Supplementary Material (ESI) for Chemical Communications

Supporting Information

Unprecedented Reactivity in the Morita–Baylis–Hillman Reaction; Intramolecular α-Alkylation of Enones Using Saturated Alkyl Halides

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Experimental Section

All oxygen- or moisture-sensitive reactions were carried out in oven-dried glassware under a positive pressure of argon. Sensitive liquids and solutions were transferred by oven dried glass syringes, or canula and were introduced through rubber septa through which a positive pressure of argon was maintained. Concentration of solutions was accomplished using a Buchi rotary evaporator with a water aspirator followed by removal of residual solvents on a vacuum line held at 0.1–1 torr.

Unless otherwise noted, all reagents and solvents were used without additional purification. Exceptions include: chromatography grade hexane and ethyl acetate which was technical grade and was distilled before use; Et_2O (ether) and THF were distilled from sodium-benzophenone ketyl under argon; pyridine, triethylamine and *t*-BuOH were distilled from CaH_2 under argon atmosphere.

Analytical thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} glass plates. Visualization on TLC achieved by use of UV light (254 nm) or exposure to basic potassium permanganate solution, or acidic anisaldehyde, or 5% phosphomolybdic acid in ethanol stain followed by heating. Flash column chromatography was carried out using Merck 60, 230–400 mesh ASTM silica gel. Additional purification was achieved through use of a CombiFlash Graduate Medium Pressure LC unit.

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) was recorded on a Varian Fourier Transform 500 (500 MHz) spectrometer. Chemical shifts are reported in units, parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-*d* or in ppm relative to the singlet at 7.15 ppm for benzene-d_6. The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, are reported in Hertz (Hz).

Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on a Varian Fourier Transform 300 (75 MHz) and was fully decoupled by broad-band decoupling. Chemical shifts are reported in ppm with the centerline of the triplet for chloroform-*d* set at 77.0 ppm or for benzene-d_6 at 128.0 ppm.

Infrared (IR) spectra were recorded as thin films on sodium chloride plates using a Perkin-Elmer FT-IR Paragon 1000 Fourier Transform spectrometer with frequencies given in reciprocal centimeters (cm^{-1}).

Mass spectra were obtained on a Jeol model JMS600H mass spectrometer using either fast atom bombardment (FAB+) or electron impact (EI) (70 eV).

Elemental analyses were performed at Atlantic Microlab Inc. in Northcross, GA.

Compounds **18**[1], **20**[2], **19** and **21**[3] have been previously reported.

Experimental Procedures

Preparation of Enone Halides

*Synthesis of **1 – 5** General Procedure*

Alkylation

A solution of diethyl allylmalonate (9.9 mL, 0.05 mol) in dry THF (14 mL) was added dropwise at room temperature to a stirred suspension of sodium hydride (60% dispersion in mineral oil, 2.40 g, 0.06 mol) in dry THF (14 mL) over a period of 30 min. The mixture was stirred for 1 h at room temperature, and a solution of 1,2-dibromoethane (5.2 mL, 0.06 mol) in dry THF (14 mL) was added dropwise over 30 min following the procedure of Kuehne *et al.*[4] The mixture was stirred for 15 h at room temperature and then poured into water. The mixture was extracted with ether and washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield the alkylated malonate as a yellow oil. Excess 1,2-dibromoethane and unreacted diethyl allylmalonate were removed by Kugelrohr distillation to yield the bromoester as a colorless oil (14.76 g, 96%).

Cross-metathesis

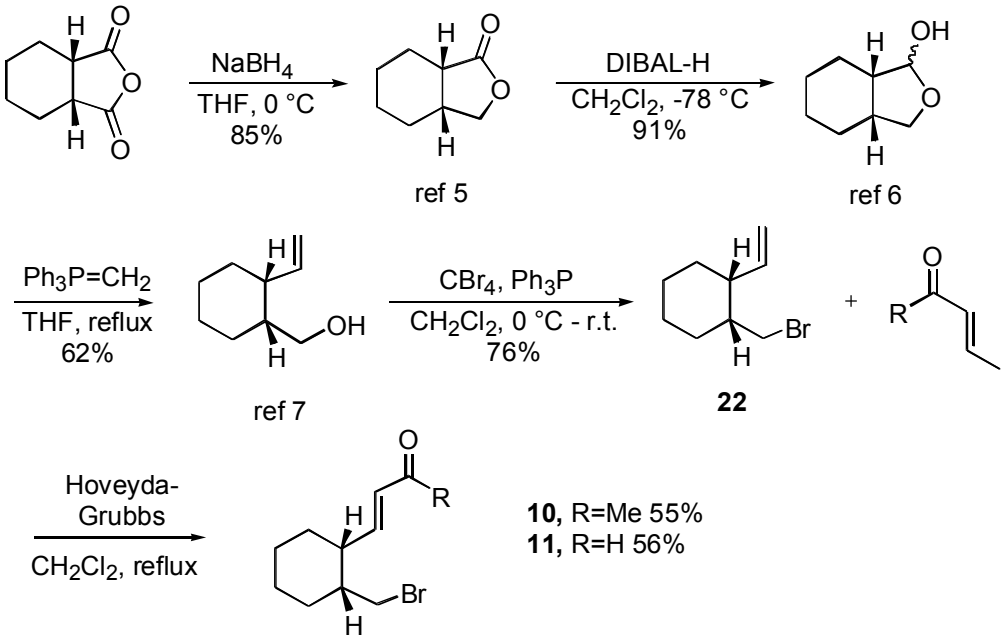
A flame-dried round-bottom flask equipped with reflux condenser was charged with alkylated malonate (2.14 g, 7 mmol), 3-penten-2-one (2.1 mL, 7 mmol), and dichloromethane (35 mL). Grubbs 2nd generation catalyst[5] (219 mg, 0.35 mmol) was subsequently added as a solid, producing a light brown/green solution which was refluxed for 12 h. The mixture was then plugged through a pad of silica gel and concentrated *in vacuo*. Purification of the residue *via* distillation under reduced pressure at 125 °C afforded the desired ester in 48% yield.

Iodination

A mixture containing excess sodium iodide (30 mg, 0.2 mmol) in acetone (0.8 mL) and 2-(2-chloro-ethyl)-2-(4-oxo-pent-2-enyl)-malonic acid diethyl ester, **4**, (50 mg, 0.16 mmol) was stirred under reflux for 24 h. The mixture was extracted with

dichloromethane, washed with water, $NaHSO_3$, brine, and then dried with Na_2SO_4. The solvent was removed under reduced pressure affording ester **5** as a thick oil (0.045 g, 71%).

*Synthesis of Compounds **10 – 11** General Procedure*



Sodium borohydride Reduction

To a suspension of sodium borohydride (1.19 g, 30.8 mmol) in THF (0.8 mL) at 0 °C was added cis-1-2-cyclohexane dicarboxylic anhydride (5.0 g, 30.8 mmol) and THF (30 mL) following the procedure of Fujiwara.[6] The mixture was stirred for 2 h followed by addition of HCl (6 M, 12 mL) and dilution with water (70 mL). Subsequent extraction with diethyl ether, drying with sodium sulfate, and concentration *in vacuo* afforded the lactone (3.65 g, 85%).

DIBAL-H Reduction

To a solution of hexahydro-isobenzofuran-1-one (3.65 g, 26.1 mmol) in dichloromethane (131 mL) at -78 °C was added DIBAL (31.3 mL, 31.3 mmol). After stirring for 2.5 h at -78 °C the mixture was quenched with methanol (0.188 mL), diluted with ether, and ground sodium sulfate decahydrate (8.41 g) was added following the procedure of Hamilton.[7] The mixture was allowed to slowly warm to room temperature and stirred overnight. The resulting suspension was plugged through a pad of Celite® and the filtrate was concentrated *in vacuo* yielding 2-hydroxymethyl-cyclohexanecarbaldehyde (3.38 g, 91%).

Wittig Olefination

A solution of methyltriphenylphosphonium bromide (30.36 g, 85 mmol) in THF (85 mL) in a heat dried round bottom flask was cooled to 0 °C. Then while stirring, *n*-butyllithium (53 mL, 1.6 M in hexane) was added slowly and the reaction mixture was allowed to warm to room temperature and stir for 0.5 h. Lactol was added to the reaction mixture slowly and refluxed for an additional 2 h following the procedure of Cho.[8] Upon completion, the reaction mixture was quenched with water and extracted with ethyl acetate. The concentrated residue was then plugged through a pad of silica gel, concentrated *in vacuo* and purified by column chromatography (hexane:ethylacetate, 5:1) to yield the desired alkene (2.26 g, 95%).

Bromination

A solution of alcohol (0.11 g, 0.79 mmol) and carbon tetrabromide (0.33 g, 1 mmol) in dichloromethane was cooled to 0 °C. Then, triphenylphosphine (0.29 g, 1.1 mmol) was added and the mixture was allowed to warm to room temperature. The mixture was stirred for 5 h and the solvent was removed *in vacuo*. The bromo alkene was purified by column chromatography, eluting with hexane:ethyl acetate (5:1). Bromide **22** was obtained as a clear oil (12 mg, 76%).

Cross-metathesis

A flame-dried round-bottom flask equipped with reflux condenser was charged with bromide **22** (1.21 g, 6 mmol), crotonaldehyde (0.49 mL, 6 mmol), and dichloromethane (30 mL). Hoveyda-Grubbs catalyst[5] (188 mg, 0.3 mmol) was subsequently added as a solid, producing a light brown/green solution which was refluxed for 12 h. The mixture was then plugged through a pad of silica gel and concentrated *in vacuo*. Yield after column chromatography (1.33 g, 56%).

*Synthesis of Compounds **14 – 17** General Procedure*

A flame-dried round-bottom flask equipped with reflux condenser was charged with 5-bromo-1-pentene (1.04 g, 7 mmol), 3-penten-2-one (2.1 mL, 7 mmol), and dichloromethane (35 mL). Grubbs 2nd generation catalyst[5] (219 mg, 0.35 mmol) was subsequently added as a solid, producing a light brown/green solution that was refluxed for 12 h. The mixture was then plugged through a pad of silica gel and concentrated *in vacuo*. Purification of the residue *via* distillation under reduced pressure at 125 °C afforded the desired ester in 75% yield.

Cyclization Reactions General Procedure

A flame-dried round bottom flask was charged with 2-(2-Bromo-ethyl)-2-(4-oxo-pent-2-enyl)-malonic acid diethyl ester, **1**, (49 mg, 0.14 mmol) and *tert*-butanol (0.28 mL). Tributylphosphine (0.04 mL, 0.14 mmol) was then added to the mixture and stirred until all starting material was consumed (TLC analysis). At this time, dichloromethane (0.07 mL), water (0.07 mL), potassium hydroxide (8 mg, 0.14 mmol), and

benzyltriethylammonium chloride (3 mg, 0.014 mmol) were added to the mixture that was allowed to stir until product was formed (TLC analysis). The mixture was extracted with DCM, washed with water, dried with sodium sulfate, plugged through a pad of silica gel, and concentrated *in vacuo* affording the cyclized product **6** (0.037 g, 99%).

Control Reaction

A flame-dried round bottom flask was charged with 1-iodohexane (0.15 mL g, 1 mmol) and *tert*-butanol (2 mL). Trimethylphosphine (0.09 mL, 1 mmol) was then added to reaction mixture which was stirred until all starting material was consumed by TLC analysis. At this time a solid precipitate was formed and the reaction mixture was concentrated *in vacuo* affording the phosphonium salt (151 mg, 94%).

Spectral Data

Bromide 1

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.64 (td, 1H, *J* = 7.93, 15.87 Hz, CH=C<u>H</u>CH_2), 6.12 (br d, 1H, *J* = 15.87 Hz, C<u>H</u>=$CHCH_2$), 4.22 (q, 4H, *J* = 7.1 Hz, C<u>H_2</u>CH_3) 3.36 (t, 2H, J = 8.1 Hz, C<u>H_2</u>CH_2C), 2.80 (dd, 2H, *J* = 1.2, 7.6 Hz, CH=CHC<u>H_2</u>) 2.46 (t, 2H, *J* = 8.1 Hz, CH_2C<u>H_2</u>C), 2.24 (s, 3H, CH_3), 1.27 (t, *J* = 7.1 Hz, C<u>H</u>CH_3)

^{13}C NMR (75 MHz, $CDCl_3$): 197.6, 169.5, 140.7, 134.6, 61.9, 57.2, 36.7, 36.5, 27.0, 26.5, 13.9

HRMS (FAB+) Calcd. For $C_{14}H_{21}O_5BrNa$ (M + Na): 371.0470, Found: 371.0467

FTIR (neat): 2981, 2938, 1701, 1677, 1630, 1446, 1366, 1300, 1253, 1194, 1176 cm^{-1}

Anal. Calcd. For $C_{14}H_{21}O_5Br$: C, 48.15; H, 6.06. Found: C, 48.18; H, 6.16.

Bromide 2

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.9 Hz, 2H, aromatic H), 7.57 (t, *J* = 7.4 Hz, 1H, aromatic H), 7.47 (t, *J* = 7.9 Hz, 2H, aromatic H) 6.94 (d, *J* = 15.2 Hz, 1H, C<u>H</u>=$CHCH_2$), 6.85 (td, *J* = 7.4, 15.2 Hz, 1H, CH=C<u>H</u>CH_2) 4.23 (q, *J* = 7.4 Hz, 4H, C<u>H_2</u>CH_3), 3.40 (t, *J* = 7.9, Hz, 2H, CCH_2C<u>H_2</u>), 2.92 (d, *J* = 7.4 Hz, 2H, CH=CHC<u>H_2</u>) 2.50 (t, *J* = 7.9 Hz, 2H, CC<u>H_2</u>CH_2) 1.27 (t, *J* = 7.4 Hz, 6H, CH_2C<u>H_3</u>)

^{13}C NMR (75 MHz, $CDCl_3$): 189.8, 169.6, 141.9, 137.3, 132.9, 129.6, 128.5, 128.4, 62.9, 57.4, 36.8, 36.7, 26.6, 14.0

HRMS (FAB+) Calcd. For $C_{19}H_{23}O_5NaBr$ (M+Na): 433.0626, Found: 433.0644.

FTIR (neat): 2980, 2937, 1730, 1674, 1624, 1447 cm^{-1}.

Anal. Calcd. For $C_{19}H_{23}O_5Br$: C, 55.49; H, 6.99. Found: C, 55.39; H, 6.95.

Bromide 3

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (m, 2H, aromatic), 7.20 (m, 3H, aromatic), 6.64 (td, *J* = 7.6, 15.6 Hz, 1H, CH=C<u>H</u>CH_2), 6.15 (d, *J* = 15.6 Hz, 1H, C<u>H</u>=$CHCH_2$), 4.21 (q, *J* = 7.1 Hz, 4H, $OC\underline{H}_2CH_3$), 3.35 (t, *J* = 8.0 Hz, 2H, $C\underline{H}_2Br$), 2.92 (m, 2H, $PhCH_2C\underline{H}_2$, or $PhC\underline{H}_2$), 2.85 (m, 2H, $PhCH_2C\underline{H}_2$, or $PhC\underline{H}_2$), 2.78 (dd, *J* = 1.2, 7.6 Hz, 2H, $CH=CHCH_2$), 2.43 (t, *J* = 8.0 Hz, 2H, $C\underline{H}_2CH_2Br$), 1.25 (t, *J* = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$).

^{13}C NMR (75 MHz, $CDCl_3$): 198.9, 169.9, 141.2, 140.2, 133.9, 128.8, 128.6, 126.4, 62.2, 57.5, 42.1, 37.0, 36.8, 30.1, 26.8, 14.3.

HRMS (FAB+) Calcd. For $C_{21}H_{27}O_5NaBr$ (M+Na): 461.0940, Found: 461.0945.

FTIR (neat): 2980, 1729, 1445, 1260 cm^{-1}.

Anal. Calcd. For $C_{21}H_{27}O_5Br$: C, 57.41; H, 6.19. Found: C, 57.03; H, 6.28.

Chloride 4

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.64 (td, *J* = 7.6, 15.9 Hz, 1H, CH=C<u>H</u>CH_2), 6.12 (br d, *J* = 15.9 Hz, 1H, C<u>H</u>=CHCH), 4.22 (q, *J* = 7.3 Hz, 4H, $C\underline{H}_2CH_3$), 3.54 (t, *J* = 7.6 Hz, 2H, $C\underline{H}_2CH_2C$), 2.82 (dd, *J* = 1.5, 7.6 Hz, 2H, $CH=CHC\underline{H}_2$) 2.38 (t, *J* = 7.6 Hz, 2H, $CH_2C\underline{H}_2C$), 2.24 (s, 3H, $C\underline{H}_3$), 1.27 (t, *J* = 7.1 Hz, 6H, $CH_2C\underline{H}_3$)

^{13}C NMR (75 MHz, $CDCl_3$): 197.5, 169.6, 140.7, 134.5, 61.8, 56.2, 39.4, 36.4, 36.2, 26.8, 13.8.

HRMS (FAB+) Calcd. For $C_{14}H_{21}O_5NaCl$ (M+Na): 327.0980, Found: 327.0975

FTIR (neat): 2982, 2908, 1731, 1700, 1678, 1632, 1446, 1254, 1180 cm^{-1}.

Anal. Calcd. For $C_{14}H_{21}O_5Cl$: C, 55.17; H, 6.95. Found: C, 54.94; H, 7.01.

Iodide 5

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.63 (dt, *J* = 7.6, 15.6 Hz, 1H, CH=C<u>H</u>CH_2), 6.11 (d, *J* = 15.6 Hz, 1H, C<u>H</u>=$CHCH_2$), 4.22 (q, *J* = 7.2, 4H, $OC\underline{H}_2CH_3$), 3.10 (m, 2H, $ICH_2C\underline{H}_2$ or $IC\underline{H}_2$), 2.77 (dd, *J* = 1.0, 7.6 Hz, 2H, $CH=CHC\underline{H}_2$), 2.48 (m, 2H, $ICH_2C\underline{H}_2$ or $IC\underline{H}_2$), 2.23 (s, 3H, -$C\underline{H}_3$), 1.26 (t, *J* = 7.2 Hz, 6H, $OCH_2C\underline{H}_3$).

^{13}C NMR (75 MHz, $CDCl_3$): 197.4, 169.2, 140.6, 134.3, 61.7, 58.6, 31.2, 36.0, 26.8, 13.8, -3.3.

HRMS (FAB+) Calcd. For $C_{14}H_{21}O_5INa$ (M+Na): 419.03312, Found: 419.0335.

FTIR (neat): 2980, 1729, 1676, 1253, 1188 cm^{-1}.

Anal. Calcd. For $C_{14}H_{21}O_5I$: C, 42.44; H, 5.35. Found: C, 42.41; H, 5.44.

Bromide 22

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.92 (ddd, *J* = 8.1, 10.3, 16.1 Hz, 1H, C<u>H</u>=CH_2), 5.14 (dd, *J* = 2.2, 16.1 Hz, 1H, C<u>H$_2$</u>=CHCH), 5.09 (dd, *J* = 2.2, 10.3 Hz, 1H, C<u>H$_2$</u>=CHCH), 3.26 (ABd, *J* = 7.3, 10.2 Hz, 1H, C<u>H$_2$</u>Br), 3.23 (ABd, *J* = 7.3, 9.5 Hz, 1H, C<u>H$_2$</u>Br), 2.60 (dddd , *J* = 3.7, 4.4, 4.4, 8.1 Hz, 1H, C<u>H</u>CH=CH_2), 1.89 (ddddd , *J* = 3.8, 3.8, 7.3, 7.3, 11.1 Hz, 1H, C<u>H</u>CH_2Br), 1.72 – 1.31 (m, 8H, cyclohexane ring).

^{13}C NMR (75 MHz, $CDCl_3$): 137.1, 116.4, 42.5, 41.8, 37.5, 30.8, 27.1, 25.0, 21.8.

FTIR (neat): 3073, 3002, 2927, 2855, 1636, 1448, 1234, 918 cm^{-1}.

Anal. Calcd. For $C_9H_{15}Br$: C, 53.22; H, 7.44. Found: C, 52.82; H, 7.73.

Bromide 10

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.90 (dd, *J* = 9.0, 15.9 Hz, 1H, CH=C<u>H</u>CH), 6.23 (dd, *J* = 0.7, 15.9 Hz, 1H, C<u>H</u>=CHCH), 3.25 (dd, *J* = 7.1, 10.3 Hz, 1H, BrC<u>H$_2$</u>) 3.14 (dd, *J* = 8.1, 10.3 Hz, 1H, BrC<u>H$_2$</u>), 2.80 (dddd, *J* = 4.2, 4.4, 4.4, 9.0 Hz, 1H, CH=CHC<u>H</u>) 2.26 (s, 3H, -CH_3), 2.01 (ddddd, *J* = 4.0, 4.2, 7.1, 8.1, 11.8 Hz, 1H, C<u>H</u>CH_2Br), 1.76-1.37 (m, 8H, cyclohexane ring). ^{13}C NMR (75 MHz, $CDCl_3$): 198.0, 146.2, 132.1, 42.5, 40.3, 36.5, 30.2, 27.5, 27.3, 24.7, 21.7..

HRMS (FAB+) Calcd. For $C_{11}H_{17}ONaBr$ (M+Na): 267.0352, Found: 267.0360.

FTIR (neat): 2929, 2857, 1696, 1674, 1622, 1450, 1254 cm^{-1}.

Anal. Calcd. For $C_{11}H_{17}OBr$: C, 53.89; H, 5.64. Found: C, 53.76; H, 5.95.

Bromide 11

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.54 (d, *J* = 7.8 Hz, 1H, aldehyde), 6.93 (dd, *J* = 8.6, 15.6 Hz, 1H, CHC<u>H</u>=CH), 6.25 (ddd, *J* = 1.0, 7.8, 15.6 Hz, 1H, CHCH=C<u>H</u>), 3.28 (dd, *J* = 7.1, 10.2 Hz, 1H, C<u>H$_2$</u>CHCH=C), 3.14 (dd, *J* = 8.1, 10.2, 1H, C<u>H$_2$</u>CHCH=C), 2.96 (dddd, *J* = 4.2, 4.4, 4.4, 8.6 Hz, 1H, C<u>H</u>CH=CH), 2.06 (ddddd, *J* = 4.0, 4.2, 7.1, 8.1, 12.0 Hz, 1H, BrCH_2C<u>H</u>) 1.79-1.65 (m, 4H, CH_2CH_2CHCH=), 1.54 (m, 2H, C<u>H$_2$</u>CHCH=), 1.41 (m, 2H, C<u>H$_2$</u>$CHCH_2$Br).

^{13}C NMR (75 MHz, $CDCl_3$): 193.3, 156.8, 133.9, 42.2, 40.4, 36.0, 29.6, 27.1, 24.4, 21.5.

HRMS (FAB+) Calcd. For $C_{10}H_{15}ONaBr$ (M+Na): 253.0204, Found: 253.0216.

FTIR (neat): 2930, 2857, 1689, 1450, 1137, 1117, 978 cm^{-1}.

Anal. Calcd. For $C_{10}H_{15}O$: C, 51.97; H, 6.54. Found: C, 51.75; H, 6.41.

Enone 6

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (tt, *J* = 2.2, 3.9 Hz, 1H, C<u>H</u>CH_2), 4.187 (ABq, *J* = 7.3, 7.3 Hz, 2H, C<u>H</u>HCH_3), 4.182 (ABq, *J* = 7.3, 7.3 Hz, 2H, CH<u>H</u>CH_3) 2.78 (td, *J* = 2.2, 3.9 Hz, 2H, C<u>H$_2$</u>CH), 2.29 (m, 2H, C<u>H$_2$</u>C=) 2.28 (s, 3H, CH_3), 2.16 (t, *J* = 6.4, Hz, 2H, C<u>H$_2$</u>CH_2C=), 1.24 (t, *J* = 7.3 Hz, 6H, C<u>H$_3$</u>CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): 198.1, 170.9, 138.2, 137.1, 61.5, 52.4, 31.3, 26.9, 25.1, 20.1, 13.9.

HRMS (FAB+) Calcd. For $C_{14}H_{20}O_5Na$ (M+Na): 291.1211, Found: 291.1208.

FTIR (neat): 2980, 1731, 1668, 1258, 1175, 1068, 1021 cm^{-1}.

Anal. Calcd. For $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.50; H, 7.65.

Hexyltrimethyl-phosphonium iodide:

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.48 (m, 2H, PC<u>H$_2$</u>), 2.21 (d, *J* = 13.9 Hz, 9H, PC<u>H$_3$</u>), 1.58 (m, 2H, PCH_2C<u>H$_2$</u>), 1.52 (m, 2H, PCH_2CH_2C<u>H$_2$</u>), 1.33 (m, 4H, C<u>H$_2$</u>C<u>H$_2$</u>CH_3), 0.89 (t, *J* = 6.6 Hz, 3H, CH_2C<u>H$_3$</u>).

^{13}C NMR (75 MHz, $CDCl_3$): 30.8, 29.9, 24.0, 23.3, 22.0, 21.3, 13.7, 9.6, 8.8.

HRMS (FAB+) Calcd. For $C_9H_{22}PNa$ (M+Na): 161.1462, Found: 161.1459.

FTIR (neat): 2959, 1298, 985, 776 cm^{-1}.

Anal. Calcd. For $C_9H_{22}PI$: C, 37.51; H, 7.70. Found: C, 37.40; H, 7.79.

Enone 7

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (m, 2H, aromatic), 7.53 (m, 1H, aromatic), 7.41 (m, 2H, aromatic), 6.53 (br s, 1H, CH_2C<u>H</u>C), 4.24 (q, *J* = 7.1 Hz, 4H, C<u>H$_2$</u>CH_3), 2.79 (m, 2H, C<u>H$_2$</u>CH), 2.50 (m, 2H, C<u>H$_2$</u>C=), 2.27 (t, *J* = 6.4 Hz, 2H, C<u>H$_2$</u>CH_2C=), 1.27 (t, *J* = 7.1 Hz, 6H, C<u>H$_3$</u>CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): 197.0, 171.0, 139.8, 138.1, 137.2, 131.6, 129.2, 128.1, 61.6, 52.6, 31.4, 27.2, 21.2, 14.0

HRMS (FAB+) Calcd. For $C_{19}H_{22}O_5Na$ (M+Na): 353.1358, Found: 353.1365.

FTIR (neat): 1729, 1245, 708 cm^{-1}.

Anal. Calcd. For $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.06; H, 6.55.

Enone 8

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (m, 3H, aromatic), 7.18 (m, 2H, aromatic), 6.82 (tt, 1H, *J* = 1.9, 3.9 Hz, $CH_2C\underline{H}C$), 4.187 (ABq, *J* =7.1, 7.1 Hz, 2H, $CH\underline{H}CH_3$), 4.182 (ABq, *J* = 7.1, 7.1 Hz, 2H, $C\underline{H}HCH_3$), 2.96 (m, 2H, $ArCH_2C\underline{H}_2$), 2.91 (m, 2H, $ArC\underline{H}_2CH_2$), 2.75 (td, *J* = 2.2, 3.9 Hz, 2H, $C\underline{H}_2CH$), 2.31 (dtt, *J* = 1.9, 2.2, 6.4 Hz, 2H, $C\underline{H}_2CCH$), 2.15 (t, *J* = 6.4 Hz, 2H, $C\underline{H}_2CH_2CCH$), 1.24 (t, *J* = 7.1 Hz, 6H, $C\underline{H}_3CH_2$).

^{13}C NMR (75 MHz, $CDCl_3$): 199.3, 171.0, 141.4, 137.8, 136.2, 128.4, 128.4, 126.0, 61.6, 52.5, 39.0, 31.3, 30.3, 27.1, 20.4, 14.0.

HRMS (FAB+) Calcd. For $C_{21}H_{26}O_5Na$ (M+Na): 381.1693, Found: 381.1678.

FTIR (neat): 2981, 1731, 1668, 1252 cm^{-1}.

Anal. Calcd. For $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.44; H, 7.21.

Enone 12

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.67 (br s, 1H, C=CH), 2.78 (m, 1H, $C\underline{H}CH=C$), 2.49 (tdd, *J* = 2.0, 8.6, 16.9 Hz, 1H, $C\underline{H}HC$), 2.30 (s, 3H, CH_3), 2.28 (m, 1H, $CH\underline{H}C$), 1.67 (dddd, *J* = 6.6, 6.6, 6.6, 13.0 Hz, 1H, $C\underline{H}_2CHCH=C$), 1.55-1.00 (m, 8H, cyclohexane ring).

^{13}C NMR (75 MHz, $CDCl_3$): 197.3, 149.4, 145.2, 45.3, 37.5, 35.4, 27.6, 27.5, 26.3, 23.3, 22.9.

FTIR (neat): 2925, 2852, 1666, 1604, 1449, 1371 cm^{-1}.

Anal. Calcd. For $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.82; H, 9.81.

Enone 13

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (s, 1H, CHO); 6.82 (br s, 1H, $C=C\underline{H}$); 2.82 (m, 1H, $C\underline{H}CHC$); 2.48 (br dd, *J* = 6.8, 15.5 Hz, 1H, $C\underline{H}HC$); 2.34 (dddt, *J* = 6.6, 6.6, 6.6, 6.8 Hz, 1H, $C\underline{H}CH_2C$); 2.26 (br dd, *J* = 5.3, 15.5 Hz, 1H, $CH\underline{H}C$); 1.71 (dddd, *J* = 5.8, 5.8, 5.8, 11.6 Hz, 1H, $C\underline{H}_2CHCHC$); 1.56-1.24 (m, 7H, cyclohexane ring).

^{13}C NMR (75 MHz, $CDCl_3$): 190.4, 158.0, 146.9, 45.2, 37.7, 33.3, 27.6, 27.3, 23.3, 22.8.

HRMS (FAB+) calc. For $C_{10}H_{14}ONa$ (M+Na): 150.1042, Found: 150.1045.

FTIR (neat): 2926, 2853, 1678, 1449 cm^{-1}.

Anal. Calcd. For $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.78; H, 9.34.

Bromide 15

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (m, 1H, aromatic H), 7.56 (m, 2H, aromatic H), 7.47 (m, 2H, aromatic H), 7.04 (td, *J* = 6.8, 15.6 Hz, 1H, CH=C<u>H</u>CH_2), 6.90 (td, *J* = 1.2, 15.6 Hz, 1H, C<u>H</u>=$CHCH_2$), 3.44 (t, *J* = 6.6 Hz, 2H, C<u>H</u>$_2CH_2CH_2CH_2CH$=CH), 2.37 (ddt, *J* = 1.2, 6.8, 7.3 Hz, 2H, C<u>H</u>$_2$CH=CH), 1.94 (m, 2H, C<u>H</u>$_2CH_2CH_2CH$=CH), 1.71 (m, 2H, C<u>H</u>$_2CH_2$CH=CH).

^{13}C NMR (75 MHz, $CDCl_3$): 190.5, 148.7, 137.8, 132.6, 128.6, 128.4, 126.2, 33.3, 32.1, 31.7, 26.6.

HRMS (FAB+) Calcd. For $C_{13}H_{15}OBrNa$ (M+Na): 289.0204, Found: 289.0204.

FTIR (neat): 2936, 1670, 1621, 1598, 1447, 1346, 1283, 693 cm^{-1}.

Anal. Calcd. For $C_{13}H_{15}OBr$: C, 58.44; H, 5.66. Found: C, 58.89; H, 5.66.

Bromide 17

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (m, 2H, aromatic H), 7.57 (m, 1H, aromatic H), 7.48 (m, 2H, aromatic H), 7.02 (td, *J* = 6.6, 15.4 Hz, 1H, CH=C<u>H</u>CH_2), 6.96 (d, *J* = 15.4 Hz, 1H, C<u>H</u>=$CHCH_2$), 3.46 (t, *J* = 6.6 Hz, 2H, C<u>H</u>$_2CH_2CH_2$CH=CH), 2.51 (td, *J* = 6.6, 7.3 Hz, 2H, C<u>H</u>$_2$CH=CH), 2.10 (tt, *J* = 6.6, 6.6 Hz, 2H, C<u>H</u>$_2CH_2$CH=CH).

^{13}C NMR (75 MHz, $CDCl_3$): 190.2, 147.0, 132.7, 128.5, 128.4, 128.1, 126.8, 32.6, 30.9, 30.8.

HRMS (FAB+) Calcd. For $C_{12}H_{13}OBrNa$ (M+Na): 275.0048, Found: 275.0048.

FTIR (neat): 2935, 1670, 1622, 1447, 1288, 1220, 972, 693 cm^{-1}.

Anal. Calcd. For $C_{12}H_{13}OBr$: C, 56.94; H, 5.18. Found: C, 56.69; H, 5.11.

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