Supporting Information

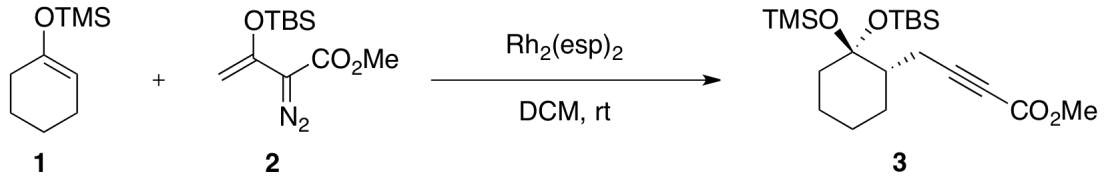
Table of Contents

General Method. All reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon. Flash chromatography was performed on silica gel 60 (230-400 mesh). Thin layer chromatography (TLC) was performed on aluminum backed plates, pre-coated with silica gel (0.25 mm, 60 F254) and developed using standard visualizing agents: UV fluorescence (254 nm) and potassium permanganate. ^{1}H NMR spectra were recorded on Varian Nuclear Magnetic Resonance spectrometers at 600, 500 or 400 MHz. The NMR data are reported as follows: chemical shift (in ppm on the δ scale relative to δH 7.26 for the residual protons in $CDCl_3$ and δH 7.16 for the residual protons in C_6D_6), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*/Hz) and integration. ^{13}C NMR spectra were recorded at 150 or 100 MHz with complete proton decoupling using the given solvent as an internal standard ($CDCl_3$, δ = 77.0 and C_6D_6, δ = 128.0). Mass spectral determinations were carried out by APCI/ESI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm^{-1}. Optical rotations were measured on a JASCO P-2000 polarimeter.

Materials. Rh_2(*S*-PTAD)$_4$,[1] Rh_2(*S*-NTTL)$_4$,[2] Rh_2(*S*-PTTL)$_4$,[3] Rh_2(*R*-BNP)$_4$,[4] Rh_2(*S*-BTPCP)$_4$,[5] Rh_2(*S*-TBPTTL)$_4$[6] were prepared according to the literature procedures and lyophilized using a SP VirTis BenchTop K freeze dryer. $Rh_2(esp)_2$ was purchased from Aldrich. Siloxyvinyldiazoacetates **2**,[7] **4,**[8] and **5**[9] were synthesized according to literature procedures. Solvents were obtained from a Grubbs-type solvent purification system.

General Procedure for the Synthesis of Alkynoates *via* Vinylogous Reactivity

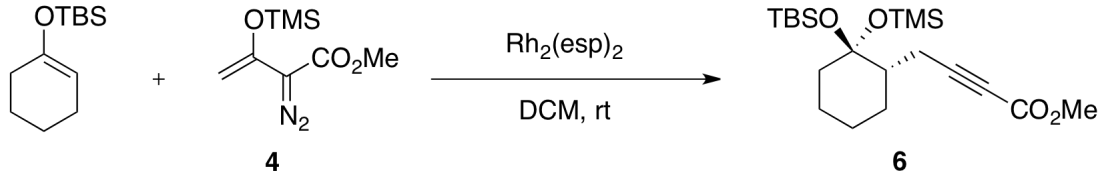
A solution of siloxyvinyldiazoacetate (1.0 mmol, 2.0 equiv) in 6 mL of dried degassed DCM was added by syringe pump over 3 h at room temperature to a flame-dried 25 mL flask containing $Rh_2(esp)_2$ (7.7 mg, 0.02 equiv) and enol ethers (0.5 mmol, 1.0 equiv) in 6 mL of dried degassed DCM under an argon atmosphere. The solution was stirred at room temperature for an additional 1 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (pentane/Et_2O) on silica gel to yield the product.



1 **2** **3**

Methyl 4-((1*SR*,2*SR*)-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclohexyl) but-2-ynoate 3: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg , 1.0 mmol, 2.0 equiv) and (cyclohex-1-en-1-yloxy)trimethylsilane **1** (85 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O) on silica gel to provide **3** as a colorless oil which crystallized on standing (0.105 g, 53% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (s, 3H), 2.71 (dd, J = 17.5, 3.0 Hz, 1H), 2.11 (dd, J = 17.5, 10.5 Hz, 1H), 1.90-1.93 (m, 1H), 1.81-1.84 (m, 1H), 1.67-1.70 (m, 1H), 1.50-1.61 (m, 3H), 1.42-1.48 (m, 1H), 1.12-1.29 (m, 2H), 0.86 (s, 9H), 0.16 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.5, 99.4, 90.8, 73.3, 52.7, 47.9, 41.8, 29.4, 26.2 (3 × C), 25.7, 24.0, 19.0, 18.3, 2.2 (3 × C), -2.3, -2.8; IR (neat): 2934, 2240, 1709, 1435, 1246,

1049, 806 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{38}O_4Si_2$ $(M+Na)^+$ 421.2201 found 421.2200; M.p. 50-52 °C.

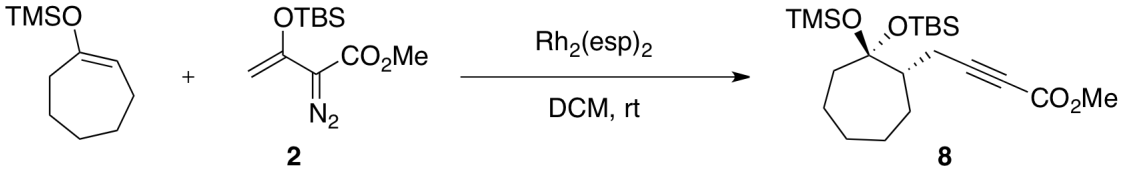


4 6

Methyl 4-((1*SR*,2*RS*)-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclohexyl) but-2-ynoate 6: Derived from methyl 2-diazo-3-((trimethylsilyl)oxy)but-3-enoate **4** (214 mg, 1.0 mmol, 2.0 equiv) and *tert*-butyl(cyclohex-1-en-1-yloxy)dimethyl silane (106 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O) on silica gel to provide **6** as a colorless oil (98 mg, 49% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.75 (s, 3H), 2.76 (dd, *J* = 17.4, 3.0 Hz, 1H), 2.18 (dd, *J* = 17.4, 10.8 Hz, 1H), 1.88-1.93 (m, 1H), 1.81-1.86 (m, 1H), 1.56-1.68 (m, 3H), 1.46-1.52 (m, 2H), 1.25 (qd, *J* = 12.6, 3.0 Hz, 1H), 1.12-1.20 (m, 1H), 0.92 (s, 9H), 0.15 (s, 6H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 99.7, 90.6, 73.2, 52.5, 47.2, 41.4, 29.0, 26.1 (3 × C), 25.2, 23.9, 18.6, 18.4, 1.9 (3 × C), -1.8, -2.6; IR (neat): 2934, 2237, 1716, 1246, 1049, 833, 729 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{38}O_4Si_2$ $(M+Na)^+$ 421.2201 found 421.2200.

2 **7**

Methyl 4-((1*SR*,2*SR*)-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclopentyl) but-2-ynoate 7: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and (cyclopent-1-en-1-yloxy)trimethylsilane (99.2 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O, R_f: 0.42) on silica gel to provide **7** as a colorless oil (0.153 g, 79% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.75 (s, 3H), 2.49 (dd, *J* = 17.4, 3.6 Hz, 1H), 2.24 (dd, *J* = 17.4, 9.0 Hz, 1H), 1.92-1.98 (m, 2H), 1.75-1.81 (m, 2H), 1.57-1.71 (m, 2H), 1.35-1.43 (m, 1H), 0.84 (s, 9H), 0.16 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.3, 106.1, 90.3, 72.6, 52.5, 48.3, 40.2, 28.0, 25.8 (3 × C), 19.7, 18.1, 17.9, 1.7 (3 × C), -2.7, -3.2; IR (neat): 2954, 2238, 1717, 1247, 831, 777 cm^{-1}; HRMS (ESI) calc. for $C_{19}H_{36}O_4Si_2Na$ $(M+Na)^+$ 407.2044 found 407.2044.



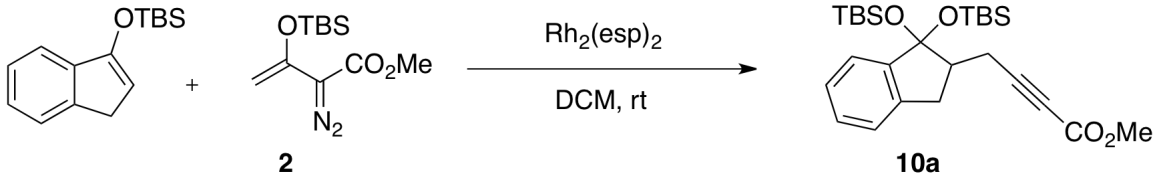
2 **8**

Methyl 4-((1*SR*,2*SR*)-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cycloheptyl)but-2-ynoate 8: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and

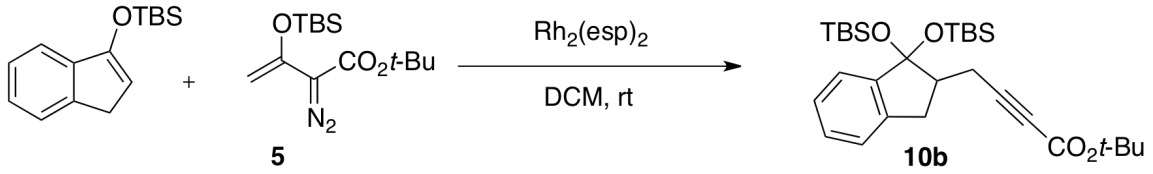
(cyclohept-1-en-1-yloxy)trimethylsilane (92 mg, 0.5 mmol, 1.0 equiv) and purified through column chromatography (30/1 pentane/Et_2O) on silica gel to provide **8** as a colorless oil (0.126 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 2.64 (dd, *J* = 17.6, 2.8 Hz, 1H), 2.12 (dd, *J* = 17.6, 11.2 Hz, 1H), 1.66-1.86 (m, 5H), 1.30-1.63 (m, 6H), 0.84 (s, 9H), 0.14 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 102.4, 91.3, 73.2, 52.7, 52.3, 42.8, 27.7, 26.5, 26.2 (3 × C), 25.9, 20.7, 20.4, 18.4, 2.28 (3 × C), -2.2, -2.8; IR (neat): 2953, 2929, 2237, 1717, 1251, 1046, 835; HRMS (ESI) calc. for $C_{21}H_{40}O_4Si_2Na$ $(M+Na)^+$ 435.2357 found 435.2361.

Methyl 4-((1*RS*,2*SR*)-1-((*tert*-butyldimethylsilyl)oxy)-1-((trimethylsilyl)oxy)-1,2,3,4-tetrahydronaphthalen-2-yl)but-2-ynoate 9: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and ((3,4-dihydronaphthalen-1-yl)oxy)trimethylsilane (109 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O, R_f: 0.38) on silica gel to provide **9** as a colorless oil (0.154 g, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55-7.57 (m, 1H), 7.15-7.19 (m, 2H), 7.03-7.05 (m, 1H), 3.78 (s, 3H), 2.76-2.87 (m, 3H), 2.31 (dd, *J* = 17.4, 11.4 Hz, 1H), 2.14-2.18 (m, 1H), 2.05 (t, *J* = 10.8 Hz, 1H), 1.81-1.88 (m, 1H), 0.78 (s, 9H), 0.17 (s, 3H), 0.09 (s, 3H), -0.05 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.2, 140.6, 135.7, 128.5, 127.7, 126.7, 125.6, 97.9, 89.7, 73.4, 52.6, 47.0, 28.3, 25.9 (3 × C),

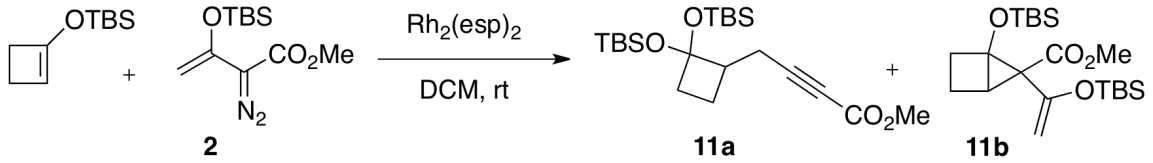
24.8, 19.1, 18.1, 1.4 (3 × C), -2.1, -2.3; IR (neat): 2953, 2929, 2238, 1717, 1249, 1069, 861, 797 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{38}O_4Si_2Na$ $(M+Na)^+$ 469.2201 found 469.2199; M.p. 43-46 °C.



(+/-)-Methyl 4-(1,1-bis((*tert*-butyldimethylsilyl)oxy)-2,3-dihydro-1*H*-inden-2-yl)but-2-ynoate 10a: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and ((1*H*-inden-3-yl)oxy)(*tert*-butyl)dimethylsilane (123 mg, 0.5 mmol, 1.0 equiv) and purified through column chromatography (30/1 pentane/Et_2O, R_f: 0.42) on silica gel to provide **10a** as a colorless oil (79.4 mg, 33% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.2 Hz, 1H), 7.25-7.27 (m, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.17 (dd, *J* = 15.0, 6.6 Hz, 1H), 2.72-2.76 (m, 1H), 2.67 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.54-2.61 (m, 2H), 0.96 (s, 9H), 0.77 (s, 9H), 0.18 (s, 3H), -0.05 (s, 3H), -0.07 (s, 3H), -0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 145.7, 140.2, 128.6, 126.3, 125.0, 122.9, 105.7, 89.1, 73.2, 52.6, 51.4, 35.0, 25.9 (3 × C), 25.7 (3 × C), 18.5, 18.2, 18.1, -2.5, -3.1, -3.2, -3.3; IR (neat): 2952, 2929, 2856, 2239, 1718, 1472, 1462, 1435, 1247, 1190, 1157, 1141, 1059, 878 cm^{-1}; HRMS (APCI) calc. for $C_{26}H_{43}O_4Si_2$ $(M+H)^+$ 475.2694 found 475.2698.

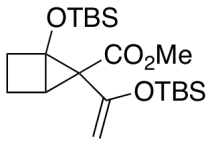


(+/-)-*tert*-Butyl 4-(1,1-bis((*tert*-butyldimethylsilyl)oxy)-2,3-dihydro-1*H*-inden-2-yl)but-2-ynoate 10b: Derived from *tert*-butyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **5** (298 mg, 1.0 mmol, 2.0 equiv) and ((1*H*-inden-3-yl)oxy)(*tert*-butyl)dimethylsilane (123 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O, R_f: 0.46) on silica gel to provide **10b** as a colorless oil (0.219 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 7.2 Hz, 1H), 7.15-7.26 (m, 3H), 3.25 (dd, J = 15.6, 6.4 Hz, 1H), 2.62-2.73 (m, 2H), 2.51-2.57 (m, 2H), 1.51 (s, 9H), 0.94 (s, 9H), 0.75 (s, 9H), 0.15 (s, 3H), -0.07 (s, 3H), -0.09 (s, 3H), -0.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.9, 145.8, 140.3, 128.6, 126.3, 125.0, 122.9, 105.8, 86.2, 83.0, 74.8, 51.4, 35.1, 28.0 (3 × C), 25.9 (3 × C), 25.8 (3 × C), 18.5, 18.2, 18.1, -2.4, -3.0, -3.1, -3.3; IR (neat): 2950, 2930, 2230, 1709, 1374, 1255, 1205, 1170, 1104, 988 cm^{-1}; HRMS (APCI) calc. for $C_{25}H_{39}O_3Si_2$ (M-OC$(CH_3)_3)^+$ 443.2438 found 443.2433.



(+/-)-Methyl 4-(2,2-bis((*tert*-butyldimethylsilyl)oxy)cyclobutyl)but-2-ynoate 11a: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and *tert*-butyl(cyclobut-1-en-1-yloxy)dimethylsilane (92 mg, 0.5 mmol,

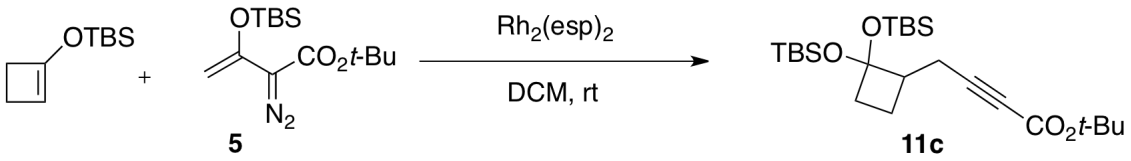
1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O, R_f: 0.42) on silica gel to provide **11a** as a colorless oil (105 mg, 51% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H), 2.60-2.68 (m, 1H), 2.41-2.54 (m, 2H), 2.14-2.21 (m, 2H), 1.84-1.92 (m, 1H), 1.31-1.40 (m, 1H), 0.89 (s, 9H), 0.88 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 98.2, 89.0, 72.7, 52.5, 48.4, 38.3, 25.8 (6 × C), 18.7, 18.5, 18.0, 17.9, -2.8 (2 × C), -3.4 (2 × C); IR (neat): 2952, 2929, 2857, 2237, 1717, 1472, 1462, 1434, 1245, 1217, 1193, 1162, 1120, 1071, 1042, 992, 938 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{41}O_4Si_2$ $(M+H)^+$ 413.2538 found 413.2533.



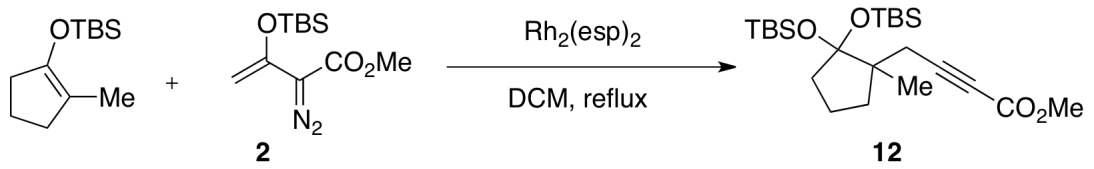
11b

Methyl 1-((*tert*-butyldimethylsilyl)oxy)-5-(1-((*tert*-butyldimethylsilyl)oxy)vinyl) bicyclo[2.1.0]pentane-5-carboxylate 11b: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and *tert*-butyl(cyclobut-1-en-1-yloxy)dimethylsilane (92 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O, R_f: 0.50) on silica gel to provide **11b** as colorless oil (94 mg, 46% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 4.44 (d, J = 0.8 Hz, 1H), 4.23 (d, J = 0.8 Hz, 1H), 3.65 (s, 3H), 2.79 (dd, J = 4.8, 1.6 Hz, 1H), 2.34 (td, J =10.8, 3.6 Hz, 1H), 2.11-2.17 (m, 1H), 1.96-2.04 (m, 1H), 1.12-1.17 (m, 1H), 0.90 (s, 9H), 0.85 (s, 9H), 0.20 (s, 6H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 150.0, 95.2, 68.7, 51.6, 45.1, 37.9, 31.5, 25.6 (3 × C), 25.5 (3 × C), 18.1, 17.7, 16.7,-4.1, -

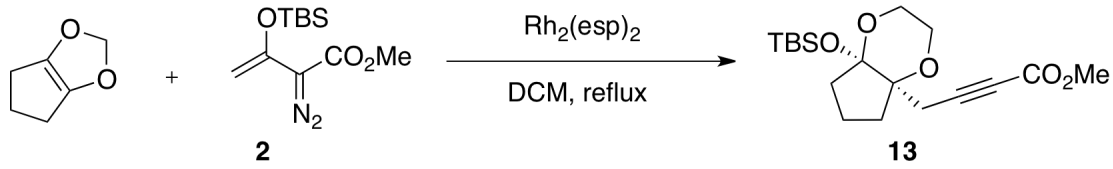
4.2, -4.7, -5.0; IR (neat): 2949, 2929, 2857, 1720, 1638, 1472, 1462, 1434, 1359, 1277, 1248, 1221, 1170, 1119, 1083, 1059, 1024, 1005, 959, 939 cm^{-1}; HRMS (APCI) calc. for $C_{21}H_{41}O_4Si_2$ $(M+H)^+$ 413.2538 found 413.2535.



(+/-)-*tert*-Butyl 4-(2,2-bis((*tert*-butyldimethylsilyl)oxy)cyclobutyl)but-2-ynoate (11c): Derived from *tert*-butyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **5** (298 mg, 1.0 mmol, 2.0 equiv) and *tert*-butyl(cyclobut-1-en-1-yloxy)dimethylsilane (92 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O, R_f: 0.42) on silica gel to provide **11c** as colorless oil (224 mg, 98% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 2.60-2.68 (m, 1H), 2.38-2.52 (m, 2H), 2.16-2.21 (m, 2H), 1.84-1.92 (m, 1H), 1.48 (s, 9H), 1.31-1.41 (m, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 98.3, 86.0, 82.7, 74.3, 48.4, 38.3, 28.0 (3 × C), 25.9 (3 × C), 25.8 (3 × C), 18.7, 18.5, 18.0, 17.9, -2.8 (2 × C), -3.4 (2 × C); IR (neat): 2953, 2930, 2896, 2857, 2237, 1708, 1472, 1463, 1391, 1368, 1250, 1218, 1161, 1120, 1069, 1042, 993, 938, 812 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{37}O_3Si_2$ $(M-OC(CH_3)_3)^+$ 381.2281 found 381.2273.

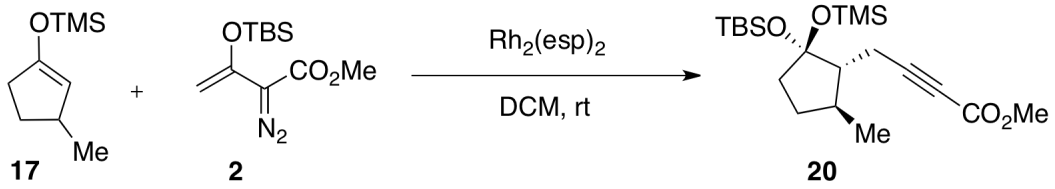


(+/-)-Methyl 4-(2,2-bis((*tert*-butyldimethylsilyl)oxy)-1-methylcyclopentyl)but-2-ynoate 12: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (154 mg, 0.6 mmol, 2.0 equiv) and *tert*-butyldimethyl((2-methylcyclopent-1-en-1-yl)oxy)silane (64 mg, 0.3 mmol, 1.0 equiv) under refluxed DCM, and purified through column chromatography (30/1 pentane/Et_2O, R_f: 0.42) on silica gel to provide **12** as a colorless oil (74 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 3H), 2.53 (d, *J* = 17.2 Hz, 1H), 2.29 (d, *J* = 17.2 Hz, 1H), 2.00-2.08 (m, 1H), 1.85-1.92 (m, 1H), 1.53-1.72 (m, 4H), 1.03 (s, 3H), 0.89 (s, 9H), 0.87 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 108.1, 90.1, 73.7, 52.5, 49.6, 36.5, 33.8, 26.1 (3 × C), 26.0 (3 × C), 25.5, 21.4, 18.4 (2 × C), 17.9, -1.6, -1.7, -2.1, -2.4; IR (neat): 2953, 2930, 2857, 2235, 1717, 1472, 1463, 1434, 1248, 1159, 1117, 1074, 1046, 1000, 938, 889 cm^{-1}; HRMS (APCI) calc. for $C_{23}H_{45}O_4Si_2$ $(M+H)^+$ 441.2778 found 441.2805.



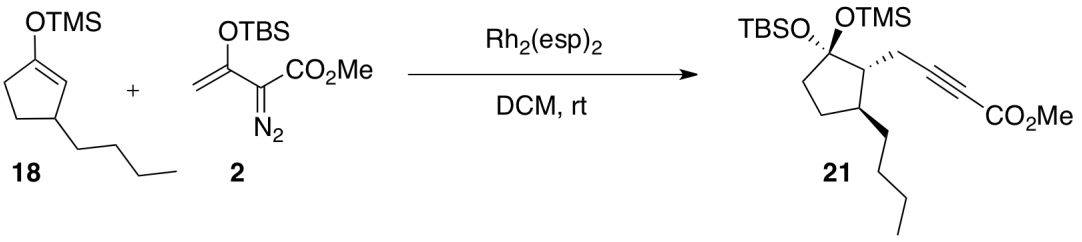
Methyl 4-((4a*RS*,7a*SR*)-7a-((*tert*-butyldimethylsilyl)oxy)hexahydro-2*H*-cyclopenta[*b*][1,4]dioxin-4a-yl)but-2-ynoate 13: Derived from methyl 3-((*tert*-

butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and 3,5,6,7-tetrahydro-2*H*-cyclopenta[*b*][1,4]dioxine (64 mg, 0.5 mmol, 1.0 equiv) under refluxed DCM, and purified through column chromatography (10/1 pentane/Et_2O, R_f: 0.26) on silica gel to provide **13** as a colorless oil (94 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89-3.95 (m, 1H), 3.76-3.83 (m, 1H), 3.73 (s, 3H), 3.56 (dt, *J* = 11.6, 2.8 Hz, 1H), 3.49 (dt, *J* = 11.6, 2.8 Hz, 1H), 2.77 (dd, *J* = 17.6, 0.8 Hz, 1H), 2.47 (d, *J* = 17.6 Hz, 1H), 2.15-2.22 (m, 1H), 1.95-2.02 (m, 1H), 1.57-1.86 (m, 4H), 0.89 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 102.2, 87.0, 81.9, 74.0, 59.8, 59.4, 52.5, 35.7, 28.1, 26.4, 25.7 (3 × C), 18.1, 17.4, -3.2, -3.3; IR (neat): 2954, 2857, 2239, 1715, 1250, 1108, 1076, 1030, 837 cm^{-1}; HRMS (ESI) calc. for $C_{18}H_{30}O_5SiNa$ $(M+Na)^+$ 377.1755 found 377.1756.

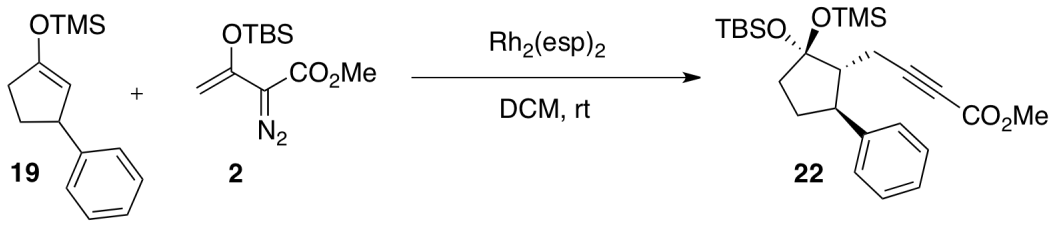


Methyl 4-((1*RS*,2*SR*,5*SR*)-2-((*tert*-butyldimethylsilyl)oxy)-5-methyl-2-((trimethylsilyl)oxy)cyclopentyl)but-2-ynoate 20: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and trimethyl((3-methylcyclopent-1-en-1-yl)oxy)silane[10] **17** (85 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (40/1 pentane/Et_2O) on neutral alumina to provide **20** as a colorless oil (114 mg, 57% yield). ^{1}H NMR (600 MHz, C_6D_6): δ 3.24 (s, 3H), 2.47 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.14 (dd, *J* = 18.0, 7.2 Hz, 1H), 1.56-1.76 (m, 4H),

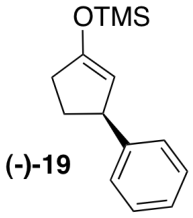
1.45-1.49 (m, 1H), 1.00 (d, J = 6.6 Hz, 3H), 0.95-0.98 (m, 1H), 0.90 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6): δ 154.0, 106.9, 89.4, 74.0, 56.0, 51.6, 39.6, 36.8, 29.6, 26.0 (3 × C), 21.0, 18.0, 17.2, 1.5 (3 × C), -2.5, -3.1; IR (neat): 2953, 2856, 2238, 1716, 1248, 1166, 1043, 832 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{38}O_4Si_2Na$ $(M+Na)^+$ 421.2201 found 421.2208.



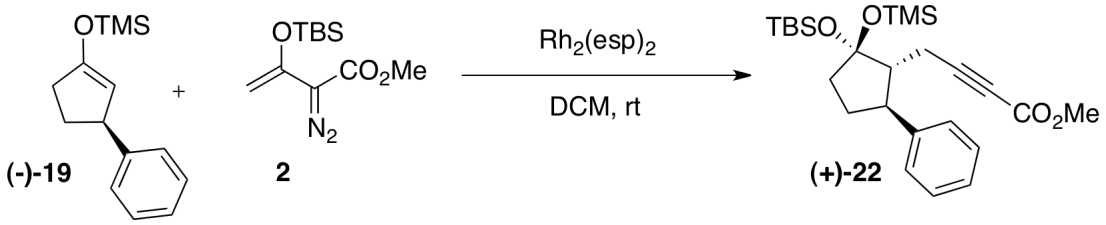
Methyl 4-((1*RS*,2*SR*,5*SR*)-5-butyl-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclopentyl)but-2-ynoate 21: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and ((3-butylcyclopent-1-en-1-yl)oxy)trimethylsilane[11] **18** (106 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (40/1 pentane/Et_2O) on neutral alumina to provide **21** as a colorless oil (111 mg, 50% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 3.22 (s, 3H), 2.49 (dd, J = 17.2, 5.2 Hz, 1H), 2.17 (dd, J = 17.2, 6.0 Hz, 1H), 1.69-1.79 (m, 1H), 1.56-1.63 (m, 4H), 1.20-1.32 (m, 4H), 1.06-1.14 (m, 3H), 0.90 (s, 9H), 0.85-0.88 (m, 3H), 0.16 (s, 3H), 0.11 (s, 3H), 0.09 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6): δ 154.0, 106.8, 89.5, 74.0, 54.1, 51.6, 42.0, 39.6, 35.6 30.0, 27.0, 26.0 (3 × C), 23.2, 18.0, 17.5, 14.2, 1.5 (3 × C), -2.5, -3.1; IR (neat): 2953, 2856, 2238, 1717, 1249, 1164, 1054, 832 cm^{-1}; HRMS (ESI) calc. for $C_{23}H_{44}O_4Si_2Na$ $(M+Na)^+$ 463.2670 found 463.2680.



Methyl 4-((1*RS*,2*SR*,5*SR*)-2-((*tert*-butyldimethylsilyl)oxy)-5-phenyl-2-((trimethylsilyl)oxy)cyclopentyl)but-2-ynoate 22: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and trimethyl((3-phenylcyclopent-1-en-1-yl)oxy)silane[11] **19** (116 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (40/1 pentane/Et_2O) on neutral alumina to provide **22** as a colorless oil (134 mg, 58% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.01-7.15 (m, 5H), 3.17 (s, 3H), 2.69-2.76 (m, 1H), 3.39-2.46 (m, 1H), 2.08-2.18 (m, 2H), 1.96-2.04 (m, 1H), 1.83-1.91 (m, 1H), 1.68-1.75 (m, 1H), 1.50-1.59 (m, 1H), 0.96 (s, 9H), 0.25 (s, 3H), 0.15 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6): δ 153.9, 145.0, 128.8 (2 × C), 127.6 (2 × C, signal overlaps with C_6D_6 solvent signal), 126.6, 106.4, 88.7, 74.0, 56.2, 51.5, 48.3, 40.5, 30.3, 26.1 (3 × C), 25.8, 18.1, 16.4, 1.6 (3 × C), -2.5, -3.0; IR (neat): 2953, 2856, 2238, 1716, 1251, 1081, 835 cm^{-1}; HRMS (ESI) calc. for $C_{25}H_{40}O_4Si_2Na$ $(M+Na)^+$ 483.2357 found 483.2357.



(−)-(*S*)-trimethyl((3-phenylcyclopent-1-en-1-yl)oxy)silane[12] 19 : Silyl enol ether **(−)-19** was prepared in accordance with the reported procedure by Hayashi and co-workers[12] and all spectroscopic data of the purified product was consistent with the reported values. $[\alpha]^{20}_{D}$ -31.6° (*c* 1.00, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis of the corresponding ketone, which was prepared by protonolysis of **(−)-19**. $[\alpha]^{20}_{D}$ -82.8° (*c* 0.92, $CHCl_3$); HPLC analysis: 98% ee, CHIRALCEL ADH, 0.5% isopropanol/hexanes, 1 mL/min, UV: 254 nm, t_R: 19.99 min (minor), 20.82 min (major).



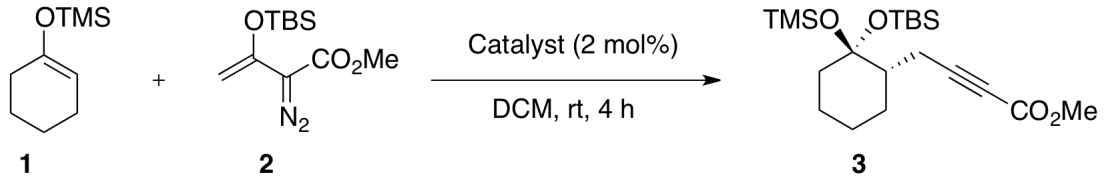
(+)-Methyl 4-((1*R*,2*S*,5*S*)-2-((*tert*-butyldimethylsilyl)oxy)-5-phenyl-2-((trimethylsilyl)oxy)cyclopentyl)but-2-ynoate 22: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (247 mg, 0.96 mmol, 2.0 equiv) and (−)-(*S*)-trimethyl((3-phenylcyclopent-1-en-1-yl)oxy)silane **(−)-19** (112 mg, 0.0.48 mmol, 1.0 equiv), and purified through column chromatography (40/1 pentane/Et_2O) on neutral alumina to provide **(+)-22** as a colorless oil (115 mg, 52% yield). $[\alpha]^{20}_{D}$ 3.6° (*c* 1.33,

$CHCl_3$); all data as previously stated. Product was determined to be 98% ee after derivatization (see **22a**).

Optimization of Conditions for the Asymmetric Alkynoate Synthesis

This study began with the evaluation of the best catalyst that could be used to access enantioenriched alkynoates. For this exercise, 1-(trimethylsiloxy)-cyclohexene **1** and methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** were selected as the substrates of choice. A series of dirhodium catalysts were tested and the results are summarized in Table 1. Although the desired alkynoate product was systematically isolated as a single diastereomer, the observed enantioselectivity was low (Table 1, entries 1-10). The best enantiomeric excess was obtained using Rh_2(*S*-PTAD)$_4$ (entry 1) and this catalyst was therefore selected to carry out further optimization studies.

General procedure for Table 1: A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (1.0 mmol, 2.0 equiv) in 6 mL of dried degassed DCM was added by syringe pump over 3 h at room temperature to a flame-dried 25 mL flask containing 1-(trimethylsiloxy)-cyclohexene **1** (0.5 mmol, 1.0 equiv) and catalyst (0.02 equiv) in 6 mL of dried degassed DCM under an argon atmosphere. The solution was stirred at room temperature for an additional 1 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (30/1 pentane/Et_2O) on silica gel to yield the product.



1 **2** **3**

Entry [a]	Catalyst	Yield [b]	d.r. [c]	ee [d]
1	*S*-PTAD	50	>20.1	37
2	*S*-NTTL	49	>20.1	-6 [e]
3	*S*-PTTL	62	>20.1	29
4	*R*-BNP	4	NA	NA
5	*S*-BTPCP	27	>20.1	24
6	*S*-PTA	38	>20.1	31
7	*S*-TBPTTL	37	>20.1	24
8	*R*-TCPTV	17	>20.1	17

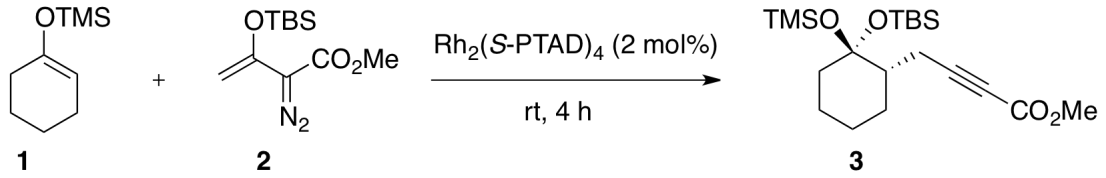
[a] Reaction condition: diazo compound **2** (1 mmol) in DCM (6 mL) was added over 3 h via a syringe pump at rt to a mixture of (cyclohex-1-en-1-yloxy)trimethylsilane **1** (0.5 mmol) and catalyst (2.0 mol%) in DCM (6 mL), and stirred for another hour at rt. [b] Isolated yield after chromatography on silica gel [c] Determined from ^{1}H NMR of the crude reaction mixture. [d] Determined by chiral HPLC after hydrolysis of the disiloxyketal. [e] Negative value indicates opposite asymmetric induction.

Table 1

A solvent screen was next performed. It was found that the enantioselectivity could be slightly improved using a different polar solvent such as TFT or DCE (Table 2, entries 2 and 3). However the use of non polar solvents had a negative impact on the reaction outcome and resulted in a significant erosion of enantioselectivity for the desired product (entries 4-6).

General procedure for Table 2: A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (1.0 mmol, 2.0 equiv) in solution (6 mL) was added by syringe pump over 3 h at room temperature to a flame-dried 25 mL flask containing 1-(trimethylsiloxy)-cyclohexene **1** (0.5 mmol, 1.0 equiv) and catalyst (0.02 equiv) in

solution (6 mL). The solution was stirred at room temperature for an additional 1 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (30/1 pentane/Et_2O) on silica gel to yield the product.



1 **2** **3**

Entry [a]	Solvent	Yield [b]	d.r. [c]	ee [d]
1	DCM	50	>20.1	37
2	TFT	57	>20.1	43
3	DCE	57	>20.1	39
4	2,2-DMB	56	>20.1	0
5	Pentane	50	>20.1	5
6	Toluene	46	>20.1	6

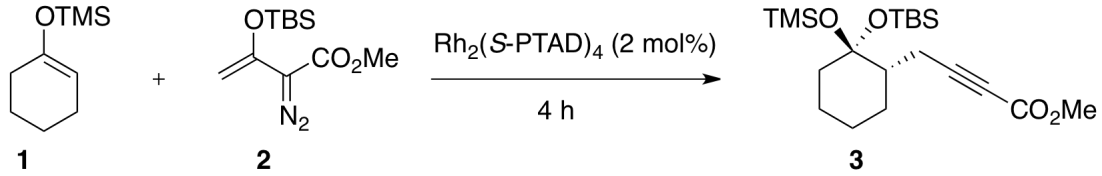
[a] Reaction condition: diazo compound **2** (1 mmol) in solution (6 mL) was added over 3 h via a syringe pump at rt to a mixture of (cyclohex-1-en-1-yloxy)trimethylsilane **1** (0.5 mmol) and Rh_2(*S*-PTAD)$_4$ (2.0 mol%) in solution (6 mL), and stirred for another hour at rt. [b] Isolated yield after chromatography on silica gel [c] Determined from ^{1}H NMR of the crude reaction mixture. [d] Determined by chiral HPLC after hydrolysis of the disiloxyketal.

Table 2

Finally, the reaction temperature was investigated (Table 3). Using TFT the enantioselectivity was improved to 60% ee when the reaction was conducted at -25 °C (Table 3, entry 3). Remarkably the reaction conversion was only slightly affected by the temperature.

General procedure for Table 3: A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (1.0 mmol, 2.0 equiv) in solution (6 mL) was added by syringe pump over 3 h to a flame-dried 25 mL flask containing 1-(trimethylsiloxy)-cyclohexene

(**1**) (0.5 mmol, 1.0 equiv) and catalyst (0.02 equiv) in solution (6 mL) at the indicated temperature. The solution was stirred at the indicated temperature for an additional 1 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (30/1 pentane/Et_2O) on silica gel to yield the product.



1 **2** **3**

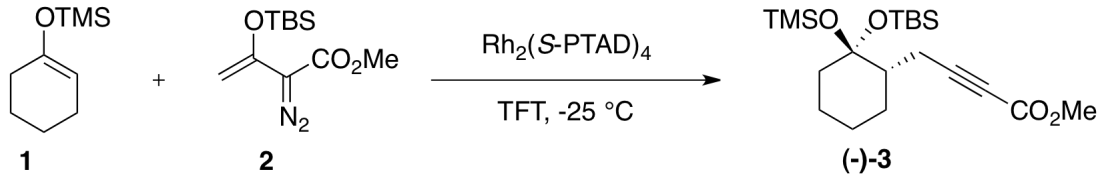
Entry [a]	Temperature (°C)	Solvent	Yield [b]	d.r. [c]	ee [d]
1	rt	TFT	57	>20.1	43
2	0	TFT	57	>20.1	49
3	-25	TFT	53	>20.1	60
4	rt	DCM	50	>20.1	37
5	-40	DCM	50	>20.1	43

[a] Reaction condition: diazo compound **2** (1 mmol) in solution (6 mL) was added over 3 h via a syringe pump at the indicated temperature to a mixture of (cyclohex-1-en-1-yloxy)trimethylsilane **1** (0.5 mmol) and Rh_2(*S*-PTAD)$_4$ (2.0 mol%) in solution (6 mL), and stirred for another hour at the indicated temperature. [b] Isolated yield after chromatography on silica gel [c] Determined from ^{1}H NMR of the crude reaction mixture. [d] Determined by chiral HPLC after hydrolysis of the disiloxyketal.

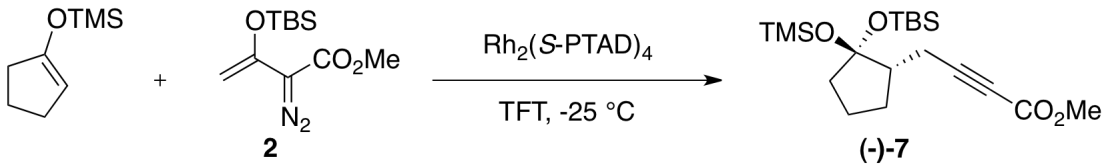
Table 3

General Procedure for the Asymmetric Alkynoate Synthesis

A solution of siloxyvinyldiazoacetate (1.0 mmol, 2.0 equiv) in 6 mL of dried degassed TFT was added by syringe pump over 3 h at -25 °C to a flame-dried 25 mL flask containing Rh_2(*S*-PTAD)$_4$ (15.6 mg, 0.02 equiv) and enol ethers (0.5 mmol, 1.0 equiv) in 6 mL of dried degassed TFT under an argon atmosphere. The solution was stirred at -25 °C for an additional 1 h. The mixture was concentrated under reduced pressure and purified by flash chromatography (pentane/Et_2O) on silica gel to yield the product.

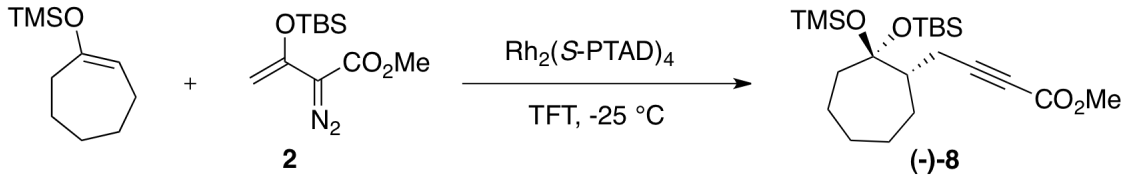


(–)-Methyl 4-(-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclohexyl)but-2-ynoate 3: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and (cyclohex-1-en-1-yloxy)trimethylsilane **1** (85 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O) on silica gel to provide **(–)-3** as a colorless oil which crystallized on standing (106 mg, 53% yield). $[\alpha]^{20}_D$ -7.1° (*c* 1.18, $CHCl_3$); all data as previously stated. Product was determined to be 60% ee after derivatization (see **(+)-16**).

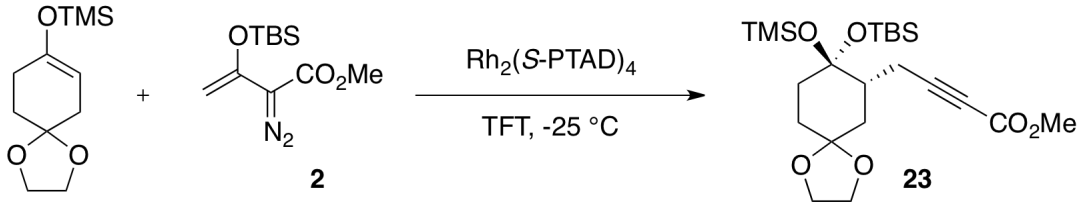


(–)-Methyl 4-((-2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclopentyl)but-2-ynoate 7: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and (cyclopent-1-en-1-yloxy)trimethylsilane (78 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O) on silica gel to provide **(–)-7** as a

colorless oil (167 mg, 87% yield). $[\alpha]^{20}_{D}$ -7.0° (*c* 1.56, $CHCl_3$); all data as previously stated. Product was determined to be 50% ee after derivatization (see **7a**).



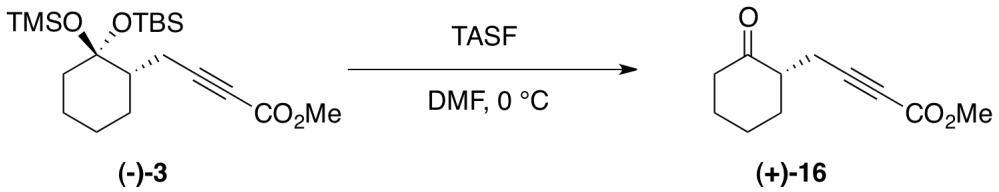
(−)-Methyl 4-(2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cycloheptyl)but-2-ynoate 8: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and (cyclohept-1-en-1-yloxy)trimethylsilane (92 mg, 0.5 mmol, 1.0 equiv), and purified through column chromatography (30/1 pentane/Et_2O) on silica gel to provide **(−)-8** as a colorless oil (0.142 g, 69% yield). $[\alpha]^{20}_{D}$ -7.1° (*c* 1.48, $CHCl_3$); all data as previously stated. Product was determined to be 70% ee after derivatization (see **8a**).



(+)-Methyl 4-(8-((*tert*-butyldimethylsilyl)oxy)-8-((trimethylsilyl)oxy)-1,4-dioxaspiro[4.5]decan-7-yl)but-2-ynoate 23: Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate **2** (256 mg, 1.0 mmol, 2.0 equiv) and (1,4-dioxaspiro[4.5]dec-7-en-8-yloxy)trimethylsilane[13] (114 mg, 0.5 mmol, 1.0 equiv), and

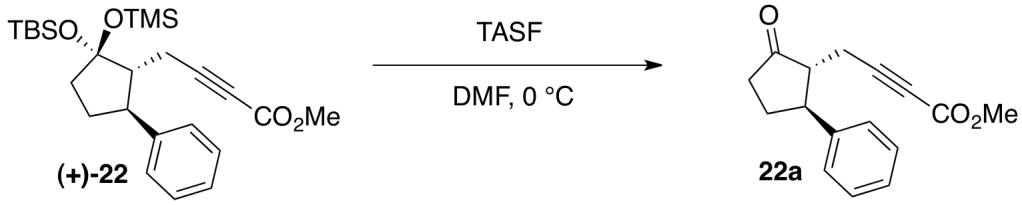
purified through column chromatography (80/20 pentane/Et_2O) on silica gel to provide **(+)-23** as a colorless oil (111 mg, 49% yield). $[\alpha]^{20}_D$ 1.9° (*c* 1.95, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 3.90-3.98 (m, 4H), 3.74 (s, 3H), 2.67 (dd, *J* = 17.2, 3.2 Hz, 1H), 2.67 (dd, *J* = 17.2, 10.4 Hz, 1H), 1.75-1.99 (m, 5H), 1.65-1.75 (m, 1H), 1.52-1.58 (m, 1H), 0.84 (s, 9H), 0.16 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 108.3, 98.7, 89.8, 73.7, 64.7, 64.5, 52.8, 44.6, 38.3, 37.6, 32.7, 26.2 (3 × C), 18.7, 18.3, 2.1 (3 × C), -2.3, -2.8; IR (neat): 2945, 2856, 2238, 1716, 1253, 1120, 1057, 835; HRMS (ESI) calc. for $C_{22}H_{40}O_6Si_2$ $(M+Na)^+$ 479.2256 found 479.2262. Product was determined to be 46% ee after derivatization (see **23a**).

General Procedure for the Deprotection of the Disiloxyketal Alkynoate Products: To a solution of alkyne (1.0 equiv) in dry DMF (1.0 mL) at 0 °C was added a solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) (0.3 equiv) in dry DMF (0.5 mL). The reaction was stirred at 0 °C for 5 min. The mixture was then diluted with EtOAc (5 mL) and poured into a separating funnel containing a pH 7 phosphate buffer solution (5 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 5 mL). The organics were dried over $MgSO_4$, concentrated under reduced pressure and purified by flash chromatography on silica gel (20% Et_2O/pentane).



(-)-3 (+)-16

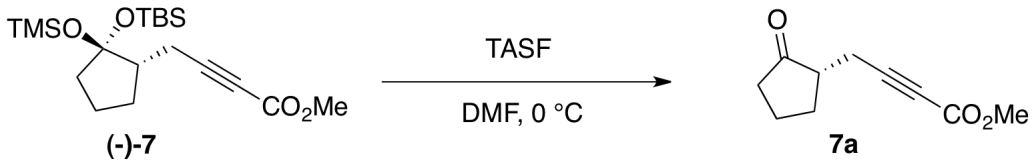
(+)-Methyl 4-(2-oxocyclohexyl)but-2-ynoate 16[14] : Derived from (–)-methyl 4-(2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclohexyl) but-2-ynoate **3** (83 mg, 0.21 mmol) and purified through column chromatography (80/20 pentane/Et_2O) on silica gel to provide **16** as a colorless oil (38 mg, 94%). $[\alpha]^{20}_D$ 2.8° (*c* 1.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 2.75 (dd, *J* = 17.6, 4.8 Hz, 1H), 2.51-2.59 (m, 1H), 2.35-2.45 (m, 2H), 2.25-2.34 (m, 2H), 2.06-2.12 (m, 1H), 1.88-1.94 (m, 1H), 1.58-1.71 (m, 2H), 1.39 (app. qd, *J* = 12.8, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 154.3, 88.1, 74.1, 52.8, 49.0, 42.1, 33.6, 27.9, 25.3, 19.3; HPLC analysis: 60% ee, CHIRALCEL ODR, 1% isopropanol/hexanes, 1 mL/min, UV: 230 nm, t_R: 16.26 min (minor), 17.60 min (major). NMR data was consistent with the literature.[14]



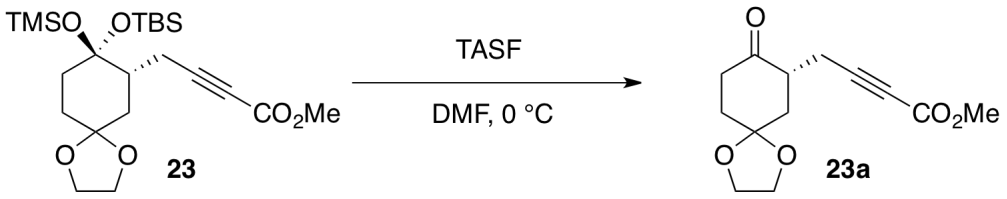
(+)-22 22a

(+)-Methyl 4-((1*R*,5*S*)-2-oxo-5-phenylcyclopentyl)but-2-ynoate 22a: Derived from (+)-Methyl 4-((1*R*,2*S*,5*S*)-2-((*tert*-butyldimethylsilyl)oxy)-5-phenyl-2-((trimethylsilyl)oxy)cyclopentyl)but-2-ynoate **22** (40 mg, 0.09 mmol) and purified through column chromatography (80/20 pentane/Et_2O) on silica gel to provide **22a** as a

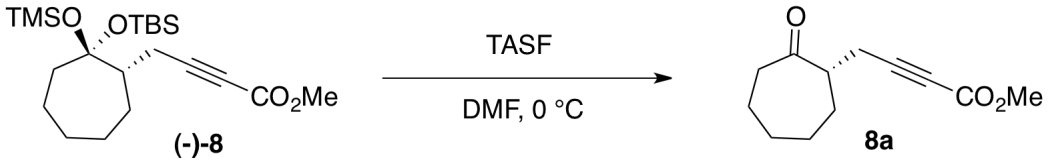
colorless oil (20 mg, 91%). $[\alpha]^{20}_{D}$ 37.3° (*c* 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.36 (m, 5H), 3.71 (s, 3H), 3.23 (td, *J* = 11.6, 6.0 Hz, 1H), 2.74 (dd, *J* = 18.8, 5.6 Hz, 1H), 2.54-2.60 (m, 1H), 2.34-2.43 (m, 3H), 2.25-2.34 (m, 1H), 1.97-2.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 216.0, 154.0, 141.4, 129.1 (2 × C), 127.5, 127.4 (2 × C), 86.0, 74.7, 54.4, 52.8, 47.2, 38.2, 29.3, 16.8; IR (neat): 2953, 2237, 1741, 1708, 1252, 721; HRMS (APCI) calc. for $C_{16}H_{15}O_3$ $(M-H)^+$ 255.1027 found 255.1027; HPLC analysis: 98% ee, CHIRALCEL ADH, 3% isopropanol/hexanes, 1 mL/min, UV: 230 nm, t_R: 15.47 min (minor), 17.26 min (major).



(–)-Methyl 4-(2-oxocyclopentyl)but-2-ynoate 7a: Derived from (–)-methyl 4-(2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cyclopentyl)but-2-ynoate **7** (30 mg, 0.08 mmol) and isolated as a colorless oil (14 mg, 97%). $[\alpha]^{20}_{D}$ -77.7° (*c* 1.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 2.72 (dd, 1H, *J* = 17.2, 4.0 Hz, 1H), 2.29-2.44 (m, 4H), 2.02-2.17 (m, 2H), 1.68-1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.0, 154.2, 87.1, 74.0, 52.9, 47.4, 37.9, 29.1, 20.6, 19.0; IR (neat): 2957, 2237, 1742, 1712, 1256; HRMS (APCI) calc. for $C_{10}H_{13}O_3$ $(M+H)^+$ 181.0859 found 181.0858; HPLC analysis: 50% ee, CHIRALCEL OBH, 5% isopropanol/hexanes, 1 mL/min, UV: 230 nm, t_R: 29.24 min (major), 31.88 min (minor).



(+)-Methyl 4-(8-oxo-1,4-dioxaspiro[4.5]decan-7-yl)but-2-ynoate 23a: Derived from (+)-Methyl 4-(8-((*tert*-butyldimethylsilyl)oxy)-8-((trimethylsilyl)oxy)-1,4-dioxaspiro[4.5]decan-7-yl)but-2-ynoate **23** (18 mg, 0.04 mmol) and purified through column chromatography (60/40 pentane/Et_2O) on silica gel to provide **23a** as a colorless oil (7 mg, 70%). $[\alpha]^{20}_D$ 1.5° (*c* 0.83, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99-4.07 (m, 4H), 3.72 (s, 3H), 2.85-2.94 (m, 1H), 2.71 (dd, *J* = 17.6, 4.8 Hz, 1H), 2.61-2.69 (m, 1H), 2.33-2.41 (m, 2H), 2.24-2.30 (ddd, *J* = 12.8, 5.6, 3.2 Hz, 1H), 1.95-2.06 (m, 2H), 1.79 (app. t, *J* = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.7, 154.2, 107.2, 87.2, 74.4, 65.1, 64.9, 52.9, 44.9, 40.0, 38.1, 34.8, 19.0; IR (neat): 2955, 2238, 1709, 1435, 1253, 1075; HRMS (ESI) calc. for $C_{13}H_{16}O_5Na$ $(M+Na)^+$ 275.0890 found 275.0890; HPLC analysis: 46% ee, CHIRALCEL ADH, 5% isopropanol/hexanes, 1 mL/min, UV: 230 nm, t_R: 14.99 min (minor), 17.97 min (major).



(−)-Methyl 4-(2-oxocycloheptyl)but-2-ynoate 8a[15] : Derived from (−)-4-(2-((*tert*-butyldimethylsilyl)oxy)-2-((trimethylsilyl)oxy)cycloheptyl)but-2-ynoate **8** (30 mg, 0.07

mmol) and purified through column chromatography (80/20 pentane/Et_2O) on silica gel to provide **8a** as a colorless oil (13 mg, 89%). $[\alpha]^{20}_D$ -41.3° (*c* 1.28, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 2.80 (tt, *J* = 8.8, 3.6 Hz, 1H), 2.66 (dd, *J* = 17.2, 4.8 Hz, 1H), 2.53-3.00 (m, 1H), 2.34-2.47 (m, 2H), 1.95-2.00 (m, 1H), 1.77-1.90 (m, 3H), 1.60-1.70 (m, 1H), 1.41-1.57 (m, 2H), 1.26-1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.2, 154.3, 88.2, 73.8, 52.9, 50.1, 43.5, 30.7, 29.5, 29.1, 23.9, 21.2; IR (neat): 2929, 2856, 2237, 1711, 1435, 1254, 1078; HRMS (APCI) calc. for $C_{12}H_{17}O_3$ $(M+H)^+$ 209.1172 found 209.1171; HPLC analysis: 70% ee, CHIRALCEL OBH, 3% isopropanol/hexanes, 1 mL/min, UV: 230 nm, t_R: 20.61 min (major), 30.08 min (minor).

References.

[1] Reddy, R. P.; Lee, G. H.; Davies, H. M. L. *Org. Lett.* **2006**, *8*, 3437.

[2] Muller, P.; Allenbach, Y.; Robert, E. *Tetrahedron Asymmetry* **2003**, *14*, 779.

[3] Tsutsui, H.; Abe, T.; Nakamura, S.; Anada, M.; Hashimoto, S. *Chem. Pharm. Bull.* **2005**, *53*, 1366.

[4] Pirrung, M. C.; Zhang, J. *Tetrahedron Lett.* **1992**, *33*, 5987.

[5] Qin, C.; Boyarskikh, V.; Hansen, J. H.; Hardcastle, K. I.; Musaev, D. G.; Davies, H. M. L. *J. Am. Chem. Soc.* **2011**, *133*, 19198.

[6] Goto, T.; Takeda, K.; Shimada, N.; Nambu, H.; Anada, M.; Shiro, M.; Ando, K.; Hashimoto, S.-I. *Angew. Chem., Int. Ed.* **2011**, *50*, 6803.

[7] Davies, H. M. L.; Ahmed, G.; Churchill, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 10774.

[8] Kundu, K.; Doyle, M. P. *Tetrahedron Asymmetry* **2006**, *17*, 574.

[9] Xu, X.; Shabashov, D.; Zavalij, P. Y.; Doyle, M. P. *Org. Lett.* **2012**, *14*, 800.

[10] Bergdahl, M.; Eriksson, M.; Nilsson, M.; Olsson, T. *J. Org. Chem.* **1993**, *58*, 7238.

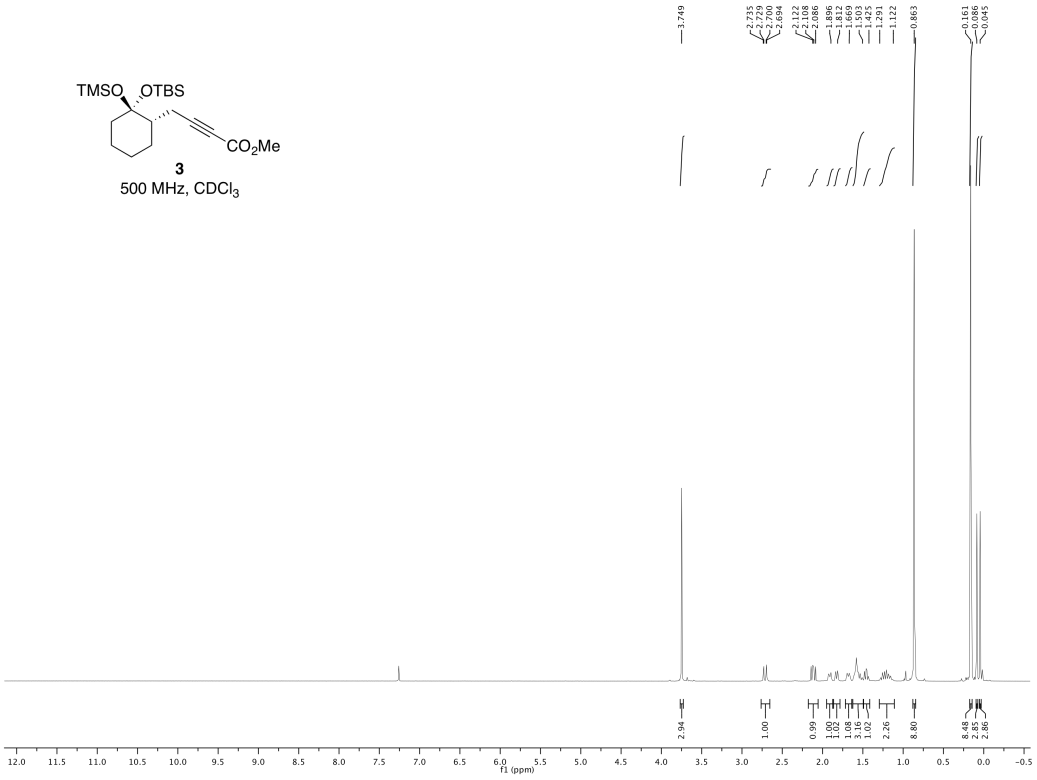
[11] Johnson, C. R.; Marren, T. J. *Tetrahedron Lett.* **1987**, *28*, 27.

[12] Tokunaga, N.; Yoshida, K.; Hayashi, T. *Proc. Natl. Acad. Sci.* **2004**, *101*, 5445.

[13] Sole, D.; Urbaneja, X.; Cordero-Vargas, A.; Bonjoch, J. *Tetrahedron* **2007**, *63*, 10177.

[14] Vizniowski, C. S.; Green, J. R.; Breen, T. L.; Dalacu, A. V. *J. Org. Chem.* **1995**, *60*, 7496.

[15] Mori, M.; Akashi, M.; Hori, M.; Hori, K.; Nishida, M.; Sato, Y. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1655.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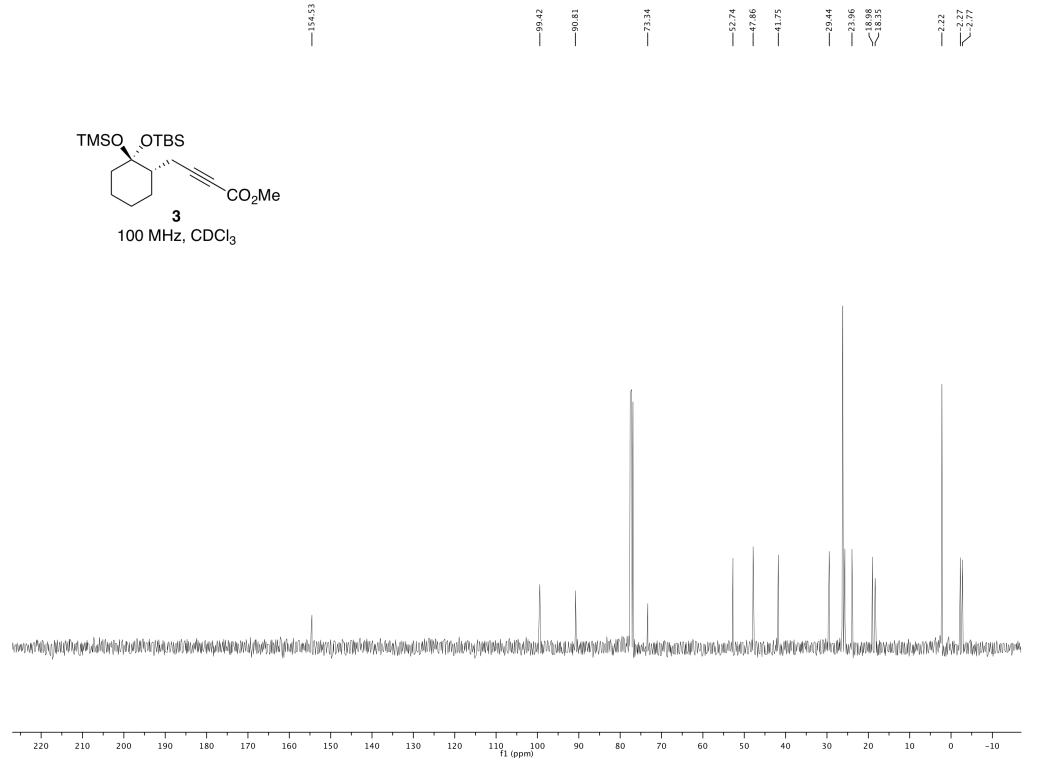
OTBS
CO2Me
3
500 MHz, CDCl3
3.749
2.735
2.729
2.700
2.694
2.122
2.108
2.086
1.896
1.812
1.660
1.503
1.425
1.291
1.122
0.863
0.161
0.086
0.045
2.94
1.00
0.99
1.00
1.02
1.08
3.16
1.02
2.26
8.80
8.48
2.85
2.86
f1 (ppm)


TMSO
OTBS
CO2Me
3
100 MHz, CDCl3
154.53
99.42
90.81
73.34
52.74
47.86
41.75
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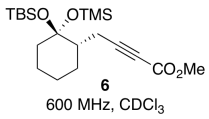
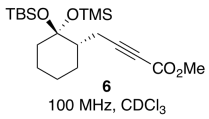
23.96
18.98
18.35
2.22
-2.27
-2.77
f1 (ppm)



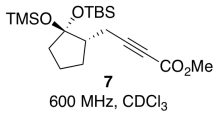
6

600 MHz, $CDCl_3$



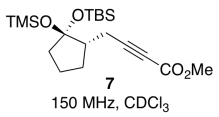
6

100 MHz, $CDCl_3$



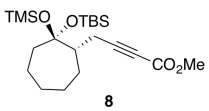
7

600 MHz, $CDCl_3$

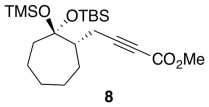


7

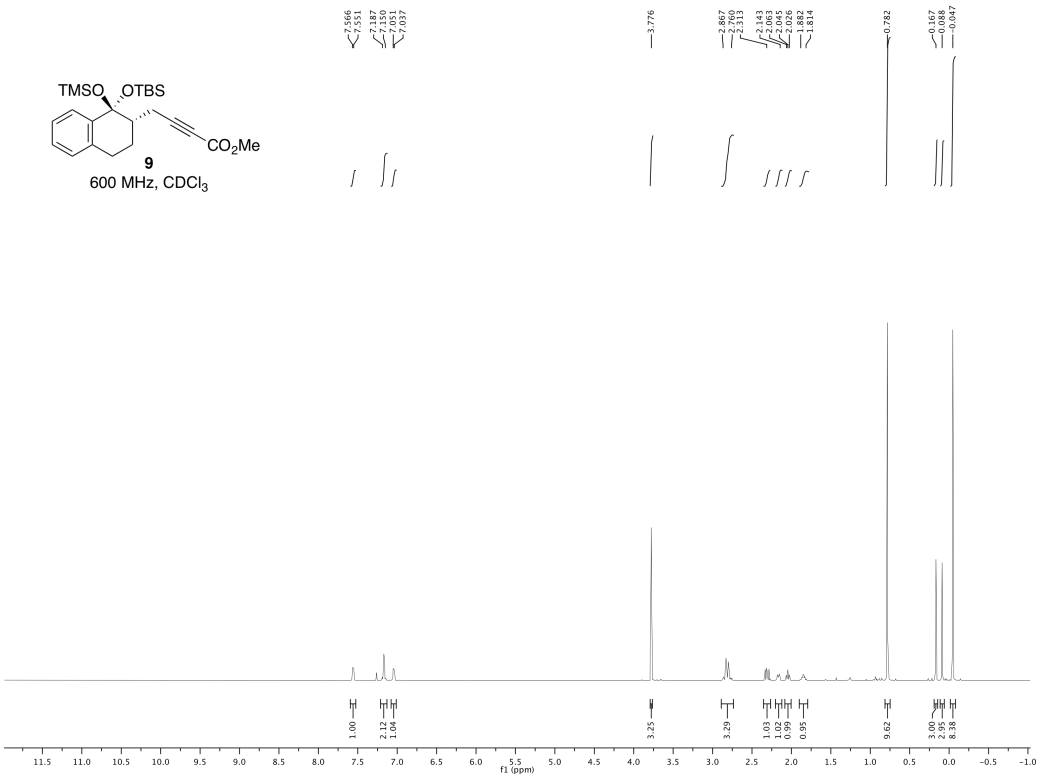
150 MHz, $CDCl_3$



8
400 MHz, $CDCl_3$



8
100 MHz, $CDCl_3$


TMSO
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9
600 MHz, CDCl3
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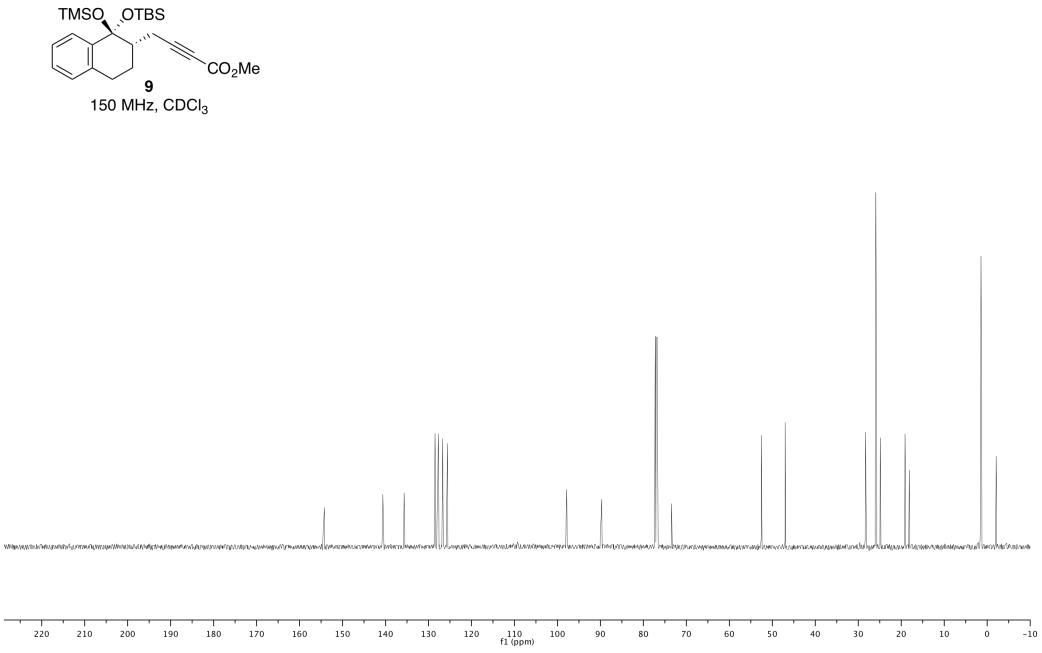
7.150
7.051
7.037
3.776
2.867
2.760
2.313
2.143
2.063
2.045
2.026
1.882
1.814
0.782
0.167
0.088
-0.047
1.00
2.12
1.04
3.25
3.29
1.03
1.02
0.99
0.95
9.62
3.00
2.95
8.38
f1 (ppm)


TMSO
OTBS
CO2Me
9
150 MHz, CDCl3
154.23
140.63
135.66
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127.67
126.72
125.59
97.85
89.69
77.21
77.00
76.79
73.42
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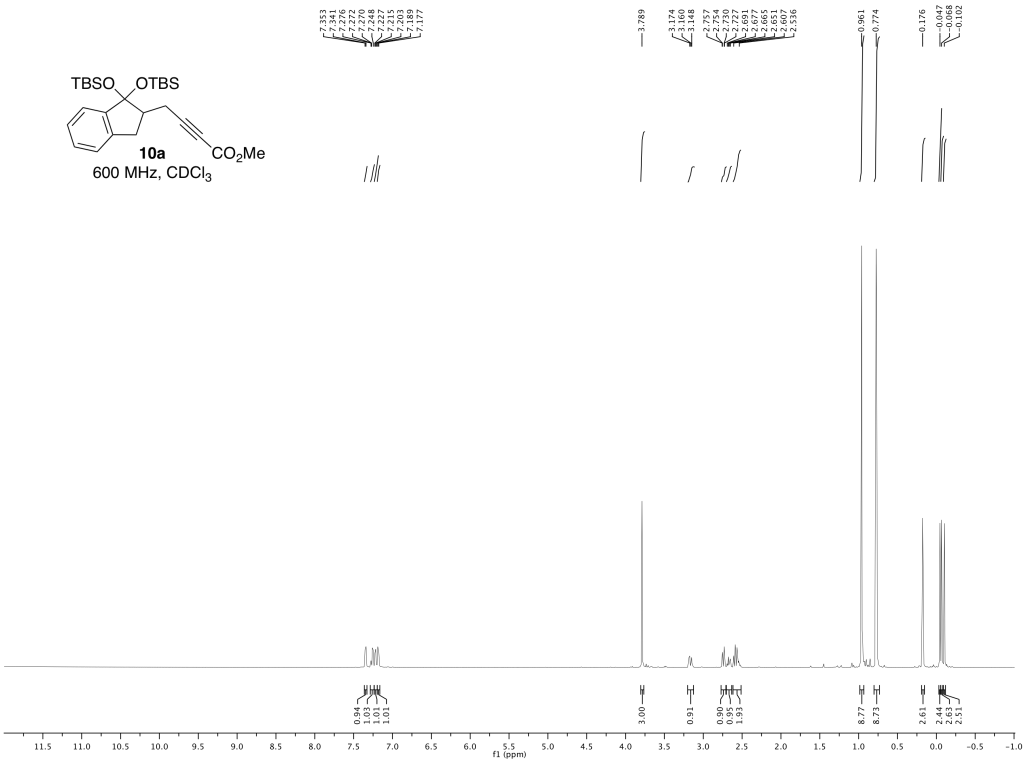
18.13
1.44
-2.10
-2.34
f1 (ppm)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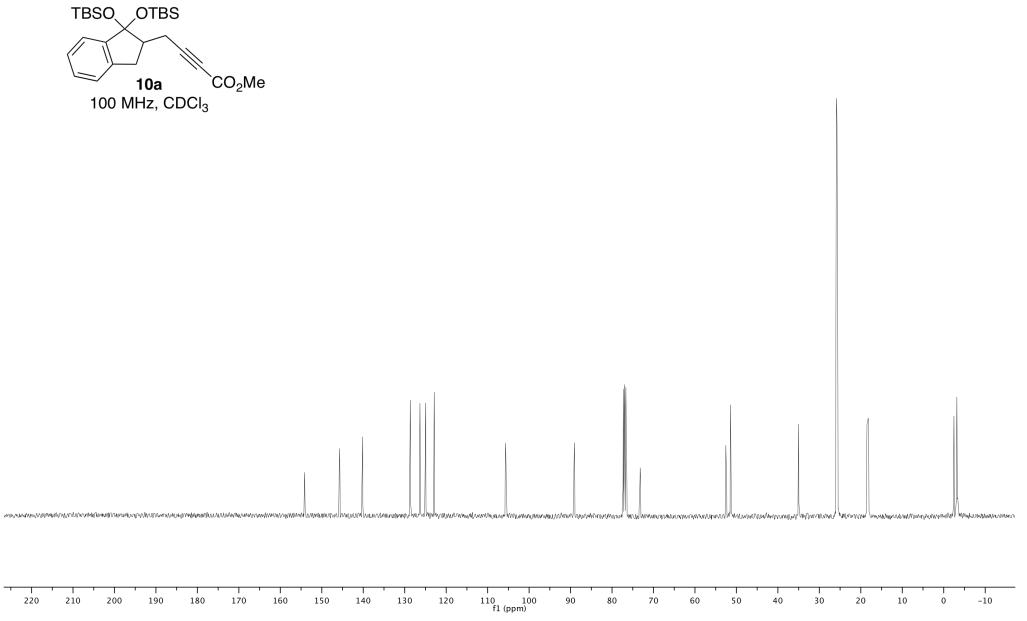
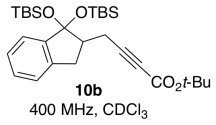
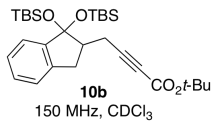
OTBS
CO2Me
10a
600 MHz, CDCl3
f1 (ppm)

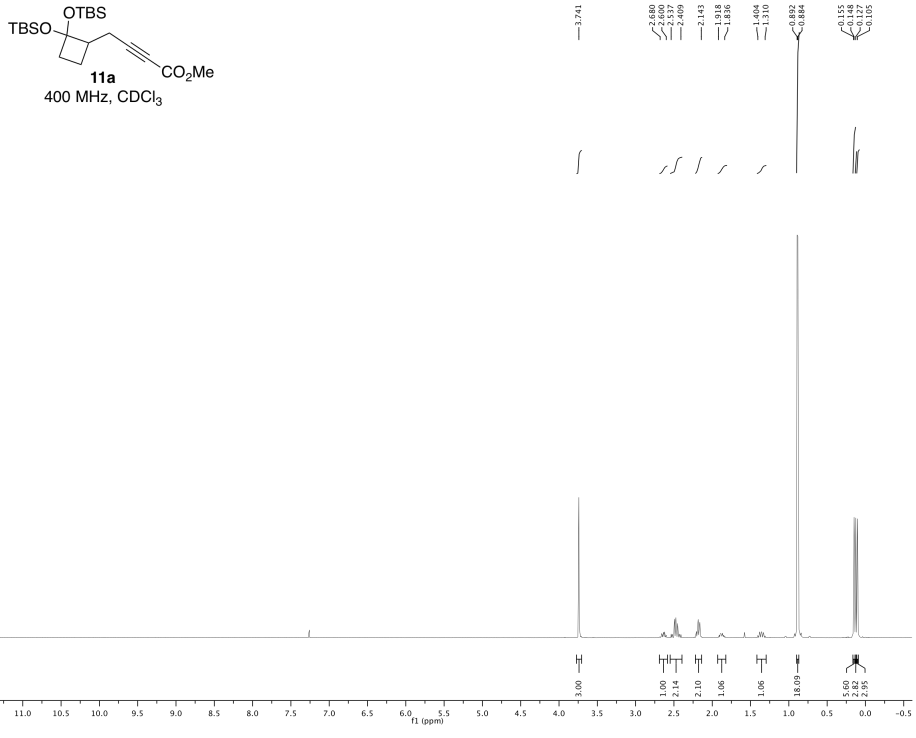

TBSO
OTBS
CO2Me
10a
100 MHz, CDCl3
f1 (ppm)



10b
400 MHz, $CDCl_3$



10b
150 MHz, $CDCl_3$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TBSO
CO2Me
11a
400 MHz, CDCl3
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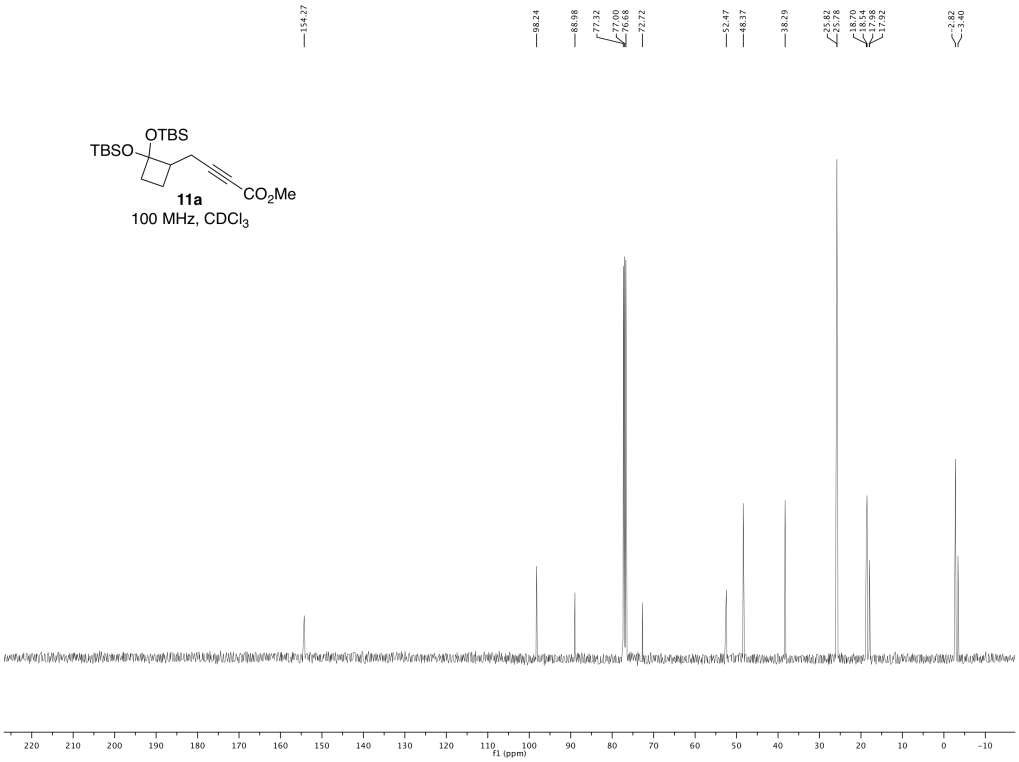
2.637
2.409
2.143
1.818
1.486
1.404
1.310
0.892
0.884
0.155
0.148
0.127
0.105
3.00
1.00
2.14
2.10
1.06
1.06
18.09
5.60
2.82
2.95
f1 (ppm)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76.68
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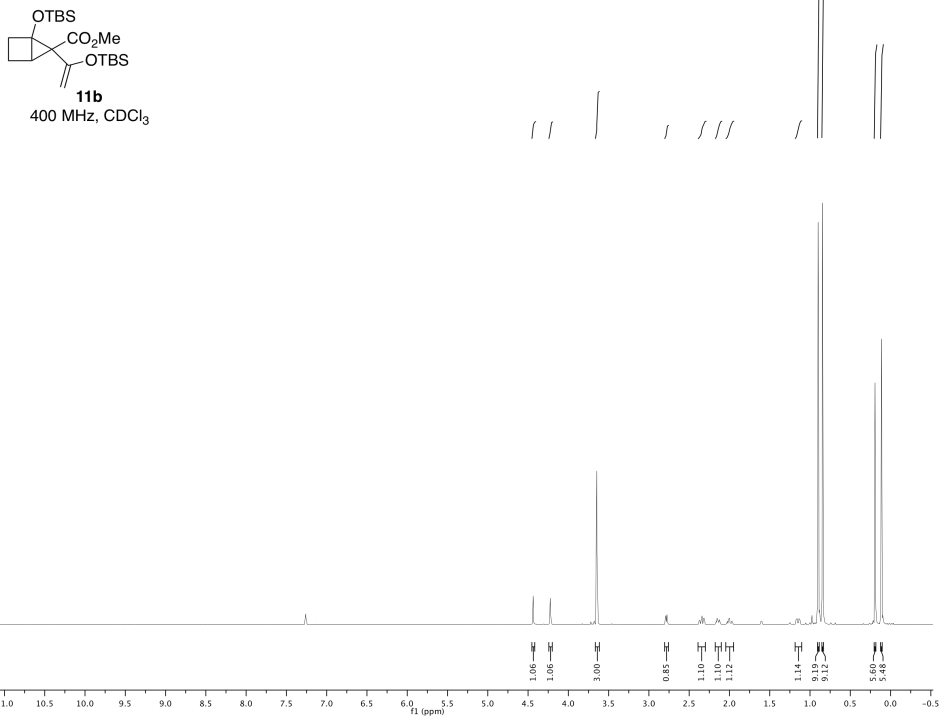
52.47
48.37
38.19
25.82
25.78
18.70
18.54
17.98
17.92
-2.82
-3.40
OTBS
TBSO
CO2Me
11a
100 MHz, CDCl3
f1 (ppm)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CO2Me
OTBS
11b
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4.223
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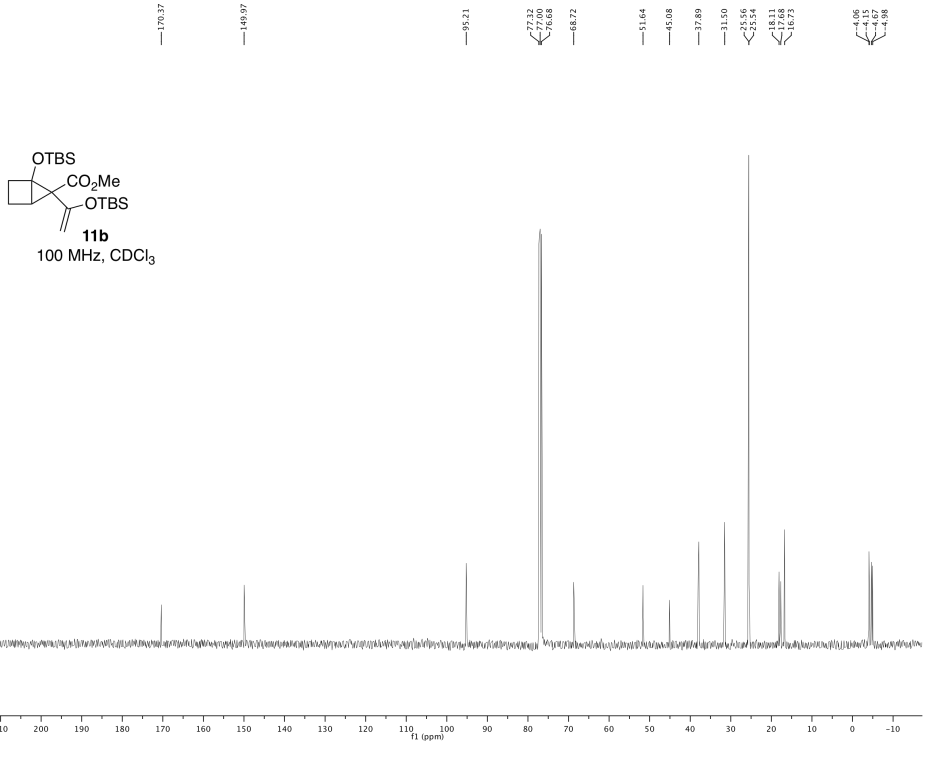
2.778
2.774
2.340
2.313
2.167
2.113
2.036
1.962
1.174
1.124
0.899
0.845
0.193
0.114
1.06
1.06
3.00
0.85
1.10
1.10
1.12
1.14
9.19
9.12
5.60
5.48
f1 (ppm)


OTBS
CO2Me
OTBS
11b
100 MHz, CDCl3
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77.00
76.68
68.72
51.64
45.08
37.89
31.50
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25.54
18.11
17.68
16.73
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-4.15
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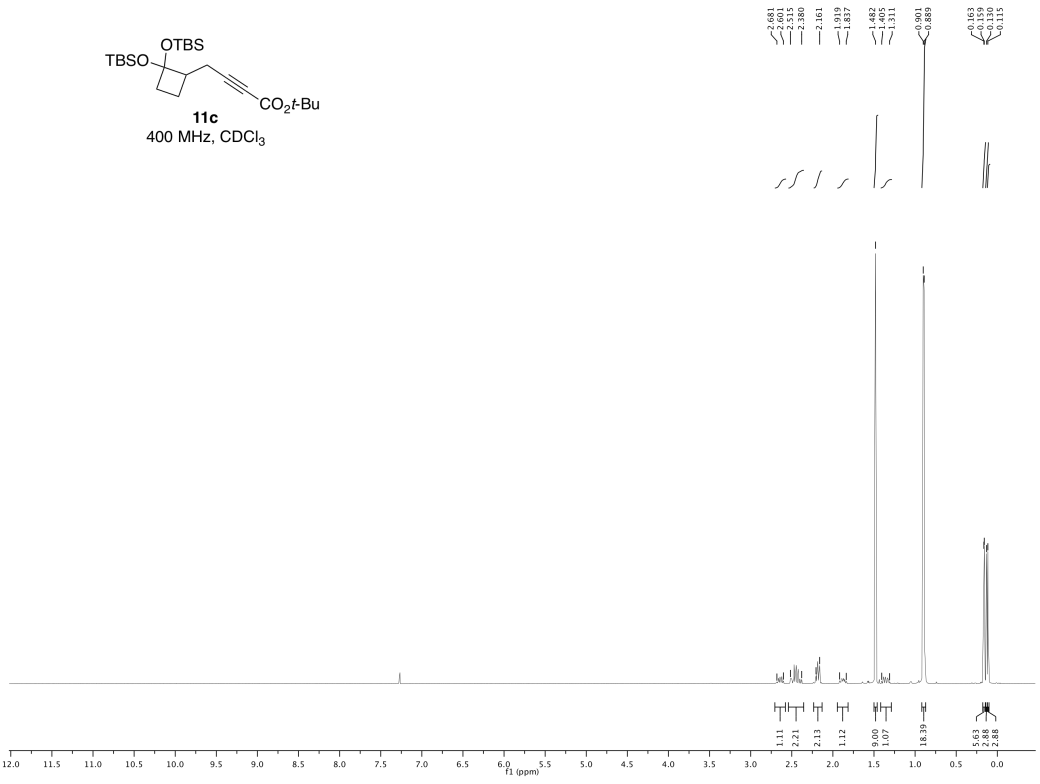
f1 (ppm)


OTBS
TBSO
CO2t-Bu
11c
400 MHz, CDCl3
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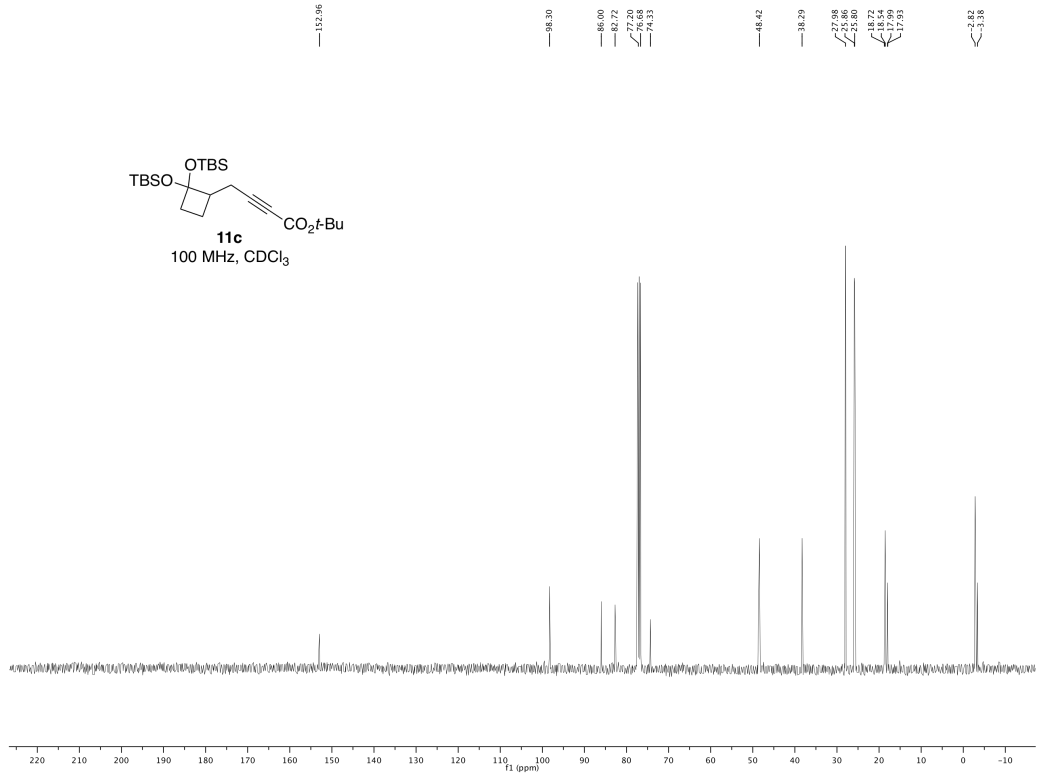
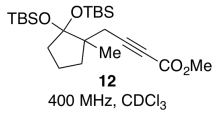
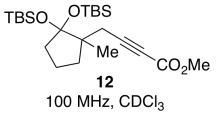
1.837
1.482
1.465
1.311
0.901
0.889
0.163
0.159
0.130
0.115
1.11
2.21
2.13
1.12
9.00
1.07
18.39
5.63
2.88
2.88
f1 (ppm)


152.96
98.30
86.00
82.72
77.20
76.68
74.33
48.42
38.29
27.98
25.86
25.80
18.72
18.54
17.99
17.93
2.82
-3.36
OTBS
TBSO
CO2t-Bu
11c
100 MHz, CDCl3
f1 (ppm)



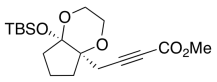
12

400 MHz, $CDCl_3$

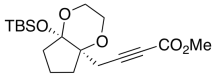


12

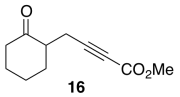
100 MHz, $CDCl_3$



13
400 MHz, $CDCl_3$

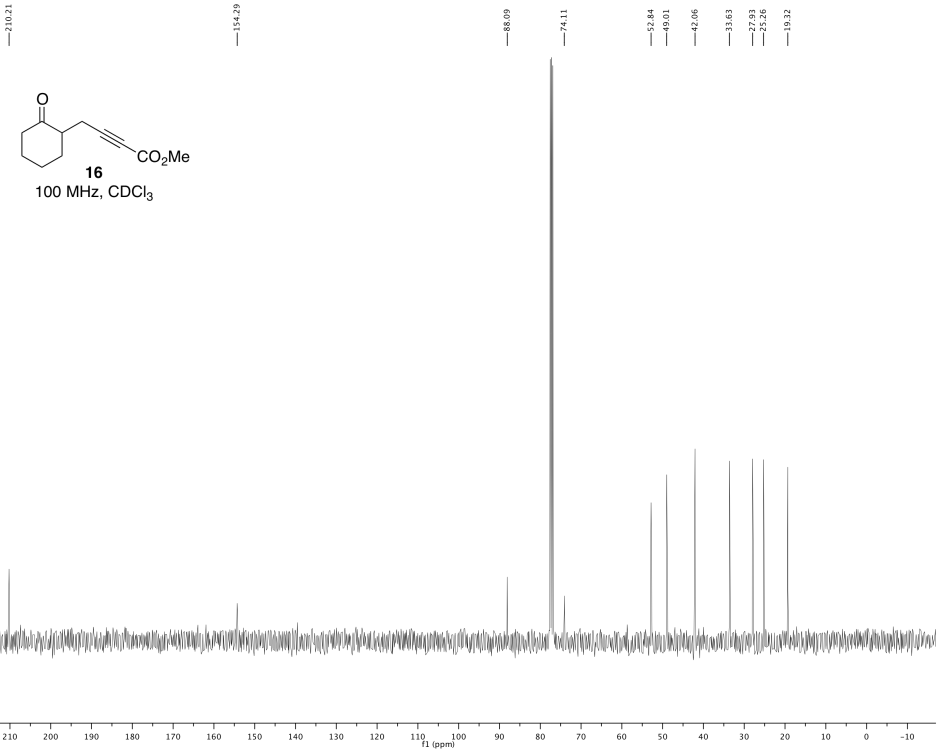


13
100 MHz, $CDCl_3$



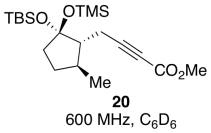
16

400 MHz, $CDCl_3$



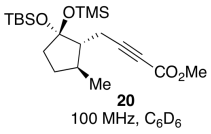
16

100 MHz, $CDCl_3$



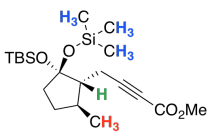
20

600 MHz, C_6D_6

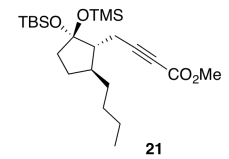


20

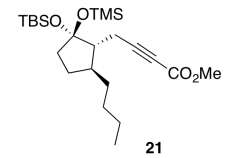
100 MHz, C_6D_6



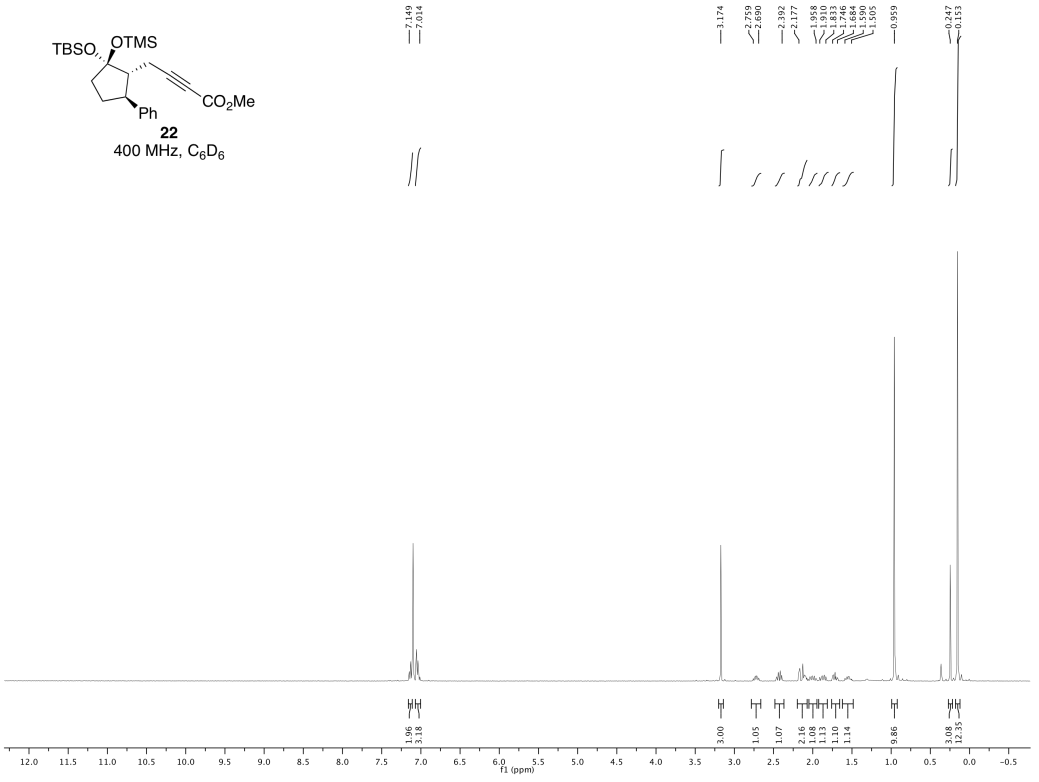
20
600 MHz, C_6D_6

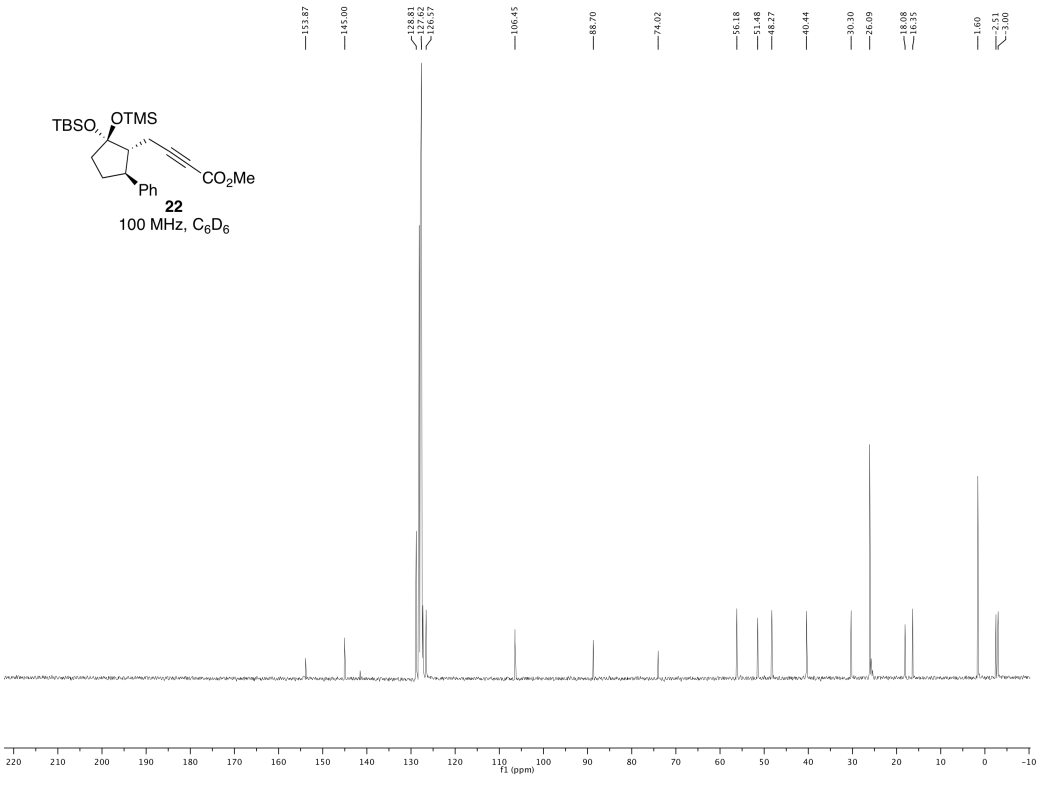


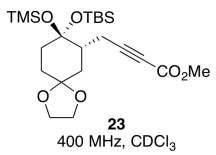
21
400 MHz, C_6D_6



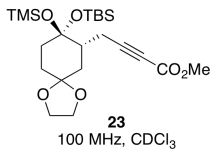
21
100 MHz, C_6D_6


TBSO
OTMS
Ph
CO2Me
22
400 MHz, C6D6
f1 (ppm)

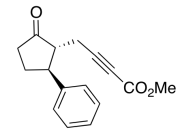

TBSO
OTMS
Ph
CO2Me
22
100 MHz, C6D6
f1 (ppm)



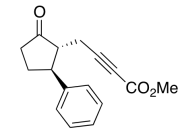
23
400 MHz, $CDCl_3$



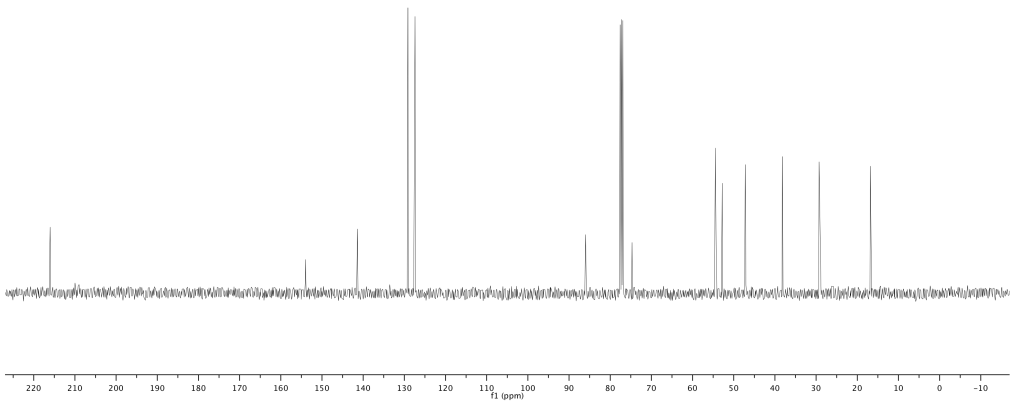
23
100 MHz, $CDCl_3$

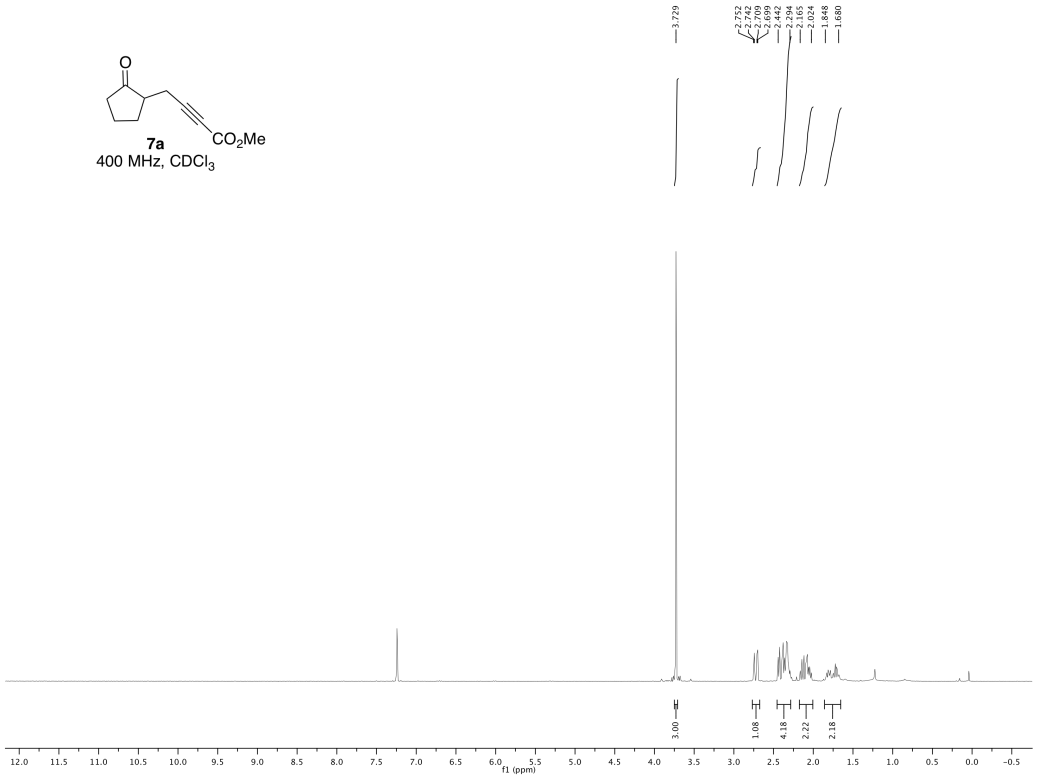


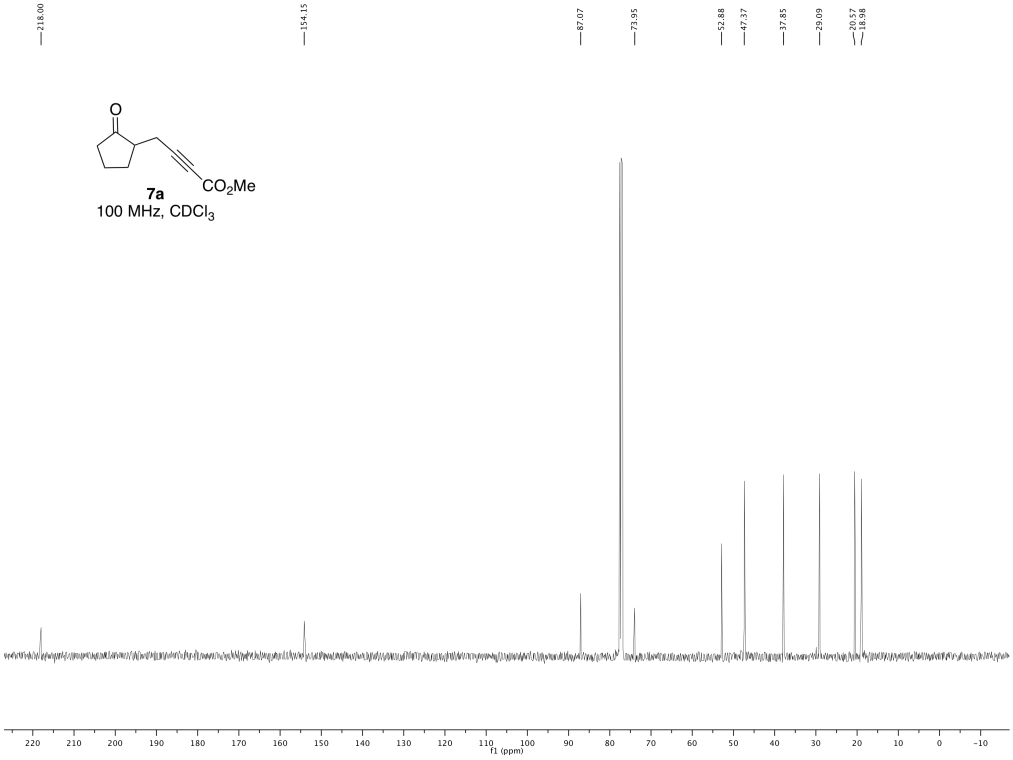
22a
400 MHz, $CDCl_3$

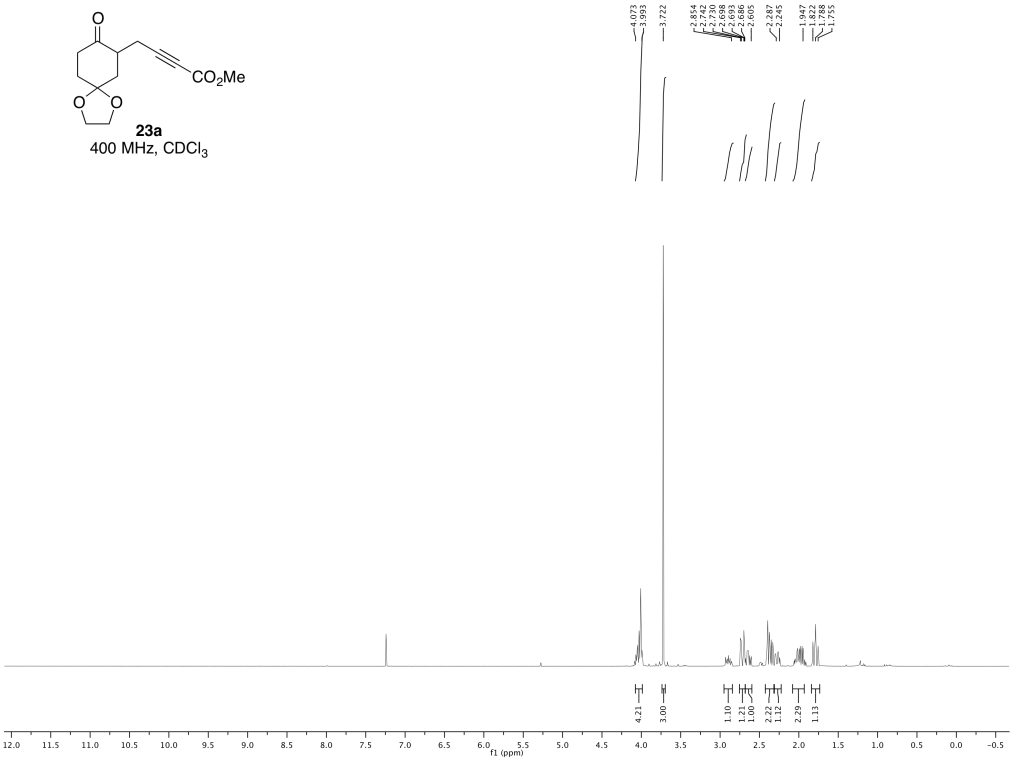


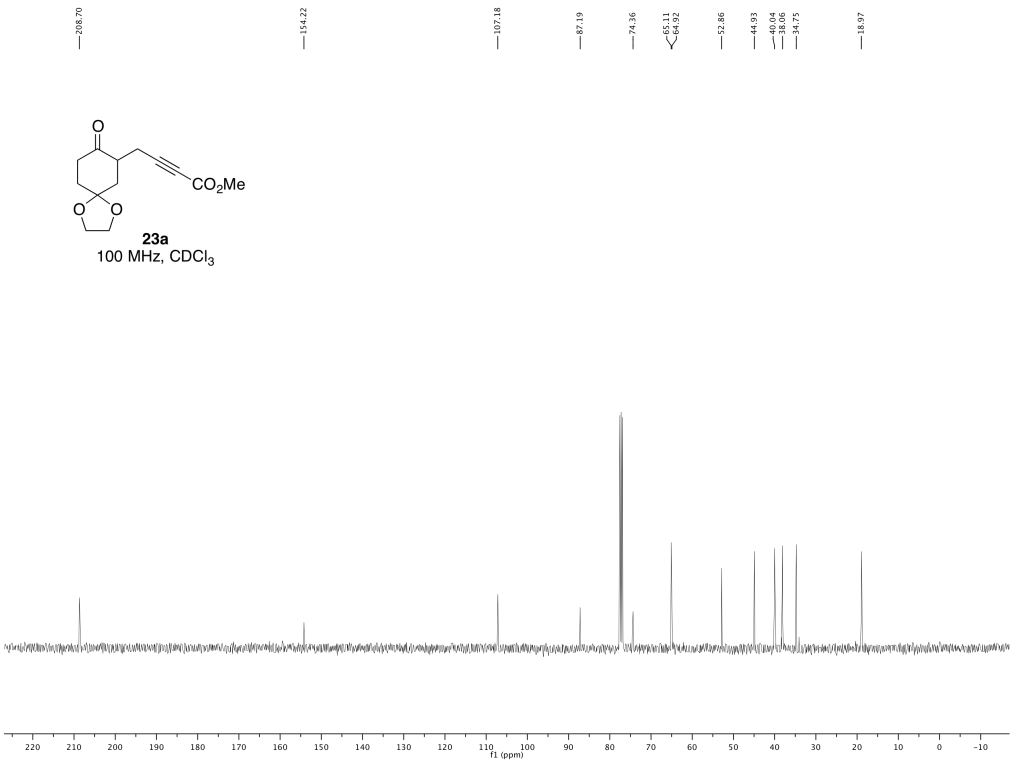
22a
100 MHz, $CDCl_3$

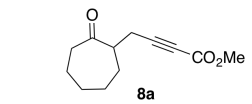



O
CO2Me
7a
400 MHz, CDCl3
3.729
2.752
2.742
2.709
2.699
2.442
2.394
2.165
2.024
1.848
1.680
3.00
1.08
4.18
2.22
2.18
f1 (ppm)

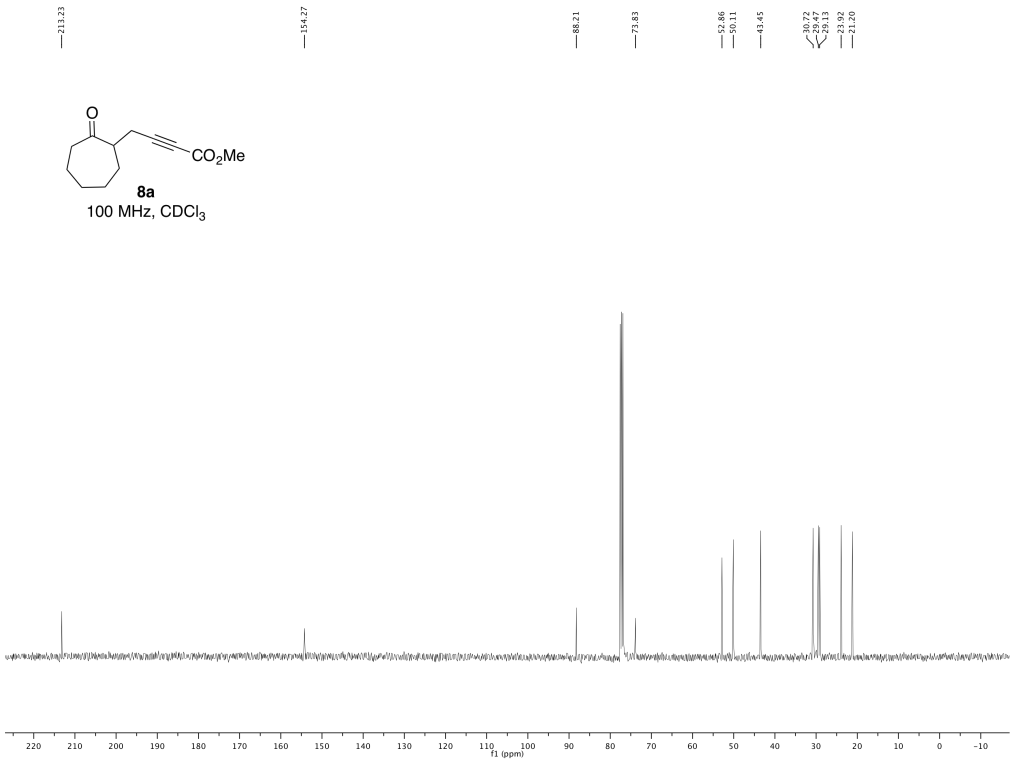

O
CO2Me
7a
100 MHz, CDCl3
218.00
154.15
87.07
73.95
52.88
47.37
37.85
29.09
20.57
18.98
f1 (ppm)


CO2Me
23a
400 MHz, CDCl3
4.073
3.993
3.722
2.854
2.732
2.730
2.698
2.695
2.686
2.605
2.287
2.245
1.987
1.962
1.788
1.755
4.21
3.00
1.10
1.21
1.00
2.22
1.12
2.29
1.13
f1 (ppm)

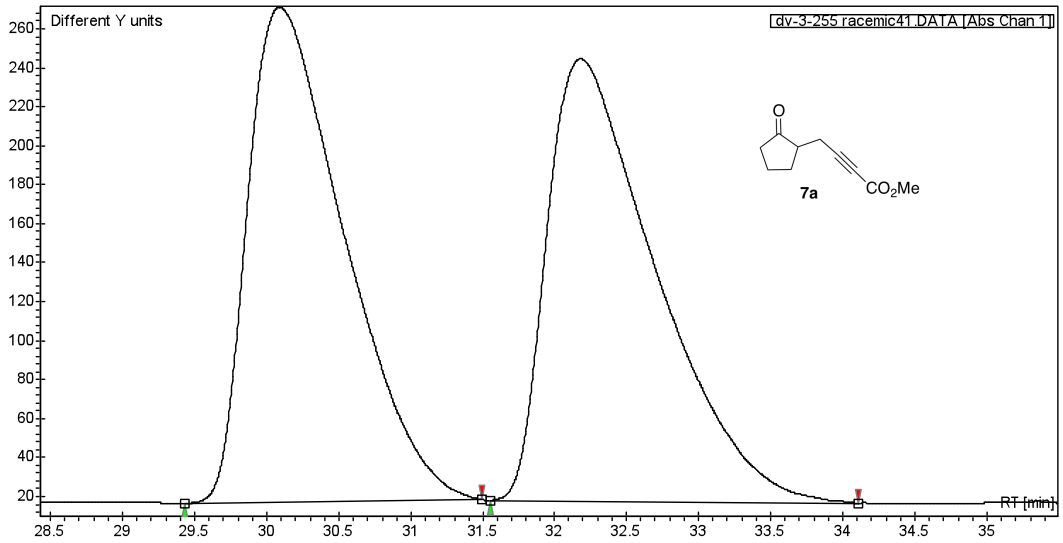

CO2Me
23a
100 MHz, CDCl3
208.70
154.22
107.18
87.19
74.36
65.11
64.92
52.86
44.93
40.04
38.06
34.75
18.97
f1 (ppm)



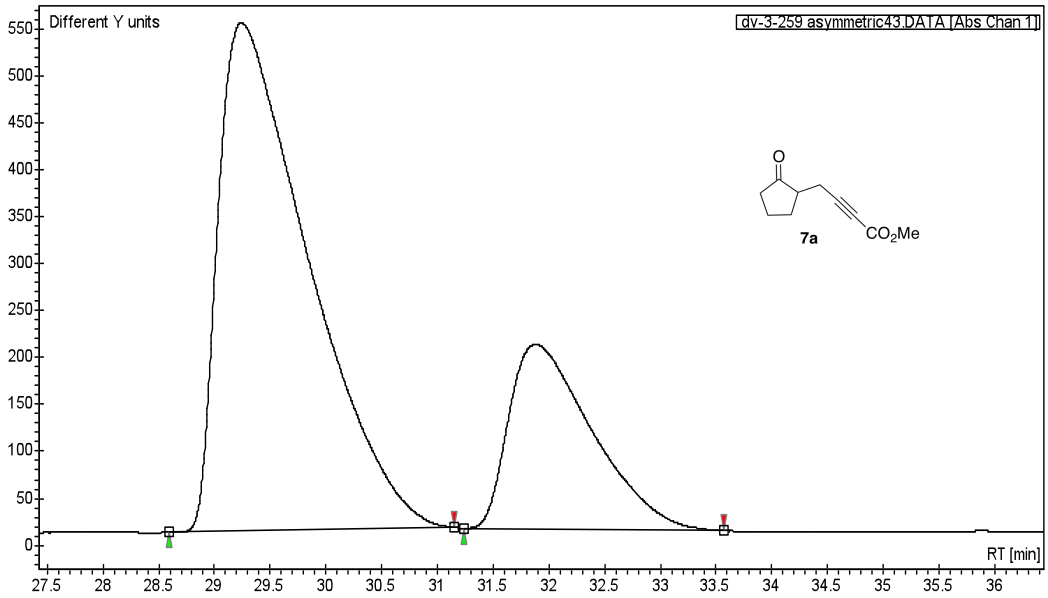
8a
400 MHz, $CDCl_3$



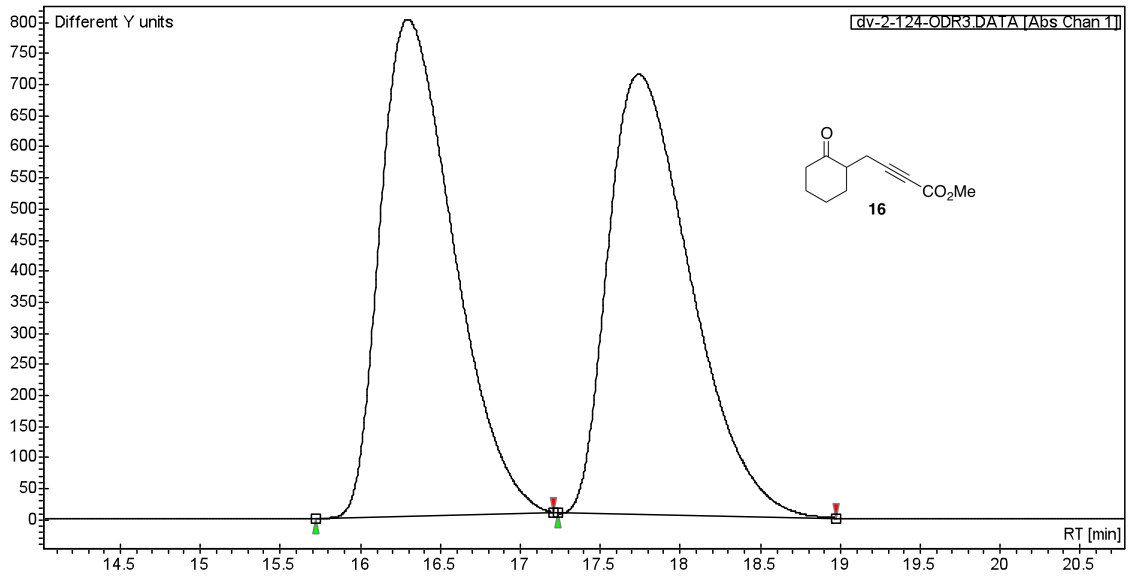
8a
100 MHz, $CDCl_3$



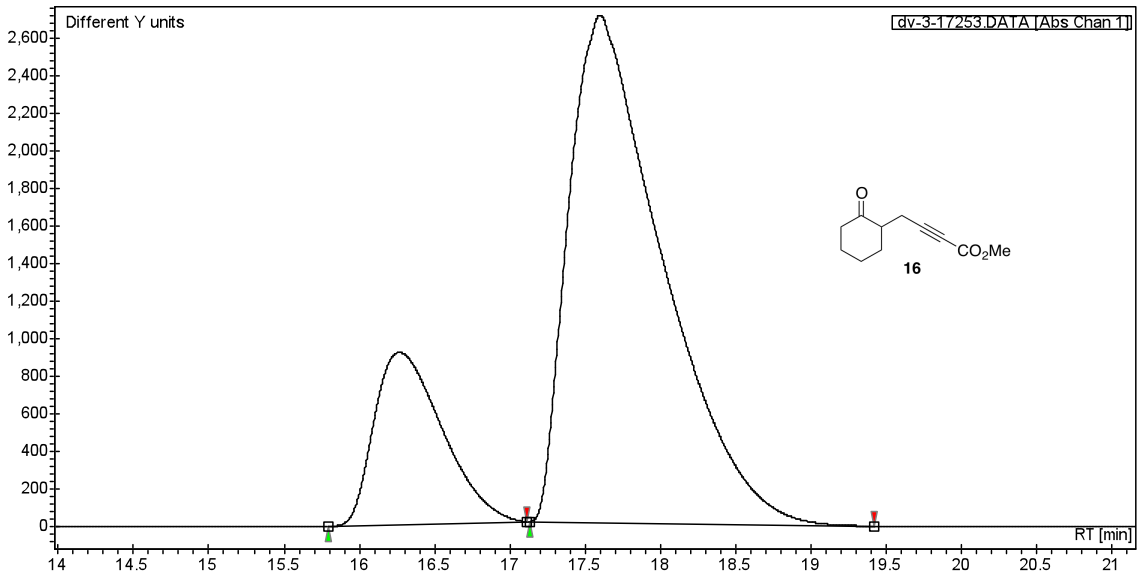
#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	30.09	49.80	254.2	197.6	49.802
2	32.18	50.20	227.1	199.2	50.198



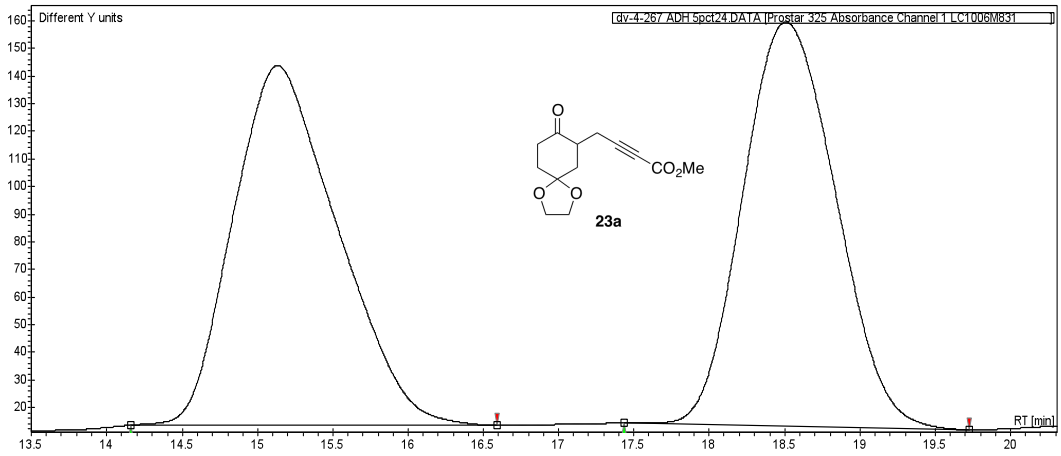
#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	29.24	74.90	541.5	507.8	74.899
2	31.88	25.10	196.4	170.2	25.101



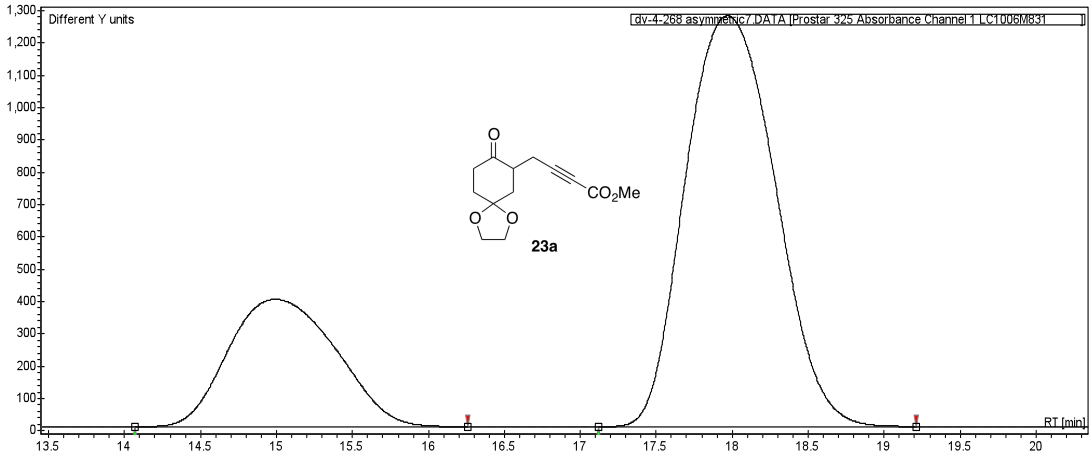
#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	16.30	50.07	799.1	425.7	50.068
2	17.74	49.93	708.1	424.6	49.932



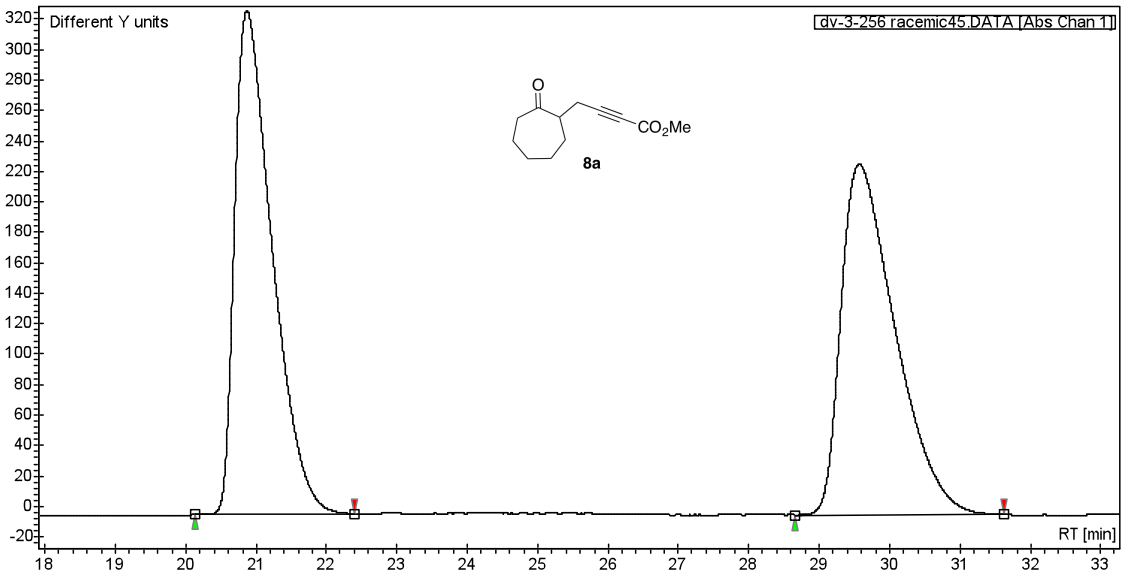
#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	16.26	19.84	918.2	483.7	19.842
2	17.60	80.16	2704.6	1954.2	80.158



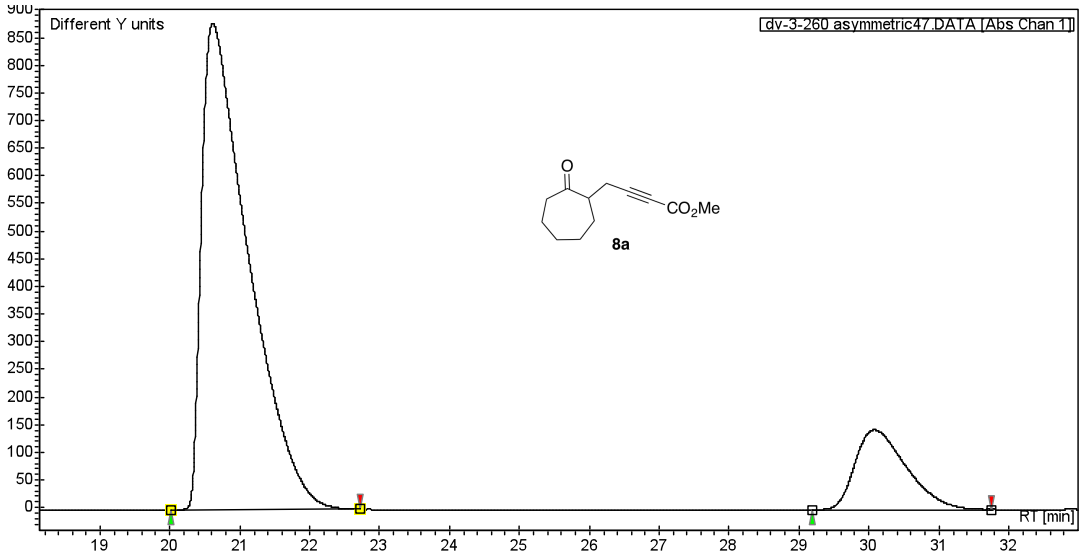
#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	15.13	49.92	130.3	104.6	49.923
2	18.51	50.08	146.5	104.9	50.077



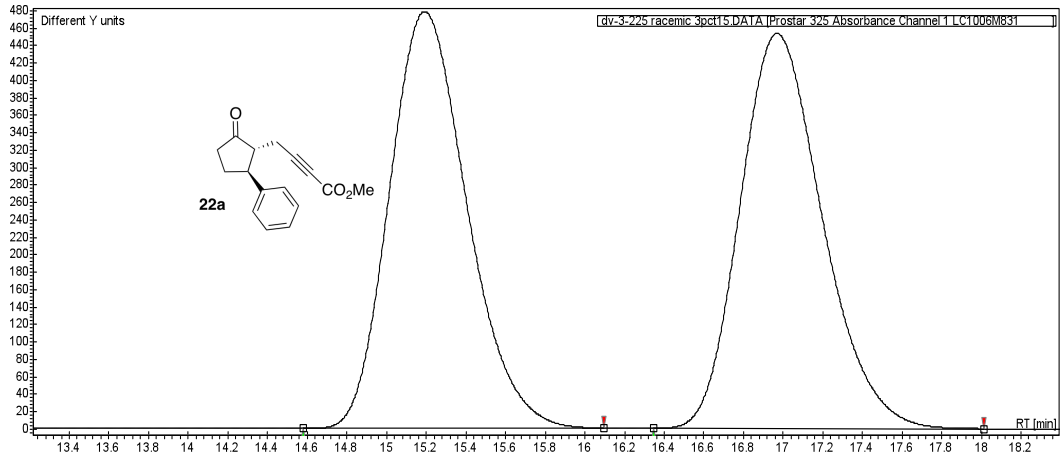
#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	14.99	27.06	394.3	324.5	27.061
2	17.97	72.94	1271.8	874.6	72.939



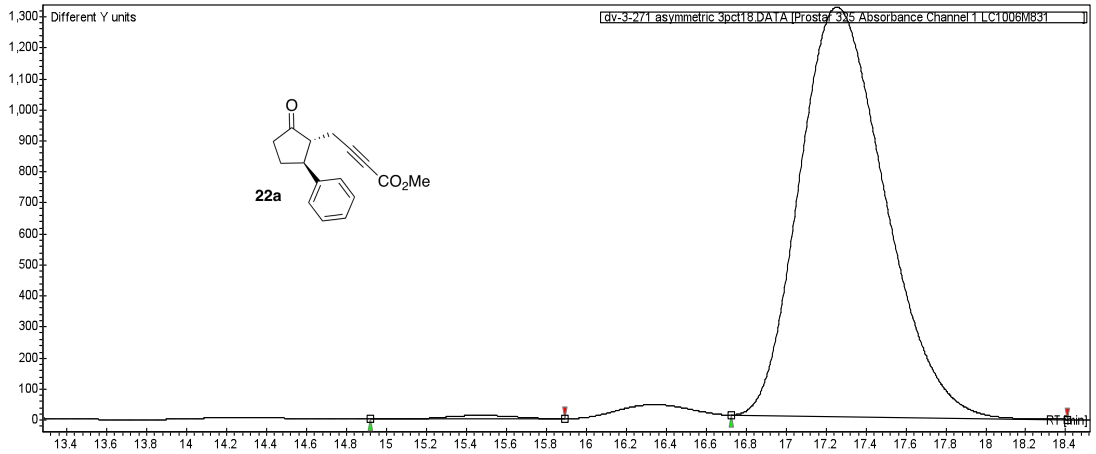
#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	20.87	49.88	330.9	204.3	49.883
2	29.57	50.12	230.4	205.2	50.117



#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	20.61	84.78	879.1	684.1	84.783
2	30.08	15.22	144.2	122.8	15.217



#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	15.19	49.92	478.2	217.0	49.915
2	16.97	50.08	453.4	217.8	50.085



#	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	15.47	0.71	11.6	4.7	0.708
2	17.26	99.29	1321.3	654.0	99.292

X-Ray Crystallographic Data for Compound 3.

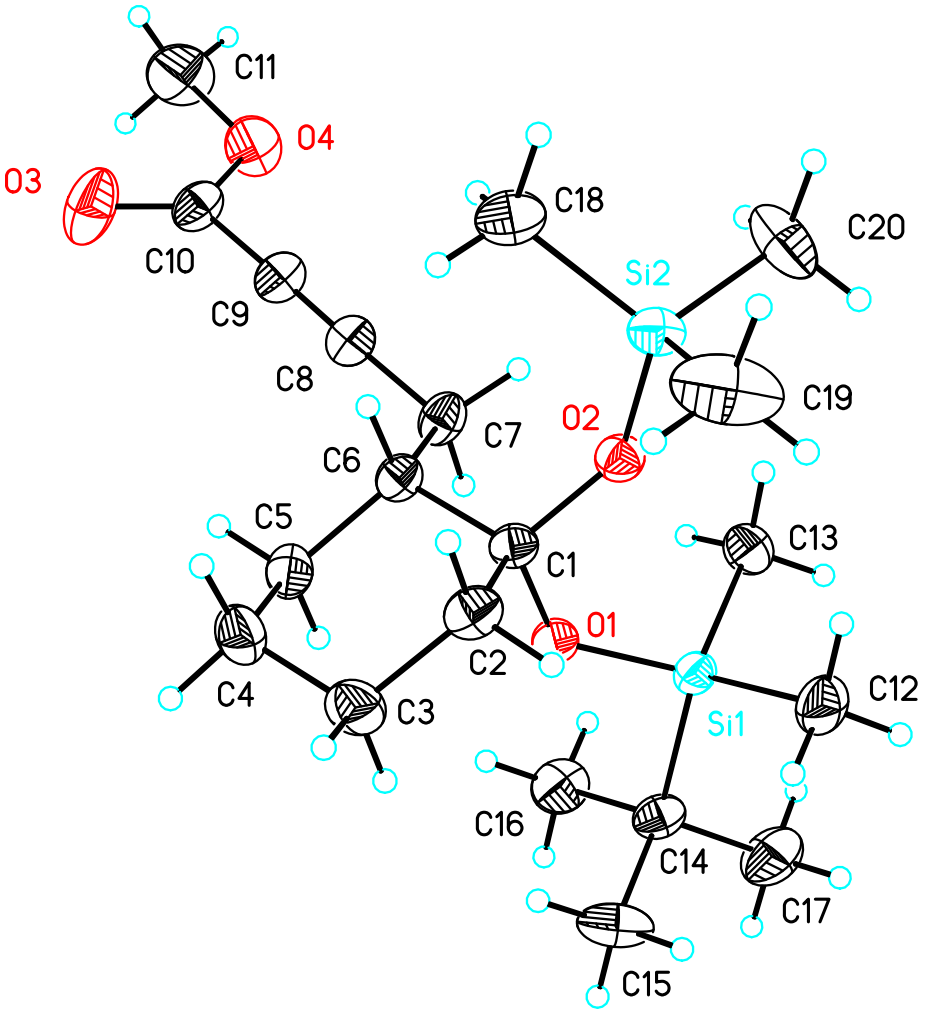


Table 1. Crystal data and structure refinement for YL_9X.

Identification code	yl_9x	
Empirical formula	C20 H38 O4 Si2	
Formula weight	398.68	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.1472(2) Å	α= 90°.
	b = 11.3292(3) Å	β= 90°.
	c = 26.4033(7) Å	γ = 90°.
Volume	2437.06(11) $Å^3$	
Z	4	
Density (calculated)	1.087 Mg/m^3	
Absorption coefficient	1.474 mm^{-1}	
F(000)	872	
Crystal size	0.34 x 0.10 x 0.04 mm^3	
Theta range for data collection	3.35 to 67.95°.	
Index ranges	-9<=h<=8, -13<=k<=10, -29<=l<=27	
Reflections collected	19192	
Independent reflections	4059 [R(int) = 0.0223]	
Completeness to theta = 67.95°	96.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9434 and 0.6342	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4059 / 0 / 236	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0835	
R indices (all data)	R1 = 0.0321, wR2 = 0.0848	
Absolute structure parameter	0.45(2)	
Largest diff. peak and hole	0.265 and -0.157 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for YL_9X. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7259(2)	9942(2)	8533(1)	34(1)
C(2)	6046(2)	10284(2)	8121(1)	44(1)
C(3)	4887(2)	9279(2)	7989(1)	52(1)
C(4)	5836(3)	8158(2)	7846(1)	53(1)
C(5)	7016(2)	7821(2)	8267(1)	45(1)
C(6)	8209(2)	8824(2)	8387(1)	36(1)
C(7)	9422(2)	8495(2)	8807(1)	42(1)
C(8)	10558(2)	7554(2)	8667(1)	42(1)
C(9)	11516(2)	6790(2)	8565(1)	43(1)
C(10)	12642(2)	5848(2)	8457(1)	45(1)
C(11)	15092(3)	4932(2)	8691(1)	81(1)
C(12)	5596(3)	11967(2)	9436(1)	55(1)
C(13)	8211(2)	10373(2)	9888(1)	49(1)
C(14)	4618(2)	9516(2)	9866(1)	41(1)
C(15)	3002(2)	9559(2)	9573(1)	63(1)
C(16)	5169(3)	8232(2)	9911(1)	56(1)
C(17)	4345(3)	10009(2)	10403(1)	66(1)
C(18)	10649(3)	10993(3)	7803(1)	73(1)
C(19)	8317(3)	12989(3)	8036(2)	104(1)
C(20)	11030(4)	12347(2)	8776(1)	75(1)
O(1)	6380(2)	9689(1)	8982(1)	36(1)
O(2)	8353(1)	10878(1)	8649(1)	38(1)
O(3)	12458(2)	5137(2)	8124(1)	79(1)
O(4)	13877(2)	5843(1)	8777(1)	66(1)
Si(1)	6247(1)	10403(1)	9526(1)	33(1)
Si(2)	9527(1)	11772(1)	8312(1)	40(1)

Table 3. Bond lengths [Å] and angles [°] for YL_9X.

C(1)-O(1)	1.415(2)
C(1)-O(2)	1.418(2)
C(1)-C(2)	1.520(2)
C(1)-C(6)	1.534(2)
C(2)-C(3)	1.521(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.533(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.518(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.529(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.531(2)
C(6)-H(6A)	1.0000
C(7)-C(8)	1.460(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.195(3)
C(9)-C(10)	1.437(3)
C(10)-O(3)	1.202(3)
C(10)-O(4)	1.314(3)
C(11)-O(4)	1.447(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-Si(1)	1.8650(19)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-Si(1)	1.8642(19)

C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(16)	1.528(3)
C(14)-C(15)	1.528(3)
C(14)-C(17)	1.539(3)
C(14)-Si(1)	1.8915(18)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-Si(2)	1.850(2)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-Si(2)	1.845(2)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-Si(2)	1.851(2)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
O(1)-Si(1)	1.6502(12)
O(2)-Si(2)	1.6529(12)

O(1)-C(1)-O(2)	106.80(13)
O(1)-C(1)-C(2)	108.82(14)
O(2)-C(1)-C(2)	111.84(14)
O(1)-C(1)-C(6)	107.36(14)
O(2)-C(1)-C(6)	110.75(13)

C(2)-C(1)-C(6)	111.05(14)
C(1)-C(2)-C(3)	112.13(16)
C(1)-C(2)-H(2A)	109.2
C(3)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2B)	109.2
C(3)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
C(2)-C(3)-C(4)	111.32(16)
C(2)-C(3)-H(3A)	109.4
C(4)-C(3)-H(3A)	109.4
C(2)-C(3)-H(3B)	109.4
C(4)-C(3)-H(3B)	109.4
H(3A)-C(3)-H(3B)	108.0
C(5)-C(4)-C(3)	110.34(17)
C(5)-C(4)-H(4A)	109.6
C(3)-C(4)-H(4A)	109.6
C(5)-C(4)-H(4B)	109.6
C(3)-C(4)-H(4B)	109.6
H(4A)-C(4)-H(4B)	108.1
C(4)-C(5)-C(6)	111.59(16)
C(4)-C(5)-H(5A)	109.3
C(6)-C(5)-H(5A)	109.3
C(4)-C(5)-H(5B)	109.3
C(6)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	108.0
C(5)-C(6)-C(7)	112.37(15)
C(5)-C(6)-C(1)	110.20(14)
C(7)-C(6)-C(1)	110.19(14)
C(5)-C(6)-H(6A)	108.0
C(7)-C(6)-H(6A)	108.0
C(1)-C(6)-H(6A)	108.0
C(8)-C(7)-C(6)	113.79(16)
C(8)-C(7)-H(7A)	108.8
C(6)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7B)	108.8
C(6)-C(7)-H(7B)	108.8

H(7A)-C(7)-H(7B)	107.7
C(9)-C(8)-C(7)	177.9(2)
C(8)-C(9)-C(10)	178.0(2)
O(3)-C(10)-O(4)	124.29(19)
O(3)-C(10)-C(9)	124.4(2)
O(4)-C(10)-C(9)	111.33(18)
O(4)-C(11)-H(11A)	109.5
O(4)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
O(4)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
Si(1)-C(12)-H(12A)	109.5
Si(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
Si(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
Si(1)-C(13)-H(13A)	109.5
Si(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
Si(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(16)-C(14)-C(15)	108.83(19)
C(16)-C(14)-C(17)	108.46(17)
C(15)-C(14)-C(17)	109.25(18)
C(16)-C(14)-Si(1)	109.67(13)
C(15)-C(14)-Si(1)	110.28(13)
C(17)-C(14)-Si(1)	110.30(15)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(2)-C(20)-H(20A)	109.5
Si(2)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(2)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(1)-O(1)-Si(1)	131.50(11)
C(1)-O(2)-Si(2)	134.90(11)
C(10)-O(4)-C(11)	115.21(19)
O(1)-Si(1)-C(13)	112.35(8)
O(1)-Si(1)-C(12)	111.95(9)
C(13)-Si(1)-C(12)	109.05(11)

O(1)-Si(1)-C(14)	101.50(8)
C(13)-Si(1)-C(14)	110.41(9)
C(12)-Si(1)-C(14)	111.44(9)
O(2)-Si(2)-C(19)	111.20(11)
O(2)-Si(2)-C(18)	112.63(10)
C(19)-Si(2)-C(18)	109.51(16)
O(2)-Si(2)-C(20)	104.01(9)
C(19)-Si(2)-C(20)	110.58(15)
C(18)-Si(2)-C(20)	108.78(14)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for YL_9X. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	33(1)	38(1)	33(1)	2(1)	3(1)	0(1)
C(2)	41(1)	51(1)	39(1)	5(1)	-2(1)	9(1)
C(3)	42(1)	66(1)	49(1)	-2(1)	-11(1)	-1(1)
C(4)	55(1)	58(1)	47(1)	-11(1)	-7(1)	-9(1)
C(5)	51(1)	41(1)	43(1)	-6(1)	2(1)	0(1)
C(6)	38(1)	39(1)	32(1)	-1(1)	2(1)	3(1)
C(7)	46(1)	44(1)	37(1)	-2(1)	-3(1)	13(1)
C(8)	45(1)	43(1)	37(1)	3(1)	0(1)	5(1)
C(9)	47(1)	42(1)	41(1)	6(1)	2(1)	8(1)
C(10)	51(1)	40(1)	45(1)	6(1)	9(1)	10(1)
C(11)	56(1)	60(2)	127(3)	4(2)	-10(2)	23(1)
C(12)	59(1)	33(1)	72(2)	0(1)	9(1)	9(1)
C(13)	43(1)	57(1)	47(1)	-8(1)	-8(1)	-3(1)
C(14)	38(1)	45(1)	40(1)	7(1)	7(1)	4(1)
C(15)	34(1)	80(2)	75(2)	26(1)	4(1)	-6(1)
C(16)	62(1)	45(1)	59(1)	14(1)	13(1)	0(1)
C(17)	71(2)	77(2)	52(1)	2(1)	22(1)	6(1)
C(18)	66(2)	83(2)	69(2)	-5(1)	31(1)	-19(1)
C(19)	62(2)	78(2)	170(3)	78(2)	-3(2)	9(1)
C(20)	89(2)	66(2)	69(2)	8(1)	-17(1)	-39(1)
O(1)	36(1)	38(1)	34(1)	0(1)	4(1)	-3(1)
O(2)	38(1)	36(1)	39(1)	2(1)	4(1)	-1(1)
O(3)	96(1)	74(1)	66(1)	-19(1)	-11(1)	39(1)
O(4)	53(1)	54(1)	90(1)	-6(1)	-18(1)	17(1)
Si(1)	32(1)	31(1)	36(1)	-2(1)	3(1)	3(1)
Si(2)	35(1)	38(1)	46(1)	11(1)	1(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for YL_9X.

	x	y	z	U(eq)
H(2A)	6658	10522	7814	52
H(2B)	5397	10972	8236	52
H(3A)	4180	9518	7702	62
H(3B)	4169	9111	8283	62
H(4A)	5054	7504	7786	64
H(4B)	6455	8296	7529	64
H(5A)	7644	7113	8164	54
H(5B)	6384	7620	8575	54
H(6A)	8853	8999	8074	44
H(7A)	10064	9205	8900	51
H(7B)	8797	8246	9110	51
H(11A)	15959	4995	8947	121
H(11B)	15570	5030	8353	121
H(11C)	14570	4155	8715	121
H(12A)	6464	12402	9259	82
H(12B)	5394	12330	9767	82
H(12C)	4587	11990	9234	82
H(13A)	8559	9553	9937	74
H(13B)	8049	10749	10218	74
H(13C)	9057	10802	9698	74
H(15A)	2170	9096	9753	94
H(15B)	3166	9230	9234	94
H(15C)	2633	10380	9545	94
H(16A)	4322	7775	10087	83
H(16B)	6197	8193	10103	83
H(16C)	5340	7903	9572	83
H(17A)	3500	9541	10575	100
H(17B)	3986	10833	10381	100
H(17C)	5373	9965	10594	100
H(18A)	9864	10686	7554	109

H(18B)	11274	10336	7948	109
H(18C)	11404	11543	7636	109
H(19A)	7722	13401	8306	156
H(19B)	7532	12670	7790	156
H(19C)	9056	13544	7865	156
H(20A)	10449	12766	9046	113
H(20B)	11786	12890	8606	113
H(20C)	11652	11688	8921	113

Table 6. Torsion angles [°] for YL_9X.

O(1)-C(1)-C(2)-C(3)	-63.2(2)
O(2)-C(1)-C(2)-C(3)	179.07(15)
C(6)-C(1)-C(2)-C(3)	54.8(2)
C(1)-C(2)-C(3)-C(4)	-54.6(2)
C(2)-C(3)-C(4)-C(5)	55.2(2)
C(3)-C(4)-C(5)-C(6)	-57.1(2)
C(4)-C(5)-C(6)-C(7)	-179.36(16)
C(4)-C(5)-C(6)-C(1)	57.3(2)
O(1)-C(1)-C(6)-C(5)	63.41(18)
O(2)-C(1)-C(6)-C(5)	179.66(14)
C(2)-C(1)-C(6)-C(5)	-55.44(19)
O(1)-C(1)-C(6)-C(7)	-61.16(18)
O(2)-C(1)-C(6)-C(7)	55.10(19)
C(2)-C(1)-C(6)-C(7)	179.99(15)
C(5)-C(6)-C(7)-C(8)	65.8(2)
C(1)-C(6)-C(7)-C(8)	-170.86(16)
C(6)-C(7)-C(8)-C(9)	169(6)
C(7)-C(8)-C(9)-C(10)	76(10)
C(8)-C(9)-C(10)-O(3)	96(7)
C(8)-C(9)-C(10)-O(4)	-82(7)
O(2)-C(1)-O(1)-Si(1)	11.1(2)
C(2)-C(1)-O(1)-Si(1)	-109.80(16)
C(6)-C(1)-O(1)-Si(1)	129.92(13)
O(1)-C(1)-O(2)-Si(2)	-168.37(11)
C(2)-C(1)-O(2)-Si(2)	-49.4(2)
C(6)-C(1)-O(2)-Si(2)	75.04(19)
O(3)-C(10)-O(4)-C(11)	2.7(3)
C(9)-C(10)-O(4)-C(11)	-179.03(19)
C(1)-O(1)-Si(1)-C(13)	-68.60(17)
C(1)-O(1)-Si(1)-C(12)	54.51(17)
C(1)-O(1)-Si(1)-C(14)	173.47(15)
C(16)-C(14)-Si(1)-O(1)	58.20(15)
C(15)-C(14)-Si(1)-O(1)	-61.64(17)
C(17)-C(14)-Si(1)-O(1)	177.60(14)

C(16)-C(14)-Si(1)-C(13)	-61.13(17)
C(15)-C(14)-Si(1)-C(13)	179.04(16)
C(17)-C(14)-Si(1)-C(13)	58.27(17)
C(16)-C(14)-Si(1)-C(12)	177.52(15)
C(15)-C(14)-Si(1)-C(12)	57.69(19)
C(17)-C(14)-Si(1)-C(12)	-63.08(17)
C(1)-O(2)-Si(2)-C(19)	79.8(2)
C(1)-O(2)-Si(2)-C(18)	-43.54(19)
C(1)-O(2)-Si(2)-C(20)	-161.16(17)