Intermolecular C–H and Si–H Insertion Reactions with Halodiazoacetates

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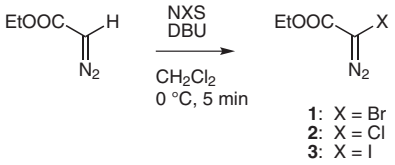
Abstract: Ethyl halodiazoacetates react with a range of substrates in regioselective rhodium(II)-catalysed C–H and Si–H insertion reactions giving α-halocarbonyl products in up to 82% yield. The halodiazoacetates are a novel class of diazo compounds that can undergo intermolecular carbenoid C–H insertion reactions, thus broadening the synthetic utility of such reactions.

Key words: C–H insertion, Si–H insertion, diazo compounds, rhodium, halides

The development of methods for selective, catalytic C–H activation is an area of immense current interest and great practical importance.[1–5] Through the functionalisation of C–H bonds that traditionally have been considered inert, new synthetic strategies are made available. One attractive method for derivatisation of C–H bonds is the metal-catalysed decomposition of diazo compounds to metal carbenoids that can insert into unactivated C–H bonds.[5–8] This results in C–H insertion reactions of high regio- and stereoselectivity, generating new C–C bonds while allowing mild conditions. Whereas the field of intramolecular metal carbenoid-induced C–H insertions is well established,[9] intermolecular versions have proved more challenging, with a rather limited choice of usable diazo compounds. The area has been dominated by rhodium(II)-stabilised donor/acceptor-substituted carbenoids,[5,7,10] containing both an electron-withdrawing group, ensuring high enough electrophilicity, and an electron-releasing group, modulating their reactivity. With such carbenoids, both yields and selectivity tend to be good. Examples of C–H insertions with other classes of diazo compounds are few and far between.[6,11] The need for specialised, non-commercial catalysts or inconvenient reaction procedures significantly reduce their synthetic utility.

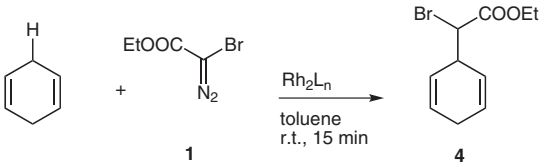
We recently described a novel method for very facile formation of halodiazoacetates (Scheme 1).[12] Ethyl diazobromoacetate (**1**), -chloroacetate (**2**) and -iodoacetate (**3**) are generated quantitatively from EDA in only five minutes reaction time, by stirring with DBU and an *N*-halosuccinimide in dichloromethane.

When used in rhodium(II)-catalysed intermolecular cyclopropanation reactions, halodiazoacetates **1**–**3** gave high yields and good diastereoselectivity, illustrating how these halogenated diazo compounds represent a novel method for selective introduction of halogens. Their utilisation in C–H insertion reactions would be a powerful synthetic tool, generating a new C–C bond as well as introducing both an ester functionality and a halogen that can be utilised in further transformations. Around 1970, Schöllkopf et al. reported the use of free carbenes generated by irradiation of **1** and **3**, bromo- and iodoethoxycarbonylcarbene, in a C–H insertion reaction with cyclohexane.[13] Only 5–6% of the respective C–H insertion products were detected, and no other substrates were tested. However, the introduction of rhodium(II) catalysts in the mid 1970s has since then resulted in an immense improvement in the synthetic use of carbene reactions. Modulation of reactivity through coordination of the carbene to the metal centre enables an increased level of both regio- and stereoselectivity. Prompted by the desirable reactivity shown by diazo compounds **1**–**3** in the rhodium(II)-catalysed cyclopropanations, we decided to investigate their effectiveness in rhodium(II)-catalysed C–H insertions as well.



Scheme 1 Formation of halodiazoacetates

Cyclohexa-1,4-diene was selected as the substrate for the initial experiments, as C–H insertion reactions are especially effective at allylic sites.[11,14] A test experiment was conducted, employing conditions analogous to the conditions used in the previously described cyclopropanation reaction:[12] 1 mol% $Rh_2(esp)_2$ dissolved in toluene was added to a solution of freshly prepared **1** and cyclohexa-1,4-diene in toluene at ambient temperature, and stirred for 15 minutes. We were pleased to see that this gave 39% of the C–H insertion product **4** (Scheme 2).



Scheme 2 Synthesis of ethyl 2-bromo-2-(cyclohexa-2,5-dienyl)acetate

Although a good catalyst in carbenoid cyclopropanation reactions[15,16] and nitrene C–H insertions,[17] $Rh_2(esp)_2$ has not yet been used successfully in a carbenoid C–H inser-

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tion reaction. A screening of catalysts was therefore performed, using the same conditions (Table 1).

Table 1 Catalyst Screening in the C–H Insertion Reaction of **1** with Cyclohexa-1,4-diene

Entry	Catalyst	Yield of **4** (%)[a]
1	$Rh_2(TPA)_4$	68
2	$Rh_2(esp)_2$	39
3	$Rh_2(TFA)_4$	29
4	$Rh_2(OOct)_4$	18
5	$Rh_2(S\text{-DOSP})_4$	15
6	$Rh_2(TMA)_4$	0
7	$AgSbF_6$	0

[a] Measured by internal standard (2-naphthaldehyde) in ^1H NMR analysis of crude reaction mixture.

The results from the screening showed that the yield of **4** was substantially affected by the ligands of the rhodium(II) catalysts, but no obvious trends were observed. The sterically encumbered tetrakis(triphenylacetato)dirhodium(II) [$Rh_2(TPA)_4$], gave the highest yield; 68% (entry 1). The chiral catalyst $Rh_2(S\text{-DOSP})_4$ is known as an efficient catalyst in C–H insertions of donor/acceptor-substituted diazo compounds,[5] but gave only 15% of **4** (entry 5), highlighting the difference between the two classes of diazo compounds. All of the tested catalysts gave complete decomposition of **1**; the only observed by-products were the products from carbene dimerisation. Even though both $Rh_2(esp)_2$ and $AgSbF_6$ have been shown to favour cyclopropanation over C–H insertion in the case of donor/acceptor-substituted diazo compounds,[15,18] no cyclopropanation products were observed in any of the experiments.

In order to examine solvent effects, an experiment was performed using $Rh_2(TPA)_4$ and the standard conditions, but with hexane instead of toluene. This lowered the yield substantially, to 41%. Slow, dropwise addition of the diazo compound to the substrate and catalyst, instead of bulk addition, was also tried, but had no effect on the outcome of the reaction. Neither did increasing the amount of cyclohexa-1,4-diene from two to five equivalents. Wanting to keep the simplicity of the procedure, no further changes in reaction conditions were tested.

Following the standard procedure, and using $Rh_2(TPA)_4$ as catalyst, C–H insertion reactions of ethyl diazochloroacetate (**2**) and ethyl diazoiodoacetate (**3**) with cyclohexa-1,4-diene were performed (Table 2). The reactions gave yields of 53 and 45% of the C–H insertion products, respectively (entries 2 and 3). Again, no cyclopropanation products were observed. The lower yields of the reactions of **2** and **3** compared to **1** may in part be explained by product instability. This was especially clear in the case of **3**, where rapid formation of free iodine was observed both during workup and storage of the C–H insertion product.

Table 2 C–H Insertion Reaction of **1**–**3** with Cyclohexa-1,4-diene

Entry	Diazo compound	Yield (%)[a]
1	ethyl diazobromoacetate (**1**)	68
2	ethyl diazochloroacetate (**2**)	53
3	ethyl diazoiodoacetate (**3**)	45

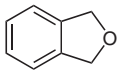
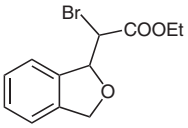
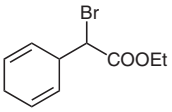
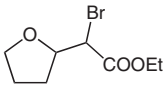
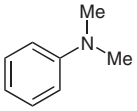
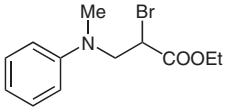
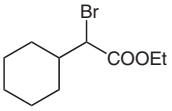
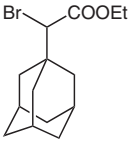
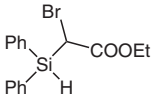
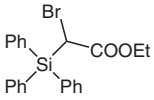
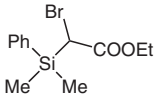
[a] Isolated yield after silica gel chromatography.

In order to examine the reaction scope, C–H and Si–H insertion reactions of **1** with a variety of substrates were carried out (Table 3). In all of the reactions the desired C–H or Si–H insertion products were formed, with yields varying from 82% with phthalan (entry 1) to 2% with the more challenging substrate adamantane (entry 6). The regioselectivity was high and predictable in all cases. The C–H insertion reactions are known to take place preferentially into the more electron-rich C–H bonds,[10] and the results were consistent with this: C–H insertion took place in the allylic position of cyclohexa-1,4-diene (entry 2), at the tertiary site in adamantane (entry 6), and into the C–H bonds of sp^3-centers α to oxygen or nitrogen in the cases of phthalan, THF, and *N*,*N*-dimethylaniline (entries 1, 3, and 4). No other regioisomers were observed.

Initially, all C–H insertion reactions were performed with $Rh_2(TPA)_4$ as the catalyst. As Si–H insertions typically are more favoured,[19,20] the lower-priced $Rh_2(esp)_2$ was used in these reactions. However, the results from the catalyst screening in Table 1 turned out not to be transferable to all of the C–H insertion substrates. In the reactions with phthalan and THF (entries 1 and 3), yields with $Rh_2(TPA)_4$ as the catalyst were rather low. Using $Rh_2(esp)_2$, however, gave good yields of 82 and 63%, respectively. This effect was not observed with neither *N*,*N*-dimethylaniline (entry 4) nor cyclohexane (entry 5), for which only trace amounts of product was observed when $Rh_2(esp)_2$ was used. With adamantane (entry 6), yields were similarly low employing both catalysts.

As rhodium(II)-catalysed decomposition of halodiazoacetates is fast at room temperature, the different yields of the various products in Table 3 are most likely a direct consequence of how efficiently the substrates trap the carbenoid. The reactivity of the substrates seems to largely mirror the reactivity observed in C–H insertions with donor/acceptor-substituted diazo compounds,[14] with C–H bonds in allylic positions being more reactive than C–H bonds α to oxygen, followed by those α to nitrogen. The nonactivated substrates give the lowest yields, with adamantane being a poorer substrate than cyclohexane. The high yield in the reaction with phthalan might be explained by the fact that the reacting C–H bond is benzylic as well as in α position to an oxygen atom, both of which are activating factors. An experiment with cyclohepta-1,3,5-triene as the substrate was also conducted. This gave

Table 3 Scope of C–H and Si–H Insertions with **1**

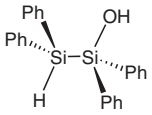
Entry	Substrate	Product	Yield (%)[a]	dr[b]
1			82[c] 35[d]	1.2:1[c] 1:2[d]
2			68[d]	–
3			63[c] 10[d]	2.5:1[c] 2.5:1[d]
4			40[d]	–
5			12[d,e]	–
6			2[c]	–
7			80[d,f]	–
8			51[c]	–
9			25[c]	–

[a] Isolated yield after silica gel chromatography.
[b] Measured by ^{1}H NMR analysis of the crude reaction mixture.
[c] Catalyst: $Rh_2(esp)_2$.
[d] Catalyst: $Rh_2(TPA)_4$.
[e] Cyclohexane was used both as reactant and solvent.
[f] Yield measured by internal standard (1,3,5-trimethoxybenzene) in the ^{1}H NMR analysis of the crude reaction mixture, as the product decomposed.

cyclopropanes as the main product, and no C–H insertion product was observed. This chemoselectivity contrasts that of donor/acceptor-substituted diazo compounds, for which C–H insertion is the dominating reaction.[14]

In the cases of phthalan and THF, diastereomeric products were formed. The relative stereochemistry of the diastereomers was assigned by comparison with an analogous compound described in the literature.[21] For phthalan (entry 1) the diastereomeric ratio (dr) was dependent on the catalyst; $Rh_2(TPA)_4$ gave a dr of 1:2, favouring the (2*R**,3*R**)-diastereomer, whereas $Rh_2(esp)_2$ gave a dr of 1.2:1, favouring the opposite diastereomer. The dr of the products formed from THF (entry 3) was 2.5:1 in both cases, with (2*R**,3*R**) as the major diastereomer. These results are in the same area as the dr reported for reactions of donor/acceptor-substituted diazo compounds.[5]

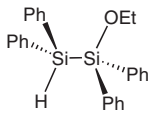
Rhodium(II)-catalysed Si–H insertion reactions are another well-established, synthetically useful class of carbenoid insertion into bonds of low polarity.[19,20] A wide range of diazo compounds readily partake in Si–H insertion reactions, including compounds that react only poorly in C–H insertion reactions. The products from Si–H insertion reactions between **1** and triphenylsilane (entry 8) and dimethylphenylsilane (entry 9) were isolated in yields of 51 and 25%, respectively. For diphenylsilane (entry 7) the yield was measured to 80% by internal standard in ^{1}H NMR spectroscopy. However, all attempts of purification by chromatography resulted in decomposition of the product; silica, neutral alumina and basic alumina all led to rapid evolution of gas. The product from this decomposition reaction was isolated and characterised as disilane **5** (Figure 1).



5

Figure 1 Product formed after attempted purification of ethyl 2-bromo-2-diphenylsilylacetate on silica gel

Assuming that the hydroxy group in **5** originated from water present in the silica gel or alumina, we decided to examine the observed reaction: The Si–H insertion reaction was repeated, but instead of the normal workup, three equivalents of ethanol was added to the crude product mixture. This resulted in evolution of gas. As always, the Si–H insertion was performed using two equivalents of diphenylsilane. ^{1}H NMR analysis of the crude mixture after stirring with ethanol for one hour at room temperature revealed that all of the excess diphenylsilane now had been consumed, whereas the Si–H insertion product remained. The mixture was then placed on a silica gel column, and once again gas evolution was observed. NMR analysis after flash chromatography showed that the Si–H insertion product now also had been consumed, and disilane **6** (Figure 2) was isolated as the main product in a yield of 24%.

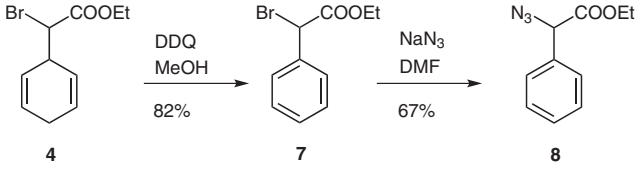


6

Figure 2 Product from the treatment of the crude mixture obtained from the reaction of **1** with ethanol and silica gel

To the best of our knowledge, this is the first example of generation of disilanes from carbenoid Si–H insertion products. Further examinations of this transformation are currently carried out, and will be reported in due time.

The products formed by C–H insertions of halodiazoacetates **1**–**3** are highly versatile building blocks in organic synthesis. The greatest synthetic possibilities may be offered by the halogen, due to the rapid development in coupling chemistry, but a variety of other transformations are also possible. One example of transformations of C–H insertion product **4** is shown in Scheme 3.



Scheme 3 Transformation of **4**

In this reaction sequence, the cyclohexadienyl ring of **4** was aromatised by oxidation with DDQ, giving **7** in 82% yield. Exploiting the presence of the halogen, the C–H insertion products can be used as precursors in the introduction of a range of other functional groups, here illustrated by a substitution with azide. Treatment of **7** with sodium azide gave 67% of **8**.

In summary, we have developed a quick and facile procedure for C–H and Si–H insertion reactions of halodiazoacetates. Ethyl diazobromoacetate (**1**), -chloroacetate (**2**) and -iodoacetate (**3**) insert regioselectively into C–H and Si–H bonds of a range of substrates, with yields up to 82%. The halodiazoacetates are a novel class of diazo compounds that can be used in intermolecular carbenoid C–H insertion reactions, thus broadening the synthetic utility of such reactions. The products from the C–H insertions of **1**–**3** are α-halocarbonyl compounds that can partake in a range of further transformations.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance spectrometer at 300 MHz and 75 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to $CHCl_3$ (7.24 and 77.00 ppm for ^{1}H and ^{13}C, respectively). Mass spectra were recorded on a Micromas Q-Tof-2 mass spectrometer (ESI) or a Fissions Instruments VG Prospec sector instrument at 70 eV (EI). For high-resolution MS measurements, perfluorokerosene was used as a reference compound.

Intermolecular C–H and Si–H Insertion Reactions with Halodiazoacetates; General Procedure

N-Halosuccinimide (0.6 mmol) was added to a solution of EDA (0.057 g, 0.5 mmol) and DBU (0.11 mL, 0.7 mmol) in CH_2Cl_2 (2.5 mL) at 0 °C, and the mixture was stirred for 5 min. The crude mixture was washed with cold 20% aq $Na_2S_2O_3$ (3 × 2 mL), dried ($MgSO_4$) at 0 °C and passed quickly through a silica gel column using cold CH_2Cl_2 as eluent. Toluene (5.0 mL) was added, and the CH_2Cl_2 was removed in vacuo at 0 °C. The appropriate substrate (1.0 mmol) was then added at 0 °C, and the temperature was slowly increased to r.t. A solution of $Rh_2(TPA)_4$ (0.007 g, 0.005 mmol) in toluene (1.0 mL) was added, and the mixture was stirred for 15 min at r.t. The solvent was evaporated in vacuo, and the crude product was purified by flash chromatography (Tables 2 and 3).

Ethyl 2-Bromo-2-(cyclohexa-2,5-dienyl)acetate (4)

Yield: 0.084 g (0.3 mmol, 68%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.31 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.62–2.66 (m, 2 H, CH_2), 3.34–3.44 (m, 1 H, CH), 4.06–4.08 (d, *J* = 7.7 Hz, 1 H, CHBr), 4.20–4.27 (q, *J* = 7.1 Hz, 2 H, CH_2), 5.54–5.60 (m, 1 H, CH), 5.81–5.93 (m, 3 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 26.6 (CH_2), 38.8 (CH), 51.1 (CHBr), 62.0 (CH_2), 124.0 (CH), 124.6 (CH), 127.4 (CH), 128.4 (CH), 168.7 (COO).

MS (EI): *m*/*z* (%) = 244/246 (2.3/2.2, [M$^+$]), 165 (53), 138 (25), 119 (18), 91 (100), 79 (93).

HRMS: *m*/*z* calcd for $C_{10}H_{13}{}^{79}BrO_2$: 244.0099; found: 244.0104 (Δ: –2.2 ppm).

Ethyl 2-Chloro-2-(cyclohexa-2,5-dienyl)acetate (Table 2, Entry 2)

Yield: 0.053 g (0.3 mmol, 53%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30–1.35 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.67–2.73 (m, 2 H, CH_2), 3.42–3.51 (m, 1 H, CH), 4.21–4.23 (d, *J* = 6.4 Hz, 1 H, CHCl), 4.24–4.31 (q, *J* = 7.1 Hz, 2 H, CH_2), 5.60–5.65 (m, 1 H, CH), 5.76–5.81 (m, 1 H, CH), 5.92–5.98 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 26.4 (CH_2), 39.5 (CH), 61.2 (CHCl), 62.0 (CH_2), 123.3 (CH), 123.7 (CH), 127.8 (CH), 128.3 (CH), 168.5 (COO).

MS (EI): *m*/*z* (%) = 200/202 (3.4/0.8, [M$^+$]), 165 (10), 111 (24), 85 (51), 71 (69), 57 (100).

HRMS: *m*/*z* calcd for $C_{10}H_{13}{}^{35}ClO_2$: 200.0604; found: 200.0600 (Δ: 2.1 ppm).

Ethyl 2-Iodo-2-(cyclohexa-2,5-dienyl)acetate (Table 2, Entry 3)

Yield: 0.065 g (0.2 mmol, 45%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.29 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.44–2.68 (m, 2 H, CH_2), 3.12–3.23 (m, 1 H, CH), 4.13–4.16 (d, *J* = 7.8 Hz, 1 H, CHI), 4.17–4.24 (m, 2 H, CH_2), 5.55–5.61 (m, 1 H, CH), 5.85–5.92 (m, 3 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 26.7 (CH_2), 29.9 (CHI), 38.5 (CH), 61.8 (CH_2), 124.8 (CH), 126.9 (CH), 127.2 (CH), 128.1 (CH), 170.3 (COO).

MS (EI): *m*/*z* (%) = 179 (8), 163 (100), 135 (15), 105 (84), 91 (29).

HRMS: *m*/*z* calcd for $C_{10}H_{12}O_2$ (M$^+$ – HI): 164.0837; found: 164.0841 (Δ: –2.3 ppm).

Ethyl 2-Bromo-2-(1,3-dihydroisobenzofuran-3-yl)acetate (Table 3, Entry 1)

Yield: 0.117 g (0.4 mmol, 82%); light yellow oil.

Data reported for a mixture of both diastereomers (DS1 and DS2). DS1 = (2*R**,3*R**).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24–1.31 (m, 2 × 3 H, CH_3), 4.34–4.30 (m, 2 × 2 H, CH_2), ca 4.26 (m, 1 H, CHBr, DS1), 4.46–4.48 (d, *J* = 5.5 Hz, 1 H, CHBr, DS2), 5.02–5.12 (m, 2 H, CH_2O, DS2), 5.16–5.25 (m, 2 H, CH_2O, DS1), 5.65–5.68 (m, 1 H, CHO, DS1), 5.71–5.74 (m, 1 H, CHO, DS2), 7.14–7.57 (8 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 14.1 (CH_3), 47.9 (CHBr, DS1), 50.5 (CHBr, DS2), 62.1 (CH_2), 62.3 (CH_2), 73.2 (CH_2O, DS2), 73.7 (CH_2O, DS1), 83.4 (CHO, DS1), 83.8 (CHO, DS2), 120.9 (CH), 121.2 (CH), 121.9 (CH), 123.6 (CH), 127.2 (CH), 128.6 (CH), 128.7 (CH), 137.4 (C), 137.5 (C), 139.6 (C), 139.8 (C), 167.5 (COO), 168.0 (COO).

MS (EI): *m/z* (%) = 205 (47), 159 (33), 131 (39), 119 (100), 91 (68).

HRMS (ESI): *m/z* calcd for $C_{12}H_{13}{}^{79}BrO_3$ + Na: 306.9945; found: 306.9939 (Δ: –2.2 ppm).

Ethyl 2-Bromo-2-(tetrahydrofuran-2-yl)acetate (Table 3, Entry 3)
Yield: 0.078 g (0.3 mmol, 63%); colourless oil.

Data reported for mixture of both diastereomers (DS1 and DS2). DS1 = (2*R**,3*R**).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23–1.30 (m, 2 × 3 H, CH_3), 1.70–2.20 (m, 2 × 2 H, CH_2), 3.79–3.93 (m, 2 × 2 H, CH_2O), 3.99–4.02 (d, *J* = 8.9 Hz, 1 H, CHBr, DS2), 4.17–4.25 (m, 2 × 2 H, CH_2), ca. 4.19 (m, 1 H, CHBr, DS1), 4.26–4.33 (m, 1 H, CHO, DS1), 4.33–4.40 (m, 1 H, CHO, DS2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 13.9 (CH_3), 25.7 (CH_2, DS2), 26.1 (CH_2, DS1), 29.6 (CH_2, DS1), 29.9 (CH_2, DS2), 47.5 (CHBr, DS2), 49.0 (CHBr, DS1), 62.0 (CH_2, DS2), 62.0 (CH_2, DS1), 68.9 (CH_2O, DS1), 69.4 (CH_2O, DS2), 79.0 (CHO, DS2), 79.2 (CHO, DS1), 168.1 (COO, DS1), 168.5 (COO, DS2).

MS (EI): *m/z* (%) = 157 (7), 111 (13), 71 (100), 43 (24).

HRMS (ESI): *m/z* calcd for $C_8H_{13}{}^{79}BrO_3$ + Na: 258.9945; found: 258.9943 (Δ: –1.1 ppm).

Ethyl 2-Bromo-3-(*N*-methyl-*N*-phenylamino)propanoate (Table 3, Entry 4)
Yield: 0.057 g (0.2 mmol, 40%); light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22-1.26 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.98 (s, 3 H, CH_3), 3.75–3.82 (dd, *J* = 5.1, 15.1 Hz, 1 H, CH_2), 3.97–4.04 (dd, *J* = 9.5, 15.1 Hz, 1 H, CH_2), 4.12–4.22 (m, 2 H, CH_2), 4.36–4.41 (dd, *J* = 5.1, 9.5 Hz, 1 H, CHBr), 6.66–7.34 (m, 5 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 39.3 (CH_3), 41.3 (CH-Br), 56.6 (CH_2), 62.2 (CH_2), 112.2 (CH), 119.8 (CH), 129.4 (CH), 147.9 (C), 169.3 (COO).

MS (EI): *m/z* (%) = 285/287 (7.4/7.4, [M$^+$]), 132 (18), 120 (100), 104 (11), 77 (30).

HRMS: *m/z* calcd for $C_{12}H_{16}{}^{79}BrNO_2$: 285.0364; found: 285.0363 (Δ: 0.4 ppm).

Ethyl 2-Bromo-2-cyclohexylacetate (Table 3, Entry 5)
Yield: 0.015 g (0.06 mmol, 12%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.30 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.51–1.66 (m, 10 H), 1.79–1.87 (m, 2 H), 1.97–2.02 (m, 3 H), 3.92 (s, 1 H, CHBr), 4.15–4.23 (m, 2H, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 28.3 (CH), 36.5 (CH_2), 39.0 (CH_2), 59.8 (CHBr), 61.5 (CH_2), 164.6 (COO).

MS (EI): *m/z* (%) = 205 (8), 166 (100), 138 (31), 95 (45), 55 (35).

Ethyl 2-Bromo-2-adamantylacetate (Table 3, Entry 6)
Yield: 0.03 g (0.01 mmol, 2%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.30 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.51–1.66 (m, 10 H), 1.79–1.87 (m, 2 H), 1.97–2.02 (m, 3 H), 3.92 (s, 1 H, CHBr), 4.15–4.23 (m, 2 H, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 28.3 (CH), 36.5 (CH_2), 39.0 (CH_2), 59.8 (CHBr), 61.5 (CH_2), 164.6 (COO).

MS (EI): *m/z* (%) = 300/302 (0.4/0.4, [M$^+$]), 272 (2), 177 (2), 135 (100), 91 (5).

HRMS: *m/z* calcd for $C_{14}H_{21}{}^{79}BrO_2$: 300.0725; found: 300.0723 (Δ: 0.8 ppm).

Ethyl 2-Bromo-2-diphenylsilylacetate (Table 3, Entry 7)
Yield: 80%, determined by internal standard (1,3,5-trimethoxybenzene) in the ^{1}H NMR spectrum of the crude product mixture.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04–1.08 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.99–4.11 (m, 2 H, CH_2), 4.20–4.21 (d, *J* = 2.9 Hz, 1 H, CH-Br), 5.31–5.23 (d, *J* = 2.9 Hz, SiH), 7.55–7.67 (m, 6 H, CH), 7.81–7.95 (m, 4 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 30.5 (CHBr), 61.9 (CH_2), 128.1 (CH), 130.6 (CH), 134.7 (C), 135.6 (CH), 169.0 (COO).

MS (EI): *m/z* (%) = 348/350 (1.7/1.7, [M$^+$]), 269 (58), 227 (60), 183 (100), 151 (56), 105 (63), 91 (40) (measured for crude product mixture.)

HRMS: *m/z* calcd for $C_{16}H_{16}{}^{79}BrO_2Si$: 347.0103; found: 347.0090 (Δ: 3.6 ppm).

Ethyl 2-Bromo-2-triphenylsilylacetate (Table 3, Entry 8)
Yield: 0.109 g (0.3 mmol, 51%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89–0.99 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.75–4.00 (m, 2 H, CH_2), 4.39 (s, CHBr), 7.35–7.48 (m, 9 H, CH), 7.63–7.67 (m, 6 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6 (CH_3), 31.6 (CHBr), 61.9 (CH_2), 127.9 (CH), 130.3 (CH), 131.3 (C), 136.3 (CH), 169.8 (COO).

MS (EI): *m/z* (%) = 424/426 (0.3/0.3, [M$^+$]), 345 (8), 259 (100), 227 (66), 181 (21), 105 (17), 77 (9).

HRMS (EI): *m/z* calcd for $C_{22}H_{21}{}^{79}BrO_2Si$: 424.0494; found: 424.0510 (Δ: –3.7 ppm).

Ethyl 2-Bromo-2-dimethylphenylsilylacetate (Table 3, Entry 9)
Yield: 0.038 g (0.1 mmol, 25%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.51 (s, 3 H, CH_3), 0.53 (s, 3 H, CH_3), 1.05–1.10 (t, *J* = 7.1 Hz, CH_3), 3.80 (s, 1 H, CHBr), 3.94–4.11 (m, 2 H, CH_2), 7.32–7.43 (m, 3 H, CH), 7.50–7.55 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.5 (CH_3), –4.2 (CH_3), 14.0 (CH_3), 34.5 (CHBr), 61.7 (CH_2), 127.9 (CH), 130.1 (CH), 133.5 (C), 134.0 (CH), 169.8 (COO).

MS (EI): *m/z* (%) = 300/302 (0.1/0.1, [M$^+$]), 221 (21), 165 (34), 135 (100), 103 (68), 75 (21).

HRMS (EI): *m/z* calcd for $C_{12}H_{17}{}^{79}BrO_2Si$: 300.0181; found: 300.0192 (Δ: –3.7 ppm).

1,1,2,2-Tetraphenyldisilanol (5)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.96 (s, 1 H, OH), 5.63 (s, 1 H, SiH), 7.34–7.46 (m, 8 H, CH), 7.55–7.67 (m, 12 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.9 (CH), 130.2 (CH), 134.3 (CH), 134.9 (C).

MS (EI): *m/z* (%) = 382 (4, [M$^+$]), 381 (5), 303 (73), 226 (100), 181 (24), 105 (11).

HRMS (EI): *m/z* calcd for $C_{24}H_{21}{}^{79}BrOSi_2$ (M$^+$ – H): 381.1131; found: 381.1122 (Δ: 2.4 ppm).

1-Ethoxy-1,1,2,2-tetraphenyldisilane (6)
Yield: 0.050 g (0.1 mmol, 24%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34–1.39 (t, *J* = 7.0 Hz, 3 H, CH_3), 3.95–4.02 (q, *J* = 7.0 Hz, 2 H, CH_2), 5.73 (s, 1 H, SiH), 7.37–7.53 (m, 8 H, CH), 7.66–7.81 (m, 12 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3 (CH_3), 58.9 (CH_2), 127.9 (CH), 130.2 (CH), 134.3 (C), 134.9 (CH).

MS (EI): *m*/*z* (%) = 382 (11), 349 (8), 303 (75), 226 (100), 181 (36), 105 (21).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{21}OSi_2$ (M^+ – Et): 381.1131; found: 381.1115 (Δ: 4.1 ppm).

Ethyl 2-Bromo-2-phenylacetate (7)[22]

A suspension of **4** (0.149 g, 0.61 mmol) and DDQ (0.275 g, 1.2 mmol) was stirred in toluene (5 mL) for 1 h at r t. The crude mixture was filtered, concentrated in vacuo, and purified by silica gel chromatography; yield: 0.121 g (0.50 mmol, 82%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23–1.30 (t, *J* = 7.1 Hz, 3 H, CH_3), 4.17–4.23 (m, 2 H, CH_2), 5.32 (s, 1 H, CH), 7.30–7.38 (m, 3 H_{arom}), 7.49–7.56 (m, 2 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 46.8 (CH), 62.5 (CH_2), 128.6 (2 × CH_{arom}), 128.8 (2 × CH_{arom}), 129.2 (CH_{arom}), 135.9 (C_{arom}), 168.3 (COO).

MS (EI): *m*/*z* (%) = 242/244 (2.5/4.5, [M^+]), 169/171 (49/49), 163 (100), 135 (14), 91 (29).

HRMS: *m*/*z* calcd for $C_{10}H_{11}{}^{79}BrO_2$: 241.9942; found: 241.9946 (Δ: –1.5 ppm).

Ethyl 2-Azido-2-phenylacetate (8)[23]

A mixture of **7** (0.115 g, 0.47 mmol) and NaN_3 (0.047 g, 0.71 mmol) was stirred in anhyd DMF (1 mL) under argon for 3 h at r t. After the addition of H_2O (4 mL), the crude mixture was extracted with CH_2Cl_2 (3 × 1 mL). The combined organic layers were washed with H_2O (2 × 4 mL), dried ($MgSO_4$), and concentrated in vacuo; yield: 0.065 g (0.32 mmol, 67%); light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19–1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 4.15–4.24 (q, *J* = 7.1 Hz, 2 H, CH_2), 4.90 (s, 1 H, CH), 7.36 (br s, 5 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 62.5 (CHN_3), 65.2 (CH_2), 127.5 (CH), 129.0 (CH), 129.1 (CH), 133.9 (C), 169.0 (COO).

MS (EI): *m*/*z* (%) = 205 (2.1, [M^+]), 180 (9), 134 (61), 104 (87), 77 (100).

HRMS: *m*/*z* calcd for $C_{10}H_{11}N_3O_2$: 205.0851; found: 205.0842 (Δ: 4.6 ppm).

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