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.

Introduction

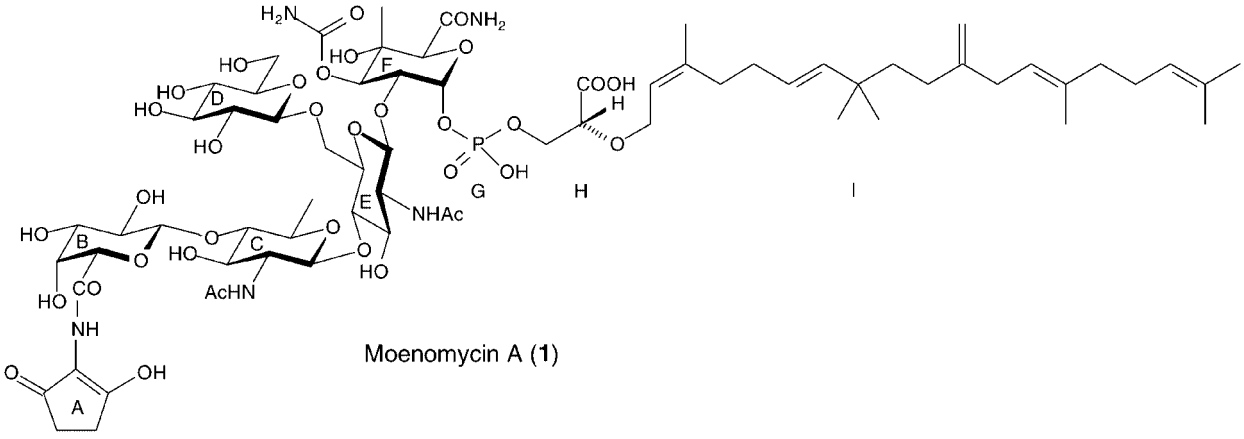
The antibiotic activity of the moenomycin antibiotics [see moenomycin A (**1**), Scheme 1] and structural analogues has been shown to be critically dependent on the presence of a suitable lipid component attached to the 2-position of the glyceric acid moiety.[1,2] Synthesis of structural analogues with 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

α-[alkynyl-hexacarbonyldicobalt]carbenium ions to give the corresponding substitution products (Nicholas reaction).[14] The activating $[Co_2(CO)_6]$ moieties can be efficiently intro-

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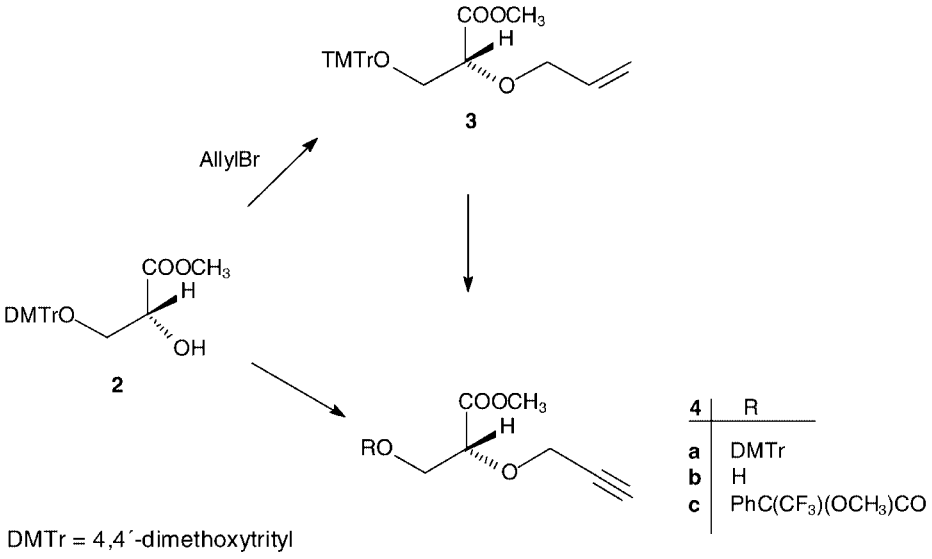
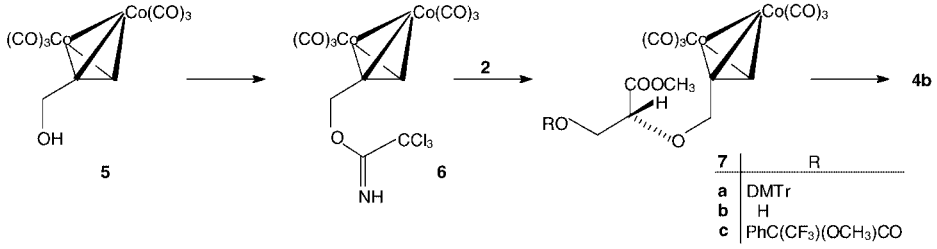


Scheme 2

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 BF_3-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 BF_3−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 (^{19}F 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)
$BF_3{\cdot}Et_2O$	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
$B(C_6F_5)_3$ [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 OsO_4/$NaIO_4$ 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, 700µL) 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 (CH_2Cl_2/acetone, 25:1). IR (KBr): $\tilde{\nu}$ = 1707, 1514, 1230, 824 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.45 (br. s, 1 H, NH), 6.10 (s, 1 H, ≡CH), 5.45 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1 (br. s, 6 × C≡O), 162.8 (C=NH), 91.3 (CCl_3), 87.3 (*C*≡CH), 72.3 (≡CH), 70.5 (CH_2) ppm. $C_{11}H_4Cl_3Co_2NO_7$ (486.38, 484.772), FAB MS: *m*/*z* (%) = 429 (65) [**8** − 2CO]$^{+\cdot}$, 401 (29) [**8** − 3CO]$^{+\cdot}$, 325 (84), 317 (35) [**8** − 6CO]$^{+\cdot}$, 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 $NaHCO_3$ (100 mL). Aqueous workup (CH_2Cl_2) and FC (toluene/acetone, 30:1) furnished **7a** (1.747 g, 78% based on **2**) as a dark red oil. R_f = 0.63 (CH_2Cl_2/acetone, 25:1). IR (KBr): $\tilde{\nu}$ = 1749, 1606, 1506, 1250, 1178, 1132, 1034, 829 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 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, ≡CH), 4.92 and 4.75 (AB system, J_{AB} = 13.0 Hz, 2 H, OCH_2), 4.34−4.28 (m, 1 H, 2-H^{glyc}), 3.84 (s, 6 H, 2 × Ar-OCH_3), 3.79 (s, 3 H, OCH_3), 3.53 (m, 2 H, CH_2-3^{glyc}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.0 (br. s, 6 × C≡O), 171.1 (−*C*OOCH$_3$), 158.7 (2 × C-$4^{methoxyphenyl}$), 144.9 (C-1^{phenyl}), 136.0 (2 × C-$1^{methoxyphenyl}$), 130.3 (4 × C-$2^{methoxyphenyl}$), 128.4 (2 × C-2^{phenyl}), 128.1 (2 × C-3^{phenyl}), 127.0 (C^{Ar}-4^{phenyl}), 113.3 (4 × C-$3^{methoxyphenyl}$), 90.7 ($C_q^{Co\ complex}$), 86.4 [*C*(Ar)$_3$], 78.9 (C-2^{glyc}), 71.9 (≡*C*H$^{Co\ complex}$), 71.2 (−*C*H$_2$−C≡), 64.4 (C-3^{glyc}), 55.3 (2 × Aryl−O*C*H$_3$), 52.0 (−COO*C*H$_3$) ppm. $C_{34}H_{28}Co_2O_{12}$ (746.46, 746.025), FAB MS: *m*/*z* (%) = 662 (20) [**7a** − 3CO]$^{+\cdot}$, 578 (53) [**7a** − 6CO]$^{+\cdot}$, 555 (3) [**7a** − 3CO − ArOMe]$^+$, 471 (20) [**7a** − 6CO − ArOMe]$^+$, 460 (9) [**7a** − $Co_2(CO)_6$]$^{+\cdot}$, 353 (14) [**7a** − $Co_2(CO)_6$ − ArOMe]$^{+\cdot}$, 303 (100) [4,4′-dimethoxytrityl]$^+$.

Methyl (*R*)-3-*O*-(4,4′-Dimethoxytrityl)-2-*O*-propargyl-glycerate (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 (CH_2Cl_2/acetone, 20:1) provided **4a** (103 mg, 56%) as a pink oil slightly contaminated with DMT-OH. R_f = 0.54 (CH_2Cl_2/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 OsO_4 (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), $NaIO_4$ (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 $NaSO_4$ 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 K_2CO_3 (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 NH_4Cl (5 mL), petroleum ether (10 mL) and diethyl ether (10 mL), the organic layer was separated, dried with Na_2SO_4 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). $[\alpha]_D^{25}$ = +9 (*c* = 0.1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 1743 cm^{-1} (CO). ^1H NMR (200 MHz, HH COSY, $CDCl_3$): 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, OCH_2^I, 2-H^H), 3.81 (s, 6 H, 2 × Ar−O−*C*H$_3$), 3.71 (s, 3 H, OCH_3), 3.44 (d, $J_{3,2}$ = 4.4 Hz, 2 H, 3-CH_2^H), 2.46 (broad s, 1 H, ≡CH) ppm. ^{13}C NMR (50.3 MHz, HETCOR, $CDCl_3$): δ = 170.86 (*C*OOCH$_3$), 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 × C-3^{phenyl}), 128.32, 127.91 (2 × C-2^{phenyl}), 125.43 (C-4^{phenyl}), 113.35, 113.19 (2 × C-$2^{methoxyphenyl}$), 86.33 (*C*Ar$_3$), 79.10 (*C*≡CH), 77.10 (C-2^H), 75.42 (C≡*C*H), 64.28 (C-3^H), 57.87 (OCH_2), 55.34 (2 × Ar−O−*C*H$_3$), 52.09 (COO*C*H$_3$) ppm. $C_{28}H_{28}O_6$ (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 (CH_2Cl_2/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 (CH_2Cl_2/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 (CH_2Cl_2/acetone, 50:1) provided **4b** (10 mg, 84%) as a colourless oil. R_f = 0.25 (CH_2Cl_2/acetone, 9:1). $[\alpha]_D^{25}$ = +176.5 (*c* = 0.1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3380 (OH), 1743 cm^{-1} (CO). ^1H NMR (200 MHz, HH COSY, $CDCl_3$): δ = 4.43 (dd, $J_{1,3}$ = 2.6, $J_{1,1'}$ = 16.1 Hz, 1 H, 1-H^I), 4.25 (dd, $J_{1,3}$ = 2.5, $J_{1',1}$ = 16.1 Hz, 1 H, 1-H'^I), 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, OCH_3), 2.50 (t, $J_{3I,1I}$ = 2.6 Hz, 1 H, C≡CH), 2.30 (s, 1 H, OH) ppm. ^{13}C NMR (50.3 MHz, HETCOR, $CDCl_3$): δ = 171.23 (*C*$OOCH_3$), 79.33 (*C*≡CH), 78.43 (C-2^H), 76.44 (C≡*C*H), 64.02 (C-3^H), 58.60 (OCH_2), 52.97 (COO*C*H_3) ppm. $C_7H_{10}O_4$ (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 (CH_2Cl_2/acetone, 15:1) furnished **7b** (107 mg, 60%) as a dark red oil. R_f = 0.31 (CH_2Cl_2/acetone, 25:1). IR (film): $\tilde{\nu}$ = 1525, 1350, 1093, 1038, 804, 731 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 6.05 (s, 1 H, ≡CH), 4.98 (d, $J_{1,1'}$ = 12.8 Hz, 1 H, 1-H^I), 4.64 (d, $J_{1',1}$ = 12.8 Hz, 1 H, 1-H'^I), 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, $COOCH_3$), 2.27 (t, $J_{3,OH}$ = 6.2, $J_{3',OH}$ = 7.3 Hz, 1 H, OH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 200.0 (br. s, 6 × C≡O), 172.8 (*C*$OOCH_3$), 91.94 (*C*≡CH), 81.2 (C-2^H), 73.1 (≡CH), 72.9 (OCH_2), 65.7 (C-3^H), 54.2 (COO*C*H_3) ppm. $C_{13}H_{10}Co_2O_{10}$ (444.08, 443.894), FAB MS: *m*/*z* (%) = 467 (2) [**7b** + Na]$^+$, 416 (6) [**7b** − CO]$^{+\cdot}$, 388 (52) [**7b** − 2CO]$^{+\cdot}$, 360 (65) [**7b** − 3CO]$^{+\cdot}$, 332 (100) [**7b** − 4CO]$^{+\cdot}$, 325 (46), 304 (8) [**7b** − 5CO]$^{+\cdot}$, 297 (49), 276 (64) [**7b** − 6CO]$^{+\cdot}$, 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 μmol), triethylamine (18.2 mg, 25 μL, 0.18 mmol) and 3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride (63 mg, 47 μL, 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). ^{19}F NMR (282 MHz, C_6D_6): two CF_3 signals, Δδ = 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 μL, 0.30 mmol, 5 equiv.), triethylamine (40 μL) and a catalytic amount of 4-(dimethylamino)pyridine in CH_2Cl_2 (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, $CDCl_3$): 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, CH_2^I), 3.42 (q, *J* = 1.0 Hz, 3 H, OCOCOCH_3), 3.07 (s, 3 H, $COOCH_3$), 1.86 (t, $J_{3I,1I}$ = 2.6 Hz, 1 H, C≡CH) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 4.46 (CF_3COOH as standard) ppm. ^{19}F NMR (188.3 MHz, C_6D_6): δ = 4.50 (CF_3COOH 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 (CH_2Cl_2/acetone, 10:1) furnished **7c** (not completely pure, 20 mg, 84%) as a red oil. ^1H NMR (200 MHz, C_6D_6): 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, ≡CH), 4.42, 4.09 (2 × d, $^2J_{1I,1'I}$ = 12.3 Hz, 2 H, OCH$_2^I$), 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, 1 H, 2-H^H), 3.47 (br. s, 3 H, C_{quat}−OCH_3), 3.20, 3.18 (2 × s, ratio 1:1.67, 3 H, COOCH_3) ppm. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.65−7.41 (m, 5 H, Ar H), 5.99 (s, 1 H, ≡CH), 4.87 (d, $^2J_{1I,1'I}$ = 12.3 Hz, 1 H, 1-H^I), 4.69−4.56 (m, 3 H, CH_2^H, 1-H'^I), 4.41 (m, 1 H, 2-H^H), 3.68 (br. s, 3 H, C_{quat}−OCH_3), 3.81, 3.54 (2 × s, ratio 1:1.65, 3 H, COOCH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 199.9 (br. s, 6 × C≡O), 168.9 (*C*$OOCH_3$), 164.6 (C_{quat}−*C*OO), 132.7, 129.8 (C^{Ar}, the other signals were hidden by the benzene signals), 124.1 (q, $^1J_{C,F}$ = 288 Hz, CF_3), 90.8 (*C*≡CH), 76.5 (C-2^H), 71.3 (≡CH), 70.9 (OCH_2), 65.7 (C-3^H), 55.5, 55.1 (OCH_3), 51.7 (COO*C*H_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4 (br. s, 6 × C≡O), 169.6 (*C*$OOCH_3$), 166.4 (C_{quat}−*C*OO), 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, $^1J_{F,C}$ = 289 Hz, CF_3), 90.0 (*C*≡CH), 76.5 (C-2^H), 71.4 (≡CH, OCH_2), 66.0 (C-3^H), 55.8, 55.6 (OCH_3), 52.4 (COO*C*H_3) ppm. ^{19}F NMR (282 MHz, C_6D_6): two CF_3 signals δ = 4.82, 4.53 ppm [ratio 1:1.7] (CF_3COOH as standard).

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