Supporting Information For:
 α -Alkylation of Ketones by Addition of Zinc Enamides to Unactivated Olefins

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General. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon or nitrogen. Air- and moisture-sensitive liquid and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25-mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). Thin layer chromatography plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating on a hot plate. Organic solutions were concentrated by rotary evaporation at c.a. 30 Torr. Flash column chromatography was performed on Kanto Silica gel 60 (spherical, neutral, 140–325 mesh) as described by Still et al.¹

Instrumentation. High-pressure reactions were conducted in a glass autoclave purchased from Taiatsu Techno Co (Hyper Glass Cylinder). Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded with JEOL AL-400 (400 MHz), JEOL ECX-400 (400 MHz) or JEOL ECA-500 (500 MHz) NMR spectrometers. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton in CDCl₃ (δ 7.26). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 125 or 100 MHz: chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of CDCl₃ (δ 77.0). Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. Gas chromatographic (GC) analyses were performed on Shimadzu GC-14B instruments equipped with an FID detector and a capillary column, HR-1 (Shinwa, 25 m $\times$ 0.25 mm i.d., 0.25 μ m film) or a CP-Chirasil-DEX CB (Chrompack, 25 $\times$ 0.25 mm i.d., 0.25 μ m film). IR spectra recorded on a FT/IR-420 (JASCO) or a React IR 1000 Reaction Analysis System equipped with DuraSample IR (ASI Applied System) are reported in cm⁻¹. High-resolution mass spectra are taken with EI (electron impact) method at JEOL GC-mate II.

Solvent. Anhydrous diethyl ether (Et₂O) and hexane were purchased from Kanto Chemical Co. and degassed and dried over molecular sieves in a storage flask. The water content of the solvent

was confirmed with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 10 ppm. Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical Co. and distilled from benzophenone ketyl at 760 Torr under argon immediately before use. Diisopropylamine and TMEDA were purchased from Aldrich Inc. and distilled before use.

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Kogyo Co., Aldrich Inc., and other commercial suppliers, and were used either after distillation. ZnCl_2 (anhydrous, beads) was purchased from Aldrich Inc. 2,4-Dimethylaniline was purchased from Wako Co. Isobutylene was purchased from Tokyo Kasei Kogyo Co. and dried over molecular sieves in an autoclave before use. Ethylene and propylene were purchased from Nippon Sanso Co.

Preparation of 2,4-dimethylphenyl-(1-ethylpropyliden)amine (33)

Molecular sieves (4A, 12 g, dry) were added to 3-pentanone (9.47 g, 110 mmol) and 2,4-dimethylaniline (12.1 g, 100 mmol). The reaction mixture was heated to reflux for 3 d. The reaction mixture was cooled to ambient temperature and then molecular sieves were filtered with a pad of celite and washed with dry Et_2O (20 mL, five times). The filtrate was evaporated *in vacuo* and distilled to yield 17.0 g (90% yield) of imine **33** as a pale yellow liquid. Bp 55 °C/0.1 mmHg; IR (neat) 1661 (C=N), 1493, 1460, 1219, 1186 946.3, 822.8; ^1H NMR (500 MHz, CDCl_3) δ 0.98 (t, J = 7.2 Hz, 3H, CH_2CH_3), 1.22 (t, J = 7.2 Hz, 3H, CH_2CH_3), 2.0 (s, 3H, NCCCH_3), 2.07 (q, J = 7.2 Hz, 2H, CH_2CH_3), 2.29 (s, 3H, CHCHCCH_3), 2.45 (q, J = 7.2 Hz, 2H, CH_2CH_3), 6.45 (d, J = 8.0 Hz, 1H, NCCCH), 6.91 (d, J = 8.0 Hz, 1H, NCCHCH), 6.95 (s, 1H, $\text{C}(\text{CH}_3)\text{CH}$); ^{13}C NMR (125 MHz, CDCl_3) δ 10.9, 11.2, 17.6, 20.7, 26.1, 30.9, 118.6, 126.6, 126.7, 130.8, 131.9, 147.4, 176.6.

2,4-Dimethylphenyl-(1-butylpentyliden)amine (34)

Bp 100 °C/0.1 mmHg; IR (neat) 1655 (C=N), 1493, 1466, 1458, 826.7; ^1H NMR (500 MHz, CDCl_3) δ 0.80 (t, J = 7.2 Hz, 3H, CH_2CH_3), 0.96 (t, J = 7.2 Hz, 3H, CH_2CH_3), 1.18 (sext, J = 7.2 Hz, 3H, CH_2CH_3), 1.35–1.46 (m, 4H, CH_2CH_3 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.67 (quint, J = 7.2 Hz, 2H,

$\text{CH}_2\text{CH}_2\text{CH}_3$), 1.99 (s, 3H, NCCCH_3), 2.04 (t, $J = 7.2$ Hz, 2H, C(=N)CH_2), 2.27 (s, 3H, CHCHCCH_3), 2.41 (t, $J = 7.2$ Hz, 2H, C(=N)CH_2), 6.42 (d, $J = 8.0$ Hz, 1H, NCCH), 6.89 (d, $J = 8.0$ Hz, 1H, NCCHCH), 6.94 (s, 1H, $\text{C(CH}_3\text{)CH}$); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 14.1, 17.8, 20.8, 22.7, 22.8, 28.8, 28.9, 32.8, 38.1, 118.6, 126.5, 126.6, 130.7, 131.7, 147.2, 174.9.

2,4-Dimethylphenyl-(cyclohexyliden)amine (35)

Bp 70 °C/0.15 mmHg; IR (neat) 1661 (C=N), 1492, 1448, 1233, 1200, 822.8, 756.3, 709.0; ^1H NMR (500 MHz, CDCl_3) δ 1.57–1.62 (m, 2H, $\text{N=CCH}_2\text{CH}_2\text{CH}_2$), 1.64–1.69 (m, 2H, $\text{N=CCH}_2\text{CH}_2\text{CH}_2$), 1.83–1.88 (m, 2H, $\text{N=CCH}_2\text{CH}_2\text{CH}_2$), 2.04 (s, 3H, NCCCH_3), 2.08 (t, $J = 6.5$ Hz, 2H, N=CCH_2), 2.28 (s, 3H, CHCHCCH_3), 2.48 (t, $J = 6.5$ Hz, 2H, N=CCH_2), 6.47 (d, $J = 8.0$ Hz, 1H, NCCH), 6.91 (d, $J = 8.0$ Hz, 1H, NCCHCH), 6.96 (s, 1H, $\text{C(CH}_3\text{)CH}$); ^{13}C NMR (125 MHz, CDCl_3) δ 17.6, 20.7, 25.8, 27.3, 27.9, 31.3, 39.1, 119.0, 126.7, 127.1, 130.8, 132.1, 147.0, 174.5.

2,4-Dimethylphenyl-(1-phenylpropyliden)amine (36)

Bp 110 °C/0.1 mmHg; IR (neat) 3087 and 3068 and 3058 and 3033 and 3023 (aromatic C–H), 1625 (C=N), 1577, 1490, 1445, 1214, 832.5, 784.3 772.7, 694.5; $E:Z = 11:1$.

E isomer; ^1H NMR (500 MHz, CDCl_3) δ 1.00 (t, $J = 7.2$ Hz, 3H, CH_2CH_3), 2.07 (s, 3H, NCCCH_3), 2.31 (s, 3H, CHCHCCH_3), 2.59 (t, $J = 7.2$ Hz, 2H, CH_2CH_3), 6.55 (d, $J = 8.0$ Hz, 1H, NCCH), 6.97 (d, $J = 8.0$ Hz, 1H, NCCHCH), 7.02 (s, 1H, $\text{C(CH}_3\text{)CH}$), 7.44 (brs, 3H, aromatic CH), 7.94 (brs, 2H, aromatic CH); ^{13}C NMR (125 MHz, CDCl_3) δ 12.3, 17.8, 20.7, 23.3, 118.1, 126.7, 126.7, 127.5 (2C), 128.4 (2C), 130.1, 131.0, 132.2, 138.1, 147.5, 170.2.

Z isomer; ^1H NMR (500 MHz, CDCl_3) δ 1.24 (t, $J = 7.2$ Hz, 3H, CH_2CH_3), 2.13 (s, 3H, NCCCH_3), 2.17 (s, 3H, CHCHCCCH_3), 2.78 (t, $J = 7.2$ Hz, 2H, CH_2CH_3), 6.21 (d, $J = 8.0$ Hz, 1H, NCCH), 6.66 (d, $J = 8.0$ Hz, 1H, NCCHCH), 7.85 (s, 1H, $\text{C}(\text{CH}_3)\text{CH}$), 7.18 (brs, 3H, aromatic CH), 7.22 (brs, 2H, aromatic CH); ^{13}C NMR (125 MHz, CDCl_3) δ 11.1, 17.8, 20.7, 34.0, 119.5, 126.4, 126.4, 127.2 (2C), 127.9 (2C), 128.2, 130.5, 131.9, 137.8, 147.0, 171.8.

Preparation of zinc enamide [Procedure A]

To a solution of diisopropylamine (0.16 mL, 1.1 mmol) in THF (1.2 mL) was added dropwise BuLi (1.55 M in hexane, 0.65 mL, 1.02 mmol) at 0 °C. After 30 min, imine **33** (0.209 mL, 1.0 mmol) was slowly added at 0 °C. After 6 h, the solvents were removed *in vacuo* (30 min, 0 °C, 0.1 mmHg). Residual sludgy lithium enamide was dissolved in Et_2O (0.5 mL) and ZnCl_2 (0.5 M in Et_2O , 2.0 mL, 1.0 mmol) was added at 0 °C. After 30 min, BuLi (1.55 M in hexane, 0.65 mL, 1.0 mmol) was added at -78 °C (or added dropwise at 0 °C) and the reaction mixture was warmed to ambient temperature.

4-Methylhexan-3-one (11) [Procedure B]

After the reaction performed according to procedure A, Et_2O was removed at 50 °C with N_2 flow. The reaction mixture was heated to 50 °C for 12 h under ethylene atmosphere (1 atm) then cooled to 0 °C. Acetic acid (1.0 mL) and water (0.5 mL) were added at 0 °C. Hydrolysis was carried out at rt for 1 h, and then water (4.5 mL) was added at that temperature. The aqueous layer was extracted five times with pentane. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate. Gas chromatography analysis was carried out (94% yield) by using decane (39.0 μL , 0.2 mmol) as an internal standard. The organic layer was chromatographed on silica gel (3 g, pentane and then 3% Et_2O in pentane) to obtain the corresponding ketone (0.068 g, 60% yield).

4,5-Dimethylhexan-3-one (12)

The addition reaction was carried out according to procedure B on a 1.0 mmol scale. Conditions; propylene balloon, 65 °C, 60 h, Hydrolysis; 65 °C, 1 h; 86% yield on GC analysis. The corresponding ketone (0.085 g, 66% yield) was obtained after silica gel column chromatography.

4,5-Dimethylundecan-3-one (8) [Procedure C]

After the reaction performed according to procedure A, the solvents was removed removed *in vacuo* (10 min, rt, 0.1 mmHg). 1-Octene (0.19 mL, 1.2 mmol) and hexane (0.1 ml) were added then the reaction mixture was heated to 65 °C for 12 h Acetic acid (1.0 mL) and water (0.5 ml) were added at 0 °C. Hydrolysis was carried out at 65 °C for 1 h, and then water (4.5 mL) was added at ambient temperature. The aqueous layer was extracted five times with pentane. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate. Gas chromatography analysis was carried out (92% yield, *syn:anti* = 7:3) by using tridecane (48.8 μ L, 0.2 mmol) as an internal standard. The organic layer was chromatographed on silica gel (5 g, pentane and then 3% Et₂O in pentane) to obtain the corresponding ketone (0.178 g, 90% yield).; R_f = 0.66, 10% Et₂O in pentane; IR(neat) 1712 (vs, C=O), 1459, 1378, 1261, 1108, 1023, 975.3, 804.5.; EI-HRMS calcd for C₁₃H₂₆O [M]⁺ 198.1984, found 198.1988.

Major diastereomer (*syn*; determined by comparison of the NMR sifts with 4,5-dimethyldecan-3-one²): ¹H NMR (400 MHz, CDCl₃) δ 0.78 (d, J = 7.2 Hz, 3H, COCHCHCH₃), 0.88 (t, J = 7.2 Hz, 3H, CH₂CH₂CH₃), 0.96 (d, J = 7.2 Hz, 3H, COCHCH₃), 1.05 (t, J = 7.2 Hz, 3H, COCH₂CH₃), 1.10–1.35 (m, 10H, CH(CH₂)₅CH₃), 1.80–1.90 (m, 1H, COCHCH), 2.37–2.51 (m, 3H, COCHCH, COCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 7.8, 11.3, 14.0, 15.3, 22.6, 27.3, 29.4 31.8, 34.5, 34.5, 35.3, 50.6, 215.3.

Minor diastereomer (*anti*): ¹H NMR (400 MHz, CDCl₃) δ 0.87 (d, J = 7.2 Hz, 3H, COCHCHCH₃), 0.88 (t, J = 7.2 Hz, 3H, CH₂CH₂CH₃), 1.01 (d, J = 7.2 Hz, 3H, COCHCH₃), 1.04 (t, J = 7.2 Hz, 3H, COCH₂CH₃), 1.10–1.35 (m, 10H, CH(CH₂)₅CH₃), 1.73–1.83 (m, 1H,

COCHCH), 2.37–2.51 (m, 3H, COCHCH, COCH₂CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 7.7, 13.1, 14.0, 17.8, 22.6, 26.7, 29.5, 32.7, 35.1, 35.1, 51.6, 215.5.

4-Methyl-6-phenylhexan-3-one (13); 4-Methyl-5-phenylhexan-3-one² (14)

The addition reaction was carried out according to procedure C on a 1.0 mmol scale. Conditions; 0.14 mL of styrene (1.2 mmol), 0.2 mL of hexane, 30 °C, 12 h, Hydrolysis; 65 °C, 1 h; *linear:branched* = 46:54, *syn:anti* = 66:34 determined by GC analysis. The corresponding ketone (0.171 g, 90% yield) was obtained after silica gel column chromatography.

4,5,5-Trimethylhexan-3-one (9) [Procedure D]

After the reaction performed according to procedure A, the solvents were removed *in vacuo* (10 min, rt, 0.1 mmHg). Isobutylene (ca. 0.5 mL) was added at –78 °C and the reaction mixture was charged in an autoclave. The autoclave was maintained at 65 °C for 60 h with stirring (4 atm), and cooled to ambient temperature. After the removal of unreacted isobutylene, the reaction mixture was moved to ice bath and added acetic acid (1.0 mL) and water (0.5 mL). Hydrolysis was carried out at 90 °C for 6 h, and then water (4.5 mL) was added at ambient temperature. The aqueous layer was extracted five times with pentane. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate. Gas chromatography analysis was carried out (85% yield), using decane (39.0 µL, 0.2 mmol) as an internal standard. The organic layer was chromatographed on silica gel (3 g, pentane and then 3% Et₂O in pentane) to obtain the corresponding ketone (0.108 g, 76% yield).

2-(1-Methyl-cyclohexyl)-pentan-3-one (15)

After the reaction performed according to procedure A, the solvents were removed *in vacuo* (20 min, rt, 0.1 mmHg). Methylenecyclohexane (0.36 mL, 3.0 mmol) was added at 0 °C. The reaction mixture was heated to 65 °C for 72 h then cooled to 0 °C. Acetic acid (1.0 mL) and water (0.5 mL) were added at 0 °C. Hydrolysis was carried out at 100 °C for 12 h, and then water (4.5 mL) was added at ambient temperature. The aqueous layer was extracted five times with pentane. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate, then chromatographed on silica gel (4 g, pentane and then 3% Et₂O in pentane) to obtain the corresponding ketone (0.140 g, 77% yield); *R*_f = 0.60, 10% Et₂O in pentane; IR (neat) 1712 (vs, C=O), 1460, 1450, 1378 1260, 1092, 1018, 803.6; ¹H NMR (500 MHz, CDCl₃) δ 0.93 (s, 3H, CCH₃), 0.97 (d, *J* = 7.2 Hz, 3H, CHCH₃), 1.00 (t, *J* = 7.2 Hz, 3H, CH₂CH₃), 1.17–1.54 (m, 10H, -C(CH₂)₅-), 2.45 (m, 2H, CH₂CH₃), 2.53 (q, *J* = 7.2 Hz, 1H, CHCH₃); ¹³C NMR (125 MHz, CDCl₃) δ 7.5, 11.6, 19.7, 21.7, 21.8, 26.2, 35.8, 35.9, 36.1, 38.5, 54.6, 216.3; EI-HRMS calcd for C₁₂H₂₂O [M]⁺ 182.1671, found 182.1666.

4-*tert*-Butylnonan-5-one (17)

The addition reaction was carried out according to procedure D on a 1.0 mmol scale. Conditions; 0.245 g of imine **34** (1.0 mmol), 0.5 mL of isobutylene, 80 °C 72 h, Hydrolysis; acetic acid (1.0 mL), water (0.5 mL), 120 °C, 12 h; The corresponding ketone (0.151 g, 76% yield) was obtained after silica gel column chromatography.

2-Ethylcyclohexanone (19)

The addition reaction was carried out according to procedure B on a 1.0 mmol scale. Conditions; 0.201 g of imine **35** (1.0 mmol), ethylene balloon, 65 °C, 24 h, Hydrolysis; rt, 1 h; 90% yield on GC analysis. The corresponding ketone (0.095 g, 75% yield) was obtained after silica gel column chromatography.

2-Isopropylcyclohexanone (20)

The addition reaction was carried out according to procedure D on a 1.0 mmol scale. Conditions; 0.201 g of imine **35** (1.0 mmol), 0.5 mL of propylene, 65 °C, 24 h, Hydrolysis; 65 °C, 1 h; 88% yield on GC analysis. The corresponding ketone (0.106 g, 76% yield) was obtained after silica gel column chromatography.

2-(2-Phenylethyl)cyclohexanone (21)

The addition reaction was carried out according to procedure D on a 1.0 mmol scale. Conditions; 0.201 g of imine **35** (1.0 mmol), 0.24 mL of styrene (2.0 mmol), 50 °C, 12 h, Hydrolysis; rt, 1 h; *linear:branched* = >98:2 determined by GC analysis. The corresponding ketone (0.176 g, 87% yield) was obtained after silica gel column chromatography.

2-*tert*-Butylcyclohexanone (22)

The addition reaction was carried out according to procedure D on a 1.0 mmol scale. Conditions; 0.201 g of imine **35** (1.0 mmol), 0.5 mL of isobutylene, 80 °C 72 h, Hydrolysis; acetic acid (1.0 mL), water (0.5 mL), 100 °C, 12 h; 24% yield on GC analysis. The corresponding ketone (0.028 g, 18% yield) was obtained after silica gel column chromatography.

2,3-Dimethyl-1-phenylbutan-1-one (24)

The addition reaction was carried out according to procedure D on a 1.0 mmol scale. Conditions; 0.237 g of imine **36** (1.0 mmol), 0.5 mL of propylene, 80 °C, 72 h, Hydrolysis; 90 °C, 1 h; The corresponding ketone (0.130 g, 74% yield) was obtained after silica gel column chromatography.

Ethyl-2-(4-methyl-5-oxoheptyl)acrylate (27)

The addition reaction was carried out according to procedure B on a 1.0 mmol scale at 50 °C for 24 h. Ethyl-2-(bromomethyl)acrylate (0.31 mL, 2.2 mmol) was slowly added to the reaction mixture at 0 °C. After 4 h, acetic acid (0.5 mL) and water (0.5 mL) were added at 0 °C. Hydrolysis was carried out at room temperature for 1 h, and then water (4.5 mL) was added. The aqueous layer was extracted five times with pentane. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate, then chromatographed on silica gel (5 g, pentane and then 5, 10, 20% Et₂O in pentane) to obtain the corresponding ketone (0.192 g, 85% yield).; $R_f = 0.18$, 10% Et₂O in pentane; IR (neat) 1711 (vs, C=O), 1631 (C=C), 1461, 1370, 1300, 1266, 1176 and 1148 (C–O), 1026, 945.4, 818.0; ¹H NMR (400 MHz, CDCl₃) δ 1.04 (t, $J = 7.2$ Hz, 3H, C(=O)CH₂CH₃), 1.07 (d, $J = 7.2$ Hz, 3H, CCHCH₃), 1.30 (t, $J = 7.2$ Hz, 3H, OCH₂CH₃), 1.32–1.47 (m, 3H, CHCHHCH₂), 1.64–1.73 (m, 1H, CHCHH), 2.29 (t, $J = 7.2$ Hz, 2H, CH₂CH₂C), 2.54 (sex, $J = 7.2$ Hz, 1H, CH), 4.21 (q, 2H, OCH₂CH₃), 5.52 (d, 1H, CHH=C), 6.14 (d, 1H, CHH=C); ¹³C NMR (100 MHz, CDCl₃) δ ; 7.7, 14.2, 16.5, 26.1, 31.8, 32.5, 34.3, 45.8, 60.6, 124.6, 140.4, 167.2, 215.2; EI-HRMS calcd for C₁₃H₂₂O₃ [M]⁺ 226.1569, found 226.1565.

6-(4-Acetylphenyl)-4-methylhexan-3-one (28) [Procedure E]

Addition reaction was carried out according to procedure B on a 10 mmol scale at 50 °C for 24 h. The solvents were removed *in vacuo*. To the reaction mixture TMEDA (3.0 mL, 20 mmol), 4-iodoacetylbenzene (5.4 g, 22 mmol), PdCl₂(PPh₃)₂ (0.35 g, 0.5 mmol), and THF (20 mL) were added in turn at 0 °C. The reaction mixture was stirred at room temperature (ca. 25 °C) for 8 h, and

then acetic acid (5 mL) and water (5 mL) were added at 0 °C. Hydrolysis was carried out at room temperature for 1 h, and then water (40 mL) was added at ambient temperature. The aqueous layer was extracted five times with Et₂O. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate then *in vacuo*. The crude product was chromatographed on silica gel (100 g, pentane and then 10, 20% Et₂O in pentane) to obtain the corresponding diketone (1.928 g, 83% yield); *R_f* = 0.18, 20% Et₂O in pentane; IR (neat) 1710 and 1679 (C=O) 1606 (aromatic C=C), 1358, 1267, 1182, 956.0, 819.9; ¹H NMR (400 MHz, CDCl₃) δ 0.96 (t, *J* = 7.2 Hz, 3H, CH₂CH₃), 1.04 (d, *J* = 7.2 Hz, 3H, CHCH₃), 1.55 (dq, *J* = 7.2, 13.5 Hz, 1H, CHCHH), 1.93 (dq, *J* = 7.2, 13.5 Hz, 1H, CHCHH), 2.30–2.50 (m, 3H, CHC(=O)CH₂), 2.49 (s, 3H, CCH₃), 2.54 (t, *J* = 7.2 Hz, 2H, CH₂Ar), 7.17 (d, *J* = 8.5 Hz, 2H, aromatic CH), 7.79 (d, *J* = 8.5 Hz, 2H, aromatic CH); ¹³C NMR (100 MHz, CDCl₃) δ; 7.6, 16.6, 26.4, 33.3, 33.9, 34.2, 45.2, 128.4 (2C), 128.4 (2C), 135.0, 147.5, 197.6, 214.6; Anal. calcd for C₁₅H₂₀O₂: C, 77.55; H, 8.68. Found: C, 77.33; H, 8.81; EI-HRMS calcd for C₁₅H₂₀O₂ [M]⁺ 232.1463, found 232.1424.

4-Methyl-6-(4-nitrophenyl)hexan-3-one (29)

Trapping was carried out according to procedure E on a 1.0 mmol scale. Conditions; 0.55 g of 4-iodonitrobenzene (2.2 mmol), room temperature (ca. 25 °C), 8 h, Hydrolysis; rt, 1 h: The corresponding ketone (0.188 g, 80% yield) was obtained after silica gel column chromatography.; *R_f* = 0.31, 20% Et₂O in pentane; IR (neat) 3080 (aromatic C–H), 1708 (C=O), 1605 (aromatic C=C), 1515 and 1342 (N=O), 1109, 848.9 (C–N), 747.6, 697.4; ¹H NMR (400 MHz, CDCl₃) δ 1.04 (t, *J* = 7.2 Hz, 3H, CH₂CH₃), 1.15 (d, *J* = 7.2 Hz, 3H, CHCH₃), 1.66 (dq, *J* = 7.2, 13.5 Hz, 1H, CHCHH), 2.04 (dq, *J* = 7.2, 13.5 Hz, 1H, CHCHH), 2.40–2.61 (m, 3H, CHC(=O)CH₂), 2.68 (t, *J* = 7.2 Hz, 2H, CH₂Ar), 7.33 (d, *J* = 8.5 Hz, 2H, aromatic CH), 8.14 (d, *J* = 8.5 Hz, 2H, aromatic CH); ¹³C NMR (100 MHz, CDCl₃) δ; 7.7, 16.8, 33.3, 33.8, 34.3, 45.2, 123.6 (2C), 129.1 (2C), 146.3, 149.7, 214.4; EI-HRMS calcd for C₁₃H₁₇NO₃ [M]⁺ 235.1208, found 235.1232.

4,5,5-Trimethylnon-8-en-3-one (30)

The addition reaction was carried out according to procedure D on a 1.0 mmol scale at 65 °C for 72 h. After the removal of unreacted isobutylene, allyl bromide (0.21 mL, 2.4 mmol) was slowly added to the reaction mixture at room temperature (ca. 25 °C). After 3 h, acetic acid (1.0 mL) and water (0.5 mL) were added at 0 °C. Hydrolysis was carried out at 90 °C for 6 h, and then water (4.5 mL) was added at ambient temperature. The aqueous layer was extracted five times with pentane. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate then chromatographed on silica gel (4 g, pentane and then 3% Et₂O in pentane) to obtain the corresponding ketone (0.149 g, 82% yield); R_f = 0.58, 10% Et₂O in pentane; IR (neat) 3079 (CH=CH₂), 1713 (C=O), 1642 (C=C), 1460, 1261, 1092, 1018 and 908.7 (CH=CH₂), 801.6; ¹H NMR (500 MHz, CDCl₃) δ 0.91 (s, 3H, CCH₃(CH₃)), 0.92 (s, 3H, CCH₃(CH₃)), 0.99 (d, J = 7.2 Hz, 3H, COCHCH₃), 1.00 (t, J = 7.2 Hz, 3H, COCH₂CH₃), 1.28–1.37 (m, 2H, CCH₂CH₂), 1.94–2.05 (m, 2H, CCH₂CH₂), 2.45 (q, J = 7.2 Hz, 2H, COCH₂CH₃), 2.53 (q, J = 7.2 Hz, 1H, COCHCH₃), 4.91 (dd, J = 2.0, 10.5 Hz, 1H, CH=CHH), 4.91 (dd, J = 2.0, 17.0 Hz, 1H, CH=CHH), 5.78 (m, 1H, CH=CH₂); ¹³C NMR (125 MHz, CDCl₃) δ 7.6, 12.3, 24.2, 24.5, 28.3, 35.6, 38.1, 39.7, 53.1, 114.1, 139.2, 215.9; EI-HRMS calcd for C₁₂H₂₂O [M]⁺ 182.1671, found 182.1665.

3-(2,2,3-Trimethyl-4-oxohexyl)cyclohexanone (31)

The addition reaction was carried out according to procedure D on a 1.0 mmol scale at 65 °C for 72 h. After the removal of unreacted isobutylene, iodomethane (0.012 mL, 0.2 mmol) was added at ambient temperature. After 30 min, unreacted iodomethane was removed *in vacuo* (10 min, rt, 0.1 mmHg) then TMEDA (0.30 mL, 2 mmol) and THF (1.0 mL) were added. The reaction mixture was poured into another vessel charged with CuCN (0.027 g, 0.3 mmol), 2-cyclohexen-1-one (0.23 mL, 2.4 mmol), and chlorotrimethylsilane (0.30 mL, 2.4 mmol) at 0 °C via cannula and rinsed with THF (0.2 mL, twice). After 6 h, Et₂O (5 mL) and aqueous NH₃ (10%, 2.0 mL) were added at 0 °C and stirred at room temperature for 30 min in air. The aqueous layer was extracted five times with

pentane. The combined organic extracts were washed with brine then *in vacuo*. The crude product was treated with acetic acid (1.0 mL) and water (0.5 mL) at 90 °C for 6 h, and then water (4.5 mL) was added at ambient temperature. The aqueous layer was extracted five times with pentane. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate, then chromatographed on silica gel (6 g, pentane and then 3, 6, 10% Et₂O in pentane) to obtain the corresponding diketone (0.169 g, 71% yield).; R_f = 0.16, 20% Et₂O in pentane; IR (neat) 1708 (vs, C=O) 1460, 1375, 1226 1114, 1094, 973.3; ¹H NMR (500 MHz, CDCl₃) δ 0.88–0.95 (m, 6H, C(CH₃)₂), 0.96–1.04 (m, 6H, CH₃CH₂COCHCH₃), 1.19–1.31 (m, 1H, CCHHCH), 1.35–1.48 (m, 2H, CCHHCH, COCH₂CHCHH), 1.61–1.71 (m, 1H, COCH₂CHH), 1.84–1.91 (m, 2H, COCH₂CHCHH), 1.99–2.10 (m, 2H, CHHCOCH₂CHH), 2.19–2.37 (m, 2H, COCH₂CH₂), 2.39–2.53 (m, 4H, CHHCOCH₂, CH₂COCH); ¹³C NMR (125 MHz, CDCl₃) δ 7.5 (7.5), 12.3 (12.3), 24.4 (24.5), 24.7 (25.1), 25.3 (25.3), 33.9 (33.9), 34.8 (34.8), 36.2 (36.3), 38.1 (38.2), 41.0 (41.1), 46.3 (46.5), 50.5 (50.5), 53.7 (53.8), 211.7 (211.8), 215.7 (215.7), ¹³C shifts of another diastereomer (*dr* = 1:1) are written in the parenthesis; EI-HRMS calcd for C₁₅H₂₆O₂ [M]⁺ 238.1933, found 238.1922.

4,5,5-Trimethyl-8-phenyloct-7-en-3-one (32)

The addition reaction was carried out according to procedure D on a 1.0 mmol scale at 65 °C for 72 h. After the removal of unreacted isobutylene, iodomethane (0.012 mL, 0.2 mmol) was added at ambient temperature. After 30 min, unreacted iodomethane was removed *in vacuo* (10 min, rt, 0.1 mmHg) then TMEDA (0.30 mL, 2 mmol) and THF (1.0 mL) were added at 0 °C. After 10 min, CuCN (0.090 g, 1.0 mmol) and β-bromostyrene (0.30 mL, 2.4 mmol) were added at 0 °C, then rinsed with THF (0.5 mL). After 8 h, Et₂O (5 mL) and aqueous NH₃ (10%, 2.0 mL) were added at 0 °C in turn. After 30 min, the aqueous layer was extracted five times with pentane. The combined organic extracts were washed with brine, and then the solvents were removed *in vacuo*. The crude product was treated with acetic acid (1.0 mL) and water (0.5 mL) at 90 °C for 6 h, and then water (4.5 mL) was added at ambient temperature. The aqueous layer was extracted five times with pentane. The combined organic extracts were washed sequentially with saturated aqueous sodium bicarbonate, 0.5-N HCl, and saturated aqueous sodium bicarbonate, then chromatographed on

silica gel (4 g, pentane and then 3% Et₂O in pentane) to obtain the corresponding ketone (0.191 g, 78% yield).; R_f = 0.50, 10% Et₂O in pentane; IR (neat) 3084 and 3061, 3026, 3076 (C=CH₂), 3025 (aromatic C–H), 1710 (vs, C=O), 1598 and 1495 (aromatic C=C), 1460, 1449, 1374, 1365, 967.5 (CH=CH), 747.6, 691.7; ¹H NMR (500 MHz, CDCl₃) δ 0.98 (s, 3H, CCH₃(CH₃), 0.99 (s, 3H, CCH₃(CH₃), 1.00 (t, J = 7.2 Hz, 3H, COCH₂CH₃), 1.04 (d, J = 7.2 Hz, 3H, COCHCH₃), 2.16 (dd, J = 7.5, 14.5 Hz, 1H, CCHHCH), 2.21 (dd, J = 7.5, 14.5 Hz, 1H, CCHHCH), 2.44 (q, J = 7.2 Hz, 2H, COCH₂CH₃), 2.55 (q, J = 7.2 Hz, 1H, COCHCH₃), 6.21 (dt, J = 7.5, 15.5 Hz, 1H, CH=CHPh), 6.37 (d, J = 15.5 Hz, 1H, CH=CHPh), 7.18–7.36 (m, 5H, aromatic CH); ¹³C NMR (125 MHz, CDCl₃) δ 7.5, 12.3, 24.5, 24.8, 36.6, 38.0, 44.0, 52.8, 125.9 (2C), 126.7, 127.0, 128.5 (2C), 132.6, 137.5, 215.8; EI-HRMS calcd for C₁₇H₂₄O [M]⁺ 244.1827, found 244.1862.

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