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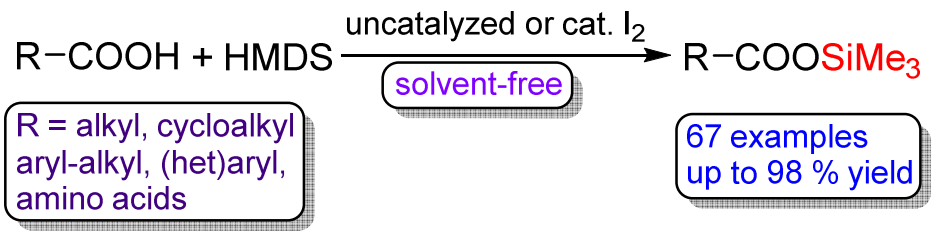
Graphical abstract



Synthesis of trimethylsilyl carboxylates by HMDS under solvent-free conditions

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Dedicated to Professor Emeritus Miha Tišler on the ocassion of his 90th birthday.

A broad set of structurally different carboxylic acids were transformed into their trimethylsilyl esters with HMDS in a practically completely solvent-free process, while a catalytic amount of iodine was required in some cases. The process has several advantages over the known methods: untreated reactants, air atmosphere, mild and neutral conditions, no evolution of hydrogen halide, no need of an additional base, low amount of waste, completely without chromatography, low consumption of energy and operational simplicity.

Keywords: Carboxylic acids, HMDS, trimethylsilyl carboxylates, solvent-free.

1. Introduction

Green and sustainable synthesis has become a necessity, in particular on an industrial scale.[1] Organic solvents represent one of the key factors contributing to the pollution, transformations under solvent-free conditions [2] bring several advantages in terms of cost-efficiency, waste-reduction, operational simplicity and health hazard. Atom economy is another important parameter of reaction effectiveness.[3]

Trimethylsilyl carboxylates (TMSC) are important derivatives in protection group chemistry,[4] and they are valuable as reactants in other transformations.[5] The introduction of the TMS group considerably enhances the volatility of the product, thus making them suitable for GC-MS analysis.[6] One of the key features of TMSC is the ease of the removal of TMS group, thus making this functional group particularly valuable in the presence of other labile functionalities.[7] A temporary TMS-protection of amino and carboxylic group in amino acids, followed by *N*-acylation brings considerable advantages in comparison with the Schotten-Baumann reaction, since the formation of oligomers is prevented.[8] TMS is an important protecting group in the transformation of antibiotics.[9] TMS is a protection of choice in the reduction of amino acids into amino alcohols.[10] Poly(trimethylsilyl esters) are an interesting family of the hydrolytically-degradable polymers with the tunable stabilities.[11]

The introduction of the TMS group into carboxylic acids could be accomplished by various TMS sources *i.e*. TMSCl,[12] allyltrimethylsilane in the presence of various catalysts,[13] hexamethyldisilathiane,[14] *N*,*N*'-bis[trimethylsilyl)urea,[15] trimethylsilyl trichloroacetate,[16] ketene methyl trialkylsilyl acetals,[17] trimethylsilyl enolate of pentane-2,4-dione/Et_3B,[18] *N*-trimethylsilyl-2-oxazolidinone,[19] hexamethyldisiloxane,[20] trimethylsilyl trimethylsilylamidosulfonate,[21] *N*,*O*-bis(trimethylsilyl)acetamide,[22] TMSOTf,[23] $TMSN_3$,[24] TMSCN,[25] trimethylsilyl *N*,*N*-dimethylcarbamate,[26] *N*,*O*-bis(trimethylsilyl)trifluoroacetamide[27] and others.

TMSC could be prepared also by other methods, *i.e*. transesterification of carboxylic esters with TMSI,[28] trimethyl(phenyl)silane/I_2,[29] TMSI/I_2,[30] TMSOTf,[31] by thermal rearrangement of (acyloxymethyl)diorganylsilanes[32] and ozonolysis of silyl diazo compounds.[33] Aldehydes and ketones could be transformed into β-lactones which spontaneously rearrange to α,β-unsaturated esters.[34] TMSC could be obtained by protodesilylation of aryltrimethylsilanes,[35] by thermal decomposition of 2-trimethylsilyl alcohols,[36] and by a reaction of TMSCl with monocarboxylates[37] in the presence of PEG400. An interesting synthesis of TMSC took place as a side reaction in the system cellulose/1-alkyl-3-methyl-imidazolium ionic liquids. The attempted trimethylsilylation of cellulose in the mentioned ionic liquids bearing acetate anion resulted in a formation of trimethylsilyl acetate instead of silylated cellulose.[38]

Hexamethyldisilazane (HMDS) was used for introduction of trimethylsilyl group in molecules with at least one weakly bonded proton, in which both TMS groups could be delivered and ammonia is the only waste product. Functionalization takes place under mild conditions, no halogen is released during the reaction, and no additional base is needed. The main drawback of HMDS is its relatively weak silylating power and, therefore, different catalysts and activators are needed. Several catalysts are metal-based, air and moisture-sensitive, expensive and hazardous. However, there are examples in which HMDS was found to be more reactive under solvent-free conditions (SFC), and reactions of the same substrate took place without a catalyst,[39] whereas a catalyst was required in a solution.[40]

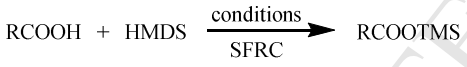
HMDS was utilized in the synthesis of TMSC in solution,[41] and there are isolated examples of its reactivity under SFC.[42] A lack of a systematic study of the reactivity of carboxylic acids with HMDS prompted us to thoroughly examine the reactivity of an extensive set of structurally different carboxylic acids with HMDS under SFC.

2. Results and discussion

Initially, the reactivity of aliphatic carboxylic acids was examined; the results are summarized in Table 1. Octanoic acid **1a** was converted into its TMS ester **2a** with 0.75 equiv. of HMDS in an uncatalyzed reaction. The excess of HMDS was removed, and the product **2a** was distilled under reduced pressure. A catalytic amount (6–9%) of iodine was required in most of the cases, the amount of HMDS also varied from acid to acid depending on the reactivity. Iodine was carefully removed after the reaction by dilution with a small amount of TBME and sodium thiosulfate, and after removal of the insoluble material by filtration; pure products were obtained following vacuum distillation. The selected acyclic, cyclic, tricyclic, dicarboxylic and halogenated aliphatic acids **1b**–**1h** were also converted into their TMSC **2b**–**2h**. Functionalization took place well regardless of the aggregate state of the acid; however, reaction time was dependent on the solubility of acid in HMDS and on the amount of starting acid.

Table 1

Functionalization of aliphatic carboxylic acids **1a**–**1h** into TMSC **2a**–**2h**.[a]



1 **2**

R = (halo)alkyl

Entry	RCOOH	**1**	HMDS (equiv.)	I_2 (mol. %)	t (h)	RCOOTMS	Yield (%)[b]
1	C_7H_{15}-	**1a**	0.75	/	22	**2a**	91
2	C_9H_{19}-	**1b**	1	6	2	**2b**	48
3	*c*-C_6H_{11}-	**1c**	1	/	96	**2c**	95
4	1-adamantyl-	**1d**	1	/	72	**2d**	94
5	-(CH_2)-	**1e**	2	9	64	**2e**	62
6	-$(CH_2)_2$-	**1f**	2	9	63	**2f**	56
7	-$(CH_2)_4$-	**1g**	3.5	9	18	**2g**	71
8	Cl_2CH-	**1h**	1	/	96	**2h**	58

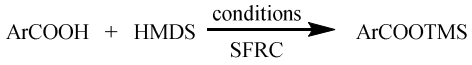
[a] Reaction conditions: **1** (5–30 mmol) and HMDS (5–35 mmol), rt.
[b] Isolated yield.

Most of the tested acids were poorly soluble in HMDS, but one has to bear in mind that no solvent was added to solubilize the acids, and reaction conditions were heterogeneous, and therefore significantly more demanding than homogenous conditions. In several examples, complete homogenization of the reaction mixture was achieved after a certain time of stirring, and this was a good indication of complete conversion, and in such cases, ^{1}H NMR analyses confirmed this. In addition, most of the starting acids were noticeably polar and sparingly soluble in $CDCl_3$, whereas all TMSC were freely soluble in $CDCl_3$, and solubility was another suggestion of full conversion.

We examined the reactivity of aryl-substituted carboxylic acids; the results are summarized in Table 2.

Table 2

Synthesis of aryl-substituted trimethylsilyl esters **4**.[a]



3 **4**

Entry	ArCOOH	**3**	HMDS (equiv.)	I_2 (mol. %)	t (h)	ArCOOTMS **4**	Yield (%)[b]
1	C_6H_5-	**3a**	1	3	18	**4a**	91
2	4-Cl-C_6H_4-	**3b**	2	6	6	**4b**	71
3	3-Cl-C_6H_4-	**3c**	2	3	60	**4c**	75
4	3-OMe-C_6H_4-	**3d**	1	3	1	**4d**	69
5	3-Me-C_6H_4-	**3e**	1	3	0.83	**4e**	70
6	4-F-C_6H_4-	**3f**	1	3	72	**4f**	54
7	2-Cl-4,5-diF-C_6H_2-	**3g**	1	6	96	**4g**	62
8	4-NO_2-C_6H_4-	**3h**	1.5	3	68	**4h**	68
9	2-Br-5-CF_3-C_6H_3-	**3i**	2	3	44	**4i**	56
10	2-I-C_6H_4-	**3j**	1	3	24	**4j**	92
11	2-Me-C_6H_4-	**3k**	1	/	46	**4k**	97
12	4-CH_2Cl-C_6H_4-	**3l**	1	6	96	**4l**	50
13	4-Me-C_6H_4-	**3m**	0.75	3	23	**4m**	89
14	3,4-di-MeO-C_6H_3-	**3n**	1	/	40	**4n**	94
15	2-MeO-C_6H_4-	**3o**	2	3	25	**4o**	61
16	4-MeO-C_6H_4-	**3p**	0.75	3	23	**4p**	74
17	2,4-di-MeO-C_6H_3-	**3q**	2	9	91	**4q**	38
18	2,4,6-tri-Me-C_6H_2-	**3r**	1	/	72	**4r**	90
19	1-Naphthyl-	**3s**	1	/	24	**4s**	92
20	2-Naphthyl-	**3t**	2	10	64	**4t**	85
21	2-COOH-C_6H_4-	**3u**	3	9	52	**4u**	46

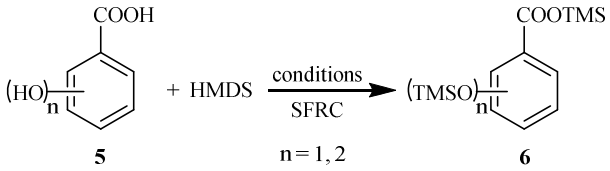
[a] Reaction conditions: **3** (4.65–30 mmol) and HMDS (4.65–30 mmol), rt.
[b] Isolated yield.

All tested acids **3** were poorly soluble solids in HMDS and therefore challenging substrates. We were pleased that acids with both electron-releasing and electron-withdrawing substituents reacted well furnishing TMSC **4a**–**4r**. Moreover, the functionalization was successful in the case of strong electron-donating groups (entries 15–17), and strong electron-withdrawing groups (entries 7–9). We prepared several halogenated products that may be significant in various coupling reactions, in medicinal or pesticide chemistry and useful substrates in nucleophilic substitutions (entries 2, 3, 6, 7, 9, 10 and 12). Sterically hindered 2,4,6-trimethylbenzoic acid **3r** reacted unexpectedly smoothly giving its derivative **4r** in an uncatalyzed reaction (entry 18). Naphthalene derivatives **3s** and **3t** efficiently produced the related **4s** and **4t** analogs in high yields (entries 19 and 20). The neighboring carboxylic groups in phthalic acid **3u** could be protected yielding **4u** despite sterical hindrance (entry 21). In most cases 3–9 mol% of iodine was required; however, some uncatalyzed reactions took place as well (entries 11, 14, 18 and 19). 0.5 equiv. of HMDS per COOH group would be theoretically a sufficient amount of reagent; however, poor solubility of acids led to very long reaction times and reactions were not complete. The lowest excess was 0.75 equiv. per COOH (entries 13 and 16); the less reactive substrates required up to 2 equiv. per COOH (entries 2, 3, 9, 15, 17 and 20).

In continuation, we focused on hydroxy-substituted acids due to the possible additional functionalization of hydroxy groups; the results are presented in Table 3.

Table 3

Functionalization of hydroxy-substituted aryl acids with HMDS.[a]



5 **6**

Entry	ArCOOH	**5**	HMDS (equiv.)	I_2 (mol. %)	t (h)	ArCOOTMS **6**	Yield (%)[b]
1	2-OH-C_6H_4-	**5a**	1.5	/	24	**6a**	89
2	2-OH-5-Cl-C_6H_3-	**5b**	2	3	27	**6b**	80
3	2-OH-5-*t*-Bu-C_6H_3-	**5c**	1	/	27	**6c**	92
4	3-OH-2-naphthyl-	**5d**	2	3	23	**6d**	63
5	4-OH-C_6H_4-	**5e**	2	3	0.67	**6e**	94
6	2,4-di-OH-C_6H_3-	**5f**	2	9	39	**6f**	44
7	2,6-di-OH-C_6H_3-	**5g**	3	9	16	**6g**	76

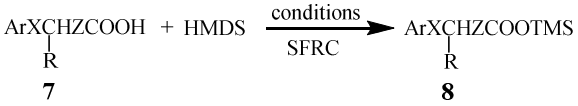
[a] Reaction conditions: **5** (5–10 mmol) and HMDS (7.5–30 mmol), rt.
[b] Isolated yield.

Initially, the reactivity of salicylic acid **5a** was tested. The functionalization of carboxy and hydroxy groups took place completely in 24 hours at room temperature thus yielding the corresponding product **6a** in 89% yield (entry 1). In the literature, **6a** was obtained in 96.5% yield after 24 hours of refluxing of **5a** and HMDS.[31a] Transformation can obviously be accomplished at room temperature at the same time. 5-chlorosalicylic acid **5b** and 5-*tert*-butylsalicylic acid **5c** were effectively converted into the related TMS-substituted products **6b** and **6c** (entries 2 and 3). 3-hydroxy-2-naphthoic acid **5d** smoothly yielded **6d** in a reasonable yield (entry 4). The adjacent position of hydroxy and carboxy groups is obviously not that sterically demanding to prevent functionalization. 4-hydroxybenzoic acid **5e** was surprisingly reactive and gave **6e** in 94% yield (entry 5). Dihydroxybenzoic acids **5f** and **5g** furnished tri-TMS-substituted products **6f** and **6g** in good yields (entries 6 and 7). We were pleased that two adjacent hydroxyl groups in **5g** did not block the functionalization of the carboxy group, and all three sites were functionalized (entry 7).

Next, we focused on variously aryl-alkyl substituted carboxylic acids; the results are presented in Table 4. Neat phenylacetic acid **7a** and its 4-methoxy derivative **7c** yielded the corresponding TMS esters **8a** and **8c** in excellent yields without catalyst (entries 1 and 3). Variously substituted acids **7b** and **7d** also furnished the expected products (entries 2 and 4).

Table 4

Functionalization of various phenyl-substituted acids into TMS derivatives **8**.[a]



7 **8**

X = CH_2, O, S, CO, /
Z = alkyl, CH=CH

Entry	ArCOOH	**7**	HMDS (equiv.)	I_2 (mol. %)	t (h)	ArCOOTMS **8**	Yield (%)[b]
1	$PhCH_2$-	**7a**	1	/	72	**8a**	98
2	4-Cl-C_6H_4-CH_2-	**7b**	1	6	24	**8b**	54
3	4-OMe-C_6H_4-CH_2-	**7c**	1	/	68	**8c**	91
4	3,4-di-OMe-C_6H_3-CH_2-	**7d**	1	3	0.17	**8d**	55
5	2-OH-C_6H_4-CH_2-	**7e**	2	3	8	**8e**	84
6	4-OH-C_6H_4-CH_2-	**7f**	3	9	1	**8f**	61
7	Ph(OH)CH-	**7g**	3	9	3	**8g**	59
8	$PhOCH_2$-	**7h**	3	9	48	**8h**	20
9	$PhSCH_2$-	**7i**	2	9	55	**8i**	82
10	$PhCH_2CH_2$-	**7j**	1	3	6	**8j**	50
11	4-OH-C_6H_4-CH_2CH_2-	**7k**	2	3	20	**8k**	92
12	C_6H_5-CH_2(Br)CH-	**7l**	1	3	21	**8l**	46
13	Ph_2CH-	**7m**	1.5	10	48	**8m**	60
14	Ph_2(Me)C-	**7n**	2	10	25	**8n**	59
15	$PhCOCH_2CH_2$-	**7o**	1	3	1	**8o**	34
16	PhCH=CH-	**7p**	1	3	40	**8p**	82
17	4-OMe-C_6H_4-CH=CH-	**7q**	1	3	68	**8q**	36
18	3,4-di-OMe-C_6H_3-CH=CH-	**7r**	1	/	22	**8r**	91
19	3,4,5-tri-OMe-C_6H_2-CH=CH-	**7s**	5	9	92	**8s**	50

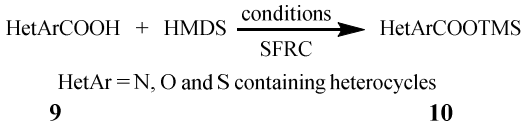
[a] Reaction conditions: **7** (5–10 mmol) and HMDS (5–30 mmol), rt.
[b] Isolated yield.

Hydroxy-substituted phenylacetic acids **7e** and **7f** yielded the related di-TMS-substituted products **8e** and **8f** (entries 5 and 6) as well as (±)-mandelic acid **7g** (entry 7). The functionalization of 2-phenoxyacetic acid **7h** gave product **8h** in low yield (entry 8) while its sulfur analogue **7i** produced **8i** in good yield (entry 9). 3-phenylpropanoic acid **7j** and its derivatives **7k** and **7l** were transformed into the related TMS-substituted derivatives (entries 10–12). Sterically demanding diphenyl-substituted acids **7m** and **7n** were converted in **8m** and **8n** in reasonable yields (entries 13 and 14). 4-oxo-4-phenylbutanoic acid **7o** yielded **8o** in modest yield (entry 15). The excess of HMDS varied from substrate to substrate; in particular, in cases of poorly soluble acids, excess HMDS partly played a role of solvent. Cinnamic acid **7p** and it derivatives **7q**–**7s** were efficiently transformed into the related derivatives **8p**–**8s** (entries 16–19); the best yields were obtained in the cases of **7p** and **7r**. It was demonstrated that various substituents are compatible with the reaction conditions *i.e*. alkyl, thioalkyl, halogen atoms as well as unsaturated functionalities.

We examined the effect of the structure of some heterocyclic carboxylic acids on the reaction with HMDS; the results are summarized in Table 5. In particular, 5-membered aromatics are acid-sensitive, and neutral reaction conditions with HMDS/I_2 may be favorable for their functionalization.

Table 5

Transformation of heteroaryl carboxylic acids **9** into TMS derivatives **10**.[a]



Entry	ArCOOH	**9**	HMDS (equiv.)	I_2 (mol. %)	t (h)	ArCOOTMS **10**	Yield (%)[b]
1	2-thienyl	**9a**	1.5	9	0.25	**10a**	67
2	2-thienylmethyl	**9b**	1	3	0.5	**10b**	53
3	3-thienylmethyl	**9c**	1	/	3	**10c**	88
4	2-furyl	**9d**	2	9	96	**10d**	31
5	3-furyl	**9e**	1	3	42	**10e**	38
6	3-pyridyl	**9f**	2	9	19	**10f**	61

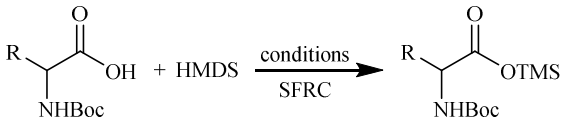
[a] Reaction conditions: **9** (10 mmol) and HMDS (10–20 mmol), rt.
[b] Isolated yield.

Thiophene-2-carboxylic acid **9a** was transformed into its TMS ester **10a** in a short reaction time (entry 1). Thiopheneacetic acids **9b** and **9c** reacted well and both trimethylsilyl acetates **10b** and **10c** were isolated in 53% and 88% yield, respectively (entries 2 and 3). Furyl-substituted acids **9d** and **9e** reacted slowly; conversion was not complete, and both required products **10d** and **10e** were isolated in moderate yield (entries 4 and 5). Nicotinic acid **9f** was converted into its TMS ester **10f** in 61% yield (entry 6). 3-Thiopheneacetic acid **9c** yielded product **10c** in high yield in an uncatalyzed reaction. Functionalization of the other substrates in Table 5 required a catalytic amount of iodine, and products were isolated in moderate yields. The reason for lower yields could be potentially ascribed to the additional complexation of iodine with the heteroatoms.

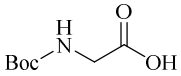
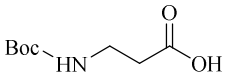
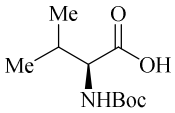
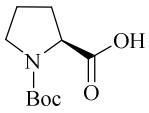
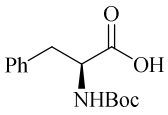
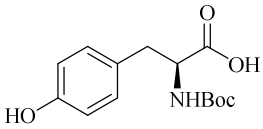
Finally, a reactivity of some Boc-protected amino acids was investigated; the results are presented in Table 6.

Table 6.

Conversion of *N*-Boc protected amino acids **11** into TMS esters **12**.[a]



11 **12**

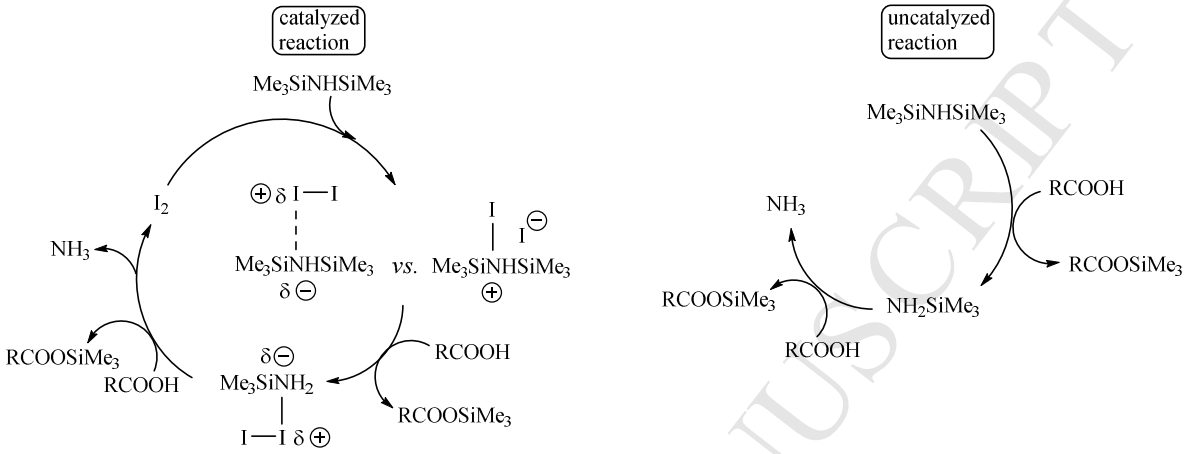
Entry	ArCOOH	**11**	HMDS (equiv.)	I_2 (mol. %)	t (h)	ArCOOTMS **12**	Yield (%)[b]
1		**11a**	1	/	45	**12a**	93
2		**11b**	1	/	24	**12b**	94
3		**11c**	1	/	3	**12c**	88
4		**11d**	1	/	17	**12d**	96
5		**11e**	1	/	24	**12e**	96
6		**11f**	2	3	0.16	**12f**	50

[a] Reaction conditions: **11** (5 mmol) and HMDS (5–10 mmol), rt.
[b] Isolated yield.

With a protected amino group, the starting amino acids **11** are considerably polar and poorly soluble in HMDS and were expected to be challenging substrates, but pleasingly neat Boc-glycine **11a** and Boc-β-alanine **11b** yielded the related TMS derivatives **12a** and **12b** in excellent yields (entries 1 and 2). Optically active Boc-L-valine **11c** reacted smoothly in 3 hours, giving the corresponding **12c** in very good yield (entry 3). Functionalization of Boc-L-proline **11d** led to the TMS-protected derivative **12d** in an excellent yield (entry 4). ^{13}C NMR spectrum of **12d** showed two sets of signals; thus indicating the coexistence of two isomeric forms due to the restricted rotation, since the adjacent Boc and COOTMS groups are sterically very demanding. To our surprise, the selected amino acids **11a**–**11e** reacted without a catalyst despite poor solubility. The initial heterogeneous reaction mixtures became completely homogeneous after a certain period of stirring. Boc-L-phenylalanine **11e** gave the related TMS derivative **12e** in an excellent yield (entry 5). A hydroxy analogue, Boc-L-tyrosine **11f** yielded its di-OTMS product **12f** in the presence of iodine in 50% yield (entry 6).

The mechanism in the case of the iodine-catalyzed reaction is probably similar to the one described by Karimi,[43] whereas the mechanism of the uncatalyzed reaction must be different (Scheme 1). A

plausible explanation could be that RCOOH attacks the silicon atom in HMDS, and TMSNH fragment traps the proton yielding RCOOTMS and $TMSNH_2$. The latter acts as a silylating reagent to some extent, because ammonia is formed as well. Reactions of salicylic acid **5a** and mandelic acid **7g** with HMDS were examined with the Nessler's reagent. In both cases, ammonia was clearly detected over the reaction mixture, and it can be concluded that both TMS groups from HMDS participate in functionalization of carboxylic acid in both catalyzed and uncatalyzed reactions.



Scheme 1. Plausible reaction pathways

The heterogeneous reaction conditions prevent establishing the structure–reactivity relationships that are common in the homogeneous solutions. There is hardly to find any correlation between the structure and reactivity in a series of the benzoic acids. The acidity and nucleophilicity parameters are not likely to be the key factors determining the reactivity of the carboxylic acids in this case. In general, the tested acids are sparingly soluble in HMDS; however, the hydrogen bonding between the carboxylic acids and HMDS might influence the solubility and reactivity of the acids. It appears that solubility of the acids in HMDS is one the main factor governing the reactivity, and consequently there is no obvious correlation between the structure and reactivity.

3. Conclusions

A structurally broad set of carboxylic acids were functionalized with neat HMDS under SFC, many acids reacted without a catalyst, and some of them required a catalytic amount of iodine. Aliphatic mono- and dicarboxylic-, cyclic- and halo-substituted acids were converted into their TMS esters. Numerous aromatic mono- and bicyclic- and several hydroxy-substituted aromatic acids were efficiently converted into their TMS derivatives; functionalization of hydroxy groups took place as well. Different phenyl-alkyl substituted- and heterocyclic carboxylic acids were converted into their TMS analogues. *N*-Boc protected amino acids were effectively transformed into the related TMS esters in uncatalyzed reactions. Despite the generally low solubility of the acids and heterogeneous reaction conditions, the reactions proceeded successfully, and a reasonable excess of HMDS was used. This functionalization is environmentally friendly for several reasons. Reactions were performed practically without any solvents, cost-effectively, completely without chromatography; products were isolated by distillation only. Neutral reaction conditions have several advantages over the alternative conditions where hydrogen halide release requires the use of an additional base. The process is remarkably operationally simpler than the majority of the reported examples, because functionalization is realizable in non-extra-dried glassware and in the presence of air without dry inert gas. Scale-up is feasible; we showed examples with up to 30 mmol of the starting acid. The

transformation is a good example of waste minimization; the excess of HMDS could be reused, and ammonia was practically the only discarded material.

4. Materials and methods

4.1. General information

Reactions were carried out in closed round-bottom flasks with stirring at room temperature without the exclusion of air. Glassware was not extra-dried, although isolated products start to hydrolyze rapidly in air. Most of the carboxylic acids and HMDS were obtained from commercial sources and used as received. All products were characterized by their ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and IR spectra, whereas novel products were characterized with CHN/HRMS analyses as well. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 DPX, Bruker Avance III 400 and Bruker Avance III 500 instruments. The ^{19}F NMR spectra were only recorded on Bruker Avance III 500 instrument. Chemical shifts are reported in δ (ppm) values relative to the TMS (δ = 0.00 ppm) and to the residual $CHCl_3$ (δ = 7.26 ppm) for ^{1}H NMR, and to the central line of $CDCl_3$ (δ = 77.00 ppm) for ^{13}C NMR. ^{19}F NMR spectra are referred to $CFCl_3$ (δ = 0.00 ppm). IR spectra were obtained with a Perkin-Elmer Spectrum 100 instrument. GC-MS spectra were obtained on Hewlett Packard HP 6890 Series (GC System and Mass Selective Detector). Optical rotations were measured with Perkin Elmer 241 MC polarimeter. The melting points were determined in open-capillaries on Büchi 535 apparatus and are uncorrected.

(±)-2-Bromo-3-phenylpropanoic acid **7l** was prepared according to the published procedure.[44] Cinnamic acids **7q**–**7s** were prepared as previously reported.[45]

4.2. Representative procedure of the non-catalyzed functionalization of carboxylic acids with HMDS under SFC

To octanoic acid **1a** (4.32 g, 30 mmol) HMDS (3.63 g, 22.5 mmol) was added, and the mixture was stirred at room temperature until the complete consumption **1a**. The initial heterogeneous reaction mixture became homogeneous, and ^{1}H NMR analysis confirmed full conversion. The excess of HMDS was distilled off under reduced pressure, and distillation of the crude product furnished trimethylsilyl octanoate **2a** (5.91 g, 91%) as a transparent oil. The distilled excess of HMDS could be reused.

4.3. Representative procedure of I_2-catalyzed functionalization of carboxylic acids with HMDS

To a mixture of decanoic acid **1b** (1.72 g, 10 mmol) and HMDS (1.61 g, 10 mmol), iodine (0.15 g, 0.6 mmol) was added, and the mixture was stirred at room temperature until the complete conversion of **1b**. The initial heterogeneous reaction mixture became homogeneous, and ^{1}H NMR analysis confirmed full conversion. A brown reaction mixture was diluted with a few drops of TBME, and anhydrous sodium thiosulfate was added in small portions during stirring at room temperature. After some time of stirring, the reaction mixture decolorized (the color of iodine disappeared). In some cases, the color of iodine persisted for hours, and then small portions of sodium thiosulfate pentahydrate were added. Further stirring reduced iodine, and the brown color disappeared. In a few cases, iodine disappeared during the reaction, and its removal was not needed. The reaction mixture was diluted with a small volume of TBME and filtered. The filtrate was concentrated under reduced pressure, and the thus-obtained reaction mixture was subjected to a vacuum distillation. After removal of excess of HMDS, the distillation of crude product gave trimethylsilyl decanoate **2b** (1.18 g, 48%) as a slightly yellow oil. The distilled excess of HMDS could be reused.

Trimethylsilyl octanoate **2a**

1a (4.32 g, 30 mmol), HMDS (3.63 g, 22.5 mmol); transparent oil, (5.91 g, 91%); IR (neat) 2927, 2857, 1708, 1413, 1252, 1053, 935, 843, 756 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.28 (t, J = 7.4 Hz, 2H), 1.62–1.51 (m, 2H), 1.35–1.19 (m, 8H), 0.87 (t, J = 6.9 Hz, 3H), 0.26 (s, 9H); δ_C (125 MHz, $CDCl_3$)

174.5, 35.9, 31.7, 29.0, 29.0, 25.0, 22.6, 14.0, −0.3; *m/z* (EI) 216 (<1 M^+), 201 (22), 117 (40), 99 (<1), 75 (100), 73 (89%); HRMS (EI): $[M-Me]^+$, found 201.1310. $[C_{10}H_{21}O_2Si]^+$ requires 201.1306.

Trimethylsilyl decanoate[5g] **2b**

1b (1.72 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.15 g, 0.6 mmol); slightly yellow oil, (1.18 g, 48%); IR (neat) 2924, 2855, 1718, 1367, 1252, 1180, 847, 762, 729 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.27 (t, J = 7.5 Hz, 2H), 1.65–1.50 (m, 2H), 1.33–1.21 (m, 12H), 0.90–0.83 (m, 3H), 0.26 (s, 9H); δ_C (75 MHz, $CDCl_3$) 174.4, 35.9, 31.8, 29.4, 29.3, 29.2, 29.1, 25.0, 22.6, 14.0, −0.3.

Trimethylsilyl cyclohexanecarboxylate[46] **2c**

1c (0.64 g, 5 mmol), HMDS (0.81 g, 5 mmol); transparent oil, (0.95 g, 95%); IR (neat) 2931, 2856, 1713, 1450, 1312, 1249, 1195, 1176, 1135, 939, 847, 763, 732 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.30–2.18 (m, 1H), 1.95–1.84 (m, 2H), 1.79–1.57 (m, 3H), 1.48–1.20 (m, 5H), 0.27 (s, 9H); δ_C (75 MHz, $CDCl_3$) 176.8, 44.4, 29.0, 25.8, 25.4, −0.2.

Trimethylsilyl adamantane-1-carboxylate[47] **2d**

1d (0.90 g, 5 mmol), HMDS (0.81 g, 5 mmol); white crystalline product, (1.18 g, 94%), m.p. 31.1–31.6 ºC; IR (neat) 2906, 2851, 1703, 1327, 1272, 1246, 1076, 909, 844, 765, 730 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.03–1.98 (m, 3H), 1.87–1.84 (m, 6H), 1.75–1.65 (m, 6H), 0.26 (s, 9H); δ_C (125 MHz, $CDCl_3$) 178.6, 41.4, 38.8, 36.5, 28.0, −0.3.

Bis(trimethylsilyl)malonate[48] **2e**

1e (1.04 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (1.54 g, 62%); IR (neat) 2962, 1715, 1411, 1335, 1282, 1252, 1195, 1156, 951, 838, 761, 714 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 3.31 (s, 2H), 0.27 (s, 18 H); δ_C (125 MHz, $CDCl_3$) 166.9, 44.8, −0.5.

Bis(trimethylsilyl)succinate[49] **2f**

1f (1.18 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.23 g, 0.9 mmol); slightly yellow crystalline solid, (1.47 g, 56%), m.p. 50.4–50.7 ºC; IR (neat) 2964, 1701, 1421, 1329, 1248, 1175, 1160, 936, 836, 800, 762, 734, 702 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.58 (s, 4H), 0.27 (s, 18H); δ_C (125 MHz, $CDCl_3$) 172.9, 30.9, −0.3.

Bis(trimethylsilyl)adipate[50] **2g**

1g (1.46 g, 10 mmol), HMDS (5.65 g, 35 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (2.07 g, 71%); IR (neat) 2958, 1714, 1368, 1252, 1181, 1147, 919, 846, 763, 730 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.35–2.25 (m, 4H), 1.65–1.55 (m, 4H), 0.25 (s, 18H); δ_C (75 MHz, $CDCl_3$) 173.9, 35.5, 24.4, −0.3.

Trimethylsilyl 2,2-dichloroacetate[51] **2h**

1h (1.29 g, 10 mmol), HMDS (1.61 g, 10 mmol); transparent oil, (1.16 g, 58%); IR (neat) 2960, 1747, 1728, 1300, 1255, 1180, 1053, 952, 843, 821, 762, 725, 680 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.88 (s, 1H), 0.36 (s, 9H); δ_C (75 MHz, $CDCl_3$) 163.8, 65.5, −0.7.

Trimethylsilyl benzoate[51] **4a**

3a (3.66 g, 30 mmol), HMDS (4.84 g, 30 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (5.32 g, 91%); IR (neat) 2961, 1698, 1452, 1314, 1284, 1252, 1175, 1115, 1069, 1026, 844, 760, 734, 707, 619 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.00–7.95 (m, 2H), 7.50–7.45 (m, 1H), 7.39–7.32 (m, 2H), 0.33 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.7, 132.9, 131.3, 130.1, 128.2, −0.2.

Trimethylsilyl 4-chlorobenzoate **4b**

3b (1.56 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.15 g, 0.6 mmol); yellow oil, (1.63 g, 71%); IR (neat) 2961, 1698, 1592, 1487, 1401, 1290, 1280, 1253, 1170, 1116, 1103, 1090, 1015, 846, 830, 768, 733, 682 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.98–7.94 (m, 2H), 7.41–7.37 (m, 2H), 0.39 (s, 9H); δ_C (125 MHz, $CDCl_3$) 165.8, 139.3, 131.5, 129.8, 128.5, −0.2; *m/z* (EI) 228 (4 M^+), 213 (66), 169 (63), 139 (100), 111 (67), 75 (50%); HRMS (EI): $[M-Me]^+$, found 213.0129. $[C_9H_{10}ClO_2Si]^+$ requires 213.0134.

Trimethylsilyl 3-chlorobenzoate **4c**

3c (1.56 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.075 g, 0.3 mmol); yellow crystalline solid, (1.72 g, 75%), m.p. 29.0–29.2 ºC; IR (neat) 2961, 1697, 1573, 1476, 1415, 1296, 1253, 1134, 1071, 883, 843, 764, 745, 717, 666 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.01–7.98 (m, 1H), 7.94–7.90 (m, 1H), 7.53–7.49 (m, 1H), 7.39–7.34 (m, 1H), 0.40 (s, 9H); δ_C (125 MHz, $CDCl_3$) 165.4, 134.3, 133.1, 132.9, 130.1, 129.5, 128.2, −0.2; *m/z* (EI) 228 (8 M^+), 213 (97), 169 (67), 139 (100), 111 (75), 75 (50%); HRMS (EI): M^+, found 228.0363. $[C_{10}H_{13}ClO_2Si]^+$ requires 228.0368.

Trimethylsilyl 3-methoxybenzoate **4d**

3d (1.52 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (1.55 g, 69%); IR (neat) 2959, 1697, 1586, 1487, 1454, 1431, 1291, 1253, 1224, 1182, 1100, 1080, 1042, 919, 906, 845, 790, 765, 734, 682 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.66–7.61 (m, 1H), 7.58–7.54 (m, 1H), 7.36–7.31 (m, 1H), 7.12–7.07 (m, 1H), 3.85 (s, 3H), 0.40 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.6, 159.5, 132.7, 129.2, 122.5, 119.4, 114.5, 55.4, −0.2; *m/z* (EI) 224 (18 M^+), 209 (68), 165 (63), 135 (100), 107 (31%); HRMS (EI): M^+, found 224.0873. $[C_{11}H_{16}O_3Si]^+$ requires 224.0864.

Trimethylsilyl 3-methylbenzoate **4e**

3e (1.36 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (1.45 g, 70%); IR (neat) 2960, 1697, 1590, 1426, 1296, 1284, 1253, 1204, 1108, 1082, 910, 847, 791, 763, 744, 682, 667 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.88–7.82 (m, 2H), 7.39–7.34 (m, 1H), 7.34–7.29 (m, 1H), 2.40 (s, 3H), 0.40 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.9, 138.0, 133.7, 131.2, 130.6, 128.1, 127.3, 21.2, −0.2; *m/z* (EI) 208 (13 M^+), 193 (84), 149 (65), 119 (100), 91 (68%); HRMS (EI): M^+, found 208.0919. $[C_{11}H_{16}O_2Si]^+$ requires 208.0914.

Trimethylsilyl 4-fluorobenzoate **4f**

3f (1.40 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (1.14 g, 54%); IR (neat) 2962, 1698, 1601, 1507, 1287, 1253, 1152, 1117, 1089, 872, 841, 774, 733, 685 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.04–7.94 (m, 2H), 7.06–6.98 (m, 2H), 0.36 (s, 9H); δ_C (125 MHz, $CDCl_3$) 165.6 (d, J = 253.6 Hz), 165.5, 132.5 (d, J = 9.3 Hz), 127.5 (d, J = 2.6 Hz), 115.2 (d, J = 22.0 Hz), −0.4; δ_F (470 MHz, $CDCl_3$) −106.4–(−106.3) (m, 1F); *m/z* (EI) 212 (3 M^+), 197 (68), 153 (70), 123 (100), 95 (73%); HRMS (EI): M^+, found 212.0670. $[C_{10}H_{13}FO_2Si]^+$ requires 212.0664.

Trimethylsilyl 2-chloro-4,5-difluorobenzoate **4g**

3g (1.93 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.15 g, 0.6 mmol); red oil, (1.65 g, 62%); IR (neat) 2963, 1719, 1698, 1595, 1503, 1399, 1307, 1252, 1220, 1178, 1108, 847, 785, 734 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.73 (dd, J = 10.5 Hz, J = 8.5 Hz, 1H), 7.22 (dd, J = 9.8 Hz, J = 6.9 Hz, 1H), 0.35 (s, 9H); δ_C (125 MHz, $CDCl_3$) 163.1, 151.9 (dd, J = 258.6 Hz, J = 13.6 Hz), 148.4 (dd, J = 250.5 Hz, J = 12.6 Hz), 130.4 (dd, J = 8.4 Hz, J = 3.6 Hz), 127.0 (t, J = 4.2 Hz,), 121.1 (dd, J = 19.8 Hz, J = 1.3 Hz), 120.3 (d, J = 20.3 Hz), −0.3; δ_F (470 MHz, $CDCl_3$) −138.7–(−138.6) (m, 1F), −129.6–(−129.5) (m, 1F); *m/z* (EI) 264 (3 M^+), 249 (57), 175 (100), 147 (63), 73 (18%); HRMS (EI): $[M-Me]^+$, found 248.9952. $[C_9H_8ClF_2O_2Si]^+$ requires 248.9945.

Trimethylsilyl 4-nitrobenzoate **4h**

3h (1.67 g, 10 mmol), HMDS (2.42 g, 15 mmol), I_2 (0.075 g, 0.3 mmol); yellow solid, (1.63 g, 68%), m.p. 105.9–106.6 ºC; [Found: C, 50.06; H 5.27; N 5.99. $C_{10}H_{13}NO_4Si$ requires C, 50.19; H 5.48; N 5.85]; IR (neat) 2962, 1689, 1605, 1521, 1425, 1347, 1310, 1278, 1248, 1101, 1011, 930, 876, 850, 821, 801, 789, 714 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.30–8.24 (m, 2H), 8.22–8.16 (m, 2H), 0.42 (s, 9H); δ_C (125 MHz, $CDCl_3$) 164.7, 150.5, 136.8, 131.2, 123.4, −0.3.

Trimethylsilyl 2-bromo-5-(trifluoromethyl)benzoate **4i**

3i (1.34 g, 5 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.04 g, 0.15 mmol); orange oil, (0.96 g, 56%). IR (neat) 2960, 1717, 1608, 1337, 1291, 1251, 1172, 1128, 1081, 1030, 844, 787, 735, 699 cm^{-1}: δ_H (500 MHz, $CDCl_3$) 8.10 (d, *J* = 1.6 Hz,1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.53 (dd, *J* = 8.3 Hz, *J* = 1.6 Hz, 1H), 0.43 (s, 9H); δ_C (125 MHz, $CDCl_3$) 164.6, 135.2, 133.8, 129.8 (q, *J* = 33.6 Hz), 128.7 (m), 126.0 (m), 123.3 (q, *J* = 274.4 Hz), −0.3; δ_F (470 MHz, $CDCl_3$) −63.4 (s); *m/z* (EI) 340 (<1 M^+), 325 (36), 281 (14), 251 (57), 223 (33), 144 (100), 75 (70), 73 (57%); HRMS (EI): M^+, found 339.9747. $[C_{11}H_{12}BrF_3O_2Si]^+$ requires 339.9737.

Trimethylsilyl 2-iodobenzoate[52] **4j**

3j (2.48 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (2.93 g, 92%); IR (neat) 2958, 1705, 1583, 1428, 1298, 1253, 1136, 1105, 1043, 1015, 850, 762, 741 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.97 (dd, *J* = 7.7 Hz, *J* = 1.1 Hz, 1H), 7.86 (dd, *J* = 7.7 Hz, *J* = 1.7 Hz, 1H), 7.36 (ddd, *J* = 7.7 Hz, *J* = 7.7 Hz, *J* = 1.1 Hz, 1H), 7.10 (ddd, *J* = 7.7 Hz, *J* = 7.7 Hz, *J* = 1.7 Hz, 1H), 0.41 (s, 9H); δ_C (75 MHz, $CDCl_3$) 166.0, 141.3, 135.7, 132.5, 131.5, 127.7, 94.3, −0.2.

Trimethylsilyl 2-methylbenzoate[53] **4k**

3k (1.36 g, 10 mmol), HMDS (1.61 g, 10 mmol); transparent oil, (2.01 g, 97%); IR (neat) 2962, 1697, 1301, 1252, 1145, 1134, 1079, 873, 836, 760, 734, 692, 661 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.05–7.97 (m, 1H), 7.46 –7.37 (m, 1H), 7.32–7.21 (m, 2H), 2.66 (s, 3H), 0.44 (s, 9H); δ_C (75 MHz, $CDCl_3$) 167.5, 140.7, 132.0, 131.7, 131.3, 130.5, 125.6, 22.0, −0.2.

Trimethylsilyl 4-(chloromethyl)benzoate **4l**

3l (1.71 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.15 g, 0.6 mmol); slightly yellow oil, (1.22 g, 50%); IR (neat) 2961, 1696, 1414, 1310, 1287, 1252, 1177, 1118, 1105, 1019, 839, 798, 709 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.06–7.99 (m, 2H), 7.48–7.41 (m, 2H), 4.61 (s, 2H), 0.40 (s, 9H); δ_C (75 MHz, $CDCl_3$) 166.2, 142.2, 131.4, 130.5, 128.4, 45.4, −0.2; *m/z* (EI) 242 (6 M^+), 227 (100), 183 (55), 153 (98), 125 (35), 89 (60), 73 (20%); HRMS (EI): M^+, found 242.0527. $[C_{11}H_{15}ClO_2Si]^+$ requires 242.0525.

Trimethylsilyl 4-methylbenzoate **4m**

3m (4.08 g, 30 mmol), HMDS (3.63 g, 22.5 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (5.56 g, 89%); IR (neat) 2959, 1696, 1611, 1408, 1284, 1252, 1176, 1109, 1052, 1020, 835, 764, 733, 688 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.96–7.91 (m, 2H), 7.25–7.19 (m, 2H), 2.41 (s, 3H), 0.40 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.8, 143.5, 130.1, 128.9, 128.6, 21.6, −0.2; *m/z* (EI) 208 (10 M^+), 193 (51), 149 (61), 119 (100), 91 (64%); HRMS (EI): M^+, found 208.0912. $[C_{11}H_{16}O_2Si]^+$ requires 208.0914.

Trimethylsilyl 3,4-dimethoxybenzoate[54] **4n**

3n (1.82 g, 10 mmol), HMDS (1.61 g, 10 mmol); transparent, viscous oil, (2.39 g, 94%); IR (neat) 2958, 1687, 1598, 1512, 1463, 1416, 1344, 1296, 1267, 1252, 1223, 1176, 1132, 1107, 1024, 930, 846, 795, 770, 735 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.66 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1H), 7.53 (d, *J* = 1.5 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 0.38 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.6, 152.9, 148.5, 124.2, 123.8, 112.3, 110.0, 55.9, 55.8, −0.2.

Trimethylsilyl 2-methoxybenzoate[55] **4o**

3o (1.52 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (1.37 g, 61%); IR (neat) 2960, 1704, 1600, 1489, 1464, 1437, 1313, 1245, 1134, 1078, 1048, 1024, 872, 831, 752, 698, 655 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.87–7.81 (m, 1H), 7.44–7.36 (m, 1H), 6.94–6.86 (m, 2H), 3.84 (s, 3H), 0.35 (s, 9H); δ_C (75 MHz, $CDCl_3$) 165.4, 159.9, 133.6, 132.4, 120.3, 119.7, 111.9, 55.7, −0.3.

Trimethylsilyl 4-methoxybenzoate[56] **4p**

3p (4.56 g, 30 mmol), HMDS (3.63 g, 22.5 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (4.95 g, 74%); IR (neat) 2959, 1690, 1605, 1510, 1287, 1250, 1165, 1118, 1101, 1030, 840, 776, 756, 734, 692 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.00–7.93 (m, 2H), 6.90–6.83 (m, 2H), 3.79 (s, 3H), 0.37 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.3, 163.2, 132.0, 123.6, 113.3, 55.1, −0.3.

Trimethylsilyl 2,4-dimethoxybenzoate **4q**

3q (1.82 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (0.96 g, 38%); IR (neat): 2959, 1698, 1674, 1605, 1574, 1504, 1461, 1439, 1416, 1248, 1210, 1162, 1136, 1082, 1029, 845, 740, 694 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.92–7.87 (m, 1H), 6.46–6.41 (m, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 0.34 (s, 9H); δ_C (125 MHz, $CDCl_3$) 164.9, 164.4, 162.2, 134.8, 112.5, 104.2, 98.7, 55.7, 55.3, −0.2; *m/z* (EI) 254 (7 M^+), 239 (12), 165 (100), 73 (9%); HRMS (EI): M^+, found 254.0976. $[C_{12}H_{18}O_4Si]^+$ requires 254.0969.

Trimethylsilyl 2,4,6-trimethylbenzoate **4r**

3r (0.76 g, 4.65 mmol), HMDS (0.75 g, 4.65 mmol); transparent oil, (0.99 g, 90%); IR (neat) 2959, 1703, 1612, 1428, 1275, 1253, 1171, 1086, 845, 743, 699 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.86 (s, 2H), 2.35 (s, 6H), 2.29 (s, 3H), 0.42 (s, 9H); δ_C (125 MHz, $CDCl_3$) 170.1, 138.9, 134.8, 132.2, 128.4, 21.1, 19.9, −0.2; *m/z* (EI) 236 (11 M^+), 221 (24), 147 (100), 119 (18), 91 (20), 73 (14%); HRMS (EI): M^+, found 236.1227. $[C_{13}H_{20}O_2Si]^+$ requires 236.1227.

Trimethylsilyl 1-naphthoate **4s**

3s (1.72 g, 10 mmol), HMDS (1.61 g, 10 mmol); slightly yellow oil, (2.26 g, 92%); IR (neat) 2959, 1689, 1509, 1282, 1243, 1197, 1137, 1001, 882, 840, 778, 727, 653, 624 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.23–9.16 (m, 1H), 8.37–8.32 (m, 1H), 8.06–8.00 (m, 1H), 7.93–7.86 (m, 1H), 7.71–7.63 (m, 1H), 7.59–7.48 (m, 2H), 0.54 (s, 9H); δ_C (75 MHz, $CDCl_3$) 167.4, 133.8, 133.6, 131.7, 131.2, 128.4, 127.7, 127.6, 126.0, 124.3, −0.1; *m/z* (EI) 244 (12 M^+), 229 (32), 185 (39), 155 (87), 127 (100%); HRMS (EI): M^+, found 244.0908. $[C_{14}H_{16}O_2Si]^+$ requires 236.0914.

Trimethylsilyl 2-naphthoate **4t**

3t (1.72 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.25 g, 1.0 mmol); bright yellow solid, (2.08 g, 85%), m.p. 71.1–72.6 °C; [Found: C, 68.45; H 6.72. $C_{14}H_{16}O_2Si$ requires C, 68.81; H 6.60]; IR (neat) 3059, 1688, 1353, 1302, 1248, 1235, 1197, 1152, 1131, 1093, 974, 895, 836, 783, 766, 734 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.64–8.60 (m, 1H), 8.12–8.05 (m, 1H), 8.00–7.93 (m, 1H), 7.92–7.84 (m, 2H), 7.63–7.50 (m, 2H), 0.47 (s, 9H); δ_C (75 MHz, $CDCl_3$) 166.9, 135.5, 132.5, 131.6, 129.3, 128.6, 128.1, 128.0, 127.7, 126.5, 125.7, −0.1.

Bis(trimethylsilyl)phthalate[57] **4u**

4u (0.83 g, 5 mmol), HMDS (2.42 g, 15 mmol), I_2 (0.11 g, 0.45 mmol); yellow oil, (0.71 g, 46%); IR (neat) 2962, 1703, 1286, 1251, 1128, 1072, 843, 760, 722, 697 cm^{-1}, δ_H (300 MHz, $CDCl_3$) 7.74–7.66 (m, 2H), 7.52–7.45 (m, 2H), 0.39 (s, 18H); δ_C (75 MHz, $CDCl_3$) 167.6, 133.6, 130.6, 128.9, −0.3.

Trimethylsilyl 2-((trimethylsilyl)oxy)benzoate[58] **6a**

5a (0.69 g, 5 mmol), HMDS (1.21 g, 7.5 mmol); yellow oil, (1.26 g, 89%); IR (neat) 2958, 1706, 1600, 1484, 1449, 1310, 1290, 1245, 1158, 1130, 1077, 1041, 920, 840, 762, 699 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.85–7.80 (m, 1H), 7.39–7.33 (m, 1H), 7.01–6.96 (m, 1H), 6.88–6.84 (m, 1H), 0.39 (s, 9H), 0.27 (s, 9H); δ_C (75 MHz, $CDCl_3$) 166.2, 155.5, 133.2, 132.2, 123.8, 121.7, 121.1, 0.3, −0.1.

Trimethylsilyl 5-chloro-2-((trimethylsilyl)oxy)benzoate **6b**

5b (1.73 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.075 g, 0.3 mmol); yellow-orange oil, (2.54 g, 80%); IR (neat) 2959, 1710, 1474, 1406, 1285, 1250, 1229, 1144, 1104, 1074, 922, 880, 840, 760, 740, 713 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.78 (d, *J* = 2.8 Hz, 1H), 7.30 (dd, *J* = 8.7 Hz, *J* = 2.8 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 0.38 (s, 9H), 0.26 (s, 9H); δ_C (125 MHz, $CDCl_3$) 164.8, 154.2, 133.0, 131.7, 126.0, 124.9, 123.1, 0.2, −0.1; *m/z* (EI) 316 (<1 M^+), 301 (7), 243 (<1), 227 (<1), 73 (100%); HRMS (EI): M^+, found 338.1739. $[C_{12}H_{18}ClO_3Si_2]^+$ requires 338.1728.

Trimethylsilyl 5-(*t*-butyl)-2-((trimethylsilyl)oxy)benzoate **6c**

5c (1.94 g, 10 mmol), HMDS (1.61 g, 10 mmol); transparent oil, (3.1 g, 92%); IR (neat) 2959, 1704, 1493, 1309, 1249, 1154, 1119, 1074, 933, 894, 836, 758 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.84 (d, *J* = 2.7 Hz, 1H), 7.38 (dd, *J* = 8.6 Hz, *J* = 2.7 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 1.31 (s, 9H), 0.40 (s, 9H), 0.27 (s, 9H); δ_C (75 MHz, $CDCl_3$) 166.9, 153.0, 143.6, 130.3, 128.7, 122.9, 121.0, 34.0, 31.3, 0.3, 0.0; *m/z* (EI) 338 (<1 M^+), 323 (30), 265 (2), 249 (4), 73 (100%); HRMS (EI): $[M-Me]^+$, found 301.0487. $[C_{17}H_{30}O_3Si_2]^+$ requires 301.0478.

Trimethylsilyl 3-((trimethylsilyl)oxy)-2-naphthoate **6d**

5d (1.88 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.075 g, 0.3 mmol); yellow, viscous oil, (2.09 g, 63%); IR (neat) 3057, 2959, 2902, 1705, 1630, 1594, 1497, 1460, 1446, 1337, 1283, 1250, 1207, 1176, 1146, 1135, 1063, 929, 892, 835, 742 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 8.33 (s, 1H), 7.80–7.75 (m, 1H), 7.65–7.60 (m, 1H), 7.45–7.39 (m, 1H), 7.33–7.28 (m 1H), 7.18 (s, 1H), 0.40 (s, 9H), 0.29 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.2, 151.6, 136.1, 133.2, 128.6, 128.2, 128.0, 126.2, 125.1, 124.4, 116.6, 0.2, −0.1; *m/z* (EI) 332 (<1 M^+), 317 (18), 259 (1), 73 (100%); HRMS (EI): M^+, found 332.1259. $[C_{17}H_{24}O_3Si_2]^+$ requires 332.1259.

Trimethylsilyl 4-((trimethylsilyl)oxy)benzoate[58] **6e**

5e (1.38 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (2.66 g, 94%); IR (neat) 2960, 1694, 1601, 1508, 1415, 1307, 1252, 1161, 1116, 1096, 909, 843, 781, 758, 737, 717 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.98–7.93 (m, 2H), 6.88–6.83 (m, 2H), 0.38 (s, 9H), 0.28 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.4, 159.6, 132.1, 124.5, 119.6, 0.1, −0.2.

Trimethylsilyl 2,4-bis((trimethylsilyl)oxy)benzoate **6f**

5f (1.54 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (1.63 g, 44%); IR (neat) 2959, 1702, 1598, 1562, 1490, 1420, 1247, 1183, 1133, 1082, 1002, 903, 836, 749 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.78 (d, *J* = 8.7 Hz, 1H), 6.48 (dd, *J* = 8.7 Hz, *J* = 2.3 Hz, 1H), 6.32 (d, *J* = 2.3 Hz, 1H), 0.36 (s, 9H), 0.27 (s, 9H), 0.27 (s, 9H); δ_C (125 MHz, $CDCl_3$) 165.7, 159.8, 157.4, 133.9, 116.9, 113.4, 113.1, 0.2, 0.2, 0.0; *m/z* (EI) 370 (<1 M^+), 355 (25), 297 (<1), 281 (5), 73 (100%); HRMS (EI): $[M-Me]^+$, found 355.1217. $[C_{15}H_{27}O_4Si_3]^+$ requires 355.1212.

Trimethylsilyl 2,6-bis((trimethylsilyl)oxy)benzoate **6g**

5g (1.54 g, 10 mmol), HMDS (4.84 g, 30 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (2.80 g, 76%); IR (neat) 2959, 1712, 1593, 1576, 1462, 1317, 1249, 1112, 1063, 837, 750 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.05 (t, *J* = 8.2 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 2H), 0.26 (s, 18H), 0.38 (s, 9H); δ_C (75 MHz, $CDCl_3$) 166.7, 153.0, 129.5, 121.7, 112.5, 0.3, −0.1; *m/z* (EI) 370 (<1 M^+), 355 (16), 297 (<1), 281 (1), 73 (100%); HRMS (EI): $[M-Me]^+$, found 355.1215. $[C_{15}H_{27}O_4Si_3]^+$ requires 355.1212.

Trimethylsilyl 2-phenylacetate[5g] **8a**

7a (1.36 g, 10 mmol), HMDS (1.61 g, 10 mmol); transparent oil, (2.05 g, 98%); IR (neat) 2959, 1714, 1251, 1221, 1171, 943, 841, 751, 724, 694 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.27–7.21 (m, 2H), 7.21–7.15 (m, 3H), 3.53 (s, 2H), 0.19 (s, 9H); δ_C (125 MHz, $CDCl_3$) 172.0, 134.3, 129.2, 128.4, 126.8, 42.8, −0.4.

Trimethylsilyl 2-(4-chlorophenyl)acetate[5g] **8b**

7b (1.71 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.15 g, 0.6 mmol); yellow oil, (1.31 g, 54%); IR (neat) 2961, 1714, 1492, 1411, 1343, 1252, 1223, 1171, 1091, 1017, 935, 842, 805, 762, 714 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.25–7.18 (m, 2H), 7.16–7.09 (m, 2H), 3.52 (s, 2H), 0.21 (s, 9H); δ_C (75 MHz, $CDCl_3$) 171.5, 132.8, 132.8, 130.6, 128.5, 42.1, −0.4.

Trimethylsilyl 2-(4-methoxyphenyl)acetate[5g] **8c**

7c (1.66 g, 10 mmol), HMDS (1.61 g, 10 mmol); transparent oil, (2.16 g, 91%); IR (neat) 2958, 1711, 1613, 1512, 1247, 1169, 1035, 946, 846, 791, 763, 724, 708 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.22–7.17 (m, 2H), 6.90–6.85 (m 2H), 3.79 (s, 3H), 3.57 (s, 2H), 0.28 (s, 9H); δ_C (125 MHz, $CDCl_3$) 172.4, 158.5, 130.2, 126.4, 113.8, 55.1, 41.9, −0.4.

Trimethylsilyl 2-(3,4-dimethoxyphenyl)acetate[5g] **8d**

7d (1.96 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (1.49 g, 55%); IR (neat) 2957, 1711, 1514, 1464, 1420, 1253, 1235, 1173, 1141, 1028, 845, 845, 791, 759, 717 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.81–6.78 (m, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.53 (s, 2H), 0.25 (s, 9H); δ_C (125 MHz, $CDCl_3$) 172.2, 148.7, 147.9, 126.8, 121.3, 112.3, 111.0, 55.7, 55.7, 42.3, −0.4.

Trimethylsilyl 2-((2-trimethylsilyl)oxy)phenyl)acetate[59] **8e**

7e (1.52 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.075 g, 0.3 mmol); transparent oil, (2.48 g, 84%); IR (neat) 2960, 1717, 1493, 1454, 1343, 1250, 1211, 1167, 933, 916, 837, 752, 723, 693 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.21–7.13 (m, 2H), 6.95–6.91 (m, 1H), 6.84–6.80 (m, 1H), 3.59 (s, 2H), 0.30 (s, 9H), 0.29 (s, 9H); δ_C (125 MHz, $CDCl_3$) 172.1, 153.6, 131.0, 128.1, 125.8, 121.2, 118.4, 37.7, 0.4, −0.3.

Trimethylsilyl 2-((4-trimethylsilyl)oxy)phenyl)acetate[59] **8f**

7f (1.52 g, 10 mmol), HMDS (4.84 g, 30 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (1.82 g, 61%); IR (neat) 2960, 1715, 1610, 1509, 1249, 1166, 912, 840, 759, 718 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.17–7.10 (m, 2H), 6.84–6.76 (m, 2H), 3.55 (s, 2H), 0.27 (s, 9H), 0.27 (s, 9H); δ_C (75 MHz, $CDCl_3$) 172.2, 154.0, 130.2, 127.3, 119.9, 42.0, 0.1, −0.4.

Trimethylsilyl 2-phenyl-((2-trimethylsilyl)oxy)acetate[60] **8g**

7g (1.52 g, 10 mmol), HMDS (4.84 g, 30 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (1.75 g, 59%); IR (neat); 2957, 1736, 1714, 1288, 1252, 1213, 1181, 1127, 1071, 949, 887, 843, 758, 726, 696 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.47–7.42 (m, 2H), 7.36–7.26 (m, 3H), 5.14 (s, 1H), 0.20 (s, 9H), 0.13 (s, 9H); δ_C (75 MHz, $CDCl_3$) 172.2, 139.3, 128.2, 128.0, 126.6, 74.8, −0.1, −0.5.

Trimethylsilyl 2-phenoxyacetate[61] **8h**

7h (1.52 g, 10 mmol), HMDS (4.84 g, 30 mmol), I_2 (0.23 g, 0.9 mmol); yellow, viscous oil, (0.46 g, 20%); IR (neat) 2960, 1743, 1717, 1599, 1494, 1304, 1253, 1199, 1174, 1086, 922, 847, 753, 690 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.32–7.26 (m, 2H), 7.01–6.96 (m, 1H), 6.93–6.88 (m, 2H), 4.58 (s, 2H), 0.33 (s, 9H); δ_C (125 MHz, $CDCl_3$) 169.0, 157.6, 129.4, 121.4, 114.5, 65.6, −0.5.

Trimethylsilyl 2-(phenythio)acetate[5g] **8i**

7i (1.68 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.23 g, 0.9 mmol); brown oil, (1.96 g, 82%); IR (neat) 2960, 1711, 1584, 1482, 1439, 1408, 1284, 1252, 1175, 1132, 942, 843, 761, 738, 689 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.42–7.37 (m, 2H), 7.32–7.26 (m, 2H), 7.24–7.18 (m, 1H), 3.64 (s, 2H), 0.24 (s, 9H); δ_C (125 MHz, $CDCl_3$): δ 169.7, 135.1, 129.8, 128.9, 126.7, 38.1, −0.5.

Trimethylsilyl 3-phenylpropanoate[59] **8j**

7j (1.50 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (1.13 g, 50%); IR (neat) 2959, 1714, 1497, 1454, 1417, 1368, 1295, 1252, 1184, 1078, 946, 846, 763, 727, 698 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.23–7.17 (m, 2H), 7.14–7.09 (m, 3H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 0.19 (s, 9H); δ_C (125 MHz, $CDCl_3$) 173.4, 140.6, 128.4, 128.2, 126.1, 37.3, 31.0, −0.3.

Trimethylsilyl 3-(4-((trimethylsilyl)oxy)phenyl)propanoate[59] **8k**

7k (1.66 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (2.87 g, 92%); IR (neat) 2960, 1715, 1610, 1510, 1248, 1184, 1101, 913, 839, 759, 733 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.09–7.04 (m, 2H), 6.79–6.74 (m, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 0.26 (s, 9H), 0.25 (s, 9H); δ_C (125 MHz, $CDCl_3$) 173.5, 153.4, 133.5, 129.2, 119.9, 37.6, 30.2, 0.1, −0.3.

Trimethylsilyl 2-bromo-3-phenylpropanoate **8l**

7l (2.30 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); slightly yellow oil, (1.39 g, 46%); [Found: C, 47.81; H 5.61. $C_{12}H_{17}BrO_2Si$ requires C, 47.84; H 5.69]; IR (neat) 2961, 1710, 1492, 1312, 1272, 1253, 1180, 1045, 977, 884, 832, 754, 727, 706, 653, 630 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.32–7.19 (m, 5H), 4.37 (dd, *J* = 8.4 Hz, *J* = 7.0 Hz, 1H), 3.42 (dd, *J* = 14.1Hz, *J* = 8.4 Hz, 1H), 3.22 (dd, *J* = 14.1 Hz, *J* = 7.0 Hz, 1H), 0.26 (s, 9H); δ_C (125 MHz, $CDCl_3$) 169.2, 136.9, 129.1, 128.5, 127.2, 47.2, 41.2, −0.6.

Trimethylsilyl 2,2-diphenylacetate[62] **8m**

7m (1.59 g, 7.5 mmol), HMDS (1.82 g, 11.25 mmol), I_2 (0.19 g, 0.75 mmol); yellow solid, (1.27 g, 60%), m.p. 76.1–76.3 ºC; IR (neat) 3025, 1701, 1497, 1449, 1411, 1308, 1282, 1250, 1222, 1198, 1168, 1079, 1033, 960, 913, 840, 747, 733, 695, 671, 637 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.20–7.07 (m, 10H), 4.85 (s, 1H), 0.12 (s, 9H); δ_C (125 MHz, $CDCl_3$) 172.7, 139.0, 128.6, 128.5, 127.1, 58.7, −0.4.

Trimethylsilyl 2,2-diphenylpropanoate **8n**

7n (1.70 g, 7.5 mmol), HMDS (2.42 g, 15 mmol), I_2 (0.19 g, 0.75 mmol); transparent oil, (1.32 g, 59%); [Found: C, 72.18; H 7.59. $C_{18}H_{22}O_2Si$ requires C, 72.44; H 7.43]; IR (neat) 2959, 1708, 1600, 1494, 1445, 1375, 1249, 1219, 1190, 1120, 1104, 1076, 1055, 1029, 901, 847, 789, 732, 698, 660 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.24–7.11 (m, 10H), 1.82 (s, 3H), 0.14 (s, 9H); δ_C (125 MHz, $CDCl_3$) 175.1, 144.5, 128.0, 127.9, 126.6, 57.4, 27.0, −0.5.

Trimethylsilyl 4-oxo-4-phenylbutanoate **8o**

7o (1.78 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow-orange oil, (0.85 g, 34%); [Found: C, 62.04; H 7.18. $C_{13}H_{18}O_3Si$ requires C, 62.37; H 7.25]; IR (neat) 2961, 1714, 1686, 1596, 1448, 1401, 1357, 1252, 1218, 1171, 887, 842, 761, 731, 688 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.99–7.93 (m, 2H), 7.57–7.51 (m, 1H), 7.47–7.40 (m, 2H), 3.25 (t, *J* = 6.6 Hz, 2H), 2.76 (t, *J* = 6.6 Hz, 2H), 0.27 (s, 9H); δ_C (100 MHz, $CDCl_3$) 198.1, 173.3, 136.5, 133.0, 128.5, 127.9, 33.4, 29.7, −0.4.

(*E*)-Trimethylsilyl 3-phenylacrylate[59] **8p**

7p (1.48 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (1.81 g, 82%); IR (neat) 2959, 1687, 1633, 1449, 1315, 1298, 1279, 1252, 1202, 1184, 974, 843, 770, 736, 710, 683 cm

$^{-1}$; δ_H (500 MHz, $CDCl_3$) 7.65 (d, *J* = 15.9 Hz, 1H), 7.54–7.49 (m, 2H), 7.41–7.34 (m, 3H), 6.42 (d, *J* = 15.9 Hz, 1H), 0.37 (s, 9H); δ_C (125 MHz, $CDCl_3$) 167.0, 145.2, 134.4, 130.1, 128.8, 128.0, 119.8, −0.2.

(*E*)-Trimethylsilyl 3-(4-methoxyphenyl)acrylate[59] **8q**

7q (1.07 g, 6 mmol), HMDS (0.97 g, 6 mmol), I_2 (0.05 g, 0.20 mmol); brown oil, (0.54 g, 36%); IR (neat) 2959, 1682, 1630, 1602, 1575, 1511, 1463, 1442, 1422, 1321, 1301, 1286, 1247, 1204, 1169, 1030, 977, 825, 784, 762, 724 cm $^{-1}$; δ_H (500 MHz, $CDCl_3$) 7.59 (d, *J* = 15.8 Hz, 1H), 7.49–7.43 (m, 2H), 6.92–6.87 (m, 2H), 6.28 (d, *J* = 15.8 Hz, 1H), 3.83 (s, 3H), 0.35 (s, 9H); δ_C (125 MHz, $CDCl_3$) 167.4, 161.3, 144.9, 129.7, 127.1, 117.3, 114.3, 55.3, −0.1.

(*E*)-Trimethylsilyl 3-(3,4-dimethoxyphenyl)acrylate[54] **8r**

7r (1.04 g, 5 mmol), HMDS (0.81 g, 5 mmol); yellow, viscous oil, (1.28 g, 91%); IR (neat) 2958, 1682, 1627, 1598, 1510, 1464, 1420, 1294, 1250, 1179, 1158, 1137, 1024, 976, 841, 806, 760, 723 cm $^{-1}$; δ_H (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 15.8 Hz, 1H), 7.00–6.91 (m, 2H), 6.77–6.71 (m, 1H), 6.19 (d, *J* = 15.8 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 0.27 (s, 9H); δ_C (125 MHz, $CDCl_3$) 166.9, 150.7, 148.8, 144.9, 127.1, 122.3, 117.2, 110.7, 109.3, 55.5, 55.4, −0.4.

(*E*)-Trimethylsilyl 3-(3,4,5-trimethoxyphenyl)acrylate[59] **8s**

7s (1.19 g, 5 mmol), HMDS (4.04 g, 25 mmol), I_2 (0.11 g, 0.45 mmol); yellow solid, (0.77 g, 50%), m.p. 75.9–78.5 ºC; IR (neat) 2968, 2942, 1674, 1580, 1505, 1464, 1420, 1277, 1246, 1127, 979, 840, 703 cm $^{-1}$; δ_H (300 MHz, $CDCl_3$) 7.54 (d, *J* = 15.8 Hz, 1H), 6.74 (s, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 3.88 (s, 6H), 3.88 (s, 3H), 0.35 (s, 9H); δ_C (75 MHz, $CDCl_3$) 166.9, 153.4, 145.1, 140.1, 130.0, 119.2, 105.3, 60.9, 56.1, −0.2.

Trimethylsilyl thiophene-2-carboxylate[24] **10a**

9a (1.28 g, 10 mmol), HMDS (2.42 g, 15 mmol), I_2 (0.23 g, 0.9 mmol); brown oil, (1.34 g, 67%); IR (neat) 2961, 1685, 1524, 1416, 1360, 1296, 1272, 1252, 1229, 1096, 1076, 1035, 841, 767, 714, 654 cm $^{-1}$; δ_H (400 MHz, $CDCl_3$) 7.76 (dd, *J* = 3.8 Hz, *J* = 1.2 Hz, 1H), 7.54 (dd, *J* = 4.9 Hz, *J* = 1.2 Hz, 1H), 7.08 (dd, *J* = 4.9 Hz, *J* = 3.8 Hz, 1H), 0.39 (s, 9H); δ_C (100 MHz, $CDCl_3$) 162.0, 135.7, 133.8, 132.6, 127.8, −0.2.

Trimethylsilyl 2-(thien-2-yl)acetate[5g] **10b**

9b (1.42 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); brown oil, (1.13 g, 53%); IR (neat) 2960, 1716, 1252, 1211, 1177, 940, 842, 761, 692 cm $^{-1}$; δ_H (400 MHz, $CDCl_3$) 7.22 (dd, *J* = 5.1 Hz, *J* = 1.3 Hz, 1H), 6.96 (dd, *J* = 5.1 Hz, *J* = 3.5 Hz, 1H), 6.91–6.94 (m, 1H), 3.84 (d, *J* = 0.7 Hz, 2H), 0.30 (s, 9H); δ_C (100 MHz, $CDCl_3$) 170.8, 135.5, 126.6, 126.6, 124.9, 37.0, −0.3.

Trimethylsilyl 2-(thien-3-yl)acetate **10c**

9c (1.42 g, 10 mmol), HMDS (1.61 g, 10 mmol); transparent oil, (1.89 g, 88%); IR (neat) 2960, 1713, 1409, 1252, 1195, 938, 841, 754, 710, 691, 611 cm $^{-1}$; δ_H (400 MHz, $CDCl_3$) 7.28 (dd, *J* = 5.0 Hz, *J* = 3.0 Hz, 1H), 7.16–7.12 (m, 1H), 7.04 (dd, *J* = 5.0 Hz, *J* = 0.9 Hz, 1H), 3.66 (s, 2H), 0.29 (s, 9H); δ_C (100 MHz, $CDCl_3$) 171.6, 134.0, 128.5, 125.5, 122.6, 37.3, −0.3; *m/z* (EI) 214 (6 M^+), 199 (7), 97 (11), 75 (29), 73 (100%); HRMS (EI): M^+, found 214.0485. $[C_9H_{14}O_2SSi]^+$ requires 214.0479.

Trimethylsilyl furan-2-carboxylate **10d**

9d (1.12 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (0.57 g, 31%); IR (neat) 2960, 1697, 1578, 1473, 1394, 1309, 1254, 1230, 1182, 1124, 1077, 1013, 934, 842, 754, 726 cm $^{-1}$; δ_H (400 MHz, $CDCl_3$) 7.58–7.54 (m, 1H), 7.16–7.12 (m, 1H), 6.50–6.46 (m, 1H), 0.38 (s, 9H);

δ_C (100 MHz, $CDCl_3$) 158.2, 146.3, 145.7, 118.3, 111.8, −0.2; *m/z* (EI) 184 (7 M^+), 169 (44), 125 (100), 95 (44%); HRMS (EI): M^+, found 184.0551. $[C_8H_{12}O_3Si]^+$ requires 184.0551.

Trimethylsilyl furan-3-carboxylate **10e**

9e (1.12 g, 10 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.075 g, 0.3 mmol); yellow oil, (0.69 g, 38%); IR (neat) 2961, 1700, 1574, 1507, 1399, 1316, 1254, 1164, 1076, 1006, 966, 845, 797, 772, 732 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.96 (dd, *J* = 1.4 Hz, *J* = 0.6 Hz, 1H), 7.41–7.38 (m, 1H), 6.71 (dd, *J* = 1.8 Hz, *J* = 0.6 Hz, 1H), 0.35 (s, 9H); δ_C (75 MHz, $CDCl_3$) 163.0, 148.3, 143.7, 120.9, 110.2, −0.2; *m/z* (EI) 184 (8 M^+), 169 (46), 125 (100), 95 (56), 73 (7), 67 (6%); HRMS (EI): M^+, found 184.0555. $[C_8H_{12}O_3Si]^+$ requires 184.0551.

Trimethylsilyl nicotinate[42b] **10f**

9f (1.23 g, 10 mmol), HMDS (3.23 g, 20 mmol), I_2 (0.23 g, 0.9 mmol); yellow oil, (1.19 g, 61%); IR (neat) 2960, 1701, 1590, 1419, 1292, 1253, 1127, 1024, 845, 828, 763, 728, 700 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.17–9.12 (m, 1H), 8.73–8.67 (m, 1H), 8.26–8.19 (m, 1H), 7.36–7.29 (m, 1H), 0.34 (s, 9H); δ_C (75 MHz, $CDCl_3$) 165.0, 153.0, 151.2, 137.5, 127.1, 123.1, −0.4.

Trimethylsilyl 2-((*t*-butoxycarbonyl)amino)acetate **12a**

11a (0.87 g, 5 mmol), HMDS (0.81 g, 5 mmol); transparent oil, (1.15 g, 93%); IR (neat) 3367, 2977, 1703, 1509, 1367, 1252, 1209, 1161, 1055, 953, 843, 762 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.14–5.00 (m, 1H), 3.87–3.77 (m, 2H), 1.40 (s, 9H), 0.25 (s, 9H); δ_C (75 MHz, $CDCl_3$) 170.5, 155.6, 79.6, 43.4, 28.2, −0.4; *m/z* (EI) 247 (<1 M^+), 191 (4), 158 (5), 73 (100), 57 (88%); HRMS (EI): $[M-C_4H_8]^+$, found 191.0611. $[C_6H_{13}NO_4Si]^+$ requires 191.0609.

Trimethylsilyl 3-((*t*-butoxycarbonyl)amino)propanoate **12b**

11b (0.95 g, 5 mmol), HMDS (0.81 g, 5 mmol); transparent oil, (1.23 g, 94%); IR (neat) 3368, 2977, 1710, 1505, 1366, 1251, 1165, 842, 762, 725 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.12–4.96 (m, 1H), 3.37–3.25 (m, 2H), 2.48 (t, *J* = 6.1 Hz, 2H), 1.40 (s, 9H), 0.25 (s, 9H); δ_C (75 MHz, $CDCl_3$) 172.9, 155.8, 79.2, 36.2, 36.1, 28.3, −0.3; *m/z* (EI) 261 (<1 M^+), 188 (7), 172 (5), 116 (15), 75 (35), 73 (33), 57 (100%); HRMS (EI): $[M-C_4H_8]^+$, found 205.0773. $[C_7H_{15}NO_4Si]^+$ requires 205.0765.

(*S*)-Trimethylsilyl 2-((*t*-butoxycarbonyl)amino)-3-methylbutanoate **12c**

11c (1.09 g, 5 mmol), HMDS (0.81 g, 5 mmol); transparent oil, (1.28 g, 88%), $[\alpha]_D^{24}$ +9.5 (*c* 1.03, CH_2Cl_2); IR (neat) 3367, 2966, 1707, 1497, 1365, 1253, 1209, 1159, 845, 763, 726 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.08–4.93 (m, 1H), 4.22–4.08 (m, 1H), 2.21–2.03 (m, 1H), 1.41 (s, 9H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H), 0.26 (s, 9H); δ_C (75 MHz, $CDCl_3$) 172.5, 155.7, 79.4, 59.3, 31.1, 28.2, 18.9, 17.4, −0.4; *m/z* (EI) 289 (<1 M^+), 200 (<1), 188 (5), 172 (12), 116 (60), 73 (50), 57 (100%).

(*S*)-1-*t*-butyl 2-(trimethylsilyl)pyrrolidine-1,2-dicarboxylate **12d**

11d (1.08 g, 5 mmol), HMDS (0.81 g, 5 mmol); transparent oil, (1.38 g, 96%); $[\alpha]_D^{24}$ -62.5 (*c* 1.04, CH_2Cl_2); IR (neat) 2975, 2881, 1728, 1699, 1391, 1365, 1252, 1201, 1159, 1118, 845, 763 cm^{-1}; δ_H (500 MHz, $CDCl_3$) two forms of product in a relative ratio 2:1; 4.21 (minor), (dd, *J* = 8.9 Hz, *J* = 3.5 Hz, 1H), 4.13 (dd, *J* = 8.9 Hz, *J* = 3.9 Hz), 3.52–3.29 (m, 2H), 2.24–2.08 (m, 1H), 1.96–1.75 (m, 3H), 1.41 (minor) (s, 9H), 1.38, 0.25 (s, 9H), 0.24 (minor); δ_C (125 MHz, $CDCl_3$) 173.3, 173.2, 154.2, 153.8, 79.6, 79.4, 59.9, 59.8, 46.4, 46.2, 30.7, 29.7, 28.3, 28.2, 24.2, 23.4, −0.4, −0.4; *m/z* (EI) 287 (<1 M^+), 186 (7), 170 (12), 114 (63), 73 (36), 70 (100), 57 (63%).

(*S*)-Trimethylsilyl 2-((*t*-butoxycarbonyl)amino)-3-phenylpropanoate **12e**

11e (1.33 g, 5 mmol), HMDS (0.81 g, 5 mmol); transparent, viscous oil, (1.62 g, 96%); $[\alpha]_D^{24}$ +42.8 (*c* 1.15, CH_2Cl_2); IR (neat) 3351, 2976, 1708, 1496, 1365, 1253, 1163, 1053, 846, 763, 731, 699 cm^{-1}; δ_H

(300 MHz, $CDCl_3$) 7.35–7.13 (m, 5H), 5.12–4.96 (m, 1H), 4.62–4.46 (m, 1H), 3.17–3.07 (m, 2H), 1.44 (s, 9H), 0.28 (s, 9H); δ_C (75 MHz, $CDCl_3$) 171.9, 155.0, 136.3, 129.4, 128.3, 126.8, 79.6, 55.3, 38.1, 28.3, −0.4; *m/z* (EI) 337 (<1 M^+), 236 (1), 220 (14), 91 (17), 73 (31), 57 (100%).

(*S*)-Trimethylsilyl 2-((*t*-butoxycarbonyl)amino)-3-(4-((trimethylsilyl)oxy)phenyl)propanoate **12f**

11f (1.41 g, 5 mmol), HMDS (1.61 g, 10 mmol), I_2 (0.04 g, 0.15 mmol); Slightly yellowish viscous oil, (1.06 g, 50%); $[\alpha]_D^{24}$ +11.4 (*c* 1.08, CH_2Cl_2); IR (neat) 3441, 2962, 1711, 1609, 1509, 1364, 1250, 1166, 914, 839, 757 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.03–6.94 (m, 2H), 6.76–6.66 (m, 2H), 5.12–4.96 (m, 1H), 4.51–4.37 (m, 1H), 3.06–2.92 (m, 2H), 1.39 (s, 9H), 0.22 (s, 9H), 0.21 (s, 9H); δ_C (75 MHz, $CDCl_3$) 171.8, 154.9, 154.0, 130.3, 129.0, 119.7, 79.3, 55.2, 37.2, 28.2, 0.0, −0.5; *m/z* (EI) 425 (<1 M^+), 308 (23), 179 (100), 73 (50), 57 (42).

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Supplementary data

Copies of ^1H, ^{13}C and ^{19}F NMR spectra of all products and mass spectra of novel compounds are provided.

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