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A novel approach towards the preparation of functionalized alkyne derivatives via ArS-mediated Ad_E reaction of cobaltcarbonyl complexed conjugated enynes

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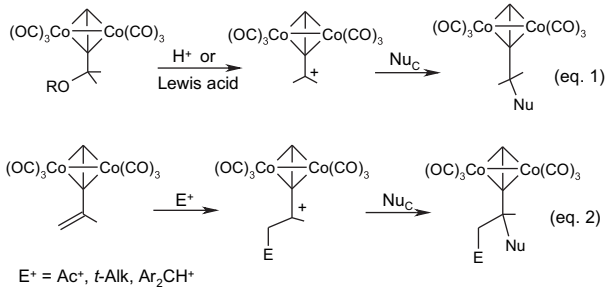
ABSTRACT

A unified protocol of three-component coupling of arenesulfenyl chloride, dicobalthexacarbonyl complexed conjugated enynes, and nucleophiles of π-donor type is applied for the synthesis of functionalized alkynes.

1. Introduction

Alkylation of π-nucleophiles with cobaltcarbonyl complexed propargylic cations (Nicholas reaction)[1,2] is widely employed as one of the most effective and convenient methods for the preparation of various functionalized alkynes (Scheme 1, Eq. 1). A useful modification of this reaction involves the controlled two-step sequence of Ad_E reactions across the double bond of dicobalthexacarbonyl (DCHC) complexes of the conjugated enynes[3,4] (Eq. 2).

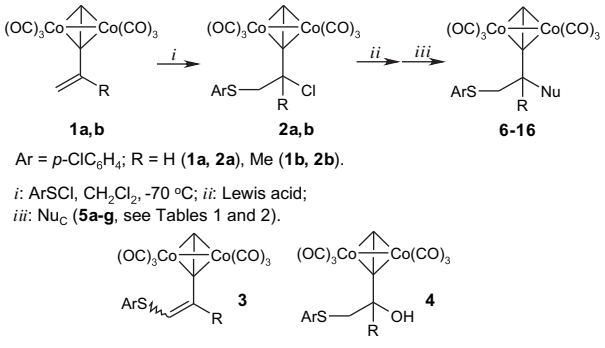


Scheme 1.

Here we present a new option of the modified Nicholas reaction based upon the use of arylsulfenium chlorides as the starting electrophiles in the abovementioned sequence (Eq. 2, E^+=ArS^+; for the preliminary results see Ref. 5).

2. Results and discussion

DCHC complexes of vinylacetylene (**1a**) and isopropenylacetylene (**1b**) were chosen as the model substrates in the reaction sequence shown in Scheme 2. *p*-Chlorobenzene sulfenyl chloride was used as a starting electrophile in step (i). Its addition across the double bond of enyne complexes **1** proceeds smoothly even at −70 °C with an almost quantitative yield (as assessed by TLC data). Arylthiochloroadducts **2** are stable at least for several hours in solution within the temperature range from −70 °C up to −20 °C. However, attempts to isolate them failed due to their lability; at temperatures above −20 °C elimination products **3** were immediately formed.



Scheme 2.

Under treatment of **2a,b** with water elimination and partial hydrolysis occur to furnish the respective products (**3** and **4**) in variable amounts. The adducts **2** formed in situ were directly treated with a Lewis acid (step ii) and then with the respective carbon nucleophile (Nu_C, step iii, Scheme 2).

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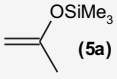
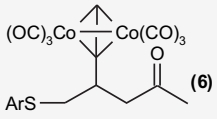
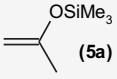
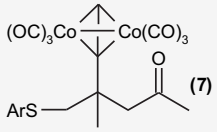
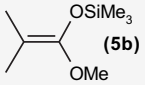
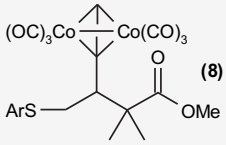
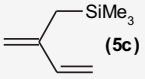
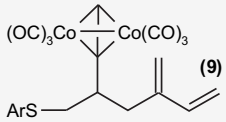
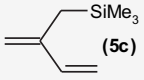
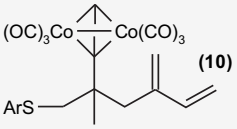
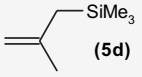
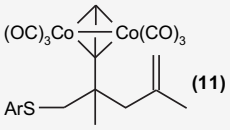
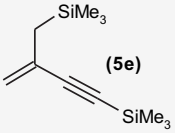
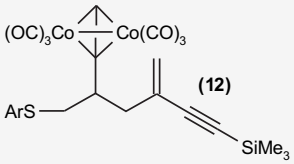
Both complexes **2a**,**b** turned out to be reactive toward a series of standard silyl-capped π-donors (**5a**–**g**) lying within the range of *N* values 4–9 (according to Mayr's scale of nucleophilicities).[6] More reactive nucleophiles (for example, enamines) exhibited high basicity and their reactions afforded only the elimination products **3**. A list of representative examples (Tables 1 and 2) demonstrates that the reaction sequence is applicable to virtually all combinations of the substrates employed; the respective products **6**–**16** were obtained in good to high yields.

alcohol[9] (Scheme 3). In fact, as was shown earlier,[9] cation **18** reacts rapidly with 1-trimethylsilyloxycyclohexene **5g** at −78 °C, whereas analogous transformation of **17a** into **15** (Table 2, entry 3) requires up to 24 h at −30 °C to proceed to completion. It is also noteworthy that the rate of the latter reaction depends on the Lewis acid used.

Moreover, the stereoselectivity for Nicholas reactions involving DCHC complexes of terminal alkynes and prochiral enolates is usually poor.[2,9,10]

Table 1
Alkylation of π-donors with DCHC complexed 1,3-enynes/ArSCl adducts according to Scheme 2

Entry	Enyne	Nu_C	Lewis acid	Product	Yield (%)
1	**1a**	 **(5a)**	$EtAlCl_2$	 **(6)**	90
2	**1b**	 **(5a)**	$EtAlCl_2$ TMSOTf Bu_2BOTf $LiClO_4/MeNO_2$ $AgSbF_6$	 **(7)**	96 40 38 27 40
3	**1a**	 **(5b)**	$EtAlCl_2$	 **(8)**	94
4	**1a**	 **(5c)**	$EtAlCl_2$	 **(9)**	81
5	**1b**	 **(5c)**	$EtAlCl_2$	 **(10)**	82
6	**1b**	 **(5d)**	$EtAlCl_2$	 **(11)**	80
7	**1a**	 **(5e)**	$EtAlCl_2$	 **(12)**	61

Various Lewis acids acted as efficient reaction promoters. While the utilization of $AgSbF_6$, TMSOTf, Bu_2BOTf, and the $LiClO_4/MeNO_2$ system furnished the desired products in rather modest yields (Table 1, entry 2; Table 2, entries 1 and 2), the use of $EtAlCl_2$, $TiCl_4$, and $ZnCl_2/Et_2O$ turned out to be optimal in most cases.[7]

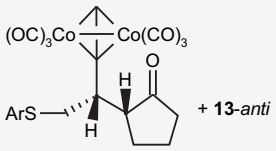
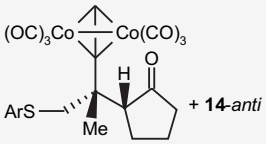
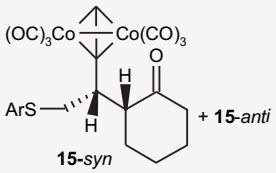
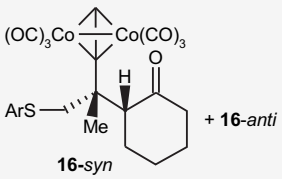
By analogy with the ample literature precedent[8] we assume that the interaction of **2** with a Lewis acid (step ii) affords the bridged cationic species, e.g., **17**. Such a description implies a contribution of the sulfur atom into the stabilization of the carbocation. Although we have no direct evidence of this contribution, there are some observations indicating the validity of this assumption.

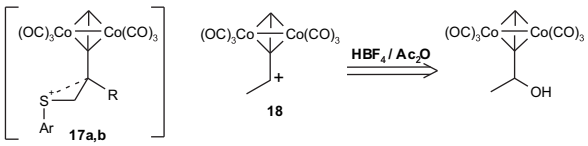
First of all, β-arylthiosubstituted cation **17a** was found to be significantly less reactive as compared to the closely similar non-bridged Nicholas' cation **18**, prepared from the respective

We found out that the secondary β-arylthiosubstituted cation **17a** prepared from **1a** reacts with 1-trimethylsilyloxycyclopentene **5f** and 1-trimethylsilyloxycyclohexene **5g** to give the corresponding adducts with good to excellent *syn*-diastereoselectivity (Table 2, entries 1 and 3) presumably due to the stereodirecting effect of the adjacent ArS-substituent. *For **13** and **15** the stereochemistry of the major isomer was rigorously established (see Experimental); that of **14** and **16** was assumed by analogy.* Surprisingly, a noticeable diastereoselection was observed even for the reactions involving a formation of the tertiary cationic intermediate **17b** (entries 2 and 4).[11]

The structures of all compounds **6**–**16** were ascertained by ^1H and ^{13}C NMR spectra and/or by the consistent analytical and NMR spectral data of the decomplexed adducts **6′**–**16′**, prepared in good

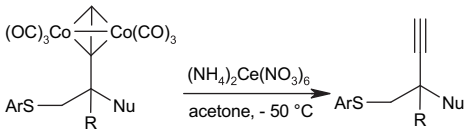
Table 2
Diastereoselective alkylation of π-donors with DCHC complexed 1,3-enynes/ArSCl adducts according to Scheme 2

Entry	Enyne	Nu_C	Lewis acid	Product	Yield (%)	dr (*syn*/*anti*)
1	**1a**	OSiMe$_3$ **(5f)**	$EtAlCl_2$ TMSOTf Bu_2BOTf $AgSbF_6$ $ZnCl_2/Et_2O$ $TiCl_4$	 + **13**-*anti* **13**-*syn*	94 55 54 40 88 86	3:1 10:1 10:1 20:1 12:1 17:1
2	**1b**	OSiMe$_3$ **(5f)**	$EtAlCl_2$ TMSOTf Bu_2BOTf $AgSbF_6$	 + **14**-*anti* **14**-*syn*	95 57 52 55	2.5:1 3.3:1 3.0:1 3.0:1
3	**1a**	OSiMe$_3$ **(5g)**	$EtAlCl_2$ $ZnCl_2/Et_2O$ TiCl4	 + **15**-*anti* **15**-*syn*	86 83 85	7:1 10:1 12:1
4	**1b**	OSiMe$_3$ **(5g)**	$EtAlCl_2$	 + **16**-*anti* **16**-*syn*	87	2.5:1



Scheme 3.

yields using the standard oxidative procedure[9] with cerium(IV) ammonium nitrate (Scheme 4).



Scheme 4.

In conclusion, we have presented a novel and efficient pathway for the one-pot preparation of the functionalized alkynes bearing ester-, keto-, allylic, or dienic fragments. Some of these products (e.g., **9** and **10**) can be considered as the substrates directly amenable for intramolecular cyclizations (for example, the Pauson–Khand reaction).[12] Further synthetic ramifications of these results are under intense study in our group.

3. Experimental

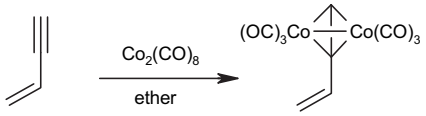
3.1. General information

All experiments were carried out under dry argon, using anhydrous solvents purified using the standard methods. TLC analysis was carried out on plates with silica. Column chromatography was performed using silica gel (220–240 mesh ASTM). *Due to the thermal lability of DCHC complexes of alkynes, the removal of solvents was carried out using a rotary evaporator with the water bath at temperature below 30 °C.* Chemical shifts are reported in parts per million as follows: chemical shift (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constant (*J*, in hertz), and integration.

Vinylacetylene was prepared from 2-methylhex-5-en-3-yn-2-ol in accordance with the described method;[13] the known procedures were modified for the preparation of the DCHC complex of vinylacetylene (**1a**)[14] and DCHC complex of isopropenylacetylene (**1b**)[3b] (vide infra). *p*-Chlorobenzene sulfenyl chloride was prepared as described previously,[15] stored and used as a 1.0 M solution in CH_2Cl_2. Silyl ketene acetal (**5b**),[16] silyl ethers (**5a**,**f**,**g**),[17] methallylsilane (**5d**),[18] and silylated enyne (**5e**)[19] were prepared using the described methods. The preparation of 2-(trimethylsilylmethyl)buta-1,3-diene (**5c**)[20] was carried out using the modified method (vide infra) described earlier; other reagents were used as received from commercial sources unless otherwise noted.

3.2. Syntheses of the starting materials

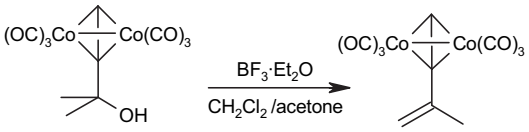
*3.2.1. DCHC complex of vinylacetylene (**1a**)[14].*



Vinylacetylene (1.21 g, 22.0 mmol) was dissolved in ether (100 ml), $Co_2(CO)_8$ (6.84 g, 20.0 mmol) was added to the solution and the mixture was stirred until the evolution of CO ceased (40 min). The reaction mixture was twice filtered through a thin

layer of silica gel using ether as the eluent. After evaporation of the solvent the residue was dissolved in hexane and again filtered through silica gel using hexane as the eluent. Removal of the solvent furnished compound **1a** (6.15 g, 91%) as a dark brownish oil (R_f 0.70, SiO_2, hexane). A 1.0 M solution of complex **1a** was stored in CH_2Cl_2 at −30 °C and was used as a stock solution.

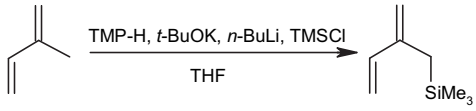
*3.2.2. DCHC complex of isopropenylacetylene (**1b**)[15].*



To a stirred solution of DCHC complex of dimethylethynyl carbinol (3.70 g, 10.0 mmol) in CH_2Cl_2 (50 ml) freshly distilled $BF_3 \cdot Et_2O$ (0.45 g, 4.0 mmol) followed by acetone* (2.0 ml) were added at 20 °C. The mixture was stirred for an additional 5 min and then quenched by Et_3N (0.45 g, 4.5 mmol) and filtered through SiO_2. After removal of the solvent, the residue was dissolved in hexane and additionally filtered through SiO_2. Removal of the solvent under reduced pressure gave complex **1b** (3.31 g, 94%).

Note: the presence of acetone was found to be crucial in order to avoid the formation of by-products.

*3.2.3. 2-(Trimethylsilylmethyl)buta-1,3-diene (**5c**)[20].*



Solutions of 2,2,6,6-tetramethylpiperidine (TMP) (7.19 g, 51.0 mmol) in dry THF (5 ml) and *t*-BuOK (6.71 g, 55.0 mmol) in dry THF (25 ml) were placed into a three-necked flask and cooled to −100 °C. Then a 1.64 M solution of *n*-BuLi in hexane (30.5 ml, 50.0 mmol) was added with stirring over 5 min keeping the temperature within the range −100 °C to −90 °C. The temperature of the reaction mixture was gradually increased to −70 °C over 20 min. The formation of a precipitate, which hindered the stirring, was observed. A solution of isoprene (1.70 g, 25.0 mmol) in dry THF (5 ml) was added in one batch and the dark red solution formed was kept at −70 °C for an additional 15 min. After that the reaction mixture was cannulated slowly to a solution of Me_3SiCl (5.45 g, 50.0 mmol) in dry THF (50 ml) keeping the temperature below −90 °C. The reaction mixture was warmed to −20 °C, quenched with water (100 ml), acidified with 0.1 M H_2SO_4 to pH 4, and extracted with ether (3×50 ml). The combined organic extracts were dried with Na_2SO_4. The solvent was removed and the residue was distilled in vacuo to give **6c** (1.44 g, 41%), bp 60 °C/30 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): 0.05 (s, 9H), 1.72 (s, 2H), 4.80 (s, 1H), 4.90 (s, 1H), 5.13 (d, J=17.4, 1H), 5.06 (d, J=10.6, 1H), 6.39 (dd, J_1=17.4, J_2=10.61, 1H).

3.3. Preparation of the products shown in Tables 1 and 2

*3.3.1. DCHC complex of 4-[(4-chlorophenylthio)methyl]-hex-5-yn-2-one (**6**).* A 1.0 M solution of the DCHC complex of vinylacetylene **1a** (1.0 ml, 1.0 mmol) was diluted with CH_2Cl_2 (6 ml) and cooled to −70 °C. Then a 1.0 M solution of *p*-ClC_6H_4SCl (1.0 ml, 1.0 mmol) in CH_2Cl_2 was added. After 5 min, a 1.0 M solution of $EtAlCl_2$ in hexane (1.0 ml, 1.0 mmol) was added followed by the addition, after 5 min, of 2-trimethylsilyloxypropene (**5a**) (195 mg, 1.5 mmol). The reaction mixture was kept at −30 °C for 1 day and then quenched with the mixture of saturated aq $NaHCO_3$ and petroleum ether, the water layer was frozen and organic phase was decanted. After an additional extraction and decantation the combined organic layer was filtered through a silica gel and evaporated. The residue after solvent removal was purified by chromatography on silica gel to give the adduct **6** (486 mg, 90%) as a dark brownish oil (R_f 0.32, ethyl acetate/hexane, 1:10). *Cobaltcomplexed alkynes thus prepared were quite stable when stored in a fridge at least for several weeks. It is not advisable to concentrate extracts without preliminary purification and to keep them at ambient temperature for a long time.*[21] The adduct **6** was then converted into the decomplexed derivative **6′** (94%) by the oxidation with CAN.[9]

Compound **6′**: R_f 0.30 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (200 MHz, $CDCl_3$): 2.17 (s, 1H), 2.20 (s, 1H), 2.79 (dd, 1H, J_1=17.3, J_2=6.6), 2.88 (dd, 1H, J_1=17.3, J_2=5.4), 3.02–3.20 (m, 3H), 7.31 and 7.37 (both d, 2H each, J=8.8). ^{13}C NMR (300 MHz, $CDCl_3$): 27.9, 31.2, 39.4, 47.8, 71.7, 85.5, 130.1, 132.3, 133.6, 134.9, 206.5. Elemental analysis calcd (%) for $C_{13}H_{13}ClOS$: C, 61.77; H, 5.18. Found (%): C, 61.87; H, 5.26.

*3.3.2. DCHC complex of 4-methyl-4-[(4-chlorophenylthio)methyl]-hex-5-yn-2-one (**7**).* Following the procedure described for **6**, the DCHC complex of isopropenylacetylene **1b** (352 mg, 1.0 mmol) and 2-trimethylsilyloxypropene (**5a**) (195 mg, 1.5 mmol) were converted into the adduct **7** (532 mg, 96%), dark brownish oil.

Compound **7**: R_f 0.33 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (200 MHz, $CDCl_3$): 1.46 (s, 3H), 2.07 (s, 3H), 2.77 and 2.89 (both d, J=18.1, 1H each), 3.32 and 3.46 (both d, J=11.9, 1H each), 6.24 (s, 1H), 7.25 (s, 4H).

Compound **7′**: 91% from **7**, R_f 0.31 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (500 MHz, $CDCl_3$): 1.39 (s, 3H), 2.14 (s, 3H), 2.22 (s, 1H), 2.69 and 2.79 (both d, J=16.1, 1H each), 3.29 (s, 2H), 7.23 and 7.33 (both d, J=8.8, 2H each). Elemental analysis calcd (%) for $C_{14}H_{15}ClOS$: C, 63.03; H, 5.67. Found (%): C, 63.28; H, 5.85.

*3.3.3. DCHC complex of methyl 2,2-dimethyl-3-[(4-chlorophenylthio)methyl]pent-4-ynoate (**8**).* A 1.0 M solution of the DCHC complex of vinylacetylene **1a** (1.0 ml, 1.0 mmol) was diluted with CH_2Cl_2 (6 ml) and cooled to −70 °C. Then a 1.0 M solution of *p*-ClC_6H_4SCl (1.0 ml, 1.0 mmol) in CH_2Cl_2 was added. After 5 min, a 1.0 M solution of $EtAlCl_2$ in hexane (1.0 ml, 1.0 mmol) was added with the subsequent addition, after 5 min, of 1-methoxy-2-methylprop-1-enyloxytrimethylsilane (**5b**) (209 mg, 1.2 mmol). The reaction mixture was kept at −50 °C for 30 min. Further work-up of the reaction mixture and the isolation of the target compound were carried out as described above (Section 3.3.1).

Compound **8**: 523 mg, 94%, dark brownish oil. R_f 0.22 (SiO_2, ethyl acetate/hexane, 1:10).

Compound **8′**: 93% from **8**, R_f 0.21 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (300 MHz, $CDCl_3$): 1.25 and 1.31 (2s, 3H each), 2.20 (d, J=2.3, 1H), 2.89 (dd, J_1=10.6, J_2=12.5, 1H), 2.94 (dd, J_1=3.6, J_2=12.5, 1H), 3.01 (ddd, J_1=2.3, J_2=3.6, J_3=10.6, 1H), 3.64 (s, 3H), 7.29 and 7.32 (both d, J=8.5, 2H each). ^{13}C NMR (75 MHz, $CDCl_3$): 19.7, 25.1, 35.9, 40.4, 45.6, 52.1, 72.5, 82.5, 129.0, 131.3, 132.5, 134.2, 176.3. Elemental analysis calcd (%) for $C_{15}H_{17}ClO_2S$: C, 60.70; H, 5.77. Found (%): C, 60.92; H, 5.56.

*3.3.4. DCHC complex of 5-[(4-chlorophenylthio)methyl]-3-methyl-enehept-1-en-6-yne (**9**).* Following the procedure described for **6**, the DCHC complex **1a** and diene **5c** (210 mg, 1.5 mmol) were converted into the adduct **9**.

Compound **9**: 445 mg, 81%, dark brownish oil. R_f 0.61 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (300 MHz, $CDCl_3$): 2.55 (dd, J_1=5.5, J_2=14.0, 1H), 2.68 (dd, J_1=7.3, J_2=14.0, 1H), 2.95 (m, 1H), 3.12–3.23 (m, 2H), 5.07 and 5.20 (both s, 1H each), 5.09 (d, J=11.0, 1H), 5.21 (d, J=17.6, 1H), 6.23 (s, 1H), 6.38 (dd, J_1=11.0, J_2=17.6, 1H), 7.25 (s, 4H).

Compound **9′**: 86% from **9**, R_f 0.59 (SiO_2, ethyl acetate/hexane, 1:10). Elemental analysis calcd (%) for $C_{15}H_{15}ClS$: C, 68.56; H, 5.75. Found (%): C, 68.63; H, 5.82.

*3.3.5. DCHC complex of 5-methyl-5-[(4-chlorophenylthio)methyl]-3-methylenehept-1-en-6-yne (**10**).* Following the procedure described for **6**, the DCHC complex **1b** (352 mg, 1.0 mmol) and diene 5**c** (210 mg, 1.5 mmol) were converted into the adduct **10**.

Compound **10**: 462 mg, 82%, dark brownish oil. R_f 0.61 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (250 MHz, $CDCl_3$): 1.33 (s, 3H), 2.54 and 2.77 (both d, J=13.5, 1H each), 3.09 (s, 2H), 5.13 (d, J=11.0, 1H), 5.20 and 5.32 (both s, 1H each), 5.35 (d, J=19.0, 1H), 6.34 (s, 1H), 6.46 (dd, J_1=11.0, J_2=19.0, 1H), 7.20 and 7.25 (both d, J=8.8, 2H each).

Compound **10′**: 82% from **10**, R_f 0.60 (SiO_2, ethyl acetate/hexane, 1:10). Elemental analysis calcd (%) for $C_{16}H_{17}ClS$: C, 69.42; H, 6.19. Found (%): C, 69.61; H, 6.43.

*3.3.6. DCHC complex of 2,4-dimethyl-4-[(4-chlorophenylthio)-methyl]-hex-1-en-5-yne (**11**).* Following the procedure described for **6**, the DCHC complex **1b** (352 mg, 1.0 mmol) and methallyltrimethylsilane (**5d**) (192 mg, 1.5 mmol) were converted into the adduct **11**.

Compound **11**: 442 mg, 80%, dark brownish oil. R_f 0.57 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (250 MHz, $CDCl_3$): 1.41 (s, 3H), 2.26 and 2.61 (both d, J=13.4, 1H each), 3.12 (s, 2H), 4.91 (s, 1H), 5.01 (s, 1H), 6.29 (s, 1H), 7.24 (s, 4H).

Compound **11′**: 82% from **11**, R_f 0.55 (SiO_2, ethyl acetate/hexane, 1:10). Elemental analysis calcd (%) for $C_{15}H_{17}ClS$: C, 68.03; H, 6.47. Found (%): C, 68.30; H, 6.20.

*3.3.7. 1,2-DCHC complex of 7-trimethylsilyl-3-[(4-chlorophenylthio)-methyl]-3-methyl-5-methylenehepta-1,6-diyne (**12**).* Following the procedure described for **6**, the DCHC complex **1a** (338 mg, 1.0 mmol) and 4-trimethylsilyl-2-trimethylsilylmethyl-2-buten-3-yne (**5e**) (315 mg, 1.5 mmol) were converted into the adduct **12**.

Compound **12**: 378 mg, 61%, dark brownish oil. R_f 0.56 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (300 MHz, $CDCl_3$): 0.10 (s, 9H), 2.31 (dd, J_1=7.2, J_2=13.8, 1H), 2.74 (dd, J_1=6.8, J_2=13.8, 1H), 3.09 (m, 2H), 3.32 (m, 1H), 5.32 (s, 1H), 5.51 (s, 1H), 6.23 (s, 1H), 7.25 and 7.30 (both d, J=7.7, 2H each). ^{13}C NMR (75 MHz, $CDCl_3$): 0.3, 40.2, 40.6, 43.6, 75.5, 95.6, 98.6, 103.9, 124.6, 129.4, 130.8, 132.3, 133.6, 134.4, 199.7.

Compound **12′**: 80% from **12**, R_f 0.53 (SiO_2, ethyl acetate/hexane, 1:10). Elemental analysis calcd (%) for $C_{18}H_{21}ClSSi$: C, 64.93; H, 6.36. Found (%): C, 65.30; H, 6.09.

*3.3.8. DCHC complex of 2-[1-(4-chlorophenylthio)but-3-yn-2-yl]-cyclopentanone (**13**).* A 1.0 M solution of the DCHC complex of vinylacetylene **1a** (1.0 ml, 1.0 mmol) was diluted with CH_2Cl_2 (6 ml) and cooled to −70 °C. Then a 1.0 M solution of *p*-ClC_6H_4SCl (1.0 ml, 1.0 mmol) in CH_2Cl_2 was added. After 5 min, a 1.47 M $ZnCl_2/Et_2O$ catalyst[7] (0.10 ml, 0.15 mmol) was added with the subsequent addition, after 5 min, of 1-trimethylsilyloxycyclopentene-1 (**5f**) (234 mg, 1.5 mmol). The reaction mixture was kept at −30 °C overnight. Further work-up of the reaction mixture and the isolation of the target compound were carried out as described in the typical experimental procedure in the main text. Product **13** was obtained as a mixture of *syn*/*anti* isomers (498 mg, 88%, dark brownish oil, R_f 0.28 (SiO_2, ethyl acetate/hexane, 1:10), *syn*/*anti*=12:1, the ratio was determined by comparison of ^{1}H NMR signal intensity). Stereochemical assignment was accomplished using two-dimensional NMR technique and ROESY experiment. In order to enrich the sample with a minor isomer the latter was treated with dioxane/HCl complex in CH_2Cl_2 solution at −30 °C. Under these conditions the mixture underwent epimerisation to give the ratio of isomers 2:1 with the predominance of *syn*-isomer.

Compound **13** (*syn*/*anti*): ^{1}H NMR (300 MHz, $CDCl_3$): 1.81 (m, 2H in all), 2.10 (m, 2H in all), 2.18 (dd, *syn*-, J_1=19.0, J_2=8.3, 1H), 2.31 (m, *anti*-, 2H), 2.40 (dd, *syn*-, J_1=19.0, J_2=7.5, 1H), 2.49 and 2.84 (both m, *anti*- and *syn*-, 1H in all), 3.01 (dd, *syn*-, J_1=13.1, J_2=10.0, 1H), 3.08 (m, *anti*-, 2H), 3.36 (dd, *syn*-, J_1=13.1, J_2=4.6, 1H), 3.52 and 3.65 (both m, *syn*- and *anti*-, 1H in all), 5.87 and 6.15 (both s, *syn*- and *anti*-, 1H in all), 7.27 and 7.31 (2d, *syn*- and *anti*-, J=8.5, 4H in all). ^{13}C NMR (125 MHz, $CDCl_3$): 20.3, 25.5, 38.5, 39.6, 41.0, 52.6, 129.3, 130.7, 131.2, 132.8, 133.6, 216.30.

Compound **13′** (*syn*/*anti*): 91% from **13**, R_f 0.27 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (500 MHz, $CDCl_3$): 1.78 (m, 1H in all), 1.92 (m, 1H in all), 2.09 (s, 1H in all), 2.11 (m, 3H in all), 2.31 (m, 1H in all), 2.51 and 2.82 (m, *syn*- and *anti*-, 1H in all), 2.93 (dd, *syn*-, J_1=11.4, J_2=8.0, 1H), 3.11 (m, 1H in all), 3.15 (dd, *syn*-, J_1=11.4, J_2=7.5, 1H), 3.27 (m, *anti*-, 2H), 7.24 and 7.31 (both d, *anti*-, J=8.8, 2H each), 7.25 and 7.29 (both d, *syn*-, J=8.5, 2H each). ^{13}C NMR (125 MHz, $CDCl_3$): 20.4, 24.9, 31.3, 37.6, 38.5, 50.2, 72.0, 82.6, 129.3, 131.6, 132.9, 133.3, 209.8. Elemental analysis calcd (%) for $C_{15}H_{15}ClOS$: C, 64.62; H, 5.42. Found (%): C, 64.81; H, 5.59.

*3.3.9. DCHC complex of 2-[2-methyl-1-(4-chlorophenylthio)but-3-yn-2-yl]cyclopentanone (**14**).* Following the procedure described for **6**, the DCHC complex **1b** (352 mg, 1.0 mmol) and trimethylsilyloxycyclopentene-1 (**5f**) (234 mg, 1.5 mmol) were converted into the mixture of *syn*/*anti* isomers of **14** (551 mg, 95%, dark brownish oil, R_f 0.29 (SiO_2, ethyl acetate/hexane, 1:10), *syn*/*anti*=3.0:1, the ratio was determined by comparison of ^{1}H NMR signal intensity).

Compound **14** (*syn*/*anti*): ^{1}H NMR (500 MHz, $CDCl_3$): 1.38 and 1.42 (both s, *syn*- and *anti*-, 3H in all), 1.70 (m, 1H in all), 2.01 (m, 2H in all), 2.17 (m, 2H in all), 2.34 (m, 1H in all), 2.58 (m, 1H in all), 3.19 and 3.52 (both d, *anti*-, J=12.5, 1H each), 3.44 and 3.52 (both d, *syn*-, J=12.5, 1H each), 6.12 and 6.16 (both s, 1H in all), 7.22 and 7.31 (both d, *syn*-, J=8.6, 2H each), 7.23 (s, *anti*-, 4H).

Compound **14′** (*syn*/*anti*): 92% from **14**, R_f 0.27 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (250 MHz, $CDCl_3$): 1.29 and 1.45 (both s, *anti*- and *syn*-, 3H in all), 1.72 (m, 1H in all), 2.14 and 2.17 (both s, *anti*- and *syn*-, 1H in all), 1.85–2.53 (m, 6H in all), 3.24 and 3.40 (both d, *syn*-, J=12.5, 1H each), 3.61 (s, *anti*-, 2H), 7.24 and 7.35 (both d, *syn*-, J=8.8, 2H each), 7.23 and 7.37 (both d, *anti*-, J=8.8, 2H each). Elemental analysis calcd (%) for $C_{16}H_{17}ClOS$: C, 65.63; H, 5.85. Found (%): C, 65.69; H, 5.76.

*3.3.10. DCHC complex of 2-[1-(4-chlorophenylthio)but-3-yn-2-yl]-cyclohexanone (**15**).* A 1.0 M solution of the DCHC complex of vinylacetylene **1a** (1.0 ml, 1.0 mmol) was diluted with CH_2Cl_2 (6 ml) and cooled to −70 °C. Then a 1.0 M solution of *p*-ClC_6H_4SCl (1.0 ml, 1.0 mmol) in CH_2Cl_2 was added. After 5 min, a 1.0 M solution of $TiCl_4$ in CH_2Cl_2 (1.1 ml, 1.1 mmol) was added with the subsequent addition, after 5 min, of 1-trimethylsilyloxycyclohexene-1 (**5g**) (255 mg, 1.5 mmol). The reaction mixture was kept at −30 °C for 1 day. Further work-up of the reaction mixture and the isolation of the target compound were carried out as described in the typical experimental procedure in the main text. Product **15** was isolated as a mixture of *syn*/*anti* diastereomers (493 mg, 85%, dark brownish oil, R_f 0.33 (SiO_2, ethyl acetate/hexane, 1:10), *syn*/*anti*=12:1, the ratio was determined by comparison of ^{1}H NMR signal intensity). Stereochemical assignment was accomplished in the same manner as for product **13**.

Compound **15**-*syn*: ^{1}H NMR (300 MHz, $CDCl_3$): 1.48 (m, 1H), 1.61 (m, 2H), 1.87 (m, 1H), 2.00 (m, 2H), 2.23 (m, 1H), 2.37 (m, 1H), 2.88 (m, 1H), 2.94 (dd, J_1=8.5, J_2=13.4, 1H), 3.31 (dd, J_1=5.5, J_2=13.4, 1H), 3.43 (m, 1H), 5.91 (s, 1H), 7.20 and 7.23 (both d, J=8.6, 2H each). ^{13}C NMR (75 MHz, $CDCl_3$): 24.9, 27.3, 29.6, 38.8, 41.3, 42.2, 53.5, 75.1, 96.1, 129.2, 131.2, 132.7, 134.1, 199.5, 210.6.

Compound **15**-*anti*: ^{1}H NMR (300 MHz, $CDCl_3$): 1.63 (m, 3H), 1.92 (m, 1H), 2.00 (m, 2H), 2.28 (m, 1H), 2.40 (m, 1H), 2.71 (m, 1H), 2.88 (m, 1H), 3.24 (dd, J_1=5.5, J_2=12.8, 1H), 3.57 (m, 1H), 6.12 (s, 1H), 7.20 and 7.27 (both d, J=8.6, 2H each). ^{13}C NMR (75 MHz, $CDCl_3$):

25.1, 27.5, 30.1, 38.1, 40.1, 42.3, 55.8, 76.4, 97.6, 129.1, 130.7, 132.6, 134.2, 199.5, 210.4.

Compound **15′** (*syn*/*anti*): 90% from **15**, R_f 0.31 (SiO_2, ethyl acetate/hexane, 1:10). Elemental analysis calcd (%) for $C_{16}H_{17}ClOS$: C, 65.63; H, 5.85. Found (%): C, 65.86; H, 6.02.

*3.3.11. DCHC complex of 2-[2-methyl-1-(4-chlorophenylthio)but-3-yn-2-yl]cyclohexanone (**16**).* Following the procedure described for **6**, the DCHC complex **1b** (352 mg, 1.0 mmol) and trimethylsilyloxycyclohexene-1 (**5g**) (255 mg, 1.5 mmol) were converted into the mixture of *syn*/*anti* isomers of **16** (517 mg, 87%, dark brownish oil, R_f 0.34 (SiO_2, ethyl acetate/hexane, 1:10), *syn*/*anti*=2.5:1, the ratio was determined by comparison of ^{1}H NMR signal intensity).

Compound **16** (*syn*/*anti*): ^{1}H NMR (250 MHz, $CDCl_3$): 1.22 and 1.41 (both s, *syn*- and *anti*-, 3H in all), 1.49–2.18 (m, 6H in all), 2.21–2.53 (m, 2H in all), 2.83 (m, 1H in all), 3.19 and 3.52 (both d, *anti*-, *J*=15.0, 1H each), 3.32 and 3.76 (both d, *syn*-, *J*=14.0, 1H each), 6.13 and 6.16 (both s, 1H in all), 7.24 and 7.35 (both d, *syn*-, *J*=8.8, 2H each), 7.27 (s, *syn*-, 4H).

Compound **16′** (*syn*/*anti*): 93% from **16**, R_f 0.33 (SiO_2, ethyl acetate/hexane, 1:10). ^{1}H NMR (250 MHz, $CDCl_3$): 1.34 and 1.40 (both s, *anti*- and *syn*-, 3H in all), 1.49–1.75 (m, 3H in all), 1.84–2.08 (m, 2H in all), 2.15 and 2.17 (both s, *syn*- and *anti*-, 1H in all), 2.10–2.42 (m, 3H in all), 2.60 and 2.75 (both m, 1H in all), 3.23 and 3.52 (both d, *syn*-, *J*=12.6, 1H each), 3.21 and 3.61 (both d, *anti*-, *J*=12.9, 1H each), 7.18 and 7.28 (both d, *syn*-, *J*=8.8, 2H each), 7.19 and 7.31 (both d, *anti*-, *J*=8.5, 2H each).

^{13}C NMR (75 MHz, $CDCl_3$): 21.4, 24.1, 24.5, 24.7, 27.1, 27.3, 28.4, 28.7, 29.1, 29.7, 42.1, 42.4, 42.5, 43.2, 53.7, 55.4, 69.8, 70.0, 75.6, 76.0, 76.3, 76.4, 127.8, 127.9, 129.9, 130.1, 209.8. Elemental analysis calcd (%) for $C_{17}H_{19}ClOS$: C, 66.54; H, 6.24. Found (%): C, 66.72; H, 6.45.

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