

One-pot synthesis of 3-hydroxymaleic anhydrides by cyclization of 1,1-bis(trimethylsilyloxy)ketene acetals with oxalyl chloride

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Abstract—Functionalized 3-hydroxymaleic anhydrides were prepared by cyclization of 1,1-bis(trimethylsilyloxy)ketene acetals with oxalyl chloride.

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1. Introduction

Functionalized maleic anhydrides represent important synthetic building blocks,¹ which have been employed, for example, in the synthesis of γ -alkylidenebutenolides,^{2a–c} maleimides,^{2d} 5-alkylidene-5*H*-pyrrol-2-ones,^{2d} numerous carba- and heterocycles (by [4+2], [3+2], and [2+2] cycloaddition reactions),³ functionalized 3-alkanoylacrylic acids and naphthoquinones (by Friedel–Crafts acylations of maleic anhydrides), 4-alkylidenebutane-1,3-diones (by reaction with enolates),^{4a} and various α,β -unsaturated carbonyl compounds (by reaction with nucleophiles).^{4b} Substituted maleic anhydrides are available by Michael reaction of nucleophiles with parent maleic anhydride and subsequent halogenation and elimination,^{4c} or by $\text{TiCl}_4/\text{N}(\text{nBu})_3$ mediated reaction of α -ketoesters with alkanolic acid anhydrides.⁵ The condensation of ethyl propionate with diethyl oxalate and subsequent methylation afforded 2-methoxy-3-methylmaleic anhydride.^{6a} 3-Methoxy-4-arylmaleic anhydrides are available by condensation of arylacetonitriles with diethyl oxalate, methylation and subsequent treatment with acid.^{6b} Notably, whereas 3,4-dihydroxymaleic anhydride,^{6c} 3,4-diacetoxymaleic anhydride,^{6d,e} and 3,4-dimethoxymaleic anhydride^{6f} are known for a long time, methods for the synthesis of unsymmetrical 3-hydroxyanhydrides have only scarcely been reported.

Oxalyl chloride represents an important building block for the synthesis of *O*-heterocycles. For example, 2,3-dihydrofuran-2,3-diones have been prepared by cyclization of silyl

enol ethers⁷ with oxalyl chloride.⁸ The cyclization of 1,3-bis(silyl enol ethers)⁹ with oxalyl chloride provides a convenient access to γ -alkylidenebutenolides.¹⁰ Recently, we reported a new method for the synthesis of 3-hydroxymaleic anhydrides by one-pot cyclization of 1,1-bis(trimethylsilyloxy)ketene acetals with oxalyl chloride.¹¹ Herein, we report full details of these studies. With regard to our preliminary communication,¹¹ we considerably extended the preparative scope.

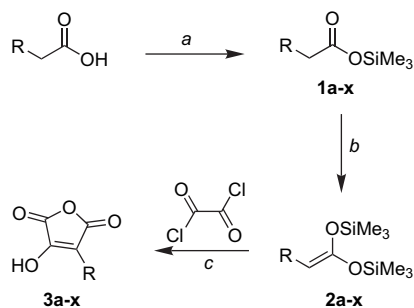
2. Results and discussion

The 1,1-bis(trimethylsilyloxy)ketene acetals **2a–x** were prepared, according to known procedures,¹² in two steps. The reaction of the carboxylic acid with pyridine, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), and trimethylchlorosilane afforded the trimethylsilyl carboxylates **1a–x** (52–92% yield). The latter were deprotonated by lithium-1,1,1,3,3,3-hexamethyldisilazide and subsequently silylated to give the 1,1-bis(trimethylsilyloxy)ketene acetals **2a–x** (47–94% yield). The reaction of **2a–x** with oxalyl chloride, in the presence of trimethylsilyl-trifluoromethanesulfonate (Me_3SiOTf), afforded the 3-hydroxymaleic anhydrides **3a–x** in 20–73% yield (Scheme 1, Table 1). The formation of **3** can be explained by Me_3SiOTf mediated attack of the carbon atom of **2** onto oxalyl chloride and subsequent cyclization via the oxygen atom. The best yields were obtained when the Lewis acid Me_3SiOTf (0.5 equiv) was employed. The yields dropped when the amount of Lewis acid was reduced.

The preparative scope was studied. The cyclization of oxalyl chloride with 1,1-bis(trimethylsilyloxy)ketene acetals **2a–k**, prepared from various alkanolic acids, afforded the alkyl-substituted 3-hydroxymaleic anhydrides **3a–k**. The products were generally isolated in moderate to good yields (except

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Scheme 1. Synthesis of **3a-x**. Reagents and conditions: (a) (1) pyridine (0.5 mL per 10 mmol of **1**, THF (1 mL per 10 mmol of **1**), 0 °C, 30 min; (2) H[N(SiMe₃)₂] (1.0 equiv), Me₃SiCl (0.5 equiv), 0 → 20 °C, 12 h; (b) (1) Li[N(SiMe₃)₂] (1.25 equiv), THF, 15 min, -78 °C; (2) Me₃SiCl (1.5 equiv), -78 → 20 °C, 12 h; (c) Me₃SiOTf (0.5 equiv), CH₂Cl₂, -78 → 20 °C, 12 h, then 20 °C, 3 h.

Table 1. Products and yields

3	R	1 ^a (%)	2 ^a (%)	3 ^a (%)
a	Me	54	62	20
b	Et	66	70	36
c	<i>n</i> -Pr	80	74	42
d	<i>n</i> -Pent	74	75	50
e	<i>n</i> -Oct	78	64	56
f	<i>n</i> -Dodec	89	94	71
g	<i>t</i> -Bu	61	92	17
h	<i>c</i> Hex	80	87	60
i	(<i>c</i> Pent)CH ₂	84	85	62
j	(<i>c</i> Hex)(CH ₂) ₂	89	78	63
k	Ph ₂ CH	91	92	30
l	Ph	92	92	70
m	4-MeC ₆ H ₄	83	87	73
n	4-ClC ₆ H ₄	77	86	65
o	4-FC ₆ H ₄	83	91	53
p	4-MeO(C ₆ H ₄)	78	83	70
q	3,4-(MeO) ₂ (C ₆ H ₃)	85	70	45
r	4-PhC ₆ H ₄	84	88	57
s	Thien-2-yl	96	83	62
t	MeO	53	53	53
u	PhO	72	92	50
v	BnO	69	47	40
w	PhS	84	86	50
x	Allyl	52	82	20

^a Yields of isolated products.

for **3a**, **3g**, and **3k**). The low yield of **3g** and **3k** can be explained by steric hindrance of the *tert*-butyl and the diphenylmethyl groups, respectively. The ketene acetals **2l-r** were prepared from various arylacetic acids. The cyclization of **2l-r** with oxalyl chloride afforded the aryl-substituted 3-hydroxymaleic anhydrides **3l-r** in moderate to good yields. The cyclization of oxalyl chloride with **2s**, prepared from (2-thienyl)acetic acid, gave the thienyl-substituted anhydride **3s**. The methoxy-, phenyloxy-, and benzyloxy-substituted 3-hydroxymaleic anhydrides **3t-v** were prepared from 1,1-bis(trimethylsilyloxy)ketene acetals **1t-v**. The cyclization of oxalyl chloride with silyl ketene acetal **2w**, prepared from (thiophenoxy)acetic acid, afforded the thiophenoxy-substituted maleic anhydride **3w**. Allyl-substituted anhydride **3x** was prepared, albeit in low yield, from silyl ketene acetal **1x** (which is available from pent-4-enoic acid).

Due to the unstable character of silyl esters **1** and silyl ketene acetals **2**, ¹³C NMR and MS spectra could not be obtained

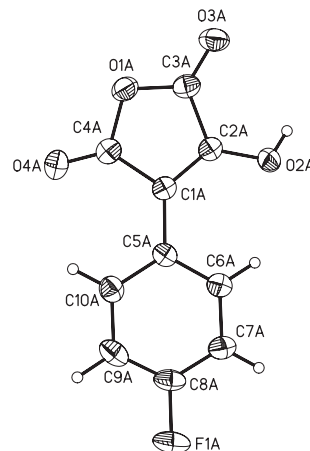


Figure 1. ORTEP plot of **3o**. The thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms.

for all compounds; in addition, elemental analyses could not be obtained. However, the purity and identity was clearly shown for all derivatives by ¹H NMR. The structure of anhydrides **3** was established by spectroscopic methods. The structure of **3o** was independently confirmed by X-ray crystal structure analysis (Fig. 1).¹³

In conclusion, a variety of functionalized 3-hydroxymaleic anhydrides were prepared by cyclization of 1,1-bis(trimethylsilyloxy)ketene acetals with oxalyl chloride.

3. Experimental section

3.1. General

All solvents were dried by standard methods and all reactions were carried out under inert atmosphere. For ¹H and ¹³C NMR spectra (¹H NMR: 300, 600 MHz; ¹³C NMR: 75, 150 MHz), the deuterated solvents indicated were used. Mass spectrometry (MS) data were obtained by using the electron ionization (70 eV), chemical ionization (CI, H₂O), or electrospray (ESI) techniques. For preparative scale chromatography, silica gel (60–200 mesh) was used.

3.2. Typical procedure for the preparation of 2-substituted trimethylsilylacetates (**1a-x**)

3.2.1. Trimethylsilyl propionate (1a). To a stirred solution of propionic acid (5.00 g, 67.56 mmol) in THF (6.7 mL) and pyridine (3.4 mL) at 0 °C was added HMDS (14.0 mL, 67.56 mmol), followed by dropwise addition of Me₃SiCl (4.24 mL, 33.78 mmol). After stirring the solution for 12 h, hexane (10 mL) was added to the mixture and the solution was filtered under argon. The solvent was removed under reduced pressure to give **1a** (5.30 g, 54%) as colorless oil. The spectroscopic data are in accordance with the data provided in the literature.^{12a} ¹H NMR (300 MHz, CDCl₃): δ=2.26 (q, 2H, ³J=7.5 Hz, CH₂), 1.04 (t, 3H, ³J=7.5 Hz, CH₃), 0.22 (s, 9H, SiMe₃).

3.2.2. Trimethylsilyl butyrate (1b). Starting with butyric acid (5.00 g, 56.80 mmol), HMDS (11.8 mL, 56.80 mmol), Me₃SiCl (3.8 mL, 28.40 mmol), THF (5.7 mL), and

pyridine (2.9 mL), **1b** (6.00 g, 66%) was isolated as colorless oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12e} ¹H NMR (300 MHz, CDCl₃): δ=2.22 (t, 2H, ³J=7.5 Hz, CH₂), 1.58–1.53 (m, 2H, CH₂), 0.88 (t, 3H, ³J=7.5 Hz, CH₃), 0.22 (s, 9H, SiMe₃).

3.2.3. Trimethylsilyl pentanoate (1c). Starting with pentanoic acid (5.00 g, 49.00 mmol), HMDS (10.2 mL, 49.00 mmol), Me₃SiCl (3.1 mL, 24.50 mmol), THF (4.9 mL), and pyridine (2.5 mL), **1c** (6.80 g, 80%) was isolated as colorless oil. ¹H NMR (300 MHz, CDCl₃): δ=2.28 (t, 2H, ³J=7.2 Hz, CH₂), 1.61–1.51 (m, 2H, CH₂), 1.36–1.25 (m, 2H, CH₂), 0.89 (t, 3H, ³J=7.5 Hz, CH₃), 0.27 (s, 9H, SiMe₃).

3.2.4. Trimethylsilyl heptanoate (1d). Starting with heptanoic acid (5.00 g, 43.04 mmol), HMDS (9.0 mL, 43.04 mmol), Me₃SiCl (2.7 mL, 21.52 mmol), THF (4.3 mL), and pyridine (2.2 mL), **1d** (6.00 g, 74%) was isolated as colorless oil. ¹H NMR (300 MHz, CDCl₃): δ=2.27 (t, 2H, ³J=7.5 Hz, CH₂), 1.60–1.55 (m, 4H, CH₂), 1.32–1.26 (m, 4H, CH₂), 0.86 (t, 3H, ³J=7.5 Hz, CH₃), 0.27 (s, 9H, SiMe₃).

3.2.5. Trimethylsilyl decanoate (1e). Starting with decanoic acid (5.00 g, 29.02 mmol), HMDS (6.0 mL, 29.02 mmol), Me₃SiCl (1.8 mL, 14.51 mmol), THF (3.0 mL), and pyridine (1.5 mL), **1e** (5.20 g, 78%) was isolated as colorless oil. ¹H NMR (300 MHz, CDCl₃): δ=2.28 (t, 2H, ³J=7.5 Hz, CH₂), 1.58 (t, 2H, ³J=7.5 Hz, CH₂), 1.26 (br s, 12H, CH₂), 0.87 (t, 3H, ³J=7.5 Hz, CH₃), 0.27 (s, 9H, SiMe₃).

3.2.6. Trimethylsilyl tetradecanoate (1f). Starting with tetradecanoic acid (7.00 g, 30.65 mmol), HMDS (6.3 mL, 30.65 mmol), Me₃SiCl (2.0 mL, 15.33 mmol), THF (3.1 mL), and pyridine (1.5 mL), **1f** (8.19 g, 89%) was isolated as yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ=2.23 (t, 2H, ³J=7.6 Hz, CH₂), 1.49–1.56 (m, 2H, CH₂), 1.20 (m, 20H, CH₂), 0.83 (t, 3H, ³J=7.0 Hz, CH₃), 0.22 (s, 9H, SiMe₃).

3.2.7. Trimethylsilyl 3,3-dimethylbutanoate (1g). Starting with 3,3-dimethylbutyric acid (7.30 g, 62.84 mmol), HMDS (13.0 mL, 62.84 mmol), Me₃SiCl (4.0 mL, 31.42 mmol), THF (6.2 mL), and pyridine (3.1 mL), **1g** (7.21 g, 61%) was isolated as yellow oil. The obtained spectroscopic data are in accordance with the data provided by the literature.^{12d} ¹H NMR (250 MHz, CDCl₃): δ=2.03 (s, 2H, CH₂), 0.82 (s, 9H, CH₃), 0.13 (s, 9H, SiMe₃).

3.2.8. Trimethylsilyl 2-(cyclohexyl)acetate (1h). Starting with cyclohexylacetic acid (10.00 g, 70.32 mmol), HMDS (14.6 mL, 70.32 mmol), Me₃SiCl (4.5 mL, 35.16 mmol), THF (7.0 mL), and pyridine (3.5 mL), **1h** (12.06 g, 80%) was isolated as yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ=2.11 (d, 2H, ³J=6.7 Hz, CH₂), 1.63–1.77 (m, 6H, CH/CH₂), 0.83–1.32 (m, 5H, CH₂), 0.22 (s, 9H, SiMe₃).

3.2.9. Trimethylsilyl 3-(cyclopropyl)propionate (1i). Starting with 3-cyclopropylpropionic acid (8.00 g, 56.25 mmol), HMDS (11.6 mL, 56.25 mmol), Me₃SiCl

(3.6 mL, 28.13 mmol), THF (5.6 mL), and pyridine (2.8 mL), **1i** (10.15 g, 84%) was isolated as yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ=2.25 (m, 2H, CH₂), 1.67–1.74 (m, 3H, CH, CH₂), 1.44–1.60 (m, 6H, CH₂), 1.00–1.08 (m, 2H, CH₂), 0.22 (s, 9H, SiMe₃).

3.2.10. Trimethylsilyl 4-(cyclohexyl)butyrate (1j). Starting with 4-cyclohexylbutyric acid (5.00 g, 29.39 mmol), HMDS (6.1 mL, 29.39 mmol), Me₃SiCl (1.9 mL, 14.69 mmol), THF (2.9 mL), and pyridine (1.5 mL), **1j** (6.33 g, 89%) was isolated as yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ=2.21 (t, 2H, ³J=7.3 Hz, CH), 1.51–1.67 (m, 5H, CH, CH₂), 1.09–1.22 (m, 6H, CH₂), 0.80–0.85 (m, 4H, CH₂), 0.22 (s, 9H, SiMe₃).

3.2.11. Trimethylsilyl 3,3-diphenylpropionate (1k). Starting with 3,3-diphenylpropionic acid (7.00 g, 30.93 mmol), HMDS (6.4 mL, 30.93 mmol), Me₃SiCl (2.0 mL, 15.47 mmol), THF (3.1 mL), and pyridine (1.5 mL), **1k** (8.40 g, 91%) was isolated as colorless oil. ¹H NMR (250 MHz, CDCl₃): δ=7.14–7.31 (m, 10H, Ph), 4.49 (t, 1H, ³J=8.0 Hz, CH), 3.05 (d, 2H, ³J=8.0 Hz, CH₂), 0.12 (s, 9H, SiMe₃).

3.2.12. Trimethylsilyl 2-phenylacetate (1l). Starting with phenylacetic acid (5.00 g, 36.72 mmol), HMDS (7.63 mL, 36.72 mmol), Me₃SiCl (2.3 mL, 18.36 mmol), THF (3.6 mL), and pyridine (1.8 mL), **1l** (7.05 g, 92%) was isolated as yellow oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12a} ¹H NMR (300 MHz, CDCl₃): δ=7.17–7.09 (m, 5H, Ph), 3.46 (s, 2H, CH₂), 0.12 (s, 9H, SiMe₃).

3.2.13. Trimethylsilyl 2-(4-tolyl)acetate (1m). Starting with *p*-tolylacetic acid (5.00 g, 33.30 mmol), HMDS (6.9 mL, 33.30 mmol), Me₃SiCl (2.1 mL, 16.65 mmol), THF (3.3 mL), and pyridine (1.7 mL), **1m** (6.15 g, 83%) was isolated as yellow oil. ¹H NMR (300 MHz, CDCl₃): δ=7.33 (d, 2H, ³J=6.7 Hz, Ar), 7.08 (d, 2H, ³J=8.1 Hz, Ar), 3.78 (s, 1H, CH₂), 2.27 (s, 3H, CH₃), 0.29 (s, 9H, SiMe₃).

3.2.14. Trimethylsilyl 2-(4-chlorophenyl)acetate (1n). Starting with (4-chlorophenyl)acetic acid (5.00 g, 29.30 mmol), HMDS (6.1 mL, 29.30 mmol), Me₃SiCl (1.8 mL, 14.65 mmol), THF (3.0 mL), and pyridine (1.5 mL), **1n** (5.50 g, 77%) was isolated as yellow oil. ¹H NMR (300 MHz, CDCl₃): δ=7.25–7.08 (m, 4H, Ar), 3.51 (s, 2H, CH₂), 0.25 (s, 9H, SiMe₃).

3.2.15. Trimethylsilyl 2-(4-fluorophenyl)acetate (1o). Starting with (4-fluorophenyl)acetic acid (6.00 g, 38.93 mmol), HMDS (8.1 mL, 38.93 mmol), Me₃SiCl (2.5 mL, 19.46 mmol), THF (3.9 mL), and pyridine (2.0 mL), **1o** (7.29 g, 83%) was isolated as colorless oil. ¹H NMR (250 MHz, CDCl₃): δ=7.03–7.11 (m, 2H, Ar), 6.80–6.90 (m, 2H, Ar), 3.44 (s, 2H, CH₂), 0.12 (s, 9H, SiMe₃).

3.2.16. Trimethylsilyl 2-(4-methoxyphenyl)acetate (1p). Starting with (4-methoxyphenyl)acetic acid (5.00 g, 30.09 mmol), HMDS (6.3 mL, 30.09 mmol), Me₃SiCl (1.9 mL, 15.04 mmol), THF (3.0 mL), and pyridine

(1.5 mL), **1p** (5.60 g, 78%) was isolated as yellow oil. ¹H NMR (250 MHz, CDCl₃): δ=7.09 (d, 2H, ³J=8.5 Hz, Ar), 6.76 (d, 2H, ³J=8.5 Hz, Ar), 3.70 (s, 3H, OCH₃), 3.46 (s, 2H, CH₂), 0.18 (s, 9H, SiMe₃).

3.2.17. Trimethylsilyl 2-(3,4-dimethoxyphenyl)acetate (1q). Starting with (3,4-dimethoxyphenyl)acetic acid (5.00 g, 25.48 mmol), HMDS (5.3 mL, 25.48 mmol), Me₃SiCl (1.6 mL, 12.74 mmol), THF (2.6 mL), and pyridine (1.3 mL), **1q** (5.80 g, 85%) was isolated as yellow oil. ¹H NMR (300 MHz, CDCl₃): δ=6.80 (br s, 3H, Ar), 3.85 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃), 3.53 (s, 2H, CH₂), 0.25 (s, 9H, SiMe₃).

3.2.18. Trimethylsilyl 2-(4-biphenyl)acetate (1r). Starting with (4-biphenyl)acetic acid (8.00 g, 37.69 mmol), HMDS (7.8 mL, 37.69 mmol), Me₃SiCl (2.4 mL, 18.85 mmol), THF (3.8 mL), and pyridine (1.9 mL), **1r** (8.97 g, 84%) was isolated as yellowish solid (mp 38 °C). ¹H NMR (250 MHz, CDCl₃): δ=7.38–7.45 (m, 4H, Ph/Ar), 7.13–7.30 (m, 5H, Ph/Ar), 3.51 (s, 2H, CH₂), 0.15 (s, 9H, SiMe₃).

3.2.19. Trimethylsilyl 2-(thien-2-yl)acetate (1s). Starting with (thien-2-yl)acetic acid (7.00 g, 49.24 mmol), HMDS (10.1 mL, 49.24 mmol), Me₃SiCl (3.1 mL, 24.62 mmol), THF (4.9 mL), and pyridine (2.5 mL), **1s** (10.13 g, 96%) was isolated as yellow oil. ¹H NMR (250 MHz, CDCl₃): δ=7.13 (dd, 1H, ³J=4.9, 5.2 Hz, H_{et}ar), 6.83–6.90 (m, 2H, H_{et}ar), 3.77 (s, 2H, CH₂), 0.24 (s, 9H, SiMe₃).

3.2.20. Trimethylsilyl 2-methoxyacetate (1t). Starting with methoxyacetic acid (5.00 g, 50.97 mmol), HMDS (10.6 mL, 50.97 mmol), Me₃SiCl (3.2 mL, 25.48 mmol), THF (6.0 mL), and pyridine (3.0 mL), **1t** (4.40 g, 53%) was isolated as colorless oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12b} ¹H NMR (300 MHz, CDCl₃): δ=3.94 (s, 2H, CH₂), 3.40 (s, 3H, OCH₃), 0.27 (s, 9H, SiMe₃).

3.2.21. Trimethylsilyl 2-(phenoxy)acetate (1u). Starting with phenoxyacetic acid (5.00 g, 32.90 mmol), HMDS (6.8 mL, 32.90 mmol), Me₃SiCl (2.1 mL, 16.44 mmol), THF (3.3 mL), and pyridine (1.6 mL), **1u** (5.30 g, 72%) was isolated as yellow oil. ¹H NMR (300 MHz, CDCl₃): δ=7.17–7.09 (m, 5H, Ph), 3.46 (s, 2H, CH₂), 0.12 (s, 9H, SiMe₃).

3.2.22. Trimethylsilyl 2-(benzyloxy)acetate (1v). Starting with (benzyloxy)acetic acid (2.00 g, 11.44 mmol), HMDS (2.4 mL, 11.44 mmol), Me₃SiCl (0.7 mL, 5.72 mmol), THF (1.1 mL), and pyridine (0.6 mL), **1v** (1.88 g, 69%) was isolated as colorless oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12c} ¹H NMR (300 MHz, CDCl₃): δ=7.37–7.25 (m, 5H, Ph), 4.63 (s, 2H, OCH₂), 4.06 (s, 2H, CH₂), 0.31 (s, 9H, SiMe₃).

3.2.23. Trimethylsilyl 2-(thiophenoxy)acetate (1w). Starting with (thiophenoxy)acetic acid (8.00 g, 47.56 mmol), HMDS (9.8 mL, 47.56 mmol), Me₃SiCl (3.0 mL, 23.78 mmol), THF (4.7 mL), and pyridine (2.4 mL), **1w** (9.56 g, 84%) was isolated as yellow oil. The spectroscopic data are in accordance with the data provided in the

literature.^{12f} ¹H NMR (250 MHz, CDCl₃): δ=7.10–7.34 (m, 5H, PhH), 3.55 (s, 2H, CH₂), 0.17 (s, 9H, SiMe₃).

3.2.24. Trimethylsilyl 2-allylacetate (1x). Starting with pent-4-enoic acid (2.00 g, 19.40 mmol), HMDS (4.0 mL, 19.40 mmol), Me₃SiCl (1.2 mL, 9.70 mmol), THF (1.9 mL), and pyridine (1.0 mL), **1x** (1.73 g, 52%) was isolated as colorless oil. ¹H NMR (300 MHz, CDCl₃): δ=5.87–5.78 (m, 1H, CH), 5.08–4.97 (m, 2H, CH₂), 2.44–2.31 (m, 4H, CH₂), 0.28 (s, 9H, SiMe₃).

3.3. Typical procedure for the preparation of 1,1-bis(trimethylsilyloxy)ketene acetals (2a–x)

3.3.1. 2-Methyl-1,1-bis(trimethylsilyloxy)ethene (2a). To a solution of HMDS (7.1 mL, 34.25 mmol) in THF (28.0 mL) was dropwise added *n*-BuLi (13.7 mL, 2.5 M solution in hexane, 34.25 mmol) at 0 °C. After stirring for 30 min at 45 °C, the mixture was cooled to –78 °C, stirred for 20 min at –78 °C and, subsequently, **1a** (4.00 g, 27.40 mmol) was slowly added. The reaction mixture was stirred for 15 min at –78 °C. Subsequently, Me₃SiCl (5.2 mL, 41.10 mmol) was dropwise added to the solution. After holding the solution at –78 °C for additional 15 min, the solution was allowed to warm-up overnight. The solvent was removed under reduced pressure and the filtration of the residue through a sintered glass funnel under argon atmosphere gave **2a** (3.70 g, 62%). The obtained spectroscopic data are in accordance with the data provided in the literature.^{12a} ¹H NMR (300 MHz, CDCl₃): δ=3.51–3.42 (m, 1H, CH), 1.47 (d, 3H, ³J=6.6 Hz, CH₃), 0.20 (s, 18H, SiMe₃).

3.3.2. 2-Ethyl-1,1-bis(trimethylsilyloxy)ethene (2b). Starting with **1b** (5.90 g, 36.87 mmol), HMDS (9.6 mL, 46.08 mmol), *n*-BuLi (18.4 mL, 46.08 mmol), Me₃SiCl (8.7 mL, 55.30 mmol), and THF (37.0 mL), **2b** (6.00 g, 70%) was isolated as colorless oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12g} ¹H NMR (300 MHz, CDCl₃): δ=3.57 (t, 1H, ³J=7.2 Hz, CH), 1.97–1.90 (m, 2H, CH₃), 0.91 (t, 3H, ³J=7.5 Hz, CH₃), 0.20 (s, 18H, SiMe₃).

3.3.3. 2-Propyl-1,1-bis(trimethylsilyloxy)ethene (2c). Starting with **1c** (6.73 g, 38.67 mmol), HMDS (10.1 mL, 48.33 mmol), *n*-BuLi (19.3 mL, 48.33 mmol), Me₃SiCl (6.9 mL, 55.00 mmol), and THF (39.0 mL), **2c** (7.05 g, 74%) was isolated as colorless oil. ¹H NMR (300 MHz, CDCl₃): δ=3.55 (t, 1H, ³J=7.2 Hz, CH), 1.31 (q, 2H, ³J=7.2 Hz, ³J=14.4 Hz, CH₂), 1.34–1.27 (m, 2H, CH₂), 0.88 (t, 3H, ³J=7.3 Hz, CH₃), 0.28 (s, 18H, SiMe₃).

3.3.4. 2-Pentyl-1,1-bis(trimethylsilyloxy)ethene (2d). Starting with **1d** (5.00 g, 24.70 mmol), HMDS (6.4 mL, 30.88 mmol), *n*-BuLi (12.4 mL, 30.88 mmol), Me₃SiCl (4.6 mL, 37.05 mmol), and THF (25.0 mL), **2d** (5.10 g, 75%) was isolated as colorless oil. ¹H NMR (300 MHz, CDCl₃): δ=3.55 (t, 1H, ³J=7.2 Hz, CH), 1.92–1.89 (m, 2H, CH₂), 1.33–1.26 (m, 6H, CH₂), 0.88 (t, 3H, ³J=7.3 Hz, CH₃), 0.28 (s, 18H, SiMe₃).

3.3.5. 2-Octyl-1,1-bis(trimethylsilyloxy)ethene (2e). Starting with **1e** (5.05 g, 22.17 mmol), HMDS (5.8 mL,

27.71 mmol), *n*-BuLi (11.1 mL, 27.71 mmol), Me₃SiCl (4.2 mL, 33.25 mmol), and THF (23.0 mL), **2e** (4.50 g, 64%) was isolated as colorless oil. ¹H NMR (300 MHz, CDCl₃): δ=3.54 (t, 1H, ³J=7.2 Hz, CH), 1.41–1.27 (m, 2H, CH₂), 1.26 (br s, 12H, CH₂), 0.88 (t, 3H, ³J=7.3 Hz, CH₃), 0.20 (s, 9H, SiMe₃), 0.18 (s, 9H, SiMe₃).

3.3.6. 2-Dodecyl-1,1-bis(trimethylsilyloxy)ethene (2f). Starting with **1f** (8.19 g, 27.25 mmol), HMDS (7.0 mL, 34.06 mmol), *n*-BuLi (13.6 mL, 34.06 mmol), and Me₃SiCl (5.2 mL, 40.88 mmol), and THF (27.0 mL), **2f** (9.51 g, 94%) was isolated as yellow oil. ¹H NMR (250 MHz, CDCl₃): δ=3.54 (t, 1H, ³J=7.3 Hz, CH), 1.65–1.95 (m, 2H, CH₂), 1.26 (m, 20H, CH₂), 0.87 (t, 3H, ³J=6.4 Hz, CH₃), 0.18 (s, 9H, SiMe₃), 0.05 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=150.3 (COSi), 83.7 (CH), 32.0, 30.7, 29.8, 29.8, 29.8, 29.6, 29.5, 29.3, 25.0, 22.8 (CH₂), 14.1 (CH₃), 2.7, 0.6 (SiMe₃).

3.3.7. 2-(tert-Butyl)-1,1-bis(trimethylsilyloxy)ethene (2g). Starting with **1g** (7.21 g, 38.28 mmol), HMDS (9.9 mL, 47.85 mmol), *n*-BuLi (19.1 mL, 47.85 mmol), Me₃SiCl (7.3 mL, 57.42 mmol), and THF (38.0 mL), **2g** (9.16 g, 92%) was isolated as colorless oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12a} ¹H NMR (250 MHz, CDCl₃): δ=3.32 (s, 1H, CH), 0.82 (s, 9H, CH₃), 0.17 (s, 9H, SiMe₃), 0.14 (s, 9H, SiMe₃).

3.3.8. 2-Cyclohexyl-1,1-bis(trimethylsilyloxy)ethene (2h). Starting with **1h** (12.07 g, 56.30 mmol), HMDS (14.6 mL, 70.35 mmol), *n*-BuLi (28.1 mL, 70.35 mmol), Me₃SiCl (10.8 mL, 84.40 mmol), and THF (56.0 mL), **2h** (14.07 g, 87%) was isolated as yellow oil. ¹H NMR (250 MHz, CDCl₃): δ=3.42 (d, 2H, ³J=8.8 Hz), 1.97–2.12 (m, 1H, CH), 1.51–1.62 (m, 5H, CH₂), 0.86–1.29 (m, 5H, CH₂), 0.15 (s, 9H, SiMe₃), 0.14 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=149.2 (COSi), 90.8, 34.8 (CH), 34.5, 26.6, 26.5 (CH₂), 0.8, 0.4 (SiMe₃).

3.3.9. 2-(Cyclopentyl)-1,1-bis(trimethylsilyloxy)ethene (2i). Starting with **1i** (10.15 g, 47.35 mmol), HMDS (12.2 mL, 59.18 mmol), *n*-BuLi (23.7 mL, 59.18 mmol), Me₃SiCl (9.1 mL, 71.03 mmol), and THF (47.0 mL), **2i** (11.52 g, 85%) was isolated as yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ=3.51 (t, 1H, ³J=7.0 Hz, CH), 1.83–1.89 (m, 2H, CH₂), 1.41–1.74 (m, 7H, CH, CH₂), 1.04–1.11 (m, 2H, CH₂), 0.16 (s, 9H, SiMe₃), 0.13 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=149.9 (COSi), 82.4, 40.7 (CH), 32.0, 30.7, 24.9 (CH₂), 0.8, 0.4 (SiMe₃).

3.3.10. 2-(Cyclohexylethyl)-1,1-bis(trimethylsilyloxy)ethene (2j). Starting with **1j** (6.33 g, 26.11 mmol), HMDS (6.8 mL, 32.64 mmol), *n*-BuLi (13.1 mL, 32.64 mmol), Me₃SiCl (5.0 mL, 39.16 mmol), and THF (26.0 mL), **2j** (6.42 g, 78%) was isolated as yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ=3.47 (t, 1H, ³J=7.3 Hz, CH), 1.55–1.90 (m, 7H, CH, CH₂), 1.09–1.19 (m, 6H, CH₂), 0.77–0.86 (m, 2H, CH₂), 0.16 (s, 9H, SiMe₃), 0.12 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=150.3 (COSi), 84.0 (CH), 38.6 (CH₂), 37.1 (CH), 33.4, 27.0, 26.9, 22.5 (CH₂), 0.9, 0.4 (SiMe₃). MS (EI, 70 eV): *m/z* (%)=314 ([M]⁺, 5), 299 (11), 271 (19), 217 (100), 204 (12), 147

(61), 73 (72). HRMS (EI): calcd for C₁₆H₃₄O₂Si₂ ([M]⁺) 314.20918, found 314.209123.

3.3.11. 2-Benzhydryl-1,1-bis(trimethylsilyloxy)ethene (2k). Starting with **1k** (8.40 g, 35.53 mmol), HMDS (9.2 mL, 44.41 mmol), *n*-BuLi (17.8 mL, 44.41 mmol), Me₃SiCl (6.8 mL, 53.29 mmol), and THF (36.0 mL), **2k** (12.13 g, 92%) was isolated as colorless oil. ¹H NMR (250 MHz, CDCl₃): δ=7.02–7.11 (m, 10H, Ph), 4.84 (d, 1H, ³J=9.2 Hz, CH), 4.06 (d, 1H, ³J=9.2 Hz, CH), 0.17 (s, 9H, SiMe₃), 0.06 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=151.2 (COSi), 146.7 (C_{Ph}), 128.7, 126.1 (CH_{Ph}), 87.7 (CH), 47.7 (CHPh₂), 0.9, 0.5 (SiMe₃). MS (EI, 70 eV): *m/z* (%)=370 ([M]⁺, 82), 293 (31), 207 (24), 180 (100), 167 (99), 147 (55), 131 (44), 73 (69). HRMS (EI): calcd for C₂₈H₃₀O₂Si₂ ([M]⁺) 370.17788, found 370.177791.

3.3.12. 2-Phenyl-1,1-bis(trimethylsilyloxy)ethene (2l). Starting with **1l** (6.87 g, 32.02 mmol), HMDS (8.6 mL, 41.28 mmol), *n*-BuLi (16.5 mL, 41.28 mmol), Me₃SiCl (6.2 mL, 49.53 mmol), and THF (34.0 mL), **2l** (8.50 g, 92%) was isolated as yellow oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12a} ¹H NMR (300 MHz, CDCl₃): δ=7.35–7.31 (m, 1H, Ph), 7.18–7.12 (m, 2H, Ph), 6.96–6.90 (m, 2H, Ph), 4.55 (s, 1H, CH), 0.24 (s, 18H, SiMe₃).

3.3.13. 2-(*p*-Tolyl)-1,1-bis(trimethylsilyloxy)ethene (2m). Starting with **1m** (6.10 g, 27.43 mmol), HMDS (7.1 mL, 34.28 mmol), *n*-BuLi (13.7 mL, 34.28 mmol), Me₃SiCl (5.2 mL, 41.14 mmol), and THF (27.0 mL), **2m** (7.00 g, 87%) was isolated as yellow oil. ¹H NMR (300 MHz, CDCl₃): δ=7.28 (d, 2H, ³J=8.4 Hz, Ar), 7.02 (d, 2H, ³J=7.8 Hz, Ar), 4.58 (s, 1H, CH₂), 2.27 (s, 3H, CH₃), 0.29 (s, 9H, SiMe₃), 0.25 (s, 9H, SiMe₃).

3.3.14. 2-(4-Chlorophenyl)-1,1-bis(trimethylsilyloxy)ethene (2n). Starting with **1n** (5.00 g, 20.60 mmol), HMDS (5.4 mL, 25.75 mmol), *n*-BuLi (10.3 mL, 25.75 mmol), Me₃SiCl (3.9 mL, 30.90 mmol), and THF (21.0 mL), **2n** (5.60 g, 86%) was isolated as yellow oil. ¹H NMR (300 MHz, CDCl₃): δ=7.25–7.08 (m, 4H, Ar), 4.48 (s, 1H, CH), 0.25 (s, 9H, SiMe₃), 0.24 (s, 9H, SiMe₃).

3.3.15. 2-(4-Fluorophenyl)-1,1-bis(trimethylsilyloxy)ethene (2o). Starting with **1o** (7.29 g, 32.20 mmol), HMDS (8.3 mL, 40.25 mmol), *n*-BuLi (16.1 mL, 40.25 mmol), Me₃SiCl (6.2 mL, 48.30 mmol), and THF (32.0 mL), **2o** (8.79 g, 91%) was isolated as yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ=7.25–7.30 (m, 2H, Ar), 6.81–6.88 (m, 2H, Ar), 4.52 (s, 1H, CH), 0.26 (s, 9H, SiMe₃), 0.12 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=159.2 (d, ¹J_{FC}=242.3 Hz, FC_{Ar}), 151.1 (COSi), 132.8 (C_{Ar}), 126.9 (d, ³J_{FC}=6.8 Hz, CH_{Ar}), 114.2 (d, ²J_{FC}=21.1 Hz, CH_{Ar}), 83.8 (CH), 0.8, 0.4 (SiMe₃). MS (EI, 70 eV): *m/z* (%)=298 ([M]⁺, 27), 197 (23), 147 (35), 136 (100). HRMS (EI): calcd for C₁₄H₂₃FO₂Si₂ ([M]⁺) 298.12151, found 298.121185.

3.3.16. 2-(4-Methoxyphenyl)-1,1-bis(trimethylsilyloxy)ethene (2p). Starting with **1p** (5.50 g, 23.07 mmol), HMDS (6.0 mL, 28.84 mmol), *n*-BuLi (11.5 mL, 28.84 mmol), Me₃SiCl (5.4 mL, 43.26 mmol), and THF (23.0 mL), **2p**

(6.00 g, 83%) was isolated as yellow oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12h} ¹H NMR (300 MHz, CDCl₃): δ=7.26 (d, 2H, ³J=8.8 Hz, Ar), 6.73 (d, 2H, ³J=8.6 Hz, Ar), 4.52 (s, 1H, CH₂), 3.68 (s, 3H, OCH₃), 0.24 (s, 9H, SiMe₃), 0.21 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=158.8 (C_{Ar}), 151.0 (COSi), 130.1 (C_{Ar}), 127.0, 113.8 (CH_{Ar}), 84.8 (CH), 55.3 (OCH₃), 0.7, 0.4 (SiMe₃). MS (EI, 70 eV): *m/z* (%)=310 ([M]⁺, 39), 267 (6), 238 (6), 209 (20), 179 (14), 148 (100), 120 (20). HRMS (EI): calcd for C₁₅H₂₆O₃Si₂ ([M]⁺) 310.14150, found 310.14146.

3.3.17. 2-(3,4-Dimethoxyphenyl)-1,1-bis(trimethylsilyloxy)ethene (2q). Starting with **1q** (5.67 g, 21.15 mmol), HMDS (5.5 mL, 26.44 mmol), *n*-BuLi (10.6 mL, 26.44 mmol), Me₃SiCl (4.0 mL, 31.72 mmol), and THF (21.0 mL), **2q** (5.00 g, 70%) was isolated as yellow oil. ¹H NMR (300 MHz, CDCl₃): δ=7.21–7.15 (m, 1H, Ar), 6.80–6.78 (m, 2H, Ar), 4.57 (s, 1H, CH), 3.88 (s, 3H, OCH₃), 3.85 (s, 3H, OCH₃), 0.29 (s, 18H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=151.1 (COSi), 148.9, 145.5, 130.6 (C_{Ar}), 118.6, 111.3, 109.4 (CH_{Ar}), 84.8 (CH), 56.0, 55.6 (OCH₃), 1.0, 0.4 (SiMe₃).

3.3.18. 2-(4-Biphenyl)-1,1-bis(trimethylsilyloxy)ethene (2r). Starting with **1r** (8.97 g, 31.54 mmol), HMDS (8.2 mL, 39.42 mmol), *n*-BuLi (15.8 mL, 39.42 mmol), Me₃SiCl (6.0 mL, 47.31 mmol), and THF (32.0 mL), **2r** (9.88 g, 88%) was isolated as yellow oil. ¹H NMR (250 MHz, CDCl₃): δ=7.13–7.53 (m, 9H, Ph/Ar), 4.60 (s, 1H, CH), 0.22 (s, 9H, SiMe₃), 0.12 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=151.7 (COSi), 140.7, 136.1, 135.4 (C_{Ar}), 128.7, 127.3, 127.1, 126.6, 126.5 (CH_{Ar}), 84.3 (CH), 0.7, 0.3 (SiMe₃). MS (EI, 70 eV): *m/z* (%)=356 ([M]⁺, 16), 284 (66), 269 (35), 240 (44), 194 (32), 165 (36), 73 (100). HRMS (EI): calcd for C₂₀H₂₈O₂Si₂ ([M]⁺) 356.16223, found 356.162565.

3.3.19. 2-(Thien-2-yl)-1,1-bis(trimethylsilyloxy)ethene (2s). Starting with **1s** (10.55 g, 49.20 mmol), HMDS (12.7 mL, 61.50 mmol), *n*-BuLi (24.6 mL, 61.50 mmol), Me₃SiCl (9.4 mL, 73.80 mmol), and THF (49.0 mL), **2s** (11.37 g, 83%) was isolated as yellow oil. ¹H NMR (250 MHz, CDCl₃): δ=6.97–7.00 (m, 1H, H_{et}ar), 6.89 (dd, 1H, ³J=5.2, 4.9 Hz, H_{et}ar), 6.70–6.73 (m, 1H, H_{et}ar), 4.99 (s, 1H, CH), 0.32 (s, 9H, SiMe₃), 0.18 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=151.2 (COSi), 140.8 (C_{H_{et}ar}), 126.0, 120.7, 120.4 (CH_{H_{et}ar}), 81.2 (CH), 2.5, 0.6 (SiMe₃). MS (EI, 70 eV): *m/z* (%)=286 ([M]⁺, 22), 185 (98), 147 (32), 124 (61), 73 (100). HRMS (EI): calcd for C₁₈H₂₂O₂Si₂ ([M]⁺) 286.08736, found 286.086880.

3.3.20. 2-Methoxy-1,1-bis(trimethylsilyloxy)ethene (2t). Starting with **1t** (4.36 g, 26.91 mmol), HMDS (7.0 mL, 33.64 mmol), *n*-BuLi (13.5 mL, 33.64 mmol), Me₃SiCl (5.1 mL, 40.36 mmol), and THF (27.0 mL), **2t** (4.00 g, 53%) was isolated as colorless oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12g} ¹H NMR (300 MHz, CDCl₃): δ=5.26 (s, 1H, CH), 3.43 (s, 3H, OCH₃), 0.22 (s, 18H, SiMe₃).

3.3.21. 2-Phenoxy-1,1-bis(trimethylsilyloxy)ethene (2u). Starting with **1u** (5.20 g, 23.18 mmol), HMDS (6.0 mL,

28.97 mmol), *n*-BuLi (11.6 mL, 28.97 mmol), Me₃SiCl (5.5 mL, 43.45 mmol), and THF (29.0 mL), **2u** (8.50 g, 92%) was isolated as yellow oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12g} ¹H NMR (300 MHz, CDCl₃): δ=7.35–7.31 (m, 1H, Ph), 7.18–7.12 (m, 2H, Ph), 6.96–6.90 (m, 2H, Ph), 4.55 (s, 1H, CH), 0.24 (s, 18H, SiMe₃).

3.3.22. 2-Benzyloxy-1,1-bis(trimethylsilyloxy)ethene (2v). Starting with **1v** (1.86 g, 7.81 mmol), HMDS (2.0 mL, 9.77 mmol), *n*-BuLi (3.9 mL, 9.77 mmol), Me₃SiCl (1.5 mL, 11.72 mmol), and THF (8.0 mL), **2v** (1.14 g, 47%) was isolated as colorless oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12c} ¹H NMR (300 MHz, CDCl₃): δ=7.38–7.33 (m, 5H, Ph), 5.35 (s, 1H, CH), 4.63 (s, 2H, CH₂), 0.24 (s, 18H, SiMe₃).

3.3.23. 2-Thiophenyl-1,1-bis(trimethylsilyloxy)ethene (2w). Starting with **1w** (9.56 g, 39.76 mmol), HMDS (10.3 mL, 49.70 mmol), *n*-BuLi (19.9 mL, 49.70 mmol), Me₃SiCl (10.8 mL, 59.64 mmol), and THF (39.0 mL), **2w** (10.66 g, 86%) was isolated as yellow oil. The obtained spectroscopic data are in accordance with the data provided in the literature.^{12f} ¹H NMR (250 MHz, CDCl₃): δ=6.94–7.21 (m, 5H, Ph), 4.31 (s, 1H, CH), 0.22 (s, 9H, SiMe₃), 0.19 (s, 9H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ=158.8 (COSi), 140.4 (C_{Ph}), 128.5, 125.5, 124.3 (CH_{Ph}), 70.1 (CH), 0.9, 0.4 (SiMe₃).

3.3.24. 1,1-Bis(trimethylsilyloxy)penta-1,4-diene (2x). Starting with **1x** (1.71 g, 9.94 mmol), HMDS (2.6 mL, 12.42 mmol), *n*-BuLi (4.0 mL, 9.94 mmol), Me₃SiCl (1.9 mL, 14.91 mmol), and THF (10.0 mL), **2x** (2.00 g, 82%) was isolated as colorless oil. The obtained spectroscopic data are in accordance with the data provided in the literature.¹²ⁱ ¹H NMR (300 MHz, CDCl₃): δ=5.83–5.74 (m, 1H, CH), 5.01–4.84 (m, 2H, =CH₂), 3.57 (t, 1H, ³J=7.3 Hz, CH), 2.05 (t, 2H, ³J=2.4 Hz, CH₂), 0.20 (s, 18H, SiMe₃).

3.4. Typical procedure for the preparation of substituted hydroxymaleic anhydrides (3a–x)

3.4.1. 3-Hydroxy-4-methylmaleic anhydride (3a). To a CH₂Cl₂ solution (22.0 mL) of oxalyl chloride (0.252 g, 2.80 mmol) and of **2a** (0.500 g, 2.15 mmol) was added CH₂Cl₂ solution (5 mL) of TMSOTf (0.19 mL, 1.07 mmol) at –78 °C. The temperature of the solution was allowed to rise to 20 °C during 12 h. After stirring for 3 h at 20 °C, an aqueous solution of HCl (10%) was added. The organic and the aqueous layer were separated and the latter was extracted three times with CH₂Cl₂. The combined organic layers were dried (Na₂SO₄), filtered, and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, hexane/EtOAc) to give **3a** (68 mg, 20%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ=1.96 (s, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ=165.7, 163.6 (CO), 152.6 (COH), 111.9 (C), 6.9 (CH₃). IR (neat, cm⁻¹): $\tilde{\nu}$ = 3430 (br), 2959 (m), 1729 (s), 1666 (s), 1614 (m), 1378 (m), 1239 (m), 1090 (m). MS (EI, 70 eV): *m/z* (%)=128 ([M]⁺, 34), 100 (28), 83 (100), 55 (96), 27 (56). Anal. Calcd for C₅H₄O₄ (128.08): C, 46.89; H, 3.15. Found: C, 47.02; H, 3.33.

3.4.2. 3-Ethyl-4-hydroxymaleic anhydride (3b). Starting with **2b** (0.500 g, 2.15 mmol), oxalyl chloride (0.251 g, 2.80 mmol), and TMSOTf (0.19 mL, 1.07 mmol), **3b** (0.100 g, 36%) was isolated as yellow oil. ^1H NMR (300 MHz, CDCl_3): δ =6.78 (s, 1H, OH), 2.40 (q, 2H, 3J =7.5 Hz, CH_2), 1.20 (t, 3H, 3J =7.5 Hz, CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ =165.2, 163.6 (CO), 151.8 (COH), 116.9 (C), 15.6 (CH_2), 11.4 (CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3440 (br), 2979 (w), 1766 (s), 1699 (s), 1398 (m), 1255 (m), 1167 (w), 899 (w). MS (EI, 70 eV): m/z (%)=142 ($[\text{M}]^+$, 25), 113 (14), 97 (100), 70 (58), 55 (24), 41 (37), 28 (36). Anal. Calcd for $\text{C}_6\text{H}_6\text{O}_4$ (142.11): C, 50.71; H, 4.26. Found: C, 50.90; H, 4.39.

3.4.3. 3-Hydroxy-4-propylmaleic anhydride (3c). Starting with **2c** (0.500 g, 2.03 mmol), oxalyl chloride (0.231 g, 2.64 mmol), and TMSOTf (0.18 mL, 1.01 mmol), **3c** (0.132 g, 42%) was isolated as yellow oil. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ =3.59 (t, 2H, 3J =7.2 Hz, CH_2), 2.85 (sext, 2H, 3J =7.8 Hz, CH_2), 2.20 (t, 3H, 3J =7.2 Hz, CH_3). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ =167.4, 164.0 (CO), 155.1 (COH), 115.7 (C), 24.9, 22.0 (CH_2), 14.6 (CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3355 (br), 2935 (w), 2875 (m), 1771 (s), 1701 (s), 1393 (s), 1233 (s), 1167 (s), 909 (s), 750 (w). MS (EI, 70 eV): m/z (%)=156 ($[\text{M}]^+$, 14), 110 (78), 97 (27), 83 (19), 70 (23), 55 (51), 41 (40), 28 (100). Anal. Calcd for $\text{C}_7\text{H}_8\text{O}_4$ (156.14): C, 53.85; H, 5.16. Found: C, 53.35; H, 6.00.

3.4.4. 3-Hydroxy-4-pentylmaleic anhydride (3d). Starting with **2d** (0.500 g, 1.82 mmol), oxalyl chloride (1.180 g, 2.37 mmol), and TMSOTf (0.16 mL, 0.91 mmol), **3d** (0.168 g, 50%) was isolated as colorless oil. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ =11.35 (s, 1H, OH), 2.32 (t, 2H, 3J =7.2 Hz, CH_2), 1.59–1.51 (m, 2H, CH_2), 1.36–1.26 (m, 4H, CH_2), 0.96 (t, 3H, 3J =7.2 Hz, CH_3). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ =167.4, 164.0 (CO), 155.0 (COH), 115.8 (C), 32.7, 28.3, 23.6, 22.9 (CH_2), 14.9 (CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3356 (br), 2923 (s), 1775 (s), 1703 (s), 1394 (s), 1207 (s), 749 (m). MS (EI, 70 eV): m/z (%)=184 ($[\text{M}]^+$, 2), 156 (10), 139 (27), 128 (50), 112 (66), 100 (34), 85 (26), 55 (50), 43 (100), 29 (50). Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}_4$ (184.19): C, 58.69; H, 6.57. Found: C, 58.90; H, 7.02.

3.4.5. 3-Hydroxy-4-octylmaleic anhydride (3e). Starting with **2e** (0.500 g, 1.58 mmol), oxalyl chloride (0.258 g, 2.97 mmol), and TMSOTf (0.21 mL, 1.14 mmol), **3e** (0.200 g, 56%) was isolated as colorless solid; mp 87 °C. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ =11.18 (s, 1H, OH), 2.36 (t, 2H, 3J =7.2 Hz, CH_2), 1.61–1.17 (m, 12H, CH_2), 0.89 (t, 3H, 3J =7.2 Hz, CH_3). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ =166.7, 163.4 (CO), 154.3 (COH), 115.4 (C), 32.5, 29.9, 28.0, 23.3, 22.3 (CH_2), 14.3 (CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3358 (s), 2924 (s), 2854 (m), 1780 (s), 1705 (s), 1397 (s), 903 (m), 750 (m). MS (EI, 70 eV): m/z (%)=226 ($[\text{M}]^+$, 7), 198 (16), 180 (17), 155 (34), 128 (57), 112 (60), 57 (79), 43 (89), 41 (100), 28 (98). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_4$ (226.27): C, 63.70; H, 8.02. Found: C, 63.33; H, 7.85.

3.4.6. 3-Dodecyl-4-hydroxymaleic anhydride (3f). Starting with **2f** (0.932 g, 2.50 mmol), oxalyl chloride (0.413 g,

3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3f** (0.544 g, 71%) was isolated as a colorless solid; mp 98 °C. ^1H NMR (250 MHz, $(\text{CD}_3)_2\text{CO}$): δ =2.40 (t, 2H, 3J =7.3 Hz, CH_2), 1.61 (m, 2H, CH_2), 1.19–1.45 (m, 18H, CH_2), 0.91 (t, 3H, 3J =6.4 Hz, CH_3). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ =166.3, 163.0 (CO), 154.0 (COH), 114.8 (C), 32.2, 30.2, 30.0, 29.9, 29.7, 29.6, 28.9, 28.7, 27.6, 22.9, 21.9 (CH_2), 14.0 (CH_3). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3353 (m), 1849 (m), 1790 (s), 1705 (s), 1275 (m), 1254 (m), 1231 (m). MS (EI, 70 eV): m/z (%)=282 ($[\text{M}]^+$, 9), 254 (40), 209 (17), 155 (25), 113 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_4$ (284.38): C, 68.06; H, 9.28. Found: C, 67.73; H, 9.40.

3.4.7. 3-tert-Butyl-4-hydroxymaleic anhydride (3g). Starting with **2g** (0.651 g, 2.50 mmol), oxalyl chloride (0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3g** (0.070 g, 17%) was isolated as colorless oil. ^1H NMR (250 MHz, $(\text{CD}_3)_2\text{CO}$): δ =1.21 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ =164.2, 162.5 (CO), 151.7 (COH), 118.8 (C), 46.3 (CMe_3), 31.4 (CH_3). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 3353 (br, m), 3057 (br, m), 1845 (m), 1773 (s), 1757 (br, s), 1684 (br, s), 1472 (br, s), 1116 (s). MS (EI, 70 eV): m/z (%)=170 ($[\text{M}]^+$, 1), 127 (100), 109 (59), 97 (73), 39 (58). HRMS (ESI): calcd for $\text{C}_8\text{H}_9\text{O}_4$ ($[\text{M}-\text{H}]^-$) 169.0506, found: 169.0498.

3.4.8. 3-Cyclohexyl-4-hydroxymaleic anhydride (3h). Starting with **2h** (0.716 g, 2.50 mmol), oxalyl chloride (0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3h** (0.292 g, 60%) was isolated as a colorless solid; mp 88 °C. ^1H NMR (250 MHz, $(\text{CD}_3)_2\text{CO}$): δ =2.52–2.64 (m, 1H, CH), 1.68–2.09 (m, 6H, CH_2), 1.25–1.45 (m, 4H, CH_2). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ =166.6, 164.2 (CO), 154.1 (COH), 119.1 (C), 34.9 (CH), 31.0, 27.3, 26.9 (CH_2). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3558 (m), 3451 (m), 2667 (br, s), 1834 (m), 1756 (s), 1687 (s), 934 (m). MS (EI, 70 eV): m/z (%)=196 ($[\text{M}]^+$, 33), 178 (18), 124 (23), 81 (62), 150 (100). HRMS (EI): calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$ ($[\text{M}]^+$) 196.0730, found 196.0729.

3.4.9. 3-(Cyclopentylmethyl)-4-hydroxymaleic anhydride (3i). Starting with **2i** (0.716 g, 2.50 mmol), oxalyl chloride (0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3i** (0.303 g, 62%) was isolated as colorless oil. ^1H NMR (250 MHz, $(\text{CD}_3)_2\text{CO}$): δ =2.37 (d, 2H, 3J =3.8 Hz, CH_2), 2.14–2.24 (m, 1H, CH), 1.45–1.83 (m, 6H, CH_2), 1.19–1.26 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ =166.6, 163.2 (CO), 154.4 (COH), 114.6 (C), 39.2 (CH), 32.7, 27.7, 25.2 (CH_2). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3441 (m), 3351 (s), 2953 (s), 2868 (m), 1844 (s), 1774 (s), 1703 (s), 1443 (m), 1394 (s). MS (EI, 70 eV): m/z (%)=196 ($[\text{M}]^+$, 1), 178 (3), 161 (13), 147 (12), 128 (100), 100 (55). HRMS (ESI): calcd for $\text{C}_{10}\text{H}_{11}\text{O}_4$ ($[\text{M}-\text{H}]^-$) 195.06573, found 195.06702.

3.4.10. 3-(Cyclohexylethyl)-4-hydroxymaleic anhydride (3j). Starting with **2j** (0.787 g, 2.50 mmol), oxalyl chloride (0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3j** (0.354 g, 63%) was isolated as a colorless solid; mp 87 °C. ^1H NMR (250 MHz, $(\text{CD}_3)_2\text{CO}$): δ =2.37 (t, 2H, 3J =7.5 Hz, CH_2), 1.61–1.80 (m, 5H, CH, CH_2), 1.41–1.50 (m, 2H, CH_2), 1.13–1.32 (m, 4H, CH_2), 0.85–0.98 (m, 2H,

(CH₂). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=166.5, 163.3 (CO), 154.4 (COH), 114.6 (C), 37.7 (CH), 35.1, 33.4, 26.9, 26.6, 19.5 (CH₂). IR (KBr, cm⁻¹): ν̄ = 3349 (s), 3261 (m), 2926 (s), 2852 (m), 1839 (m), 1779 (br, s), 1708 (s), 1456 (m), 1391 (s). MS (CI pos.): *m/z* (%)=225 ([M+H]⁺, 100). Anal. Calcd for C₁₂H₁₆O₄ (284.38): C, 64.27; H, 7.19. Found: C, 64.44; H, 9.31.

3.4.11. 3-Benzhydryl-4-hydroxymaleic anhydride (3k). Starting with **2k** (0.927 g, 2.50 mmol), oxalyl chloride (0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3k** (0.212 g, 30%) was isolated as colorless oil. ¹H NMR (250 MHz, (CD₃)₂CO): δ=7.27–7.37 (m, 10H, Ph), 5.43 (s, 1H, CH). ¹³C NMR (62.5 MHz, (CD₃)₂CO): δ=165.9, 163.0 (CO), 155.0 (COH), 140.8 (C_{Ph}), 129.2, 128.8, 127.3 (CH_{Ph}), 114.8 (C), 45.5 (CH). IR (neat, cm⁻¹): ν̄ = 3596 (w), 3062 (m), 3029 (m), 2633 (br, m), 1849 (s), 1763 (s), 909 (s). MS (EI, 70 eV): *m/z* (%)=280 ([M]⁺, 59), 262 (9), 252 (34), 235 (50), 167 (100). HRMS (EI): calcd for C₁₇H₁₂O₄ ([M]⁺) 280.0730, found: 280.0729.

3.4.12. 3-Hydroxyphenylmaleic anhydride (3l). Starting with **2l** (0.500 g, 1.8 mmol), oxalyl chloride (0.20 mL, 2.3 mmol), and TMSOTf (0.16 mL, 0.9 mmol), **3l** (240 mg, 70%) was isolated as a yellow solid; mp 164 °C. ¹H NMR (300 MHz, CDCl₃): δ=7.42–7.50 (m, 3H, Ph), 8.05–8.08 (m, 2H, Ph). ¹³C NMR (75 MHz, CDCl₃): δ=163.5, 163.4 (CO), 149.4 (COH), 130.3, 129.1, 128.8 (CH_{Ph}), 126.9 (C_{Ph}), 112.0 (C). IR (neat, cm⁻¹): ν̄ = 3244 (s), 3123 (w), 1840 (s), 1760 (s), 1673 (s), 1393 (s), 1262 (s), 939 (s), 762 (s). MS (EI, 70 eV): *m/z* (%)=190 ([M]⁺, 43), 162 (100), 145 (22), 118 (27), 105 (15), 89 (81), 77 (8). Anal. Calcd for C₁₀H₆O₄ (190.15): C, 63.16; H, 3.18. Found: C, 62.87; H, 3.63.

3.4.13. 3-Hydroxy-4-(4-tolyl)maleic anhydride (3m). Starting with **2m** (0.501 g, 1.70 mmol), oxalyl chloride (0.192 g, 2.21 mmol), and TMSOTf (0.15 mL, 0.85 mmol), **3m** (0.253 g, 73%) was isolated as brown solid; mp 102 °C. ¹H NMR (300 MHz, (CD₃)₂CO): δ=7.95 (d, 2H, ³J=8.4 Hz, Ar), 7.30 (d, 2H, ³J=8.4 Hz, Ar), 2.29 (s, 3H, CH₃). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=166.0, 163.9 (CO), 153.0 (COH), 140.7 (C_{Ar}), 130.7, 129.6 (CH_{Ar}), 126.8 (C_{Ar}), 111.9 (C), 22.0 (CH₃). IR (KBr, cm⁻¹): ν̄ = 3455 (br), 2925 (w), 1767 (s), 1680 (m), 1387 (s), 1173 (w), 825 (w). MS (EI, 70 eV): *m/z* (%)=204 ([M]⁺, 36), 176 (76), 149 (31), 131 (30), 105 (100), 77 (40), 51 (18), 28 (10). Anal. Calcd for C₁₁H₈O₄ (204.18): C, 64.71; H, 3.95. Found: C, 65.00; H, 4.01.

3.4.14. 4-(4-Chlorophenyl)-3-hydroxymaleic anhydride (3n). Starting with **2n** (0.500 g, 1.60 mmol), oxalyl chloride (1.042 g, 2.0 mmol), and TMSOTf (0.14 mL, 0.80 mmol), **3n** (0.230 g, 65%) was isolated as yellow solid; mp 150 °C. ¹H NMR (300 MHz, (CD₃)₂CO): δ=8.09 (d, 2H, ³J=2.4 Hz, Ar), 7.55 (d, 2H, ³J=7.2 Hz, Ar). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=165.9, 163.6 (CO), 154.2 (COH), 135.9, 135.5 (C_{Ar}), 132.5, 131.2, 130.3, 129.8 (CH_{Ar}), 110.6 (C). IR (KBr, cm⁻¹): ν̄ = 3319 (s), 3100 (w), 1755 (s), 1697 (s), 1388 (s), 1092 (m), 864 (m). MS (EI, 70 eV): *m/z* (%)=224 ([M]⁺, 36), 196 (100), 151 (32), 125 (57), 89 (52), 63 (24), 28 (10). Anal. Calcd for C₁₀H₅ClO₄ (224.60): C, 53.48; H, 2.24. Found: C, 53.29; H, 2.56.

3.4.15. 4-(4-Fluorophenyl)-3-hydroxymaleic anhydride (3o). Starting with **2o** (0.746 g, 2.50 mmol), oxalyl chloride (0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3o** (0.232 g, 45%) was isolated as colorless solid; mp 115 °C. ¹H NMR (500.13 MHz, (CD₃)₂CO): δ=10.9 (br, 1H, OH); 8.12 (m, 2H, ⁴J_{F,H}=5.5 Hz, *o*-Ph), 7.27 (m, 2H, ³J_{F,H}=9.0 Hz, *m*-Ph). ¹³C NMR (125.8 MHz, (CD₃)₂CO): δ=165.3, 160.0 (C-1, C-4), 163.6 (d, ¹J_{F,C}=249.3 Hz, *p*-Ph), 152.6 (d, ⁶J_{F,C}=1.5 Hz, C-2); 131.3 (d, ³J_{F,C}=8.4 Hz, *o*-Ph), 125.4 (d, ⁴J_{F,C}=3.4 Hz, *i*-Ph), 116.4 (d, ²J_{F,C}=22.0 Hz, *m*-Ph); 110.3 (C-3). ¹⁹F NMR (235 MHz): δ=-111.8 (*p*-CF). IR (KBr, cm⁻¹): ν̄ = 3308 (br, s), 1843 (m), 1773 (br, s), 1676 (m), 1606 (m), 1514 (m), 1419 (w), 1392 (br, s). MS (EI, 70 eV): *m/z* (%)=208 ([M]⁺, 34), 180 (100), 163 (12), 135 (45), 107 (89). HRMS (EI): calcd for C₁₀H₅FO₄ ([M]⁺) 208.0166, found: 208.0168.

3.4.16. 3-Hydroxy-4-(4-methoxyphenyl)maleic anhydride (3p). Starting with **2p** (0.500 g, 1.61 mmol), oxalyl chloride (0.180 g, 2.10 mmol), and TMSOTf (0.15 mL, 0.80 mmol), **3p** (0.190 g, 53%) was isolated as yellow solid; mp 115 °C. ¹H NMR (300 MHz, (CD₃)₂CO): δ=8.07–8.02 (m, 2H, Ar), 7.07–7.02 (m, 2H, Ar), 3.85 (s, 3H, OCH₃). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=165.8, 163.6, 161.2 (CO), 151.8 (COH), 131.3, 130.6 (CH_{Ar}), 121.7 (C), 115.0, 114.6 (CH_{Ar}), 111.1 (C), 55.8 (OCH₃). IR (KBr, cm⁻¹): ν̄ = 3484 (br), 2927 (m), 1761 (s), 1604 (s), 1515 (s), 1251 (s), 1028 (m), 836 (m). MS (EI, 70 eV): *m/z* (%)=220 ([M]⁺, 43), 192 (100), 135 (64), 121 (85), 77 (36), 51 (45), 28 (50). Anal. Calcd for C₁₁H₈O₅ (220.18): C, 60.00; H, 3.66. Found: C, 59.95; H, 4.17.

3.4.17. 4-(3,4-Dimethoxyphenyl)-3-hydroxymaleic anhydride (3q). Starting with **2q** (0.500 g, 1.47 mmol), oxalyl chloride (0.161 g, 1.91 mmol), and TMSOTf (0.14 mL, 0.17 mmol), **3q** (0.261 g, 70%) was isolated as yellow solid; mp 214 °C. ¹H NMR (300 MHz, (CD₃)₂CO): δ=7.72–7.68 (m, 2H, Ar), 7.07 (t, 1H, ³J=8.4 Hz, Ar), 3.87 (s, 6H, OCH₃). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=166.2, 163.9 (CO), 151.9 (COH), 151.7, 150.7 (C_{Ar}), 123.4 (CH_{Ar}), 122.8 (C_{Ar}), 113.1, 113.1 (CH_{Ar}), 112.2 (C), 56.7, 56.7 (OCH₃). IR (KBr, cm⁻¹): ν̄ = 3401 (s), 2927 (m), 1765 (s), 1714 (s), 1242 (s), 1022 (s), 915 (m), 822 (m). MS (EI, 70 eV): *m/z* (%)=250 ([M]⁺, 46), 220 (100), 207 (18), 148 (20), 77 (10), 28 (33). Anal. Calcd for C₁₂H₁₀O₆ (250.20): C, 57.60; H, 4.03. Found: C, 58.01; H, 3.72.

3.4.18. 4-(4-Biphenyl)-3-hydroxymaleic anhydride (3r). Starting with **2r** (0.892 g, 2.50 mmol), oxalyl chloride (0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3r** (0.379 g, 57%) was isolated as yellowish solid; mp 180 °C. ¹H NMR (250 MHz, (CD₃)₂CO): δ=8.31 (d, 2H, ³J=8.5 Hz, Ph/Ar), 7.58–7.64 (m, 4H, Ph/Ar), 7.37–7.44 (m, 2H, Ph/Ar), 7.27–7.34 (m, 1H, Ph/Ar). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=177.5, 168.0 (CO), 150.3 (COH), 141.7, 139.4, 131.8 (C), 129.9, 128.2, 127.7, 127.7, 127.4 (CH_{Ar}). IR (Nujol, cm⁻¹): ν̄ = 1810 (br, s), 1733 (br, m), 1620 (br, s), 1300 (br, m), 1240 (m), 1181 (m), 1077 (w). HRMS (ESI): calcd for C₁₆H₉O₄ ([M-H]⁻) 265.0506, found: 265.0622.

3.4.19. 3-Hydroxy-4-(thien-2-yl)maleic anhydride (3s). Starting with **2s** (0.716 g, 2.50 mmol), oxalyl chloride

(0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3s** (0.305 g, 62%) was isolated as yellowish solid; mp 151 °C. ¹H NMR (250 MHz, (CD₃)₂CO): δ=7.88 (dd, 1H, ³J=3.7 Hz, ⁴J=1.2 Hz, H_{et}ar), 7.77 (dd, 1H, ³J=5.2 Hz, ⁴J=1.2 Hz, H_{et}ar), 7.27 (dd, 1H, ³J=5.2 Hz, ³J=3.7 Hz, H_{et}ar). ¹³C NMR (62.5 MHz, (CD₃)₂CO): δ=165.2, 163.4 (CO), 150.3 (COH), 130.4, 130.1 (CH_{H_{et}ar}), 130.0 (C_{H_{et}ar}), 129.0 (CH_{H_{et}ar}), 109.3 (C). IR (Nujol, cm⁻¹): ν̄ = 3182 (br, m), 3109 (m), 1829 (m), 1758 (s), 1676 (m), 1277 (s), 1230 (m). MS (CI pos.): *m/z* (%)=197 ([M+H]⁺, 100). HRMS (CI, neg.): calcd for C₈H₃O₄S ([M-H]⁻) 194.9747, found: 194.9750.

3.4.20. 3-Hydroxy-4-methoxymaleic anhydride (3t). Starting with **2t** (0.500 g, 2.13 mmol), oxalyl chloride (0.252 g, 2.77 mmol), and TMSOTf (0.19 mL, 1.06 mmol), **3t** (0.159 g, 53%) was isolated as yellow oil. ¹H NMR (300 MHz, (CD₃)₂CO): δ=4.10 (s, 3H, OCH₃). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=163.5, 162.4 (CO), 153.3 (COH), 133.6 (C), 60.0 (OCH₃). IR (neat, cm⁻¹): ν̄ = 3436 (br), 2966 (m), 1773 (s), 1714 (s), 1353 (s), 1155 (s), 917 (w). MS (EI, 70 eV): *m/z* (%)=144 ([M]⁺, 3), 118 (6), 89 (7), 73 (14), 59 (23), 45 (100), 29 (77), 28 (21). Anal. Calcd for C₇H₄O₅ (144.08): C, 41.68; H, 2.80. Found: C, 41.80; H, 3.20.

3.4.21. 3-Hydroxy-4-phenoxy-maleic anhydride (3u). Starting with **2u** (0.500 g, 1.69 mmol), oxalyl chloride (0.192 g, 2.19 mmol), and TMSOTf (0.15 mL, 0.84 mmol), **3u** (0.178 g, 50%) was isolated as colorless solid; mp 164 °C. ¹H NMR (300 MHz, (CD₃)₂CO): δ=8.67–8.60 (m, 2H, Ph), 8.49–8.38 (m, 3H, Ph). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=162.6, 162.3 (CO), 157.1 (COH), 143.8, 133.1 (C), 131.3, 125.4, 117.8 (CH_{Ph}). IR (KBr, cm⁻¹): ν̄ = 3220 (br), 2960 (w), 1766 (s), 1721 (s), 1489 (s), 1381 (s), 1198 (s), 930 (s). MS (EI, 70 eV): *m/z* (%)=206 ([M]⁺, 6), 180 (35), 151 (36), 107 (47), 105 (54), 77 (100), 51 (33), 28 (10). Anal. Calcd for C₁₀H₆O₅ (206.15): C, 58.26; H, 2.93. Found: C, 58.00; H, 3.02.

3.4.22. 3-Hydroxy-4-benzyloxymaleic anhydride (3v). Starting with **2v** (0.500 g, 1.61 mmol), oxalyl chloride (1.051 g, 2.10 mmol), and TMSOTf (0.14 mL, 0.80 mmol), **3v** (0.145 g, 40%) was isolated as colorless oil. ¹H NMR (300 MHz, (CD₃)₂CO): δ=7.49–7.34 (m, 5H, Ph), 5.46 (s, 2H, CH₂). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=163.4, 162.6 (CO), 137.6, 136.8 (C), 130.1, 130.0, 129.9, 129.8, 129.7 (CH), 128.0 (C), 74.6 (CH₂). IR (KBr, cm⁻¹): ν̄ = 3428 (br), 3035 (w), 1747 (s), 1208 (m), 743 (m), 699 (m). MS (EI, 70 eV): *m/z* (%)=220 ([M]⁺, 1), 107 (4), 91 (100), 66 (14), 39 (6), 29 (6). Anal. Calcd for C₁₁H₈O₅ (220.18): C, 60.00; H, 3.66. Found: C, 59.69; H, 3.20.

3.4.23. 3-Hydroxy-4-thiophenoxymaleic anhydride (3w). Starting with **2w** (0.782 g, 2.50 mmol), oxalyl chloride (0.413 g, 3.25 mmol), and TMSOTf (0.14 mL, 0.75 mmol), **3w** (0.277 g, 50%) was isolated as yellow oil. ¹H NMR (250 MHz, (CD₃)₂CO): δ=7.06–7.57 (br m, 5H, Ph). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=172.1, 167.8, 167.0, 138.8 (C), 128.9, 126.3, 125.0 (CH_{Ph}). IR (KBr, cm⁻¹): ν̄ = 3419 (br, m), 3058 (m), 1829 (m), 1696 (m), 1618 (s), 1480 (m), 1439 (m), 1402 (m).

HRMS (ESI): calcd for C₁₀H₅O₄ ([M-H]⁻) 220.9914, found: 220.9925.

3.4.24. 3-Allyl-4-hydroxymaleic anhydride (3x). Starting with **2x** (1.900 g, 7.78 mmol), oxalyl chloride (5.061 g, 10.12 mmol), and TMSOTf (0.70 mL, 3.90 mmol), **3x** (0.134 g, 20%) was isolated as yellow oil. ¹H NMR (300 MHz, (CD₃)₂CO): δ=5.82 (q, 1H, ³J=10.2 Hz, CH), 5.17 (d, 2H, ³J_{trans}=17 Hz, ³J_{gem}=2 Hz, 1H, CH), 5.01 (d, 2H, ³J_{cis}=12 Hz, ³J_{gem}=2 Hz, 1H, CH). ¹³C NMR (75 MHz, (CD₃)₂CO): δ=166.4, 163.4 (CO), 155.1 (COH), 133.3 (CH), 117.1 (CH), 112.2 (C), 26.3 (CH₂). IR (KBr, cm⁻¹): ν̄ = 3344 (Br), 2982 (m), 1769 (s), 1673 (m), 1227 (m), 923 (m), 759 (m). MS (EI, 70 eV): *m/z* (%)=154 ([M]⁺, 17), 108 (60), 107 (89), 83 (50), 55 (100), 27 (50). Anal. Calcd for C₇H₆O₄ (154.12): C, 54.55; H, 3.92. Found: C, 54.92; H, 4.01.

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