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Quick Access to Diverse Polymerizable Molecules (a Monomer Library) by Catalytic [2 + 2 + 2] Cycloaddition Reactions of Functionalized Alkynes

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ABSTRACT: The [2 + 2 + 2] cycloaddition reactions of 1,6-diynes and alkynes with a functional group(s), such as epoxide, oxetane, ester, alcohol, phenol, amine, borate, styrene, and methacrylate, catalyzed by a dipimp/$CoCl_2 \cdot 6H_2O$/Zn reagent [dipimp: 2-(2,6-diisopropylphenyl)-iminomethyl-pyridine] yielded a variety of polymerizable molecules (monomers) having a 2,3-dihydro-1*H*-indene core structure. Similarly, the [2 + 2 + 2] cycloaddition reactions of 1,6-diynes and nitriles with a functional group(s) catalyzed by a dppe/$CoCl_2 \cdot 6H_2O$/Zn reagent [dppe: 1,2-bis(diphenylphosphino)ethane] gave a variety of polymerizable molecules (monomers) with a 6,7-dihydro-5*H*-cyclopenta[*c*]pyridine core structure. Among the resulting monomers, 5-phenyl-1,3-dihydrospiro[indene-2,3′-oxetane] prepared from 3,3-di(prop-2-ynyl)oxetane and phenylacetylene was representatively polymerized in the presence of BF_3 catalyst. A cationic random copolymerization of one of 1,3-dihydrospiro-[indene-2,3′-oxetane] derivatives with 3-ethyl-3-(phenoxymethyl)oxetane and radical random copolymerization of diethyl 5-(4-vinylphenyl)-1*H*-indene-2,2(3*H*)-dicarboxylate with styrene have also been demonstrated.

Introduction

In the study of functional materials, polymer science is increasingly important. For bottom-up development of new functional polymers, the preparation of new polymerizable molecules (monomers) with functional handles for compositional versatility is desired.[1]

In contrast to the conventional, individual preparation of monomers for planned polymerization, we propose a convergent process that couples simple molecules having a polymerizable functional group (PG) and a functional group(s) necessary for the desired properties of the resulting polymers, the synthesis of which enables a quick and easy access to diverse monomers (a monomer library) and the corresponding polymers. To realize this idea, the coupling reaction must have high functional group compatibility. In this context, Fréchet and Hawker et al. have developed a synthesis of a variety of monomers comprised with a 4-vinyl-1,3,5-triazole structure by the Cu(I)-catalyzed cycloaddition of azides and alkynes and demonstrated their radical polymerizations.[2] Herein is reported synthesis of a wider range of polymerizable molecules of types **4** and **5** from diynes **1** with alkynes **2** or nitriles **3** by using a catalytic [2 + 2 + 2] cycloaddition reaction as the coupling process (Scheme 1). Attributed to molecular assembly by a combination of the starting alkynes and nitriles, various monomers **4** and **5** can be prepapred; their polymerization will give a variety of polymers such as types I, II, and III. Alternative copolymerization with a combination of these new monomers and also with conventional monomers might open a broad range of new polymer families.

Results and Discussion

Although a variety of functional groups tolerated under the reaction conditions of catalyzed [2 + 2 + 2] alkyne-cycloaddition reactions developed so far,[3] the compatibility of polymerizable functional groups (PGs) has not been investigated systematically. First, we explored the stability of such functional moieties under the conditions of the cycloaddition reaction catalyzed by a dipimp/$CoCl_2 \cdot 6H_2O$/Zn reagent [dipimp: 2-(2,6-diisopropylphenyl)-iminomethylpyridine] that we developed.[4] Thus, the cycloaddition reaction of diyne **1a** with phenylacetylene (**2a**) catalyzed by a dipimp/$CoCl_2 \cdot 6H_2O$/Zn reagent was carried out in the presence of the model molecules **6** having the PG depicted in Scheme 2.

As a result, the reaction showed reasonably high PG compatibility. Thus, except for the reaction with carboxylic acid **6o** and aryl bromide **6p**, the cycloaddition reaction proceeded smoothly to produce adduct **4aa** in good to quantitative yields. After the workup, styrene (**6a**), 1,3-diene **6b**, methacrylate **6c**, phenol **6d**, amides **6e** and **6f**, aldehyde **6g**, aryl chloride **6h**, epoxide **6i**, oxetane **6j**, and borate **6k** were quantitatively recovered as themselves. The reaction in the presence of acrylate **6l**, acrylamide **6m**, or isocyanate **6n** provided **4aa** in good yield but they were not recovered due to their polymerization (**6l** and **6m**) or reaction with water (**6n**). In the presence of compounds **6o** and **6p**, the cycloaddition reaction did not proceed.

With these results in hand, we pursued synthesis of various polymerizable molecules by the coupling of a series of diynes and their alkyne (or nitrile) counterparts, **1a**−**e** and **2a**−**m** (or **3a**−**c**) (see Supporting Information for their structure). Representative results are illustrated in Figure 1, where the part derived from diyne **1** and the part derived from alkyne **2** (or nitrile **3**) are indicated in red and blue, respectively. Thus, the reaction of **1** and **2** with a dipimp/$CoCl_2 \cdot 6H_2O$/Zn catalyst in tetrahydrofuran (THF) at ambient temperature gave 2,3-dihydro-1*H*-indenes **4** having a polymerizable functionality such as an epoxide (**4ab**), active alkene (**4ac**, **4ad, 4be**, **4af**, **4el**), oxetane (**4ca**, **4cg**, **4ck**, **4el**, **4cn**), ester (**4ab**, **4ac**, **4ad**, **4af**, **4ah**, **4ai**, **4dj**, **4di**, **4am**), alcohol (**4be**, **4dj**, **4am**), phenol (**4ah**), amine (**4ai**, **4di**) and borate (**4cn**)

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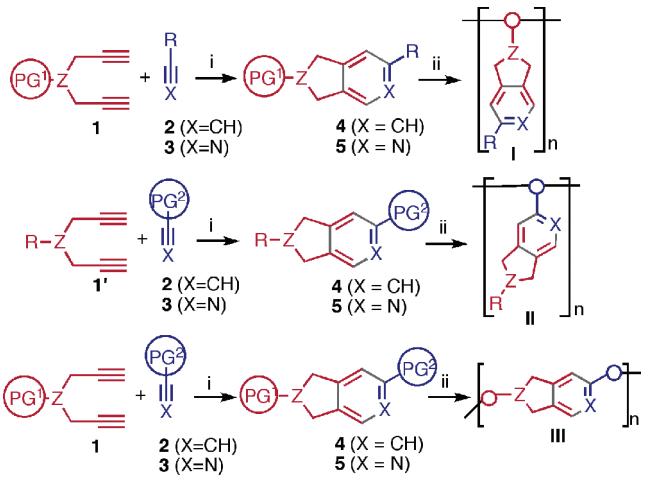
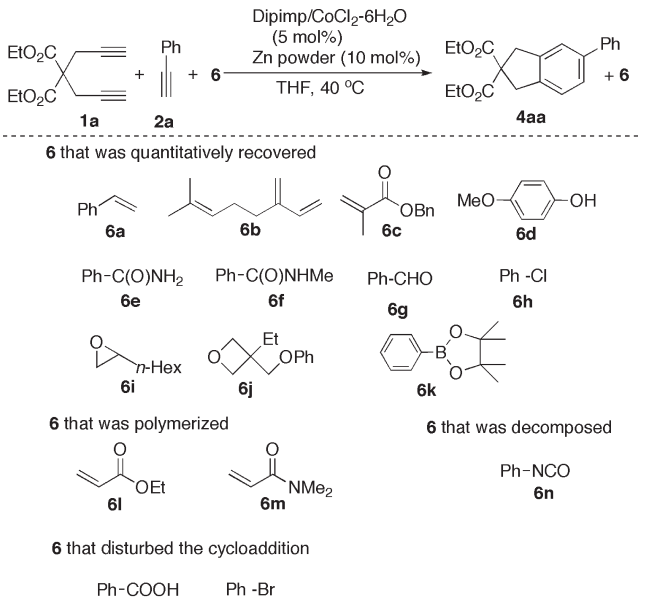
Scheme 1. Concept of Rapid Assembly of Polymerizable Molecules by [2 + 2 + 2] Cycloaddition Reactions[a]



[a] PG^1, PG^2 = polymerizable functional groups. Keys: (i) alkyne [2 + 2 + 2] cycloaddition reaction; (ii) polymerization.

Scheme 2. Investigation on Polymerizable-Functional Group Compatibility[a]



[a] Key: dipimp = 2-(2,6-diisopropylphenyl)iminomethylpyridine; THF = tetrahydrofuran.

in good to excellent yields. In all these syntheses, no oligomeric or polymeric byproduct derived from **1**, **2**, and the resulting **4** was detected. As exemplified by conversion of **4am** to **4am′**, styrene derivatives were also prepared from the corresponding alcoholic adducts by a dehydration reaction.

Similarly, with use of a dppe/$CoCl_2 \cdot 6H_2O$/Zn [dppe: 1,2-bis(diphenylphosphino)ethane] catalyst[5] instead of dipimp/$CoCl_2 \cdot 6H_2O$/Zn, 6,7-dihydro-5*H*-cyclopenta-[*c*]pyridines **5** were obtained by the reaction of diynes **1** and nitriles **3**, albeit in a low yield of **5cb**.

Among these monomers **4** obtained here, a few compounds were representatively used for polymerization (Scheme 3). Thus, a cationic polymerization of oxetane **4ca** was carried out by treatment with a catalytic amount of BF_3 in CH_2Cl_2 at 0 °C to yield the corresponding *poly*-**4ca** (M_n = 4.56 × 10^4, M_w = 2.23 × 10^5, M_w/M_n = 4.89 based on gel permeation chromatography (GPC) analysis, Tg = 106.9 °C) in 82% yield. A 5:1 mixture of styrene and **4ac** with a catalytic amount of 2,2′-azobis(isobutyronitrile) (AIBN) in toluene was heated to 60 °C to provide the corresponding copolymer *poly*-(styrene-*co*-**4ac**) (M_n = 9.25 × 10^4, M_w = 2.21 × 10^5, M_w/M_n = 2.39 based on GPC analysis, Tg = 102.9 °C, 81% of styrene incorporation) in 68% yield. Treatment of a

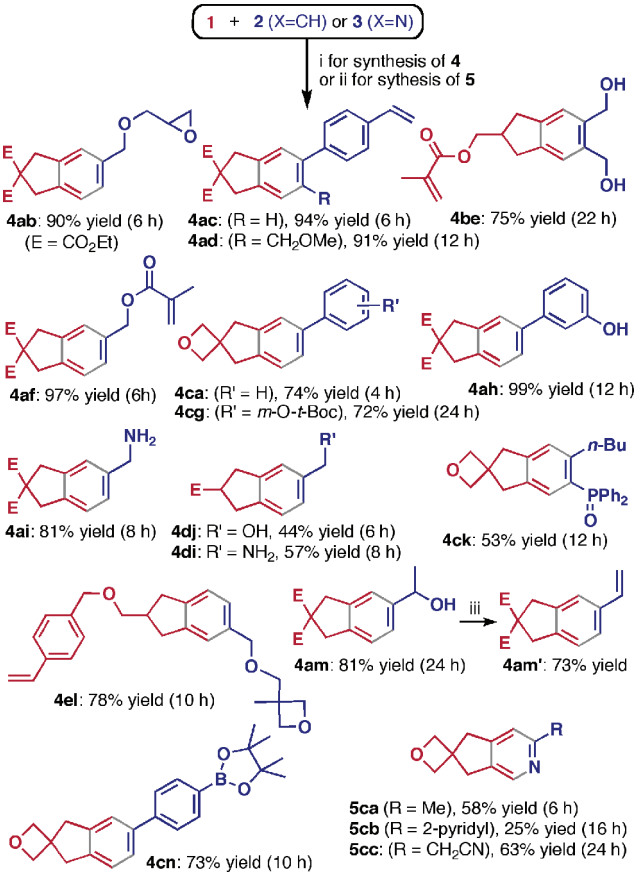
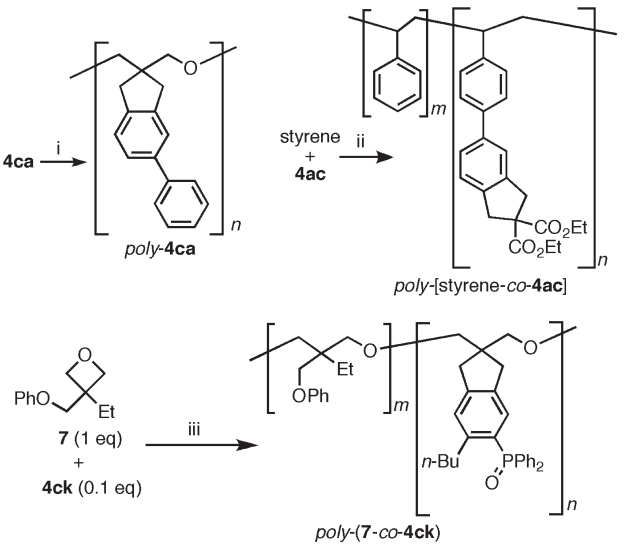


Figure 1. Synthesis of polymerizable molecules by [2 + 2 + 2] cycloaddition reaction; dipimp = 2-(2,6-diisopropylphenyl)iminomethylpyridine, dppe = 1,2-bis(diphenylphosphino)ethane, THF = tetrahydrofuran, NMP = *N*-methyl-2-pyrrolidone, DMSO = dimethylsulfoxide, BHT = 2,6-di(*tert*-butyl)-4-methylphenol.

Scheme 3. Representative Polymerization of New Monomers 4[a]



[a] AIBN = 2,2′-azobis(isobutyronitrile).

mixture of **7** and **4ck** (0.1 equiv) with 13 mol % of BF_3-OEt_2 in CH_2Cl_2 afforded *poly*-(**7**-*co*-**4ck**) bearing triaryl phosphine oxide pendants [$M_n = 3.89 \times 10^3$, $M_w = 1.09 \times 10^4$, $M_w/M_n = 2.81$ based on GPC analysis, *m*:*n* = 10:1, ^{31}P NMR ($CDCl_3$, 202 MHz) δ −14.05] in 40% yield.

Conclusion

We have demonstrated that a cobalt-catalyzed [2 + 2 + 2] cycloaddition of functionalized alkynes yielded a variety of polymerizable molecules (monomers). Their polymerization will give a variety of polymers, and alternative copolymerization with these new monomers and also conventional monomers might open a broad range of new polymer families.

Experimental Section

General Data. NMR spectra were recorded in $CDCl_3$ at 600, 500, 270, and 90 MHz for ^1H and 150, 125, 67.5, and 22.5 MHz for ^{13}C on JEOL JNM-ECA600, -ECA500, -EX270, and HITACHI R-1900 spectrometers, respectively. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si (δ 0.00) or residual $CHCl_3$ (δ 7.26 for ^1H NMR) and $CDCl_3$ (δ 77.0 for ^{13}C NMR). IR spectra were recorded on JASCO IR FT/IR 4100 spectrometer. High-resolution mass spectra (HR−MS) were measured on JEOL Accu TOF T-100 equipped with an ESI ionization unit. The M_n and M_w/M_n of polymers were measured with a TOSOH HLC-8020 gel-permeation chromatography (GPC) unit (eluent: tetrahydrofuran (THF); calibration: polystyrene standards) using two TSK-gel columns (2 × Multipore H_{XL}-M). Thermogravimetry/differential thermal analysis (TG/DTA) was carried out with Seiko Instruments Inc. EXSTAR6000 TG/DTA6200 under nitrogen (heating rate:10 °C/min).

All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. Dry solvents [tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), dichloromethane (CH_2Cl_2), toluene, *N*-methyl-2-pyrrolidone (NMP) and diethyl ether (ether)] were purchased from Kanto Chemicals. 2-(2,6-Diisopropylphenyliminomethyl)pyridine (dipimp) was prepared from pyridine 2-carboxaldehyde and 2,6-diisopropylaniline by the reported procedure.[6] For the structures and preparation of diynes **1a**−**e**, alkynes **2a**−**m** and nitriles **3a**−**c**, see the Supporting Information.

General Procedure for Investigating Functional Group Compatibility of Cobalt-Catalyzed [2 + 2 + 2] Cycloaddition Reaction. A solution of $CoCl_2 \cdot 6H_2O$ (5.9 mg, 0.025 mmol) and dipimp (7.9 mg, 0.030 mmol) in THF (1.0 mL) was added to zinc powder (3.3 mg, 0.05 mmol). The resulting mixture was stirred at ambient temperature for 1 h. A solution of α,α-dipropargyl malonic diethyl ester (**1a**) (118.1 mg, 0.5 mmol), ethynylbenzene (**2a**) (66.4 mg, 0.65 mmol), compound **6** (0.50 mmol) in THF (1.0 mL) was added, and the resulting mixture was stirred at room temperature. The reaction progress was checked by TLC analysis. After complete consumption of diyne **2a**, Et_2O was added and the mixture was passed through a pad of Celite with Et_2O. After concentration, the crude residue was analyzed by ^1H NMR to confirm the progress of the reaction and recovery of compound **6**.

Typical Procedure for Synthesis of Monomers 4 from Diynes 1 and Alkynes 2. A 20 mL Schlenk tube was charged with zinc powder (40−100 mesh, 6.5 mg, 0.10 mmol) and purged with argon. A solution of $CoCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol) and dipimp (16.0 mg, 0.06 mmol) in THF (2.0 mL) was added, and the resulting mixture was stirred at ambient temperature for 1 h. A solution of α,α-dipropargyl diethyl malonate (**1a**) (236 mg, 1.0 mmol) and 2-((prop-2-ynyloxy)methyl)oxirane (**2b**) (168 mg, 1.5 mmol) in THF (2.0 mL) was added and the mixture was stirred at 40 °C. The reaction progress was checked by TLC analysis. After complete consumption of **1a**, Et_2O (4 mL) was added and the mixture was passed through a pad of Celite with Et_2O. The filtrate was concentrated to dryness and the resulting colored residue was chromatographed on silica gel to give 314 mg of diethyl 5-((oxiran-2-ylmethoxy)methyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (**4ab**) in 90% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.19 (s, 1H, Ar), 7.17 (d, J = 7.5 Hz, 1H, Ar), 7.14 (d, J = 7.5 Hz, 1H, Ar), 4.56 (d, J = 11.5 Hz, 1H, ArCH_2O), 4.50 (d, J = 11.5 Hz, 1H, ArCH_2O), 4.20 (q, J = 7.2 Hz, 4H, OCH_2CH$_3$), 3.75 (dd, J = 3.5, 11.5 Hz, 1H, epoxide), 3.58 (s, 2H, ArCH_2C), 3.57 (s, 2H, ArCH_2C), 3.42 (dd, J = 5.5, 11.5 Hz, 1H, epoxide), 3.20 − 3.16 (m, 1H, epoxide), 2.80 (dd, J = 4.0, 5.0 Hz, 1H, epoxide), 2.61 (dd, J = 2.8, 5.0 Hz, 1H, epoxide), 1.25 (t, J = 7.2 Hz, 6H, OCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.5, 140.3, 139.6, 136.6, 126.7, 124.1, 123.7, 73.3, 70.7, 61.6, 60.4, 50.8, 44.2, 40.3, 40.1, 14.0. IR (neat): 2982, 2934, 2905, 1732, 1466, 1445, 1366, 1253, 1185, 1158, 1094, 1012, 903, 825 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $C_{19}H_{24}NaO_6$ $[M + Na]^+$, 371.1471; found, 371.1481.

Diethyl 5-(4-Vinylphenyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4ac). The title (342 mg) compound was obtained from **1a** (236 mg, 1.0 mmol) and **2c** (192 mg, 1.5 mmol) in 94% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.50 (d, J = 8.0 Hz, 2H, Ar), 7.43 (d, J = 8.0 Hz, 2H, Ar), 7.40 (s, 1H, Ar), 7.38 (d, J = 7.5 Hz, 1H, Ar), 7.23 (d, J = 7.5 Hz, 1H, Ar), 6.72 (dd, J = 11.0, 17.5 Hz, 1H, ArCH=CH$_2$), 5.75 (d, J = 17.5 Hz, 1H, ArCH=CH_2), 5.23 (d, J = 11.0 Hz, 1H, ArCH=CH_2), 4.20 (q, J = 7.5 Hz, 4H, OCH_2CH$_3$), 3.64 (s, 2H, ArCH_2C), 3.62 (s, 2H, ArCH_2C), 1.24 (t, J = 7.5 Hz, 6H, OCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.5, 140.6, 140.5, 139.6, 139.2, 136.3, 127.0, 126.5, 125.8, 124.4, 122.6, 113.6, 61.6, 60.4, 40.4, 40.1, 14.0, 13.9. IR (neat): 2980, 2936, 2904, 1733, 1628, 1488, 1365, 1277, 1244, 1186, 1157, 1067, 819 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $C_{23}H_{24}NaO_4$ $[M + Na]^+$, 387.1572; found, 387.1556.

Diethyl 5-(Methoxymethyl)-6-(4-vinylphenyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4ad). The title compound (371 mg) was obtained from **1a** (236 mg, 1.0 mmol) and **2d** (258 mg, 1.5 mmol) in 91% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.45 (d, J = 8.3 Hz, 2H, Ar), 7.36 (s, 1H, Ar), 7.31 (d, J = 8.3 Hz, 2H, Ar), 7.11 (s, 1H, Ar), 6.76 (dd, J = 11.0, 17.5 Hz, 1H, ArCH = CH$_2$), 5.80 (d, J = 17.5 Hz, 1H, ArCH=CH_2), 5.28 (d, J = 11.0 Hz, 1H, ArCH=CH_2), 4.27 (s, 2H, ArCH_2O), 4.22 (q, J = 7.0 Hz, 4H, OCH_2CH$_3$), 3.64 (s, 2H, ArCH_2C), 3.61 (s, 2H, ArCH_2C), 3.33 (s, 3H, OCH_3), 1.27 (t, J = 7.0 Hz, 6H, OCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.6, 140.5, 140.4, 139.7, 139.5, 136.5, 136.2, 134.2, 129.5, 125.9, 125.6, 124.9, 113.8, 76.7, 72.5, 61.7, 60.5, 58.1, 40.2, 14.0. IR (neat): 2980, 2929, 2901, 1729, 1628, 1446, 1245, 1068, 907, 850 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $C_{25}H_{28}NaO_5$ $[M + Na]^+$, 431.1834; found, 431.1809.

(5,6-Bis(hydroxymethyl)-2,3-dihydro-1*H*-inden-2-yl)methyl 2-Methylprop-2-enoate (4be). The title compound (207 mg) was obtained from **1b** (190 mg, 1.0 mmol) and **2e** (261 mg, 3.0 mmol) in 75% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.20 (s, 2H, Ar), 6.08 (s, 1H, C=CH_2), 5.58−5.55 (m, 1H, C=CH_2), 4.69 (s, 4H, ArCH_2OH), 4.23 (s, 2H, OH), 4.16 (d, J = 7.5 Hz, 2H, OCH_2CH), 3.08 (dd, J = 8.0, 15.5 Hz, 2H, ArCH_2CH), 2.88 (quint, J = 6.7 Hz, 1H, CH(CH$_2$)$_3$), 2.76 (dd, J = 6.3, 16.3 Hz, 2H, ArCH_2CH), 1.93 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 142.8, 137.8, 136.2, 126.1, 125.6, 67.6, 64.2, 38.4, 35.7, 18.3. IR (KBr): 3358, 2929, 2873, 1713, 1634, 1453, 1299, 1173 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $C_{16}H_{20}NaO_4$ $[M + Na]^+$, 299.1259; found, 299.1281.

Diethyl 5-((2-Methylprop-2-enoyloxy)methyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4af). The title compound (350 mg) was obtained from **1a** (236 mg, 1.0 mmol) and **2f** (372 mg, 3.0 mmol) in 97% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.21 (s, 1H, Ar), 7.18 (br s, 2H, Ar), 6.14 (br s, 1H, C=CH_2), 5.59 − 5.50 (m, 1H, C=CH_2), 5.14 (s, 2H, ArCH_2O), 4.20 (q, J = 7.3 Hz, 4H, OCH_2CH$_3$), 3.59 (s, 2H, ArCH_2C), 3.58 (s, 2H, ArCH_2C), 1.96 (s, 3H, CH_3), 1.26 (t, J = 7.3 Hz, 6H,

OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 171.5,167.3, 140.5, 140.1, 136.2, 134.9, 127.1, 125.8, 124.2, 124.1, 66.4, 61.7, 60.4, 40.3, 40.2, 18.3, 14.0. IR (neat): 2982, 2936, 2905, 2874, 1730, 1635, 1589, 1445, 1368, 1317, 1294, 1252, 1184, 1157, 1069, 1053, 1013, 943, 860, 816 cm^{-1}. HRMS−ESI (m/z): calcd for $C_{20}H_{24}NaO_6$ $[M + Na]^+$, 383.1471; found, 383.1451.

5-Phenyl-1,3-dihydrospiro[indene-2,3′-oxetane] (4ca). The title compound (175 mg) was obtained from **1c** (134 mg, 1.0 mmol) and **2a** (153 mg, 1.5 mmol) in 74% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.55 (d, J = 6.5 Hz, 2H, Ar), 7.47 − 7.36 (m, 4H, Ar), 7.33 (d, J = 7.5 Hz, 1H, Ar), 7.28 (d, J = 8.0 Hz, 1H, Ar), 4.71 (s, 4H, oxetane ring), 3.31 (s, 2H, $ArCH_2C$), 3.29 (s, 2H, $ArCH_2C$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.3, 141.3, 140.7, 140.2, 128.7, 127.09, 127.05, 125.9, 124.8, 123.4, 83.6, 47.0, 44.1, 43.8. IR (neat): 2947, 2905, 2924, 2849, 1476, 1427, 1304, 1223, 974, 943, 829, 732, 692 cm^{-1}. HRMS−ESI (m/z): calcd for $C_{17}H_{16}NaO$ $[M + Na]^+$, 259.1108; found, 259.1099.

***tert*-Butyl 3-(1,3-dihydrospiro[indene-2,3′-oxetane]-5-yl)phenyl Carbonate (4cg).** The title compound (254 mg) was obtained from **1c** (134 mg, 1.0 mmol) and **2g** (327 mg, 1.5 mmol) in 72% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.44−7.32 (m, 5H, Ar), 7.25 (d, J = 8.0 Hz, 1H, Ar), 7.16−7.12 (m, 1H, Ar), 4.70 (s, 4H, oxetane ring), 3.29 (s, 2H, $ArCH_2C$), 3.28 (s, 2H, $ArCH_2C$), 1.58 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 151.8, 151.3, 142.8, 142.3, 141.1, 139.0, 129.5, 125.8, 124.8, 124.3, 123.3, 119.9, 119.8, 83.45, 83.42, 46.9, 43.9, 43.7, 27.6. IR (neat): 2975, 2939, 2860, 1752, 1474, 1427, 1369, 1279, 1253, 1157, 973 cm^{-1}. HRMS−ESI (m/z): calcd for $C_{22}H_{24}NaO_4$ $[M + Na]^+$, 375.1572; found, 375.1595.

Diethyl 5-(3-Hydroxyphenyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4ah). The title compound (351 mg) was obtained from **1a** (236 mg, 1.0 mmol) and **2h** (177 mg, 1.5 mmol) in 99% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.37 (s, 1H, Ar), 7.35 (d, J = 7.4 Hz, 1H, Ar), 7.28−7.20 (m, 2H, Ar), 7.10 (d, J = 7.4 Hz, 1H, Ar), 7.00 (d, J = 2.3 Hz, 1H, Ar), 6.79 (dd, J = 3.4, 8.0 Hz, 1H, Ar), 5.42 (br, 1H, ArO*H*), 4.22 (q, J = 7.2 Hz, 4H, OCH_2CH_3), 3.64 (s, 2H, $ArCH_2C$), 3.62 (s, 2H, $ArCH_2C$), 1.26 (t, J = 7.2 Hz, 6H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.8, 156.0, 142.9, 140.6, 139.9, 139.3, 129.8, 126.1, 124.4, 122.9, 119.5, 114.0, 113.9, 61.8, 60.5, 40.4, 40.2, 14.0. IR (neat): 3444, 2980, 2936, 2905, 1730, 1714, 1599, 1573, 1478, 1248, 1068, 782, 695 cm^{-1}. HRMS−ESI (m/z): calcd for $C_{21}H_{22}NaO_5$ $[M + Na]^+$, 377.1395; found, 377.1365.

Diethyl 5-(Aminomethyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4ai). The title compound (236 mg) was obtained from **1a** (236 mg, 1.0 mmol) and **2i** (165 mg, 3.0 mmol) in 81% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.17 (s, 1H, Ar), 7.15 (d, J = 7.5 Hz, 1H, Ar), 7.11 (d, J = 7.5 Hz, 1H, Ar), 4.20 (q, J = 7.2 Hz, 4H, OCH_2CH_3), 3.82 (s, 2H, $ArCH_2NH_2$), 3.57 (s, 2H, $ArCH_2C$), 3.56 (s, 2H, $ArCH_2C$), 1.99 (br, 2H, $ArCH_2NH_2$), 1.25 (t, J = 7.2 Hz, 6H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.6, 141.6, 140.5, 138.7, 126.1, 124.2, 123.1, 61.7, 60.5, 46.2, 40.4, 40.1, 14.0. IR (neat): 3370, 3299, 2935, 2905, 2871, 1671, 1584, 1525, 1495, 1386, 1115, 1012, 943, 901, 819 cm^{-1}. HRMS−ESI (m/z): calcd for $(C_{16}H_{22}NO_4)^+$ 292.1549; found, 292.1545.

Ethyl 5-(Hydroxymethyl)-2,3-dihydro-1*H*-indene-2-carboxylate (4dj). The title compound (97 mg) was obtained from **1d** (164 mg, 1.0 mmol) and **2j** (168 mg, 3.0 mmol) in 44% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.23 (s, 1H, Ar), 7.19 (d, J = 7.5 Hz, 1H, Ar), 7.15 (d, J = 7.5 Hz,1H, Ar), 4.65 (s, 2H, $ArCH_2OH$), 4.18 (q, J = 7.0 Hz, 2H, OCH_2CH_3), 3.33 (quint, J = 8.5 Hz, 1H, $CH(CH_2)_3$), 3.28 − 3.17 (m, 4H, $ArCH_2CH$), 1.28 (t, J = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 176.1, 143.0, 142.1, 140.3, 126.5, 125.2, 124.0, 66.3, 61.5, 44.6, 36.9, 36.8, 15.1. IR (neat): 3445, 2979, 2937, 2855, 1731, 1493, 1440, 1372, 1348, 1261, 1208, 1173, 1033, 820 cm^{-1}. HRMS−ESI (m/z): calcd for $C_{13}H_{16}NaO_3$ $[M + Na]^+$, 243.0997; found, 243.0981.

Ethyl 5-(Aminomethyl)-2,3-dihydro-1*H*-indene-2-carboxylate (4di). The title compound (125 mg) was obtained from **1d** (164 mg, 1.0 mmol) and **2i** (165 mg, 3.0 mmol) in 57% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.18 (s, 1H, Ar), 7.16 (d, J = 8.0 Hz, 1H, Ar), 7.10 (d, J = 8.0 Hz,1H, Ar), 4.17 (q, J = 7.3 Hz, 2H, OCH_2CH_3), 4.15 (s, 2H, $ArCH_2NH_2$), 3.31 (quint, J = 8.4 Hz, 1H, $CH(CH_2)_3$), 3.26 − 3.15 (m, 4H, $ArCH_2CH$), 2.66 (br s, 2H, NH_2), 1.28 (t, J = 7.3 Hz, 3H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 175.2, 142.1, 140.7, 140.4, 125.8, 124.3, 123.3, 60.6, 46.0, 43.7, 36.0, 35.8, 14.2. IR (neat): 3383, 2978, 2947, 2909, 2872, 1732, 1566, 1532, 1483, 1435, 1371, 1335, 1231, 1211, 1175, 1034, 812 cm^{-1}. HRMS−ESI (m/z): calcd for $(C_{13}H_{18}NO_2)^+$ 220.1338; found, 220.1354.

(5-Butyl-1,3-dihydrospiro[indene-2,3′-oxetane]-6-yl)diphenylphosphine Oxide (4ck). The title compound (221 mg) was obtained from **1c** (201 mg, 1.5 mmol) and **2k** (282 mg, 1.0 mmol) in 53% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.68−7.55 (m, 4H, Ar), 7.55−7.52 (m, 2H, Ar), 7.48−7.45 (m, 4H, Ar), 7.19 (d, 1H, J_{P-H} = 3.5 Hz, Ar), 6.94 (d, 1H, J_{P-H} = 14.0 Hz, Ar), 4.66 (d, 2H, J = 6.5 Hz, oxetane), 4.63 (d, 2H, J = 6.5 Hz, oxetane), 3.26 (s, 2H, cyclic CH_2), 3.11 (s, 2H, cyclic CH_2), 2.77 (t, 2H, J = 8.0 Hz, $ArCH_2CH_2$), 1.29 (m, 2H, acyclic CH_2), 1.10 (m, 2H, acyclic CH_2), 0.70 (t, 3H, J = 7.3 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.1 (d, J_{CP} = 9.6 Hz), 146.2 (d, J_{CP} = 2.9 Hz), 138.5 (d, J_{CP} = 14 Hz), 131.93, 131.9 (d, J_{CP} = 9.6 Hz), 131.6 (d, J_{CP} = 2.9 Hz), 129.3 (d, J_{CP} = 13 Hz), 129.2 (d, J_{CP} = 14 Hz), 128.4 (d, J_{CP} = 12 Hz), 126.9 (d, J_{CP} = 11 Hz), 83.4, 46.8, 44.1, 43.6, 34.0 (d, J_{CP} = 4.8 Hz), 33.6, 22.7, 13.8. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 31.30. IR (neat): 2956, 2928, 2867, 2607, 1465, 1437, 1164 cm^{-1}. HRMS−ESI (m/z): calcd for $(C_{30}H_{35}O_3P)^+$ 417.19834; found, 417.20139.

3-Ethyl-3-(((2-((4-vinylbenzyloxy)methyl)-2,3-dihydro-1*H*-inden-5-yl)methoxy)methyl)oxetane (4el). The title compound (295 mg) was obtained from **1e** (201 mg, 1.0 mmol) and **2l** (210 mg, 1.5 mmol) in 78% yield. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.39 (d, 2H, J = 8.2 Hz, Ar), 7.30 (d, 2H, J = 8.2 Hz, Ar), 7.17 (s, 1H, Ar), 7.16 (d, 1H, J = 7.9 Hz, Ar), 7.10 (d, 1H, J = 7.9 Hz, Ar), 6.71 (dd, 1H, J = 10.7, 17.2 Hz, $ArCH$ = CH_2), 5.74 (d, 1H, J = 17.2 Hz, $ArCH{=}CH_2$), 5.24 (d, 1H, J = 10.7 Hz, $ArCH{=}CH_2$), 4.524 (s, 2H, $ArCH_2O$), 4.520 (s, 2H, $ArCH_2O$), 4.51 (d, 2H, J = 5.4 Hz, oxetane), 4.36 (d, 2H, J = 5.4 Hz, oxetane), 3.51 (s, 2H, OCH_2C), 3.48 (d, 2H, J = 6.9 Hz, OCH_2CH), 3.10 − 3.03 (m, 2H, CH_2CHCH_2), 2.86 −2.78 (m, 1H, CH_2CHCH_2), 2.77 − 2.70 (m, 2H, CH_2CHCH_2), 1.33 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 143.2, 142.5, 138.1, 136.9, 136.5, 136.3, 127.8, 126.2, 125.9, 124.5, 124.1, 113.7, 80.2, 75.3, 74.0, 73.6, 72.8, 39.8, 39.2, 36.1, 35.9, 21.4. IR (neat): 2931, 2862, 1628, 1511, 1361, 1093 cm^{-1}. HRMS−ESI (m/z): calcd for $C_{25}H_{30}NaO_3$ $[M + Na]^+$, 401.2093; found, 401.2041.

Diethyl 5-(1-hydroxyethyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4am). The title compound (248 mg) was obtained from **1a** (236 mg, 1.0 mmol) and **2m** (210 mg, 3.0 mmol) in 81% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.22 (s, 1H, Ar), 7.16 (br s, 2H, Ar), 4.86 (q, J = 6.9 Hz, 1H, $ArCHOH$), 4.20 (q, J = 7.3 Hz, 4H, OCH_2CH_3), 3.58 (s, 2H, $ArCH_2C$), 3.57 (s, 2H, $ArCH_2C$), 1.75 (br, 1H, ArCHO*H*), 1.48 (d, 1H, J = 6.9 Hz, $CH(OH)CH_3$), 1.26 (t, J = 7.3 Hz, 6H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.9, 145.0, 139.6, 127.6, 124.6, 124.4, 121.5, 70.7, 62.0, 60.7, 40.7, 40.4, 25.4, 14.3. IR (neat): 3526, 2977, 2932, 2905, 1729, 1445, 1250, 1069, 1012, 860 cm^{-1}. HRMS−ESI (m/z): calcd for $C_{17}H_{22}NaO_5$ $[M + Na]^+$, 329.1365; found, 329.1362.

2-(4-(1,3-Dihydrospiro[indene-2,3′-oxetane]-5-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4cn). The title compound (264 mg) was obtained from **1c** (201 mg, 1.5 mmol) and **2n** (228 mg, 1.0 mmol) in 73% yield. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.86 (d, J = 8.0 Hz, 2H, Ar), 7.57 (d, J = 8.0 Hz, 2H, Ar), 7.46 (s, 1H, Ar), 7.42 (d, J = 8.0 Hz, 1H, Ar), 7.27 (d, J = 8.0 Hz, 1H, Ar), 4.70 (s, 4H, oxetane ring), 3.30 (s, 2H, $ArCH_2C$), 3.29 (s, 2H, $ArCH_2C$), 1.36 (s, 12H, $OCCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.0, 142.3, 141.1, 139.9,

135.2, 126.37, 126.35, 126.0, 124.9, 123.4, 83.8, 83.5, 47.0, 44.0, 43.8, 24.9. IR (neat): 2980, 2931, 2861, 1608, 1396, 1360, 1144 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $C_{23}H_{27}BKO_3$ $[M + K]^+$, 401.1960; found, 401.1936.

Diethyl 5-Vinyl-1*H*-indene-2,2(3*H*)-dicarboxylate (4am′). *p*-Toluene sulfonic acid hydrate (5.2 mg, 0.03 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (∼0.1 mg, ∼0.5 μmol) were added to a solution of **4am** (306 mg, 1.0 mmol) in dimethyl sulfoxide (3.3 mL) and the resulting mixture was heated to 140 °C for 3 h. After being cooled to room temperature, the mixture was quenched by addition of aqueous saturated $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel to give **4am′** (210 mg) in 73% yield as an yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.26 (s, 1H, Ar), 7.21 (d, *J* = 7.8 Hz, 1H, Ar), 7.14 (d, *J* = 7.8 Hz, 1H, Ar), 6.68 (dd, *J* = 10.9, 17.2 Hz, 1H, ArC*H* = CH_2), 5.69 (d, *J* = 17.2 Hz, 1H, ArCH=CH_2), 5.18 (d, *J* = 10.9 Hz, 1H, ArCH=CH_2), 4.20 (q, *J* = 7.2 Hz, 4H, OC$H_2$$CH_3$), 3.58 (s, 2H, ArC$H_2$C), 3.57 (s, 2H, ArC$H_2$C), 1.26 (t, *J* = 7.3 Hz, 6H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.5, 140.2, 139.8, 136.8, 136.6, 125.4, 124.2, 121.7 113.1, 61.7, 60.4, 40.3, 40.2, 14.0. IR (neat): 2981, 2936, 2905, 1730, 1455, 1278, 903, 860, 827 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $C_{17}H_{20}NaO_4$ $[M + Na]^+$, 311.1259; found, 311.1227.

General Procedure for Synthesis of Monomers 5 from Diynes 1 and Alkynes 3. A solution of $CoCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol) and 1,2-bis(diphenylphosphino)ethane (23.9 mg, 0.06 mmol) in *N*-methyl-2-pyrrolidone (2.0 mL for synthesis of **5cb** and **5cc**) or acetonitrile (4.0 mL for synthesis of **5ca**) was added to a mixture of diyne **1c** (134 mg, 1.0 mmol), nitrile **3** (2-cyanopyridine: 312 mg, 3.0 mmol or malononitrile: 99 mg, 1.5 mmol) and zinc powder (6.5 mg, 0.10 mmol), and the resulting mixture was stirred at 50 °C. The reaction progress was checked by TLC analysis. After complete consumption of **1c**, ethyl acetate was added and the mixture was passed through a pad of Celite with ethyl acetate. The filtrate was concentrated to dryness and the resulting colored residue was chromatographed on silica gel to give the corresponding pyridine **5**.

3-Methyl-5,7-dihydrospiro[cyclopenta[*c*]pyridine-6,3′-oxetane] (5ca). The title compound (102 mg) was obtained from **1c** (134 mg, 1.0 mmol) and acetonitrile (**3a**: 4.0 mL, ∼80 mmol) in 58% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.33 (s, 1H, Py), 7.03 (s, 1H, Py), 4.68 (d, *J* = 6.3 Hz, 2H, oxetane), 4.66 (d, *J* = 6.3 Hz, 2H, oxetane), 3.24 (s, 2H, PyCH_2C), 3.22 (s, 2H, PyCH_2C), 2.51 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.5, 151.5, 144.9, 134.6, 119.5, 83.1, 46.9, 43.6, 41.1, 24.2. IR (neat): 3007, 2928, 2862, 1611, 1561, 1487, 1429, 1392, 1247, 1233, 977, 923, 830 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $(C_{11}H_{14}NO)^+$ 176.1075; found, 176.1067.

3-(Pyridin-2-yl)-5,7-dihydrospiro[cyclopenta[*c*]pyridine-6,3′-oxetane] (5cb). The title compound (59 mg) was obtained from **1c** (134 mg, 1.0 mmol) and 2-cyanopyridine (**3b**: 312 mg, 3.0 mmol) in 25% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.66 (d, *J* = 4.5 Hz, 1H, Py), 8.65 (s, 1H, Py), 8.34 (d, *J* = 8.0 Hz, 1H, Py), 8.27 (s, 1H, Py), 7.81−7.78 (m, 1H, Py), 7.30−7.27 (m, 1H, Py), 4.70 (d, *J* = 6.3 Hz, 2H, oxetane), 4.69 (d, *J* = 6.3 Hz, 2H, oxetane), 3.32 (s, 4H, PyCH_2C). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.2, 154.9, 152.1, 149.0, 145.0, 137.8, 136.8, 123.4, 121.0, 117.2, 83.0, 46.9, 43.6, 41.3. IR (KBr) 2958, 2948, 2920, 2877, 2854, 1605, 1586, 1552, 1464, 1425, 1381, 974, 795, 746 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $C_{15}H_{14}ClN_2O$ $[M + Cl]^-$ 275.0765; found, 275.0714.

2-(5,7-Dihydrospiro[cyclopenta[*c*]pyridine-6,3′-oxetane]-3-yl)-ethanenitrile (5cc). The title compound (126 mg) was obtained from **1c** (134 mg, 1.0 mmol) and malononitrile (**3c**: 99 mg, 1.5 mmol) in 25% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.41 (s, 1H, Py), 7.32 (s, 1H, Py), 4.70 (d, *J* = 6.3 Hz, 2H, oxetane), 4.68 (d, *J* = 6.3 Hz, 2H, oxetane), 3.90 (s, 2H, PyCH_2CN), 3.29 (br s, 2H, PyCH_2C). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.9, 148.6, 145.7, 137.2, 118.6, 117.2, 82.9, 46.9, 43.6, 41.1, 26.4. IR (neat): 2961, 2930, 2864, 2252, 1608, 1485, 1260, 1094, 1022, 974, 801 cm^{-1}. HRMS−ESI (*m*/*z*): calcd for $C_{12}H_{12}N_2NaO_1$ $[M + Na]^+$, 223.0847; found, 223.0826.

BF_3−Catalyzed Cationic Polymerization of 4ca. $BF_3 \cdot Et_2O$ (2.1 mg, 0.1 mmol) was added to a solution of **4ca** (236 mg, 1.0 mmol) in dry CH_2Cl_2 (0.4 mL). After stirring for 8 h at 0 °C, the reaction mixture was poured into methanol containing a few drops of aqueous ammonia and was filtered. The cake was dried under reduced pressure. The residue was twice precipitated in chloroform/methanol, and the solid was dried in *vacuo* to yield *poly*-**4ca** (194 mg) in 82% yield as a white solid: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48−7.41 (m, 2H × *n*, Ar), 7.34−7.19 (m, 5H × *n*, Ar), 7.09−7.03 (br s, 1H × *n*, Ar), 3.26 (br s, 4H × *n*, OCH_2C), 2.74 (br s, 1H × *n*, ArCH_2C), 2.73 (br s, 1H × *n*, ArCH_2C). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.3, 141.8, 139.7, 137.2, 136.4, 128.3, 126.4, 125.9, 124.4, 122.4, 83.6, 79.8, 46.9, 44.1, 43.7, 43.6, 41.7. IR (film) 3057, 3029, 2845, 2788, 1600, 1570, 1480, 1457, 1433, 1362, 1263, 1223, 1109, 1020, 898, 758, 697 cm^{-1}. $M_n = 4.56 \times 10^4$, $M_w = 2.23 \times 10^5$, $M_w/M_n = 4.89$ based on GPC analysis. T_g = 106.9 °C.

BF_3-Catalyzed Cationic Random Copolymerization of Oxetanes 7 and 4ck. $BF_3 \cdot Et_2O$ (35.1 mg, 0.25 mmol) was added to a solution of oxetane **7** (365 mg, 1.9 mmol) and **4ck** (80.0 mg, 0.19 mmol) in CH_2Cl_2 (18.5 mL) at 0 °C. The solution was stirred for 72 h at room temperature and then quenched by addition of aqueous saturated $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2. The combined organic layers were washed with aqueous NaCl, dried over Na_2SO_4, filtered through a pad of Celite, and concentrated in *vacuo*. The residue was twice precipitated in ether/hexane and dried *in vacuo* to give *poly*(**7**-*co*-**4ck**) (172 mg) in 40% yield as a white solid: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72−7.60 (br, 4H × *n*, Ar), 7.55−7.37 (br, 6H × *n*, Ar), 7.23−7.10 (br, 2H × *n*, Ar), 6.93−6.67 (br, 3H, Ar), 3.92−3.58 (br, 2H × *n*, CC_H_2O), 3.42−3.00 (br, 4H × *n*, CH_2CCH_2), 2.81−2.35 (br, 4H × *n*, cyclic), 1.59−1.22 (br, 2H × *n*, CCH_2CH_3), 0.93−0.54 (br, 3H × *n*, CCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.4, 131.94, 131.86, 129.2, 128.4, 128.3, 120.3, 114.5, 71.5, 68.6, 43.1, 33.9, 33.6, 23.3, 23.17, 23.14, 22.7, 13.8, 7.7. ^{31}P NMR ($CDCl_3$, 202 MHz): δ −14.05. IR (film) 2963, 2905, 1599, 1497, 1261, 1169, 1096 cm^{-1}. $M_n = 3.89 \times 10^3$, $M_w = 1.09 \times 10^4$, $M_w/M_n = 2.81$ based on GPC analysis.

Radical Random Copolymerization of 4ac and Styrene. A solution of 2,2′-azobis(isobutyronitrile) (5.4 mg, 0.028 mmol) in dry toluene (1.0 mL) was added to a mixture of **4ac** (364 mg, 1.0 mmol) and styrene (521 mg, 5.0 mmol). After heating to 60 °C for 24 h, the reaction mixture was poured into methanol and the precipitated solid was collected by filtration. The resulting solid was dried under reduced pressure. The residue was twice precipitated in chloroform/methanol and dried in *vacuo* to give *poly*(styrene-*co*-**4ac**) (194 mg) in 68% yield as a white solid: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45−6.27 (br, Ar from **4ac** and styrene), 4.22 (br s, OC$H_2$$CH_3$ from **4ac**), 3.95 (br s, ArCH_2C from **4ac**), 2.11−1.20 (br s, ArC*H*CH_2, ArCHCH_2, OCH_2CH_3 from **4ac** and ArC*H*CH_2, ArCHCH_2 from styrene). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.7, 145.2, 140.6, 138.7, 127.9, 127.8, 127.6, 127.4, 127.3, 126.6, 125.9, 125.6, 125.5, 124.4, 122.7, 61.7, 60.5, 40.5, 40.2, 14.0. IR (film) 3081, 3059, 3025, 2979, 2924, 2849, 1732, 1600, 1582, 1492, 1452, 1366, 1244, 1186, 1156, 1067, 817, 759, 543 cm^{-1}. $M_n = 9.25 \times 10^4$, $M_w = 2.21 \times 10^5$, M_w/M_n = 2.39 based on GPC analysis, T_g = 102.9 °C. ^{1}H NMR spectra indicated 81% of styrene incorporation.

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Supporting Information Available: Text giving a detailed experimental section including experimental procedures and

figures showing the structures and spectroscopic data of compounds **1**, **2**, **4**, **5** and the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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