Supporting Information

for

Gold-catalyzed cyclization of allenyl acetal derivatives

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Experimental details

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(I) Representative synthetic procedures:

(a) General procedure:

Unless otherwise noted, all the reactions were performed in oven-dried glassware under nitrogen atmosphere with freshly distilled solvents. The THF was dried with sodium/benzophenone and distilled before use. N,N-dimethylformamide (DMF) and dichloromethane (DCM) were distilled from CaH₂ under nitrogen. DMF and triethylamine (Et₃N) were stored over 4 Å molecular sieves prior to use. All other commercial reagents were used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Varian 400, Bruker 400 and a Bruker 600 MHz spectrometer using chloroform-d (CDCl₃) and benzene-d₆ (C₆D₆) as internal standard.

(b) Typical procedure for the synthesis of 1-(dimethoxymethyl)-2-(3-methylbuta-1,2-dienyl)cyclohex-1-ene (1a). [1,2]

\[ \text{Scheme S1:} \]

(b-1) Synthesis of 1-bromo-2-(dimethoxymethyl)cyclohex-1-ene (s-1). [1]

To dry DMF (11.8 mL, 152.9 mmol) in DCM (100 mL) was slowly added PBr₃ (12.0 mL, 127.5 mmol) at 0 °C and the mixture was stirred for 1 h at this temperature before the addition of cyclohexanone (5 g, 51.0 mmol) in dry DCM. The resulting solution was stirred for 8 h at room temperature. After completion of the reaction, the residue was carefully and slowly added to crushed ice and neutralized with saturated NaHCO₃ solution and extracted with EtOAc (3 × 50
mL). The combined organic extracts were initially washed with saturated aqueous NaHCO$_3$, followed by water and brine. The organic phase was dried over MgSO$_4$, filtered, and concentrated in vacuo to afford the crude bromocyclohex-1-enecarbaldehyde (5.30 g, 28.0 mmol, 55%) as yellow oil. To this yellow oil, 15.3 mL (140.2 mmol) of trimethyl orthoformate and PTSA (0.48 g, 2.80 mmol) were added and stirred at 25–30 °C until complete consumption of the aldehyde (8 h, TLC). After completion of the reaction, the mixture was diluted with hexane and neutralized by using saturated aqueous NaHCO$_3$ solution. The resulting mixture was then extracted with hexane (2 × 20 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure to afford the crude product (s-1) (6.06 g, 25.8 mmol, 92%) as pale yellow oil that was used for the next step without further purification.

(b-2) Synthesis of 2-(dimethoxymethyl)cyclohex-1-enecarbaldehyde (s-2).

To a THF (100 mL) solution of crude compound (s-1) (6.06 g, 25.8 mmol) was added n-butyllithium (12.4 mL, 30.9 mmol, 2.5 M) at −78 °C, and the mixtures were stirred for 30 min. The reaction was quenched by adding dried DMF (2.99 mL, 38.7 mmol), and the resulting mixture was allowed to reach room temperature for another 30 min. The resulting solution was partitioned between 50 mL hexane and saturated Na$_2$CO$_3$ (aq) (1:1, v/v), and the aqueous layer was extracted with hexane (2 × 30 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was eluted through a triethylamine-pretreated silica gel column to give compound (s-2) (3.89 g, 21.1 mmol, 82%) as pale yellow oil.

(b-3) Synthesis of 1-(2-(dimethoxymethyl)cyclohex-1-enyl)but-2-ynyl acetate (s-3).

A THF (100 mL) solution of 1-bromo-1-propene (2.71 mL, 31.7 mmol) was cooled to −78 °C before addition of n-butyllithium (17.7 mL, 44.4 mmol, 2.5 M). The reaction was kept at −78 °C for 30 min, and to this solution was added a THF (5 mL) solution of compound (s-2) (3.89 g, 21.1 mmol) and the reaction was allowed to reach room temperature for 30 min, followed by addition of acetic anhydride (2.99 mL, 31.7 mmol) at 0 °C. The resulting mixture was stirred at room temperature for another 1 h before it was quenched with saturated aqueous Na$_2$CO$_3$. The aqueous solution was extracted with hexane (30 mL × 3). The combined organic layer was dried
over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The crude product s-3 (4.89 g, 18.4 mmol, 87%) was obtained as pale yellow oil and used for next step without further purification.

(b-4) Synthesis of 1-(dimethoxymethyl)-2-(3-methylbuta-1,2-dienyl)cyclohex-1-ene (1a). [2]

To a well stirred mixture of lithium bromide (3.19 g, 36.8 mmol) and copper iodide (6.98 g, 36.8 mmol) in THF (100 mL) at 0 °C was added methylmagnesium chloride (12.3 mL, 36.8 mmol, 3 M), and the solution was stirred for 20 min at 0 °C. The propargylic ester (s-3) (4.89 g, 18.4 mmol) in THF (5 mL) was added dropwise and the resulting mixture was slowly warmed to rt and stirred for an additional 5 h. At the completion of the reaction indicated by TLC, the mixture was poured into a saturated aqueous solution of ammonium chloride and partitioned between hexane/saturated Na$_2$CO$_3$ (aq) (1:2, v/v). The aqueous layer was extracted with hexane (2 × 100 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was purified on a triethylamine-pretreated silica column to afford desired vinylallenyl acetal (1a) (3.35 g, 14.1 mmol, 76.6%) as a yellow oil.

(c) Synthesis of 4-(2-(dimethoxymethyl)-5,5-dimethylcyclohex-1-enyl)-2-methylbut-3-yn-2-yl acetate (5a):

Scheme S2:
(c-1) Synthesis of 2-bromo-4,4-dimethylcyclohex-1-enecarbaldehyde (s-4). [1]

To dry DMF (9.20 mL, 118.9 mmol) in chloroform (100 mL) was slowly added PBr$_3$ (9.31 mL, 99.0 mmol) at 0 °C and the mixture was stirred for 1 h at this temperature before addition of 3,3-dimethylcyclohexanone (5 g, 39.6 mmol) in dry DCM. The resulting solution was stirred for 8 h at room temperature. After completion of the reaction, the residue was carefully added to crushed ice and neutralized with saturated NaHCO$_3$ solution and extracted with EtOAc (3 × 50 mL). The combine organic extracts were initially washed with saturated aqueous NaHCO$_3$ followed by water and brine. The organic phase was dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography (hexane/ethyl acetate, 9:1) to afford 2-bromo-4,4-dimethylcyclohex-1-enecarbaldehyde (s-4) (7.31 g, 85%, 33.7 mmol) as a yellow oil.

(c-2) Synthesis of 2-methylbut-3-yn-2-yl acetate (s-5).

To a DCM (200 mL) solution of 2-methylbut-3-yn-2-ol (10 g, 118.9 mmol) was added Ac$_2$O (18.2 g, 178.4 mmol), Et$_3$N (24.1 g, 237.8 mmol) and several crystals of DMAP (1.45 g, 11.9 mmol). The mixture was stirred overnight at room temperature. Upon completion of the reaction as indicated by TLC, the solution was then quenched with saturated ammonium chloride (aq). The resulting mixture was partitioned between 200 mL hexane and saturated Na$_2$CO$_3$ (aq) (1:1, v/v), and the aqueous layer was extracted with hexane (2 × 50 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was eluted through a triethylamine-pretreated silica gel column to afford compound (s-5) (13.4 g, 89%, 106.2 mmol) as pale yellow oil.

(c-3) Synthesis of 4-(2-formyl-5,5-dimethylcyclohex-1-enyl)-2-methylbut-3-yn-2-yl acetate (s-6).

To a suspension of PdCl$_2$(PPh$_3$)$_2$ (1.18 g, 1.68 mmol) and CuI (0.641 g, 3.37 mmol) in 50 mL triethylamine at room temperature compound (s-4) (7.31 g, 33.7 mmol) was added and stirred for 15 min. To this solution, 2-methylbut-3-yn-2-yl acetate (s-5) (5.10 g, 40.4 mmol) was added dropwise using a standard syringe. After stirring the mixture at room temperature for 8 h the resulting solution was filtered through a small celite bed and washed three times with ethyl acetate. It was then concentrated and purified by column chromatography, which yielded the product s-6 (6.00 g, 68%, 22.9 mmol) as yellow oil.

(c-4) Synthesis of 4-(2-(dimethoxymethyl)-5,5-dimethylcyclohex-1-enyl)-2-methylbut-3-yn-2-yl acetate (5a). [3]

A mixture of aldehyde (s-6) (6.00 g, 22.9 mmol), p-TsOH monohydrate (0.394 g, 2.29 mmol) and trimethyl orthoformate (12.53 mL, 114.5 mmol) was stirred at 25 °C for 8 h and then concentrated in vacuo. The residue was diluted with hexane, washed with saturated NaHCO$_3$ solution, water, and brine. The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography with
pretreated triethylamine silica gel to afford the desired propargylic ester acetal (5a) (6.22 g, 20.2 mmol, 88%) as yellow oil.

**References:**

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3. a) Kumar, R.; Kumar D.; Chakraborti, A. K., *Synthesis.* **2007**, *2*, 299. DOI: 10.1055/s-2006-958948; b) Chakraborti, A. K.; Gulhane, R., *Chem. Commun.* **2003**, *1896*. DOI: 10.1039/B304178F

**(II) General procedure for gold-catalyzed carbocyclization:**

(a) General procedure for the gold (I)-catalyzed carbocyclization of vinylallenyl acetal:

![Chemical Structure](image)

A two-necked flask was charged with chloro(triphenylphosphine)gold(I) (11.1 mg, 0.022 mmol) and silver triflate (5.8 mg, 0.022 mmol), and CH$_2$Cl$_2$ (2.0 mL) was added. The resulting mixture was stirred at room temperature for 10 min. To this mixture was added CH$_2$Cl$_2$ (2.5 mL) solution of vinylallenyl acetal (1a) (100 mg, 0.45 mmol) dropwise and the mixture was kept stirring at 25 °C for 30 min before it was filtered over a short silica bed. The solvent was evaporated under reduced pressure. The crude product was eluted through a short silica column (3% ethyl acetate in hexane) affords the desired ketone 4a (70.6 mg, 0.40 mmol, 89%) as a pale yellow oil.
(b) General procedure for the gold(I)-catalyzed carbocyclization of propargylic ester acetals:

Chloro(triphenylphosphine)gold (I) (8.0 mg, 0.016 mmol) and silver triflate (4.2 mg, 0.016 mmol) was added to a dried Schlenk tube under an N₂ atmosphere, and then freshly distilled DCM (1.0 mL) was introduced by a syringe. The resulting mixture was stirred at room temperature for 10 minutes before the addition of propargylic ester acetal (5a) (100 mg, 0.32 mmol) in DCM (2.2 mL). The reaction mixture was stirred for another 5 minutes at 25 °C (reaction monitored by TLC). After completion of the reaction, the brown suspension was filtered through a short bed of silica gel and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography to afford the desired ketone 6a (58 mg, 0.25 mmol, 76%) as dark yellow oil.

(III) Spectral data of Compounds 1a to 6g:

Spectral data for 1-(dimethoxymethyl)-2-(3-methylbuta-1,2-dienyl)cyclohex-1-ene (1a). [1]

Compound 1a was prepared according to the known literature procedure [1] reported by our laboratory.
Spectral data for 1-(dimethoxymethyl)-2-(3-methylbuta-1,2-dienyl)cyclopent-1-ene (1b).

Yellow oil, IR (neat, cm$^{-1}$): 2962 (s), 1649 (w), 1441 (m), 1086 (s); $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 6.15–6.12 (m, 1H), 5.02 (s, 1H), 3.28 (s, 6H), 2.47–2.38 (m, 4H), 1.83–1.77 (m, 2H), 1.75 (s, 3H), 1.73 (s, 3H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 205.3, 137.2, 134.7, 101.5, 97.0, 87.2, 53.6 (2 x OCH$_3$), 35.2, 33.6, 21.9, 20.6 (2 x CH$_3$); HRMS calcd for C$_{13}$H$_{20}$O$_2$: 208.1463, found: 208.1462.

Spectral data for (4-(2-(dimethoxymethyl)cyclopent-1-enyl)buta-2,3-dien-2-yl)benzene (1c).

Yellow oil, IR (neat, cm$^{-1}$): 2978 (s), 1638 (w), 1464 (m), 1064 (s), 867 (s), 692 (s); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41–7.38 (m, 2H), 7.33–7.29 (m, 2H), 7.22–7.18 (m, 1H), 6.66 (q, $J = 2.8$ Hz, 1H), 5.12 (s, 1H), 3.37 (s, 3H), 3.36 (s, 3H), 2.56–2.52 (m, 2H), 2.50–2.45 (m, 2H), 2.14 (d, $J = 2.8$ Hz, 3H), 1.87–1.80 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 208.4, 136.7, 135.8, 135.5, 128.3, 126.6, 125.7, 102.1, 101.2, 90.8, 53.6, 53.5, 34.8, 33.3, 21.4, 17.0; HRMS calcd for C$_{18}$H$_{22}$O$_2$: 270.1620, found: 270.1618.

Spectral data for (1- (2-(dimethoxymethyl)cyclopent-1-enyl)penta-1,2-dien-3-yl)benzene (1d).

Pale yellow oil, IR (neat, cm$^{-1}$): 2978 (s), 1638 (w), 1464 (m), 1064 (s), 878 (s), 686 (s); $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 7.44–7.42 (m, 2H), 7.19–7.15 (m, 2H), 7.07–7.03 (m, 1H), 6.99 (t, $J =$
3.2 Hz, 1H), 5.10 (s, 1H), 3.18 (s, 3H), 3.17 (s, 3H), 2.67–2.62 (m, 2H), 2.51–2.46 (m, 2H), 2.38–2.31 (m, 2H), 1.72–1.66 (m, 2H), 1.10 (t, J = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $\text{C}_6\text{D}_6$): δ 208.2, 137.1, 136.5, 135.4, 128.7, 127.0, 126.4, 109.5, 101.4, 93.7, 52.8, 52.7, 35.3, 34.5, 23.5, 21.8, 12.9; HRMS calcd for C$_{19}$H$_{24}$O$_2$: 284.1776, found: 284.1773.

Spectral data for (1,1-dimethoxy-2,6-dimethylhepta-2,4,5-trien-3-yl)benzene (1e).

![Spectral data for (1,1-dimethoxy-2,6-dimethylhepta-2,4,5-trien-3-yl)benzene (1e).](image)

Pale yellow oil, IR (neat, cm$^{-1}$): 1647 (w), 1453 (m), 1048 (s), 869 (s); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.28–7.24 (m, 2H), 7.21–7.19 (m, 5H), 7.08–7.04 (m, 3H), 6.28–6.25 (m, 1H), 6.15–6.12 (m, 1H), 5.24 (s, 1H), 4.40 (s, 1H), 3.41 (s, 6H), 3.17 (s, 3H), 1.85 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 207.2, 206.6, 140.9, 139.8, 137.3, 137.0, 129.5, 129.3, 128.9 (1 x CH, 1 x C), 127.5, 127.3, 126.5, 126.4, 105.3, 102.8, 97.4, 97.2, 92.4, 91.0, 54.6 (2 x OCH$_3$), 54.3 (2 x OCH$_3$), 19.7 (2 x CH$_3$), 19.6 (2 x CH$_3$), 14.5, 11.0; HRMS calcd for C$_{17}$H$_{22}$O$_2$: 258.3554, found: 258.3552.

Spectral data for (3-(2-(dimethoxymethyl)cyclohex-1-enyl)propa-1,2-dienyl)benzene (1f).

![Spectral data for (3-(2-(dimethoxymethyl)cyclohex-1-enyl)propa-1,2-dienyl)benzene (1f).](image)

Colourless oil, IR (neat, cm$^{-1}$): 2957 (s), 1633 (w), 1465 (m), 1063 (s), 872 (s), 681 (s); $^1$H NMR (400 MHz, $\text{C}_6\text{D}_6$): δ 7.33–7.30 (m, 2H), 7.20–7.15 (m, 2H), 7.08–7.04 (m, 1H), 7.00 (d, J = 6.4 Hz, 1H), 6.41 (d, J = 6.4 Hz, 1H), 5.13 (s, 1H), 3.25 (s, 3H), 3.21 (s, 3H), 2.43–2.40 (m, 2H), 2.33–2.28 (m, 1H), 2.23–2.12 (m, 1H), 1.55–1.47 (m, 4H); $^{13}$C NMR (100 MHz, $\text{C}_6\text{D}_6$): δ 208.4, 134.8, 133.7, 129.2, 129.0, 127.3, 127.1, 102.7, 98.0, 96.8, 53.7, 53.4, 27.7, 25.3, 22.8, 22.7; HRMS calcd for C$_{18}$H$_{22}$O$_2$: 270.1620, found: 270.1621.
Spectral data for (4-(2-(dimethoxymethyl)cyclohex-1-enyl)buta-2,3-dien-2-yl)benzene (1g).

Yellow oil, IR (neat, cm\(^{-1}\)): 2934 (s), 1647 (w), 1471 (m), 1085 (s), 869 (s), 687 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.42–7.40 (m, 2H), 7.34–7.30 (m, 2H), 7.23–7.19 (m, 1H), 6.69–6.67 (m, 1H), 5.16 (s, 1H), 3.39 (s, 3H), 3.38 (s, 3H), 2.21–2.14 (m, 7H), 1.62–1.61 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 206.9, 136.8, 131.8, 130.5, 128.3, 126.6, 125.6, 103.2, 102.8, 94.1, 54.4, 54.3, 27.4, 24.1, 22.4, 22.3, 17.0; HRMS calcd for C\(_{19}\)H\(_{24}\)O\(_2\): 284.1776, found: 284.1779.

Spectral data for (1-(2-(dimethoxymethyl)cyclohex-1-enyl)penta-1,2-dien-3-yl)benzene (1h).

Yellow oil, IR (neat, cm\(^{-1}\)): 2945 (s), 1638 (w), 1442 (m), 1048 (s), 872 (s), 691 (s); \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)): \(\delta\) 7.43–7.41 (m, 2H), 7.17–7.13 (m, 2H), 7.05–7.01 (m, 1H), 6.93 (t, \(J = 3.2\) Hz, 1H), 5.13 (s, 1H), 3.18 (s, 3H), 3.16 (s, 3H), 2.39–2.31 (m, 4H), 2.23–2.17 (m, 2H), 1.51–1.39 (m, 4H), 1.08 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, C\(_6\)D\(_6\)): \(\delta\) 206.6, 137.1, 132.9, 129.9, 128.7, 127.0, 126.3, 110.6, 102.7, 96.9, 53.7, 53.5, 27.8, 25.1, 23.5, 22.9, 22.8, 12.9; HRMS calcd for C\(_{20}\)H\(_{26}\)O\(_2\): 298.1933, found: 298.1931.

Spectral data for 1-(dimethoxymethyl)-2-(3-methylbuta-1,2-dienyl)cyclohex-1-ene (d\(_1\)-1a).

Pale yellow oil, IR (neat, cm\(^{-1}\)): 2932 (s), 1645 (w), 1439 (m), 1012 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.12–6.09 (m, 1H), 3.29 (s, 6H), 2.14–1.99 (m, 4H), 1.68 (s, 3H), 1.67 (s, 3H), 1.56–1.53 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 203.5, 131.4, 130.4, 97.6, 90.0, 54.2 (2 x OCH\(_3\)), 27.2, 23.4, 22.5, 22.4, 20.4 (2 x CH\(_3\)); HRMS calcd for C\(_{14}\)H\(_{21}\)DO\(_2\): 223.1683, found: 223.1689.
Spectral data for 4-(2-(dimethoxymethyl)-5,5-dimethylcyclohex-1-enyl)-2-methylbut-3-yn-2-yl acetate (5a).

Pale yellow oil, IR (neat, cm⁻¹): 2961 (s), 1721 (s), 1642 (w), 1468 (m), 1048 (s); ¹H NMR (400 MHz, CDCl₃): δ 5.22 (s, 1H), 3.36 (s, 6 H), 2.13–2.10 (m, 2H), 1.97 (s, 3 H), 1.92–1.91 (m, 2H), 1.63 (s, 6H), 1.31 (t, J = 6.5 Hz, 2H), 0.86 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 169.1, 141.0, 118.1, 105.2, 93.0, 83.0, 72.3, 55.2 (2 x OCH₃), 43.4, 34.3, 29.0 (2 x CH₃), 28.7, 27.9 (2 x CH₃), 21.9, 19.6; HRMS calcd for C₁₈H₂₈O₄: 308.1988, found: 308.1984.

Spectral data for 1-((2-(dimethoxymethyl)cyclopent-1-enyl)ethynyl)cyclopentyl acetate (5b).

Yellow oil, IR (neat, cm⁻¹): 2932 (s), 1728 (s), 1631 (w), 1427 (m), 1042 (s); ¹H NMR (400 MHz, C₆D₆): δ 5.44 (s, 1H), 3.37 (s, 6 H), 2.63–2.58 (m, 2H), 2.43–2.38 (m, 2H), 2.30–2.15 (m, 4H), 1.65 (s, 3H), 1.61–1.50 (m, 6H); ¹³C NMR (100 MHz, C₆D₆): δ 168.7, 149.0, 122.3, 102.5, 95.3, 81.1, 80.9, 54.6 (2 x OCH₃), 40.7 (2 x CH₂), 37.0, 31.4, 23.5 (2 x CH₂), 22.6, 21.3; HRMS calcd for C₁₇H₂₄O₄: 292.1675, found: 292.1670.

Spectral data for 3-(2-(dimethoxymethyl)cyclohex-1-enyl)-1-phenylprop-2-ynyl acetate (5c).
Yellow oil, IR (neat, cm^{-1}): 2946 (s), 1730 (s), 1635 (w), 1442 (m), 1063 (s), 887 (s), 691 (s); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.52–7.49 (m, 2H), 7.39–7.31 (m, 3H), 6.56 (s, 1H), 5.12 (s, 1H), 3.33 (s, 3H), 3.30 (s, 3H), 2.20–2.19 (m, 2H), 2.12–2.11 (m, 2H), 2.08 (s, 3H), 1.60–1.57 (m, 4H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 169.7, 143.5, 137.2, 128.8, 128.6, 127.6, 118.7, 105.2, 89.0, 86.1, 66.2, 55.2 (2 x OCH\textsubscript{3}), 29.8, 22.0, 21.9, 21.4, 21.0; HRMS calcd for C\textsubscript{20}H\textsubscript{24}O\textsubscript{4}: 328.1675, found: 328.1673.

**Spectral data for 4-(2-(dimethoxymethyl)cyclohex-1-eny1)-2-methylbut-3-yn-2-yl acetate (5d).**

![Diagram of 5d](image)

Yellow oil, IR (neat, cm^{-1}): 2954 (s), 1722 (s), 1628 (w), 1463 (m), 1054 (s); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 5.19 (s, 1H), 3.33 (s, 6H), 2.11–2.09 (m, 2H), 2.06–2.04 (m, 2H), 1.94 (s, 3H), 1.60 (s, 6H), 1.54–1.50 (m, 4H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 169.0, 142.3, 118.9, 105.3, 93.3, 82.7, 72.2, 55.1 (2 x OCH\textsubscript{3}), 29.8, 28.9 (2 x CH\textsubscript{3}), 22.1, 21.8, 21.7, 21.5; HRMS calcd for C\textsubscript{16}H\textsubscript{24}O\textsubscript{2}: 280.1675, found: 280.1678.

**Spectral data for 3-(2-(dimethoxymethyl)phenyl)-1-phenylprop-2-ynyl acetate (5e).**

![Diagram of 5e](image)

Yellow oil, IR (neat, cm^{-1}): 3059 (m), 1735 (s), 1636 (w), 1438 (m), 1051 (s), 896 (s), 689 (s); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.62 (d, J = 7.4 Hz, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.42–7.34 (m, 4H), 7.29–7.25 (m, 1H), 6.70 (s, 1H), 5.58 (s, 1H), 3.35 (s, 3H), 3.34 (s, 3H), 2.12 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 169.6, 140.4, 137.2, 132.5, 129.0, 128.9, 128.7, 128.4, 127.8, 126.2, 121.0, 102.5, 90.3, 84.8, 66.2, 54.2, 54.1, 20.9; HRMS calcd for C\textsubscript{20}H\textsubscript{20}O\textsubscript{4}: 324.1362, found: 324.1366.
Spectral data for 4-(2-(dimethoxymethyl)phenyl)but-3-yn-2-yl acetate (5f).

Yellow oil, IR (neat, cm\(^{-1}\)): 3068 (m), 1730 (s), 1628 (w), 1459 (m), 1060 (s), 901 (s), 698 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.54 (dd, \(J = 7.6, 1.1\) Hz, 1H), 7.41 (dd, \(J = 7.6, 1.1\) Hz, 1H), 7.31 (td, \(J = 7.6, 1.1\) Hz, 1H), 7.23 (td, \(J = 7.6, 1.1\) Hz, 1H), 5.66 (q, \(J = 6.7\) Hz, 1H), 5.57 (s, 1H), 3.38 (s, 3H), 3.37 (s, 3H), 2.06 (s, 3H), 1.57 (d, \(J = 6.7\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 169.8, 140.0, 132.4, 128.6, 128.2, 125.9, 121.1, 102.6, 91.9, 82.0, 60.7, 54.4 (2 x OMe), 21.3, 21.0; HRMS calcd for C\(_{15}\)H\(_{18}\)O\(_4\): 262.1205, found: 262.1209.

Spectral data for 1-(2-(dimethoxymethyl)phenyl)hept-1-yn-3-yl acetate (5g).

Yellow oil, IR (neat, cm\(^{-1}\)): 3073 (m), 1734 (s), 1636 (w), 1448 (m), 1053 (s), 912 (s), 686 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.51 (dd, \(J = 7.4, 1.2\) Hz, 1H), 7.38 (dd, \(J = 7.4, 1.2\) Hz, 1H), 7.26 (td, \(J = 7.4, 1.2\) Hz, 1H), 7.19 (td, \(J = 7.4, 1.2\) Hz, 1H), 5.56–5.53 (m, 2H), 3.33 (s, 3H), 3.32 (s, 3H), 2.04 (s, 3H), 1.84–1.79 (m, 2H), 1.50–1.42 (m, 2H), 1.39–1.29 (m, 2H), 0.88 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 169.7, 139.9, 132.3, 128.4, 128.1, 125.9, 121.1, 102.4, 91.1, 82.5, 64.4, 54.1 (2 x OMe), 34.3, 27.0, 22.1, 20.8, 13.7; HRMS calcd for C\(_{18}\)H\(_{24}\)O\(_4\): 304.1675, found: 304.1671.

Spectral data for 2-(propan-2-ylidene)-2,3,4,5,6,7-hexahydro-1H-inden-1-one (4a).
Pale yellow oil, IR (neat, cm\(^{-1}\)): 2967 (s), 1672 (s), 1652 (m); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.91 (s, 2H), 2.28–2.25 (m, 5H), 2.14–2.10 (m, 2H), 1.81 (s, 3H), 1.70–1.65 (m, 2H), 1.64–1.60 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.4, 162.7, 143.7, 141.7, 129.1, 35.8, 27.5, 23.8, 22.2, 21.7, 20.1, 19.4; HRMS calcd for C\(_{12}\)H\(_{16}\)O: 176.1201, found: 176.1191.

**Spectral data for 2-(propan-2-ylidene)-2,3,5,6-tetrahydropentalen-1(4\(H\))-one (4b).**

![Structure of 4b](image)

Yellow solid, IR (neat, cm\(^{-1}\)): 2959 (s), 1671 (s), 1642 (m); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.98 (s, 2H), 2.55–2.51 (m, 2H), 2.43–2.38 (m, 2H), 2.29–2.21 (m, 5H), 1.82 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 192.6, 175.1, 152.0, 144.1, 134.5, 31.6, 31.3, 27.0, 25.3, 23.7, 19.4; HRMS calcd for C\(_{11}\)H\(_{14}\)O: 162.1045, found: 162.1041.

**Spectral data for (\(E\))-2-(1-phenylethylidene)-2,3,5,6-tetrahydropentalen-1(4\(H\))-one (4c).**

![Structure of 4c](image)

Pale yellow oil, IR (neat, cm\(^{-1}\)): 2972 (s), 1682 (s), 1651 (m), 891 (s), 698 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.37–7.33 (m, 2H), 7.29–7.26 (m, 1H), 7.22–7.20 (m, 2H), 2.89 (s, 2H), 2.58 (s, 3H), 2.50–2.44 (m, 4H), 2.29–2.22 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 193.2, 177.4, 151.8, 146.3, 143.7, 135.8, 128.3, 127.4, 126.9, 32.4, 31.6, 27.0, 25.3, 19.6; HRMS calcd for C\(_{16}\)H\(_{16}\)O: 224.1201, found: 224.1200.

| Irradiation | Intensity increase |
|-------------|--------------------|
| H\(_1\) (\(\delta\) 2.89) | H\(_2\) (\(\delta\) 7.22–7.20, 3.00 %). |
| H\(_2\) (\(\delta\) 7.22–7.20) | H\(_1\) (\(\delta\) 2.89, 1.75%), H\(_3\) (\(\delta\) 2.58, 1.51%). |
| H\(_3\) (\(\delta\) 2.58) | H\(_2\) (\(\delta\) 7.22–7.20, 0.76%). |
Spectral data for \((E)-2-\text{(1-phenylpropylidene)-2,3,5,6-tetrahydropentalen-1(4H)-one (4d).}

![Image of 4d]

Pale yellow oil, IR (neat, cm\(^{-1}\)): 2963 (s), 1674 (s), 1656 (m), 887 (s), 695 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.37–7.32 (m, 2H), 7.30–7.26 (m, 1H), 7.17–7.14 (m, 2H), 3.12 (q, \(J = 7.5\) Hz, 2H), 2.81 (s, 2H), 2.48–2.42 (m, 4H), 2.28–2.21 (m, 2H), 0.98 (t, \(J = 7.5\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 192.8, 177.3, 152.8, 151.9, 142.2, 135.2, 128.2, 127.3, 127.2, 32.3, 31.6, 27.0, 25.4, 25.3, 12.8; HRMS calcd for C\(_{17}\)H\(_{18}\)O: 238.1358, found: 238.1364.

Spectral data for 2-methyl-3-phenyl-5-(propan-2-ylidene)cyclopent-2-enone (4e).

![Image of 4e]

Pale yellow oil, IR (neat, cm\(^{-1}\)): 1680 (s), 1645 (m), 897 (s), 687 (s); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.54–7.53 (m, 2H), 7.45–7.43 (m, 2H), 7.39–7.36 (m, 1H), 3.40 (s, 2H), 2.36 (s, 3H), 2.01 (t, \(J = 1.4\) Hz, 3H), 1.94 (s, 3H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 196.9, 156.6, 145.6, 139.7, 136.3, 129.1, 128.6 (1 x CH, 1 x C), 127.8, 35.2, 24.1, 20.0, 10.3; HRMS calcd for C\(_{15}\)H\(_{16}\)O: 212.1201, found: 212.1197.

| Irradiation | Intensity increase |
|-------------|--------------------|
| H\(_d\) (\(\delta\) 3.40) | Ha (\(\delta\) 1.94, 3.38%), He (\(\delta\) 7.52–7.54, 3.86%) |
| Ha (\(\delta\) 1.94) | H\(_d\) (\(\delta\) 3.40, 2.38%) |
| Hc (\(\delta\) 2.00) | Ha (\(\delta\) 1.94, 3.38%), He (\(\delta\) 7.52–7.54, 3.86%) |
| He,\(_e\) (\(\delta\) 7.52–7.54) | H\(_d\) (\(\delta\) 3.40, 2.52%) |

Spectral data for \((E)-2\text{-benzylidene-2,3,4,5,6,7-hexahydro-1H-inden-1-one (4f).}

![Image of 4f]
Pale yellow oil, IR (neat, cm⁻¹): 2958 (s), 1669 (s), 1645 (m), 893 (s), 691 (s); ¹H NMR (600 MHz, CDCl₃): δ 7.56–7.55 (m, 2H), 7.40–7.37 (m, 2H), 7.34–7.31 (m, 2H), 3.36 (s, 2H), 2.42–2.40 (m, 2H), 2.27–2.24 (m, 2H), 1.79–1.75 (m, 2H), 1.71–1.68 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 196.5, 166.7, 140.2, 135.7, 133.7, 130.2, 129.8, 129.0, 128.8, 36.0, 28.0, 22.3, 21.7, 20.4; HRMS calcd for C₁₆H₁₆O: 224.1201, found: 224.1195.

| Irradiation | Intensity increase       |
|-------------|--------------------------|
| Ha (δ 3.36) | Hb (δ 7.55, 4.83%)       |
| Hb (δ 7.55) | Hd (δ 3.36, 2.94%)       |

Spectral data for (E)-2-(1-phenylethylidene)-2,3,4,5,6,7-hexahydro-1H-inden-1-one (4g).

Yellow oil, IR (neat, cm⁻¹): 2963 (s), 1672 (s), 1651 (m), 886 (s), 698 (s); ¹H NMR (400 MHz, CDCl₃): δ 7.37–7.34 (m, 2H), 7.30–7.26 (m, 1H), 7.24–7.21 (m, 2H), 2.87 (s, 2H), 2.59 (s, 3H), 2.24–2.17 (m, 4H), 1.70–1.63 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 197.2, 165.0, 145.8, 143.9, 141.7, 130.6, 128.3, 127.4, 127.0, 36.8, 27.5, 22.2, 21.7, 20.2, 19.6; HRMS calcd for C₁₇H₁₈O: 238.1358, found: 238.1361.

Spectral data for (E)-2-(1-phenylpropylidene)-2,3,4,5,6,7-hexahydro-1H-inden-1-one (4h).

Yellow oil, IR (neat, cm⁻¹): 2961 (s), 1676 (s), 1662 (m), 876 (s), 693 (s); ¹H NMR (400 MHz, CDCl₃): δ 7.37–7.33 (m, 2H), 7.30–7.26 (m, 1H), 7.18–7.16 (m, 2H), 3.14 (q, J = 7.5 Hz, 2H), 2.79 (s, 2H), 2.21–2.17 (m, 4H), 1.70–1.60 (m, 4H), 0.98 (t, J = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 196.7, 164.9, 152.4, 142.4, 141.8, 129.9, 128.2, 127.3, 127.2, 36.7, 27.5, 25.5, 22.2, 21.8, 20.2, 12.8; HRMS calcd for C₁₈H₂₀O: 252.1514, found: 252.1512.
Spectral data for 2-(propan-2-ylidene)-2,3,4,5,6,7-hexahydro-1H-inden-1-one (d1-4a).

Pale yellow oil, IR (neat, cm\(^{-1}\)): 2969 (s), 1674 (s), 1650 (m); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.92 (s, 1H), 2.31–2.28 (m, 5H), 2.16–2.12 (m, 2H), 1.83 (s, 3H), 1.73–1.60 (m, 4H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.5, 162.8, 143.8, 141.9, 129.2, 35.5 (\(J = 19.7\) Hz), 27.6, 23.9, 22.3, 21.8, 20.2, 19.5; HRMS calcd for C\(_{12}\)H\(_{15}\)DO: 177.1264, found: 177.1271.

Spectral data for 6,6-dimethyl-2-(propan-2-ylidene)-2,3,4,5,6,7-hexahydro-1H-inden-1-one (6a).

Pale yellow oil, IR (neat, cm\(^{-1}\)): 2959 (s), 1663 (s), 1652 (m); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 4.93 (s, 1H), 2.94 (s, 3H), 2.43–2.36 (m, 1H), 2.30 (s, 3H), 2.27–2.20 (m, 1H), 1.99–1.96 (m, 5H), 1.46 (t, \(J = 7.6\) Hz, 2H), 0.91 (s, 3H), 0.89 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.8, 160.4, 149.3, 144.6, 128.4, 77.9, 50.2, 35.0, 33.7, 29.2, 28.0, 27.9, 23.0, 22.4, 20.1; HRMS calcd for C\(_{15}\)H\(_{22}\)O\(_2\): 234.1620, found: 234.1623.

Spectral data for 2-cyclopentylidene-3-methoxy-2,3,5,6-tetrahydropentalen-1(4H)-one (6b).

Dark yellow oil, IR (neat, cm\(^{-1}\)): 2975 (s), 1673 (s), 1648 (m), 1121 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 4.81 (s, 1H), 3.13 (s, 3H), 2.88–2.84 (m, 2H), 2.65–2.33 (m, 6H), 2.32–2.25 (m, 2H), 1.74–1.59 (m, 4H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 190.2, 174.2, 159.5, 155.0, 130.6, 75.5, 52.8, 32.7, 32.0, 30.0, 26.9, 26.3, 25.3, 25.2; HRMS calcd for C\(_{14}\)H\(_{18}\)O\(_2\): 218.1307, found: 218.1301.
Spectral data for \((E)-2\text{-benzylidene-3-methoxy-2,3,4,5,6,7-hexahydro-1H-inden-1-one}\) (6c).

Yellow oil, IR (neat, cm\(^{-1}\)): 2973 (s), 1672 (s), 1641 (m), 1124 (s), 885 (s), 691 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.82–7.80 (m, 2H), 7.47 (d, \(J = 1.3\) Hz, 1H), 7.41–7.32 (m, 3H), 5.31 (s, 1H), 2.92 (s, 3H), 2.53–2.47 (m, 1H), 2.34–2.29 (m, 3H), 1.85–1.69 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.1, 164.9, 144.1, 134.1, 133.8, 131.5, 131.3, 129.6, 128.6, 76.6, 49.7, 24.7, 21.8, 21.5, 20.1; HRMS calcd for C\(_{17}\)H\(_{18}\)O\(_2\): 254.1307, found: 254.1312.

Spectral data for 3-methoxy-2-(propan-2-ylidene)-2,3,4,5,6,7-hexahydro-1H-inden-1-one (6d).

Brown oil, IR (neat, cm\(^{-1}\)): 2965 (s), 1669 (s), 1636 (m), 1120 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 4.90 (s, 1H), 2.95 (s, 3H), 2.42–2.35 (m, 1H), 2.30 (s, 3H), 2.24–2.13 (m, 3H), 1.95 (s, 3H), 1.79–1.66 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.6, 161.5, 149.2, 145.1, 128.2, 78.2, 50.2, 24.5, 23.1, 22.0, 21.6, 20.1, 19.9; HRMS calcd for C\(_{13}\)H\(_{18}\)O\(_2\): 206.1307, found: 206.1313.

Spectral data for \((E)-2\text{-benzylidene-3-methoxy-2,3-dihydro-1H-inden-1-one}\) (6e).

Yellow oil, IR (neat, cm\(^{-1}\)): 2982 (m), 1672 (s), 1642 (m), 891 (s), 692 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.95–7.92 (m, 2H), 7.89 (d, \(J = 7.7\) Hz, 1H), 7.82 (d, \(J = 1.5\) Hz, 1H), 7.74–7.66 (m, 2H), 7.53–7.49 (m, 1H), 7.47–7.40 (m, 3H), 5.95 (d, \(J = 1.5\) Hz, 1H), 2.91 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 192.4, 148.5, 138.8, 138.6, 135.1, 134.0, 133.4, 131.9, 130.4, 129.8, 128.8, 126.2, 123.7, 74.7, 50.4; HRMS calcd for C\(_{17}\)H\(_{14}\)O\(_2\): 250.0994, found: 250.0991.
Spectral data for (E)-2-ethylidene-3-methoxy-2,3-dihydro-1H-inden-1-one (6f).

![Image of 6f]

Yellow oil, IR (neat, cm$^{-1}$): 2953 (m), 1668 (s), 1642 (m), 887 (s), 697 (s); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85 (d, $J = 7.8$ Hz, 1H), 7.71–7.65 (m, 2H), 7.52–7.48 (m, 1H), 7.19–7.13 (m, 1H), 5.73 (s, 1H), 3.00 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.2, 148.5, 138.9, 138.3, 136.7, 134.9, 129.6, 126.2, 123.8, 74.8, 51.2, 14.8; HRMS calcd for C$_{12}$H$_{12}$O$_2$: 188.0837, found: 188.0841.

Spectral data for (E)-3-methoxy-2-pentylidene-2,3-dihydro-1H-inden-1-one (6g).

![Image of 6g]

Yellow oil, IR (neat, cm$^{-1}$): 2957 (m), 1670 (s), 1645 (m), 895 (s), 691 (s); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.84 (d, $J = 7.6$ Hz, 1H), 7.69–7.63 (m, 2H), 7.50–7.46 (m, 1H), 7.07 (td, $J = 7.8$ Hz, 1.7 Hz, 1H), 5.70 (s, 1H), 2.98 (s, 3H), 2.51–2.45 (m, 2H), 1.56–1.49 (m, 2H), 1.44–1.35 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.4, 148.5, 143.6, 139.0, 135.6, 134.9, 129.7, 126.2, 123.8, 74.9, 51.2, 30.5, 28.8, 22.6, 13.8; HRMS calcd for C$_{15}$H$_{18}$O$_2$: 230.1307, found: 230.1310.
DV-1150
\[ \text{Ph} \equiv \text{Me} \]

1e

E/Z : 3.1

ppm

10 9 8 7 6 5 4 3 2 1
5e

S45
S63
4h
DV-1173
$^{1}H$ NOE spectra of compounds 4c, 4e, and 4f
NOE of compound 4c
NOE of compound 4c
NOE of compound 4c
NOE of compound 4e
NOE of compound 4e
NOE of compound 4e
NOE of compound 4f
NOE of compound 4f
X-ray structure of compound 6a
Table 1. Crystal data and structure refinement for 08NV24_0m.

| Property                           | Value                                      |
|------------------------------------|--------------------------------------------|
| Identification code                | 08nv24_0m                                  |
| Empirical formula                  | C15 H22 O2                                  |
| Formula weight                     | 234.33                                     |
| Temperature                        | 296(2) K                                   |
| Wavelength                         | 0.71073 Å                                  |
| Crystal system                     | Triclinic                                  |
| Space group                        | P-1                                        |
| Unit cell dimensions               | a = 8.0947(3) Å, b = 9.4471(3) Å, c = 9.5269(3) Å |
|                                   | α = 79.573(2)°, β = 87.361(2)°, γ = 72.261(2)° |
| Volume                             | 682.41(4) Å³                               |
| Z                                  | 2                                          |
| Density (calculated)               | 1.140 Mg/m³                                 |
| Absorption coefficient             | 0.074 mm⁻¹                                  |
| F(000)                             | 256                                        |
| Crystal size                       | 0.30 x 0.30 x 0.30 mm³                      |
| Theta range for data collection    | 2.17 to 28.32°                             |
| Index ranges                       | -10 ≤ h ≤ 10, -12 ≤ k ≤ 10, -11 ≤ l ≤ 12   |
| Reflections collected              | 12717                                      |
| Independent reflections            | 3373 [R(int) = 0.0189]                      |
| Completeness to theta = 28.32°    | 99.3 %                                     |
| Absorption correction              | Empirical                                  |
| Max. and min. transmission         | 0.7454 and 0.7120                          |
| Refinement method                  | Full-matrix least-squares on F²            |
| Data / restraints / parameters     | 3373 / 0 / 159                             |
| Description                                      | Value           |
|--------------------------------------------------|-----------------|
| Goodness-of-fit on $F^2$                         | 1.071           |
| Final R indices [I>2sigma(I)]                    | R1 = 0.0464, wR2 = 0.1411 |
| R indices (all data)                             | R1 = 0.0580, wR2 = 0.1523 |
| Largest diff. peak and hole                      | 0.220 and -0.146 e.Å$^{-3}$ |
Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 08NV24_0m. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

|      | x       | y       | z       | $U(\text{eq})$ |
|------|---------|---------|---------|---------------|
| C(4) | 7020(1) | 2004(1) | 8695(1) | 43(1)         |
| C(1) | 3985(2) | 2370(1) | 8785(1) | 46(1)         |
| C(3) | 6592(2) | 1712(1) | 10219(1)| 45(1)         |
| C(9) | 5578(2) | 2369(1) | 7899(1) | 44(1)         |
| C(2) | 4680(2) | 1980(1) | 10305(1)| 44(1)         |
| C(5) | 8792(2) | 1899(2) | 8124(1) | 50(1)         |
| C(6) | 8748(2) | 2636(2) | 6542(1) | 52(1)         |
| C(11)| 3732(2) | 1883(2) | 11493(1)| 50(1)         |
| C(8) | 5564(2) | 2737(2) | 6312(1) | 58(1)         |
| C(7) | 7398(2) | 2228(2) | 5736(1) | 61(1)         |
| C(13)| 4487(2) | 1514(2) | 12972(1)| 64(1)         |
| C(12)| 1806(2) | 2175(2) | 11428(2)| 69(1)         |
| C(15)| 8273(2) | 4342(2) | 6431(2) | 74(1)         |
| C(14)| 10536(2)| 2058(2) | 5895(2) | 76(1)         |
| C(10)| 2965(2) | 5043(2) | 8723(2) | 73(1)         |
| O(1) | 2604(1) | 3748(1) | 8429(1) | 60(1)         |
| O(2) | 7643(1) | 1320(1) | 11202(1)| 66(1)         |
Table 3. Bond lengths [Å] and angles [°] for 08NV24_0m.

| Bond                  | Length/Angle  |
|-----------------------|---------------|
| C(4)-C(9)             | 1.3415(16)    |
| C(4)-C(3)             | 1.4734(16)    |
| C(4)-C(5)             | 1.4918(16)    |
| C(1)-O(1)             | 1.4307(15)    |
| C(1)-C(9)             | 1.5080(17)    |
| C(1)-C(2)             | 1.5183(16)    |
| C(1)-H(1)             | 0.9800        |
| C(3)-O(2)             | 1.2223(14)    |
| C(3)-C(2)             | 1.4909(16)    |
| C(9)-C(8)             | 1.4879(17)    |
| C(2)-C(11)            | 1.3435(18)    |
| C(5)-C(6)             | 1.5389(17)    |
| C(5)-H(5A)            | 0.9700        |
| C(5)-H(5B)            | 0.9700        |
| C(6)-C(15)            | 1.524(2)      |
| C(6)-C(14)            | 1.5268(19)    |
| C(6)-C(7)             | 1.5404(19)    |
| C(11)-C(13)           | 1.5004(18)    |
| C(11)-C(12)           | 1.5006(19)    |
| C(8)-C(7)             | 1.524(2)      |
| C(8)-H(8A)            | 0.9700        |
| C(8)-H(8B)            | 0.9700        |
| C(7)-H(7A)            | 0.9700        |
| C(7)-H(7B)            | 0.9700        |
| C(13)-H(13A)          | 0.9600        |
| Bond                  | Distance  |
|-----------------------|-----------|
| C(13)-H(13B)         | 0.9600    |
| C(13)-H(13C)         | 0.9600    |
| C(12)-H(12A)         | 0.9600    |
| C(12)-H(12B)         | 0.9600    |
| C(12)-H(12C)         | 0.9600    |
| C(15)-H(15A)         | 0.9600    |
| C(15)-H(15B)         | 0.9600    |
| C(15)-H(15C)         | 0.9600    |
| C(14)-H(14A)         | 0.9600    |
| C(14)-H(14B)         | 0.9600    |
| C(14)-H(14C)         | 0.9600    |
| C(10)-O(1)           | 1.417(2)  |
| C(10)-H(10A)         | 0.9600    |
| C(10)-H(10B)         | 0.9600    |
| C(10)-H(10C)         | 0.9600    |
| C(9)-C(4)-C(3)       | 109.78(11)|
| C(9)-C(4)-C(5)       | 125.11(11)|
| C(3)-C(4)-C(5)       | 125.11(10)|
| O(1)-C(1)-C(9)       | 112.35(10)|
| O(1)-C(1)-C(2)       | 116.54(10)|
| C(9)-C(1)-C(2)       | 103.15(9) |
| O(1)-C(1)-H(1)       | 108.1     |
| C(9)-C(1)-H(1)       | 108.1     |
| C(2)-C(1)-H(1)       | 108.1     |
| O(2)-C(3)-C(4)       | 124.99(11)|
| O(2)-C(3)-C(2)       | 127.94(11)|
C(4)-C(3)-C(2) 107.07(9)
C(4)-C(9)-C(8) 123.24(12)
C(4)-C(9)-C(1) 112.71(10)
C(8)-C(9)-C(1) 124.04(10)
C(11)-C(2)-C(3) 127.07(11)
C(11)-C(2)-C(1) 125.72(11)
C(3)-C(2)-C(1) 107.22(10)
C(4)-C(5)-C(6) 112.14(10)
C(4)-C(5)-H(5A) 109.2
C(6)-C(5)-H(5A) 109.2
C(4)-C(5)-H(5B) 109.2
C(6)-C(5)-H(5B) 109.2
H(5A)-C(5)-H(5B) 107.9
C(15)-C(6)-C(14) 109.12(13)
C(15)-C(6)-C(5) 109.15(12)
C(14)-C(6)-C(5) 109.43(11)
C(15)-C(6)-C(7) 110.18(12)
C(14)-C(6)-C(7) 109.58(12)
C(5)-C(6)-C(7) 109.37(11)
C(2)-C(11)-C(13) 123.42(12)
C(2)-C(11)-C(12) 121.64(12)
C(13)-C(11)-C(12) 114.92(12)
C(9)-C(11)-C(12) 114.92(12)
C(9)-C(8)-C(7) 110.65(10)
C(9)-C(8)-H(8A) 109.5
C(7)-C(8)-H(8A) 109.5
C(9)-C(8)-H(8B) 109.5
C(7)-C(8)-H(8B) 109.5
H(8A)-C(8)-H(8B) 108.1
C(8)-C(7)-C(6) 113.82(11)
C(8)-C(7)-H(7A) 108.8
C(6)-C(7)-H(7A) 108.8
C(8)-C(7)-H(7B) 108.8
C(6)-C(7)-H(7B) 108.8
H(7A)-C(7)-H(7B) 107.7
C(11)-C(13)-H(13A) 109.5
C(11)-C(13)-H(13B) 109.5
H(13A)-C(13)-H(13B) 109.5
C(11)-C(13)-H(13C) 109.5
H(13A)-C(13)-H(13C) 109.5
H(13B)-C(13)-H(13C) 109.5
C(11)-C(12)-H(12A) 109.5
C(11)-C(12)-H(12B) 109.5
H(12A)-C(12)-H(12B) 109.5
C(11)-C(12)-H(12C) 109.5
H(12A)-C(12)-H(12C) 109.5
H(12B)-C(12)-H(12C) 109.5
C(6)-C(15)-H(15A) 109.5
C(6)-C(15)-H(15B) 109.5
H(15A)-C(15)-H(15B) 109.5
C(6)-C(15)-H(15C) 109.5
H(15A)-C(15)-H(15C) 109.5
H(15B)-C(15)-H(15C) 109.5
C(6)-C(14)-H(14A) 109.5
C(6)-C(14)-H(14B) 109.5
H(14A)-C(14)-H(14B)  109.5  
C(6)-C(14)-H(14C)  109.5  
H(14A)-C(14)-H(14C)  109.5  
H(14B)-C(14)-H(14C)  109.5  
O(1)-C(10)-H(10A)  109.5  
O(1)-C(10)-H(10B)  109.5  
H(10A)-C(10)-H(10B)  109.5  
O(1)-C(10)-H(10C)  109.5  
H(10A)-C(10)-H(10C)  109.5  
H(10B)-C(10)-H(10C)  109.5  
C(10)-O(1)-C(1)  114.56(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å² x 10³) for 08NV24_0m. The anisotropic displacement factor exponent takes the form: -2\pi² \[ h^2 a^* U_{11} + ... + 2 h k a^* b^* U_{12} \]

|       | U¹¹  | U²²  | U³³  | U²³  | U¹³  | U¹²  |
|-------|------|------|------|------|------|------|
| C(4)  | 38(1)| 44(1)| 42(1)| -6(1)| -4(1)| -6(1)|
| C(1)  | 40(1)| 52(1)| 46(1)|-10(1)| -5(1)| -11(1)|
| C(3)  | 42(1)| 44(1)| 42(1)|-5(1)| -5(1)| -5(1)|
| C(9)  | 42(1)| 48(1)| 41(1)|-8(1)| -5(1)| -10(1)|
| C(2)  | 42(1)| 46(1)| 42(1)|-9(1)| -3(1)| -10(1)|
| C(5)  | 39(1)| 59(1)| 49(1)|-6(1)| -3(1)| -9(1)|
C(6)  47(1)  61(1)  48(1)  -6(1)  2(1)  -17(1)
C(11)  49(1)  53(1)  48(1)  -14(1)  3(1)  -15(1)
C(8)  55(1)  80(1)  41(1)  -6(1)  -8(1)  -23(1)
C(7)  62(1)  83(1)  43(1)  -13(1)  2(1)  -27(1)
C(13)  69(1)  78(1)  44(1)  -12(1)  3(1)  -20(1)
C(12)  53(1)  92(1)  66(1)  -22(1)  10(1)  -27(1)
C(15)  72(1)  63(1)  85(1)  2(1)  -4(1)  -26(1)
C(14)  56(1)  103(1)  66(1)  -16(1)  14(1)  -23(1)
C(10)  60(1)  55(1)  90(1)  -10(1)  -10(1)  2(1)
O(1)  39(1)  67(1)  66(1)  -10(1)  -13(1)  -4(1)
O(2)  49(1)  89(1)  46(1)  1(1)  -13(1)  -7(1)
Table 5. Hydrogen coordinates \((x \times 10^4)\) and isotropic displacement parameters \((\text{Å}^2 \times 10^3)\) for 08NV24_0m.

|     | x   | y   | z   | U(eq) |
|-----|-----|-----|-----|-------|
| H(1) | 3580 | 1542 | 8603 | 55    |
| H(5A) | 9476 | 845  | 8229 | 61    |
| H(5B) | 9353 | 2391 | 8678 | 61    |
| H(8A) | 5068 | 3818 | 6008 | 70    |
| H(8B) | 4847 | 2240 | 5928 | 70    |
| H(7A) | 7390 | 2685 | 4738 | 74    |
| H(7B) | 7749 | 1142 | 5788 | 74    |
| H(13A) | 5714 | 1365 | 12917 | 97 |
| H(13B) | 4276 | 610  | 13474 | 97 |
| H(13C) | 3954 | 2333 | 13472 | 97 |
| H(12A) | 1226 | 3171 | 11613 | 103 |
| H(12B) | 1479 | 1446 | 12131 | 103 |
| H(12C) | 1481 | 2093 | 10496 | 103 |
| H(15A) | 7184 | 4703 | 6893 | 111 |
| H(15B) | 8177 | 4812 | 5444 | 111 |
| H(15C) | 9158 | 4587 | 6887 | 111 |
| H(14A) | 11373 | 2325 | 6390 | 113 |
| H(14B) | 10505 | 2506 | 4904 | 113 |
| H(14C) | 10855 | 980  | 5984 | 113 |
| H(10A) | 3019 | 4986 | 9737 | 109 |
| H(10B) | 2063 | 5933 | 8321 | 109 |
| H(10C) | 4057 | 5087 | 8311 | 109 |
|--------|------|------|------|-----|

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