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Diastereoselective Reductive Nitro-Mannich Reactions

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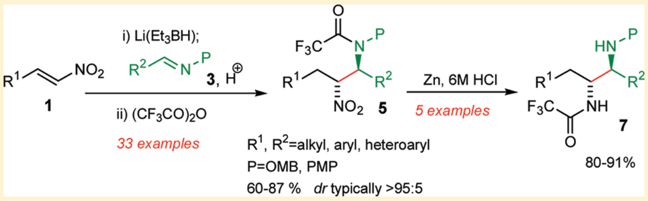
Ⓢ *Supporting Information*

ABSTRACT: A range of nitroalkenes **1** and imines **3** derived from alkyl, aryl, and heteroaryl aldehydes underwent a tandem 1,4-hydride addition nitro-Mannich reaction to afford *anti*-rich *β*-nitroamines **4**. The crude *anti*-*β*-nitroamines **4** could be converted to the corresponding *anti*-*β*-nitroacetamides **5** (33 examples) to allow purification in good yield from the parent nitroalkenes (60−87%), and with a high diastereomeric ratio (90:10 to mostly >95:5). A representative selection of *anti*-*β*-nitroacetamides **5** (five examples) were reduced to vicinal diamines **7** with zinc hydrochloride; concomitant acyl migration provided differentially protected vicinal diamines **7** in good yield (80−91%).

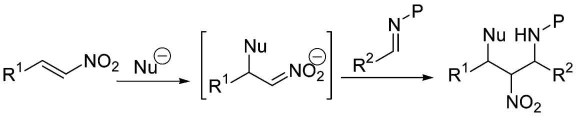


INTRODUCTION

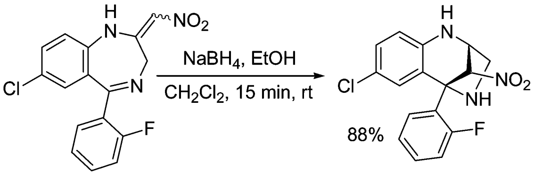
Among the most widely employed C−C bond-forming reactions in organic chemistry is the addition of activated C−H nucleophiles to C═X π-bonds. Encompassed within this description is the well-known aldol reaction[1] and its aza analogues: the nitro aldol or Henry reaction,[2] the Mannich reaction,[3] and the least explored analogue, the nitro-Mannich reaction.[4] Although the nitro-Mannich reaction was first reported in 1896,[4] little progress was made until the characterization of efficient stereoselective versions more than 100 years later.[5] The product *β*-nitroamines are highly versatile synthetic intermediates, allowing access to a range of important functionalities, including vicinal diamines[5a,6] and *β*-amino carbonyl compounds.[7] There are now a range of metal and organocatalyzed procedures that access both the more common *anti*- and rare *syn*-*β*-nitroamines, many in enantiomerically enriched form.[5b,c,8]

Despite these advances, the nitro-Mannich reaction still suffers from some limitations. For instance, there are relatively few examples of the use of the nitro-Mannich reaction in total synthesis,[9] and we believe its versatility has been limited by the availability of more complex nitroalkanes.[10] We have been addressing this issue by the development of conjugate addition nitro-Mannich reactions (Scheme 1). The conjugate addition of a nucleophile to a nitroalkene, abundantly available from the Henry reaction, and the subsequent trapping of the nitronate anion with an imine give wider access to acyclic *β*-nitroamines and do not require a prerequisite synthesis of a nitroalkane (most often prepared from a nitroalkene). We have recently reported an enantioselective conjugate addition nitro-Mannich protocol, initiated by asymmetric copper-catalyzed dialkyl zinc additions, which affords *anti*- or *syn*-*β*-nitroamines with exquisite control of stereochemistry over three contiguous centers.[11] The initial stereocenter from the conjugate addition reaction effectively controls the formation of the two new additional stereocenters from the nitro-Mannich reaction.

Scheme 1. Conjugate Addition Nitro-Mannich Reaction



We have been investigating other nucleophiles in this process, and although we found conditions that allowed the addition of cyanide anions to nitroalkenes in good yield,[12] all subsequent attempts at a nitro-Mannich reaction failed. The development of a conjugate reduction nitro-Mannich reaction proved to be more successful. We found an isolated example of this reaction in the literature whereby an unexpected intramolecular cyclization took place upon reduction of a nitroalkene in the presence of an imine, during an investigation of the synthesis of some imidazobenzodiazepines (eq 1).[13] One



(1)

could envisage a chiral reduction of a suitable nitroalkene would furnish a stereocenter that would control the stereoselectivity of the following nitro-Mannich reaction as we have found for the conjugate addition nitro-Mannich reaction with dialkyl zincs.[11]

In this paper, we report the broad generality of the reductive nitro-Mannich reaction and show that it is diastereoselective for a wide range of alkyl, aryl, and heteroaryl substituents. We also

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Scheme 2. Reductive Nitro-Mannich Reaction with OMB-Imines

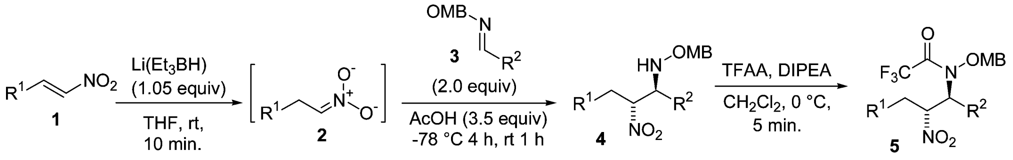


Table 1. Scope of the Reductive Nitro-Mannich Reaction with OMB-Imines

nitro alkene	R^1	imine	R^2	**4** conv. (%)[a]	dr (*anti*:*syn*)[b]	product	yield of **5** (%, two steps)[c]	dr (*anti*:*syn*)[b]
1a	*n*-pentyl	**3a**	Ph	84	95:5	**5aa**	72	95:5
1b	Cy	**3a**	Ph	88	90:10	**5ba**	75	95:5
1c	*t*-Bu	**3a**	Ph	91	80:20	**5ca**	60	95:5
1d	Ph	**3a**	Ph	<5	–	**5da**	–	–
1e	Bn	**3a**	Ph	92	90:10	**5ea**	65	90:10
1f	*p*-MeO-C$_6$H$_4$	**3a**	Ph	<5	–	**5fa**	–	–
1g	*p*-CF$_3$-C$_6$H$_4$	**3a**	Ph	80	70:30	**5ga**	47	95:5
1h	*p*-F-C$_6$H$_4$	**3a**	Ph	<5	–	**5ha**	–	–
1i	2-furyl	**3a**	Ph	49	75:25	**5ia**	30	95:5
1a	*n*-pentyl	**3b**	2-furyl	85	80:20	**5ab**	55	95:5
1a	*n*-pentyl	**3c**	*n*-pentyl	95	90:10	**5ac**	68	95:5

[a]Determined by ^{1}H NMR and mass balance. [b]Determined by ^{1}H NMR. [c]Isolated yield.

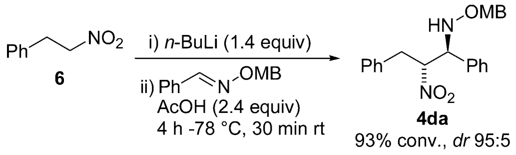
show that the usually unstable product β-nitroamines can be isolated as their corresponding trifluoroacetamides, which allows their subsequent reduction with zinc hydrochloride to give differentially protected 1,2-diamines.

■ RESULTS AND DISCUSSION

Central to our strategy was the selection of a suitable hydride source. We reasoned that a precise hydride stoichiometry was required to prevent competitive imine reduction that could occur with reagents such as sodium borohydride.[14] Mindful of this, we employed Superhydride,[15] as Kalbalka has shown that nitroalkenes can be efficiently reduced to nitroalkanes with Superhydride and silica gel.[16] We intended to intercept the nitronate intermediate of this reaction with an imine to give a nitro-Mannich reaction.

Treatment of nitroalkene **1**[17] with a slight excess of Superhydride in THF at rt for 10 min followed by cooling to −78 °C and addition of *o*-methoxybenzyl (OMB)-protected imine **3** (2 equiv) and AcOH allowed the isolation of the crude nitro-Mannich products **4** (Scheme 2 and Table 1).[18] Because of the relative instability of β-nitroamines, we isolated the products as their trifluoroacetamides **5** by treatment of the crude reaction mixtures with trifluoroacetic anhydride (TFAA) in the presence of diisopropylethylamine (DIPEA).[19] These products were stable to chromatography, and the *anti* stereoselectivity was often upgraded during purification.[20]

A range of aliphatic nitroalkenes **1a–c,e** smoothly underwent the Superhydride reductive nitro-Mannich reaction with imine **3a** (Table 1). A dramatic difference in reactivity was observed with aromatic and heteroaromatic nitroalkenes **1d,i**. While some reactivity was retained with the 2-furyl analogue **1i**, no reaction was observed with β-nitrostyrene; instead, complete recovery of unreacted imine **3a** and nitroethylbenzene **6** was observed. Reductive nitro-Mannich reactivity was restored by either moving the phenyl ring farther from the nitronate (**1e**) or modifying the electronic properties of the aryl ring (**1f–h**). Interestingly, β-nitroamine **4da** can be prepared from nitroethylbenzene **6** by a standard nitro-Mannich reaction, suggesting that putative nitronate **2d** will participate in a nitro-Mannich reaction, albeit in the absence of triethylborane (eq 2).



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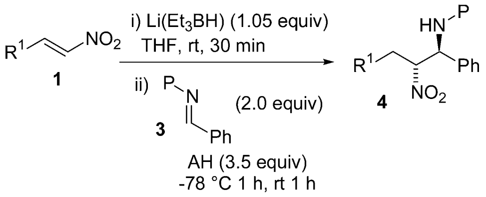
Also, quenching of nitronate **2d**, derived from the Superhydride reduction of **1d**, with d_4-AcOH gave complete deuterium incorporation at the α position, suggesting that the nitronate species remains intact in solution but does not undergo a nitro-Mannich coupling in this case. We conducted further investigations focusing on the nature of the imine protecting group and the use of the stronger carboxylic acid, trifluoroacetic acid (TFA), to promote the reaction (Scheme 3 and Table 2)

Scheme 3. Reductive Nitro-Mannich Reaction of Nitrostyrenes



Changing the protecting group of the imine from OMB **3a** to allyl **3d** reinstated reactivity to some extent (60% conversion). The *p*-methoxyphenyl (PMP)-protected imine **3e** was used in the presence of a stronger acid, trifluoroacetic acid (TFA), to promote the reaction. We attribute the necessity of using a stronger acid to the lower basicity of the PMP-imine lone pair versus the OMB-imine lone pair (a $\mathrm{p}K_\mathrm{a}$H for PMP-imine of $\sim$3 vs a $\mathrm{p}K_\mathrm{a}$H for OMB-imine of $\sim$7). Use of the PMP-imine **3e** led to a near-quantitative conversion in a very high diastereomeric ratio of 95:5. Using TFA to promote the reaction with OMB-imine **3a**

Table 2. Investigating the Lack of Nitrostyrene Reactivity

nitro alkene	R^1	imine	P	AH	product	4 conv. (%)[a]	dr (*anti*:*syn*)[b]
1d	Ph	**3a**	OMB	AcOH	**4da**	<5	–
1d	Ph	**3d**	allyl	AcOH	**4dd**	60	90:10
1d	Ph	**3e**	PMP	CF_3CO_2H	**4de**	>95	95:5
1d	Ph	**3a**	OMB	CF_3CO_2H	**4da**	90	90:10
1b	Cy	**3e**	PMP	AcOH	**4be**	50[c]	>95:5
1b	Cy	**3e**	PMP	CF_3CO_2H	**4be**	>95	90:10

[a]Determined by ^{1}H NMR and mass balance. [b]Determined by ^{1}H NMR. [c]At −78 °C for 4 h and rt for 1 h.

also led to efficient conversion (90%) with a slightly decreased diastereomeric ratio of 90:10. We observed that the intermediate nitronate adduct formed from the reduction of **1d** with Superhydride was insoluble in the reaction solvent THF. However, when TFA was added, the solid dissolved, whereas with AcOH, the solid remained. We think that the nitrostyrene **1d** and OMB-imine **3a** reaction does not work with AcOH because the nitronate species remains solid in the reaction. Use of TFA instead dissolves the solid nitronate adduct, and the homogeneous reaction mixture then allows an efficient nitro-Mannich reaction. To support this, treatment of cyclohexyl nitroalkene **1b** with PMP-imine **3e** in the presence of AcOH led to a 50% conversion with nearly complete control of diastereoselectivity. In this case, the aliphatic nitroalkene becomes soluble upon addition of AcOH, but the ensuing reaction with PMP-imine is slower because of the reduced basicity of the imine lone pair being less able to accept a proton and facilitate the nitro-Mannich reaction. Use of trifluoroacetic acid in the same reaction resulted in quantitative conversion with a 90:10 dr. The acid could solubilize the nitronate adduct by protonation to form the nitronic acid or some alteration of the boron species to give a soluble nitronate species. As the nitrostyrene **1d**−PMP-imine **3e** reaction with TFA had given nearly complete conversion and diastereoselectivity, and PMP-imines had led to excellent stereoselectivites in our conjugate addition nitro-Mannich reaction with dialkyl zincs,[11] we now turned to this imine and acid promoter to explore the full scope of the reductive nitro-Mannich reaction. Optimization studies revealed that the amount of imine could be reduced to 1.1 equiv, the amount of trifluoroacetic acid could be reduced to 2.5 equiv, and the nitro-Mannich reaction needed only 5 min at room temperature to give the same high yield and diastereoselectivity. Because of the relative instability of the β-nitroamines, we isolated the products as their trifluoroacetamides by treatment of the crude reaction mixtures with TFAA in the presence of pyridine (Scheme 4 and Table 3).[19,21]

Scheme 4. Scope of the Reductive Nitro-Mannich Reaction with Respect to Nitroalkenes Using PMP-Imine 3e

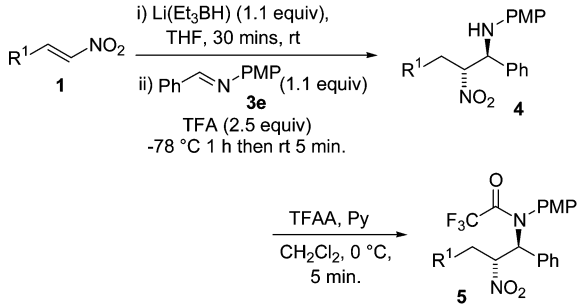


Table 3. Scope of the Reductive Nitro-Mannich Reaction with PMP-Imine 3e

nitro alkene	R^1	product	yield of **5** (%, two steps)[a]	dr (*anti*:*syn*)[b]
1a	*n*-pentyl	**5ae**	82	95:5
1b	Cy	**5be**	87	90:10
1d	Ph	**5de**	82	>95:5
1f	*p*-MeO-C_6H_4	**5fe**	86	>95:5
1j	*o*-MeO-C_6H_4	**5je**	79	95:5
1g	*p*-CF_3-Ph	**5ge**	81	>95:5
1i	2-furyl	**5ie**	79	>95:5
1k	*o*-CF_3-C_6H_4	**5ke**	79	>95:5
1l	*p*-Me-C_6H_4	**5le**	75	>95:5
1m	*o*-Me-C_6H_4	**5me**	72	95:5
1n	*N*-Me-2-pyrrole	**5ne**	63[c]	>95:5
1o	*N*-Ts-2-pyrrole	**5oe**	74	>95:5
1p	2-pyridyl	**5pe**	65	>95:5

[a]Isolated yield. [b]Determined by ^{1}H NMR. [c]In addition to *N*-trifluoroacetylation, the electron rich pyrrole ring was trifluoroacetylated at position 5.

With respect to nitroalkenes, the reaction worked well with a variety of alkyl, aryl, and heteroaryl substituents. Electron-donating or -withdrawing substituents on the phenyl ring, pyridine, and pyrrole groups all gave uniformly high diastereoselectivities. The *N*-methyl-pyrrole nitroalkene **1n** was employed because the unprotected pyrrole product was unstable and would degrade at rt. The product **5ne** from the *N*-methyl-pyrrole nitroalkene was trifluoroacetylated at position 5 in addition to *N*-trifluoroacetylation under our standard protection conditions (5 equiv of TFAA and 5 equiv of Py). Reduction of the TFAA/Py combination to 1.1 equiv did not lead to selective N-trifluoroacetylation, but instead to a complex mixture of N-trifluoroacetylated and heterocycle trifluoroacetylated products. The corresponding pyridine nitroalkene **1p** has a tendency to polymerize but is stable for weeks at −20 °C and works well in the reaction. The product from the pyridine nitroalkene **5pe** was unstable at room temperature, turning from a yellow oil to a black oil over 4 days. Examination of the ^{1}H NMR revealed that the product had turned to an ∼1:1 mixture of diastereoisomers with no evidence of retro products. This is the only example of epimerization of any of the trifluoroacetamide-protected products in this and our previous work. It is possible that the epimerization is intramolecular (Figure 1) from the pyridine nitrogen despite the discrepancies in the pK_a of pyridine (∼5) versus nitroalkane (∼10).

Although using the optimized conditions (Scheme 4) to survey the reaction with respect to different PMP-imines led to >95% conversion, in general we noted lower diastereoselectivites for electron rich imines. For example, 2-furyl PMP-imine **3f** gave a dr of ∼65:35. We speculated that the more electron

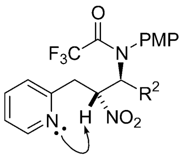


Figure 1. Possible epimerization mechanism.

rich imines were more easily protonated and led to faster, nonselective reactions. To investigate this, we optimized the reaction with respect to temperature, acid, and reaction solvent (Scheme 5 and Table 4).

Scheme 5. Optimization of Electron Rich PMP-Imines

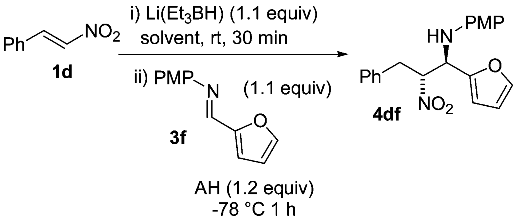


Table 4. Optimization of Electron Rich PMP-Imines

entry	acid AH[a]	solvent	conv. (%)[b]	dr (*anti*:*syn*)[c]
1[e]	CF_3CO_2H[d]	THF	>95	65:35
2	CF_3CO_2H[d]	THF	>95	65:35
3[f]	CF_3CO_2H[d]	THF	>95	65:35
4	CF_3CO_2H	THF	>95	75:25
5	AcOH	THF	<5	–
6[g]	AcOH	THF	<5	–
7	$BrCH_2CO_2H$	THF	<5	–
8[g]	$BrCH_2CO_2H$	THF	40	65:35
9	$Cl_2CH_2CO_2H$	THF	80	70:30
10	$Cl_3CH_2CO_2H$	THF	>95	80:20
11	CF_3CO_2H[h]	THF	>95	80:20
12	$MeSO_3H$	THF	50	80:20
13	CF_3SO_3H	THF	>95	80:20
14	CF_3SO_3H	CH_2Cl_2	>95	80:20
15	CF_3CO_2H[h]	CH_2Cl_2	>95	90:10
16	CF_3CO_2H[h]	Et_2O	>95	65:35
17	CF_3CO_2H[h]	PhMe	>95	85:15

[a] Added in 1 mL of solvent. [b] Determined by ^1H NMR and mass balance. [c] Determined by ^1H NMR. [d] 2.5 equiv of CF_3CO_2H. [e] Reaction temperature of −78 °C and then rt for 5 min. [f] Reaction temperature of −100 °C for 1 h. [g] Reaction temperature of −78 °C for 1 h and then rt for 1 h. [h] Neat CF_3CO_2H added.

Scheme 6. Scope of the Reductive Nitro-Mannich Reaction with Respect to PMP-Imine with Nitrostyrene 1d

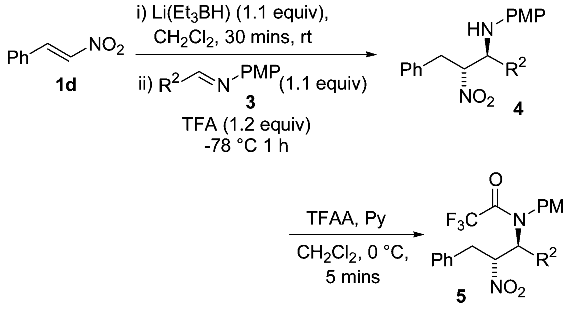


Table 5. Scope of the Reductive Nitro-Mannich Reaction with Nitrostyrene 1d

imine	R^2	product	yield[a] of **5** (%)	dr (*anti*:*syn*)[b]
3i	2-furyl	**5di**	83	90:10
3j	*o*-MeO-C_6H_4	**5dj**	87	90:10
3p	*m*-MeO-C_6H_4	**5dp**	86	>95:5
3f	*p*-MeO-C_6H_4	**5df**	80	>95:5
3k	*o*-CF_3-C_6H_4	**5dk**	76	95:5
3g	*p*-CF_3-C_6H_4	**5dg**	78	>95:5
3m	*o*-Me-C_6H_4	**5dm**	72	>95:5
3q	*n*-pentyl	**5dq**	84	>95:5
3r	Cy	**4dr**[c]	58[d]	>95:5
3o	2-pyridyl	**5do**	60[e]	>95:5
3s	3-pyridyl	**5ds**	80	>95:5
3t	2-pyrrole	**4dt**	15[f]	50:50
3n	*N*-Me-2-pyrrole	**4dn**	75[f]	55:45
3u	*N*-Ts-2-pyrrole	**5du**	74	>95:5
3v	3-indole	**4dv**	80[f]	50:50
3w	*N*-Ts-3-indole	**5dw**	64[g]	>95:5

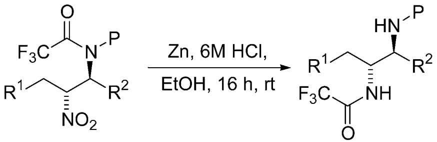
[a] Isolated yield over two steps from nitro alkene **1**. [b] Determined by ^1H NMR. [c] *β*-Nitroamine was resistant to TFA protection. [d] Conversion to **4dr** of 88% with a 75:25 dr. [e] Conversion to **4do** of 95% with a 75:25 dr. [f] The crude product was not TFA protected or characterized because of the low yield and/or low dr. [g] Conversion to **4dw** of >95% with a 90:10 dr.

Not allowing the nitro-Mannich reaction mixture to warm to room temperature (entry 2) or even cooling to −100 °C (entry 3) led to no change in dr (cf. entry 1). Reducing the amount of trifluoroacetic acid to 1.2 equiv had a small beneficial effect on dr (entry 4), and this amount was adopted as the standard amount.[22] Acids weaker than trifluoroacetic acid failed to promote the reaction (entries 4–6). Allowing a bromoacetic acid-promoted nitro-Mannich reaction mixture to warm to rt for 1 h led to poor conversion and a low dr (entry 8). Dichloroacetic acid and trichloroacetic acid were able to promote the reaction at −78 °C and gave a slight improvement in diastereoselectivity up to 80:20 (entries 9 and 10, respectively). This diastereoselectivity could be repeated via addition of neat trifluoroacetic acid (entry 11), but attemps to add neat trichloroacetic acid were thwarted because of the fact it is a sticky solid. Methanesulfonic acid (entry 12) and triflic acid (entry 13) produced the same dr (80:20), but methanesulfonic acid was unable to promote the reaction as efficiently (50% conversion). Changing the solvent had no effect with triflic acid (entries 13 and 14) but affected the dr with trifluoroacetic acid (entries 11 and 15–17), with CH_2Cl_2 providing >95% conversion and a dr of 90:10. Despite the reaction being performed in CH_2Cl_2, there was still a small amount of THF present from the Superhydride stock solution (1 M in THF). Evaporating to dryness after the reduction step and redissolving in pure CH_2Cl_2 for the nitro-Mannich reaction produced no change in dr. With these improved conditions in hand, a survey of the scope of the reaction toward different PMP-imines was conducted (Scheme 6 and Table 5).

The reaction worked well in terms of yield and diastereoselectivity for electron rich, electron deficient, and more sterically demanding aryl imines with ortho substituents. Straight chain alkyl imine **3q** gave good results; however, the branched cyclohexyl imine **3r** gave an 88% yield of the product *β*-nitroamine **4dr** with a low dr (75:25), and it would not undergo trifluoroacetylation even with excess TFAA and pyridine. It could however be isolated by rapid column chromatography in 58% yield as a single diastereoisomer. Nitrogen heterocycle 2-pyridyl PMP-imine **3o** gave a poor dr (75:25) for the crude **4do** and a corresponding low 60% yield of the isolated product **5do** (>95:5 dr), whereas the 3-pyridyl PMP-imine **3s** gave a higher 80% yield of final product **5ds** (>95:5 dr) because of a more diastereoselective nitro-Mannich reaction. Pyrrole PMP-imines **3t** and **3n** were poorly selective, and the unprotected pyrrole **3t** gave a low level of conversion. Protecting the pyrrole group (**3u**) with an electron-withdrawing tosyl group resulted in the normally high yield and a >95:5 dr. A similar pattern was observed with the indole imines **3v** and **3w**, where once more a tosyl protecting group was required to give good diastereoselectivity.

The reduction of β-nitroamines **4** is complicated by the inherent instability of the β-nitroamines.[18] The use of SmI_2 is good for very sensitive substrates but unfortunately requires 6 equiv of freshly prepared reagent.[18b,20] Because of these limitations, we developed the use of aluminum amalgam to reduce the nitro function to a hydroxylamine, which can then be further reduced to the amine by hydrogenolysis or $LiAlH_4$ depending on the nature of the substituents.[23] The enhanced stability of β-nitroacetamides **5** versus that of β-nitroamines **4** allowed us to investigate other compatible reducing agents. A survey of reducing systems was conducted that included iron,[24] zinc,[25] indium,[26] aluminum amalgam,[23] nickel boride,[27] $LiAlH_4$,[28] hydrogenation [with Pd-C,[29] Ra-Ni,[30] and $Pd(OH)_2$[31]], and transfer hydrogenation.[32] Of the reducing agents examined, zinc hydrochloride (Zn/HCl) was found to be superior. In the representative examples that were examined, reduction was accompanied by concomitant transacylation to the sterically less encumbered amine to give **7** (Scheme 7). The OMB/PMP and TFA groups are orthogonal protecting groups and render these differentially protected vicinal diamines as attractive intermediates in target synthesis.

Scheme 7. Representative Syntheses of 1,2-Diamines 7



5aa P=OMB, R^1=*n*-pent, R^2=Ph **7aa** 87%
5ia P=OMB, R^1=2-furyl, R^2=Ph **7ia** 91%
5ab P=OMB, R^1=*n*-Pn, R^2=2-furyl **7ab** 91%
5de P=PMP, R^1=Ph, R^2=Ph **7de** 85%
5oe P=PMP, R^1=*N*-Ts-2-pyrrole, R^2=Ph **7oe** 80%

■ CONCLUSION

We have demonstrated the first example of a reductive nitro-Mannich reaction that provides β-nitroamines with excellent conversion and diastereoselectivity for a wide range of alkyl, aryl, and heteroaryl substituents. The moderate instability of the reaction products was overcome by smooth conversion to β-nitroacetamides that were found to be highly stable intermediates. Reduction with concomitant acyl migration can be effected by treatment with Zn/HCl. This work represents a significant advance in the scope of the nitro-Mannich reaction, demonstrates a powerful method for the isolation of sensitive β-nitroamines, and describes an efficient conversion to differentially protected vicinal diamines.

■ EXPERIMENTAL SECTION

General Procedure for the Synthesis of OMB-β-Nitroamines 4 by the Reductive Nitro-Mannich Reaction (Table 1). A solution of nitroalkene **1** (1.0 mmol) in THF (10 mL) was added to Superhydride (1.05 mmol, 1 M in THF) by cannula under N_2. The suspension was then stirred for 30 min at rt before being cooled to −78 °C over 30 min. A solution of imine **3** (2.0 mmol) in THF (10 mL) was added by cannula and the mixture stirred at −78 °C for 10 min. A solution of AcOH (3.5 mmol) in THF (2 mL) was added by cannula and the reaction mixture stirred for 4 h at −78 °C before being allowed to warm to rt over 1 h. Saturated aqueous $NaHCO_3$ and Et_2O were then added. The organic phase was washed with saturated aqueous $NaHCO_3$ and dried ($MgSO_4$), and the solvents were removed in vacuo to afford crude nitroamine **4**. Diastereoselectivities were calculated by analysis of the ^{1}H NMR integrals for the ArCH_2N (~3.7 ppm) protons unless otherwise stated.

***4aa** (1S*,2R*)-N-(2-Methoxybenzyl)-2-nitro-1-phenyloctan-1-amine.* Nitroalkene **1a** (210 mg, 1.47 mmol) afforded crude β-nitroamine **4aa** (859 mg, 84% conv., 95:5 dr) as a yellow oil by the general procedure for Table 1: IR υ_{max} 3330, 2837, 1549, 1242 cm^{-1}; ^{1}H NMR^{anti} δ 0.87 (3H, J = 7.2), 1.26 (8H, m), 1.91 (1H, m), 2.08 (1H, m), 3.52 (1H, d, J = 13.2), 3.78 (1H, d, J = 13.2), 3.80 (3H, s), 4.04 (1H, d, J = 6.4), 4.63 (1H, ddd, J = 10.9, 6.4, 2.9), 6.85 (1H, d, J = 8.4), 7.05 (1H, dd, J = 7.4, 1.6), 7.32 (7H, m); ^{1}H NMR^{syn} ($CDCl_3$) δ 3.47 (1H, d, J = 13.3), 3.95 (1H, d, J = 9.2) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 14.2 (CH_3), 22.7 (CH_2), 26.2 (CH_2), 28.9 (CH_2), 29.3 (CH_2), 31.6 (CH_2), 47.8 (CH_2), 64.5 (CH), 93.9 (CH), 110−130 (9C, *Ar*), 130−150 (3C, *C*); ^{13}C NMR^{syn} ($CDCl_3$) δ 47.1 (CH_2), 64.3 (CH), 94.3 (CH) (the remaining signals could not be distinguished); MS (EI+) *m*/*z* 371 (100%, MH^+), 355 (19%, MH^+ − CH_3), 256 (38%); HRMS $C_{22}H_{30}N_2O_3H^+$ calcd 371.2329, found 371.2324.

***4ba** (1S*,2R*)-3-Cyclohexyl-N-(2-methoxybenzyl)-2-nitro-1-phenylpropan-1-amine.* Nitroalkene **1b** (244 mg, 1.57 mmol) afforded crude β-nitroamine **4ba** (999 mg, 88% conv., 90:10 dr) as a yellow oil by the general procedure for Table 1: IR υ_{max} 3200, 3050, 1548, 1492, 1241 cm^{-1}; ^{1}H NMR^{anti} δ 0.70−1.70 (12H, m), 2.06 (1H, ddd, J = 15.5, 11.5, 4.0), 3.54 (1H, d, J = 10.5), 3.81 (3H, s), 4.03 (1H, d, J = 6.0), 4.77 (1H, ddd, J = 13.5, 6.0, 2.5), 6.85−7.09 (2H, m), 7.25−7.45 (7H, m); ^{1}H NMR^{syn} δ 3.47 (1H, d, J = 14.0) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 25.7 (CH_2), 25.8 (CH_2), 26.1 (CH_2), 31.6 (CH_2), 34.7 (CH), 36.5 (CH_2), 47.6 (CH_2), 55.1 (CH_3), 64.7 (CH), 91.2 (CH), 110−130 (9C, *Ar*), 130−150 (3C, *C*); ^{13}C NMR^{syn} δ 47.4 (CH_2), 65.1 (CH), 91.8 (CH) (the remaining signals could not be distinguished); MS (EI+) *m*/*z* 383 (100%, MH^+), 367 (36%, MH^+ − CH_3), 298 (28%), 256 (77%); HRMS $C_{23}H_{30}N_2O_3H^+$ calcd 383.2329, found 383.2327.

***4ca** (1S*,2R*)-N-(2-Methoxybenzyl)-4,4-dimethyl-2-nitro-1-phenylpentan-1-amine.* Nitroalkene **1c** (156 mg, 1.20 mmol) afforded crude β-nitroamine **4ca** (881 mg, 91% conv., 80:20 dr) as a yellow oil by the general procedure for Table 1: IR (neat) υ_{max} 3050, 2838, 1549, 1242 cm^{-1}; ^{1}H NMR^{anti} δ 0.76 (9H, s), 1.45 (1H, b), 1.82 (1H, d, J = 16.0), 2.17 (1H, dd, J = 16.0, 1.0), 3.50 (1H, d, J = 13.0), 3.79 (1H, d, J = 13.5), 3.79 (3H, s), 4.03 (1H, d, J = 5.0), 4.69 (1, dd, J = 10.0, 5.5), 6.85 (2H, m), 7.25 (7H, m); ^{1}H NMR^{syn} δ 0.73 (9H, s), 1.24 (1H, d, J = 15.5), 1.99 (1H, dd, J = 15.5, 10.0), 3.56 (1H, d, J = 14.0), 3.88 (1H, t, J = 10.0) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 28.8 (CH_3), 29.8 (C), 41.0 (CH_2), 47.6 (CH_2), 55.2 (CH_3), 64.4 (CH), 90.6 (CH), 110−130 (9C, *Ar*), 130−150 (3C, *C*); ^{13}C NMR^{syn} δ 30.3 (CH_3), 40.8 (CH_2), 47.5 (CH_2), 55.1 (CH_3), 65.7 (CH), 90.9 (CH) (the remaining signals could not be distinguished); MS (EI+) *m*/*z* 357 (100%, MH^+), 341 (15%, MH^+ − Me), 256 (16%); HRMS $C_{21}H_{28}N_2O_3H^+$ calcd 357.2173, found 357.2159.

***4ea** (1S*,2R*)-N-(2-Methoxybenzyl)-2-nitro-1,4-diphenylbutan-1-amine.* Nitroalkene **1e** (142 mg, 0.872 mmol) afforded crude β-nitroamine **4ea** (312 mg, 92% conv., 90:10 dr) as a yellow oil by the general procedure for Table 1: IR υ_{max} 3150, 2938, 1553, 1492, 1463, 1292 cm^{-1}; ^{1}H NMR^{anti} δ 2.28 (1H, m), 2.44 (1H, m), 2.51 (1H, m), 2.66 (1H, ddd, J = 14.0, 10.0, 4.5), 3.53 (1H, d, J = 13.5), 3.78 (1H, d, J = 13.5), 4.09 (1H, d, J = 6.5), 4.67 (1H, ddd, J = 10.5, 6.1, 2.5), 6.82

(1H, d, *J* = 8.0), 7.05 (1H, dd, *J* = 7.5, 3.5), 7.10 (2H, d, *J* = 7.0), 7.20−7.40 (10H, m); ^{13}C NMR^{anti} δ 30.8 (CH$_2$), 32.2 (CH$_2$), 47.6 (CH$_2$), 55.4 (CH$_3$), 64.4 (CH), 92.7 (CH), 110−130 (14C, CH), 130−150 (4C, C); ^{1}H NMR^{syn} δ 3.49 (1H, d, *J* = 13.4), 4.00 (1H, d, *J* = 10.5) (the remaining signals could not be distinguished); ^{13}C NMR^{syn} δ 47.4 (CH$_2$), 55.1 (CH$_3$), 64.8 (CH), 93.2 (CH) (the remaining signals could not be distinguished); MS (EI$^+$) *m*/*z* 391 (100%, MH$^+$), 421 (36%); HRMS $\mathrm{C_{24}H_{26}N_2O_3H^+}$ calcd 391.2016, found 391.2000.

4ga _(1S*,2R*)-N-(2-Methoxybenzyl)-2-nitro-1-phenyl-3-[4-(trifluoromethyl)phenyl]propan-1-amine._ Nitroalkene **1g** (55 mg, 0.25 mmol) afforded crude nitroamine **4ga** (189 mg, 80% conv., 70:30 dr) as a yellow oil by the general procedure for Table 1: IR υ_{max} 3200, 3009, 2941, 1556, 1326, 1244 cm^{-1}; ^{1}H NMR^{anti} δ 3.38 (2H, m), 3.58 (1H, d, *J* = 13.5), 3.72 (1H, d, *J* = 14.0), 3.81 (3H, s), 4.18 (1H, d, *J* = 6.0), 4.88 (1H, m), 6.80−7.50 (13H, m); ^{1}H NMR^{syn} δ 2.73 (1H, dd, *J* = 14.5, 3.0), 3.07 (1H, dd, *J* = 14.5, 11.0), 3.50 (1H, d, *J* = 13.5), 3.75 (3H, s), 4.05 (1H, d, *J* = 9.0), 4.88 (1H, m), 6.80−7.50 (13H, m); ^{13}C NMR^{anti} δ 34.8 (CH$_2$), 47.7 (CH$_2$), 55.2 (CH$_3$), 64.3 (CH), 94.3 (CH), 110−130 (13C, CH), 130−150 (4C, *C*) (the signals corresponding to CF$_3$ and CCF$_3$ could not be distinguished); ^{13}C NMR^{syn} δ 34.8 (CH$_2$), 47.7 (CH$_2$), 55.2 (CH$_3$), 64.3 (CH), 94.3 (CH) (the remaining signals could not be distinguished); MS (EI+) *m*/*z* 445 (100%, MH$^+$), 475 (20% MNa$^+$), 501 (9%); HRMS $\mathrm{C_{24}H_{23}F_3N_2O_3H^+}$ calcd 445.1734, found 445.1737.

4ia _(1S*,2R*)-3-(Furan-2-yl)-N-(2-methoxybenzyl)-2-nitro-1-phenylpropan-1-amine._ Nitroalkene **1i** (105 mg, 0.751 mmol) afforded crude β-nitroamine **4ia** (799 mg, 49% conv., 75:25 dr) as an orange oil by the general procedure for Table 1: IR υ_{max} 3064, 1556, 1245 cm^{-1}; ^{1}H NMR^{anti} δ 3.32 (1H, dd, *J* = 16.0, 3.0), 3.47 (1H, dd, *J* = 16.0, 11.0), 3.55 (1H, d, *J* = 13.5), 3.81 (1H, d, *J* = 13.5), 3.81 (3H, s), 4.14 (1H, d, *J* = 6.0), 4.98 (1H, m), 6.15 (1H, dd, *J* = 3.5, 1.0), 6.31 (1H, dd, *J* = 3.5, 1.0), 6.85 (1H, d, *J* = 8.0), 7.07 (1H, dt, *J* = 7.5, 2.5), 7.23−7.40 (7H, m), 7.47 (1H, d, *J* = 3.5); ^{1}H NMR^{syn} δ 2.72 (1H, dd, *J* = 16.0, 3.0), 3.14 (1H, dd, *J* = 16.0, 11.0), 3.50 (1H, d, *J* = 13.5), 3.75 (3H, s), 4.02 (1H, d, *J* = 9.0), 4.98 (1H, m), 5.96 (1H, d, *J* = 3.0), 6.21 (1H, dd, *J* = 3.0, 2.0), 6.80 (1H, m) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 30.0 (CH$_2$), 47.6 (CH$_2$), 55.2 (CH$_3$), 64.0 (CH), 91.5 (CH), 107.6 (*C*H), 110.3 (*C*H), 110−130 (9C, *C*H), 130−150 (3C, *C*), 150.0 (*C*); ^{13}C NMR^{syn} δ 29.8 (CH$_2$), 47.4 (CH$_2$), 55.1 (CH$_3$), 64.5 (CH), 92.2 (CH) (the remaining signals could not be distinguished); MS (EI+) *m*/*z* 367 (100%, MH$^+$), 397 (56%), 422 (23%); HRMS $\mathrm{C_{21}H_{22}N_2O_4H^+}$ calcd 367.1652, found 367.1644.

4ab _(1R*,2R*)-1-(Furan-2-yl)-N-(2-methoxybenzyl)-2-nitrooctan-1-amine._ Nitroalkene **1a** (118 mg, 0.880 mmol) afforded crude nitroamine **4ab** (792 mg, 85% conv., 80:20 dr) as an orange oil by the general procedure for Table 1: IR υ_{max} 3150, 3009, 2840, 1589, 1493, 1242 cm^{-1}; ^{1}H NMR^{anti} δ 0.77 (3H, t, *J* = 8.0), 1.27 (8H, m), 2.02 (2H, m), 3.61 (1H, d, *J* = 13.2), 3.70 (1H, m), 3.82 (3H, s), 4.12 (1H, d, *J* = 6.8), 6.23 (1H, d, *J* = 3.2), 6.33 (1H, dd, *J* = 3.2, 1.6), 6.85 (1H, d, *J* = 8.4), 6.97 (1H, m), 7.15 (1H, dd, *J* = 7.6, 1.2), 7.20 (1H, td, *J* = 7.2, 1.2), 7.39 (1H, m); ^{1}H NMR^{syn} δ 3.58 (1H, d, *J* = 13.2), 3.76 (3H, s), 4.07 (1H, d, *J* = 10.0), 4.76 (1H, dd, *J* = 10.2, 3.2) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 14.1 (CH$_3$), 22.5 (CH$_2$), 26.0 (CH$_2$), 28.7 (CH$_2$), 29.8 (CH$_2$), 31.5 (CH$_2$), 47.6 (CH$_2$), 55.2 (CH$_3$), 58.3 (CH), 91.3 (CH), 105−160 (10C, 7 CH, 3 C); ^{13}C NMR^{syn} δ 47.2 (CH$_2$), 55.2 (CH$_3$), 58.5 (CH), 91.4 (CH) (the remaining signals could not be distinguished); MS (EI$^+$) *m*/*z* 361 (54%, MH$^+$), 401 (100%); HRMS $\mathrm{C_{20}H_{28}N_2O_4H^+}$ calcd 361.2122, found 361.2132.

4ac _(6S*,7R*)-N-(2-Methoxybenzyl)-7-nitrotridecan-6-amine._ Nitroalkene **1a** (98 mg, 0.684 mmol) afforded crude β-nitroamine **4ac** (525 mg, 95% conv., 90:10 dr) as an orange oil by the general procedure for Table 1: IR υ_{max} 3320, 2932, 1546, 1244 (OMe) cm^{-1}; ^{1}H NMR^{anti} ($\mathrm{C_6D_6}$) δ 0.8−1.5 (22H, m), 2.89 (1H, ddd, *J* = 9.0, 6.0, 3.5), 3.13 (1H, b), 3.34 (3H, s), 3.81 (1H, d, *J* = 13.5), 3.89 (1H, d, *J* = 13.5), 4.51 (1H, ddd, *J* = 10.5, 5.5, 3.0), 6.53 (1H, d, *J* = 8.5), 6.57 (1H, t, *J* = 7.5), 6.87 (1H, t, *J* = 7.3), 7.25 (1H, dd, *J* = 7.5, 1.5); ^{1}H NMR^{syn} ($\mathrm{C_6D_6}$) δ 3.01 (1H, m, C*H*) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} ($\mathrm{C_6D_6}$) δ 10.1 (CH$_3$), 10.2 (CH$_3$), 22.6 (CH$_2$), 22.7 (CH$_2$), 25.7 (CH$_2$), 26.4 (CH$_2$), 28.9 (CH$_2$), 30.0 (CH$_2$), 21.7 (CH$_2$), 36.0 (CH$_2$), 47.0 (CH$_2$), 54.4 (CH$_3$), 59.9 (CH), 91.3 (CH), 110−130 (4C, CH), 130−150 (2C, C); MS (EI+) *m*/*z* 362 (100%), 365 (99%, MH$^+$); HRMS $\mathrm{C_{21}H_{36}N_2O_3H^+}$ calcd 365.2799, found 365.2790.

Synthesis of **4da** (1S*,2R*)-N-(2-Methoxybenzyl)-2-nitro-1,3-diphenylpropan-1-amine from **6**. A solution of *n*-BuLi (2.5 M in hexanes, 0.13 mL, 0.33 mmol) was added to a solution of nitroalkane **6** (50 mg, 0.33 mmol 1.4 mmol) in THF (5 mL) over 10 min at −78 °C under N$_2$(g) and the mixture stirred for 10 min. A solution of imine **3a** (54.1 mg, 0.24 mmol) in THF (10 mL) was added and the mixture stirred for 10 min. AcOH (33 μL, 0.56 mmol) was added and the mixture stirred for a further 20 min before being warmed to rt over 30 min. The mixture was partitioned between saturated aqueous NaHCO$_3$ (5 mL) and Et$_2$O (10 mL) and the aqueous phase further extracted with Et$_2$O (10 mL). The combined organic phases were dried (MgSO$_4$), and the volatile material was removed in vacuo to leave crude β-nitroamine **4da** (242 mg, 93% conv., >20:1 dr) as a yellow oil: IR υ_{max} 3068, 1555, 1261 cm^{-1}; ^{1}H NMR^{anti} δ 3.19 (1H, dd, *J* = 10.8, 3.6), 3.23 (1H, m), 3.47 (1H, d, *J* = 13.3), 3.70 (3H, s), 3.73 (1H, d, *J* = 13.2), 4.06 (1H, d, *J* = 6.1), 4.79 (1H, ddd, *J* = 10.2, 6.1, 4.3), 6.50−7.20 (14H, m); ^{1}H NMR^{syn} δ 2.72 (1H, dd, *J* = 14.6, 3.4), 3.05 (1H, dd, *J* = 14.6, 11.2), 3.78 (3H, s), 4.09 (1H, d, *J* = 9.2), 4.94 (1H, m) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 35.1 (CH$_2$), 47.7 (CH$_2$), 55.2 (CH$_3$), 64.4 (CH), 94.8 (CH), 110−130 (14C, CH), 130−160 (4C, C); ^{13}C NMR^{syn} δ 37.3 (CH$_2$), 47.4 (CH$_2$), 55.2 (CH$_3$), 59.9 (CH), 95.5 (CH) (the remaing signals could not be distinguished); MS (EI+) *m*/*z* 377 (100%, MH$^+$), 319 (22%); HRMS $\mathrm{C_{23}H_{24}N_2O_3H^+}$ calcd 377.1865, found 377.1852.

4dd _N-[(1S*,2R*)-2-Nitro-1,3-diphenylpropyl]prop-2-en-1-amine (Table 2)._ Nitroalkene **1d** (50 mg, 0.33 mmol) afforded crude β-nitroamine **4dd** (166 mg, 60% conv., 90:10 dr) as a yellow oil by the general procedure for Table 1: IR υ_{max} 3300, 3009, 1555 cm^{-1}; ^{1}H NMR^{anti} δ 1.69 (1H, b), 3.07 (1H, ddt, *J* = 14.1, 6.6, 1.0), 3.22 (1H, ddt, *J* = 14.1, 5.4, 1.0), 3.32 (1H, dd, *J* = 14.8, 10.2), 3.39 (1H, dd, *J* = 14.8, 3.8), 4.20 (1H, d, *J* = 6.6), 4.91 (1H, ddd, *J* = 10.2, 6.6, 3.9), 5.16 (2H, m), 5.86 (1H, dddd, *J* = 16.9, 12.0, 6.5, 5.4), 7.00−7.50 (10H, m); ^{1}H NMR^{syn} δ 2.66 (1H, dd, *J* = 14.4, 3.4), 3.09 (3H, m), 4.07 (1H, d, *J* = 9.4), 4.82 (1H, ddd, *J* = 11.1, 9.5, 3.4), 5.04 (2H, m), 7.71 (1H, dddd, *J* = 17.0, 15.7, 6.6, 5.4) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 35.8 (CH$_2$), 50.0 (CH), 64.2 (CH$_2$), 94.5(CH), 116.8 (CH$_2$), 126−129 (10 × CH), 136.1 (CH), 140.2 (2C); ^{13}C NMR^{syn} (CDCl$_3$) δ 37.5 (CH$_2$), 49.5 (CH$_2$), 64.4 (CH), 95.2 (CH); MS (EI+) *m*/*z* 297 (100%, MH$^+$); HRMS $\mathrm{C_{18}H_{20}N_2O_2H^+}$ calcd 297.1598, found 297.1598.

4be (Table 2) was characterized as β-nitroacetamides **5be** (Table 3).

4de (Table 2) was characterized as β-nitroacetamides **5de** (Table 3).

General Procedure for the Synthesis of β-Nitroacetamides 5 (Table 1). To a stirred solution of crude β-nitroamine (1.0 mmol) in CH$_2$Cl$_2$ (5 mL) at 0 °C was added DIPEA (1.1 mmol), followed by TFAA (1.1 mmol), and the solution was returned to rt over 10 min. A solution of 2 M HCl (10 mL) was then added and the organic phase separated. The organic phase was washed with brine and dried (MgSO$_4$), and the solvents were removed in vacuo to afford crude material that was purified by column chromatography to give β-nitroacetamides **5**.

5aa _2,2,2-Trifluoro-N-(2-methoxybenzyl)-N-[(1S*,2R*)-2-nitro-1-phenyloctyl]acetamide._ Crude nitroamine **4aa** (859 mg) gave after purification by column chromatography (5% EtOAc/hexanes) **5aa** (494 mg, 72% over two steps) as colorless crystals: mp 68−70 °C; R_f = 0.38 (10% EtOAc/hexanes); IR υ_{max} 2929, 1689, 1553, 1247 (C−O), 1140 cm^{-1}; ^{1}H NMR^{anti} δ 0.87 (3H, t, *J* = 7.2), 1.16 (8H, m), 1.35, (1H, m), 1.58 (1H, m), 3.87 (3H, s), 4.65 (1H, d, *J* = 16.0), 4.69 (1H, d, *J* = 16.0), 4.84 (1H, d, *J* = 10.8), 5.82 (1H, t, *J* = 10.8), 6.94 (1H, d, *J* = 8.4), 6.99 (1H, t, *J* = 7.4), 7.24 (4H, m), 7.36 (3H, m); ^{1}H NMR^{rotamer} δ 1.79 (1H, m), 4.00 (3H, s), 4.49 (1H, d, *J* = 15.6), 4.75 (1H, d, *J* = 15.2), 5.27 (1H, t, *J* = 10.8), 5.58 (1H, d, *J* = 10.8) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 14.0 (CH$_3$), 22.5 (CH$_2$), 25.5 (CH$_2$), 28.3 (CH$_2$), 31.3 (CH$_2$), 31.4 (CH$_2$), 46.8 (CH$_2$), 55.3 (OCH$_3$), 62.1 (CH), 89.5 (CH), 111.1 (CH), 116.5

(q, J = 287.1, $\mathrm{CF_3}$), 121.1 (CH), 121.8 (CH), 128.8 (CH), 129.1 (CH), 129.1 (CH), 129.2 (CH), 129.6 (CH), 129.7 (CH), 130.7 (CH), 130.9 (CH), 134.7 (CH), 157.7 (q, J = 35.8, C=O), 157.8 (C); ^{13}C NMR$^{\mathrm{rotamer}}$ δ 14.0 ($\mathrm{CH_3}$), 26.0 ($\mathrm{CH_2}$), 28.3 ($\mathrm{CH_2}$), 31.8 ($\mathrm{CH_2}$), 39.6 ($\mathrm{CH_2}$), 55.6 ($\mathrm{CH_3}$), 62.1 (CH), 87.6 (CH), 110.9 (CH), 121.5 (CH), 124.7 (C), 128.2 (CH), 129.6 (CH), 131.0 (CH), 133.0 (C), 156.2 (C) (the remaining signals could not be distinguished); ^{19}F NMR δ −68.5 (3F, s, CF_3); MS (EI+) m/z 489 (100%, $\mathrm{MNa^+}$), 484 (2%, $\mathrm{MNH_4^+}$), 420 (14%); HRMS $\mathrm{C_{24}H_{29}F_3N_2O_4Na^+}$ calcd 489.1972, found 489.1994. Anal. Calcd for $\mathrm{C_{24}H_{29}F_3N_2O_4}$: C, 61.79; H, 6.27; N, 6.01. Found: C, 62.15; H, 6.37; N, 5.90.

5ba _N-[(1S*,2R*)-3-Cyclohexyl-2-nitro-1-phenylpropyl]-2,2,2-trifluoro-N-(2-methoxybenzyl)acetamide._ Crude nitroamine **4ba** (999 mg) gave after purification by column chromatography (5% EtOAc/hexanes) **5ba** (591 mg, 75% over two steps) as colorless crystals: mp 55−57 °C; R_f = 0.21 (5% EtOAc/hexanes); IR $\upsilon_{\max}$ 2928, 1690, 1554, 1152 cm^{-1}; ^{1}H NMR^{anti} δ 0.84 (2H, m), 1.05 (1H, m), 1.16 (3H, m), 1.34 (3H, m), 1.62 (2H, m), 1.67 (1H, m), 1.93 (1H, bd, J = 12.4), 3.89 (3H, s), 4.66 (1H, d, J = 15.2), 4.71 (1H, d, J = 15.2), 4.75 (1H, d, J = 10.8), 6.05 (1H, td, J = 10.8, 3.2), 6.95 (1H, d, J = 8.0), 7.00 (1H, td, J = 10.0, 0.8), 7.27 (5H, m), 7.36 (2H, m), 7.40 (1H, td, J = 8.4, 1.6); ^{1}H NMR$^{\mathrm{rotamer}}$ δ 3.98 (3H, s), 4.63 (1H, m), 5.46 (1H, m), 5.58 (1H, d, J = 10.4) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 25.6 (*Cy*), 26.6 (*Cy*), 26.2 (*Cy*), 31.3 (*Cy*), 33.9 (*Cy*), 34.0 (*Cy*), 38.8 ($\mathrm{CH_2}$), 47.1 ($\mathrm{CH_2}$), 55.3 ($\mathrm{CH_3}$), 65.2 (CH), 87.1 (CH), 111.0 (CH), 116.4 (1C, q, J = 286.0, $\mathrm{CF_3}$), 121.0 (CH), 121.8 (C), 128.7 (CH), 128.7 (CH), 129.1 (CH), 129.1 (CH), 129.2 (CH *r*), 130.4 (CH), 130.7 (CH), 134.7 (C), 1575 (1C, q, J = 36.0, C=O), 157.8 (C); ^{13}C NMR$^{\mathrm{rotamer}}$ δ 55.6 ($\mathrm{CH_3}$), 62.5 (CH), 85.0 (CH) (the remaining signals could not be distinguished); ^{19}F NMR δ −68.5 (3F, s, CF_3); MS (EI+) m/z 501 (100%, $\mathrm{MNa^+}$), 432 (16%), 496 (5%, $\mathrm{MNH_4^+}$); HRMS $\mathrm{C_{25}H_{29}F_3N_2O_4Na^+}$ calcd 501.1972, found 501.1947. Anal. Calcd for $\mathrm{C_{25}H_{29}F_3N_2O_4}$: C, 62.75; H, 6.11; N, 5.85. Found: C, 62.52; H, 6.15; N, 5.73.

5ca _N-[(1S*,2R*)-4,4-Dimethyl-2-nitro-1-phenylpentyl]-2,2,2-trifluoro-N-(2-methoxybenzyl)acetamide._ Crude nitroamine **4ca** (881 mg) gave after purification by column chromatography (10% EtOAc/hexanes) **5ca** (325 mg, 60% over two steps) as a colorless oil: R_f = 0.31 (10% EtOAc/hexanes); IR $\upsilon_{\max}$ 2963, 1691, 1556, 1152 cm^{-1}; ^{1}H NMR^{anti} δ 0.85 (9H, s), 1.44 (1H, dd, J = 15.0, 2.0), 1.50 (1H, dd, J = 15.5, 10.0), 3.87 (3H, s), 4.58 (1H, d, J = 11.0), 4.67 (1H, d, J = 15.0), 4.71 (1H, d, J = 15.5), 6.10 (1H, td, J = 10.5, 2.0), 6.95 (1H, d, J = 8.0), 7.00 (1H, td, J = 7.5, 0.5), 7.25 (5H, m), 7.36 (2H, dd, J = 8.5, 1.5), 7.40 (1H, td, J = 8.0, 2.0); ^{1}H NMR$^{\mathrm{rotamer}}$ δ 0.70 (9H, s), 3.97 (3H, s), 5.43 (1H, t, J = 11.5), 5.52 (1H, d, J = 10.5) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 29.0 [$\mathrm{(CH_3)_3}$], 30.3 (C), 43.6 ($\mathrm{CH_2}$), 47.4 ($\mathrm{CH_2}$), 55.3 ($\mathrm{CH_3}$), 66.3 (CH), 86.6 (CH), 11.0 (CH), 118.7 (1C, q, J = 286.3, $\mathrm{CF_3}$), 121.1 (CH), 123.8 (C), 128.7 (CH), 128.8 (CH), 129.1 (CH), 129.3 (CH), 129.8 (CH), 130.7 (CH), 131.3 (CH), 134.3 (C), 157.4 (1C, q, J = 35.0, C=O), 157.9 (C); ^{13}C NMR$^{\mathrm{rotamer}}$ δ 28.6 (C), 29.8 [$\mathrm{(CH_3)_3}$], 55.6 ($\mathrm{CH_3}$), 63.4 (CH), 84.3 (CH) (the remaining signals could not be distinguished); ^{19}F NMR δ −68.5 (3F, s, $\mathrm{CF_3}$); MS (EI+) m/z 475 (100%, $\mathrm{MNa^+}$), 470 (3%, $\mathrm{MNH_4^+}$); HRMS $\mathrm{C_{23}H_{27}F_3N_2O_4Na^+}$ calcd 475.1815, found 475.1819. Anal. Calcd for $\mathrm{C_{23}H_{27}F_3N_2O_4}$: C, 61.05; H, 6.01; N, 6.19. Found: C, 61.32; H, 6.18; N, 6.38.

5ea _2,2,2-Trifluoro-N-(2-methoxybenzyl)-N-[(1S*,2R*)-2-nitro-1,4-diphenylbutyl]acetamide._ Crude nitroamine **4ea** (460 mg) gave after purification by column chromatography (5% EtOAc/hexanes) **5ea** (254 mg, 65% over two steps) as a yellow oil: R_f = 0.42 (10% EtOAc/hexanes); IR $\upsilon_{\max}$ 2929, 1690, 1554, 1152 cm^{-1}; ^{1}H NMR^{anti} δ 1.64 (1H, dtd, J = 16.0, 11.0, 5.0), 1.93 (1H, dddd, J = 17.0, 11.5, 6.0, 2.5), 2.45 (1H, ddd, J = 14.0, 11.5, 5.5), 2.54 (1H, ddd, J = 14.0, 11.5, 5.5), 3.70 (3H, s), 4.58 (1H, d, J = 15.0), 4.70 (1H, d, J = 15.0), 4.89 (1H, d, J = 10.5), 5.89 (1H, td, J = 11.0, 2.5), 6.84 (1H, d, J = 8.5), 6.93 (1H, t, J = 7.5), 7.07 (2H, d, J = 7.5), 7.18 (1H, d, J = 7.5), 7.40 (9H, m); ^{1}H NMR$^{\mathrm{rotamer}}$ δ 1.79 (1H, m), 2.09 (1H, m), 4.00 (3H, s), 4.49 (1H, d, J = 15.0), 4.81 (1H, d, J = 15.0), 5.41 (1H, t, J = 11.0), 5.62 (1H, d, J = 11.0) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 31.8 ($\mathrm{CH_2}$), 33.1 ($\mathrm{CH_2}$), 47.12 ($\mathrm{CH_2}$), 55.1 (CH), 64.6 ($\mathrm{CH_3}$), 89.1 (CH), 11.0 (CH), 116.4 (1C, q, J = 287.5, $\mathrm{CF_3}$), 121.0 (CH), 121.7 (*Ar-C*), 126.5 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.6 (CH), 128.9 (CH), 128.9 (CH), 129.0 (CH), 129.0 (CH), 129.8 (CH), 130.8 (CH), 131.2 (C), 134.5 (C), 139.7 (CH), 157.8 (C), 157.8 (1C, q, J = 35.0, C=O); ^{13}C NMR$^{\mathrm{rotamer}}$ δ 32.3 ($\mathrm{CH_2}$), 33.5 ($\mathrm{CH_2}$), 39.7 ($\mathrm{CH_2}$), 55.6 ($\mathrm{CH_3}$), 61.9 (CH), 87.2 (CH) (the remaining signals could not be distinguished); ^{19}F NMR δ −68.5 (3F, s, CF_3); MS (EI+) m/z 509 (100%, $\mathrm{MNa^+}$), 440 (10%), 504 (3%, $\mathrm{MNH_4^+}$); HRMS $\mathrm{C_{26}H_{25}F_3N_2O_4Na^+}$ calcd 509.1659, found 509.1646. Anal. Calcd for $\mathrm{C_{26}H_{25}F_3N_2O_4}$: C, 64.19; H, 5.18; N, 5.76. Found: C, 63.94; H, 5.20; N, 5.45.

5ga _2,2,2-Trifluoro-N-(2-methoxybenzyl)-N-{(1S*,2R*)-2-nitro-1-phenyl-3-[4-(trifluoromethyl)phenyl]propyl}acetamide._ Crude β-nitroamine **4ga** (189 mg) gave after purification by column chromatography (33% DCM/hexanes) **5ga** (63 mg, 47% over two steps) as a yellow oil: R_f = 0.50 (50% DCM/hexanes); IR $\upsilon_{\max}$ 2923, 1692, 1558 cm^{-1}; ^{1}H NMR^{anti} δ 2.51 (1H, dd, J = 14.2, 11.7), 3.08 (1H, dd, J = 14.2, 2.0), 3.93 (3H, s), 4.73 (1H, d, J = 15.1), 4.76 (1H, d, J = 15.2), 4.94 (1H, d, J = 10.7), 6.10 (1H, apt. td, J = 11.2, 2.7), 7.04 (1H, d, J = 8.4), 7.07 (1H, td, J = 7.5, 0.8), 7.15 (2H, d, J = 8.1), 7.33 (4H, m), 7.41 (2H, m), 7.48 (1H, td, J = 7.9, 1.6), 7.52 (2H, d, J = 8.1); ^{1}H NMR$^{\mathrm{rotamer}}$ δ 2.95 (1H, d, J = 14.4), 3.15 (1H, d, J = 14.0), 3.97 (3H, s), 4.68 (1H, d, J = 15.3), 4.89 (1H, d, J = 15.4), 5.44 (1H, t, J = 9.1), 5.75 (1H, d, J = 10.9), 6.45 (1H, d, J = 8.0) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 37.4 ($\mathrm{CH_2}$), 46.9 ($\mathrm{CH_2}$), 55.6 ($\mathrm{CH_3}$), 65.0 (CH), 91.2 (CH), 11.3 (2 × CH), 116.5 (1C, q, J = 286.7, $\mathrm{CF_3}$), 121.3 (2 × CH), 122.2 (C), 124.0 (1C, q, J = 127.0, $\mathrm{CF_3}$), 125.8 (1C, q, J = 3.3), 128.9 (2 × CH), 129.1 (2 × CH), 129.6 (CH), 129.9 (1C, q, J = 32.5, $\mathrm{CCF_3}$), 131.0 (CH), 131.2 (CH), 134.3 (C), 138.9 (C), 157.9 (C), 158.1 (1C, q, J = 35.8, C=O); ^{13}C NMR$^{\mathrm{rotamer}}$ δ 37.8 ($\mathrm{CH_2}$), 55.8 ($\mathrm{CH_3}$), 62.6 (CH), 88.5 (CH), 111.5 (CH), 122.1 (CH), 128.1 (CH), 128.6 (CH), 130.0 (CH), 132.4 (CH), 138.4 (CH), 156.7 (C) (the remaining signals could not be distinguished); ^{19}F NMR δ −63.1 (3F, s, CF_3), −68.4 (3F, s, CF_3); MS (EI+) m/z 563 (100%, $\mathrm{MNa^+}$), 427 (2%); HRMS $\mathrm{C_{26}H_{22}F_6N_2O_4H^+}$ calcd 541.1557, found 541.1555.

5ia _2,2,2-Trifluoro-N-[(1S*,2R*)-3-(furan-2-yl)-2-nitro-1-phenylpropyl]-N-(2-methoxybenzyl)acetamide._ Crude nitroamine **4ia** (799 mg) gave after purification by column chromatography (10% $\mathrm{Et_2O}$/hexanes) **5ia** (104 mg, 30% over two steps) as colorless crystals: mp 94−95 °C; R_f = 0.51 (20% $\mathrm{Et_2O}$/hexanes); IR $\upsilon_{\max}$ 3042, 2963, 1963, 1559, 1151 cm^{-1}; ^{1}H NMR^{anti} δ 2.77 (1H, dd, J = 15.6, 10.8), 3.07 (1H, dd, J = 15.6, 2.8), 3.93 (3H, s), 4.67 (1H, d, J = 15.2), 4.73 (1H, d, J = 15.2), 4.99 (1H, d, J = 11.2), 6.04 (1H, d, J = 3.2), 6.09 (1H, td, J = 10.8, 3.2), 6.26 (1H, dd, J = 2.8, 1.6), 6.97 (1H, d, J = 8.0), 7.02 (1H, td, J = 7.6, 0.8), 7.23 (1H, dd, J = 7.2, 0.8), 7.25−7.38 (5H, m), 7.42 (1H, td, J = 7.8, 1.6); ^{1}H NMR$^{\mathrm{rotamer}}$ δ 2.76 (1H, dd, J = 15.6, 11.2), 3.06 (1H, dd, J = 15.6, 2.8), 3.88 (3H, s), 4.54 (1H, d, J = 17.2), 4.79 (1H, d, J = 17.6), 5.72 (2H, m), 6.21 (1H, s) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 30.3 ($\mathrm{CH_2}$), 46.9 ($\mathrm{CH_2}$), 55.3 ($\mathrm{CH_3}$), 64.3 (CH), 88.1 (CH), 108.1 (CH), 110.5 (CH), 111.1 (CH), 116.4 (1C, q, J = 287.0, $\mathrm{CF_3}$), 121.1 (CH), 121.6 (C), 129.1 (CH), 129.1 (CH), 129.3 (CH), 129.4 (CH), 129.8 (CH), 130.8 (CH), 130.9 (CH), 134.2 (C), 142.5 (CH), 148.3 (C), 157.8 (C), 158.0 (1C, q, J = 36.0, C=O); ^{19}F NMR δ −68.44 (3F, s, CF_3); MS (EI+) m/z 485 (100%, $\mathrm{MNa^+}$), 517 (17%); HRMS $\mathrm{C_{23}H_{21}F_3N_2O_5Na^+}$ calcd 485.1295, found 485.1300. Anal. Calcd for $\mathrm{C_{23}H_{21}F_3N_2O_5}$: C, 59.74; H, 4.58; N, 6.06. Found: C, 59.58; H, 4.45; N, 6.01.

5ab _2,2,2-Trifluoro-N-[(1R*,2R*)-1-(furan-2-yl)-2-nitrooctyl]-N-(2-methoxybenzyl)acetamide._ Crude nitroamine **4ab** (1.12 g) gave after purification by column chromatography (30% DCM/hexanes) **5ab** (494 mg, 55%) as a yellow oil: R_f = 0.32 (30% DCM/hexanes); IR $\upsilon_{\max}$ 3100, 2931, 1693, 1557, 1250, 1155 cm^{-1}; ^{1}H NMR^{anti} δ 0.88 (3H, t, J = 7.0), 0.97 (1H, hex, J = 7.0), 1.20−1.33 (8H, m), 1.54 (1H, m), 3.88 (3H, s), 4.72 (1H, d, J = 15.5), 4.76 (1H, d, J = 15.5), 5.38 (1H, s, J = 10.5), 5.46 (1H, apt. td, J = 10.5, 2.0), 6.26 (1H, dd, J = 3.0, 1.5), 6.37 (1H, d, J = 3.0), 6.94 (1H, d, J = 8.0), 6.98 (1H, t, J = 8.0), 7.18 (1H, d, J = 7.5), 7.37 (2H, m); ^{1}H NMR^{syn} δ 0.83 (3H, t, J = 7.0), 1.11−1.28 (9H, m), 1.75 (1H, m), 3.73 (3H, s), 4.47 (1H, d, J = 16.0), 4.86 (1H, d, J = 16.0), 5.09 (1H, d, J = 10.8), 5.74 (1H, apt. td,

J = 10.8, 2.8), 6.23 (1H, dd, J = 3.2, 2.0), 6.34 (1H, d, J = 3.2), 6.80 (1H, d, J = 8.4), 6.85 (1H, t, J = 7.4), 6.93 (1H, d, J = 7.1), 7.08 (1H, d, J = 0.8), 7.27 (1H, td, J = 7.1); ^{1}H NMR$^{\text{rotamer}}$ δ 0.69 (1H, m), 0.85 (3H, t, J = 7.5), 1.05−1.40 (8H, m), 1.76 (1H, qd, J = 10.5, 4.5), 3.95 (3H, s), 4.52 (1H, d, J = 15.5), 4.77 (1H, d, J = 15.5), 5.13 (1H, t, J = 10.8), 5.62 (1H, d, J = 11.0), 6.34 (1H, d, J = 3.0), 6.90 (1H, d, J = 8.1), 7.27 (1H, m), 7.31 (1H, d, J = 7.5) (the remaining signals could not be distinguished); ^{13}C NMR^{anti} δ 14.0 (CH_3), 22.4 (CH_2), 25.4 (CH_2), 28.4 (CH_2), 30.6 (CH_2), 31.3 (CH_2), 47.1 (CH_2), 55.3 (CH_3), 57.1 (CH), 88.0 (CH), 110.4 (CH), 110.5 (CH), 110.7 (CH), 116.3 (1C, q, J = 286.0, CF_3), 120.9 (CH), 121.9 (C), 130.4 (CH), 130.7 (CH), 142.8 (CH), 147.6 (C), 157.4 (1C, q, J = 36.0, C═O), 157.8 (C); ^{13}C NMR$^{\text{rotamer}}$ δ 25.7 (CH_2), 28.2 (CH_2), 40.4 (CH_2), 55.4 (CH_3), 56.8 (CH), 87.4 (CH), 121.4 (CH), 124.3 (C), 129.5 (CH), 143.7 (C), 156.3 (C) (the remaining signals could not be distinguished); ^{19}F NMR δ −68.5 (3F, s, CF_3); MS (EI+) m/z 479 (100%, MNa^+), 410 (2.8%); HRMS $C_{22}H_{27}F_3N_2O_5Na^+$ calcd 479.1764, found 479.1769.

***5ac** 2,2,2-Trifluoro-N-(2-methoxybenzyl)-N-[(6S*,7R*)-7-nitrotridecan-6-yl]acetamide.* Crude nitroamine **4ac** (739 mg) gave after purification by column chromatography (4% Et_2O/hexanes) **5ac** (265 mg, 68%) as a yellow oil: R_f = 0.38 (4% Et_2O/hexanes); IR υ_{max} 2841, 1783, 1591 cm^{-1}; ^{1}H NMR^{anti} δ 0.67 (2H, m), 0.77 (3H, t, J = 7.2), 0.87 (3H, t, J = 6.8), 0.98 (2H, m), 1.25 (8H, m), 1.46 (1H, m), 1.67 (1H, m), 1.79 (2H, m), 3.61 (1H, m), 3.84 (3H, s), 4.14 (1H, d, J = 14.8), 4.82 (1H, d, J = 14.8), 5.27 (1H, td, J = 10.6, 2.8), 6.90 (1H, d, J = 8.0), 6.99 (1H, td, J = 7.6, 1.2), 7.23 (1H, dd, J = 7.6, 1.6), 7.37 (1H, td, J = 8.0, 1.5); ^{13}C NMR^{anti} δ 13.9 (CH_3), 14.0 (CH_3), 22.4 (CH_2), 25.6 (CH_2), 29.7 (CH_2), 29.9 (CH_2), 31.0 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 48.5 (CH_2), 55.1 (CH_3), 62.5 (CH), 88.1 (CH), 110.7 (CH), 116.2 (1C, q, J = 287.0, CF_3), 121.1 (CH), 122.1 (CH), 130.5 (CH), 131.7 (C), 157.9 (1C, q, J = 36.0, C═O), 158.1 (C); ^{19}F NMR δ −62.9 (3F, s, CF_3); MS (EI+) m/z 483 (100%, MNa^+), 478 (7%, MNH_4^+); HRMS $C_{23}H_{35}F_3N_2O_4Na^+$ calcd 483.2441, found 483.2455. Anal. Calcd for $C_{23}H_{35}F_3N_2O_4$: C, 59.98; H, 7.66; N, 6.08. Found: C, 59.93; H, 7.84; N, 5.87.

General Procedure for the Reductive Nitro-Mannich Reaction Using PMP-Imine 3e To Give β-Nitroacetamides 5 (Table 3). To a solution of nitroalkene **1** (1 mmol) in THF (6 mL) was added Superhydride (1.10 mmol, 1 M in THF). The suspension was then stirred for 30 min at rt before being cooled to −78 °C over 30 min. A solution of imine **3e** (1.1 mmol) in THF (6 mL) was added via cannula and the mixture stirred at −78 °C for 10 min. A solution of TFA (2.5 mmol) in THF (2 mL) was added by cannula and the reaction mixture stirred for 1 h at −78 °C. The reaction was then quenched with saturated brine (10 mL) and the mixture diluted with Et_2O (20 mL). The organic phase was washed with saturated aqueous NaCl (10 mL) and dried ($MgSO_4$). Solvents were removed in vacuo to afford crude β-nitroamines **4**. Crude β-nitroamine **4** (1.0 mmol) was then dissolved in DCM (5 mL) and cooled to 0 °C. To this solution was added trifluoroacetic anhydride (5.0 mmol), followed by pyridine (5.0 mmol), and the solution was warmed to rt over 10 min. The reaction was quenched with 2 M HCl (10 mL) and the mixture extracted with DCM (2 × 5 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (10 mL) and saturated brine (10 mL). The organic phase was then dried ($MgSO_4$), and the solvents were removed in vacuo to afford crude β-nitrotrifluoroacetamides **5** that were then purified by column chromatography.

***5ae** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-2-nitro-1-phenyloctyl]acetamide.* Nitroalkene **1a** (72 mg, 0.50 mmol) afforded after purification by column chromatography (7.5% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5ae** (184 mg, 0.41 mmol, 82% yield) as a yellow oil: IR υ_{max} 2931, 1698, 1554, 1510, 1254, 1206, 1180, 1152 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (3H, t, J = 6.6), 1.30−1.50 (8H, m), 2.14 (1H, m), 2.26 (1H, m), 3.80 (3H, s), 5.30 (1H, br s), 6.03 (1H, br s), 6.27 (1H, br s), 6.66 (1H, d, J = 9.0), 6.88 (1H, dd, J = 9.0, 3.0), 6.92 (1H, d, J = 8.4), 7.07 (2H, d, J = 7.8), 7.24 (2H, d, J = 7.8), 7.31 (1H, t, J = 7.2); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.51 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_2), 25.9 (CH_2), 28.6 (CH_2), 31.6 (CH_2), 32.0 (CH_2), 55.6 (CH_3), 64.3 (CH), 88.0 (CH), 114.0 (CH), 114.3 (CH), 116.3 (1C, q, J = 289.3, CF_3), 127.7 (CN), 128.8 (CH), 129.2 (CH), 129.7 (CH), 130.1 (CH), 132.4 (CH), 133.5 (C), 158.0 (1C, q, J = 34.4, C═O), 160.5 (C); MS m/z 452 (32%, M), 219 (100%, MH^+ − $C_{14}H_{20}NO_2$); HRMS $C_{23}H_{27}F_3N_2O_4$ calcd 452.19174, found 452.19160.

***5be** N-[(1S*,2R*)-3-Cyclohexyl-2-nitro-1-phenylpropyl]-2,2,2-trifluoro-N-(4-methoxyphenyl)acetamide.* Nitroalkene **1b** (78 mg, 0.50 mmol) afforded after purification by column chromatography (4% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5be** (405 mg, 0.87 mmol, 87% yield) as a yellow solid: mp 164−167 °C; IR υ_{max} 2927, 1701, 1555, 1256, 1209, 1156 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.01 (1H, qd, J = 12.0, 3.0), 1.08 (1H, qd, J = 12.0, 3.0), 1.25 (4H, m), 1.70 (3H, m), 1.80 (1H, br d, J = 13.2), 1.90 (1H, m), 2.09 (1H, br d, J = 12.0), 2.28 (1H, m), 3.82 (3H, s), 5.45 (1H, br s), 6.03 (1H, br s), 6.24 (1H, br s), 6.66 (1H, br d, J = 10.2), 6.89 (1H, dd, J = 9.0, 3.0), 6.96 (1H, br d, J = 7.8), 7.06 (2H, d, J = 7.8), 7.24 (2H, t, J = 7.8), 7.31 (1H, t, J = 7.8); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.6 (3F, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.0 (CH_2), 26.2 (CH_2), 26.3 (CH_2), 31.9 (CH_2), 34.1 (CH_2), 34.5 (CH), 39.5 (CH_2), 55.6 (CH_3), 64.3 (CH), 85.6 (CH), 113.9 (CH), 114.3 (CH), 116.3 (1C, q, J = 288.7, CF_3), 127.6 (br s, CN), 128.8 (CH), 129.3 (CH), 129.7 (CH), 130.2 (CH), 132.5 (br s, CH), 133.4 (C), 158.0 (1C, q, J = 35.9, C═O), 160.47 (C); MS (EI) m/z 464 (38%, M), 219 (78%, MH^+ − $C_{15}H_{20}NO_2$); HRMS $C_{24}H_{27}F_3N_2O_4$ calcd 464.19173, found 464.19051, Anal. Calcd for $C_{24}H_{27}F_3N_2O_4$: C, 62.06; H, 5.86; N, 6.03. Found: C, 61.89; H, 5.84; N, 5.97.

***5de** 2,2,2-Trifluoro-N-[(1S*,2R*)-2-nitro-1,3-diphenylpropyl]-N-(4-methoxyphenyl)acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5de** (188 mg, 0.41 mmol, 82% yield) as a yellow solid: mp 128−131 °C; IR υ_{max} 2936, 1699, 1557, 1511, 1254, 1209, 1169 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.47 (1H, dd, J = 14.4, 10.8), 3.56 (1H, dd, J = 14.4, 3.0), 3.83 (3H, s), 5.61 (1H, br s), 6.06 (1H, br s), 6.39 (1H, br s), 6.72 (1H, dd, J = 8.4, 2.4), 6.93 (1H, dd, J = 8.4, 2.4), 7.04 (1H, br d, J = 7.8), 7.12 (2H, d, J = 7.2), 7.22−7.27 (3H, m), 7.29−7.38 (5H, m); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.8 (3F, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 38.4 (CH_2), 55.7 (CH_3), 65.2 (CH), 89.8 (CH), 114.1 (CH), 114.5 (CH), 116.3 (1C, q, J = 286.5, CF_3), 128.0 (2C, CH, C), 128.7 (CH), 128.9 (CH), 129.2 (CH), 129.4 (CH), 129.9 (CH), 130.2 (CH), 132.2 (CH), 133.2 (C), 134.6 (C), 158.3 (1C, q, J = 36.0, C═O), 160.1 (C); MS (EI) m/z 458 (17%, M), 219 (96%, MH^+ − $C_{15}H_{14}NO_2$); HRMS $C_{24}H_{21}F_3N_2O_4$ calcd 458.14479, found 458.14563. Anal. Calcd for $C_{24}H_{21}F_3N_2O_4$: C, 62.88; H, 4.62; N, 6.11. Found: C, 62.47; H, 4.49; N, 6.06.

***5fe** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-3-(4-methoxyphenyl)-2-nitro-1-phenylpropyl]acetamide.* Nitroalkene **1f** (80 mg, 0.50 mmol) afforded after purification by column chromatography (10% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5fe** (211 mg, 0.432 mmol, 86% yield) as a brown oil: IR υ_{max} 2935, 2840, 1697, 1556, 1510, 1301, 1250, 1207, 1179, 1155 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.43 (1H, dd, J = 14.4, 10.8), 3.53 (1H, dd, J = 14.4, 3.0), 3.77 (3H, s), 3.80 (3H, s), 5.59 (1H, br s), 6.09 (1H, br s), 6.40 (1H, br s), 6.72 (1H, dd, J = 9.0, 2.4), 6.88 (2H, dm, J = 8.4), 6.93 (1H, dd, J = 8.4, 3.0), 7.08 (1H, d, J = 7.8), 7.13 (2H, d, J = 7.2), 7.16 (2H, dm, J = 9.0), 7.24 (2H, t, J = 7.8), 7.32 (1H, t, J = 7.8); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.6 (3F, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 37.6 (CH_2), 55.3 (CH_3), 55.6 (CH_3), 65.2 (CH), 90.0 (CH), 114.1 (CH), 114.6 (CH), 116.4 (1C, q, J = 288.7, CF_3), 126.5 (C), 128.0 (CN), 128.9 (CH), 129.4 (CH), 129.8 (CH), 130.2 (CH), 132.2 (CH), 133.3 (C), 158.1 (1C, q, J = 35.5, C═O), 159.3 (C), 160.6 (C); MS (EI) m/z 488 (46%, M); HRMS $C_{25}H_{23}F_3N_2O_5$ calcd 488.15536, found 488.15500.

***5je** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-3-(2-methoxyphenyl)-2-nitro-1-phenylpropyl]acetamide.* Nitroalkene **1j** (80 mg, 0.50 mmol) afforded after purification by column chromatography (10% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5je** (192 mg, 0.393 mmol, 79% yield) as a yellow solid: mp 146−150 °C; IR υ_{max} 2938, 1698, 1556, 1513, 1496, 1248, 1208, 1155 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.31 (1H, dd, J = 14.4, 12.0), 3.78 (1H, dd, J = 14.4, 3), 3.82 (3H, s), 4.00 (3H, s), 5.54 (1H, br t, J = 9.6), 6.08 (1H, br d, J = 7.2), 6.52 (1H br d, J = 8.4), 6.57 (1H, dd, J = 8.4, 2.4), 6.89 (1H, td, J = 7.8, 0.6), 6.93 (1H, d, J = 7.8), 6.96 (1H, dd, J = 8.4, 2.4), 6.99 (2H, d, J = 7.2), 7.03 (1H, dd, J = 7.8, 1.8), 7.19 (2H, t, J = 8.4), 7.26–7.30 (2H, m), 7.53 (1H, d, J = 7.2); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.42 (3F, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.2 (CH_2), 55.5 (CH_3), 55.6 (CH_3), 62.9 (CH), 87.1 (CH), 110.4 (CH), 113.6 (CH), 114.0 (CH), 116.4 (1C, q, J = 287.6, CF_3), 121.4 (CH), 122.7 (C), 127.0 (CN), 128.7 (CH), 129.4 (CH), 129.5 (CH), 129.6 (CH), 130.7 (CH), 131.2 (CH), 132.9 (C), 133.1 (CH), 157.1 (C), 158.1 (1C, q, J = 35.6, C═O), 160.4 (C); MS (EI) m/z 488 (5%, M); HRMS $C_{25}H_{23}F_3N_2O_5$ calcd 488.15535, found 488.15396. Anal. Calcd for $C_{25}H_{23}F_3N_2O_5$: C, 61.47; H, 4.75; N, 5.74. Found: C, 61.84; H, 4.75; N, 5.70.

5ge *2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-{(1S*,2R*)-2-nitro-1-phenyl-3-[4-(trifluoromethyl)phenyl]propyl}acetamide.* Nitroalkene **1g** (109 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5ge** (213 mg, 0.405 mmol, 81% yield) as a yellow oil: IR υ_{max} 2939, 1697, 1557, 1510, 1324, 1254, 1209, 1157, 1111 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.54 (1H, dd, J = 14.4, 11.4), 3.60 (1H, dd, J = 14.4, 3.0), 3.83 (3H, s), 5.69 (1H, br s), 5.95 (1H, br s), 6.48 (1H, br s), 6.75 (1H, dd, J = 8.4, 1.8), 6.92 (1H, dd, J = 8.4, 2.4), 7.00 (1H, d, J = 7.8), 7.13 (2H, d, J = 7.8), 7.26 (2H, t, J = 7.8), 7.34 (1H, t, J = 7.2), 7.37 (2H, d, J = 7.8), 7.61 (2H, d, J = 7.8); ^{19}F NMR (300 MHz, $CDCl_3$) δ −63.1 (3F, s, ArCF_3), −67.7 (3F, s, CF_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.0 (CH_2), 55.6 (CH_3), 66.0 (C), 89.6 (CH), 114.2 (CH), 114.7 (CH), 116.3 (1C, q, J = 289.0, F_3CC═O), 124.1 (1C, q, J = 271.8, F_3CAr), 126.2 (1C, q, J = 4.5, CH), 128.2 (br s, CN), 129.1 (CH), 129.2 (CH), 129.3 (CH), 130.0 (CH), 130.1 (CH), 130.4 (1C, q, J = 33.2, CH), 131.9 (CH), 133.0 (C), 138.6 (C), 158.3 (1C, q, J = 35.9, C═O), 160.6 (C); MS (EI) m/z 526 (7%, M), 261 (100%, M − $C_9H_8N_2O_4$); HRMS $C_{25}H_{20}F_6N_2O_4$ calcd 526.13218, found 526.13172. Anal. Calcd for $C_{25}H_{20}F_6N_2O_4$: C, 57.04; H, 3.83; N, 5.32. Found: C, 56.99; H, 3.75; N, 5.25.

5ie *2,2,2-Trifluoro-N-[(1S*,2R*)-3-(furan-2-yl)-2-nitro-1-phenylpropyl]-N-(4-methoxyphenyl)acetamide.* Nitroalkene **1i** (70 mg, 0.50 mmol) afforded after purification by column chromatography (10% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5ie** (176 mg, 0.393 mmol, 79% yield) as a yellow solid: mp 118–121 °C; IR υ_{max} 2939, 1699, 1558, 1511, 1255, 1208, 1182, 1156 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.57 (1H, dd, J = 16.2, 3.6), 3.63 (1H, dd, J = 16.2, 10.2), 3.83 (3H, s), 5.24, (1H, br t, J = 10.2), 6.17 (1H, d, J = 7.8), 6.21 (1H, d, J = 3.0), 6.32 (1H, br s), 6.34 (1H, dd, J = 3.0, 1.8), 6.64 (1H, dd, J = 9.0, 3.0), 6.97 (1H, dd, J = 8.4, 2.4), 7.04 (2H, d, J = 7.2), 7.15 (1H, dd, J = 8.4, 2.4), 7.24 (2H, t, J = 7.8), 7.33 (1H, m), 7.44 (1H, d, J = 1.2); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.5 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 31.2 (CH_2), 55.6 (CH_3), 62.8 (CH), 86.6 (CH), 108.9 (CH), 110.9 (CH), 114.1 (CH), 114.2 (CH), 116.3 (1C, q, J = 288.4, CF_3), 127.8 (CN), 128.8 (CH), 129.3 (CH), 129.9 (CH), 130.4 (CH), 132.7 (C), 132.9 (CH), 142.9 (CH), 148.2 (C), 158.3 (1C, q, J = 36.2, C═O), 160.6 (C); MS (CI) m/z 449 (3%, MH$^+$), 402 (88%, M − NO_2); HRMS $C_{22}H_{19}F_3N_2O_5H^+$ calcd 449.13243, found 449.13101. Anal. Calcd for $C_{22}H_{19}F_3N_2O_5$: C, 58.93; H, 4.27; N, 6.25. Found C, 58.74; H, 4.21; N, 6.20.

5ke *2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-{(1S*,2R*)-2-nitro-1-phenyl-3-[2-(trifluoromethyl)phenyl]propyl}acetamide.* Nitroalkene **1k** (109 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5ke** (209 mg, 0.397 mmol, 79% yield) as an off-white solid: mp 108–112 °C; IR υ_{max} 2939, 1698, 1558, 1511, 1315, 1209, 1180, 1110 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.65 (1H, dd, J = 14.4, 12.0), 3.82 (3H, s), 3.85 (1H, dd, J = 15.0, 3.0), 5.74 (1H, br s), 6.17 (1H, br s), 6.33 (1H, br s), 6.65 (1H, d, J = 6.6), 6.92 (1H, dd, J = 9.0, 3.0), 7.10 (2H, d, J = 7.2), 7.15 (1H, d, J = 7.8), 7.24 (2H, t, J = 7.8), 7.29–7.33 (2H, m), 7.42 (1H, t, J = 7.8), 7.51 (1H, t, J = 7.8), 7.71 (1H, d, J = 7.8); ^{19}F NMR (300 MHz, $CDCl_3$) δ −59.5 (3F, s, ArCF_3), −67.7 (3F, s, CF_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.1 (CH_2), 55.6 (CH_3), 65.8 (CH), 88.5 (CH), 113.9 (CH), 114.5 (CH), 116.3 (1C, q, J = 288.7, F_3CC═O), 124.6 (1C, q, J = 273.9, F_3CAr), 126.7 (1C, q, J = 5.7, CH), 128.3 (CH), 128.7 (1C, q, J = 30.0, C), 128.9 (CH), 129.8 (CH), 130.4 (CH), 131.8 (CH), 132.1 (CH), 132.7 (C), 132.8 (CH), 132.9 (C), 158.4 (1C, q, J = 36.2, C═O), 160.5 (C); MS (EI) m/z 526 (27%, M), 262 (100%, M − $C_9H_7N_2O_4$); HRMS $C_{25}H_{20}F_6N_2O_4$ calcd 526.13218, found 526.13351. Anal. Calcd for $C_{25}H_{20}F_6N_2O_4$: C, 57.04; H, 3.83; N, 5.32. Found: C, 56.75; H, 3.71; N, 5.20.

5le *2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-2-nitro-1-phenyl-3-(p-tolyl)propyl]acetamide.* Nitroalkene **1l** (82 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5le** (176 mg, 0.373 mmol, 75% yield) as a yellow solid: mp 92–96 °C; IR υ_{max} 2932, 1699, 1557, 1511, 1255, 1209, 1168 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.33 (3H, s), 3.43 (1H, dd, J = 14.4, 10.8), 3.51 (1H, dd, J = 14.4, 3.0), 3.83 (3H, s), 5.57 (1H, br s), 6.06 (1H, br s), 6.38 (1H, br s), 6.71 (1H, dd, J = 8.4, 2.4), 6.93 (1H, dd, J = 9.0, 3.0), 7.05 (1H, d, J = 8.4), 7.10–7.13 (4H, m), 7.15 (2H, d, J = 7.8), 7.25 (2H, t, J = 7.8), 7.33 (1H, m); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.6 (3F, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.2 (CH_3), 38.0 (CH_2), 55.6 (CH_3), 65.2 (CH), 89.8 (CH), 114.1 (CH), 114.5 (CH), 116.3 (1C, q, J = 289.0, CF_3), 128.0 (CN), 128.6 (CH), 128.9 (CH), 129.4 (CH), 129.7 (CH), 129.9 (CH), 130.2 (CH), 131.5 (C), 132.2 (CH), 133.2 (C), 137.7 (C), 158.1 (1C, q, J = 35.9, C═O), 160.5 (C); MS (EI) m/z 472 (3%, M), 219 (40%, MH$^+$ − $C_{16}H_{16}NO_2$); HRMS $C_{25}H_{23}F_3N_2O_4$ calcd 472.16044, found 472.16064. Anal. Calcd for $C_{25}H_{23}F_3N_2O_4$: C, 63.55; H, 4.91; N, 5.93. Found: C, 63.24; H, 4.92; N, 5.80.

5me *2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-2-nitro-1-phenyl-3-(o-tolyl)propyl]acetamide.* Nitroalkene **1m** (82 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5me** (170 mg, 0.360 mmol, 72% yield) as an off-white solid: mp 143–145 °C; IR υ_{max} 2937, 1699, 1558, 1511, 1254, 1210, 1168 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (3H, s), 3.54 (2H, m), 3.84 (3H, s), 5.82 (2H, m), 6.57 (1H, br s), 6.77 (1H, d, J = 7.2), 6.89 (1H, dd, J = 8.4, 2.4), 6.98 (1H, d, J = 8.4), 7.14–7.21 (6H, m), 7.27 (2H, t, J = 7.8), 7.34 (1H, m); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.8 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 19.7 (CH_3), 35.5 (CH_2), 55.7 (CH_3), 67.3 (CH), 88.4 (CH), 114.1 (CH), 114.7 (CH), 116.3 (1C, q, J = 288.7, CF_3), 126.7 (CH), 128.0 (CH), 129.0 (CH), 129.3 (CH), 129.5 (CH), 129.8 (CH), 130.3 (CH), 131.0 (CH), 131.6 (CH), 132.6 (C), 133.4 (C), 136.6 (C), 158.1 (1C, q, J = 35.6, C═O), 160.5 (C); MS (EI) m/z 472 (4%, M), 219 (77%, MH$^+$ − $C_{16}H_{16}NO_2$); HRMS $C_{25}H_{23}F_3N_2O_4$ calcd 472.16044, found 472.16057. Anal. Calcd for $C_{25}H_{23}F_3N_2O_4$: C, 63.55; H, 4.91; N, 5.93. Found: C, 63.26; H, 4.81; N, 5.86.

5ne *2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-{(1S*,2R*)-3-[1-methyl-5-(2,2,2-trifluoroacetyl)-1H-pyrrol-2-yl]-2-nitro-1-phenylpropyl}-acetamide.* Nitroalkene **1n** (76 mg, 0.50 mmol) afforded after purification by column chromatography (50% CH_2Cl_2/Petrol) pure β-nitrotrifluoroacetamide **5ne** (175 mg, 0.315 mmol, 63% yield) as a yellow foam: IR υ_{max} 2963, 1686, 1672 1560, 1511, 1210, 1181, 1147 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.48 (1H, d, J = 16.0), 3.68 (1H, dd, J = 16.0, 11.0), 3.83 (3H, s), 3.98 (3H, s), 5.8 (2H, br s), 6.25 (1H, d, J = 4.4), 6.54 (1H, br s), 6.78 (1H, dd, J = 8.7, 2.3), 6.84 (1H, d, J = 8.5), 6.88 (1H, dd, J = 8.7, 2.6), 7.15 (2H, d, J = 7.6), 7.20 (1H, dd, J = 4.0, 1.9), 7.29 (2H, t, J = 7.7), 7.37 (1H, t, J = 7.4); ^{19}F NMR (300 MHz, $CDCl_3$), δ −71.6 (3F, s), −67.7 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 29.2 (CH_2), 33.7 (CH_3), 55.7 (CH_3), 66.8 (CH), 87.0 (CH), 110.9 (CH), 114.2 (CH), 114.9 (CH), 116.2 (1C, q, J = 288.7, CF_3), 117.1 (1C, q, J = 290.8, CF_3), 124.0 (1C, q, J = 3.9, CH), 125.9 (C), 128.3 (C), 129.2 (CH), 129.4 (CH), 130.1 (CH), 130.2 (CH), 131.5 (CH), 132.6 (C), 158.5 (1C, q, J = 36.2, C═O), 160.7 (C), 170.1 (1C, q, J = 34.7, C═O); MS (ES$^+$) m/z 558 (18%, MH$^+$), 511 (32%, M − NO_2); HRMS $C_{25}H_{21}F_6N_3O_5H^+$ calcd 558.1464, found 558.1451.

5oe *2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-2-nitro-1-phenyl-3-(1-tosyl-1H-pyrrol-2-yl)propyl]acetamide.* Nitroalkene **1o** (113 mg, 0.39 mmol) afforded after purification by column chromatography (50% CH_2Cl_2/Petrol) pure β-nitrotrifluoroacetamide **5oe** (173 mg, 0.288 mmol, 74% yield) as a yellow foam: IR υ_{max} 2968, 1698, 1558, 1512, 1366, 1208, 1180, 1153 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (3H, s), 3.60 (1H, dd, J = 15.8, 11.2), 3.70 (1H, dd, J = 15.7, 3.1), 3.80 (3H, s), 5.62 (1H, td, *J* = 11.0, 2.5), 6.07−6.13 (2H, m), 6.22 (1H, t, *J* = 3.4), 6.34 (1H, d, *J* = 9.9), 6.53 (1H, dd, *J* = 8.8, 2.8), 6.93−6.98 (3H, m), 7.17 (2H, t, *J* = 7.8), 7.24−7.28 (1H, m), 7.31 (2H, d, *J* = 8.2), 7.34 (1H, dd, *J* = 3.3, 1.6), 7.60 (1H, d, *J* = 7.7), 7.63 (2H, d, *J* = 8.4); ^{19}F NMR (300 MHz, $CDCl_3$), δ − 67.38; ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.8 (CH_3), 30.8 (CH_2), 55.6 (CH_3), 63.9 (CH), 88.2 (CH), 112.6 (CH), 113.8 (CH), 114.2 (CH), 116.4 (CH), 116.4 (1C, q, *J* = 288.9, CF_3), 124.1 (CH), 126.5 (CH), 127.2 (C), 127.3 (C), 128.7 (CH), 129.6 (CH), 129.7 (CH), 130.5 (CH), 131.0 (CH), 132.4 (C), 132.7 (CH), 135.8 (C), 145.7 (C), 158.4 (1C, q, *J* = 35.6, *C*═O), 160.3 (C); MS (ES$^+$) *m/z* 624 (56%, MNa$^+$), 555 (100%, M − NO_2); HRMS $C_{29}H_{26}F_3N_3O_6SNa^+$ calcd 624.1384, found 624.1392.

***5pe** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-2-nitro-1-phenyl-3-(pyridin-2-yl)propyl]acetamide.* Nitroalkene **1p** (75 mg, 0.50 mmol) afforded after purification by column chromatography (20% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5pe** (149 mg, 0.324 mmol, 65% yield) as a yellow oil: IR υ_{max} 2935, 1696, 1555, 1255, 1206, 1180, 1152 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.66 (1H, dd, *J* = 15.0, 10.5), 3.72 (1H, dd, *J* = 15.0, 3.5), 3.82 (3H, s), 5.94 (1H, td, *J* = 11.0, 3.5), 6.13 (1H, d, *J* = 7.0), 6.50 (1H, d, *J* = 11.5), 6.60 (1H, dd, *J* = 8.5, 3.0), 7.01 (1H, dd, *J* = 9.0, 3.0), 7.04 (2H, d, *J* = 7.5), 7.15 (1H, d, *J* = 7.5), 7.20−7.23 (3H, m), 7.30 (1H, m), 7.52 (1H, dd, *J* = 8.5, 2.5), 7.63 (1H, td, *J* = 7.5, 2.0), 8.65 (1H, m); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.3 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 40.3 (CH_2), 55.6 (CH_3), 62.5 (CH), 87.8 (CH), 114.0 (CH), 114.1 (CH), 116.4 (1C, q, *J* = 288.4, CF_3), 122.8 (CH), 123.8 (CH), 126.6 (C), 128.7 (CH), 129.5 (CH), 129.7 (CH), 131.0 (CH), 132.6 (C), 133.0 (CH), 137.1 (CH), 150.2 (CH), 155.1 (C), 158.3 (1C, q, *J* = 36.2, *C*═O), 160.5 (C); MS (ES$^+$) *m/z* 560 (86%, MH$^+$), 413 (48%, M − NO_2); HRMS $C_{23}H_{20}F_3N_3O_4H^+$ calcd 460.1484, found 460.1494.

The method was that for the general procedure for Table 3 altering reaction solvent, identity, and equivalents of acid as detailed in Table 4.

General Procedure for the Reductive Nitro-Mannich Reaction Using Electron Rich PMP-Imines with 1d (Table 5). To a solution of nitroalkene **1d** (1 mmol) in CH_2Cl_2 (6 mL) was added Superhydride (1.10 mmol, 1 M in THF). The suspension was then stirred for 30 min at rt before being cooled to −78 °C over 30 min. A solution of imine **3** (1.1 mmol) in CH_2Cl (6 mL) was added via cannula and the mixture stirred at −78 °C for 10 min. Neat trifluoroacetic acid (1.2 mmol) was added dropwise, and the mixture was stirred for 1 h at −78 °C. The reaction was then quenched with saturated brine (10 mL) and the mixture diluted with Et_2O (20 mL). The organic phase was washed with saturated aqueous NaCl (10 mL) and dried ($MgSO_4$). Solvents were removed in vacuo to afford crude β-nitroamines **4**. Crude β-nitroamine **4** (1.0 mmol) was then redissolved in DCM (5 mL) and cooled to 0 °C. To this solution was added trifluoroacetic anhydride (5.0 mmol), followed by pyridine (5.0 mmol), and the solution was warmed to rt over 10 min. The reaction was quenched with 2 M HCl (10 mL) and the mixture extracted with DCM (2 × 5 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (10 mL) and saturated brine (10 mL). The organic phase was then dried ($MgSO_4$), and the solvents were removed in vacuo to afford crude β-nitrotrifluoroacetamides **5** that were then purified by column chromatography.

***5di** 2,2,2-Trifluoro-N-[(1R*,2R*)-1-(furan-2-yl)-2-nitro-3-phenylpropyl]-N-(4-methoxyphenyl)acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5di** (186 mg, 0.415 mmol, 83% yield) as a yellow solid: mp 120−123 °C; IR υ_{max} 2937, 1698, 1557, 1509, 1253, 1207, 1180, 1152 cm^{-1}; ^{1}H NMR (600 MHz, CDCl3) δ 3.41 (1H, dd, *J* = 14.4, 10.8), 3.49 (1H, dd, *J* = 15.0, 3.6), 3.83 (3H, s), 5.35 (1H, td, *J* = 11.4, 3.6), 6.27 (2H, dd, *J* = 0.6), 6.33 (1H, d, *J* = 10.8), 6.47 (1H, d, *J* = 8.4), 6.75 (1H, dd, *J* = 9.0, 2.4), 6.96 (1H, dd, *J* = 8.4, 6.0), 7.20 (2H, d, *J* = 7.2), 7.29−7.37 (4H, m); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.68 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.8 (CH_2), 55.6 (CH_3), 58.0 (CH), 88.6 (CH), 111.0 (CH), 111.9 (CH), 114.2 (CH), 114.7 (CH), 116.2 (1C, q, *J* = 288.7, CF_3), 127.9 (CN), 128.1 (CH), 128.7 (CH), 129.2 (CH), 130.0 (CH), 131.1 (CH), 134.3 (C), 143.4 (CH), 146.2 (C), 158.0 (1C, q, *J* = 36.2, *C*═O), 160.6 (C); MS (CI) *m/z* 449 (24%, MH$^+$), 402 (97%, M − NO_2); HRMS $C_{22}H_{19}F_3N_2O_5H^+$ calcd 449.1324, found 449.1313. Anal. Calcd for $C_{22}H_{19}F_3N_2O_5$: C, 58.93; H, 4.27; N, 6.25. Found: C, 59.07; H, 4.20; N, 6.21.

***5dj** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-1-(2-methoxyphenyl)-2-nitro-3-phenylpropyl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5dj** (212 mg, 0.434 mmol, 87% yield) as a yellow solid: mp 136−140 °C; IR υ_{max} 2940, 1698, 1555, 1510, 1495, 1298, 1252, 1206, 1180, 1152 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.50−3.57 (2H, m), 3.77 (3H, s), 3.80 (3H, s), 5.48 (1H, m), 6.20 (1H, d, *J* = 7.8), 6.59 (1H, dd, *J* = 8.8, 2.8), 6.70 (1H, t, *J* = 7.5), 6.79 (1H, br d, *J* = 11.0), 6.83 (1H, br d, *J* = 6.2), 6.86 (1H, d, *J* = 8.2), 6.92 (1H, dd, *J* = 8.7, 2.9), 7.08 (1H, dd, *J* = 8.6, 2.1), 7.23−7.28 (3H, m), 7.30 (1H, m), 7.36 (2H, t, *J* = 7.6); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.5 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.4 (CH_2), 55.6 (CH_3), 55.7 (CH_3), 57.3 (CH), 89.2 (CH), 110.9 (CH), 113.7 (CH), 114.1 (CH), 116.5 (1C, q, *J* = 288.9, CF_3), 120.4 (CH), 121.3 (C), 127.7 (CN), 127.9 (CH), 128.7 (CH), 129.2 (CH), 130.1 (CH), 130.8 (CH), 132.2 (CH), 135.0 (C), 157.9 (1C, q, *J* = 35.5, *C*═O), 157.9 (C), 160.3 (C); MS (EI) *m/z* 488 (8%, M), 224 (100%, M − $C_9H_7F_3N_2O_4$); HRMS $C_{25}H_{23}F_3N_2O_5$ calcd 488.1554, found 488.1543. Anal. Calcd for $C_{25}H_{23}F_3N_2O_5$: C, 61.47; H, 4.75; N, 5.74. Found: C, 61.28; H, 4.57; N, 5.70.

***5dp** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-1-(3-methoxyphenyl)-2-nitro-3-phenylpropyl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5dp** (210 mg, 0.430 mmol, 86% yield) as a yellow solid: mp 130−134 °C; IR υ_{max} 2938, 1697, 1557, 1510, 1254, 1207, 1180, 1154 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.48 (1H, dd, *J* = 14.4, 11.4), 3.59 (1H, dd, *J* = 15.0, 3.0), 3.68 (3H, s), 3.81 (3H, s), 5.62 (1H, br s), 6.07 (1H, br s), 6.48 (1H, br s), 6.70 (2H, br s), 6.74 (1H, dd, *J* = 9.0, 2.4), 6.87 (1H, dd, *J* = 7.8, 1.8), 6.94 (1H, dd, *J* = 9.0, 3.0), 7.09 (1H, br d, *J* = 7.8), 7.15 (1H, t, *J* = 7.8), 7.26 (2H, d, *J* = 7.2), 7.31 (1H, t, *J* = 7.2), 7.36 (2H, t, *J* = 7.2); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.5 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.4 (CH_2), 55.3 (CH_3), 55.6 (CH_3), 65.2 (CH), 89.8 (CH), 114.1 (CH), 114.6 (CH), 114.7 (CH), 115.6 (CH), 116.4 (1C, q, *J* = 289.0, CF_3), 121.6 (CH), 128.1 (CH), 128.8 (CH), 129.2 (CH), 129.9 (CH), 130.2 (CH), 132.2 (CH), 134.5 (C), 134.6 (C), 158.2 (1C, q, *J* = 35.9, *C*═O), 159.8 (C), 160.6 (C); MS (EI) *m/z* 488 (5%, M); HRMS $C_{25}H_{23}F_3N_2O_5$ calcd 488.1554, found 488.1558. Anal. Calcd for $C_{25}H_{23}F_3N_2O_5$: C, 61.47; H, 4.75; N, 5.74. Found: C, 61.40; H, 4.67; N, 5.72.

***5df** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-1-(4-methoxyphenyl)-2-nitro-3-phenylpropyl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5df** (195 mg, 0.400 mmol, 80% yield) as a brown oil: IR υ_{max} 2939, 1695, 1555, 1512, 1252, 1209, 1183, 1152 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.48 (1H, dd, *J* = 14.6, 10.9), 3.57 (1H, dd, *J* = 14.6, 3.2), 3.80 (3H, s), 3.86 (3H, s), 5.59 (1H, br t, *J* = 9.5), 6.01 (1H, br s), 6.47 (1H, br d, *J* = 7.2), 6.70−6.80 (3H, m), 6.95 (1H, dd, *J* = 8.7, 2.8), 7.00−7.10 (3H, m), 7.20−7.30 (2H, m), 7.30−7.40 (3H, m); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.6 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.3 (CH_2), 55.4 (CH_3), 55.7 (CH_3), 64.9 (CH), 90.1 (CH), 114.1 (CH), 114.2 (CH), 114.6 (CH), 116.3 (1C, q, *J* = 291.4, CF_3), 125.0 (CN), 128.0 (CH), 128.7 (CH), 129.2 (CH), 130.2 (CH), 130.7 (CH), 132.3 (CH), 134.7 (C), 158.1 (1C, q, *J* = 34.7, *C*═O), 160.5 (2C, C); MS (EI) *m/z* 488 (4%, M), 441 (3%, M − NO_2H); HRMS $C_{25}H_{23}F_3N_2O_5$ calcd 488.1554, found 488.1557. Anal. Calcd for $C_{25}H_{23}F_3N_2O_5$: C, 61.47; H, 4.75; N, 5.74. Found: C, 61.40; H, 4.68; N, 5.70.

***5dk** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-{(1S*,2R*)-2-nitro-3-phenyl-1-[2-(trifluoromethyl)phenyl]propyl}acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (7.5% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5dk** (201 mg, 0.382 mmol, 76% yield) as a yellow sticky solid: mp 126−128 °C; IR υ_{max} 2939, 1704, 1557, 1511, 1312, 1209, 1181, 1154, 1121 cm^{-1};

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.53 (1H, dd, J = 15.0, 3.0), 3.64 (1H, dd, J = 15.0, 11.4), 3.80 (3H, s), 5.40 (1H, td, J = 11.4, 3.0), 6.04 (1H, dd, J = 9.0, 1.8), 6.51 (1H, dd, J = 9.0, 3.0), 6.68 (1H, d, J = 5.4), 6.98 (1H, dd, J = 8.4, 3.0), 7.06 (1H, d, J = 10.9), 7.14−7.19 (2H, m), 7.23−7.26 (2H, m), 7.32 (1H, t, J = 7.2), 7.35−7.41 (3H, m), 7.74 (1H, d, J = 7.8); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.7 (3F, s, CF_3), −60.2 (3F, s, $ArCF_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.3 (CH_2), 55.6 (CH_3), 57.1 (CH), 89.9 (CH), 114.0 (CH), 114.4 (CH), 116.3 (1C, q, J = 288.7, F_3C), 127.0 (1C, q, J = 274.4, F_3), 126.4 (CN), 127.0 (1C, q, J = 5.7, CH), 128.1 (CH), 128.7 (CH), 129.3 (CH), 129.8 (CH), 130.2 (C), 130.3 (1C, q, J = 30.7, C), 130.4 (CH), 131.3 (CH), 133.0 (CH), 134.7 (C), 157.9 (1C, q, J = 35.9, C=O), 160.6 (C); MS (EI) m/z 526 (7%, M), 261 (100%, M − $C_9H_8N_2O_4$); HRMS $C_{25}H_{20}F_6N_2O_4$ calcd 526.1322, found 526.1327. Anal. Calcd for $C_{25}H_{20}F_6N_2O_4$: C, 57.04; H, 3.83; N, 5.32. Found: C, 56.79; H, 3.69; N, 5.30.

***5dg** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-{(1S*,2R*)-2-nitro-3-phenyl-1-[4-(trifluoromethyl)phenyl]propyl}acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol and then neat toluene) pure β-nitrotrifluoroacetamide **5dg** (204 mg, 0.388 mmol, 78% yield) as a yellow solid: mp 122−126 °C; IR υ_{max} 2941, 1700, 1557, 1510, 1325, 1211, 1165, 1119 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.50 (1H, dd, J = 14.4, 11.4), 3.62 (1H, dd, J = 14.4, 2.4), 3.82 (3H, s), 5.70 (1H, br s), 6.11 (1H, br s), 6.49 (1H, br s), 6.78 (1H, d, J = 6.6), 6.97 (1H, dd, J = 8.4, 2.4), 7.08 (1H, br d, J = 7.2), 7.26 (2H, d, J = 7.2), 7.29−7.34 (3H, m), 7.37 (2H, t, J = 7.2), 7.55 (2H, d, J = 7.8); ^{19}F NMR (300 MHz, $CDCl_3$) δ −63.3 (3F, s, $ArCF_3$), −67.7 (3F, s, CF_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.3 (CH_2), 55.6 (CH_3), 65.0 (CH), 89.7 (CH), 114.4 (CH), 114.8 (CH), 116.3 (1C, q, J = 289.0, F_3C), 123.8 (1C, q, J = 272.9, F_3C), 125.9 (1C, q, J = 3.6, CH), 127.9 (CN), 128.2 (CH), 128.7 (CH), 129.3 (CH), 129.9 (CH), 130.2 (CH), 131.9 (CH), 131.9 (1C, q, J = 32.6, CH), 134.3 (C), 137.2 (C), 158.4 (1C, q, J = 35.9, C=O), 160.8 (C); MS (EI) m/z 526 (100%, M), 261 (100%, M − $C_9H_8N_2O_4$); HRMS $C_{25}H_{20}F_6N_2O_4$ calcd 526.1322, found 526.1319. Anal. Calcd for $C_{25}H_{20}F_6N_2O_4$: C, 57.04; H, 3.83; N, 5.32. Found: C, 57.02; H, 3.76; N, 5.32.

***5dm** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-2-nitro-3-phenyl-1-(o-tolyl)propyl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% EtOAc/Petrol and then neat toluene) pure β-nitrotrifluoroacetamide **5dm** (169 mg, 0.358 mmol, 72% yield) as an off-white solid: mp 143−145 °C; IR υ_{max} 2938, 1696, 1556, 1510, 1255, 1207, 1180, 1154 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.36 (3H, s), 3.56 (2H, m), 3.81 (3H, s), 5.47 (1H, br s), 6.13 (1H, br s), 6.59 (1H, dd, J = 8.4, 2.4), 6.66 (1H, br s), 6.89 (1H, t, J = 7.2), 6.93 (1H, dd, J = 8.4, 3.0), 7.07 (1H, d, J = 7.8), 7.15−7.20 (2H, m), 7.25 (2H, d, J = 7.8), 7.32 (1H, t, J = 7.2), 7.37 (2H, t, J = 7.2); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.2 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 19.8 (CH_3), 38.4 (CH_2), 55.6 (CH_3), 59.2 (CH), 89.7 (CH), 113.9 (CH), 114.6 (CH), 116.5 (1C, q, J = 290.5, CF_3), 125.9 (CH), 127.0 (CN), 128.0 (CH), 128.2 (CH), 128.7 (CH), 129.2 (CH), 129.5 (CH), 130.0 (CH), 131.0 (C), 138.1 (C), 158.2 (1C, q, J = 34.1, C=O), 160.5 (C); MS (EI) m/z 472 (14%, M), 426 (8%, M − NO_2); HRMS $C_{25}H_{23}F_3N_2O_4$ calcd 472.1604, found 472.1607. Anal. Calcd for $C_{25}H_{23}F_3N_2O_4$: C, 63.55; H, 4.91; N, 5.93. Found: C, 63.26; H, 4.82; N, 5.86.

***5dq** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(2R*,3S*)-2-nitro-1-phenyloctan-3-yl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% Me_2CO/Petrol) pure β-nitrotrifluoroacetamide **5dq** (190 mg, 0.412 mmol, 84% yield) as a yellow oil: IR υ_{max} 2931, 2861, 1701, 1556, 1511, 1255, 1209, 1183, 1157 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 7.0), 1.20−1.35 (4H, m), 1.40−1.50 (3H, m), 1.65 (1H, br s), 3.30−3.40 (2H, m), 3.88 (3H, s), 4.87 (1H, br s), 4.97 (1H, br s), 6.96−7.01 (2H, m), 7.14 (2H, d, J = 7.0), 7.19 (2H, d, J = 7.0), 7.26−7.29 (1H, m), 7.30−7.33 (2H, m); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.4 (s, CF_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.5 (CH_2), 26.1 (CH_2), 28.2 (CH_2), 31.3 (CH_2), 37.8 (CH_2), 55.7 (CH_3), 61.1 (CH), 91.5 (CH), 114.7 (CH), 114.9 (CH), 116.3 (1C, q, J = 288.4, CF_3), 127.6 (C), 127.9 (CH), 128.6 (CH), 129.2 (CH), 130.3 (CH), 131.1 (CH), 134.7 (C), 158.7 (1C, q, J = 36.2, C=O), 160.6 (C); MS (EI) m/z 452 (84%, M), 406 (13%, M − NO_2); HRMS $C_{23}H_{27}F_3N_2O_4$ calcd 452.1917, found 452.1921.

***4dr** N-[(1S*,2R*)-1-Cyclohexyl-2-nitro-3-phenylpropyl]-4-methoxyaniline.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **4dr major** (*anti*) (107 mg, 0.290 mmol, 58% yield) as a yellow oil: IR υ_{max} 3405, 2927, 2853, 1545, 1509, 1234 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.00−1.20 (2H, m), 1.20−1.30 (3H, m), 1.50−1.60 (1H, m), 1.60 (1H, br d, J = 9.0), 1.67 (1H, br d, J = 13.2), 1.73 (1H, br d, J = 10.2), 1.78 (1H, br d, J = 13.2), 1.85 (1H, br d, J = 12.6), 3.26−3.32 (2H, m), 3.41 (1H, d, J = 10.2), 3.80 (3H, s), 3.82 (1H, m), 4.81 (1H, ddd, J = 7.8, 4.8), 6.61−6.64 (2H, m), 6.77−6.80 (2H, m), 7.13 (2H, d, J = 7.2), 7.22−7.25 (1H, m), 7.28 (2H, t, J = 7.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.0 (CH_2), 26.2 (CH_2), 26.3 (CH_2), 31.2 (CH_2), 36.6 (CH_2), 40.6 (CH), 55.9 (CH_3), 62.1 (CH), 91.7 (CH), 114.5 (CH), 115.2 (CH), 127.4 (CH), 128.8 (CH), 128.9 (CH), 136.3 (C), 142.0 (C), 152.6 (C); MS (EI) m/z 368 (8%, M), 239 (52%), 218 (100%); HRMS $C_{22}H_{28}N_2O_3$ calcd 368.2094, found 368.2089. It also gave **4dr minor** (*syn*) (55 mg, 0.149 mmol, 30% yield) as a yellow oil: IR υ_{max} 3395, 2925, 2853, 1547, 1510, 1232 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.00−1.30 (5H, m), 1.50−1.60 (1H, m), 1.68 (1H, br d, J = 12.0), 1.76 (2H, br d, J = 12.8), 1.86 (2H, br s), 3.16 (1H, dd, J = 14.4, 8.4), 3.40 (1H, dd, J = 14.0, 8.0), 3.51 (1H, m), 3.78 (3H, s), 3.91 (1H, d), 5.08 (1H, apt. dt, J = 9.2, 5.6), 6.56−6.61 (2H, m), 6.77−6.81 (2H, m), 7.11−7.13 (2H, m), 7.27−7.33 (3H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.0 (CH_2), 26.1 (CH_2), 26.2 (CH_2), 29.2 (CH_2), 30.7 (CH_2), 37.6 (CH_2), 41.6 (CH), 55.8 (CH_3), 60.8 (CH), 91.0 (CH), 114.1 (CH), 115.0 (CH), 127.4 (CH), 128.8 (CH), 128.9 (CH), 135.7 (C), 142.5 (C), 152.2 (C); MS (EI) m/z 368 (33%, M), 239 (23%), 218 (47%); HRMS $C_{22}H_{28}N_2O_3$ calcd 368.2094, found 368.2086.

***5do** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1R*,2R*)-2-nitro-3-phenyl-1-(pyridin-2-yl)propyl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (20% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5do** (138 mg, 0.300 mmol, 60% yield) as an off-white solid: mp 109−112 °C; IR υ_{max} 2919, 1698, 1555, 1510, 1253, 1207, 1182, 1152 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.41 (1H, dd, J = 14.4, 10.8), 3.60 (1H, dd, J = 14.4, 3.0), 3.80 (3H, s), 5.63 (1H, td, J = 10.8, 3.0), 6.08 (1H, d, J = 7.2), 6.59 (2H, d, J = 10.8), 6.94 (1H, d, J = 7.2), 7.19−7.24 (4H, m), 7.28−7.32 (1H, m), 7.35 (2H, t, J = 6.6), 7.48 (1H, d, J = 7.8), 7.71 (1H, td, J = 7.8, 1.8), 8.31 (1H, d, J = 4.8); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.3 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.1 (CH_2), 55.6 (CH_3), 62.6 (CH), 87.4 (CH), 114.1 (CH), 114.5 (CH), 116.4 (1C, q, J = 289.0, F_3C), 124.1 (CH), 124.6 (CH), 127.1 (CH), 128.0 (CH), 128.8 (CH), 129.1 (CH), 130.3 (CH), 131.6 (CH), 134.6 (C), 137.4 (C), 149.1 (CH), 153.7 (C), 158.4 (1C, q, J = 35.9, C=O), 160.5 (C); MS (ES^+) m/z 460 (100%, MH^+), 413 (95%, M − NO_2); HRMS $C_{23}H_{20}F_3N_3O_4H^+$ calcd 460.1491, found 460.1484. Anal. Calcd for $C_{23}H_{20}F_3N_3O_4$: C, 60.13; H, 4.39; N, 9.15. Found: C, 60.19; H, 4.30; N, 9.14.

***5ds** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-2-nitro-3-phenyl-1-(pyridin-3-yl)propyl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (30% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5ds** (183 mg, 0.398 mmol, 80% yield) as an off-white solid: mp 147−150 °C; IR υ_{max} 3032, 2970, 1700, 1557, 1511, 1255, 1211, 1182, 1168 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.47 (1H, dd, J = 14.5, 11.1), 3.55 (1H, dd, J = 14.5, 3.0), 3.83 (3H, s), 5.68 (1H, br s), 5.95 (1H, br s), 6.53 (1H, br s), 6.79 (1H, dd, J = 8.8, 2.6), 6.95 (1H, dd, J = 8.7, 2.8), 7.03 (1H, d, J = 7.1), 7.20−7.24 (3H, m), 7.31 (1H, m), 7.36 (2H, m), 7.53 (1H, d, J = 7.0), 8.34 (1H, d, J = 1.8), 8.59 (1H, dd, J = 4.8, 1.2); ^{19}F NMR (300 MHz, $CDCl_3$) δ −67.8 (3F, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.2 (CH_2), 55.7 (CH_3), 63.9 (CH), 89.5 (CH), 114.6 (CH), 115.0 (CH), 116.1 (1C, q, J = 289.0, CF_3), 123.7 (CH), 128.0 (C), 128.2 (CH), 128.7 (CH), 129.1 (C), 129.3 (CH), 131.8 (CH), 134.1 (C), 136.7 (CH), 150.6 (CH), 151.2 (CH), 158.3 (1C, q, J = 36.2, C=O), 160.8 (C); MS (EI) m/z 459 (15%, M), 413 (7%, M − NO_2); HRMS $C_{23}H_{20}N_3F_3O_4$ calcd 459.1400, found 459.1408. Anal. Calcd for

$C_{23}H_{20}F_3N_3O_4$: C, 60.13; H, 4.39; N, 9.15. Found: C, 59.80; H, 4.33; N, 9.06.

***5du** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1R*,2R*)-2-nitro-3-phenyl-1-(1-tosyl-1H-pyrrol-2-yl)propyl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5du** (225 mg, 0.374 mmol, 75% yield) as a yellow solid: mp 192−196 °C; IR υ_{max} 2938, 1702, 1557, 1511, 1370, 1179, 1154 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 2.47 (3H, s), 3.34 (1H, dd, J = 14.4, 10.8), 3.40 (1H, dd, J = 15.0, 4.2), 3.80 (3H, s), 4.96 (1H, td, J = 10.8, 4.2), 5.74 (1H, dd, J = 3.6, 1.2), 5.97 (1H, t, J = 3.6), 6.51 (1H, dd, J = 8.9, 2.2), 6.64 (1H, dd, J = 8.9, 2.9), 6.72 (1H, d, J = 11.0), 6.90 (1H, dd, J = 8.6, 2.9), 7.02 (1H, dd, J = 8.6, 2.6), 7.14 (2H, d, J = 7.0), 7.27−7.30 (1H, m), 7.31−7.35 (1H, m), 7.40−7.43 (3H, m), 7.86 (2H, d, J = 8.4); ^{19}F NMR (300 MHz, CDCl$_3$) δ −68.0 (3F, s); ^{13}C NMR (151 MHz, CDCl$_3$) δ 21.9 (CH$_3$), 38.0 (CH$_2$), 54.8 (CH), 55.6 (CH$_3$), 90.0 (CH), 111.0 (CH), 113.8 (CH), 114.4 (CH), 116.3 (1C, q, J = 288.6, CF$_3$), 117.9 (CH), 124.5 (C), 124.7 (CH), 127.7 (C), 127.7 (CH), 128.0 (CH), 128.6 (CH), 129.2 (CH), 129.7 (CH), 130.4 (CH), 132.0 (CH), 134.7 (C), 134.8 (C), 146.1 (C), 158.2 (1C, q, J = 36.2, C═O), 160.4 (C); MS (CI) m/z 602 (4%, MH$^+$), 555 (6%, M − NO$_2$), 383 (100%, M − $C_9H_7F_3NO_2$); HRMS $C_{29}H_{26}N_3F_3O_6SH^+$ calcd 602.1573, found 602.1586. Anal. Calcd for $C_{29}H_{26}N_3F_3O_6S$: C, 57.90; H, 4.36; N, 6.98. Found: C, 57.82; H, 4.28; N, 6.95.

***5dw** 2,2,2-Trifluoro-N-(4-methoxyphenyl)-N-[(1S*,2R*)-2-nitro-3-phenyl-1-(1-tosyl-1H-indol-3-yl)propyl]acetamide.* Nitroalkene **1d** (75 mg, 0.50 mmol) afforded after purification by column chromatography (10% EtOAc/Petrol) pure β-nitrotrifluoroacetamide **5dw** (208 mg, 0.319 mmol, 64% yield) as an off-white solid: mp 90−95 °C; IR υ_{max} 2934, 1698, 1557, 1511, 1448, 1371, 1210 1171 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 2.31 (3H, s), 3.51 (1H, dd, J = 14.5, 11.5), 3.61 (1H, dd, J = 14.6, 2.8), 3.84 (3H, s), 5.33 (1H, br s), 6.09 (1H, br s), 6.54 (1H, d, J = 7.3), 6.68 (1H, br s), 6.97 (1H, dd, J = 8.6, 2.2), 7.13−7.22 (4H, m), 7.24 (2H, d, J = 7.2), 7.28−7.40 (5H, m), 7.51 (1H, br s), 7.57 (2H, d, J = 8.3), 7.95 (1H, d, J = 8.3); ^{19}F NMR (300 MHz, CDCl$_3$), δ −67.61 (3F, s); ^{13}C NMR (151 MHz, CDCl$_3$) δ 21.7 (CH$_3$), 38.0 (CH$_2$), 54.9 (CH), 55.7 (CH$_3$), 89.8 (CH), 114.0 (CH), 114.2 (CH), 114.7 (CH), 114.8 (C), 116.2 (1C, q, J = 288.5, CF$_3$), 119.3 (CH), 124.4 (CH), 125.9 (CH), 126.6 (CH), 127.0 (CH), 128.2 (CH), 128.6 (CH), 129.2 (C), 129.3 (CH), 129.8 (CH), 130.1 (CH), 132.0 (CH), 134.2 (C), 134.3 (C), 134.6 (C), 145.6 (C), 158.5 (1C, q, J = 36.2, C═O), 160.7 (C); MS (ES$^+$) m/z 674 (21%, MNa$^+$), 605 (16%, M − NO$_2$); HRMS $C_{33}H_{28}F_3N_3O_6SNa^+$ calcd 674.1549, found 674.1558.

General Procedure for the Synthesis of Differentially Protected 1,2-Diamines 7 by Reduction of β-Nitroacetamides 5. To a vigorously stirred solution of β-nitroacetamide **5** (1 mmol) in EtOH (10 mL) at 0 °C was added 6 M HCl (5 mL), followed by zinc dust (60 mmol) in three portions over 20 min (**Caution:** *Effervescence*). The mixture was allowed to warm to rt overnight. The reaction was monitored by TLC, and further zinc (20 mmol) and 6 M HCl (2 mL) were added if required. Once the reaction was complete, the EtOH was removed in vacuo. The residual slurry was partitioned between EtOAc and saturated NaHCO$_3$ (**Caution:** *Effervescence*). If necessary, further NaHCO$_3$ was added to attain a pH of >7 in the aqueous layer. The aqueous layer was further extracted with EtOAc; the organics layers were combined and dried (MgSO$_4$), and the solvent was removed in vacuo to afford crude material that was purified by column chromatography to give 1,2-diamines **7**.

***7aa** 2,2,2-Trifluoro-N-{(1S*,2R*)-1-[(2-methoxybenzyl)amino]-1-phenyloctan-2-yl}acetamide.* Pure β-nitroacetamide **5aa** (124 mg, 0.271 mmol) afforded crude amine **7aa** as a yellow oil that was purified by column chromatography (5% EtOAc/hexanes) to give **7aa** (102 mg, 87%) as a yellow oil: R_f = 0.51 (10% EtOAc/hexanes); IR υ_{max} 3420, 3065, 2958, 1720, 1169 cm^{-1}; ^{1}H NMR δ 0.83 (3H, t, J = 7.3), 1.10−1.25 (9H, m), 1.41 (1H, m), 3.50 (1H, d, J = 13.0), 3.85 (5H, m), 4.18 (1H, m), 6.62 (1H, d, J = 9.5), 6.88 (1H, d, J = 8.0), 6.91 (1H, td, J = 7.5, 1.0), 7.12 (1H, dd, J = 7.5, 1.5), 7.26 (1H, td, J = 8.0, 1.5), 7.32 (1H, d, J = 7.0), 7.33 (1H, td, J = 7.0, 1.0), 7.40 (1H, t, J = 7.0), 7.41 (1H, t, J = 8.0); ^{13}C NMR δ 14.2 (CH$_3$), 22.7 (CH$_2$), 26.0 (CH$_2$), 29.0 (CH$_2$), 30.0 (CH$_2$), 31.9 (CH$_2$), 47.3 (CH$_2$), 54.1 (CH$_2$), 55.3 (CH$_3$), 64.6 (CH), 110.4 (CH), 116.1 (1C, q, J = 286.3, CF$_3$), 120.5 (CH), 127.6 (CH), 127.8 (CH), 127.8 (CH), 127.9 (C), 128.6 (CH), 128.7 (CH), 130.1 (CH), 138.8 (C), 157.3 (1C, q, J = 36.3, C═O), 157.8 (C); ^{19}F NMR δ −68.8 (3F, s, CF_3); MS (EI+) m/z 437 (100%, MH$^+$); HRMS $C_{24}H_{31}F_3N_2O_2H^+$ calcd 437.2412, found 437.2419.

***7ia** 2,2,2-Trifluoro-N-{(1S*,2R*)-3-(furan-2-yl)-1-[(2-methoxybenzyl)amino]-1-phenylpropan-2-yl}acetamide.* Pure β-nitroamide **5ia** (92 mg, 0.20 mmol) afforded crude **7ia** that was purified by column chromatography (10% EtOAc/hexanes) to give **7ia** (136 mg, 91%) as a colorless oil: R_f = 0.66 (20% EtOAc/hexanes); IR υ_{max} 3419, 3009, 1723 cm^{-1}; ^{1}H NMR δ 2.10 (1H, b), 2.73 (1H, dd, J = 15.0, 8.0), 2.86 (1H, dd, J = 15.0, 4.5), 3.56 (1H, d, J = 13.0), 3.87 (3H, s), 3.90 (1H, d, J = 15.0), 3.92 (1H, d, J = 5.0), 4.52 (1H, apt. tt, J = 8.7, 4.8), 6.05 (1H, d, J = 3.0), 6.31 (1H, dd, J = 3.0, 1.5), 6.74 (1H, bd, J = 9.0), 6.91 (1H, d, J = 8.5), 6.95 (1H, td, J = 7.5, 0.5), 7.15 (1H, dd, J = 7.0, 1.5), 7.31 (1H, td, J = 8.0, 1.5, 7.3), 7.38 (1H, d, J = 1.0), 7.40 (3H, m), 7.47 (2H, m); ^{13}C NMR δ 28.5 (CH$_2$), 47.4 (CH$_2$), 53.1 (CH), 55.2 (CH$_3$), 63.7 (CH), 107.4 (CH), 110.4 (CH), 110.5 (CH), 115.9 (1C, q, J = 286.7, CF$_3$), 127.6 (2 × CH), 127.9 (C), 128.0 (CH), 128.6 (CH), 128.9 (2 × CH), 130.0 (CH), 138.6 (C), 141.9 (CH), 151.2 (CH), 156.7 (1C, q, J = 36.8, CCF$_3$), 157.7 (C); ^{19}F NMR δ −76.4 (3F, s, CF_3); MS (EI+) m/z 433 (100%, MH$^+$); HRMS $C_{23}H_{23}F_3N_2O_3H^+$ calcd 433.1734, found 433.1736. Anal. Calcd for $C_{23}H_{23}F_3N_2O_3$: C, 63.88; H, 5.36; N, 6.48. Found: C, 63.84; H, 5.49; N, 6.38.

***7ab** 2,2,2-Trifluoro-N-{(1R*,2R*)-1-(furan-2-yl)-1-[(2-methoxybenzyl)amino]octan-2-yl}acetamide.* Pure β-nitroamide **5ab** (160 mg, 0.351 mmol) afforded crude **7ab** as a yellow oil that was purified by column chromatography (20% EtOAc/hexanes) to give **7ab** (136 mg, 91%) as a colorless oil: R_f 0.72 (20% EtOAc/hexanes); IR υ_{max} 3419, 2931, 1720, 1466 cm^{-1}; ^{1}H NMR δ 0.85 (3H, t, J = 7.0), 1.25 (9H, m), 1.40 (1H, m), 1.93 (1H, b), 3.62 (1H, d, J = 13.2), 3.84 (3H, s), 3.86 (1H, d, J = 4.0), 3.88 (1H, d, J = 13.2), 4.27 (1H, m), 6.27 (1H, d, J = 3.0), 6.38 (1H, dd, J = 3.0, 1.7), 6.88 (1H, d, J = 8.3), 6.91 (1H, d, J = 7.5), 6.94 (1H, d, J = 7.3), 7.18 (1H, d, J = 7.3), 7.26 (2H, m), 7.43 (1H, s); ^{13}C NMR δ 14.1 (CH$_3$), 22.6 (CH$_2$), 25.6 (CH$_2$), 29.0 (CH$_2$), 30.8 (CH$_2$), 31.6 (CH$_2$), 47.6 (CH$_2$), 52.9 (CH), 55.3 (CH$_3$), 58.2 (CH), 108.1 (CH), 110.3 (CH), 110.4 (CH), 116.1 (1C, q, J = 286.3, CF$_3$), 120.5 (CH), 127.6 (C), 128.7 (CH), 130.1 (CH), 153.2 (C), 157.1 (1C, q, J = 36.3, CCF$_3$), 157.8 (C); ^{19}F NMR δ −76.4 (3F, s, CF_3); MS (EI+) m/z 427 (100%, MH$^+$), 449 (19%, MNa$^+$); HRMS $C_{22}H_{29}F_3N_2O_3H^+$ calcd 427.2203, found 427.2219. Anal. Calcd for $C_{22}H_{29}F_3N_2O_3$: C, 61.96; H, 6.85; N, 6.57. Found: C, 62.27; H, 6.97; N, 6.41.

***7de** 2,2,2-Trifluoro-N-{(1S*,2R*)-1-[(4-methoxyphenyl)amino]-1,3-diphenylpropan-2-yl}acetamide.* Pure β-nitrotrifluoroacetamide **5de** (50 mg, 0.11 mmol) afforded pure **7de** (40 mg, 0.935 mmol, 85% yield) as an off-white solid without the need for chromatography: mp 150−153 °C; IR υ_{max} 3307, 3039, 1702, 1511, 1178 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) δ 2.69 (1H, dd, J = 14.2, 8.8), 2.98 (1H, dd, J = 14.2, 5.2), 3.68 (3H, s), 4.25 (1H, br s), 4.58 (1H, d, J = 3.1), 4.73 (1H, dddd, J = 9.0, 9.0, 4.7, 4.7), 6.14 (1H, d, J = 9.3), 6.44 (2H, dm, J = 6.8), 6.67 (2H, dm, J = 8.9), 7.14 (2H, d, J = 7.1),7.23−7.37 (6H, m), 7.40 (2H, t, J = 7.5); ^{19}F NMR (300 MHz, CDCl$_3$) δ −76.31 (3F, s); ^{13}C NMR (151 MHz, CDCl$_3$) δ 36.9 (CH$_2$), 55.6 (CH), 55.8 (CH$_3$), 61.5 (CH), 114.8 (CH), 115.3 (CH), 115.8 (1C, q, J = 288.0, CF$_3$), 127.3 (CH), 127.4 (CH), 128.3 (CH), 129.0 (CH), 129.1 (CH), 129.2 (CH), 136.3 (C), 138.3 (C), 140.5 (C), 152.7 (C), 157.5 (1C, q, J = 36.2, C═O); MS (EI) m/z 428 (3%, M); HRMS $C_{24}H_{23}F_3N_2O_2$ calcd 428.1706, found 428.1703.

***7oe** 2,2,2-Trifluoro-N-{(1S*,2R*)-1-[(4-methoxyphenyl)amino]-1-phenyl-3-(1-tosyl-1H-pyrrol-2-yl)propan-2-yl}acetamide.* Pure β-nitrotrifluoroacetamide **5oe** (60 mg, 0.10 mmol) afforded after purification by column chromatography (20% Me$_2$CO/Petrol) pure **7oe** (46 mg, 0.080 mmol, 80% yield) as an off-white solid: mp 144−146 °C; IR υ_{max} 3321, 2929, 1699, 1514, 1353, 1239, 1172 cm^{-1}; ^{1}H NMR (600 MHz, CD$_3$CN) δ 2.40 (3H, s), 2.91 (1H, dd, J = 15.7, 11.2), 3.30 (1H, dd, J = 15.7, 2.0), 3.67 (3H, s), 4.50−4.57 (1H, m), 4.59 (1H, dd, J = 9.3, 7.1), 4.82 (1H, d, J = 9.2), 6.08 (1H, s), 6.22 (1H, t, J = 3.4), 6.61 (2H, d, J = 8.9), 6.71 (2H, d, J = 8.9), 7.27−7.31 (2H, m), 7.34−7.38 (4H, m), 7.39−7.44 (3H, m), 7.57 (2H, d, J = 8.3); ^{19}F NMR (300 MHz, $CDCl_3$) δ − 76.38; ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.8 (CH_3), 28.2 (CH_2), 55.7 (CH), 55.8 (CH_3), 62.3 (CH), 112.2 (CH), 114.8 (CH), 115.0 (CH), 115.1 (CH), 115.4 (1C, q, J = 290.2, CF_3), 123.3 (CH), 126.7 (CH), 127.5 (CH), 128.3 (CH), 129.0 (CH), 129.5 (C), 130.3 (CH), 135.9 (C), 138.6 (C), 140.8 (C), 145.5 (C), 152.5 (C), 158.0 (1C, q, J = 37.3, C); MS (ES$^+$) m/z 594 (50%, MNa$^+$), 572 (100%, MH$^+$); HRMS $C_{29}H_{28}F_3N_3O_4SH^+$ calcd 572.1829, found 572.1831.

■ ASSOCIATED CONTENT

Supporting Information

General experimental details, X-ray representations, and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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