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Catalytic Staudinger Reduction at Room Temperature

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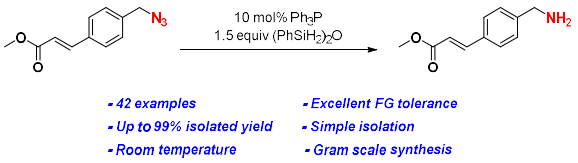


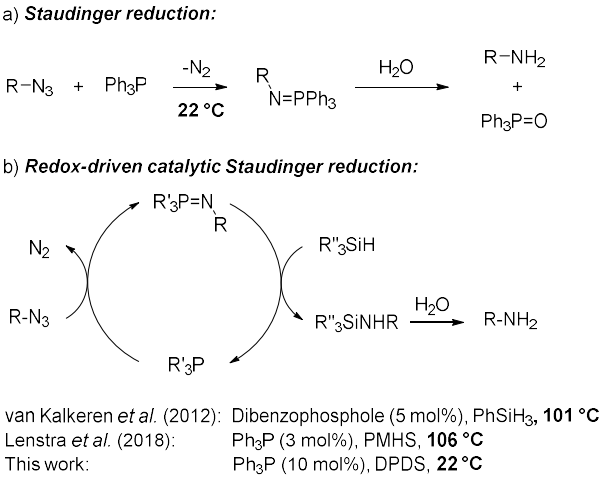
ABSTRACT: We report an efficient catalytic Staudinger reduction at room temperature that enables the preparation of a structurally diverse set of amines from azides in excellent yields. The reaction is based on the use of catalytic amounts of triphenylphosphine as a phosphine source, and diphenyldisiloxane as a reducing agent. Our catalytic Staudinger reduction exhibits a high chemoselectivity, as exemplified by reduction azides over other common functionalities, including nitriles, alkenes, alkynes, esters, and ketones.

The Staudinger reduction (also known as the Staudinger reaction), a phosphine-mediated conversion of organic azides to amines, presents an important synthetic method in the repertoire of chemical reactions that transformed organic chemistry in the past century (Scheme 1a). Since its first report in 1919 by Staudinger and Meyer,[1] the Staudinger reduction has found a widespread use in chemistry, ranging from synthetic organic chemistry and material science to medicinal chemistry and chemical biology.[2] Only recently, two organocatalytic versions of the Staudinger reduction have been developed, both at elevated temperatures (Scheme 1b).[3] Along with recent advances in development of other phosphine-catalyzed reactions, including the Wittig,[4] Appel,[5] and Mitsunobu[6] reactions, the Staudinger ligation,[7] and several other transformations,[8] we are currently lacking efficient catalytic methods that are carried out at room temperature. Here we report the development of the first efficient catalytic Staudinger reaction at room temperature.

Redox-driven organophosphorus catalysis typically relies on efficient hydrosilane-based *in situ* reduction of phosphine oxides (P(V)) to the corresponding phosphines (P(III)).[9] For instance, phenylsilane was used as a reducing agent in the catalytic Staudinger ligation, Staudinger reduction, (Aza-)Wittig, and Mitsunobu reaction. Other frequently used silanes include diphenylsilane,[4c] diethoxymethylsilane,[8c] tetramethyldisiloxane (TMDS),[10] and poly(methylhydrosiloxane) (PMHS).[3a] Even though these reactive silanes have been successfully applied as reducing agents in various organophosphorus-catalyzed reactions, the major drawback is high temperature (typically >100 °C) required for reduction of phosphine oxide to phosphine.[11] Recently, a few methods for the reduction of phosphine oxides to phosphines at room temperature have been reported. Li *et al.* developed an iodine-catalyzed reduction in the presence of phosphites.[12] Aldrich and co-workers found that phosphine oxides can be efficiently reduced in the presence of diphenyldisiloxane ($(PhSiH_2)_2O$,

DPDS)/bis(4-nitrophenyl) phosphate.[13] A third method utilizes pinacol borane, HBpin, as a reducing agent, however, the scope is limited to secondary phosphine oxides.[14]

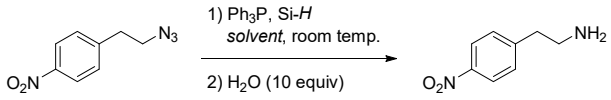
Scheme 1. (a) Classic Staudinger reduction; (b) Organophosphorus-catalyzed Staudinger reduction in the presence of hydrosilane-based reducing agents



We hypothesized that DPDS alone has an ability to reduce at room temperature the iminophosphorane intermediate (unlike the more stable phosphine oxide) that is formed during the catalytic cycle of the Staudinger reduction (Scheme 1b). We started our investigations by testing whether DPDS is a good reducing agent for the catalytic Staudinger reaction, under conditions similar to our previously reported PMHS-mediated reaction.[3a] For this purpose, 4-nitrophenethyl azide (0.5 mmol) was reacted with catalytic amounts of Ph_3P (10 mol%) and diphenyldisiloxane (DPDS, 1.5 equiv) at room temperature (22 °C) for 24 hours in various organic solvents (Table 1, entries 1–4). The amount of 4-nitrophenetylamine formed was determined by ^1H NMR spectroscopy, using 1,3,5-trimethoxybenzene as an internal standard. We were pleased to find that the reaction proceeded very well in toluene, as 96% of 4-nitrophenethylamine was formed from 4-nitrophenethyl azide (Table 1, entry 1). The reaction also works perfectly well in ethereal solvents such as dioxane (98%), THF (99%), and

cyclopentyl methyl ether (CPME, >99% NMR yield). From these ethereal solvents, we were particularly interested in using CPME because it is an environmentally friendly alternative to THF and dioxane.[15] Besides being a sustainable solvent produced from bio-mass, the use of CPME is also safer compared to THF as it resists peroxide formation (i.e. no stabilizers are required).[16]

Table 1. Optimization of the catalytic Staudinger reduction at room temperature[a]



Entry	Phosphorus (equiv)	Silane (equiv)	Solvent	Yield (%)[b]
1	Ph_3P (0.1)	DPDS (1.5)	Toluene	96
2	Ph_3P (0.1)	DPDS (1.5)	Dioxane	98
3	Ph_3P (0.1)	DPDS (1.5)	THF	99
4	Ph_3P (0.1)	DPDS (1.5)	CPME[c]	>99
5	Ph_3P (0.05)	DPDS (1.5)	CPME	80
6	Ph_3P (0.02)	DPDS (1.5)	CPME	27
7[d]	Ph_3P (0.1)	DPDS (1.5)	CPME	97
8[e]	Ph_3P (0.1)	DPDS (1.5)	CPME	44
9[f]	Ph_3P (0.05)	DPDS (1.5)	CPME	98
10[g]	Ph_3P (0.05)	DPDS (1.5)	CPME	>99
11	Ph_3P (0.1)	DPDS (1.1)	CPME	79
12	Ph_3P (0.1)	DPDS (0.6)	CPME	60
13	Ph_3P (0.1)	PMHS (1.5)	CPME	10
14	Ph_3P (0.1)	$PhSiH_3$ (1.5)	CPME	12
15	Ph_3P (0.1)	Ph_2SiH_2 (1.5)	CPME	4
16	-	DPDS (1.5)	CPME	0
17	Ph_3P (0.1)	-	CPME	8
18	Ph_3PO (0.1)	DPDS (1.5)	CPME	0

[a]4-nitrophenethyl azide (0.5 mmol), DPDS (1.5 equiv), Ph_3P (0.1 equiv), solvent (2.0 mL, 0.25 M), 24 h, rt. [b]NMR yield, using 1,3,5-trimethoxybenzene as an internal standard. [c]cyclopentyl methyl ether (CPME). [d]20 h reaction time. [e]8 h reaction time. [f]4 h at 60 °C. [g]30 min at 106 °C.

We then investigated whether we could lower the amount of Ph_3P and found that with 5 mol% of Ph_3P the reaction still proceeds very well, affording 80% of 4-nitrophenethylamine

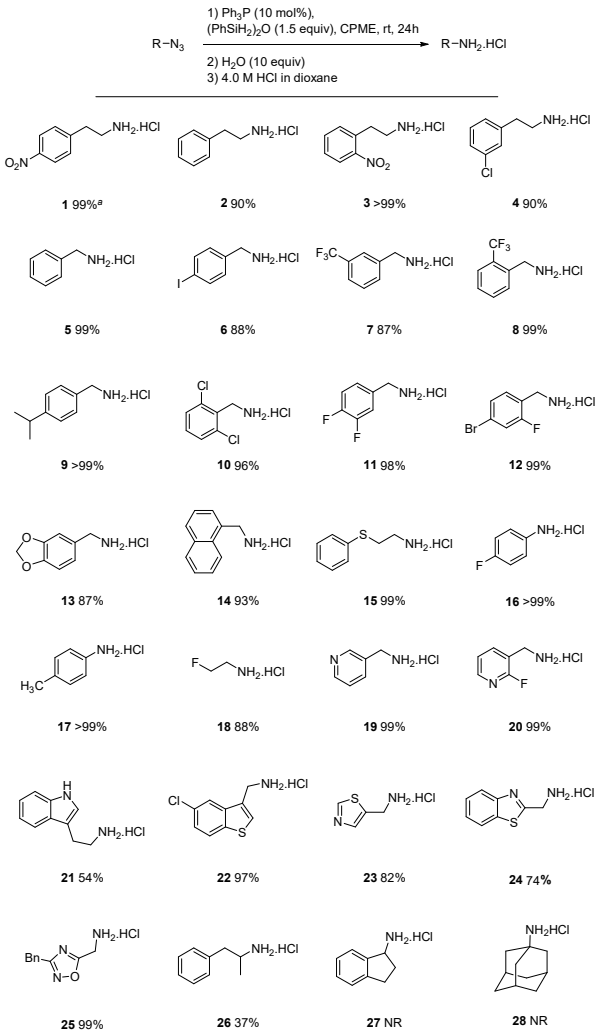
(Table 1, entry 5). When 2 mol% of Ph_3P was used, however, we observed only 27% of the amine product after 24 hours (Table 1, entry 6). A slight decrease in yield of 4-nitrophenethyl amine was observed when the reaction proceeded for 20 hours with 10 mol% Ph_3P (97%), whereas only 44% of amine was obtained after 8 hours (Table 1, entries 7 and 8). We observed that the model reaction proceeded much faster, even in the presence of lower amounts (5 mol%) of Ph_3P, at elevated temperatures: in the presence of 5 mol% Ph_3P the reaction took 4 hours for completion at 60 °C (Table 1, entry 9). Remarkably, a full conversion of 4-nitrophenetyl azide to 4-nitrophenethylamine was observed with 5 mol% Ph_3P in only 30 minutes at 106 °C (with 2 mol% Ph_3P in 1 h), highlighting that our newly reported method is far more efficient when compared to the PMHS-based method developed recently (Table 1, entry 10).[3a] More details on the catalytic Staudinger reduction at room temperature and elevated temperatures can be found in Figures S1 and S2 in Supporting Information. DPDS contains 4 Si-H bonds, thus employing 1.5 equiv of DPDS corresponds to 6 equiv of Si-H. To investigate whether the Si-H excess is required for efficient Staudinger reduction, we examined reactions in the presence of 1.1 (4.4 Si-H) and 0.6 (2.4 Si-H) equiv of DPDS, respectively: we found that decreased amounts of DPDS led to somewhat lower yields (79 and 60%, respectively) (Table 1, entries 11 and 12).

Having shown that a combination of Ph_3P and DPDS enables an efficient catalytic Staudinger reduction at room temperature (Table 1, entry 4), we carried out several important control experiments. Notably, other silane reagents that are commonly used in organophosphorus catalysis, such as poly(methylhydrosiloxane), phenylsilane, and diphenylsilane, are not amenable to the room temperature organophosphorus-catalyzed Staudinger reduction under our conditions (Table 1, entries 13–15). The model reaction in the absence of Ph_3P did not yield detectable amounts of 4-nitrophenethylamine, demonstrating that the reaction is phosphine-catalyzed (Table 1, entry 16). In the absence of DPDS, the Staudinger reduction gave 8% of the amine product; in this case, the small amount of amine was produced

via classic Staudinger reduction in the presence of 10 mol% Ph_3P (Table 1, entry 17). In line with the findings of Aldrich and co-workers[13] that triphenylphosphine oxide is not reduced by DPDS at room temperature without bis(4-nitrophenyl) phosphate additive, we observed no Staudinger reduction in a reaction in which catalytic amounts of triphenylphosphine oxide were used instead of triphenylphosphine (Table 1, entry 18).

With the optimized conditions in hand, we set out to explore the scope of the room temperature organophosphorus-catalyzed Staudinger reduction. The reduction of various substituted phenethyl azides afforded the corresponding amines in very good to excellent isolated yields (Scheme 2, **1**–**4**); the amine products were obtained as hydrochloride salts upon precipitation with 4M HCl (in dioxane), thus making the reaction operationally very simple. It is worth noting that for compounds **1** and **3** we did not observe reduction of the nitro group. The reaction proceeds very well for the reduction of benzyl azide as benzylamine was obtained quantitatively (Scheme 2, **5**). Notably, a gram scale (1.3 gram, 10 mmol) reduction of benzyl azide to benzylamine was also carried out; benzylamine was obtained in excellent 94% isolated yield. Furthermore, various mono- and disubstituted benzylic azides were found to be excellent substrates for this transformation with yields in the range of 87–99% (Scheme 2, **6**–**14**). Thioether **15** was also obtained with an excellent 99% isolated yield. In contrast to our previously reported PMHS-mediated method,[3a] the room temperature organophosphorus-catalyzed Staudinger reduction works very well for aryl azides, as *p*-fluoroaniline **16** and *p*-toluidine **17** were both obtained in quantitative (>99%) isolated yield. Furthermore, 2-fluoroethyl azide was reduced to afford 88% of 2-fluoroethylamine (Scheme 2, **18**).

Scheme 2. Substrate scope for the catalytic Staudinger reduction at room temperature.



[a]isolated yield.

Next, the substrate scope of the reaction with respect to heteroaromatic azides was investigated. The catalytic reduction of pyridines **19** and **20** proceeded very well (99% yield), whereas tryptamine **21** was obtained in a moderate yield (54%). The reaction with benzothiophene-derived azide also underwent nearly quantitative conversion (97%) to the corresponding amine **22**. In addition, thiazole **23** and benzothiazole **24** were formed with good yields of 82% and 74%, respectively. Furthermore, an azide containing a functionalized

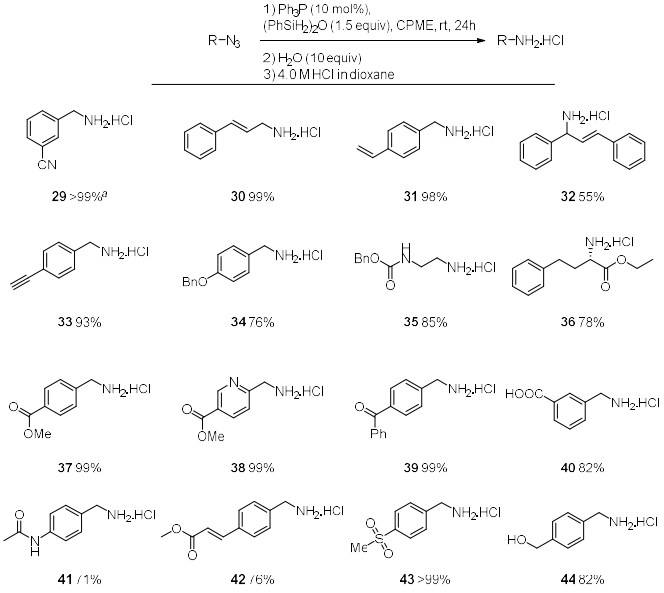
oxadiazole ring was efficiently converted to the corresponding amine **25** with 99% isolated yield.

The reaction scope for secondary and tertiary organic azides was also evaluated. It was found that the reaction is less efficient for secondary azides. 2-Amino-1-phenylpropane **26** was obtained in moderate 37% isolated yield, whereas the reduction of 2-azidoindane did not yield detectable amounts of the amine product (Scheme 2, **27**). In addition, when we attempted a catalytic Staudinger reduction on sterically demanding 1-azidoadamantane, no amine product was obtained, implying that steric effects play an important role in the efficient reduction (Scheme 2, **28**).

Having shown that the catalytic Staudinger reduction proceeds very efficiently for a large panel of primary azides, we explored the scope of the room temperature catalytic Staudinger reduction for azides bearing functional groups that are prone to reduction (Scheme 3). We found that the reaction is highly chemoselective for reduction of azides to amines in the presence of various common functional groups, which would be reduced under catalytic hydrogenation conditions.[17] Notably, under our reaction conditions, we did not observe any reduction of the nitrile (**29**, 99%), alkene (**30**–**32**, 55–99%), alkyne (**33**, 93%), benzyl ether (**34**, 76%), and benzyl carbamate (**35**, 85%) functionalities. As an alternative to the Staudinger reaction, the reduction of organic azides can also be achieved in the presence of metal hydride reagents.[18] Unfortunately, these reagents, such as lithium aluminium hydride, also reduce many other functional groups, including esters, ketones, carboxylic acids, and amides.[19] We were very pleased to find that these carbonyl-containing functional groups remained unaffected under our conditions using Ph_3P and DPDS; in all cases the azide was selectively reduced and the desired amines were obtained in very good to excellent isolated yields in the range of 71–99% (Scheme 3, **36**–**41**). It is worth noting that a combination of reduction-sensitive functional groups is also tolerated well, as exemplified by the chemoselective reduction of an azide bearing both alkene

and ester functionalities (**42** in 76% yield). Furthermore, sulfone containing amine **43** was obtained with virtually quantitative yield (>99%). A chemoselective reduction of azide to amine also proceeds in the presence of alcohol (**44**, 82%). We also attempted to carry out chemoselective reduction of 4-formylbenzyl azide, however, we found that no amine product was obtained.

Scheme 3. Extended substrate scope highlighting the chemoselective nature of the catalytic Staudinger reduction.



[a]isolated yield.

To investigate the mechanism of the room temperature catalytic Staudinger reduction, we carried out various experiments and followed these by NMR spectroscopy. We started by confirming that DPDS does not reduce 4-nitrophenetyl azide in the absence of Ph_3P in 24 hours at room temperature, confirming that no product was formed in an optimization experiment (Table 1, entry 16, Figure S3). Importantly, in agreement with the control experiment (Table 1, entry 18), ^{1}H and ^{31}P NMR data showed that Ph_3PO does not catalyze the conversion of 4-nitrophenetyl azide to 4-nitrophenetylamine in the presence of DPDS, hence excluding the

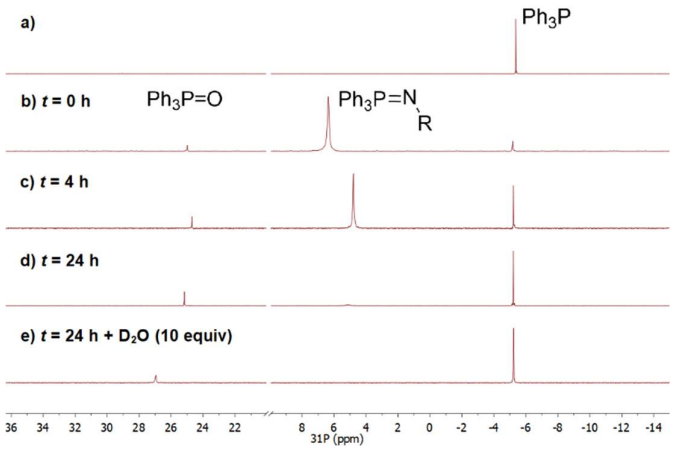


Figure 1. Time-course of the room temperature organophosphorus-catalyzed Staudinger reduction performed in toluene-d_8 followed by *in situ* ^{31}P NMR spectroscopy. ^{31}P NMR spectra of [a]Ph_3P (δ -5.22 ppm); [b]preactivation: Ph_3P mixed with 4-nitrophenethyl azide but absence of DPDS showing formation of iminophosphorane (Ph_3P=N-R, δ 6.35 ppm); [c]postactivation: 4 h after initiation of the reaction with DPDS; [d]24 h reaction time, before quenching; [e]after quenching of the reaction in D_2O.

possibility that the catalytic Staudinger reduction proceeds via the Ph_3PO-mediated pathway (Figure S4). Finally, we monitored the catalytic Staudinger reaction by *in situ* ^{31}P NMR spectroscopy (Figure 1). The iminophosphorane (Ph_3P=N-R, δ 6.35 ppm) was formed immediately upon pre-mixing of 4-nitrophenethyl azide and 10 mol% of Ph_3P (but before the addition of DPDS), and persisted until the reaction was complete. Eventually, Ph_3P (δ -5.22 ppm) was reformed, whereas only traces of Ph_3PO (δ 25.98 ppm) were present from the start of the reaction. In contrast, in the stoichiometric reaction at room temperature, Ph_3P was rapidly consumed to form the iminophosphorane, which was hydrolyzed by water over time to exclusively form Ph_3PO and the amine product: no reformation of Ph_3P was observed (Figure S5). Furthermore, NMR analyses reveal that many different intermediates are present before quenching of the reaction: *i*) all nitrogen that is present in the reaction is either in the form of the silylamine species or has already formed the amine product, and *ii*) multiple hydrides per molecule of DPDS participate in the reaction, as different R_3SiH, R_2SiH_2 and $RSiH_3$ species are formed (Figures S6-S8). Taken together, these observations lead to the conclusion that the

room temperature catalytic Staudinger reduction proceeds via the DPDS-mediated P=N reduction pathway (Scheme 1b).

In summary, we have developed the first efficient organophosphorus-catalyzed Staudinger reduction that proceeds at room temperature. The catalytic Staudinger reduction, which is based on the presence of Ph_3P as a phosphine source and DPDS as a silane source, provides a structurally diverse panel of amines in excellent isolated yields (up to 99%). We demonstrate that the catalytic Staudinger reduction displays a broad substrate scope, and is very tolerant to functional groups that are prone to reduction, as exemplified by chemoselective reduction of azide to amine in the presence of alkenes, alkyne, ester, carboxylic acid, ketone, amide, nitro, nitrile, benzyl ether, carbamate, and sulfone functionalities.

EXPERIMENTAL SECTION

General experimental. All chemicals and solvents were obtained from commercial suppliers and used without further purification. 4-Azidotoluene solution in MTBE (CAS 2101-86-2), 1-Azido-4-fluorobenzene solution in MTBE (CAS 3296-02-4), and 1-azidoadamantane (CAS 24886-73-5) were purchased from Sigma-Aldrich. Phenylsilane (CAS 694-53-1), copper chloride (CAS 7447-39-4), copper iodide (CAS 7681-65-4) and 1-azido-2-fluoroethane (CAS 894792-94-0) were purchased from Fluorochem. Reactions were carried out with constant magnetic stirring under atmospheric conditions. The reaction progress was monitored using thin-layer chromatography (TLC) in the indicated solvent mixture on EMD Silica Gel 60 F_{254} glass plates. Visualisation of the developed plates was performed under UV light (254 nm) and/or staining with ninhydrin or $KMnO_4$.

Nuclear magnetic spectroscopy (NMR) data were recorded at ambient temperature on a Bruker Avance III 400 (400 MHz), or Bruker Avance III 500 (500 MHz, equipped with a Prodigy cryoprobe) spectrometer in the indicated solvents. ^1H NMR chemical shifts are reported as δ in

units of parts per million (ppm) relative to the internal standard tetramethylsilane (TMS, δ = 0 ppm). $^{13}C\{^{1}H\}$ NMR shifts are reported as δ in units of parts per million (ppm) and the spectra were internally referenced to the residual solvent signal ($CHCl_3$ δ = 77.0 ppm, MeOH δ = 49.0 ppm). ^{31}P NMR shifts are reported as δ in units of ppm with respect to Ph_3P (δ -5.2 ppm).[7c] Multiplicities are given as: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), hept (heptet), m (multiplet), app. (apparent). Coupling constants are reported as *J*-values in Hertz (Hz). Infrared spectra (IR-ATR, cm^{-1}) were recorded on a Bruker Tensor 27. Mass spectra (MS, *m/z*) were recorded on a LCQ Advantage MAX (Finnigan) mass spectrometer. High resolution mass spectra (HRMS, ESI+) were recorded on a JEOL AccuTOF CS JMS-T100CS mass spectrometer.

4-Nitrophenethyl azide, phenethyl azide, 2-nitrophenethyl azide, 3-chlorophenethyl azide, benzyl azide, 4-bromo-2-fluorobenzyl azide, 3,4-(methylenedioxy)benzyl azide (piperonyl azide), 1-(azidomethyl)naphthalene, (2-azidoethyl) phenyl sulfide, 2-fluoro-3-(azidomethyl)pyridine, 3-(2-azidoethyl) indole, 5-(azidomethyl) thiazole, 1-phenyl-2-azidopropane, 1-azidoindane, 3-cyanobenzyl azide, cinnamyl azide, 4-benzyloxybenzyl azide, methyl 4-(azidomethyl) benzoate, methyl 6-(azidomethyl) nicotinate, 4-benzoylbenzyl azide, 4-acetamidobenzyl azide, 4-(methylsulfonyl)benzyl azide, and 4-(hydroxymethyl)benzyl azide were synthesized as previously described.[3a]

General procedure I (GPI) for the synthesis of azides from alkyl halides. To a 20 mL mixture of acetone and water (4:1) were subsequently added alkyl halide (4 mmol, 0.2 M final concentration, 1.0 equiv) and NaN_3 (4.8 mmol, 1.2 equiv). The mixture was stirred at room temperature (22 °C, alkyl bromides) or 60 °C (alkyl chlorides) until TLC analysis showed the reaction was complete (typically overnight). After this, brine (50 mL) was added and the product was extracted with Et_2O (3x20 mL). The combined organic layer was dried over

$MgSO_4$, and filtered. After evaporation of the solvent, ^{1}H NMR was taken and if necessary the crude azide was purified by flash column chromatography.

4-Iodobenzyl azide (770 mg, 99% isolated yield, pale yellow oil) was synthesized according to GPI starting from 4-iodobenzyl bromide (890 mg, 4.0 mmol). R_f = 0.50 (EtOAc/*n*-heptane = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 4.32 (s, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.0, 135.0, 130.0, 93.9, 54.2. Data are in accordance to that previously reported.[20]

3-(Trifluoromethyl)benzyl azide (699 mg, 87% isolated yield, pale yellow oil) was synthesized according to GPI starting from 3-(trifluoromethyl)benzyl chloride (778 mg, 4.0 mmol). R_f = 0.60 (EtOAc/*n*-heptane = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 2H), 7.54 – 7.50 (m, 2H), 4.44 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 136.5, 131.3 (q, *J* = 1.2 Hz), 131.2 (q, *J* = 32.3 Hz), 129.4, 125.1 (q, *J* = 3.7 Hz), 124.8 (q, *J* = 3.9 Hz), δ 123.9 (q, *J* = 272.4 Hz), 54.17; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.8. Data are in accordance to that previously reported.[21]

2-(Trifluoromethyl)benzyl azide (526 mg, 87% isolated yield, colorless oil) was synthesized according to GPI starting from (trifluoromethyl)benzyl bromide (717 mg, 3.0 mmol). R_f = 0.60 (EtOAc/*n*-heptane = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 4.60 (s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 133.9 (q, *J* = 1.7 Hz), 132.3, 130.3, 128.3 (q, *J* = 30.6 Hz), 128.3, 126.2 (q, *J* = 5.6 Hz), 124.1 (q, *J* = 273.8 Hz), 51.1 (q, *J* = 2.5 Hz). Data are in accordance to that previously reported.[22]

4-Isopropylbenzyl azide (425 mg, 61% isolated yield, colorless oil) was synthesized according to GPI starting from 4-isopropylbenzyl chloride (675 mg, 4.0 mmol). R_f = 0.65 (EtOAc/*n*-heptane = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 4H), 4.30 (s, 2H), 2.92 (hept, *J* = 6.9

Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.1, 132.7, 128.3, 126.9, 54.7, 33.9, 23.9. Data are in accordance to that previously reported.[23]

2,6-Dichlorobenzyl azide (799 mg, 99% isolated yield, pale yellow oil) was synthesized according to GPI starting from 2,6-dichlorobenzyl chloride (782 mg, 4.0 mmol). R_f = 0.60 (EtOAc/*n*-heptane = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.27 – 7.23 (m, 1H), 4.68 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 136.4, 131.5, 130.3, 128.6, 49.2. Data are in accordance to that previously reported.[23]

3,4-Difluorobenzyl azide (454 mg, 90% isolated yield, colorless oil) was synthesized according to GPI starting from 3,4-difluorobenzyl chloride (487.7 mg, 3.0 mmol). R_f = 0.45 (EtOAc/*n*-heptane = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 2H), 7.09 – 7.04 (m, 1H), 4.34 (s, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 150.4 (dd, *J* = 249.6, 12.9 Hz), 150.2 (dd, *J* = 249.2, 12.6 Hz), 132.4 (dd, *J* = 3.9, 1.4 Hz), 124.1 (dd, *J* = 6.5, 3.7 Hz), 117.4 (dd, *J* = 63.8, 17.6 Hz), 65.2 (d, *J* = 0.9 Hz). Data are in accordance to that previously reported.[24]

3-(Azidomethyl)pyridine (204 mg, 38% isolated yield, colorless oil) was synthesized according to GPI starting from 3-(chloromethyl)pyridine (656 mg, 4.0 mmol). The crude azide was purified by flash column chromatography using 30-50% EtOAc in *n*-heptane. R_f = 0.30 (EtOAc/*n*-heptane = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.51 (m, 2H), 7.73 – 7.62 (m, 1H), 7.34 (ddd, *J* = 7.8, 4.9, 0.9 Hz, 1H), 4.40 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 149.8, 149.4, 135.7, 131.1, 123.7, 52.2. Data are in accordance to that previously reported.[25]

3-(Azidomethyl)-5-chlorobenzo[b]thiophene (636 mg, 95% isolated yield, light yellow solid) was synthesized according to GPI starting from 3-(bromomethyl)-5-chlorobenzo[b]thiophene (784 mg, 3.0 mmol). R_f = 0.60 (EtOAc/*n*-heptane = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.51 – 7.47 (m, 1H), 7.36 (ddd, *J* = 8.6, 2.0, 0.5 Hz, 1H), 4.54 (d, *J* = 0.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 138.8, 138.7, 131.0, 129.8, 127.5, 125.4, 123.9, 121.5, 48.5.

2-(Azidomethyl)benzo[d]thiazole (680 mg, 89% isolated yield, pale green oil) was synthesized according to GPI starting from 2-(chloromethyl)benzo[d]thiazole (735 mg, 4.0 mmol). R_f = 0.70 (EtOAc/*n*-heptane = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 1H), 7.93 – 7.89 (m, 1H), 7.55 – 7.48 (m, 1H), 7.45 – 7.40 (m, 1H), 4.80 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 165.8, 153.1, 135.2, 126.4, 125.6, 123.3, 121.8, 52.1. Data are in accordance to that previously reported.[26]

5-(Azidomethyl)-3-benzyl-1,2,4-oxadiazole (604 mg, 94% isolated yield, pale yellow oil) was synthesized according to GPI starting from 5-(chloromethyl)-3-benzyl-1,2,4-oxadiazole (626 mg, 3.0 mmol). R_f = 0.20 (EtOAc/*n*-heptane = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 4.52 (s, 2H), 4.10 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.0, 169.9, 135.0, 129.0, 128.8, 127.3, 45.1, 32.3.

4-Vinylbenzyl azide (636 mg, 99% isolated yield, pale yellow oil) was synthesized according to GPI starting from 4-vinylbenzyl chloride (610 mg, 4.0 mmol). R_f = 0.55 (100% *n*-heptane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.28 (dd, *J* = 10.9, 0.8 Hz, 1H), 4.32 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.7, 136.2, 134.8, 128.5, 126.6, 114.5, 54.6. Data are in accordance to that previously reported.[27]

4-(Azidomethyl)benzaldehyde (416 mg, 84% isolated yield, yellow oil): To a stirred solution of 4-(azidomethyl)benzyl alcohol (500 mg, 3.06 mmol) in DCM (15 mL) was added pyridinium chlorochromate (1.12 g, 5.21 mmol, 1.7 equiv). The reaction was left to stir at room temperature for 1 hour. Subsequently, the reaction mixture was filtered over a pad of silica gel on a fritted funnel. The solvent was removed *in vacuo* to afford the desired azide without further purification. R_f = 0.75 (EtOAc/*n*-heptane = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 4.46 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz,

$CDCl_3$) δ 191.6, 142.1, 136.2, 130.2, 128.5, 54.3. Data are in accordance to that previously reported.[27]

4-Ethynylbenzyl azide (108 mg, 55% isolated yield, colorless oil): To a stirred solution of 4-(azidomethyl)benzaldehyde (200 mg, 1.25 mmol) and K_2CO_3 (343 mg, 2.5 mmol, 1.5 equiv) in MeOH (20 mL) was added dimethyl (1-diazo-2-oxopropyl)phosphonate solution (Bestmann-Ohira reagent, 1.3 equiv) at room temperature. The reaction mixture was left to stir at room temperature overnight, after which it was quenched by the addition of sat. aq. $NaHCO_3$ (10 mL). The crude mixture was concentrated *in vacuo* in order to remove the MeOH. Subsequently, the solution was diluted with EtOAc (10 mL), washed with water (2 x 10 mL), brine (1 x 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude alkyne was purified by flash column chromatography (0-5% EtOAc in *n*-heptane). R_f = 0.50 (EtOAc/*n*-heptane = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.35 (s, 2H), 3.10 (s, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 136.1, 132.6, 128.1, 122.2, 83.1, 54.4. Data are in accordance to that previously reported.[28]

Benzyl (2-azidoethyl)carbamate (515 mg, 78% isolated yield, colorless oil) was synthesized according to GPI starting from benzyl (2-chloroethyl)carbamate (641 mg, 3.0 mmol). R_f = 0.30 (EtOAc/*n*-heptane = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 5.12 (s, 2H), 5.04 (bs, 1H), 3.45 (t, *J* = 5.5 Hz, 2H), 3.38 (t, *J* = 5.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.2, 136.3, 128.6, 128.2, 128.1, 67.0, 51.2, 40.5. Data are in accordance to that previously reported.[29]

3-(Azidomethyl)benzoic acid (495 mg, 93% isolated yield, off-white solid) was synthesized according to GPI starting from 3-(chloromethyl)benzoic acid (512 mg, 3.0 mmol). R_f = 0.30 (EtOAc/*n*-heptane = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 2H), 7.59 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.52 (td, *J* = 7.7, 0.6 Hz, 1H), 4.44 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ

171.6, 136.1, 133.4, 130.1, 129.9, 129.8, 129.1, 54.3. Data are in accordance to that previously reported.[30]

Methyl (E)-3-(4-(azidomethyl)phenyl)acrylate (650 mg, >99% isolated yield, pale yellow oil) was synthesized according to GPI starting from methyl (*E*)-3-(4-(bromomethyl)phenyl)acrylate (765 mg, 4.0 mmol). R_f = 0.30 (EtOAc/*n*-heptane = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.39 (s, 2H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.3, 144.0, 137.6, 134.4, 128.6, 128.5, 118.4, 54.4, 51.8.

General procedure II (GPII) for the synthesis of azides from alcohols.[31] In a dried reaction flask under a protected atmosphere, the respective alcohol (1.0 equiv) was dissolved in dry DCM to obtain a 0.1 M solution. The mixture was cooled to -30 °C followed by the addition of triethylamine (1.5 equiv) and methanesulfonyl chloride (1.3 equiv). The reaction mixture was allowed to stir at -30 °C for 5 hours after which it was allowed to warm to room temperature. After additional stirring at room temperature for 30 minutes the solvent was removed *in vacuo*. The obtained solid was redissolved in anhydrous dimethylformamide (DMF, 0.1 M) followed by the addition of NaN_3 (2.0 equiv). The reaction was left to stir at room temperature for 20 h. The reaction mixture was diluted by the addition of water (50 mL) and extracted with Et_2O (3x20 mL). The combined organic layers were washed with brine (1x50 mL), dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo*, and the crude azide was purified by flash column chromatography.

(E)-(3-Azidoprop-1-ene-1,3-diyl)dibenzene (541 mg, 58% isolated yield, colorless oil) was synthesized according to GPII starting from (*E*)-1,3-diphenylprop-2-en-1-ol (841.1 mg, 4.0 mmol). The crude azide was purified by flash column chromatography using 1% EtOAc in *n*-heptane. R_f = 0.60 (EtOAc/*n*-heptane = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.23 (m, 10H), 6.72 (dd, *J* = 15.7, 1.4 Hz, 1H), 6.29 (dd, *J* = 15.7, 7.2 Hz, 1H), 5.21 (dd, *J* = 7.2, 1.4 Hz,

1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 138.6, 135.9, 133.0, 128.8, 128.6, 128.3, 128.2, 127.1, 126.9, 126.7, 67.2. Data are in accordance to that previously reported.[32]

Ethyl (S)-2-azido-4-phenylbutanoate (213 mg, 23% isolated yield, colorless oil) was synthesized according to GPII. R_f = 0.65 (EtOAc/*n*-heptane = 3:7); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.81 (dd, *J* = 8.9, 5.0 Hz, 1H), 2.84 – 2.64 (m, 2H), 2.21 – 2.11 (m, 1H), 2.10 – 2.01 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.4, 140.1, 128.6, 128.5, 126.4, 61.8, 61.2, 32.9, 31.8, 14.2. Data are in accordance to that previously reported.[3a]

General procedure for the catalytic Staudinger reduction. Azide (0.25 or 0.5 mmol, 1.0 equiv) and diphenyldisiloxane (DPDS, 1.5 equiv) were combined in a glass vial containing a magnetic stir bar. The mixture was dissolved in CPME (0.25 M final conc.) and to this Ph_3P (0.1 equiv) was added. Gas evolves from the reaction immediately. The reaction was left to stir at room temperature (22 °C) for 24 h, after which it was quenched by the addition of water (10 equiv). The mixture was allowed to stir until gas stopped evolving, subsequently, the mixture was diluted two times with Et_2O. The desired amine was obtained as the corresponding hydrochloride salt by precipitation with 0.5 mL of 4.0 M HCl in dioxane.

4-Nitrophenethylamine hydrochloride (Compound **1**, 105 mg, 99% isolated yield, off-white solid) was synthesized according to GPIII starting from 4-nitrophenethyl azide (96 mg, 0.5 mmol). ^1H NMR (400 MHz, CD_3OD) δ 8.26 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 3.29 (t, *J* = 7.8 Hz, 2H), 3.14 (t, *J* = 7.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 149.5, 146.6, 131.9, 125.8, 42.1, 35.0; MS (ESI) *m*/*z* 167.3 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

Phenethylamine hydrochloride (Compound **2**, 72 mg, 90% isolated yield, white solid) was synthesized according to GPIII starting from phenethyl azide (74 mg, 0.5 mmol). ^1H NMR (400

MHz, CD_3OD) δ 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 3.20 (t, *J* = 8.3 Hz, 2H), 2.97 (t, *J* = 8.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 138.8, 130.9, 130.6, 129.2, 42.8, 35.4; MS (ESI) *m*/*z* 122.3 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

2-Nitrophenethylamine hydrochloride (Compound **3**, 104 mg, >99% isolated yield, off-white solid) was synthesized according to GPIII starting from 2-nitrophenethyl azide (97.09 mg, 0.5 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.52 – 7.47 (m, 2H), 7.41 – 7.35 (m, 2H), 7.32 – 7.27 (m, 1H), 3.27 (t, *J* = 7.0 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 151.7, 135.8, 134.6, 133.7, 130.8, 127.1, 42.0, 32.8; MS (ESI) *m*/*z* 167.3 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

3-Chlorophenethylamine hydrochloride (Compound **4**, 43.1 mg, 90% isolated yield, white solid) was synthesized according to GPIII starting from 3-chlorophenethyl azide (45.4 mg, 0.25 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.42 – 7.33 (m, 1H), 7.36 – 7.22 (m, 1H), 3.22 (t, *J* = 7.8 Hz, 1H), 3.00 (dd, *J* = 8.7, 6.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 141.1, 136.6, 132.4, 130.8, 129.3, 129.1, 42.5, 35.0; MS (ESI) *m*/*z* 156.2 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

Benzylamine hydrochloride (Compound **5**, 90 mg, 93% isolated yield, white solid) was synthesized according to GPIII starting from benzyl azide (91 mg, 0.5 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.54 – 7.40 (m, 4H), 4.15 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 134.4, 130.1, 130.1, 130.1, 44.3; MS (ESI) *m*/*z* 107.9 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

4-Iodobenzylamine hydrochloride (Compound **6**, 59.0 mg, 88% isolated yield, white solid) was synthesized according to GPIII starting from 4-iodobenzyl azide (64.8 mg, 0.25 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.11 (s, 2H);

$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 138.0, 132.7, 130.7, 94.3, 42.4; MS (ESI) *m/z* 233.8 $[M+H]^+$. Data are in accordance to that previously reported.[33]

3-(Trifluoromethyl)benzylamine hydrochloride (Compound **7**, 41.0 mg, 78% isolated yield, white solid) was synthesized according to GPIII starting from 3-(trifluoromethyl)benzyl azide (50.3 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.90 – 7.84 (m, 1H), 7.82 – 7.74 (m, 2H), 7.72 – 7.64 (m, 1H), 4.26 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 134.4, 132.6 (q, *J* = 1.3 Hz), 131.0 (q, *J* = 32.6 Hz), 129.7, 125.5 (dq, *J* = 4.0, 0.6 Hz), 124.0 (q, *J* = 271.7 Hz), 42.3; ^{19}F NMR (377 MHz, CD_3OD) δ -64.2; MS (ESI) *m/z* 175.9 $[M+H]^+$. Data are in accordance to that previously reported.[34]

2-(Trifluoromethyl)benzylamine hydrochloride (Compound **8**, 52.0 mg, 99% isolated yield, white solid) was synthesized according to GPIII starting from 2-(trifluoromethyl)benzyl azide (50.3 mg, 0.25 mmol). ^{1}H NMR (500 MHz, CD_3OD) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.82 – 7.72 (m, 2H), 7.69 – 7.63 (m, 1H), 4.35 (s, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 132.9, 131.0, 130.8, 129.44, 128.5 (q, *J* = 30.5 Hz), 126.3 (q, *J* = 5.6 Hz), 124.2 (q, *J* = 272.9 Hz), 39.3 (q, *J* = 2.9 Hz); ^{19}F NMR (377 MHz, CD_3OD) δ -60.54; MS (ESI) *m/z* 175.9 $[M+H]^+$. Data are in accordance to that previously reported.[34]

4-Isopropylbenzylamine hydrochloride (Compound **9**,46.1 mg, >99% isolated yield, white solid) was synthesized according to GPIII starting from4-isopropylbenzyl azide (43.8 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.11 (s, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 150.0, 130.4, 128.7, 126.8, 42.7, 33.8, 22.9; MS (ESI) *m/z* 149.8 $[M+H]^+$. Data are in accordance to that previously reported.[35]

2,6-Dichlorobenzylamine hydrochloride (Compound **10**, 60.0 mg, 96% isolated yield, white solid) was synthesized according to GPIII starting from 2,6-dichlorobenzyl azide (50.5 mg, 0.25

mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.60 – 7.53 (m, 1H), 7.48 (dd, *J* = 9.1, 7.0 Hz, 1H), 4.50 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 136.3, 131.8, 129.0, 128.7, 37.9; MS (ESI) *m/z* 175.9 $[M+H]^+$. Data are in accordance to that previously reported.[36]

3,4-Difluorobenzylamine hydrochloride (Compound **11**, 44.0 mg, 98% isolated yield, white solid) was synthesized according to GPIII starting from 3,4-difluorobenzyl azide (42.3 mg, 0.25 mmol). ^{1}H NMR (500 MHz, CD_3OD) δ 7.49 (ddd, *J* = 11.2, 7.6, 1.8 Hz, 1H), 7.45 – 7.28 (m, 2H), 4.16 (s, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 150.6 (dd, *J* = 248.6, 12.2 Hz), 150.2 (dd, *J* = 247.5, 12.4 Hz), 130.4 (dd, *J* = 6.1, 4.0 Hz), 125.8 (dd, *J* = 6.8, 3.7 Hz), 118.1 (d, *J* = 18.5 Hz), 117.7 (d, *J* = 17.7 Hz), 41.9; ^{19}F NMR (377 MHz, CD_3OD) δ -139.2 (d, *J* = 20.7 Hz), -139.8 (d, *J* = 20.7 Hz); IR (cm^{-1}) 2975, 1526, 1290, 826, 773; MS (ESI) *m/z* 143.9 $[M+H]^+$; HRMS (ESI) found *m/z* 144.0640 $[M+H]^+$, calcd for $C_7H_8F_2N^+$ *m/z* 144.0619.

4-Bromo-2-fluorobenzylamine hydrochloride (Compound **12**, 127 mg, 99% isolated yield, off-white solid) was synthesized according to GPIII starting from 4-bromo-2-fluorobenzyl azide (155 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.59 – 7.44 (m, 3H), 4.20 (d, *J* = 1.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 163.2 (d, *J* = 252.0 Hz), 134.6 (d, *J* = 3.7 Hz), 130.3 (d, *J* = 3.7 Hz), 125.9 (d, *J* = 9.8 Hz), 121.8 (d, *J* = 15.0 Hz), 121.4 (d, *J* = 24.9 Hz), 38.4 (d, *J* = 4.1 Hz); ^{19}F NMR (377 MHz, CD_3OD) δ -116.0; MS (ESI) *m/z* 204.2 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

3,4-(Methylenedioxy)benzylamine (piperonylamine) hydrochloride (Compound **13**, 82 mg, 87% isolated yield, off-white solid) was synthesized according to GPIII starting from piperonyl azide (89 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.00 – 6.95 (m, 2H), 6.92 – 6.88 (m, 1H), 6.02 (s, 2H), 4.05 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 150.7, 150.6, 128.8, 125.0, 111.1, 110.5, 103.8, 45.1; MS (ESI) *m/z* 152.1 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

1-Naphthylmethylamine hydrochloride (Compound **14**, 90 mg, 93% isolated yield, off-white solid) was synthesized according to GPIII starting from 1-(azidomethyl)naphthalene (91 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 8.15 (dq, J = 8.4, 1.0 Hz, 1H), 8.06 – 7.97 (m, 2H), 7.74 – 7.54 (m, 4H), 4.67 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 136.3, 133.2, 132.0, 131.1, 131.0, 129.7, 129.2, 128.4, 127.4, 124.5, 42.2; MS (ESI) *m*/*z* 157.9 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

(2-Aminoethyl) phenyl sulfide hydrochloride (Compound **15**, 100 mg, 99% isolated yield, off-white solid) was synthesized according to GPIII starting from (2-azidoethyl) phenyl sulfide (89 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.54 – 7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.32 – 7.27 (m, 1H), 3.27 (t, J = 7.0 Hz, 2H), 3.13 (t, J = 7.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 133.6, 130.2, 129.1, 127.0, 38.4, 30.6;MS (ESI) *m*/*z* 154.3 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

4-Fluoroaniline hydrochloride (Compound **16**, 92 mg, >99% isolated yield, off-white solid) was synthesized according to GPIII starting from 1-azido-4-fluorobenzene (84 mg, 0.6 mmol, 0.5M in MTBE). ^{1}H NMR (400 MHz, CD_3OD) δ 7.55 (dd, J = 9.0, 4.5 Hz, 2H), 7.31 (dd, J = 9.0, 8.3 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 164.7 (d, J = 247.3 Hz), 128.8 (d, J = 3.2 Hz), 127.3 (d, J = 8.9 Hz), 118.8 (d, J = 23.8 Hz). ^{19}F NMR (377 MHz, CD_3OD) δ -114.25; MS (ESI) *m/z* 112.3 $[M+H]^+$. Data are in accordance to that previously reported.[37]

p-Toluidine hydrochloride (Compound **17**, 89 mg, >99% isolated yield, yellow solid) was synthesized according to GPIII starting from 1-azido-4-methylbenzene (82 mg, 0.6 mmol, 0.5M in MTBE). ^{1}H NMR (400 MHz, CD_3OD) δ 7.37 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.42 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 141.5, 132.6, 130.1, 124.7, 21.8; MS (ESI) *m*/*z* 108.3 $[M+H]^+$. Data are in accordance to that previously reported.[38]

2-Fluoroethylamine hydrochloride (Compound **18**, 44 mg, 88% isolated yield, white solid) was synthesized according to GPIII starting from 1-azido-2-fluoroethane (45 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 4.82 – 4.78 (m, 1H), 4.70 – 4.67 (m, 1H), 3.37 (t, J = 4.7 Hz, 1H), 3.30 (t, J = 4.7 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 82.1 (d, J = 167.2 Hz), 42.1 (d, J = 20.0 Hz); ^{19}F NMR (377 MHz, CD_3OD) δ -228.13; MS (ESI): *m/z* 64.2 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

3-(Aminomethyl)pyridine hydrochloride (Compound **19**, 35.9 mg, 99% isolated yield, white solid) was synthesized according to GPIII starting from 3-(azidomethyl)pyridine (33.5 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 9.16 – 9.10 (d, J = 2.0 Hz, 1H), 8.99 (dt, J = 5.8, 1.0 Hz, 1H), 8.89 – 8.81 (m, 1H), 8.24 (ddd, J = 8.1, 5.8, 1.0 Hz, 1H), 4.50 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 147.5, 142.4, 142.1, 133.8, 127.5, 39.4; MS (ESI) *m/z* 109.1 $[M+H]^+$. Data are in accordance to that previously reported.[39]

2-Fluoro-3-(aminomethyl)pyridine hydrochloride (Compound **20**, 97 mg, 99% isolated yield, off-white solid) was synthesized according to GPIII starting from 2-fluoro-3-(azidomethyl)pyridine (85 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 8.32 (ddd, J = 5.0, 1.9, 1.1 Hz, 1H), 8.10 (ddd, J = 9.6, 7.5, 1.9 Hz, 1H), 7.45 (ddd, J = 7.5, 5.0, 1.9 Hz, 1H), 4.26 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 163.8 (d, J = 239.2 Hz), 150.6 (d, J = 14.4 Hz), 144.7 (d, J = 4.1 Hz), 124.4 (d, J = 4.4 Hz), 117.7 (d, J = 30.0 Hz), 38.7; ^{19}F NMR (377 MHz, CD_3OD) δ -73.58; MS (ESI) *m/z* 127.0 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

3-(2-Aminoethyl)indole hydrochloride (Compound **21**, 53mg, 54% isolated yield, grey solid) was synthesized according to GPIII starting from 3-(2-azidoethyl) indole (93 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.57 (dt, J = 8.1, 1.0 Hz, 1H), 7.38 (dt, J = 8.1, 0.9 Hz, 1H), 7.18 (bs, 1H), 7.16 – 7.10 (m, 1H), 7.08 – 7.02 (m, 1H), 3.24 (t, J = 7.3 Hz, 2H), 3.13 (t, J = 7.3 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 138.4, 128.2, 124.3, 122.8, 120.0, 118.9,

112.6, 110.2, 41.3, 24.5; MS (ESI) *m/z* 161.22 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

3-(Aminomethyl)-5-chlorobenzo[d]thiazole hydrochloride (Compound **22**, 56.6 mg, 97% isolated yield, off-white solid) was synthesized according to GPIII starting from 3-(azidomethyl)-5-chlorobenzo[d]thiazole (55.9 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 8.03 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.92 (s, 1H), 7.45 (dd, *J* = 8.6, 2.0 Hz, 1H), 4.43 (s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD) δ 138.7, 138.5, 130.9, 129.7, 127.4, 125.1, 123.9, 120.9, 35.7; IR (cm^{-1}) 2965, 1588, 1427, 1151, 1079, 783 ; MS (ESI) *m/z* 197.8 $[M+H]^+$; HRMS (ESI) found *m/z* 198.0158 $[M+H]^+$, calcd for $C_9H_9ClNS^+$ *m/z* 198.0139.

5-(Aminomethyl)thiazole hydrochloride (Compound **23**, 67 mg, 82% isolated yield, white solid) was synthesized according to GPIII starting from 5-(azidomethyl)thiazole (61 mg, 0.43 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 9.75 (s, 1H), 8.36 (d, *J* = 1.0 Hz, 1H), 4.58 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 160.9, 142.0, 134.8, 36.6; MS (ESI) *m/z* 115.0 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

2-(Aminomethyl)benzo[d]thiazole hydrochloride (Compound **24**, 37.0 mg, 74% isolated yield, light brown solid) was synthesized according to GPIII starting from 2-(azidomethyl)benzo[d]thiazole (47.6 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 8.11 – 8.02 (m, 2H), 7.58 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.50 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 4.67 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 162.3, 152.3, 135.3, 126.4, 125.7, 122.8, 121.7, 40.3; MS (ESI) *m/z* 164.9 $[M+H]^+$. Data are in accordance to that previously reported.[40]

(3-Benzyl-1,2,4-oxadiazol-5-yl)methanamine hydrochloride (Compound **25**, 55.6 mg, 99% isolated yield, off-white solid) was synthesized according to GPIII starting from 5-(azidomethyl)-3-benzyl-1,2,4-oxadiazole (53.8 mg, 0.25 mmol). ^{1}H NMR (500 MHz, CD_3OD) δ 7.38 – 7.21 (m, 5H), 4.52 (s, 2H), 4.14 (s, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD) δ 174.3,

171.2, 136.7, 130.1, 129.7, 128.2, 36.1, 32.7; IR (cm^{-1}) 2933, 1600, 717, 695; MS (ESI) *m/z* 189.9 $[M+H]^+$; HRMS (ESI) found *m/z* 190.0978 $[M+H]^+$, calcd for $C_{10}H_{12}N_3O^+$ *m/z* 190.0975.

1-Phenyl-2-aminopropane hydrochloride (Compound **26**, 32 mg, 37% isolated yield, off-white solid) was synthesized according to GPIII starting from 1-phenyl-2-azidopropane (80 mg, 0.5 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.42 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 3.56 (dt, *J* = 8.1, 6.3 Hz, 1H), 3.05 (dd, *J* = 13.5, 6.3 Hz, 1H), 2.84 (dd, *J* = 13.5, 8.1 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 138.3, 131.2, 130.8, 129.2, 51.2, 42.6, 19.1; MS (ESI) *m/z* 136.3 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

3-Cyanobenzylamine hydrochloride (Compound **29**, 88 mg, >99% isolated yield, white solid) was synthesized according to GPIII starting from 3-cyanobenzyl azide (80 mg, 0.5 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.97 (t, *J* = 1.5 Hz, 1H), 7.90 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.82 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 4.29 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 136.9, 135.9, 134.7, 134.6, 132.2, 120.0, 114.8, 44.3; MS (ESI) *m/z* 133.3 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

Cinnamyl amine hydrochloride (Compound **30**, 85 mg, 99% isolated yield, off-white solid) was synthesized according to GPIII starting from cinnamyl azide (80 mg, 0.5 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.51 – 7.47 (m, 2H), 7.42 – 7.29 (m, 3H), 6.85 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.9 Hz, 1H), 3.75 (d, *J* = 6.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 138.7, 138.0, 130.7, 130.5, 128.6, 122.0, 43.4; MS (ESI) *m/z* 134.2 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

4-Vinylbenzylamine hydrochloride (Compound **31**, 41.4 mg, 98% isolated yield, off-white solid) was synthesized according to GPIII starting from 4-vinylbenzyl azide (39.8 mg, 0.25 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.78 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.31 (dd, *J* = 10.9, 0.9 Hz, 1H),

4.13 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 138.5, 135.9, 132.4, 128.9, 126.5, 113.9, 42.7; MS (ESI) *m/z* 133.8 $[M+H]^+$. Data are in accordance to that previously reported.[41]

(E)-1,3-Diphenyl-2-propene-1-amine hydrochloride (Compound **32**, 33.5 mg, 55% isolated yield, white solid) was synthesized according to GPIII starting from (*E*)-1,3-diphenyl-2-propene-1-azide (58.8 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ7.60 – 7.40 (m, 7H), 7.38 – 7.25 (m, 3H), 6.82 (d, *J* = 15.9 Hz, 1H), 6.54 (dd, *J* = 15.9, 7.6 Hz, 1H), 5.16 (d, *J* = 7.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 136.5, 135.5, 134.8, 129.1, 128.9, 128.4, 128.4, 127.0, 126.5, 124.2, 56.9; MS (ESI) *m/z* 210.2 $[M+H]^+$. Data are in accordance to that previously reported.[42]

4-Ethynylbenzylamine hydrochloride (Compound **33**, 39.0 mg, 93% isolated yield, white solid) was synthesized according to GPIII starting from 4-ethynylbenzyl azide (39.3 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 4.16 (s, 2H), 3.61 (s, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 133.6, 132.3, 128.8, 123.3, 82.2, 78.6, 42.6; MS (ESI) *m/z* 131.8 $[M+H]^+$. Data are in accordance to that previously reported.[43]

4-Benzyloxybenzylamine hydrochloride (Compound **34**, 95 mg, 76% isolated yield, off-white solid) was synthesized according to GPIII starting from 4-benzyloxybenzyl azide (120 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.47 – 7.29 (m, 7H), 7.08 (d, *J* = 8.7 Hz, 1H), 5.13 (s, 2H), 4.07 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 161.6, 139.2, 132.5, 130.4, 129.8, 129.4, 127.4, 117.4, 71.8, 44.7; MS (ESI) *m/z* 214.1 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

Benzyl (2-aminoethyl)carbamate hydrochloride (Compound **35**, 49.3 mg, 85% isolated yield, off-white solid) was synthesized according to GPIII starting from benzyl (2-azidoethyl)carbamate (55.1 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.45 – 7.23 (m, 5H), 5.12 (s, 2H), 3.44 (t, *J* = 5.9 Hz, 2H), 3.09 (t, *J* = 5.9 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz,

CD_3OD) δ 157.9, 136.6, 128.1, 127.7, 127.6, 66.5, 39.7, 38.1; MS (ESI) *m/z* 194.9 $[M+H]^+$. Data are in accordance to that previously reported.[44]

Ethyl (S)-2-amino-4-phenylbutanoate hydrochloride (Compound **36**, 47.8 mg, 78% isolated yield, white solid) was synthesized according to GPIII starting from ethyl (*S*)-2-azido-4-phenylbutanoate (58.3 mg, 0.25 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.41 – 7.13 (m, 5H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.07 (t, *J* = 6.3 Hz, 1H), 2.92 – 2.69 (m, 2H), 2.36 – 2.11 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 169.0, 139.7, 128.3, 128.1, 126.2, 62.3, 52.2, 32.1, 30.6, 13.1; MS (ESI) *m/z* 208.0 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

Methyl (4-aminomethyl)benzoate hydrochloride (Compound **37**, 100 mg, 99% isolated yield, white solid) was synthesized according to GPIII starting from methyl (4-azidomethyl)benzoate (95 mg, 0.5 mmol). ^1H NMR (400 MHz, CD_3OD) δ 8.16 – 8.08 (m, 2H), 7.66 – 7.58 (m, 2H), 4.24 (s, 2H), 3.95 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 168.7, 140.4, 132.9, 132.1, 131.0, 53.7, 44.7; MS (ESI) *m/z* 165.9 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

Methyl 6-(aminomethyl)nicotinate hydrochloride (Compound **38**, 117 mg, 99% isolated yield, off-white solid) was synthesized according to GPIII starting from methyl 6-(azidomethyl)nicotinate (95 mg, 0.5 mmol). ^1H NMR (400 MHz, CD_3OD) δ 9.25 (dd, *J* = 2.1, 0.8 Hz, 1H), 8.52 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.73 (dd, *J* = 8.2, 0.8 Hz, 1H), 4.47 (s, 2H), 4.00 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 167.1, 158.1, 151.4, 141.2, 128.6, 124.8, 54.0, 44.5; MS (ESI) *m/z* 167.1 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

4-Benzoylbenzylamine hydrochloride (Compound **39**, 122 mg, 99% isolated yield, off-white solid) was synthesized according to GPIII starting from 4-benzoylbenzyl azide (119 mg, 0.50 mmol). ^1H NMR (400 MHz, CD_3OD) δ 7.90 – 7.85 (m, 2H), 7.83 – 7.78 (m, 2H), 7.73 – 7.65

(m, 3H), 7.58 (dddd, J = 8.4, 6.6, 1.5, 0.9 Hz, 2H), 4.28 (s, 2H), 3.38 (s, 1H); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 196.3, 138.0, 137.5, 137.1, 132.7, 130.2, 129.6, 128.7, 128.2, 42.5; MS (ESI) *m/z* 212.0 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

3-(Aminomethyl)benzoic acid hydrochloride (Compound **40**, 38.5 mg, 82% isolated yield, white solid) was synthesized according to GPIII starting from 3-(azidomethyl)benzoic acid (44.3 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 8.18 (t, J = 1.5 Hz, 1H), 8.09 (dt, J = 7.7, 1.5 Hz, 1H), 7.75 (dt, J = 7.7, 1.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 4.23 (s, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 167.6, 133.5, 133.2, 131.5, 130.0, 129.9, 129.0, 42.6; MS (ESI) *m/z* 151.9 $[M+H]^+$. Data are in accordance to that previously reported.[45]

4-Acetamidobenzylamine hydrochloride (Compound **41**, 84 mg, 71% isolated yield, light yellow solid) was synthesized according to GPIII starting from 4-acetamidobenzyl azide (94 mg, 0.50 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.72 – 7.64 (m, 2H), 7.48 – 7.40 (m, 2H), 4.11 (s, 2H), 2.17 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 172.7, 141.7, 131.5, 130.6, 122.3, 44.8, 24.7; MS (ESI) *m/z* 164.0 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

Methyl (E)-3-(4-(aminomethyl)phenyl)acrylate hydrochloride (Compound **42**, 43.1 mg, 76% isolated yield, off-white solid) was synthesized according to GPIII starting from methyl (*E*)-3-(4-(azidomethyl)phenyl)acrylate (54.3 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.76 – 7.69 (m, 3H), 7.56 – 7.52 (m, 2H), 6.61 (d, J = 16.1 Hz, 1H), 4.18 (s, 2H), 3.81 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 167.4, 143.7, 135.1, 135.1, 129.2, 128.5, 118.5, 50.9, 42.5; IR (cm^{-1}) 2928, 1714, 1640, 1313, 1167, 982, 905; MS (ESI) *m/z* 191.8$[M+H]^+$; HRMS (ESI) found *m/z* 192.1027 $[M+H]^+$, calcd for $C_{11}H_{14}NO_2^+$ *m/z* 192.1025.

4-(Methylsulfonyl)benzyl amine hydrochloride (Compound **43**, 115 mg, 99% isolated yield, white solid) was synthesized according to GPIII starting from 4-(methylsulfonyl)benzyl azide (107 mg, 0.5 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 8.11 – 8.03 (m, 2H), 7.80 – 7.72 (m, 2H),

4.29 (s, 2H), 3.17 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD) δ 143.8, 141.3, 131.9, 130.1, 45.1, 44.5. MS (ESI) *m/z* 185.9 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

(4-Hydroxymethyl)benzyl amine hydrochloride (Compound **44**, 35.4 mg, 82% isolated yield, white solid) was synthesized according to GPIII starting from 4-(hydroxymethyl)benzyl azide (40.8 mg, 0.25 mmol). ^{1}H NMR (400 MHz, CD_3OD) δ 7.52 – 7.41 (m, 4H), 4.65 (s, 2H), 4.14 (s, 2H); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 142.6, 131.8, 128.7, 127.2, 63.2, 42.7; MS (ESI) *m/z* 137.9 $[M+H]^+$. Data are in accordance to that previously reported.[3a]

Diphenyldisiloxane ($(PhSiH_2)_2O$, DPDS) was synthesized as previously described.[46] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 4H), 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 4H), 5.15 (s, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 134.4, 134.0, 130.9, 128.5; ^{29}Si NMR (80 MHz, $CDCl_3$) δ -25.3.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Supplementary figures, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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