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Supporting Information

Acceleration Effect of Allylic Hydroxy Group on Ring-Closing Enyne Metathesis of Terminal Alkynes: Scope, Application and Mechanistic Insights

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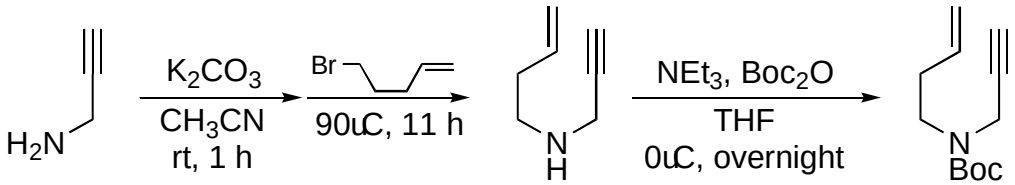
General Comments: NMR spectra were recorded on JNM-EX270 (20 MHz) spectrometer, JEOL JNM-AL400 (400 MHz) spectrometer, JNM-EX400 (400 MHz) spectrometer and JNM-EX600 (600 MHz) pectrometer in $CDCl_3$, C_6D_6, D_2O and CD_2Cl_2. ^{13}C-NMR spectra were recorded using broad band proton decoupling. Residual $CHCl_3$ signal or tetramethylsilane was used as an internal standard for ^{1}H- and ^{13}C-NMR in $CDCl_3$. The C_6D_6 itself was used as an internal standard for ^{13}C-NMR in C_6D_6. The residual non-deuterated H_2O signal was used as internal standard for ^{1}H-NMR and acetonitrile was used as an internal standard in ^{13}C-NMR in D_2O. CD_2Cl_2 was used in NMR studies and kinetic studies with ^{1}H-NMR spectrum. In NMR studies, the residual non-deuterated CH_2Cl_2 was used as an internal standard in chemical shift. In kinetic studies, CH_2ClCH_2Cl was used as internal standard in chemical shift and concentration. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, m = multiplet, br s = broad singlet, br d = broad doublet, dd = double-doublet and ddd = double-double-doublet. Mass spectra were recorded on JEOL JMN-DX303 or JEOL JMA-DA5000 spectrometer. IR spectra were measured with Perkin-Elmer 1725 X series FT-IR spectrometer. CH_2Cl_2 was bubbled with Ar well before use in ring-closing enyne metathesis. LDA = lithium diisopropylamide, LAH = lithium alminum hydride, PCC = pyridiniume chlorochromate, DIBAH = diisobutylalminum hydride

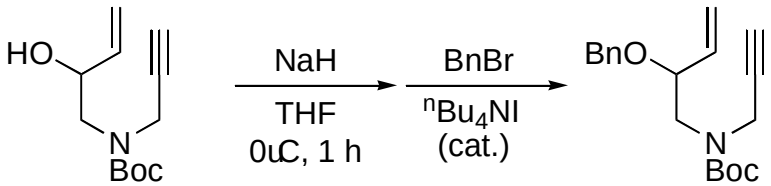
Synthesis of enyne substrates with an allylic or other hydroxy group



1a

***tert*-Butyl but-3-enylprop-2-ynylcarbamate (1a):** To a solution of propargylamine (3.0 mmol) in CH_3CN (12 mL) was added K_2CO_3 (3.0 mmol) at rt and the mixture was stirred for 1 hour. Then 4-bromo-1-butene (3.0 mmol) was added to the mixture and the mixture was warmed to 90 °C. After stirring for 11 hours at 90 °C, the mixture was concentrated in vacuo and the residue was diluted with CH_2Cl_2. The mixture was washed with saturated aqueous solution of $NaHCO_3$ and the organic layer was dried over K_2CO_3. The solvent was evaporated in vacuo and the residue was dissolved in THF (11 mL). Triethylamine (7.5 mmol) and Boc_2O (3.6 mmol) were added to the solution at rt and the mixture was stirred overnight. The solvent of the reaction mixture was evaporated in vacuo and the residue was diluted with Et_2O. The mixture was washed with 1N HCl and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain 313 mg of **1a** (50% yield for 2 steps).

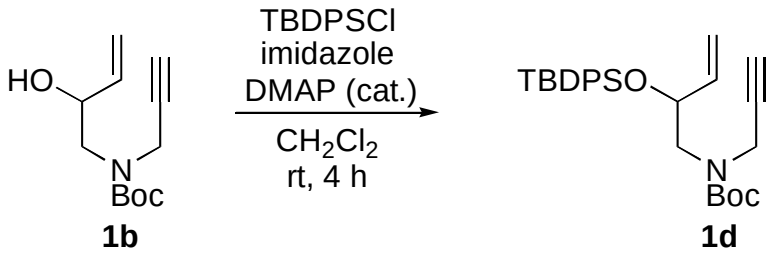
1a: ^{1}H-NMR (400 MHz, $CDCl_3$): *d* = 1.47 (s, 9H), 2.21 (t, *J* = 2.4 Hz, 1H), 2.30-2.35 (m, 2H), 3.38 (t, *J* = 7.2, 2H), 4.07 (br s, 2H), 5.01-5.11 (m, 2H), 5.72-5.83 ppm (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): *d* = 28.3, 32.6, 36.0, 45.9, 71.4, 80.1, 85.1, 116.6, 135.3, 146.7 ppm; IR (neat): $\tilde{n}$ = 1697 cm^{-1}; EI-Ms: *m/z*: 209 (M^+); HRMS: *m/z*: Calcd for $C_{12}H_{19}NO_2$: 209.1416, Found: 209.1410.



1b **1c**

***tert*-Butyl 2-(benzyloxy)but-3-enylprop-2-ynylcarbamate (1c):** To a solution of **1b** (1.2 mmol) in THF (3.0 mL) was added NaH (2.3 mmol) at 0 °C and the mixture was stirred for 1 hour. Then benzyl bromide (3.5 mmol) and *n*-Bu_3NI (20 mg) was added to the mixture at 0 °C. After stirring for 2 hours at 0 °C, the mixture was diluted with Et_2O and washed with saturated aqueous solution of NH_4Cl, H_2O and brine. The organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain 280 mg of **1c** (76% yield).

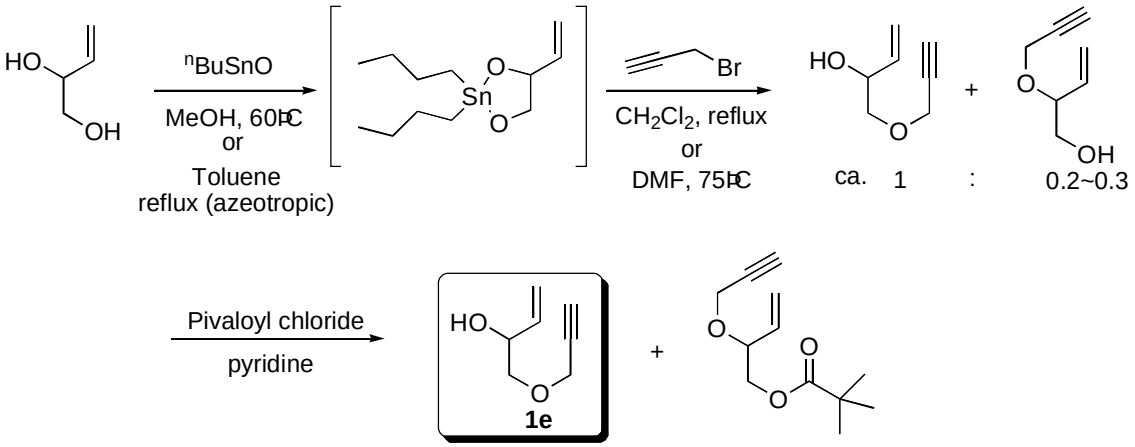
1c: ^{1}H-NMR (400 MHz, $CDCl_3$): d = 1.43 (d, J = 24.6 Hz, 9H), 2.17 (s, 1H), 3.30-3.55 (m, 1H), 4.02-4.26 (m, 3H), 4.35 (d, J = 11.6 Hz, 1H), 4.60 (d, J = 12.1 Hz, 2H), 5.27-5.35 (m, 2H), 5.69-5.78 (m, 1H), 7.23-7.34 ppm (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): d = 28.3, 30.9, 37.2, 38.2, 50.4, 70.4, 70.9, 71. 4, 79.5, 80.2, 118.4, 118.7, 127.5, 128.3, 136.1, 136.3, 154.9 ppm; IR (neat): $\tilde{n}$ = 1698 cm^{-1}; EI-Ms: *m/z*: 315 (M^+); HRMS: *m/z*: Calcd for $C_{12}H_{25}NO_3$: 315.1834, Found: 315.1823.



1b **1d**

***tert*-Butyl 2-(*tert*-butyldiphenylsilyloxy)but-3-enylprop-2-ynylcarbamate (1d):** To a solution of **1b** (0.43 mmol) in CH_2Cl_2 (2.0 mL) was added imidazole (0.65 mmol), DMAP (0.0086 mmol) and TBDPSCl (0.47 mmol) at rt and the mixture was stirred for 4 hours. Then the reaction mixture was filtered with a pad of celite. The filtrate was washed with brine and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain 280 mg of **1d** (86% yield).

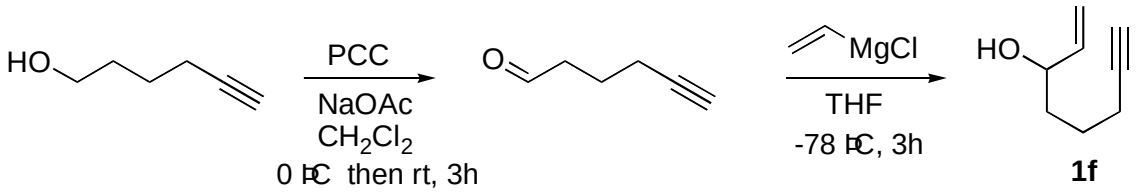
1d: ^{1}H-NMR (400 MHz, $CDCl_3$): d = 1.09 (s, 9H), 1.40 (d, J = 29.5 Hz, 9H), 2.10 (s, 1H), 3.33-3.38 (m, 2H), 3.78-4.03 (m, 2H), 4.34-4.40 (m, 1H), 4.92-5.01 (m, 2H), 5.71-5.80 (m, 1H), 7.25-7.44 (m, 6H), 7.62-7.70 ppm (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): d = 19.2, 27.0, 28.3, 37.0, 37.7, 52.0, 70.9, 71.4, 73.6, 79.7, 80.2, 116.0, 116.2, 127.4, 127.6, 129.6, 129.7, 133.7, 133.8, 135.9, 136.0, 138.2, 138.4, 154.9 ppm; IR (neat): $\tilde{n}$ = 1700 cm^{-1}; EI-Ms: *m/z*: 463(M^+), 464 (M^++H); HRMS: *m/z*: Calcd for $C_{28}H_{37}NO_3Si$: 463.2543, Found: 463.2532.



1-(Prop-2-ynyloxy)but-3-en-2-ol (1e): To a solution of *n*-Bu_2SnO (10 mmol) in MeOH (50 mL) was added 3,4-dihydroxy-1-butene (10 mmol) at rt and the mixture was warmed to 60 °C. After stirring overnight, the mixture was heated under reflux for 2 hours. The mixture was concentrated in vacuo and the residue was dissolved in CH_2Cl_2 (25 mL). Propargyl bromide (10 mmol) was added to the solution at rt and the mixture was heated under reflux for 28 hours. The reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was

dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain a mixture of **1e** and regio-isomer (>27% yield, **1e** : regio-isomer = ca. 1:0.2-0.3 from ^{1}H-NMR). The mixture of regio-isomers was dissolved in CH_2Cl_2 (8 mL) and pyridine (2 mL). Then pivaloyl chloride (1.4 mmol) was added to the solution at 0°C. After stirring overnight, the reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous solution of $NaHCO_3$ and saturated aqueous solution of NH_4Cl. The organic layer was dried over Na_2SO_4. Then the solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1e** (53% yield).

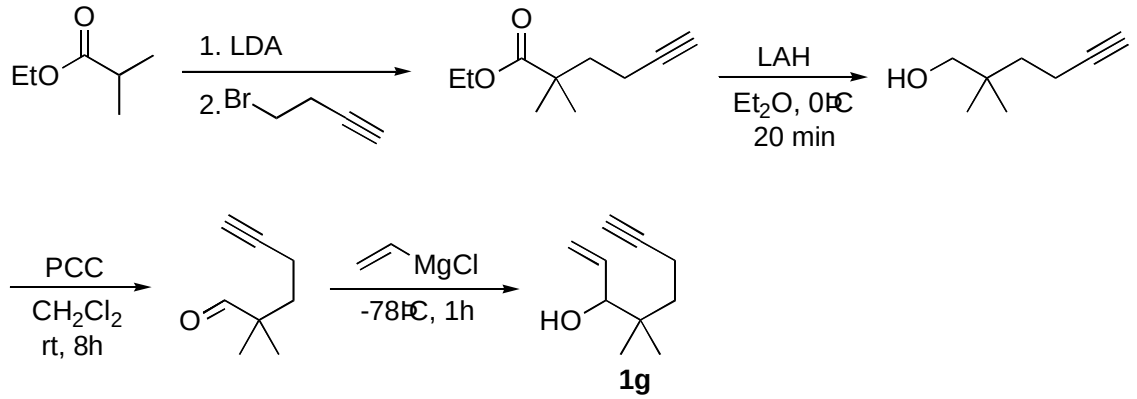
1e: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.30 (d, J = 3.4 Hz, 1H), 2.46 (t, J = 2.4 Hz, 1H), 3.43 (dd, J = 9.7 Hz, 8.2 Hz, 1H), 3.64 (dd, J = 9.7, 3.4 Hz, 1H), 4.22 (dd, J = 3.4, 2.4 Hz, 2H), 4.36 (m, 1H), 5.23 (dt, J = 9.2 Hz, 1.5 Hz, 1H), 5.39 (dt, J = 15.9 Hz, 1.5 Hz, 1H), 5.81-5.90 ppm (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 58.5, 71.3, 73.7, 74.9, 79.3, 116.6, 136.3 ppm; IR (neat): $\tilde{\nu}$ = 3424, 2116, 1647 cm^{-1}; EI-Ms: *m/z*: 125 (M^+-H); HRMS: *m/z*: Calcd for $C_7H_{10}O_2$: 125.0603, Found: 125.0592.



1f

Oct-1-en-7-yn-3-ol (1f): To a solution of PCC (26.7 mmol) and NaOAc (2.7 mmol) in CH_2Cl_2 (25 mL) was added 5-hexyn-1-ol (17.7 mmol) at 0 °C and the mixture was stirred at the temperature. After stirring for 2 hours, the reaction mixture was filtered with a pad of silica gel. The filtrate was concentrated in vacuo. Then the residue was dissolved in THF (60 mL) under Ar atmosphere. Vinylmagnesium chloride (1.44 M THF solution, 17.7 mmol) was added to the solution at -78 °C and the mixture was stirred at the temperature. After stirring for 2 hours, further 0.5 equivalent of vinylmagnesium chloride was added to the mixture to complete reaction. Then the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1f** (>16% yield for 2 steps).

1f: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.47-1.70 (m, 4H), 1.96 (t, J = 2.4 Hz, 1H), 2.24 (m, 2H), 4.14 (m, 1H), 5.13 (d, J = 10.2 Hz, 1H), 5.24 (d, J = 17.1 Hz, 1H), 5.84-5.92 ppm (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 18.3, 24.3, 35.8, 68.5, 72.7, 84.2, 114.9, 140.9 ppm; IR (neat): $\tilde{\nu}$ = 3302, 2116, 1645, 1431 cm^{-1}; EI-Ms: *m/z*: 123 (M^+-H); HRMS: *m/z*: Calcd for $C_8H_{12}O$: 123.0810, Found: 123.0798.

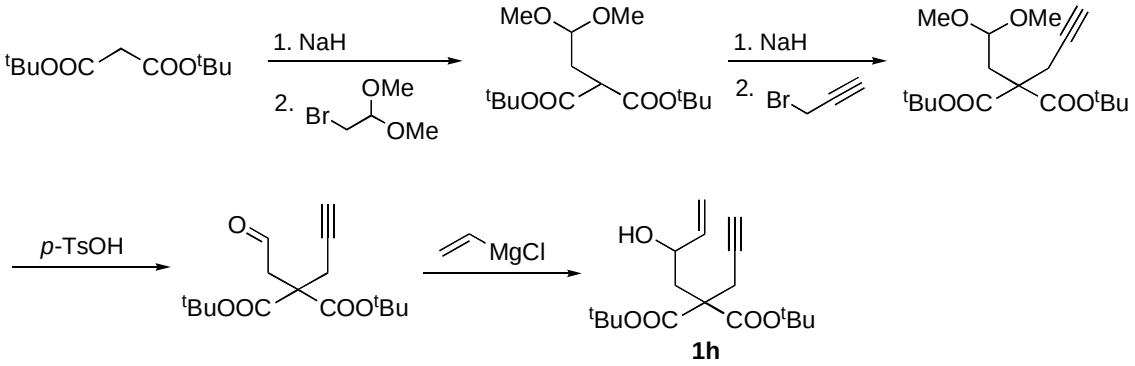


1g

4,4-Dimethyloct-1-en-7-yn-3-ol (1g): To a solution of LDA (5.2 mmol) in THF (7 mL) was added ethyl isobutylate (5.0 mmol) at -78 °C and the mixture was stirred at 0 °C. After stirring for 10 minutes, 4-bromo butyne was added to the solution at -78 °C. The mixture was allowed to warm to ambient temperature and stirred for 3 hours. Then the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was

evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain ethyl 2,2-dimethylhex-5-ynoate (31% yield). To a solution of LAH (1.0 M Et_2O solution, 1.53 mmol) in Et_2O (5 mL) under Ar atmosphere was added a solution of ethyl 2,2-dimethylhex-5-ynoate (1.53 mmol) in Et_2O (2 mL) at 0 °C and the mixture was stirred for 20 minutes at the temperature. Then 10% aqueous solution of KOH was added dropwise to the mixture at 0 °C. The mixture was allowed to warm to rt and stirred. After stirring for 1 hour, the reaction mixture was filtered with a pad of celite and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chlomatography to obtain 2,2-dimethylhex-5-yn-1-ol (71% yield). To a solution of 2,2-dimethylhex-5-yn-1-ol (0.94 mmol) and celite (900 mg) in CH_2Cl_2 (5.5 mL) was added PCC (2.8 mmol) at rt and the mixture was stirred for 6.5 hours. Then the reaction mixture was filtered with a pad of silica gel and the filtrate was concentrated in vacuo. The residue was dissolved in THF (3.3 mL) under Ar atmosphere. Vinylmagnesium chloride (1.44 M THF solution, 0.95 mmol) was added to the solution at -78 °C and the mixture was stirred at the temperature. After stirring for 1 hour, the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1g** (40% yield for 2 steps).

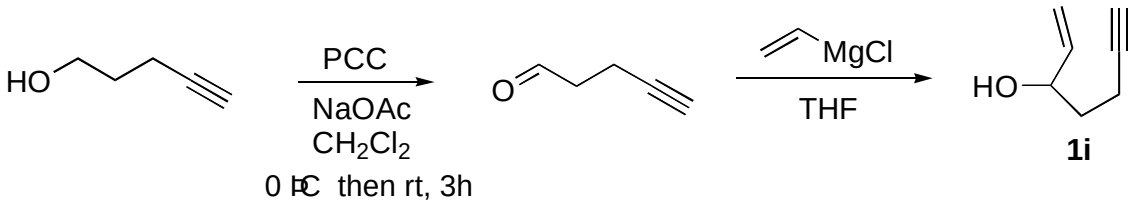
1g: ^{1}H-NMR (400 MHz, $CDCl_3$): d = 0.88 (s, 3H), 0.89 (s, 3H), 1.46-1.58 (m, 2H), 1.65-1.73 (m, 1H), 1.94 (t, J = 2.4 Hz, 1H), 2.18-2.24 (m, 2H), 3.83 (t, J = 5.4 Hz, 1H), 5.20 (d, J = 10.2 Hz, 1H), 5.25 (d, J = 17.1 Hz, 1H), 5.93 ppm (ddd, J = 17.1, 10.2, 6.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): d = 13.4, 22.5, 22.7, 37.2, 37.6, 67.9, 79.6, 85.4, 116.8, 137.6 ppm; IR (neat): $\tilde{n}$ = 3445, 2117, 1642 cm^{-1}; EI-Ms: *m/z*: 152 (M^+); HRMS: *m/z*: Calcd for $C_{10}H_{16}O$: 152.1201, Found: 152.1177.



1h

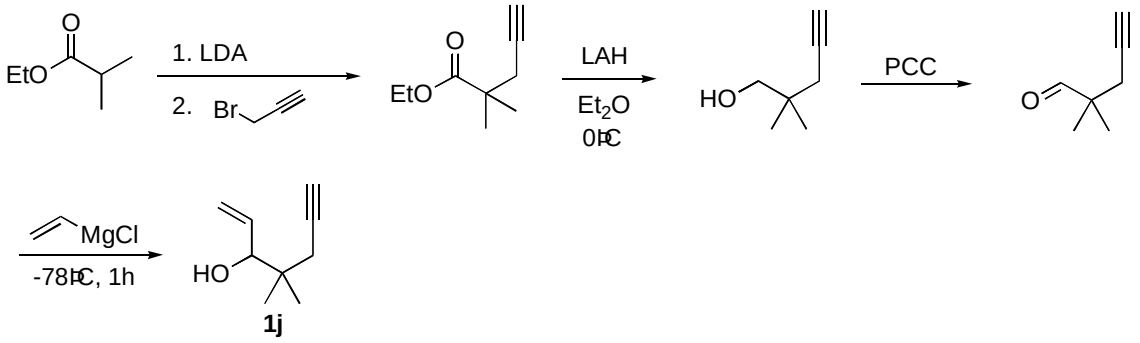
Di-*tert*-butyl 2-(2-hydroxybut-3-enyl)-2-(prop-2-ynyl)malonate (1h): To a solution of NaH (41.3 mmol) in THF (50 mL) was added di-*tert*-butyl malonate (20.2 mmol) at 0 °C and the mixture was stirred at rt. After stirring for 1 hour, 2-bromo-1,1-dimethoxyethane (19.7 mmol) was added to the mixture at rt. Then the mixture was allowed to warm to ambient temperature and stirred for 3 hours. The reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain di-*tert*-butyl 2-(2,2-dimethoxyethyl)malonate (12.3% yield). To a solution of NaH (6.1 mmol) in THF (10 mL) was added di-*tert*-butyl 2-(2,2-dimethoxyethyl)malonate (5.1 mmol) in THF (2.5 mL) at 0 °C and the mixture was stirred at rt. After stirring for 30 min, propargyl bromide (7.6 mmol) was added to the mixture at 0 °C. Then the mixture was allowed to warm to ambient temperature and stirred for 3 hours. The reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was dissolved in acetone (20 mL) and H_2O (0.25 mL). *p*-Toluene sulfonic acid monohydrate (0.25 mmol) was added to the solution at rt and the mixture was stirred overnight. The reaction mixture was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain di-*tert*-butyl 2-(formylmethyl)-2-(prop-2-ynyl)malonate (>40% yield for 2 steps). To a solution of di-*tert*-butyl 2-(formylmethyl)-2-(prop-2-ynyl)malonate (2.0 mmol) in THF (6 mL) was added vinylmagnesium chloride (1.48 M THF solution, 2.0 mmol) at -78 °C and the mixture was stirred at the temperature. After stirring for 1 hour, the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was

washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1h** (>15% yield).
1h: ^{1}H-NMR (400 MHz, $CDCl_3$): d = 1.44 (d, , J = 1.5 Hz, 18H), 2.00 (t, J = 2.4 Hz, 1H), 2.18-2.20 (m, 3H), 2.78 (dd, J = 14.5, 2.4 Hz, 1H), 2.58 (dd, J =14.5, 2.4 Hz, 1H), 4.24 (m, 1H), 5.08 (d, J = 10.1 Hz, 1H), 5.24 (d, J = 17.4 Hz, 1H), 5.88 (ddd, J = 17.4, 10.1, 5.3 Hz, 1H), 5.93 ppm (ddd, J = 17.1, 10.2, 6.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): d = 23.4, 27.7, 39.0, 56.6, 69.4, 71.3, 79.5, 82.0, 114.3, 141.1, 169.5, 160.7 ppm; IR (neat): $\tilde{n}$ = 3543, 2122, 1732, 1715, 1645 cm^{-1}; EI-Ms: *m/z*: 325 (M^++H); HRMS: *m/z*: Calcd for $C_{18}H_{29}O_5$: 325.2015, Found: 325.2018.



1i

Hept-1-en-6-yn-3-ol (1i): To a solution of 4-pentyn-1-ol (36.3 mmol) in CH_2Cl_2 (220 mL) was added celite (36g) and PCC (109.1 mmol) at rt and the mixture was stirred at the temperature. After stirring for 3 hours, the reaction mixture was filtered with a pad of silica gel. The filtrate was concentrated in vacuo. Then the residue was dissolved in THF (130 mL) under Ar atmosphere. Vinylmagnesium chloride (1.48 M THF solution, 37.0 mmol) was added to the solution at -78 °C and the mixture was stirred at the temperature. After stirring for 10 minutes, the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1i** (>24% yield for 2 steps).
1i: ^{1}H-NMR (400 MHz, $CDCl_3$): d = 1.70-1.77 (m, 3H), 1.98 (t, J = 2.4 Hz, 1H), 2.24-2.40 (m, 2H), 4.28 (m, 1H), 5.15 (dd, J = 10.6, 1.4 Hz, 1H), 5.28 (dd, J = 16.9, 1.4 Hz, 1H), 5.87 ppm (ddd, J = 16.9, 10.6, 6.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): d = 14.6, 35.3, 68.8, 71.8, 83.9, 115.2, 140.3 ppm; IR (neat): $\tilde{n}$ = 3366, 2117, 1645, 1431 cm^{-1}; EI-Ms: *m/z*: 110 (M^+); HRMS: *m/z*: Calcd for $C_7H_{10}O$: 110.0732, Found: 110.0734.

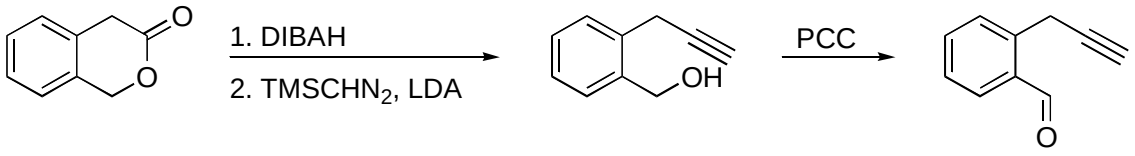


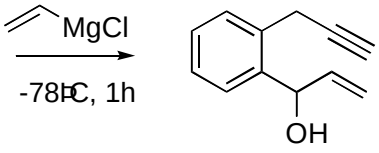
1j

4,4-Dimethylhept-1-en-7-yn-3-ol (1j): To a solution of LDA (10.4 mmol) in THF (14 mL) was added ethyl isobutylate (10.0 mmol) at -78 °C and the mixture was stirred at 0 °C. After stirring for 10 minutes, propargyl bromide was added to the solution at -78 °C. The mixture was allowed to warm to ambient temperature and stirred for 1 hour. Then the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain ethyl 2,2-dimethylpent-4-ynoate (84% yield). To a solution of LAH (1.0 M Et_2O solution, 9.2 mmol) in Et_2O (30 mL) under Ar atmosphere was added a solution of ethyl 2,2-dimethylpent-4-ynoate (8.4 mmol) in Et_2O (10 mL) at 0 °C and the mixture was stirred for 20 minutes at the temperature. Then 10% aqueous solution of KOH was added dropwise to the mixture at 0 °C. The mixture was allowed to warm to rt and stirred for 1 hour. The reaction

mixture was filtered with a pad of celite and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chlomatography to obtain 2,2-dimethylpent-4-yn-1-ol (76% yield). To a solution of 2,2-dimethylpent-4-yn-1-ol (6.4 mmol) and celite (6.2 g) in CH_2Cl_2 (38 mL) was added PCC (4.2 mmol) at rt and the mixture was stirred overnight. Then the reaction mixture was filtered with a pad of silica gel and the filtrate was concentrated in vacuo. The residue was dissolved in THF (23 mL) under Ar atmosphere. Vinylmagnesium chloride (1.44 M THF solution, 6.5 mmol) was added to the solution at -78 °C and the mixture was stirred at the temperature. After stirring for 10 minutes, the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1j** (>13% yield for 2 steps).

1j: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 3H), 0.99 (s, 3H), 1.64 (d, J = 4.3 Hz, 1H), 2.01 (t, J = 2.4 Hz, 1H), 2.13 (dd, J = 16.4, 2.4 Hz, 1H), 2.30 (dd, J = 16.4, 2.4 Hz, 1H), 4.00 (br t, J = 5.8 Hz, 1H), 5.22 (d, J = 10.6 Hz, 1H), 5.28 (dt, , J = 16.9, 1.4 Hz, 1H), 5.93 ppm (ddd, , J = 16.9, 10.6, 6.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 22.1, 23.2, 28.7, 37.5, 70.3, 78.8, 82.3, 117.0, 137.4 ppm; IR (neat): $\tilde{\nu}$ = 3422, 2116, 1642 cm^{-1}; EI-Ms: *m/z*: 138 (M^+); HRMS: *m/z*: Calcd for $C_9H_{14}O$: 138.1045, Found: 138.1044.

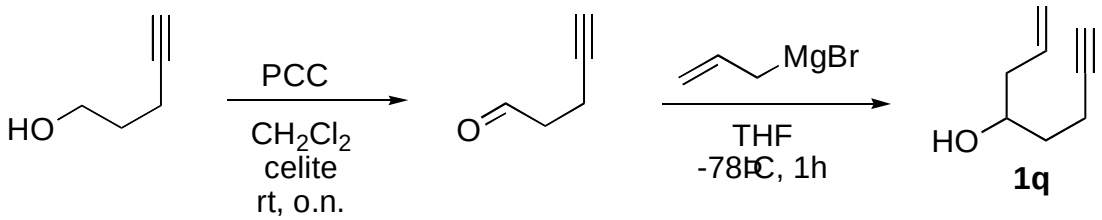




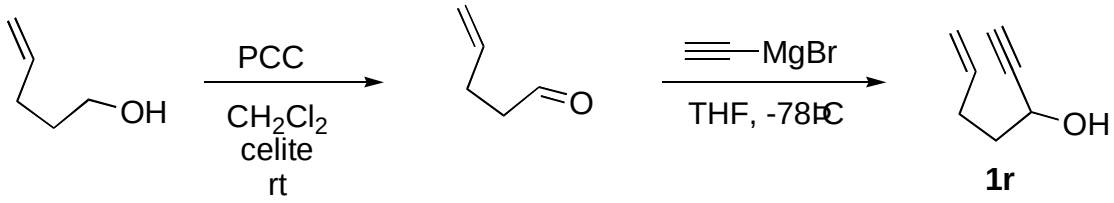
1k

1-(2-(Prop-2-ynyl)phenyl)prop-2-en-1-ol (1k): To a solution of 3-isochromanone (3.3 mmol) in CH_2Cl_2 (10 mL) was added DIBAH (3.7 mmol) at -78 °C under Ar atmosphere and the mixture was stirred at the temperature. After stirring for 2 hours, the reaction was quenched with 1N HCl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. Then the solvent was evaporated in vacuo to obtain crude 3,4-dihydro-1*H*-isochromen-3-ol. To a solution of LDA (7.6 mmol) in THF (10 mL) was added tetramethyl diazomethane (3.8 mmol) at -78 °C under Ar atmosphere and the mixture was stirred for 30 minutes at the temperature. Then a solution of crude 3,4-dihydro-1*H*-isochromen-3-ol in THF (2 mL) was added dropwise to the solution at -78 °C and the mixture was stirred for 30 minutes at the temperature. The mixture was allowed to warm to ambient temperature gradually. The reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with Et_2O. The mixture was washed with water and brine, and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain (2-(prop-2-ynyl)phenyl)methanol (88% yield for 2 steps). To a solution of (2-(prop-2-ynyl)phenyl)methanol (2.9 mmol) and celite (2.8 g) in CH_2Cl_2 (16 mL) was added PCC (8.7 mmol) at rt and the mixture was stirred 1 hour. Then the reaction mixture was filtered with a pad of silica gel and the filtrate was concentrated in vacuo. The residue was dissolved in THF (10 mL) under Ar atmosphere. Vinylmagnesium chloride (1.44 M THF solution, 2.9 mmol) was added to the solution at -78 °C and the mixture was stirred at the temperature. After stirring for 1.5 hours, the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1k** (>76% yield for 2 steps).

1k: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.05 (br s, 1H), 2.26 (t, J = 2.4 Hz, 1H), 3.74 (t, J = 2.4 Hz, 1H), 5.30 (dd, J = 10.6, 1.4 Hz, 1H), 5.42 (dd, J = 17.4, 1.4 Hz, 1H), 5.55 (br d, J = 4.8 Hz, 1H), 6.12 (ddd, J = 17.4, 10.6, 1.4 Hz, 1H), 7.33-7.37 (m, 2H), 7.50-7.55 ppm (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 22.2, 71.0, 71.7, 82.0, 115.5, 126.8, 127.5, 128.2, 129.2, 133.7, 139.0, 139.8 ppm; IR (neat): $\tilde{\nu}$ = 3296, 2119, 1641 cm^{-1}; EI-Ms: *m/z*: 172 (M^+); HRMS: *m/z*: Calcd for $C_{12}H_{12}O$: 172.0888, Found: 172.0894.



Oct-1-en-7-yn-4-ol (1q): To a solution of 4-pentyn-1-ol (19.3 mmol) in CH_2Cl_2 (120 mL) was added celite (19.4g) and PCC (58.2 mmol) at rt and the mixture was stirred at the temperature. After stirring overnight, the reaction mixture was filtered with a pad of silica gel. The filtrate was concentrated in vacuo. Then the residue was dissolved in THF (70 mL) under Ar atmosphere. Allylmagnesium bromide (1.0 M Et_2O solution, 20.0 mmol) was added to the solution at -78 °C and the mixture was stirred at the temperature. After stirring for 1 hour, the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1i** (>17% yield for 2 steps).
1q: ^{1}H-NMR (400 MHz, $CDCl_3$): d = 1.57-1.78 (m, 3H), 1.97 (t, J = 2.4 Hz, 1H), 2.15-2.22 (m, 1H), 2.28-2.37 (m, 3H), 3.77-3.85 (m, 1H), 5.15 (d, J = 12.6 Hz, 2H), 5.78-5.88 ppm (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): d = 15.0, 35.1, 41.9, 68.7, 69.4, 84.1, 118.4, 134.4 ppm; IR (neat): $\tilde{n}$ = 3304, 2117, 1642, 1435 cm^{-1}; EI-Ms: *m/z*: 110 (M^+); HRMS: *m/z*: Calcd for $C_8H_{12}O$: 124.0888, Found: 124.0840.

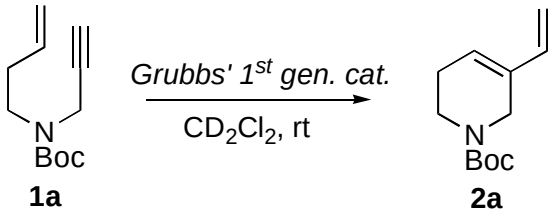


Hept-6-en-1-yn-3-ol (1r): To a solution of 4-penten-1-ol (19.3 mmol) in CH_2Cl_2 (120 mL) was added celite (19.4g) and PCC (58.2 mmol) at rt and the mixture was stirred at the temperature. After stirring 1 hour, the reaction mixture was filtered with a pad of silica gel. The filtrate was concentrated in vacuo. Then the residue was dissolved in THF (70 mL) under Ar atmosphere. Ethynylmagnesium bromide (0.5 M THF solution, 20.0 mmol) was added to the solution at -78 °C and the mixture was stirred at the temperature. After stirring for 10.5 hours, the reaction was quenched with aqueous solution of NH_4Cl and the reaction mixture was diluted with CH_2Cl_2. The mixture was washed with water and the organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by silica gel column chlomatography to obtain **1i** (>10% yield for 2 steps).
1q: ^{1}H-NMR (400 MHz, $CDCl_3$): d = 1.79-1.86 (m, 3H), 2.22-2.28 (m, 2H), 2.48 (d, , J = 1.9, 1H), 2.28-2.37 (m, 1H), 5.01 (dt, J = 8.7, 1.4 Hz, 1H), 5.08 (m, 1H), 5.78-5.89 ppm (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): d = 29.2, 36.6, 61.8, 73.2, 84.6, 115.4, 137.5 ppm; IR (neat): $\tilde{n}$ = 3305, 2115, 1642 cm^{-1}; EI-Ms: *m/z*: 109 (M^+-H); HRMS: *m/z*: Calcd for C_7H_9O: 109.0653, Found: 109.0495.

Procedure for kinetic studies to confirm the change of rate-determining step

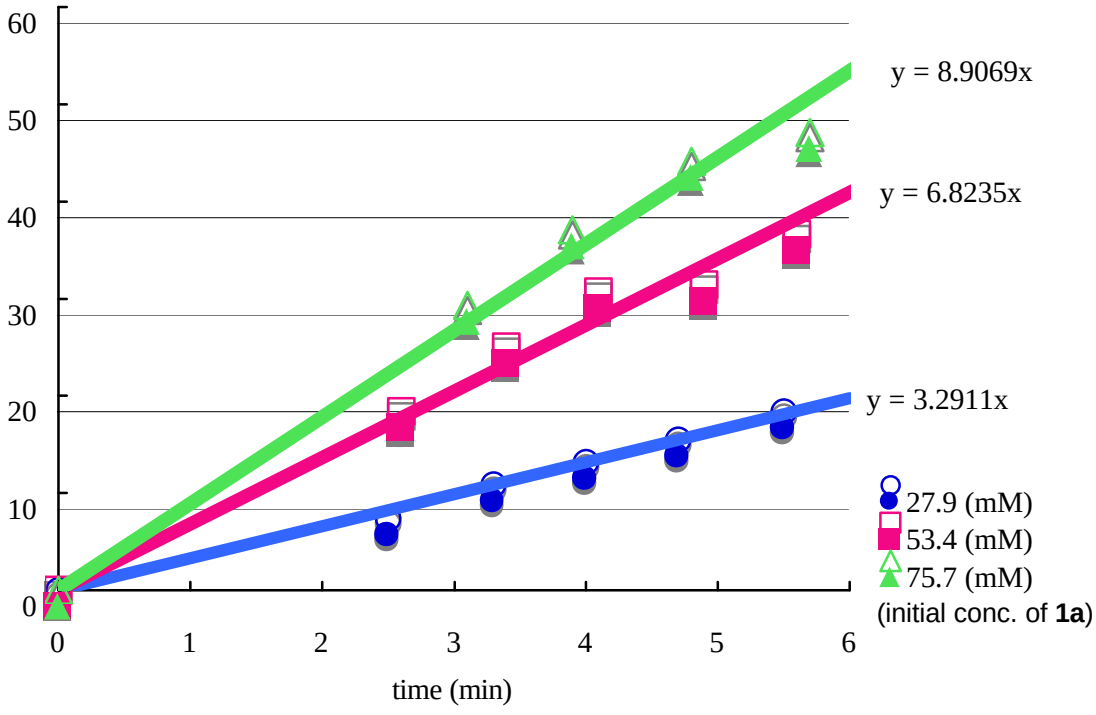
Grubbs' 1st generation catalyst was dried in vacuo for 30 min and appropriate amount of CD_2Cl_2 was added under Ar atmosphere to prepare 0.002 M solution of Grubbs' 1st generation catalyst in CD_2Cl_2. 1,2-Dichloroethane was added to the solution as an internal standard (ca. 0.03378 M). Then 0.6 mL of this solution was transferred to a dried NMR tube. Just before measurement of ^{1}H-NMR, a corresponding amount of N-tert-Butoxycarbonyl-3-vinyl-3-piperidene (**1a**) or 4-dimethylhept-1-en-6-yn-3-ol (**1j**) was added to the NMR tube and the tube was shaken intensively. Then ^{1}H-NMR was measured continuously. The concentration of the desired product (**2a** or **2j)** was estimated from the integration of 1,2-

Dichloroethane as an internal standard. Initial reaction rates were estimated from the approximated curves (first order) of first 5 minutes on each conditions.

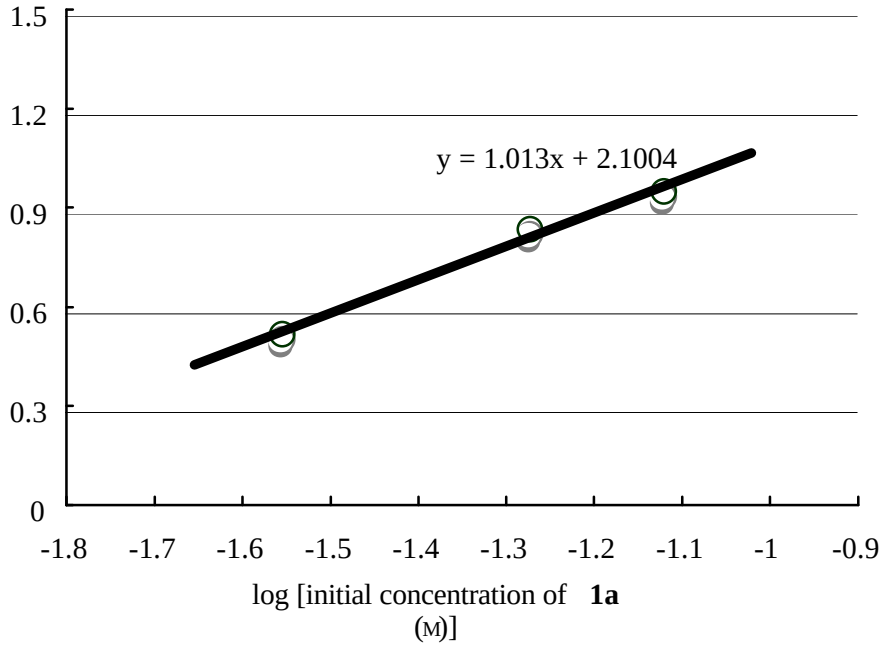


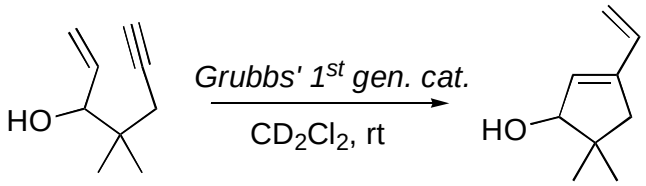
1a **2a**

initial conc. of **1a** = 27.9 (mM)						
time (min)	0	2.5	3.3	4	4.7	5.5
conc. of **2a** (mM)	0	7.4	10.9	13.2	15.5	18.4
initial conc. of **1a** = 53.4 (mM)						
time(min)	0	2.6	3.4	4.1	4.9	5.6
conc. of **2a** (mM)	0	18.4	25.0	30.7	31.4	36.6
initial conc. of **1a** = 75.7 (mM)						
time(min)	0	3.1	3.9	4.8	5.7	
conc. of **2a** (mM)	0	29.3	37.1	44.1	47.1	



initial conc. of **1a** (mM)	27.9	53.4	75.7
rate constant (mMmin^{-1})	3.2911	6.8235	8.9069
log [initial conc. of **1a** (M)]	-1.554822518	-1.272815922	-1.121166383
log [rate constant (mMmin^{-1})]	0.517341078	0.834007195	0.949726576

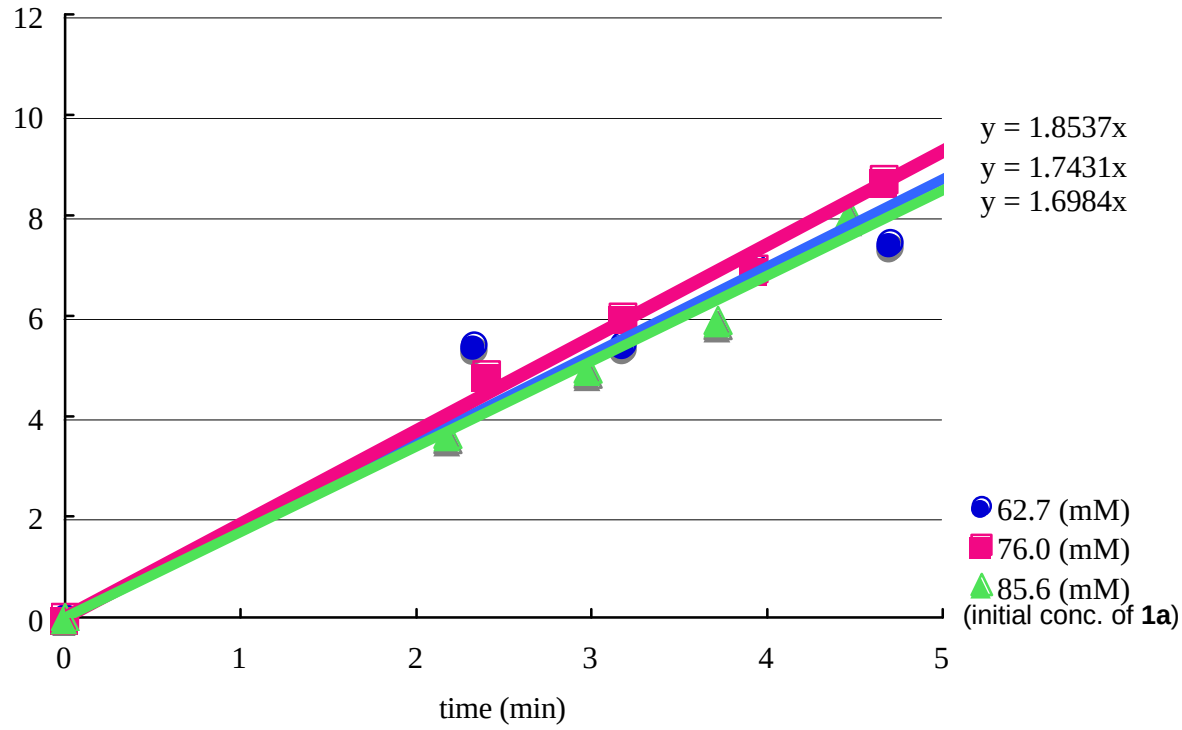




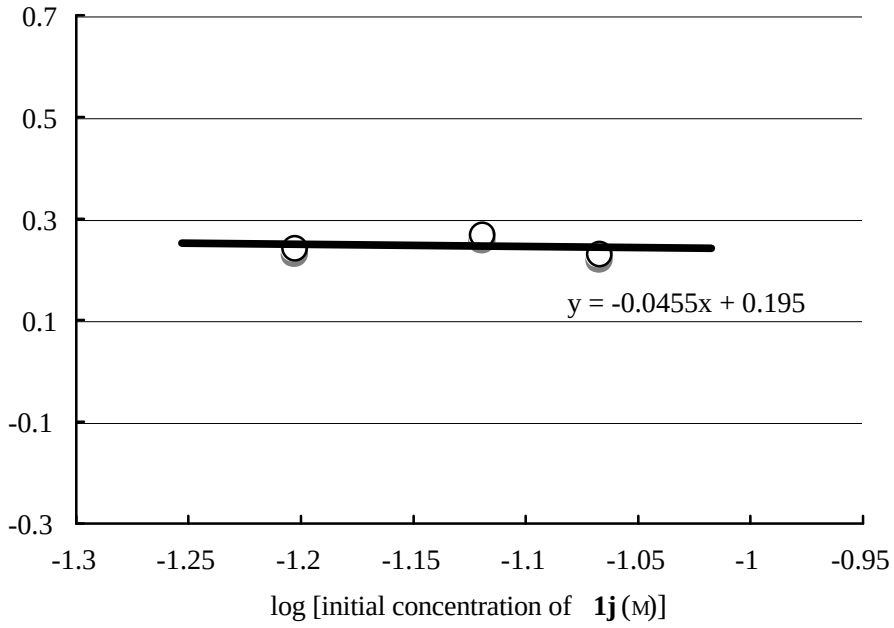
1j **2j**

initial conc. of **1j** = 62.7 (mM)					
time (min)	0	2.3	3.2	3.9	4.7
conc. of **1j** (mM)	0	5.43	5.44	7.00	7.46
initial conc. of **1j** = 76.0 (mM)					
time (min)	0	2.4	3.2	3.9	4.7
conc. of **1j** (mM)	0	4.83	5.98	6.93	8.70
initial conc. of **1j** = 85.6 (mM)					

time (min)	0	2.2	3.0	3.7	4.5
conc. of **1j** (mM)	0	3.64	4.95	5.91	8.03



initial conc. of **1j** (mM)	62.7	76	85.6
rate constant ($mMmin^{-1}$)	1.7431	1.8537	1.6984
log [initial conc. of **1j** (M)]	-1.202677639	-1.119340427	-1.067423255
log [rate constant ($mMmin^{-1}$)]	0.241322302	0.268039449	0.230039981


0.7
0.5
0.3
0.1
-0.1
-0.3
y = -0.0455x + 0.195
-1.3
-1.25
-1.2
-1.15
-1.1
-1.05
-1
-0.95
log [initial concentration of 1j (M)]