Nucleophilic Addition/Double Cyclization Cascade Processes Between Enynyl Fischer Carbene Complexes and Alkynyl Malonates

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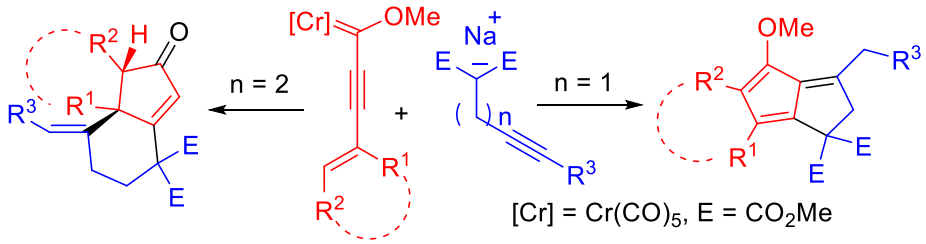


ABSTRACT: Two new selective cascade processes for enynyl Fischer carbene complexes **1** are described in their reaction with alkynyl malonates. When carbene complexes **1** react with the sodium enolate of homopropargyl malonates **3** a consecutive Michael type addition/cyclopentannulation/6-*exo* cyclization takes place leading, in a regio and stereoselective way, to n/5/6 angular tricyclic compounds **5**. Furthermore, when propargylic malonates are used, a delayed protonation of the reaction mixture allows intermediate 1,4-addition adduct **Ia** to evolve through a 5-*exo* cyclization, consisting in an intramolecular nucleophilic attack from the central carbon of the allenylmetallate over the triple C-C bond. Further spontaneous cyclopentannulation of the resulting metallatriene gives rise to bicyclic and linear polycyclic compounds **6** and **7**, some of them bearing a polyquinane framework.

■ INTRODUCTION

Cascade reactions are among the most advantageous tools in organic synthesis.[1] They include multiple benefits, such as atom economy, reduction of workup and purification steps, as well as decreased production of waste. It has been demonstrated that Fischer carbene complexes (FCCs) can participate in many cascade and multicomponent reactions,[2] due to the ability of the metal pentacarbonyl moiety to activate consecutive reaction steps. Thus, enynyl Fischer metal carbenes **1** are the popular substrates for these kinds of reactions, which may generate at least two rings in a single operation. In this context, a well developed strategy comprises first a cycloaddition involving the activated C-C triple bond followed by ring closure through the C-metal and C-C double bonds. Figure 1 illustrates three different processes, i) [6+2] cycloaddition/cyclopentannulation (compound A),[3] ii) [4+2] cycloaddition/benzannulation (compound B),[4] iii) triple [4+2] cycloaddition/cyclopentannulation (compound C).[5]

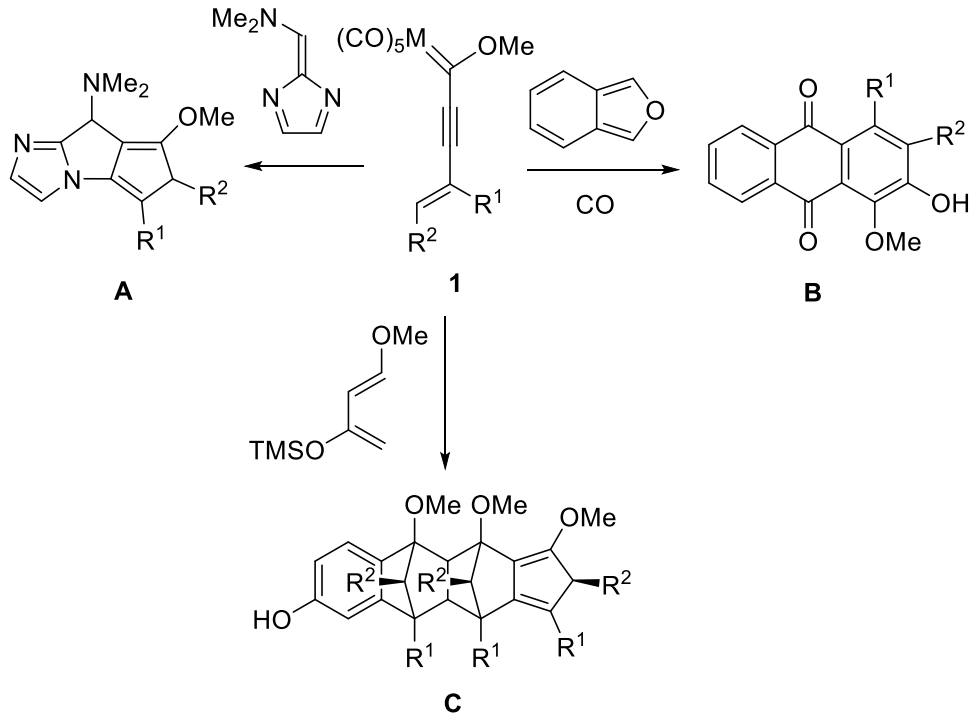
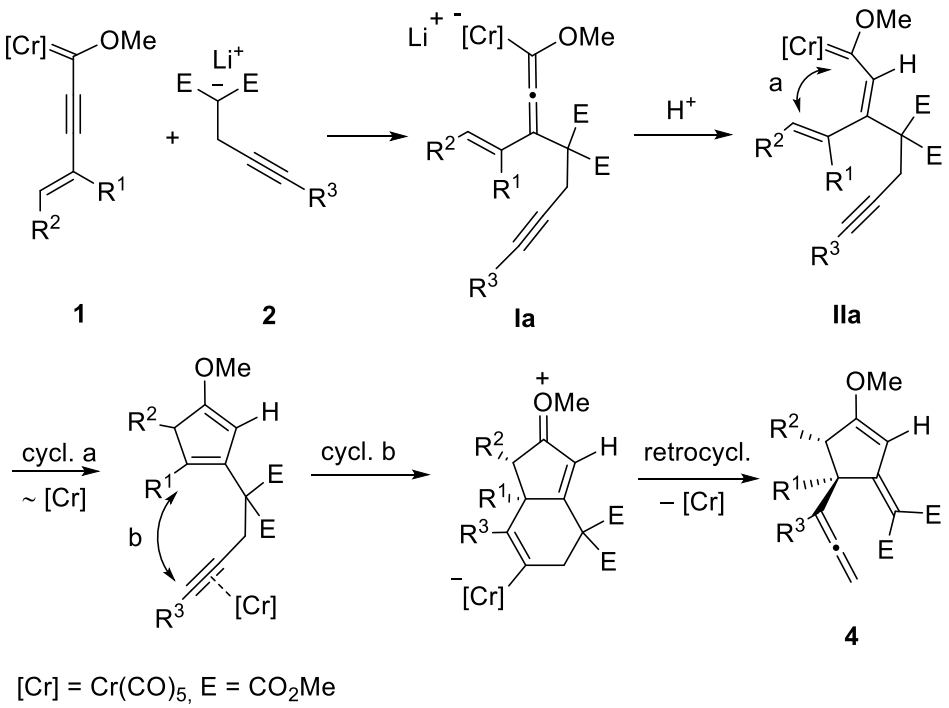


Figure 1. Cascade reactions of enynyl FCCs **1**.

In contrast, cascade reactions initiated by 1,4-conjugate addition of nucleophiles to enynyl FCCs have been less studied.[6] Recently we described a new entry to cyclopentenones consisting in a 1,4-addition of enolates to enynylcarbenes, followed by cyclopentannulation.[7] We considered that the use of appropriately functionalized nucleophiles, e.g. readily accessible alkyne-containing malonates **2, 3**, might provide an alternative pathway. Thus, we observed that cyclopentene derivatives **4** were isolated by mixing enynyl carbenes **1** and dimethyl propargylmalonates **2** at low temperature followed by rapid quenching (30 min) and further stirring at room temperature (Scheme 1).[8] The complete process involves, i) 1,4-addition of enolate, ii) protonation and regeneration of the metal carbene function, iii) cyclopentannulation (cyclization a), iv) chromium-promoted intramolecular nucleophilic addition (cyclization b), and v) retrocyclization.

Scheme 1. Reaction between enynyl FCCs **1** and propargylmalonates **2** (ref 8).



Considering the participation of the key allenyl chromium metalate intermediate **Ia**, other reaction pathways might be realized by appropriate variation on its structure, such as using a longer enolate-alkyne tether like an homopropargylmalonate derivative. Moreover, delaying the protonation would allow intermediate **I** to survive and likely attack an electrophilic center. Herein is reported new cascade polycyclizations from enynyl chromium carbenes **1** and dimethyl propargyl and homopropargylmalonates **2**

and **3** leading to bicyclic and tricyclic systems of potential interest (Figure 2). Specifically, compounds **5** were formed from homopropargyl malonates **3** (cyclizations a and c), while compounds **6** resulted from the reaction of **1** and propargyl malonates **2** followed by late quenching (cyclizations d and a).

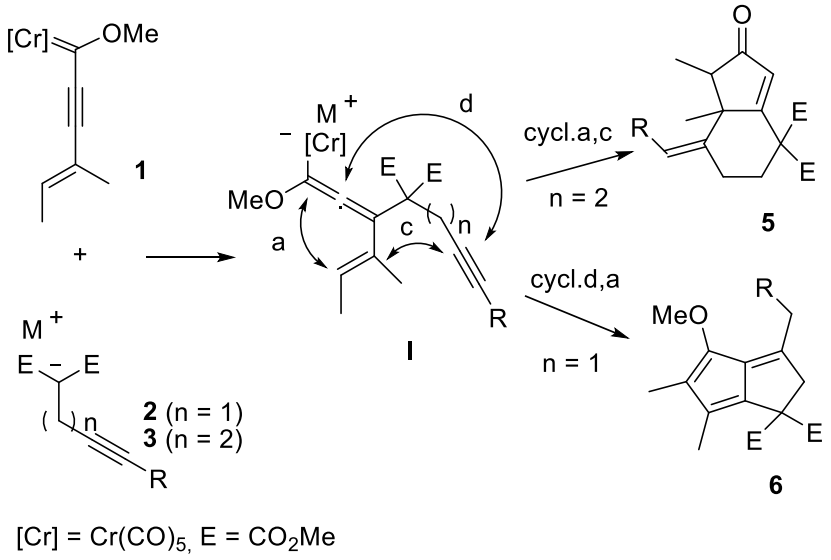
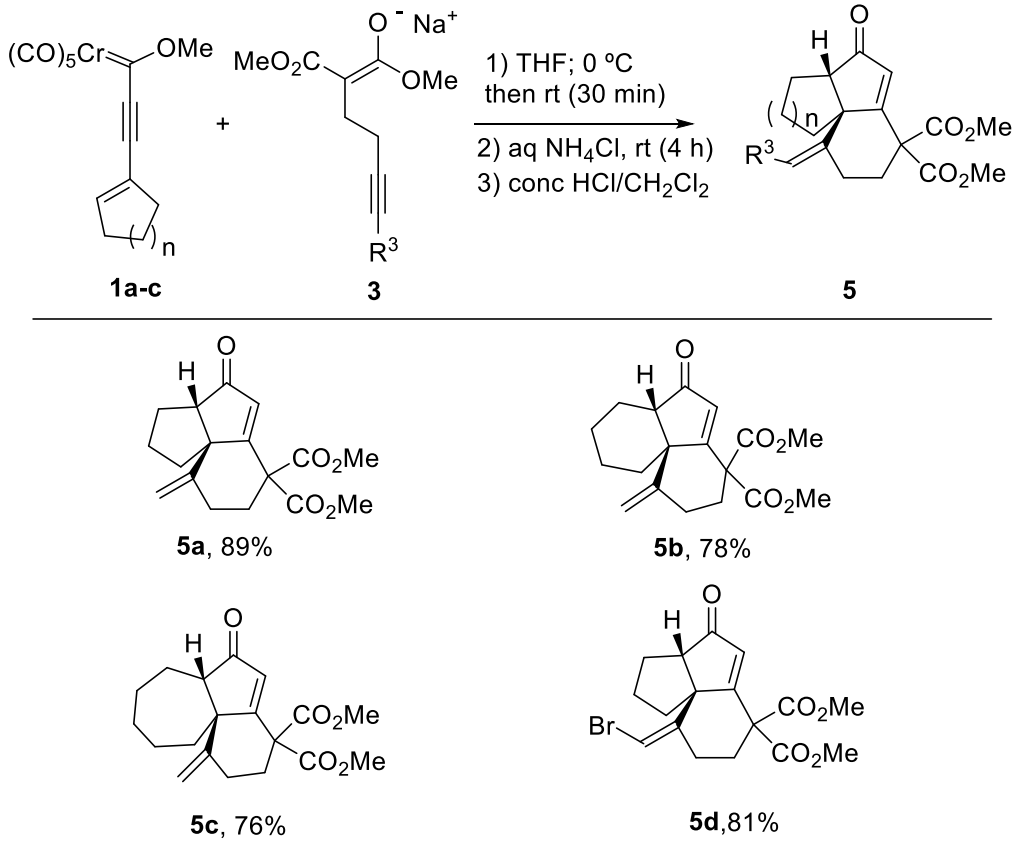


Figure 2. Cascade cyclizations reported in this work.

■ RESULTS AND DISCUSSION

Reaction of enynyl FCCs 1a-c and homopropargylmalonates 3: 1,4-Nucleophilic addition/double cyclization process: We started our study by reacting the corresponding enolate of homopropargylmalonates **3** with enynyl carbene complexes **1**. Thus, carbene complexes **1a-c** dissolved in THF were added to a THF solution of sodium enolates **3**. After stirring for 30 min, the reaction was quenched with an aq saturated solution of NH_4Cl. Purification gave tricycles **5** in 89%-76% yield with complete diastereoselectivity.[9]

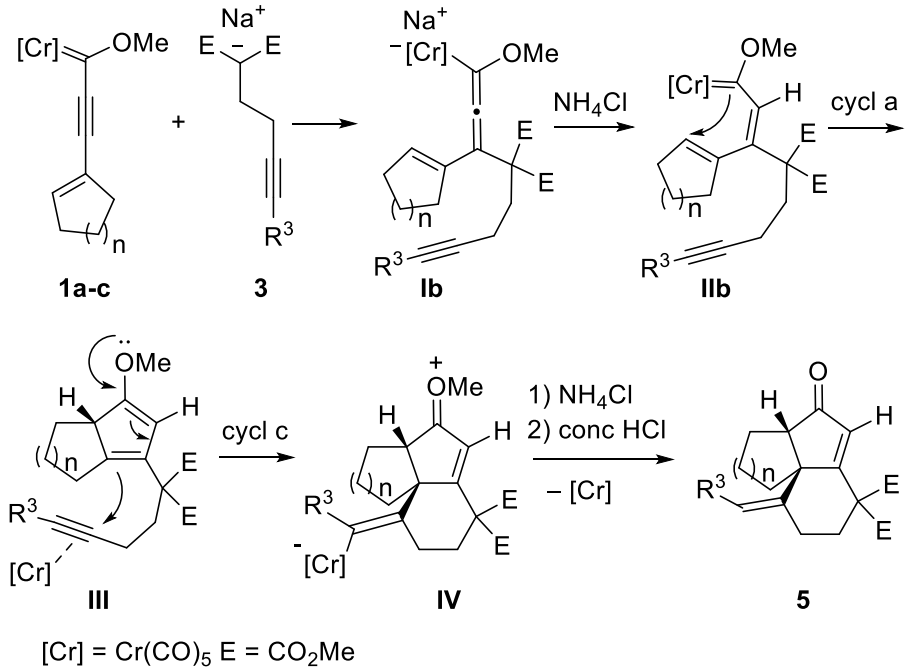
Scheme 2 Synthesis of tricycles **5** from enynyl FCCs **1a-c** and homopropargylmalonate enolates **3.**



The structural arrangement and stereochemistry of compounds **5** are in accordance with the spectroscopic data (^{1}H and ^{13}C NMR, HRMS) and the full structure was unambiguously determined for **5c** by X-ray analysis of crystals grown from hexanes/chloroform.[10] The process tolerates well the bromo-C(sp) function (**5**; R^3 = Br)[11] affording stereoselectively the *Z*-bromoalkenyl derivative **5d** whose structure was also confirmed by X-ray analysis[10]

The consecutive processs leading to tricycles **5** can be explained as depicted in Scheme 3. Thus, Michael type addition of the homopropargylmalonate enolate **3** to carbenes **1a-c** would produce allenyl intermediate **Ib** (n = 2), which then would undergo protonation on addition of NH_4Cl to regenerate the metal carbene functionality. The resulting metallatriene **IIb** would provide the intermediate **III** upon cyclopentannulation (cyclization a), metal fragment liberation and alkyne-$Cr(CO)_5$ coordination. Finally, the formation of compounds **5** is thought to occur via 6-*exo* cyclization (cyclization c) by attack from the C4 of the methoxydiene function over the C-C triple bond (intermediate **IV**) followed by protodemetallation.[12]

Scheme 3. Mechanism proposed for the formation of tricycles **5**.

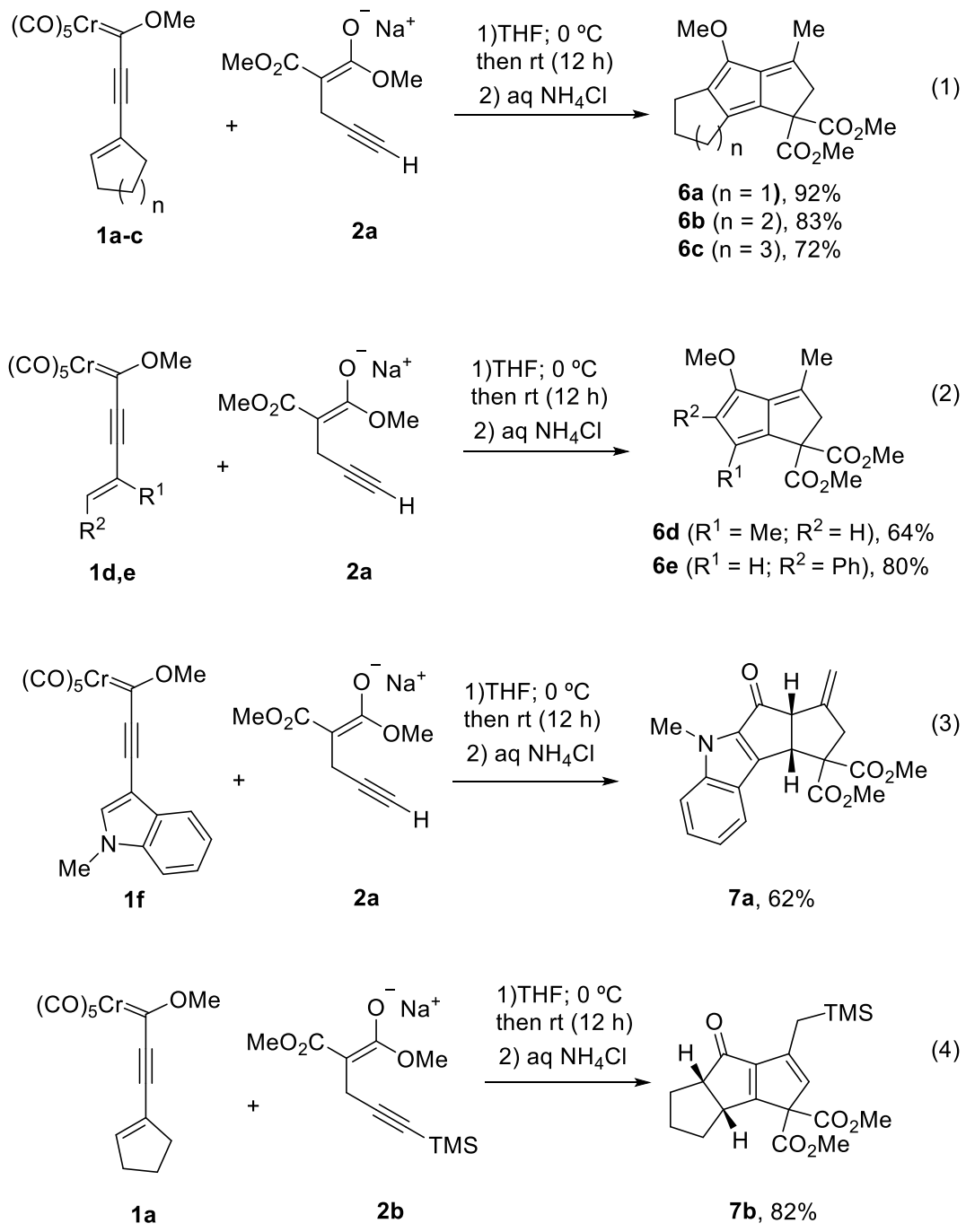


It is worth noting that this 1,4-addition/double cyclization cascade sequence represents a stereoselective access to functionalized 5/5/6, 6/5/6 and 7/5/6 angular tricyclic frameworks[13] in a single operation from simple starting materials. Some of these structures are present in the skeleton of natural and bioactive products.[14]

Reaction of propargylmalonates 2 and enynyl FCCs 1. 1,4-Nucleophilic addition/double cyclization process: Taking in mind the experimental conditions and the associated mechanisms shown in the cycloaddition reactions of propargylmalonates (see Scheme 1, Ref. 8) and homopropargylmalonates (see Schemes 2,3) it seems that the rapid quenching of intermediates **Ia**[8] (Scheme 1) and **Ib** (Scheme 3) resulted in the generation of reactive dienylcarbene species **II**. If the quenching of these intermediates **I** were delayed, it could allow new modes of cyclization to develop. Thus, a THF solution of carbenes **1** was added at 0ºC to a THF solution of sodium propargylic enolates **2**. After stirring for 12 h, the reaction was quenched

with an aq saturated solution of NH_4Cl. Purification gave enol ethers **6** and ketones **7** in good yields (62-92%) (Scheme 4). The structures of compounds **6** and **7** were confirmed by mono and bidimensional NMR experiments and by X-ray analysis of compound **6e**.[10]

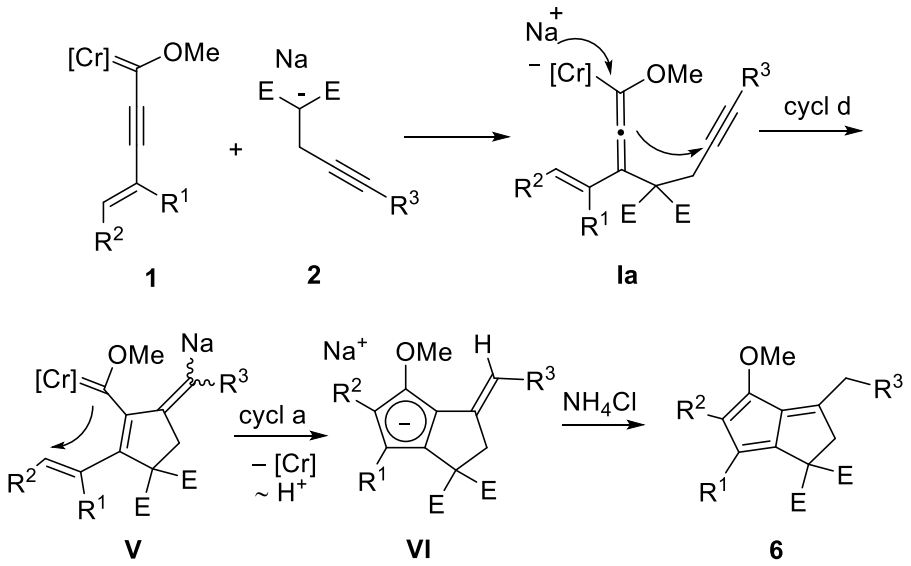
Scheme 4. Reaction between enynyl FCCs **1** and propargylic enolates **2** to give polycycles **6** and **7**.



As shown in Scheme 4, a variety of polycyclic compounds, depending on the structure of the enynyl FCCs, were readily accessible by taking advantage of this strategy. Thus, tricyclic (**6a-c,** Scheme 4, eq 1) and bicyclic (**6d,e**, Scheme 4, eq 2) structures, some of them with an interesting functionalized polyquinane

framework,[15] were formed in very satisfactory yields. The reaction also worked well for indol-substituted alkynylcarbene, where the C2-C3 of 1-methylindole is able to participate as the alkenyl moiety ($R^1C=CR^2$ in **1**) providing a complex tetracyclic indol framework (compound **7a**, Scheme 4, eq 3).[16] Finally, TMS-substituted propargylmalonate **2b** (R^3 = TMS) has been successfully used to generate the linear triquinane **7b** in high yield (Scheme 4, eq 4).[16] A plausible mechanism for this new process involving a Michael type addition and a double cyclization is depicted in Scheme 5. In this case, the allenylmetallate **Ia**, resulting from the addition of the propargylmalonate enolate to the Fischer carbene, would undergo an intramolecular 5-*exo* cyclization by nucleophilic attack over the C-C triple bond to give cyclic metallatriene **V** (cyclization d).[17] The latter readily would undergo cyclopentannulation and proton rearrangement to cyclopentadienyl anion intermediate **VI** (cyclization a); then, protonation gives rise to compounds **6** and **7**.[18]

Scheme 5. Mechanism proposed for the formation of **6**.



■ CONCLUSIONS

We have described two new 1,4-nucleophilic addition/double cyclization cascade processes involving enynyl FCCs. Functionalized tricyclic angular compounds **5** can be obtained selectively from cyclic enynyl

FCCs **1a-c** and homopropargylmalonates **3** by a 1,4-nucleophilic addition/cyclopentannulation/6-*exo* cyclization process. This reaction represents a simple approach to a variety of 5/5/5, 5/5/6 and 5/5/7 angular tricyclic compounds, the basic structure of some of them being present in bioactive molecules.[14] Moreover, new transformations can be achieved when the protonation of the allenylmetallate addition adducts **Ia** is delayed. Thus, the intramolecular 5-*exo* nucleophilic addition to the triple bond from the central carbon of the allenyl moiety can be favored to produce metallatriene intermediates that spontaneouly cyclize to a variety of polycyclic compounds (**6** and **7)**, several of them bearing an interesting polyquinane structure.[15]

■ EXPERIMENTAL SECTION

General. All reactions involving air sensitive compounds were carried out under a N_2 atmosphere (99.99%). All glassware was oven-dried (120°C), evacuated and purged with nitrogen. Enynyl Fischer carbene complexes **1**, were prepared following described procedures.[5] Enynes, were purchased (2-methyl-1-buten-3-yne, 1-ethynylcyclohexene) or synthesized following described procedures[19] (1-ethynylcyclopentene and 1-ethynylcycloheptene). Dimethyl 2-(2-propynyl)-malonate was purchased; dimethyl 2-(3-trimethylsilyl-2-propynyl)-malonate,[20] dimethyl 2-(3-butynyl)-malonate[21] and dimethyl 2-(4-bromo-3-butynyl)-malonate[21] were synthesized. Solvents were dried by standard methods and distilled prior to use. Flash column chromatography was carried out on silica gel 60, 230-240 mesh. Deactivated silica gel was prepared by treatment with a 4% potassium hydrogenophosphate aqueous solution. NMR experiments were recorded on 300; 400 and 600 MHz spectrometers with tetramethylsilane (δ = 0.0) as the internal standard. NMR chemical shifts are reported in ppm. ^{1}H NMR splitting pattern abbreviations are: s, singlet; d, doublet; m, multiplet; brs, broad singlet. ^{13}C NMR spectra were recorded with complete proton decoupling and the multiplicities were determined by DEPT. High resolution mass spectra (HRMS) were obtained with electron ionization techniques (EI) (70 eV) using a magnetic sector analyzer.

General procedure for the 1,4-nucleophilic addition/cyclopentannulation/6-exo-cyclization process. Preparation of compounds ***5***. The corresponding homopropargylmalonate (1.3 mmol) was added to a THF (3 mL) suspension of NaH (1.6 mmol) at 0ºC, and stirred for 10 min. Then, a THF solution (2 mL) of chromium enynyl carbene **1** (1 mmol) was added dropwise at the same temp. The

mixture was warmed to rt, stirred for 30 min, quenched with a saturated aq solution of NH_4Cl (10 mL). The mixture was stirred for 4 h and extracted with diethyl ether (2 x 10 mL). After solvent removal, the resulting crude material was dissolved in CH_2Cl_2 (5 mL) and treated with concd HCl (1 mL), after 12 h at rt the mixture was extracted with CH_2Cl_2 and the solvent removed. Purification of the crude by column chromatrography (silica gel, hexanes/ethyl acetate, 5:1) gave tricycles **5** as solids (76-89%).

*cis-Dimethyl9-methylene-4-oxo-2,3,3a,4,8,9-hexahydro-1H-cyclopenta[c]indene-6,6(7H)-dicarboxylate (**5a**).* White solid; 271 mg, 89% yield; mp 119-121ºC (decomposes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49-1.52 (m, 2H), 1.67-1.84 (m, 3H), 1.95-2.0 (m, 1H), 2.11-2.15 (m, 1H), 2.35-2.59 (m, 2H), 2.62-2.66 (m, 1H), 2.95-2.98 (m, 1H), 3.79 (s, 6H), 4.75 (brs, 1H), 4.80 (brs, 1H), 5.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9 (CH_2), 27.9 (CH_2), 29.7 (CH_2), 33.2 (CH_2), 39.7 (CH_2), 53.1 (CH_3), 53.3 (CH_3), 55.8 (CH), 59.3 (C), 61.8 (C), 107.0 (CH_2), 130.9 (CH), 150.2 (C), 168.7 (C), 169.8 (C), 174.4 (C), 209.9 (C); HRMS calcd for $C_{17}H_{20}O_5$ (M^+) 304.1311, found 304.1313.

*cis-Dimethyl 1-methylene-6-oxo-2,3,6,6a,7,8,9,10-octahydrobenzo[c]indene-4,4(1H)-dicarboxylate (**5b**).* White solid; 248 mg, 78% yield; mp 121-124 ºC (decomposes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11-1.24 (m, 3H), 1.30-141 (m, 1H), 1,58-171 (m, 2H), 1.87-192 (m, 1H), 2.01-2.13 (m, 1H), 2.28-243 (m, 2H), 2.43-2.75 (m, 3H), 3.77 (s, 6H), 4.85 (brs, 1H), 5.00 (brs, 1H), 6.05 (s 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3 (CH_2), 22.0 (CH_2), 23.0 (CH_2), 28.9 (CH_2), 33.8 (CH_2), 37.7 (CH_2), 52.5 (2 x CH_3), 53.0 (CH), 53.2 (C), 58.7 (C), 111.0 (CH_2), 129.7 (CH), 148.9 (C), 168.5 (C), 170.1 (C), 176.0 (C), 206.8 (C); HRMS calcd for $C_{18}H_{22}O_5$ (M^+) 318.1467, found 318.1461.

*cis-Dimethyl 1-methylene-6-oxo-2,3,6a,7,8,9,10,11-octahydro-1H-benzo[c]azulene-4,4(6H) dicarboxylate (**5c**).* White solid; 252 mg, 76% yield; mp 129-130 ºC (decomposes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93-1.05 (m, 1H), 1.17-1.25 (m, 1H), 1.35-1.46 (m, 1H), 1.50-1.65 (m, 4H), 1.75-1.86 (m, 1H), 1.87-1.95 (m, 1H), 2.08-2.23 (m, 2H), 2.26-2.42 (m, 1H), 2.51-2.63 (m, 1H), 2.70-2.73 (m, 1H), 2.82.92 (m, 1H), 3.76 (s, 3H), 3.78 (s, 3H), 4.80 (brs, 1H), 4.90 (brs, 1H), 6.12 (s, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 22.7 (CH_2), 25.0 (CH_2), 25.5 (CH_2), 29.2 (CH_2), 30.6 (CH_2), 33.7 (CH_2), 37.7 (CH_2), 53.1 (CH_3), 53.3 (CH_3), 55.6 (CH), 58.5 (C), 58.8 (C), 109.2 (CH_2), 132.7 (CH), 152.6 (C), 168.8 (C), 170.2 (C), 173.3 (C), 207.9 (C); HRMS calcd for $C_{19}H_{24}O_5$ (M^+) 332.1622, found 332.1627; Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.39; H, 7.41.

*(3aR/S,9aR/S,Z)-Dimethyl-9-(bromomethylene)-4-oxo-2,3,3a,4,8,9-hexahydro-1H-cyclopenta[c]indene-6,6(7H)-dicarboxylate (**5d**).* White solid; 310 mg, 81% yield; mp 143-145 ºC (decomposes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-1.45 (m, 1H), 1.64-1.79 (m, 2H), 1.89-2.09 (m, 2H), 2.20-2.35 (m, 1H), 2.40-2.52 (m, 4H), 3.39 (d, J = 10 Hz, 1H), 3.77 (s, 3H), 3.81(s, 3H), 6.03 (s, 1H), 6.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5 (CH_2), 29.1 (CH_2), 31.1 (CH_2), 31.8 (CH_2), 36.8 (CH_2), 53.3 (CH_3), 53.4 (CH_3), 55.7 (CH), 58.1 (C), 59.7 (C), 99.1 (CH), 135.7 (CH), 145.7 (C), 169.2 (C), 169.8 (C), 171.9 (C), 210.5 (C); HRMS calcd for $C_{17}H_{19}BrO_5$ (M^+): 382.0421, found: 382.0416.

*General procedure for the 1,4-nucleophylic addition/5-exo-cyclization/ cyclopentannulation process. Preparation of compounds **6** and **7**.* A THF solution (2 mL) of chromium enynyl carbene **1** (1 mmol) was added dropwise at 0 ºC, to a THF (3 mL) solution of sodium enolate **2**, prepared in situ by the addition of the corresponding propargylmalonate (1,3 mmol) to a NaH (1,6 mmol) THF suspension. The mixture was stirred at rt for 12 h, and then quenched with a saturated aq solution of NH_4Cl (10 mL). The resulting crude was isolated by extraction with diethyl ether (2 x 10 mL), followed by solvent removal, and then purified by column chromatography (deactivated SiO_2, hexanes/ethyl acetate, 5:1) to get compounds **6** and **7** (72-92%).

*Dimethyl7-methoxy-6-methyl-2,3-dihydro-1H-cyclopenta[a]pentalene-4,4(5H) dicarboxylate (**6a**).* Colorless oil; 280 mg, 92% yield;:^{1}H NMR (300 MHz, $CDCl_3$) δ 2.12 (s, 3H), 2.15-2.25 (m, 2H), 2.36-2.47 (m, 2H), 2.67-2.76 (m, 2H), 3.52 (s, 2H), 3.76 (s, 6H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1 (CH_3), 24.4 (CH_2), 26.4 (CH_2), 30.5 (CH_2), 52.4 (CH_2), 52.7 (2 x CH_3), 57.2 (C), 57.8

(CH_3), 120.1 (C), 130.6 (C), 140.4 (C), 141.1 (C), 145.0 (C), 145.7 (C), 170.6 (2 x C); HRMS calcd for $C_{17}H_{20}O_5$ (M^+) 304.1311, found 304.1325.

*Dimethyl8-methoxy-1-methyl-4,5,6,7-tetrahydrocyclopenta[a]indene-3,3(2H)-dicarboxylate (**6b**).* Colorless oil; 264 mg, 83% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58-1.64 (m 4H), 2.15 (s, 3H), 2.49-2,55 (m, 2H), 2.58-2.65 (m, 2H), 3.50-3.54 (s, 2H), 3.75 (s, 6H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.6 CH_3), 23.0 (CH_2), 23.1 (CH_2), 23.8 (CH_2), 24.4 (CH_2), 52.7 (2 x CH_3), 53.0 (CH_2), 57.8 (C), 60.5 (CH_3), 126.2 (C), 130.1 (C), 131.4 (C), 140.1 (C), 142.7 (C), 146.2 (C), 170.4 (2 x C); HRMS calcd for $C_{18}H_{22}O_5$ (M^+) 318.1467, found 318.1471.

*Dimethyl 9-methoxy-1-methyl-5,6,7,8-tetrahydro-2H-cyclopenta[a]azulene-3,3(4H)-dicarboxylate (**6c**).* Colorless oil, 239 mg, 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54-1.57 (m, 6H), 2.17 (s, 3H), 2.44-2.57 (m, 4H), 3.55 (s, 2H), 3.70 (s, 3H), 3.76 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.7 (CH_3), 26.1 (CH_2), 28.5 (CH_2), 29.4 (CH_2), 29.8 (CH_2), 32.8 (CH_2), 52.8 (2 x CH_3), 53.2 (CH_2), 57.8 (C), 62.4 (CH_3), 127.6 (C), 135.7 (C), 140.0 (C), 140.7 (C), 142.7 (C), 145.3 (C), 170.7 (2 x C); HRMS calcd for $C_{19}H_{24}O_5$ (M^+) 332.1624, found 332.1627.

*Dimethyl 4-methoxy-3,6-dimethylpentalene-1,1(2H)-dicarboxylate (**6d**).* Colorless oil; 178 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.15 (s, 3H), 3.55 (s, 2H), 3.69 (s, 3H), 3.76 (s, 6H), 5.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 15.4 (CH_3), 52.7 (2 x CH_3), 53.2 (CH_2), 56.8 (CH_3), 57.7 (C), 110.8 (CH), 125.9 (C), 129.3 (C), 140.2 (C), 147.3 (C), 151.3 (C), 170.7 (2 x C); HRMS calcd for $C_{15}H_{18}O_5$ (M^+) 278.1154, found 278.1160.

*Dimethyl 4-methoxy-3-methyl-5-phenylpentalene-1,1(2H)-dicarboxylate (**6e**).*White solid; 272 mg, 80% yield; mp 103-105 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.66 (s, 2H), 3.73 (s, 3H), 3.79 (s, 6H), 6.46 (s, 1H), 7.21-7.29 (m, 1H), 7.32-7.41 (m, 2H), 7.71-7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7 (CH_3), 53.5 (CH_2), 53.6 (2 x CH_3), 58.5 (C), 61.6 (CH_3), 118.2 (CH), 127.2 (CH), 127.5 (2 x

CH), 128.7 (2 x CH), 134.1 (C), 135.3 (C), 136.7 (C), 141.6 (C), 152.5 (C), 170.5 (2 x C); HRMS calcd for $C_{20}H_{20}O_5$ (M^+) 340.1311, found 340.1315; Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.35; H, 6.15.

*cis-Dimethyl5-methyl-3-methylene-4-oxo-2,3,3a,4-tetrahydro-1H-pentaleno[2,1-b]indole-1,1(5H,9cH)-dicarboxylate (**7a**).* Colorless oil, 219 mg, 62% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.74 (d, J = 15.3 Hz, 1H), 3.06 (d, J = 15.3 Hz, 1H), 3.60 (s, 3H), 3.80 (s, 3H), 3.90 (m, 1H), 3.93 (s, 3H), 4.85 (m, 1H), 5.11 (brs, 1H), 5.33 (brs, 1H), 7.10-7.21 (m, 1H), 7.26-7.30 (m, 2H), 7.36-7.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.5 (CH), 39.9 (CH_2), 45.1 (CH), 53.3 (CH_3), 53.6 (CH_3), 61.7 (C), 63.6 (CH_3), 111.50 (CH_2), 111.6 (CH), 121.0 (CH), 122.9 (CH), 123.1 (C), 127.5 (CH), 139.6 (C), 140.8 (C), 142.9 (C), 145.6 (C), 170.5 (C), 171.9 (C), 191.9 (C); HRMS calcd for $C_{20}H_{19}NO_5$ (M^+): 353.1263, found 353.1271.

*cis-Dimethyl7-oxo-6-((trimethylsilyl)methyl)-3,3a,7,7a-tetrahydro-1H-cyclopenta[a]pentalene-4,4(2H)-dicarboxylate (**7b**):* Colorless oil; 297 mg, 82% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 9H), 1.33-1.43 (m, 1H), 1.58-1.78 (m, 4H), 1.86-1.93 (m, 1H), 2.81-2.89 (m, 1H), 3.10 (s, 2H), 3.54-3.58 (m, 1H), 3.79 (s, 3H), 3.80 (s, 3H), 6.36 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.2 (3 x CH_3), 25.5 (CH_2), 27.4 (CH_2), 29.4 (CH_2), 30.3 (CH_2), 48.2 (CH), 52.2 (CH), 53.6 (CH_3), 53.7 (CH_3), 61.5 (C), 99.7 (C), 101.1 (C), 135.1 (CH), 169.5 (C), 173.8 (2 x C), 212.0 (C); HRMS calcd for $C_{19}H_{26}O_5Si$ (M^+): 362.1550, found 362.1556.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all compounds, X-ray data and CIF files for compounds **5c**, **5d** and **6e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) See supporting Information

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