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Generation and Reactions of ε-Carbonyl Cations via Group 13 Catalysis

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Abstract: The generation of ε-carbonyl cations and their reactions with nucleophiles is accomplished readily without transition metal cation stabilization, using the ε-bromide dienoate or dienone starting materials and GaCl₃ or InCl₃ catalysis. Arene nucleophiles are somewhat more straightforward than allyltrimethylsilane, but allyltrimethylsilane and propiophenone trimethysilyl enol ether each react successfully with InCl₃ catalysis. The viability of these cations is supported by DFT calculations.

Keywords: ε-carbonyl cations; catalysis; umpolung; electrophilic aromatic substitution; allylation

1. Introduction

The reaction of electrophilic allyl and propargyl compounds with nucleophiles is a commonly used technique in organic chemistry. However, this chemistry becomes challenging when the system involves an electron-withdrawing group, such as a carbonyl. As a result, the generation and reaction of cations at the site γ- to a carbonyl or carbonyl equivalent (1 and 2) has seen only limited work, although it constitutes a fundamental form of umpolung chemistry (Figure 1). A modest but growing number of methods have been developed to obtain synthetic equivalents of these species. Propargyldicobalt [1] and allyliron [2] cations bearing electron withdrawing groups have been successfully generated and reacted with nucleophiles at the γ-site and are highly electrophilic. Activated cyclopropanes may serve as γ-carbonyl cation equivalents in the presence of Lewis acids, and they have close to the same level of electrophilicity [3]. Allylpalladiums and -iridiums bearing EWG’s are significantly less electrophilic but act catalytically and react well with stronger nucleophiles [4-6]. Methods giving an equivalent overall transformation, involving cationic species but not γ-carbonyl cations themselves, are known [9]. Nevertheless, methodology involving direct generation of γ-carbonyl cations without additional stabilization has remained elusive.

Figure 1. γ- and ε-carbonyl cations.

Research on vinylogous versions of γ-carbonyl cations, specifically on equivalents of ε-carbonyl cation equivalents (3), is still more scattered (Figure 2). The Green group has reported vinylogous Nicholas reactions involving compounds 4-5 to functionalize the site ε- to the carbonyl or carbonyl equivalent [10]. Activated vinylcyclopropanes (6) can, in principle, serve as ε-carbonyl cation equivalents, but Lewis acid mediated openings of these systems often favor reaction at the γ-site [3,11-13]. Transition metal mediated couplings are, in general, ε-selective, but again are only modestly electrophilic [14-21]. As a
consequence, there the is an absence of work on ε-carbonyl cations or their equivalents that features both catalysis and high electrophilicity. Furthermore, the existence of a number of natural products containing ε-arylated carbonyls indicates significant synthetic utility to any methods capable of accessing such cations [22–24]. Unlike the γ-carbonyl cations themselves, the further conjugation possible to ε-carbonyl potentially ameliorates the effect of the electron-withdrawing group. As a result, we considered it worth investigating whether the ε-carbonyl cations themselves (3) could be generated, and whether this would be amenable to Lewis acid catalysis.

![Figure 2](image-url)

**Figure 2.** Existing ε-carbonyl cation equivalent precursors.

### 2. Results

The viability of direct generation of ε-carbonyl cations was initially addressed computationally, using DFT calculations employing the B3LYP functional and 6-311++G(d,p) basis set. The allyl bromide (7) to allyl cation (7+) transformation was the benchmark with which to compare results, as the viability of experimentally verified allyl cation synthetic chemistry has been established, most notably with indium(III) and related catalysts [25–28]. Compared to this was ionization of 5-bromo-1,3-pentadiene (8a) to give pentadienyl cation (8a+), and the analogous ionizations of ethyl 6-bromosorbate (8b), 6-bromo-1-phenyl-2,4-butan-1-one (8c). In addition, the ethyl 4-bromocrotonate (9) to γ-carbonyl cation species 9+ transformation was included, as an example of a process that has proven difficult experimentally (Scheme 1, Table 1).

![Scheme 1](image-url)

**Scheme 1.** Allyl- and dienyl bromide ionization reactions.

**Table 1.** Ionization energies of select allyl- and dienyl bromides.

| Molecule | E Ionization (a.u.) | E Ionization (kcal/mol) | E (rel) (kcal/mol) |
|----------|---------------------|-------------------------|--------------------|
| 7-Br     | 0.7034              | 441.4                   | 0                  |
| 8a-Br    | 0.6766              | 424.6                   | −16.8              |
| 8b-Br    | 0.6861              | 430.5                   | −10.9              |
| 8c-Br    | 0.6832              | 428.7                   | −12.7              |
| 9-Br     | 0.7144              | 448.3                   | +6.9               |

1 Calculations at the B3LYP 6-311++G(d,p)+ ZPVE level, in CH2Cl2.

The results of the calculations were promising. The ionization energy of 8a to dienyl cation 8a+ was unsurprisingly the most favored, the process being 16.8 kcal/mol lower in energy than allyl cation generation. Somewhat to our surprise, the ionizations of the ε-carbonyl cation precursors 8b and 8c also were found to be favored substantially (by
10.9 kcal and 12.7 kcal, respectively), relative to the process with allyl bromide. Finally, the analogous ionization of ethyl 4-bromocrotonate was found to be 6.9 kcal/mol higher in energy than that of allyl bromide, consistent with the difficulty in discrete generation of γ-carbonyl cations. As a result of these findings, we chose to test these observations with an experiment. Given the notably mild conditions reported in the group 13 catalyzed electrophilic reactions of allyl bromides [25–28], we chose to pursue the analogous approach for ε-carbonyl cations.

The ester- and phenyl ketone-substituted dienyl bromides, 8b–8c, were chosen as substrates. Ethyl 6-bromohexadienoate (ethyl 6-bromosorbate, 8b) was obtained by literature radical bromination of ethyl sorbate [29]. Phenyl ketone 8c was prepared from 1-phenyl-2,4-butadienone [30], by HG-II-induced cross metathesis with allyl bromide (Scheme 2) [31].

![Scheme 2. Preparation of phenyl ketone 8c.](image1)

In addition, a third substrate chosen for the study was 10, employing an aryl spacer rather than one of the alkene spacers between the ester and bromide. Compound 10 was prepared by the radical bromination of cinnamate ester derivative 11 (10, 77%) (Scheme 3), itself being prepared by the Wittig reaction of o-tolualdehyde [32].

![Scheme 3. Preparation of benzylic bromide 10.](image2)

Experimental work began with ethyl 6-bromohexadienoate (ethyl 6-bromosorbate, 8b). Test reactions were undertaken with mesitylene (5 equiv) as the nucleophile, and catalytic amounts (10 mol%) of Lewis acids CuCl, SnCl4, InCl3, GaCl3, and BiI3, in CH2Cl2 with 4 Å molecular sieves (Table 2, Scheme 4). CuCl and BiI3 afforded no product and minimal amounts of product, respectively. Conversely, GaCl3, InCl3, and SnCl4 gave more significant amounts of conversion to 12a over 24 h, although small amounts of starting material remained. Repetition of the reactions at reflux afforded complete starting material consumption, but also gave some polar decomposition byproduct. Ultimately, GaCl3 at room temperature proved to be the most successful Lewis acid, giving 12a in a 68% yield. Reducing the amount of GaCl3 to 5 mol% decreased the yield noticeably (47%), while an increase to 15 mol% made a negligible difference (67% yield). Omission of the 4 Å molecular sieves also gave a decrease in the yield of 12a (51%, 58% brsm).

![Scheme 4. Formation of 12a as a model reaction.](image3)
The characterization of 12a was most clearly defined from the $^1$H NMR spectrum, which revealed a doublet ($J = 15.4$ Hz) at 5.77 ppm (H$_a$), a doublet of doublets ($J = 15.4, 11.0$ Hz) at 7.30 ppm (H$_b$), a doublet of doublets ($J = 15.2, 11.0$ Hz) at 6.02 ppm (H$_y$), and doublet of triplets ($J = 15.2, 5.7$ Hz) at 6.23 ppm (H$_z$), indicative of the conjugated diene of (E, E)-geometry resulting from $\varepsilon$-substitution. A small amount (<5% of the mixture) of isomeric material was co-eluted with the main product. Most of the $^1$H NMR spectral resonances are obscured by the dominant isomer due to the similar $^1$H spectral features, but with the H$_y$ methylene observable as a doublet of doublets ($J = 7.4, 1.5$ Hz) at 3.65 ppm, and with the H$_z$ observable as a doublet of doublets ($J = 15.1, 11.6$ Hz) at 7.85 ppm, we have assigned this minor compound as the (2E, 4Z)-isomer of 12a.

These conditions were adopted for other arene nucleophiles, with the exception that the yields were found to be, in general, superior for other nucleophiles at reflux (Scheme 5, Table 3). p-Xylene, under analogous conditions, gave a modest yield of 12b at rt (33% yield, 54% brsm), but better yields (65%) at reflux. 1,3-Dimethoxybenzene gave 12c in 56% yield at reflux, while 1,3,5-trimethoxybenzene required 20 mol% GaCl$_3$ for complete conversion, giving 12d in 51% yield. Thiophene gave a 63% yield of product, as a 72:28 mixture C-2 (12e) and C-3 (12e') substitutions. With allyltrimethylsilane, no condensation product was observed with 10 mol% GaCl$_3$. Switching the catalyst to InCl$_3$ was much more successful; 10 mol% InCl$_3$ in CH$_2$Cl$_2$ at reflux gave approximately 80% conversion and 53% of 12f, while 20 mol% InCl$_3$ gave 12g in a 66% yield. Finally, the phenyl ketone 8c and mesitylene with GaCl$_3$ at reflux gave 12g in a 50% yield.

Table 2. Optimization of 12a formation.

| Entry | Lewis Acid | T      | Yield 12a (%) |
|-------|------------|--------|---------------|
| 1     | CuCl (10 mol%) | rt    | 0             |
| 2     | Bi$_3$ (10 mol%) | rt    | 11            |
| 3     | SnCl$_4$ (10 mol%) | rt    | 36            |
| 4     | SnCl$_4$ (10 mol%) | 40 $^\circ$C | 51            |
| 5     | InCl$_3$ (10 mol%) | rt    | 43            |
| 6     | InCl$_3$ (10 mol%) | 40 $^\circ$C | 53            |
| 7     | GaCl$_3$ (10 mol%) | rt    | 68            |
| 8     | GaCl$_3$ (10 mol%) | 40 $^\circ$C | 63            |
| 9     | GaCl$_3$ (5 mol%) |        | 47            |
| 10    | GaCl$_3$ (15 mol%) | rt    | 67            |
| 11    | GaCl$_3$ (10 mol%) | 1      | 51 (58 brsm)  |

1 Reaction conducted in the absence of 4 Å sieves. 2 brsm = based on recovered starting material.
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Results for reactions of 1,3-dimethoxybenzene (13).

Table 3. Results for condensation reactions of 8b, 8c.

| Entry | Substrate | Nucleophile | Catalyst (mol%) | Time (h) | Product | Yield (%) |
|-------|-----------|-------------|-----------------|----------|---------|-----------|
| 1     | 8b        | mesitylene 1 | GaCl₃, 10       | 26       | 12a     | 68        |
| 2     | 8b        | p-xylene 1   | GaCl₃, 10       | 24       | 12b     | 33 (54)²  |
| 3     | 8b        | 1,3-dimethoxybenzene | GaCl₃, 10 | 23   | 12b     | 65        |
| 4     | 8b        | 1,3,5-trimethoxybenzene | GaCl₃, 20  | 24   | 12d     | 51        |
| 5     | 8b        | thiophene    | GaCl₃, 10       | 23       | 12e/12e’ | 63 (72/28)³ |
| 6     | 8b        | allyltrimethylsilane | InCl₃, 10  | 24   | 12f     | 53        |
| 7     | 8b        | allyltrimethylsilane | InCl₃, 20  | 14   | 12f     | 66        |
| 8     | 8c        | mesitylene   | GaCl₃, 10       | 20       | 12g     | 50        |

¹ Reaction conducted at room temperature. ² Yield based on recovered SM. ³ 12:12’ ratio.

The benzylic bromide analogue, 10, also reacted under the optimized conditions, again at reflux (Scheme 6, Table 4). Mesitylene afforded 13a in a 73% yield, with no evidence of even trace amounts of isomeric products present. p-Xylene (13b, 76% yield), 1,3-dimethoxybenzene (13c, 77% yield), and 1,3,5-trimethoxybenzene (13d, 75% yield) behaved analogously. Thiophene worked well, again affording an isomeric mixture of C-2 and C-3 substitution products (13e and 13e’, 92% yield, 13e:13e’ = 71:29). The aromatic nucleophiles could be extended to benzene itself (13f, 72% yield), although a greater amount of GaCl₃ catalyst (30 mol%) was required.

![Scheme 6. Reactions of ε-bromo aryl alkenoate 10.](image)

Table 4. Results for reactions of 10.

| Entry | Substrate | Nucleophile | Catalyst (mol%) | Time (h) | Product | Yield (%) |
|-------|-----------|-------------|-----------------|----------|---------|-----------|
| 1     | 10        | mesitylene  | GaCl₃, 10       | 24       | 13a     | 73        |
| 2     | 10        | p-xylene  | GaCl₃, 10       | 21       | 13b     | 76        |
| 3     | 10        | 1,3-diethoxybenzene | GaCl₃, 10  | 22   | 13c     | 77        |
| 4     | 10        | 1,3,5-trimethoxybenzene | GaCl₃, 20  | 22   | 13d     | 75        |
| 5     | 10        | thiophene   | GaCl₃, 10       | 20       | 13e/13e’ | 92 (71/29)¹ |
| 6     | 10        | benzene     | GaCl₃, 30       | 30       | 13f     | 72        |
| 7     | 10        | allyltrimethylsilane | GaCl₃, 10  | 24   | 13g     | 0         |
| 8     | 10        | allyltrimethylsilane | GaCl₃, 50  | 24   | 13g     | 46        |
| 9     | 10        | Allyltrimethylsilane ² | InCl₃, 10 | 24   | 13g     | 29        |
| 10    | 10        | Allyltrimethylsilane ² | InCl₃, 20 | 19   | 13g     | 64 (78)²  |
| 11    | 10        | propiophenone TMS enol ether ³ | InCl₃, 20 | 15   | 13h     | 82        |

¹ 13:13’ ratio. ² Yield based on recovered SM. ³ Reaction conducted in CH₂Cl₂ at reflux.
The reaction with allyltrimethylsilane was again more difficult than for arene nucleophiles with GaCl₃ catalysis. In this case, while 10 mol% GaCl₃ showed no significant conversion, 50 mol% GaCl₃ gave a 46% yield of 13g. InCl₃ again proved to be a superior catalyst with allyltrimethylsilane; 10 mol% of InCl₃ afforded a 29% yield of 13g, while raising the catalyst amount to 20 mol% InCl₃ gave 13g in 64% (78% brsm). Finally, a switch to higher temperature reaction conditions (1,2-dichloroethane, reflux) demonstrated that propiophenone trimethylsilyl enol ether was also amenable to reaction with 10 (13h, 82% yield) with the use of InCl₃ as the catalyst.

3. Discussion

An analysis of the results suggests several issues worth discussing. First of all, despite the unmanageable superficial appearance of ε-carbonyl cations, they are quite viable. Transition metal stabilization of the cationic dienyl (or enynyl) unit is not mandatory. The use of dienyl bromides and Ga(III) or In(III) catalysts is capable of generating ε-carbonyl cations that react with nucleophiles in moderate yields with 8b–c, and in good yields with 10. The reactions require somewhat more vigorous conditions than with allyl bromide itself, and we attribute this to the presence of the Lewis basic carbonyl functions in the substrates, and in some cases, the reacting nucleophiles. Arene nucleophiles react with greater facility than allylsilanes using GaCl₃, although conditions can normally be found using InCl₃ that give synthetically useful yields of 12f and 13g. InCl₃ also allows the successful reaction of an enol silane (13h). The successful incorporation of benzene as a nucleophile (13f) indicates that the current protocol can allow incorporation of less reactive nucleophiles than the Nicholas reaction-based ε-carbonyl cation equivalents [10] and far less reactive nucleophiles than the analogous transition metal catalyzed equivalents [14–21]. The question of competitive conjugate addition does not appear problematic with the arene, allylsilane, or enol silane nucleophiles. For example, the crude reaction product of 8b and allyltrimethylsilane showed no evidence of conjugate addition byproducts. Conversely, trial reactions with triethylsilane, a substantially stronger nucleophile than arenes or allyltrimethylsilane [33], appeared to give mixtures whose 1H NMR spectra included multiple aliphatic resonances, suggesting the conjugate addition may be a major reaction pathway there.

4. Materials and Methods

The starting materials and reagents involved in the reactions were purchased from commercial sources, unless otherwise noted. GaCl₃ and InCl₃ were stored under an inert atmosphere prior to use. Purification of synthesized products was conducted by either column chromatography (using SilaFlash® P60, 230–400 mesh, SiliCycle, Quebec City, QC, Canada), preparative TLC (SiliaPlate, 1000 µm thickness, SiliCycle, Quebec City, QC, Canada) or radial chromatography (Silica gel, 2000 µm thickness, EM Science, Gibbstown, NJ, USA). Analytical thin layer chromatography (TLC) was performed using Silicycle aluminum-backed sheets (SiliCycle, Quebec City, QC, Canada). Dichloromethane and tetrahydrofuran solvents (Sigma-Aldrich Canada, Milton, ON, Canada) were obtained from a solvent purification system. All of the reactions were performed under an atmosphere of nitrogen unless otherwise stated. Prior to reaction, all glassware was dried in an oven at 110 °C for a minimum of one hour and subsequently cooled in a desiccator. Reactions conducted at greater than 25 °C were conducted in a heated oil bath.

All of the NMR spectral analyses were conducted on 300 MHz and 500 MHz spectrometers (Bruker Canada, Milton, ON, Canada) at room temperature in solutions of CDCl₃ (CIL, Andover, MA, USA). The residual CHCl₃ peak was set to 7.27 ppm and 77.0 ppm for the 1H NMR and 13C NMR spectra, respectively. 1H NMR spectral data are listed with units of ppm for peak position (δ) and Hz for coupling constant (J). The following symbols were used for peak appearance: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; q, quartet; m, multiplet. The 1H and 13C NMR spectra are available in the Supplementary Materials. The IR analysis was conducted on an ATR infrared (FTIR)
spectrometer (Bruker Canada, Milton, ON, Canada). For IR spectra listed in the characterization of compounds and the absorption peaks with the greatest functional group relevance are reported in wavenumbers (cm⁻¹). High resolution mass spectrometry results were obtained by direct insertion probe on a Waters Xevo G2-MS Time-of-Flight Mass Spectrometer (Waters, Toronto, ON, Canada) in ASAP(+) mode at the University of Windsor Mass Spectrometry lab. The computational calculations were conducted with Gaussian 0.9 and B3LYP/6-31+G(d,p) to optimize the structures studied, both with and without solvation in dichloromethane. Final coordinates are available in the Supplementary Materials.

4.1. 6-Bromo-1-phenyl-2,4-hexadiene (8c)

A procedure for synthesis of similar compounds had previously been reported,[31] so this procedure was adapted to use on 1-phenyl-2,4-hexadiene. To a solution of 1-phenyl-2,4-hexadiene (0.2287 g, 1.33 mmol) and allyl bromide (0.56 mL, 6.6 mmol, 5 equiv.) in dichloromethane (40 mL) were added to the Hoveyda-Grubbs II catalyst (0.021 g, 0.034 mmol, 2.5 mol%). After stirring under N₂ for 24 h, another portion of Hoveyda Grubbs II catalyst (0.021 g, 0.034 mmol, 2.5 mol%) was added. After 48 h total, the solvent was evaporated under reduced pressure and the product was subjected to flash chromatography (5:1 PE:EtO) to yield 8c as a yellow solid (0.0902 g, 68%). 

4.2. Methyl 3-[2-(Bromomethyl)phenyl]acrylate (10)

Bromination was conducted with methods derived from those described by Snead[34]. Methyl 3-(2-methylphenyl)acrylate 11 (1.1761 g, 4.2 mmol) and N-bromosuccinimide (1.6947 g, 9.522 mmol) were heated to reflux in chloroform (35 mL). Once at reflux, benzoyl peroxide (0.1670 g, 0.6894 mmol) was added. The reaction was stirred at reflux for 22 h after the reagents were added. This afforded the product was also made by methods outlined below in General Procedure 1, where the solvent was evaporated under reduced pressure and the product was subjected to flash chromatography (5:1 PE:EtO) to yield 8c as a yellow solid (0.0982 g, 29%).

4.3. Ethyl 6-(2,4,6-Trimethylphenyl)-2,4-hexadienoate (12a)

To a suspension of GaCl₃ (0.009 g, 0.05 mmol, 10 mol%) and 4Å molecular sieves (ca. 0.4 g), CH₂Cl₂ (6 mL) was added to mesitylene (0.37 mL, 2.67 mmol, 5 equiv.) and 8b (0.1161 g, 0.5299 mmol) at room temperature. The reaction was stirred under N₂ and monitored by TLC for 26 h. Following removal of volatiles under reduced pressure and flash chromatography (10:1 PE:EtO), 12a (0.0902 g, 68%) was isolated as a yellow oil. This compound was also made by methods outlined below in General Procedure 1, where the reaction was brought to reflux for 22 h after the reagents were added. This afforded the product 12a in a 63% yield. 

4.4. 12a product was obtained. The mp was 84.5–85.5°C. 1H NMR (300 MHz, CDCl₃) δ 7.95 (d, J = 8.7 Hz, 2H), 7.58 (apparent t, J = 7.4 Hz, 1H), 7.49 (apparent t, J = 7.6 Hz, 2H), 7.39 (dd, J = 15.1, 11.0 Hz, 1H), 7.02 (d, J = 15.1 Hz, 1H), 6.53 (dd, J = 15.0 Hz, 11.0 Hz, 1H), 6.36 (m, 1H), and 4.07 (d, J = 7.7 Hz, 2H); 13C NMR (125 MHz, CDCl₃) δ 190.2, 142.5, 137.8, 132.9, 132.6, 128.6, 128.4, 127.0, and 31.3; the HRMS m/e for C₁₂H₁₁BrO calculated (M + 1)+ 251.0072, found 251.0068.

4.5. Ethyl 6-(2,4,6-Trimethylphenyl)-2,4-hexadienoate (12a)

To a suspension of GaCl₃ (0.009 g, 0.05 mmol, 10 mol%) and 4Å molecular sieves (ca. 0.4 g), CH₂Cl₂ (6 mL) was added to mesitylene (0.37 mL, 2.67 mmol, 5 equiv.) and 8b (0.1161 g, 0.5299 mmol) at room temperature. The reaction was stirred under N₂ and monitored by TLC for 26 h. Following removal of volatiles under reduced pressure and flash chromatography (10:1 PE:EtO), 12a (0.0902 g, 68%) was isolated as a yellow oil. This compound was also made by methods outlined below in General Procedure 1, where the reaction was brought to reflux for 22 h after the reagents were added. This afforded the product 12a in a 63% yield. 

4.6. 12a product was obtained. The mp was 84.5–85.5°C. 1H NMR (300 MHz, CDCl₃) δ 7.95 (d, J = 8.7 Hz, 2H), 7.58 (apparent t, J = 7.4 Hz, 1H), 7.49 (apparent t, J = 7.6 Hz, 2H), 7.39 (dd, J = 15.1, 11.0 Hz, 1H), 7.02 (d, J = 15.1 Hz, 1H), 6.53 (dd, J = 15.0 Hz, 11.0 Hz, 1H), 6.36 (m, 1H), and 4.07 (d, J = 7.7 Hz, 2H); 13C NMR (125 MHz, CDCl₃) δ 190.2, 142.5, 137.8, 132.9, 132.6, 128.6, 128.4, 127.0, and 31.3; the HRMS m/e for C₁₂H₁₁BrO calculated (M + 1)+ 251.0072, found 251.0068.
4.4. Ethyl 6-(2,5-Dimethylphenyl)-2,4-hexadienoate (12b)

**General Procedure 1.** To a suspension of GaCl₃ (0.004 g, 0.02 mmol, 10 mol%) and 4Å molecular sieves (ca. 0.4 g), CH₂Cl₂ (6 mL) was added to para-xylene (0.14 mL, 1.1 mmol, 5 equiv.) and 8b (0.048 g, 0.22 mmol) at room temperature. The mixture was heated to reflux, stirred under N₂ and monitored by TLC for 23 h. Following removal of volatiles under reduced pressure and flash chromatography (5:1 PE:Et₂O), 12b (0.0349 g, 65%) was isolated as a yellow oil. This compound was also prepared where the reaction was stirred at room temperature for 23 h, and the yield of product 12b was 34%. IR (neat) 2979, 2925, 1710, 1640, 1131, 1000, and 810 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.29 (dd, J = 15.3 Hz, 10.5 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 6.96 (m, 2H), 6.26 (dt, J = 15.3 Hz, 6.0 Hz, 1H), 6.12 (dd, J = 15.9 Hz, 10.5 Hz, 1H), 5.80 (d, J = 15.0 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.46 (d, J = 6.3 Hz, 2H), 2.31 (s, 3H), 2.24 (s, 3H), and 1.29 (t, J = 6.9 Hz, 3H); ₁³C NMR (75 MHz, CDCl₃) δ 167.0, 144.4, 141.6, 136.5, 135.4, 132.9, 130.0, 129.8, 128.9, 127.1, 119.7, 60.0, 36.6, 20.7, 18.7, and 14.1; the HRMS m/e for C₁₆H₂₀O₂ calculated (M + 1)+ 245.1550, and found 245.1539.

4.5. Ethyl 6-(2,4,4'-Dimethoxyphenyl)-2,4-hexadienoate (12c)

General Procedure 1 was carried out with GaCl₃ (0.005 g, 0.030 mmol, 10 mol%), 1,3-dimethoxybenzene (0.20 mL, 1.5 mmol, 5 equiv.) and 8b (0.0653 g, 0.298 mmol). The reaction was monitored by TLC for 23 h under reflux and N₂, and after purification by flash chromatography (3:1 PE:Et₂O), 12c (0.0460 g, 56%) was isolated as a yellow oil. IR (neat) 2935, 2837, 1708, 1207, 1155, 1132, and 1035 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.28 (dd, J = 10.8 Hz, 5.1 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.50 (m, 2H), 6.21 (m, 2H), 5.78 (d, J = 15.3 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.80 (s, 6H), 3.42 (d, J = 6.6 Hz, 2H), and 1.29 (t, J = 6.9 Hz, 3H); ₁³C NMR (75 MHz, CDCl₃) δ 167.1, 159.5, 157.9, 144.8, 142.6, 129.9, 128.4, 119.3, 103.8, 98.4, 59.9, 55.2, 32.8, and 14.1; the HRMS m/e for C₁₆H₂₀O₄ calculated (M + 1)+ 277.1440, and found 277.1440.

4.6. Ethyl 6-(2,4,6-Trimesoxyphenyl)-2,4-hexadienoate (12d)

General Procedure 1 was carried out with GaCl₃ (0.010 g, 0.057 mmol, 20 mol%), 1,3,5-trimesoxybenzene (0.2521 g, 1.499 mmol, 5 equiv.) and 8b (0.0629 g, 0.287 mmol). The reaction was monitored by TLC for 24 h under reflux and N₂, and after purification by flash chromatography (3:1 PE:Et₂O), 12d (0.0446 g, 51%) was isolated as a beige solid, and the mp was 69–70.5 °C. IR (neat) 2941, 2837, 1697, 1595, and 1149 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.25 (dd, J = 15.3 Hz, 11.0 Hz, 1H), 6.22 (dt, J = 15.1, 6.4 Hz, 1H), 6.15 (s, 2H), 6.10 (m, 2H), 5.74 (d, J = 15.3 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 6H), 3.43 (d, J = 6.4 Hz, 2H), and 1.27 (t, J = 7.2 Hz, 3H); ₁³C NMR (75 MHz, CDCl₃) δ 167.3, 159.8, 158.7, 145.5, 143.2, 127.6, 118.8, 107.6, 90.6, 60.0, 55.7, 55.3, 26.1, and 14.3; the HRMS m/e for C₁₇H₂₀O₅ calculated (M + 1)+ 307.1654, and found 307.1539.

4.7. Ethyl 6-(2-Thienyl)-2,4-hexadienoate (12e) and Ethyl 6-(3-Thienyl)-2,4-hexadienoate (12e′)

General Procedure 1 was carried out with GaCl₃ (0.004 g, 0.02 mmol, 10 mol%), thiophene (0.17 mL, 2.1 mmol, 10 equiv.) and 8b (0.0476 g, 0.217 mmol). The reaction was monitored by TLC for 23 h under reflux and N₂, and after purification by flash chromatography (4:1 PE:Et₂O), an 12e/12e′ mixture (0.0306 g, 63%) was isolated as a yellow oil. The product contained a 72:28 12e:12e′ based on ¹H NMR spectral integration of the resonances at 3.70 ppm (12e), and 3.52 ppm (12e′) corresponding to the hydrogen atoms bonded to the sp² carbon adjacent to the thiophene, but these two compounds were not able to be separated. IR (neat) 2980, 2934, 1707, 1253, and 1131 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.25–7.34 (m, 1H), 7.18 (d, J = 5.1 Hz, 1H), 6.96 (dd, 5.1, 3.5 Hz, 1H), 6.83 (m, 1H), 6.19–6.31 (m, 2H), 5.86 (d, J = 15.0 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.70 (d, J = 5.7 Hz, 2H), and 1.30 (t, J = 7.2 Hz, 3H). Resonances from minor product 12e′ were observed at: δ 6.98 (m, 1H), 6.93 (dd, J = 4.9, 1.2 Hz, 1H), 5.83 (d, J = 15.3 Hz, 1H), and 3.52 (d, J = 5.4 Hz, 2H); ₁³C NMR (125 MHz, CDCl₃) δ 167.0, 144.0, 141.3, 140.6, 129.5, 127.0, 125.8, 125.1, 124.0, 120.8, 60.3, 33.1, and 14.3. Resonances from minor product 12e′ were
observed at: $\delta$ 167.1, 144.3, 139.0, 129.3, 128.1, 125.8, 121.2, 120.3, 60.2, and 33.7; the HRMS m/e for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{S}$ calculated (M + 1)$^+$ 223.0793, and found 223.0797.

4.8. Ethyl 2,4,6-Nonanitroate (12f)

A mixture of InCl$_3$ (0.0127 g, 20 mol%), 4Å molecular sieves, 8b (0.0633 g, 0.289 mmol) and allyltirimethylsilane (0.23 mL, 5 equiv) in CH$_2$Cl$_2$ (7 mL) were heated to reflux under N$_2$ for 14 h. Following a conventional workup, preparative TLC (7:5:1 hexanes: Et$_2$O) afforded 12f (0.0343 g, 66%) as a faintly tan oil. IR (neat) $\nu$$_\text{max}$ 2980, 2928, 1712, 1253, 1136, and 998 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.25 (dd, $\text{J}$ = 15.4 Hz, 10.5 Hz, 1H), 6.19 (d of $\frac{1}{2}$ AB, $\text{J}$ = 10.5, 15.2 Hz, 1H), 6.11 (t of $\frac{1}{2}$ AB, $\text{J}$ = 6.5, 15.2 Hz, 1H), 5.73–5.84 (m, 2H), 5.03 (dd, $\text{J}$ = 17.1, 1.6 Hz, 1H), 4.99 (dd, $\text{J}$ = 10.2, 1.6 Hz, 1H), 4.19 (q, $\text{J}$ = 7.2 Hz, 2H), 2.27 (m, 2H), 2.19 (m, 2H), and 1.28 (t, $\text{J}$ = 7.2 Hz, 3H). Resonances from the minor (2E, 4Z) isomer can be observed at 6.89 (dd, $\text{J}$ = 15.7, 7.5 Hz, 1H), 5.73 (m, 1H), 5.10 (d, $\text{J}$ = 10.3 Hz, 1H), and 4.18 (obscured q, $\text{J}$ = 7.1 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.2, 144.8, 143.3, 137.4, 128.7, 119.5, 115.3, 60.1, 32.7, 32.2, and 14.3; the HRMS m/e for $\text{C}_{12}\text{H}_{16}\text{O}_2$ calculated (M + 1)$^+$ 181.1228, and found 181.1228.

4.9. 6-(2,4,6-Trimethylphenyl)-1-phenyl-2,4-hexadiene (12g)

To a suspension of GaCl$_3$ (0.003 g, 0.02 mmol, 10 mol%), and 4Å molecular sieves (ca. 0.4 g), CH$_2$Cl$_2$ (6 mL) was added to mesitylene (0.12 mL, 0.86 mmol, 5 equiv.) and 8c (0.0438 g, 0.17 mmol) at room temperature. The reaction was heated to reflux, stirred under N$_2$ and monitored by TLC for 20 h. Following the removal of volatiles under reduced pressure and flash chromatography (10:1 PE:Et$_2$O), 12g (0.0251 g, 50%) was isolated as a yellow oil. IR (neat) $\nu$$_\text{max}$ 3000, 2917, 2851, 1587, 1000, 693 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.92 (d, $\text{J}$ = 7.2 Hz, 2H), 7.55 (m, 1H), 7.36–7.50 (m, 3H), 6.90 (s, 2H), 6.83 (d, $\text{J}$ = 15.0 Hz, 1H), 6.37 (dt, $\text{J}$ = 15.0 Hz, 5.7 Hz, 1H), 6.10 (dd, $\text{J}$ = 15.0 Hz, 11.1 Hz, 1H), 3.54 (d, $\text{J}$ = 5.1 Hz, 2H), 2.30 (s, 3H), and 2.27 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 190.8, 144.9, 143.0, 138.2, 136.5, 135.9, 132.5, 131.9, 129.0, 128.9, 128.5, 128.3, 124.0, 32.8, 20.9, and 19.8; the HRMS m/e for $\text{C}_{21}\text{H}_{22}O$ calculated (M + 1)$^+$ 291.1745, and found 291.1745.

4.10. Methyl 3-[2-(2,4,6-Trimethylbenzyl)phenyl]acrylate (13a)

General procedure 2. To a suspension of GaCl$_3$ (0.004 g, 0.02 mmol, 10 mol%), and 4Å molecular sieves (ca. 0.4 g), CH$_2$Cl$_2$ (6 mL) was added to mesitylene (0.15 mL, 5 equiv.) and 10 (0.0532 g, 0.210 mmol) at room temperature. The reaction was heated to reflux, stirred under N$_2$ and monitored by TLC for 24 h. Following removal of volatiles under reduced pressure and chromatography (5:1 PE:Et$_2$O), 13a (0.0449 g, 73%) was obtained as a beige solid; mp was 81.5–83.0 °C. IR (neat) $\nu$$_\text{max}$ 3050, 2969, 2948, 2915, 1713, 1164, 982, and 760 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 (d, $\text{J}$ = 15.6 Hz, 1H), 7.59 (dd, $\text{J}$ = 6.9 Hz, 2.1 Hz, 1H), 7.14–7.23 (m, 2H), 6.93 (s, 2H), 6.60 (d, $\text{J}$ = 7.8 Hz, 1H), 6.44 (d, $\text{J}$ = 15.9 Hz, 1H), 4.10 (s, 2H), 3.86 (s, 3H), 3.43 (m, 2H), and 2.15 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.4, 142.2, 139.1, 137.2, 135.9, 133.4, 132.7, 130.3, 128.9, 127.2, 126.5, 126.3, 119.5, 51.7, 31.8, 20.9, and 19.9; the HRMS m/e for $\text{C}_{20}\text{H}_{23}O_2$ calculated (M + 1)$^+$ 295.1698, and found 295.1699.

4.11. Methyl 3-[2-(2,5-Dimethylbenzyl)phenyl]acrylate (13b)

General procedure 2 was carried out with GaCl$_3$ (0.004 g, 0.02 mmol, 10 mol%), para-xylene (0.13 mL, 5 equiv.) and 10 (0.0540 g, 0.213 mmol). The reaction was monitored by TLC for 21 h under reflux and N$_2$, and after evaporation under reduced pressure and purification by flash chromatography (5:1 PE:Et$_2$O), 13b (0.0452 g, 76%) was obtained as a faintly yellow solid; mp was 51.0–53.0 °C. IR (neat) $\nu$$_\text{max}$ 3015, 2949, 2923, 2892, 1714, 1172, 1015, 977, and 765 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.03 (d, $\text{J}$ = 15.9 Hz, 1H), 7.61 (dd, $\text{J}$ = 7.5 Hz, 1.5 Hz, 1H), 7.24–7.32 (m, 2H), 7.10 (d, $\text{J}$ = 7.8 Hz, 1H), 6.98 (m, 2H), 6.75 (s, 1H), 6.38 (d, $\text{J}$ = 15.9 Hz, 1H), 4.07 (s, 2H), 3.81 (s, 3H), 2.26 (s, 3H), and 2.23 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 167.3, 142.4, 139.8, 137.7, 135.5, 133.5, 133.3, 130.4, 130.13, 130.11, 129.9,
127.2, 126.7, 126.6, 119.5, 51.7, 36.2, 21.0, and 19.1; the HRMS m/e for C_{19}H_{22}O_{2} calculated (M + 1)^+ 281.1541, and found 281.1544.

4.12. Methyl 3-[2-(2,4-Dimethoxybenzyl)phenyl]acrylate (13c)

General procedure 2 was carried out with GaCl₃ (0.003 g, 0.02 mmol, 10 mol%), 1,3-dimethoxybenzene (0.11 mL, 0.84 mmol, 5 equiv.) and 10 (0.0445 g, 0.175 mmol). The reaction was monitored by TLC for 22 h under reflux and N₂, and after evaporation under reduced pressure and purification by flash chromatography (4:1 PE:Et₂O), 13c (0.0423 g, 77%) was isolated as a light yellow viscous oil. IR (neat) λ_max 2934, 2878, 2837, 1716, 1241, 1114, and 1036 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.11 (d, J = 15.9 Hz, 1H), 7.58 (dd, J = 7.5 Hz, 1.2 Hz, 1H), 7.20–7.34 (m, 2H), 7.17 (dd, J = 6.0 Hz, 1.2 Hz, 1H), 6.81 (d, J = 8.3 Hz, 1H), 6.48 (d, J = 2.4 Hz, 1H), 6.38 (dd, J = 8.3, 2.4 Hz, 2H), 6.36 (d, J = 15.9 Hz, 1H), 4.03 (s, 2H), 3.83 (s, 3H), 3.80 (s, 3H), and 3.79 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 159.5, 157.9, 142.9, 140.7, 133.5, 130.6, 130.3, 130.0, 126.5, 126.4, 121.0, 119.0, 104.0, 98.4, 55.3, 51.6, and 32.1; the HRMS m/e for C_{19}H_{20}O_{4} calculated (M + 1)^+ 313.1440, and found 313.1441.

4.13. Methyl 3-[2-(2,4,6-Trimethoxybenzyl)phenyl]acrylate (13d)

General procedure 2 was carried out with GaCl₃ (0.004 g, 0.02 mmol, 10 mol%), 1,3,5-trimethoxybenzene (0.1907 g, 1.134 mmol, 5 equiv.) and 10 (0.0547 g, 0.215 mmol). The reaction was monitored by TLC for 22 h under reflux and N₂, and after evaporation under reduced pressure and purification by flash chromatography (5:1 PE:Et₂O), 13d (0.0552 g, 75%) was obtained as a colorless solid; the mp was 84–85 °C. IR (neat) λ_max 2949, 2839, 1702, 1118, 949, and 764 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.43 (d, J = 15.9 Hz, 1H), 7.53 (dd, J = 7.5 Hz, 1.2 Hz, 1H), 7.14–7.25 (m, 2H), 7.11 (m, 1H), 6.37 (d, J = 15.9 Hz, 1H), 6.17 (s, 2H), 4.06 (s, 2H), 3.84 (s, 3H), 3.83 (s, 3H), and 3.77 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.7, 159.9, 158.9, 143.8, 141.6, 133.1, 129.7, 129.3, 126.1, 125.8, 124.6, 118.4, 109.0, 90.5, 55.1, 55.3, 51.5, and 25.5; the HRMS m/e for C_{20}H_{25}O_{5} calculated (M + 1)^+ 343.1545, and found 343.1547.

4.14. Methyl 3-[2-(2-Methylthienyl)phenyl]acrylate (13e) and Methyl 3-[2-(3-methylthienyl)phenyl]acrylate (13e')

General procedure 2 was carried out with GaCl₃ (0.003 g, 0.02 mmol, 10 mol%), thiophene (0.075 mL, 0.94 mmol, 5 equiv.) and 10 (0.0465 g, 0.183 mmol). The reaction was monitored by TLC for 20 h under reflux and N₂, and after purification by flash chromatography (5:1 PE:Et₂O), the 13e/13e' mixture (0.0437 g, 92% combined) was found as a light yellow oil. Based on ¹H NMR integration of the hydrogen atoms bonded to the sp³ carbon adjacent to the thiophene group (4.27 ppm for 13e and 4.10 ppm for 13e'), the product is an inseparable mixture of 13e:13e' in a ratio of 71:29. IR (neat) λ_max 2949, 1711, 1170, 977, 763, 731, and 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, J = 15.6 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.28 (m, 3H), 7.12 (d, J = 5.1 Hz, 1H), 6.88 (m, 1H), 6.72 (d, J = 3.0 Hz, 1H), 6.34 (d, J = 15.9 Hz, 1H), 4.27 (s, 2H), and 3.78 (s, 2H). Most resonances from minor product 13e' were superimposed on those from 13e, but the following resonances from 13e were clearly observed: δ 6.83 (s, 1H), and 4.10 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 167.1, 143.0, 141.9, 139.5, 133.1, 130.3, 130.2, 127.2, 126.8, 126.7, 125.1, 124.0, 119.6, 51.6, and 33.3. Some resonances from minor product 13e' were superimposed on those from 13e but the following resonances from 13e' were clearly observed: δ 142.2, 139.8, 133.2, 130.4, 130.1, 128.0, 126.9, 126.6, 125.7, 125.2, 121.4, 119.3, and 33.8; the HRMS m/e for C_{15}H_{13}O_{2}S calculated (M + 1)^+ 259.0793, and found 259.0801.

4.15. Methyl 3-[2-Benzylphenyl]acrylate (13f)

General procedure 2 was carried out with GaCl₃ (0.0107 g, 0.061 mmol, 30 mol%), benzene (0.25 mL, 14 equiv.) and 10 (0.0518 g, 0.204 mmol). The reaction was monitored by TLC for 30 h under reflux and N₂, and following a conventional (CH₂Cl₂) extractive workup and purification by preparative TLC (7:1 PE:Et₂O), 13f (0.0367 g, 72%) was obtained as a faintly tan oil. IR (neat) λ_max 3062, 3026, 2950, 1714, 1172, 1634, and 1599 cm⁻¹; ¹H
NMR (300 MHz, CDCl₃) δ 8.06, (d, J = 15.8 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.10–7.40 (m, 8H), 6.36 (d, J = 15.8 Hz, 1H), 4.16 (s, 2H), and 3.80 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 142.4, 140.14, 140.05, 133.5, 130.8, 130.1, 128.7, 128.5, 126.9, 126.7, 126.2, 119.4, 51.6, and 38.9; MS m/e 252 (M⁺).

4.16. Methyl 3-[2-(3-Butenyl)phenyl]acrylate (13g)

To a suspension of InCl₃ (0.008 g, 0.04 mmol, 20 mol%) and 4Å molecular sieves (ca. 0.4 g), CH₂Cl₂ (6 mL) was added to allyltrimethylsilane (0.15 mL, 0.94 mmol, 5 equiv.) and 10 (0.0455 g, 0.179 mmol) at room temperature. The reaction was heated to reflux, stirred under N₂ and monitored by TLC for 19 h. Following removal of volatiles under reduced pressure and purification by flash chromatography (5:1 PE:Et₂O), 13g was isolated as a light beige oil (0.0246 g, 64%, 78% BRMS). Continued elution afforded starting 10 (0.0083 g, 18%) in subsequent fractions.

IR (neat) λmax 3066, 2948, 1715, 1169, 979, and 763 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.03 (d, J = 15.9 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.32 (m, 1H), 7.18-7.27 (m, 2H), 6.38 (d, J = 15.9 Hz, 1H), 5.87 (m, 1H), 4.97–5.11 (m, 2H), 3.83 (s, 3H), 2.86 (dd, J = 9.7, 6.0 Hz, 2H), and 2.34 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 167.4, 142.3, 141.4, 137.4, 132.9, 130.0, 126.6, 126.5, 119.1, 115.4, 51.7, 35.4, and 32.7; the HRMS m/e for C₁₄H₁₆O₂ calculated (M + 1)⁺ 217.1228, and found 217.1230.

4.17. Methyl 3-(2-(2-Methyl-3-oxo-3-phenylpropylphenyl)acrylate (13h)

To a suspension of InCl₃ (0.0065 g, 0.029 mmol, 18 mol%) and 4Å molecular sieves (ca. 0.4 g) in 1,2-dichloroethane (5 mL) were added propiophenone trimethylsilyl enol ether (0.229 g, 1.11 mmol, 6.7 equiv.) and 10 (0.0422 g, 0.165 mmol) at room temperature. The reaction was heated to reflux, stirred under N₂ and monitored by TLC for 15 h. Following a conventional extractive (CH₂Cl₂) workup and purification by preparative TLC (3:1 hexane:Et₂O), 13h was isolated as a light beige oil (0.0420 g, 82%).

IR (neat) λmax 3061, 2950, 1717, 1681, 1632, and 1597 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.10 (d, J = 15.8 Hz, 1H), 7.88 (m, 2H), 7.55 (m, 2H), 7.45 (m, 2H), 7.17–7.31 (m, 3H), 6.40 (d, J = 15.8 Hz, 1H), 3.84 (s, 3H), 3.72 (m, 1H), 3.30 (dd, J = 14.0, 6.6 Hz, 1H), 3.17 (dd, J = 14.0, 7.8 Hz), and 1.19 (d, J = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 203.4, 167.2, 142.2, 139.4, 136.3, 133.3, 133.0, 131.2, 130.0, 128.7, 128.2, 127.0, 119.6, 51.7, 42.1, 36.6, and 17.3; MS m/e for C₁₄H₁₆O₂ calculated (M + 1)⁺ 217.1228, and found 217.1230.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27103078/s1. Copies of the ¹H NMR and ¹³C NMR spectra of all new compounds. Final coordinates for the computationally determined structures.

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