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Maleimide-Modified Phosphonium Ionic Liquids: A Template Towards (Multi)Task-Specific Ionic Liquids

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Abstract: The synthesis and characterization of several compounds representing a new class of multitask-specific phosphonium ionic liquids that contain a maleimide functionality is reported. The maleimide moiety of the ionic liquid (IL) is shown to undergo Michael-type additions with substrates containing either a thiol or amine moiety, thus, serving as a template to introduce wide structural diversity into the IL. Multitask-specific ILs are accessible by reaction of the maleimide with Michael donors that are capable of serving some function. As a model example to illustrate this concept, a redox active ferrocenyl thiol was incorporated and examined by cyclic voltammetry. Because the maleimide moiety is highly reactive to additions, the task-specific ionic liquids (TSILs) are prepared as the furan-protected Diels–Alder maleimide. The maleimide moiety can then be liberated when required by simple heating.

Keywords: high-pressure chemistry · ionic liquids · maleimide · Michael addition · phosphonium

Introduction

Recent advances in the synthesis and development of novel ionic liquids (ILs) have diverged from their conventional predecessors, such as N-alkylated imidazolium salts, to focus on producing task-specific ionic materials. The initial concept and the corresponding definition of a task-specific ionic liquid (TSIL) was first proposed by J. H. Davis, Jr. who defined TSILs as an organic salt that has a covalently bound functional group on the cation and/or anion, and behaves not only as the reaction medium, but serves secondary function, for example, as a reactant, or a catalyst.[1] The structural design and functionality of the organic salt imposes the desired property or characteristic for the intended purpose, such as ILs that act as ligands for transition-metal catalysts,[2] or capture agents for CO_2[3] and heavy metals.[4] Task-specific ionic liquids do not need to be limited to molecules that fit the initial description given by Davis, Jr., but rather can include any molecule that exhibits the defining properties of an ionic liquid, such as melting point below 100 °C, negligible vapor pressure, large liquid range, and most importantly, contains a covalently bound substituent, which performs any function for a target application. Thus, any ionic liquid synthesized for a specific application may be deemed a TSIL even though it may not necessarily be used as the reaction medium or solvent. Examples include functionalized salts that act as reactive precursors for functional materials, such as thiol-terminated phosphonium ionic liquids (PILs) for superhydrophobic coatings[5] or disulfide-tethered imidazolium salts, which are used to form IL-protected Au nanoparticles.[6]

In the aforementioned examples, each TSIL was separately synthesized for the required task, which can often be a complicated and time consuming process. A more practical approach is to prepare an ionic liquid that contains a functional group moiety that is reactive towards a broad variety of substrates, which can then be utilized as a template to introduce task-specific functionality from a single starting material.[7] Task-specific ionic liquids that bear a reactive hydroxyl functional group, pioneered by Bazureau et al.[8] and further extended by others,[7,9] exploited this type of concept and developed TSILs as liquid supports for ionic-liquid-

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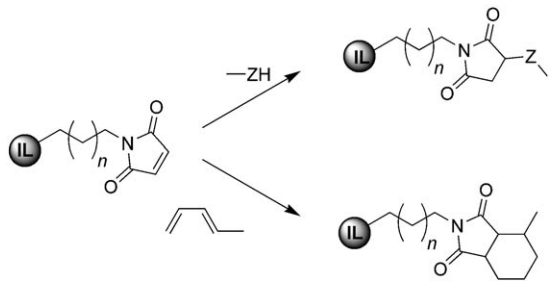
phase organic synthesis; a methodology that is analogous to solid-support synthesis.

An alternative and versatile reactive moiety that could be incorporated into the structure of an IL to serve as a template TSIL, which is presented in this work, is the N-substituted maleimide. Maleimide is a cyclic unsaturated imide and has a symmetrical and activated double bond that can act as a dienophile in [4+2] cycloaddition reactions, as a dipolarophile in [3+2] cycloaddition reactions, as well as an electrophile in Michael-type addition reactions (Scheme 1).



Scheme 1. Schematic representation of a maleimide-functionalized IL that participates in Michael addition (top) and Diels–Alder (bottom) reactions.

By incorporating the maleimide moiety into the structure of an IL its wide reactivity allows one to incorporate additional functionality for specific tasks as required. The reaction of particular interest here, as proof of concept, is the Michael addition reaction. Michael additions to maleimides are often high yielding and versatile because maleimides react with a variety of nucleophiles (thiols, amines, carbanions) that can be used to incorporate structural diversity from a single IL platform, circumventing the tedious synthesis of a unique IL for each task. The versatility is such that many maleimide-modified reagents are sold commercially. They are mostly incorporated as thiol-reactive dyes to prepare fluorescent peptides, proteins, and oligonucleotides for probing biological structure and function. A number of research groups have also anchored maleimide moieties onto flat SiO_2[10] and Au self-assembled monolayers (Au/SAMs)[11] to serve as traps for thiols by the Michael addition reaction. Thiols and amines are the primary nucleophiles that are used in the formation of biochip assemblies on SiO_2 and Au/SAMs. For example, biomolecules,[11a,b] carbohydrates,[11c,d] as well as a number of peptides have been used.[11e]

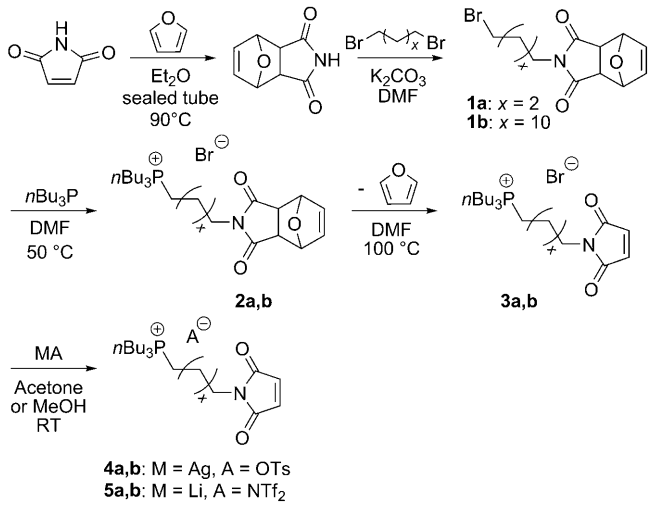
As far as we are aware, there are no reports for the preparation of maleimide-modified ILs, and incorporating this versatile and reactive functionality into the ionic framework is an attractive concept specifically for the formation of TSILs. In this context, tethering maleimide to a phosphonium salt can alter the solubility properties of the system and combines the benefits of ionic liquids, such as large electrochemical windows, negligible vapor pressures, and high thermal stabilities, with multifaceted functionality. Herein, we describe the synthesis and characterization of maleimide-functionalized phosphonium ionic liquids, which can be utilized as TSIL. Given the maleimide renders the material available for further reactivity, such as Michael addition reaction, the maleimide PIL subsequently behaves as a template, which enables the synthesis of a library of TSILs. With a particular focus on the Michael addition reaction, we demonstrate a facile and an unprecedented method for the preparation of highly functionalized ionic liquids. Ionic liquids based on the phosphonium cation were used herein for their higher thermal and chemical stability and to showcase their potential in alternative applications.

One of the shortcomings of maleimide-modified reagents is the poor storage capability, given its highly reactive nature to Michael addition reactions with nucleophiles. Based on a method by Workentin et al. previously employed to modify monolayer-protected gold nanoparticles,[12] maleimide can be stored as its Diels–Alder-protected furan derivative, which releases the desired maleimide by simple heating. Such strategies, taking advantage of the reversibility of the maleimide–furan Diels–Alder reaction, has been used for the preparation of thermally responsive polymers and dendrimers.[13] Here the reversible Diels–Alder reaction is used simply as a maleimide protecting group. Upon deprotection, if the Michael addition reaction utilizes a donor substituent, which itself can perform a particular function, such as a ferrocenyl thiol that acts as an electrochemical tag, the maleimide-modified PIL then functions as a multitask specific IL as demonstrated herein.

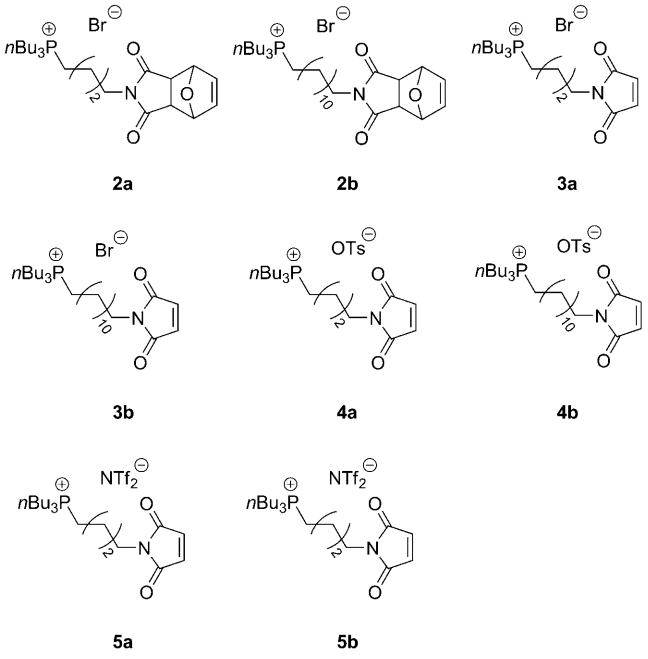
Results and Discussion

The first approach to prepare the maleimide-tethered phosphonium salts **3a** and **3b** involved the quaternization of tri-*n*-butylphosphine with *N*-(bromobutyl)maleimide. However, characterization of the resulting product displayed evidence for the Michael addition of the $n\mathrm{Bu_3P}$ across the C=C of the maleimide ($^{31}P\{^1H\}$ NMR: $\delta = 17$ ppm).[14] An alternate procedure, in which the maleimide moiety was first protected as its furan Diels–Alder product was selected in order to avoid these complications.

Specifically, and as illustrated in Scheme 2, to encourage the formation of a phosphonium salt by an S_N2 mechanism, the maleimide was protected with furan through a Diels–Alder cycloaddition in a sealed tube at 90 °C. This substrate was then converted to compounds **1a** and **1b** by reaction with the corresponding 1,4-dibromobutane (**a**) or 1,12-dibromododecane (**b**) in DMF with potassium carbonate. After the addition of **1a** or **1b** to a solution of tri-*n*-butylphosphine the quaternization reaction proceeded, which was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Upon complete consumption of $n\mathrm{Bu_3P}$ ($^{31}P\{^1H\}$ NMR: $\delta = -32$ ppm), the solvent was removed in vacuo. Characterization of the resulting yellow viscous liquid by multinuclear NMR spectroscopy displayed the distinctive phosphonium chemical shift ($^{31}P\{^1H\}$ NMR: $\delta = 33$ ppm vs. $\delta(n\mathrm{Bu_4P^+}) = 32$ ppm),[15] which in conjunction with mass spectrometry and elemental analy-



Scheme 2. Synthetic route for the preparation of maleimide-modified phosphonium ionic liquids.



sis confirmed the presence of the furan-protected phosphonium salts **2a** and **2b**. The salts were isolated in good yields (81–86%) and no further purification was required. Subsequently, **2a** and **2b** were dissolved in DMF and heated to 100°C in an open vial for ≈18 h to deprotect the maleimide by liberating furan, which easily dissipated, to yield **3a** and **3b**. Proton NMR spectroscopy of **3a** and **3b** revealed the complete disappearance of signals that correspond to those of alkenyl and bridgehead protons associated with the furan–maleimide Diels–Alder adduct (^{1}H NMR: $\delta = 5.52$, 5.21, 2.90 ppm) and the emergence of the alkenyl protons on the maleimide (^{1}H NMR: $\delta = 5.72$ ppm), thus, confirming that the retro-Diels–Alder reaction proceeded quantitatively yielding the deprotected maleimide phosphonium salts **3a** and **3b**.

Given that the melting point and other physical properties of ionic liquids can be tuned by exchanging the cation–anion pair, several counter anions were incorporated by using metathetical routes. Anion exchange of **3a** and **3b** was carried out by using LiOTs or LiNTf$_2$ (OTs = *p*-toluenesulfonate, NTf$_2$ = bis(trifluoromethanesulfonyl)imide) in acetone or methanol to afford the corresponding products **4a** and **4b** and **5a** and **5b**. The metathesis of **2a** and **2b** followed by the thermal deprotection to yield **4a** and **4b** or **5a** and **5b** was complicated because the high temperatures prompted the Michael-type addition between the anion and the maleimide upon release of the furan. Evidence for this addition was observed by ^{1}H NMR spectroscopy, which revealed the loss of the alkenyl protons on the maleimide and the formation of the characteristic proton splitting pattern imposed by the generation of the chiral center on the succinimide. Further characterization and isolation of this adduct was not pursued.

The essential thermal characteristics of the phosphonium ionic liquids **2**–**5** were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 1). In all cases, the phosphonium salts were viscous liquids with glass transitions ranging from −24 to −49°C. There were no crystallization or melting points observed for the viscous liquids indicating that the materials were completely amorphous. The salt **2a** was the only exception. At room temperature the material is a waxy solid and exhibits a melting point slightly greater than 100°C. Thermogravimetric analysis studies by using heat ramp analysis depicted decomposition temperatures ranging from 365 to 446°C, suggesting the ionic liquids have excellent thermal stabilities. Thermogravimetric analysis is also an exceptional tool to observe the retro-Diels–Alder deprotection of the phosphonium salts **2**. A step corresponding to 10–12% mass loss (calculated: 13.58% (**2a**), 11.10% (**2b**); experimental: 12% (**2a**), 10% (**2b**)) correlates to the liberation of furan. The subsequent step clearly reflects the formation of the maleimide PIL and, given the onset temperature, occurs at exactly the same temperature as the decomposition of the maleimide PIL **3** (Figure 1a, Table 1). The exchange of anions does indeed effect the thermal properties of the PILs, especially in the case of **5** where the thermal stability is increased by 70°C (Table 1).

Table 1. Thermal characteristics of the phosphonium ionic liquids.

Entry	PIL	T_g [°C][a]	T_d [°C][b]	T_{MA} [°C][c]
1	**2a**	112[d]	134[e] 365	254
2	**2b**	−42	132[e] 374	224
3	**3a**	−36	365	194
4	**4a**	−24	395	242
5	**5a**	−49	440	296
6	**3b**	−35	373	216
7	**4b**	−40	426	241
8	**5b**	−35	446	291

[a] Onset of glass transition. [b] Onset of decomposition. [c] T_{MA} = onset temperature for the Michael addition. [d] Melting point. [e] Onset temperature for retro-Diels–Alder reaction.

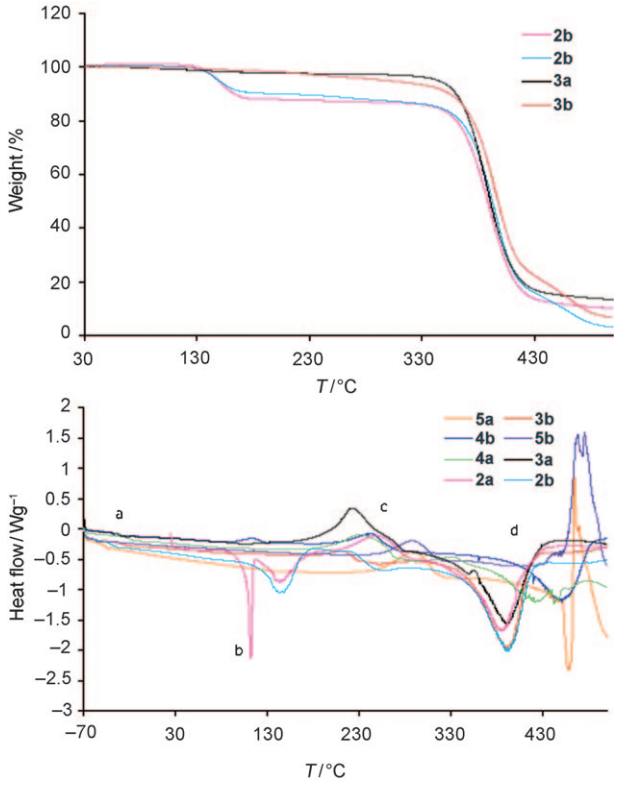
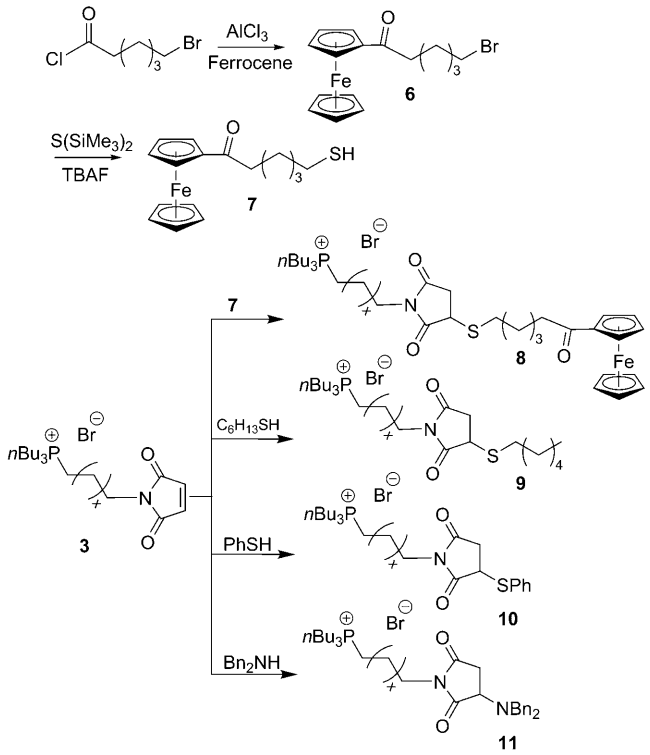


Figure 1. a) Comparison of TGA thermograms of **2** displaying the liberation of furan followed by subsequent decomposition of the resulting deprotected phosphonium salt and **3**, the synthesized maleimide PILs; b) DSC thermograms of **2–5** displaying the exotherm for T_g (a), T_m (b), the Michael-type addition (c),and the decomposition (d).



Scheme 3. Schematic representation of the Michael addition reactivity of **3** with thiols and an amine (TBAF = tetra-*n*-butylammonium fluoride).

The DSC experiments included heating the samples past the decomposition temperatures to determine if any phase transitions indicative of chemical transformations with zero mass loss occurred. An exotherm was observed for compounds **3–5** ranging from 200 to 300 °C, which is indicative of a Michael-type addition of the anion to the C=C on the maleimide (Figure 1b, Table 1). This result, along with the observations from the attempted anion exchange reactions of **2**, further suggests that Michael addition with the anion occurs at elevated temperatures. The same type of exotherm was noted for **2** in the DSC thermogram after the feature representing the retro-Diels–Alder deprotection. Therefore the salts **3–5** are only stable at temperatures less than 300 °C in the solid state and approximately 120 °C in solution, which nonetheless, is more than sufficient for most applications given that the maleimide is reactive, especially towards Michael addition with sulfhydryl groups.

With the maleimide-tethered phosphonium ionic liquids **3** in hand, as proof of concept, we next investigated their reactivity towards a few model thiol (**7**, hexanethiol, and benzenethiol) and amine (dibenzylamine) nucleophiles to form the corresponding Michael adducts **8–11** (Scheme 3). The 6-ferrocene-hexanone-1-thiol (**7**) was synthesized to act both as a Michael donor and as a probe on account of the existence of the electrochemically active center ferrocene. In order to prepare such a complex, first 6-bromo-1-ferrocene-hexanone (**6**) was synthesized by a Friedel–Crafts acylation between ferrocene and 6-bromo-hexanoxyl chloride, which was then converted to **7** in the presence of hexamethyldisilylthiane. Proton NMR spectroscopy was used to assess the formation of the ferrocenyl thiol **7**, where the most salient feature was the emergence of a triplet and an overlapping doublet of triplets (^{1}H NMR: $\delta = 1.44$ and 2.55 ppm, respectively) indicative of the thiol and the adjacent methylene protons, thereby, conclusively revealing the generation of **7**.

Preliminary assessment of the Michael addition reactivity of **3** with hexanethiol at room temperature and atmospheric pressure in $CDCl_3$ was sluggish and required long reaction times (60 h) to afford product **9**. Increasing the reaction temperature to 60 °C reduced the reaction time. Michael additions and similar transformations are also known to experience acceleration at high pressures;[16] thus, hyperbaric conditions were employed to prepare **8** and **11**. Indeed, the duration of the reaction was shortened significantly for the ferrocenyl thiol **7** and dibenzylamine when the reactions were carried out at 11 Katm (the default operating pressure of our reactor). Evidence for the complete transformation to the succinimide adducts **8** and **11** was easily revealed by using ^{1}H NMR spectroscopy, which established the disappearance of the alkenyl protons and the appearance of the distinctive proton splitting pattern enforced by the generation of the chiral center on the resulting succinimide. The isolation of **8** involved the removal of the excess thiol by extraction with hexane and **11** was merely subjected to high vacuum at elevated temperatures (100 °C) to remove the

excess dibenzylamine, affording the viscous liquids in high yields (80–99%) with no need for further purification. Therefore, even sluggish nucleophiles were added efficiently either by gentle heating or at high pressure to eliminate any competing reactions where the anion acts as a nucleophile at raised temperatures.

As an alternative to the conventional and high-pressure methodologies employed to afford products, **8**, **9**, and **11** a one-pot approach was selected for the synthesis of **10**. This was accomplished simply by heating neat **2a/b** at 100 °C in the presence of the nucleophile, benzenethiol, for 30 h to yield product **10**. It should be noted that **2a** and **2b** are solids at room temperature and upon heating to 100 °C, which activates the retro Diels–Alder reaction and liberates furan, the resulting product **3** is a liquid. This ionic liquid is then used as both the reaction medium, as well as a reagent in classical TSIL fashion and participates in a Michael-type addition with the nearby nucleophile. After extraction with hexane product **10** was isolated in good yield (88%), showing that a one pot approach may be employed as a more practical way to afford Michael adducts.

The maleimide PIL is task-specific given its propensity to react as a Michael acceptor. Nucleophiles, which are capable of performing some function, for example, as an electrophore, fluorophore, or acid/base donor/acceptor, facilitate the formation of multitask-specific ILs. The reaction of **3** with ferrocenyl thiol **7** produces **8** and introduces an electroactive ferrocenyl group, illustrating this concept. Cyclic voltammetry (CV) of **8** was used to verify the addition of the ferrocenyl thiol **7** (Figure 2). Cyclic voltammetry of 1 mM solutions of compound **8a** and **8b** in dichloromethane that contain 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte show reversible redox waves with standard oxidation potentials of $E°=255$ and 253 mV, respectively, relative to ferrocene ($E°=0$ mV). In comparison, compound **3** has no significant redox activity with the exception of a broad irreversible oxidation due to the bromide counterion in **3b**. The oxidation of the Br^- counterion gives rise to the slightly broadened oxidative waves of **8a** and **8b**. Comparatively, the CV of a 1 mM solution of the NTf_2 salt of **8b** in CH_2Cl_2/0.1 M TBAP has a sharper oxidative wave and $E°=321$ mV versus ferrocene given the lack of the redox active Br^- counterion. After each experiment the system was calibrated against ferrocene/ferrocenium couple set to 0.0 mV.

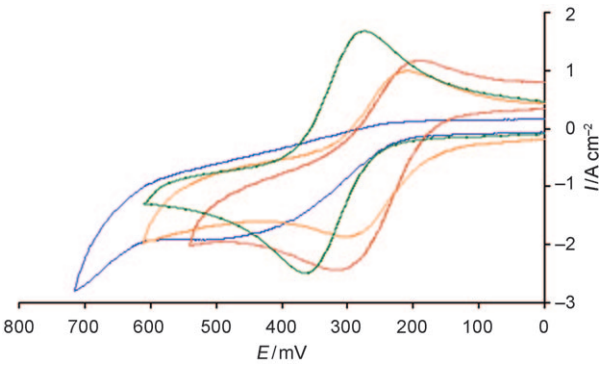


Figure 2. Cyclic voltammograms of the maleimide PIL **3b** (blue) and the ferrocenyl thiol Michael adducts **8a** (orange), **8b** (red) and the NTf_2 salt of **8b** (green).

Conclusion

The synthesis and characterization of maleimide-modified phosphonium ionic liquids, which showcase a versatile platform for the preparation of other ILs have been reported. Subsequent formation of the succinimidyl PILs by Michael addition with reactive nucleophiles clearly demonstrates the feasibility of incorporating additional substituents into the IL framework and reflects their capability to act as a task-specific ionic liquid. Using the methodology of protecting the maleimide fragment by employing Diels–Alder chemistry allows the storage of the PIL until further reactivity is required. A one-pot approach where the deprotection through liberation of the furan to generate the maleimide in the presence of a nucleophile to form the corresponding Michael adduct in a single step was also realized. The flexibility of the reactivity at the maleimide moiety allows the attachment of fluorophores, electrophores, or biomolecules, which may lead to further applications of these ILs as functional materials in sensor technology. Such functionalities and others may also alter the IL in order to improve the solubility or bioavailability. It is important to note that non-composite IL sensors are novel commodities that remain elusive in the literature and our methodology is conducive to realizing such materials. The strategy employed here of using a maleimide-tagged ionic liquid as a template for a TSIL can be extended to other IL platforms easily and several methods are currently under investigation, including studies that explore the reactivity of dienophiles and 1,3-dipoles with maleimide PILs in Diels–Alder and 1,3-cycloaddition chemistry.

Experimental Section

The tri-*n*-butylphosphine was received from Cytec Industries and was distilled prior to use (0.01 Torr; 80 °C) and stored in a nitrogen-filled MBraun Labmaster 130 glove box. The compounds 1,12-dibromododecane, 1,4-dibromobutane, furan, silver *p*-toluenesulfonate (Aldrich), maleimide (Alfa Aesar), potassium carbonate, diethyl ether, and *N*,*N*-dimethylformamide (Caledon) were used as received. Lithium bis(trifluoromethanesulfonyl)imide (Fluka) was used as received and stored in the glove box. The precursors to **2**, including 6-*endo*/*exo*-tetrahydrophthalimide and (3,6-*endo*/*exo*-tetrahydrophthalimide)bromoalkane, were prepared by using modified literature procedures.[12b] All manipulations with phosphines were carried out in a nitrogen-filled MBraun Labmaster 130 glove box or by using standard Schlenk techniques. The *N*,*N*-dimethylformamide was dried by using an Innovative Technologies Inc. controlled atmospheres solvent purification system, which utilize dual-alumina columns, and was collected under vacuum and stored under a nitrogen atmosphere in a Strauss flask. Deuterated solvents, [D_3]chloroform and [D_6]acetone (Cambridge Isotope Laboratories) were stored over 4 Å sieves.

Solution ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer unless otherwise noted (^{1}H: 400.09 MHz; ^{13}C: 100.52 MHz; ^{31}P: 161.82 MHz). All samples for ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectroscopy were referenced to the residual protons or ^{13}C nuclei in the NMR solvent relative to $(CH_3)_4Si$ (δ [ppm]); ^{1}H: [D_3]chloroform $\delta = 7.26$, [D_6]acetone $\delta = 2.05$ ppm; $^{13}C\{^{1}H\}$: [D_3]chloroform $\delta = 77.0$ ppm). ^{31}P chemical shifts were reported relative to an external standard (85% H_3PO_4: $\delta = 0.00$ ppm). The high-pressure reactions were carried out on a LECOTempres High-Pressure chemical reactor at 11000 atm, which is the default pressure under normal operating conditions. (CAUTION: Working with high-pressure reactors can be dangerous. Follow manufacturer guidelines for safe operation.) Mass spectrometry measurements were recorded in positive and negative ion modes by using an electrospray ionization Micromass LCT spectrometer and exact masses were recorded on a MAT 8200 Finnigan High Resolution Mass Spectrometer. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. The decomposition temperatures were determined by using Thermoravimetric analysis (TGA) on a TGA/SDTA 851^{e} Mettler Toledo instrument. A 0.005–0.010g sample was loaded in an Al_2O_3 crucible (70 μL) and heated at a rate of 10 °C min^{-1} over a temperature range of 25–600 °C under a flow of N_2 (100 mL min^{-1}). Melting and glass transition points were determined by using differential scanning calorimetry (DSC) on a DSC 822^{e} Mettler Toledo instrument. A 0.005–0.010 g sample was loaded in a sealed, pierced aluminum pan (40 μL) and cooled to −70 °C where the temperature was sustained for 15 min, followed by heating to 500 °C with 10 °C min^{-1}. Cyclic voltammetry was preformed by using a Perkin–Elmer Par 263A potentiostat interfaced to a computer equipped with PAR 270 electrochemistry software. The working electrode was a 1 mm diameter glassy carbon rod, Tokai, GC-20, sealed in glass tubing. The counter electrode was a Pt wire. The reference electrode was a silver wire immersed in a glass tube with a sintered end containing 0.1 M tetrabutylammonium perchlorate (TBAP) in dichloromethane. After each experiment, the system was calibrated against the ferrocene/ferricinium couple at 0.5 V versus saturated calomel electrode (SCE).

Preparation of 2a: Neat tri-*n*-butylphosphine (0.351 g, 1.732 mmol) was added dropwise to a solution of 4-(3,6-endoxo-Δ4-tetrahydrophthalimide)bromobutane (0.518 g, 1.732 mmol) in dry DMF (5 mL) in the glove box and was subsequently heated to 50 °C for 17 h under a flow of nitrogen. The DMF was removed by oil pump vacuum. The viscous oil was dissolved in CH_2Cl_2 (2 mL) and titrated with Et_2O (20 mL). The resulting emulsion was cooled to −30 °C and upon separation of product, the solvent was decanted and the extraction procedure was repeated. The residual solvent was removed in vacuo, yielding the 4-(3,6-endoxo-Δ4-tetrahydrophthalimide)butyl-tri-*n*-butylphosphonium bromide (**2a**) as a viscous yellow oil (0.705 g, 1.406 mmol, 81%). $T_m = 112$ °C; $T_d = 134$ °C (12% mass loss), 365 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.52$ (s, 2H), 5.21 (s, 2H), 3.56 (t, $^{3}J = 4$ Hz, 2H), 2.93 (s, 2H), 2.54 (m, 2H), 2.41 (m, 6H), 1.83 (quintet, $^{3}J = 4$ Hz, 2H), 1.52 (m, 14H), 0.97 ppm (t, $^{3}J = 8$ Hz, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 173$, 131, 80.7, 47.3, 37.0, 28.0 (d, ^{3}J(C,P) = 15.7 Hz), 23.7 (d, ^{3}J(C,P) = 15.2 Hz), 23.4 (d, ^{2}J(C,P) = 4.7 Hz), 18.7 (d, ^{1}J(C,P) = 49 Hz), 18.6 (d, ^{1}J(C,P) = 48.1 Hz), 18.3 (d, ^{2}J(C,P) = 4.5 Hz), 13.2 ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 33.6$ ppm (s); MS (ESI): m/z^+ (%): 422.1 ([M^+], 35), 925.5 ([M_2Br^+], 2); m/z^- (%): 582.0 ([MBr_2^-], 50), 1083.3 ([$M_2Br_3^-$], 17).

Preparation of 2b: Tri-*n*-butylphosphine (0.216 g, 1.067 mmol) was added dropwise to a solution of 12-(3,6-endoxo-Δ4-tetrahydrophthalimide)bromododecane (0.400 g, 0.973 mmol) in dry DMF (10 mL) and heated to 50 °C for 17 h under a flow of nitrogen. A workup procedure analogous to **2a** yielded **2b** as a viscous yellow oil (0.456 g, 0.743 mmol, 86%). $T_g = -42$ °C; $T_d = 132$ °C (10% mass loss, −furan), 374 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.51$ (s, 2H), 5.26 (s, 2H), 3.46 (t, $^{3}J = 7.6$ Hz, 2H), 2.83 (s, 2H), 2.48 (m, 8H), 1.53 (m, 20H), 1.24 (m, 12H), 0.98 ppm (t, $^{3}J = 7.2$ Hz, 9H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): $\delta = 176.0$, 133, 80.6, 47.1, 38.7, 32.5, 30.5 (d, ^{3}J(C,P) = 13.7 Hz), 29.11, 29.06, 28.98, 28.7 (d, ^{4}J(C,P) = 11.5 Hz), 27.3, 23, 25.5, 23.7 (d, ^{3}J(C,P) = 14.9 Hz), 23.5 (d, ^{2}J(C,P) = 4.5 Hz), 21.6 (d, ^{2}J(C,P) = 4.5 Hz), 19.1 (d, ^{1}J(C,P) = 48.3 Hz), 18.9 (d, ^{1}J(C,P) = 42 Hz), 13.2 ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 33.4$ ppm (s); MS (ESI): m/z^+ (%): 534.4 ([M^+], 100), 1147.7 ([M_2Br^+], 17); m/z^- (%): 699.9 ([MBr_2^-], 70).

Preparation of 3a: The 4-(3,6-endoxo-Δ4-tetrahydrophthalimide)butyl-tri-*n*-butylphosphonium bromide (**2a**) (0.667 g, 1.331 mmol) was dissolved in DMF (7 mL) and heated in an open vial at 100 °C for 20 h to liberate furan. ^{1}H NMR spectroscopy confirmed the reaction was quantitative. The DMF was removed in vacuo, the resulting mixture was dissolved in CH_2Cl_2 (2 mL) and Et_2O (20 mL) was added. The emulsion was cooled to −30 °C and upon separation of product, the solvent was decanted and the extraction procedure was repeated. The residual solvent was removed in vacuo to afford 4-(maleimidyl)butyl-tri-*n*-butylphosphonium bromide (**3a**) as a clear brown viscous liquid (0.437 g, 1.009 mmol, 76%). $T_g = -36$ °C; $T_d = 365$ °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.72$ (s, 2H), 3.60 (t, $^{3}J = 4$ Hz, 2H), 2.64 (m, 2H), 2.44 (m, 6H), 1.83 (quintet, $^{3}J = 8$ Hz, 2H), 1.53 (m, 14H), 0.98 ppm (t, $^{3}J = 8$ Hz, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 170.6$, 134.0, 35.9, 29.2 (d, ^{3}J(C,P) = 15.6 Hz), 23.7 (d, ^{3}J(C,P) = 15.3 Hz), 23.5 (d, ^{2}J(C,P) = 4.7 Hz), 18.8 (d, ^{1}J(C,P) = 47.0 Hz), 18.6 (d, ^{1}J(C,P) = 47.7 Hz), 18.7 (d, ^{2}J(C,P) = 4.1 Hz), 13.2 ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 33.7$ ppm (s); MS (ESI): m/z^+ (%): 353.9 ([M^+], 100), 787.5 ([M_2Br^+], 30), 1222.5 ([$M_3Br_2^+$], 1); m/z^- (%): 514.1 ([MBr_2^-], 25), 947.3 ([$M_2Br_3^-$], 1).

Preparation of 3b: The 12-(3,6-endoxo-Δ4-tetrahydrophthalimide)dodecyl-tri-*n*-butylphosphonium bromide (**2b**) (0.627 g, 1.022 mmol) was dissolved in DMF (7 mL) and heated in an open vial at 100 °C for 15 h to remove furan. ^{1}H NMR spectroscopy confirmed the reaction was quantitative. A workup procedure analogous to **3a** afforded 12-(maleimidyl)dodecyl-tri-*n*-butylphosphonium bromide (**3b**) as a clear brown viscous liquid (0.355 g, 0.650 mmol, 64%). $T_g = -35$ °C; $T_d = 373$ °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.68$ (s, 2H), 3.50 (t, $^{3}J = 7.2$ Hz, 2H), 2.47 (m, 8H), 1.54 (m, 18H), 0.98 ppm (t, $^{3}J = 8$ Hz, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 170.1$, 133.4, 37.0, 32.0, 30.0 (d, ^{3}J(C,P) = 14.5 Hz), 28.6, 28.5, 28.4, 28.2 (d, ^{4}J(C,P) = 9.7 Hz), 27.7, 25.9, 25.1, 23.1 (d, ^{3}J(C,P) = 15.2 Hz), 23.0 (d, ^{2}J(C,P) = 4.7 Hz), 21.0 (d, ^{2}J(C,P) = 4.5 Hz), 18.5 (d, ^{1}J(C,P) = 47 Hz), 18.3 (d, ^{1}J(C,P) = 47.1 Hz), 12.7 ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 33.5$ ppm (s); MS (ESI): m/z^+ (%): 463 ([M^+], 100), 1013.7 ([M_2Br^+], 5); m/z^- (%): 631.2 ([MBr_2^-], 100).

Preparation of 4a: A vial wrapped in aluminum foil was charged with silver *p*-toluenesulfonate (0.367 g, 1.315 mmol) and a solution of 4-(maleimidyl)butyl-tri-*n*-butylphosphonium bromide (**3a**) (0.380 g, 0.876 mmol) in MeOH (5 mL) was added. The mixture stirred for 72 h and centrifuged, the supernatant was decanted and the AgBr was washed with MeOH (5 mL) and then CH_2Cl_2 (5 mL). The combined supernatant was filtered through a Celite column (0.5×4 cm) and the solvent was removed in vacuo at 35 °C for 1 h. The liquid was redissolved in CH_2Cl_2 (5 mL), filtered through a Celite column, and the solvent was removed in vacuo at 35 °C for 1 h, then the filtration procedure was repeated one more time. The residual solvent was removed in vacuo at 35 °C for 13 h and then at RT for 14 h to afford 4-(maleimidyl)butyl-tri-*n*-butylphosphonium *p*-toluenesulfonate (**4a**) as a clear brown viscous liquid (0.415 g, 0.789 mmol, 90%). $T_g = -24$ °C; $T_d = 395$ °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (d, $^{3}J = 7.6$ Hz, 2H), 6.95 (d, $^{3}J = 8.0$ Hz, 2H), 5.57 (s, 2H), 3.36 (t, $^{3}J = 8$ Hz, 2H), 2.18 (m, 5H), 2.04 (m, 6H), 1.55 (quintet, $^{3}J = 8$ Hz, 2H), 1.28 (m, 14H), 0.76 ppm (t, $^{3}J = 8$ Hz, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 170.5$, 144.3, 138.3, 133.9, 128.0, 125.5, 35.7, 28.9 (d, ^{3}J(C,P) = 15.9 Hz), 23.4 (d, ^{3}J(C,P) = 15.3 Hz), 23.1 (d, ^{2}J(C,P) = 4.7 Hz), 20.8, 18.3 (d, ^{2}J(C,P) = 4.1 Hz), 17.9 (d, ^{1}J(C,P) = 47.1 Hz), 17.7 (d, ^{1}J(C,P) = 47.6 Hz), 13.0 ppm; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 33.7$ ppm (s); MS (ESI): m/z^+ (%): 354.6 ([M^+], 100), 879.1 ([M_2OTs^+], 40), 1403.4 ([$M_3OTs_2^+$], 1); m/z^- (%): 692 ([$MOTs_2^-$], 80).

Preparation of 4b: A vial wrapped in aluminum foil was charged with silver *p*-toluenesulfonate (0.119 g, 0.426 mmol) and a solution of 12-(maleimidyl)dodecyl-tri-*n*-butylphosphonium bromide (**3b**) (0.155 g, 0.284 mmol) in MeOH (3 mL) was added. The mixture was stirred for 72 h. A workup procedure analogous to **4a** gave 12-(maleimidyl)dodecyl-tri-*n*-butylphosphonium *p*-toluenesulfonate (**4b**) as a clear brown viscous liquid (0.129 g, 0.202 mmol, 71%). $T_g = -40$ °C; $T_d = 426$ °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.77$ (d, $^{3}J = 8.0$ Hz, 2H), 7.10 (d, $^{3}J = 7.6$ Hz, 2H), 5.68 (s, 2H), 3.50 (t, $^{3}J = 7.6$ Hz, 2H), 2.32 (m, 11H), 1.49 (m, 18H), 1.24

(m, 14H), 0.96 ppm (t, ^3J=8 Hz, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ=170.7, 144.4, 138.3, 133.9, 128.1, 125.8, 37.6, 32.6, 30.5 (d, ^3J(C,P)=14.6 Hz), 29.19, 29.16, 29.05, 28.6 (d, ^4J(C,P)=10.8 Hz), 28.3, 25, 25.6, 23.7 (d, ^3J(C,P)=15.2 Hz), 23.5 (d, ^2J(C,P)=4.8 Hz), 21.5 (d, ^2J(C,P)=4.5 Hz), 21.0, 18.6 (d, ^1J(C,P)=48 Hz), 18.4 (d, ^1J(C,P)=47.2 Hz), 13.2 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ=33.5 ppm (s); MS (ESI): m/z^+ (%): 466 ([M^+], 100), 1102.8 ([M_2OTs^+], 45); m/z^- (%):808.4 ([$MOTs_2^-$], 10), 1445.8 ([$M_2OTs_3^-$], 1).

Preparation of 5a: A solution of 4-(maleimidyl)butyl-tri-*n*-butylphosphonium bromide (**3a**) (0.282 g, 0.650 mmol) in acetone (5 mL) was added to lithium bis(trifluoromethanesulfonyl)imide (0.280 g, 0.976 mmol) and stirred for 72 h. The solvent was removed in vacuo, CH_2Cl_2 (5 mL) was added and the mixture was filtered twice through a Celite column (0.5×4 cm). The solvent was concentrated to 2 mL and was extracted with H_2O (2×18 mL). The aqueous layers were tested with an aqueous solution of $AgNO_3$ (10%) to confirm the complete removal of LiBr. The organic fraction was dried with $MgSO_4$ and the residual solvent was removed in vacuo to afford 4-(maleimidyl)butyl-tri-*n*-butylphosphonium bis(trifluoromethanesulfonyl)imide (**5a**) as a clear brown viscous liquid (0.362 g, 0.413 mmol, 88%). T_g=−49°C; T_d=440°C; ^1H NMR (400 MHz, $CDCl_3$): δ=5.71 (s, 2H), 3.59 (t, ^3J=6 Hz, 2H), 2.25 (m, 2H), 2.12 (m, 6H), 1.80 (quintet, ^3J=6 Hz, 2H), 1.51 (m, 14H), 0.98 ppm (t, ^3J=6 Hz, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ=170.8, 134.0, 119.6 (quartet, ^1J(C,F)=320.0 Hz), 35.5, 28.9 (d, ^3J(C,P)=15.7 Hz), 23.5 (d, ^3J-(C,P)=15.3 Hz), 23.0 (d, ^2J(C,P)=4.7 Hz), 18.0 (d, ^1J(C,P)=47.4 Hz), 18.2 (d, ^3J(C,P)=4.2 Hz), 17.7 (d, ^1J(C,P)=48.1 Hz), 12.9 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ=33.9 ppm (s); FTIR (dropcast on KBr, ranked intensity): 659 (10), 695 (5), 750 (4), 832 (6), 918 (9), 968 (16), 1099 (13), 1140 (7), 1242 (11), 1382 (12), 1408 (2), 1442 (8), 1463 (18), 1636 (20), 1705 (1), 1769 (17), 2456 (19), 2873 (14), 2933 (15), 2960 cm^{-1} (3); MS (ESI): m/z^+ (%): 354.2 ([M^+], 100), 988.4 ([M_2-(NTf_2)$^+$], 27); m/z^- (%): 279.9 ([(NTf_2)$^-$], 100), 914.0 ([M(NTf_2)$_2^-$], 1).

Preparation of 5b: A solution of 12-(maleimidyl)dodecyl-tri-*n*-butylphosphonium bromide (**3b**) (0.166 g, 0.304 mmol) in acetone (5 mL) was added to lithium bis(trifluoromethanesulfonyl)imide (0.131 g, 0.456 mmol) and stirred for 72 h. A workup procedure analogous to **5a** yielded 12-(maleimidyl)dodecyl-tri-*n*-butylphosphonium bis(trifluoromethanesulfonyl)imide (**5b**) as a clear brown viscous liquid (0.172 g, 0.230 mmol, 76%). T_g=−53°C; T_d=446°C; ^1H NMR (400 MHz, $CDCl_3$): δ=5.68 (s, 2H), 3.50 (t, ^3J=7.2 Hz, 2H), 2.14 (m, 8H), 1.52 (m, 20H), 1.26 (m, 12H), 0.99 ppm (t, ^3J=5.6 Hz, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ=170.8, 134.0, 119.8 (quartet, ^1J(C,F)=319.9 Hz), 37.8, 32.7, 30.4 (d, ^3J(C,P)=14.6 Hz), 29.4, 29.3, 29.0 (d, ^4J(C,P)=13.6 Hz), 28.7, 28.4, 26, 25.6, 23.6 (d, ^3J(C,P)=15.0 Hz), 23.3 (d, ^2J(C,P)=4.6 Hz), 21.4 (d, ^2J(C,P)=4.6 Hz), 18.6 (d, ^1J(C,P)=47.1 Hz), 18.3 (d, ^1J-(C,P)=47.3 Hz), 13.1 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ=33.7 ppm (s); FTIR (dropcast on KBr ranked intensity): 660 (8), 696 (6), 752 (4), 827 (5), 917 (12), 969 (15), 1006 (17), 1099 (10), 1115 (20), 1243 (9), 1381 (3), 1407 (11), 1442 (14), 1464 (7), 1627 (19), 1706 (1), 1769 (18), 2455 (16), 2857 (13), 2929 cm^{-1} (2); MS (ESI): m/z^+ (%): 463 ([M^+], 100), 1212.6 ([M_2(NTf_2)$^+$], 25); m/z^- (%): 279.9 ([(NTf_2)$^-$], 100), 1022 ([M(NTf_2)$_2^-$], 1).

Preparation of 6: Ferrocene (5.54 g, 35.2 mmol) was dissolved in CH_2Cl_2 (15 mL) and cooled to −15–−20°C in an ice/NaCl bath. Aluminum trichloride (2.19 g, 14 mmol) was added immediately. A solution of 6-bromo-hexanoxyl chloride (2.71 g, 12.7 mmol) in CH_2Cl_2 (5 mL) was added while the solution was kept in the ice/NaCl bath. The solution was then stirred for 2 h while warming to room temperature. The reaction was quenched by adding the solution to ice cold water (15 mL). The contents were transferred to a separation funnel and the organic layer was isolated. The aqueous layer was washed with CH_2Cl_2 (2×10 mL) and the combined organic layers were washed with distilled water until the aqueous layer became clear colorless. The organic fraction was dried with $MgSO_4$ and the solvent was removed by rotary evaporation to reveal an orange oil. 6-Bromo-1-ferrocene-hexanone was then purified by liquid column chromatography (ethyl acetate/hexane, 3:1) to yield **6** (3.78 g, 10.4 mmol, 82%). ^1H NMR (600 MHz, $CDCl_3$): δ=4.78 (t, ^3J=2.0 Hz, 2H), 4.49 (t, ^3J=2.0 Hz, 2H), 4.18 (s, 5H), 3.44 (t, ^3J=6 Hz, 2H), 2.73 (t, ^3J=7.0 Hz, 2H), 1.93 (m, 2H), 1.74 (m, 2H), 1.53 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=204.3, 79.2, 72.4, 69.9, 69.5, 39.6, 34.0, 32.8, 28.3, 23.8 ppm; FTIR (dropcast on NaCl): 3094, 2935, 2861, 1667, 1455, 1411, 1378, 1258, 1232, 1105, 1054, 1026, 1002, 824, 533, 482 cm^{-1}; HRMS: m/z: calcd for $C_{16}H_{19}OBrFe$: 361.9969; found: 361.9973.

Preparation of 7: Compound **6** (1.08 g, 3.0 mmol) and hexamethyldisilathiane (0.64 g, 0.75 mL, 3.59 mmol) were dissolved in dry THF (6 mL) and cooled to −15–−20°C in an ice/NaCl bath. A solution of TBAF in THF (1 M, 3.30 mL, 3.30 mmol) was added. The mixture was allowed to warm to room temperature over 45 min. The reaction was quenched by adding the solution to ice cold water (15 mL). The organic layer was then diluted with Et_2O and washed with water (5×30 mL). The organic layer was collected and dried with $MgSO_4$ and the solvent was removed in by rotary evaporation to yield a reddish-orange oil. The 6-ferrocene-hexanone-1-thiol was then purified by liquid column chromatography (hexane/ethyl acetate, 1:1) to afford **7** (0.66 g, 2.10 mmol, 70%). ^1H NMR (600 MHz, $CDCl_3$): δ=4.78 (t, ^3J=2.0 Hz, 2H), 4.49 (t, ^3J=2.0 Hz, 2H), 4.18 (s, 5H), 2.70 (t, ^3J=7.4 Hz, 2H) 2.55 (dt, ^3J=7.8, 7.2 Hz, 2H) 1.69 (m, 4H) 1.48 (m, 2H), 1.44 ppm (t, ^3J=7.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=204.6, 79.3, 72.4, 69.9, 69.5, 39.7, 39.0, 34.1, 29.3, 28.6, 28.4, 24.7, 24.3, 24.1 ppm; FTIR (dropcast on NaCl): 3096, 2932, 2857, 1667, 1454, 1410, 1378, 1264, 1238, 1105, 1055, 1026, 1002, 824, 533, 483 cm^{-1}; HRMS: m/z: calcd for $C_{16}H_{20}OSFe$: 316.0584; found: 316.0577.

Preparation of 8a: Compound **3a** (0.015 g, 0.034 mmol) was dissolved in $CDCl_3$ (3 mL) and **7** (0.032 g, 0.101 mmol) was dissolved in $CDCl_3$ (3 mL) and several drops of anhydrous MeOH. Each solution was degassed with nitrogen until the volume was reduced by half. The solutions were then transferred to a brass-clamp sealed PTFE tube and placed in the LECO Tempres high-pressure reactor at 11000 atm for 16 h. The solvent was removed in vacuo and the residue was redissolved in CH_2Cl_2 (0.5 mL). The solution was extracted with hexane (4×10 mL) to remove excess 6-ferrocene-hexanone-1-thiol. The residual solvent was removed in vacuo yielding **8a** as a viscous red-brown, clear liquid (0.025 g, 0.033 mmol, 99%). ^1H NMR (400 MHz, $CDCl_3$): δ=4.75 (dd, ^3J=1.6, 2.0 Hz, 2H), 4.48 (dd, ^3J=1.6, 2.0 Hz, 2H), 4.17 (s, 5H), 3.92 (dd, ^3J=3.2, 8.4 Hz, 1H), 3.56 (t, ^3J=6.0 Hz, 2H), 3.34 (dd, ^3J=9.2, 18.8 Hz, 1H), 2.93–2.74 (m, 2H), 2.70 (t, ^3J=7.2 Hz, 2H), 2.54–2.35 (m, 9H), 1.80 (quintet, ^3J=5.6 Hz, 2H), 1.74–1.58 (m, 6H), 1.55–1.45 (m, 14H), 0.96 ppm (t, ^3J=6.0 Hz, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ=204.2, 177.1, 175.3, 79.0, 72.1, 69.7, 69.2, 39.3, 39.2, 37.0, 34, 31.7, 28.9, 28.5, 28.3 (d, ^3J(C,P)=11 Hz), 23.91 (d, ^3J(C,P)=15.3 Hz), 23.88, 23.7 (d, ^2J(C,P)=5.3 Hz), 18.9 (d, ^1J(C,P)=47.3 Hz), 18.85 (d, ^2J(C,P)=3.4 Hz), 18.80 (d, ^1J(C,P)=47.7 Hz), 13.5 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ=34.0 ppm (s); FTIR (dropcast on KBr, ranked intensity): 639 (12), 729 (4), 825 (10), 923 (5), 1026 (17), 1053 (19), 1098 (15), 1146 (7), 1236 (16), 1312 (20), 1383 (13), 1401 (2), 1439 (18), 1456 (6), 1664 (14), 1702 (1), 1773 (9), 2176 (11), 2873 (8), 2933 cm^{-1} (3); MS (ESI): m/z^+ (%): 670.3 ([M^+], 100), 1421.6 ([M_2Br^+], 2).

Preparation of 8b: Compound **3b** (0.032 g, 0.058 mmol) was dissolved in $CDCl_3$ (4 mL) and **7** (0.055 g, 0.174 mmol) was dissolved in $CDCl_3$ (4 mL) and several drops of anhydrous MeOH. Each solution was degassed with nitrogen until the volume was reduced by half. The solutions were then transferred to a brass-clamp sealed PTFE tube and placed in the LECO Tempres high-pressure reactor at 11000 atm for 16 h. A workup procedure analogous to **8a** yielded **8b** as a viscous red-brown, clear liquid (0.040 g, 0.046 mmol, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ=4.77 (s, 2H), 4.50 (s, 2H), 4.19 (s, 5H), 3.71 (dd, ^3J=3.6, 9.2 Hz, 1H), 3.49 (t, ^3J=7.2 Hz, 2H), 3.12 (dd, ^3J=9.2, 18.8 Hz, 1H), 2.92–2.72 (m, 2H), 2.71 (t, ^3J=7.2 Hz, 2H), 2.49–2.34 (m, 9H), 1.73–1.64 (m, 4H), 1.58–1.41 (m, 20H), 1.32–1.17 (m, 14H), 0.97 ppm (br s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ=204.1, 175, 174.7, 78.9, 72.1, 69.6, 69.1, 39.2, 38.91, 38.87, 36.0, 31.4, 30.7 (d, ^3J(C,P)=14.6 Hz), 29.3, 29.2, 29.1, 28.9, 28.8 (d, ^4J(C,P)=9.5 Hz), 28.4, 27.4, 25, 23.9 (d, ^3J(C,P)=15.4 Hz), 23.8 (d, ^2J(C,P)=4.5 Hz), 21.8 (d, ^2J(C,P)=4.6 Hz), 19.4 (d, ^1J-(C,P)=47.6 Hz), 19.2 (d, ^1J(C,P)=47.5 Hz), 13.4 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ=33.7 ppm (s); FTIR (dropcast on KBr, ranked intensity): 483 (13), 659 (15), 751 (4), 825 (7), 923 (6), 1003 (18), 1026 (17), 1054 (20), 1099 (14), 1135 (9), 1240 (12), 1382 (16), 1399 (3), 1456 (5),

1665 (8), 1703 (1), 1774 (11), 2174 (19), 2857 (10), 2929 cm^{-1} (2); MS (ESI): m/z^+ (%): 782.4 ([M^+], 100), 1645.8 ([M_2Br^+], 2).

Preparation of 9b: Compound **3b** (0.052 g, 0.097 mmol) was combined with hexanethiol (0.034 g, 0.291 mmol) in $CDCl_3$ (3 mL) and the solution was divided and transferred to two NMR tubes. One tube was left at atmospheric pressure and 25 °C, while the other was kept at atmospheric pressure and 60 °C. The progress of the reactions was monitored by ^1H NMR spectroscopy. After each reaction was deemed to have gone to completion (ca. 64 h at 25 °C and 30 h at 60 °C) a similar workup procedure analogous to **8** was used to give product **9b**, a viscous orange-red clear liquid. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.63$ (dd, $^1J = 3.67$, $^2J = 9.08$ Hz, 1H), 3.43 (t, $J = 7.4$ Hz, 2H), 3.05 (dd, $^1J = 9.09$, $^2J = 18.68$ Hz, 1H), 2.84–2.78 (m, 1H), 2.71–2.64 (m, 1H), 2.47 (d, $^3J = 3.53$ Hz, 1H), 2.40 (m, 8H), 1.49–1.44 (m, 20H), 1.26–1.18 (m, 20H), 0.91 (t, $^3J = 92$ Hz, 9H), 0.82 ppm (t, $^3J = 93$ Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta =$ 177.2, 177, 83.4, 79.0, 49.4, 49.3, 45.5, 37.9, 37.4, 35.7, 32.5, 31.3, 29.4, 28.6, 28.1 (d, $^3J(C,P) = 16.0$ Hz), 24.0 (d, $^3J(C,P) = 15.2$ Hz), 23.7 (d, $^2J(C,P) = 4.5$ Hz), 22.5, 18.94 (d, $^1J(C,P) = 47.3$ Hz), 18.85 (d, $^1J(C,P) = 47.4$ Hz), 18.5 (d, $^2J(C,P) = 4.3$ Hz), 14.0, 13.5 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 34.0$ ppm (s); FTIR (dropcast on NaCl): 3751, 3675, 3628, 2927, 2856, 1736, 1714, 1651, 1559, 1541, 1521, 1458, 1401, 1082, 1059 cm^{-1}; HRMS: m/z: calcd for $C_{34}H_{67}NO_2NPS^+$: 584.4625; found 584.4622.

Preparation of 11a: A brass-clamp sealed PTFE tube was charged with **3a** (0.030 g, 0.069 mmol) in $CDCl_3$ (3 mL), dibenzylamine (0.041 g, 0.208 mmol) and anhydrous MeOH (2 drops). The tube was placed in the LECOTempres high-pressure reactor at 11000 atm for 3 h. The solvent and excess dibenzylamine was removed in vacuo at 100 °C for 19 h yielding **11a** as a viscous orange clear liquid (0.043 g, 0.068 mmol, 98%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$ (d, $^3J = 7.2$ Hz, 4H), 7.31 (t, $^3J = 7.8$ Hz, 4H), 7.24 (t, $^3J = 7.2$ Hz, 2H), 3.98 (dd $^3J = 4.8$, 9.2 Hz, 1H), 3.70 (dd, $^3J = 13.2$, 64.4 Hz, 4H), 3.53 (t, $^3J = 6$ Hz, 2H), 2.78 (dd, $^2J = 18.6$, $^3J = 9.6$ Hz, 1H), 2.64–2.55 (m, 3H), 2.42–2.37 (m, 6H), 1.77 (quintet,$^3J = 7.2$ Hz, 2H), 1.58–1.45 (m, 14H), 0.95 ppm (t, $^3J = 7.2$ Hz, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 177.4$, 175.3, 137.9, 128.7, 128.4, 127.5, 57.6, 54.7, 37, 31.8, 28.7 (d, $^3J(C,P) = 15.3$ Hz), 23.8 (d, $^3J(C,P) = 15.3$ Hz), 23.7 (d, $^2J(C,P) = 5.3$ Hz), 18.9 (d, $^1J(C,P) = 45$ Hz), 19.0 (d, $^2J(C,P) = 4.5$ Hz), 18.8 (d, $^1J(C,P) = 52.6$ Hz), 13.4 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 33.7$ ppm (s); FTIR (dropcast on KBr, ranked intensity): 639 (15), 700 (9), 732 (4), 825 (16), 924 (19), 973 (19), 1028 (17), 1099 (20), 1144 (6), 1382 (14), 1400 (2), 1455 (7), 1494 (11), 1701 (1), 1773 (12), 2174 (13), 2873 (8), 2933 (10), 2960 (3), 3029 cm^{-1} (18); MS (ESI): m/z^+ (%): 551.3 ([M^+], 100), 1183.6 ([M_2Br^+], 8).

Preparation of 11b: A brass-clamp sealed PTFE tube was charged with **3b** (0.038 g, 0.069 mmol) in $CDCl_3$ (3 mL), dibenzylamine (0.041 g, 0.208 mmol) and anhydrous MeOH (2 drops). The tube was placed in the LECO Tempres high-pressure reactor at 11000 atm for 3 h. A workup procedure analogous to **11a** gave **11b** as a viscous orange clear liquid (0.046 g, 0.062 mmol, 89%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.39$ (d, $^3J = 8.0$ Hz, 4H), 7.32 (t, $^3J = 8.0$ Hz, 4H), 7.25 (t, $^3J = 4$ Hz, 2H), 3.91 (dd, $^3J = 5.6$, 9.2 Hz, 1H), 3.72 (dd, $^3J = 13.2$, 73.2 Hz, 4H), 3.47 (t, $^3J = 7.2$ Hz, 2H), 2.75 (dd, $^2J = 18.4$, $^3J = 9.2$ Hz, 1H), 2.60 (dd, $^2J = 18.4$, $^3J = 4.8$ Hz, 1H), 2.50–2.40 (m, 8H), 1.59–1.46 (m, 18H), 1.35–1.19 (m, 14H), 0.97 ppm (t, $^3J = 8$ Hz, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 177.3$, 175.2, 138.2, 128.7, 128.4, 127.4, 57.3, 54.5, 38.5, 32.1, 30.7 (d, $^3J(C,P) = 14.4$ Hz), 29.4, 29.3, 29.3, 29.2, 29.0, 28.9, 27.7, 28, 23.9 (d, $^3J(C,P) = 15.3$ Hz), 23.8 (d, $^2J(C,P) = 3.8$ Hz), 21.9 (d, $^2J(C,P) = 4.6$ Hz), 19.3 (d, $^1J(C,P) = 45$ Hz), 19.1 (d, $^3J(C,P) = 47.2$ Hz), 13.5 ppm; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta = 33.5$ ppm (s); FTIR (dropcast on KBr, ranked intensity): 639 (15), 700 (9), 732 (4), 825 (14), 924 (7),1028 (16), 1133 (8), 1383 (13), 1399 (3), 1456(5),1494 (11), 1702 (1), 1773 (10), 2170 (12), 2856 (6), 2928 cm^{-1} (2); MS (ESI): m/z^+ (%): 663.5 ([M^+], 100), 1407.9 ([M_2Br^+], 5).

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