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Nickel-Catalyzed Intermolecular [3+2+2] and [2+2+2] Cocyclizations of Bicyclopropylidene and Alkynes[1]

Ligang Zhao[a] and Armin de Meijere[a,*]

[a] Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstr. 2, 37077 Göttingen, Germany
Fax: (+49)-551-39-9475; e-mail: Armin.deMeijere@chemie.uni-goettingen.de

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Dedicated to Professor Paul Binger on the occasion of his 70th birthday.

Abstract: Under the catalysis of bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$, in the presence of triphenylphosphane, two molecules of bicyclopropylidene (**1**) and one molecule of a terminal alkyne **2** at ambient temperature undergo an intermolecular [3+2+2] cocyclization to furnish the bis-spirocyclopropanated cyclopropylidenecycloheptene derivatives **3** in 45–93% yield (15 examples plus 2 examples with 8 and 25% yield, respectively). With the same catalyst system, [2+2+2] cocyclizations of two molecules of an arylmethyl (aryl = phenyl, furyl) propargyl ether and one molecule of bicyclopropylidene (**1**) occur to provide regioisomeric dispiro[2.0.2.4]deca-7,9-diene derivatives **9**/**10** (2 examples, 57 and 44% yield, respectively).

Keywords: [2+2+2] cocyclization; [3+2+2] cocyclization; homogeneous catalysis; nickel; seven-membered rings; small rings

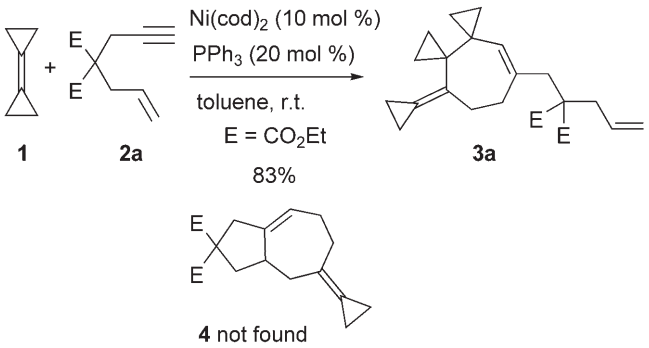
Introduction

Transition metal-catalyzed cocyclizations, formal cycloadditions of alkenes and alkynes as well as carbon monoxide, are among the most efficient ways of constructing complex cyclic and oligocyclic compounds from simple starting materials under mild conditions.[2] Whereas a large number of publications deals with the construction of four-, five- and six-membered rings by transition metal-catalyzed cocyclization reactions, only a limited number of accesses to seven-membered rings has been reported.[3–6] Towards five- and seven-membered rings, the cyclopropyl group in methylenecyclopropanes and vinylcyclopropanes has mostly served as the provider of a three-carbon fragment.[7] Bicyclopropylidene (**1**),[8] which is a symmetrical bis(methylenecyclopropane), has been employed as a highly reactive building block in a number of transition metal-catalyzed cross-coupling[9,10] and cocyclization[11,12] reactions. Under nickel(0) catalysis, it can undergo cocyclizations as an alkene without participation of one of the cyclopropane rings,[11a,12] or as a methylenecyclopropane with opening of one three-membered ring.[12] These results and our recent finding that bicyclopropylidene (**1**) is almost as good a ligand on nickel(0) as an alkyne is,[13] prompted us to further explore nickel(0)-catalyzed cocyclization reactions of bicyclopropylidene (**1**) with different alkynes **2**.

Results and Discussion

Initially, the enyne **2a** was tested, as it was expected to first react intramolecularly, before the thus formed bicyclic nickelacyclopentene intermediate[14] would incorporate bicyclopropylidene (**1**).

When bicyclopropylidene (**1**) (2 mmol) was mixed with the enyne **2a** (1 mmol) in the presence of bis(cyclooctadiene)nickel (10 mol%) and triphenylphosphane (20 mol%), a rapid exothermal reaction occurred, but no defined product could be isolated. However, slow addition (using a syringe pump) of **1** and **2** in toluene solution to a solution of $Ni(cod)_2$ and PPh_3 afforded the [3+2+2] cocyclization product **3a** in 83% yield as a single regioisomer (Scheme 1). The yield was significantly lower, when only **1** was added to a solution of **2** and the catalyst, or only **2** was added to **1** and the catalyst. The yield was better with triphenylphosphane (PPh_3) than with other added ligands such as DPPE, DPPF, P(*o*-Tol)$_3$, P(*n*-Bu)$_3$, P(Cy)$_3$, P(*t*-Bu)$_3$. The structure of the cycloadduct **3a** was assigned on the basis of its NMR (^{1}H and ^{13}C) spectra, and the molecular mass as determined by mass spec-



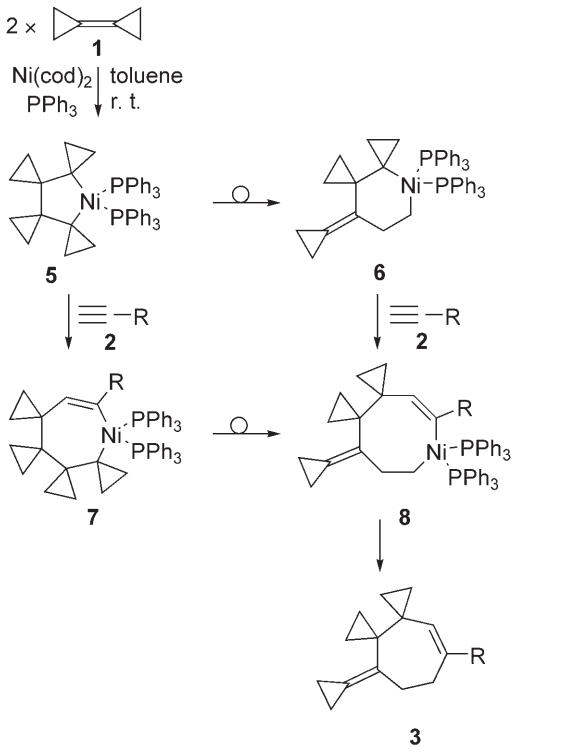
Scheme 1.

trometry confirmed that it was a [3+2+2] cocyclization product of two molecules of bicyclopropylidene (**1**) with one molecule of the enyne **2a**,[15] and not the expected product **4** that would have resulted from an intra-intermolecular cascade reaction of **2a** with incorporation of one molecule of **1**.

Especially this result with the enyne **2a** gives a certain hint about the mechanism for the formation of **3a**. Although none of the postulated intermediates has actually been identified, the mere fact that the double bond in **2a** does not participate in the reaction, indicates a preferred initial complexation of two molecules of bicyclopropylidene (**1**) on nickel,[13] leading to the tetraspirocyclopropanated nickelacyclopentane **5** after two-fold insertion (Scheme 2).[16]

A cyclopropylcarbinylmetal to homoallylmetal rearrangement[17] – corresponding to a β-carbon elimination – in **5** would yield the nickelacyclohexane intermediate **6** which could insert the alkyne **2**, and the resulting nickelacyclooctene **8** would furnish the observed cycloheptene derivative **3** by reductive elimination. As the transition structure for the rearrangement of **5** to **6** most probably would be highly strained, it is more likely that insertion of the alkyne **2** occurs at the stage of the nickelacyclopentane intermediate **5** to give **7**, which subsequently undergoes the cyclopropylcarbinylmetal to homoallylmetal rearrangement[17] to furnish **8**, the immediate precursor to **3**.

To establish the scope and limitations of this new reaction, various alkynes were employed (Table 1), and the loading of the catalyst was varied. Usually, higher catalyst loading [10 mol% $Ni(cod)_2$, 20 mol% PPh_3] gave higher yields than lower [(5 mol% $Ni(cod)_2$, 10 mol% PPh_3), compare entries 1 and 2, 4 and 5, as well as 7 and 8]. Most of the tested terminal alkynes **2**, especially the ones with bulky (**2b–e**), aromatic (**2f**), aliphatic (**2g** and **h**) and electron-donating (**2j**) substituents afforded the corresponding formal [3+2+2] cycloadducts **3** in good to high yields (entries 1–12). The reaction can be also carried out under an atmosphere of acetylene (**2i**) provided in a balloon,



Scheme 2. Nickel(0)-catalyzed intermolecular [3+2+2] cocyclizations of bicyclopropylidene (**1**) and terminal alkynes **2**. For further details see Table 1.

and it afforded **3i** in 77% yield. The product **3j** obtained with ethoxyethyne (**2j**) was not stable on silica gel and hydrolyzed to 11-cyclopropylidenedispiro-[2.0.2.5]undecan-8-one upon chromatographic purification. The reaction with methyl propiolate **2k** was sluggish and produced a very low yield of **3k**. Protection of the hydroxy group in propargyl alcohol (**2l**) was beneficial for obtaining higher yields (compare entries 14 and 15–16). It is noteworthy that most of these reactions proceeded with high degrees of chemo- and regioselectivity. Only in the case of **2f** was a trace of a regioisomeric product detected.

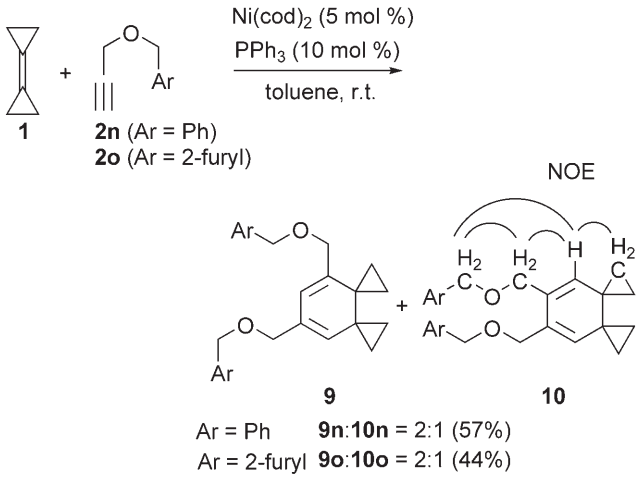
With the benzyl propargyl ether **2n** and the furfuryl propargyl ether **2o**, traces of the formal [2+2+2] cycloadducts[18] **9n/10n** and **9o/10o** could be isolated. Employing the alkyne **2n** or **2o** and the alkene **1** in a ratio of 2:1 led to increased yields of **9n/10n** and **9o/10o** of 57 and 44%, respectively (Scheme 3). The two isomers **9** and **10** were assigned on the basis of their NMR spectra (^1H-^1H NOESY, COESY, HMBC and HMQC).

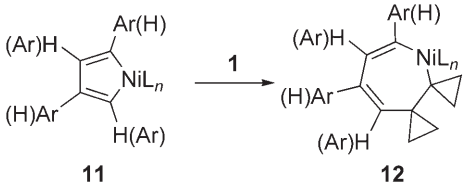
Apparently, the reaction mode of these cocyclizations is controlled by a delicate balance between the ligating abilities and thereby reactivities of bicyclopropylidene (**1**) and the respective alkyne. The propargyl ethers **2n** and **2o** must be slightly more reactive towards $Ni(cod)_2$ than **1** so that a nickelacyclopenta-

Table 1. Nickel(0)-catalyzed intermolecular [3+2+2] cocyclizations of bicyclopropylidene (**1**) and terminal alkynes **2** (see Scheme 2).

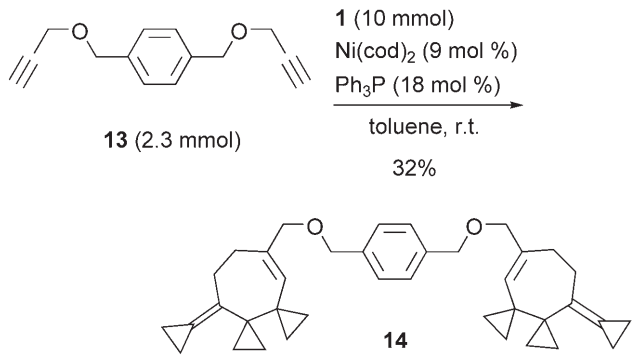
Entry	Alkyne	R	Product	Yield [%][a]
1	**2b**	*t*-Bu	**3b**	93[b]
2	**2b**	*t*-Bu	**3b**	86[c]
3	**2c**	Me_3Si	**3c**	92[b]
4	**2d**	Cpr(Me)	**3d**	87[b]
5	**2d**	Cpr(Me)	**3d**	91[d]
6	**2e**	Cpr	**3e**	92[b]
7	**2f**	Ph	**3f**	45[b,e]
8	**2f**	Ph	**3f**	65[d,e]
9	**2g**	$CH_2CH(CO_2Me)_2$	**3g**	50[b]
10	**2h**	*n*-Bu	**3h**	79[b]
11	**2i**	H	**3i**	77[f]
12	**2j**	OEt	[**3j**][g]	57[d]
13	**2k**	CO_2Me	**3k**	8[b,h]
14	**2l**	CH_2OH	**3l**	25[b]
15	**2m**	CH_2OTHP	**3m**	60[b]
16	**2n**	CH_2OBn	**3n**	65[b,i]
17	**2o**	CH_2OCH_2(2-furyl)	**3o**	57[b,i]

[a] Isolated yields.
[b] Reaction was performed by employing $Ni(cod)_2$ (27.5 mg, 0.10 mmol, 5.0 mol%) and PPh_3 (52.5 mg, 0.20 mmol, 10.0 mol%) in anhydrous toluene (1.0 mL), 5.0 mmol of **1** and 2.0 mmol of **2** in toluene (1.0 mL).
[c] $Ni(cod)_2$ (14.0 mg, 0.05 mmol, 2.5 mol%) and PPh_3 (26.0 mg, 0.10 mmol, 5.0 mol%) were used.
[d] $Ni(cod)_2$ (55.0 mg, 0.20 mmol, 10.0 mol%) and PPh_3 (105.0 mg, 0.40 mmol, 20.0 mol%) were used.
[e] A trace amount (<5%) of the 11-phenyl regioisomer of **3f** was detected in the NMR spectra.
[f] $Ni(cod)_2$ (27.5 mg, 0.10 mmol, 2.0 mol%) and PPh_3 (52.5 mg, 0.20 mmol, 4.0 mol%), acetylene (balloon, 1atm, excess), **1** (400 mg, 5.0 mmol) were used, catalyst loading and yield of **3i** was based on **1**.
[g] The enol ether **3j** underwent hydrolysis to 11-cyclopropylidenedispiro[2.0.2.5]undecan-8-one upon purification by column chromatography on silica gel.
[h] No other products could be identified and no starting material could be recovered.
[i] Trace amounts of the corresponding formal [2+2+2] cycloadducts of type **9** and **10** were also isolated (Scheme 3).





Scheme 3. Nickel-catalyzed intermolecular [2+2+2] cocyclizations of one molecule of bicyclopropylidene (**1**) and two molecules of propargyl ether **2n** or **2o**.



Scheme 4. Two-fold [3+2+2] cocyclization of the bispropargyl ether **13** and bicyclopropylidene (**1**).

diene **11** (two regioisomers) is formed initially before bicyclopropylidene (**1**) is inserted to yield **12** (two regioisomers). Interestingly, **12** then undergoes reductive elimination without a cyclopropylcarbinyl to homoallyl rearrangement.

The reactivity balance is so delicate that it can even be influenced by modifying the ratio of cocyclization substrates. Thus, the bispropargyl ether **13**, with a roughly five-fold excess of bicyclopropylidene (**1**) per triple bond gave the two-fold [3+2+2] cocyclization product **14** in 32% yield (Scheme 4).

Conclusion and Outlook

A novel nickel-catalyzed intermolecular [3+2+2] cocyclization of bicyclopropylidene (**1**) and terminal alkynes **2** provides access to seven-membered carbocycles with good regioselectivity. In these reactions, the peculiar methylenecyclopropane derivative **1** acts as both a three- and a two-carbon component. The reaction mode switches to a [2+2+2] cocyclization, when an excess of a propargyl ether **2n** or **2o** is employed. These new cocyclizations hold a certain potential for

combinatorial applications since various enynes including non-terminal ones, diynes and non-terminal alkynes as well as acceptor-substituted bicyclopropylidenes can be employed. More detailed studies on the scope of these reactions are in progress.

Experimental Section

All reagents were used as purchased from commercial suppliers without further purification. All reactions in non-aqueous solvents were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were purified and dried according to conventional methods prior to use; toluene was freshly distilled from sodium/benzophenone and acetonitrile was freshly distilled from CaH_2. ^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AM 250 or Varian UNITY-300 instrument. Chemical shifts δ are given in ppm relative to resonances of solvent (^1H: 7.26 ppm for residual $CHCl_3$ in $CDCl_3$; ^{13}C: 77.0 ppm for $CDCl_3$), coupling constants J are given in Hertz. Characterization of the multiplicities of signals: s = singlet, br s = broad singlet, d = doublet, t = triplet, m = multiplet. The multiplicities of ^{13}C NMR signals were determined by the DEPT technique: DEPT: + = primary or tertiary (positive DEPT signal), − = secondary (negative DEPT signal), C_{quat} = quaternary C-atoms; or the APT technique: APT: + = primary or tertiary (positive APT signal), − = secondary or quaternary (negative DEPT signal). IR: Bruker IFS 66. MS and HR-MS: Finnigan MAT 95 spectrometer: pre-selected ion peak matching at R *ca.* 10000 to be within ±2 ppm of the exact masses. Chromatography: separations were carried out on Merck Silica gel 60 (0.063–0.200 mm, 70–230 mesh ASTM). The dimensions of the columns are given as "diameter × height of the silica column". TLC: Macherey–Nagel, TLC plates Alugram® Sil G/UV_{254}. Detection under UV light at 254 nm, development with MOPS reagent (10% molybdophosphoric acid, solution in ethanol). Melting points: apparatus according to Dr. Tottoli (Büchi); values are uncorrected. Elemental analyses: Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen. Bicyclopropylidene (**1**)[8] and 1,4-bis(prop-2-ynyloxymethyl)benzene (**13**)[19] were prepared according to published procedures.

General Procedure (GP) for Nickel(0)-Catalyzed Cocyclizations of Bicyclopropylidene (1) and Alkynes (2)

To a dark red solution of $Ni(cod)_2$ and PPh_3 in anhydrous toluene was added at ambient temperature under nitrogen dropwise with a syringe pump a solution of bicyclopropylidene (**1**) and the respective alkyne **2** in anhydrous toluene within 3 h. The reaction mixture was stirred until the alkyne had disappeared (usually overnight), monitoring the progress by TLC. After removal of the solvent in a rotary evaporator under reduced pressure at ambient temperature, the residue was subjected to chromatography on silica gel eluting with pentane/diethyl ether.

Diethyl 2-[(11-Cyclopropylidenedispiro[2.0.2.5]undec-7-en-8-yl)methyl]-2-(prop-2-enyl)malonate (3a)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (0.5 mL) and a solution of **1** (160 mg, 2.0 mmol) as well as diethyl 2-allyl-2-prop-2-ynylmalonate (**2a**) (238 mg, 1.0 mmol) in toluene (0.5 mL) **3a** was obtained after chromatography (2 × 20 cm column, R_f = 0.81, eluting with pentane/diethyl ether 5:1) as a colorless oil; yield: 329 mg (0.83 mmol, 83%); IR (film): $\tilde{\nu}$ = 3078, 2978, 1734, 1640, 1437, 1388, 1366, 1284, 1211, 1054, 920, 858 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.39–0.47 (m, 4H, Cpr-H), 0.53–0.55 (m, 2H, Cpr-H), 0.72–0.77 (m, 2H, Cpr-H), 0.79–0.90 (m, 2H, Cpr-H), 1.00–1.06 (m, 2H, Cpr-H), 1.21–1.31 (m, 6H, 2 CH_3), 2.23–2.27 (m, 2H, CH_2), 2.65–2.68 (m, 6H, 3 CH_2), 4.06–4.26 (m, 4H, 2 OCH_2), 4.96 (s, 1H, vinyl-H), 5.03 (s, 1H, vinyl-H), 5.07–5.09 (m, 1H, vinyl-H), 5.59–5.76 (m, 1H, vinyl-H); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = −0.43 (−, Cpr-C), 3.42 (−, Cpr-C), 12.04 (−, 2 × Cpr-C), 14.05 (+, 2 × CH_3), 14.58 (−, 2 × Cpr-C), 24.61 (−, Cpr-C_{quat}), 27.53 (−, Cpr-C_{quat}), 31.78 (−, CH_2), 34.26 (−, CH_2), 36.63 (−, CH_2), 42.91 (−, CH_2), 57.68 (−, C_{quat}), 61.04 (−, 2 OCH_2), 112.41 (−, vinyl-C_{quat}), 118.68 (−, vinyl-CH_2), 132.34 (−, vinyl-C_{quat}), 133.03 (+, vinyl-CH), 135.30 (−, vinyl-C_{quat}), 138.27 (+, vinyl-CH), 171.26 (−, 2 CO); MS (70 eV, EI): *m/z* (%) = 398 (2) [M^+], 370 (40), 325 (4), 296 (8), 250 (12), 237 (22), 223 (8), 198 (26), 170 (100), 155 (48), 141 (46), 129 (36), 115 (20), 91 (28), 79 (10), 41 (18); elemental analysis: calcd. for $C_{25}H_{34}O_4$ (398.54): C 75.34, H 8.60; found: C 75.66, H 8.31.

8-*tert*-Butyl-11-cyclopropylidenedispiro[2.0.2.5]undec-7-ene (3b)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in anhydrous toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as 3,3-dimethyl-1-butyne (**2b**) (164 mg, 2.0 mmol) in toluene (1.0 mL) **3b** was obtained after chromatography (2 × 30 cm column, R_f = 0.95, eluting with pentane) as a colorless oil; yield: 450 mg (1.86 mmol, 93%).

The same procedure with 2.5 mol% of $Ni(cod)_2$ and 5.0 mol% of PPh_3 afforded **3b** in 86% yield. IR (film): $\tilde{\nu}$ = 3077, 2966, 2869, 1465, 1361, 1016 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.34–0.37 (m, 2H, Cpr-H), 0.43–0.47 (m, 2H, Cpr-H), 0.51–0.55 (m, 2H, Cpr-H), 0.62–0.66 (m, 2H, Cpr-H), 0.85–0.89 (m, 2H, Cpr-H), 1.02–1.05 (m, 2H, Cpr-H), 1.01 (s, 9H, *t*-Bu), 2.42–2.48 (m, 2H, CH_2), 2.55–2.58 (m, 2H, CH_2), 4.90 (s, 1H, H-7); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = 0.14 (−, Cpr-C), 3.24 (−, Cpr-C), 11.41 (−, 2 Cpr-C), 14.17 (−, 2 Cpr-C), 24.57 (−, Cpr-C_{quat}), 26.51 (−, C-10), 27.49 (−, C_{quat}), 28.86 (+, *t*-Bu), 34.91 (−, C-9), 36.45 (−, *t*-Bu-C_{quat}), 113.75 (−, Cpr-C_{quat}), 128.13 (+, C-7), 132.57 (−, C-8), 148.83 (−, C-11); MS (70 eV, EI): *m/z* (%) = 242 (16) [M^+], 229 (24), 214 (96), 199 (60), 185 (40), 171 (36), 157 (100), 143 (60), 129 (76), 91 (78); HR-MS: $C_{18}H_{26}$ (242.40): calcd. [M^+]: 242.2035 (correct HR-MS).

11-Cyclopropylidene-8-trimethylsilyldispiro[2.0.2.5]-undec-7-ene (3c)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg,

5.0 mmol) as well as trimethylsilylethyne **2c** (196 mg, 2.0 mmol) in toluene (1.0 mL) **3c** was obtained after chromatography (2×30 cm column, R_f=0.91, eluting with pentane) as a colorless oil; yield: 474 mg (1.84 mmol, 92%); IR (film): $\tilde{\nu}$=3078, 3002, 2954, 1457, 1419, 1247, 836, 751 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ=0.02 (s, 9H, 3 CH_3), 0.36–0.53 (m, 8H, Cpr-H), 0.82–0.91 (m, 2H, Cpr-H), 0.99–1.09 (m, 2H, Cpr-H), 2.43–2.51 (m, 2H, CH_2), 2.61–2,70 (m, 2H, CH_2), 5.16 (s, 1H, H-7); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=−2.02 (+, 3 CH_3), 0.22 (−, Cpr-C), 3.05 (−, Cpr-C), 11.50 (−, 2 Cpr-C), 14.09 (−, 2 Cpr-C), 26.71 (−, Cpr-C_{quat}), 27.11 (−, C-10), 27.72 (−, Cpr-C_{quat}), 35.03 (−, C-9), 114.79 (−, Cpr-C_{quat}), 131.95 (−, C-8), 139.79 (−, C-11), 146.01 (+, C-7); MS (70 eV, EI): *m/z* (%)=258 (4) [M^+], 245 (4), 230 (6), 185 (4), 73 (100); elemental analysis: calcd. for $C_{17}H_{26}Si$ (258.47): C 79.00, H 10.14; found: C 79.02, H 9.88.

11-Cyclopropylidene-8-(1-methylcyclopropyl)-dispiro[2.0.2.5]undec-7-ene (3d)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol, 5 mol%) and PPh_3 (52.5 mg, 0.2 mmol, 10 mol%) in anhydrous toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as 1-methylcyclopropyl-1-ethyne (**2d**) (160 mg, 2.0 mmol) in toluene (1.0 mL) **3d** was obtained after chromatography (2× 30 cm column, R_f=0.95, eluting with pentane) as a colorless oil; yield: 419 mg (1.75 mmol, 87%).

The same procedure with $Ni(cod)_2$ (55 mg, 0.2 mmol, 10 mol%) and PPh_3 (105 mg, 0.40 mmol, 20 mol%) afforded **3d** in 91% yield. IR (film): $\tilde{\nu}$=3076, 3001, 2957, 2873, 1456, 1424, 1377, 1016 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ= 0.33–0.38 (m, 4H, Cpr-H), 0.44–0.46 (m, 2H, Cpr-H), 0.50–0.54 (m, 4H, Cpr-H), 0.66–0.70 (m, 2H, Cpr-H), 0.81–0.88 (m, 2H, Cpr-H), 1.00–1.07 (m, 2H, Cpr-H), 1.12 (s, 3H, CH_3), 2.40–2.46 (m, 2H, CH_2), 2.62–2.68 (m, 2H, CH_2), 5.41 (s, 1H, H-7); ^{13}C NMR (75 MHz, $CDCl_3$, APT): δ=−0.13 (−, Cpr-C), 3.27 (−, Cpr-C), 11.69 (−, Cpr-C), 12.95 (−, Cpr-C), 14.17 (−, Cpr-C), 23.93 (−, Cpr-C_{quat}), 24.35 (+, C-Me), 24.46 (−, Cpr-C_{quat}), 27.50 (−, Cpr-C_{quat}), 29.06 (−, C-10), 34.62 (−, C-9), 113.36 (−, Cpr-C_{quat}), 131.75 (+, C-7), 132.58 (−, C-11), 144.24 (−, C-8); MS (70 eV, EI): *m/z* (%)=240 (20) [M^+], 225 (18), 211 (48), 197 (100), 183 (60), 169 (64), 155 (62), 129 (42), 115 (30), 105 (24), 41 (46); elemental analysis: calcd. for $C_{18}H_{24}$ (240.38): C 89.94, H 10.06; found: C 89.60, H 9.85.

8-Cyclopropyl-11-cyclopropylidenedispiro[2.0.2.5]-undec-7-ene (3e)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as cyclopropylethyne (**2e**) (2.0 mmol, in 70% toluene solution, 188 mg) in toluene (1.0 mL) **3e** was obtained after chromatography (2×30 cm column, R_f=0.95, eluting with pentane) as a colorless oil; yield: 416 mg (1.84 mmol, 92%); IR (film): $\tilde{\nu}$=3078, 3002, 2973, 2929, 1457, 1419, 1017 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ= 0.31–0.56 (m, 10H, Cpr-H), 0.66–0.71 (m, 2H, Cpr-H), 0.76–0.86 (m, 2H, Cpr-H), 0.99–1.06 (m, 2H, Cpr-H), 1.25–1.42 (m, 1H, Cpr-H), 2.17–2.23 (m, 2H, CH_2), 2.62–2.68 (m, 2H, CH_2), 4.91 (s, 1H, H-7); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=−0.26 (−, Cpr-C), 3.30 (−, Cpr-C), 4.34 (−, Cpr-C), 11.88 (−, Cpr-C), 14.23 (−, Cpr-C), 18.91 (+, Cp-C), 24.30 (−, Cpr-C_{quat}), 27.65 (−, Cpr-C_{quat}), 28.42 (−, C-10), 34.04 (−, C-9), 113.12 (−, Cpr-C_{quat}), 130.61 (+, C-7), 132.59 (−, C-11), 140.89 (−, C-8); MS (70 eV, EI): *m/z* (%)=226 (6) [M^+], 211 (20), 183 (100), 168 (30), 153 (40), 141 (38), 128 (40); HR-MS: $C_{17}H_{22}$ (226.36): calcd. [M^+]: 226.1721 (correct HR-MS).

11-Cyclopropylidene-8-phenyldispiro[2.0.2.5]undec-7-ene (3f)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in anhydrous toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as phenylethyne (**2f**) (204 mg, 2.0 mmol) in toluene (1.0 mL) **3f** was obtained after chromatography (2×30 cm column, R_f=0.65, eluting with pentane) as a colorless oil; yield: 237 mg (0.90 mmol, 45%).

The same procedure with $Ni(cod)_2$ (55 mg, 0.20 mmol, 10 mol%) and PPh_3 (105 mg, 0.40 mmol, 20 mol%) afforded **3d** in 65% yield. IR (film): $\tilde{\nu}$=3078, 3001, 2971, 2828, 1772, 1718, 1598, 1492, 1444, 1020, 759, 698 cm^{-1}, ^1H NMR (250 MHz, $CDCl_3$): δ=0.54–0.59 (m, 4H, Cpr-H), 0.67–0.71 (m, 2H, Cpr-H), 0.79–0.83 (m, 2H, Cpr-H), 0.89–0.94 (m, 2H, Cpr-H), 1.08–1.14 (m, 2H, Cpr-H), 2.90 (s, 4H, 2 CH_2), 5.41 (s, 1H, H-7), 7.21–7.38 (m, 5H, Ar-H); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=−0.13 (−, Cpr-C), 3.35 (−, Cpr-C), 11.95 (−, 2 Cpr-C), 14.74 (−, 2 Cpr-C), 25.46 (−, Cpr-C_{quat}), 27.44 (−, Cpr-C_{quat}), 30.86 (−, C-10), 34.41 (−, C-9), 113.55 (−, Cpr-C_{quat}), 128.07 (+, 2 Ar-C), 126.22 (+, Ar-C), 125.79 (+, 2 Ar-C), 132.21 (−, C-11), 136.50 (+, C-7), 140.50 (−, C-8), 145.16 (−, Ar-C_{quat}); MS (70 eV, EI): *m/z* (%)=262 (20) [M^+], 247 (22), 234 (100), 219 (80), 205 (56), 191 (40), 178 (36), 165 (44), 155 (24), 143 (42), 128 (48), 115 (50), 91 (80), 77 (40); elemental analysis: calcd. for $C_{20}H_{22}$ (262.39): C 91.55, H 8.45; found: C 91.35, H 8.21.

Dimethyl 2-(11-Cyclopropylidenedispiro[2.0.2.5]-undec-7-en-8-ylmethyl)malonate (3g)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) and dimethyl 2-prop-2-ynylmalonate (**2g**) (340 mg, 2.0 mmol) in toluene (1.0 mL) **3g** was obtained after chromatography (2×20 cm column, R_f=0.45, eluting with pentane/diethyl ether 5:1) as a colorless oil; yield: 330 mg (1.0 mmol, 50%); IR (film): $\tilde{\nu}$=3076, 3002, 2953, 1738, 1436, 1343, 1235, 1153, 1025 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.35–0.45 (m, 4H, Cpr-H), 0.51–0.55 (m, 2H, Cpr-H), 0.69–0.73 (m, 2H, Cpr-H), 0.80–0.90 (m, 2H, Cpr-H), 1.01–1.06 (m, 2H, Cpr-H), 2.30–2.35 (m, 2H), 2.56 (d, J=8.0 Hz, 2H, H-8-CH_2), 2.67–2.71 (m, br. 2H), 3.57 [t, J= 8.0 Hz, 1H, $CH(COOMe)_2$], 3.71 (s, 6H, 2 CH_3), 4.96 (s, 1H, H-7); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=−0.39 (−, Cpr-C), 3.36 (−, Cpr-C), 11.94 (−, 2 Cpr-C), 14.36 (−, 2 Cpr-C), 24.29 (−, Cpr-C_{quat}), 27.53 (−, Cpr-C_{quat}), 30.63 (−, CH_2), 33.90 (−, C-10), 39.53 (−, C-9), 50.86 (+, CH), 52.28 (+, 2×C-OMe), 112.87 (−, Cpr-C_{quat}), 132.23 (−, C-11), 135.57 (+, C-7), 135.90 (−, C-8), 169.47 (−, 2 CO); MS (70 eV, EI): *m/z* (%)=330 (4) [M^+], 302 (40), 267 (2), 238 (4), 223 (3), 210 (12), 198 (14), 171 (24), 170 (100), 155 (50), 129 (40), 115 (28), 91 (36), 77 (20); HR-MS: $C_{20}H_{26}O_4$ (330.42): calcd. [M^++1]: 331.19094 (correct HR-MS).

8-Butyl-11-cyclopropylidenedispiro[2.0.2.5]undec-7-ene (3h)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as 1-butyne **2h** (164 mg, 2.0 mmol) in toluene (1.0 mL) **3h** was obtained after chromatography (2× 20 cm column, R_f=0.85, eluting with pentane) as a colorless oil; yield: 380 mg (1.57 mmol, 79%); IR (film): $\tilde{\nu}$=3078, 3042, 3000, 2956, 2928, 1466, 1457, 1417, 1018 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.38–0.40 (m, 2H, Cpr-H), 0.45–0.48 (m, 2H, Cpr-H), 0.50–0.52 (m, 2H, Cpr-H), 0.70–0.74 (m, 2H, Cpr-H), 0.84–0.91 (m, 5H, Cpr-H and CH_3), 1.02–1.05 (m, 2H, Cpr-H), 1.32–1.34 (m, 4H, CH_2-Bu), 1.93–1.98 (t, J=7.25 Hz, 2H, CH_2-Bu), 2.31–2.35 (m, 2H, CH_2), 2.67–2.72 (m, 2H, CH_2), 4.87 (s, 1H, H-7); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=−0.34 (−, Cpr-C), 3.37 (−, Cpr-C), 11.99 (−, 2 Cpr-C), 14.05 (+, CH_3), 14.27 (−, 2 Cpr-C), 22.30 (−, CH_2-C_{Bu}), 24.24 (−, Cpr-C_{quat}), 27.81 (−, Cpr-C_{quat}), 30.44 (−, CH_2-C_{Bu}), 30.99 (−, CH_2-C_{Bu}), 34.10 (−, C-10), 40.10 (−, C-9), 112.63 (−, Cpr-C_{quat}), 131.69 (+, C-7), 132.95 (−, C-11), 140.86 (−, C-8); MS (70 eV, EI): *m/z* (%)=242 (8) [M^+], 214 (100), 185 (20), 171 (36), 157 (84), 129 (44), 91 (40), 77 (20); HR-MS: $C_{18}H_{26}$ (242.40): calcd. [M^+]: 242.2035, found: 242.2034.

11-Cyclopropylidenedispiro[2.0.2.5]undec-7-ene (3i)

According to the GP, to $Ni(cod)_2$ (27.5 mg, 0.1 mmol, 2 mol%) and PPh_3 (52.5 mg, 0.2 mmol, 4 mol%) in anhydrous toluene (1.0 mL) kept under an atmosphere of acetylene (**2i**) (balloon, 1 atm), was added a solution of **1** (400 mg, 5.0 mmol) in anhydrous toluene (1.0 mL) within 3 h, and the mixture was stirred overnight. Chromatography (2×20 cm column, R_f=0.67, eluting with pentane) gave **3i** as a colorless oil; yield: 360 mg (1.93 mmol, 77%); IR (film): $\tilde{\nu}$= 3078, 3005, 2973, 2931, 2838, 1433, 1019, 728 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.42–0.49 (m, 4H, Cpr-H), 0.55–0.58 (m, 2H, Cpr-H), 0.71–0.75 (m, 2H, Cpr-H), 0.85–0.89 (m, 2H, Cpr-H), 1.02–1.08 (m, 2H, Cpr-H), 2.35–2.43 (m, 2H, CH_2), 2.69–2.75 (m, 2H, CH_2), 5.05 (dt, 1H, J=11.3, 1.5 Hz, H-7), 5.59 (dt, 1H, J=11.3, 5.5 Hz, H-8); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=−0.15 (−, Cpr-C), 3.30 (−, Cpr-C), 11.90 (−, 2 Cpr-C), 14.07 (−, 2 Cpr-C), 25.37 (−, Cpr-C_{quat}), 27.15 (−, C-10), 27.52 (−, C_{quat}), 34.35 (−, C-9), 113.76 (−, Cpr-C_{quat}), 128.46 (+, C-7). 132.38 (−, C-11). 138.12 (−, C-8); MS (70 eV, EI): *m/z* (%)=186 (2) [M^+], 171 (8), 158 (24), 143 (30), 129 (24), 115 (18), 91 (100); HR-MS: $C_{14}H_{18}$ (186.29): calcd. [M^+]: 186.1409 (correct HR-MS).

11-Cyclopropylidenedispiro[2.0.2.5]undecan-8-one

According to the GP, from $Ni(cod)_2$ (55.0 mg, 0.2 mmol) and PPh_3 (105 mg, 0.4 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as ethoxyethyne **2j** (50 wt% in hexane, 280 mg, 2.0 mmol) in toluene (1.0 mL) after chromatography (2×20 cm column, R_f=0.63, eluting with pentane/diethyl ether 3:1) 11-cyclopropylidenedispiro[2.0.2.5]undecan-8-one was obtained as a colorless oil; yield: 230 mg (1.14 mmol, 57%); The intermediate 11-cyclopropylidene-8-ethoxydispiro[2.0.2.5]undec-7-ene (**3j**) was observed in the TLC (R_f=0.85, pentane/diethyl ether 8:1). IR (film): $\tilde{\nu}$= 3080, 2974, 2939, 1703, 1419, 1019, 733 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.32–0.49 (m, 2H, Cpr-H), 0.40–0.44 (m, 2H, Cpr-H), 0.47–0.51 (m, 2H, Cpr-H), 0.68–0.72 (m, 2H, Cpr-H), 0.87–0.96 (m, 2H, Cpr-H), 1.05–1.21 (m, 2H, Cpr-H), 2.48 (s, 2H, CH_2), 2.63 (s, 4H, 2 CH_2); ^{13}CNMR (75.5 MHz, $CDCl_3$, APT): δ=−0.08 (−, Cpr-C), 3.54 (−, Cpr-C), 11.64 (−, 2 Cpr-C), 12.04 (−, 2 Cpr-C), 21.04 (−, Cpr-C_{quat}), 30.11 (−, Cpr-C_{quat}), 30.71 (−, C-10), 43.37 (−, C-9), 53.01 (−, C-7), 117.40 (−, Cpr-C_{quat}), 130.62 (−, Cpr-C_{quat}), 213.46 (−, C-8); MS (70 eV, EI): *m/z* (%)=202 (2) [M^+], 187 (8), 174 (28), 159 (36), 145 (68), 131 (76), 117 (84), 105 (50), 91 (100); HR-MS: $C_{14}H_{18}O$ (202.29): calcd. [M^+]: 202.1358 elemental analysis: calcd. for $C_{14}H_{18}O$ (202.29): C 83.12, H 8.97; found: C 82.89, H 8.77.

Methyl 11-cyclopropylidenedispiro[2.0.2.5]undec-7-ene-8-carboxylate (3k)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as methyl propynoate (**2k**) (168 mg, 2.0 mmol) in toluene (1.0 mL) was obtained after chromatography (2×20 cm column, R_f=0.25, eluting with pentane/dichloromethane 3:1) **3k** (40 mg, 0.16 mmol, 8%) as a colorless oil. - IR (Film): $\tilde{\nu}$=2974, 2948, 1709, 1635, 1435, 1280, 1224, 1092, 1022 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ= 0.48–0.50 (m, 1H, Cpr-H), 0.64–0.66 (m, 1H, Cpr-H), 0.71–0.77 (m, 4H, Cpr-H), 0.86–0.89 (m, 2H, Cpr-H), 1.01–1.04 (m, 2H, Cpr-H), 1.08–1.14 (m, 2H, Cpr-H), 2.69–2.74 (m, 2H, CH_2), 2.79–2.90 (m, 2H, CH_2), 3.73 (s, 3H, CH_3), 6.33 (s, 1H, H-7); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=0.15 (−, Cpr-C), 3.07 (−, Cpr-C), 11.56 (−, 2 Cpr-C), 15.24 (−, 2 Cpr-C), 24.42 (−, C-10), 26.02 (−, Cpr-C_{quat}), 26.90 (−, Cpr-C_{quat}) 34.02 (−, C-9), 51.72 (+, CH_3), 115.18 (−, Cpr-C_{quat}), 130.66 (−, C-11), 130.76 (−, C-8), 150.76 (+, C-7), 168.93 (−, CO); MS (70 eV, EI): *m/z* (%)=244 (4) [M^+], 229 (8), 216 (64), 201 (44), 185 (100), 169 (20), 157 (90), 141 (60), 129 (84), 115 (60); HR-MS: $C_{16}H_{20}O_2$ (244.33): calcd. [M^+]: 244.1463 (correct HR-MS).

(11-Cyclopropylidenedispiro[2.0.2.5]undec-7-en-8-yl)-methanol (3l)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as prop-2-yn-1-ol (**2l**) (112 mg, 2.0 mmol) in toluene (1.0 mL) **3l** was obtained after chromatography (2×20 cm column, R_f=0.38, eluting with pentane/ethyl acetate 6:1) as a colorless oil; yield: 106 mg (0.49 mmol, 25%); IR (film): $\tilde{\nu}$=3310, 3078, 3000, 2971, 2927, 1430, 1086, 1018 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.43–0.48 (m, 4H, Cpr-H), 0.56–0.58 (m, 2H, Cpr-H), 0.69–0.73 (m, 2H, Cpr-H), 0.86–0.89 (m, 2H, Cpr-H), 1.02–1.07 (m, 2H, Cpr-H), 2.40 (s, br, 1H, OH), 2.43–2.45 (m, 2H, H-10), 2.70–2.75 (m, 2H, H-9), 3.98 (s, 2H, OCH_2), 5.08 (s, 1H, H-7); ^{13}C NMR (50 MHz, $CDCl_3$, DEPT): δ=−0.12 (−, Cpr-C), 3.22 (−, Cpr-C), 11.74 (−, 2 Cpr-C), 14.09 (−, 2 Cpr-C), 24.67 (C_{quat}, Cpr-C), 27.18 (C_{quat}, Cpr-C), 27.75 (−, C-10), 33.93 (−, C-9), 68.97 (−, OCH_2), 113.96 (C_{quat}, Cpr-C), 131.97 (C_{quat}, C-11), 133.69 (+, C-7), 139.46 (C_{quat}, C-8); MS (70 eV, EI): *m/z* (%)=216 (6) [M^+], 201 (4), 185 (90), 157

(84), 141 (60), 129 (100), 128 (64), 115 (60), 91 (76); HR-MS: $C_{15}H_{20}O$ (216.32): calcd. [M^+]: 216.1514.

2-(11-Cyclopropylidenedispiro[2.0.2.5]undec-7-en-8-ylmethoxy)tetrahydropyran (3m)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as 2-prop-2-ynyloxytetrahydropyran (**2m**) (280 mg, 2.0 mmol) in toluene (1.0 mL) **3m** was obtained after chromatography (2×20 cm column, R_f=0.26, eluting with pentane) as a colorless oil; yield: 360 mg (1.2 mmol, 60%); IR (film): $\tilde{\nu}$=3078, 2999, 2939, 2870, 1440, 1117, 1021 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.43–0.47 (m, 4H, Cpr-H), 0.54–0.58 (m, 2H, Cpr-H), 0.69–0.73 (m, 2H, Cpr-H), 0.82–0.90 (m, 2H, Cpr-H), 1.02–1.08 (m, 2H, Cpr-H), 1.50–1.86 (m, 6H, THP), 2.40–2.45 (m, 2H, H-10), 2.70–2.74 (m, 2H, H-9), 3.47–3.51 (m, 1H, THP), 3.82–3.88 (m, 2H, 1H, THP and 1H, OCH_2), 4.10 (d, J=11.8 Hz, 1H, OCH_2), 4.62 (t, J=3.5 Hz, 1H, THP), 5.10 (s, 1H, H-7); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=−0.14 (−, Cpr-C), 3.25 (−, Cpr-C), 11.73 (−, Cpr-C), 11.87 (−, Cpr-C), 14.08 (−, Cpr-C), 14.22 (−, Cpr-C), 19.56 (−, THP-C), 24.75 (−, Cpr-C), 25.49 (−, THP-C), 27.26 (−, Cpr-C), 28.00 (−, C-10), 30.65 (−, THP-C), 33.85 (−, C-9), 62.19 (−, OCH_2), 72.93 (−, OCH_2), 97.09 (+, CHO_2), 113.71 (−, Cpr-C), 132.17 (−, C-11), 135.49 (+, C-7), 139.44 (−, C-8); MS (70 eV, EI): m/z (%)=300 (2) [M^+], 272 (6), 243 (2), 215 (2), 198 (4), 185 (6), 170 (34), 115 (12), 129 (10), 85 (100); HR-MS: $C_{20}H_{28}O_2$ (300.44): calcd. [M^+]: 300.2089 (correct HR-MS).

8-Benzyloxymethyl-11-cyclopropylidenedispiro-[2.0.2.5]undec-7-ene (3n)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as prop-2-ynyloxymethylbenzene (**2n**) (292 mg, 2.0 mmol) in toluene (1.0 mL) **3n** was obtained after chromatography (2×20 cm column, R_f=0.56, eluting with pentane/diethyl ether 8:1) as a colorless oil; yield: 398 mg (1.3 mmol, 65%); IR (film): $\tilde{\nu}$=3077, 3028, 3000, 2971, 2928, 2851, 1496, 1454, 1352, 1087, 1072, 1018, 735, 697 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.43–0.50 (m, 4H, Cpr-H), 0.57–0.60 (m, 2H, Cpr-H), 0.72–0.76 (m, 2H, Cpr-H), 0.85–0.89 (m, 2H, Cpr-H), 1.03–1.06 (m, 2H, Cpr-H), 2.44–2.48 (m, 2H, H-10), 2.72–2.74 (m, 2H, H-9), 3.89 (s, 2H, OCH_2), 4.46 (s, 2H, OCH_2), 5.11 (s, 1H, H-7), 7.27–7.35 (m, 5H, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$, APT, HMBC, HMQC): δ=−0.14 (−, Cpr-C), 3.30 (−, Cpr-C), 11.88 (−, 2 Cpr-C), 14.24 (−, 2 Cpr-C), 24.77 (−, Cpr-C), 27.32 (−, Cpr-C), 28.00 (−, C-10), 33.89 (−, C-9), 71.22 (−,OCH_2), 76.44 (−, OCH_2), 113.63 (−, Cpr-C), 127.43 (+, Ar-C), 127.78 (+, 2 Ar-C), 128.29 (+, 2 Ar-C), 132.17 (−, C-11), 136.17 (+, C-7), 136.71 (−, C-8), 138.61 (−, Ar-C); MS (70 eV, EI): m/z (%)=278 (3) [$M^+-C_2H_4$], 249 (4), 221 (1), 197 (2), 185 (5), 157 (8), 143 (8), 129 (10), 91 (100); elemental analysis: calcd. for $C_{22}H_{26}O$ (306.44): C 86.23, H 8.55; found: C 86.13, H 8.25.

2-(11-Cyclopropylidenedispiro[2.0.2.5]undec-7-en-8-ylmethoxymethyl)furan (2o)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (400 mg, 5.0 mmol) as well as 2-prop-2-ynyloxymethylfuran (**2o**) (272 mg, 2.0 mmol) in toluene (1.0 mL) **3o** was obtained after chromatography (2×20 cm column, R_f=0.71, eluting with pentane/diethyl ether 10:1) as a colorless oil; yield: 340 mg (1.15 mmol, 57%); IR (film): $\tilde{\nu}$=3076, 3000, 2972, 2930, 2851, 1434, 1353, 1151, 1071, 1016, 742, 696 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.44–0.49 (m, 4H, Cpr-H), 0.56–0.59 (m, 2H, Cpr-H), 0.71–0.75 (m, 2H, Cpr-H), 0.85–0.88 (m, 2H, Cpr-H), 1.02–1.08 (m, 2H, Cpr-H), 2.41–2.46 (m, 2H, H-10), 2.71–2.75 (m, 2H, H-9), 3.88 (d, J=1.0 Hz, 2H, OCH_2), 4.40 (s, 2H, OCH_2), 5.11 (d, J=1.0 Hz, 1H, H-7), 6.28–6.29 (m, 1H, Ar-H), 6.32–6.34 (m, 1H, Ar-H), 7.40–7.41 (m, 1H, Ar-H); ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=−0.14 (−, Cpr-C), 3.28 (−, Cpr-C), 11.84 (−, 2 Cpr-C), 14.23 (−, 2 Cpr-C), 24.79 (−, Cpr-C_{quat}), 27.27 (−, Cpr-C_{quat}), 27.90 (−, C-10), 33.84 (−, C-9), 62.93 (−, OCH_2), 76.25 (−, OCH_2), 109.01 (+, Ar-C), 110.15 (+, Ar-C), 113.66 (−, Cpr-C_{quat}), 132.12 (−, C-11), 136.38 (−, Ar-C_{quat}), 136.54 (+, C-7), 142.60 (+, Ar-C), 152.07 (−, C-8); MS (70 eV, EI): m/z (%)=296 (3) [M^+], 270 (1), 268 (8), 239 (6), 185 (12), 157 (6), 143 (4), 129 (10), 81 (100); elemental analysis: calcd. for $C_{20}H_{24}O_2$ (296.40): C 81.04, H 8.16; found: C 81.11, H 7.91.

7,9-Bisbenzyloxymethyldispiro[2.0.2.4]deca-7,9-diene (9n) and 8,9-Bisbenzyloxymethyldispiro[2.0.2.4]deca-7,9-diene (10n)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (160 mg, 2.0 mmol) as well as prop-2-ynyloxymethylbenzene (**2n**) (584 mg, 4.0 mmol) in toluene (1.0 mL) a mixture of **9n** and **10n** (ratio 2:1) was obtained after chromatography (2× 20 cm column, R_f=0.41, eluting with pentane/diethyl ether 8:1) as a colorless oil; yield: 424 mg (1.14 mmol, 57%); IR (film): $\tilde{\nu}$=3063, 3029, 3003, 2856, 1718, 1701, 1496, 1453, 1069, 737, 698 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.37–0.54 [m, 6 H(**9n**)+8 H(**10n**), Cpr-H], 0.73–0.76 [m, 2 H(**9n**), Cpr-H], 3.86 [s, 2 H(**9n**), OCH_2], 4.03 [s, 2 H(**9n**), OCH_2], 4.15 [s, 4 H(**10n**), 2 OCH_2], 4.47 [s, 2 H(**9n**)+4 H(**10n**), 3 OCH_2], 4.52 [s, 2 H(**9n**), OCH_2], 5.22 [s, 1H, 8-H(**9n**)], 5.25 [s, 2H, 7,10-H(**10n**)], 6.16 [s, 1H, 10-H(**9n**)], 7.28–7.36 [m, 10 H(**9n**)+10 H(**10n**), Ar-H]; ^{13}C NMR (75 MHz, $CDCl_3$, APT, HMBC, HMQC): δ=8.82 [−, 2 Cpr-C(**9n**)], 11.45 [−, 2 Cpr-C(**9n**)], 11.55 [−, 4 Cpr-C(**10n**)], 20.38 [−, 3,4-C_{quat}, 2 Cpr-C(**10n**)], 21.52 [−, 4-C_{quat}, Cpr-C(**9n**)], 21.66 [−, 3-C_{quat}, Cpr-C(**9n**)], 70.73 [−, 2 C(**10n**)-OCH_2], 71.01 [−, C(**9n**)-OCH_2], 71.38 [−, C(**9n**)-OCH_2], 71.60 [−, C(**9n**)-OCH_2], 71.76 [−, 2 C(**10n**)-OCH_2], 71.88 [−, C(**9n**)-OCH_2], 124.92 [+, 10-C(**9n**)], 127.43 (+, Ar-C), 127.46 (+, Ar-C), 127.59 (+, Ar-C), 127.67 (+, Ar-C), 127.78 (+, Ar-C), 127.87 (+, Ar-C), 128.24 (+, Ar-C), 128.27 (+, Ar-C), 131.75 (−, C_{quat}, vinyl-C), 131.82 (−, C_{quat}, vinyl-C), 132.12 [+, 8-C(**9n**)], 134.03 [+, 7,10-C(**10n**)], 136.63 [−, C_{quat}, vinyl-C(**9n**)], 138.29 (−, Ar-C_{quat}), 138.34 (−, Ar-C_{quat}), 138.40 (−, Ar-C_{quat}); MS (DCI, NH_3): m/z (%)=390 (100) [$M+NH_4^+$], 762 (8) [$2M+NH_4^+$]; HR-MS (DCI): $C_{26}H_{28}O_2$ (372.51): found [$M + NH_4]^+$: 390.2428

7,9-Bis(2-furfuryloxymethyl)dispiro[2.0.2.4]deca-7,9-diene (9o) and 8,9-Bis(2-furfuryloxymethyl)dispiro-[2.0.2.4]deca-7,9-diene (10o)

According to the GP, from $Ni(cod)_2$ (27.5 mg, 0.1 mmol) and PPh_3 (52.5 mg, 0.2 mmol) in toluene (1.0 mL) and **1** (160 mg, 2.0 mmol) as well as 2-prop-2-ynyloxymethylfuran (**2o**) (584 mg, 4.0 mmol) in toluene (1.0 mL) a mixture of **9o** and **10o** (ratio 2:1) was obtained after chromatography (2× 20 cm column, $R_f = 0.44$, eluting with pentane/diethyl ether 7:1) as a colorless oil; yield: 310 mg (0.88 mmol, 44%); IR (film): $\tilde{\nu} = 3120$, 3077, 3001, 2856, 1594, 1503, 1356, 1150, 1067, 739, 600 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.34$–0.53 [m, 6 H(**9n**)+8 H(**10n**), Cpr-H], 0.69–0.73 [m, 2 H(**9n**), Cpr-H], 3.82 [s, 2 H(**9n**), OCH_2], 4.01 [s, 2 H(**9n**), OCH_2], 4.11 [s, 4 H(**10n**), OCH_2], 4.39 [s, 2 H(**9n**), OCH_2], 4.42 [s, 4 H(**10n**), OCH_2], 4.44 [s, 2 H(**9n**), OCH_2], 5.22 [s, 1 H(**9n**), vinyl], 5.23 [s, 2 H(**10n**), vinyl], 6.11 [s, 1 H(**9n**), vinyl], 6.29–6.35 [m, 4 H(**9n**)+4 H(**10n**), Ar-H], 7.39–7.41 [m, 2 H(**9n**)+2 H(**10n**), Ar-H]; ^{13}C NMR (50 MHz, $CDCl_3$, APT, HMBC, HMQC): $\delta = 8.77$ [–, 2 Cpr-C(**9n**)], 11.43 [–, 2 Cpr-C(**9n**)], 11.53 [–, 4 Cpr-C(**10n**)], 20.35 [–, 2 C(**10n**)-Cpr-C_{quat}], 21.39 [–, C(**9n**)-Cpr-C_{quat}], 21.66 [–, C(**9n**)-Cpr-C_{quat}], 62.84 [–, C(**9n**)-OCH_2], 63.31 [–, C(**9n**)-OCH_2], 63.43 [–, 2 C(**10n**)-OCH_2], 70.49 [–, 2 C(**10n**)-OCH_2], 70.58 [–, C(**9n**)-OCH_2], 71.65 [–, C(**9n**)-OCH_2], 109.15 (+), 109.21 (+), 109.24 (+), 110.15 (+), 125.35 (+), 131.38 (–), 131.51 (–), 132.63 (+), 134.40 (+), 136.31 (–), 142.54 (+), 142.62 (+), 142.64 (+), 151.72 (–), 151.81 (–), 151.96 (–); MS (DCI, NH_3): *m/z* (%) = 370 (100) [$M+NH_4^+$], 722 (16) [$2M+NH_4^+$]; elemental analysis: calcd. for $C_{22}H_{24}O_4$ (352.42): C 74.98, H 6.86; found: C 74.79, H 6.62.

1,4-Bis(11-cyclopropylidenedispiro[2.0.2.5]undec-7-en-8-ylmethoxymethyl)benzene (14)

According to the GP, from $Ni(cod)_2$ (55 mg, 0.20 mmol, 8.8 mol%) and PPh_3 (105 mg, 0.40 mmol, 17.6 mol%) in toluene (1.0 mL) and **1** (800 mg, 10.0 mmol) as well as 1,4-bis-prop-2-ynyloxymethylbenzene (**13**)[19] (484 mg, 2.26 mmol) in toluene (1.0 mL) **14** was obtained after chromatography (2×20 cm column, $R_f = 0.43$, eluting with pentane/diethyl ether 10:1) as a colorless oil; yield: 384 mg (0.72 mmol, 36% or 32%); IR (film): $\tilde{\nu} = 3078$, 2999, 2972, 2927, 2849, 1457, 1352, 1086, 1019 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.44$–0.49 (m, 8H, Cpr-H), 0.57–0.61 (m, 4H, Cpr-H), 0.72–0.76 (m, 4H, Cpr-H), 0.83–0.90 (m, 4H, Cpr-H), 1.02–1.09 (m, 4H, Cpr-H), 2.44–2.49 (m, 4H, H-10), 2.72–2.75 (m, 4H, H-9), 3.88 (s, 4H, OCH_2), 4.46 (s, 4H, OCH_2), 5.11 (s, 2H, H-7), 7.32 (s, 4H, Ar-H); ^{13}C NMR (50 MHz, $CDCl_3$, APT): $\delta = -0.14$ (–, 2 Cpr-C), 3.29 (–, 2 Cpr-C), 11.86 (–, 4 Cpr-C), 14.23 (–, 4 Cpr-C), 24.75 (–, 2 Cpr-C_{quat}), 27.30 (–, 2 Cpr-C_{quat}), 27.98 (–, 2 C-10), 33.87 (–, 2 C-9), 70.98 (–, 2 C-OCH_2), 76.43 (–, 2 C-OCH_2), 113.62 (–, 2 Cpr-C_{quat}), 127.81 (+, 4 Ar-C), 132.16 (–, 2 C-11), 136.14 (+, 2 C-7), 136.69 (–, 2 C-8), 137.84 (–, 2 Ar-C_{quat}); MS (70 eV, EI): *m/z* (%) = 534 (3) [M^+], 385 (1), 336 (4), 291 (6), 215 (8), 198 (24), 185 (100), 143 (50), 105 (90), 91 (56); elemental analysis: calcd. for $C_{38}H_{46}O_2$ (534.77): C 85.35, H 8.67; found: C 85.55, H 8.44.

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