

Synthesis of Methyl (*R*)-2-*O*-Propargylglycerate, a Precursor to Analogues of the 2-*O*-Alkylglycerate Part of the Moenomycins

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Conditions allowing optically active methyl glycerate to be converted, without racemization, into the 2-*O*-propargyl derivative, via the 2-*O*-allyl derivative, are reported.

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Introduction

The antibiotic activity of the moenomycin antibiotics [see moenomycin A (**1**), Scheme 1] and structural analogues has been shown to be critically dependent on the presence of a suitable lipid component attached to the 2-position of the glyceric acid moiety.^[1,2] Synthesis of structural analogues with modified lipid chains has been hampered by the inconvenience of access to 2-*O*-alkyl glycerates.^[3–7]

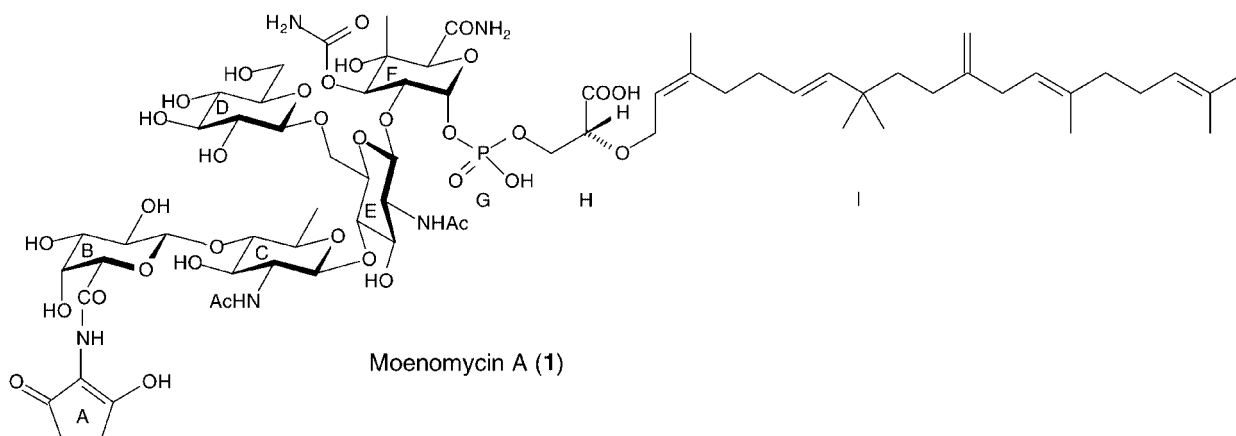
The only efficient procedure so far reported is the silver oxide-promoted reaction between a suitably protected glycerate **2** and allyl bromide, which gives the 2-*O*-allylated derivative **4** in very high yield (Scheme 2) and without measurable racemization. The 2-allyl derivative could then

be used to prepare an array of new 2-*O*-alkylglycerates by cross metathesis followed by catalytic hydrogenation.^[8]

Here we wish to describe the synthesis of methyl 2-*O*-propargylglycerate (**4b**). This compound should also allow various 2-*O*-substituted glycerates to be prepared by known methods.

Results

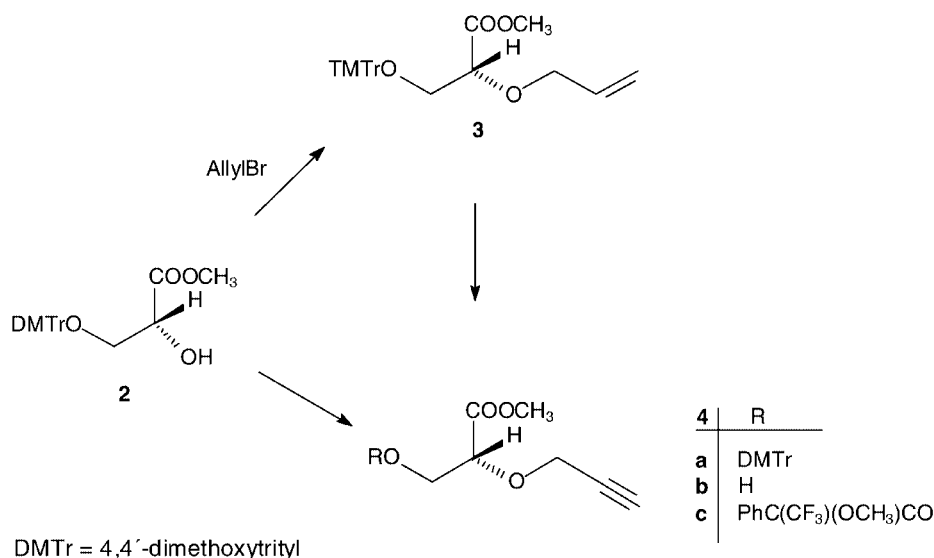
Direct treatment of **2** with propargyl bromide failed.^[9] It is known, however, that nucleophilic reagents such as electron-rich aromatic compounds,^[10] β -dicarbonyl compounds,^[11] allylsilanes,^[12] enols^[13] and alcohols react with



Scheme 1

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α -[alkynyl-hexacarbonyldicobalt]carbenium ions to give the corresponding substitution products (Nicholas reaction).^[14] The activating $[\text{Co}_2(\text{CO})_6]$ moieties can be efficiently intro-

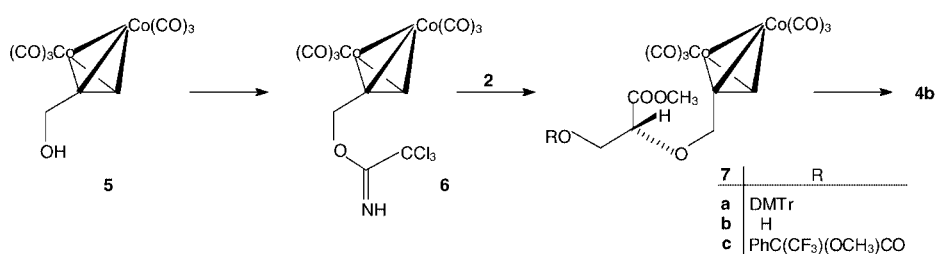


Scheme 2

duced (by treatment of the alkyne with octacarbonyldicobalt) and removed (by treatment with ceriumammonium nitrate).^[15,16] The reaction between **2** and **6** in the presence of several Lewis acids as promoters, at -20 to 0 °C, was unsuccessful.^[17] When, however, the OH group of **5** was activated as a trichloroacetimidate,^[18] the thus formed **6** gave the desired ether **7a** in a BF₃-mediated reaction in yields of 30–40%. Careful optimization of the reaction conditions (i.e., reduction both of the excess of trichloroacetonitrile used in the formation of **6** and of the amount of BF₃–diethyl ether used in the formation of **7a**) increased the yield of **6** to 91% and that of **7a** to 78% (Scheme 3). Use of other Lewis acids (see Table 1) gave lower yields. On the pathway to **4b** it turned out to be advantageous first to

remove the dimethoxytrityl group and then to release the triple bond with ceriumammonium nitrate. Mosher ester analysis^[19] performed both with **4b** (sample obtained from **7b**) and with **7b** revealed that the Nicholas reaction between **2** and **7** was accompanied by substantial racemization, the ratio of the two stereoisomers being about 1:1.6. The analysis showed that racemization occurred in the coupling step rather than during cleavage of the cobalt complex. Analysis of the Mosher esters **7c** obtained by making use of other Lewis acids in the substitution step revealed somewhat better stereoisomer ratios (¹⁹F NMR).

The results called for a more suitable method for the preparation of stereohomogeneous **4b**. It is known that aldehydes can be converted into terminal alkynes by use of



Scheme 3

Table 1. Reaction between **2** and **7**^[17]

Lewis-acid	Yield of 7a	Reaction temperature	Amount of promoter	Ratio of stereoisomers 7c (¹⁹ F NMR)
BF ₃ ·Et ₂ O	78%	-20 °C	0.33 equiv.	1:1.6
Sc(OTf) ₃ ^[19]	35%	-10 °C	0.10 equiv.	1:2.23
TfOH	23%	0 °C	0.20 equiv.	1:1.86
TfOSiMe ₃	<10%	-20 °C	0.10–0.50 equiv.	not determined
B(C ₆ F ₅) ₃ ^[20]	<10%	-20 °C	0.10–0.50 equiv.	not determined

the Ohira-Bestmann modification^[22,23] of a reaction discovered by Colvin and Hamill.^[24] In the event, treatment of the anion of dimethoxy(diazomethyl)phosphonate with the aldehyde obtained from **3** on treatment with OsO₄/NaIO₄ afforded alkyne **4a** in 84% yield (Scheme 2). 2-*O*-Propargylglycerate **4b** was converted into the corresponding Mosher ester **4c**. NMR revealed that no racemization had occurred under these conditions.

Thus, as well as the allyl ether **3**, the new building block **4a** is now available for the preparation of glycerates with different substituents connected to the 2-position through an ether linkage.

Experimental Section

General Methods: see ref.^[25]

NMR spectra: The protons and carbons of the glyceric acid unit are labelled as ^H and those of the 2-*O*-substituent as ^I, according to moenomycin nomenclature (see Scheme 1).

Propargyl Trichloroacetimidate Hexacarbonyldicobalt Complex (6): Trichloroacetonitrile (2.7 mL, 26.8 mmol) and DBU (dropwise, 4.47 mmol, 700 µL) were added at –10 °C to a solution of the hexacarbonyldicobalt complex of propargyl alcohol (**5**,^[26] 6.10 g, 17.89 mmol) in dry dichloromethane (60 mL). After completion of the reaction (monitoring by TLC) the mixture was quickly filtered through silica gel. Washing with dichloromethane and solvent evaporation furnished crude **6** as a red oil (7.98 g, 91%), which was unstable and was used without further purification. *R*_f = 0.60 (CH₂Cl₂/acetone, 25:1). IR (KBr): $\tilde{\nu}$ = 1707, 1514, 1230, 824 cm^{–1}. ¹H NMR (300 MHz, CDCl₃): δ = 8.45 (br. s, 1 H, NH), 6.10 (s, 1 H, $\equiv$ CH), 5.45 (s, 2 H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 199.1 (br. s, 6 $\times$ C=O), 162.8 (C=NH), 91.3 (CCl₃), 87.3 (C $\equiv$ CH), 72.3 ($\equiv$ CH), 70.5 (CH₂) ppm. C₁₁H₄Cl₃Co₂NO₇ (486.38, 484.772), FAB MS: *m/z* (%) = 429 (65) [**8** – 2CO]⁺, 401 (29) [**8** – 3CO]⁺, 325 (84), 317 (35) [**8** – 6CO]⁺, 297 (100), 269 (45), 241 (31).

Methyl (R)-3-*O*-(4,4'-Dimethoxytrityl)-2-*O*-propargylglycerate Hexacarbonyldicobalt Complex (7a): Borontrifluoride–diethyl ether (142 mg, 127 µL, 1 mmol) was slowly added at –20 °C to a solution of **2** (1.267 g, 3 mmol) and **6** (1.703 g, 3.5 mmol) in dry dichloromethane (60 mL). The mixture was stirred at –20 °C for 2 h. With vigorous stirring, the reaction mixture was then added to an ice-cold saturated aqueous solution of NaHCO₃ (100 mL). Aqueous workup (CH₂Cl₂) and FC (toluene/acetone, 30:1) furnished **7a** (1.747 g, 78% based on **2**) as a dark red oil. *R*_f = 0.63 (CH₂Cl₂/acetone, 25:1). IR (KBr): $\tilde{\nu}$ = 1749, 1606, 1506, 1250, 1178, 1132, 1034, 829 cm^{–1}. ¹H NMR (300 MHz, CDCl₃): δ = 7.45–7.41 (d, 2 H, Ar H), 7.34–7.16 (m, 7 H, Ar H), 6.84–6.79 (d, 4 H, Ar H), 6.09 (s, 1 H, $\equiv$ CH), 4.92 and 4.75 (AB system, *J*_{AB} = 13.0 Hz, 2 H, OCH₂), 4.34–4.28 (m, 1 H, 2-H^{glyc}), 3.84 (s, 6 H, 2 $\times$ Ar-OCH₃), 3.79 (s, 3 H, OCH₃), 3.53 (m, 2 H, CH₂-3^{glyc}) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 200.0 (br. s, 6 $\times$ C=O), 171.1 (–COOCH₃), 158.7 (2 $\times$ C-4^{methoxyphenyl}), 144.9 (C-1^{phenyl}), 136.0 (2 $\times$ C-1^{methoxyphenyl}), 130.3 (4 $\times$ C-2^{methoxyphenyl}), 128.4 (2 $\times$ C-2^{phenyl}), 128.1 (2 $\times$ C-3^{phenyl}), 127.0 (C-Ar₄^{phenyl}), 113.3 (4 $\times$ C-3^{methoxyphenyl}), 90.7 (C^{Co} complex), 86.4 [C(Ar₃)], 78.9 (C-2^{glyc}), 71.9 ($\equiv$ CH^{Co} complex), 71.2 (–CH₂–C $\equiv$), 64.4 (C-3^{glyc}), 55.3 (2 $\times$ Aryl–OCH₃), 52.0 (–COOCH₃) ppm. C₃₄H₂₈Co₂O₁₂ (746.46, 746.025), FAB MS: *m/z* (%) = 662 (20) [**7a** – 3CO]⁺, 578 (53) [**7a**

– 6CO]⁺, 555 (3) [**7a** – 3CO – ArOMe]⁺, 471 (20) [**7a** – 6CO – ArOMe]⁺, 460 (9) [**7a** – Co₂(CO)₆]⁺, 353 (14) [**7a** – Co₂(CO)₆ – ArOMe]⁺, 303 (100) [4,4'-dimethoxytrityl]⁺.

Methyl (R)-3-*O*-(4,4'-Dimethoxytrityl)-2-*O*-propargylglycerate (4a). **a)** From **7a**: Ceriumammonium nitrate (CAN, 660 mg, 1.20 mmol) was added at 0 °C to a solution of **7a** (300 mg, 0.40 mmol) in acetone (8 mL). After the mixture had been stirred at 0 °C for 10 min, evolution of CO was no longer observed and TLC (toluene/acetone, 10:1) indicated completion of the reaction. Solvent evaporation, addition of water and usual workup (diethyl ether), followed by FC (CH₂Cl₂/acetone, 20:1) provided **4a** (103 mg, 56%) as a pink oil slightly contaminated with DMT-OH. *R*_f = 0.54 (CH₂Cl₂/acetone, 25:1). IR (KBr): $\tilde{\nu}$ = 1747, 1608, 1508, 1248, 1176, 1101, 1034, 785, 762 cm^{–1}.

b) From **4a**: A catalytic amount of OsO₄ (0.05 mL) in water (1 mL) was added to a solution of **4a** (400 mg, 0.85 mmol) in diethyl ether (10 mL). After the reaction mixture had turned black (15 min), NaIO₄ (370 mg, 2 equiv.) in water (5 mL) was added. After 18 h the reaction mixture was diluted with diethyl ether, and the organic layer was separated and washed with water, dried with NaSO₄ and concentrated. TLC showed only one substance. Because of its very low stability the aldehyde was used in the next step without any purification. A solution of dimethoxy(diazomethyl)phosphonate (210 mg, 1.5 equiv.) and the crude aldehyde (350 mg) in dry methanol (5 mL) and THF (3 mL) was added at 0 °C under argon to a suspension of K₂CO₃ (250 mg, 2.2 equiv.) in THF (1 mL). The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 6 h. After addition of aqueous saturated NH₄Cl (5 mL), petroleum ether (10 mL) and diethyl ether (10 mL), the organic layer was separated, dried with Na₂SO₄ and concentrated. The crude product was purified by FC on silica gel, eluted with toluene/acetone (50:1), to give **4a** (290 mg, 84% after two steps). *R*_f = 0.45 (toluene/acetone, 9:1). [α]_D²⁵ = +9 (*c* = 0.1, CHCl₃). IR (film): $\tilde{\nu}$ = 1743 cm^{–1} (CO). ¹H NMR (200 MHz, HH COSY, CDCl₃): δ = 7.49–7.16 (m, 9 H, Ar H), 6.89–6.83 (m, 4 H, Ar H), 4.39–4.34 (m, 3 H, OCH₂, 2-H^I), 3.81 (s, 6 H, 2 $\times$ Ar–O–CH₃), 3.71 (s, 3 H, OCH₃), 3.44 (d, *J*_{3,2} = 4.4 Hz, 2 H, 3-CH₂^I), 2.46 (broad s, 1 H, $\equiv$ CH) ppm. ¹³C NMR (50.3 MHz, HETCOR, CDCl₃): δ = 170.86 (COOCH₃), 158.69 (*p*-methoxyphenyl-C), 144.83 (C-1^{phenyl}), 139.68 (C'-1^{methoxyphenyl}), 135.98 (C-1^{methoxyphenyl}), 130.22 (C-3^{methoxyphenyl}), 129.28, 129.15 (2 $\times$ C-3^{phenyl}), 128.32, 127.91 (2 $\times$ C-2^{phenyl}), 125.43 (C-4^{phenyl}), 113.35, 113.19 (2 $\times$ C-2^{methoxyphenyl}), 86.33 (CAr₃), 79.10 (C $\equiv$ CH), 77.10 (C-2^H), 75.42 (C $\equiv$ CH), 64.28 (C-3^H), 57.87 (OCH₂), 55.34 (2 $\times$ Ar–O–CH₃), 52.09 (COOCH₃) ppm. C₂₈H₂₈O₆ (460.52, 460.19), ESI MS: *m/z* = [M + Na]⁺ calcd. 483.17781; found 483.17804.

Methyl 2-*O*-Propargylglycerate (4b)

a) Mixture of Enantiomers Obtained by the Nicholas Route:

aa) A solution of **4a** (80 mg, 0.174 mmol) in aqueous acetic acid (80%, 5 mL) was stirred at 20 °C for 48 h. Azeotropic solvent removal [toluene (5 mL) and pyridine (1 mL)] and subsequent FC (CH₂Cl₂/acetone, 10:1) provided **4b** (15 mg, 55%) as a pink oil.

ab) Compound **7a** (312 mg, 0.703 mmol) was treated with CAN (1.156 g, 2.11 mmol) as described above. Workup and FC (CH₂Cl₂/acetone, 10:1) furnished **4b** (64 mg, 58%) as a pink oil.

b) Compound 4b Obtained by the Ohira–Bestmann Route:

A solution of **4a** (35 mg, 0.08 mmol) in acetic acid (80%, 3 mL) was stirred at 20 °C for 4 h. The reaction mixture was then diluted with a pyridine/water mixture and the solvents were evaporated.

Dry pyridine (2 mL) was added and the solvent was removed under reduced pressure. FC (CH₂Cl₂/acetone, 50:1) provided **4b** (10 mg, 84%) as a colourless oil. *R*_f = 0.25 (CH₂Cl₂/acetone, 9:1). [α]_D²⁵ = +176.5 (*c* = 0.1, CHCl₃). IR (film): $\tilde{\nu}$ = 3380 (OH), 1743 cm⁻¹ (CO). ¹H NMR (200 MHz, HH COSY, CDCl₃): δ = 4.43 (dd, *J*_{1,3} = 2.6, *J*_{1,1'} = 16.1 Hz, 1 H, 1-H¹), 4.25 (dd, *J*_{1,3} = 2.5, *J*_{1',1} = 16.1 Hz, 1 H, 1-H^{1'}), 4.29 (m, 1 H, 2-H^H), 3.92 (dd, *J*_{3,2} = 3.6, *J*_{3,3'} = 11.7 Hz, 1 H, 3-H^H), 3.82 (dd, *J*_{3',2} = 5.5, *J*_{3',3} = 11.7 Hz, 1 H, 3-H^{H'}), 3.78 (s, 3 H, OCH₃), 2.50 (t, *J*_{3,1,11} = 2.6 Hz, 1 H, C $\equiv$ CH), 2.30 (s, 1 H, OH) ppm. ¹³C NMR (50.3 MHz, HETCOR, CDCl₃): δ = 171.23 (COOCH₃), 79.33 (C $\equiv$ CH), 78.43 (C-2^H), 76.44 (C $\equiv$ CH), 64.02 (C-3^H), 58.60 (OCH₂), 52.97 (COOCH₃) ppm. C₇H₁₀O₄ (158.15, 158.06), ESI MS: *m/z* = 159.0 [M + H]⁺, 278.9 [M + Na]⁺.

Methyl 2-*O*-Propargyl-glycerate Hexacarbonyldicobalt Complex (7b, Mixture of Enantiomers): The dimethoxyltrityl group was removed from **7a** (300 mg, 0.402 mmol) as described for **4a**. FC (CH₂Cl₂/acetone, 15:1) furnished **7b** (107 mg, 60%) as a dark red oil. *R*_f = 0.31 (CH₂Cl₂/acetone, 25:1). IR (film): $\tilde{\nu}$ = 1525, 1350, 1093, 1038, 804, 731 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 6.05 (s, 1 H, $\equiv$ CH), 4.98 (d, *J*_{1,1'} = 12.8 Hz, 1 H, 1-H¹), 4.64 (d, *J*_{1',1} = 12.8 Hz, 1 H, 1-H^{1'}), 4.28–4.24 (dd, *J*_{2,3} = 3.7, *J*_{2,3'} = 5.1 Hz, 1 H, 2-H^H), 4.05–3.96 (dt, *J*_{3,3'} = 11.7, *J*_{3,2} = 3.7, *J*_{3,OH} = 6.2 Hz, 1 H, 3-H^H), 3.93–3.84 (dt, *J*_{3',3} = 11.7, *J*_{3',2} = 5.1, *J*_{3',OH} = 7.3 Hz, 1 H, 3-H^{H'}), 3.80 (s, 3 H, COOCH₃), 2.27 (t, *J*_{3,OH} = 6.2, *J*_{3',OH} = 7.3 Hz, 1 H, OH) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 200.0 (br. s, 6 $\times$ C=O), 172.8 (COOCH₃), 91.94 (C $\equiv$ CH), 81.2 (C-2^H), 73.1 ($\equiv$ CH), 72.9 (OCH₂), 65.7 (C-3^H), 54.2 (COOCH₃) ppm. C₁₃H₁₀Co₂O₁₀ (444.08, 443.894), FAB MS: *m/z* (%) = 467 (2) [7b + Na]⁺, 416 (6) [7b – CO]⁺, 388 (52) [7b – 2CO]⁺, 360 (65) [7b – 3CO]⁺, 332 (100) [7b – 4CO]⁺, 325 (46), 304 (8) [7b – 5CO]⁺, 297 (49), 276 (64) [7b – 6CO]⁺, 269 (18), 241 (14).

Methyl 2-*O*-Propargyl-3-*O*-[(*R*)-3,3,3-trifluoro-2-methoxy-2-phenyl]-propionyl]glycerate (4c)

a) Mixture of Stereoisomers Obtained by the Nicholas Route: DMAP (0.7 mg, 6.3 μ mol), triethylamine (18.2 mg, 25 μ L, 0.18 mmol) and 3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride (63 mg, 47 μ L, 0.24 mmol) were added at 20 °C to a solution of **4b** (20 mg, 0.12 mmol) in dry dichloromethane (2 mL) and the mixture was stirred at 20 °C overnight. TLC indicated complete consumption of **4b**. Solvent evaporation and FC (toluene/acetone, 25:1) furnished **4c** (38.4 mg 83%) as a colourless oil. *R*_f = 0.56 (toluene/acetone, 10:1). ¹⁹F NMR (282 MHz, C₆D₆): two CF₃ signals, $\Delta\delta$ = 0.2 ppm [ratio 1:1.6].

b) Compound 4c Obtained by the Ohira–Bestmann Route: A mixture of **4b** (10 mg, 0.06 mmol), 3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride (40 μ L, 0.30 mmol, 5 equiv.), triethylamine (40 μ L) and a catalytic amount of 4-(dimethylamino)pyridine in CH₂Cl₂ (0.5 mL) was stirred under argon for 15 h. The solvents were evaporated. Purification by FC (petroleum ether/ethyl acetate, 3:1) furnished **4c** (18 mg, 85%). ¹H NMR (200 MHz, CDCl₃): δ = 7.68–7.63 (m, 2 H, Ar H), 7.07–6.94 (m, 3 H, Ar H), 4.42 (dd, *J*_{3,2} = 3.3, *J*_{3,3'} = 11.4 Hz, 1 H, 3-H^H), 4.08 (dd, *J*_{3',2} = 5.1, *J*_{3',3} = 11.4 Hz, 1 H, 3-H^{H'}), 4.23–4.15 (dd, *J*_{2,3} = 3.3, *J*_{2,3'} = 5.1 Hz, 1 H, 2-H^H), 3.96 (t, *J*_{1,3} = 2.6 Hz, 2 H, CH₂), 3.42 (q, *J* = 1.0 Hz, 3 H, OCOC(=O)CH₃), 3.07 (s, 3 H, COOCH₃), 1.86 (t, *J*_{3,1,11} = 2.6 Hz, 1 H, C $\equiv$ CH) ppm. ¹⁹F NMR (188.3 MHz, CDCl₃): δ = 4.46 (CF₃COOH as standard) ppm. ¹⁹F NMR (188.3 MHz, C₆D₆): δ = 4.50 (CF₃COOH as standard) ppm.

Methyl 2-*O*-Propargyl-3-*O*-[(*R*)-3,3,3-trifluoro-2-methoxy-2-phenyl]propionyl]glycerate Hexacarbonyldicobalt Complex (7c, Mixture of Stereoisomers): Complex **7b** was converted into **7c** as described for **4b**. FC (CH₂Cl₂/acetone, 10:1) furnished **7c** (not completely pure, 20 mg, 84%) as a red oil. ¹H NMR (200 MHz, C₆D₆): δ = 7.78–7.65 (dd, 2 H, 2-H^{Ar}), 7.16–7.08 (m, 3 H, 3-H^{Ar}, 4-H^{Ar}), 5.40 (s, 1 H, $\equiv$ CH), 4.42, 4.09 (2 $\times$ d, ²*J*_{1,1',1} = 12.3 Hz, 2 H, OCH₂), 4.51–4.43 (dd, *J*_{3,3'} = 11.7, *J*_{3,2} = 3.7 Hz, 1 H, 3-H^H), 4.38–4.29 (dd, *J*_{3',3} = 11.7, *J*_{3',2} = 5.1 Hz, 1 H, 3-H^{H'}), 3.82–3.78 (dd, *J*_{2,3} = 3.7, *J*_{2,3'} = 5.1 Hz, 2 H, 2-H^H), 3.47 (br. s, 3 H, C_{quat}–OCH₃), 3.20, 3.18 (2 $\times$ s, ratio 1:1.67, 3 H, COOCH₃) ppm. ¹H NMR (200 MHz, CDCl₃): δ = 7.65–7.41 (m, 5 H, Ar H), 5.99 (s, 1 H, $\equiv$ CH), 4.87 (d, ²*J*_{1,1',1} = 12.3 Hz, 1 H, 1-H¹), 4.69–4.56 (m, 3 H, CH₂^H, 1-H^{1'}), 4.41 (m, 1 H, 2-H^H), 3.68 (br. s, 3 H, C_{quat}–OCH₃), 3.81, 3.54 (2 $\times$ s, ratio 1:1.65, 3 H, COOCH₃) ppm. ¹³C NMR (75 MHz, C₆D₆): δ = 199.9 (br. s, 6 $\times$ C=O), 168.9 (COOCH₃), 164.6 (C_{quat}–COO), 132.7, 129.8 (C^{Ar}, the other signals were hidden by the benzene signals), 124.1 (q, ¹*J*_{C,F} = 288 Hz, CF₃), 90.8 (C $\equiv$ CH), 76.5 (C-2^H), 71.3 ($\equiv$ CH), 70.9 (OCH₂), 65.7 (C-3^H), 55.5, 55.1 (OCH₃), 51.7 (COOCH₃) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 199.4 (br. s, 6 $\times$ C=O), 169.6 (COOCH₃), 166.4 (C_{quat}–COO), 132.1 (C-1^{Ar}), 130.0, 129.8 (C-4^{Ar}), 128.8, 128.6 (C-3^{Ar}), 127.5, 127.4 (C-2^{Ar}), 123.3 (q, ¹*J*_{F,C} = 289 Hz, CF₃), 90.0 (C $\equiv$ CH), 76.5 (C-2^H), 71.4 ($\equiv$ CH, OCH₂), 66.0 (C-3^H), 55.8, 55.6 (OCH₃), 52.4 (COOCH₃) ppm. ¹⁹F NMR (282 MHz, C₆D₆): two CF₃ signals δ = 4.82, 4.53 ppm [ratio 1:1.7] (CF₃COOH as standard).

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