Supporting Information

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“N-Acyliiminium Ion Pool” as Hetero Diene in [4+2] Cycloaddition Reaction

Seiji Suga,* Aiichiro Nagaki, Yamato Tsutsui, and Jun-ichi Yoshida*

Department of Synthetic Chemistry & Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Experimental Section

General Remarks. GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused silica capillary. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Varian Gemini 2000 or JEOL A-500 spectrometer with Me_4Si as an internal standard unless otherwise noted. NMR spectra of the carbamates were usually very broad and sometimes separated to two signals due to the existence of rotamers. Mass spectra were obtained on JEOL JMS SX-102A mass spectrometer. IR spectra were measured with a SHIMADZU FTIR 1600 spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F₂₅₄ plates (thickness 0.25 mm). Flush chromatography was carried out on a column of silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100 μm). Gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using CHCl_3 as eluent. All reactions were carried out under Ar

atmosphere unless otherwise noted. A micromixer was purchased from Institut für Mikrotechnik Mainz GmbH (IMM). The micromixer constructed of stainless steel body has 40 µm mixing channels (silver) which were fabricated by means of the LIGA (Lithographie, Galvanoformung, Abformung) process. Introduction of two solutions to the mixer was performed by two syringe pumps, Harvard Model 11.

Materials. Dichloromethane (CH₂Cl₂) was washed with water, distilled from P₂O₅, redistilled from dried K₂CO₃ to remove a trace amount of acid, and stored over molecular sieves 4A.

***N*-Methoxycarbonyl-*N*-(trimethylsilylmethyl)butylamine (1).** To a suspension of sodium hydride (60 wt% dispersion in mineral oil, 7.91 g, 197 mmol) in DMF (200 mL), *N*-(methoxycarbonyl)butylamine (21.6 g, 165 mmol) was added at 0 °C. The mixture was stirred for 120 min at 60 °C and iodo(trimethylsilyl)methane (42.6 g, 199 mmol) was added at 0 °C. The reaction mixture was stirred for 14.5 h at 60 °C, and then poured into water (300 mL). The organic phase was separated and the aqueous phase was extracted with ether (300 mL x 3). The combined organic phase was dried over Na₂SO₄, and solvent was removed to give the crude product. After purification with flash chromatography (hexane/ethyl acetate 10 : 1), the compound was further purified by distillation (120 °C, 20 mmHg) to obtain the title compound (36.0 g, 76%): *t*_R = 6.92 min (column, OV-17; 0.25 mm x 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min): TLC *R*_f 0.54 (hexane/ethyl acetate 5:1); ¹H NMR (300 MHz, CDCl₃) δ 0.03 (s, 9H), 0.90 (t, 3H, *J* =

7.2 Hz), 1.16-1.36 (m, 2H), 1.39-1.55 (m, 2H), 2.68 (s) and 2.72 (s) (total 2H, two rotamers), 3.06-3.26 (m, 2H), 3.64 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ - 1.8 and - 1.6, 13.7, 19.8, 29.4 and 29.8, 37.9 and 38.6, 48.7 and 49.3, 51.9 and 52.3, 156.6; IR (neat) 2957, 1701, 1473, 1225 cm^{-1} ; LRMS (EI) m/e 217 (M^+), 202 ($\text{M}^+ - \text{CH}_3$), 186 ($\text{M}^+ - \text{OMe}$), 158 ($\text{M}^+ - \text{CO}_2\text{Me}$); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{23}\text{NO}_2\text{Si}$ (M^+): 217.1498, found: 217.1501.

Generation of Iminium Cation Pool 2. Typical Procedure. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 $^\circ\text{C}$ /1 mmHg for 1 h before use) and a platinum plate cathode (60 mm x 30 mm). In the anodic chamber was placed a solution of **1** (610.3 mg, 2.81 mmol) in 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ (56.0 mL). In the cathodic chamber were placed 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ (56.0 mL) and trifluoromethanesulfonic acid (1.05 g, 7.00 mmol). The constant current electrolysis (30 mA) was carried out at -78 $^\circ\text{C}$ with magnetic stirring until 2.5 F/mol of electricity was consumed.

NMR Analysis of the Pool of Iminium Cation 2 generated from 1. ^1H and ^{13}C NMR spectra were recorded in CD_2Cl_2 on a JEOL A-500 spectrometer. Chemical shifts are reported using methylene signals at δ 5.32 (^1H NMR) and δ 53.80 (^{13}C NMR) as standards. The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber was placed a solution of **1** (45.0 mg, 0.206 mmol) in 4.0 mL of 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CD}_2\text{Cl}_2$. In the cathodic chamber were placed trifluoromethanesulfonic acid (72.3 mg, 0.482 mmol) and 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CD}_2\text{Cl}_2$ (4.0 mL). The constant current electrolysis (5.0 mA) was carried out at -78 $^\circ\text{C}$ with magnetic stirring. After 2.5 F/mol of electricity was consumed, the reaction mixture of the anodic chamber was transferred to a 5 mm NMR tube with a septum cap under Ar atmosphere at -78 $^\circ\text{C}$.

The NMR measurement was carried out at -80 °C: ^1H NMR (500 MHz, CD_2Cl_2 , selected) δ 4.01-4.20 (m, 5H), 8.56 (s, 1H), 8.83 (s, 1H); ^{13}C NMR (125.65 MHz, CD_2Cl_2 , selected) δ 174.7, 147.3, 58.6, 56.6, 29.3. In the NMR spectra the other signals could not be assigned because of overlap of the signals of Bu_4NBF_4 used as electrolyte.

General Procedure of Batch Mixing (Method A). To a cation pool (**2**, 10 mL, cooled at -78 °C) generated from **1** (0.500 mmol) was added a solution of nucleophile (0.417 mmol) in CH_2Cl_2 (10 mL, cooled at -78 °C) by syringe pump (flow rate, 5.0 mL/min). (At this time the solutions of **2** and **3** were quickly transferred to syringes, which were kept cool with dry ice, and immediately introduced to a mixer cooled at -78 °C. Decomposition of **2** was thus avoided.) The reaction mixture was immediately quenched by addition of Et_3N (1 mL) at the same temperature.

In the reactions of Table 1, the reaction mixture was immediately warmed to 0 °C or -27 °C and then stirred for 10 min before quenching by addition of Et_3N (1 mL) at the same temperature.

After quenching the mixture was warmed to room temperature and the solvent was removed under reduced pressure. The residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (300 mL). The combined solution was concentrated to give a crude product, which was purified by flash chromatography.

General Procedure of Batch Mixing (Method B). To a solution of nucleophile (0.417 mmol) in CH_2Cl_2 (10 mL, cooled at -78 °C) was added a cation pool (**2**, 10 mL, cooled at -78 °C) generated from **1** (0.500 mmol) by syringe pump (flow rate, 5.0 mL/min). Immediately after mixing, the reaction mixture was quenched by addition of Et_3N (1 mL) at

the same temperature. The mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (300 mL). The combined solution was concentrated to give a crude product, which was purified by flash chromatography.

General Procedure of Batch Mixing (Method C). A solution of nucleophile (0.417 mmol) in CH_2Cl_2 (10 mL, cooled at $-78\text{ }^\circ\text{C}$) and a cation pool (**2**, 10 mL, cooled at $-78\text{ }^\circ\text{C}$) generated from **1** (0.500 mmol) were simultaneously introduced to the reaction vessel using syringe pumps (flow rate is 5.0 mL/min). Immediately after mixing, the reaction mixture was quenched by addition of Et_3N (1 mL) at the same temperature. The mixture was warmed to room temperature. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (300 mL). The combined solution was concentrated to give a crude product, which was purified by flash chromatography.

General Procedure of Micromixing. A solution of nucleophile (0.417 mmol) in CH_2Cl_2 (10 mL, cooled at $-78\text{ }^\circ\text{C}$) and a cation pool (**2**, 10 mL, cooled at $-78\text{ }^\circ\text{C}$) generated from **1** (0.500 mmol) were simultaneously introduced to the micromixer (channel width = 40 μm), which is dipped in a coolant at $-78\text{ }^\circ\text{C}$, using syringe pumps (flow rate is 5.0 mL/min). Then, the reaction mixture coming out from the outlet of the micromixer was collected with a round bottom flask, and immediately quenched by Et_3N (1 mL) at $-78\text{ }^\circ\text{C}$. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (300 mL). The combined solution was concentrated to give a crude product,

which was purified by flash chromatography.

3-Butyl-6-decyl-[1,3]oxazinan-2-one. Prepared from **1** (10.0 mL, 0.499 mmol) and 1-dodecene (71.4 mg, 0.424 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): Isolated yield 72% (91.3 mg, purified with flash chromatography, hexane/ethyl acetate 6:1): TLC *R_f* 0.61 (hexane/ethyl acetate 3:1): ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, 3H, *J* = 6.8 Hz), 0.93 (t, 3H, *J* = 7.4 Hz), 1.18-1.39 (m, 17H), 1.41-1.62 (m, 4H), 1.62-1.85 (m, 2H), 1.90-2.03 (m 1H), 3.20-3.42 (m, 4H), 4.10-4.24 (m, 1H); ¹³C NMR (75 MHz, CDCl₃, some signals were on top of the others) δ 13.8, 14.1, 19.9, 22.6, 24.7, 27.2, 29.1, 29.2, 29.4, 29.4, 29.5, 29.5, 31.8, 34.9, 44.4, 49.0, 76.9, 153.7; IR (neat) 2923, 1688, 1667, 1487 cm⁻¹; LRMS (EI) *m/e* 297 (M⁺), 282 (M⁺ - Me), 254 (M⁺ - C₃H₇), 240 (M⁺ - C₄H₉); HRMS (EI) calcd for C₁₈H₃₅NO₂ (M⁺): 297.2668, found: 297.2664.

3-Butyl-*trans*-5,6-dimethyl-[1,3]oxazinan-2-one.^{1a,b} Prepared from **1** (10.0 mL, 0.491 mmol) and *E*-2-butene (23.3 mg, 0.415 mmol) by Method A (The mixture was stirred at -27 °C for 10 min before treatment of Et₃N): Isolated yield 68% (52.5 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC *R_f* 0.21 (hexane/ethyl acetate 1:1): ¹H NMR (300 MHz, CDCl₃) δ 0.93 (t, 3H, *J* = 7.4 Hz), 0.98 (d, 3H, *J* = 6.9 Hz), 1.34 (d,

3H, $J = 6.3$ Hz), 1.33 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.45-1.65 (m, 2H), 1.80-1.95 (m, 1H), 2.98 (dd, 1H, $J = 10.7$ Hz, $J = 11.6$ Hz), 3.18 (dd, 1H, $J = 5.6$ Hz, $J = 11.9$ Hz), 3.20-3.45 (m, 2H), 3.98 (dq, 1H, $J = 9.5$ Hz, $J = 6.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 13.7, 14.0, 18.7, 19.8, 29.0, 33.1, 48.7, 51.5, 78.2, 153.5; IR (neat) 2961, 1694, 1491, 1248 cm^{-1} ; LRMS (EI) m/e 185 (M^+), 170 ($\text{M}^+ - \text{Me}$), 142 ($\text{M}^+ - \text{C}_3\text{H}_7$); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_2$ (M^+): 185.1416, found: 185.1415.

3-Butyl-*cis*-5,6-dimethyl-[1,3]oxazinan-2-one. ^{1a,b} Prepared from **1** (10.0 mL, 0.503 mmol) and *Z*-2-butene (23.5 mg, 0.419 mmol) by Method A (The mixture was stirred at -27 $^{\circ}\text{C}$ for 10 min before treatment of Et_3N): Isolated yield 65% (50.2 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC R_f 0.21 (hexane/ethyl acetate 1:1): ^1H NMR (300 MHz, CDCl_3) δ 0.94 (t, 3H, $J = 7.4$ Hz), 1.02 (d, 3H, $J = 7.2$ Hz), 1.28 (d, 3H, $J = 6.6$ Hz), 1.33 (tq, 2H, $J = 7.5$ Hz, $J = 7.5$ Hz), 1.45-1.65 (m, 2H), 2.09-2.22 (m, 1H), 3.01 (dd, 1H, $J = 5.3$ Hz, $J = 11.6$ Hz), 3.20-3.40 (m, 2H), 3.40 (dd, 1H, $J = 5.1$ Hz, $J = 11.4$ Hz), 4.43 (dq, 1H, $J = 3.0$ Hz, $J = 6.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 11.5, 13.7, 16.4, 19.8, 28.9, 29.9, 48.9, 50.6, 75.4, 153.1; IR (neat) 2961, 1694, 1491, 1237 cm^{-1} ; LRMS (EI) m/e 185 (M^+), 170 ($\text{M}^+ - \text{Me}$), 156 ($\text{M}^+ - \text{C}_2\text{H}_5$), 142 ($\text{M}^+ - \text{C}_3\text{H}_7$), 128 ($\text{M}^+ - \text{C}_4\text{H}_9$); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_2$ (M^+): 185.1416, found: 185.1416.

3-Butyl-5,6-cis-tetramethylenetetrahydrooxazin-2-one.^{1c} Prepared from **1** (10.0 mL, 0.507 mmol) and cyclohexene (34.7 mg, 0.423 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): Isolated yield 84% (75.1 mg, purified with flash chromatography, hexane/ethyl acetate 1:1): TLC *R_f* 0.32 (hexane/ethyl acetate 1:2): ¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, 3H, *J* = 7.3 Hz), 1.16-1.35 (m, 3H), 1.36-1.72 (m, 8H), 1.80-1.98 (m, 2H), 2.88 (dd, 1H, *J* = 2.0 Hz, *J* = 11.5 Hz), 3.12-3.35 (m, 2H), 3.42 (dd, 1H, *J* = 5.3 Hz, *J* = 11.8 Hz), 4.38 (d, 1H, *J* = 3.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 13.7, 19.3, 19.7, 24.1, 24.6, 28.9, 29.8, 32.1, 48.7, 50.1, 74.6, 153.3; IR (neat) 2934, 1686, 1489, 1233 cm⁻¹; LRMS (EI) *m/e* 211 (M⁺), 196 (M⁺ - Me), 168 (M⁺ - C₃H₇); HRMS (EI) calcd for C₁₂H₂₁NO₂ (M⁺): 211.1572, found: 211.1574.

3-Butyl-6-trimethylsilyl-[1,3]oxazinan-2-one. Prepared from **1** (10.0 mL, 0.491 mmol) and vinylsilane (40.2 mg, 0.401 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): Isolated yield 86% (79.3 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC *R_f* 0.49 (hexane/ethyl acetate 1:1): ¹H NMR (300 MHz, CDCl₃) δ 0.07 (s, 9H), 0.89 (t, 3H, *J* = 7.2 Hz), 1.29 (tq, 2H, *J* = 7.5 Hz, *J* = 7.5 Hz), 1.43-1.64 (m, 2H), 1.80-2.04 (m, 2H), 3.12-3.28 (m, 2H), 3.29-3.48 (m, 2H), 3.91 (dd, 1H, *J* = 4.1 Hz, *J* = 10.7 Hz); ¹³C NMR (75 MHz, CDCl₃) δ -4.4, 13.8, 19.9, 23.5, 29.1, 46.5, 49.3, 71.8, 154.8; IR (neat) 2957, 1684, 1456, 1250 cm⁻¹; LRMS (EI) *m/e* 229 (M⁺), 214 (M⁺ - Me), 186 (M⁺ - C₃H₇); HRMS (EI) calcd for C₁₁H₂₃NO₂Si (M⁺): 229.1498, found: 229.1493.

3-Butyl-6-acetoxy-[1,3]oxazinan-2-one. Prepared from **1** (10.0 mL, 0.491 mmol) and vinylacetate (35.4 mg, 0.411 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): GC yield 81% (72.0 mg, *t*_R 16.7 min, column, OV-1; 0.80 mm x 1 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min): TLC *R*_f 0.48 (hexane/ethyl acetate 1:1): ¹H NMR (300 MHz, CDCl₃) δ 0.95 (t, 3H, *J* = 7.2 Hz), 1.35 (tq, 2H, *J* = 7.5 Hz, *J* = 7.5 Hz), 1.53-1.68 (m, 2H), 1.96-2.10 (m, 1H), 2.12 (s, 3H), 2.13-2.28 (m, 1H), 3.18-3.32 (m, 1H), 3.37 (dt, 2H, *J* = 4.5 Hz, *J* = 7.2 Hz), 3.55 (dt, 1H, *J* = 4.8 Hz, *J* = 11.6 Hz), 6.48 (t, 1H, *J* = 3.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 13.7, 19.7, 20.8, 25.3, 28.9, 40.3, 49.3, 90.2, 150.6, 168.6; IR (neat) 2959, 1759, 1718, 1491 cm⁻¹; LRMS (EI) *m/e* 215 (M⁺), 172 (M⁺ - C₃H₇), 156 (M⁺ - CH₃CO₂); HRMS (EI) calcd for C₁₀H₁₇NO₄ (M⁺): 215.1158, found: 215.1157.

3-Butyl-5,6-*cis*-(3,4-dihydrotetramethylene)tetrahydrooxazin-2-one.^{1c}

Prepared from **1** (10.0 mL, 0.507 mmol) and 1,3-cyclohexadiene (33.9 mg, 0.423 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): Isolated yield 70% (61.9 mg, purified with flash chromatography, hexane/ethyl acetate 1:1): TLC *R*_f 0.32 (hexane/ethyl acetate 1:2): ¹H NMR (300 MHz, CDCl₃) δ 0.93 (t, 3H, *J* = 7.4 Hz),

1.33 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.48-1.70 (m, 3H), 1.71-1.89 (m, 1H), 2.10-2.24 (m, 3H), 3.10 (dd, 1H, $J = 4.2$ Hz, $J = 12.0$ Hz), 3.21-3.40 (m, 2H), 3.50 (dd, 1H, $J = 5.6$ Hz, $J = 12.2$ Hz), 4.73 (t, 1H, $J = 4.1$ Hz), 5.80-5.90 (m, 1H), 5.92-6.04 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 19.8, 21.5, 24.0, 29.1, 30.1, 48.5, 49.0, 72.1, 124.6, 132.1, 152.6; IR (neat) 2957, 1699, 1487, 1244 cm^{-1} ; LRMS (EI) m/e 209 (M^+), 180 ($\text{M}^+ - \text{C}_2\text{H}_5$), 166 ($\text{M}^+ - \text{C}_3\text{H}_7$); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{NO}_2$ (M^+): 209.1416, found: 209.1416.

3-Butyl-*trans*-5,6-diphenyl-[1,3]oxazinan-2-one.^{1a,b} Prepared from **1** (10.0 mL, 0.496 mmol) and *E*-1,2-diphenylethene (76.0 mg, 0.422 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et_3N): Isolated yield 87% (113.7 mg, purified with flash chromatography, hexane/ethyl acetate 3.5:1): TLC R_f 0.57 (hexane/ethyl acetate 1:1): ^1H NMR (300 MHz, CDCl_3) δ 0.95 (t, 3H, $J = 7.4$ Hz), 1.37 (tq, 2H, $J = 7.5$ Hz, $J = 7.5$ Hz), 1.57-1.72 (m, 2H), 3.23-3.55 (m, 4H), 3.68 (dd, 1H, $J = 11.0$ Hz, $J = 11.9$ Hz), 5.34 (d, 1H, $J = 9.6$ Hz), 7.01-7.29 (m, 10H); ^{13}C NMR (125.65 MHz, CDCl_3 , some signals were on top of the others) δ 13.8, 19.9, 29.1, 45.9, 49.2, 51.0, 83.0, 126.7, 127.6, 128.0, 128.2, 128.7, 136.7, 137.3, 153.2; IR (KBr) 2963, 1690, 1482, 1238 cm^{-1} ; LRMS (FAB) m/e 310 (MH^+); HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_2$ (MH^+): 310.1807, found: 310.1807. X-ray data: $\text{C}_{20}\text{H}_{23}\text{NO}_2$, $M = 309.41$, monoclinic, space group $\text{P}2_1/\text{c}$ (No. 14), $a = 10.1579(8)$ Å, $b = 10.7574(8)$ Å, $c = 16.195(2)$ Å, $V = 1723.1(2)$ Å³, $Z = 4$, $D_c = 1.193$ g/cm³, $\mu = 0.76$ cm⁻¹. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). The data were

collected at 23 ± 1 °C to a maximum 2θ value of 55.0° . A total of 14787 reflections were collected. The structure was solved by direct methods and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement on F was based on 2013 observed reflections ($I > 3.00\sigma(I)$) and 244 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.055$ ($R_w = 0.112$). The standard deviation of an observation of unit weight was 2.41. All calculation were performed using the CrystalStructure crystallographic software package.

Figure. Ortep drawing of 3-Butyl-*trans*-5,6-diphenyl-[1,3]oxazinan-2-one.

Table A. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	Beq
O(1)	0.3596(6)	0.1629(5)	1.0134(3)	5.7(1)
O(2)	0.5366(5)	0.1696(5)	0.9562(3)	4.8(1)
N(1)	0.3445(6)	0.0625(6)	0.8886(4)	4.4(1)
C(1)	0.4085(8)	0.1314(7)	0.9547(5)	4.3(2)
C(2)	0.4043(8)	0.0249(7)	0.8193(5)	4.7(2)
C(3)	0.5179(8)	0.1119(8)	0.8094(5)	4.5(2)
C(4)	0.6131(8)	0.1295(7)	0.8946(4)	4.4(2)
C(5)	0.5847(7)	0.0626(7)	0.7414(4)	4.1(2)
C(6)	0.5615(8)	0.1217(7)	0.6639(5)	5.0(2)
C(7)	0.613(1)	0.0752(9)	0.5989(5)	6.0(2)
C(8)	0.6869(9)	-0.0316(9)	0.6094(6)	6.0(2)
C(9)	0.7116(8)	-0.0925(8)	0.6852(5)	5.4(2)
C(10)	0.6613(8)	-0.0455(7)	0.7515(5)	4.8(2)
C(11)	0.7216(8)	0.2258(7)	0.8967(4)	4.0(2)
C(12)	0.6933(8)	0.3510(7)	0.8940(4)	4.3(2)
C(13)	0.7944(9)	0.4369(7)	0.8976(5)	5.2(2)
C(14)	0.9240(9)	0.3999(9)	0.9034(6)	6.2(2)
C(15)	0.9525(9)	0.2769(9)	0.9049(7)	7.3(3)
C(16)	0.8533(9)	0.1901(8)	0.9023(6)	6.0(2)
C(17)	0.2028(8)	0.0252(7)	0.8817(5)	5.1(2)
C(18)	0.1778(8)	-0.1116(7)	0.8680(5)	5.4(2)
C(19)	0.031(1)	-0.143(1)	0.8592(9)	7.0(3)
C(20)	0.002(1)	-0.279(1)	0.8453(8)	9.7(4)
H(1)	0.3358(8)	0.0293(7)	0.7685(5)	5.6(2)
H(2)	0.4370(8)	-0.0580(7)	0.8276(5)	5.6(2)
H(3)	0.479(8)	0.198(8)	0.800(5)	7.6(2)
H(4)	0.663(7)	0.044(7)	0.912(4)	5.4(2)
H(5)	0.5115(8)	0.1971(7)	0.6558(5)	5.9(2)
H(6)	0.594(1)	0.1168(9)	0.5458(5)	7.3(3)
H(7)	0.7209(9)	-0.0635(9)	0.5636(6)	7.3(3)
H(8)	0.7636(8)	-0.1667(8)	0.6930(5)	6.5(2)
H(9)	0.6782(8)	-0.0880(7)	0.8043(5)	5.6(2)
H(10)	0.6029(8)	0.3785(7)	0.8888(4)	5.1(2)

H(11)	0.7721(9)	0.5228(7)	0.8960(5)	6.2(2)
H(12)	0.9941(9)	0.4592(9)	0.9060(6)	7.6(3)
H(13)	1.0428(9)	0.2504(9)	0.9085(7)	9.0(3)
H(14)	0.8760(9)	0.1043(8)	0.9045(6)	7.3(3)
H(15)	0.1465(8)	0.0696(7)	0.8364(5)	6.1(2)
H(16)	0.1801(8)	0.0472(7)	0.9336(5)	6.1(2)
H(17)	0.2019(8)	-0.1317(7)	0.8163(5)	6.3(2)
H(18)	0.2327(8)	-0.1578(7)	0.9130(5)	6.3(2)
H(19)	-0.014(9)	-0.099(8)	0.820(5)	6.3(3)
H(20)	-0.000(8)	-0.113(8)	0.909(5)	6.3(2)
H(21)	0.027(1)	-0.302(1)	0.7942(8)	11.1(4)
H(22)	0.056(1)	-0.324(1)	0.8914(8)	11.1(4)
H(23)	-0.090(1)	-0.297(1)	0.8411(8)	11.1(4)

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table B. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(1)	0.089(4)	0.072(4)	0.064(3)	-0.015(3)	0.035(3)	-0.012(3)
O(2)	0.071(3)	0.066(3)	0.047(3)	-0.020(3)	0.017(2)	-0.012(3)
N(1)	0.057(4)	0.053(4)	0.057(4)	-0.008(3)	0.014(3)	-0.007(3)
C(1)	0.067(5)	0.044(4)	0.053(4)	-0.008(4)	0.014(4)	0.003(3)
C(2)	0.067(5)	0.060(5)	0.050(4)	-0.011(4)	0.009(4)	-0.010(4)
C(3)	0.068(5)	0.052(5)	0.052(4)	-0.006(4)	0.013(4)	-0.005(4)
C(4)	0.069(5)	0.055(4)	0.045(4)	-0.007(4)	0.012(4)	-0.005(4)
C(5)	0.056(4)	0.050(4)	0.047(4)	-0.014(4)	0.007(3)	-0.009(3)
C(6)	0.080(6)	0.049(4)	0.058(5)	-0.009(4)	0.011(4)	0.002(4)
C(7)	0.103(7)	0.079(6)	0.049(5)	-0.021(6)	0.022(5)	0.002(4)
C(8)	0.080(6)	0.091(7)	0.062(5)	-0.015(5)	0.027(5)	-0.017(5)
C(9)	0.061(5)	0.068(5)	0.076(6)	0.000(4)	0.014(4)	-0.014(5)
C(10)	0.066(5)	0.062(5)	0.049(4)	-0.004(4)	0.004(4)	0.000(4)
C(11)	0.064(5)	0.048(4)	0.041(4)	-0.012(4)	0.012(3)	-0.007(3)

C(12)	0.061(5)	0.056(4)	0.044(4)	-0.003(4)	0.008(3)	0.002(3)
C(13)	0.087(6)	0.049(5)	0.062(5)	-0.009(4)	0.019(4)	0.002(4)
C(14)	0.075(6)	0.070(6)	0.095(7)	-0.023(5)	0.027(5)	-0.011(5)
C(15)	0.063(6)	0.079(7)	0.143(9)	-0.009(5)	0.039(6)	-0.020(7)
C(16)	0.073(6)	0.055(5)	0.103(7)	0.001(5)	0.028(5)	-0.013(5)
C(17)	0.058(5)	0.061(5)	0.074(5)	-0.002(4)	0.013(4)	0.002(4)
C(18)	0.065(5)	0.060(5)	0.074(5)	-0.009(4)	0.002(4)	0.007(4)
C(19)	0.065(6)	0.082(7)	0.106(9)	-0.018(5)	-0.003(6)	0.020(7)
C(20)	0.105(8)	0.090(8)	0.16(1)	-0.039(7)	-0.007(8)	0.018(8)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table C. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
O(1)	C(1)	1.216(8)	O(2)	C(1)	1.359(8)
O(2)	C(4)	1.462(8)	N(1)	C(1)	1.342(9)
N(1)	C(2)	1.450(9)	N(1)	C(17)	1.474(9)
C(2)	C(3)	1.52(1)	C(3)	C(4)	1.51(1)
C(3)	C(5)	1.52(1)	C(4)	C(11)	1.51(1)
C(5)	C(6)	1.38(1)	C(5)	C(10)	1.39(1)
C(6)	C(7)	1.37(1)	C(7)	C(8)	1.36(1)
C(8)	C(9)	1.36(1)	C(9)	C(10)	1.39(1)
C(11)	C(12)	1.38(1)	C(11)	C(16)	1.37(1)
C(12)	C(13)	1.37(1)	C(13)	C(14)	1.36(1)
C(14)	C(15)	1.35(1)	C(15)	C(16)	1.37(1)
C(17)	C(18)	1.50(1)	C(18)	C(19)	1.50(1)
C(19)	C(20)	1.49(1)			

Table D. Bond angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	O(2)	C(4)	123.6(5)	C(1)	N(1)	C(2)	124.0(6)
C(1)	N(1)	C(17)	119.8(6)	C(2)	N(1)	C(17)	116.1(6)
O(1)	C(1)	O(2)	117.5(7)	O(1)	C(1)	N(1)	124.6(7)
O(2)	C(1)	N(1)	117.9(7)	N(1)	C(2)	C(3)	111.8(6)
C(2)	C(3)	C(4)	108.9(6)	C(2)	C(3)	C(5)	109.7(6)
C(4)	C(3)	C(5)	114.2(6)	O(2)	C(4)	C(3)	109.4(6)
O(2)	C(4)	C(11)	106.4(6)	C(3)	C(4)	C(11)	114.8(6)
C(3)	C(5)	C(6)	119.2(7)	C(3)	C(5)	C(10)	122.7(7)
C(6)	C(5)	C(10)	118.0(7)	C(5)	C(6)	C(7)	121.0(8)
C(6)	C(7)	C(8)	120.6(8)	C(7)	C(8)	C(9)	119.9(8)
C(8)	C(9)	C(10)	119.8(8)	C(5)	C(10)	C(9)	120.7(8)
C(4)	C(11)	C(12)	121.7(7)	C(4)	C(11)	C(16)	120.3(7)
C(12)	C(11)	C(16)	118.0(7)	C(11)	C(12)	C(13)	120.6(7)
C(12)	C(13)	C(14)	120.6(8)	C(13)	C(14)	C(15)	119.2(8)
C(14)	C(15)	C(16)	120.9(9)	C(11)	C(16)	C(15)	120.7(8)
N(1)	C(17)	C(18)	114.1(7)	C(17)	C(18)	C(19)	111.6(8)
C(18)	C(19)	C(20)	113.2(1)

3-Butyl-*cis*-5,6-diphenyl-[1,3]oxazinan-2-one.^{1a,b} Prepared from **1** (10.0 mL, 0.495 mmol) and *Z*-1,2-diphenylethene (73.1 mg, 0.406 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): Isolated yield 80% (95.9 mg, purified with flash chromatography, hexane/ethyl acetate 3.5:1)(*cis*/*trans* 55:45 by ¹H NMR). The following data for the *cis*-isomer were measured after the purification using gel permeation chromatography: TLC *R_f* 0.57 (hexane/ethyl acetate 1:1): ¹H NMR (300 MHz, CDCl₃) δ 0.97 (t, 3H, *J* = 7.4 Hz), 1.40 (tq, 2H, *J* = 7.4 Hz, *J* = 7.4 Hz), 1.57-1.76 (m, 2H), 3.42-3.62 (m, 4H), 3.72 (t, 1H, *J* = 7.1 Hz), 5.62 (d, 1H, *J* = 3.0 Hz), 6.78-6.95 (m, 4H), 7.09-7.30 (m, 6H); ¹³C NMR (125.65 MHz, CDCl₃, some signals were on top of the others) δ 13.9, 20.1, 29.0, 43.1, 48.7, 49.4, 80.8, 126.2, 127.8, 128.3, 128.5, 136.4, 136.4, 153.4; IR (KBr) 2957, 1680, 1497, 1264 cm⁻¹; LRMS (EI) *m/e* 309 (M⁺), 266 (M⁺ - C₃H₇); HRMS (EI) calcd for C₂₀H₂₃NO₂ (M⁺): 309.1729, found: 309.1726.

3-Butyl-*trans*-5,6-methylphenyl-[1,3]oxazinan-2-one.^{1a,b} Prepared from **1** (10.0 mL, 0.496 mmol) and *E*-1-methyl-2-phenylethene (49.1 mg, 0.415 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): Isolated yield 88% (90.6 mg, purified with flash chromatography, hexane/ethyl acetate 3:1): TLC *R_f* 0.49 (hexane/ethyl acetate 1:1): ¹H NMR (300 MHz, CDCl₃) δ 0.83 (d, 3H, *J* = 6.9 Hz), 0.96 (t, 3H, *J* = 7.4 Hz), 1.36 (tq, 2H, *J* = 7.5 Hz, *J* = 7.5 Hz), 1.50-1.73 (m, 2H), 2.17-2.36 (m, 1H),

3.12 (dd, 1H, $J = 11.6$ Hz, $J = 10.4$ Hz), 3.18-3.50 (m, 3H), 4.80 (d, 1H, $J = 9.6$ Hz), 7.28-7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 14.2, 19.9, 29.1, 33.4, 49.0, 51.5, 84.2, 126.8, 128.4, 128.5, 137.6, 153.4; IR (KBr) 2956, 1676, 1483, 1256 cm^{-1} ; LRMS (EI) m/e 247 (M^+), 232 ($\text{M}^+ - \text{Me}$), 204 ($\text{M}^+ - \text{C}_3\text{H}_7$); HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_2$ (M^+): 247.1572, found: 247.1575.

3-Butyl-*cis*-5,6-methylphenyl-[1,3]oxazinan-2-one.^{1a,b} Prepared from **1** (10.0 mL, 0.493 mmol) and *Z*-1-methyl-2-phenylethene (48.9 mg, 0.414 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et_3N): Isolated yield 83% (85.4 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) (*cis*/*trans* 56:44 by ^1H NMR). The following data for the *cis*-isomer were measured after the purification using gel permeation chromatography: TLC R_f 0.49 (hexane/ethyl acetate 1:1): ^1H NMR (300 MHz, CDCl_3) δ 0.85 (d, 3H, $J = 7.2$ Hz), 0.96 (t, 3H, $J = 7.4$ Hz), 1.37 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.50-1.73 (m, 2H), 2.35-2.48 (m, 1H), 3.05 (dd, 1H, $J = 11.7$ Hz, $J = 3.6$ Hz), 3.25-3.50 (m, 2H), 3.60 (dd, 1H, $J = 11.6$ Hz, $J = 5.0$ Hz), 5.40 (d, 1H, $J = 2.7$ Hz), 7.28-7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 11.3, 13.8, 19.9, 29.0, 31.5, 49.1, 50.9, 80.2, 125.5, 127.7, 128.2, 137.5, 153.0; IR (KBr) 2961, 1689, 1489, 1279 cm^{-1} ; LRMS (EI) m/e 247 (M^+), 232 ($\text{M}^+ - \text{Me}$), 204 ($\text{M}^+ - \text{C}_3\text{H}_7$); HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_2$ (M^+): 247.1572, found: 247.1573.

3-Butyl-6-hexyl-3,4-dihydro-[1,3]oxazin-2-one. Prepared from **1** (10.0 mL, 0.503 mmol) and 1-octyne (46.8 mg, 0.425 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): Isolated yield 64% (64.6 mg, purified with flash chromatography, hexane/ethyl acetate 15:1): TLC *R_f* 0.32 (hexane/ethyl acetate 10:1): ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, 3H, *J* = 6.9 Hz), 0.94 (t, 3H, *J* = 7.2 Hz), 1.20-1.65 (m, 12H), 2.09 (dt, 2H, *J* = 0.9 Hz, *J* = 7.5 Hz), 3.34 (t, 2H, *J* = 7.5 Hz), 3.77-3.84 (m, 2H), 4.76-4.80 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 13.8, 14.0, 19.9, 22.5, 25.9, 28.3, 28.6, 31.5, 32.3, 45.2, 48.6, 93.6, 150.7, 151.8; IR (neat) 2957, 1725, 1456, 1173 cm⁻¹; LRMS (EI) *m/e* 239 (M⁺), 238 (M⁺ - H); HRMS (EI) calcd for C₁₄H₂₅NO₂ (M⁺): 239.1885, found: 239.1883.

3-Butyl-6-phenyl-3,4-dihydro-[1,3]oxazin-2-one. Prepared from **1** (10.0 mL, 0.500 mmol) and phenylacetylene (43.0 mg, 0.421 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et₃N): Isolated yield 46% (44.6 mg, purified with flash chromatography, hexane/ethyl acetate 10:1): TLC *R_f* 0.76 (hexane/ethyl acetate 1:1): ¹H NMR (300 MHz, CDCl₃) δ 0.96 (t, 3H, *J* = 7.2 Hz), 1.38 (tq, 2H, *J* = 7.4 Hz, *J* = 7.4 Hz), 1.57-1.70 (m, 2H), 3.41 (t, 2H, *J* = 7.5 Hz), 4.01 (d, 2H, *J* = 3.3 Hz), 5.56 (t, 1H, *J* = 3.6 Hz), 7.34-7.43 (m, 3H), 7.57-7.69 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.8, 19.9, 28.4, 45.5, 48.7, 94.1, 124.5, 128.4, 129.1, 131.7, 148.8, 150.4; IR (neat) 2959, 1723, 1449,

1227 cm^{-1} ; LRMS (EI) m/e 231 (M^+), 203 ($M^+ - \text{CO}$), 187 ($M^+ - \text{CO}_2$); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ (M^+): 231.1259, found: 231.1258.

3-Butyl-6-trimethylsilyl-3,4-dihydro-[1,3]oxazin-2-one. Prepared from **1** (10.0 mL, 0.504 mmol) and trimethylsilylacetylene (41.2 mg, 0.419 mmol) by Method A (The mixture was stirred at 0 °C for 10 min before treatment of Et_3N): Isolated yield 90% (85.5 mg, purified with flash chromatography, hexane/ethyl acetate 10:1): TLC R_f 0.69 (hexane/ethyl acetate 3:1): ^1H NMR (300 MHz, CDCl_3) δ 0.16 (s, 9H), 0.94 (t, 3H, $J = 7.2$ Hz), 1.35 (tq, 2H, $J = 7.6$ Hz, $J = 7.6$ Hz), 1.52-1.66 (m, 2H), 3.33 (t, 2H, $J = 7.5$ Hz), 3.85 (d, 2H, $J = 3.3$ Hz), 5.25 (t, 1H, $J = 3.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.1, 13.7, 19.8, 28.2, 45.7, 48.7, 108.5, 150.8, 157.9 ; IR (neat) 2959, 1717, 1483, 1250 cm^{-1} ; LRMS (EI) m/e 227 (M^+), 212 ($M^+ - \text{Me}$), 199 ($M^+ - \text{CO}$); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{21}\text{NO}_2\text{Si}$ (M^+): 227.1342, found: 227.1342.

3-Butyl-6-phenyltetrahydrooxazin-2-one. Prepared from **1** (10.0 mL, 0.492 mmol) and styrene (43.2 mg, 0.414 mmol) by Method A: Isolated yield 57% (55.3 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymerized product (15.5 mg, 35% yield based on styrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.492 mmol) and styrene (43.2 mg, 0.414 mmol) by Method B:

Isolated yield 20% (19.4 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymerized product (33.4 mg, 77% yield based on styrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.497 mmol) and styrene (43.1 mg, 0.414 mmol) by Method C: Isolated yield 55% (53.0 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymerized product (24.5 mg, 56% yield based on styrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.491 mmol) and styrene (45.3 mg, 0.435 mmol) by Micomixing: Isolated yield 79% (79.8 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymerized product (10.1 mg, 23% yield based on styrene, purified with gel permeation chromatography): TLC R_f 0.32 (hexane/ethyl acetate 1:1): ^1H NMR (300 MHz, CDCl_3) δ 0.95 (t, 3H, $J = 6.3$ Hz), 1.35 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.52-1.69 (m, 2H), 2.02-2.34 (m, 2H), 3.21-3.52 (m, 4H), 5.28 (dd, 1H, $J = 2.7$ Hz, $J = 9.6$ Hz), 7.25-7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 19.9, 29.1, 29.6, 44.2, 49.2, 77.9, 125.5, 128.2, 128.5, 139.0, 153.4. The NMR spectra data were identical to those reported in the literature.²

3-Butyl-6-(4-chloro-phenyl)-[1,3]oxazinan-2-one. Prepared from **1** (10.0 mL, 0.500 mmol) and *p*-chlorostyrene (60.9 mg, 0.440 mmol) by Method A: Isolated yield 43% (50.1 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymerized product (39.2 mg, 64% yield based on *p*-chlorostyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.500 mmol) and *p*-chlorostyrene (60.9 mg,

0.440 mmol) by Method B: Isolated yield 12% (14.6 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymerized product (50.9 mg, 83% yield based on *p*-chlorostyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.500 mmol) and *p*-chlorostyrene (60.9 mg, 0.440 mmol) by Method C: Isolated yield 54% (63.3 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymerized product (34.1 mg, 56% yield based on *p*-chlorostyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.500 mmol) and *p*-chlorostyrene (60.9 mg, 0.440 mmol) by Micromixing: Isolated yield 70% (82.1 mg, purified with flash chromatography, hexane/ethyl acetate 2:1) with polymerized product (25.4 mg, 42% yield based on *p*-chlorostyrene, purified with gel permeation chromatography): ^1H NMR (300 MHz, CDCl_3) δ 0.94 (t, 3H, $J = 7.4$ Hz), 1.34 (tq, 2H, $J = 7.4$ Hz, $J = 7.4$ Hz), 1.49-1.70 (m, 2H), 1.99-2.17 (m, 1H), 2.18-2.28 (m, 1H), 3.20-3.52 (m, 4H), 5.25 (dd, 1H, $J = 2.9$ Hz, $J = 10.1$ Hz), 7.28-7.39 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.7, 19.8, 29.0, 29.5, 44.0, 49.1, 77.2, 126.9, 128.6, 133.9, 137.6, 153.0; IR (KBr) 2959, 1678, 1489, 1096 cm^{-1} ; LRMS (EI) m/e 267 (M^+), 252 ($\text{M}^+ - \text{Me}$), 224 ($\text{M}^+ - \text{C}_3\text{H}_7$), 210 ($\text{M}^+ - \text{C}_4\text{H}_9$); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}\text{ClNO}_2$ (M^+): 267.1026, found: 267.1024.

3-Butyl-6-*p*-tolyl-[1,3]oxazinan-2-one. Prepared from **1** (10.0 mL, 0.504 mmol) and *p*-methylstyrene (50.6 mg, 0.428 mmol) by Method A: Isolated yield 45% (47.4 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) with polymerized product

(39.5 mg, 78% yield based on *p*-methylstyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.503 mmol) and *p*-methylstyrene (50.4 mg, 0.426 mmol) by Method B: Isolated yield 16% (16.5 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) with polymerized product (50.8 mg, 100% yield based on *p*-methylstyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.503 mmol) and *p*-methylstyrene (50.4 mg, 0.426 mmol) by Method C: Isolated yield 58% (60.9 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) with polymerized product (43.0 mg, 85% yield based on *p*-methylstyrene, purified with gel permeation chromatography): Prepared from **1** (10.0 mL, 0.503 mmol) and *p*-methylstyrene (50.4 mg, 0.426 mmol) by Micromixing: Isolated yield 66% (69.3 mg, purified with flash chromatography, hexane/ethyl acetate 3:1) with polymerized product (24.5 mg, 49% yield based on *p*-methylstyrene, purified with gel permeation chromatography): ^1H NMR (300 MHz, CDCl_3) δ 0.97 (t, 3H, $J = 7.5$ Hz), 1.37 (tq, 2H, $J = 7.5$ Hz, $J = 7.5$ Hz), 1.52-1.71 (m, 2H), 2.05-2.33 (m, 2H), 2.38 (s, 3H), 3.21-3.52 (m, 4H), 5.28 (dd, 1H, $J = 3.0$ Hz, $J = 9.6$ Hz), 7.17-7.32 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 19.9, 21.1, 29.1, 29.6, 44.2, 49.2, 77.9, 125.5, 129.2, 136.1, 138.0, 153.5; IR (KBr) 2957, 1682, 1495, 1460 cm^{-1} ; LRMS (EI) m/e 247 (M^+), 232 ($\text{M}^+ - \text{Me}$), 204 ($\text{M}^+ - \text{C}_3\text{H}_7$); HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_2$ (M^+): 247.1572, found: 247.1574.

DFT calculations. The DFT calculations were carried out at B3LYP/6-31G(d) level using the Gaussian 98W, Revision A.7.³ Cartesian coordinates and energies of computationally characterized species are as follows: The transition state was verified to have exactly one negative eigenvalue. Negative eigenvalue was animated using NEC

MolStudio R3.1 and proved to be the transition state for formation of the expected bond.

The reaction path was followed using IRC method and it was confirmed that there is only one transition state between the precomplex and the cycloadduct.

Precomplex:

6	-2.09055	-0.26021	-0.28202
7	-0.72729	0.29708	-0.42826
6	-0.4478	1.54878	-0.23526
6	0.41149	-0.59689	-0.75477
8	1.53405	-0.17538	-0.77676
8	-0.04697	-1.80361	-0.97982
6	0.95449	-2.8144	-1.32812
1	-2.379	-0.7422	-1.21673
1	-2.7774	0.55338	-0.04919
1	-2.09181	-1.00017	0.52031
1	0.56613	1.88233	-0.41751
1	-1.24523	2.25402	-0.03913
1	0.38375	-3.72928	-1.46911
1	1.66791	-2.91013	-0.50871
1	1.46175	-2.51431	-2.24583
6	-0.35606	2.10687	2.55208
6	0.93138	1.97699	2.19241
1	-0.84455	3.07821	2.58447

1	-0.94231	1.2579	2.89683
1	1.44333	1.01813	2.21777
1	1.53414	2.83766	1.9114

E = -440.773009376

TS:

6	-2.19201	-0.31048	-0.2821
7	-0.86874	0.33794	-0.37929
6	-0.66592	1.63309	-0.05096
6	0.30051	-0.44004	-0.56466
8	1.39944	0.03093	-0.32363
8	0.01557	-1.66187	-0.96545
6	1.15044	-2.54899	-1.19243
1	-2.40283	-0.8314	-1.21696
1	-2.9474	0.45784	-0.1162
1	-2.20567	-1.03244	0.53871
1	0.2075	2.09781	-0.48966
1	-1.56492	2.23684	0.01668
1	0.70834	-3.47983	-1.54102
1	1.69344	-2.69661	-0.25764
1	1.80701	-2.11585	-1.94839
6	-0.1415	1.90825	1.86508
6	1.11011	1.33244	1.88879

1	-0.20806	2.99391	1.8141
1	-0.9655	1.40819	2.36973
1	1.27244	0.31359	2.22467
1	1.99714	1.88426	1.59133

E = -440.765149303

Cycloadduct:

6	-1.73061	1.39093	-0.89173
7	-0.43499	0.81382	-0.48862
6	0.77025	1.63745	-0.74512
6	-0.35269	-0.36083	0.10792
8	0.77014	-0.94558	0.43441
8	-1.45584	-0.98855	0.40277
6	-1.39709	-2.31857	1.01148
6	2.05173	-0.33589	0.04373
6	1.93663	1.17278	0.12121
1	-2.49978	0.62199	-0.89752
1	-1.62064	1.80515	-1.89696
1	-2.01112	2.18861	-0.19748
1	0.50337	2.6736	-0.51979
1	1.00612	1.57405	-1.81368
1	-2.44088	-2.60459	1.11892
1	-0.90567	-2.25451	1.98257

1	-0.86757	-3.00376	0.34882
1	2.27311	-0.69623	-0.96485
1	2.76829	-0.75646	0.74801
1	1.79072	1.48207	1.16191
1	2.86533	1.63111	-0.23204

E = -440.837433174

References and Notes

1. Stereochemistry was determined by the coupling constant of ^1H NMR spectroscopies referring to the following papers: (a) Barluenga, J.; Olano, B.; Fustero, S. *J. Org. Chem.* **1985**, *50*, 4052. (b) Yamamoto, Y.; Komatsu, T.; Maruyama, K. *J. Org. Chem.* **1985**, *50*, 3115. (c) Bernath, G.; Gondos, G. Y.; Kovacs, K.; Sohar, P. *Tetrahedron* **1971**, *29*, 981.
2. Fujiwara, M.; Baba, A.; Matsuda, H. *J. Heterocyclic. Chem.* **1989**, *26*, 1659.
3. Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M.

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