**Tandem Nucleophilic Addition/Fragmentation Reactions and Synthetic Versatility
of Vinylogous Acyl Triflates**

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Supporting Information

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General information

^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 (300 MHz) spectrometer using CDCl_3 as a solvent. The chemical shifts (δ) are reported in parts per million (ppm) relative to the chloroform peak (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR). The coupling constants (J) are reported in Hertz (Hz). IR spectra were recorded on a Perkin-Elmer FTIR Paragon 1000 spectrometer using NaCl discs. Mass spectra were recorded on a JEOL JMS600H spectrometer. All chemicals were used as received unless otherwise noted. Tetrahydrofuran (THF) and toluene were dried through a solvent purification system packed with alumina and molecular sieves under Ar atmosphere. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone (DMPU) was distilled from CaH_2 under reduced pressure. The Grignard solutions were titrated with iodine dissolved in ether. The purifications of the compounds were performed by flash chromatography using silica gel F-254 (230-499 mesh particle size).

Experimental procedures

Representative procedure for the preparation of triflates (1).¹ To a CH_2Cl_2 solution (60 mL) of 2-methyl-1,3-cyclohexanedione (1.26 g, 10.0 mmol) and pyridine (1.6 mL, 20 mmol) was added TiF_4 (2.0 mL, 12 mmol) slowly at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred for another 10 min at $-78\text{ }^\circ\text{C}$ and warmed to $0\text{ }^\circ\text{C}$. After the consumption of the starting diketone, the mixture was acidified with HCl (1 N, aqueous) and extracted with ether. The organic layer was washed with aqueous Na_2CO_3 solution and water, dried over Na_2SO_4 , and evaporated. The residue was purified by chromatography on a silica gel column (hexanes/AcOEt = 10/1 to 5/1) to yield 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (100%, 2.60 g).

Typical procedure for the reactions between triflates and aryl Grignard reagents (Table 1).^{1a} Phenylmagnesium bromide (0.53 mL, 0.50 mmol; 0.95 M in THF) was added dropwise to a THF solution (2 mL) of 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (142 mg, 0.55 mmol) at $0\text{ }^\circ\text{C}$ under Ar atmosphere. The mixture was stirred at $0\text{ }^\circ\text{C}$ for 10 min and then at room temperature for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and

concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 10/1) to give 1-phenyl-5-heptynone (**2a**) in 83% yield (77 mg). The second run was carried out following the same procedure as above, using 1 mmol of phenylmagnesium bromide (1.05 mL), 1.1 mmol of 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (248 mg), and 4 mL of THF. 1-Phenyl-5-heptynone was obtained in 76% yield (141 mg).

Typical procedure for the reactions between triflates and phenyllithium reagent (Table 1).^{1a} Phenyllithium (0.28 mL, 0.50 mmol; 1.8 M in Bu₂O) was added dropwise to a THF solution (2 mL) of 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (142 mg, 0.55 mmol) at -78 °C under Ar atmosphere. The mixture was stirred at -78 °C for 10 min, at 0 °C for 10 min and then at room temperature for 30 min. Saturated aqueous NH₄Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO₄, filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 10/1) to give 1-phenyl-5-heptynone (**2a**) in 91% yield (85 mg). The second run was carried out following the same procedure as above, using 1.0 mmol of phenyllithium (0.56 mL), 1.10 mmol of 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (248 mg), and 4 mL of THF. 1-Phenyl-5-heptynone was obtained in 95% yield (177 mg).

Procedure for the reactions between triflates and phenyllithium reagent (Table 2).^{1a} Phenyllithium (0.28 mL, 0.50 mmol; 1.8 M in Bu₂O) was added dropwise to a THF solution (2 mL) of 3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1b**) (134 mg, 0.55 mmol) at -78 °C under Ar atmosphere. The mixture was stirred at -78 °C for 10 min, at 0 °C for 10 min, at room temperature for 30 min, and then at 60 °C for 30 min. Saturated aqueous NH₄Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO₄, filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 10/1) to give 1-phenyl-5-hexynone (**2g**) in 65% yield (55 mg).

Typical procedure for the reactions between triflates and alkyllithium reagents (Table 3 and 4). To a toluene solution (2 mL) of *n*-BuLi (0.20 mL, 0.50 mmol; 2.5 M solution in hexanes) was added 2-methyl-3-(trifluoromethanesulfonyloxy)-2-

cyclohexenone (**1a**) (102 μ L, 0.55 mmol) at -78 $^{\circ}$ C under Ar atmosphere. The mixture was stirred at -78 $^{\circ}$ C for 10 min, at 0 $^{\circ}$ C for 10 min, and then at rt for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 20/1) to give 9-undecyn-5-one (**2k**) in 76% yield (63 mg).

Typical procedure for the reactions between triflates and alkyl Grignard reagents (Table 3). To a toluene solution (2 mL) of *n*-BuMgCl (0.25 mL, 0.50 mmol; 2.0 M solution in ether) was added 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (142 μ L, 0.55 mmol) at -78 $^{\circ}$ C under Ar atmosphere. The mixture was stirred at -78 $^{\circ}$ C for 10 min, at 0 $^{\circ}$ C for 10 min, at rt for 30 min, and then at 60 $^{\circ}$ C for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 20/1) to give 9-undecyn-5-one (**2k**) in 63% yield (52 mg).

Typical procedure for the reactions between triflates and alkynyl and vinyl lithium reagents (Table 5). To a THF solution (2 mL) of phenylacetylene (70 μ L, 0.60 mmol) was added *n*-BuLi (0.20 mL, 0.50 mmol; 2.5 M solution in hexanes) at -78 $^{\circ}$ C and stirred for 30 min at the same temperature under Ar atmosphere. Then, 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (102 μ L, 0.55 mmol) was added to the mixture at -78 $^{\circ}$ C. The mixture was stirred at -78 $^{\circ}$ C for 10 min, at 0 $^{\circ}$ C for 10 min, and then at rt for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 20/1) to give 1-phenyl-1,7-nonadiyn-3-one (**2v**) in 56% yield (59 mg).

Vinyl lithium species was generated by treating 3,4-dihydro-2*H*-pyran with *t*-BuLi at -78 $^{\circ}$ C for 10 min and 0 $^{\circ}$ C for 20 min in THF under Ar atmosphere.

Procedure for the synthesis of alkynols (eq 8). To a toluene solution (2 mL) of *n*-BuLi (0.44 mL, 1.1 mmol; 2.5 M solution in hexanes) was added 2-methyl-3-

(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (129 mg, 0.50 mmol) at $-78\text{ }^{\circ}\text{C}$ under Ar atmosphere. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 10 min, at $0\text{ }^{\circ}\text{C}$ for 10 min, and then at rt for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 4/1) to give 5-butyl-9-undecyn-5-ol (**7b**) in 77% yield (86 mg).

Procedure for the synthesis of cyclohexenone derivatives (eq 9). To a toluene solution (2 mL) of PhMgBr (0.18 mL, 0.55 mmol; 3.0 M solution in ether) was added 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (129 mg, 0.50 mmol) at $-78\text{ }^{\circ}\text{C}$ under Ar atmosphere. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 10 min and then at $0\text{ }^{\circ}\text{C}$ for 10 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 80/1 to 4/1) to give 2-methyl-3-phenyl-2-cyclohexen-1-one (**6a**) in 91% yield (84 mg).

Procedure for the synthesis of substituted triflates (eq 10). To a THF solution (2 mL) of 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (129 mg, 0.50 mmol) was added LiHMDS (0.52 mL, 0.52 mmol; 1.0 M solution in THF) was added at $-78\text{ }^{\circ}\text{C}$ under Ar atmosphere. After stirring at $-78\text{ }^{\circ}\text{C}$ for 25 min, DMPU (1 mL) was added and stirred at $-78\text{ }^{\circ}\text{C}$ for another 5 min. Then, to the reaction mixture was added allyl iodide (91 μL , 1.0 mmol), and the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then at $0\text{ }^{\circ}\text{C}$ for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 20/1) to give 6-allyl-2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexen-1-one (**8a**) in 59% yield (88 mg).

Typical procedure for the Claisen-type condensation of triflates with lithium enolates and their analogues (Tables 6 and 7).² To a THF solution (2 mL) of acetophenone (0.14 mL, 1.2 mmol) was added LiHMDS (1.1 mL, 1.1 mmol; 1.0 M solution in THF) at $-78\text{ }^{\circ}\text{C}$ under Ar atmosphere. After stirred for 30 min at $-78\text{ }^{\circ}\text{C}$, 2-

methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (93 μ L, 0.50 mmol) was added to the resultant solution. The mixture was stirred at -78 °C for 10 min, at 0 °C for 10 min, at rt for 30 min, and then at 60 °C for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/ether = 100/1 to 20/1) to give 1-phenyl-1,3-dioxo-7-nonyne (**3a**) in 85% yield (96 mg).

Typical procedure for the reductive ring opening reactions of triflates using LiBHEt_3 (Table 9). To a THF solution (2.0 mL) of LiBHEt_3 (1.1 mL, 1.1 mmol; 1.0 M in THF) was added 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (93 μ L, 0.5 mmol) under Ar atmosphere. The mixture was stirred at -78 °C for 10 min, at 0 °C for 10 min, and then at rt for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/AcOEt = 100/1 to 3/1) to give 5-heptyn-1-ol (**4a**) in 73% yield (40 mg).

Procedure for the synthesis of cyclohexenol **9a and the reaction with LiBHEt_3 (eq 11).** To a THF solution (2.0 mL) of 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (93 μ L, 0.50 mmol) was added DIBALH (1.1 mL, 0.55 mmol; 1.0 M in heptane) under Ar atmosphere. The mixture was stirred at -78 °C for 10 min, at 0 °C for 10 min, at rt for 30 min, and then at 60 °C for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether after the treatment with aqueous NaOH solution. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/AcOEt = 10/1 to 2/1) to give 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexen-1-ol (**9a**) in 99% yield (128 mg). To a THF solution (2.0 mL) of LiBHEt_3 (1.1 mL, 1.1 mmol; 1.0 M in THF) was added **9a** (130 μ g, 0.5 mmol) under Ar atmosphere. The mixture was stirred at -78 °C for 10 min, at 0 °C for 10 min, and then at rt for 30 min. Saturated aqueous NH_4Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , filtered, and concentrated. The residue was

purified by chromatography on a silica gel column (hexanes/AcOEt = 100/1 to 4/1) to give 5-heptyn-1-ol (**4a**) in 70% yield (39 mg).

Typical procedure for the amidative ring opening reactions of triflates using lithium amides (Tables 10 and 11). To a THF solution (2.0 mL) of PrNH₂ (0.10 mL, 1.2 mmol) was added *n*-BuLi (0.44 mL, 1.1 mmol; 2.5 M solution in hexanes) at –78 °C and stirred for 30 min at the same temperature under Ar atmosphere. Then, 2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexenone (**1a**) (93 µL, 0.50 mmol) was added to the mixture at –78 °C. The mixture was stirred at –78 °C for 10 min, at 0 °C for 10 min, at rt for 30 min, and then at 60 °C for 30 min. Saturated aqueous NH₄Cl solution was added to quench the reaction and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO₄, filtered, and concentrated. The residue was purified by chromatography on a silica gel column (hexanes/AcOEt = 10/1 to 1/1) to give *N*-propyl-5-heptynamide (**5a**) in 91% yield (76 mg).

Analytical data

Compounds 2a–j, see reference 1a for the data.

9-undecyn-5-one (2k): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.3$ Hz), 1.30 (2H, sextet, $J = 7.3$ Hz), 1.55 (2H, quintet, $J = 7.3$ Hz), 1.73 (2H, quintet, $J = 7.3$ Hz), 1.77 (3H, t, $J = 2.5$ Hz), 2.15 (2H, tq, $J = 7.3, 2.5$ Hz), 2.40 (2H, t, $J = 7.3$ Hz), 2.51 (2H, t, $J = 7.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 13.8, 18.1, 22.3, 22.8, 25.9, 41.3, 42.6, 76.2, 78.2, 210.8; IR (neat) 1713, 1454, 1410, 1371, 1216, 1126 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$ (M^+) 166.1357. Found 166.1357.

2-methyl-7-nonyn-3-one (2l): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.10 (6H, d, $J = 6.9$ Hz), 1.73 (2H, quintet, $J = 7.0$ Hz), 1.77 (3H, t, $J = 2.5$ Hz), 2.15 (2H, tq, $J = 7.0, 2.5$ Hz), 2.56 (2H, t, $J = 7.0$ Hz), 2.61 (1H, septet, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 18.1, 18.2, 22.8, 38.9, 40.9, 76.1, 78.3, 214.3; IR (neat) 1708, 1466, 1382, 1365, 1214, 1084, 1020 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{10}\text{H}_{17}\text{O}$ ($[\text{M}+\text{H}]^+$) 153.1279. Found 153.1282.

2,2-dimethyl-7-nonyn-3-one (2m): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.14 (9H, s), 1.72 (2H, quintet, $J = 7.0$ Hz), 1.77 (3H, t, $J = 2.4$ Hz), 2.15 (2H, tq, $J = 7.0, 2.4$ Hz), 2.60 (2H, t, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 18.0, 23.0, 26.3, 35.1, 44.1, 76.0, 78.4, 215.5; IR (neat) 1697, 1615, 1479, 1365, 1222, 1088 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{11}\text{H}_{19}\text{O}$ ($[\text{M}+\text{H}]^+$) 167.1436. Found 167.1435.

6-octyn-2-one (2n) [24395-06-0]: colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.73 (2H, apparent quintet, $J = 7.0$ Hz), 1.77 (3H, t, $J = 2.4$ Hz), 2.15 (3H, s), 2.12–2.19 (2H, m), 2.55 (2H, t, $J = 8.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 18.0, 22.8, 29.9, 42.2, 76.2.

1-(2-pyridyl)-6-octyn-2-one (2o): yellow oil; keto:enol = 20:1; keto-form: ^1H NMR (300 MHz, CDCl_3) δ 1.74 (2H, quintet, $J = 7.0$ Hz), 1.75 (3H, t, $J = 2.4$ Hz), 2.14 (2H, tq, $J = 7.0, 2.4$ Hz), 2.66 (2H, t, $J = 7.0$ Hz), 3.92 (2H, s), 7.17 (1H, m), 7.22 (1H, m), 7.65 (1H, m), 8.55 (1H, m); assignable peaks of enol-form: δ 1.82 (2H, quintet, $J = 7.4$ Hz), 2.21 (2H, tq, $J = 7.4, 2.4$ Hz), 2.36 (2H, t, $J = 7.4$ Hz), 5.33 (2H, s), 6.80–6.93 (2H, m), 7.54 (1H, m), 8.20 (1H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 17.9, 22.6, 41.3, 52.3, 76.2, 78.1, 121.8, 124.0, 136.5, 149.4, 154.7, 206.9; IR (neat) 3410 (br), 1714, 1650, 1595, 1474, 1435, 1149 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$ (M^+) 201.1153. Found 201.1145.

1-(2-methyl-[1,3]dithian-2-yl)-5-heptyn-1-one (2p): colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.67 (3H, s), 1.77 (3H, t, $J = 2.5$ Hz), 1.78 (2H, quintet, $J = 7.2$ Hz), 1.84 (1H, m), 2.09 (1H, m), 2.17 (2H, tq, $J = 7.2, 2.5$ Hz), 2.61 (2H, ddd, $J = 13.5, 3.5, 3.5$ Hz), 2.79 (2H, t, $J = 7.2$ Hz), 3.10 (2H, ddd, $J = 13.5, 13.5, 3.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 18.0, 23.8, 24.0, 24.7, 27.9, 34.3, 54.5, 76.2, 78.1, 203.7; IR (neat) 1713, 1434, 1372, 1277, 1072, 1000 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{18}\text{OS}_2$ (M^+) 242.0799. Found 242.0789.

1-phenyl-6-octyn-2-one (2q): colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.71 (2H, quintet, $J = 7.1$ Hz), 1.74 (3H, t, $J = 2.4$ Hz), 2.12 (2H, tq, $J = 7.1, 2.4$ Hz), 2.57 (2H, t, $J = 7.1$ Hz), 3.70 (2H, s), 7.19-7.22 (2H, m), 7.28-7.35 (3H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 17.9, 22.8, 40.5, 50.1, 76.2, 78.1, 126.9, 128.6, 129.3, 134.2, 207.9; IR (neat) 1713, 1602, 1495, 1453, 1367, 1093, 1031, 734, 700 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{14}\text{H}_{17}\text{O}$ ($[\text{M}+\text{H}]^+$) 201.1279. Found 201.1276.

9-decyn-5-one (2r) [55183-18-1]: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.4$ Hz), 1.31 (2H, sextet, $J = 7.4$ Hz), 1.55 (2H, quintet, $J = 7.4$ Hz), 1.78 (2H, quintet, $J = 7.1$ Hz), 1.95 (1H, t, $J = 2.5$ Hz), 2.22 (2H, td, $J = 7.1, 2.5$ Hz), 2.41 (2H, t, $J = 7.4$ Hz), 2.55 (2H, t, $J = 7.1$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 17.7, 22.1, 22.2, 25.9, 40.9, 42.6, 68.9, 83.5, 210.5.

6,6-dimethyl-9-decyn-5-one (2s): colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.4$ Hz), 1.12 (6H, s), 1.29 (2H, sextet, $J = 7.4$ Hz), 1.53 (2H, quintet, $J = 7.4$ Hz), 1.80 (2H, virtual t, $J = 8.1$ Hz), 1.93 (1H, t, $J = 2.7$ Hz), 2.07 (2H, td, $J = 8.1, 2.7$ Hz), 2.46 (2H, t, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 14.2, 22.3, 24.1, 25.8, 36.5, 38.4, 47.1, 68.4, 84.1, 214.8; IR (neat) 3311, 2118, 1703, 1470, 1367, 1118, 1050 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{12}\text{H}_{20}\text{ONa}$ ($[\text{M}+\text{Na}]^+$) 203.1412. Found 203.1418.

9-dodecyn-5-one (2t): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.0$ Hz), 1.30 (2H, sextet, $J = 7.0$ Hz), 1.47-1.60 (4H, m), 1.69 (2H, quintet, $J = 7.0$ Hz), 1.94 (1H, t, $J = 2.4$ Hz), 2.20 (2H, td, $J = 7.0, 2.4$ Hz), 2.39 (2H, t, $J = 7.0$ Hz), 2.42 (2H, t, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 13.8, 18.2, 22.3, 22.8, 25.9, 27.9, 42.0, 42.5, 68.4, 84.0, 210.9; IR (neat) 3309, 2117, 1712, 1666, 1460, 1378, 1126, 1091, 1035 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{11}\text{H}_{18}\text{ONa}$ ($[\text{M}+\text{Na}]^+$) 189.1255 Found 189.1248.

8-decyn-5-one (2u): yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.4$ Hz), 1.31 (2H, sextet, $J = 7.4$ Hz), 1.56 (2H, quintet, $J = 7.4$ Hz), 1.75 (3H, t, $J = 2.4$ Hz), 2.38 (2H, tq, $J = 7.4, 2.4$ Hz), 2.41 (2H, t, $J = 7.4$ Hz), 2.59 (2H, t, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 13.3, 13.8, 22.3, 25.8, 41.8, 42.5, 75.9, 77.7, 209.4; IR (neat) 1731, 1455, 1378, 1213, 1140 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{10}\text{H}_{16}\text{O}$ (M^+) 152.1201. Found 152.1200.

1-phenyl-1,7-nonadiyn-3-one (2v): viscous yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.78 (3H, t, $J = 2.5$ Hz), 1.90 (2H, quintet, $J = 7.2$ Hz), 2.24 (2H, tq, $J = 7.2, 2.5$ Hz), 2.80 (2H, t, $J = 7.2$ Hz), 7.36-7.48 (3H, m), 7.57 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 18.0, 23.3, 44.3, 76.6, 77.9, 87.7, 90.6, 119.9, 128.5, 130.6, 133.0, 187.4; IR (neat) 2200, 1667, 1489, 1443, 1096, 1040, 758, 689 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{15}\text{H}_{14}\text{ONa}$ ($[\text{M}+\text{Na}]^+$) 233.0942. Found 233.0945.

1-trimethylsilyl-1,7-nonadiyn-3-one (2w): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.24 (9H, s), 1.77 (3H, t, $J = 2.4$ Hz), 1.82 (2H, quintet, $J = 7.1$ Hz), 2.18 (2H, tq, $J = 7.1, 2.4$ Hz), 2.68 (2H, t, $J = 7.1$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ -0.8, 3.3, 17.9, 23.0, 44.0, 76.5, 77.8, 97.6, 101.9, 187.1; IR (neat) 2149, 2092, 1676, 1252, 1111, 846, 765 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{12}\text{H}_{19}\text{OSi}$ ($[\text{M}+\text{H}]^+$) 207.1205. Found 207.1208.

1-(5,6-dihydro-4H-pyran-2-yl)-5-heptynone (2x): colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.73-1.80 (2H, m), 1.77 (3H, t, $J = 2.4$ Hz), 1.80-1.88 (2H, quintet, $J = 5.1$ Hz), 2.14-2.23 (4H, m), 2.71 (2H, t, $J = 7.3$ Hz), 4.08 (2H, t, $J = 5.1$ Hz), 5.98 (1H, t, $J = 4.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 18.1, 20.5, 21.4, 23.1, 36.1, 66.0, 76.0, 78.3, 109.5, 151.0, 196.2; IR (neat) 1698, 1632, 1445, 1287, 1057, 916, 863 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{12}\text{H}_{17}\text{O}_2$ ($[\text{M}+\text{H}]^+$) 193.1228. Found 193.1226.

Compounds 3a–e, see reference 2 for the data.

1-cyano-6-octyn-2-one (3f): yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.77 (3H, t, $J = 2.5$ Hz), 1.80 (2H, apparent quintet, $J = 6.9$ Hz), 2.21 (2H, tq, $J = 6.6, 2.5$ Hz), 2.75 (2H, t, $J = 7.0$ Hz), 3.48 (2H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 17.8, 22.4, 32.0, 40.7, 77.1, 77.5, 113.6, 197.1; IR (neat) 2260, 1728, 1618, 1372, 1087 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_9\text{H}_{11}\text{ON}$ (M^+) 149.0840. Found 149.0842.

5-heptyn-1-ol (4a) [58944-42-6]: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.31 (1H, br s), 1.50-1.60 (2H, m), 1.63-1.71 (2H, m), 1.77 (3H, t, $J = 2.5$ Hz), 2.17 (2H, dt, J

= 6.9, 2.5 Hz), 3.67 (2H, br t, $J = 6.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 18.4, 25.2, 31.7, 62.4, 75.7, 78.8.

6-phenyl-5-hexyn-1-ol (4b) [69936-53-4]: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.31 (1H, br s), 1.64-1.81 (4H, m), 2.46 (2H, t, $J = 6.6$ Hz), 3.71 (2H, br t, $J = 5.9$ Hz), 7.26 (3H, m), 7.39 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 19.1, 24.9, 31.8, 62.3, 80.8, 89.8, 123.8, 127.5, 128.1, 131.4.

2,2-dimethyl-5-hexyn-1-ol (4d): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.89 (6H, s), 1.49 (1H, br t, $J = 6.0$ Hz), 1.56 (2H, t, $J = 7.9$ Hz), 1.95 (1H, t, $J = 2.6$ Hz), 2.19 (2H, td, $J = 7.9, 2.6$ Hz), 3.35 (2H, d, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 19.1, 23.9, 29.2, 43.0, 70.8, 78.9; IR (neat) 3305 (br), 2117, 1687, 1471, 1416, 1215, 1142, 1048 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_8\text{H}_{15}\text{O}$ ($[\text{M}+\text{H}]^+$) 127.1123. Found 127.1121.

3,3-dimethyl-5-hexyn-1-ol (4e):³ colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.01 (6H, s), 1.09 (1H, br s), 1.64 (2H, t, $J = 7.3$ Hz), 2.00 (1H, t, $J = 2.7$ Hz), 2.12 (2H, d, $J = 2.7$ Hz), 3.72 (2H, t, $J = 7.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 27.0, 32.0, 32.6, 43.5, 59.7, 70.1, 82.2.

4,4-dimethyl-5-hexyn-1-ol (4f):⁴ pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.22 (6H, s), 1.28 (1H, br t, $J = 5.5$ Hz), 1.43-1.50 (2H, m), 1.69-1.79 (2H, m), 2.08 (1H, s), 3.68 (2H, br q, $J = 5.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 28.6, 29.0, 30.7, 39.1, 63.1, 67.9, 91.6.

6-heptyn-1-ol (4g) [63478-76-2]: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.25 (1H, br s), 1.42-1.64 (6H, m), 1.94 (3H, t, $J = 2.5$ Hz), 2.21 (2H, dt, $J = 6.6, 2.5$ Hz), 3.66 (2H, br q, $J = 5.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 18.3, 24.8, 28.1, 32.1, 62.6, 68.2, 84.3.

N-propyl-5-heptynamide (5a): yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.3$ Hz), 1.52 (2H, sextet, $J = 7.3$ Hz), 1.77 (3H, t, $J = 2.4$ Hz), 1.80 (2H, quintet, $J = 7.1$ Hz), 2.19 (2H, tq, $J = 6.6, 2.4$ Hz), 2.28 (2H, t, $J = 7.5$ Hz), 3.21 (2H, q, $J = 6.7$ Hz), 5.48 (1H, br s); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 11.2, 18.1, 22.7, 24.8, 35.3, 41.0, 76.1, 78.0, 172.4. IR (neat) 3295 (br), 1644, 1556, 1455, 1256, 1160, 1044 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{10}\text{H}_{17}\text{ONNa}$ ($[\text{M}+\text{Na}]^+$) 190.1207. Found 190.1210.

N-isopropyl-5-heptynamide (5b): white solid; ^1H NMR (300 MHz, CDCl_3) δ 1.14 (6H, t, $J = 6.6$ Hz), 1.79 (2H, quintet, $J = 7.4$ Hz), 1.78 (3H, t, $J = 2.5$ Hz), 2.18 (2H, tq, $J = 6.6,$

2.5 Hz), 2.24 (2H, t, $J = 7.4$ Hz), 4.07 (1H, octet, $J = 6.6$ Hz), 5.28 (1H, br s); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 18.1, 22.6, 24.8, 35.4, 41.0, 76.1, 78.1, 171.5; IR (CCl_4) 3299 (br), 1640, 1546, 1455, 1251, 1175 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{10}\text{H}_{18}\text{ON}$ ($[\text{M}+\text{H}]^+$) 168.1388. Found 168.1389.

***N*-(*tert*-butyl)-5-hepynamide (5c):** yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.34 (9H, s), 1.77 (2H, quintet, $J = 7.4$ Hz), 1.78 (3H, t, $J = 2.4$ Hz), 2.16 (2H, m), 2.20 (2H, t, $J = 7.4$ Hz), 5.30 (1H, br s); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 18.0, 24.7, 28.7, 36.2, 51.0, 76.2, 78.2, 171.8; IR (neat) 3305 (br), 1651, 1537, 1454, 1362, 1224, 1073 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{11}\text{H}_{20}\text{ON}$ ($[\text{M}+\text{H}]^+$) 182.1544. Found 182.1540.

***N*-benzyl-5-hepynamide (5d):** white solid; ^1H NMR (300 MHz, CDCl_3) δ 1.75 (3H, t, $J = 2.5$ Hz), 1.83 (2H, quintet, $J = 7.2$ Hz), 2.21 (2H, tq, $J = 6.6, 2.5$ Hz), 2.34 (2H, t, $J = 7.2$ Hz), 4.45 (2H, d, $J = 5.7$ Hz), 5.74 (1H, br s), 7.26-7.37 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 3.2, 18.0, 24.6, 35.0, 43.2, 76.2, 78.0, 127.1, 127.4, 128.4, 138.2, 172.4; IR (CCl_4) 3294 (br), 1654, 1647, 1542, 1453, 1218, 1027 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{14}\text{H}_{18}\text{ON}$ ($[\text{M}+\text{H}]^+$) 216.1388. Found 216.1388.

***N*-phenyl-5-hepynamide (5e):** yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 1.79 (3H, t, $J = 2.5$ Hz), 1.90 (2H, quintet, $J = 7.1$ Hz), 2.26 (2H, tq, $J = 6.6, 2.5$ Hz), 2.49 (2H, t, $J = 7.1$ Hz), 7.10 (1H, br t, $J = 7.4$ Hz), 7.21 (1H, br s), 7.32 (2H, br t, $J = 7.8$ Hz), 7.51 (2H, br d, $J = 7.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 18.1, 24.5, 36.2, 76.6, 78.0, 119.8, 124.1, 128.8, 137.8, 171.0; IR (CCl_4) 3312 (br), 1660, 1651, 1547, 1531, 1445, 758 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{15}\text{ON}$ (M^+) 201.1153. Found 201.1153.

***N*-(*p*-methoxyphenyl)-5-hepynamide (5f):** white solid; ^1H NMR (300 MHz, CDCl_3) δ 1.79 (3H, t, $J = 2.4$ Hz), 1.89 (2H, quintet, $J = 7.1$ Hz), 2.25 (2H, tq, $J = 6.6, 2.4$ Hz), 2.46 (2H, t, $J = 7.1$ Hz), 3.79 (3H, s), 6.86 (2H, d, $J = 9.0$ Hz), 7.09 (1H, br s), 7.41 (2H, d, $J = 9.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 18.1, 24.7, 36.0, 55.3, 76.4, 78.0, 113.9, 121.8, 131.0, 156.2, 170.9; IR (CCl_4) 3321 (br), 1660, 1513, 1405, 1033 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{NNa}$ ($[\text{M}+\text{Na}]^+$) 254.1157. Found 254.1146.

***N*-(*p*-trifluoromethylphenyl)-5-hepynamide (5g):** pale yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 1.79 (3H, t, $J = 2.4$ Hz), 1.90 (2H, quintet, $J = 7.1$ Hz), 2.27 (2H, tq, $J = 6.6, 2.4$ Hz), 2.52 (2H, t, $J = 7.1$ Hz), 7.32 (1H, br s), 7.57 (2H, d, $J = 8.7$ Hz), 7.65 (2H, d, $J = 8.7$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 18.1, 24.4, 36.2, 76.8, 77.7, 119.4,

123.9 ($^1J(\text{C}, \text{F}) = 269 \text{ Hz}$), 125.6, 126.1 ($^2J(\text{C}, \text{F}) = 126.1 \text{ Hz}$), 140.9, 171.5; IR (CCl_4) 3313 (br), 1682, 1599, 1526, 1405, 1324, 1157, 1115 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{14}\text{H}_{15}\text{ONF}_3$ ($[\text{M}+\text{H}]^+$) 270.1105. Found 270.1103.

***N*-phenyl-6-phenyl-5-hexynamide (5i)**: yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 2.04 (2H, quintet, $J = 7.0 \text{ Hz}$), 2.53-2.59 (4H, m), 7.10 (1H, br t, $J = 7.4 \text{ Hz}$), 7.20 (1H, br s), 7.26-7.34 (5H, m), 7.40 (2H, m), 7.51 (2H, br d, $J = 8.1 \text{ Hz}$); ^{13}C NMR (75 MHz, CDCl_3) δ 18.7, 24.2, 36.2, 81.7, 88.8, 119.7, 123.5, 124.2, 127.7, 128.2, 128.9, 131.5, 137.8, 170.5; IR (CCl_4) 3255 (br), 1660, 1599, 1538, 1441, 1329, 1256 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{18}\text{H}_{18}\text{NO}$ ($[\text{M}+\text{H}]^+$) 264.1388. Found 264.1386.

***N*-phenyl-5-hexynamide (5j)**: dark yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 1.89 (2H, quintet, $J = 7.0 \text{ Hz}$), 1.95 (1H, t, $J = 2.4 \text{ Hz}$), 2.26 (2H, td, $J = 6.6, 2.4 \text{ Hz}$), 2.45 (2H, t, $J = 7.3 \text{ Hz}$), 7.04 (1H, br t, $J = 7.4 \text{ Hz}$), 7.20 (1H, br s), 7.26 (2H, br t, $J = 7.8 \text{ Hz}$), 7.45 (2H, d, $J = 7.8 \text{ Hz}$); ^{13}C NMR (75 MHz, CDCl_3) δ 17.7, 23.9, 35.8, 69.3, 83.3, 119.9, 124.2, 128.8, 137.8, 170.7; IR (CCl_4) 3311 (br), 2117, 1660, 1600, 1538, 1498, 1442, 1253 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{12}\text{H}_{14}\text{NO}$ ($[\text{M}+\text{H}]^+$) 188.1075. Found 188.1073.

***N*-phenyl-2,2-dimethyl-5-hexynamide (5k)**: yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.32 (6H, s), 1.90 (2H, t, $J = 7.8 \text{ Hz}$), 1.93 (1H, t, $J = 2.6 \text{ Hz}$), 2.24 (2H, td, $J = 7.8, 2.6 \text{ Hz}$), 7.11 (1H, t, $J = 7.4 \text{ Hz}$), 7.26-7.41 (4H, m), 7.50 (2H, br d, $J = 7.8 \text{ Hz}$).

***N*-phenyl-6-heptynamide (5l)**: yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 1.61 (2H, quintet, $J = 7.5 \text{ Hz}$), 1.86 (2H, quintet, $J = 7.5 \text{ Hz}$), 1.96 (1H, t, $J = 2.4 \text{ Hz}$), 2.23 (2H, td, $J = 6.9, 2.4 \text{ Hz}$), 2.38 (2H, t, $J = 7.5 \text{ Hz}$), 7.09 (1H, br t, $J = 7.4 \text{ Hz}$), 7.30 (2H, br t, $J = 7.8 \text{ Hz}$), 7.41 (1H, br s), 7.51 (2H, br d, $J = 7.8 \text{ Hz}$); ^{13}C NMR (75 MHz, CDCl_3) δ 18.0, 24.5, 27.7, 36.7, 68.6, 83.9, 120.0, 124.1, 128.7, 137.8, 171.4; IR (CCl_4) 3310 (br), 2117, 1659, 1600, 1537, 1498, 1442, 1310, 1250 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{13}\text{H}_{16}\text{NO}$ ($[\text{M}+\text{H}]^+$) 202.1231. Found 202.1231.

***N*-phenyl-4-hexynamide (5m)**: yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 1.81 (3H, t, $J = 2.1 \text{ Hz}$), 2.51-2.57 (4H, m), 7.11 (1H, br t, $J = 7.4 \text{ Hz}$), 7.32 (2H, br t, $J = 7.8 \text{ Hz}$), 7.50-7.52 (1H, br s), 7.51 (2H, br d, $J = 7.8 \text{ Hz}$); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 15.1, 36.8, 76.5, 77.51, 119.8, 124.2, 128.9, 137.8, 169.7; IR (CCl_4) 3296 (br), 1661, 1602, 1547, 1498, 1441, 1317, 1246, 1191 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_{12}\text{H}_{14}\text{NO}$ ($[\text{M}+\text{H}]^+$) 188.1075. Found 188.1073.

2,2-dimethyl-2-cyclohexen-1-one (6a) [1122-20-9]: yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.72 (3H, br s), 1.88 (3H, br s), 1.88 (2H, quintet, $J = 6.5$ Hz), 2.29 (2H, br t, $J = 6.5$ Hz), 2.34 (2H, t, $J = 6.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 10.7, 21.4, 22.2, 32.7, 37.5, 130.9, 155.1, 199.0.

3-phenyl-2-cyclohexene-1-one (6b) [10345-87-6]: yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 2.15 (2H, quintet, $J = 6.4$ Hz), 2.49 (2H, t, $J = 6.4$ Hz), 2.78 (2H, td, $J = 6.0, 1.2$ Hz), 6.42 (1H, t, $J = 1.2$ Hz), 7.40-7.43 (3H, m), 7.51-7.55 (2H, m).

2-methyl-3-butyl-2-cyclopenten-1-one (6c) [5760-60-1]: yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.93 (3H, t, $J = 7.3$ Hz), 1.35 (2H, sextet, $J = 7.3$ Hz), 1.51 (2H, quintet, $J = 7.3$ Hz), 1.69 (3H, br s), 2.36 (2H, m), 2.41 (2H, t, $J = 7.3$ Hz), 2.49 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 7.9, 13.8, 22.6, 29.1, 29.3, 30.9, 34.0, 136.0, 173.8, 210.1.

2-methyl-3-phenyl-2-cyclohexen-1-one (6d) [30708-63-5]: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.72 (3H, t, $J = 2.0$ Hz), 2.09 (2H, quintet, $J = 6.5$ Hz), 2.52 (2H, t, $J = 6.5$ Hz), 2.63 (2H, tq, $J = 6.5, 2.0$ Hz), 7.19 (2H, m), 7.29-7.42 (3H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 12.8, 22.7, 32.8, 37.6, 127.0, 127.7, 128.2, 131.7, 141.2, 156.5, 199.9.

2-methyl-6-octyn-2-ol (7a): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.22 (6H, s), 1.24 (1H, br s), 1.54-1.56 (4H, m), 1.77 (3H, t, $J = 2.4$ Hz), 2.15 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 3.4, 19.1, 23.9, 29.2, 43.0, 70.8, 75.7, 78.9; IR (neat) 3390 (br), 1469, 1366, 1208, 1151, 1126 cm^{-1} ; IR (neat) 3390 (br), 1469, 1366, 1208, 1151, 1126 cm^{-1} ; HRMS (CI) Calcd for $\text{C}_9\text{H}_{17}\text{O}$ ($[\text{M}+\text{H}]^+$) 141.1279. Found 141.1275.

5-butyl-9-undecy-5-ol (7b): yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.91 (6H, t, $J = 6.8$ Hz), 1.19 (1H, s), 1.24-1.34 (12H, m), 1.42 (2H, m), 1.50 (2H, m), 1.78 (3H, t, $J = 2.4$ Hz), 2.13 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 3.3, 14.0, 19.2, 23.22, 23.25, 25.5, 38.3, 38.9, 74.1, 75.6, 79.0; IR (neat) 3417 (br), 1544, 1378, 1140 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{15}\text{H}_{28}\text{ONa}$ ($[\text{M}+\text{Na}]^+$) 247.2038. Found 247.2036.

6-allyl-2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexen-1-one (8a): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.72-1.84 (1H, m), 1.86 (3H, t, $J = 2.0$ Hz), 2.09-2.20 (2H, m), 2.33-2.43 (1H, m), 2.59-2.67 (1H, m), 2.72-2.86 (2H, m), 5.07 (1H, br d, $J = 10.8$ Hz), 5.08 (1H, br d, $J = 16.2$ Hz), 5.74 (1H, ddt, $J = 16.2, 10.8, 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 9.4, 25.3, 27.9, 33.5, 44.9, 117.4, 118.2 ($^1J(\text{C}, \text{F}) = 317$ Hz),

127.5, 135.1, 161.1, 198.7; IR (neat) 1681, 1416, 1347, 1212, 1139, 1035 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4\text{SF}_3$ ($[\text{M}+\text{H}]^+$) 299.0564. Found 299.0566.

6-(ethoxycarbonylmethyl)-2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexen-1-one (8b): pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.27 (3H, t, $J = 7.2$ Hz), 1.87 (3H, t, $J = 2.0$ Hz), 1.90 (1H, m), 2.18 (1H, m), 2.33 (1H, m), 2.66 (1H, m), 2.76-2.99 (3H, m), 4.16 (2H, qd, $J = 7.2, 0.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 9.4, 14.0, 26.3, 28.4, 34.2, 42.3, 60.7, 118.1 ($^1J(\text{C}, \text{F}) = 316$ Hz), 127.4, 161.1, 171.7, 197.6; IR (neat) 1735, 1686, 1420, 1346, 1214, 1139, 1032 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{12}\text{H}_{15}\text{O}_6\text{SF}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$) 367.0439. Found 367.0440.

2-methyl-3-(trifluoromethanesulfonyloxy)-2-cyclohexen-1-ol (9a):⁵ colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.60 (1H, t, $J = 7.5$ Hz), 1.71-1.90 (4H, m), 1.88 (3H, t, $J = 2.1$ Hz), 2.34 (2H, m), 4.22 (1H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 13.7, 18.4, 27.7, 30.9, 69.2, 118.2 ($^1J(\text{C}, \text{F}) = 317$ Hz), 128.0, 146.4; IR (neat) 3365 (br), 1703, 1415, 1208, 1140, 1034 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_8\text{H}_{11}\text{O}_4\text{SF}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$) 283.0228. Found 283.0230.

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¹H NMR charts