Nazarov cyclization of divinyl ketones bearing ester group at β-position: remarkable effect of α-substitution and alkene geometry on regioselectivity

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1. General Information

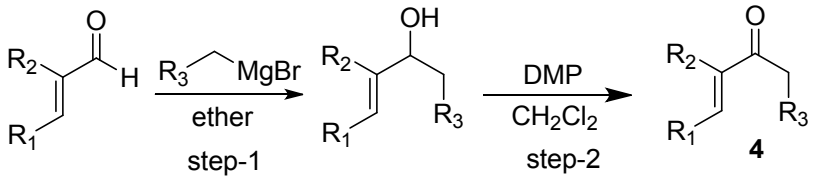
Anhydrous solvents were dried and distilled by standard methods prior to use. Commercially available reagents were used without further purification unless otherwise specified. All the reactions were performed under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring. Column chromatography was carried out using silica gel (60-120 or 100-200 or 230-400 mesh), the column was eluted with ethyl acetate-hexanes. Visualization of the spots on TLC plates was achieved either by UV light or by staining the plates in methanolic anisaldehyde-sulphuric acid-acetic acid or in methanol-phosphomolybdic acid-sulphuric acid solution and charring on a hot plate.

^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ solvent on 600 MHz, 500 MHz, 400MHz, 300 MHz and 75 MHz, 100MHz, 125 MHz spectrometer, respectively at ambient temperature. Chemical shifts are reported as δ values relative to internal $CHCl_3$ δ 7.26 or TMS δ 0.0 for ^{1}H NMR and $CHCl_3$ δ 77.0 for ^{13}C NMR. ^{1}H NMR data is recorded as follows: chemical shift [multiplicity, coupling constant(s) *J* (Hz), relative integral] where multiplicity is defined as: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublet; dt = doublet of triplet; dq = doublet of quartet; m = multiplet; br s = broad singlet, br d = broad doublet. FTIR spectra were recorded as KBr thin films or neat. Mass spectra were recorded for ESI and are given in mass units (m/z). High resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double focusing spectrometer. Melting points were determined using Cintex melting point apparatus and are uncorrected.

2. Experimental Procedures

2.1. Typical procedure for the preparation of benzyl/alkyl-vinylketone 4:

Method A:



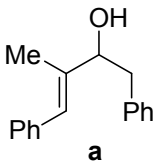
Step-1: General procedure for the synthesis of allylic alcohol: In a dry 2- neck round bottom flask equipped with a magnetic stirring bar, nitrogen inlet, reflux condenser, rubber septum, one iodine pinch and magnesium turnings (1.5 equiv) was stirred with dry diethyl ether (1 mL/1 mmol). Then alkyl/benzyl halide (1 equiv) was added drop wise until an exothermic reaction began. When all of the bromide had been added, the Grignard reagent was kept for reflux for 45 min and then stand for some time at rt. This Grignard reagent was added to an ice cooled solution of *α,β*-unsaturated aldehyde (0.9 equiv) in dry diethyl ether (3 mL/mmol) at 0 °C and stirred for 30 min. The reaction was monitored by TLC, after completion of the starting material, the reaction was quenched with saturated aq NH_4Cl, extracted with EtOAc. The organic layer was washed with saturated aq NaCl and dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by using silica gel flash column chromatography (EtOAc/hexanes) to give pure allylic alcohol.

Step-2: General procedure for the synthesis of benzyl/alkyl-vinyl ketone (4): To an allylic alcohol solution in CH_2Cl_2 (3 mL/1mmol) was cooled to 0 °C. Then added portion wise Dess-Martin periodinane (DMP) (1.2 equiv). The reaction mixture was slowly warmed to rt. The reaction was monitored by TLC and after completion of the starting material, the reaction mixture was filtered through Celite and the organic solution was washed with a saturated aq $NaHCO_3$ solution, brine, dried over Na_2SO_4, filtered and evaporated under

reduced pressure. The residue was purified by using silica gel column chromatography to afford pure ketone **4**.

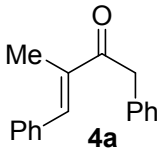
(*E*)-3-Methyl-1,4-diphenylbut-3-en-2-one (4a):

Step-1: Yield: 87%; colorless oil; R_f = 0.3 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.15 (m, 10H), 6.42 (s, 1H), 4.34 (m, 1H), 2.99-2.81 (m, 2H), 1.92 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.0, 137.9, 137.1, 129.0, 128.5, 128.0, 127.7, 126.0, 125.6, 78.2, 41.8, 13.4; IR (neat): ν_{max} 3398, 3026, 2926, 1600, 1494, 1447, 1016, 744, 698 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{17}O$ $[M-H]^+$ 237.1273, found 237.1280.



a

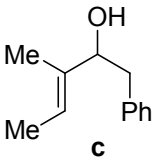
Step-2:[1] Yield: 86%; colorless oil; R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.42-7.19 (m, 10H), 4.11 (s, 2H), 2.06 (d, J = 0.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.6, 139.7, 136.8, 135.6, 135.2, 129.6, 129.1, 128.5, 128.3, 126.6, 44.5, 13.2; IR (neat): ν_{max} 3059, 1664, 1495, 1447, 1209, 1052, 769, 698 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{16}O$ $[M+H]^+$ 237.1273, found 237.1274.



4a

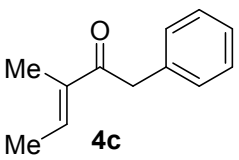
(*E*)-3-Methyl-1-phenylpent-3-en-2-one (4c):

Step-1:[2] Yield: 88%; colorless oil; R_f = 0.3 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (m, 2H), 7.16 (m, 3H), 5.38 (q, J = 6.8 Hz, 1H), 4.13 (t, J = 6.1 Hz, 1H), 2.80-2.76 (m, 2H), 2.05 (bs, 1H), 1.64 (s, 3H), 1.55 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5, 136.8, 129.0, 127.9, 125.9, 120.4, 78.2, 41.7, 12.7, 11.7; IR (neat): ν_{max} 3395, 2922, 1494, 1381, 1012, 737, 695 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{15}O$ $[M-H]^+$ 175.1117, found 175.1111.



c

Step-2:[3] Yield: 88%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (m, 2H), 7.18 (m, 3H), 6.84 (q, J = 6.8 Hz, 1H), 3.94 (s, 2H), 1.82 (d, J = 6.8 Hz, 3H), 1.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$):

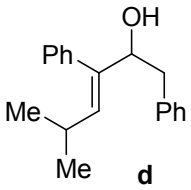


4c

δ 198.6, 138.3, 137.7, 135.3, 128.9, 128.2, 126.2, 43.8, 14.6, 10.9; IR (neat): ν_{max} 3028, 2927, 1660, 1495, 1382, 1070, 770 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{15}O$ $[M+H]^+$ 175.1117, found 175.1116.

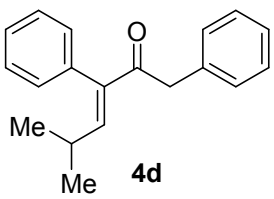
(*E*)-5-Methyl-1,3-diphenylhex-3-en-2-one (4d):

Step-1: Yield: 86%; colorless oil; R_f = 0.3 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.40-7.12 (m, 10H), 5.48 (d, J = 10.1 Hz, 1H), 4.49 (dd, J = 4.1, 8.6 Hz, 1H), 2.85 (dd, J = 4.1, 13.7 Hz, 1H), 2.59 (dd, J = 8.4, 13.7 Hz, 1H), 2.26 (m, 1H), 1.79 (br s, 1H), 0.92 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.1, 138.6, 138.4, 135.8, 129.3, 129.1, 128.2, 128.0, 126.8, 126.2, 76.8, 42.4, 27.4, 23.1, 23.0; IR (neat): ν_{max} 3400, 2956, 1452, 1366, 1218, 1079, 1030, 699 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{22}O_2Na$ $[M+Na]^+$ 289.1562, found 289.1558.



d

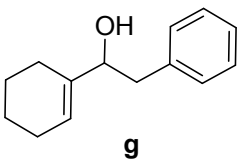
Step-2: Yield: 87%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.40-7.15 (m, 6H), 7.06 (m, 4H), 6.72 (d, J = 10.3 Hz, 1H), 3.83 (s, 2H), 2.32 (m, 1H), 0.96 (d, J = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.5, 150.4, 139.7, 136.1, 134.7, 129.4, 129.3, 128.3, 128.1, 127.3, 126.5, 46.3, 28.6, 22.0; IR (neat): ν_{max} 2962, 2866, 1678, 1614, 1494, 1452, 1314, 1245, 1105, 956, 701 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{21}O$ $[M+H]^+$ 265.1586, found 265.1580.



4d

1-(Cyclohex-1-en-1-yl)-2-phenylethanone (4g):

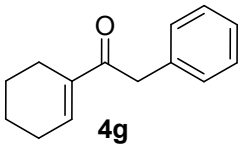
Step-1:[4] Yield: 91%; colorless oil; R_f = 0.3 (15% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.30-7.15 (m, 5H), 5.59 (m, 1H), 4.12 (dd, J = 3.0, 5.2 Hz, 1H), 2.79 (m, 2H), 2.16-1.92 (m, 4H), 1.88 (bs, 1H), 1.71-1.49 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.0, 138.5, 129.1, 128.1, 126.0, 122.9,



g

76.9, 41.9, 24.7, 23.9, 22.5, 22.4; IR (neat): ν_{max} 3395, 2925, 1495, 1446, 1271, 1140, 916, 740 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{17}$ $[M\text{-}OH]^+$ 185.1324, found 185.1316.

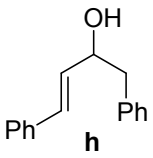
Step-2**:**[5] Yield: 92%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.34-7.15 (m, 5H), 7.02 (m, 1H), 3.93 (s, 2H), 2.23 (m, 4H), 1.59 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.5, 141.0, 138.8, 135.3, 129.1, 128.3, 126.4, 43.8, 26.0, 23.1, 21.7, 21.3; IR (neat): ν_{max} 2931, 1660, 1495, 1379, 1273, 1187, 703 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{17}O$ $[M+H]^+$ 201.1273, found 201.1273.



4g

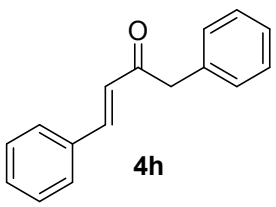
(*E*)-1,4-Diphenylbut-3-en-2-one (4h):

Step-1:[6] Yield: 81%; light yellow oil; R_f = 0.2 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.18 (m, 10H), 6.57 (d, J = 15.8 Hz, 1H), 6.26 (dd, J = 6.4, 15.8 Hz, 1H), 4.50 (q, J = 6.4 Hz, 1H), 2.91 (m, 2H), 1.87 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.6, 136.6, 131.4, 130.2, 129.5, 128.4, 127.5, 126.5, 126.4, 73.4, 44.1; IR (neat): ν_{max} 3398, 3027, 2855, 1713, 1493, 1029, 745, 697 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{15}O$ $[M\text{-}H]^+$ 223.1117, found 223.1111.



h

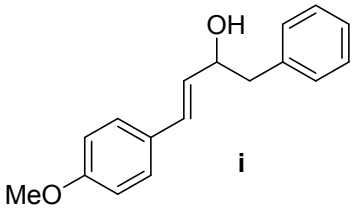
Step-2:[7] Yield: 83%; yellow solid; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, J = 15.8 Hz, 1H), 7.50 (m, 2H), 7.38-7.23 (m, 8H), 6.77 (d, J = 15.8 Hz, 1H), 3.93 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.1, 143.2, 134.3, 130.4, 129.3, 128.8, 128.6, 128.2, 126.9, 125.0, 48.2; IR (neat): ν_{max} 3029, 1690, 1603, 1450, 1168, 979, 745, 690 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{15}O$ $[M+H]^+$ 223.1117, found 223.1111.



4h

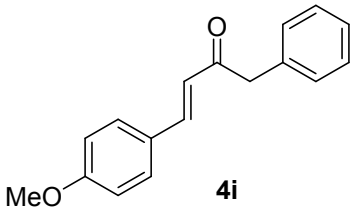
(*E*)-4-(4-Methoxyphenyl)-1-phenylbut-3-en-2-one (4i):

Step-1:[8] Yield: 85%; yellow soild; R_f = 0.2 (15% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.17 (m, 7H), 6.82 (d, J = 9.0 Hz, 2H), 6.48 (d, J = 15.8 Hz, 1H), 6.10 (dd, J = 6.0, 15.8 Hz, 1H), 4.44 (q, J = 6.0 Hz, 1H), 3.75 (s, 3H), 2.88 (m, 2H), 2.11 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 137.7, 129.7, 129.4, 129.2, 129.1, 128.3, 127.5, 126.3, 113.8, 73.4, 55.1, 44.0; IR (neat): ν_{max} 3499, 2926, 1599, 1508, 1250, 988, 809, 749, 690 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{17}O_2$ $[M-H]^+$ 253.1223, found 253.1221.



i

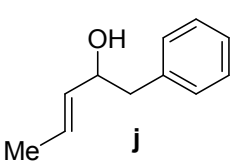
Step-2:[9] Yield: 86%; light yellow solid; R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 15.8 Hz, 1H), 7.46 (d, J = 8.6 Hz, 2H), 7.33 (m, 2H), 7.26 (m, 3H), 6.88 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 15.8 Hz, 1H), 3.91 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 161.5, 143.1, 134.6, 130.0, 129.4, 128.6, 126.8, 122.9, 114.2, 55.3, 48.2; IR (neat): ν_{max} 2925, 1683, 1596, 1509, 1252, 1171, 1029, 832, 700 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{17}O_2$ $[M+H]^+$ 253.1223, found 253.1224.



4i

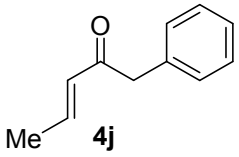
(*E*)-1-Phenylpent-3-en-2-one (4j)

Step-1:[10] Yield: 86%; colorless oil; R_f = 0.3 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (m, 2H), 7.19 (m, 3H), 5.61 (m, 1H), 5.51 (m, 1H), 4.22 (q, J = 6.7 Hz, 1H), 2.76 (m, 2H), 2.01 (bs, 1H), 1.66 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 133.0, 129.3, 128.1, 126.6, 126.1, 73.3, 43.9, 17.5; IR (neat): ν_{max} 3389, 2922, 1494, 1027, 967, 744, 699 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{15}O$ $[M+H]^+$ 163.1117, found 163.1116.



j

Step-2:[11] Yield: 87%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (m, 2H), 7.24 (d, J = 7.3 Hz, 1H), 7.20 (d, J = 7.3 Hz,

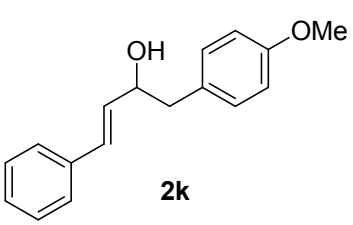


4j

2H), 6.92 (m, 1H), 6.16 (dq, J = 1.6, 15.7 Hz, 1H), 3.80 (s, 2H), 1.86 (dd, J = 1.6, 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 143.6, 134.4, 130.8, 129.3, 128.5, 126.7, 47.3, 18.2; IR (neat): ν_{max} 2920, 1672, 1628, 1442, 1185, 967, 738, 698 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{13}O$ $[M+H]^+$ 161.0960, found 161.0953.

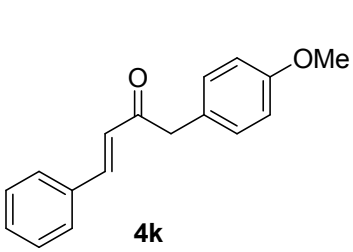
(*E*)-1-(4-Methoxyphenyl)-4-phenylbut-3-en-2-one (4k):

Step-1:[12] Yield: 76%; light yellow oil; R_f = 0.3 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 7.3 Hz, 2H), 7.29 (t, J = 7.3 Hz, 2H), 7.21 (m, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 15.9 Hz, 1H), 6.25 (dd, J = 6.3, 15.9 Hz, 1H), 4.44 (q, J = 6.3 Hz, 1H), 3.76 (s, 3H), 2.84 (m, 2H), 1.98 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 136.6, 131.4, 130.4, 130.1, 129.5, 128.4, 127.5, 126.3, 113.8, 73.4, 55.1, 43.1; IR (neat): ν_{max} 3419, 2924, 1609, 1510, 1244, 1032, 749, 694 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{17}O_2$ $[M-H]^+$ 253.1223, found 253.1215.



2k

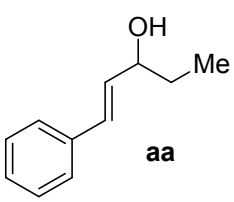
Step-2:[13] Yield: 82%; light yellow solid; R_f = 0.4 (15% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, J = 16.0 Hz, 1H), 7.49 (m, 2H), 7.35 (m, 3H), 7.17 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 16.0 Hz, 1H), 3.85 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4, 158.4, 143.0, 134.2, 130.3, 128.7, 128.1, 126.2, 124.9, 114.0, 55.0, 47.3; IR (neat): ν_{max} 2925, 1679, 1607, 1509, 1244, 1172, 1031, 744, 689 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{17}O_2$ $[M+H]^+$ 253.1223, found 253.1213.



4k

(*E*)-1-Phenylpent-1-en-3-one (4aa):

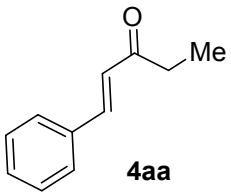
Step-1:[14] Yield: 86%; colorless oil; R_f = 0.3 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, J = 7.7 Hz, 2H), 7.25 (t, J = 7.3 Hz, 2H), 7.18 (m,



aa

1H), 6.50 (d, J = 15.8 Hz, 1H), 6.15 (dd, J = 6.7, 15.8 Hz, 1H), 4.12 (q, J = 6.7 Hz, 1H), 2.88 (br s, 1H), 1.68-1.53 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.6, 132.1, 130.0, 128.3, 127.3, 126.2, 74.0, 29.9, 9.5; IR (neat): ν_{max} 3393, 3025, 2967, 1609, 1495, 963, 747, 690 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{13}O$ $[M-H]^+$ 161.0960, found 161.0957.

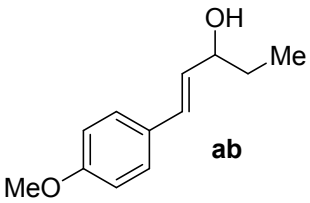
Step-2:[15] Yield: 85%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (m, 3H), 7.39 (m, 3H), 6.74 (d, J = 16.1 Hz, 1H), 2.70 (q, J = 7.3 Hz, 2H), 1.17 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.9, 141.4, 129.7, 128.3, 127.6, 125.4, 33.3, 7.5; IR (neat): ν_{max} 2977, 1663, 1611, 1494, 1352, 1187, 1119, 978, 745, 690 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{13}O$ $[M+H]^+$ 161.0960, found 161.0954.



4aa

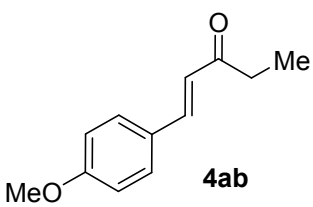
(*E*)-1-(4-Methoxyphenyl)pent-1-en-3-one (4ab):

Step-1:[16] Yield: 83%; colorless oil; R_f = 0.3 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 15.8 Hz, 1H), 6.06 (dd, J = 7.0, 15.8 Hz, 1H), 4.16 (q, J = 7.0 Hz, 1H), 3.79 (s, 3H), 1.91 (bs, 1H), 1.64 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 130.0, 129.9, 129.4, 127.5, 113.9, 74.5, 55.2, 30.1, 9.7; IR (neat): ν_{max} 3448, 2923, 2842, 1602, 1506, 1246, 1173, 1032, 940, 824 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{15}O_2$ $[M-H]^+$ 191.1066, found 191.1060.



ab

Step-2:[17] Yield: 87%; colorless oil; R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 16.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H), 2.67 (q, J = 7.3 Hz, 2H), 1.16 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz,

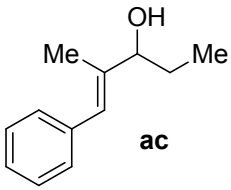


4ab

$CDCl_3$): δ 200.8, 161.3, 141.9, 129.8, 127.1, 123.7, 114.2, 55.2, 33.7, 8.2; IR (neat): ν_{max} 2932, 2843, 1655, 1594, 1507, 1250, 1174, 1116, 1029, 981, 826 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{15}O_2$ $[M+H]^+$ 191.1066, found 191.1055.

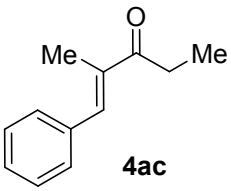
(*E*)-2-Methyl-1-phenylpent-1-en-3-one (4ac):

Step-1:[18] Yield: 86%; colorless oil; R_f = 0.3 (15% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.32-7.11 (m, 5H), 6.43 (s, 1H), 4.03 (t, J = 6.6 Hz, 1H), 2.93-2.53 (br s, 1H), 1.81 (s, 3H), 1.63 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.9, 137.7, 128.7, 127.8, 126.1, 125.6, 79.2, 27.6, 12.8, 9.9; IR (neat): ν_{max} 3391, 2964, 2873, 1448, 1377, 1327, 993, 744, 694 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{15}O$ $[M-H]^+$ 175.1117, found 175.1118.



ac

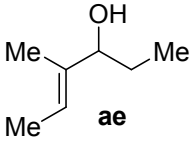
Step-2:[19] Yield: 91%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.41 (m, 4H), 7.34 (m, 1H), 2.83 (q, J = 7.3 Hz, 2H), 2.07 (d, J = 0.9 Hz, 3H), 1.17 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.3, 137.8, 136.7, 135.6, 129.3, 128.0, 30.3, 12.8, 8.4; IR (neat): ν_{max} 2976, 2928, 1664, 1492, 1369, 1206, 1086, 926, 695 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{15}O$ $[M+H]^+$ 175.1117, found 175.1116.



4ac

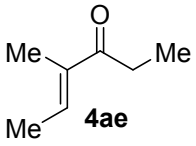
(*E*)-4-Methylhex-4-en-3-one (4ae):

Step-1:[20] Yield: 82%; colorless oil; R_f = 0.3 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 5.40 (m, 1H), 3.83 (t, J = 6.8 Hz, 1H), 3.62 (br s, 1H), 1.59 (d, J = 6.7 Hz, 3H) 1.55 (s, 3H), 1.49 (m, 2H), 0.80 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.2, 119.5, 78.5, 26.9, 12.1, 9.9, 9.4; IR (neat): ν_{max} 3374, 2966, 2872, 1452, 1380, 1094, 996, 825 cm^{-1}; HRMS (ESI): calcd for $C_7H_{13}O$ $[M-H]^+$ 113.0960, found 113.0959.



ae

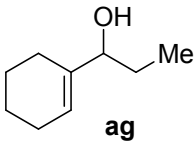
Step-2:[21] Yield: 81%; colorless oil; R_f = 0.6 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.75 (m, 1H), 2.68 (q, J = 7.3 Hz, 2H), 1.86 (d, J = 7.3 Hz, 3H) 1.78 (s, 3H), 1.09 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.1, 137.8, 136.5, 30.0, 14.5, 10.8, 8.6; IR (neat): ν_{max} 2921, 2855, 1714, 1457, 1375, 1241, 910, 743 cm^{-1}; HRMS (ESI): calcd for $C_7H_{13}O$ $[M+H]^+$ 113.0960, found 113.0962.



4ae

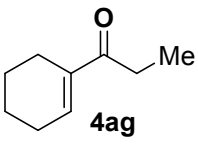
1-(Cyclohex-1-en-1-yl)propan-1-one (4ag):

Step-1:[22] Yield: 91%; colorless oil; R_f = 0.3 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.63 (s, 1H), 3.86 (m, 1H), 2.03 (m, 3H), 1.88 (m, 2H), 1.70-1.48 (m, 6H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.5, 123.0, 78.0, 27.4, 24.8, 23.1, 22.5, 9.9; IR (neat): ν_{max} 3354, 2925, 2868, 1448, 1239, 1003, 919, 841, 748 cm^{-1}; HRMS (ESI): calcd for $C_9H_{15}O$ $[M-H]^+$ 139.1117, found 139.1116.



ag

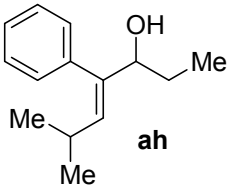
Step-2:[23] Yield: 87%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91 (s, 1H), 2.66 (q, J = 7.5 Hz, 2H), 2.24 (m, 4H), 1.68-1.58 (m, 4H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.8, 139.1, 138.7, 29.9, 25.8, 23.0, 21.8, 21.2, 8.5; IR (neat): ν_{max} 2931, 2864, 1666, 1429, 1382, 1201, 975, 843 cm^{-1}; HRMS (ESI): calcd for $C_9H_{15}O$ $[M+H]^+$ 139.1117, found 139.1119.



4ag

(*E*)-6-Methyl-4-phenylhept-4-en-3-one (4ah):

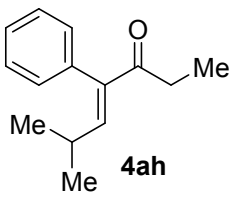
Step-1: Yield: 87%; colorless oil; R_f = 0.3 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, J = 8.0 Hz, 2H), 7.27 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 5.48 (d, J = 10.0 Hz, 1H), 4.16 (t, J = 6.2 Hz, 1H), 2.23 (m,



ah

1H), 1.60 (bs, 1H), 1.54-1.45 (m, 1H), 1.45-1.36 (m, 1H), 0.94-0.88 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.5, 138.4, 136.1, 129.1, 127.9, 126.7, 77.9, 28.1, 27.5, 23.1, 23.0, 9.8; IR (neat): ν_{max} 3362, 2959, 2868, 1457, 1377, 1104, 1021, 877, 703 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{19}$ [M-OH]$^+$ 187.1481, found 187.1486.

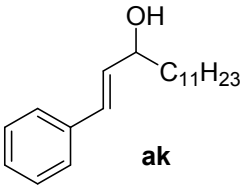
Step-2: Yield: 91%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (m, 2H), 7.32 (m, 1H), 7.10 (m, 2H), 6.66 (d, J = 10.3 Hz, 1H), 2.53 (q, J = 7.3 Hz, 2H), 2.32 (m, 1H), 1.05 (t, J = 7.3 Hz, 3H), 0.98 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.7, 148.8, 139.9, 136.5, 129.3, 128.1, 127.2, 32.9, 28.5, 22.1, 8.2; IR (neat): ν_{max} 2964, 1682, 1622, 1456, 1348, 1236, 1130, 1060, 911, 702 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{19}O$ [M+H]$^+$ 203.1430, found 203.1434.



4ah

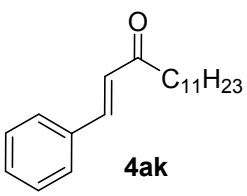
(*E*)-1-Phenyltetradec-1-en-3-one (4ak):

Step-1: Yield: 83%; colorless oil; R_f = 0.2 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.17 (m, 5H), 6.54 (d, J = 16.0 Hz, 1H), 6.20 (dd, J = 6.7, 16.0 Hz, 1H), 4.24 (q, J = 6.7 Hz, 1H), 1.98 (bs, 1H), 1.60 (m, 2H), 1.50-1.16 (m, 18H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.6, 132.5, 130.0, 128.4, 127.4, 126.3, 73.0, 37.3, 31.8, 29.5, 29.3, 25.4, 22.6, 14.0; IR (neat): ν_{max} 3356, 2921, 2853, 1456, 1019, 746, 692 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{31}O$ [M-H]$^+$ 287.2369, found 287.2367.



ak

Step-2: Yield: 84%; colorless oil; R_f = 0.6 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.46 (m, 3H), 7.34 (m, 3H), 6.72 (d, J = 16.0 Hz, 1H), 2.62 (t, J = 7.5, 1H), 1.66 (t, J = 6.7 Hz, 2H), 1.39-1.16 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.1, 141.9, 134.3,

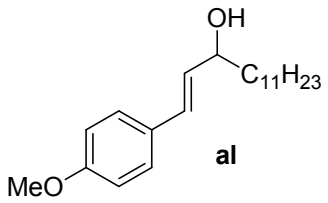


4ak

130.0, 128.6, 127.9, 125.9, 40.7, 31.7, 29.4, 29.2, 29.1, 24.1, 22.4, 13.9; IR (neat): ν_{max} 2922, 2853, 1734, 1665, 1612, 1496, 1239, 1180, 978, 747, 691 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{30}ONa$ $[M+Na]^+$ 309.2188, found 309.2185.

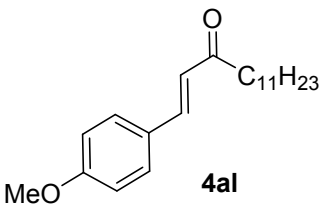
(*E*)-1-(4-Methoxyphenyl)tetradec-1-en-3-one (4al):

Step-1: Yield: 78%; light yellow oil; R_f = 0.3 (15% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.48 (d, J = 15.8 Hz, 1H), 6.06 (dd, J = 6.9, 15.8 Hz, 1H), 4.22 (q, J = 6.9 Hz, 1H), 3.79 (s, 3H), 1.95 (bs, 1H), 1.59 (m, 2H), 1.44-1.15 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 130.4, 129.7, 127.6, 127.5, 113.9, 73.2, 55.1, 37.3, 31.8, 29.5, 29.3, 25.3, 22.6, 14.0; IR (neat): ν_{max} 3432, 2922, 2852, 1605, 1510, 1460, 1248, 1035 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{33}O_2$ $[M-H]^+$ 317.2475, found 317.2473.



al

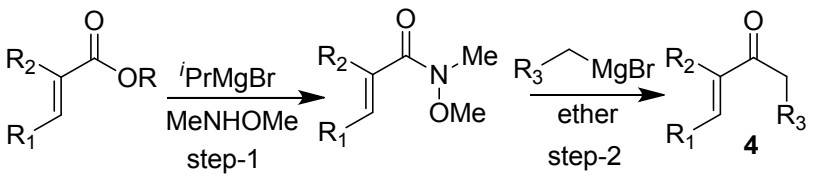
Step-2: Yield: 84%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (m, 3H), 6.91 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 16.0, 1H), 3.84 (s, 3H), 2.63 (t, J = 7.3 Hz, 1H), 1.67 (m, 2H), 1.36-1.22 (m, 16H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.7, 161.4, 142.0, 129.8, 127.2, 124.0, 114.3, 55.3, 40.8, 31.8, 29.5, 29.4, 29.3, 29.3, 24.5, 22.6, 14.0; IR (neat): ν_{max} 2917, 2849, 1656, 1606, 1512, 1250, 1109, 973, 759 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{33}O_2$ $[M+H]^+$ 317.2475, found 317.2470.



4al

Typical procedure for preparation of benzyl/alkyl-vinylketone 4:

Method B:

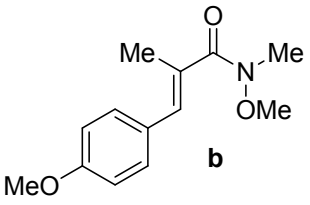


Step-1: General procedure for the synthesis of Weinreb amide: To a stirred solution of the ester in THF (3 mL/mmol) was cooled to 0 °C and added *N*,*O*-dimethylhydroxylamine hydrochloride (3 equiv). To the resultant suspension, ^{i}PrMgBr (6 equiv of 1 M solution in THF) was added drop wise at 0 °C and continued stirring at the same temperature for 1 h. After completion of the reaction (TLC), it was quenched by addition of the saturated aq NH_4Cl solution, extracted with EtOAc. The combined organic layer was washed with brine, dried with Na_2SO_4, filtered, and concentrated. The residue was purified by using silica gel column chromatography.

Step-2: General procedure for the synthesis of allyl ketone (4): Weinreb amide (1 equiv) in dry diethyl ether (3 mL/mmol) was cooled to 0 °C. A freshly prepared solution of benzyl or alkyl magnesium bromide (1 M in Et_2O, 1.5 equiv/mmol) was added slowly and the resulting mixture was stirred at the same temperature for 3 h. It was cautiously quenched by the addition of saturated aq NH_4Cl solution and the mixture was extracted with Et_2O. The organic layers were combined, washed with brine, dried with Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by using silica gel column chromatography to give the ketone compound.

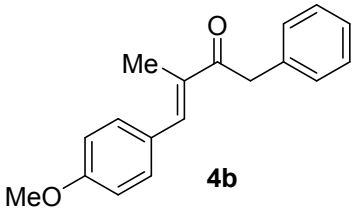
(*E*)-4-(4-Methoxyphenyl)-3-methyl-1-phenylbut-3-en-2-one (4b):

Step-1:[24] Yield: 87%; colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.80 (s, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.28 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.9, 158.8, 131.5, 130.5, 130.3, 128.4, 113.5, 60.8, 55.0, 33.5, 15.7; IR (neat): ν_{max} 2929, 1643, 1606, 1509, 1249, 1177, 1028, 827 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{17}NO_3Na$ $[M+Na]^+$ 258.1100, found 258.1102.



b

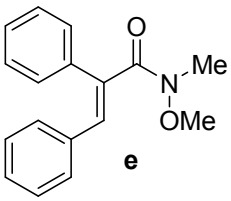
Step-2: Yield: 86%; light yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.31 (m, 2H), 7.24 (m, 3H), 6.93 (d, J = 8.6 Hz, 2H), 4.11 (s, 2H), 3.82 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5, 159.8, 139.7, 135.5, 134.9, 131.5, 129.1, 128.4, 128.2, 126.5, 113.8, 55.2, 44.4, 13.2; IR (neat): ν_{max} 2923, 1658, 1599, 1507, 1251, 1175, 1031, 831, 701 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{19}O_2$ $[M+H]^+$ 267.1379, found 267.1389.



4b

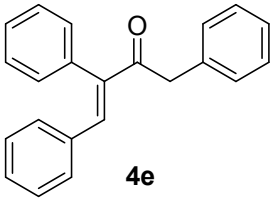
(*E*)-1,3,4-Triphenylbut-3-en-2-one (4e):

Step-1:[25] To a stirred solution of α-phenylcinnamic acid (3.0 g, 13.4 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added *N*,*O*-dimethyihydroxylamine hydrochloride (1.95 g, 20.1 mmol), *N*-ethyldiisopropylamine (3.6 mL, 20.1 mmol), DCC (3.59 g, 17.4 mmol) and DMAP (0.82 g, 6.69 mmol) and the reaction was allowed to stir at rt. After 16 h, the reaction mixture was filtered and washed with 5% aq $KHSO_4$ (2×15 mL), saturated aq $NaHCO_3$ (2×15 mL), brine (2×15 mL), dried with Na_2SO_4, and concentrated in vacuo. Then, hexane (10 mL) was added and the precipitated dicyclohexylurea was filtered off. The remaining solution was purified by using silica gel column chromatography to give **e** (3.255 g, 91%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.27 (m, 5H), 7.17-7.14 (m, 3H), 7.10-7.06 (m, 2H), 6.99 (s, 1H), 3.26 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 137.2, 136.0, 135.1, 132.5, 129.6, 128.9, 128.4, 127.9, 127.8, 127.7, 60.4, 33.3; IR (neat): ν_{max} 3056, 2931, 1647, 1490, 1369, 1172, 1114, 1021, 764 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{18}O_2N$ $[M+H]^+$ 268.1332, found 268.1330.



e

Step-2:[26] Yield: 87%; light yellow solid; R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.39-7.36 (m, 3H), 7.28-7.24 (m, 2H), 7.23-7.16 (m, 2H), 7.15-7.07 (m, 6H), 7.01 (d, J = 7.6 Hz, 2H), 3.87

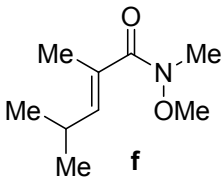


4e

(s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8, 140.2, 139.0, 136.6, 134.6, 134.5, 130.8, 129.6, 129.3, 129.1, 128.9, 128.3, 128.1, 127.9, 126.6, 46.6; IR (neat): ν_{max} 3059, 3028, 1677, 1599, 1494, 1446, 1323, 1211, 1100, 698 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{19}O$ $[M+H]^+$ 299.1430, found 299.1442.

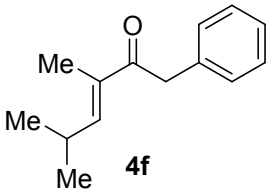
(*E*)-3,5-Dimethyl-1-phenylhex-3-en-2-one (4f):

Step-1:[27] Yield: 92%; colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.58 (m, 1H), 3.56 (s, 3H), 3.15 (s, 3H), 2.53 (m, 1H), 1.79 (d, J = 1.1 Hz, 3H), 0.94 (d, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.7, 140.4, 128.4, 60.6, 33.6, 26.9, 22.0, 13.6; IR (neat): ν_{max} 2959, 1642, 1458, 1368, 994, 835, 729 cm^{-1}; HRMS (ESI): calcd for $C_9H_{17}NO_2Na$ $[M+Na]^+$ 194.1151, found 194.1157.



f

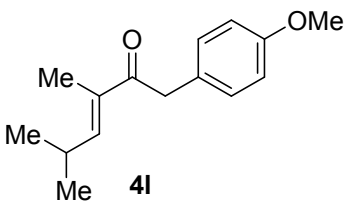
Step-2: Yield: 87%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (m, 2H), 7.19 (m, 3H), 6.54 (d, J = 9.3 Hz, 1H), 3.96 (s, 2H), 2.69 (m, 1H), 1.78 (s, 3H), 1.03 (d, J = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.3, 150.1, 135.4, 134.3, 129.0, 128.2, 126.2, 43.8, 28.1, 21.7, 11.1; IR (neat): ν_{max} 2961, 1665, 1454, 1265, 1055, 734, 699 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{19}O$ $[M+H]^+$ 203.1430, found 203.1433.



4f

(*E*)-1-(4-Methoxyphenyl)-3,5-dimethylhex-3-en-2-one (4l):

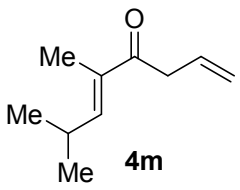
Step-2: Yield: 76%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): 7.09 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.53 (d, J = 9.2 Hz, 1H), 3.90 (s, 2H), 3.75 (s, 3H), 2.76-2.61 (m, 1H), 1.78 (d, J = 1.1 Hz, 3H), 1.04 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.7, 158.0, 149.9, 134.3, 130.0, 129.1, 127.3, 113.6, 54.9, 54.8,



4l

42.9, 28.1, 21.7, 11.2; IR (neat): ν_{max} 2959, 1663, 1510, 1459, 1242, 1177, 1036, 824, 670 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{20}O_2Na$ $[M+Na]^+$ 255.1355, found 255.1351.

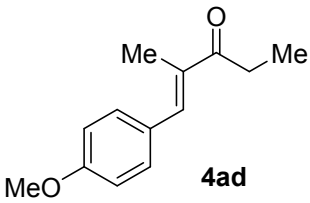
(*E*)-5,7-Dimethylocta-1,5-dien-4-one (4m):



4m

Step-2: Yield: 82%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 6.45 (d, J = 8.3 Hz, 2H), 5.97 (m, 1H), 5.23-5.06 (m, 2H), 3.45 (d, J = 6.7 Hz, 2H), 2.80-2.64 (m, 1H), 1.79 (d, J = 1.5 Hz, 3H), 1.05 (d, J = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7, 149.6, 134.3, 131.9, 117.5, 42.1, 28.1, 21.7, 11.0; IR (neat): ν_{max} 2962, 1668, 1461, 1053, 992, 914 cm^{-1}; HRMS (ESI): calcd for $C_{10}H_{17}O$ $[M+H]^+$ 153.1273, found 153.1281.

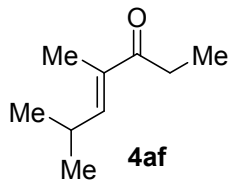
(*E*)-1-(4-Methoxyphenyl)-2-methylpent-1-en-3-one (4ad):



4ad

step-2:[28] Yield: 78%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.48 (s, 1H), 7.40 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.82 (q, J = 7.3 Hz, 2H), 2.08 (s, 3H), 1.16 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.6, 159.6, 137.9, 135.0, 131.3, 128.3, 113.7, 55.1, 30.4, 13.0, 8.8; IR (neat): ν_{max} 2934, 1661, 1602, 1509, 1252, 1176, 1031, 829 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{17}O_2$ $[M+H]^+$ 205.1223, found 205.1227.

(*E*)-4,6-Dimethylhept-4-en-3-one (4af):

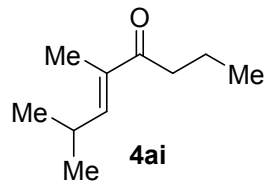


4af

step-2:[29] Yield: 83%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 6.42 (m, 1H), 2.75-2.65 (m, 3H), 1.79 (d, J = 1.3 Hz, 3H), 1.09 (t, J = 7.3 Hz, 3H), 1.05 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.7, 148.4, 134.4, 30.1, 28.0, 21.8, 11.1, 8.7; IR (neat): ν_{max}

2963, 1669, 1460, 1371, 1239, 1046, 799 cm^{-1}; HRMS (ESI): calcd for $C_9H_{17}O$ $[M+H]^+$ 141.1273, found 141.1274.

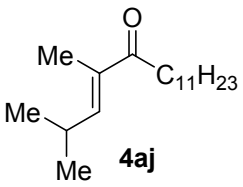
(*E*)-5,7-Dimethyloct-5-en-4-on (4ai):



4ai

step-2: Yield: 86%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 6.42 (d, J = 9.1 Hz, 1H), 2.73 (m, 1H), 2.63 (t, J = 7.3 Hz, 2H), 1.78 (s, 3H), 1.63 (m, 2H), 1.05 (d, J = 6.6 Hz, 6H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.2, 148.5, 134.7, 38.9, 28.0, 21.8, 18.2, 13.7, 11.0; IR (neat): ν_{max} 2960, 1667, 1460, 1371, 1133, 1052 cm^{-1}; HRMS (ESI): calcd for $C_{10}H_{19}O$ $[M+H]^+$ 155.1430, found 155.1424.

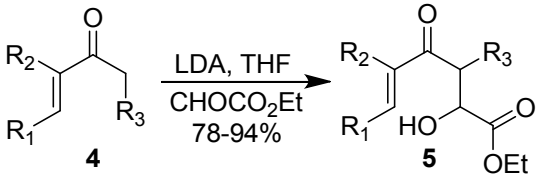
(*E*)-2,4-Dimethylhexadec-3-en-5-one (4aj):



4aj

Step-2: Yield: 78%; colorless oil; R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 6.40 (d, J = 9.2 Hz, 1H), 2.71 (m, 1H), 2.64 (t, J = 7.3 Hz, 2H), 1.78 (d, J = 0.9 Hz, 3H), 1.58 (m, 2H), 1.35-1.19 (m, 16H), 1.05 (d, J = 6.7 Hz, 6H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.7, 148.7, 134.8, 37.2, 31.8, 29.6, 29.5, 29.4, 29.3, 28.1, 25.0, 22.6, 22.0, 14.0, 11.2; IR (neat): ν_{max} 2922, 2855, 1669, 1513, 1460, 1129, 722 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{35}O$ $[M+H]^+$ 267.2682, found 267.2667.

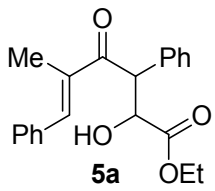
2.2. Typical procedure for the preparation of 5:



To a solution of diisopropylamine (1.2 equiv) in THF (3 mL/mmol) at −78 °C was added drop wise ^{n}BuLi (1 equiv). After 30 min, a solution of the ketone **4** (1 equiv) in a minimal

amount of THF was added *via* cannula over 10 min. After stirring the reaction for 1 h, ethylglyoxalate (2 equiv) was added. After 20 min, the reaction was quenched with saturated aq NH_4Cl, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, the solvent was evaporated, and purified by using silica gel column chromatography to afford **5** in mixture of diastereomers.

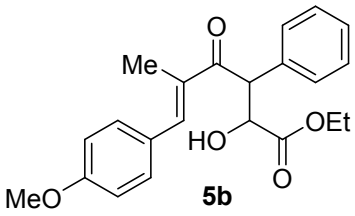
Ethyl (*E*)-2-hydroxy-5-methyl-4-oxo-3,6-diphenylhex-5-enoate (5a): *dr* 1.5:1; Yield: 92%;



5a

colorless oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.40-7.22 (m, 10H), 4.92 (m, 1.6H), 4.68 (t, J = 6.9 Hz, 0.4H), 4.20 (m, 1.3H), 4.05 (m, 0.7H), 3.60 (d, J = 8.4 Hz, 0.3H), 3.41 (bs, 0.5H), 2.03 (s, 3H), 1.22 (t, J = 7.1 Hz, 1.9H), 1.05 (t, J = 7.1 Hz, 1.2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.6, 200.5, 172.9, 172.3, 140.8, 140.5, 136.0, 135.6, 135.2, 135.1, 134.7, 129.5, 129.0, 128.7, 128.5, 128.1, 127.5, 73.7, 72.4, 61.4, 61.0, 56.2, 55.5, 13.8, 13.5, 13.2, 13.1; IR (neat): ν_{max} 3470, 2981, 1730, 1658, 1492, 1448, 1185, 1084, 761, 699 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{22}O_4Na$ $[M+Na]^+$ 361.1410, found 361.1412.

(*E*)-Ethyl 2-hydroxy-6-(4-methoxyphenyl)-5-methyl-4-oxo-3-phenylhex-5-enoate (5b): *dr*

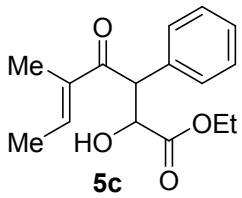


5b

1.5:1; Yield: 91%; light yellow oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 1H), 7.34-7.24 (m, 7H), 6.88 (d, J = 8.0 Hz, 2H), 4.92 (m, 1.6H), 4.70 (m, 0.4H), 4.18 (m, 1.3H), 4.03 (m, 0.8H), 3.79 (s, 3H), 3.74 (bs, 0.3H), 3.58 (bs, 0.5H), 2.04 (m, 3H), 1.20 (t, J = 7.1 Hz, 1.8H), 1.04 (t, J = 7.1 Hz, 1.2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.6, 200.5, 173.0, 172.3, 159.9, 141.0, 140.8, 135.5, 134.9, 134.0, 133.6, 131.7, 131.6, 129.0, 128.7, 128.6, 127.8, 127.5, 113.7, 73.9, 72.5, 61.4, 61.1, 56.0, 55.4, 55.1, 13.9, 13.7, 13.3, 13.2; IR (neat): ν_{max} 3470, 2925,

1731, 1653, 1600, 1509, 1253, 1176, 1027, 827, 762, 702 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{24}O_5Na$ $[M+Na]^+$ 391.1516, found 391.1527.

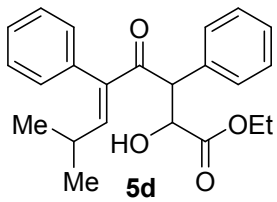
(*E*)-Ethyl 2-hydroxy-5-methyl-4-oxo-3-phenylhept-5-enoate (5c): *dr* 1.5:1; Yield: 93%;



5c

colorless oil; R_f = 0.2 (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.33-7.20 (m, 5H), 6.79 (m, 1H), 4.78 (m, 1.6H), 4.63 (t, J = 6.8 Hz, 0.4H), 4.16 (m, 1.2H), 4.00 (m, 0.9H), 3.74 (br s, 0.4H), 3.55 (br s, 0.5H), 1.75 (s, 6H), 1.19 (t, J = 7.0 Hz, 1.7H), 1.01 (t, J = 7.1 Hz, 1.3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8, 199.7, 172.8, 172.2, 139.9, 139.6, 137.2, 136.8, 135.3, 134.8, 128.9, 128.6, 128.5, 128.4, 127.3, 73.7, 72.4, 61.2, 60.8, 55.5, 54.8, 14.8, 14.7,13.7, 13.5, 11.0, 10.9; IR (neat): ν_{max} 3471, 2979, 1730, 1653, 1450, 1379, 1189, 1080, 1026, 700 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{21}O_4$ $[M+H]^+$ 277.1434, found 277.1430.

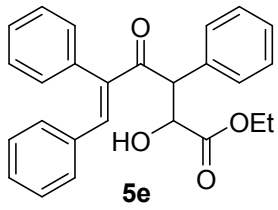
(*E*)-Ethyl 2-hydroxy-7-methyl-4-oxo-3,5-diphenyloct-5-enoate (5d): *dr* 2.3:1; Yield: 86%;



5d

light yellow oil; R_f = 0.2 (20% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.30-7.19 (m, 6H), 6.98 (m, 2H), 6.84 (m, 1H), 6.70 (m, 1H), 4.85 (t, J = 4.7 Hz, 0.7H), 4.50 (m, 1.3H), 4.15 (q, J = 7.1 Hz, 1.4H), 4.03 (q, J = 7.1 Hz, 0.6H), 3.53 (m, 0.3H), 3.25 (t, J = 3.9 Hz, 0.6H), 2.20 (m, 1H), 1.19 (t, J = 7.1 Hz, 2H), 1.05 (t, J = 7.1 Hz, 1H), 0.93 (d, J = 6.6 Hz, 3H), 0.81 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8, 199.4, 172.8, 172.1, 151.8, 151.7, 139.2, 138.9, 135.5, 135.4, 134.4, 133.7, 129.5, 129.4, 129.1, 128.4, 128.3, 127.9, 127.5, 127.3, 73.5, 71.9, 61.4, 61.1, 57.7, 57.0, 28.5, 21.9, 21.7, 13.9, 13.7; IR (neat): ν_{max} 3488, 2964, 2865, 1731, 1675, 1612, 1454, 1303, 1234, 1096, 948, 701 cm^{-1}; HRMS (ESI): calcd for $C_{23}H_{27}O_4$ $[M+H]^+$ 367.1903, found 367.1901.

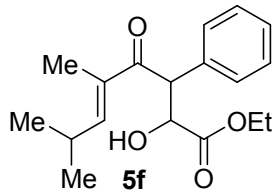
(*E*)-Ethyl 2-hydroxy-4-oxo-3,5,6-triphenylhex-5-enoate (5e): *dr* 1.5:1; Yield: 88%; light yellow oil; R_f = 0.3 (20% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.35-



5e

7.18 (m, 6H), 7.17-7.03 (m, 3H), 7.02-6.86 (m, 6H), 4.88 (m, 0.6H), 4.55 (m, 1.4H), 4.16 (q, J = 7.5 Hz, 1.2H), 4.02 (q, J = 7.5 Hz, 0.9H), 3.65 (m, 0.6H), 3.27 (d, J = 4.5 Hz, 0.5H), 1.20 (t, J = 7.5 Hz, 1.8H), 1.04 (t, J = 7.5 Hz, 1.3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.9, 199.4, 172.8, 172.2, 140.1, 140.0, 139.6, 139.4, 135.9, 135.8, 134.2, 134.1, 134.0, 133.4, 130.9, 130.8, 129.7, 129.5, 129.4, 129.3, 129.2, 128.6, 128.4, 128.3, 128.0, 127.8, 127.7, 127.5, 73.6, 72.2, 61.4, 61.1, 57.7, 57.0, 13.9, 13.7; IR (neat): ν_{max} 3476, 2981, 2926, 1730, 1671, 1592, 1491, 1448, 1378, 1192, 1031, 699 cm^{-1}; HRMS (ESI): calcd for $C_{26}H_{25}O_4$ $[M+H]^+$ 401.1747, found 401.1767.

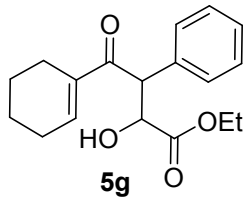
(*E*)-Ethyl 2-hydroxy-5,7-dimethyl-4-oxo-3-phenyloct-5-enoate (5f): *dr* 1.5:1; Yield: 86%; colorless oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.17 (m,



5f

5H), 6.45 (d, J = 9.8 Hz, 0.3H), 6.41 (d, J = 9.8 Hz, 0.7H), 4.85 (t, J = 4.5 Hz, 0.6H), 4.77 (t, J = 7.5 Hz, 1H) 4.65 (m, 0.4H), 4.17 (q, J = 6.0 Hz, 1.2H), 4.01 (q, J = 6.7 Hz, 0.8H); 3.67 (d, J = 8.3 Hz, 0.4H), 3.52 (d, J = 4.5 Hz, 0.6H), 2.672-2.49 (m, 1H), 1.74 (s, 3H), 1.19 (t, J = 6.7 Hz, 1.8H), 1.02 (t, J = 6.7 Hz, 1.2H), 0.99 (d, J = 6.7 Hz, 3.2H), 0.81 (m, 3.1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.4, 200.4, 172.8, 172.3, 151.6, 151.2, 135.5, 135.0, 133.6, 133.1, 128.9, 128.4, 128.3, 127.2, 73.5, 72,2, 61.2, 60.8, 55.7, 55.1, 28.0, 21.5, 21.3, 13.8, 13.5, 11.3, 11.2; IR (neat): ν_{max} 3469, 2964, 1733, 1660, 1457, 1231, 1192, 1038, 702 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{24}O_4Na$ $[M+Na]^+$ 327.1566, found 327.1558.

Ethyl 4-(cyclohex-1-en-1-yl)-2-hydroxy-4-oxo-3-phenylbutanoate (5g): *dr* 2.3:1; Yield: 94%; colorless oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.20

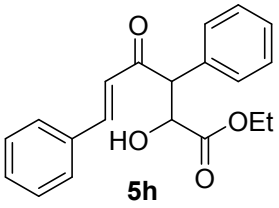


5g

(m, 5H), 6.93 (m, 1H), 4.84 (m, 0.6H), 4.73 (m, 1H), 4.63 (t, J = 8.1 Hz, 0.4H), 4.22-4.08 (m, 1.3H), 4.01 (m, 0.7H), 3.68 (d, J = 8.3 Hz,

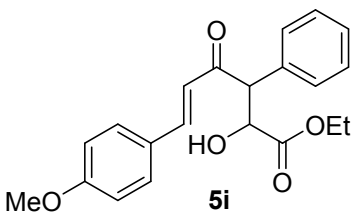
0.3H), 3.52 (d, J = 3.0 Hz, 0.6H), 2.31-2.05 (m, 4H), 1.53 (m, 4H), 1.20 (t, J = 7.1 Hz, 2H) 1.02 (t, J = 7.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.5, 199.4, 172.9, 172.2, 142.3, 142.1, 138.3, 137.8, 135.3, 134.7, 128.9, 128.6, 128.4, 127.4, 73.8, 72.4, 61.3, 61.0, 55.3, 54.6, 26.0, 23.0, 22.9, 21.5, 21.1, 21.0, 13.8, 13.6; IR (neat): ν_{max} 3468, 2932, 1730, 1655, 1492, 1448, 1180, 1089, 702 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{22}O_4Na$ $[M+Na]^+$ 325.1410, found 325.1401.

(*E*)-Ethyl 2-hydroxy-4-oxo-3,6-diphenylhex-5-enoate (5h): *dr* 1.5:1; Yield: 89%; light yellow oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, J = 15.8 Hz, 0.4H), 7.63 (d, J = 16.0 Hz, 0.6H), 7.42 (d, J = 7.6 Hz, 2H), 7.37-7.27 (m, 8H), 6.65 (d, J = 15.8 Hz, 0.4H), 6.63 (d, J = 16.0 Hz, 0.6H), 5.02 (d, J = 3.8 Hz, 0.4H), 4.63 (br s, 0.6H), 4.45 (d, J = 5.9 Hz, 0.6H), 4.42 (d, J = 4.2 Hz, 0.4H), 4.18 (m, 0.8H), 4.09 (m, 1.2H), 3.68 (br s, 0.5H), 3.34 (br s, 0.4H), 1.21 (t, J = 7.1 Hz, 1.2H), 1.09 (t, J = 7.1 Hz, 1.8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.7, 197.1, 172.7, 172.4, 143.9, 143.7, 134.4, 134.0, 133.9, 133.4, 130.6, 130.5, 129.9, 129.3, 128.8, 128.7, 128.3, 127.9, 124.4, 123.9, 73.0, 71.1, 61.5, 61.2, 60.3, 59.9, 14.0, 13.7; IR (neat): ν_{max} 3467, 2925, 1732, 1684, 1606, 1450, 1196, 1086, 751, 698 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{21}O_4$ $[M+H]^+$ 325.1434, found 325.1425.



5h

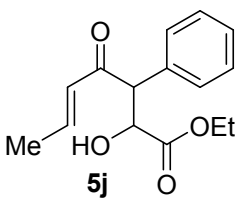
(*E*)-Ethyl 2-hydroxy-6-(4-methoxyphenyl)-4-oxo-3-phenylhex-5-enoate (5i): *dr* 2.3:1; Yield: 89%; light yellow oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (m, 1H), 7.42-7.26 (m, 7H), 6.82 (d, J = 8.6 Hz, 2H), 6.52 (m, 1H), 5.02 (m, 0.4H), 4.64 (m, 0.6H), 4.43 (m, 1H), 4.22-4.03 (m, 2H), 3.81 (br s, 0.6H), 3.78 (s, 3H), 3.50 (br s, 0.4H), 1.21 (t, J = 6.9 Hz, 1H), 1.08 (d, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.8, 197.3, 172.8, 172.4, 161.6, 143.8, 143.6, 134.7, 133.6,



5i

130.2, 130.1, 129.8, 129.3, 128.7, 128.6, 127.7, 126.6, 122.1, 121.7, 114.1, 73.1, 71.2, 61.4, 61.1, 60.1, 59.7, 55.2, 13.9, 13.7; IR (neat): ν_{max} 3468, 2929, 1732, 1677, 1591, 1510, 1251, 1169, 1026, 702 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{22}O_5Na$ $[M+Na]^+$ 377.1359, found 377.1367.

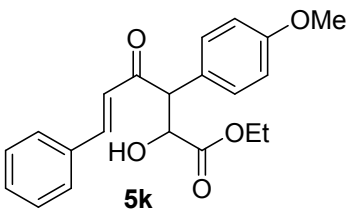
(*E*)-Ethyl 2-hydroxy-4-oxo-3-phenylhept-5-enoate (5j): *dr* 4:1; Yield: 78%; colorless oil;



5j

R_f = 0.2 (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37-7.21 (m, 5H), 6.95 (m, 1H), 6.06 (m, 1H), 4.94 (s, 0.9H), 4.56 (m, 0.2H), 4.31 (m, 1H), 4.16 (m, 1.8H), 4.07 (m, 0.3H), 3.28 (br s, 0.7H), 2.03 (d, *J* = 7.1 Hz, 0.3H), 1.80 (dd, *J* = 1.6, 7.0 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 2.5H), 1.08 (t, *J* = 7.0 Hz, 0.7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8, 197.2, 172.7, 172.3, 144.7, 144.4, 133.4, 130.1, 129.8, 129.6, 129.2, 129.0, 128.8, 128.6, 128.4, 127.9, 127.8, 73.0, 71.1, 61.5, 61.2, 59.5, 59.1, 18.1, 13.9, 13.7; IR (neat): ν_{max} 3478, 2924, 1732, 1688, 1628, 1445, 1223, 1093, 1028, 770, 700 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{19}O_4$ $[M+H]^+$ 263.1277, found 263.1265.

(*E*)-Ethyl 2-hydroxy-3-(4-methoxyphenyl)-4-oxo-6-phenylhex-5-enoate (5k): *dr* 1.5:1;

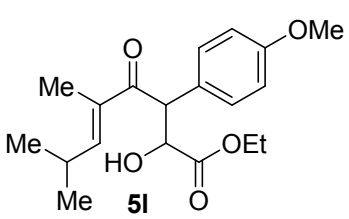


5k

Yield: 83%; light yellow oil; R_f = 0.2 (20% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.5 Hz, 0.4H), 7.61 (d, *J* = 7.5 Hz, 0.5H), 7.44 (m, 1.6H), 7.33 (m, 2.5H), 7.26 (d, *J* = 3.5 Hz, 0.7H), 7.21 (d, *J* = 8.8 Hz, 1.1H), 6.88 (m, 1.6H), 6.74 (m, 0.1), 6.64 (dd, *J* = 5.6, 16.0 Hz, 0.8H), 6.08 (m, 0.1H), 5.00 (d, *J* = 3.9 Hz, 0.3H), 4.59 (d, *J* = 5.6 Hz, 0.4H), 4.39 (d, *J* = 5.8 Hz, 0.5H), 4.36 (d, *J* = 3.9 Hz, 0.3H), 4.28-4.03 (m, 2.4H), 3.77 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 1.9H), 1.12 (t, *J* = 7.1 Hz, 1.1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.9, 197.4, 172.8, 172.4, 159.2, 143.7, 143.5, 134.0, 133.9, 131.0, 130.5, 128.7, 128.3, 126.2, 125.0, 124.2, 123.8, 114.2, 114.1, 77.4, 76.9, 76.5, 72.9, 71.0, 61.5, 61.2, 59.5,

59.1, 55.0, 29.5, 14.0, 13.8; IR (neat): ν_{max} 3466, 2923, 1733, 1681, 1606, 1509, 1453, 1296, 1027, 748, 692 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{23}O_5$ $[M+H]^+$ 355.1540, found 355.1528.

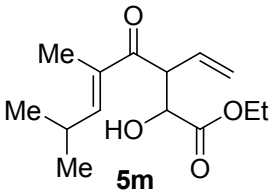
(*E*)-Ethyl 2-hydroxy-3-(4-methoxyphenyl)-5,7-dimethyl-4-oxooct-5-enoate (5l): *dr* 1.5:1;



5l

Yield: 87%; colorless oil; R_f = 0.2 (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.64 (m, 0.4H), 6.43 (m, 0.6H), 4.81 (m, 0.6H), 4.75-4.68 (m, 1H), 4.63 (m, 0.4H), 4.17 (m, 1.3H), 4.02 (q, J = 6.9 Hz, 0.8H), 3.76 (s, 3H), 2.66-2.52 (m, 1H), 1.74 (s, 1H), 1.21 (t, J = 7.1 Hz, 2H), 1.04 (t, J = 6.9 Hz, 1.2H), 1.04 (d, J = 6.6 Hz, 3H); 0.85 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 172.9, 172.3, 158.7, 151.4, 151.1, 133.5, 133.0, 130.0, 129.5, 127.3, 126.8, 113.9, 113.8, 73.6, 72.2, 61.2, 60.9, 54.7, 54.1, 28.0, 21.5, 13.8, 13.6, 11.4, 11.3; IR (neat): ν_{max} 3476, 2962, 1733, 1659, 1460, 1247, 1181, 1031, 819 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{26}O_5Na$ $[M+Na]^+$ 357.1672, found 357.1667.

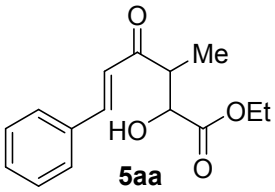
(*E*)-Ethyl 2-hydroxy-5,7-dimethyl-4-oxo-3-vinyloct-5-enoate (5m): *dr* 1:1; Yield: 83%;



5m

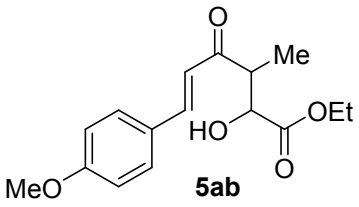
colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 6.52 (d, J = 9.0 Hz, 1H), 6.01-5.83 (m, 1H), 5.29-5.17 (m, 2H), 4.53 (m, 0.5H), 4.43 (m, 0.5H), 4.34-4.13 (m, 3H), 3.81 (d, J = 9.1 Hz, 0.5H), 3.68 (d, J = 4.2 Hz, 0.5H), 2.73 (m, 1H), 1.79 (d, J = 8.0 Hz, 3H), 1.28 (m, 3H), 1.06 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.4, 200.5, 172.6, 172.3, 151.3, 151.0, 134.0, 133.6, 133.1, 132.7, 119.7, 119.4, 72.8, 72.7, 71.9, 71.8, 61.4, 61.0, 53.5, 53.4, 53.1, 28.2, 21.6, 21.5, 13.9, 11.2, 11.1; IR (neat): ν_{max} 3497, 2964, 1765, 1663, 1635, 1370, 1195, 1092, 863, 667 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{22}O_4Na$ $[M+Na]^+$ 277.1410, found 277.1421.

(*E*)-Ethyl 2-hydroxy-3-methyl-4-oxo-6-phenylhex-5-enoate (5aa): *dr* 4:1; Yield: 90%; colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 15.5 Hz, 0.2H), 7.63 (d, J = 16.0 Hz, 0.8H), 7.59 (m, 0.4H), 7.57 (m, 1.7H), 7.41 (m, 3H), 7.14 (d, J = 15.5 Hz, 0.2H), 6.81 (d, J = 16.0 Hz, 0.8H), 4.31 (m, 1H), 4.22 (m, 2H), 3.48 (d, J = 8.5 Hz, 0.9H), 3.40 (m, 0.9H), 3.22 (m, 0.1H), 3.27 (d, J = 4.5 Hz, 0.1H), 1.39-1.29 (m, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.4, 197.2, 173.0, 168.4, 145.6, 143.6, 134.0, 130.5, 128.7, 128.2, 124.0, 120.1, 72.6, 71.0, 68.9, 61.3, 58.4, 47.2, 17.0, 13.9, 13.3, 11.0; IR (neat): ν_{max} 3398, 2923, 2855, 1735, 1683, 1608, 1455, 1206, 1035, 770 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{19}O_4$ $[M+H]^+$ 263.1277, found 263.1268.



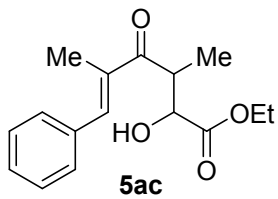
5aa

(*E*)-Ethyl 2-hydroxy-6-(4-methoxyphenyl)-3-methyl-4-oxohex-5-enoate (5ab): *dr* 1.5:1; Yield: 88%; colorless oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (m, 1H), 7.52 (m, 2H), 6.91 (m, 2H), 6.76 (d, J = 15.8 Hz, 0.6H), 6.69 (d, J = 15.8 Hz, 0.4H), 4.60 (m, 0.6H), 4.27 (m, 2.4H), 4.21 (m, 1H), 3.84 (m, 3H), 3.39 (m, 0.4H), 3.31 (m, 0.6H), 1.37-1.22 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.6, 200.5, 173.1, 173.0, 161.7, 161.6, 143.4, 130.0, 126.7, 121.8, 121.5, 114.2, 72.8, 71.1, 61.6, 61.3, 55.1, 47.4, 46.9, 13.9, 13.5, 11.1; IR (neat): ν_{max} 3468, 2928, 2848, 1733, 1678, 1592, 1510, 1249, 1171, 1026, 826 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{21}O_5$ $[M+H]^+$ 293.1383, found 293.1368.



5ab

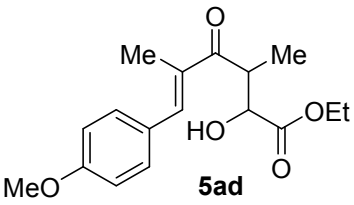
(*E*)-Ethyl 2-hydroxy-3,5-dimethyl-4-oxo-6-phenylhex-5-enoate (5ac): *dr* 4:1; Yield: 91%; colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (s, 0.8H), 7.52 (s, 0.2H), 7.45-7.40 (m, 3.8H), 7.39-7.33 (m, 1H), 4.35 (m, 0.2H), 4.28 (m, 1.8H), 4.20 (m, 0.4H), 3.90 (m, 0.2H), 3.85 (m, 0.8H), 3.67 (m, 0.2H), 3.41 (m, 0.7H), 2.09 (d, J = 1.0 Hz, 2.4H), 2.06 (d,



5ac

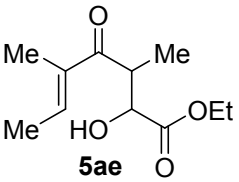
J = 1.0 Hz, 0.6H), 1.36-1.23 (m, 5.6H), 1.21 (m, 0.7H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.7, 203.4, 173.0, 139.1, 138.8, 136.2, 135.9, 135.3, 135.2, 129.4, 128.3, 128.1, 73.2, 71.9, 63.8, 61.3, 61.0, 43.0, 42.5, 24.8, 14.2, 13.8, 13.0, 12.8; IR (neat): ν_{max} 3470, 2982, 1731, 1660, 1450, 1373, 1208, 1024, 767 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{20}O_4Na$ $[M+Na]^+$ 299.1253, found 299.1248.

(*E*)-Ethyl 2-hydroxy-6-(4-methoxyphenyl)-3,5-dimethyl-4-oxohex-5-enoate (5ad): *dr* 4:1; Yield: 88%; colorless oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 0.8H), 7.49 (s, 0.2H), 7.44 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 4.52 (br s, 0.8H), 4.34 (br s, 0.2H), 4.32-4.25 (m, 1.6H), 4.22-4.16 (m, 0.5H), 3.85 (m, 3.9H), 3.80 (m, 0.2H), 3.56 (m, 0.7H), 2.10 (s, 2.4H), 2.08 (s, 0.6H), 1.36-1.23 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.1, 203.8, 173.1, 159.9, 139.6, 139.3, 134.2, 133.9, 131.7, 131.6, 128.0, 127.9, 113.8, 72.6, 72.1, 61.6, 61.2, 55.1, 42.8, 42.2, 14.9, 14.0, 13.2, 13.1, 13.0; IR (neat): ν_{max} 3469, 2927, 1731, 1655, 1600, 1510, 1249, 1176, 1020, 829 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{22}O_5Na$ $[M+Na]^+$ 329.1359, found 329.1367.



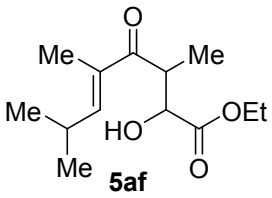
5ad

(*E*)-Ethyl 2-hydroxy-3,5-dimethyl-4-oxohept-5-enoate (5ae): *dr* 4:1; Yield: 91%; colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80 (m, 1H), 4.43 (t, J = 3.7 Hz, 0.7H), 4.30-4.16 (m, 2.2H), 3.77-3.63 (m, 1.2H), 3.48 (d, J = 3.7 Hz, 0.7H), 1.90 (d, J = 6.7 Hz, 3H), 1.80 (s, 2.3H), 1.77 (s, 0.7H), 1.30 (t, J = 7.5 Hz, 2.4H), 1.25 (m, 0.6H), 1.23 (d, J = 3.0 Hz, 0.6H), 1.18 (d, J = 7.5 Hz, 2.4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.2, 173.1, 138.2, 137.1, 72.0, 61.6, 42.5, 14.8, 14.0, 12.8, 11.1; IR (neat): ν_{max} 3469, 2979, 2927, 1729, 1656, 1454, 1206, 1025, 856 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{18}O_4Na$ $[M+Na]^+$ 237.1097, found 237.1093.



5ae

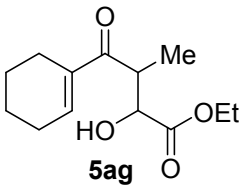
(*E*)-Ethyl 2-hydroxy-3,5,7-trimethyl-4-oxooct-5-enoate (5af): *dr* 2.3:1; Yield: 87%;



5af

colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.45 (d, J = 9.3 Hz, 1H), 4.44 (q, J = 3.5 Hz, 0.8H), 4.30-4.24 (m, 1.8H), 4.22-4.14 (m, 0.4H), 3.76-3.65 (m, 1.2H), 3.44 (m, 0.7H), 2.79-2.69 (m, 1H), 1.80 (s, 2.3H), 1.78 (s, 0.8H), 1.34-1.29 (m, 2.4H), 1.28-1.23 (m, 1.5 H), 1.19 (d, J = 7.1 Hz, 2.5H), 1.07 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.3, 203.9, 173.1, 150.4, 150.1, 134.0, 133.6, 73.5, 72.0, 61.6, 61.2, 42.6, 42.0, 28.3, 21.8, 15.0, 14.0, 12.9, 11.3, 11.2; IR (neat): ν_{max} 3487, 2965, 1733, 1662, 1458, 1372, 1201, 1025 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{22}O_4Na$ $[M+Na]^+$ 265.1410, found 265.1404.

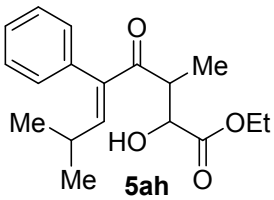
Ethyl 4-(cyclohex-1-en-1-yl)-2-hydroxy-3-methyl-4-oxobutanoate (5ag): *dr* 4:1; Yield:



5ag

92%; colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97 (s, 1H), 4.43 (t, J = 4.4 Hz, 0.7H), 4.29-4.22 (m, 1.7H), 4.19 (t, J = 6.8, Hz, 0.4H), 3.78 (d, J = 9.3 Hz, 0.2H), 3.70-3.62 (m, 1H), 3.56 (d, J = 4.4 Hz, 0.7H), 2.32-2.19 (m, 4H), 1.69-1.59 (m, 4H), 1.30 (t, J = 7.1 Hz, 2H), 1.28-1.23 (m, 1.5H), 1.18 (d, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.9, 202.6, 173.0, 172.9, 141.1, 140.7, 138.2, 137.8, 73.4, 71.8, 61.4, 61.0, 42.2, 41.7, 25.9, 22.9, 22.7, 21.6, 21.5, 21.2, 21.1, 14.6, 13.9, 12.6; IR (neat): ν_{max} 3469, 2933, 1732, 1660, 1452, 1197, 988, 926 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{20}O_4Na$ $[M+Na]^+$ 263.1253, found 263.1260.

(*E*)-Ethyl 2-hydroxy-3,7-dimethyl-4-oxo-5-phenyloct-5-enoate (5ah): *dr* 9:1; Yield: 89%;

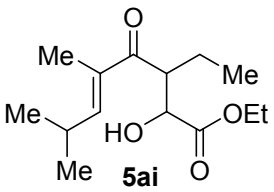


5ah

colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.32 (m, 1H), 7.13 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 8.3 Hz, 1H), 4.46 (t, J = 4.4 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.51 (m, 1H), 3.41 (br s, 1H), 2.40 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.21 (d, J = 7.1 Hz, 0.4H), 1.15 (d, J = 7.1 Hz, 2.6H), 1.03-0.97 (m, 6H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ 204.3, 202.6, 172.9, 150.7, 150.5, 139.2, 138.9, 135.6, 135.4, 129.1, 128.0, 127.3, 73.1, 71.4, 61.4, 61.1, 44.1, 43.6, 28.6, 21.9, 13.9, 12.1; IR (neat): ν_{max} 3491, 2966, 1732, 1676, 1617, 1455, 1371, 1211, 1030, 704 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{24}O_4Na$ $[M+Na]^+$ 327.1566, found 327.1573.

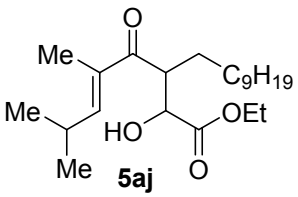
(*E*)-Ethyl 3-ethyl-2-hydroxy-5,7-dimethyl-4-oxooct-5-enoate (5ai): *dr* 4:1; Yield: 83%;



5ai

colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 6.46 (d, *J* = 9.6 Hz, 0.8H), 6.43 (d, *J* = 12.3 Hz, 0.2H), 4.35 (t, *J* = 5.1 Hz, 0.8H), 4.31 (m, 0.2H), 4.24 (q, *J* = 7.1 Hz, 1.5H), 4.16 (q, *J* = 7.1 Hz, 0.4H), 3.90 (d, *J* = 10.0 Hz, 0.2H), 3.57 (m, 1H), 3.36 (d, *J* = 4.7 Hz, 0.7H), 2.78-2.70 (m, 1H), 1.81 (s, 2.7H), 1.78 (s, 1H), 1.76-1.67 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 2.4H), 1.24 (t, *J* = 7.0 Hz, 0.6H), 1.07 (d, *J* = 6.7 Hz, 6H), 0.96 (t, *J* = 7.4 Hz, 0.6H), 0.87 (t, *J* = 7.4 Hz, 2.5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.8, 203.4, 173.4, 173.2, 150.9, 150.3, 135.2, 135.1, 71.6, 71.3, 61.5, 61.0, 49.4, 47.8, 29.4, 28.2, 22.8, 21.7, 13.8, 11.8, 11.7, 11.1, 10.9; IR (neat): ν_{max} 3484, 2964, 1733, 1658, 1459, 1373, 1197, 1036 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{24}O_4Na$ $[M+Na]^+$ 279.1566, found 279.1578.

(*E*)-Ethyl 3-(2,4-dimethylpent-2-enoyl)-2-hydroxytridecanoate (5aj): *dr* 9:1; Yield: 86%;

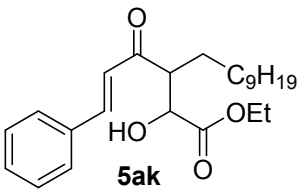


5aj

colorless oil; R_f = 0.3 (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 6.45 (d, *J* = 9.3 Hz, 0.9H), 6.42 (d, *J* = 9.4 Hz, 0.1H), 4.33 (t, *J* = 4.7 Hz, 0.9H), 4.28 (t, *J* = 3.9 Hz, 0.1H), 4.25 (q, *J* = 7.1 Hz, 1.8H), 4.15 (q, *J* = 7.1 Hz, 0.3H), 3.89 (d, *J* = 10.2 Hz, 0.1H), 3.63 (m, 1H), 3.28 (d, *J* = 4.5 Hz, 0.8H), 2.74 (m, 1H), 1.81 (d, *J* = 1.2 Hz, 2.5H), 1.77 (d, *J* = 1.2 Hz, 0.5H), 1.73 (m, 1H), 1.64 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.23 (m, 12.3H), 1.07 (d, *J* = 6.7 Hz, 6H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.7, 173.5, 150.4, 135.2, 71.6, 71.5, 61.6, 48.1, 48.0, 31.7, 29.5, 29.4, 29.3, 29.2, 28.5, 28.3, 27.4, 22.5, 21.9, 21.8, 14.0, 11.3; IR

(neat): ν_{max} 3479, 2923, 2856, 1733, 1661, 1460, 1217, 1096, 1034 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{41}O_4$ $[M+H]^+$ 369.2999, found 369.3015.

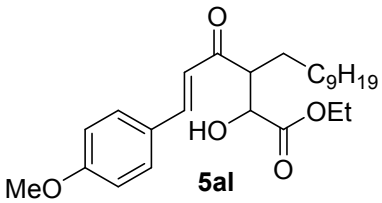
Ethyl 3-cinnamoyl-2-hydroxytridecanoate (5ak): *dr* 1:1; Yield: 88%; colorless oil; R_f = 0.3



5ak

(20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72-7.48 (m, 3H), 7.40 (s, 3H), 6.87 (d, J = 16.0 Hz, 0.5H), 6.81 (d, J = 16.2 Hz, 0.5H), 4.47 (m, 0.5H), 4.39-4.12 (m, 2.6H), 3.68 (d, J = 9.0 Hz, 0.5H), 3.39-3.22 (m, 1.5H), 1.81 (m, 1.8H), 1.65 (m, 0.8H), 1.47-1.07 (m, 20.4H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.3, 200.7, 173.3, 143.8, 143.3, 134.2, 134.0, 130.6, 130.5, 128.8, 128.3, 125.2, 125.0, 71.4, 70.9, 70.8, 61.7, 61.3, 53.5, 52.1, 31.7, 29.4, 29.1, 28.4, 27.3, 22.5, 13.9; IR (neat): ν_{max} 3473, 2922, 2855, 1733, 1678, 1607, 1454, 1199, 1092, 760, 695 cm^{-1}; HRMS (ESI): calcd for $C_{24}H_{37}O_4$ $[M+H]^+$ 389.2686, found 389.2688.

(*E*)-Ethyl 2-hydroxy-3-(3-(4-methoxyphenyl)acryloyl)tridecanoate (5al): *dr* 1:1; Yield:

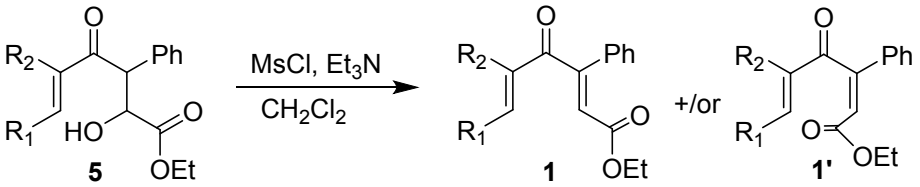


5al

86%; colorless oil; R_f = 0.2 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64-7.50 (m, 3H), 6.92 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 16.0 Hz, 0.6H), 6.67 (d, J = 16.0 Hz, 0.5H), 4.46 (t, J = 4.2 Hz, 0.5H), 4.34-4.23 (m, 2H), 4.19 (m, 1H), 3.85 (s, 3H), 3.72 (d, J = 9.6 Hz, 0.5H), 3.30 (m, 1H), 3.25 (m, 1H), 1.89-1.72 (m, 2H), 1.34-1.20 (m, 20H), 0.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.6, 200.9, 173.5, 173.4, 161.8, 161.7, 143.4, 130.2, 126.9, 126.7, 123.1, 122.9, 114.3, 71.1, 70.9, 61.8, 61.4, 53.3, 51.7, 31.8, 29.4, 29.2, 28.7, 27.6, 27.5, 27.4, 22.6, 14.0; IR (neat): ν_{max} 3469, 2923, 2853, 1734, 1677, 1595, 1511, 1252, 1171, 983, 826 cm^{-1}; HRMS (ESI): calcd for $C_{25}H_{39}O_5$ $[M+H]^+$ 419.2792, found 419.2784.

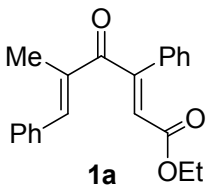
2.3. Typical procedure for the preparation of divinylketones 1 or/and 1':

Method A:



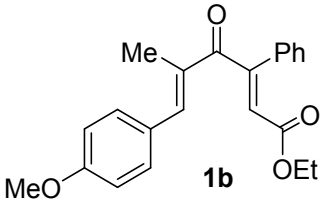
A round-bottomed flask was charged with alcohol **5** (1.0 equiv) and CH_2Cl_2 (3 mL). The resulting solution was stirred and cooled to 0 °C before adding sequentially Et_3N (10.0 equiv) and methanesulfonyl chloride (4.0 equiv). The resulting solution was stirred at rt until TLC showed the complete consumption of starting material. The resulting suspension was diluted with EtOAc, quenched with saturated aq $NaHCO_3$, extracted with EtOAc and washed with saturated aq NaCl solution. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in *vacuo.* The obtained crude product was purified by using silica gel column chromatography to give **1** or separable **1** and **1'.**

Ethyl (2*E*,5*E*)-5-methyl-4-oxo-3,6-diphenylhexa-2,5-dienoate (1a): Yield: 82% (from **5a**);



colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.44-7.32 (m, 10H), 6.16 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 2.13 (d, J = 1.2 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 165.1, 153.4, 145.0, 135.8, 135.1, 134.6, 129.8, 129.1, 128.6, 128.4, 128.1, 128.0, 121.6, 60.5, 13.7, 13.0; IR (neat): ν_{max} 2926, 1721, 1652, 1620, 1444, 1365, 1237, 1194, 1028, 761, 696 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_3$ $[M+H]^+$ 321.1485, found 321.1474.

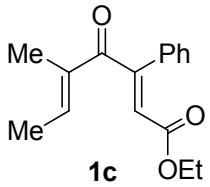
Ethyl (2*E*,5*E*)-6-(4-methoxyphenyl)-5-methyl-4-oxo-3-phenylhexa-2,5-dienoate (1b):



Yield: 86% (from **5b**); light yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.44-7.38 (m, 4H), 7.35 (m, 3H), 6.92 (d, J = 8.8 Hz, 2H), 6.12 (s,

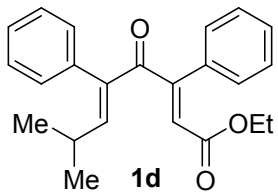
1H), 4.10 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 2.14 (d, J = 0.7 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 165.1, 160.3, 153.8, 145.3, 134.7, 133.5, 131.9, 128.9, 127.9, 127.6, 121.0, 113.9, 60.8, 55.1, 13.7, 12.9; IR (neat): ν_{max} 2925, 1718, 1644, 1597, 1508, 1257, 1166, 1028, 831, 767, 698 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{23}O_4$ $[M+H]^+$ 351.1590, found 351.1602.

Ethyl (2*E*,5*E*)-5-methyl-4-oxo-3-phenylhepta-2,5-dienoate (1c): Yield: 79% (from **5c**);



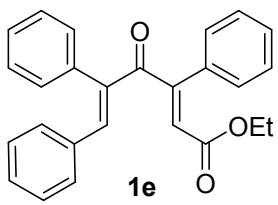
colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.30 (m, 5H), 6.57 (m, 1H), 6.35 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 1.96 (s, 3H) 1.80 (d, J = 6.9 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.8, 164.8, 156.2, 141.5, 138.2, 134.7, 129.9, 128.7, 126.3, 116.9, 60.3, 14.6, 13.8, 10.2; IR (neat): ν_{max} 2982, 2926, 1711, 1652, 1446, 1365, 1272, 1168, 1029, 769, 690 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{19}O_3$ $[M+H]^+$ 259.1328, found 259.1326.

(2*E*,5*E*)-ethyl 7-methyl-4-oxo-3,5-diphenylocta-2,5-dienoate (1d): Yield: 87% (from **5d**);



colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.28 (m, 6H), 7.21 (m, 2H), 6.99 (m, 2H), 6.60 (d, J = 10.3 Hz, 1H), 6.29 (s, 1H), 4.07 (q, J = 7.1 Hz, 2H), 2.44 (m, 1H), 1.11 (t, J = 7.1 Hz, 3H), 0.94 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.1, 165.2, 154.7, 153.5, 138.7, 134.7, 134.4, 129.2, 128.4, 128.2, 128.0, 127.8, 127.4, 122.7, 60.5, 28.6, 21.9, 13.7; IR (neat): ν_{max} 2923, 2858, 1719, 1662, 1623, 1451, 1369, 1168, 1031, 699 cm^{-1}; HRMS (ESI): calcd for $C_{23}H_{25}O_3$ $[M+H]^+$ 349.1798, found 349.1795.

(2*E*,5*E*)-Ethyl 4-oxo-3,5,6-triphenylhexa-2,5-dienoate (1e): Yield: 71% (from **5e**); white

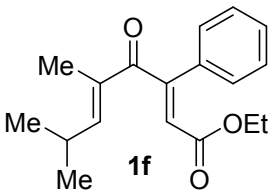


solid, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.32-7.28 (m, 6H), 7.25-7.20 (m, 3H), 7.17-7.13 (m, 2H), 7.05-7.00 (m, 4H), 6.35 (s, 1H), 4.08 (q, J = 7.1 Hz, 2H), 1.12 (t,

J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.3, 165.2, 153.6, 143.2, 139.6, 135.0, 134.1, 130.7, 129.6, 129.5, 128.7, 128.6, 128.2, 127.9, 122.8, 60.6, 13.8; IR (neat): ν_{max} 2923, 1717, 1549, 1499,1452, 1222, 1144, 1017, 696 cm^{-1}; HRMS (ESI): calcd for $C_{26}H_{23}O_3$ $[M+H]^+$ 383.1641, found 383.1663.

*Compounds **1f** (59%) and **1'f** (19%) were obtained from **5f**.*

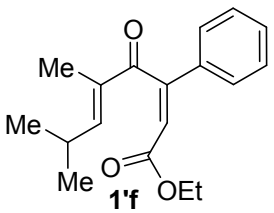
(2*E*,5*E*)-Ethyl 5,7-dimethyl-4-oxo-3-phenylocta-2,5-dienoate (1f): colorless oil, R_f = 0.45



1f

(10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.28 (m, 5H), 6.49 (m, 1H), 6.04 (s, 1H), 4.8 (q, J = 7.1 Hz, 2H) 2.76-2.62(m, 1H), 1.83 (d, J = 1.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H), 0.99 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 165.1, 155.9, 153.4, 134.8, 133.5, 128.3, 127.8, 127.7, 121.3, 60.3, 28.3, 21.5, 13.6, 11.0; IR (neat): ν_{max} 2965, 1721, 1652, 1457, 1252, 1202, 1167, 1031, 697 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{21}O_3$ $[M-H]^+$ 285.1485, found 285.1479.

(2*Z*,5*E*)-Ethyl 5,7-dimethyl-4-oxo-3-phenylocta-2,5-dienoate (1'f): colorless oil, R_f = 0.4

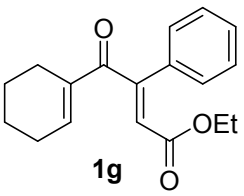


1'f

(10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-7.29 (m, 5H), 6.36 (s, 1H), 6.27 (d, J = 9.2 Hz, 1H) , 4.15 (q, J = 7.1 Hz, 2H), 2.78-2.64 (m, 1H), 1.96 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H), 0.94 (d, J = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 165.0, 155.9, 153.2, 135.2, 130.0, 128.8, 126.6, 117.4, 60.6, 28.2, 21.5, 14.0, 10.7; IR (neat): ν_{max} 2963, 1713, 1658, 1453, 1271, 1173, 1032, 772, 690 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{22}O_3Na$ $[M+Na]^+$ 309.1461, found 309.1453.

*Compounds **1g** (59%) and **1'g** (25%) were obtained from **5g**.*

(*E*)-Ethyl 4-(cyclohex-1-en-1-yl)-4-oxo-3-phenylbut-2-enoate (1g): colorless oil, R_f = 0.45

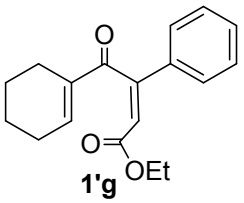


1g

(10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (m, 5H),

7.01 (m, 1H), 6.01 (s, 1H), 4.07 (q, J = 7.1 Hz, 2H), 2.29-2.25 (m, 4H), 1.67-1.58 (m, 4H), 1.11 (m, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3, 165.1, 153.0, 147.0, 138.1, 134.5, 128.4, 127.9, 127.8, 121.0, 60.4, 26.2, 22.7, 21.4, 21.2, 13.6; IR (neat): ν_{max} 2931, 1719, 1644, 1490, 1445, 1230, 1189, 1032, 772, 699 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485, found 285.1478.

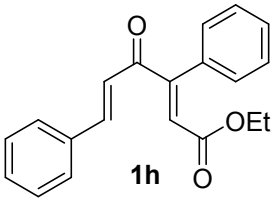
(*Z*)-Ethyl 4-(cyclohex-1-en-1-yl)-4-oxo-3-phenylbut-2-enoate (1'g): colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (m, 2H), 7.38 (m, 3H), 6.71 (m, 1H), 6.34 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.42 (m, 2H), 2.17 (m, 2H), 1.69 (m, 2H), 1.61 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 165.0, 156.0, 143.9, 139.3, 134.9, 130.0, 128.8, 126.5, 117.2, 60.5, 25.9, 22.3, 21.5, 21.4, 13.9; IR (neat): ν_{max} 2935, 1706, 1668, 1618, 1447, 1379, 1272, 1172, 1032, 769, 693 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485, found 285.1478.



1'g

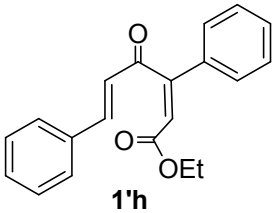
*Compounds **1h** (59%) and **1'h** (19%) were obtained from **5h**.*

(2*E*,5*E*)-ethyl 4-oxo-3,6-diphenylhexa-2,5-dienoate (1h): light yellow oil; R_f = 0.45 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.39 (m, 4H), 7.34 (d, J = 16.3 Hz, 1H), 7.31-7.25 (m, 6H), 6.85 (d, J = 16.3 Hz, 1H), 6.34 (s, 1H), 4.08 (q, J = 7.1 Hz, 2H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.6, 164.9, 155.5, 145.3, 134.1, 130.6, 130.3, 128.9, 128.7, 128.3, 126.8, 117.3, 60.8, 13.9; IR (neat): ν_{max} 2923, 1710, 1654, 1611, 1347, 1275, 1169, 770, 692 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1328, found 307.1319.



1h

(2*Z*,5*E*)-ethyl 4-oxo-3,6-diphenylhexa-2,5-dienoate (1'h): light yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 15.8 Hz, 1H), 7.39 (m, 2H), 7.33 (m, 3H), 7.29 (m, 3H), 7.22 (m, 2H), 6.78 (d,

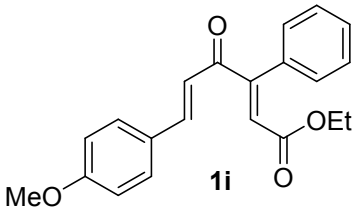


1'h

J = 15.8 Hz, 1H), 6.65 (s, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.0, 165.5, 151.8, 145.8, 134.5, 134.2, 130.9, 129.0, 128.8, 128.6, 128.5, 128.2, 125.3, 122.8, 60.7, 13.8; IR (neat): ν_{max} 2923, 1710, 1654, 1611, 1347, 1275, 1169, 770, 692 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1328, found 307.1318.

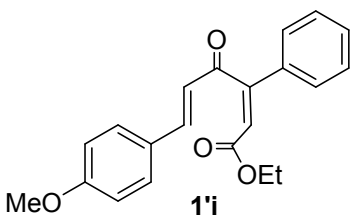
*Compounds **1i** (55%) and **1'i** (21%) were obtained from **5i**.*

(2*E*,5*E*)-ethyl 6-(4-methoxyphenyl)-4-oxo-3-phenylhexa-2,5-dienoate (1i): light yellow oil; R_f = 0.4 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (m, 2H), 7.43 (m, 3H), 7.38 (m, 3H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 16.3 Hz, 1H), 6.41 (s, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5, 165.0, 161.7, 155.7, 145.3, 134.3, 130.2, 128.9, 126.8, 124.6, 117.2, 114.2, 60.7, 55.3, 14.0; IR (neat): ν_{max} 2924, 1710, 1647, 1593, 1508, 1252, 1159, 1099, 1026, 825, 753, 686 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{20}O_4Na$ $[M+Na]^+$ 359.1253, found 359.1257.



1i

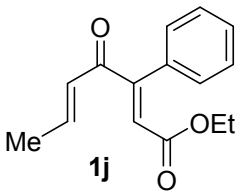
(2*Z*,5*E*)-ethyl 6-(4-methoxyphenyl)-4-oxo-3-phenylhexa-2,5-dienoate (1'i): light yellow oil; R_f = 0.45 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 15.7 Hz, 1H), 7.44-7.39 (m, 5H), 7.30 (m, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 15.7 Hz, 1H), 6.70 (s, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.0, 165.6, 162.0, 152.2, 145.8, 134.8, 130.5, 128.6, 128.5, 128.1, 127.0, 124.0, 120.6, 114.4, 60.7, 55.3, 13.8; IR (neat): ν_{max} 2924, 1710, 1647, 1593, 1508, 1251, 1159, 1100, 1027, 826, 763, 690 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1434, found 337.1419.



1'i

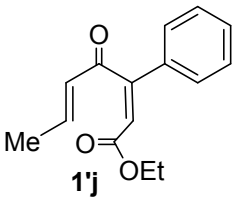
*Compounds **1j** (56%) and **1'j** (14%) were obtained from **5j**.*

(2*E*,5*E*)-ethyl 4-oxo-3-phenylhepta-2,5-dienoate (1j): colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (m, 2H), 7.39 (m, 3H), 6.73 (m, 1H), 6.36-6.31 (dq, *J* = 1.5, 15.8 Hz, 1H), 6.34 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.89 (dd, *J* = 1.6, 6.8 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.5, 165.1, 155.8, 146.3, 132.4, 130.1, 128.8, 126.6, 117.0, 60.7, 18.4, 13.9; IR (neat): ν_{max} 2923, 2854, 1716, 1645, 1627, 1445, 1176, 1025, 849, 769, 697 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1161.



1j

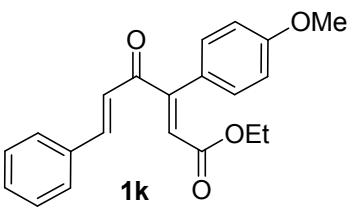
(2*Z*,5*E*)-Ethyl 4-oxo-3-phenylhepta-2,5-dienoate (1'j): colorless oil, R_f = 0.45 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 3H), 7.24 (m, 2H), 7.03 (m, 1H), 6.58 (s, 1H), 6.28 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 1.88 (dd, *J* = 1.6, 7.0 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.3, 165.4, 151.7, 146.9, 134.4, 128.4, 128.0, 124.9, 60.6, 18.5, 13.7; IR (neat): ν_{max} 2926, 1720, 1640, 1623, 1446, 1178, 1030, 969, 771, 700 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1164.



1'j

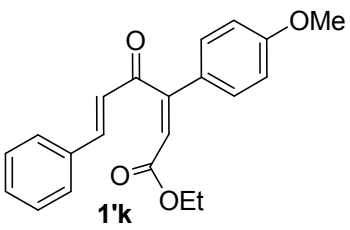
*Compounds **1m** (34%) and **1'm** (48%) were obtained from **5m**.*

(2*E*,5*E*)-Ethyl 3-(4-methoxyphenyl)-4-oxo-6-phenylhexa-2,5-dienoate (1k): light yellow oil; R_f = 0.4 (15% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.32 (m, 8H), 6.94 (d, *J* = 15.1 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.34 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.2, 165.3, 161.4, 155.2, 145.2, 134.2, 130.6, 128.8, 128.5, 128.4, 126.9, 114.7, 114.4, 60.7, 55.3, 14.0; IR (neat): ν_{max} 2922, 2853, 1708, 1654, 1596, 1511, 1254, 1166, 1029, 832 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1434, found 337.1423.



1k

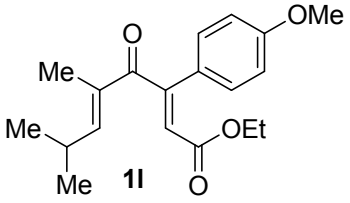
(2*Z*,5*E*)-Ethyl 3-(4-methoxyphenyl)-4-oxo-6-phenylhexa-2,5-dienoate (1'k): light yellow oil; R_f = 0.45 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, J = 15.8 Hz, 1H), 7.48 (m, 2H), 7.36 (m, 3H), 7.26 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 15.8 Hz, 1H), 6.61 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 165.6, 159.9, 151.8, 145.7, 134.2, 130.8, 130.3, 128.8, 128.5, 126.3, 123.9, 123.1, 113.6, 60.6, 55.1, 13.9; IR (neat): ν_{max} 2925, 1717, 1662, 1601, 1510, 1250, 1171, 1030, 834, 769 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1434, found 337.1421.



1'k

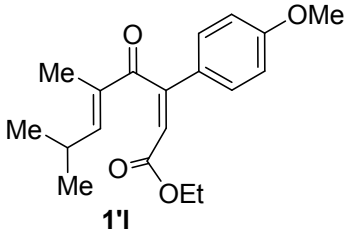
*Compounds **1n** (67%) and **1'n** (17%) were obtained from **5n**.*

(2*E*,5*E*)-Ethyl 3-(4-methoxyphenyl)-5,7-dimethyl-4-oxoocta-2,5-dienoate (1l): colorless oil, R_f = 0.45 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.46 (d, J = 9.6 Hz, 1H), 5.95 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.80 (d, J = 1.2 Hz, 3H), 2.74-2.64 (m, 1H), 1.82 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H), 0.99 (d, J = 6.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.1, 165.4, 159.9, 156.2, 153.5, 133.6, 129.7, 126.8, 119.9, 113.3, 60.4, 55.2, 55.1, 28.4, 21.6, 13.9, 11.1; IR (neat): ν_{max} 2963, 1719, 1651, 1606, 1510, 1250, 1168, 1030, 833 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{24}O_4Na$ $[M+Na]^+$ 339.1566, found 339.1562.



1l

(2*Z*,5*E*)-Ethyl 3-(4-methoxyphenyl)-5,7-dimethyl-4-oxoocta-2,5-dienoate (1'l): colorless oil, R_f = 0.4 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.28 (s, 1H), 6.26 (m, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.82 (s, 1H), 2.75-2.67 (m, 1H), 1.96 (d, J = 1.3 Hz, 3H), 1.25 (t, J = 7.1

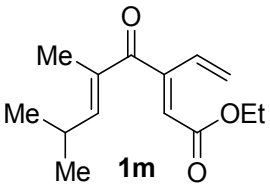


1'l

Hz, 3H), 0.94 (d, J = 6.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.2, 165.2, 161.1, 155.5, 153.1, 135.2, 128.3, 127.4, 114.8, 114.2, 60.4, 55.3, 55.2, 28.1, 21.6, 14.1, 10.7; IR (neat): ν_{max} 2962, 1710, 1658, 1597, 1512, 1255, 1168, 1030, 833 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{24}O_4Na$ $[M+Na]^+$ 339.1566, found 339.1561.

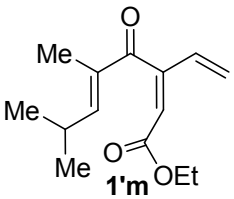
*Compounds **1m** (64%) and **1'm** (18%) were obtained from **5m**.*

(2*E*,5*E*)-Ethyl 5,7-dimethyl-4-oxo-3-vinylocta-2,5-dienoate (1m): colorless oil, R_f = 0.5



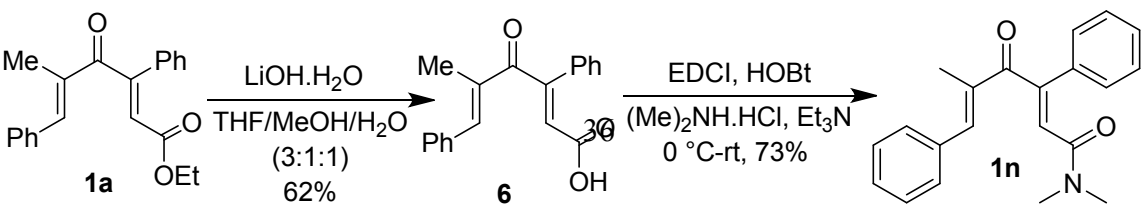
(15% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (dd, J = 10.9, 17.9 Hz, 1H), 6.36 (d, J = 9.4 Hz, 1H), 5.60 (s, 1H), 5.50 (d, J = 10.9 Hz, 1H), 5.30 (d, J = 17.9 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.77-2.61 (m, 1H), 1.82 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 0.99 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.2, 165.2, 156.9, 153.7, 134.2, 131.0, 130.9, 124.5, 117.7, 60.4, 28.5, 21.5, 14.1, 10.5; IR (neat): ν_{max} 2965, 1714, 1657, 1587, 1264, 1213, 1162, 998, 867 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1485, found 237.1494.

(2*Z*,5*E*)-Ethyl 5,7-dimethyl-4-oxo-3-vinylocta-2,5-dienoate (1'm): colorless oil, R_f = 0.4

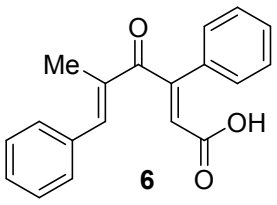


(15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.44 (m, 1H), 6.19 (dq, J = 1.3, 9.4 Hz, 1H), 5.87 (s, 1H), 5.46 (d, J= 10.6 Hz, 1H), 5.29 (d, J= 17.5 Hz, 1H), 4.07 (q, J = 7.1 Hz, 1H), 2.74-2.64 (m, 1H), 1.88 (d, J = 1.3 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H), 0.95 (d, J = 6.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.3, 164.9, 154.7, 153.1, 135.2, 134.8, 124.0, 120.0, 60.5, 28.1, 21.6, 14.0, 10.4; IR (neat): ν_{max} 2964, 1713, 1661, 1598, 1368, 1261, 1218, 1152, 999, 875 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1485, found 237.1493.

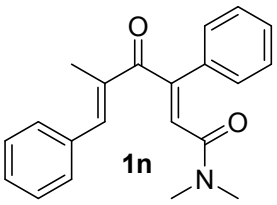
Synthesis of 1n from 1a:



(2*E*,5*E*)-5-Methyl-4-oxo-3,6-diphenylhexa-2,5-dienoic acid (6): To an ester **1a** (260 mg, 0.813 mmol) in THF/MeOH/H_2O (3:1:1, 5 mL) at 0 °C was added $LiOH{\cdot}H_2O$ (68.0 mg, 1.625 mmol), and the reaction was allowed to stir for 4 h. The reaction mixture was acidified to pH 2 with 1 N HCl, the residue was extracted with EtOAc (25 mL) and washed with H_2O and brine, and the organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by using silica gel column chromatography (EtOAc/hexane) to furnish the acid **6** (147 mg, 62%). R_f = 0.3 (50% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 1.2 Hz, 1H), 7.43-7.39 (m, 5H), 7.35 (m, 4H), 7.27 (m, 1H), 6.11 (s, 1H), 2.12 (d, J = 1.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.5, 169.9, 156.0, 145.6, 135.7, 135.0, 134.0, 129.9, 129.3, 129.1, 128.5, 128.2, 128.0, 120.0, 12.9; IR (neat): ν_{max} 3026, 2923, 1682, 1652, 1448, 1391, 1285, 1218, 1074, 925, 757, 695 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{15}O_3$ $[M\text{-}H]^+$ 291.1015, found 291.1026.

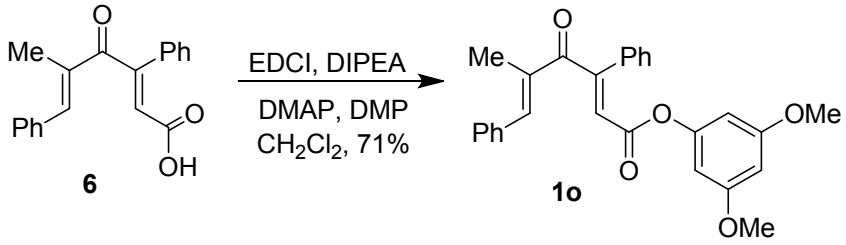


(2E,5E)-N,N,5-trimethyl-4-oxo-3,6-diphenylhexa-2,5-dienamide(1n): To a solution of acid **6** (60 mg, 0.21 mmol) in 2 mL of CH_2Cl_2 was added sequentially HOBt (53.8 mg, 0.41 mmol), EDCI (78.4 mg,0.41 mmol) and *N,N′*-dimethylamine hydrochloride (24.9 mg, 0.30 mmol) at 0 °C. Then, Et_3N (0.17 mL, 1.24 mmol) was added at 0 °C and the mixture was stirred for 5 h at rt. After completion of the reaction, diluted with CH_2Cl_2 (5 mL), sequentially washed with 1N HCl, saturated aq $NaHCO_3$ and brine. The organic layer was dried with Na_2SO_4, concentrated and purified by column chromatography over silica gel to give amide compound **1n** as colorless oil (48 mg, 73%). R_f : 0.3 (50% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.38 (m, 2H), 7.33-7.17 (m, 9H), 6.67 (s, 1H), 3.08 (s, 3H), 2.88 (s, 3H), 2.16 (d, J = 1.2 Hz, 3H);



^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 165.2, 152.9, 141.1, 137.3, 135.9, 135.8, 129.8, 129.4, 128.9, 128.4, 128.1, 126.5, 118.6, 37.8, 35.5, 12.9; IR (neat): ν_{max} 2927, 1644, 1494, 1398, 1200, 1144, 1069, 923, 761, 696 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{22}O_2N$ $[M+H]^+$ 320.1645, found 320.1642.

Synthesis of 1o from 6:

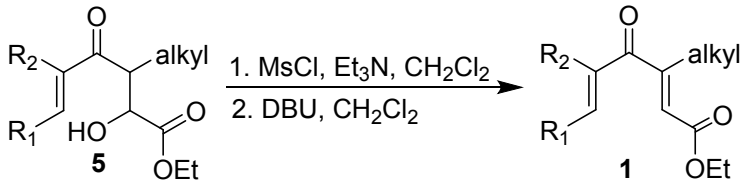


(2*E*,5*E*)-3,5-Dimethoxyphenyl 5-methyl-4-oxo-3,6-diphenylhexa-2,5-dienoate (1o): EDCI [1-ethyl-3-(dimethylaminopropyl)carbodiimide] (157.5 mg, 0.82 mmol) and DIPEA (0.29 mL, 1.64 mmol) were added to a stirred solution of acid **6** (120 mg, 0.41 mmol) in CH_2Cl_2 (3 mL) at 0 °C, and the reaction mixture was stirred for 10 min. 3,5-Dimethoxyphenol (126.5 mg, 0.82 mmol) was added to this reaction mixture, followed by DMAP (10 mg, 0.082 mmol). Then, the reaction mixture was allowed to stir for overnight. The reaction mixture was diluted with EtOAc, and the mixture was sequentially washed with 1N HCl, saturated aq $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by using silica gel column chromatography to give ester **1o** (124.5 mg, 71%) as a colorless oil. R_f = 0.3 (20% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.55 (m, 2H), 7.44 (m, 3H), 7.40-7.35 (m, 5H), 7.32 (m, 1H), 6.63 (s, 1H), 6.31 (t, J = 2.4 Hz, 1H), 6.24 (d, J = 2.4 Hz, 2H), 3.71 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 163.2, 161.0, 158.2, 151.8, 142.5, 137.4, 135.3, 134.7, 130.7, 129.8, 129.1, 128.9, 128.3,

126.8, 116.4, 99.9, 98.4, 55.3, 12.5; IR (neat): ν_{max} 2924, 2852, 1730, 1657, 1613, 1464, 1349, 1200, 1147, 1059, 769 cm^{-1}; HRMS (ESI): calcd for $C_{27}H_{25}O_5$ $[M+H]^+$ 429.1696, found 429.1704.

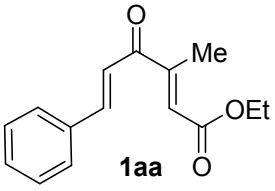
Typical procedure for preparation of divinylketones 1 or/and 1':

Method B:



A round-bottom flask was charged with alcohol **5** (1.0 equiv) and CH_2Cl_2 (3 mL). The resulting solution was stirred and cooled to 0 °C before adding sequentially Et_3N (10.0 equiv) and methanesulfonyl chloride (4.0 equiv). The resulting solution was stirred at rt until TLC showed the complete consumption of starting material. The resulting suspension was diluted with EtOAc, quenched with saturated aq $NaHCO_3$, extracted with EtOAc and washed with saturated aq NaCl solution. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in *vacuo.* Without column purification, it was proceeded to the next step. To the crude mesylated compound in dry THF (3 mL/mmol), DBU (2.0 equiv) was added and stirring continued at rt. After completion of the reaction, it was quenched with H_2O, extracted with EtOAc, and washed with saturated aq NaCl solution. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The obtained product was purified by using silica gel column chromatography to give **1**.

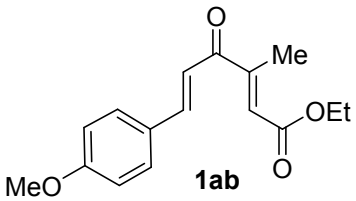
(2*E*,5*E*)-Ethyl 3-methyl-4-oxo-6-phenylhexa-2,5-dienoate (1aa): Yield: 78% (from **5aa**);



colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 15.7 Hz, 1H), 7.59 (m, 2H), 7.41 (m, 3H), 7.15 (d, J = 15.7 Hz, 1H), 6.54 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.36 (d, J

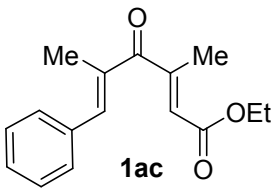
= 1.5 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.7, 165.9, 152.1, 145.5, 134.3, 130.6, 128.8, 128.3, 124.4, 121.3, 60.5, 14.1, 14.0; IR (neat): ν_{max} 2983, 2309, 1717, 1660, 1601, 1448, 1214, 1073, 983, 767, 693 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1165.

(2*E*,5*E*)-Ethyl 6-(4-methoxyphenyl)-3-methyl-4-oxohexa-2,5-dienoate (1ab): Yield: 86% (from **5ab**); colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, J = 15.7 Hz, 1H), 7.54 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 15.7 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 6.50 (s, 1H), 4.25 (q, J = 7.3 Hz, 2H), 3.83 (s, 3H), 2.35 (s, 3H), 1.33 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.8, 166.0, 161.7, 152.4, 145.4, 130.2, 127.0, 123.8, 119.0, 114.3, 60.4, 55.2, 14.2, 14.0; IR (neat): ν_{max} 2925, 2845, 1716, 1658, 1587, 1510, 1213, 1172, 1030, 822 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{19}O_4$ $[M+H]^+$ 275.1277, found 275.1266.



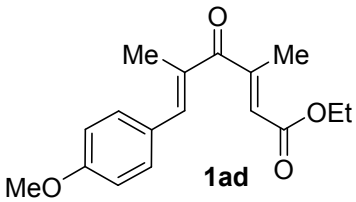
1ab

(2*E*,5*E*)-Ethyl 3,5-dimethyl-4-oxo-6-phenylhexa-2,5-dienoate (1ac): Yield: 82% (from **5ac**); colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.33 (m, 5H), 7.31 (m, 1H), 6.95 (q, J = 1.5 Hz, 1H), 4.09 (q, J = 6.7 Hz, 2H), 2.18 (d, J = 1.5 Hz, 3H), 2.14 (d, J = 1.5 Hz, 3H), 1.19 (t, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.6, 164.6, 155.5, 141.2, 135.7, 135.4, 129.7, 128.7, 128.3, 119.3, 60.4, 22.3, 13.9, 12.2; IR (neat): ν_{max} 2980, 1714, 1651, 1443, 1366, 1255, 1185, 1037, 772, 696 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{19}O_3$ $[M+H]^+$ 259.1328, found 259.1326.



1ac

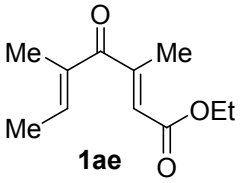
(2*E*,5*E*)-Ethyl 6-(4-methoxyphenyl)-3,5-dimethyl-4-oxohexa-2,5-dienoate (1ad): Yield: 81% (from **5ad**); colorless oil, R_f = 0.3 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 8.8 Hz, 2H), 7.30 (s, 1H), 6.95 (d, J = 8.8 Hz, 2H), 6.01 (q, J = 1.5 Hz, 1H), 4.23



1ad

(q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 2.40 (d, J = 1.5 Hz, 3H), 2.15 (d, J = 1.2 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.1, 165.7, 160.2, 153.9, 143.5, 133.1, 131.7, 127.7, 121.5, 113.9, 60.2, 55.1, 16.4, 14.0, 13.1; IR (neat): ν_{max} 2929, 1715, 1641, 1598, 1509, 1249, 1180, 1031, 828 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{27}O_4$ $[M+H]^+$ 289.1434, found 289.1436.

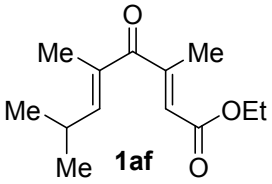
(2*E*,5*E*)-Ethyl 3,5-dimethyl-4-oxohepta-2,5-dienoate (1ae): Yield: 87% (from **5ae**);



1ae

colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.61 (qd, J = 1.3, 6.8 Hz, 1H), 5.90 (q, J = 1.5 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.30 (d, J = 1.5 Hz, 3H), 1.89 (m, 3H), 1.84 (m, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.3, 165.5, 153.4, 142.6, 136.3, 121.4, 60.1, 16.0, 14.7, 13.9, 10.9; IR (neat): ν_{max} 2927, 1719, 1646, 1268, 1201, 1044, 745 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{15}O_3$ $[M+H]^+$ 195.1015, found 195.1017.

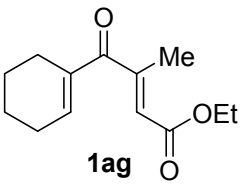
(2*E*,5*E*)-Ethyl 3,5,7-trimethyl-4-oxoocta-2,5-dienoate (1af): Yield: 90% (from **5af**);



1af

colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.27 (d, J = 9.6 Hz, 1H), 5.92 (s, 1H), 4.22 (q, J = 7.0 Hz, 2H), 2.74 (m, 1H), 2.31 (s, 3H), 1.85 (s, 3H), 1.31 (t, J = 7.0 Hz, 3H), 1.09 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.1, 165.8, 154.3, 153.5, 133.0, 121.7, 60.2, 28.3, 21.6, 16.2, 14.1, 11.3; IR (neat): ν_{max} 2964, 1718, 1644, 1459, 1260, 1198, 1109, 1040, 873 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{21}O_3$ $[M+H]^+$ 225.1485, found 225.1484.

(*E*)-Ethyl 4-(cyclohex-1-en-1-yl)-3-methyl-4-oxobut-2-enoate (1ag): Yield: 94% (from

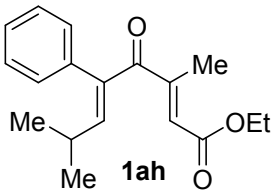


1ag

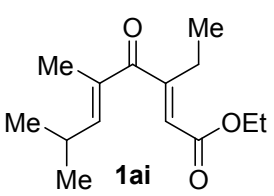
5ag); colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.78 (s, 1H), 5.93 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.35-2.23 (m, 7H), 1.73-1.60 (m, 4H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6, 165.5, 152.9, 144.9, 137.2, 121.4, 60.0, 25.9, 22.8, 21.4, 21.2, 15.8,

13.9; IR (neat): ν_{max} 2934, 1717, 1638, 1436, 1242, 1184, 1123, 1038, 723 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{19}O_3$ $[M+H]^+$ 223.1328, found 223.1334.

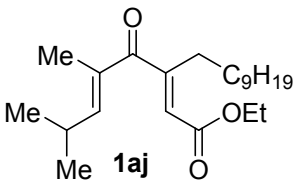
(2*E*,5*E*)-ethyl 3,7-dimethyl-4-oxo-5-phenylocta-2,5-dienoate (1ah): Yield: 92% (from **5ah**); colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.32 (m, 1H), 7.14 (m, 2H), 6.39 (d, *J* = 10.3 Hz, 1H), 6.17 (q, *J* = 1.5 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.59-2.52 (m, 1H), 2.32 (d, *J* = 1.5 Hz, 3H), 1.31 (q, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.5, 165.7, 153.4, 138.3, 135.0, 129.1, 128.1, 127.5, 123.3, 60.4, 28.7, 22.1, 15.8, 14.1; IR (neat): ν_{max} 2966, 2867, 1718, 1657, 1450, 1368, 1248, 1206, 1086, 1036, 773, 703 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{23}O_3$ $[M+H]^+$ 287.1641, found 287.1647.



(2*E*,5*E*)-Ethyl 3-ethyl-5,7-dimethyl-4-oxoocta-2,5-dienoate (1ai): Yield: 83% (from **5ai**); colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 6.29 (d, *J* = 9.6 Hz, 1H), 5.81 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.87 (q, *J* = 7.5 Hz, 2H), 2.81-2.67 (m, 1H), 1.86 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.8, 165.3, 159.1, 154.6, 133.9, 120.3, 60.1, 28.3, 22.8, 21.5, 13.9, 12.3, 11.0; IR (neat): ν_{max} 2968, 1718, 1642, 1458, 1192, 1035, 866, 762 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{23}O_3$ $[M+H]^+$ 239.1641, found 239.1650.

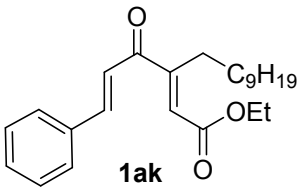


(*E*)-Ethyl 3-((*E*)-2,4-dimethylpent-2-enoyl)tridec-2-enoate (1aj): Yield: 89% (from **5aj**); colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 6.28 (d, *J* = 9.4 Hz, 1H), 5.83 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.74 (m, 1H), 1.85 (s, 3H), 1.40 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.25 (m, 14H), 1.05 (d, *J* = 6.6 Hz, 6H), 0.87 (t, *J* = 6.5 Hz,



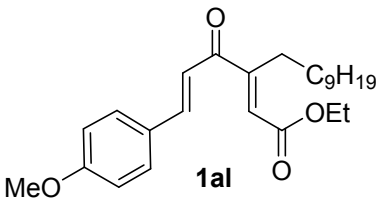
3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.1, 165.6, 158.2, 154.5, 133.8, 120.9, 60.2, 31.8, 29.6, 29.4, 29.2, 28.4, 28.2, 22.5, 21.7, 14.1, 14.0, 11.2; IR (neat): ν_{max} 2924, 2856, 1720, 1646, 1460, 1259, 1166, 1035, 879 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{39}O_3$ $[M+H]^+$ 351.2893, found 351.2910.

(*E*)-Ethyl 3-cinnamoyltridec-2-enoate (1ak): Yield: 89% (from **5ak**); colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 15.8 Hz, 1H), 7.59 (m, 2H), 7.41 (m, 3H), 7.11 (d, J = 15.8 Hz, 1H), 6.42 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 1.46 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.31-1.20 (m, 14H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3, 165.7, 157.1, 145.6, 134.3, 130.7, 128.8, 128.4, 123.5, 122.3, 60.5, 31.8, 29.7, 29.4, 29.2, 28.8, 27.9, 22.6, 14.1, 14.0; IR (neat): ν_{max} 2923, 2854, 1720, 1662, 1602, 1452, 1175, 856, 687 cm^{-1}; HRMS (ESI): calcd for $C_{24}H_{35}O_3$ $[M+H]^+$ 371.2580, found 371.2581.



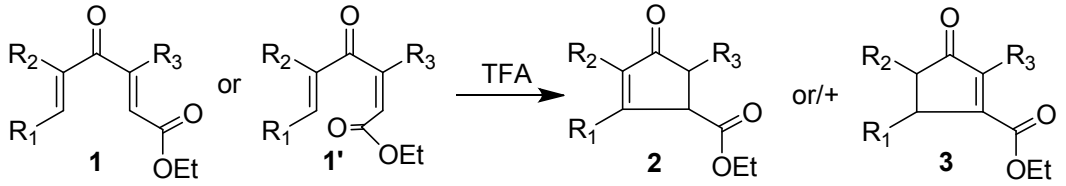
1ak

(*E*)-Ethyl 3-((*E*)-3-(4-methoxyphenyl)acryloyl)tridec-2-enoate (1al): Yield: 83% (from **5al**); colorless oil, R_f = 0.3 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, J = 16.0 Hz, 1H), 7.55 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 16.0 Hz, 1H), 6.93 (d, J = 8.6 Hz, 2H), 6.38 (s, 1H), 4.25 (q, J = 6.9 Hz, 2H), 3.86 (s, 3H), 2.89 (t, J = 7.1 Hz, 2H), 1.45 (m, 2H), 1.33 (t, J = 6.9 Hz, 3H), 1.30-1.20 (m, 14H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6, 165.9, 161.8, 157.6, 145.6, 130.3, 127.1, 123.0, 120.2, 114.4, 60.5, 55.3, 31.8, 29.8, 29.5, 29.3, 29.2, 28.8, 28.6, 28.1, 14.1, 14.0; IR (neat): ν_{max} 2923, 2853, 1720, 1659, 1591, 1511, 1254, 1171, 1032, 826 cm^{-1}; HRMS (ESI): calcd for $C_{25}H_{36}O_4Na$ $[M+Na]^+$ 423.2505, found 423.2496.



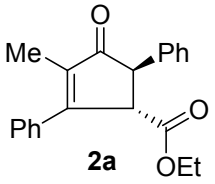
1al

2.4. Typical procedure for the preparation of cyclopentenone 2/3 from 1 or 1':



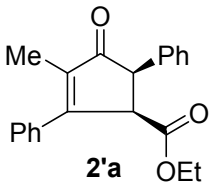
To a divinylketone, was added TFA (10 equiv) at 0 °C, then the reaction mixture was slowly warmed to rt, stirring continued at the same temperature. The reaction was monitored by TLC, after completion of the starting material, the reaction was quenched with saturated aq $NaHCO_3$, and extracted with EtOAc. The organic layer was washed with saturated aq NaCl, and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/ hexanes) to give **2** or/and **3**.

Ethyl 3-methyl-4-oxo-2,5-diphenylcyclopent-2-ene-1-carboxylate (2a): Yield: 84%; light



yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 7.3 Hz, 2H), 7.44 (m, 3H), 7.34 (t, J = 7.1 Hz, 2H), 7.27 (t, J = 7.1 Hz, 1H), 7.20 (d, J = 7.3 Hz, 2H), 4.25 (m, 1H), 4.00 (m, 2H), 3.94 (m, 1H), 2.01 (d, J = 1.9 Hz, 3H), 0.97 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.2, 171.7, 163.0, 137.9, 134.0, 129.6, 128.7, 128.3, 127.8, 127.7, 127.2, 61.0, 56.2, 55.2, 13.6, 10.0; IR (neat): ν_{max} 2979, 1707, 1631, 1495, 1378, 1169, 1025, 696 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_3$ $[M+H]^+$ 321.1485, found 321.1485.

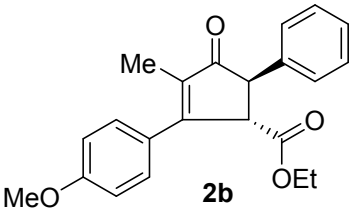
Ethyl 3-methyl-4-oxo-2,5-diphenylcyclopent-2-ene-1-carboxylate (2a & 2'a (0.6:1)**):** ^{1}H



NMR (500 MHz, $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.40-7.35 (m, 4H), 7.28 (m, 1H), 7.23-7.19 (m, 4H), 7.19-7.16 (m, 2H), 7.14-7.10 (m, 3H), 4.53 (dq, J = 1.6, 7.9 Hz, 1H), 4.17 (dd, J = 1.98, 3.0 Hz, 0.6H), 4.08 (d, J = 7.9 Hz, 1H), 3.94 (m, 1.3H), 3.86 (d, J = 3.0 Hz, 0.6H), 3.44 (m, 2H), 2.03 (d, J = 1.6 Hz, 3H), 1.95 (d, J = 1.9 Hz, 1.7H), 0.91 (t, J = 7.1 Hz, 1.7H), 0.63 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.5, 206.2, 171.8, 169.8, 163.1, 162.3, 139.0, 138.0, 137.2, 135.5, 135.0,

134.2, 129.8, 129.5, 128.8, 128.6, 128.5, 128.1, 127.8, 127.5, 127.3, 61.2, 60.7, 56.3, 55.3, 54.5, 54.2, 13.7, 13.3, 10.2, 10.1.

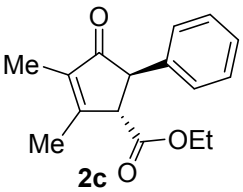
Ethyl 2-(4-methoxyphenyl)-3-methyl-4-oxo-5-phenylcyclopent-2-ene-1-carboxylate (2b):



2b

Yield: 76%; light yellow oil; R_f = 0.4 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 8.8 Hz, 2H), 7.34 (m, 2H), 7.28 (m, 1H), 7.18 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 4.22 (m, 1H), 4.04 (m, 2H), 3.89 (d, J = 3.0 Hz, 1H), 3.86 (s, 3H), 2.05 (d, J = 1.9 Hz, 3H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.2, 172.1, 162.5, 160.7, 138.3, 135.7, 129.7, 128.8, 127.8, 127.3, 126.6, 113.9, 61.2, 56.2, 55.4, 55.3, 13.9, 10.4; IR (neat): ν_{max} 2924, 2852, 1729, 1700, 1604, 1511, 1253, 1177, 1027, 839, 768, 699 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{23}O_4$ $[M+H]^+$ 351.1590, found 351.1601.

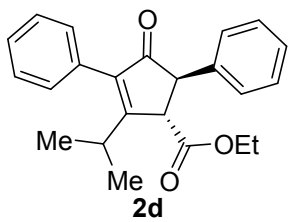
Ethyl 2,3-dimethyl-4-oxo-5-phenylcyclopent-2-enecarboxylate (2c): Yield: 78%; colorless



2c

oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (m, 2H), 7.25 (m, 1H), 7.11 (d, J = 8.3 Hz, 2H), 4.23 (m, 2H), 3.87 (d, J = 3.0 Hz, 1H), 3.65 (m, 1H), 2.13 (s, 3H) 1.80 (d, J = 0.7 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.3, 171.6, 164.2, 138.2, 137.2, 128.7, 127.7, 127.1, 61.4, 58.0, 54.9, 15.5, 14.1, 8.4; IR (neat): ν_{max} 2923, 1712, 1652, 1603, 1495, 1448, 1323, 1168, 1028, 770 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{19}O_3$ $[M+H]^+$ 259.1328, found 259.1325.

Ethyl 2-isopropyl-4-oxo-3,5-diphenylcyclopent-2-enecarboxylate (2d): Yield: 72%; light

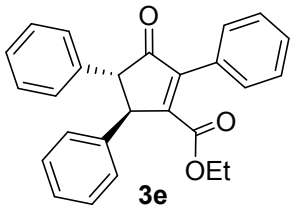


2d

yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (m, 2H), 7.35 (m, 3H), 7.27 (m, 3H), 7.18 (m, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.95 (d, J = 1.9 Hz, 1H), 3.89 (d, J = 1.9 Hz, 1H), 3.26 (m, 1H), 1.32 (t, J = 7.1 Hz, 3H), 1.24 (d, J = 6.8 Hz, 3H) 1.17 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.8, 174.7, 172.6, 140.9,

138.3, 131.4, 129.2, 128.9, 128.3, 128.1, 127.4, 127.3, 61.6, 56.3, 53.6, 30.0, 20.7, 14.0; IR (neat): ν_{max} 2972, 1717, 1634, 1492, 1455, 1316, 1254, 1164, 1030, 700 cm^{-1}; HRMS (ESI): calcd for $C_{23}H_{25}O_3$ $[M+H]^+$ 349.1798, found 349.1794.

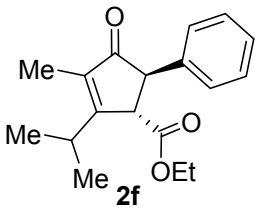
Ethyl 4-oxo-2,3,5-triphenylcyclopent-2-enecarboxylate (3e): Yield: 67%; white solid, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.50 (m, 2H), 7.42 (m, 3H), 7.37-7.31 (m, 4H), 7.31-7.26 (m, 2H), 7.20 (d, J = 7.0 Hz, 2H), 7.15 (d, J = 7.0 Hz, 2H), 4.48 (d, J = 3.5 Hz, 1H), 4.11-4.00 (m, 2H), 3.73 (d, J = 3.5 Hz, 1H), 0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.9, 165.3, 158.4, 143.7, 139.8, 137.7, 129.6, 129.1, 128.9, 128.0, 127.9, 127.5, 127.4, 62.3, 61.3, 55.0, 13.6; IR (neat): ν_{max} 2923, 1717, 1549, 1499, 1452, 1222, 1144, 1017, 696 cm^{-1}; HRMS (ESI): calcd for $C_{26}H_{23}O_3$ $[M+H]^+$ 383.1641, found 383.1652.



3e

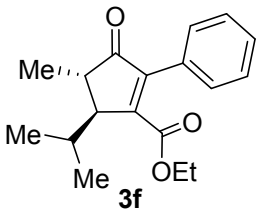
*Compound **2f** (54%) and **3f** (23%) were obtained from **1f**; and only **3f** (86%) were obtained from **1'f**.*

Ethyl 2-isopropyl-3-methyl-4-oxo-5-phenylcyclopent-2-enecarboxylate (2f): colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.35-7.20 (m, 3H), 7.08 (d, J = 8.1 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 3.77 (d, J = 2.6 Hz, 1H), 3.71 (d, J = 2.6 Hz, 1H), 3.17-3.09 (m, 1H), 1.85 (d, J = 1.7 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H), 1.27 (d, J = 7.1 Hz, 3H), 1.16 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.8, 173.2, 172.8, 138.3, 136.7, 128.8, 127.3, 127.2, 61.4, 55.7, 54.6, 29.9, 19.9, 14.0, 8.7; IR (neat): ν_{max} 2923, 1709, 1639, 1458, 1170, 1026, 695 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{23}O_3$ $[M+H]^+$ 287.1641, found 287.1635.



2f

Ethyl 5-isopropyl-4-methyl-3-oxo-2-phenylcyclopent-1-enecarboxylate (3f): colorless oil,

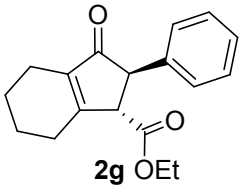


3f

R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.31 (m, 5H), 4.21 (q, J = 7.1 Hz, 2H), 2.89 (m, 1H), 2.38 (qd, J = 2.1, 7.4 Hz, 1H), 2.24-2.15 (m, 1H), 1.29 (d, J = 7.4 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.4, 166.9, 160.2, 142.5, 130.1, 128.7, 128.6, 127.9, 61.3, 54.1, 41.5, 29.2, 21.1, 17.5, 16.6, 13.8; IR (neat): ν_{max} 2925, 1715, 1634, 1458, 1224, 1159, 696 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{23}O_3$ $[M+H]^+$ 287.1641, found 287.1638.

*Compound **2g** (61%) and **3g** (21%) were obtained from **1g**; and **2g** (8%) and **3g** (73%) were obtained from **1'g**.*

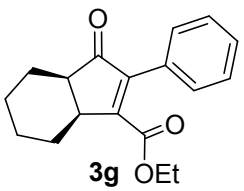
Ethyl 3-oxo-2-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indene-1-carboxylate (2g): colorless oil,



2g

R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (m, 2H), 7.25 (m, 1H), 7.13 (d, J = 8.5 Hz, 2H), 4.22 (m, 2H), 3.92 (d, J = 3.0 Hz, 1H), 3.66 (m, 1H), 2.41 (m, 2H), 2.23 (m, 2H), 1.83-1.69 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.5, 171.3, 167.8, 139.4, 138.3, 128.7, 127.8, 127.1, 61.4, 57.1, 55.1, 26.8, 22.1, 21.2, 20.3, 14.1; IR (neat): ν_{max} 2937, 1715, 1646, 1499, 1449, 1385, 1232, 1179, 1022, 771 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485, found 285.1478.

Ethyl 1-oxo-2-phenyl-3a,4,5,6,7,7a-hexahydro-1*H*-indene-3-carboxylate (3g): colorless



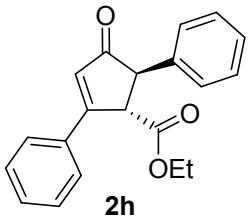
3g

oil, R_f = 0.5 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.32 (m, 5H), 4.21 (m, 2H), 3.27 (m, 1H), 2.70 (m, 1H), 2.25 (m, 1H), 2.18 (m, 1H), 1.73 (m, 1H), 1.62 (m, 3H), 1.38 (m, 1H), 1.25 (m, 1H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.1, 166.1, 160.2, 143.3, 130.4, 128.8, 128.6, 127.8, 61.1, 47.0, 39.7, 29.6, 22.6, 21.9, 21.6, 13.7; IR (neat): ν_{max} 2939,

1719, 1639, 1550, 1448, 1278, 1227, 1019, 770 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485, found 285.1478.

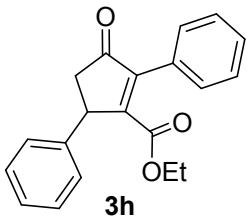
*Compound **2h** (61%) and **3h** (15%) were obtained from **1h**; and **2h** (4%) and **3h** (74%) were obtained from **1'h**.*

Ethyl 4-oxo-2,5-diphenylcyclopent-2-enecarboxylate (2h): light yellow oil; R_f = 0.4 (15% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (m, 2H), 7.47 (m, 3H), 7.33 (m, 3H), 7.19 (m, 2H), 6.72 (d, J = 1.3 Hz, 1H), 4.36 (m, 1H), 4.14 (m, 2H), 3.92 (d, J = 2.6 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.6, 171.5, 170.0, 138.0, 132.6, 131.6, 128.9, 128.2, 127.6, 127.5, 127.2, 61.6, 57.0, 55.9, 13.9; IR (neat): ν_{max} 2922, 2853, 1715, 1635, 1454, 1221, 1151, 760, 697 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1328, found 307.1321.



2h

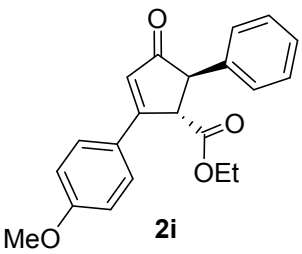
Ethyl 3-oxo-2,5-diphenylcyclopent-1-enecarboxylate (3h): light yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.43-7.38 (m, 5H), 7.33 (m, 2H), 7.27 (m, 1H), 7.22 (m, 2H), 4.48 (dd, J = 2.4, 7.3 Hz, 1H), 4.02 (m, 2H), 3.17 (dd, J = 7.3, 19.3 Hz, 1H), 2.64 (dd, J = 2.4, 19.3 Hz, 1H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.6, 165.3, 159.7, 144.7, 140.4, 129.7, 129.0, 128.9, 128.0, 127.4, 127.3, 61.2, 44.9, 13.6; IR (neat): ν_{max} 2922, 2853, 1714, 1645, 1454, 1290, 1150, 758, 696 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{19}O_3$ $[M+H]^+$ 307.1328, found 307.1322.



3h

*Compound **2i** (63%) and **3i** (15%) were obtained from **1i**; and **2i** (5%) and **3i** (75%) were obtained from **1'i**.*

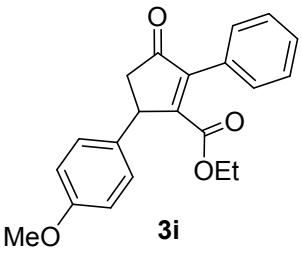
Ethyl 2-(4-methoxyphenyl)-4-oxo-5-phenylcyclopent-2-enecarboxylate (**2i**): light yellow



2i

oil; R_f = 0.4 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, J = 9.0 Hz, 2H), 7.34 (m, 2H), 7.28 (m, 1H), 7.19 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 1.2 Hz, 1H), 4.30 (m, 1H), 4.16 (m, 2H), 3.89 (d, J = 2.5 Hz, 1H), 3.87 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.5, 171.8, 169.6, 162.4, 138.3, 129.2, 128.9, 127.6, 127.4, 126.2, 125.2, 114.4, 61.6, 61.1, 56.0, 55.4, 14.0; IR (neat): ν_{max} 2927, 1715, 1696, 1596, 1510, 1257, 1174, 1027, 833, 754, 699 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1434, found 337.1421.

Ethyl 5-(4-methoxyphenyl)-3-oxo-2-phenylcyclopent-1-enecarboxylate (3i): light yellow

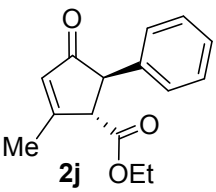


3i

oil; R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.37 (m, 5H), 7.14 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 4.44 (dd, J = 2.4, 7.3 Hz, 1H), 4.09-3.97 (m, 2H), 3.79 (s, 3H), 3.15 (dd, J = 7.3, 19.3 Hz, 1H), 2.60 (dd, J = 2.4, 19.3 Hz, 1H), 0.97 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.8, 165.5, 160.0, 158.8, 144.2, 132.2, 129.7, 128.9, 128.3, 128.0, 114.3, 61.2, 55.2, 45.0, 44.1, 13.6; IR (neat): ν_{max} 2925, 1728, 1694, 1594, 1510, 1257, 1173, 1027, 833, 759, 699 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1434, found 337.1420.

*Compounds **2j** (32%) and **3j** (48%) were obtained from **1j**; and **2j** (8%) and **3j** (62%) were obtained from **1'j**.*

Ethyl 2-methyl-4-oxo-5-phenylcyclopent-2-enecarboxylate (2j): colorless oil, R_f = 0.4

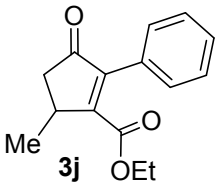


2j

(10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.23 (m, 3H), 7.13 (d, J = 8.3 Hz, 2H), 6.12 (s, 1H), 4.24 (m, 2H), 3.95 (d, J = 3.2 Hz, 1H), 3.74 (m, 1H), 2.23 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125

MHz, $CDCl_3$): δ 206.2, 172.9, 170.8, 137.9, 131.1, 128.8, 127.7, 127.3, 61.6, 59.1, 56.2, 17.9, 14.1; IR (neat): ν_{max} 2924, 2854, 1720, 1638, 1628, 1446, 1257, 1026, 849, 768, 698 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1162.

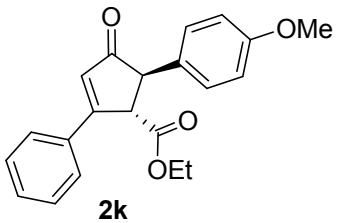
Ethyl 5-methyl-3-oxo-2-phenylcyclopent-1-enecarboxylate (3j): colorless oil, R_f = 0.5 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.44-7.29 (m, 5H), 4.22 (m, 2H), 3.35 (m, 1H), 2.89 (dd, J = 6.7, 19.0 Hz, 1H), 2.26 (dd, J = 2.0, 19.0 Hz, 1H), 1.31 (d, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.4, 166.1, 162.3, 143.8, 130.0, 128.6, 127.9, 126.7, 61.3, 43.3, 33.9, 19.3, 13.7; IR (neat): ν_{max} 2923, 2834, 1716, 1642, 1627, 1445, 1176, 1072, 849, 766 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1162.



3j

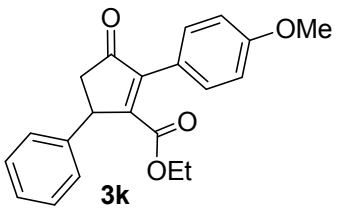
*Compound **2k** (72%) and **3k** (6%) were obtained from **1k**; and only **3k** (82%) were obtained from **1'k**.*

Ethyl 5-(4-methoxyphenyl)-4-oxo-2-phenylcyclopent-2-enecarboxylate (2k): light yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (m, 2H), 7.47 (m, 3H), 7.11 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.71 (d, J = 1.6 Hz, 1H), 4.31 (dd, J = 1.6, 2.8 Hz, 1H), 4.14 (m, 2H), 3.87 (d, J = 2.8 Hz, 1H) 3.80 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.0, 171.6, 169.9, 158.9, 132.8, 131.5, 130.1, 129.0, 128.7, 128.2, 127.3, 114.4, 61.6, 56.4, 56.2, 55.3, 13.9; IR (neat): ν_{max} 2922, 2853, 1704, 1636, 1603, 1511, 1250, 1173, 1031, 772 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1434, found 337.1424.



2k

Ethyl 2-(4-methoxyphenyl)-3-oxo-5-phenylcyclopent-1-enecarboxylate (3k): light yellow oil; R_f = 0.6 (15% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, J = 8.8 Hz, 2H), 7.32 (m, 2H), 7.27-7.20 (m,

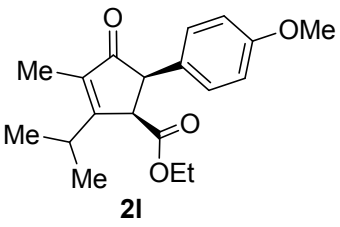


3k

3H), 6.94 (d, J = 8.8 Hz, 2H), 4.45 (dd, J = 2.4, 7.3 Hz, 1H), 4.04 (m, 2H), 3.83 (s, 3H), 3.15 (dd, J = 7.3, 19.3 Hz, 1H), 2.61 (dd, J = 2.4, 19.3 Hz, 1H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.0, 165.5, 160.2, 158.2, 144.0, 140.6, 130.6, 128.8, 127.3, 121.8, 113.5, 61.1, 55.2, 44.9, 44.8, 13.6; IR (neat): ν_{max} 2922, 2852, 1712, 1642, 1604, 1509, 1218, 1153, 1025, 832, 699 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{21}O_4$ $[M+H]^+$ 337.1434, found 337.1424.

*Compound **2l** (86%) only obtained from **1l**; and **2l** (16%) and **3l** (63%) were obtained from **1'l**.*

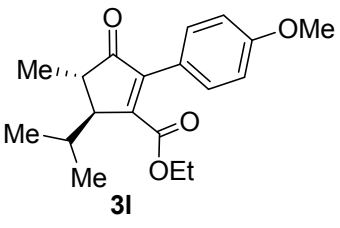
Ethyl 2-isopropyl-5-(4-methoxyphenyl)-3-methyl-4-oxocyclopent-2-enecarboxylate (2l):



2l

colorless oil, R_f = 0.3 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.12 (d, J = 7.5 Hz, 1H), 3.88 (d, J = 7.5 Hz, 1H), 3.76 (s, 3H), 3.64 (q, J = 7.1 Hz, 2H), 3.04 (m, 1H), 1.88 (s, 3H), 1.20 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.9, 171.6, 170.6, 158.6, 138.0, 130.9, 127.1, 113.3, 60.6, 55.0, 53.9, 52.6, 29.7, 20.1, 20.0, 13.5, 8.6; IR (neat): ν_{max} 2966, 1702, 1642, 1512, 1460, 1317, 1247, 1172, 1031, 820 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{24}O_4Na$ $[M+Na]^+$ 339.1566, found 339.1560.

Ethyl 5-isopropyl-2-(4-methoxyphenyl)-4-methyl-3-oxocyclopent-1-enecarboxylate (3l):



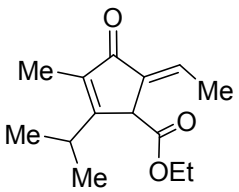
3l

colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 2.87 (m, 1H), 2.36 (m, 1H), 2.23-2.11 (m, 1H), 1.28 (d, J = 7.3 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H), 1.06 (d, J = 6.7 Hz, 3H), 0.81 (d, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.7, 167.2, 159.9, 158.8, 141.8, 130.2, 122.4, 113.4, 61.2, 55.2, 54.0, 41.4, 29.2, 21.1,

17.5, 16.6, 13.9; IR (neat): ν_{max} 2922, 1711, 1640, 1510, 1458, 1219, 1164, 1028, 830 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{24}O_4Na$ $[M+Na]^+$ 339.1566, found 339.1563.

*Compound **2m** (72%) and **2'm** (6%) were obtained from **1m**; and only **2m** (87%) were obtained from **1'm**.*

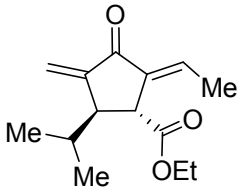
(*E*)-Ethyl 5-ethylidene-2-isopropyl-3-methyl-4-oxocyclopent-2-enecarboxylate (2m):



2m

colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 6.67 (m, 1H), 4.22 (s, 1H), 4.15 (m, 2H), 3.05 (m, 1H), 1.90-1.83 (m, 6H), 1.27-1.19 (m, 6H), 1.12 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.3, 171.3, 167.5, 139.1, 135.3, 130.3, 61.1, 48.3, 29.3, 20.1, 20.0, 14.2, 13.9, 8.6; IR (neat): ν_{max} 2925, 1729, 1643, 1461, 1373, 1225, 1169, 1034, 943 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1485, found 237.1496.

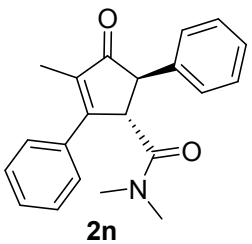
(*E*)-Ethyl 2-ethylidene-5-isopropyl-4-methylene-3-oxocyclopentanecarboxylate (2'm):



2'm

colorless oil, R_f = 0.45 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 6.93 (qd, J = 1.7, 7.3 Hz, 1H), 6.24 (s, 1H), 5.43 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.57 (m, 1H), 2.99 (m, 1H), 1.92 (d, J = 7.3 Hz, 3H), 1.87 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H), 0.92 (d, J = 6.7 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 173.0, 147.5, 137.8, 136.9, 120.3, 61.0, 48.6, 45.0, 33.3, 19.3, 18.3, 15.2, 14.0; IR (neat): ν_{max} 2923, 1732, 1666, 1631, 1460, 1152, 960 cm^{-1} ; HRMS (ESI): calcd for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1485, found 237.1495.

***N,N*,3-trimethyl-4-oxo-2,5-diphenylcyclopent-2-enecarboxamide(2n):** Yield: 83%;



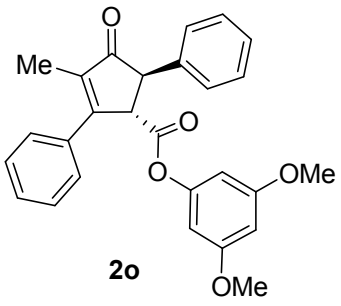
2n

colorless oil, R_f = 0.3 (50% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.18 (m, 8H), 7.12 (d, J = 8.3 Hz, 2H), 4.41 (m, 1H), 3.72 (d, J = 3.0 Hz, 1H), 2.80 (s, 3H), 2.70 (s, 3H), 1.91 (d, J = 1.8 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8, 171.5, 165.0, 138.7, 137.8, 135.3, 129.3, 129.0, 128.6, 127.8, 127.4, 127.3, 56.6, 53.5, 37.6, 35.9, 10.0; IR (neat): ν_{max} 2925, 2856, 1701, 1642, 1450, 1399, 1339, 1143, 1050, 698 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{22}O_2N$ $[M+H]^+$ 320.1645, found 320.1638.

*Compound **2o** (42%) and **7** (21%) were obtained from **1o**.*

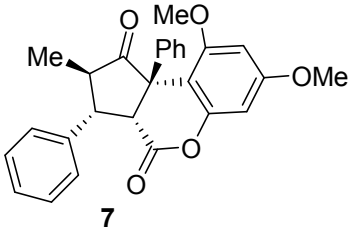
3,5-Dimethoxyphenyl 3-methyl-4-oxo-2,5-diphenylcyclopent-2-enecarboxylate (2o): light



2o

yellow oil; R_f = 0.5 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (m, 2H), 7.52 (m, 2H), 7.48 (m, 1H), 7.40 (m, 2H), 7.33 (m, 1H), 7.27 (m, 2H), 6.25 (app. t, J = 2.2 Hz, 1H), 5.76 (d, J = 2.2 Hz, 2H), 4.46 (m, 1H), 4.10 (d, J = 3.3 Hz, 1H), 3.66 (s, 6H) 2.06 (d, J = 2.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.9, 170.3, 162.6, 160.9, 151.7, 137.8, 137.7, 134.1, 129.9, 129.0, 128.7, 128.1, 127.9, 127.6, 99.6, 98.4, 56.4, 55.4, 55.3, 10.2; IR (neat): ν_{max} 2922, 2853, 1753, 1704, 1604, 1460, 1336, 1196, 1050, 974, 829, 734 cm^{-1}; HRMS (ESI): calcd for $C_{27}H_{24}O_5Na[M+Na]^+$ 451.1516, found 451.1523.

7,9-Dimethoxy-2-methyl-3,9b-diphenyl-3,3a-dihydrocyclopenta[c]chromene-

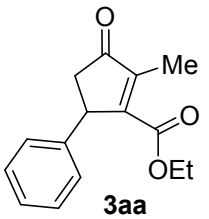


7

1,4(2*H*,9b*H*)-dione (7): light yellow oil; R_f = 0.45 (15% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.25 (m, 3H), 7.22-7.16 (m, 3H), 6.98 (d, J = 7.1 Hz, 2H), 6.80 (d, J = 7.1 Hz, 2H), 6.38 (d, J = 2.4 Hz, 1H), 5.92 (d, J = 2.4 Hz, 1H), 3.87 (d, J = 11.5 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.50 (dd, J = 8.5, 11.5 Hz, 1H), 3.18 (m, 1H), 1.23 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.4, 166.3, 161.7, 157.9, 153.6, 137.7, 137.2, 128.4, 128.2, 128.1, 127.6, 127.5, 102.1, 95.9, 94.6, 56.9, 55.9, 55.6,

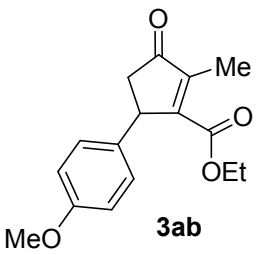
51.5, 46.9, 42.8, 13.8; IR (neat): ν_{max} 2923, 2854, 1759, 1619, 1590, 1497, 1457, 1344, 1208, 1151, 1108, 699 cm^{-1}; HRMS (ESI): calcd for $C_{27}H_{25}O_5$ $[M+H]^+$ 429.1696, found 429.1691.

Ethyl 2-methyl-3-oxo-5-phenylcyclopent-1-enecarboxylate (3aa): Yield: 91%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.27 (m, 3H), 7.11 (d, J = 6.7 Hz, 2H), 4.33 (m, 1H), 4.25-4.02 (m, 2H), 2.98 (dd, J = 7.1, 19.2 Hz, 1H), 2.43 (dd, J = 1.8, 19.2 Hz, 1H), 2.13 (d, J = 1.8 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.0, 164.6, 157.0, 141.6, 128.6, 126.9, 126.8, 119.8, 60.8, 44.4, 44.3, 13.7, 9.6; IR (neat): ν_{max} 2982, 2926, 1715, 1497, 1328, 1221, 1074, 767 cm^{-1}; HRMS (ESI): calcd for $C_{25}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1167.



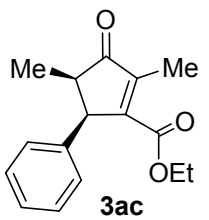
3aa

Ethyl 5-(4-methoxyphenyl)-2-methyl-3-oxocyclopent-1-enecarboxylate (3ab): Yield: 89%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.03 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.29 (m, 1H), 4.15 (m, 2H), 3.77 (s, 3H), 2.97 (dd, J = 7.1, 19.4 Hz, 1H), 2.4 (dd, J = 1.8, 19.4 Hz, 1H), 2.10 (d, J = 1.8 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.2, 164.8, 158.4, 157.3, 145.8, 133.4, 127.9, 113.9, 60.8, 55.0, 44.5, 43.5, 13.8, 9.5; IR (neat): ν_{max} 2925, 2844, 1712, 1642, 1511, 1216, 1035, 833 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{19}O_4$ $[M+H]^+$ 275.1277, found 275.1266.



3ab

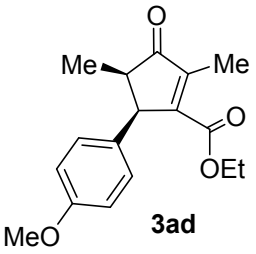
Ethyl 2,4-dimethyl-3-oxo-5-phenylcyclopent-1-enecarboxylate (3ac): Yield: 80%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.24 (m, 3H), 6.96 (m, 2H), 4.46 (m, 1H), 4.14 (m, 2H), 2.81 (m, 1H), 2.18 (d, J = 1.5 Hz, 3H), 1.13 (t, J = 6.7 Hz, 3H), 0.74 (d, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.7, 165.0, 154.9, 146.3, 138.3, 128.3,



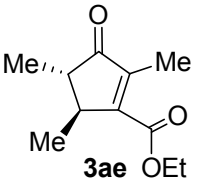
3ac

127.0, 60.9, 49.6, 45.5, 13.8, 11.9, 9.9; IR (neat): ν_{max} 2924, 1718, 1511, 1452, 1378, 1226, 1086, 769 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{19}O_3$ $[M+H]^+$ 259.1328, found 259.1327.

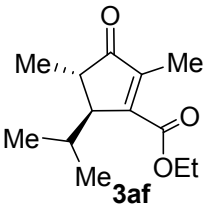
Ethyl 5-(4-methoxyphenyl)-2,4-dimethyl-3-oxocyclopent-1-enecarboxylate (3ad): Yield: 56%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 6.82 (m, 4H), 4.42 (dq, J = 1.8, 7.0 Hz, 1H), 4.20-4.09 (m, 2H), 3.77 (s, 3H), 2.77 (m, 1H), 2.15 (d, J = 1.8 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 0.74 (d, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.0, 165.1, 158.5, 155.1, 145.8, 130.1, 129.3, 128.0, 113.7, 60.9, 55.1, 48.9, 45.5, 13.9, 11.9, 9.9; IR (neat): ν_{max} 2944, 1715, 1642, 1600, 1510, 1251, 1183, 1038, 829 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{21}O_4$ $[M+H]^+$ 289.1434, found 289.1438.



Ethyl 2,4,5-trimethyl-3-oxocyclopent-1-enecarboxylate (3ae): Yield: 76%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 4.34 (m, 2H), 2.72 (m, 1H), 2.02 (m, 1H), 1.99 (d, J = 2.2 Hz, 3H), 1.38 (t, J = 6.7 Hz, 3H), 1.25 (d, J = 6.7 Hz, 3H), 1.20 (d, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.0, 165.1, 157.3, 144.0, 60.6, 48.2, 42.2, 18.4, 14.7, 13.9, 9.4; IR (neat): ν_{max} 2975, 1707, 1640, 1453, 1213, 1049, 789 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{15}O_3$ $[M-H]^+$ 195.1015, found 195.1014.

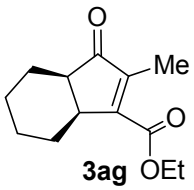


Ethyl 5-isopropyl-2,4-dimethyl-3-oxocyclopent-1-enecarboxylate (3af): Yield: 87%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 4.33 (m, 2H), 2.76 (m, 1H), 2.2 (m, 2H), 1.97 (d, J = 2.2 Hz, 3H), 1.37 (t, J = 6.7 Hz, 3H), 1.19 (d, J = 6.7 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H), 0.66 (d, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.2, 166.0, 157.4, 143.9, 61.0, 53.6, 40.8, 28.9, 21.2, 17.7, 16.4, 14.1, 9.6; IR (neat): ν_{max} 2961, 1710, 1639,



1458, 1374, 1214, 1053 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{21}O_3$ $[M+H]^+$ 225.1485, found 225.1484.

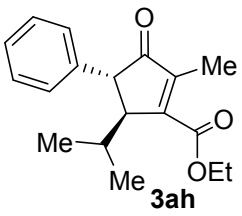
Ethyl 2-methyl-1-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indene-3-carboxylate (3ag): Yield:



3ag

92%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 4.32 (m, 2H), 3.14 (m, 1H), 2.49 (m, 1H), 2.24 (m, 1H), 2.15 (m, 1H), 2.05 (d, J = 1.5 Hz, 3H), 1.65 (m, 1H), 1.57 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H), 1.27 (m, 1H), 1.12 (m, 1H), 0.90 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.4, 165.3, 157.8, 144.9, 60.8, 46.5, 39.1, 30.3, 22.3, 22.2, 21.8, 14.1, 9.8; IR (neat): ν_{max} 2913, 2854, 1708, 1635, 1448, 1207, 1065 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{19}O_3$ $[M+H]^+$ 223.1328, found 223.1334.

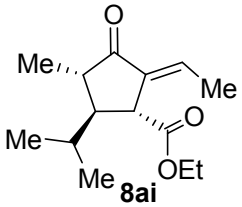
Ethyl 5-isopropyl-2-methyl-3-oxo-4-phenylcyclopent-1-enecarboxylate (3ah): Yield:



3ah

92%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.35-7.18 (m, 3H), 7.11 (d, J = 7.1 Hz, 2H), 4.36 (m, 2H), 3.40 (br d, J = 1.5 Hz, 1H), 3.34 (m, 1H), 2.29 (m, 1H), 2.04 (d, J = 1.8 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H), 0.98 (d, J = 6.9 Hz, 3H), 0.77 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.6, 165.6, 158.3, 144.3, 139.6, 128.7, 127.4, 126.8, 61.1, 54.1, 52.8, 29.6, 21.3, 16.6, 14.1, 9.7; IR (neat): ν_{max} 3026, 1710, 1600, 1494, 1455, 1330, 1214, 1066, 749, 699 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{23}O_3$ $[M+H]^+$ 287.1641, found 287.1643.

(*E*)-Ethyl 2-ethylidene-5-isopropyl-4-methyl-3-oxocyclopentanecarboxylate (8ai): Yield:

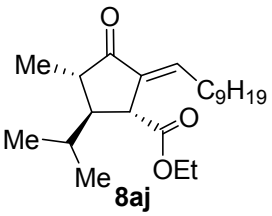


8ai

87%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$): δ 6.80 (dq, J = 2.8, 7.4 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.45 (m, 1H), 2.15 (m, 1H), 2.06 (m, 1H), 1.89 (m, 1H), 1.81 (dd, J = 1.8, 7.4 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.21 (d, J = 7.0 Hz, 3H), 0.96 (dd, J = 2.8, 6.8 Hz, 6H);

^{13}C NMR (75 MHz, $CDCl_3$): δ 206.4, 174.3, 137.0, 135.2, 60.9, 51.6, 45.9, 45.4, 30.4, 19.7, 18.5, 15.6, 14.6, 14.0; IR (neat): ν_{max} 2964, 1725, 1648, 1458, 1165, 928, 856 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{23}O_3$ $[M+H]^+$ 239.1641, found 239.1651.

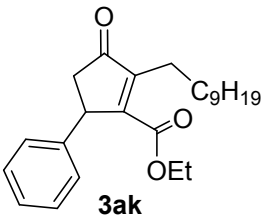
(*E*)-Ethyl 2-decylidene-5-isopropyl-4-methyl-3-oxocyclopentanecarboxylate (8aj): Yield: 82%; colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.71 (td, J = 2.5, 7.6 Hz, 1H), 4.17 (m, 2H), 3.44 (d, J = 6.7 Hz, 1H), 2.13 (m, 3H), 2.05 (m, 1H), 1.89 (m, 1H), 1.43 (m, 2H), 1.34-1.23 (m, 15H), 1.21 (d, J = 7.0 Hz, 3H), 0.96 (dd, J = 2.5, 6.8 Hz, 6H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.8, 174.5, 140.6, 135.7, 60.9, 51.7, 46.2, 46.1, 45.5, 31.8, 30.5, 29.4, 29.3, 29.2, 29.1, 28.1, 22.6, 19.7, 18.6, 15.8, 14.0; IR (neat): ν_{max} 2925, 2857, 1727, 1646, 1460, 1161, 964 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{39}O_3$ $[M+H]^+$ 351.2893, found 351.2910.



8aj

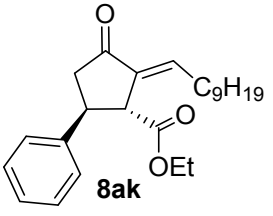
*Compound **3ak** (73%) and **8ak** (13%) were obtained from **1ak**.*

Ethyl 2-decyl-3-oxo-5-phenylcyclopent-1-enecarboxylate (3ak): colorless oil, R_f = 0.45 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (t, J = 7.0 Hz, 2H), 7.21 (m, 1H), 7.10 (d, J = 7.0 Hz, 2H), 4.32 (m, 1H), 4.20-4.05 (m, 2H), 2.97 (dd, J = 7.1, 19.3 Hz, 1H), 2.57 (t, J = 7.6 Hz, 2H), 2.41 (dd, J = 2.1, 19.3 Hz, 1H), 1.54-1.45 (m, 2H), 1.39-1.22 (m, 14H), 1.13 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.0, 164.7, 157.0, 150.5, 141.7, 128.7, 127.0, 60.9, 44.7, 44.4, 44.3, 31.8, 29.8, 29.5, 29.3, 29.2, 28.6, 24.1, 22.6, 14.0, 13.8; IR (neat): ν_{max} 2922, 2855, 1714, 1605, 1212, 761, 700cm^{-1}; HRMS (ESI): calcd for $C_{24}H_{35}O_3$ $[M+H]^+$ 371.2580, found 371.2582.



3ak

(*E*)-Ethyl 2-decylidene-3-oxo-5-phenylcyclopentanecarboxylate (8ak): colorless oil, R_f = 0.4 (10% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, J =

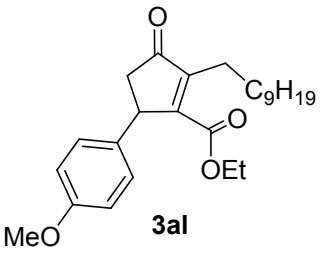


8ak

7.1 Hz, 2H), 7.23 (m, 1H), 7.14 (d, J = 7.1 Hz, 2H), 6.82 (td, J = 1.6, 7.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.78 (m, 2H), 3.04 (dd, J = 8.0, 18.4 Hz, 1H), 2.56 (dd, J = 4.8, 18.4 Hz, 1H), 2.18 (m, 2H), 1.43 (m, 2H), 1.25 (m, 15H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.1, 172.6, 143.3, 141.5, 134.8, 128.8, 127.0, 126.5, 61.2, 52.7, 44.6, 42.1, 31.8, 29.7, 29.6, 29.4, 29.3, 29.2, 28.2, 22.6, 14.1, 14.0; IR (neat): ν_{max} 2921, 2853, 1727, 1647, 1458, 1218, 1030, 700 cm^{-1}; HRMS (ESI): calcd for $C_{24}H_{35}O_3$ $[M+H]^+$ 371.2580, found 371.2582.

*Compound **3al** (64%) and **8al** (24%) were obtained from **1al**.*

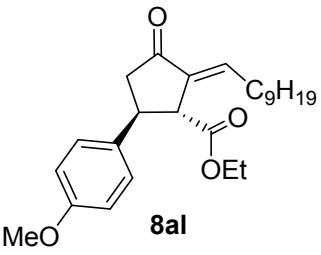
Ethyl 2-decyl-5-(4-methoxyphenyl)-3-oxocyclopent-1-enecarboxylate (3al): colorless oil,



3al

R_f = 0.45 (15% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 4.29 (m, 1H), 4.22-4.05 (m, 2H), 3.77 (s, 3H), 2.95 (dd, J = 7.1, 19.2 Hz, 1H), 2.55 (t, J = 7.3, Hz, 2H), 2.38 (dd, J = 2.0, 19.2 Hz, 1H), 1.49 (m, 2H), 1.40-1.21 (m, 14H), 1.16 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.2, 164.8, 158.5, 157.3, 149.9, 133.5, 128.0, 114.1, 60.9, 55.1, 44.7, 43.6, 31.8, 29.7, 29.5, 29.3, 29.2, 28.6, 24.0, 22.6, 14.0, 13.9; IR (neat): ν_{max} 2923, 2850, 1714, 1640, 1511, 1459, 1244, 1033, 831 cm^{-1}; HRMS (ESI): calcd for $C_{25}H_{37}O_4$ $[M+H]^+$ 401.2686, found 401.2682.

(*E*)-Ethyl 2-decylidene-5-(4-methoxyphenyl)-3-oxocyclopentanecarboxylate (8al):

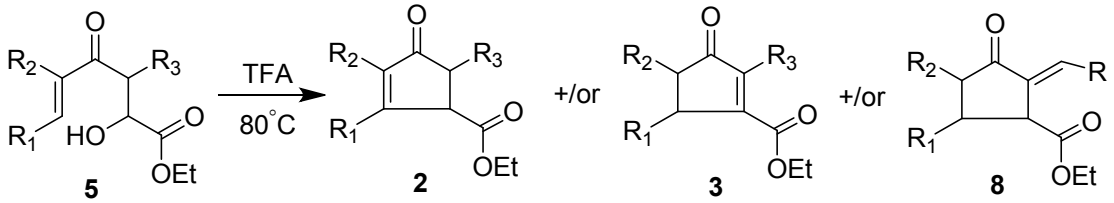


8al

colorless oil, R_f = 0.4 (15% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.80 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.73 (m, 2H), 3.02 (dd, J = 7.7, 18.1 Hz, 1H), 2.52 (dd, J = 4.7, 18.1 Hz, 1H), 2.17 (m, 2H), 1.43 (m, 2H), 1.34-1.13 (m, 15H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ 204.2, 172.7, 158.5, 141.4, 135.3, 134.8, 127.6, 114.1, 61.1, 55.2, 53.0, 44.7, 41.5, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 28.2, 22.6, 14.0; IR (neat): ν_{max} 2923, 2854, 1727, 1646, 1513, 1460, 1250, 1176, 1034, 829 cm^{-1}; HRMS (ESI): calcd for $C_{25}H_{37}O_4$ $[M+H]^+$ 401.2686, found 401.2686.

2.5. General procedure for the synthesis of cyclopentenones 2/3/8 from 5:

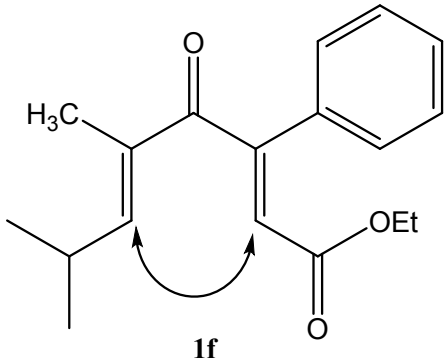


5 **2** **3** **8**

To an alcohol **5** was added TFA (10 equiv) at rt and the reaction mixture was slowly warmed to 80 °C. The reaction was monitored by TLC, after completion of the starting material, the reaction was cooled and quenched with saturated aq $NaHCO_3$, and extracted with EtOAc. The organic layer was washed with saturated aq NaCl, and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by using silica gel column chromatography (EtOAc/ hexanes) to give **2** or/and **3** or/and **8**.

3. 2D NMR experiments of compounds 1f, 1'f, 2a, 3e, 7, 8ai:

The relative stereochemistry and the regio isomers of the compounds **1f**, **1'f**, **2a**, **3e**, 7, **8ai** were determined by 2D NMR experiments. The scalar couplings as well as distinctive nOe correlations as shown in the figures 1-6, were extensively used to characterize and confirm the structures of the these compounds.



1f

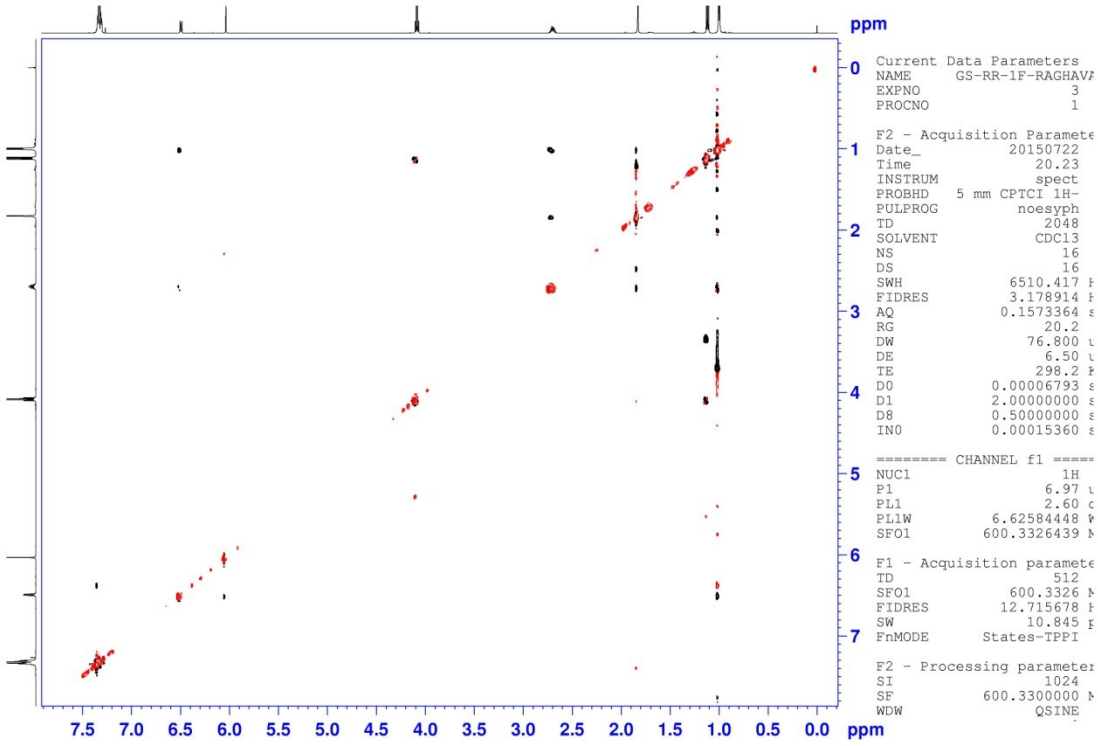
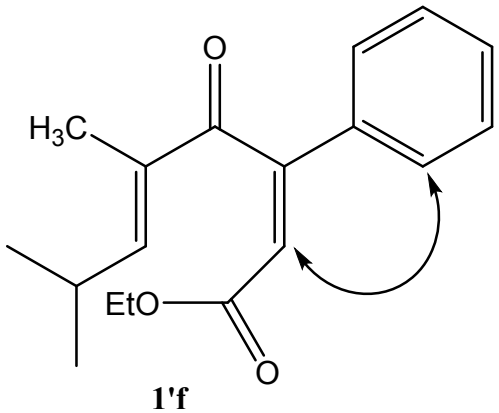


Figure 1. Compound **1f** nOe correlations



1'f

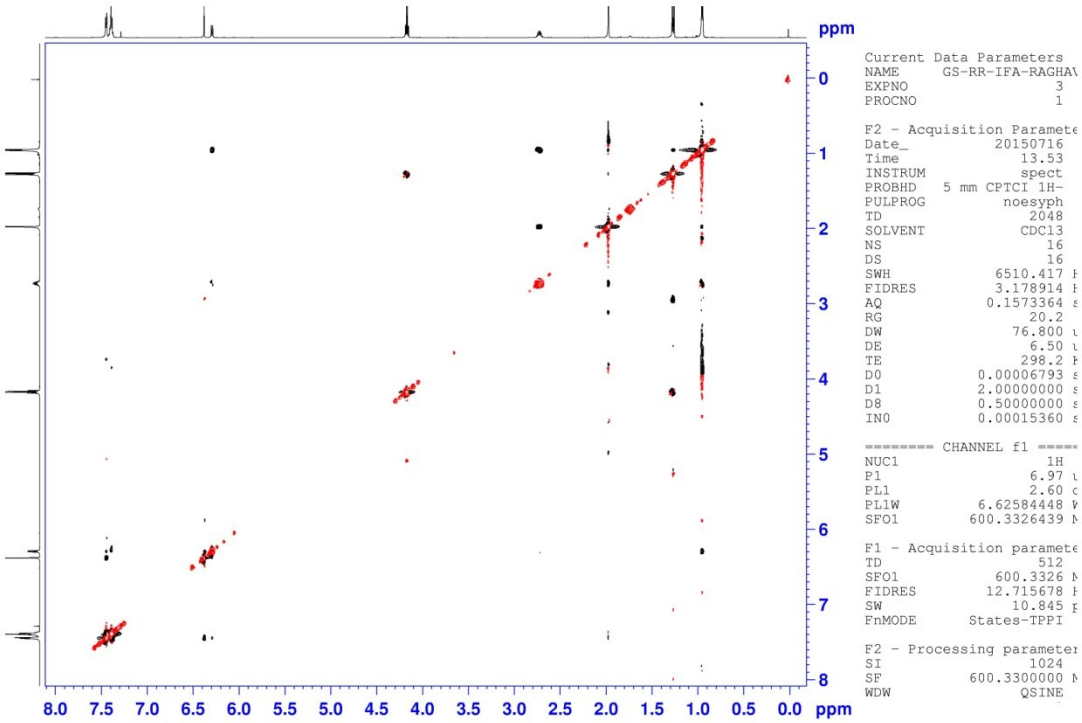
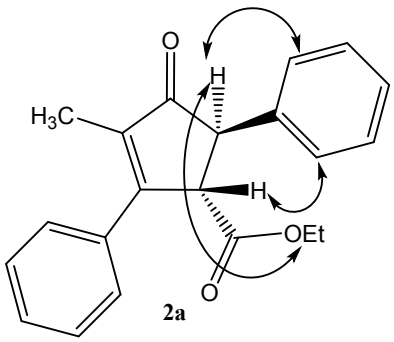


Figure 2. Compound **1'f** nOe correlations



2a

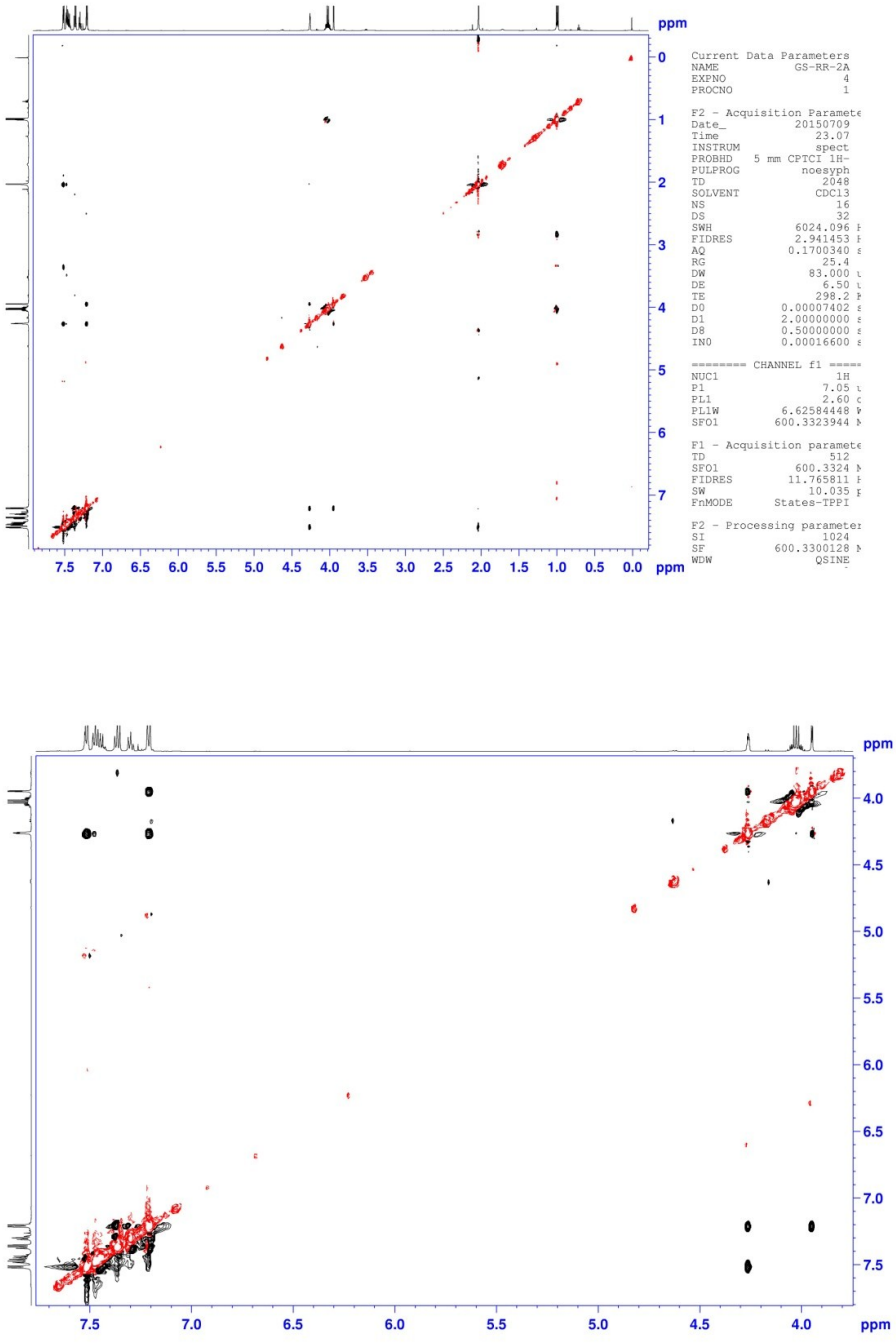
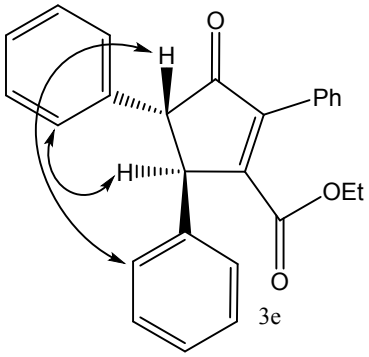


Figure 3. Compound **2a** nOe correlations



3e

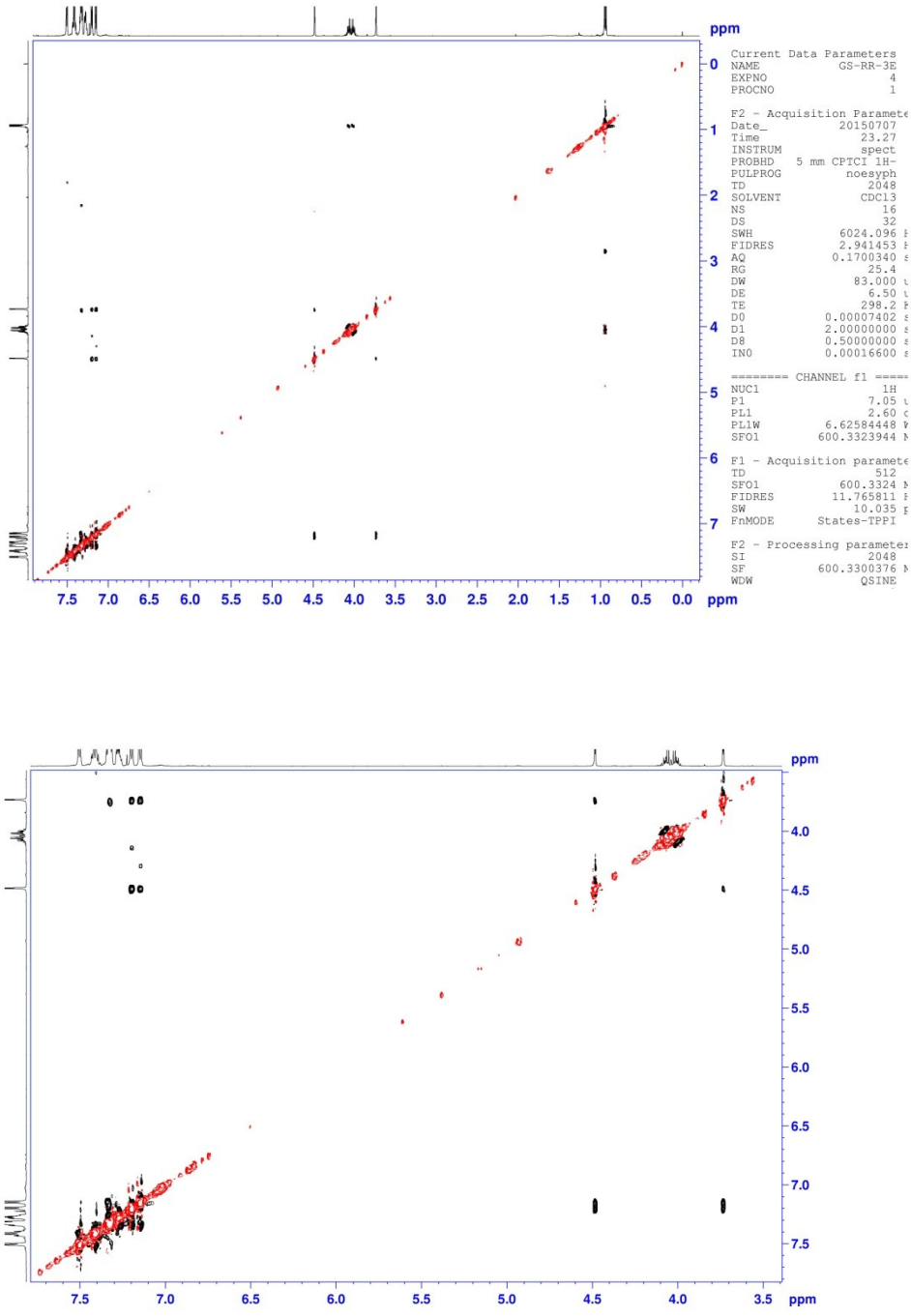
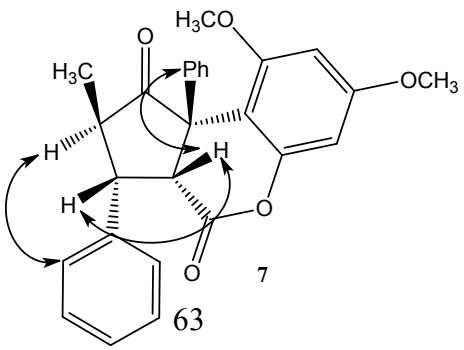


Figure 4. Compound **3e** nOe correlations



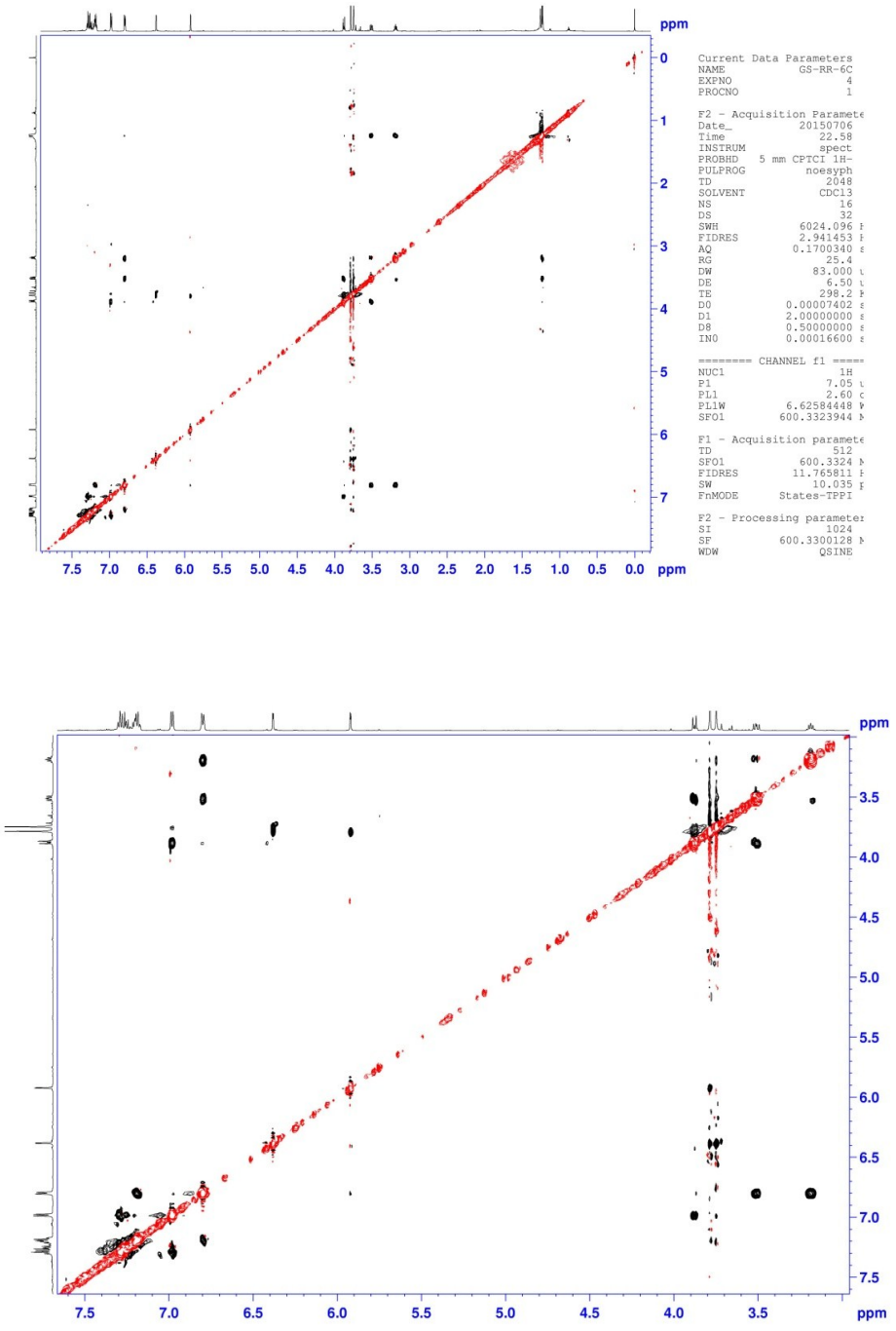
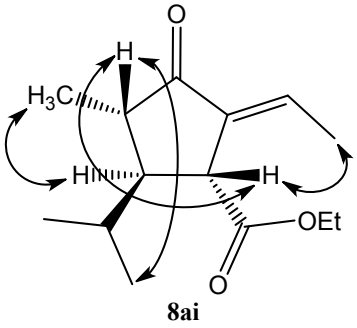


Figure 5. Compound **7** nOe correlations



8ai

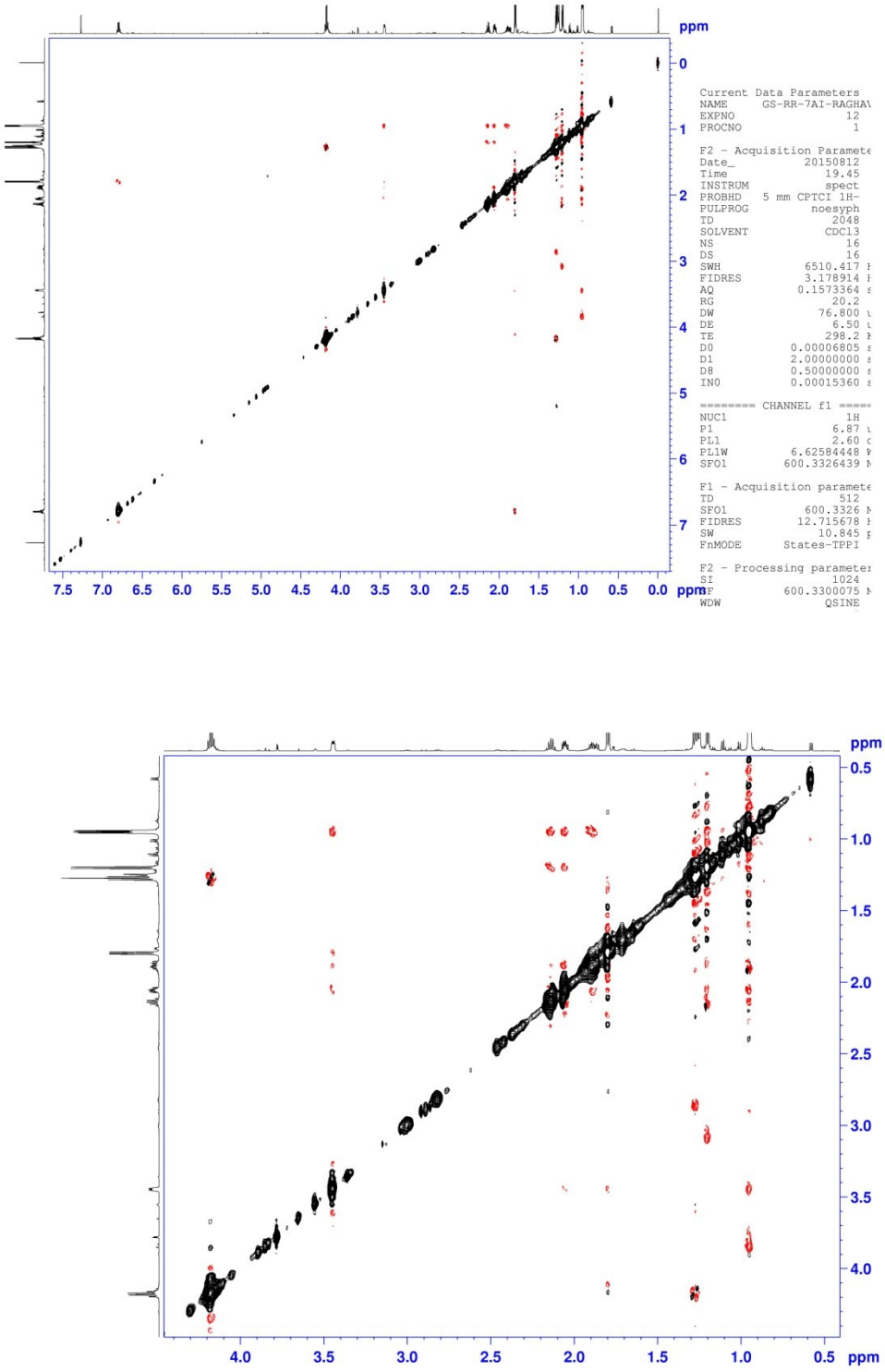


Figure 6. Compound **8ai** nOe correlations

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