Inverse Electron Demand Diels-Alder Reactions of *N*-Sulfonyl α,β-Unsaturated Imines: A General Approach to Implementation of the 4π Participation of 1-Aza-1,3-butadienes in Diels-Alder Reactions

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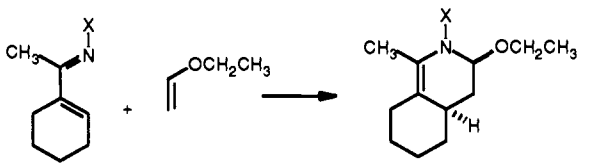
Abstract: Full details of a study of the inverse electron demand Diels-Alder reactions of *N*-sulfonyl-1-aza-1,3-butadienes are described. The α,β-unsaturated *N*-sulfonylimines proved accessible through clean, homolytic rearrangement of in situ generated oxime *O*-sulfinyl compounds or through direct condensation of sulfonamides with α,β-unsaturated aldehydes. Thermal- or pressure-promoted [4 + 2] cycloaddition reactions of the *N*-sulfonyl-1-aza-1,3-butadienes with electron-rich olefins generally provided a single cycloadduct derived from predominant (≥20:1) cycloaddition through an endo transition state. The complementary C3 addition of an electron-withdrawing substituent to the *N*-sulfonyl-1-aza-1,3-butadienes substantially accelerated their participation in the $LUMO_{diene}$-controlled Diels-Alder reactions and such reactions may be conducted at 25 °C. Characteristic of a concerted [4 + 2] cycloaddition reaction, the reactions were found to proceed with full preservation of the dienophile olefin stereochemistry, to exhibit little solvent dependency on the [4 + 2] cycloaddition rate, trans 1,2-disubstituted dienophiles were shown to be more reactive than cis 1,2-disubstituted dienophiles, and the cis versus trans 1,2-disubstituted dienophiles were shown to exhibit a preferential pressure-induced rate acceleration. In addition, the noncomplementary C2 or C4 addition of an electron-withdrawing substituent to the *N*-sulfonyl-1-aza-1,3-butadienes accelerated the azadiene participation in $LUMO_{diene}$-controlled Diels-Alder reactions (25 °C) that maintain the regioselectivity and endo diastereoselectivity of the parent azadienes and that display characteristics consistent with concerted [4 + 2] cycloaddition reactions. Computational studies support the observed endo diastereoselectivity that may be derived from a pronounced, stabilizing secondary orbital interaction. However, the unusually high endo diastereoselectivity (≥20:1) suggests this may only be part of the origin of the cycloaddition selectivity. It is suggested that the endo [4 + 2] cycloaddition transition state in which the lone pair on nitrogen and the σ C-O bond of the dienophile lie trans periplanar further benefits from a n-σ* stabilization in a manner analogous to the product ground-state conformation (anomeric effect).

The Diels-Alder 4π participation of simple α,β-unsaturated imines is rarely observed and typically suffers low conversions, competitive imine addition, and/or imine tautomerization precluding [4 + 2] cycloaddition.[1,2] Consequently, only a limited number of 1-aza-1,3-butadiene structural variations and modified or restricted reaction conditions have been introduced that have permitted the productive 4π participation of α,β-unsaturated imines in [4 + 2] cycloaddition reactions.[3-7] These include the use of the intramolecular [4 + 2] cycloaddition reactions of in situ generated *N*-acyl-1-aza-1,3-butadienes[3] (flash vacuum pyrolysis) and in situ generated *o*-quinomethide monoimines,[4] the $HOMO_{diene}$-controlled Diels-Alder reactions of α,β-unsaturated

Scheme I



equiv. of dienophile, temp °C or pressure kbar, (time, h), solvent

1a X = OH	5, 12 kbar (72), CH_2Cl_2	**2a**	no rxn
1b X = OCH_3	5, 12 kbar (72), CH_2Cl_2	**2b**	no rxn
1c X = $P(O)Ph_2$	5, 12 kbar (135), CH_2Cl_2	**2c**	75%
1d X = SO_2Ph	5, 12 kbar (87), CH_2Cl_2	**2d**	89%
	5, 110° C (48), toluene		79%

N,*N*-dimethylhydrazones (N^1-(dimethylamino)-1-aza-1,3-butadienes),[5] and the Lewis acid catalyzed intramolecular [4 + 2] cycloaddition reactions of in situ generated 2-(*tert*-butyldimethylsilyl)oxy]- and 2-[(trimethylsilyl)oxy]-1-aza-1,3-butadienes.[6,7] In the conduct of synthetic studies on the [4 + 2] cycloaddition reactions of hetero dienes,[8,9] we have examined alternative approaches to promote the 4π participation of 1-aza-1,3-butadienes in intermolecular [4 + 2] cycloaddition reactions. The complementary N1 or C3 substitution of an α,β-unsaturated imine with an electron-withdrawing substituent would be expected to accentuate the inherent electron-deficient nature of the 1-aza-1,3-butadiene and accelerate its potential [4 + 2] cycloaddition reaction with electron-rich dienophiles in $LUMO_{diene}$-controlled Diels-Alder reactions.[1-2] In addition, a bulky electron-withdrawing N1 substituent would be expected to preferentially decelerate

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Table I

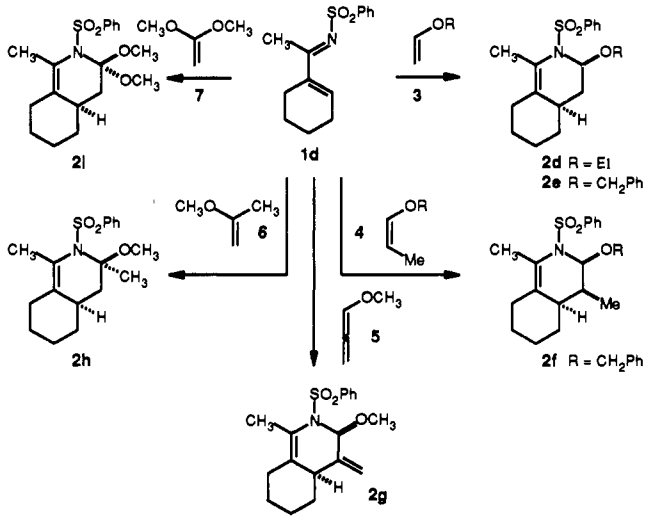
dienophile, R	conditions[a] temp (°C), time (h), solvent, pressure (kbar)	product, endo:exo (% yield)
3a, Et	25, 87, CH_2Cl_2, 12	**2d**, >20:1 (89)
3a, Et	110, 48, toluene	**2d**, >20:1 (79)
3b, CH_2Ph	25, 70, neat, 12	**2e**, >20:1 (74)
4b, CH_2Ph[b]	25, 72, CH_2Cl_2, 12	**2f**, >20:1 (28)
5	25, 72, CH_2Cl_2, 12	**2g**, >20:1 (54)
5	140, 24, mesitylene	**2g**, >20:1 (23)
6	25, 76, CH_2Cl_2, 12	**2h**, >20:1 (82)
7	25, 96, CH_2Cl_2, 12	**2i**, (63)

[a] A total of 5 equiv of dienophile employed unless otherwise indicated. [b] A total of 2 equiv of dienophile employed, 66% recovered diene.

1,2-imine addition relative to [4 + 2] cycloaddition and stabilize [4 + 2] cycloaddition product (deactivated enamine) to the reaction conditions while enhancing the electron-deficient nature of the diene. Herein, we provide full details of a comparative study of the 4π participation of N^1-substituted α,β-unsaturated imines in $LUMO_{diene}$-controlled Diels–Alder reactions that have revealed the general, well-defined 4π participation of α,β-unsaturated *N*-sulfonylimines in regiospecific and endo-specific inverse electron demand Diels–Alder reactions suitable for the diastereoselective preparation of substituted 1,2,3,4-tetrahydropyridines.[10-14]

***N*-Sulfonyl-1-aza-1,3-butadienes: Synthesis and Comparative [4 + 2] Cycloaddition Reactivity.** Representative results of initial studies employing stable imine derivatives of 1-acetyl-1-cyclohexene are summarized in Scheme I. The use of derivatives of 1-acetylcyclohexene for initial study represented the selection of a test 1-aza-1,3-butadiene system (1) that is capable of imine tautomerization, (2) that possesses no selected *s*-*Z*- versus *s*-*E*-diene conformational bias, (3) that presents substantial diene–dienophile steric interactions in the developing [4 + 2] transition state (N1, C2, C3, and C4 diene substituents), and (4) that suffers from the introduction of $A^{1,2}$-strain accompanying the [4 + 2] cycloaddition. This latter effect generally conveys a preference for 1,2- versus 1,4-addition to such systems. Thus, the derivatives **2a–d** were selected for initial comparison with expectations that the observation of [4 + 2] cycloaddition with electron-rich dienophiles would prove generally applicable. As illustrated by the results summarized in Scheme I, N^1-substitution of a 1-aza-1,3-butadiene with an electron-withdrawing substituent ($-SO_2Ph$, $-P(O)Ph_2$) was found to facilitate its participation in $LUMO_{diene}$-controlled Diels–Alder reactions. The *N*-(phenylsulfonyl)imine **1d**[15,16] and *N*-(diphenylphosphinyl)imine **1c**[17] proved to be stable imine derivatives capable of simple isolation and purification (SiO_2 or Florisil chromatography), both exhibited good thermal [4 + 2] cycloaddition reactivity with ethyl vinyl ether

Scheme II



(**1c** ≅ **1d** ≫ **1a,b**), and the [4 + 2] cycloadducts **2c,d** proved stable to isolation and purification.[18]

Given the ease of its preparation and the anticipated synthetic generality of working with sulfonamides, **1d** was selected for further study. The results of a study of the scope of the Diels–Alder reactions of **1d** with a range of electron-rich olefins are summarized in Scheme II and Table I.[18] Both the thermal- and pressure-promoted [4 + 2] cycloaddition reactions cleanly provided the Diels–Alder cycloadducts, and the reactions proved to proceed predominately if not exclusively (≥95%) through an endo transition state with full preservation of the dienophile olefin geometry in the stereochemistry of the reaction products. Even in instances where the endo [4 + 2] cycloaddition is decelerated by destabilizing steric interactions introduced by an additional dienophile cis substituent (e.g., **4b**), the exclusive formation of the product derived from [4 + 2] cycloaddition through an endo transition state (e.g., **2f**) was observed albeit with formation at slower rates.

The results of the extension of these observations to the $LUMO_{diene}$-controlled Diels–Alder reaction of ethyl vinyl ether with a full range of *N*-(phenylsulfonyl)-1-aza-1,3-butadienes derived from α,β-unsaturated ketones and aldehydes are summarized in Scheme III and Table II. The *N*-(phenylsulfonyl)-imines proved to be readily accessible through the clean, homolytic rearrangement of in situ generated oxime *O*-phenylsulfinyl[15] compounds (aldehyde and ketone precursors) or through the direct condensation of benzenesulfonamide with selected α,β-unsaturated aldehydes.[16] In each instance, the thermal- or pressure-promoted [4 + 2] cycloaddition provided a single cycloadduct derived from the expected [4 + 2] cycloaddition regioselectivity that proved to be derived from predominate if not exclusive (≥95%) cycloaddition through an endo transition state. The *N*-phenylsulfonyl aldimines proved more reactive than *N*-phenylsulfonyl ketimines ($R^1 = H > R^1 = CH_3, C_6H_5$), and the complementary addition of a C3 electron-withdrawing substituent to the azadiene ($R^2 = CO_2R^1 \gg R^2 = H, CH_3$) substantially accelerated the *N*-(phenylsulfonyl)-1-aza-1,3-butadiene participation in the $LUMO_{diene}$-controlled Diels-Alder reaction. Thus, the reaction of N^1-(phenylsulfonyl)imine **1j** possessing the additional C3 electron-withdrawing substituent was found to react with 1,1-dimethoxyethylene *within 5 min at 25 °C* to provide the Diels–Alder adduct **14** (79%). Further consistent with the characteristics of a concerted [4 + 2] cycloaddition reaction, the reactions were found to proceed with full preservation of the dienophile olefin

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(18) The [4 + 2] cycloaddition products were purified by chromatography on Florisil and on occasion have proven somewhat unstable to silica gel. For example, the cycloadducts **2g–l** are not completely stable to this method of purification and **14** proved unstable to chromatography on Florisil. To date, we have not detected epimerization of the cycloadduct C2 center resulting from the conditions of purification and the products have proven configurationally stable.

Table II

diene, method (% yield)	dienophile	conditions:[a] equiv dienophile, temp or pressure, time (h), solvent	product, endo:exo (% yield)
1e, A (15)	**3a**	10, 60 °C (12), neat	**8**, (73)
1f, A (90)	**3a**	5, 12 kbar (80), CH_2Cl_2	**9**, >20:1 (69)
1g, A (50)	**3a**	5, 12 kbar (45), CH_2Cl_2	**10**, >20:1 (77)
1h, B (50–68)	**3a**	5, 12 kbar (45), CH_2Cl_2	**11a**, >20:1 (72)
1h, A (28)	**4b**	5, 6 kbar (144), CH_2Cl_2	**11b**, >20:1 (54)
1i, C (56)	**3a**	5, 12 kbar (45), CH_2Cl_2	**12**, (72)
1i, A (55)	**3a**	10, 40 °C (11), CH_2Cl_2	**12**, (82)
1j, A (47)[b]	**3a**	5, 100 °C (12), dioxane	**13**, >20:1 (56)
1j	**3a**	10, 100 °C (72), dioxane	**13**, >20:1 (89)
1j	**7**	10, 25 °C (5 min), CH_2Cl_2	**14**, (79)

[a] All pressure-promoted reactions were conducted at 25 °C. [b] The (methylsulfonyl)imine was similarly prepared in 75% yield.

Table III. Theoretical Highest Occupied π Orbital (HOMO) and Lowest Unoccupied π Orbital (LUMO) of Azadienes and Enol Ether Dienophiles: AM1[a] (MNDO)[b] Results

diene	*E* (eV)	coefficients				
$H_2C{=}CH{-}CH{=}CH_2$		C1	C2	C3	C4	
HOMO	−9.4 (−9.2)	0.56 (0.56)	0.43 (0.44)	−0.43 (−0.44)	−0.56 (−0.56)	
LUMO	0.5 (0.4)	0.57 (0.57)	−0.42 (−0.43)	−0.42 (−0.43)	0.57 (0.57)	
$H_2C{=}CH{-}CH{=}NH$		N1	C2	C3	C4	
HOMO	−10.1 (−10.0)	0.46 (0.42)	0.24 (0.20)	−0.59 (−0.62)	−0.62 (−0.63)	
LUMO	0.4 (0.3)	0.50 (0.48)	−0.45 (−0.45)	−0.43 (−0.44)	0.60 (0.61)	
$H_2C{=}CH{-}CH{=}NSO_2Ph$		N1	C2	C3	C4	
HOMO	−11.1 (−10.8)	0.32 (0.39)	0.11 (0.10)	−0.47 (−0.66)	−0.46 (−0.62)	
LUMO	−0.9 (−0.7)	0.50 (0.47)	−0.58 (0.58)	−0.30 (−0.30)	0.53 (0.57)	
$H_2C{=}CH{-}C(CO_2CH_3){=}NSO_2Ph$		N1	C2	C3	C4	CO_2CH_3
HOMO	−11.2 (−10.9)	0.32 (0.20)	0.12 (0.10)	−0.55 (−0.68)	−0.55 (−0.64)	0.05 (0.12)
LUMO	−1.1 (−0.7)	0.53 (0.54)	−0.60 (−0.68)	−0.21 (−0.19)	0.47 (0.34)	−0.10 (−0.14)
$H_2C{=}C(CO_2CH_3){-}CH{=}NSO_2Ph$		N1	C2	C3	C4	CO_2CH_3
HOMO	−11.5 (−11.2)	0.41 (0.30)	0.14 (0.11)	−0.58 (−0.64)	−0.54 (−0.58)	0.04 (0.01)
LUMO	−1.3 (−0.8)	0.40 (0.39)	−0.42 (−0.47)	−0.34 (−0.33)	0.63 (0.51)	−0.18 (−0.05)
$HC(CO_2CH_3){=}CH{-}CH{=}NSO_2Ph$		N1	C2	C3	C4	CO_2CH_3
HOMO	−11.5 (−11.3)	0.32 (0.21)	0.11 (0.09)	−0.47 (−0.63)	−0.49 (−0.63)	−0.02 (−0.03)
LUMO	−1.5 (−0.6)	0.43 (0.46)	−0.46 (−0.57)	−0.49 (−0.42)	0.46 (0.47)	0.00 (0.08)
$H_2C{=}CHOCH_3$		OCH_3	C1	C2		
HOMO	−9.5 (−9.4)	−0.51 (−0.46)	0.48 (0.51)	0.69 (0.71)		
LUMO	1.4 (1.2)	0.21 (0.20)	0.72 (0.71)	−0.66 (−0.66)		

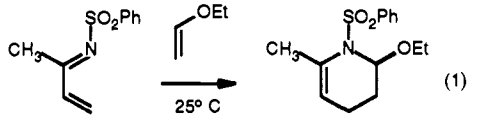
[a] AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. [b] MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4894.

Table IV

16 R^1	**17** (% yield)	**18** (% yield)	**19** or **20** (% yield)	**21** or **22**,[a] endo:exo (% yield)
C_6H_5	**17a** (94)	**18a** (82)	**19a** (69)	**21a**, >20:1 (80)
			20a (64)	**22a**, >20:1 (61)
$(CH_2)_5CH_3$	**17b** (89)	**18b** (55)	**19b** (64)	**21b**, >20:1 (55)
			20b (59)	**22b**, >20:1 (53)
CH_3	**17c** (72)	**18c** (72)	**19c** (45)	**21c**, >20:1 (51)
			20c (56)	**22c**, >20:1 (59)

[a] A total of 4 equiv of ethyl vinyl ether employed.

stereochemistry, to exhibit little solvent dependency on the [4 + 2] cycloaddition rate (k_{rel}(ethyl vinyl ether): CH_3CN (2), CH_2Cl_2 (1.5), toluene (1) for **1e** (eq 1)) and were found to react more



(1)

rel. rates: CH_3CN (2), CH_2Cl_2 (1.5), toluene (1)

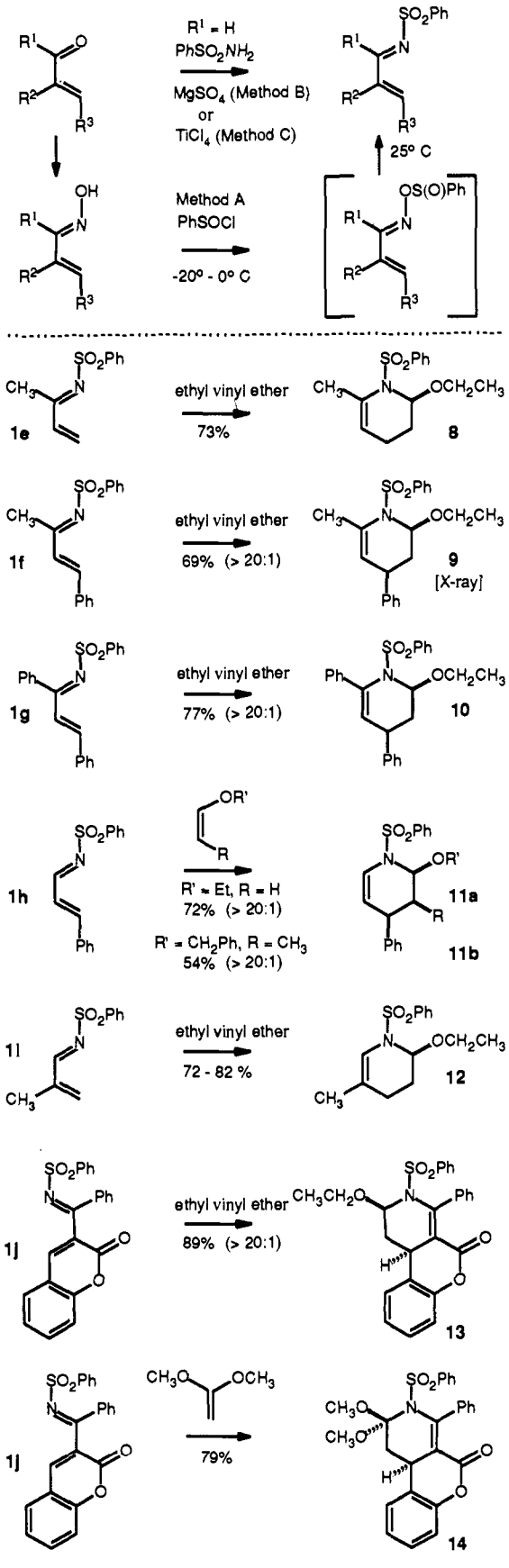
rapidly with trans 1,2-disubstituted dienophiles than with cis 1,2-disubstituted dienophiles (1-(benzyloxy)propene: $k(E)/k(Z)$ = 6.3 for **1h**).[19] In addition, even the α,β-unsaturated N^1-(phenylsulfonyl)imines that preferentially exist in the extended *s*-*E*-diene conformation (e.g., **1h**) were found to participate readily in the $LUMO_{diene}$-controlled Diels–Alder reactions. The stereochemistry of the [4 + 2] cycloaddition reaction products was established by spectroscopic techniques[20] and was unambiguously confirmed with the single-crystal X-ray structure determination of adduct **9**.[21a]

(19) Treatment of **1h** with a 64:36 mixture of (*Z*)-:(*E*)-benzyl 1-propenyl ether (55% yield, 42 h, toluene, 6 kbar, 25 °C) provided a 22:78 mixture of the corresponding [4 + 2] cycloaddition products, $k(E)/k(Z)$ = 6.3.

(20) The X-ray crystal structure of **9** was consistent with the spectroscopically (^{1}H NMR) assigned structure and stereochemistry ($J_{C2\text{-}H_{eq}/C3\text{-}H_{ax}} \leq 2.0$–$2.5$ Hz, $J_{C2\text{-}H_{eq}/C3\text{-}H_{eq}} \leq 4.0$ Hz, $J_{C3\text{-}H_{ax}/C4\text{-}H_{eq}} = 7.0$–$9.0$ Hz, $J_{C3\text{-}H_{eq}/C4\text{-}H_{eq}} \cong 4.0$ Hz, $^1J_{C2/H2} = 160$–165 Hz). For **9**: $J_{C2\text{-}H_{eq}/C3\text{-}H_{ax}} = 2.3$ Hz, $J_{C2\text{-}H_{eq}/C3\text{-}H_{eq}} = 4.0$ Hz, $J_{C3\text{-}H_{ax}/C4\text{-}H_{eq}} = 8.6$ Hz, $J_{C3\text{-}H_{eq}/C4\text{-}H_{eq}} = 4.0$ Hz, $^1J_{C2/H2} = 163$ Hz. The stereochemistry of **2c–l** and **8–14** was assigned spectroscopically. For example, the all-cis stereochemistry for **11b** and the axial C2 OEt orientation were established spectroscopically: $J_{C2\text{-}H_{eq}/C3\text{-}H_{ax}} = 2.3$ Hz; $J_{C3\text{-}H_{ax}/C4\text{-}H_{eq}} = 7.7$ Hz, $^1J_{C2/H2} = 166$ Hz. The ^1J for an axial C–H adjacent to N (or O) in a six-membered ring is significantly smaller (ca. 10 Hz) than ^1J for an equatorial C–H, $^1J_{C\text{-}H_{ax}} < {}^1J_{C\text{-}H_{eq}}$. Takeuchi, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 210; Binst, G. V.; Tourwe, D. *Heterocycles* **1973**, *1*, 257. This characteristically large C2/H2 coupling constant proved diagnostic in the conformational assignment (i.e., axial OR) and subsequent spectroscopic interpretation of coupling constants.

(21) (a) Full details of the X-ray structure determination of **9** have been provided elsewhere.[10] Supplementary material includes an ORTEP representation of **9** that illustrates the C2/C4 relative stereochemistry, the axial orientation of C2 OEt, the pseudoaxial orientation of C4 phenyl, and the near-planar N^1-nitrogen that lies approximately 0.21 Å above the plane of the attached substituents syn to the C2 OEt. (b) Full details of the X-ray structure determination of **21a** and **28a** have been provided elsewhere.[11] Supplementary material includes an ORTEP representation of **21a** and **28a**. (c) Full details of the X-ray structure determinations of **40**-endo, **45**-endo, and **48**-endo have been provided elsewhere.[12] Supplementary material includes ORTEP representations of the structures.

Scheme III



Computational studies summarized in Table III support the observation of the expected [4 + 2] cycloaddition regioselectivity and endo diastereoselectivity. The magnitude of the $LUMO_{diene}$ C4 coefficient proved largest of the diene termini supporting the observed cycloaddition regioselectivity. In the instances where the diene termini LUMO coefficients proved comparable in magnitude, the strong secondary orbital interactions ($LUMO_{diene}$ C2 and $HOMO_{dienophile}$ OR) may serve to dictate the reaction regioselectivity as well as the reaction diastereoselectivity. The sequential N1 and C3 addition of electron-withdrawing substituents ($-SO_2Ph$ and $-CO_2Me$, respectively) substantially lowers the azadiene E_{LUMO} supporting the observed rate acceleration in the $LUMO_{diene}$-controlled [4 + 2] cycloaddition. In addition, the computational studies suggest that the unusually high endo diastereoselectivity may be derived in part from a pronounced stabilizing secondary orbital interaction between diene C2 (LUMO) and the dienophile OR (HOMO). However, the degree of endo diastereoselectivity observed with the *N*-sulfonyl-1-aza-1,3-butadienes exceeds that customarily observed in thermal [4 + 2] cycloaddition reactions, suggesting that this stabilizing secondary orbital interaction may only be part of the origin of the diastereoselectivity. In addition and as a consequence of the boat transition state for the [4 + 2] cycloaddition reaction, the lone pair on nitrogen and the σ C–O bond of the dienophile lie trans periplanar to each other in the preferred endo transition state, suggesting a n–σ^* stabilization of the endo transition state comparable to that responsible for the ground-state anomeric effect. A similar stabilizing n–σ^* interaction is not present in the exo [4 + 2] cycloaddition transition state, and this difference may further contribute to the unusually high endo diastereoselectivity observed in the Diels–Alder reactions of such systems (Figure 1).

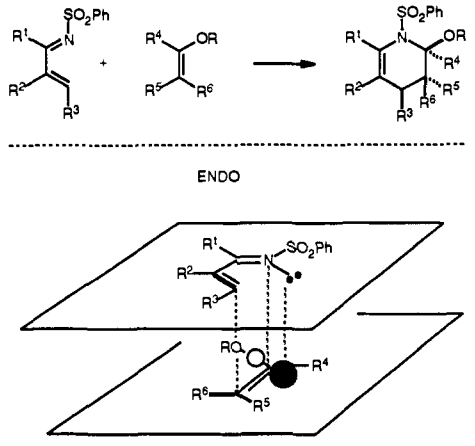


Figure 1.

Room-Temperature, Endo-Specific 1-Aza-1,3-butadiene Diels–Alder Reactions: Acceleration of the $LUMO_{diene}$-Controlled [4 + 2] Cycloaddition Reactions through Noncomplementary Azadiene Substitution. In the preceding efforts, the 4π participation of simple, stable *N*-(phenylsulfonyl)-1-aza-1,3-butadienes in regiospecific and endo-specific inverse electron demand Diels–Alder reactions was observed under the mild thermal conditions of ca. 100 °C, and the complementary substitution of the 1-aza-1,3-butadienes with a C3 electron-withdrawing substituent was shown to predictably accelerate the [4 + 2] cycloadditioin reaction to the extent that the reaction may be observed at 25 °C. In contrast to the complementary C3 addition of an electron-withdrawing substituent to the 1-aza-1,3-butadiene system, the noncomplementary C2 or C4 addition of an electron-withdrawing group would not be expected to additionally stabilize a developing zwitterionic or biradical transition state for a [4 + 2] cycloaddition reaction. However, the AM1 computational studies detailed in Table III illustrate that the *noncomplementary* C2 and/or C4 addition of an electron-withdrawing substituent to the 1-azadiene lowers the $LUMO_{diene}$ and may serve to accelerate its participation in a $LUMO_{diene}$-controlled reaction. This, as well as the effect of the size of sulfonyl substituent on the diastereoselectivity of the [4 + 2] cycloaddition reaction, was examined through the preparation and study of *N*-(phenylsulfonyl)- and *N*-(methylsulfonyl)-2-(ethoxycarbonyl)-1-aza-1,3-butadienes **19** and **20**.

Scheme IV

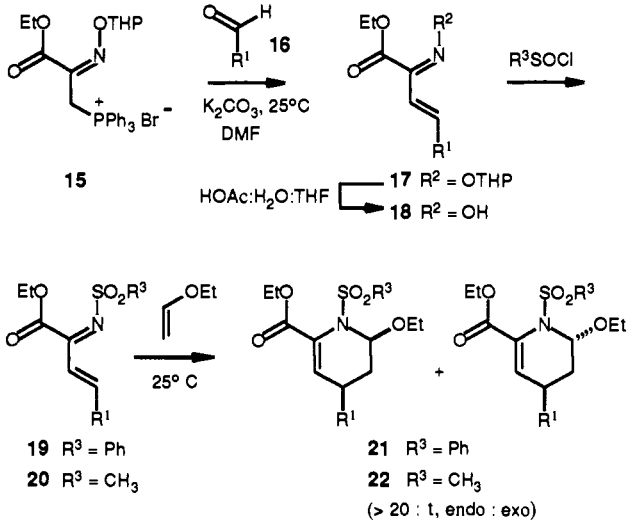


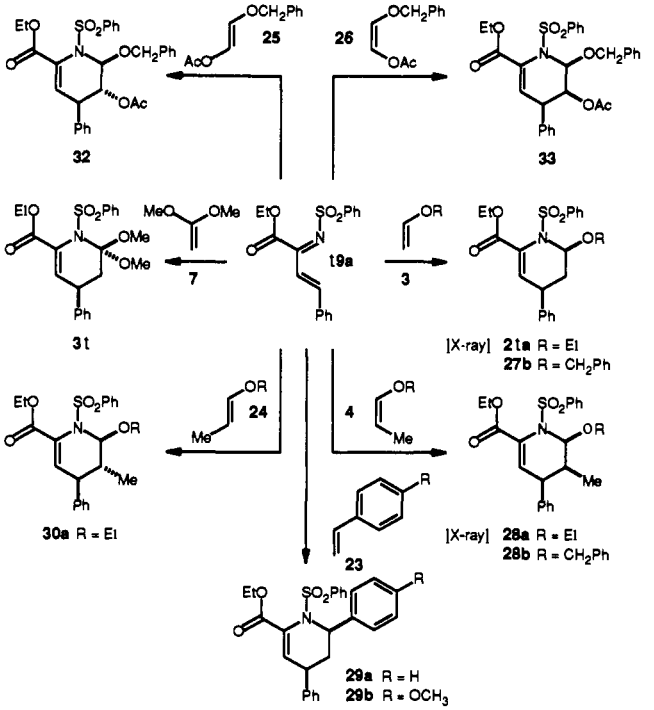
Table V

dienophile, R	conditions:[a] temp (°C), time (h), solvent, pressure (kbar)	product, endo:exo (% yield)
3a, Et	25, 24, CH_2Cl_2	**21a**, >20:1 (80)
3b, CH_2Ph	25, 15, CH_2Cl_2	**27b**, >20:1 (84)
4a, Et	25, 120, CH_2Cl_2	**28a**, >20:1 (49)
4a, Et	25, 96, CH_2Cl_2, 6.2	**28a**, >20:1 (54)
4b, CH_2Ph	25, 104, CH_2Cl_2, 6.2	**28b**, >20:1 (50)
23a, H	25, 96, CH_2Cl_2	**29a**, (0)
23a, H	80, 7 days, toluene	**29a**, (0)
23a, H	25, 67, CH_2Cl_2, 6.2	**29a**, >20:1 (37)
23a, H	25, 97, CH_2Cl_2, 13.0	**29a**, >20:1 (48)
23b, OCH_3	25, 72, CH_2Cl_2	**29b**, >20:1 (12)
23b, OCH_3	80, 48, toluene	**29b**, >20:1 (46)
23b, OCH_3	25, 97, CH_2Cl_2, 13.0	**29b**, >20:1 (87)
24a, Et	25, 36, CH_2Cl_2 6.2	**30a**, >20:1 (65)
7	25, 1, CH_2Cl_2	**31**, (58)
25	25, 97, CH_2Cl_2, 6.2	**32**, >20:1 (50)
26	25, 97, CH_2Cl_2, 6.2	**33**, >20:1 (68)

[a] A total of 4 equiv of dienophile employed.

The 4-substituted *N*-(phenylsulfonyl)- and *N*-(methylsulfonyl)-2-(ethoxycarbonyl)-1-aza-1,3-butadienes **19** and **20** were prepared through Wittig reaction of the stabilized phosphorane generated in situ from the phosphonium salt **15**[22] (K_2CO_3, 25 °C, DMF) with aldehydes (25 °C, DMF, 20–40 h, 94–72%) followed by acid-catalyzed removal of the tetrahydropyranyl (THP) group (HOAc/H_2O/THF, 3:1:1, 55 °C, 37–53 h),[23] *O*-phenylsulfinyl or *O*-methylsulfinyl formation (PhSOCl or CH_3SOCl, Et_3N, 0 °C, CCl_4 or Et_2O, 0.5–1.0 h), and subsequent in situ homolytic rearrangement (25 °C, 1–3 h) to provide **19** and **20** (Scheme IV and Table IV).[24] The results of the [4 + 2] cycloaddition reaction of **19** and **20** with ethyl vinyl ether (25 °C, CH_2Cl_2, 0.2–0.5 M, 17–26 h) *conducted at room temperature* are detailed in Table IV, and the comparative results of the reaction of **19a** with a range of dienophiles are summarized in Scheme V and Table V. The

Scheme V



assigned stereochemistry of the [4 + 2] cycloadducts was derived initially from diagnostic ^1H NMR chemical shifts and coupling constants,[25] was supported by 2-D NOE experiments,[26] and was unambiguously established with the single-crystal X-ray structure determinations of **21a**[21b] and **28a**[21b] coupled with chemical correlation (e.g., **30**).

The [4 + 2] cycloaddition reactions of **19** and **20** with vinyl ethers were determined to proceed predominantly if not exclusively (≥95%) through an endo transition state, and the endo diastereoselectivity proved independent of the size of the *N*-sulfonyl substituent (R^3 = Ph = CH_3). In addition, the [4 + 2] cycloaddition reactions were found to proceed with full preservation of the dienophile olefin geometry in the stereochemistry of the reaction products (Scheme V), to exhibit little solvent dependency on the [4 + 2] cycloaddition rate (k_{rel}(ethyl vinyl ether): CH_3CN and CH_2Cl_2 (2), C_6H_6 (1) for **19a**), and the noncomplementary C2 addition of an electron-withdrawing group ($-CO_2Et$) to the *N*-(phenylsulfonyl)-1-aza-1,3-butadiene was determined to substantially accelerate the rate of [4 + 2] cycloaddition, eqs 2 and 3 (k(**19a**)/k(**1f** or **1h**) > 20).[27] Further consistent with the characteristics of a concerted Diels–Alder reaction, trans 1,2-disubstituted dienophiles were found to react more rapidly than cis 1,2-disubstituted dienophiles with **19a** ($k(E)/k(Z)$ = 9.2 (1 atm), 5.6 (6.2 kbar) for 1-ethoxypropene),[28] the cis 1,2-disubstituted dienophiles exhibited a preferential pressure-induced rate acceleration, and the [4 + 2] cycloaddition reactions of the cis

(22) For the related preparation and Wittig reactions of $EtO_2CC(NOCH_3)CH_2PPh_3^+Br^-$, see: Bicknell, A. J.; Burton, G.; Elder, J. S. *Tetrahedron Lett.* **1988**, *29*, 3361.

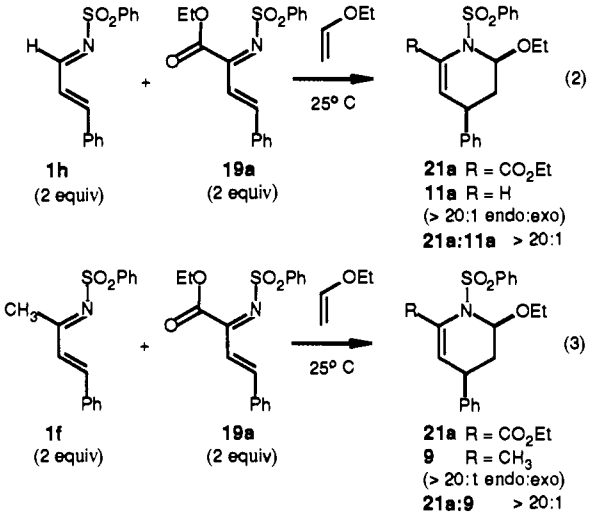
(23) Since the conduct of this work, we have found that deprotection of the tetrahydropyranyl ethers may be accomplished in shorter reaction times by using catalytic Amberlyst H-15 in an ethanolic solution of the tetrahydropyranyl oxime. Bongini, A.; Cardillo, G.; Orena, M.; Sergio, S. *Synthesis* **1979**, 618.

(24) Consistent with intuitive expectations, the *N*-sulfonylimines **19** and **20** proved more sensitive to hydrolysis by adventitious water than *N*-sulfonyl azadienes lacking the C2 ethoxycarbonyl group but may be purified by rapid chromatography (SiO_2, Florisil) with partial but not extensive loss of material.

(25) Characteristic coupling constants (C2-OR axial): $J_{C2\text{-}H_{eq}/C3\text{-}H_{eq}}$ = 2.7–5.0 Hz, $J_{C2\text{-}H_{eq}/C3\text{-}H_{ax}}$ = 2.5–4.4 Hz, $J_{C3\text{-}H_{eq}/C4\text{-}H_{eq}}$ = 1.7–3.3 Hz, $J_{C3\text{-}H_{ax}/C4\text{-}H_{eq}}$ = 8.9–9.3 Hz, $J_{C4\text{-}H_{eq}/C5\text{-}H}$ = 3.2–3.6 Hz, $^1J_{C2/H2}$ = 163–158 Hz. The exceptions (**30**, **32**, **29**) may exist in the all-equatorial conformation: for **30** $J_{C2\text{-}H_{ax}/C3\text{-}H_{ax}}$ = 4.4 Hz, $J_{C3\text{-}H_{ax}/C4\text{-}H_{ax}}$ = 13 Hz, $J_{C4\text{-}H_{ax}/C5\text{-}H}$ = 3.6 Hz, $^1J_{C2/H2}$ = 156.6 Hz; for **32** $^1J_{C2/H2}$ = 153.7 Hz; for **29** $^1J_{C2/H2}$ = 140–145 Hz. The single-crystal X-ray structure determinations of **21a** and **28a** established the C2/C4 and C2/C3/C4 cis relative stereochemistry that must arise through endo [4 + 2] cycloaddition and proved consistent with the ^1H NMR spectroscopically assigned structures and stereochemistry. For **19a**: $J_{C2\text{-}H_{eq}/C3\text{-}H_{eq}}$ = 2.5 Hz, $J_{C2\text{-}H_{eq}/C3\text{-}H_{ax}}$ = 4.1 Hz, $J_{C3\text{-}H_{eq}/C4\text{-}H_{eq}}$ = 3.0 Hz, $J_{C3\text{-}H_{ax}/C4\text{-}H_{eq}}$ = 9.3 Hz, $J_{C4\text{-}H_{eq}/C5\text{-}H}$ = 3.6 Hz, $^1J_{C2/H2}$ = 158.5 Hz. For **28a**: $J_{C2\text{-}H_{eq}/C3\text{-}H_{ax}}$ = 2.8 Hz, $J_{C3\text{-}H_{ax}/C4\text{-}H_{eq}}$ = 8.9 Hz, $J_{C4\text{-}H_{ax}/C5}$ = 3.4 Hz, $^1J_{C2/H2}$ = 159.9 Hz.

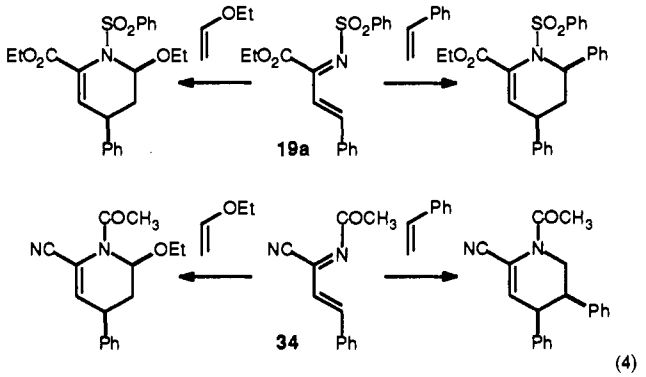
(26) Full details of the studies conducted are presented in supplementary material.

(27) No trace of the Diels–Alder products derived from **1h** or **1f** was detected in the reaction mixture.



1,2-disubstituted dienophiles were found to proceed predominantly (>95%) through an endo transition state despite the increased destabilizing steric interactions (e.g., **28a**). The azadiene **19a** proved sufficiently reactive to undergo intermolecular [4 + 2] cycloaddition with a full range of dienophiles including the relatively unreactive olefins **23** (R = OCH_3 > H, Scheme V), suggesting a broad and general scope for such 1-aza-1,3-butadiene Diels–Alder reactions.[29] In addition, the studies demonstrate that the *noncomplementary* addition of a C2 electron-withdrawing substituent ($-CO_2Et$) to the *N*-sulfonyl-1-aza-1,3-butadienes predictably accelerates their 4π participation in $LUMO_{diene}$-controlled [4 + 2] cycloaddition reactions, maintains the expected cycloaddition regioselectivity, maintains or enhances the cycloaddition endo diastereoselectivity (>95%), and illustrates that the reactions display characteristics consistent with a concerted $LUMO_{diene}$-controlled [4 + 2] cycloaddition reaction.

Room-Temperature, Endo-Selective $LUMO_{diene}$-Controlled [4 + 2] Cycloaddition Reactions of *N*-Sulfonyl-4-(ethoxycarbonyl)-1-aza-1,3-butadienes. Concurrent with our efforts, Fowler and Teng[13] have examined the intra- and intermolecular [4 + 2] cycloaddition reactions of *N*-acyl-2-cyano-1-aza-1,3-butadienes and have disclosed that such dienes participate in [4 + 2] cycloaddition reactions with electron-rich dienophiles with a reactivity, regioselectivity, and diastereoselectivity comparable to the *N*-sulfonyl-2-(ethoxycarbonyl)-1-aza-1,3-butadienes. However, in contrast to our observation of the 2-aryl-1,2,3,4-tetrahydropyridine cycloaddition regioisomer derived from the [4 + 2] cycloaddition of styrenes with **19a**, Fowler and Teng[13] have described the observation of the predominant 3-aryl-1,2,3,4-tetrahydropyridines with **34** albeit in mixtures (8–1:1) with the 2-aryl regioisomer, eq 4. Consequently, in efforts to define the



Scheme VI

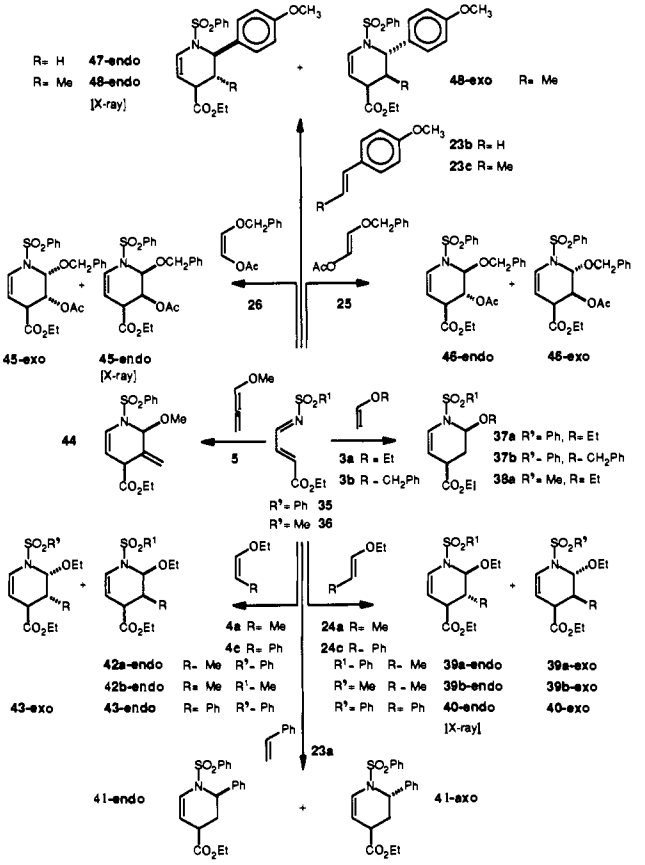


Table VI

diene	dienophile, R (equiv)	conditions: temp (°C), time (h), solvent, pressure (kbar)	product, endo:exo (% yield)
35	**3a**, Et (5)	21, 46, CH_2Cl_2	**37a**, >20:1 (82)
35	**3b**, CH_2Ph (5)	21, 46, CH_2Cl_2	**37b**, >20:1 (88)
36	**3a**, Et (5)	21, 56, CH_2Cl_2	**38a**, >20:1 (73)
35	**24a**, Me (3)	21, 37, CH_2Cl_2	**39a**, 2.2:1 (93)
36	**24a**, Me (3)	21, 43, CH_2Cl_2	**39b**, 2.2:1 (91)
35	**24c**, Ph (2.5)	21, 61, CH_2Cl_2	**40**, 5:1 (61)
35	**24c**, Ph (2.5)	21, 47.5, CH_2Cl_2, 13.3	**40**, 4:1 (57)
35	**23a** (5)	80, 69, C_6H_6	**41**, 6.5:1 (45)
35	**23a** (2.5)	21, 45.5, CH_2Cl_2, 13.3	**41**, 11:1 (48)
35	**4a**, Me (4)	21, 69, CH_2Cl_2	**42a**, >20:1 (48)
35	**4a**, Me (2)	21, 45.5, CH_2Cl_2, 13.3	**42a**, >20:1 (50)
36	**4a**, Me (4)	21, 66, CH_2Cl_2	**42b**, >20:1 (36)
35	**4c**, Ph (2)	40, 64, CH_2Cl_2	**43**, 1:3 (41)
35	**4c**, Ph (2.5)	21, 49.5, CH_2Cl_2, 13.3	**43**, 2.2:1 (42)
35	**5** (5)	0, 82, CH_2Cl_2	**44**, >20:1 (56)
35	**26** (3)	21, 49.5, CH_2Cl_2, 13.3	**45**, >20:1 (42)
35	**26** (3)	80, 21, C_6H_6	**45**, 8:1 (32)
35	**25** (3)	21, 135, CH_2Cl_2	**46**, 2.4:1 (71)
35	**25** (2.5)	21, 49.5, CH_2Cl_2, 13.3	**46**, 2.2:1 (74)
35	**23b**, H (5)	21, 46, CH_2Cl_2	**47**, >20:1 (63)
35	**23c**, Me (2)	80, 53, C_6H_6	**48**, 4:1 (44)
35	**23c**, Me (2.5)	21, 47.5, CH_2Cl_2, 13.3	**48**, 4:1 (60)

origin of the differences in the two systems, we have examined the [4 + 2] cycloaddition reactions of *N*-(phenylsulfonyl)- and *N*-(methylsulfonyl)-4-(ethoxycarbonyl)-1-aza-1,3-butadiene (**35** and **36**).

Controlled ozonolysis of ethyl sorbate[30] followed by condensation of ethyl 4-oxo-2-butenoate with benzene- or methanesulfonamide

(28) The relative rates of [4 + 2] cycloaddition were derived from product distributions obtained from the reaction of a mixture of (*Z*)- and (*E*)-ethyl-1-propenyl ether (2.8:1, 10 equiv) with **19a** (25 °C, 96 h, CH_2Cl_2, 1 atm), **28a**/**20a** ((1.0:3.3), 54% and 25 °C, 96 h, CH_2Cl_2, 6.2 kbar), **28a**/**30a** (1.0:2.0), 65%).

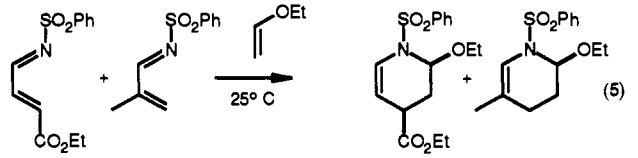
(29) Diene **19a** failed to participate in a [4 + 2] cycloaddition reaction with 1-octene, methyl acrylate, and *p*-benzoquinone, and diene **35** failed to react with methyl acrylate and *p*-benzoquinone under reaction conditions detailed herein.

(0.5 equiv of $TiCl_4$, CH_2Cl_2, 0 °C for 8 h) provided *N*-(phenylsulfonyl)- and *N*-(methylsulfonyl)-4-(ethoxycarbonyl)-1-aza-1,3-butadiene (**35** and **36**, 60–46%).[31] The results of a survey of [4 + 2] cycloaddition reactions of **35** and **36** with a full range of dienophiles are summarized in Scheme VI and Table VI. The structure and stereochemistry of the [4 + 2] cycloadducts were assigned initially on the basis of diagnostic ^1H NMR chemical shifts and coupling constants,[32] were firmly established through NOE difference experiments,[26] and were unambiguously established with the single-crystal X-ray structure determinations[21c] of **40**-endo, **45**-endo, and **48**-endo in conjunction with the deliberate epimerization and interconversion studies.[26]

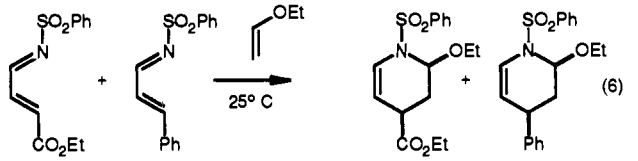
The [4 + 2] cycloaddition reactions of **35** and **36** were established to proceed predominantly or exclusively (2.2:1 to >20:1) through an endo transition state independent of the size of the *N*-sulfonyl substituent (R^1 = Ph = CH_3). Like observations made in earlier studies, the reactions of **35** and **36** with simple vinyl ethers (**3** and **5**), cis 1,2-disubstituted vinyl ethers possessing a small C2 substituent (CH_3 or OAc, **4a** and **26**), and unsubstituted styrenes (**23a,b**) proceed with high (11:1 for **23a**) or near exclusive (>20:1 for **3**, **4a**, **5**, **23b**, and **26**) endo diastereoselectivity. In contrast to the endo-specific cycloaddition reactions of the preceding dienes, the reactions of **35** and **36** with trans 1,2-disubstituted dienophiles (**23c**, **24**, **25**) and a cis 1,2-disubstituted vinyl ether possessing a large C2 substituent (Ph, **4c**) proceed predominantly (2.2–5:1) but not exclusively through an endo transition state. The modest endo diastereoselectivity of the reaction of the *N*-phenylsulfonyl diene **35** with (*E*)-1-ethoxypropene proved comparable to the results obtained with the *N*-methylsulfonyl diene **36** (2.2:1), highlighting the observation that the cycloaddition diastereoselectivity has proven independent of the size of the *N*-sulfonyl substituent. Consistent with expectations, the endo diastereoselectivity decreases with increasing reaction temperature and increases with increasing reaction pressure. From a comparison of the thermal and high pressure (13 kbar) results for the preparation of **43** (endo versus exo), the estimate for the $\Delta\Delta V^{\ddagger}$ (endo versus exo transition state) derived from the Drude–Nernst equation is −4 cm³/mol (25 °C). The [4 + 2] cycloaddition reactions were found to exhibit little solvent dependency on the cycloaddition rate (k_{rel}(**35**): CH_3CN (0.9), CH_2Cl_2 (1), C_6H_6 (1) for ethyl vinyl ether)[33] and were found to proceed with full preservation of the dienophile olefin geometry in the stereochemistry of the reaction products. Further characteristic of a concerted Diels–Alder reaction, trans 1,2-disubstituted dienophiles were found to react more rapidly than cis 1,2-disubstituted dienophiles with **35** ($k(E)/k(Z)$ = 13.4 (1 atm) for 1-ethoxypropene).[34] Most impressively, the noncomplementary C4 addition of an electron-withdrawing group to the *N*-(phenylsulfonyl)-1-aza-1,3-butadiene was found to substantially accelerate the rate of [4 + 2] cycloaddition [k(**35**)/k(**1h** or **1i**) > 20], eqs 5 and 6.[35] As such, the dienes **35** and **36** were found to be sufficiently reactive to participate in intermolecular [4 + 2] cycloaddition reactions with a full range of dienophiles, including ketene acetals, substituted vinyl ethers, (*E*)- and (*Z*)-2-benzyloxy vinyl acetate, and the relatively unreactive alkenes **23** ((k(**23b**)/k(**23a**) > 20)) (Scheme VI). Notably, even the styrenes provide a single cycloaddition regioisomer in which the inherent regioselectivity of the [4 + 2] cycloaddition reaction is unaltered by the diene C4 ethoxycarbonyl group and the room-temperature, endo-specific reaction of **23b** (**23b** ≫ **23a**) is consistent with the diene participation in a $LUMO_{diene}$-controlled Diels–Alder reaction. Remarkably, under pressure-promoted reaction conditions (21 °C, 13.3 kbar, CH_2Cl_2, 6 days), diene **35** proved sufficiently reactive to undergo [4 + 2] cycloaddition with the unactivated dienophile, 1-octene, to provide a single cycloaddition regioisomer derived through the compact endo transition state albeit in modest conversion (18%, **49**).[29] Thus, the studies demonstrate that the noncomplementary C4 addition of an electron-withdrawing group (−CO_2Et) to the electron-deficient 1-azadienes accelerates their 4π participation in $LUMO_{diene}$-controlled [4 + 2] cycloaddition reactions, maintains the [4 + 2] cycloaddition regioselectivity and endo diastereoselectivity of the parent *N*-sulfonyl-1-aza-1,3-butadienes, and that the [4 + 2] cycloaddition reactions display characteristics consistent with concerted $LUMO_{diene}$-controlled [4 + 2] cycloaddition reactions.

Table VII. C2–H2 Coupling Constants (Hz, $CDCl_3$, 50 Hz)[20]

8	161	**27b**	159	**39**-endo	164
9	164	**28a**	159	**40**-endo	166
11a	159	**28b**	158	**41**-endo	144
11b	166	**29a**	141	**42**-endo	162
12	151	**29b**	144	**43**-endo	162
21a	159	**30a**	157	**43**-exo	164
21b	159	**32**	154	**45**-endo	166
21c	159	**33**	160	**47**-endo	142
22a	163	**37a**-endo	164	**48**-endo	137
22b	163	**37b**-endo	159		
22c	162	**38b**-endo	164		



35 (2 equiv) **1l** (2 equiv) **37a** **37a:12** **12** (>20:1)



35 (2 equiv) **1h** (2 equiv) **37a** **37a:11a** **11a** (>20:1)

Experimental Section[36]

General Procedures for the Preparation of α,β-Unsaturated *N*-(Phenylsulfonyl)imines. Method A: 1-(1-Cyclohexenyl)-1-[(phenylsulfonyl)-

(30) Stotter, P. L.; Eppner, J. B. *Tetrahedron Lett.* **1973**, 2417.

(31) Unlike simple *N*-sulfonylimines, **35** and **36** proved sensitive to hydrolysis by adventitious water and could not be purified by chromatography without extensive loss of material. All yields of cycloadducts of **35** and **36** are based on pure material isolated by chromatography (Florisil, 100–200 mesh) or recrystallization. Cycloadducts with endo/exo ratios of 5:1 or less were separated chromatographically and independently characterized fully. Cycloadducts with endo/exo ratios of 11:1 or greater were separated and the major diastereomer characterized fully. Endo/exo diastereomer ratios were established spectroscopically (^1H NMR, integration) as detailed in the experimental section.

(32) Characteristic coupling constants: C2-OR axial $J_{C2\text{-}H_{eq}/C3\text{-}H_{ax}}$ = 1.2–2.3 Hz, $J_{C2\text{-}H_{eq}/C3\text{-}H_{eq}}$ = < 1–2.7 Hz, $J_{C3\text{-}H_{ax}/C4\text{-}H_{eq}}$ = 5.5–7.6 Hz, $J_{C3\text{-}H_{eq}/C4\text{-}H_{eq}}$ = 1.2–2.5 Hz; C2-aryl axial $J_{C2\text{-}H_{eq}/C3\text{-}H_{ax}}$ = 3.7–5.1 Hz, $J_{C2\text{-}H_{eq}/C3\text{-}H_{eq}}$ = < 1 Hz, $J_{C3\text{-}H_{ax}/C4\text{-}H_{eq}}$ = 6.8–7.0 Hz, $J_{C3\text{-}H_{eq}/C4\text{-}H_{eq}}$ < 1 Hz.

(33) The solvent rate study was conducted in deuterated solvents and monitored by ^1H NMR (300 or 500 MHz) where the comparison of the amount of starting material to product could easily be determined. A solution of **35** in solvent was cooled to 0 °C and treated with ethyl vinyl ether (5 equiv).

(34) A solution of **35** (CH_2Cl_2, 0 °C) was treated with a mixture of (*Z*)- and (*E*)-ethyl-1-propenyl ether (2.8:1, 20 equiv) and stirred while gradually warming to 21 °C. After 44 h, a 4.8:1 ratio of cycloadducts arising from (*E*)- and (*Z*)-ethyl 1-propenyl ether, respectively, was observed by ^1H NMR (300 MHz, $CDCl_3$).

(35) A solution of **35** (0.16 mmol) and diene **1i**/**1h** (0.16 mmol) in CH_2Cl_2 was cooled to 0 °C and treated with ethyl vinyl ether (0.08 mmol). Inspection of the crude product by ^1H NMR (500 MHz, $CDCl_3$) showed a >20:1 (**37a**/**11a** or **12**) ratio of products after 52 h.

imino]ethane (1d). A solution of 1-acetylcyclohexene oxime (2.00 g, 14.4 mmol) in carbon tetrachloride (100 mL, 0.14 M) cooled to 0 °C under nitrogen was treated sequentially with triethylamine (1.75 g, 2.40 mL, 17.3 mmol, 1.2 equiv) and benzenesulfinyl chloride (2.54 g, 1.95 mL, 15.8 mmol, 1.1 equiv), and the resulting reaction mixture was stirred at 0 °C for 15 min. The triethylamine hydrochloride was removed by filtration, and the filtrate was stirred at 25 °C for 12 h under nitrogen. The intermediate *O*-phenylsulfinyl oximes were observed by TLC and were found to have a slightly higher R_f value than the α,β-unsaturated *N*-(phenylsulfonyl)imines. The reaction mixture was washed with water (2 × 100 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Moisture-sensitive imines were not washed with water. Flash chromatography (SiO_2, 5 cm × 13 cm, 10% EtOAc/hexane eluant) afforded pure **1d** (2.60 g, 3.79 g theoretical, 69%) as a pale yellow oil.

Method B: (*E*)-3-Phenyl-1-[(phenylsulfonyl)imino]-2-propene (1h). A solution of cinnamaldehyde (2.00 g, 15.1 mmol) in toluene (150 mL) was treated with benzenesulfonamide (2.62 g, 16.6 mmol, 1.1 equiv) and $MgSO_4$ (2 g/mmol, 30.0 g), and the reaction mixture was stirred at reflux for 120 h. The reaction mixture was cooled to room temperature, the $MgSO_4$ was removed by filtration, and the filtrate was concentrated in vacuo. Flash chromatography (SiO_2, 6 cm × 13 cm, 15% EtOAc/hexane eluant) afforded **1h** (2.05 g, 4.10 g theoretical, 50%) as a pale yellow solid.

Method C: 2-Methyl-1-[(phenylsulfonyl)imino]-2-propene (1i). A solution of methacrolein (2.00 g, 28.5 mmol) in dichloromethane (150 mL) was cooled to 0 °C under nitrogen and treated with triethylamine (8.65 g, 11.9 mL, 85.5 mmol, 3.0 equiv) and benzenesulfonamide (4.48 g, 28.5 mmol, 1.0 equiv). Titanium tetrachloride (2.97 g, 15.7 mmol, 0.55 equiv) was added dropwise to the reaction solution, and the mixture was stirred for an additional 30 min at 0 °C. The titanium salts were removed by filtration of the reaction mixture through Celite. The Celite pad was washed with dichloromethane (150 mL), and the combined filtrates were concentrated in vacuo to provide the reactive (phenylsulfonyl)imine **1i**. Rapid purification (SiO_2, 6 cm × 10 cm, 15% EtOAc/hexane eluant) afforded **1i** (3.32 g, 5.96 g theoretical, 56%) as a clear oil that was used immediately in subsequent reactions.

General Procedure for the [4 + 2] Cycloaddition Reactions of α,β-Unsaturated *N*-(Phenylsulfonyl)imines. Pressure-Promoted [4 + 2] Cycloaddition. 1-(1-Cyclohexenyl)-1-[(phenylsulfonyl)imino]ethane (**1d**, 208 mg, 0.790 mmol) was placed in a Teflon tube sealed with a brass clamp at one end and treated with a solution of ethyl vinyl ether (285 mg, 3.95 mmol, 5.0 equiv) in dichloromethane (0.79 mL). The mixture was purged with nitrogen and sealed with a brass clamp with the exclusion of air/nitrogen. The reaction vessel was placed in a pressure reactor (13 kbar) at 25 °C for 87 h. After depressurization, the reaction mixture was transferred to a round-bottom flask and concentrated in vacuo. Flash chromatography (Florisil, 100–200 mesh, 2 cm × 18 cm, 5% EtOAc/hexane eluant) afforded pure **2d** (235 mg, 265 mg theoretical, 89%) as a pale yellow solid.

Thermal Cycloaddition. A solution of **1d** (0.40 g, 1.5 mmol) in mesitylene (3.0 M, 0.48 mL) was placed in a Kontes vial and treated with ethyl vinyl ether (0.54 g, 7.5 mmol, 0.72 mL, 5.0 equiv). The reaction vessel was purged with nitrogen, sealed, and placed in an oil bath (115 °C) for 48 h. The cooled reaction mixture was transferred to a round-bottom flask and concentrated in vacuo. Flash chromatography (Florisil, 100–200 mesh, 2 cm × 13 cm, 5% EtOAc/hexane eluant) afforded **2d** (0.40 g, 0.50 g theoretical, 80%) as a pale yellow solid.

1-(1-Cyclohexenyl)-1-[(diphenylphosphinyl)imino]ethane (1c): ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.93 (4 H, m), 7.38 (6 H, m), 6.80 (1 H, m, CH=C), 2.60 (3 H, s, CH_3), 2.50 (2 H, m), 2.25 (2 H, m), 1.66 (4 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) 182.0, 140.8, 140.4, 139.3, 136.0, 134.3, 131.5, 131.0, 128.2, 128.1, 26.4, 24.6, 22.3, 21.4, 21.2; IR (neat) ν_{max} 3056, 2930, 1616, 1438, 1276, 1248, 1200, 1120, 998, 860, 796, 724, 696 cm^{-1}; EIMS *m/e* (relative intensity) 323 (43, M^+), 246 (13), 216 (21), 201 (base), 157 (18), 122 (68), 77 (89); CIMS (2-methylpropane) *m/e* (relative intensity) 324 (M + H^+, base); EIHRMS *m/e* 323.1439 ($C_{20}H_{22}NOP$ requires 323.1439).

1-(1-Cyclohexenyl)-1-[(phenylsulfonyl)imino]ethane (1d): mp 56–59 °C (EtOAc/hexane); ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.99 (2 H, d, J = 8 Hz), 7.50 (3 H, m), 6.90 (1 H, t, J = 4 Hz, C=CH), 2.66 (3 H, s, CH_3), 2.25 (2 H, m), 2.15 (2 H, m), 1.50 (4 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) 180.0 (e), 142.4 (o), 141.7 (e), 138.7 (e), 132.0 (o), 128.4 (o), 126.3 (o), 26.5 (e), 23.8 (e), 21.6 (e), 20.4 (e), 18.8 (o); IR (neat) ν_{max} 3064, 2936, 2862, 1626, 1566, 1480, 1448, 1384, 1306, 1254, 1152, 1090, 1024, 994, 952, 860 cm^{-1}; EIMS *m/e* (relative intensity) 263 (2, M^+), 157 (10), 141 (13), 122 (33), 109 (13), 93 (16), 81 (31), 79 (28), 77 (base), 67 (25), 55 (20), 51 (39); CIMS (2-methylpropane) *m/e* (relative intensity) 264 (M + H^+, base); EIHRMS *m/e* 263.0980 ($C_{14}H_{17}NO_2S$ requires 263.0980). Anal. Calcd for $C_{14}H_{17}NO_2S$: C, 63.85; H, 6.51; N, 5.32, S, 12.18. Found: C, 63.46; H, 6.22; N, 5.16; S, 12.29.

2-[(Phenylsulfonyl)imino]-3-butene (1e): ^1H NMR (C_6D_6, 300 MHz, ppm) 8.04 (2 H, d, J = 7 Hz), 7.05 (3 H, m), 6.03 (1 H, dd, J = 18, 10 Hz, CH=C), 5.53 (1 H, d, J = 18 Hz, CH_tH_c=C), 5.23 (1 H, d, J = 10 Hz, CH_tH_c=C), 1.73 (3 H, s, CH_3); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 179.1, 142.3, 138.6, 132.6, 128.9, 128.3, 128.0, 127.7, 127.3, 19.0; IR (neat) ν_{max} 3064, 2926, 1622, 1576, 1448, 1308, 1154, 1090, 1022, 846, 730, 688 cm^{-1}; EIMS *m/e* (relative intensity) 209 (14, M^+), 141 (52), 125 (11), 77 (base), 51 (22); CIMS (2-methylpropane) *m/e* (relative intensity) 210 (M + H^+, base); CIHRMS *m/e* 210.0588 ($C_{10}H_{11}NO_2S$ requireis 210.0588).

(*E*)-4-Phenyl-2-[(phenylsulfonyl)imino]-3-butene (1f): ^1H NMR (C_6D_6, 300 MHz, ppm) 8.20 (2 H, d, J = 7.4 Hz), 6.96 (8 H, m), 6.89 (1 H, d, J = 16 Hz, C=CH), 6.45 (1 H, d, J = 16 Hz, C=CH), 2.73 (3 H, s, CH_3); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 179.0 (e), 145.8 (o), 143.7 (o), 142.9 (e), 135.0 (e), 132.6 (o), 130.8 (o), 129.6 (o), 129.3 (o), 129.2 (o), 129.0 (o), 128.6 (o), 127.6 (o), 123.3 (o), 20.3 (o); IR (neat) ν_{max} 3062, 1624, 1560, 1448, 1372, 1306, 1210, 1152, 1090, 1026, 970, 884, 740, 688, 656, 636 cm^{-1}; CIMS (2-methylpropane) *m/e* (relative intensity) 286 (M + H^+, 41), 158 (base); EIHRMS *m/e* 285.0820 ($C_{16}H_{15}NO_2S$ requires 285.0822).

(*E*)-1,3-Diphenyl-1-[(phenylsulfonyl)imino]-2-propene (1g): ^1H NMR (C_6D_6, 300 MHz, ppm) 8.05 (2 H, d, J = 7 Hz), 7.61 (6 H, m), 7.50 (1 H, d, J = 16 Hz, C=CH), 7.43 (4 H, m), 7.26 (3 H, m), 7.06 (1 H, d, J = 16 Hz, CH=C); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 177.3, 148.5, 142.8, 134.7, 132.4, 131.7, 130.9, 130.4, 130.2, 130.1, 129.2, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 123.1, 102.3; IR (neat) ν_{max} 3050, 1616, 1578, 1540, 1448, 1320, 1152, 1086, 860, 810, 754, 688, 654 cm^{-1}; CIMS (2-methylpropane) *m/e* 348 (M + H^+, base); CIHRMS *m/e* 348.1058 ($C_{21}H_{17}NO_2S$ requires 348.1058).

(*E*)-3-Phenyl-1-[(phenylsulfonyl)imino]-2-propene (1h): mp 107–109 °C (EtOAc/hexane); ^1H NMR (C_6D_6, 300 MHz, ppm) 8.80 (1 H, d, J = 9 Hz, CH=N), 7.95 (2 H, d, J = 7.7 Hz), 7.40–7.70 (9 H, m), 7.00 (1 H, dd, J = 16, 9 Hz, CH=C); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 171.1, 153.1, 133.1, 131.3, 129.1, 128.8, 128.4, 128.3, 128.0, 127.7, 124.8; IR (neat) ν_{max} 3062, 1618, 1580, 1448, 1318, 1260, 1156, 1088, 1012, 966, 858, 784, 752, 724, 686, 632 cm^{-1}; EIMS *m/e* (relative intensity) 270 (4), 206 (16), 141 (68), 130 (39), 129 (base), 125 (43), 102 (29), 77 (53), 64 (11), 51 (30), 50 (23), 48 (23), 39 (28), 38 (15); CIMS (2-methylpropane) *m/e* (relative intensity) 272 (M + H^+, 1), 259 (11),

(36) Proton nuclear magnetic resonance spectra (^1H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded on a Gemini 200, QE-300, or VSR-500S spectrometer, and chemical shifts are reported in parts per million (ppm) relative to internal tetramethylsilane (0.00 ppm). For APT ^{13}C NMR, *e* = even and *o* = odd number of attached protons. Infrared spectra (IR) were recorded on a Perkin Elmer 1420 or Perkin Elmer Model 1800 FTIR as KBr pellets (solids) and thin films (liquids and oils). Melting points (mp) were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Electron impact mass spectra (EIMS) and chemical ionization mass spectra (CIMS) were recorded on a Finnegan 4000 mass spectrometer. Electron impact (EI) and chemical ionization (CI) high-resolution mass spectra (HRMS) were recorded on a Kratos MS-50 spectrometer. All high-pressure reactions were performed in a Leco hydraulically pressurized apparatus[37] containing a castor oil media using Teflon vessels sealed at both ends with brass screw clamps. Flash chromatography was performed on 230–400 mesh silica gel (SiO_2) and 100–200 mesh Florisil. Tetrahydrofuran (THF), ether (Et_2O), and benzene (C_6H_6) were distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from phosphorus pentoxide. Carbon tetrachloride (CCl_4), triethylamine (Et_3N), and *N*,*N*-dimethylformamide (DMF) were distilled from calcium hydride. Methanol (CH_3OH) was distilled from magnesium turnings. All extraction and chromatographic solvents: ethyl ether (Et_2O), dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), and hexane were distilled prior to use. All reactions requiring anhydrous conditions and/or an inert atmosphere were performed under a positive pressure of argon or nitrogen. Ethyl vinyl ether, 1,1-dimethoxyethylene, 2-methoxypropene, (*E*)-4-propenylanisole, styrene, and 4-vinylanisole were obtained from Aldrich Chemical Co., Inc. 1,1-Dimethoxyethylene was obtained from Wiley Organics. Ethyl-1-propenyl ether was obtained as a 2.8:1 (*Z*/*E*) mixture from Fluka Chemical Corp. and separated by gas chromatography. Benzyl vinyl ether,[36a] (*Z*)-benzyl 1-propenyl ether,[36b] (*E*)-1-ethoxy-2-phenylethylene,[36c] (*Z*)-1-ethoxy-2-phenylethylene,[36d] 1-methoxy-1,2-propadiene,[36e] (*E*)-1-acetoxy-2-(benzyloxy)ethylene,[36f] and (*Z*)-1-acetoxy-2-(benzyloxy)ethylene[36f] were prepared according to the following procedures: (a) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828. (b) Rautenstrauch, V.; Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1974**, *96*, 2576. (c) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393. (d) Baldwin, J. E.; Walker, L. E. *J. Org. Chem.* **1966**, *31*, 3985. (e) Hoff, S.; Brandsma, L.; Arens, J. F. *Rec. Trav. Chim. Pays-Bas* **1968**, *87*, 916. (f) Boger, D. L.; Robarge, K. D. *J. Org. Chem.* **1988**, *53*, 5976.

186 (10), 143 (8), 130 (base); CIHRMS *m/e* 272.0745 ($C_{15}H_{13}NO_2S$ requires 272.0745). Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16; S, 11.82. Found: C, 66.03; H, 4.94; N, 5.12; S, 11.83.

2-Methyl-1-[(phenylsulfonyl)imino]-2-propene (1i), ^{1}H NMR (C_6D_6, 300 MHz, ppm) 8.60 (1 H, s, CH=N), 7.98 (2 H, dd, *J* = 8, 1 Hz), 6.88–7.16 (3 H, m), 5.22 (1 H, s, CH*H*=C), 5.06 (1 H, s, C*H*H=C), 1.52 (3 H, s, CH_3); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 171.9, 135.3, 132.8, 128.8, 127.5, 15.5; IR (neat) ν_{max} 3066, 2924, 1624, 1578, 1448, 1328, 1308, 1160, 1090, 1026, 810, 754, 726, 688; EIMS *m/e* (relative intensity) 209 (2, M^+), 157 (12), 141 (21), 93 (11), 77 (base), 51 (21); CIMS (2-methylpropane) *m/e* (relative intensity) 210 (M + H^+, base); EIHRMS *m/e* 209.0510 ($C_{10}H_{11}NO_2S$ requires 209.0510).

2-Oxo-3-[1-phenyl-1-[(phenylsulfonyl)imino]methyl]-2*H*-1-benzopyran (1j): mp 189–193 °C (EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 8.10 (2 H, d, *J* = 7 Hz), 7.90 (3 H, m), 7.65–7.50 (6 H, m), 7.43–7.33 (4 H, m); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) 157.6 (e), 154.2 (o), 142.6 (o), 135.0 (o), 134.4 (o), 133.2 (o), 133.0 (o), 129.8 (o), 128.9 (o), 127.6 (o), 125.0 (o), 124.6 (o), 117.9 (e), 117.0 (o); IR (neat) ν_{max} 3062, 1726, 1608, 1588, 1560, 1490, 1448, 1366, 1320, 1266, 1244, 1158, 1122, 1088, 1020, 926, 834 cm^{-1}; EIMS *m/e* (relative intensity) 389 (17, M^+), 248 (base), 89 (30), 77 (93), 63 (8), 51 (21); CIMS (2-methylpropane) *m/e* (relative intensity) 390 (M + H^+, base); EIHRMS *m/e* 389.0721 ($C_{22}H_{15}NO_4S$ requires 389.0721). Anal. Calcd for $C_{22}H_{15}NO_4S$: C, 67.85; H, 3.88; N, 3.60; S, 8.23. Found: C, 67.90; H, 3.77; N, 3.66; S, 8.12.

(3*S,4a*R**)-3-Ethoxy-1-methyl-2-(diphenylphosphinyl)-2,3,4,4a,5,6,7,8-octahydroisoquinoline (2c)**: ^{1}H NMR (C_6D_6, 300 MHz, ppm) 8.10 (2 H, m), 7.95 (2 H, m), 7.05 (6 H, m), 4.66 (1 H, dd, *J* = 8, 2 Hz, C3-H), 4.11 (1 H, dq, *J* = 10, 7 Hz, OC*H*HCH$_3$), 3.43 (1 H, dq, *J* = 10, 7 Hz, OCH*H*CH$_3$), 2.44 (1 H, m, C4-H_{ax}), 2.01 (3 H, s, CH_3), 1.80–1.45 (6 H, m), 1.40–1.20 (4 H, m), 1.11 (3 H, t, *J* = 7 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 136.8 (e), 135.1 (e), 133.4 (o), 133.3 (o), 133.1 (o), 132.4 (o), 132.3 (o), 129.6 (o), 129.5 (o), 129.2 (e), 129.1 (o), 128.9 (o), 128.8 (e), 123.0 (e), 84.2 (o), 63.8 (e), 37.6 (e), 35.1 (o), 31.1 (e), 29.0 (e), 28.7 (e), 19.7 (o), 16.2 (o); IR (neat) ν_{max} 3058, 2930, 2858, 2362, 1728, 1438, 1386, 1288, 1210, 1168, 1120, 1058, 996, 750, 724, 698, 678 cm^{-1}; EIMS *m/e* (relative intensity) 349 (26), 201 (14), 148 (54), 84 (base), 77 (50), 55 (31), 49 (52); CIMS (2-methylpropane) *m/e* (relative intensity) 396 (M + H^+, 1), 350 (base); EIHRMS *m/e* 395.2006 ($C_{24}H_{30}NO_2P$ requires 395.2014).

(3*S,4a*R**)-3-Ethoxy-1-methyl-2-(phenylsulfonyl)-2,3,4,4a,5,6,7,8-octahydroisoquinoline (2d)**: mp 62–64 °C (EtOAc/hexane); ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.70 (2 H, d, *J* = 7 Hz), 7.50 (3 H, m), 5.20 (1 H, t, *J* = 3 Hz, C3-H), 3.65 (1 H, dq, *J* = 10, 7 Hz, OC*H*HCH$_3$), 3.45 (1 H, dq, *J* = 10, 7 Hz, OC*H*HCH$_3$), 2.63 (1 H, dd, *J* = 12, 2 Hz, C4-H_{ax}), 2.14 (3 H, s, C=CCH$_3$), 1.70 (2 H, m), 1.60 (2 H, m), 1.40 (2 H, m), 1.20 (2 H, m), 1.14 (3 H, t, *J* = 7 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 140.4 (e), 132.2 (o), 130.4 (e), 129.1 (o), 128.6 (o), 121.0 (e), 84.2 (o), 63.2 (e), 36.7 (e), 33.8 (o), 32.7 (e), 30.7 (e), 27.5 (e), 27.2 (e), 19.3 (o), 15.2 (o); IR (neat) ν_{max} 2930, 2856, 1446, 1346, 1256, 1236, 1198, 1172, 1154, 1110, 1080, 1054, 986, 964, 924, 860 cm^{-1}; EIMS *m/e* (relative intensity) 335 (4, M^+), 194 (8), 148 (base), 172 (2), 107 (14), 81 (22), 79 (22), 77 (66), 51 (8); CIMS (2-methylpropane) *m/e* (relative intensity) 336 (M + H^+, 2), 290 (base); EIHRMS *m/e* 335.1555 ($C_{18}H_{25}NO_3S$ requires 335.1555). Anal. Calcd for $C_{18}H_{25}NO_3S$: C, 64.44; H, 7.53; N, 4.18. Found: C, 64.46; H, 7.82; N, 4.33.

(3*S,4a*R**)-3-(Benzyloxy)-1-methyl-2-(phenylsulfonyl)-2,3,4,4a,5,6,7,8-octahydroisoquinoline (2e)**: ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.62 (2 H, d, *J* = 7 Hz), 7.26 (2 H, d, *J* = 7 Hz), 7.06–7.18 (3 H, m), 6.89–6.99 (3 H, m), 5.37 (1 H, m, C4-H), 4.73 (1 H, d, *J* = 12 Hz, OC*H*HPh), 4.50 (1 H, d, *J* = 12 Hz, OCH*H*Ph), 2.48 (1 H, m), 2.20 (3 H, s, CH_3), 1.80 (1 H, m), 1.50 (2 H, m), 1.23 (6 H, m), 1.25 (1 H, m); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 140.3 (e), 139.1 (e), 132.1 (o), 130.4 (e), 128.8 (o), 127.7 (o), 127.5 (o), 121.3 (o), 84.2 (o), 69.7 (e), 36.8 (e), 33.7 (o), 32.6 (e), 30.8 (e), 27.5 (e), 19.6 (o); IR (neat) ν_{max} 2930, 2854, 1654, 1446, 1348, 1258, 1198, 1172, 1076, 1050, 966, 720, 690 cm^{-1}; EIMS *m/e* (relative intensity) 397 (1, M^+), 148 (28), 91 (base), 77 (33), 65 (9), 51 (9); CIMS (2-methylpropane) *m/e* (relative intensity) 398 (M + H^+, 2), 290 (base); CIHRMS *m/e* 398.1789 ($C_{23}H_{27}NO_3S$ requires 398.1789). Anal. Calcd for $C_{23}H_{27}NO_3S$: C, 69.48; H, 6.86; N, 3.52. Found: C, 69.44; H, 6.98; N, 3.44.

(3*S,4*S**,4a*R**)-3-(Benzyloxy)-1,4-dimethyl-2-(phenylsulfonyl)-2,3,4,4a,5,6,7,8-octahydroisoquinoline (2f)**: mp 104–107 °C (EtOAc/hexane); ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.85 (2 H, d, *J* = 7 Hz), 7.30 (2 H, d, *J* = 7 Hz), 7.00–7.20 (3 H, m), 6.88–6.96 (3 H, m), 5.45 (1H, d, *J* = 3 Hz, C3-H), 4.67 (1 H, d, *J* = 12 Hz, OCH*H*Ph), 4.55 (1 H, d, *J* = 12 Hz, OC*H*HPh), 2.30 (1 H, ddd, *J* = 14, 4.5, 4.0 Hz, C4-H_{ax}), 2.04 (3 H, s, CH_3), 1.80 (1 H, ddq, *J* = 7, 4.5, 3 Hz), 1.0–1.7 (8 H, m), 0.95 (3 H, d, *J* = 7 Hz, C4-CH_3); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 142.9 (e), 138.9 (e), 132.0 (o), 128.7 (o), 128.3 (o), 128.0 (o), 127.8 (o), 127.7 (o), 127.6 (e), 122.4 (e), 90.5 (o), 70.3 (e), 41.6 (o), 40.6 (o), 32.8 (e), 28.8 (e), 26.1 (e), 25.7 (e), 18.7 (o), 17.6 (o); IR (neat) ν_{max} 2930, 2854, 1728, 1498, 1448, 1348, 1260, 1172, 1026, 802, 750, 718, 692 cm^{-1}; EIMS *m/e* (relative intensity) 411 (1, M^+), 288 (6), 162 (28), 120 (5), 108 (2), 107 (11), 91 (base), 79 (14), 77 (21); CIMS (2-methylpropane) *m/e* (relative intensity) 304 (base, M + H^+ – $PhCH_2OH$); CIHRMS *m/e* 412.1938 ($C_{24}H_{29}NO_3S$ requires 412.1946).

(3*S,4a*R**)-3-Methoxy-1-methyl-4-methylene-2-(phenylsulfonyl)-2,3,4,4a,5,6,7,8-octahydroisoquinoline (2g)**: mp 96–99 °C (EtOAc/hexane); ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.62 (2 H, d, *J* = 7 Hz), 6.80–7.00 (3 H, m), 5.42 (1 H, s, C3-H), 4.55 (1 H, s, C*H*H=C), 4.35 (1 H, s, CH*H*=C), 3.30 (3 H, s, OCH_3), 2.43 (1 H, dd, *J* = 12, 1.3 Hz, C4-H_{ax}), 2.25 (3 H, s, CH_3), 1.90–1.60 (2 H, m), 1.50–1.30 (2 H, m), 1.20–1.00 (2 H, m); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 144.4 (e), 139.6 (e), 132.5 (o), 128.7 (o), 128.3 (o), 122.0 (e), 113.5 (e), 91.1 (o), 55.5 (o), 42.3 (o), 38.0 (e), 30.3 (e), 27.1 (e), 27.0 (e), 19.6 (e); IR (neat) ν_{max} 2932, 2856, 1446, 1348, 1198, 1170, 1144, 1094, 1070, 1042, 984, 950, 914, 750, 724, 690, 662 cm^{-1}; EIMS *m/e* (relative intensity) 333 (8, M^+), 318 (5), 302 (6), 160 (47), 151 (38), 141 (11), 119 (17), 105 (11), 93 (14), 91 (46), 77 (base), 57 (52), 51 (39); CIMS (2-methylpropane) *m/e* (relative intensity) 334 (M + H^+, 7) 302 (base); EIHRMS *m/e* 333.1400 ($C_{18}H_{23}NO_3S$ requires 333.1398). Anal. Calcd for $C_{18}H_{23}NO_3S$: C, 64.83; H, 6.97; N, 4.20. Found: C, 65.20; H, 6.97; N, 4.26.

(3*S,3*R**,4a*R**)-3-Methoxy-1,3-dimethyl-2-(phenylsulfonyl)-2,3,4,4a,5,6,7,8-octahydroisoquinoline (2h)**: mp 104–106 °C (EtOAc/hexane); ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.90 (2 H, m), 6.93 (3 H, m), 3.09 (3 H, s, C3-OCH_3), 2.50 (1 H, dd, *J* = 13, 1 Hz, C4-H_{ax}), 2.33 (3 H, s, C1-CH_3), 1.50 (6 H, m), 1.29 (3 H, s, C3-CH_3), 1.20 (2 H, m); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 142.4 (e), 132.4 (e), 131.9 (o), 131.9 (e), 128.5 (o), 127.6 (o), 127.2 (o), 50.2 (o), 39.5 (e), 35.7 (o), 35.3 (e), 30.4 (e), 27.1 (e), 26.7 (e), 22.8 (o), 21.6 (o); IR (neat) ν_{max} 2928, 1448, 1348, 1158, 988, 690 cm^{-1}; EIMS *m/e* (relative intensity) 335 (1, M^+), 194 (41) 162 (27), 136 (18), 77 (36), 73 (base), 72 (63); CIMS (2-methylpropane) *m/e* (relative intensity) 336 (M + H^+, 2), 304 (base); EIHRMS *m/e* 335.1557 ($C_{18}H_{25}NO_3S$ requires 335.1554). Anal. Calcd for $C_{18}H_{25}NO_3S$: C, 64.44; H, 7.53; N, 4.18. Found: C, 64.38; H, 7.61; N, 4.17.

(4a*R)-3,3-Dimethoxy-1-methyl-2-(phenylsulfonyl)-2,3,4,4a,5,6,7,8-octahydroisoquinoline (2i)**: ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.95 (2 H, m), 7.03 (3 H, m), 2.84 (3 H, s, OCH_3), 2.83 (3 H, s, OCH_3), 2.52 (1 H, d, *J* = 12 Hz, C4-H_{ax}), 2.30 (3 H, s, CH=CC*H*$_3$), 2.03 (2 H, m), 1.60 (4 H, m), 1.20 (2 H, m); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 132.3 (e), 131.4 (o), 128.3, 128.1, 127.9, 123.3, 48.5 (o), 48.1 (o), 36.5 (o), 35.3 (e), 34.5 (e), 30.3 (e), 27.3 (e), 26.6 (e), 26.5 (e), 20.2 (o); IR (neat) ν_{max} 2928, 2854, 1448, 1324, 1152, 1118, 1050, 690, 660 cm^{-1}; EIMS *m/e* (relative intensity) 351 (2, M^+), 210 (18), 196 (11), 179 (16), 178 (base), 136 (22), 91 (10), 88 (80), 77 (57), 56 (19), 51 (23); CIMS (2-methylpropane) *m/e* (relative intensity) 352 (M + H^+, 1), 178 (base); CIHRMS *m/e* 352.1582 ($C_{18}H_{25}NO_4S$ requires 352.1528).

(2*S)-2-Ethoxy-6-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (8)**: mp 58–61 °C (EtOAc); ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.69 (2 H, d, *J* = 7), 7.01 (3 H, m), 5.50 (1 H, dd, *J* = 2.8, 1.3 Hz, C*H*OCH$_2$CH$_3$), 4.81 (1 H, dd, *J* = 4.6, 2.5 Hz, C=CH), 3.85 (1 H, dq, *J* = 10.5, 7 Hz, OC*H*HCH$_3$), 3.60 (1 H, dq, *J* = 10.5, 7 Hz, OCH*H*CH$_3$), 2.20 (3 H, s, CH_3), 2.07 (dddd, *J* = 16, 7, 2.5, 2 Hz, C4-H_{eq}), 1.55 (1 H, dddd, *J* = 13, 7, 2, 1.3 Hz, C3-H_{eq}), 1.40 (1 H, dddd, *J* = 16, 7, 2.5, 2 Hz, C4-H_{ax}), 1.10 (3 H, t, *J* = 7 Hz, OCH$_2$C*H*$_3$), 0.91 (1 H, dddd, *J* = 13, 3, 7, 2.8 Hz, C3-H_{ax}); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 132.3 (o), 129.0 (e), 128.0 (o), 127.7 (o), 127.2 (e), 127.1 (o), 114.0 (o), 84.0 (o), 63.2 (e), 25.6 (e), 23.9 (o), 18.6 (e), 15.2 (o); IR (neat) ν_{max} 2974, 2932, 1664, 1480, 1446, 1386, 1348, 1310, 1248, 1190, 1168, 1120, 1100, 1062, 1016, 968, 928, 848, 802, 758, 732, 690, 604 cm^{-1}; EIMS *m/e* (relative intensity) 281 (8, M^+), 236 (12), 140 (26), 94 (base), 77 (59), 51 (21); CIMS (2-methylpropane) *m/e* (relative intensity) 282 (M + H^+, 3), 236 (base); EIHRMS *m/e* 281.1088 ($C_{14}H_{19}NO_3S$ requires 281.1085). Anal. Calcd for $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98; S, 11.40. Found: C, 60.06; H, 6.74; N, 4.87; S, 11.02.

(2*S,4*R**)-2-Ethoxy-6-methyl-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (9)**: mp 96–98 °C (EtOAc/hexane): ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.70 (2 H, d, *J* = 7 Hz), 7.10 (8 H, m), 5.48 (1 H, dd, *J* = 4, 2.3 Hz, C2-H), 5.20 (1 H, d, *J* = 1.3 Hz, C5-H), 3.75 (1 H, dq, *J* = 10, 7 Hz, OC*H*HCH$_3$), 3.43 (1 H, dq, *J* = 10, 7 Hz, OC*H*HCH$_3$), 2.50 (1 H, ddd, *J* = 8.6, 4.0, 1.3, C4-H_{eq}), 2.24 (3 H, s, CH=CC*H*$_3$), 1.85 (1 H, ddd, *J* = 14.3, 4.0, 2.3 Hz, C3-H_{eq}), 1.69 (1 H, ddd, *J* = 14.3, 8.6, 4.0 Hz, C3-H_{ax}), 1.00 (3 H, t, *J* = 7 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 145.5 (e), 140.9 (e), 132.4 (o), 132.0 (e), 129.0 (o), 128.3 (o), 127.9 (o), 127.6 (e), 127.2 (o), 126.4 (o), 121.0 (o), 84.3 (o), 63.3 (e), 36.4 (o), 36.3 (e), 23.5 (o), 15.0 (o);

IR (neat) ν_{max} 2929, 1652, 1443, 1346, 1167, 1109, 1050, 1024, 952, 758, 732 cm^{-1}; EIMS *m/e* (relative intensity) 357 (1, M$^+$), 312 (2), 216 (6), 170 (base), 144 (18), 143 (10), 129 (31), 128 (10), 103 (14), 91 (13), 77 (90), 51 (20); CIMS (2-methylpropane) *m/e* (relative intensity) 358 (M + H$^+$, 1), 312 (base); EIHRMS *m/e* 357.1401 ($C_{20}H_{23}NO_3S$ requires 357.1398). Anal. Calcd for $C_{20}H_{23}NO_3S$: C, 67.77; H, 6.23; N, 3.72. Found: C, 67.37; H, 6.22; N, 3.93.

The structure of **9** was unambiguously established in a single-crystal X-ray structure determination.[21a]

(2*S,4*R**)-2-Ethoxy-4,6-diphenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (10)**: ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.70 (2 H, d, *J* = 7 Hz), 7.60 (2 H, d, *J* = 7 Hz), 7.20 (5 H, m), 6.90 (6 H, m), 5.85 (1 H, d, *J* = 3.2 Hz, C=CH), 5.67 (1 H, dd, *J* = 5.8, 4 Hz, C*H*OCH$_2$CH$_3$), 4.13 (1 H, dq, *J* = 10, 7 Hz, OC*H*HCH$_3$), 3.66 (1 H, dq, *J* = 10, 7 Hz, OCH*H*CH$_3$), 2.40 (1 H, dd, *J* = 7.6, 7.4 Hz, C4-H$_{eq}$), 2.06 (1 H, ddd, *J* = 14, 7.4, 5.8 Hz, C3-H$_{eq}$), 1.95 (1 H, *J* = 14, 7.6, 4 Hz, C3-H$_{ax}$), 1.12 (3 H, t, *J* = 7 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 145.5, 138.5, 133.3, 129.7, 129.6, 129.4, 129.2, 129.1, 129.0, 128.9, 128.5, 127.9, 127.5, 121.2, 119.3, 86.0, 64.8, 40.5, 38.5, 15.1; IR (neat) ν_{max} 2974, 1684, 1654, 1596, 1560, 1542, 1492, 1446, 1356, 1170, 1060, 954, 762, 738, 690 cm^{-1}; EIMS *m/e* (relative intensity) 278 (7), 232 (49), 231 (base), 230 (91), 202 (15), 154 (13), 129 (17), 102 (18), 77 (69), 51 (39); CIMS (2-methylpropane) *m/e* 420 (M + H$^+$, 6), 232 (base); CIHRMS *m/e* 420.1625 ($C_{25}H_{25}NO_3S$ requires 420.1633).

(2*S,4*R**)-2-Ethoxy-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (11a)**: ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.73 (2 H, d, *J* = 7 Hz), 7.10 (7 H, m), 6.83 (1 H, d, *J* = 8.4 Hz, C6-H), 5.24 (1 H, m, C2-H), 5.04 (1 H, *J* = 8.4, 4.7 Hz, C5-H), 3.56 (1 H, dq, *J* = 9.4, 7 Hz, OC*H*HCH$_3$), 3.15 (1 H, dq, *J* = 9.4, 7 Hz, OCH*H*CH$_3$), 2.88 (1 H, dd, *J* = 8, 2.5 Hz, C4-H$_{eq}$), 1.90 (1 H, dd, *J* = 14, 2.5 Hz, C3-H$_{eq}$), 1.30 (1 H, ddd, *J* = 14, 8, 3 Hz, C3-H$_{ax}$), 0.76 (3 H, t, *J* = 7 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 144.5 (e), 132.4 (o), 129.1 (o), 129.0 (o), 128.1 (e), 128.0 (o), 127.9 (o), 127.7 (o), 127.5 (o), 127.2 (o), 126.1 (o), 123.9 (o), 114.9 (o), 112.1 (o), 81.9 (o), 63.0 (e), 34.8 (o), 33.8 (e), 14.6 (o); IR (neat) ν_{max} 2976, 1654, 1560, 1542, 1490, 1448, 1398, 1352, 1252, 1170, 1108, 1060, 1024, 920, 758, 730, 690 cm^{-1}; EIMS *m/e* (relative intensity) 343 (13, M$^+$), 297 (32), 156 (44), 130 (23), 129 (22), 115 (13), 103 (19), 91 (23), 77 (base), 72 (25), 69 (17), 51 (42); CIMS (2-methylpropane) *m/e* 344 (M + H$^+$, 1), 298 (base); EIHRMS *m/e* 343.1167 ($C_{19}H_{21}NO_3S$ requires 343.1163).

(2*R,3*S**,4*R**)-2-(Benzyloxy)-3-methyl-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (11b)**: ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.68 (2 H, d, *J* = 7 Hz), 7.10 (10 H, m), 6.90 (3 H, m), 6.85 (1 H, d, *J* = 8.1 Hz, C6-H), 5.25 (1 H, d, *J* = 2.3 Hz, C2-H), 5.16 (1 H, dd, *J* = 8.1, 4.5 Hz, C5-H), 4.92 (1 H, d, *J* = 12.3 Hz, OC*H*HPh), 4.66 (1 H, d, *J* = 12.3 Hz, OCH*H*Ph), 2.66 (1 H, dd, *J* = 7.7, 4.5 Hz, C4-H$_{eq}$), 1.38 (1 H, ddq, *J* = 7.7, 7, 2.3 Hz, C3-H$_{ax}$), 0.64 (3 H, d, *J* = 7 Hz, CHC*H*$_3$); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 132.6, 131.6, 129.3, 128.4, 128.3, 128.1, 127.6, 127.2, 126.8, 123.0, 115.2, 86.2, 70.4, 41.8, 36.8, 15.7; IR (neat) ν_{max} 2930, 1654, 1560, 1492, 1448, 1370, 1348, 1172, 1136, 1092, 1064, 1012, 904, 732, 700, 672 cm^{-1}; EIMS *m/e* (relative intensity) 419 (1, M$^+$), 296 (25), 91 (base); CIMS (2-methylpropane) *m/e* (relative intensity) 420 (M + H$^+$, 1), 312 (base); EIHRMS *m/e* 419.1548 ($C_{25}H_{25}NO_3S$ requires 419.1555).

(2*S)-2-Ethoxy-5-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (12)**: mp 56–58 °C (EtOAc/hexane); ^{1}H NMR (C_6D_6, 300 MHz, ppm) 7.70 (2 H, d, *J* = 7 Hz), 6.88 (3 H, m), 6.57 (1 H, s, C=CH), 5.24 (1 H, dd, *J* = 2.8, 1.1 Hz, C*H*OCH$_2$CH$_3$), 4.00 (1 H, dq, *J* = 10, 7 Hz, OCH*H*CH$_3$), 3.70 (1 H, dq, *J* = 10, 7 Hz, OC*H*HCH$_3$), 2.10 (1 H, ddd, *J* = 15.6, 13, 6 Hz, C4-H$_{eq}$), 1.60 (1 H, dddd, *J* = 13, 6, 2, 1.1 Hz, C3-H$_{eq}$), 1.34 (3 H, s, CH=CC*H*$_3$), 1.20 (1 H, ddd, *J* = 15.6, 6, 2 Hz, C4-H$_{ax}$), 1.10 (3 H, t, *J* = 7 Hz, OCH$_2$C*H*$_3$), 0.70 (1 H, dddd, *J* = 13, 13, 6, 2.8 Hz, C3-H$_{ax}$); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 140.2 (e), 132.3 (o), 129.0 (o), 128.3 (o), 127.7 (o), 127.1 (o), 119.4 (e), 117.1 (o), 81.1 (o), 63.2 (e), 25.9 (e), 22.3 (e), 20.8 (o), 15.9 (o); IR (neat) ν_{max} 2928, 1684, 1654, 1560, 1352, 1164, 1102, 1070, 938, 838, 722, 690, 634 cm^{-1}; EIMS *m/e* (relative intensity) 281 (8, M$^+$), 236 (12), 140 (26), 94 (base), 82 (21), 77 (59); CIMS (2-methylpropane) *m/e* 282 (M + H$^+$, 3); EIHRMS *m/e* 281.1085 ($C_{14}H_{19}NO_3S$ requires 281.1085). Anal. Calcd for $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98; S, 11.40. Found: C, 59.54; H, 6.63; N, 4.87; S, 11.11.

(6*S)-2-Oxo-2*H*-1-benzopyran[3,4-*c*]-6-ethoxy-2-phenyl-1-(phenylsulfonyl)-1,4,5,6-tetrahydropyridine (13)**: mp 132–135 °C (EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 7.40 (2 H, m), 7.25 (2 H, m), 7.03 (4 H, m), 5.86 (6 H, m), 5.88 (1 H, dd, *J* = 5.2, 4.2 Hz, C*H*OCH$_2$CH$_3$), 3.38 (1 H, dq, *J* = 9, 7 Hz, OC*H*HCH$_3$), 3.25 (1 H, dd, *J* = 8, 6 Hz, C4-H), 3.15 (1 H, dq, *J* = 9, 7 Hz, OCH*H*CH$_3$), 2.30 (1 H, ddd, *J* = 14, 6, 5.2 Hz, C5-H), 2.11 (1 H, ddd, *J* = 14, 8, 4.2 Hz, C5-H), 0.84 (3 H, t, *J* = 7 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6, 75 MHz, ppm) 159.1, 150.7, 149.3, 141.1, 135.0, 132.4, 131.8, 129.0, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 127.5, 127.1, 126.6, 123.6, 123.4, 116.9, 84.1, 64.1, 38.1, 32.6, 14.7; IR (neat) ν_{max} 3061, 2977, 1726, 1606, 1478, 1447, 1365, 1321, 1267, 1245, 1159, 1139, 1088, 789, 756, 725, 689, 651, 600 cm^{-1}; CIMS (2-methylpropane) *m/e* (relative intensity) 462 (M + H$^+$, 13), 274 (base); CIHRMS *m/e* 462.1371 ($C_{26}H_{23}NO_5S$ requires 462.1375).

2-Oxo-2*H*-1-benzopyran[3,4-*c*]-6,6-dimethoxy-2-phenyl-1-(phenylsulfonyl)-1,4,5,6-tetrahydropyridine (14): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 7.69 (2 H, d, *J* = 7 Hz), 7.50 (2 H, m), 7.16 (3 H, m), 6.90 (6 H, m), 6.69 (1 H, m), 3.75 (1 H, dd, *J* = 11, 8 Hz, C4-H), 2.93 (3 H, s, OCH$_3$), 2.89 (3 H, s, OCH$_3$), 2.62 (1 H, dd, *J* = 12, 11 Hz, C5-H), 2.31 (1 H, dd, *J* = 12, 8 Hz, C5-H); IR (neat) ν_{max} 2926, 1750, 1618, 1490, 1456, 1360, 1210, 1172, 1116, 1062, 1040, 974, 888, 756, 688 cm^{-1}; EIMS *m/e* (relative intensity) 404 (2), 390 (5), 248 (50), 89 (29), 77 (base); CIMS (2-methylpropane) *m/e* (relative intensity) 478 (M + H$^+$, 2), 250 (base); CIHRMS *m/e* 478.1314 ($C_{26}H_{23}NO_6S$ requires 478.1324).

[2-(Ethoxycarbonyl)-2-[(2-tetrahydropyranyloxy)imino]ethyl]triphenylphosphonium Bromide (15). Hydroxylamine hydrochloride (3.48 g, 50.0 mmol) was added to a stirred solution of ethyl bromopyruvate (9.76 g, 50.0 mmol) in anhydrous chloroform (150 mL) and anhydrous methanol (100 mL) at 23 °C. The reaction mixture was stirred at 23 °C for 18 h and concentrated under reduced pressure. The residue was dissolved in dichloromethane (300 mL), washed with 5% aqueous hydrochloric acid and saturated aqueous sodium chloride, dried (Na_2SO_4), filtered, and concentrated in vacuo. Recrystallization afforded ethyl 2-(hydroxyimino)-3-bromopropanoate (9.66 g, 10.5 g theoretical, 92%) as a white solid: mp 75–77 °C (CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$, 200 MHz, ppm) 4.38 (2 H, q, *J* = 7.2 Hz, OCH_2CH$_3$), 4.27 (2 H, s, CH_2Br), 1.39 (3 H, t, *J* = 7.2 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 161.9 (C=O), 147.9 (C=N), 62.5 (OCH_2), 14.9 (CH_2Br), 13.8 (CH$_3$); IR (neat) ν_{max} 3182, 2996, 1736, 1604, 1406, 1318, 1236, 1200, 1122, 1032, 860 cm^{-1}; EIMS *m/e* (relative intensity) 209/211 (3/3, M$^+$), 181/183 (18/18), 129 (21), 101 (base); CIMS (2-methylpropane) *m/e* (relative intensity) 210/212 (M + H$^+$, base); EIHRMS *m/e* 208.9688 ($C_5H_8BrNO_3$ requires 208.9688).

A stirred solution of the oxime (9.12 g, 43.4 mmol) in anhydrous dichloromethane (225 mL) was treated with 3,4-dihydro-2*H*-pyran (5.11 g, 60.7 mmol, 1.4 equiv). A catalytic amount of pyridinium *p*-toluenesulfonate (820 mg, 3.25 mmol, 0.075 equiv) was added, and the mixture was stirred under nitrogen at 23 °C for 21 h. The reaction mixture was diluted with diethyl ether (100 mL) and washed with half-saturated aqueous sodium chloride (50 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated in vacuo. Flash chromatography (SiO_2, 5 cm × 25 cm, 12% ethyl acetate/hexane eluant) afforded ethyl 2-[(2-tetrahydropyranyloxy)imino]-3-bromopropanoate (12.0 g, 12.8 g theoretical, 94%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 200 MHz, ppm) 5.57 (1 H, apparent t, *J* = 2.1 Hz, OC*H*O), 4.40 (2 H, q, *J* = 7.1 Hz, OCH_2CH$_3$), 4.27 (2 H, s, CH_2Br), 3.91 (1 H, m, OC*H*HCH$_2$), 3.72 (1 H, m, OCH*H*CH$_2$), 1.88 (2 H, m, CHCH_2CH$_2$), 1.66 (4 H, m, CH$_2$CH$_2$), 1.34 (3 H, t, *J* = 7.1 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 161.9 (C=O), 148.6 (C=N), 102.1 (OCHO), 62.2 (CO$_2$CH_2CH$_3$), 62.0 (OCH_2CH$_2$), 28.0 (CH_2Br), 24.6 (O$_2$CHCH_2), 18.3 (OCH$_2$CH_2), 15.9 (CH$_2$CH_2CH$_2$), 13.7 (CO$_2$CH$_2$CH_3); IR (neat) ν_{max} 2948, 1722, 1374, 1334, 1206, 1188, 1118, 1040, 1020, 986, 964, 900, 866 cm^{-1}; CIMS (2-methylpropane) *m/e* (relative intensity) 294/296 (M + H$^+$, 21/20), 250 (9), 216 (14), 85 (base); CIHRMS *m/e* 294.0338 ($C_{10}H_{16}BrNO_4$ requires 294.0341).

Triphenylphosphine (5.62 g, 21.4 mmol) was added to a solution of the oxime THP ether (6.29 g, 21.4 mmol) in anhydrous tetrahydrofuran (60 mL) and anhydrous benzene (30 mL), and the reaction mixture was warmed at 80 °C under nitrogen for 18 h. The reaction mixture was allowed to cool to 23 °C and further cooled to 0 °C with an ice–water bath. The precipitate was collected by filtration and washed with diethyl ether (2 × 70 mL). The remaining solid was dried in vacuo to afford **15** (10.9 g, 11.9 g theoretical, 91%) as a white solid: mp 164–165 °C; ^{1}H NMR ($CDCl_3$, 200 MHz, ppm) 7.64–7.96 (15 H, m, ArH), 5.46 (1 H, apparent t, *J* = 15.2 Hz, CH*H*P), 5.30 (1 H, apparent t, *J* = 2.2 Hz, OC*H*O), 5.24 (1 H, apparent t, *J* = 15.0 Hz, C*H*HP), 4.07 (2 H, q, *J* = 7.2 Hz, OCH_2CH$_3$), 3.72 (1 H, m, OC*H*HCH$_2$), 3.54 (1 H, m, OCH*H*CH$_2$), 1.64 (2 H, m, CHCH_2CH$_2$), 1.49 (4 H, m, CH$_2$CH$_2$), 1.11 (3 H, t, *J* = 7.2 Hz, OCH$_2$CH_3); IR (neat) ν_{max} 2956, 1706, 1586, 1436, 1376, 1332, 1250, 1208, 1110, 1052, 1038, 982, 956, 894, 850 cm^{-1}. Anal. Calcd for $C_{28}H_{31}BrNO_4P$: C, 60.43; H, 5.63; Br, 14.36; N, 2.52; P, 5.57. Found: C, 60.14; H, 5.86; Br, 14.01; N, 2.42; P, 5.32.

General Procedure for the Wittig Reaction of 15 with Aldehydes: Ethyl (*E*)-4-Phenyl-2-[(2-tetrahydropyranyloxy)imino]-3-butenoate (17a). A stirred suspension of **15** (4.40 g, 7.91 mmol, 1.0 equiv) in anhydrous *N,N*-dimethylformamide (16 mL) was treated with anhydrous potassium carbonate (1.20 g, 8.68 mmol, 1.1 equiv). The slurry was stirred under

nitrogen for 5 min at 23 °C and was treated with benzaldehyde (840 mg, 7.91 mmol, 1.0 equiv). The reaction mixture was stirred at 23 °C for 27 h. The mixture was diluted with water (50 mL) and extracted with ether (5 × 50 mL), and the combined extracts were washed with water (2 × 100 mL) and saturated aqueous sodium chloride (1 × 100 mL), dried (Na_2SO_4), and concentrated in vacuo. Flash chromatography (SiO_2, 5 cm × 13 cm, 10–15% ethyl acetate/hexane gradient elution) afforded **3a** (2.25 g, 2.40 g theoretical, 94%) as a yellow, viscous oil. ^1H NMR ($CDCl_3$, 200 MHz, ppm) 7.61 (1 H, d, J = 16.5 Hz, CH=), 7.36–7.52 (5 H, m, ArH), 7.28 (1 H, d, J = 16.7 Hz, =CH), 5.52 (1 H, apparent t, J = 3.3 Hz, OC*H*O), 4.40 (2 H, q, J = 7.2 Hz, OCH_2CH$_3$), 3.90 (1 H, m, OC*H*HCH$_2$), 3.69 (1 H, m, OCH*H*CH$_2$), 1.89 (2 H, m, CHCH_2), 1.61 (4 H, m, CH$_2$CH$_2$), 1.36 (3 H, t, J = 7.2 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 163.5 (C=O), 149.3 (C=N), 140.4 (CH=), 136.4 (C aromatic), 129.6 (CH aromatic), 128.9 (CH aromatic), 127.7 (CH aromatic), 113.9 (=CH), 102.0 (OCHO), 62.8 (COCH_2CH$_3$), 61.8 (OCH_2CH$_3$), 28.5 (O$_2$CHCH$_2$), 24.8 (OCH$_2$CH_2), 19.3 (CH$_2$CH$_2$CH$_2$), 13.9 (CH$_3$); IR (neat) ν_{max} 2946, 2872, 1722, 1448, 1356, 1320, 1262, 1206, 1176, 1154, 1130, 1118, 1102, 1076, 1064, 1042, 1020, 956, 904, 874 cm^{-1}; EIMS m/e (relative intensity) 219 (7), 129 (3), 85 (base), 77 (3), 67 (9), 57 (13); CIMS (2-methylpropane) m/e (relative intensity) 304 (M + H$^+$, base), 220 (65), 85 (8); CIHRMS m/e 304.1546 ($C_{17}H_{21}NO_4$ requires 304.1548). Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.30; H, 6.99; N, 4.62. Found: C, 67.65; H, 7.27; N, 4.98.

Ethyl (*E*)-2-[(2-tetrahydropyranyloxy)imino]-3-decenoate (17b): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 6.66 (1 H, dt, J = 16.2, 6.5 Hz, =CH), 6.65 (1 H, d, J = 16.2 Hz, CH=), 5.44 (1 H, apparent t, J = 3.7 Hz, OC*H*O), 4.31 (2 H, q, J = 7.2 Hz, OCH_2CH$_3$), 3.84 (1 H, m, OC*H*HCH$_2$), 3.63 (1 H, m, OCH*H*CH$_2$), 2.22 (2 H, apparent q, J = 6.5 Hz, =CHCH_2), 1.84 (2 H, m, O$_2$CHCH_2), 1.56 (4 H, m, CH$_2$CH$_2$), 1.35 (3 H, t, J = 7.2 Hz, OCH$_2$CH_3), 1.39–1.28 (8 H, m, (CH$_2$)$_4$), 0.89 (3 H, t, J = 6.7 Hz, CH$_2$CH_3); IR (neat) ν_{max} 2932, 2858, 1722, 1370, 1320, 1204, 1184, 1116, 1042, 1020, 952, 904 cm^{-1}; CIMS (2-methylpropane) m/e (relative intensity) 312 (M + H$^+$, 9), 228 (base), 85 (44); EIHRMS m/e 311.2096 ($C_{17}H_{29}NO_4$ requires 311.2097).

Ethyl (*E*)-2-[(2-tetrahydropyranyloxy)imino]-3-pentenoate (17c): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 6.64 (1 H, dq, J = 16.1, 5.5 Hz, =C*H*CH$_3$), 6.51 (1 H, d, J = 16.2 Hz, CH=), 5.37 (1 H, apparent t, J = 3.7 Hz, OC*H*O), 4.24 (2 H, q, J = 7.1 Hz, OCH_2CH$_3$), 3.81 (1 H, m, OC*H*HCH$_2$), 3.61 (1 H, m, OCH*H*CH$_2$), 1.85 (3 H, d, J = 5.2 Hz, =CHCH_3), 1.78 (2 H, m, O$_2$CHCH_2), 1.57 (4 H, m, CH$_2$CH$_2$), 1.29 (3 H, t, J = 7.1 Hz, OCH$_2$CH_3); IR (neat) ν_{max} 2946, 2872, 1722, 1444, 1372, 1206, 1180, 1116, 1042, 1020, 958, 904 cm^{-1}; CIMS (2-methylpropane) m/e (relative intensity) 242 (M + H$^+$, 22), 158 (base), 132 (23), 85 (51); CIHRMS m/e 242.1406 ($C_{12}H_{19}NO_4$ requires 242.1392).

General Procedure for the Deprotection of Oxime Tetrahydropyranyl Ethers: Ethyl (*E*)-2-(Hydroxyimino)-4-phenyl-3-butenoate (18a). A solution of **17a** (1.29 g, 4.25 mmol, 0.07 M) in glacial acetic acid/water/tetrahydrofuran (3:1:1, 60 mL) was warmed at 55 °C for 37 h. The cooled reaction mixture was diluted with water (100 mL) and extracted with ethyl acetate (3 × 100 mL). The combined extracts were washed with saturated aqueous sodium bicarbonate (3 × 100 mL), water (2 × 100 mL), and saturated aqueous sodium chloride (1 × 100 mL), dried (Na_2SO_4), and concentrated in vacuo. Flash chromatography (SiO_2, 3 cm × 10 cm, 5–10% ethyl acetate/hexane gradient elution) afforded **18a** (0.76 g, 0.93 g theoretical, 82%) as a white solid: mp 87–90 °C (EtOAc/hexane); ^1H NMR ($CDCl_3$, 200 MHz, ppm), 9.98 (1 H, br s, NO*H*), 7.85 (1 H, d, J = 16.8 Hz, CH=), 7.56 (2 H, dd, J = 7.8, 1.7 Hz, *o*-ArH), 7.36 (3 H, m, *m*,*p*-ArH), 7.27 (1 H, d, J = 16.7 Hz, =CH), 4.40 (2 H, q, J = 7.2 Hz, OCH_2CH$_3$), 1.42 (3 H, t, J = 7.2 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 163.2 (C=O), 146.8 (C=N), 140.7 (=CH), 136.5 (C aromatic), 129.6 (CH aromatic), 128.9 (CH aromatic), 127.7 (CH aromatic), 113.2 (=CH), 61.8 (CO$_2$CH$_2$CH$_3$), 31.8 (CO$_2$CH$_2$CH$_3$); IR (neat) ν_{max} 3408, 2980, 1732, 1448, 1420, 1384, 1312, 1262, 1172, 1024, 1002, 976 cm^{-1}; EIMS m/e (relative intensity) 219 (M$^+$, 27), 218 (51), 202 (7), 128 (base), 115 (43), 102 (21), 77 (19); CIMS (2-methylpropane) m/e (relative intensity) 220 (M + H$^+$, base); EIHRMS m/e 219.0896 ($C_{12}H_{13}NO_3$ requires 219.0895). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.73; H, 5.99; N, 6.39. Found: C, 65.76; H, 6.05; N, 6.74.

Ethyl (*E*)-2-(hydroxyimino)-3-decenoate (18b): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 9.36 (1 H, br s, NO*H*), 6.89 (1 H, dt, J = 16.2, 7.0 Hz, =CH), 6.57 (1 H, d, J = 16.2 Hz, CH=), 4.32 (2 H, q, J = 7.1 Hz, OCH_2CH$_3$), 2.23 (2 H, apparent q, J = 6.7 Hz, =CHCH_2), 1.47–1.28 (8 H, m, (CH$_2$)$_4$), 1.36 (3 H, t, J = 7.1 Hz, OCH$_2$CH_3), 0.89 (3 H, t, J = 7.1 Hz, CH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 163.4 (C=O), 147.2 (C=N), 145.5 (=CH), 115.6 (=CH), 61.7 (CO$_2$CH$_2$CH$_3$), 33.9 (CH$_2$), 31.4 (CH$_2$), 28.5 (CH$_2$), 28.3 (CH$_2$), 22.3 (CH$_2$), 13.7 (CO$_2$CH$_2$CH$_3$), 10.2 (CH$_2$CH$_3$); IR (neat) ν_{max} 3264, 2958, 2930, 2858, 1730, 1420, 1374, 1318, 1182, 1022, 978 cm^{-1}; EIMS m/e (relative intensity) 227 (8, M$^+$), 154 (12), 142 (76), 114 (70), 97 (57), 85 (47), 67 (27), 55 (base); CIMS (2-methylpropane) m/e (relative intensity) 228 (M + H$^+$, base); EIHRMS m/e (relative intensity) 227.1511 ($C_{12}H_{21}NO_3$ requires 227.1521).

Ethyl (*E*)-2-(hydroxyimino)-3-pentenoate (18c): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 10.60 (1 H, br s, NO*H*), 7.03 (1 H, dq, J = 16.2, 6.8 Hz, =CH), 6.60 (1 H, d, J = 16.2 Hz, CH=), 4.32 (2 H, q, J = 7.1 Hz, OCH_2CH$_3$), 1.92 (3 H, d, J = 6.8 Hz, =CHCH_3), 1.35 (3 H, t, J = 7.1 Hz, OCH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 163.5 (C=O), 146.7 (C=N), 140.6 (=CH), 117.3 (=CH), 61.8 (CO$_2$CH$_2$CH$_3$), 19.6 (CH$_3$), 13.9 (CO$_2$CH$_2$CH$_3$); IR (neat) ν_{max} 3268, 2984, 2940, 1730, 1444, 1374, 1318, 1280, 1180, 1160, 1022, 974 cm^{-1}; EIMS m/e (relative intensity) 157 (13, M$^+$), 142 (83), 114 (base), 96 (54), 68 (45); CIMS (2-methylpropane) m/e (relative intensity) 158 (M + H$^+$, base); EIHRMS m/e 157.0739 ($C_7H_{11}NO_3$ requires 157.0738).

General Procedure for the Preparation of *N*-(Phenylsulfonyl)- or *N*-(Methylsulfonyl)-1-aza-1,3-butadienes: Ethyl (*E*)-4-Phenyl-2-[(phenylsulfonyl)imino]-3-butenoate (19a). A solution of **18a** (500 mg, 2.28 mmol, 1.0 equiv) in anhydrous carbon tetrachloride (11.4 mL, 0.20 M) was cooled to 0 °C under nitrogen and treated sequentially with triethylamine (280 mg, 0.38 mL, 2.73 mmol, 1.2 equiv) and benzenesulfinyl chloride (400 mg, 0.29 mL, 2.48 mmol). The resulting reaction mixture was stirred at 0 °C for 25 min. The triethylamine hydrochloride was removed by filtration. The filtrate was stirred at 23 °C for 2 h and then concentrated in vacuo. Flash chromatography (Florisil, 3 cm × 9 cm, 10% ethyl acetate/hexane eluant) afforded **19a** (0.54 g, 0.78 g theoretical, 69%) as a gold oil: ^1H NMR ($CDCl_3$, 200 MHz, ppm) 8.02 (2 H, d, J = 6.6 Hz, *o*-SO$_2$ArH), 7.61 (1 H, d, J = 16.9 Hz, CH=), 7.34–7.68 (8 H, m, ArH, *m*,*p*-SO$_2$ArH), 6.84 (1 H, d, J = 16.5 Hz, =CH), 4.56 (2 H, q, J = 7.1 Hz, OCH_2CH$_3$), 1.46 (3 H, t, J = 7.0 Hz, OCH$_2$CH_3); IR (neat) ν_{max} 3064, 2840, 1735, 1614, 1560, 1474, 1448, 1391, 1370, 1268, 1165, 1014, 970, 868 cm^{-1}; CIMS (2-methylpropane) m/e (relative intensity) 344 (M + H$^+$, base); CIHRMS m/e 344.0939 ($C_{18}H_{17}NO_4S$ requires 344.0957). Anal. Calcd for $C_{18}H_{17}NO_4S$: C, 62.95; H, 5.00; N, 4.08; S, 9.34. Found: C, 62.66; H, 5.18; N, 3.99; S, 8.96.

Ethyl (*E*)-2-[(phenylsulfonyl)imino]-3-decenoate (19b): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 7.99 (2 H, d, J = 6.7 Hz, *o*-SO$_2$ArH), 7.64–7.54 (3 H, m, *m*,*p*-SO$_2$ArH), 6.79 (1 H, dt, J = 16.0, 6.8 Hz, =C*H*CH$_2$), 6.20 (1 H, d, J = 16.1 Hz, CH=), 4.42 (2 H, q, J = 7.0 Hz, OCH_2CH$_3$), 2.30 (2 H, apparent q, J = 7.0 Hz, =CHCH_2), 1.47–1.28 (8 H, m, (CH$_2$)$_4$), 1.33 (3 H, t, J = 7.0 Hz, OCH$_2$CH_3), 0.87 (3 H, apparent t, CH$_2$CH_3); IR (neat) ν_{max} 2930, 2858, 1740, 1580, 1448, 1330, 1310, 1186, 1166, 1148, 1090, 752 cm^{-1}; EIMS m/e (relative intensity) 278 (2), 77 (base); CIMS (2-methylpropane) m/e (relative intensity) 352 (M + H$^+$, base); CIHRMS m/e 352.1583 ($C_{18}H_{25}NO_4S$ requires 352.1583).

Ethyl (*E*)-2-[(phenylsulfonyl)imino]-3-pentenoate (19c): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 7.96 (2 H, d, J = 7.8 Hz, *o*-SO$_2$ArH), 7.51 (3 H, m, *m*,*p*-SO$_2$ArH), 6.78 (1 H, dq, J = 16.2, 6.3 Hz, =C*H*CH$_3$), 6.22 (1 H, d, J = 15.8 Hz, CH=), 4.46 (2 H, q, J = 6.9 Hz, OCH_2CH$_3$), 1.98 (3 H, d, J = 6.2 Hz, =CHCH_3), 1.43 (3 H, t, J = 7.0 Hz, OCH$_2$CH_3); IR (neat) ν_{max} 2980, 2936, 1738, 1636, 1580, 1448, 1370, 1328, 1256, 1166, 1016, 964, 862 cm^{-1}; EIMS m/e (relative intensity) 281 (1, M$^+$), 208 (10), 77 (base); CIMS (2-methylpropane) m/e (relative intensity) 282 (M + H$^+$, base); EIHRMS m/e 281.0728 ($C_{13}H_{15}NO_4S$ requires 281.0722).

Ethyl (*E*)-2-[(methylsulfonyl)imino]-4-phenyl-3-butenoate (20a): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 7.55 (2 H, m, *o*-ArH), 7.45 (1 H, d, J = 12.3 Hz, CH=), 7.44 (3 H, m, *m*,*p*-ArH), 6.90 (1 H, d, J = 12.1 Hz, =CH), 4.46 (2 H, q, J = 7.3 Hz, OCH_2CH$_3$), 3.16 (3 H, s, SO$_2$CH$_3$), 1.40 (3 H, t, J = 7.2 Hz, OCH$_2$CH_3); IR (neat) ν_{max} 2984, 2938, 1738, 1614, 1576, 1450, 1392, 1370, 1268, 1182, 1150, 1014, 968, 870 cm^{-1}; EIMS m/e (relative intensity) 204 (5), 131 (base), 103 (28), 77 (16); CIMS (2-methylpropane) m/e (relative intensity) 282 (M + H$^+$, base); EIHRMS m/e 281.0725 ($C_{13}H_{15}NO_4$ requires 281.0721).

Ethyl (*E*)-2-[(methylsulfonyl)imino]-3-decenoate (20b): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 6.79 (1 H, dt, J = 15.7, 7.1 Hz, =C*H*CH$_2$), 6.23 (1 H, d, J = 16.1 Hz, CH=), 4.38 (2 H, q, J = 7.0 Hz, OCH_2CH$_3$), 3.17 (3 H, s, SO$_2$CH$_3$), 2.31 (2 H, q, J = 7.0 Hz, =CHCH_2), 1.37 (3 H, t, J = 7.0 Hz, OCH$_2$CH_3), 1.27 (8 H, m, (CH$_2$)$_4$), 0.87 (3 H, apparent t, J = 6.3 Hz, CH$_2$CH_3); IR (neat) ν_{max} 2930, 2858, 1740, 1620, 1588, 1466, 1370, 1326, 1148, 1018, 968 cm^{-1}; EIMS m/e (relative intensity) 216 (16), 210 (13), 138 (base), 79 (51), 55 (54); CIMS (2-methylpropane) m/e (relative intensity) 290 (M + H$^+$, base); CIHRMS m/e 290.1424 ($C_{13}H_{23}NO_4S$ requires 290.1426).

Ethyl (*E*)-2-[(methylsulfonyl)imino]-3-pentenoate (20c): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 6.81 (1 H, dq, J = 16.0, 6.9 Hz, =C*H*CH$_3$), 6.25 (1 H, d, J = 16.5 Hz, CH=), 4.37 (2 H, q, J = 7.0 Hz, OCH_2CH$_3$), 3.17 (3 H, s, SO$_2$CH$_3$), 2.02 (3 H, d, J = 6.6 Hz, =CHCH_3), 1.36 (3

H, t, J = 7.1 Hz, OCH_2CH_3); IR (neat) ν_{max} 2938, 1736, 1636, 1586, 1372, 1318, 1184, 1148, 1016, 964, 810 cm^{-1}; CIMS (2-methylpropane) m/e (relative intensity) 220 (M + H^+, base); EIHRMS m/e 219.0564 ($C_8H_{13}NO_4S$ requires 219.0565).

General Procedures for the [4 + 2] Cycloaddition Reactions of N-(Phenylsulfonyl)- or N-(Methylsulfonyl)-1-aza-1,3-butadienes. Room-Temperature [4 + 2] Cycloaddition: (2R*,4S*)-2-Ethoxy-6-(ethoxycarbonyl)-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (21a). A solution of **19a** (88.0 mg, 0.26 mmol, 1.0 equiv) in anhydrous dichloromethane (0.51 mL, 0.50 M) under argon at 23 °C was treated with ethyl vinyl ether (73.9 mg, 1.02 mmol, 4.0 equiv). The reaction mixture was stirred at 23 °C for 24 h and then concentrated in vacuo. Flash chromatography (Florisil, 1.5 cm × 13 cm, 7% ethyl acetate/hexane eluant) afforded **21a** (85.0 mg, 106 mg theoretical, 80%) as a pale yellow solid: mp 101–102 °C (EtOAc/hexane); ^1H NMR (C_6D_6, 200 MHz, ppm) 8.10 (2 H, dd, J = 5.4, 1.9 Hz, o-SO_2ArH), 7.07 (5 H, m, ArH), 6.95 (3 H, dd, J = 5.8, 1.8 Hz, m,p-SO_2ArH), 6.69 (1 H, d, J = 2.6 Hz, =C*H*), 5.11 (1 H, dd, J = 5.0, 2.5 Hz, NC*H*O), 4.18 (2 H, dq, J = 7.1, 2.7 Hz, CO_2CH_2CH), 3.78 (1 H, dq, J = 7.1, 2.4 Hz, $OCHHCH_3$), 3.08 (1 H, dq, J = 7.0, 2.4 Hz, $OCHHCH_3$), 2.89 (1 H, dt, J = 9.3, 3.0 Hz, C*H*Ph), 2.11 (1 H, ddd, J = 14.5, 9.1, 4.1, CH_aH_e), 1.98 (1 H, dt, J = 14.3, 2.5 Hz, CH_aH_e), 1.05 (3 H, t, J = 7.2 Hz, $CO_2CH_2CH_3$), 0.92 (3 H, t, J = 7.0 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 165.4 (C=O), 143.7 (C, C6), 139.0 (C aromatic), 133.5 (CH aromatic), 133.1 (CH aromatic), 129.2 (CH aromatic), 128.5 (CH aromatic), 128.4 (CH aromatic), 128.1 (CH aromatic), 128.0 (C aromatic), 126.8 (CH, C5), 82.1 (CH, C2), 63.1 ($CO_2CH_2CH_3$), 61.4 (OCH_2CH_3), 36.5 (CH, C4), 35.6 (CH_2, C3), 14.3 ($CO_2CH_2CH_3$), 13.9 (OCH_2CH_3); IR (neat) ν_{max} 2976, 2932, 1724, 1638, 1448, 1344, 1324, 1238, 1168, 1092, 1062, 1044, 962, 758 cm^{-1}; EIMS m/e (relative intensity) 415 (2, M^+), 274 (17), 228 (base), 154 (26), 141 (36), 129 (27), 77 (86); CIMS (2-methylpropane) m/e (relative intensity) 371 (22), 370 (base), 228 (4), 205 (8); EIHRMS m/e 415.1448 ($C_{22}H_{25}NO_5S$ requires 415.1453). Anal. Calcd for $C_{22}H_{25}NO_5S$: C, 63.58; H, 6.08; N, 3.37; S, 7.72. Found: C, 63.27; H, 6.11; N, 3.54; S, 7.79.

The structure of **21a** was unambiguously established in a single-crystal X-ray structure determination.[21b]

Base-Catalyzed Epimerization of (2R*,4S*)-2-Ethoxy-6-(ethoxycarbonyl)-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (21a): Preparation of (2R*,4R*)-2-Ethoxy-6-(ethoxycarbonyl)-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine. A solution of **21a** (10.0 mg, 24.0 μmol, 1.0 equiv) in anhydrous benzene (120 μL, 0.20 M) at 23 °C was treated with a solution of DBU (2 M in benzene, 3 μL, 0.25 equiv). The reaction mixture was stirred at 23 °C for 1.5 h. The resulting reaction mixture was diluted with ether (10 mL), washed with 2% aqueous hydrochloric acid (2 × 5 mL) and saturated aqueous sodium chloride (1 × 5 mL), dried ($MgSO_4$), and concentrated in vacuo: ^1H NMR of the mixture revealed a 1:2.5 ratio of endo/exo isomers. For *exo*-**21a**: ^1H NMR (C_6D_6, 200 MHz, ppm) 7.81 (2 H, m, o-SO_2ArH), 7.00–6.81 (8 H, m, PhH, m,p-SO_2ArH), 6.23 (1 H, dd, J = 4.4, 2.2 Hz, =CH), 5.40 (1 H, t, J = 3.4 Hz, NC*H*O), 3.93 (2 H, q, J = 7.1 Hz, $CO_2CH_2CH_3$), 3.45 (3 H, m, OCH_2CH_3, C*H*Ph), 2.55 (1 H, apparent d, J = 17 Hz, $CH_{ax}H_{eq}$), 2.20 (1 H, dm, J = 17 Hz, $CH_{ax}H_{eq}$), 1.05 (3 H, t, J = 7.4 Hz, $CO_2CH_2CH_3$), 0.90 (3 H, t, J = 7.1 Hz, OCH_2CH_3).

Pressure-Promoted [4 + 2] Cycloaddition. (2R*,3R*,4S*)-2-Ethoxy-6-(ethoxycarbonyl)-3-methyl-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (28a). Ethyl (*E*)-4-phenyl-2-[(phenylsulfonyl)imino]-3-butenoate (**19a**; 28.0 mg, 81.5 μmol, 1.0 equiv) was placed in a Teflon tube sealed with a brass clamp at one end. A solution of (*Z*)-ethyl-1-propenyl ether (31.0 mg, 360 μmol, 4.4 equiv) in anhydrous dichloromethane (160 μL, 0.50 M) was added to the reaction vessel, and the mixture was purged with argon and sealed with another brass clamp. The reaction vessel was placed in a pressure reactor (6.2 kbar)[37] at 25 °C for 96 h. After depressurization, the reaction mixture was transferred to a round-bottom flask and concentrated in vacuo. Flash chromatography (Florisil, 1 cm × 14 cm, 5% ethyl acetate/hexane eluant) afforded **28a** (19.0 mg, 35.0 mg theoretical, 54%) as a pale yellow solid: mp 73–74 °C ($CHCl_3$/hexane); ^1H NMR ($CDCl_3$, 200 MHz, ppm) 8.07 (2 H, dd, J = 7.9, 1.3 Hz, o-SO_2ArH), 7.55 (3 H, m, m,p-SO_2ArH), 7.19 (5 H, s, ArH), 6.47 (1 H, d, J = 3.4 Hz, =C*H*), 4.77 (1 H, d, J = 2.8 Hz, NC*H*O), 4.34 (2 H, dq, J = 7.1, 3.7 Hz, $CO_2CH_2CH_3$), 3.57 (1 H, dq, J = 7.1, 2.3 Hz, $OCHHCH_3$), 3.38 (1 H, dd, J = 8.8, 3.3 Hz, C*H*Ph), 3.01 (1 H, dq, J = 7.0, 2.3 Hz, $OCHHCH_3$), 2.16 (1 H, qdd, J = 7.3, 3.3, 2.4 Hz, $CHCH_3$), 1.36 (3 H, t, J = 7.1, $CO_2CH_2CH_3$), 0.98 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 0.67 (3 H, d, J = 7.3 Hz, $CHCH_3$); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 165.8 (C=O), 139.3 (C, C6), 138.9 (C aromatic), 133.5 (CH aromatic), 131.1 (CH aromatic), 130.9 (CH aromatic), 129.2 (CH aromatic), 128.3 (CH aromatic), 127.6 (CH aromatic), 127.4 (C aromatic), 126.8 (CH, C5), 86.0 (CH, C2), 63.6 ($CO_2CH_2CH_3$), 61.5 (OCH_2CH_3), 42.4 (CH, C4), 35.8 (CH, C3), 14.7 (CH_3, C3), 14.3 ($CO_2CH_2CH_3$), 13.9 (OCH_2CH_3); IR (neat) ν_{max} 2978, 2930, 1728, 1642, 1448, 1360, 1276, 1204, 1170, 1092, 984, 774 cm^{-1}; EIHRMS m/e (relative intensity) 384 (3), 288 (11), 242 (54), 168 (24), 141 (25), 131 (40), 103 (25), 86 (74), 77 (base), 58 (52); CIMS (2-methylpropane) m/e (relative intensity) 384 (base), 288 (16), 242 (22), 205 (31), 143 (36); EIHRMS m/e 429.1616 ($C_{23}H_{27}NO_5S$ requires 429.1610).

The structure of **28a** was unambiguously established in a single-crystal X-ray structure determination.[21b]

(2R*,4S*)-2-Ethoxy-6-(ethoxycarbonyl)-4-*n*-hexyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (21b): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 7.93 (2 H, dd, J = 6.7, 1.7 Hz, o-SO_2ArH), 7.16 (3 H, m, m,p-SO_2ArH), 6.46 (1 H, d, J = 3.2 Hz, =CH), 5.04 (1 H, t, J = 3.6 Hz, NC*H*O), 4.30 (2 H, dq, J = 7.2, 3.3 Hz, $CO_2CH_2CH_3$), 3.60 (1 H, dq, J = 7.7, 2.4 Hz, $OCHHCH_3$), 3.18 (1 H, dq, J = 7.0, 2.6 Hz, $OCHHCH_3$), 1.81 (1 H, m, =CHC*H*), 1.65–1.52 (2 H, m, CH_2, C3), 1.35 (3 H, t, J = 7.2 Hz, $CO_2CH_2CH_3$), 1.23 (10 H, m, $(CH_2)_5$), 0.99 (3 H, t, J = 7.1 Hz, OCH_2CH_3), 0.84 (3 H, t, J = 6.9 Hz, CH_2CH_3); IR (neat) ν_{max} 2956, 2930, 2858, 1732, 1636, 1448, 1362, 1312, 1272, 1170, 1126, 1096, 1018, 998, 756 cm^{-1}; EIMS m/e (relative intensity) 423 (2, M^+), 250 (21), 236 (base), 152 (18), 141 (32), 77 (56); CIMS (2-methylpropane) m/e (relative intensity) 379 (23), 378 (base), 236 (44); EIHRMS m/e 423.2078 ($C_{22}H_{33}NO_5S$ requires 423.2080).

(2R*,4S*)-2-Ethoxy-6-(ethoxycarbonyl)-4-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (21c): ^1H NMR (C_6D_6, 200 MHz, ppm) 8.07 (2 H, dd, J = 5.6, 3.1 Hz, o-SO_2ArH), 7.89 (3 H, m, m,p-SO_2ArH), 6.37 (1 H, d, J = 2.4 Hz, =CH), 5.08 (1 H, dd, J = 2.4, 1.4 Hz, NC*H*O), 4.20 (2 H, dq, J = 7.1, 2.7 Hz, $CO_2CH_2CH_3$), 3.73 (1 H, dq, J = 7.1, 2.8 Hz, $OCHHCH_3$), 3.07 (1 H, dq, J = 7.1, 2.8 Hz, $OCHHCH_3$), 1.70 (1 H, m, $CHCH_3$), 1.56 (1 H, ddd, J = 14.2, 7.9, 3.8 Hz, $CH_{ax}H_{eq}$), 1.40 (1 H, dt, J = 13.8, 1.2 Hz, $CH_{ax}H_{eq}$), 1.09 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 0.93 (3 H, t, J = 7.2 Hz, OCH_2CH_3), 0.89 (3 H, d, J = 7.9 Hz, $CHCH_3$); IR (neat) ν_{max} 2978, 2934, 1728, 1642, 1446, 1390, 1302, 1264, 1172, 1068, 1026, 972, 760 cm^{-1}; EIMS m/e (relative intensity) 353 (9, M^+), 308 (50), 166 (base), 77 (95); CIMS (2-methylpropane) m/e (relative intensity) 308 (base), 166 (4); EIHRMS m/e 353.1287 ($C_{17}H_{23}NO_5S$ requires 353.1296).

(2R*,4S*)-2-Ethoxy-6-(ethoxycarbonyl)-4-phenyl-1-(methylsulfonyl)-1,2,3,4-tetrahydropyridine (22a): ^1H NMR ($CDCl_3$, 200 MHz, ppm) 7.28 (5 H, s, ArH), 6.72 (1 H, d, J = 3.3 Hz, =C*H*), 5.40 (1 H, t, J = 3.7 Hz, NC*H*O), 4.23 (2 H, dq, J = 7.2, 3.5 Hz, $CO_2CH_2CH_3$), 3.67 (1 H, dq, J = 7.1, 1.7 Hz, $OCHHCH_3$), 3.60 (1 H, dt, J = 9.2, 3.3 Hz, C*H*Ph), 3.42 (1 H, dq, J = 7.1, 1.5 Hz, $OCHHCH_3$), 3.35 (3 H, s, SO_2CH_3), 2.58 (1 H, ddd, J = 13.6, 9.2, 4.4 Hz, $CH_{ax}H_{eq}$), 2.30 (1 H, dt, J = 14.3, 3.3 Hz, $CH_{ax}H_{eq}$), 1.33 (3 H, t, J = 7.1 Hz, $CO_2CH_2CH_3$), 1.17 (3 H, t, J = 7.1 Hz, OCH_2CH_3); IR (neat) ν_{max} 2978, 2936, 1724, 1644, 1452, 1390, 1346, 1322, 1240, 1218, 1160, 1120, 1070, 960, 778 cm^{-1}; EIMS m/e (relative intensity) 228 (70), 200 (11), 182 (16), 154 (32), 131 (base), 103 (49), 77 (32); CIMS (2-methylpropane) m/e (relative intensity) 340 (24), 308 (base), 262 (15), 228 (73), 81 (86); EIHRMS m/e 353.1296 ($C_{17}H_{23}NO_5S$ requires 353.1297).

(2R*,4S*)-2-Ethoxy-6-(ethoxycarbonyl)-4-*n*-hexyl-1-(methylsulfonyl)-1,2,3,4-tetrahydropyridine (22b): ^1H NMR (C_6D_6, 200 MHz, ppm) 6.58 (1 H, d, J = 3.2 Hz, =CH), 5.31 (1 H, dd, J = 3.7, 2.6 Hz, NC*H*O), 4.07 (2 H, dq, J = 6.9, 3.7 Hz, $CO_2CH_2CH_3$), 3.61 (1 H, dq, J = 7.0, 1.8 Hz, $OCHHCH_3$), 3.03 (1 H, dq, J = 7.0, 1.8 Hz, $OCHHCH_3$), 2.97 (3 H, s, SO_2CH_3), 2.02 (1 H, ddd, J = 12.4, 8.4, 3.6 Hz, $CH_{ax}H_{eq}$), 1.80 (2 H, apparent d, J = 12.6 Hz, $CH_{ax}H_{eq}$, =CHC*H*), 1.36–1.12 (10 H, m, $(CH_2)_5$), 0.97 (3 H, t, J = 7.2 Hz, $CO_2CH_2CH_3$), 0.96 (3 H, t, J = 7.1 Hz, OCH_2CH_3), 0.88 (3 H, t, J = 7.1 Hz, CH_2CH_3); IR (neat) ν_{max} 2928, 2958, 1726, 1642, 1466, 1348, 1324, 1232, 1162, 1090, 962 cm^{-1}; EIMS m/e (relative intensity) 361 (2, M^+), 282 (13), 236 (base), 152 (59), 72 (20); CIMS (2-methylpropane) m/e (relative intensity) 316 (base), 238 (17), 81 (14); EIHRMS m/e 316.1923 ($C_{17}H_{31}NO_5S$ requires 361.1923).

(2R*,4S*)-2-Ethoxy-6-(ethoxycarbonyl)-4-methyl-1-(methylsulfonyl)-1,2,3,4-tetrahydropyridine (22c): ^1H NMR (C_6D_6, 200 MHz, ppm) 6.40 (1 H, d, J = 2.4 Hz, =C*H*), 5.27 (1 H, t, J = 2.6 Hz, NC*H*O), 4.03 (2 H, dq, J = 7.0, 2.1 Hz, $CO_2CH_2CH_3$), 3.62 (1 H, dq, J = 7.0, 2.0 Hz, $OCHHCH_3$), 2.97 (1 H, dq, J = 7.0, 2.1 Hz, $OCHHCH_3$), 2.95 (3 H, s, SO_2CH_3), 1.95 (2 H, m, $CH_{ax}H_{eq}$, $CHCH_3$), 1.60 (1 H, d, J = 13.5 Hz, $CH_{ax}H_{eq}$), 0.94 (9 H, m, $CO_2CH_2CH_3$, OCH_2CH_3, OCH_2CH_3); IR (neat) ν_{max} 2934, 2362, 1722, 1640, 1456, 1392, 1370, 1320, 1258, 1228, 1162, 1092, 1072, 968 cm^{-1}; EIMS m/e (relative intensity) 291 (5, M^+), 246 (10), 212 (16), 166 (base); CIMS (2-methylpropane) m/e (relative intensity) 246 (base), 212 (2);

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EIHRMS *m/e* 291.1149 ($C_{12}H_{21}NO_5S$ requires 291.1140).

(2*R,4*S**)-2-(Benzyloxy)-6-(ethoxycarbonyl)-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (27b)**: ^{1}H NMR (C_6D_6, 200 MHz, ppm) 8.05 (2 H, dd, *J* = 4.3, 2.2 Hz, *o*-SO_2ArH), 7.10–6.85 (13 H, m, ArH), 6.71 (1 H, d, *J* = 3.2 Hz, =CH), 5.19 (1 H, t, *J* = 3.6 Hz, NC*H*O), 4.85 (1 H, d, *J* = 11.7 Hz, OC*H*HPh), 4.23 (2 H, q, *J* = 7.3 Hz, $CO_2CH_2CH_3$), 4.22 (1 H, d, *J* = 11.4 Hz, OCH*H*Ph), 2.85 (1 H, dt, *J* = 8.9, 3.4 Hz, C*H*Ph), 2.10 (1 H, ddd, *J* = 11.1, 9.0, 4.1 Hz, $CH_{ax}H_{eq}$), 1.95 (1 H, dt, *J* = 11.1, 4.0 Hz, $CH_{ax}H_{eq}$), 1.06 (3 H, t, *J* = 7.3 Hz, $CO_2CH_2CH_3$); IR (neat) ν_{max} 3064, 2938, 1736, 1642, 1496, 1448, 1360, 1288, 1214, 1170, 1056, 964 cm^{-1}; EIMS *m/e* (relative intensity) 230 (19), 91 (base), 65 (4); CIMS (2-methylpropane) *m/e* (relative intensity) 370 (base), 336 (4), 230 (10); CIHRMS *m/e* 478.1674 ($C_{27}H_{27}NO_5S$ requires 478.1688).

(2*R*,3*R,4*S**)-2-(Benzyloxy)-6-(ethoxycarbonyl)-3-methyl-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (28b)**, ^{1}H NMR ($CDCl_3$, 200 MHz, ppm) 8.10 (2 H, dd, *J* = 6.7, 1.5 Hz, *o*-SO_2ArH), 7.70–7.54 (3 H, m, *m,p*-SO_2ArH), 7.29–7.02 (10 H, m, ArH), 6.51 (1 H, d, *J* = 3.2 Hz, =CH), 4.88 (1 H, d, *J* = 2.6 Hz, NC*H*O), 4.64 (1 H, d, *J* = 12.0 Hz, OC*H*HPh), 4.37 (2 H, dq, *J* = 7.0, 3.7 Hz, $CO_2CH_2CH_3$), 4.07 (1 H, d, *J* = 11.9 Hz, OCH*H*Ph), 3.42 (1 H, dd, *J* = 8.9, 3.3, Hz, C*H*Ph), 2.17 (1 H, qdd, *J* = 7.2, 8.8, 2.6 Hz, C*H*CH_3), 1.35 (3 H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 0.69 (3 H, d, *J* = 7.2 Hz, CHC*H*$_3$); IR (neat) ν_{max} 2926, 1728, 1642, 1494, 1362, 1276, 1204, 1170, 1090, 1050, 874 cm^{-1}; CIMS (2-methylpropane) *m/e* (relative intensity) 384 (base), 350 (12), 244 (19), 143 (20); EIHRMS *m/e* 491.1765 ($C_{28}H_{29}NO_5S$ requires 491.1766).

(2*R,4*R**)-6-(Ethoxycarbonyl)-2,4-diphenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (29a)**. ^{1}H NMR (C_6D_6, 200 MHz, ppm) 8.08 (2 H, d, *J* = 7.3 Hz, *o*-SO_2ArH), 7.20–6.90 (11 H, m), 6.66 (1 H, d, *J* = 3.1 Hz, =CH), 6.44 (2 H, d, *J* = 7.2 Hz, *o*-PhH), 5.22 (1 H, t, *J* = 6.4 Hz, NC*H*Ph), 4.23 (2 H, dq, *J* = 7.3, 3.7 Hz, $CO_2CH_2CH_3$), 2.91 (1 H, td, *J* = 6.1, 3.7 Hz, C*H*Ph), 2.31 (1 H, ddd, *J* = 14.0, 6.7, 6.1 Hz, $CH_{ax}H_{eq}$), 2.00 (1 H, ddd, *J* = 14.0, 6.7, 6.0 Hz, $CH_{ax}H_{eq}$), 1.45 (3 H, t, *J* = 7.3 Hz, $CO_2CH_2CH_3$); IR (neat) ν_{max} 3030, 2926, 2854, 1728, 1638, 1602, 1496, 1448, 1364, 1256, 1168, 1140, 1094, 964, 846 cm^{-1}; EIMS *m/e* (relative intensity) 306 (23), 231 (18), 131 (20), 103 (32), 91 (30), 77 (base), 51 (28); CIMS (2-methylpropane) *m/e* (relative intensity) 448 (M + H$^+$, base); EIHRMS *m/e* 447.1504 ($C_{26}H_{25}NO_4S$ requires 447.1504).

(2*R,4*R**)-6-(Ethoxycarbonyl)-2-(4′-methoxyphenyl)-4-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (29b)**. ^{1}H NMR (C_6D_6, 200 MHz, ppm) 8.15 (2 H, dd, *J* = 6.9, 2.9 Hz, *o*-SO_2ArH), 7.20–6.90 (8 H, m, *m,p*-SO_2ArH, PhH), 6.66 (1 H, d, *J* = 3.4 Hz, =CH), 6.51 (4 H, d, *J* = 8.8 Hz, $ArOCH_3$), 5.18 (1 H, t, *J* = 6.6 Hz, NC*H*Ph), 4.25 (2 H, dq, *J* = 7.1, 3.6 Hz, $CO_2CH_2CH_3$), 3.23 (3 H, s, OCH_3), 2.95 (1 H, dt, *J* = 6.6, 3.5 Hz, C*H*Ph), 2.35 (1 H, ddd, *J* = 13.8, 6.2, 6.1 Hz, $CH_{ax}H_{eq}$), 2.10 (1 H, ddd, *J* = 13.8, 7.0, 6.8 Hz, $CH_{ax}H_{eq}$), 1.10 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$); IR (neat) ν_{max} 2928, 1728, 1612, 1514, 1448, 1362, 1250, 1168, 1032, 754 cm^{-1}; EIMS *m/e* (relative intensity) 477 (12, M$^+$), 404 (8), 336 (60), 134 (base), 77 (51); CIMS (2-methylpropane) *m/e* (relative intensity) 478 (M + H$^+$, 68), 338 (base); EIHRMS *m/e* 477.1610 ($C_{27}H_{27}NO_5S$ requires 477.1610).

(2*R,3*S**,4*S**)-2-Ethoxy-6-(ethoxycarbonyl)-3-methyl-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (30)**: ^{1}H NMR (C_6D_6, 200 MHz, ppm) 8.01 (2 H, d, *J* = 7.6 Hz, *o*-SO_2ArH), 7.00–6.84 (8 H, m, ArH), 6.67 (1 H, dd, *J* = 3.6, 1.8 Hz, =CH), 5.07 (1 H, d, *J* = 4.4 Hz, NC*H*O), 4.16 (2 H, dq, *J* = 7.0, 3.3 Hz, $CO_2CH_2CH_3$), 4.00 (1 H, dq, *J* = 7.4, 1.8 Hz, OC*H*HCH$_3$), 3.42 (1 H, dq, *J* = 7.0, 1.7 Hz, OCH*H*CH$_3$), 2.20 (1 H, m, C*H*CH$_3$), 2.08 (1 H, dd, *J* = 10.2, 3.0 Hz, C*H*Ph), 1.09 (6 H, m, $CO_2CH_2CH_3$, OCH_2CH_3), 0.77 (3 H, d, *J* = 6.6 Hz, CHC*H*$_3$); IR (neat) ν_{max} 2976, 2928, 1734, 1636, 1560, 1448, 1362, 1172, 1088, 1030, 750 cm^{-1}; EIMS *m/e* (relative intensity) 288 (21), 242 (38), 196 (12), 168 (25), 141 (34), 86 (94), 77 (base), 58 (61); CIMS (2-methylpropane) *m/e* (relative intensity 384 (base), 244 (5); EIHRMS *m/e* 429.1614 ($C_{23}H_{27}NO_5S$ requires 429.1610).

(4*R)-6-(Ethoxycarbonyl)-2,2-dimethoxy-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (31)**: ^{1}H NMR (C_6D_6, 200 MHz, ppm) 8.45 (2 H, dd, *J* = 6.3, 1.4 Hz, *o*-SO_2ArH), 7.05–6.96 (8 H, m, ArH), 6.58 (1 H, d, *J* = 3.5 Hz, =C*H*), 4.16 (2 H, dq, *J* = 7.3, 1.4 Hz, $CO_2CH_2CH_3$), 3.60 (1 H, td, *J* = 9.9, 3.5 Hz, C*H*Ph), 3.10 (3 H, s, OCH_3), 2.74 (3 H, s, OCH_3), 2.51 (1 H, t, *J* = 10.9 Hz, $CH_{ax}H_{eq}$), 2.32 (1 H, dd, *J* = 9.1, 5.0 Hz, $Ch_{ax}H_{eq}$), 1.01 (3 H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); IR (neat) ν_{max} 3062, 2946, 1726, 1648, 1492, 1450, 1324, 1274, 1168, 1124, 1088, 1050, 980 cm^{-1}; EIMS *m/e* (relative intensity) 290 (33), 141 (9), 121 (16), 88 (base), 77 (39), 58 (29), 51 (12); CIMS (2-methylpropane) *m/e* (relative intensity) 432 (M + H$^+$, base); CIHRMS *m/e* 432.1481 ($C_{22}H_{25}NO_6S$ requires 432.1481).

(2*R,3*S**,4*R**)-3-Acetoxy-2-(benzyloxy)-6-(ethoxycarbonyl)-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (32)**: ^{1}H NMR ($CDCl_3$, 200 MHz, ppm) 8.10 (2 H, dd, *J* = 6.9, 1.3 Hz, *o*-SO_2ArH), 7.56 (3 H, m, *m,p*-SO_2ArH), 7.20 (3 H, m, *m,p*-CH_2ArH), 7.15 (5 H, m, Ph), 6.95 (2 H, m, *o*-CH_2ArH), 6.50 (1 H, dd, *J* = 3.5, 0.9 Hz, =C*H*), 5.47 (1 H, d, *J* = 2.7 Hz, NC*H*OBn), 5.27 (1 H, dd, *J* = 2.8, 1.7 Hz, C*H*OAc), 4.38 (1 H, d, *J* = 11.5 Hz, OC*H*HPh), 4.35 (2 H, dq, *J* = 7.1, 2.8 Hz, $CO_2CH_2CH_3$), 4.00 (1 H, d, *J* = 11.4 Hz, OCH*H*Ph), 3.43 (1 H, t, *J* = 3.4 Hz, C*H*Ph), 2.05 (3 H, s, $COCH_3$), 1.35 (3 H, t, *J* = 7.1 Hz, $CO_2CH_2CH_3$); IR (neat) ν_{max} 2926, 1730, 1642, 1448, 1370, 1352, 1280, 1244, 1154, 1092, 1052, 868 cm^{-1}; EIMS *m/e* (relative intensity) 368 (23), 141 (14), 128 (17), 115 (19), 105 (36), 91 (86), 77 (base), 57 (25), 51 (34); CIMS (2-methylpropane) *m/e* (relative intensity) 405 (base), 317 (40), 288 (23), 244 (19), 228 (65), 218 (23), 143 (62); CIHRMS *m/e* 536.1738 ($C_{29}H_{29}NO_7S$ requires 536.1743).

(2*R,3*R**,4*R**)-3-Acetoxy-2-(benzyloxy)-6-(ethoxycarbonyl)-4-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (33)**: ^{1}H NMR ($CDCl_3$, 200 MHz, ppm) 8.07 (2 H, dd, *J* = 7.0, 1.5 Hz, *o*-SO_2ArH), 7.61 (3 H, m, *m,p*-SO_2ArH), 7.23 (3 H, m, *m,p*-CH_2ArH), 7.13 (5 H, s, PhH), 7.05 (2 H, m, *o*-CH_2ArH), 6.50 (1 H, d, *J* = 3.3 Hz, =C*H*), 5.15 (1 H, d, *J* = 3.5 Hz, NC*H*OBn), 4.95 (1 H, dd, *J* = 9.1, 3.5 Hz, C*H*OAc), 4.65 (1 H, d, *J* = 12.0 Hz, OC*H*HPh), 4.35 (2 H, dq, *J* = 7.1, 1.1 Hz, $CO_2CH_2CH_3$), 4.17 (1 H, d, *J* = 12.0 Hz, OCH*H*Ph), 3.90 (1 H, dd, *J* = 9.1, 3.3 Hz, C*H*Ph), 1.70 (3 H, s, $COCH_3$), 1.35 (3 H, t, *J* = 7.25 Hz, *J* = $CO_2CH_2CH_3$); IR (neat) ν_{max} 3032, 2930, 2856, 1734, 1646, 1448, 1368, 1316, 1280, 1236, 1170, 1060, 928 cm^{-1}; EIMS *m/e* (relative intensity) 368 (16), 288 (9), 141 (9), 91 (base), 77 (31); CIMS (2-methylpropane) *m/e* (relative intensity) 428 (base), 405 (25), 288 (12), 228 (19), 143 (24); CIHRMS *m/e* 536.1728 ($C_{29}H_{29}NO_7S$ requires 536.1743).

Ethyl (*E*)-4-[(Phenylsulfonyl)imino]-2-butenoate (35). A solution of ethyl 4-oxo-2-butenoate[30] (826 mg, 6.45 mmol) and benzenesulfonamide (1.50 g, 6.70 mmol, 1.03 equiv) in methylene chloride (25 mL) was cooled to 0 °C and treated with triethylamine (2.1 mL, 15 mmol, 2.33 equiv). The mixture was cooled to −5 °C, and a solution of titanium tetrachloride in methylene chloride (6.0 mL, 0.64 m, 3.8 mmol, 0.59 equiv) was added dropwise over 20 min. The resulting reaction mixture was stirred for 9 h at −5 to 0 °C and at 22 °C for 1 h. Filtration of the mixture through Celite and concentration of the filtrate afforded a brown solid. Redissolution of the solid in ether (50 mL, 2 h), filtration, and concentration of the filtrate afforded **35** (1.04 g, 1.72 g theoretical, 60%), which was sufficiently pure by ^{1}H NMR (homogeneous) for use in the Diels–Alder reactions: yelow solid; mp 87–89 °C (ether/hexane (1:1); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 8.74 (d, 1 H, C4-H, *J* = 9.3 Hz), 7.97 (d, 2 H, aromatic) 7.60 (m, 3 H, aromatic), 7.31 (dd, 1 H, C3-H, *J* = 9.3, 15.7 Hz), 6.73 (d, 1 H, C2-H, *J* = 15.7 Hz), 4.28 (q, 2 H, $CO_2CH_2CH_3$, *J* = 7.2 Hz), 1.32 (t, 3 H, $CO_2CH_2CH_3$, *J* = 7.2 Hz); IR (KBr) ν_{max} 3062, 2984, 1713, 1632, 1602, 1576, 1450, 1354, 1323, 1288, 1181, 1171, 1149, 1091, 1043, 996 cm^{-1}; EIMS *m/e* (relative intensity) 141 (24), 126 (7), 98 (6), 93 (5), 78 (7), 77 (base), 73 (11), 56 (16); CIMS (2-methylpropane) *m/e* (relative intensity) 268 (M + H$^+$, base). Anal. Calcd for $C_{12}H_{13}NO_4S$: C, 53.93; H, 4.90; N, 5.24. Found: C, 53.90; H, 5.06; N, 5.49.

Ethyl (*E*)-4-[(Methylsulfonyl)imino]-2-butenoate (36). A solution of ethyl 4-oxo-2-butenoate[30] (497 mg, 3.88 mmol) and methanesulfonamide (374 mg, 3.93 mmol, 1.03 equiv) in methylene chloride (15 mL) was cooled to 0 °C and treated with triethylamine (1.25 mL, 8.90 mmol, 2.3 equiv). The resulting reaction mixture was cooled to −6 °C, and a solution of titanium tetrachloride in methylene chloride (3.6 mL, 0.64 M, 2.3 mmol, 0.59 equiv) was added dropwise over 14 min. The reaction mixture was stirred at −2 to 0 °C for 9.5 h and allowed to warm to 25 °C over 30 min. Filtration of the mixture through Celite and concentration of the filtrate afforded a brown solid. Redissolution of the solid in ether (30 mL, 2 h), filtration, and concentration of the filtrate afforded crude **36** as a yellow oil that solidified on standing at 4 °C (367 mg, 795 mg theoretical, 46%) and that was sufficiently pure by ^{1}H NMR (homogeneous) for use in the Diels–Alder reactions: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 8.73 (d, 1 H, C4-H, *J* = 9.5 Hz), 7.34 (dd, 1 H, C3-H, *J* = 9.5, 15.8 Hz), 6.75 (d, 1 H, C2-H, *J* = 15.8 Hz), 4.30 (q, 2 H, $CO_2CH_2CH_3$, *J* = 7.3 Hz), 3.10 (s, 3 H, CH_3SO_2), 1.35 (t, 3 H, $CO_2CH_2CH_3$, *J* = 7.3 Hz); IR (neat) ν_{max} 3277, 2935, 1718, 1636, 1597, 1560, 1370, 1308, 1261, 1191, 1154, 1028, 969, 801 cm^{-1}; EIMS *m/e* (relative intensity) 205 (4, M$^+$), 160 (4), 132 (13), 126 (6), 99 (4), 98 (44), 96 (25), 95 (27), 83 (20), 82 (25), 81 (10), 80 (base), 79 (68), 64 (13), 55 (29), 54 (25); CIMS (2-methylpropane) *m/e* (relative intensity) 206 (M + H, base); CIHRMS *m/e* 206.0489 ($C_7H_{11}NO_4S$ requires 206.0487).

General Procedure for Room-Temperature Diels–Alder Reaction of 35 and 36. (2*R,4*S**)-2-(Benzyloxy)-4-(ethoxycarbonyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (37b).** A solution of **35** (71.1 mg, 0.27 mmol) in methylene chloride (0.53 mL, 0.50 M) was cooled to 0 °C and treated with benzyl vinyl ether (190 mg, 1.41 mmol, 5.3 equiv), and

the mixture was allowed to warm gradually to 21 °C. Small aliquots were removed from the reaction mixture to monitor the progress by ^{1}H NMR. The reaction was judged complete (30:1 endo/exo) after 45.5 **h**. Evaporation of solvent in vacuo and purification of the residue by flash column chromatography (Florisil, 12 × 1.5 cm, 20% ethyl acetate/hexane eluant) afforded **37b** as a white solid (94 mg, 107 mg theoretical, 88%, 25:1 endo/exo). For pure **37b**: mp 79–80.5 °C (white needles, ether/hexane (1:1)); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 7.76 (m, 2 H, aromatic), 7.51 (m, 3 H, aromatic), 7.27 (m, 5 H, aromatic), 6.67 (dt, 1 H, C6-H, J = 1.3, 8.2 Hz), 5.65 (m, 2 H, C2-H and C5-H), 4.71 (d, 1 H, OC*H*HPh, J = 11.8 Hz), 4.57 (d, 1 H, OCH*H*Ph, J = 11.8 Hz), 3.92 (m, 2 H, $CO_2CH_2CH_3$), 2.81 (m, 1 H, C4-H), 2.70 (dt, 1 H, C3-H_{eq}, J = 1.3, 13.8 Hz), 1.20 (ddd, 1 H, C3-H_{ax}, J = 2.3, 7.6, 13.8 Hz), 1.07 (t, 3 H, $CO_2CH_2CH_3$, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.7 (*C*O_2Et), 139.6 (C aromatic) 138.1 (C aromatic), 133.4 (CH aromatic), 129.7 (CH aromatic), 128.4 (CH aromatic), 127.9 (CH aromatic), 127.7 (CH aromatic), 127.1 (CH aromatic), 122.9 (CH, C6), 108.1 (CH, C5), 81.0 (CH, C2), 69.7 (OCH_2Ph), 61.0 ($CO_2CH_2CH_3$), 34.0 (CH, C4), 28.4 (CH_2, C3), 13.9 ($CO_2CH_2CH_3$); IR (KBr) ν_{max} 2976, 2937, 2895, 1728, 1450, 1363, 1348, 1333, 1311, 1293, 1271, 1253, 1214, 1175, 1160, 1135, 1106, 1057, 1030, 932, 734, 691 cm^{-1}; EIMS *m/e* (relative intensity) 294 (2), 220 (4), 152 (2), 141 (5), 132 (6), 108 (2), 107 (4), 105 (6), 91 (base), 80 (9), 79 (8), 78 (6), 65 (5); CIMS (2-methylpropane) *m/e* (relative intensity) 294 (M + H$^+$ – $HOCH_2$Ph, base); EIHRMS *m/e* 401.1307 ($C_{21}H_{23}NO_5S$ requires 401.1297). Anal. Calcd for $C_{21}H_{23}NO_5S$: C, 62.83; H, 5.77; N, 3.49. Found: C, 62.75; H, 5.91; N, 3.72.

(2*R,4*S**)-2-Ethoxy-4-(ethoxycarbonyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (37a).** Conditions: ethyl vinyl ether (5 equiv), 0.28 mmol scale, 46 h, 21 °C. Examination of the crude product by ^{1}H NMR (500 MHz) showed a 29.5:1 mixture of endo/exo isomers (isolated **37a** 82%, 22:1 (endo/exo)). For pure **37a**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 7.80 (d, 2 H, aromatic, J = 7.0 Hz), 7.50 (m, 3 H, aromatic), 6.65 (dd, 1 H, C6-H, J = 1.3, 9.7 Hz), 5.30 (ddd, 1 H, C5-H, J = 1.2, 6.0, 9.7 Hz), 5.26 (broad s, 1 H, C2-H), 4.10 (m, 2 H, $CO_2CH_2CH_3$), 3.67 (m, 1 H, OC*H*HCH$_3$), 3.51 (m, 1 H, OCH*H*CH$_3$), 2.79 (apparent t, 1 H, C4-H, J = 6.0 Hz), 2.60 (dt, 1 H, C3-H_{eq}, J = 1.2, 12.8 Hz), 1.23 (t, 3 H, OCH_2CH_3, J = 7.2 Hz), 1.18 (m, 1 H, C3-H_{ax}, C3), 1.05 (t, 3 H, $CO_2CH_2CH_3$, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.9 (*C*O_2Et), 139.9 (C aromatic), 133.3 (CH aromatic), 129.6 (CH aromatic), 127.1 (CH aromatic), 123.0 (CH, C6), 107.6 (CH, C5), 81.0 (CH, C2), 63.3 ($CO_2CH_2CH_3$), 61.0 (OCH_2CH_3), 34.0 (CH, C4), 28.4 (CH_2, C3), 14.7 ($CO_2CH_2CH_3$), 14.1 (OCH_2CH_3); IR (neat) ν_{max} 2977, 2929, 1730, 1701, 1685, 1654, 1447, 1396, 1364, 1350, 1337, 1311, 1267, 1172, 1108, 1046, 919, 728 cm^{-1}; EIMS *m/e* (relative intensity) 294 (13), 266 (26), 220 (11), 152 (21), 141 (17), 124 (15), 103 (25), 96 (25), 81 (10); 80 (base), 77 (36), 73 (32), 68 (10); CIMS (2-methylpropane) *m/e* (relative intensity) 294 (M + H$^+$ – EtOH, base); EIHRMS *m/e* 339.1136 ($C_{16}H_{21}NO_5S$ requires 339.1140). Anal. Calcd for $C_{16}H_{21}NO_5S$: C, 56.62; H, 6.24; N, 4.13. Found: C, 56.73; H, 6.54; N, 4.18.

Diagnostic ^{1}H NMR signals utilized for the estimation of the endo/exo ratio (by integration) for the minor cycloadduct are as follows: 3.34 (m, 1 H, C4–H), 2.15 (m, 1 H, C3–H_{ax}). This was established to be the exo diastereomer by deliberate epimerization as detailed in the following text.

Base-Catalyzed Epimerization of (2*R,4*S**)-2-Ethoxy-4-(ethoxycarbonyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (37a): Preparation of (2*R**,4*R**)-2-Ethoxy-4-(ethoxycarbonyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine.** A solution of **37a** (9.3 mg, 27 μmol) in dry benzene (0.12 mL) was treated with a solution of DBU (2 M in benzene, 10 μmol, 1 equiv), and the mixture was stirred at 21 °C for 1.5 h. The resulting reaction mixture was diluted with ether (5 mL) and washed with aqueous hydrochloric acid (2%, 2 × 3 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. A 4.5:1 mixture of isomers was obtained (4.5:1 C4 epimers) with the major isomer having the (2*R**,4*R**) relative configuration: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 7.77 (dd, 2 H, aromatic, J = 1.6, 7 Hz), 7.53 (m, 3 H, aromatic), 6.59 (ddd, 1 H, C6-H, J = 1.26, 2.50, 8.3 Hz), 5.25 (m, 2 H, C5-H and C2-H), 4.09 (q, 2 H, $CO_2CH_2CH_3$, J = 7.1 Hz), 3.82 (m, 1 H, OC*H*HCH$_3$), 3.64 (m, 1 H, OCH*H*CH$_3$), 3.34 (m, 1 H, C4-H), 2.15 (m, 1 H, C3-*H*$_{eq}$), 1.20 (m, 7 H, $CO_2CH_2CH_3$, OCH_2CH_3 and C3-H_{ax}).

(2*R,4*S**)-2-Ethoxy-4-(ethoxycarbonyl)-1-(methylsulfonyl)-1,2,3,4-tetrahydropyridine (38a),** Conditions: ethyl vinyl ether (5 equiv), 0.26 mmol scale, 56 h, 21 °C. Examination of the crude product by ^{1}H NMR (300 MHz) showed a 27.5:1 mixture of endo/exo isomers (isolated **38a** 73%, 21:1 (endo/exo)). For pure **38a**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 6.52 (d, 1 H, C6-H, J = 8.3 Hz), 5.28 (m, 2 H, C5-H and C2-H), 4.15 (q, 2 H, $CO_2CH_2CH_3$, J = 7.1 Hz), 3.53 (q, 2 H, OCH_2CH_3, J = 7.0 Hz), 3.01 (m, 1 H, C4-H), 2.97 (s, 3 H, CH_3SO_2), 2.98 (dd, 1 H, C3-H_{eq}, J = 1.2, 14.1 Hz), 1.82 (ddd, 1 H, C3-H_{ax}, J = 1.7, 7.3, 14.1 Hz), 1.27 (t, 3 H, $CO_2CH_2CH_3$, J = 7.1 Hz), 1.13 (t, 3 H, OCH_2CH_3, J = 7.0 Hz); diagnostic ^{1}H NMR signals utilized for the estimation of the endo/exo ratio (by integration) for the minor cycloadduct were 3.40 (m, 1 H, C4-H), 2.45 (m, 1 H, C3-H); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.9 (*C*O_2Et), 123.3 (CH, C6), 105.5 (CH, C5), 81.2 (CH, C2), 63.5 ($CO_2CH_2CH_3$), 61.1 (OCH_2CH_3), 41.0 (CH_3SO_2), 33.9 (CH, C4), 27.8 (CH_2, C3), 14.8 ($CO_2CH_2CH_3$), 14.2 (OCH_2CH_3); IR (neat) ν_{max} 2978, 1730, 1654, 1438, 1336, 1268, 1211, 1166, 1102, 1046, 952, 922, 762 cm^{-1}; EIMS *m/e* (relative intensity) 232 (11), 204 (55), 198 (7), 158 (22), 124 (91), 96 (12), 81 (13), 80 (base), 72 (10), 68 (13), 53 (9); CIMS (2-methylpropane) *m/e* (relative intensity) 232 (M + H$^+$ – EtOH, base); EIHRMS *m/e* 277.0984 ($C_{11}H_{19}NO_5S$ requires 277.0984). Anal. Calcd for $C_{11}H_{19}NO_5S$: C, 47.64; H, 6.91; N, 5.05. Found: C, 47.81; H, 7.24; N, 4.77.

(2*S,3*S**,4*R**)-2-Ethoxy-4-(ethoxycarbonyl)-3-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (39a-endo).** Conditions: (*E*)-ethyl-1-propenyl ether (3.1 equiv), 0.17 mmol scale, 37 h, 21 °C. Examination of crude ^{1}H NMR (300 MHz) showed a 2:1 mixture of endo/exo isomers (isolated **39a** 93%, 2.2:1 (endo/exo)). For pure **39a**-endo: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 7.82 (m, 2 H, aromatic), 7.45 (m, 3 H, aromatic), 6.63 (d apparent triplet, 1 H, C6-H, J = 1.1, 8.5 Hz), 5.11 (ddd, 1 H, C5-H, J = 1.3, 5.5, 8.5 Hz), 5.01 (d, 1 H, C2-H, J = 1.3 Hz), 4.09 (m, 2 H, $CO_2CH_2CH_3$), 3.54 (m, 2 H, OCH_2CH_3), 2.85 (ddq, 1 H, C3-H, J = 1.3, 5.5, 7.3 Hz), 2.51 (d, 1 H, C4-H, J = 5.5 Hz), 1.23 (t, 3 H, $CO_2CH_2CH_3$, J = 7.1 Hz), 1.01 (t, 3 H, OCH_2CH_3, J = 7.0 Hz), 0.47 (d, 3 H, CH_3CH, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.9 (*C*O_2Et), 140.6 (C aromatic), 133.4 (CH aromatic), 129.4 (CH aromatic), 127.4 (CH aromatic), 122.0 (CH, C6), 103.9 (CH, C5), 85.6 (CH, C2), 63.5 ($CO_2CH_2CH_3$), 60.9 (OCH_2CH_3), 41.3 (CH, C4), 32.7 (CH, C3), 15.9 ($CO_2CH_2CH_3$), 14.8 (OCH_2CH_3), 14.2 (CH_3CH); IR (neat) ν_{max} 2977, 2931, 1735, 1654, 1480, 1448, 1363, 1341, 1257, 1172, 1112, 1092, 1027, 995, 928, 909, 881, 853, 759, 729 cm^{-1}; EIMS *m/e* (relative intensity) 292 (46), 280 (25), 141 (15), 138 (13), 110 (16), 94 (base), 86 (48), 84 (6), 82 (17), 72 (45), 58 (25); CIMS (2-methylpropane) *m/e* (relative intensity) 308 (M + H$^+$ – EtOH, base); EIHRMS *m/e* 353.1297 ($C_{17}H_{23}NO_5S$ requires 353.1297).

Irradiation of C4–H resulted in a 7.6% increase in the adjacent methyl signal (CH_3CH) and a 12.7% increase in the C5–H signal in the NOE difference spectrum. Irradiation of the methyl substituent at C3 (C-H_3CH) resulted in a 4% increase in the signal due to the ortho hydrogens of the phenyl ring, a 4.1% increase in C2–H, a 7.8% increase in C4–H and a 7.6% increse in C3–H. Irradiation of C3–H resulted in a 12% increase in C2–H and an 8.4% increase in the adjacent methyl group (CHCH_3) in the NOE difference spectrum ($CDCl_3$, 200 MHz).

(2*R,3*S**,4*S**)-2-Ethoxy-4-(ethoxycarbonyl)-3-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (39a-exo),** Minor adduct **39a**-exo: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 7.83 (m, 2 H, aromatic), 7.52 (m, 3 H, aromatic), 6.57 (d, apparent triplet, 1 H, C6-H, J = 1.3, 7.5 Hz), 5.16 (d, apparent triplet, 1 H, C5-H, J = 1.5, 7.5 Hz), 4.99 (apparent t, 1 H, C2-H, J = 1.2 Hz), 4.13 (m, 2 H, $CO_2CH_2CH_3$), 3.78 (m, 1 H, OC*H*HCH$_3$), 3.70 (m, 1 H, OCH*H*CH$_3$), 3.50 (m, 1 H, C4-H), 2.45 (m, 1 H, C3-H), 1.23 (t, 3 H, $CO_2CH_2CH_3$, J = 7.2 Hz), 1.16 (t, 3 H, OCH_2CH_3, J = 7.1 Hz), 0.30 (d, 3 H, CH_3CH, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 173.1 (*C*O_2Et), 140.6 (C aromatic), 133.4 (CH aromatic), 129.5 (CH aromatic), 127.5 (CH aromatic), 122.3 (CH, C6), 103.8 (CH, C5), 86.5 (CH, C2), 63.8 ($CO_2CH_2CH_3$), 60.9 (OCH_2CH_3), 38.3 (CH, C4), 32.0 (CH, C3), 15.1 ($CO_2CH_2CH_3$), 14.2 (OCH_2CH_3), 11.1 (CH_3CH); IR (neat) ν_{max} 2978, 2928, 1737, 1701, 1654, 1448, 1363, 1337, 1285, 1242, 1170, 1108, 1092, 1054, 1031, 970, 934, 869, 729 cm^{-1}; EIMS *m/e* (relative intensity) 308 (14), 292 (base), 280 (23), 141 (29), 138 (16), 110 (25), 94 (91), 86 (41), 84 (22), 82 (27), 78 (11), 77 (90), 67 (10), 58 (30), 57 (20), 55 (13), 51 (28); CIMS (2-methylpropane) *m/e* (relative intensity) 308 (M + H$^+$ – EtOH, base); EIHRMS *m/e* 353.1297 ($C_{17}H_{23}NO_5S$ requires 353.1297).

Irradiation of the methyl substituent at C3 (CHCH_3) resulted in a 4.8% increase in the C3–H signal, a 2.5% increase in the C2–H signal and a 4.1% increase in the signal for the ortho hydrogens of the phenyl ring in the NOE difference spectrum. Irradiation of C3–H resulted in a 6% increase in the signal due to the methyl substituent, at 18% increase in the C4–H signal and a 12.1% increase in the C2–H signal in the NOE difference spectrum ($CDCl_3$, 200 MHz).

(2*R,3*S**,4*R**)-2-Ethoxy-4-(ethoxycarbonyl)-3-methyl-1-(methylsulfonyl)-1,2,3,4-tetrahydropyridine (39b-endo),** Conditions: (*E*)-ethyl 1-propenyl ether (3 equiv), 0.21 mmol scale, 43 h, 21 °C. Examination of crude ^{1}H NMR (300 MHz) showed a 2.2:1 mixture of endo/exo isomers (isolated **39b** 91%, 2.2:1 (endo/exo)). For pure **39b**-endo: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 6.48 (dd, 1 H, C6-H, J = 8.5, 1.0 Hz), 5.15 (m, 1 H, C5-H), 4.95 (d, 1 H, C2-H, J = 2.2 Hz), 4.14 (m, 2 H, OCH_2CH_3), 3.52 (m, 2 H, OCH_2CH_3), 3.01 (s, 1 H, CH_3SO_2), 2.99 (m,

1 H, C3-H), 2.67 (d, 1 H, C4-H, J = 5.5 Hz), 1.27 (t, 3 H, OCH_2CH_3, J = 7.1 Hz), 1.10 (t, 3 H, OCH_2CH_3, J = 7.0 Hz), 0.99 (d, 3 H, CH_3CH, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.9 (CO_2Et), 122.2 (CH, C6), 103.1 (CH, C5), 85.9 (CH, C2), 63.7 ($CO_2CH_2CH_3$), 61.1 (OCH_2CH_3), 41.5 (CH, C4), 41.1 (CH_3SO_2), 31.5 (CH, C3), 16.4 ($CO_2CH_2CH_3$), 15.0 (OCH_2CH_3), 14.2 (CH_3CH); IR (neat) ν_{max} 2978, 1734, 1718, 1701, 1696, 1685, 1654, 1636, 1559, 1507, 1473, 1458, 1340, 1259, 1167, 1082, 1027, 998, 964, 933, 768, 728 cm^{-1}; EIMS m/e (relative intensity) 291 (M^+, 4), 246 (5), 230 (15), 218 (32), 172 (13), 110 (14), 94 (base), 86 (45), 82 (18), 58 (37); CIMS (2-methylpropane) m/e (relative intensity) 246 (M + H^+ – EtOH, base); EIHRMS m/e 291.1143 ($C_{12}H_{21}NO_5S$ requires 291.1140).

Minor adduct **39b**-exo could not be separated from **39b**-endo. Diagnostic ^1H NMR signals utilized for the estimation of endo/exo ratio (by integration) for the minor cycloadduct are as follows: 5.24 (dt, 1 H, C5-H, J = 8.5, 1.5 Hz), 3.70 (q, 2 H, OCH_2CH_3, J = 7 Hz), 2.6 (m, 1 H, C3-H), 0.82 (d, 3 H, CH_3CH, J = 7.2 Hz).

(2*R,3*R**,4*R**)-2-Ethoxy-4-(ethoxycarbonyl-3-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (40-endo).** Conditions: (*E*)-1-ethoxy-2-phenylethylene[36c] (2.5 equiv), 0.29 mmol scale, 61 h, 21 °C. Examination of crude ^1H NMR (300 MHz) showed a 5:1 mixture of endo/exo isomers (isolated **40** 61%, 5:1 (endo/exo)). For pure **40**-endo: mp 109–110 °C (EtOAc/hexane); ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.4–6.9 (m, 10 H, aromatic), 6.67 (d apparent t, 1 H, C6-H, J = 1.4, 8.4 Hz), 5.45 (ddd, 1 H, C5-H, J = 1.1, 5.0, 8.4 Hz), 5.40 (dd, 1 H, C2-H, J = 1.4, 2.7 Hz), 4.15 (m, 3 H, OCH_2CH_3 and C3-H), 3.67 (m, 2 H, OCH_2CH_3), 3.12 (d, 1 H, C4-H, J = 5.0 Hz), 1.28 (t, 3 H, OCH_2CH_3), 1.13 (t, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.7 (CO_2Et), 139.9 (C aromatic), 138.8 (C aromatic), 132.6 (CH aromatic), 129.2 (CH aromatic), 128.7 (CH aromatic), 127.7 (CH aromatic), 127.6 (CH aromatic), 126.8 (CH aromatic), 122.3 (CH, C6), 105.6 (CH, C5), 86.1 (CH, C2), 63.5 (OCH_2CH_3), 61.3 (OCH_2CH_3), 44.0 (CH, C4), 39.3 (CH, C3), 14.8 (CH_3CH_2O), 14.2 (CH_3CH_2O); IR (neat) ν_{max} 2977, 1735, 1701, 1696, 1685, 1654, 1636, 1560, 1448, 1363, 1337, 1257, 1168, 1101, 1075, 1034, 934, 899, 753, 737 cm^{-1}; EIMS m/e (relative intensity) 415 (M^+, 3), 369 (11), 292 (18), 274 (21), 200 (11), 172 (35), 156 (base), 148 (53), 144 (36), 128 (11), 120 (23), 91 (24), 77 (73), 51 (16); CIMS (2-methylpropane) m/e (relative intensity) 370 (M + H^+ – EtOH, base); EIHRMS m/e 415.1453 ($C_{22}H_{25}NO_5$ requires 415.1453). Anal. Calcd for $C_{22}H_{25}NO_5S$: C, 63.60; H, 6.06; N, 3.37. Found: C, 63.78; H, 6.42; N, 3.42.

A single-crystal X-ray structure determination confirmed the structure of **40**-endo.[21e]

(2*R,3*R**,4*S**)-2-Ethoxy-4-(ethoxycarbonyl)-3-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (40-exo).** Minor adduct **40**-exo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.41–6.85 (m, 10 H, aromatic), 6.63 (ddd, 1 H, C6-H, J = 1.3, 2.7, 8.3 Hz), 5.58 (d apparent t, 1 H, C5-H, J = 1.6, 8.3 Hz), 5.36 (apparent t, 1 H, C2-H, J = 1.3 Hz), 3.93–3.71 (m, 6 H, C3-H, C4-H, OCH_2CH_3, OCH_2CH_3), 1.26 (t, 3 H, CH_3CH_2O, J = 7.0 Hz), 0.82 (t, 3 H, CH_3CH_2O, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.3 (CO_2Et), 140.0 (C aromatic), 136.9 (C aromatic), 132.7 (CH aromatic), 129.3 (CH aromatic), 128.6 (CH aromatic), 128.2 (CH aromatic), 127.6 (CH aromatic), 126.9 (CH aromatic), 123.3 (CH, C6), 105.8 (CH, C5), 87.0 (CH, C2), 63.9 (OCH_2CH_3), 60.76 (OCH_2CH_3), 43.9 (CH, C4), 37.8 (CH, C3), 15.1 (CH_3CH_2O), 13.8 (CH_3CH_2O); IR (neat) ν_{max} 2977, 1735, 1701, 1697, 1685, 1654, 1560, 1497, 1448, 1363, 1340, 1267, 1168, 1098, 1066, 935, 899, 742, 735 cm^{-1}; EIMS m/e (relative intensity) 415 (M^+, 5), 370 (27), 369 (27), 342 (15), 296 (14), 292 (44), 274 (24), 200 (18), 172 (30), 157 (10), 156 (99), 148 (base), 144 (13), 141 (14), 120 (53), 91 (17), 77 (29); CIMS (2-methylpropane) m/e (relative intensity) 370 (M + H^+ – EtOH, base); EIHRMS m/e 415.1453 ($C_{22}H_{25}NO_5S$ requires 415.1453).

(2*R,4*R**)-4-(Ethoxycarbonyl)-2-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (41-endo).** Conditions: styrene (2.5 equiv), 0.27 mmol scale, 45.5 h, CH_2Cl_2, 21 °C, 13.3 kbar. Examination of the crude product by ^1H NMR (300 MHz) showed a 11:1 mixture of endo/exo isomers (isolated **41**-endo 48%, 11:1 (endo/exo)). For pure **41**-endo: mp 120–122 °C (ether/hexane); ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.5 (d, 2 H, aromatic, J = 7.5 Hz), 7.44 (m, 3 H, aromatic), 7.13 (m, 6 H, 5 H aromatic, C6-H), 5.25 (dd, 1 H, C5-H, J = 5.7, 9.4 Hz), 5.24 (broad (overlapping) s, 1 H, C2-H), 3.48 (m, 2 H, $CO_2CH_2CH_3$), 2.86 (t, 1 H, C4-H, J = 5.7 Hz), 2.72 (d, 1 H, C3-H_{eq}, J = 13.7 Hz), 1.80 (ddd, 1 H, C3-H_{ax}, J = 5.7, 6.8, 13.7 Hz), 0.91 (t, 3 H, $CO_2CH_2CH_3$, J = 7.1 Hz); diagnostic ^1H NMR signals utilized for the estimation of the endo/exo ratio (by integration) for the minor cycloadduct 4.10 (q, 2 H, $CO_2CH_2CH_3$, J = 7 Hz), 2.21 (m, 1 H, C3-H_{eq}), 1.68 (m, 1 H, C3-H_{ax}), 1.20 (t, 3 H, $CO_2CH_2CH_3$, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 171.9 (CO_2Et), 139.5 (C aromatic), 138.3 (C aromatic), 133.3 (CH aromatic), 129.4 (CH aromatic), 128.3 (CH aromatic), 127.6 (CH aromatic), 127.3 (CH aromatic), 126.8 (CH aromatic), 125.6 (CH, C6), 105.9 (CH, C5), 60.9 (CH, C2), 55.3 ($CO_2CH_2CH_3$), 34.8 (CH, C4), 29.8 (CH_2, C3), 13.7 ($CO_2CH_2CH_3$); IR (neat) ν_{max} 2905, 2724, 2672, 1460, 1378, 1314, 1188, 1172, 1160, 1104, 1076, 1028, 874, 812, 744, 722, 702 cm^{-1}; EIMS m/e (relative intensity) 371 (M^+, 27), 299 (14), 298 (99), 230 (8), 157 (33), 156 (base), 141 (12), 129 (8), 104 (15), 80 (29), 78 (10), 77 (58), 51 (10); CIMS (2-methylpropane) m/e (relative intensity) 372 (M + H^+, base); EIHRMS m/e 371.1191 ($C_{20}H_{21}NO_4S$ requires 371.1191). Anal. Calcd for $C_{20}H_{21}NO_4S$: C, 64.67; H, 5.70; N, 3.77. Found: C, 64.35; H, 5.64; N, 3.64.

(2*R,3*R**,4*R**)-2-Ethoxy-4-(ethoxycarbonyl)-3-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (42a-endo).** Conditions: (*Z*)-ethyl-1-propenyl ether (3.8 equiv), 0.21 mmol scale, 69 h, 21 °C. Examination of the crude product by ^1H NMR (300 MHz) showed a 25:1 mixture of endo/exo isomers (isolated **42a**-endo 48%, 22.7:1 (endo/exo)). For pure **42a**-endo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.77 (d, 2 H, aromatic, J = 7.3 Hz), 7.56 (m, 3 H, aromatic), 6.62 (d, 1 H, C6-H, J = 8.1 Hz), 5.19 (dd, 1 H, C5-H, J = 5.5, 8.1 Hz), 4.96 (broad s, 1 H, C2-H), 4.12 (m, 2 H, $CO_2CH_2CH_3$), 3.80 (m, $OCHHCH_3$), 3.51 (m, 1 H, $OCHHCH_3$), 2.72 (apparent triplet, 1 H, C4-H, J = 5.5 Hz), 1.44 (m, 1 H, C3-H), 1.23 (t, 3 H, $CO_2CH_2CH_3$, J = 7.2 Hz), 1.20 (d, 3 H, CH_3CH, J = 7.1 Hz), 1.09 (t, 3 H, OCH_2CH_3, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 171.6 (CO_2Et), 139.8 (C aromatic), 133.3 (CH aromatic), 129.7 (CH aromatic), 127.0 (CH aromatic), 123.1 (CH, C6), 109.1 (CH, C5), 85.7 (CH, C2), 64.0 ($CO_2CH_2CH_3$), 60.6 (OCH_2CH_3), 39.5 (CH, C4), 35.3 (CH, C3), 15.5 ($CO_2CH_2CH_3$), 14.6 (OCH_2CH_3), 14.2 ($CHCH_3$); IR (neat) ν_{max} 2977, 2928, 1724, 1701, 1654, 1448, 1350, 1311, 1233, 1173, 1079, 1017, 981, 756, 725 cm^{-1}; EIMS m/e (relative intensity) 353 (M^+, 6), 308 (31), 293 (18), 292 (base), 280 (31), 141 (19), 138 (14), 110 (8), 94 (96), 86 (23), 82 (20), 77 (57), 58 (24), 57 (12); CIMS (2-methylpropane) m/e (relative intensity) 308 (M + H^+ – EtOH, base); EIHRMS m/e 353.1297 ($C_{17}H_{23}NO_5S$ requires 353.1297).

Irradiation of C4-H resulted in a 13% increase in the C3-H signal and an 11% increase in the C5-H signal in the NOE difference spectrum ($CDCl_3$, 200 MHz).

Base-Catalyzed Epimerization of (2*R,3*R**,4*R**)-2-Ethoxy-4-(ethoxycarbonyl)-3-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (42a-endo): Preparation of (2*R**,3*R**,4*S**)-2-Ethoxy-4-(ethoxycarbonyl)-3-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine.** A solution of **42a**-endo (4.1 mg, 0.12 mmol) in dry benzene (0.6 mL) was treated with a solution of DBU (2 M in benzene, 6 μL, 1 equiv), and the mixture was stirred at 21 °C for 2 h. The resulting reaction mixture was diluted with ether (8 mL) and washed with 2% aqueous hydrochloric acid (2 × 5 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. ^1H NMR (300 Mhz) of the crude product revealed a mixture of the starting material and **42a**-exo (1:12): ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.70 (d, 2 H, aromatic, J = 7.3 Hz), 7.52 (m, 3 H, aromatic), 6.57 (dd, 1 H, C6-H, J = 1.3, 8 Hz), 5.04 (dd, 1 H, C5-H, J = 2.1, 8 Hz), 4.95 (broad s, 1 H, C2-H), 4.09 (q, 2 H, $CO_2CH_2CH_3$, J = 7.1 Hz), 3.84 (m, 1 H, $OCHHCH_3$), 3.59 (m, 1 H, $OCHHCH_3$), 2.99 (dt, 1 H, C4-H, J = 2.1, 11.4 Hz), 1.39 (m, 1 H, C3-H), 1.21 (t, 3 H, $CO_2CH_2CH_3$, J = 7.1 Hz), 1.17 (t, 3 H, OCH_2CH_3, J = 7.0 Hz), 0.94 (d, 3 H, CH_3CH, J = 6.7 Hz).

(2*R,3*R**,4*R**)-2-Ethoxy-4-(ethoxycarbonyl)-3-methyl-1-(methylsulfonyl)-1,2,3,4-tetrahydropyridine (42b-endo).** Conditions: (*Z*)-ethyl-1-propenyl ether (4 equiv), 0.16 mmol scale, 66 h, 21 °C. Examination of crude ^1H NMR (300 MHz) showed a single diastereomer (isolated **42b** 36% >20:1 (endo/exo)). For pure **42b**-endo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 6.52 (d, 1 H, C6-H, J = 8.50 Hz), 5.19 (dd, 1 H, C5-H, J = 8.6, 5.30 Hz), 5.02 (broad s, 1 H, C2-H), 4.11 (m, 2 H, $CO_2CH_2CH_3$), 3.79 (m, 1 H, $OCHHCH_3$), 3.54 (m, 1 H, $OCHHCH_3$), 2.99 (m, 1 H, C4-H), 2.95 (s, 3 H, CH_3SO_2), 2.18 (m, 1 H, C3-H), 1.34 (d, 3 H, CH_3CH, J = 7.24 Hz), 1.26 (t, 3 H, OCH_2CH_3, J = 7.05 Hz), 1.13 (t, 3 H, OCH_2CH_3, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 171.9 (CO_2Et), 123.3 (CH, C6), 107.3 (CH, C5), 86.2 (CH, C2), 65.5 ($CO_2CH_2CH_3$), 60.8 (OCH_2CH_3), 40.9 (CH, C4), 39.9 (CH_3SO_2), 29.9 (CH, C3), 15.2 ($CO_2CH_2CH_3$), 15.1 (OCH_2CH_3), 14.4 (CH_3CH); IR (neat) ν_{max} 2977, 2929, 1718, 1654, 1637, 1559, 1541, 1508, 1458, 1374, 1340, 1235, 1169, 1121, 1068, 1030, 961, 922, 765, 734 cm^{-1}; EIMS m/e (relative intensity) 291 (M^+, 3), 246 (10), 230 (46), 218 (33), 110 (15), 95 (12), 94 (base), 86 (57), 82 (18), 58 (43), 57 (23), 55 (16); CIMS (2-methylpropane) m/e (relative intensity) 246 (M + H^+ – EtOH, base); EIHRMS m/e 291.1142 ($C_{12}H_{21}NO_5S$ requires 291.1140).

(2*S,3*R**,4*S**)-2-Ethoxy-4-(ethoxycarbonyl)-3-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (43-endo).** Conditions: (*Z*)-1-ethoxy-2-phenylethylene[36d] (2.5 equiv), 0.24 mmol scale, 49.5 h, CH_2Cl_2, 21 °C, 13.3 kbar. Examination of the crude product by ^1H NMR (300 MHz) showed a 2.2:1 mixture of endo/exo isomers, (isolated **43** 42%, 2.2:1 (endo/exo)). For pure **43**-endo: mp 91–93 °C (ether/hexane); ^1H

NMR ($CDCl_3$, 300 MHz, ppm) 7.73 (m, 2 H, aromatic), 7.57 (m, 1 H, aromatic), 7.50 (m, 2 H, aromatic), 7.28 (m, 3 H, aromatic), 7.17 (m, 2 H, aromatic), 6.70 (d apparent t, 1 H, C6-H, J = 1.4, 8.2 Hz), 5.48 (t, 1 H, C2-H, J = 1.1 Hz), 5.37 (dd, 1 H, C5-H, J = 5.6, 8.2 Hz), 3.94 (m, 1 H, $OCHHCH_3$), 3.87 (m, 2 H, OCH_2CH_3), 3.69 (m, 1 H, $OCHHCH_3$), 3.07 (m, 1 H, C4-H), 2.50 (d, 1 H, C3-H, J = 5.6 Hz), 1.23 (t, 3 H, CH_3CH_2O, J = 7.0 Hz), 0.93 (t, 3 H, CH_3CH_2O, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 170.9 (CO_2Et), 139.4 (C aromatic), 133.5 (C aromatic), 129.8 (CH aromatic), 128.8 (CH aromatic), 128.3 (CH aromatic), 127.3 (CH aromatic), 127.1 (CH aromatic), 123.0 (CH, C6), 110.1 (CH, C5), 84.0 (CH, C2), 63.6 (CH_3CH_2O), 60.4 (CH_3CH_2O), 45.9 (CH, C4), 41.3 (CH, C3), 14.8 (CH_3CH_2O), 13.7 (CH_3CH_2O); IR (neat) ν_{max} 3064, 2978, 2928, 1734, 1718, 1701, 1696, 1685, 1670, 1654, 1647, 1636, 1559, 1540, 1507, 1496, 1473, 1457, 1448, 1395, 1340, 1261, 1171, 1136, 1096, 1056, 927, 725, 689 cm^{-1}; EIMS m/e (relative intensity) 369 (15), 292 (35), 274 (18), 200 (11), 172 (28), 151 (15), 156 (base), 148 (75), 144 (25), 141 (17), 129 (11), 128 (14), 127 (10), 120 (40), 115 (13), 105 (29), 91 (43), 78 (12), 77 (84), 51 (15); CIMS (2-methylpropane) m/e (relative intensity) 370 (M + H^+ - EtOH, base); EIHRMS m/e 415.1445 ($C_{22}H_{25}NO_5S$ requires 415.1453). Anal. Calcd for $C_{22}H_{25}NO_5S$: C, 63.60; H, 6.06; N, 3.37. Found: C, 63.22; H, 5.94; N, 3.62.

Irradiation of C4-H resulted in a 6.5% increase in the signal for the ortho hydrogens of the phenyl substituent at C3, a 13.3% increase in the signal for C5-H, and a 10.7% increase in the signal for C3-H. Irradiation of C3-H resulted in a 4.1% increase in the signal for the ortho hydrogens of the phenylsulfonyl substituent at N1, a 16.4% increase in the ortho hydrogens of the phenyl substituent at C3, a 8.4% increase in the C2-H signal, and a 14.4% increase in the C4-H signal in the NOE difference spectrum ($CDCl_3$, 500 MHz).

(2*R,3*S**,4*S**)-2-Ethoxy-4-(ethoxycarbonyl)-3-phenyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (43-exo).** Minor product **43**-exo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.34–6.89 (m, 10 H, aromatic), 6.59 (d, apparent t, 1 H, C6-H, J = 1.5, 8.5 Hz), 5.39 (ddd, 1 H, C5-H, J = 1.2, 5.1, 8.5 Hz), 5.33 (dd, 1 H, C2-H, J = 1.5, 2.8 Hz), 4.09 (m, 3 H, OCH_2CH_3 and C3-H), 3.61 (m, 2 H, OCH_2CH_3), 3.05 (d, 1 H, C4-H, J = 5.1 Hz), 1.21 (t, 3 H, OCH_2CH_3), 1.06 (t, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.7 (CO_2Et), 140.0 (C aromatic), 138.8 (C aromatic), 132.6 (CH aromatic), 129.2 (CH aromatic), 128.9 (CH aromatic), 128.5 (CH aromatic), 127.7 (CH aromatic), 127.6 (CH aromatic), 126.8 (CH aromatic), 123.3 (CH, C6), 105.6 (CH, C5), 86.1 (CH, C2), 63.6 (OCH_2CH_3), 61.3 (OCH_2CH_3), 44.1 (CH, C4), 39.3 (CH, C3), 14.9 (OCH_2CH_3), 14.2 (OCH_2CH_3); IR (neat) ν_{max} 2977, 1735, 1701, 1697, 1685, 1654, 1448, 1363, 1340, 1260, 1170, 1101, 933, 800, 754, 737 cm^{-1}; EIMS m/e (relative intensity) 415 (M^+, 3), 369 (15), 342 (32), 292 (19), 274 (41), 200 (10), 172 (28), 156 (84), 148 (47), 144 (27), 141 (15), 128 (11), 120 (27), 105 (56), 91 (30), 78 (11), 77 (base), 51 (19); CIMS (2-methylpropane) m/e (relative intensity) 370 (M + H^+ - EtOH, base); EIHRMS m/e 415.1453 ($C_{22}H_{25}NO_5S$ requires 415.1453).

Irradiation of C4-H resulted in a 17.5% signal increase in the ortho hydrogens of the phenyl substituent at C3, a 10% increase in the C5-H signal, and a 7.3% increase in the C3-H signal in the NOE difference spectrum ($CDCl_3$, 500 MHz).

(2*R,4*R**)-4-(Ethoxycarbonyl)-3-methylidene-2-methoxy-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (44).** Conditions: 1-methoxy-1,2-propadiene[36e] (5 equiv), 0.16 mmol scale, 82 h, 0 °C; examination of the crude product by ^1H NMR (300 MHz) revealed no trace of the exo cycloadduct, **44**: 56%; ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.78 (d, 2 H, J = 7.5 Hz, aromatic), 7.52 (m, 3 H, aromatic), 6.59 (d, 1 H, C6-H, J = 8.1 Hz), 5.30 (s, 1 H, C2-H), 5.26 (dd, 1 H, C5-H, J = 3.4, 8.1 Hz), 5.10 (d, 2 H, $C{=}CH_2$, J = 9.2 Hz), 4.13 (m, 2 H, $CO_2CH_2CH_3$), 3.45 (d, 1 H, C4-H, J = 3.4 Hz), 3.32 (s, 3 H, OCH_3), 1.21 (t, 3 H, $CO_2CH_2CH_3$, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 170.6 (CO_2Et), 139.9 (C aromatic), 136.3 (C, C3), 133.5 (CH aromatic), 129.5 (CH aromatic), 127.5 (CH aromatic), 123.4 (CH, C6), 118.5 ($C{=}CH_2$), 107.3 (CH, C5), 87.4 (CH, C2), 61.7 ($CO_2CH_2CH_3$), 55.2 (OCH_3), 43.5 (CH, C4), 14.2 ($CO_2CH_2CH_3$); IR (neat) ν_{max} 3278, 3070, 2936, 1730, 1654, 1448, 1392, 1362, 1171, 1129, 1098, 1076, 1023, 998, 942, 907, 874, 757, 727, 689 cm^{-1}; EIMS m/e (relative intensity) 337 (M^+, 3), 306 (21), 265 (11), 264 (85), 150 (19), 141 (20), 134 (13), 123 (12), 122 (22), 119 (14), 108 (29), 94 (11), 93 (17), 92 (57), 78 (21), 77 (base), 74 (13), 65 (25), 59 (47), 57 (10), 53 (15), 51 (43), 50 (18); CIMS (2-methylpropane) m/e (relative intensity) 338 (M + H^+, 10), 306 (M + H^+ - CH_3OH, base); EIHRMS m/e 337.0986 ($C_{16}H_{19}NO_5S$ requires 337.0984).

(2*R,3*R**,4*R**)-3-Acetoxy-2-(benzyloxy)-4-(ethoxycarbonyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (45-endo).** Conditions: (*Z*)-1-acetoxy-2-(benzyloxy)ethylene[36f] (110 mg, 0.57 mmol, 3.1 equiv) 13.3 kbar, 49.5 h, 21 °C. Examination of the crude material by ^1H NMR (300 MHz) showed a single diastereomer. Isolated **45**-endo (35.9 mg, 83.9 mg theoretical, 42%), mp 90–92 °C (white needles, ether/hexane); ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.80 (d, 2 H, aromatic, J = 7.4 Hz), 7.59 (m, 1 H, aromatic), 7.51 (m, 2 H, aromatic), 7.36–7.28 (m, 5 H, aromatic), 6.64 (d, 1 H, C6-H, J = 8.2 Hz), 5.32 (d, 1 H, C2-H, J = 1.6 Hz), 5.14 (dd, 1 H, C5-H, J = 5.4, 8.2 Hz), 4.81 (d, 1 H, $OCHHPh$, J = 12 Hz), 4.68 (d, 1 H, $OCHHPh$, J = 12 Hz), 4.31 (dd, 1 H, C3-H, J = 2.3, 7.3 Hz), 4.00 (m, 1 H, $OCHHCH_3$), 3.85 (m, 1 H, $OCHHCH_3$), 3.43 (m, 1 H, C4-H), 2.07 (s, 3 H, $COCH_3$), 1.08 (t, 3 H, CH_3CH_2O); diagnostic ^1H NMR signals utilized for the determination of endo/exo ratio (by integration) for the minor cycloadduct were 6.82 (dt, 1 H, C6-H, J = 8.4, 1.0 Hz), 2.92 (d, 1 H, C4-H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 170.9 (CO_2Et), 169.5 ($OCOCH_3$), 139.4 (C aromatic), 137.8 (C aromatic), 133.9 (CH aromatic), 130.0 (CH aromatic), 128.6 (CH aromatic), 128.3 (CH aromatic), 128.1 (CH aromatic), 127.2 (CH aromatic), 123.2 (CH, C6), 106.1 (CH, C5), 82.1 (CH, C2), 70.8 ($PhCH_2O$), 70.3 (CH, C3), 61.2 (OCH_2CH_3), 37.5 (CH, C4), 21.1 (CH_3CO_2), 14.1 (CH_3CH_2O); IR (neat) ν_{max} 3065, 2937, 1734, 1701, 1696, 1685, 1654, 1636, 1559, 1507, 1497, 1473, 1448, 1363, 1312, 1231, 1172, 1102, 1066, 908, 731 cm^{-1}; EIMS m/e (relative intensity) 292 (17), 220 (3), 141 (4), 91 (base), 77 (23), 65 (5), 51 (5); CIMS (2-methylpropane) m/e (relative intensity) 352 (M + H^+ - $HOCH_2Ph$, base); EIHRMS m/e 459.1352 ($C_{23}H_{25}NO_7S$ requires 459.1352).

A single-crystal X-ray structure determination confirmed the structure of **45**-endo.[21c]

(2*R,3*S**,4*R**)-3-Acetoxy-2-(benzyloxy)-4-(ethoxycarbonyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (46-endo).** Conditions: (*E*)-1-acetoxy-2-(benzyloxy)ethylene[36f] (3 equiv), 0.09 mmol scale, 135 h, 21 °C. Examination of the crude product by ^1H NMR (300 MHz) showed a 2.4:1 mixture of endo/exo isomers (isolated **46** 71%, 2.4:1 (endo/exo)). For pure **46**-endo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.87 (d, 2 H, aromatic), 7.49 (m, 3 H, aromatic), 7.19 (m, 5 H, aromatic), 6.77 (d, 1 H, C6-H, J = 8.3 Hz), 5.64 (t, 1 H, C3-H, J = 1.3 Hz), 5.34 (d, 1 H, C2-H, J = 2.6 Hz), 5.19 (m, 1 H, C5-H), 4.66 (d, 1 H, $OCHHPh$, J = 11.7 Hz), 4.54 (d, 1 H, $OCHHPh$, J = 11.7 Hz), 3.85 (m, 2 H, $CO_2CH_2CH_3$), 2.91 (d, 1 H, C4-H, J = 4.7 Hz), 1.33 (s, 3 H, $OCOCH_3$), 0.99 (t, 3 H, $CO_2CH_2CH_3$, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 170.1 (CO), 168.4 (CO), 140.6 (C aromatic), 137.5 (C aromatic), 133.3 (CH aromatic), 129.7 (CH aromatic), 128.6 (CH aromatic), 128.1 (CH aromatic), 127.40 (CH aromatic), 126.8 (CH aromatic), 122.6 (CH, C6), 103.8 (CH, C5), 81.1 (CH, C2), 70.4 (OCH_2Ph), 67.4 (CH, C3), 61.5 (OCH_2CH_3), 40.6 (CH, C4), 20.4 ($OCOCH_3$), 13.9 (OCH_2CH_3); IR (neat) ν_{max} 2927, 1741, 1701, 1697, 1685, 1654, 1447, 1369, 1345, 1229, 1172, 1072, 1030, 912, 741 cm^{-1}; EIMS m/e (relative intensity) 292 (57), 157 (15), 141 (26), 93 (16), 91 (base), 78 (10), 77 (79), 51 (31); CIMS (2-methylpropane) m/e (relative intensity) 352 (M + H^+ - $PhCH_2OH$, base); CIHRMS m/e 460.1412 ($C_{23}H_{25}NO_7S$ requires 460.1430).

(2*R,3*S**,4*S**)-3-Acetoxy-2-(benzyloxy)-4-(ethoxycarbonyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (46-exo).** Minor adduct **46**-exo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.81 (d, 2 H, aromatic, 7.3 Hz), 7.52 (m, 3 H, aromatic), 7.33 (m, 5 H, aromatic), 6.83 (d, 1 H, C6-H, J = 7.9 Hz), 5.37–5.31 (m, 3 H, C2-H, C3-H, C5-H), 4.92 (d, 1 H, $OCHHPh$, J = 11.7 Hz), 4.75 (d, 1 H, $OCHHPh$, J = 11.7 Hz), 4.12 (m, 2 H, $CO_2CH_2CH_3$), 3.62 (t, 1 H, C4-H, J = 2.6 Hz), 1.23 (s, 3 H, $OCOCH_3$), 1.18 (t, 3 H, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 170.3 (CO), 170.2 (CO), 140.5 (C aromatic), 137.6 (C aromatic), 133.4 (CH aromatic), 129.8 (CH aromatic), 128.8 (CH aromatic), 128.3 (CH aromatic), 127.5 (CH aromatic), 122.9 (CH, C6), 103.3 (CH, C5), 81.3 (CH, C2), 70.5 (OCH_2Ph), 65.7 (CH, C3), 61.4 (OCH_2CH_3), 38.6 (CH, C4), 20.1 (O_2CCH_3), 14.2 ($CO_2CH_2CH_3$); IR (neat) ν_{max} 2926, 1735, 1701, 1697, 1685, 1676, 1654, 1649, 1618, 1577, 1561, 1555, 1497, 1449, 1370, 1234, 1170, 1038, 956, 915 cm^{-1}; EIMS m/e (relative intensity) 293 (2), 292 (16), 220 (2), 141 (7), 105 (2), 96 (2), 92 (7), 91 (base), 79 (2), 78 (4), 77 (28); CIMS (2-methylpropane) m/e (relative intensity) 460 (M + H^+, 16), 352 (M + H^+ - $PhCH_2OH$, base); EIHRMS m/e 459.1359 ($C_{23}H_{25}NO_7S$ requires 459.1352).

(2*R,4*R**)-4-(Ethoxycarbonyl)-2-(4′-methoxyphenyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (47-endo).** Conditions: 4-vinyl anisole (5 equiv), 0.27 mmol scale, 46 h, 21 °C. Examination of crude product by ^1H NMR (300 MHz) showed a 33:1 mixture of endo/exo isomers (isolated **47** 63%, 33:1 (endo/exo)). For pure **47**-endo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.72 (m, 2 H, aromatic), 7.53 (m, 1 H, aromatic), 7.44 (m, 2 H, aromatic), 7.04 (m, 3 H, 2 H aromatic and C6-H), 6.70 (m, 2 H, aromatic), 5.25 (ddd, 1 H, C5-H, J = 1.2, 5.5, 8.7 Hz), 5.18 (apparent triplet, 1 H, C2-H, J = 3.7 Hz), 3.73 (s, 3 H, OCH_3), 3.57 (m, 2 H, $CO_2CH_2CH_3$, J = 7.1 Hz), 2.86 (m, 1 H, C4-H), 2.67 (m, 1 H, C3-H_{eq}), 1.28 (ddd, 1 H, C3-H_{ax}, J = 2.2, 7, 14 Hz), 0.94 (t, 3 H, $CO_2CH_2CH_3$, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm)

171.9 (CO_2Et), 158.9 (C aromatic), 139.3 (C aromatic), 132.9 (CH aromatic), 130.0 (C aromatic), 129.3 (CH aromatic), 129.2 (CH aromatic), 127.8 (CH aromatic), 127.0 (CH aromatic), 126.5 (CH aromatic), 125.3 (CH aromatic), 113.4 (CH, C6), 105.6 (CH, C5), 60.6 ($CO_2CH_2CH_3$), 55.2 (OCH_3), 54.7 (CH, C2), 34.5 (CH, C4), 29.7 (CH_2, C3), 13.5 ($CO_2CH_2CH_3$); IR (neat) ν_{max} 2927, 1725, 1654, 1612, 1513, 1446, 1339, 1249, 1169, 1098, 1035, 910, 830, 747, 725 cm^{-1}; EIMS *m/e* (relative intensity) 401 (M^+, 24), 328 (22), 260 (73), 259 (11), 187 (24), 186 (66), 157 (38), 141 (21), 134 (91), 94 (12), 93 (38), 84 (11), 80 (16), 77 (base), 51 (39), 49 (22); CIMS (2-methylpropane) *m/e* (relative intensity) 402 ($M + H^+$, base); EIHRMS *m/e* 401.1297 ($C_{21}H_{23}NO_5S$ requires 401.1297). Anal. Calcd for $C_{21}H_{23}NO_5S$: C, 62.83; H, 5.77; N, 3.49. Found: C, 62.82; H, 5.75; N, 3.67.

Irradiation of C3-H_{ax} resulted in a 23% increase in the C3-H_{eq} signal, a 17% increase in the C4-H signal, a 6% increase in the C2-H signal, and a 4% increase in the signal for the ortho hydrogens of the phenylsulfonamide in the NOE difference spectrum. Irradiation of C3-H_{eq} resulted in a 23% increase in the C3-H_{ax} signal, a 9% increase in the C2-H signal, and a 18% increase in the signal for the ortho hydrogens of the *p*-methoxyphenyl substituent at C2 in the NOE difference spectrum ($CDCl_3$, 200 MHz).

Diagnostic ^1H NMR signals utilized for the determination of the endo/exo ratio (by integration) for the minor cycloadduct are as follows: 3.78 (s, 3 H, CH_3O), 2.18 (ddd, 1 H, C3-H_{eq}, J = 12.5, 2.4, 2.1 Hz), 1.63 (dt, 1 H, C3-H_{ax}, J = 12.5, 4.3 Hz). This was further established to be the exo diastereomer by deliberate epimerization as detailed in the following text.

Base-Catalyzed Epimerization of (2*R,4*R**)-4-(Ethoxycarbonyl)-2-(4′-methoxyphenyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (47-endo): Preparation of (2*R**,4*S**)-4-(Ethoxycarbonyl)-2-(4′-methoxyphenyl)-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine.** Following the procedure for epimerization of **37b**, **47**-endo afforded a 5.5:1 ratio of C4 epimers with the (2*R**,4*S**) epimer as the major product: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.70 (d, 2 H, aromatic, J = 7.5 Hz), 7.50 (m, 3 H, aromatic), 7.08 (d, 2 H, aromatic, J = 8.6 Hz), 6.98 (dd, 1 H, C6-H, J = 2.1, 8.4 Hz), 6.78 (d, 2 H, aromatic, J = 8.6 Hz), 5.18 (m, 2 H, C5-H and C2-H), 4.07 (q, 2 H, OCH_2CH_3, J = 7.1 Hz), 3.78 (s, 3 H, CH_3O), 2.72 (dt, 1 H, C4-H, J = 12, 2.4 Hz), 2.18 (ddd, 1 H, C3-H_{eq}, J = 12.5, 2.4, 2.1 Hz), 1.63 (dt, 1 H, C3-H_{ax}, C3, J = 12.5, 4.3 Hz), 1.08 (t, 3 H, CH_3CH_2O, J = 7.1 Hz).

(2*R,3*R**,4*S**)-4-(Ethoxycarbonyl)-2-(4′-methoxyphenyl)-3-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (48-endo).** Conditions: (*E*)-4-propenyl anisole (2 equiv), 0.22 mmol scale, 53 h, benzene, 80 °C. Examination of crude ^1H NMR (300 MHz) showed a 4.5:1 (endo/exo) mixture of isomers (isolated **48** 44%, 4:1 (endo/exo)). For pure **48**-endo: mp 139–140 °C (EtOAc/hexane); ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.72 (m, 2 H, aromatic), 7.52 (m, 1 H, aromatic), 7.41 (m, 2 H, aromatic), 7.04 (d, 1 H, C6-H, J = 8.5 Hz), 6.75 (m, 2 H, aromatic), 6.65 (m, 2 H, aromatic), 5.06 (ddd, 1 H, C5-H, J = 1.35, 5.4, 8.5 Hz), 4.91 (broad s, 1 H, C2-H), 3.72 (s, 3 H, OCH_3), 3.49 (m, 2 H, OCH_2CH_3), 2.96 (m, 1 H, C3-H), 2.53 (d, 1 H, C4-H, J = 5.5 Hz), 0.93 (t, 3 H, OCH_2CH_3, J = 7.09 Hz), 0.79 (d, 3 H, CH_3CH, J = 7.12 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 171.9 (CO_2Et), 159.1 (C aromatic), 140.1 (C aromatic), 133.2 (CH aromatic), 130.7 (C aromatic), 129.3 (CH aromatic), 127.9 (CH aromatic), 124.4 (CH aromatic), 113.6 (CH, C6), 102.3 (CH, C5), 60.8 (CH_3CH_2O and CH, C2), 55.4 (OCH_3), 41.8 (CH, C4), 35.2 (CH, C3), 20.0 (CH_3CH), 13.8 (CH_3CH_2O); IR (KBr) ν_{max} 2970, 2361, 1725, 1701, 1697, 1685, 1654, 1613, 1513, 1448, 1405, 1363, 1249, 1170, 1089, 1068, 1036, 1005, 916, 853, 729 cm^{-1}; EIMS *m/e* (relative intensity) 415 (M^+, 12), 342 (11), 274 (32), 201 (13), 200 (33), 148 (base), 137 (17), 135 (31), 121 (13), 94 (12), 77 (37); CIMS (2-methylpropane) *m/e* (relative intensity) 416 ($M + H^+$, base); EIHRMS *m/e* 415.1453 ($C_{22}H_{25}NO_5S$ requires 415.1453). Anal. Calcd for $C_{22}H_{25}NO_5S$: C, 63.60; H, 6.06; N, 3.37. Found: C, 63.81; H, 6.33; N, 3.41.

A single-crystal X-ray structure determination confirmed the structure of **48**-endo.[21c]

(2*R,3*R**,4*R**)-4-(Ethoxycarbonyl)-2-(4′-methoxyphenyl)-3-methyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (48-exo).** Minor product **48**-exo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.72 (m, 2 H, aromatic), 7.52 (m, 1 H, aromatic), 7.41 (m, 2 H, aromatic), 7.04 (m, 2 H, aromatic), 6.98 (dd, 1 H, C6-H, J = 2.2, 8.5 Hz), 6.77 (m, 2 H, aromatic), 5.12 (d apparent t, 1 H, C5-H, J = 1.3, 8.5 Hz), 4.86 (d, 1 H, C2-H, J = 1.8 Hz), 4.08 (m, 2 H, OCH_2CH_3), 3.77 (s, 3 H, OCH_3), 2.85 (m, 1 H, C4-H), 2.42 (m, 1 H, C3-H), 1.18 (t, 3 H, OCH_2CH_3, J = 7.1 Hz), 0.57 (d, 3 H, CH_3CH, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 172.9 (CO_2Et), 159.4 (C aromatic), 140.0 (C aromatic), 133.2 (CH aromatic), 132.9 (C aromatic), 129.4 (CH aromatic), 127.3 (CH aromatic), 127.1 (CH aromatic), 124.7 (CH aromatic), 114.3 (CH, C6), 101.6 (CH, C5), 62.5 (CH, C2), 61.0 (OCH_2CH_3), 55.5 (OCH_3), 38.1 (CH, C4), 34.5 (CH, C3), 14.3 (CH_3CH), 14.2 (CH_3CH_2O); IR (neat) ν_{max} 2921, 2361, 2345, 1830, 1773, 1756, 1749, 1740, 1730, 1718, 1707, 1701, 1696, 1685, 1676, 1670, 1663, 1654, 1647, 1636, 1628, 1047, 1025, 995, 940 cm^{-1}; EIMS *m/e* (relative intensity) 415 (M^+, 3), 292 (8), 274 (4), 201 (6), 200 (17), 186 (6), 148 (base), 147 (10), 121 (9), 94 (9), 77 (46); CIMS (2-methylpropane) *m/e* (relative intensity) 416 ($M + H^+$, base); EIHRMS *m/e* 415.1459 ($C_{22}H_{25}NO_5S$ requires 415.1453).

(2*R,4*S**)-4-(Ethoxycarbonyl)-2-*n*-hexyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydropyridine (49).** Conditions: 1-octene (3 equiv) 0.21 mmol scale, 6 d, CH_2Cl_2, 13.3 kbar. Examination of crude ^1H NMR (300 MHz) showed a 4.5:1 (endo/exo) mixture of isomers (isolated **49**: 18% 5:1 (endo/exo)). **49**-endo: ^1H NMR ($CDCl_3$, 300 MHz, ppm) 7.78 (m, 2 H, aromatic), 7.53 (m, 3 H, aromatic), 6.70 (dd, 1 H, C6-H, J = 8.2, 1.5 Hz), 5.27 (ddd, 1 H, C5-H, J = 1, 4.5, 8.2 Hz), 4.12 (m, 2 H, $CO_2CH_2CH_3$), 2.93 (m, 1 H, C2-H), 2.77 (m, 1 H, C4-H), 2.27 (d, 1 H, C3-H_{eq}, J = 13.9 Hz), 1.25 (m, 14 H, $(CH_2)_5CH_3$, and C3-H_{ax}), 0.87 (t, 3 H, OCH_2CH_3, J = 6.9 Hz); diagnostic ^1H NMR signals utilized for the estimation of endo/exo ratio (by integration) for the minor cycloadduct 3.05 (m, 1 H, C4-H), 1.84 (m, 1 H, C3-H_{eq}); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm) 173.4 (CO_2Et), 159.7 (C aromatic), 133.2 (CH aromatic), 129.7 (CH aromatic), 127.4 (CH aromatic), 124.7 (CH, C6), 107.2 (CH, C5), 61.4 ($CO_2CH_2CH_3$), 53.0 (CH, C2), 35.0 (CH, C4), 31.9 (CH_2), 31.8 (CH_2), 29.3 (CH_2, C3), 26.5 (CH_2), 25.8 (CH_2), 22.8 (CH_3), 14.2 ($CO_2CH_2CH_3$); IR (neat) ν_{max} 2928, 2857, 1734, 1685, 1654, 1559, 1541, 1508, 1458, 1447, 1362, 1339, 1171, 1096, 1030, 914, 727 cm^{-1}; EIMS *m/e* (relative intensity) 379 (M^+, 4), 307 (9), 306 (46), 238 (34), 220 (14), 141 (20), 94 (14), 81 (17), 80 (base), 78 (11), 77 (79), 69 (12), 67 (13), 57 (11), 55 (22), 53 (15), 51 (10); CIMS (2-methylpropane) *m/e* (relative intensity) 380 ($M + H^+$, base); EIHRMS *m/e* 379.1821 ($C_{20}H_{29}NO_4S$ requires 379.1817).

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Supplementary Material Available: ORTEPS of the single-crystal X-ray structures of **9**, **21a**, **28a**, **40**-endo, **45**-endo, and **48**-endo, NOE summary, and summary of epimerization studies (9 pages). Ordering information is given on any current masthead page.