Supporting Information

A New Co₂(CO)₈-Mediated Tandem [5+1]/[2+2+1]-Cycloaddition Reactions: One-Pot Synthesis of Tricyclic γ -Lactones from *cis*-Epoxy Ene-ynes

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(1) Synthetic procedures for *cis*-epoxy ene-yne **1**, **4**, **7-16**.

Scheme S-1

Synthesis of *cis*-allylic alcohol (**S-2a**):

To a mixture of PdCl₂(Ph₃P)₂ (350 mg, 0.51 mmol) and CuI (40 mg, 0.25 mmol) in Et₃NH (50 ml) was added compound **S-1** (5.0 g, 25.55 mmol) at RT under N₂ atmosphere and stirred for 10 min before the addition of phenylacetylene (3.13 g, 30.66 mmol). The reaction mixture was allowed to stir at RT for 8 h. The reaction was quenched by an aq NH₄Cl solution and it was extracted with ether and washed with H₂O. The organic layer was dried using anhydrous MgSO₄ and concentrated. The residue was subjected to column chromatography (silica gel, hexane-ether, 2:1) resulting in **S-2a** (3.5 g, 20.32 mmol, 80 %).

Synthesis of *cis*-allylic bromide (**S-3a**):

To a CH₂Cl₂ solution containing Ph₃P (5.86 g, 22.35 mmol) at 0 °C was added Br₂ (3.56 g, 22.35 mmol) dropwise under N₂ atmosphere. After 20 min stirring, alcohol **S-2a** (3.5 g, 20.32 mmol) was added and the reaction mixture was stirred for 20 minutes. The reaction was quenched with water and it was extracted with hexane. The combine organic layers was dried (Na₂SO₄) and concentrated. The elution of the

residue through a short silica column gave the *cis*-allylic bromide **S-3a** (4.38 g, 18.62 mmol, 92 %).

Synthesis of *cis*-allylic methyl ether (**S-4a**):

To a THF solution (15 ml) containing NaH (380 mg, 16.5 mmol), allylic alcohol **S-2b** (2.1 g, 13.8 mmol) was added in THF (1.0 ml) at 0 °C and the mixture was stirred for 1 h before addition of methyl iodide (1.96 g, 13.8 mmol) and the reaction mixture was allowed to stir at RT under N₂ atmosphere for 8 h. To the solution was added a saturated NH₄Cl solution, followed by extraction with diethyl ether and was dried over MgSO₄. The concentrated residue was subjected to column chromatography (hexane-ether, 3:1) gave *cis*-allylic methyl ether as a light yellow color oil (2.3 g, 11.8 mmol, 85.7 %).

Synthesis of *cis*-allylic benzyltosylate (**S-4b**):

To a THF solution (20 ml) containing NaH (118 mg, 4.93 mmol), benzyltosylate (1.0 g, 3.82 mmol) was added in THF (1.0 ml) at 0 °C and the mixture was stirred for 1 h before addition of *cis*-allylic bromide **S-3c** (1.0 g, 4.11 mmol) and the reaction mixture was allowed to stir at 23 °C under N₂ atmosphere for 8 h. The reaction was quenched by an aqueous NH₄Cl solution and the organic layer was extracted with ether and washed with H₂O. The combined organic layers was dried over MgSO₄ and concentrated. The residue was eluted through a silica column (hexane-ether, 9:1) to give tosylate **S-4b** as a colorless solid (1.77 g, 10.6 mmol, 77 %).

Synthesis of *cis*-epoxyalkyne (**1a**):

To a CH₂Cl₂ solution (20 ml) of *cis*-allyl methyl ether **S-4a** (1.0 g, 6.0 mmol) was added *m*-chloroperbenzoic acid (1.24 g, 7.2 mmol) and the mixtures were stirred for 12 h at RT under a N₂ atmosphere. The resulting solution was quenched with an aqueous NaHCO₃ solution, extracted with diethyl ether, dried over anhydrous MgSO₄. The resulting solution was filtered through a small Al₂O₃ (basic) bed, then concentrated and eluted

through a Et₃N-pretreated silica column (diethyl ether-hexane, 1:1) to afford the *cis*-epoxyalkyne **1a** as a colourless oil (0.80 g, 4.40 mmol, 73 %).

Synthesis of *cis*-epoxyalkyne (**1b**):

To a CH₂Cl₂ solution (20 ml) of *cis*-allylic benzylosylate **S-4b** (1.0 g, 2.36 mmol) was added *m*-chloroperbenzoic acid (0.49 g, 2.8 mmol) and the mixtures were stirred for 12 h at RT under N₂ atmosphere. The resulting solution was quenched with aq NaHCO₃ solution, extracted with diethyl ether, dried over anhydrous MgSO₄. The resulting solution was filtered through a small bed of basic Al₂O₃, then concentrated and eluted through a Et₃N-pretreated silica column (diethyl ether: hexane, 1:1) to afford the *cis*-epoxyalkyne **1b** as a colourless oil (0.70 g, 1.60 mmol, 68 %).

Synthesis of *cis*-diene (**S-5a**):

To an ether solution (20 ml) of *cis*-allylic bromide **s-3a** (2.0 g, 8.5 mmol) at -78°C was added allyl magnesium bromide (8.5 ml, 8.5 mmol) and the mixtures were stirred at 23°C 10 h. The resulting solution was then quenched with an aqueous NH₄Cl solution and

extracted with diethyl ether. The combined organic layers was dried over anhydrous MgSO_4 and concentrated. The resulting residue was then passed through a small silica bed to afford the *cis*-dienes-**5a** (1.44 g, 7.35 mmol, 87 %).

Synthesis of *cis*-epoxyalkyne (**4**):

To a CH_2Cl_2 solution (10 ml) of *cis*-diene **s-5a** (0.63 g, 2.99 mmol) was added *m*-chloroperbenzoic acid (0.62 g, 3.59 mmol) and the mixtures were stirred for 12 h at 25 °C under a N_2 atmosphere. The resulting solution was quenched with an aqueous NaHCO_3 solution, extracted with diethyl ether, and dried over MgSO_4 . The resulting solution was filtered through a short Al_2O_3 (basic) bed, then concentrated and eluted through a Et_3N -pretreated silica column (diethyl ether-hexane, 1:1) to afford the *cis*-epoxyalkyne **4** as a yellow oil (0.40 g, 1.80 mmol, 61 %).

Synthesis of *cis*-allylic alcohol (**s-6**):

To a 50 ml two-necked flask was placed 1.22 ml (14.0 mmol) of oxalyl chloride and 10 ml of dry dichloromethane. The solution was cooled to -60 °C to -70 °C and a CH_2Cl_2 (20 mL) of DMSO (2.0 mL, 28.0 mmol) was added. After 20 min, a CH_2Cl_2 solution (5.0 mL) of alcohol **s-2c** (2.30 g, 12.7 mmol) was added over a period of 5 min. To this mixture was added triethylamine (9.76 mL, 70 mmol) at -50 °C, and the mixtures were stirred for 0.5 h before it was brought to 23 °C. The reaction mixture was poured into water and the organic layer was extracted with dichloromethane. The extracts were washed with brine, dried over magnesium sulfate, and concentrated. The residues were chromatographed (hexane-ethylacetate, 10:1) on a silica gel to afford the aldehyde. To a THF solution (10 mL) of this aldehyde (1.94 g, 10.8 mmol) was added allylmagnesium bromide (13.0 ml, 13.0 mmol) at -78 °C and the mixture was stirred at 23 °C for 8 h. The reaction was quenched with a aqueous NH_4Cl solution, extracted with

diethyl ether, dried over Na₂SO₄. The residues were chromatographed through a silica column (silica gel, hexane-ether 1:1) to give the alcohol **s-6** (2.0 g, 9.0 mmol, 84 %).

Synthesis of *cis*-epoxy alcohol (s-7):

To a CH₂Cl₂ solution (20 ml) of allylic alcohol **s-6** (1.00 g, 4.50 mmol) was added *m*-chloroperbenzoic acid (0.94 g, 5.71 mmol) and the mixtures were stirred at 23 °C for 8 h. The resulting solution was quenched with NaHCO₃ solution, extracted with diethyl ether, and dried over anhydrous MgSO₄. The resulting solution was filtered through a small Al₂O₃ bed, then concentrated and eluted through a Et₃N-pretreated silica column (diethyl ether-hexane, 1:1) to afford the epoxyalcohol **s-7** as a colorless oil (0.90g, 3.82 mmol, 84 %).

Synthesis of *cis*-epoxyalkyne (8a)

To a CH₂Cl₂ solution (20 ml) of epoxy alcohol **s-7** (1.00g, 4.23 mmol) was added pyridine (1.00 ml, 12.7 mmol) at 0 °C. After 10 min, the mixture was added acetyl chloride (0.60 ml, 8.43 mmol), and the resulting mixtures were stirred for 2 h. The resulting solution was quenched with water, extracted with diethyl ether, and dried over anhydrous MgSO₄. The residues were chromatographed through a short silica bed to afford epoxyalkyne **8a** as a color oil (0.95 g, 3.44 mmol, 81.0 %).

Synthesis of *cis*-epoxyalkyne (8b):

To a THF solution (50 ml) containing NaH (61 mg, 2.5 mmol), epoxyalcohol **s-7** (0.5 g, 2.1 mmol) was added in THF (1 ml) at 0 °C and the mixtures were stirred for 1 h before addition of methyl iodide (330 mg, 2.3 mmol). The reaction mixture was stirred for 4 h at 23 °C under a N₂ atmosphere. To the solution was added a NH₄Cl solution, and the organic layer was extracted with diethyl ether and dried over MgSO₄. The concentrated residues were chromatographed through a silica column (hexane-ether, 1:1) to give epoxyalkyne **8b** as a colorless oil (0.40 g, 1.61 mmol, 76.0 %).

Synthesis of *cis*-epoxyalkyne (9):

To a CH₂Cl₂ solution (20 ml) of compound **s-3c** (1.20 g, 3.50 mmol) was added *m*-chloroperbenzoic acid (0.743 g, 4.3 mmol) and the mixtures were stirred for 12 h at 23 °C before quenching with a NaHCO₃ solution. The organic layer was extracted with diethyl ether, dried over MgSO₄. The solution was filtered through a short Al₂O₃ bed, then concentrated and eluted through a Et₃N-pretreated silica column (diethyl ether-hexane, 2:1) to afford epoxyalkyne **9** as a colourless oil (0.9 g, 2.5 mmol, 71.4 %).

Synthesis of *cis*-epoxyalkyne (10):

To a CH₂Cl₂ solution (20 ml) of compound **s-8a** (0.50 g, 2.27 mmol) was added *m*-chloroperbenzoic acid (0.39 g, 2.5 mmol) and the mixtures were stirred for 12 h at 23 °C before quenching with NaHCO₃ solution. The organic layer was extracted with diethyl ether, dried over MgSO₄. The resulting solution was filtered through a small Al₂O₃ bed, concentrated and eluted through a Et₃N-pretreated silica column (diethyl ether-hexane, 2:1) to afford the epoxyalkyne **10** as a colourless oil (0.352 mg, 1.49 mmol, 65 %).

Synthesis of *cis*-epoxyalkyne (11):

To a CH₂Cl₂ solution (20 ml) of compound **s-8b** (2.47 g, 6.61 mmol) was added *m*-chloroperbenzoic acid (1.48 g, 8.59 mmol) and the mixtures were stirred at 23 °C for 12 h before quenching with NaHCO₃. The organic layer was extracted with diethyl ether, and dried over MgSO₄. The resulting solution was filtered through a small Al₂O₃ bed, concentrated and eluted through a Et₃N-pretreated silica column (diethyl ether-hexane, 2:1) to afford the epoxyalkyne **11** as a colourless oil (1.67 g, 4.68 mmol, 65 %).

Synthesis of epoxyalkyn-enes 12a,b-16 followed the procedures for related analogues 4, 7-11 using the following starting material

(2) (a) Experimental procedure for cyclization of *cis*-epoxy ene-yne to tricyclic cyclopentanone. Synthesis of compound 5. To a benzene solution (5 mL) of *cis*-epoxy ene-yne **4** (100 mg, 0.47 mmol) was added $\text{Co}_2(\text{CO})_8$ (177 mg, 0.51 mmol) under nitrogen and the mixture was stirred for 2 h at 23 °C. The solution was transferred to a high pressure reactor under CO (50 psi) and heated at 80 °C for 24 h. The solution was filtered over a short silica bed and the filtrate was concentrated, eluted through a silica column (diethyl ether/hexane=1/1) to afford tricyclic cyclopentanone as colorless solid (93 mg, 0.34 mmol, 74 %).

(b) Experimental procedure for cyclization of *cis*-epoxy ene-yne to tricyclic cyclobutane. Synthesis of compound 6. To a benzene solution (5 mL) of *cis*-epoxy ene-yne **4** (100 mg, 0.47 mmol) was added $\text{Co}_2(\text{CO})_8$ (177 mg, 0.51 mmol) under nitrogen and the mixture was stirred for 2 h at 23 °C. The mixture was heated at 75 °C under nitrogen for 24 h. The solution was filtered over a short silica bed and the filtrate was concentrated, eluted through a silica column (diethyl ether/hexane=1/2) to afford tricyclic cyclobutane **6** as a colorless solid (84 mg, 0.35 mmol, 75 %).

(3) Spectra data for compounds 1-30:

3-Methyl-5-phenyl-pent-2-en-4-yn-1-ol (S-2a). IR (neat, cm^{-1}): 3348 (vs), 2241(m), 1633(w); ^1H NMR (400 MHz, CDCl_3): 7.41~7.45 (m, 2 H), 7.28~7.33 (m, 3 H), 5.91

(t, $J = 4.4$ Hz, 1 H), 4.39 (d, $J = 5.2$ Hz, 2 H), 1.95 (s, 3 H), 1.82 (b, OH); ^{13}C NMR (100 MHz, CDCl_3): 135.6, 131.4, 128.3, 128.3, 123.0, 120.8, 94.3, 87.3, 61.48, 23.1; Mass (75 eV, m/z): 172 (M^+).

5-Bromo-3-methyl-pent-3-en-1-ynyl-benzene (S-3a). IR(neat, cm^{-1}): 2240(m), 1654(w), 1633(w); ^1H NMR (400 MHz, CDCl_3): 7.44~7.46 (m, 2 H), 7.31~7.34 (m, 3 H), 5.88 (t, $J = 14.0$ Hz, 1 H), 4.34 (d, $J = 8.0$ Hz, 2 H), 1.98 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 131.6, 131.5, 128.5, 128.3, 123.4, 122.8, 95.7, 86.5, 42.4, 23.0; Mass (75 eV, m/z): 234 (M^+).

1-Methoxy-3-methyl-non-2-en-4-yne (S-4a). IR (neat, cm^{-1}): 2254(m), 1651(w); ^1H NMR (300 MHz, CDCl_3): 5.67 (t, $J = 7.2$ Hz, 1 H), 4.07 (d, $J = 6.6$ Hz, 2 H), 3.30 (s, 3 H), 2.31 (t, $J = 6.8$ Hz, 2 H), 1.83 (s, 3 H), 1.52~1.36 (m, 4 H), 0.897 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): 131.4, 122.5, 95.5, 79.0, 70.5, 57.8, 30.8, 23.5, 21.9, 19.0, 13.5; Mass (75 eV, m/z): 194 (M^+).

N-Benzyl-4-methyl-N-(3-methyl-undec-2-en-4-ynyl)-benzenesulfonamide (S-4b). IR (neat, cm^{-1}): 2239(m), 1656(w), 1634(w); ^1H NMR (400 MHz, CDCl_3): 7.72 (d, $J = 8.0$ Hz, 2 H), 7.31~7.25 (m, 7 H), 5.27 (t, $J = 7.2$ Hz, 1 H), 4.29 (s, 2 H), 3.94 (d, $J = 7.6$ Hz, 2 H), 2.42 (s, 3 H), 1.63 (s, 3 H), 2.18 (t, $J = 6.8$ Hz, 2 H), 1.30~1.19 (m, 4 H), 0.97 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 143.0, 137.3, 136.5, 129.5, 128.5, 128.3, 128.2, 127.4, 127.2, 123.1, 96.0, 78.4, 50.6, 47.1, 31.3, 28.5, 28.4, 23.3, 22.4, 21.4, 19.2, 13.9; Mass (75 eV, m/z): 423 (M^+).

2-Hex-1-ynyl-3-methoxymethyl-2-methyl-oxirane (1a). IR (neat, cm^{-1}): 2242(w); ^1H NMR (400 MHz, CDCl_3): 3.70 (dd, $J = 11.2, 4.4$ Hz, 1 H), 3.55 (dd, $J = 11.2, 5.6$ Hz, 1 H), 3.39 (s, 3 H), 3.02 (t, $J = 6.0$ Hz, 1 H), 2.18 (t, $J = 1.6$ Hz, 2 H), 1.53 (s, 3 H), 1.49~1.38 (m, 4 H), 0.884 (t, $J = 1.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 85.9, 81.2, 72.1, 62.5, 59.2, 51.6, 30.6, 23.8, 22.0, 18.5, 13.7; Mass (75 eV, m/z): 182 (M^+).

N-Benzyl-4-methyl-N-(3-methyl-3-oct-1-ynyl-oxiranylmethyl)-benzenesulfonami

de (1b). IR (neat, cm^{-1}): 2239(m), 1627(w); ^1H NMR (400 MHz, CDCl_3): 7.75 (d, $J = 6.8$ Hz, 2 H), 7.34~7.24 (m, 7 H), 4.59 (d, $J = 14.8$ Hz, 1 H), 4.23 (d, $J = 15.2$ Hz, 1 H), 3.48 (dd, $J = 15.2, 4.8$ Hz, 1 H), 3.36 (dd, $J = 14.8, 6.0$ Hz, 1 H), 2.80 (t, $J = 4.8$ Hz, 1 H), 2.43 (s, 3 H), 2.48 (t, $J = 6.0$ Hz, 2 H), 1.42~1.19 (m, 4 H), 1.18 (s, 3 H), 0.848 (t, $J = 6.4$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 143.4, 136.7, 136.6, 129.7, 128.4, 128.2, 127.6, 127.2, 86.3, 76.8, 62.2, 52.6, 52.5, 48.1, 31.7, 28.4, 28.2, 22.9, 22.4, 21.4, 18.5, 13.9; Mass (75 eV, m/z): 439 (M^+).

3-Methyl-octa-3,7-dien-1-ynyl-benzene (s-5a). IR (neat, cm^{-1}): 2241(m), 1647(w), 1624(w); ^1H NMR (400 MHz, CDCl_3): 7.37~7.44 (m, 2 H), 7.28~7.34 (m, 3 H), 5.85 (m, 1 H), 5.73 (t, $J = 6.6$ Hz, 1 H), 5.06 (dd, $J = 17.6, 2.4$ Hz, 1 H), 4.99 (dd, $J = 10.4, 2.4$ Hz, 1 H), 2.41 (q, $J = 14.4$ Hz, 2 H), 2.16 (q, $J = 13.8$ Hz, 2 H), 1.91 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 138.1, 137.3, 131.3, 128.2, 127.8, 123.6, 118.3, 114.7, 92.9, 88.7, 33.2, 30.04, 22.9; Mass (75 eV, m/z): 196 (M^+).

6-Methyl-tetradeca-1,5-dien-7-yn-4-ol (s-6). IR (neat, cm^{-1}): 3423(vs); 2238(m), 1644(w), 1625(w); ^1H NMR (300 MHz, CDCl_3): 5.85~5.74 (m, 1 H), 5.58 (dd, $J = 8.22, 1.16$ Hz, 1 H), 5.13 (d, $J = 8.9$ Hz, 1 H), 5.08 (d, $J = 1.28$ Hz, 1 H), 4.63~4.56 (m, 1 H), 2.32~2.26 (m, 2 H), 1.81 (s, 3 H), 1.55~1.46 (m, 2 H), 1.42~1.18 (m, 8 H), 0.867 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): 137.4, 134.3, 120.8, 117.8, 95.7, 79.0, 69.7, 41.2, 31.2, 28.6, 28.5, 23.5, 22.5, 19.4, 14.0; Mass (75 eV, m/z): 220 (M^+).

1-(3-Methyl-3-oct-1-ynyl-oxiranyl)-but-3-en-1-ol (s-7). IR (neat, cm^{-1}): 3383(vs); 2241(m); ^1H NMR (400 MHz, CDCl_3): 5.92~5.82 (m, 1 H), 5.20 (d, $J = 3.6$ Hz, 1 H), 5.14 (d, $J = 10.4$ Hz, 1 H), 3.76~3.70 (m, 1 H), 3.52 (dd, $J = 3.6, 1.6$ Hz, 1 H), 3.02 (dd, $J = 8.0, 4.4$ Hz, 1 H), 2.45~2.38 (m, 2 H), 2.20 (t, $J = 6.8$ Hz, 2 H), 1.52~1.22 (m, 11 H), 0.883 (t, $J = 7.6$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 133.2, 118.1, 87.7, 74.1, 70.8, 60.4, 52.2, 37.8, 31.2, 28.4, 28.2, 23.9, 22.4, 18.6, 13.9; Mass (75 eV, m/z): 236 (M^+).

3-Butyl-5-hydroxy-6-methoxymethyl-5-methyl-5,6-dihydro-pyran-2-one (2a). IR (neat, cm^{-1}): 3351(vs), 1713(s); ^1H NMR (400 MHz, CDCl_3): 6.43 (s, 1 H), 4.42 (t, $J = 6.8$ Hz, 1 H), 3.72 (d, $J = 7.2$ Hz, 2 H), 3.42 (s, 1 H), 2.28~2.19 (m, 2 H), 1.45~1.27 (m, 4 H), 1.25 (s, 3 H), 0.879 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 163.8, 147.1, 129.5, 78.6, 70.8, 69.0, 59.6, 29.9, 29.8, 22.1, 21.0, 13.7; HRMS calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_4$: 228.1352, Found: 228.1358.

N-Benzyl-N-(5-hexyl-3-hydroxy-3-methyl-6-oxo-3,6-dihydro-2H-pyran-2-ylmethyl)-4-methyl-benzenesulfonamide (2b). IR (neat, cm^{-1}): 3351(vs), 1721(s), 1622(w); ^1H NMR (500 MHz, CDCl_3): 7.66 (d, $J = 8.0$ Hz, 2 H), 7.25~7.17 (m, 7 H), 6.88 (s, 1 H), 5.19 (t, $J = 7.0$ Hz, 1 H), 4.26 (s, 2 H), 3.80 (d, $J = 6.5$ Hz, 2 H), 2.38 (s, 3 H), 2.17 (t, $J = 7.5$ Hz, 2 H), 1.50 (s, 3 H), 1.35~1.15 (m, 8 H), 0.812 (t, $J = 4.0$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): 173.1, 143.4, 137.2, 135.6, 135.4, 131.1, 129.7, 128.6, 128.3, 127.9, 127.1, 76.7, 66.0, 50.86, 44.3, 31.5, 29.9, 29.4, 27.3, 22.6, 21.5, 15.9, 14.0; HRMS calcd. for $\text{C}_{27}\text{H}_{35}\text{NO}_5\text{S}$: 485.2236, Found: 485.2232.

N-Benzyl-N-(5-hexyl-3-methyl-6-oxo-6H-pyran-2-ylmethyl)-4-methyl-benzenesulfonamide (3b). IR (neat, cm^{-1}): 1713(s), 1622(w); ^1H NMR (500 MHz, CDCl_3): 7.64 (d, $J = 8.5$ Hz, 2 H), 7.31~7.22 (m, 7 H), 6.56 (s, 1 H), 4.44 (s, 2 H), 4.06 (s, 2 H), 2.39 (s, 3 H), 2.22 (t, $J = 8.5$ Hz, 2 H), 1.29~1.25 (m, 8 H), 0.871 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): 162.1, 150.7, 143.5, 141.9, 136.1, 135.8, 129.6, 128.3, 128.2, 127.6, 127.0, 113.8, 52.6, 45.8, 31.5, 31.4, 30.1, 28.9, 27.7, 22.5, 21.5, 14.6, 14.0; HRMS calcd. for $\text{C}_{27}\text{H}_{33}\text{NO}_4\text{S}$: 467.2130, Found: 467.2133.

3-But-3-enyl-2-methyl-2-phenylethynyl-oxirane (4). IR (neat, cm^{-1}): 2215(w), 1645(w), 1622(w); ^1H NMR (400 MHz, CDCl_3): 7.40~7.43 (m, 2 H), 7.25~7.30 (m, 3 H), 5.82~5.92 (m, 1 H), 5.08 (dd, $J = 17.6, 3.2$ Hz, 1 H), 5.00 (dd, $J = 10.8, 2.0$ Hz, 1 H), 2.93 (t, $J = 6.4$ Hz, 1 H), 2.25~2.32 (m, 2 H), 1.85~1.90 (m, 2 H), 1.61 (s, 3 H); ^{13}C NMR (100 MHz): 137.4, 131.8, 128.5, 128.2, 122.2, 115.2, 86.8, 84.1, 64.8, 52.8,

30.1, 29.5, 23.4; Mass (75 eV, m/z): 212 (M^+).

Spectral data of tricyclic cyclopentanone (5). IR (neat, cm^{-1}): 1730(s), 1723(s), 1644(w), 1613(w); ^1H NMR (400 MHz, CDCl_3): 7.34~7.39 (m, 3 H), 7.28~7.31 (m, 2 H), 4.88 (t, $J = 8.8$ Hz, 1 H), 2.74 (dd, $J = 19.6, 8.0$ Hz, 1 H), 2.50 (dd, $J = 15.6, 9.2$ Hz, 1 H), 2.33~2.40 (m, 1 H), 2.27 (d, $J = 19.6$ Hz, 1 H), 2.02~2.16 (m, 2 H), 1.40~1.50 (m, 1 H), 1.44 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 203.4, 163.3, 147.2, 132.4, 130.5, 130.3, 129.3, 127.3, 86.8, 48.3, 43.8, 41.2, 30.7, 29.1, 22.4; HRMS Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$: 268.1094; Found: 268.1099.

Spectral data of tricyclic cyclobutane (6). IR (neat, cm^{-1}): 1729(s), 1642(w), 1622(w); ^1H NMR (400 MHz, CDCl_3): 7.30~7.36 (m, 2 H), 7.25~7.28 (m, 3 H), 4.58 (t, $J = 10.0$ Hz, 1 H), 3.71 (dd, $J = 16.2, 9.6$ Hz, 1 H), 2.60 (d, $J = 13.6$ Hz, 2 H), 2.14~2.26 (m, 2 H), 1.85~1.91 (m, 1 H), 1.68~1.74 (m, 1 H), 1.53 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 158.3, 132.5, 129.7, 128.3, 128.2, 127.8, 127.6, 86.1, 53.1, 40.8, 39.9, 31.7, 27.4, 17.6; HRMS Calcd for: $\text{C}_{16}\text{H}_{16}\text{O}_2$: 240.1175 ; Found: 240.1177.

3-But-3-enyl-2-methyl-2-oct-1-ynyl-oxirane (7a). IR (neat, cm^{-1}): 2234(w), 1642(w); ^1H NMR (400 MHz, CDCl_3): 5.89~5.79 (m, 1 H), 5.05 (dd, $J = 17.2, 1.6$ Hz, 1 H), 4.98 (dd, $J = 10.4, 1.6$ Hz, 1 H), 2.81 (t, $J = 6$ Hz, 1 H), 2.49~2.16 (m, 4 H), 1.80~1.74 (m, 2 H), 1.48 (s, 3 H), 1.48~1.22 (m, 8 H), 0.86 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 137.5, 114.9, 85.2, 77.7, 64.3, 52.6, 31.1, 30.0, 29.3, 28.3, 23.6, 22.4, 18.5, 13.8; Mass (75 eV, m/z): 220 (M^+).

(3-But-3-enyl-2-methyl-oxiranylethynyl)-trimethylsilane (7b). IR (neat, cm^{-1}): 1644(w); ^1H NMR (400 MHz, CDCl_3): 5.78~5.86 (m, 1 H), 5.01 (d, $J = 17.2$ Hz, 1 H), 4.97 (d, $J = 8.0$ Hz, 1 H), 2.81 (t, $J = 6.0$ Hz, 1 H), 2.19~2.26 (m, 2 H), 1.73~1.83 (m, 2 H), 1.49 (s, 3 H), 0.130 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): 137.3, 114.9, 103.0, 89.2, 64.4, 52.3, 29.9, 29.2, 23.0, -0.39 (3 CH_3); Mass (75 eV, m/z): 208 (M^+).

Acetic acid 1-(3-methyl-3-oct-1-ynyl-oxiranyl)-but-3-enyl ester (8a). IR (neat,

cm⁻¹): 2233(w), 1718(s), 1642(w); ¹H NMR (400 MHz, CDCl₃): 5.83~5.73 (m, 1 H), 5.11 (d, *J* = 15.2 Hz, 1 H), 5.08 (d, *J* = 7.2 Hz, 1 H), 4.92~4.87 (m, 1 H), 2.94 (d, *J* = 7.8 Hz, 1 H), 2.58~2.44 (m, 2 H), 2.20 (t, *J* = 4.8 Hz, 2 H), 2.05 (s, 3 H), 1.55~1.27 (m, 11 H), 0.869 (t, *J* = 5.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): 170.2, 132.6, 118.3, 86.7, 79.2, 73.9, 64.6, 52.2, 36.3, 31.4, 28.6, 28.5, 23.9, 22.6, 21.2, 18.8, 14.2; Mass (75 eV, *m/z*): 278 (M⁺).

3-(1-Methoxy-but-3-enyl)-2-methyl-2-oct-1-ynyl-oxirane (8b). IR(neat, cm⁻¹): 2243(w), 1644(w); ¹H NMR (300 MHz, CDCl₃): 5.90~5.78 (m, 1 H), 5.11 (d, *J* = 15.2 Hz, 1 H), 5.04 (d, *J* = 7.2 Hz, 1 H), 3.35 (s, 3 H), 3.26~3.19 (m, 1 H), 2.78 (d, *J* = 7.8 Hz, 1 H), 2.36 (t, *J* = 7.2 Hz, 1 H), 2.16 (t, *J* = 7.0 Hz, 1 H), 1.53~1.23 (m, 11 H), 0.859 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (75 MHz, CDCl₃): 134.0, 117.0, 85.8, 80.8, 79.5, 66.5, 57.9, 49.2, 36.5, 31.2, 28.4, 22.5, 23.7, 22.5, 18.6, 14.0; Mass (75 eV, *m/z*): 250 (M⁺).

2-Allyl-2-(3-methyl-3-oct-1-ynyl-oxiranylmethyl)-malonic acid dimethyl ester (9). IR (neat, cm⁻¹): 2231(w), 1715(s), 1640(w); ¹H NMR (400 MHz, CDCl₃): 5.74~5.61 (m, 1 H), 5.09 (d, *J* = 11.2 Hz, 1 H), 5.06 (d, *J* = 1.6 Hz, 1 H), 3.71 (s, 6 H), 2.90 (t, *J* = 6.0 Hz, 1 H), 2.70 (t, *J* = 7.2 Hz, 2 H), 2.22 (d, *J* = 6.0 Hz, 2 H), 2.16 (t, *J* = 6.8 Hz, 2 H), 1.44 (s, 3 H), 1.31~1.22 (m, 8 H), 0.868 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): 171.1, 132.1, 119.4, 85.9, 76.8, 61.1, 56.2, 52.6, 52.5, 52.4, 38.5, 33.8, 31.2, 28.3, 23.6, 22.4, 18.6, 13.9; Mass (75 eV, *m/z*): 350 (M⁺).

3-Allyloxymethyl-2-methyl-2-oct-1-ynyl-oxirane (10). IR (neat, cm⁻¹): 2230(w), 1640(w); ¹H NMR (400 MHz, CDCl₃): 5.85-5.94 (m, 1 H), 5.32 (d, *J* = 15.2 Hz, 1 H), 5.18 (d, *J* = 10.0 Hz, 1 H), 3.98~4.11 (m, 2 H), 3.74 (dd, *J* = 11.2, 4.8 Hz, 1 H), 3.59 (dd, *J* = 12.4, 6.0 Hz, 1 H), 3.03 (t, *J* = 5.2 Hz, 1 H), 2.17 (t, *J* = 7.2 Hz, 2 H), 1.49 (s, 3 H), 1.48~1.24 (m, 9 H), 0.85 (t, *J* = 4.4 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): 134.4, 117.1, 85.6, 72.1, 69.5, 65.7, 62.4, 51.5, 31.2, 28.3, 23.5, 22.4, 18.5, 15.1, 13.9;

Mass (75 eV, m/z): 236 (M^+).

N-Allyl-4-methyl-N-(3-methyl-3-oct-1-ynyl-oxiranylmethyl)-benzenesulfonamide

(11). IR (neat, cm^{-1}): 2235(w), 1643(w); ^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.0$ Hz, 2 H), 7.26 (d, $J = 8.0$ Hz, 2 H), 5.63~5.67 (m, 1 H), 5.18 (d, $J = 17.6$ Hz, 1 H), 5.11 (d, $J = 10.4$ Hz, 1 H), 3.87, 3.84 (ABq, $J = 14.0, 6.0$ Hz, 2 H), 3.47 (dd, $J = 14.6, 4.8$ Hz, 1 H), 3.31 (dd, $J = 15.4, 5.2$ Hz, 1 H), 2.96 (t, $J = 5.0$ Hz, 1 H), 2.38 (s, 3 H), 2.12 (t, $J = 7.0$ Hz, 2 H), 1.32~1.43 (m, 4 H), 1.21~1.30 (m, 4 H), 0.82 (t, $J = 5.4$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 143.2, 137.2, 133.0, 129.6, 127.3, 127.2, 118.5, 86.3, 62.5, 52.2, 51.3, 47.9, 31.1, 28.4, 28.3, 23.3, 22.3, 21.3, 18.6, 13.7; Mass (75 eV, m/z): 389 (M^+).

2-But-3-enyl-3-oct-1-ynyl-oxirane (12a). IR (neat, cm^{-1}): 2233(w), 1640(w); ^1H NMR (400 MHz, CDCl_3): 5.93-5.81 (m, 1 H), 5.06 (d, $J = 18.8$ Hz, 1 H), 4.99 (d, $J = 9.6$ Hz, 1 H), 3.41~3.39 (m, 1 H), 3.01~2.98 (m, 1 H), 2.28~2.18 (m, 4 H), 1.84~1.69 (m, 2 H), 1.53~1.21 (m, 8 H), 0.870 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 137.4, 115.0, 86.4, 74.8, 57.2, 45.3, 31.2, 30.0, 28.5, 28.3, 28.26, 22.4, 18.6, 13.9; Mass (75 eV, m/z): 206 (M^+).

2-But-3-enyl-3-phenylethynyl-oxirane (12b). IR (neat, cm^{-1}): 2251(w), 1642(w); ^1H NMR (400 MHz, CDCl_3): 7.44~7.42 (m, 2 H), 7.32~7.27 (m, 3 H), 5.81~5.41 (m, 1 H), 5.09(dd, $J = 17.2, 1.6$ Hz, 1 H), 5.01 (d, $J = 10$ Hz, 1 H), 3.64 (d, $J = 4.4$ Hz, 1 H), 3.17~3.13 (m, 1 H), 2.33~2.28 (m, 2 H), 1.91~1.54 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): 1137.2, 131.7, 128.5, 128.1, 122.1, 115.0, 85.1, 84.3, 57.6, 45.2, 29.9, 28.7; Mass (75 eV, m/z): 198 (M^+).

Acetic acid 1-(3-oct-1-ynyl-oxiranyl)-but-3-enyl ester (13). IR (neat, cm^{-1}): 2230(w), 1722(s), 1640(w); ^1H NMR (400 MHz, CDCl_3): 5.83~5.72 (m, 1 H), 5.18 (d, $J = 8.0$ Hz, 1 H), 5.15 (d, $J = 9.6$ Hz, 1 H), 4.98~4.92 (m, 1 H), 3.53~3.51 (m, 1 H), 3.10 (dd, $J = 8.4, 4.0$ Hz, 1 H), 2.58~2.43 (m, 2 H), 2.22~2.18 (m, 2 H), 2.09 (s, 3 H), 1.54~1.20

(m, 8 H), 0.878 (t, $J = 6.0$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 170.3, 132.4, 118.6, 88.1, 73.9, 73.5, 58.1, 44.6, 36.1, 31.4, 28.7, 28.4, 22.7, 21.3, 18.9, 14.2; Mass (75 eV, m/z): 264 (M^+).

2-Allyl-2-(3-oct-1-ynyl-oxiranylmethyl)-malonic acid dimethyl ester (14). IR (neat, cm^{-1}): 2241(w), 1734(w), 1643(w); ^1H NMR (300 MHz, CDCl_3): 5.71~5.62 (m, 1 H), 5.11 (d, $J = 9.4$ Hz, 1 H), 5.07 (s, 1 H), 3.71 (s, 6 H), 3.37 (dd, $J = 3.8, 1.6$ Hz, 1 H), 3.11~3.06 (m, 1 H), 2.73 (d, $J = 7.2$ Hz, 2 H), 2.28 (dd, $J = 15.2, 6.0$ Hz, 1 H), 2.20~2.12 (m, 3 H), 1.52~1.42 (m, 2 H), 1.36~1.25 (m, 6 H), 0.857 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): 171.3, 132.3, 119.7, 87.5, 74.5, 56.5, 54.5, 52.8, 52.7, 45.4, 38.6, 33.2, 31.5, 28.7, 28.5, 22.7, 18.9, 14.2; Mass (75 eV, m/z): 336 (M^+).

2-Allyloxymethyl-3-hex-1-ynyl-oxirane (15). IR (neat, cm^{-1}): 2230(w), 1641(w); ^1H NMR (400 MHz, CDCl_3): 5.596~5.81 (m, 1 H), 5.28 (d, $J = 17.2$ Hz, 1 H), 5.18 (d, $J = 10$ Hz, 1 H), 4.11~3.97 (m, 2 H), 3.76 (dd, $J = 11.6, 4.8$ Hz, 1 H), 3.60 (dd, $J = 11.2, 6$ Hz, 1 H), 3.47~3.46 (m, 1 H), 3.23~3.20 (m, 1 H), 2.19 (t, $J = 6.8$ Hz, 2 H), 1.49~1.32 (m, 4 H), 0.88 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 134.1, 116.7, 86.4, 74.0, 71.8, 68.8, 55.4, 43.6, 30.0, 21.4, 18.0, 13.1; Mass (75 eV, m/z): 194 (M^+).

N-Allyl-4-methyl-N-(3-oct-1-ynyl-oxiranylmethyl)-benzenesulfonamide (16). IR (neat, cm^{-1}): 2230(w), 1618(w); ^1H NMR (400 MHz, CDCl_3): 7.69 (d, $J = 8.0$ Hz, 2 H), 7.26 (d, $J = 8.0$ Hz, 2 H), 5.69~5.61 (m, 1 H), 5.18 (d, $J = 16.8$ Hz, 1 H), 5.12 (d, $J = 10.4$ Hz, 1 H), 3.86~3.88 (m, 2 H), 3.52 (dd, $J = 14.8, 4.4$ Hz, 1 H), 3.29 (dd, $J = 15.6, 6.0$ Hz, 1 H), 3.37 (d, $J = 4.4$ Hz, 1 H), 3.11 (t, $J = 6.2$ Hz, 1 H), 2.38 (s, 3 H), 2.14 (t, $J = 7.2$ Hz, 2 H), 1.37~1.44 (m, 2 H), 1.22~1.33 (m, 6 H), 0.83 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 143.3, 136.9, 132.7, 129.6, 127.1, 118.8, 87.6, 74.0, 55.7, 51.2, 47.0, 44.6, 31.1, 28.4, 28.1, 22.4, 21.4, 18.6, 13.9; Mass (75 eV, m/z): 375 (M^+).

Spectral data of tricyclic cyclopentanone (17a). IR (neat, cm^{-1}): 1725(s), 1710(s), 1622(w); ^1H NMR (400 MHz, CDCl_3): 4.77 (t, $J = 8.0$ Hz, 1 H), 2.92~2.85 (m, 1 H),

2.68 (dd, $J = 18.8$, 8 Hz, 1 H), 2.62~2.57 (m, 1 H), 2.42 (q, $J = 9.6$ Hz, 1 H), 2.31 (d, $J = 19.2$ Hz, 1 H), 2.31~2.21 (m, 1 H), 2.11~2.01 (m, 1 H), 1.92~1.86 (m, 1 H), 1.29 (s, 3 H), 1.42~1.22 (m, 9 H), 0.84 (t, $J = 7.6$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 206.1, 163.7, 146.7, 135.7, 87.1, 48.0, 44.1, 41.5, 31.4, 30.8, 29.3, 29.2, 29.1, 25.6, 22.5, 22.4, 14.0; HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3$, 276.1716, Found 276.1718

Spectral data of tricyclic cyclopentanone (17b). IR (neat, cm^{-1}): 1723(s), 1710(s), 1626(w); 1615(w); ^1H NMR (400 MHz, CDCl_3): 4.74 (t, $J = 8.2$ Hz, 1 H), 2.66 (dd, $J = 19.6$, 8.0 Hz, 1 H), 2.44 (dd, $J = 15.6$, 9.2 Hz, 1 H), 2.28 (d, $J = 19.6$ Hz, 1 H), 2.19~2.27 (m, 1 H), 2.05~2.13 (m, 1 H), 1.79~1.87 (m, 1 H), 1.32~1.38 (m, 1 H), 1.25 (s, 3 H), 0.22 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): 207.2, 162.7, 138.5, 123.2, 86.9, 51.8, 43.1, 39.8, 30.2, 29.7, 21.2, -0.29 (3 CH_3); HRMS Calcd For $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Si}$: 264.1230 ; Found: 264.1235.

Spectral data of tricyclic cyclopentanone (18a). IR (neat, cm^{-1}): 1728(s), 1706(s), 1622(w); ^1H NMR (400 MHz, CDCl_3): 5.16~5.12 (m, 1 H), 4.77 (d, $J = 6.0$ Hz, 1 H), 2.81~2.61 (m, 4 H), 2.34 (d, $J = 19.6$ Hz, 1 H), 2.07 (s, 3 H), 2.01~1.98 (m, 2 H), 1.42~1.27 (m, 11 H), 0.866 (t, $J = 6.4$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 204.9, 170.2, 162.8, 146.7, 136.4, 89.9, 78.2, 46.0, 43.9, 39.3, 36.4, 31.4, 29.1, 25.9, 22.6, 22.4, 20.8, 14.0; HRMS calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_5$: 334.4067, Found: 334.4063.

Spectral data of tricyclic cyclopentanone (18b). IR (neat, cm^{-1}): 1728(s), 1700(s), 1622(w); ^1H NMR (400 MHz, CDCl_3): 4.63 (d, $J = 4.4$ Hz, 1 H), 3.87~3.84 (m, 1 H), 3.37 (s, 3 H), 2.87~2.85 (m, 1 H), 2.70 (d, $J = 7.2$ Hz, 1 H), 2.64~2.62 (m, 2 H), 2.31 (d, $J = 18.4$ Hz, 1 H), 2.13~2.06 (m, 1 H), 1.72~1.61 (m, 2 H), 1.40~1.27 (m, 11 H), 0.868 (t, $J = 6.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): 205.5, 163.2, 146.9, 136.0, 92.7, 85.8, 57.4, 47.1, 43.5, 39.9, 36.9, 31.4, 29.1, 25.6, 22.5, 14.0; HRMS calcd. for $\text{C}_{18}\text{H}_{26}\text{O}_4$: 306.1831, Found: 306.1829.

Spectral data of tricyclic cyclopentanone (19). IR (neat, cm^{-1}): 1720(s), 1714(s),

1628(w); ^1H NMR (500 MHz, CDCl_3): 4.68 (dd, $J = 12.0, 5.5$ Hz, 1 H), 3.77 (s, 3 H), 3.69 (s, 3 H), 2.93~2.90 (m, 1 H), 2.77~2.66 (m, 3 H), 2.41~2.31 (m, 2 H), 2.01 (d, $J = 19.5$ Hz, 1 H), 1.69 (t, $J = 12.5$ Hz, 1 H), 1.42~1.11 (m, 11 H), 0.848 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): 204.9, 170.3, 169.8, 163.5, 144.4, 137.6, 79.8, 53.6, 53.2, 53.0, 44.1, 40.7, 36.5, 34.8, 32.7, 31.4, 29.25, 29.21, 25.5, 25.0, 22.5, 14.0; HRMS calcd. for $\text{C}_{22}\text{H}_{30}\text{O}_7$: 406.1992, Found: 406.1988.

NOE-map of compound **19**.

Irradiation	Increase (%)
	H^1 (δ 4.68)	$\text{Me } \delta$ 1.25 (3.44%)
	$\text{Me } (\delta$ 1.25)	$\text{H}^1 \delta$ 4.68 (2.19 %) $\text{H}^2 \delta$ 2.31 (2.02 %)
	H^2 (δ 2.31)	$\text{Me } \delta$ 1.25 (2.18 %) $\text{H}^4 \delta$ 2.01 (2.34 %)

Spectral data of tricyclic cyclopentanone (20). IR (neat, cm^{-1}): 1730(s), 1716(s), 1642(w); ^1H NMR (400 MHz, CDCl_3): 4.56 (dd, $J = 11.2, 6.4$ Hz, 1 H), 4.05 (dd, $J = 11.2, 6.0$ Hz, 1 H), 3.91 (, dd, $J = 12.4, 6.4$ Hz, 1 H), 3.18 (t, $J = 11.6$ Hz, 1 H), 2.99~2.93 (m, 1 H), 2.82 (t, $J = 12.4$ Hz, 1 H), 2.70~2.64 (m, 2 H), 2.45~2.39 (m, 1 H), 1.99 (d, $J = 18.8$ Hz, 1 H), 1.34 (s, 3 H), 1.36-1.15 (m, 8 H), 0.850 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 204.6, 163.8, 144.1, 138.0, 77.4, 70.1, 64.8, 40.0, 39.6, 38.5, 31.8, 29.4, 29.3, 25.9, 25.3, 22.8, 14.0; HRMS calcd for. $\text{C}_{17}\text{H}_{24}\text{O}_4$: 292.1675, Found 292.1670.

NOE-map of Compound **20**:

Irradiation	Increase (%)
	H^1 (δ 4.56)	$\text{Me } \delta$ 1.39 (2.27 %)
	$\text{Me } (\delta$ 1.39)	$\text{H}^1 \delta$ 4.56 (1.98 %) $\text{H}^2 \delta$ 2.42 (1.92%)
	H^2 (δ 2.42)	$\text{Me } \delta$ 1.39 (2.54%) $\text{H}^4 \delta$ 2.66 (2.28 %)

Spectral data of tricyclic cyclopentanone (21). IR (neat, cm^{-1}): 1729(s), 1720(s), 1636(w); ^1H NMR (400 MHz, CDCl_3): 7.56 (d, $J = 8.0$ Hz, 2 H), 7.30 (d, $J = 8.0$ Hz, 2 H), 4.66 (dd, $J = 11.0, 6.4$ Hz, 1 H), 4.00 (dd, $J = 16.1, 6.4$ Hz, 1 H), 3.77 (dd, $J = 16.1, 6.4$ Hz, 1 H), 2.82~2.77 (m, 1 H), 2.71 (dd, $J = 19.2, 7.2$ Hz, 1 H), 2.48~2.61 (m, 2 H), 2.39 (s, 3 H), 2.10 (dd, $J = 22.8, 13.2$ Hz, 2 H), 1.68 (t, $J = 12.0$ Hz, 1 H), 1.38 (s, 3 H), 1.22~1.12 (m, 6 H), 0.85~0.78 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3): 203.9, 162.8, 144.4, 143.2, 137.8, 132.6, 130.0, 127.5, 78.6, 48.7, 46.1, 40.9, 40.3, 38.4, 31.3, 29.1, 28.9, 25.4, 24.9, 22.3, 21.5, 14.0; HRMS Calcd For $\text{C}_{24}\text{H}_{31}\text{NO}_5\text{S}$: 445.1930 ; Found: 445.1932.

NOE-map of Compound **21**:

Irradiation	Increase (%)
H ¹ (δ 4.66)	Me δ 1.38 (2.99 %)
Me (δ 1.38)	H ¹ δ 4.66 (2.07 %)
	H ² δ 2.52 (1.80 %)
H ² (δ 2.52)	Me δ 1.38 (2.77 %)
	H ⁴ δ 2.72 (3.4 %)

Spectral data of tricyclic cyclopentanone (22a). IR (neat, cm^{-1}): 1720(s), 1711(s), 1623(w); ^1H NMR (400 MHz, CDCl_3): 5.12 (q, $J = 8$ Hz, 1 H), 3.31 (t, $J = 6.8$ Hz, 1 H), 2.91~2.77 (m, 2 H), 2.70~2.59 (m, 2 H), 2.35 (d, $J = 19.2$ Hz, 1 H), 2.28~2.19 (m, 1 H), 2.08~1.88 (m, 2 H), 1.48~1.17 (m, 9 H), 0.830 (t, $J = 6$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 206.0, 163.8, 141.5, 136.3, 81.3, 45.4, 43.4, 35.1, 31.4, 31.1, 29.8, 29.2, 29.1, 25.6, 22.4, 13.9; HRMS calcd for. $\text{C}_{16}\text{H}_{22}\text{O}_3$: 262.1569, Found 262.1566.

Spectral data of tricyclic cyclopentanone (22b). IR (neat, cm^{-1}): 1720(s), 1711(s), 1623(w), 1612(w); ^1H NMR (400 MHz, CDCl_3): 7.40~7.30 (m, 5 H), 5.23 (q, $J = 8.0$ Hz, 1 H), 3.55 (t, $J = 7.6$ Hz, 1 H), 2.91 (q, $J = 7.6$ Hz, 1 H), 2.74 (dd, $J = 19.6, 8.4$ Hz, 1 H), 2.41~2.30 (2 m, H), 2.17~2.05 (m, 2 H), 1.54~1.49 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): 203.2, 163.4, 142.3, 133.0, 130.4, 129.4, 127.3, 81.1, 45.3, 43.6, 34.6, 31.0,

29.8; HRMS calcd for $C_{16}H_{14}O_3$, 254.0948, Found 254.0950

Spectral data of tricyclic cyclopentanone (23). IR (neat, cm^{-1}): 1720(s), 1711(s), 1612(w); 1H NMR (500 MHz, $CDCl_3$): 5.22 (q, $J = 6.5$ Hz, 1 H), 5.06 (dd, $J = 7.5$, 6.0 Hz, 1 H), 3.42 (t, $J = 6.4$ Hz, 1 H), 3.08~2.98 (m, 1 H), 2.82~2.79 (m, 1 H), 2.66 (dd, $J = 19.0$, 8.0 Hz, 2 H), 2.38 (d, $J = 19.5$ Hz, 1 H), 2.05 (s, 3 H), 1.99 (t, $J = 8.0$ Hz, 2 H), 1.43~1.38 (m, 2 H), 1.29~1.18 (m, 6 H), 0.851 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): 204.7, 170.2, 162.9, 141.4, 137.2, 84.7, 78.6, 45.3, 41.3, 36.7, 32.9, 31.4, 29.3, 29.2, 26.0, 22.5, 20.8, 14.0; HRMS calcd. for $C_{18}H_{24}O_5$: 320.1624, Found: 320.1628.

Spectral data of tricyclic cyclopentanone (24). IR (neat, cm^{-1}): 1720(s), 1711(s), 1612(w); 1H NMR (400 MHz, $CDCl_3$): 5.02~4.95 (m, 1 H), 3.76 (s, 3 H), 3.69 (s, 3 H), 3.33~3.32 (m, 1 H), 2.70~2.53 (m, 4 H), 2.29 (d, $J = 17.2$ Hz, 2 H), 1.73 (t, $J = 12.4$ Hz, 1 H), 1.40~1.16 (m, 8 H), 0.844 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 204.6, 170.6, 170.0, 164.0, 139.3, 138.6, 73.9, 54.3, 53.4, 53.2, 46.6, 38.3, 33.1, 31.7, 31.5, 30.1, 29.4, 29.3, 25.8, 22.7, 14.2; HRMS calcd. for $C_{21}H_{28}O_7$: 392.1835, Found: 392.1837.

Spectral data of tricyclic cyclopentanone (25). IR (neat, cm^{-1}): 1720(s), 1711(s), 1610(w); 1H NMR (400 MHz, $CDCl_3$): 4.90~4.84 (m, 1 H), 4.00 (dd, $J = 11.6$, 6.0 Hz, 1 H), 3.89 (dd, $J = 11.2$, 5.6 Hz, 1 H), 3.52 (t, $J = 6.4$ Hz, 1 H), 3.25 (t, $J = 11.6$ Hz, 1 H), 3.02~2.95 (m, 1 H), 2.90~2.67 (m, 3 H), 2.51 (dd, $J = 18.4$, 6.8 Hz, 1 H), 2.14 (d, $J = 18.4$, 1 H), 1.44~1.31 (m, 4 H), 0.89 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 204.2, 163.5, 138.5, 138.4, 71.5, 68.3, 64.5, 41.9, 36.9, 31.8, 31.3, 25.4, 22.7, 13.7; HRMS calcd for $C_{14}H_{18}O_4$: 250.1214, Found 250.1217.

Spectral data of tricyclic cyclopentanone (26). IR (nujol, cm^{-1}): 1721(s), 1712(s), 1610(w); 1H NMR (400 MHz, $CDCl_3$): 7.58 (d, $J = 8.0$ Hz, 2 H), 7.31 (d, $J = 8.0$ Hz, 2 H), 4.95~5.01 (m, 1 H), 3.98 (dd, $J = 18.0$, 2.4 Hz, 1 H), 3.77 (dd, $J = 10.2$, 1.6 Hz, 1 H),

3.47 (t, $J = 6.0$ Hz, 1 H), 2.90~2.79 (m, 2 H), 2.65~2.61 (m, 1 H), 2.59 (dd, $J = 18.4, 7.2$ Hz, 1 H), 2.41 (s, 3 H), 2.20 (dd, $J = 14.8, 10.4$ Hz, 2 H), 1.75 (t, $J = 12.2$ Hz, 1 H), 1.23~1.13 (m, 8 H), 0.81 (t, $J = 16.4$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 203.5, 163.0, 144.4, 138.7, 137.8, 132.7, 130.0, 127.4, 72.6, 47.2, 44.7, 43.4, 37.4, 32.0, 31.3, 29.0, 29.0, 25.5, 22.3, 21.5, 14.0; HRMS Calcd For $\text{C}_{23}\text{H}_{29}\text{NO}_5\text{S}$: 431.1763 ; Found: 431.1769.

Spectral data of tricyclic cyclobutane (28a). IR (nujol, cm^{-1}): 1712(s), 1610(w); ^1H NMR (500 MHz, CDCl_3): 4.46 (t, $J = 8.5$ Hz, 1 H), 3.32 (dd, $J = 15, 9$ Hz, 1 H), 2.52 (d, $J = 15$ Hz, 1 H), 2.45 (t, $J = 9$ Hz, 1 H), 2.24~2.06 (4 H, m), 1.92~1.83 (m, 1 H), 1.74~1.70 (m, 1 H), 1.40 (t, $J = 7$ Hz, 2 H), 1.35 (s, 3 H), 1.24~1.18 (m, 8 H), 0.81 (t, $J = 7$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): 163.7, 156.5, 123.4, 86.6, 52.1, 40.1, 37.3, 32.1, 31.4, 29.1, 27.9, 27.7, 27.0, 22.5, 17.7, 13.9; HRMS cald. For, $\text{C}_{16}\text{H}_{24}\text{O}_2$, 248.1780, Found, 248.1783

Spectral data of tricyclic cyclobutane (28b). IR (nujol, cm^{-1}): 1714(s), 1612(w); ^1H NMR (400 MHz, CDCl_3): 4.48 (t, $J = 8.4$ Hz, 1 H), 3.51 (dd, $J = 12.4, 9.6$ Hz, 1 H), 2.65 (dd, $J = 15.6, 1.6$ Hz, 1 H), 2.47 (t, $J = 8.6$ Hz, 1 H), 2.10~2.17 (m, 2 H), 1.81~1.90 (m, 1 H), 1.72~1.77 (m, 1 H), 1.38 (s, 3 H), 0.180 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): 174.2, 128.6, 124.1, 86.0, 53.2, 40.4, 39.7, 31.41, 29.8, 17.6, -0.86 (3 CH_3); HRMS Calcd For $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si}$: 236.1231 ; Found: 236.1235.

Spectral data of tricyclic cyclobutane (28c). IR (nujol, cm^{-1}): 1723(s), 1713(s), 1615(w); ^1H NMR (400 MHz, CDCl_3): 5.51~5.45 (q, $J = 8.0$ Hz, 1 H), 4.44 (d, $J = 6.0$ Hz, 1 H), 3.38 (dd, $J = 15.2, 9.2$ Hz, 1 H), 2.64 (d, $J = 14.8, 1$ Hz), 2.60 (d, $J = 9.2, 1$ Hz), 2.39 (dd, $J = 14.4, 8.0$ Hz, 1 H), 2.24~2.14 (m, 2 H), 2.02 (s, 3 H), 1.87~1.83 (m, 1 H), 1.46~1.26 (m, 11 H), 0.863 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 170.32, 162.9, 155.9, 124.5, 89.5, 80.0, 49.3, 38.6, 37.8, 34.5, 31.4, 29.1, 27.8, 27.1, 22.5, 20.8, 17.7, 14.0; HRMS calcd. for $\text{C}_{18}\text{H}_{26}\text{O}_4$: 306.1831, Found: 306.1835.

Spectral data of tricyclic cyclobutane (28d). IR (nujol, cm^{-1}): 1721(s), 1714(s), 1615(w); ^1H NMR (500 MHz, CDCl_3): 4.30 (d, $J = 5.0$ Hz, 1 H), 4.24~4.20 (m, 1 H), 3.36 (s, 3 H), 2.58 (dd, $J = 13.5, 9.2$ Hz, 2 H), 2.27~2.19 (m, 1 H), 2.17~2.11 (m, 3 H), 1.99~1.94 (m, 1 H), 1.45~1.41 (m, 2 H), 1.38 (s, 3 H), 0.865 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): 163.4, 156.5, 124.1, 92.2, 87.4, 57.7, 50.4, 38.6, 38.0, 35.1, 31.5, 29.2, 27.9, 27.0, 22.6, 18.0, 14.0; HRMS calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_3$: 278.1882, Found: 278.1880.

3-(2,2-Dimethyl-but-3-enyl)-2-methyl-2-oct-1-ynyl-oxirane (29). IR (nujol, cm^{-1}): 2231(w), 1645(w); ^1H NMR (400 MHz, CDCl_3): 5.85 (dd, $J = 16.0, 12.0$ Hz, 1 H), 4.98 (d, $J = 8.0$ Hz, 1 H), 4.94 (s, 1 H), 2.78 (t, $J = 6.0$ Hz, 1 H), 2.20 (t, $J = 7.2$ Hz, 2 H), 1.73 (dd, $J = 14.0, 5.6$ Hz, 1 H), 1.67 (dd, $J = 14.0, 5.6$ Hz, 1 H), 1.58~1.20 (m, 11 H), 0.991 (s, 3 H), 0.980 (s, 3 H), 0.875 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 147.5, 110.8, 85.7, 78.0, 62.4, 52.4, 42.0, 36.0, 31.2, 28.4, 27.0, 26.9, 23.7, 22.5, 18.6, 14.0; Mass (75 eV, m/z): 248 (M^+).

Spectral data of tricyclic cyclobutane (30). IR (nujol, cm^{-1}): 1715(s), 1611(w); ^1H NMR (400 MHz, CDCl_3): 4.52 (t, $J = 8.0$ Hz, 1 H), 3.20 (dd, $J = 15.2, 9.6$ Hz, 1 H), 2.76 (d, $J = 16.0$ Hz, 1 H), 2.29~2.22 (m, 1 H), 2.14 (dd, $J = 14.8, 7.6$ Hz, 1 H), 2.06 (dd, $J = 16.0, 8.4$ Hz, 1 H), 1.95 (dd, $J = 13.2, 8.4$ Hz, 1 H), 1.43~1.35 (m, 5 H), 1.26~1.18 (m, 6 H), 1.00 (s, 3 H), 0.915 (s, 3 H), 0.858 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): 164.3, 156.3, 123.6, 85.0, 52.2, 51.1, 45.3, 38.8, 33.0, 31.7, 29.6, 28.2, 27.2, 26.1, 22.8, 19.2, 14.2; HRMS calcd. for $\text{C}_{18}\text{H}_{28}\text{O}_2$: 276.2089, Found: 276.2085.

(5) **x-ray data for compounds 5, 6, 22b, 28b** including a summary of crystallographic data, ORTEP drawings, full tables of bond distances and angles, atomic coordinates and thermal parameters.

(a) x-ray data for compound 5.

Table 1. Crystal data and structure refinement for 02OT23.

Identification code	ot23m	
Empirical formula	C17 H16 O3	
Formula weight	268.30	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 12.8933(8) Å	$\alpha = 90^\circ$
	b = 8.7035(6) Å	$\beta = 90^\circ$
	c = 24.4720(16) Å	$\gamma = 90^\circ$
Volume	2746.2(3) Å ³	
Z	8	
Density (calculated)	1.298 Mg/m ³	
Absorption coefficient	0.088 mm ⁻¹	
F(000)	1136	
Crystal size	0.6 x 0.4 x 0.3 mm ³	
Theta range for data collection	1.66 to 28.28°	
Index ranges	-16 ≤ h ≤ 15, -11 ≤ k ≤ 11, -32 ≤ l ≤ 24	
Reflections collected	16232	
Independent reflections	5688 [R(int) = 0.0428]	
Completeness to theta = 28.28°	96.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.96570 and 0.85167	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5688 / 0 / 360	
Goodness-of-fit on F ²	1.012	
Final R indices [I > 2sigma(I)]	R1 = 0.0554, wR2 = 0.1189	
R indices (all data)	R1 = 0.0901, wR2 = 0.1313	
Absolute structure parameter	0.7(14)	
Largest diff. peak and hole	0.153 and -0.138 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02OT23. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	4389(2)	6081(3)	161	60(1)
O(2)	4971(2)	3749(3)	216(1)	71(1)
O(3)	6117(2)	6875(3)	2057(1)	74(1)
O(4)	2980(2)	1109(3)	-449(1)	59(1)
O(5)	2365(2)	-1226(3)	-462(1)	72(1)
O(6)	1358(2)	1594(3)	-2383(1)	82(1)
C(1)	5374(2)	5340(3)	977(1)	40(1)
C(2)	4910(2)	4979(4)	430(2)	50(1)
C(3)	4326(2)	7658(4)	387(2)	59(1)
C(4)	5287(3)	8623(4)	254(2)	76(1)
C(5)	5348(3)	9770(4)	711(2)	85(1)
C(6)	4612(2)	9263(4)	1176(2)	61(1)
C(7)	5129(3)	9023(4)	1726(2)	71(1)
C(8)	5521(2)	7395(4)	1730(2)	51(1)
C(9)	5049(2)	6610(3)	1238(1)	42(1)
C(10)	4240(2)	7641(3)	1001(2)	51(1)
C(11)	3148(2)	7238(4)	1196(2)	76(1)
C(12)	6159(2)	4216(3)	1179(1)	43(1)
C(13)	6109(2)	3670(4)	1714(2)	57(1)
C(14)	6831(3)	2660(5)	1904(2)	74(1)
C(15)	7615(3)	2146(4)	1569(2)	73(1)
C(16)	7673(2)	2646(4)	1042(2)	63(1)
C(17)	6937(2)	3696(3)	840(2)	52(1)
C(18)	1983(2)	281(3)	-1247(2)	42(1)
C(19)	2444(2)	-12(4)	-695(2)	50(1)
C(20)	3027(2)	2647(4)	-681(2)	58(1)
C(21)	2087(3)	3634(4)	-544(2)	79(1)
C(22)	1988(3)	4762(4)	-997(2)	79(1)
C(23)	2678(2)	4211(4)	-1478(2)	59(1)
C(24)	2091(3)	3912(4)	-2011(2)	62(1)
C(25)	1849(2)	2238(4)	-2027(2)	52(1)

C(26)	2320(2)	1517(3)	-1527(1)	43(1)
C(27)	3104(2)	2644(3)	-1294(2)	48(1)
C(28)	4189(2)	2269(4)	-1507(2)	66(1)
C(29)	1205(2)	-847(3)	-1433(1)	41(1)
C(30)	1268(2)	-1519(3)	-1945(2)	55(1)
C(31)	522(3)	-2549(4)	-2115(2)	72(1)
C(32)	-289(3)	-2947(4)	-1776(2)	85(1)
C(33)	-356(3)	-2288(4)	-1257(2)	71(1)
C(34)	383(2)	-1257(3)	-1093(2)	55(1)

Table 3. Bond lengths [Å] and angles [°] for 02OT23.

O(1)-C(2)	1.343(4)
O(1)-C(3)	1.482(4)
O(2)-C(2)	1.195(3)
O(3)-C(8)	1.197(4)
O(4)-C(19)	1.339(4)
O(4)-C(20)	1.456(4)
O(5)-C(19)	1.205(4)
O(6)-C(25)	1.214(4)
C(1)-C(9)	1.345(4)
C(1)-C(12)	1.493(4)
C(1)-C(2)	1.498(4)
C(3)-C(10)	1.508(5)
C(3)-C(4)	1.531(5)
C(4)-C(5)	1.500(6)
C(5)-C(6)	1.547(5)
C(6)-C(7)	1.516(5)
C(6)-C(10)	1.551(5)
C(7)-C(8)	1.504(5)
C(8)-C(9)	1.513(4)
C(9)-C(10)	1.493(4)
C(10)-C(11)	1.528(4)
C(12)-C(17)	1.378(4)
C(12)-C(13)	1.393(4)
C(13)-C(14)	1.362(5)
C(14)-C(15)	1.375(6)
C(15)-C(16)	1.363(6)
C(16)-C(17)	1.408(5)
C(18)-C(26)	1.347(4)
C(18)-C(29)	1.476(4)
C(18)-C(19)	1.499(4)
C(20)-C(27)	1.503(5)
C(20)-C(21)	1.522(5)
C(21)-C(22)	1.486(6)
C(22)-C(23)	1.553(5)

C(23)-C(24)	1.530(5)
C(23)-C(27)	1.538(4)
C(24)-C(25)	1.491(4)
C(25)-C(26)	1.504(4)
C(26)-C(27)	1.519(4)
C(27)-C(28)	1.528(4)
C(29)-C(30)	1.385(4)
C(29)-C(34)	1.393(4)
C(30)-C(31)	1.379(5)
C(31)-C(32)	1.380(6)
C(32)-C(33)	1.395(6)
C(33)-C(34)	1.369(5)
C(2)-O(1)-C(3)	120.4(2)
C(19)-O(4)-C(20)	121.0(2)
C(9)-C(1)-C(12)	126.4(2)
C(9)-C(1)-C(2)	118.2(2)
C(12)-C(1)-C(2)	115.4(2)
O(2)-C(2)-O(1)	117.2(3)
O(2)-C(2)-C(1)	123.6(3)
O(1)-C(2)-C(1)	119.2(3)
O(1)-C(3)-C(10)	111.5(3)
O(1)-C(3)-C(4)	112.6(3)
C(10)-C(3)-C(4)	106.0(3)
C(5)-C(4)-C(3)	104.5(3)
C(4)-C(5)-C(6)	109.0(3)
C(7)-C(6)-C(5)	115.0(3)
C(7)-C(6)-C(10)	104.8(3)
C(5)-C(6)-C(10)	104.3(3)
C(8)-C(7)-C(6)	106.5(3)
O(3)-C(8)-C(7)	125.2(3)
O(3)-C(8)-C(9)	128.2(3)
C(7)-C(8)-C(9)	106.5(3)
C(1)-C(9)-C(10)	121.8(3)
C(1)-C(9)-C(8)	128.7(2)
C(10)-C(9)-C(8)	108.6(3)

C(9)-C(10)-C(3)	110.0(3)
C(9)-C(10)-C(11)	112.6(3)
C(3)-C(10)-C(11)	112.4(3)
C(9)-C(10)-C(6)	102.9(2)
C(3)-C(10)-C(6)	104.1(3)
C(11)-C(10)-C(6)	114.1(3)
C(17)-C(12)-C(13)	119.2(3)
C(17)-C(12)-C(1)	120.6(3)
C(13)-C(12)-C(1)	120.2(2)
C(14)-C(13)-C(12)	120.6(3)
C(13)-C(14)-C(15)	120.6(4)
C(16)-C(15)-C(14)	120.0(3)
C(15)-C(16)-C(17)	120.2(3)
C(12)-C(17)-C(16)	119.4(3)
C(26)-C(18)-C(29)	126.5(3)
C(26)-C(18)-C(19)	117.8(3)
C(29)-C(18)-C(19)	115.8(2)
O(5)-C(19)-O(4)	118.0(3)
O(5)-C(19)-C(18)	122.9(3)
O(4)-C(19)-C(18)	119.1(3)
O(4)-C(20)-C(27)	113.0(3)
O(4)-C(20)-C(21)	113.6(3)
C(27)-C(20)-C(21)	105.9(3)
C(22)-C(21)-C(20)	106.1(3)
C(21)-C(22)-C(23)	108.2(3)
C(24)-C(23)-C(27)	106.0(3)
C(24)-C(23)-C(22)	114.6(3)
C(27)-C(23)-C(22)	104.8(3)
C(25)-C(24)-C(23)	107.0(3)
O(6)-C(25)-C(24)	125.4(3)
O(6)-C(25)-C(26)	127.0(3)
C(24)-C(25)-C(26)	107.6(3)
C(18)-C(26)-C(25)	128.0(3)
C(18)-C(26)-C(27)	122.7(3)
C(25)-C(26)-C(27)	107.7(2)
C(20)-C(27)-C(26)	109.3(2)

C(20)-C(27)-C(28)	113.7(3)
C(26)-C(27)-C(28)	110.1(2)
C(20)-C(27)-C(23)	105.5(3)
C(26)-C(27)-C(23)	103.0(2)
C(28)-C(27)-C(23)	114.6(3)
C(30)-C(29)-C(34)	118.5(3)
C(30)-C(29)-C(18)	121.3(2)
C(34)-C(29)-C(18)	120.2(3)
C(31)-C(30)-C(29)	120.4(3)
C(30)-C(31)-C(32)	120.7(4)
C(31)-C(32)-C(33)	119.4(3)
C(34)-C(33)-C(32)	119.5(4)
C(33)-C(34)-C(29)	121.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for O2OT23. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	65(1)	65(1)	50(1)	5(1)	-18(1)	1(1)
O(2)	85(2)	64(2)	64(2)	-14(1)	-27(1)	-3(1)
O(3)	72(1)	96(2)	54(1)	-17(1)	-19(1)	16(1)
O(4)	69(1)	65(1)	44(1)	-1(1)	-17(1)	3(1)
O(5)	93(2)	58(2)	64(2)	22(1)	-21(1)	2(1)
O(6)	105(2)	81(2)	60(2)	20(1)	-33(1)	-24(1)
C(1)	37(1)	46(2)	37(2)	7(1)	-2(1)	-3(1)
C(2)	50(2)	48(2)	54(2)	-1(2)	-4(1)	-7(1)
C(3)	61(2)	60(2)	57(2)	13(2)	-10(2)	7(2)
C(4)	83(2)	65(2)	81(3)	19(2)	20(2)	-13(2)
C(5)	96(3)	60(2)	98(3)	16(2)	-1(2)	-17(2)
C(6)	59(2)	51(2)	74(2)	1(2)	5(2)	8(2)
C(7)	83(2)	61(2)	68(2)	-15(2)	1(2)	2(2)
C(8)	45(2)	64(2)	43(2)	-9(2)	7(1)	-2(1)
C(9)	40(1)	47(2)	39(2)	3(1)	3(1)	2(1)
C(10)	44(1)	49(2)	60(2)	9(2)	5(2)	4(1)
C(11)	42(2)	79(2)	108(4)	24(2)	19(2)	9(2)
C(12)	41(1)	42(1)	47(2)	-2(1)	-4(1)	-5(1)
C(13)	60(2)	60(2)	50(2)	8(2)	-1(2)	0(1)
C(14)	77(2)	77(3)	68(3)	18(2)	-12(2)	13(2)
C(15)	71(2)	50(2)	97(3)	3(2)	-31(2)	10(2)
C(16)	51(2)	53(2)	86(3)	-21(2)	6(2)	5(2)
C(17)	53(2)	46(2)	57(2)	-12(1)	4(1)	-2(1)
C(18)	43(1)	42(2)	40(2)	0(1)	2(1)	8(1)
C(19)	49(2)	60(2)	39(2)	-3(2)	-7(1)	10(1)
C(20)	57(2)	55(2)	62(2)	-14(2)	-10(2)	-4(1)
C(21)	100(3)	71(3)	66(3)	-13(2)	16(2)	15(2)
C(22)	81(2)	77(2)	78(3)	-18(2)	2(2)	15(2)
C(23)	52(2)	47(2)	78(2)	5(2)	2(2)	-6(2)
C(24)	77(2)	50(2)	59(2)	7(2)	2(2)	15(2)
C(25)	47(2)	62(2)	48(2)	12(2)	2(1)	-3(1)

C(26)	38(1)	46(2)	44(2)	-1(1)	-1(1)	5(1)
C(27)	40(1)	52(2)	52(2)	-5(1)	0(1)	-5(1)
C(28)	41(1)	75(2)	81(3)	-13(2)	3(2)	-3(2)
C(29)	40(1)	37(1)	44(2)	3(1)	-2(1)	4(1)
C(30)	65(2)	44(2)	54(2)	-3(1)	-9(2)	3(1)
C(31)	96(3)	39(2)	81(3)	-9(2)	-34(2)	3(2)
C(32)	76(2)	50(2)	130(4)	24(3)	-48(3)	-13(2)
C(33)	50(2)	66(2)	97(3)	26(2)	-12(2)	-7(2)
C(34)	50(2)	56(2)	60(2)	15(2)	3(2)	4(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02OT23.

	x	y	z	U(eq)
H(3A)	3771	8186	206	80
H(4A)	5270	9143	-112	80
H(4B)	6026	7960	223	80
H(5A)	5974	9540	832	80
H(5B)	5212	10931	518	80
H(6A)	4029	9928	1187	80
H(7A)	4822	9147	2095	80
H(7B)	5711	9823	1759	80
H(11A)	2998	6030	1044	80
H(11B)	3136	7222	1647	80
H(11C)	2708	8017	1055	80
H(13A)	5554	4032	1965	80
H(14A)	6980	2268	2297	80
H(15A)	8021	1313	1724	80
H(16A)	8207	2488	722	80
H(17A)	6979	4081	433	80
H(20A)	3639	3080	-535	80
H(21A)	2065	4061	-201	80
H(21B)	1346	2835	-597	80
H(22A)	1283	4908	-1121	80
H(22B)	2491	5470	-899	80
H(23A)	3215	4877	-1550	80
H(24A)	1437	4545	-2002	80
H(24B)	2283	4442	-2383	80
H(28A)	4378	1259	-1339	80
H(28B)	4234	1994	-1822	80
H(28C)	4564	3097	-1482	80
H(30A)	1809	-1102	-2190	80
H(31A)	616	-3083	-2475	80
H(32A)	-866	-3831	-1879	80

H(33A)	-980	-2606	-1084	80
H(34A)	290	-870	-728	80

(b) x-ray data for compound 6.

Table 1. Crystal data and structure refinement for 02JL21.

Identification code	j121m	
Empirical formula	C16 H16 O2	
Formula weight	240.29	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.6228(6) Å	$\alpha = 90^\circ$.
	b = 12.2008(12) Å	$\beta = 110.754(2)^\circ$.
	c = 8.4401(8) Å	$\gamma = 90^\circ$.
Volume	637.74(10) Å ³	
Z	2	
Density (calculated)	1.251 Mg/m ³	
Absorption coefficient	0.081 mm ⁻¹	
F(000)	256	
Crystal size	0.90 x 0.50 x 0.30 mm ³	
Theta range for data collection	2.58 to 28.25°.	
Index ranges	-7 ≤ h ≤ 8, -13 ≤ k ≤ 15, -11 ≤ l ≤ 10	
Reflections collected	3956	
Independent reflections	2399 [R(int) = 0.0234]	
Completeness to theta = 28.25°	94.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.96931 and 0.83649	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2399 / 0 / 162	
Goodness-of-fit on F ²	1.103	
Final R indices [I > 2σ(I)]	R1 = 0.0451, wR2 = 0.1105	
R indices (all data)	R1 = 0.0494, wR2 = 0.1132	
Absolute structure parameter	0.9(16)	
Largest diff. peak and hole	0.136 and -0.215 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02JL21. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	6691(2)	7548	599(2)	64(1)
O(2)	8320(3)	7204(2)	3301(2)	80(1)
C(1)	3656(4)	4807(3)	3396(3)	54(1)
C(2)	3936(5)	3913(3)	4454(3)	66(1)
C(3)	5984(6)	3519(3)	5318(3)	73(1)
C(4)	7728(5)	4022(3)	5132(3)	71(1)
C(5)	7471(4)	4915(2)	4069(3)	55(1)
C(6)	5416(3)	5326(2)	3162(2)	42(1)
C(7)	5013(3)	6238(2)	1944(2)	39(1)
C(8)	6784(3)	7029(2)	2044(3)	52(1)
C(9)	4896(3)	7371(2)	-996(3)	52(1)
C(10)	5064(4)	6310(3)	-1908(3)	61(1)
C(11)	2716(4)	6000(3)	-2931(3)	67(1)
C(12)	1343(3)	6433(3)	-1952(3)	55(1)
C(13)	1274(3)	5729(3)	-434(3)	59(1)
C(14)	3160(3)	6408(2)	658(2)	41(1)
C(15)	2808(3)	7275(2)	-672(2)	46(1)
C(16)	1782(5)	8335(3)	-370(4)	72(1)

Table 3. Bond lengths [Å] and angles [°] for 02JL21.

O(1)-C(8)	1.356(3)
O(1)-C(9)	1.463(3)
O(2)-C(8)	1.200(3)
C(1)-C(2)	1.380(3)
C(1)-C(6)	1.400(3)
C(2)-C(3)	1.379(4)
C(3)-C(4)	1.366(4)
C(4)-C(5)	1.383(4)
C(5)-C(6)	1.397(3)
C(6)-C(7)	1.474(3)
C(7)-C(14)	1.335(2)
C(7)-C(8)	1.498(3)
C(9)-C(15)	1.506(3)
C(9)-C(10)	1.531(3)
C(10)-C(11)	1.534(4)
C(11)-C(12)	1.524(3)
C(12)-C(15)	1.555(3)
C(12)-C(13)	1.557(3)
C(13)-C(14)	1.510(3)
C(14)-C(15)	1.499(3)
C(15)-C(16)	1.525(3)
C(8)-O(1)-C(9)	121.47(16)
C(2)-C(1)-C(6)	121.4(2)
C(3)-C(2)-C(1)	119.9(2)
C(4)-C(3)-C(2)	119.7(2)
C(3)-C(4)-C(5)	120.9(2)
C(4)-C(5)-C(6)	120.6(2)
C(5)-C(6)-C(1)	117.3(2)
C(5)-C(6)-C(7)	123.58(18)
C(1)-C(6)-C(7)	119.07(17)
C(14)-C(7)-C(6)	124.85(17)
C(14)-C(7)-C(8)	114.91(18)
C(6)-C(7)-C(8)	120.17(16)

O(2)-C(8)-O(1)	117.8(2)
O(2)-C(8)-C(7)	124.5(2)
O(1)-C(8)-C(7)	117.72(16)
O(1)-C(9)-C(15)	110.10(17)
O(1)-C(9)-C(10)	114.03(18)
C(15)-C(9)-C(10)	105.09(18)
C(9)-C(10)-C(11)	104.57(19)
C(12)-C(11)-C(10)	106.87(19)
C(11)-C(12)-C(15)	105.07(17)
C(11)-C(12)-C(13)	116.9(2)
C(15)-C(12)-C(13)	89.19(15)
C(14)-C(13)-C(12)	86.57(16)
C(7)-C(14)-C(15)	124.95(17)
C(7)-C(14)-C(13)	137.2(2)
C(15)-C(14)-C(13)	93.13(16)
C(14)-C(15)-C(9)	106.39(16)
C(14)-C(15)-C(16)	115.68(17)
C(9)-C(15)-C(16)	117.1(2)
C(14)-C(15)-C(12)	87.01(16)
C(9)-C(15)-C(12)	108.22(17)
C(16)-C(15)-C(12)	118.12(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02JL21. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	52(1)	70(1)	63(1)	6(1)	11(1)	-23(1)
O(2)	66(1)	80(1)	68(1)	-3(1)	-8(1)	-31(1)
C(1)	59(1)	56(1)	49(1)	2(1)	24(1)	3(1)
C(2)	91(2)	62(2)	57(1)	4(1)	39(1)	-3(1)
C(3)	116(2)	54(2)	49(1)	14(1)	30(1)	10(2)
C(4)	78(2)	66(2)	55(1)	7(1)	5(1)	23(1)
C(5)	55(1)	55(1)	47(1)	-2(1)	9(1)	6(1)
C(6)	47(1)	41(1)	35(1)	-7(1)	12(1)	3(1)
C(7)	39(1)	36(1)	41(1)	-5(1)	13(1)	-1(1)
C(8)	47(1)	46(1)	54(1)	-3(1)	8(1)	-9(1)
C(9)	47(1)	57(1)	51(1)	8(1)	16(1)	-4(1)
C(10)	52(1)	77(2)	57(1)	2(1)	25(1)	11(1)
C(11)	69(1)	73(2)	53(1)	-9(1)	14(1)	-1(1)
C(12)	36(1)	68(2)	49(1)	6(1)	1(1)	3(1)
C(13)	35(1)	69(2)	65(1)	9(1)	7(1)	-8(1)
C(14)	38(1)	38(1)	49(1)	1(1)	18(1)	1(1)
C(15)	45(1)	43(1)	49(1)	4(1)	16(1)	6(1)
C(16)	92(2)	53(2)	78(2)	16(1)	40(2)	28(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 02JL21.

	x	y	z	U(eq)
H(1A)	2279	5122	2944	80
H(2A)	2713	3546	4619	80
H(3A)	6120	2928	5991	80
H(4A)	9085	3837	5670	80
H(5A)	8639	5272	3879	80
H(9A)	4968	8020	-1595	80
H(10A)	5945	6374	-2624	80
H(10B)	5679	5741	-1082	80
H(11A)	2562	5202	-3033	80
H(11B)	2278	6377	-4012	80
H(12A)	56	6634	-2694	80
H(13A)	-13	5800	-178	80
H(13B)	1667	4913	-395	80
H(16A)	528	8246	-25	80
H(16B)	1706	8834	-1203	80
H(16C)	2921	8705	622	80

(c) x-ray data for compound 22b.

Fig. : The molecular structure of IC9068, thermal ellipsoids drawn at the 30% probability level.

Table 1. Crystal data and structure refinement for ic9068.

Identification code	ic9068
Empirical formula	$C_{13}H_{20}O_2Si$
Formula weight	236.38
Diffractometer used	NONIUS KappaCCD
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pmma
Unit cell dimensions	$a = 8.41840(10)$ Å $\alpha = 90^\circ$ $b = 10.8733(2)$ Å $\beta = 90^\circ$ $c = 15.0011(3)$ Å $\gamma = 90^\circ$
Volume, Z	$1373.14(4)$ Å ³ , 4
Density (calculated)	1.143 Mg/m ³
Absorption coefficient	0.156 mm ⁻¹
F(000)	512
Crystal size	$0.45 \times 0.28 \times 0.20$ mm
θ range for data collection	2.31 to 27.50°
Limiting indices	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-18 \leq l \leq 19$
Reflections collected	8125
Independent reflections	1646 ($R_{int} = 0.0326$)
Completeness to $\theta = 27.50^\circ$	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.975 and 0.890
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1646 / 1 / 119
Goodness-of-fit on F^2	1.143
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0718$, $wR2 = 0.1872$
R indices (all data)	$R1 = 0.0951$, $wR2 = 0.2080$
Extinction coefficient	$0.34(4)$
Largest diff. peak and hole	0.412 and -0.383 eÅ ⁻³

This structure was solved by Gene-Hsiang Lee at NTU Instrumentation Center.

Table 2. Bond lengths [Å] and angles [°] for ic9068.

Si(1)-C(12)#1	1.851(3)	Si(1)-C(12)	1.851(3)
Si(1)-C(11)	1.854(4)	Si(1)-C(2)	1.870(3)
O(1)-O(1)#1	0.578(13)	O(1)-C(1)	1.338(4)
O(1)-C(5)	1.457(5)	O(1)-C(5)#1	1.636(5)
O(2)-O(2)#1	0.57(2)	O(2)-C(1)	1.234(5)
C(1)-O(2)#1	1.234(5)	C(1)-O(1)#1	1.338(4)
C(1)-C(2)	1.474(4)	C(2)-C(3)	1.386(4)
C(2)-C(3)#1	1.386(4)	C(3)-C(3)#1	0.868(8)
C(3)-C(4)	1.523(6)	C(3)-C(9)	1.547(5)
C(3)-C(4)#1	1.786(6)	C(4)-C(4)#1	1.006(8)
C(4)-C(5)#1	1.088(6)	C(4)-C(6)#1	1.418(11)
C(4)-C(5)	1.466(6)	C(4)-C(8)	1.489(5)
C(4)-C(10)	1.505(14)	C(4)-C(7)#1	1.593(6)
C(4)-C(3)#1	1.786(6)	C(5)-C(5)#1	0.959(9)
C(5)-C(4)#1	1.088(6)	C(5)-C(6)	1.546(12)
C(5)-O(1)#1	1.636(5)	C(5)-C(10)#1	1.709(15)
C(6)-C(10)#1	0.507(12)	C(6)-C(4)#1	1.418(11)
C(6)-C(7)	1.562(11)	C(7)-C(10)#1	1.279(17)
C(7)-C(8)	1.590(4)	C(7)-C(4)#1	1.593(6)
C(8)-C(4)#1	1.489(5)	C(8)-C(9)	1.560(6)
C(8)-C(7)#1	1.590(4)	C(9)-C(3)#1	1.547(5)
C(10)-C(6)#1	0.507(12)	C(10)-C(7)#1	1.279(17)
C(10)-C(5)#1	1.709(15)		
C(12)#1-Si(1)-C(12)	109.4(2)	C(12)#1-Si(1)-C(11)	109.42(13)
C(12)-Si(1)-C(11)	109.42(13)	C(12)#1-Si(1)-C(2)	109.73(10)
C(12)-Si(1)-C(2)	109.73(10)	C(11)-Si(1)-C(2)	109.09(16)
O(1)#1-O(1)-C(1)	77.5(3)	O(1)#1-O(1)-C(5)	97.5(3)
C(1)-O(1)-C(5)	120.0(3)	O(1)#1-O(1)-C(5)#1	62.0(3)
C(1)-O(1)-C(5)#1	108.6(3)	C(5)-O(1)-C(5)#1	35.5(3)
O(2)#1-O(2)-C(1)	76.7(5)	O(2)-C(1)-O(2)#1	26.6(10)
O(2)-C(1)-O(1)	111.4(3)	O(2)#1-C(1)-O(1)	117.6(3)
O(2)-C(1)-O(1)#1	117.6(3)	O(2)#1-C(1)-O(1)#1	111.4(3)
O(1)-C(1)-O(1)#1	24.9(5)	O(2)-C(1)-C(2)	123.2(3)
O(2)#1-C(1)-C(2)	123.2(3)	O(1)-C(1)-C(2)	119.2(2)
O(1)#1-C(1)-C(2)	119.2(2)	C(3)-C(2)-C(3)#1	36.5(3)
C(3)-C(2)-C(1)	112.0(3)	C(3)#1-C(2)-C(1)	112.0(3)
C(3)-C(2)-Si(1)	127.0(2)	C(3)#1-C(2)-Si(1)	127.0(2)
C(1)-C(2)-Si(1)	117.52(19)	C(3)#1-C(3)-C(2)	71.76(16)
C(3)#1-C(3)-C(4)	92.6(2)	C(2)-C(3)-C(4)	123.1(3)
C(3)#1-C(3)-C(9)	73.71(15)	C(2)-C(3)-C(9)	129.2(3)
C(4)-C(3)-C(9)	94.3(3)	C(3)#1-C(3)-C(4)#1	58.38(19)
C(2)-C(3)-C(4)#1	106.8(3)	C(4)-C(3)-C(4)#1	34.2(3)
C(9)-C(3)-C(4)#1	84.6(3)	C(4)#1-C(4)-C(5)#1	88.8(3)
C(4)#1-C(4)-C(6)#1	163.7(4)	C(5)#1-C(4)-C(6)#1	74.9(5)
C(4)#1-C(4)-C(5)	47.9(2)	C(5)#1-C(4)-C(5)	40.8(4)
C(6)#1-C(4)-C(5)	115.8(5)	C(4)#1-C(4)-C(8)	70.27(17)
C(5)#1-C(4)-C(8)	148.5(5)	C(6)#1-C(4)-C(8)	124.0(5)
C(5)-C(4)-C(8)	114.3(3)	C(4)#1-C(4)-C(10)	157.2(5)
C(5)#1-C(4)-C(10)	80.7(8)	C(6)#1-C(4)-C(10)	19.7(5)
C(5)-C(4)-C(10)	118.9(8)	C(8)-C(4)-C(10)	109.6(7)
C(4)#1-C(4)-C(3)	87.4(2)	C(5)#1-C(4)-C(3)	116.3(4)
C(6)#1-C(4)-C(3)	100.6(4)	C(5)-C(4)-C(3)	107.5(3)
C(8)-C(4)-C(3)	86.8(3)	C(10)-C(4)-C(3)	115.4(6)
C(4)#1-C(4)-C(7)#1	130.3(2)	C(5)#1-C(4)-C(7)#1	126.4(4)

C(6)#1-C(4)-C(7)#1	62.2(4)	C(5)-C(4)-C(7)#1	149.8(4)
C(8)-C(4)-C(7)#1	62.0(3)	C(10)-C(4)-C(7)#1	48.6(7)
C(3)-C(4)-C(7)#1	102.3(4)	C(4)#1-C(4)-C(3)#1	58.38(19)
C(5)#1-C(4)-C(3)#1	111.6(4)	C(6)#1-C(4)-C(3)#1	128.5(4)
C(5)-C(4)-C(3)#1	86.0(3)	C(8)-C(4)-C(3)#1	77.8(3)
C(10)-C(4)-C(3)#1	144.4(6)	C(3)-C(4)-C(3)#1	29.0(3)
C(7)#1-C(4)-C(3)#1	119.8(4)	C(5)#1-C(5)-C(4)#1	91.2(3)
C(5)#1-C(5)-O(1)	82.5(3)	C(4)#1-C(5)-O(1)	127.0(4)
C(5)#1-C(5)-C(4)	47.9(2)	C(4)#1-C(5)-C(4)	43.3(4)
O(1)-C(5)-C(4)	110.9(4)	C(5)#1-C(5)-C(6)	153.5(4)
C(4)#1-C(5)-C(6)	62.3(5)	O(1)-C(5)-C(6)	113.4(5)
C(4)-C(5)-C(6)	105.6(5)	C(5)#1-C(5)-O(1)#1	62.0(3)
C(4)#1-C(5)-O(1)#1	122.9(4)	O(1)-C(5)-O(1)#1	20.5(5)
C(4)-C(5)-O(1)#1	94.7(3)	C(6)-C(5)-O(1)#1	132.0(4)
C(5)#1-C(5)-C(10)#1	145.6(5)	C(4)#1-C(5)-C(10)#1	60.3(6)
O(1)-C(5)-C(10)#1	129.2(5)	C(4)-C(5)-C(10)#1	101.5(6)
C(6)-C(5)-C(10)#1	17.0(5)	O(1)#1-C(5)-C(10)#1	148.7(5)
C(10)#1-C(6)-C(4)#1	90(3)	C(10)#1-C(6)-C(5)	100(3)
C(4)#1-C(6)-C(5)	42.8(4)	C(10)#1-C(6)-C(7)	48(3)
C(4)#1-C(6)-C(7)	64.4(5)	C(5)-C(6)-C(7)	101.4(6)
C(10)#1-C(7)-C(6)	17.1(6)	C(10)#1-C(7)-C(8)	116.7(7)
C(6)-C(7)-C(8)	109.1(5)	C(10)#1-C(7)-C(4)#1	62.1(6)
C(6)-C(7)-C(4)#1	53.4(4)	C(8)-C(7)-C(4)#1	55.8(2)
C(4)#1-C(8)-C(4)	39.5(3)	C(4)#1-C(8)-C(9)	95.1(3)
C(4)-C(8)-C(9)	95.1(3)	C(4)#1-C(8)-C(7)#1	100.7(3)
C(4)-C(8)-C(7)#1	62.2(3)	C(9)-C(8)-C(7)#1	103.2(3)
C(4)#1-C(8)-C(7)	62.2(3)	C(4)-C(8)-C(7)	100.7(3)
C(9)-C(8)-C(7)	103.2(3)	C(7)#1-C(8)-C(7)	149.6(6)
C(3)#1-C(9)-C(3)	32.6(3)	C(3)#1-C(9)-C(8)	83.6(3)
C(3)-C(9)-C(8)	83.6(3)	C(6)#1-C(10)-C(7)#1	115(3)
C(6)#1-C(10)-C(4)	70(2)	C(7)#1-C(10)-C(4)	69.3(8)
C(6)#1-C(10)-C(5)#1	63(3)	C(7)#1-C(10)-C(5)#1	106.3(9)
C(4)-C(10)-C(5)#1	38.9(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+3/2, z

(d) x-ray data for compound 28b.

Table 1. Crystal data and structure refinement for 02OT01.

Identification code	ot01m	
Empirical formula	C ₁₆ H ₁₄ O ₃	
Formula weight	254.27	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 14.2689(15) Å	α = 90°.
	b = 10.3045(11) Å	β = 90°.
	c = 17.3186(17) Å	γ = 90°.
Volume	2546.4(5) Å ³	
Z	8	
Density (calculated)	1.327 Mg/m ³	
Absorption coefficient	0.091 mm ⁻¹	
F(000)	1072	
Crystal size	0.40 x 0.30 x 0.30 mm ³	
Theta range for data collection	2.35 to 28.28°.	
Index ranges	-18 ≤ h ≤ 7, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23	
Reflections collected	15062	
Independent reflections	3116 [R(int) = 0.0355]	
Completeness to theta = 28.28°	98.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.97864 and 0.91567	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3116 / 0 / 172	
Goodness-of-fit on F ²	1.025	
Final R indices [I > 2σ(I)]	R1 = 0.0508, wR2 = 0.1102	
R indices (all data)	R1 = 0.0848, wR2 = 0.1213	
Largest diff. peak and hole	0.188 and -0.157 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02OT01. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	1870(1)	1414(1)	2253(1)	55(1)
O(2)	-897(1)	-331(1)	633(1)	67(1)
O(3)	1005(1)	3140(1)	2431(1)	65(1)
C(1)	318(1)	-1892(2)	909(1)	62(1)
C(2)	-204(1)	-629(2)	991(1)	48(1)
C(3)	325(1)	185(2)	1565(1)	40(1)
C(4)	303(1)	1475(2)	1669(1)	39(1)
C(5)	1068(1)	2075(2)	2146(1)	46(1)
C(6)	1988(1)	107(2)	1943(1)	49(1)
C(7)	2347(1)	68(2)	1116(1)	56(1)
C(8)	2085(1)	-1281(2)	843(1)	58(1)
C(9)	1249(1)	-1746(2)	1338(1)	52(1)
C(10)	1079(1)	-638(2)	1919(1)	44(1)
C(11)	-420(1)	2384(2)	1376(1)	39(1)
C(12)	-1370(1)	2110(2)	1470(1)	47(1)
C(13)	-2046(1)	2973(2)	1225(1)	58(1)
C(14)	-1793(1)	4121(2)	879(1)	63(1)
C(15)	-854(1)	4413(2)	780(1)	61(1)
C(16)	-172(1)	3556(2)	1031(1)	50(1)

Table 3. Bond lengths [Å] and angles [°] for 02OT01.

O(1)-C(5)	1.3442(19)
O(1)-C(6)	1.4594(19)
O(2)-C(2)	1.207(2)
O(3)-C(5)	1.2068(19)
C(1)-C(2)	1.506(2)
C(1)-C(9)	1.529(3)
C(2)-C(3)	1.504(2)
C(3)-C(4)	1.342(2)
C(3)-C(10)	1.501(2)
C(4)-C(11)	1.483(2)
C(4)-C(5)	1.502(2)
C(6)-C(10)	1.508(2)
C(6)-C(7)	1.522(2)
C(7)-C(8)	1.514(3)
C(8)-C(9)	1.546(3)
C(9)-C(10)	1.540(2)
C(11)-C(16)	1.394(2)
C(11)-C(12)	1.394(2)
C(12)-C(13)	1.380(2)
C(13)-C(14)	1.374(3)
C(14)-C(15)	1.384(3)
C(15)-C(16)	1.384(2)
C(5)-O(1)-C(6)	121.04(12)
C(2)-C(1)-C(9)	107.34(14)
O(2)-C(2)-C(3)	127.52(16)
O(2)-C(2)-C(1)	125.24(16)
C(3)-C(2)-C(1)	107.19(14)
C(4)-C(3)-C(10)	121.42(14)
C(4)-C(3)-C(2)	129.01(14)
C(10)-C(3)-C(2)	108.41(13)
C(3)-C(4)-C(11)	126.62(14)
C(3)-C(4)-C(5)	117.69(14)
C(11)-C(4)-C(5)	115.68(13)

O(3)-C(5)-O(1)	117.90(14)
O(3)-C(5)-C(4)	123.05(15)
O(1)-C(5)-C(4)	119.04(14)
O(1)-C(6)-C(10)	112.36(13)
O(1)-C(6)-C(7)	114.17(14)
C(10)-C(6)-C(7)	104.46(13)
C(8)-C(7)-C(6)	103.58(14)
C(7)-C(8)-C(9)	107.60(14)
C(1)-C(9)-C(10)	104.75(14)
C(1)-C(9)-C(8)	115.58(14)
C(10)-C(9)-C(8)	104.68(13)
C(3)-C(10)-C(6)	109.90(12)
C(3)-C(10)-C(9)	105.27(13)
C(6)-C(10)-C(9)	105.11(13)
C(16)-C(11)-C(12)	118.22(15)
C(16)-C(11)-C(4)	121.17(14)
C(12)-C(11)-C(4)	120.56(14)
C(13)-C(12)-C(11)	120.93(16)
C(14)-C(13)-C(12)	120.32(16)
C(13)-C(14)-C(15)	119.74(17)
C(14)-C(15)-C(16)	120.20(17)
C(15)-C(16)-C(11)	120.59(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02OT01. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	41(1)	58(1)	65(1)	-17(1)	-12(1)	4(1)
O(2)	55(1)	72(1)	74(1)	-10(1)	-20(1)	-8(1)
O(3)	56(1)	61(1)	77(1)	-31(1)	-11(1)	4(1)
C(1)	72(1)	47(1)	66(1)	-12(1)	-1(1)	-7(1)
C(2)	47(1)	49(1)	47(1)	0(1)	0(1)	-14(1)
C(3)	38(1)	45(1)	37(1)	1(1)	2(1)	-5(1)
C(4)	35(1)	45(1)	37(1)	-2(1)	3(1)	-4(1)
C(5)	41(1)	53(1)	44(1)	-9(1)	0(1)	-1(1)
C(6)	46(1)	47(1)	55(1)	-5(1)	-8(1)	7(1)
C(7)	49(1)	52(1)	68(1)	-4(1)	13(1)	2(1)
C(8)	61(1)	55(1)	58(1)	-4(1)	4(1)	7(1)
C(9)	65(1)	37(1)	53(1)	4(1)	-3(1)	3(1)
C(10)	50(1)	44(1)	38(1)	5(1)	-1(1)	0(1)
C(11)	39(1)	44(1)	35(1)	-5(1)	2(1)	0(1)
C(12)	41(1)	56(1)	45(1)	-3(1)	3(1)	-3(1)
C(13)	40(1)	80(1)	53(1)	-5(1)	0(1)	7(1)
C(14)	61(1)	77(1)	52(1)	-1(1)	-3(1)	25(1)
C(15)	74(1)	51(1)	56(1)	6(1)	6(1)	8(1)
C(16)	49(1)	51(1)	50(1)	0(1)	6(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 02OT01.

	x	y	z	U(eq)
H(1A)	399	-2105	392	80
H(1B)	-80	-2561	1141	80
H(6A)	2448	-258	2311	80
H(7A)	3015	246	1079	80
H(7B)	2007	733	772	80
H(8A)	1900	-1288	322	80
H(8B)	2613	-1843	924	80
H(9A)	1393	-2537	1605	80
H(10A)	870	-867	2458	80
H(12A)	-1528	1306	1701	80
H(13A)	-2706	2772	1304	80
H(14A)	-2265	4748	711	80
H(15A)	-680	5227	519	80
H(16A)	494	3740	986	80