Lewis acid catalyzed cascade annulation of alkynols with α-ketoesters: A facile access to γ-spiroketal-γ-lactones

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1. **General Information:**

All reactions were performed under argon atmosphere with oven (80 °C) or flame-dried glassware with septum seal. Tetrahydrofuran (THF) was distilled from sodium-benzophenone under argon atmosphere immediately prior to use. Dichloromethane and acetonitrile were freshly distilled over calcium hydride under argon atmosphere. 30 °C corresponds to the room temperature (rt) of the laboratory when the experiments were carried out. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. Analytical thin layer chromatography (TLC) was performed on TLC Silica gel 60 F254. Visualization was accomplished with short wave UV light, anisaldehyde or KMnO₄ staining solutions followed by heating. Chromatography was performed on silica gel (100-200 mesh) by standard techniques eluting with solvents as indicated. $^1$H and $^{13}$C NMR spectra were recorded on Bruker AV 400 and 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δ H = 7.26 ppm, δ C = 77.16 ppm), the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; AB q, AB quartet; dd, doublet of doublet; td, triplet doublet; and br, broad. HRMS data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Experimental procedures for all new compounds and known compounds without published experimental procedures are described below. Compounds that are not presented in the main text (manuscript) are numbered starting from S1.
2. *General Procedure* for the synthesis of unsaturated γ-spiroketal-γ-lactones from alkynols and α-ketoesters:

Alkynol 1a (0.66 mmol)/or 4 (0.66 mmol) and α-ketoester 2 (0.66 mmol) were taken in a single neck round bottom flask, then dissolved in 5 mL of anhydrous CH$_2$Cl$_2$. Bi(OTf)$_3$ (0.13 mmol) was added under argon atmosphere at room temperature (rt). The resulting reaction mixture was stirred at rt for respective reaction time. After completion of the reaction (typically after 12 h, monitored by TLC, visualized using UV, anisaldehyde, and KMnO$_4$ staining solutions) the reaction was quenched with saturated aqueous-NaHCO$_3$ solution, then extracted with CH$_2$Cl$_2$ (2x10 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, and filtered through sintered glass funnel. The filtrate was concentrated under reduced pressure and purified using silica-gel column chromatography (100-200 mesh) to afford the corresponding unsaturated γ-spiroketal-γ-lactone 3 or 6.

3. Synthesis of alkynols:

(see below experimental procedures)
(1-(Prop-2-yn-1-yl) cyclohexyl) methanol (1a):

(1-(prop-2-yn-1-yl) cyclohexyl) methanol (1a) was prepared using known procedure. \(^{1}\) \(\text{H NMR (CDCl}_3, 400 \text{ MHz): } \delta 3.55 \text{ (s, 2H), 2.26 (d, } J = 2.45 \text{ Hz, 2H), 2.01 (t, } J = 2.69 \text{ Hz, 1H), 1.84 (br s, 1H), 1.35-1.51 (m, 10H); } \text{C NMR (CDCl}_3, 101 \text{ MHz): } \delta 82.0, 70.4, 68.5, 37.6, 31.8, 26.1, 25.1, 21.5, \text{ HRMS (ESI) m/z calcd for C}_{10}H_{17}O \ [M+H]^+ 153.1274, \text{ found 153.1280.}

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((1-(Prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S2):

(1-(prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S2):

To a cold (0 °C) mixture of (1-(prop-2-yn-1-yl)cyclohexyl) methanol (1a) (14 g, 100 mmol) and 3, 4-dihydro-2H-pyran (9.1 mL, 100 mmol) in 30 mL of anhydrous CH\(_2\)Cl\(_2\) was added camphor sulfonic acid (CSA, 2 g, 10 mmol). The reaction mixture was warmed slowly to rt and stirred for 3 h. Then the reaction was quenched with saturated aqueous NaHCO\(_3\) solution, extracted with CH\(_2\)Cl\(_2\) (2x50 mL). The combined organic layers were dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (SiO\(_2\), 2% EtOAc/hexanes) to afford ((1-(prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S2), (18.5 g, 85%) as colourless liquid. TLC: \(R_f = 0.40\) (SiO\(_2\), 10% EtOAc/hexanes); \(^{1}\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 4.64 - 4.57 \text{ (m, 1H), 3.96 - 3.85 (m, 1H), 3.65 (d, } J = 9.8 \text{ Hz, 1H), 3.52 (d, } J = 11.6 \text{ Hz, 1H), 3.21 (d, } J = 9.2 \text{ Hz, 1H), 2.35-2.23 \text{ (m, 2H), 1.80 (t, } J = 2.4 \text{ Hz, 3H), 1.84-1.79 \text{ (m, 1H), 1.74-1.51 \text{ (m, 5H), 1.5-1.36 \text{ (m, 10H); } \text{C NMR (CDCl}_3, 101 \text{ MHz) } \delta 98.8, 82.2, 72.1, 69.9, 61.7, 36.9, 32.3, 32.1, 30.6, 26.1, 25.6, 21.6, 19.2; \text{ HRMS (ESI) m/z calcd for C}_{12}H_{25}O_2 \ [M+H]^+ 237.1849, \text{ found 237.1846.}}

2-((1-(But-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S3):

![S3](image)

To a solution of ((1-(prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S2) (1 g, 4.2 mmol) in anhydrous THF, nBuLi (1.6 M in hexane, 8.1 mL, 5.1 mmol) was added at -78 °C and stirred this reaction mixture for 45 min at -78 °C under argon atmosphere. Then the solution of CH₃I (1.8 mL, 12.7 mmol) in anhydrous HMPA (1 mL) was added at same temperature and resulting reaction mixture was slowly warmed to room temperature and further stirred for 6 h. Then the reaction mixture was quenched with saturated NH₄Cl solution at 0 °C and extracted with ethyl acetate (3x25 mL). The combined extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Crude product was purified by silica gel chromatography (SiO₂, 2% EtOAc/hexanes) to afford 2-((1-(but-2-yn-1-yl)cyclohexyl) methanol (S3) (1.23 g, 78%) as a colourless liquid. TLC: R₂ = 0.5 (SiO₂, 10% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 4.62 (t, J = 3.43 Hz, 1H), 3.94-3.87 (m, 1H), 3.66 (d, J = 9.54 Hz, 1H), 3.56-3.49 (m, 1H), 3.22 (d, J = 9.16 Hz, 1H), 2.24-2.2 (m, 2H), 1.8 (t, J = 2.67 Hz, 3H), 1.89-1.37 (m, 16H); ¹³C NMR (CDCl₃, 101 MHz) δ 98.9, 72.3, 61.6, 37.1, 32.3, 32.1, 30.6, 26.2, 25.9, 25.6, 21.7, 19.2, 3.5; HRMS (ESI) m/z calcd for C₁₆H₂₇O₂ [M+H]+ 251.2006, found 251.2001.

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(1-(But-2-yn-1-yl) cyclohexyl) methanol (4a):

![4a](image)

To a solution of 2-((1-(but-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S3) (1 g, 4 mmol) in methanol was added p-toluenesulfonic acid (PTSA, 0.075 g, 0.4 mmol) at 0 °C and then it was slowly warmed to rt. The resulting reaction mixture was stirred for 6 h at rt, then the methanol was evaporated under reduced pressure, diluted with ethyl acetate and quenched with saturated aqueous NaHCO₃ solution and extracted with ethyl acetate (3x25
mL). Combined organic layers were dried over anhydrous Na₂SO₄, filtered using sintered funnel, concentrated under reduced pressure to afford the crude product, which was purified by silica gel column chromatography (SiO₂, 10% EtOAc/hexanes) to afford (1-(but-2-yn-1-yl) cyclohexyl) methanol (4a), (0.59 g, 74%) as a colourless liquid. TLC: Rf = 0.2 (SiO₂, 20% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 3.54 (s, 2 H), 2.22-2.15 (m, 2 H), 1.82 (br. s., 1H), 1.8 (t, J = 2.44 Hz, 3H), 1.53 - 1.32 (m, 10 H); ¹³C NMR (CDCl₃, 101 MHz) δ 77.9, 76.4, 69.1, 37.7, 32.0, 26.2, 25.7, 21.6, 3.5; HRMS (ESI): m/z calcd for C₁₁H₁₉O [M+H]⁺ 167.2617, found 167.2619.

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2-((1-(Pent-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S4):

To a solution of (1-(prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S2) (1.5 g, 6.3 mmol) in anhydrous THF, nBuLi (1.6 M in hexane, 5 mL, 7.6 mmol) was added, and stirred this reaction mixture for 45 min at -78 °C under argon atmosphere. Then the solution of EtI (1.56 mL, 1.9 mmol) in anhydrous HMPA (1 mL) was added at -78 °C and resulting reaction mixture was stirred for 6 h at rt. The reaction mixture was quenched with saturated solution of NH₄Cl and extracted with ethyl acetate (2x25 mL). Combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure, crude product was purified by silica gel column chromatography (SiO₂, 10% EtOAc/hexanes) to give 2-((1-(pent-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S4) (1.1 g, 66%) as a colourless liquid. TLC: Rf = 0.45 (SiO₂, 10% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz) δ 4.60 (m, 1H), 3.95 - 3.79 (m, 1H), 3.64 (d, J = 9.8 Hz, 1H), 3.56-3.44 (m, 1H), 3.2 (d, J = 9.8 Hz, 1H), 2.25 - 2.2 (m, 2H), 2.2-2.11 (m, 2 H), 1.89-1.36 (m, 16H), 1.12 (t, J = 7.32 Hz, 3H); ¹³C NMR (CDCl₃, 101 MHz) δ 98.8, 83.3, 76.9, 72.3, 61.5, 37.0, 32.3, 32.1, 30.6, 26.3, 25.9, 25.6, 21.7, 19.2, 14.5, 12.5; HRMS (ESI): m/z calcd for C₁₇H₂₀O₂ [M+H]⁺ 265.2162, found 265.2161.

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(1-(Pent-2-yn-1-yl) cyclohexyl) methanol (4b):

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\text{OH}
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4b

To a solution of 2-((1-(pent-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S4) (1.1 g, 4.16 mmol) in methanol was added PTSA at 0 °C and then it was warmed to room temperature, the resulting reaction mixture was stirred at rt for 6 h. Then methanol was evaporated under reduced pressure, diluted with ethyl acetate (25 mL) and washed with saturated solution of sodium bicarbonate and brine solution. The residue was dried over anhydrous sodium sulphate, filtered using sintered funnel, concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (SiO\(_2\), 10% EtOAc/hexanes) to afford (1-(pent-2-yn-1-yl) cyclohexyl) methanol 4b (0.59 g, 78%) as a colourless liquid. TLC: \(R_f = 0.5\) (SiO\(_2\), 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.53 (s, 2H), 2.24 - 2.11 (m, 4H), 1.85 (br. s., 1H), 1.51 - 1.32 (m, 10H), 1.12 (t, \(J = 7.32\) Hz, 3H); \(^13\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 84.2, 76.6, 69.2, 37.6, 32.0, 26.2, 25.8, 21.6, 14.3, 12.4; HRMS (ESI): m/z calcd for C\(_{12}\)H\(_{20}\)ONa [M+H]\(^+\) 203.1406, found 203.1405.

(1-(3-Phenylprop-2-yn-1-yl) cyclohexyl) methanol (4c):

\[
\text{OH}
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4c

(1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (4c) was prepared according to the literature.\(^2\) Pd(PPh\(_3\))\(_4\) (0.023 g, 0.019 mmol) and CuI (0.08 g, 0.039 mmol) were added to the solution of iodobenzene (S1) (0.45 ml, 3.94 mmol) and (1-(prop-2-yn-1-yl) cyclohexyl) methanol (0.3 g, 1.97 mmol) (1a) in triethylamine (2.76 mL, 19.7 mmol) and THF (10 mL) under argon atmosphere. The reaction mixture was stirred at rt for 12 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford the (1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (4c) as a brown oil (0.27 g, 60%). TLC: \(R_f = 0.5\) (SiO\(_2\), 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.47-7.36 (m, 2H), 7.36-7.22 (m, 3H), 7.36-7.22 (m, 3H), 3.62
(s, 2H), 2.49 (s, 2H), 1.92 (br s, 1H), 1.61 - 1.34 (m, 10H); $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 131.6, 128.2, 127.6, 123.8, 87.6, 82.8, 68.7, 38.2, 32.0, 26.2, 26.1, 21.6; HRMS (ESI): m/z calcd for C$_{16}$H$_{23}$O [M+H]$^+$ 229.1587, found 229.1586.

(1-(Prop-2-yn-1-yl) cyclopentyl) methanol (1b):$^1$

(1-(prop-2-yn-1-yl) cyclopentyl) methanol (1b) was prepared using known procedure.$^1$ $^1$H NMR (CDCl$_3$, 400 MHz) δ 3.47 (s, 2H), 2.35 (s, 1H), 2.27 (d, $J = 2.45$ Hz, 2H), 1.94 (t, $J = 2.45$ Hz, 1H), 1.68-1.54 (m, 4H), 1.53-1.42 (m, 4H), $^{13}$C NMR (CDCl$_3$, 101 MHz): δ 82.9, 69.3, 68.5, 46.9, 34.0, 26.5, 25.2; HRMS (ESI) m/z calcd for C$_9$H$_{15}$O [M+H]$^+$ 139.1117, found 139.116.

(1-(3-Phenylprop-2-yn-1-yl) cyclopentyl) methanol (4d):

(1-(3-phenylprop-2-yn-1- cyclopentyl) methanol (4d) was prepared according to the literature procedure.$^1$ Pd(PPh$_3$)$_4$ (0.042 g, 0.036 mmol) and CuI (0.014 g, 0.072 mmol) were added to the solution of iodobenzene (S1) (0.82 mL, 7.24 mmol) and (1-(prop-2-yn-1-yl) cyclopentyl) methanol (1b) (0.5 g, 3.62 mmol) in triethylamine (5 mL, 36.2 mmol) and THF (10 mL) under argon atmosphere. The reaction mixture was stirred at rt for 12 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford (1-(3-phenylprop-2-yn-1- cyclopentyl) methanol (4d) (0.5 g, 64%) as brownish oil, TLC: $R_f = 0.5$ (20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.44-7.34 (m, 2H), 7.32 - 7.18 (m, 3H), 3.57 (s, 2H), 2.50 (s, 2H), 1.82-1.45 (m, 8H); $^{13}$C NMR (CDCl$_3$, 101 MHz): δ 131.6, 128.2, 127.7, 123.8, 88.5, 81.7, 69.1, 47.6, 34.3, 27.7, 25.3; HRMS (ESI) m/z calcd for C$_{15}$H$_{19}$O [M+H]$^+$ 215.1430, found 215.1426.
5-Phenylpent-4-yn-1-ol (4e):

5-phenylpent-4-yn-1-ol (4e) was prepared according to the literature procedure.\(^1\) Pd(PPh\(_3\))\(_4\) (0.137 g, 0.12 mmol) and CuI (0.045 g, 0.24 mmol) were added to the solution of iodobenzene (S1) (2.7 mL, 23.77 mmol) and pent-4-yn-1-ol (1c) (1 g, 11.89 mmol) in triethylamine (16 mL, 118.9 mmol) and anhydrous THF (15 mL) under argon atmosphere. The reaction mixture was stirred at rt for 6 h. Then the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford 5-phenylpent-4-yn-1-ol (4e) (1.9 g, 98%) brown oil. TLC: \(R_f= 0.4\) (20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.46-7.38 (m, 2H), 7.34-7.25 (m, 3H), 3.89-3.68 (m, 2H), 2.59-2.51 (m, 2H), 2.1 (br. s., 1H), 1.93-1.82 (m, 2H); \(^13\)C NMR (CDCl\(_3\), 126 MHz) \(\delta\) 131.6, 128.3, 127.7, 123.8, 89.4, 81.1, 61.7, 61.6, 31.4, 16.0; HRMS (ESI): m/z calcd for C\(_{11}\)H\(_{13}\)O [M+H]\(^+\) 161.0961, found 161.0958.

4. Synthesis of \(\alpha\)-ketoesters:\(^2, 3,4,5\)

\(2a\), \(2b\) were purchased from commercial sources.
\(5\) see the next page for preparation.
Ethyl 2-(4-nitrophenyl)-2-oxoacetate (2e)\(^6\):

Bromine (3.51 mL, 68 mmol) was added drop wise over 20 min to anhydrous 1,4-dioxane (20 mL) at 25–30 °C under argon atmosphere and the mixture was kept under these conditions for 30 min. A solution of 1-(4-nitrophenyl)ethan-1-one (S5) (5 g, 34 mmol) in dioxane (20 mL) was added and the mixture was stirred for another 3 h. The reaction was then quenched with ice-cold water (400 mL, 10 volumes with respect to 1,4-dioxane) and the solid was filtered off and washed with chilled hexane to give 2,2-dibromo-1-(4-nitrophenyl)ethan-1-one (S6), which was used in the next step without further purification. The crude S6 was dissolved in anhydrous DMSO (60 mL) under argon. The solution was then slowly heated to 70–75 °C and stirred at this temperature for 16 h. The mixture was then cooled to rt, then EtOH (3.97 mL, 0.6 mol) was added, and the mixture was stirred for 2 h at rt. The mixture was then diluted with H\(_2\)O (100 mL) and extracted with EtOAc (4 × 30 mL). The combined organic layers were washed successively with water (3×30 mL) and brine solution, dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. The pure product was isolated by silica gel column chromatography (12% EtOAc/hexanes) to give 3.21 g (47%) of 2e as a yellow oil. TLC: \(R_f = 0.35\) (20% EtOAc/hexanes). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.32 (d, \(J = 8.55\) Hz, 2H), 8.21 (d, \(J = 8.55\) Hz, 2H), 4.47 (q, \(J = 7.32\) Hz, 2H), 1.43 (t, \(J = 7.32\) Hz, 3H); \(^1^3\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 184.2, 162.3, 151.1, 137.0, 131.2, 123.9, 63.0, 14.0; HRMS (ESI): m/z calcd for C\(_{10}\)H\(_{10}\)O\(_5\)N [M+H]\(^+\) 224.0553, found 224.0549.

5. *Synthesis and Characterization* of unsaturated \(\gamma\)-spiroketal-\(\gamma\)-lactones from alkynols possessing terminal alkyne functionality:

3-Methyl-1, 14-dioxadispiro \([4.1.5.2^5]\) tetradec-3-en-2-one (3aa):

Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl) cyclohexyl) methanol (1a) (0.100 g, 0.66 mmol) and ethyl pyruvate (2a) (0.104 g, 0.66 mmol) in anhydrous CH\(_2\)Cl\(_2\) (5 mL) was added Bi(OTf)\(_3\) (0.090 g, 0.13 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO\(_2\), 5% EtOAc/hexanes) afforded 3-methyl-1, 14-dioxadispiro \([4.1.5.2^5]\) tetradec-3-en-2-one (3aa) (0.117 g, 80%). TLC: \(R_f\) = 0.40 (SiO\(_2\), 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 6.74-6.65 (m, 1H), 3.95 (d, \(J = 8.8\) Hz, 1H), 3.86 (d, \(J = 8.3\) Hz, 1H), 2.12 (d, \(J = 13.7\) Hz, 1H), 2.01 (d, \(J = 14.2\) Hz, 1H), 1.91 (d, \(J = 0.98\) Hz, 3H), 1.77-1.64 (m, 2H), 1.57-1.36 (m, 8H); \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \(\delta\) 171.6, 145.1, 132.5, 113.2, 80.4, 47.1, 43.6, 37.4, 35.5, 25.5, 23.8, 23.7, 10.4; HRMS (ESI) m/z calcd for C\(_{13}\)H\(_{19}\)O\(_3\) [M+H]\(^+\) 223.1329, found 223.1326.

3-Phenyl-1, 14-dioxadispiro \([4.4.5.2^5]\) tetradec-3-en-2-one (3ab):

Following the *General Procedure*, to the mixture of (1-(prop-2-yn-1-yl) cyclohexyl) methanol (1a) (0.100 g, 0.66 mmol) and ethyl phenylglyoxylate (2b) (0.104 g, 0.66 mmol) in anhydrous CH\(_2\)Cl\(_2\) (5 mL) was added Bi(OTf)\(_3\) (0.09 g, 0.13 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 12 h. Purification of the crude product by column chromatography (SiO\(_2\), 2% EtOAc/hexanes) afforded 3-phenyl-
1,14-dioxadispiro[4.4.5.7.2]tetradec-3-en-one (3ab) as a crystalline solid (0.142 g, 76%). TLC: \( R_f = 0.75 \) (SiO2, 20% EtOAc/hexanes); \(^1\)H NMR (CDCl3, 400 MHz): \( \delta \) 7.89-7.79 (m, 2H), 7.42 (d, \( J = 3.7 \) Hz, 3H), 7.18 (s, 1H), 4.03 (d, \( J = 7.9 \) Hz, 1H), 3.94 (d, \( J = 8.5 \) Hz, 1H), 2.20 (dd, \( J = 36.01, 13.4 \) Hz, 2H), 1.81-1.69 (m, 2H), 1.62-1.38 (m, 8H); \(^13\)C NMR (CDCl3, 101 MHz): \( \delta \) 169.3, 143.7, 133.6, 129.7, 129.0, 128.7, 127.5, 112.4, 80.5, 47.4, 43.8, 37.4, 35.5, 25.6, 23.9, 23.8; HRMS (ESI) m/z calcd for C18H21O3 [M+H]^+ 285.1485, found 285.1483.

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3-(4-Methoxyphenyl)-1,14-dioxadispiro [4.1.5.7.2]tetradec-3-en-2-one (3ac):

Following the General Procedure, to the mixture of (1-(prop-2-yn-1-yl) cyclohexyl) methanol (1a) (0.05 g, 0.33 mmol) and ethyl anisylglyoxylate (2c) (0.054 g, 0.33 mmol) in anhydrous CH2Cl2 (3 mL) was added Bi(OTf)3 (0.045 g, 0.066 mmol) under argon atmosphere at room temperature and stirred the reaction mixture for 12 h. Purification of the crude product by column chromatography (SiO2, 5% EtOAc/hexanes) afforded 3-(4-methoxyphenyl)-1, 14-dioxadispiro [4.1.5.7.2] tetradec-3-en-2-one (3ac) (0.06 g, 72%). TLC: \( R_f = 0.75 \) (SiO2, 20% EtOAc/hexanes); \(^1\)H NMR (CDCl3, 400 MHz): \( \delta \) 7.81 (d, \( J = 8.8 \) Hz, 2H), 7.05 (s, 1H), 6.93 (d, \( J = 8.8 \) Hz, 2H), 4.01 (d, \( J = 8.3 \) Hz, 1H), 3.92 (d, \( J = 8.3 \) Hz, 1H), 3.84 (s, 3H), 2.16 (dd, \( J = 38.15, 13.7 \) Hz, 2H), 1.77-1.69 (m, 2H), 1.59-1.40 (m, 8H); \(^13\)C NMR (CDCl3, 101 MHz): \( \delta \) 169.6, 160.7, 141.3, 132.9, 129.0, 121.5, 114.1, 112.4, 80.5, 55.3, 47.4, 43.8, 37.4, 35.5, 25.6, 23.9, 23.8; HRMS (ESI) m/z calcd for C19H23O4 [M+H]^+ 315.1591, found 315.1588.

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3-(p-Tolyl)-1, 14-dioxadispiro [4.1.5\(^7\).2\(^5\)] tetradec-3-en-2-one (3ad):

Following the General Procedure, to the reaction mixture of (1-(prop-2-yn-1-yl)cyclohexyl) methanol (1a) (0.05 g, 0.32 mmol) and ethyl p-tolylglyoxylate (2d) (0.063 g, 0.32 mmol) in anhydrous CH\(_2\)Cl\(_2\) (4 mL) was added Bi(OTf)_3 (0.042 g, 0.064 mmol) under argon atmosphere at room temperature and stirred the reaction mixture for 12 h. Purification of the crude product by column chromatography (SiO\(_2\), 2% EtOAc/hexanes) afforded 3-(p-tolyl)-1, 14-dioxadispiro [4.1.5\(^7\).2\(^5\)] tetradec-3-en-2-one (3ad) (0.067 g, 70%) as a crystalline solid. TLC: R\(_f\) = 0.60 (SiO\(_2\), 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 7.75 (d, \(J = 8.01\) Hz, 2H), 7.22 (d, \(J = 8.01\) Hz, 2H), 7.12 (s, 1H), 4.02 (d, \(J = 8.4\) Hz, 1H), 3.93 (d, \(J = 8.4\) Hz, 1H), 2.38 (s, 3H), 2.23 (d, \(J = 14.11\) Hz, 1H), 2.13 (d, \(J = 13.73\) Hz, 1H), 1.78-1.68 (m, 2H), 1.61-1.31 (m, 8H); \(^1^3\)C NMR (CDCl\(_3\), 126 MHz): \(\delta\) 169.4, 142.7, 139.9, 133.5, 129.4, 127.4, 126.1, 112.3, 80.5, 43.8, 37.4, 35.6, 25.6, 23.9, 23.8, 21.4; HRMS (ESI) m/z calcd for C\(_{19}\)H\(_{23}\)O\(_3\) [M+H]+ 299.1642 found 299.1634.

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3-Methyl-1, 13-dioxadispiro [4.1.4\(^7\).2\(^5\)] tridec-3-en-2-one (3ba):

Following the General Procedure, to the mixture of (1-(prop-2-yn-1-yl)cyclopentyl)methanol (1b) (0.1 g, 0.72 mmol) and ethylpyruvate (2a) (0.083 g, 0.72 mmol) in anhydrous CH\(_2\)Cl\(_2\) (5 mL) was added Bi(OTf)_3 (0.09 g, 0.144 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO\(_2\), 5% EtOAc/hexanes) afforded 3-
methyl-1,13-dioxadispiro[4.1.4.2]tridec-3-en-2-one (3ba) (0.117 g, 78%) as a white solid. TLC: $R_f = 0.3$ (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 6.72-6.69 (m, 1H), 4.01 (d, $J = 8.4$ Hz, 1H), 3.85 (d, $J = 8.4$ Hz, 1H), 2.18 (s, 2H), 1.92 (d, $J = 1.14$ Hz, 3H), 1.86-1.81 (m, 2H), 1.74-1.58 (m, 6H); $^{13}$C NMR (CDCl$_3$, 126 MHz): $\delta$ 171.6, 145.2, 132.5, 113.3, 81.1, 50.3, 47.4, 38.0, 37.2, 24.6, 24.4, 10.4; HRMS (ESI): calcd for C$_{12}$H$_{17}$O$_3$ [M+H]$^+$ 209.1172, found 209.1171.

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3-Phenyl-1, 13-dioxadispiro [4.1.4.2] tridec-3-en-one (3bb):

Following the General Procedure, to the mixture of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (1b) (0.1 g, 0.72 mmol) ethyl phenylglyoxylate (2b) (0.128 g, 0.72 mmol) in anhydrous CH$_2$Cl$_2$ (6 mL) was added Bi(OTf)$_3$ (0.09 g, 0.144 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO$_2$, 5% EtOAc /hexanes) afforded 3-phenyl-1,13-dioxadispiro[4.1.4.2]tridec-3-en-one (3bb) (0.136 g, 70%). TLC: $R_f = 0.5$ (SiO$_2$, 20% EtOAc /hexanes); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.87-7.81 (m, 2H), 7.45-7.39 (m, 3H), 7.19 (s, 1H), 4.08 (d, $J = 8.0$ Hz, 1H), 3.92 (d, $J = 8.0$ Hz, 1H), 2.31 (dd, $J = 17.55$, 13.73 Hz, 2H), 1.91-1.87 (m, 2H), 1.79-1.63 (m, 6H); $^{13}$C NMR (CDCl$_3$, 126 MHz): $\delta$ 169.3, 143.7, 133.6, 129.7, 129.0, 128.7, 127.5, 112.4, 81.2, 50.5, 47.7, 38.0, 37.2, 24.7, 24.4; HRMS (ESI): calcd for C$_{17}$H$_{19}$O$_3$ [M+H]$^+$ 271.1329, found 271.1328.

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3-(4-Methoxyphenyl)-1, 13-dioxadispiro [4.1.4.7.2.5] tridec-3-en-2-one (3bc):

Following the General Procedure, to the reaction mixture of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (1b) (0.1 g, 0.72 mmol) and ethyl anisyglyoxylate (2c) (0.15 g, 0.72 mmol) in anhydrous CH$_2$Cl$_2$ (2 mL) was added Bi(OTf)$_3$ (0.094 g, 0.14 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of crude product by column chromatography (SiO$_2$, 8% EtOAc /hexanes) afforded 3-(4-methoxyphenyl)-1,13-dioxadispiro[4.1.4.7.2.5]tridec-3-en-2-one (3bc) crystalline solid (0.151 g, 70%). TLC: $R_f$ = 0.60 (SiO$_2$, 20% EtOAc /hexanes); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.88-7.80 (m, 2H), 7.06 (s, 1H), 6.96-6.91 (m, 2H), 4.07 (d, $J$ = 8.01 Hz, 1H), 3.91 (d, $J$ = 8.01 Hz, 1H), 3.84 (s, 3H), 2.29 (dd, $J$ = 13.35, 3.43 Hz, 2H), 1.91-1.85 (m, 2H), 1.78-1.63 (m, 6H); $^{13}$C NMR (126MHz, CDCl$_3$): $\delta$ 169.6, 160.7, 141.3, 132.9, 129.0, 121.6, 114.1, 112.4, 81.2, 55.3, 50.5, 47.7, 38.1, 37.2, 29.7, 24.7, 24.4; HRMS (ESI) m/z calcd for C$_{18}$H$_{21}$O$_4$ [M+H]$^+$ 300.1434 found 301.1425.

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3-(p-Tolyl)-1, 13-dioxadispiro [4.1.4.7.2.5] tridec-3-en-2-one (3bd):

Following the General Procedure, to the reaction mixture of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (1b) (0.05 g, 0.36 mmol) and ethyl $p$-tolylglyoxylate (2d) (0.069 g, 0.36 mmol) in anhydrous CH$_2$Cl$_2$ (3 mL) was added Bi(OTf)$_3$ (0.042 g, 0.072 mmol) under argon atmosphere at room temperature and stirred for 12 h at rt. Purification of the crude
product by column chromatography (SiO$_2$, 2% EtOAc /hexanes) afforded 3-(p-tolyl)-1,13-dioxadispiro[4.1.4.7.2.5]tridec-3-en-2-one (3bd) (0.073 g, 72%) as a white solid. TLC: $R_f = 0.60$ (SiO$_2$, 20% EtOAc /hexanes); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.75 (d, $J = 8.5$ Hz, 2H), 7.22 (d, $J = 7.9$ Hz, 2H), 7.13 (s, 1H), 4.07 (d, $J = 8.5$ Hz, 1H), 3.91 (d, $J = 7.9$ Hz, 1H), 2.39 (s, 3H), 2.29 (dd, $J = 14.404$, 1.22 Hz, 2H), 1.93-1.85 (m, 2H), 1.80-1.61 (m, 6H); $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 169.4, 142.7, 139.9, 133.4, 129.4, 127.4, 126.1, 112.4, 81.2, 50.5, 47.7, 38.0, 37.2, 24.7, 24.4, 21.4; HRMS (ESI) m/z calcd for C$_{18}$H$_{21}$O$_3$ [M+H]$^+ 285.1485$ found 285.1476.

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3-(4-Nitrophenyl)-1,13-dioxadispiro [4.1.4.7.2.5] tridec-3-en-2-one (3be):

Following the General Procedure, to the mixture of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (1b) (0.112 g, 0.811 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (2e) (0.181 g, 0.811 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added Bi(OTf)$_3$ (0.106 g, 0.162 mmol) at room temperature under argon atmosphere and the mixture was stirred for 12 h at rt. Quenched with aqueous NaHCO$_3$ solution (5 mL), stirred for 5 min then extracted with CH$_2$Cl$_2$ (2x5 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated. Resulting solid was dissolved in hexanes (5 mL) and slowly added the minimum amount of CH$_2$Cl$_2$, then resulting solution was stand at room temperature until all solvents were evaporated to form crystalline product 3-(4-nitrophenyl)-1,13-dioxadispiro[4.1.4.7.2.5]tridec-3-en-2-one (3be) (0.144 g, 78%). TLC: $R_f = 0.75$ (SiO$_2$, 20% EtOAc /hexanes); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.28 (d, $J = 8.5$ Hz, 2H), 8.05 (d, $J = 9.2$ Hz, 2H), 7.38 (s, 1H), 4.10 (d, $J = 8.5$ Hz, 1H), 3.94 (d, $J = 7.9$ Hz, 1H), 2.39-2.27 (m, 2H), 1.95-1.83 (m, 2H), 1.81-1.62 (m, 6H); $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 168.3, 148.3, 147.0, 135.0, 131.7, 128.5, 123.9, 112.6, 81.5, 50.6, 47.6, 37.9, 37.1, 24.7, 24.4; HRMS (ESI) m/z calcd for C$_{17}$H$_{18}$O$_3$N [M+H]$^+ 316.1179$, found 316.1171.

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3-Methyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3ca):

Following the General Procedure, to the reaction mixture of pent-4-yn-1-ol (1c) (0.1 g, 1.1 mmol) and ethyl pyruvate (2a) (0.137 g, 1.1 mmol) in anhydrous CH₂Cl₂ (5 mL) was added Bi(OTf)₃ (0.154 g, 0.22 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 48 h at rt. Purification of crude product by column chromatography (SiO₂, 5% EtOAc /hexanes) afforded 3-methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ca) (0.106 g, 58%) as a yellow oily liquid. TLC: $R_f = 0.60$ (SiO₂, 20% EtOAc /hexanes); $^1$H NMR (CDCl₃, 500 MHz): δ 6.73-6.70 (m, 1H), 4.65-4.19 (m, 1H), 4.10-4.03 (m, 1H), 2.34-2.23 (m, 1H), 2.22-2.06 (m, 3H), 1.93 (d, $J = 1.91$ Hz, 3H); $^{13}$C NMR (CDCl₃, 126 MHz): δ 171.4, 144.4, 133.3, 112.7, 70.3, 35.3, 24.2, 10.5; HRMS (ESI) m/z calcd for C₈H₁₁O₃ [M+H]⁺ 154.0703 found 155.0699.

3-Phenyl-1, 6-dioxaspiro [4, 4] non-3-en-2-one (3cb):

Following the General Procedure, to the mixture of 4-pentyne-1-ol (1c) (0.1 g, 1.19 mmol) and ethyl phenylglyoxylate (2b) (0.21 g, 1.19 mmol) in anhydrous CH₂Cl₂ (5 mL) was added Bi(OTf)₃ (0.249 g, 0.238 mmol) under argon atmosphere at room temperature and the resulting mixture was stirred for 48 h at rt. Purification of the crude product by column chromatography (SiO₂, 5% EtOAc /hexane) afforded 3-phenyl-1, 6-dioxaspiro [4, 4] non-3-en-2-one (3cb) (0.138 g, 54%). TLC: $R_f = 0.45$ (SiO₂, 20% EtOAc /hexanes); $^1$H NMR (CDCl₃, 400 MHz): δ 7.90-7.80 (m, 2H), 7.49-7.34 (m, 3H), 7.21 (s, 1H), 4.28 (td, $J = 8.2, 3.7$ Hz, 1H), 4.11 (q, $J = 7.5$ Hz, 1H), 2.42-2.14 (m, 4H); $^{13}$C NMR (CDCl₃, 101 MHz): δ 169.2, 143.1, 134.3, 129.8, 129.0, 128.7, 128.2, 128.1, 127.7, 127.5, 127.3, 111.9, 70.5, 35.7, 24.3; HRMS (ESI) m/z calcd for C₁₃H₁₃O₃ [M+H]⁺ 217.0859, found 217.0857.
3-(4-Methoxyphenyl)-1,6-dioxaspiro[4,4]non-3-en-2-one (3cc):

Following the General Procedure, to the mixture of 4-pentyne-1-ol (1c) (0.3 g, 3.57 mmol) and ethyl anisylglyoxylate (2c) (0.743 g, 3.57 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (6 mL) was added Bi(OTf)\textsubscript{3} (0.465 g, 0.714 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 48 h at rt. Purification of the crude product by column chromatography (SiO\textsubscript{2}, 5% EtOAc/hexanes) afforded 3-(4-methoxyphenyl)-1,6-dioxaspiro[4,4]non-3-en-2-one (3cc) (0.46 g, 52%). TLC: \( R_f = 0.40 \) (SiO\textsubscript{2}, 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\textsubscript{3}, 500 MHz): \( \delta 7.82 \text{ (d, } J = 8.8 \text{ Hz, 2H)}, 7.07 \text{ (s, 1H)}, 6.92 \text{ (d, } J = 8.8 \text{ Hz, 2H)}, 4.31-4.24 \text{ (m, 1H)}, 4.15-4.08 \text{ (m, 1H)}, 3.83 \text{ (s, 3H)}, 2.38-2.12 \text{ (m, 4H)}; ^{13}\text{C NMR (CDCl}_3, 126 MHz): \( \delta 169.5, 160.8, 140.5, 133.7, 129.0, 121.6, 114.1, 111.9, 70.4, 35.7, 24.3; \text{ HRMS (ESI): calcd for C}_{14}H_{15}O_4 [M+H]^+ 247.0965, found 247.0964.

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3-(p-Tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (3cd):

Following the General Procedure, to the reaction mixture of pent-4-yn-1-ol (1c) (0.1 g, 1.1 mmol) and ethyl p-tolyglyoxylate (2d) (0.228 g, 1.1 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (5 mL) was added Bi(OTf)\textsubscript{3} (0.154 g, 0.22 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 48 h at rt. Purification of crude product by column chromatography (SiO\textsubscript{2}, 8% EtOAc/hexanes) afforded 3-(p-tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (3cd) crystalline solid (0.084 g, 62%). TLC: \( R_f = 0.60 \) (SiO\textsubscript{2}, 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \( \delta 7.76 \text{ (d, } J = 7.9 \text{ Hz, 2H)}, 7.23 \text{ (d, } J = 7.9 \text{ Hz, 2H)}, 7.15 \text{ (s, 1H)}, 4.33-4.25 \text{ (m, 1H)}, 4.17-4.08 \text{ (m, 1H)}, 2.38 \text{ (s, 3H)}, 2.43-2.12 \text{ (m, 4H)}; ^{13}\text{C NMR (CDCl}_3, 101 MHz): \( \delta 169.3, 141.9, 140.0, 134.2, 129.4, 127.4, 126.2, 111.8, 70.4, 35.7, 24.3, 21.4; \text{ HRMS (ESI) m/z calcd for C}_{14}H_{15}O_3 [M+H]^+ 230.1016 found 231.1009. \)
2, 2-diphenylpent-4-yn-1-ol (1d):

![Image](image1.png)

Compound (1d) was prepared using known procedure.\(^7\) \(^1\)H NMR (CDCl\(_3\), 500MHz) \(\delta\) 7.33-7.27 (m, 4H), 7.25-7.20 (m, 6H), 4.30 (s, 2H), 3.08 (d, \(J = 2.29\) Hz, 2H), 1.93 (t, \(J = 2.7\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \(\delta\) 144. 4, 128.9, 128.02, 126.7, 81.4, 71.5, 68.3, 51.5, 27.4; HRMS (ESI) m/z calcd for C\(_{17}\)H\(_{17}\)O [M+H]\(^+\) 237.1274, found 237.1274.

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3-methyl-8, 8-diphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3da):

![Image](image2.png)

Following the General Procedure, to the mixture of 2, 2-diphenylpent-4-yn-1-ol (1d) (0.1 g, 0.42 mmol) and ethyl pyruvate (2a) (0.049 g, 0.42mmol) in anhydrous CH\(_2\)Cl\(_2\) (5 mL) was added Bi(OTf)\(_3\) (0.055 g, 0.08 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO\(_2\), 5% EtOAc /hexanes) afforded 3-methyl-8, 8-diphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3da) (0.80 g, 62%). TLC: \(R_f = 0.5\) (SiO\(_2\), 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.36-7.28 (m, 6H), 7.27-7.23 (m, 2H), 7.21-7.18 (m, 2H), 6.35 (d, \(J =1.53\) Hz 1H), 4.86 (d, \(J =8.7\) Hz, 1H), 4.49 (d, \(J = 9.1\) Hz, 1H), 3.27 (d, \(J = 14.1\)Hz, 1H), 2.95 (d, \(J = 13.7\) Hz, 1H), 1.86 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \(\delta\) 171.4, 145.6, 145.2, 143.6, 131.7, 128.7, 128.3, 127.1, 127.0, 126.8, 112.9, 77.9, 56.3, 47.5, 10.3; HRMS (ESI) m/z calcd for C\(_{20}\)H\(_{19}\)O\(_3\) [M+H]\(^+\) 307.1329, found 307.1326.

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3, 8, 8-triphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3db):

Following the General Procedure, to the mixture of 2, 2-diphenylpent-4-yn-1-ol (1d) (0.1 g, 0.42 mmol) and ethyl phenylglyoxylate (2b) (0.075 g, 0.42 mmol) in anhydrous CH₂Cl₂ (5 mL) was add Bi(OTf)₃ (0.055 g, 0.28 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO₂, 5% EtOAc /hexanes) afforded 3,8,8-triphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3db) (0.109 g, 70%). TLC: Rf = 0.40 (SiO₂, 20% EtOAc/hexanes); ¹H NMR(CDCl₃, 400 MHz) δ 7.80-7.71 (m, 2H), 7.40-7.30 (m, 9H), 7.29-7.20 (m, 4H), 6.79 (s, 1H), 4.91(d, J = 9.1 Hz, 1H), 4.55 (d, J = 9.1 Hz, 1H), 3.36 (d, J = 14 Hz, 1H), 3.07 (d, J = 14 Hz, 1H); ¹³C NMR (CDCl₃, 101 MHz) δ 169, 145.5, 143.5, 132.7, 128.8, 129.8, 128.7, 128.6, 127.5, 127.1, 126.9, 126.8, 112.1, 78.1, 56.4, 47.8; HRMS (ESI) m/z calcd for C₂₅H₂₁O₃ [M+H]+ 369.1485, found 369.1469.

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1-phenylpent-4-yn-1-ol (1e):

Compound 1e was prepared using known procedure.⁸ PhMgBr (1.0 M in THF, 18 mL, 1.82 mmol) was added drop wise to a solution of pent-4-ynal (S7) (0.5 g, 0.605 mmol) in THF (20 mL) at room temperature, the reaction mixture was stirred at rt for 2 h. Reaction was quenched by adding ice cold water (10 mL), then neutralized with 2N HCl (20 mL), extracted with EtOAc (20 mL), which was washed once with 2N HCl (20 mL) and brine solution (20 mL). Organic layer was dried over anhydrous MgSO₄. Filtration and evaporation of the solvent under reduced pressure afforded the desired product 1-phenylpent-4-yn-1-ol (1e) (0.72 g, 70 %).¹H NMR (CDCl₃, 200 MHz) δ 7.45-7.11 (m, 5H), 4.77-4.64 (m, 1H), 2.96 (d, J = 14 Hz, 1H), 2.79-2.71 (m, 2H), 2.28-2.20 (m, 2H), 1.28-1.20 (m, 2H), 0.96 (d, J = 6 Hz, 3H), 0.87 (t, J = 7 Hz, 3H), 0.82 (d, J = 6 Hz, 3H), 0.78 (t, J = 7 Hz, 3H); ¹³C NMR (CDCl₃, 101 MHz) δ 169, 145.5, 143.5, 132.7, 128.8, 129.8, 128.7, 128.6, 127.5, 127.1, 126.9, 126.8, 112.1, 78.1, 56.4, 47.8; HRMS (ESI) m/z calcd for C₂₃H₂₆O [M+H]+ 369.1815, found 369.1814.

$J = 3.66 \text{ Hz, 1H), 2.36-2.06 (m, 2H), 2.03-1.66 (m, 3H); HRMS (ESI) m/z calcd for C}_{11}\text{H}_{13}\text{O [M+H]$^+$} 161.0963, found 161.0961.

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3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):

Following the General Procedure, to the mixture of 1-phenylpent-4-yn-1-ol (1e) (0.1 g, 0.062 mmol) and ethyl pyruvate (2a) (0.072 g, 0.062 mmol) in anhydrous CH$_2$Cl$_2$ (2 mL) was added Bi(OTf)$_3$ (0.081 g, 0.012 mmol), then reaction mixture was stirred under reflux conditions (40 °C) for 12 h. The reaction mixture was cooled to room temperature and quenched using aqueous NaHCO$_3$ solution. Extracted with dichloromethane (2x10 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated. Purification of the crude product by silica gel column chromatography (SiO$_2$, 6% EtOAc/hexanes) afforded two separable diastereomers of 3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea-Isomer-1, 27% yield (0.038 g), 3ea-Isomer-2, 29% yield (0.041 mg), in dr approx 1:1) as a yellow oil.

3ea-Isomer-1: TLC: $R_f = 0.3$ (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.52-7.22 (m, 5H), 6.89 (s, 1H), 5.45 (t, $J = 5.72$ Hz, 1H), 2.81-2.69 (m, 1H), 2.37-2.26 (m, 2H), 2016-2.08 (m, 1H), 1.97 (s, 3H); $^{13}$C NMR (CDCl$_3$, 126 MHz) $\delta$ 171.4, 144.3, 141.3, 133.3, 128.5, 127.8, 125.5, 112.8, 82.4, 34.4, 32.5, 10.5.

3ea-Isomer-2: TLC: $R_f = 0.28$ (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.52-7.22 (m, 5H), 6.79 (s, 1H), 5.21 (t, $J = 4.88$ Hz, 1H), 2.57-244 (m, 1H), 2.41-2.21 (m, 3H), 1.97 (s, 3H); $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 171.4, 144.5, 141.0, 133.5, 128.6, 128.4, 128.1, 126.3, 112.7, 85.0, 37.2, 34.1, 10.6; HRMS (ESI) m/z calcd for C$_{14}$H$_{13}$O$_3$ [M+H]$^+$ 231.1016, found 231.1016.
2-(prop-2-yn-1-yl)cyclohexan-1-ol (1f):

![Structure of 1f](image)

Compound 1f was prepared using analogous literature procedure: 

\[ \text{1H NMR (CDCl}_3, 500 MHz): \delta 3.38 (td, J = 9.9, 4.4 Hz, 1H), 2.50-2.42 (m, 1H), 2.32 (ddd, J = 16.8, 6.9, 2.7 Hz, 1H), 2.03-1.94 (m, 3H), 1.91-1.84 (m, 1H), 1.80-1.65 (m, 2H), 1.38-1.49 (m, 1H), 1.30-1.15 (m, 4H); \]

\[ \text{13}^\text{C NMR (CDCl}_3, 126 MHz): \delta 83.0, 73.5, 69.7, 43.9, 35.5, 30.3, 25.4, 24.9, 21.8; \text{HRMS (ESI) m/z calcd for C}_9\text{H}_{15}\text{O} [\text{M+H}]^+ 139.1117, \text{found 139.1114.} \]

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4'-methyl-3a,4,5,6,7,7a-hexahydro-3\textsuperscript{H},5\textsuperscript{H}-spiro[benzofuran-2,2'-furan]-5'-one (3fa and 3fa\textsuperscript{1}):

![Structures of 3fa and 3fa\textsuperscript{1}](image)

Following the General Procedure, to the mixture of 2-(prop-2-yn-1-yl)cyclohexan-1-ol (1f) (0.15 g, 1.09 mmol) and ethyl pyruvate (2a) (0.12 g, 1.09 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (5 mL) was added Bi(OTf)\textsubscript{3} (0.073 g, 0.22 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 24 h at rt. Purification of the crude product by silica gel column chromatography (SiO\textsubscript{2}, 8% EtOAc/hexanes) afforded two separable diastereomers of 4'-methyl-3a,4,5,6,7,7a-hexahydro-3\textsuperscript{H},5\textsuperscript{H}-spiro[benzofuran-2,2'-furan]-5'-one (0.095 g of 3fa (42%) and 0.048 g of 3fa\textsuperscript{1} (21%); α:β = 7:3) as a white solid.

\[ \text{3fa: TLC: } R_f = 0.6 \text{ (SiO}_2, 20\text% EtOAc/hexanes); \text{Relative stereochemistry was assigned based on NOE analysis (see below).} \]

\[ \text{1H NMR (CDCl}_3, 400 MHz): \delta 6.72 (s, 1H), 3.66-3.53 (m, 1H), 2.35 (dd, J = 13.4, 7.9 Hz, 1H), 2.20-2.06 (m, 2H), 1.99-1.93 (m, 1H), 1.91 (s, 3H), 1.88 (d, J = 11.6 Hz, 1H), 1.78 (d, J = 7.3 Hz, 1H), 1.63-1.51 (m, 1H), 1.45-1.30 \]

(m, 2H), 1.28-1.20 (m, 2H); $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 171.9, 145.7, 131.2, 111.8, 84.7, 46.3, 39.8, 30.5, 28.5, 25.5, 24.0, 10.3; HRMS (ESI) m/z calcd for C$_{12}$H$_{17}$O$_3$ [M+H]$^+$ 209.1172, found 209.1173.

Figure 1. Key NOE interactions in compound 3fa.

3fa$^1$: $R_f = 0.58$ (SiO$_2$, 20% EtOAc/hexanes), Relative stereochemistry was assigned based on analogy to 3fa; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 6.72 (d, $J$ = 1.5 Hz, 1H), 3.39 (td, $J$ = 10.7, 3.8 Hz, 1H), 2.17-2.11 (m, 2H), 2.0 (d, $J$ = 14.1 Hz, 1H), 1.97-1.92 (m, 1H), 1.91 (d, $J$ = 1.5 Hz, 3H), 1.88-1.85 (m, 1H), 1.78-1.73 (m, 1H), 1.50 (qd, $J$ = 11.7, 3.8 Hz, 1H), 1.31-1.24 (m, 3H), 1.17 (td, $J$ = 12.2, 3.4 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 126 MHz): $\delta$ 171.3, 145.9, 132.4, 111.4, 86.7, 43.7, 41.5, 31.3, 28.5, 25.5, 24.2, 10.4; HRMS (ESI) m/z calcd for C$_{12}$H$_{17}$O$_3$ [M+H]$^+$ 209.1172, found 209.1174.

2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (S9) and 2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (S10)

To a flame dried (100 mL) two neck round bottom flask, anhydrous THF (20 mL) was added under argon atmosphere and cooled it to 0 °C, to this diisopropylamine (0.42 mL, 4.16 mmol) followed by $n$-butyllithium (1.6 M in hexanes, 2.837 mL,) was added drop wise at 0
°C and stirred for 45 min at 0 °C to generate LDA solution. To this LDA solution was added 1-indanone (S8) (0.5 g, 3.78 mmol) in THF (20 mL) and stirred the reaction mixture at -78 °C for 30 min, then warmed to 0 °C and stirred for another 30 min. Reaction mixture was cooled back to -78 °C and propargyl bromide (80% in toluene, 0.2 mL, 3.78 mmol) was added drop wise. The resulting mixture was stirred at -78 °C for 1 h and warmed to 25 °C and stirred for overnight. The reaction was quenched with saturated aqueous NH₄Cl solution and extracted with EtOAc (3x25 mL), combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (S9) (0.2 g, 25%) and (S10) 2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (0.64 g, 42%) TLC: Rf = 0.6 and 0.59 (SiO₂, 20% EtOAc/hexanes); S9: ¹H NMR (CDCl₃, 200 MHz): δ 7.78 (d, J = 7.6 Hz, 1H), 7.69-7.58 (m, 1H), 7.53-7.45 (m, 1H), 7.44-7.34 (m, 1H), 3.32 (s, 2H), 2.71-2.44 (m, 4H), 1.88 (t, J = 2.7 Hz, 2H); HRMS (ESI) m/z calcd for C₁₅H₁₂NaO [M+Na]⁺ 231.0780, found 231.0774.

S10: ¹H NMR (CDCl₃, 500 MHz): δ 7.76 (d, J = 7.3 Hz, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.49 (d, J = 7.3 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 3.40 (dd, J = 17.7, 8.54 Hz, 1H), 3.10 (dd, J = 17.1, 4.3 Hz, 1H), 2.89-2.84 (m, 1H), 2.81-2.74 (m, 1H), 2.54 (ddd, J = 16.4, 7.9, 2.4 Hz, 1H), 1.90 (t, J = 2.7 Hz, 1H); HRMS (ESI) m/z calcd for C₁₂H₁₁O [M+H]⁺ 171.0804, found 171.0799.

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2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-ol (1g):

To a solution of 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (S9) (0.13 g 0.66 mmol) in methanol (3 mL), sodium borohydride (0.015 g, 0.4 mmol) was slowly added at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then for 2.5 h at room temperature, after which the solvent was evaporated under reduced pressure. Aqueous NH₄Cl solution (5 mL) was added to the resulting suspension, and then extracted with EtOAc (3×5 mL). Organic phases were combined and dried over anhydrous Na₂SO₄, filtered and the
solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO$_2$, 6% EtOAc/hexanes) to afford 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-ol (1g) (0.12 g, 87%) as a colourless liquid. TLC: $R_f = 0.4$ (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.46-7.36 (m, 1H), 7.32-7.22 (m, 3H), 5.13 (s, 1H), 3.09 (d, $J = 15.9$ Hz, 1H), 2.92 (d, $J = 15.9$ Hz, 1H), 2.66 (dd, $J = 17.1, 2.4$ Hz, 1H), 2.62-2.52 (m, 2H), 2.44 (dd, $J = 17.1, 2.4$ Hz, 1H), 2.28 (br s, 1H), 2.12 (t, $J = 2.4$ Hz, 1H), 2.05 (t, $J = 2.7$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 126 MHz): $\delta$ 142.8, 140.5, 128.6, 127.1, 125.2, 124.7, 81.9, 81.6, 80.7, 71.4, 70.6, 50.0, 40.1, 26.0, 22.1; HRMS (ESI) m/z calcd for C$_{15}$H$_{15}$O [M+H]$^+$ 211.1117, found 211.1119.

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4-methyl-3a'-((prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5H-spiro[furan-2,2'-indenophen][1,2-b][furan]-5-one (3ga, 3ga$^1$)

Following the General Procedure, to the mixture of 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-ol (1g) (0.05 g, 0.24 mmol) and ethyl pyruvate (2a) (0.027 g, 0.24 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added Bi(OTf)$_3$ (0.032 g, 0.05 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO$_2$, 5% EtOAc/hexanes) afforded 4-methyl-3a'-((prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5H-spiro[furan-2,2'-indenophen][1,2-b][furan]-5-one and its diastereomer (77% yield; 0.04 g of 3ga (60%) and 0.011 g of 3ga$^1$ (17%) isolated yield $dr$: 8:2).

3ga: TLC: $R_f = 0.4$ (SiO$_2$, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on NOE analysis (see below); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.43-7.25 (m, 4H), 6.56 (s, 1H), 5.59 (s, 1H), 3.30 (d, $J = 16.5$ Hz, 1H), 3.10 (d, $J = 17.1$ Hz, 1H), 2.88 (ABq, $J = 17.0, 3.0$ Hz, 2H), 2.50 (d, $J = 13.4$ Hz, 1H), 2.21 (d, $J = 14.0$ Hz, 1H), 1.99 (t, $J = 2.7$ Hz, 1H), 1.93 (d, $J = 1.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 126 MHz): $\delta$ 171.2, 144.5, 141.2, 140.8, 127.1, 125.2, 124.7, 81.9, 81.6, 80.7, 71.4, 70.6, 50.0, 40.1, 26.0, 22.1; HRMS (ESI) m/z calcd for C$_{15}$H$_{15}$O [M+H]$^+$ 211.1117, found 211.1119.
133.3, 129.4, 127.5, 125.7, 125.4, 113.2, 93.7, 81.4, 70.0, 52.6, 46.8, 43.0, 27.4, 10.5; HRMS (ESI) m/z calcd for C\textsubscript{18}H\textsubscript{17}O\textsubscript{3} [M+H]\textsuperscript{+} 281.1172, found 281.1175.

**Figure 2.** Key NOE interactions in compound 3ga.

3ga\textsuperscript{1}: TLC: \(R_f = 0.38\) (SiO\textsubscript{2}, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on analogy to 3ga; \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 7.40 (d, \(J = 7.3\) Hz, 1H), 7.37-7.30 (m, 1H), 7.27-7.22 (m, 2H), 6.77 (s, 1H), 5.47 (s, 1H), 3.61 (d, \(J = 16.5\) Hz, 1H), 3.04 (d, \(J = 16.5\) Hz, 1H), 2.67-2.56 (m, 2H), 2.53-2.45 (m, 1H), 2.38 (d, \(J = 13.4\) Hz, 1H), 2.06 (br s., 1H), 1.91 (s, 3H); \(^1^3\)C NMR (CDCl\textsubscript{3}, 101 MHz): \(\delta\) 171.4, 144.6, 142.7, 139.6, 133.3, 129.6, 127.4, 126.1, 125.3, 113.9, 94.4, 80.8, 70.6, 52.6, 46.5, 43.7, 28.4, 10.4; HRMS (ESI) m/z calcd for C\textsubscript{18}H\textsubscript{17}O\textsubscript{3} [M+H]\textsuperscript{+} 281.1172, found 281.1175.

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4-phenyl-3a',(prop-2-yn-1-yl)-3',4',8b'-tetrahydro-5H-spiro[furan-2,2'-indeno[1,2-b]furan]-5-one (3gb)

Following the General Procedure, to the mixture of 2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-ol (1h) (0.1 g, 0.48 mmol) and ethyl phenyl glyoxylate (2b)(0.08 g, 0.48 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (5 mL) was added Bi(OTf)\textsubscript{3} (0.06 g, 0.1 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt.
Purification of the crude product by silica gel column chromatography (SiO₂, 3% EtOAc/hexanes) afforded inseparable diastereomeric mixture of 4-phenyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5H-spiro[furan-2,2'-indeno[1,2-b]furan]-5-one (3gb) in 0.104 g (64% yield, dr: 1:1) as a solid. TLC: \( R_f = 0.5 \) (SiO₂, 20% EtOAc/hexanes); (3gb; mixture of two diastereomers): Relative stereochemistry was assigned based on analogy to 3ga¹. \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta \) 7.84-7.74 (m, 2H), 7.45-7.12 (m, 9H), 7.02 (s, 1H), 5.63 (s, 1H), 3.76-3.67 (m, 1H), 3.35-3.25 (m, 1H), 3.2-3.07 (m, 2H), 3.03-2.94 (m, 1H), 2.93-2.81 (m, 3H), 2.62-2.47 (m, 4H), 2.34-2.21 (m, 2H), 2.09-1.95 (m, 2H); \(^1^\)C NMR (CDCl₃, 101 MHz): \( \delta \) 168.9, 143.1, 141.1, 140.8, 134.3, 129.9, 129.5, 128.8, 128.7, 127.6, 127.5, 127.4, 127.2, 125.8, 125.4, 125.3, 124.7, 112.4, 93.8, 81.4, 71.1, 70.2, 52.8, 50.6, 50.2, 48.8, 47.1, 43.7, 43.4, 42.9, 28.5, 27.4; HRMS (ESI) m/z calcd for C₂₃H₁₉O₃ [M+H]^+ 343.1329, found 343.1335.

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2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1h)

To a flame dried (100 mL) two neck round bottom flask, anhydrous THF (50 mL) was added under argon atmosphere and cooled it to 0 °C, to this diisopropylamine (3.16 mL, 22.2 mmol) followed by n-butyllithium (1.6 M in hexanes, 12.82 mL,) was added drop wise at 0 °C and stirred for 45 min at 0 °C to generate LDA solution. To this LDA solution was added 1-tetralone (S11) (2.5 g, 17.1 mmol) in THF (10 mL) and stirred the reaction mixture at -78 °C for 30 min, then warmed to 0 °C and stirred for another 30 min. Reaction mixture was cooled back to -78 °C and propargyl bromide (80% in toluene, 1.2 mL, 17.1 mmol) was added drop wise. The resulting mixture was stirred at -78 °C for 1 h and warmed to 25 °C and stirred for overnight. The reaction was quenched with saturated aqueous NH₄Cl solution and extracted with EtOAc (4x50 mL), combined organic layers were dried over anhydrous Na₂SO₄, concentrated under reduced pressure to give the crude product S12 in (1 g, 26% yield), which was subjected to next reaction without further purification. To a solution of S12 (0.3 g, 1.35 mmol) in methanol (10 mL), sodium borohydride (0.05 g, 1.35 mmol) was slowly
added at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then for 2.5 h at room temperature, after which the solvent was evaporated under reduced pressure. Aqueous NH₄Cl solution (5 mL) was added to the resulting suspension, and then extracted with EtOAc (3×10 mL). Organic phases were combined and dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO₂, 8% EtOAc/hexanes) to afford 2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1h) (0.28 g, 92%) as a solid as a colourless liquid. TLC: \( R_f = 0.35 \) (SiO₂, 20% EtOAc/hexanes); \(^1\)H NMR (CDCl₃, 200 MHz) \( \delta \) 7.46-7.40 (m, 1H), 7.26-7.20 (m, 2H), 7.17-7.11 (m, 1H), 4.68 (d, \( J = 5.3 \) Hz, 1H), 2.92-2.76 (m, 2H), 2.44 (AB q, \( J = 2.2 \) Hz, 16.7 Hz, 2H), 2.43 (AB q, \( J = 17.1, 2.2 \) Hz, 2H), 2.15 (d, \( J = 5.7 \) Hz, 1H), 2.09 (t, \( J = 2.7 \) Hz, 1H), 2.06 (t, \( J = 2.7 \) Hz, 1H), 1.98-1.90 (m, 1H), 1.90-1.83 (m, 1H); \(^1^3\)C NMR (CDCl₃, 126 MHz): \( \delta \) 136.7, 135.7, 129.4, 128.9, 127.9, 126.5, 81.1, 80.8, 72.6, 71.0, 70.9, 39.9, 26.6, 25.4, 23.8, 23.2; HRMS (ESI) m/z calcld for C_{16}H_{17}O \[M+H]^+ \) 225.1274, found 225.1268.

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4-methyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'H,5H-spiro[furan-2,2'-naphtho[1,2-b]furan]-5-one (3ha, 3ha¹)

Following the *General Procedure*, to the mixture of 2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1h) (0.1 g, 0.45 mmol) and ethyl pyruvate (2a) (0.05 g, 0.45 mmol) in anhydrous CH₂Cl₂ (5 mL) was added Bi(OTf)₃ (0.05 g, 0.09 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 5% EtOAc/hexanes) afforded 4-methyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'H,5H-spiro[furan-2,2'-naphtho[1,2-b]furan]-5-one along with their partially separable diastereomer (70% yield,: 0.069 g (52%) and 0.023 g (18%) isolated yield (3ha:3ha¹; \( dr: \beta: \alpha: 8.57:1.43 \)) as a solid.
**3ha:** TLC: $R_f = 0.3$ (SiO$_2$, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on NOE analysis (see below); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.38 (d, 7.3 Hz, 1H), 7.33-7.23 (m, 2H), 7.22-7.17 (m, 1H), 6.67 (s, 1H), 5.0 (s, 1H), 2.85-2.75 (m, 2H), 2.65-2.52 (m, 3H), 2.34 (d, $J = 14.0$ Hz, 1H), 2.07-1.97 (m, 2H), 1.97-1.87 (m, 4H); $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 171.5, 144.7, 137.2, 132.8, 132.3, 130.9, 128.7, 128.5, 126.7, 111.2, 83.9, 80.5, 70.8, 46.4, 43.9, 31.1, 26.6, 25.8, 10.4; HRMS (ESI) m/z calcd for C$_{19}$H$_{19}$O$_3$ [M+H]$^+$ 295.1329, found 295.1318.

**Figure 3.** Key NOE interactions in compound 3ha.

**3ha**$^1$ impure with 3ha (3ha+3ha$^1$; dr: $\beta$: $\alpha$: 1 : 1.25): TLC: $R_f = 0.3$-0.29 (SiO$_2$, 20% EtOAc/hexanes); Relative stereochemistry was assigned based on analogy to 3ha; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.43-7.35 (m, 2H), 7.32-7.17 (m, 9H), 6.81 (d, $J = 1.1$ Hz, 1H), 6.67 (d, $J = 1.5$ Hz, 1H), 5.01 (s, 1H), 4.93 (s, 1H), 2.97- 2.31 (m, 13H), 2.13-1.9 (m, 10H); $^{13}$C NMR (CDCl$_3$, 126 MHz): $\delta$ 171.5, 171.2, 145.7, 144.7, 137.2, 136.2, 132.9, 132.6, 132.3, 132.2, 130.9, 130.7, 128.7, 128.7, 128.5, 128.5, 126.7, 126.6, 111.9, 111.2, 83.9, 83.8, 80.5, 80.3, 71.5, 70.8, 46.6, 46.4, 43.9, 43.2, 31.2, 29.7, 28.3, 26.6, 25.8, 25.5, 10.4, 10.4; HRMS (ESI) m/z calcd for C$_{19}$H$_{19}$O$_3$ [M+H]$^+$ 295.1329, found 295.1319.

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4-phenyl-3a'-((prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'H,5H-spiro[furan-2,2'-naphtho[1,2-b]furan]-5-one (3hb)

Following the General Procedure, to the mixture of 2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1h) (0.1 g, 0.45 mmol) and ethyl phenylglyoxylate (2b) (0.08 g, 0.45 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added Bi(OTf)$_3$ (0.05 g, 0.09 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO$_2$, 5% EtOAc/hexanes) afforded 0.097 g of inseparable diastereomeric mixture of 4-phenyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'H,5H-spiro[furan-2,2'-naphtho[1,2-b]furan]-5-one 3hb (61% yield, (dr: 8:2)) as a solid. TLC: $R_f = 0.5$ (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.89-7.79 (m, 2H), 7.48-7.10 (m, 12H), 5.08 (s, 1H), 3.5-2.2 (m, 12H), 2.16-1.75 (m, 5H); $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 169.2, 144.2, 143.2, 137.2, 133.8, 132.2, 131.0, 130.8, 130.1, 129.8, 129.4, 128.8, 128.7, 128.6, 127.5, 126.8, 126.6, 126.5, 126.4, 110.4, 84.0, 83.9, 80.5, 71.4, 70.9, 51.1, 46.8, 46.7, 44.1, 42.8, 40.2, 31.2, 28.2, 26.6, 26.5, 25.8, 25.3; HRMS (ESI) m/z calcd for C$_{24}$H$_{21}$O$_3$ [M+H]$^+$ 357.1485, found 357.1473.

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(E)-3-styryl-1,13-dioxadispiro[4.1.4.7.2]tridec-3-en-2-one (3bf)

Following the General Procedure, to the mixture of 1-(pent-2-yn-1-yl) cyclopentyl methanol (1b) (0.1 g, 0.14 mmol) and ethyl (E)-2-oxo-4-phenylbut-3-enoate (2f)$^{10}$ (0.294 g, 0.14 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added Bi(OTf)$_3$ (0.189 g, 0.028 mmol) under

argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 5% EtOAc/hexanes) afforded \((E)-3\text{-styryl-1,13-dioxadispiro}[4.1.4.2^5]\text{tridec-3-en-2-one (3bf)}\) (0.135 g, 63%) as a solid. TLC: \(R_f = 0.6\) (SiO₂, 20% EtOAc/hexanes); \(^1\text{H NMR (CDCl}_3, 500 \text{ MHz) \(\delta\) 7.71 (d, } J = 16.44 \text{ Hz, 1H}, 7.51 (d, } J = 7.3 \text{ Hz, 2H}, 7.39-7.30 (m, 3H), 6.90 (s, 1H), 6.81 (d, } J = 14.44 \text{ Hz, 1H}, 4.06 (d, } J = 8.54 \text{ Hz, 1H}, 3.9 (d, } J = 8.54 \text{ Hz, 1H} 2.27 (s, 2H), 1.93-1.84 (m, 2H), 1.52-1.78 (m, 6H); \(^{13}\text{C NMR (CDCl}_3, 126 \text{ MHz) \(\delta\) 169.4, 143.0, 136.6, 136.2, 131.4, 128.7, 127.1, 116.1, 113.1, 81.2, 50.5, 47.8, 38.0, 24.6, 24.4; HRMS (ESI) m/z calcd for C₁₉H₂₁O₃ [M+H]^+ 297.1486, found 297.1485.

6. Synthesis and Characterization of unsaturated \(\gamma\)-spiroketal-\(\gamma\)-lactones from alkynols possessing internal alkyne functionality:

3, 4-Dimethyl-1, 14-dioxadispiro \([4.1.5.2^5]\text{tetradec-3-en-2-one (6aa)}\):

Following the General Procedure, to the mixture of (1-(but-2-yn-1-yl) cyclohexyl)methanol (4a) (0.05 g, 0.3 mmol) and ethyl pyruvate 2a (0.05 g, 0.3 mmol) in anhydrous CH₂Cl₂ (3 mL) was added Bi(OTf)₃ (0.04 g, 0.06 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 5% EtOAc/hexanes) gave 3, 4-dimethyl-1, 14-dioxadispiro \([4.1.5.2^5]\text{tetradec-3-en-2-one (6aa)}\) (0.046 g, 65%) as a yellow oil. TLC: \(R_f = 0.7\) (SiO₂, 20% EtOAc/hexanes); \(^1\text{H NMR (CDCl}_3, 500 \text{ MHz}) \(\delta\) 3.95 (d, } J = 8.8 \text{ Hz, 1H), 3.85 (d, } J = 8.8 \text{ Hz, 1H), 2.04-1.94 (m, 2H), 1.90 (s, 3H), 1.80 (s, 3H), 1.72-1.65 (m, 2H), 1.53-1.39 (m, 8H); \(^{13}\text{C NMR (CDCl}_3, 126 \text{ MHz}) \(\delta\) 171.7, 154.9, 126.0, 114.5, 80.6, 45.7, 43.4, 37.4, 35.6, 25.5, 23.8, 23.7, 10.5, 8.6; HRMS (ESI) m/z calcd for C₁₄H₂₁O₃ [M+H]^+ 237.1485, found 237.1486.
4-Methyl-3-phenyl-1, 14-dioxadispiro [4.1.5.7.2.5] tetradec-3-en-2-one (6ab):

Following the *General Procedure*, to the mixture of (1-(but-2-yn-1-yl) cyclohexyl) methanol (4a) (0.05 g, 0.3 mmol) and ethyl phenylglyoxylate (2b) (0.054 g, 0.3 mmol) in dry CH₂Cl₂ (3 mL) was added Bi(OTf)₃ (0.04 g, 0.066 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO₂, 3% EtOAc/hexanes) afforded 4-methyl-3-phenyl-1, 14-dioxadispiro[4.1.5.7.2.5] tetradec-3-en-2-one (6ab) (0.062 g, 68%) as a crystalline solid. TLC: *R*ᵣ = 0.5 (SiO₂, 20% EtOAc/hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 7.53-7.34 (m, 5H), 4.06 (d, *J* = 8.5 Hz, 1H), 3.95 (d, *J* = 7.9 Hz, 1H), 2.23-2.05 (m, 2H), 2.13 (s, 3H), 1.83-1.72 (m, 2H), 1.60-1.45 (m, 8H); ¹³C NMR (CDCl₃, 101 MHz): δ 169.9, 156.0, 129.6, 129.0, 128.98, 128.7, 128.5, 113.9, 80.9, 46.1, 43.7, 37.4, 35.6, 25.5, 23.9, 23.8, 11.5; HRMS (ESI) m/z calcd for C₁₉H₂₃O₃ [M+H]^+ 299.1642, found 299.1643.

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3-(4-Methoxyphenyl)-4-methyl-1, 14-dioxadispiro [4.1.5.7.2.5] tetradec-3-en-2-one (6ac):

Following the *General Procedure*, to the mixture of (1-(but-2-yn-1-yl) cyclohexyl) methanol (4a) (0.050 g, 0.3 mmol) and ethyl anisylglyoxylate (2c) (0.063 g, 0.3 mmol) in anhydrous CH₂Cl₂ (3 mL) was added Bi(OTf)₃ (0.04 g, 0.066 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO₂, 5% EtOAc/hexanes) afforded 3-(4-
methoxyphenyl)-4-methyl-1, 14-dioxadispiro [4.1.5.2\textsuperscript{5}] tetradec-3-en-2-one (6ac) (0.062 g, 62%) as a crystalline solid. TLC: \( R_f = 0.45 \) (SiO\(_2\), 20\% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta 7.46 \) (d, \( J = 8.5 \) Hz, 2H), 6.97 (d, \( J = 8.5 \) Hz, 2H), 4.05 (d, \( J = 7.9 \) Hz, 1H), 3.94 (d, \( J = 8.5 \) Hz, 1H), 3.85 (s, 3H), 2.12 (s, 3H), 2.21-2.04 (m, 2H), 1.76-1.7 (m, 2H), 1.61-1.41 (m, 8H); \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \( \delta 170.2\), 159.8, 154.3, 130.4, 128.4, 122.0, 113.9, 80.8, 55.3, 46.1, 43.6, 37.4, 35.7, 25.6, 23.9, 23.8, 11.6; HRMS (ESI) m/z calcd for C\(_{20}\)H\(_{25}\)O\(_4\) [M+H]\(^+\) 329.1747, found 329.1739.

4-Methyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5.2\textsuperscript{5}] tetradec-3-en-2-one (6ad):

Following the \textit{General Procedure}, to the mixture of (1-(but-2-yn-1-yl) cyclohexyl) methanol (4a) (0.05 g, 0.3 mmol) and ethyl p-tolylglyoxylate (2d) (0.058 g, 0.3 mmol) in anhydrous CH\(_2\)Cl\(_2\) (3 mL) was added Bi\((\text{OTf})_3\) (0.04 g, 0.066 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO\(_2\), 4\% EtOAc/hexanes) gave 4-methyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5.2\textsuperscript{5}] tetradec-3-en-2-one (6ad) (0.068 g, 72%) as a crystalline solid. TLC: \( R_f = 0.45 \) (SiO\(_2\), 20\% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta 7.40 \) (d, \( J = 7.9 \) Hz, 2H), 7.26 (d, \( J = 7.9 \) Hz, 2H), 4.06 (d, \( J = 8.5 \) Hz, 1H), 3.94 (d, \( J = 8.5 \) Hz, 1H), 2.40 (s, 3H), 2.12 (s, 3H), 2.21-2.05 (m, 2H), 1.81-1.72 (m, 2H), 1.56-1.34 (m, 8H); \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \( \delta 170.0\), 159.8, 154.3, 130.4, 128.4, 122.0, 113.9, 80.8, 55.3, 46.1, 43.6, 37.4, 35.7, 25.6, 23.9, 23.8, 11.6; HRMS (ESI) m/z calcd for C\(_{20}\)H\(_{25}\)O\(_3\) [M+H]\(^+\) 313.1798, found 313.1808.

4-Ethyl-3-methyl-1, 14-dioxadispiro [4.1.5.2\textsuperscript{5}] tetradec-3-en-2-one (6ba):
Following the **General Procedure**, to the mixture of (1-(pent-2-yn-1-yl) cyclohexyl) methanol (4b) (0.1 g, 0.55 mmol) and ethyl pyruvate (2a) (0.064 g, 0.55 mmol) in anhydrous \( \text{CH}_2\text{Cl}_2 \) (3 mL) was added Bi(OTf\(_3\)) (0.073 g, 0.11 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO\(_2\), 5% EtOAc/hexanes) provided 4-ethyl-3-methyl-1, 14-dioxadispiro [4.1.5.2\(^5\)] tetradec-3-en-2-one (6ba) (0.093 g, 68%) as a colourless oil. TLC: \( R_f = 0.45 \) (SiO\(_2\), 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 3.96 (d, \( J = 8.5 \text{ Hz} \), 1H), 3.86 (d, \( J = 7.9 \text{ Hz} \), 1H), 2.44-2.31 (m, 1H), 2.31-2.2 (m, 1H), 2.06-1.96 (m, 2H), 1.84 (s, 3H), 1.74-1.67 (m, 2H), 1.55-1.39 (m, 8H), 1.17 (t, \( J = 7.6 \text{ Hz} \), 3H); \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): \( \delta \) 171.9, 159.4, 126.0, 114.9, 80.5, 45.9, 43.3, 37.6, 35.7, 25.5, 23.9, 23.7, 18.9, 12.3, 8.6; HRMS (ESI) m/z calcd for C\(_{15}\)H\(_{23}\)O\(_3\) [M+H\(^+\)] 251.1642, found 251.1644.

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**4-Ethyl-3-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6bb):**

![6bb](image)

Following the **General Procedure**, to the mixture of (1-(pent-2-yn-1-yl) cyclohexyl) methanol (4b) (0.1 g, 0.55 mmol) and ethyl phenylglyoxylate (2b) (0.099 g, 0.55 mmol) in anhydrous \( \text{CH}_2\text{Cl}_2 \) (3 mL) was added Bi(OTf\(_3\)) (0.073 g, 0.11 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO\(_2\), 3% EtOAc/hexanes) afforded 4-ethyl-3-phenyl-1, 14-dioxadispiro [4.1.5^7.2^5] tetradec-3-en-2-one (6bb) (0.122 g, 70%) as a solid. TLC: \( R_f = 0.5 \) (SiO\(_2\), 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 500 MHz): \( \delta \) 7.55-7.34 (m, 5H), 4.06 (d, \( J = 8.4 \text{ Hz} \), 1H), 3.95 (d, \( J = 8.4 \text{ Hz} \), 1H), 2.68-2.58 (m, 1H), 2.46-2.37 (m, 1H), 2.18 (s, 2H), 1.81-1.74 (m, 2H), 1.62-1.43 (m, 8H), 1.18 (t, \( J = 7.6 \text{ Hz} \), 3H); \(^{13}\)C NMR (CDCl\(_3\), 126 MHz): \( \delta \) 170.1, 160.5, 129.8, 129.4, 129.1, 128.9, 128.7, 128.4, 114.6, 80.7, 46.3, 43.5, 37.6, 35.7, 25.6, 23.9, 23.8, 19.4, 12.5; HRMS (ESI) m/z calcd for C\(_{20}\)H\(_{25}\)O\(_3\) [M+H\(^+\)] 313.1798, found 313.1797.

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4-Ethyl-3-(4-methoxyphenyl)-1, 14-dioxadispiro [4.1.5.7.2^5] tetradec-3-en-2-one (6bc):

![Structure of 6bc]

Following the General Procedure, to the mixture of (1-(pent-2-yn-1-yl) cyclohexyl) methanol (4b) (0.1 g, 0.55 mmol) and ethyl anisylglyoxylate (2c) (0.114 g, 0.55 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added Bi(OTf)$_3$ (0.073 g, 0.11 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO$_2$, 2% EtOAc/hexanes) gave 4-ethyl-3-(4-methoxyphenyl)-1, 14-dioxadispiro [4.1.5.7.2^5] tetradec-3-en-2-one (6bc) (0.146 g, 72%) as a solid. TLC: $R_f$ = 0.5 (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.44 (d, $J$ = 8.5 Hz, 2H), 6.96 (d, $J$ = 8.5 Hz, 2H), 4.03 (d, $J$ = 8.5 Hz, 1H), 3.93 (d, $J$ = 8.5 Hz, 1H), 3.84 (s, 3H), 2.69-2.54 (m, 1H), 2.47-2.32 (m, 1H), 2.15 (s, 2H), 1.82-1.71 (m, 2H), 1.60-1.41 (m, 8H), 1.18 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 170.4, 159.8, 159.0, 130.2, 128.7, 122.2, 114.5, 113.9, 80.6, 55.3, 46.3, 43.4, 37.6, 35.7, 25.6, 23.9, 23.8, 19.4, 12.5; HRMS (ESI) m/z calcd for C$_{21}$H$_{27}$O$_4$ [M+H]$^+$ 343.1904, found 343.1905.

4-Ethyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5.7.2^5] tetradec-3-en-2-one (6bd):

![Structure of 6bd]

Following the General Procedure, to the mixture of (1-(pent-2-yn-1-yl) cyclohexyl) methanol (4b) (0.1 g, 0.55 mmol) and ethyl p-tolylglyoxylate (2d) (0.106 g, 0.55 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added Bi(OTf)$_3$ (0.073 g, 0.11 mmol) under argon atmosphere at room temperature and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO$_2$, 2% EtOAc/hexanes) afforded 4-ethyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5.7.2^5] tetradec-3-en-2-one (6bd) (0.13 g, 76%) as a solid. TLC: $R_f$ = 0.6 (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.38 (d, $J$ = 8.4 Hz, 2H), 7.25 (d, $J$ = 7.6 Hz, 2H), 4.05 (d, $J$ = 8.4 Hz, 1H), 3.95 (d, $J$ = 8.8 Hz, 1H), 2.68-
2.58 (m, 1H), 2.4 (s, 3H), 2.46-2.36 (m, 1H), 2.17 (s, 2H), 1.81-1.74 (m, 2H), 1.63-1.43 (m, 8H), 1.19 (t, J = 7.6 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 126 MHz): δ 170.3, 159.8, 138.7, 129.3, 129.2, 128.8, 127.3, 126.9, 114.5, 80.6, 46.3, 43.4, 37.6, 35.8, 25.6, 23.9, 23.8, 21.3, 19.4, 12.5; HRMS (ESI) m/z calculated for C$_{21}$H$_{27}$O$_3$ [M+H]$^+$ 327.1955, found 327.1959.

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3-Methyl-4-phenyl-1, 14-dioxadispiro [4.1.5.2] tetradec-3-en-2-one (6ca):

Following the General Procedure, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclohexyl) methanol (4c) (0.1 g, 0.43 mmol) and ethyl pyruvate (2a) (0.052 g, 0.43 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added Bi(OTf)$_3$ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO$_2$, 3% EtOAc/hexanes) afforded 3-methyl-4-phenyl-1, 14-dioxadispiro [4.1.5.2] tetradec-3-en-2-one (6ca) (0.097g, 74%) as a white solid. TLC: $R_f$ = 0.60 (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 500 MHz): δ 7.56-7.40 (m, 5H), 4.09 (d, J = 8.5 Hz, 1H), 3.94 (d, J = 8.5 Hz, 1H), 2.09 (d, J = 14.0 Hz, 1H), 2.0 (s, 3H), 1.86 (d, J = 14.0 Hz, 1H), 1.78-1.71 (m, 2H), 1.54-1.44 (m, 2H), 1.42-1.29 (m, 6H); $^{13}$C NMR (CDCl$_3$, 126 MHz): δ 171.7, 154.8, 131.1, 129.6, 128.7, 128.4, 127.1, 115.0, 80.9, 43.3, 37.4, 35.8, 25.5, 23.9, 23.6, 9.9; HRMS (ESI) m/z calculated for C$_{19}$H$_{23}$O$_3$ [M+H]$^+$ 299.1642, found 299.1644.

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3, 4-Diphenyl-1, 14-dioxadispiro [4.1.5.2] tetradec-3-en-2-one (6cb):
Following the General Procedure, to the mixture of (1-(3-phenylprop-2-yn-1-yl)cyclohexyl) methanol (4e) (0.1 g, 0.43 mmol) and ethyl phenylglyoxylate (2b) (0.078 g, 0.43 mmol) in anhydrous CH₂Cl₂ (5 mL) was added Bi(OTf)₃ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature the reaction mixture was stirred for 12 h at rt. Purification of the crude product by crystallization (hexane:CH₂Cl₂ (8.2)) afforded 3, 4-diphenyl-1, 14-dioxadispiro [4.1.5.7.2] tetradec-3-en-2-one, (6cb) (0.187 g, 73%) as a solid. TLC: Rf = 0.5 (SiO₂, 20% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz): δ 7.43-7.34 (m, 7H), 7.34-7.29 (m, 3H), 4.15 (d, J = 8.4 Hz, 1H), 3.98 (d, J = 8.4 Hz, 1H), 2.20 (d, J = 13.7 Hz, 1H), 1.93 (d, J = 13.7 Hz, 1H), 1.84-1.76 (m, 2H), 1.56-1.48 (m, 2H), 1.44-1.31 (m, 6H); ¹³C NMR (CDCl₃, 101 MHz): δ 169.8, 155.2, 131.0, 129.7, 129.5, 129.4, 128.9, 128.7, 128.71, 128.4, 114.4, 81.0, 43.4, 37.3, 35.8, 25.5, 23.9, 23.7; HRMS (ESI) m/z calcd for C₂₄H₂₅O₃ [M+H]⁺ 361.1798, found 361.1798.

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3-(4-Methoxyphenyl)-4-phenyl-1, 14-dioxadispiro [4.1.5.7.2] tetradec-3-en-2-one (6cc):

Following the General Procedure, to the mixture of (1-(3-phenylprop-2-yn-1-yl)cyclohexyl) methanol (4e) (0.1 g, 0.43 mmol) and ethyl anisylglyoxylate (2c) (0.091 g, 0.43 mmol) in anhydrous CH₂Cl₂ (5 mL) was added Bi(OTf)₃ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 5% EtOAc/hexanes) afforded 3-(4-methoxyphenyl)-4-phenyl-1, 14-dioxadispiro [4.1.5.7.2] tetradec-3-en-2-one (6cc) (0.116 g, 68%) as a solid. TLC: Rf = 0.45 (SiO₂, 20% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz): δ 7.46-7.33 (m, 7H), 6.82 (d, J = 8.5 Hz, 2H), 4.13 (d, J = 8.5 Hz, 1H), 3.95 (d, J = 8.5 Hz, 1H), 3.81 (s, 3H), 2.17 (d, J = 13.4 Hz, 1H), 1.90 (d, J = 14.0 Hz, 1H), 1.82-1.74 (m, 2H), 1.54-1.47 (m, 2H), 1.43-1.25 (m, 6H); ¹³C NMR (CDCl₃, 101 MHz): δ 170.2, 160.0, 153.5, 131.4, 130.9, 129.5, 128.7, 128.7, 128.3, 121.7, 114.4, 113.8, 80.9, 55.2, 43.4, 37.3, 35.8, 29.7, 25.5, 23.9, 23.7; HRMS (ESI) m/z calcd for C₂₅H₂₅O₄ [M+H]⁺ 391.1904, found 391.1901.
4-Phenyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5.7.2.5] tetradec-3-en-2-one (6cd):

Following the General Procedure, to the mixture of (1-(3-phenylprop-2-yn-1-yl)cyclohexyl) methanol (4c) (0.1 g, 0.43 mmol) and ethyl p-tolylglyoxylate (2d) (0.084 g, 0.43 mmol) in anhydrous CH₂Cl₂ (5 mL) was added Bi(OTf)₃ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature, the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 3% EtOAc/hexanes) afforded 4-phenyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5.7.2.5] tetradec-3-en-2-one (6cd) (0.088 g, 66%) as a white solid. TLC: Rf = 0.5 (SiO₂, 20% EtOAc/hexanes); ¹H NMR (CDCl₃, 500 MHz): δ 7.45-7.28 (m, 7H), 7.14-7.07 (m, 2H), 4.15 (d, J = 8.5 Hz, 1H), 3.96 (d, J = 8.5 Hz, 1H), 2.34 (s, 3H), 2.18 (d, J = 13.4 Hz, 1H), 1.91 (d, J = 14.0 Hz, 1H), 1.82-1.72 (m, 2H), 1.57-1.46 (m, 2H), 1.43-1.28 (m, 6H); ¹³C NMR (CDCl₃, 126 MHz): δ 170.0, 154.4, 138.9, 131.2, 129.6, 129.4, 129.1, 128.8, 128.7, 126.4, 114.4, 81.0, 46.5, 43.4, 37.3, 35.8, 25.5, 24.0, 23.7, 21.4; HRMS (ESI) m/z calcd for C₂₅H₂₇O₃ [M+H]⁺ 375.1955, found 375.1956.

3-(4-Nitrophenyl)-4-phenyl-1, 14-dioxadispiro [4.1.5.7.2.5] tetradec-3-en-2-one (6ce):

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Following the General Procedure, to the mixture of (1-(3-phenylprop-2-yn-1-yl)cyclohexyl) methanol (4c) (0.1 g, 0.43 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (2e) (0.97 g, 0.43 mmol) in anhydrous CH₂Cl₂ (5 mL) was added Bi(OTf)₃ (0.057 g, 0.086 mmol) under argon atmosphere at room temperature, the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 3% EtOAc/hexanes) afforded 3-(4-nitrophenyl)-4-phenyl-1,14-dioxadispiro[4.1.5.2]tetradec-3-en-2-one (6ce) (0.125 g, 70%) as a yellow solid. TLC: Rf = 0.65 (SiO₂, 20% EtOAc/hexanes); ¹H NMR (CDCl₃, 500 MHz): δ 8.16 (d, J = 8.54 Hz, 2H), 7.61 (d, J = 9.16 Hz, 2H), 7.51-7.35 (m, 5H), 4.17 (d, J = 8.55 Hz, 1H), 3.98 (d, J = 8.55 Hz, 1H), 2.22 (d, J = 14.04 Hz, 1H), 1.93 (d, J = 14.04 Hz, 1H), 1.84-1.74 (m, 2H), 1.56-1.48 (m, 2H), 1.44-1.25 (m, 6H); ¹³C NMR (CDCl₃, 126 MHz): δ 168.8, 158.4, 147.8, 130.6, 130.5, 129.2, 128.5, 123.5, 114.6, 81.3, 53.4, 43.6, 37.2, 35.8, 25.5, 23.9, 23.6; HRMS (ESI) m/z calcd for C₂₄H₂₂O₅N [M+H]⁺ 406.1649, found 406.1640.

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3-Methyl-4-phenyl-1,13-dioxadispiro[4.1.4.2]tridec-3-en-2-one (6da):

Following the General Procedure, to the mixture of (1-(3-phenylprop-2-yn-1-yl)cyclopentyl) methanol (4d) (0.05 gm, 0.23 mmol) and ethyl pyruvate (2a) (0.027 g, 0.23 mmol) in anhydrous CH₂Cl₂ (3 mL) was added Bi(OTf)₃ (0.03 g, 0.046 mmol) under argon atmosphere at room temperature the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 3% EtOAc/hexane) afforded 3-methyl-4-phenyl-1,13-dioxadispiro[4.1.4.2]tridec-3-en-2-one one (6da) (0.036 g, 64%) as a solid. TLC: Rf = 0.6 (SiO₂, 20% EtOAc/hexane); ¹H NMR (CDCl₃, 500 MHz): δ 7.55 - 7.44 (m, 5H), 4.14 (d, J = 8.0 Hz, 1H), 3.93 (d, J = 8.0 Hz, 1H), 2.15-2.04 (m, 2H), 2.01 (s, 3H), 1.95 - 1.85 (m, 2H), 1.73-1.53 (m, 6H); ¹³C NMR (CDCl₃, 126 MHz): δ 171.7, 155.0, 131.1, 129.6, 128.7, 128.3, 127.1, 115.0, 81.5, 50.1, 47.0, 37.9, 37.7, 24.6, 24.3, 9.8; HRMS (ESI) m/z calcd for C₁₈H₂₁O₃ [M+H]⁺ 285.1485, found 285.1482.

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3-(4-Nitrophenyl)-4-phenyl-1, 13-dioxadispiro [4.1.4\(^7\).2\(^5\)] tridec-3-en-2-one (6de):

Following the General Procedure, to the mixture of (1-(3-phenylprop-2-yn-1-yl) cyclopentyl) methanol (4d) (0.05 g, 0.23 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (2e) (0.051 g, 0.23 mmol) in anhydrous CH\(_2\)Cl\(_2\) (3 mL) was added Bi(OTf)_3 (0.03 g, 0.046 mmol) under argon atmosphere at room temperature, the reaction mixture was stirred for 12 h at rt. Purification of the crude product by silica gel column chromatography (SiO\(_2\), 3% EtOAc/hexanes) afforded 3-(4-nitrophenyl)-4-phenyl-1, 13-dioxadispiro [4.1.4\(^7\).2\(^5\)] tridec-3-en-2-one (6de) as a solid (0.05 g, 68%). TLC: \(R_f = 0.58\) (SiO\(_2\), 20% EtOAc/hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 8.15\) (m, \(J = 8.5\) Hz, 2H), 7.60 (d, \(J = 8.5\) Hz, 2H), 7.50-7.32 (m, 5H), 4.19 (d, \(J = 7.9\) Hz, 1H), 3.96 (d, \(J = 7.9\) Hz, 1H), 2.24 (d, \(J = 13.4\) Hz, 1H), 2.12 (d, \(J = 14.0\) Hz, 1H), 1.99-1.85 (m, 2H), 1.78-1.37 (m, 6H); \(^1^3\)C NMR (CDCl\(_3\), 101 MHz): \(\delta 168.7, 158.6, 147.7, 136.0, 130.54, 130.47, 130.2, 129.2, 128.5, 126.8, 123.5, 114.6, 81.9, 50.3, 47.0, 37.8, 37.5, 24.7, 24.3\); HRMS (ESI) m/z calcd for C\(_{23}\)H\(_{22}\)O\(_5\)N [M+H]\(^+\) 392.1492, found 392.1483.

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3-Methyl-4-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6ea):

Following the General Procedure, to the mixture of 5-phenylpent-4-yn-1-ol (4e) (0.3 g, 1.87 mmol) and ethyl pyruvate (2a) (0.23 g, 1.87 mmol) in anhydrous CH\(_2\)Cl\(_2\) (8 mL) was added Bi(OTf)_3 (0.09 g, 0.37 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 48 h at rt. Purification of the crude product by silica gel
column chromatography (SiO₂, 5% EtOAc/hexanes) afforded 3-methyl-4-phenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6ea) (0.038 g, 35%) as a solid. TLC: Rf = 0.45 (SiO₂, 20% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz): δ 7.56-7.49 (m, 2H), 7.48-7.42 (m, 3H), 4.33 (dt, J = 8.5, 4.3 Hz, 1H), 4.19-4.09 (m, 1 H), 2.39-2.27 (m, 1 H), 2.19-2.10 (m, 1 H), 2.08-1.96 (m, 5H); ¹³C NMR (CDCl₃, 101 MHz): δ 171.5, 154.3, 131.1, 129.6, 128.7, 128.3, 127.3, 114.3, 70.4, 34.9, 24.4, 9.97; HRMS (ESI) m/z calcd for C₁₄H₁₅O₃ [M+H]⁺ 231.1016, found 231.1013.

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3,4-Diphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6eb):

Following the General Procedure, to the mixture of 5-phenylpent-4-yn-1-ol (4e) (0.3 g, 1.87 mmol) and ethyl phenylglyoxylate (2b) (0.333 g, 1.87 mmol) in anhydrous CH₂Cl₂ (8 mL) was added Bi(OTf)₃ (0.245 g, 0.37 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 48 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 5% EtOAc/hexanes) afforded 3,4-diphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6eb) (0.23 g, 42%) as a solid. TLC: Rf = 0.6 (SiO₂, 20% EtOAc/hexanes); ¹H NMR (CDCl₃, 400 MHz): δ 7.46-7.23 (m, 10H), 4.37 (td, J = 8.2, 3.7 Hz, 1H), 4.16 (m, 1H), 2.43-2.30 (m, 1H), 2.30-2.19 (m, 1H), 2.12-1.97 (m, 2H); ¹³C NMR (CDCl₃, 126 MHz): δ 169.7, 154.8, 131.0, 129.8, 129.5, 129.4, 129.1, 128.9, 128.8, 128.7, 128.4, 113.7, 70.4, 34.9, 24.5; HRMS (ESI) m/z calcd for C₁₉H₁₇O₃ [M+H]⁺ 293.1172, found 293.1168.

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3-(4-Nitrophenyl)-4-phenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6ee):
Following the General Procedure, to the mixture of 5-phenylpent-4-yn-1-ol (4e) (0.15 g, 0.72 mmol) and ethyl 2-(4-nitrophenyl)-2-oxoacetate (2e) (0.115 g, 0.72 mmol) in anhydrous CH₂Cl₂ (6 mL) was added Bi(OTf)₃ (0.095 g, 0.14 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 48 h at rt. Purification of the crude product by silica gel column chromatography (SiO₂, 5% EtOAc/hexanes) afforded 3-(4-nitrophenyl)-4-phenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6ee) (0.052 g, 48%) as a solid. TLC: R_f = 0.45 (SiO₂, 10% EtOAc/hexanes); ^1H NMR (CDCl₃, 500 MHz): δ 8.16 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.48-7.42 (m, 1H), 7.42-7.35 (m, 4H), 4.42 (td, J = 8.4, 3.8 Hz, 1H), 4.21 (q, J = 8.0 Hz, 1H), 2.45-2.35 (m, 1H), 2.35-2.27 (m, 1H), 2.15-2.01 (m, 2H); ^13C NMR (CDCl₃, 126 MHz): δ 168.6, 157.9, 147.8, 136.0, 130.6, 130.5, 130.1, 129.2, 128.5, 127.1, 123.6, 113.9, 71.0, 34.9, 24.6; HRMS (ESI) m/z calcd for C₁₉H₁₆O₅N [M+H]^+ 338.1023, found 338.1018.

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2,2,5-triphenylpent-4-yn-1-ol (4f):

Compound (4f) was prepared using literature procedure. ^11Pd(PPh₃)₄ (0.015 g, 0.012 mmol) and Cul (0.048 g, 0.025 mmol) were added to the solution of iodobenzene (S1) (0.29 ml, 2.53 mmol) and 2,2-diphenylpent-4-yn-1-ol (1d) (0.3 g, 1.27 mmol) in triethylamine (1.78 mL, 12.7 mmol) and THF (10 mL) under argon atmosphere. The reaction mixture was stirred at rt for 12 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford the 2,2,5-triphenylpent-4-yn-1-ol (4f) as a brown oil (0.21 g, 53%). TLC: R_f = 0.5 (SiO₂, 20% EtOAc/hexanes); ^1H NMR (CDCl₃, 400 MHz) δ 7.39-7.23 (m, 15H), 4.39 (d, J = 6.1 Hz, 2H), 3.30 (s, 2H); ^13C NMR (CDCl₃, 101 MHz) δ 144.5, 131.5, 128.2, 128.1, 127.7, 126.7, 87.1, 83.7, 68.5, 52.2, 28.4; HRMS (ESI) m/z calcd for C₂₃H₂₁O [M+H]^+ 313.1587, found 313.1587.

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3-methyl-4, 8, 8-triphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6fa):

Following the General Procedure, to the mixture of 2,2,5-triphenylpent-4-yn-1-ol (4f) (0.05 g, 0.16 mmol) and ethyl pyruvate (2a) (0.019 g, 0.16 mmol) in anhydrous CH$_2$Cl$_2$ (2 mL) was added Bi(OTf)$_3$ (0.02 g, 0.032 mmol) under argon atmosphere at room temperature, the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO$_2$, 5% EtOAc/hexanes) afforded 3-methyl-4,8,8-triphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6fa) (0.038 g, 62%). TLC: $R_f = 0.5$ (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.39-7.24 (m, 10H), 7.20-7.12 (m, 3H), 7.1-7.0 (m, 2H), 4.87 (d, $J = 9.1$ Hz, 1H), 4.77 (d, $J = 9.7$ Hz, 1H), 3.13 (d, $J = 14$ Hz, 1H), 2.90 (d, $J = 14$ Hz, 1H), 1.98 (s, 3H); $^{13}$C NMR (CDCl$_3$, 101 MHz) 171.3, 154.8, 146.1, 144.6, 130.4, 129.5, 128.6, 128.5, 128.3, 127.7, 127.4, 126.7, 126.4, 114.6, 79.3, 55.9, 48.2, 29.7, 9.8; HRMS (ESI) m/z calcld for C$_{26}$H$_{23}$O$_3$ [M+H]$^+$ 383.1642, found 383.1642.

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2-(3-phenylprop-2-yn-1-yl) cyclohexan-1-ol (4g):

2-(3-phenylprop-2-yn-1-yl) cyclohexan-1-ol (4g) was prepared according to the known procedure. $^2$ Pd(PPh$_3$)$_4$ (0.012 g, 0.011 mmol) and Cul (0.004 g, 0.021 mmol) were added to the solution of iodobenzene (S1) (0.24 ml, 2.17 mmol) and 2-(prop-2-yn-1-yl)cyclohexan-1-ol (0.15 g, 1.086 mmol) (1f) in triethylamine (1.5 mL, 10.86 mmol) and THF (10 mL) under argon atmosphere. The reaction mixture was stirred at rt for 12 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. Purified by silica gel column chromatography (10% EtOAc/hexanes) to afford 2-(3-phenylprop-2-yn-1-yl) cyclohexan-1-ol (4g) as brown oil (0.16 g, 69 %). TLC: $R_f = 0.5$ (SiO$_2$, 20% EtOAc/hexanes); $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.46-7.39 (m, 2H), 7.33-7.26 (m, 3H), 3.53-
3.39 (m, 1H), 2.69 (dd, J = 16.4, 4.2 Hz, 1H), 2.56 (d, J = 17.1, 6.7 Hz, 1H), 2.05 – 1.91 (m, 2H), 1.87-1.65 (m, 3H), 1.64 - 1.48 (m, 1H), 1.35-1.22 (m, 4H); 13C NMR (CDCl3, 101 MHz) δ 131.5, 128.2, 127.6, 123.8, 88.5, 82.1, 73.8, 44.4, 35.5, 30.5, 25.5, 24.9, 22.8; HRMS (ESI) m/z calcd for C15H19O [M+H]+ 215.1430, found 215.1431.

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4'-methyl-3'-phenyl-3a, 4, 5, 6, 7, 7a-hexahydro-3H, 5'H-spiro [benzofuran-2, 2'-furan]-5'-one (6ga):

Following the General Procedure, to the mixture of 2-(3-phenylprop-2-yn-1-yl)cyclohexan-1-ol (6ga) (0.1 g, 0.46 mmol) and ethyl pyruvate (2a) (0.053g, 0.46mmol) in anhydrous CH2Cl2 (5 mL) was added Bi(OTf)3 (0.060 g, 0.092 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 12 h at rt. Purification of the crude product by column chromatography (SiO2, 5% EtOAc /hexanes) afforded separable 1:1 diastereomeric mixture of (3a,7a)-4'-methyl-3'-phenyl-3a,4,5,6,7,7a-hexahydro-3H,5'H-spiro[benzofuran-2,2'-furan]-5'-one (43 mg of 6ga and 43.5 mg of 6ga1 (overall yield 64%).

6ga: TLC: Rf = 0.60 (SiO2, 20% EtOAc/hexanes); 1H NMR (CDCl3, 400 MHz) δ 7.44-7.38 (m, 5H), 3.25 (td, J = 3.81, 10.3 Hz, 1H), 2.82 (dd, J = 3.8, 12.9 Hz, 1H), 2.12-2.02 (m, 2H), 1.97 (s, 3H), 1.84-1.73 (m, 2H), 1.7-1.62 (m, 1H), 1.57-1.37 (m, 3H), 1.24-1.17 (m, 2H); 13C NMR (CDCl3, 101 MHz) δ 171.5, 158.4, 136, 129.6, 129.0, 126.4, 123.3, 104.9, 78.1, 44.6, 31.7, 31.5, 31.2, 30.9, 25.2, 24.5, 8.5; HRMS (ESI) m/z calcd for C18H21O3 [M+H]+ 285.1486, found 285.1485.

6ga1: TLC: Rf = 0.53 (SiO2, 20% EtOAc/hexanes); 1H NMR(CDCl3, 500 MHz) δ 7.44-7.38 (m, 5H), 3.2 (td, J = 4.2, 10.7 1H), 2.82 (dd, J = 4.2, 13.35, 1H), 2.18 (s, 2H), 2.1-2.02 (m, 2H), 1.97 (s, 3H), 1.85-1.73 (m, 2H), 1.7-1.6 (m, 1H), 1.53-1.4 (m, 3H); 13C NMR (CDCl3, 126 MHz) δ 171.5, 158.4, 136, 129.6, 129.0, 126.4, 123.3, 104.92, 78.1, 44.6, 31.7, 31.5, 31.2, 25.2, 24.5, 8.5; HRMS (ESI) m/z calcd for C18H21O3 [M+H]+ 285.1487, found 285.1485.
7. Supporting experiments for the postulated reaction mechanism:

**Eq. 1:** To a dry 10 mL round bottom flask, equipped with a magnetic stir bar was added (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.1 g, 0.72 mmol) and ethyl pyruvate (**2a**) (0.083 g, 0.72 mmol) followed by anhydrous CH₂Cl₂ (5 mL) and stirred the reaction mixture at rt for 24 h under argon atmosphere without the addition of Bi(OTf)₃. Reaction monitored by TLC, which shown two starting materials (**1b** and **2a**) were remained intact even after 24 h. (This confirmed the role of the catalyst in the reaction).

**Eq. 2:** To a 10 mL round bottom flask, equipped with a magnetic stir bar was added activated molecular sieves (MS-4Å) powder and CH₂Cl₂ (5 mL). Then, added CH₂Cl₂ solution of (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.1 g, 0.72 mmol) and ethyl pyruvate (**2a**) (0.083 g, 0.72 mmol).Then Bi(OTf)₃ (0.09 g, 0.144 mmol) was added. The reaction mixture was stirred 24 h at rt under argon atmosphere. Interestingly, under these reaction conditions, the desired product was not observed (monitored by TLC). (This confirmed the role of in situ released water in the product (**3ba**) formation).

**Eq. 3:** NMR-Scale Catalytic Reaction: (1-(prop-2-yn-1-yl) cyclopentyl) methanol (**1b**) (0.01 g, 0.072 mmol) and ethyl pyruvate (**2a**) (0.0083 g, 0.072 mmol) were weighed in to a vial, and 500 µL CDCl₃ was added by syringe. The solution was mixed well and then transferred to a NMR tube, then Bi(OTf)₃ (0.009 g, 0.014 mmol) was added to the mixture in NMR tube, was monitored by ¹H NMR spectroscopy at 27 °C in between 0 to 5 h to identify reaction intermediates and by products to propose the reaction mechanism (Figure 1).
Figure 1. $^1$H NMR spectra (500 MHz, CDCl$_3$): $tc = 0$ h, $tc = 0.5$ h, $tc = 1$ h, $tc = 3$ h and $tc = 5$ h are the spectrums belongs to respective reaction times.

An interesting observation in the above cascade annulation reaction is the various intermediates and products detected in the $^1$H NMR spectroscopy as shown in Figure 1. Through, careful $^1$H NMR analysis and by comparing with reported literature, we confirmed this reaction proceeds through immediate formation of exocyclic-enolether (1b-C), which then reacts slowly with ethylpyruvate (2a) and gives the unsaturated γ-spiroketal-γ-lactone and EtOH as reaction products. These observations are consistent with Marks’s reports (Eq 3. Figure 1).$^{12}$

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8. Synthetic utility of unsaturated γ-spiroketal γ-lactones

3-Methyl-1, 13-dioxadispiro [4.1.4\textsuperscript{7}.2\textsuperscript{5}] tridecan-2-one (7):

To the mixture of 3-methyl-1,13-dioxadispiro[4.1.4\textsuperscript{7}.2\textsuperscript{5}]tridec-3-en-2-one (3ba) (0.05 g, 0.24 mmol) and Pd/C (0.025 g, 0.024 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (5 mL) was added Et\textsubscript{3}N (0.005 g, 0.048 mmol) at 0 °C under argon atmosphere, then argon was replaced with H\textsubscript{2} (in a balloon) and stirred the reaction mixture at room temperature for 3 h. After completion of the reaction, H\textsubscript{2} atmosphere was removed and the mixture passed through Celite-sintered glass funnel, filtrate was concentrated under reduced pressure. Purification of the crude product by silica gel column chromatography (5% EtOAc/hexane) afforded 3-methyl-1, 13-dioxadispiro [4.1.4\textsuperscript{7}.2\textsuperscript{5}] tridecan-2-one (7) as crystalline solid (mixture of two diastereomers) (0.038 g, 76%). TLC: \( R_f = 0.65 \) (20% EtOAc/hexane). \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): δ (mixture of two diastereomers) 3.96-3.85 (m, 1H), 3.83 - 3.72 (m, 1H), 3.01 - 2.86 and 2.77-2.63 (m, 1H), 2.54-2.42 (m, 1H), 2.34-2.22 (m, 1H), 2.12-1.92 (m, 2H), 1.83-1.50 (m, 8H), 1.35 (minor isomer) (d, \( J = 7.32 \) Hz, ) and 1.26 (major isomer) (d, \( J = 6.71 \) Hz) for 3H); \(^{13}\)C NMR (CDCl\textsubscript{3}, 101 MHz): δ (mixture of two diastereomers) 179, 115.5, 114.1, 80.4, 80.0, 49.75, 49.67, 49.63, 48.86, 41.16, 40.14, 38.58, 38.49, 37.10, 37.05, 36.01, 34.97, 24.47, 24.31, 16.55, 15.01; HRMS (ESI) m/z calcd for C\textsubscript{12}H\textsubscript{19}O\textsubscript{3} [M+H]\textsuperscript{+} 211.1329, found 211.1324.

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3, 4-Dihydroxy-3-methyl-1, 13-dioxadispiro [4.1.4\textsuperscript{7}.2\textsuperscript{5}] tridecan-2-one (8):

\[ X-ray, \text{CCDC No: 1510253} \quad \text{ORTEP Diagram} \]
To a solution of 3-methyl-1,13-dioxadispiro[4.1.4.25.7]tridec-3-en-2-one (3ba) (0.15 g, 0.721 mmol) in 5:1 mixture of THF/H2O (10 mL) was added N-methylmorpholine N-oxide hydrate (0.25 g, 2.16 mmol) and osmium tetroxide (0.1 M in toluene, 0.36 mL, 0.036 mmol). The reaction mixture was stirred at rt for 12 h. The resulting black mixture was quenched by saturated sodium sulphite solution and stirred at room temperature for 1 h. The aqueous layer was extracted with EtOAc (3x15 mL) and the combined organic layers were dried over anhydrous sodium sulphate, concentrated under reduced pressure and purified by silica gel column chromatography (SiO2, 25% EtOAc/hexanes) to afford 3, 4-dihydroxy-3-methyl-1,13-dioxadispiro [4.1.4.25.7] tridecan-2-one (8) as a white crystalline solid (0.124 g, 71%).

TLC: Rf = 0.5 (SiO2, 50% EtOAc/hexanes); 1H NMR (CDCl3, 400 MHz): δ 3.98 (d, J = 8.5 Hz, 1H), 3.88 (s, 1H), 3.83 (d, J = 8.5 Hz, 1H), 3.48 (br. s., 1H), 3.25 (br. s, 1H), 2.48 (d, J = 14.6 Hz, 1H), 2.21 (d, J = 14.0 Hz, 1H), 1.64 (s, 3H), 1.84-1.54 (m, 8H); 13C NMR (CDCl3, 101 MHz): δ 177.9, 116.8, 81.3, 78.1, 77.2, 74.7, 48.7, 45.2, 37.8, 36.9, 24.6, 24.3, 23.0; HRMS (ESI): m/z calcd for C12H19O5 [M+H]+ 243.1227, found 243.1222.
9.

$^1H$ and $^{13}C$ NMR Spectra
(1-(Prop-2-yn-1-yl)cyclohexyl)methanol (1a):

$^1$H NMR, 400 MHz
CDCl$_3$

$^{13}$C NMR, 101 MHz
CDCl$_3$
2-((1-(Prop-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S2):

[^1]H NMR, 400 MHz
CDC\textsubscript{3}

[^1]C NMR, 101 MHz
CDC\textsubscript{3}
2-((1-(But-2-yn-1-yl) cyclohexyl) methoxy) tetrahydro-2H-pyran (S3):

$^1$H NMR, 400 MHz
CDCl$_3$

$^{13}$C NMR, 101 MHz
CDCl$_3$
(1-(But-2-yn-1-yl) cyclohexyl) methanol (4a):

$^1$H NMR, 400 MHz
CDCl$_3$

$^{13}$C NMR, 101 MHz
CDCl$_2$
2-((1-(Pent-2-yn-1-yl)cyclohexyl)methoxy)tetrahydro-2H-pyran (S4):

\[
\text{\chem{S4}} \\
\text{\textsuperscript{1}H NMR, 400 MHz} \\
\text{CDCl\textsubscript{3}}
\]

\[
\text{\chem{S4}} \\
\text{\textsuperscript{13}C NMR, 101 MHz} \\
\text{CDCl\textsubscript{3}}
\]
(1-(Pent-2-yn-1-yl) cyclohexyl) methanol (4b):

\[ \text{H NMR, 400 MHz} \]
\[ \text{CDCl}_3 \]

\[ \text{^13C NMR, 100 MHz} \]
\[ \text{CDCl}_3 \]
(1-(Phenylprop-2-yl)cyclohexyl)methanol (4c):

$^{1}$H NMR 400 MHz
CDCl$_3$
(1-(Prop-2-yn-1-yl) cyclopentyl) methanol (1b):
(1-(3-Phenylprop-2-yn-1-yl) cyclopentyl) methanol (4d):

\[\text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{\( \text{
5-Phenylpent-4-yn-1-ol (4e):

[Chemical Structure Image]

$^1$H NMR, 500 MHz
CDCl$_3$

[Chemical Structure Image]

$^{13}$C NMR, 126 MHz
CDCl$_3$
Ethyl 2-(4-nitrophenyl)-2-oxoacetate (2e):

$\text{O}_2\text{N} \quad \text{2e}$

$^{1}H$ NMR, 400 MHz
$\text{CDCl}_3$

$\text{O} \quad \text{O} \quad \text{O} \quad \text{2e} \quad \text{O} \quad \text{2} \quad \text{N}$

$^{13}C$ NMR, 101 MHz
$\text{CDCl}_3$
3-Methyl-1, 14-dioxadispiro [4.1.5.2.7] tetradec-3-en-2-one (3aa):

\[ \text{Chemical Shift (ppm)} \]

\[ \begin{align*}
    & 8.33 \quad 2.07 \quad 3.06 \quad 1.03 \quad 1.04 \quad 1.03 \quad 1.00 \quad 1.01 \\
    & 7.28 \quad 6.69 \quad 6.69 \quad 3.99 \quad 3.97 \quad 3.95 \quad 3.88 \quad 3.86 \\
    & 2.14 \quad 2.11 \quad 2.03 \quad 2.00 \quad 1.96 \quad 1.92 \quad 1.92 \quad 1.69 \\
    & 1.51 \quad 1.48 \quad 1.47 \quad 0.00
\end{align*} \]

\[ \text{Chemical Shift (ppm)} \]

\[ \begin{align*}
    & 171.58 \quad 145.13 \quad 132.53 \quad 113.22 \quad 80.38 \quad 77.36 \quad 77.05 \quad 76.73 \\
    & 47.05 \quad 43.58 \quad 37.39 \quad 35.53 \quad 25.55 \quad 23.82 \quad 23.71 \quad 10.42
\end{align*} \]

\[ \text{Chemical Shift (ppm)} \]

\[ \begin{align*}
    & 171.58 \quad 145.13 \quad 132.53 \quad 113.22 \quad 80.38 \quad 77.36 \quad 77.05 \quad 76.73 \\
    & 47.05 \quad 43.58 \quad 37.39 \quad 35.53 \quad 25.55 \quad 23.82 \quad 23.71 \quad 10.42
\end{align*} \]
3-Phenyl-1, 14-dioxadispiro [4.4.5.2\(^7\)5\(^7\)2\(^5\)] tetradec-3-en-one (3ab):
3-(4-Methoxyphenyl)-1,14-dioxadispiro[4.1.5.7.2.5]tetradec-3-en-2-one (3ac):

$^1$H NMR, 400 MHz
CDCl$_3$

$^{13}$C NMR, 101 MHz
CDCl$_3$
3-(p-Tolyl)-1, 14-dioxadispiro [4.1.5.2][tetrade-c-3-en-2-one (3ad):

**1H NMR, 500 MHz**

CDCl$_3$

**13C NMR, 126 MHz**

CDCl$_3$
3-Methyl-1,13-dioxadispiro[4.1.4.7.25]tridec-3-en-2-one (3ba):

$^{1}H$ NMR, 500 MHz
CDCl$_3$

$^{13}C$ NMR, 126 MHz
CDCl$_3$
3-Phenyl-1,13-dioxadispiro[4.1.4.2]7.5tridec-3-en-one(3bb):

\[ \text{1}^\text{H} \text{NMR, 500 MHz} \]
\[ \text{CDCl}_3 \]

\[ \text{\textsuperscript{13}C NMR, 126 MHz} \]
\[ \text{CDCl}_3 \]
3-(4-Methoxyphenyl)-1,13-dioxadispiro[4.1.4.7.2]tridec-3-en-2-one (3bc):

$^1$H NMR, 500 MHz
CDCl$_3$

$^{13}$C NMR, 126 MHz
CDCl$_3$
3-(p-Tolyl)-1,13-dioxadispiro[4.1.4.2.5]tridec-3-en-2-one (3bd):

1H NMR, 400 MHz
CDCl₃

13C NMR, 101 MHz
CDCl₃
3-(4-Nitrophenyl)-1, 13-dioxadispiro [4.1.4.2] tridec-3-en-2-one (3be):

$\text{[Chemical Structure Image]}

$^1\text{H NMR, 400 MHz}$
$\text{CDCl}_3$

$\text{[Chemical Structure Image]}

$^{13}\text{C NMR, 101 MHz}$
$\text{CDCl}_3$
3-Methyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ca):

3ca

$^1$H NMR, 500 MHz
CDCl$_3$

3ca

$^{13}$C NMR, 126 MHz
CDCl$_3$
3-Phenyl-1,6-dioxaspiro[4,4]non-3-en-2-one (3cb):
3-(4-Methoxyphenyl)-1,6-dioxaspiro[4,4]non-3-en-2-one(3cc):

\[ \text{Chemical Shift (ppm)} \]

\[ \begin{align*}
\text{H NMR, 500 MHz} \\
\text{CDCl}_3
\end{align*} \]

\[ \text{Chemical Shift (ppm)} \]

\[ \begin{align*}
\text{\^C NMR, 126 MHz} \\
\text{CDCl}_3
\end{align*} \]
3-(p-Tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one (3cd):

$\text{3cd}$

$^1\text{H NMR, 400 MHz}$

$\text{CDCl}_3$

$\text{13C NMR, 101 MHz}$

$\text{CDCl}_2$
2, 2-diphenylpent-4-yn-1-ol (1d):

\[ \text{Ph} \quad \text{OH} \quad \text{Ph} \]

\[ 1d \]

\[ ^1H \text{NMR}, 500 \text{ MHz} \]

\[ \text{CDCl}_3 \]

\[ 7.32, 7.30, 7.29, 7.24, 7.23 \]

\[ 6.23, 4.30, 3.09, 3.08, 1.94, 1.93, 1.93, 0.00 \]

\[ ^13C \text{NMR}, 126 \text{ MHz} \]

\[ \text{CDCl}_3 \]

\[ 144.37, 129.28, 128.02, 126.75 \]

\[ 81.39, 77.32, 76.81, 71.56, 51.55, 27.46 \]
3-methyl-8, 8-diphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3da):

\[
\text{\textbf{3da}}
\]

\text{\textsuperscript{1}H NMR, 500 MHz}
\text{CDCl}_3

\[
\text{\textbf{3da}}
\]

\text{\textsuperscript{13}C NMR, 126 MHz}
\text{CDCl}_3
3, 8, 8-triphenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (3db):
3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):

\[ \text{1H NMR, 500 MHz, CDCl}_3 \]

\[ \text{13C NMR, 126 MHz, CDCl}_3 \]
3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):

13C DEPT NMR, 126 MHz
CDCl₃

3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):

1H NMR, 400 MHz
CDCl₃
3-methyl-7-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (3ea):
2-(prop-2-yn-1-yl)cyclohexan-1-ol (1f):

\[ \text{If} \]

$^1$H NMR-500 MHz
$^{13}$C NMR-126 MHz
CDCl$_3$
4'-methyl-3a,4,5,6,7,7a-hexahydro-3H,5'H-spiro[benzofuran-2,2'-furan]-5'-one (3fa)

1H NMR-400 MHz
CDCl₃

13C NMR-101 MHz
CDCl₃
COSY: (3fa)

HMBC: (3fa)
HSQC: (3fa)

NOESY: (3fa)
4'-methyl-3a,4,5,6,7a-hexahydro-3H,5'H-spiro[benzofuran-2,2'-furan]-5'-one (3fa)

$^1$H NMR - 500 MHz
CDCl$_3$

$^{13}$C NMR - 126 MHz
CDCl$_3$
2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (S9)

[Chemical structure image of S9]

$^1$H NMR 200 MHz
CDCl$_3$

2-(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-one (S10)

[Chemical structure image of S10]

$^1$H NMR 500 MHz
CDCl$_3$
2,2-di(prop-2-yn-1-yl)-2,3-dihydro-1H-inden-1-ol (1g)

1H NMR-500 MHz
CDCl₃

13C NMR-126 MHz
CDCl₃
4-methyl-3a'-(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5H-spiro[furan-2,2'-indeno[1,2-b]furan]-5-one (3ga)

\[ \text{3ga} \]

\(^1\text{H NMR-500 MHz} \]
\[ \text{CDCl}_3 \]

\[ \text{13C NMR-126 MHz} \]
\[ \text{CDCl}_3 \]
COSY: (3ga)

HMBC: (3ga)
HSQC: (3ga)

NOESY: (3ga)
NOESY: (3ga)
4-methyl-3a'-{(prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5H-spiro[furan-2,2'-indeno[1,2-b]furan]-5-one (3ga¹)

¹H NMR-400 MHz
CDCl₃

¹³C NMR-101 MHz
CDCl₃
4-phenyl-3a'-((prop-2-yn-1-yl)-3',3a',4',8b'-tetrahydro-5H-spiro[furan-2,2'-indeno[1,2-
b]furan]-5-one (3gb)

\[\text{(3gb)}\]

\[\text{\(\text{H NMR-400 MHz}\)}\]
\[\text{\(\text{CDCl}_3\)}\]

\[\text{\(\text{\(\text{C NMR-101 MHz}\)}\)}\]
\[\text{\(\text{CDCl}_3\)}\]

Chemical Shift (ppm)
2,2-di(prop-2-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1h)

$^1$H NMR-200 MHz
CDCl$_3$

$^{13}$C NMR-50 MHz
CDCl$_3$
4-methyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'H,5H-spiro[furan-2,2'-naphtho[1,2-b]furan]-5-one (3ha)

$^{1}H$ NMR-400 MHz
CDCl$_3$

$^{13}C$ NMR-101 MHz
CDCl$_3$
COSY: (3ha)

HMBC: (3ha)
NOESY: (3ha)
4-methyl-3a'-{(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'H,5H-spiro[furan-2,2'-naphtho[1,2-b][furan]-5-one (3ha')

\[\text{(3ha':3ha') = 1:1.25}\]

\[\text{3ha + 3ha'}\]

$^1\text{H NMR}, 500 \text{ MHz}$

$^1\text{C NMR}, 126 \text{ MHz}$

$\text{CDCl}_3$
4-phenyl-3a'-(prop-2-yn-1-yl)-3a',4',5',9b'-tetrahydro-3'H,5H-spiro[furan-2,2'-naphtho[1,2-b][furan]-5-one (3hb)
(E)-3-styryl-1,13-dioxadispiro[4.1.4.7.2.5]tridec-3-en-2-one (3bf)
3, 4-Dimethyl-1, 14-dioxadispiro [4.1.5.2] tetradec-3-en-2-one (6aa):

\[ \text{6aa} \]

\[^1H\text{NMR, 500 MHz} \]
\[ \text{CDCl}_3 \]

\[ \text{13C NMR, 126 MHz} \]
\[ \text{CDCl}_3 \]
4-Methyl-3-phenyl-1, 14-dioxadispiro [4.1.5.2] tetradec-3-en-2-one (6ab):
3-(4-Methoxyphenyl)-4-methyl-1, 14 dioxadispiro[4.1.5.2]tetradec-3-en-2-one (6ac):

$^1$H NMR, 400 MHz
CDCl$_3$

$^{13}$C NMR, 101 MHz
CDCl$_3$
4-Methyl-3-(p-tolyl)-1, 14-dioxadispiro [4.1.5.7.2] tetradec-3-en-2-one (6ad):

**1H NMR, 400 MHz**

CDCl₃

**13C NMR, 101 MHz**

CDCl₃
4-Ethyl-3-methyl-1, 14-dioxadispiro [4.1.5.7.2.5] tetradec-3-en-2-one (6ba):

$^1$H NMR, 400 MHz
CDCl$_3$

$^{13}$C NMR, 101 MHz
CDCl$_3$
4-Ethyl-3-phenyl-1, 14-dioxadispiro [4.1.5.2] tetradec-3-en-2-one (6bb):

$^1$H NMR, 500 MHz
CDCl$_3$

$^1$C NMR, 126 MHz
CDCl$_3$
4-Ethyl-3-(4-methoxyphenyl)-1, 14-dioxadispiro [4.1.5.7.2] tetradec-3-en-2-one (6bc):

\[ \text{6bc} \]

\(^1\)H NMR, 400 MHz
CDCl\(_3\)

\[ \text{6bc} \]

\(^1^3\)C NMR, 101 MHz
CDCl\(_3\)
4-Ethyl-3-(p-toly)-1, 14-dioxadispiro [4.1.5.2.5] tetradec-3-en-2-one (6bd):

\[\text{6bd}\]

\[^1H\text{ NMR, 500 MHz}\]
\[\text{CDCl}_3\]

\[\text{13C NMR, 126 MHz}\]
\[\text{CDCl}_3\]
3-Methyl-4-phenyl-1,14-dioxadispiro[4.1.5.2\textsuperscript{7}.2\textsuperscript{5}]tetradec-3-en-2-one (6ca):

\begin{align*}
\text{\textbf{6ca}} \\
\text{\textsuperscript{1}H NMR, 500 MHz} \\
\text{CDCl}_3
\end{align*}

\begin{align*}
\text{\textbf{6ca}} \\
\text{\textsuperscript{13}C NMR, 126 MHz} \\
\text{CDCl}_3
\end{align*}
3,4-Diphenyl-1,14-dioxadispiro[4.1.5^7.2^5]tetradec-3-en-2-one (6cb):

$^1$H NMR, 400 MHz
CDCl$_3$

$^{13}$C NMR, 101 MHz
CDCl$_3$
3-(4-Methoxyphenyl)-4-phenyl-1,14-dioxadispiro [4.1.5.2^7.2^5] tetradec-3-en-2-one (6cc):

\[\text{6cc}\]

$^1\text{H NMR, 400 MHz}$

$\text{CDCl}_3$

\[\text{6cc}\]

$^{13}\text{C NMR, 101 MHz}$

$\text{CDCl}_3$
4-Phenyl-3-(p-tolyl)-1,14-dioxadispiro[4.1.5.2.7]tetradec-3-en-2-one (6cd):

![NMR Spectra](image)

$^1$H NMR, 500 MHz
CDCl$_3$

$^{13}$C NMR, 126 MHz
CDCl$_3$
3-(4-Nitrophenyl)-4-phenyl-1, 14-dioxadispiro [4.1.5.2] tetradec-3-en-2-one (6ce):

$\text{H NMR, 500 MHz}$
$\text{CDCl}_3$

$\text{C NMR, 126 MHz}$
$\text{CDCl}_3$
3-Methyl-4-phenyl-1, 13-dioxadispiro [4.1.4.2] tridec-3-en-2-one (6da):

6da

$^1$H NMR, 500 MHz
CDCl$_3$

6da

$^{13}$C NMR, 126 MHz
CDCl$_3$
3-(4-Nitrophenyl)-4-phenyl-1, 13-dioxadispiro [4.1.4.7.2] tridec-3-en-2-one (6de):
3-Methyl-4-phenyl-1, 6-dioxaspiro [4.4] non-3-en-2-one (6ea):

\[ 
\begin{align*}
  & \begin{array}{c}
    \text{6ea} \\
    \text{\textsuperscript{1}H NMR, 400 MHz} \\
    \text{CDCl\textsubscript{3}}
  \end{array} \\
  & \begin{array}{c}
    \text{6ea} \\
    \text{\textsuperscript{13}C NMR, 101 MHz} \\
    \text{CDCl\textsubscript{3}}
  \end{array}
\end{align*}
\]
3,4-Diphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6eb)

{\text{6eb}}

$^1$H NMR-400 MHz

CDCl$_3$

$^{13}$C NMR, 101 MHz

CDCl$_3$
3-(4-Nitrophenyl)-4-phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one (6ee):

![Diagram of 6ee]

**H NMR, 500 MHz**

CDCl₃

![1H NMR spectrum]

**C NMR, 126 MHz**

CDCl₃

![13C NMR spectrum]
2, 2, 5-triphenylpent-4-yn-1-ol (4f):

**$^1$H NMR, 400 MHz**

CDCl$_3$

**$^{13}$C NMR, 101 MHz**

CDCl$_3$
3-methyl-4, 8, 8-triphenyl-1, 6-dioxaspiro[4.4] non-3-en-2-one (6fa):

\[ \text{\begin{center}
\includegraphics[width=0.5\textwidth]{structure}
\end{center}} \]

\[ \text{\begin{center}
6fa
\text{\H NMR, 400 MHz}
\text{\CDCl}_3
\end{center}} \]

\[ \text{\begin{center}
\includegraphics[width=0.5\textwidth]{nmr}
\end{center}} \]

\[ \text{\begin{center}
6fa
\text{\C NMR, 101 MHz}
\text{\CDCl}_3
\end{center}} \]
2-(3-phenylprop-2-yn-1-yl) cyclohexan-1-ol (4g):

$\text{H NMR, 400 MHz}$

$\text{CDCl}_3$

$\text{13C NMR, 101 MHz}$

$\text{CDCl}_3$
4'-methyl-3'-phenyl-3a, 4, 5, 6, 7, 7a-hexahydro-3\textit{H}, 5'\textit{H}-spiro [benzofuran-2, 2'-furan]-5'-one (6ga):

\textbf{6ga}

TLC: \textit{Rf} = 0.60
(SiO\textsubscript{2}, 20\% EtOAc/hexanes);

\textit{\textit{1}H} NMR, 500 MHz
CDCl\textsubscript{3}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{NMR spectrum of 6ga.}
\end{figure}

\textbf{6ga}

TLC: \textit{Rf} = 0.60 (SiO\textsubscript{2}, 20\% EtOAc/hexanes);

\textit{\textit{13}C} NMR, 126 MHz
CDCl\textsubscript{3}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{NMR spectrum of 6ga.}
\end{figure}
4'-methyl-3'-phenyl-3a, 4, 5, 6, 7, 7a-hexahydro-3\(^\text{H}\), 5'\(^\text{H}\)-spiro [benzofuran-2, 2'-furan]-5'-one (6ga\(^1\)):

TLC: \(R_f = 0.53\) (SiO\(_2\), 20% EtOAc/hexanes);

\(^1\)H NMR, 500 MHz
CDCl\(_3\)

\( ^{13} \)C NMR, 126 MHz
CDCl\(_3\)
3-Methyl-1, 13-dioxadispiro [4.1.4\(^7\).2\(^5\)] tridecan-2-one (7):

\[\begin{align*}
\text{\textsuperscript{1}H NMR, 400 MHz} \\
\text{CDCl}_3
\end{align*}\]

\[\begin{align*}
\text{\textsuperscript{13}C NMR, 101 MHz} \\
\text{CDCl}_3
\end{align*}\]
3, 4-Dihydroxy-3-methyl-1, 13-dioxadispiro [4.1.4.7^2^5] tridecan-2-one (8):

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