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High-Load, Oligomeric Dichlorotriazine: A Versatile ROMP-Derived Reagent and Scavenger

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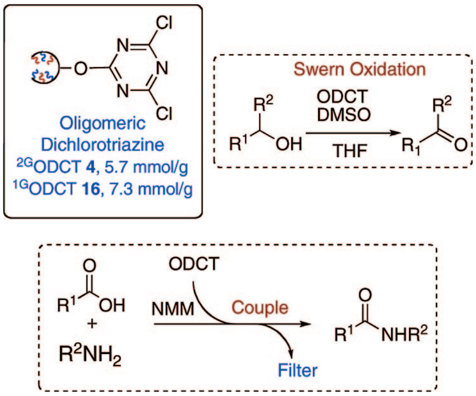
Received July 16, 2008



A new high-load, soluble oligomeric dichlorotriazine (ODCT) reagent derived from ring-opening metathesis polymerization (ROMP) is reported as an effective coupling reagent, scavenger of nucleophilic species, and activator of DMSO for the classic Swern oxidations. Two variants of this reagent ^{2G}ODCT **4** and ^{1G}ODCT **16**, possessing theoretical loads of 5.3 and 7.3 mmol/g, respectively, have been synthesized. Preparation was accomplished via simple synthetic protocols affording free flowing powders, amenable for large-scale production. Removal of the spent oligomeric reagent was achieved via either precipitation of the spent reagent or simple filtration utilizing a silica SPE, followed by solvent removal, to deliver products in excellent yield and purity. In addition, the corresponding norbornenyl monomer **3** was successfully demonstrated in a couple-ROMP-filter protocol utilizing in situ polymerization, achieving comparable results versus the corresponding oligomeric variant.

Introduction

Trichlorotriazine (TCT) has been widely used over the years for facilitating an array of transformations, most notably as both a facile scavenger of nucleophilic species and an effective coupling reagent.[1] However, in spite of its utility, TCT is a toxic, unstable reagent with a strong stench and hence is an undesirable reagent for large scale use and application in the preparation of combinatorial libraries. To overcome these limitations, a number of immobilized TCT derivatives and other polymer-supported acyl group-activating reagents have been reported.[2] More recently a cross-linked, polymeric ROMPgel derivative of TCT was reported and demonstrated as a dehydrocondensing reagent for the formation of amides.[3] Despite these reports, the design

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10.1021/jo801578f CCC: $40.75

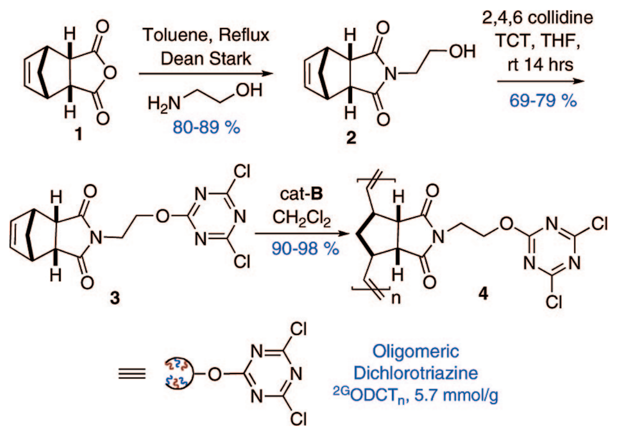
of new and improved variants of TCT that are user-friendly, offering a high degree of versatility, is warranted.[4]

Ring-opening metathesis (ROM) polymerization of functionalized norbornenes has emerged in recent years as a powerful tool for the generation of high-load, supported reagents with tunable properties.[5] Originally pioneered by Barrett and coworkers, ROM oligomers/polymers have several salient features which address classical limitations associated with traditional methods of immobilization and therefore positions them as ideal supports for both reagents and scavengers.[5,6] Our continued interest in the development of purification protocols based on norbornenyl tagged reagents and ROMP strategies leads us to report the titled oligomeric dichlorotriazine (ODCT) derivatives, designed as readily prepared, scalable reagents with optimal characteristics for versatile use in synthetic methodology and parallel synthesis.

Results and Discussion

Initial efforts toward the development of a soluble, ROMP-derived DCT-variant focused on the synthesis of an oligomeric DCT derivative (^{2G}ODCT$_{50}$ **4**) in a three-step protocol.[7] Thus, condensation of commercially available carbic anhydride **1** with ethanolamine, using a Dean−Stark trap, generated the desired alcohol **2** in high yield (80−89%, Scheme 1).[8] Alcohol **2** was subsequently treated with trichlorotriazine (TCT) to afford the desired norbornene monomer **3** in good yield (69−79%). It is worth noting that use of bases other than 2,4,6-collidine yielded additional byproduct attributed to multiple additions of alcohol **2** into TCT. With monomer **3** in hand, polymerization was carried out utilizing 2 mol % of the Grubbs second-generation catalyst [(IMesH$_2$)(PCy$_3$)(Cl)$_2$Ru═CHPh; cat-**B**][9] to afford the corresponding oligomeric reagent **4** (50-mer) as a free-flowing powder in high yield (90−98%). Quenching of the ROM polymerization reaction with ethyl vinyl ether, followed by precipitation with diethyl ether, provided the desired reagents as a free-flowing reagent **4** (^{2G}ODCT$_{50}$, theoretical load 5.7 mmol/g)[10] in excellent yield and on large scale (15 g, Scheme 1).[11] The high load nature of this soluble oligomeric ROMP reagent/scavenger **4** (5.7 mmol/g) represents a significant advantage over commercially available scavengers and coupling reagents: 1.0−1.6 mmol/g for PS-BnCHO, 3−5 mmol/g for PS-Trisamine, PS-HOBt(HL) 0.9−1.4 mmol/g, and PS-carbodiimide 1.0−1.5 mmol/g.[12]

SCHEME 1



With oligomer **4** in hand, the solubility in a range of organic solvents was examined. It was found that ^{2G}ODCT$_{50}$ **4** (50 mer) was soluble in CH$_2$Cl$_2$, DMF, THF, and DMSO and insoluble in Et$_2$O, EtOAc, toluene, and hexane. This wide solubility profile allows for reactions to be conducted in CH$_2$Cl$_2$ followed by removal of the spent oligomer via precipitation in EtOAc. It is worth noting that ROMP technology enables one to tune the length of the polymer (n = 10, 20, 50, and 100 mer) by controlling the amount of catalyst (mol %).[13] Thus, the solubility profile and hence the physical properties of the oligomer can be tailored. In general, longer chained polymers (n = 100, 200) in comparison to shorter chained polymers (n = 10, 20, 50) are soluble in a smaller range of organic solvents.

Initially, we evaluated the scavenging ability of ^{2G}ODCT **4** to sequester nucleophilic species such as amines and alcohols.[14] This was undertaken by using the corresponding monomer **3**, allowing for direct monitoring of the crude monomer using both GC and ^{1}H NMR. With the successful scavenging of excess amines and alcohols utilizing **3**, we evaluated the removal of excess amines with **4** in the formation of simple amides (Table 1).[15]

With these results in hand, we next evaluated the application of ^{2G}ODCT$_{50}$ **4** as a coupling reagent for the formation of amides from commercially available amines and acids (Table 2).

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(7) ^{X}ODCT$_y$ (X = generation of Grubbs catalyst, y = polymer length/number of monomer units in the oligomeric chain).

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(10) Loading of ODCT is calculated as mmol Cl/g.

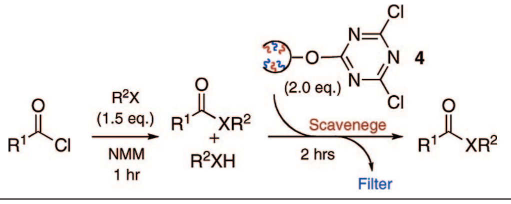
(11) We have previously found that there is a good correlation between the mol % of Grubbs catalyst added and the Gaussian distribution of oligomers formed, which is the case with several other oligomers formed [see ref 5d]. We have made these reagents several times with good reproducibility and consistency. MALDITOF and/or GPC data are normally attained on all oligomers; however, both methods have failed to give good results for our previously published reactive oligomeric bis-acid chloride (OBAC) and sulfonyl chloride resin (OSC).

(12) www.biotage.com (5-11-08).

(13) We have previously found that there is good correlation between the mol % of Grubbs catalyst added and the Gaussian distribution of oligomers formed, which we believe is the case with the ODCT shown in Scheme 1. We have made this reagent several times (i.e., the preparation and reactivity are repeatable and consistently reliable). We normally obtain MALDI-TOF and/or GPC data on all oligomers formed; however, both methods have failed to give good results for this reactive oligomer.

(14) For additional ROMP-derived scavengers, see: (a) Moore, J. D.; Herpel, R. H.; Lichtsinn, J. R.; Flynn, D. L.; Hanson, P. R. *Org. Lett.* **2003**, *5*, 105–107. (b) Moore, J. D.; Byrne, R. J.; Vedantham, P.; Flynn, D. L.; Hanson, P. R. *Org. Lett.* **2003**, *5*, 4241–4244. (c) Herpel, R. H.; Vedantham, P.; Flynn, D. L.; Hanson, P. R. *Tetrahdron Lett.* **2006**, *47*, 6429–6432. (d) Stoianova, D. S.; Yao, L.; Rolfe, A.; Samarakoon, T.; Hanson, P. R. *Tetrahedron Lett.* **2008**, *49*, 4553–4555.

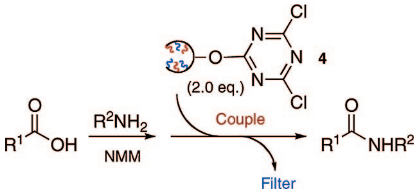
TABLE 1. Application of $^{2G}\mathrm{ODCT}_{50}$ 4 as a Facile Scavenger of Amines and Alcohols



entry[a]	R¹C(O)Cl	R²XH	product	yield (%)[c]	purity (%)[b]
1	BnC(O)Cl	BnNH$_2$	**5**	92	>95
2	BnC(O)Cl	^{i}PrNH$_2$	**6**	92	>95
3	BnC(O)Cl	C$_5$H$_8$NH	**7**	94	>95
4	*p*-TolC(O)Cl	^{i}PrNH$_2$	**8**	91	>95
5	*p*-TolC(O)Cl	C$_5$H$_8$NH	**9**	94	>95

[a] All reactions were carried out on 0.164 mmol scale, with 2.0 equiv of R^{2}XH, and scavenged with 1 equiv of **4** unless stated otherwise. [b] Purity by GC analysis and confirmed by ^{1}H NMR. [c] Yields were calculated from pure products after purification via elution through a silica SPE.

TABLE 2. Application of $^{2G}\mathrm{ODCT}_{50}$ 4 as an Efficient Coupling Reagent

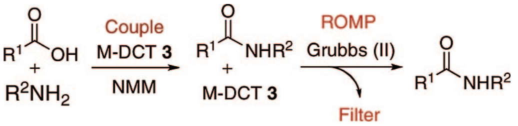


entry	R¹CO$_2$H	R²NH$_2$	product	yield (%)[c]	purity (%)[b]
1	BnCO$_2$H	BnNH$_2$	**5**	94	>95
2	BnCO$_2$H	^{i}PrNH$_2$	**6**	92	>95
3	BnCO$_2$H	C$_5$H$_8$NH	**7**	93	>95
4	*p*-TolCO$_2$H	^{i}PrNH$_2$	**8**	96	>95
5	*p*-TolCO$_2$H	C$_5$H$_8$NH	**9**	97	>95
6	4-OMe-3-MeBnCO$_2$H	C$_5$H$_8$NH	**10**	93	>95
7	C$_7$H$_{15}$CO$_2$H	BnNH$_2$	**11**	95	>95
9	C$_2$H$_5$CO$_2$H	BnNH$_2$	**12**	93	>95
10	C$_2$H$_5$(CH$_3$)CO$_2$H	^{i}PrNH$_2$	**13**	94	>95

[a] All reactions were carried out on 0.164 mmol scale, with addition of 2.0 equiv of **4** unless stated otherwise. [b] Purity by GC analysis and confirmed by ^{1}H NMR. [c] Yields were calculated from pure products after purification via elution through a silica SPE.

Coupling was achieved by using 1 equiv of acid, 1.1 equiv of amine, 3 equiv of *N*-methylmorpholine (NMM), and 2 equiv of $^{2G}\mathrm{ODCT}_{50}$ **4**. After the solution was stirred for 2 h at room temperature, silica was added to the crude mixture, the solvent was removed, and the crude was loaded onto a silica SPE and eluted with solvent (1:1 EtOAc:hexane) to yield the desired product with no residual oligomer observed in the crude ^{1}H NMR. Additionally, it is worth noting that less than 2 equiv of **4** can be used; however, slower reaction rates were observed, along with residual amine in certain cases. In the latter case, it is believed that the extra equivalent of $^{2G}\mathrm{ODCT}_{50}$ **4** scavenged excess amine in the crude reaction yielding the desired amide in good purity. This latter function displays the dual role inherent to the titled reagents.[16]

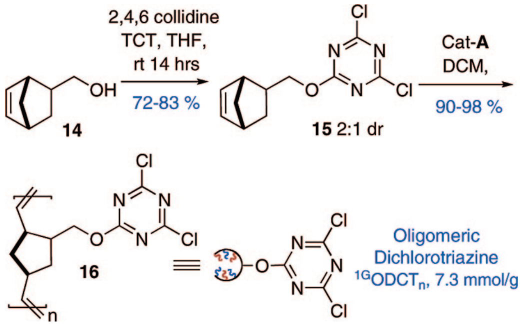
TABLE 3. Application of DCT Monomer 3 in a Couple-ROMP-Filter Protocol



entry	R¹CO$_2$H	R²NH$_2$	yield (%)[c]	purity (%)[b]
1	BnCO$_2$H	BnNH$_2$	95	>95
2	C$_9$H$_{19}$CO$_2$H	BnNH$_2$	93	>95
3	*p*-TolCO$_2$H	^{i}PrNH$_2$	92	>95
4	*p*-TolCO$_2$H	C$_5$H$_8$NH	93	>95
5	4-OMe-3-MeBnCO$_2$H	C$_5$H$_8$NH	96	>95

[a] All reactions were carried out on 0.164 mmol scale, with addition of 2.0 equiv of **3** unless stated otherwise. [b] Purity by GC and confirmed by ^{1}H NMR. [c] Yields were calculated from pure products after purification via elution through a silica SPE.

SCHEME 2. Synthesis of Monomer 15 and Oligomer ^{1G}ODCT 16



To demonstrate the versatility of oligomer **4** and its corresponding monomer **3**, a couple-ROMP-filter protocol was examined, whereby **3** was utilized as a coupling reagent for the synthesis of simple amides (Table 3).[17] Once the reaction had gone to completion (monitoring via GC/TLC), cat-**B** was added and the reaction was heated to reflux to initiate in situ polymerization of the spent monomer. Subsequent removal of the spent, oligomerized reagent was achieved by simple precipitation and filtration. Alternatively, the crude reaction mixture can be dry loaded onto silica and eluted through a SiO$_2$ SPE.

In our continued efforts to develop and generate new high-load oligomeric reagents and scavengers, a second derivative of ODCT possessing a higher load was synthesized (Scheme 2). In this example, commercially available norbornene-2-methanol **14** was condensed with TCT yielding the desired DCT monomer **15** in good yield. Initially, polymerization of the monomer **15** was attempted with cat-**B**; however, problems occurred with both the polymerization event and precipitation procedure. To circumvent these problems, polymerization and successful precipitation were accomplished with the utilization of the Grubbs first generation catalyst $(\mathrm{PCy_3})_2(\mathrm{Cl})_2\mathrm{Ru{=}CHPh}$ (cat-**A**),[18] followed by precipitation in hexanes to generate **16** in high yield (90−98%).

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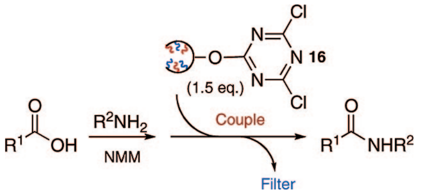
(16) As observed in the crude ^{1}H NMR spectra of reactions where spent-oligomer was removed by precipitation in Et$_2$O, followed by filtration and removal of solvent under reduced pressure.

(17) Of notable importance is the seminal advances made by Barrett and co-workers demonstrating the concept of reagent annihilation (norbornenyl-tagged DEAD), see: (a) Barrett, A. G. M.; Roberts, R. S.; Schröder, J. *Org. Lett.* **2000**, *2*, 2999–3002. For additional examples of in situ scavenging, see: (b) Moore, J. D.; Harned, A. M.; Henle, J.; Flynn, D. L.; Hanson, P. R. *Org. Lett.* **2002**, *4*, 1847–1849.

TABLE 4. Application of ^{1G}ODCT$_{50}$ 16 for the Formation of Simple Amides



entry	R^1CO_2H	R^2NH_2	product	yield (%)[c]	purity (%)[b]
1	$BnCO_2H$	$BnNH_2$	**5**	92	>95
3	$BnCO_2H$	C_5H_8NH	**7**	94	>95
4	*p*-TolCO_2H	$^iPrNH_2$	**8**	92	>95
5	*p*-TolCO_2H	C_5H_8NH	**9**	95	>95
6	4-OMe-3-MeBnCO_2H	C_5H_8NH	**10**	94	>95
7	$C_7H_{15}CO_2H$	$BnNH_2$	**11**	93	>95

[a] All reactions were carried out on 0.164 mmol scale, with addition of 2.0 equiv of **16** unless stated otherwise. [b] Purity by GC analysis and confirmed by ^1H NMR of crude isolated products. [c] Yields were calculated from pure products after purification via elution through a silica SPE.

With use of the aforementioned protocol, a range of oligomeric lengths were generated (20, 50, and 100 mer), which in comparison to ODCT **4**, demonstrated a differential solubility profile. In this regard, a greater solubility in a range of organic solvents was observed, including solubility in CH_2Cl_2, DMF, THF, and DMSO, with the notable inclusion of acetone and Et_2O. Due to its solubility in Et_2O, precipitation of the desired polymer after ROM polymerization was accomplished by using hexane.

As demonstrated with ^{2G}ODCT **4**, the application of ^{1G}ODCT$_{50}$ **16** was implemented successfully for the coupling of simple amines and acids giving comparable results as reported with oligomer **4** (Table 4).

Along with its application as a scavenger and coupling reagent, TCT and the corresponding DCT derivatives have been reported as reagents for a number of other applications, which include chlorination, dehydration of amides to nitriles, deoxygenation of sulfoxides, and the Swern oxidation.[19] In this regard we examined the application of ^{1G}ODCT$_{50}$ (**16**) as an activator for the classical Swern oxidation (Scheme 3).

SCHEME 3. Activation of DMSO Utilizing ^{1G}ODCT$_{50}$ 16

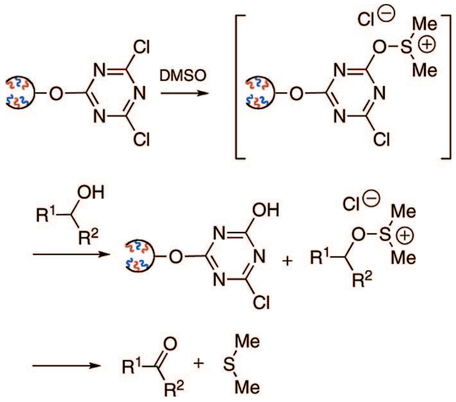
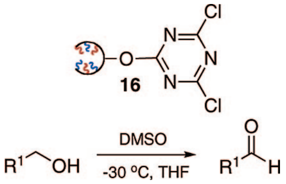


TABLE 5. Application of ^{1G}ODCT$_{50}$ 16 in the Swern Oxidation of Primary Alcohols



entry	R^1OH	product	yield (%)[a]
1	C_4H_9OH	**17**	90
2	$(CH_3)_2CHCH_2OH$	**18**	40
3	$C_8H_{17}OH$	**19**	92
4	2,4-OMeBnOH	**20**	94
5	4-NO_2BnOH	**21**	90
6	4-OMeBnOH	**22**	95

[a] All reactions were carried out on 0.164 mmol scale, with addition of 1.5 equiv of **16** unless stated otherwise. [b] Purity by GC and confirmed by ^1H NMR of crude isolated products. [c] Yields were calculated from pure products after purification via elution through a silica SPE.

TCT has been reported as an effective activator in the Swern oxidation of alcohols.[19e] Activation of DMSO can be violent and very exothermic, requiring low temperatures as observed with thionyl or oxalyl chloride. Despite previous success with use of TCT, the utilization of TCT as an activator is limited due to its inherent toxicity and moisture sensitivity. With this in mind, ROMP-derived ODCT represents an ideal reagent for the activation of DMSO. To explore this reaction pathway with the application of ^{1G}ODCT **16**, the Swern oxidation of simple primary alcohols to the corresponding aldehydes was investigated (Table 5).[20] In this regard, ^{1G}ODCT **16** and DMSO were stirred together at −30 °C, forming the activated DMSO complex in situ. Subsequent addition of the corresponding primary alcohol, followed by addition of Et_3N resulted in a homogeneous solution. The crude mixture was then absorbed onto silica, loaded onto a silica SPE, and flushed with an eluent of hexane:EtOAc (2:1) to yield the desired product in high yield and purity.

In conclusion, we have synthesized a high-load oligomeric variant of TCT derived from ROM polymerization. Initially, a norbornenyl maleimide variant of this reagent was prepared, ^{2G}ODCT$_n$ **4** (5.3 mmol/g), and successfully applied as a facile scavenger of amines and alcohols in addition to its application as a facile coupling reagent for the preparation of simple amides. Expanding the utility of this reagent, the corresponding monomer **3** was successfully utilized in a couple-ROMP-filter protocol for the formation of amides. A second variant of ^{1G}ODCT$_{50}$ **16** was synthesized possessing a significant increase in load. Like ^{2G}ODCT$_{50}$ **4**, ^{1G}ODCT$_{50}$ **16** was successfully applied as both a facile scavenger and coupling reagent. Additional versatility of the reagent was demonstrated with the successful application as an activating reagent of DMSO for the Swern oxidation of a variety of alcohols. Overall, ODCT **4** and **16** offer a high-load, versatile reagent that is readily synthesized from inexpensive starting materials with application to large-scale production.

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Experimental Section

***exo*-Norborenyl Alcohol 2.** Into a flame-dried flask fitted with a Dean−Stark apparatus under Ar was added exocarbic anhydride **1** (1 g, 6.10 mmol). After addition of dry toluene (8.7 mL) and stirring for 5 min at rt, ethanolamine (0.75 mL, 12.2 mmol) was added. The reaction was heated at reflux for 14 h, then upon completion (monitoring via TLC) cooled to rt and concentrated under reduced pressure. The resulting crude solid was dissolved in DCM (20 mL), filtered through a silica plug, and concentrated to give 1.12 g (89% yield) of **2** as a white solid. Mp 90−92 °C; FTIR (neat) 3442, 2945, 1766, 1696, 1174 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11 (t, J = 1.8 Hz, 2H), 3.63 (t, J = 4.9 Hz, 2H), 3.55 (t, J = 5.5 Hz, 2H), 3.39 (m, 2H), 3.29 (dd, J = 2.9, 1.5 Hz, 2H), 1.74 (t, J = 1.6 Hz, 1H), 1.72 (t, J = 1.6 Hz, 1H), 1.56 (m, 1H), 1.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.4, 134.4, 60.8, 52.2, 45.8, 44.9, 41.2; HRMS calcd for $C_{11}H_{13}NO_3Na$ $(M + Na)^+$ 230.0793, found 230.0786 (TOF MS ES+).

DCT Norborenyl Monomer 3. Into a flame dried flask under Ar was added TCT (1.78 g, 9.7 mmol). This was dissolved in dry THF (12 mL) and the solution was cooled to 0 °C and stirred for 15 min. After such time, 2,4,6-colidine (2.53 mL, 19.2 mmol) was added followed by addition of **2** (2.0 g, 9.6 mmol). Upon stirring for an additional 15 min at 0 °C, the reaction was warmed to rt and stirred for 10 h. The reaction was then concentrated in situ and purified by flash chromatography (6:4 hexane:EtOAc) to afford 2.59 g (79% yield) of the **3** as a light brown solid. FTIR (neat) 1770, 1699, 1549, 1514, 1255 cm $^{-1}$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11 (t, J = 1.8 Hz, 2H), 4.52 (t, J = 3.3 Hz, 2H), 3.78 (t, J = 5.5 Hz, 2H), 3.38 (m, 2H), 3.28 (dd, J = 2.9, 1.5 Hz, 2H), 1.73 (t, J = 1.6 Hz, 1H), 1.72 (t, J = 1.6 Hz, 1H), 1.54 (m, 1H), 1.52 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ177.4, 172.5, 170.7, 134.3, 65.9, 56.0, 45.9, 45.0, 36.2; HRMS calcd for $C_{14}H_{12}Cl_2N_4O_3Na$ $(M + Na)^+$ 377.0184, found 377.0186 (TOF MS ES+).

General Procedure for the Polymerization of DCT Norborenyl Monomer 3 to Generate 4. Norbornenyl monomer **3** (0.5 g, 1.41 mmol) was dissolved in degassed CH_2Cl_2 (0.085 M, 16.6 mL), to which cat-**B** (23.9 mg, 28 μmol) was added, and the reaction was refluxed for 2 h under Ar. After such time, the reaction was cooled to rt, ethyl vinyl ether (0.05 mL) was added, and the reaction was stirred for 15 min. The crude reaction mixture was concentrated and precipitated by dropwise addition to a stirring solution of Et_2O (100 mL). The resulting precipitate was filtered, washed with Et_2O, and dried under vacuum to produce 0.49 g (98% yield) of **4** as a light brown, free-flowing solid.

The following represents general experimental procedures for the implementation of the titled oligomer reagents in synthetic transformations. Specific experimental details and characterization data for the aforementioned compounds and other new compounds can be found in the Supporting Information.

General Procedure A for the Scavenging of Amines or Alcohols ODCT$_{50}$ 4/16 or Monomer 3/15. A vial equipped with a stir bar was charged with amine/alcohol (0.246 mmol, 1.5 equiv), Et_3N, and CH_2Cl_2 (0.075 M). After the mixture was stirred for 5 min, acid chloride (0.164 mmol, 1 equiv) was added and the reaction was stirred for 1 h at rt. After the stated time, ODCT$_{50}$ **4/16** or monomer **3/15** (0.328 mmol, 2.0 equiv) was added and the crude reaction was stirred for an additional 2 h. This was monitored by ^{1}H NMR and GC when monomer **3** was applied.

General Procedure B for the Amide Coupling of Simple Acids and Amines Utilizing ODCT$_{50}$ 4/16. A vial equipped with a stir bar was charged with ODCT$_{50}$ **4/16** (0.328 mmol, 2.0 equiv), CH_2Cl_2 (0.075 M), acid (0.164 mmol, 1 equiv), and NMM (0.492 mmol, 3 equiv). After the mixture was stirred for 10 min, amine (0.328 mmol, 2 equiv) was added and the reaction was stirred at rt for 2 h. After such time, the crude mixture was added dropwise to a stirring solution of dry Et_2O (10 mL), precipitating the spent oligometric reagent. After successful precipitation, the crude mixture was filtered through a SiO_2 SPE, yielding the desired products **5**−**13**.

General Procedure C for the Amide Coupling of Simple Acids and Amines Utilizing ODCT$_{50}$ 4/16. A 1 dram vial equipped with a stir bar was charged with ODCT$_{50}$ **4/16** (0.328 mmol, 2.0 equiv), CH_2Cl_2 (0.075 M), acid (0.164 mmol, 1 equiv), and NMM (0.492 mmol, 3 equiv). After the mixture was stirred for 10 min, amine (0.328 mmol, 2 equiv) was added and the reaction was stirred for 2 h. Silica was added to the reaction mixture, the solvent was removed under reduced pressure, and the resulting powder was loaded onto a silica SPE and eluted with solvent (1:1 EtOAc:hexane) to yeild the desired products **5**−**13** in high purity.

General Procedure D for the Amide Coupling of Simple Acids and Amines. A vial equipped with a stir bar was charged with DCT monomer **3** (0.328 mmol, 2.0 equiv), dry CH_2Cl_2 (0.075 M), acid (0.164 mmol, 1 equiv), and NMM (0.492 mmol, 3 equiv). After the mixture was stirred for 10 min, amine (0.328 mmol, 2 equiv) was added to the crude mixture and the reaction was stirred at rt for 2 h. After the stated time, cat-**B** (2 mol %) was added to the crude mixture, which was heated at reflux for 1 h. After such time, the reaction was cooled to rt, quenched via the addition of ethyl vinyl ether (50 μL), and stirred for 15 min. The spent oligomer was precipitated by the slow addition of the crude mixture to a stirring solution of Et_2O (5 mL) and filtered through a silica SPE with solvent (1:1 EtOAc:hexane) to afford the desired products **5**−**13** in good purity.

DCT Norborenyl Monomer 15. Into a flame-dried flask under Ar, a solution of TCT (1.55 g, 8.4 mmol) in dry THF (10.0 mL) was cooled to 0 °C and stirred for 15 min. After such time, 2,4,6-collidine (2.12 mL, 16.0 mmol) was added, followed by the slow addition of alcohol **14** (1.0 g, 8.0 mmol). After being stirred for an additional 15 min at 0 °C, the reaction was warmed to rt and stirred for 10 h. Purification of the crude reaction mixture entailed in situ concentration followed by flash chromatography (6:4 EtOAc: hexane) to give 1.86 g (83% yield) of **15** (2:1 mixture of diastereoisomers) as a brown viscous oil. FTIR (neat) 1769, 1695, 1550, 1510, 1248 cm $^{-1}$; [major isomer] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.21 (dd, J = 5.7, 3.1 Hz, 1H), 5.97 (dd, J = 5.7, 2.9 Hz, 1H), 4.26 (dd, J = 10.5, 6.6 Hz, 1H), 4.06 (dd, J = 10.4, 9.7 Hz, 1H), 2.99 (s, 1H), 2.87 (s, 1H), 1.92 (ddd, J = 11.9, 9.3, 3.8 Hz, 2H), 1.50 (dd, J = 8.3, 2.1 Hz, 1H), 1.30 (d, J = 8.3 Hz, 1H), 0.64 (ddd, J = 11.8, 4.4, 2.6 Hz, 1H); [minor] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11 (t, J = 1.8 Hz, 2H), 4.56 (dd, J = 10.6, 6.4 Hz, 1H), 4.36 (dd, J = 10.6, 9.4 Hz, 1H), 2.89 (s, 1H), 2.83 (d, J = 1.5 Hz, 1H), 1.92 (ddd, J = 11.9, 9.3, 3.8 Hz, 2H), 1.42−1.37 (m, 1H), 1.37−1.32 (m, 1H), 1.24 (ddd, J = 11.9, 4.5, 3.5 Hz, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 172.4, 170.9, 138.1, 137.0, 136.0, 131.9, 74.4, 73.8, 49.4, 44.9, 43.7, 43.5, 42.1, 41.6, 37.7, 37.4, 29.3, 28.7; HRMS calcd for $C_{11}H_{11}Cl_2N_3ONa$ $(M + Na)^+$ 294.0177, found 294.0182 (TOF MS ES+).

General Procedure for the Polymerization of DCT Norborenyl Monomer 15 to Generate 16. Norbornenyl monomer **15** (1.67 g, 6.14 mmol) was dissolved in degassed CH_2Cl_2 (0.085 M, 72.2 mL), to which cat-**A** (0.104 g, 0.123 mmol) was added. The reaction refluxed for 2 h and subsequently cooled to rt, upon which time the reaction was quenched by the addition of ethyl vinyl ether (0.1 mL). After being stirred for 15 min, the crude mixture was concentrated and precipitated via dropwise addition to a stirring solution of hexane (200 mL). The resulting precipitate was filtered, washed with hexanes, and dried under vacuum to produce 1.63 g (98% yield) of **16** as a light brown, free-flowing solid.

General Procedure E for the Swern Oxidation of Simple Primary Alcohols Utilizing ^{1G}ODCT$_{50}$ 16. To a stirring solution of ^{1G}ODCT$_{50}$ **16** (0.246, 1.5 equiv) in dry THF (1 mL) at −30 °C was added DMSO (0.984 mmol, 6 equiv) slowly under Ar. After being stirred for 30 min, a solution of alcohol (0.164 mmol, 1 equiv) in dry THF (0.5 mL) was slowly added maintaining the reaction temperature at −30 °C. After the mixture was stirred for 30 min,

Et_3N (0.825 mmol, 5 equiv) was added and the reaction mixture was stirred for an additional 30 min. After being warmed to rt, silica was added to the reaction mixture, solvent was removed, and the resulting powder was loaded onto an SiO_2 SPE. The desired products **17−22** were isolated via elution with a solvent mixture (2:1 hexane:EtOAc).

Acknowledgement. This work was generously supported by funds provided by an NIH STTR Grant (R41 GM076765 STTR-Phase-I), the Center for Chemical Methodologies and Library Development at the University of Kansas (KU-CMLD) [P50 GM069663], and NIH COBRE award P20 RR015563 with additional funds from the State of Kansas. Undergraduate funding was provided by the NIH K-INBRE award (K.V.) and the KU Center of Research (K.V.). The authors also thank the Umaer Basha Research fellowship for student support (I.O.) and Materia, Inc. for supplying catalyst and helpful discussion.

Supporting Information Available: Copies of NMR spectra are provided along with experimental details and data for products **5−13** and **17−22**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO801578F