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Reductive Nitro-Mannich Route for the Synthesis of 1,2-Diamine Containing Indolines and Tetrahydroquinolines

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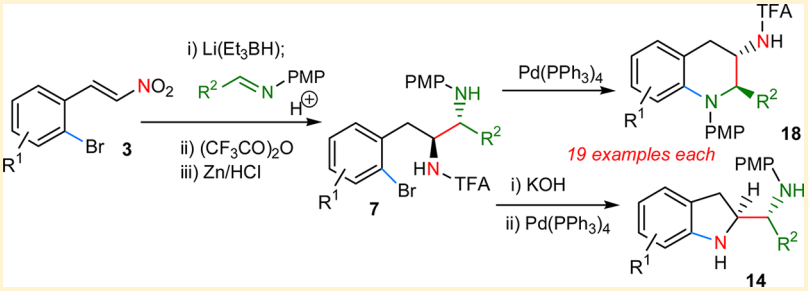
Supporting Information



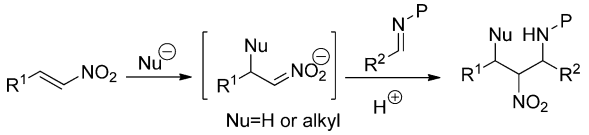
ABSTRACT: A one-pot, 1,4-hydride addition nitro-Mannich reaction between a set of nitroalkenes **3** and a wide range of *N*-*p*-methoxyphenyl-protected aldimines, derived from alkyl, aryl and heteroaryl aldehydes, followed by Zn/HCl reduction leads to stereochemically defined 1,2-diamines. These underwent palladium-catalyzed cyclization and depending upon the presence or not of the trifluoroacetamide protecting group gave either tetrahydroquinolines **18** or indolines **14** in high overall yield and diastereoselectivity (19 examples each). In each case, the more nucleophilic pendant amine cyclizes to give a benzofused saturated heterocyclic 5- or 6-membered ring, with an additional vicinal amino stereocenter in each.

INTRODUCTION

The nitro-Mannich (or aza-Henry) reaction is a powerful synthetic tool for the construction of C−C bonds. It enables the formation of β-nitroamines with two contiguous stereocenters, often with high levels of enantio- and diastereoselectivity.[1] These useful synthetic intermediates provide access to other valuable moieties such as α-amino acids (via Nef reaction), vicinal diamines (via nitro reduction), and peptides.[2] Although first reported by Henry in 1896,[3] the nitro-Mannich reaction received little attention for over a century until the first acyclic diastereoselective examples.[4] There have since been huge advances in this field with the advent of numerous asymmetric transition-metal-catalyzed, lanthanide-catalyzed, and organocatalytic methods.[5−7] These now provide easy access to a range of β-nitroamines with highly selective procedures available for the formation of both *anti*- and *syn*-diastereomers. The synthetic utility of this reaction has been further demonstrated through its successful use in the synthesis of a number of natural products and pharmaceuticals.[8]

Although there have been considerable advances in the scope and efficiency of nitro-Mannich protocols, limitations still exist with respect to the complexity of the nitroalkane used. Recently, our group disclosed an enantioselective conjugate addition nitro-Mannich reaction in which addition of dialkylzincs to nitroalkenes generates zinc nitronates. These are subsequently trapped with an imine to generate complex β-nitroamines with excellent diastereocontrol over three contiguous stereocenters.[9] Our group also recently published an achiral reductive nitro-Mannich reaction in which $LiHBEt_3$ is used as a hydride source in the conjugate addition (Scheme 1).[10] The use of nitroalkenes (prepared via the Henry reaction) provides easy access to more structurally complex nitro coupling partners, thereby generating β-nitroamines with higher levels of functionality which may be further manipulated to produce a range of useful intermediates.

Scheme 1. Conjugate Addition Nitro-Mannich Reactions



We envisaged the use of nitroalkenes bearing a pendant *o*-halo-aromatic group which could later be utilized in intramolecular *N*-arylation reactions to form a variety of fused heterocyclic structures (Scheme 2). Synthetic routes to structurally diverse fused nitrogen heterocycles are of interest because of their importance in medicinal chemistry and abundance in biologically active natural products.[11,12] Herein, we report an expedient and highly diastereoselective synthesis of both 2-aminomethylene indolines **1** and 3-aminotetrahydroquinolines **2** by utilizing a diamine derived from a reductive nitro-Mannich reaction in selective intramolecular *N*-arylations.

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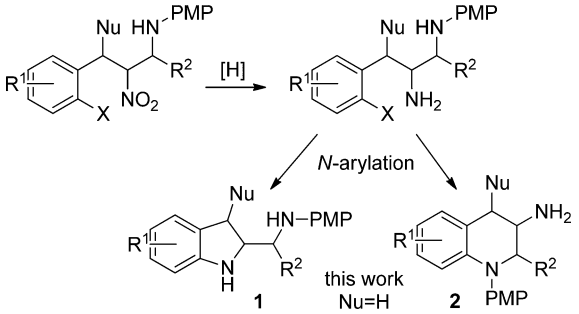
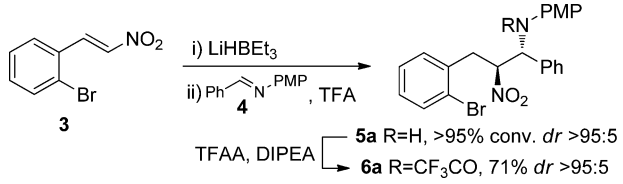
Scheme 2. Synthesis of 1,2-Diamine-Containing Fused Nitrogen Heterocycles



RESULTS AND DISCUSSION

Initial studies began with the $LiHBEt_3$-mediated reductive nitro-Mannich reaction between 2-bromo-β-nitrostyrene (**3**) and *N*-*p*-methoxyphenyl (PMP)-phenyl imine (**4**). Using conditions previously developed by us, the reaction proceeded smoothly to provide β-nitroamine **5a** with complete conversion and >95:5 diastereomeric ratio (dr) in favor of the *anti*-diastereomer.[10] Because of the susceptibility of PMP-protected β-nitroamines to retro-addition, the product was protected by treatment with trifluoroacetic anhydride (TFAA) in the presence of diisopropylethylamine (DIPEA) to provide β-nitroacetamide **6a** in 71% yield over two steps from nitroalkene **3** (Scheme 3).[9] The relative stereochemistry of the major diastereomer was confirmed by single-crystal X-ray crystallography (see the Supporting Information).

Scheme 3. Synthesis of β-Nitrotrifluoroacetamide 6a



The next stage in the synthesis was reduction of the nitro group to form the 1,2-diamine required for the intramolecular *N*-arylation reactions. The reduction of β-nitroacetamide **6a** to form β-aminoacetamide **7a** initially proved to be problematic due to complications caused by the lability of the aromatic bromide (resulting in the formation of **8** or **9**) and the difficulty in reducing the hydroxylamine intermediate **10**. Concomitant transacylation of the trifluoroacetyl group was observed during reduction, which is in agreement with previous studies on similar systems.[9,10] This transacylation process, however, also resulted in a number of complications due to the formation of dihydroimidazole **11** and both diastereomers of imidazolidine **12** via elimination of water during transacylation and subsequent reduction of the C=N bond (Scheme 4, Table 1). Initial attempts using well-established reduction protocols gave poor conversions to **7a**. Hydrogenation resulted in complete debromination to form **9** with no observed reduction of the nitro group, and Raney nickel/N_2H_4 showed only trace amounts of hydroxylamine **10** (Table 1, entries 1 and 2).[13,14] Nickel boride resulted in complete reduction of **6a** but with debrominated diamine **8** formed as the major product (Table 1, entry 3).[15] Using zinc hydrochloride (Zn/HCl) in EtOH gave a mixture of the desired diamine **7a**, hydroxylamine **10**, and two diastereomers of imidazolidine **12** in a 2:1 dr (Table 1, entry 4).[16] Although diamine **7a** was formed as the minor product, the stability of the aromatic bromide under the Zn/HCl conditions prompted further optimization studies. Increasing the equivalents of both Zn and HCl increased the amount of reduction of hydroxylamine **10** but resulted in formation of imidazolidine **12** (2.5:1 dr) as the major product (Table 1, entry 5). It was found that using an excess of HCl with respect to Zn greatly reduced the formation imidazolidine **12**, instead giving rise to larger amounts of dihydroimidazole **11** and the desired product **7a** (Table 1, entries 6–9). Complete reduction of hydroxylamine **10** was accomplished by addition of the Zn in two portions, although the additional zinc resulted in the formation of small amounts of debromination product **8** (Table 1, entry 10). Using a mixture of EtOH and EtOAc aided solubilization of the reactants and enabled the reactions to be conducted at higher concentration. Hydrolysis of dihydroimidazole **11**, by treating the crude product with 6 M HCl, provided near-quantitative conversion to diamine **7a** and gave a purified yield of 89% (Table 1, entry 11).

At this stage, the trifluoroacetyl protecting group could be removed by treating **7a** with KOH in EtOH and H_2O, providing monoprotected diamine **13** in 94% yield (Scheme 5). With conditions developed that provided ready access to both bis- and monoprotected diamines **13** and **7a** attention was turned to the intramolecular *N*-arylation reaction.

To generate the indoline and tetrahydroquinoline structures, we investigated the use of intramolecular Buchwald–Hartwig chemistry,[17] which has previously been successfully applied to the formation of 5- and 6-membered ring heterocycles containing a single amine group.[18] Although selective intermolecular monoarylations of poly- and diamines have been reported,[19] intramolecular examples are far less common and have mainly been applied to the formation of polyazamacrocycles in low to moderate yields.[20] We began our investigations by applying catalyst systems that had

Scheme 4. Products from Nitro Reduction

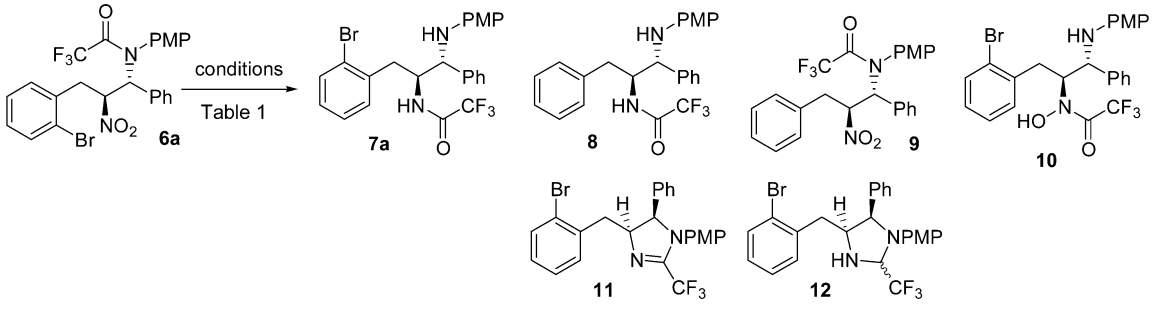


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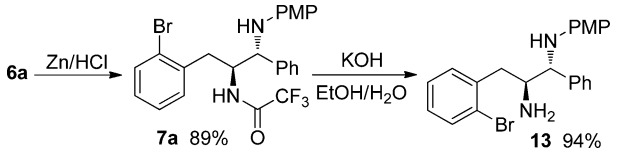
Table 1. Optimization of Nitro Reduction

		conversion (%)[a]					
entry	conditions	**7a**	**8**	**9**	**10**	**11**	**12**
1	H_2, Pd/C, MeOH	0	0	100	0	0	0
2	Raney Ni/N_2H_4	0	<5	0	0	0	0
3	$NiCl_2.6H_2O$, $NaBH_4$, MeOH	35	43	0	21	2	0
4	Zn (60 equiv), 6 M HCl (30 equiv), EtOH	9	0	0	53	0	38
5	Zn (80 equiv), 6 M HCl (40 equiv), EtOH	32	0	0	19	1	48
6	Zn (60 equiv), 6 M HCl (100 equiv), EtOH	62	0	0	28	9	1
7	Zn (60 equiv), 6 M HCl (200 equiv), EtOH	74	0	0	13	13	0
8	Zn (60 equiv), 6 M HCl (300 equiv), EtOH	67	0	0	13	20	0
9	Zn (100 equiv), 6 M HCl (300 equiv), EtOH	62	5	0	8	25	0
10[b]	Zn (75 equiv), 6 M HCl (300 equiv), EtOH	78	6	0	0	16	0
11[b,c]	Zn (75 equiv), 6 M HCl (250 equiv), EtOH, EtOAc	95 (89)	5	0	0	0	0

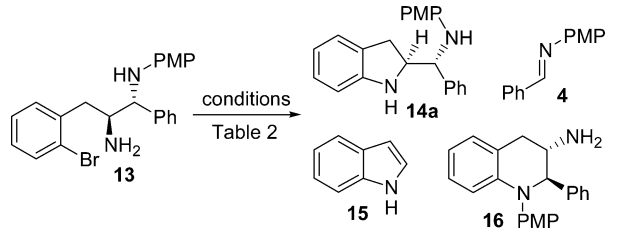
[a]Determined by ^{1}H NMR. Numbers in parentheses show purified yield. [b]Zinc added in two portions (50 and 25 equiv). [c]Crude product treated with 6 M HCl (20 equiv) in EtOH for 1 h.

Scheme 5. Synthesis of Bis- and Monoprotected Diamines 7a and 13



previously been used by Buchwald et al. for the formation of simple indoline and tetrahydroquinoline structures.[18a] Initial attempts to affect the cyclization of monoprotected diamine **13** (Scheme 6) were very promising with a 54% yield of indoline

Scheme 6. Indoline Formation



14a obtained by treatment with $Pd(PPh_3)_4$, NaO-*t*-Bu, and K_2CO_3 in toluene at 90 °C (Table 2, entry 1). The product was accompanied by trace amounts of imine **4** and indole **15**, formed due to the slight instability of **14a** to oxidative cleavage under the reaction conditions (Scheme 6). Rigorous drying of the bases, degassing of the solvent, and performing the reaction at 100 °C gratifyingly increased the yield of **14a** to 91% (Table 2, entry 2). Various other catalyst systems were also investigated, but none proved to be as effective as $Pd(PPh_3)_4$ (Table 2, entries 2–6). Using conditions employed by the groups of Jackson and Buchwald for the synthesis of 2-substituted indolines gave poor conversion to the desired product (Table 2, entry 3).[18b,c] $Pd(dppf)Cl_2$/dppf and $Pd_2(dba)_3$/BINAP catalyst systems gave moderate yields of indoline **14a** and also resulted in small amounts of tetrahydroquinoline **16** (Table 2, entries 3 and 4). It was found that the cyclization could also be performed with only NaO*t*Bu as a base, however, the reaction did not proceed as cleanly as those with two bases resulting in a lower yield of 77% (Table 2, entry 8). Using only K_2CO_3 reduced the rate of

Table 2. Optimization of Indoline Formation

		conversion (%)[a]		
entry	conditions	**14a**	**4 + 15**	**16**
1	$Pd(PPh_3)_4$ (5 mol %), NaO*t*Bu (1.6 equiv), K_2CO_3 (1.6 equiv), toluene, 90 °C	94 (54)	6	0
2[b]	$Pd(PPh_3)_4$ (5 mol %), NaO*t*Bu (1.6 equiv), K_2CO_3 (1.6 equiv), toluene, 100 °C, 4 h	>95 (91)	<5	0
3	$Pd_2(dba)_3$ (3.3 mol %), P(*o*-tol)$_3$ (13.3 mol %), $CsCO_3$ (4.0 equiv), toluene, 100 °C	21	<5	0
4	$Pd(dppf)Cl_2$ (5 mol %), dppf (15 mol %), NaO*t*Bu (1.6 equiv), toluene, 100 °C, 5 h	70 (65)	<5	5
5	$Pd_2(dba)_3$ (5 mol %), BINAP (15 mol %), NaO*t*Bu (1.6 equiv), toluene, 100 °C, 5 h	73 (51)	6	9
6	$Pd(OAc)_2$ (5 mol %), P(*o*-tol)$_3$ (15 mol %), NaO*t*Bu (1.6 equiv), toluene, 100 °C, 5 h	27	5	0
7	$Pd(PPh_3)_4$ (5 mol %), NaO*t*Bu (1.6 equiv), toluene, 100 °C, 5 h	32	<5	0
8	$Pd(PPh_3)_4$ (5 mol %), NaO*t*Bu (2.5 equiv), toluene, 100 °C, 18 h	85 (77)	6	6
9	$Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (1.6 equiv), toluene, 100 °C, 5 h	24	0	<5
10	$Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (2.5 equiv), toluene, 100 °C, 18 h	69 (48)	0	17
11	$Pd(PPh_3)_4$ (5 mol %), Cs_2CO_3 (1.6 equiv), toluene, 100 °C, 5 h	30	0	0

[a]Determined by ^{1}H NMR. Numbers in parentheses show purified yield. [b]Reaction performed with rigorously dried bases and degassed solvent.

reaction and resulted in an increased amount of tetrahydroquinoline **16** formation (Table 2, entry 10).

Although small amounts of the tetrahydroquinoline **16** were formed in several reactions (Table 2, entries 4, 5, and 8–10) further attempts to switch selectivity to favor tetrahydroquinoline formation were unsuccessful. This was assumed to be due to the significant difference in rates of formation of the 5- and 6-membered rings. Attention was therefore shifted to the cyclization of orthogonally protected diamine **7a** (Scheme 7, Table 3). It was postulated that the presence of the trifluoroacetyl protecting group would enable selective tetrahydroquinoline formation due to the significantly lower nucleophilicity of the amide nitrogen. Gratifyingly, complete reversal of selectivity was observed when **7a** was submitted to the *N*-arylation conditions, with no formation of the trifluoroacetyl-protected indoline **17** observed (Table 3, entry 1). Tetrahydroquinoline **18a** was formed in 54% yield,

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Scheme 7. Tetrahydroquinoline Formation

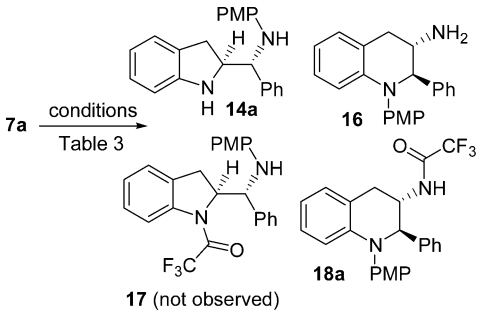


Table 3. Optimization of Tetrahydroquinoline Formation

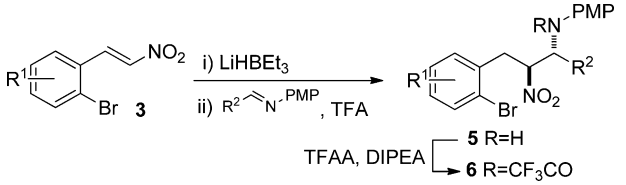
		conversion (%)[a]		
entry	conditions	18a	16	14a
1	$Pd(PPh_3)_4$ (5 mol %), NaO*t*Bu (1.6 equiv), K_2CO_3 (1.6 equiv), toluene, 90 °C, 18 h	72 (54)	10	12 (7)
2	$Pd(dppf)Cl_2$ (5 mol %), dppf (15 mol %), NaO*t*Bu (1.4 equiv), toluene, 90 °C, 18 h	20	0	5
3	$Pd_2(dba)_3$ (2.5 mol %), BINAP (7.5 mol %), NaO*t*Bu (1.4 equiv), toluene, 90 °C, 5 h	<5	0	<5
4	$Pd(PPh_3)_4$ (5 mol %), NaO*t*Bu (1.6 equiv), toluene, 90 °C, 18 h	71 (54)	19	<5
5	$Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (1.6 equiv), toluene, 90 °C, 18 h	90 (76)	0	0
6	$Pd(PPh_3)_4$ (5 mol %), LiHMDS (1.6 equiv), toluene, 90 °C, 18 h	<10	0	0
7	$Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (2.5 equiv), toluene, 100 °C, 18 h	100 (98)	0	0

[a]Determined by ^1H NMR. Numbers in parentheses show purified yield.

accompanied by deprotected tetrahydroquinoline **16** and indoline **14a** (Scheme 7). These additional products are presumably formed via deprotection of the trifluoroacetyl group by *tert*-butoxide anions present in the reaction. Deprotection prior to cyclization results in the formation of monoprotected diamine **13**, which can then undergo cyclization forming indoline **14a**. Various other catalyst systems were investigated but all failed to compete with the $Pd(PPh_3)_4$-catalyzed reaction (Table 3, entries 2 and 3). By varying the bases used in the reaction it became clear that the trifluoroacetyl group would not tolerate NaO*t*Bu, with deprotection occurring both before and after cyclization to give multiple products (Table 3, entry 4). Using only K_2CO_3 gave a very clean reaction affording 76% of **18a** (Table 3, entry 5). Increasing the equivalents of K_2CO_3 and increasing the temperature to 100 °C resulted in complete conversion to tetrahydroquinoline **18a**, which was isolated in 98% yield (Table 3, entry 7).

Following the successful synthesis of both indoline **14a** and tetrahydroquinoline **18a**, with excellent levels of diastereoselectivity and high yield, attention was then turned to investigating the scope of the methodology. This began with the reductive nitro-Mannich reaction, which was applied to a range of imines and nitroalkenes (Scheme 8, Table 4). The nitro-Mannich reactions to form **5** proceeded with excellent diastereoselectivity and the subsequent trifluoroacetamides **6** were formed in good yield for a wide range of imines derived from aryl, heteroaryl, and alkyl substituents (Table 4, entries 1–15). Enhancement of the diastereoselectivity of the *β*-

Scheme 8. Scope of Reductive Nitro-Mannich Route to Cyclization Precursors 6



nitroacetamide products **6** was achieved by separation of the two diastereomers during purification by flash column chromatography. The imines derived from cyclohexyl and *tert*-butyl aldehydes performed well in the nitro-Mannich reaction, with good conversion and diastereoselectivity, but failed to undergo trifluoroacetyl protection (Table 4, entries 6 and 7). The product derived from 2-trifluoromethylbenzaldehyde also suffered from a slower rate in the trifluoroacetyl protection and required the use of additional TFAA and base to achieve satisfactory yields (Table 4, entry 15). A number of substituted 2-bromo-*β*-nitrostyrenes were also employed in the reaction and gave uniformly high yields and diastereoselectivities (Table 4, entries 16–19). Likewise, the nitroalkene derived from 2-chloro-3-pyridine carboxaldehyde also gave a good yield of the desired product (Table 4, entry 20).

The successfully synthesized *β*-nitroacetamides **6a–d,g–t** were then used to investigate the scope of the nitro reduction (Scheme 9, Table 5). The reduction gave uniformly high yields in the majority of cases with yields ranging from 79% to 95% (Table 5, entries 1–6 and 8–15). Problems arising from debromination occurred when forming compounds **7i**, **7r**, and **7s** (Table 5, entries 7, 16, and 17). Although trace amounts of the respective debrominated products were formed in the majority of cases, these could be removed either by column chromatography or recrystallization. The reductions to form compounds **7i**, **7r**, and **7s**, however, resulted in significant amounts of debrominated product which could not be removed by either column chromatography or recrystallization, thereby preventing the isolation of these products in pure form. It should be noted that debromination of dibromo analogue **7i** occurred at the C–Br bond in the R^2 substituent, resulting in the formation of **7a**. The reactive C–Cl bond in pyridine analogue **6t** was not stable under the reduction conditions and complete dechlorination resulted (Table 5, entry 18).

To overcome these dehalogenation problems and resolve the problem associated with the failure of compounds **5f** and **5g** to undergo trifluoroacetyl protection, alternative routes to the orthogonally protected diamines were investigated (Scheme 10). Previous studies within our group have shown that unstable *β*-nitroamines can be cleanly reduced to *β*-aminohydroxylamines by using aluminum amalgam and MeOH.[21] The stable *β*-aminohydroxylamines could then be reduced to 1,2-diamines by either hydrogenation or with $LiAlH_4$. Initial investigations focused on the reduction of cyclohexyl analogue **5f** (Scheme 10, route A). Using slightly modified conditions to those reported previously,[21] the reduction proceeded smoothly to yield *β*-aminohydroxylamine **19** in 56% yield and with excellent dr after separation of the diastereomers by column chromatography. The *anti*-configuration of **19** was confirmed by single-crystal X-ray crystallography (see the Supporting Information). Further reduction with $LiAlH_4$, followed by protection of the crude diamine yielded 81% of orthogonally protected diamine **7f**. The use of the Zn/HCl reduction on the

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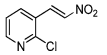
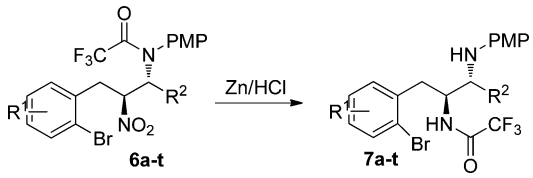
Table 4. Scope of the Reductive Nitro-Mannich Reaction

Entry	R^1	R^2	**5** (% conv.)[a]	*dr* (*anti*:*syn*)[a]	**6** (%,from **3**)[b]	*dr* (*anti*:*syn*)[a]
1	H	Ph	**a** (>95%)	>95:5	**a** (71%)	>95:5
2	H	2-furyl	**b** (>95%)	85:15	**b** (70%)	>95:5
3	H	3-furyl	**c** (>95%)	85:15	**c** (69%)	>95:5
4	H	2-thienyl	**d** (>95%)	90:10	**d** (74%)	>95:5
5	H	*n*-pentyl	**e** (>95%)	95:5	**e** (85%)	>95:5
6	H	cyclohexyl	**f** (>95%)	80:20	**f** (-)[c]	-
7	H	*tert*-butyl	**g** (90%)	85:15	**g** (-)[c]	-
8	H	2-Me-C_6H_4	**h** (>95%)	90:10	**h** (81%)	>95:5
9	H	2-Br-C_6H_4	**i** (>95%)	90:10	**i** (83%)	>95:5
10	H	2-MeO-C_6H_4	**j** (>95%)	90:10	**j** (83%)	>95:5
11	H	3-MeO-C_6H_4	**k** (>95%)	>95:5	**k** (83%)	>95:5
12	H	4-MeO-C_6H_4	**l** (95%)	>95:5	**l** (82%)	>95:5
13	H	2-CF_3-C_6H_4	**m** (>95%)	90:10	**m** (60%)[d]	>95:5
14	H	3-CF_3-C_6H_4	**n** (>95%)	>95:5	**n** (91%)	>95:5
15	H	4-CF_3-C_6H_4	**o** (>95%)	>95:5	**o** (90%)	>95:5
16	5-F	Ph	**p** (>95%)	>95:5	**p** (82%)	>95:5
17	4-MeO,5-MeO	Ph	**q** (>95%)	>95:5	**q** (88%)	>95:5
18	4-MeO,5-MeO	2-MeO-C_6H_4	**r** (>95%)	85:15	**r** (72%)	>95:5
19	3-OBn,4-MeO	Ph	**s** (>95%)	>95:5	**s** (82%)	>95:5
20		Ph	**t** (>95%)	>95:5	**t** (59%)	>95:5

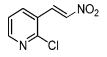
[a]Determined by ^{1}H NMR. [b]Isolated yields. [c]No reaction occurred. [d]Protection performed with 5.0 equiv TFAA and 5.0 equiv pyridine.

Scheme 9. Scope of Nitro Reduction



crude β-nitroamines was also investigated. It was previously thought that these compounds would not be stable to acidic reduction conditions due to their propensity to undergo retro-addition. However, in the absence of a trifluoroacetyl-protecting group the reduction becomes much more facile and can be performed with only 20 equiv of HCl and 10 equiv of zinc. The rate of reduction is also increased and therefore minimizes the amount of retro-addition that occurs. These conditions were used to reduce β-nitroamine **5f** which, after subsequent trifluoroacetyl protection of the diamine, gave a 68% yield of orthogonally protected diamine **7f** and with no observed debromination (Scheme 5, route B). It was found that separation of the diastereomers of **7f** could not be achieved effectively by column chromatography, but recrystallization could be used to obtain the major *anti*-diastereomer with dr > 95:5. The use of Zn/HCl was found to be preferable to aluminum amalgam as it gave a higher overall yield, required only a single chromatographic purification, and also avoided the use of toxic mercury reagents. These conditions enabled the formation of orthogonally protected 1,2-diamines **7g**, **7i**, **7r**, and **7s** in moderate to good yields (Scheme 6). Because of the high reactivity of the C−Cl bond in pyridine analogue **5t**,

Table 5. Scope of Nitro Reduction

Entry	R^1	R^2	Product	Yield (%)[a]
1	H	Ph	**7a**	89
2	H	2-furyl	**7b**	91
3	H	3-furyl	**7c**	93
4	H	2-thienyl	**7d**	82
5	H	*n*-pentyl	**7e**	95
6	H	2-Me-C_6H_4	**7h**	91
7	H	2-Br-C_6H_4	**7i**	75% conv. (25%)[b,c]
8	H	2-MeO-C_6H_4	**7j**	94
9	H	3-MeO-C_6H_4	**7k**	82
10	H	4-MeO-C_6H_4	**7l**	91
11	H	2-CF_3-C_6H_4	**7m**	82
12	H	3-CF_3-C_6H_4	**7n**	88
13	H	4-CF_3-C_6H_4	**7o**	88
14	5-F	Ph	**7p**	89
15	4-MeO,5-MeO	Ph	**7q**	79
16	4-MeO,5-MeO	2-MeO-C_6H_4	**7r**	90% conv. (10%)[b,c]
17	3-OBn,4-MeO	Ph	**7s**	65% conv. (35%)[b,c]
18		Ph	**7t**	0% conv. (>95%)[b]

[a]Isolated yields. [b]Determined by ^{1}H MNR. Numbers in parentheses show conversion to dehalogenated β-aminoacetamide. [c]Debromination caused inseparable mixture of products.

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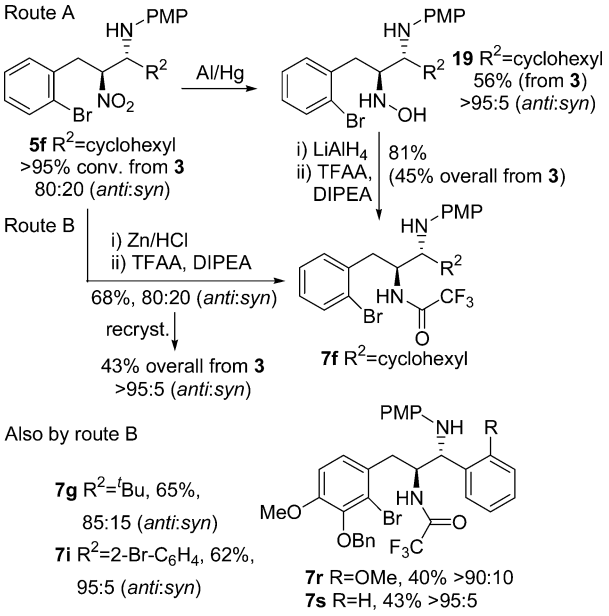
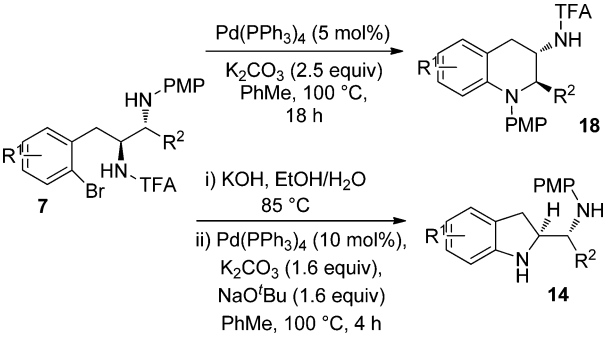
Scheme 10. Alternative Reduction Strategy



application of the Zn/HCl reduction protocol again resulted in dechlorination, with no desired product isolated. This was also the case when the Al/Hg reduction protocol was used, as the reduction of the hydroxylamine intermediate with $LiAlH_4$ resulted in dechlorination. The failure to synthesize diamine **7t** represents a limitation of the current synthesis and further investigations into milder reduction protocols are required.

With all of the desired orthogonally protected diamines formed, the synthesis of the fused heterocycles was surveyed (Scheme 11, Table 6). The tetrahydroquinolines **18** were formed in excellent yields in nearly all cases.

Scheme 11. Heterocycle Formation



Examples containing bulky alkyl substituents, such as cyclohexyl and *tert*-butyl analogues **18f** and **18g**, were formed in lower yields due to the unexpected formation of indolines **20** and **21** in 15% and 38% yield, respectively (Scheme 12). The use of 10 mol % of $Pd(PPh_3)_4$ was required to achieve a good yield of **18f** due to the instability of **7f** under the reaction conditions.

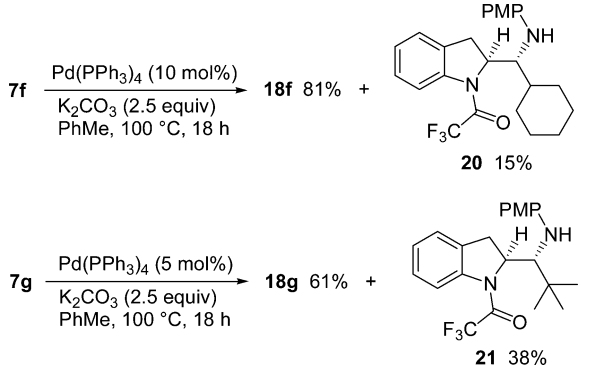
When dibromo analogue **7i** was submitted to the cyclization conditions, **18i** was formed in only 27% yield because of competing oxidative addition of the palladium catalyst to both C−Br bonds. Although the yield was low, the reaction demonstrates surprisingly high selectivity (ca. 85:15) for the desired C−Br bond, considering this selectivity arises from

Table 6. Scope of Heterocycle Formation

entry	R^1	R^2	**18** (%)[a]	**14** (%, two steps)[a]
a	H	Ph	98	86[b]
b	H	2-furyl	92	69
c	H	3-furyl	94	66
d	H	2-thienyl	91	73
e	H	*n*-pentyl	89	66
f	H	cyclohexyl	81[c]	80
g	H	*tert*-butyl	61	87
h	H	2-Me-C_6H_4	88	74
i	H	2-Br-C_6H_4	54[c] (27)[d]	83[e]
j	H	2-MeO-C_6H_4	98	56
k	H	3-MeO-C_6H_4	90	66
l	H	4-MeO-C_6H_4	98	64
m	H	2-CF_3-C_6H_4	97	65
n	H	3-CF_3-C_6H_4	99	59
o	H	4-CF_3-C_6H_4	99	78
p	5-F	Ph	93	50
q	4-MeO, 5-MeO	Ph	91	48
r	4-MeO, 5-MeO	2-MeO-C_6H_4	88	42
s	3-OBn, 4-MeO	Ph	31	58

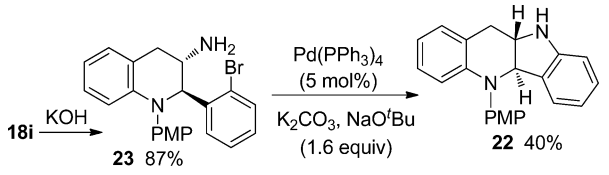
[a]Isolated yields. [b]5 mol % of $Pd(PPh_3)_4$. [c]10 mol % of $Pd(PPh_3)_4$. [d]Yield obtained when using 5 mol % of $Pd(PPh_3)_4$. [e]NaO-*t*-Bu (3.2 equiv) and K_2CO_3 (3.2 equiv).

Scheme 12. Trifluoroacetyl-Protected Indoline Formation



relatively small steric differences between each C−Br bond. The yield of **18i** could be improved to 54% by doubling the amount of catalyst to 10 mol %. This product was then used to synthesize tetracycle **22**, first by removal of the trifluoroacetyl group, furnishing primary amine **23** in 87% yield, and subsequent cyclization, to give **22** in 40% yield (Scheme 13).

Scheme 13. Synthesis of Tetracycle 22



The modest yield of the final cyclization reaction is believed to be due to the formation of a relatively strained *trans*-fused ring system. The cyclization also failed to provide a satisfactory yield of tetrahydroquinoline **18s**, presumably due to the formation of a sterically crowded product with the PMP and OBn groups in close proximity to one another (Table 6).

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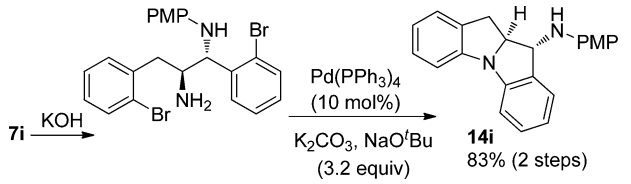
The final set of cyclizations to be performed were the indoline syntheses, requiring initial trifluoroacetyl deprotection of orthogonally protected diamines **7a–s** and subsequent cyclization of the monoprotected diamines (Table 6). Although the original conditions developed for the synthesis of indoline **14a** from diamine **13** used 5 mol % of $Pd(PPh_3)_4$, it was found that the byproduct resulting from the instability of some of the indoline products **14** caused a decrease in catalyst efficiency and that more reproducible results could be obtained by increasing the amount of $Pd(PPh_3)_4$ to 10 mol %. This catalyst loading was then used in the investigation into the scope of indoline formation. The reactions proceeded with moderate to high yield over the two steps to furnish indoline products **14a–s**. The yields were consistent for a range of aryl, heteroaryl and alkyl containing analogues (Table 6). The yields of the substituted indolines **14p–s** were found to be lower as a result of their lower stabilities, which resulted in difficult purifications (Table 6). The product formed from the reaction of dibromo analogue **7i** was tetracycle **14i** (Table 6 and Scheme 14). This resulted from a double cyclization reaction which required the use of additional base for the reaction to reach completion.

Scheme 14. Synthesis of Tetracycle 14i



The yields for the formation of indolines **14a–s** were generally found to be lower than those obtained for the formation of tetrahydroquinolines **18a–s**. This is due to the lower stability of the indoline products, some of which proved to be difficult to purify due to degradation during column chromatography. This was particularly evident for the substituted indolines **14p–r** which could only be isolated in relatively modest yields (Table 6).

CONCLUSION

In conclusion, we have developed an expedient and highly diastereoselective synthesis of both 3-aminotetrahydroquinolines **18a–s** and 2-aminomethylene indolines **14a–s** that relies upon a reductive nitro-Mannich reaction and reduction to form a stereochemically defined 1,2-diamine. A chemoselective intramolecular *N*-arylation reaction is dictated by the most nucleophilic amine which is controlled by the presence or not of a trifluoroacetamide protecting group. This short and efficient reaction sequence has allowed access to an array of fused heterocyclic structures, thereby demonstrating the synthetic potential of the nitro-Mannich reaction. The demonstration of carbon and heteroatom nucleophiles in this process and other cyclization strategies to synthesize heterocycles is currently under investigation, as is the development of an asymmetric variant and the application of this methodology to natural product synthesis.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of β-Nitroamines 5 by the Reductive Nitro-Mannich Reaction (Table 4). To a solution of nitroalkene (1.00 mmol) in CH_2Cl_2 (5.0 mL) at room temperature was added dropwise lithium triethylborohydride (1.0 M in THF, 1.05 mmol). The mixture was stirred at room temperature for 20 min to give a white precipitate before being cooled to −78 °C. A solution of imine (1.10 mmol) in CH_2Cl_2 (2.8 mL) was added and the mixture stirred for 10 min before the dropwise addition of trifluoroacetic acid (1.15 mmol) over 30 s. The reaction was stirred at −78 °C for 90 min before being removed from the cold bath and allowed to warm for 5 min giving a yellow solution. The reaction was quenched by the addition of satd aq $NaHCO_3$ and the product extracted into Et_2O. The combined organic phases were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give the crude β-nitroamine which was used without further purification.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-phenylpropyl)-4-methoxyaniline (**5a**).* Nitroalkene **3** (299 mg, 1.31 mmol) afforded crude β-nitroamine **5a** as a yellow solid (812 mg, >95% conv, >95:5 dr): IR ν_{max} (neat) 3393, 3058–2833, 1552, 1511, 1243 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.43 (1H, dd, *J* = 14.7, 10.9), 3.55 (1H, dd, *J* = 14.7, 2.8), 3.72 (3H, s), 4.26 (1H, d, *J* = 6.8), 4.93 (1H, t, *J* = 6.4), 5.19 (1H, ddd, *J* = 10.9, 5.9, 2.9), 6.60 (2H, dm, *J* = 8.9), 6.74 (2H, dm, *J* = 8.9), 7.10–7.26 (3H, m), 7.32–7.42 (5H, m), 7.53 (1H, dd, *J* = 7.9, 0.9); ^{13}C NMR (101 MHz, $CDCl_3$) δ 35.7 (CH_2), 55.7 (CH_3), 62.1 (CH), 91.7 (CH), 114.8 (CH), 115.9 (CH), 124.3 (*C*), 127.1 (CH), 127.9 (CH), 128.7 (CH), 129.1 (CH), 129.3 (CH), 131.6 (CH), 133.2 (CH), 135.0 (*C*), 137.4 (*C*), 139.9 (*C*), 153.1 (*C*); MS (ESI^+) *m*/*z* 441 + 443 (1:1, 42, M + H^+), 212 (67, $PhCH^+NHPMP$); HRMS $C_{22}H_{22}(^{79}Br)N_2O_3$ calcd 441.0808, found 441.0798.

N-((1S,2S*)-3-(2-Bromophenyl)-1-(furan-2-yl)-2-nitropropyl)-4-methoxyaniline (**5b**).* Nitroalkene **3** (1.01 g, 4.42 mmol) afforded crude β-nitroamine **5b** as a yellow oily solid (2.59 g, >95% conv, 85:15 dr): IR ν_{max} (neat) 3368, 3124–2834, 1551, 1510, 1240, 1034 cm^{-1}; ^1H NMR^{anti} (400 MHz, $CDCl_3$) δ 3.47 (1H, dd, *J* = 14.7, 10.0), 3.64 (1H, dd, *J* = 14.6, 3.9), 3.75 (3H, s), 4.16 (1H, br d, *J* = 9.6), 5.02 (1H, dd, *J* = 9.9, 6.1), 5.25 (1H, ddd, *J* = 10.0, 6.1, 4.0), 6.30–6.34 (2H, m), 6.64–6.68 (2H, m), 6.75–6.80 (2H, m), 7.12–7.27 (3H, m), 7.41 (1H, m), 7.57 (1H, m); ^1H NMR^{syn} (400 MHz, $CDCl_3$) δ 3.30 (1H, dd, *J* = 14.3, 4.7), 3.41 (1H, dd, *J* = 14.3, 9.6), 3.74 (3H, s), 4.16 (1H, br d, *J* = 9.6), 4.90 (1H, dd, *J* = 10.7, 7.9), 5.33 (1H, ddd, *J* = 9.6, 7.9, 4.8), 6.30–6.34 (2H, m), 6.64–6.68 (2H, m), 6.75–6.80 (2H, m), 7.12–7.27 (3H, m), 7.41 (1H, m), 7.55 (1H, m); ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 36.4 (CH_2), 55.8 (CH_3), 56.5 (CH), 89.3 (CH), 108.9 (CH), 110.7 (CH), 115.0 (CH), 116.4 (CH), 124.5 (*C*), 128.1 (CH), 129.5 (CH), 131.8 (CH), 133.3 (CH), 135.1 (*C*), 139.6 (*C*), 143.0 (CH), 150.1 (*C*), 153.6 (*C*); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 37.5 (CH_2), 55.7 (CH_3), 56.4 (CH), 90.0 (CH), the remaining signals could not be determined; MS (EI) *m*/*z* 430 + 432 (1:1, 5, M^+), 202 (96, $FurylCH^+NHPMP$); HRMS $C_{20}H_{19}(^{79}Br)N_2O_4$ calcd 430.0523, found 430.0531.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(furan-3-yl)-2-nitropropyl)-4-methoxyaniline (**5c**).* Nitroalkene **3** (1.29 g, 5.65 mmol) afforded crude β-nitroamine **5c** as a yellow oily solid (3.20 g, >95% conv, 85:15 dr): IR ν_{max} (neat) 3392, 3131–2834, 1551, 1510, 1241, 1025 cm^{-1}; ^1H NMR^{anti} (600 MHz, $CDCl_3$) δ 3.43 (1H, dd, *J* = 14.6, 10.3), 3.59 (1H, dd, *J* = 14.6, 3.5), 3.76 (3H, s), 4.00 (1H, br s), 4.91 (1H, d, *J* = 4.5), 5.16 (1H, ddd, *J* = 10.2, 6.3, 3.8), 6.41 (1H, m), 6.66 (2H, dm, *J* = 8.9), 6.79 (2H, dm, *J* = 8.9), 7.16 (1H, td, *J* = 7.6, 1.8), 7.20 (1H, dd, *J* = 7.6, 1.7), 7.25 (1H, td, *J* = 7.5, 1.0), 7.42 (1H, m), 7.47 (1H, s), 7.57 (1H, dd, *J* = 8.0, 0.9); ^1H NMR^{syn} (600 MHz, $CDCl_3$) δ 0.35 (1H, dd, *J* = 14.3, 9.7), 3.39 (1H, dd, *J* = 14.4, 5.0), 3.75 (3H, s), 4.06 (1H, br s), 4.81 (1H, br m), 5.22 (1H, ddd, *J* = 9.6, 7.3, 5.0), the remaining signals could not be determined; ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 36.7 (CH_2), 54.7 (CH), 55.8 (CH_3), 90.3 (CH), 108.6 (CH), 115.0 (CH), 116.3 (CH), 122.2 (*C*), 124.5 (*C*), 128.1 (CH), 129.5 (CH), 131.7 (CH), 133.3 (CH), 135.0 (*C*), 139.7 (*C*), 140.8 (CH), 144.1 (CH), 153.5 (*C*); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 37.7 (CH_2), 54.3 (CH), 55.7 (CH_3), 91.1 (CH), the remaining signals could not be determined; MS (EI) *m*/*z* 432 + 430 (1:1, 25, M^+), 202 (98, $FurylCH^+NHPMP$); HRMS $C_{20}H_{19}(^{79}Br)N_2O_4$ calcd 430.0523, found 430.0518.

N-((1S,2S*)-3-(2-Bromophenyl)-2-nitro-1-(thiophene-2-yl)-propyl)-4-methoxyaniline (**5d**).* Nitroalkene **3** (85 mg, 0.37 mmol) afforded crude β-nitroamine **5d** as a yellow solid (173 mg, >95% conv,

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90:10 dr): IR ν_{max} (neat) 3387, 3069−2833, 1551, 1509, 1241, 1026 cm^{-1}; ^1H NMR^{anti} (600 MHz, $CDCl_3$) δ 3.48 (1H, m), 3.67 (1H, dd, J = 14.7, 2.7), 3.74 (3H, s), 4.17 (1H, br d, J = 7.4), 5.18−5.22 (2H, m), 6.66 (2H, dm, J = 8.9), 6.77 (2H, dm, J = 8.9), 6.99 (1H, dd, J = 5.0, 3.6), 7.07 (1H, d, J = 3.5), 7.15 (1H, td, J = 7.6, 1.9), 7.20 (1H, dd, J = 7.6, 1.8), 7.25 (1H, td, J = 7.4, 1.1), 7.27 (1H, m), 7.56 (1H, dd, J = 8.0, 1.1); ^1H NMR^{syn} (600 MHz, $CDCl_3$) δ 3.35 (1H, m), 3.73 (3H, s), 5.08 (1H, dd, J = 9.7, 7.8), 5.26 (1H, ddd, J = 8.9, 7.8, 5.6), the remaining signals could not be determined; ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 36.5 (CH_2), 55.7 (CH_3), 58.2 (*C*H), 91.6 (*C*H), 115.0 (*C*H), 116.2 (*C*H), 124.5 (*C*), 125.7 (*C*H), 125.9 (*C*H), 127.5 (*C*H), 128.1 (*C*H), 129.6 (*C*H), 131.7 (*C*H), 133.3 (*C*H), 134.9 (*C*), 139.6 (*C*), 141.5 (*C*), 153.6 (*C*); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 38.0 (CH_2), 55.7 (CH_3), 58.0 (*C*H), 92.0 (*C*H), the remaining signals could not be determined; MS (EI) m/z 448 + 446 (1:1, 20, M^+), 217 (96, thiophenylCH$^+$NHPMP); HRMS $C_{20}H_{19}(^{79}Br)N_2O_3S$ calcd 446.0294, found 446.0310.

N-((2S,3R*)-1-(2-Bromophenyl)-2-nitrooctan-3-yl)-4-methoxyaniline (**5e**).* Nitroalkene **3** (968 mg, 4.24 mmol) afforded crude β-nitroamine **5e** as a yellow oil (2.73 g, >95% conv, 95:5 dr): IR ν_{max} (neat) 3379, 3060−2834, 1546, 1509, 1466, 1441, 1234, 1036, 1025 cm^{-1}; ^1H NMR^{anti} (600 MHz, $CDCl_3$) δ 0.90 (3H, t, J = 6.9), 1.29−1.44 (6H, m), 1.61 (1H, m), 1.81 (1H, m), 3.39 (1H, dd, J = 14.5, 5.0), 3.45 (1H, dd, J = 14.4, 9.2), 3.76 (3H, s), 3.78 (1H, m), 4.96 (1H, dt, J = 9.2, 4.7), 6.53 (2H, dm, J = 8.9), 6.77 (2H, dm, J = 8.9), 7.15 (1H, td, J = 7.6, 1.6), 7.21 (1H, dd, J = 7.6, 1.7), 7.25 (1H, td, J = 7.3, 1.0), 7.57 (1H, dd, J = 8.0, 0.9); ^1H NMR^{syn} (600 MHz, $CDCl_3$) δ 3.27 (1H, dd, J = 14.3, 5.1), 3.73 (3H, s), 5.13 (1H, dt, J = 9.9, 4.4), the remaining signals could not be determined; ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 14.2 (CH_3), 22.6 (CH_2), 26.1 (CH_2), 30.9 (CH_2), 31.7 (CH_2), 36.4 (CH_2), 55.8 (CH_3), 57.4 (*C*H), 89.4 (*C*H), 115.1 (*C*H), 115.5 (*C*H), 124.6 (*C*), 128.0 (*C*H), 129.4 (*C*H), 131.7 (*C*H), 133.3 (*C*H), 135.4 (*C*), 140.4 (*C*), 152.9 (*C*); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 55.6 (CH_3), 56.9 (*C*H), 89.7 (*C*H), the remaining signals could not be determined; MS (EI) m/z 436 + 434 (1:1, 10, M^+), 206 (100, $CH_3(CH_2)_4CH^+$NHPMP); HRMS $C_{21}H_{28}(^{79}Br)N_2O_3$ calcd 434.1200, found 434.1204.

N-((1R,2S*)-3-(2-Bromophenyl)-1-cyclohexyl-2-nitropropyl)-4-methoxyaniline (**5f**).* Nitroalkene **3** (103 mg, 0.452 mmol) afforded crude β-nitroamine **5f** as a yellow solid (250 mg, >95% conv, 80:20 dr): IR ν_{max} (neat) 3408, 3062−2853, 1547, 1510, 1241, 1027 cm^{-1}; ^1H NMR^{anti} (600 MHz, $CDCl_3$) δ 1.08−1.29 (4H, m), 1.33 (1H, qd, J = 12.3, 3.1), 1.53 (1H, m), 1.64−1.85 (5H, m), 3.25 (1H, dd, J = 14.6, 11.2), 3.42 (1H, d, J = 10.5), 3.55 (1H, dd, J = 14.6, 2.8), 3.76 (3H, s), 3.84 (1H, m), 4.96 (1H, ddd, J = 11.2, 8.4, 2.8), 6.68 (2H, m), 6.80 (2H, m), 7.12 (2H, m), 7.21 (1H, td, J = 7.4, 1.1), 7.54 (1H, d, J = 8.0); ^1H NMR^{syn} (600 MHz, $CDCl_3$) δ 1.04−1.37 (5H, m), 1.52−1.94 (5H, m), 3.32 (1H, dd, J = 14.3, 4.0), 3.41 (1H, dd, J = 14.3, 10.1), 3.61 (1H, m), 3.76 (3H, s), 3.84 (1H, d, J = 10.9), 5.22 (1H, ddd, J = 10.0, 5.6, 4.3), 6.62 (2H, m), 6.78 (2H, m), 7.08 (1H, dd, J = 7.5, 1.7), 7.13−7.20 (2H, m), 7.57 (1H, m); ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 26.0 (CH_2), 26.2 (CH_2), 26.3 (CH_2), 26.4 (CH_2), 31.3 (CH_2), 37.4 (CH_2), 40.2 (*C*H), 55.9 (CH_3), 62.2 (*C*H), 89.9 (*C*H), 114.6 (*C*H), 115.2 (*C*H), 124.2 (*C*), 128.1 (*C*H), 129.3 (*C*H), 131.5 (*C*H), 133.2 (*C*H), 135.5 (*C*), 142.1 (*C*), 152.6 (*C*); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 26.1 (CH_2), 26.1 (CH_2), 26.2 (CH_2), 28.9 (CH_2), 30.9 (CH_2), 38.5 (CH_2), 41.5 (*C*H), 55.9 (CH_3), 61.7 (*C*H), 89.4 (*C*H), 114.2 (*C*H), 115.1 (*C*H), 124.4 (*C*), 128.1 (*C*H), 129.5 (*C*H), 131.7 (*C*H), 133.3 (*C*H), 135.1 (*C*), 142.4 (*C*), 152.2 (*C*); MS (EI) m/z 446 + 448 (1:1, 11, M^+), 317 + 319 (1:1, 31, M-(Cy + NO_2)), 218 (100, CyCH$^+$NHPMP); HRMS $C_{22}H_{27}(^{79}Br)N_2O_3$ calcd 446.1200, found 446.1200.

N-((2S,3R*)-1-(2-Bromophenyl)-4,4-dimethyl-2-nitropentan-3-yl)-4-methoxyaniline (**5g**).* Nitroalkene **3** (1.03 g, 4.52 mmol) afforded crude β-nitroamine **5g** as a yellow oil (2.20 g, 92% conv, 85:15 dr): IR ν_{max} (neat) 3415, 3060−2833, 1548, 1509, 1471, 1232, 1036, 1024 cm^{-1}; ^1H NMR^{anti} (600 MHz, $CDCl_3$) δ 1.07 (9H, s), 3.18 (1H, dd, J = 14.3, 12.0), 3.56 (1H, dd, J = 14.5, 3.0), 3.56 (1H, m), 3.78 (3H, s), 3.90 (1H, dd, J = 8.6, 6.5), 5.12 (1H, ddd, J = 11.6, 6.3, 3.2), 6.78 (2H, dm, J = 8.9), 6.84 (2H, dm, J = 8.9), 7.06 (1H, dd, J = 7.5, 1.3), 7.13 (1H, td, J = 7.7, 1.6), 7.20 (1H, td, J = 7.5, 1.0), 7.55 (1H, dd, J = 7.9, 0.7); ^1H NMR^{syn} (600 MHz, $CDCl_3$) δ 1.04 (9H, s), 3.14 (1H, dd, J = 14.4, 3.7), 3.38 (1H, dd, J = 14.4, 10.3), 3.43 (1H, d, J = 10.5), 4.51 (1H, d, J = 10.7), 5.38 (1H, m), the remaining signals could not be determined; ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 26.7 (CH_3), 37.5 (*C*), 38.7 (CH_2), 55.9 (CH_3), 65.7 (*C*H), 90.2 (*C*H), 114.0 (*C*H), 115.3 (*C*H), 124.1 (*C*), 128.0 (*C*H), 129.3 (*C*H), 131.7 (*C*H), 133.1 (*C*H), 135.5 (*C*), 142.6 (*C*), 152.4 (*C*); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 27.1 (CH_3), 37.3 (*C*), 40.4 (CH_2), 55.6 (CH_3), 65.2 (*C*H), 87.7 (*C*H), the remaining signals could not be determined; MS (EI) m/z 420 + 422 (1:1, 14, M^+), 317 + 319 (1:1, 100, M^+ − ($C(CH_3)_3$ + NO_2)), 192 (49, PMPNHCH$^+$C$(CH_3)_3$); HRMS $C_{20}H_{25}(^{79}Br)N_2O_3$ calcd 420.1043, found 420.1045.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-(o-tolyl)propyl)-4-methoxyaniline (**5h**).* Nitroalkene **3** (64 mg, 0.28 mmol) afforded crude β-nitroamine **5h** as a yellow oily solid (148 mg, >95% conv, 90:10 dr): IR ν_{max} (neat) 3399, 3057−2833, 1549, 1509, 1233, 1026 cm^{-1}; ^1H NMR^{anti} (600 MHz, $CDCl_3$) δ 2.54 (3H, s), 3.53 (1H, dd, J = 14.7, 11.2), 3.59 (1H, dd, J = 14.7, 2.6), 3.74 (3H, s), 4.19 (1H, br s), 5.22 (1H, ddd, J = 11.1, 5.7, 2.6), 5.29 (1H, d, J = 5.7), 6.62 (2H, dm, J = 8.9), 6.78 (2H, dm, J = 8.9), 7.12 (1H, m), 7.22−7.27 (5H, m), 7.52 (2H, m); ^1H NMR^{syn} (600 MHz, $CDCl_3$) δ 2.62 (3H, s), 3.32 (1H, dd, J = 14.1, 4.4), 3.72 (3H, s), 5.09 (1H, d, J = 6.7), the remaining signals could not be determined; ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 19.4 (CH_3), 34.9 (CH_2), 55.8 (CH_3), 58.7 (*C*H), 90.4 (*C*H), 115.0 (*C*H), 115.8 (*C*H), 124.2 (*C*), 126.3 (*C*H), 127.0 (*C*H), 128.1 (*C*H), 128.5 (*C*H), 129.5 (*C*H), 131.5 (*C*H), 131.7 (*C*H), 133.3 (*C*H), 135.3 (*C*), 135.9 (*C*), 136.0 (*C*), 140.4 (*C*), 153.2 (*C*); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 19.6 (CH_3), 37.8 (CH_2), 55.7 (CH_3), 57.3 (*C*H), 91.9 (*C*H), the remaining signals could not be determined; MS (EI) m/z 456 + 454 (1:1, 13, M^+), 226 (100, ArCH$^+$NHPMP); HRMS $C_{23}H_{23}(^{79}Br)N_2O_3$ calcd 454.0887, found 454.0876.

N-((1R,2S*)-1,3-Bis(2-bromophenyl)-2-nitropropyl)-4-methoxyaniline (**5i**).* Nitroalkene **3** (61 g, 0.27 mmol) afforded crude β-nitroamine **5i** as a yellow solid (196 mg, >95% conv, 90:10 dr). The *anti* diastereomer could be obtained in pure form by recrystallization from Et_2O/petroleum ether to give a yellow solid: mp 117−119 °C; R_f^{anti} 0.25 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3400, 3063−2834, 1550, 1511, 1244, 1025 cm^{-1}; ^1H NMR^{anti} (600 MHz, $CDCl_3$) δ 3.40 (1H, br m), 3.48 (1H, dd, J = 14.6, 11.7), 3.71 (3H, s), 4.52 (1H, br s), 5.40 (1H, br s), 5.43 (1H, br d, J = 11.4), 6.54 (2H, d, J = 8.9), 6.73 (2H, dm, J = 8.9), 7.11 (1H, m), 7.19−7.23 (3H, m), 7.33 (1H, m), 7.49 (1H, d, J = 7.9), 7.52 (1H, br d, J = 7.4), 7.64 (1H, dd, J = 8.0, 0.8); ^1H NMR^{syn} (600 MHz, $CDCl_3$) δ 3.46 (1H, dd, J = 13.7, 4.7), 3.63 (1H, dd, J = 14.0, 9.1), 3.71 (3H, s), 4.95 (1H, d, J = 9.9), 5.23 (1H, dd, J = 9.8, 5.6), 5.35 (1H, dt, J = 9.7, 5.6), 6.52 (2H, dm, J = 8.9), 6.73 (2H, dm, J = 8.9), 7.14−7.30 (6H, m), 7.57 (1H, dd, J = 2.7, 0.9), 7.58 (1H, dd, J = 2.6, 1.1); ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 34.1 (CH_2), 55.7 (CH_3), 61.2 (*C*H), 88.8 (*C*H), 114.9 (*C*H), 115.8 (*C*H), 123.7 (*C*), 124.3 (*C*), 128.0 (*C*H), 128.2 (*C*H), 129.5 (*C*H), 129.7 (*C*H), 130.3 (*C*H), 131.7 (*C*H), 133.3 (*C*H), 133.9 (*C*H), 135.0 (*C*), 136.0 (*C*), 139.6 (*C*), 153.3 (*C*); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 37.8 (CH_2), 55.7 (CH_3), 58.3 (*C*H), 90.4 (*C*H), 114.9 (*C*H), 115.0 (*C*H), the remaining signals could not be determined; MS (EI) m/z 522 + 520 + 518 (10:20:10, M^+), 292+ 290 (1:1, 100, ArCH$^+$NHPMP); HRMS $C_{22}H_{20}(^{79}Br)_2N_2O_3$ calcd 517.9835, found 517.9843. Anal. Calcd for $C_{22}H_{20}Br_2N_2O_3$: C, 50.79; H, 3.88; N, 5.38; Found: C, 50.65; H, 3.85; N, 5.28.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(2-methoxyphenyl)-2-nitropropyl)-4-methoxyaniline (**5j**).* Nitroalkene **3** (52 mg, 0.23 mmol) afforded crude β-nitroamine **5j** as a yellow oil (134 mg, >95% conv, 90:10 dr): IR ν_{max} (neat) 3402, 3063−2836, 1549, 1510, 1488, 1464, 1439, 1235, 1023 cm^{-1}; ^1H NMR^{anti} (600 MHz, $CDCl_3$) δ 3.40 (1H, dd, J = 14.7, 11.5), 3.70 (1H, m), 3.74 (3H, s), 3.96 (3H, s), 4.61 (1H, br s), 5.13 (1H, d, J = 5.6), 5.54 (1H, ddd, J = 11.5, 7.4, 2.4), 6.70 (2H, dm, J = 8.9), 6.78 (2H, dm, J = 8.9), 6.92 (1H, td, J = 7.5, 0.7), 6.93 (1H, d, J = 8.2), 7.12 (1H, m), 7.19−7.30 (4H, m), 7.55 (1H, dd, J = 8.0, 0.8); ^1H NMR^{syn} (600 MHz, $CDCl_3$) δ 3.19 (1H, dd, J = 14.0, 3.8), 3.36 (1H, dd, J = 14.2, 10.4), 4.76 (1H, br s), 5.06 (1H, d, J = 6.7), the remaining signals could not be determined; ^{13}C NMR^{anti} (151

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MHz, $CDCl_3$) δ 36.4 (CH_2), 55.7 (CH_3), 55.8 (CH_3), 60.1 (CH), 90.0 (CH), 111.3 (CH), 114.9 (CH), 115.9 (CH), 121.1 (CH), 124.4 (C), 125.0 (C), 128.0 (CH), 129.3 (CH), 129.7 (CH), 129.8 (CH), 131.6 (CH), 133.2 (CH), 135.7 (C), 140.7 (C), 153.0 (C), 157.3 (C); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 38.4 (CH_2), 55.5 (CH_3), 55.5 (CH_3), 90.6 (CH), the remaining signals could not be determined; MS (EI) m/z 470 + 472 (1:1, 6, M^+), 242 (100, $ArCH^+NHPMP$); HRMS $C_{23}H_{23}(^{79}Br)N_2O_4$ calcd 470.0836, found 470.0820.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(3-methoxyphenyl)-2-nitropropyl)-4-methoxyaniline (**5k**).* Nitroalkene **3** (177 mg, 0.776 mmol) afforded crude β-nitroamine **5k** as a yellow oil (486 mg, >95% conv, >95:5 dr): IR ν_{max} (neat) 3381, 3057−2834, 1551, 1511, 1242, 1037 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.45 (1H, dd, J = 14.8, 11.2), 3.56 (1H, dd, J = 14.8, 2.7), 3.73 (3H, s), 3.80 (3H, s), 4.29 (1H, br s), 4.93 (1H, d, J = 5.9), 5.21 (1H, ddd, J = 11.1, 6.0, 2.7), 6.62 (2H, dm, J = 8.9), 6.76 (2H, dm, J = 8.9), 6.87 (1H, dd, J = 8.0, 2.3), 6.96 (1H, t, J = 2.0), 7.02 (1H, d, J = 7.7), 7.12 (1H, td, J = 7.6, 1.8), 7.18 (1H, dd, J = 7.7, 1.8), 7.22 (1H, td, J = 7.4, 1.0), 7.30 (1H, t, J = 7.9), 7.53 (1H, dd, J = 8.0, 1.0); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.8 (CH_2), 55.4 (CH_3), 55.8 (CH_3), 62.1 (CH), 91.7 (CH), 113.2 (CH), 113.9 (CH), 114.9 (CH), 115.9 (CH), 119.5 (CH), 124.4 (C), 128.1 (CH), 129.5 (CH), 130.3 (CH), 131.7 (CH), 133.3 (CH), 135.1 (C), 139.2 (C), 140.1 (C), 153.2 (C), 160.1 (C); MS (EI) m/z 470 + 472 (1:1, 4, M^+), 349 + 351 (1:1, 2, M^+ − PMPNH), 242 (53, $ArCH^+NHPMP$); HRMS $C_{23}H_{23}(^{79}Br)N_2O_4$ calcd 470.0836, found 470.0845.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(4-methoxyphenyl)-2-nitropropyl)-4-methoxyaniline (**5l**).* Nitroalkene **3** (1.09 g, 4.79 mmol) afforded crude β-nitroamine **5l** as a yellow oily solid (2.70 g, 95% conv, >95:5 dr): IR ν_{max} (neat) 3401, 3065−2835, 1551, 1510, 1244, 1032 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.44 (1H, dd, J = 14.8, 11.1), 3.57 (1H, dd, J = 14.7, 2.6), 3.72 (3H, s), 3.79 (3H, s), 4.28 (1H, br s), 4.90 (1H, d, J = 5.7), 5.19 (1H, ddd, J = 11.0, 6.1, 2.7), 6.62 (2H, dm, J = 8.9), 6.76 (2H, dm, J = 8.9), 6.90 (2H, dm, J = 8.7), 7.13 (1H, td, J = 7.6, 1.7), 7.18 (1H, dd, J = 7.6, 1.6), 7.22 (1H, td, J = 7.5, 0.7), 7.33 (2H, dm, J = 8.6), 7.54 (1H, dd, J = 7.9, 0.6); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.0 (CH_2), 55.4 (CH_3), 55.8 (CH_3), 61.6 (CH), 91.9 (CH), 114.5 (CH), 114.9 (CH), 115.9 (CH), 124.4 (C), 128.1 (CH), 128.4 (CH), 129.4 (C), 129.5 (CH), 131.7 (CH), 133.3 (CH), 135.2 (C), 140.1 (C), 153.1 (C), 159.8 (C); MS (CI) m/z 472 + 470 (1:1, 7, M^+), 426 + 424 (1:1, 20, M^+ − NO_2), 242 (100, $PMPCH^+NHPMP$); HRMS $C_{23}H_{23}(^{79}Br)N_2O_4$ calcd 470.0836, found 470.0850.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-(2-(trifluoromethyl)-phenyl)propyl)-4-methoxyaniline (**5m**).* Nitroalkene **3** (739 mg, 3.24 mmol) afforded crude β-nitroamine **5m** as a yellow oil (2.00 g, >95% conv, 90:10 dr): IR ν_{max} (neat) 3392, 3068−2835, 1552, 1511, 1309, 1243, 1160, 1115, 1034 cm^{-1}; ^{1}H NMR^{anti} (600 MHz, $CDCl_3$) δ 3.45 (1H, dd, J = 14.6, 2.1), 3.55 (1H, dd, J = 14.6, 11.7), 3.72 (3H, s), 4.39 (1H, br s), 5.32 (1H, ddd, J = 11.7, 4.5, 2.3), 5.53 (1H, d, J = 4.3), 6.61 (2H, dm, J = 8.9), 6.75 (2H, dm, J = 8.9), 7.09−7.13 (1H, m), 7.22 (2H, d, J = 4.2), 7.47−7.50 (2H, m), 7.61 (1H, t, J = 7.5), 7.79 (1H, d, J = 7.7), 7.90 (1H, d, J = 7.9); ^{1}H NMR^{syn} (600 MHz, $CDCl_3$) δ 3.43−3.48 (2H, m), 3.71 (3H, s), 4.92 (1H, br s), 5.23 (1H, br s), 5.28−2.31 (1H, m), the remaining signals could not be determined; ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 33.7 (CH_2), 55.7 (CH), 57.9 (CH_3), 90.2 (CH), 114.9 (CH), 116.0 (CH), 124.2 (C), 124.4 (1C, q, J = 274.2, C), 127.2 (1C, q, J = 6.0, CH), 128.1 (CH), 129.0 (2 × CH), 129.5 (CH), 131.7 (CH), 132.8 (CH), 133.3 (CH), 134.8 (C), 136.6 (C), 139.5 (C), 153.4 (C); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 34.0 (CH_2), 55.6 (CH), 55.7 (CH_3), 89.7 (CH), the remaining signals could not be determined; ^{19}F NMR^{anti} (282 MHz, $CDCl_3$) δ −58.3 (3F, s); MS (EI) m/z 508 + 510 (1:1, 16, M^+), 279 (100, $ArCH^+NHPMP$); HRMS $C_{23}H_{20}(^{79}Br)F_3N_2O_3$ calcd 508.0604, found 508.0615.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-(3-(trifluoromethyl)-phenyl)propyl)-4-methoxyaniline (**5n**).* Nitroalkene **3** (142 mg, 0.623 mmol) afforded crude β-nitroamine **5n** as a yellow oil (448 mg, >95% conv, >95:5 dr): IR ν_{max} (neat) 3405, 3061−2836, 1552, 1511, 1327, 1243, 1165, 1123, 1072, 1034, 1026 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.45 (1H, dd, J = 14.8, 10.5), 3.49 (1H, dd, J = 14.8, 3.3), 3.73 (3H, s), 4.34 (1H, br s), 5.03 (1H, d, J = 5.7), 5.21 (1H, ddd, J = 10.5, 5.6, 3.4), 6.59 (2H, dm, J = 8.9), 6.77 (2H, dm, J = 9.0), 7.14 (1H, td, J = 7.6, 1.7), 7.18 (1H, dd, J = 7.7, 1.8), 7.23 (1H, td, J = 7.5, 1.1), 7.52 (1H, t, J = 7.7), 7.53 (1H, dd, J = 8.0, 1.1), 7.63 (1H, t, J = 9.4), 7.72 (1H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.5 (CH_2), 55.7 (CH_3), 61.8 (CH), 91.4 (CH), 115.0 (CH), 116.0 (CH), 124.1 (1C, q, J = 272.5, C), 124.2 (1C, q, J = 3.5, CH), 124.3 (C), 125.7 (1C, q, J = 3.5, CH), 128.1 (CH), 129.7 (CH), 129.8 (CH), 130.7 (CH), 131.5 (1C, q, J = 32.4, C), 131.7 (CH), 133.3 (CH), 134.6 (C), 138.8 (C), 139.5 (C), 153.5 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.0 (3F, s); MS (EI) m/z 508 + 510 (5, M^+), 338 + 340 (5, M^+ − (NHPMP + NO_2)), 279 (100, $ArCH^+NHPMP$); HRMS $C_{23}H_{20}(^{79}Br)F_3N_2O_3$ calcd 508.0604, found 508.0619.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-(4-(trifluoromethyl)-phenyl)propyl)-4-methoxyaniline (**5o**).* Nitroalkene **3** (211 mg, 0.925 mmol) afforded crude β-nitroamine **5o** as a yellow oil (550 mg, >95% conv, >95:5 dr): IR ν_{max} (neat) 3395, 3057−2835, 1552, 1510, 1323, 1241, 1165, 1121, 1113, 1066, 1035, 1027, 1017 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.46 (1H, dd, J = 14.8, 11.0), 3.55 (1H, dd, J = 14.7, 2.7), 3.73 (3H, s), 4.33 (1H, br s), 5.02 (1H, s), 5.22 (1H, ddd, J = 10.9, 6.0, 2.8), 6.59 (2H, dm, J = 8.9), 6.77 (2H, dm, J = 8.9), 7.14 (1H, td, J = 7.6, 1.7), 7.18 (1H, dd, J = 7.7, 1.7), 7.23 (1H, td, J = 7.4, 1.0), 7.55 (1H, dd, J = 8.1, 1.0), 7.56 (2H, d, J = 8.3), 7.65 (2H, d, J = 8.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.8 (CH_2), 55.7 (CH_3), 61.7 (CH), 91.4 (CH), 115.0 (CH), 116.0 (CH), 124.0 (1C, q, J = 272.2, C), 124.3 (C), 126.2 (1C, q, J = 3.5, CH), 127.8 (CH), 128.2 (CH), 129.7 (CH), 131.0 (1C, q, J = 32.5, C), 131.7 (CH), 133.3 (CH), 134.6 (C), 139.4 (C), 141.7 (C), 153.5 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.0 (3F, s); MS (EI) m/z 508 + 510 (1:1, 15, M^+), 280 ($ArCH^+NHPMP$); HRMS $C_{23}H_{20}(^{79}Br)F_3N_2O_3$ calcd 508.0604, found 508.0616.

N-((1R,2S*)-3-(2-Bromo-5-fluorophenyl)-2-nitro-1-phenylpropyl)-4-methoxyaniline (**5p**).* 2-Bromo-5-fluoro-β-nitrostyrene (118 mg, 0.480 mmol) afforded crude β-nitroamine **5p** as a yellow oil (304 mg, >95% conv, >95:5 dr): IR ν_{max} (neat) 3401, 3066−2834, 1551, 1510, 1470, 1235, 1030 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.43 (1H, dd, J = 14.8, 11.0), 3.51 (1H, dd, J = 14.8, 2.7), 3.73 (3H, s), 4.27 (1H, br s), 4.97 (1H, d, J = 5.6), 5.20 (1H, ddd, J = 11.0, 5.9, 2.7), 6.63 (2H, dm, J = 8.9), 6.76 (2H, dm, J = 8.9), 6.87 (1H, td, J = 8.3, 3.0), 6.94 (1H, dd, J = 8.9, 3.0), 7.35 (1H, m), 7.38−7.43 (4H, m), 7.48 (1H, dd, J = 8.8, 5.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.7 (CH_2), 55.8 (CH_3), 62.2 (CH), 91.4 (CH), 114.9 (CH), 116.0 (CH), 116.7 (1C, d, J = 22.6, CH), 118.5 (1C, d, J = 3.1, C), 118.8 (1C, d, J = 23.2, CH), 127.2 (CH), 128.9 (CH), 129.2 (CH), 134.4 (1C, d, J = 7.9, CH), 137.1 (1C, d, J = 7.7, C), 137.3 (C), 139.9 (C), 153.3 (C), 161.9 (1C, d, J = 248.5, C); ^{19}F NMR (126 MHz, $CDCl_3$) δ −114.1 (1F, m); MS (EI) m/z 458 + 460 (5, M^+), 290 + 292 (10, M^+ − (NHPMP + NO_2)), 212 (100, $PhCH^+NHPMP$); HRMS $C_{22}H_{20}(^{79}Br)FN_2O_3$ calcd 458.0636, found 458.0635.

N-((1R,2S*)-3-(2-Bromo-4,5-dimethoxyphenyl)-2-nitro-1-phenylpropyl)-4-methoxyaniline (**5q**).* 2-Bromo-4,5-dimethoxy-β-nitrostyrene (136 mg, 0.472 mmol) afforded crude β-nitroamine **5q** as a yellow solid (273 mg, >95% conv, >95:5 dr): IR ν_{max} (neat) 3389, 3005−2837, 1551, 1509, 1260, 1243, 1219, 1166 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.35 (1H, dd, J = 14.9, 11.1), 3.44 (1H, dd, J = 14.8, 2.7), 3.72 (3H, s), 3.79 (3H, s), 3.84 (3H, s), 4.28 (1H, br d, J = 4.6), 4.92 (1H, br d, J = 4.9), 5.16 (1H, ddd, J = 11.0, 5.7, 2.7), 6.59 (2H, dm, J = 8.9), 6.64 (1H, s), 6.74 (2H, dm, J = 8.9), 6.97 (1H, s), 7.33 (1H, m), 7.36−7.41 (4H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.0 (CH_2), 55.3 (CH_3), 55.7 (CH_3), 55.8 (CH_3), 61.7 (CH), 91.6 (CH), 113.6 (CH), 113.8 (C), 114.5 (CH), 115.4 (CH), 115.5 (CH), 126.5 (C), 126.8 (CH), 128.3 (CH), 128.7 (CH), 137.1 (C), 139.6 (C), 148.2 (C), 148.7 (C), 152.7 (C); MS (EI) m/z 500 + 502 (1:1, 2, M^+), 289 + 291 (1:1, 16, M^+ − PMPNHBn), 242 + 244 (1:1, 46, M^+ − (PMPNHCHPh + NO_2)), 211 (91, $PhCH^+NHPMP$); HRMS $C_{24}H_{25}(^{79}Br)N_2O_5$ calcd 500.0941, found 500.0936.

N-((1R,2S*)-3-(2-Bromo-4,5-dimethoxyphenyl)-1-(2-methoxyphenyl)-2-nitropropyl)-4-methoxyaniline (**5r**).* 2-Bromo-4,5-dimethoxy-β-nitrostyrene (775 mg, 2.69 mmol) afforded crude β-nitroamine **5r** as a yellow oil (2.27 g, >95% conv, 85:15 dr): IR ν_{max} (neat) 3392, 3001−2838, 1550, 1509, 1258, 1237, 1219, 1164, 1025 cm^{-1}; ^{1}H NMR^{anti} (600 MHz, $CDCl_3$) δ 3.29 (1H, dd, J = 14.8, 11.4),

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3.57 (1H, dd, J = 14.8, 1.9), 3.72 (3H, s), 3.80 (3H, s), 3.83 (3H, s), 3.95 (3H, s), 4.56 (1H, br s), 5.09 (1H, br d, J = 6.1), 5.45 (1H, ddd, J = 11.4, 7.1, 2.5), 6.65 (2H, dm, J = 8.9), 6.65 (1H, s), 6.75 (2H, dm, J = 8.9), 6.90−6.93 (2H, m), 6.97 (1H, s), 7.22 (1H, dd, J = 7.5, 1.5), 7.26−7.29 (1H, m); ^{1}H NMR^{syn} (600 MHz, $CDCl_3$) δ 3.21 (1H, dd, J = 14.0, 5.9), 4.82 (1H, br s), 4.92 (1H, br s), 5.45 (1H, dt, J = 9.1, 6.5), 6.54 (2H, dm, J = 8.9), 6.62 (1H, s), 6.69 (2H, dm, J = 8.9), 7.00 (1H, s), 7.18 (1H, dd, J = 7.7, 1.5), the remaining signals could not be determined; ^{13}C NMR^{anti} (151 MHz, $CDCl_3$) δ 36.0 (CH_2), 55.7 (CH_3), 55.8 (CH_3), 56.1 (CH_3), 56.2 (CH_3), 59.9 (CH), 90.3 (CH), 111.2 (CH), 114.0 (CH), 114.2 (C), 114.9 (CH), 115.7 (CH), 115.8 (CH), 121.1 (CH), 125.0 (C), 127.5 (C), 129.6 (CH), 129.8 (CH), 140.6 (C), 148.5 (C), 149.0 (C), 153.0 (C), 157.3 (C); ^{13}C NMR^{syn} (151 MHz, $CDCl_3$) δ 37.9 (CH_2), 55.5 (CH_3), 55.6 (CH_3), 55.7 (CH_3), 55.8 (CH_3), 57.2 (CH), 90.0 (CH); the remaining signals could not be determined; MS (EI) m/z 530 + 532 (1:1, 4, M^+), 242 (100, $ArCH^+NHPMP$); HRMS $C_{25}H_{27}(^{79}Br)N_2O_6$ calcd 530.1047, found 530.1055.

N-((1R,2S*)-3-(3-(Benzyloxy)-2-bromo-4-methoxyphenyl)-2-nitro-1-phenylpropyl)-4-methoxyaniline (**5s**).* 3-Benzyloxy-2-bromo-4-methoxy-β-nitrostyrene (426 mg, 1.17 mmol) afforded crude β-nitroamine **5s** as a yellow oily foam (835 mg, >95% conv, >95:5 dr): IR ν_{max} (neat) 3389, 3065−2836, 1551, 1511, 1485, 1268, 1241, 1032 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.41 (1H, dd, J = 14.9, 11.1), 3.54 (1H, dd, J = 14.9, 2.6), 3.73 (3H, s), 3.84 (3H, s), 4.32 (1H, s), 4.95 (1H, d, J = 5.9), 5.03 (2H, s), 5.19 (1H, ddd, J = 11.1, 5.9, 2.7), 6.62 (2H, dm, J = 8.9), 6.76 (2H, dm, J = 8.9), 6.79 (1H, d, J = 8.6), 6.93 (1H, d, J = 8.5), 7.33−7.44 (8H, m), 7.55−7.56 (1H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.5 (CH_2), 55.8 (CH_3), 56.2 (CH_3), 62.1 (CH), 74.7 (CH_2), 92.1 (CH), 111.5 (CH), 114.9 (CH), 115.9 (CH), 120.4 (C), 126.6 (CH), 127.3 (CH), 127.7 (C), 128.3 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.2 (CH), 137.2 (C), 137.6 (CH), 140.1 (C), 145.6 (C), 153.1 (C), 153.3 (C); MS (EI) m/z 576 + 578 (1:1, 2, M^+), 365 + 367 (1:1, 11, M^+ − PhCHNHPMP), 319 + 321 (1:1, 54, M^+ − (PhCHNHPMP + NO_2)), 212 (100, $PhCH^+NHPMP$); HRMS $C_{30}H_{29}(^{79}Br)N_2O_5$ calcd 576.1254, found 576.1239.

N-((1R,2S*)-3-(2-Chloropyridin-3-yl)-2-nitro-1-phenylpropyl)-4-methoxyaniline (**5t**).* 2-Chloro-3-((E)-2-nitrovinyl)pyridine (41 mg, 0.22 mmol) afforded crude β-nitroamine **5t** as a yellow oil (98 mg, >95% conv, >95:5 dr): IR ν_{max} (neat) 3372, 3059−2834, 1550, 1510, 1410, 1238 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.41 (1H, dd, J = 14.9, 11.2), 3.52 (1H, dd, J = 14.9, 2.4), 3.72 (3H, s), 4.21 (1H, br s), 4.99 (1H, d, J = 5.8), 5.21 (1H, ddd, J = 11.2, 5.9, 2.5), 6.62 (2H, dm, J = 8.9), 6.75 (2H, dm, J = 8.9), 7.16 (1H, dd, J = 7.6, 4.8), 7.33−7.40 (5H, m), 7.53 (1H, dd, J = 7.6, 1.7), 8.30 (1H, dd, J = 4.7, 1.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 33.0 (CH_2), 55.8 (CH_3), 62.2 (CH), 90.9 (CH), 114.9 (CH), 116.1 (CH), 123.1 (CH), 127.0 (CH), 128.9 (CH), 129.3 (CH), 130.3 (C), 137.1 (C), 139.7 (C), 140.4 (CH), 149.1 (CH), 151.2 (C), 153.3 (C); MS (EI) m/z 397 (3, M^+), 212 (31%, M^+ − $C_7H_6ClN_2O_2$); HRMS $C_{21}H_{20}ClN_3O_3$ calcd 397.1188, found 397.1196.

General Procedure for the Synthesis of β-Nitroacetamides 6 (Table 4). To a solution of crude β-nitroamine **5** (1.00 mmol) in CH_2Cl_2 (10.0 mL) at −78 °C was added DIPEA (2.50 mmol) quickly followed by the dropwise addition of TFAA (2.50 mmol). The mixture was stirred at −78 °C for 60 min before being allowed to warm to room temperature over 30 min. The reaction was quenched by the addition of 2 M HCl (15 mL). The phases were separated, and the aqueous portion was further extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), filtered, and concentrated in vacuo to give the crude β-nitroacetamide **6** which was purified by flash column chromatography.

N-[(1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-phenylpropyl]-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6a**).* Prepared using general procedure H. Crude β-nitroamine **5a** (1.31 mmol) afforded crude β-nitroacetamide **6a** as a brown oil. Purification by flash column chromatography (40% CH_2Cl_2/petroleum ether followed by 10% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6a** as a white solid (500 mg, 71%, >95:5 dr): mp 118−120 °C; R_f 0.24 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3062−2841, 1699, 1559, 1512, 1255, 1183, 1169, 1033 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.61 (1H, dd, J = 14.4, 11.4), 3.79 (1H, dd, J = 14.5, 3.8), 3.82 (3H, s), 5.76 (1H, td, J = 11.2, 3.6), 6.27 (1H, d, J = 9.0), 6.31 (1H, d, J = 11.3), 6.63 (1H, dd, J = 8.8, 2.8), 6.92 (1H, dd, J = 8.7, 2.9), 7.08 (2H, d, J = 7.3), 7.16−7.33 (6H, m), 7.41 (1H, dd, J = 8.7, 1.4), 7.61−7.63 (1H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.7 (CH_2), 55.6 (CH_3), 64.8 (CH), 87.2 (CH), 113.8 (CH), 114.3 (CH), 116.3 (1C, q, J = 288.7, C), 124.1 (C), 127.6 (C), 128.4 (CH), 128.8 (CH), 129.6 (CH), 129.8 (CH), 129.9 (CH), 130.8 (CH), 131.7 (CH), 132.4 (CH), 132.8 (C), 133.3 (CH), 133.9 (C), 158.3 (1C, q, J = 35.7, C), 160.4 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.1 (3F, s); MS (ESI^+) m/z 559 + 561 (1:1, 100, M^+ + Na); HRMS $C_{24}H_{20}(^{79}Br)F_3N_2O_4Na$ calcd 559.0430, found 559.0451. Anal. Calcd for $C_{24}H_{20}BrF_3N_2O_4$: C, 53.65; H, 3.75; N, 5.21. Found: C, 53.93; H, 3.84; N, 4.95.

N-((1S,2S*)-3-(2-Bromophenyl)-1-(furan-2-yl)-2-nitropropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6b**).* Crude β-nitroamine **5b** (4.42 mmol) afforded crude β-nitroacetamide **6b** as a brown solid. Purification by flash column chromatography (45% CH_2Cl_2/petroleum ether) yielded pure β-nitroacetamide **6b** as a white solid (2.03 g, 87%, 95:5 dr). Subsequent recrystallization from toluene/petroleum ether gave β-nitroacetamide **6b** as a single *anti* diastereomer (1.63 g, 70%): mp 134−137 °C; R_f 0.44 (45% CH_2Cl_2/petroleum ether); IR ν_{max} (neat) 3130−2841, 1701, 1556, 1510, 1253, 1206, 1180, 1154, 1029 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.51 (1H, dd, J = 14.3, 11.7), 3.71 (1H, dd, J = 14.3, 3.8), 3.83 (3H, s), 5.57 (1H, td, J = 11.1, 3.7), 6.26 (1H, dd, J = 3.2, 1.4), 6.27 (1H, d, J = 3.4), 6.45 (1H, d, J = 10.7), 6.49 (1H, d, J = 8.1), 6.71 (1H, dd, J = 8.8, 2.8), 6.93 (1H, dd, J = 8.8, 2.9), 7.14 (1H, dd, J = 7.7, 1.4), 7.19 (1H, td, J = 7.7, 1.6), 7.27 (1H, td, J = 7.5, 0.9), 7.32 (1H, d, J = 1.1), 7.48 (1H, dd, J = 8.7, 2.1), 7.61 (1H, dd, J = 7.9, 0.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.3 (CH_2), 55.6 (CH_3), 58.4 (CH), 86.3 (CH), 111.0 (CH), 112.1 (CH), 113.9 (CH), 114.5 (CH), 116.2 (1C, q, J = 288.6, C), 124.1 (C), 128.0 (C), 128.4 (CH), 130.0 (CH), 130.6 (CH), 131.0 (CH), 131.7 (CH), 133.3 (CH), 133.6 (C), 143.4 (CH), 145.9 (C), 158.2 (1C, q, J = 36.0, C), 160.5 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.6 (3F, s); MS (CI) m/z 527 + 529 (1:1, 4, M^+), 480 + 482 (1:1, 100, M^+ − NO_2); HRMS $C_{22}H_{18}(^{79}Br)F_3N_2O_5$ calcd 527.0429, found 527.0438. Anal. Calcd for $C_{22}H_{18}BrF_3N_2O_5$: C, 50.11; H, 3.44; N, 5.31. Found: C, 50.23; H, 3.50; N, 5.20%.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(furan-3-yl)-2-nitropropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6c**).* Crude β-nitroamine **5c** (5.65 mmol) afforded crude β-nitroacetamide **6c** as a brown oily solid. Purification by flash column chromatography (50% CH_2Cl_2/petroleum ether followed by 20% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6c** as a white solid (2.47 g, 83%, 95:5 dr). Subsequent recrystallization from toluene/petroleum ether gave β-nitroacetamide **6c** as a single *anti* diastereomer (2.06 g, 69%): mp 120−122 °C; R_f 0.36 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3137−2842, 1697, 1557, 1510, 1253, 1207, 1180, 1155, 1025 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.49 (1H, dd, J = 14.3, 11.6), 3.71 (1H, dd, J = 14.3, 3.5), 3.85 (3H, s), 5.67 (1H, m), 5.91 (1H, br m), 6.11 (1H, s), 6.80 (1H, br d, J = 8.8), 6.82 (1H, dd, J = 8.7, 2.6), 6.93 (1H, dd, J = 8.8, 2.7), 7.14 (1H, dd, J = 7.6, 1.6), 7.18 (1H, td, J = 7.7, 1.7), 7.26 (1H, td, J = 7.5, 1.2), 7.30 (1H, app t, J = 1.1), 7.33 (1H, s), 7.35 (1H, br d, J = 9.1), 7.60 (1H, dd, J = 8.0, 1.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.3 (CH_2), 55.7 (CH_3), 58.8 (CH), 88.3 (CH), 110.5 (CH), 114.2 (CH), 114.7 (CH), 116.2 (1C, q, J = 288.6, C), 117.8 (C), 124.2 (C), 128.3 (CH), 128.8 (C), 129.8 (CH), 130.4 (CH), 131.5 (CH), 131.8 (CH), 133.3 (CH), 133.8 (C), 142.9 (CH), 143.6 (CH), 158.2 (1C, q, J = 35.9, C), 160.5 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.8 (3F, s); MS (EI) m/z 526 + 528 (1:1, 4, M^+), 480 + 482 (1:1, 46, M^+ − NO_2); HRMS $C_{22}H_{18}(^{79}Br)F_3N_2O_5$ calcd 526.0346, found 526.0338. Anal. Calcd for $C_{22}H_{18}BrF_3N_2O_5$: C, 50.11; H, 3.44; N, 5.31. Found: C, 49.96; H, 3.32; N, 5.27.

N-((1S,2S*)-3-(2-Bromophenyl)-2-nitro-1-(thiophene-2-yl)-propyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6d**).* Crude β-nitroamine **5d** (4.39 mmol) afforded crude β-nitroacetamide **6d** as a brown oil. Purification by flash column chromatography (50% CH_2Cl_2/petroleum ether followed by 20% Et_2O/petroleum ether)

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yielded pure β-nitroacetamide **6d** as a white solid (1.76 g, 74%, >95:5 dr): mp 126−128 °C; R_f 0.25 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3082−2841, 1698, 1557, 1510, 1254, 1207, 1180, 1156, 1033 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.54 (1H, dd, *J* = 14.2, 11.6), 3.77 (1H, dd, *J* = 14.3, 3.6), 3.84 (3H, s), 5.81 (1H, br m), 6.23 (1H, br s), 6.69 (1H, br s), 6.78 (2H, m), 6.86 (1H, dd, *J* = 5.0, 3.7), 6.93 (1H, dd, *J* = 8.7, 2.8), 7.15−7.19 (2H, m), 7.26 (1H, td, *J* = 7.5, 1.1), 7.31 (1H, dd, *J* = 5.1, 0.9), 7.34 (1H, br d, *J* = 8.0), 7.61 (1H, dd, *J* = 8.0, 1.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.5 (CH_2), 55.6 (CH_3), 61.9 (CH), 88.9 (CH), 114.1 (CH), 114.7 (CH), 116.2 (1C, q, *J* = 288.5, *C*), 124.2 (*C*), 126.9 (CH), 128.0 (CH), 128.4 (CH), 128.8 (*C*), 129.8 (CH), 129.9 (CH), 130.5 (CH), 131.2 (CH), 131.5 (CH), 133.3 (CH), 133.7 (*C*), 134.2 (*C*), 158.1 (1C, q, *J* = 36.1, *C*), 160.6 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.8 (3F, s); MS (CI) *m*/*z* 543 + 545 (1:1, 3, $M^+ + H$), 496 + 498 (1:1, 5, $M^+ - NO_2$), 324 + 326 (1:1, 86, M^+ − PMPNTFA); HRMS $C_{22}H_{19}(^{79}Br)F_3N_2O_4S$ calcd 543.0201, found 543.0185. Anal. Calcd for $C_{22}H_{18}BrF_3N_2O_4S$: C, 48.63; H, 3.34; N, 5.16. Found: C, 48.32; H, 3.19; N, 4.95.

N-((2S,3R*)-1-(2-Bromophenyl)-2-nitrooctan-3-yl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6e**).* Prepared following general procedure for the synthesis of **6** except using TFAA (5.0 mmol) and pyridine (5.0 mmol). Crude β-nitroamine **5e** (4.24 mmol) afforded crude β-nitroacetamide **6e** as a brown oil. Purification by flash column chromatography (60% CH_2Cl_2/petroleum ether followed by 20% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6e** as a white solid (1.91 g, 85%, >95:5 dr): mp 88−90 °C; R_f 0.33 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3059−2862, 1698, 1554, 1511, 1255, 1205, 1182, 1171, 1154, 1028 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.0), 1.20−1.53 (7H, m), 1.74−1.79 (1H, m), 3.42 (1H, dd, *J* = 14.5, 11.4), 3.55 (1H, dd, *J* = 14.5, 3.7), 3.87 (3H, s), 4.93 (1H, br s), 5.21 (1H, td, *J* = 10.1, 3.4), 6.96 (2H, dm, *J* = 9.2), 7.13 (1H, dd, *J* = 7.6, 1.5), 7.16 (1H, td, *J* = 7.7, 1.8), 7.21 (1H, br m), 7.25 (1H, td, *J* = 7.4, 1.3), 7.38 (1H, br d, *J* = 7.6), 7.58 (1H, dd, *J* = 7.9, 1.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.5 (CH_2), 26.4 (CH_2), 28.0 (CH_2), 31.3 (CH_2), 38.1 (CH_2), 55.7 (CH_3), 62.5 (CH), 89.2 (CH), 114.6 (CH), 116.3 (1C, q, *J* = 288.7, *C*), 124.2 (*C*), 128.2 (*C*), 128.2 (CH), 129.7 (CH), 130.6 (CH), 130.8 (CH), 131.5 (CH), 133.3 (CH), 134.1 (*C*), 158.7 (1C, q, *J* = 35.2, *C*), 160.5 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.4 (3F, s); MS (EI) *m*/*z* 530 + 532 (1:1, 18, M^+), 265 + 267 (1:1, M^+ − (PMPNTFA + NO_2)), 219 (55, $PMPN^+TFA$); HRMS $C_{23}H_{26}(^{79}Br)F_3N_2O_4$ calcd 530.1023, found 530.1024. Anal. Calcd for $C_{23}H_{26}BrF_3N_2O_4$: C, 51.99; H, 4.93; N, 5.27. Found: C, 52.05; H, 4.91; N, 5.21.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-(o-tolyl)propyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6h**).* Crude β-nitroamine **5h** (5.10 mmol) afforded crude β-nitroacetamide **6h** as a yellow oil. Purification by flash column chromatography (35% CH_2Cl_2/petroleum ether) yielded β-nitroacetamide **6h** as a white solid (2.28 g, 81%, >95:5 dr): mp 154−156 °C; R_f 0.34 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3067−2841, 1697, 1557, 1511, 1255, 1207, 1180, 1167, 1155, 1032 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.45 (3H, s), 3.67 (1H, dd, *J* = 14.3, 11.6), 3.80 (3H, s), 3.80 (1H, dd, *J* = 14.2, 3.9), 5.64 (1H, td, *J* = 10.8, 2.6), 6.00 (1H, d, *J* = 6.5), 6.51 (1H, dd, *J* = 8.8, 2.8), 6.55 (1H, br s), 6.84 (1H, t, *J* = 7.4), 6.85 (1H, br m), 6.92 (1H, dd, *J* = 8.7, 3.0), 7.14−7.21 (4H, m), 7.27 (1H, td, *J* = 7.4, 1,2), 7.54 (1H, br d, *J* = 7.9), 7.63 (1H, dd, *J* = 8.0, 1.0); ^{13}C NMR (151 MHz, $CDCl_3$) δ 19.8 (CH_3), 38.7 (CH_2), 55.6 (CH_3), 59.0 (CH), 87.2 (CH), 113.5 (CH), 114.2 (CH), 116.4 (1C, q, *J* = 288.6, *C*), 124.0 (*C*), 125.9 (CH), 126.8 (*C*), 128.2 (CH), 128.5 (CH), 129.4 (CH), 129.9 (CH), 130.8 (CH), 130.8 (*C*), 131.1 (CH), 131.9 (CH), 132.7 (CH), 133.2 (CH), 134.0 (*C*), 138.0 (*C*), 158.4 (1C, q, *J* = 35.7, *C*), 160.4 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.3 (3F, s); MS (EI) *m*/*z* 551 + 553 (1:1, 27, $M^+ + H$), 550 + 552 (1:1, 100, M^+), 504 + 506 (1:1, 19, $M^+ - NO_2$); HRMS $C_{25}H_{22}(^{79}Br)F_3N_2O_4$ calcd 550.0710, found 550.0714. Anal. Calcd for $C_{25}H_{22}BrF_3N_2O_4$: C, 54.46; H, 4.02; N, 5.08. Found: C, 54.45; H, 3.93; N, 5.06.

N-((1R,2S*)-1,3-Bis(2-bromophenyl)-2-nitropropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6i**).* Crude β-nitroamine **5i** (4.39 mmol) afforded crude β-nitroacetamide **6i** as a yellow oil. Purification by flash column chromatography (40% CH_2Cl_2/petroleum ether) and subsequent recrystallization from toluene/petroleum ether yielded pure β-nitroacetamide **6i** as a white solid (2.24 g, 83%, >95:5 dr): mp 197−198 °C; R_f 0.34 (40% CH_2Cl_2/petroleum ether); IR ν_{max} (neat) 3067−2840, 1702, 1556, 1511, 1256, 1207, 1181, 1167, 1156, 1030 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.71 (1H, dd, *J* = 14.3, 11.6), 3.78 (3H, s), 3.79 (1H, dd, *J* = 14.3, 3.9), 5.64 (1H, td, *J* = 11.3, 3.8), 6.22 (1H, d, *J* = 7.7), 6.50 (1H, dd, *J* = 8.9, 2.9), 6.71 (1H, d, *J* = 7.7), 6.90 (1H, dd, *J* = 8.8, 2.9), 6.97 (1H, m), 7.00 (1H, d, *J* = 11.0), 7.13 (1H, td, *J* = 7.7, 1.4), 7.16 (1H, dd, *J* = 7.5, 1.6), 7.20 (1H, td, *J* = 7.7, 1.7), 7.28 (1H, td, *J* = 7.5, 1.1), 7.53 (1H, dd, *J* = 8.7, 2.5), 7.63 (2H, dt, *J* = 8.0, 1.6); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.7 (CH_2), 55.6 (CH_3), 61.9 (CH), 87.2 (CH), 113.6 (CH), 114.4 (CH), 116.4 (1C, q, *J* = 288.5, *C*), 123.9 (*C*), 126.1 (*C*), 127.0 (*C*), 127.4 (CH), 128.5 (CH), 129.7 (CH), 130.0 (CH), 130.8 (CH), 130.9 (CH), 131.9 (CH), 132.2 (CH), 132.3 (*C*), 133.2 (CH), 133.7 (CH), 133.9 (*C*), 158.1 (1C, q, *J* = 35.9, *C*), 160.4 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.4 (3F, s); MS (EI) *m*/*z* 618 + 616 + 614 (1:2:1, 15, M^+), 535 + 537 (1:1, 4, M^+ − Br), 353 + 351 + 349 (1:2:1, 45, M^+ − (NO_2 + PMPNTFA)); HRMS $C_{24}H_{19}(^{79}Br)_2F_3N_2O_4$ calcd 613.9658, found 613.9667. Anal. Calcd for $C_{24}H_{19}Br_2F_3N_2O_4$: C, 46.78; H, 3.11; N, 4.55. Found: C, 47.02; H, 3.00; N, 4.48.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(2-methoxyphenyl)-2-nitropropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6j**).* Crude β-nitroamine **5j** (4.80 mmol) afforded crude β-nitroacetamide **6j** as a brown oil. Purification by flash column chromatography (35% Et_2O/petroleum ether followed by 50% CH_2Cl_2/petroleum ether) yielded pure β-nitroacetamide **6j** as a white solid (2.25 g, 83%, >95:5 dr): mp 130−132 °C; R_f 0.35 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3071−2841, 1699, 1556, 1511, 1252, 1206, 1180, 1166, 1154, 1026 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.65 (1H, dd, *J* = 14.3, 11.7), 3.79 (3H, s), 3.79 (1H, dd, *J* = 14.4, 3.9), 3.81 (3H, br s), 5.69 (1H, td, *J* = 11.2, 3.1), 6.14 (1H, d, *J* = 8.2), 6.52 (1H, dd, *J* = 8.9, 2.9), 6.67 (1H, t, *J* = 7.5), 6.77 (1H, br d, *J* = 5.9), 6.86 (1H, d, *J* = 8.2), 6.89 (1H, dd, *J* = 8.7, 2.9), 6.96 (1H, br d, *J* = 11.2), 7.16 (1H, dd, *J* = 7.5, 1.7), 7.18 (1H, td, *J* = 7.7, 1.7), 7.24 (1H, m), 7.26 (1H, td, *J* = 7.4, 1.1), 7.50 (1H, dd, *J* = 8.7, 2.2), 7.62 (1H, dd, *J* = 8.0, 1.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.8 (CH_2), 55.5 (CH_3), 55.8 (CH_3), 57.4 (CH), 86.8 (CH), 110.9 (CH), 113.4 (CH), 114.0 (CH), 116.5 (1C, q, *J* = 288.7, *C*), 120.4 (CH), 121.1 (*C*), 124.0 (*C*), 127.5 (*C*), 128.4 (CH), 129.2 (CH), 129.8 (CH), 130.8 (CH), 130.9 (CH), 131.9 (CH), 132.1 (CH), 133.2 (CH), 134.2 (*C*), 157.8 (*C*), 158.1 (1C, q, *J* = 35.3, *C*), 160.2 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.3 (3F, s, CF_3); MS (EI) *m*/*z* 566 + 568 (1:1, 5, M^+); HRMS $C_{25}H_{22}(^{79}Br)F_3N_2O_5$ calcd 566.0659, found 566.0642. Anal. Calcd for $C_{25}H_{22}BrF_3N_2O_5$: C, 52.92; H, 3.91; N, 4.94. Found: C, 52.81; H, 3.83; N, 4.90.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(3-methoxyphenyl)-2-nitropropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6k**).* Crude β-nitroamine **5k** (0.776 mmol) afforded crude β-nitroacetamide **6k** as a dark yellow oil. Purification by flash column chromatography (45% CH_2Cl_2/petroleum ether followed by 40% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6k** as a white solid (387 mg, 88%, >95:5 dr): mp 132−133 °C; R_f 0.50 (40% Et_2O/petroleum ether); IR ν_{max} (neat) 3056−2839, 1698, 1557, 1511, 1255, 1208, 1181, 1168, 1156, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.59 (1H, dd, *J* = 14.4, 11.4), 3.70 (3H, s), 3.78 (1H, dd, *J* = 14.4, 3.7), 3.83 (3H, s), 5.73 (1H, td, *J* = 11.1, 3.3), 6.26 (1H, br d, *J* = 10.1), 6.35 (1H, br d, *J* = 7.8), 6.63−6.68 (3H, m), 6.85 (1H, ddd, *J* = 8.3, 2.3, 0.9), 6.92 (1H, dd, *J* = 8.7, 2.9), 7.13 (1H, t, *J* = 8.2), 7.17−7.21 (2H, m), 7.27 (1H, td, *J* = 7.5), 7.41 (1H, br d, *J* = 8.0), 7.61−7.63 (1H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.7 (CH_2), 55.4 (CH_3), 55.6 (CH_2), 64.7 (CH), 87.2 (CH), 113.8 (CH), 114.4 (CH), 114.9 (CH), 115.6 (CH), 116.3 (1C, q, *J* = 288.7, *C*), 121.8 (CH), 124.1 (*C*), 127.7 (*C*), 128.4 (CH), 129.8 (CH), 129.9 (CH), 130.8 (CH), 131.6 (CH), 132.4 (CH), 133.3 (CH), 133.9 (*C*), 134.2 (*C*), 158.3 (1C, q, *J* = 35.8, *C*), 159.7 (*C*), 160.5 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.5 (3F, s); MS (EI) *m*/*z* 566 + 568 (1:1, 15, M^+), 367 (30, $M^+ - C_8H_9BrO$), 302 + 304 (1:1, 52%, M^+ − (PMPNTFA + NO_2)), 219 (87, $PMPN^+TFA$); HRMS $C_{25}H_{22}(^{79}Br)F_3N_2O_5$ calcd 566.0659, found 566.0645. Anal.

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Calcd for $C_{25}H_{22}BrF_3N_2O_5$: C, 52.92; H, 3.91; N, 4.94. Found: C, 52.95; H, 3.82; N, 4.88.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(4-methoxyphenyl)-2-nitropropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6l**).* Crude β-nitroamine **5l** (4.79 mmol) afforded crude β-nitroacetamide **6l** as a brown oil. Purification by flash column chromatography (60% CH_2Cl_2/petroleum ether followed by 30% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6l** as a white solid (2.23 g, 82%, >95:5 dr): mp 114−116 °C; R_f 0.36 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3007−2841, 1698, 1557, 1511, 1256, 1207, 1177, 1169, 1156, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.59 (1H, dd, *J* = 14.3, 11.6), 3.77 (3H, s), 3.77 (1H, dd, *J* = 14.3, 3.7), 3.83 (3H, s), 5.70 (1H, br m), 6.26 (1H, br s), 6.31 (1H, br s), 6.67 (1H, dd, *J* = 8.6, 2.2), 6.74 (2H, d, *J* = 8.8), 6.92 (1H, dd, *J* = 8.8, 2.9), 6.98 (2H, br d, *J* = 8.0), 7.17−7.19 (2H, m), 7.25−7.28 (1H, m), 7.42 (1H, br d, *J* = 7.6), 7.61 (1H, d, *J* = 7.9); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.6 (CH_2), 55.4 (CH_3), 55.6 (CH_3), 64.5 (*C*H), 87.5 (*C*H), 113.8 (*C*H), 114.1 (*C*H), 114.4 (*C*H), 116.4 (1C, q, *J* = 288.7, *C*), 124.1 (*C*), 124.7 (*C*), 127.7 (*C*), 128.4 (*C*H), 129.8 (*C*H), 130.8 (*C*H), 130.9 (*C*H), 131.7 (*C*H), 132.6 (*C*H), 133.3 (*C*H), 134.0 (*C*), 158.2 (1C, q, *J* = 35.6, *C*), 160.4 (*C*), 160.5 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.5 (3F, s); MS (EI) *m*/*z* 566 + 568 (4, M^+), 520 + 522 (12, $M^+ - NO_2$), 348 + 350 (M^+ − PMPNHTFA), 302 + 304 ($M^+ - (NO_2$ + PMPNHTFA); HRMS $C_{25}H_{22}(^{79}Br)F_3N_2O_5$ calcd 566.0659, found 566.0638. Anal. Calcd for $C_{25}H_{22}BrF_3N_2O_5$: C, 52.92; H, 3.91; N, 4.94. Found: C, 53.01; H, 3.84; N, 4.76.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-(2-(trifluoromethyl)-phenyl)propyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6m**).* Prepared following the general procedure for the synthesis of **6** except using TFAA (5.0 mmol) and pyridine (5.0 mmol). Crude β-nitroamine **5m** (3.24 mmol) afforded crude β-nitroacetamide **6m** as a brown oil. Purification by flash column chromatography (40% CH_2Cl_2/petroleum ether followed by 30% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6m** as a white solid (1.33 g, 68%, 90:10 dr). Subsequent recrystallization from toluene/petroleum ether gave β-nitroacetamide **6m** as a single *anti* diastereomer (1.18 g, 60%): mp 153−154 °C; R_f 0.33 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3057−2843, 1705, 1557, 1512, 1313, 1257, 1210, 1182, 1159, 1125, 1038 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.71 (1H, dd, *J* = 14.4, 11.6), 3.79 (3H, s), 3.80 (1H, dd, *J* = 14.3, 3.8), 5.62 (1H, td, *J* = 11.1, 3.8), 6.04 (1H, dd, *J* = 8.8, 2.0), 6.46 (1H, dd, *J* = 8.8, 2.9), 6.67 (1H, d, *J* = 7.9), 6.95 (1H, dd, *J* = 8.7, 3.0), 7.14 (1H, d, *J* = 10.5), 7.15 (2H, dd, *J* = 7.5, 1.7), 7.20 (1H, td, *J* = 7.7, 1.6), 7.27 (1H, td, *J* = 7.5, 1.2), 7.38 (1H, t, *J* = 7.7), 7.63 (1H, dd, *J* = 7.9, 1.1), 7.64 (1H, dd, *J* = 8.7, 2.6), 7.74 (1H, d, *J* = 7.6); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.9 (CH_2), 55.6 (CH_3), 57.5 (*C*H), 87.7 (*C*H), 113.7 (*C*H), 114.3 (*C*H), 116.3 (1C, q, *J* = 288.4, *C*), 123.8 (1C, q, *J* = 274.1, *C*), 123.9 (*C*), 126.6 (*C*), 126.9 (1C, q, *J* = 5.9, *C*H), 128.6 (*C*H), 129.7 (*C*H), 130.0 (*C*H), 130.2 (1C, q, *J* = 30.4, *C*), 130.4 (*C*), 130.4 (*C*H), 131.2 (*C*H), 131.4 (*C*H), 132.0 (*C*H), 132.6 (*C*H), 133.2 (*C*H), 133.8 (*C*), 158.1 (1C, q, *J* = 35.9, *C*), 160.5 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.6 (3F, s), −60.2 (3F, s); MS (EI) *m*/*z* 604 + 606 (1:1, 32, M^+), 339 + 341 (1:1, 85, M^+ − (PMPNHTFA + NO_2)), 261 (38, M^+ − (PMPNHTFA + Br + NO_2)), 218 (100, $PMPN^+TFA$); HRMS $C_{25}H_{19}(^{79}Br)F_6N_2O_4$ calcd 604.0427, found 604.0411. Anal. Calcd for $C_{25}H_{19}BrF_6N_2O_4$: C, 49.60; H, 3.16; N, 4.63. Found: C, 49.24; H, 3.03; N, 4.57.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-(3-(trifluoromethyl)-phenyl)propyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6n**).* Crude β-nitroamine **5n** (0.623 mmol) afforded crude β-nitroacetamide **6n** as a brown oil. Purification by flash column chromatography (40% CH_2Cl_2/petroleum ether followed by 30% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6n** as an off-white solid (344 mg, 91%, >95:5 dr): mp 57−60 °C; R_f 0.53 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3061−2841, 1700, 1557, 1511, 1328, 1257, 1209, 1180, 1164, 1127, 1076, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.61 (1H, dd, *J* = 14.4, 11.4), 3.81 (1H, dd, *J* = 14.2, 3.6), 3.82 (3H, s), 5.75 (1H, td, *J* = 11.1, 3.4), 6.26 (1H, d, *J* = 8.0), 6.36 (1H, d, *J* = 10.7), 6.66 (1H, dd, *J* = 8.8, 2.8), 6.96 (1H, dd, *J* = 8.8, 2.9), 7.16−7.22 (2H, m), 7.23 (1H, s), 7.28 (1H, td, *J* = 7.5, 1.3), 7.33 (1H, d, *J* = 7.9), 7.39 (1H, d, *J* = 7.8), 7.42 (1H, d, *J* = 8.4), 7.59 (1H, d, *J* = 7.7), 7.63 (1H, dd, *J* = 7.9, 1.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.6 (CH_2), 55.7 (CH_3), 64.3 (*C*H), 87.2 (*C*H), 114.4 (*C*H), 114.5 (*C*H), 116.2 (1C, q, *J* = 288.6, *C*), 123.5 (1C, q, *J* = 272.6, *C*), 124.1 (*C*), 126.5 (1C, q, *J* = 3.7, *C*H), 126.7 (1C, q, *J* = 3.6, *C*H), 127.3 (*C*), 128.5 (*C*H), 129.5 (*C*H), 130.0 (*C*H), 130.8 (*C*H), 131.2 (1C, q, *J* = 32.7, *C*), 131.6 (*C*H), 132.3 (*C*H), 133.0 (*C*H), 133.3 (*C*H), 133.6 (*C*), 133.7 (*C*), 158.4 (1C, q, *J* = 36.0, *C*), 160.8 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.6 (3F, s), −63.2 (3F, s); MS (EI) *m*/*z* 604 + 606 (1:1, 6, M^+), 339 + 341 (1:1, 10, M^+ − (PMPNTFA + NO_2)); HRMS $C_{25}H_{19}(^{79}Br)F_6N_2O_4$ calcd 604.0427, found 604.0424. Anal. Calcd for $C_{25}H_{19}BrF_6N_2O_4$: C, 49.60; H, 3.16; N, 4.63. Found: C, 49.65; H, 3.10; N, 4.55.

N-((1R,2S*)-3-(2-Bromophenyl)-2-nitro-1-(4-(trifluoromethyl)-phenyl)propyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6o**).* Crude β-nitroamine **5o** (0.925 mmol) afforded crude β-nitroacetamide **6o** as a brown oil. Purification by flash column chromatography (35% CH_2Cl_2/petroleum ether) yielded pure β-nitroacetamide **6o** as a white solid (507 g, 91%, >95:5 dr): mp 126−128 °C; R_f 0.20 (30% CH_2Cl_2/petroleum ether); IR ν_{max} (neat) 3060−2843, 1702, 1558, 1511, 1325, 1256, 1211, 1180, 1167, 1124, 1069, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.59 (1H, dd, *J* = 14.3, 11.4), 3.82 (1H, dd, *J* = 14.4, 3.7), 3.84 (3H, s), 5.82 (1H, td, *J* = 11.1, 3.4), 6.27 (1H, br d, *J* = 10.5), 6.36 (1H, br d, *J* = 7.2), 6.70 (1H, dd, *J* = 8.8, 2.7), 6.94 (1H, dd, *J* = 8.7, 2.8), 7.17 (1H, dd, *J* = 7.5, 1.7), 7.20 (1H, td, *J* = 7.6, 1.9), 7.24−7.27 (2H, m), 7.28 (1H, td, *J* = 7.5, 1.3), 7.38 (1H, br d, *J* = 7.9), 7.52 (2H, d, *J* = 8.2), 7.63 (1H, dd, *J* = 7.9, 1.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.7 (CH_2), 55.7 (CH_3), 64.8 (*C*H), 87.1 (*C*H), 114.2 (*C*H), 114.6 (*C*H), 116.2 (1C, q, *J* = 288.6, *C*), 123.7 (1C, q, *J* = 272.5, *C*), 124.1 (*C*), 125.9 (1C, q, *J* = 3.7, *C*H), 127.7 (*C*), 128.5 (*C*H), 130.0 (*C*H), 130.0 (*C*H), 130.8 (*C*H), 131.6 (*C*H), 131.9 (1C, q, *J* = 32.8, *C*), 132.0 (*C*H), 133.3 (*C*H), 133.6 (*C*), 136.7 (*C*), 158.4 (1C, q, *J* = 36.1, *C*), 160.7 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.6 (3F, s), −63.3 (3F, s); MS (EI) *m*/*z* 604 + 606 (1:1, 13, M^+), 339 + 441 (1:1, 12, M^+ − (PMPNHTFA + NO_2)), 219 (97, M^+ − $PMPN^+TFA$); HRMS $C_{25}H_{19}(^{79}Br)F_6N_2O_4$ calcd 604.0427, found 604.0424. Anal. Calcd for $C_{25}H_{19}BrF_6N_2O_4$: C, 49.60; H, 3.16; N, 4.63. Found: C, 49.80; H, 3.16; N, 4.54.

N-((1R,2S*)-3-(2-Bromo-5-fluorophenyl)-2-nitro-1-phenylpropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6p**).* Crude β-nitroamine **5p** (0.480 mmol) afforded crude β-nitroacetamide **6p** as a yellow oil. Purification by flash column chromatography (40% CH_2Cl_2/petroleum ether followed by 25% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6p** as a white solid (219 mg, 82%, >95:5 dr): mp 118−120 °C; R_f 0.51 (25% Et_2O/petroleum ether); IR ν_{max} (neat) 3069−2842, 1698, 1557, 1511, 1474, 1255, 1208, 1181, 1155, 1032 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.58 (1H, dd, *J* = 14.4, 11.4), 3.74 (1H, dd, *J* = 14.4, 3.7), 3.82 (3H, s), 5.78 (1H, td, *J* = 11.2, 3.5), 6.24 (1H, br d, *J* = 10.7), 6.31 (1H, br d, *J* = 8.2), 6.65 (1H, dd, *J* = 8.8, 2.8), 6.93 (2H, td, *J* = 8.4, 3.1), 6.94 (1H, d, *J* = 8.2), 7.09 (2H, d, *J* = 7.4), 7.24 (2H, t, *J* = 7.5), 7.30−7.36 (2H, m), 7.56−7.60 (1H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.6 (CH_2), 55.6 (CH_3), 65.1 (*C*H), 87.0 (*C*H), 113.9 (*C*H), 114.4 (*C*H), 116.3 (1C, q, *J* = 288.5, *C*), 117.2 (1C, d, *J* = 22.2, *C*H), 118.3 (1C, d, *J* = 3.2, *C*), 118.7 (1C, d, *J* = 23.1, *C*H), 127.7 (*C*), 128.9 (*C*H), 129.6 (*C*H), 129.9 (*C*H), 130.7 (*C*H), 132.3 (*C*H), 132.6 (*C*), 134.5 (1C, d, *J* = 7.9, *C*H), 135.9 (1C, d, *J* = 7.6, *C*), 158.3 (1C, q, *J* = 35.8, *C*), 160.5 (*C*), 162.1 (1C, d, *J* = 248.8, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −113.5 (1F, m), −67.5 (3F, s); MS (EI) *m*/*z* 554 + 556 (1:1, 7, M^+), 335 + 337 (1:1, 9, M^+ − PMPNTFA); HRMS $C_{24}H_{19}(^{79}Br)F_4N_2O_4$ calcd 554.0459, found 554.0465. Anal. Calcd for $C_{24}H_{19}BrF_4N_2O_4$: C, 51.91; H, 3.45; N, 5.04. Found: C, 52.04; H, 3.39; N, 5.00.

N-((1R,2S*)-3-(2-Bromo-4,5-dimethoxyphenyl)-2-nitro-1-phenylpropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6q**).* Crude β-nitroamine **5q** (0.472 mmol) afforded crude β-nitroacetamide **6q** as a yellow foam. Purification by flash column chromatography (50% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6q** as an off-white solid (248 mg, 88%, >95:5 dr): mp 72−75 °C; R_f 0.48 (50% Et_2O/petroleum ether); IR ν_{max} (neat) 3008−2842, 1697, 1556, 1509, 1258, 1206, 1180, 1155, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ

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3.52 (1H, dd, J = 14.4, 11.4), 3.72 (1H, dd, J = 14.4, 3.8), 3.82 (3H, s), 3.82 (3H, s), 3.87 (3H, s), 5.71 (1H, td, J = 11.1, 3.5), 6.26 (1H, br d, J = 8.0), 6.31 (1H, br d, J = 11.0), 6.63 (1H, m), 6.64 (1H, s), 6.92 (1H, dd, J = 8.7, 2.8), 7.05 (1H, s), 7.06 (2H, m), 7.23 (2H, t, J = 7.5), 7.27−7.33 (1H, m), 7.42 (1H, br d, J = 7.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.4 (CH_2), 55.6 (CH_3), 56.2 (CH_3), 56.3 (CH_3), 64.7 (CH), 87.4 (CH), 113.8 (CH), 113.9 (CH), 114.0 (C), 114.3 (CH), 115.6 (CH), 116.3 (1C, q, J = 288.7, C), 125.6 (C), 127.6 (C), 128.8 (CH), 129.5 (CH), 129.8 (CH), 130.8 (CH), 132.5 (CH), 132.8 (C), 148.8 (CO), 149.4 (CO), 158.3 (1C, q, J = 35.7, C), 160.5 (CO); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.5 (3F, s); MS (ES^+) m/z 619 + 621 (1:1, 43%, M^+ + Na), 550 + 552 (86, $M^+ - NO_2$), 331 + 333 (1:1, 18%, M^+ − PMPNTFA), 228 + 230 (75, $M^+ - C_{17}H_{14}F_3N_2O_4$); HRMS $C_{26}H_{24}(^{79}Br)F_3N_2O_6Na$ calcd 619.0668, found 619.0672.

*N-((1R,2S)-3-(2-Bromo-4,5-dimethoxyphenyl)-1-(2-methoxyphenyl)-2-nitropropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6r**).* Crude β-nitroamine **5r** (2.69 mmol) afforded crude β-nitroacetamide **6r** as a brown oil. Purification by flash column chromatography (70% CH_2Cl_2/petroleum ether followed by 60% Et_2O/petroleum ether) yielded pure β-nitroacetamide **6r** as a white solid (1.22 g, 72%, >95:5 dr): mp 81−83 °C; R_f 0.32 (50% Et_2O/petroleum ether); IR ν_{max} (neat) 3005−2842, 1700, 1556, 1511, 1496, 1255, 1207, 1181, 1167, 1033 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.56 (1H, dd, J = 14.4, 11.5), 3.73 (1H, dd, J = 14.4, 4.0), 3.79 (3H, s), 3.81 (6H, s), 3.88 (3H, s), 5.65 (1H, td, J = 11.3, 3.8), 6.14 (1H, d, J = 8.0), 6.52 (1H, dd, J = 8.8, 2.9), 6.63 (1H, s), 6.67 (1H, t, J = 7.4), 6.76 (1H, d, J = 7.2), 6.86 (1H, d, J = 8.9), 6.89 (1H, dd, J = 8.8, 2.9), 6.95 (1H, d, J = 11.3), 7.05 (1H, s), 7.23−7.27 (1H, m), 7.50 (1H, dd, J = 8.7, 2.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.6 (CH_2), 55.5 (CH_3), 55.8 (CH_3), 56.1 (CH_3), 56.3 (CH_3), 57.2 (CH), 86.9 (CH), 110.9 (CH), 113.4 (CH), 113.9 (C), 113.9 (CH), 114.1 (CH), 115.5 (CH), 116.5 (1C, q, J = 288.6, C), 120.4 (CH), 121.1 (C), 125.9 (C), 127.5 (C), 129.3 (CH), 130.8 (CH), 130.9 (CH), 132.2 (CH), 148.8 (C), 149.3 (C), 157.8 (C), 158.1 (1C, q, J = 35.3, C), 160.2 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.3 (3F, s); MS (EI) m/z 626 + 628 (1:1, 20, M^+), 361 + 363 (1:1, 100, M^+ − (PMPNHTFA + NO_2)), 229 + 231 (1:1, 98, $M^+ - C_{18}H_{17}F_3N_2O_5$); HRMS $C_{27}H_{26}(^{79}Br)F_3N_2O_7$ calcd 626.0870, found 626.0847. Anal. Calcd for $C_{27}H_{26}BrF_3N_2O_7$: C, 51.69; H, 4.18; N, 4.46. Found: C, 51.95; H, 4.14; N, 4.45.

N-((1R,2S*)-3-(3-(Benzyloxy)-2-bromo-4-methoxyphenyl)-2-nitro-1-phenylpropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6s**).* Crude β-nitroamine **5s** (1.17 mmol) afforded crude β-nitroacetamide **6s** as a brown oil. Purification by flash column chromatography (60% CH_2Cl_2/petroleum ether) and subsequent recrystallization from Et_2O/petroleum ether yielded pure β-nitroacetamide **6s** as a white solid (550 mg, 82%, >95:5 dr): mp 168−169 °C; R_f 0.33 (60% CH_2Cl_2/petroleum ether); IR ν_{max} (neat) 3064−2840, 1699, 1557, 1511, 1487, 1300, 1270, 1256, 1208, 1181, 1170, 1156, 1033 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.56 (1H, dd, J = 14.4, 11.4), 3.78 (1H, dd, J = 14.4, 3.8), 3.82 (3H, s), 3.86 (3H, s), 5.06 (2H, s), 5.71 (1H, td, J = 11.2, 3.5), 6.22 (1H, d, J = 8.1), 6.36 (1H, d, J = 10.5), 6.61 (1H, dd, J = 8.8), 6.83 (1H, d, J = 8.6), 6.91 (1H, d, J = 8.5), 6.92 (1H, dd, J = 8.8, 2.9), 7.06 (2H, d, J = 7.3), 7.23 (2H, t, J = 7.5), 7.29−7.44 (4H, m), 7.46 (1H, d, J = 8.7), 7.56−7.58 (2H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 38.6 (CH_2), 55.6 (CH_3), 56.1 (CH_3), 64.5 (CH), 74.8 (CH_2), 87.3 (CH), 111.7 (CH), 113.7 (CH), 114.3 (CH), 116.4 (1C, q, J = 289.0, C), 120.2 (C), 126.5 (C), 126.7 (CH), 127.5 (C), 128.3 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 129.6 (CH), 129.7 (CH), 130.9 (CH), 132.5 (CH), 132.9 (C), 137.1 (C), 145.5 (C), 153.6 (C), 158.3 (1C, q, J = 35.8, C), 160.4 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.4 (3F, s); MS (FAB^+) m/z 695 + 697 (1:1, 8, M^+ + Na), 549 + 551 (1:1, 5, $M^+ - C_8H_{10}O$); HRMS $C_{32}H_{28}(^{79}Br)F_3N_2O_6Na$ calcd 695.0981, found 695.0968. Anal. Calcd for $C_{32}H_{28}BrF_3N_2O_6$: C, 57.07; H, 4.19; N, 4.16. Found: C, 57.40; H, 4.20; N, 4.05.

N-((1R,2S*)-3-(2-Chloropyridin-3-yl)-2-nitro-1-phenylpropyl)-N-(4-methoxyphenyl)-2,2,2-trifluoroacetamide (**6t**).* Crude β-nitroamine **5t** (0.99 mmol) afforded crude β-nitroacetamide **6t** as a brown oil. Purification by flash column chromatography (25% EtOAc/petroleum ether) yielded pure β-nitroacetamide **6t** as a white solid (290 mg, 59%, >95:5 dr): mp 53−55 °C; R_f 0.32 (25% EtOAc/petroleum ether); IR ν_{max} (neat) 3039−2851, 1697, 1557, 1510, 1411, 1254, 1207, 1180, 1155 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (1H, dd, J = 14.5, 11.6), 3.79 (1H, dd, J = 14.5, 3.6), 3.82 (3H, s), 5.70 (1H, td, J = 11.3, 3.5), 6.20 (1H, d, J = 8.1), 6.39 (1H, d, J = 10.0), 6.62 (1H, dd, J = 8.8, 2.9), 6.95 (1H, dd, J = 8.7, 2.9), 7.05 (2H, d, J = 7.4), 7.20−7.25 (3H, m), 7.32 (1H, m), 7.38 (1H, br dd, J = 8.7, 1.9), 7.52 (1H, dd, J = 7.6, 1.9), 8.37 (1H, dd, J = 4.7, 1.9); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.0 (CH_2), 55.5 (CH_3), 64.0 (CH), 86.6 (CH), 113.7 (CH), 114.4 (CH), 116.2 (1C, q, J = 288.6, C), 123.3 (CH), 127.0 (C), 128.8 (CH), 129.0 (C), 129.4 (CH), 129.8 (CH), 130.4 (CH), 132.3 (C), 132.5 (CH), 140.3 (CH), 149.5 (CH), 150.8 (C), 158.4 (1C, q, J = 35.9, C), 160.5 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.5 (3F, s); MS (ES^+) m/z 494 (80, M^+), 447 (100, $M^+ - NO_2$), 230 (50, $C_{14}H_{12}ClN$); HRMS $C_{23}H_{20}ClF_3N_3O_4$ calcd 494.1094, found 494.1103.

General Procedure for the Synthesis of β-Aminoacetamides 7 (Table 5). To a solution of β-nitroacetamide (1.00 mmol) in EtOAc (30.0 mL) and EtOH (40.0 mL) at 0 °C was added 6 M aq HCl (250 mmol). The colorless solution was vigorously stirred, and zinc dust (50.0 mmol) was added in three portions over 10 min. The gray suspension was removed from the cold bath and allowed to warm to rt over 2 h to give a colorless solution. Zinc dust (25.0 mmol) was added in one portion, and the resultant gray suspension stirred at room temperature for a further 1 h. The EtOH and EtOAc were removed in vacuo, and the resultant aqueous solution was neutralized by the addition of $NaHCO_{3(s)}$ and extracted with EtOAc. The combined organic phases were washed with 2 M HCl and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was dissolved in EtOH (40.0 mL), 6 M $HCl_{(aq)}$ (20.0 mmol) was added and the mixture stirred at rt for 1 h before removal of the EtOH in vacuo. To the residue was added H_2O, and the product was extracted into EtOAc. The combined organic phases were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give crude β-aminoacetamide which was purified by column chromatography.

N-((1R,2S*)-3-(2-Bromophenyl)-1-((4-methoxyphenyl)amino)-1-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (**7a**).* β-Nitroacetamide **6a** (893 mg, 1.66 mmol) afforded crude β-aminoacetamide **7a** as a brown solid. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7a** as a white solid (751 mg, 89%): mp 166−169 °C; R_f 0.33 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3303, 3065−2834, 1702, 1512, 1180 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.84 (1H, dd, J = 14.1, 11.1), 3.15 (1H, dd, J = 14.1, 3.7), 3.71 (3H, s), 4.33 (1H, br s), 4.70 (1H, d, J = 3.7), 4.75 (1H, m), 6.39 (1H, br d, J = 9.4), 6.56 (2H, dm, J = 8.9), 6.72 (2H, dm, J = 8.9), 7.10 (2H, m), 7.22 (1H, td, J = 7.5, 0.9), 7.35 (1H, m), 7.40- 7.43 (4H, m), 7.52 (1H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.7 (CH_2), 55.4 (CH), 55.8 (OCH_3), 62.2 (CH), 114.9 (CH), 115.5 (CH), 115.7 (1C, q, J = 288.0, C), 124.9 (C), 127.3 (CH), 127.9 (CH), 128.3 (CH), 129.0 (CH), 129.1 (CH), 131.0 (CH), 133.1 (CH), 136.1 (C), 138.3 (C), 140.6 (C), 152.8 (C), 157.4 (1C, q, J = 37.2, C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.4 (3F, s); MS (ESI^+) m/z 507 + 509 (26, M^+ + H), 429 (100, M^+ − Br); HRMS $C_{24}H_{23}(^{79}Br)F_3N_2O_2$ calcd 507.0890, found 507.0879. Anal. Calcd for $C_{24}H_{22}BrF_3N_2O_2$: C, 56.82; H, 4.37; N, 5.52. Found: C, 56.63; H, 4.31; N, 5.29.

N-((1S,2S*)-3-(2-Bromophenyl)-1-(furan-2-yl)-1-((4-methoxyphenyl)amino)propan-2-yl)-2,2,2-trifluoroacetamide (**7b**).* β-Nitroacetamide **6b** (586 mg, 1.11 mmol) afforded crude β-aminoacetamide **7b** as a brown solid. Purification by flash column chromatography (20% EtOAc/petroleum ether) and subsequent recrystallization from toluene/petroleum ether yielded pure β-aminoacetamide **7b** as a white solid (501 mg, 91%): mp 131−133 °C; R_f 0.24 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3306, 3113−2834, 1703, 1511, 1244, 1232, 1207, 1167 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.94 (1H, dd, J = 14.0, 10.2), 3.13 (1H, dd, J = 14.0, 4.8), 3.74 (3H, s), 3.98 (1H, br s), 4.71 (1H, d, J = 4.0), 4.80 (1H, ddd, J = 14.4, 9.7, 4.6), 6.32 (1H, d, J = 3.3), 6.37 (1H, dd, J = 3.3, 1.9), 6.62 (2H, dm, J = 8.9), 6.67 (1H, br d, J = 9.4), 6.76 (2H, dm, J = 8.9), 7.12 (1H, td, J = 7.6, 1.6), 7.21 (1H, dd, J = 7.7, 1.7), 7.25 (1H, td, J = 7.5,

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1.2), 7.45 (1H, dd, J = 1.7, 0.7), 7.55 (1H, dd, J = 8.0, 1.0); ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.0 (CH_2), 54.0 (*C*H), 55.8 (CH_3), 56.5 (*C*H), 108.8 (*C*H), 110.8 (*C*H), 114.9 (*C*H), 115.8 (1C, q, J = 288.3, *C*), 116.1 (*C*H), 125.0 (*C*), 127.8 (*C*H), 129.0 (*C*H), 131.3 (*C*H), 133.2 (*C*H), 136.2 (*C*), 140.3 (*C*), 142.8 (*C*H), 152.0 (*C*), 153.4 (*C*), 157.2 (1C, q, J = 37.0, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (EI) m/z 496 + 498 (4, M^+), 202 (100, $M^+ - C_{10}H_8BrF_3NO$); HRMS $C_{22}H_{20}(^{79}Br)F_3N_2O_3$ calcd 496.0604, found 496.0614. Anal. Calcd for $C_{22}H_{20}BrF_3N_2O_3$: C, 53.13; H, 4.05; N, 5.63. Found: C, 53.44; H, 4.16; N, 5.89.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(furan-3-yl)-1-((4-methoxyphenyl)amino)propan-2-yl)-2,2,2-trifluoroacetamide (**7c**).* β-Nitroacetamide **6c** (511 mg, 0.969 mmol) afforded crude β-aminoacetamide **7c** as a brown solid. Purification by flash column chromatography (20% EtOAc/petroleum ether) and subsequent recrystallization from toluene/petroleum ether yielded pure β-aminoacetamide **7c** as a white solid (448 mg, 93%): mp 131−133 °C; R_f 0.46 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3398, 3312, 3111−2835, 1705, 1511, 1244, 1230, 1209, 1164, 1027 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.91 (1H, dd, J = 13.9, 10.9), 3.17 (1H, dd, J = 14.0, 4.0), 3.74 (1H, s), 3.90 (1H, br s), 4.65 (1H, d, J = 3.2), 4.72 (1H, m), 6.45 (1H, s), 6.52 (1H, d, J = 9.3), 6.63 (2H, dm, J = 8.9), 6.77 (2H, dm, J = 8.9), 7.12 (1H, td, J = 7.7, 1.5), 7.17 (1H, dd, J = 7.6, 1.4), 7.25 (1H, t, J = 7.4), 7.45−7.47 (2H, m), 7.55 (1H, d, J = 8.0); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.6 (CH_2), 54.5 (*C*H), 55.4 (*C*H), 55.8 (CH_3), 109.3 (*C*H), 115.0 (*C*H), 115.7 (1C, q, J = 288.2, *C*), 115.8 (*C*H), 123.8 (*C*), 124.9 (*C*), 127.9 (*C*H), 129.1 (*C*H), 131.2 (*C*H), 133.2 (*C*H), 136.1 (*C*), 140.5 (*C*H), 140.6 (*C*), 144.2 (*C*H), 153.2 (*C*), 157.3 (1C, q, J = 37.2, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (EI) m/z 496 + 498 (1:1, 2, M^+), 202 (100, $M^+ - C_{10}H_8BrF_3NO$); HRMS $C_{22}H_{20}(^{79}Br)F_3N_2O_3$ calcd 496.0604, found 496.0598. Anal. Calcd for $C_{22}H_{20}BrF_3N_2O_3$: C, 53.13; H, 4.05; N, 5.63. Found: C, 53.27; H, 4.02; N, 5.52.

N-((1S,2S*)-3-(2-Bromophenyl)-1-((4-methoxyphenyl)amino)-1-(thiophene-2-yl)propan-2-yl)-2,2,2-trifluoroacetamide (**7d**).* β-Nitroacetamide **6d** (516 mg, 0.950 mmol) afforded crude β-aminoacetamide **7d** as a brown solid. Purification by flash column chromatography (20% EtOAc/petroleum ether) and subsequent recrystallization from toluene/petroleum ether yielded pure β-aminoacetamide **7d** as a white solid (402 mg, 82%): mp 131−133 °C; R_f 0.46 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3298, 3104−2834, 1700, 1512, 1244, 1233, 1207, 1178 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.93 (1H, dd, J = 14.0, 10.8), 3.20 (1H, dd, J = 14.1, 4.1), 3.73 (3H, s), 4.23 (1H, d, J = 6.7), 4.79 (1H, m), 4.93 (1H, dd, J = 6.6, 3.5), 6.49 (1H, br d, J = 9.4), 6.61 (2H, dm, J = 8.9), 6.75 (2H, dm, J = 8.9), 7.07 (1H, dd, J = 5.0, 3.5), 7.11−7.14 (2H, m), 7.18 (1H, dd, J = 7.7, 1.7), 7.26 (1H, td, J = 7.5, 1.4), 7.31 (1H, dd, J = 5.1, 1.1), 7.55 (1H, dd, J = 8.0, 1.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.0 (CH_2), 55.2 (*C*H), 55.8 (CH_3), 59.0 (*C*H), 114.9 (*C*H), 115.7 (*C*H), 115.7 (1C, q, J = 288.3, *C*), 125.0 (*C*), 125.5 (*C*H), 125.6 (*C*H), 127.5 (*C*H), 127.9 (*C*H), 129.1 (*C*H), 131.1 (*C*H), 133.2 (*C*H), 136.0 (*C*), 140.4 (*C*), 143.0 (*C*), 153.2 (*C*), 157.6 (1C, q, J = 37.3, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (EI) m/z 514 + 512 (3, M^+), 218 (100, $M^+ - C_{10}H_8BrF_3NO$); HRMS $C_{22}H_{20}(^{79}Br)F_3N_2O_2S$ calcd 512.0376, found 512.0374. Anal. Calcd for $C_{22}H_{20}BrF_3N_2O_2S$: C, 51.47; H, 3.93; N, 5.46. Found: C, 51.62; H, 3.86; N, 5.41.

N-((2S,3R*)-1-(2-Bromophenyl)-3-((4-methoxyphenyl)amino)-octan-2-yl)-2,2,2-trifluoroacetamide (**7e**).* β-Nitroacetamide **6e** (999 mg, 1.88 mmol) afforded crude β-aminoacetamide **7e** as a pale brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7e** as an off-white solid (899 mg, 95%): mp 51−53 °C; R_f 0.23 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3391, 3297, 3105−2834, 1702, 1510, 1232, 1208, 1178, 1163, 1039 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (3H, t, J = 6.9), 1.24−1.32 (4H, m), 1.37−1.47 (2H, m), 1.55−1.61 (1H, m), 1.65−1.71 (1H, m), 2.84 (1H, dd, J = 13,7, 11.3), 3.13 (1H, br s), 3.20 (1H, dd, J = 13.7, 3.9), 3.55 (1H, m), 3.77 (3H, s), 4.49 (1H, m), 6.61−6.65 (3H, m), 6.79 (2H, dm, J = 8.9), 7.12 (1H, td, J = 7.7, 1.5), 7.19 (1H, dd, J = 7.6, 1.5), 7.25 (1H, td, J = 7.4, 0.8), 7.55 (1H, dd, J = 8.0, 0.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_2), 26.3 (CH_2), 31.8 (CH_2), 33.5 (CH_2), 35.1 (CH_2), 53.6 (*C*H), 55.8 (CH_3), 59.0 (*C*H), 115.2 (*C*H), 115.6 (*C*H), 115.8 (1C, q, J = 288.2, *C*), 125.0 (*C*), 127.7 (*C*H), 128.9 (*C*H), 131.3 (*C*H), 133.1 (*C*H), 136.5 (*C*), 142.0 (*C*), 153.0 (*C*), 156.6 (1C, q, J = 36.9, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.4 (3F, s); MS (EI) m/z 500 + 502 (4, M^+), 206 (100, $M^+ - C_{10}H_8BrF_3NO$); HRMS $C_{23}H_{28}(^{79}Br)F_3N_2O_2$ calcd 500.1281, found 500.1289. Anal. Calcd for $C_{23}H_{28}BrF_3N_2O_2$: C, 55.10; H, 5.63; N, 5.59. Found: C, 55.33; H, 5.65; N, 5.61.

N-((1R,2S*)-3-(2-Bromophenyl)-1-((4-methoxyphenyl)amino)-1-(o-tolyl)propan-2-yl)-2,2,2-trifluoroacetamide (**7h**).* β-Nitroacetamide **6h** (159 mg, 0.288 mmol) afforded crude β-aminoacetamide **7h** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7h** as a white solid (138 mg, 91%): mp 190−192 °C; R_f 0.51 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3409, 3327, 3063−2834, 1703, 1511, 1243, 1232, 1211, 1169, 1034 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.55 (3H, s), 2.88 (1H, dd, J = 13.7, 11.9), 3.14 (1H, dd, J = 13.8, 3.0), 3.71 (3H, s), 4.24 (1H, br s), 4.65 (1H, m), 4.96 (1H, d, J = 3.8), 6.58 (2H, dm, J = 8.9), 6.70 (1H, br d, J = 9.2), 6.74 (2H, dm, J = 8.9), 7.06 (1H, dd, J = 7.6, 1.0), 7.08 (1H, dd, J = 7.7, 1.4), 7.19−7.26 (4H, m), 7.31−7.33 (1H, m), 7.50 (1H, d, J = 7.9); ^{13}C NMR (151 MHz, $CDCl_3$) δ 19.6 (CH_3), 35.1 (CH_2), 54.2 (*C*H), 55.8 (CH_3), 58.5 (*C*H), 115.0 (*C*H), 115.7 (1C, q, J = 288.2, *C*), 115.9 (*C*H), 124.8 (*C*), 125.9 (*C*H), 126.5 (*C*H), 127.8 (*C*H), 127.9 (*C*H), 129.0 (*C*H), 131.0 (*C*H), 131.5 (*C*H), 133.1 (*C*H), 136.2 (*C*), 136.3 (*C*), 136.4 (*C*), 140.5 (*C*), 153.1 (*C*), 157.1 (1C, q, J = 37.1, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (EI) m/z 520 + 522 (10, M^+), 226 (100, $M^+ - C_{10}H_8BrF_3NO$); HRMS $C_{25}H_{24}(^{79}Br)F_3N_2O_2$ calcd 520.0968, found 520.0974. Anal. Calcd for $C_{25}H_{24}BrF_3N_2O_2$: C, 57.59; H, 4.64; N, 5.37. Found: C, 57.88; H, 4.63; N, 5.29.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(2-methoxyphenyl)-1-((4-methoxyphenyl)amino)propan-2-yl)-2,2,2-trifluoroacetamide (**7j**).* β-Nitroacetamide **6j** (154 mg, 0.271 mmol) afforded crude β-aminoacetamide **7j** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7j** as a white solid (136 mg, 94%): mp 137−138 °C; R_f 0.41 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3373, 3062−2836, 1710, 1511, 1235, 1208, 1163, 1027 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.87 (1H, dd, J = 14.2, 10.7), 3.36 (1H, dd, J = 14.2, 3.7), 3.71 (3H, s), 3.94 (3H, s), 4.39 (1H, br s), 4.71 (1H, qdd, J = 10.0, 6.2, 3.8), 4.96 (1H, d, J = 6.1), 6.57 (2H, dm, J = 8.9), 6.70 (1H, d, J = 9.3), 6.72 (2H, dm, J = 8.9), 6.92−6.94 (2H, m), 7.09 (1H, td, J = 7.6, 1.6), 7.16 (1H, dd, J = 7.7, 1.7), 7.22 (1H, td, J = 7.4, 1.2), 7.24−7.28 (2H, m), 7.52 (1H, dd, J = 8.0, 1.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.6 (CH_2), 54.5 (*C*H), 55.6 (CH_3), 55.8 (CH_3), 57.5 (*C*H), 110.8 (*C*H), 114.9 (*C*H), 115.4 (*C*H), 115.8 (1C, q, J = 288.3, *C*), 121.3 (*C*H), 125.0 (*C*), 126.5 (*C*), 127.7 (*C*H), 128.2 (*C*H), 128.7 (*C*H), 129.2 (*C*H), 131.2 (*C*H), 133.0 (*C*H), 136.8 (*C*), 140.7 (*C*), 152.7 (*C*), 156.8 (1C, q, J = 36.8, *C*), 157.1 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.6 (3F, s); MS (CI) m/z 537 + 539 (1:1, 12, M^+ + H), 414 + 416 (1:1, 15, M^+ − NHPMP), 301 + 303 (5%, $M^+ - C_9H_9F_3N_2O_2$), 242 (25, $M^+ - C_{10}H_8BrF_3NO$); HRMS $C_{25}H_{25}(^{79}Br)F_3N_2O_3$ calcd 537.1001, found 537.1013. Anal. Calcd for $C_{25}H_{24}BrF_3N_2O_3$: C, 55.88; H, 4.50; N, 5.21. Found: C, 55.58; H, 4.40; N, 5.25.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(3-methoxyphenyl)-1-((4-methoxyphenyl)amino)propan-2-yl)-2,2,2-trifluoroacetamide (**7k**).* β-Nitroacetamide **6k** (177 mg, 0.312 mmol) afforded crude β-aminoacetamide **7k** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) followed by recrystallization from toluene/petroleum ether yielded pure β-aminoacetamide **7k** as a white solid (137 mg, 82%): mp 130−131 °C; R_f 0.31 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3389, 3306, 3107−2836, 1701, 1511, 1242, 1232, 1208, 1158, 1037 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.84 (1H, dd, J = 13.9, 11.3), 3.15 (1H, dd, J = 14.1, 3.6), 3.71 (3H, s), 3.81 (3H, s), 4.29 (1H, br s), 4.66 (1H, br s), 4.75 (1H, m), 6.42 (1H, d, J = 9.4), 6.56 (2H, d, J = 6.2), 6.72 (2H, d, J = 8.9), 6.87 (1H, dd, J = 8.2, 2.1), 6.95 (1H, s), 7.00 (1H, d, J = 7.6), 7.09−7.12 (2H, m), 7.22 (1H, td, J = 7.4, 0.7), 7.33 (1H, t, J = 7.9), 7.53

(1H, d, J = 8.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.8 (CH_2), 55.2 (CH), 55.4 (CH_3), 55.8 (CH_3), 62.3 (CH), 112.9 (CH), 113.6 (CH), 114.9 (CH), 115.5 (CH), 115.7 (1C, q, J = 288.1, C), 119.6 (CH), 124.9 (C), 127.9 (CH), 129.0 (CH), 130.2 (CH), 131.0 (CH), 133.1 (CH), 136.1 (C), 140.0 (C), 140.6 (C), 152.8 (C), 157.4 (1C, q, J = 37.3, C), 160.2 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (ES$^-$) m/z 536 + 538 (1:1, 25, M^-), 535 + 537 (1:1, 100, M − H^+), 457 (18, M^- − Br); HRMS $C_{25}H_{23}(^{79}Br)F_3N_2O_3$ calcd 535.0844, found 535.0837. Anal. Calcd for $C_{25}H_{24}BrF_3N_2O_3$: C, 55.88; H, 4.50; N, 5.21. Found: C, 55.60; H, 4.40; N, 5.16.

N-((1R,2S*)-3-(2-Bromophenyl)-1-(4-methoxyphenyl)-1-((4-methoxyphenyl)amino)propan-2-yl)-2,2,2-trifluoroacetamide (**7l**).* β-Nitroacetamide **6l** (169 mg, 0.298 mmol) afforded crude β-aminoacetamide **7l** as a pale brown solid. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7l** as a white solid (146 mg, 91%): mp 173−175 °C; R_f 0.35 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3399, 3302, 3107−2836, 1702, 1510, 1243, 1209, 1175, 1033 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.81 (1H, dd, J = 14.0, 11.2), 3.15 (1H, dd, J = 14.1, 3.8), 3.71 (3H, s), 3.83 (3H, s), 4.28 (1H, br s), 4.64 (1H, br s), 4.73 (1H, m), 6.33 (1H, d, J = 9.4), 6.54 (2H, d, J = 8.6), 6.71 (2H, d, J = 8.9), 6.94 (2H, dm, J = 8.7), 7.09−7.10 (1H, m), 7.11 (1H, d, J = 7.4), 7.22 (1H, td, J = 7.5, 1.1), 7.32 (2H, dm, J = 8.6), 7.53 (1H, dd, J = 8.3, 1.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.9 (CH_2), 55.4 (CH_3 + CH), 55.8 (CH_3), 61.7 (CH), 114.5 (CH), 114.9 (CH), 115.5 (CH), 115.7 (1C, q, J = 288.2, C), 124.9 (C), 127.9 (CH), 128.4 (CH), 129.0 (CH), 130.0 (C), 131.0 (CH), 133.1 (CH), 136.1 (C), 140.6 (C), 152.7 (C), 157.5 (1C, q, J = 37.2, C), 159.5 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (CI) m/z 537 + 539 (1:1, 100, M^+ + H), 536 + 538 (1:1, 23, M^+), 242 (44, M^+ − $C_{10}H_8BrF_3NO$); HRMS $C_{25}H_{25}(^{79}Br)F_3N_2O_3$ calcd 537.1001, found 537.1008. Anal. Calcd for $C_{25}H_{24}BrF_3N_2O_3$: C, 55.88; H, 4.50; N, 5.21. Found: C, 56.03; H, 4.48; N, 5.16.

N-((1R,2S*)-3-(2-Bromophenyl)-1-((4-methoxyphenyl)amino)-1-(2-(trifluoromethyl)phenyl)propan-2-yl)-2,2,2-trifluoroacetamide (**7m**).* β-Nitroacetamide **6m** (824 mg, 1.36 mmol) afforded crude β-aminoacetamide **7m** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) and subsequent recrystallization from toluene/petroleum ether yielded pure β-aminoacetamide **7m** as a white solid (642 mg, 82%): mp 140−142 °C; R_f 0.38 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3362, 3066−2836, 1712, 1512, 1310, 1243, 1234, 1212, 1161, 1118, 1035 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.06 (1H, dd, J = 14.1, 10.1), 3.55 (1H, dd, J = 14.1, 3.4), 3.71 (3H, s), 4.30 (1H, br s), 4.55 (1H, m), 4.98 (1H, d, J = 6.6), 6.40 (1H, d, J = 8.8), 6.63 (2H, d, J = 8.8), 6.74 (2H, d, J = 8.8), 7.11 (1H, td, J = 7.6, 1.4), 7.19 (1H, dd, J = 7.5, 1.4), 7.24 (1H, t, J = 7.4), 7.38 (1H, t, J = 7.7), 7.52−7.55 (2H, m), 7.68 (2H, d, J = 8.0); ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.7 (CH_2), 55.5 (CH), 55.7 (CH_3), 58.7 (CH), 114.9 (CH), 115.5 (1C, q, J = 288.2, C), 115.9 (CH), 124.7 (1C, q, J = 273.9, C), 124.8 (C), 126.2 (1C, q, J = 5.9, CH), 127.8 (CH), 127.9 (CH), 128.2 (1C, q, J = 29.4, C), 128.3 (CH), 129.1 (CH), 131.3 (CH), 132.8 (CH), 133.2 (CH), 136.1 (C), 138.9 (C), 139.8 (C), 153.2 (C), 156.4 (1C, q, J = 37.2, C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.8 (3F, s), −57.2 (3F, s); MS (EI) m/z 574 + 576 (1:1, 3, M^+), 280 (100, M^+ − $C_8H_{10}BrF_3NO$); HRMS $C_{25}H_{21}(^{79}Br)F_6N_2O_2$ calcd 574.0685, found 574.0696. Anal. Calcd for $C_{25}H_{21}BrF_6N_2O_2$: C, 52.19; H, 3.68; N, 4.87. Found: C, 51.92; H, 3.45; N, 4.94.

N-((1R,2S*)-3-(2-Bromophenyl)-1-((4-methoxyphenyl)amino)-1-(3-(trifluoromethyl)phenyl)propan-2-yl)-2,2,2-trifluoroacetamide (**7n**).* β-Nitroacetamide **6n** (688 mg, 1.14 mmol) afforded crude β-aminoacetamide **7n** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7n** as a white solid (579 mg, 89%): mp 133−134 °C; R_f 0.24 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3408, 3292, 3108−2836, 1699, 1511, 1327, 1242, 1233, 1210, 1162, 1124, 1072, 1033 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.88 (1H, dd, J = 14.0, 11.0), 3.16 (1H, dd, J = 14.1, 3.8), 3.72 (3H, s), 4.40 (1H, br s), 4.72 (1H, m), 4.77 (1H, d, J = 3.8), 6.41 (1H, d, J = 9.1), 6.55 (2H, dm, J = 8.9), 6.74 (2H, dm, J = 8.9), 7.10−7.12 (2H, m), 7.23 (1H, t, J = 7.5), 7.52−7.54 (2H, m), 7.61 (2H, t, J = 8.5), 7.67 (1H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.3 (CH_2), 55.5 (CH), 55.8 (CH_3), 62.1 (CH), 115.0 (CH), 115.6 (CH), 115.6 (1C, q, J = 288.0, C), 124.0 (1C, q, J = 272.5, C), 124.2 (1C, q, J = 3.6, CH), 124.8 (C), 125.2 (1C, q, J = 3.5, CH), 128.0 (CH), 129.2 (CH), 129.6 (CH), 130.6 (CH), 131.0 (CH), 131.4 (1C, q, J = 32.4, C), 133.2 (CH), 135.7 (C), 139.9 (C), 140.0 (C), 153.1 (C), 157.6 (1C, q, J = 37.4, C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.4 (3F, s), −63.0 (3F, s); MS (CI) m/z 575 + 577 (5, M^+ + H), 280 (100, M^+ − $C_8H_{10}BrF_3NO$); HRMS $C_{25}H_{22}(^{79}Br)F_6N_2O_2$ calcd 575.0769, found 575.0778. Anal. Calcd for $C_{25}H_{21}BrF_6N_2O_2$: C, 52.19; H, 3.68; N, 4.87. Found: C, 52.27; H, 3.57; N, 4.85.

N-((1R,2S*)-3-(2-Bromophenyl)-1-((4-methoxyphenyl)amino)-1-(4-(trifluoromethyl)phenyl)propan-2-yl)-2,2,2-trifluoroacetamide (**7o**).* β-Nitroacetamide **6o** (176 mg, 0.291 mmol) afforded crude β-aminoacetamide **7o** as a pale brown solid. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7o** as a white solid (147 mg, 88%): mp 154−156 °C; R_f 0.45 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3402, 3293, 3106−2836, 1701, 1512, 1326, 1243, 1211, 1166, 1125, 1068 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.88 (1H, dd, J = 14.1, 10.8), 3.15 (1H, dd, J = 14.1, 3.8), 3.71 (3H, s), 4.40 (1H, d, J = 5.5), 4.73−4.78 (2H, m), 6.41 (1H, d, J = 8.9), 6.53 (2H, dm, J = 8.9), 6.73 (2H, dm, J = 8.9), 7.10−7.13 (2H, m), 7.23 (1H, td, J = 7.5, 1.1), 7.52−7.53 (1H, m), 7.54 (2H, d, J = 8.1), 7.66 (2H, d, J = 8.2); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.3 (CH_2), 55.4 (CH), 55.8 (CH_3), 62.0 (CH), 115.0 (CH), 115.5 (CH), 115.6 (1C, q, J = 288.2, C), 124.0 (1C, q, J = 272.2, C), 124.8 (C), 126.0 (1C, q, J = 3.4, CH), 127.7 (CH), 128.0 (CH), 129.2 (CH), 130.5 (1C, q, J = 32.5, C), 131.0 (CH), 133.2 (CH), 135.6 (C), 140.0 (C), 142.8 (C), 153.1 (C), 157.6 (1C, q, J = 37.4, C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s), −63.0 (3F, s); MS (CI) m/z 575 + 577 (1:1, 100, M^+ + H), 574 + 576 (1:1, 7, M^+); HRMS $C_{25}H_{22}(^{79}Br)F_6N_2O_2$ calcd 575.0769, found 575.0771. Anal. Calcd for $C_{25}H_{21}BrF_6N_2O_2$: C, 52.19; H, 3.68; N, 4.87. Found: C, 52.06; H, 3.60; N, 4.85.

N-((1R,2S*)-3-(2-Bromo-5-fluorophenyl)-1-((4-methoxyphenyl)-amino)-1-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (**7p**).* β-Nitroacetamide **6p** (649 mg, 1.17 mmol) afforded crude β-aminoacetamide **7p** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7p** as a white solid (546 mg, 89%): mp 148−150 °C; R_f 0.26 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3397, 3301, 3107−2835, 1700, 1512, 1471, 1236, 1210, 1179, 1033 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.80 (1H, dd, J = 14.0, 11.2), 3.13 (1H, dd, J = 14.0, 3.5), 3.71 (3H, s), 4.27 (1H, br s), 4.70 (1H, s), 4.74 (1H, m), 6.47 (1H, d, J = 9.4), 6.57 (2H, d, J = 8.5), 6.72 (2H, dm, J = 8.9), 6.83−6.86 (2H, m), 7.33−7.36 (1H, m), 7.39−7.43 (4H, m), 7.47 (1H, dd, J = 9.6, 5.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.8 (CH_2), 55.1 (CH), 55.8 (CH_3), 62.2 (CH), 114.9 (CH), 115.7 (CH), 115.7 (1C, q, J = 288.2, C), 116.3 (1C, d, J = 22.3, CH), 118.0 (1C, d, J = 22.8, CH), 118.9 (1C, d, J = 3.2, C), 127.2 (CH), 128.4 (CH), 129.2 (CH), 134.3 (1C, d, J = 8.1, CH), 138.1 (C), 138.3 (1C, d, J = 7.4, C), 140.4 (C), 153.0 (C), 157.4 (1C, q, J = 37.3, C), 161.9 (1C, d, J = 248.2, C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −114.6 (1F, m), −76.3 (3F, s); MS (EI) m/z 524 + 526 (1:1, 5, M^+), 446 (3, M^+ − Br), 212 (100, M^+ − $C_{10}H_7BrF_4NO$); HRMS $C_{24}H_{21}(^{79}Br)F_4N_2O_2$ calcd 524.0717, found 524.0704. Anal. Calcd for $C_{24}H_{21}BrF_4N_2O_2$: C, 54.87; H, 4.03; N, 5.33. Found: C, 54.91; H, 3.97; N, 5.28.

N-((1R,2S*)-3-(2-Bromo-4,5-dimethoxyphenyl)-1-((4-methoxyphenyl)amino)-1-phenylpropan-2-yl)-2,2,2-trifluoroacetamide (**7q**).* β-Nitroacetamide **6q** (89 mg, 0.15 mmol) afforded crude β-aminoacetamide **7q** as a pale brown oil. Purification by flash column chromatography (60% Et_2O/petroleum ether) yielded pure β-aminoacetamide **7q** as a white solid (67 mg, 79%): mp 167−169 °C; R_f 0.27 (60% Et_2O/petroleum ether); IR ν_{max} (neat) 3410, 3296, 3113−2837, 1695, 1509, 1259, 1241, 1217, 1178, 1166, 1034 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.81 (1H, dd, J = 14.3, 10.7), 3.10 (1H, dd, J = 14.3, 3.6), 3.70 (3H, s), 3.77 (3H, s), 3.84 (3H, s), 4.33 (1H, d, J = 6.1), 4.68 (1H, d, J = 5.2), 4.70 (1H, m), 6.37 (1H, br d, J = 9.0), 6.55 (2H, dm, J = 8.9), 6.57 (1H, s), 6.71 (2H, dm, J = 8.9), 6.96 (1H,

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s), 7.33 (1H, m), 7.40 (4H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.3 (CH_2), 55.6 (*C*H), 55.8 (CH_3), 56.1 (CH_3), 56.2 (CH_3), 62.3 (*C*H), 113.1 (*C*H), 114.7 (*C*), 114.9 (*C*H), 115.5 (*C*H), 115.5 (*C*H), 115.7 (1C, q, J = 288.2, *C*), 127.3 (*C*H), 127.8 (*C*), 128.3 (*C*H), 129.1 (*C*H), 138.4 (*C*), 140.5 (*C*), 148.7 (*C*), 148.8 (*C*), 152.8 (*C*), 157.5 (1C, q, J = 37.2, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (FAB$^+$) m/z 591 + 589 (12, M + Na$^+$), 212 (100, $C_{12}H_{12}BrF_3NO_3$); HRMS $C_{26}H_{26}(^{79}Br)F_3N_2O_4Na$ calcd 589.0926, found 589.0912. Anal. Calcd for $C_{26}H_{26}BrF_3N_2O_4$: C, 55.04; H, 4.62; N, 4.94. Found: C, 55.38; H, 4.53; N, 4.75.

N-((1R,2S*)-3-(2-Bromophenyl)-1-cyclohexyl-2-(hydroxyamino)-propyl)-4-methoxyaniline (**19**).* To a solution of crude β-nitroamine **5f** (0.452 mmol) in THF (2.5 mL) at 0 °C was added MeOH (274 μL, 6.78 mmol) followed by the portionwise addition of freshly amalgamated Al foil (61.0 mg, 2.26 mmol) [coils of Al foil (~1.00 mmol) were soaked in Et_2O to remove machining oils and individually immersed in sat. $HgCl_{2(aq)}$ solution for 30 s, washed in H_2O for 5 s, roughly dried on tissue, and added to the reaction mixture]. The mixture was allowed to warm to rt and rigorously stirred for 2 h to give a dark gray suspension. The mixture was filtered through Celite and washed with Et_2O (2 × 15 mL) and MeOH (15 mL) and the solvents removed in vacuo to give crude β-aminohydroxylamine **19** as a yellow oil. Purification by flash column chromatography (30% EtOAc/petroleum ether) yielded pure β-aminohydroxylamine **19** as a colorless solid (109 mg, 56%, >95:5 dr): mp 139−141 °C; R_f 0.60 (30% EtOAc/petroleum ether); IR ν_{max} (neat) 3356, 3242, 3056−2850, 1509, 1233, 1037, 1024 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.99 (1H, qd, J = 12.3, 3.1), 1.10−1.28 (4H, m), 1.62−1.68 (2H, m), 1.71−1.76 (2H, m), 1.86 (2H, m), 2.66 (1H, dd, J = 14.0, 11.0), 2.99 (1H, dd, J = 14.0, 3.2), 3.17 (1H, br d, J = 7.1), 3.31 (1H, ddd, J = 11.0, 4.3, 3.5), 3.63 (1H, br s), 3.76 (3H, s), 6.72 (2H, dm, J = 9.0), 6.77 (2H, dm, J = 9.1), 7.10 (1H, ddd, J = 8.0, 6.8, 2.2), 7.24−7.28 (2H, m), 7.55 (1H, dd, J = 8.0, 0.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.3 (2 × CH_2), 26.5 (CH_2), 29.8 (CH_2), 31.2 (CH_2), 33.2 (CH_2), 41.4 (*C*H), 55.9 (CH_3), 59.8 (*C*H), 63.0 (*C*H), 114.4 (*C*H), 115.1 (*C*H), 124.8 (*C*), 127.5 (*C*H), 128.1 (*C*H), 131.9 (*C*H), 133.0 (*C*H), 139.0 (*C*), 144.6 (*C*), 151.8 (*C*); MS (CI) m/z 433 + 435 (1:1, 25, M$^+$ + H), 432 + 434 (1:1, 18, M$^+$), 418 + 420 (1:1, 42, M$^+$ − CH_2), 415 + 417 (1:1, 35, M$^+$−OH), 218 (28, M$^+$ − C_8H_9BrNO); HRMS $C_{22}H_{30}(^{79}Br)N_2O_2$ calcd 433.1491, found 433.1487. Anal. Calcd for $C_{22}H_{29}BrN_2O_2$: C, 60.97; H, 6.74; N, 6.46. Found: C, 61.07; H, 6.79; N, 6.30.

N-((1R,2S*)-3-(2-Bromophenyl)-1-cyclohexyl-1-((4-methoxyphenyl)amino)propan-2-yl)-2,2,2-trifluoroacetamide (**7f**).* To a solution of β-aminohydroxylamine **19** (146 mg, 0.337 mmol) in toluene (6.7 mL) at 0 °C was added dropwise $LiAlH_4$ (2 M in THF, 843 μL, 1.69 mmol). The reaction was stirred at 0 °C for 1 h before being allowed to warm to rt and stirred until the reaction was complete by TLC analysis (3 h). The mixture was cooled to 0 °C before being quenched by the careful dropwise addition of ^{i}PrOH (0.35 mL per mmol $LiAlH_4$ = 0.61 mL) and brine (0.10 mL per mmol $LiAlH_4$ = 0.17 mL). The mixture was dried ($MgSO_4$) and filtered through Celite, and the solvents were removed in vacuo to give the crude 1,2-diamine. To a solution of the crude 1,2-diamine in CH_2Cl_2 (3.4 mL) at −78 °C was added DIPEA (88.1 μL, 0.506 mmol) quickly followed by the dropwise addition of TFAA (70.3 μL, 0.506 mmol). The reaction was stirred at −78 °C for 30 min before being allowed to warm to rt over 30 min. The reaction was quenched by the addition of 2 M HCl (5 mL), the layers were separated and the aqueous layer further extracted with CH_2Cl_2 (2 × 5 mL). The combined organic extracts were dried ($MgSO_4$) and filtered and the solvents removed in vacuo to give crude β-aminoacetamide **7f** as a yellow oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7f** as a white solid (141 mg, 81%): mp 60−63 °C; R_f 0.52 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3360, 3305, 3105−2853, 1703, 1509, 1243, 1232, 1207, 1162, 1039, 1027 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.90 (1H, qd, J = 12.6, 2.9), 1.11−1.30 (4H, m), 1.50−1.56 (1H, m), 1.67 (1H, d, J = 10.9), 1.71 (1H, d, J = 11.5), 1.80−1.82 (1H, m), 1.91 (1H, d, J = 13.2), 2.04 (1H, d, J = 12.4), 2.87 (1H, dd, J = 13.7, 11.6), 3.14 (1H, dd, J = 13.8, 3.7), 3.24 (1H, d, J = 9.2), 3.32 (1H, td, J = 9.0, 3.5), 3.76 (3H, s), 4.66 (1H, m), 6.62 (2H, dm, J = 8.9), 6.67 (1H, d, J = 9.5), 6.78 (2H, dm, J = 8.9), 7.10 (1H, td, J = 7.7, 1.6), 7.19 (1H, dd, J = 7.6, 1.7), 7.24 (1H, td, J = 7.5, 1.0), 7.54 (1H, dd, J = 8.1, 1.0); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.0 (CH_2), 26.0 (CH_2), 26.2 (CH_2), 30.5 (CH_2), 30.5 (CH_2), 34.6 (CH_2), 42.2 (*C*H), 51.8 (*C*H), 55.8 (CH_3), 63.9 (*C*H), 114.6 (*C*H), 115.2 (*C*H), 115.8 (1C, q, J = 288.2, *C*), 125.1 (*C*), 127.7 (*C*H), 128.8 (*C*H), 131.4 (*C*H), 133.0 (*C*H), 136.5 (*C*), 143.3 (*C*), 152.7 (*C*), 156.4 (1C, q, J = 36.8, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.4 (3F, s); MS (EI) m/z 512 + 514 (1:1, 5, M$^+$), 218 (100, M$^+$ − $C_{10}H_8BrF_3NO$); HRMS $C_{24}H_{28}(^{79}Br)F_3N_2O_2$ calcd 512.1281, found 512.1276. Anal. Calcd for $C_{24}H_{28}BrF_3N_2O_2$: C, 56.15; H, 5.50; N, 5.46. Found: C, 55.92; H, 5.48; N, 5.42.

General Procedure for the Synthesis of β-Aminoacetamides 7 (Scheme 10). To a solution of β-nitroamine **5** (1.00 mmol) in EtOH (20.0 mL) and EtOAc (20.0 mL) at rt was added 6 M HCl (20.0 mmol) followed by Zn dust (10.0 mmol) in one portion. The gray suspension was stirred vigorously rt for 1 h before removal of the solvents in vacuo. The residue was neutralized by the addition of $NaHCO_{3(s)}$ and the product extracted into EtOAc. The combined organic extracts were washed with water, brine, dried ($MgSO_4$), filtered and the solvents removed in vacuo to give crude 1,2-diamine. To a solution of the crude 1,2-diamine in CH_2Cl_2 (10.0 mL) at −78 °C was added DIPEA (1.50 mmol) quickly followed by the dropwise addition of TFAA (1.50 mmol). The reaction was stirred at −78 °C for 30 min before being allowed to warm to rt over 30 min. The reaction was quenched by the addition of 2 M HCl, the layers were separated and the aqueous layer further extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), filtered and the solvents removed in vacuo to give crude β-aminoacetamide, which was purified by flash column chromatography.

***7g** N-((2S*,3R*)-1-(2-Bromophenyl)-3-((4-methoxyphenyl)-amino)-4,4-dimethylpentan-2-yl)-2,2,2-trifluoroacetamide.* Crude β-nitroamine **5g** (4.52 mmol) afforded crude β-aminoacetamide **7g** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7g** as a white solid (1.42 g, 65%, 85:15 dr): mp 82−84 °C; R_f 0.51 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3399, 3311, 3062−2833, 1706, 1509, 1243, 1231, 1207, 1159, 1038, 1023 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.14 (9H, s), 2.91 (1H, dd, J = 13.6, 12.1), 3.23 (1H, dd, J = 13.7, 3.6), 3.45 (1H, br s), 3.54 (1H, br s), 3.76 (3H, s), 4.74 (1H, m), 6.55 (1H, br d, J = 9.2), 6.66 (2H, dm, J = 9.0), 6.79 (2H, dm, J = 9.0), 7.10 (1H, td, J = 7.6, 1.7), 7.14 (1H, dd, J = 7.7, 1.7), 7.23 (1H, td, J = 7.5, 1.2), 7.53 (1H, dd, J = 8.0, 1.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.1 (CH_3), 36.2 (CH_2), 36.4 (*C*), 52.3 (*C*H), 55.9 (CH_3), 67.0 (*C*H), 114.7 (*C*H), 115.3 (*C*H), 115.7 (1C, q, J = 288.4, *C*), 125.0 (*C*), 127.7 (*C*H), 128.8 (*C*H), 131.4 (*C*H), 133.0 (*C*H), 136.5 (*C*), 143.3 (*C*), 152.6 (*C*), 156.0 (1C, q, J = 36.9, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.5 (3F, s); MS (EI) m/z 486 + 488 (1:1, 13%, M$^+$), 429 + 431 (1:1, 22%, M$^+$-C(CH_3)$_3$), 192 (100%, PMPNHCH$^+$C(CH_3)$_3$); HRMS $C_{22}H_{26}(^{79}Br)F_3N_2O_2$ calcd 486.1124, found 486.1134; Anal. Calcd for $C_{22}H_{26}BrF_3N_2O_2$: C, 54.22; H, 5.38; N, 5.75; found: C, 54.11; H, 5.32; N, 5.72%.

***7i** N-((1R*,2S*)-1,3-Bis(2-bromophenyl)-1-((4-methoxyphenyl)-amino)propan-2-yl)-2,2,2-trifluoroacetamide.* Crude β-nitroamine **5i** (4.15 mmol) afforded crude β-aminoacetamide **7i** as a brown oil. Purification by flash column chromatography (15% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7i** as a white solid (1.50 g, 62%, 95:5 dr): mp 176−178 °C; R_f 0.27 (15% EtOAc/petroleum ether); IR ν_{max} (neat) 3409, 3268, 3106−2832, 1702, 1510, 1240, 1232, 1208, 1182, 1157, 1033, 1017 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.30 (1H, dd, J = 14.1, 11.0), 3.43 (1H, dd, J = 14.2, 3.5), 3.71 (3H, s), 4.47 (1H, br s), 4.69 (1H, m), 5.09 (1H, br s), 6.54 (2H, br d, J = 7.5), 6.56 (1H, br d, J = 10.3), 6.73 (2H, d, J = 8.8), 7.11 (1H, td, J = 7.7, 1.6), 7.16 (1H, td, J = 7.7, 1.4), 7.17 (1H, dd, J = 7.6, 1.5), 7.23 (1H, td, J = 7.4, 0.9), 7.29 (1H, td, J = 7.6, 0.7), 7.40 (1H, dd, J = 7.8, 1.4), 7.53 (1H, dd, J = 8.0, 0.8), 7.59 (1H, dd, J = 8.0, 0.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.2 (CH_2), 54.8 (*C*H), 55.8 (CH_3), 60.9 (*C*H), 115.0 (*C*H), 115.3 (*C*H), 115.6 (1C, q, J = 287.9, *C*), 124.6 (*C*), 124.9 (*C*), 127.9 (*C*H), 128.2 (*C*H), 128.4 (*C*H), 129.1 (*C*H), 129.8 (*C*H), 131.2 (*C*H), 133.2 (*C*H), 133.3 (*C*H), 136.1 (*C*), 137.8 (*C*), 139.9 (*C*),

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152.9 (*C*), 156.9 (1C, q, *J* = 37.2, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.5 (3F, s); MS (EI) *m*/*z* 584 + 586 + 588 (1:2:1, 97%, M^+), 290 + 292 (1:1, 100%, M^+-$C_{10}H_8BrF_3NO$); HRMS $C_{24}H_{21}(^{79}Br)_2F_3N_2O_2$ calcd 583.9916, found 583.9924; Anal. Calcd for $C_{24}H_{21}Br_2F_3N_2O_2$: C, 49.17; H, 3.61; N, 4.78; found: C, 49.43; H, 3.34; N, 4.97%.

7r *N-((1R*,2S*)-3-(2-Bromo-4,5-dimethoxyphenyl)-1-(2-methoxyphenyl)-1-((4-methoxyphenyl)amino)propan-2-yl)-2,2,2-trifluoroacetamide.* Crude β-nitroamine **5r** (3.30 mmol) afforded crude β-aminoacetamide **7r** as a brown oil. Purification by flash column chromatography (30% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7r** as a white solid (793 mg, 40%, 90:10 dr): mp 73−75 °C; R_f 0.38 (30% EtOAc/petroleum ether); IR ν_{max} (neat) 3365, 3069−2840, 1714, 1508, 1463, 1439, 1258, 1234, 1214, 1161, 1028 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.90 (1H, dd, *J* = 14.3, 9.9), 3.31 (1H, dd, *J* = 14.4, 3.0), 3.69 (3H, s), 3.71 (3H, s), 3.84 (3H, s), 3.92 (3H, s), 4.65 (1H, dtd, *J* = 7.9, 7.9, 3.4), 4.92 (1H, d, *J* = 6.5), 6.56 (2H, d, *J* = 8.3), 6.69 (1H, s), 6.71 (2H, dm, *J* = 8.9), 6.83 (1H, br s), 6.91−6.93 (2H, m), 6.98 (1H, s), 7.25 (2H, t, *J* = 7.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 37.0 (CH_2), 54.8 (*C*H), 55.6 (CH_3), 55.8 (CH_3), 55.9 (CH_3), 56.2 (CH_3), 57.0 (*C*H), 110.8 (*C*H), 113.5 (*C*H), 114.8 (*C*), 114.9 (*C*H), 115.5 (*C*H), 115.5 (*C*H), 115.8 (1C, q, *J* = 288.4, *C*), 121.3 (*C*H), 126.6 (*C*), 128.1 (*C*H), 128.4 (*C*), 129.2 (*C*H), 140.5 (*C*), 148.5 (*C*), 148.6 (*C*), 152.8 (*C*), 156.8 (1C, q, *J* = 36.7, *C*), 157.1 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.5 (3F, s); MS (ES^-) *m*/*z* 596 + 598 (30%, M^-), 595 + 597 (100%, M-H^+); Accurate HRMS could not be obtained.

7s *N-((1R*,2S*)-3-(3-(Benzyloxy)-2-bromo-4-methoxyphenyl)-1-((4-methoxyphenyl)amino)-1-phenylpropan-2-yl)-2,2,2-trifluoroacetamide.* Crude β-nitroamine **5s** (1.15 mmol) afforded crude β-aminoacetamide **7s** as a pale brown solid. Purification by flash column chromatography (30% EtOAc/petroleum ether) yielded pure β-aminoacetamide **7s** as a white solid (882 mg, 43%, >95:5 dr): mp 68−70 °C; R_f 0.34 (30% EtOAc/petroleum ether); IR ν_{max} (neat) 3393, 3303, 3089−2838, 1702, 1511, 1485, 1454, 1440, 1296, 1271, 1241, 1210, 1163, 1033 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.83 (1H, dd, *J* = 14.0, 11.1), 3.13 (1H, dd, *J* = 14.2, 3.5), 3.71 (3H, s), 3.83 (3H, s), 4.36 (1H, br s), 4.69−4.74 (2H, m), 4.96 (1H, d, *J* = 10.5), 5.00 (1H, d, *J* = 10.6), 6.39 (1H, d, *J* = 9.2), 6.55 (2H, d, *J* = 7.3), 6.72 (2H, d, *J* = 8.8), 6.80 (1H, d, *J* = 8.5), 6.85 (1H, d, *J* = 8.5), 7.33−7.41 (8H, m), 7.54 (2H, d, *J* = 7.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 36.3 (CH_2), 55.7 (CH_3), 55.8 (*C*H), 56.2 (CH_3), 62.2 (*C*H), 74.7 (CH_2), 111.5 (*C*H), 114.9 (*C*H), 115.5 (*C*H), 115.8 (1C, q, *J* = 288.2, *C*), 121.1 (*C*), 125.8 (*C*H), 127.4 (*C*H), 128.2 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 128.6 (*C*H), 128.9 (*C*), 129.1 (*C*H), 137.2 (*C*), 138.4 (*C*), 140.6 (*C*), 145.5 (*C*), 152.7 (*C*), 152.9 (*C*), 157.5 (1C, q, *J* = 37.2, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s); MS (ES^-) *m*/*z* 642 + 644 (1:1, 32%, M^-), 641 + 643 (1:1, 97%, M-H^+); HRMS $C_{32}H_{29}(^{79}Br)F_3N_2O_4$ calcd 641.1263, found 641.1230; Anal. Calcd for $C_{32}H_{30}BrF_3N_2O_4$: C, 59.73; H, 4.35; N, 4.87; found: C, 59.79; H, 4.70; N, 4.35%.

General Procedure for the Synthesis of 3-Aminotetrahydroquinolines 18 (Table 6). A flame-dried Schenk tube was charged with β-aminoacetamide (1.00 mmol), $Pd(PPh_3)_4$ (5.00 mol %) and K_2CO_3 (2.50 mmol). The tube was triple evacuated/N_2 filled before the addition of toluene (10.0 mL). The resulting mixture was stirred while N_2 was bubbled through it, using a needle, for 15 min. The N_2 needle was removed and the reaction was heated to 100 °C for 18 h to give a dark brown mixture. The reaction was allowed to cool to rt before being filtered through Celite and washed with EtOAc, and the solvents were removed in vacuo to give crude tetrahydroquinoline, which was purified by flash column chromatography.

2,2,2-Trifluoro-N-[(2R,3S*)-1-(4-methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl]acetamide (**18a**).* β-Aminoacetamide **7a** (100 mg, 0.197 mmol) afforded crude tetrahydroquinoline **18a** as a brown solid. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18a** as a white solid (82 mg, 98%): mp 162−164 °C; R_f 0.31 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3418, 3284, 3065−2838, 1709, 1508, 1491, 1456, 1240, 1205, 1167 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.71 (1H, d, *J* = 17.0), 2.96 (1H, dd, *J* = 17.0, 4.2), 3.80 (3H, s), 4.58 (1H, m), 4.89 (1H, s), 6.66 (1H, br d, *J* = 7.3), 6.69 (1H, d, *J* = 8.3), 6.77 (1H, t, *J* = 7.3), 6.87 (2H, dm, *J* = 8.7), 7.05−7.11 (4H, m), 7.28−7.36 (5H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.7 (CH_2), 47.6 (*C*H), 55.5 (CH_3), 66.2 (*C*H), 113.7 (*C*H), 115.2 (*C*H), 115.7 (1C, q, *J* = 288.0, *C*), 115.8 (*C*), 118.0 (*C*H), 126.4 (*C*H), 127.7 (*C*H), 127.9 (*C*H), 128.1 (*C*H), 128.9 (*C*H), 130.7 (*C*H), 139.1 (*C*), 141.0 (*C*), 143.7 (*C*), 156.9 (1C, q, *J* = 37.2, *C*), 157.6 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s); MS (EI) *m*/*z* 427 (22, M + H^+), 426 (100, M^+); HRMS $C_{24}H_{21}F_3N_2O_2$ calcd 426.1550, found 426.1539. Anal. Calcd for $C_{24}H_{21}F_3N_2O_2$: C, 67.60; H, 4.96; N, 6.57. Found: C, 67.62; H, 4.95; N, 6.57.

2,2,2-Trifluoro-N-[(2S,3S*)-2-(furan-2-yl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl]acetamide (**18b**).* β-Aminoacetamide **7b** (107 mg, 0.215 mmol) afforded crude tetrahydroquinoline **18b** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18b** as a white solid (84 mg, 92%): mp 127−130 °C; R_f 0.32 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3414, 3300, 3073−2838, 1710, 1509, 1492, 1457, 1243, 1207, 1180 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.79 (1H, d, *J* = 17.2), 3.12 (1H, dd, *J* = 17.1, 4.7), 3.82 (3H, s), 4.77 (1H, ddd, *J* = 10.4, 5.1, 2.7), 4.83 (1H, m), 6.19 (1H, dd, *J* = 2.5, 0.7), 6.30 (1H, dd, *J* = 3.3, 1.8), 6.59 (1H, d, *J* = 8.2), 6.65 (1H, br d, *J* = 7.7), 6.76 (1H, td, *J* = 7.4, 1.0), 6.89 (2H, dm, *J* = 8.9), 7.02−7.06 (2H, m), 7.07 (2H, dm, *J* = 8.9), 7.38 (1H, dd, *J* = 1.7, 0.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 29.2 (CH_2), 45.8 (*C*H), 55.6 (CH_3), 60.8 (*C*H), 108.4 (*C*H), 110.5 (*C*H), 114.5 (*C*H), 115.2 (*C*H), 115.8 (1C, q, *J* = 288.0, *C*), 116.7 (*C*), 118.6 (*C*H), 127.8 (*C*H), 128.0 (*C*H), 130.6 (*C*H), 138.6 (*C*), 142.5 (*C*H), 143.1 (*C*), 153.0 (*C*), 156.9 (1C, q, *J* = 37.3, *C*), 157.8 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s); MS (EI) *m*/*z* 417 (28%, M^++H), 416 (100, M^+), 303 (26, M^+ − NHTFA), 196 (48, M^+ − $C_{22}H_{19}F_3N_2O_3$); HRMS $C_{22}H_{19}F_3N_2O_3$ calcd 416.1342, found 416.1334. Anal. Calcd for $C_{22}H_{19}F_3N_2O_3$: C, 63.46; H, 4.60; N, 6.73. Found: C, 63.44; H, 4.52; N, 6.55.

2,2,2-Trifluoro-N-[(2R,3S*)-2-(furan-2-yl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl]acetamide (**18c**).* β-Aminoacetamide **7c** (104 mg, 0.209 mmol) afforded crude tetrahydroquinoline **18c** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18c** as a yellow solid (82 mg, 94%): mp 139−141 °C; R_f 0.70 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3413, 3302, 3143−2838, 1713, 1508, 1492, 1457, 1242, 1207, 1160, 1036, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (1H, d, *J* = 17.3), 3.14 (1H, dd, *J* = 17.2, 4.8), 3.81 (3H, s), 4.53 (1H, ddd, *J* = 10.4, 5.0, 2.7), 4.73 (1H, t, *J* = 1.4), 6.32 (1H, dd, *J* = 1.6, 0.8), 6.64 (1H, d, *J* = 8.1), 6.64 (1H, br m), 6.76 (1H, td, *J* = 7.4, 1.0), 6.88 (2H, dm, *J* = 9.0), 7.02−7.06 (2H, m), 7.09 (2H, dm, *J* = 9.0), 7.30 (1H, m), 7.38 (1H, t, *J* = 1.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.5 (CH_2), 47.2 (*C*H), 55.6 (CH_3), 59.1 (*C*H), 108.9 (*C*H), 114.6 (*C*H), 115.2 (*C*H), 115.8 (1C, q, *J* = 288.1, *C*), 116.7 (*C*), 118.6 (*C*H), 125.5 (*C*), 127.5 (*C*H), 127.9 (*C*H), 130.7 (*C*H), 139.0 (*C*), 140.6 (*C*H), 143.0 (*C*), 143.8 (*C*H), 156.9 (1C, q, *J* = 37.2, *C*), 157.6 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s); MS (EI) *m*/*z* 416 (6, M^+), 220 (18, M^+ − $C_7H_7F_3O_3$), 205 (39, M^+ − $C_7H_7F_3NO_3$); HRMS $C_{22}H_{19}F_3N_2O_3$ calcd 416.1342, found 416.1354. Anal. Calcd for $C_{22}H_{19}F_3N_2O_3$: C, 63.46; H, 4.60; N, 6.73. Found: C, 63.33; H, 4.54; N, 6.64.

2,2,2-Trifluoro-N-((2S,3S*)-1-(4-methoxyphenyl)-2-(thiophene-2-yl)-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18d**).* β-Aminoacetamide **7d** (102 mg, 0.199 mmol) afforded crude tetrahydroquinoline **18d** as a brown oil. Purification by flash column chromatography (20% Et_2O/petroleum ether) yielded pure tetrahydroquinoline **18d** as an off- white solid (79 mg, 91%): mp 134−136 °C; R_f 0.41 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3413, 3295, 3075−2838, 1709, 1508, 1491, 1456, 1242, 1206, 1168, 1036 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.78 (1H, d, *J* = 17.3), 3.18 (1H, dd, *J* = 17.2, 4.7), 3.81 (3H, s), 4.63 (1H, m), 5.06 (1H, m), 6.64 (1H, br d, *J* = 7.6), 6.67 (1H, d, *J* = 7.9), 6.79 (1H, td, *J* = 7.4, 1.0), 6.88 (2H, dm, *J* = 8.9), 6.95−6.97 (2H, m), 7.07 (2H, m), 7.12 (2H, dm, *J* = 9.0), 7.22 (1H, dd, *J* = 4.8, 1.4); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.3 (CH_2), 48.1 (*C*H), 55.6 (CH_3), 62.5 (*C*H), 114.9 (*C*H), 115.2 (*C*H), 115.8 (1C, q, *J* = 288.1, *C*), 116.5 (*C*), 118.8 (*C*H), 125.0 (*C*H), 125.1 (*C*H), 127.3

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(CH), 127.6 (CH), 128.0 (CH), 130.7 (CH), 139.0 (C), 142.8 (CH), 144.3 (C), 157.0 (1C, q, J = 37.4, C), 157.7 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s); MS (EI) m/z 432 (18%, M^+); HRMS $C_{22}H_{19}F_3N_2O_2S$ calcd 432.1114, found 432.1116. Anal. Calcd for $C_{22}H_{19}F_3N_2O_2S$: C, 61.10; H, 4.43; N, 6.48. Found: C, 61.15; H, 4.38; N, 6.42.

2,2,2-Trifluoro-N-((2R,3S*)-1-(4-methoxyphenyl)-2-pentyl-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18e**).* β-Aminoacetamide **7e** (187 mg, 0.373 mmol) afforded crude tetrahydroquinoline **18e** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18e** as a white solid (137 mg, 87%): mp 93−94 °C; R_f 0.50 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3415, 3292, 3066−2860, 1712, 1507, 1492, 1456, 1242, 1204, 1157, 1037 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (3H, t, J = 6.8), 1.22−1.45 (6H, m), 1.52 (1H, dddd, J = 19.3, 14.3, 10.0, 5.1), 1.75 (1H, dddd, J = 16.4, 13.9, 11.0, 5.5), 2.82 (1H, d, J = 17.3), 3.23 (1H, dd, J = 17.3, 4.7), 3.56 (1H, m), 3.84 (3H, s), 4.50 (1H, m), 6.57 (1H, d, J = 8.3), 6.64 (1H, br d, J = 7.3), 6.74 (1H, t, J = 7.3), 6.94 (2H, dm, J = 8.6), 6.99 (1H, t, J = 7.7), 7.07 (1H, d, J = 7.4), 7.11 (2H, dm, J = 8.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.1 (CH_3), 22.6 (CH_2), 25.2 (CH_2), 28.2 (CH_2), 31.7 (CH_2), 31.8 (CH_2), 44.8 (C), 55.6 (CH_3), 62.7 (CH), 115.3 (CH), 115.5 (CH), 115.8 (1C, q, J = 288.0, C), 117.0 (C), 118.4 (CH), 127.6 (CH), 128.2 (CH), 130.6 (CH), 139.3 (C), 142.6 (C), 156.7 (1C, q, J = 37.1, C), 157.4 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (EI) m/z 420 (10, M^+), 349 (100, M^+ − ^{n}pentyl); HRMS $C_{23}H_{27}F_3N_2O_2$ calcd 420.2019, found 420.2002. Anal. Calcd for $C_{23}H_{27}F_3N_2O_2$: C, 65.70; H, 6.47; N, 6.66. Found: C, 65.93; H, 6.51; N, 6.67.

N-((2R,3S*)-2-Cyclohexyl-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroacetamide (**18f**).* Prepared using the general for the synthesis of 3-aminotetrahydroquinolines except with 10 mol % $Pd(PPh_3)_4$. β-Aminoacetamide **7f** (63 mg, 0.12 mmol) afforded crude tetrahydroquinoline **18f** as a pale brown oil. Purification by flash column chromatography (20% Et_2O/petroleum ether) yielded pure tetrahydroquinoline **18f** as an off-white solid (43 mg, 81%): mp 95−97 °C; R_f 0.46 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3410, 3304, 3067−2852, 1721, 1506, 1491, 1456, 1272, 1244, 1229, 1203, 1174, 1037 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.10−1.26 (5H, m), 1.39−1.46 (1H, m), 1.69 (1H, m), 1.78−1.86 (3H, m), 2.10 (1H, d, J = 12.1), 2.86 (1H, d, J = 17.8), 3.16 (1H, dd, J = 17.8, 5.5), 3.48 (1H, dd, J = 10.0, 2.2), 3.80 (3H, s), 4.62 (1H, m), 6.53 (1H, br d, J = 7.0), 6.83 (2H, dm, J = 9.0), 6.86 (1H, td, J = 7.4, 0.9), 6.94 (1H, d, J = 8.1), 7.06 (1H, td, J = 7.7, 0.9), 7.11−7.13 (3H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.3 (CH_2), 26.3 (CH_2), 26.5 (CH_2), 28.7 (CH_2), 29.5 (CH_2), 31.7 (CH_2), 39.0 (CH), 45.5 (CH), 55.7 (CH_3), 67.2 (CH), 115.1 (CH), 115.6 (1C, q, J = 288.2, C), 120.4 (CH), 120.5 (CH), 120.9 (C), 123.5 (CH), 127.3 (CH), 130.6 (CH), 141.5 (C), 143.3 (C), 155.5 (C), 156.5 (1C, q, J = 37.0, C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.4 (3F, s); MS (CI) m/z 433 (100, M^+ + H), 432 (44, M^+), 349 (32, M^+ − Cy); HRMS $C_{24}H_{28}F_3N_2O_2$ calcd 433.2103, found 433.2115. Anal. Calcd for $C_{24}H_{27}F_3N_2O_2$: C, 66.65; H, 6.29; N, 6.48. Ffound: C, 66.64; H, 6.49; N, 6.16.

N-((2R,3S*)-2-tert-Butyl-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroacetamide (**18g**).* β-Aminoacetamide **7g** (94 mg, 0.19 mmol) afforded crude tetrahydroquinoline **18g** as a dark brown oil. Purification by flash column chromatography (20% Et_2O/petroleum ether) yielded pure tetrahydroquinoline **18g** as a white solid (48 mg, 61%): mp 119−121 °C; R_f 0.46 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3418, 3291, 3080−2838, 1712, 1507, 1491, 1456, 1243, 1205, 1157, 1038 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.00 (9H, s), 2.83 (1H, d, J = 7.6), 3.27 (1H, dd, J = 17.5, 5.2), 3.57 (1H, t, J = 1.8), 3.81 (3H, s), 4.75 (1H, td, J = 5.4, 2.5), 6.46 (1H, br d, J = 7.0), 6.78−6.80 (2H, m), 6.88 (2H, dm, J = 8.9), 7.02 (1H, t, J = 7.7), 7.07 (1H, d, J = 7.6), 7.12 (2H, dm, J = 8.9); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.6 (CH_3), 30.0 (CH_2), 36.9 (C), 45.0 (CH), 55.6 (CH_3), 71.2 (CH), 115.0 (CH), 115.7 (1C, q, J = 288.1, C), 117.4 (CH), 118.4 (C), 119.3 (CH), 126.8 (CH), 127.7 (CH), 130.6 (CH), 142.7 (C), 143.8 (C), 156.4 (1C, q, J = 37.1, C), 156.5 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (CI) m/z 407 (100, M^++ H), 407 (12, M^+), 349 (17, M^+ − $C(CH_3)_3$); HRMS $C_{22}H_{26}F_3N_2O_2$ calcd 407.1946, found 407.1953. Anal. Calcd for $C_{22}H_{25}F_3N_2O_2$: C, 65.01; H, 6.20; N, 6.89. Found: C, 64.75; H, 6.23; N, 6.61.

2,2,2-Trifluoro-N-((2R,3S*)-1-(4-methoxyphenyl)-2-(o-tolyl)-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18h**).* β-Aminoacetamide **7h** (114 mg, 0.219 mmol) afforded crude tetrahydroquinoline **18h** as a brown oil. Purification by flash column chromatography (15% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18h** as an orange solid (85 mg, 88%): mp 62−65 °C; R_f 0.67 (15% EtOAc/petroleum ether); IR ν_{max} (neat) 3418, 3285, 3063−2838, 1719, 1601, 1528, 1508, 1491, 1456, 1280, 1239, 1206, 1166, 1035 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.48 (3H, s), 2.71 (1H, d, J = 16.9), 3.07 (1H, dd, J = 16.9, 3.4), 3.80 (3H, s), 4.51 (1H, m), 5.03 (1H, d, J = 1.3), 6.61 (1H, d, J = 8.4), 6.65 (1H, br d, J = 6.4), 6.77 (1H, t, J = 7.4), 6.87 (2H, br d, J = 7.8), 7.04 (2H, br d, J = 8.1), 7.08−7.10 (2H, m), 7.15 (1H, t, J = 7.3), 7.19−7.23 (2H, m), 7.35 (1H, d, J = 7.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 19.0 (CH_3), 27.9 (CH_2), 45.6 (CH), 55.5 (CH_3), 64.1 (CH), 113.2 (CH), 114.9 (C), 115.3 (CH), 115.9 (1C, q, J = 288.1, C), 117.7 (CH), 126.4 (CH), 126.8 (CH), 127.8 (CH), 128.3 (CH), 128.6 (CH), 130.8 (CH), 131.2 (CH), 135.1 (C), 139.1 (C), 139.1 (C), 144.5 (C), 157.2 (1C, q, J = 37.2, C), 157.9 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.1 (3F, s); MS (EI) m/z 441 (27, M^+ + H), 440 (100, M^+); HRMS $C_{25}H_{23}F_3N_2O_2$ calcd 440.1706, found 440.1712; Anal. Calcd for $C_{25}H_{23}F_3N_2O_2$: C, 68.17; H, 5.26; N, 6.36. Found: C, 67.84; H, 5.23; N, 6.36.

N-((2R,3S*)-2-(2-Bromophenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroacetamide (**18i**).* Prepared using the general for the synthesis of 3-aminotetrahydroquinolines except with 10 mol % $Pd(PPh_3)_4$. β-Aminoacetamide **7i** (90 mg, 0.15 mmol) afforded crude tetrahydroquinoline **18i** as a brown oil. Purification by flash column chromatography (20% Et_2O/petroleum ether) yielded pure tetrahydroquinoline **18i** as a white solid (42 mg, 54%): mp 145−146 °C; R_f 0.36 (10% Et_2O/petroleum ether); IR ν_{max} (neat) 3421, 3311, 3065−2838, 1725, 1508, 1491, 1457, 1240, 1205, 1167, 1036, 1023 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.77 (1H, d, J = 17.0), 2.91 (1H, dd, J = 17.0, 4.1), 3.80 (3H, s), 4.84 (1H, dt, J = 11.3, 3.4), 5.09 (1H, s), 6.59 (1H, br d, J = 8.0), 6.65 (1H, d, J = 8.2), 6.79 (1H, td, J = 7.3, 0.5), 6.87 (2H, d, J = 8.9), 7.03 (2H, d, J = 8.6), 7.07 (1H, d, J = 7.4), 7.08 (1H, t, J = 7.8), 7.17 (1H, td, J = 7.7, 1.6), 7.25 (1H, td, J = 7.6, 0.8), 7.41 (1H, dd, J = 7.8, 1.4), 7.57 (1H, dd, J = 7.9, 1.0); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.4 (CH_2), 44.9 (CH), 55.6 (CH_3), 66.7 (CH), 113.6 (CH), 115.4 (CH), 115.8 (C), 115.9 (1C, q, J = 288.3, C), 118.5 (CH), 122.0 (C), 127.9 (CH), 128.2 (CH), 128.3 (CH), 128.6 (CH), 129.7 (CH), 130.9 (CH), 133.7 (CH), 138.6 (C), 139.4 (C), 143.8 (C), 156.7 (1C, q, J = 37.1, C), 157.9 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.1 (3F, s); MS (CI) m/z 506 + 508 (1:1, 29, M^+ + H_2), 505 + 507 (1:1, 100, M^+ + H), 504 + 506 (1:1, 8, M^+); HRMS $C_{24}H_{21}(^{79}Br)F_3N_2O_2$ calcd 505.0739, found 505.0746. Anal. Calcd for $C_{24}H_{20}BrF_3N_2O_2$: C, 57.04; H, 3.99; N, 5.54. Found: C, 57.17; H, 3.84; N, 5.73.

2,2,2-Trifluoro-N-((2R,3S*)-2-(2-methoxyphenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18j**).* β-Aminoacetamide **7j** (113 mg, 0.210 mmol) afforded crude tetrahydroquinoline **18j** as a brown solid. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18j** as an orange solid (94 mg, 98%): mp 168−170 °C; R_f 0.63 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3417, 3313, 3069−2838, 1722, 1600, 1508, 1488, 1456, 1283, 1238, 1202, 1160, 1097, 1031 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.72 (1H, d, J = 17.0), 2.87 (1H, dd, J = 16.9, 4.2), 3.79 (3H, s), 3.87 (3H, s), 4.79 (1H, m), 5.09 (1H, s), 6.65 (1H, d, J = 7.9), 6.69 (1H, d, J = 8.3), 6.76 (1H, t, J = 7.3), 6.85−6.89 (3H, m), 6.90 (1H, d, J = 8.1), 7.03 (1H, d, J = 7.4), 7.06−7.10 (3H, m), 7.26−7.29 (2H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.8 (CH_2), 44.9 (CH), 55.4 (CH_3), 55.6 (CH_3), 62.2 (CH), 110.6 (CH), 113.6 (CH), 115.2 (CH), 115.9 (1C, q, J = 288.2, C), 116.3 (C), 118.1 (CH), 120.6 (CH), 127.6 (CH), 127.9 (2 × CH), 128.4 (C), 129.0 (CH), 130.8 (CH), 139.3 (C), 144.0 (C), 155.9 (C), 156.7 (1C, q, J = 36.8, C), 157.6 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s); MS (EI) m/z 457 (27, M^+), 456 (100, M^+), 342 (37, M^+ − $_3H_5F_3O$); HRMS $C_{25}H_{23}F_3N_2O_3$ calcd 456.1655, found

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456.1659.Anal. Calcd for $C_{25}H_{23}F_3N_2O_3$: C, 65.78; H, 5.08; N, 6.14. Found; C, 65.55; H, 5.01; N, 6.03.

2,2,2-Trifluoro-N-((2R,3S*)-2-(3-methoxyphenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18k**).* β-Aminoacetamide **7k** (130 mg, 0.242 mmol) afforded crude tetrahydroquinoline **18k** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure tetrahydroquinoline **18k** as a white solid (99 mg, 90%): mp 114−116 °C; R_f 0.38 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3418, 3306, 3069−2837, 1712, 1601, 1508, 1489, 1456, 1278, 1238, 1205, 1151, 1037 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.70 (1H, d, J = 17.0), 2.97 (1H, dd, J = 17.0, 4.2), 3.75 (3H, s), 3.80 (3H, s), 4.59 (1H, m), 4.85 (1H, s), 6.66−6.68 (1H, br m), 6.68 (1H, d, J = 8.3), 6.75 (1H, t, J = 7.4), 6.83 (1H, dd, J = 8.2, 2.2), 6.86−6.88 (3H, m), 6.95 (1H, d, J = 7.6), 7.06 (2H, t, J = 8.3), 7.09 (2H, d, J = 8.2), 7.26 (1H, t, J = 7.9); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.9 (CH_2), 47.7 (*C*H), 55.3 (CH_3), 55.6 (CH_3), 66.2 (*C*H), 112.3 (*C*H), 113.0 (*C*H), 113.9 (*C*H), 115.3 (*C*H), 115.8 (1C, q, J = 288.0, *C*), 116.0 (*C*), 118.1 (*C*H), 118.7 (*C*H), 127.9 (*C*H), 128.1 (*C*H), 130.1 (*C*H), 130.8 (*C*H), 139.2 (*C*), 142.8 (*C*), 143.7 (*C*), 157.0 (1C, q, J = 37.2, *C*), 157.6 (*C*), 160.0 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s); MS (EI) m/z 457 (28, M^+ + H), 456 (100, M^+), 342 (68, $M^+ - C_3H_5F_3O$), 236 (47, $M^+ - C_9H_9F_3NO_2$); HRMS $C_{25}H_{23}F_3N_2O_3$ calcd 456.1655, found 456.1652. Anal. Calcd for $C_{25}H_{23}F_3N_2O_3$: C, 65.78; H, 5.08; N, 6.14. Found: C, 65.98; H, 5.23; N, 5.96.

2,2,2-Trifluoro-N-((2R,3S*)-2-(4-methoxyphenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18l**).* β-Aminoacetamide **7l** (123 mg, 0.229 mmol) afforded crude tetrahydroquinoline **18l** as a brown oil. Purification by flash column chromatography (15% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18l** as an orange solid (102 mg, 98%): mp 118−120 °C; R_f 0.51 (15% EtOAc/petroleum ether); IR ν_{max} (neat) 3418, 3300, 3067−2837, 1709, 1608, 1508, 1491, 1456, 1240, 1206, 1170, 1105, 1032 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.69 (1H, d, J = 17.0), 2.97 (1H, dd, J = 17.0, 4.4), 3.79 (3H, s), 3.79 (3H, s), 4.52 (1H, m), 4.80 (1H, s), 6.62 (1H, br d, J = 7.7), 6.66 (1H, d, J = 8.3), 6.75 (1H, t, J = 7.4), 6.85−6.87 (4H, m), 7.04−7.08 (4H, m), 7.24 (2H, dm, J = 8.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.7 (CH_2), 47.8 (*C*H), 55.4 (CH_3), 55.6 (CH_3), 65.8 (*C*H), 113.8 (*C*H), 114.3 (*C*H), 115.2 (*C*H), 115.8 (1C, q, J = 288.0, *C*), 116.0 (*C*), 118.0 (*C*H), 127.6 (*C*H), 128.0 (*C*H), 128.1 (*C*H), 130.8 (*C*H), 133.0 (*C*), 139.1 (*C*), 143.8 (*C*), 157.0 (1C, q, J = 37.2, *C*), 157.6 (*C*), 159.2 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s); MS (EI) m/z 457 (27, M^+ + H), 456 (100, M^+), 342 (42, $M^+ - C_3H_5F_3O$); HRMS $C_{25}H_{23}F_3N_2O_3$ calcd 456.1655, found 456.1662. Anal. Calcd for $C_{25}H_{23}F_3N_2O_3$: C, 65.78; H, 5.08; N, 6.14. Found: C, 65.88; H, 5.04; N, 6.14.

2,2,2-Trifluoro-N-((2R,3S*)-1-(4-methoxyphenyl)-2-(2-trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18m**).* β-Aminoacetamide **7m** (85 mg, 0.15 mmol) afforded crude tetrahydroquinoline **18m** as a pale brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18m** as a white solid (71 mg, 97%): mp 176−178 °C; R_f 0.31 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3418, 3312, 3075−2855, 1726, 1509, 1492, 1457, 1311, 1280, 1245, 1209, 1157, 1122, 1105, 1037 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.85 (1H, dd, J = 16.9, 2.3), 3.10 (1H, dd, J = 16.9, 4.0), 3.78 (3H, s), 4.69 (1H, app dt, J = 12.0, 3.6), 5.15 (1H, d, J = 2.0), 6.57 (2H, d, J = 8.3), 6.80 (1H, td, J = 7.4, 0.7), 6.84 (2H, d, J = 8.8), 6.96 (2H, d, J = 8.2), 7.08 (1H, t, J = 7.8), 7.11 (1H, d, J = 7.4), 7.41 (1H, t, J = 7.6), 7.51 (1H, t, J = 7.6), 7.64 (1H, d, J = 7.9), 7.66 (1H, d, J = 7.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.5 (CH_2), 46.6 (*C*H), 55.5 (CH_3), 63.4 (*C*H), 113.7 (*C*H), 115.3 (*C*H), 115.8 (1C, q, J = 288.2, *C*), 116.0 (*C*), 118.5 (*C*H), 124.2 (1C, q, J = 274.3, *C*), 126.6 (1C, q, J = 5.9, *C*H), 127.8 (1C, q, J = 30.3, *C*), 128.3 (*C*H), 128.4 (*C*H), 128.8 (*C*H), 129.0 (*C*H), 130.9 (*C*H), 132.3 (*C*H), 138.0 (*C*), 139.9 (*C*), 144.3 (*C*), 156.4 (1C, q, J = 37.2, *C*), 158.0 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s), −58.6 (3F, s); MS (EI) m/z 494 (30, M^+), 380 (100, $M^+ - C_3H_5F_3O$), 236 (62, $M^+ - C_9H_6F_6NO$); HRMS $C_{25}H_{20}F_6N_2O_2$ calcd 494.1424, found 494.1428. Anal. Calcd for $C_{25}H_{20}F_6N_2O_2$: C, 60.73; H, 4.08; N, 5.67. Found: C, 60.58; H, 3.76; N, 5.58.

2,2,2-Trifluoro-N-((2R,3S*)-1-(4-methoxyphenyl)-2-(3-trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18n**).* β-Aminoacetamide **7n** (119 mg, 0.207 mmol) afforded crude tetrahydroquinoline **18n** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18n** as a white solid (101 mg, 99%): mp 169−171 °C; R_f 0.32 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3419, 3301, 3072−2840, 1710, 1508, 1492, 1458, 1328, 1316, 1242, 1205, 1163, 1125, 1074, 1038 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.72 (1H, d, J = 17.1), 2.91 (1H, dd, J = 17.0, 4.3), 3.80 (3H, s), 4.57 (1H, m), 4.96 (1H, s), 6.60 (1H, br d, J = 7.4), 6.67 (1H, d, J = 8.2), 6.79 (1H, td, J = 7.4, 0.9), 6.87 (2H, dm, J = 8.9), 7.02 (2H, dm, J = 8.8), 7.07 (1H, d, J = 7.5), 7.10 (1H, t, J = 8.3), 7.47 (1H, t, J = 7.7), 7.56−7.57 (2H, m), 7.60 (1H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.6 (CH_2), 47.6 (*C*H), 55.6 (CH_3), 66.0 (*C*H), 114.1 (*C*H), 115.4 (*C*H), 115.5 (*C*), 115.7 (1C, q, J = 287.9, *C*), 118.5 (*C*H), 123.4 (1C, q, J = 3.5, *C*H), 124.0 (1C, q, J = 272.5, *C*), 124.9 (1C, q, J = 3.7, *C*H), 128.1 (*C*H), 128.4 (*C*H), 129.6 (*C*H), 130.0 (*C*H), 130.8 (*C*H), 131.4 (1C, q, J = 32.5, *C*), 138.8 (*C*), 142.2 (*C*), 143.5 (*C*), 157.1 (1C, q, J = 37.5, *C*), 157.9 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s), −63.0 (3F, s); MS (CI) m/z 496 (23, $M^+ + H_2$), 495 (100, M^+ + H), 494 (45, M^+); HRMS $C_{25}H_{21}F_6N_2O_2$ calcd 495.1507, found 495.1490. Anal. Calcd for $C_{25}H_{20}F_6N_2O_2$: C, 60.73; H, 4.08; N, 5.67. Found: C, 60.62; H, 4.08; N, 5.57.

2,2,2-Trifluoro-N-((2R,3S*)-1-(4-methoxyphenyl)-2-(4-trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinolin-3-yl)acetamide (**18o**).* β-Aminoacetamide **7o** (139 mg, 0.242 mmol) afforded crude tetrahydroquinoline **18o** as a brown oil. Purification by flash column chromatography (20% Et_2O/petroleum ether) yielded pure tetrahydroquinoline **18o** as an off-white solid (118 mg, 99%): mp 162−164 °C; R_f 0.41 (20% Et_2O/petroleum ether); IR ν_{max} (neat) 3417, 3281, 3069−2848, 1710, 1509, 1492, 1457, 1323, 1244, 1208, 1164, 1124, 1106, 1067, 1037 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.72 (1H, d, J = 17.2), 2.90 (1H, dd, J = 17.1, 4.1), 3.80 (3H, s), 4.56 (1H, m), 4.95 (1H, s), 6.62 (1H, br d, J = 6.6), 6.68 (1H, d, J = 8.3), 6.79 (1H, t, J = 7.4), 6.87 (2H, d, J = 8.8), 7.03 (2H, d, J = 8.5), 7.07 (1H, d, J = 7.4), 7.10 (1H, t, J = 7.9), 7.49 (2H, d, J = 8.0), 7.61 (2H, d, J = 8.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.6 (CH_2), 47.5 (*C*H), 55.6 (CH_3), 66.0 (*C*H), 114.1 (*C*H), 115.4 (*C*H), 115.5 (*C*), 115.7 (1C, q, J = 287.8, *C*), 118.5 (*C*H), 124.1 (1C, q, J = 272.1, *C*), 126.0 (1C, q, J = 3.6, *C*H), 127.0 (*C*H), 128.0 (*C*H), 128.4 (*C*H), 130.2 (1C, q, J = 32.6, *C*), 130.8 (*C*H), 138.8 (*C*), 143.5 (*C*), 145.1 (*C*), 157.1 (1C, q, J = 37.5, *C*), 157.9 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.2 (3F, s), −63.0 (3F, s); MS (CI) m/z 496 (28%, $M^+ + H_2$), 495 (100, M^+ + H), 494 (17, M^+), 406 (52), 280 (32); HRMS $C_{25}H_{21}F_6N_2O_2$ calcd 495.1507, found 495.1512. Anal. Calcd for $C_{25}H_{20}F_6N_2O_2$: C, 60.73; H, 4.08; N, 5.67. Found: C, 60.68; H, 3.98; N, 5.63.

2,2,2-Trifluoro-N-[(2R,3S*)-6-fluoro-1-(4-methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl]acetamide (**18p**).* β-Aminoacetamide **7p** (115 mg, 0.219 mmol) afforded crude tetrahydroquinoline **18p** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18p** as a white solid (91 mg, 93%): mp 112−124 °C; R_f 0.35 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3416, 3291, 3066−2838, 1709, 1508, 1497, 1243, 1209, 1178, 1034 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.68 (1H, d, J = 17.3), 2.90 (1H, dd, J = 17.2, 4.2), 3.79 (3H, s), 4.58 (1H, m), 4.85 (1H, s), 6.61 (1H, br d, J = 7.5), 6.65 (1H, dd, J = 9.0, 4.8), 6.77−6.82 (2H, m), 6.85 (2H, dm, J = 8.9), 7.05 (2H, dm, J = 8.8), 7.28−7.36 (5H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.1 (CH_2), 47.6 (*C*H), 55.6 (CH_3), 66.1 (*C*H), 115.0 (1C, d, J = 22.2, *C*H), 115.0 (1C, d, J = 7.3, *C*H), 115.3 (*C*H), 115.8 (1C, q, J = 288.0, *C*), 116.7 (1C, d, J = 22.3, *C*H), 117.5 (1C, d, J = 7.0, *C*), 126.3 (*C*H), 127.5 (*C*H), 127.9 (*C*H), 129.0 (*C*H), 139.4 (*C*), 139.9 (1C, d, J = 1.6, *C*), 140.7 (*C*), 155.8 (1C, d, J = 237.3, *C*), 157.0 (1C, q, J = 37.3, *C*), 157.6 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −127.4 (1H, m), −76.2 (3F, s); MS (EI) m/z 445 (23, M^+ + H), 444 (100, M^+), 330 (53, $M^+ - C_3H_5F_3O$), 254 (33, $M^+ - C_8H_7F_3NO$); HRMS $C_{24}H_{20}F_4N_2O_2$ calcd 444.1455, found 444.1459. Anal. Calcd for $C_{24}H_{20}F_4N_2O_2$: C, 64.86; H, 4.54; N, 6.30. Found: C, 64.94; H, 4.57; N, 6.15.

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N-[(2R,3S*)-6,7-Dimethoxy-1-(4-methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl]-2,2,2-trifluoroacetamide (**18q**).* β-Aminoacetamide **7q** (49 mg, 86 μmol) afforded crude tetrahydroquinoline **18q** as a brown oil. Purification by flash column chromatography (50% Et_2O/petroleum ether) yielded pure tetrahydroquinoline **18q** as a white solid (38 mg, 91%): mp 136−138 °C; R_f 0.40 (50% Et_2O/petroleum ether); IR ν_{max} (neat) 3416, 3292, 3064−2836, 1709, 1507, 1465, 1451, 1443, 1241, 1209, 1176, 1143, 1032 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.60 (1H, d, *J* = 16.9), 2.81 (1H, dd, *J* = 16.8, 4.4), 3.69 (3H, s), 3.79 (3H, s), 3.83 (3H, s), 4.58 (1H, m), 4.84 (1H, s), 6.38 (1H, s), 6.54 (1H, s), 6.66 (1H, br d, *J* = 7.9), 6.84 (2H, d, *J* = 8.9), 7.07 (2H, d, *J* = 8.5), 7.28−7.35 (5H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.6 (CH_2), 48.0 (CH), 55.6 (CH_3), 55.9 (CH_3), 56.5 (CH_3), 65.8 (CH), 99.5 (CH), 107.7 (C), 113.9 (CH), 115.1 (CH), 115.8 (1C, q, *J* = 288.0, C), 126.4 (CH), 126.6 (CH), 127.7 (CH), 129.0 (CH), 137.0 (C), 140.1 (C), 140.8 (C), 142.2 (C), 148.9 (C), 156.9 (1C, q, *J* = 37.1, C), 157.0 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (EI) *m*/*z* 487 (28, M^+ + H), 486 (100, M^+), 471 (26, $M^+ - CH_3$), 372 (14, $M^+ - C_3H_5F_3O$); HRMS $C_{26}H_{25}F_3N_2O_4$ calcd 486.1761, found 486.1746. Anal. Calcd for $C_{26}H_{25}F_3N_2O_4$: C, 64.19; H, 5.18; N, 5.76. Found: C, 64.32; H, 5.17; N, 5.63.

N-((2R,3S*)-6,7-Dimethoxy-2-(2-methoxyphenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroacetamide (**18r**).* β-Aminoacetamide **7r** (112 mg, 0.187 mmol) afforded crude tetrahydroquinoline **18r** as a brown oil. Purification by flash column chromatography (30% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18r** as a white solid (85 mg, 88%): mp 159−161 °C; R_f 0.44 (30% EtOAc/petroleum ether); IR ν_{max} (neat) 3416, 3311, 3066−2837, 1720, 1508, 1489, 1464, 1452, 1441, 1284, 1240, 1211, 1178, 1147, 1031 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.64 (1H, d, *J* = 16.7), 2.74 (1H, dd, *J* = 16.7, 4.5), 3.69 (3H, s), 3.79 (3H, s), 3.83 (3H, s), 3.87 (3H, s), 4.80 (1H, m), 5.05 (1H, s), 6.39 (1H, s), 6.53 (1H, s), 6.69 (1H, br d, *J* = 8.0), 6.84 (2H, d, *J* = 8.8), 6.86 (1H, t, *J* = 7.5), 6.90 (1H, d, *J* = 8.1), 7.09 (2H, d, *J* = 8.5), 7.25−7.29 (2H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 28.5 (CH_2), 45.4 (CH), 55.4 (CH_3), 55.6 (CH_3), 55.9 (CH_3), 56.5 (CH_3), 61.9 (CH), 99.3 (CH), 108.1 (C), 110.5 (CH), 114.0 (CH), 115.1 (CH), 115.9 (1C, q, *J* = 288.3, C), 120.7 (CH), 126.6 (CH), 127.6 (CH), 128.3 (C), 129.0 (CH), 137.3 (C), 140.2 (C), 142.1 (C), 148.8 (C), 155.9 (C), 156.7 (1C, q, *J* = 36.8, C), 157.0 (C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.3 (3F, s); MS (EI) *m*/*z* 517 (29, M^+ + H), 516 (100, M^+), 501 (17, $M^+ - CH_3$), 402 (15, $M^+ - C_3H_5F_3O$); HRMS $C_{27}H_{27}F_3N_2O_5$ calcd 516.1867, found 516.1870. Anal. Calcd for $C_{27}H_{27}F_3N_2O_5$: C, 62.78; H, 5.27; N, 5.42. Found: C, 63.11; H, 5.31; N, 5.38.

N-((2R,3S*)-8-(Benzyloxy)-7-methoxy-1-(4-methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-2,2,2-trifluoroacetamide (**18s**).* β-Aminoacetamide **7s** (88 mg, 0.14 mmol) afforded crude tetrahydroquinoline **18s** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure tetrahydroquinoline **18s** as a white solid (24 mg, 31%): mp 126−128 °C; R_f 0.38 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3411, 3302, 3066−2853, 1709, 1506, 1490, 1448, 1288, 1241, 1206, 1162, 1136, 1099, 1033 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.76 (1H, dd, *J* = 17.2, 2.2), 2.81 (1H, dd, *J* = 17.3, 4.5), 3.74 (3H, s), 3.84 (3H, s), 4.66 (1H, m), 4.71 (1H, d, *J* = 10.7), 4.82 (1H, d, *J* = 10.6), 5.08 (1H, d, *J* = 3.9), 6.61 (1H, d, *J* = 8.5), 6.62 (1H, br m), 6.72 (2H, dm, *J* = 8.9), 6.81 (1H, d, *J* = 8.5), 6.90−6.94 (4H, m), 7.16−7.19 (3H, m), 7.27−7.35 (5H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.7 (CH_2), 48.7 (CH), 55.8 (CH_3), 55.9 (CH_3), 67.3 (CH), 73.4 (CH_2), 105.5 (CH), 114.5 (CH), 114.8 (C), 115.6 (1C, q, *J* = 288.2, C), 122.2 (CH), 125.6 (CH), 126.0 (CH), 127.5 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 129.0 (CH), 135.8 (C), 137.5 (C), 138.1 (C), 140.4 (C), 144.7 (C), 153.2 (C), 155.7 (C), 156.9 (1C, q, *J* = 37.2, C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.4 (3F, s); MS (ES^+) *m*/*z* 564 (20, $M^+ + H_2$), 563 (65, M^+ + H), 472 (100, $M^+ - PhCH_2$), 433 (55, $M^+ - C_3H_4F_3O_2$); HRMS $C_{32}H_{30}F_3N_2O_4$ calcd 563.2158, found 563.2131.

(1R,2S*)-3-(2-Bromophenyl)-N[1]-(4-methoxyphenyl)-1-phenylpropane-1,2-diamine (**13**).* A stirred suspension of β-aminoacetamide **7a** (164 mg, 0.323 mmol) and KOH (272 mg, 4.85 mmol) in EtOH (5.0 mL) and H_2O (1.0 mL) was heated to 85 °C to give a homogeneous solution. The reaction was heated until complete by TLC analysis (4 h) and allowed to cool to rt, H_2O was added, and the product was extracted into EtOAc. The combined organic extracts were washed with water, brine, dried ($MgSO_4$), and filtered and the solvents removed in vacuo to give crude 1,2-diamine **13** as a pale brown oil. Purification by passing through a short plug of silica and eluting with EtOAc yielded pure 1,2-diamine **13** as a pale yellow oil (124 mg, 94%): R_f 0.31 (50% EtOAc/petroleum ether); IR ν_{max} (neat) 3382, 3059−2830, 1511, 1240, 1037 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.42 (1H, dd, *J* = 13.5, 10.5), 3.17 (1H, dd, *J* = 13.5, 2.7), 3.47 (1H, ddd, *J* = 10.4, 4.7, 2.9), 3.70 (3H, s), 4.41 (1H, d, *J* = 4.7), 6.54 (2H, dm, *J* = 8.9), 6.69 (2H, dm, *J* = 8.9), 7.10 (1H, td, *J* = 7.6, 1.4), 7.16 (1H, dd, *J* = 7.5, 1.4), 7.23 (1H, t, *J* = 7.2), 7.28 (1H, t, *J* = 7.3), 7.36 (2H, t, *J* = 7.6), 7.42 (2H, d, *J* = 7.4), 7.55 (1H, d, *J* = 7.9); ^{13}C NMR (151 MHz, $CDCl_3$) δ 41.7 (CH_2), 55.6 (CH), 55.8 (CH_3), 63.0 (CH), 114.8 (CH), 114.9 (CH), 125.0 (C), 127.5 (CH), 127.5 (CH), 127.9 (CH), 128.3 (CH), 128.6 (CH), 131.7 (CH), 133.2 (CH), 138.7 (C), 140.1 (C), 141.6 (C), 151.9 (C); MS (ESI^+) *m*/*z* 411 + 413 (1:1, 100, M^+ + H), 290 + 288 (1:1, 33, M^+ − NHPMP); HRMS $C_{22}H_{24}(^{79}Br)N_2O$ calcd 411.1064, found 411.1067.

N-((R)-((S*)-Indolin-2-yl)(phenyl)methyl)-4-methoxyaniline (**14a**).* A flame-dried Schenk tube was charged with $Pd(PPh_3)_4$ (28.0 mg, 24.3 μmol, NaO^{t}Bu (74.7, 0.778 mmol) and K_2CO_3 (107 mg, 0.778 mmol). The tube was triple evacuated/N_2 filled before the addition of a solution of 1,2-diamine **13** (200 mg, 0.486 mmol) in toluene (9.7 mL). The resulting mixture was stirred while N_2 was bubbled through it, using a needle, for 15 min. The N_2 needle was removed and the reaction was heated to 100 °C for 4 h to give a dark brown mixture. The reaction was allowed to cool to rt before being filtered through Celite, washed with EtOAc and the solvents removed in vacuo to give crude indoline **14a** as a brown solid. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14a** as a pale yellow solid (148 mg, 91%): mp 51−55 °C; R_f 0.27 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3359, 3027−2832, 1609, 1509, 1483, 1466, 1454, 1237, 1035 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.91 (1H, dd, *J* = 15.9, 8.8), 3.18 (1H, dd, *J* = 15.9, 8.7), 3.70 (3H, s), 4.16 (1H, dt, *J* = 8.3, 7.1), 4.37 (1H, d, *J* = 6.4), 6.49 (2H, dm, *J* = 8.9), 6.61 (1H, d, *J* = 7.7), 6.68 (2H, d, *J* = 8.7), 6.73 (1H, t, *J* = 7.4), 7.05 (1H, t, *J* = 7.7), 7.07 (1H, d, *J* = 7.3), 7.30 (1H, t, *J* = 7.2), 7.37 (2H, t, *J* = 7.4), 7.42 (2H, d, *J* = 7.4); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.3 (CH_2), 55.8 (CH_3), 62.2 (CH), 65.3 (CH), 109.2 (CH), 114.8 (CH), 115.4 (CH), 119.1 (CH), 125.0 (CH), 127.1 (CH), 127.5 (CH), 127.6 (CH), 128.2 (C), 128.9 (CH), 141.3 (C), 141.7 (C), 150.5 (C), 152.4 (C); MS (EI) *m*/*z* 330 (3, M^+), 213 (93, $M^+ - C_8H_7N$), 212 (99, $M^+ - C_8H_8N$), 118 (100, $M^+ - C_{14}H_{14}NO$); HRMS $C_{22}H_{22}N_2O$ calcd 330.1727, found 330.1735. Anal. Calcd for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found: C, 79.79; H, 6.69; N, 8.24.

General Procedure for the Synthesis of Indolines 14 (Table 6). A stirred suspension of β-nitroacetamide **7** (1.00 mmol) and KOH (15.0 mmol) in EtOH (15.0 mL) and H_2O (3.0 mL) was heated to 85 °C to give a homogeneous solution. The reaction was heated until complete by TLC analysis (2−6 h), allowed to cool to rt, H_2O was added and the product extracted into EtOAc. The combined organic extracts were washed with water, brine, dried ($MgSO_4$), filtered and the solvents removed in vacuo to give crude 1,2-diamine, which was purified by passing through a short plug of silica. A flame-dried Schenk tube was charged with $Pd(PPh_3)_4$ (10.0 mol %), NaO-*t*-Bu (1.60 mmol), and K_2CO_3 (1.60 mmol). The tube was triple evacuated/N_2 filled before the addition of a solution of 1,2-diamine (1.00 mmol) in toluene (20.0 mL). The resulting mixture was stirred while N_2 was bubbled through it, using a needle, for 15 min. The N_2 needle was removed, and the reaction was heated to 100 °C for 4 h to give a dark brown mixture. The reaction was allowed to cool to rt before being filtered through Celite, washed with EtOAc and the solvents removed in vacuo to give crude indoline **14**, which was purified by flash column chromatography.

N-((S)-Furan-2-yl((S*)-indolin-2-yl)methyl)-4-methoxyaniline (**14b**).* β-Aminoacetamide **7b** (92 mg, 0.18 mmol) afforded crude

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indoline **14b** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14b** as an off-white semisolid (41 mg, 69%): R_f 0.55 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3365, 3112−2833, 1609, 1509, 1484, 1465, 1234, 1035 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.18 (2H, d, J = 8.0), 3.73 (3H, s), 4.24 (1H, q, J = 7.9), 4.41 (1H, d, J = 7.6), 6.27 (1H, d, J = 3.2), 6.33 (1H, dd, J = 3.2, 1.9), 6.59 (2H, dm, J = 8.9), 6.62 (1H, d, J = 7.7), 6.73−6.76 (3H, m), 7.05 (1H, t, J = 7.6), 7.10 (1H, d, J = 7.3), 7.39 (1H, dd, J = 1.7, 0.5); ^{13}C NMR (151 MHz, $CDCl_3$) δ 33.3 (CH_2), 55.8 (CH_3), 57.1 (CH), 62.5 (CH), 107.9 (CH), 109.4 (CH), 110.4 (CH), 114.8 (CH), 115.6 (CH), 119.0 (CH), 125.0 (CH), 127.5 (CH), 128.1 (C), 141.3 (C), 142.2 (CH), 150.4 (C), 152.8 (C), 154.3 (C); MS (CI) m/z 321 (5, M^+ + H), 320 (2, M^+), 202 (17, $M^+ - C_8H_8N$), 118 (100, $M^+ - C_{12}H_{12}NO_2$); HRMS $C_{20}H_{21}N_2O_2$ calcd 321.1603, found 321.1607.

N-((R)-Furan-3-yl((S*)-indolin-2-yl)methyl)-4-methoxyaniline (**14c**).* β-Aminoacetamide **7c** (54 mg, 0.11 mmol) afforded crude indoline **14c** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14c** as a pale brown semisolid (23 mg, 66%): R_f 0.30 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3359, 3138−2832, 1609, 1510, 1485, 1466, 1239, 1035, 1020 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.09 (1H, dd, J = 16.0, 8.8), 3.13 (1H, dd, J = 16.0, 8.0), 3.73 (3H, s), 4.14 (1H, q, J = 7.9), 4.33 (1H, d, J = 6.7), 6.42 (1H, d, J = 0.7), 6.58 (2H, dm, J = 8.9), 6.61 (1H, d, J = 7.7), 6.72−6.75 (3H, m), 7.04 (1H, t, J = 7.6), 7.08 (1H, d, J = 7.3), 7.41 (1H, t, J = 1.5), 7.42 (1H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.8 (CH_2), 55.0 (CH), 55.8 (CH_3), 63.8 (CH), 109.1 (CH), 109.3 (CH), 114.8 (CH), 115.6 (CH), 119.1 (CH), 125.0 (CH), 125.7 (C), 127.5 (CH), 128.3 (C), 140.4 (CH), 141.6 (C), 143.7 (CH), 150.5 (C), 152.6 (C); MS (ESI^+) m/z 320 (4, M^+), 202 (100, $M^+ - C_8H_8N$), 118 (92, $M^+ - C_{12}H_{12}NO_2$); HRMS $C_{20}H_{20}N_2O_2$ calcd 320.1519, found 320.1526.

N-((S)-((S*)-Indolin-2-yl)(thiophene-2-yl)methyl)-4-methoxyaniline (**14d**).* β-Aminoacetamide **7d** (165 mg, 0.322 mmol) afforded crude indoline **14d** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14d** as an pale yellow solid (79 mg, 73%): mp 46−49 °C; R_f 0.33 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3360, 3051−2832, 1609, 1508, 1483, 1465, 1233, 1035 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.12 (1H, dd, J = 16.1, 9.0), 3.18 (1H, dd, J = 16.1, 7.9), 3.73 (3H, s), 4.00 (2H, br s), 4.18 (1H, q, J = 7.9), 4.63 (1H, d, J = 6.8), 6.59 (2H, dm, J = 9.0), 6.63 (1H, d, J = 7.7), 6.73−6.76 (3H, m), 7.01 (1H, dd, J = 5.0, 3.5), 7.06 (2H, m), 7.10 (1H, d, J = 7.3), 7.24 (1H, dd, J = 5.0, 1.1); ^{13}C NMR (151 MHz, $CDCl_3$) δ 33.0 (CH_2), 55.8 (CH_3), 59.1 (CH), 64.9 (CH), 109.3 (CH), 114.8 (CH), 115.6 (CH), 119.1 (CH), 124.7 (CH), 124.8 (CH), 125.0 (CH), 127.1 (CH), 127.6 (CH), 128.1 (C), 141.3 (C), 146.3 (C), 150.3 (C), 152.8 (C); MS (CI) m/z 337 (30, M^+ + H), 253 (5, $M^+ - C_4H_3S$), 218 (95, $M^+ - C_8H_8N$), 123 (100, $M^+ - C_{13}H_{11}NS$), 118 (19, $M^+ - C_{12}H_{12}NOS$); HRMS $C_{20}H_{21}N_2OS$ calcd 337.1375, found 337.1386. Anal. Calcd for $C_{20}H_{20}N_2OS$: C, 71.40; H, 5.99; N, 8.33. Found: C, 71.46; H, 6.02; N, 8.10.

N-((R)-1-((S*)-Indolin-2-yl)hexyl)-4-methoxyaniline (**14e**).* β-Aminoacetamide **7e** (164 mg, 0.327 mmol) afforded crude indoline **14e** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14e** as an pale brown oil (70 mg, 66%): R_f 0.48 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3370, 3052−2855, 1609, 1509, 1485, 1465, 1232, 1038 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.90 (3H, t, J = 5.7), 1.26−1.53 (7H, m), 1.66−1.71 (1H, m), 2.95 (1H, dd, J = 16.0, 8.5), 3.17 (1H, dd, J = 16.0, 9.3), 3.39 (1H, dt, J = 6.9, 5.0), 3.77 (3H, s), 4.05 (1H, td, J = 8.9, 5.8), 6.60 (2H, d, J = 8.8), 6.61 (1H, d, J = 7.9), 6.72 (1H, t, J = 7.4), 6.79 (2H, dm, J = 8.8), 7.04 (1H, t, J = 7.6), 7.09 (1H, d, J = 7.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.2 (CH_3), 22.8 (CH_2), 25.8 (CH_2), 31.7 (CH_2), 32.2 (CH_2), 32.9 (CH_2), 55.9 (CH_3), 58.4 (CH), 62.5 (CH), 109.4 (CH), 114.6 (CH), 115.1 (CH), 118.8 (CH), 124.8 (CH), 127.5 (CH), 128.8 (C), 142.5 (C), 151.1 (C), 152.0 (C); MS (CI) m/z 326 (23, $M^+ + H_2$), 325 (100, M^+ + H), 324 (6, M^+), 118 (15, $M^+ - C_{13}H_{20}NO$); HRMS $C_{21}H_{29}N_2O$ calcd 325.2280, found 325.2282. Anal. Calcd for $C_{21}H_{28}N_2O$: C, 77.74; H, 8.70; N, 8.63. Found: C, 77.54; H, 8.73; N, 8.65.

N-((R)-Cyclohexyl((S*)-indolin-2-yl)methyl)-4-methoxyaniline (**14f**).* β-Aminoacetamide **7f** (65 mg, 0.13 mmol) afforded crude indoline **14f** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure indoline **14f** as an off-white solid (34 mg, 80%): mp 85−88 °C; R_f 0.39 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3384, 3051−2851, 1609, 1509, 1485, 1465, 1236, 1039 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.12−1.32 (5H, m), 1.65−1.83 (6H, m), 2.88 (1H, dd, J = 16.0, 8.5), 3.14 (1H, dd, J = 16.0, 8.9), 3.34 (1H, dd, J = 8.1, 3.9), 3.75 (3H, s), 3.98 (1H, q, J = 8.6), 6.56 (2H, dm, J = 8.9), 6.61 (1H, d, J = 7.7), 6.71 (1H, t, J = 7.4), 6.75 (2H, dm, J = 8.6), 7.02 (1H, t, J = 7.7), 7.05 (1H, d, J = 7.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.5 (CH_2), 26.6 (CH_2), 26.6 (CH_2), 27.1 (CH_2), 31.2 (CH_2), 34.1 (CH_2), 40.9 (CH), 55.9 (CH_3), 61.9 (CH), 63.7 (CH), 109.5 (CH), 114.1 (CH), 115.0 (CH), 119.0 (CH), 124.8 (CH), 127.4 (CH), 128.9 (C), 143.6 (C), 150.7 (C), 151.7 (C); MS (ES^+) m/z 337 (19, M^+ + H), 214 (100, M^+ − NHPMP); HRMS $C_{22}H_{29}N_2O$ calcd 337.2280, found 337.2285. Anal. Calcd for $C_{22}H_{28}N_2O$: C, 78.53; H, 8.39; N, 8.33. Found: C, 78.07; H, 8.59; N, 7.75.

N-((R)-1-((S*)-Indolin-2-yl)-2,2-dimethylpropyl)-4-methoxyaniline (**14g**).* β-Aminoacetamide **7g** (58 mg, 0.12 mmol) afforded crude indoline **14g** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure indoline **14g** as a colorless oil (32 mg, 87%): R_f 0.34 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3375, 3053−2832, 1610, 1509, 1486, 1466, 1232, 1038 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.06 (9H, s), 3.00 (1H, dd, J = 15.8, 9.9), 3.05 (1H, dd, J = 15.8, 8.9), 3.32 (1H, d, J = 4.9), 3.74 (3H, s), 4.23 (1H, td, J = 9.4, 4.8), 6.53−6.57 (3H, m), 6.69 (1H, t, J = 7.3), 6.73 (2H, dm, J = 8.9), 6.99 (1H, t, J = 7.6), 7.05 (1H, d, J = 7.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.9 (CH_3), 33.3 (CH_2), 36.2 (C), 55.9 (CH_3), 62.2 (CH), 66.9 (CH), 109.6 (CH), 114.2 (CH), 114.9 (CH), 118.9 (CH), 124.5 (CH), 127.3 (CH), 129.0 (C), 144.3 (C), 150.9 (C), 151.6 (C); MS (ES^+) m/z 311 (43, M^+ + H), 280 (92, $M^+ - OCH_3$), 192 (18, $M^+ - C_8H_8N$), 188 (100, M^+ − NHPMP); HRMS $C_{20}H_{27}N_2O$ calcd 311.2123, found 311.2130.

N-((R)-((S*)-Indolin-2-yl)(o-tolyl)methyl)-4-methoxyaniline (**14h**).* β-Aminoacetamide **7h** (65 mg, 0.13 mmol) afforded crude indoline **14h** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14h** as an off-white solid (32 mg, 74%): mp 47−50 °C; R_f 0.34 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3355, 3053−2832, 1610, 1510, 1484, 1466, 1236, 1036 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.45 (3H, s), 2.90 (1H, dd, J = 15.9, 8.8), 3.24 (1H, dd, J = 15.9, 8.8), 3.70 (3H, s), 3.75 (1H, br s), 4.18 (1H, q, J = 8.0), 4.20 (1H, br s), 4.64 (1H, d, J = 6.3), 6.43 (2H, dm, J = 8.9), 6.60 (1H, d, J = 7.7), 6.68 (2H, dm, J = 8.9), 6.73 (1H, t, J = 7.4), 7.04 (1H, t, J = 7.6), 7.09 (1H, d, J = 7.3), 7.19−7.22 (3H, m), 7.52−7.54 (1H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 19.7 (CH_3), 32.3 (CH_2), 55.8 (CH_3), 58.0 (CH), 64.0 (CH), 109.2 (CH), 114.8 (CH), 115.1 (CH), 119.0 (CH), 125.0 (CH), 126.4 (CH), 126.8 (CH), 127.2 (CH), 127.5 (CH), 128.3 (C), 130.8 (CH), 135.6 (C), 139.2 (C), 142.0 (C), 150.7 (C), 152.3 (C); MS (CI) m/z 345 (18, M^+ + H), 226 (17, $M^+ - C_8H_8N$), 220 (100, $M^+ - C_{16}H_{15}NO$); HRMS $C_{23}H_{25}N_2O$ calcd 345.1967, found 345.1950.

(10R,10aS*)-N-(4-Methoxyphenyl)-10a,11-dihydro-10H-indolo-[1,2-a]indol-10-amine (**14i**).* Prepared using general procedure for the synthesis of indolines except with 3.2 equiv NaO*t*Bu and 3.2 equiv K_2CO_3. β-Aminoacetamide **7i** (73 mg, 0.12 mmol) afforded crude indoline **14i** as a brown oil. Purification by flash column chromatography (20% EtOAc/petroleum ether) yielded pure indoline **14i** as a yellow solid (34 mg, 83%): mp 47−50 °C; R_f 0.17 (20% EtOAc/petroleum ether); IR ν_{max} (neat) 3367, 3028−2832, 1592, 1509, 1478, 1456, 1233, 1036 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.28 (1H, dd, J = 15.9, 8.6), 3.41 (1H, dd, J = 15.9, 9.5), 3.80 (3H, s), 4.58 (1H, td, J = 9.1, 5.5), 5.15 (1H, d, J = 5.3), 6.70 (2H, dm, J = 8.8), 6.86 (2H, dm, J = 8.8), 6.95−6.98 (2H, m), 7.19−7.23 (4H, m), 7.29 (1H, t, J = 7.8), 7.31 (1H, d, J = 7.4); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.7 (CH_2), 55.9 (CH_3), 63.8 (CH), 73.4 (CH), 113.2 (CH), 113.7 (CH), 115.2 (CH), 115.2 (CH), 122.1 (CH), 122.4 (CH), 125.2 (CH), 125.5 (CH), 127.8 (CH), 129.7 (CH), 132.5 (C), 133.4 (C),

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141.3 (*C*), 148.2 (*C*), 149.2 (*C*), 152.7 (*C*); MS (CI) *m*/*z* 329 (39, M^+ + H), 328 (14, M^+), 220 (42, M^+ − PMPH), 206 (46, M^+ − NHPMP); HRMS $C_{22}H_{21}N_2O$ calcd 329.1654, found 329.1649. Anal. Calcd for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.13; H, 6.13; N, 8.65.

N-((R)-((S*)-Indolin-2-yl)(2-methoxyphenyl)methyl)-4-methoxyaniline (**14j**).* β-Aminoacetamide **7j** (152 mg, 0.282 mmol) afforded crude indoline **14j** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14j** as an off-white oily foam (57 mg, 56%): R_f 0.24 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3361, 3030−2834, 1601, 1509, 1485, 1463, 1439, 1233, 1026 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.89 (1H, dd, *J* = 15.9, 8.9), 3.18 (1H, dd, *J* = 16.0, 8.2), 3.70 (3H, s), 3.89 (3H, s), 4.39 (1H, q, *J* = 7.9), 4.68 (1H, s), 6.50 (2H, dm, *J* = 8.8), 6.59 (1H, d, *J* = 7.9), 6.69 (2H, dm, *J* = 8.9), 6.73 (1H, t, *J* = 7.0), 6.93−6.95 (2H, m), 7.04 (1H, t, *J* = 7.6), 7.08 (1H, d, *J* = 7.3), 7.25−7.28 (1H, m), 7.40 (1H, d, *J* = 7.3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.3 (CH_2), 55.5 (CH_3), 55.8 (CH_3), 57.7 (*C*H), 62.4 (*C*H), 109.2 (*C*H), 110.8 (*C*H), 114.7 (*C*H), 115.3 (*C*H), 118.9 (*C*H), 121.0 (*C*H), 125.0 (*C*H), 127.4 (*C*H), 128.5 (*C*H), 128.5 (*C*), 128.6 (*C*), 128.9 (*C*H), 142.2 (*C*), 150.9 (*C*), 152.2 (*C*), 157.1 (*C*); MS (CI) *m*/*z* 361 (30, M^+ + H), 342 (31, M^+ − C_8H_8N), 123 (100, M^+ − $C_{16}H_{15}NO$), 118 (35, M^+ − $C_{15}H_{16}NO_2$); HRMS $C_{23}H_{25}N_2O_2$ calcd 361.1911, found 361.1916.

N-((R)-((S*)-Indolin-2-yl)(3-methoxyphenyl)methyl)-4-methoxyaniline (**14k**).* β-Aminoacetamide **7k** (140 mg, 0.261 mmol) afforded crude indoline **14k** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14k** as an off-white solid (62 mg, 66%): mp 53−56 °C; R_f 0.29 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3360, 3052−2833, 1608, 1585, 1509, 1483, 1465, 1436, 1233, 1036 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.93 (1H, dd, *J* = 16.0, 8.8), 3.18 (1H, dd, *J* = 16.0, 8.6), 3.71 (3H, s), 3.82 (3H, s), 4.14 (1H, q, *J* = 7.9), 4.20 (1H, br s), 4.33 (1H, d, *J* = 6.5), 6.51 (2H, dm, *J* = 8.9), 6.61 (1H, d, *J* = 7.7), 6.70 (2H, dm, *J* = 8.9), 6.74 (1H, t, *J* = 7.4), 6.85 (1H, dd, *J* = 8.2, 2.3), 7.00 (1H, s), 7.03 (1H, d, *J* = 7.5), 7.06 (1H, t, *J* = 7.6), 7.09 (1H, d, *J* = 7.2), 7.30 (1H, t, *J* = 7.9); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.4 (CH_2), 55.3 (CH_3), 55.8 (CH_3), 62.2 (*C*H), 65.2 (*C*H), 109.2 (*C*H), 112.7 (*C*H), 112.8 (*C*H), 114.8 (*C*H), 115.4 (*C*H), 119.1 (*C*H), 119.4 (*C*H), 125.0 (*C*H), 127.5 (*C*H), 128.2 (*C*), 129.9 (*C*H), 141.8 (*C*), 143.3 (*C*), 150.5 (*C*), 152.4 (*C*), 160.1 (*C*); MS (EI) *m*/*z* 361 (5%, M^+ + H), 360 (8, M^+); HRMS $C_{23}H_{24}N_2O_2$ calcd 360.1832, found 360.1835. Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.42; H, 6.91; N, 7.81.

N-((R)-((S*)-Indolin-2-yl)(4-methoxyphenyl)methyl)-4-methoxyaniline (**14l**).* β-Aminoacetamide **7l** (54 mg, 0.10 mmol) afforded crude indoline **14l** as a brown oil. Purification by flash column chromatography (15% EtOAc/petroleum ether) yielded pure indoline **14l** as a pale brown oil (23 mg, 64%): R_f 0.23 (15% EtOAc/petroleum ether); IR ν_{max} (neat) 3363, 3052−2833, 1609, 1509, 1484, 1465, 1238, 1174, 1034 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.93 (1H, dd, *J* = 15.9, 8.8), 3.16 (1H, dd, *J* = 15.9, 8.6), 3.70 (3H, s), 3.82 (3H, s), 4.11 (1H, q, *J* = 8.0), 4.31 (1H, d, *J* = 6.5), 6.49 (2H, d, *J* = 8.9), 6.60 (1H, d, *J* = 7.7), 6.69 (2H, d, *J* = 8.8), 6.73 (1H, t, *J* = 7.4), 6.91 (2H, d, *J* = 8.6), 7.04 (1H, t, *J* = 7.6), 7.08 (1H, d, *J* = 7.2), 7.33 (2H, d, *J* = 8.5); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.4 (CH_2), 55.4 (CH_3), 55.8 (CH_3), 61.6 (*C*H), 65.4 (*C*H), 109.2 (*C*H), 114.3 (*C*H), 114.8 (*C*H), 115.4 (*C*H), 119.0 (*C*H), 125.0 (*C*H), 127.5 (*C*H), 128.1 (*C*H), 128.3 (*C*), 133.3 (*C*), 141.8 (*C*), 150.5 (*C*), 152.3 (*C*), 159.0 (*C*); MS (CI) *m*/*z* 361 (4, M^+ + H), 242 (100, M^+ − C_8H_8N); HRMS $C_{23}H_{25}N_2O_2$ calcd 361.1911, found 361.1907.

N-((R)-((S*)-Indolin-2-yl)(2-(trifluoromethyl)phenyl)methyl)-4-methoxyaniline (**14m**).* β-Aminoacetamide **7m** (29 mg, 50 μmol) afforded crude indoline **14m** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure indoline **14m** as a pale brown oil (13 mg, 65%): R_f 0.36 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3357, 3031−2834, 1609, 1511, 1484, 1467, 1308, 1246, 1238, 1162, 1116, 1035 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.60 (1H, dd, *J* = 15.8, 8.9), 3.29 (1H, dd, *J* = 15.3, 11.1), 3.69 (3H, s), 4.41 (1H, td, *J* = 9.5, 3.6), 4.91 (1H, d, *J* = 3.8), 6.48 (2H, d, *J* = 8.8), 6.66−6.68 (3H, m), 6.74 (1H, t, *J* = 7.4), 7.05−7.07 (2H, m), 7.41 (1H, t, *J* = 7.5), 7.54 (1H, t, *J* = 7.7), 7.75 (1H, d, *J* = 7.9), 7.99 (1H, d, *J* = 7.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 30.2 (CH_2), 55.8 (CH_3), 56.9 (*C*H), 64.3 (*C*H), 109.6 (*C*H), 114.7 (*C*H), 115.8 (*C*H), 119.4 (*C*H), 124.8 (1C, q, *J* = 274.3, *C*), 124.9 (*C*H), 126.7 (1C, q, *J* = 6.0, *C*H), 127.6 (*C*H), 127.7 (*C*H), 127.7 (1C, q, *J* = 29.5, *C*), 128.2 (*C*), 128.8 (*C*H), 132.6 (*C*H), 140.0 (*C*), 141.3 (*C*), 150.6 (*C*), 152.8 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −58.1 (3F, s); MS (CI) *m*/*z* 399 (100%, M^+ + H), 398 (10, M^+), 274 (19, M^+ − $C_7H_{10}NO$); HRMS $C_{23}H_{22}F_3N_2O$ calcd 399.1679, found 399.1684.

N-((R)-((S*)-Indolin-2-yl)(3-(trifluoromethyl)phenyl)methyl)-4-methoxyaniline (**14n**).* β-Aminoacetamide **7n** (64 mg, 0.11 mmol) afforded crude indoline **14n** as a brown oil. Purification by flash column chromatography (25% Et_2O/petroleum ether) yielded pure indoline **14n** as a pale brown oil (26 mg, 59%): R_f 0.27 (25% Et_2O/petroleum ether); IR ν_{max} (neat) 3359, 3053−2834, 1610, 1509, 1484, 1467, 1436, 1326, 1237, 1195, 1164, 1121, 1071, 1036 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.85 (1H, dd, *J* = 15.9, 8.9), 3.14 (1H, dd, *J* = 15.9, 9.2), 3.70 (3H, s), 4.21 (1H, m), 4.44 (1H, d, *J* = 6.0), 6.47 (2H, d, *J* = 8.8), 6.63 (1H, d, *J* = 7.7), 6.70 (2H, d, *J* = 8.8), 6.74 (1H, t, *J* = 7.4), 7.04−7.07 (2H, m), 7.49 (1H, t, *J* = 7.7), 7.56 (1H, d, *J* = 7.6), 7.65 (1H, d, *J* = 7.7), 7.70 (1H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 31.9 (CH_2), 55.8 (CH_3), 62.1 (*C*H), 65.1 (*C*H), 109.4 (*C*H), 114.8 (*C*H), 115.6 (*C*H), 119.4 (*C*H), 123.8 (1C, q, *J* = 3.6, *C*H), 124.6 (1C, q, *J* = 272.3, *C*), 124.6 (1C, q, *J* = 3.6, *C*H), 125.0 (*C*H), 127.7 (*C*H), 127.9 (*C*), 129.4 (*C*H), 130.6 (*C*H), 131.2 (1C, q, *J* = 32.2, *C*), 141.2 (*C*), 142.5 (*C*), 150.3 (*C*), 152.7 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.8 (3F, s); MS (CI) *m*/*z* 399 (52, M^+ + H), 398 (10, M^+), 280 (84, M^+ − C_8H_8N); HRMS $C_{23}H_{22}F_3N_2O$ calcd 399.1679, found 399.1681.

N-((R)-((S*)-Indolin-2-yl)(4-(trifluoromethyl)phenyl)methyl)-4-methoxyaniline (**14o**).* β-Aminoacetamide **7o** (178 mg, 0.309 mmol) afforded crude indoline **14o** as a brown oil. Purification by flash column chromatography (30% Et_2O/petroleum ether) yielded pure indoline **14o** as a pale brown solid (96 mg, 78%): mp 57−60 °C; R_f 0.37 (30% Et_2O/petroleum ether); IR ν_{max} (neat) 3358, 3054−2835, 1610, 1511, 1484, 1467, 1324, 1238, 1163, 1122, 1066, 1036, 1017 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.85 (1H, dd, *J* = 16.0, 8.9), 3.16 (1H, dd, *J* = 15.9, 9.3), 3.72 (3H, s), 4.20 (1H, td, *J* = 9.0, 6.2), 4.46 (1H, d, *J* = 6.0), 6.46 (2H, dm, *J* = 8.9), 6.64 (1H, d, *J* = 7.6), 6.71 (2H, dm, *J* = 8.8), 6.76 (1H, t, *J* = 7.4), 7.06−7.09 (2H, m), 7.58 (2H, d, *J* = 8.0), 7.65 (2H, d, *J* = 7.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.0 (CH_2), 55.8 (CH_3), 61.9 (*C*H), 65.1 (*C*H), 109.4 (*C*H), 114.8 (*C*H), 115.5 (*C*H), 119.4 (*C*H), 124.3 (1C, q, *J* = 272.0, *C*), 125.0 (*C*H), 125.9 (1C, q, *J* = 3.7, *C*H), 127.5 (*C*H), 127.7 (*C*H), 128.0 (*C*), 129.9 (1C, q, *J* = 32.4, *C*), 141.3 (*C*), 145.6 (*C*), 150.4 (*C*), 152.7 (*C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.8 (3F, s); MS (CI) *m*/*z* 399 (13, M^+), 280 (100, M^+ − C_8H_8N); HRMS $C_{23}H_{22}F_3N_2O$ calcd 399.1679, found 399.1671. Anal. Calcd for $C_{23}H_{21}F_3N_2O$: C, 69.34; H, 5.31; N, 7.03. Found: C, 68.95; H, 5.29; N, 6.81.

N-((R)-((S*)-5-Fluoroindolin-2-yl)(phenyl)methyl)-4-methoxyaniline (**14p**).* β-Aminoacetamide **7p** (57 mg, 0.11 mmol) afforded crude indoline **14p** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure indoline **14p** as a pale yellow oily solid (19 mg, 50%): R_f 0.18 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3354, 3060−2833, 1511, 1488, 1451, 1236, 1036 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.89 (1H, dd, *J* = 16.2, 8.8), 3.15 (1H, dd, *J* = 16.2, 8.8), 3.69 (3H, s), 4.18 (1H, dd, *J* = 15.3, 8.6), 4.36 (1H, d, *J* = 6.5), 6.48−6.51 (3H, m), 6.68 (2H, dm, *J* = 8.8), 6.73 (1H, td, *J* = 8.9, 2.1), 6.78 (1H, d, *J* = 8.3), 7.29 (1H, t, *J* = 7.2), 7.36 (2H, t, *J* = 7.5), 7.41 (2H, d, *J* = 7.4); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.6 (CH_2), 55.8 (CH_3), 62.1 (*C*H), 65.9 (*C*H), 109.4 (1C, d, *J* = 8.3, *C*H), 112.4 (1C, d, *J* = 23.9, *C*H), 113.4 (1C, d, *J* = 23.2, *C*H), 114.8 (*C*H), 115.5 (*C*H), 127.1 (*C*H), 127.7 (*C*H), 128.9 (*C*H), 129.9 (1C, d, *J* = 8.1, *C*), 141.0 (*C*), 141.5 (*C*), 146.5 (*C*), 152.5 (*C*), 157.2 (1C, d, *J* = 235.5, *C*); ^{19}F NMR (282 MHz, $CDCl_3$) δ −126.4 (1F, m); MS (EI) *m*/*z* 348 (11, M^+), 212 (100, M^+ − C_8H_7FN), 136 (92, M^+ − $C_{14}H_{14}NO$); HRMS $C_{22}H_{21}FN_2O$ calcd 348.1632, found 348.1624.

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N-((R)-((S*)-5,6-Dimethoxyindolin-2-yl)(phenyl)methyl)-4-methoxyaniline (**14q**).* β-Aminoacetamide **7q** (136 mg, 0.240 mmol) afforded crude indoline **14q** as a brown oil. Purification by flash column chromatography (80% Et_2O/petroleum ether) yielded pure indoline **14q** as a pale yellow solid (45 mg, 48%): mp 58−61 °C; R_f 0.38 (70% Et_2O/petroleum ether); IR ν_{max} (neat) 3351, 3061−2833, 1509, 1481, 1464, 1237, 1195, 1175, 1109, 1034 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.85 (1H, dd, *J* = 15.6, 8.9), 3.11 (1H, dd, *J* = 15.5, 8.7), 3.69 (3H, s), 3.81 (3H, s), 3.82 (3H, s), 4.14 (1H, q, *J* = 7.9), 4.37 (1H, d, *J* = 6.4), 6.30 (1H, s), 6.49 (2H, dm, *J* = 8.9), 6.68 (2H, dm, *J* = 8.9), 6.70 (1H, s), 7.27−7.30 (1H, m), 7.36 (2H, t, *J* = 7.6), 7.42 (2H, d, *J* = 7.4); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.4 (CH_2), 55.8 (CH_3), 56.2 (CH_3), 57.1 (CH_3), 62.3 (CH), 66.0 (CH), 95.6 (CH), 110.2 (CH), 114.7 (CH), 115.4 (CH), 118.9 (C), 127.1 (CH), 127.6 (CH), 128.9 (CH), 141.4 (C), 141.8 (C), 142.7 (C), 144.3 (C), 149.0 (C), 152.3 (C); MS (EI) *m*/*z* 390 (4, M^+), 213 (37, $M^+ - C_{10}H_{11}NO_2$), 212 (47, $M^+ - C_{10}H_{12}NO_2$), 178 (100, $M^+ - C_{14}H_{14}NO$); HRMS $C_{24}H_{26}N_2O_3$ calcd 390.1938, found 390.1942. Anal. Calcd for $C_{24}H_{26}N_2O_3$: C, 73.82; H, 6.71; N, 7.17. Found: C, 73.46; H, 6.73; N, 6.94.

N-((R)-((S*)-5,6-Dimethoxyindolin-2-yl)(2-methoxyphenyl)-methyl)-4-methoxyaniline (**14r**).* β-Aminoacetamide **7r** (61 mg, 0.10 mmol) afforded crude indoline **14r** as a brown oil. Purification by flash column chromatography (70% Et_2O/petroleum ether) yielded pure indoline **14r** as an off-white solid (18 mg, 42%): mp 65−68 °C; R_f 0.52 (70% Et_2O/petroleum ether); IR ν_{max} (neat) 3357, 2997−2834, 1509, 1489, 1463, 1236, 1195, 1029 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.83 (1H, dd, *J* = 15.6, 9.0), 3.10 (1H, dd, *J* = 15.7, 8.1), 3.69 (3H, s), 3.81 (3H, s), 3.82 (3H, s), 3.88 (3H, s), 4.36 (1H, td, *J* = 8.3, 6.7), 4.67 (1H, d, *J* = 6.1), 6.28 (1H, s), 6.49 (2H, dm, *J* = 8.9), 6.68 (2H, dm, *J* = 8.9), 6.71 (1H, s), 6.91−6.93 (2H, m), 7.25 (1H, td, *J* = 7.8, 1.6), 7.38 (1H, d, *J* = 7.4); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.5 (CH_2), 55.5 (CH_3), 55.8 (CH_3), 56.2 (CH_3), 57.1 (CH_3), 57.9 (CH), 63.0 (CH), 95.7 (CH), 110.3 (CH), 110.8 (CH), 114.7 (CH), 115.3 (CH), 119.3 (C), 120.9 (CH), 128.4 (CH), 128.6 (C), 128.9 (CH), 142.2 (C), 142.6 (C), 144.7 (C), 148.9 (C), 152.2 (C), 157.1 (C); MS (EI) *m*/*z* 420 (10, M^+), 243 (51, $M^+ - C_{10}H_{11}NO_2$), 242 (100, $M^+ - C_{10}H_{12}NO_2$), 178 (31, $M^+ - C_{15}H_{16}NO_2$); HRMS $C_{25}H_{28}N_2O_4$ calcd 420.2044, found 420.2041.

N-((R)-((S*)-7-(Benzyloxy)-6-methoxyindolin-2-yl)(phenyl)-methyl)-4-methoxyaniline (**14s**).* β-Aminoacetamide **7s** (67 mg, 0.10 mmol) afforded crude indoline **14s** as a brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure indoline **14s** as a pale yellow oily solid (28 mg, 58%): R_f 0.17 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3365, 3064−2835, 1622, 1511, 1495, 1465, 1454, 1266, 1237, 1090, 1038 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.79 (1H, dd, *J* = 15.4, 8.6), 3.10 (1H, dd, *J* = 15.4, 9.1), 3.70 (3H, s), 3.86 (3H, s), 3.98 (1H, m), 4.29 (1H, d, *J* = 6.1), 4.99 (2H, q, *J* = 10.4), 6.30 (1H, d, *J* = 7.9), 6.48 (2H, d, *J* = 8.6), 6.69 (2H, d, *J* = 8.2), 6.73 (1H, d, *J* = 7.9), 7.29−7.39 (10H, m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 32.1 (CH_2), 55.8 (CH_3), 56.2 (CH_3), 62.2 (CH), 66.3 (CH), 74.6 (CH_2), 102.7 (CH), 114.7 (CH), 115.6 (CH), 119.7 (CH), 122.2 (C), 127.1 (CH), 127.6 (CH), 128.2 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 132.1 (C), 138.1 (C), 141.1 (C), 141.5 (C), 144.8 (C), 152.4 (C), 152.5 (C); MS (ES^+) *m*/*z* 467 (5, M^+ + H), 344 (100, M^+ − NHPMP), 253 (33%, $M^+ - C_{14}H_{15}NO$); HRMS $C_{30}H_{31}N_2O_3$ calcd 467.2315, found 467.2335.

1-((S)-2-((R*)-Cyclohexyl((4-methoxyphenyl)amino)methyl)-indolin-1-yl)-2,2,2-trifluoroethanone (**20**).* Formed as a byproduct during the synthesis of tetrahydroquinoline **18f**. Prepared using the general procedure for the preparation of 3-aminotetrahydroquinolines except with 10 mol % $Pd(PPh_3)_4$. β-Aminoacetamide **7f** (63 mg, 0.12 mmol) afforded crude indoline **20** as a pale brown oil. Purification by flash column chromatography (10% Et_2O/petroleum ether) yielded pure indoline **20** as a pale brown oil (10 mg, 15%): R_f 0.31 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3393, 3035−2853, 1677, 1509, 1249, 1229, 1200, 1179, 1144 cm^{-1}; ^1H NMR (400 MHz, C_6D_6, 90 °C) δ 1.10−1.37 (6H, m), 1.57−1.66 (4H, m), 1.87 (1H, d, *J* = 13.0), 2.52 (1H, d, *J* = 16.1), 2.76 (1H, dd, *J* = 16.1, 9.2), 3.40 (3H, s), 3.69 (1H, br s), 4.83 (1H, d, *J* = 8.6), 6.06 (2H, d, *J* = 8.4), 6.58 (2H, dm, *J* = 9.0), 6.83−6.89 (3H, m), 7.61 (1H, br s); ^1H $NMR^{rotamerA}$ (600 MHz, C_6D_6, 25 °C, 65:35 ratio of rotamers A:B) δ 0.71−1.65 (10H, m), 1.83 (1H, d, *J* = 12.5), 2.28 (1H, d, *J* = 16.0), 2.57 (1H, dd, *J* = 16.0, 9.1), 3.31 (3H, s), 3.51 (1H, d, *J* = 8.0), 4.69 (1H, d, *J* = 8.6), 5.99 (2H, d, *J* = 8.4), 6.61 (2H, d, *J* = 8.8), 6.70−6.87 (3H, m), 8.01 (1H, d, *J* = 7.2); ^1H $NMR^{rotamerB}$ (600 MHz, C_6D_6, 25 °C) δ 0.71−1.65 (10H, m), 1.87 (1H, br m), 2.25−2.27 (1H, m), 2.46−2.51 (1H, m), 3.35 (3H, s), 3.92 (1H, br s), 4.82 (1H, br s), 6.10 (2H, br s), 6.61 (2H, m), 6.70−6.87 (3H, m), 6.98−7.00 (1H, m); ^{13}C $NMR^{rotamerA}$ (151 MHz, C_6D_6, 25 °C) δ 26.3 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 29.3 (CH_2), 30.1 (CH_2), 30.6 (CH_2), 41.1 (CH), 55.2 (CH_3), 61.7 (CH), 63.7 (CH), 113.8 (CH), 115.0 (CH), 117.2 (1C, q, *J* = 288.4, C), 119.4 (CH), 123.1 (CH), 125.5 (CH), 127.5 (CH), 131.9 (C), 142.5 (C), 143.2 (C), 152.5 (C), 154.0 (1C, q, *J* = 36.6, C); ^{13}C $NMR^{rotamerB}$ (151 MHz, C_6D_6, 25 °C) δ 26.3 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 27.7 (CH_2), 30.0 (CH_2), 30.2 (CH_2), 40.6 (CH), 55.3 (CH_3), 58.9 (CH), 65.1 (CH), 113.8 (CH), 115.0 (CH), 115.8 (CH), 124.7 (CH), 125.1 (CH), 127.3 (CH), 133.6 (C), 140.0 (C), 152.5 (C), the remaining signals could not be determined; ^{19}F $NMR^{rotamerA}$ (282 MHz, C_6D_6, 25 °C) δ −69.5 (3F, s); ^{19}F $NMR^{rotamerB}$ (282 MHz, C_6D_6, 25 °C) δ −70.6 (3F, s); MS (CI) *m*/*z* 434 (26, $M^+ + H_2$), 433 (100, M^+ + H), 432 (16, M^+), 218 (15, $M^+ - C_{10}H_7F_3NO$); HRMS $C_{24}H_{28}F_3N_2O_2$ calcd 433.2103, found 433.2106.

2,2,2-Trifluoro-1-((S)-2-((R*)-1-((4-methoxyphenyl)amino)-2,2-dimethylpropyl)indolin-1-yl)ethanone (**21**).* Formed as a byproduct during the synthesis of tetrahydroquinoline **18g**. β-Aminoacetamide **7g** (94 mg, 0.19 mmol) afforded crude indoline **21** as a dark brown oil. Purification by flash column chromatography (10% EtOAc/petroleum ether) yielded pure indoline **21** as a pale brown oil (30 mg, 38%): R_f 0.38 (10% EtOAc/petroleum ether); IR ν_{max} (neat) 3410, 2957−2833, 1672, 1510, 1230, 1199, 1170, 1143 cm^{-1}; ^1H NMR (400 MHz, C_6D_6, 90 °C) δ 0.92 (9H, s), 2.69 (1H, dd, *J* = 16.2, 1.5), 2.81 (1H, dd, *J* = 16.2, 9.0), 3.38 (3H, s), 3.77 (1H, s), 4.99 (1H, d, *J* = 8.5), 6.05 (2H, br s), 6.53 (2H, dm, *J* = 9.0), 6.76−6.85 (3H, m), 7.45 (1H, br s); ^1H $NMR^{rotamerA}$ (600 MHz, C_6D_6, 25 °C, 55:45 ratio of rotamers A:B) δ 0.80 (9H, s), 2.59 (1H, d, *J* = 15.7), 2.66 (1H, dd, *J* = 16.1, 8.6), 3.30 (3H, s), 3.58 (1H, s), 4.82 (1H, d, *J* = 7.7), 5.99 (2H, d, *J* = 6.5), 6.55 (2H, d, *J* = 8.9), 6.66−6.81 (3H, m), 8.01 (1H, d, *J* = 6.5); ^1H $NMR^{rotamerB}$ (600 MHz, C_6D_6, 25 °C) δ 0.93 (9H, s), 2.46 (1H, d, *J* = 16.2), 2.56 (1H, dd, *J* = 16.4, 9.4), 3.32 (3H, s), 3.94 (1H, s), 4.94 (1H, d, *J* = 6.8), 6.03 (2H, br s), 6.55 (2H, d, *J* = 8.9), 6.66−6.81 (3H, m), 6.95 (1H, d, *J* = 7.7); ^{13}C $NMR^{rotamerA}$ (151 MHz, C_6D_6, 25 °C) δ 27.9 (CH_3), 30.9 (CH_2), 35.7 (C), 55.2 (CH_3), 61.5 (CH), 67.5 (CH), 114.0 (CH), 114.9 (CH), 117.1 (1C, q, *J* = 288.3, C), 119.5 (CH), 122.9 (CH), 125.6 (CH), 127.5 (CH), 132.0 (C), 139.6 (C), 142.9 (C), 152.7 (C), 154.1 (1C, q, *J* = 36.6, C); ^{13}C $NMR^{rotamerB}$ (151 MHz, C_6D_6, 25 °C) δ 27.8 (CH_3), 28.9 (CH_2), 35.7 (C), 55.3 (CH_3), 63.5 (CH), 64.4 (CH), 114.1 (CH), 114.9 (CH), 115.4 (CH), 116.9 (1C, q, *J* = 286.2, C), 124.5 (CH), 125.1 (CH), 127.3 (CH), 133.7 (C), 139.6 (C), 143.4 (C), 152.7 (C), 153.7 (1C, q, *J* = 39.1, C); ^{19}F $NMR^{rotamerA}$ (282 MHz, C_6D_6, 25 °C) δ −69.2 (3F, s); ^{19}F $NMR^{rotamerB}$ (282 MHz, C_6D_6, 25 °C) δ −70.8 (3F, s); MS (CI) *m*/*z* 407 (55, M^+ + H), 192 (100, $M^+ - C_{10}H_7F_3NO$); HRMS $C_{22}H_{26}F_3N_2O_2$ calcd 407.1946, found 407.1949.

(2R,3S*)-2-(2-Bromophenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-amine (**23**).* Prepared using the same procedure that was used for the preparation of 1,2-diamine **13**. Tetrahydroquinoline **18i** (82 mg, 0.16 mmol) afforded crude primary amine **23** as a pale brown solid. Purification by passing through a short plug of silica and eluting with EtOAc yielded pure primary amine **23** as an off-white solid (57 mg, 87%): R_f 0.19 (50% EtOAc/petroleum ether); IR ν_{max} (neat) 3363, 3062−2836, 1600, 1507, 1491, 1456, 1439, 1241, 1034, 1021 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.62 (1H, d, *J* = 16.3), 2.86 (1H, dd, *J* = 16.3, 3.8), 3.57 (1H, d, *J* = 2.3), 3.79 (3H, s), 4.92 (1H, s), 6.55 (1H, d, *J* = 8.3), 6.72 (1H, t, *J* = 7.3), 6.86 (2H, d, *J* = 8.8), 7.01 (1H, t, *J* = 7.6), 7.07 (1H, d, *J* = 7.3), 7.11 (1H, td, *J* = 7.4, 1.3), 7.13 (2H, d, *J* = 8.5), 7.25 (1H, t, *J* = 7.4), 7.45 (1H, dd, *J* = 7.8, 1.0), 7.51 (1H, d, *J* = 7.7); ^{13}C NMR (151 MHz, $CDCl_3$) δ 31.5 (CH_2), 46.7 (CH), 55.5 (CH_3), 71.2 (CH), 112.8 (CH), 115.1 (CH), 117.6 (CH), 117.7 (C), 122.4 (C), 127.4 (CH), 127.7 (CH), 128.7

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(CH), 128.9 (CH), 129.0 (CH), 130.9 (CH), 133.2 (CH), 139.5 (C), 141.7 (C), 144.4 (C), 157.5 (C); MS (EI) *m/z* 409 + 411 (1:1, 25, M^+ + H), 408 + 410 (1:1, 100, M^+); HRMS $C_{22}H_{21}(^{79}Br)N_2O$ calcd 408.0832, found 408.0836.

(5aR,10aS*)-5-(4-Methoxyphenyl)-5a,10,10a,11-tetrahydro-5H-indolo[3,2-b]quinoline (**22**).* Prepared using the same procedure that was used for the preparation of indoline **14a**. Primary amine **23** (52 mg, 0.13 mmol) afforded crude tetrahydroindoloquinoline **22** as a black oil. Purification by flash column chromatography (15% EtOAc/petroleum ether) yielded pure tetrahydroindoloquinoline **22** as an off-white solid (17 mg, 40%): mp 175−180 °C dec; R_f 0.49 (15% EtOAc/petroleum ether); IR ν_{max} (neat) 3351, 3052−2774, 1607, 1508, 1485, 1461, 1453, 1324, 1241, 1220, 1033 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.21 (1H, dd, *J* = 14.8, 4.9), 3.44 (1H, t, *J* = 13.4), 3.92 (3H, s), 4.05 (1H, td, *J* = 11.7, 4.9), 4.66 (1H, d, *J* = 11.2), 5.93 (1H, d, *J* = 7.6), 6.36 (1H, d, *J* = 8.3), 6.55 (1H, t, *J* = 7.5), 6.77 (1H, t, *J* = 7.3), 6.79 (1H, d, *J* = 8.5), 6.98 (1H, t, *J* = 7.7), 7.04−7.06 (3H, m), 7.15 (1H, d, *J* = 7.4), 7.30 (2H, d, *J* = 8.8); ^{13}C NMR (151 MHz, $CDCl_3$) δ 35.5 (CH_2), 55.6 (CH_3), 63.7 (CH), 66.3 (CH), 111.1 (CH), 115.1 (CH), 115.8 (CH), 118.7 (CH), 119.6 (CH), 121.3 (C), 124.7 (CH), 127.2 (CH), 128.0 (CH), 129.0 (C), 130.7 (CH), 131.3 (CH), 138.6 (C), 148.4 (C), 150.8 (C), 158.7 (C); MS (EI) *m/z* 329 (18, M^+ + H), 328 (100, M^+), 327 (34, M^+ − H); HRMS $C_{22}H_{20}N_2O$ calcd 328.1570, found 328.1568.

■ ASSOCIATED CONTENT

Supporting Information

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

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