# A New Reaction for Organoselenium Compounds: Alkyl Transfer from Diorganoselenium(IV) Dibromides to Alkenoic Acids To Give γ- and δ-Lactones

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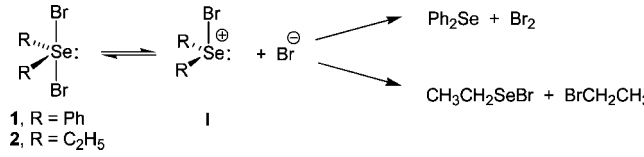
Various 1-[[bis(1-methylethyl)amino]carbonyl]-2-(dibromo-*n*-alkylseleno)ferrocene derivatives reacted with 2 equiv of 4-pentenoic acid or 5-hexenoic acid to give the corresponding γ- or δ-lactones, respectively, from transfer of the alkyl group bound to selenium to the terminal alkene carbon. In the lactone cyclization, 1-[[bis(1-methylethyl)amino]carbonyl]-2-(bromoselenenyl)ferrocene (**25**) is formed and reacts with a second equivalent of the alkenoic acid to give either 5-[1-[[bis(1-methylethyl)amino]carbonyl]ferrocene-2-selenenylmethyl]tetrahydro-2-furanone (**23**) or 6-[1-[[bis(1-methylethyl)amino]carbonyl]ferrocene-2-selenenylmethyl]tetrahydro-2*H*-pyran-2-one (**26**) as a mixture of diastereomers in yields comparable to the corresponding γ- or δ-lactone. The addition of 1-[[bis(1-methylethyl)amino]carbonyl]-2-(dibromo-*n*-butylseleno)ferrocene to 3-butenoic acid gave alkyl transfer to the internal alkene carbon and formation of the γ-lactone. Density functional theory (DFT) geometry optimizations were performed on several idealized *n*-alkyldibromselenoferrocene structures to examine the role of iron in the alkyl transfer and the role of various structural features on the alkyl carbon−selenium bond length. The results of the computations suggested that the ferrocenyl iron was not involved in the alkyl transfer reactions.

## Introduction

Although organoselenium compounds have found utility in a variety of synthetic transformations,[1] the chemistry of diorgano selenium(IV) dihalides remains largely undeveloped. Dibromodiphenylselenium (**1**, Scheme 1), upon heating over an open flame, gives a mixture of diphenyl selenide and bis(4-bromophenyl) selenide.[2] Similarly, heating **1** to 200 °C under a stream of $N_2$ gives melting, gas evolution, and a quantitative recovery of diphenylselenide.[3] The gas evolution associated with the heating of **1** is most likely the formation of bromine. Compound **1** is a brominating agent for a variety of organic substrates.[4] In contrast, heating dibromodialkylselenium or dibromoalkylarylselenium compounds leads to the corresponding bromoalkane and selenenyl bromide, as illustrated in Scheme 1 for the conversion of dibromodiethylselenium (**2**) to bromoethane and ethylselenenyl bromide.[5]

The reactions of both **1** and **2** involve the formation of the bromoselenonium ion (**I**) as an intermediate (Scheme 1). For reactions of **1**, intermediate **I** is the active brominating specie or nucleophilic attack by bromide can produce elemental bromine.[3,4,6] For reactions of **2**, nucleophilic attack of bromide on the alkyl carbon of bromoselenonium intermediate **I** leads to ethylselenenyl bromide and bromoethane.[5]

**Scheme 1**




Organoselenium trihalides also undergo reactions in which the selenium−halogen bond is broken. Tribromophenylselenium dissociates in solution to give a mixture of phenylselenenyl bromide and bromine.[7] Engman developed trichlorophenylselenium as a reagent for adding $Cl^-$ and $(PhSeCl_2)^+$ across olefins.[8]

In reactions of dibromodiorganoselenium compounds, relative rates of debromination and dealkylation have not been established. As described herein, we examined a series of dibromoalkylarylselenium compounds with 4-pentenoic acid in order to compare the ratio of bromination to dealkylation. This series also included several examples with a suitable substituent to act as an intramolecular ligand for Se(IV).[9]

Compound **1** illustrates the stability of the selenium(IV) derivatives with two electronegative bromide ligands. X-ray structures of **1** and related compounds reveal a trigonal bipyramidal geometry with the two phenyl substituents and the lone pair of electrons on selenium occupying the equatorial sites.[10] The two bromide ligands form a nearly linear array with the central Se(IV) with the distortion from linearity due to the

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(1) (a) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22–30. (b) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *39*, 3740–3749. (c) Uemura, S. *Phosphorus, Sulfur Silicon* **2005**, *180*, 721–728.

(2) Bradt, W. E.; Green, J. F. *J. Org. Chem.* **1937**, *1*, 540–543.

(3) Detty, M. R.; Friedman, A. E.; McMillan, M. *Organometallics* **1994**, *13*, 3338–3345.

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(9) Coles, M. P. *Curr. Org. Chem.* **2006**, *10*, 1993–2005.

(10) McCullough, J. D.; Hamburger, G. *J. Am. Chem. Soc.* **1941**, *63*, 803.

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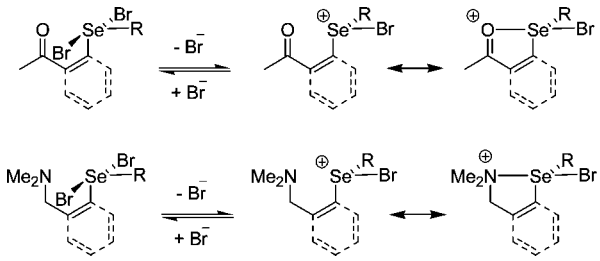
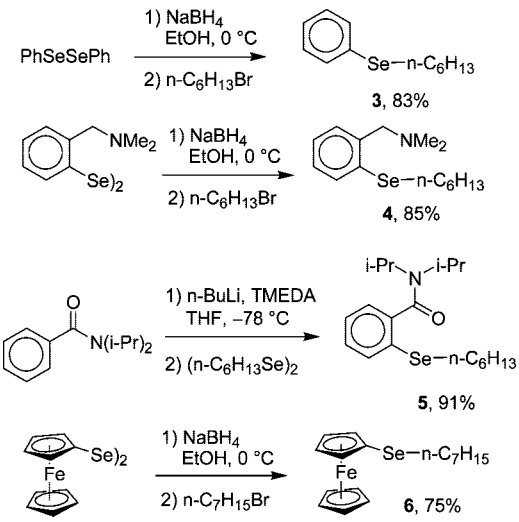
**Scheme 2**



**Scheme 3**



selenium lone pair, which is stereochemically active. The Br−Se−Br array is an example of so-called three-center, four-electron bonds, in which the two electronegative bromide ligands each donate a pair of electrons to an empty p-orbital on the central selenium atom.[11] The resulting Se−Br bonds are long and correspond to approximately 50% covalent character. In the bromoselenonium intermediate **I**, a suitably placed substituent can interact with the selenonium center to stabilize the intermediate via the formation of new three-center, four-electron bonds, as shown in Scheme 2.

In the series of dibromoalkylarylselenium compounds discussed here, dealkylation (formally reductive elimination of bromoalkane) was observed with no indication of competitive bromination. However, in one system, a new reaction for organo Se(IV) compounds was observed: a formal reductive elimination of alkyl bromide with transfer of primary alkyl groups from Se(IV) to 4-pentenoic acid and other alkenoic acids to form new carbon−carbon bonds in a series of $\gamma$- and $\delta$-lactones.

## Results and Discussion

**Synthesis of Organoselenium Compounds.** The selenides **3**−**6** were prepared as shown in Scheme 3. Reduction of diphenyl diselenide with sodium borohydride in ethanol followed by treatment of the resulting solution of sodium phenyl selenide with 1-bromohexane gave (*n*-hexylseleno)benzene (**3**)[12] in 83% isolated yield. Similarly, *N,N*-dimethyl-2-(*n*-hexylseleno)-benzenemethanamine (**4**) was prepared in 85% isolated yield by treating the corresponding diselenide[13] with sodium borohydride and 1-bromohexane. Directed metalation of *N,N*-bis(1-methylethyl)benzamide with *n*-butyllithium and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)[14] gave the ortho-lithiated benzamide derivative, which was quenched with di-*n*-hexyl diselenide to give *N,N*-bis(1-methylethyl)-2-(*n*-hexylseleno)benzamide **5** in 91% isolated yield. Diferrocenyl diselenide[15] was reduced with sodium borohydride in ethanol and the resulting solution of sodium ferrocenyl selenide was quenched with 1-bromoheptane to give (*n*-heptylseleno)ferrocene (**6**) in 75% isolated yield.

Organoselenides **7** were prepared as shown in Scheme 4. Directed metalation of [[bis(1-methylethyl)amino]carbonyl]ferrocene with *n*-butyllithium/TMEDA at −78 °C in ether gives 2-lithio-1-[bis(1-methylethyl)amino]carbonyl]ferrocene (**8**).[16,17] The anion **8** was quenched with dipropyl,[18] dibutyl,[19] dipentyl,[18] dihexyl,[19] diheptyl,[20] or diisopropyl[19] diselenide to give the corresponding selenides **7c**−**h** in 60−94% isolated yield. Alternatively, the anion **8** reacted with selenium powder in ether at ambient temperature to give diselenide **9** in 62% isolated yield following air oxidation of the intermediate selenide anion. The diselenide **9** was reduced with sodium borohydride and the resulting ferrocenyl selenide anion was quenched with iodomethane, iodoethane, 1-bromoheptane, or 2-bromopropane to give 1-[[bis(1-methylethyl)amino]carbonyl]-2-(alkylseleno)ferrocene derivatives **7a**, **7b**, **7f**, and **7g**, respectively, in 75−85% isolated yields, as indicated in Scheme 4.

The organoselenides **3**−**7** were our precursors to the corresponding Se(IV) dibromides **10**−**14** (Chart 1). Dibromides **10** and **13** have no competing intramolecular ligands for the Se(IV) and would be expected to form the symmetrical Br−Se−Br three-center, four-electron array. Selenium(IV) derivative **11** has the 2-dimethylaminomethyl substituent, which can compete as an intramolecular ligand.[9] If analogy to the corresponding Te(IV) and Se(IV) derivatives **15** and **16**, respectively, is appropriate (Chart 1),[3,4] then **11** is correctly written in the ionic form for oxidative addition of bromine. The X-ray crystal structure of **15** shows that the linear three-center, four-electron bond involves the N−Te−O array and that the bromide counterion is located to form a Br−Te···Br− interaction with a 90° angle.[3] Selenium(IV) compounds **12** and **14** have carboxamide substituents that can similarly compete as intramolecular ligands for Se(IV).[9]

The addition of 1 equiv of bromine to a solution of the organoselenides **3**−**7** gave a rapid color change from red to yellow. Attempts to isolate the selenium(IV) dibromides were unsuccessful. The products decomposed (lost bromine and/or bromoalkane) upon standing. The $^1$H NMR spectra of these materials displayed broadened peaks consistent with exchange processes. As a consequence, the Se(IV) derivatives were generated and used in situ in subsequent reactions. Our earlier work using stopped-flow spectroscopy indicated that the oxidative addition of bromine to organoselenides is rapid and is thermodynamically favored.[3]

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**Scheme 4**

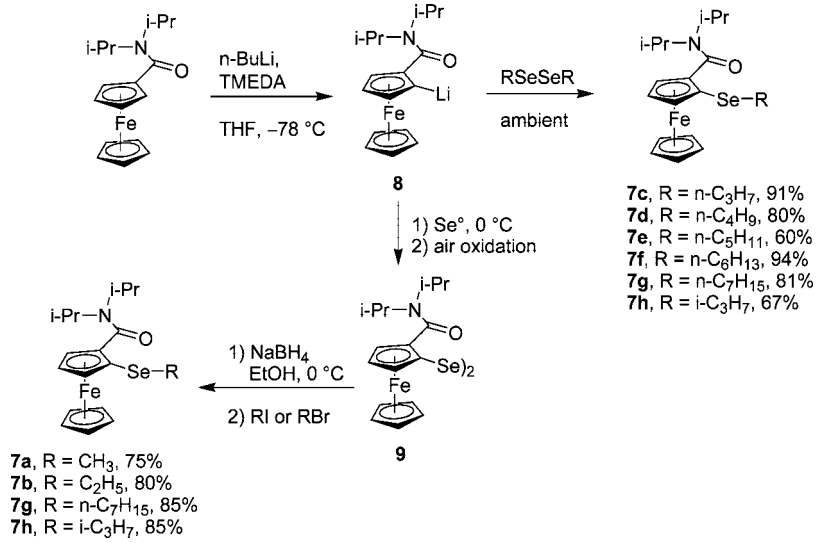
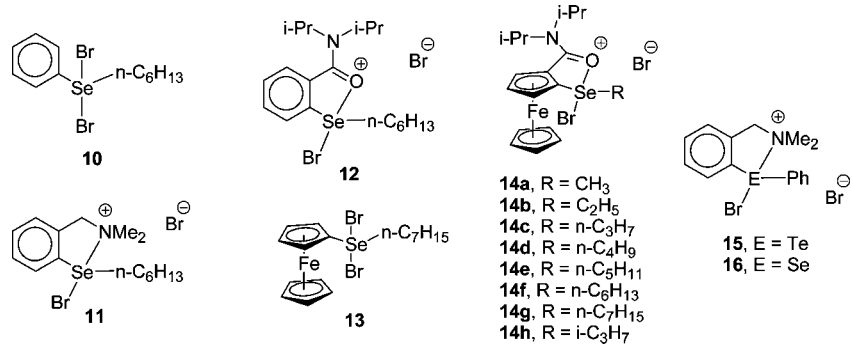
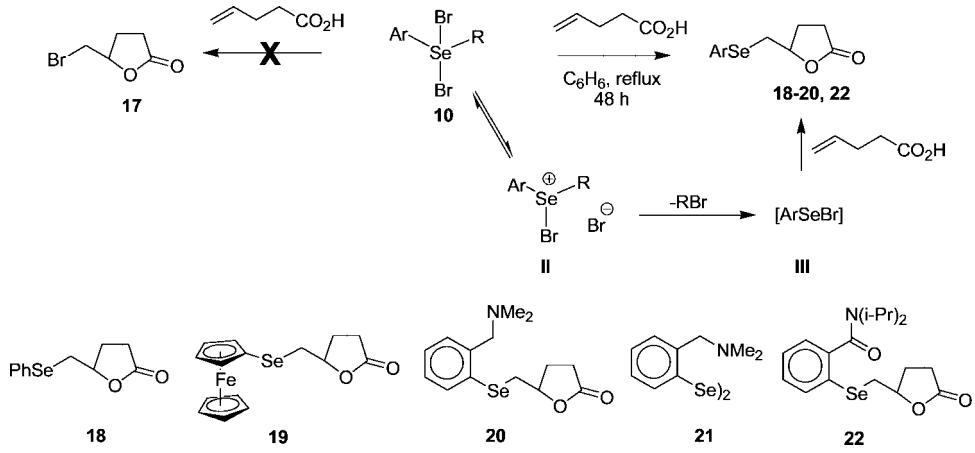



**Chart 1**



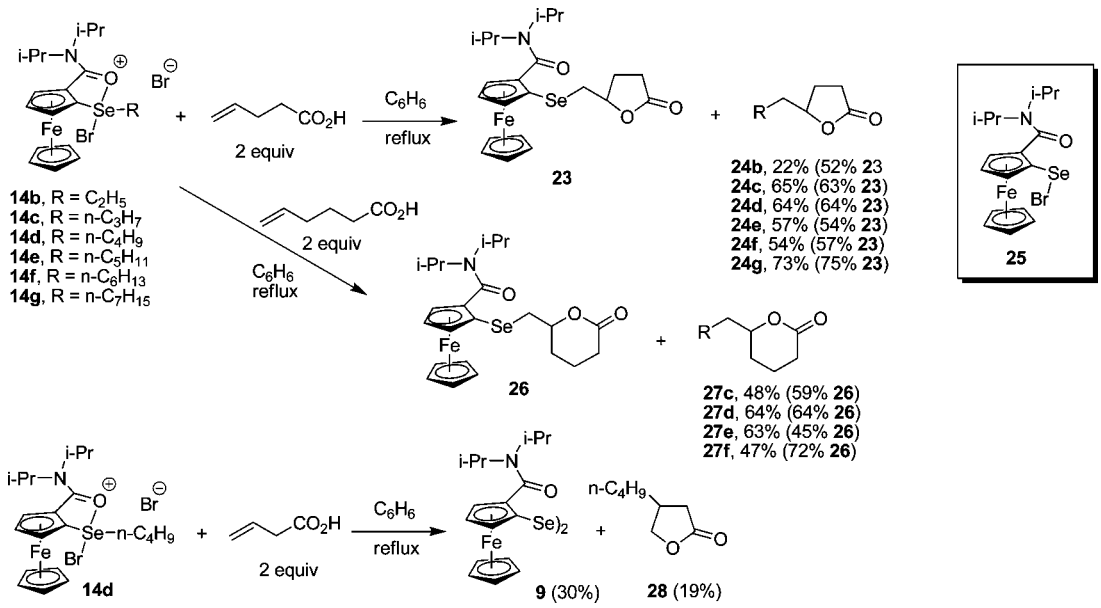

**Scheme 5**




**Reactions of Selenium(IV) Derivatives 10−13.** 4-Pentenoic acid is an excellent substrate for comparing bromination and dealkylation reactions of the Se(IV) derivatives. Bromination of 4-pentenoic acid gives bromomethyl-substituted lactone **17**.[4] Selenium(IV) derivatives **10**−**13** were prepared by adding 1 equiv of bromine to a benzene solution of the selenide **3**−**6** at 0 °C, followed by the addition of 4-pentenoic acid at room temperature. The resulting solutions were heated at reflux for 48 h. As shown in Scheme 5, none of the derivatives **10**−**13** gave lactone **17** as an isolable compound and instead gave products derived from initial loss of bromoalkane from the Se(IV) derivative. From **10**, phenylseleno-substituted lactone **18**[21] was isolated in 65% yield. Ferrocenyl derivative **13** gave ferrocenylseleno-substituted lactone **19** in 77% yield, along with traces of diferrocenyl diselenide (<5%). Selenium(IV) derivative **11**, with an intramolecular dimethylamino ligand for Se(IV), gave arylseleno-substituted lactone **20** in 8% yield and bis[2-[(dimethylamino)methyl]phenyl] diselenide (**21**) in 47% isolated yield, perhaps via disproportionation of the corresponding selenenyl bromide. Compound **12**, with an amide

(21) Clive, D. J.; Hittattu, G. *J. Chem. Soc. Chem. Com.* **1977**, 484–485.

**Scheme 6**




substituent, upon heating with 4-pentenoic acid gave selenolactone **22** in 65% isolated yield.

As shown in Scheme 5, loss of bromide from the Se(IV) derivatives produces the bromoselenonium intermediates **II**, which must undergo dealkylation via nucleophilic attack of bromide at carbon to produce bromoalkane and arylselenenyl bromide intermediates **III**. The selenenyl bromides **III** then undergo electrophilic addition to 4-pentenoic acid to form the arylseleno-substituted lactones **18**−**20** and **22**.

The bromoalkane product was detected in the reaction mixtures from amide-substituted derivative **12** (1-bromohexane observed in $^1$H NMR and mass spectra of the reaction mixture) and ferrocenyl derivative **13** (lactone **19** and 1-bromoheptane were both observed by $^1$H NMR spectroscopy; see Supporting Information for NMR spectrum of mixture). The reaction between **13** and 4-pentenoic acid was repeated at 80 °C in benzene-$d_6$ and relative amounts of ferrocenylseleno-substituted lactone **19** and 1-bromoheptane increased in a 1:1 ratio as a function of time.

The arylseleno-substituted $\gamma$-lactones **17**, **19**, **20**, and **22** share NMR spectral features consistent with the proposed $\gamma$-lactone structures (Supporting Information). In their $^1$H NMR spectra, all five compounds displayed the methine proton on the lactone ring as a multiplet centered between $\delta$ 4.58 and 4.69. The $^{13}$C NMR spectra displayed lactone carbonyl signals at $\delta$ 176.7−176.8 and signals in the range $\delta$ 32.3−33.6 for the carbon $\alpha$ to the carbonyl, $\delta$ 28.6−28.9 for the carbon $\beta$ to the carbonyl, and $\delta$ 27.4−27.8 for the carbon $\gamma$ to the carbonyl. The IR spectra of these derivatives all displayed the lactone carbonyl at 1774−1775 cm$^{-1}$. The remaining signals in both $^1$H and $^{13}$C NMR spectra were consistent with appropriate groups to define the compound. The $^{13}$C NMR spectrum of **22** displayed an extra set of signals for the amide functionality, which may be due to "free" and selenium-associated amide carbonyl groups. However, mass spectral and elemental analyses were consistent with an empirical formula of $C_{18}H_{25}NO_3Se$.

**Reactions of Se(IV) Derivatives 14.** The selenium(IV) derivatives **14** were all prepared by the addition of 1 equiv of bromine to a benzene solution of the selenide **7** at 0 °C. The 4-pentenoic acid was added at room temperature and the resulting solution was heated at reflux for 48 h. As was observed with the Se(IV) derivatives **10**−**13**, no bromomethyl-substituted lactone **17** was observed in the product mixture. Ferrocenylseleno-substituted lactone **23** was formed from all of the derivatives **14**. However, compounds **14b**−**14g** gave a new product that was not observed from reactions of **10**−**13** with 4-pentenoic acid−$\gamma$-lactones **24** (Scheme 6). The corresponding bromoalkanes were not observed in the product mixtures. Loss of the alkyl group from **14** would generate ferrocenylselenenyl bromide **25**, which would then add to 4-pentenoic acid to generate ferrocenylseleno-substituted lactone **23**.

With the exception of the ethylseleno derivative **14b**, where ferrocenylseleno-substituted lactone **23** was isolated in 52% yield and lactone **24b** in 22% yield, the alkylseleno derivatives **14c**−**14g** gave ferrocenylseleno-substituted lactone **23** and lactone **24** in comparable yields, as shown in Scheme 6. The methyl derivative **14a** gave ferrocenylseleno-substituted lactone **23** in 51% isolated yield, but the corresponding ethyl-$\gamma$-lactone **24a** (R = Me) was not detected. The isopropyl derivative **14h** was much less reactive in refluxing benzene. After 48 h, workup and purification of the product mixture via chromatography on silica gave gave the reduced selenide **7h** in 75% yield and trace amounts of ferrocenylseleno-substituted lactone **23** (5%). The $\gamma$-lactones **24** are all known and well-characterized compounds.[22]

The NMR spectra of compound **23** were complicated by the presence of two diastereomers in nearly equal amounts based on the *R,S*-stereochemistry of the ferrocenyl group[16,17] and the chiral methine carbon of the lactone ring. Most of the $^{13}$C NMR peaks were doubled, as were the $^1$H NMR peaks. However, the mass spectrum of the mixture of diastereomers displayed one peak via electrospray ionization corresponding to the empirical formula for **23** ($C_{22}H_{29}NO_3FeSe$). The combustion analysis also corresponded to the same empirical formula.

The reactions of **14** with 4-pentenoic acid also gave **23** and lactones **24** when the reactions were run in acetonitrile as solvent. However, the reaction gave higher yields and fewer biproducts when conducted in benzene, which was used in subsequent reactions. The presence of an added base such as pyridine or lutidine had no impact, favorable or unfavorable, on the reaction.

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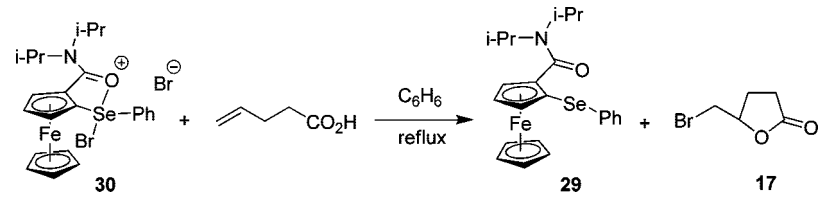
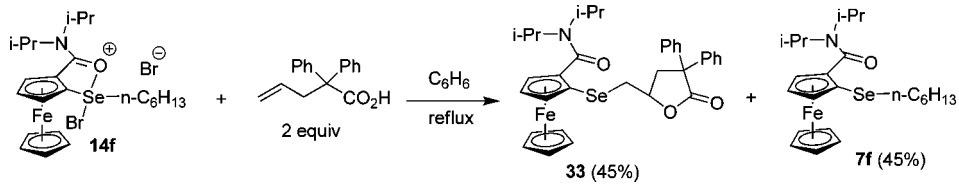
**Scheme 7**




**Scheme 8**




As shown in Scheme 6, heating compounds **14** with 2 equiv of 5-hexenoic acid in refluxing benzene gave ferrocenylseleno-substituted $\delta$-lactone **26** and alkyl transfer to give $\delta$-lactones **27**. Again, comparable yields for both **26** and **27** were obtained (Scheme 6). The $\delta$-lactones **27** are all known and well-characterized compounds.[23]

Like the characterization of **23**, characterization of the ferrocenylseleno-substituted $\delta$-lactone **26** was also complicated by the presence of nearly equal amounts of two diastereomers resulting from the *R,S*-stereochemistry of the ferrocenyl group[16,17] and the chiral methine carbon of the $\delta$-lactone ring. NMR signals were doubled in both $^1$H and $^{13}$C NMR spectra. The mass spectrum of the mixture of diastereomers of **26** displayed one peak via electrospray ionization corresponding to the empirical formula for **26** ($C_{23}H_{31}NO_3FeSe$).

Heating **14d** with 2 equiv of 3-butenoic acid gave $\gamma$-lactone **28**[24] (see Supporting Information for NMR spectra) in 19% yield and diselenide **9** in 51% yield (Scheme 6). Disproportionation of **25** would produce **9**. No ferrocenylseleno-substituted lactones were observed in the product mixture.

**Reactions of a Ferrocenyl Phenyl Se(IV) Derivative.** The alkyl-transfer chemistry was only observed with compounds **14**. In order to examine whether bromination would occur in a system incapable of alkyl transfer, we prepared (phenylseleno)-ferrocene (**29**).[17] Compound **29** reacted with 1 equiv of bromine at 0 °C to give (dibromophenylseleno)ferrocene **30** (Scheme 7). One equivalent of 4-pentenoic acid was added and the resulting solution was heated at reflux for 24 h. Bromomethyl-substituted lactone **17**[25] was isolated in 38% yield and (phenylseleno)ferrocene (**29**) was recovered in 85% yield. No products were observed from selenenyl bromide **25** addition to the 4-pentenoic acid, and no products were observed corresponding to transfer of the phenyl group. Compound **30** acted similarly to other dibromodiarylselenium compounds and brominated 4-pentenoic acid.[4]

**Reactions with Other Alkenes.** The alkyl transfer chemistry was not observed with all alkenoic acids and with simple alkenes. The hexylseleno derivative **14f** reacted with 2,2-diphenyl-4-pentenoic acid to give ferrocenylseleno-substituted lactone **33** in 45% yield and the reduced selenide **7f** in 45% yield (Scheme 8). No alkyl transfer product was observed in the reaction mixture. The reaction of cyclohexene with **14f** gave a mixture of products corresponding to bromination, the addition of selenenyl bromide **25**, as well as a mixture of debromination products under conditions identical to the reaction of Se(IV) derivatives **14** with alkenoic acids. No products corresponding to tranfer of the *n*-hexyl group were detected in the reaction mixture.

**Mechanistic Considerations.** We examined several control reactions in order to gain some insight into possible mechanistic pathways. Does the alkyl transfer chemistry come from the formation of ferrocenylseleno-substituted lactone **23** and the bromoalkane? As shown in Scheme 9a, a mixture of **23**, *n*-bromohexane, and 4-pentenoic acid gave no reaction after 48 h in refluxing benzene, suggesting that reaction of **23** and the bromoalkane are not responsible for the alkyl-transfer reaction. Is bromination rapid to give bromomethyl-substituted lactone **17**, and does **17** react with the reduced selenide **7** to give the alkyl transfer chemistry? As shown in Scheme 9b, a mixture of **17**, selenide **7f**, and 4-pentenoic acid gave no reaction after 48 h in refluxing benzene. If formation of the selenenyl bromide **25** and bromoalkane were rapid, then the formation of **23** would lead to a buildup of bromoalkane in the reaction mixture. There are two questions to consider in this context: (1) Is the loss of alkyl bromide reversible, and (2) does the alkyl bromide buildup accelerate or retard the reaction? To address these questions, we conducted a third control reaction in which a mixture of Se(IV) derivative **14f**, 4-pentenoic acid, and 1-bromopropane (5 equiv) was heated in refluxing benzene-$d_6$ for 48 h, as shown in Scheme 9c. Although the data are qualitative, no apparent change in rate was observed in the presence of 5 equiv of free bromoalkane. As with the other reactions, reaction was complete after 48 h. The mass spectrum of the product mixture following aqueous workup showed lactone **24c** as the predominant lactone product, with the expected product from **14f**, lactone **24f**, as the minor component. Clearly, the alkyl groups can scramble, suggesting that loss of bromoalkane from **14** is reversible.

The mechanism for the alkyl transfer reactions to alkenoic acids is not all clear. Precedented reactions of diorganoselenium(IV) dibromides do not appear to be involved in the alkyl transfer chemistry, as demonstrated by the control reactions a and b in Scheme 9. The products of bromination [bromomethyl-substituted lactone **17** and (alkylseleno)ferrocene derivatives **7**] and the products of bromoalkane loss (ferrocenylseleno-substituted lactone **23** and 1-bromoalkane) do not react with

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**Scheme 9**

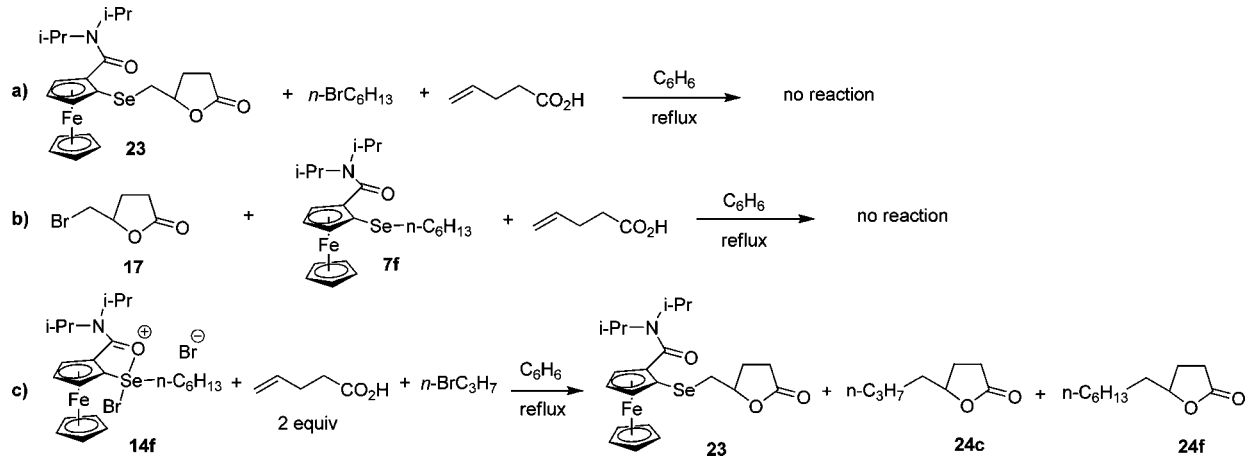
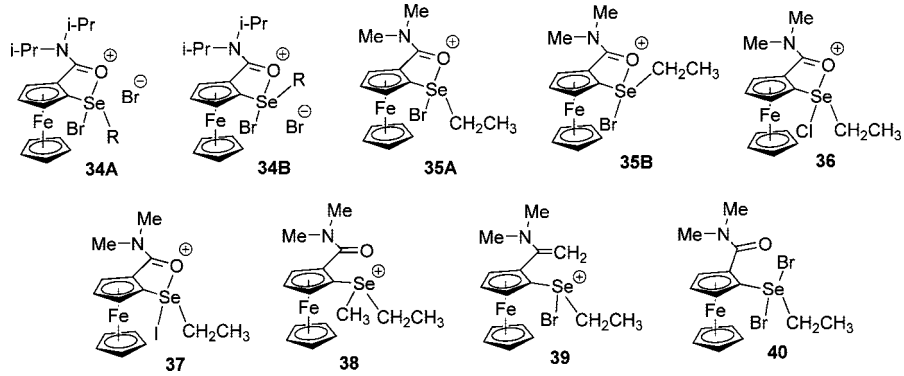



**Chart 2**




pentenoic acid under the conditions of reaction to give the $\gamma$-lactones **24**. The reduced reactivity of the isopropyl derivative **14h** and the lack of rearrangement products in lactone formation argue against a free carbocation being involved. The addition of 1-bromopropane to the reaction of hexylseleno derivative **14f** with 4-pentenoic acid, as shown in Scheme 9c, gave scrambling of the alkyl groups, producing a mixture of $\gamma$-lactones **24c** and **24f** as well as selenolactone **23**. This reaction suggests that the loss of bromoalkane from Se(IV) derivatives **14** to give selenides **7** is reversible.

**Does Iron Participate?** One can ask the obvious question of what role, if any, does Fe(II) play in the alkyl transfer reaction? Ferrocenyl derivative **13** gave dealkylation upon heating with formation of 1-bromoheptane. No alkyl transfer to 4-pentenoic acid was observed. Only the ferrocenyl derivatives **14** with the amide substituents displayed the alkyl transfer chemistry. Two of the possible conformations of these derivatives are shown in Chart 2 as conformers **34A** and **34B**. If Fe(II) were involved in the alkyl transfer, one might anticipate that conformer **34A** would be involved, since the alkyl group would be closest to the Fe atom.

Density functional theory (DFT) geometry optimizations were performed for structures derived from **34A**, at the B3LYP/LANL2DZ and BP86/TZP levels of theory.[26,27] (See the Experimental Section for details.) To lower the computational effort, the isopropyl groups of compounds **14** were replaced by methyl groups. For the group R in **34A**, we chose ethyl, again, to simplify the calculations. This parent compound **35A** (Chart 2), related to **14b** and conformer **34A**, was optimized first, yielding an eclipsed conformation for the ferrocene moiety after starting from a staggered conformation. The minimized structure is shown in Figure S1 (Supporting Information). We note that the Cp rotational barrier is known to be very low, and an essentially free rotation takes place at room temperature. For comparison with **35A**, **35B**, a conformation with the R group pointing away from the Fe center as in **34B**, was also considered and found to be about 3 kcal mol$^{-1}$ lower in energy (B3LYP/

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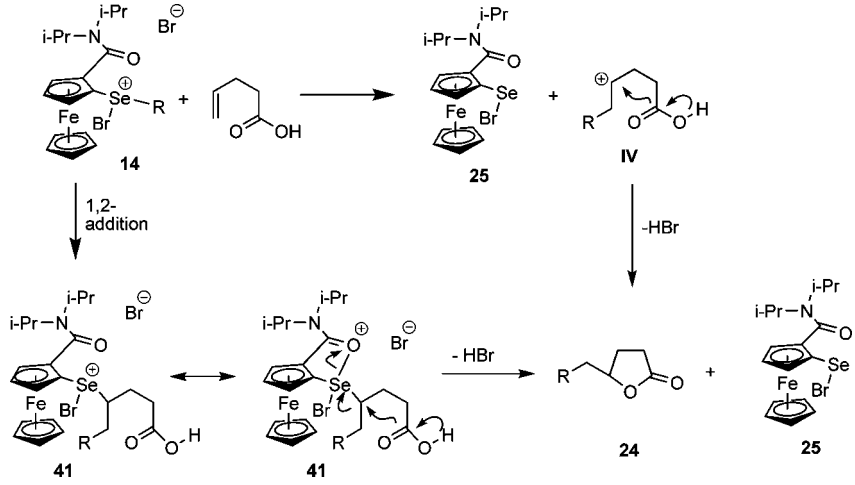
**Scheme 10**



LANL2DZ). The computations also did not indicate interactions between the Fe center and the ethyl group in either **35A** or **35B**, suggesting that iron does not participate in the breaking of the Se−C bond.

If iron were not involved in the alkyl transfer, then perhaps structural features of compounds **14** are weakening the Se−C bond, facilitating heterolytic cleavage. To address this question, we examined several structural variations shown in Chart 2 in order to examine substituent effects on the Se−C bond length. The Br ligand was replaced with Cl, I, and Me, as shown in **36**−**38**, respectively (Chart 2). The electronegative O atom in the amide carbonyl was replaced with a methylene to give **39**, and the Se···O interaction was removed by the introduction of a second Br ligand, as shown in structure **40**. In all structures considered, the Se−C bond distance from Se to the ethyl group was 203−206 pm, with the shortest distance of 203 pm for structure **38** with a Me for Br substitution. The longest Se−C distance of 206 pm was calculated for the **35B** conformer. This variation across the set of molecules considered is rather small and does not give a compelling indication that, for instance, the Se−Br or Se−O interaction has an obviously strong effect on the Se−C bond. At the BP86/TZP level of theory, the calculated Se−C bond distances were consistently slightly shorter, between 198 and 202 pm, again with the shortest distance for **38** and overall little variation. Due to the Se−alkyl bond pointing away from the ferrocene moiety, the Fe center and the alkyl group are spaced too far apart for direct interaction. At the levels of theory used in this study, there is no indication for interactions between Fe and the alkyl group.

## Conclusions

The reaction of 1-[[bis(1-methylethyl)amino]carbonyl]-2-(alkylseleno)ferrocene derivatives **14b**−**14g** with 4-pentenoic acid and 5-hexenoic acid gave $\gamma$-lactones **24** and $\delta$-lactones **27**, respectively, as well as comparable amounts of product from the addition of selenenyl bromide **25** to the alkeneoic acid to give ferrocenylseleno-substituted lactones **23** and **26**, respectively. The reaction of **14d** with 3-butenoic acid gave $\gamma$-lactone **28** in low yield (19%). This is a new C−C bond forming reaction of organoselenium compounds. It is not (yet) a general reaction. Steric interactions may be important, since 2,2-diphenyl-4-pentenoic acid did not undergo the alkyl-transfer chemistry. A simple alkene such as cyclohexene did not undergo the alkyl-transfer chemistry.

In the reactions of compounds **14** with alkenoic acids, the alkyl-transfer reaction is accompanied by the formation of selenenyl bromide **25**, which then adds to the alkenoic acid to give ferrocenylseleno-substituted lactones **23** or **26**. When selenenyl bromide **25** forms is not entirely clear. With the exception of reactions of **14a** and **14b**, the products of alkyl transfer to the alkenoic acid and the addition of **25** are formed in comparable amounts. This is suggestive of a common process. The reaction of **14a** with 4-pentenoic acid gives ferrocenylseleno-substituted lactone **23** as the only product isolated. None of the $\gamma$-lactone **24a** was detected in the product mixture. The reaction of **14b** with 4-pentenoic acid gave **23** in 53% isolated yield and $\gamma$-lactone **24b** in 22% isolated yield. One might argue that **14a** and **14b** have rapid loss of bromomethane and bromoethane, respectively, to form **25**. Since these bromoalkanes are more volatile, readdition to regenerate **14a** and **14b** may limit the availability of the alkyl-transfer pathway. However, loss of bromoalkane would give **25**, allowing the formation of ferrocenylseleno-substituted lactone **23**.

What might the common process be? If iron is not involved in the alkyl-transfer chemistry, then the alkyl group of compounds **14b**−**14g** must be acting like an electrophile, as summarized in Scheme 10. Direct transfer of the alkyl group from **14** to the 4-pentenoic acid would give selenenyl bromide **25** and a secondary carbocation intermediate **IV**, which would be intercepted by the carboxyl group to give lactones **24**. Alternatively, compounds **14** might undergo a 1,2-addition to the alkene to give compounds **41**, which would be similar to Engman's addition of phenylselenium trichloride.[8] Lactone-forming attack by the carboxyl group at the selenium-bearing carbon of **41** would generate **24**, with selenenyl bromide **25** lost as a leaving group.

Obviously, the scope of this reaction needs to be explored further with respect to both the Se(IV) derivatives capable of giving alkyl transfer and the substrates capable of reacting with the Se(IV) derivatives. Furthermore, directed metalation of [bis(1-methylethyl)amino]carbonyl]ferrocene with *n*-butyllithium and (−)-sparteine at −78 °C in ether gives 2-lithio-1-[bis(1-methylethyl)amino]carbonyl]ferrocene **8** (Scheme 4) in a highly enantioselective manner.[16] Quenching of **8** with various diselenides gives selenides **7** with high enantioselectivity.[16] An enantioselective variant of this reaction would provide a novel means of transferring a primary alkyl group in a chiral manner.

## Experimental Section

**General Methods.** Solvents and reagents were used as received from Sigma-Aldrich Chemical Co., unless otherwise noted. Diethyl ether, dichloromethane, and TMEDA were dried over $CaH_2$ under

nitrogen atmosphere and freshly distilled prior to use. Benzene was dried over 3A molecular sieves. Chromatography was performed with silica gel (230−400 mesh, 60 Å). Bis(ferrocenyl) diselenide,[15] [[bis(1-methylethyl)amino]carbonyl]ferrocene,[16,17] di-*n*-heptyl diselenide,[20] di-*n*-hexyl diselenide,[19] di-*n*-pentyl diselenide,[18] di-*n*-butyl diselenide,[19] di-*n*-propyl diselenide,[18] diisopropyl diselenide,[19] 1-[[bis(1-methylethyl)amino]carbonyl]-2-(butylseleno)ferrocene (**7d**),[16] 1-[[bis(1-methylethyl)amino]carbonyl]-2-(phenylseleno)ferrocene (**29**),[16,17] and (*n*-hexylseleno)benzene (**3**)[12] were prepared by literature procedures. Concentration in vacuo was performed on a Büchi rotary evaporator. NMR spectra were recorded on a Varian Gemini-300 or Inova 500 instrument with residual solvent signal of $CDCl_3$ as internal standard ($\delta$ 7.26 for proton, $\delta$ 77.1 for carbon). Infrared spectra were recorded on a Perkin-Elmer FT-IR instrument. Elemental analyses were conducted by Atlantic Microlabs, Inc. The lactone products **24**,[22] **27**,[23] and **28**[24] are known compounds, and spectral characterization is compiled in the Supporting Information.

**Preparation of 2-*N*,*N*-Dimethylaminobenzyl Hexyl Selenide (4).** Sodium borohydride (100 mg, 3.0 mmol) was added to bis(2-*N*,*N*-dimethylaminobenzyl) diselenide[13] (426 mg, 1.0 mmol) in EtOH (15 mL) at 0 °C under Ar. The resulting solution was stirred 0.5 h at 0 °C. 1-Bromohexane (0.28 mL, 2 mmol) was added via syringe and the resulting mixture was stirred for an additional 1 h. The reaction mixture was poured into saturated $NaHCO_3$ (50 mL), and the organic products were extracted with ether (4 × 10 mL). The combined organic extracts were washed with water, dried over $Na_2SO_4$, and concentrated in vacuo. Selenide **4** was obtained as a colorless liquid (508 mg, 85%). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.41 (m, 1H), 7.23 (m, 1H), 7.12 (m, 2H), 3.49 (s, 2H), 2.78 (t, $J$ = 6.8 Hz, 2H), 2.23 (s, 6H), 1.72 (m, 2H), 1.48−1.16 (m, 6H), 0.86 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 139.9, 133.9, 130.4, 129.7, 127.6, 125.5, 64.3, 45.0, 31.3, 29.8, 29.7, 26.8, 22.6, 14.0; HRMS (ESI) *m*/*z* 299.1146 (calcd for $C_{15}H_{25}N^{80}Se$: 299.1146).

**Preparation of 2-*N*,*N*-Diisopropylbenzamide Hexyl Selenide (5).** *n*-Butyllithium (3.1 mL of a 1.3 M solution in cyclohexane/hexane, 4.0 mmol) was added slowly to TMEDA (0.59 mL, 3.9 mmol) in THF (10 mL) at −78 °C under Ar. After 10 min, *N*,*N*-diisopropylbenzamide (616 mg, 3.0 mmol) in THF (4 mL) was added dropwise via syringe and the resulting solution was stirred for 1 h at −78 °C. Dihexyl diselenide (1.31 g, 4 mmol) in THF (2 mL) was added via syringe and the resulting mixture was stirred for an additional 1 h at −78 °C and for 1 h at room temperature. The reaction mixture was poured into a mixture of ice (25 g) and brine (20 mL) and the products were extracted with ether (3 × 15 mL). The combined ether extracts were dried over $Na_2SO_4$ and concentrated in vacuo to give a yellow oil. The crude product was purified via column chromatography on $SiO_2$ eluted with hexanes/ethyl acetate (9:1) to give 1.00 g (91%) of **5** as a colorless liquid: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.52 (dd, $J$ = 6.5, 2.5 Hz, 1H), 7.22 (m, 2H), 7.11 (dd, $J$ = 6.5, 2.5, 1H), 3.57 (dm, $J$ = 6.0 Hz, 2H), 2.93 (br d, 2H), 1.68 (m, $J$ = 7.5 Hz, 1H), 1.62−1.59 (many signals, 6H), 1.39 (m, $J$ = 7.0 Hz, 2H), 1.30−1.23 (m, 4H), 1.20 (br d, 3H), 1.06 (br s, 3H), 0.87 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$)$\delta$169.7, 142.7, 133.6, 128.5, 127.2, 127.0, 125.6, 51.0 (br), 45.9 (br), 31.4, 30.2, 29.7, 28.4, 22.7, 20.9, 14.1; IR (film, NaCl) 1634 cm$^{-1}$; ESMS (ESI) *m*/*z* 392.1454 (calcd for $C_{19}H_{31}NO^{80}Se + Na^+$: 392.1463).

**Preparation of Ferrocenyl Heptyl Selenide (6).** Sodium borohydride (290 mg, 7.6 mmol) was added in one portion to a solution of diferrocenyl diselenide (2.00 g, 3.8 mmol) in EtOH (15 mL) cooled to 0 °C under Ar. After the reaction had stirred for 1 h, 1-bromoheptane (1.24 mL, 1,44 g, 7.6 mmol) was added via syringe at room temperature. The reaction mixture was stirred for an additional 3 h and poured into water, and the products were extracted with ether (2 × 15 mL). The combined ether extracts were washed with water, dried over $Na_2SO_4$, and concentrated in vacuo. The crude product was purified via chromatography on $SiO_2$ eluted with hexanes to give 412 mg (75%) of **6** as a yellow liquid: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.31 (t, $J$ = 2.0 Hz, 2H), 4.19 (t, $J$ = 2.0, 2H), 4.18 (s, 5H), 2.59 (t, $J$ = 7.5 Hz, 2H), 1.59 (m, 2H), 1.33−1.22 (m, 4H), 0.87 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 75.2, 69.6, 69.4, 31.9, 30.7, 29.9, 29.8, 28.9, 22.7, 14.2; IR (film, NaCl) 2954, 2924, 2853, 1466, 1150, 1106, 1020, 1001, 881, 818 cm$^{-1}$; HRMS (ESI) *m*/*z* 364.0387 (calcd for $C_{17}H_{24}Fe^{80}Se$: 364.0393).

**General Procedure for the Preparation of 1-[[Bis(1-methylethyl)amino]carbonyl]-2-(alkylseleno)ferrocenes 7. Preparation of 1-[[Bis(1-methylethyl)amino]carbonyl]-2-(*n*-hexylseleno)ferrocene (7f).** [[Bis(1-methylethyl)amino]carbonyl]ferrocene (1.878 g, 6.0 mmol) in ether (10 mL) was added via cannula to a solution of TMEDA (1.55 g, 13.4 mmol) and *n*-BuLi (5.30 mL of a 2.5 M solution in hexanes, 13.3 mmol) in ether (10 mL) at −78 °C under Ar. The resulting orange-colored reaction mixture was stirred for 45 min at −78 °C. Di-*n*-hexyl diselenide (8.21 g, 25 mmol) was added via syringe and stirring was continued for 15 min at −78 °C and then 0.5 h at room temperature. During this time, the heterogeneous reaction mixture became homogeneous. The reaction mixture was quenched with saturated, aqueous $NH_4Cl$ solution (50 mL), and the organic products were extracted with ether (3 × 25 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The crude product was purified via chromatography on $SiO_2$ eluted with hexanes/ethyl acetate (95/5) to give 2.70 g (94%) of **7f** as an orange oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.37 (m, 1H), 4.31 (s, 5H), 4.28 (m, 1H), 4.18 (t, $J$ = 3 Hz, 1H), 3.59 (br s, 1H), 3.48 (br s, 1H), 2.70 (t, $J$ = 7.5 Hz, 2H), 1.68−1.62 (m, 2H), 1.51 (br s, 1H), 1.43−1.24 (m, 8H), 1.09 (br s, 6H), 0.88 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 167.0, 89.8, 74.9, 72.8, 71.1, 67.3, 67.1, 65.7, 50.2 (br), 45.8 (br), 31.2, 30.4, 30.3, 29.4, 28.5, 22.4, 20.9, 15.2, 13.9; IR (film, NaCl) 1637 cm$^{-1}$; HRMS (ESI) *m*/*z* 477.1222 (calcd for $C_{23}H_{35}NOFe^{80}Se$: 477.1228).

**Preparation of 1-[[Bis(1-methylethyl)amino]carbonyl]-2-(*n*-propylseleno)ferrocene (7c).** Propyl selenide **7c** was prepared as described for **7f** using [[bis(1-methylethyl)amino]carbonyl]ferrocene and di-*n*-propyl diselenide at 0.5 mmol scale. The product yield was 197 mg (91%) of **7c** as a yellow oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.36 (m, 1H), 4.31 (s, 5H), 4.28 (m, 1H), 4.17 (t, $J$ = 2.5 Hz, 1H), 3.92 (br s, 1H), 3.41 (br s, 1H), 2.68 (t, $J$ = 7.5 Hz, 2H), 1.66 (t, $J$ = 7.5 Hz, 2H), 1.50 (br s, 6H), 1.07 (br s, 6H), 0.97 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 167.2, 94.9, 90.1, 75.0, 73.1, 71.4, 67.4, 67.4, 50.4 (br), 46.0 (br), 31.0, 23.9, 21.0, 14.6; IR (film, NaCl) 1637 cm$^{-1}$; HRMS (ESI) *m*/*z* 458.0656 (calcd for $C_{20}H_{29}NOFe^{80}Se + Na^+$: 458.0656).

**Preparation of 1-[[Bis(1-methylethyl)amino]carbonyl]-2-(*n*-pentylseleno)ferrocene (7e).** Pentyl selenide **7e** was prepared as described for **7f** using [[bis(1-methylethyl)amino]carbonyl]ferrocene and di-*n*-pentyl diselenide at 1.0 mmol scale. The product yield was 610 mg (60%) of **7e** as a yellow oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.30 (t, $J$ = 2.0 Hz, 1H), 4.18 (m, $J$ = 2.0, 1H), 4.18 (s, 5H), 4.28 (m, 1H), 4.18 (t, $J$ = 3.0 Hz, 1H), 3.93 (br s, 1H), 3.41 (br s, 1H), 2.70 (t, $J$ = 7.5 Hz, 2H), 1.68−1.62 (m, 2H), 1.51 (br s, 1H), 1.43−1.24 (m, 8H), 1.09 (br s, 6H), 0.88 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 167.2, 90.0, 72.9, 72.9, 71.3, 67.4, 67.3, 50.3 (br), 46.0 (br), 32.7, 32.2, 30.3, 28.7, 28.4, 23.1, 22.3, 21.0, 14.0; IR (film, NaCl) 1636 cm$^{-1}$; HRMS (ESI) *m*/*z* 463.1087 (calcd for $C_{23}H_{33}NOFe^{80}Se$: 463.1071).

**Preparation of 1-[[Bis(1-methylethyl)amino]carbonyl]-2-(*n*-heptylseleno)ferrocene (7g).** Heptyl selenide **7g** was prepared as described for **7f** using [[bis(1-methylethyl)amino]carbonyl]ferrocene and di-*n*-heptyl diselenide at 1.0 mmol scale. The product yield was 396 mg (81%) of **7g** as a yellow oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.36 (m, 1H), 4.31 (s, 5H), 4.28 (m, 1H), 4.17 (t, $J$ = 3.0 Hz, 1H), 3.93 (br s, 1H), 3.39 (br s, 1H), 2.70 (t, $J$ = 7.5 Hz,

2H), 1.69−1.61(m, 2H), 1.51 (br s, 1H), 1.38−1.22 (m, 10H), 1.09 (br s, 6H), 0.87 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 167.2, 90.0, 76.7, 75.1, 72.9, 71.2, 67.4, 67.3, 50.3 (br), 45.9 (br), 31.8, 30.6, 30.0, 28.9, 28.8, 22.7, 21.0, 14.1; IR (film, NaCl) 1636 cm$^{-1}$; HRMS (ESI) *m/z* 492.1469 (calcd for $C_{24}H_{38}NOFe^{80}Se$: 492.1463).

**Preparation of 1-[[Bis(1-methylethyl)amino]carbonyl]-2-(isopropylseleno)ferrocene (7h).** Isopropyl selenide **7h** was prepared as described for **7f** using [[bis(1-methylethyl)amino]carbonyl]ferrocene and diisopropyl diselenide at 1.0 mmol scale. The product yield was 290 mg (67%) of **7h** as a yellow oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.37 (m, 1H), 4.27 (m, 1H), 4.27 (s, 5H), 4.18 (t, $J =$ 2.0 Hz, 1H), 3.94 (br s, 1H), 3.37 (br s, 1H), 3.07 (heptet, $J =$ 7.0 Hz, 1H), 1.47 (br s, 6H), 1.32 (d, $J = 6.5$ Hz, 3H), 1.28 (d, $J = 6.5$ Hz, 3H), 1.07 (br s, 3H), 1.01 (br s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 167.0, 90.5, 75.0, 73.4, 71.3, 67.7, 67.2, 50.2 (br), 45.9 (br), 33.3, 24.5, 24.3, 21.0; IR (film, NaCl) 1667 cm$^{-1}$; HRMS (ESI) *m/z* 458.0656 (calcd for $C_{20}H_{29}NOFe^{80}Se$ + $Na^+$: 458.0656).

**Preparation of [[Bis(1-methylethyl)amino]carbonyl]ferrocenyl Diselenide (9).** *n*-Butyllithium (2.2 mL of a 2.3 M solution in hexane, 5.0 mmol) was added to TMEDA (0.58 g, 5.0 mmol) in THF (10 mL) at −78 °C and the resulting solution was stirred for 15 min at −78 °C. [[Bis(1-methylethyl)amino]carbonyl]ferrocene (626 mg, 2.0 mmol) in THF (5 mL) was added dropwise, and the resulting orange solution was stirred for 45 min at −78 °C. Selenium powder (0.80 g, 10 mmol) was added under a brisk flow of Ar, and the resulting mixture was warmed to 0 °C and stirred for 0.5 h, during which time all of the Se was consumed. The reaction mixture was poured over 50 g of ice and stirred for 2 h. The organic products were extracted with ether (3 × 15 mL) and the combined ether extracts were dried over $Na_2SO_4$ and concentrated in vacuo to give a red oil. The crude product was purified by column chromatography on $SiO_2$ eluting with hexanes/ethyl acetate (90:10). The product was recrystallized from hexanes/ether to give 480 mg (62%) of orange crystals: mp 145−147 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.52 (t, $J = 1.5$ Hz, 1H), 4.38 (m, 2H), 4.28 (s, 5H), 4.23 (t, $J = 1.5$ Hz, 1H), 4.10 (br s, 1H), 3.44 (br s, 1H), 1.50 (br s, 6 H), 1.20 (br s, 6H), 1.13 (br s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 167.9, 85.4, 80.2, 73.8, 71.7, 71.4, 68.4, 67.6, 50.0, 46.2, 22.3 (br), 21.2 (br); IR (KBr) 1634 cm$^{-1}$. Anal. Calcd for $C_{34}H_{44}N_2O_2Fe_2Se_2$: C, 52.21; H, 5.67; N, 3.58. Found: C, 52.30; H, 5.74; N, 3.61.

**General Procedure for the Preparation of 1-[[Bis(1-methylethyl)amino]carbonyl]-2-(alkylseleno)ferrocene from Diselenide 9. Preparation of 1-[[Bis(1-methylethyl)amino]carbonyl]-2-(ethylseleno)ferrocene (7b).** Sodium borohydride (190 mg, 5.0 mmol) was added in one portion to a cold solution of diselenide **9** (490 mg, 0.62 mmol) in EtOH (15 mL) at 0 °C under Ar. The resulting mixture was stirred for 0.5 h at 0 °C and 0.5 h at room temperature. Ethyl iodide (0.78 mL, 10 mmol) was added via syringe at 0 °C, and the resulting mixture was stirred for 0.5 h at 0 °C and 2 h at room temperature. The reaction mixture was poured into brine (50 mL), and the products were extracted with ether (4 × 25 mL). The combined ether extracts were dried over $Na_2SO_4$ and concentrated in vacuo. The crude prodect was purified via column chromatography on $SiO_2$ eluting with ethyl acetate/hexanes (5:95) to give 0.419 g (80%) of **7b** as a yellow liquid: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.38 (m, 1H), 4.31 (s, 5H), 4.29 (m, 1H), 4.19 (t, $J = 2.5$ Hz, 1H), 3.97 (br s, 1H), 3.42 (br s, 1H), 2.71 (q, $J = 7.5$ Hz, 2H), 1.50 (br s, 6H), 1.36 (t, $J = 8.0$ Hz, 3H), 1.07 (br s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 167.2, 90.1, 74.7, 73.1, 71.3, 67.4, 50.3 (br), 45.9 (br), 22.0, 21.0, 15.8; IR (film, NaCl) 1667 cm$^{-1}$; HRMS (ESI) *m/z* 444.0487 (calcd for $C_{19}H_{25}NOFeNa^{80}Se$: 444.0499).

Compound **7a** was prepared in 75% yield, and compounds **7g** and **7h** were each isolated in 85% yield using this procedure.

**Reaction of (Dibromo-*n*-hexylseleno)benzene (10) with 4-Pentenoic Acid. Preparation of 5-(Phenylselenomethyl)tetrahydro-2-furanone (18).** Bromine (1 mL of a 1 M solution in benzene, 1.0 mmol) was added to a solution of (*n*-hexylseleno)benzene (**3**, 241 mg, 1.0 mmol) in benzene (5 mL) at 0 °C under Ar. After 45 min, 4-pentenoic acid (200 mg, 2.0 mmol) was added and the resulting dark red mixture was heated at reflux for 48 h. The reaction mixture was concentrated in vacuo and the residue was dissolved in $CH_2Cl_2$ (15 mL). The resulting solution was washed with 10% aqueous $K_2CO_3$ (2 × 15 mL) and water (15 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The crude product was purified via chromatography on $SiO_2$ eluted with hexanes/ethyl acetate (from 90:10 to 70:30) to give 0.212 g (65%) of **18**[17] as a pale yellow liquid: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.58 (m, 2H), 7.32 (m, 3H), 4.69 (m, 1H) 3.32 (dd, $J = 6.0$, 16.0 Hz, 1H), 3.05 (dd, $J = 10.0$, 16.0 Hz, 1H), 2.67−2.41 (m, 3H), 2.00 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 176.7, 133.0, 129.3, 128.9, 127.6, 79.2, 31.7, 28.6, 27.4; IR (film, NaCl) 1774 cm$^{-1}$; HRMS (ESI) *m/z* 392.1454 (calcd for $C_{19}H_{31}NO^{80}Se$ + $Na^+$: 392.1463).

**Reaction of *N*,*N*-Dimethyl-2-(dibromo-*n*-hexylseleno)benzenemethanamine (11) with 4-Pentenoic Acid.** Bromine (1 mL of a 1 M solution in benzene, 1.0 mmol) was added to a solution of *N*,*N*-dimethyl-2-(*n*-hexylseleno)benzenemethanamine (**4**, 298 mg, 1.0 mmol) in benzene (5 mL) at 0 °C under Ar. After 45 min, 4-pentenoic acid (200 mg, 2.0 mmol) was added and the resulting dark red mixture was heated at reflux for 48 h. The reaction mixture was concentrated in vacuo and the residue was dissolved in $CH_2Cl_2$ (15 mL). The resulting solution was washed with 10% aqueous $K_2CO_3$ (2 × 15 mL) and water (15 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The crude product was purified via chromatography on $SiO_2$ eluted with hexanes/ethyl acetate (from 90:10 to 70:30) to give 104 mg (47%) of di-2-*N*,*N*-(dimethylaminomethyl)phenyl diselenide (**21**)[12] and 24 mg (8%) of selenolactone **20** as a pale yellow liquid.

For **20**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.53 (m, 1H), 7.36 (m, 1H), 7.22 (dd, $J = 3.2$, 6.0 Hz, 2H), 4.56 (m, 1H), 3.68 (s, 2H), 3.27 (dd, $J = 4.8$, 12.8 Hz, 1H), 3.32 (dd, $J = 8.0$, 12.4 Hz, 1H), 2.62−2.36 (m, 6H), 2.32 (s, 6H), 1.93 (m, 1H); IR (film, NaCl) 1775 cm$^{-1}$; ESMS (ESI) *m/z* 314.0661 (calcd for $C_{14}H_{19}NO_2{}^{80}Se$ + $H^+$: 314.0654).

**Reaction of *N*,*N*-Bis(1-methylethyl)-2-(dibromo-*n*-hexylseleno)benzamide (12) with 4-Pentenoic Acid. Preparation of 5-[(2-*N*,*N*-Bis(1-methylethyl)benzamidoseleno)methyl]tetrahydro-2-furanone (22).** A benzene (10 mL) solution of 2-*n*-hexylselenobenzamide **5** (310 mg, 0.85 mmol) was cooled to 0 °C, and a solution of bromine (0.85 mL of a 1 M solution in benzene, 0.85 mmol) was added dropwise under argon. The resulting yellow solution was stirred for 0.5 h at 0 °C and 1 h at room temperature. 4-Pentenoic acid (0.17 g, 1.7 mmol) was added via syringe and the resulting mixture was stirred for 0.5 h at room temperature and was then heated at reflux for 48 h. The reaction mixture was concentrated in vacuo and the residue was dissolved in $CH_2Cl_2$ (20 mL). The resulting solution was washed with 10% HCl (3 × 20 mL) and 10% aqueous $K_2CO_3$ (20 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The crude red oil was purified via chromatography on $SiO_2$ eluted with ethyl acetate/hexanes (from 15:85 to 25:75) to give 212 mg (65%) of **22**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.66 (d, $J = 7.5$ Hz, 1H), 7.33 (t, $J = 7.0$ Hz, 1H), 7.26 (t, $J =$ 7.0, 1H), 7.16 (d, $J = 7.5$ Hz, 1H), 4.68 (br s, 1H), 3.60−3.49 (m, 2H), 3.16 (br s, 1H), 2.59−2.47 (m, 2H), 2.419 (br m, 1H), 1.59−1.87 (m, 1H), 1.57 (br s, 6H), 1.85 (br s, 3H), 1.07 br s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 176.8, 169.4, 169.3, 144.0, 136.1, 128.9, 128.8, 128.6, 125.7, 79.7, 51.2, 45.9, 32.8, 28.9, 28.8, 27.7, 20.7; IR (film, NaCl) 1775 cm$^{-1}$; ESMS (ESI) *m/z* 383.1002 (calcd for $C_{18}H_{25}NO_3{}^{80}Se$: 383.0994). Anal. Calcd for $C_{18}H_{25}NO_3Se$: C, 56.54; H, 6.59; N, 3.66. Found: C, 56.17; H, 6.22; N, 3.98.

**Reaction of (Dibromo-*n*-heptylseleno)ferrocene (13) with 4-Pentenoic Acid. (A) Preparation of 5-[(Ferrocenylseleno)-methyl]tetrahydro-2-furanone (19).** Bromine (1 mL of a 1 M solution in benzene, 1.0 mmol) was added to a solution of (*n*-heptylseleno)ferrocene (**6**, 364 mg, 1.0 mmol) in benzene (5 mL) at 0 °C under Ar. After 45 min, 4-pentenoic acid (200 mg, 2.0 mmol) was added and the resulting dark red mixture was heated at reflux for 48 h. The reaction mixture was concentrated in vacuo and the residue was dissolved in $CH_2Cl_2$ (15 mL). The resulting solution was washed with 10% aqueous $K_2CO_3$ (2 × 15 mL) and water (15 mL), dried over $Na_2SO_4$, and concentrated in vacuo. The crude product was purified via chromatography on $SiO_2$ eluted with hexanes/ethyl acetate (from 90:10 to 70:30) to give 2.82 g (77%) of **19** as an orange liquid and trace amounts (<5%) of diferrocenyl diselenide.

For **19**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.58 (m, 1H), 4.36 (m, 1H), 4.30 (m, 1H), 4.22 (m, 2H), 4.19 (s, 5H), 2.94 (dd, $J$ = 5.0, 12.5 Hz, 1H), 2.71 (dd, $J$ = 8.0, 12.5 Hz, 1H), 2.54 (m, 2H), 2.38 (m, 1H), 1.92 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 176.7, 79.8, 75.6, 75.4, 70.1, 70.0, 69.4, 69.3, 33.6, 28.9, 27.6; IR (film, NaCl) 1775 cm$^{-1}$; HRMS (ESI) *m*/*z* 363.9669 (calcd for $C_{15}H_{16}O_2Fe^{80}Se$: 363.9659).

**(B) In Benzene-$d_6$.** Bromine (0.20 mL of a 1 M solution in benzene-$d_6$, 0.20 mmol) was added to a solution of (*n*-heptylseleno)ferrocene (**6**, 73 mg, 0.20 mmol) in benzene-$d_6$ (1 mL) at 0 °C under Ar in a 5-mm NMR tube. After 0.5 h, 4-pentenoic acid (40 mg, 0.40 mmol) was added and the mixture was warmed to room temperature. The $^1$NMR spectrum of the resulting solution was recorded. The NMR tube was placed in an 80 °C bath and the $^1$NMR spectrum of the mixture contained in the tube was recorded every 24 h. Selenolactone **19** and 1-bromoheptane were formed in equimolar amounts (integral of signals at $\delta$ 4.58 for **19** and $\delta$ 3.42 for 1-bromoheptane). Mass spectral analysis (ESI) of the product mixture gave peaks corresponding to **19** (*m*/*z* 364 for $C_{15}H_{16}O_2Fe^{80}Se$) and to 1-bromoheptane (*m*/*z* 179 for $C_7H_{15}{}^{79}Br + H^+$ and *m*/*z* 181 for $C_7H_{15}{}^{81}Br + H^+$ in a 1:1 ratio).

**General Procedure for the Reaction of 1-[[Bis(1-methylethyl)-amino]carbonyl]-2-(dibromoalkylseleno)ferrocene with Enoic Acids. Preparation of (Ferrocenylselenomethyl)tetrahydro-2-furanone (23) and 5-*n*-Butyldihydro-2(3*H*)furanone (24c).** Bromine (0.5 mL of a 1 M solution in benzene, 1.0 mmol) was added to selenide **7c** (216 mg, 0.5 mmol) in benzene (5 mL) at 0 °C and the resulting solution was stirred for 0.5 h at 0 °C and 0.5 h at room temperature. 4-Pentenoic acid (100 mg, 1 mmol) was added and the resulting mixture was heated at reflux for 48 h. The reaction mixture was diluted with 20 mL of $CH_2Cl_2$. The resulting solution was washed with 10% (by volume) of aqueous HCl (3 × 50 mL), 10% aqueous $K_2CO_3$, and water; dried over $Na_2SO_4$; and concentrated in vacuo. The crude product was purified via chromatography on $SiO_2$ eluted with ethyl acetate/hexanes (10:90 to 25:75) to give 51 mg (65%) of $\gamma$-lactone **24c**[22] as a colorless oil and 113 mg (62%) of **23** as an orange solid: mp 45−48 °C.

For **23**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.68 (m, 1H), 4.61 (m, 1H), 4.45 (t, $J$ = 2.5 Hz, 1H), 4.38 (t, $J$ = 2.5 Hz, 1H), 4.31 (m, 2H), 4.29 (s, 5H), 4.28(s, 5H), 4.21 (m, 2H), 4.21 (br s, 1H), 3.97 (br s, 1H), 3.38 (br s, 2H), 3.01 (dd, 1H), 3.01 (dd, 1H), 2.85−2.79 (m, 2H), 2.61−2.40 (m, 6H), 1.96 (m, 2H), 1.48 (br s, 12H), 1.07 (br s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 176.8, 176.7, 167.2, 167.0, 89.4, 88.4, 79.9, 79.6, 76.7, 74.9, 73.9, 73.6, 71.4, 71.4, 68.1, 68.0, 67.6, 67.5, 50.3 (b), 46.1 (b), 33.0, 32.3, 28.8, 28.8, 27.8, 27.8, 21.2, 21.0; IR (film, NaCl) 1774 cm$^{-1}$; ESMS *m*/*z* 492.1 (calcd for $C_{22}H_{29}NO_3FeSe + H^+$: 492.1). Anal. Calcd for $C_{22}H_{29}NO_3FeSe$: C, 53.90; H, 5.96; N, 2.86. Found: C, 54.07; H, 6.12; N, 3.00.

**Preparation 5-*n*-Pentyldihydro-2(3*H*)furanone (24d).** Selenide **7d** (200 mg, 0.45 mmol), bromine (0.45 mmol), and 4-pentenoic acid (90 mg, 0.90 mmol) were treated as described to give 130 mg (64%) of selenolactone **23** and 65 mg (64%) of $\gamma$-lactone **24d**.[22]

**Preparation of 5-*n*-Hexyldihydro-2(3*H*)furanone (24e).** Selenide **7e** (460 mg, 1.0 mmol), bromine (1.0 mmol), and 4-pentenoic acid (200 mg, 2.0 mmol) were treated as described to give 266 mg (54%) of selenolactone **23** and 94 mg (57%) of $\gamma$-lactone **24e**.[22]

**Preparation of 5-*n*-Heptyldihydro-2(3*H*)furanone (24f).** Selenide **7f** (474 mg, 1.0 mmol), bromine (1.0 mmol), and 4-pentenoic acid (200 mg, 2.0 mmol) were treated as described to give 266 mg (54%) of selenolactone **23** and 94 mg (54%) of $\gamma$-lactone **24f**.[22]

**Preparation of 5-Octyldihydro-2(3*H*)furanone (24g).** Selenide **7g** (244 mg, 0.50 mmol), bromine (0.50 mmol), and 4-pentenoic acid (100 mg, 1.0 mmol) were treated as described to give 246 mg (75%) of selenolactone **23** and 70 mg (73%) of $\gamma$-lactone **24g**.[22]

**Preparation of 5-(Ferrocenylselenomethyl)tetrahydro-2*H*-pyran-2-one 26 and 6-*n*-Butyltetrahydro-2*H*-pyran-2-one (27c).** Selenide **7c** (325 mg, 0.75 mmol), bromine (0.75 mmol), and 5-hexenoic acid (171 mg, 1.5 mmol) were treated as described to give 229 mg (59%) of selenolactone **26** and 49 mg (48%) of $\delta$-lactone **27c**.[23c]

For **26**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.91 (m, 1H), 4.42 (t, $J$ = 1.5 Hz, 1H),4.415 (m, 1H), 4.38 (t, $J$ = 1.5 Hz, 1H), 4.29 (s, 5H), 4.27(s, 5H), 4.20 (m, 2H), 4.08 (br s, 1H), 3.96 (br s, 1H), 3.40 (br s, 2H), 3.03 (dd, $J$ = 5, 12.5 Hz 1H), 2.93 (dd, $J$ = 5, 12.5 Hz, 1H), 2.86−2.81 (m, 2H), 2.59−2.51 (m, 2H), 2.42 (m, 2 H), 2.20 (m, 1H), 2.13 (m, 1H), 1.94−174 (m, 4H), 1.61−1.34 (m, 16 H), 1.07 (br s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 171.2, 171.1, 167.2, 167.0, 89.4, 88.2, 80.4, 80.2, 75.6, 74.9, 73.3, 71.3, 68.1, 68.0, 67.9, 67.6, 67.6, 65.9, 50.3 (br), 46.0 (br), 33.2, 32.9, 29.5, 29.4, 27.4, 27.3, 21.1, 18.4, 15.3; IR (film, NaCl) 1737 cm$^{-1}$; HRMS (ESI) *m*/*z* 505.0815 (calcd for $C_{23}H_{31}NO_3Fe^{80}Se$: 505.0813).

**Preparation of 6-*n*-Pentyltetrahydro-2*H*-pyran-2-one (27d).** Selenide **7d** (222 mg, 0.50 mmol), bromine (0.50 mmol), and 5-hexenoic acid (114 mg, 1.0 mmol) were treated as described to give 163 mg (64%) of selenolactone **26** and 54 mg (64%) of $\delta$-lactone **27d**.[23d]

**Preparation of 6-*n*-Hexyltetrahydro-2*H*-pyran-2-one (27e).** Selenide **7e** (468 mg, 1.0 mmol), bromine (1.0 mmol), and 5-hexenoic acid (228 mg, 2.0 mmol) were treated as described to give 227 mg (45%) of selenolactone **26** and 116 mg (63%) of $\delta$-lactone **27e**.[23a]

**Preparation of 6-*n*-Heptyltetrahydro-2*H*-pyran-2-one (27f).** Selenide **7f** (427 mg, 0.90 mmol), bromine (0.90 mmol), and 5-hexenoic acid (225 mg, 1.8 mmol) were treated as described to give 326 mg (72%) of selenolactone **26** and 80 mg (47%) of $\delta$-lactone **27f**.[23d]

**Preparation of 4-*n*-Butyldihydro-2(3*H*)-furanone (28).** Selenide **7d** (222 mg, 0.50 mmol), bromine (0.50 mmol), and 3-butenoic acid (86 mg, 1.0 mmol) were treated as described to give 14 mg (19%) of $\gamma$-lactone **28**[21] and 60 mg (51%) of diselenide **9**.

**Preparation of 5-(Ferrocenylselenomethyl)-3,3-diphenyltetrahydro-2-furanone 33.** Selenide **7f** (238 mg, 0.50 mmol), bromine (0.50 mmol), and 2,2-diphenyl-4-butenoic acid (126 mg, 0.5 mmol) were treated as described to give 159 mg (45%) of lactone **33** as a mixture of diastereomers and 10 mg (45%) of selenide **7f**.

For **33**: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.2−7.5 (m, 10H), 4.58 (m, 1H), {[4.42 (s), 4.45 (t, $J$ = 2.5 Hz), 4.38 (t, $J$ = 2.5 Hz), 4.31 (m), 4.19 (s), 4.17 (s), 4.24 (s), 4.22 (s)], 8H}, 4.05 (br m, 2H), {[3.24 (m), 3.17 (m), 2.90 (m), 2.70 (m)], 4H}, 2.55 (br s, 3H), 2.50 (br s, 3H), 1.05 (br s, 3H), 1.00 (br s, 3H); IR (film, NaCl) 1774 cm$^{-1}$; HRMS (ESI) *m*/*z* 643.1282 (calcd for $C_{34}H_{37}FeNO_3{}^{80}Se$: 643.1288). Anal. Calcd for $C_{36}H_{43}FeNO_3Se$: C, 64.29; H, 6.44; N, 2.08. Found: C, 64.32; H, 6.37; N, 1.96.

**Preparation of 5-(Bromomethyl)dihydro-2(3*H*)furanone (17).** Bromine (1 mL of a 1 M solution in benzene, 1.0 mmol) was added to a solution of **29** (342 mg, 1.0 mmol)[16,17] in 5 mL of benzene at 0 °C. After 0.5 h, 4-pentenoic acid (100 mg, 1.0 mmol) was added and the resulting mixture was heated at reflux for 24 h. The reaction

mixture was diluted with 20 mL of $CH_2Cl_2$. The resulting solution was washed with 10% HCl (3 × 50 mL), 10% $K_2CO_3$ (20 mL), and water; dried over $Na_2SO_4$; and concentrated in vacuo. The crude product was purified via chromatography on $SiO_2$ eluted with ethylacetate/hexanes (10:90) to give 68 mg (38%) of bromolactone **17**[25] and 290 mg (85%) of selenide **29**.

**Computational Details.** Density functional theory (DFT) computations were performed using the Gaussian 03 (G03)[26] and the Amsterdam Density Functional (ADF)[27] software packages. The three-parameter hybrid functional B3LYP was used for the G03 computations, along with the LANL2DZ pseudopotential Gaussian-type basis set. In the ADF calculations, we have used the BP86 functional, a polarized triple-ζ Slater-type frozen core basis (TZP, with the 1s shell frozen for C, N, O, F; 1s3p frozen for Se and Br; 1s2p frozen for Fe; and 1s4p frozen for iodine), and the spin-free zeroth-order regular approximation (ZORA) for relativistic effects. Optimized structures were initially obtained with B3LYP/LANL2DZ and characterized by harmonic frequencies computations. Although the LANL2DZ basis is not particularly flexible, trends among related structures should be able to demonstrate whether there are any noteworthy interactions for the Se−C bond related to the Se environment that might be related to the peculiar reactivity observed experimentally. The computations at the BP86/TZP level were carried out to confirm whether using a more flexible basis set leads to the same conclusions.

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**Supporting Information Available:** List of spectral data for lactones **24**, **27**, and **28**; $^1$H and $^{13}$C NMR spectra for selenides **4**−**6**, **7c**, and **7f**−**h** and diselenide **9**; $^1$H NMR spectrum of the reaction mixture from the reaction of **13** with 4-pentenoic acid; $^1$H and $^{13}$C NMR spectra for selenolactones **19**, **22**, and **23**, γ-lactone **24g**, selenolactone **26**, δ-lactone **27f**, and γ-lactone **28**; Figure S1 for the DFT optimized geometry of **35A**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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