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Preparation of Enantiomerically Pure Perfluorobutanesulfinamide and Its Application to the Asymmetric Synthesis of α-Amino Acids

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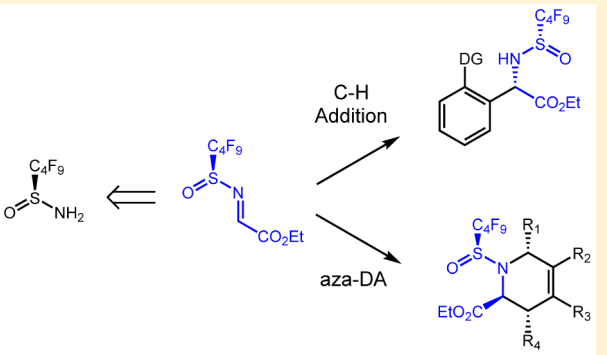
Supporting Information

ABSTRACT: A high yielding and practical two-step synthesis of enantiomerically pure perfluorobutanesulfinamide from Senanayake's 2-aminoindanol-derived sulfinyl transfer reagent was developed and carried out on a multigram scale. Straightforward condensation of this sulfinamide with ethyl glyoxylate provided the *N*-perfluorobutanesulfinyl imino ester. The utility of this activated *N*-sulfinyl imino ester was demonstrated for reactions that gave either no product or very low yields with the corresponding less electrophilic *N*-*tert*-butanesulfinyl derivative. Specifically, the Rh(III)-catalyzed C−H bond addition of aromatic compounds to the *N*-perfluorobutanesulfinyl imino ester provided arylglycines with very high diastereoselectivities for a range of directing groups including pyrrolidine amide, azo, sulfoximine, 1-pyrazole, and 1,2,3-triazole functionalities. Thermal asymmetric aza-Diels−Alder reactions also proceeded in good yields and with high selectivity, including for the substituted dienes (*E*)-1,3-pentadiene and (2*E*,4*E*)-2,4-hexadiene.



INTRODUCTION

α-Amino acids were one of the first classes of compounds to be targeted for asymmetric synthesis due to their pervasive biological roles,[1] and their asymmetric syntheses continue to be important to numerous drug discovery and chemical biology applications.[2] In this regard, *N*-*tert*-butanesulfinyl imino esters have proven to be extremely versatile intermediates for the asymmetric synthesis of α-amino acids.[3] The addition of a variety of organometallic reagents proceeds with high diastereoselectivities, including lithium,[4] magnesium,[5] indium,[6] and zinc[7] reagents, and through the use of transition-metal catalysts, also organoboron reagents.[8] Transition-metal catalysts have also been applied to the addition of allyl alcohols via isomerization pathways[9] and for the hydrogen-mediated reductive coupling of alkynes.[10] Stabilized anions such as enolates[11] and nitronate[12] anions also have been added with good selectivities. Moreover, Lewis acids have been employed to catalyze Friedel−Craft reactions with electron-rich aromatic[13] and heteroaromatic compounds,[14] Mannich-type additions of silyl enol ethers,[15] and aza-Diels−Alder cycloadditions with dienes.[16]

However, for some reactions of *N*-*tert*-butanesulfinyl imino esters, little to no conversion to the desired addition products was observed because the imines were not sufficiently electrophilic.[16a,17] In seminal work, Liu and co-workers have reported on the preparation of enantiomerically pure perfluoroalkanesulfinamides and on their conversion to *N*-perfluoroalkanesulfinyl aldimines. They have further shown that these more electrophilic imines can be effective substrates for the addition of a number of nucleophiles.[18]

Herein, we describe a practical two-step synthesis of perfluorobutanesulfinamide from Senanayake's 2-aminoindanol-derived sulfinyl transfer reagent in good overall yield and high enantiopurity.[19] Condensation with ethyl glyoxylate to provide the corresponding *N*-perfluorobutanesulfinyl imino ester is also described. We further report that the enhanced electrophilicity of this *N*-perfluorobutanesulfinyl imino ester enables transformations to be performed that are shown not to proceed with the corresponding *N*-*tert*-butanesulfinyl imino ester. Specifically, Rh(III)-catalyzed, highly diastereoselective addition of aromatic C−H bonds enables the asymmetric synthesis of arylglycines, a class of compounds present in many drugs including glycopeptide antibiotics such as vancomycin, many β-lactam antibiotics such as cefprozil, and the cardiovascular agent Plavix.[20] Moreover, the asymmetric synthesis of pipecolic acid derivatives has been accomplished by thermal aza-Diels−Alder cycloaddition reactions with substituted dienes, including those that have been reported to give low cycloaddition yields for the corresponding *N*-*tert*-butanesulfinyl imino ester.[16a] The pharmaceutical relevance of these aza-Diels−Alder reactions is highlighted by the AIDs drug Saquinavir and the blockbuster HCV drug Ledipasvir, each of which incorporates a pipecolic acid derivative.[20]

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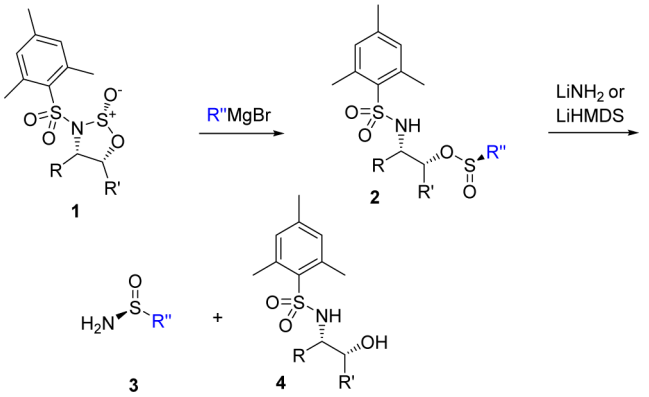
RESULTS AND DISCUSSION

An effective route to enantiomerically pure perfluoroalkanesulfinamides has been developed,[21] but significant quantities of material are difficult to access due to the multistep sequence that includes several purification steps. For this reason, we investigated alternative methods for the preparation of perfluorobutanesulfinamide. The most practical and by far the most extensively used method for the asymmetric synthesis of the more commonly used *tert*-butanesulfinamide is catalytic enantioselective oxidation of inexpensive *tert*-butyl disulfide, followed by addition of $LiNH_2$.[22] Unfortunately, this approach is not relevant to the synthesis of perfluoroalkanesulfinamides because the corresponding disulfides are not commercially available and are inconvenient to prepare. The chiral sulfinyl transfer auxiliary approach developed by Senanayake and coworkers is an alternative general and efficient method for the preparation of a broad range of enantiomerically pure sulfinamides (Scheme 1).[19] Addition of a Grignard reagent to

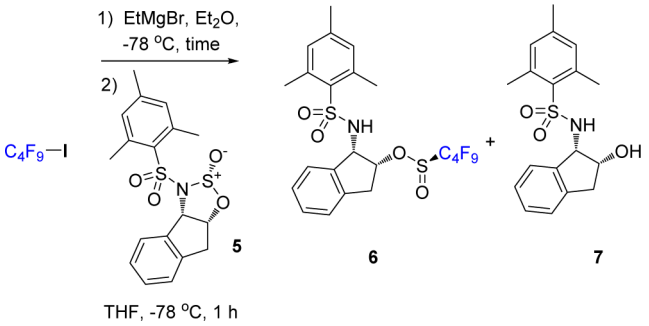
Scheme 1. Senanayake's Sulfinyl Transfer Approach



the sulfinyl transfer reagent **1** proceeds with inversion of stereochemistry to give sulfinate ester **2**. Treatment of **2** with an amide nucleophile then provides sulfinamide **3** and the chiral auxiliary **4**, which then can be recycled back to the sulfinyl transfer reagent **1** by reaction with thionyl chloride.

The key challenge to applying this approach to the perfluoroalkanesulfinamide is the well-documented instability of perfluoroalkyl Grignard reagents, which, unless maintained at low temperature, rapidly decompose through facile elimination of fluoride.[23] We, therefore, investigated the preparation and reaction of the perfluorobutyl Grignard reagent by transmetalation of perfluorobutyl iodide with ethylmagnesium bromide at −78 °C, followed by slow addition of a THF solution of the precooled 2-aminoindanol-derived sulfinyl transfer reagent **5** (Table 1). A slight excess of perfluorobutyl iodide relative to ethylmagnesium bromide was employed to prevent competitive formation of the undesired ethanesulfinate ester byproduct. Moreover, exactly 1 equiv of the Grignard reagent was used to prevent overaddition of the Grignard reagent to the desired sulfinate ester product **6**, which would give a sulfoxide byproduct. The duration of the transmetalation step was evaluated at both 30 and 60 min (entries 1 and 2), with 60 min providing the highest yield (entry 2). To minimize reagent waste, the stoichiometry of the perfluorobutyl iodide was lowered to 1.05 equiv without any reduction in yield (entry 3). Additionally, the reaction can be conducted at a higher concentration, which is preferable when performed on larger

Table 1. Addition of Perfluorobutyl Grignard Reagent[a]



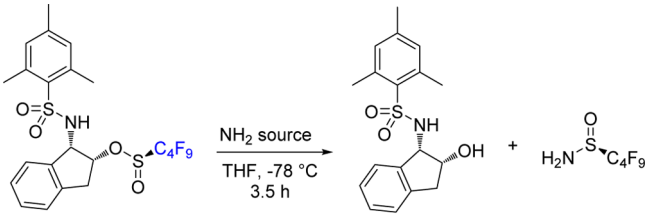
entry	C_4F_9I (equiv)	EtMgBr (equiv)	time (min)	concn **5** (M)	**6** (%)	**7** (%)
1	1.1	1.0	30	0.13	79	3
2	1.1	1.0	60	0.13	89	5
3	1.05	1.0	60	0.13	88	3
4	1.05	1.0	60	0.30	90	2

[a]Yields of **6** and **7** determined by ^{1}H NMR integration relative to 2,6-dimethoxytoluene as an external standard.

scales (entry 4). The solubility of sulfinyl transfer reagent **5** prevented a concentration higher than 0.3 M from being used. The only observed impurity was a small amount of byproduct **7**, which has no detrimental effects on the subsequent step of the synthesis (vide infra). Therefore, the crude material obtained after extractive isolation was employed in the next step without further purification.

Various amine nucleophiles were next evaluated for cleavage of **6** to provide the sulfinamide product **8** (Table 2). Initially, we speculated that the electron-withdrawing perfluorobutyl group might render sulfinate ester **6** sufficiently reactive for cleavage with the most practical and inexpensive source of ammonia, ammonium hydroxide. However, when **6** was treated with excess ammonium hydroxide, either neat or with THF as a

Table 2. Sulfinate Ester Cleavage[a]



entry	NH_2 source	conc **6** (M)	**8** (%)[a]
1[b]	$NH_4OH_{(aq)}$ (excess)	0.05	0
2[c]	$NH_4OH_{(aq)}$ (excess)	0.05	0
3[d]	LiHMDS (5 equiv)	0.10	59
4[d]	LiHMDS (2 equiv)	0.10	41
5[d]	LiHMDS (3 equiv)	0.10	48
6[d]	NaHMDS (5 equiv)	0.10	73
7[d]	NaHMDS (3 equiv)	0.10	74
8[d]	KHMDS (3 equiv)	0.10	59
9[d]	NaHMDS (3 equiv)	0.30	73

[a]Isolated yields after column chromatography. [b]Neat or with THF as solvent at rt for 24 h. [c]Neat NH_4OH with heating in a pressure tube at 110 °C for 3 h. [d]Workup by treatment with aqueous NH_4Cl to cleave the *N*-TMS substituents from the initial addition product.

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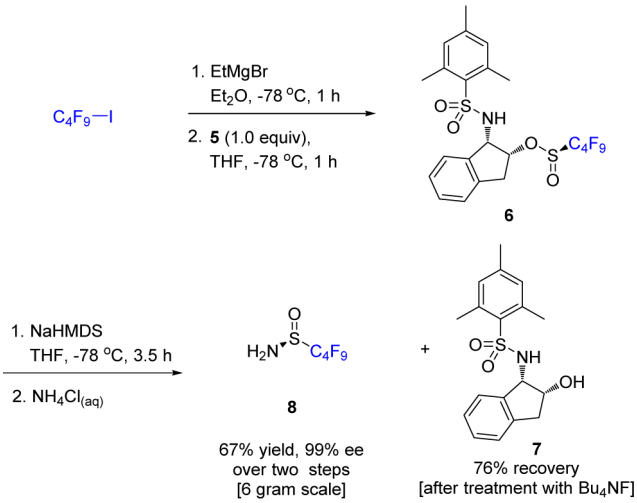
cosolvent, no reaction was observed at rt (entry 1). While complete consumption of the sulfinate ester **6** could be achieved by heating in a sealed tube, and though the alcohol byproduct **7** was detected, none of the desired sulfinamide **8** was observed (entry 2). The absence of sulfinamide **8** could in part be due to preferential saponification of **6** under the reaction conditions. However, control experiments also established that **8** was not stable to concentrated NH_4OH even at rt. LiHMDS, one of the most commonly used nucleophiles for sulfinate ester cleavage,[19] was next investigated. Addition of 5 equiv of LiHMDS provided sulfinamide **8** in 59% yield after chromatography (entry 3). Only 2 equiv of base is required, 1 equiv to serve as a nucleophile and the second equivalent to deprotonate the sulfonamide group in **6**. Unfortunately, attempts to reduce the amount of LiHMDS to either 2.0 or 3.0 equiv led to diminished yields (entries 4 and 5, respectively). In contrast, addition of 5 equiv of NaHMDS in place of LiHMDS resulted in a higher yield of **8** (entry 6). Furthermore, decreasing the amount of NaHMDS to 3.0 equiv did not significantly affect the reaction yield (entry 7). Because at least 2 equiv of this strong base is needed, further reduction in the number of equivalents of base was not investigated. The more costly KHMDS also gave a slightly lower yield than NaHMDS under identical reaction conditions (entry 8). Finally, addition of NaHMDS at triple the reaction concentration provided pure sulfinamide **8** in the same yield as observed at the lower concentration (entry 9).

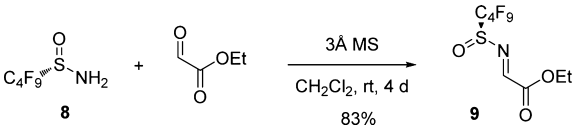
With optimal conditions identified for the preparation and cleavage of sulfinate ester **6**, perfluorobutanesulfinamide (**8**) was next prepared on a multigram scale from sulfinyl transfer reagent **5** in a two-step sequence (Scheme 2). Sulfinamide **8**

Scheme 2. A Practical Asymmetric Synthesis of Perfluorobutanesulfinamide



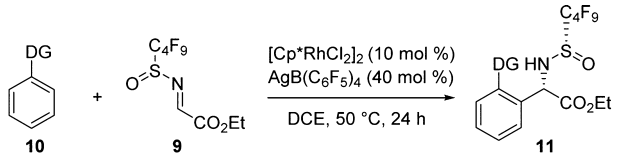
was isolated in 67% overall yield for the two steps with the sole purification being straightforward chromatographic separation from the byproduct **7** and its *O*-TMS ether. Importantly, sulfinamide **8** was obtained in 99% ee as determined by chiral HPLC analysis. Chiral auxiliary **7** also can be recovered in pure form in 76% overall yield from **5** by treating the mixture of **7** and its silyl ether with Bu_4NF, followed by extractive isolation and recrystallization.

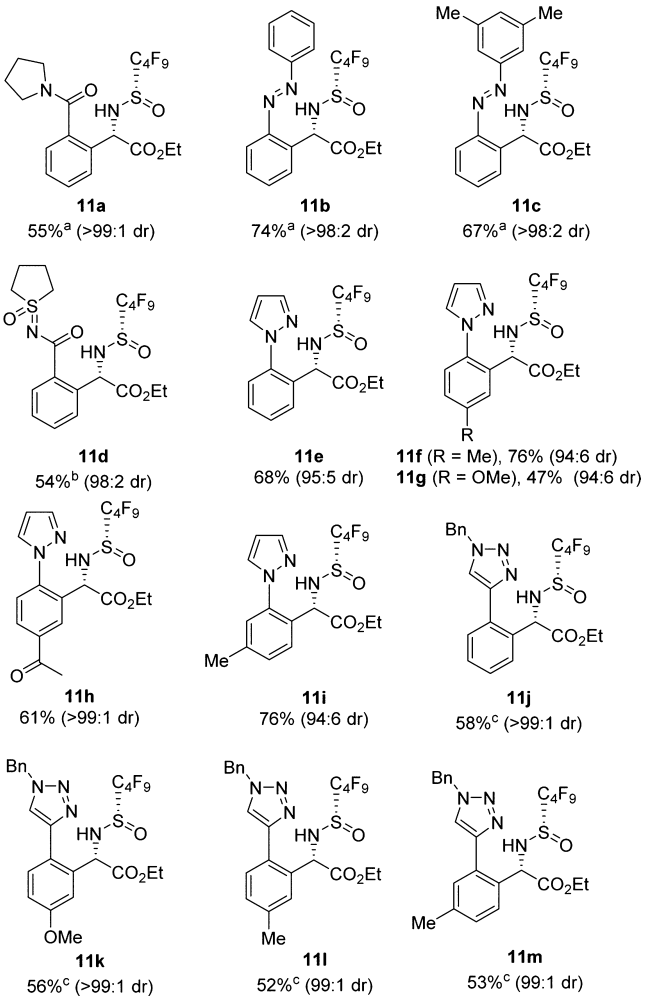
We next focused on the preparation of *N*-perfluorobutanesulfinyl imino ester **9** as a versatile intermediate for the asymmetric synthesis of α-amino acids. Condensation of **8** with ethyl glyoxylate was performed with molecular sieves as the dehydrating reagent (eq 1). Although *N*-sulfinyl imino ester **9** is not stable to column chromatography, it is sufficiently pure that it can be directly used in subsequent reactions after filtration to remove the sieves, followed by concentration.



Recently, we reported on the first asymmetric addition of C–H bonds to *N*-perfluorobutanesulfinyl imines.[17a] This study included the asymmetric syntheses of the three arylglycines **11a–c** by Rh(III)-catalyzed C–H bond addition to perfluorobutanesulfinyl imine **9** (Table 3). Here, an expanded set of

Table 3. Asymmetric Synthesis of Arylglycines





[a]Conditions: in DCE (0.75 M) for 48 h. [b]Conditions: **10** (0.225 mmol), **9** (0.150 mmol) in DCE (0.75 M) at room temperature for 24 h. [c]Conditions: AgOAc (20 mol %) was added to the reaction mixture.

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directing groups and compatibility with different functionalities and substitution patterns has been demonstrated (**11d**–**11m**). All Rh(III)-catalyzed C–H bond additions were performed at ≤60 °C because rapid decomposition of perfluorobutanesulfinyl imino ester **9** occurs at higher temperatures. A number of directing groups proved to be effective for this reaction. In addition to the previously reported benzamide (**11a**) and azo (**11b** and **c**) directing groups, sulfoximine (**11d**), pyrazoles (**11e**–**i**), and 1,2,3-triazoles (**11j**–**m**) also were shown to be effective. Good scope was also observed for substitution on the arene ring with an electron-deficient and reactive keto functionality (**11h**) and electron-donating groups (**11f**, **11g**, **11i**, and **11k**–**11m**). The desired products were obtained in moderate to good yield and, in all cases, with excellent diastereoselectivities, as rigorously determined by HPLC analysis using an authentic mixture of diastereomer standards.[24]

The absolute configuration of **11a** was established by X-ray structure determination of its 4-chlorobenzamide derivative. The stereochemistry of all of the other addition products **11** was assigned by analogy. The sense of induction is consistent with the stereochemical model that we reported for C–H bond addition to aromatic imines (Figure 1). Enantiomeric rhodacycles **A** and **B** are based upon the X-ray structures of corresponding cationic rhodacycles derived from 2-phenylpyridine.[25,26] The observed sense of induction is obtained if the reaction occurs through **C** with the C_4F_9 substituent pointing away from the reaction center. This model is consistent with prior mechanistic studies on the addition of 2-phenylpyridine to *N*-sulfonyl and *N*-carbamoyl imines.[27] The high diastereoselectivity requires equilibration between enantiomeric rhodacycles **A** and **B** either before or after coordination of *N*-sulfinyl iminoester **9**.

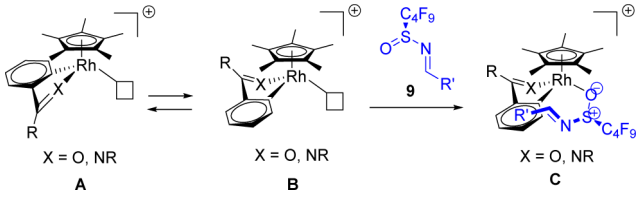
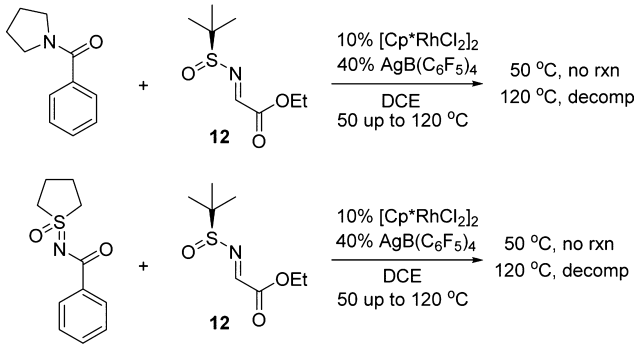


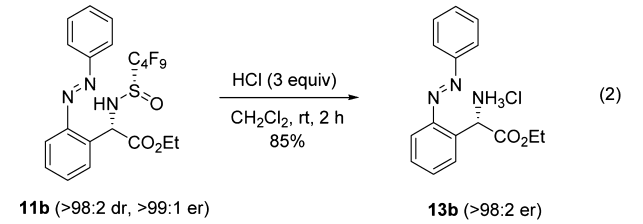
Figure 1. Stereochemical model consistent with sense of induction.

We and others had previously reported that Rh(III)-catalyzed C–H bond additions to *N*-*tert*-butanesulfinyl benzaldimine were unsuccessful,[17] in contrast to the additions to the corresponding *N*-perfluorobutanesulfinyl derivative.[17a] However, because the carboxy group of *N*-sulfinyl imino esters activates the imine for addition, as a further control, we now also have evaluated Rh(III)-catalyzed C–H bond additions to *tert*-butanesulfinyl imino ester **12** (Scheme 3). The desired addition products were not obtained for either the amide or sulfoximine directing groups. At 50 °C, no reaction was observed, and upon incremental heating up to 120 °C, only decomposition occurred.

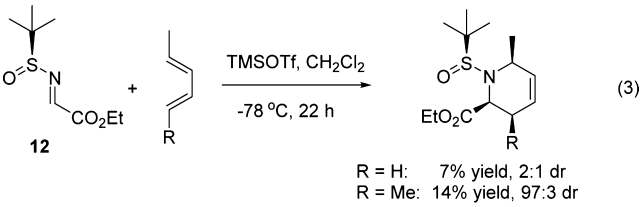
As shown in eq 2, the *N*-perfluorobutanesulfinyl group readily can be cleaved by treatment with HCl in CH_2Cl_2 at rt to provide the hydrochloride salt **13b** in high yield and without any loss in stereochemical purity.[17a]

Scheme 3. Attempted C–H Additions to *N*-*tert*-Butanesulfinyl Imino Ester 12





Gautun and co-workers have previously reported highly diastereoselective aza-Diels–Alder reaction of *tert*-butanesulfinyl imino ester **12** with dienes with TMSOTf as a Lewis acid catalyst.[16] While cycloaddition with unhindered dienes proceeded in high yields and with high selectivity, for more hindered diene substrates, the aza-Diels–Alder products were obtained in very low yields (eq 3).



The synthetic utility of *N*-perfluorobutanesulfinyl imino ester **9** was, therefore, evaluated for aza-Diels–Alder reactions (Table 4). When TMSOTf or $BF_3{\cdot}Et_2O$ was employed as Lewis acid for cycloaddition of **9** with 2-methylbutadiene (**14a**) under the conditions previously reported for the aza-Diels–Alder reaction of *N*-*tert*-butanesulfinyl imino ester **12**,[16] no desired product was obtained due to the rapid decomposition of **9** (entries 1 and 2, respectively). However, when the reaction solution was heated to 50 °C without a Lewis acid catalyst, good conversion to the desired cycloaddition product **15a** was observed (entry 3). The higher boiling point solvent 1,2-dichloroethane (DCE) resulted in higher conversion (entry 4), and increasing the reaction concentration of **9** to 1.0 M led to a higher yield of **15a** with almost complete consumption of starting material **9** (entry 5). Increasing the temperature above 50 °C resulted in a lower yield due to competitive decomposition of imino ester **9** (entry 6). The reaction also proceeded at 2.0 M (entry 7) and even without solvent (entry 8).

The thermal aza-Diels–Alder reaction of the corresponding *N*-*tert*-butanesulfinyl imino ester **12** was also evaluated for comparison purposes (eq 4). At 50 °C, no reaction occurred, and incremental heating up to 120 °C only resulted in the decomposition of imine **12**.

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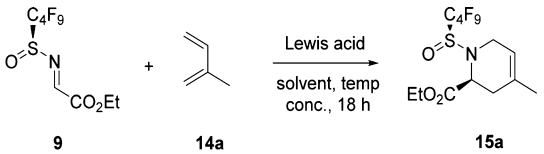
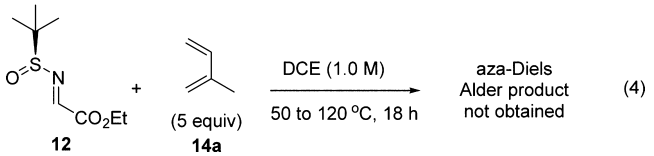
Table 4. Optimization of Aza-Diels-Alder Reaction[a]



9 14a 15a

entry	14a (equiv)	Lewis acid	solv	temp (°C)	conc (M)	15a (%)	9 (%)
1	20	TMSOTf[b]	CH_2Cl_2	−78	0.13	0	0
2	5	$BF_3{\cdot}Et_2O$[c]	CH_2Cl_2	0	0.13	0	7
3	5		CH_2Cl_2	50	0.25	44	13
4	5		DCE	50	0.25	61	11
5	5		DCE	50	1.0	76	3
6	5		DCE	75	1.0	69	0
7	5		DCE	50	2.0	70	2
8	5			50	neat	74	1

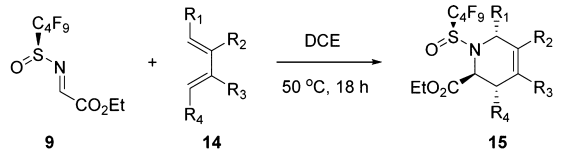
[a]Determined by ^{1}H NMR analysis relative to 2,6-dimethoxytoluene as an external standard. [b]10 equiv of TMSOTF was used. [c]1 equiv of TMSOTf was used.



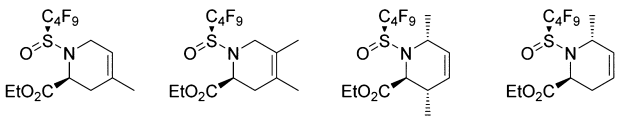
12 14a (4)

The thermal aza-Diels−Alder reaction of the *N*-perfluorobutanesulfinyl imino ester **9** was next evaluated for several dienes (Table 5). For the reactive dienes 2-methylbutadiene

Table 5. Scope of Aza-Diels-Alder Reaction



9 14 15



15a	15b	15c	15d
81%	71%	69%	65%
(>98:2 dr)	(>98:2 dr)	(10:1 exo/endo)	(8:1 exo/endo)

and 2,3-dimethylbutadiene, the aza-Diels−Alder products **15a** and **15b** were obtained in high yields and with very high diastereoselectivity. However, it should be noted that, for these dienes, the TMSOTF catalyzed aza-Diels−Alder reaction with *tert*-butanesulfinyl imino ester **12** had previously been shown to be efficient.[16] Much more significantly, the reaction also proceeded in good yields and selectivity for the less reactive dienes (*E*)-1,3-pentadiene and (2*E*,4*E*)-2,4-hexadiene to give **15c** and **15d**. For these dienes, Lewis acid catalyzed addition to *tert*-butanesulfinyl imino ester **12** had previously been shown to proceed in very low yields (see eq 3).[16a] The absolute configuration of the pipecolic acid derivative **15d** was rigorously determined by X-ray crystal structure analysis, and the remainder of the products were assigned by analogy.

CONCLUSIONS

In conclusion, a high yielding and practical two-step synthesis of enantiomerically pure perfluorobutanesulfinamide from Senanayake's 2-aminoindanol-derived sulfinyl transfer reagent was developed and carried out on a multigram scale. Straightforward preparation of the *N*-perfluorobutanesulfinyl imine from ethyl glyoxylate also proceeded cleanly and in high yield. The enhanced reactivity of the *N*-perfluorobutanesulfinyl imino ester allowed for the Rh(III)-catalyzed addition of aryl C−H bonds using a wide range of directing groups to provide arylglycines in moderate to good yields and with high diastereoselectivity. We further demonstrated the utility of the *N*-perfluorobutanesulfinyl imino ester for the asymmetric synthesis of pipecolic acid derivatives via aza-Diels−Alder reaction. We anticipate that *N*-perfluorobutanesulfinyl imino esters may prove effective when the corresponding less electrophilic *N*-*tert*-butanesulfinyl imino esters are determined to have insufficient reactivity.

EXPERIMENTAL SECTION

General Information. Unless noted, all catalytic reactions were set up inside a nitrogen-filled glovebox using oven-dried (150 °C) glassware that was evacuated hot prior to use. Unless otherwise indicated, all reagents and starting materials were obtained from commercial suppliers and used without further purification. Heating in addition to workup and isolation of the products of the reactions were performed on the benchtop using standard techniques. Tetrahydrofuran and diethyl ether were purified by passage through activated alumina using a solvent purification system. $[Cp^*RhCl_2]_2$,[28] $AgB(C_6F_5)_4$,[29] benzoylpyrrolidine,[30] azobenzenes,[31] sulfoximine,[32] *N*-aryl-1*H*-pyrazoles,[33] and 1-benzyl-4-phenyl-1*H*-1,2,3-triazoles[34] were synthesized according to published procedures. 1,2-Dichloroethane (DCE) was deoxygenated by sparging with nitrogen gas, followed by storage over activated 3 Å molecular sieves for 48 h prior to use. Ethylmagnesium bromide was titrated[35] before use, and the oxathiazolidine oxide chiral sulfinyl transfer auxiliary (**5**) was prepared according to a published procedure.[36] Ethyl glyoxylate was prepared following a published procedure.[37] Flash column chromatography was performed with 230−400 mesh silica gel. The products were visualized on TLC by either UV or staining with $KMnO_4$. Normal phase chromatography was performed on 230−240 mesh silica gel or preparative thin-layer chromatography plates (1 mm SiO_2, 20 × 20 cm). Reverse phase chromatography was performed with C18 columns using an automated purification system. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR characterization data were collected at ambient temperature, and chemical shifts are reported in parts per million relative to $CDCl_3$ (^{1}H NMR; 7.26 ppm, ^{13}C{^{1}H} NMR; 77.16 ppm) or MeOD (^{1}H NMR; pentet, 3.31 ppm). Only partial data are provided for IR spectra. Melting points are reported uncorrected. High-resolution mass spectra

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(HRMS) were obtained using electrospray ionization (ESI) on a time-of-flight (TOF) mass spectrometer. Enantiomeric excess and diastereomeric ratio were determined using an HPLC (1.0 mL/min flow rate) equipped with a multiwavelength detector and a Chiralpak IB column or an Microsorb 100−5 Si 250 × 4.6 mm silica column, respectively.

(1*S*,2*R*)-1-(2,4,6-Trimethylbenzenesulfonamido)-2,3-dihydro-1*H*-inden-2-yl-(*S*)-nonafluorobutane-1-sulfinate (6). A flame-dried, 250 mL, three-neck round-bottom flask cooled under nitrogen was equipped with a magnetic stir bar and rubber septa. The flask was flushed with nitrogen for 10 min and then charged with diethyl ether (48 mL) before it was cooled to −78 °C using a dry ice−acetone bath. The flask was then charged with nonafluoro-1-iodobutane (5.74 mL, 33.4 mmol, 1.05 equiv) before ethylmagnesium bromide (12.0 mL, 2.65 M in ether, 31.8 mmol, 1.00 equiv) was added dropwise with stirring via syringe over 5 min. After the addition, the flask was covered with aluminum foil to protect it from light, and the Grignard mixture was stirred for 1 h at −78 °C. While the Grignard mixture was being stirred, a separate one-neck oven-dried, 100 mL, round-bottom flask was charged with oxathiazolidine oxide[36] (12.0 g, 31.8 mmol, 1.00 equiv) and 45 mL of anhydrous THF, and the resulting mixture was heated to 50 °C until complete dissolution had occurred. The resulting THF solution was cooled to −78 °C with a dry ice−acetone bath before it was transferred via cannula to the 250 mL flask containing the Grignard reagent (1 h after ethylmagnesium bromide addition). The resulting reaction mixture in the 250 mL flask was stirred at −78 °C for 1 h before the reaction was quenched by addition of 15.5 mL of 4.1 M acetic acid in THF (2 equiv) over 5 min. The solution was allowed to warm to rt over ∼30 min, and then the mixture was transferred to a separatory funnel. Additional deionized water (60 mL) was added, and the aqueous layer was separated and extracted with ethyl acetate (3 × 30 mL). The combined organic layer was shaken with saturated aqueous $Na_2S_2O_3$ solution (30 mL) until the orange color disappeared. The organic layer was then washed with brine (30 mL), dried over sodium sulfate, and concentrated to dryness under reduced pressure to afford crude product **6** (17.3 g, 91% yield) as an off-white solid. The crude product was determined to be of sufficient purity by ^{1}H NMR and was used directly in the subsequent step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.26 (m, 1H), 7.24−7.20 (m, 2H), 7.18−7.14 (m, 1H), 7.01 (s, 2H), 5.26−5.20 (m, 2H), 5.00 (dd, J = 10.5, 4.3 Hz, 1H), 3.27−3.09 (m, 2H), 2.73 (s, 6H), 2.32 (s, 3H).

(*S*)-Perfluorobutanesulfinamide (8). To a flame-dried three-neck, 250 mL, indented style (Morton) round-bottom flask equipped with a magnetic stir bar and cooled under nitrogen was added 17.3 g of crude perfluorobutanesulfinate ester **6**. The flask was then fitted with an oven-dried, 125 mL addition funnel and rubber septa before flushing with nitrogen for 10 min. Anhydrous THF (53 mL) was then added via syringe with stirring until all the solids had dissolved to give a clear solution. The solution of **7** in THF was cooled to −78 °C using a dry ice−acetone bath before 43.4 mL (86.9 mmol, 3 equiv assuming that crude **6** was 100% pure) of a 2.0 M solution of NaHMDS in THF was added dropwise via an addition funnel over 10 min. The resulting reaction mixture was stirred for 3.5 h at −78 °C before it was quenched by dropwise addition of a saturated aqueous NH_4Cl solution (50 mL). After allowing it to warm to rt over ∼30 min, the biphasic mixture was stirred at room temperature for 16 h before being transferred to a separatory funnel. The aqueous layer was separated and extracted with ethyl acetate (3 × 30 mL). The combined organic layer was washed with brine (30 mL), dried over sodium sulfate, and concentrated under reduced pressure to afford a dark red-brown oil. Purification by flash column chromatography with 10% MTBE in CH_2Cl_2 as eluent (**8** has an R_f value of 0.31) afforded the product **8** (6.0 g, 67% yield over two steps) as an off-white solid that was determined to be of >99% ee as determined by chiral HPLC analysis (Chiralpak IB, EtOH/hexanes 10:90, 1.0 mL/min. 230 nm) of **8**: t_R = 7.4 min (*S*) and 11.4 min (*R*); mp 73−75 °C [lit. 64−66 °C].[18d] The analytical data for this compound are consistent with previously reported data.[18d] IR (film): 3349, 1264, 1205, 1136, 1021, 731, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 119.4−107.7 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.82 (tt, J = 9.8, 2.3 Hz, 3F), −121.43 to −121.72 (m, 2F), −121.08 to −122.05 (m, 1F), −122.50 to −123.32 (m, 1F), −126.12 to −126.25 (m, 2F); $[\alpha]_D^{20}$ = −16.2 (c 0.46, CH_3OH); Anal. Calcd for $C_4H_2F_9NOS$: C, 16.97; H, 0.71; N, 4.95. Found: C, 17.09; H, 0.71; N, 5.34.

Recovery of *N*-((1*S*,2*R*)-2-Hydroxy-2,3-dihydro-1*H*-inden-1-yl)-2,4,6-trimethylbenzenesulfonamide (7). From the column chromatography purification of **8**, fractions that contain **7** (R_f = 0.59, 10% MTBE in CH_2Cl_2) or its *O*-TMS ether (R_f = 0.90, 10% MTBE in CH_2Cl_2) were combined and concentrated to give 12.0 g of a dark red-brown oil. The material was transferred to a one-neck, 250 mL, round-bottom flask using 100 mL of THF to solubilize the material and assist with transfer. To the stirred solution at ambient temperature was then added 30 mL of 1 M TBAF solution in THF. After being stirred at ambient temperature for 1 h, the mixture was transferred to a 250 mL separatory funnel. Additional ethyl acetate (50 mL) and deionized water (50 mL) were used to assist transfer. The aqueous layer was separated and further extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with deionized water (2 × 30 mL) and saturated aqueous NaCl solution (30 mL) and then dried over sodium sulfate. The drying agent was removed by vacuum filtration, and the filtrate was concentrated to dryness on a rotary evaporator before it was triturated with 50 mL of hexanes and vacuum filtered through a Buchner funnel equipped with a filter paper to afford 10.0 g of a light brown solid material, which was diluted with 40 mL of ethyl acetate in a 250 mL Erlenmeyer flask. The mixture was heated to 50 °C with swirling to dissolve all the material, and then 80 mL of hexanes was layered on top and the flask was covered with aluminum foil. The flask was stored at −20 °C overnight (16 h). The crystalline product was isolated by vacuum filtration using a Buchner funnel equipped with a filter paper. The crystalline solid was crushed to powder using a porcelain mortar and pestle before it is dried under high vacuum to provide 8.0 g (76% recovery from **5**) of **7** as an off-white solid; mp 148−150 °C [lit. 149−150 °C].[36] The analytical data for this compound are consistent with previously reported data.[36] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.10 (m, 4H), 7.01 (s, 2H), 5.33 (d, J = 9.5 Hz, 1H), 4.63 (dd, J = 9.5, 4.8 Hz, 1H), 4.44−4.39 (m, 1H), 3.09 (dd, J = 16.8, 5.1 Hz, 1H), 2.92 (d, J = 16.5 Hz, 1H), 2.72 (s, 6H), 2.33 (s, 3H), 2.17 (d, J = 4.9 Hz, 1H).

(*S*,*E*)-Ethyl-2-(((perfluorobutyl)sulfinyl)imino)acetate (9). To a 20 mL screw-top scintillation vial equipped with magnetic stir bar and flushed with nitrogen was weighed out distilled ethyl glyoxylate (108.2 mg, 1.06 mmol, 1.0 equiv) before addition of anhydrous CH_2Cl_2 (3.5 mL, [sulfinyl imino ester] = 0.30 M). To the solution were added 3 Å molecular sieves and (*S*)-nonafluorobutanesulfinamide (300 mg, 1.06 mmol, 1.0 equiv) before the vial was capped. The resulting mixture was stirred at room temperature over 4 days with the reaction conversion monitored by ^{1}H NMR. After complete conversion was observed, the resulting mixture was filtered through a fine glass frit funnel to remove the molecular sieves and the flask and funnel were washed with additional CH_2Cl_2. The combined filtrate was concentrated under reduced pressure to give crude product **9** (322 mg, 83% yield) as a clear yellow-orange liquid which was of sufficient purity to be used in subsequent transformations. The analytical data for this compound are consistent with previously reported data.[17a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H).

General Procedure for Synthesis of 1-Benzyl-4-Aryl-1*H*-1,2,3-Triazoles. The following procedure was adapted from the literature.[34a] In a 20 mL scintillation vial equipped with a magnetic stir bar was added the indicated benzyl bromide (4.40 mmol, 1.1 equiv) to a stirred solution of DMF−H_2O (10 mL; 4:1). Following this, $CuSO_4$·$5H_2O$ (499 mg, 2.00 mmol, 0.5 equiv), sodium azide (312 mg, 4.80 mmol, 1.2 equiv), L-ascorbic acid (705 mg, 4.00 mmol, 1.0 equiv), and sodium carbonate (424 mg, 4.00 mmol, 1.0 equiv) were added. After the solution was stirred for 5 min, the indicated ethynylarene was added (4.00 mmol, 1.0 equiv), and the reaction mixture was stirred at ambient temperature for 16 h. The reaction mixture was transferred to a stirred 0.1 M solution of EDTA (disodium salt, dihydrate) in DI

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water (100 mL), followed by the addition of 100 mL of NH_4OH (28−30% *v*/*v*). The resulting mixture was then stirred vigorously at 1200 rpm for 30 min before being diluted with CH_2Cl_2 (200 mL) and transferred to a separatory funnel. The mixture was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic layers were washed with DI water (50 mL) and brine (50 mL), dried with $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography with EtOAc/hexanes afforded the 1-benzyl-4-aryl-1*H*-1,2,3-triazole.

*1-Benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (**10k**).* The general procedure was followed with benzyl bromide (753 mg, 4.40 mmol, 1.1 equiv) and 4-ethynylanisole (529 mg, 4.00 mmol, 1.0 equiv). Purification by flash column chromatography (10−30% EtOAc in hexanes gradient) afforded the product (**10k**) (729 mg, 69% yield) as an off-white solid. mp: 142−143 °C [lit.[34b] 141−142 °C]. The analytical data for this compound are consistent with previously reported data.[34b]

*1-Benzyl-4-(p-tolyl)-1H-1,2,3-triazole (**10l**).* The general procedure was followed with benzyl bromide (753 mg, 4.40 mmol, 1.1 equiv) and 4-ethynyltoluene (465 mg, 4.00 mmol, 1.0 equiv). Purification by flash column chromatography (10−20% EtOAc in hexanes gradient) afforded the product (893 mg, 90% yield) as a white solid. mp: 152−154 °C [lit.[34b] 150−152 °C]. The analytical data for this compound are consistent with previously reported data.[34b]

*1-Benzyl-4-(m-tolyl)-1H-1,2,3-triazole (**10m**).* The general procedure was followed with benzyl bromide (753 mg, 4.40 mmol, 1.1 equiv) and 3-ethynyltoluene (465 mg, 4.00 mmol, 1.0 equiv). Purification by flash column chromatography (10−25% EtOAc in hexanes gradient) afforded the product (758 mg, 76% yield) as a white solid. 146−147 °C [lit.[34c] 144−146 °C]. The analytical data for this compound are consistent with previously reported data.[34c]

Synthesis and Characterization of Arylglycines 11a−11c. Synthetic procedures, full analytical characterization, and NMR spectra were previously reported for arylglycines **11a−c**.[17a]

*Ethyl (S)-2-(4-Chlorobenzamido)-2-(2-(pyrrolidine-1-carbonyl)-phenyl)acetate (**11a-amide**).* To a flame-dried, 1 dram vial equipped with a magnetic stir bar was added **11a** (60 mg, 0.11 mmol, 1 equiv). Anhydrous CH_2Cl_2 (1 mL) was added, and the solution was cooled to 0 °C with an ice bath, followed by dropwise addition of 4 M HCl in dioxane (0.14 mL, 0.55 mmol, 5 equiv). The mixture was stirred at 0 °C for 2 h and then concentrated to dryness under reduced pressure. The resulting solid residue was dissolved in anhydrous CH_2Cl_2 (1 mL), and Et_3N (0.038 mL, 0.28 mmol, 2.5 equiv) was added. After cooling the mixture to 0 °C with an ice bath, a solution of benzoyl chloride (20.3 mg, 0.12 mmol, 1.05 equiv) in anhydrous CH_2Cl_2 (1 mL) was added slowly dropwise. The reaction mixture was warmed up slowly to room temperature and stirred for 2 h before concentrating to dryness under reduced pressure. Purification by flash column chromatography (50% EtOAc in hexanes) afforded the product **11a-amide** (39.5 mg, 86% yield) as an off-white solid; mp 118−120 °C. IR (film): 3286, 1743, 1660, 1614, 1594, 1521, 1479, 1432, 1338, 1320, 1206, 1180, 1091, 1014, 847, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 7.4 Hz, 1H), 7.45−7.31 (m, 5H), 6.02 (d, J = 8.8 Hz, 1H), 4.24−4.02 (m, 2H), 3.64−3.53 (m, 2H), 3.38−3.29 (m, 1H), 3.26−3.19 (m, 1H), 2.02−1.77 (m, 4H), 1.22 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 170.5, 165.3, 137.9, 136.0, 134.7, 132.3, 132.0, 130.4, 129.0, 128.8, 128.3, 127.7, 61.9, 56.9, 49.7, 46.2, 26.3, 24.7, 14.3; $[\alpha]_D^{20}$ = +39.0 (*c* 0.32, CH_3OH); HRMS (ESI/$[M + H]^+$) calcd. for $C_{22}H_{23}ClN_2O_4$: 415.1419. Found 415.1390.

X-ray quality crystals of the **11a-amide** were obtained according to the following procedure: In a flame-dried, 1 dram vial, 10 mg of **11a-amide** was dissolved in 1.0 mL of Et_2O with heating. The 1 dram vial containing the solution of **11a-amide** in Et_2O was placed inside a 20 mL scintillation vial filled with 5 mL of pentane. The scintillation vial was sealed and allowed to sit at room temperature for 2 days, after which single crystals formed.

Procedure for Synthesis of Ethyl (*S*)-2-(2-((1-Oxidotetrahydrothiophen-1-ylidene)carbamoyl)phenyl)-2-(((*S*)-(perfluorobutyl)sulfinyl)amino)acetate (11d). In a N_2-filled glovebox, perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) was weighed out into a 1 mL conical screw-capped vial, followed by benzoylsulfoximine **10d** (50.2 mg, 0.225 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol, 10 mol %), and $AgB(C_6F_5)_4(Et_2O)_2$ (56.1 mg, 0.06 mmol, 40 mol %). To this mixture were added DCE (0.200 mL, [sulfinyl imine] = 0.750 M) and a triangular magnetic stir bar before the vial was sealed with a cap containing a PTFE septum and was removed from the glovebox. The reaction mixture was stirred at ambient temperature for 24 h before it was filtered through a plug of Celite in a pipet with CH_2Cl_2 (4 mL). The filtrate was then concentrated and subjected to purification by flash column chromatography on silica gel to afford the product **11d** (45.1 mg, 55% yield) as a yellow oil. IR (film): 1739, 1612, 1595, 1573, 1309, 1196, 1093, 746, 723, 692 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 5.66 (d, J = 7.4 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.81−3.73 (m, 1H), 3.72−3.64 (m, 1H), 3.41−3.31 (m, 2H), 2.42−2.32 (m, 2H), 2.35−2.22 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 176.8, 170.3, 136.7, 134.4, 132.2, 131.8, 131.1, 128.9, 120.5−106.3 (m), 62.3, 59.9, 53.1, 52.7, 23.9, 23.7, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.86 (t, J = 9.7 Hz, 3F), −117.84 (dt, J = 249.1, 13.1 Hz, 1F), −121.64 to −121.91 (m, 2F), −122.44 to −123.39 (m, 1F), −126.12 to −126.35 (m, 2F); HRMS (ESI/$[M + H]^+$) calcd. for $C_{19}H_{19}F_9N_2O_5S_2$: 591.0664. Found 591.0659.

General Procedure for Synthesis of Arylglycines 11e−11i. In a N_2-filled glovebox, perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv), the indicated 1-aryl-1*H*-pyrazole (**10e−10i**)[33] (0.300 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol, 0.10 equiv), and $AgB(C_6F_5)_4$ (62.0 mg, 0.060 mmol, 0.40 equiv, 23.8% *w*/*w* toluene) were added to a 0.5−2.0 mL microwave vial equipped with a triangular magnetic stir bar, followed by the addition of 1,2-dichloroethane (200 μL, [sulfinyl imine] = 0.75 M). The vial was sealed and removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath preset to 50 °C and was stirred for 24 h. The vial was removed from the oil bath and cooled to ambient temperature before the reaction vessel was unsealed. The crude mixture was purified directly by silica gel chromatography.

*Ethyl (S)-2-(2-(1H-Pyrazol-1-yl)phenyl)-2-(((S)-(perfluorobutyl)-sulfinyl)amino)acetate (**11e**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-phenyl-1*H*-pyrazole (43.3 mg, 0.300 mmol, 2.0 equiv). Purification by flash column chromatography (10−20% EtOAc in hexanes gradient) afforded the product **11e** (52.0 mg, 68% yield) as a light yellow oil. IR (film): 1739, 1521, 1396, 1351, 1195, 1138, 1099, 1015, 941, 864, 758, 723, 692, 619, 577, 515, 428 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 1.9 Hz, 1H), 7.68 (d, J = 2.2 Hz, 1H), 7.51−7.40 (m, 4H), 7.33 (dd, J = 7.4, 1.8 Hz, 1H), 6.47 (t, J = 1.9 Hz, 1H), 5.45 (d, J = 9.0 Hz, 1H), 4.00−3.87 (m, 2H), 1.08 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 169.1, 141.2, 138.7, 132.7, 132.2, 130.7, 130.0, 129.0, 125.4, 120.4−106.5 (m), 107.8, 62.4, 58.0, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.81 (t, J = 9.5 Hz, 3F), −117.51 (dt, J = 249.0, 12.7 Hz, 1F), −122.69 to −122.85 (m, 2F), −124.30 (dt, J = 249.0, 12.7 Hz, 1F), −126.29 to −128.07 (m, 2F); HRMS (ESI/$[M + H]^+$) calcd. for $C_{17}H_{15}F_9N_3O_3S$: 512.0685. Found 512.0684.

*Ethyl (S)-2-(5-Methyl-2-(1H-pyrazol-1-yl)phenyl)-2-(((S)-(perfluorobutyl)sulfinyl)amino)acetate (**11f**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-(*p*-tolyl)-1*H*-pyrazole[33a] (47.5 mg, 0.300 mmol, 2.0 equiv). Purification by flash column chromatography (10−20% EtOAc in hexanes gradient) afforded the product **11f** (59.6 mg, 76% yield) as a light yellow oil. IR (film): 1738, 1522, 1396, 1351, 1195, 1138, 1099, 1024, 942, 862, 822, 746, 722, 692, 620, 576, 519, 436 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, J = 1.9 Hz, 1H), 7.62 (d, J = 2.2 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.30 (s, 1H), 7.26−7.23 (m, 1H), 7.20 (d, J = 8.0 Hz, 1H), 6.44 (t, J = 2.2 Hz, 1H), 5.39 (d, J = 9.0 Hz, 1H), 3.98−3.87 (m, 2H), 2.40 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 169.1, 140.9, 139.2, 136.3, 132.6, 132.6, 130.7, 130.5, 125.4, 120.4−106.4 (m), 107.6, 62.3,

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57.6, 21.0, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.86 (tt, J = 9.6, 2.4 Hz, 3F), −117.34 (dt, J = 248.9, 12.9 Hz, 1F), −122.75 to −122.90 (m, 2F), −124.57 (dt, J = 248.9, 11.6 Hz, 1F), −126.32 to −128.10 (m, 2F); HRMS (ESI/[M + H]$^+$) calcd. for $C_{18}H_{17}F_9N_3O_3S$: 526.0841. Found 526.0840.

*Ethyl (S)-2-(5-Methoxy-2-(1H-pyrazol-1-yl)phenyl)-2-(((S)-(perfluorobutyl)sulfinyl)amino)acetate (**11g**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-(4-methoxyphenyl)-1*H*-pyrazole[33a] (52.3 mg, 0.300 mmol, 2.0 equiv). Purification by preparative thin-layer silica gel chromatography using 25% EtOAc/hexanes afforded the product **11g** (38.3 mg, 47% yield) as a light yellow oil. IR (film): 1740, 1523, 1196, 1138, 1043, 1018, 943, 864, 816, 746, 723, 692, 613, 435 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 1.9 Hz, 1H), 7.58 (d, J = 2.2 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 2.8 Hz, 1H), 6.95 (dd, J = 8.7, 2.8 Hz, 1H), 6.43 (t, J = 2.2 Hz, 1H), 5.36 (d, J = 8.8 Hz, 1H), 4.00−3.88 (m, 2H), 3.85 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 168.9, 159.7, 140.8, 134.4, 131.9, 131.0, 127.2, 116.7, 115.0, 120.4−106.4 (m), 107.4, 62.4, 57.3, 55.8, 13.9; ^{19}F NMR (471 MHz, $CDCl_3$): δ −81.87 (t, J = 9.5 Hz, 3F), −117.38 (dt, J = 249.2, 13.2 Hz, 1F), −122.71 to −122.88 (m, 2F), −124.49 (ad, J = 249.2, 1F), −126.48 to −127.98 (m, 2F); HRMS (ESI/[M + H]$^+$) calcd. for $C_{18}H_{17}F_9N_3O_4S$: 542.0791. Found 542.0790.

*Ethyl (S)-2-(5-Acetyl-2-(1H-pyrazol-1-yl)phenyl)-2-(((S)-(perfluorobutyl)sulfinyl)amino)acetate (**11h**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-(4-(1*H*-pyrazol-1-yl)phenyl)ethan-1-one[33b] (55.9 mg, 0.300 mmol, 2.0 equiv). Purification by preparative thin-layer silica gel chromatography using 25% EtOAc/hexanes afforded the product **11h** (50.6 mg, 61% yield) as a light yellow waxy solid. IR (film): 1726, 1697, 1607, 1524, 1395, 1191, 1137, 1033, 943, 759, 746, 722, 692, 613, 514, 457 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, J = 2.0 Hz, 1H), 8.04 (dd, J = 8.2, 2.0 Hz, 1H), 7.76 (d, J = 2.2 Hz, 1H), 7.74 (d, J = 2.0 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.40 (d, J = 9.1 Hz, 1H), 6.51 (t, J = 2.2 Hz, 1H), 5.58 (d, J = 9.1 Hz, 1H), 4.00−3.88 (m, 2H), 2.63 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 196.3, 168.7, 141.9, 141.8, 136.6, 132.9, 132.3, 130.5, 129.8, 124.8, 120.3−106.4 (m), 108.6, 62.5, 58.3, 26.8, 13.9; ^{19}F NMR (471 MHz, $CDCl_3$): δ −82.10 (t, J = 9.5 Hz, 3F), −117.80 (dt, J = 248.9, 13.5 Hz, 1F), −122.93 to −123.09 (m, 2F), −124.53 (ad, J = 248.9 Hz, 1F), −126.72 to −128.91 (m, 2F); HRMS (ESI/[M + H]$^+$) calcd. for $C_{19}H_{17}F_9N_3O_4S$: 554.0791. Found 554.0793.

*Ethyl (S)-2-(4-Methyl-2-(1H-pyrazol-1-yl)phenyl)-2-(((S)-(perfluorobutyl)sulfinyl)amino)acetate (**11i**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-(*m*-tolyl)-1*H*-pyrazole[33a] (47.5 mg, 0.300 mmol, 2.0 equiv). Purification by flash column chromatography (10−20% EtOAc in hexanes gradient) afforded the product **11i** (60.1 mg, 76% yield) as a light yellow oil. IR (film): 1738, 1519, 1394, 1351, 1194, 1138, 1101, 1014, 955, 859, 746, 722, 692, 619, 580, 437 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, J = 1.8 Hz, 1H), 7.67 (d, J = 2.2 Hz, 1H), 7.38−7.35 (m, 2H), 7.23 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 6.46 (t, J = 2.2 Hz, 1H), 5.40 (d, J = 8.9 Hz, 1H), 3.98−3.88 (m, 2H), 2.40 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 169.2, 141.1, 140.4, 138.5, 131.9, 130.6, 129.7, 129.6, 126.1, 120.4−106.4 (m), 107.6, 62.3, 57.6, 21.1, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.87 (tt, J = 9.4, 2.6 Hz, 3F), −117.57 (dt, J = 249.1, 13.0 Hz, 1F), −122.72 to −122.89 (m, 2F), −124.33 (dt, J = 249.1, 12.2 Hz, 1F), −126.33 to −128.10 (m, 2F); HRMS (ESI/[M + H]$^+$) calcd. for $C_{18}H_{17}F_9N_3O_3S$: 526.0841. Found 526.0842.

General Procedure for the Synthesis of Arylglycines 11j−11m. In a N_2-filled glovebox, perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv), the indicated 1-benzyl-4-aryl-1*H*-1,2,3-triazole (**10j−10m**)[34] (0.300 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol, 0.10 equiv), $AgB(C_6F_5)_4$ (62.0 mg, 0.060 mmol, 0.40 equiv, 23.8% *w*/*w* toluene), and AgOAc (5.0 mg, 0.030 mmol, 0.20 equiv) were added to a 0.5−2.0 mL microwave vial equipped with a triangular magnetic stir bar, followed by the addition of 1,2-dichloroethane (200 μL, [sulfinyl imine] = 0.75 M). The vial was sealed and removed from the glovebox. The reaction vial was then placed in a temperature-controlled oil bath preset to 50 °C. After the solution was stirred for 24 h, the vial was removed from the oil bath and cooled to ambient temperature before the reaction vessel was unsealed. The crude mixture was purified directly by chromatography.

*Ethyl (S)-2-(2-(1-Benzyl-1H-1,2,3-triazol-4-yl)phenyl)-2-(((S)-(perfluorobutyl)sulfinyl)amino)acetate (**11j**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-benzyl-4-phenyl-1*H*-1,2,3-triazole[34a] (70.6 mg, 0.300 mmol, 2.0 equiv). Preparative thin-layer silica gel chromatography using 50% Et_2O/pentane provided the first step of the purification process. Pure product was then obtained by C18 reverse phase column chromatography with loading of the isolated material onto the column as a solution in 1 mL of DMSO. Reverse phase purification was performed with 15.5 g of reverse phase media and a 95 column volume gradient from 10 to 65% CH_3CN:H_2O containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were then washed with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated to afford the product **11j** (52.1 mg, 58% yield) as a colorless oil. IR (film): 1738, 1352, 1196, 1138, 1014, 763, 721, 692, 581 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.42−7.28 (m, 10H), 5.78 (d, J = 8.0 Hz, 1H), 5.59 (d, J = 14.8 Hz, 1H), 5.55 (d, J = 14.8 Hz, 1H), 4.01−3.92 (m, 2H), 1.03 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 169.9, 147.4, 135.4, 134.4, 130.4, 130.1, 129.3, 129.3, 129.1, 129.1, 128.3, 122.0, 120.4−106.2 (m), 62.1, 58.6, 54.5, 13.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ −81.88 (t, J = 9.5 Hz, 3F), −117.99 (dt, J = 249.0, 12.6 Hz, 1F), −122.03 to −123.54 (m, 2F), −123.56 (ad, J = 249.0 Hz, 1F), −126.52 to −127.93 (m, 2F); HRMS (ESI/[M + H]$^+$) calcd. for $C_{23}H_{20}F_9N_4O_3S$: 603.1107. Found 603.1108.

*Ethyl (S)-2-(2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-5-methoxyphenyl)-2-(((S)-(perfluorobutyl)sulfinyl)amino)acetate (**11k**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (79.6 mg, 0.300 mmol, 2.0 equiv). Preparative thin-layer silica gel chromatography using 50% Et_2O/pentane provided the first step in the purification process. Pure product was then obtained by C18 reverse phase column chromatography with loading of the isolated material onto the column as a solution in 1 mL of DMSO. Reverse phase purification was performed with 15.5 g of reverse phase media and an 80 column volume gradient from 10 to 70% CH_3CN:H_2O containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were then washed with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated to afford the product **11k** (53.0 mg, 56% yield) as a yellow oil. IR (film): 1738, 1615, 1493, 1459, 1351, 1196, 1138, 864, 814, 746, 721, 693, 580 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.41−7.30 (m, 7H), 6.93 (d, J = 2.6 Hz, 1H), 6.88 (dd, J = 8.6, 2.6 Hz, 1H), 5.73 (d, J = 7.9 Hz, 1H), 5.58 (d, J = 14.9 Hz, 1H), 5.53 (d, J = 14.9 Hz, 1H), 4.01−3.93 (m, 2H), 3.81 (s, 3H), 1.03 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 169.8, 160.0, 147.3, 136.8, 134.4, 131.5, 129.3, 129.0, 128.3, 121.8, 121.5, 115.6, 114.7, 120.4−106.4 (m), 62.2, 58.4, 55.5, 54.5, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.85 (t, J = 9.6 Hz, 3F), −117.85 (dt, J = 249.0, 13.0 Hz, 1F), −121.83 to −123.66 (m, 2F), −123.74 (ad, J = 249.0 Hz, 1F), −126.35 to −128.08 (m, 2F); HRMS (ESI/[M + H]$^+$) calcd. for $C_{24}H_{22}F_9N_4O_4S$: 633.1213. Found 633.1214.

*Ethyl (S)-2-(2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-5-methylphenyl)-2-(((S)-(perfluorobutyl)sulfinyl)amino)acetate (**11l**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (74.8 mg, 0.300 mmol, 2.0 equiv). Preparative thin-layer silica gel chromatography using 50% Et_2O/pentane provided the first step in the purification process. Pure product was then obtained by C18 reverse phase column chromatography with loading of the isolated material onto the column as a solution in 1 mL of DMSO. Reverse

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phase purification was performed with 15.5 g of reverse phase media and a 70 column volume gradient from 10 to 60% CH_3CN:H_2O containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were then washed with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated to afford the product **11l** (48.3 mg, 52% yield) as a colorless oil. IR (film): 1739, 1459, 1351, 1232, 1197, 1138, 1015, 820, 721, 692, 578 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.41−7.28 (m, 7H), 7.22 (s, 1H), 7.17 (d, J = 8.0 Hz, 1H), 5.73 (d, J = 8.0 Hz, 1H), 5.58 (d, J = 14.8 Hz, 1H), 5.53 (d, J = 14.8 Hz, 1H), 4.02−3.91 (m, 2H), 2.36 (s, 3H), 1.03 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 170.0, 147.5, 139.4, 135.2, 134.4, 131.2, 130.0, 129.9, 129.3, 129.0, 128.3, 126.4, 121.7, 120.4−106.2 (m), 62.1, 58.5, 54.5, 21.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.86 (t, J = 9.6 Hz, 3F), −117.83 (dt, J = 248.9, 12.6 Hz, 1F), −121.89 to −123.71 (m, 2F), −123.80 (ad, J = 248.9 Hz, 1F), −126.36 to −128.09 (m, 2F); HRMS (ESI/$[M + H]^+$) calcd. for $C_{24}H_{22}F_9N_4O_3S$: 617.1263. Found 617.1261.

*Ethyl (S)-2-(2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-4-methylphenyl)-2-(((S)-(perfluorobutyl)sulfinyl)amino)acetate (**11m**).* The general procedure was followed with perfluorobutanesulfinyl imino ester **9** (55.1 mg, 0.150 mmol, 1.0 equiv) and 1-benzyl-4-(*m*-tolyl)-1*H*-1,2,3-triazole (74.8 mg, 0.300 mmol, 2.0 equiv). Preparative thin-layer silica gel chromatography using 50% Et_2O/pentane provided the first step in the purification process. Pure product was then obtained by C18 reverse phase column chromatography with loading of the isolated material onto the column as a solution in 1 mL of DMSO. Reverse phase purification was performed with 15.5 g of reverse phase media and a 75 column volume gradient from 10 to 60% CH_3CN:H_2O containing 0.1% TFA. Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were then washed with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated to afford the product **11m** (49.1 mg, 53% yield) as a colorless waxy solid. IR (film): 1739, 1459, 1352, 1197, 1138, 1014, 862, 819, 786, 746, 721, 692, 575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.42−7.37 (m, 3H), 7.34−7.28 (m, 3H), 7.24 (d, J = 1.8 Hz, 1H), 7.20−7.17 (m, 2H), 5.73 (d, J = 7.9 Hz, 1H), 5.59 (d, J = 14.8 Hz, 1H), 5.55 (d, J = 14.8 Hz, 1H), 4.02−3.94 (m, 2H), 2.34 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 170.1, 147.5, 139.1, 134.4, 132.4, 130.8, 130.3, 130.0, 129.3, 129.1, 129.1, 128.3, 121.9, 120.4−106.4 (m), 62.1, 58.3, 54.6, 21.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.84 (t, J = 9.5 Hz, 3F), −117.91 (dt, J = 249.2, 13.3 Hz, 1F), −121.84 to −123.69 (m, 2F), −123.59 (ad, J = 249.2 Hz, 1F), −126.34 to −128.07 (m, 2F); HRMS (ESI/$[M + H]^+$) calcd. for $C_{24}H_{22}F_9N_4O_3S$: 617.1263. Found 617.1260.

General Procedure for the Aza-Diels−Alder Reaction. In a N_2-filled glovebox, perfluorobutanesulfinyl imino ester **9** (183.6 mg, 0.50 mmol, 1.0 equiv) was weighed into a 1 mL conical screw-capped vial. DCE (0.20 mL, [sulfinyl imine] = 1.0 M) and a triangular magnetic stir bar were then added. The vial was sealed with a screw-top cap containing a PTFE septum and was removed from the glovebox. The cap was removed, and the corresponding diene (**14a**−**14d**) (2.5 mmol, 5.0 equiv) was added by syringe before the vial was sealed again with the cap. The vial was then heated in a temperature-controlled aluminum-heating block set at 50 °C and was stirred for 16 h, and the vial was removed from the heating block and allowed to cool to ambient temperature. Excess diene and solvent were removed under reduced pressure, and the remaining crude material was purified by silica gel flash column chromatography.

*Ethyl (S)-4-Methyl-1-((S)-(perfluorobutyl)sulfinyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (**15a**).* The general procedure using isoprene **14a** (0.25 mL, 2.5 mmol, 5.0 equiv) was followed. Purification by flash column chromatography (10% EtOAc in hexanes) afforded the product **15a** (154 mg, 71% yield) as a colorless oil. IR (film): 2920, 1740, 1350, 1196, 1138, 1112, 1009, 921, 746, 721, 691 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.42−5.37 (m, 1H), 4.57 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 4.00 (d, J = 17.5 Hz, 1H), 3.82 (d, J = 17.1 Hz, 1H), 2.51−2.45 (m, 2H), 1.72 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.1, 131.4, 116.6, 120.6−106.3 (m), 62.0, 52.6, 42.9, 32.2, 23.5, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.88 (t, J = 9.5 Hz, 3F), −114.90 (dt, J = 248.3, 12.9 Hz, 1F), −120.58 to −123.54 (m, 3F), −125.27 to −127.14 (m, 2F); HRMS (ESI/$[M + Na]^+$) calcd. for $C_{13}H_{14}F_9NO_3S$: 458.0443. Found 458.0447.

*Ethyl (S)-4,5-Dimethyl-1-((S)-(perfluorobutyl)sulfinyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (**15b**).* The general procedure using dimethylbutadiene **14b** (0.29 mL, 2.5 mmol, 5.0 equiv) was followed. Purification by flash column chromatography (10% EtOAc in hexanes) afforded the product **15b** (182 mg, 81% yield) as a colorless oil. IR (film): 2917, 1742, 1350, 1232, 1196, 1134, 1009, 998, 746, 721, 690 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 4.51 (s, 1H), 4.19 (qd, J = 7.1, 2.3 Hz, 2H), 3.89 (d, J = 16.5 Hz, 1H), 3.59 (d, J = 16.6 Hz, 1H), 2.52−2.41 (m, 2H), 1.65 (s, 3H), 1.60 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.0, 123.1, 121.6, 120.7−106.0 (m), 61.6, 52.5, 46.2, 33.0, 18.7, 15.9, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.85 (t, J = 9.5 Hz, 3F), −114.85 (dt, J = 248.6, 12.7 Hz, 1F), −121.46 to −123.53 (m, 3F), −125.28 to −127.13 (m, 2F); HRMS (ESI/$[M + Na]^+$) calcd. for $C_{14}H_{16}F_9NO_3S$: 472.0599. Found 472.0598.

*Ethyl (2S,3S,6R)-3,6-Dimethyl-1-((S)-(perfluorobutyl)sulfinyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (**15c**).* The general procedure using 2,4-hexadiene **14c** (0.29 mL, 2.5 mmol, 5.0 equiv) was followed. Purification by flash column chromatography (10% EtOAc in hexanes) afforded the product **15c** (154 mg, 69% yield) as a colorless oil. IR (film): 2978, 1749, 1233, 1189, 1137, 1110, 1018, 997, 746, 722, 692 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.71 (ddd, J = 10.4, 5.5, 2.0 Hz, 1H), 5.57−5.51 (m, 1H), 4.60−4.54 (m, 1H), 4.49 (s, 1H), 4.24−4.12 (m, 2H), 2.78 (p, J = 5.8 Hz, 1H), 1.45 (d, J = 6.8 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.2, 129.6, 128.3, 121.7−106.1 (m), 61.5, 54.0, 50.8, 32.7, 20.2, 19.8, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.88 (t, J = 9.6 Hz, 3F), −108.89 to −115.20 (m, 1F), −122.28 to −122.42 (m, 2F), −125.14 to −127.34 (m, 3F); HRMS (ESI/$[M + Na]^+$) calcd. for $C_{14}H_{16}F_9NO_3S$: 472.0599. Found 472.0591.

*Ethyl (2S,6R)-6-Methyl-1-((S)-(perfluorobutyl)sulfinyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (**15d**).* The general procedure using 1,3-pentadiene **14d** (0.25 mL, 2.5 mmol, 5.0 equiv) was followed. Purification by flash column chromatography (10% EtOAc in hexanes) afforded the product **15d** (141 mg, 65% yield) as a colorless oil and as an inseparable exo/endo diastereomeric mixture (dr = 8/1, ^1H NMR). IR (film): 2987, 1742, 1350, 1191, 1136, 1109, 1007, 746, 721, 691 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) major isomer only δ 5.80−5.73 (m, 1H), 5.65−5.58 (m, 1H), 4.76 (s, 1H), 4.56−4.50 (m, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.61−2.55 (m, 1H), 2.51−2.45 (m, 1H), 1.43 (d, J = 6.9 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, selected signals) δ 170.0, 130.5, 122.9, 121.1−106.2 (m), 61.7, 50.1, 28.6, 23.4 19.8, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.86 (t, J = 9.5 Hz, 3F), −110.20 to −115.41 (m, 1F), −122.29 (app. q, J = 9.6 Hz, 2F), −125.10 to −127.46 (m, 3F); HRMS (ESI/$[M + Na]^+$) calcd. for $C_{13}H_{14}F_9NO_3S$: 458.0443. Found 458.0438. HPLC (Microsorb 100−5 Si, EtOH/hexanes. 2:98, 1.0 mL/min. 230 nm) of **15d**: t_R = 4.78 (minor) and 5.05 min (major). A 1:1 mixture of endo/exo diastereomers of **15d** was obtained by collecting enriched fractions (t_R = 4.7 to 5.0 min). The enriched fractions from multiple runs were combined and concentrated to give 2.0 mg of the 1:1 mixture (**15d-mix**). Relative configurations were determined from 2D NOE experiments of **15d-mix**.

The absolute configuration of the major exo diastereomer was determined by sulfinyl group cleavage and then X-ray structural analysis of the 2,4,6-trinitrobenzenesulfonate salt of the resulting amine. To a flame-dried, 1 dram vial equipped with a magnetic stir bar was added **15d** (31.7 mg, 0.073 mmol, 1 equiv), followed by 2 M HCl in Et_2O (0.36 mL, 0.73 mmol, 10 equiv). The mixture was stirred and heated to 50 °C for 8 h and then concentrated to dryness under reduced pressure. The concentrate was dissolved in 10 mL of 0.1 M aqueous HCl, transferred to a separatory funnel, and washed with Et_2O (1 × 5 mL) before aqueous Na_2CO_3(sat) was added with stirring until a pH of 10−11 was reached. The basic aqueous layer was

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extracted with Et_2O (3 × 10 mL), and the combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford the free amine (6.7 mg. 54% yield). To 4.8 mg of the unpurified free amine in a 1 dram vial was added 7.5 mg (0.9 equiv) of 2,4,6-trinitrobenzenesulfonic acid, followed by 0.5 mL of toluene, which resulted in a cloudy mixture. To this cloudy mixture was added methanol dropwise with swirling until the solution turned clear (10 drops). The clear solution was transferred into an NMR tube and layered with 1.0 mL of HPLC grade hexanes. The NMR tube was allowed to sit at ambient temperature for 3 days, after which single crystals were formed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02700.

^1H, ^{13}C, and ^{19}F NMR spectra and HPLC chromatograms of new compounds, and X-ray structures of the 4-chlorobenzamide derivative of **11a** and the amine salt of **15d** (PDF)

Crystallographic data for **11a-amide** (CIF)

Crystallographic data for **15d-amine** (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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