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An Efficient Synthesis of Geminal-Dialkyl Dienes for Olefin Metathesis Polymerization

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General Considerations

Unless otherwise stated, all reactions were performed under argon atmosphere using oven dried glassware. Anhydrous solvents were dried using activated alumina and stored in Schlenk flasks over activated 3 Å molecular sieves. All reagents were purchased from commercial suppliers (TiCl₄ was purchased from Acros Organics, all other reagents and solvents were purchased from Millipore Sigma) and used as received. CDCl₃ (99.8% D) was purchased from Cambridge Isotope Laboratories, Inc. and used as received. Methyl 9-decenoate was a donation from Elevance Renewable Sciences. The second generation Ru metathesis catalyst was received as a donation from Materia Inc. NMR spectra were collected using Varian 500 or 600 MHz spectrometers or a Bruker 400 MHz spectrometer. Mass spectrometry was performed at the Caltech Mass spectrometry facility. Differential Scanning Calorimetry was performed using a Mettler Toledo DSC 3+ Star System. Ethyl-(E)-hex-4-enoate, i and nona-1,8-dien-5-one ii were synthesized according to literature precedent.

Experimental Procedures

\[(Z)-\text{cyclooct-4-en-1-one (11):}\] According to a known procedure, iii a solution of hydrogen peroxide (35% in water, 5 mL, 60 mmol) was added to a mixture of palladium acetate (90 mg, 0.4 mmol), benzoquinone (87 mg, 0.8 mmol) and 1,5-cyclooctadiene (5.4 mL, 40 mmol). The mixture was stirred for 5 days at 30° C. The mixture was poured into Et₂O (100 mL) and water was added (100 mL) then the mixture was slowly basified with 1M NaOH solution while cooling with ice. The layers were separated and the aqueous layer was extracted with Et₂O (2 × 100 mL). The combined organic layers were twice washed with 1M NaOH and dried over Na₂SO₄. Distillation under reduced pressure afforded ketone 11 (1.36 g, 27% yield) as a colorless oil. Spectral data matched those reported in the literature.iv
(Z)-2,2-dimethylcyclooct-4-en-1-one (12): To a stirred solution of KOt-Bu (5.61 g, 2.5 equiv) in THF (100 mL) was added ketone 11 (2.48 g, 20.0 mmol) in THF (20 mL). The solution was stirred for 1 hour at –40 ºC, and MeI (6.3 mL, 5.0 equiv) was added. The reaction mixture was slowly warmed to 23 ºC and stirring was continues for 20 hours. Water (50 mL) was then added and the aqueous phase was extracted by Et₂O (3 × 50 mL). GC analysis showed > 50:1 ratio of products 12 and 13, and pure compound 12 can be isolated by column chromatography (SiO₂, 10:1 pentane/Et₂O) as a colorless liquid (1.29 g, 42%).

TLC (10:1 pentane/Et₂O): Rf = 0.4 (KMnO₄).

¹H NMR (400 MHz, CDCl₃) δ 5.69 – 5.56 (m, 1H), 2.45 (dd, J = 8.0, 4.0 Hz, 1H), 2.25 (d, J = 7.2 Hz, 1H), 2.15 – 2.07 (m, 1H), 1.64 – 1.54 (m, 1H), 1.06 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 217.5, 131.9, 129.2, 52.6, 37.8, 36.5, 27.3, 26.3, 23.7.


(Z)-4,4-dimethylcyclooct-1-ene (16): Ketone 12 (2.10 g, 13.8 mmol) in THF (50 mL) was added to a solution of Red-Al (16.6 mmol, 1.2 equiv) in THF (40 mL) dropwise at –78 ºC under argon atmosphere. After stirring at the same temperature for 3 hours, the solution was quenched with 0.1 M HCl (100 mL), and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were then washed with saturated aqueous NaHCO₃ (50 mL) and brine (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was filtered through a plug of silica with Et₂O wash. The crude alcohol product 14 was obtained as a colorless oil (2.23 g), which was used in the next step without further purification.

To a suspension of NaH (60% in mineral oil, 2.24 g, 96 mmol, 4.0 equiv) in THF (100 mL) at 0 ºC was added alcohol 14 (2.23 g, 14 mmol, 1.0 equiv) in THF (20 mL). The mixture was stirred for 30 min, at which point CS₂ (8.4 mL, 140 mmol, 10.0 equiv) was added. The mixture was stirred for an additional 30 min, at which point iodomethane (8.7 mL, 140 mmol, 10.0 equiv) was added. The reaction mixture was allowed to warm to room temperature for 3 hours before being quenched with MeOH (50 mL) and evaporated in vacuo. The residue was dissolved in EtOAc (100 mL), washed with water (50 mL) and brine (50 mL). The organic layer was dried over Na₂SO₄ and concentrated. Column chromatography (SiO₂, hexanes) afforded crude xanthate 15 (4.42 g) as a yellow oil.

Then, methyl xanthate 15 (733 mg, 3 mmol, 1.0 equiv) was dissolved in a flame-dried 500 mL flask with benzene (100 mL), combined with H₂O (0.27 mL, 15 mmol, 5.0 equiv) and allowed to stir for 1 h. Argon gas was then bubbled through the solution for a period of 1 h, after which, a solution of BEt₃ (1.0 M in THF, 15 mL, 15 mmol, 5.0 equiv) was added via syringe pump over 1 h. On completion of BEt₃ addition, dry oxygen (54 mL, 2.4 mmol O₂, 0.8 equiv) was introduced.
via syringe pump at a rate of 1.2 ml/hr through a stainless steel cannula positioned beneath the reaction surface. Upon completion of air addition, hydrogen peroxide (30 % in water, 50 mL) and sodium hydroxide (3.0 M in water, 50 mL) were introduced simultaneously into the reaction mixture (Caution: reaction is exothermic). After stirring for 10 min, the solution was diluted with brine (100 mL), and the aqueous layer was extracted with EtOAc (3 × 100 mL). Combined organic portions were dried over anhydrous sodium sulfate, filtered, and concentrated. Distillation under reduced pressure afforded 16 as a colorless oil (297 mg, 72%).

TLC (pentane): Rf = 0.9 (KMnO₄).

**¹H NMR** (400 MHz, CDCl₃) δ 5.85 – 5.48 (m, 2H), 2.17 – 2.04 (m, 2H), 1.92 (d, J = 8.2 Hz, 2H), 1.49 (dd, J = 6.0, 3.2 Hz, 4H), 1.33 – 1.23 (m, 2H), 0.89 (s, 6H).

**¹³C NMR** (126 MHz, CDCl₃) δ 131.4, 128.9, 39.7, 37.5, 36.1, 30.3, 29.0, 26.8, 23.5.


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**Nonadeca-1,18-dien-10-one (18):** A 100 mL three-necked round bottom flask was fitted with a dropping funnel and two ground glass stoppers and charged with a magnetic stir bar, NaH (60 wt% in mineral oil, 3.7 g, 92 mmol, 1.2 equiv), and toluene (25 mL). This suspension was heated to 100 °C and a solution of methyl 9-decenolate (14.3 g, 80 mmol, 1 equiv) in toluene (10 mL) was added dropwise over the course of 30 min. The reaction mixture was then heated to 110 °C with stirring for 24 h, cooled to ambient temperature and quenched by the slow addition of MeOH. The solvent was removed in vacuo and the residue was suspended in EtOH (50 mL) and water (25 mL). NaOH (1.6 g, 1.0 equiv) was added and the reaction mixture was heated to reflux for 2 h. After cooling to ambient temperature, the reaction mixture was extracted with Et₂O (3 × 50 mL) and the combined organic layers were washed with water (3 × 50 mL), brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated. Crystallization with MeOH afforded 18 as a white solid (10.2 g, 90% yield over two steps) Spectral data matched those reported in the literature.

**Trideca-1,12-dien-7-one (26):** To a stirred solution of hydrazone 25 (4.0 g, 40 mmol, 1.0 equiv) in THF (80 mL) was added n-butyl lithium solution (16.8 mL, 2.5 M solution in hexanes, 42 mmol, 1.05 equiv). After stirring 30 minutes at 0 °C, 5-bromo-1-pentene (4.8 mL, 40 mmol, 1.0 equiv) was added and the reaction mixture was stirred for 1 hour at 23 °C. Then the reaction mixture was cooled to 0 °C again and n-butyl lithium solution (16.8 mL, 2.5 M solution in hexanes, 42 mmol, 1.05 equiv) was added. After stirring 30 minutes at 0 °C, 5-bromo-1-pentene (4.8 mL, 40 mmol, 1.0 equiv) was added again and the reaction mixture was stirred for 2 hours at 23 °C before quenched by saturated NH₄Cl solution (100 mL). The aqueous layer was extracted with Et₂O (2 × 100 mL) and the combined organic phases were washed with brine (100 mL), dried over anhydrous
MgSO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was dissolved in CH₂Cl₂ (40 mL), and HCl solution (16 mL, 3.0 M) was added. After 12 h, the phases were separated and the aqueous phase was extracted with CH₂Cl₂ (2 × 50 mL). The combined organic phases are washed with saturated NaHCO₃ solution (100 mL). Column chromatography (SiO₂, 10:1 hexanes/EtOAc) gave 26 as a colorless oil (7.0 g, 90% yield).

**¹H NMR** (400 MHz, CDCl₃): δ 5.66 (ddt, J = 16.9, 10.2, 6.5 Hz, 2H), 4.94 – 4.77 (m, 4H), 2.32 – 2.23 (m, 4H), 1.97 – 1.88 (m, 4H), 1.46 (dt, J = 15.2, 7.3 Hz, 4H), 1.30 – 1.20 (m, 4H).

**¹³C NMR** (101 MHz, CDCl₃): δ 211.2, 138.5, 114.6, 42.6, 33.6, 28.5, 23.3.

**HRMS (EI+, m/z):** calc’d for C₁₃H₂₂O [M]⁺ 194.1671, found: 194.1646.

Henicosa-1,20-dien-11-one (29): A 500 mL flamed-dried round bottom flask charged with ethyl 10-undecenoate (21.0 g, 100 mmol, 1.0 equiv) and sodium ethoxide (3.4 g, 50 mmol, 0.5 equiv) was equipped with a reflux condenser and a vacuum adapter. The reaction was stirred at 100 ºC under a dynamic vacuum (2 torr) for 12 hours to remove the ethanol produced. After the reaction was cooled to 23 ºC, the crude β-keto ester 29a was dissolved in ethanol (50 mL) and 2 M NaOH solution (20 mL, 1.0 equiv) was added. The reaction mixture was warmed to reflux for 2 hours and cooled to 23 ºC. A white solid precipitated and was collected by filtration and recrystallized from refluxing methanol, to give ketone 29 as a white solid (7.47 g, 63% yield over two steps).

**¹H NMR** (400 MHz, CDCl₃): δ 5.73 (ddt, J = 16.9, 10.1, 6.6 Hz, 2H), 4.97 – 4.82 (m, 4H), 2.31 (t, J = 7.5 Hz, 4H), 2.01 – 1.91 (m, 4H), 1.49 (q, J = 7.0 Hz, 4H), 1.34 – 1.25 (m, 4H), 1.24 – 1.17 (m, 16H).

**¹³C NMR** (101 MHz, CDCl₃): δ 211.7, 139.2, 114.2, 42.8, 33.8, 29.4, 29.3, 29.3, 28.9, 23.9.

**HRMS (EI+, m/z):** calc’d for C₂₁H₃₈O [M]⁺ 306.2923, found: 306.2927.

An oven-dried 500 mL three-necked round bottom flask was equipped with a magnetic stirbar and fitted with two rubber septa and a ground glass flow adaptor to introduce inert atmosphere. This flask was charged with (E)-hex-4-enoate (20 g, 140 mmol) and NBu₃ (17 mL, 140 mmol) via syringe. Anhydrous toluene (350 mL) was added by cannula, and the reaction mixture was cooled to –78 ºC. TiCl₄ (18.4 mL, 168 mmol) was added dropwise via syringe over twenty minutes, causing the reaction mixture to become deep red in color. The reaction mixture was stirred with warming to ambient temperature for 10 h, and saturated aqueous NaHCO₃ was carefully added to quench the reaction. The organic layer was separated, the aqueous layer was
extracted with Et₂O (3 × 25 mL), and the combined organic layers were washed with water (20 mL), brine (2 × 20 mL), dried over MgSO₄, and concentrated to a clear, yellow oil.

The yellow oil was dissolved in EtOH (200 mL) and water (50 mL) and NaOH pellets were added (3 g). The reaction mixture was heated to 85 °C and monitored by TLC (5% Et₂O in hexanes) until the starting material was fully consumed. The reaction mixture was concentrated and extracted with Et₂O (3 × 50 mL), and the combined organic layers were washed with water (3 × 25 mL) and brine (25 mL), dried over MgSO₄, filtered and concentrated. The product 31 was purified by column chromatography (SiO₂, 5% Et₂O in hexanes) to yield a clear, pale yellow oil (11 g, 60 mmol, 85%)

1H NMR (600 MHz, CDCl₃) δ 5.49 – 5.34 (m, 4H), 2.43 (t, J = 7.4 Hz, 4H), 2.28 – 2.19 (m, 4H), 1.65 – 1.59 (m, 6H).

13C NMR (101 MHz, CDCl₃) δ 210.4, 129.7, 126.0, 42.8, 26.9, 18.0.

HRMS (El+) calc’d for C₁₁H₁₈O[M]⁺ 166.1358; found 166.1346

(Z)-dibenzy1 oct-4-ene-1,8-diyl bis(carbonate) (38): In a nitrogen-filled glovebox, 4-penten-1-ol (1.72 g, 20 mmol) was dissolved in 6 mL THF in a 20 mL vial equipped with a stir bar, and Ru-2 (13.5 mg, 0.1 mol%) was added. The vial was placed on a 35 ºC stir plate without capping and stirring was continued for 4 hours. At that time the reaction progress was monitored by GC analysis to ensure full conversion, and the vial was brought outside the glovebox and the reaction mixture was quenched with a few drops of ethyl vinyl ether. Column chromatography (SiO₂, 2:1 hexanes/EtOAc) gave 38a as a colorless oil (1.06 g, 74% yield).

To the diol 38a (1.06 g, 7.35 mmol, 1.0 equiv) in 30 mL CH₂Cl₂, pyridine (3.0 mL, 36.75 mmol, 5.0 equiv) and DMAP (180 mg, 1.47 mmol, 0.2 equiv) was added sequentially at 0 ºC. Then benzyl chloroformate (4.2 mL, 29.4 mmol, 4.0 equiv) was added dropwisely. The mixture was left to stir at 23 ºC for overnight before it was quenched with 1 M HCl (30 mL). The aqueous phase was extracted by Et₂O three times. The combined organic phases were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Column chromatography (SiO₂, 9:1 hexanes/EtOAc) gave 38 as a colorless oil (2.52 g, 83% yield).

1H NMR (400 MHz, CDCl₃) δ 7.43 – 7.30 (m, 10H), 5.38 (ddd, J = 5.6, 4.4, 1.1 Hz, 2H), 5.15 (s, 4H), 4.13 (t, J = 6.6 Hz, 4H), 2.18 – 2.03 (m, 4H), 1.72 (dq, J = 8.2, 6.7 Hz, 4H).
\[ ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 155.3, 135.4, 129.5, 128.7, 128.6, 128.5, 69.6, 67.7, 28.6, 23.4. \]

\[ \text{HRMS (FAB+, m/z): calc'd for C}_{24} \text{H}_{29} \text{O}_6 \ [\text{M+H}]^{+} \ 413.1964, \text{found: 413.1961.} \]

**General Procedure A for gem-dimethylation of ketones:**

![Chemical reaction](image)

In a flame-dried round-bottom flask, ketone (1.0 equiv) was dissolved in THF and the reaction mixture was cooled to 0 °C. Methylmagnesium bromide solution (3.0 M solution in diethyl ether, 1.5 equiv) was added dropwise, and the reaction mixture was slowly warmed to 23 °C. After 1 hour, the reaction mixture was cooled to 0 °C, and quenched by saturated NH\textsubscript{4}Cl solution. The aqueous phase was extracted with Et\textsubscript{2}O twice, dried over anhydrous MgSO\textsubscript{4}, and concentrated under reduced pressure.

The crude tertiary alcohol was transferred into a Schlenk flask (with one side arm fitted with a glass stopcock) with dry CH\textsubscript{2}Cl\textsubscript{2}. The residual solvent was removed by connecting the side arm to vacuum. The flask was back-filled with argon and cooled to 0 °C, and then SOCl\textsubscript{2} (2.5 equiv) was added slowly. A minimal amount of CH\textsubscript{2}Cl\textsubscript{2} can be added to aid with stirring. The reaction mixture was stirred at 0 °C for 1 hour, and the reaction progress can be monitored by TLC (using Al\textsubscript{2}O\textsubscript{3} plate). The side arm of the Schlenk flask was reconnected to vacuum and excess SOCl\textsubscript{2} was removed at 0 °C. Then the crude tertiary chloride product was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (0.3 M) and the reaction mixture was cooled to –78 °C. Trimethylaluminum (2.0 M solution in hexanes, 2.0 equiv) was added dropwise. The reaction mixture was slowly warmed to 23 °C and stirred for 4 hours and then quenched with aqueous HCl solution (1.0 M) at 0 °C. The aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2}, dried over anhydrous MgSO\textsubscript{4}, filtered, and concentrated under reduced pressure. The gem-dimethylation products were purified by column chromatography (SiO\textsubscript{2}, 100% hexanes) or distillation.

**10,10-dimethylnonadeca-1,18-diene (21):** Prepared according to General Procedure A from ketone 18 (10.2 g, 37 mmol) as a colorless liquid (9.1 g, 83% yield).

\[ ^{1}H \text{ NMR} \ (600 \text{ MHz, CDCl}_3) \delta 5.82 \ (ddt, J = 16.9, 10.1, 6.7 \text{ Hz}, 2H), 5.00 \ (dq, J = 17.1, 1.7 \text{ Hz}, 2H), 4.93 \ (ddt, J = 10.2, 2.4, 1.2 \text{ Hz}, 2H), 2.07 – 2.00 \ (m, 4H), 1.42 – 1.09 \ (m, 24H), 0.81 \ (s, 6H). \]

\[ ^{13}C \text{ NMR} \ (126 \text{ MHz, CDCl}_3) \delta 139.3, 114.1, 42.0, 33.8, 32.6, 30.6, 29.6, 29.2, 29.0, 27.3, 24.0. \]

\[ \text{HRMS (EI+, m/z): calc’d for C}_{21} \text{H}_{40} \ [\text{M}]^{+} \ 292.3130, \text{found: 292.3144.} \]
5,5-dimethylnona-1,8-diene (24): Prepared according to General Procedure A from ketone 23 (25 g, 181 mmol) as a colorless liquid (13 g, 58% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.81 (ddt, $J = 16.9, 10.2, 6.6$ Hz, 2H), 4.99 (dq, $J = 17.1, 1.7$ Hz, 2H), 4.94 – 4.86 (m, 2H), 2.02 – 1.93 (m, 4H), 1.30 – 1.22 (m, 4H), 0.86 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.80, 113.77, 41.06, 32.65, 28.58, 27.08.

HRMS (EI+, m/z): calc’d for C$_{11}$H$_{20}$ [M]$^+$ 152.1565, found: 152.1561.

7,7-dimethyltrideca-1,12-diene (27): Prepared according to General Procedure A from ketone 26 (1.94 g, 10 mmol) as a colorless liquid (1.2 g, 58% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.75 (ddt, $J = 16.9, 10.1, 6.7$ Hz, 2H), 4.98 – 4.81 (m, 4H), 2.03 – 1.94 (m, 4H), 1.32 – 1.23 (m, 4H), 1.19 – 1.05 (m, 8H), 0.75 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.3, 114.1, 41.8, 33.9, 32.7, 29.9, 27.3, 23.5.

HRMS (EI+, m/z): calc’d for C$_{15}$H$_{28}$ [M]$^+$ 208.2191, found: 208.2177.

11,11-dimethylhenicosa-1,20-diene (30): Prepared according to General Procedure A from ketone 29 (7.47 g, 24.4 mmol) as a colorless liquid (5.66 g, 72% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.84 (ddt, $J = 16.9, 10.2, 6.7$ Hz, 2H), 5.08 – 4.89 (m, 4H), 2.14 – 2.00 (m, 4H), 1.40 (q, $J = 6.9$ Hz, 4H), 1.35 – 1.12 (m, 24H), 0.84 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.4, 114.2, 42.1, 34.0, 32.7, 30.8, 29.8, 29.7, 29.3, 29.1, 27.5, 24.2.

HRMS (EI+, m/z): calc’d for C$_{23}$H$_{44}$ [M]$^+$ 320.3443, found: 320.3425.

5,5-diethylnona-1,8-diene (33): Prepared according to modified General Procedure A from ketone 23 (276 mg, 2.0 mmol), EtMgBr, and AlEt$_3$ to afford 33 as a clear, colorless oil (230 mg, 63% yield).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 5.82 (ddt, $J = 16.9, 10.2, 6.6$ Hz, 2H), 5.00 (dq, $J = 17.1, 1.6$ Hz, 2H), 4.91 (ddt, $J = 10.0, 2.3, 1.2$ Hz, 2H), 1.96 – 1.87 (m, 4H), 1.26 – 1.19 (m, 8H), 0.75 (t, $J = 7.5, 1.0$ Hz, 6H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.9, 113.9, 37.3, 34.9, 28.0, 27.7, 7.6.

HRMS (EI+) calc’d for C$_{13}$H$_{24}$ [M]$^+$ 180.1878; found 180.1894.

11-butyl-11-ethylhenicosa-1,20-diene (34): Prepared according to modified General Procedure A from ketone 29 (918 mg, 3 mmol) with n-butylmagnesium chloride solution (2.0 M solution in diethyl ether, 1.5 equiv) and triethylaluminum (2.0 equiv). 34 was obtained as a colorless liquid (680 mg, 60% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.74 (ddt, $J$ = 17.0, 10.2, 6.7 Hz, 2H), 4.96 – 4.82 (m, 4H), 2.01 – 1.92 (m, 4H), 1.35 – 1.25 (m, 4H), 1.25 – 1.11 (m, 24H), 1.07 – 0.99 (m, 8H), 0.82 (td, $J$ = 7.2, 2.0 Hz, 3H), 0.64 (t, $J$ = 7.5 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.4, 114.2, 37.5, 37.1, 36.2, 35.9, 33.9, 33.9, 33.5, 30.8, 30.3, 29.8, 29.7, 29.7, 29.3, 29.1, 28.7, 26.8, 25.4, 23.8, 23.3, 23.1, 14.4, 14.4, 7.7.

HRMS (EI+, m/z): calc’d for C$_{27}$H$_{52}$ [M]$^+$ 376.4069, found: 376.4120.

11-ethyl-11-octylhenicosa-1,20-diene (35): Prepared according to modified General Procedure A from ketone 29 (153 mg, 0.5 mmol) with n-octylmagnesium chloride solution (2.0 M solution in THF, 1.5 equiv) and triethylaluminum (2.0 equiv). 35 was obtained as a colorless liquid (154 mg, 71% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.74 (ddt, $J$ = 16.9, 10.2, 6.7 Hz, 2H), 4.99 – 4.80 (m, 4H), 2.04 – 1.90 (m, 4H), 1.34 – 1.26 (m, 4H), 1.25 – 1.10 (m, 34H), 1.05 – 1.00 (m, 6H), 0.83 – 0.78 (m, 3H), 0.64 (t, $J$ = 7.5 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.4, 114.2, 37.5, 37.2, 36.2, 34.0, 33.8, 32.1, 30.8, 30.8, 30.5, 30.3, 30.3, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.3, 29.1, 28.7, 26.8, 23.1, 22.9, 14.3, 7.7.

HRMS (EI+, m/z): calc’d for C$_{31}$H$_{60}$ [M]$^+$ 432.4695, found: 432.4714.

(2E,9E)-6,6-dimethylundeca-2,9-diene (36): Prepared according to general procedure A from ketone 31 (258 mg, 1.6 mmol) as a colorless liquid (230 mg, 82%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 5.49 – 5.39 (m, 4H), 1.96 – 1.89 (m, 4H), 1.66 (dt, $J$ = 4.8, 1.3 Hz, 6H), 1.27 – 1.21 (m, 4H), 0.86 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 132.3, 124.2, 41.8, 32.6, 27.3, 27.1, 18.0.
HRMS (EI+) calc’d for C_{13}H_{24} [M]^{+} 180.1878; found 180.1865.

**General Procedure B for gem-dialkylation of ketones:**

In a flame-dried round-bottom flask, ketone (1.0 equiv) was dissolved in THF and the reaction mixture was cooled to 0 °C. Methylmagnesium bromide solution (3.0 M solution in diethyl ether, 1.5 equiv) was added dropwise, and the reaction mixture was slowly warmed to 23 °C. After 1 hour, the reaction mixture was cooled to 0 °C, and quenched by saturated NH₄Cl solution. The aqueous phase was extracted with Et₂O twice, dried over anhydrous MgSO₄, filtered over a short silica plug, and concentrated under reduced pressure.

A 100 mL round bottom flask equipped with a magnetic stirbar was charged with the tertiary alcohol (1.0 equiv) and dissolved in anhydrous CH₂Cl₂ (1 M). This solution was cooled to 0 °C and PBr₃ (0.35 equiv) was added dropwise. The reaction mixture was stirred for 2 h at 0 °C, and then concentrated in vacuo. The flask was fitted with a short path distillation head and the residue was distilled under vacuum to afford the tertiary bromide as a clear, colorless oil.

A 250 mL round bottom flask equipped with a magnetic stirbar was charged with ZnCl₂ (0.1 equiv) and the tertiary bromide (1 equiv) and dissolved in anhydrous CH₂Cl₂ (0.5 M). This solution was cooled to –40 °C and the dialkylzinc reagent (1.0 equiv) was added dropwise via syringe. The reaction mixture was stirred with warming to ambient temperature for 12 h, and then quenched by the dropwise addition of MeOH. The reaction mixture was washed with 1 M HCl, the organic layer was separated, washed with brine, dried over MgSO₄, and concentrated in vacuo. The product was purified by distillation.

**5-ethyl-5-methylnona-1,8-diene (32):** Prepared according to general procedure B from ketone 23 (5.86 g, 42.5 mmol) and Et₂Zn to afford 32 as a clear, colorless oil (4.3 g, 61% yield).

^1H NMR (600 MHz, CDCl₃) δ 5.79 (ddt, J = 16.9, 10.1, 6.6 Hz, 2H), 4.97 (dt, J = 17.0, 1.8 Hz, 2H), 4.92 – 4.86 (m, 2H), 1.96 – 1.88 (m, 4H), 1.27 – 1.18 (overlapping m, 6H), 0.79 (s, 3H), 0.76 (t, J = 7.5 Hz, 3H).

^13C NMR (101 MHz, CDCl₃) δ 139.8, 113.7, 38.1, 34.9, 31.4, 28.1, 24.4, 7.9.

HRMS (EI+) calc’d for C_{12}H_{22} [M]^{+} 166.1722; found 166.1700.

**General Procedure C for ADMET Polymerization:**
In a nitrogen-filled glovebox, monomer 30 (320 mg, 1 mmol) in 0.5 mL CH₂Cl₂ was transferred into a 50 mL Schlenk flask equipped with a stir bar, followed by Grubbs 2nd Generation Catalyst (4.2 mg, 0.5 mol%) in 0.5 mL CH₂Cl₂. The Schlenk tube was sealed and removed from the glovebox and placed under static vacuum after one freeze-pump-thaw cycle. Then the Schlenk flask was placed in a 60 ºC oil bath for 12 hours. The valve was opened to dynamic vacuum and stirring was continued for 2 hours until the mixture turned viscous and became difficult to stir. The Schlenk tube was sealed and taken into the glovebox where the CTA 38 (20.6 mg, 0.05 mmol, 20:1 monomer: CTA ratio) in 2 mL toluene was added. The Schlenk tube was removed from the glovebox and the side arm was flame dried under vacuum and backfilled three times with argon. Then the Schlenk tube was opened to the argon line and placed in a 60 °C oil bath for 72 h. The reaction mixture was transferred into a flame-dried round bottom flask and the solvent was removed under reduced pressure to obtain crude polymer poly-30a.

\(^1\text{H NMR}\) (500 MHz, CDCl₃) \(\delta 7.47 – 7.14\) (m, 5H), 5.47 – 5.32 (m, 11H), 5.16 (s, 1H), 4.21 – 4.10 (m, 1H), 2.08 – 1.91 (m, 21H), 1.46 – 1.06 (m, 131H), 0.82 (s, 29H). \(^1\text{H NMR determined}\) \(n = 22, M_n = 6800.\) GPC data: \(M_n = 5400;\) PDI (\(M_w/M_n\)) = 1.2.

The crude polymer poly-30a was dissolved in toluene (10 mL) and 10% palladium on carbon (100 mg, 0.1 equiv) was added in a round-bottom flask with a stir bar. The flask was sealed with a septum and back-filled with argon for three times, and then back-filled with H₂ using a balloon. The reaction was allowed to stir at 23 ºC for 24 hours under an atmosphere of hydrogen (1 atm H₂ balloon). After that time the reaction mixture was filtered through a short pad of Celite (caution: Palladium on carbon is highly flammable and the palladium waste must be collected separately and covered with water). The filtered solution was concentrated upon heating under high vacuum to obtain the hydroxyl telechelic polymer poly-30b (286 mg, 97% yield). \(^1\text{H NMR}\) (500 MHz, CDCl₃) \(\delta 3.65\) (t, \(J = 6.6\) Hz, 1H), 1.39 – 1.10 (m, 210H), 0.82 (s, 32H). \(^1\text{H NMR determined}\) \(n = 21, M_a = 6300.\) GPC data: \(M_n = 7600;\) PDI (\(M_w/M_n\)) = 1.1.
Table S1. Summary of Telechelic Polymer Samples Prepared.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer/CTA ratio</th>
<th>Yield (%)</th>
<th>(n)</th>
<th>(M_n)(NMR)(Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly-21b</td>
<td>10:1</td>
<td>95</td>
<td>15</td>
<td>4200</td>
</tr>
<tr>
<td>poly-24b</td>
<td>22:1</td>
<td>55</td>
<td>16</td>
<td>2200</td>
</tr>
<tr>
<td>poly-27b</td>
<td>12:1</td>
<td>99</td>
<td>10</td>
<td>2000</td>
</tr>
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<td>99</td>
<td>10</td>
<td>3100</td>
</tr>
<tr>
<td>poly-30b-2</td>
<td>20:1</td>
<td>97</td>
<td>21</td>
<td>6300</td>
</tr>
<tr>
<td>poly-30b-3</td>
<td>50:1</td>
<td>96</td>
<td>58</td>
<td>17200</td>
</tr>
<tr>
<td>poly-30b-4</td>
<td>100:1</td>
<td>89</td>
<td>97</td>
<td>28700</td>
</tr>
<tr>
<td>poly-32b</td>
<td>22:1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly-34b</td>
<td>20:1</td>
<td>95</td>
<td>19</td>
<td>6800</td>
</tr>
</tbody>
</table>

Telechelic polymer poly-21b: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.57 (t, \(J = 6.6\) Hz, 1H), 1.62 – 1.48 (m, 7H), 1.32 – 1.00 (m, 122H), 0.74 (s, 22H). \(^1\)H NMR determined \(n = 15, M_n = 4200\). GPC data: \(M_n = 2800\); PDI (\(M_w/M_n\)) = 1.44.

Telechelic polymer poly-24b: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 3.63 (t, \(J = 6.7\) Hz, 1H), 1.59 – 1.52 (m, 1H), 1.36 – 1.04 (m, 46H), 0.80 (s, 20H).

Telechelic polymer poly-27b: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.65 (t, \(J = 6.6\) Hz, 1H), 1.43 – 1.09 (m, 58H), 0.82 (s, 13H).

poly-30b-1: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.65 (dt, \(J = 6.5, 4.8\) Hz, 1H), 1.41 – 1.17 (m, 94H), 0.82 (s, 15H).

poly-30b-2: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.65 (t, \(J = 6.6\) Hz, 1H), 1.34 – 1.11 (m, 208H), 0.82 (s, 32H).

poly-30b-3: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.65 (dt, \(J = 6.7, 5.6\) Hz, 1H), 1.32 – 1.12 (m, 571H), 0.82 (s, 88H).
poly-30b-4: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.65 (dt, $J = 6.6, 5.5$ Hz, 1H), 1.35 – 1.11 (m, 943H), 0.82 (s, 146H). $^1$H NMR determined $n = 97$, $M_n = 28700$.

Telechelic polymer poly-32b: $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 3.63 (t, $J = 6.7$ Hz, 1H), 1.55 (q, $J = 6.9$ Hz, 2H), 1.38 – 1.05 (m, 83H), 0.78 – 0.68 (m, 34H). $^1$H NMR determined $n = 22$, $M_n = 3200$. GPC data: $M_n$ =6800; PDI ($M_w/M_n$) = 1.1.

poly-34b: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.65 (q, $J = 6.4$ Hz, 1H), 1.34 – 1.19 (m, 265H), 1.14 – 1.09 (m, 56H), 0.92 – 0.87 (m, 29H), 0.72 (t, $J = 7.5$ Hz, 14H). $^1$H NMR determined $n = 19$, $M_n = 6800$.

5,5-dimethylcyclohept-1-ene (37): After the polymerization of 24, the cyclic olefin was removed by vacuum distillation from the reaction mixture (23 °C, 100 mTorr).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.60 (ddd, $J = 3.8, 2.9, 0.8$ Hz, 2H), 2.06 – 1.94 (m, 4H), 1.40 – 1.32 (m, 4H), 0.87 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 131.5, 40.3, 33.7, 29.3, 24.4.

HRMS (EI+, m/z) calc’d for C$_9$H$_{16}$ [M]$^{+}$ 124.1252, found: 124.1264.

5-ethyl-5-methylcyclohept-1-ene (39): After the polymerization of 32, the cyclic olefin was removed by vacuum distillation from the reaction mixture (23 °C, 100 mTorr).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 5.63 (t, $J = 3.2$ Hz, 2H), 2.09 – 2.01 (m, 4H), 1.49 – 1.33 (m, 4H), 1.29 (q, $J = 7.5$ Hz, 2H), 0.83 (s, 3H), 0.80 (t, $J = 7.5$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 131.4, 38.3, 35.9, 33.6, 25.2, 24.1, 8.1.

HRMS (EI+, m/z) calc’d for C$_{10}$H$_{18}$ [M]$^{+}$ 138.1409, found: 138.1413.

DSC was performed using a Mettler Toledo DSC 3+ Star System. Scan rates of 10 K/min for heating and 5K/min for cooling were used.
Figure S1. DSC Traces for Different Gem-dimethyl Polymer Samples

(poly-21b) $M_n = 4200$ Da
(poly-24b) $M_n = 2000$ Da
(poly-27b) $M_n = 2000$ Da
(poly-30b-1) $M_n = 3100$ Da
(poly-30b-2) $M_n = 6300$ Da
(poly-30b-3) $M_n = 17200$ Da
(poly-30b-4) $M_n = 28700$ Da
(poly-32b) $M_n = 3200$ Da
(poly-34b) $M_n = 6800$ Da
$^1$H NMR (400 MHz, CDCl$_3$) of compound 12.
$^1$C NMR (101 MHz, CDCl$_3$) of compound 12.
$^1$H–$^1$H COSY NMR (400 MHz, CDCl$_3$) of compound 12.

$^1$H–$^{13}$C HSQC NMR (400 MHz, CDCl$_3$) of compound 12.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 16.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 16.
$^{1}\text{H}^{1}\text{H}$ COSY NMR (400 MHz, CDCl$_3$) of compound 16.

$^{1}\text{H}^{13}\text{C}$ HSQC NMR (400 MHz, CDCl$_3$) of compound 16.
$^{1}\text{H} \text{ NMR (400 MHz, CDCl}_3\text{)}$ of compound 26.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 26.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 29.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 29.
$^1$H NMR (600 MHz, CDCl$_3$) of compound 31.

CDCl$_3$ – 7.26
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 31.
$^1$H NMR (600 MHz, CDCl$_3$) of compound 38.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 38.
$^1$H NMR (600 MHz, CDCl$_3$) of compound 21.

![NMR spectrum of compound 21](image)
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 21.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 24.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 24.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 27.

Me  Me

CDCl$_3$ - 7.26
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 27.
$^{1}$H NMR (400 MHz, CDCl$_3$) of compound 30.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 30.
$^1$H NMR (600 MHz, CDCl$_3$) of compound 33.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 33.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 34.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 34.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 35.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 35.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 36.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 36.
$^1$H NMR (600 MHz, CDCl$_3$) of compound 32.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 32.
$^1$H NMR (400 MHz, CDCl$_3$) of compound poly-21b.
$^1$H NMR (600 MHz, CDCl$_3$) of compound poly-24b.
$^1$H NMR (500 MHz, CDCl$_3$) of compound poly-27b.
$^1$H NMR (500 MHz, CDCl$_3$) of compound poly-30b-1.
$^1$H NMR (500 MHz, CDCl$_3$) of compound poly-30b-2.
$^1$H NMR (500 MHz, CDCl$_3$) of compound poly-30b-3.
$^1$H NMR (500 MHz, CDCl$_3$) of compound **poly-30b-4**.
$^1$H NMR (500 MHz, CDCl$_3$) of compound poly-32b.
$^1$H NMR (500 MHz, CDCl$_3$) of compound poly-34b.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 37.
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) of compound 37.
$^1$H NMR (600 MHz, CDCl$_3$) of compound 39.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 39.


