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Convenient synthesis of *O*-functionalized mandelic acids *via* Lewis acid mediated transformation of 1,3-dioxolan-4-ones

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ABSTRACT

An efficient method for the synthesis of *O*-substituted mandelic acids containing alkenyl, alkynyl, methoxycarbonyl, or phenacyl fragments *via* the Lewis acid-catalyzed reaction of 1,3-dioxolan-4-ones with different *C*-nucleophiles is proposed.

1. Introduction

The structural motif of *O*-substituted mandelic acid occurs in many bioactive compounds; for example, compound **1** and Mandipropamid (**4**) possess antifungicidal activity [1], derivatives of *O*-methylated mandelic acid **2** possess growth-regulating activity [2], compound **3** is a potential PPAR α/γ agonist for the treatment of type 2 diabetes [3], and mandelic acid hydrazide **5** is a selective inhibitor of phosphodiesterase 10A (Fig. 1) [4].

The most common methods for the preparation of *O*-substituted mandelic acids can be divided into several main types: a) oxidative transformations of α-functionalized *O*-substituted benzyl alcohols [5]; b) *O*-functionalization of mandelic acids [6]; c) rhodium-catalyzed transformations of 2-diazophenylacetic acids [7]; and d) the reaction n of 1,3-dioxolan-4-ones (also referred to as Seebach chiral templates) [8] with different nucleophiles (Fig. 2) [9].

Among methods for the preparation *O*-substituted mandelic acids, those using 1,3-dioxolan-4-ones are, in our opinion, most promising, but are associated with the use of organometallic reagents and the need to perform reactions on cooling to −78 °C. At the same time, in the short communication [10] we have shown that the reaction between 1,3-dioxolan-4-ones and different *C*-nucleophilic reagents can afford both mono- and bis-addition products depending on the nature of the nucleophile used. In the present work, we developed this research trend as applied to the synthesis of *O*-substituted mandelic acids.

2. Results and discussion

There are several protocols for the synthesis of 1,3-dioxolan-4-ones based on the condensation of carbonyl compounds with α-hydroxycarboxylic acids in the presence of mineral acids [11]. However, the modified procedure [12] based on the use of $BF_3 \cdot OEt_2$ as a catalyst in the acetonitrile medium is, in our opinion, the most convenient and applicable for a wide range of substrates (Table 1). Using this procedure, we obtained the corresponding 1,3-dioxolan-4-ones in reasonable yields from commercially available racemic and optically pure mandelic acid (Entry 1), and 4-fluoro-, 4-fluoromethyl-, 4-bromomandelic acids (Examples 5–7).

The exact configuration of compound **3a** was determined by X-ray diffraction which showed both stereoisomers to have *cis* configuration (Fig. 3).

Such Lewis acids as $TiCl_4$ and $BF_3 \cdot OEt_2$ have been used earlier as catalysts for the reactions of 1,3-dioxolan-4-ones with silicon-containing nucleophiles and found to be efficient when the reaction was performed at very low temperatures [9]. At the same time, $FeCl_3$ is known to exhibit excellent catalytic activity in the reactions of acetals with allylsilanes and silyl ketene acetals and is also efficient in an amount of 5–10 mol. % in room-temperature reactions [13]. Therefore, first we studied the reactions of 1,3-dioxolan-4-

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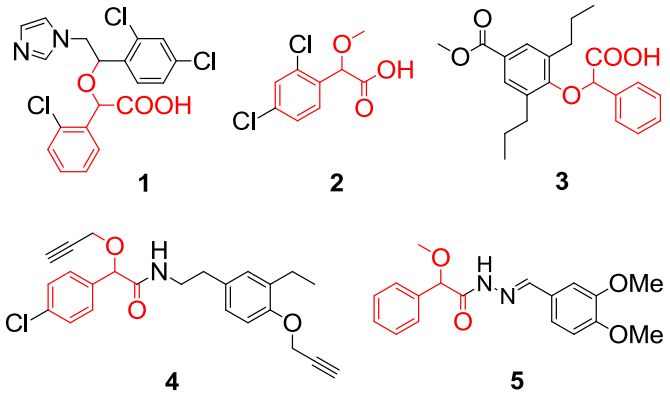


Fig. 1. Examples of bioactive compounds containing the *O*-substituted mandelic acid moiety.

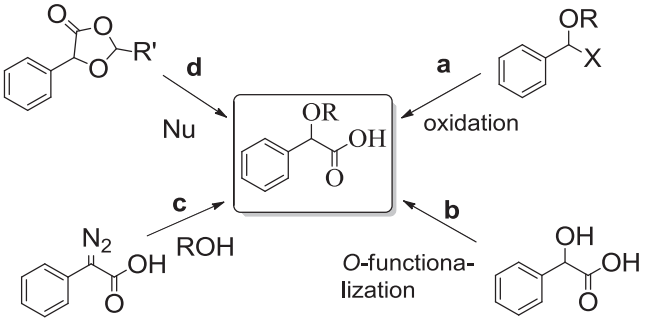
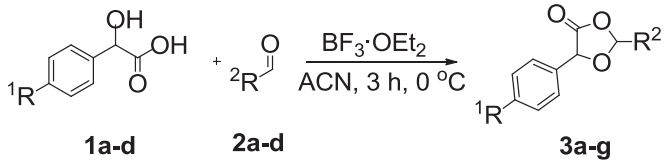


Fig. 2. Main methods for the preparation of *O*-substituted mandelic acids.

Table 1
Synthesis of 1,3-dioxalan-4-ones **3a-g**.[a]



1a-d **2a-d** **3a-g**

Entry		R [1]	R [2]	Yield[b,d] (%)
1	**3a**	H	Ph	59 (56)[c]
2	**3b**	H	*p*-NO_2Ph	72
3	**3c**	H	*p*-BrPh	48
4	**3d**	H	*t*-Bu	57
5	**3e**	F	Ph	64
6	**3f**	CF_3	Ph	71
7	**3g**	Br	Ph	59

[a] The reaction was performed using racemic mandelic acid **1a-d** (15 mmol) and aldehyde **2** (10 mmol) in acetonitrile (30 mL) in the presence of $BF_3 \cdot OEt_2$ (15 mmol) in an argon atmosphere at 0 °C.
[b] Yield after recrystallization.
[c] The yield in parentheses is given for 1,3-dioxolan-4-one **S-3a** obtained from (S)-(+)-mandelic acid.
[d] The ratio of *cis*/*trans*-isomers was 91:9 for **S-3a**, 68:32 for **3b**, 86:14 for **3e**, 74:26 for **3f**, 75:25 for **3g**, and >99:1 for compounds **3a**, **3c** and **3d** (according to the NMR data).

ones **1** with different silicon-containing nucleophiles **4** in the presence of 10 mol. % $FeCl_3$ (Table 2).

The reaction of 1,3-dioxolan-4-ones **3a,e-g** with allyltrimethylsilane **4a** proceeds smoothly at room temperatures; according to the GC/MS data, the reagents are consumed within

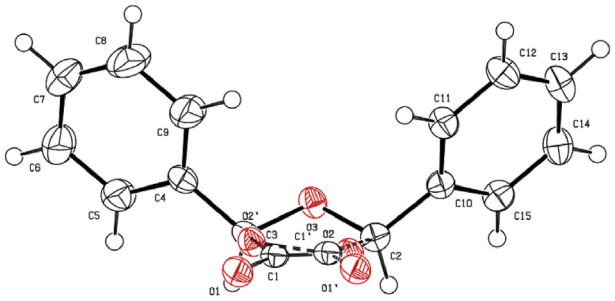


Fig. 3. Crystal structure of compound **3a** with labeling schemes and 50% thermal ellipsoids.

30 min and the preparative-scale yield of substituted mandelic acids **5a-d** in this case reaches 84% (Entry 1–4). In the case of *tert*-butyl-substituted 1,3-dioxolan-4-one **3d**, the complete conversion of the reagents requires keeping the reaction mixture for 24 h at room temperature (Entry 5). Methallyltrimethylsilane **4b** also affords the corresponding substituted mandelic acid in yield of 78% (Entry 6).

The experiment on allylation of 1,3-dioxolan-4-one **S-3a** prepared from (S)-(+)-mandelic acid showed that, in this case, there is no difference in the diastereomeric ratio of products compared to the use of 1,3-dioxolan-4-one **3a** prepared from racemic mandelic acid (Fig. 4). This fact is indirect evidence that the reaction proceeds through the intermediate formation of the planar oxocarbenium cation shown in Fig. 6.

The reactions of 1,3-dioxolan-4-ones with silyl ketene acetal **4c** also proceeds readily at room temperature (Entry 7–9). The reaction of **3a** with silylenol **4d** (Entry 10) requires cooling of the reaction mixture to −10°, since a mixture of products, which is difficult to separate, is produced at room temperature according to the data from TLC. The formation of a mixture of diastereomers, whose ratio was determined by ^{1}H NMR spectroscopy, was observed in all cases. In some of examples, we succeeded in preparative-scale isolation of diastereomers by flash chromatography on silica gel (in the case of **5a,f,j** and **7c**).

The crystal structure of major diastereomer of compound **5f** is shown on Fig. 5. This product corresponds to the attack of the metalylsilane **4b** to the oxocarbenium cation **8** (see Fig. 6) from the side opposite to the carboxyl group, as it is less sterically hindered.

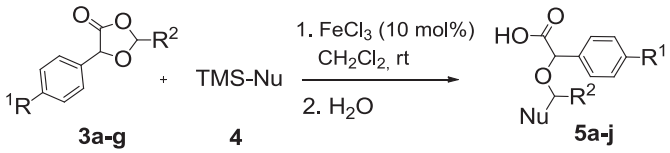
In the case when the nucleophile was vinyltrimethylsilane or (phenylethynyl)trimethylsilane, no formation of reaction product was detected.

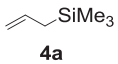
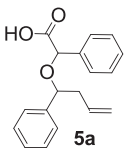
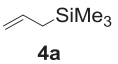
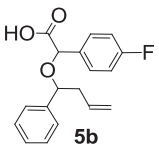
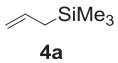
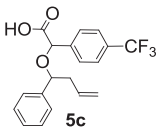
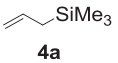
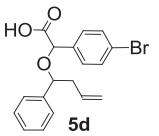
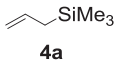
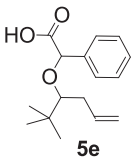
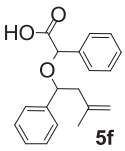
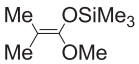
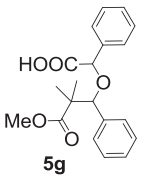
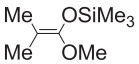
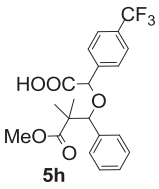
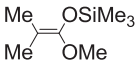
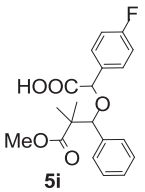
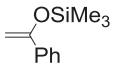
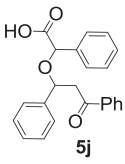
It is known that activation of not only substrate, but also nucleophile is used in order to generate electrophilic species. For example, activation through the formation of corresponding metal acetylides is often used for 1-alkynes whose nucleophilicity on the Mayr scale [14] is considerably lower than that of silicon-containing nucleophiles **4a-d**. A convenient technique was applied earlier by Carreira [15] and Downey [16a] to activate 1-alkynes in the reactions with carbonyl compounds and by Watson [16b] for the reactions with acetals, which consisted in generation of zinc or copper acetyldies in the presence of $ZnBr_2$ or CuI and DIPEA.

The use of this methodology in combination with TMSOTf to generate the oxocarbenium cation from 1,3-dioxolan-4-ones **3a-g** allowed us to obtain alkynylation products **7a-k** (Table 3).

Arylalkynes **6a-d** with both donor and acceptor substituents, as well as trimethylsilylacetylene **6e** undergo this reaction. As Table 2 shows, the presence of the electron-donating substituent in 1-alkyne (Entry 9) increases the reaction time and decreases the

Table 2
Reaction of 1,3-dioxolan-4-ones **3a,d-g** with silicon-containing nucleophiles **4a-d**.[a]



Entry	Nucleophile	Product	Time (h)	Yield[b] (%)	Entry	Nucleophile	Product	Time (h)	Yield[b] (%)
1	 **4a**	 **5a**	0.5	84 (62:38)[c]	**6**	 **4a**	 **5b**	1.5	78 (68:32)
2	 **4a**	 **5c**	0.5	62 (61:39)	**7**	 **4a**	 **5d**	2	63 (64:36)[b]
3	 **4a**	 **5e**	0.5	82 (57:43)	**8**	 **4b**	 **5f**	2	53 (73:27)
4	 **4c**	 **5g**	0.5	80 (55:45)	**9**	 **4c**	 **5h**	2	66 (74:26)
5	 **4c**	 **5i**	24	76 (76:24)	**10**	 **4d**	 **5j**	1	55[d] (61:39)

[a] The reaction was carried out using dioxolan-4-one (0.60 mol) in CH_2Cl_2 (5.5 mL), nucleophile (0.90 mol in the case of **5a-f**, 0.66 mol in the case of **5g-i**, or 0.60 mol in the case of **5j**), and $FeCl_3$ (0.06 mol) in an argon atmosphere at r.t.
[b] Yield of pure products (the ratio of diastereomers is given in parentheses).
[c] Ratio of diastereomers according to NMR spectra.
[d] The reaction was carried out at −10 °C.

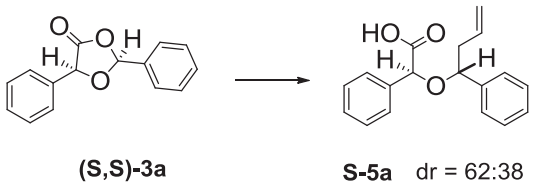


Fig. 4. Allylation of the optical isomer **S-3a**.

product yield to 45%, which is likely due to a lower acidity of methoxyphenylacetylene **6c** and, consequently, a slower formation of acetylide. Also, an increase in the reaction time along with a decrease in the product yield is observed upon introduction of an electron-withdrawing substituent to the starting dioxalanone **3b** (Entry 6) or replacement of the benzene ring with the *tert*-butyl group in **3d** (Entry 7). This fact can be explained by a worse stabilization of the oxocarbenium intermediate in this case.

In all cases, the reaction products form as a mixture of diastereomers in a ratio from 1 : 1.5 to 1 : 4. We assign this to the assumption of that the intermediate oxocarbenium cation **8** has a planar structure and can be attacked by a nucleophile on either side; however, steric hindrances created by substituents make one-side attack more preferred. To confirm this assumption, we performed quantum chemical calculations of the oxocarbenium intermediate **8**, which showed its planar structure (Fig. 6).

3. Conclusion

Thus, we have proposed a simple method for the preparation of *O*-functionalized mandelic acids containing alkenyl, alkynyl, methoxycarbonyl, or phenacyl fragments *via* the Lewis acid-catalyzed reaction between 1,3-dioxolan-4-ones and different *C*-nucleophiles.

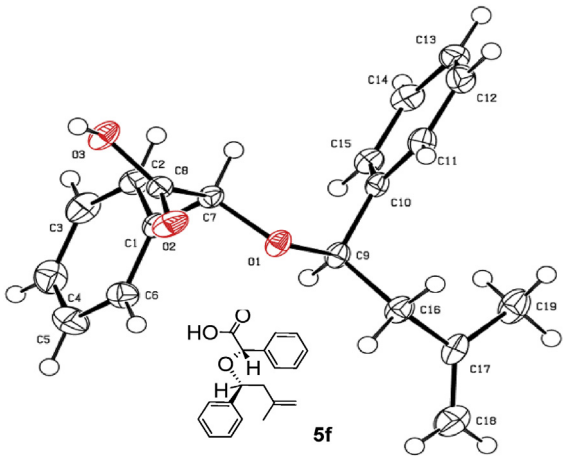


Fig. 5. Crystal structure of major diastereomer of compound **5f** with labeling schemes and 50% thermal ellipsoids.

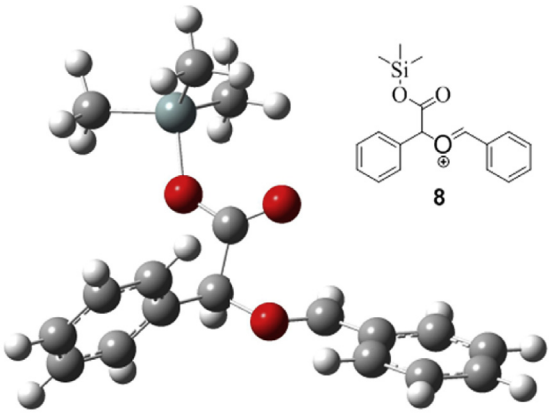


Fig. 6. Computed structure of the oxocarbenium intermediate **8** optimazed at the RB3LYP level with 6-31 + G basis set in toluene.

4. Experimental section

4.1. General information

Reactions were monitored by GC-2010 (Shimadzu) with mass-selective detector QP-2010 Plus (Shimadzu): Supelko SLB-5ms column, 30 m, programmable heating from 60 to 265°C 30 °C/min and thin layer chromatography (TLC). Column chromatography was performed using Silica 60 (40–63 μm, Mecherey-Nagel). ^{1}H NMR and ^{13}C NMR spectra were acquired on an ECA400 (JEOL) (400 and 100 MHz, respectively) and BRUKER AVANCE-600 (600 and 150 MHz, respectively) spectrometers in $CDCl_3$ at room temperature. Chemical shifts δ were measured in ppm and were referenced to the residual solvent resonances ([1]H: $CDCl_3$, $\delta = 7.26$ ppm, ^{13}C: $CDCl_3$, $\delta = 77.2$ ppm). Splitting patterns are designated as *s*, singlet; *d*, doublet; *t*, triplet; *m*, multiplet; *dd*, double doublet. Coupling constants (*J*) are given in Hertz. IR spectra were recorded on a IR Prestige (Shimadzu) for tablets of samples with potassium bromide or for chloroform solution. Mass spectra were recorded on a GCMS–QP2010 Plus Shimadzu, EI ionization (70 eV, ionization chamber temperature 250°C). The procedure of preliminary derivatization to the corresponding ethyl esters described previously was used for compounds **5a-i** and **7a-k** [17]. Melting points were determined on an Stuart SMP30 apparatus and are uncorrected. All chemicals used were of commercial grade and were used without further purification.

4.2. A typical procedure for synthesis of 2,5-diphenyl-1,3-dioxolan-4-one (**3a**)

To a stirring solution of 4 g (26 mmol) D,L-mandelic acid and 1,75 mL (17.3 mmol) benzaldehyde in 80 mL ACN at 0°C in an argon atmosphere, was added 3,33 mL (26 mmol) $BF_3 \cdot OEt_2$. The reaction mixture was stirred for 3 h at 0°C, poured to saturated sodium carbonate solution and extracted DCM. The organic phase was washed consistently with saturated sodium carbonate solution and distilled water, dried with anhydrous Na_2SO_4 and evaporated. The residue was recrystallized from 110 mL *i*-octane. Yield of **3a** 2.21 g (53%) as a colourless crystals, mp 100–101°C. ^{1}H NMR (600 MHz, $CDCl_3$): 7.60–7.61 (m, 2H, H_{Ar}), 7.49–7.52 (m, 5H, H_{Ar}), 7.41–7.45 (m, 3H, H_{Ar}), 6.58 (s, 1H, CH), 5.44 (s, 1H, CH) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.45, 134.4, 133.4, 130.9, 129.5, 129.0 (2C), 128.9 (2C), 127.1 (2C), 126.9 (2C), 103.4, 77.4 ppm. IR: 1784, 1398, 1331, 1221, 1207, 1192, 1055, 748, 694 cm^{-1}. MS (EI, 70 eV) *m/z*: 196 ([$M^+ - 44$], 100%); 195 (49); 167 (97); 105 (80); 90 (61); 89 (61); 77 (68).

4.2.1. (2S,5S)-2,5-Diphenyl-1,3-dioxolan-4-one (**S-3a**)

Colourless crystals, mp 88–89°C (i-octane). ^{1}H NMR (400 MHz, $CDCl_3$): 7.59–7.62 (m, 2H, H_{Ar}), 7.41–7.53 (m, 9H, H_{Ar}), 6.70 (s, 0.1H, CH, minor), 6.58 (d, $J = 0.4$ Hz, 1H, CH, major), 5.53 (s, 0.1H, CH, minor), 5.43 (s, 1H, CH, major) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 134.4, 133.5, 130.9, 129.5, 129.0 (2C), 128.9 (2C), 127.1 (2C), 126.9 (2C), 103.4, 77.4 ppm. IR: 1784, 1396, 1329, 1221, 1192, 1055, 750, 694 cm^{-1}. MS (EI, 70 eV) *m/z*: 196 ([$M^+ - 44$], 100%); 195 (50); 167 (75); 105 (68); 90 (42); 89 (40); 77 (53).

The products **3c-g** were prepared by the similar procedure.

4.2.2. 2-(4-Bromophenyl)-5-phenyl-1,3-dioxolan-4-one (**3c**)

Colourless crystals, mp 105–106°C (MeOtBu:Hex). ^{1}H NMR (400 MHz, $CDCl_3$): 7.60–7.64 (m, 2H, H_{Ar}), 7.41–7.49 (m, 7H, H_{Ar}), 6.53 (d, $J = 0.4$ Hz, 1H, CH), 5.42 (d, $J = 0.4$ Hz, 1H, CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 133.5, 133.2, 132.2 (2C), 129.6, 129.0 (2C), 128.5 (2C), 127.1 (2C), 125.2, 102.6, 77.3 ppm. IR: 1792, 1217, 1196, 1178, 1063, 1011, 827, 762, 698 cm^{-1}. MS (EI, 70 eV) *m/z*: 276 ([M^+, ^{81}Br]-44, 43%); 274 ([M^+, ^{79}Br]-44, 43%); 195 (78); 90 (51); 89 (100); 77 (66); 51 (40).

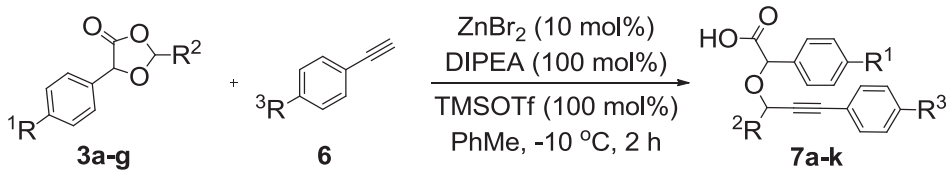
4.2.3. 2-(tert-butyl)-5-phenyl-1,3-dioxolan-4-one (**3d**)

Colourless crystals, mp 109–110°C (*i*-octane). ^{1}H NMR (400 MHz, $CDCl_3$): 7.39–7.48 (m, 5H, H_{Ar}), 5.32 (d, $J = 0.8$ Hz, 1H, CH), 5.24 (s, 1H, CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 133.7, 129.3, 128.9 (2C), 127.2 (2C), 109.5, 77.2, 34.6, 23.8 (3C) ppm. IR: 2980, 2959, 1800, 1776, 1275, 1207, 1184, 976, 760, 696 cm^{-1}. MS (EI, 70 eV) *m/z*: 176 ([$M^+ - 44$], 52%); 135 (77); 107 (100); 79 (52); 70 (98); 57 (72); 41 (43).

4.2.4. 5-(4-Fluorophenyl)-2-phenyl-1,3-dioxolan-4-one (**3e**)

Colourless crystals, mp 90–91°C (*i*-octane). ^{1}H NMR (400 MHz, $CDCl_3$): 7.56–7.59 (m, 2H, H_{Ar}), 7.46–7.52 (m, 5H, H_{Ar}), 7.10–7.15 (m, 2H, H_{Ar}), 6.69 (s, 0.16H, CH, minor), 6.57 (s, 1H, CH, major), 5.48 (s, 0.16H, CH, minor), 5.41 (s, 1H, CH, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 171.1, 163.4 (d, $J^1_{C\text{-}F} = 247.1$ Hz, major), 163.3 (d, $J^1_{C\text{-}F} = 247.1$ Hz, minor), 135.1, 134.3, 131.0, 130.7, 129.3 (d, $J^3_{C\text{-}F} = 3.1$ Hz, major + minor), 129.1 (2C), 129.0 (2C), 128.2 (d, $J^2_{C\text{-}F} = 8.4$ Hz, major + minor), 126.9, 126.4, 116.3, 116.14, 116.08, 115.9, 103.8, 103.4, 76.7, 74.9 ppm. IR: 2920, 1802, 1510, 1402, 1226, 1186, 1059, 837 cm^{-1}. MS (EI, 70 eV) *m/z*: 214 ([$M^+ - 44$], 100%); 213 (37), 185 (61); 108 (44), 107 (32); 105 (39); 90 (27); 77 (39).

Table 3
Reaction of 1,3-dioxolan-4-ones **3a-g** with 1-alkynes **6a-e**.[a]



3a-g **6** **7a-k**

Entry	Nucleophile	Product	Yield (%)	Entry	Nucleophile	Product	Yield[b] (%)
1	Ph— **6a**	**7a**	75 (60:40)[c]	7	Ph— **6a**	**7b**	33[f] (83:17)
2	Ph— **6a**	**7c**	64 (57:43)	8	Ph— **6a**	**7d**	73[d] (80:20)
3	Ph— **6a**	**7e**	54 (75:25)	9	Ph— **6a**	**7f**	45[e] (80:20)
4	Ph— **6a**	**7g**	58 (81:19)	10	O_2N— **6b**	**7h**	67 (75:25)
5	MeO— **6c**	**7i**	53 (75:25)	11	Cl— **6d**	**7j**	50 (75:25)
6	Me_3Si— **6e**	**7k**	45[f] (82:18)				

[a] The reaction was carried out using dioxolan-4-one (0.50 mmol) in toluene (5 mL), 1-alkyne (0.60 mmol), DIPEA (0.50 mmol), TMSOTf (0.50 mmol), and $ZnBr_2$ (0.05 mmol) under an argon atmosphere at −10 °C.
[b] Yield of pure products (the ratio of diastereomers is given in parentheses).
[c] Ratio of diastereomers according to the NMR analysis.
[d] The reaction was carried out for 3 h.
[e] The reaction was carried out for 4.5 h at 0 °C.
[f] The reaction was carried out for 4 h at 0 °C and, then, for 24 h at 5 °C.

*4.2.5. 2-Phenyl-5-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-4-one (**3f**)*

Colourless crystals, mp 110–111°C (i-octane:$CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): 7.65–7.72 (m, 6H, H_{Ar}), 7.56–7.59 (m, 3H, H_{Ar}), 7.47–7.52 (m, 4H, H_{Ar}), 6.71 (s, 0.36H, CH, minor), 6.61 (d, J = 0.8 Hz, 1H, CH, major), 5.54 (s, 0.36H, CH, minor), 5.48 (s, 1H, CH, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 137.3, 137.1, 134.9, 134.2, 131.5 (q, $J^2_{C\text{-}F}$ = 32.5 Hz), 131.1, 130.8, 129.0, 127.0, 126.8, 126.42, 126.39, 126.1 (q, $J^3_{C\text{-}F}$ = 3.6 Hz, minor), 125.9 (q, $J^3_{C\text{-}F}$ = 3.6 Hz, major), 124.0 (q, $J^1_{C\text{-}F}$ = 270.8 Hz), 104.1, 103.7, 76.3, 74.7 ppm. IR: 2914, 1794, 1402, 1333, 1117, 1069, 831 cm^{-1}. MS (EI, 70 eV) m/z: 264 ([M^+ − 44], 100%); 246 (24), 235 (50); 195 (33); 167 (30), 105 (52); 90 (50); 77 (50).

*4.2.6. 5-(4-Bromophenyl)-2-phenyl-1,3-dioxolan-4-one (**3g**)*

Colourless crystals, mp 87–88°C (i-octane). ^1H NMR (400 MHz, $CDCl_3$): 7.54–7.60 (m, 5.6H, H_{Ar}), 7.46–7.52 (m, 4H, H_{Ar}), 7.44 (d, J = 8.4 Hz, 0.75H, H_{Ar}, minor), 7.39 (d, J = 8.4 Hz, 2H, H_{Ar}, major), 6.68 (s, 0.35H, CH, minor), 6.57 (d, J = 0.4 Hz, 1H, CH, major), 5.46 (s, 0.34H, CH, minor), 5.39 (s, 1H, CH, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 170.8, 134.9, 134.2, 132.4, 132.3 (2C), 132.1 (3C), 131.0, 130.7, 129.0 (4C), 128.5 (2C), 127.8 (2C), 126.8 (2C), 126.4 (2C), 123.6,

123.5, 103.9, 103.5, 76.6, 74.8 ppm. IR: 2922, 1792, 1398, 1227, 1207, 1070, 920 cm^{-1}. MS (EI, 70 eV) *m/z*: 276 (45); 274 (47), 195 (100), 167 (46); 166 (33), 105 (53); 90 (40); 89 (88); 77 (51).

4.3. A typical procedure for synthesis of 2-(4-nitrophenyl)-5-phenyl-1,3-dioxolan-4-one (**3b**)

To a stirring solution of 1.14 g (7.5 mmol) D,L-mandelic acid and 0.756 g (5 mmol) of *p*-nitrobenzaldehyde in 20 mL ACN at 0°C in the argon atmosphere, was added 0,95 mL (7,5 mmol) BF_3*OEt_2. The reaction mixture was stirred for 3 h at 0°C, poured to saturated sodium carbonate solution and extracted DCM. The organic phase was washed consistently with saturated sodium carbonate solution and distilled water, dried with anhydrous Na_2SO_4 and evaporated. The residue was purified by column chromatography using MeOt-Bu:Hex = 1:4 → 1:2 as the eluent and recrystallized from mixture of i-octane: chloroform, to give compound **3b** (cis diastereomer) (700 mg, 49%) and **3b′** (trans diastereomer) (326 mg, 23%) as colorless crystals.

*2-(4-nitrophenyl)-5-phenyl-1,3-dioxolan-4-one (**3b**, cis*-diastereomer): colourless crystals, mp 103.5–104.5°C (*i*-octane:$CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 8.33 (dt, *J* = 8.8 Hz, *J* = 2 Hz, 2H, H_{Ar}), 7.78 (dt, *J* = 8.8 Hz, *J* = 2 Hz, 2H, H_{Ar}), 7.42–7.46 (m, 5H, H_{Ar}), 6.67 (s, 1H, CH), 5.48 (d, *J* = 0.8 Hz, 1H, CH). ppm. ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.6, 149.4, 141.0, 132.9, 129.7, 129.1 (2C), 127.8 (2C), 127.1 (2C), 124.2 (2C), 101.4, 77.2. ppm. IR: 1813, 1794, 1528, 1350, 1271, 1223, 1182, 854, 735, 696 cm^{-1}. MS (EI, 70 eV) *m/z*: 241 ([M^+ – 44], 100%); 212 (26); 166 (22); 165 (24); 135 (57); 105 (58); 90 (83); 89 (65); 77 (68).

*2-(4-nitrophenyl)-5-phenyl-1,3-dioxolan-4-one (**3b′**, trans*-diastereomer): colourless crystals, mp 125,8–126,5°C (*i*-octane:$CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 8.33 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 7.7 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 7.53–7.56 (m, 2H, H_{Ar}), 7.43–7.49 (m, 3H, H_{Ar}), 6.76 (s, 1H, CH), 5.51 (s, 1H, CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.4, 149.3, 141.7, 132.6, 129.6, 129.3 (2C), 127.5 (2C), 126.3 (2C), 124.2 (2C), 102.0, 75.4 ppm. IR: 1796, 1521, 1224, 1198, 1180, 1072, 1005, 743, 735 cm^{-1}. MS (EI, 70 eV) *m/z*: 241 ([M^+ – 44], 100%); 212 (27); 135 (63); 105 (67); 90 (91); 89 (72); 77 (73).

4.4. A typical procedure for synthesis of acids **5a-j**

To a solution of dioxolanone **3a** (144 mg, 0.6 mmol) and allyltrimethylsilane **4a** (144 μL, 0.9 mmol) in dry CH_2Cl_2 (5.5 mL) under an argon atmosphere, $FeCl_3$ (9.7 mg, 0.06 mmol) was added at room temperature. The reaction mixture was stirred for 30 min, poured into water, and extracted with EtOAc. The organic phase was dried with anhydrous Na_2SO_4 and evaporated. The residue was purified by column chromatography using EtOAc:Hex (1 : 9) as eluent to give compound **5a** (142 mg, 84%) as a colorless solid (dr = 1 : 1.5).

*2-phenyl-2-((1-phenylbut-3-en-*1-yl*)oxy)acetic acid* (**5a**) (minor diastereomer): colourless crystals, mp 119–120°C. ^{1}H NMR (600 MHz, $CDCl_3$): 10.27 (bs, 1H, OH), 7.40–7.41 (m, 2H, H_{Ar}), 7.31–7.36 (m, 6H, H_{Ar}), 7.27–7.28 (m, 2H, H_{Ar}), 5.88–5.95 (m, 1H, CH_2=C-H), 5.10–5.15 (m, 2H, =CH_2), 4.82 (s, 1H, CH), 4.58 (t, *J* = 6.6 Hz, 1H, CH), 2.72–2.77 (m, 1H, CH_2), 2.52–2.56 (m, 1H, CH_2) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 176.6, 140.4, 136.2, 134.5, 128.8, 128.7 (4C), 128.3, 127.2 (2C), 127.1 (2C), 117.8, 81.6, 77.8, 42.6 ppm. IR: 3028, 2903, 1722, 1703, 1454, 1238, 1188, 1113, 727, 698 cm^{-1}. MS (EI, 70 eV) *m/z*: 269 (8%); 163 (21); 135 (13); 132 (11); 131 (100); 107 (13); 91 (29); 79 (12); 77 (13).

*2-phenyl-2-((1-phenylbut-3-en-*1-yl*)oxy)acetic acid* (**5a**) (major diastereomer): colourless crystals. mp 89–90°C. ^{1}H NMR (600 MHz, $CDCl_3$): 9.94 (bs, 1H, OH), 7.34–7.42 (m, 8H, H_{Ar}), 7.27–7.28 (m, 2H, H_{Ar}), 5.66–5.73 (m, 1H, CH_2=C-H), 5.01–5.04 (m, 2H, =CH_2), 4.74 (s, 1H, CH), 4.26 (t, *J* = 10.2 Hz, 1H, CH), 2.69–2.74 (m, 1H, CH_2), 2.46–2.51 (m, 1H, CH_2) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 174.4, 139.8, 135.5, 134.1, 129.2, 128.90 (2C), 128.86 (2C), 128.5, 127.9 (2C), 127.2 (2C), 117.7, 79.5, 77.3, 42.3 ppm. IR: 3028, 2903, 1722, 1703, 1454, 1238, 1188, 1113, 727, 698 cm^{-1}. MS (EI, 70 eV) *m/z*: 269 (8%); 163 (21); 135 (13); 132 (11); 131 (100); 107 (13); 91 (29); 79 (12); 77 (13).

The products **5b-j** were prepared by the similar procedure.

4.4.1. 2-(4-fluorophenyl)-2-((1-phenylbut-3-en-1-yl)oxy)acetic acid (**5b**)

Colourless crystals, mp 79–81°C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.85 (bs, 1H, OH), 7.29–7.39 (m, 8H, H_{Ar}), 7.22–7.26 (m, 3.7H, H_{Ar}), 7.09 (t, *J* = 8.8 Hz, 1.4H, CH, minor), 7.00 (t, *J* = 8.8 Hz, 2H, CH, major), 5.83–5.93 (m, 1H, =CH, major), 5.63–5.73 (m, 0.64H, =CH, minor), 5.00–5.15 (m, 3.3H, =CH_2, major + minor), 4.77 (s, 1H, CH, major), 4.72 (s, 0.63H, CH, minor), 4.54 (t, *J* = 6.8 Hz, 1H, CH, major), 4.22 (t, *J* = 6.8 Hz, 0.65H, CH, minor), 2.65–2.76 (m, 1.7H, CH_2, major + minor), 2.43–2.55 (m, 1.7H, CH_2, major + minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 175.7, 174.0, 163.3 (d, $J^1_{C\text{-}F}$ = 246.8 Hz, minor), 163.0 (d, $J^1_{C\text{-}F}$ = 246.1 Hz, major), 140.3, 139.7, 134.4, 134.0, 132.1 (d, $J^3_{C\text{-}F}$ = 3.1 Hz, 2C, major), 131.4 (d, $J^3_{C\text{-}F}$ = 2.9 Hz, 2C, minor), 131.36, 129.8, 129.7, 129.0, 128.95 (2C), 128.7 (2C), 128.6, 128.4, 127.2, 127.0, 117.9, 117.8, 116.0 (d, $J^2_{C\text{-}F}$ = 21.6 Hz, 2C, minor), 115.6 (d, $J^2_{C\text{-}F}$ = 21.6 Hz, 2C, major), 81.8, 79.7, 77.3, 76.7, 42.6, 42.2 ppm. IR: 3078, 3030, 2976, 2903, 1724, 1510, 1223, 1113, 1094, 760, 700 cm^{-1}. Major diastereomer: ret. time 8.565 MS (EI, 70 eV) *m/z*: 287 (6%); 181 (30); 153 (6); 132 (11); 131 (100); 129 (8), 125 (15); 109 (13); 91 (15). Minor diastereomer: ret. time 8.625 MS (EI, 70 eV) *m/z*: 287 (9%); 181 (52); 153 (10); 132 (11); 131 (100); 125 (21); 109 (20); 91 (17). HRMS: [M – H]$^-$, found 299.1089, $C_{18}H_{16}FO_3$ requires 299.1089.

4.4.2. 2-((1-Phenylbut-3-en-1-yl)oxy)-2-(4-(trifluoromethyl)-phenyl)acetic acid (**5c**)

Colourless crystals, mp 95–96°C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.87 (bs, 1.9H, OH), 7.67 (d, *J* = 8.4 Hz, 2.6H, H_{Ar}, major), 7.58 (d *J* = 8.4 Hz, 2H, H_{Ar}, minor), 7.50–7.54 (m, 4.7H, H_{Ar}, major + minor), 7.30–7.40 (m, 6.7H, H_{Ar}, major + minor), 7.21–7.26 (m, 5H, H_{Ar}, major + minor), 5.83–5.94 (m, 1H, =CH, minor), 5.64–5.75 (m, 1.3H, =CH, major), 5.05–5.16 (m, 3.4H, =CH_2, major + minor), 5.02 (s, 1.3H, =CH_2, major), 4.84 (s, 1H, CH, minor), 4.80 (s, 1.3H, CH, major), 4.57 (dd, *J* = 7.6 Hz, *J* = 5.6 Hz, 1H, CH, minor), 4.23 (dd, *J* = 7.2 Hz, *J* = 6.4 Hz,1.3H, CH, major), 2.68–2.77 (m, 2.4H, CH_2, major + minor), 2.45–2.57 (m, 2.4H, CH_2, major + minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 175.5, 173.7, 140.0 (2C), 139.6, 139.4, 134.3, 133.8, 131.4 (q, $J^2_{C\text{-}F}$ = 32.3 Hz, major), 130.9 (q, $J^2_{C\text{-}F}$ = 32.3 Hz, minor), 129.0 (2C), 128.8 (3C), 128.5, 128.2 (2C), 127.4 (2C), 127.2 (2C), 127.0 (2C), 125.9 (d, $J^3_{C\text{-}F}$ = 3.6 Hz, 2C, major), 125.6 (d, $J^3_{C\text{-}F}$ = 3.6 Hz, 2C, minor), 124.1 (q, $J^1_{C\text{-}F}$ = 270.8 Hz, minor), 124.0 (q, $J^1_{C\text{-}F}$ = 270.9 Hz, major), 118.1, 118.0, 82.0, 80.3, 77.4, 77.2, 42.6, 42.2 ppm. IR: 3069, 2909, 1728, 1420, 1325, 1163, 1128, 914, 702 cm^{-1}. Minor diastereomer: ret. time 8.350 MS (EI, 70 eV) *m/z*: 337 (20%); 231 (30); 203 (18); 175 (17); 159 (13); 132 (11); 131 (100); 129 (10); 127 (11); 91 (21). Major diastereomer: ret. time 8.385 MS (EI, 70 eV) *m/z*: 337 (40%); 231 (63); 203 (38); 175 (34); 159 (26); 131 (100); 129 (13); 127 (19); 91 (26). HRMS: [M – H]$^-$, found 349.1056, $C_{19}H_{16}O_3F_3O_3$ requires 349.1057.

4.4.3. 2-(4-bromophenyl)-2-((1-phenylbut-3-en-1-yl)oxy)acetic acid (**5d**)

Pale oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.61 (bs, 1.3H, OH), 7.52–7.54 (m, 2H, H_{Ar}), 7.43–7.46 (m, 1.7H, H_{Ar}), 7.29–7.39 (m, 5.6H, H_{Ar}), 7.21–7.26 (m, 7.8H, H_{Ar}), 5.82–5.90 (m, 0.8H, =CH, minor), 5.62–5.73 (m, 1H, =CH, major), 5.00–5.14 (m, 3.8H, =CH_2, major + minor), 4.73 (s, 0.8H, CH, minor), 4.69 (s, 1H, CH, major), 4.53 (dd, *J* = 7.6 Hz, *J* = 5.6 Hz, 0.9H, CH, minor), 4.22 (dd, *J* = 7.6 Hz,

J = 6.0 Hz, 1H, CH, major), 2.65–2.75 (m, 1.9H, CH_2, major + minor), 2.43–2.54 (m, 1.9H, CH_2, major + minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 173.7, 140.1, 139.5, 135.2, 134.6, 134.3, 133.9, 132.2 (2C), 131.8 (2C), 129.5 (2C), 129.0 (2C), 128.8 (2C), 128.75 (2C), 128.69, 128.4, 127.2 (2C), 127.0 (2C), 123.5, 123.0, 118.0, 117.9, 81.8, 79.9, 77.4, 76.7, 42.6, 42.2 ppm. IR: 3067, 2913, 1728, 1713, 1487, 1186, 1092, 1013, 918, 760 cm^{-1}. Minor diastereomer: ret. time 10.095 MS (EI, 70 eV) m/z: 349 (3%); 347 (3); 243 (13); 241 (13); 187 (4); 185 (5); 162 (5); 132 (11); 131 (100); 129 (8); 91 (15); 77 (7). Major diastereomer: ret. time 10.165 MS (EI, 70 eV) m/z: 349 (4%); 347 (4); 243 (19); 241 (20); 185 (7); 162 (7); 132 (11); 131 (100); 129 (9); 91 (16); 77 (9).

4.4.4. 2-((2,2-Dimethylhex-5-en-3-yl)oxy)-2-phenylacetic acid (**5e**)

Colourless crystals, mp 53–54°C. ^1H NMR (400 MHz, $CDCl_3$): 9.72 (bs, 1H, OH), 7.43–7.45 (m, 2H, H_{Ar}), 7.33–7.38 (m, 4.6H, H_{Ar}), 5.87–5.95 (m, 0.3H, =CH, minor), 5.53–5.63 (m, 1H, =CH, major), 5.08–5.18 (m, 0.5H, $=CH_2$, minor), 5.08 (s, 1H, CH, major), 5.04 (s, 0.33H, CH, minor), 4.82–4.93 (m, 2H, $=CH_2$, major), 3.28 (dd, J = 6.4 Hz, J = 4 Hz, 1H, CH, major), 3.20 (dd, J = 7.6 Hz, J = 3.6 Hz, 0.32H, CH, minor), 2.47–2.52 (m, 0.32H, CH_2, minor), 2.32–2.40 (m, 1.32H, CH_2, major + minor), 2.14–2.21 (m, 1H, CH_2, major), 1.00 (s, 9H, *t*-Bu, major), 0.83 (s, 3H, *t*-Bu, minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 174.2, 137.0, 136.8, 136.6, 136.1, 129.0, 128.8, 128.7 (2C), 128.6 (2C), 128.1 (2C), 127.5 (2C), 117.6, 116.4, 87.7, 87.4, 81.0, 80.5, 36.3, 35.8, 35.7, 35.6, 26.65 (3C), 26.58 (3C) ppm. IR: 2957, 1726, 1705, 1261, 1219, 1186, 1099, 1074, 719 cm^{-1}. MS (EI, 70 eV) m/z: 163 (100%); 135 (34); 111 (32); 107 (50); 91 (30); 79 (23); 69 (32).

4.4.5. 2-((3-methyl-1-phenylbut-3-en-1-yl)oxy)-2-phenylacetic acid (**5f**)

Minor diastereomer: colourless crystals, mp 80.1–80.6°C. ^1H NMR (400 MHz, $CDCl_3$): 7.28–7.35 (m, 8H, H_{Ar}), 7.24–7.26 (m, 1H, H_{Ar}), 4.92 (s, 1H, $=CH_2$), 4.88 (s, 1H, $=CH_2$), 4.80 (s, 1H, CH), 4.58 (dd, J = 8.8 Hz, J = 4.8 Hz, 1H, CH), 2.72 (dd, J = 14.0 Hz, J = 8.8 Hz, 1H, CH_2), 2.39 (dd, J = 14.0 Hz, J = 4.8 Hz, 1H, CH_2), 1.83 (s, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 142.5, 140.4, 136.1, 128.75, 128.68 (2C), 128.64 (2C), 128.3, 127.0 (2C), 126.94 (2C), 114.3, 80.8, 78.2, 46.9, 22.9 ppm. IR: 3075, 2899, 1717, 1456, 1242, 1119, 885, 723 cm^{-1}. MS (EI, 70 eV) m/z: 269 (20%); 163 (45); 145 (100); 135 (26); 129 (14); 117 (12); 107 (12); 91 (19); 79 (13); 77 (12).

Major diastereomer: colourless crystals, mp 82–83°C. ^1H NMR (400 MHz, $CDCl_3$): 7.30–7.39 (m, 8H, H_{Ar}), 7.23–7.25 (m, 2H, H_{Ar}), 4.77 (s, 1H, $=CH_2$), 4.71 (s, 1H, CH), 4.67 (s, 1H, $=CH_2$), 4.34 (dd, J = 8.4 Hz, J = 5.2 Hz, 1H, CH), 2.67 (dd, J = 14.0 Hz, J = 8.4 Hz, 1H, CH_2), 2.36 (dd, J = 14.0 Hz, J = 5.2 Hz, 1H, CH_2), 1.58 (s, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 141.6, 140.0, 135.3, 129.3, 128.9 (4C), 128.6, 128.0 (2C), 127.2 (2C), 113.8, 78.2, 77.3, 46.4, 22.7 ppm. IR: 3088, 2966, 1763, 1452, 1306, 1092, 1065, 868, 779 cm^{-1}. MS (EI, 70 eV) m/z: 269 (35%); 163 (89); 145 (100); 135 (50); 129 (17); 117 (13); 107 (21); 91 (30); 79 (22); 77 (18). HRMS: $[M-H]^-$, found 295.1337, $C_{19}H_{19}O_3$ requires 295.1340.

4.4.6. 2-(3-methoxy-2,2-dimethyl-3-oxo-1-phenylpropoxy)-2-phenylacetic acid (**5g**)

Colourless crystals, mp 83–85°C. ^1H NMR (400 MHz, $CDCl_3$): 7.64 (bs, 1.3H, OH), 7.30–7.37 (m, 11H, H_{Ar}), 7.17–7.24 (m, 5H, H_{Ar}), 4.94 (s, 0.56H, CH, minor), 4.75 (s, 0.56H, CH, minor), 4.67 (s, 1H, CH, major), 4.52 (s, 1H, CH, major), 3.79 (s, 1.6H, OCH_3, minor), 3.54 (s, 3H, OCH_3, major), 1.27 (s, 1.7H, CH_3, minor), 1.20 (s, 3H, CH_3, major), 1.06 (s, 1.7H, CH_3, minor), 1.00 (s, 3H, CH_3, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 176.5, 173.9, 173.0, 136.6, 135.5, 135.3, 135.1, 129.4 (2C), 128.9 (2C), 128.8 (4C), 128.7 (2C), 128.6 (2C), 128.4 (2C), 128.3 (4C), 126.8 (2C), 85.1, 84.0, 78.1, 77.9, 52.8, 52.0, 47.8 (2C), 23.3, 22.8, 19.4, 18.7 ppm. IR: 3462, 3453, 2990, 1740, 1726, 1263, 1188, 1136, 1096, 706 cm^{-1}. Minor diastereomer: ret. time 9.790 MS (EI, 70 eV) m/z: 297 (24%); 191 (65); 163 (80); 135 (44); 131 (28); 121 (32); 91 (42); 73 (100). Major diastereomer: ret. time 9.880 MS (EI, 70 eV) m/z: 269 (21%); 191 (54); 163 (100); 135 (47); 131 (26); 121 (31); 107 (29); 105 (22); 91 (48); 73 (88).

4.4.7. 2-(3-methoxy-2,2-dimethyl-3-oxo-1-phenylpropoxy)-2-(4-(trifluoromethyl)phenyl)acetic acid (**5h**)

Pale oil. ^1H NMR (400 MHz, $CDCl_3$): 7.74 (bs, 1H, OH), 7.58–7.64 (m, 3H, H_{Ar}), 7.49–7.51 (m, 0.8H, H_{Ar}), 7.32–7.39 (m, 5.2H, H_{Ar}), 7.23–7.23 (m, 2.3H, H_{Ar}), 7.14–7.16 (m, 0.8H, H_{Ar}), 4.96 (s, 0.37H, CH, minor), 4.79 (s, 0.38H, CH, minor), 4.73 (s, 1H, CH, major), 4.53 (s, 1H, CH, major), 3.79 (s, 1.1H, OCH_3, minor), 3.53 (s, 3H, OCH_3, major), 1.25 (s, 1H, CH_3, minor), 1.21 (s, 3H, CH_3, major), 1.06 (s, 1.1H, CH_3, minor), 0.99 (s, 3H, CH_3, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 176.6, 173.4, 173.1, 140.3, 139.4, 135.4, 135.0, 131.4 (q, J^2_{C-F} = 32.5 Hz, major), 130.6 (q, J^2_{C-F} = 32.3 Hz, minor), 129.0, 128.9, 128.8, 128.7 (2C), 128.52 (4C), 128.48 (2C), 128.4, 127.1 (2C), 125.7 (q, J^3_{C-F} = 3.6 Hz, 2C, major), 125.6 (q, J^3_{C-F} = 3.6 Hz, 2C, minor), 124.1 (q, J^1_{C-F} = 270.7 Hz, minor), 124.0 (q, J^3_{C-F} = 270.8 Hz, minor), 85.4, 84.7, 77.5, 77.3, 52.8, 52.0, 47.9, 47.8, 22.85, 22.78, 19.3, 18.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.59, 62.61 ppm. IR: 3030, 2986, 2951, 1730, 1713, 1454, 1325, 1126, 1018, 756, 706 cm^{-1}. Minor + major diastereomer: ret. time 9.300 MS (EI, 70 eV) m/z: 337 (48%); 231 (100); 203 (48); 191 (54); 175 (39); 159 (34); 131 (36); 73 (63).

4.4.8. 2-(4-fluorophenyl)-2-(3-methoxy-2,2-dimethyl-3-oxo-1-phenylpropoxy)acetic acid (**5i**)

Colourless oil. ^1H NMR (400 MHz, $CDCl_3$): 8.42 (bs, 1.1H, OH), 7.29–7.39 (m, 4.8H, H_{Ar}), 7.15–7.24 (m, 4.9H, H_{Ar}), 6.98–7.07 (m, 2.9H, H_{Ar}), 4.92 (s, 0.36H, CH, minor), 4.71 (s, 0.36H, CH, minor), 4.65 (s, 1H, CH, major), 4.50 (s, 1H, CH, major), 3.79 (s, 1.1H, OCH_3, minor), 3.55 (s, 3H, OCH_3, major), 1.26 (s, 1.3H, CH_3, minor), 1.20 (s, 3H, CH_3, major), 1.05 (s, 1.1H, CH_3, minor), 0.99 (s, 3H, CH_3, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 176.5, 174.0, 173.4, 163.3 (d, J^1_{C-F} = 247 Hz, major), 162.9 (d, J^1_{C-F} = 245.8 Hz, minor), 135.4, 135.2, 132.4 (d, J^4_{C-F} = 3.1 Hz, minor), 131.0 (d, J^4_{C-F} = 2.9 Hz, major), 130.1 (d, J^3_{C-F} = 8.4 Hz, 2C, major), 128.87 (2C), 128.85 (2C), 128.82 (2C), 128.7 (2C), 128.6, 128.5 (2C), 128.3, 115.8 (d, J^2_{C-F} = 21.8 Hz, 2C, major), 115.6 (d, J^2_{C-F} = 21.5 Hz, 2C, minor), 85.2, 84.0, 77.4, 77.2, 52.8, 52.0, 47.85, 47.80, 23.2, 22.8, 19.3, 18.7 ppm. IR: 3028, 2986, 1728, 1713, 1605, 1508, 1225, 1090, 835, 756 cm^{-1}. Minor diastereomer: ret. time 9.550 MS (EI, 70 eV) m/z: 315 (23%); 287 (10); 192 (16); 191 (97); 181 (87); 135 (25); 131 (38); 125 (30); 121 (44); 109 (38); 73 (100). Major diastereomer: ret. time 9.595 MS (EI, 70 eV) m/z: 315 (17%); 287 (12); 191 (72); 182 (13); 181 (100); 153 (19); 135 (19); 131 (28); 125 (30); 121 (33); 109 (39); 73 (78). HRMS: $[M-H]^-$, found 359.1297, $C_{20}H_{20}FO_5$ requires 359.1300.

4.4.9. 2-(3-oxo-1,3-diphenylpropoxy)-2-phenylacetic acid (**5j**)

Minor diastereomer: colourless crystals, mp 104–106°C. ^1H NMR (400 MHz, $CDCl_3$): 12.36 (bs, 1H, OH), 8.01–8.03 (m, 2H, H_{Ar}), 7.62–7.66 (m, 1H, H_{Ar}), 7.48–7.51 (m, 2H, H_{Ar}), 7.38–7.42 (m, 3H, H_{Ar}), 7.31–7.35 (m, 8H, H_{Ar}), 5.16 (dd, J = 10.4 Hz, J = 1.6 Hz, 1H, CH), 4.85 (s, 1H, CH), 3.72 (dd, J = 18.0 Hz, J = 10.4 Hz, 1H, CH_2), 3.39 (dd, J = 18.0 Hz, J = 1.6 Hz, 1H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 172.6, 138.7, 136.5, 135.8, 134.5, 129.3 (2C), 129.2, 129.0 (2C), 128.73, 128.68 (2C), 128.64 (2C), 127.1 (2C), 127.0 (2C), 78.5, 77.0, 46.6 ppm. IR: 3510, 3387, 1705, 1670, 1327, 1219, 1107, 702, 691 cm^{-1}. MS (EI, 70 eV) m/z: 208 (M^+, 83%); 207 (100); 131 (38); 105 (44); 103 (52); 77 (86); 51 (42).

Major diastereomer: colourless crystals, mp 104–106°C. ^1H NMR (400 MHz, $CDCl_3$): 8.14 (bs, 1H, OH), 7.89–7.91 (m, 2H, H_{Ar}), 7.52–7.56 (m, 1H, H_{Ar}), 7.41–7.44 (m, 2H, H_{Ar}), 7.27–7.37 (m, 10H, H_{Ar}), 4.93 (dd, J = 7.6 Hz, J = 5.6 Hz, 1H, CH), 4.74 (s, 1H, CH), 3.70

(dd, $J = 16.4$ Hz, $J = 7.6$ Hz, 1H, CH_2), 3.28 (dd, $J = 16.4$ Hz, $J = 5.6$ Hz, 1H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 174.2, 139.5, 137.0, 135.0, 133.4, 129.3, 129.0 (2C), 128.8 (2C), 128.74, 128.70 (2C), 128.3 (2C), 127.9 (2C), 127.3 (2C), 77.5, 75.9, 46.9 ppm. IR(смесь): 3510, 3387, 1705, 1670, 1327, 1219, 1107, 702, 691 cm^{-1}. MS (EI, 70 eV) *m/z*: 208 (M^+, 83%); 207 (100); 131 (38); 105 (44); 103 (52); 77 (86); 51 (42).

4.5. A typical procedure for synthesis of acids **7a-k**

To a solution of phenylacetylene (66 μL, 0.6 mmol) in dry toluene (4 mL) under an argon atmosphere, DIPEA (87 μL, 0.5 mmol) and $ZnBr_2$(11.3 mg, 0.5 mmol) were added at room temperature. The reaction mixture was stirred for 30 min at room temperature and cooled to −10°C. A cooled to −10 °C solution of dioxolanone **3a** (120.1 mg, 0.5 mmol) and TMSOTf (90 μL, 0.5 mmol) in toluene (1 mL) was added. The resulting mixture was stirred for 2 h, poured into water acidified with 2 N HCl (1 mL), and extracted with EtOAc. The organic phase was dried with anhydrous Na_2SO_4 and evaporated. The residue was purified by column chromatography using gradient elution with EtOAc:Hex (1:10 → 1:6) to give compound **7a** (128.4 mg, 75%) as a pale oil (dr = 1:1.5).

*2-((1,3-diphenylprop-2-yn-*1-yl*)oxy)-2-phenylacetic acid* (**7a**). Pale oil. ^1H NMR (600 MHz, $CDCl_3$): 9.57 (bs, 2H, OH), 7.66–7.67 (m, 3H, H_{Ar}), 7.56–7.60 (m, 4H, H_{Ar}), 7.47–7.52 (m, 9H, H_{Ar}), 7.31–7.43 (m, 23H, H_{Ar}), 5.66 (s, 1.5H, CH, major), 5.49 (s, 1H, CH, minor), 5.40 (s, 1.5H, CH, major), 5.38 (s, 1H, CH, minor) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 174.8, 137.7, 137.6, 135.7, 135.2, 132.0 (4C), 130.3, 129.4, 129.1, 129.04, 129.02, 129.0, 128.9 (2C), 128.81 (2C), 128.77 (2C), 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.0 (4C), 127.9 (2C), 127.6 (2C), 122.2, 122.1, 89.3,89.0, 85.8, 85.3, 78.1, 77.6, 71.4, 70.5 ppm. IR: 3032, 1721, 1452, 1278, 1217, 1067, 756, 696 cm^{-1}. MS (EI, 70 eV) *m/z*: 207 (31%); 192 (18); 191 (100); 189 (14); 164 (8) 105 (7).

The products **7b-k** were prepared by the similar procedure.

4.5.1. 2-((1,3-diphenylprop-2-yn-1-yl)oxy)-2-(4-fluorophenyl)-acetic acid (**7b**)

Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): 8.03 (bs, 1.1H, OH), 7.63–7.65 (m, 2H, H_{Ar}), 7.51–7.58 (m, 3.1H, H_{Ar}), 7.46–7.52 (m, 5.7H, H_{Ar}), 7.32–7.43 (m, 11.4H, H_{Ar}), 7.10–7.14 (m, 1.6H, H_{Ar}), 7.03–7.07 (m, 2H, H_{Ar}), 5.65 (s, 1H, CH, major), 5.44 (s, 0.74H, CH, minor), 5.37 (s, 1H, CH, major), 5.36 (s, 0.77H, CH, minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 174.4, 163.4 (d, $J^1_{C\text{-}F} = 247$ Hz, minor), 163.1 (d, $J^1_{C\text{-}F} = 246.4$ Hz, major), 137.5, 137.4, 132.0 (4C), 131.6 (d, $J^4_{C\text{-}F} = 2.9$ Hz, minor), 131.1 (d, $J^4_{C\text{-}F} = 3.1$ Hz, major), 129.8 (d, $J^3_{C\text{-}F} = 8.4$ Hz, 2C, minor), 129.4 (d, $J^3_{C\text{-}F} = 8.3$ Hz, 2C, major), 129.1 (2C), 129.0 (2C), 128.8 (2C), 128.7 (2C), 128.52 (2C), 128.49 (2C), 127.95 (2C), 127.87 (2C), 122.1, 122.0, 116.1 (d, $J^2_{C\text{-}F} = 21.8$ Hz, 2C, minor), 115.8 (d, $J^2_{C\text{-}F} = 21.5$ Hz, 2C, major), 89.5, 89.2, 85.6, 85.1, 77.4, 76.9, 71.5, 70.7 ppm. IR: 3063, 2922, 1728, 1713, 1603, 1504, 1225, 1082, 835, 758 cm^{-1}. Ret. time 14.045 MS (EI, 70 eV) *m/z*: 208 (6%); 207 (35); 192 (19); 191 (100); 190 (6); 189 (13); 165 (4); 123 (5). HRMS: $[M - H]^-$, found 359.1082, $C_{23}H_{16}FO_3$ requires 359.1089.

4.5.2. 2-((1,3-diphenylprop-2-yn-1-yl)oxy)-2-(4-(trifluoromethyl)-phenyl)acetic acid (**7c**)

Major diastereomer: colourless crystals, mp 104–105°C. ^1H NMR (400 MHz, $CDCl_3$): 7.63–7.65 (m, 6H, H_{Ar}), 7.40–7.44 (m, 5H, H_{Ar}), 7.29–7.35 (m, 3H, H_{Ar}), 5.70 (s, 1H, CH), 5.47 (s, 1H, CH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 139,7, 137.4, 131.9 (2C), 131.1 (q, $J^2_{C\text{-}F} = 32.4$ Hz), 129.1 (2C), 128.8 (2C), 128.5 (2C), 127.94 (2C), 127.86 (2C), 125.7 (q, $J^3_{C\text{-}F} = 3.3$ Hz, 2C), 124.0 (q, $J^1_{C\text{-}F} = 270.8$ Hz), 122.0, 89.6, 85.3, 77.0, 71.9, ppm. IR: 3030, 2904, 1701, 1491, 1329, 1161, 1126, 1069, 754 cm^{-1}. Ret. time 13.055 MS (EI, 70 eV) *m/z*: 208 (13%); 207 (79); 192 (18); 191 (100); 190 (7); 189 (17); 165 (7); 129 (9); 105 (7). HRMS: $[M - H]^-$, found 409.1034, $C_{24}H_{16}F_3O_3$ requires 409.1057.

Mixture of diastereomers: pale oil. ^1H NMR (400 MHz, $CDCl_3$): 8.12 (bs, 1H, OH), 7.69 (m, 1,3H, H_{Ar}), 7.63–7.65 (m, 6.1H, H_{Ar}), 7.29–7.46 (m, 11,6H, H_{Ar}), 5.70 (s, 1H, CH, major), 5.50 (s, 0.34H, CH, minor), 5.46 (s, 1H, CH, major), 5.42 (s, 0.34H, CH, minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 174.0, 139,7, 139.3, 137.4, 137.2, 131.9 (4C), 131.1 (q, $J^2_{C\text{-}F} = 32.3$ Hz, 2C, major + minor), 129.25, 129.20, 129.1 (2C), 128.9, 128.8 (3C), 128.5 (4C), 128.2, 127.94 (3C), 127.90, 127.86 (3C), 126.0 (q, $J^3_{C\text{-}F} = 3.5$ Hz, 2C, minor), 125.7 (q, $J^3_{C\text{-}F} = 3.5$ Hz, 2C, major), 124.0 (q, $J^1_{C\text{-}F} = 270.8$ Hz, 2C, major + minor), 122.0, 121.8, 89.8, 89.6, 85.3, 84.9, 77.4, 77.0, 71.9, 71.3 ppm. IR: 3065, 2926, 1728, 1713, 1491, 1325, 1167, 1069, 758 cm^{-1}. Ret. time 13.060 MS (EI, 70 eV) *m/z*: 208 (14%); 207 (79); 192 (18); 191 (100); 190 (7); 189 (17); 165 (5); 129 (8); 105 (7).

4.5.3. 2-(4-bromophenyl)-2-((1,3-diphenylprop-2-yn-1-yl)oxy)-acetic acid (**7d**)

Coloureless oil. ^1H NMR (400 MHz, $CDCl_3$): 8.83 (bs, 0.9H, OH), 7.62–7.64 (m, 2H, H_{Ar}), 7.56–7.58 (m, 1H, H_{Ar}), 7.48–7.51 (m, 2.3H, H_{Ar}), 7.43–7.46 (m, 2.9H, H_{Ar}), 7.31–7.41 (m, 9.8H, H_{Ar}), 5.66 (s, 1H, CH, major), 5.41 (s, 0.23H, CH, minor), 5.38 (s, 0.24H, CH, minor), 5.34 (s, 1H, CH, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 174.3, 137.5, 137.3, 134.8, 134.3, 132.3 (2C), 132.0 (6C), 129.5, 129.2 (2C), 129.14 (2C), 129.05 (2C), 128.9 (2C), 128.8 (2C), 128.52 (3C), 128.49 (2C), 127.93 (2C), 127.88 (2C), 123.6, 123.2, 122.1, 121.9, 89.6, 89.3, 85.5, 85.0, 77.4, 76.9, 71.7, 70.9 ppm. IR: 3030, 2924, 1724, 1489, 1215, 1072, 1013, 756 cm^{-1}. Ret. time 21.125 MS (EI, 70 eV) *m/z*: 208 (7%); 207 (38); 192 (19); 191 (100); 190 (6); 189 (14); 165 (4); 105 (4).

4.5.4. 2-((1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)oxy)-2-phenylacetic acid (**7e**)

Pale oil. ^1H NMR (400 MHz, $CDCl_3$): 8.37 (bs, 1H, OH), 7.42–7.55 (m, 12.5H, H_{Ar}), 7.32–7.39 (m, 7.3H, H_{Ar}), 5.61 (s, 1H, CH, major), 5.46 (s, 0.33H, CH, minor), 5.39 (s, 1H, CH, major), 5.30 (s, 0.38H, CH, minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 174.6, 136.8, 136.7, 135.6, 135.0, 132.1 (2C), 132.0 (2C), 131.9 (2C), 131.8 (2C), 129.7, 129.6 (2C), 129.5 (2C), 129.2, 129.1 (2C), 128.9 (2C), 128.80, 128.76, 128.54 (2C), 128.51 (2C), 128.0 (2C), 127.6 (2C), 123.1, 123.0, 122.0, 121.8, 89.6, 89.4, 85.2, 84.7, 78.2, 77.7, 70.8, 69.8 ppm. IR: 3032, 2924, 1719, 1487, 1069, 1030, 754, 691 cm^{-1}. MS (EI, 70 eV) *m/z*: 287 (30%); 285 (31); 271 (100); 270 (19); 269 (99); 189 (47); 164 (48). HRMS: $[M - H]^-$, found 419.0273, $C_{23}H_{16}BrO_3$ requires 419.0288.

4.5.5. 2-((1-(4-nitrophenyl)-3-phenylprop-2-yn-1-yl)oxy)-2-phenylacetic acid (**7f**)

Pale oil. ^1H NMR (400 MHz, $CDCl_3$): 8.66 (bs, 1H, OH), 8.25 (d, $J = 8.8$ Hz, 2H, H_{Ar}, major), 8.24 (d, $J = 8.8$ Hz, 0.47H, H_{Ar}, minor), 7.86 (d, $J = 8.8$ Hz, 2H, H_{Ar}, major), 7.76 (d, $J = 8.4$ Hz, 0.45H, H_{Ar}, minor), 7.56–7.58 (m, 0.4H, H_{Ar}), 7.45–7.54 (m, 5.3H, H_{Ar}), 7.32–7.41 (m, 7H, H_{Ar}), 5.78 (s, 1H, CH, major), 5.52 (s, 0.23H, CH, minor), 5.50 (s, 1H, CH, major), 5.40 (s, 0.22H, CH, minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 175.1, 148.1 (2C), 144.8, 144.7, 135.4, 134.6, 132.0 (4C), 129.8, 129.42, 129.38, 129.30, 129.26 (2C), 128.9 (2C), 128.6 (6C), 128.4 (2C), 128.0 (2C), 127.5 (2C), 123.94 (2C), 123.85 (2C), 121.6, 121.5, 90.2, 90.1, 84.3, 84.0, 78.4, 78.0, 70.3, 69.0 ppm. IR: 3021, 2926, 1720, 1524, 1491, 1348, 1072, 756 cm^{-1}.

4.5.6. 2-((4,4-dimethyl-1-phenylpent-1-yn-3-yl)oxy)-2-phenylacetic acid (**7g**)

Colourless crystals, mp 136–137°C. ^1H NMR (400 MHz, $CDCl_3$): 9.02 (bs, 1H, OH), 7.53–7.56 (m, 2H, H_{Ar}), 7.46–7.50 (m, 1H, H_{Ar}), 7.30–7.41 (m, 10H, H_{Ar}), 5.44 (s, 1H, CH, major), 5.36 (s, 0.21H, CH, minor), 4.27 (s, 1H, CH, major), 3.89 (s, 0.21H, CH, minor), 1.15 (s, 9H,

t-Bu, major), 1.09 (s, 2H, t-Bu, minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 174.2, 136.6, 135.3, 131.9 (4C), 129.3, 128.9, 128.8, 128.7 (2C), 128.61 (2C), 128.55 (2C), 128.49, 128.40 (2C), 127.9 (2C), 127.2 (2C), 122.7, 122.4, 88.4, 87.9, 86.1, 85.2, 78.5, 78.3, 78.1, 77.3, 36.3, 35.9, 26.1 (6C) ppm. IR: 2972, 2953, 2864, 1721, 1703, 1493, 1315, 1240, 1124, 754, 723, 690 cm^{-1}. Minor: RT 9.935MS (EI, 70 eV) *m*/*z*: 171 (68%); 164 (63); 163 (100); 156 (39); 143 (30); 135 (44); 91 (42). Major: RT 9.895 MS (EI, 70 eV) *m*/*z*: 171 (100%); 164 (70); 163 (89); 156 (55); 143 (39); 135 (35); 91 (41).

*4.5.7. 2-((3-(4-nitrophenyl)-1-phenylprop-2-yn-1-yl)oxy)-2-phenylacetic acid (**7h**)*

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.34 (bs, 1H, OH), 8.14–8.34 (m, 2.6H, H_{Ar}), 7.37–7.61 (m, 16H, H_{Ar}), 5.61 (s, 1H, CH, major), 5.41 (s, 0.25H, CH, minor), 5.36 (s, 0.25H, CH, minor), 5.28 (s, 1H, CH, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 171.6, 147.5 (2C), 136.96, 136.90, 135.4, 134.9, 132.7 (4C), 129.3 (4C), 129.1 (2C), 129.0 (2C), 128.9 (6C), 127.85 (2C), 127.82 (2C), 127.77 (2C), 127.6 (2C), 123.71 (2C), 123.68 (2C),91.3, 90.8, 86.9, 86.6, 78.3, 77.8, 71.1, 70.5 ppm. IR: 3065, 3030, 1721, 1593, 1344, 1107, 1067, 856, 750 cm^{-1}.

*4.5.8. 2-((3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl)oxy)-2-phenylacetic acid (**7i**)*

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.99 (bs, 1H, OH), 7.64–7.66 (m, 2H, H_{Ar}), 7.55–7.59 (m, 1H, H_{Ar}), 7.49–7.51 (m, 2H, H_{Ar}), 7.35–7.44 (m, 10.7H, H_{Ar}), 6.83–6.87 (m, 2.7H, H_{Ar}),5.64 (s, 1H, CH, major), 5.49 (s, 0.24H, CH, minor), 5.39 (s, 1H, CH, major), 5.37 (s, 0.25H, CH, minor) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 174.4, 160.2, 160.1, 137.9, 137.8, 135.8, 135.2, 133.5 (4C), 129.4, 129.1, 129.0, 128.9, 128.85, 128.79 (4C), 128.75, 128.67 (4C), 128.0 (4C), 127.9, 127.6 (4C), 114.3, 114.12, 114.07 (4C), 89.4, 89.0, 84.4, 83.8, 78.1, 77.6, 71.5, 70.7, 55.4 (2C) ppm. IR: 3028, 3018, 1721, 1605, 1510, 1290, 1250, 1217, 756 cm^{-1}. MS (EI, 70 eV) *m*/*z*: 238 (16%); 237 (84); 222 (23); 221 (100); 178 (14); 105 (15); 77 (9).

*4.5.9. 2-((3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)oxy)-2-phenylacetic acid (**7j**)*

Pale oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.61 (bs, 1H, OH), 7.60–7.60 (m, 2H, H_{Ar}), 7.52–7.52 (m, 1.5H, H_{Ar}), 7.47–7.50 (m, 2H, H_{Ar}), 7.35–7.42 (m, 11.6H, H_{Ar}), 7.28–7.30 (m, 2H, H_{Ar}), 5.61 (s, 1H, CH, major), 5.41 (s, 0.34H, CH, minor), 5.36 (s, 0.34H, CH, minor), 5.31 (s, 1H, CH, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 174.5, 137.5, 137.4, 135.6, 135.13, 135.09, 135.0, 133.2 (4C), 129.5, 129.13, 129.11, 129.0, 128.9 (4C), 128.80 (4C), 128.79 (4C), 127.9 (4C), 127.8 (2C), 127.6 (2C), 120.7, 120.6, 88.1, 87.7, 86.9, 86.4, 78.2, 77.7, 71.3, 70.6 ppm. IR: 3032, 2924, 1719, 1489, 1276, 1091, 827, 696 cm^{-1}. MS (EI, 70 eV) *m*/*z*: 243 (9%); 241 (26); 227 (34); 226 (18); 225 (100); 189 (15); 164 (17).

*4.5.10. 2-Phenyl-2-((1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl) oxy)acetic acid (**7k**)*

Colourless crystals, mp 127–129°C. ^{1}H NMR (400 MHz, $CDCl_3$): 9.96 (bs, 1H, OH), 7.57–7.59 (m, 2H, H_{Ar}), 7.49–7.53 (m, 1.5H, H_{Ar}), 7.35–7.47 (m, 10H, H_{Ar}), 5.45 (s, 1H, CH, major), 5.40 (s, 0.34H, CH, minor), 5.32 (s, 1H, CH, major), 5.14 (s, 0.34H, CH, minor), 5.14 (s, 0.34H, CH, minor), 0.23 (s, 3H, CH_3, minor), 0.21 (s, 9H, CH_3, major) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 174.4, 137.4, 137.2, 135.8, 135.1, 129.4, 129.1, 129.01, 128.97, 128.87 (2C), 128.78 (2C), 128.71 (2C), 128.6 (2C), 127.99 (2C), 127.94 (2C), 127.92 (2C), 127.6 (2C), 101.6, 101.0, 95.0, 94.6, 78.0, 77.5, 71.4, 70.5, 0.1 (6C) ppm. IR: 3034, 2959, 1728, 1707, 1252, 1117, 1040, 858, 841, 698 cm^{-1}. MS (EI, 70 eV) *m*/*z*: 221 (8%); 164 (9); 116 (12); 115 (100); 89 (7); 77 (7).

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Appendix A. Supplementary data

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