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Diastereoselective Baylis–Hillman type reactions of chiral non-racemic *N*-sulfinimines with cyclopent-2-en-1-one

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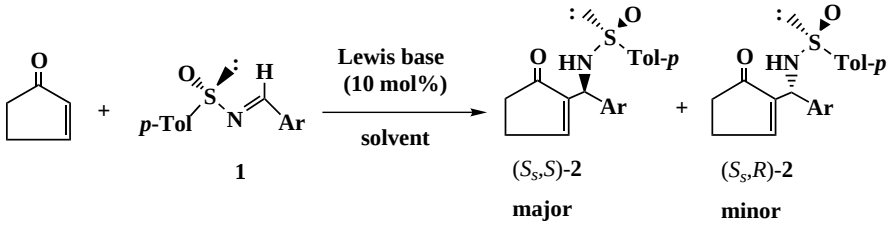
Abstract—In the Baylis–Hillman type reaction of chiral non-racemic *N*-sulfinimines **1** with cyclopent-2-en-1-one, we found that in the presence of a catalytic amount of the Lewis base $PhPMe_2$ (10 mol%), diastereoselective reaction could be achieved in toluene at room temperature to give the normal Baylis–Hillman adducts **2** in good yields and high diastereoselectivities.

1. Introduction

Since Baylis and Hillman reported the reaction of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of a catalytic amount of strong Lewis base in 1972,[1,2] great progress has been made in what has become known as the Baylis–Hillman reaction,[3–26] and the methodology now includes a catalytic asymmetric version.[27] However, to date the catalytic asymmetric Baylis–Hillman reaction has not been fully exploited and only a few papers have reported the use of α,β-unsaturated ketones or acrylates, such as ethyl vinyl ketone (71% ee),[8] cyclopent-2-en-1-one (56% ee)[28] or 1,1,1,3,3,3-hexafluoroisopropyl acrylate (99% ee),[25] as acceptors. Very recently, Aggarwal and co-workers disclosed that in the asymmetric Baylis–Hillman reaction of enantiomerically pure *N*-*p*-toluenesulfinimines with methyl acrylate, good yields and high diastereoselectivities could be achieved in the presence of DABCO (100 mol%), $Ln(OTf)_3$ (5 mol%), and other additives with a reaction time of 7 days.[29] Herein, we wish to report an unprecedented catalytic asymmetric Baylis–Hillman type reaction of chiral non-racemic *N*-sulfinimines **1**[30] with cyclopent-2-en-1-one in which excellent yields and high diastereoselectivities (86% de) have been achieved using only a catalytic amount of $PhPMe_2$ (10 mol%) as the Lewis base over 7 days.

2. Results and discussion

Previously, we reported that when using PBu_3 as a Lewis base in the Baylis–Hillman reaction of *N*-benzylidene-4-methylbenzenesulfonamide with cyclopent-2-en-1-one, the normal Baylis–Hillman adducts could be obtained in very high yields within 5 h.[31] Based on this result, we then attempted the diastereoselective Baylis–Hillman type reaction of chiral non-racemic *N*-sulfinimines **1** with cyclopent-2-en-1-one in the presence of Lewis base PBu_3 (10 mol%). The conditions for the reaction of **1** with cyclopent-2-en-1-one were systematically examined (Scheme 1, Table 1). We found that the



Scheme 1.

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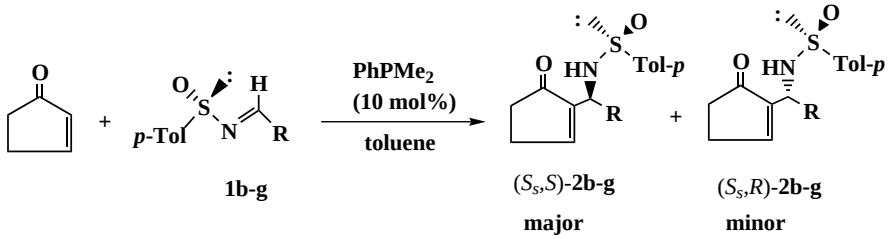
Table 1. Baylis–Hillman reactions of chiral *N*-sulfinimines (1.0 equiv.) with cyclopent-2-en-1-one (1.0 equiv.) in the presence of Lewis base (10 mol%)

Entry	Ar	Lewis base	Solvent	Time	Temp. (°C)	Yield of **2** (%)[a]	De (%)[b]
1	C_6H_5	PBu_3	THF	3 days	20	85	50 (75:25)
2	C_6H_5	PBu_3	DMF	12 h	20	96	46 (73:27)
3	C_6H_5	PBu_3	MeCN	7 h	20	92	36 (68:32)
4	C_6H_5	PBu_3	CH_2Cl_2	2 days	20	95	54 (77:23)
5	C_6H_5	PBu_3	Toluene	2 days	20	69	68 (84:16)
6	C_6H_5	PBu_3	Benzene	2 days	20	50	64 (82:18)
7	C_6H_5	PBu_3	CCl_4	2 days	20	25	33 (66:34)
8	C_6H_5	PBu_3	MeCN/toluene (1/5)	2 days	20	53	48 (74:26)
9	C_6H_5	$PhPMe_2$	THF	3 days	0	37	74 (87:13)
10	C_6H_5	$PhPMe_2$	THF	5 days	20	67	70 (85:15)
11	C_6H_5	$PhPMe_2$	Toluene	4 days	20	72	82 (91:9)
12	*m*-FC_6H_4	$PhPMe_2$	THF	1.5 days	0	93	72 (86:14)
13	*p*-ClC_6H_4	$PhPMe_2$	THF	5 days	20	95	78 (89:11)
14	C_6H_5	PBu_3	MeCN	5 days	−20	80	35 (67:32)
15	C_6H_5	PPh_3	THF	3 days	20	–	–
16	C_6H_5	Ph_2PMe	THF	3 days	20	–	–
17	C_6H_5	DABCO	THF	3 days	20	–	–

[a] Isolated yields.
[b] Determined by ^1H NMR spectral data.

solvents and Lewis bases played very important roles in this reaction. For example, using 10 mol% of PBu_3 as a Lewis base in DMF or MeCN at 20°C, the reaction proceeded very well to give the corresponding normal Baylis–Hillman adduct **2** in good yields (96 and 92%) within 12 and 7 h, respectively. However, the diastereoselectivities achieved are only 46 and 36%, respectively (Table 1, entries 2 and 3). In solvents such as THF, CH_2Cl_2 or CCl_4, the reactions are relatively slow with moderate diastereoselectivities (Table 1, entries 1, 4, and 7). However, it was found that when using toluene or benzene as solvent the diastereoselectivities can reach 68 and 64% with moderate yields, although the reactions were still relatively slow (Table 1, entries 5 and 6). Using the mixed solvent system of MeCN and toluene (1/5) did not improve the reaction rate or the diastereoselectivity (Table 1, entry 8). In order to achieve higher diastereoselectivities, we used $PhPMe_2$ as a Lewis base for this reaction (Table 1, entries 9–13). We were delighted to find that in toluene the diastereoselectivity reached 82% (Table 1, entry 11) and in THF the observed diastereoselectivity is 70% (Table 1, entry 10), although the reactions required 7 days. For other chiral non-racemic *N*-sulfinimines **1** having electron-withdrawing group, similar diastereoselectivities were obtained with higher yields (Table 1, entries 12 and 13). At lower reaction temperature, no improvement in the diastereoselectivity was realized (Table 1, entries 9, 12, and 14). Using 10 mol% of Ph_2PMe, PPh_3 or DABCO as a Lewis base, no reactions occurred (Table 1, entries 15–17). Using cyclohex-2-en-1-one as a substrate for the reaction with *N*-sulfinimines **1** under the same conditions, no reaction occurred either.

Under the optimized reaction conditions, we then examined the Baylis–Hillman reaction of other chiral non-racemic *N*-sulfinimines **1** with cyclopent-2-en-1-one using a catalytic amount of $PhPMe_2$ as a Lewis base in toluene (Scheme 2). The results were summarized in Table 2. In general, the similar results were obtained. The achieved highest diastereoselectivity is 86% (de) with 83% yield (Table 2, entry 6). The major diastereoisomers of **2** can be easily separated by silica gel column chromatography (SiO_2). The structures of **2** including minor diastereoisomers were established by spectroscopic data. The crystal structure of the major



b: R= *p*-EtC_6H_4, c: R= $C_6H_5CH_2CH_2$, d: R= $MeCH_2CH_2CH_2$, e: R= *p*-ClC_6H_4, f: R= *p*-BrC_6H_4, g: R= *m,p*-$Cl_2C_6H_3$.

Scheme 2.

Table 2. Baylis–Hillman reactions of chiral *N*-sulfinimines (1.0 equiv.) with cyclopent-2-en-1-one (1.0 equiv.) in the presence of Lewis base $PhPMe_2$ (10 mol%) in toluene

Entry	R	Time (days)	Yield of **2** (%)[a]	De (%)[b]
1	*p*-EtC_6H_4	7	70	82 (91:9)
2	$C_6H_5CH_2CH_2$	7	71	84 (92:8)
3	$MeCH_2CH_2CH_2$	9	52	82 (91:9)
4	*m*-FC_6H_4	4	76	76 (88:12)
5	*p*-ClC_6H_4	3	80	82 (91:9)
6	*p*-BrC_6H_4	5	83	86 (93:7)
7	*m*,*p*-$Cl_2C_6H_3$	4	80	80 (90:10)

[a] Isolated yields.
[b] Determined by ^1H NMR spectral data.

diastereoisomer **2c** was determined by X-ray analysis (Fig. 1).[32] Thus, the absolute configurations of the major isomers of **2** can be unambiguously assigned as (S_s,*S*). No highly enantioselective Baylis–Hillman reaction (>80% ee or de) involving α,β-unsaturated cyclic ketones such as cyclopent-2-en-1-one or cyclohex-2-en-1-one have been disclosed until now.

In Fig. 2, we propose a transition state for this novel diastereoselective Baylis–Hillman reaction. Using chiral non-racemic *N*-sulfinimines **1** as the substrate to react with cyclopent-2-en-1-one in the presence of Lewis base, (S_s,*S*)-**2** should be the major product. We believe that PBu_3 or $PPhMe_2$ behave as simple Lewis bases in this reaction. PBu_3 has greater nucleophilicity than $PhPMe_2$, but $PPhMe_2$ is the more stable of the two, which is important when long reaction times are used. Additionally, $PPhMe_2$ is more sterically encumbered

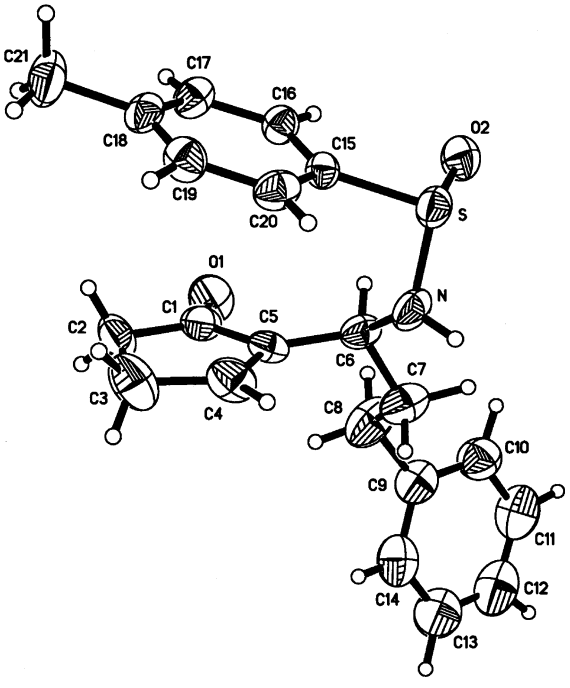


Figure 1. The crystal structure of major isomer-**2c**.

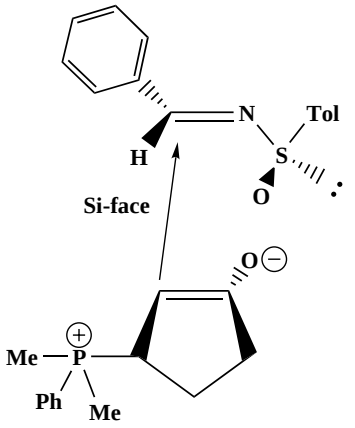


Figure 2. The transition state in the Baylis–Hillman reaction of cyclopent-2-en-1-one with chiral non-racemic *N*-sulfinimine **1**.

than PBu_3. These factors may explain why the use of $PPhMe_2$ gives higher diastereoselectivities than PBu_3.

3. Conclusion

In conclusion, we have found a very simple system using catalytic amounts of Lewis base such as PBu_3 or $PhPMe_2$ to achieve asymmetric Baylis–Hillman type reaction with high diastereoselectivities. Using $PhPMe_2$ (10 mol%) as a Lewis base in the reaction of chiral non-racemic *N*-sulfinimines **1** with cyclopent-2-en-1-one in toluene, the Baylis–Hillman adduct was formed in good yields with high diastereoselectivities. Efforts are now underway to elucidate the mechanistic details of this reaction and the key factors with respect to Lewis bases and to disclose the full scope and limitations of this reaction.

4. Experimental

4.1. General remarks

Unless otherwise stated, all reactions were carried out under argon atmosphere. All solvents were purified by distillation. Methyl vinyl ketone and tributyl phosphine were obtained from Tokyo Chemical Industry (Tokyo Kasei Co. Ltd.) and used without purification. All *N*-tosyl imines were prepared according to the literature. Infrared spectra were measured on a Perkin–Elmer 983 spectrometer. ^1H NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points were obtained by means of a micro melting point apparatus and are uncorrected.

4.2. Typical procedure for the Baylis–Hillman reaction of chiral non-racemic *N*-sulfinimines 1 with cyclopent-2-en-1-one in the presence of $PhPMe_2$ (10 mol%)

To a mixture of (*S*)-(+)-*N*-(*p*-bromobenzylidene)–*p*-toluenesulfinamide (96.6 mg, 0.3 mmol) in toluene (0.5 mL) was added cyclopent-2-en-1-one (29 μL, 24.6 mg, 0.3 mmol) and $PhPMe_2$ (5 μL, 6.9 mg, 0.03 mmol). The reaction mixture was stirred at room temperature for 5 days. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (eluent: EtOAc/petroleum ether = 1/2) to give the major isomer **2f** (S_s,*S*) (93 mg, 77%) and minor isomer **2f** (S_s,*R*) (7 mg, 6%). It should be emphasized here that the major products **2** (S_s,*S*) can be easily isolated as a sole product, but the minor products **2** (S_S,*R*) always contain a small amount of **2** (S_s,*S*). Thus, for minor products **2** (S_S,*R*), we only report their ^{1}H NMR spectral data in Section 4.

4.2.1. Reaction of *N*-sulfinimine 1a with cyclopent-2-en-1-one. Major product: (S_s,*S*)-4-Methylbenzenesulfinic acid [(4-ethylphenyl)(5-oxocyclopent-1-enyl)methyl]-amide, (S_s,*S*)-**2a**: mp 168–170°C; $[\alpha]_D = +113.3$ (*c* 0.39, $CHCl_3$); IR (KBr) *v* 1698 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.35–2.39 (2H, m, CH_2), 2.40 (3H, s, CH_3), 2.50–2.53 (2H, m, CH_2), 5.15 (1H, d, $J = 5.5$ Hz, CH), 5.41 (1H, d, $J = 5.5$ Hz, NH), 7.27–7.43 (7H, m, Ar), 7.39 (1H, t, $J = 1.8$ Hz, =CH), 7.58 (2H, d, $J = 8.6$ Hz, Ar); MS (EI) *m*/*z* 277 (M^+−50, 24.05), 187 (M^+−141, 100). Anal. found: C, 70.09; H, 5.96; N, 4.14. $C_{19}H_{21}NO_2S$ requires: C, 69.69; H, 6.46; N, 4.28%.

Minor product: (S_s,*R*)-4-Methylbenzenesulfinic acid [(4-ethylphenyl)(5 - oxocyclopent - 1 - enyl)methyl]amide, (S_s,*R*)-**2a**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.39 (3H, s, CH_3), 2.41–2.44 (2H, m, CH_2), 2.62–2.65 (2H, m, CH_2), 5.24 (1H, d, $J = 6.7$ Hz, CH), 5.46 (1H, d, $J = 6.7$ Hz, NH), 7.20–7.35 (7H, m, Ar), 7.32 (1H, t, $J = 1.8$ Hz, =CH), 7.55 (2H, d, $J = 8.5$ Hz, Ar).

4.2.2. Reaction of *N*-sulfinimine 1b with cyclopent-2-en-1-one. Major product: (S_s,*S*)-4-Methylbenzenesulfinic acid [(4-ethylphenyl)(5-oxocyclopent-1-enyl)methyl]-amide, (S_s,*S*)-**2b**: mp 151–153°C; $[\alpha]_D = +104.9$ (*c* 0.50, $CHCl_3$); IR (KBr) *v* 1692 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.23 (3H, t, $J = 7.6$ Hz, CH_3), 2.34–2.36 (2H, m, CH_2), 2.41 (3H, s, CH_3), 2.50–2.54 (2H, m, CH_2), 2.63 (2H, q, $J = 7.6$ Hz, CH_2), 5.11 (1H, d, $J = 5.9$ Hz, CH), 5.39 (1H, d, $J = 5.9$ Hz, NH), 7.18 (2H, d, $J = 8.4$ Hz, Ar), 7.27 (1H, t, $J = 1.6$ Hz, =CH), 7.29 (2H, d, $J = 8.2$ Hz, Ar), 7.33 (2H, d, $J = 8.4$ Hz, Ar), 7.59 (2H, d, $J = 8.2$ Hz, Ar); MS (EI) *m*/*z* 220 (M^+−141, 100), 205 (M^+−156, 88.66). Anal. found: C, 70.78; H, 6.96; N, 3.67. $C_{21}H_{25}NO_2S$ requires: C, 70.95; H, 7.09; N, 3.94%.

Minor product: (S_s,*R*)-4-Methylbenzenesulfinic acid [(4 - ethylphenyl)(5 - oxocyclopent - 1 - enyl)methyl]amide, (S_s,*R*)-**2b**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 1.22 (3H, t, $J = 7.6$ Hz, CH_3), 2.39 (3H, s, CH_3), 2.42–2.44 (2H, m, CH_2), 2.54–2.58 (2H, m, CH_2), 2.64 (2H, q, $J = 7.6$ Hz, CH_2), 5.30 (1H, d, $J = 4.6$ Hz, CH), 5.49 (1H, d, $J = 4.6$ Hz, NH), 7.07 (2H, d, $J = 6.3$ Hz, Ar), 7.28 (2H, d, $J = 8.4$ Hz, Ar), 7.39 (1H, t, $J = 1.6$ Hz, =CH), 7.56 (2H, d, $J = 8.4$ Hz, Ar), 7.62 (2H, d, $J = 6.3$ Hz, Ar).

4.2.3. Reaction of *N*-sulfinimine 1c with cyclopent-2-en-1-one. Major product: (S_s,*S*)-4-Methylbenzenesulfinic acid [1-(5-oxocyclopent-1-enyl)-3-phenylpropyl]amide, (S_s,*S*)-**2c**: mp 115–116°C; $[\alpha]_D = +85.3$ (*c* 0.67, $CHCl_3$); IR (KBr) *v* 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.06–2.18 (2H, m, CH_2), 2.37–2.42 (2H, m, CH_2), 2.41 (3H, s, CH_3), 2.48–2.52 (2H, m, CH_2), 2.64–2.77 (2H, m, CH_2), 4.22 (1H, dt, $J = 9.0$, 8.1 Hz, CH), 4.94 (1H, d, $J = 9.0$ Hz, NH), 7.20–7.35 (7H, m), 7.27 (1H, t, $J = 2.2$ Hz, =CH), 7.58 (2H, d, $J = 8.4$ Hz, Ar); MS (EI) *m*/*z* 214 (M^+−141, 37.20), 139 (M^+−216, 100). Anal. found: C, 71.08; H, 6.79; N, 3.90. $C_{21}H_{25}NO_2S$ requires: C, 70.95; H, 7.09; N, 3.94%.

Minor product: (S_s,*R*)-4-Methylbenzenesulfinic acid [1-(5-oxocyclopent-1-enyl)-3-phenylpropyl]amide, (S_s,*R*)-**2c**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.24–2.28 (2H, m, CH_2), 2.40 (3H, s, CH_3), 2.42–2.46 (2H, m, CH_2), 2.55–2.59 (2H, m, CH_2), 2.72–2.82 (2H, m, CH_2), 4.02 (1H, dt, $J = 8.4$, 7.5 Hz, CH), 5.26 (1H, d, $J = 8.4$ Hz, NH), 7.03 (2H, d, $J = 8.0$ Hz, Ar), 7.18 (2H, d, $J = 8.0$ Hz, Ar), 7.34 (2H, d, $J = 8.3$ Hz, Ar), 7.42 (1H, t, $J = 2.2$ Hz, =CH), 7.65 (2H, d, $J = 8.3$ Hz, Ar).

4.2.4. Reaction of *N*-sulfinimine 1d with cyclopent-2-en-1-one. Major product: (S_s,*S*)-4-Methylbenzenesulfinic acid [1-(5-oxocyclopent-1-enyl)pentyl]amide, (S_s,*S*)-**2d**: mp 88–89°C; $[\alpha]_D = +122.5$ (*c* 1.05, $CHCl_3$); IR (KBr) *v* 1689 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 0.88 (3H, t, $J = 7.4$ Hz, CH_3), 1.24–1.34 (4H, m, CH_2CH_2), 1.69–1.76 (2H, m, CH_2), 2.33–2.40 (2H, m, CH_2), 2.40 (3H, s, CH_3), 2.47–2.51 (2H, m, CH_2), 4.13 (1H, dt, $J = 8.2$, 7.5 Hz, CH), 4.94 (1H, d, $J = 8.2$ Hz, NH), 7.22 (1H, t, $J = 2.0$ Hz, =CH), 7.32 (2H, d, $J = 7.9$ Hz, Ar), 7.52 (2H, d, $J = 7.9$ Hz, Ar); MS (EI) *m*/*z* 293 (M^+−1, 0.99), 139 (M^+−155, 100). Anal. found: C, 65.57; H, 7.89; N, 4.59. $C_{16}H_{24}NO_2S$ requires: C, 65.30; H, 8.16; N, 4.76%.

Minor product: (S_s,*R*)-4-Methylbenzenesulfinic acid [1-(5-oxocyclopent-1-enyl)pentyl]amide, (S_s,*R*)-**2d**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 0.91 (3H, t, $J = 7.4$ Hz, CH_3), 1.18–1.26 (4H, m, CH_2CH_2), 1.89–1.91 (2H, m, CH_2), 2.41 (3H, s, CH_3), 2.42–2.45 (2H, m, CH_2), 2.47–2.52 (2H, m, CH_2), 4.82 (1H, dt, $J = 7.5$, 6.2 Hz, CH), 4.98 (1H, d, $J = 7.5$ Hz, NH), 7.35 (2H, d, $J = 8.4$ Hz, Ar), 7.65 (2H, d, $J = 8.4$ Hz, Ar), 7.67 (1H, t, $J = 2.1$ Hz, =CH).

4.2.5. Reaction of *N*-sulfinimine 1e with cyclopent-2-en-1-one. Major product: (S_s,*S*)-4-Methylbenzenesulfinic acid [(4-chlorophenyl)(5-oxocyclopent-1-enyl)methyl]-amide, (S_s,*S*)-**2e**: mp 151–153°C; $[\alpha]_D = +107$ (*c* 0.19, $CHCl_3$); IR (KBr) *v* 1698 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.36–2.39 (2H, m, CH_2), 2.41 (3H, s, CH_3), 2.53–2.54 (2H, m, CH_2), 5.20 (1H, d, $J = 6.2$ Hz, CH), 5.36 (1H, d, $J = 6.2$ Hz, NH),

7.26 (4H, d, $J=8.2$ Hz, Ar), 7.27 (1H, t, $J=1.8$ Hz, =CH), 7.28 (2H, d, $J=8.2$ Hz, Ar), 7.57 (2H, d, $J=8.2$ Hz, Ar); MS (EI) m/z 220 (M^+-141, 100), 205 (M^+-156, 88.66). Anal. found: C, 63.09; H, 5.37; N, 3.68. $C_{19}H_{18}ClNO_2S$ requires: C, 63.06; H, 5.57; N, 3.87%.

Minor product: (S_s,S)-4-Methylbenzenesulfinic acid [(4-chlorophenyl)(5 - oxocyclopent - 1 - enyl)methyl]amide, (S_s,R)-**2e**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.39 (3H, s, CH_3), 2.42–2.47 (2H, m, CH_2), 2.62–2.68 (2H, m, CH_2), 5.21 (1H, d, $J=6.6$ Hz, CH), 5.59 (1H, d, $J=6.6$ Hz, NH), 7.09 (2H, d, $J=8.5$ Hz, Ar), 7.16 (1H, t, $J=2.0$ Hz, =CH), 7.22 (2H, d, $J=8.5$ Hz, Ar), 7.30 (2H, d, $J=8.3$ Hz, Ar), 7.57 (2H, d, $J=8.3$ Hz, Ar).

4.2.6. Reaction of *N*-sulfinimine 1f with cyclopent-2-en-1-one. Major product: (S_s,S)-4-Methylbenzenesulfinic acid [(4-bromophenyl)(5-oxocyclopent-1-enyl)methyl]-amide, (S_s,S)-**2f**: mp 139–141°C; $[\alpha]_D=+106.4$ (c 2.40, $CHCl_3$); IR (KBr) ν 1697 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.35–2.38 (2H, m, CH_2), 2.41 (3H, s, CH_3), 2.50–2.53 (2H, m, CH_2), 5.14 (1H, d, $J=5.8$ Hz), 5.35 (1H, d, $J=5.8$ Hz), 7.26 (4H, d, $J=8.2$ Hz, Ar), 7.27 (1H, t, $J=1.8$ Hz), 7.48 (2H, d, $J=8.4$ Hz, Ar), 7.57 (2H, d, $J=8.4$ Hz, Ar); MS (EI) m/z 264 (M^+-128, 100), 139 (M^+-253, 94.54). Anal. found: C, 56.54; H, 4.56; N, 3.34. $C_{19}H_{18}NBrO_2S$ requires: C, 56.49; H, 4.46; N, 3.40%.

Minor product: (S_s,R)-4-Methylbenzenesulfinic acid [(4-bromophenyl)(5 - oxocyclopent - 1 - enyl)methyl]amide, (S_s,R)-**2f**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.43 (3H, s, CH_3), 2.47–2.52 (2H, m, CH_2), 2.63–2.72 (2H, m, CH_2), 5.20 (1H, d, $J=6.8$ Hz), 5.56 (1H, d, $J=6.8$ Hz), 7.05 (2H, d, $J=8.4$ Hz, Ar), 7.23 (2H, d, $J=8.0$ Hz, Ar), 7.35 (2H, d, $J=8.4$ Hz, Ar), 7.55 (2H, d, $J=8.0$ Hz, Ar), 7.56 (1H, t, $J=1.8$ Hz).

4.2.7. Reaction of *N*-sulfinimine 1g with cyclopent-2-en-1-one. Major product: (S_s,S)-4-Methylbenzenesulfinic acid [(2,3-dichlorophenyl)(5-oxocyclopent-1-enyl)-methyl]amide, (S_s,S)-**2g**: mp 138–140°C; $[\alpha]_D=+144.6$ (c 1.05, $CHCl_3$); IR (KBr) ν 1697 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.38–2.41 (2H, m, CH_2), 2.43 (3H, s, CH_3), 2.60 (2H, dd, $J=2.8$, 1.4 Hz, CH_2), 5.50 (1H, d, $J=7.5$ Hz), 5.81 (1H, d, $J=7.5$ Hz), 7.25 (1H, d, $J=8.2$ Hz, Ar), 7.28 (2H, d, $J=8.4$ Hz, Ar), 7.39 (1H, dd, $J=8.2$, 8.2 Hz, Ar), 7.51 (1H, t, $J=1.8$ Hz, =CH), 7.53 (1H, d, $J=8.2$ Hz, Ar), 7.59 (2H, d, $J=8.4$ Hz, Ar); MS (EI) m/z 358 (M^+-37, 50.06), 254 (M^+-141, 100). Anal. found: C, 57.70; H, 4.69; N, 3.52. $C_{19}H_{19}Cl_2NO_2S$ requires: C, 57.58; H, 4.80; N, 3.54%.

Minor product: (S_s,R)-4-Methylbenzenesulfinic acid [(2,3 - dichlorophenyl)(5 - oxocyclopent - 1 - enyl)methyl]-amide, (S_s,R)-**2g**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.34 (3H, s, CH_3), 2.45–2.50 (2H, m, CH_2), 2.65–2.68 (2H, m, CH_2), 5.70 (1H, d, $J=8.1$ Hz), 6.05 (1H, d, $J=8.1$ Hz), 7.06 (2H, d, $J=8.5$ Hz, Ar), 7.22–7.34 (2H, m, Ar), 7.42 (1H, dd, $J=8.2$, 8.2 Hz, Ar), 7.52 (1H, t, $J=1.8$ Hz, =CH), 7.61 (2H, d, $J=8.4$ Hz, Ar).

4.2.8. Reaction of *N*-sulfinimine 1h with cyclopent-2-en-1-one. Major isomer: (S_s,S)-4-Methylbenzenesulfinic acid [(3-fluorophenyl)(5-oxocyclopent-1-enyl)methyl]-amide, (S_s,S)-**2h**: mp 144–146°C; $[\alpha]_D=+104.7$ (c 0.91, $CHCl_3$); IR (KBr) ν 1698 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.37–2.40 (2H, m, CH_2), 2.42 (3H, s, CH_3), 2.50–2.53 (2H, m, CH_2), 5.17 (1H, d, $J=6.0$ Hz, CH), 5.40 (1H, d, $J=6.0$ Hz, NH), 6.99 (1H, ddd, $J=8.7$, 8.4, 2.3 Hz, Ar), 7.12 (1H, dd, $J=8.7$, 2.1 Hz, Ar), 7.20 (1H, d, $J=8.4$ Hz, Ar), 7.29 (1H, s, Ar), 7.31 (2H, d, $J=8.4$ Hz, Ar), 7.35 (1H, t, $J=1.9$ Hz, =CH), 7.59 (2H, d, $J=8.4$ Hz, Ar); MS (EI) m/z 205 (M^+-140, 100), 295 (M^+-50, 23.36). Anal. found: C, 66.18; H, 5.63; N, 3.94. $C_{19}H_{20}FNO_2S$ requires: C, 66.06; H, 5.84; N, 4.05%.

Minor product: (S_s,R)-4-Methylbenzenesulfinic acid [(3-fluorophenyl)(5 - oxocyclopent - 1 - enyl)methyl]amide, (S_s,R)-**2h**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 2.40 (3H, s, CH_3), 2.48 (2H, td, $J=3.5$, 1.9 Hz, CH_2), 2.62–2.66 (2H, m, CH_2), 5.22 (1H, d, $J=7.2$ Hz, CH), 5.61 (1H, d, $J=7.2$ Hz, NH), 6.86 (1H, ddd, $J=9.1$, 8.9, 1.6 Hz, Ar), 6.94 (1H, d, $J=8.9$ Hz, Ar), 6.98 (1H, d, $J=9.1$ Hz, Ar), 7.27 (2H, d, $J=8.0$ Hz, Ar), 7.28 (1H, s, Ar), 7.55 (2H, d, $J=8.0$ Hz, Ar), 7.57 (1H, t, $J=1.9$ Hz, =CH).

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