Palladium-Catalyzed Silane/Siloxane Reductions in the One-Pot Conversion of Nitro Compounds into Their Amines, Hydroxylamines, Amides, Sulfonamides, and Carbamates

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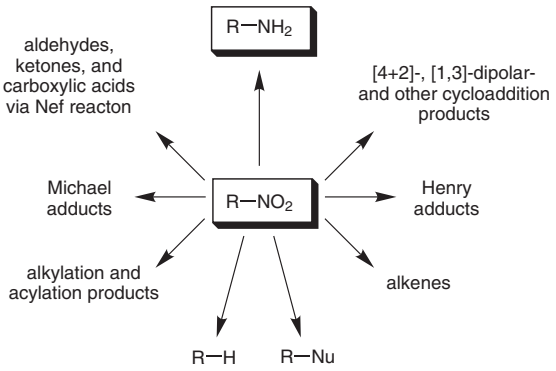
Abstract: A combination of palladium(II) acetate, aqueous potassium fluoride, and polymethylhydrosiloxane (PMHS) facilitates the room-temperature reduction of aromatic nitro compounds to anilines. These reactions tend to be quick (30 min), high-yielding, and tolerate a range of other functional groups. Replacement of PMHS/KF with triethylsilane allows for the reduction of aliphatic nitro compounds to their corresponding hydroxylamines. Depending on the substrate, both conditions can allow for the in situ conversion of the product amines into amides, sulfonamides, and carbamates.

Key words: reduction, amines, nitro compounds, palladium, silicon hydride, hydroxylamines

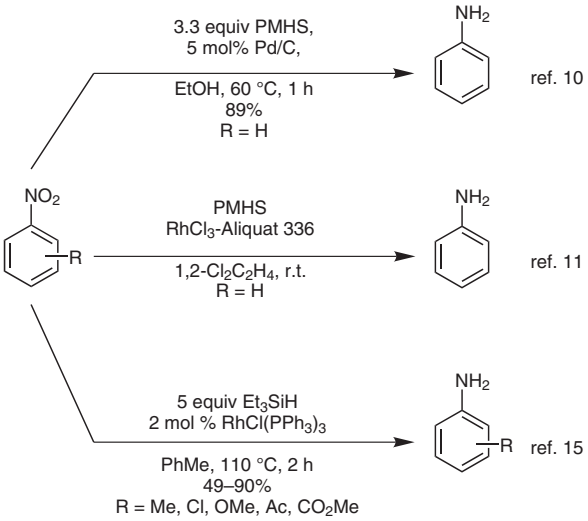
Nitro compounds are versatile building blocks for organic synthesis. Many are articles of commerce or can be easily prepared.[1,2] Furthermore, advances in asymmetric catalysis have made for ready access to stereodefined aliphatic nitro compounds.[3–5] Once in hand, nitro compounds can be alkylated, acylated, halogenated, made to undergo Nef reactions, substituted with nucleophiles, eliminated, allowed to participate in cycloadditions, as well as Henry and Michael reactions (Scheme 1).[1]



Scheme 1 Nitro compounds: versatile building blocks in synthesis

The nitro group has also served as a precursor to amines.[1] Reductions of nitro compounds to amines have been carried out under hydrogenation, electron-transfer, electrochemical, and hydride-transfer conditions.[6] Despite the wide use of several such protocols, environmental concerns, the demands of combinatorial syntheses, and/or issues of functional group compatibility continue to spur the invention of new reduction methods.[7]

Owing to their low toxicity and relatively mild nature, silanes and siloxanes would appear to be attractive hydride sources for such reductions.[8] Indeed, over thirty years ago Andrianov and co-workers[9] began reporting on the silane reductions of nitroarenes to anilines. Unfortunately, their reductions were plagued by incomplete reactions and low yields. Lipowitz and Bowman[10] had better success with polymethylhydrosiloxane (PMHS) in the Pd/C-catalyzed reduction of nitrobenzene to aniline as did Blum and Vollhardt[11] who also used PMHS to reduce nitrobenzene via rhodium-catalyzed transfer hydrogenation. Given the advantages associated with PMHS (low toxicity and cost, stability to air and moisture, and high functional-group tolerance),[12] it is somewhat surprising that, to the best of our knowledge, no other successful PMHS reductions of other nitro compounds had appeared in the literature prior to our own preliminary communication.[13,14] Moreover, only Brinkman and Miles' application of triethylsilane and Wilkinson's catalyst toward the reduction of several functionalized nitrobenzenes[15] (Scheme 2) had served to advance Andrianov's early use of silanes in nitro reductions.



Scheme 2 Previous examples of nitroarene reductions using silyl hydrides[10,11,15]

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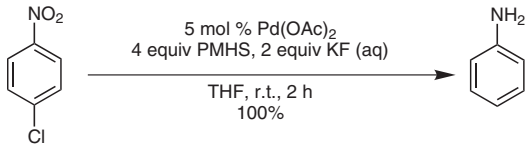
Our interest in using silanes or siloxanes for the reduction of nitro compounds was born out of our own experiences with PMHS as a reducing agent. Namely, we had previously used hypercoordinate PMHS to reduce Sn–X bonds[16] and discovered that catalytic $Pd(OAc)_2$, PMHS, and aqueous KF could together effect the room-temperature hydrodehalogenation of aryl chlorides.[17] During those chlorodehalogenation studies, we found that 1-chloro-4-nitrobenzene was quantitatively transformed to aniline at room temperature (Scheme 3).



Scheme 3 Preliminary $Pd(OAc)_2$/PMHS/KF nitro reduction

This preliminary result, suggested a greater level of reactivity over that previously observed by Lipowitz and Bowman.[10] Such an increase made sense given the ability of fluoride to activate the PMHS[12,16,18] and in light of Chauhan's finding that PMHS and $Pd(OAc)_2$ form highly active palladium nanoparticles.[19] With that background and given the limited prior use of silicon hydrides in that context, we decided to conduct a full study on the $Pd(OAc)_2$/PMHS/KF promoted reduction of nitro compounds.

To begin testing the generality of the $Pd(OAc)_2$/PMHS/KF conditions, we subjected nitrobenzene to the optimized dehalogenation conditions. Exposure to these conditions quantitatively afforded aniline after less than 30 minutes. We next screened a variety of palladium, fluoride, silicon hydride sources, and solvents in the reduction of 2-nitrotoluene. This screening clearly revealed the necessity of palladium catalysis as no amine formation occurred after stirring 2-nitrotoluene for one day in the presence of only two equivalents of PMHS and aqueous KF. Of the Pd catalysts tested, $Pd(OAc)_2$ (70%) proved best, but Pd/C (62%), $PdCl_2$ (59%), and Pd_2dba_3 (55%) all worked reasonably well. On the other hand, the presence of phosphine, either added as Ph_3P or in the form of phosphine-bearing catalysts, was detrimental to the reduction. We assume phosphine ligands disrupt the dispersion of Pd throughout the PMHS matrix[19] and as a consequence disrupt nanoparticle formation.

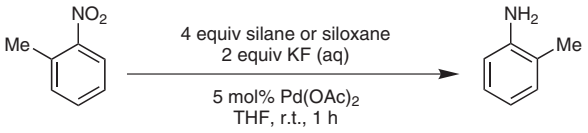
Taking into account palladium acetate's performance in the preliminary screens, its synergy with PMHS[19] in other reductions,[17,18a] and its relatively low cost, all future optimization studies would employ that catalyst. The first of these aimed to establish the best source of fluoride for the reduction. First, we reacted 2-nitrotoluene with 5 mol% $Pd(OAc)_2$ and 4 equivalents PMHS, but no fluoride. No amine product was observed after one hour, but at 24 hours 2-aminotoluene was obtained in 50% yield. Thus, it became clear that while the formation a polycoordinate siloxane species was not required, the presence of fluoride certainly seemed to facilitate hydride transfer from the silicon. LiF, NaF, CsF, and potassium fluoride were also examined in the reaction and all performed as well as KF. TBAF could also be employed, but only when used in substoichiometric amounts (10 mol%) and under cryogenic (–78 °C) conditions. Use of one equivalent of TBAF at –78 °C or in any amount at room temperature caused the reaction mixtures to turn into a solid mass via sol-gel formation.

Whereas most changes in the fluoride source had relative little impact on the reaction, the same could not be said of solvent. Reduction of 2-nitrotoluene with 5 mol% $Pd(OAc)_2$, 2 equivalents PMHS, and 2 equivalents of aqueous KF in THF and EtOAc gave the highest amine yields (70% and 67%, respectively), whereas reactions in 1,4-dioxane (24%), benzene (31%), hexanes (17%), CH_2Cl_2 (33%), and MeCN (30%) gave low yields. DMF and NMP were even worse as only starting material was recovered from reactions attempted in these solvents. Perhaps most surprisingly, Et_2O also turned out to be an incompatible solvent as precipitation of the catalyst and gel formation was observed after prolonged reaction times.

With solvent, fluoride, and palladium screening complete, we next looked at the use of other silanes and siloxanes. As shown in Table 1, several Si–H reagents efficiently reduced 2-nitrotoluene to 2-aminotoluene. However none showed a definitive advantage over the non-toxic, cheap,[20] and stable[21] PMHS. Thus, after considerable experimentation, the original $Pd(OAc)_2$/PMHS/KF combination remained unsurpassed as our conditions of choice.

We were now ready to study the reaction of a variety of nitro-substituted arenes and heteroarenes with 5 mol% of

Table 1 Silane/Siloxane Screening

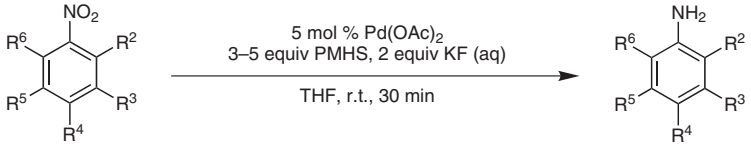


Entry	Si–H species	Yield (%)[a]
1	PMHS	100
2	Et_3SiH	100
3	TMS_3SiH	23
4	$EtO(Me)_2SiH$	100
5	$TMSO(Me)_2SiH$	100
6	$Me(MeO)_2SiH$	97
7	$Me(TMSO)_2SiH$	90
8	$(TMSO)_3SiH$	0
9	1,3-bis(trimethylsiloxy)-1,3-dimethyldisiloxane	100
10	methylhydrocyclosiloxanes	30

[a] Determined by ^1H NMR spectroscopy with CH_2Cl_2 as an internal standard (average of two runs).

$Pd(OAc)_2$, 4 equivalents of PMHS, and 2 equivalents of aqueous KF in THF at room temperature (Table 2). For the most part, the nitroarenes could be substituted at all ring positions. The steric hindrance of one ortho functional group did not affect reaction times, but the reduction of 2-nitro-*m*-xylene (Table 2, entry 3) was considerably slower (180 vs. 30 min). Electron-donating functional groups were well tolerated with quantitative formation of the corresponding anilines typically observed (Table 2, entries 4–9, 11–13). An exception to this rule was 4-nitrothioanisole, which gave a complex mixture of products containing ~10% of the expected amine (Table 2, entry 10). In this case, we assume sulfur is scavenging or in some way poisoning the catalyst. In terms of electron-withdrawing functional groups the system was accepting of carboxylic acids (Table 2, entry 19), esters (Table 2, entries 16–18, 21), amides (Table 2, entry 20–21), and trifluorotoluene (Table 2, entry 25).

Table 2 Anilines Formed by the Reduction of Nitroarenes with $Pd(OAc)_2$/PMHS/KF



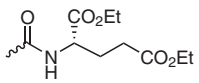
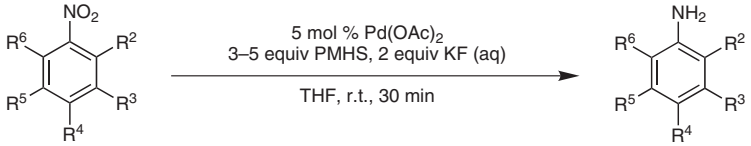
Entry	R^2	R^3	R^4	R^5	R^6	PMHS (equiv)	Yield (%)[a]	Side product	Yield (%)[a]
1	Me	H	H	H	H	4	quant.		
2	H	H	Me	H	H	4	94		
3	Me	H	H	H	Me	5	quant.		
4[b]	NH_2	H	H	H	H	4	97		
5	H	NH_2	H	H	H	4	97		
6	H	H	NH_2	H	H	4	95		
7[b]	OH	H	H	H	H	4	98		
8	H	OH	H	H	H	4	93		
9[b]	H	H	OH	H	H	4	97		
10	H	H	SMe	H	H	4	10		
11	H	H	OMe	H	H	4	98		
12	H	H	OAc	H	H	4	94		
13	H	H	OTBS	H	H	3	92	4-aminophenol	7
14	H	H	OBn	H	H	4	27	4-nitrophenol	54
15	H	H	$CO_2(CH_2)_6OBn$	H	H	4	quant.		
16	CO_2Me	H	H	H	H	4	quant.		
17	H	CO_2Me	H	H	H	4	quant.		
18	H	H	CO_2Me	H	H	4	quant.		
19[c]	H	H	CO_2H	H	H	4	94		
20	H	$CONH_2$	H	H	H	4	92		
21	H	H		H	H	4	quant.		
22[d]	CN	H	H	H	H	4	97		
23[d]	H	CN	H	H	H	4	98		
24[d]	H	H	CN	H	H	4	8	4-hydroxyaminobenzonitrile	77

Table 2 Anilines Formed by the Reduction of Nitroarenes with $Pd(OAc)_2$/PMHS/KF (continued)



Entry	R^2	R^3	R^4	R^5	R^6	PMHS (equiv)	Yield (%)[a]	Side product	Yield (%)[a]
25	H	H	CF_3	H	H	4	99		
26	H	Ac	H	H	H	3.5	97		
27	H	H	Ac	H	H	3	95		
28	H	H	CHO	H	H	3	73	(4-nitrophenyl)methanol	24
29	H	H		H	H	4	80		
30	H	H	Br	H	H	4	0	aniline	100
31	H	H	Cl	H	H	4	0	aniline	100
32	F	H	H	H	H	4	97		
33	H	F	H	H	H	4	96		
34	H	H	F	H	H	4	97		
35	H	H	$CO_2(CH_2)_6Br$	H	H	4	82	hexyl 4-aminobenzoate	15
36	H	H	$CO_2(CH_2)_6Br$	H	H	3.5	quant.		
37	H	H	NO_2	H	H	4	72	1,4-diamine	20
38[e]	H	CF_3	H	OMe	H	5	99		
39	OMe	H	H	CF_3	H	4	quant.		
40	H	CF_3	OMe	H	H	4	98		
41	CN	H	H	CF_3	H	4	78	2-amino-4-(trifluoromethyl)benzamide	20
42[f]	H	OMe	CN	H	H	4	99		
43	H	CN	CN	H	H	4	mixture		
44	H	CF_3	H	CF_3	H	4	20–80	*N*-hydroxylamine	20–80

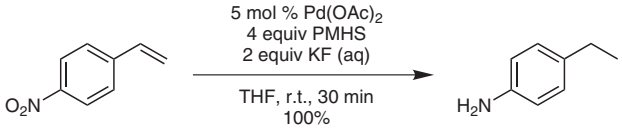
[a] Isolated yields after flash chromatography.
[b] Isolated as the acetamide.
[c] Isolated as acetylamino benzoic acid.
[d] Stirred for 12 h or 4 h with 4 equiv KF.
[e] Stirred for 12 h.
[f] Stirred for 1 h.

Adjustment of the PMHS concentration to 3–3.5 equivalents allowed selective reduction of a nitro group in the presence of a benzylic ketone (Table 2, entries 26–27), but with the use of 4 equivalents of PMHS reduction of the benzylic ketone occurred after complete reduction of the nitro group. Reduction of the nitro group was favored with 4-nitrobenzaldehyde affording the aniline in 73% yield (Table 2, entry 28), but intrusive reduction of the aldehyde to the alcohol (24%) was unavoidable (reductive amination was not witnessed). Again, reactions were typically complete within 30 minutes, with formation of the amino-substituted benzonitriles being notable exceptions (Table 2, entries 22–24). For these substrates, 12 hour reaction times were necessary, unless KF concentrations were increased. With four equivalents of KF, the 2- and 3-nitrobenzonitriles could be quantitatively reduced to their aniline derivatives within four hours. However, even under these more forcing conditions 4-nitrobenzonitrile could only be partially reduced to the *N*-hydroxylamine (Table 2, entry 24). The sluggish reactivity of this substrate may be attributable to increased resonance stabilization of its intermediates.

In addition to the functional-group compatibility mentioned above, it should be noted that despite the presence of KF, the TBS-protected aminophenol (Table 2, entry 13) was isolated in high yield accompanied by only 7% of the desilylated phenol. This was not the case with 1-(benzyloxy)-4-nitrobenzene where debenzylation of the protected phenol was the major reduction pathway, affording the benzyl-protected aminophenol in only 27% yield (Table 2, entry 14). A nitro group could be selectively reduced to the amine in the presence of a less activated benzyl ether (Table 2, entry 15). Chemoselective nitro reductions were not achieved in the presence of an aromatic bromide or chloride (Table 2, entries 30, 31). On the other hand aromatic fluorides were not dehalogenated under these conditions (Table 2, entries 32–34). In the case of an aliphatic bromide, nitro reduction was favored over dehalogenation, but after reduction of the nitro group was complete unconsumed PMHS could promote the dehalogenation of an aliphatic bromide. With 4 equivalents of PMHS full reduction of the nitro to the amine was accomplished, followed by 15% dehalogenation (Table 2, entry 35). By simply adjusting the PMHS concentration to 3.5 equivalents, only reduction of the nitro group was seen (Table 2, entry 36).

Arenes that were disubstituted with an electron-donating and an electron-withdrawing group (Table 2, entries 38–40) afforded their anilines in near quantitative yield. Even though the nitrobenzonitriles required prolonged reaction times, a nitroarene containing a nitrile and a trifluoromethyl substituent (Table 2, entry 41) was reduced in the prototypical reaction time of 30 min accompanied with 20% hydrolysis of the nitrile to the amide. Anderson[22] also reported that 2-nitro-4-(trifluoromethyl)benzonitrile is reduced and hydrolyzed completely to 2-amino-4-(trifluoromethyl)benzamide with standard palladium hydrogenolysis conditions (Pd/C, H_2, MeOH, rt). What should be noted is that under our system only 20% amide formation occurs. A methoxy-substituted nitrobenzonitrile (Table 2, entry 42) was reduced to the *N*-hydroxylamine after 30 min, which itself underwent quantitative reduction to the amine after an hour. 4-Nitrophthalonitrile was completely consumed after 30 min, but only a complex mixture of products was isolated (Table 2, entry 43). Complete consumption of starting material was also observed with 1-nitro-3,5-bis(trifluoromethyl)benzene (Table 2, entry 44), but the reaction was inconsistent affording varying ratios of *N*-hydroxylamine and amine with each run.

The substrates in Table 2 reveal that the nitro reductions can be performed in the company of a variety of functional groups. Absent though were any substrates containing alkene-bearing substituents. Such groups pose a potential problem as PMHS has been used for the reduction of alkenes and alkynes under transition-metal catalysis.[12,19b,c] Likewise, we too had previously witnessed examples where $Pd(OAc)_2$/PMHS/KF reduced activated olefins and alkynes,[18] including enones.[23] As such we were not taken aback when subjection of 4-nitrostyrene to the reaction conditions quantitatively produced 4-ethylaniline (Scheme 4).



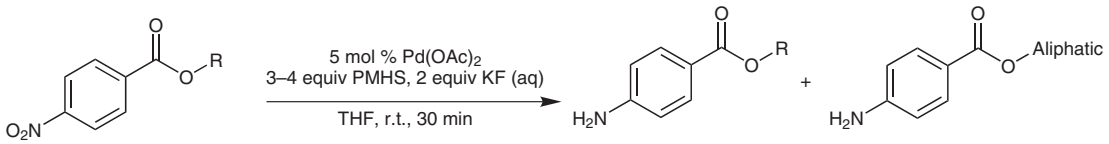
Scheme 4 Over-reduction of 4-nitrostyrene

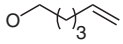
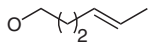
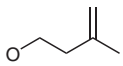
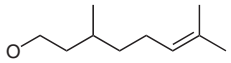
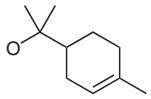
Nonetheless, the uncertainty of whether unactivated olefins and alkynes could survive the conditions remained. To answer that question, a variety of unactivated mono-, di-, and tri-substituted olefin-containing esters were prepared from 4-nitrobenzoic acid and the corresponding alcohols. Reaction of these substrates (Table 3) revealed that nitro group reduction was only slightly favored over saturation of the mono-substituted olefin, selectively yielding the olefin-containing aniline in 27% yield along with 73% of the doubly reduced product (Table 3, entry 2). Selectivity was increased when the alkene substituent was vicinally (51%) (Table 3, entry 3) or geminally disubstituted (60–64%) (Table 3, entries 5–7). In the latter case, the products contained 13–20% of the isomerized tri-substituted olefins. With some adjustment of the PMHS equivalency, nitro compounds containing tri-substituted olefins showed high preference for reduction of the nitro group (Table 3, entries 9 and 11), though even here reduction of the double bond could not be completely stopped with 4% and 7% over reduced material being formed.

We similarly explored the ability of alkynes to survive the reduction conditions. Based on the results in Scheme 5, it would appear that they do not. Reduction of a nitrobenzoate containing a TBS-protected alkyne saw the alkyne being converted into the vinyl silane before reduction of the nitro group to the amine. Moreover, olefin isomerization and saturation of the aliphatic chain could not be avoided. Increasing the PMHS concentration to six equivalents efficiently reduced the nitro group to the amine and the alkyne to the alkane[24] (Scheme 5). Reduction of the alkyne and isomerization likely involves a palladium-mediated transfer hydrogenation mechanism.[25]

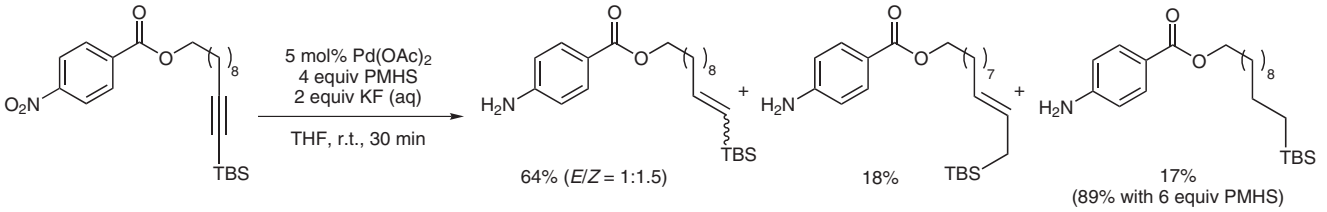
Another group of substrates where selectivity was evaluated was that of dinitro compounds (Table 4). Attempted mono reduction of 1,4-dinitrobenzene afforded 4-nitroaniline (Table 4, entry 2) in 72% yield along with 20% of the diamine. Selectivity diminished with bis(4-nitrophenyl)methane (Table 4, entry 3), but doubling the PMHS and KF concentrations could afford the diamine in high yield (Table 4, entries 4, 5). Mono reduction of 1-methoxy-2,4-dinitrobenzene occurs in 69% yield, but without selectivity for either nitro group (Table 4, entry 6). Again the diamine was afforded in good yield upon doubling the PMHS and KF concentrations (Table 4, entry 7). As seen previously, multiple nitrile subtituents proved capricious. In entries 8 and 9, all starting material was consumed, but this only led to a complex mixture of products.

Table 3 Determining the Tolerance of Unactivated Olefins and Alkynes



Entry	OR	PMHS (equiv)	Yield (%) of aniline[a]	Yield (%) of reduced olefin[a]
1		3	19	55
2		4	27	73
3		3	51	22
4		4	41	54
5		3	60 (13)[b]	10
6		3.5	64 (18)[b]	15
7		4	60 (20)[b]	19
8		3	75	1
9		3.5	90	4
10		4	68	32
11		3.5	93	7
12		4	49	50

[a] Isolated yields after flash chromatography.
[b] Yield (%) in parentheses reflects the amount of double-bond-isomerized material.



Scheme 5 Testing the compatibility of unactivated alkynes

Table 4 Reduction of Dinitroarenes[a]

Entry	Starting material	PMHS (equiv)	KF (equiv)	Monoamine	Diamine
1	1,4-dinitrobenzene	3	2	44	0
2	1,4-dinitrobenzene	4	2	72	20
3	bis(4-nitrophenyl)methane	3	2	48	30
4	bis(4-nitrophenyl)methane	6	4	17	83
5	bis(4-nitrophenyl)methane	8	4	0	93
6	1-methoxy-2,4-dinitrobenzene	4	2	69 (1:1)	0
7	1-methoxy-2,4-dinitrobenzene	8	4	0	89
8	2,4-dinitrobenzonitrile	4	2	complex mixture	complex mixture
9	2,4-dinitrobenzonitrile	8	4	complex mixture	complex mixture

[a] Conditions: dinitroarene (1 mmol), $Pd(OAc)_2$ (5 mol%), PMHS, KF, THF (5 mL), H_2O (2 mL), r.t., 30 min.
[b] Isolated yields after flash chromatography.

Extension of the methodology to nitro-substituted heteroaromatics afforded the expected amines in high yields, but not without some subtle changes to the experimental procedure (Table 5). In all previous reactions PMHS was added last to the reaction. When this was done during the reaction of 5-nitrobenzimidazole an atypical color change

was observed and the starting substrate was unchanged. We hypothesized that formation of the active Pd-PMHS complex was hindered by coordination of the substrate to the metal. To overcome this problem, we simply premixed the reagents, so as to allow nanoparticle formation in advance of exposure to 5-nitrobenzimidazole. This protocol, where the substrate was added after nanoparticle formation, gave the expected amine in high yield (Table 5, entry 2). Application of the modified protocol to 2-methyl-4(5)-nitroimidazole resulted in consumption of all of the starting material, but only a complex mixture of products was isolated. Attempts to inhibit decomposition of the desired amine by protection/derivatization of one of the imidazole nitrogens (Ac, Bn, CH_2CH_2CN) was partially successful (entry 4), unfortunately the amine products could never be cleanly isolated. On the other hand, a nitro-substituted pyrazole was reduced without incident (Table 5, entry 5). In contrast to the aforementioned heterocycles, the standard conditions were capable of quantitatively reducing a nitro group on or in the presence of a pyridine (Table 5, entries 6–8). Methyl 5-nitro-2-furanoate likewise was reduced in 89% yield (Table 5, entry 1). Whereas thioanisole was a problem substrate, thioimidazoles were not (Table 5, entries 9,10). 2-Nitrothiophene was also easily reduced to the amine (Table 5, entry 12). However, isolation of the product was difficult and could only be achieved after its in situ protection as a Boc carbamate. As was the case with the imidazoles, a nitro group could be reduced in the presence of a 1,2,3-thiadiazole (Table 5, entry 11), but only a complex mixture of products was afforded.

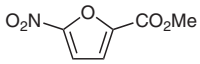
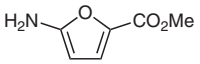
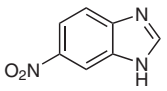
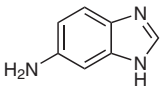
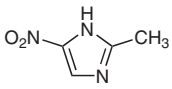
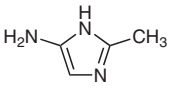
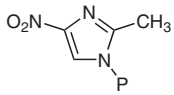
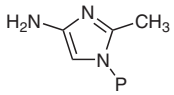
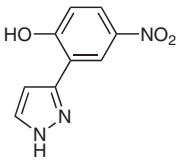
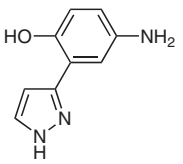
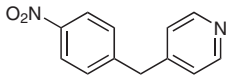
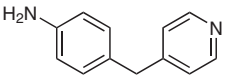
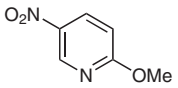
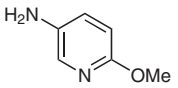
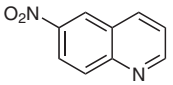
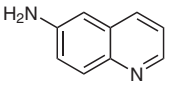
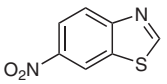
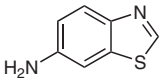
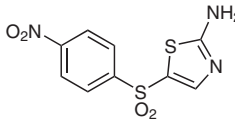
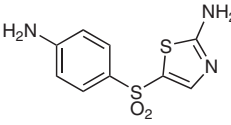
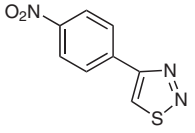
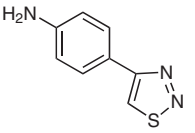
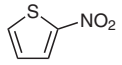
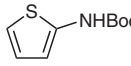
Having examined aromatic and heteroaromatic nitro compounds, we next sought to extend the reduction method to aliphatic nitro compounds. Our first attempt to convert 1-nitrodecane into its corresponding amine only yielded a small amount of *N*-hydroxyl-1-aminodecane (15–20%), the corresponding nitroso compound (40%), and unreacted starting material (23%). As only a handful of methods have been developed for the synthesis of *N*-hydroxylamines from aliphatic nitro compounds,[1,6,26] we wanted to capitalize on the small amount of the *N*-hydroxylamine formed during the reaction.

N-Hydroxylamines are found in natural products and biologically active compounds. They are important components in the synthesis of nitrones[1,27] and Bode and coworkers have utilized them in a decarboxylative condensation with α-keto acids for the formation of amides.[28] As mentioned above, reductive routes to these compounds are few and the available methods tend to have low functional group compatibility, require harsh reaction conditions, and/or are low-yielding. Likewise, the oxidation of aliphatic amines to *N*-hydroxylamines can also be fraught with problems.[1,26] Thus we sought to expand our $Pd(OAc)_2$/PMHS/KF system to include aliphatic *N*-hydroxylamines from the corresponding aliphatic nitro compounds.

Utilizing 1-nitrodecane as the test substrate, adjustments to the catalyst loading, PMHS concentration, fluoride source, and temperature were examined. While some of these changes improved yields slightly, none of the conditions tested could be described as synthetically viable.

Reaction monitoring suggested that side reactions were competing with the 1-nitrodecane for the hydride. In an attempt to bias the reactions toward nitro reduction, we decreased the reactivity of the PMHS by removing the

Table 5 Reduction of Nitro-Substituted Heteroaromatics[a]

Entry	Nitro compound	Product	Yield (%)[b]
1			89
2			89
3			complex mixture
4	 P = Ac, Bn, CH_2CH_2CN	 P = Ac, Bn, CH_2CH_2CN	–
5			87
6			99
7			quant.
8			99
9			71
10			94
11			complex mixture
12[c]			81

[a] Conditions: substrate (1 mmol), $Pd(OAc)_2$ (5 mol%), PMHS (4 equiv), aq KF (2 equiv), THF (5 mL), and H_2O (2 mL H_2O) at r.t. for 30 min.
[b] Isolated yields after flash chromatography.
[c] Worked up with Boc_2O.

fluoride from the reaction. This proved beneficial, as running the reaction in the absence of KF led to ~60% conversion of the 1-nitrodecane into its *N*-hydroxylamine. Still, complete reduction never occurred as under these conditions concomitant sol-gel formation took place. This likely contributed to shutting the reaction down by encapsulating the catalyst (and the substrate).

To determine if the sol-gel formation was indeed preventing the reaction from going to completion, we decided to swap PMHS for a non-polymeric silicon hydride. Our initial optimization studies had already established a number of non-polymeric silanes and siloxanes capable of reducing aromatic nitro compounds (Table 1). Rescreening these silane and siloxanes for nitroalkane reductions saw triethylsilane converting 85% of 1-nitrodecane into *N*-hydroxyl-1-aminodecane in two hours. It should be noted, that even though the fluoride source was removed, *the addition of water remained critical to the reaction's success* as anhydrous conditions gave low product yields. Also, six equivalents of triethylsilane were needed to ensure complete consumption of the nitroalkane and reproducible yields.

With these results in hand, the screening of aliphatic nitro compounds was initiated (Table 6). Primary and secondary nitro groups responded favorably to 5 mol% $Pd(OAc)_2$, six equivalents Et_3SiH, in THF–H_2O, with high-yielding reductions occurring within two hours. In contrast, tertiary nitro aliphatics reacted poorly. The highly oxygenated 1,3-diacetoxy-2-acetoxymethyl-2-nitropropane was reduced to the *N*-hydroxylamine in a modest 31% yield (Table 6, entry 4). Only trace amounts of the reduced product could be isolated from the reaction of methyl 4-methyl-4-nitropentanoate (Table 6, entry 5). It should be noted that in this last example only 64% of the starting material was recovered. Therefore we cannot rule out the possibility that the hydroxylamine (or the hydroxylamine derived *N*-hydroxylactam) decomposed prior to isolation. Indeed, evidence suggested that for the tertiary nitroacetonide of entry 6 the newly formed hydroxylamine was in fact prone to decomposition.

A look at more elaborated nitroalkanes revealed that a Henry adduct could be reduced in high yield with complete retention of the stereochemistry (Table 6, entry 7). However, protection of that Henry adduct's alcohol with a variety of standard protective groups (TES, TBS, Ac, Me) gave substrates that consistently yielded their hydroxylamines in diminished yields (44–49%) (Table 6, entries 8–15). In these cases, increasing the triethylsilane concentration to 10 equivalents produced only a ~10% increase in product yield (54–57%), except in the case of entry 16 where reduction of the methylated substrate afforded the product in 84% yield.

We could also follow the nitro reduction with intra- or intermolecular trapping of an electrophile. For example, the Henry adduct's hydroxylamine was trapped with 1,1′-carbonyldiimidazole and transformed into a *N*-hydroxyloxazolidinone (Table 6, entry 7). A nitro-containing Michael adduct saw the intermediate hydroxylamine condense with the ketone to form the cyclic nitrone (also known as Reissig nitrone synthesis) with no loss of stereochemistry (Table 6, entries 17–20).[29] For this process an optimal yield of 77% was achieved with 10 equivalents Et_3SiH, but even under these conditions starting material remained. In an attempt to force the reaction to consume all of the Michael adduct, the silane amount was upped to 12 equivalents, but this only served to decrease the nitrone yield, while doing little to drive the reaction to completion. The reduction was also run with a catalytic amount of KF (0.25 equiv). This, too, resulted in full consumption of the starting material, but also decreased the yield of the nitrone. In both cases, the lowered yields were attributed to over-reduction of the nitrone. Usefully, protection of the Michael adduct's ketone as the ketal did not inhibit the reduction (Table 6, entry 21).

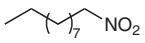
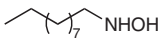
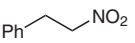
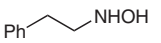
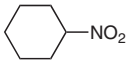
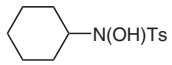
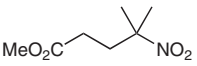
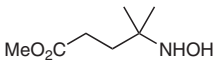
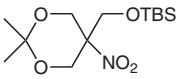
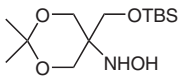
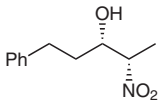
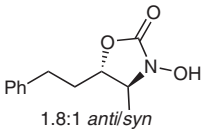
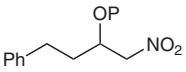
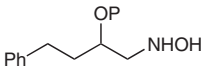
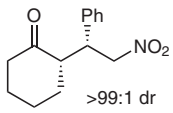
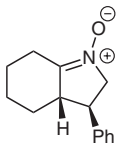
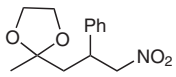
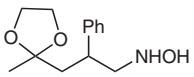
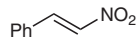
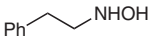
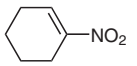
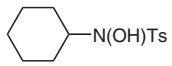
Finally, we examined vinyl nitro compounds. With 8 equivalents of triethylsilane, nitrostyrene and nitrocyclohexene were efficiently reduced to the primary and secondary *N*-hydroxylamimes respectively (Table 6, entries 22,23).

Crude amine products generated by other reduction methods have been alkylated,[30] transformed into heterocycles,[31] or heteroaromatics.[32] Methods have also been developed for reductive one-pot transformations of nitro compounds to their carbamates,[33] acetamides,[34] and formamides.[35] However generic conditions for the direct synthesis of amides from nitro compounds remain elusive. As described above, we were able to subject the reduction products to further chemistry. In fact, such derivatization was necessary for the efficient isolation of some reaction products (e.g. aminobenzoic acids and 2-aminothiophene). With this in mind, we next investigated if such one-pot reduction/amidations could be broadly developed.

Starting conservatively, 4-nitrobenzoic acid was subjected to the reaction conditions, where once TLC indicated complete consumption of the nitro compound, one equivalent of acetic anhydride was added. This procedure afforded 4-acetamidobenzoic acid in 40%. The yield of the amide steadily improved as the amount of anhydride was increased, two equivalents of Ac_2O providing the amide in 94% yield. In an attempt to streamline the protocol further, the anhydride was added at the beginning of the reduction. Unfortunately, such conditions completely inhibited the reduction and only starting material was isolated. Furthermore, addition of the anhydride to the reaction mixture before complete consumption of the nitro arene immediately halts any further reduction.

Knowing that the anhydrides would have to be added after the reductions were complete, a cross-section of anhydrides were tested against electron-rich, electron-poor, and sterically congested nitroarenes (Table 7). 4-Nitroanisole performed extremely well, generally affording the corresponding amides, a carbamate, and sulfonamides in high yields (79–99%) (Table 7, entries 1, 4, 7, 10, 13, 14,

Table 6 Reduction of Aliphatic Nitro Compounds to *N*-Hydroxylamines with $Pd(OAc)_2/Et_3SiH$ in a THF–H_2O Mixture[a]

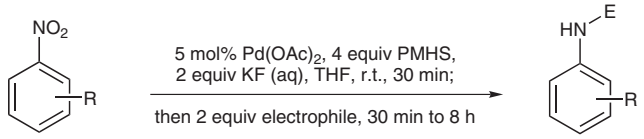
Entry	Aliphatic nitro compound	Reduction product	Et_3SiH (equiv)	Yield (%)[b]
1			6	83
2			6	58
3[c]			6	89
4	$(AcOCH_2)_3C-NO_2$	$(AcOCH_2)_3C-NHOH$	6	31 (66% SM)
5			6	trace (64% SM)
6			6	0 (77% SM)
7	 1.8:1 *syn*/*anti*	 1.8:1 *anti*/*syn*	6	82
8				
9	P = TES	P = TES	6	44
10			10	56
11	P = TBS	P = TBS	6	45
12			10	57
13	P = Ac	P = Ac	6	49
14			10	54
15	P = Me	P = Me	6	56
16			10	84
17	 >99:1 dr		6	39 (37% SM)
18			10	77 (19% SM)
19			12	45 (10% SM)
20			10 + KF (0.25 equiv)	67 (0% SM)
21			6	51
22			8	53
23[c]			8	88

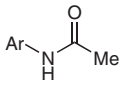
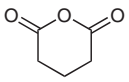
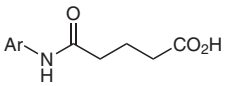
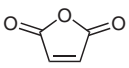
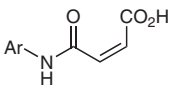
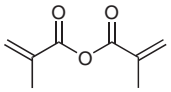
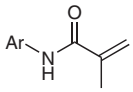
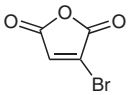
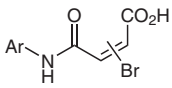
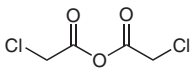
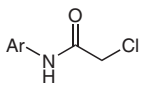
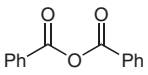
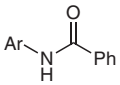
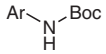
[a] Conditions: aliphatic nitro compound (1 mmol), $Pd(OAc)_2$ (5 mol%), PMHS, THF–H_2O (5:2 mL), r.t., 2–4 h.
[b] Isolated yields after flash chromatography.
[c] Reaction quenched with Ts_2O. The NTs (vs. OTs) assignment is based on IR data and should be considered tentative.

19, 22, 25, and 28). Exceptions to this trend were reactions quenched with trichloroacetic or trifluoroacetic anhydrides (Table 7, entries 17 and 18). In these cases, the aqueous reaction conditions hydrolyzed the anhydrides before they could react with the amines.[36] It should also be noted that although $Pd(OAc)_2$/PMHS/KF will reduce activated olefins and organic halides, anhydrides containing these functional groups were well tolerated (Table 7, entries 7–16).

Reduced methyl 3-nitrobenzoate also behaved well when forming the amides and sulfonamides (78–100%) (Table 7, entries 2, 5, 8, 11, 15, 20, 23, and 26), but only 22% of the carbamate (Table 7, entry 29) was obtained. Despite being readily reduced, the sterically hindered 2-nitro-*m*-xylene proved to be a difficult substrate in the combined reduction/amidation protocol with amide yields ranging from 0–72% (Table 7, entries 3, 6, 9, 12, 16, 21, 24, 27, and 30).

Table 7 One-Pot Reductive Conversion of Nitroarenes into Amides, Carbamates or Sulfonamides



Entry	Nitroarene	Electrophile	Reduction product	Yield (%)[a]
1	4-nitroanisole	Ac_2O		99
2	methyl 3-nitrobenzoate			quant.
3	2-nitro-*m*-xylene			0
4	4-nitroanisole			96
5	methyl 3-nitrobenzoate			87
6	2-nitro-*m*-xylene			0
7	4-nitroanisole			95
8	methyl 3-nitrobenzoate			84
9	2-nitro-*m*-xylene			29
10	4-nitroanisole			99
11	methyl 3-nitrobenzoate			94
12	2-nitro-*m*-xylene			0
13	4-nitroanisole			89 (1:1.3)
14	4-nitroanisole			96
15	methyl 3-nitrobenzoate			84
16	2-nitro-*m*-xylene			<73[b]
17	4-nitroanisole	trichloroacetic anhydride	4-$MeOC_6H_4NHC(O)CCl_3$	0
18	4-nitroanisole	trifluoroacetic anhydride	4-$MeOC_6H_4ArNHC(O)CF_3$	0
19	4-nitroanisole			97
20	methyl 3-nitrobenzoate			89
21	2-nitro-*m*-xylene			59
22	4-nitroanisole	Ms_2O		79
23	methyl 3-nitrobenzoate			78
24	2-nitro-*m*-xylene			30
25	4-nitroanisole	Ts_2O		97
26	methyl 3-nitrobenzoate			98
27	2-nitro-*m*-xylene			72
28	4-nitroanisole	Boc_2O		98
29	methyl 3-nitrobenzoate			22
30	2-nitro-*m*-xylene			50

[a] Isolated yields after flash chromatography.
[b] The yield includes a small amount of an unknown contaminant.

The in situ functionalization of the aliphatic hydroxylamine products was not as successful. Yields typically ranged from 0–30%, irrespective of the electrophile used. In these cases, no hydroxylamine was isolated after addition of the electrophile. Thus it appears that the hydroxylamines or their derivatives were not stable to the reaction conditions and/or flash chromatography. One exception to the above findings was the reaction of *N*-hydroxylcyclohexylamine with Ts_2O, which formed the *N*-hydroxylsulfonamide in good yield (Table 6, entry 3).

Based on findings discussed herein and previous work[19] with palladium-PMHS nanoparticles, we propose these reductions advance via a nitroso (possibly in equilibrium with its oxime) and then hydroxylamine intermediates/products. The precise method by which these intermediates are formed and subsequently reduced is not entirely clear. However, as the presence of water had a dramatic influence on reaction efficiency and rate, we are tempted to suggest a palladium-mediated transfer hydrogenation process where σ-bond metathesis between the silicon hydride and water leads to the generation of hydrogen gas. In such a scenario, reduction of the nitro group to the nitroso would most likely occur through hydrogenolysis.

To partly evaluate this hypothesis, nitrobenzene was subjected to $Pd(OAc)_2$, PMHS, and *anhydrous* THF. Unfortunately, this only gave a solid mass via sol-gel formation. However, swapping PMHS with triethylsilane eliminated sol-gel formation. Moreover, NMR analysis of the crude reaction mixture indicated some formation of *N*-phenyl-*O*-(triethylsilyl)hydroxylamine. Thus it is possible that other pathways to the nitroso compounds are, at least in part, operative. For example, past literature precedent[37] suggests that the nitro group could also be oxidizing a silicon coordinated to the palladium resulting in nitroso formation.

As for the actual reduction of the nitroso compound, based on the aforementioned control reactions and intermediates isolated from the aliphatic substrates, we favor a process involving an initial hydrogenolysis or hydrosilylation to afford the hydroxylamine, which then undergoes hydrogenolysis to the amine. That said, much work is needed before settling on a mechanism for this process.

Finally, irrespective of mechanism we recognized that 5 mol% $Pd(OAc)_2$ represents a relatively high catalyst loading. As such, the amount of palladium was systematically decreased while screening against three aromatic nitro compounds (Table 8). Lowering the catalyst loading to 1 mol% increased the reaction times for aromatic substrates to three hours, but resulted in no loss in product yields. Similarly, yields were maintained with the employment of 0.5 mol% $Pd(OAc)_2$, although not without increasing reaction times to 15 hours. Importantly, at this level of catalyst loading similar results were obtained when the reductions were run from 1-mmol to 45-mmol scale. Diminishing results did set in when the catalyst loading was taken to 0.1 mol%. Here the reductions became substrate-dependent, with only methyl 4-nitrobenzoate responding well to such conditions.

In summary, nanoparticles formed from $Pd(OAc)_2$ and PMHS, in combination with aqueous KF, rapidly and mildly reduce nitro-substituted arenes and heteroarenes to their corresponding amines in high yields. Substituting PMHS/KF with Et_3SiH, allows for the room-temperature reduction of aliphatic nitro groups to hydroxylamines. Both variations of the method exhibit good functional group compatibility with short reaction times. The amine products could also be transformed to amides, sulfonamides, or carbamates in one pot, by the addition of an electrophile (anhydride). The one-pot reduction/amidation was not as successful with the nitroaliphatics. Future investigations aimed at reducing nitroarenes to their hydroxylamines, nitroalkanes to amines, and a better mechanistic understanding of the chemistry will be described as they develop.

Table 8 Determining the Usable $Pd(OAc)_2$ Concentration[a]

Entry	Substrate	Pd (mol%)	Time (h)	Yield (%)
1	methyl 4-nitrobenzoate	5	0.5	100
2	methyl 4-nitrobenzoate	1	3	100
3	methyl 4-nitrobenzoate	0.5	15	92
4	methyl 4-nitrobenzoate	0.1	48	100
5	4-nitroanisole	5	0.5	98
6	4-nitroanisole	1	3	94
7	4-nitroanisole	0.5	15	98
8	4-nitroanisole	0.1	48	51
9	methyl 5-nitro-2-furoate	5	0.5	89
10	methyl 5-nitro-2-furoate	1	3	90
11	methyl 5-nitro-2-furoate	0.5	15	91
12	methyl 5-nitro-2-furoate	0.1	48	mixture

[a] Conditions: nitroarene (1 mmol), $Pd(OAc)_2$, PMHS (4 mmol), KF (2 mmol), THF (5 mL), degassed H_2O (2 mL), r.t.

All reactions were carried out in oven-dried glassware under N_2, with magnetic stirring, and monitored by TLC with 0.25-mm precoated silica gel plates, unless otherwise noted. THF was freshly distilled from sodium/benzophenone under N_2. Anhyd A.C.S. grade KF and polymethylydrosiloxane (PMHS), and triethylsilane were used without purification. 4-Acetoxynitrobenzene,[38] *tert*-butyldimethyl(4-nitrophenoxy)silane,[39] 6-bromohexyl 4-nitrobenzoate,[13] 2-nitrothiophene,[40] 1-nitrodecane,[41] (2-nitroethyl)benzene,[41] 1,3-diacetoxy-2-acetoxymethyl-2-nitropropane,[42] 4-nitro-1-phenylpentan-3-ol,[43] and *syn*-2-(2-nitrophenylethyl)cyclohexanone[3f] were prepared following literature procedures. The remaining nitro compounds were purchased and used without purification, except for 4-nitroanisole, which was recrystallized from hexanes before use. $Pd(OAc)_2$ was purchased from Strem.[44] Flash chromatography (FC) was performed with silica gel 60 Å (230–400 mesh). Yields refer to chromatographically and spectroscopically pure compounds unless other wise stated. ^1H NMR and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer (300 MHz for ^1H, respectively, and 75 MHz for ^{13}C, respectively), with chemical shifts reported relative to the residue peaks of solvent $CHCl_3$ (δ = 7.24 for ^1H and 77 for ^{13}C) or DMSO (δ = 2.50 for ^1H and 39.5 for ^{13}C). Melting points were measured on a capillary melting point apparatus and are uncorrected.

Reduction of Nitroarenes to Anilines; General Procedure

A round-bottom flask was charged with $Pd(OAc)_2$ (0.05 mmol, 11 mg), the nitroarene (1 mmol), and freshly distilled THF (5 mL). The flask was sealed and purged with N_2. While purging the flask with N_2, a solution of aq KF was added via syringe (2 mmol KF, 116 mg in 2 mL of degassed H_2O). The N_2 inlet was replaced with a balloon filled with N_2. PMHS (4 mmol, 0.24 mL; 1 mmol of hydride is 0.06 mL) was slowly added dropwise via syringe (***Caution!*** *Rapid addition of PMHS can result in uncontrollable gas evolution!*). The reaction was stirred for 30 min or until complete as judged by TLC. At that time, the reaction flask was opened to the air, diluted with Et_2O (5–10 mL), and stirred for 5 min. The layers were separated and the aqueous layer was back-extracted with Et_2O. The combined organics were filtered through a plug of Celite (top layer) and neutral alumina (bottom layer) in a 1 cm diameter column by flushing with EtOAc. The filtrate was concentrated and subjected to flash chromatography eluting with gradients of hexanes–EtOAc and/or EtOAc–MeOH.

2-Aminotoluene (Table 2, entry 1)

Yellow oil; yield: 107 mg (quant.); R_f 0.55 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06 (m, 2 H), 6.79–6.62 (m, 2 H), 3.60 (br s, 2 H), 2.18 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.4, 130.3, 126.8, 122.2, 118.5, 114.8, 17.2.

4-Aminotoluene (Table 2, entry 2)

Yellow-orange solid; yield: 101 mg (94%); mp 40–44 °C; R_f 0.2 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97 (d, *J* = 8.24 Hz, 2 H), 6.61 (d, *J* = 8.24 Hz, 2 H), 3.52 (br s, 2 H), 2.24 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.7, 129.6, 127.6, 115.2, 20.3.

2,6-Dimethylaniline (Table 2, entry 3)

2,6-Dimethylnitrobenzene was subjected to the general procedure for reducing nitro arenes with 5 equiv of PMHS. Light yellow oil; yield 121 mg (quant.); R_f 0.35 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 95:5, then 80:20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 7.14 Hz, 2 H), 6.70 (t, *J* = 7.69 Hz, 1 H), 3.57 (br s, 2 H), 2.23 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7, 128.1, 121.5, 117.9, 17.5.

***N,N′*-(1,2-Phenylene)diacetamide** (Table 2, entry 4)

To obtain the 2-aminoaniline free of all palladium it was isolated as the diacetamide, by the addition of Ac_2O (4 mmol, 0.376 mL) to the reaction mixture with an additional 30 min of stirring; white solid; yield: 190 mg (99%); mp 183–185 °C; R_f 0.1 (EtOAc); silica gel FC (EtOAc–MeOH, 100:0, then 50:50).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.31 (s, 2 H), 7.53 (m, 2 H), 7.10 (m, 2 H), 2.05 (s, 6 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.6, 130.4, 124.7, 124.5, 23.6.

1,3-Benzenediamine (Table 2, entry 5)

Green oil; yield 108 mg (99%); R_f 0.1 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 6.56 (t, *J* = 7.69 Hz, 1 H), 5.74 (dd, *J* = 2.19, 8.24 Hz, 2 H), 5.69 (t, *J* = 2.19 Hz, 1 H), 3.61 (s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 147.1, 129.0, 104.5, 100.8.

1,4-Benzenediamine (Table 2, entry 6)

Purple solid; yield 103 mg (95%); mp 141 °C; R_f 0.1 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 6.32 (s, 4 H), 3.28 (br s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 138.1, 116.0.

2-Aminophenol (Table 2, entry 7)

The general procedure for reducing nitroarenes afforded 103 mg (94%) of 2-aminophenol and 5.2 mg (~4%) of what appeared to be a *p*-quinonimine.

Red-yellow solid; yield: 103 mg (94%); R_f 0.3 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50).

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 8.38 (br s, 1 H), 6.56–6.25 (m, 4 H), 3.62 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 144.0, 134.8, 119.4, 117.7, 114.9, 114.4.

2-Aminophenol Isolated as 2-Acetamidophenol

Analytically pure material was obtained by following the general amidation procedure with Ac_2O (2 mmol, 0.188 mL) and an additional 30 min of stirring; white solid; yield: 148 mg (98%); mp 205 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.70 (s, 1 H), 9.29 (s, 1 H), 7.64 (d, *J* = 7.69 Hz, 2 H), 6.90–6.70 (m, 3 H), 2.05 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 169.1, 147.9, 126.4, 124.7, 122.4, 119.0, 115.9, 23.6.

3-Aminophenol (Table 2, entry 8)

Tan solid; yield: 103 mg (94%); mp 119–120 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50).

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 8.31 (br s, 1 H), 6.60 (t, *J* = 8.24 Hz, 1 H), 5.84 (dt, *J* = 1.64, 9.89 Hz, 3 H), 3.62 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 157.4, 147.6, 129.2, 105.7, 104.5, 101.4.

4-Aminophenol (Table 2, entry 9)

The general procedure for reducing nitroarenes afforded 994 mg (91%) of 4-aminophenol and 8 mg (7%) of the oxidized product.

Tan solid; yield: 99 mg (91%); R_f 0.15 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50).

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 6.28 (d, *J* = 8.24 Hz, 2 H), 6.19 (d, *J* = 8.24 Hz, 2 H), 3.00 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 148.85, 138.41, 115.58, 115.22.

4-Aminophenol Isolated as Acetamidophenol

Analytically pure material was obtained by following the general amidation procedure with Ac_2O (2 mmol, 0.188 mL) and an additional 30 min of stirring; off-white solid; yield: 150 mg (99%); mp 166–168 °C; R_f 0.05 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.61 (s, 1 H), 9.11 (s, 1 H), 7.31 (d, *J* = 8.79 Hz, 2 H), 6.64 (d, *J* = 8.79 Hz, 2 H), 1.94 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 167.7, 153.2, 131.1, 121.0, 115.1, 23.8.

4-Methoxyaniline (Table 2, entry 11)

Tan solid; yield: 121 mg (98%); mp 55–56 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.73 (d, *J* = 8.79 Hz, 2 H), 6.61 (d, *J* = 8.79 Hz, 2 H), 3.71 (s, 3 H), 3.40 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.5, 139.8, 116.2, 114.6, 55.6.

4-Acetoxyaniline (Table 2, entry 12)

Tan-red solid; yield: 143 mg (94%); mp 73 °C; R_f 0.3 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 (d, *J* = 8.79 Hz, 2 H), 6.59 (d, *J* = 8.79 Hz, 2 H), 3.62 (br s, 2 H), 2.22 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.0, 144.2, 142.4, 121.9, 115.3, 20.8.

4-*tert*-Butyldimethylsiloxyaniline (Table 2, entry 13)

Following the general procedure for reducing nitroarenes with 3 equiv PMHS afforded 4-*tert*-butyldimethylsiloxyaniline and 7.5 mg (7%) of 4-aminophenol.

Dark yellow oil; yield: 205 mg (92%); R_f 0.45 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

IR (neat): 3460, 2957, 2930, 2858, 1591, 1510, 1336, 1248, 912, 841, 781 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.65 (d, *J* = 8.79 Hz, 2 H), 6.56 (d, *J* = 8.79 Hz, 2 H), 3.91 (br s, 2 H), 0.94 (s, 9 H), 0.13 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 126.0, 120.6, 116.5, 115.5, 18.1, –4.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 224 (11), 223 (93), 167 (29), 166 (100), 138 (38), 109 (12), 93 (7), 73 (17), 65 (34).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{21}NOSi$: 223.1392; found: 223.1398.

4-(Benzyloxy)aniline (Table 2, entry 14)

The general procedure for reducing nitroarenes afforded 4-(benzyloxy)aniline, along with 78 mg (56%) of 4-nitrophenol and 16 mg (14%) of 4-aminophenol.

Red-orange solid; yield: 55 mg (28%); mp 56 °C; R_f 0.3 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (m, 5 H), 6.80 (d, *J* = 8.69 Hz, 2 H), 6.62 (d, *J* = 8.79 Hz, 2 H), 4.97 (s, 2 H), 3.43 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.9, 140.1, 137.4, 128.4, 127.7, 127.4, 116.3, 116.0, 70.7.

6-(Benzyloxy)hexyl 4-Aminobenzoate (Table 2, entry 15)

White solid; yield 327 mg (quant.); mp 58–59 °C; R_f 0.1 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (PTFE card, neat): 3470, 3366, 3235, 2936, 2858, 1689, 1603, 1309, 1275, 1170, 1109, 843, 771, 736, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.79 Hz, 2 H), 7.31 (m, 5 H), 6.59 (d, *J* = 8.79 Hz, 2 H), 4.48 (s, 2 H), 4.22 (t, *J* = 6.59 Hz, 2 H), 4.03 (br s, 2 H), 3.45 (t, *J* = 6.59 Hz, 2 H), 1.71 (t, *J* = 6.59 Hz, 2 H), 1.64 (t, *J* = 6.59 Hz, 2 H), 1.41 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 150.7, 138.5, 131.5, 128.3, 127.5, 127.4, 119.9, 113.7, 72.8, 70.2, 64.3, 29.6, 28.7, 25.9, 25.8.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{25}NO_3$: 327.1834; found: 327.1832.

Methyl 2-Aminobenzoate (Table 2, entry 16)

Bright yellow oil; yield: 151 mg (quant.); R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 1.64, 8.24 Hz, 1 H), 7.23 (dt, *J* = 1.64, 7.14 Hz, 1 H), 6.61 (m, 2 H), 5.69 (br s, 2 H), 3.83 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 150.3, 133.9, 131.2, 116.5, 116.1, 110.5, 51.3.

Methyl 3-Aminobenzoate (Table 2, entry 17)

Light yellow oil; yield: 151 mg (quant.); R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 7.69 Hz, 1 H), 7.29 (m, 1 H), 7.13 (t, 7.69 Hz, 1 H), 6.78 (m, 1 H), 3.85 (br s, 2 H), 3.81 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 146.5, 130.8, 129.0, 125.2, 119.2, 115.5, 51.8.

Methyl 4-Aminobenzoate (Table 2, entry 18)

Yellow solid; yield: 151 mg (quant.); mp 108 °C; R_f 0.15 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.24 Hz, 2 H), 6.57 (d, *J* = 8.79 Hz, 2 H), 4.13 (br s, 2 H), 3.79 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 150.9, 131.4, 119.1, 113.5, 51.4.

4-Acetylaminobenzoic Acid (Table 2, entry 19)

To aid isolation, 4-aminobenzoic acid was converted into its amide following the general amidation procedure with Ac_2O (2 mmol, 0.188 mL) and an additional 30 min of stirring; white solid; yield 169 mg (94%); mp 259–262 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes, EtOAc, 50:50, 0:100, then EtOAc–MeOH, 80:20).

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 9.98 (s, 1 H), 7.90 (d, *J* = 8.24 Hz, 2 H), 7.68 (d, *J* = 8.24 Hz, 2 H), 2.12 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 168.7, 167.2, 142.9, 130.1, 124.9, 118.1, 23.9.

3-Aminobenzamide (Table 2, entry 20)

White solid; yield: 125 mg (92%); mp 117–117.5 °C; R_f 0.2 (EtOAc); silica gel FC (EtOAc–MeOH, 100:0, then 80:20).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.69 (br s, 1 H), 7.11 (br s, 1 H), 7.05–6.86 (m, 3 H), 6.62 (d, *J* = 7.69 Hz, 1 H), 5.14 (br s, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.2, 148.6, 135.1, 128.6, 116.5, 114.7, 113.1.

(*S*)-Diethyl 2-(4-Aminobenzamido)pentanedioate (Table 2, entry 21)

White solid; yield: 322 mg (quant.); mp 134–136 °C; R_f 0.5 (EtOAc); silica gel FC (hexanes–EtOAc, 0:100).

IR (PTFE card, neat): 3445, 3314, 2974, 1726, 1638, 1606, 1529, 1504, 1298, 1182, 1103, 1022 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.24 Hz, 2 H), 6.80 (d, *J* = 7.14 Hz, 1 H), 6.57 (d, *J* = 8.79 Hz, 2 H), 4.71 (dt, *J* = 4.94, 8.24 Hz, 1 H), 4.15 (q, *J* = 7.14 Hz, 2 H), 4.03 (q, *J* = 7.14 Hz, 2 H), 4.2–3.9 (br s, 2 H), 2.38 (m, 2 H), 2.23 (m, 1 H), 2.05 (pent, *J* = 7.14 Hz, 1 H), 1.22 (t, *J* = 7.14 Hz, 3 H), 1.14 (t, *J* = 7.14 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.1, 172.2, 166.8, 149.9, 128.8, 122.8, 113.9, 61.5, 60.6, 52.0, 30.4, 27.3, 14.0.

HRMS (EI): *m*/*z* calcd for $C_{16}H_{22}N_2O_5$: 322.1529; found: 322.1527.

2-Aminobenzonitrile (Table 2, entry 22)

Subjection of 2-nitrobenzonitrile to the general procedure for reducing nitroarenes required 12 h of stirring. The reaction time was decreased to 4 h using 4 equiv of KF (4 mmol, 232 mg); tan solid; yield: 115 mg (97%); mp 52 °C; R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.22 (m, 2 H), 6.69 (m, 2 H), 4.42 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.6, 133.9, 132.2, 117.7, 115.0, 95.7.

3-Aminobenzonitrile (Table 2, entry 23)

Subjection of 3-nitrobenzonitrile to the general procedure for reducing nitroarenes required 12 h of stirring. The reaction time was decreased to 4 h using 4 equiv of KF (4 mmol, 232 mg); yellow-orange solid; yield: 116 mg (98%); mp 49–50 °C; R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 7.96 Hz, 1 H), 6.94 (m, 1 H), 6.88–6.78 (m, 2 H), 3.85 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.9, 129.8, 121.6, 119.1, 119.1, 117.2, 112.5.

Reduction of 4-Nitrobenzonitrile (Table 2, entry 24)

Subjection of 4-nitrobenzonitrile to the general procedure for reducing nitroarenes required 12 h of stirring. The reaction time was decreased to 4 h using 4 equiv of KF (4 mmol, 232 mg). The general procedure afforded 9.4 mg (8%) of 4-aminobenzonitrile and the major product 4-(hydroxyamino)benzonitrile as a mixture.

4-(Hydroxyamino)benzonitrile

Bright yellow solid; yield: 140 mg (78%); R_f 0.45 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.37 (d, *J* = 8.79 Hz, 2 H), 7.29 (br s, 1 H), 6.87 (d, *J* = 8.24 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.5, 133.5, 132.9, 119.7, 114.1, 112.8, 102.1.

1-Amino-4-(trifluoromethyl)benzene (Table 2, entry 25)

Yellow oil; yield 161 mg (99%, 90% purity, contaminated with ca. 18 mg siloxane); R_f 0.55 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc: 80:20, then 50:50).

Pure product could be obtained by following the general procedure for reducing nitroarenes with the following modifications. After filtration through the plug of Celite/alumina, the filtrate was stirred with 5 mol% TBAF for 4 h. The mixture was concentrated and subjecting to flash chromatography to afford 1-amino-4-(trifluoromethyl)benzene that was contaminated with TBA and traces of siloxane (quantitative yield, 95% purity). Short-path distillation of this crude material afforded 145 mg (91%) of analytically pure 1-amino-4-(trifluoromethyl)benzene; bp 75 °C/1 mm Hg.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 8.24 Hz, 2 H), 6.65 (d, *J* = 8.24 Hz, 2 H), 3.91 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 126.67, 126.62, 126.56, 126.52, 123.0, 120.1, 119.7, 114.1, 107.9.

3-Aminoacetophenone (Table 2, entry 26)

3-Nitroacetophenone was subjected to the general procedure for reducing nitroarenes with 3.5 equiv of PMHS (3.5 mmol, 0.21 mL); cream-yellow solid; yield: 132 mg (97%); mp 94–95 °C; R_f 0.25 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.12 (m, 3 H), 6.80 (dd, *J* = 2.19, 7.69 Hz, 1 H), 3.86 (br s, 2 H), 2.49 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.4, 146.7, 137.9, 129.2, 119.5, 118.5, 113.8, 26.5.

4-Aminoacetophenone (Table 2, entry 27)

4-Nitroacetophenone was subjected to the general procedure for reducing nitroarenes with 3 equiv of PMHS (3 mmol, 0.18 mL); yellow solid; yield: 129 mg (95%); mp 102 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 6.59 Hz, 2 H), 6.69 (d, *J* = 6.59 Hz, 2 H), 4.47 (br s, 2 H), 2.54 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.4, 151.0, 130.7, 127.7, 113.6, 26.0.

4-Aminobenzaldehyde (Table 2, entry 28)

Subjection of 4-nitrobenzaldehyde to the general procedure for reducing nitroarenes with 3 equiv of PMHS (3 mmol, 0.18 mL) afforded an inseparable mixture of 88 mg (73%) of 4-aminobenzaldehyde and 38 mg (24%) of (4-nitrophenyl)methanol as a yellow solid containing residual EtOAc. Upon complete removal of EtOAc a yellow solid formed, which was insoluble in all solvents tested (presumable from polymerization of the two products); R_f 0.4 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.62 (s, 1 H), 7.58 (d, *J* = 6.59 Hz, 2 H), 6.62 (d, *J* = 6.59 Hz, 2 H), 4.55 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.6, 152.8, 132.3, 126.9, 113.8.

(4-Nitrophenyl)methanol

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 6.59 Hz, 2 H), 7.46 (d, *J* = 7.14 Hz, 2 H), 4.73 (s, 2 H), 3.70 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.6, 126.8, 123.4, 63.6.

***N*-[4-(1,3-Dioxolan-2-yl)phenyl]acetamide** (Table 2, entry 29)

To aid isolation, 4-(1,3-dioxolan-2-yl)aniline was converted into its amide following the general amidation procedure with Ac_2O (2 mmol, 0.188 mL) and an additional 30 min of stirring; light yellow solid; yield: 165 mg (80%); mp 110 °C; R_f 0.1 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

IR (PTFE card, neat): 3310, 3127, 3063, 2885, 1670, 1604, 1539, 1419, 1371, 1313, 1078, 941, 835 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60 (br s, 1 H), 7.45 (d, *J* = 8.79 Hz, 2 H), 7.32 (d, *J* = 8.79 Hz, 2 H), 5.68 (s, 1 H), 3.98 (m, 4 H), 2.02 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.0, 138.8, 133.2, 126.9, 119.6, 103.2, 64.9, 24.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 207 (0.36), 163 (41), 121 (85), 120 (83), 119 (100), 92 (45), 77 (4), 73 (3), 43 (83).

HRMS (CI): *m*/*z* calcd for $[C_{11}H_{13}NO_3 + H]^+$: 208.0974; found: 208.0970.

2-Fluoroaniline (Table 2, entry 32)

Light yellow oil; yield: 109 mg (97%); R_f 0.3 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00–6.86 (m, 2 H), 6.78–6.18 (m, 2 H), 3.67 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.2, 150.0, 134.5, 124.4, 124.3, 118.5, 118.4, 116.8, 115.2.

3-Fluoroaniline (Table 2, entry 33)

Light yellow oil; yield: 107 mg (96%); R_f 0.2 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03 (q, *J* = 8.24 Hz, 1 H), 6.45–6.28 (m, 3 H), 3.74 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 162.1, 148.3, 148.1, 130.3, 130.2, 110.5, 104.9, 104.6, 101.9, 101.6.

4-Fluoroaniline (Table 2, entry 34)

Light yellow oil; yield: 105 mg (95%); R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.83 (m, 2 H), 6.60 (m, 2 H), 3.51 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 154.7, 142.3, 116.0, 115.9, 115.7, 115.4.

6-Bromohexyl 4-Aminobenzoate (Table 2, entry 36)

6-Bromohexyl 4-nitrobenzoate was subjected to the general procedure for reducing nitroarenes with PMHS (3.5 mmol, 0.21 mL, 3.5 equiv); white solid; yield: 300 mg (quant.); mp 77–78 °C; R_f 0.15 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 95:5 then 50:50).

IR (THF solution): 3445, 3360, 3238, 2937, 1705, 1604, 1518, 1275, 1170, 1113, 844, 773 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.79 Hz, 2 H), 6.58 (d, *J* = 8.79 Hz, 2 H), 4.21 (t, *J* = 6.59 Hz, 2 H), 4.07 (br s, 2 H), 3.35 (t, *J* = 6.59 Hz, 2 H), 1.82 (pent, *J* = 6.59 Hz, 2 H), 1.69 (pent, *J* = 6.59 Hz, 2 H), 1.42 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 150.8, 131.3, 119.4, 113.5, 64.1, 33.7, 32.4, 28.4, 27.6, 25.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 300 (12), 299 (11), 138 (12), 137 (100), 80 (7), 79 (100), 92 (40), 65 (15), 64 (14).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{18}BrNO_2$: 299.0521; found: 299.0525.

4-Nitroaniline (Table 2, Entry 37; Table 4, entry 2)

Orange solid; yield: 99 mg (72%); mp 147–148 °C; R_f 0.4 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, 0:100, then EtOAc–MeOH, 80:20); and 22 mg (20%) of 1,4-diaminobenzene was also isolated as a tan solid.

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 7.68 (d, J = 8.79 Hz, 2 H), 6.32 (d, J = 9.34 Hz, 2 H), 5.27 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 153.7, 136.7, 125.6, 112.2.

3-Methoxy-5-(trifluoromethyl)aniline (Table 2, entry 38)

1-Methoxy-3-nitro-5-(trifluoromethyl)benzene was subjected to the general procedure for reducing nitroarenes with 5 equiv of PMHS (5 mmol, 0.3 mL) and stirred for 12 h; yellow oil; yield: 190 mg (99%); mp 50 °C; R_f 0.15 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.51 (s, 1 H), 6.48 (s, 1 H), 6.31 (s, 1 H), 3.92 (br s, 2 H), 3.75 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.9, 148.0, 132.6, 132.2, 125.8, 122.2, 104.45, 104.40, 103.6, 100.7, 55.2.

2-Methoxy-5-(trifluoromethyl)aniline (Table 2, entry 39)

White solid; yield: 191 mg (quant.); mp 56–57 °C; R_f 0.2 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.96 (d, J = 8.24 Hz, 1 H), 6.89 (s, 1 H), 6.77 (d, J = 8.24 Hz, 1 H), 3.90 (br s, 2 H), 3.86 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.3, 136.4, 126.3, 123.3, 122.7, 115.49, 115.43, 111.0, 110.9, 109.5, 55.4.

4-Methoxy-3-(trifluoromethyl)aniline (Table 2, entry 40)

Yellow solid; yield: 188 mg (98%); mp 55–57 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (Nujol): 3431, 3314, 3211, 1643, 1599, 1508, 1437, 1344, 1236, 1101, 1053, 1022, 877, 815, 709 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.87 (d, J = 2.74 Hz, 1 H), 6.80 (m, 1 H), 6.76 (dd, J = 2.74, 8.79 Hz, 1 H), 3.78 (s, 3 H), 3.53 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 139.3, 125.1, 121.1, 119.0, 118.8, 113.7, 113.6, 113.56, 113.50, 56.2.

LRMS (EI, 70 eV): m/z (%) = 192 (8), 191 (78), 177 (12), 176 (100), 175 (10), 148 (42), 129 (13), 128 (30), 101 (30), 98 (21), 77 (10), 51 (25).

HRMS (EI): m/z calcd for $C_8H_8F_3NO$: 191.0558; found: 191.0555.

2-Amino-4-(trifluoromethyl)benzonitrile (Table 2, entry 41)

The general procedure for reducing nitroarenes afforded 41 mg (20%) of 2-amino-4-(trifluoromethyl)benzamide and 2-amino-4-(trifluoromethyl)benzonitrile.

Yellow solid; yield: 145 mg (78%); mp 85 °C; R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, J = 8.24 Hz, 1 H), 6.95 (s, 1 H), 6.90 (d, J = 8.24 Hz, 1 H), 4.71 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 135.8, 135.4, 133.1, 124.9, 121.2, 116.3, 114.04, 114.00, 111.86, 111.80, 98.6.

4-Amino-2-methoxybenzonitrile (Table 2, entry 42)

4-Nitro-2-methoxybenzonitrile was subjected to the general procedure for reducing nitroarenes for 1 h. Burgundy solid; yield: 147 mg (99%); mp 94 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (PTFE card, neat): 1603, 1512, 1471, 1342, 1130, 1028, 833, 636 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, J = 8.24 Hz, 1 H), 6.18 (dd, J = 2.19, 8.24 Hz, 1 H), 6.13 (m, 1 H), 4.26 (br s, 2 H), 3.78 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9, 152.4, 134.7, 117.9, 106.9, 96.7, 89.6, 55.6.

LRMS (EI, 70 eV): m/z (%) = 148 (100), 119 (36), 118 (29), 105 (28), 104 (28), 91 (23), 78 (25), 77 (10).

HRMS (EI): m/z calcd for $C_8H_8N_2O$: 148.0637; found: 148.0633.

Hex-5-enyl 4-Aminobenzoate (Table 3, entry 2)

Subjection of hex-5-enyl 4-nitrobenzoate to the general procedure for reducing nitroarenes afforded 221 mg of hex-5-enyl 4-aminobenzoate (27%) and hexyl 4-aminobenzoate (73%) as an inseparable mixture in a 1:2.7 ratio; yellow solid; R_f 0.15 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.79 Hz, 2 H), 6.59 (d, J = 8.79 Hz, 2 H), 5.42 (m, 3 H, measured 0.81 H), 4.21 (t, J = 6.59 Hz, 2 H), 4.05 (br s, 2 H), 2.08 (m, 2 H, measured 0.54 H), 1.83–1.53 (m, 3 H), 1.45–1.20 (m, 3.5 H), 0.87 (t, J = 6.59 Hz, 3 H, measured 2.15 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 150.8, 131.4, 130.0, 125.6, 119.7, 113.6, 64.4, 63.7, 31.3, 28.9, 28.6, 28.5, 25.6, 22.4, 17.7, 13.9.

(*E*)-Hex-4-enyl 4-Aminobenzoate (Table 3, entry 3)

Subjection of (*E*)-hex-4-enyl 4-nitrobenzoate to the general procedure for reducing nitroarenes with 3 equiv of PMHS (3 mmol, 0.18 mL), afforded 160 mg of (*E*)-hex-4-enyl 4-aminobenzoate (51%) and hexyl 4-aminobenzoate (22%) as an inseparable mixture in a 2.25:1 ratio; tan solid; R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.79 Hz, 2 H), 6.58 (d, J = 8.79 Hz, 2 H), 5.41 (m, 2 H, measured 1.38 H), 4.21 (t, J = 6.59 Hz, 2 H), 4.11 (br s, 2 H), 2.07 (m, 2 H, measured 1.38 H), 1.75 (m, 2 H), 1.61 (m, 3 H, measured 2.08 H), 1.31 (m, 6 H, measured 1.84 H), 0.86 (t, J = 6.59 Hz, 3 H, measured 0.92 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 166.6, 150.9, 150.8, 131.3, 129.5, 125.5, 119.5, 119.4, 113.5, 64.3, 63.7, 31.3, 28.8, 28.6, 28.4, 25.5, 22.3, 17.7, 13.8.

3-Methylbut-3-enyl 4-Aminobenzoate (Table 3, entry 6)

Subjection of 3-methylbut-3-enyl 4-nitrobenzoate to the general procedure for reducing nitroarenes with 3.5 equiv of PMHS (3.5 mmol, 0.21 mL), afforded 201 mg of 3-methylbut-3-enyl 4-aminobenzoate (64%), 3-methylbut-2-enyl 4-aminobenzoate (18%), and isopentyl 4-aminobenzoate (15%) as an inseparable mixture in a 4.1:1.2:1.0 ratio; yellow solid; R_f 0.2 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.24 Hz, 2 H), 6.57 (d, J = 8.24 Hz, 2 H), 5.41 (m, 1 H, measured 0.19 H), 4.77 (d, J = 7.69 Hz, 2 H, measured 1.36 H), 4.72 (d, J = 7.14 Hz, 2 H, measured 0.36 H), 4.33 (t, J = 7.14 Hz, 2 H, measured 1.31 H), 4.25 (t, J = 7.14 Hz, 2 H, measured 0.37 H), 4.11 (br s, 2 H), 2.41 (t, J = 6.59 Hz, 2 H, measured 1.31 H), 1.75 (s, 3 H, measured 1.97 H), 1.70 (d, J = 7.69 Hz, 6 H, measured 1.09 H), 1.60 (q, J = 6.59 Hz, 2 H, measured 0.32 H), 0.91 (d, J = 6.59 Hz, 6 H, measured 0.96 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 150.9, 150.8, 141.8, 138.4, 131.4, 119.5, 118.9, 113.6, 112.1, 62.8, 62.5, 61.1, 37.3, 36.7, 25.6, 25.0, 22.43, 22.40, 17.9.

3,7-Dimethyloct-6-enyl 4-Aminobenzoate (Table 3, entry 9)

Subjection of 3,7-dimethyloxt-6-enyl 4-nitrobenzoate (1 mmol, 305 mg) to the general procedure for reducing nitroarenes with 3.5 equiv PMHS (3.5 mmol, 0.21 mL) afforded 13 mg (5%) of 3,7-dimethyloctyl 4-aminobenzoate and 249 mg (91%) of 3,7-dimethyloct-6-

enyl 4-aminobenzoate as an inseparable mixture; yellow oil; yield: 249 mg (91%); R_f 0.2 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20).

IR (neat): 3478, 3372, 3231, 2961, 2926, 1893, 1624, 1604, 1278, 1172, 1115 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.79 Hz, 2 H), 6.59 (d, *J* = 8.79 Hz, 2 H), 5.06 (m, 1 H), 4.26 (m, 2 H), 4.09 (br s, 2 H), 1.97 (m, 2 H), 1.81–1.08 (m, 12 H), 0.93 (d, *J* = 6.59 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 150.8, 131.4, 131.1, 124.5, 119.7, 113.6, 62.7, 36.8, 35.4, 29.4, 25.5, 25.2, 19.3, 17.5.

HRMS (EI): *m*/*z* calcd for $C_{17}H_{25}NO_2$: 275.1885; found: 275.1883.

2-(4-Methylcyclohex-3-enyl)propan-2-enyl 4-Aminobenzoate (Table 3, entry 11)

Subjection of 2-(4-methylcyclohex-3-enyl)propan-2-yl 4-nitrobenzoate (1 mmol, 303 mg) to the general procedure for reducing nitroarenes with 3.5 equiv PMHS (3.5 mmol, 0.21 mL) afforded 20 mg (7%) of 2-(4-methylcyclohexyl)propan-2-yl 4-aminobenzoate and 254 mg (93%) of 2-(4-methylcyclohex-3-enyl)propan-2-yl 4-aminobenzoate as an inseparable mixture; clear viscous oil; yield: 254 mg (93%); R_f 0.2 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20).

IR (neat): 3478, 3370, 3229, 2928, 1684, 1616, 1516, 1437, 1311, 1172, 1115, 912, 844, 771, 734 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.79 Hz, 2 H), 6.56 (d, *J* = 8.24 Hz, 2 H), 5.35 (s, 1 H), 4.07 (br s, 2 H), 2.2–1.8 (m, 7 H), 1.62 (s, 3 H), 1.54 (s, 3 H), 1.51 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.7, 150.5, 133.7, 131.1, 121.3, 120.3, 113.5, 84.3, 43.0, 30.8, 26.3, 23.8, 23.4, 23.1.

HRMS (EI): *m*/*z* calcd for $C_{17}H_{22}NO_2$: 273.1729; found: 273. 1736.

4,4′-Diaminodiphenylmethane (Table 4, entry 5)

Bis(4-nitrophenyl)methane was subjected to the general procedure for reducing nitro arenes with 8 equiv of PMHS (8 mmol, 0.48 mL) and 4 equiv KF (4 mmol, 232 mg); yellow-orange solid; yield: 185 mg (93%); mp 89 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

^1H NMR (300 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 8.24 Hz, 4 H), 6.61 (d, *J* = 8.24 Hz, 4 H), 3.79 (s, 2 H), 3.54 (br s, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1, 131.7, 129.4, 115.1, 40.0.

4-Methoxybenzene-1,3-diamine (Table 4, entry 7)

1-Methoxy-2,4-dinitrobenzene was subjected to the general procedure for reducing nitroarenes with 8 equiv of PMHS (8 mmol, 0.48 mL) and 4 equiv KF (4 mmol, 232 mg); tan solid; yield: 122 mg (89%); mp 65 °C; R_f 0.25 (EtOAc); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

^1H NMR (300 MHz, $CDCl_3$): δ = 6.58 (d, *J* = 7.69 Hz, 1 H), 6.03 (m, 2 H), 3.73 (s, 3 H), 3.54 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.6, 136.9, 112.1, 104.5, 103.2, 56.0.

Methyl 5-Amino-2-furoate (Table 5, entry 1)

Yellow solid; yield: 124 mg (89%); mp 134–135 °C; R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.02 (d, *J* = 3.29 Hz, 1 H), 6.41 (br s, 2 H), 5.01 (d, *J* = 3.29 Hz, 1 H), 3.61 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.7, 158.0, 132.2, 123.6, 84.2, 50.4.

6-Amino-1*H*-benzimidazole (Table 5, entry 2)

A dry 25-mL round-bottom flask was charged with $Pd(OAc)_2$ (0.05 mmol, 11 mg), sealed, and placed under a positive pressure of N_2. THF (5 mL) and aq KF (2 mmol, 116 mg, in 2 mL of degassed H_2O) were added sequentially. PMHS (0.67 mmol, 0.04 mL) was added dropwise via syringe and the reaction was stirred ~15–45 seconds to preform the PMHS-$Pd(OAc)_2$ nanoparticles. The reaction was then opened to the air and 6-nitro-1*H*-benzimidazole (1 mmol, 163 mg) was added in a single portion. The reaction flask was resealed and purged with N_2. The remaining PMHS (3.3 mmol, 0.20 mL) was then added dropwise. The N_2 inlet was replaced by a balloon filled with N_2 and the reaction was stirred for 30 min. Following the general extraction protocol, the organics were filtered though a plug of Celite, concentrated and subjected to flash chromatography. (Note: In lieu of opening the reaction system to the air, 6-nitro-1*H*-benzimidazole can be dissolved in a THF–H_2O mixture (2 mL:1 mL) and added to the reaction via syringe; cream-colored solid; yield: 133 mg [89%, containing residual (~10%) H_2O]; mp 160–165 °C; R_f 0.6 (EtOAc–MeOH, 60:40); silica gel FC (EtOAc–MeOH, 100:0, 80:20, then 50:50).

IR (MeOH solution): 3175, 2820, 1635, 1522, 1491, 1361, 1265, 1209, 1028, 949, 812, 619 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 11.85 (br s, 1 H), 7.92 (s, 1 H), 7.29 (d, *J* = 8.24 Hz, 1 H), 6.71 (s, 1 H), 6.54 (d, *J* = 8.24 Hz, 1 H), 4.91 (br s, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 144.5, 139.6, 136.9, 132.9, 117.1, 111.6, 96.8.

LRMS (EI, 70 eV): *m*/*z* (%) = 132, 116, 106, 105, 78, 66, 52.

HRMS (EI): *m*/*z* calcd for $C_7H_7N_3$: 133.0640; found: 133.0637.

4-Amino-2-(1*H*-pyrazol-3-yl)phenol (Table 5, entry 5)

A dry 25-mL round-bottom flask was charged with $Pd(OAc)_2$ (0.05 mmol, 11 mg), sealed, and placed under a positive pressure of N_2. THF (5 mL) and aq KF (2 mmol, 116 mg, in 2 mL of degassed H_2O) were added sequentially. PMHS (0.67 mmol, 0.04 mL) was added dropwise via syringe and the reaction was stirred ~15–45 seconds to preform the PMHS-$Pd(OAc)_2$ nanoparticles. The reaction was then opened to the air and 4-nitro-2-(1*H*-pyrazol-3-yl)phenol (1 mmol, 205 mg) was added in a single portion. The reaction flask was resealed and purged with N_2. The remaining PMHS (3.3 mmol, 0.20 mL) was then added dropwise. The N_2 inlet was replaced by a balloon filled with N_2 and the reaction was stirred for 30 min. Following the general extraction protocol, the organics were filtered though a plug of Celite, concentrated and subjected to flash chromatography.

The general procedure for reducing nitroarenes afforded an inseparable mixture of 8.6 mg (5%) of the partially reduced product and 4-amino-2-(1*H*-pyrazol-3yl)phenol; yellow solid; yield: 156 mg (89%); mp 160–165 °C; R_f 0.4 (EtOAc); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then EtOAc).

^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 10.15 (br s, 1 H), 7.22 (d, *J* = 2.74 Hz, 1 H), 6.61 (d, *J* = 2.74 Hz, 1 H), 6.42 (m, 1 H), 6.23 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 149.8, 147.4, 138.3, 128.7, 116.2, 116.0, 115.8, 112.0, 100.5,

***N*-(4-Hydroxy-3-(1*H*-pyrazol-3-yl)phenyl)acetamide**

To aid isolation, analytically pure material 4-amino-2-(1*H*-pyrazol-3-yl)phenol was subjected to the general amidation procedure with Ac_2O (2 mmol, 0.188 mL) and an additional 30 min of stirring; white solid; yield: 189 mg (87%); mp 172–176 °C; R_f 0.2 (EtOAc); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 10.37 (br s, 1 H), 8.99 (s, 1 H), 7.37 (d, *J* = 2.74 Hz, 1 H), 7.07 (d, *J* = 2.74 Hz, 1 H), 6.78

(dd, J = 2.19, 8.79 Hz, 1 H), 6.33 (d, J = 8.79 Hz, 1 H), 6.06 (d, J = 2.19 Hz, 1 H), 1.57 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 167.4, 150.7, 149.1, 129.7, 128.6, 120.1, 117.3, 115.4, 115.3, 100.2, 22.7.

HRMS (EI): m/z calcd for $C_{11}H_{11}N_3O_2$: 217.0851; found: 217.0848.

4-(Pyridin-4-ylmethyl)aniline (Table 5, entry 6)

White solid; yield: 183 mg (99%); mp 157 °C; R_f 0.2 (EtOAc); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 8.17 (d, J = 6.04 Hz, 2 H), 6.82 (d, J = 6.04 Hz, 2 H), 6.66 (d, J = 8.24 Hz, 2 H), 6.36 (d, J = 8.24 Hz, 2 H), 3.69 (br s, 2 H), 3.56 (s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 150.4, 148.9, 144.9, 129.1, 127.3, 123.4, 114.5,

6-Methoxypyridin-3-amine (Table 5, entry 7)

Amber oil; yield: 124 mg (100%); R_f 0.15 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, J = 2.74 Hz, 1 H), 6.93 (dd, J = 2.74, 8.79 Hz, 1 H), 6.52 (d, J = 8.79 Hz, 1 H), 3.78 (s, 3 H), 3.38 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8, 136.6, 132.6, 127.4, 110.5, 53.1.

Quinolin-6-amine (Table 5, entry 8)

Yellow solid; yield: 144 mg (quant.); mp 118–120 °C; R_f 0.2 (EtOAc); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (dd, J = 1.64, 4.39 Hz, 1 H), 7.83 (d, J = 8.79 Hz, 1 H), 7.77 (d, J = 8.24 Hz, 1 H), 7.16 (dd, J = 4.39, 8.24 Hz, 1 H), 7.05 (dd, J = 2.74, 8.79 Hz, 1 H), 6.77 (d, J = 2.74 Hz, 1H), 4.04 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 144.6, 143.1, 133.6, 130.1, 129.6, 121.4, 121.1, 107.1.

5-(4-Aminophenylsulfonyl)thiazol-2-amine (Table 5, entry 10)

A dry 25-mL round-bottom flask was charged with $Pd(OAc)_2$ (0.05 mmol, 11 mg), sealed, and placed under a positive pressure of N_2. THF (3 mL) and aq KF (2 mmol, 116 mg, in 1.5 mL of degassed H_2O) were added sequentially. PMHS (0.67 mmol, 0.04 mL) was added dropwise via syringe and the reaction was stirred ~15–45 seconds to preform the PMHS-$Pd(OAc)_2$ nanoparticles. At that point 2-amino-5-(4-nitrophenylsulfonyl)thiazole (1 mmol, 285 mg) dissolved in a mixture of anhyd THF and H_2O (2 mL:0.5 mL) was injected, followed by the dropwise addition of the remaining PMHS (3.3 mmol, 0.20 mL). A balloon filled with N_2 replaced the N_2 inlet and the reaction was stirred for 30 min. Following the general extraction protocol, the organics were filtered though a plug of Celite, concentrated and subjected to flash chromatography; yellow solid; yield: 241 mg (94%); mp 170 °C; R_f 0.35 (EtOAc); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.05 (s, 1 H), 8.70 (s, 1 H), 7.85 (br s, 2 H), 7.58 (d, J = 8.79 Hz, 2 H), 6.84 (d, J = 8.79 Hz, 2 H), 7.46 (s, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 174.1, 155.6, 145.8, 130.5, 127.8, 123.6, 111.4.

2-Aminothiophene (Table 5, entry 12)

Note: 2-Aminothiophene decomposes immediately when exposed to air,[45] so the reaction system should not be opened to the air until the amine is protected.

2-Nitrothiophene (1 mmol, 129 mg) was subjected to the general procedure for reducing nitroarenes with the following modification. After complete consumption of the starting material as judged by TLC (ca. 30 min), di(*tert*-butyl) dicarbonate (2 mmol, 436 mg) dissolved in THF (0.5 mL) was injected into the reaction followed by an additional 4 h of stirring. Following the general extraction protocol, the organics were filtered though a plug of Celite. Concentration of the crude material and flash chromatography afforded *tert*-butyl thiophen-2-ylcarbamate; white solid; yield: 161 mg (81%); mp 150 °C; R_f 0.2 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 95:5, then 80:20.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.91 (br s, 1 H), 6.78 (m, 2 H), 6.49 (dd, J = 1.64, 3.29 Hz, 1 H), 1.49 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.4, 140.2, 124.3, 116.9, 111.1, 81.3, 28.2.

Reduction of Aliphatic Nitro Compounds; General Procedure

A round bottom flask was charged with $Pd(OAc)_2$ (0.05 mmol, 11 mg), the nitroarene (1 mmol), and freshly distilled anhyd THF (5 mL). The flask was sealed and purged with N_2. While purging the flask with N_2, degassed H_2O (2 mL) was injected via a syringe. The N_2 inlet was replaced with a balloon of N_2. Et_3SiH (6 mmol, 0.96 mL) was slowly added dropwise via a syringe. The reaction was stirred for 2 h or until complete as judged by TLC. At that time, the reaction flask was opened to the air and diluted with Et_2O (5–10 mL). The layers were separated and the aqueous layer was back-extracted with Et_2O. The combined organics were concentrated and subjected to flash chromatography eluting with gradients of hexanes–EtOAc and/or EtOAc–MeOH.

***N*-Decylhydroxylamine** (Table 6, entry 1)

White solid; yield: 145 mg (83%); mp 79 °C; R_f 0.05 (hexanes–EtOAc, 90:10); silica gel FC (hexanes–EtOAc, 90:10, then 0:100).

IR (KBr): 3270, 3159, 2931, 2865, 1473, 1153, 1061, 891, 721 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (br s, 2 H), 2.90 (t, J = 7.14 Hz, 2 H), 1.49 (m, 2 H), 1.22 (m, 14 H), 0.84 (t, J = 7.14 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.9, 31.9, 29.5, 29.3, 27.1, 26.9, 22.6, 14.1.

LRMS (EI, 70 eV): m/z (%) = 173 (3), 157 (3), 142 (1), 70 (19), 46 (100).

HRMS (EI): m/z calcd for $C_{10}H_{23}N_3O$: 173.1780; found: 173.1781.

***N*-Phenethylhydroxylamine** (Table 6, entry 2)

White solid; yield: 80 mg (58%); mp 85 °C; R_f 0.2 (EtOAc); silica gel FC (EtOAc–MeOH, 100:0, then 80:20).

IR (neat): 3246, 3152, 2862, 1496, 1454, 1059, 740, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m, 2 H), 7.22 (m, 3 H), 6.33 (br s, 2 H), 3.17 (t, J = 7.14 Hz, 2 H), 2.87 (t, J = 7.14 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0, 128.7, 128.5, 126.2, 54.7, 33.1.

LRMS (EI, 70 eV): m/z (%) = 137 (1), 136 (1), 121 (8), 105 (13), 104 (24), 92 (83), 91 (100), 77 (13), 76 (17), 46 (32), 45 (34).

HRMS (EI): m/z calcd for $C_8H_{11}NO$ 137.0841; found: 137.0843.

Isolation of *N*-Hydroxylaminocyclohexane as *N*-Cyclohexyl-*N*-hydroxy-4-methylbenzenesulfonamide (Table 6, entry 3)

Nitrocyclohexane (1 mmol, 0.122 mL) was subjected to the general procedure for reducing aliphatic nitro compounds with the following modification. After complete consumption of the starting material (as judged by TLC), 2 equiv *p*-toluenesulfonic anhydride (2 mmol, 652 mg) was added to the reaction followed by an additional 2 h of stirring to afford after the general workup *N*-cyclohexyl-*N*-hydroxy-4-methylbenzenesulfonamide [The NTs (vs. OTs) assignment was based on IR data and should be considered tentative]; white solid; yield: 239 mg (89%); mp 127–129 °C; R_f 0.7 (hexanes–

EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

IR (PTFE card): 3366, 2930, 2855, 1334, 1185, 1082, 665, 584 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.24 Hz, 2 H), 7.29 (d, *J* = 8.24 Hz, 2 H), 6.64 (s, 1 H), 3.62 (tt, *J* = 3.84, 10.98 Hz, 1 H), 2.41 (s, 3 H), 1.72–0.85 (m, 10 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 133.8, 129.5, 128.8, 60.3, 28.9, 25.3, 25.2, 21.6.

LRMS (EI, 70 eV): *m*/*z* (%) = 269 (1), 253 (3), 157 (78), 139 (46), 91 (100), 83 (44), 77 (7), 76 (9), 55 (46), 54 (44), 41 (53).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{19}NO_3S$: 269.1086; found: 269.1090.

1,3-Diacetoxy-2-acetoxymethyl-2-(*N*-hydroxy)aminopropane (Table 6, entry 4)

Clear oil; yield: 82 mg (31%); R_f 0.45 (EtOAc); silica gel FC (hexanes–EtOAc, 80:20, then 0:100).

IR (neat): 3372, 2963, 1734, 1653, 1437, 1379, 1226, 1047, 952, 908 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.21 (br s, 2 H), 4.14 (s, 6 H), 2.05 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 62.0, 61.0, 20.7.

LRMS (EI, 70 eV): *m*/*z* (%) = 263 (0.5), 232 (40), 190 (30), 172 (9), 113 (74), 102 (13), 54 (7), 43 (100).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{17}NO_7$: 263.1005; found: 269.0997.

3-Hydroxy-4-methyl-5-phenethyloxazolidin-2-one (Table 6, entry 7)

4-Nitro-1-phenylpentan-3-ol (1 mmol, 209 mg, *syn*/*anti* mixture = 1.77:1) was subjected to the general procedure for reducing aliphatic nitro compounds with the following modifications. After stirring for 4 h, the starting material was completely consumed (as judged by TLC). At that time 2 equiv of *N,N*′-carbonyldiimidazole (2 mmol, 324 mg) was added and the reaction was stirred an additional 6 h to afford after the general workup of 3-hydroxy-4-methyl-5-phenethyloxazolidin-2-one (*anti*/*syn* = 1.8:1); clear solid; yield: 182 mg (89%); R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

IR (neat): 3267, 2936, 1757, 1496, 1456, 1387, 1228, 1111, 1035, 752, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.76 (br s, 1 H), 7.32–7.12 (m, 5 H), 4.43 (ddd, *J* = 3.84, 7.14, 10.43 Hz, 0.35H), 3.96 (m, 1 H), 3.55 (dq, *J* = 2.19, 6.04 Hz, 0.63 H), 2.85 (m, 1 H), 2.66 (m, 1 H), 2.10–1.73 (m, 2 H), 1.29 (d, *J* = 6.04 Hz, 2.04 H), 1.20 (d, *J* = 6.59 Hz, 1.14 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.5, 160.4, 140.2, 140.1, 128.5, 128.4, 128.3, 126.2, 79.8, 76.0, 60.5, 57.8, 34.5, 31.3, 30.9, 16.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 221 (20), 220 (13), 204 (12), 146 (9), 116 (39), 105 (44), 104 (67), 99 (15), 91 (100), 77 (50), 41 (100).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{15}NO_3$: 221.1052; found: 221.1055.

***N*-[4-Phenyl-2-(triethylsilyloxy)butyl]hydroxylamine** (Table 6, entry 10)

Subjection of triethyl(1-nitro-4-phenylbutan-2-yloxy)silane (1 mmol, 309 mg) to the general procedure for reducing aliphatic nitro compounds with 10 equiv triethylsilane (10 mmol, 1.6 mL) afforded *N*-[4-phenyl-2-(triethylsilyloxy)butyl]hydroxylamine and 118 mg (38%) of starting material.

Light yellow oil; yield: 165 mg (56%); R_f 0.15 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (neat): 3267, 2953, 2930, 2856, 1471, 1255, 1097, 1068, 837, 777, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.28 (m, 2 H), 7.19 (m, 2 H), 6.16 (br s, 2 H), 4.07 (m, 1 H), 3.04 (dd, $J_{A,A}$ = 3.84 Hz, $J_{A,B}$ = 3.29 Hz, 1 H), 2.92 (dd, $J_{B,B}$ = 7.14 Hz, $J_{B,A}$ = 7.69 Hz, 1 H), 2.66 (t, *J* = 8.79 Hz, 2 H), 1.83 (m, 2 H), 0.99 (t, *J* = 8.24 Hz, 6 H), 0.65 (q, *J* = 8.24 Hz, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.0, 128.3, 128.2, 125.7, 68.4, 59.0, 37.6, 31.4, 6.8, 4.9.

HRMS (EI): *m*/*z* calcd for $C_{16}H_{29}NO_2Si$: 295.1968; found: 295.1964.

***N*-[2-(*tert*-Butyldimethylsilyloxy)-4-phenylbutyl]hydroxylamine** (Table 6, entry 12)

Subjection of *tert*-butyldimethyl(1-nitro-4-phenylbutan-2-yloxy)silane (1 mmol, 309 mg) to the general procedure for reducing aliphatic nitro compounds with 10 equiv triethylsilane (10 mmol, 1.6 mL) afforded *N*-[2-(*tert*-butyldimethylsilyloxy)-4-phenylbutyl]hydroxylamine, and 97 mg (31%) of starting material.

Light yellow oil; yield: 169 mg (57%); R_f 0.15 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (neat): 3267, 2953, 2930, 2856, 1471, 1255, 1097, 1068, 837, 777, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.14 (m, 5 H), 6.29 (br s, 2 H), 4.06 (m, 1 H), 3.03 (dd, $J_{A,A}$ = 3.84 Hz, $J_{A,B}$ = 3.29 Hz, 1 H), 2.94 (dd, $J_{B,B}$ = 7.14 Hz, $J_{B,A}$ = 7.14 Hz, 1 H), 2.64 (t, *J* = 7.69 Hz, 2 H), 1.81 (m, 2 H), 0.96 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.1, 128.3, 128.2, 125.7, 68.3, 59.0, 37.6, 31.3, 25.8, 18.0, –4.4, –4.6.

LRMS (EI, 70 eV): *m*/*z* (%) = 249 (24), 248 (10), 147 (6), 132 (5), 131 (35), 117 (36), 115 (14), 91 (83), 77 (6), 75 (63), 74 (15), 73 (100), 72 (11), 57 (10).

HRMS (EI): *m*/*z* calcd for $C_{16}H_{29}NO_2Si$: 295.1968; found: 295.1974.

1-(Hydroxyamino)-4-phenylbutan-2-yl Acetate (Table 6, entry 14)

Subjection of 1-nitro-4-phenylbutan-2-yl acetate (1 mmol, 237 mg) to the general procedure for reducing aliphatic nitro compounds with 10 equiv triethylsilane (10 mmol, 1.6 mL) afforded 1-(hydroxyamino)-4-phenylbutan-2-yl acetate; orange solid; yield: 121 mg (54%); R_f 0.05 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50, 0:100, then EtOAc–MeOH, 80:20).

***N*-(2-Methoxy-4-phenylbutyl)hydroxylamine** (Table 6, entry 15)

Clear oil; yield: 109 mg (56%); R_f 0.05 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50, 0:100, then EtOAc–MeOH, 80:20).

IR (neat): 3267, 3026, 2930, 2828, 1496, 1456, 1103, 1057, 910, 733 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.12 (m, 5 H), 6.28 (br s, 2 H), 3.51 (m, 1H), 3.39 (s, 3 H), 3.05 (dd, $J_{A,A}$ = 3.29 Hz, $J_{A,B}$ = 3.84 Hz, 1 H), 2.91 (dd, $J_{B,B}$ = 8.24 Hz, $J_{B,A}$ = 7.69 Hz, 1 H), 2.66 (t, *J* = 7.69 Hz, 2 H), 1.82 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.8, 128.3, 128.2, 125.8, 76.7, 57.0, 56.7, 33.6, 31.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 149 (9), 131 (6), 118 (4), 117 (29), 105 (6), 91 (100), 77 (5).

HRMS (EI): *m*/*z* calcd for $C_{11}H_{17}NO_2$: 195.1259; found: 195.1258.

3-Phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indol-1-oxide (Table 6, entry 18)

Subjection of 2-(2-nitro-1-phenylethyl)cyclohexanone (1 mmol, 247 mg) to the general procedure for reducing aliphatic nitro compounds with 10 equiv triethylsilane (10 mmol, 1.6 mL) afforded the nitrone 3-phenyl-3,3a,4,5,6,7-hexahydro-2*H*-indol-1-oxide; amber oil; yield: 165 mg (77%); R_f 0.1 (EtOAc–MeOH, 90:10); silica gel FC (EtOAc–MeOH, 100:0, 90:10, then 80:20).

IR (neat): 3391, 2937, 2860, 2206, 1624, 1498, 1448, 1379, 1251, 1230, 1180, 925, 731 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.11 (m, 5 H), 4.30–4.03 (m, 2 H), 3.18 (m, 2 H), 2.76 (m, 1 H), 2.12–1.85 (m, 3 H), 1.79 (m, 1 H), 1.45–1.09 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.9, 139.7, 128.9, 127.3, 127.1, 68.1, 50.5, 45.7, 32.2, 24.1, 23.7, 23.4.

LRMS (EI, 70 eV): *m*/*z* (%) = 215 (64), 198 (18), 111 (73), 104 (18), 91 (38), 84 (23), 77 (23).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{17}NO$: 215.1310; found: 215.1307.

***N*-[3-(2-Methyl-1,3-dioxolan-2-yl)-2-phenylpropyl]hydroxylamine** (Table 6, entry 21)

Clear oil; yield: 121 mg (51%); R_f 0.1 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50, 0:100, then EtOAc–MeOH, 70:30).

IR (neat): 3410, 3271, 2982, 2941, 2885, 1495, 1454, 1379, 1251, 1221, 1143, 1076, 1049, 910, 734, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.08 (m, 5 H), 5.60 (br s, 2 H), 3.83 (m, 4 H), 3.17 (m, 2 H), 2.92 (m, 1H), 2.00 (m, 2 H), 1.17 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.9, 128.5, 127.7, 126.4, 109.7, 64.4, 64.2, 59.9, 42.8, 38.2, 24.4.

LRMS (EI, 70 eV): *m*/*z* (%) = 175 (6), 161 (2), 160 (2), 159 (2), 158 (5), 118 (2), 117 (7), 116 (2), 115 (6), 104 (12), 91 (11), 88 (17), 87 (100), 86 (38), 77 (5), 43 (80).

HRMS (methane CI): *m*/*z* calcd for $[C_{13}H_{19}NO_3 + H]^+$: 238.1443; found: 238.1434.

***N*-Phenethylhydroxylamine** (Table 6, entry 22)

trans-β-Nitrostyrene (1 mmol, 149 mg) was subjected to the general procedure for reducing aliphatic nitro compounds with 8 equiv of triethylsilane (8 mmol, 1.28 mL) affording 73 mg (53%) of *N*-phenethylhydroxylamine. For product characterization, see above (Table 6, entry 2).

***N*-Cyclohexyl-*N*-hydroxy-4-methylbenzenesulfonamide** (Table 6, entry 23)

1-Nitro-1-cylcohexene (1 mmol, 0.113 mL) was subjected to the general procedure for reducing aliphatic nitro compounds with 8 equiv of triethylsilane (8 mmol, 1.28 mL) and with the following modifications. After complete consumption of the starting material (as judged by TLC) 2 equiv *p*-toluenesulfonic anhydride (2 mmol, 652 mg) was added to the reaction followed by an additional 2 h of stirring to afford after the general workup 237 mg (88%) of *N*-cyclohexyl-*N*-hydroxy-4-methylbenzenesulfonamide. For product characterization, see above (Table 6, entry 3).

One-Pot Reductive Conversion of Nitroarenes into Amides, Carbamates or Sulfonamides; General Procedure

A round-bottom flask was charged with $Pd(OAc)_2$ (0.05 mmol, 11 mg), the nitroarene (1 mmol), and freshly distilled anhyd THF (5 mL). The flask was sealed and purged with N_2. While purging the flask with N_2, a solution of aq KF was added via a syringe (2 mmol KF, 116 mg in 2 mL of degassed H_2O). The N_2 inlet was replaced with a balloon filled with N_2. PMHS (4 mmol, 0.24 mL; 1 mmol of hydride is 0.06 mL) was slowly added dropwise via syringe (***Caution!*** *Rapid addition PMHS can result in uncontrollable gas evolution!*) The reaction was stirred for 30 min or until complete as judged by TLC. At that time, the reaction flask was opened to the air and the anhydride (2 mmol), sulfonic anhydride (2 mmol), or dicarbonate (2 mmol) was added quickly. The flask was resealed and flushed with N_2. [Note: The anhydride (or dicarbonate) can also be dissolved in 0.5 mL of THF an injected into the reaction mixture without exposing the reaction to the air]. The reaction was stirred for an additional 30 min or until complete as judged by TLC. The layers were separated and the aqueous layer was back-extracted with Et_2O. The combined organics were concentrated and subjected to flash chromatography eluting with gradients of hexanes–EtOAc and/or EtOAc–MeOH.

***N*-(4-Methoxyphenyl)acetamide** (Table 7, entry 1)

White solid; yield: 164 mg (99%); mp 129 °C; R_f 0.15 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

^1H NMR (300 MHz, $CDCl_3$): δ = 8.72 (s, 1 H), 7.31 (d, *J* = 8.79 Hz, 2 H), 6.67 (d, *J* = 8.79 Hz, 2 H), 3.63 (s, 3 H), 1.97 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6, 155.7, 131.3, 121.6, 113.5, 55.1, 23.7.

Methyl 3-Acetamidobenzoate (Table 7, entry 2)

White solid; yield: 193 mg (quant.); mp 136 °C; R_f 0.2 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 9.48 (s, 1 H), 8.04 (s, 1 H), 7.77 (d, *J* = 8.24 Hz, 1 H), 7.56 (d, *J* = 7.69 Hz, 1 H), 7.20 (dd, *J* = 7.69, 8.24 Hz, 1 H), 3.73 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 168.8, 166.2, 138.6, 129.8, 128.2, 123.9, 123.7, 120.1, 51.4, 23.6.

5-(4-Methoxyphenylamino)-5-oxopentanoic Acid (Table 7, entry 4)

White solid; yield: 228 mg (96%); mp 140 °C; R_f 0.2 (EtOAc); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

IR (Nujol): 3314, 1695, 1658, 1541, 1516, 1458, 1414, 1304, 1267, 1236, 1186, 1033, 846, 808 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 9.34 (s, 1 H), 7.36 (d, *J* = 8.79 Hz, 2 H), 6.67 (d, *J* = 8.79 Hz, 2 H), 3.62 (s, 3 H), 2.21 (m, 4 H), 1.82 (q, *J* = 7.14 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$ +DMSO-d_6): δ = 174.6, 170.6, 155.3, 132.0, 121.1, 113.4, 55.0, 35.5, 33.1, 20.6.

LRMS (EI, 70 eV): *m*/*z* (%) = 237 (12), 123 (100), 108 (65), 92 (3), 87 (6), 77 (2), 45 (9), 43 (4), 42 (5), 41 (10).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{15}NO_4$: 237.1001; found: 237.1001.

5-[3-(Methoxycarbonyl)phenylamino]-5-oxopentanoic Acid (Table 7, entry 5)

White solid; yield: 230 mg (87%); mp 110 °C; R_f 0.1 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, 50:50, then 0:100).

IR (Nujol): 3348, 3275, 1714, 1695, 1664, 1593, 1545, 1433, 1302, 1275, 1232, 1082, 925, 760, 688 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 8.98 (br s, 1 H), 8.02 (s, 1 H), 7.81 (d, *J* = 8.24 Hz, 1 H), 7.60 (d, *J* = 7.69 Hz, 1 H), 7.24 (dd, *J* = 7.69, 8.24 Hz, 1 H), 3.77 (s, 3 H), 2.35 (t, *J* = 7.14 Hz, 2 H), 2.29 (t, *J* = 7.14 Hz, 2 H), 1.91 (q, *J* = 7.14 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 175.3, 171.3, 166.6, 138.7, 130.3, 128.6, 124.4, 124.0, 120.4, 51.8, 35.9, 33.0, 20.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 265 (5), 151 (100), 120 (24), 119 (31), 115 (13), 93 (13), 92 (27), 91 (13), 90 (11), 87 (13), 86 (20), 77 (6), 59 (6) 45 (27), 44 (14), 43 (31), 42 (15), 41 (25).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{15}NO_5$: 265.0950; found: 265.0948.

(*Z*)-4-(4-Methoxyphenylamino)-4-oxobut-2-enoic Acid (Table 7, entry 7)

Bright yellow solid; yield: 211 mg (95%); mp 180 °C; R_f 0.3 (EtOAc–MeOH, 80:20); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

IR (Nujol): 3256, 3061, 1713, 1633, 1539, 1508, 1468, 1412, 1280, 1248, 1176, 1035, 854, 825 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 10.40 (s, 1H), 7.51 (d, *J* = 8.79 Hz, 2 H), 6.85 (d, *J* = 8.79 Hz, 2 H), 6.44 (d, *J* = 12.08 Hz, 1H), 6.25 (d, *J* = 12.08 Hz, 1 H), 3.66 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 166.8, 163.2, 156.1, 132.0, 131.4, 131.3, 121.5, 114.1, 55.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 222 (1), 221 (11), 203 (27), 188 (12), 123 (69), 122 (44), 108 (100), 77 (8), 44 (6).

HRMS (EI): *m*/*z* calcd for $C_{11}H_{11}NO_4$: 221.0688; found: 221.0684.

(*Z*)-4-(3-(Methoxycarbonyl)phenylamino)-4-oxobut-2-enoic Acid (Table 7, entry 8)

White solid; yield: 209 mg (84%); mp 170 °C; R_f 0.05 (hexanes–EtOAc, 50:50); silica gel FC (EtOAc–MeOH, 100:0, then 80:20).

IR (Nujol): 3317, 3157, 2926, 2855, 1724, 1628, 1591, 1558, 1496, 1296, 1257, 1203, 1105, 1082, 968, 893, 846, 760, 609 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 10.90 (br s, 1 H), 8.11 (s, 1 H), 7.82 (d, *J* = 7.69 Hz, 1 H), 7.67 (d, *J* = 8.24 Hz, 1 H), 7.30 (dd, *J* = 7.69, 8.24 Hz, 1 H), 6.47 (d, *J* = 12.63 Hz, 1 H), 6.19 (d, *J* = 12.63 Hz, 1 H), 3.73 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 165.8, 165.4, 163.9, 137.3, 133.3, 132.5, 130.2, 128.6, 125.6, 124.6, 120.9, 51.7.

LRMS (EI, 70 eV): *m*/*z* (%) = 249 (6), 204 (5), 200 (36), 172 (20), 152 (11), 151 (51), 150 (71), 135 (1), 120 (45), 119 (70), 115 (10), 99 (12), 98 (18), 97 (10), 92 (100), 77 (5), 65 (16), 64 (32), 63 (16), 62 (15), 54 (26), 53 (36).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{11}NO_5$: 249.0637; found: 249.0633.

(*Z*)-4-(2,6-Dimethylphenylamino)-4-oxobut-2-enoic Acid (Table 7, entry 9)

White solid; yield: 63 mg (29%); mp 170–173 °C; R_f 0.05 (hexanes–EtOAc, 50:50); silica gel FC (EtOAc–MeOH, 100:0, then 80:20).

^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 9.94 (s, 1 H), 6.53 (m, 3 H), 6.15 (d, *J* = 13.18 Hz, 1 H), 5.77 (d, *J* = 12.63 Hz, 1 H), 1.65 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 163.9, 163.5, 133.6, 133.4, 131.6, 130.8, 126.8, 126.4, 17.0.

***N*-(4-Methoxyphenyl)methacrylamide** (Table 7, entry 10)

White solid; yield: 189 mg (99%); mp 80 °C; R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.43 (s, 1 H), 7.43 (d, *J* = 8.79 Hz, 2 H), 6.83 (d, *J* = 8.79 Hz, 2 H), 5.75 (s, 1 H), 5.40 (s, 1 H), 3.76 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 156.4, 140.6, 130.8, 121.9, 119.5, 114.0, 55.3, 18.6.

Methyl 3-Methacrylamidobenzoate (Table 7, entry 11)

Light yellow oil; yield: 207 mg (94%); R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

IR (neat): 3337, 2953, 1718, 1668, 1593, 1541, 1489, 1437, 1298, 1232, 1163, 1109, 929, 756 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.06 (t, *J* = 1.64 Hz, 1 H), 7.95 (br s, 1 H), 7.89 (m, 1 H), 7.72 (dt, *J* = 1.64, 8.24 Hz, 1 H), 7.33 (t, *J* = 8.24 Hz, 1 H), 5.77 (s, 1 H), 5.42 (s, 1 H), 3.83 (s, 3 H), 2.00 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 166.6, 140.5, 138.0, 130.7, 129.0, 125.3, 124.6, 121.0, 120.0, 52.1, 18.5.

LRMS (EI, 70 eV) *m*/*z* (%) = 219 (6), 151 (23), 135 (1), 120 (10), 119 (5), 91 (10), 69 (100), 41 (75).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{13}NO_3$: 219.0895; found: 219.0893.

(*E*)-2-Bromo-4-(4-methoxyphenylamino)-4-oxobut-2-enoic Acid and (*E*)-3-Bromo-4-(4-methoxyphenylamino)-4-oxobut-2-enoic Acid (1:1.26) (Table 7, entry 13)

Yellow-brown solid; yield: 268 mg (89%); R_f 0.05 (EtOAc); silica gel FC (hexanes–EtOAc, 50:50, then 0:100).

^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 10.25 (s, 1 H, measured 0.56 H), 10.15 (s, 1 H, measured 0.44 H), 7.43 (d, *J* = 8.79 Hz, 2 H), 6.76 (d, *J* = 9.33 Hz, 2 H), 6.70 (s, 1 H, measured 0.44 H), 6.36 (s, 1 H, measured 0.56 H), 3.66 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 163.5, 161.3, 155.7, 131.8, 131.3, 125.3, 121.1, 120.7, 113.6, 113.5, 106.8, 66.5, 54.9, 28.7, 23.4.

2-Chloro-*N*-(4-methoxyphenyl)acetamide (Table 7, entry 14)

White solid; yield: 191 mg (96%); mp 117–119 °C; R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

IR (Nujol): 3294, 1674, 1545, 1512, 1466, 1414, 1300, 1248, 1180, 1030, 831, 788, 711, 688 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.12 (br s, 1 H), 7.41 (d, *J* = 8.79 Hz, 2 H), 6.86 (d, *J* = 8.79 Hz, 2 H), 4.14 (s, 3 H), 3.77 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 157.0, 129.6, 122.0, 114.2, 55.4, 42.8.

LRMS (EI, 70 eV): *m*/*z* (%) = 201 (16), 200 (4), 199 (50), 124 (14), 123 (32), 122 (64), 121 (43), 108 (100), 77 (10).

HRMS (EI): *m*/*z* calcd for $C_9H_{10}ClNO_2$: 199.0400; found: 199.0397.

Methyl 3-(2-Chloroacetamido)benzoate (Table 7, entry 15)

Tan solid; yield: 190 mg (84%); mp 83 °C; R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

IR (Nujol): 1732, 1668, 1408, 1244, 1084, 814, 754 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.59 (br s, 1 H), 8.03 (m, 1 H), 7.82 (dq, *J* = 1.09, 8.24 Hz, 1 H), 7.74 (dt, *J* = 1.09, 7.69 Hz, 1 H), 7.33 (dd, *J* = 7.69, 8.24 Hz, 1 H), 4.13 (s, 2 H), 3.82 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.4, 164.3, 136.9, 130.8, 129.1, 125.9, 124.5, 121.0, 52.1, 42.8.

LRMS (EI, 70 eV): *m*/*z* (%) = 229 (9), 228 (3), 227 (28), 178 (21), 150 (99), 120 (100), 92 (67), 91 (26), 77 (11), 76 (17), 59 (4).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{10}ClNO_3$: 227.0349; found: 227.0352.

2-Chloro-*N*-(2,6-dimethylphenyl)acetamide (Table 7, entry 16)

White-pink solid; isolated: 144 mg (<72%; product contaminated with a small amount of an unknown material; mp 114–117 °C; R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

IR (PTFE card, neat): 3254, 1662, 1533, 1177, 1142, 767 cm^{-1}.

IR (Nujol): 3217, 1680, 1653, 1539, 1473, 1431, 1323, 1147, 979, 760, 707, 665 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.83 (br s, 1 H), 7.08 (m, 3 H), 4.22 (s, 2H), 2.21 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3, 135.3, 128.3, 127.8, 107.9, 42.7, 18.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 199 (7), 198 (2), 197 (21), 148 (100), 121 (31), 120 (23), 119 (36), 105 (24), 104 (16), 77 (40).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{12}ClNO$: 197.0607; found: 197.0603.

***N*-(4-Methoxyphenyl)benzamide** (Table 7, entry 19)

White solid; yield: 220 mg (97%); mp 153 °C; R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.51 (br s, 1 H), 7.85 (d, *J* = 6.59 Hz, 2 H), 7.56 (d, *J* = 8.79 Hz, 2 H), 7.37 (m, 3 H), 6.77 (d, *J* = 8.79 Hz, 2 H), 3.69 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 155.3, 134.6, 131.3, 130.6, 127.5, 126.9, 121.7, 113.1, 54.6.

Methyl 3-Benzamidobenzoate (Table 7, entry 20)

White solid; yield: 227 mg (89%); mp 122–123 °C; R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

IR (Nujol): 3283, 1724, 1651, 1595, 1529, 1431, 1292, 1226, 1124, 1072, 925, 754, 694 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.15 (br s, 1 H), 8.21 (s, 1 H), 7.95 (m, 1 H), 7.82 (d, *J* = 7.14 Hz, 2 H), 7.66 (d, *J* = 7.69 Hz, 1 H), 7.48–7.22 (m, 4 H), 3.74 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.0, 166.6, 138.4, 134.3, 132.7, 131.5, 129.5, 128.6, 128.2, 128.0, 127.2, 125.0, 121.4, 51.9.

LRMS (EI, 70 eV): *m*/*z* (%) = 255 (8), 105 (100), 91 (2), 77 (66).

HRMS (EI): *m*/*z* calcd for $C_{15}H_{13}NO_3$: 255.0895; found: 255.0902.

***N*-(2,6-Dimethylphenyl)benzamide** (Table 7, entry 21)

White solid; yield: 133 mg (59%); mp 162 °C; R_f 0.2 (hexanes–EtOAc, 80:20); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (br s, 1 H), 7.83 (d, *J* = 7.14 Hz, 2 H), 7.49 (m, 1 H), 7.36 (m, 2 H), 7.05 (m, 3 H), 2.16 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 135.5, 134.1, 133.9, 131.5, 128.4, 128.0, 127.2, 127.1, 18.2.

***N*-(4-Methoxyphenyl)methanesulfonamide** (Table 7, entry 22)

Pink-purple solid; yield: 159 mg (79%); mp 115 °C; R_f 0.3 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (Nujol): 3256, 1512, 1462, 1323, 1284, 1143, 1026, 974, 825, 767 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 8.79 Hz, 2 H), 6.96 (br s, 1 H), 6.84 (d, *J* = 8.79 Hz, 2 H), 3.75 (s, 3 H), 2.91 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 129.1, 124.5, 114.6, 55.4, 38.6.

LRMS (EI, 70 eV): *m*/*z* = 203 (0.75), 202 (1), 201 (17), 122 (100), 95 (42), 79 (11), 78 (10), 77 (4).

HRMS (EI): *m*/*z* calcd for $C_8H_{11}NO_3S$: 201.0460; found: 201.0464.

Methyl 3-(Methylsulfonamido)benzoate (Table 7, entry 23)

White solid; yield: 179 mg (78%); mp 124–125 °C; R_f 0.3 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (Nujol): 3426, 3246, 1718, 1589, 1475, 1437, 1332, 1296, 1155, 1036, 1005, 821, 758 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (br s, 1 H), 7.82 (s, 1 H), 7.67 (d, *J* = 7.69 Hz, 1 H), 7.41 (d, *J* = 7.14 Hz, 1 H), 7.28 (t, *J* = 7.69 Hz, 1 H), 3.79 (s, 3 H), 2.87 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3, 137.9, 131.0, 129.3, 125.3, 124.6, 120.9, 52.0, 39.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 231 (1), 230 (4), 229 (32), 198 (15), 170 (2), 151 (26), 150 (100), 120 (68), 119 (22), 118 (12), 105 (15), 93 (11), 92 (40), 91 (65), 90 (36), 77 (20), 66 (44), 65 (25), 64 (38), 63 (38), 59 (11) 44 (12).

HRMS (EI): *m*/*z* calcd for $C_9H_{11}NO_4S$: 229.0409; found: 229.0409.

***N*-(2,6-Dimethylphenyl)methanesulfonamide** (Table 7, entry 24)

White solid; yield: 60 mg (30%); mp 125 °C; R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

IR (Nujol): 3267, 3011, 1396, 1319, 1147, 983, 900, 769 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08 (m, 3 H), 6.16 (br s, 1 H), 3.05 (s, 3 H), 2.39 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.3, 132.7, 128.8, 127.9, 41.7, 19.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 201 (0.4), 200 (0.9), 199 (11), 120 (100), 90 (12), 77 (15).

HRMS (EI): *m*/z calcd for $C_9H_{13}NO_2S$: 199.0667; found: 199.0670.

***N*-(4-Methoxyphenyl)-4-methylbenzenesulfonamide** (Table 7, entry 25)

White solid; yield: 269 mg (97%); mp 112 °C; R_f 0.9 (EtOAc); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (Nujol): 3267, 3011, 1610, 1597, 1510, 1396, 1332, 1290, 1251, 1219, 1161, 1091, 1030, 912, 812, 679 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.24 Hz, 2 H), 7.20 (s, 1 H), 7.14 (d, *J* = 7.69 Hz, 2 H), 6.97 (d, *J* = 9.33 Hz, 2 H), 6.69 (d, *J* = 8.79 Hz, 2 H), 3.68 (s, 3 H), 2.31 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 143.5, 135.7, 129.4, 129.0, 127.2, 124.9, 114.2, 55.2, 21.4.

LRMS (EI, 70 eV): *m*/*z* (%) = 277 (9), 122 (100), 91 (20), 77 (3), 64 (20).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{15}NO_3S$: 277.0773; found: 277.0768.

Methyl 3-(4-Methylphenylsulfonamido)benzoate (Table 7, entry 26)

White solid; yield: 298 mg (98%); mp 152–154 °C; R_f 0.5 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

IR (Nujol): 3227, 1703, 1593, 1477, 1439, 1404, 1336, 1300, 1219, 1159, 1089, 985, 852, 814, 754, 661 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 9.54 (br s, 1 H), 7.65 (s, 1 H), 7.54 (d, *J* = 8.24 Hz, 2 H), 7.23 (m, 1 H), 7.18 (t, *J* = 7.69 Hz, 1 H), 7.06 (d, *J* = 8.24 Hz, 2 H), 3.72 (s, 3 H), 2.21 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ = 166.4, 143.3, 137.8, 136.3, 130.9, 129.4, 129.0, 127.0, 125.2, 124.8, 121.3, 52.0, 21.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 305 (11), 155 (32), 150 (8), 120 (9), 119 (5), 118 (10), 91 (100), 77 (5), 43 (15).

HRMS (EI): *m*/*z* calcd for $C_{15}H_{15}NO_4S$: 305.0722; found: 305.0720.

***N*-(2,6-Dimethylphenyl)-4-methylbenzenesulfonamide** (Table 7, entry 27)

White solid; yield: 199 mg (72%); mp 129–131 °C; R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, 80:20, then 50:50).

IR (Nujol): 3271, 1597, 1473, 1369, 1325, 1159, 1091, 898, 817, 781, 673 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.24 Hz, 2 H), 7.21 (d, *J* = 8.24 Hz, 2 H), 7.05 (m, 1 H), 6.99 (m, 2 H), 6.32 (br s, 1 H), 2.39 (s, 3 H), 2.02 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.5, 137.76, 137.70, 132.5, 129.5, 128.6, 127.6, 127.1, 21.4, 18.6.

LRMS (EI, 70 eV): *m*/*z* (%) = 275 (9), 120 (100), 91 (31), 77 (16)

HRMS (EI): *m*/*z* calcd for $C_{15}H_{17}NO_2S$: 275.0980; found: 275.0982.

***tert*-Butyl 4-Methoxyphenylcarbamate** (Table 7, entry 28)

White solid; yield: 220 mg (99%); mp 90–91 °C; R_f 0.7 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.79 Hz, 2 H), 6.79 (d, *J* = 8.79 Hz, 2 H), 6.50 (br s, 1H), 3.72 (s, 3 H), 1.47 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 153.1, 131.4, 120.5, 114.0, 80.1, 55.3, 28.2.

Methyl 3-(*tert*-Butoxycarbonylamino)benzoate (Table 7, entry 29)

White solid; yield: 56 mg (22%); mp 103 °C; R_f 0.7 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 80:20, then 50:50).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 7.65 (m, 2 H), 7.32 (m, 1H), 6.71 (br s, 1 H), 3.87 (s, 3 H), 1.49 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 152.6, 138.6, 130.8, 129.0, 124.0, 122.8, 119.3, 80.8, 52.1, 28.2.

***tert*-Butyl 2,6-Dimethylphenylcarbamate** (Table 7, entry 30)

Light yellow oil; yield: 111 mg (50%); R_f 0.6 (hexanes–EtOAc, 50:50); silica gel FC (hexanes–EtOAc, 95:5, then 80:20).

IR (Nujol): 3341, 3003, 1695, 1506, 1248, 1122, 1055, 771 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.03 (s, 3 H), 5.92 (br s, 1 H), 2.23 (s, 6 H), 1.50 (br s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.7, 134.0, 127.9, 126.7, 79.7 28.2, 27.3, 18.2.

LRMS (EI, 70 eV): *m*/*z* (%) = 222 (0.1), 221 (1), 165 (23), 121 (46), 119 (20), 105 (18), 91 (5), 77 (11), 59 (20), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{19}NO_2$: 221.1416; found: 221.1409.

Starting Nitro Compounds

6-(Benzyloxy)hexyl 4-Nitrobenzoate (Table 2 entry 15)

A flame-dried 100-mL round-bottom flask was charged with 4-nitrobenzoic acid (20 mmol, 3.34 g), 6-(benzyloxy)hexan-1-ol[46] (20 mmol, 4.16 g), *N*,*N*-dimethylaminopyridine (4 mmol, 0.49 g), and 20 mL of anhyd CH_2Cl_2 under N_2. DCC as a 1 M solution in CH_2Cl_2 (30 mmol, 30 mL) was slowly injected into the reaction and the mixture was stirred overnight (14 h). The mixture was filtered and the solid white material rinsed with CH_2Cl_2. The filtrate was sequentially washed with aq 10% HCl and aq sat. $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated. The crude material was subjected to flash chromatography (hexanes–EtOAc, 95:5) affording 5.51 g (77%) of 6-(benzyloxy)hexyl 4-nitrobenzoate as a pale yellow solid; mp 38–40 °C.

IR (Nujol): 1718, 1608, 1525, 1454, 1346, 1273, 1105, 873, 742, 715 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.79 Hz, 2 H), 8.15 (d, *J* = 8.79 Hz, 2 H), 7.29 (m, 5 H), 4.47 (s, 2 H), 4.33 (t, *J* = 6.59 Hz, 2 H), 3.45 (t, *J* = 6.59 Hz, 2 H), 1.77 (m, 2 H), 1.63 (m, 2 H), 1.44 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 150.4, 138.5, 135.8, 130.6, 128.3, 127.5, 127.4, 123.4, 72.8, 70.1, 65.9, 29.6, 28.5, 25.9, 25.8.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{23}NO_5$: 357.1576; found: 357.1580.

2-(4-Nitrophenyl)-1,3-dioxolane (Table 2 entry 29)

A flame-dried 500-mL round-bottom flask was connected to a Dean–Stark trap with a reflux condenser and drying tube. The flask was charged with 4-nitrobenzaldehyde (30 mmol, 4.53 g), *p*-toluenesulfonic acid monohydrate (1.8 mmol, 0.34 g), ethylene glycol (600 mmol, 33.5 mL), and anhyd benzene (300 mL). The flask was then placed in an oil-bath at 100 °C and the mixture was refluxed for 8 h. The mixture was cooled to r.t. and then poured into a separatory funnel containing 10% aq K_2CO_3. The organic layer was dried ($MgSO_4$), filtered, and concentrated to afford 3.89 g (66%) of pure 2-(4-nitrophenyl)-1,3-dioxolane as a light yellow solid.

IR (PTFE card, neat): 1522, 1358, 1184, 1126, 1080, 846, 750, 667 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.79 Hz, 2 H), 7.62 (d, *J* = 8.79 Hz, 2 H), 5.86 (s, 1 H), 4.07 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.3, 144.9, 127.4, 123.5, 102.2, 65.4.

Nitroarenes Containing an Unactivated Olefin; General Procedure (Table 3)

A flame-dried 100-mL round-bottom flask under a nitrogen atmosphere was charged with 4-nitrobenzoic acid (20 mmol, 3.34 g), the aliphatic alcohol (24–40 mmol), *N*,*N*-dimethylaminopyridine (4 mmol, 0.49 g), and anhyd CH_2Cl_2 (20 mL) under N_2. DCC as a 1 M solution in CH_2Cl_2 (24 mmol, 24 mL) was slowly injected into the flask and the reaction mixture was stirred overnight (14 h). The mixture was filtered and the solid white material rinsed with CH_2Cl_2. The filtrate was sequentially washed with aq 10% HCl and aq sat. $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated. The crude material was subjected to flash chromatography.

Hex-5-enyl 4-Nitrobenzoate (Table 3, entries 1, 2)

Yellow oil; yield: 4.31 g (87%); silica gel FC (hexanes–EtOAc, 95:5).

IR (neat): 2939, 1726, 1529, 1350, 1277, 1118, 1103, 1014, 914, 873, 719 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.79 Hz, 2 H), 8.16 (d, *J* = 8.79 Hz, 2 H), 5.78 (m, 1 H), 4.96 (m, 2 H), 4.34 (t, *J* = 7.14 Hz, 2 H), 2.10 (q, *J* = 7.14 Hz, 2 H), 1.78 (m, 2 H), 1.51 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.4, 138.0, 135.7, 130.6, 123.4, 114.9, 65.8, 33.2, 27.9, 25.1.

HRMS (methane CI): *m*/*z* calcd for $[C_{13}H_{15}NO_4 + H]^+$: 250.1079; found: 250.1085.

(*E*)-Hex-4-enyl 4-Nitrobenzoate (Table 3, entries 3,4)

Pale yellow solid; yield: 4.31 g (87%); mp 44 °C; silica gel FC (hexanes–EtOAc, 95:5).

IR (Nujol): 1728, 1604, 1531, 1348, 1319, 1275, 1103, 968, 871, 843, 788, 717 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.79 Hz, 2 H), 8.17 (d, *J* = 8.79 Hz, 2 H), 5.42 (m, 2 H), 4.34 (t, *J* = 6.59 Hz, 2 H), 2.11 (m, 2 H), 1.82 (q, *J* = 6.59 Hz, 2 H), 1.63 (d, *J* = 4.94 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.4, 135.7, 134.8, 130.6, 129.6, 126.1, 123.4, 65.4, 28.8, 28.3, 17.8.

HRMS (methane CI): *m*/*z* calcd for $[C_{13}H_{15}NO_4 + H]^+$: 250.1079; found: 250.1077.

3-Methylbut-3-enyl 4-Nitrobenzoate (Table 3, entries 5–7)

Yellow oil; yield: 3.05 g (65%); silica gel FC (hexanes–EtOAc, 95:5).

IR (neat): 1716, 1522, 1348, 1284, 1103, 906, 871, 715 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.79 Hz, 2 H), 8.15 (d, *J* = 8.79 Hz, 2 H), 4.79 (d, *J* = 13.18 Hz, 2 H), 4.45 (t, *J* = 6.59 Hz, 2 H), 2.46 (t, *J* = 6.59 Hz, 2 H), 1.77 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.5, 150.4, 141.2, 135.6, 130.6, 123.4, 112.6, 63.8, 36.6, 22.3.

HRMS (methane CI): *m*/*z* calcd for $[C_{12}H_{13}NO_4 + H]^+$: 236.0923; found: 236.0919.

3,7-Dimethyloct-6-enyl 4-Nitrobenzoate (Table 3, entries 8–10)

Yellow oil; yield: 7.82 g (85%); silica gel FC (hexanes–CH_2Cl_2, 50:50).

IR (neat): 2963, 2926, 1726, 1608, 1529, 1456, 1350, 1277, 1116, 1103, 873, 835, 785, 719 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.79 Hz, 2 H), 8.16 (d, *J* = 8.79 Hz, 2 H), 5.05 (t, *J* = 7.14 Hz, 1 H), 4.37 (m, 2H), 1.97 (q, *J* = 7.69 Hz, 2 H), 1.80 (m, 1H), 1.63 (s, 3 H), 1.56 (s, 3 H), 1.36 (m, 2 H), 1.22 (m, 2 H), 0.94 (d, *J* = 6.59 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 150.4, 135.8, 131.4, 130.6, 124.3, 123.4, 64.4, 36.9, 35.3, 29.5, 25.6, 25.3, 19.4, 17.6.

HRMS (methane CI): *m*/*z* calcd for $[C_{17}H_{23}NO_4 + H]^+$: 306.1705; found: 306.1700.

2-(4-Methylcyclohex-3-enyl)propan-2-yl 4-Nitrobenzoate (Table 3, entries 11,12)

Light yellow solid; yield: 3.49 g (58%); mp 140 °C; silica gel FC (hexanes–CH_2Cl_2, 50:50).

IR (PTFE card, neat): 3111, 3001, 2959, 2924, 2897, 2855, 1711, 1523, 1348, 1309, 1203, 1147, 1103, 924, 717cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.79 Hz, 2 H), 8.09 (d, *J* = 8.79 Hz, 2 H), 5.35 (s, 1 H), 2.21–1.78 (m, 7 H), 1.62 (s, 3 H), 1.58 (s, 3 H), 1.55 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5, 150.2, 137.4, 134.0, 130.4, 123.3, 120.0, 87.2, 43.0, 30.8, 26.4, 24.0, 23.3, 23.2.

HRMS (methane CI): *m*/*z* calcd for $[C_{17}H_{21}NO_4 + H]^+$: 304.1549; found: 304.1550.

11-(*tert*-Butyldimethylsilyl)undec-10-yn-1-ol (Scheme 5)

A dry 1-L round-bottom flask was placed in an ice-bath and charged with 10-undecyn-1-ol (67 mmol, 12.9 mL), anhyd THF (250 mL), and *n*-BuLi (1.6 M in hexanes, 50 mL, 80 mmol). The reaction mixture was stirred for 30 min at which time an additional amount *n*-BuLi (1.6 M in hexanes, 50 mL, 80 mmol) was added. The reaction flask was removed from the ice-bath and TBSCl (80 mmol, 12.1 g) dissolved in THF (10 mL) was added in four portions with manual shaking of the reaction flask between each addition. The mixture was stirred for 10 h and then poured into a separatory funnel containing Et_2O and H_2O. The layers were separated and the organic layer was dried ($MgSO_4$), filtered, concentrated, and subjected to flash chromatography (hexanes–EtOAc, 80:20) to afford 5.51 g (21%) of *tert*-butyl[11-(*tert*-butyldimethylsilyl)undec-10-ynyloxy]dimethylsilane and 12.9 g (68%) of 11-(*tert*-butyldimethylsilyl)undec-10-yn-1-ol as clear oils.

IR (neat): 3321, 2937, 2856, 2174, 1471, 1250, 1055, 837, 773, 680 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.59 (m, 2 H), 2.18 (t, *J* = 6.59 Hz, 2 H), 1.58–1.16 (m, 14 H), 0.88 (s, 9 H), 0.03 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 108.2, 108.1, 82.1, 62.9, 32.7, 29.4, 29.3, 28.9, 28.6, 26.1, 25.9, 25.6, 19.7, 16.4, –4.4.

11-(*tert*-Butyldimethylsilyl)undec-10-ynyl 4-Nitrobenzoate (Scheme 5)

A flame-dried 100-mL round-bottom flask was charged with 4-nitrobenzoic acid (20 mmol, 3.34 g), 11-(*tert*-butyldimethylsilyl)undec-10-yn-1-ol (22 mmol, 6.21 mL), *N,N*-dimethylaminopyridine (4 mmol, 0.49 g), and anhyd CH_2Cl_2 (20 mL) under N_2. DCC as a 1 M solution in CH_2Cl_2 (30 mmol, 30 mL) was slowly injected into the flask and the reaction mixture was stirred overnight (18 h). The mixture was filtered and the solid white material rinsed with CH_2Cl_2. The filtrate was sequentially washed with aq 10% HCl and aq sat. $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated. The crude material was subjected to flash chromatography (hexanes–EtOAc, 80:20) affording 7.86 g (91%) of 11-(*tert*-butyldimethylsilyl)undec-10-ynyl 4-nitrobenzoate as a clear, light yellow oil. The oil was further purified by Kugelrohr distillation (225 °C/0.1 mmHg) to afford 7.10 g (82%) of the pure product.

IR (neat): 2930, 2856, 2172, 1728, 1531, 1471, 1350, 1275, 1120, 1103, 1014, 837, 775, 719 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.79 Hz, 2 H), 8.17 (d, *J* = 8.79 Hz, 2 H), 4.33 (t, *J* = 7.14 Hz, 2 H), 1.75 (q, *J* = 6.59 Hz, 2 H), 1.54–1.21 (m, 12 H), 0.88 (s, 9 H), 0.04 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.7, 150.4, 135.8, 130.6, 123.4, 108.0, 82.3, 66.0, 29.3, 29.1, 28.9, 28.6, 28.5, 26.0, 25.9, 19.7, 16.5, –4.4.

HRMS (methane CI): *m*/*z* calcd for $[C_{24}H_{37}NO_4Si + H]^+$: 432.2570; found: 432.2575.

Triethyl(1-nitro-4-phenylbutan-2-yloxy)silane (Table 6, entries 9, 10)

A dry 25-mL round-bottom flask was charged with 1-nitro-4-phenylbutan-2-ol[47] (10 mmol, 1.95 g), imidazole (25 mmol, 1.70 g), and 5 mL of anhyd DMF (5 mL). The flask was sealed and placed under N_2, followed by injecting chlorotriethylsilane (12 mmol, 2.01 mL) into the reaction. After stirring for 12 h, the mixture was diluted with H_2O and extracted with CH_2Cl_2. The aqueous layer was back-extracted with CH_2Cl_2 and the combined organics were washed with brine, dried ($MgSO_4$), filtered, and concentrated. The crude material was subjected to flash chromatography (hexanes–EtOAc, 95:5, then 80:20) affording 1.657 (53.5%) of triethyl(1-nitro-4-phenylbutan-2-yloxy)silane as a dark yellow oil.

IR (neat): 2957, 2878, 1558, 1456, 1415, 1385, 1240, 1116, 1005, 733 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.12 (m, 5 H), 4.45 (m, 1 H), 4.35 (m, 2 H), 2.66 (m, 2 H), 1.86 (m, 2 H), 0.94 (t, *J* = 8.24 Hz, 9 H), 0.58 (q, *J* = 8.24 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.9, 128.6, 128.1, 126.2, 80.9, 69.5, 36.9, 31.0, 6.6, 4.8.

HRMS (methane CI): *m*/*z* calcd for $[C_{16}H_{27}NO_3Si + H]^+$: 310.1838; found: 310.1829.

***tert*-Butyldimethyl(1-nitro-4-phenylbutan-2-yloxy)silane** (Table 6, entries 11, 12)

This compound was prepared via the procedure described immediately above; yellow oil; yield: 2.22 g (72%), silica gel FC (hexanes–Et_2O, 100:0, then 85:15).

IR (neat): 2955, 2930, 2858, 1556, 1471, 1387, 1257, 1115, 1003, 837, 779, 748, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.34 (m, 5 H), 4.51–4.30 (m, 3 H), 2.67 (dt, *J* = 2.74, 7.69 Hz, 2 H), 1.88 (m, 2 H), 0.88 (s, 9 H), 0.08 (s, 3 H), 0.02 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.9, 128.6, 128.1, 126.2, 80.8, 69.5, 36.8, 30.8, 25.6, 17.9, –4.6, –5.1.

HRMS (methane CI): *m*/*z* calcd for $[C_{16}H_{27}NO_3Si + H]^+$: 310.1838; found: 310.1845.

1-Nitro-4-phenylbutan-2-yl Acetate (Table 6, entries 13,14)

A dry 100-mL round-bottom flask was charged with 1-nitro-4-phenylbutan-2-ol[47] (10 mmol, 1.95 g) and placed under N_2. Freshly distilled CH_2Cl_2 (20 mL), pyridine (14 mmol, 1.13 mL), and acetyl chloride (12 mmol, 0.85 mL) were injected sequentially, and the reaction mixture was stirred for 14 h. The mixture was quenched with aq sat. $NaHCO_3$, transferred to a separatory funnel, and the organic layer washed with brine. The organics were then dried (Na_2SO_4), filtered, and concentrated. The crude material was subjected to flash chromatography (hexanes–EtOAc, 95:5, then 80:20) affording 1.01 g (43%) of 1-nitro-4-phenylbutan-2-yl acetate as a yellow oil.

IR (neat): 3028, 2932, 1747, 1558, 1375, 1230, 1047, 943, 752, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.11 (m, 5 H), 5.42 (m, 1 H), 4.48 (m, 2 H), 2.67 (m, 2 H), 2.03 (s, 3 H), 1.96 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.8, 140.0, 128.5, 128.1, 126.3, 77.1, 69.4, 32.9, 31.1, 20.6.

HRMS (methane CI): *m*/*z* calcd for $[C_{12}H_{15}NO_4 + H]^+$: 238.1079; found: 238.1079.

(3-Methoxy-4-nitrobutyl)benzene[48] (Table 6, entries 15,16)

A dry 250-mL round-bottom flask was charged with Proton-Sponge® (61.13 mmol, 13.1 g) and methyl trifluoromethanesulfonate (50.94 mmol, 5.76 mL), connected to a reflux condenser, and placed under a positive pressure of N_2. 1-Nitro-4-phenylbutan-2-ol[47] (10.19 mmol, 1.99 g) in freshly distilled $CHCl_3$ (50 mL) were added through the reflux condenser followed by another quantity of freshly distilled $CHCl_3$ (40 mL). The N_2 inlet was removed, the flask was placed in an oil-bath, and the reaction mixture was refluxed for 14 h. After cooling to r.t., concd NH_4OH (3 mL) was added and the mixture was stirred for an additional 2 h. The mixture was poured into a separatory funnel containing H_2O, extracted with CH_2Cl_2, and the organics were washed with aq 10% HCl. The organics were dried ($MgSO_4$), filtered, and concentrated. The crude material was subjected to flash chromatography (hexanes–EtOAc: 90:10) affording 1.31 g (61%) of (3-methoxy-4-nitrobutyl)benzene as a light red-yellow oil.

IR (neat): 2936, 1558, 1456, 1387, 1116, 750, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.13 (m, 5 H), 4.40 (m, 2 H), 3.54 (m, 1 H), 3.39 (s, 3 H), 2.70 (m, 2 H), 1.87 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7, 128.5, 128.2, 126.2, 78.3, 77.3, 57.7, 33.2, 30.9.

2-Methyl-2-(3-nitro-2-phenylpropyl)-1,3-dioxolane (Table 6, entry 21)

This compound was prepared following literature procedures via a proline-catalyzed Michael reaction between acetone and *trans*-nitrostyrene[3f] followed by protection of the ketone as the ketyl;[49] clear oil; yield: 4.26 g (85%).

IR (neat): 2984, 2889, 1552, 1381, 1219, 1142, 1043, 763, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.14 (m, 5 H), 4.86 (dd, *J* = 6.04, 12.63 Hz, 1 H), 4.50 (dd, *J* = 9.33, 12.08 Hz, 1 H), 3.91 (m, 4 H), 3.72 (m, 1 H), 2.06 (dd, *J* = 6.04, 7.69 Hz, 2 H), 1.24 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8, 128.7, 128.2, 127.2, 108.9, 80.7, 64.6, 64.3, 42.0, 39.7, 24.2.

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