Synthesis of a Novel Chiral Cubane-Based Schiff Base Ligand and Its Application in Asymmetric Nitro-Aldol (Henry) Reactions

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Abstract: The first reported cubane-based chiral Schiff base ligand has been successfully synthesized. This ligand has been evaluated on the nitro-aldol (Henry) reaction. The reactions were performed in the presence of four different copper salts, using eight different solvents, and five different temperatures. The highest enantioselectivity obtained for this novel ligand was ~39% ee.

Key words: cubane, aldol reactions, chirality, Schiff base, catalysis

In 1964, the first successful synthesis of pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, more commonly known as cubane, was accomplished at the University of Chicago by Philip E. Eaton and Tom Cole Jr.[1] Since this first synthesis, much work has been performed on a large number of its derivatives. Octanitrocubane has been classified as the most powerful non-nuclear explosive,[2] cubylamines have shown antiviral acitivity,[3] dicubyl disulfide[4] and its derivatives[5] have revealed unique bond lengths and intramolecular hydrogen-bonding. Cubanes have also been shown to rearrange with silver(I)[6] and rhodium(I)[7] ions to cuneane and *syn*-tricyclooctadiene, respectively. Recently, it was reported that 4-iodo-1-vinylcubane rearranged under heat, and/or in the presence of a Lewis acid, to yield 4-vinyl-*trans*-β-iodostyrene.[8] Polymers of cubane have also been synthesized[9,10] and some have undergone cage-opening once incorporated within the polymer.[10] One area of cubane chemistry that has not been examined is its application in asymmetric synthesis. The bulkiness of the cubane makes it an attractive moiety for incorporation into a chiral ligand.

A classical C–C bond forming reaction is the nitro-aldol (Henry) reaction. This reaction was first reported in 1895;[11] however, the first asymmetric version was only accomplished in 1992.[12] This reaction couples a nitroalkane with a carbonyl compound in the presence of a base, yielding β-nitroalcohols. This methodology has been successfully used in the stereoselective synthesis of several β-blockers, including (*S*)-metoprolol,[13] (*S*)-pindolol,[14] and (*S*)-propranolol.[15] Numerous chiral ligands have been used in this copper- and zinc-catalyzed reaction, including bis(oxazoline),[16] amino alcohols,[17] tridentate-bis(thiazole),[18] and Schiff base ligands.[19] Herein, we report the synthesis of a cubane-based chiral Schiff base ligand and its use in the enantioselective Henry reaction.

In order to synthesize our desired cubane-based chiral Schiff base ligand, we required the dimethyl-1,4-cubane dicarboxylate (**5**), which was synthesized according to Tsanaktsidis' procedure (Scheme 1).[20] Initially, we started with cyclopentanone (**1**), which was ketalized to **2** with ethane-1,2-diol in the presence of Dowex 50W-X8 (H) cation-exchange resin. After treatment with bromine in 1,4-dioxane, the unpurified tribromide was dimerized to **3** in refluxing methanol. The formation of the dione **4** was accomplished with concentrated sulfuric acid, which was irradiated, hydrolyzed, induced to undergo two consecutive Favorskii ring contractions, and subsequently esterified to afford the dimethyl-1,4-cubane dicarboxylate (**5**). After addition of one equivalent of sodium hydroxide, cubane **5** was converted into the corresponding acid ester **6**. A subsequent Moriarty reaction,[21] followed immediately by another base-mediated hydrolysis yielded the iodo acid **7**. Borane reduction of the carboxylic acid, then a Swern oxidation afforded aldehyde **9**. Finally, the cubane-based chiral ligand **10** was formed by reacting two equivalents of **9** with *trans*-(1*R*,2*R*)-(–)-1,2-cyclohexanediamine. All intermediates were characterized by ^{1}H NMR and compared to literature values.[8,20,22] Ligand **10** was fully characterized through ^{1}H and ^{13}C NMR as well as HRMS.

Ligand **10** was evaluated in the Henry reaction described by Jiang and Shi.[23] Typical conditions were 10 mol% ligand **10** and 5 mol% copper(I) triflate in methanol at room temperature for 48 hours. This provided a high conversion (>99%) with only 13% ee. We next compared different copper salt sources (entries 1–4, Table 1). Copper(II) triflate gave both poor conversion and poor enantiomeric excess (entry 2, Table 1). When using copper(I) triflate tetrakisacetonitrile or copper(I) chloride, we obtained near quantitative conversion and an increase in enantiomeric excess to 27 and 32% ee, respectively. Next, we focused on the use of these two copper salts with ligand **10**, in a range of solvents. After screening eight solvents with copper(I) chloride, we found near quantitative conversion in each case (entries 4–11, Table 1). Only a moderate increase in enantiomeric excess was observed with diethyl ether (entry 8) and dichloromethane (entry 9). The same solvent systems were also examined with copper(I) triflate tetrakisacetonitrile (entries 12–18, Table 1).

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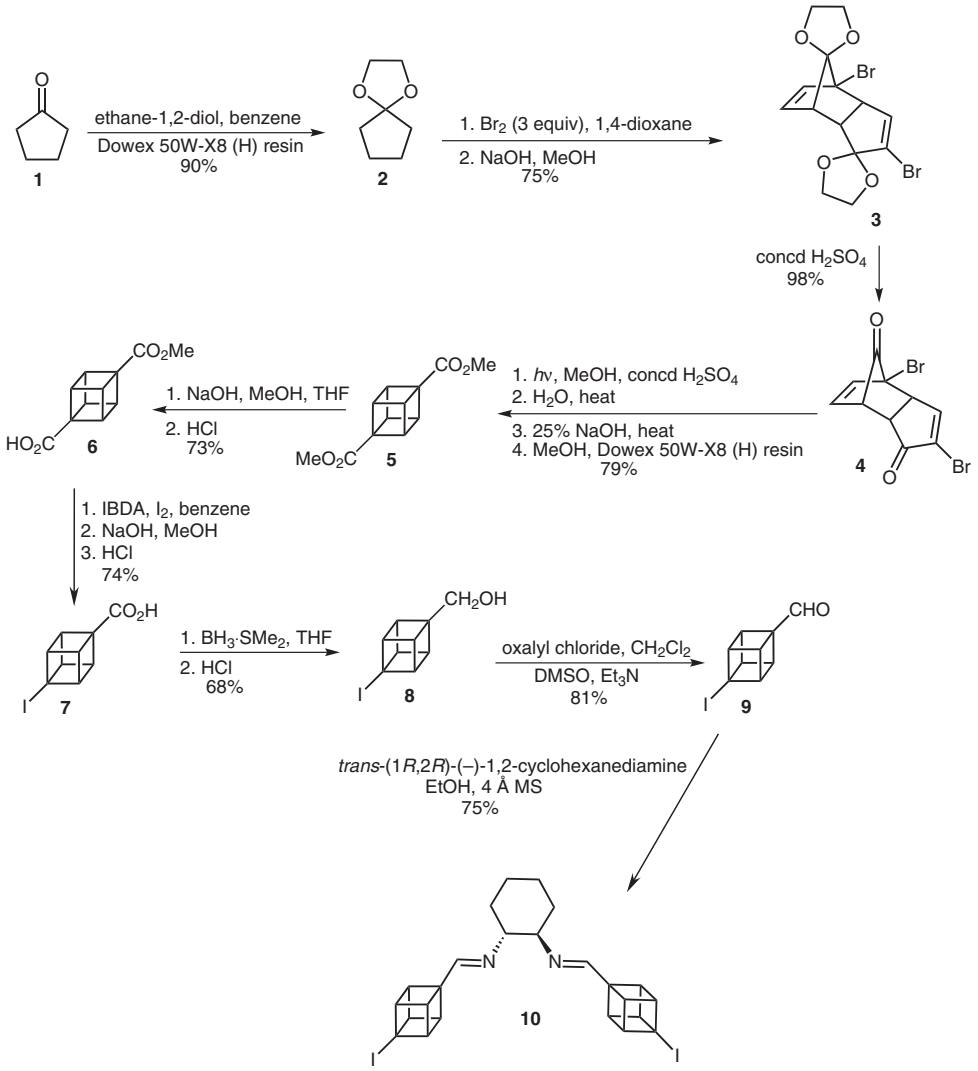


Scheme 1 Synthesis of the cubane-based chiral Schiff base ligand

Only diethyl ether (entry 15) provided a higher enantiomeric excess compared to the initial study in methanol (entry 3), but gave a lower conversion after 48 hours. Ligand **10**, with copper(I) triflate tetrakisacetonitrile in dichloromethane gave the lowest conversion (72.2%) as well as yielding the opposite enantiomer in 11% ee (entry 16).

Finally, we examined the reaction in the presence of ligand **10** and copper(I) chloride in methanol at different temperatures (entries 4 and 19–22, Table 1). Surprisingly, the highest enantiomeric excess (39% with >99.0% conversion) was observed at 65 °C. The enantiomeric excess as well as the level of conversion decreased with temperature, which was unexpected, however within experimental error, excluding the –80 °C data point.

In conclusion, we have successfully synthesized the first reported cubane-based chiral Schiff base ligand and have demonstrated its use in the enantioselective copper-catalyzed Henry reaction. Further applications of this novel ligand are currently underway.

Purchased chemicals were reagent grade. 1,4-Dioxane was distilled over potassium benzophenone ketyl immediately prior to use. Melting points were obtained on a Gallenkamp apparatus and are uncorrected. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were obtained on a Varian instrument with the indicated solvent. HPLC measurements were performed with Varian Polaris HPLC model 325. Separations were carried out on a Diacel Chiralcel AD column (hexane–*i*-PrOH, 65:35; 0.7 mL/min; 230 nm; t_{minor} = 10.595 min, t_{major} = 13.106 min).

Synthesis of Cubane-Based Chiral Schiff Base

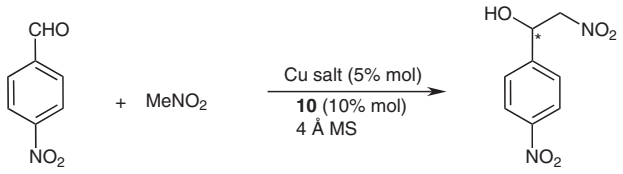
Cyclopentanone Ethylene Ketal (2)

Cyclopentanone (**1**; 250 ml, 3.0 mol), ethane-1,2-diol (200 mL, 3.59 mol), and Dowex 50W-X8 (H) cation-exchange resin (3 g) were refluxed in benzene (500 mL) with simultaneous azeotropic removal of H_2O over 30 h. The yellow solution that remained was cooled to r.t., filtered, and washed with aq NaOH (4%, 250 mL) and brine (500 mL), dried with $MgSO_4$ and concentrated by distillation through a Vigreux column (35 cm). Simple distillation of the residue (59–63 °C/23 mmHg; Lit.[24] 57 °C/18 mmHg) yielded the ketal **2**.

Yield: 326.2 g (90%); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58–1.81 (m, 8 H), 3.87 (s, 4 H).

Table 1 Optimization of the Copper-Catalyzed Asymmetric Henry Reaction between *p*-Nitrobenzaldehyde and Nitromethane



Entry	Metal	Temp (°C)	Solvent	Conv. (%)[a]	ee (%)[b]
1	Cu(OTf) toluene complex	25	MeOH	>99.0	13 (*R*)
2	$Cu(OTf)_2$	25	MeOH	54.2	2 (*R*)
3	Cu(OTf) tetrakisacetonitrile	25	MeOH	97.9	27 (*R*)
4	CuCl	25	MeOH	97.8	32 (*R*)
5	CuCl	25	EtOH	>99.0	20 (*R*)
6	CuCl	25	THF	>99.0	31 (*R*)
7	CuCl	25	Toluene	96.3	17 (*R*)
8	CuCl	25	Et_2O	>99.0	36 (*R*)
9	CuCl	25	CH_2Cl_2	>99.0	34 (*R*)
10	CuCl	25	*i*PrOH	95.2	25 (*R*)
11	CuCl	25	MeCN	>99.0	25 (*R*)
12	Cu(OTf) tetrakisacetonitrile	25	EtOH	93.0	26 (*R*)
13	Cu(OTf) tetrakisacetonitrile	25	THF	97.1	5 (*R*)
14	Cu(OTf) tetrakisacetonitrile	25	Toluene	91.1	13 (*R*)
15	Cu(OTf) tetrakisacetonitrile	25	Et_2O	73.1	30 (*R*)
16	Cu(OTf) tetrakisacetonitrile	25	CH_2Cl_2	72.2	11 (*S*)
17	Cu(OTf) tetrakisacetonitrile	25	*i*PrOH	>99.0	19 (*R*)
18	Cu(OTf) tetrakisacetonitrile	25	MeCN	98.0	15 (*R*)
19	CuCl	65	MeOH	>99.0	39 (*R*)
20	CuCl	5	MeOH	27.9	32 (*R*)
21	CuCl	–5	MeOH	23.3	31 (*R*)
22	CuCl	–80	MeOH	16.2	8 (*R*)

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture.
[b] Determined by chiral HPLC using Diacel Chiralcel AD column.

endo-2,4-Dibromodicyclopentadiene-1,8-dione Bisethylene Ketal (3)

Anhydrous 1,4-dioxane (25 kg) was transferred into a 100 L reaction vessel under nitrogen. To this was added cyclopentanone ethylene ketal (**2**; 6.3 kg, 49.2 mol) and the mixture was stirred under nitrogen. The system was cooled to ~10 °C while stirring at ~200 rpm. Anhydrous liquid bromine (25 kg, 156 mol) was added slowly under nitrogen to the vigorously stirred reaction mixture keeping the temperature between 10–15 °C and ensuring the bromine was added directly into the stirred solution. Addition of bromine was complete after ~6 h. The mixture was stirred at r.t. with nitrogen blowing through the delivery vessel and over the reaction mixture to ensure removal of HBr. NaOH (11 kg, 275 mol) in MeOH (55 L) was added slowly, so as to maintain the temperature below 10 °C. After half the NaOH solution had been added, the mixture turned a dark-green color. After ~4 h, the addition was complete with the color having turned to brown. The mixture was then heated to reflux and left stirring for 16 h then subsequently cooled to r.t. and pumped out of the reactor into ice water (80 L). The precipitate was then collected by vacuum filtration, washed with deionized H_2O (90 L) and cold MeOH (5 L). The solid was then air-dried to yield the bisketal **3**.

Yield: 7.46 kg (74.7%); solid; mp 174–176 °C (Lit.[25] 172–174 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.69–2.76 (m, 1 H), 3.02–3.13 (m, 1 H), 3.46–3.55 (m, 1 H), 3.83–4.30 (m, 8 H), 5.84 (d, *J* = 6.5 Hz, 1 H), 6.07 (d, *J* = 2.3 Hz, 1 H), 6.19 (dd, *J* = 3.5, 6.5 Hz, 1 H).

endo-2,4-Dibromodicyclopentadiene-1,8-dione (4)

The bisketal **3** (14 kg, 34.5 mol) was slowly added to concd H_2SO_4 (45 L) keeping the temperature below 25 °C. The mixture was then stirred at r.t. for 24 h, then pumped from the reactor onto ice water (~120 L) while stirring. The precipitate was then collected by vacuum filtration washed with H_2O (2 × 20 L) and air-dried, yielding the dione **4**.

Yield: 10.8 kg (98.4%); colorless solid; mp 156–157 °C (Lit[25] 155–155.5 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.15–3.25 (m, 1 H), 3.48–3.63 (m, 2 H), 6.24–6.36 (m, 2 H), 7.67 (d, *J* = 2.9 Hz, 1 H).

Dimethyl 1,4-Cubanedicarboxylate (5)

The dione **4** (4.00 kg, 12.6 mol) was dissolved in MeOH (68 L), deionized H_2O (12 L) and concd H_2SO_4 (103 mL) in a 100 L reactor. The solution was circulated through the Symantec large-scale photolysis unit irradiating the solution with UV light (2 kW Hg vapor lamp). Cooling was applied to the reactor to maintain a temperature of ~25 °C. Conversion into the caged dione was quite slow, with a maximum conversion rate of ~10 g per hour (monitored by ^{1}H NMR). When conversion was complete, the reaction solution was concentrated to dryness under reduced pressure. The crude solid caged dione was dissolved in aq NaOH (30%, 38 L) and the mixture was heated to reflux for 3 h. The solution was then cooled to 0 °C and acidified by the slow addition of concd HCl (24 L) with vigorous stirring while maintaining the temperature below 10 °C. The resulting precipitate of crude cubane diacid, was collected by vacuum filtration and washed with ice-cold H_2O (2 × 2 L). The solid cake was again washed with ice-cold H_2O (2 × 5 L) and then air-dried. The cubane diacid was dissolved in MeOH (15 L), washed Dowex 50W-X8 ion-exchange resin [75 g; pre-washed with MeOH (500 mL)] was added and the solution was heated at reflux overnight. The mixture was cooled to r.t., filtered, and evaporated to dryness under reduced pressure. The crude product was then purified by sublimation (100–120 °C/0.01 mmHg) to afford **5**.

Yield: 563 g (78.7%); white solid; mp 161–162 °C (Lit.[26] 161–162 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.70 (s, 6 H, CH_3), 4.24 (s, 6 H, cubyl H).

4-Methoxycarbonyl-cubanecarboxylic Acid (6)

To a solution of dimethyl 1,4-cubane dicarboxylate (**5**; 2.498 g, 11.3 mmol) dissolved in THF (85 mL) at r.t., was added dropwise a solution of NaOH (0.438 g, 10.9 mmol) dissolved in MeOH (7.1 mL). The mixture was stirred overnight and evaporated to dryness. The resulting white solid was dissolved in H_2O (100 mL), extracted with $CHCl_3$ (3 × 25 mL), dried with $MgSO_4$, filtered and evaporated to afford the excess starting material (0.125 g, 5.5%). The aqueous layer from the extraction was acidified with concd HCl to pH ~1, extracted with $CHCl_3$ (3 × 50 mL), dried with $MgSO_4$, filtered and

evaporated to afford 4-methoxycarbonyl cubane carboxylic acid (**6**).

Yield: 1.70 g (73.0%); mp 181–183 °C (Lit.[22a] 182–183 °C).

^{1}H NMR (400 MHz, CD_3OD): δ = 3.71 (s, 3 H, CH_3), 4.20 (s, 6 H, cubyl H).

4-Iodocubanecarboxylic Acid (7)

A suspension of 4-methoxycarbonyl-cubanecarboxylic acid (**6**; 1.94 g, 9.38 mmol) was prepared in anhydrous benzene (150 mL) under argon. To it, iodobenzenediacetate (9.06 g, 28.1 mmol) and I_2 (7.14 g, 28.1 mmol) were added and the mixture was refluxed for 7 h. The mixture was then cooled to r.t. and hexanes (75 mL) was added. The solution was washed with sat. Na_2SO_3 (2 × 25 mL), H_2O (25 mL), and brine (25 mL), dried with $MgSO_4$, filtered, and evaporated to near dryness. The resulting red-brown liquid was dissolved in THF (50 mL) and a mixture of NaOH (3.75 g, 93.8 mmol) dissolved in MeOH (40 mL) and H_2O (15 mL) was added. The mixture was stirred overnight then the solution was evaporated to near dryness. The residue was dissolved in H_2O (25 mL), and acidified with concd HCl to pH <1, whereby a white precipitate formed which was collected under vacuum filtration, yielding 4-iodocubanecarboxylic acid (**7**).

Yield: 1.91 g (74.3%); mp 212 °C (dec.) [Lit.[22a] 215 °C (dec.)].

^{1}H NMR (400 MHz, CD_3OD): δ = 4.24 (m, 3 H, cubyl H), 4.36 (m, 3 H, cubyl H).

1-Iodo-4-(hydroxymethyl)cubane (8)

4-Iodocubanecarboxylic acid (**7**; 676 mg, 2.46 mmol) was dissolved in anhydrous THF (25 mL) under argon and cooled to 0 °C. To it, borane dimethyl sulfide complex (0.78 mL, 3.91 mmol) was added and the mixture was stirred for 20 min at 0 °C, then at r.t. for 4 h. The reaction was quenched with H_2O (20 mL) and stirred overnight. After adding EtOAc (20 mL), the solution was washed with H_2O (2 × 15 mL) and brine (20 mL), dried with $MgSO_4$, filtered, and evaporated to dryness. Column chromatography ($CHCl_3$–EtOAc, 1:1) afforded 1-iodo-4-(hydroxymethyl)cubane (**8**).

Yield: 438 mg (68.4%); white solid; mp 109–111 °C (Lit.[22a] 109–111 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 2 H, CH_2), 4.07 (m, 3 H, cubyl H), 4.23 (m, 3 H, cubyl H).

1-Iodocubane-4-carboxaldehyde (9)

A stirring solution of oxalyl chloride (0.16 mL, 1.89 mmol) in anhydrous CH_2Cl_2 (4 mL) was prepared under argon at –78 °C. To it, anhydrous DMSO (0.28 mL, 3,86 mmol) in anhydrous CH_2Cl_2 (4 mL) was added dropwise. After 20 min at –78 °C, 1-iodo-4-(hydroxymethyl)cubane (**8**; 403 mg, 1.56 mmol) dissolved in anhydrous CH_2Cl_2 (17 mL) under argon was added to the system dropwise. The system was maintained at –78 °C for 1.5 h and anhydrous Et_3N (7.02 mmol) was added via syringe. The mixture was warmed to r.t. and quenched with H_2O (15 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL) and the organic layers were combined and washed with H_2O (15 mL) and brine (15 mL), dried with $MgSO_4$, filtered, and evaporated to dryness. Column chromatography (CH_2Cl_2) afforded 1-iodocubane-4-carboxaldehyde (**9**).

Yield: 326 mg (80.9%); white solid; mp 106–109 °C (Lit.[27] 108–110 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (m, 3 H, cubyl H), 4.53 (m, 3 H, cubyl H), 9.76 (s, 1 H, CHO).

Cubane-Based Chiral Schiff Base Ligand (10)

trans-(1*R*,2*R*)-(–)-1,2-Cyclohexanediamine (50.3 mg, 0.438 mmol) and 1-iodocubane-4-carboxaldehyde (**9**; 226 mg, 0.876 mmol) and oven-dried 4 Å molecular sieves (0.05 g) were combined together in EtOH (1.1 mL) at r.t. and stirred for 30 min. The mixture was evaporated to dryness, affording an off-white solid. The solid was collected and washed with cold EtOH under vacuum filtration, yielding **10**.

Yield: 195 mg (75.0%); white solid; mp 95–97 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36–1.40 (m, 2 H), 1.61–1.84 (m, 6 H) 3.06–3.09 (m, 2 H), 4.21–4.32 (m, 6 H), 7.66 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 73.7, 59.0, 54.7, 49.9, 37.5, 32.6, 24.4.

HRMS (ESI): *m/z* [M + H^+] calcd for $C_{24}H_{25}N_2I_2$: 595.0102; found: 595.01074.

General Procedure for Henry Reaction

To the solvent (1.5 mL) at r.t., 4 Å molecular sieves (20 mg), the copper salt (0.00841 mmol), and cube ligand **10** (10 mg, 0.0168 mmol) were added and the mixture was stirred for 10 min. 4-Nitrobenzaldehyde (25.4 mg, 0.168mmol) and excess $MeNO_2$ (1 mL) were added and the reaction was stirred for 48 h. The mixture was evaporated to near dryness, dissolved in CH_2Cl_2 (10 mL) and 1 M HCl (10 mL) was added until the mixture became clear. Work-up with CH_2Cl_2 (2 × 10 mL), washing with H_2O (2 × 10 mL) and brine (10 mL), drying with $MgSO_4$, filtering and evaporating to dryness afforded the dark-yellow glutinous product which was used directly to determine conversion and enantioselectivity.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.49–4.60 (m, 2 H, CH_2), 5.62 (dd, *J* = 4.4, 8.0 Hz, 1 H, CH), 7.63 (d, *J* = 9.2 Hz, 2 H, Ar), 8.28 (d, *J* = 9.2 Hz, 2 H, Ar).

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References

(1) Eaton, P. E.; Cole, T. W. Jr. *J. Am. Chem. Soc.* **1964**, *96*, 962 and 3157.
(2) (a) Service, R. F. *Science* **2000**, *287*, 564. (b) Zhang, M.-X.; Eaton, P. E.; Gilardi, R. *Angew. Chem.* **2000**, *39*, 401. (c) Kortus, J.; Pederson, M. R.; Richardson, S. L. *Chem. Phys. Lett.* **2000**, *322*, 224. (d) Hrovat, D. A.; Borden, W. T.; Eaton, P. E.; Kahr, B. *J. Am. Chem. Soc.* **2001**, *123*, 1289.
(3) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421.
(4) Priefer, R.; Lee, Y. J.; Barrios, F.; Wosnick, J. H.; Lebuis, A.-M.; Farrell, P. G.; Harpp, D. N.; Sun, A.; Wu, S.; Snyder, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 5626.
(5) Priefer, R.; Martineau, E.; Harpp, D. N. *J. Sulfur Chem.* **2007**, *28*, 529.
(6) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 6366.
(7) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515.
(8) Carroll, V. M.; Harpp, D. N.; Priefer, R. *Tetrahedron Lett.* **2008**, *49*, 2677.
(9) Priefer, R.; Nguyen, S.; Farrell, P. G.; Harpp, D. N. *Macromolecules* **2003**, *36*, 5435.
(10) McGonagle, A. E.; Savage, G. P. *Aust. J. Chem.* **2009**, *62*, 145.
(11) Henry, L. *C. R. Hebd. Seances Acad. Sci.* **1895**, *120*, 1265.
(12) Sasai, H.; Suzuki, T.; Arai, S.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1992**, *114*, 4418.

(13) Sasai, H.; Suzuki, T.; Itoh, N.; Arai, S.; Shibasaki, M. *Tetrahedron Lett.* **1993**, *34*, 2657.
(14) Sasai, H.; Yamada, Y. M. A.; Suzuki, T.; Shibasaki, M. *Tetrahedron* **1994**, *50*, 12313.
(15) Sasai, H.; Itoh, N.; Suzuki, T.; Shibasaki, M. *Tetrahedron Lett.* **1993**, *34*, 855.
(16) Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2003**, *125*, 12692.
(17) Palomo, C.; Oiarbide, M.; Laso, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 3881.
(18) Lu, S. F.; Du, D. M.; Zhang, S. W.; Xu, J. *Tetrahedron: Asymmetry* **2004**, *15*, 3433.
(19) Gan, C.; Lai, G.; Zhang, Z.; Wang, Z.; Zhou, M.-M. *Tetrahedron: Asymmetry* **2006**, *17*, 3315.
(20) Bliese, M.; Tsanaktsidis, J. *Aust. J. Chem.* **1997**, *50*, 189.
(21) (a) Moriarty, R. M.; Khosrowshahi, J. S.; Dalecki, T. M. *J. Chem. Soc., Chem. Commun.* **1987**, 675. (b) Concepcion, J. I.; Francisco, C. G.; Freire, R.; Hernandez, R.; Salazar, J. A.; Suarez, E. *J. Org. Chem.* **1986**, *51*, 402.
(22) (a) Priefer, R.; Farrell, P. G.; Harpp, D. N. *Synthesis* **2002**, 2671. (b) Priefer, R.; Farrell, P. G.; Harpp, D. N. *Tetrahedron Lett.* **2002**, *43*, 8781.
(23) Jiang, J.-J.; Shi, M. *Tetrahedron: Asymmetry* **2007**, *18*, 1376.
(24) Salmi, E. J. *Chem. Ber.* **1938**, *71*, 1803.
(25) Chapman, N. B.; Key, J. M.; Toyne, K. J. *J. Org. Chem.* **1970**, *35*, 3860.
(26) Stock, L. M.; Luh, T.-Y. *J. Org. Chem.* **1972**, *37*, 338.
(27) Eaton, P. E.; Galoppini, E.; Gilardi, R. *J. Am. Chem. Soc.* **1994**, *116*, 7588.