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# Supporting Information

for

# Ring-closing metathesis of prochiral oxaenediynes to racemic 4-alkenyl-2-alkynyl-3,6-dihydro-2*H*-pyrans

Viola Kolaříková, Markéta Rybáčková, Martin Svoboda and Jaroslav Kvíčala

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# Synthesis of compounds 2, 4, and 7–11, copies of $^{1}$H and $^{13}$C NMR spectra of compounds 2, 10–12, and 14, and XYZ files of all computed structures

# Table of contents

## 1. Experimental details of synthesis of compounds 2, 4, and 7–11

Synthesis of starting oxaenediynes

### Hepta-1,6-diyn-4-ol (4a) [1]

A mixture of Mg (6.69 g, 275 mmol) and $HgCl_2$ (122 mg, 449 mmol) in diethyl ether (130 mL) under an inert atmosphere was cooled to 0 °C and an 80% solution of propargyl bromide in toluene (30 mL, 269 mmol) was added dropwise over 1 h. The mixture was stirred at 0 °C for 1 h, then ethyl formate (7.5 mL, 8.18 g, 92.8 mmol) was added, the mixture was stirred for 2 h at 0 °C, and then quenched with ice water (130 mL) and HCl (1.2 M solution, 260 mL). The organic layer was extracted with $Et_2O$ (3 × 130 mL), the combined organic layers were washed with a saturated $NaHCO_3$ solution (30 mL), and dried over $Na_2SO_4$. Evaporation gave crude alcohol **4a**, which was distilled at reduced pressure to give the desired hepta-1,6-diyn-4-ol (**4a**) as clear oil (9.02 g, 90%, bp 88-91°C at 3.5 kPa). $^1$H NMR: δ 2.09 (t, *J* = 2.7 Hz, 2H, C**H**≡C), 2.22 (d, *J* = 5.4 Hz, 1H, O**H**), 2.44-2.63 (m, 4H, C**H**$_2$), 3.97 (m, 1H, C**H**-$CH_2$).

### 4-(*tert*-Butyldimethylsilyloxy)hepta-1,6-diyne (7a) [1]

*tert*-Butyldimethylsilyl chloride (2.51 g, 16.7 mmol) and imidazole (1.14 g, 16.7 mmol) were added to a solution of hepta-1,6-diyn-4-ol (**4a**, 1.39 g, 12.8 mmol) in DCM (23 mL) at 0 °C. The reaction mixture was allowed to warm to rt and stirred for 20 h. After quenching with water (23 mL), extraction with DCM (3 × 23 mL), and drying over anhydr. $MgSO_4$, the solvent was evaporated and the crude product was purified by column chromatography (eluent hexane/EtOAc 40:1, Rf = 0.48) to give the desired silyl ether **7a** as clear oil (2.86 g, quant.). $^1$H NMR [1]: δ 0.12 (s, 6H, Si-C**H**$_3$), 0.91 (s, 9H, C**H**$_3$), 2.00 (t, *J* = 2.6 Hz, 2H, C**H**≡C), 2.44 (ddd, *J* = 16.7 Hz, *J* = 5.9 Hz, *J* = 2.6 Hz, 2H, C**H**$_2$), 2.51 (ddd, *J* = 16.7 Hz, *J* = 5.9 Hz, *J* = 2.6 Hz, 2H, C**H**$_2$), 3.97 (quint, *J* = 5.9 Hz, 1H, C**H**-$CH_2$).

**2-(Hepta-1,6-diyn-4-yloxy)tetrahydro-*2H*-pyran (8a)**

*p*-TsOH·$H_2O$ (69 mg, 0.36 mmol) was added to a solution of hepta-1,6-diyn-4-ol (**4a**, 3.89 g, 36.0 mmol) in dichloromethane (57 mL) at 0 °C. Then, 3,4-dihydro-2*H*-pyran (3.33 g, 39.6 mmol) was slowly added, the mixture was stirred for 5 min at 0 °C, and then for further 55 min at rt. The reaction was quenched with satd. $NaHCO_3$ solution (38 mL), the layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 67 mL). The combined organic layers were dried over anhydr. $MgSO_4$, the solvent was carefully evaporated under reduced pressure, and the crude product was purified by column chromatography (eluent hexane/EtOAc 32:1, Rf =0.21) to give the target pyran **8a** as clear oil (6.58 g, 96%). $^1$H NMR: $\delta$ 1.50-1.91 (m, 6H, C**H**$_2$), 2.02 (dt, *J* = 8.8 Hz, *J* = 2.5 Hz, 2H, C≡C**H**), 2.53 (ddd, *J* = 17 Hz, *J* = 5.8 Hz, *J* = 2.7 Hz, 1H, C-C**H**$_2$), 2.57-2.69 (m, 3H, C-C**H**$_2$), 3.46-3.58 (m, 1H, O-C**H**$_2$), 3.90-4.01 (m, 2H, O-C**H**$_2$ + C**H**-$CH_2$), 4.82 (t, *J* = 3.5 Hz, 1H, O-C**H**-O). $^{13}$C NMR: $\delta$ 19.2 (s, 1C, **C**$H_2$-$CH_2$), 22.9 (s, 1C, **C**$H_2$-C), 24.5 (s, 1C, **C**$H_2$-C), 25.3 (s, 1C, **C**$H_2$-$CH_2$), 30.5 (s, 1C, **C**$H_2$-$CH_2$), 62.3 (s, 1C, O-**C**$H_2$), 70.1 (s, 1C, **C**≡C), 70.3 (s, 1C, **C**≡CH), 72.9 (s, 1C, **C**H-O), 80.3 (s, 1C, C≡**C**H), 80.5 (s, 1C, C≡**C**H), 97.9 (s, 1C, O-**C**H-O). MS (EI$^+$), *m/z* (%): 153.1 $[M\text{-}C_3H_3]^+$ (30), 101.1 $[C_5H_9O_2]^+$ (40), 91.0 $[C_7H_7]^+$ (95), 85.7 $[C_6H_{13}]^+$ (100), 85.0 $[C_5H_9O]$ (95), 67.0 $[C_5H_7]^+$ (88), 65.0 $[C_5H_5]^+$ (95), 56.1 $[C_3H_4O]^+$ (74). HRMS (EI$^+$): calcd. for $C_{12}H_{15}O_2$ ($[M-H]^+$) 191.1072, found 191.1077.

***tert*-Butyldimethyl(nona-2,7-diyn-5-yloxy)silane (7b)**

Butyllithium (6.0 mL, 14.4 mmol, 2.4 M solution in hexanes) was added dropwise at −78 °C to a solution of TBS ether **7a** (800 mg, 3.60 mmol) in dry THF (15 mL). The mixture was stirred at −78 °C for 1 h, then methyl iodide (2.04 g, 14.4 mmol) was

added, the mixture was allowed to warm to rt, and stirred overnight. After quenching with saturated $NH_4Cl$ solution (48 mL), the aqueous layer was extracted with diethyl ether (3 × 40 mL), and dried over anhydr. $MgSO_4$. Evaporation of the solvents and subsequent column chromatography (eluent hexane/EtOAc 60:1, Rf = 0.38) gave TBS ether **7b** as clear oil (850 mg, 94%). $^1$H NMR: $\delta$ 0.11 (s, 6H, Si-C**H**$_3$), 0.91 (s, 9H, C**H**$_3$), 1.78 (t, *J* = 2.4 Hz, 6H, C≡C-C**H**$_3$), 2.31 (dm, *J* = 16.4 Hz, 2H, C**H**$_2$), 2.41 (dm, *J* = 16.4 Hz, 2H, C**H**$_2$), 3.86 (quint, *J* = 6.0 Hz, 1H, C**H**-CH$_2$). $^{13}$C NMR: $\delta$ -4.7 (s, 2C, Si-**C**H$_3$), 3.5 (s, 2C, C≡C-**C**H$_3$), 18.2 (s, 1C, Si-**C**), 25.8 (s, 3C, Si-C-**C**H$_3$), 27.2 (s, 2C, **C**H$_2$), 71.0 (s, 1C, **C**H), 76.2 (s, 1C, **C**≡C-CH$_3$), 77.3 (s, 1C, C≡**C**-CH$_3$). MS (ESI$^+$), *m/z* (%): 273.1 [M+Na]$^+$ (40). HRMS (ESI): calcd. for $C_{15}H_{27}OSi$ ([M+H]$^+$) 251.1826, found 251.1827. HRMS (ESI): calcd. for $C_{15}H_{26}ONaSi$ ([M+Na]$^+$) 273.1645, found 273.1645.

**_tert_-Butyldimethyl(undeca-3,8-diyn-6-yloxy)silane (7c)**

Butyllithium (3.75 mL, 9.00 mmol, 2.4 M solution in hexanes) was added dropwise at −78 °C to a solution of TBS ether **7a** (667 mg, 3.00 mmol) in dry THF (13 mL). The mixture was stirred at −78 °C for 1 h, then ethyl iodide (2.11 g, 13.5 mmol) was added, the mixture was allowed to warm to rt, and then refluxed for 6 h. After quenching with saturated $NH_4Cl$ solution (25 mL), the aqueous layer was extracted with diethyl ether (3 × 25 mL), and dried over anhydr. $MgSO_4$. Evaporation of the solvents and subsequent column chromatography (eluent hexane/$CH_2Cl_2$ 7:1, Rf = 0.23) gave TBS ether **7c** as clear oil (417 mg, 50%). $^1$H NMR: $\delta$ 0.11 (s, 6H, Si-C**H**$_3$), 0.91 (s, 9H, C**H**$_3$), 1.12 (t, *J* = 7.5 Hz, 6H, CH$_2$-C**H**$_3$), 2.16 (qt, *J* = 7.5 Hz, *J* = 2.3 Hz, 4H, C**H**$_2$-CH$_3$), 2.33 (ddt, *J* = 16.3 Hz, *J* = 6.1 Hz, *J* = 2.3 Hz, 2H, CH-C**H**$_2$), 2.43 (ddt, *J* = 16.3 Hz, *J* = 6.1 Hz, *J* = 2.3 Hz, 2H, CH-C**H**$_2$), 3.85 (quint, *J* = 6.1 Hz, 1H,

C**H**-$CH_2$). $^{13}$C NMR: δ -4.6 (s, 2C, Si-**C**$H_3$), 12.5 (s, 2C, C**H**$_2$-$CH_3$), 14.2 (s, 2C, $CH_2$**C**$H_3$), 18.1 (s, 1C, Si-**C**), 25.8 (s, 3C, Si-C-**C**$H_3$), 27.3 (s, 2C, CH-**C**$H_2$), 71.0 (s, 1C, **C**H), 76.4 (s, 1C, **C**≡C-$CH_2$-$CH_3$), 83.3 (s, 1C, C≡**C**-$CH_2$-$CH_3$). MS ($CI^+$), *m/z* (%): 263.2 $[M\text{-}CH_3]^+$ (51), 221.1 $[M\text{-}C_4H_9]^+$ (100), 211.1 $[M\text{-}C_5H_7]^+$ (98), 147.1 $[M\text{-}C_6H_{15}OSi]^+$ (52), 73.0 $[C_4H_9O]^+$ (47). HRMS ($CI^+$): calcd. for $C_{17}H_{31}OSi$ ($[M+H]^+$) 279.2144, found 279.2140.

**2-(Nona-2,7-diyn-5-yloxy)tetrahydro-2*H*-pyran (8b)**

Butyllithium (27 mL, 60 mmol, 2.25 M solution in hexanes) was added dropwise at −78 °C to a solution of THP ether **8a** (2.88 g, 15.0 mmol) in dry THF (60 mL). The mixture was stirred at −78 °C for 1 h, then methyl iodide (8.52 g, 60.0 mmol) was added, the mixture was allowed to warm to rt, and stirred for 20 h. After quenching with saturated $NH_4Cl$ solution (120 mL), the aqueous layer was extracted with diethyl ether (3 × 100 mL) and dried over anhydr. $MgSO_4$. Evaporation of the solvents and subsequent column chromatography (eluent hexane/EtOAc 97:3, Rf = 0.22) gave THP ether **8b** as clear oil (2.88 g, 87%). $^1$H NMR: δ 1.47-1.90 (m, 12H, 3 × C**H**$_2$ + 2 × C**H**$_3$), 2.35-2.59 (m, 4H, C-C**H**$_2$), 3.46-3.56 (m, 1H, O-C**H**$_2$), 3.80-3.89 (m, 1H, C**H**-$CH_2$), 3.92-4.02 (m, 1H, O-C**H**$_2$), 4.82 (t, *J* = 3.5 Hz, 1H, O-C**H**-O). $^{13}$C NMR: δ 3.49 (s, 1C, **C**$H_3$), 3.53 (s, 1C, **C**$H_3$), 19.4 (s, 1C, **C**$H_2$-$CH_2$), 23.2 (s, 1C, **C**$H_2$-C), 25.0 (s, 1C, **C**$H_2$-C), 25.4 (s, 1C, **C**$H_2$-$CH_2$), 30.7 (s, 1C, **C**$H_2$-$CH_2$), 62.2 (s, 1C, O-**C**$H_2$), 73.9 (s, 1C, $CH_2$-**C**H-O), 75.3 (s, 1C, **C**≡C), 75.5 (s, 1C, **C**≡C), 77.2 (s, 1C, C≡**C**), 77.3 (s, 1C, C≡**C**), 97.7 (s, 1C, O-**C**H-O). MS ($CI^+$), *m/z* (%): 119.1 $[M\text{-}C_5H_9O_2]^+$ (52), 85.1 $[C_5H_9O]^+$ (100), 83.0 $[C_5H_7O]^+$ (44). HRMS ($CI^+$): calcd. for $C_{14}H_{21}O_2$ ($[M+H]^+$) 221.1542, found 221.1540.

**2-(Undeca-3,8-diyn-6-yloxy)tetrahydro-2*H*-pyran (8c)**

Butyllithium (6.0 mL, 14.4 mmol, 2.4 M solution in hexanes) was added dropwise at −78 °C to a solution of THP ether **8a** (1.00 g, 5.20 mmol) in dry THF (20 mL). The mixture was stirred at −78 °C for 1 h, then ethyl iodide (3.24 g, 20.8 mmol) was added, the mixture was allowed to warm to rt, and then refluxed for 6 h. After quenching with saturated $NH_4Cl$ solution (48 mL), the aqueous layer was extracted with diethyl ether (3 × 40 mL) and dried over anhydr. $MgSO_4$. Evaporation of the solvents and subsequent column chromatography (eluent hexane/EtOAc 25:1, Rf = 0.27) gave THP ether **8c** as clear oil (660 mg, 51%). $^1$H NMR: δ 1.12 (t, *J* = 7.5 Hz, 6H, C**H**$_3$), 1.48-1.91 (m, 6H, CH-C**H**$_2$-C**H**$_2$-C**H**$_2$), 2.11-2.21 (m, 4H, C**H**$_2$-CH$_3$), 2.42 (ddt, *J* = 16.6 Hz, *J* = 6.2 Hz, *J* = 2.5 Hz, 1H, C-C**H**$_2$-CH), 2.48-2.62 (m, 3H, C-C**H**$_2$-CH), 3.45-3.55 (m, 1H, O-C**H**$_2$), 3.86 (m, 1H, C**H**-CH$_2$), 3.92-4.05 (m, 1H, O-C**H**$_2$), 4.86 (t, *J* = 3.6 Hz, 1H, O-C**H**-O). $^{13}$C NMR: δ 12.4 (s, 1C, **C**H$_2$-CH$_3$), 12.5 (s, 1C, **C**H$_2$-CH$_3$), 14.2 (s, 1C, **C**H$_3$), 14.2 (s, 1C, **C**H$_3$), 19.4 (s, 1 C, **C**H$_2$-CH$_2$), 23.5 (s, 1C, C-**C**H$_2$-CH), 25.2 (s, 1C, C-**C**H$_2$-CH), 25.5 (s, 1C, **C**H$_2$-CH$_2$), 30.7 (s, 1C, **C**H$_2$-CH$_2$), 62.2 (s, 1C, O-**C**H$_2$), 74.1 (s, 1C, C-CH$_2$-**C**H), 75.7 (s, 1C, **C**≡C-CH$_2$-CH$_3$), 75.9 (s, 1C, **C**≡C-CH$_2$-CH$_3$), 83.3 (s, 1C, C≡**C**-CH$_2$-CH$_3$), 83.5 (s, 1C, C≡**C**-CH$_2$-CH$_3$), 97.8 (s, 1C, O-**C**H-O). MS (ESI$^+$), *m/z* (%): 272.2 [M+Na]$^+$ (100). HRMS (ESI$^+$): calcd. for $C_{16}H_{24}O_2Na$ ([M+Na]$^+$) 271.1669, found 271.1669.

**2-(Trideca-4,9-diyn-7-yloxy)tetrahydro-2*H*-pyran (8d)**

Butyllithium (16.8 mL, 42.0 mmol, 2.5 M solution in hexanes) was added dropwise at −78 °C to a solution of THP ether **8a** (2.31 g, 12.0 mmol) in dry THF (48 mL). The mixture was stirred at −78 °C for 1 h, then propyl iodide (10.2 g, 60.0 mmol) was added, the mixture was allowed to warm to rt, and then refluxed for 24 h. After

quenching with saturated $NH_4Cl$ solution (90 mL), the aqueous layer was extracted with diethyl ether (3 × 75 mL) and dried over anhydr. $MgSO_4$. Filtration, careful evaporation of solvents, and subsequent column chromatography (eluent hexane/EtOAc 30:1, Rf = 0.24) gave THP ether **8d** as clear oil (2.31 g, 70%). $^1$H NMR: δ 0.97 (t, *J* = 7.4 Hz, 6H, C**H**$_3$), 1.44-1.95 (m, 10H, C**H**$_2$-$CH_3$ + CH-C**H**$_2$-C**H**$_2$-C**H**$_2$), 2.08-2.18 (m, 4H, C**H**$_2$-$CH_2$-$CH_3$), 2.44 (ddt, *J* = 16.7 Hz, *J* = 6.2 Hz, *J* = 2.4 Hz, 1H, C-C**H**$_2$-CH), 2.49-2.62 (m, 3H, C-C**H**$_2$-CH), 3.46-3.56 (m, 1H, O-C**H**$_2$), 3.81-3.92 (m, 1H, C**H**-$CH_2$), 3.93-4.04 (m, 1H, O-C**H**$_2$), 4.86 (t, *J* = 3.5 Hz, 1H, O-C**H**-O). $^{13}$C NMR: δ 13.5 (s, 1C, $CH_2$-**C**$H_3$), 13.5 (s, 1C, $CH_2$-**C**$H_3$), 19.4 (s, 1C, **C**$H_2$-$CH_2$), 20.8 (s, 1C, **C**$H_2$-$CH_2$-$CH_3$), 20.8 (s, 1C, **C**$H_2$-$CH_2$-$CH_3$), 22.4 (s, 1C, **C**$H_2$-$CH_3$), 22.4 (s, 1C, **C**$H_2$-$CH_3$), 23.4 (s, 1C, C-**C**$H_2$-CH), 25.2 (s, 1C, C-**C**$H_2$-CH), 25.5 (s, 1C, **C**$H_2$-$CH_2$), 30.7 (s, 1C, **C**$H_2$-$CH_2$), 62.2 (s, 1C, O-**C**$H_2$), 74.2 (s, 1C, C-$CH_2$-**C**H), 76.5 (s, 1C, **C**≡C-$CH_2$-$CH_2$), 77.2 (s, 1C, **C**≡C-$CH_2$-$CH_2$), 81.8 (s, 1C, C≡**C**-$CH_2$-$CH_2$), 81.9 (s, 1C, C≡**C**-$CH_2$-$CH_2$), 97.8 (s, 1C, O-**C**H-O). MS (ESI$^+$), *m/z* (%): 299.3 $[M+Na]^+$ (100). HRMS (ESI$^+$): calcd. for $C_{18}H_{28}O_2Na$ ($[M+Na]^+$) 299.1982, found 299.1982.

**Nona-2,7-diyn-5-ol (4b)**

From TBS ether **7b**: tetrabutylammonium fluoride (1.18 g, 3.39 mmol, 75% solution in water) in THF (5 mL) was added to TBS ether **7b** (850 mg, 3.39 mmol) in THF (8 mL) and the mixture was stirred for 46 h. Evaporation of the solvents and column chromatography (eluent hexane/EtOAc 20:3, Rf = 0.26) gave alcohol **4b** as clear oil (351 mg, 76%).

From THP ether **8b**: a mixture of THP ether **8b** (2.87 g, 13.0 mmol) and pyridinium *p*-toluenesulfonate (327 mg, 1.30 mmol) in methanol (60 mL) was stirred for 3 days. Evaporation of the solvents and column chromatography (eluent hexane/EtOAc 20:3,

Rf = 0.26) gave alcohol **4b** as clear oil (1.33 g, 75%). $^{1}$H NMR: δ 1.81 (t, *J* = 2.4 Hz, 6H, C-C**H**$_3$), 2.35-2.54 (m, 4H, C**H**$_2$), 3.82 (quint, *J* = 5.9 Hz, 1H, C**H**-CH$_2$). $^{13}$C NMR: δ 3.6 (s, 2C, **C**H$_3$), 26.4 (s, 2C, **C**H$_2$), 69.0 (s, 1C, **C**H), 74.7 (s, 2C, CH$_2$-**C**≡C), 78.6 (s, 2C, C≡**C**-CH$_3$). MS (ESI$^+$), *m/z* (%): 159.1 [M+Na]$^+$ (27). HRMS (ESI$^+$): calcd. for $C_9H_{12}ONa$ ([M+Na]$^+$) 159.0781, found 159.0782.

**Undeca-3,8-diyn-6-ol (4c)**

From TBS ether **7c**: tetrabutylammonium fluoride (272 mg, 0.779 mmol, 75% solution in water) in THF (2 mL) was added to TBS ether **7c** (217 mg, 0.779 mmol) in THF (1 mL) and the mixture was stirred for 5 days. Evaporation of the solvents and column chromatography (eluent hexane/EtOAc 5:1, Rf = 0.48) gave alcohol **4c** as clear oil (100 mg, 78%).

From THP ether **8c**: a mixture of THP ether **8c** (639 mg, 2.57 mmol) and pyridinium *p*-toluenesulfonate (65 mg, 0.26 mmol) in methanol (13 mL) was stirred for 4 days. Evaporation of solvents and column chromatography (eluent hexane/EtOAc 5:1, Rf = 0.48) gave alcohol **8c** as clear oil (272 mg, 64%). $^{1}$H NMR: δ 1.14 (t, *J* = 7.5 Hz, 6H, CH$_2$-C**H**$_3$), 2.19 (qt, *J* = 7.5 Hz, *J* = 2.4 Hz, 4H, C**H**$_2$-CH$_3$), 2.22-2.26 (bs, 1H, OH), 2.37-2.55 (m, 4H, CH-C**H**$_2$), 3.77-3.88 (m, 1H, C**H**-CH$_2$). $^{13}$C NMR: δ 12.4 (s, 2C, **C**H$_2$-CH$_3$), 14.2 (s, 2C, **C**H$_3$), 26.4 (s, 2C, CH-**C**H$_2$), 69.0 (s, 1C, **C**H), 74.9 (s, 1C, **C**≡C-CH$_2$-CH$_3$), 84.7 (s, 1C, C≡**C**-CH$_2$-CH$_3$). MS (EI$^+$), *m/z* (%): 135.1 [M-$C_2H_5$]$^+$ (35), 97.1 [M-$C_5H_7$]$^+$ (37), 79.1 [M-$C_5H_9O$]$^+$ (37), 67.0 [M-$C_6H_9O$]$^+$(100), 53.0 [$C_4H_5$]$^+$(53). HRMS (EI$^+$): calcd. for $C_{11}H_{15}O$ ([M-H]$^+$) 163.1123, found 163.1125.

**Trideca-4,9-diyn-7-ol (4d)**

A mixture of THP ether **8d** (2.31 g, 8.35 mmol) and pyridinium *p*-toluenesulfonate (210 mg, 0.835 mmol) in methanol (41 mL) was stirred for 3 days. Evaporation of the solvents and column chromatography (eluent hexane/EtOAc 7:1, Rf = 0.46) gave alcohol **4d** as clear oil (851 mg, 53%). $^{1}$H NMR: δ 0.98 (t, *J* = 7.4 Hz, 6H, $CH_2$-C**H**$_3$), 1.47-1.57 (m, 4H, C**H**$_2$-$CH_3$), 2.15 (tt, *J* = 7.0 Hz, *J* = 2.4 Hz, 4H, C**H**$_2$-$CH_2$-$CH_3$), 2.23 (d, *J* = 5.3 Hz, 1H, OH), 2.40-2.53 (m, 4H, CH-C**H**$_2$), 3.78-3.87 (m, 1H, C**H**-$CH_2$). $^{13}$C NMR: δ 13.5 (s, 2C, $CH_2$-**C**$H_3$), 20.8 (s, 2C, **C**$H_2$-$CH_2$-$CH_3$), 22.4 (s, 2C, $CH_2$-**C**$H_2$-$CH_3$), 26.4 (s, 2C, CH-**C**$H_2$), 69.1 (s, 1C, **C**H), 75.7 (s, 1C, **C**≡C-$CH_2$-$CH_2$), 83.2(s, 1C, C≡**C**-$CH_2$-$CH_2$). MS (EI$^+$), *m/z* (%): 163.1 [M-$C_2H_5$]$^+$ (45), 145.1 [M-$C_2H_7O$]$^+$ (55), 93.1 [$C_7H_9$]$^+$ (57), 91.0 [$C_7H_7$]$^+$ (52), 79.1 [$C_6H_7$]$^+$ (51), 77.0 [$C_6H_5$]$^+$ (48), 67.0 [$C_5H_7$]$^+$(100), 53.0 [$C_4H_5$]$^+$(63). HRMS (EI$^+$): calcd. for $C_{13}H_{19}O$ ([M-H]$^+$) 191.1436, found 191.1432.

**4-(Allyloxy)hepta-1,6-diyne (2a)**

Sodium hydride (1.12 g, 60% in oil, 28.0 mmol) was added to a mixture of hepta-1,6-diyn-4-ol (**4a**, 1.84 g, 16.0 mmol), allyl bromide (3.39 g, 28.0 mmol) and tetraethylammonium iodide (477 mg, 1.86 mmol) in dry THF (40 mL) at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C for 10 min, then allowed to warm to rt, and stirred for 2 days. After the addition of satd. $NH_4Cl$ solution (20 mL), the mixture was extracted with $Et_2O$ (3 × 30 mL) and dried over anhydr. $MgSO_4$. Filtration and evaporation gave the crude product, which was purified by column chromatography (hexane/EtOAc 25:1, Rf = 0.5) to give 4-(allyloxy)hepta-1,6-diyne (**2a**) as pale yellow oil (2.22 g, 94%). $^{1}$H NMR: δ 2.00 (t, *J* = 2.7 Hz, 2H, C≡C**H**), 2.44-2.57 (m, 4H, CH-C**H**$_2$), 3.62 (quint, *J* = 5.7 Hz, 1H, C**H**), 4.07 (dm, *J* = 6.0 Hz, 2H, O-

C**H**$_2$), 5.15 (d, *J* = 10.3 Hz, 1H, CH=C**H**$_2$), 5.27 (dm, *J* = 17.2 Hz, 1H, CH=C**H**$_2$), 5.83-5.94 (m, 1H, C**H**=CH$_2$). $^{13}$C NMR: δ 23.2 (s, 2C, C-**C**H$_2$), 70.3 (s, 1C, O-**C**H$_2$), 70.5 (s, 2C, **C**≡C), 75.0 (s, 1C, **C**H-CH$_2$), 80.2 (s, 2C, C≡**C**H), 117.2 (s, 1C, CH=**C**H$_2$), 134.4 (s, 1C, **C**H=CH$_2$). MS (ESI$^-$), *m/z* (%): 147 [M-H]$^-$ (20), 127 [M-H$_2$-H$_2$O]$^-$ (26), 109 [M-C$_3$H$_3$]$^-$ (34), 89 [M-C$_3$H$_7$O]$^-$ (36), 87 [M-C$_3$H$_9$O]$^-$ (59), 75 [M-C$_4$H$_{10}$O]$^-$ (100), 67 [M-C$_5$H$_5$O]$^-$ (96). HRMS (ESI$^-$): calcd. for C$_{10}$H$_{11}$O ([M-H]$^-$) 147.0815, found 147.0812.

**5-(Allyloxy)nona-2,7-diyne (2b)**

Sodium hydride (131 mg, 60% in oil, 3.27 mmol) was added to a mixture of nona-2,7-diyn-5-ol (**4b**, 254 mg, 1.87 mmol), allyl bromide (396 g, 3.27 mmol), and tetraethyl-ammonium iodide (60 mg, 0.22 mmol) in dry Et$_2$O (20 mL) at 0 °C. The mixture was stirred at 0 °C for 10 min, then allowed to warm to rt and stirred for 3 days. After the addition of saturated NH$_4$Cl solution (7 mL), the mixture was extracted with Et$_2$O (2 × 17 mL), washed with brine (17 mL), and dried over anhydr. MgSO$_4$. Filtration and evaporation gave the crude product, which was purified by column chromatography (eluent hexane/EtOAc 50:1, Rf = 0.23) to give 5-(allyloxy)nona-2,7-diyne (**2b**) as clear oil (314 mg, 95%). $^1$H NMR: δ 1.78 (t, *J* = 2.5 Hz, 6H, C**H**$_3$), 2.37-2.56 (m, 4H, C-C**H**$_2$), 3.54 (quint, *J* = 5.7 Hz, 1H, C**H**), 4.09 (dt, *J* = 5.7 Hz, *J* = 1.4 Hz, 2H, C**H**$_2$), 5.17 (ddm, *J* = 10.4 Hz, *J* = 1.4 Hz, 1H, CH=C**H**$_2$), 5.29 (dm, *J* = 17.2 Hz, 1H, CH=C**H**$_2$), 5.85-6.00 (m, 1H, C**H**=CH$_2$). $^{13}$C NMR: δ 3.6 (s, 2C, **C**H$_3$), 23.7 (s, 2C, C-**C**H$_2$), 70.6 (s, 1C, O-**C**H$_2$), 75.2 (s, 1C, **C**H), 76.2 (s, 1C, CH$_2$-**C**≡C), 77.5 (s, 1C, C≡**C**-CH$_3$), 117.1 (s, 1C, CH=**C**H$_2$), 134.9 (s, 1C, **C**H=CH$_2$). MS (ESI$^+$), *m/z* (%): 199.1 [M+Na]$^+$ (100). HRMS (ESI$^+$): calcd. for C$_{12}$H$_{17}$O ([M+H]$^+$) 177.1274, found 177.1275. HRMS (ESI$^+$): calcd. for C$_{12}$H$_{16}$ONa ([M+Na]$^+$) 199.1093, found 199.1094.

**6-(Allyloxy)undeca-3,8-diyne (2c)**

Sodium hydride (116 mg, 60% in oil, 2.90 mmol) was added to a mixture of undeca-3,8-diyn-6-ol (**4c**, 272 mg, 1.66 mmol), allyl bromide (351 mg, 2.90 mmol), and tetraethylammonium iodide (53 mg, 0.19 mmol) in dry THF (7 mL) at 0 °C. The mixture was stirred at 0 °C for 10 min, then allowed to warm to rt and stirred for 4 days. After the addition of saturated $NH_4Cl$ solution (7 mL), the mixture was extracted with $Et_2O$ (2 × 16 mL) and dried over anhydr. $MgSO_4$. Filtration and careful evaporation gave the crude product, which was purified by column chromatography (eluent hexane/EtOAc 50:1, Rf = 0.25) to give 6-(allyloxy)undeca-3,8-diyne (**2c**) as clear oil (303 mg, 89%). $^1$H NMR: $\delta$ 1.13 (t, *J* = 7.5 Hz, 6H, C**H**$_3$), 2.18 (qt, *J* = 7.5 Hz, *J* = 2.4 Hz, 4H, C**H**$_2$-$CH_3$), 2.38-2.57 (m, 4H, CH-C**H**$_2$), 3.56 (quint, *J* = 5.8 Hz, 1H, C**H**), 4.12 (dm, *J* = 5.6 Hz, 2H, O-C**H**$_2$), 5.18 (dm, *J* = 10.4 Hz,1H, CH=C**H**$_2$), 5.31 (dm, *J* = 17.2 Hz, 1H, CH=C**H**$_2$), 5.86-6.02 (m, 1H, C**H**=$CH_2$). $^{13}$C NMR: $\delta$ 12.5 (s, 2C, **C**H$_2$-$CH_3$), 14.2 (s, 2C, **C**H$_3$), 23.9 (s, 2C, CH-**C**H$_2$), 70.7 (s, 1C, O-**C**H$_2$), 75.6 (s, 1C, **C**≡C-$CH_2$-$CH_3$), 76.4 (s, 1C, **C**H), 83.5 (s, 1C, C≡**C**-$CH_2$-$CH_3$), 117.0 (s, 1C, CH=**C**H$_2$), 135.0 (s, 1C, **C**H=$CH_2$). MS (EI$^+$), *m/z* (%): 137.1 [M-$C_5H_7$]$^+$ (97), 95.0 [$C_7H_{11}$]$^+$ (72), 91.0 [$C_7H_7$]$^+$ (84), 79.0 [$C_6H_7$]$^+$ (85), 67.0 [$C_5H_7$]$^+$ (100), 57.0 [$C_3H_5O$]$^+$ (95). HRMS (EI$^+$): calcd. for $C_{14}H_{19}O$ ([M-H]$^+$) 203.1436, found 203.1432.

**7-(Allyloxy)trideca-4,9-diyne (2d)**

Sodium hydride (313 mg, 60% in oil, 7.83 mmol) was added to a mixture of trideca-4,9-diyn-7-ol (**4d**, 851 mg, 4.47 mmol), allyl bromide (947 mg, 7.83 mmol), and tetraethylammonium iodide (144 mg, 0.519 mmol) in dry $Et_2O$ (19 mL) at 0 °C. The mixture was stirred at 0 °C for 10 min, then allowed to warm to rt and stirred for 2 days. After the addition of saturated $NH_4Cl$ solution (19 mL), the mixture was

extracted with $Et_2O$ (3 × 29 mL) and dried over anhydr. $MgSO_4$. Filtration and evaporation gave the crude product, which was purified by column chromatography (eluent hexane/EtOAc 50:1, Rf = 0.35) to give 7-(allyloxy)trideca-4,9-diyne (**2d**) as clear oil (927 mg, 89%). $^1$H NMR: $\delta$ 0.98 (t, *J* = 7.5 Hz, 6H, C**H**$_3$), 1.52 (m, 4H, C**H**$_2$-$CH_3$), 2.14 (tt, *J* = 7.0 Hz, *J* = 2.4 Hz, 4H, C**H**$_2$-$CH_2$-$CH_3$), 2.43-2.56 (m, 4H, CH-C**H**$_2$), 3.57 (quint, *J* = 5.8 Hz, 1H, C**H**), 4.12 (dt, *J* = 5.6 Hz, *J* =1.4 Hz, 2H, O-C**H**$_2$), 5.18 (dm, *J* = 10.4 Hz,1H, CH=C**H**$_2$), 5.31 (dm, *J* = 17.3 Hz, 1H, CH=C**H**$_2$), 5.88-5.99 (m, 1H, C**H**=$CH_2$). $^{13}$C NMR: $\delta$ 13.5 (s, 2C, **C**$H_3$), 20.8 (s, 2C, **C**$H_2$-$CH_2$-$CH_3$), 22.4 (s, 2C, $CH_2$-**C**$H_2$-$CH_3$), 23.9 (s, 2C, CH-**C**$H_2$), 70.7 (s, 1C, O-**C**$H_2$), 76.4 (s, 1C, **C**≡C-$CH_2$-$CH_2$), 76.5 (s, 1C, **C**H), 82.0 (s, 1C, C≡**C**-$CH_2$-$CH_2$), 117.0 (s, 1C, CH=**C**$H_2$), 135.0 (s, 1C, **C**H=$CH_2$). MS ($CI^+$), *m/z* (%): 175.1 $[M-C_3H_5O]^+$ (23), 151.1 $[M-C_6H_9]^+$ (100), 133.1 $[M-C_6H_{11}O]^+$ (30), 81.1 $[C_6H_9]^+$ (31). HRMS ($CI^+$): calcd. for $C_{16}H_{25}O$ ($[M+H]^+$) 233.1905, found 233.1906.

**5-[(2-Methylallyl)oxy]nona-2,7-diyne (9b)**

Sodium hydride (105 mg, 60% in oil, 2.62 mmol) was added to a mixture of nona-2,7-diyn-5-ol (**4b**, 204 mg, 1.50 mmol), 2-methylprop-2-enyl chloride (407 mg, 4.49 mmol), and tetraethylammonium iodide (125 mg, 0.449 mmol) in dry $Et_2O$ (6 mL) at 0 °C. The mixture was stirred at 0 °C for 10 min, then allowed to warm to rt and stirred for 5 days. After the addition of saturated $NH_4Cl$ solution (6 mL), the mixture was extracted with $Et_2O$ (2 × 10 mL) and dried over anhydr. $MgSO_4$. Filtration, evaporation, and separation by column chromatography (eluent hexane/EtOAc 50:1, Rf = 0.30) gave ether **9b** as clear oil (217 mg, 76%). $^1$H NMR: $\delta$ 1.77-1.81 (m, 9H, C**H**$_3$), 2.39-2.57 (m, 4H, CH-C**H**$_2$), 3.53 (quint, *J* = 5.7 Hz, 1H, C**H**), 4.00 (s, 2H, O-C**H**$_2$), 4.91 (s, 1H, CH=C**H**$_2$), 5.00 (s, 1H, CH=C**H**$_2$). $^{13}$C NMR: $\delta$ 3.6 (s, 2C, C≡C-

**C**$H_3$), 19.5 (s, 1C, $CH_2$=C-**C**$H_3$), 23.6 (s, 2C, CH-**C**$H_2$), 73.3 (s, 1C, O-**C**$H_2$), 75.3 (s, 1C, **C**≡C-$CH_3$), 75.9 (s, 1C, **C**H), 77.4 (s, 1C, C≡**C**-$CH_3$), 112.7 (s, 1C, C=**C**$H_2$), 142.3 (s, 1C, **C**=$CH_2$). MS ($ESI^+$), *m/z* (%): 213.1 $[M+Na]^+$ (100). HRMS ($ESI^+$): calcd. for $C_{13}H_{19}O$ ($[M+H]^+$) 191.1430, found 191.1429. HRMS ($ESI^+$): calcd. for $C_{13}H_{18}ONa$ ($[M+Na]^+$) 213.1250, found 213.1248.

**7-[(2-Methylallyl)oxy]trideca-4,9-diyne (9d)**

Sodium hydride (70 mg, 60% in oil, 1.8 mmol) was added to a mixture of trideca-4,9-diyn-7-ol (**4d**, 192 mg, 1.00 mmol), 2-methylprop-2-enyl chloride (272 mg, 3.00 mmol), and tetraethylammonium iodide (83 mg, 0.30 mmol) in dry $Et_2O$ (4 mL) at 0 °C. The mixture was stirred at 0 °C for 10 min, then allowed to warm to rt and stirred for 7 days. After the addition of saturated $NH_4Cl$ solution (4 mL), the mixture was extracted with $Et_2O$ (2 × 7 mL) and dried over anhydr. $MgSO_4$. Filtration, evaporation, and separation by gradient column chromatography (eluent hexane/EtOAc 65:1→20:1, Rf = 0.32 for hexane/EtOAc 55:1) gave ether **9d** as clear oil (131 mg, 53%). Starting trideca-4,9-diyn-7-ol (73 mg, 38%) was partially recovered. $^1$H NMR: δ 0.97 (t, *J* = 7.5 Hz, 6H, $CH_2$-C**H**$_3$), 1.44-1.57 (m, 4H, C**H**$_2$-$CH_3$), 2.14 (tt, *J* = 7.0 Hz, *J* = 2.3 Hz, 4H, C**H**$_2$-$CH_2$-$CH_3$), 2.41-2.58 (m, 4H, CH-C**H**$_2$), 3.55 (quint, *J* = 5.7 Hz, 1H, C**H**), 4.01 (s, 2H, O-C**H**$_2$), 4.88-4.91 (s, 1H, C=C**H**$_2$), 4.99-5.02 (s, 1H, C=C**H**$_2$). $^{13}$C NMR: δ 13.5 (s, 2C, $CH_2$-**C**$H_3$), 19.5 (s, 1C, $CH_2$=C-**C**$H_3$), 20.8 (s, 2C, **C**$H_2$-$CH_2$-$CH_3$), 22.4 (s, 2C, $CH_2$-**C**$H_2$-$CH_3$), 23.8 (s, 2C, CH-**C**$H_2$), 73.4 (s, 1C, O-**C**$H_2$), 76.3 (s, 1C, **C**H), 76.4 (**C**≡C-$CH_2$-$CH_2$), 81.9 (s, 1C, **C**≡C-$CH_2$-$CH_2$), 112.5 (s, 1C, C=**C**$H_2$), 142.4 (s, 1C, **C**=$CH_2$). MS ($EI^+$), *m/z* (%): 165.1 $[M-C_6H_9]^+$ (100), 123.1 $[C_8H_{11}O]^+$ (57), 121.1 $[C_8H_9O]^+$ (90), 109.1 $[C_7H_9O]^+$ (68), 105.1 $[C_7H_5O]^+$ (74), 95.1 $[C_6H_7O]^+$ (75), 93.1 $[C_7H_9]^+$ (98), 91.0 $[C_6H_3O]^+$ (85), 81.0 $[C_6H_9]^+$ (65), 79.0

$[C_6H_7]^+$ (93), 77.0 $[C_6H_5]^+$ (67), 71.0 $[C_4H_7O]^+$ (85), 55.0 $[C_3H_3O]^+$ (95). HRMS ($EI^+$): calcd. for $C_{17}H_{26}O$ ($[M]^+$) 246.1984, found 246.1985.

**Dimethyl 5-(allyloxy)nona-2,7-diynedioate (2e)**

Butyllithium (3.4 mL, 7.7 mmol, 2.3 M solution in hexanes) was added dropwise at −78 °C to a solution of oxaenediyne **2a** (520 mg, 3.51 mmol) in dry THF (13 mL). The mixture was stirred at −78 °C for 1 h, then methyl chloroformate (1.53 g, 16.1 mmol) was added, and the mixture was allowed to warm to rt over 4 h. After quenching with saturated $NH_4Cl$ solution (13 mL), the aqueous layer was extracted with diethyl ether (3 × 13 mL) and dried over anhydr. $MgSO_4$. Filtration and evaporation of the solvents and subsequent column chromatography (eluent hexane/$Et_2O$ 3:1, Rf=0.26) gave diester **2e** as clear oil (751 mg, 81%). $^1$H NMR: $\delta$ 2.70 (d, *J* = 5.6 Hz, 4H, CH-C**H**$_2$), 3.73-3.83 (m, 7H, C**H**-O + C**H**$_3$), 4.11 (dm, *J* = 5.7 Hz, 2H, O-C**H**$_2$), 5.23 (dm, *J* = 10.2 Hz, 1H, CH=C**H**$_2$), 5.32 (dm, *J* = 17.4 Hz, 1H, CH=C**H**$_2$), 5.84-5.98 (m, 1H, C**H**=$CH_2$). $^{13}$C NMR: $\delta$ 24.1 (s, 2C, CH-**C**$H_2$), 52.7 (s, 2C, **C**$H_3$), 71.1 (s, 1C, O-**C**$H_2$), 73.9 (s, 1C, **C**H-O), 74.9 (s, 2C, **C**≡C-CO), 84.7 (s, 2C, C≡**C**-CO), 118.0 (s, 1C, CH=**C**$H_2$), 134.0 (s, 1C, **C**H=$CH_2$), 153.8 (s, 2C, **C**=O). MS ($CI^+$), *m/z* (%): 265.1 $[M+H]^+$ (38), 201.1 $[M-C_2H_7O_2]^+$ (47), 191.0 $[M-C_3H_5O_2]^+$ (45), 173.1 $[M-C_3H_7O_3]^+$ (85), 167.1 $[M-C_5H_5O_2]^+$ (100), 145.1 $[M-C_4H_7O_4]^+$ (65), 117.1 $[M-C_5H_7O_5]^+$ (46), 107.1 $[C_8H_{11}]^+$ (61), 79.1 $[C_6H_7]^+$ (64). HRMS ($CI^+$): calcd. for $C_{14}H_7O_5$ ($[M+H]^+$) 265.1076, found 265.1078.

**[4-(Allyloxy)hepta-1,6-diyne-1,7-diyl]bis(trimethylsilane) (2f)**

Butyllithium (2.7 mL, 6.1 mmol, 2.25 M solution in hexanes) was added dropwise at −78 °C to a solution of oxaenediyne **2a** (222 mg, 1.50 mmol) in dry THF (7 mL). The

mixture was stirred at −78 °C for 1 h, then trimethylsilyl chloride (660 mg, 6.08 mmol) was added, the mixture was allowed to warm to rt, and then stirred for 26 h. After quenching with saturated $NH_4Cl$ solution (8 mL), the aqueous layer was extracted with diethyl ether (3 × 5 mL) and dried over anhydr. $Na_2SO_4$. Evaporation of the solvents and subsequent column chromatography (eluent hexane/EtOAc 98:2, Rf = 0.34) gave silylated oxaenediyne **2f** as clear oil (140 mg, 32%). $^1$H NMR (299.97 MHz, $CDCl_3$): $\delta$ 0.16 (s, 18H, Si-C**H**$_3$), 2.46-2.61 (m, 4H, C**H**$_2$), 3.66 (quint, *J* = 6.0 Hz, 1H, C**H**), 4.16 (dm, *J* = 5.3 Hz, 2H, O-C**H**$_2$), 5.19 (d, *J* = 10.3 Hz, 1H, CH=C**H**$_2$), 5.32 (dm, *J* = 17.1 Hz, 1H, CH=C**H**$_2$), 5.87-6.01 (m, 1H, C**H**=CH$_2$). $^{13}$C NMR (75.44 MHz, $CDCl_3$): $\delta$ 0.0 (s, 6C, Si-**C**H$_3$), 25.5 (s, 2C, **C**H$_2$-C≡C), 71.1 (s, 1C, O-**C**H$_2$), 75.9 (s, 1C, **C**H), 86.6 (s, 2C, C≡**C**-Si), 103.3 (s, 2C, **C**≡C-Si), 117.1 (s, 1C, CH=**C**H$_2$), 134.8 (s, 1C, **C**H=CH$_2$). MS (ESI$^+$), *m/z* (%): 315.2 [M+Na]$^+$ (21), 156.1 [$C_8H_{16}OSi$]$^+$ (81), 116.1 [$C_6H_{16}Si$]$^+$ (78), 105.1 [$C_7H_5O$]$^+$ (100). HRMS (ESI$^+$): calcd. for $C_{16}H_{28}ONaSi_2$ ([M+Na]$^+$) 315.1571, found 315.1567.

**Hepta-1,6-diyn-4-yl acrylate (10a)**

Freshly distilled acryloyl chloride (462 mg, 5.10 mmol) in $CH_2Cl_2$ was added dropwise to a solution of diynol **4a** (368 mg, 3.40 mmol) and triethylamine (688 mg, 6.80 mmol) in $CH_2Cl_2$ (10 mL). After stirring for 10 min at 0 °C, the mixture was allowed to warm to rt and stirred for 6 h. The reaction was quenched with water (20 mL), extracted with $CH_2Cl_2$ (3 × 10 mL), and dried over anhydr. $Na_2SO_4$. Careful evaporation gave the crude product, which was purified by column chromatography (eluent hexane/EtOAc 95:5, Rf = 0.42) to give acrylate **10a** as clear oil (329 mg, 60%). $^1$H NMR: $\delta$ 2.04 (t, *J* = 2.7 Hz, 2H, C≡C**H**), 2.61-2.78 (m, 4H, C-C**H**$_2$), 5.12 (quint, *J* = 5.8 Hz, 1H, CH$_2$-C**H**), 5.89 (dd, *J* = 10.4 Hz, *J* = 1.4 Hz, 1H, CH=C**H**$_2$), 6.15 (dd, *J* =

17.3 Hz, *J* = 10.4 Hz, 1H, CH=C**H**$_2$), 6.47 (dd, *J* = 17.3 Hz, *J* = 1.4 Hz, 1H, **C**H=CH$_2$). $^{13}$C NMR: δ 22.8 (s, 2C, CH-**C**H$_2$), 69.7 (s, 1C, **C**H-CH$_2$), 71.0 (s, 1C, **C**≡CH), 78.8 (s, 1C, C≡**C**H), 128.1 (s, 1C, **C**H=CH$_2$), 131.6 (s, 1C, CH=**C**H$_2$), 165.3 (s, 1C, **C**=O). MS (CI$^+$), *m/z* (%): 163.1 [M+H]$^+$ (50), 123.0 [M-C$_3$H$_3$]$^+$ (100), 91.1 [M-C$_3$H$_3$O$_2$]$^+$ (80). HRMS (CI$^+$): calcd. for C$_{10}$H$_{11}$O$_2$ ([M+H]$^+$) 163.0759, found 163.0757.

**Nona-2,7-diyn-5-yl acrylate (10b)**

Nona-2,7-diyn-5-ol (**4b**, 250 mg, 1.84 mmol) and triethylamine (372 mg, 3.68 mmol) were dissolved in dry CH$_2$Cl$_2$ (6 mL) and the mixture was cooled to 0 °C. Freshly distilled acryloyl chloride (250 mg, 2.76 mmol) was added dropwise and the mixture was stirred for 1 h at 0 °C. After quenching with brine (4 mL), the layers were separated, the aqueous phase extracted with Et$_2$O (2 × 6 mL), and the combined organic layers were dried over anhydr. Na$_2$SO$_4$. Careful evaporation gave the crude product, which was purified by column chromatography (eluent hexan/EtOAc 97:3, Rf = 0.32) to give acrylate **10b** as clear oil (328 mg, 94%). $^1$H NMR: δ 1.79 (t, *J* = 2.5 Hz, 6H, C**H**$_3$), 2.50-2.68 (m, 4H, C-C**H**$_2$), 5.01 (quint, *J* = 6.0 Hz, 1H, CH$_2$-C**H**), 5.85 (dd, *J* = 10.0 Hz, *J* = 1.4 Hz, 1H, CH=C**H**$_2$), 6.15 (dd, *J* = 17.5 Hz, *J* = 10.4 Hz, 1H, C**H**=CH$_2$), 6.45 (dd, *J* = 17.3 Hz, *J* = 1.4 Hz, 1H, CH=C**H**$_2$). $^{13}$C NMR: δ 3.5 (s, 2C, **C**H$_3$), 23.2 (s, 2C, CH-**C**H$_2$), 71.0 (s, 1C, **C**H-CH$_2$), 73.4 (s, 1C, **C**≡C-CH$_3$), 78.1 (s, 1C, C≡**C**-CH$_3$), 128.5 (s, 1C, **C**H=CH$_2$), 131.0 (s, 1C, CH=**C**H$_2$), 165.4 (s, 1C, **C**=O). MS (ESI$^+$), *m/z* (%): 213.1 [M+Na]$^+$ (100). HRMS (ESI$^+$): calcd. for C$_{12}$H$_{15}$O$_2$ ([M+H]$^+$) 191.1067, found 191.1065. HRMS (ESI$^+$): calcd. for C$_{12}$H$_{14}$O$_2$Na ([M+Na]$^+$) 213.0886, found 213.0885.

**Trideca-4,9-diyn-7-yl acrylate (10d)**

Trideca-4,9-diyn-7-ol (**4d**, 192 mg, 1.00 mmol) and triethylamine (202 mg, 2.00 mmol) were dissolved in dry $CH_2Cl_2$ (3.5 mL) and the mixture was cooled to 0 °C. Freshly distilled acryloyl chloride (136 mg, 1.50 mmol) was added dropwise and the mixture was stirred for 90 min at 0 °C. After quenching with brine (2.5 mL), the layers were separated, the aqueous phase extracted with $Et_2O$ (2 × 3.5 mL), and the combined organic layers were dried over $Na_2SO_4$. Careful evaporation gave the crude product, which was purified by column chromatography (eluent hexan/EtOAc 55:1, Rf = 0.24) to give acrylate **10d** as clear oil (166 mg, 67%). $^1$H NMR: $\delta$ 0.97 (t, *J* = 7.4 Hz, 6H, C**H**$_3$), 1.44-1.56 (m, 4H, C**H**$_2$-CH$_3$), 2.13 (tt, *J* = 7.0 Hz, *J* = 2.3 Hz, 4H, C**H**$_2$-CH$_2$-CH$_3$), 2.53-2.69 (m, 4H, CH-C**H**$_2$), 5.04 (quint, *J* = 5.9 Hz, 1H, C**H**-CH$_2$), 5.85 (dd, *J* = 10.5 Hz, *J* = 1.4 Hz, 1H, CH=C**H**$_2$), 6.15 (dd, *J* = 17.0 Hz, *J* = 10.5 Hz, 1H, C**H**=CH$_2$), 6.44 (dd, *J* = 17.0 Hz, *J* = 1.4 Hz, 1H, CH=C**H**$_2$). $^{13}$C NMR: $\delta$ 13.4 (s, 2C, **C**H$_3$), 20.7 (s, 2C, **C**H$_2$-CH$_2$-CH$_3$), 22.3 (s, 2C, CH$_2$-**C**H$_2$-CH$_3$), 23.3 (s, 2C, CH-**C**H$_2$), 71.0 (s, 1C, **C**H-CH$_2$), 74.9 (s, 1C, **C**≡C-CH$_2$-CH$_2$), 82.6 (s, 1C, C≡**C**-CH$_2$-CH$_2$), 128.5 (s, 1C, **C**H=CH$_2$), 130.9 (s, 1C, CH=**C**H$_2$), 165.4 (s, 1C, **C**=O). MS (EI$^+$), *m/z* (%): 145.1 [M-C$_5$H$_9$O$_2$]$^+$ (96), 131.1 [M-C$_6$H$_{11}$O$_2$]$^+$ (58), 117.1 [M-C$_7$H$_{13}$O$_2$]$^+$ (80), 91.0 [C$_7$H$_7$]$^+$ (48), 55.0 [C$_3$H$_3$O]$^+$ (100). HRMS (EI$^+$): calcd. for C$_{16}$H$_{22}$O$_2$ ([M]$^+$) 246.1620, found 246.1622.

**Nona-2,7-diyn-5-yl methacrylate (11b)**

Triethylamine (559 mg, 5.52 mmol) and 4-(dimethylamino)pyridine (34 mg, 0.28 mmol) were slowly added to a solution of nona-2,7-diyn-5-ol (**4b**, 250 mg, 1.84 mmol) in dry $CH_2Cl_2$ (5 mL) at 0 °C. Methacryloyl chloride (385 mg, 3.68 mmol) was added dropwise, the mixture was allowed to warm to rt, and stirred for 24 h. After quenching with saturated $NH_4Cl$ (5 mL), the layers were separated, the aqueous

phase was extracted with $Et_2O$ (2 × 5 mL), and the combined organic layers were dried over anhydr. $MgSO_4$. Evaporation and purification by column chromatography (eluent hexan/EtOAc 97:3, Rf = 0.43) gave methacrylate **11b** as clear oil (161 mg, 43%). $^1$H NMR: δ 1.78 (t, *J* = 2.6 Hz, 6H, C≡C-C**H**$_3$), 1.96 (s, 3H, C**H**$_3$), 2.49-2.67 (m, 4H, C-C**H**$_2$), 4.97 (quint, *J* = 5.9 Hz, 1H, $CH_2$-C**H**), 5.57-5.60 (m, 1H, C=C**H**$_2$), 6.14-6.16 (m, 1H, C=C**H**$_2$). $^{13}$C NMR: δ 3.2 (s, 2C, C≡C-**C**$H_3$), 17.9 (s, 1C, **C**$H_3$), 22.8 (s, 2C, C-**C**$H_2$), 70.8 (s, 1C, **C**H), 73.6 (s, 1C, **C**≡C-$CH_3$), 77.6 (s, 1C, C≡**C**-$CH_3$), 125.4 (s, 1C, C=**C**$H_2$), 136.0 (s, 1C, **C**=$CH_2$), 166.3 (s, 1C, **C**=O). MS (ESI$^+$), *m/z* (%): 227.1 $[M+Na]^+$ (100). HRMS (ESI$^+$): calcd. for $C_{13}H_{17}O_2$ ($[M+H]^+$) 205.1223, found 205.1224. HRMS (ESI$^+$): calcd. for $C_{13}H_{16}O_2Na$ ($[M+Na]^+$) 227.1043, found 227.1044.

**Trideca-4,9-diyn-7-yl methacrylate (11d)**

Triethylamine (405 mg, 4.00 mmol) and 4-(dimethylamino)pyridine (24 mg, 0.20 mmol) were slowly added to a solution of trideca-4,9-diyn-7-ol (**4d**, 192 mg, 1.00 mmol) in dry $CH_2Cl_2$ (3 mL) at 0 °C. Methacryloyl chloride (209 mg, 2.00 mmol) was added dropwise, the mixture was allowed to warm to rt, and stirred for 20 h. After quenching with saturated $NH_4Cl$ (3 mL), the layers were separated, the aqueous phase was extracted with $Et_2O$ (2 × 3 mL), and the combined organic layers were dried over anhydr. $MgSO_4$. Careful evaporation and purification by column chromatography (eluent hexan/EtOAc 55:1, Rf = 0.23) gave methacrylate **11d** as clear oil (234 mg, 90%). $^1$H NMR: δ 0.96 (t, *J* = 7.3 Hz, 6H, $CH_2$-C**H**$_3$), 1.43-1.56 (m, 4H, C**H**$_2$-$CH_3$), 1.96 (s, 3H, C**H**$_3$), 2.12 (tt, *J* = 7.0 Hz, *J* = 2.3 Hz, 4H, C**H**$_2$-$CH_2$-$CH_3$), 2.53-2.69 (m, 4H, CH-C**H**$_2$), 5.01 (quint, *J* = 5.6 Hz, 1H, $CH_2$-C**H**), 5.56-5.59 (m, 1H, C=C**H**$_2$), 6.15 (s, 1H, C=C**H**$_2$). $^{13}$C NMR: δ 13.4 (s, 2C, $CH_2$-**C**$H_3$), 18.2 (s, 1C, **C**$H_3$), 20.7 (s, 2C, **C**$H_2$-$CH_2$-$CH_3$), 22.3 (s, 2C, $CH_2$-**C**$H_2$-$CH_3$), 23.4 (s, 2C, CH-**C**$H_2$), 71.1

(s, 1C, **C**H-$CH_2$), 75.0 (s, 2C, **C**≡C-$CH_2$-$CH_2$), 82.5 (s, 2C, C≡**C**-$CH_2$-$CH_2$), 125.6 (s, 1C, C=**C**$H_2$), 136.3 (s, 1C, **C**=$CH_2$), 166.6 (s, 1C, **C**=O). MS ($EI^+$), *m/z* (%): 174.1 [M-M-$C_4H_6O_2$]$^+$ (62), 159.1 [M-$C_5H_9O_2$]$^+$ (55), 145.1 [M-$C_6H_{11}O_2$]$^+$ (100), 131.1 [M-$C_7H_{13}O_2$]$^+$ (80), 117.1 [M-$C_8H_{15}O_2$]$^+$ (95), 91.0 [$C_7H_7$]$^+$ (70). HRMS ($EI^+$): calcd. for $C_{17}H_{24}O_2$ ([M]$^+$) 260.1776, found 260.1775.

## 2. Copies of $^{1}H$ and $^{13}C$ NMR spectra

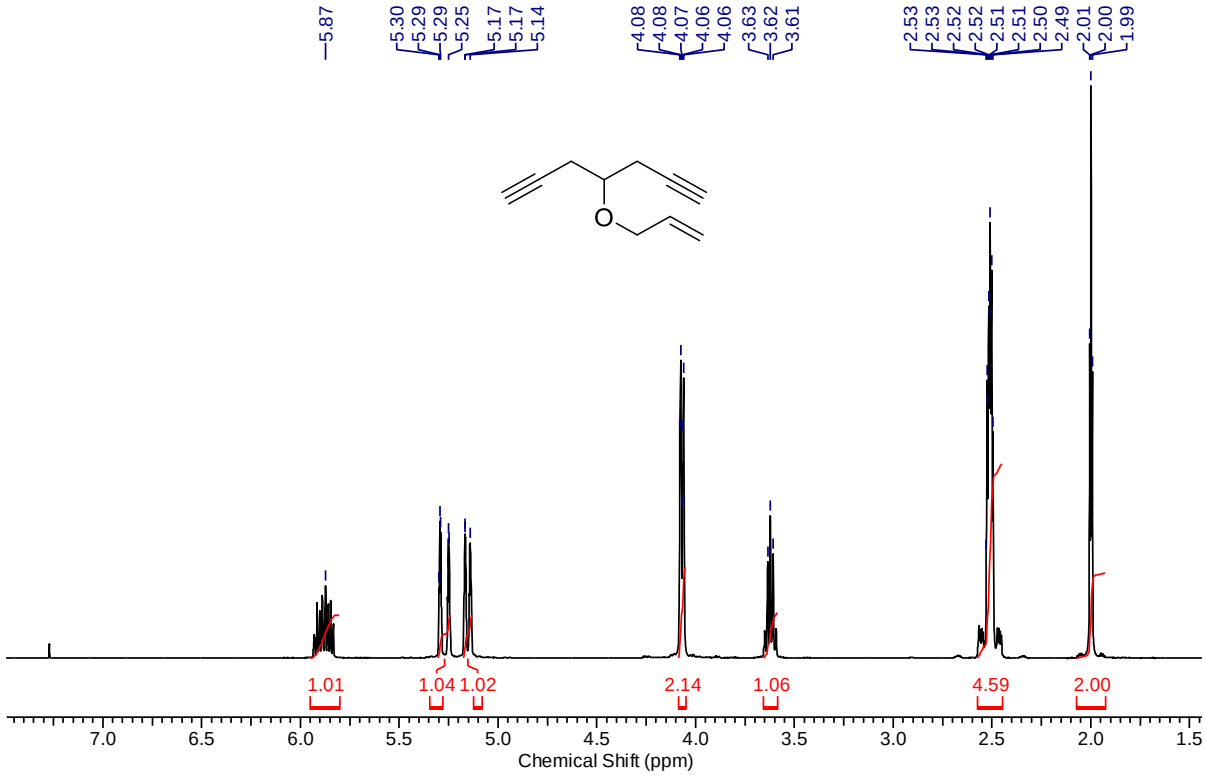


Figure S1. $^{1}H$ NMR spectrum, 299.97 MHz, $CDCl_3$, 4-(allyloxy)hepta-1,6-diyne (**2a**).

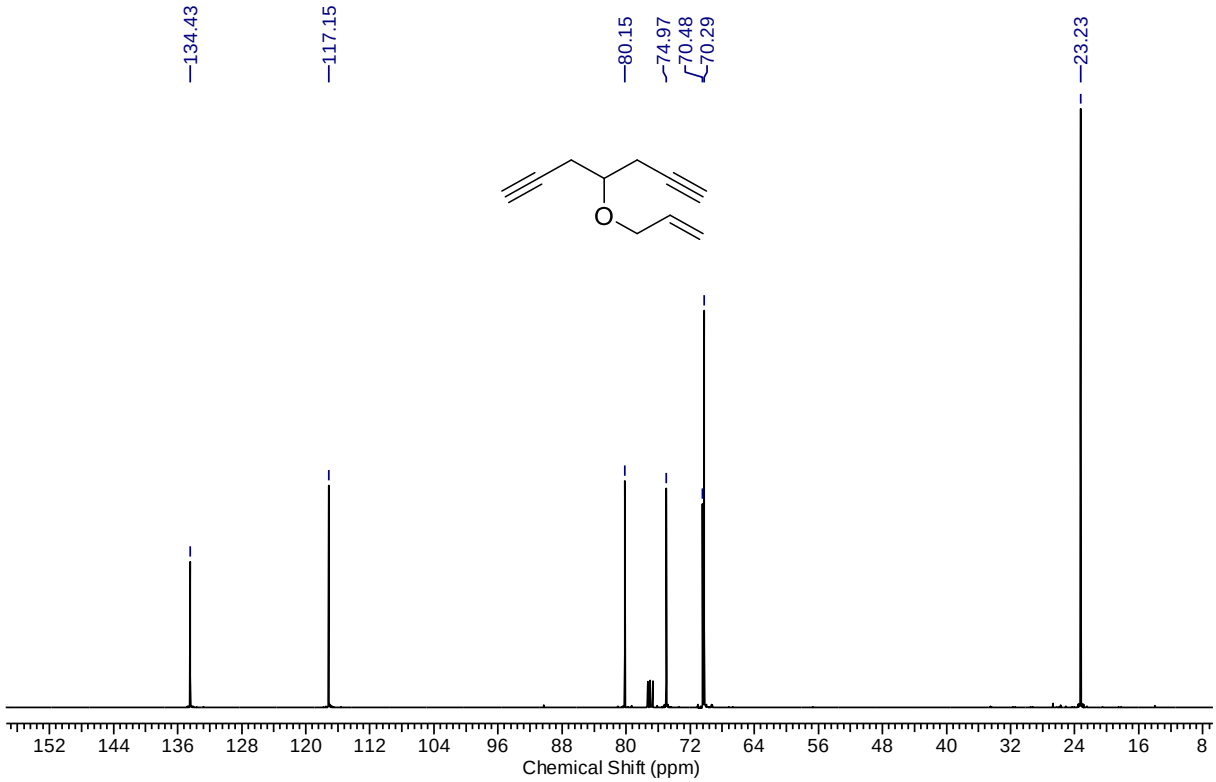


Figure S2. $^{13}C\{1H\}$ NMR spectrum, 75.44 MHz, $CDCl_3$, 4-(allyloxy)hepta-1,6-diyne (**2a**).

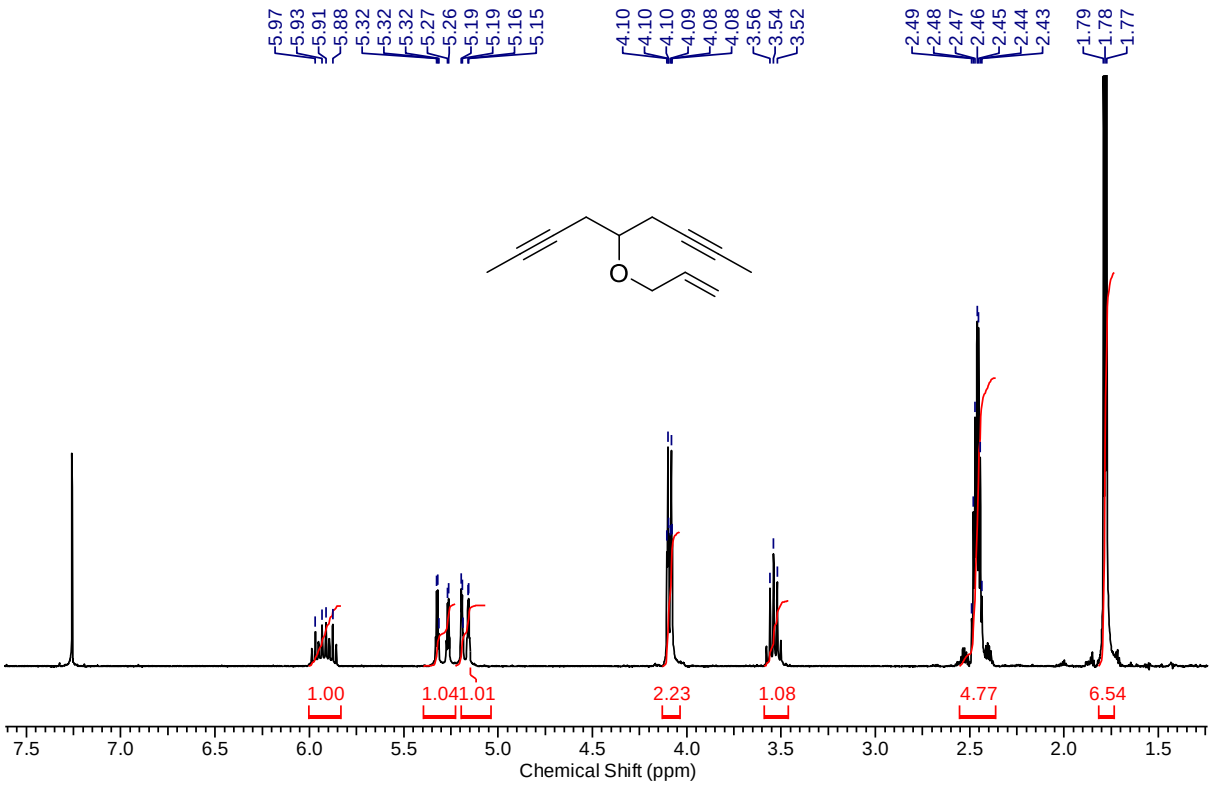


Figure S3. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 5-(allyloxy)nona-2,7-diyne (**2b**).

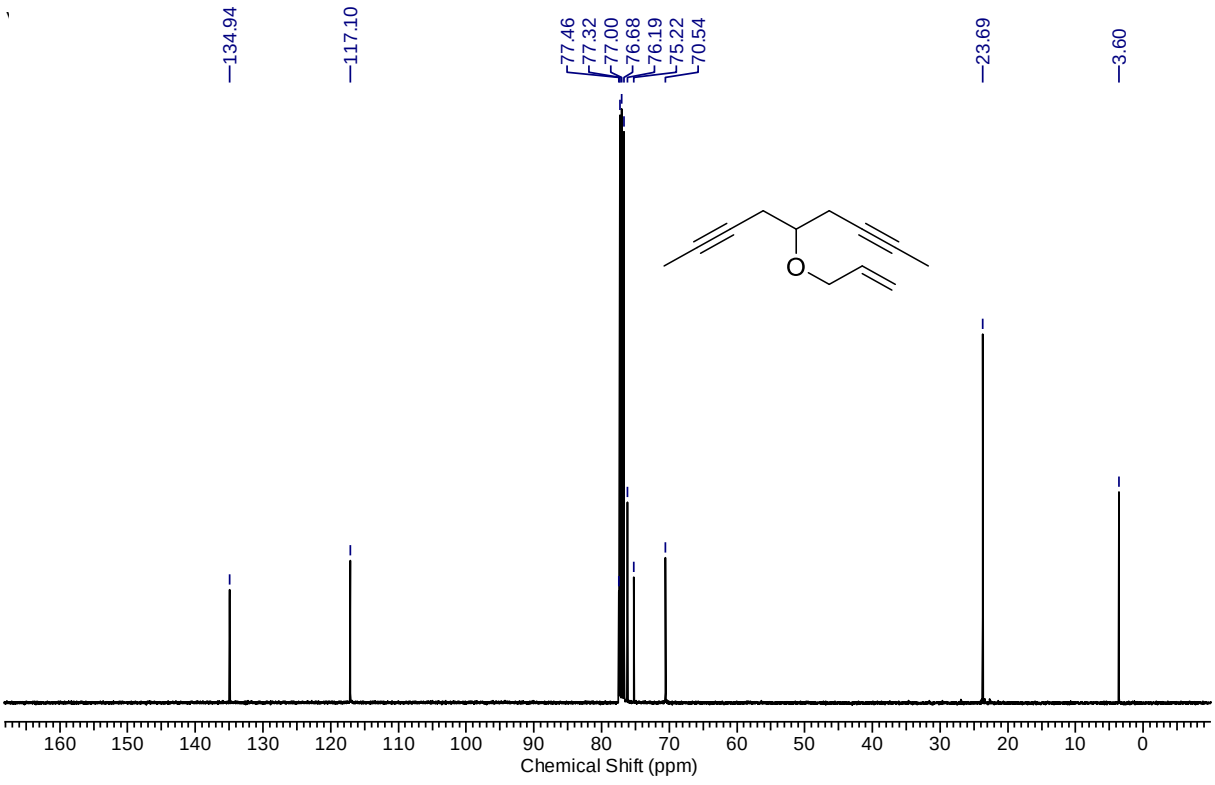


Figure S4. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 5-(allyloxy)nona-2,7-diyne (**2b)**.

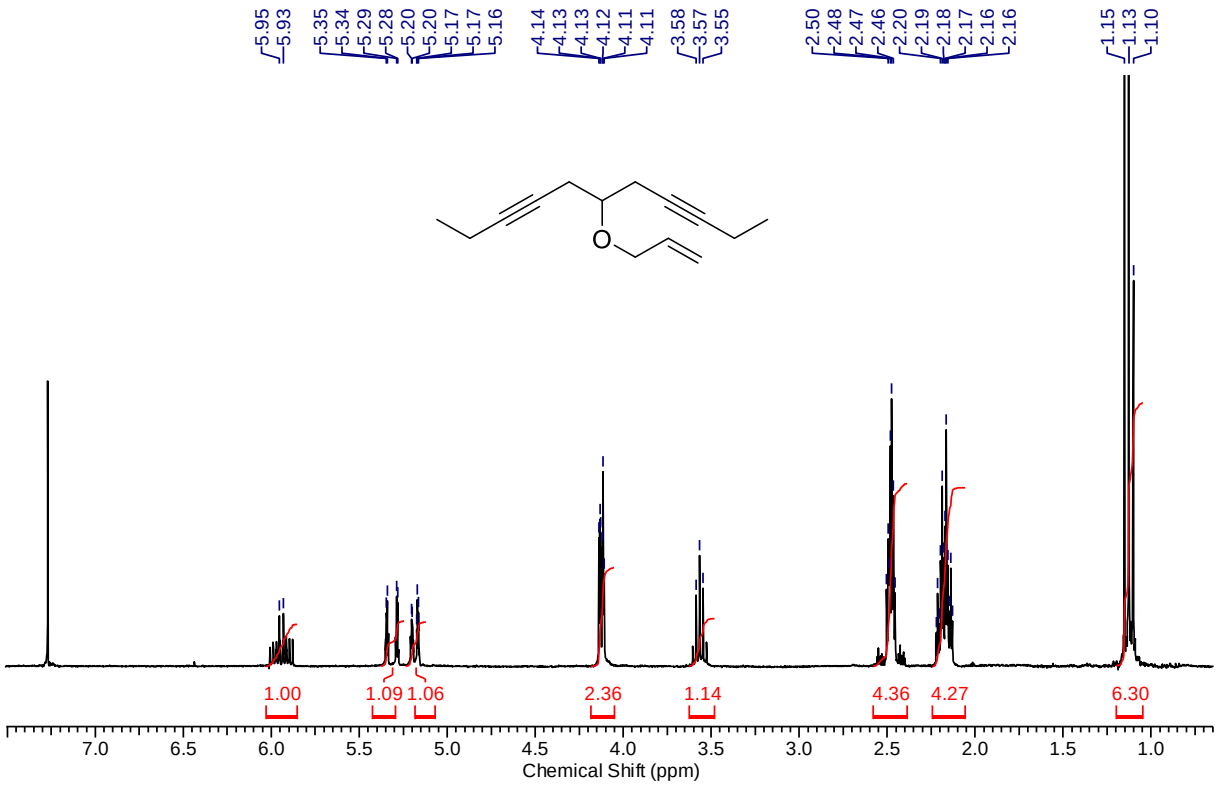


Figure S5. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 6-(allyloxy)undeca-3,8-diyne (**2c**).

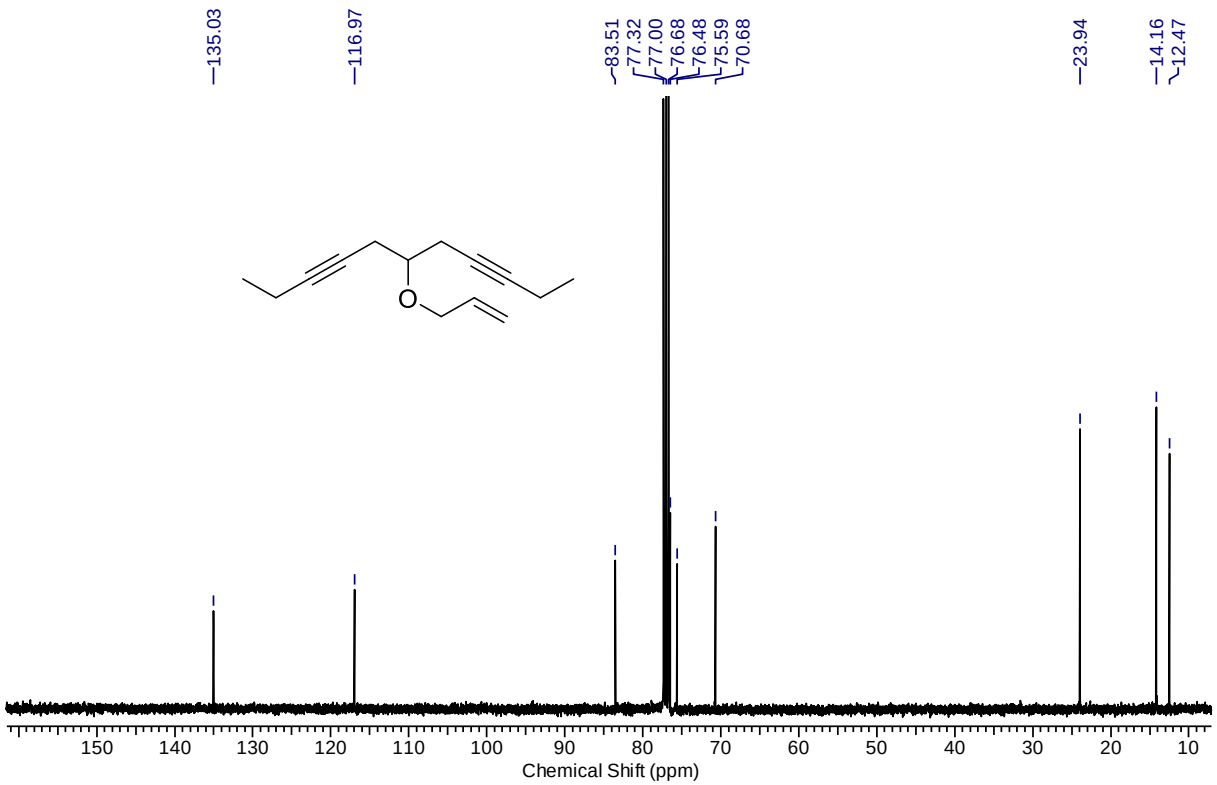


Figure S6. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 6-(allyloxy)undeca-3,8-diyne (**2c**).

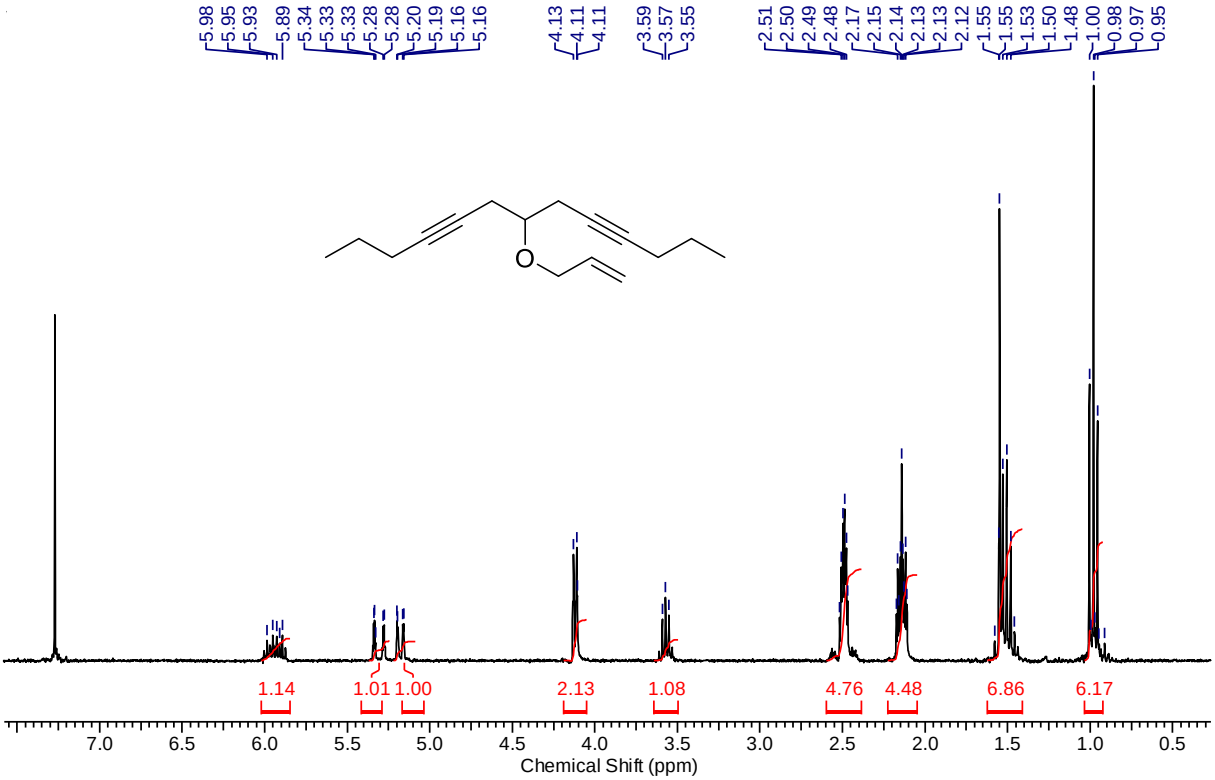


Figure S7. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 7-(allyloxy)trideca-4,9-diyne (**2d**).

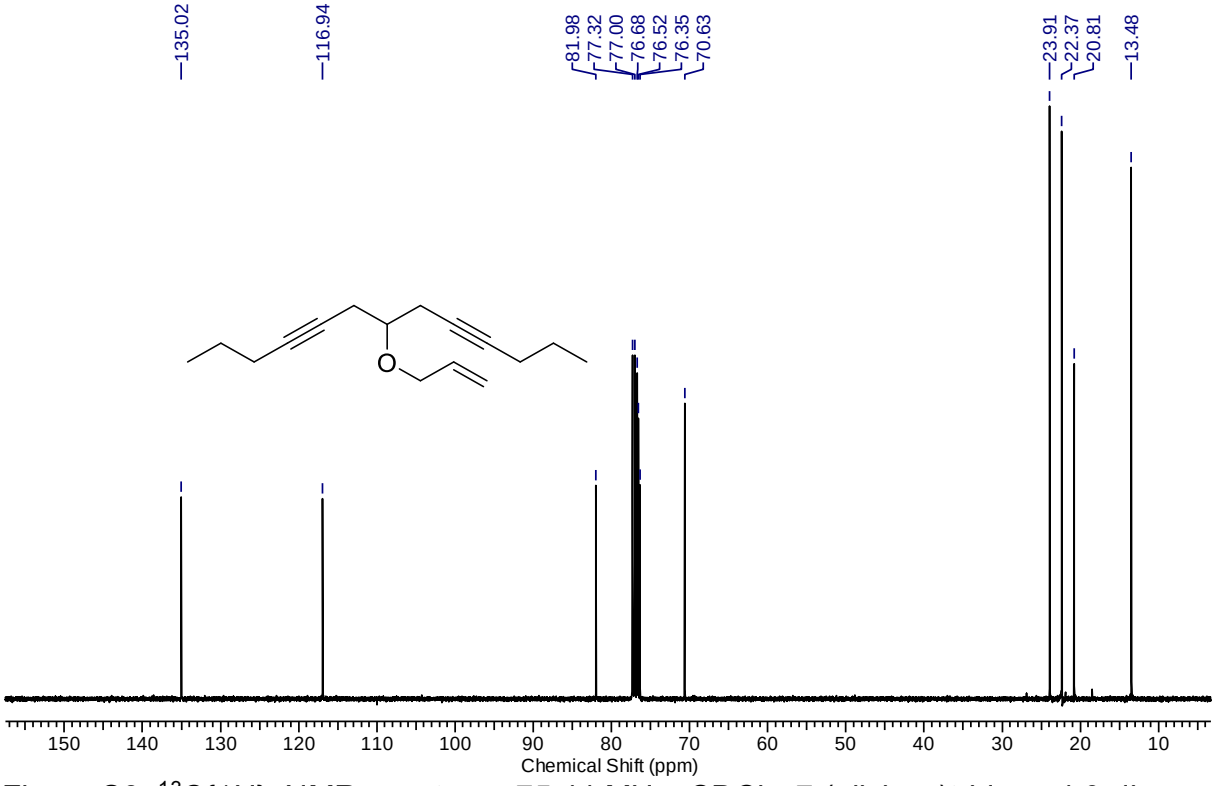


Figure S8. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 7-(allyloxy)trideca-4,9-diyne (**2d**).

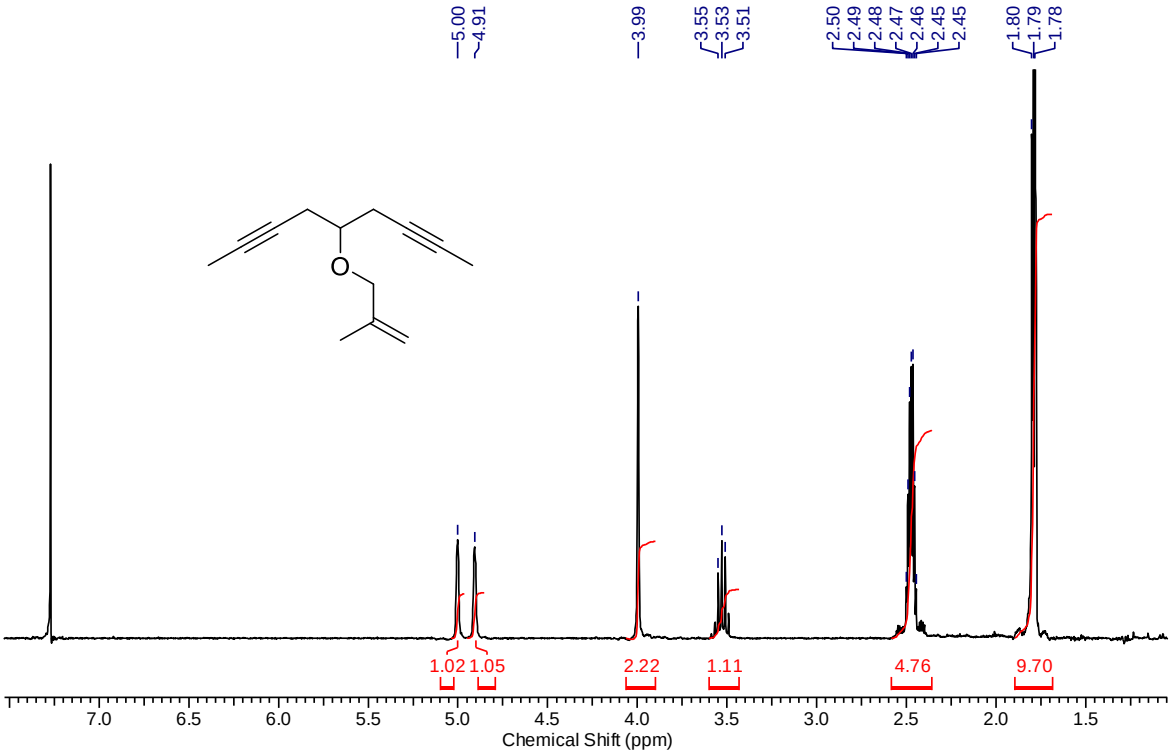


Figure S9. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 5-((2-methylallyl)oxy)nona-2,7-diyne (**9b**).

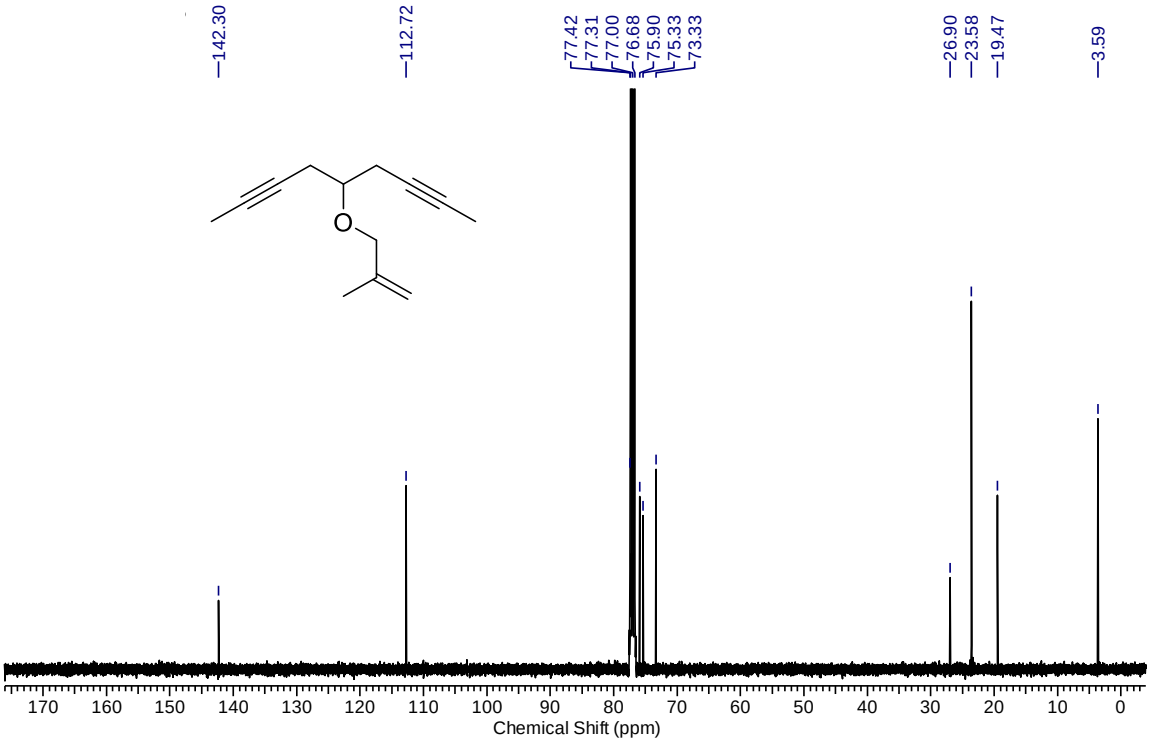


Figure S10. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 5-((2-methylallyl)oxy)nona-2,7-diyne (**9d**).

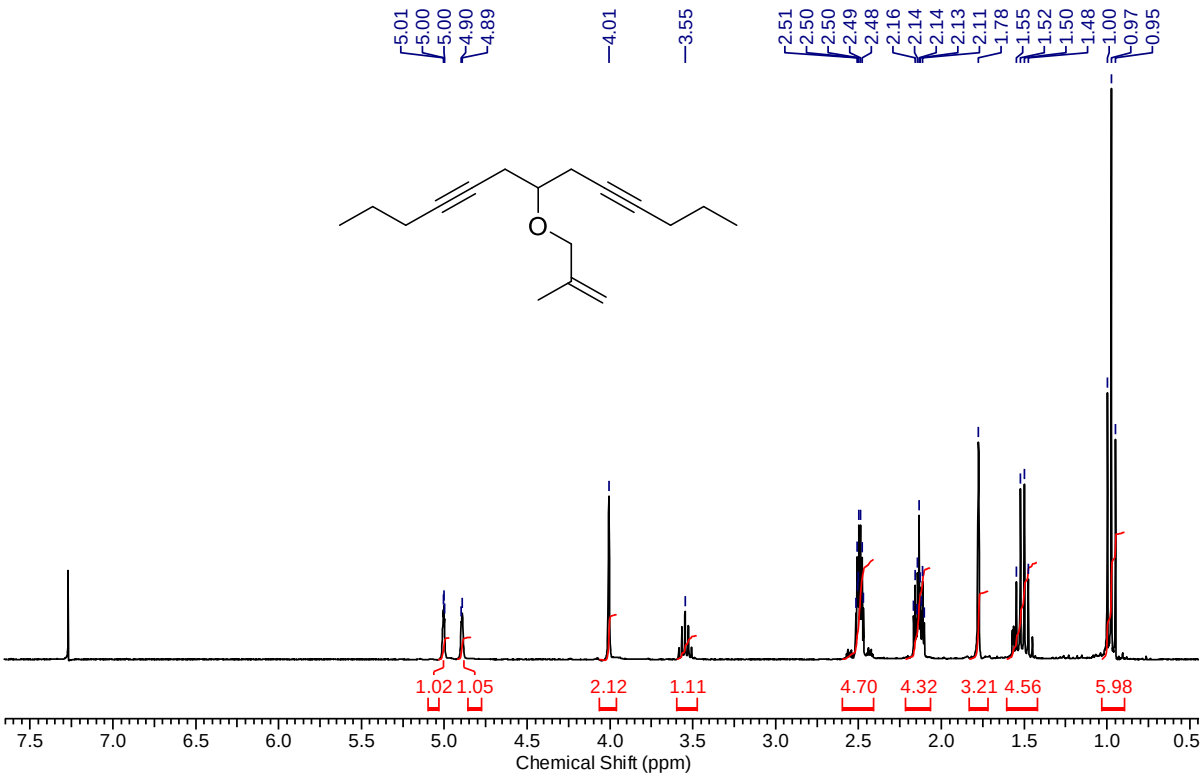


Figure S11. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 7-((2-methylallyl)oxy)trideca-4,9-diyne (**9d**).

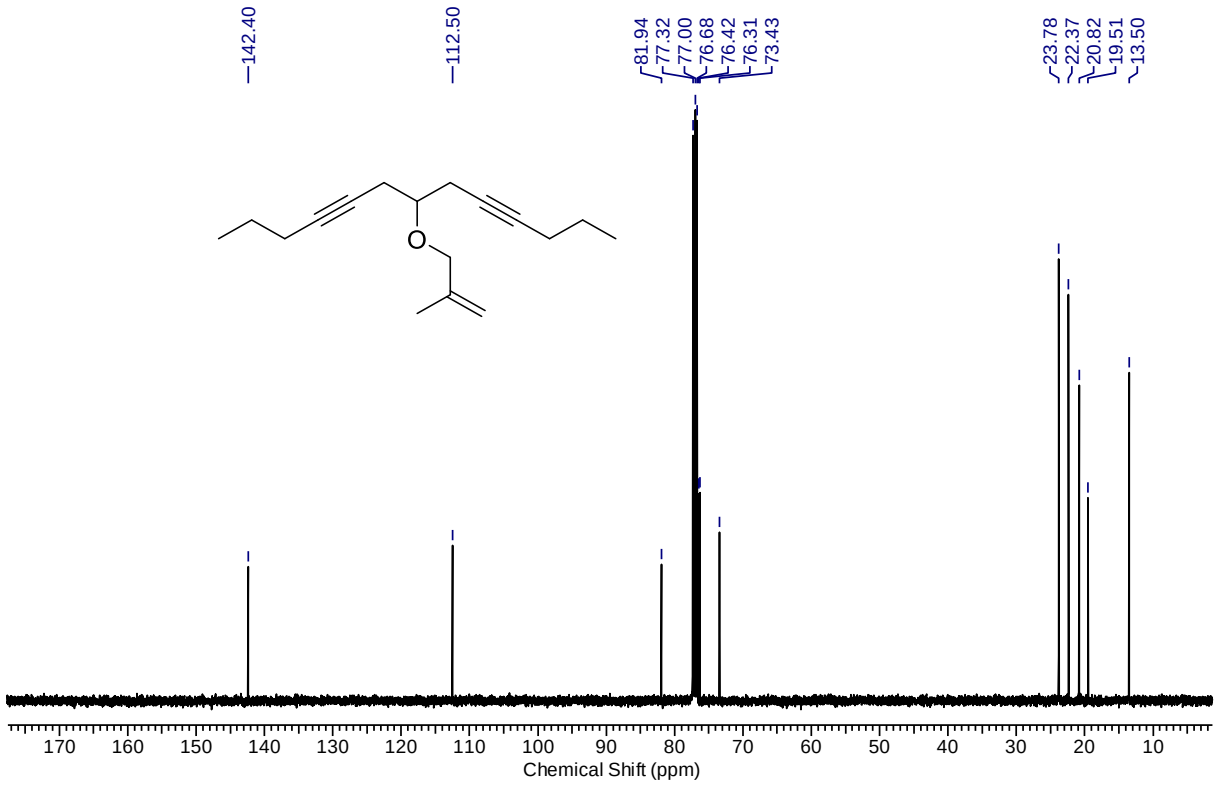


Figure S12. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 7-((2-methylallyl)oxy)trideca-4,9-diyne (**9d**).

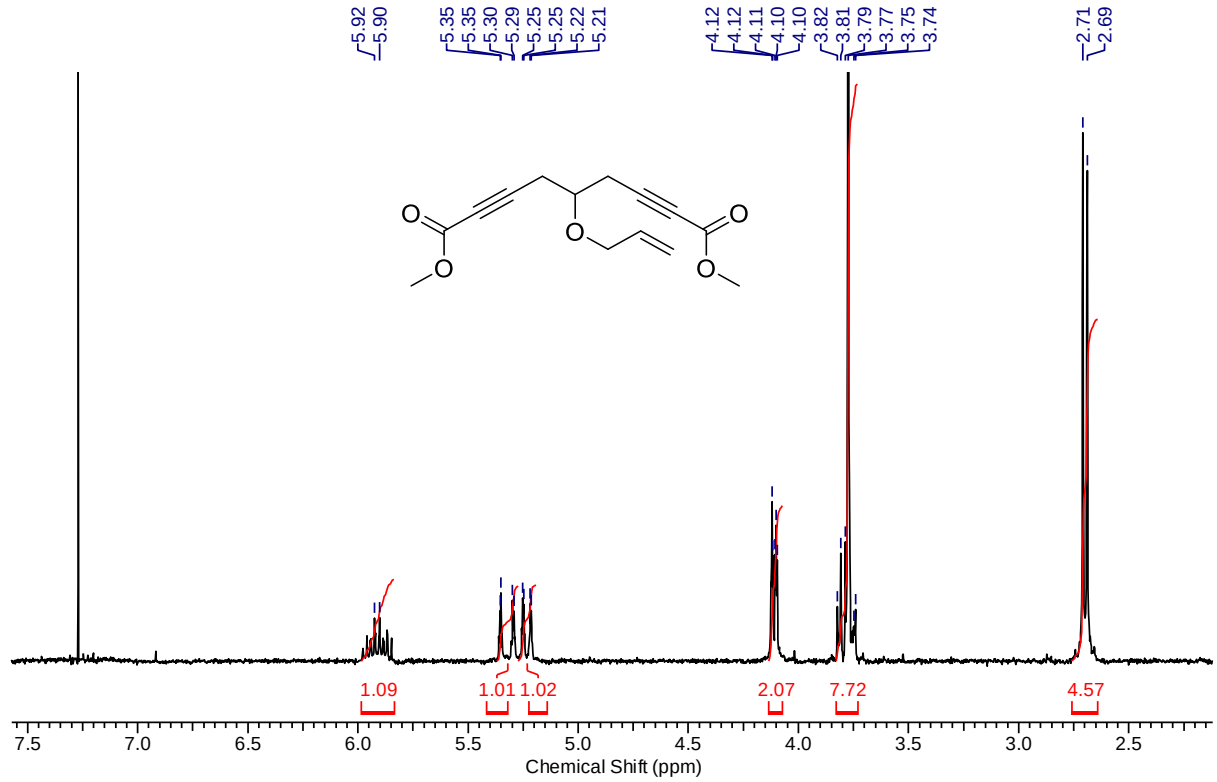


Figure S13. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, dimethyl 5-(allyloxy)nona-2,7-diynedioate (**2e**).

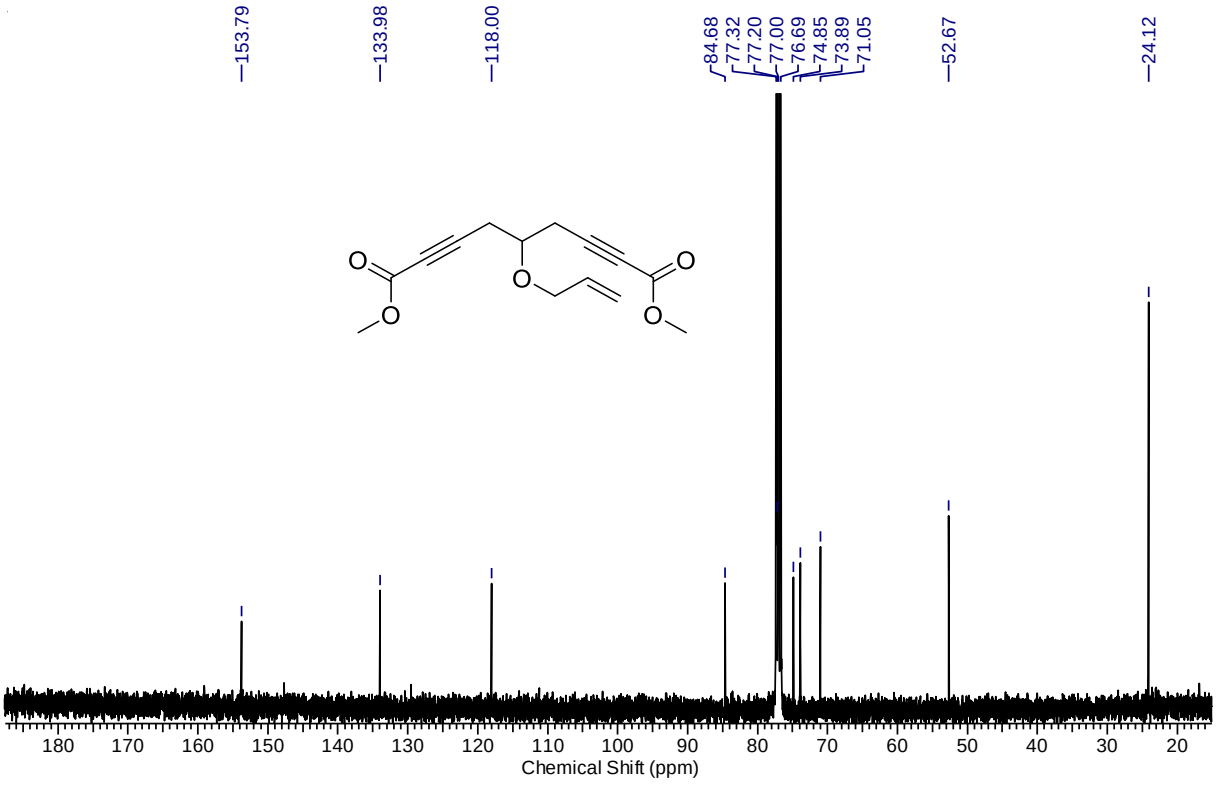


Figure S14. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, dimethyl 5-(allyloxy)nona-2,7-diynedioate (**2e**).

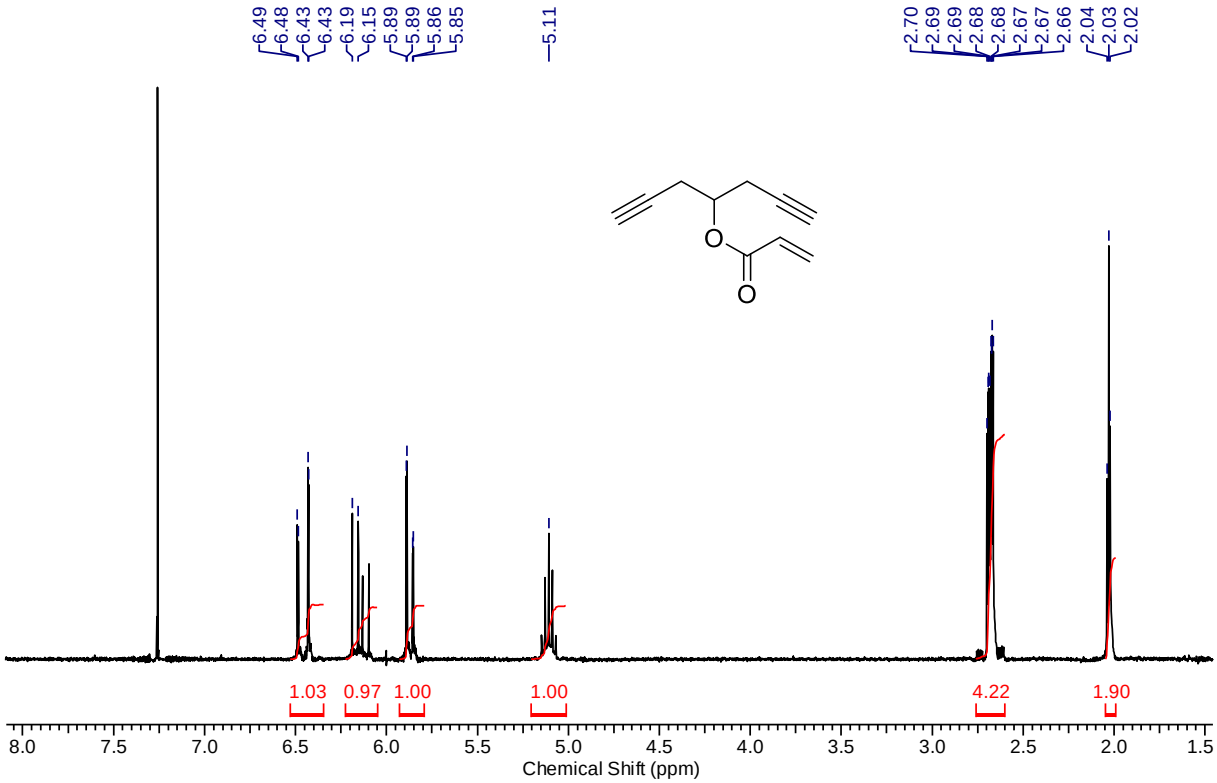


Figure S15. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, hepta-1,6-diyn-4-yl acrylate (**10a**).

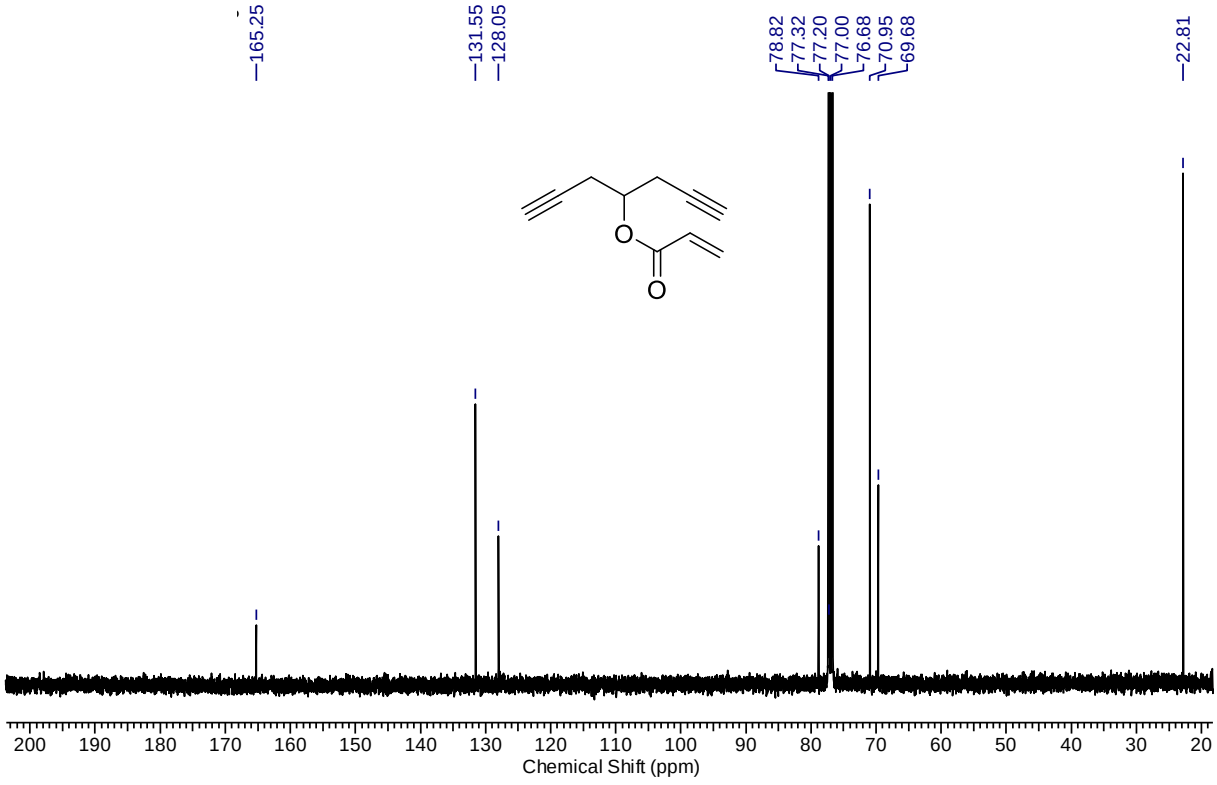


Figure S16. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, hepta-1,6-diyn-4-yl acrylate (**10a**).

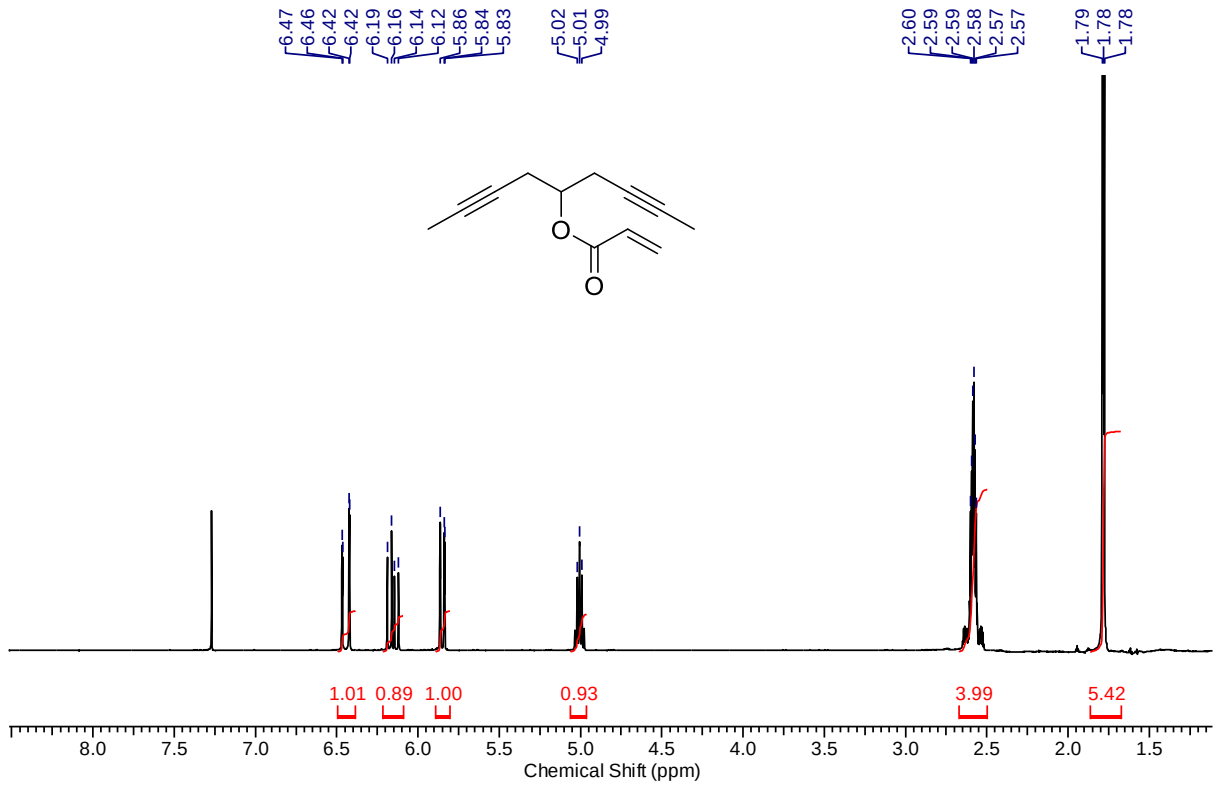


Figure S17. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, nona-2,7-diyn-5-yl acrylate (**10b**).

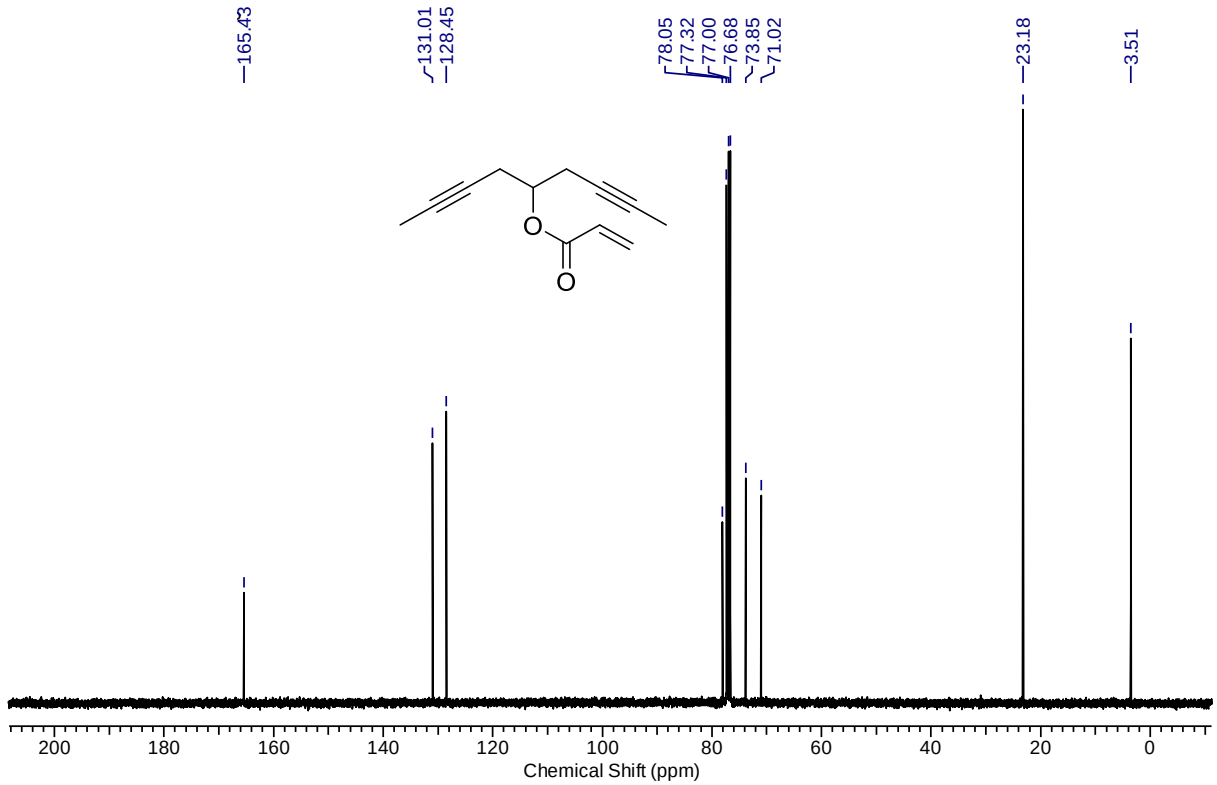


Figure S18. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, nona-2,7-diyn-5-yl acrylate (**10b**).

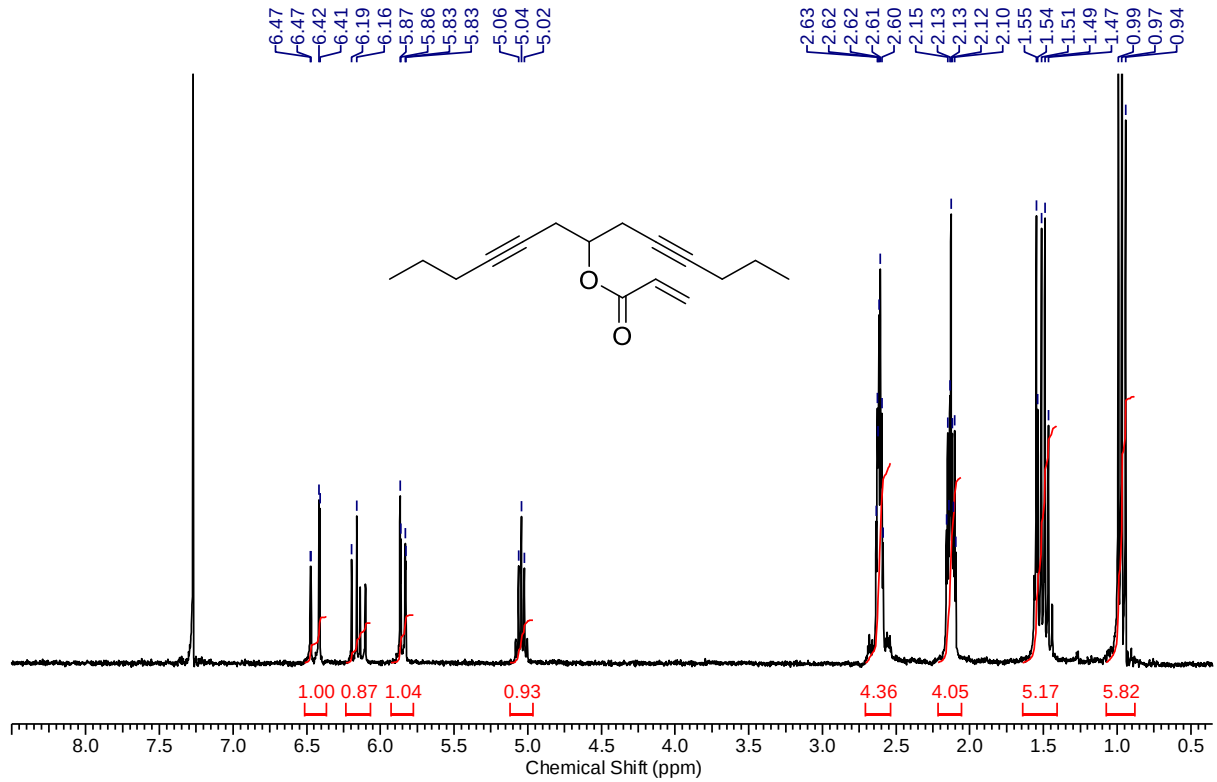


Figure S19. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, trideca-4,9-diyn-7-yl acrylate (**10d**).

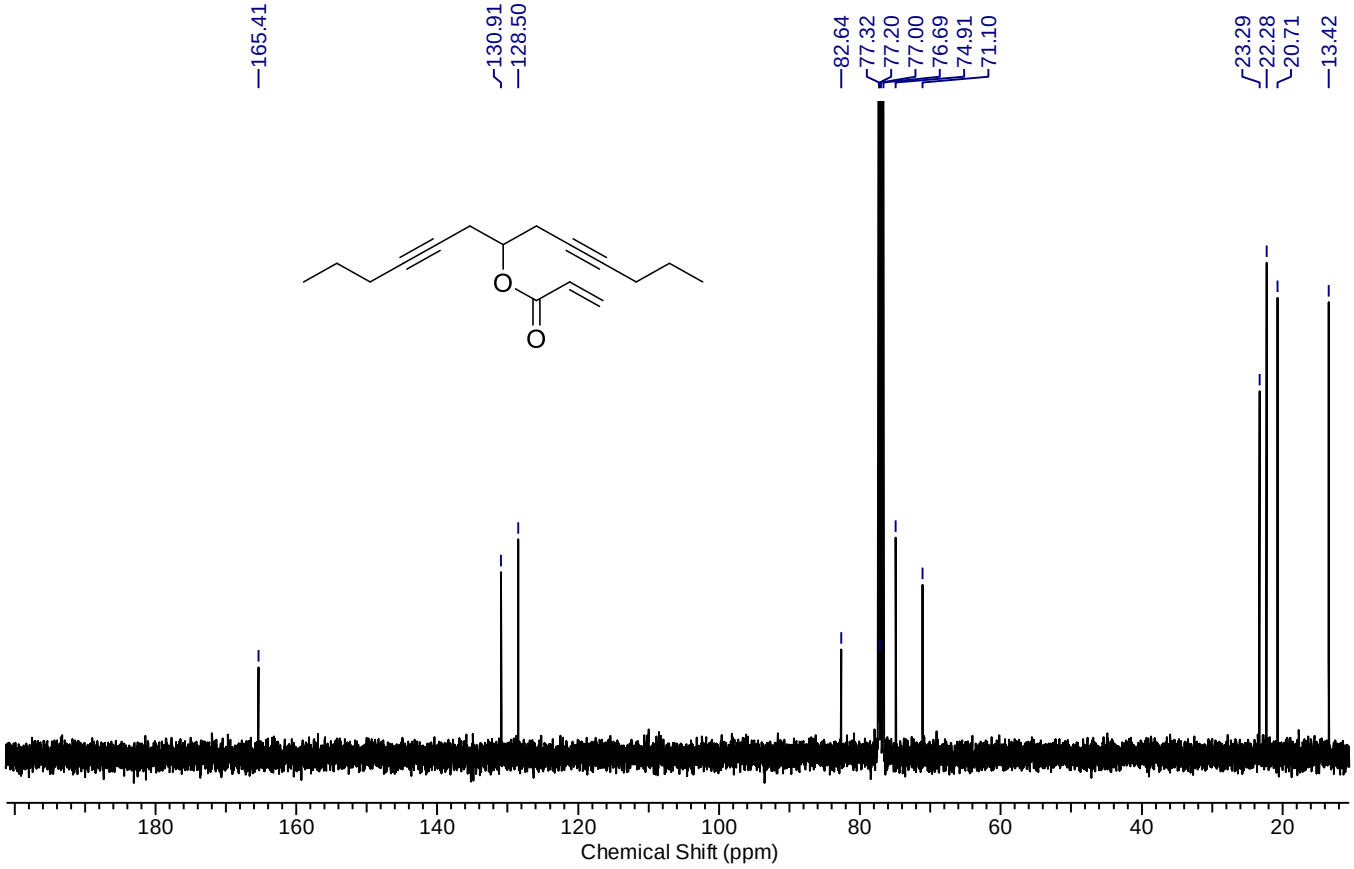


Figure 20. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, trideca-4,9-diyn-7-yl acrylate (**10d**).

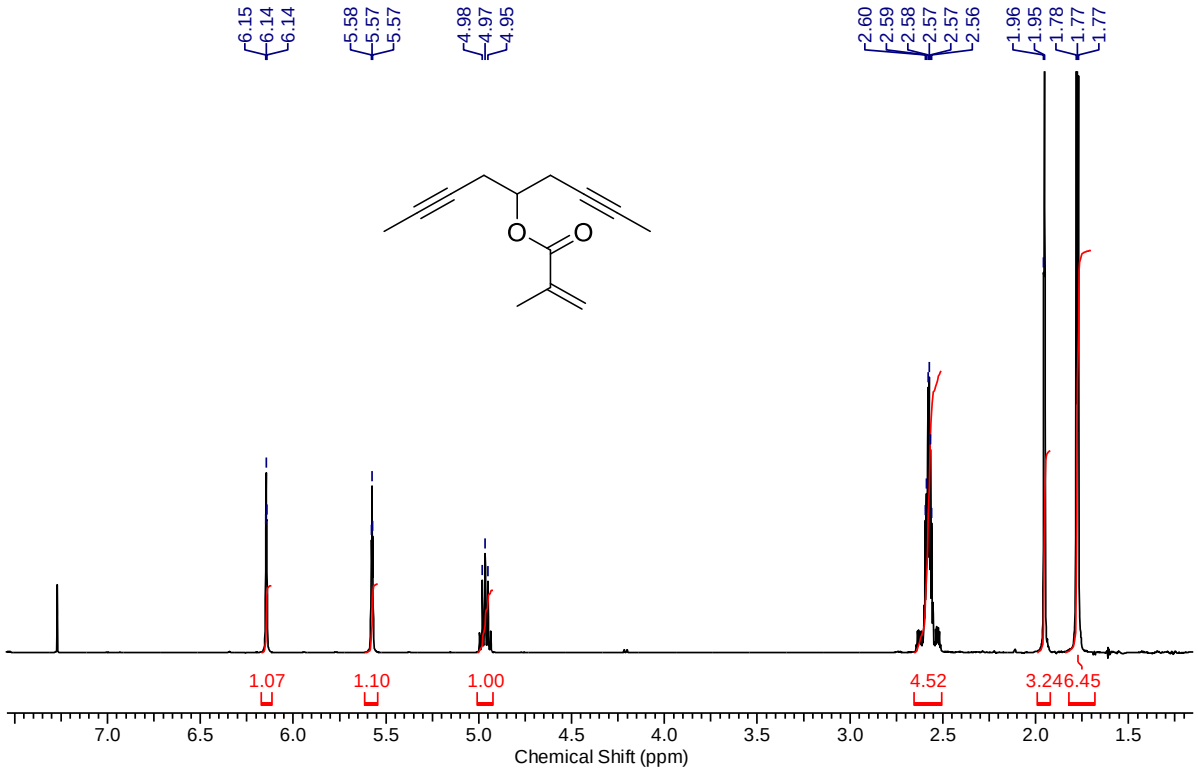


Figure S21. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, nona-2,7-diyn-5-yl methacrylate (**11b**).

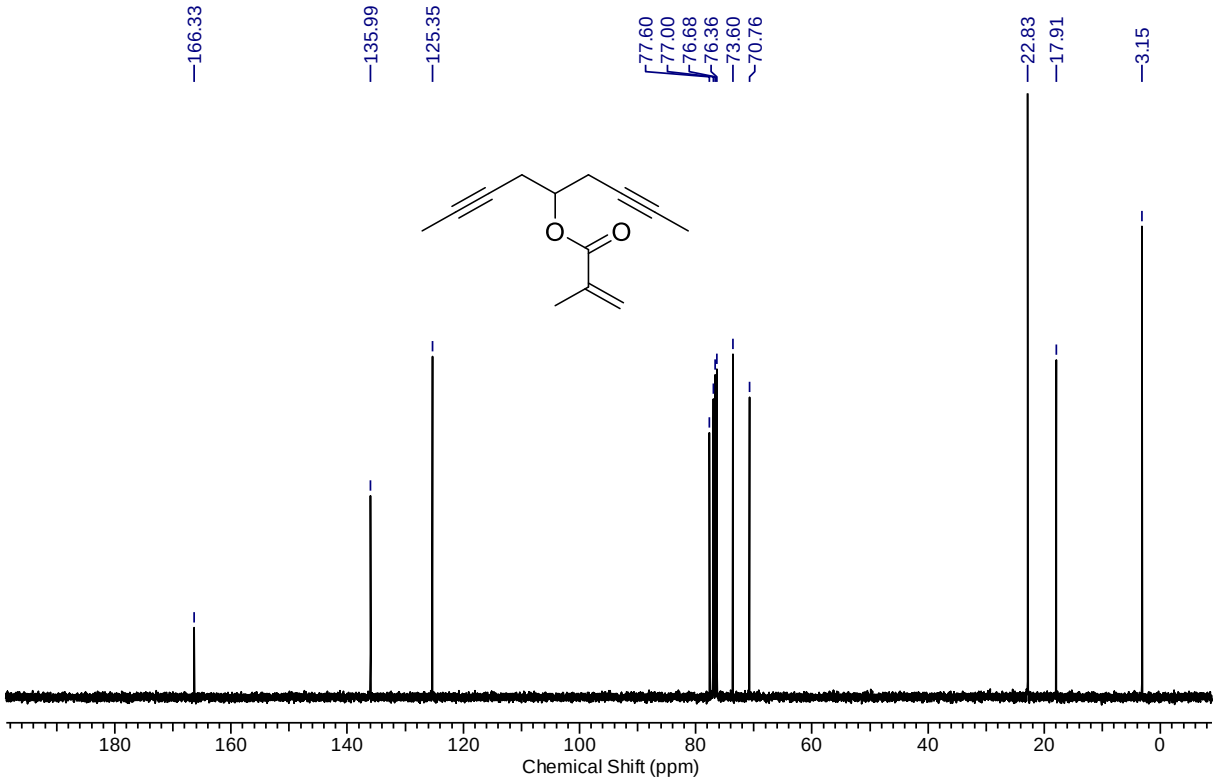


Figure S22. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, nona-2,7-diyn-5-yl methacrylate (**11b**).

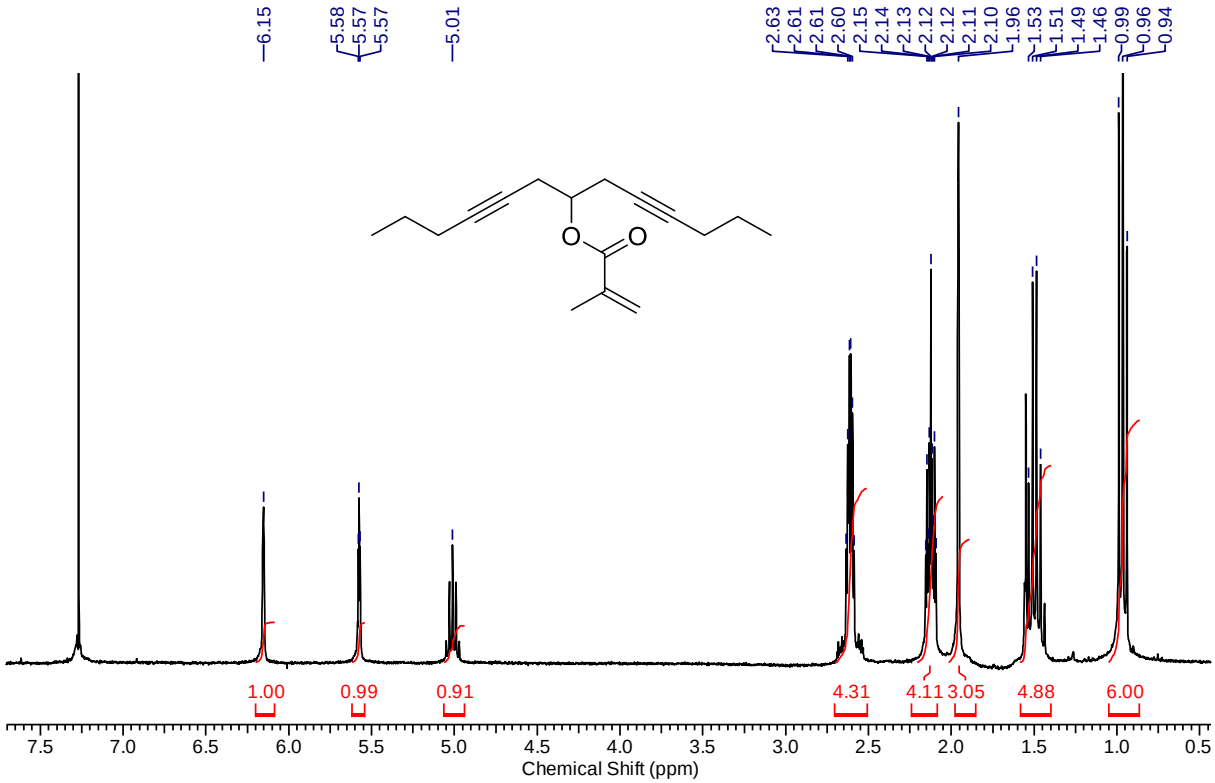


Figure S23. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, trideca-4,9-diyn-7-yl methacrylate (**11d**).

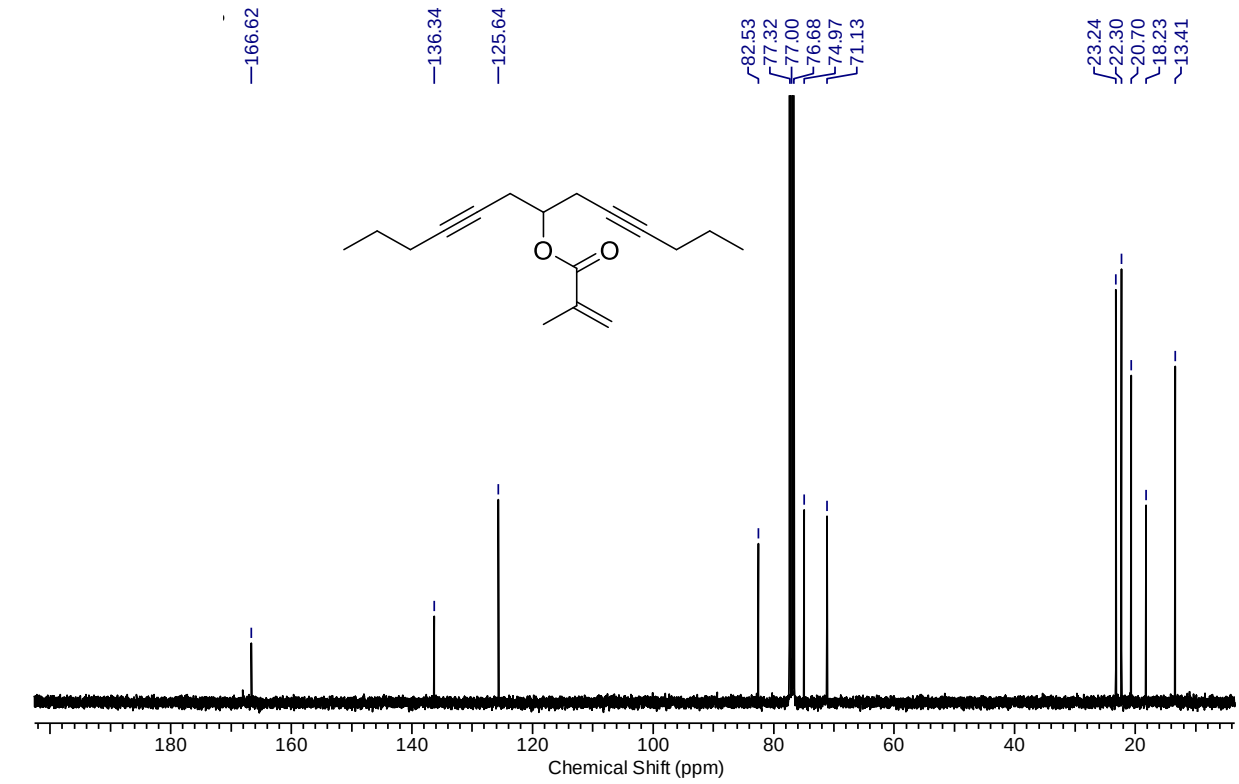


Figure S24. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, trideca-4,9-diyn-7-yl methacrylate (**11d**).

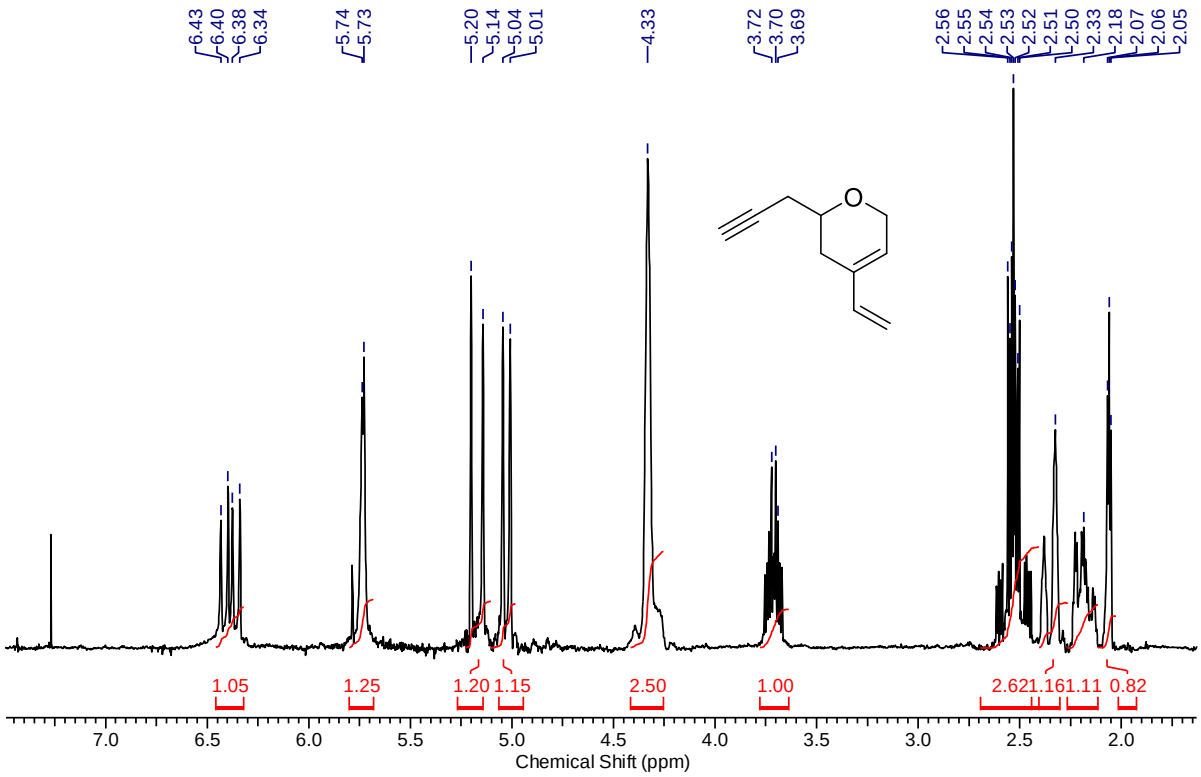


Figure S25. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 4-ethenyl-2-prop-2-yn-1-yl-3,6-dihydro-*2H*-pyran (**12a**).

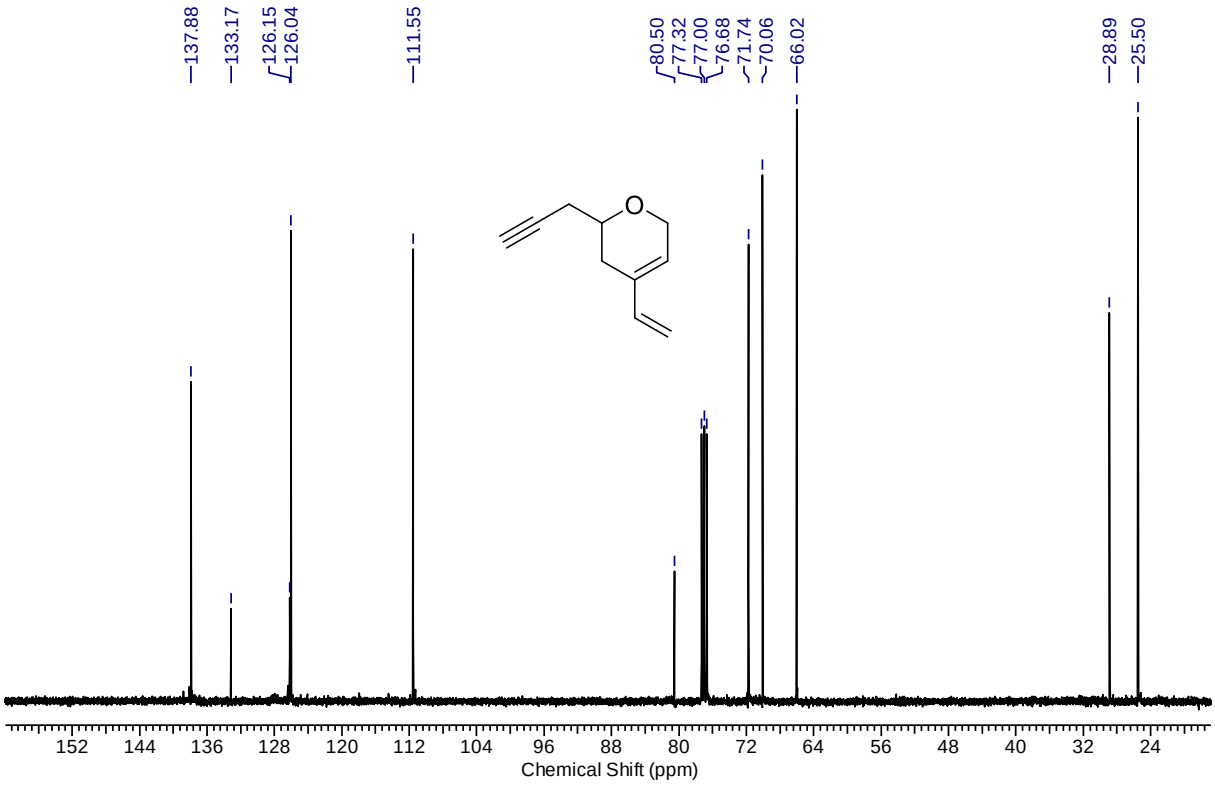


Figure S26. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 4-ethenyl-2-prop-2-yn-1-yl-3,6-dihydro-*2H*-pyran (**12a**).

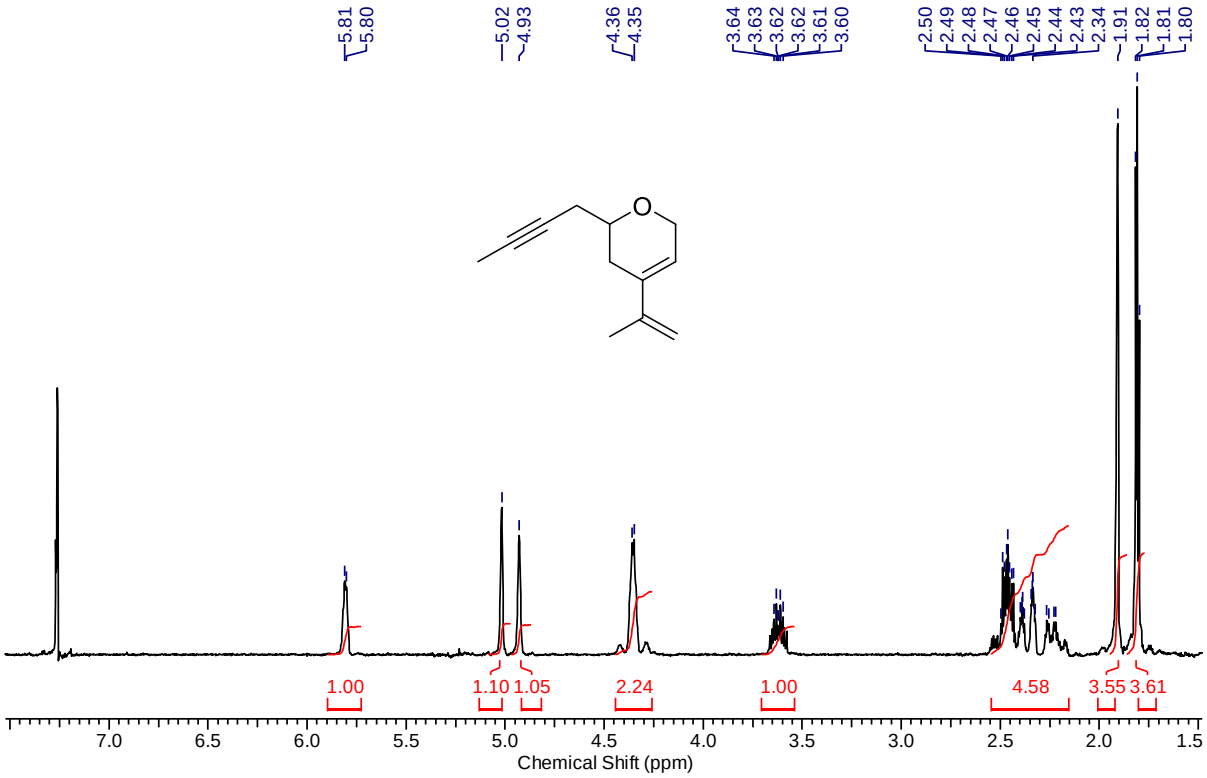


Figure S27. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 2-(but-2-yn-1-yl)-4-(prop-1-en-2-yl)-3,6-dihydro-2*H*-pyran (**12b**).

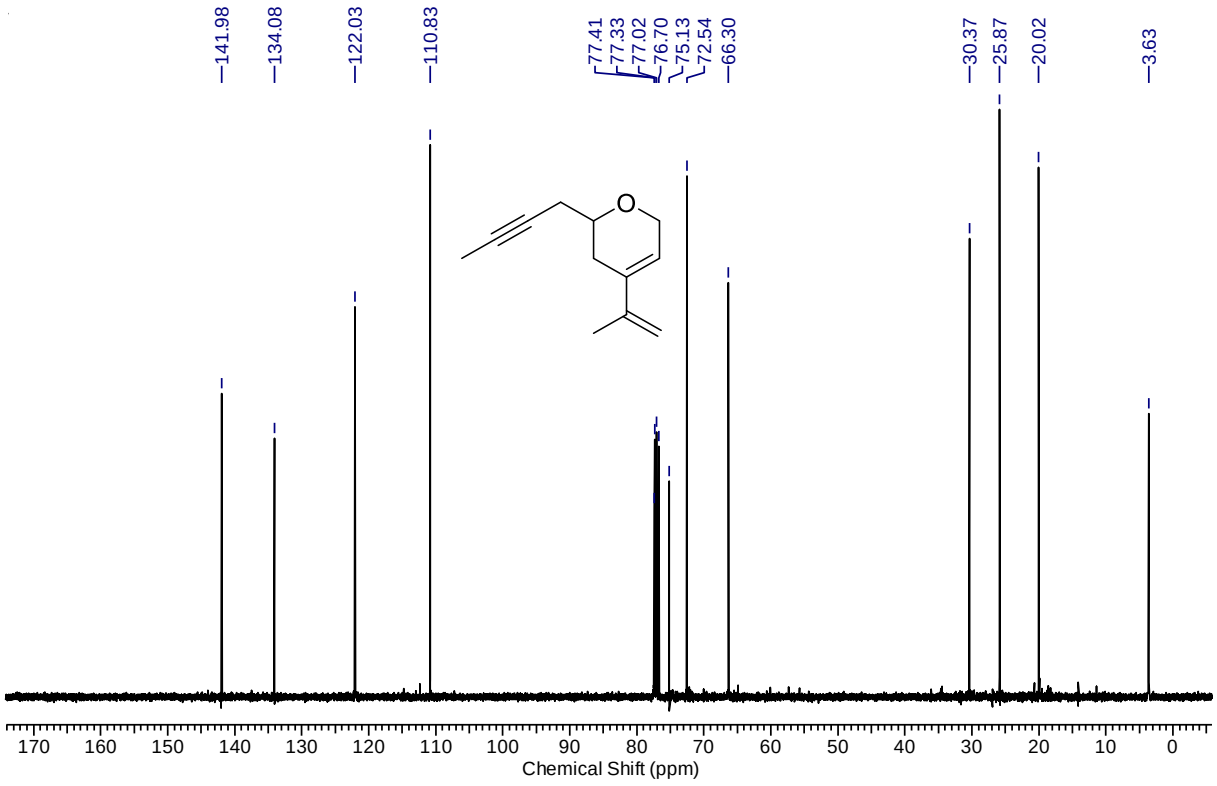


Figure S28. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 2-(but-2-yn-1-yl)-4-(prop-1-en-2-yl)-3,6-dihydro-2*H*-pyran (**12b**).

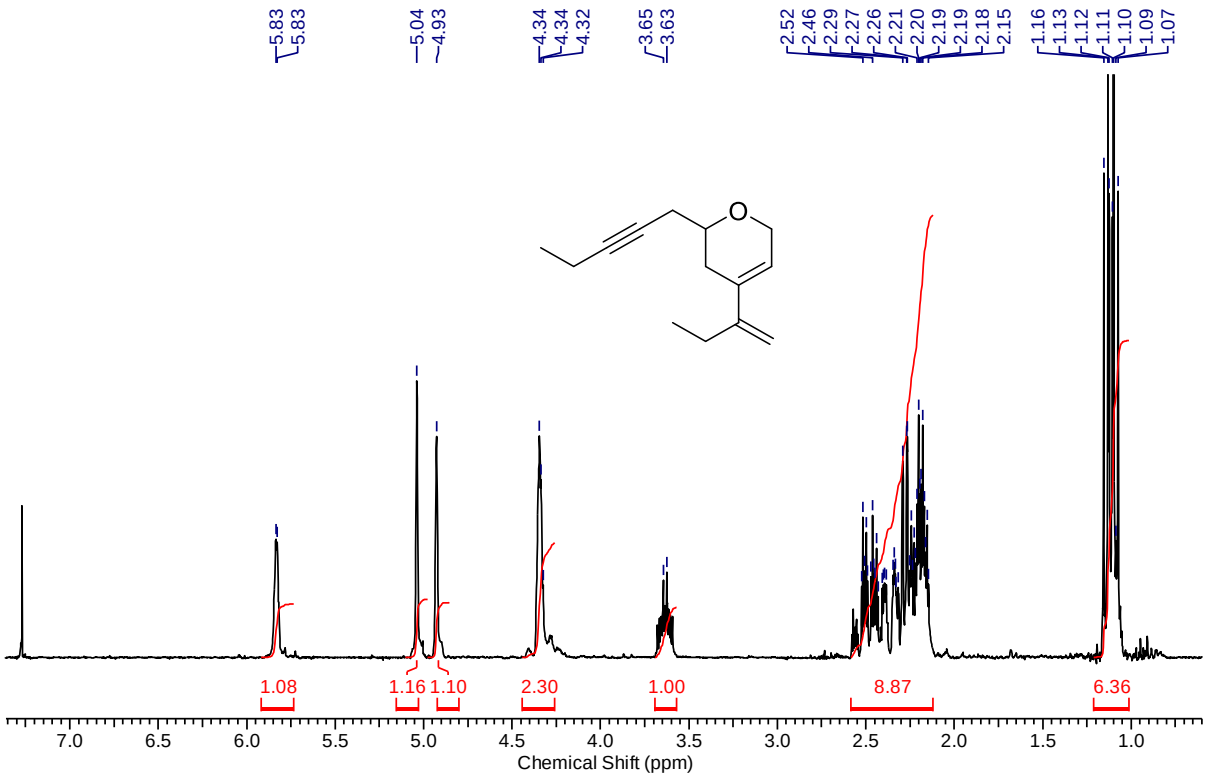


Figure S29. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 4-(but-1-en-2-yl)-2-(pent-2-yn-1-yl)-3,6-dihydro-2*H*-pyran (**12c**).

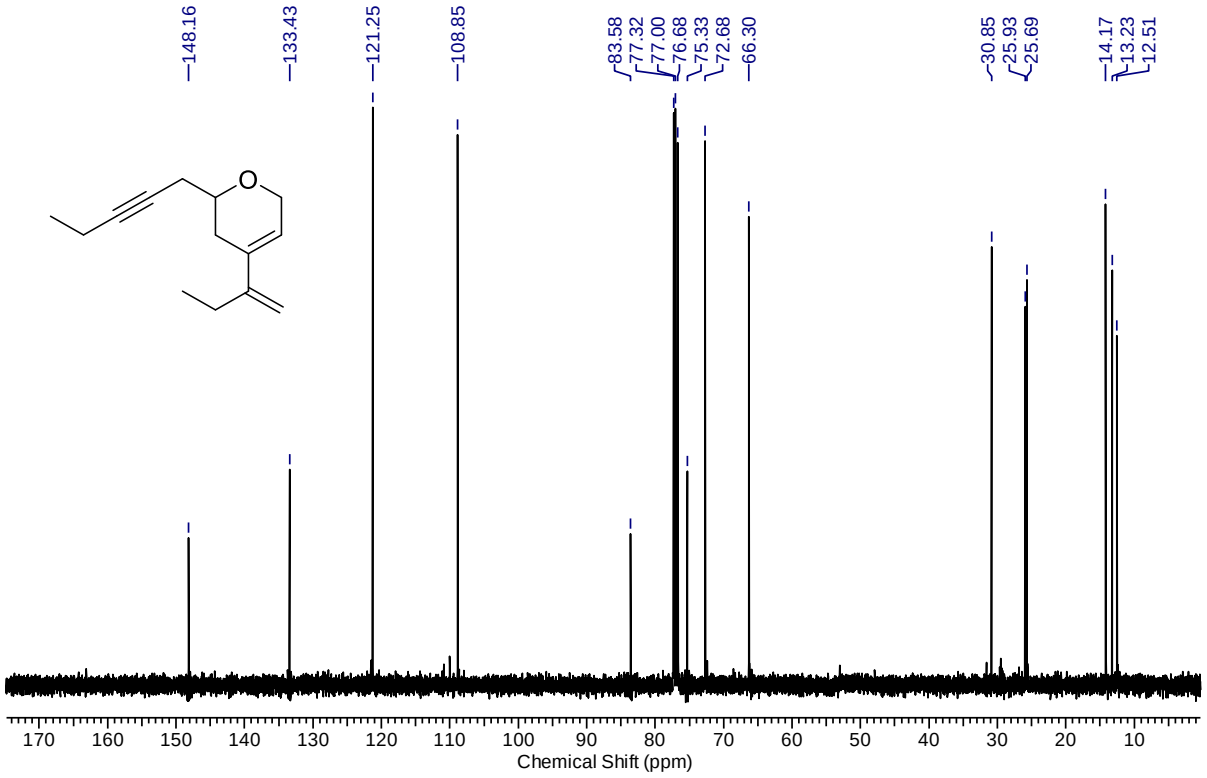


Figure S30. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 4-(but-1-en-2-yl)-2-(pent-2-yn-1-yl)-3,6-dihydro-2*H*-pyran (**12c**).

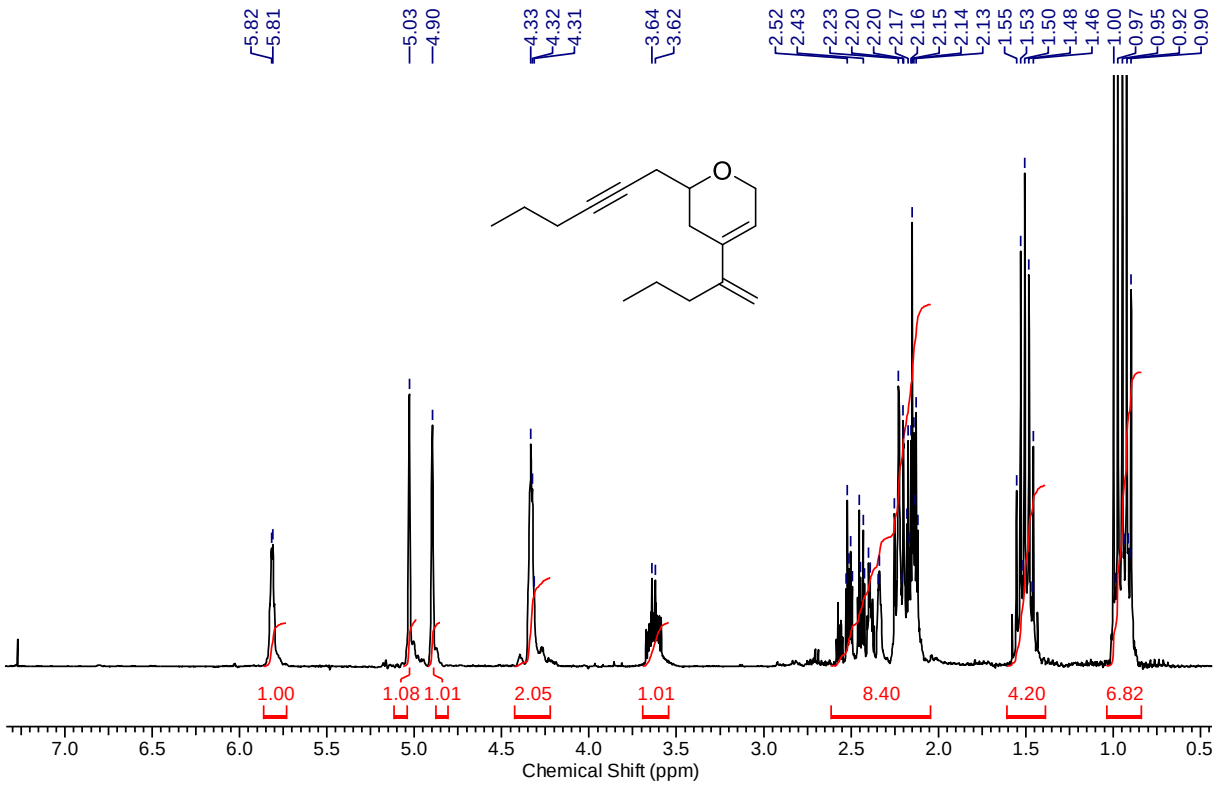


Figure S31. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 2-(hex-2-yn-1-yl)-4-(pent-1-en-2-yl)-3,6-dihydro-2*H*-pyran (**12d**).

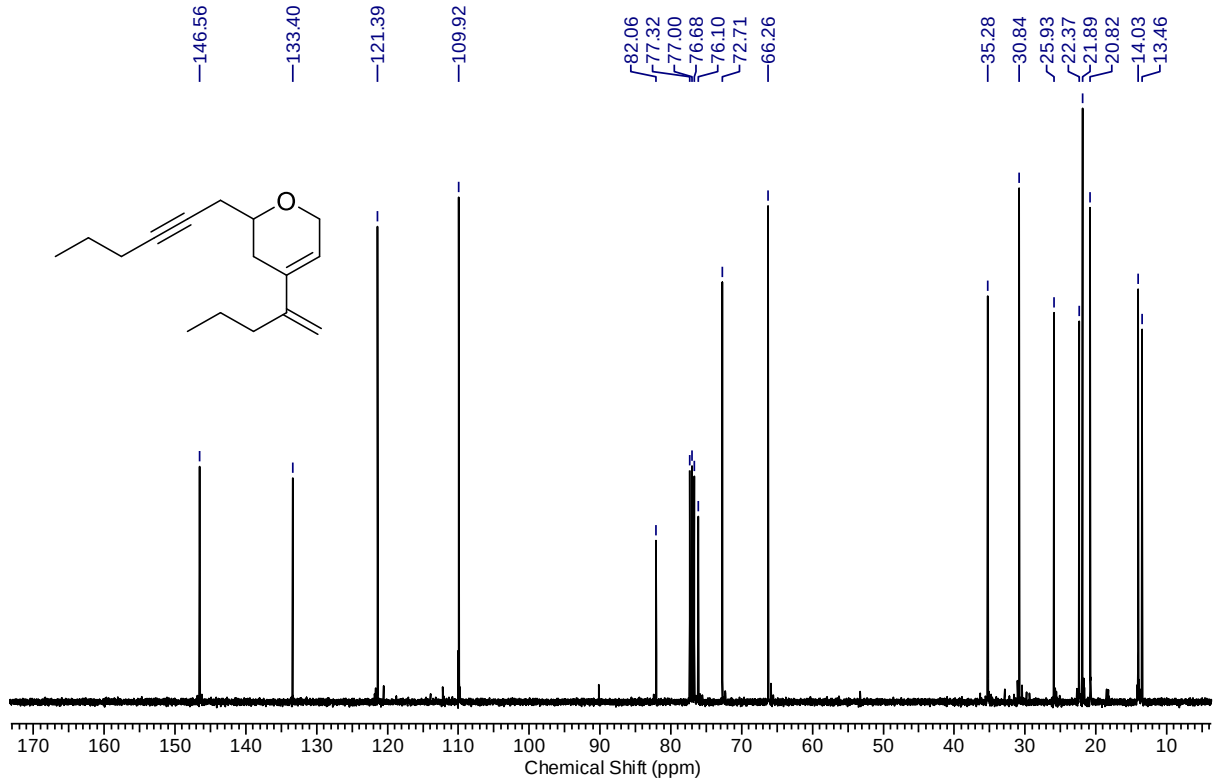


Figure S32. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 2-(hex-2-yn-1-yl)-4-(pent-1-en-2-yl)-3,6-dihydro-2*H*-pyran (**12d**).

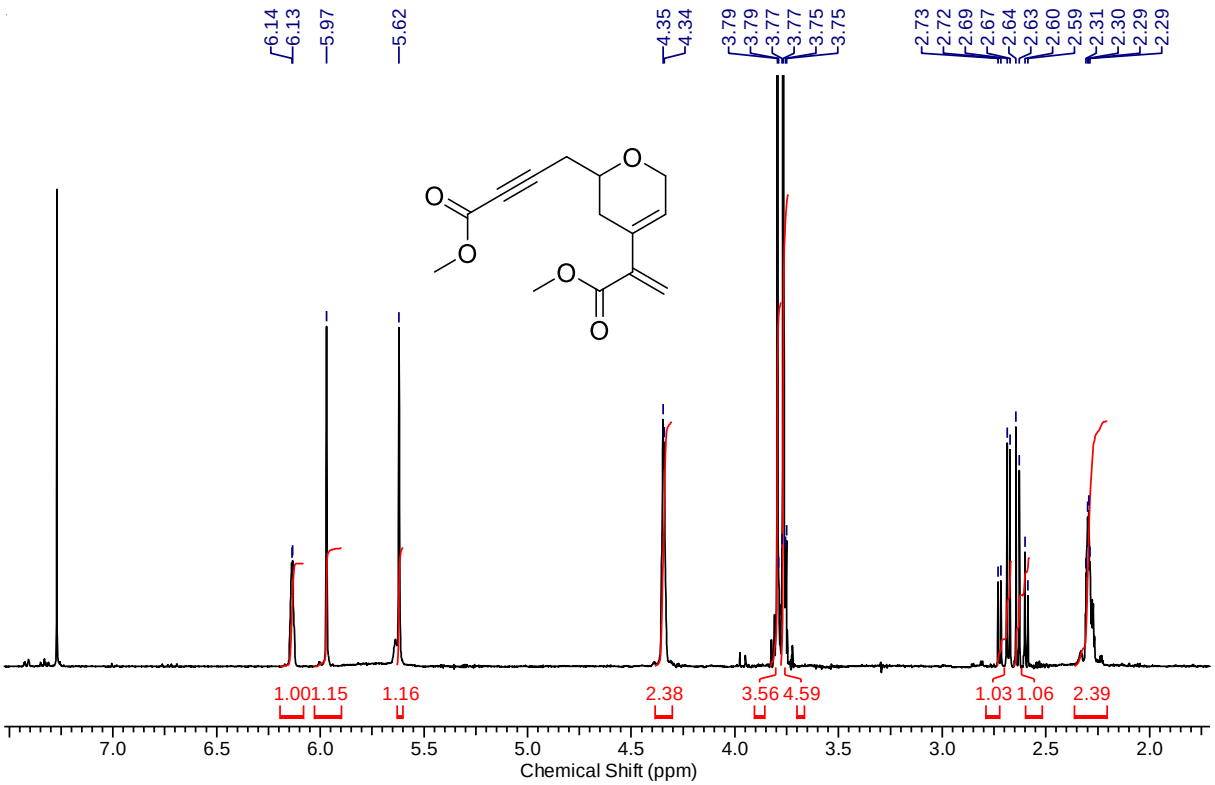


Figure S33. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, methyl 4-(4-(3-methoxy-3-oxoprop-1-en-2-yl)-3,6-dihydro-2*H*-pyran-2-yl)but-2-ynoate (**12e**).

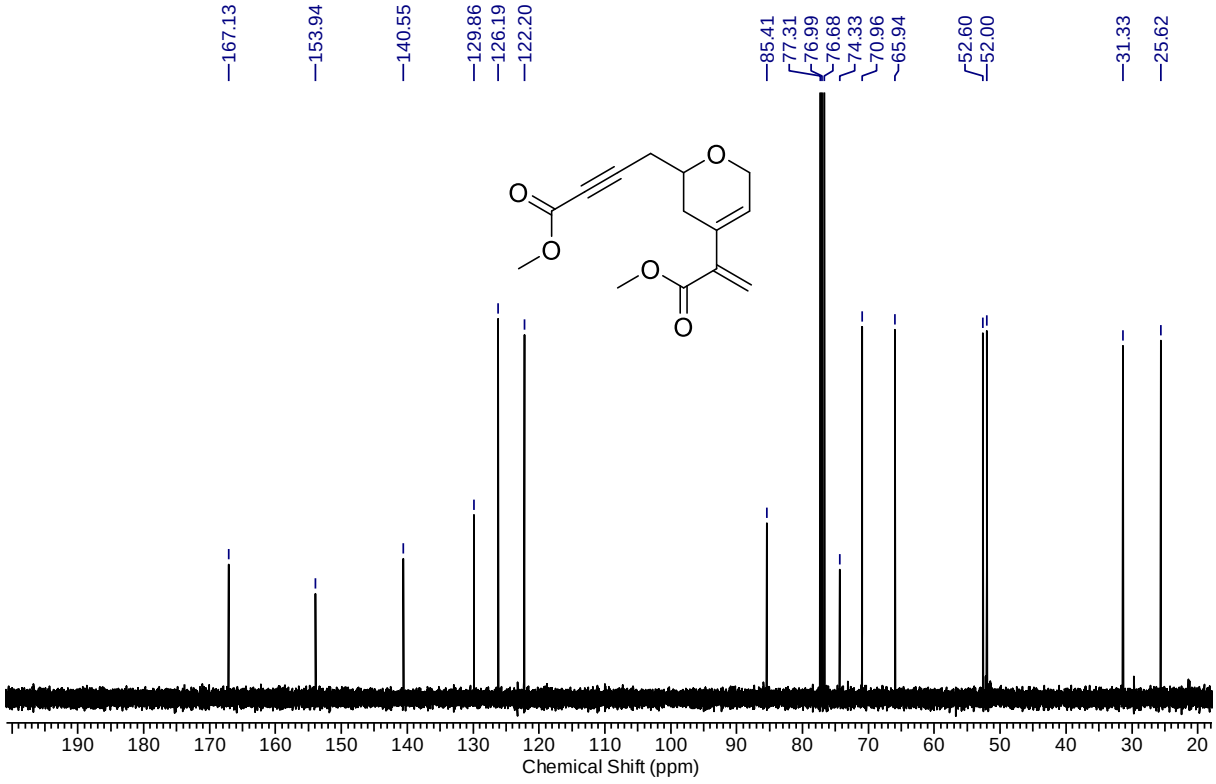


Figure S34. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, methyl 4-(4-(3-methoxy-3-oxoprop-1-en-2-yl)-3,6-dihydro-2*H*-pyran-2-yl)but-2-ynoate (**12e**).

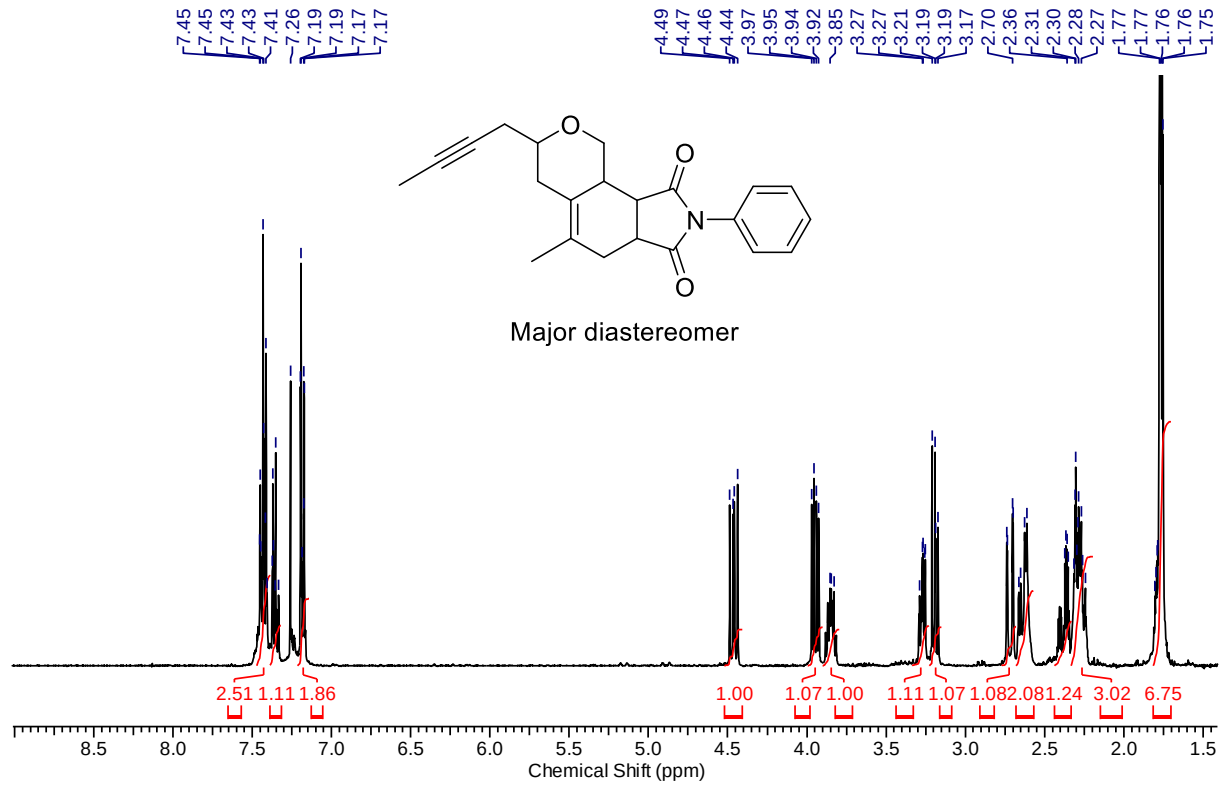


Figure S35. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 3-(but-2-yn-1-yl)-5-methyl-8-phenyl-3,4,6,6a,9a,9b-hexahydropyrano[3,4-e]isoindole-7,9(1*H*,8*H*)-dione (**14**, major diastereoisomer).

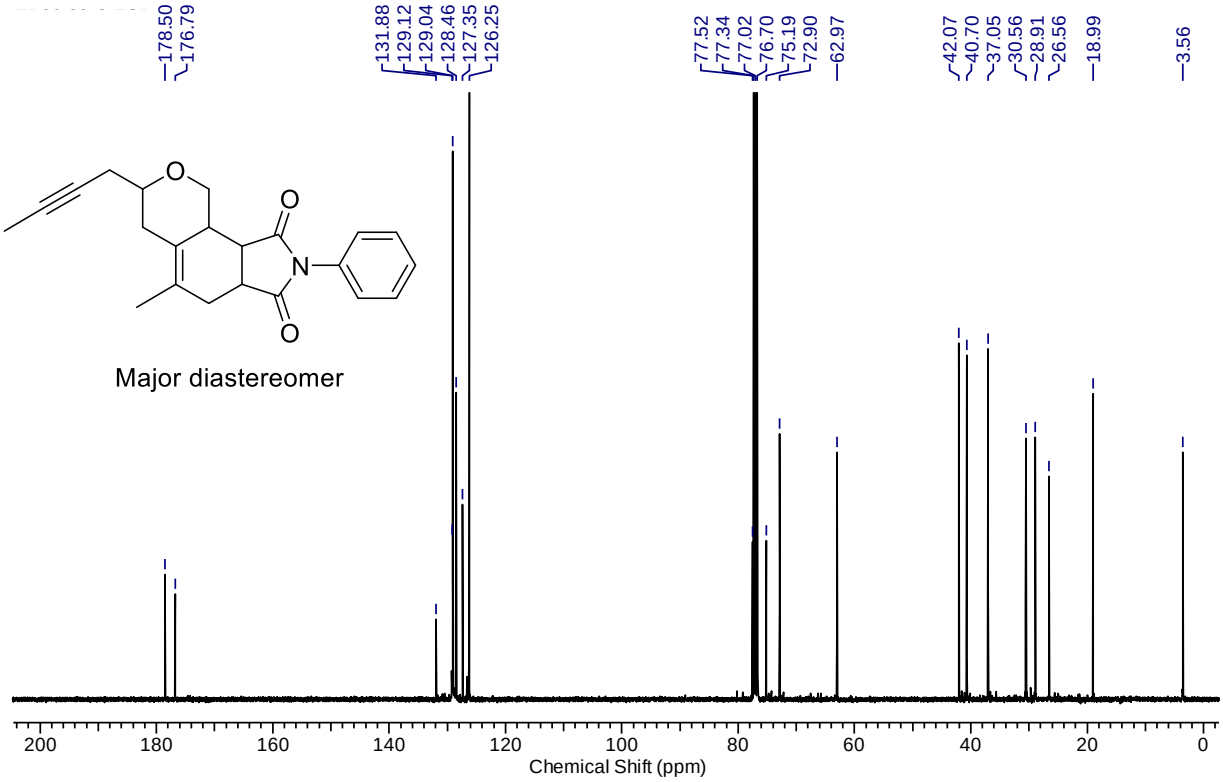


Figure S36. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 3-(but-2-yn-1-yl)-5-methyl-8-phenyl-3,4,6,6a,9a,9b-hexahydropyrano[3,4-e]isoindole-7,9(1*H*,8*H*)-dione (**14**, major diastereoisomer).

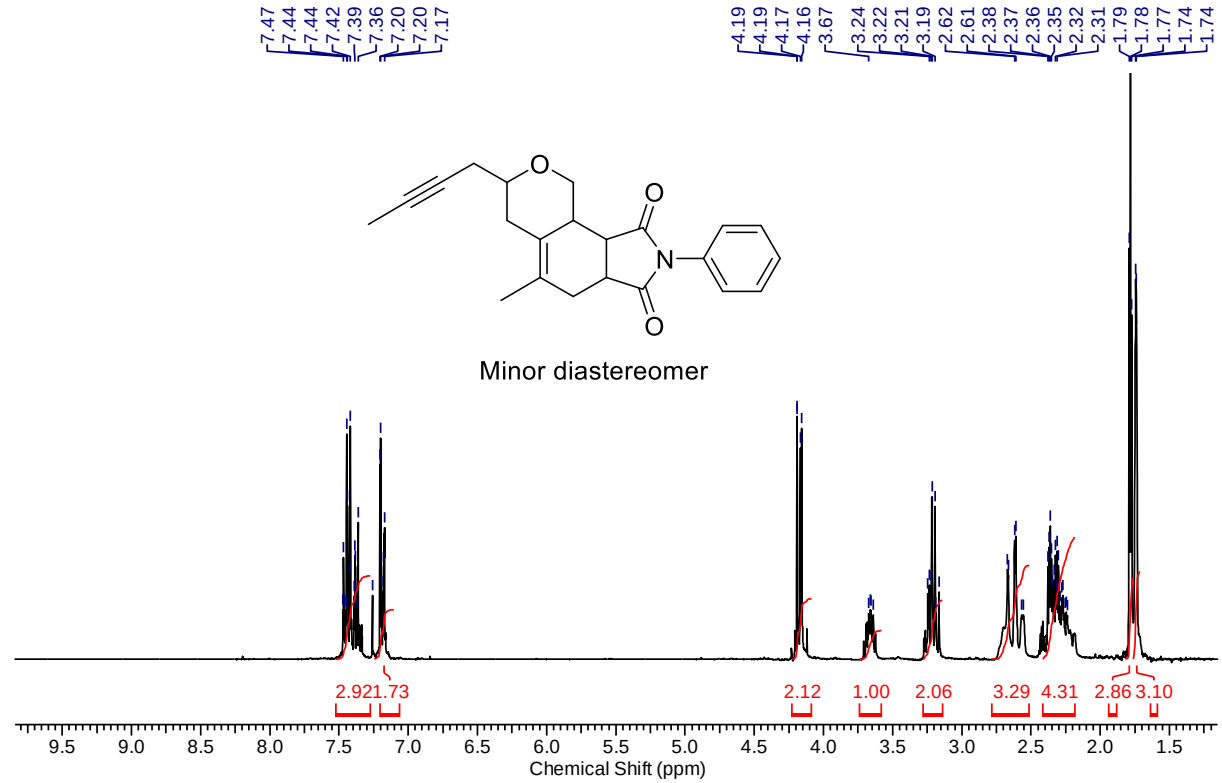


Figure S37. $^{1}$H NMR spectrum, 299.97 MHz, $CDCl_3$, 3-(but-2-yn-1-yl)-5-methyl-8-phenyl-3,4,6,6a,9a,9b-hexahydropyrano[3,4-e]isoindole-7,9(1*H*,8*H*)-dione (**14**, minor diastereoisomer).

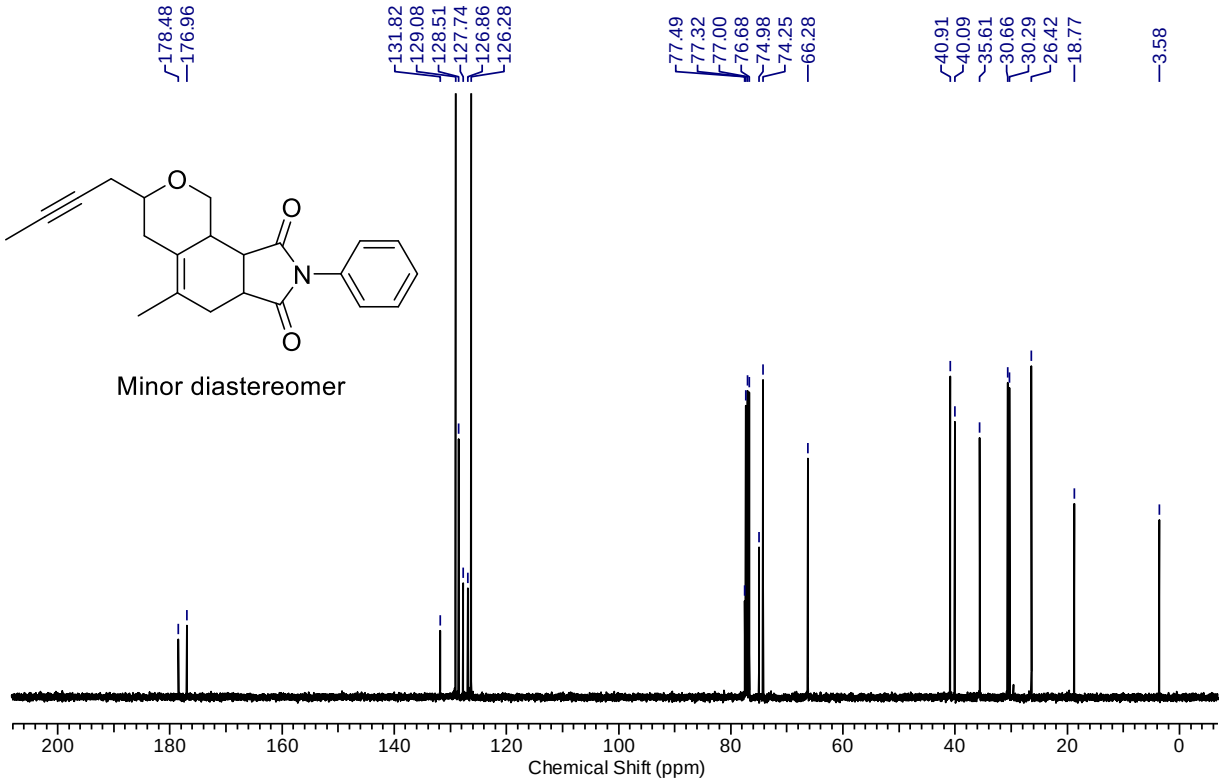


Figure S38. $^{13}$C{1H} NMR spectrum, 75.44 MHz, $CDCl_3$, 3-(but-2-yn-1-yl)-5-methyl-8-phenyl-3,4,6,6a,9a,9b-hexahydropyrano[3,4-e]isoindole-7,9(1*H*,8*H*)-dione (**14**, minor diastereoisomer).

## 3. XYZ of all computed geometries (SMD(DCM)-RI-M06L/def2-SVP)

### 12b + 13, *endo-cis* complex

Gibbs free energy: -2969959.217 kJ/mol

| | | | |
|---|---|---|---|
| C | -0.57768 | -0.31897 | 1.62671 |
| C | -0.49889 | -1.63417 | 1.91955 |
| C | -1.38480 | -2.65302 | 1.29139 |
| C | -2.68845 | -0.92227 | 0.39258 |
| C | -1.65526 | 0.15469 | 0.68642 |
| H | -0.79902 | -3.52919 | 0.95512 |
| H | -3.36372 | -1.02034 | 1.27250 |
| H | -1.20964 | 0.51700 | -0.26321 |
| H | -2.17335 | 1.03272 | 1.11412 |
| H | -2.11287 | -3.05236 | 2.03749 |
| O | -2.06694 | -2.17518 | 0.15910 |
| H | 0.22198 | -2.00070 | 2.66328 |
| C | 0.34512 | 0.69042 | 2.19922 |
| C | 1.58970 | 0.37195 | 2.60495 |
| H | 2.25660 | 1.13246 | 3.03429 |
| H | 1.99968 | -0.64054 | 2.50298 |
| C | -0.14119 | 2.10692 | 2.27409 |
| H | -0.36907 | 2.51436 | 1.27083 |
| H | -1.07509 | 2.19569 | 2.86161 |
| H | 0.61324 | 2.76783 | 2.73307 |
| C | -3.52433 | -0.62884 | -0.84909 |
| H | -4.21082 | -1.48083 | -1.01421 |
| H | -2.84430 | -0.61277 | -1.72464 |
| C | -4.27205 | 0.61622 | -0.77137 |
| C | -4.88837 | 1.66299 | -0.69569 |
| C | -5.62002 | 2.91118 | -0.60861 |
| H | -5.03747 | 3.75627 | -1.01821 |
| H | -6.57065 | 2.86837 | -1.17020 |
| H | -5.87160 | 3.16452 | 0.43717 |
| C | 2.10224 | -1.90746 | -0.29258 |
| C | 1.19123 | -2.96877 | -0.78789 |
| C | 0.33674 | -2.43234 | -1.66582 |
| C | 0.65175 | -0.98778 | -1.82109 |
| H | 1.26318 | -3.99925 | -0.43314 |
| H | -0.47334 | -2.90754 | -2.22213 |
| O | 2.98015 | -2.01226 | 0.53223 |
| O | 0.10617 | -0.18451 | -2.54301 |
| N | 1.73956 | -0.72314 | -0.96754 |
| C | 2.37121 | 0.53391 | -0.80423 |
| C | 1.61066 | 1.70986 | -0.82298 |
| C | 3.75498 | 0.60517 | -0.59951 |
| C | 2.22962 | 2.94134 | -0.62319 |
| H | 0.53176 | 1.66160 | -0.98874 |
| C | 4.36077 | 1.84258 | -0.38746 |
| H | 4.35741 | -0.30630 | -0.60044 |
| C | 3.60410 | 3.01490 | -0.39481 |

| | | | |
|---|---|---|---|
| H | 1.62204 | 3.85405 | -0.63431 |
| H | 5.44344 | 1.88674 | -0.22116 |
| H | 4.08716 | 3.98482 | -0.22938 |

**12b + 13, *endo-trans* complex**

Gibbs free energy: -2969956.083 kJ/mol

| | | | |
|---|---|---|---|
| C | 1.66431 | 1.37212 | 0.73828 |
| C | 2.39841 | 1.74359 | -0.33764 |
| C | 1.87847 | 2.63942 | -1.40417 |
| C | -0.27254 | 2.36947 | -0.51109 |
| C | 0.23139 | 1.83525 | 0.82057 |
| H | 2.60555 | 3.44803 | -1.60893 |
| H | -0.41726 | 1.51622 | -1.20951 |
| H | 0.12699 | 2.61778 | 1.60118 |
| H | -0.42860 | 1.00859 | 1.14294 |
| H | 1.77589 | 2.07262 | -2.36035 |
| O | 0.66871 | 3.26920 | -1.07258 |
| H | 3.44109 | 1.42335 | -0.45064 |
| C | 2.19807 | 0.53635 | 1.83327 |
| C | 3.47133 | 0.08154 | 1.85964 |
| H | 3.82185 | -0.55401 | 2.68333 |
| H | 4.21518 | 0.33996 | 1.09719 |
| C | 1.26427 | 0.17313 | 2.94826 |
| H | 0.82985 | 1.07045 | 3.42704 |
| H | 0.40695 | -0.42724 | 2.59386 |
| H | 1.77724 | -0.41231 | 3.72892 |
| C | -1.57538 | 3.15213 | -0.40258 |
| H | -1.83089 | 3.52757 | -1.41176 |
| H | -1.37965 | 4.05318 | 0.21257 |
| C | -2.69315 | 2.40412 | 0.15015 |
| C | -3.64548 | 1.80845 | 0.61904 |
| C | -4.79385 | 1.11975 | 1.17387 |
| H | -5.54018 | 1.83457 | 1.56639 |
| H | -5.30562 | 0.49798 | 0.41760 |
| H | -4.51220 | 0.45473 | 2.01016 |
| C | 1.67074 | -2.24701 | 0.23665 |
| C | 2.98170 | -1.86599 | -0.34521 |
| C | 2.77345 | -1.10108 | -1.42759 |
| C | 1.31695 | -0.93521 | -1.62683 |
| H | 3.92171 | -2.21569 | 0.08694 |
| H | 3.50149 | -0.65409 | -2.10836 |
| O | 1.45635 | -2.95504 | 1.19403 |
| O | 0.74952 | -0.33516 | -2.51347 |
| N | 0.68681 | -1.64175 | -0.57668 |
| C | -0.70812 | -1.86256 | -0.46385 |
| C | -1.50144 | -1.98274 | -1.61415 |
| C | -1.30395 | -1.98268 | 0.79951 |
| C | -2.87161 | -2.20789 | -1.49462 |
| H | -1.04520 | -1.90862 | -2.60353 |

| | | | |
|---|---|---|---|
| C | -2.67316 | -2.21960 | 0.90483 |
| H | -0.69260 | -1.91206 | 1.70167 |
| C | -3.46545 | -2.32929 | -0.23808 |
| H | -3.47871 | -2.29945 | -2.40277 |
| H | -3.12416 | -2.31656 | 1.89951 |
| H | -4.54266 | -2.51238 | -0.15027 |

**12b + 13, *exo-cis* complex**

Gibbs free energy: -2969957.267 kJ/mol

| | | | |
|---|---|---|---|
| C | 1.40275 | 0.24960 | -1.22815 |
| C | 0.95328 | -0.91748 | -1.73596 |
| C | 1.55186 | -2.23316 | -1.38458 |
| C | 3.36178 | -1.09423 | -0.41879 |
| C | 2.64031 | 0.24465 | -0.37134 |
| H | 0.75504 | -2.94365 | -1.09445 |
| H | 3.88017 | -1.18769 | -1.39965 |
| H | 2.38107 | 0.50136 | 0.67870 |
| H | 3.33755 | 1.03760 | -0.70061 |
| H | 2.06159 | -2.68829 | -2.26640 |
| O | 2.43923 | -2.16440 | -0.29257 |
| H | 0.09366 | -0.93673 | -2.41925 |
| C | 0.70481 | 1.53633 | -1.44680 |
| C | -0.62276 | 1.58794 | -1.67824 |
| H | -1.13006 | 2.54494 | -1.86133 |
| H | -1.24498 | 0.68324 | -1.71198 |
| C | 1.51710 | 2.79264 | -1.35137 |
| H | 1.93595 | 2.93197 | -0.33662 |
| H | 2.38114 | 2.77805 | -2.04246 |
| H | 0.91111 | 3.68396 | -1.58357 |
| C | 4.37852 | -1.27979 | 0.70147 |
| H | 4.78742 | -2.30512 | 0.62559 |
| H | 3.83955 | -1.24227 | 1.66943 |
| C | 5.45859 | -0.30596 | 0.68596 |
| C | 6.36508 | 0.50582 | 0.66057 |
| C | 7.44627 | 1.47068 | 0.63587 |
| H | 7.35165 | 2.21485 | 1.44728 |
| H | 8.43080 | 0.98294 | 0.75376 |
| H | 7.47275 | 2.02997 | -0.31677 |
| C | -1.75112 | 0.82235 | 1.72110 |
| C | -0.37887 | 0.31277 | 1.96987 |
| C | -0.21796 | -0.84467 | 1.31474 |
| C | -1.47750 | -1.16344 | 0.58896 |
| H | 0.33035 | 0.85159 | 2.60285 |
| H | 0.66229 | -1.49187 | 1.25880 |
| O | -2.26700 | 1.82787 | 2.15037 |
| O | -1.71029 | -2.11225 | -0.12541 |
| N | -2.37435 | -0.12166 | 0.88153 |
| C | -3.69692 | -0.02492 | 0.38784 |
| C | -4.52129 | -1.15659 | 0.37188 |
| C | -4.17870 | 1.19905 | -0.09237 |

| | | | |
|---|---|---|---|
| C | -5.81685 | -1.06150 | -0.13192 |
| H | -4.14501 | -2.10930 | 0.75534 |
| C | -5.48160 | 1.28553 | -0.57874 |
| H | -3.53202 | 2.08087 | -0.08399 |
| C | -6.30339 | 0.15778 | -0.60584 |
| H | -6.45576 | -1.95212 | -0.14478 |
| H | -5.85414 | 2.24752 | -0.94938 |
| H | -7.32538 | 0.22951 | -0.99528 |

**12b + 13, *exo-trans* complex**

Gibbs free energy: -2969955.92 kJ/mol

| | | | |
|---|---|---|---|
| C | 1.40275 | 0.24960 | -1.22815 |
| C | 0.95328 | -0.91748 | -1.73596 |
| C | 1.55186 | -2.23316 | -1.38458 |
| C | 3.36178 | -1.09423 | -0.41879 |
| C | 2.64031 | 0.24465 | -0.37134 |
| H | 0.75504 | -2.94365 | -1.09445 |
| H | 3.88017 | -1.18769 | -1.39965 |
| H | 2.38107 | 0.50136 | 0.67870 |
| H | 3.33755 | 1.03760 | -0.70061 |
| H | 2.06159 | -2.68829 | -2.26640 |
| O | 2.43923 | -2.16440 | -0.29257 |
| H | 0.09366 | -0.93673 | -2.41925 |
| C | 0.70481 | 1.53633 | -1.44680 |
| C | -0.62276 | 1.58794 | -1.67824 |
| H | -1.13006 | 2.54494 | -1.86133 |
| H | -1.24498 | 0.68324 | -1.71198 |
| C | 1.51710 | 2.79264 | -1.35137 |
| H | 1.93595 | 2.93197 | -0.33662 |
| H | 2.38114 | 2.77805 | -2.04246 |
| H | 0.91111 | 3.68396 | -1.58357 |
| C | 4.37852 | -1.27979 | 0.70147 |
| H | 4.78742 | -2.30512 | 0.62559 |
| H | 3.83955 | -1.24227 | 1.66943 |
| C | 5.45859 | -0.30596 | 0.68596 |
| C | 6.36508 | 0.50582 | 0.66057 |
| C | 7.44627 | 1.47068 | 0.63587 |
| H | 7.35165 | 2.21485 | 1.44728 |
| H | 8.43080 | 0.98294 | 0.75376 |
| H | 7.47275 | 2.02997 | -0.31677 |
| C | -1.75112 | 0.82235 | 1.72110 |
| C | -0.37887 | 0.31277 | 1.96987 |
| C | -0.21796 | -0.84467 | 1.31474 |
| C | -1.47750 | -1.16344 | 0.58896 |
| H | 0.33035 | 0.85159 | 2.60285 |
| H | 0.66229 | -1.49187 | 1.25880 |
| O | -2.26700 | 1.82787 | 2.15037 |
| O | -1.71029 | -2.11225 | -0.12541 |
| N | -2.37435 | -0.12166 | 0.88153 |
| C | -3.69692 | -0.02492 | 0.38784 |

| | | | |
|---|---|---|---|
| C | -4.52129 | -1.15659 | 0.37188 |
| C | -4.17870 | 1.19905 | -0.09237 |
| C | -5.81685 | -1.06150 | -0.13192 |
| H | -4.14501 | -2.10930 | 0.75534 |
| C | -5.48160 | 1.28553 | -0.57874 |
| H | -3.53202 | 2.08087 | -0.08399 |
| C | -6.30339 | 0.15778 | -0.60584 |
| H | -6.45576 | -1.95212 | -0.14478 |
| H | -5.85414 | 2.24752 | -0.94938 |
| H | -7.32538 | 0.22951 | -0.99528 |

***endo-cis*-14A (*(3S,6aS,9aR,9bS)-14*)**

Gibbs free energy: -2970096.053 kJ/mol

| | | | |
|---|---|---|---|
| C | -1.20326 | -1.19442 | 0.41326 |
| C | -0.80565 | -1.88743 | -0.87152 |
| C | -1.54898 | -1.26915 | -2.04597 |
| C | -3.33884 | -0.45868 | -0.67842 |
| C | -2.17475 | -0.06986 | 0.23831 |
| H | -1.19864 | -0.24232 | -2.26629 |
| H | -4.06155 | -1.06483 | -0.09752 |
| H | -1.64783 | 0.79819 | -0.21370 |
| H | -2.57745 | 0.29127 | 1.19859 |
| H | -1.41002 | -1.85993 | -2.96720 |
| O | -2.93389 | -1.28629 | -1.76621 |
| H | -1.14533 | -2.94303 | -0.81763 |
| C | -0.63913 | -1.63225 | 1.55905 |
| C | 0.35786 | -2.75511 | 1.41956 |
| H | 0.90186 | -2.93153 | 2.36362 |
| H | -0.15625 | -3.70542 | 1.17297 |
| C | -0.87583 | -1.09098 | 2.92749 |
| H | 0.05833 | -0.67338 | 3.35325 |
| H | -1.64080 | -0.29813 | 2.96125 |
| H | -1.18950 | -1.89250 | 3.62434 |
| C | -4.07406 | 0.76004 | -1.25002 |
| H | -4.84270 | 0.38932 | -1.95492 |
| H | -3.35816 | 1.34415 | -1.86291 |
| C | -4.68863 | 1.60878 | -0.24162 |
| C | -5.20433 | 2.29493 | 0.62192 |
| C | -5.82241 | 3.11796 | 1.64259 |
| H | -6.56183 | 3.81681 | 1.21116 |
| H | -6.35359 | 2.50653 | 2.39424 |
| H | -5.07748 | 3.72715 | 2.18579 |
| C | 1.37418 | -0.62738 | -1.28201 |
| C | 0.72942 | -1.96753 | -0.99833 |
| C | 1.37067 | -2.45396 | 0.30659 |
| C | 2.29737 | -1.33712 | 0.73685 |
| H | 0.97839 | -2.62410 | -1.85169 |
| H | 2.00067 | -3.34594 | 0.13702 |
| O | 1.19192 | 0.08926 | -2.23971 |
| O | 2.95376 | -1.28276 | 1.75057 |

| | | | |
|---|---|---|---|
| N | 2.25971 | -0.33430 | -0.23830 |
| C | 3.03584 | 0.85427 | -0.16997 |
| C | 4.41373 | 0.76526 | 0.04807 |
| C | 2.42189 | 2.10160 | -0.31334 |
| C | 5.17636 | 1.92906 | 0.12320 |
| H | 4.88519 | -0.21679 | 0.15479 |
| C | 3.19482 | 3.25986 | -0.24530 |
| H | 1.34040 | 2.16281 | -0.47059 |
| C | 4.57072 | 3.17776 | -0.02567 |
| H | 6.25631 | 1.85733 | 0.29596 |
| H | 2.71214 | 4.23741 | -0.35874 |
| H | 5.17349 | 4.09145 | 0.03071 |

***endo-trans*-14B (*(3S,6aR,9aS,9bR)-14*)**

Gibbs free energy: -2970099.658 kJ/mol

| | | | |
|---|---|---|---|
| C | -1.20478 | -1.80903 | -0.03738 |
| C | -0.51110 | -2.08340 | 1.28543 |
| C | -0.99974 | -1.07892 | 2.32149 |
| C | -1.87932 | 0.46118 | 0.71771 |
| C | -2.34316 | -0.84110 | 0.06202 |
| H | -2.02292 | -1.33299 | 2.66455 |
| H | -1.31697 | 1.05373 | -0.03112 |
| H | -3.16171 | -1.27792 | 0.67161 |
| H | -2.78605 | -0.60967 | -0.91916 |
| H | -0.35327 | -1.06308 | 3.21345 |
| O | -0.95713 | 0.22661 | 1.78033 |
| H | -0.79668 | -3.09959 | 1.62675 |
| C | -0.77677 | -2.42764 | -1.15836 |
| C | 0.45908 | -3.27943 | -1.04115 |
| H | 0.86914 | -3.51270 | -2.03911 |
| H | 0.24288 | -4.25272 | -0.55681 |
| C | -1.36995 | -2.29764 | -2.51962 |
| H | -2.28893 | -1.69078 | -2.55310 |
| H | -0.63958 | -1.84882 | -3.22125 |
| H | -1.61481 | -3.29346 | -2.93769 |
| C | -3.03586 | 1.30885 | 1.25869 |
| H | -2.60331 | 2.20030 | 1.75198 |
| H | -3.54268 | 0.73517 | 2.06110 |
| C | -3.99771 | 1.71409 | 0.24601 |
| C | -4.78866 | 2.04744 | -0.61753 |
| C | -5.73496 | 2.44755 | -1.64005 |
| H | -6.52981 | 1.69303 | -1.78201 |
| H | -6.23279 | 3.40078 | -1.38537 |
| H | -5.24267 | 2.58980 | -2.61913 |
| C | 1.88511 | -1.23086 | -0.90053 |
| C | 1.50525 | -2.53486 | -0.22257 |
| C | 1.04522 | -2.11294 | 1.17107 |
| C | 1.67133 | -0.75033 | 1.36371 |
| H | 2.43463 | -3.13197 | -0.14846 |
| H | 1.43094 | -2.76970 | 1.96754 |

| | | | |
|---|---|---|---|
| O | 2.07527 | -1.05212 | -2.08188 |
| O | 1.90222 | -0.18004 | 2.40306 |
| N | 1.99773 | -0.24948 | 0.09032 |
| C | 2.42260 | 1.08464 | -0.13778 |
| C | 1.75537 | 2.13210 | 0.50851 |
| C | 3.49099 | 1.35323 | -0.99928 |
| C | 2.16278 | 3.44604 | 0.28993 |
| H | 0.91823 | 1.90507 | 1.17680 |
| C | 3.88321 | 2.67306 | -1.21729 |
| H | 4.01319 | 0.53043 | -1.49534 |
| C | 3.22424 | 3.72175 | -0.57409 |
| H | 1.63894 | 4.26434 | 0.79738 |
| H | 4.71942 | 2.88145 | -1.89469 |
| H | 3.53890 | 4.75760 | -0.74598 |

***exo-cis*-14C (*(3S,6aR,9aS,9bS)-14*)**

Gibbs free energy: -2970091.474 kJ/mol

| | | | |
|---|---|---|---|
| C | -1.79110 | 0.73608 | 0.31920 |
| C | -0.69001 | -0.30721 | 0.40276 |
| C | -1.21287 | -1.73980 | 0.30823 |
| C | -3.44273 | -1.17867 | 0.02905 |
| C | -3.21290 | 0.32633 | 0.02128 |
| H | -0.44289 | -2.41656 | -0.09247 |
| H | -3.56329 | -1.52974 | 1.07925 |
| H | -3.49170 | 0.71031 | -0.98210 |
| H | -3.92159 | 0.80420 | 0.72309 |
| H | -1.48258 | -2.10600 | 1.32219 |
| O | -2.33331 | -1.85158 | -0.53578 |
| H | -0.18422 | -0.20576 | 1.38513 |
| C | -1.40644 | 2.02940 | 0.38192 |
| C | 0.06771 | 2.29982 | 0.47991 |
| H | 0.29566 | 3.37295 | 0.36676 |
| H | 0.45699 | 2.00713 | 1.47676 |
| C | -2.31627 | 3.20484 | 0.26839 |
| H | -2.11253 | 3.77893 | -0.65780 |
| H | -3.38528 | 2.93732 | 0.26154 |
| H | -2.15475 | 3.91766 | 1.10006 |
| C | -4.66923 | -1.60102 | -0.77254 |
| H | -4.73120 | -2.70568 | -0.75374 |
| H | -4.50012 | -1.32645 | -1.83291 |
| C | -5.91154 | -1.01764 | -0.29170 |
| C | -6.94556 | -0.52667 | 0.12208 |
| C | -8.17976 | 0.05670 | 0.60890 |
| H | -8.03118 | 0.58469 | 1.56824 |
| H | -8.59619 | 0.79009 | -0.10516 |
| H | -8.95638 | -0.71116 | 0.77772 |
| C | 2.29800 | 1.47930 | -0.33210 |
| C | 0.81476 | 1.49626 | -0.59809 |
| C | 0.38511 | 0.02803 | -0.66586 |
| C | 1.66362 | -0.76119 | -0.48473 |

| | | | |
|---|---|---|---|
| H | 0.66080 | 1.99840 | -1.57057 |
| H | -0.03195 | -0.23828 | -1.65444 |
| O | 3.02020 | 2.43362 | -0.16167 |
| O | 1.80445 | -1.96302 | -0.50901 |
| N | 2.71516 | 0.14295 | -0.27389 |
| C | 4.05543 | -0.25348 | -0.01817 |
| C | 4.31827 | -1.24154 | 0.93650 |
| C | 5.10716 | 0.35195 | -0.71327 |
| C | 5.63411 | -1.62451 | 1.18854 |
| H | 3.49166 | -1.70749 | 1.48087 |
| C | 6.42045 | -0.03052 | -0.44531 |
| H | 4.89696 | 1.11633 | -1.46671 |
| C | 6.68826 | -1.01857 | 0.50317 |
| H | 5.83504 | -2.40102 | 1.93550 |
| H | 7.24261 | 0.44831 | -0.98944 |
| H | 7.72244 | -1.31829 | 0.70816 |

***exo-trans*-14D (*(3S,6aS,9aR,9bR)-14*)**

Gibbs free energy: -2970098.673 kJ/mol

| | | | |
|---|---|---|---|
| C | 1.77907 | 0.68999 | 0.48522 |
| C | 0.71576 | -0.39105 | 0.46967 |
| C | 1.37180 | -1.74255 | 0.20099 |
| C | 3.42702 | -0.84314 | -0.60131 |
| C | 3.18081 | 0.16773 | 0.52378 |
| H | 1.88217 | -2.12056 | 1.11104 |
| H | 3.63561 | -0.29145 | -1.53799 |
| H | 3.35976 | -0.33335 | 1.49837 |
| H | 3.93170 | 0.97074 | 0.45611 |
| H | 0.62502 | -2.49794 | -0.08871 |
| O | 2.27312 | -1.63153 | -0.88031 |
| H | 0.21969 | -0.43015 | 1.46352 |
| C | 1.39379 | 1.98280 | 0.47224 |
| C | -0.08712 | 2.25142 | 0.43084 |
| H | -0.30066 | 3.31807 | 0.24732 |
| H | -0.54442 | 2.01242 | 1.41388 |
| C | 2.29018 | 3.17406 | 0.50610 |
| H | 3.36307 | 2.92431 | 0.52160 |
| H | 2.10869 | 3.83030 | -0.36711 |
| H | 2.08305 | 3.79935 | 1.39653 |
| C | 4.60474 | -1.78254 | -0.31056 |
| H | 4.68396 | -2.50054 | -1.14894 |
| H | 4.35585 | -2.38790 | 0.58436 |
| C | 5.87159 | -1.09623 | -0.11338 |
| C | 6.92015 | -0.49776 | 0.04419 |
| C | 8.17334 | 0.20635 | 0.23131 |
| H | 9.04200 | -0.45332 | 0.05450 |
| H | 8.26947 | 1.06151 | -0.46187 |
| H | 8.27088 | 0.60588 | 1.25703 |
| C | -2.26493 | 1.42375 | -0.50112 |
| C | -0.76376 | 1.39938 | -0.65117 |

| | | | |
|---|---|---|---|
| C | -0.36549 | -0.07502 | -0.58688 |
| C | -1.65224 | -0.82154 | -0.32127 |
| H | -0.51872 | 1.83706 | -1.63515 |
| H | 0.02307 | -0.42192 | -1.56254 |
| O | -2.98711 | 2.39277 | -0.51167 |
| O | -1.79386 | -2.01069 | -0.14755 |
| N | -2.70120 | 0.10794 | -0.29358 |
| C | -4.05553 | -0.23974 | -0.04022 |
| C | -4.37368 | -1.01351 | 1.08021 |
| C | -5.06366 | 0.20436 | -0.90066 |
| C | -5.70305 | -1.34539 | 1.33406 |
| H | -3.57963 | -1.34750 | 1.75506 |
| C | -6.39137 | -0.12566 | -0.63323 |
| H | -4.80557 | 0.80509 | -1.77830 |
| C | -6.71464 | -0.90133 | 0.48134 |
| H | -5.94997 | -1.95202 | 2.21294 |
| H | -7.18067 | 0.22582 | -1.30758 |
| H | -7.75978 | -1.16005 | 0.68635 |

***endo-cis*-15A (TS 12b + 13 to 14A)**

Gibbs free energy: -2969894.554 kJ/mol

One imaginary frequency detected

| | | | |
|---|---|---|---|
| C | -2.13171 | -0.04501 | 0.82617 |
| C | -2.92082 | -0.21455 | -0.28334 |
| C | -3.31562 | 0.93387 | -1.13884 |
| C | -2.02517 | 2.42821 | 0.18329 |
| C | -1.65733 | 1.33719 | 1.19517 |
| H | -2.70098 | 0.95282 | -2.07016 |
| H | -2.20783 | 3.36944 | 0.72905 |
| H | -0.56285 | 1.34501 | 1.35787 |
| H | -2.08764 | 1.58979 | 2.18390 |
| H | -4.36133 | 0.82087 | -1.47542 |
| O | -3.25864 | 2.16402 | -0.45837 |
| H | -3.40673 | -1.16914 | -0.48893 |
| C | -1.72085 | -1.16953 | 1.61535 |
| C | -2.14431 | -2.46071 | 1.27820 |
| H | -1.83373 | -3.28251 | 1.93661 |
| H | -3.13358 | -2.60494 | 0.82960 |
| C | -0.68856 | -0.97519 | 2.67733 |
| H | -0.45070 | -1.91751 | 3.19610 |
| H | 0.25761 | -0.56116 | 2.27509 |
| H | -1.03218 | -0.24770 | 3.43766 |
| C | -0.91727 | 2.70630 | -0.84858 |
| H | -1.35567 | 3.34054 | -1.64331 |
| H | -0.60298 | 1.76704 | -1.34901 |
| C | 0.22935 | 3.37736 | -0.25823 |
| C | 1.15645 | 3.95301 | 0.28186 |
| C | 2.26844 | 4.63818 | 0.91119 |
| H | 2.68336 | 4.05705 | 1.75467 |
| H | 3.09454 | 4.81672 | 0.19926 |

| | | | |
|---|---|---|---|
| H | 1.96713 | 5.62319 | 1.31208 |
| C | -0.26986 | -1.23379 | -1.57792 |
| C | -1.38484 | -2.15187 | -1.48027 |
| C | -1.18347 | -3.01787 | -0.40695 |
| C | 0.21143 | -2.79195 | 0.08302 |
| H | -2.18135 | -2.18186 | -2.22547 |
| H | -1.59795 | -4.02975 | -0.35366 |
| O | -0.05706 | -0.31744 | -2.35189 |
| O | 0.83444 | -3.43708 | 0.89847 |
| N | 0.65788 | -1.63561 | -0.55917 |
| C | 1.94053 | -1.06842 | -0.38296 |
| C | 3.07838 | -1.88450 | -0.34596 |
| C | 2.07406 | 0.31809 | -0.25622 |
| C | 4.33697 | -1.31045 | -0.17557 |
| H | 2.97482 | -2.96741 | -0.45737 |
| C | 3.33784 | 0.88478 | -0.10174 |
| H | 1.18219 | 0.95156 | -0.27649 |
| C | 4.47291 | 0.07380 | -0.05688 |
| H | 5.22306 | -1.95530 | -0.14726 |
| H | 3.43303 | 1.97322 | -0.01371 |
| H | 5.46539 | 0.52178 | 0.06881 |

***endo-trans*-15B (TS 12b + 13 to 14B)**

Gibbs free energy: -2969909.821 kJ/mol

One imaginary frequency detected

| | | | |
|---|---|---|---|
| C | 1.65942 | 1.27923 | 0.83545 |
| C | 2.39027 | 1.70431 | -0.24744 |
| C | 1.83881 | 2.63059 | -1.26820 |
| C | -0.29519 | 2.29239 | -0.35120 |
| C | 0.23503 | 1.75832 | 0.97003 |
| H | 2.54935 | 3.45598 | -1.46025 |
| H | -0.41589 | 1.44206 | -1.05880 |
| H | 0.16732 | 2.54963 | 1.74499 |
| H | -0.42306 | 0.94030 | 1.31614 |
| H | 1.73033 | 2.08277 | -2.23493 |
| O | 0.62060 | 3.22503 | -0.90283 |
| H | 3.45490 | 1.47398 | -0.33743 |
| C | 2.17757 | 0.31036 | 1.75551 |
| C | 3.37398 | -0.35743 | 1.47939 |
| H | 3.72541 | -1.09685 | 2.21137 |
| H | 4.18210 | 0.14412 | 0.93690 |
| C | 1.33937 | -0.13163 | 2.90944 |
| H | 1.05772 | 0.72979 | 3.54456 |
| H | 0.38368 | -0.59167 | 2.59636 |
| H | 1.86830 | -0.86165 | 3.54225 |
| C | -1.62075 | 3.03322 | -0.22968 |
| H | -1.88132 | 3.42479 | -1.23141 |
| H | -1.45747 | 3.92463 | 0.40833 |
| C | -2.71811 | 2.23632 | 0.29546 |
| C | -3.65340 | 1.59524 | 0.73828 |

| | | | |
|---|---|---|---|
| C | -4.78252 | 0.85816 | 1.27041 |
| H | -5.48424 | 1.52609 | 1.80279 |
| H | -5.35723 | 0.35330 | 0.47283 |
| H | -4.46602 | 0.08170 | 1.99003 |
| C | 1.64420 | -2.10583 | 0.22764 |
| C | 2.98058 | -1.54800 | -0.14501 |
| C | 2.80016 | -0.79344 | -1.29737 |
| C | 1.39590 | -0.71810 | -1.62128 |
| H | 3.87176 | -2.14387 | 0.07493 |
| H | 3.56727 | -0.37101 | -1.94928 |
| O | 1.39734 | -2.92960 | 1.08218 |
| O | 0.84172 | -0.15982 | -2.55297 |
| N | 0.70899 | -1.48196 | -0.61180 |
| C | -0.68727 | -1.70878 | -0.57031 |
| C | -1.45095 | -1.73216 | -1.74815 |
| C | -1.32515 | -1.92678 | 0.66116 |
| C | -2.82643 | -1.94930 | -1.68321 |
| H | -0.96772 | -1.58481 | -2.71514 |
| C | -2.69708 | -2.16093 | 0.70925 |
| H | -0.74179 | -1.93562 | 1.58418 |
| C | -3.45860 | -2.16749 | -0.45967 |
| H | -3.40776 | -1.96154 | -2.61284 |
| H | -3.17565 | -2.33638 | 1.68019 |
| H | -4.53925 | -2.34664 | -0.41728 |

***exo-cis*-15C (TS 12b + 13 to 14C)**

Gibbs free energy: -2969900.209 kJ/mol

One imaginary frequency detected

| | | | |
|---|---|---|---|
| C | 1.66258 | 0.52882 | -0.51091 |
| C | 0.78143 | -0.53167 | -0.55057 |
| C | 1.18207 | -1.90768 | -0.16523 |
| C | 3.41167 | -1.21440 | -0.05652 |
| C | 3.07159 | 0.26673 | -0.04928 |
| H | 0.39408 | -2.37016 | 0.45961 |
| H | 3.51061 | -1.55869 | -1.11080 |
| H | 3.21245 | 0.66849 | 0.97635 |
| H | 3.79163 | 0.81693 | -0.68319 |
| H | 1.25730 | -2.54415 | -1.07963 |
| O | 2.37590 | -1.95423 | 0.57015 |
| H | -0.18781 | -0.44359 | -1.05356 |
| C | 1.21653 | 1.87320 | -0.67846 |
| C | -0.14388 | 2.14105 | -0.82227 |
| H | -0.47204 | 3.18424 | -0.91707 |
| H | -0.79123 | 1.42190 | -1.33853 |
| C | 2.16584 | 2.99323 | -0.40242 |
| H | 2.58367 | 2.93746 | 0.62226 |
| H | 3.03731 | 2.96842 | -1.08314 |
| H | 1.68129 | 3.97647 | -0.51636 |
| C | 4.69287 | -1.54716 | 0.69891 |
| H | 4.82557 | -2.64555 | 0.68452 |

| | | | |
|---|---|---|---|
| H | 4.54528 | -1.27620 | 1.76325 |
| C | 5.87629 | -0.88897 | 0.16864 |
| C | 6.86142 | -0.33478 | -0.28276 |
| C | 8.03927 | 0.32232 | -0.81367 |
| H | 7.78421 | 1.01551 | -1.63550 |
| H | 8.56173 | 0.91264 | -0.03939 |
| H | 8.76715 | -0.40548 | -1.21594 |
| C | -2.35848 | 1.61683 | 0.60078 |
| C | -0.93583 | 1.64272 | 1.05523 |
| C | -0.59542 | 0.34200 | 1.41970 |
| C | -1.69415 | -0.55134 | 1.09603 |
| H | -0.55036 | 2.54618 | 1.53632 |
| H | 0.24619 | 0.01652 | 2.03397 |
| O | -3.06411 | 2.55492 | 0.30133 |
| O | -1.79604 | -1.75406 | 1.25260 |
| N | -2.72275 | 0.26500 | 0.53482 |
| C | -3.93755 | -0.22723 | 0.00960 |
| C | -3.92895 | -1.36093 | -0.81450 |
| C | -5.14949 | 0.41292 | 0.29875 |
| C | -5.12474 | -1.85190 | -1.33431 |
| H | -2.98130 | -1.85667 | -1.04621 |
| C | -6.33770 | -0.07695 | -0.24132 |
| H | -5.15828 | 1.29117 | 0.94970 |
| C | -6.33258 | -1.21003 | -1.05590 |
| H | -5.10885 | -2.74198 | -1.97427 |
| H | -7.28131 | 0.43296 | -0.01383 |
| H | -7.27070 | -1.59509 | -1.47198 |

***exo-trans*-15D (TS 12b + 13 to 14D)**

Gibbs free energy: -2969880.25 kJ/mol

One imaginary frequency detected

| | | | |
|---|---|---|---|
| C | 1.62290 | 0.35465 | 1.10791 |
| C | 0.68670 | -0.65782 | 1.00000 |
| C | 1.17152 | -2.03222 | 0.71920 |
| C | 3.19468 | -1.05959 | -0.21653 |
| C | 3.04319 | -0.11841 | 0.97391 |
| H | 1.51398 | -2.50773 | 1.66933 |
| H | 3.08769 | -0.46067 | -1.14630 |
| H | 3.33425 | -0.66831 | 1.89312 |
| H | 3.76330 | 0.70747 | 0.86553 |
| H | 0.35642 | -2.66754 | 0.33237 |
| O | 2.20038 | -2.07625 | -0.24970 |
| H | -0.34319 | -0.54684 | 1.35593 |
| C | 1.25673 | 1.72736 | 1.12675 |
| C | -0.08987 | 2.07102 | 1.03049 |
| H | -0.37347 | 3.13108 | 0.99969 |
| H | -0.85571 | 1.41231 | 1.45675 |
| C | 2.30397 | 2.78636 | 0.97281 |
| H | 3.06809 | 2.72984 | 1.76911 |
| H | 2.85062 | 2.69054 | 0.01404 |

| | | | |
|---|---|---|---|
| H | 1.86559 | 3.79695 | 1.00544 |
| C | 4.55428 | -1.76326 | -0.25053 |
| H | 4.53578 | -2.48996 | -1.08482 |
| H | 4.65634 | -2.36722 | 0.67292 |
| C | 5.68568 | -0.86126 | -0.39535 |
| C | 6.62105 | -0.09108 | -0.51367 |
| C | 7.74356 | 0.81553 | -0.65439 |
| H | 8.70792 | 0.27836 | -0.60335 |
| H | 7.71939 | 1.35136 | -1.62050 |
| H | 7.75442 | 1.58036 | 0.14306 |
| C | -2.09128 | 1.55781 | -0.72442 |
| C | -0.62363 | 1.43982 | -0.95228 |
| C | -0.33296 | 0.08871 | -1.12240 |
| C | -1.54686 | -0.69166 | -0.89589 |
| H | -0.08832 | 2.26506 | -1.42902 |
| H | 0.53829 | -0.35392 | -1.60763 |
| O | -2.76216 | 2.56259 | -0.63540 |
| O | -1.72116 | -1.89313 | -0.95169 |
| N | -2.57048 | 0.24526 | -0.58607 |
| C | -3.88880 | -0.10731 | -0.21999 |
| C | -4.09514 | -1.10174 | 0.74490 |
| C | -4.98694 | 0.52694 | -0.81343 |
| C | -5.39160 | -1.46039 | 1.10738 |
| H | -3.23447 | -1.59010 | 1.21328 |
| C | -6.28007 | 0.17099 | -0.43248 |
| H | -4.82534 | 1.29546 | -1.57447 |
| C | -6.48843 | -0.82398 | 0.52379 |
| H | -5.54376 | -2.24100 | 1.86193 |
| H | -7.13554 | 0.67342 | -0.89905 |
| H | -7.50741 | -1.10410 | 0.81475 |

## References

1. Nicolaou, K. C.; Skokotas, G.; Furaya, S.; Suemune, H.; Nicolaou, D. C., *Angew. Chem.* **1990,** *102*, 1066-1068.