Direct Stereodivergent Olefination of Carbonyl Compounds with Sulfur Ylides

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ABSTRACT: The reactivity of phosphorus and sulfur ylides toward carbonyl compounds constitutes a well-known dichotomy that is a common educational device in organic chemistry—the former gives olefins, while the latter gives epoxides. Herein, we report a stereodivergent carbonyl olefination that challenges this dichotomy, showcasing thiouronium ylides as valuable olefination reagents. With this method, aldehydes are converted to Z-alkenes with high stereoselectivity and broad substrate scope, while N-tosylimines provide a similarly proficient entry to E-alkenes. In-depth computational and experimental studies clarified the mechanistic details of this unusual reactivity.

INTRODUCTION

Alkenes are among the most prevalent functional groups in natural products and industrial chemicals, with one cheminformatics study estimating that 40% of the former contain an alkene.1 As such, the development of olefination methods has been a central and rewarding challenge to organic chemistry,2 contributing some of the most valued reactions in the “synthetic toolbox”.3 Nevertheless, the wide structural and electronic parameters of olefin chemical space continue to pose a challenge, implying that no single method is universally apt for their synthesis. As a result, the development of complementary olefination methods remains an active area of research.

The Wittig olefination is part of a mechanistic dichotomy that is a common educational device in organic chemistry.4 It is generally accepted to proceed by the addition of a phosphorus ylide to an aldehyde or ketone to give an oxaphosphetane, which then undergoes cycloreversion to produce an alkene and a phosphine oxide (Figure 1A).6,7 The major thermodynamic driving force for this reaction is known to be the strength of the resulting phosphorus–oxygen double-bond.8 Notably, the reaction of a sulfur-ylide—the Corey–Chaykovsky reaction—follows a different pathway, involving an intermediate betaine and resulting in the formation of an epoxide by displacement of the sulfonium group (Figure 1A).8−10 This textbook difference in reactivity is attributed to the lower oxophilicity of sulfur, the better leaving-group ability of the sulfonium group, and kinetic factors.5,11,12 The sulfur–phosphorus ylide dichotomy is therefore commonly used in chemical education to convey the concepts of
leaving group ability, oxophilicity, as well as kinetic/thermodynamic reaction control.16

Our group’s long-standing interest in novel olefination methods13,14 and sulfur ylide reactivity15 led us to interrogate the universality of the phosphorus/sulfur ylide dichotomy in organic chemistry. Herein, we report a novel carbonyl olefination method relying on thiouronium ylides, which challenges this dichotomy (Figure 1B). This method selectively affords Z-alkenes from aldehydes and E-alkenes from N-tosylimines, typically in greater than 20:1 selectivity, while exhibiting broad substrate scope, making it suitable for late-stage functionalization.

## RESULTS AND DISCUSSION

Our group recently reported the reaction of thiouronium salts with alcohols to afford thioethers without requiring the use of thiol reactants.16 The formation of a stable urea (C=O) in exchange for a less stable thiourea (C=S) derivative was identified as a plausible thermodynamic driving force of the reaction.17

By analogy, we surmised that the reaction of thiouronium ylides with carbonyl compounds might also be thermodynamically biased toward the formation of a urea byproduct and thus favor an olefination pathway, in a manner akin to the Wittig reaction. These considerations, along with the potential tunability of reactivity that is offered by thiouronium salts (by modulation of their N-substituents), prompted us to investigate them as olefination reagents.

Between 1976 and 1978, Burgess and co-workers described syntheses of thiouronium compounds and a preliminary assessment of their reactivity with aldehydes.18 Interestingly, the authors reported the formation of both epoxide and olefin products, as typified by the reaction of 1 with benzaldehyde to give methyl cinnamate (2a) and 3 in a 1:1 ratio (Figure 2A). This precedent provided initial support for our hypotheses and a starting point for our investigations.18a

**Figure 2. Revisiting Burgess’ observations in carbonyl olefination with thiouronium ylides.**

First, we examined the reaction of 1 with 2-naphthaldehyde and benzaldehyde. While we did observe the formation of alkenes (2) with low E/Z selectivity, no epoxide products were detected under a range of different reaction conditions (Figure 2B and the Supporting Information (SI)). Instead, we found that episulfide 4 was the major byproduct of the reaction, prompting us to consider the possibility that 3 had been misassigned by Burgess and co-workers.18a Unfortunately, characterization data for the compound 3 was not reported by Burgess, and we can only speculate that the true identity of originally described epoxide 3 was that of its episulfide congener 4. With proof of principle in hand, we sought to optimize this reaction to improve its stereoselectivity and yield, as well as to suppress the formation of the episulfide byproduct.

Early in our investigations, we found that the solubility of bromide 1 was poor in ethereal solvents, preventing us from investigating strong bases at cryogenic temperatures. We later found that solubility could be increased by exchanging the bromide counterion for bistriﬂumide (N(Tf2)), and thiouronium 5a thus became the starting point for optimization. First, we examined the influence of the base on the reaction outcome, noting that olefin 2b was produced in moderate to high yield (55−93%, Table 1, entries 1−4, and SI) with several bases stronger than triethylamine, including DBU, LDA, and Barton’s base (BMTG). Unfortunately, the stereoselectivity observed with thiouronium 5a was poor even at low temperature, and we decided to explore modulation of the reagent structure. To this end, we treated reagent 5a, carrying bulkier N-substituents, with BMTG in the presence of 2-naphthaldehyde. Pleasingly, a marked increase in stereoselectivity was observed. In the case of reagent 5c, Z-alkene 2b was delivered as the single detectable isomer in 92% yield when 1.2 eq of BMTG was deployed.

These optimized conditions for Z-selective olefination were then applied to a broad range of substrates (Figure 3, 2c). Aromatic and heteroaromatic aldehydes performed well, delivering a range of substituted acrylates (2a and c−i) in high yield and >20:1 stereoselectivity, which compared favorably with the bench-mark Still–Gennari protocol (Z/E 2.5:1−11.5:1), as did several other examples—see color coding in Figure 3. Ferrocenecarboxaldehyde was also found to be a competent substrate (2j). Aliphatic aldehydes performed well, being cleanly converted to the respective Z-alkenes—again with typically high stereoselectivity. Among these substrates...
were notable chiral pool building blocks N-Boc-D-phenylalaninal, citronellal and (R)-glyceraldehyde acetonide. Importantly, no racemization of the sensitive chiral center of N-Boc-D-phenylalaninal took place and 2n was formed with 99% ee (100% ee). Next, we extended the scope of aliphatic aldehydes to enals, which were found to react with similarly high yields and selectivities, including important monoterpene perillaldehyde (giving 2u).

We then sought to validate this Z-selective olefination on complex bioactive scaffolds. A derivative of hypertension drug losartan was found to smoothly undergo olefination to give 2v in >20:1 stereoselectivity. Pleasingly, even spiramycin, a large macrolide antibiotic bearing unprotected alcohols, tertiary amines, a 1,3-diene, and glycosides, could be converted into the desired Z-acrylate 2w in 61% yield, showcasing the synthetic potential of this olefination.

Regarding the thiouronium reactant, modification of the ester group was well-tolerated, and synthetically useful tert-butyl, ethylene-TMS, and benzyl esters were installed (2x, 2y, and 2z) in essentially identical yield and selectivity compared to the model methyl ester 2b. Additionally, gram-scale synthesis of 2b proceeded with near identical efficiency (88%).

Having established that thiouronium ylides can indeed be competent olefination reagents, we sought to probe how general this divergence from canonical S-ylide reactivity was. N-Tosylimines are known to react with sulfur ylides to give N-tosylaziridines, in analogy to the Corey-Chaykovsky epoxidation.8−10,19 We surmised that thiouronium ions might also contradict this reactivity paradigm.

Preliminary investigations of the reactivity of 1 with N-tosylimines indeed showed a clear bias toward olefination.20 Interestingly, the E-olefin was formed preferentially, presenting the possibility of developing a general method for divergent access to both olefin geometries. We optimized the reaction for E-stereoselectivity, finding the sterically unencumbered thiouronium bromide 1 to be ideal and the reaction to proceed smoothly at −40 °C.

We then examined the substrate scope of the reaction, focusing initially on the imine component (Figure 4). Treatment of a range of N-tosylimines with 1.1 equiv of 1 and 1.2 equiv of Barton’s base delivered the respective olefins as single stereoisomers in good to excellent yields (6a−6p, 2a).

![Figure 3. Substrate scope of the Z-selective olefination of aldehydes; reaction conditions: aldehyde (0.2 mmol), thiouronium salt (0.22 mmol), BMTG (0.24 mmol) at −78 °C in THF (1.0 M) for 2 h;1 Still−Gennari Z/E ratios given from two separate literature reports;2 Still−Gennari reaction executed in-house—see the SI refs to all other Still−Gennari data;3 combined yield by 1H NMR.](https://pubs.acs.org/jacs/2022/144/12538)

- **Figure 3.** Substrate scope of the Z-selective olefination of aldehydes; reaction conditions: aldehyde (0.2 mmol), thiouronium salt (0.22 mmol), BMTG (0.24 mmol) at −78 °C in THF (1.0 M) for 2 h;1 Still−Gennari Z/E ratios given from two separate literature reports;2 Still−Gennari reaction executed in-house—see the SI refs to all other Still−Gennari data;3 combined yield by 1H NMR.
substituents—all delivering the products in moderate to high yield, in greater than 20:1 selectivity in all cases but one (6p).

At this stage we sought to shed light on the mechanisms at play. In the early work of Burgess, a quasi-Wittig reaction mechanism involving oxasulfetane 7 was proposed (Figure 5A). However, we deemed the presence of such an intermediate unlikely due to the necessary production of thiourea S-oxide 8, which was never observed in our investigations. Instead, we persistently observed urea by-products, alongside elemental sulfur and in some cases episulfide 4b (Figure 5B). This led us to consider episulfide 4b as an intermediate en route to the olefin 2b, and indeed, we observed the stereospecific formation of olefin 2b when diastereomerically pure episulfide 4b was treated with DBU or BTMG. With these experimental observations in mind, we initiated an in-depth computational study to interrogate the precise mechanism of the olefination reactions.

Density functional theory (DFT) calculations were performed at the PBE0-D3BJ/def2-TZVP,SMD//PBE0-D3BJ/def2-SVP,SMD level of theory (see the SI for details and discussion). The mechanisms for the formation of products syn-4a and anti-4a were calculated for the coupling of the in situ generated thiouronium ylide 9 with benzaldehyde (Figure 6a) and N-tosyl imine 10 with thiouronium ylide 11 (Figure 6b).
The Gibbs free energy profile for the reaction with benzaldehyde (Figure 6) shows an irreversible (3 + 2)-cycloaddition-type transition state (TSAld-Z-AB), with simultaneous C−S bond cleavage to give a diastereomeric pair of acyclic intermediates (trans, Ald-Z-B or cis, Ald-E-B). From both of these structures, an SN2-type attack of the sulfi de breaks the C−O bond, forming the urea and leading to the corresponding episulfides Ald-Z-C, via TSAld-Z-BC (profile in blue, major), and Ald-E-C via TSAld-E-BC (profile in gray, minor). The lower activation barrier for the formation of the major episulfide, Ald-Z-C (ΔG‡(Ald-A*→Ald-Z-B) = 17.3 kcal mol⁻¹) while

\[ \Delta G^\ddagger(Ald-A^* \rightarrow Ald-E-B) = 21.2 \text{ kcal mol}^{-1} \]

strongly suggests that the reaction is kinetically controlled. Energy decomposition analysis revealed that a greater steric clash in TSAld-E-BC compared with TSAld-Z-BC accounts for this kinetic selectivity (see the SI for details). Unlike the case of aldehyde olefi nation, episulfide formation of N-tosylimine 10 with 11 (Figure 6B) is a stepwise process. This fi rst entails C−C bond formation via an acyclic transition state (TSTsI-E-AB or TSTsI-Z-AB), yet again generating two possible epimeric pathways (steps Tsi-A*-→Tsi-E-B in the pro fi le in blue and Tsi-A*-→Tsi-Z-B in the pro fi le in gray).

Nucleophilic attack of the tosyl amide at the thiouronium moiety of Tsi-E-B or Tsi-Z-B leads to C−N bond formation, producing discrete thiazolidines Tsi-E-C and Tsi-Z-C via TSTsI-E-CD and TSTsI-Z-CD, respectively. Thiazolidine intermediates Tsi-E-C and Tsi-Z-C readily ring open by C−S bond

Figure 6. Energy profi les of the C−C coupling of ylide 9 with benzaldehyde (A), and 11 and tosyl imine 10 (B) for the two possible epimers: cis-episulfide or trans-episulfide. Favored profi le shown in blue and disfavored shown in gray. Relative Gibbs free energies are presented in kcal mol⁻¹ (298 K). The separated reactants (Ald/Tsi-A*) serve as a reference (0.0 kcal mol⁻¹). Calculations were performed at the PBE0-D3BJ/def2-TZVP,SMD//PBE0-D3BJ/def2-SVP,SMD level of theory (see the SI for details and discussion).
cleavage, forming the intermediates Tsi-E-E and Tsi-Z-Z, respectively. Similarly to the scenario described in Figure 6A, the last step is an $S_2$-type attack, which cleaves the C–N bond and yields the episulfides with inversion of the configuration. Therefore, in contrast to the reaction with the aldehyde electrophile, the bulkiness of the N-tosylimine promotes a stepwise mechanism toward formation of the experimentally observed trans-episulphide Tsi-E-E, which is both thermodynamically and kinetically favorable.

The observed selective formation of Z-olefin from the cis-episulfide and E-olefin from the trans-episulfide (Figure 5 and the SI) indicated that the sulfur extrusion mechanism is stereospecific. Our calculations were consistent with this observation, showing that excision of a sulfur atom from either episulfide anti-4a or syn-4a by BTMG to selectively yield the corresponding olefin was thermodynamically feasible under the reaction conditions (Figure 7 and the SI). Together with the formation of an olefin, the BTMG-sulfur adduct 14 would then be generated. The initial stoichiometry of BTMG is 1.2 equiv, of which 1 equiv is required to form the thiouronium ylide. Given that only 0.2 equiv of base would remain, desulfurization evidently did not require stoichiometric base, and we sought to interrogate if BTMG could be regenerated in a pseudocatalytic process. As such, the pathway for base regeneration was also studied (Figure 7), considering the experimentally observed formation of elemental sulfur.

The obtained Gibbs free energy profile showed that nucleophilic attack on the episulfide was kinetically more favorable when performed by the BTMG-sulfur adduct 14 [ΔG° ($\text{growth phase, first step}$) = 13.3 kcal mol$^{-1}$] than by BTMG alone [ΔG° = 19.5 kcal mol$^{-1}$]. This suggested that the formation of BTMG-sulfur adduct 14 served as an initiation step and that ensuing sulfur extrusion steps would form a BTMG-polysulfide adduct through iterative S–S bond formation (termed the growth phase, Figure 7). Our calculations showed that early termination of the growth phase through release of $S_2$ was kinetically and thermodynamically unfavorable. Instead, termination of the growth phase by release of $S_2$ from BTMG-octasulfide adduct 15 was shown to be a favorable pathway to BTMG regeneration.

**CONCLUSION**

In summary, we have developed a stereodivergent olefination method based on thiouronium ylides. This selective transformation, suitable for complex molecule synthesis and late-stage functionalization, challenges the canonical reactivity of S-ylides toward carbonyl derivatives. In-depth computational studies revealed that selective episulfide generation is at the heart of the olefination process, while clarifying the role of the base in a domino sulfur extrusion event. While enhancing the "synthetic toolbox" for carbonyl olefination, we believe this work adds a subtle new layer to the textbook phosphorus/sulfur ylide dichotomy.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c05637.

Discussions of general information, reaction optimization, mechanistic studies, computational studies, Cartesian coordinates, preparation of substrates, Z-selective olefination of aldehydes, E-selective olefination of N-tosylimines, and limitations, tables of preliminary investigations, and figures of NMR study, energy profiles, Newman representation, results of SAPT analysis, 3D and schematic representations of geometry, direct Gibbs free energy comparison, and NMR spectra (PDF)

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Notes
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REFERENCES
(1) Ertl, P.; Schuhmann, T. A Systematic Chemoinformatics Analysis of Functional Groups Occurring in Natural Products. J. Nat. Prod. 2019, 82 (5), 1258−1263.
(2) The Nobel Prize in Chemistry 1979. https://www.nobelprize.org/prizes/chemistry/1979/summary/ (accessed 2021-05-09).
(3) a) Wittig, G.; Grisar, G. Zur Reaktionsweise Des Pentaphenyloxydiphenylamidophosphors Und Einiger Derivate. Justus Liebigs Ann. Chem. 1953, 580 (1), 44−57. (b) Peterson, D. J. Carbonyl Olefination Reaction Using Silyl-Substituted Organometallic Compounds. J. Org. Chem. 1968, 33 (2), 780−784. (c) Baudin, J.; Hareau, G.; Julia, S.; Ruel, O. A Direct Synthesis of Olefins by Reaction of Carbonyl Compounds with Lithio Derivatives of 2-Alkyl- or (2-Alkyl)- or Benzyl-Sulfonyl]-Benzothiazoles. Tetrahedron Lett. 1991, 32 (9), 1175−1178. (d) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. Olefin Homologation with Titanium Methylene Compounds. J. Am. Chem. Soc. 1978, 100 (11), 3611−3613. (e) Horner, L.; Hoffmann, H.; Wippel, H. G. Phosphororganische Verbindungen, XII. Phosphosine als Olefinierungsreagenzien. Chem. Ber. 1958, 91 (1), 61−63. (f) Wadsworth, W. S.; Bersons, W. G. The Utility of Phosphonate Carbanions in Olefin Synthesis. J. Am. Chem. Soc. 1961, 83 (7), 1733−1738. (g) Julia, M.; Paris, J.-M. Syntheses a l’aide de Sulfones v(+) - Methode de Synthese Generale de Doubles Liaisons. Tetrahedron Lett. 1973, 14 (49), 4833−4836. (h) Kocienski, P. J.; Lythgoe, H.; Rustom, S. Scope and Stereochemistry of an Olefin Synthesis from β-Hydroxysulphones. J. Chem. Soc. Perkin 1 1978, No. 8, 829−834. (i) Takeda, T. Modern carbonyl olefination; Wiley-VCH: Weinheim, 2004. (j) Normant, J. F.; Alexakis, A. Carbomethylation (C-Methylation) of Alkenes: Stereo-specific Synthesis of Alkenyl Derivatives. Synthesis 1981, 1981 (11), 841−870. (k) Müller, D. S.; Marek, I. Copper Mediated Carbomethylation Reactions. Chem. Soc. Rev. 2016, 45 (16), 4552−4566. (l) Flynn, A. B.; Ogilvie, W. W. Stereocontrolled Synthesis of Tetrasubstituted Olefins. Chem. Rev. 2007, 107 (11), 4698−4745. (m) Chakraborty, S.; Basu, K.; Saha, C. Distinction between the Reactivity of Phosphorus Ylide vs. Sulfur Ylide with the Carbonyl Group: A First Principle and Quantum Mechanical Study. J. Am. Chem. Soc. 2013, 135 (19), 7312−7323. (n) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. Asymmetric Ylide Reactions: Epoxidation, Cyclopropanation, Aziridination, Olefination, and Rearrangement. Chem. Rev. 1997, 97 (6), 2341−2372. (o) Volatron, F.; Eisenstein, O. Theoretical Study of the Reactivity of Phosphonium and Sulfinium Ylides with Carbonyl Groups. J. Am. Chem. Soc. 1984, 106 (20), 6117−6119. (p) Aggarwal, V. K.; Harvey, J. N.; Robiette, R. On the Importance of Leaving Group Ability in Reactions of Ammonium, Oxonium, Phosphonium, and Sulfinium Ylides. Angew. Chem., Int. Ed. 2005, 44 (34), 5468−5471. (q) Niyomchon, S.; Oppedissano, A.; Allard, P.; Maulide, N. A Three-Membered Ring Approach to Carbonyl Olefination. Nat. Commun. 2017, 8 (1), 1091. (r) Neuhau, J. D.; Bauer, A.; Pinto, A.; Maulide, N. A Catalytic Cross-Olefination of Diazoc Compounds with Sulfoxonium Ylides. Angew. Chem., Int. Ed. 2018, 57 (49), 16215−16218. (s) a) Huang, X.; Goddard, R.; Maulide, N. A Direct Ylide Transfer to Carbonyl Derivatives and Heteroaromatic Compounds. Angew. Chem., Int. Ed. 2010, 49 (47), 8979−8983. (b) Huang, X.; Patil, M.; Fares, C.; Thiel, W.; Maulide, N. Sulfur(IV)-Mediated Transformations: From Ylide Transfer to Metal-Free Auration of Carbonyl Compounds. J. Am. Chem. Soc. 2013, 135 (19), 7312−7323. (c) Huang, X.; Peng, B.; Luparia, M.; Gomes, L. F. R.; Veiros, L. F.; Maulide, N. Gold-Catalyzed Synthesis of Furans and Furanones from Sulfur Ylides. Angew. Chem., Int. Ed. 2012, 51 (35), 8886−8890. (d) Kaiser, D.; Klose, I.; Oost, R.; Neuhaus, J.; Maulide, N. Bond-Forming and -Breaking Reactions at Sulfur(IV): Sulfoxides, Sulfinium Salts, Sulfur Ylides, and Sulfinate Salts. Chem. Rev. 2019, 119 (14), 8701−8780. (e) Klimczyk, S.; Misale, A.; Huang, X.; Maulide, N. Dimeric TADDOL Phosphoramidites in Asymmetric Catalysis: Domino Deracemization and Cyclopropanation of Sulfinium Ylides. Angew. Chem., Int. Ed. 2015, 54 (35), 10365−10369. (f) Klose, I.; Misale, A.; Maulide, N. Synthesis and Photocatalytic Catalysis of Vinylsulfonium Ylides. J. Org. Chem. 2016, 81 (16), 7201−7210. (g) Neuhau, J. D.; Oost, R.; Merad, J.; Maulide, N. Sulfur-Based Ylides in Transition-Metal-Catalysed Processes. Top. Curr. Chem. 2018, 376 (3), 15. (h) Neuhau, J. D.; Oost, R.; Merad, J.; Maulide, N. Sulfur-Based Ylides in Transition-Metal-Catalysed Processes. In Sulfur Chemistry; Jiang, X., Ed.; Topics in Current Chemistry Collections; Springer International Publishing: Cham, 2019; pp 429−475: (i) Neuhau, J. D.; Angyal, P.; Oost, R.; Maulide, N. (3 + 2) Cycloadditions of Thioironium Ylides: A Room-Temperature, One-Pot Approach to Dihydrothiophenes. J. Org. Chem. 2018, 83 (4), 2479−2485. (j) Oost, R.; Neuhaus, J. D.; Merad, J.; Maulide, N. Sulfur Ylides in Organic Synthesis and Transition Metal Catalysis. In Modern Ylide Chemistry: Applications in Ligand Design, Organic and Catalytic Transformations; Gesner, V. H., Ed.; Structure and Bonding; Springer International Publishing: Cham, 2018; pp 73−115. (k) Sabbatani, J.; Huang, X.; Veiros, L. F.; Maulide, N. Gold-Catalyzed Intermolecular Synthesis of Alkylideneacyclop propane through Catalytic Allene Activation. Chem. Eur. J. 2014, 20 (34), 10636−10639.
(16) Merad, J.; Matyášovský, J.; Stopka, T.; Bruitt, B. R.; Pinto, A.; Drescher, M.; Maulide, N. Stable and Easily Available Sulfide Surrogates Allow a Stereoselective Activation of Alcohols. Chem. Sci. 2021, 12, 7770.
(17) The instability of various thiocarbonyl compounds in comparison to their oxo-analogues is well-documented, see: Hadad, C. M.; Rablen, P. R.; Wiberg, K. B. C−O and C−S Bonds: Stability, Bond Dissociation Energies, and Resonance Stabilization. J. Org. Chem. 1998, 63 (24), 8668−8681.
(18) a) Burgess, E. M.; Pulcran, M. C. Thione S-Methylides as Quasi-Wittig Reagents. J. Am. Chem. Soc. 1978, 100 (20), 6538−6539. (b) Ardengo, A. J.; Burgess, E. M. Syntheses and Reactions of Substituent Stabilized Thione Methylides. J. Am. Chem. Soc. 1976, 98 (16), 5020−5021. (c) Ardengo, A. J.; Burgess, E. M. Tricoordinate Hypervalent Sulfur Compounds. J. Am. Chem. Soc. 1977, 99 (7), 2376−2378. (d) Ardengo, A. J.; Burgess, E. M. The Structure of a Substituent Stabilized Thione Methylide. J. Am. Chem. Soc. 1976, 98 (16), 5021−5023. (e) Representative examples of Corey-Chaykovsky aziridination: (a) Degenarro, L.; Trinchera, P.; Luisi, R. Recent Advances in the
by Ring Expansion of 3-(Di-Tert-Butylmethylene)-Tetramethylcyclobutanone. J. Org. Chem. 1990, 55 (6), 1909–1915.