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Note

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Experiments Probing the Viability of Donor–Acceptor Norbornenes for (5 + 2)-Annulation

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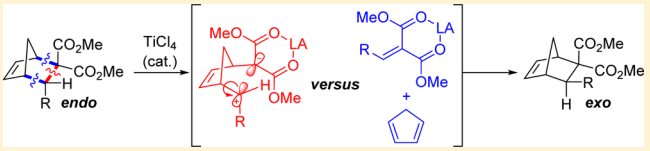
Supporting Information

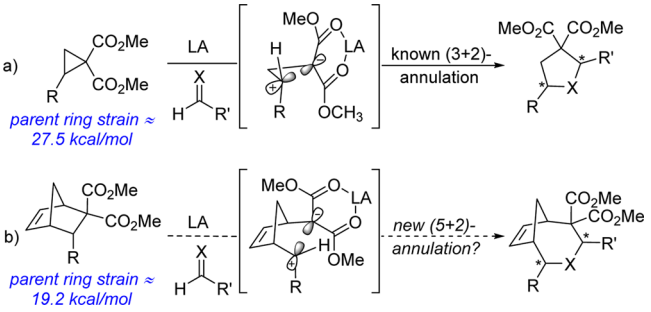
ABSTRACT: This Note details experiments that probe the mechanism by which donor–acceptor norbornene systems epimerize. A number of mechanistic studies indicate that epimerization in these systems occurs via a Lewis acid catalyzed retro-Diels–Alder/Diels–Alder sequence, rather than bond rotation in an intimate ion pair. These results suggest that, under the reaction conditions examined, the ring strain present in norbornene is inadequate to induce zwitterion formation analogous to that observed with donor–acceptor cyclopropanes.



Donor–acceptor (D-A) cyclopropanes are being deployed in a growing number of reactions.[1,2] These strained building blocks are excellent reaction partners in (3 + *n*)-annulations that generate a variety of hetero- and carbocyclic ring systems.[3] A common embodiment of the transformation involves the reaction of a cyclopropane 1,1-diester with a 2π component in the presence of a Lewis acid catalyst. Much of the appeal associated with these reactions lies in the simple and scalable access to the starting materials and the utility of the tetrahydrofuran, pyrrolidine, and related products. With the goal of extending the product types that might be possible via Lewis acid-catalyst ring strain-release annulations, we became interested in testing the notion that other easily accessible strained systems might be fruitful reaction partners. The evaluation of that hypothesis in the context of "donor–acceptor norbornenes" is the subject of this Note.

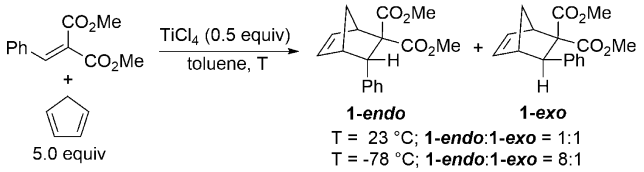
Mechanistic studies of the cyclopropane/aldehyde annulation have implicated the existence of a Lewis acid-coordinated intimate ion pair as the key reactive intermediate (Scheme 1a).[4] Enantiomerically pure cyclopropanes can racemize via this intermediate by single bond rotation and reclosure, either in the absence of "dipolarophile" or in the presence of a poorly reactive trap. This configurational instability provides a useful stereochemical probe for intimate ion pair formation. We wondered whether a 5-norbornene-2,2-dicarboxylic diester might be sufficiently strained to undergo intimate ion pair formation and ultimate trapping by appropriately selected reagents (Scheme 1b). Because of the strain difference in the parent hydrocarbons, 27.5 kcal/mol for cyclopropane versus 19.2 kcal/mol for norbornene,[5] this extrapolation was an open question at the outset of our studies. A potential merit of this type of building block was the expectation that it could be easily accessed via the Diels–Alder reaction.

Scheme 1. Annulations Utilizing Strained Ring Systems



We prepared donor–acceptor norbornene **1** via a $TiCl_4$-promoted Diels–Alder reaction (Scheme 2). Of immediate interest was the discovery that the reaction diastereoselectivity was temperature dependent. Conducting the cycloaddition at room temperature for 24 h resulted in a 1:1 ratio of **1-*endo*/1-*exo***; conversely, at a reaction temperature of −78 °C, **1-*endo*/1-*exo*** were obtained in a combined 33% yield and an 8:1 ratio.

Scheme 2. Synthesis of 1



This change in *endo*/*exo* ratio could be the result of either strongly temperature-dependent kinetic diastereoselectivity during cycloadduct formation or epimerization of **1** under thermodynamic control at higher temperature. The latter might suggest that donor–acceptor norbornene ring-opening was possible. Accordingly, we began an epimerization study to determine the cause of the variable *endo*/*exo* ratio by subjecting **1-*endo*** to catalytic quantities of $TiCl_4$ (10 mol %) at room temperature. Within 28.5 h, we observed a turnover of the ratio

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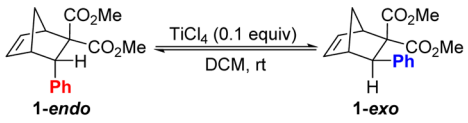
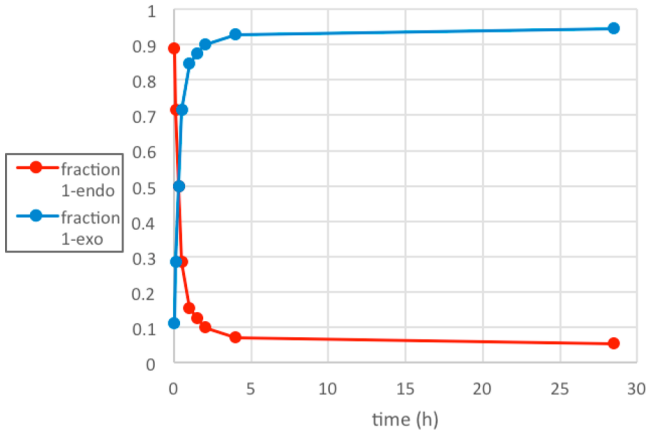
of **1**-*endo*/**1**-*exo* from 8:1 to 1:17 (Chart 1). We considered two limiting mechanisms that could lead to this equilibration:

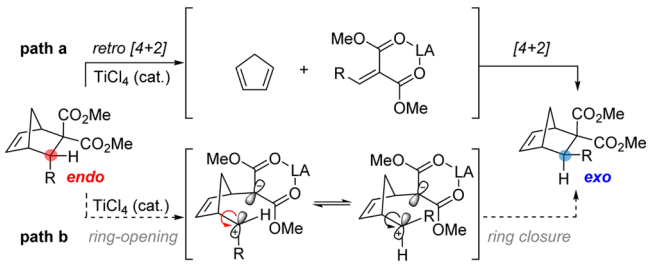
Chart 1. $TiCl_4$-Catalyzed Epimerization of 1





either ring-opening and bond rotation (Scheme 3, path b)[4] or a retro-[4 + 2]/[4 + 2] sequence (Scheme 3, path a)[6] could deliver the thermodynamically favored product.

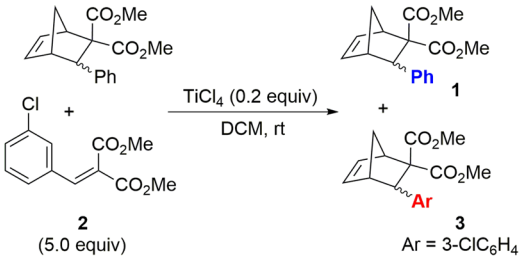
Scheme 3. Possible Mechanisms of Norbornene Epimerization

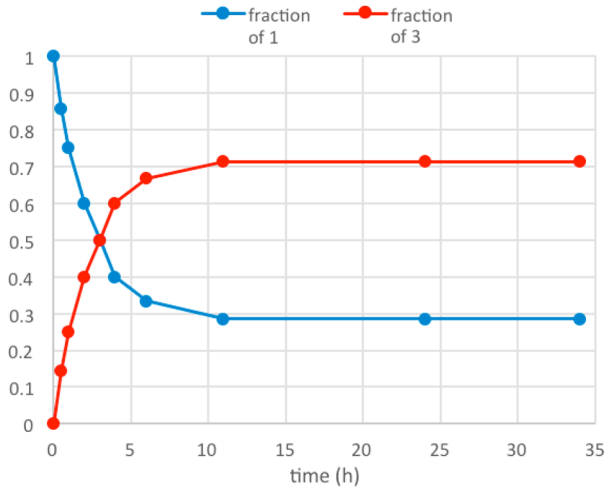


We evaluated retro-[4 + 2]/[4 + 2]-cycloaddition as a mechanism of epimerization via a crossover experiment using 5.0 equiv of a crossover dienophile **2** in the presence of **1** and 10 mol % $TiCl_4$. These conditions resulted in very little epimerization (or crossover) over the course of 48 h. The superstoichiometric quantities of **2** may serve to inhibit catalyst activity relative to that noted in Chart 1. This finding is in accord with literature studies involving reactions of chelating substrates catalyzed by divalent Lewis acids.[7] Accordingly, for the purposes of the crossover study, we increased the loading of $TiCl_4$ to 20 mol % and used ^1H NMR spectroscopy to monitor the ratio of **1**/**3** over the course of 48 h. Diels–Alder reaction of **2** with liberated cyclopentadiene[8] over this time produced the crossover product **3**. At the completion of this time trial, we observed a 2.5:1 ratio of crossover product **3** to starting norbornene **1**, strongly suggesting that epimerization was occurring via the retro-[4 + 2]/[4 + 2] sequence (Chart 2).

To further probe whether ring-opening (intimate ion pair formation) was happening in parallel with retro-[4 + 2]/[4 + 2]

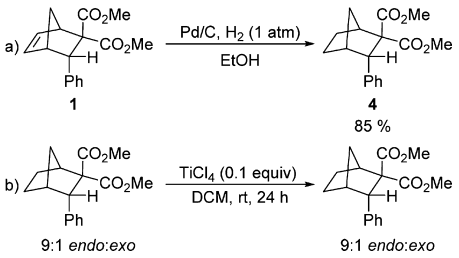
Chart 2. [4 + 2] Crossover Experiment





cycloaddition, we prepared norbornane **4** via catalytic hydrogenation of norbornene **1** (Scheme 4a). The saturated variant,

Scheme 4. Evaluation of Donor–Acceptor Norbornanes for Ring-Opening



which is unable to undergo retro-Diels–Alder reaction, was subjected to the standard epimerization conditions. After 24 h, the *endo*/*exo* ratio of **4** remained unchanged, excluding epimerization via ring-opening for that particular compound (Scheme 4b). The extrapolation back to norbornene **1** is imperfect, however, since the parent ring strain energies are different (parent norbornane ring strain = 14.4 kcal/mol).[5] We note that initial exploratory experiments to probe the viability of Scheme 1b under conditions optimal for related [3 + 2]-annulations (e.g., aryl aldehydes with Lewis acids like $Sc(OTf)_3$) have to date been unsuccessful, further suggesting the need for more strained systems to achieve donor–acceptor cycloalkane reactivity.

Collectively, the results presented here indicate that under Lewis acidic conditions, the epimerization of donor–acceptor norbornene systems occurs via a retro-[4 + 2]/[4 + 2] sequence, rather than ring-opening to an intimate ion pair and bond rotation. This suggests that the strain present and polarization in these particular norbornene systems is

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insufficient under the conditions examined to promote zwitterion formation, excluding at the present time their use in [5 + 2] annulations.

EXPERIMENTAL SECTION

Methods. Proton and carbon magnetic resonance spectra (^{1}H NMR at 400 MHz and ^{13}C NMR at 150 MHz) were recorded with solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm, and ^{13}C NMR, $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, bs = broad singlet, d = doublet, m = multiplet), and coupling constants (Hz). Analytical thin layer chromatography (TLC) visualization was accomplished with UV light or aqueous potassium permanganate ($KMnO_4$) followed by heating. Yield refers to isolated yield of analytically pure material unless otherwise noted. Mass spectra samples of the reported analytes were prepared via dilution using 0.1 M formic acid in methanol.

Materials. Alkylidene malonates were prepared according to known literature procedures.[9] Dichloromethane (DCM) and toluene were dried by passage through a column of neutral alumina under nitrogen prior to use.

General Procedure A for the Preparation of Norbornenes (1-*endo*, 3-*endo*). The title compounds were prepared based on a literature Diels–Alder reaction of di-*l*-menthyl (acetoxymethylene)-malonate and cyclopentadiene.[10] To a flame-dried round-bottomed flask equipped with a magnetic stir bar under N_2 atmosphere was added alkylidene malonate (1.0 equiv) and toluene (0.2 M). The solution was cooled to −78 °C, and cyclopentadiene (5.0 equiv; distilled prior to use) was added, followed by $TiCl_4$ (0.5 equiv). The mixture was stirred at −78 °C overnight then quenched with water. The biphasic solution was diluted with ethyl acetate (EtOAc), and the layers were separated. The organic layer was washed with water (2×) and brine and dried over Na_2SO_4. This was filtered, concentrated *in vacuo*, and purified by flash chromatography using 2% EtOAc/hexanes ($KMnO_4$) to provide the norbornene products, which were stored neat in the freezer.

*Dimethyl-3-phenylbicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate (**1-endo**).* The title compound was prepared according to general procedure A using dimethyl-2-benzylidene malonate (16.6 g, 75.0 mmol), cyclopentadiene (31.5 mL, 375 mmol), and $TiCl_4$ (4.12 mL, 37.5 mmol) affording **1-*endo*** (7.12 g, 24.9 mmol, 33%, 8:1 *endo*/*exo*) as a pale yellow solid that was stored in the freezer. Analytical data for **1-*endo***: mp 68–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.12 (5H, m), 6.74–6.72 (1H, m), 6.34–6.32 (1H, m), 4.45–4.44 (1H, d, J = 3.2 Hz), 3.78 (3H, s), 3.45 (1H, br s), 3.12 (3H, s), 3.06 (1H, s), 1.59–1.57 (1H, m), 1.51–1.48 (1H, m). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.1, 170.4, 140.8, 137.7, 135.8, 128.63, 128.60, 127.7, 126.5, 69.3, 53.4, 53.0, 51.6, 51.5, 49.5, 48.0. IR (thin film): 3035, 2958, 1780, 1206, 1088 cm^{-1}. TLC (13:1 hexanes/EtOAc): R_f = 0.35. HRMS (ESI, ion trap) Calcd for $C_{17}H_{18}O_4$ ($[M + NH_4]^+$): 304.1549. Found: 304.1543.

*Dimethyl-3-(3-chlorophenyl)bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate (**3-endo**).* The title compound was prepared according to general procedure A using dimethyl-2-(3-chlorobenzylidene) malonate **2** (3.67 g, 14.4 mmol), cyclopentadiene (6.04 mL, 72.0 mmol), and $TiCl_4$ (0.79 mL, 7.2 mmol) affording **3-*endo*** (1.59 g, 5.0 mmol, 34%, 13:1 *endo*/*exo*) as a pale yellow solid that was stored in the freezer. Analytical data for **3-*endo***: mp 69–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15–7.08 (3H, m), 7.01–6.98 (1H, m), 6.73–6.71 (1H, m), 6.28–6.26 (1H, m), 4.39 (1H, d, J = 3.2 Hz), 3.76 (3H, s), 3.44–3.43 (1H, m), 3.16 (3H, s), 3.02 (1H, s), 1.56–1.54 (1H, m), 1.49–1.47 (1H, m). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.9, 170.1, 143.1, 138.1, 135.4, 133.6, 128.9, 128.9, 126.7, 126.6, 69.2, 53.1, 53.0, 51.7, 51.6, 49.4, 48.0. IR (thin film): 2958, 1730, 1205, 1081, 834 cm^{-1}. TLC (13:1 hexanes/EtOAc): R_f = 0.35. HRMS (ESI, ion trap) Calcd for $C_{17}H_{17}ClO_4$ ($[M + NH_4]^+$): 338.1159. Found: 338.1144.

Preparation of Dimethyl-3-phenylbicyclo[2.2.1]heptane-2,2-dicarboxylate (4). A flame-dried 10 mL round-bottomed flask equipped with a magnetic stir bar was charged with 10% Pd/C (0.057 g). To the flask was added degassed ethanol (4 mL) and dimethyl-3-phenylbicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate, **1** (0.573 g, 2.0 mmol). The reaction vessel was purged with H_2 (3 times) and then put under 1 atm of H_2 (balloon). The reaction mixture was stirred for 24 h, filtered through Celite with diethyl ether (Et_2O), then concentrated *in vacuo* providing **4** as a colorless oil without need for further purification (0.489 g, 85%, 9:1 *endo*/*exo*). Analytical data for **4**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.24 (2H, m), 7.21–7.15 (3H, m), 4.03–4.02 (1H, d, J = 3.6 Hz), 3.76 (3H, s), 3.32 (3H, s), 2.98–2.97 (1H, m), 2.55 (1H, m), 2.17–2.14 (1H, m), 1.78–1.73 (1H, m), 1.64–1.58 (2H, m), 1.46–1.38 (2H, m). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.7, 169.9, 139.3, 128.5, 127.5, 125.7, 63.6, 52.7, 51.3, 51.3, 45.5, 42.3, 38.4, 23.8, 22.1. IR (thin film): 2958, 2889, 1730, 1498, 1206, 1081 cm^{-1}. TLC (13:1 hexanes/EtOAc): R_f = 0.35. HRMS (ESI, ion trap) Calcd for $C_{17}H_{20}O_4$ ($[M + NH_4]^+$): 306.1705. Found: 306.1705.

General Procedure B for the Epimerization of Norbornenes (1-*exo*, 3-*exo*, 4). A flame-dried round-bottomed flask equipped with a magnetic stir bar was charged with norbornene (1.0 equiv) and DCM (0.05 M). $TiCl_4$ (0.1 equiv) was added; the reaction was stirred overnight and then was filtered through silica gel with Et_2O, concentrated *in vacuo*, and purified by flash chromatography using 2% EtOAc/hexanes ($KMNO_4$). Further purification was carried out via preparative HPLC using 5% isopropanol/hexanes to provide the *exo*-norbornene products. Due to the difficulty in separating the *endo* and *exo* isomers, isolated yields are low and ^{1}H NMR yields are provided using mesitylene as an internal standard.

*Dimethyl-3-phenylbicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate (**1-exo**).* The title compound was prepared according to general procedure B using dimethyl-3-phenylbicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate, **1-*endo***, (0.286 g, 1.0 mmol) and $TiCl_4$ (0.01 mL, 0.1 mmol), providing **1** (75% ^{1}H NMR yield, 1:14 *endo*/*exo* ratio) and dimethyl-2-benzylidene malonate (19% ^{1}H NMR yield). Flash chromatography followed by preparative HPLC provided **1-*exo*** as a colorless oil (0.036 g, 0.13 mmol, 13%). Analytical data for **1-*exo***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.22 (4H, m), 7.18–7.15 (1H, m), 6.53–6.51 (1H, m), 6.07–6.05 (1H, m), 3.77 (1H, m), 3.72 (3H, s), 3.41 (1H, bs), 3.05 (4H, br s), 2.64–2.62 (1H, d, J = 9.2 Hz), 1.81–1.78 (1H, m). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.8, 171.0, 142.5, 140.0, 135.0, 128.7, 127.8, 126.5, 66.3, 52.6, 51.7, 51.5, 50.1, 48.1, 46.7. IR (thin film): 3012, 2958, 1780, 1206, 1120, 1058 cm^{-1}. TLC (13:1 hexanes/EtOAc): R_f = 0.35. HRMS (ESI, ion trap) Calcd for $C_{17}H_{18}O_4$ ($[M + NH_4]^+$): 304.1549. Found: 304.1545.

*Methyl-3-(3-chlorophenyl)-2-((methylperoxy)-l2-methyl)bicyclo-[2.2.1]hept-5-ene-2-carboxylate (**3-exo**).* The title compound was prepared according to general procedure B using dimethyl-3-(3-chlorophenyl)bicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate, **3-*endo*** (0.321 g, 1.0 mmol), and $TiCl_4$ (0.01 mL, 0.1 mmol), providing **3** (81% ^{1}H NMR yield, 1:10 *endo*/*exo* ratio) and dimethyl-2-(3-chlorobenzylidene) malonate **2** (14% ^{1}H NMR yield). Flash chromatography followed by preparative HPLC provided **3-*exo*** as a colorless oil (6.7 mg, 0.02 mmol, 2%). Analytical data for **3-*exo***. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.26 (2H, m), 7.18–7.17 (2H, m), 6.52–6.50 (1H, m), 6.08–6.06 (1H, m), 3.73 (3H, s), 3.42 (1H, bs), 3.05 (1H, s), 3.15 (3H, s), 2.58–2.56 (1H, d, J = 8.8 Hz), 1.82–1.79 (1H, m). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.6, 170.8, 142.29, 142.25, 135.2, 133.7, 129.04, 128.99, 126.7, 66.3, 52.7, 51.9, 51.2, 50.2, 48.1, 46.5. IR (thin film): 3059, 2989, 2309, 1730, 1429, 1267, 896 cm^{-1}. TLC (13:1 hexanes/EtOAc): R_f = 0.35. HRMS (ESI, ion trap) Calcd for $C_{17}H_{17}ClO_4$ ($[M + NH_4]^+$): 338.1159. Found: 338.1127.

*Dimethyl-3-phenylbicyclo[2.2.1]heptane-2,2-dicarboxylate (**4**).* The title compound was subjected to the conditions in general procedure B using dimethyl-3-phenylbicyclo[2.2.1]heptane-2,2-dicarboxylate **4** (0.215 g, 0.75 mmol) and $TiCl_4$ (0.75 mL, 0.075 mmol of a 0.1 M solution of $TiCl_4$ in DCM). Epimerization was not observed.

Procedure C To Determine the Rate of Epimerization of 1-*endo*. A 50 mL flame-dried round-bottomed flask equipped with a magnetic stir bar was charged with dimethyl-3-phenylbicyclo[2.2.1]-hept-5-ene-2,2-dicarboxylate (**1-*endo***, 0.286 g, 1.0 mmol, 1.0 equiv) and DCM (20 mL, 0.05 M). To this solution was added $TiCl_4$ (1.0

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mL, 0.2 mmol, of a 0.1 M solution of $TiCl_4$ in DCM). At indicated time points, a 1.0 mL aliquot was taken from the reaction mixture and filtered through silica gel with Et_2O. ^1H NMR analysis was utilized for each sample to determine the *endo*/*exo* ratio.

Procedure D To Determine the Epimerization Mechanism as Retro-[4 + 2]/[4 + 2]. A 50 mL flame-dried round-bottomed flask equipped with a magnetic stir bar was charged with dimethyl-3-phenylbicyclo[2.2.1]hept-5-ene-2,2-dicarboxylate (**1-*endo***, 0.286 g, 1.0 mmol, 1.0 equiv), DCM (20 mL, 0.05 M), and dimethyl-2-(3-chlorobenzylidene) malonate **2** (1.273 g, 5.0 mmol, 5.0 equiv). $TiCl_4$ (0.02 mL, 0.2 mmol, 0.2 equiv) was then added to this solution. At indicated time points, a 1 mL aliquot was taken from the reaction mixture and filtered through silica gel with Et_2O. ^1H NMR analysis was utilized for each sample to determine the ratio of **1** to **3**.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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