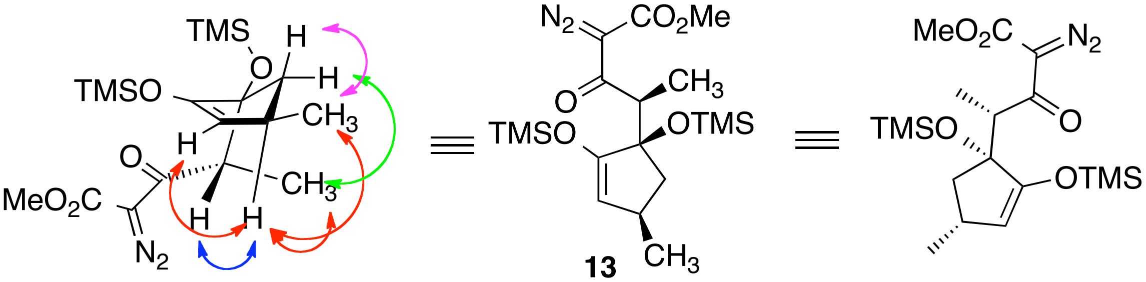
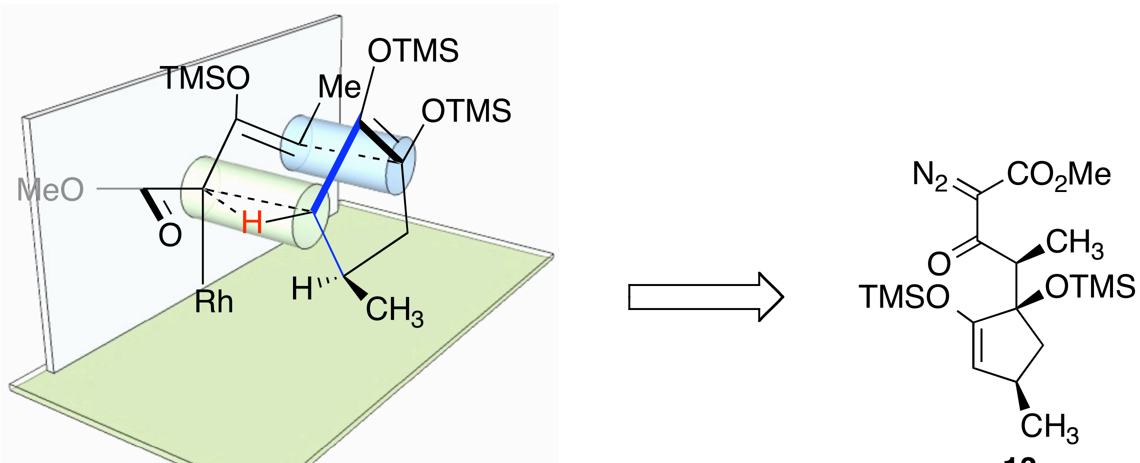
CONTENTS

^{1}H nOe assignment of Product **13**



13

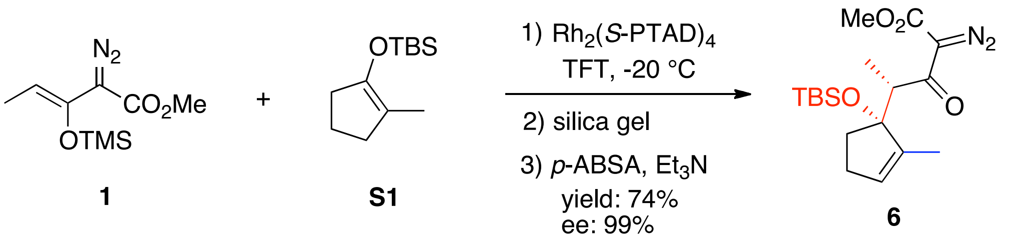
Proposed transition state of making product **13**.



13

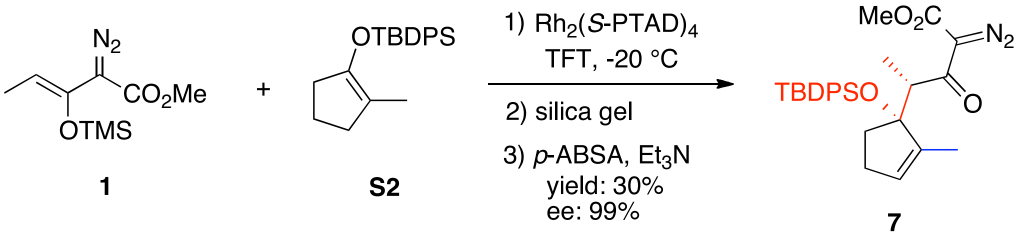
s-*cis/boat* approach **D**

Reaction Equations for Table **1**



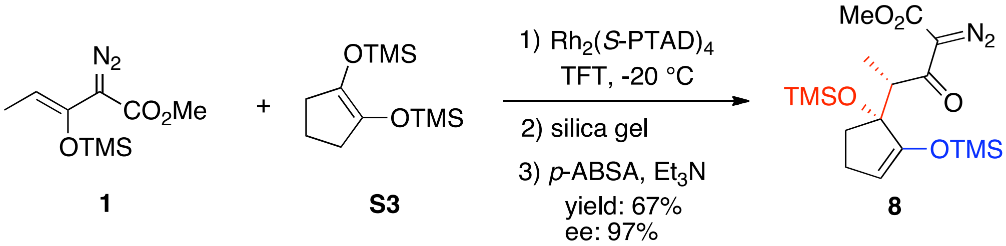
1 + **S1** → **6**

1) Rh_2(*S*-PTAD)$_4$, TFT, -20 °C
2) silica gel
3) *p*-ABSA, Et_3N
yield: 74%
ee: 99%



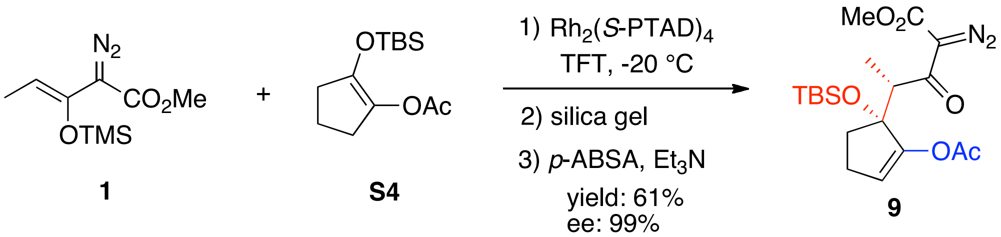
1 + **S2** → **7**

1) Rh_2(*S*-PTAD)$_4$, TFT, -20 °C
2) silica gel
3) *p*-ABSA, Et_3N
yield: 30%
ee: 99%



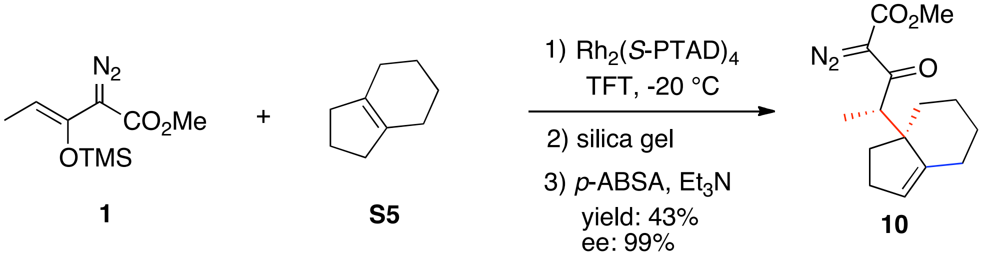
1 + **S3** → **8**

1) Rh_2(*S*-PTAD)$_4$, TFT, -20 °C
2) silica gel
3) *p*-ABSA, Et_3N
yield: 67%
ee: 97%



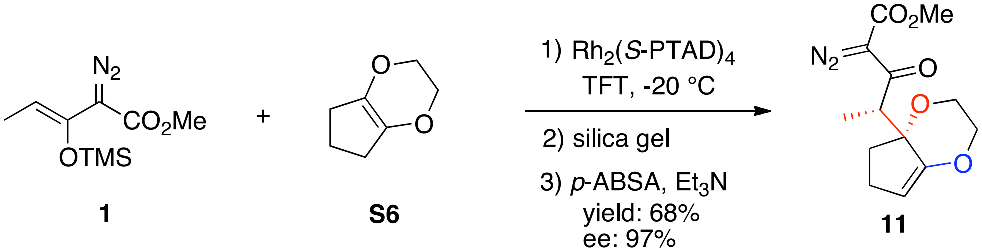
1 + **S4** → **9**

1) Rh_2(*S*-PTAD)$_4$, TFT, -20 °C
2) silica gel
3) *p*-ABSA, Et_3N
yield: 61%
ee: 99%



1 + **S5** → **10**

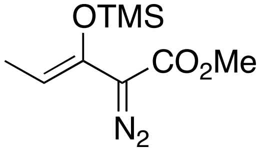
1) Rh_2(*S*-PTAD)$_4$, TFT, -20 °C
2) silica gel
3) *p*-ABSA, Et_3N
yield: 43%
ee: 99%



1 + **S6** → **11**

1) Rh_2(*S*-PTAD)$_4$, TFT, -20 °C
2) silica gel
3) *p*-ABSA, Et_3N
yield: 68%
ee: 97%

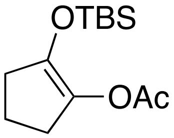
General Methods: All experiments were performed under anhydrous conditions in an atmosphere of argon except where stated, using flame-dried glassware. Toluene and methylenechloride were dried by a solvent purification system (passed through activated alumina columns). Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded at 400 or 600 MHz. Data are presented as follows: chemical shift (in ppm on the δ scale relative to δH 7.26 for the residual protons in $CDCl_3$ and δH 7.15 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), integration. Coupling constants were taken directly from the spectra and are uncorrected. ^{13}C NMR spectra were recorded at 100 or 150 MHz, and all chemical shift values are reported in ppm on the δ scale, with an internal reference of δC 77.0 for $CDCl_3$. Mass spectral determinations were carried out by using APCI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm^{-1}. Analytical TLC was performed on silica gel plates using UV light or potassium permanganate stain if stated. Flash column chromatography was performed on silica gel 60A (230-400 mesh). Optical rotations were measured on Jasco polarimeters. Analytical enantioselective chromatographies were measured on Varian Prostar instrument and used isopropanol/hexane as gradient.



(*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (1):

Triethylamine (2.0 mL, 14.3 mmol, 1.4 equiv) was added to a stirring solution of methyl 2-diazo-3-oxopentanoate (1.58 g, 10.1 mmol, 1.0 equiv) in dichloromethane (26 mL) at 0 °C under an inert argon atmosphere. Trimethylsilyl trifluoromethanesulfonate (2.3 mL, 12.2 mmol, 1.2 equiv) was added over 5 min and the mixture was further stirred for 30 min at 0 °C. The reaction mixture was diluted with pentane (100 mL), and the organic phase was subsequently washed with dilute aqueous sodium bicarbonate (100 mL) and brine (100 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure to yield the title product as a reddish oil (essentially quantitative yield), which was used without further purification.

^{1}H NMR (400 MHz, C_6D_6): δ 5.71 (q, *J* = 7.0 Hz, 1H), 3.29 (s, 3H), 1.63 (d, *J* = 6.7 Hz, 3H), 0.10 (s, 9H); ^{13}C NMR (150 MHz, C_6D_6): δ 165.0, 133.5, 106.7, 51.7, 12.4, 0.4; IR (neat): 2084, 1709, 1436, 1341, 1253, 1098, 1059, 842, 754 cm^{-1}.



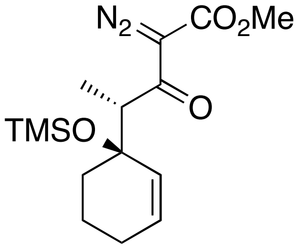
2-((*tert*-butyldimethylsilyl)oxy)cyclopent-1-en-1-yl acetate (S4):

To an oven-dried flask containing 2-oxocyclopentyl acetate (2.13 g, 15.0 mmol, 1.0 equiv) and Et_3N (4.2 mL, 30 mmol, 2.0 equiv) in 20 mL DCM was added slowly with TBSOTf (4.5 mL, 19.5 mmol, 1.3 equiv) at 0 °C. The mixture was stirred for 2 h and was quenched by saturated $NaHCO_3$ solution and extracted by pentane (2 X 50 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (20/1 pentane/ether, R_f: 0.41) on silica gel to provide product as a colorless oil (1.98 g, 52% yield).

^{1}H NMR (400 MHz, C_6D_6): δ 2.46-2.51 (m, 2H), 2.08-2.14 (m, 2H), 1.75 (s, 3H), 1.56-1.64 (m, 2H), 0.98 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 168.1, 138.8, 128.8, 30.9, 28.3, 26.1, 20.7, 18.6, 17.7, –3.8; IR (neat): 2930, 2857, 1757, 1709, 1340, 1204, 1070, 892, 837, 780 cm^{-1}; HRMS (APCI) calc. for $C_{13}H_{25}O_3Si$ $(M+H)^+$ 257.1568 found 257.1566.

General procedure for making *β*-keto diazoacetates:

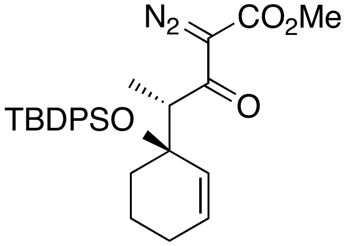
To an oven-dried 25 mL flask containing Rh_2(*S*-PTAD)$_4$ (16.5 mg, 0.01 equiv) and substrate (1.0 mmol, 1.0 equiv) in 6 mL dried trifluorotoluene under argon atmosphere was added a solution of (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv) in 6 mL dried trifluorotoluene by syringe pump over 3 h at -20 °C. The solution was warmed up to room temperature over 2 h. The mixture was concentrated under reduced pressure and then stirred with 5 g silica gel in 15 mL hexane for 30 mins. The mixture was filtrated and washed with several portions of Et_2O. The organic layer was concentrated under vacuum and the residue was purified by flash chromatography on silica gel to provide a colorless oil, which was dissolved in 5 mL dried CH_3CN containing *p*-ABSA (240 mg, 1.0 mmol, 1.0 equiv.), Et_3N (0.30 ml, 2.0 mmol, 2.0 equiv.) The mixture was stirred for additional 3h and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to provide *β*-keto diazoacetates.



(*S*)-methyl 2-diazo-3-oxo-4-((*R*)-1-((trimethylsilyl)oxy)cyclohex-2-en-1-yl)pentanoate (3a):

Derived from (cyclohex-1-en-1-yloxy)trimethylsilane (**2a**) (170.3 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.25) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et$_2$O, R$_f$: 0.32) on silica gel to provide **3a** as a yellow oil (240 mg, 74% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 5.82-5.84 (m, 2H), 3.96-4.06 (br, 1H), 3.82 (s, 3H), 1.53-2.02 (m, 6H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.03 (s, 9H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 194.9, 161.8, 131.9, 129.6, 74.8, 52.0, 50.1, 33.8, 25.0, 18.1, 12.2, 2.3; IR (neat): 2954, 2135, 1722, 1652, 1299, 1200, 1127, 1029, 998, 836 cm^{-1}; HRMS (ESI) calc. for $C_{15}H_{24}O_4N_2NaSi$ (M+Na)$^+$ 347.1398 found 347.1340; $[\alpha]^{25}_D$ 131.9 (*c* = 1.34, CHCl$_3$). HPLC: (OD-H, 0.2% isopropanol in hexane, 0.7 mL/min) retention times of 14.4 min (minor) and 16.7 min (major), 89% ee.

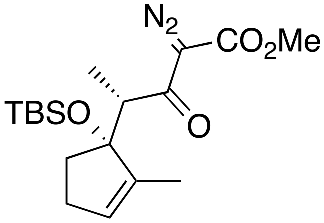


(*S*)-methyl 4-((*R*)-1-((*tert*-butyldiphenylsilyl)oxy)cyclohex-2-en-1-yl)-2-diazo-3-oxopentanoate (3b):

Derived from *tert*-butyl(cyclohex-1-en-1-yloxy)diphenylsilane (**2b**) (336.5 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (10/1 pentane/Et$_2$O, R$_f$: 0.42) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (10/1 pentane/Et$_2$O, R$_f$: 0.52) on silica gel to provide **3b** as a yellow powder (230.1 mg, 47% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.68-7.73 (m, 4H), 7.31-7.42 (m, 6H), 5.58-5.66 (m, 1H), 5.35-5.43 (m, 1H), 4.22-4.34 (m, 1H), 3.81 (s, 3H), 1.95-2.07 (m, 1H), 1.74-1.83 (m, 1H), 1.54-1.67 (m, 1H), 1.21-1.38 (m, 3H), 1.25 (d, *J* = 7.6 Hz, 3H), 1.03 (s, 9H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 194.6, 161.6, 136.5, 136.4, 135.6, 135.5, 131.2, 130.3, 129.1, 127.0, 76.0, 52.0, 51.0 33.6, 27.1, 24.4, 19.5, 18.9, 12.6; IR (neat): 2933, 2136, 1720, 1654, 1427, 1300, 1108, 994, 739, 700 cm^{-1}; HRMS (APCI) calc. for $C_{28}H_{35}O_4Si$ (M-

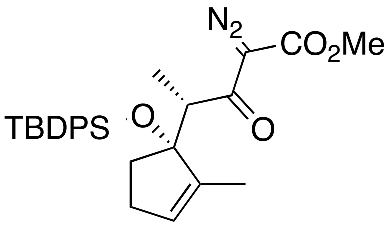
N_2+H)$^+$ 463.2299 found 463.2296; $[\alpha]^{25}_D$ 107.9 (*c* = 1.28, $CHCl_3$). HPLC: (AD-H, 100% hexane, 1.0 mL/min) retention times of 12.3 min (minor) and 12.8 min (major), 97% ee.



(*S*)-methyl 4-((*R*)-1-((*tert*-butyldimethylsilyl)oxy)-2-methylcyclopent-2-en-1-yl)-2-diazo-3-oxopentanoate (6):

Derived from *tert*-butyldimethyl((2-methylcyclopent-1-en-1-yl)oxy)silane (**S1**) (212.4 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.44) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.39) on silica gel to provide **6** as a yellow oil (226 mg, 62% yield).

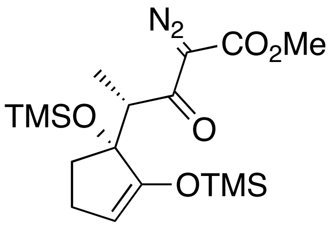
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.53 (d, *J* = 1.2 Hz, 1H), 4.27 (br, 1H), 3.81 (s, 3H), 2.76 (ddd, *J* = 15.3, 9.5, 4.3 Hz, 1H), 2.28-2.38 (m, 1H), 2.11-2.20 (m, 1H), 1.76 (ddd, *J* = 14.9, 9.2, 4.6 Hz, 1H), 1.70 (q, *J* = 2.0 Hz, 3H), 0.87 (d, *J* = 7.6 Hz, 3H), 0.77 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.4, 161.9, 142.0, 129.5, 92.4, 52.0, 45.5, 31.8, 30.0, 25.6, 18.2, 12.3, 11.7, -3.3, -3.7; IR (neat): 2954, 2929, 2856, 2123, 1724, 1655, 1436, 1301, 1211, 1195, 1127, 1066, 773 cm^{-1}; HRMS (ESI) calc. for $C_{18}H_{30}O_4N_2NaSi$ (M+Na)$^+$ 389.1867 found 389.1866; $[\alpha]^{25}_D$ -1.5 (*c* = 1.39, $CHCl_3$). HPLC: (AD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 6.8 min (major) and 7.6 min (minor), 99% ee.



(*S*)-methyl 4-((*R*)-1-((*tert*-butyldiphenylsilyl)oxy)-2-methylcyclopent-2-en-1-yl)-2-diazo-3-oxopentanoate (7):

Derived from *tert*-butyl((2-methylcyclopent-1-en-1-yl)oxy)diphenylsilane (**S2**) (336.5 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (20/1 pentane/Et$_2$O, R$_f$: 0.27) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (10/1 pentane/Et$_2$O, R$_f$: 0.42) on silica gel to provide as a yellow powder (145 mg, 30% yield).

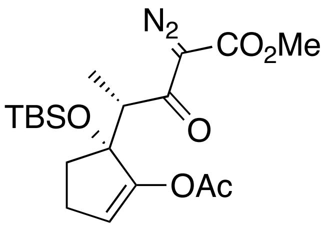
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.59-7.63 (m, 2H), 7.52-7.55 (m, 2H), 7.34-7.39 (m, 2H), 7.29-7.33 (m, 2H), 7.24-7.28 (m, 2H), 4.87 (d, *J* = 1.4 Hz, 1H), 4.52 (br, 1H), 3.86 (s, 3H), 2.77-2.82 (m, 1H), 1.81-1.88 (m, 1H), 1.73-1.80 (m, 1H), 1.60 (d, *J* = 1.4 Hz, 3H), 1.38-1.45 (m, 1H), 0.96 (s, 9H), 0.87 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 196.8, 162.0, 140.1, 136.1, 136.0, 135.1, 134.6, 130.2, 129.3, 129.2, 127.1, 126.9, 94.1, 52.0, 45.2, 32.3, 30.0, 27.1, 19.2, 12.2, 11.8; IR (neat): 2930, 2134, 1720, 1647, 1430, 1304, 1189, 1106, 1058, 1011, 736, 700 cm^{-1}; HRMS (ESI) calc. for $C_{28}H_{34}O_4N_2NaSi$ $(M+Na)^+$ 513.2180 found 513.2178; $[\alpha]^{25}_D$ -55.3 (*c* = 1.27, CHCl$_3$); HPLC: (AD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 9.2 min (minor) and 11.8 min (major), 99% ee.



(*S*)-methyl 4-((*R*)-1,2-bis((trimethylsilyl)oxy)cyclopent-2-en-1-yl)-2-diazo-3-oxopentanoate (8):

Derived from 1,2-bis((trimethylsilyl)oxy)cyclopent-1-ene (**S3**) (336.5 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.18) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.24) on silica gel to provide as a yellow oil (267 mg, 67% yield).

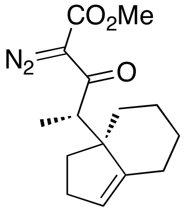
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74 (t, *J* = 4.2 Hz, 1H), 3.93 (br, 1H), 3.82 (s, 3H), 2.54 (ddd, *J* = 13.7, 9.5, 4.3 Hz, 1H), 2.19-2.31 (m, 1H), 2.04-2.12 (m, 1H), 1.59-1.66 (m, 1H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.25 (s, 9H), 0.02 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.2, 162.1, 153.4, 104.5, 88.2, 52.1, 46.0, 30.5, 25.2, 12.0, 1.4, -0.2; HRMS (ESI) calc. for $C_{17}H_{30}O_5N_2NaSi_2$ $(M+Na)^+$ 421.1586 found 421.1586; $[\alpha]^{25}_D$ 26.1 (*c* = 2.06, $CHCl_3$). HPLC: (OD-H, 0.1% isopropanol in hexane, 0.4 mL/min) retention times of 21.9 min (minor) and 25.6 min (major), 97% ee.



(*S*)-methyl 4-((*R*)-2-acetoxy-1-((*tert*-butyldimethylsilyl)oxy)cyclopent-2-en-1-yl)-2-diazo-3-oxopentanoate (9):

Derived from 2-((*tert*-butyldimethylsilyl)oxy)cyclopent-1-en-1-yl acetate (**S4**) (256.4 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (85/15 pentane/Et_2O, R_f: 0.29) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.24) on silica gel to provide **9** as a yellow oil (250 mg, 61% yield).

^1H NMR (400 MHz, $CDCl_3$): δ 5.89 (t, *J* = 2.4 Hz, 1H), 4.26 (br, 1H), 3.80 (s, 3H), 2.76 (ddd, *J* = 15.0, 9.2, 3.8 Hz, 1H), 2.36-2.46 (m, 1H), 2.22-2.30 (m, 1H), 2.22 (s, 3H), 1.74 (ddd, *J* = 15.0, 9.4, 4.2 Hz, 1H), 0.95 (d, *J* = 7.6 Hz, 3H), 0.77 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.4, 168.2, 161.6, 148.5, 116.9, 88.0, 52.0, 45.5, 30.4, 26.5, 25.4, 21.4, 18.1, 12.5, -3.6, -3.8; IR (neat): 2929, 2857, 2137, 1768, 1724, 1653, 1303, 1193, 1072, 835, 775 cm^{-1}; HRMS (ESI) calc. for $C_{19}H_{30}O_6N_2NaSi$ $(M+Na)^+$ 433.1765 found 433.1766; $[\alpha]^{25}_D$ 11.2 (*c* = 1.18, $CHCl_3$). HPLC: (OD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 8.8 min (minor) and 10.4 min (major), 99% ee.

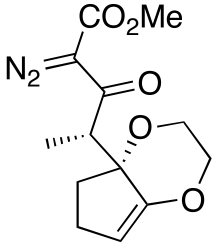


(*S*)-methyl 2-diazo-4-((*S*)-2,4,5,6,7,7a-hexahydro-1*H*-inden-7a-yl)-3-oxopentanoate (10):

Derived from 2,3,4,5,6,7-hexahydro-1*H*-indene (**S5**) (122.2 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.30) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f: 0.41) on silica gel to provide **10** as a yellow oil (119 mg, 43% yield).

^1H NMR (600 MHz, $CDCl_3$): δ 5.34 (d, *J* = 1.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 1H), 3.84 (s, 3H), 2.73 (ddd, *J* = 14.3, 8.6, 3.8 Hz, 1H), 2.29-2.32 (m, 1H), 2.17-2.28 (m, 2H), 1.98-2.03 (m, 1H), 1.87 (d, *J* = 13.8 Hz, 1H), 1.77-1.82 (m, 1H), 1.42-1.61 (m, 3H), 1.18-1.27 (m, 2H), 1.01 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.1, 161.6, 146.6, 122.6, 53.1, 52.1, 41.8, 39.9, 33.3, 31.4, 28.1, 26.2, 22.4, 12.8; IR (neat): 2930, 2852, 2135, 1715, 1655, 1436, 1297, 1195, 1128, 988, 731 cm^{-1}; HRMS (ESI) calc. for

$C_{15}H_{20}O_3N_2Na$ $(M+Na)^+$ 299.1366 found 299.1367; $[\alpha]^{25}_D$ -31.6 (*c* = 1.85, $CHCl_3$). HPLC: (OD-H, 0.5% isopropanol in hexane, 0.7 mL/min) retention times of 9.1 min (minor) and 10.4 min (major), 99% ee.



(*S*)-methyl 2-diazo-3-oxo-4-((*R*)-3,4a,5,6-tetrahydro-2*H*-cyclopenta[*b*][1,4]dioxin-4a-yl)pentanoate (11):

Derived from 3,5,6,7-tetrahydro-2*H*-cyclopenta[*b*][1,4]dioxine (**S6**)[1] (126.1 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.26) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.29) on silica gel to provide **11** as a yellow oil (190 mg, 68% yield).

^1H NMR (400 MHz, C_6D_6): δ 5.10 (t, *J* = 2.4 Hz, 1H), 4.80 (q, *J* = 7.1 Hz, 1H), 4.23-4.28 (m, 1H), 3.72-3.77 (m, 1H), 3.56-3.60 (m, 2H), 3.18 (s, 3H), 3.11-3.17 (m, 1H), 1.93-2.05 (m, 3H), 1.20 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ 194.7, 162.1, 154.7, 107.3, 87.2, 68.7, 61.9, 51.7, 45.3, 34.5, 26.0, 12.6; IR (neat): 2139, 1716, 1648, 1436, 1302, 1199, 1127, 1001, 899 cm^{-1}; HRMS (APCI) calc. for $C_{13}H_{17}O_5N_2$ $(M+H)^+$ 281.1132 found 281.1133; $[\alpha]^{25}_D$ -17.0 (*c* = 1.76, CH_3CN). HPLC: (AD-H, 2% isopropanol in hexane, 0.7 mL/min) retention times of 15.3 min (minor) and 18.8 min (major), 97% ee.

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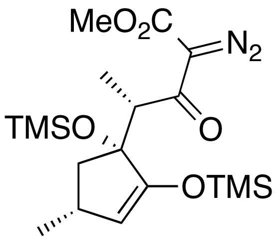
[1] Fjeldskaar, I. R.; Rongved, P.; Skattebøl, L. *Acta Chem. Scand.* **1987**, 477.

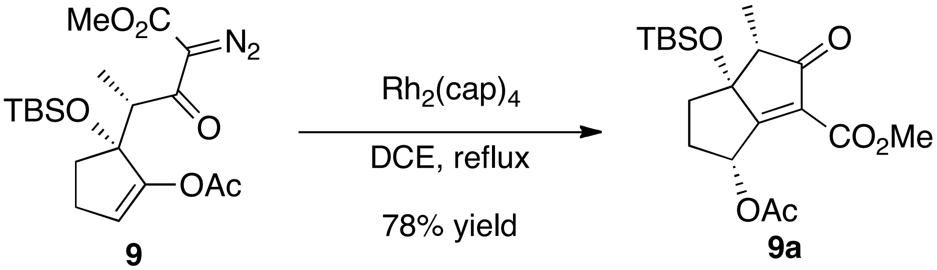


(*S*)-methyl 2-diazo-4-((1*R*,4*R*)-4-methyl-1,2-bis((trimethylsilyl)oxy)cyclopent-2-en-1-yl)-3-oxopentanoate (13):

Derived from ((4-methylcyclopent-1-ene-1,2-diyl)bis(oxy))bis(trimethylsilane) (**12**) (258.5 mg, 1.0 mmol, 1.0 equiv) and (*Z*)-methyl 2-diazo-3-((trimethylsilyl)oxy)pent-3-enoate (**1**) (365 mg, 1.6 mmol, 1.6 equiv), and purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.36) on silica gel to provide the corresponding *β*-keto ester. The diazo transferred residue was purified by flash chromatography (10/1 pentane/Et_2O, R_f: 0.40) on silica gel to provide **13** as a yellow oil (166 mg, 40% yield).

^{1}H NMR (400 MHz, C_6D_6): δ 4.60 (d, *J* = 2.4 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 1H), 3.29 (s, 3H), 3.23-3.34 (m, 1H), 2.28-2.38 (m, 1H), 1.45 (dd, *J* = 14.3, 8.2 Hz, 1H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.22 (s, 9H), 0.21 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.3, 162.1, 154.0, 111.0, 89.3, 76.4, 51.7, 42.1, 33.7, 23.1, 12.4, 2.6, 0.2; IR (neat): 2956, 2120, 1728, 1645, 1301, 1248, 1209, 1128, 1044, 837, 751 cm^{-1}; HRMS (ESI) calc. for $C_{18}H_{32}O_5N_2NaSi_2$ $(M+Na)^+$ 435.1742 found 435.1739; $[\alpha]^{25}_D$ 46.6 (*c* = 1.84, $CHCl_3$). HPLC: (OD-H, 0.1% isopropanol in hexane, 0.7 mL/min) retention times of 13.1 min (minor) and 17.2 min (major), 99% ee.

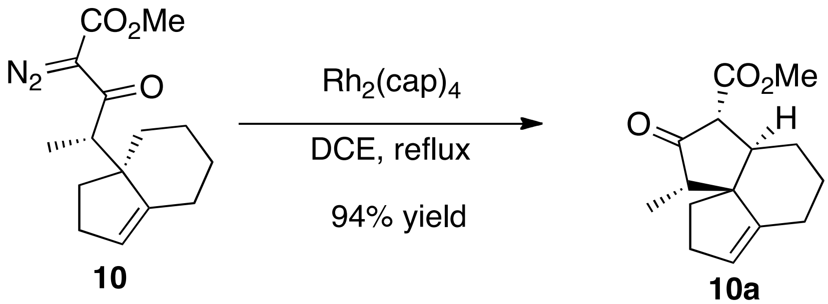
Procedure of making derivatives 9a and 10a



(3*S*,3a*R*,6*R*)-methyl 6-acetoxy-3a-((*tert*-butyldimethylsilyl)oxy)-3-methyl-2-oxo-2,3,3a,4,5,6-hexahydropentalene-1-carboxylate (9a):

To an oven-dried 10 mL flask containing $Rh_2(cap)_4$ (1.3 mg, 0.02 equiv) and Diazoacetate **9** (41.1 mg, 0.1 mmol, 1.0 equiv) in 5 mL anhydrous Dichloroethane was heated to reflux for 1h under argon atmosphere. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (1/1 pentane/Et_2O, R_f: 0.31) on silica gel to provide **9a** as a colorless powder (29.7 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 2.51 (dt, *J* = 13.3, 7.6 Hz, 1H), 2.34 (q, *J* = 7.2 Hz, 2H), 2.20-2.27 (m, 1H), 2.11 (s, 3H), 1.55-1.61 (m, 1H), 1.21 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 9H), 0.10 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 181.8, 169.8, 161.9, 130.6, 85.6, 68.9, 55.7, 52.2, 36.3, 32.7, 25.9, 20.8, 18.6, 8.6, -2.0, -2.3; IR (neat): 2954, 1746, 1736, 1235, 1114, 1049, 777 cm^{-1}; M.p. 117-120 °C; HRMS (APCI) calc. for $C_{19}H_{31}O_6Si$ $(M+H)^+$ 383.1884 found 383.1883; $[\alpha]^{25}_D$ 48.2 (*c* = 0.70, $CHCl_3$).

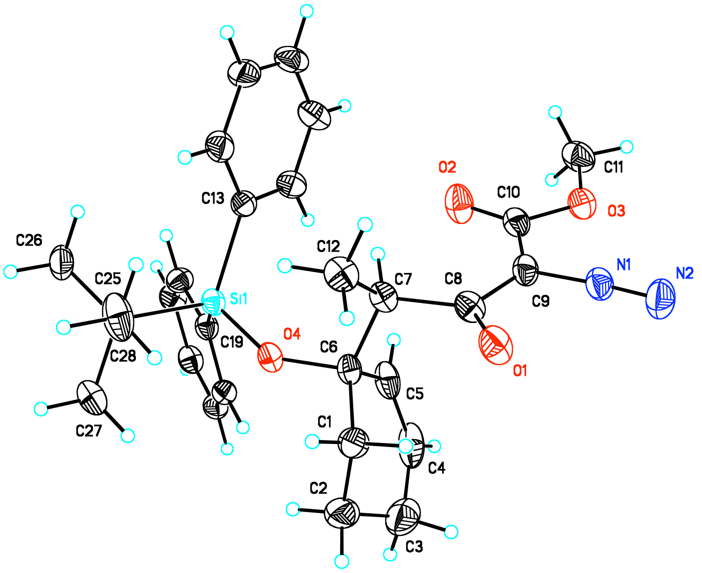


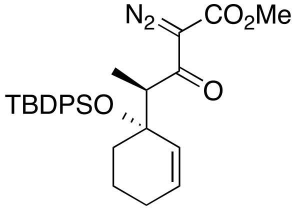
(1*R*,3*S*,3a*R*,9a*R*)-methyl 3-methyl-2-oxo-2,3,4,5,7,8,9,9a-octahydro-1*H*-cyclopenta[*d*]indene-1-carboxylate (10a):

To an oven-dried 10 mL flask containing $Rh_2(cap)_4$ (1.3 mg, 0.02 equiv) and Diazoacetate **10** (27.7 mg, 0.1 mmol, 1.0 equiv) in 5 mL anhydrous Dichloroethane was heated to reflux for 1h under argon atmosphere. The mixture was concentrated under reduced pressure and the residue was purified by flash chromatography (7/3 pentane/Et_2O, R_f: 0.35) on silica gel to provide **10a** as a colorless powder (23.4 mg, 94% yield).

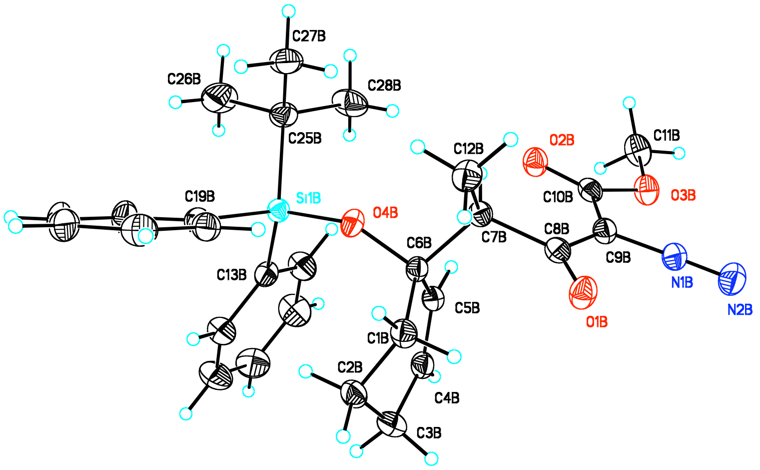
^{1}H NMR (400 MHz, C_6D_6): δ 5.28-5.30 (m, 1H), 3.37 (s, 3H), 2.83 (s, 1H), 2.28 (ddd, *J* = 12.5, 5.6, 1.8 Hz, 1H), 2.19 (q, *J* = 7.0 Hz, 1H), 2.11 (dm, *J* = 13.4 Hz, 1H), 1.87-2.04 (m, 4H), 1.56 (t, *J* = 13.6 Hz, 1H), 1.33-1.44 (m, 2H), 1.04-1.12 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.72-0.84 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ 209.9, 169.8, 144.0, 124.8, 60.5, 56.1, 52.2, 49.2, 48.2, 36.4, 31.63, 31.58, 26.8, 25.8, 8.0; IR (neat): 2932, 1753, 1725, 1436, 1256, 1151, 990 cm^{-1}; M.p. 74-76 °C; HRMS (APCI) calc. for $C_{15}H_{21}O_3$ $(M+H)^+$ 249.1485 found 249.1482; $[\alpha]^{25}_D$ 170.0 (*c* = 0.98, $CHCl_3$).

Crystal structure of *ent*-3b

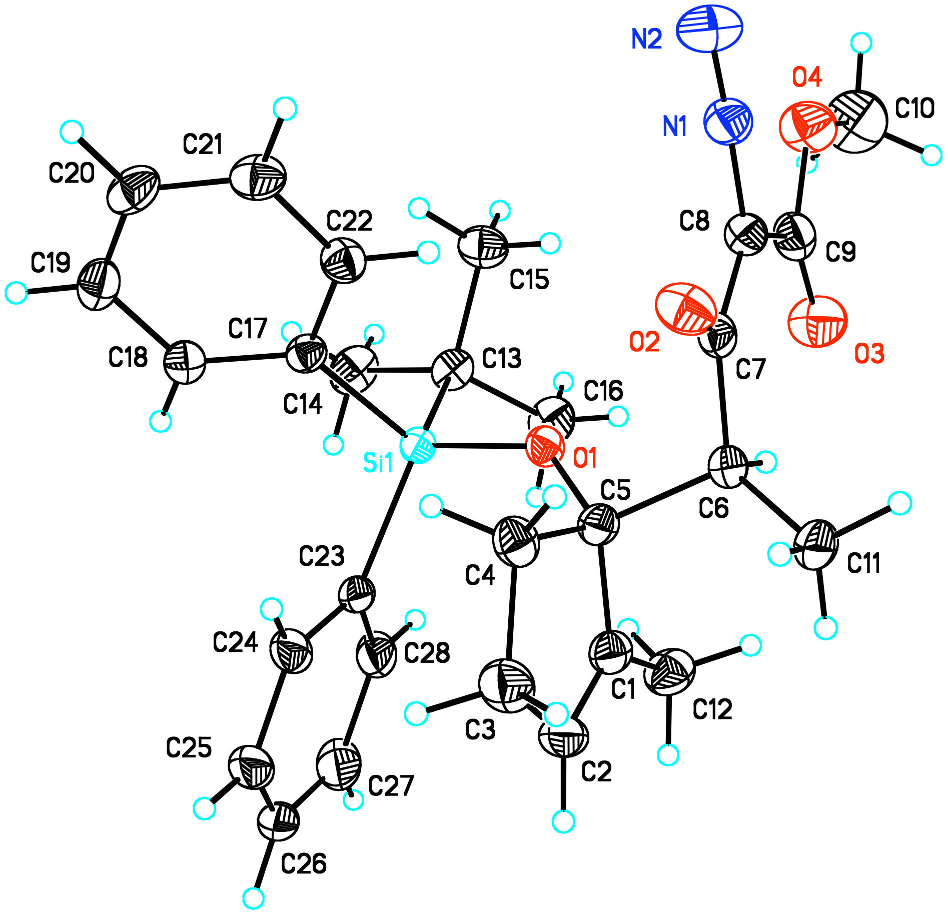


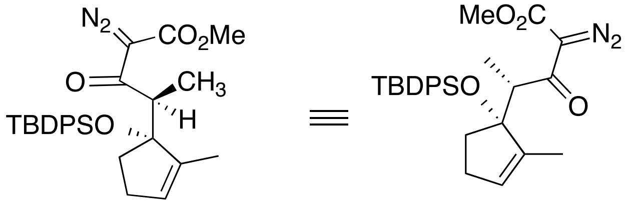


***ent*-3b**



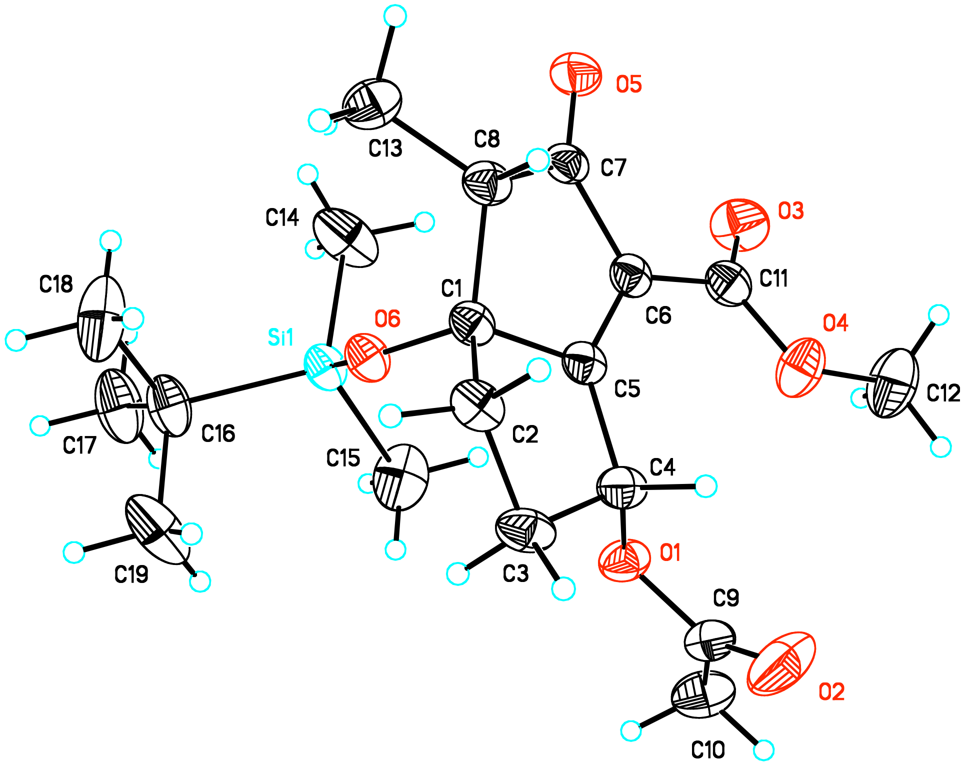
Crystal structure of 7

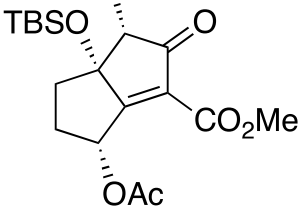




7

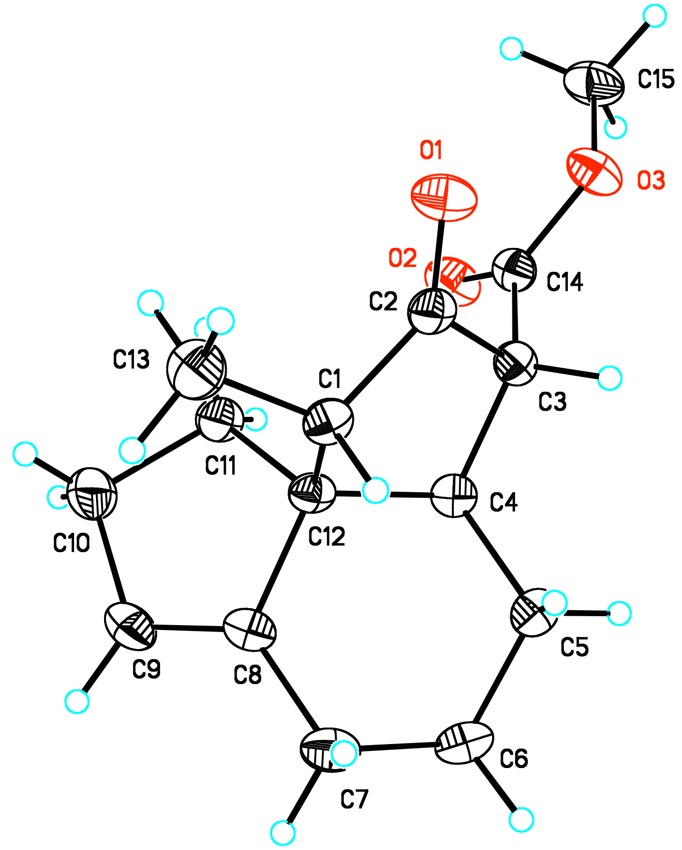
Crystal structure of 9a

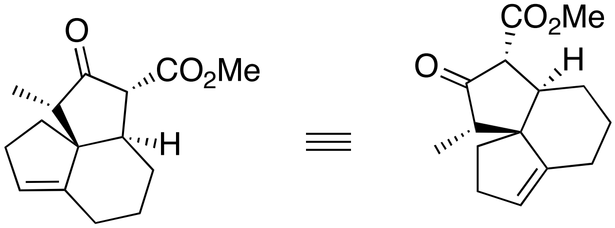




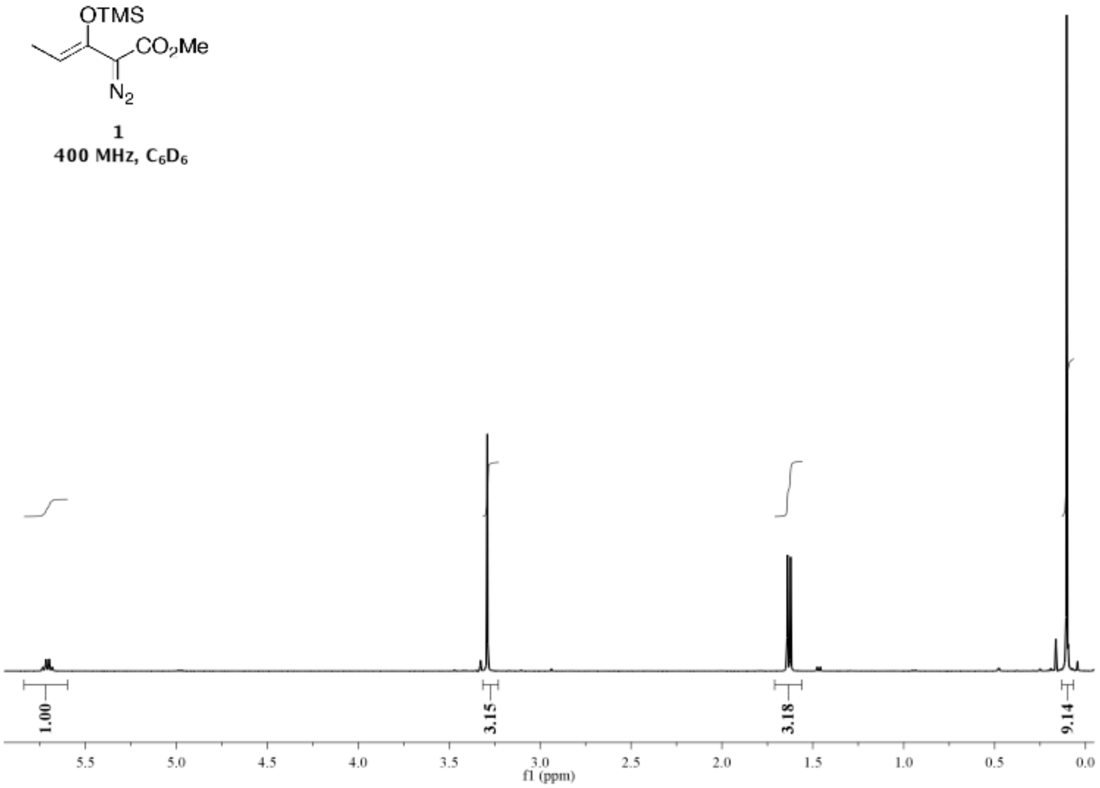
9a

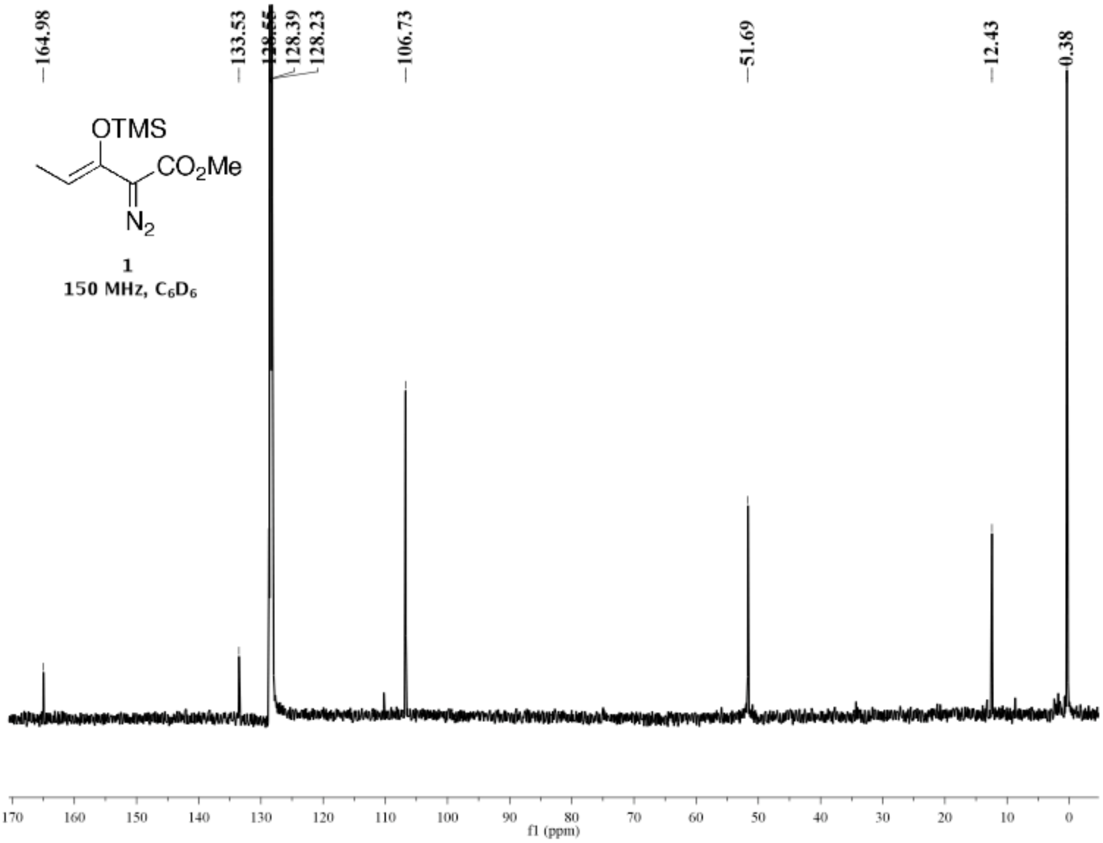
Crystal structure of 10a

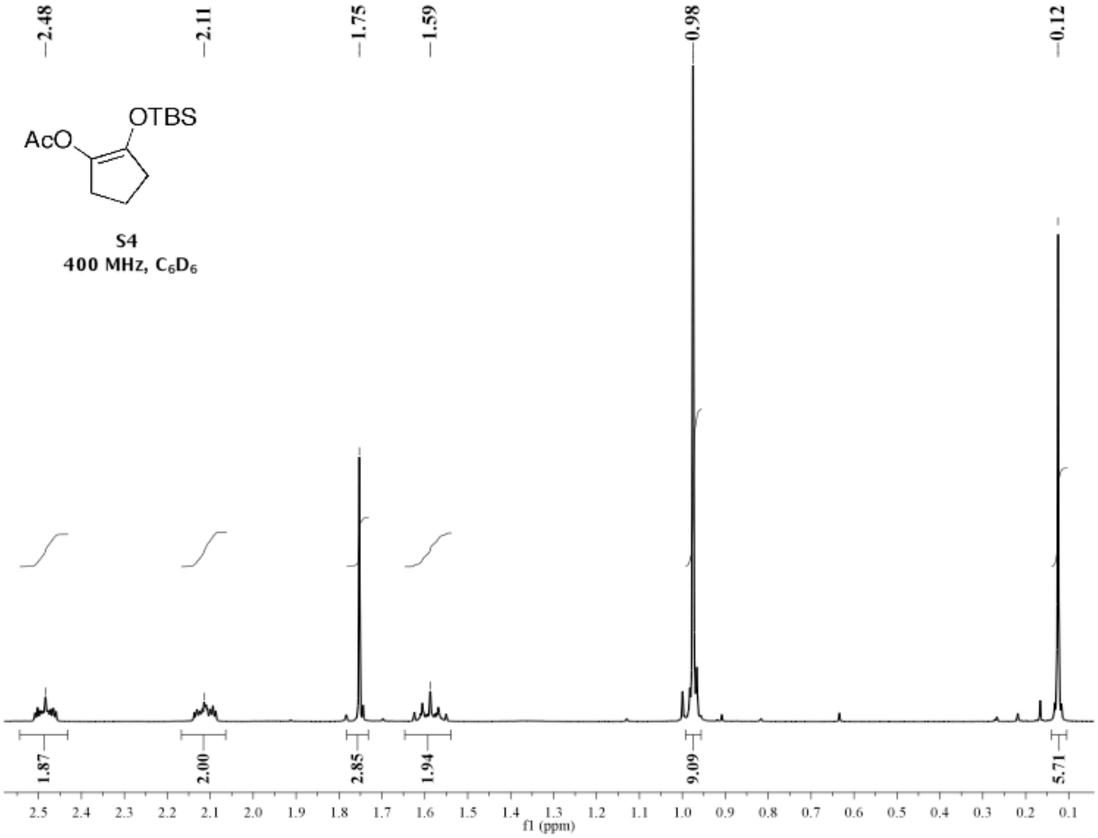




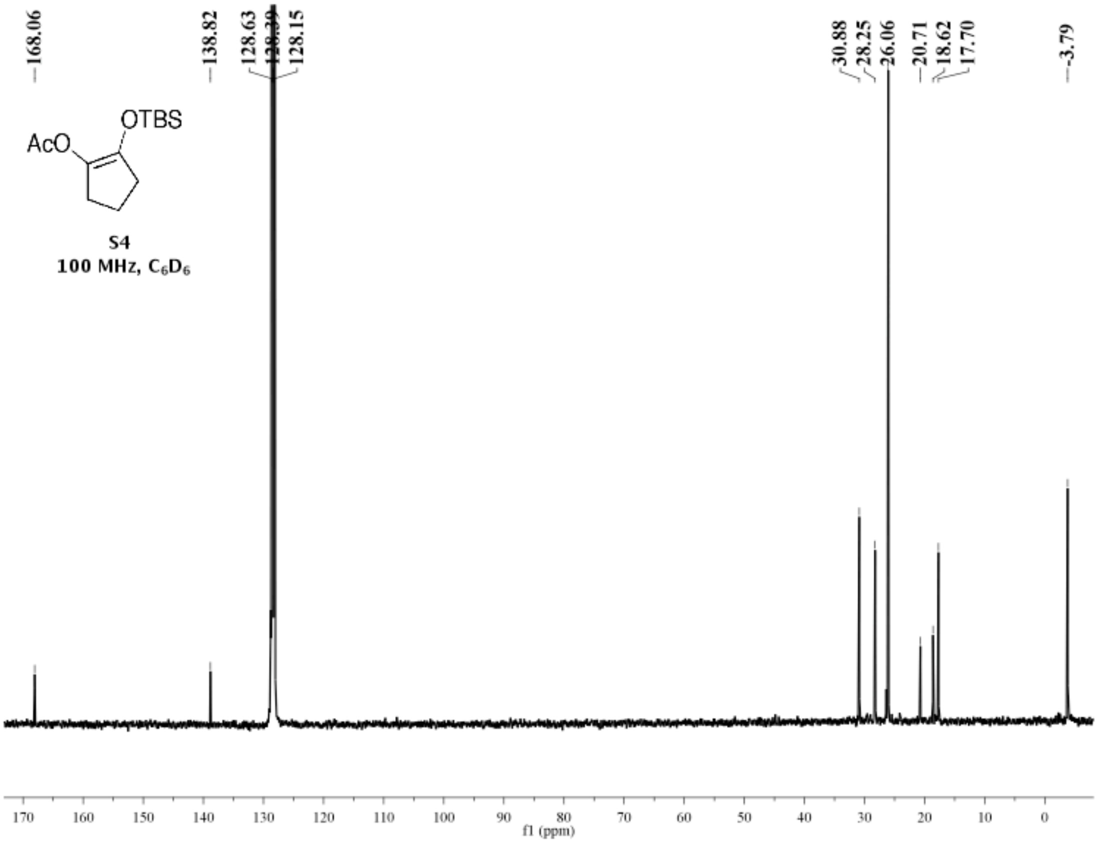
10a


OTMS
CO2Me
N2
1
400 MHz, C6D6
1.00
3.15
3.18
9.14
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

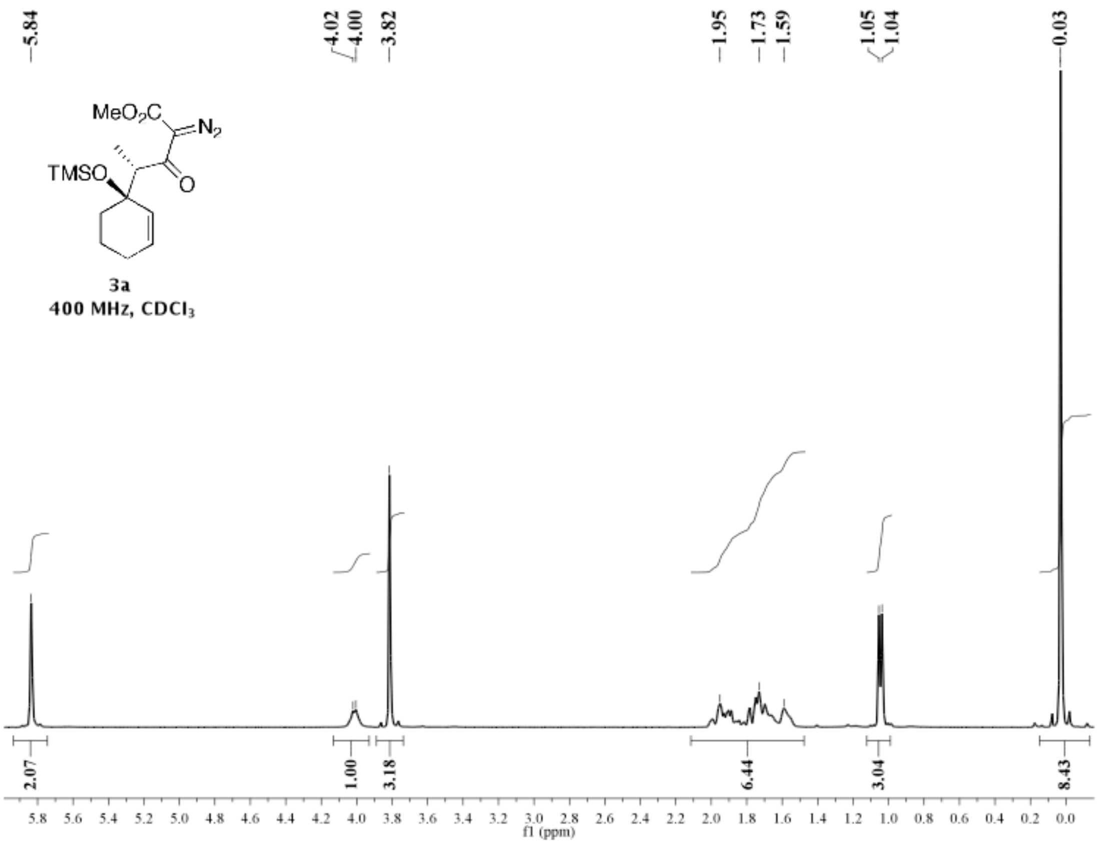

164.98
133.53
128.55
128.39
128.23
106.73
51.69
12.43
0.38
OTMS
CO2Me
N2
1
150 MHz, C6D6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

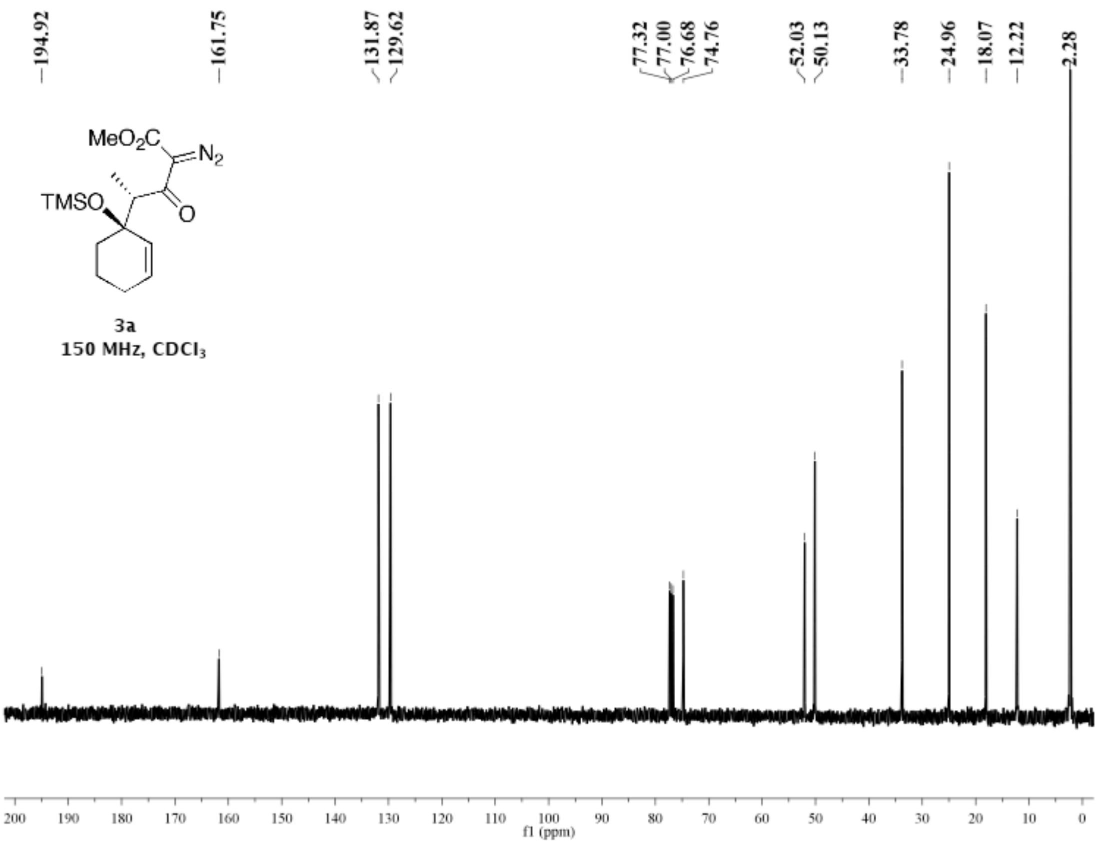


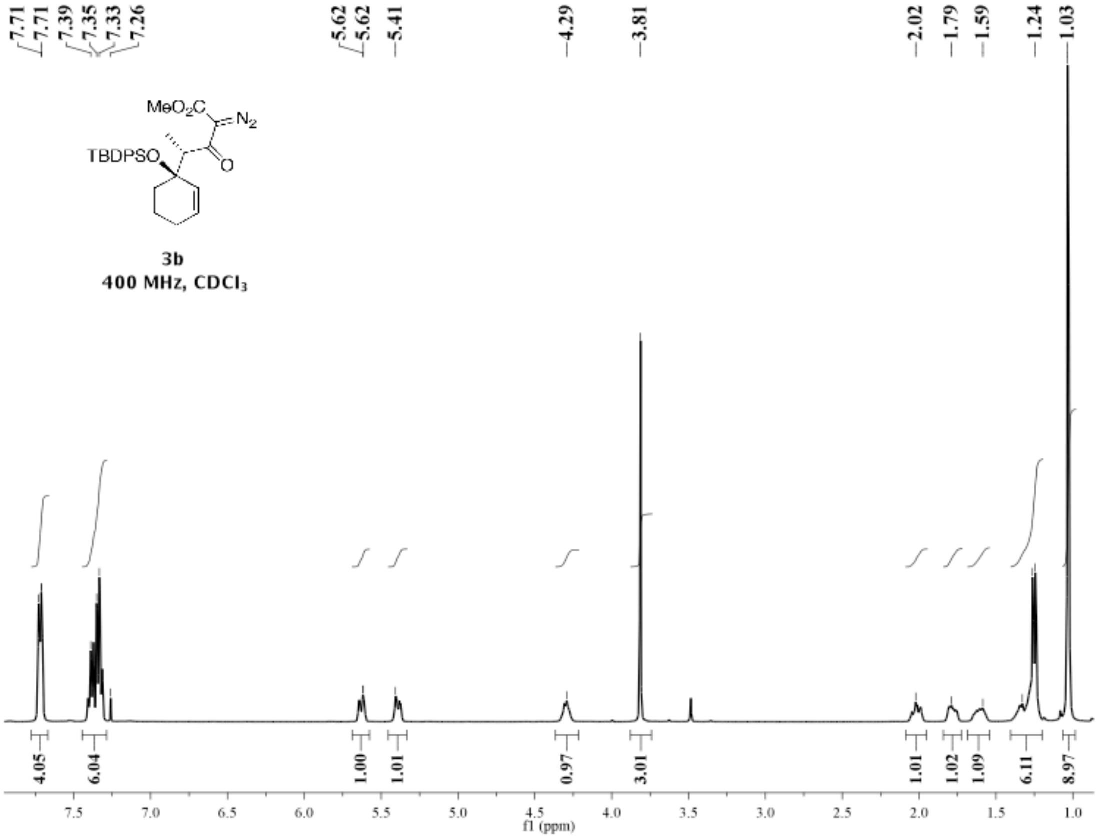
2.48
2.11
1.75
1.59
0.98
0.12
OTBS
AcO
S4
400 MHz, C_6D_6
1.87
2.00
2.85
1.94
9.09
5.71
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
f1 (ppm)



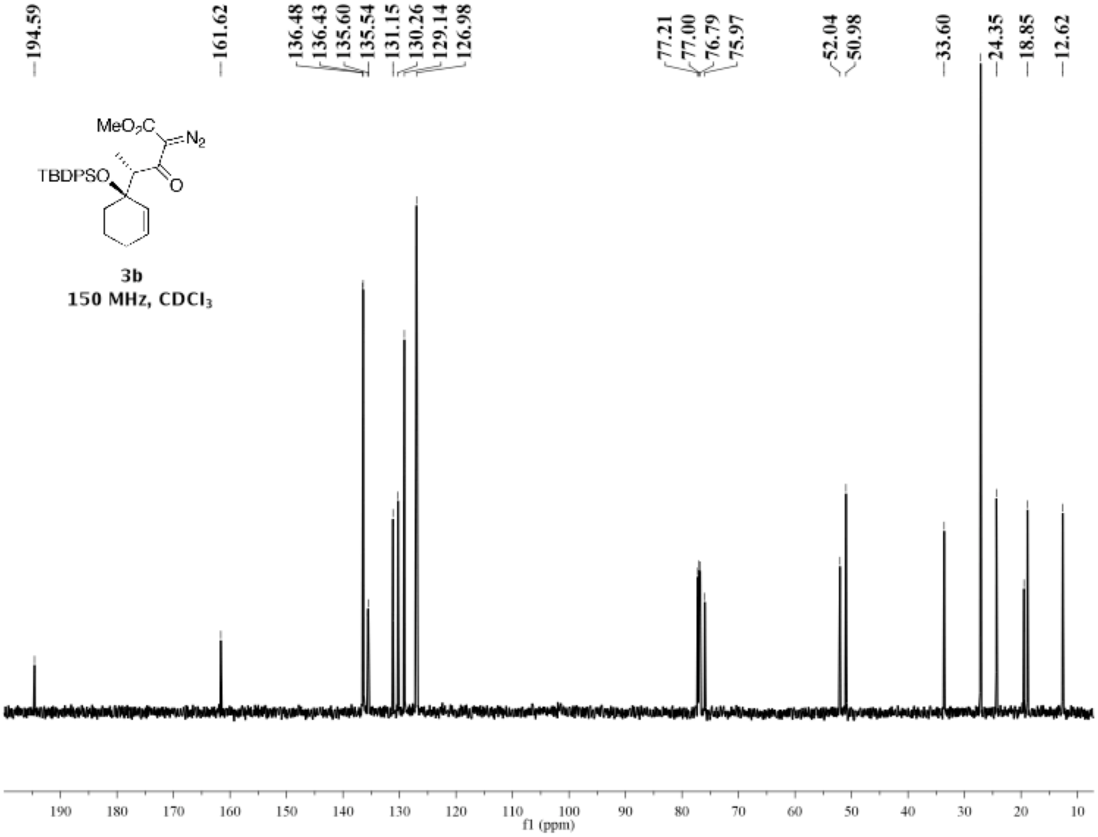
168.06
138.82
128.63
128.39
128.15
30.88
28.25
26.06
20.71
18.62
17.70
-3.79
OTBS
AcO
S4
100 MHz, C_6D_6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


5.84
4.02
4.00
3.82
1.95
1.73
1.59
1.05
1.04
0.03
MeO2C
N2
TMSO
O
3a
400 MHz, CDCl3
2.07
1.00
3.18
6.44
3.04
8.43
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
f1 (ppm)

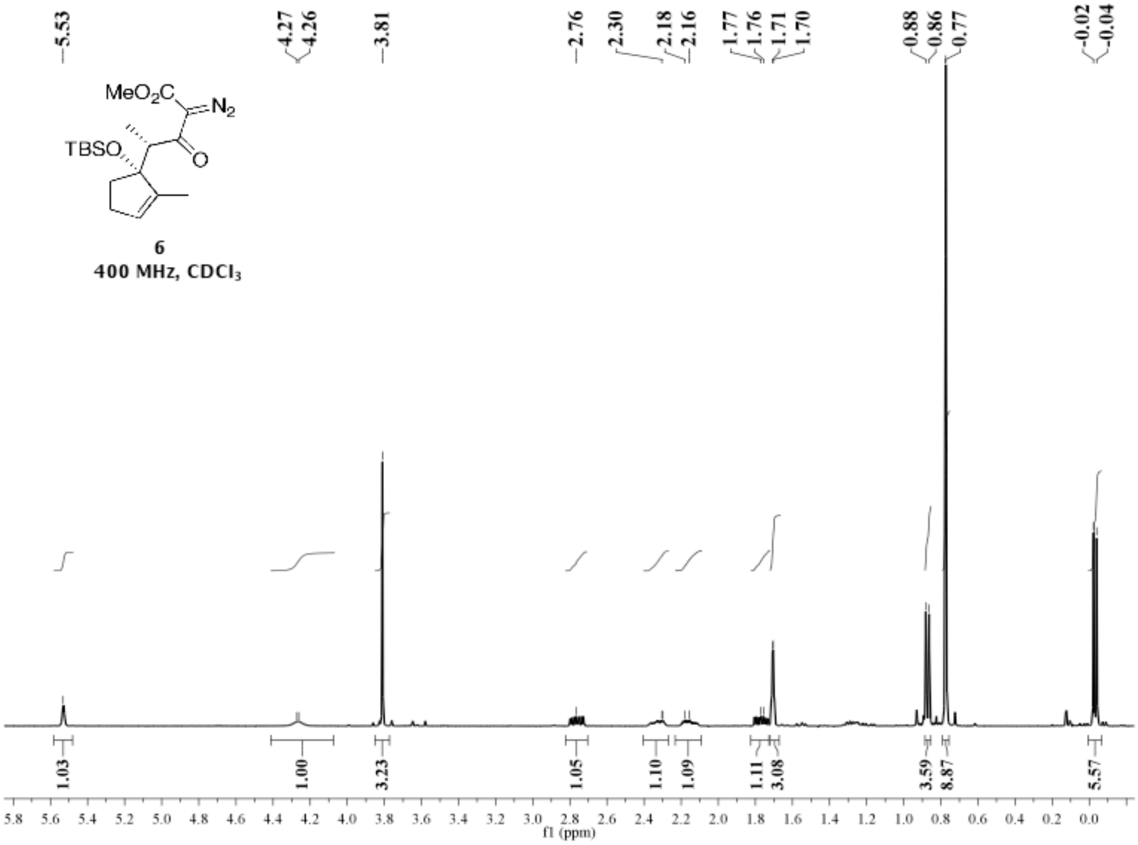

194.92
161.75
131.87
129.62
77.32
77.00
76.68
74.76
52.03
50.13
33.78
24.96
18.07
12.22
2.28
MeO2C
N2
TMSO
O
3a
150 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

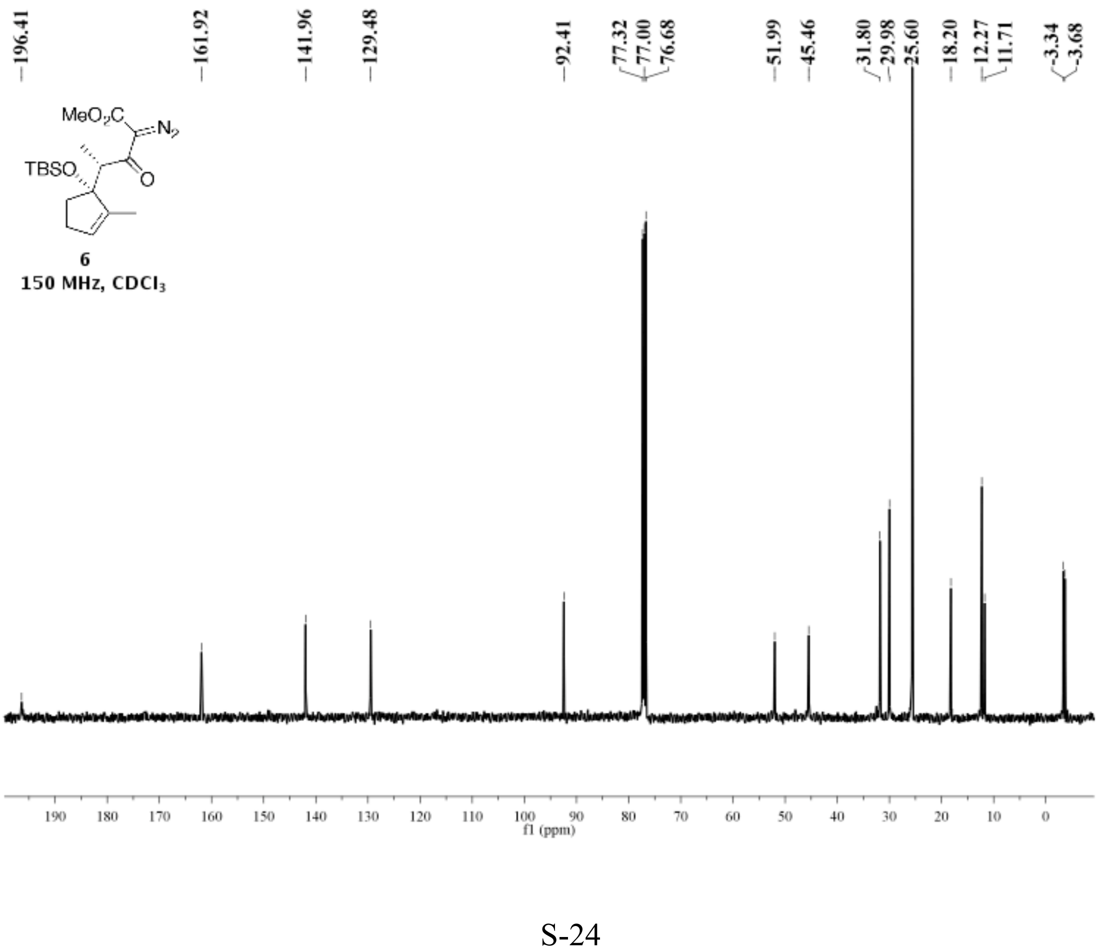


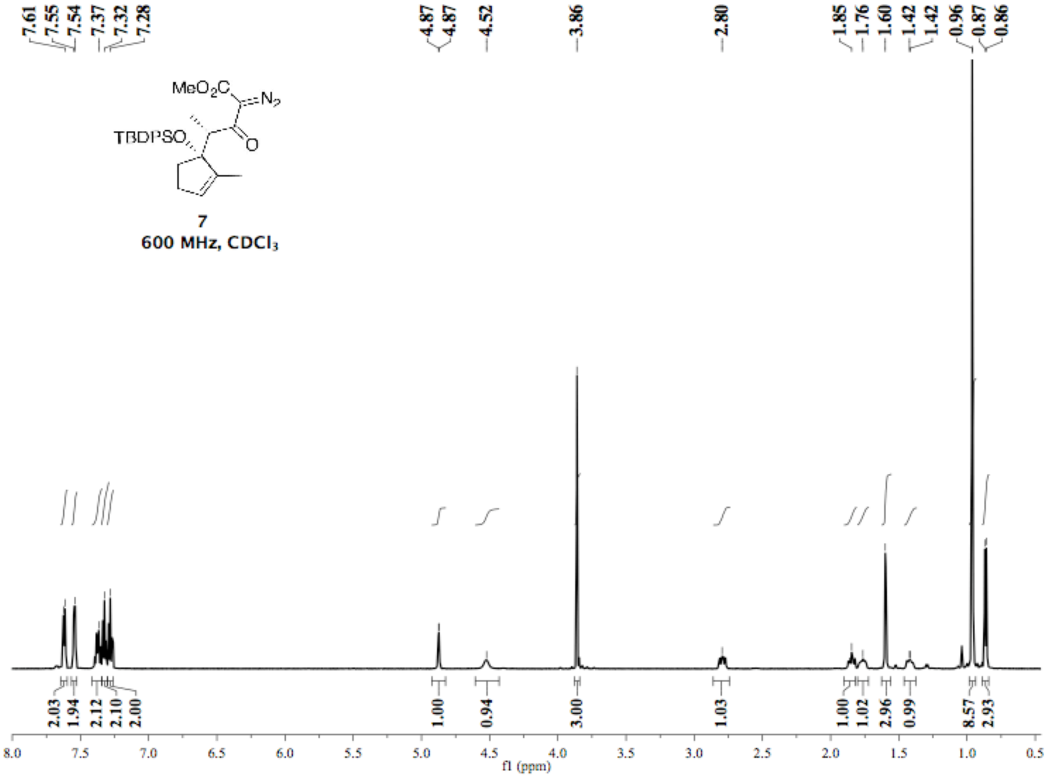
3b
400 MHz, $CDCl_3$

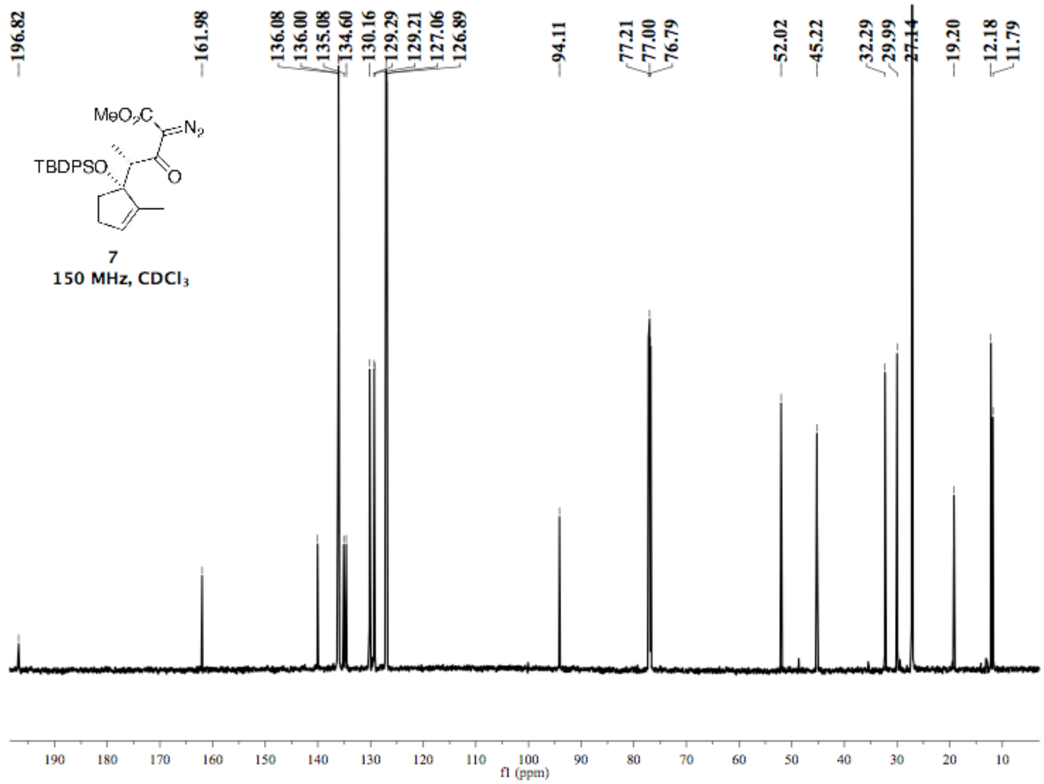


3b
150 MHz, $CDCl_3$


5.53
4.27
4.26
3.81
2.76
2.30
2.18
2.16
1.77
1.76
1.71
1.70
0.88
0.86
0.77
-0.02
-0.04
MeO_2C
N_2
TBSO
O
6
400 MHz, $CDCl_3$
1.03
1.00
3.23
1.05
1.10
1.09
1.11
3.08
3.59
8.87
5.57
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f1 (ppm)


196.41
161.92
141.96
129.48
92.41
77.32
77.00
76.68
51.99
45.46
31.80
29.98
25.60
18.20
12.27
11.71
-3.34
-3.68
MeO_2C
N_2
TBSO
O
6
150 MHz, $CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.61
7.55
7.54
7.37
7.32
7.28
4.87
4.87
4.52
3.86
2.80
1.85
1.76
1.60
1.42
1.42
0.96
0.87
0.86
MeO2C
N2
TBDPSO
O
7
600 MHz, CDCl3
2.03
1.94
2.12
2.10
2.00
1.00
0.94
3.00
1.03
1.00
1.02
2.96
0.99
8.57
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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161.98
136.08
136.00
135.08
134.60
130.16
129.29
129.21
127.06
126.89
94.11
77.21
77.00
76.79
52.02
45.22
32.29
29.99
27.14
19.20
12.18
11.79
MeO2C
N2
TBDPSO
O
7
150 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
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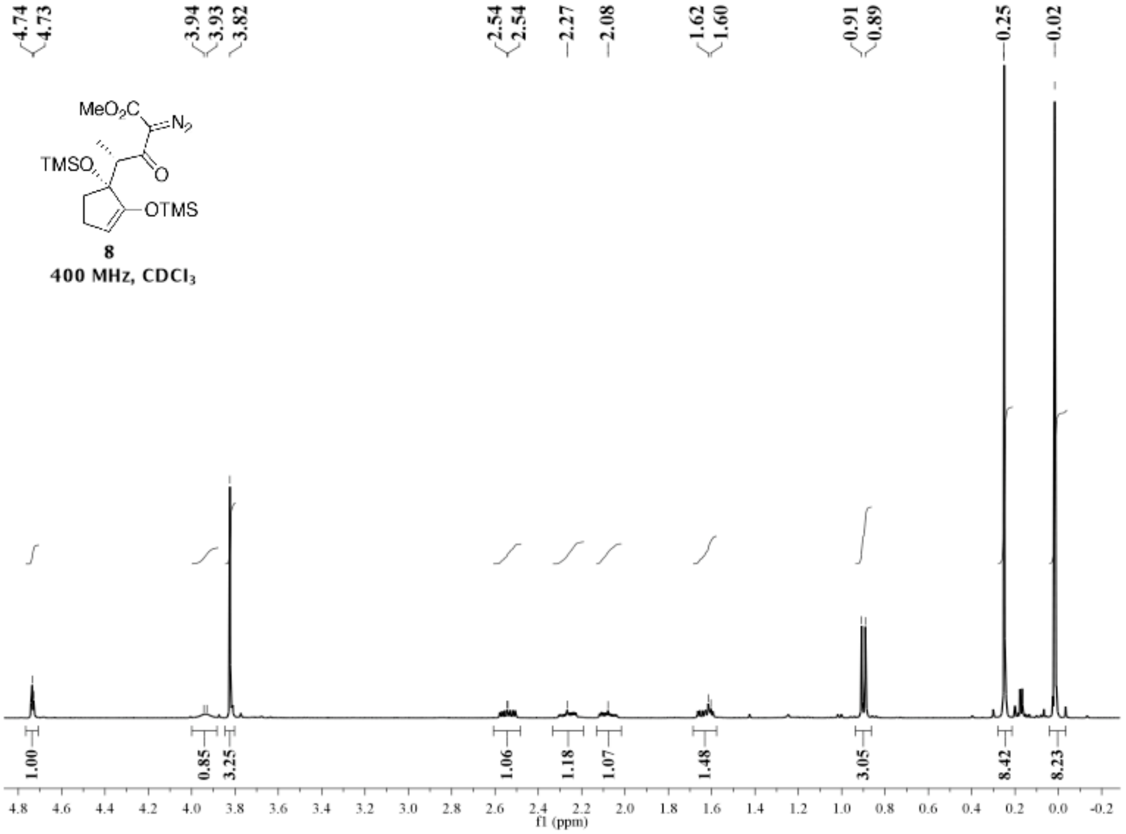
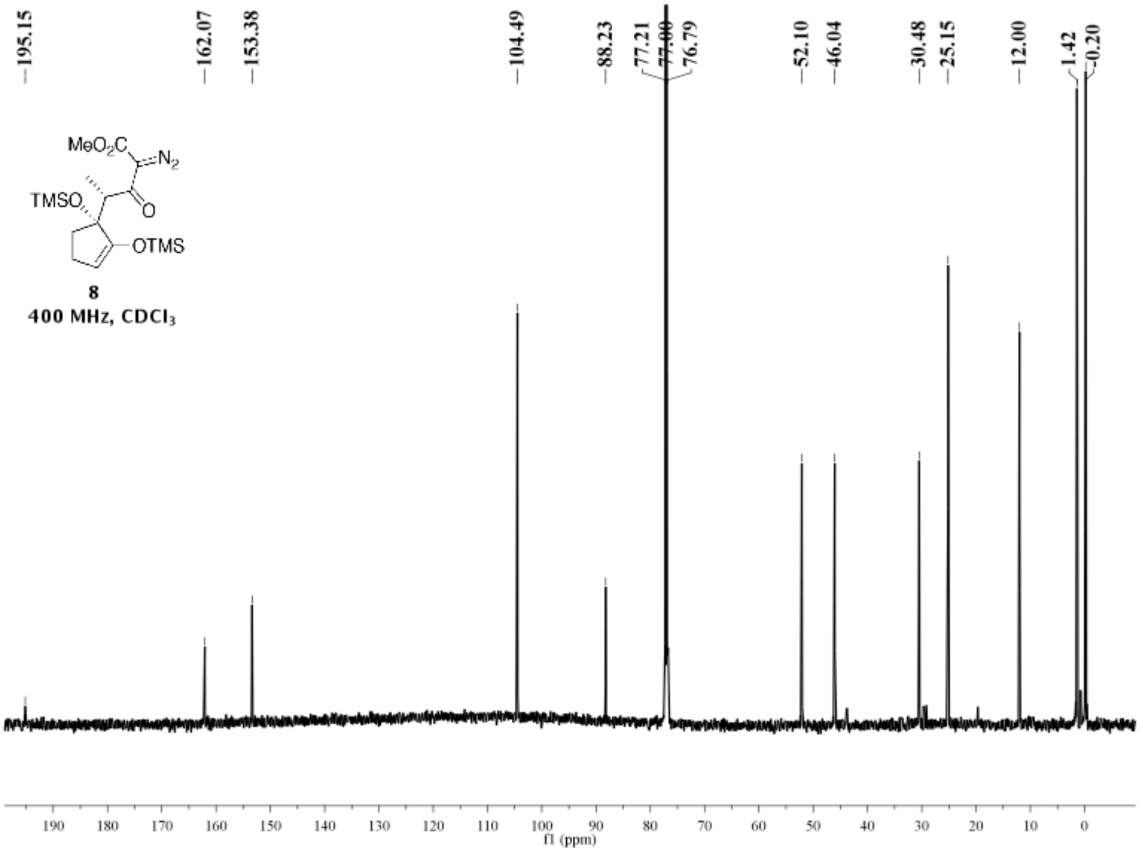
40
30
20
10
f1 (ppm)



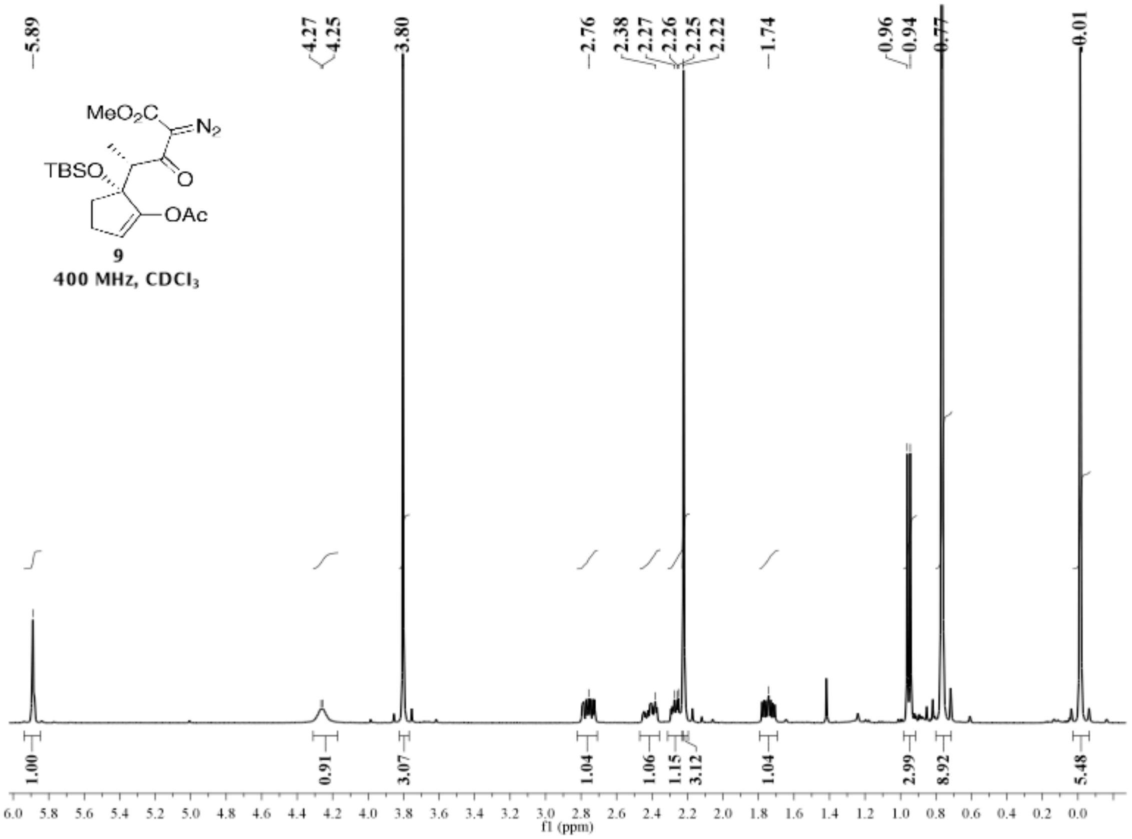
8

400 MHz, CDCl$_3$

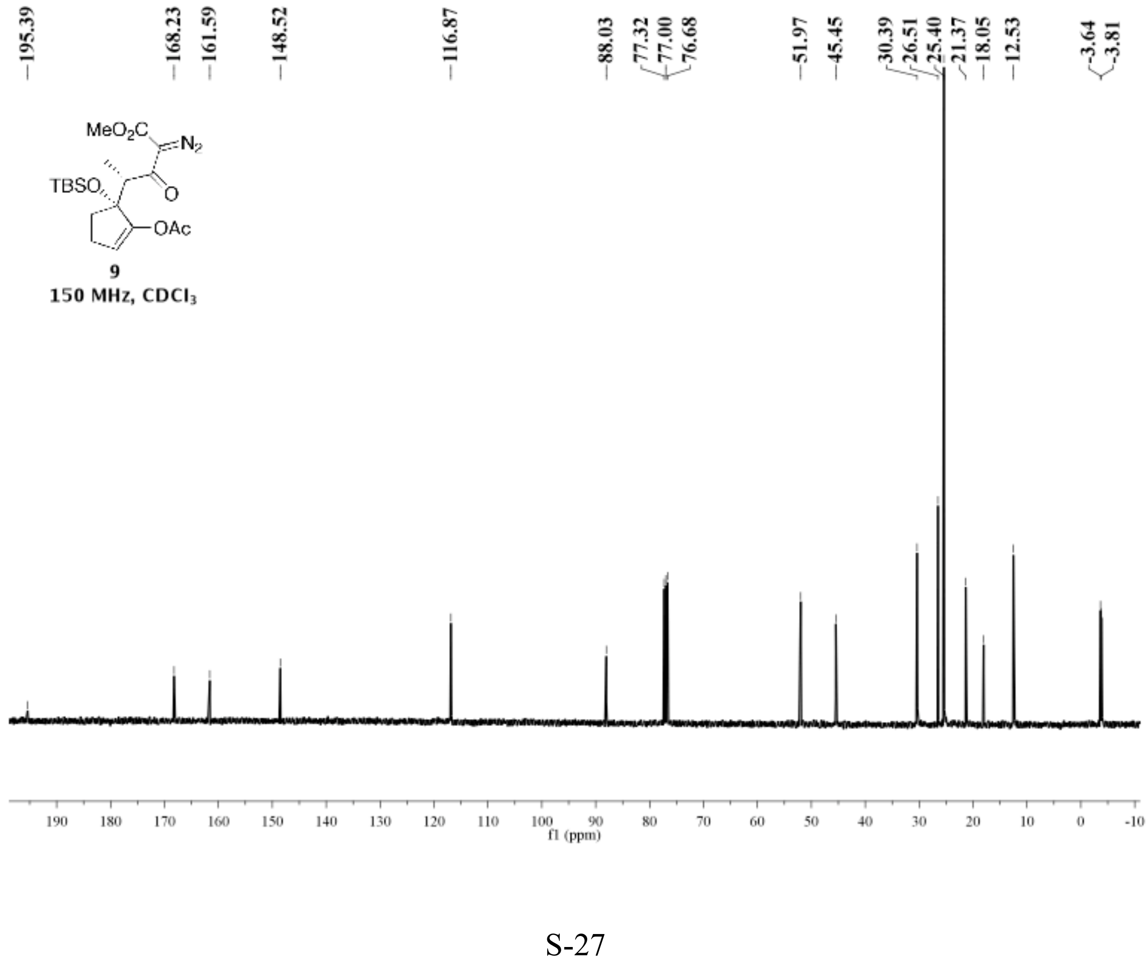


8

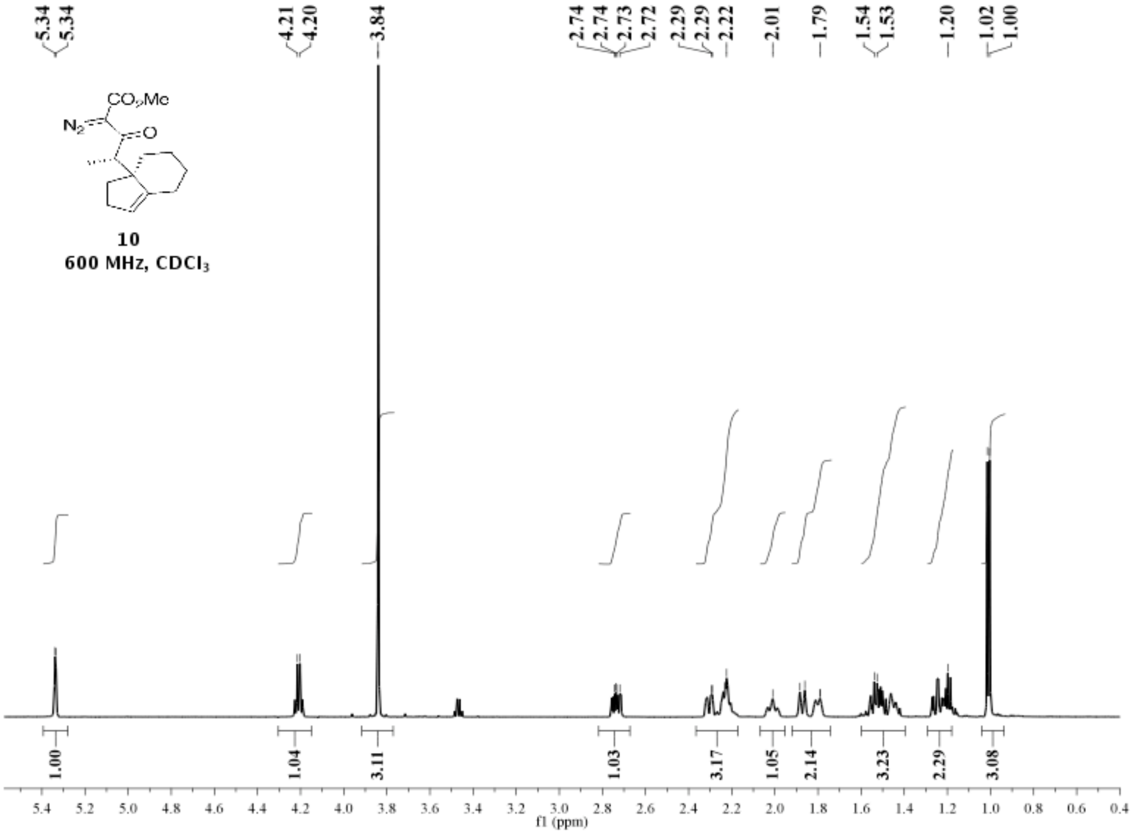
400 MHz, CDCl$_3$

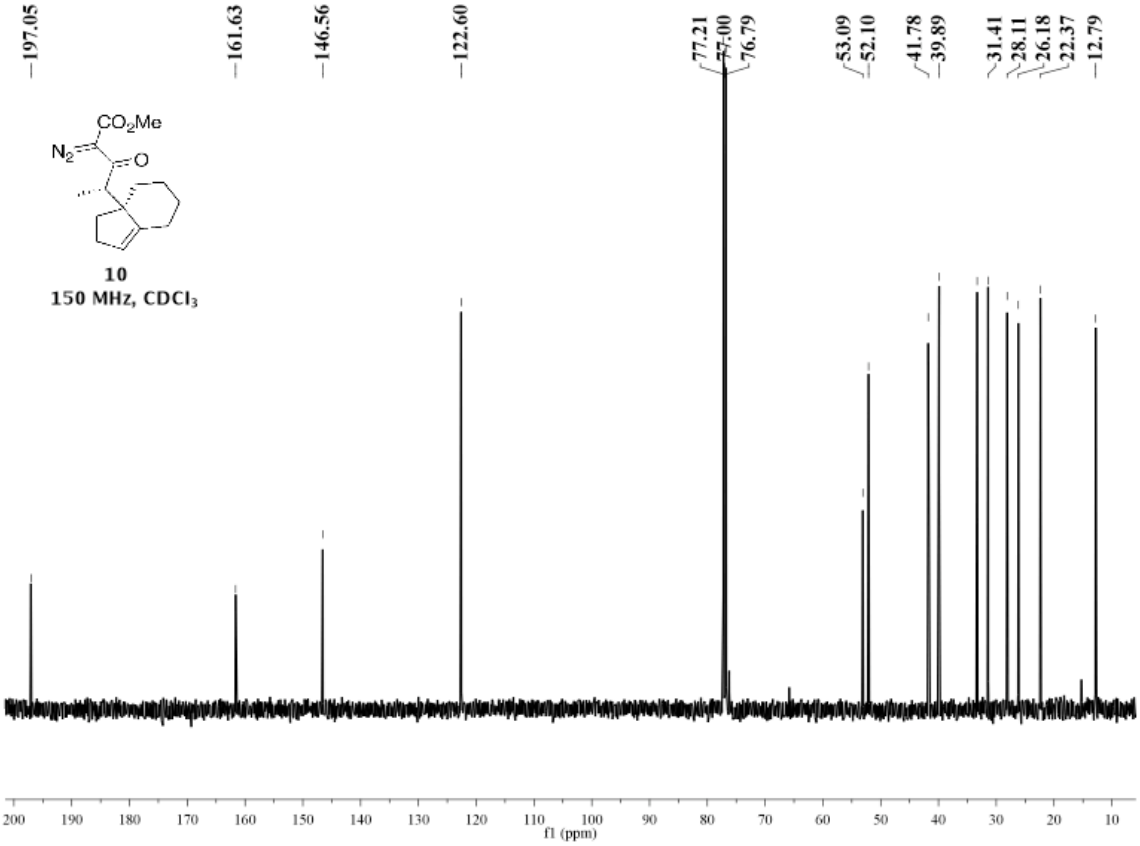


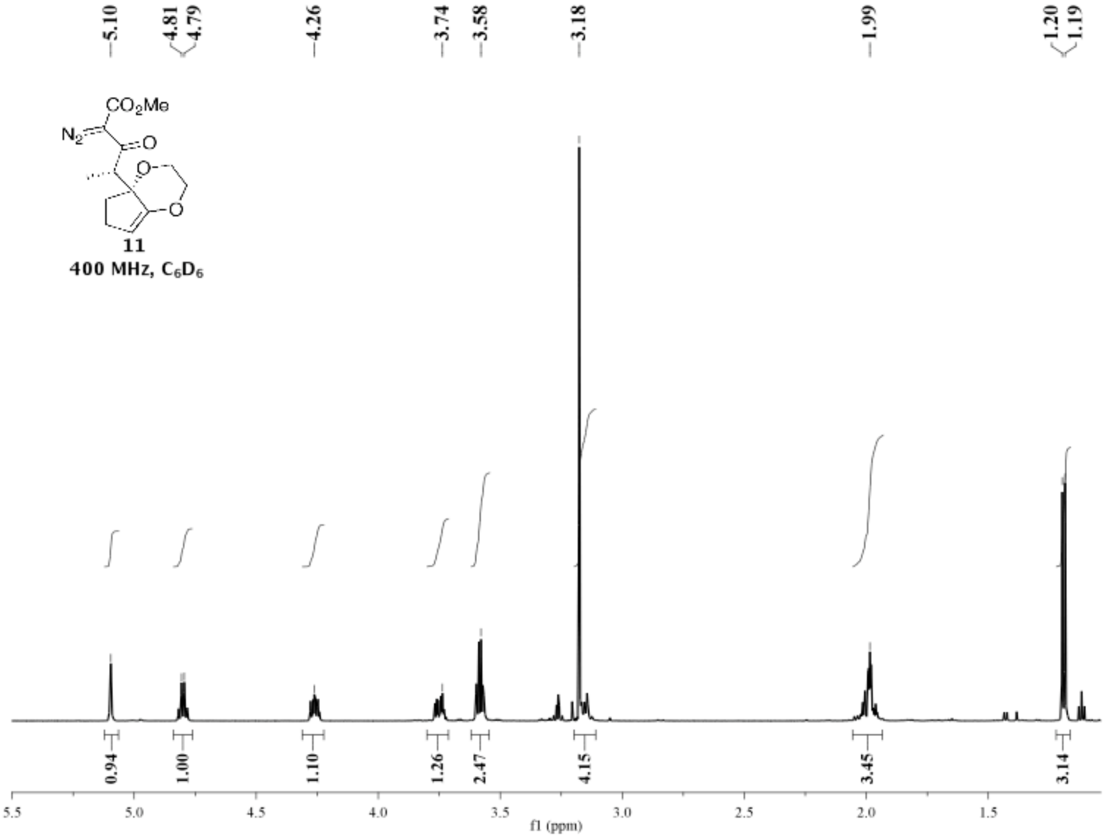
9
400 MHz, $CDCl_3$

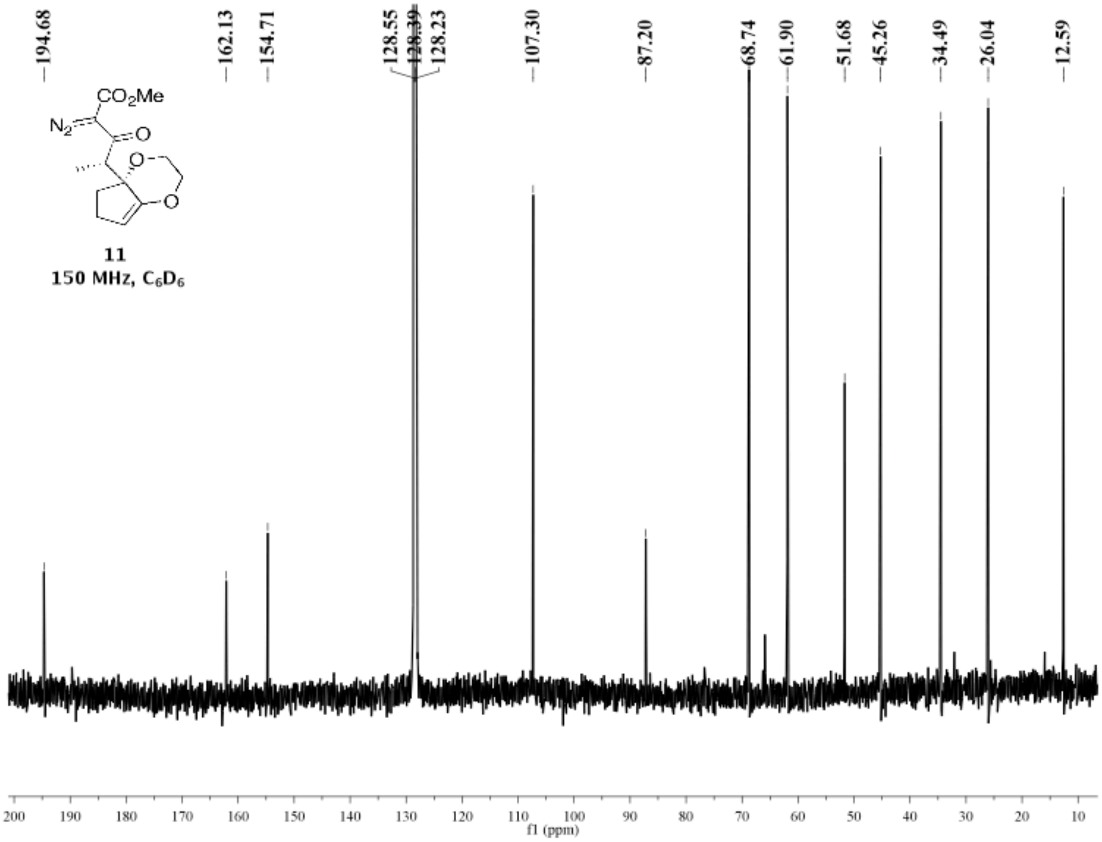


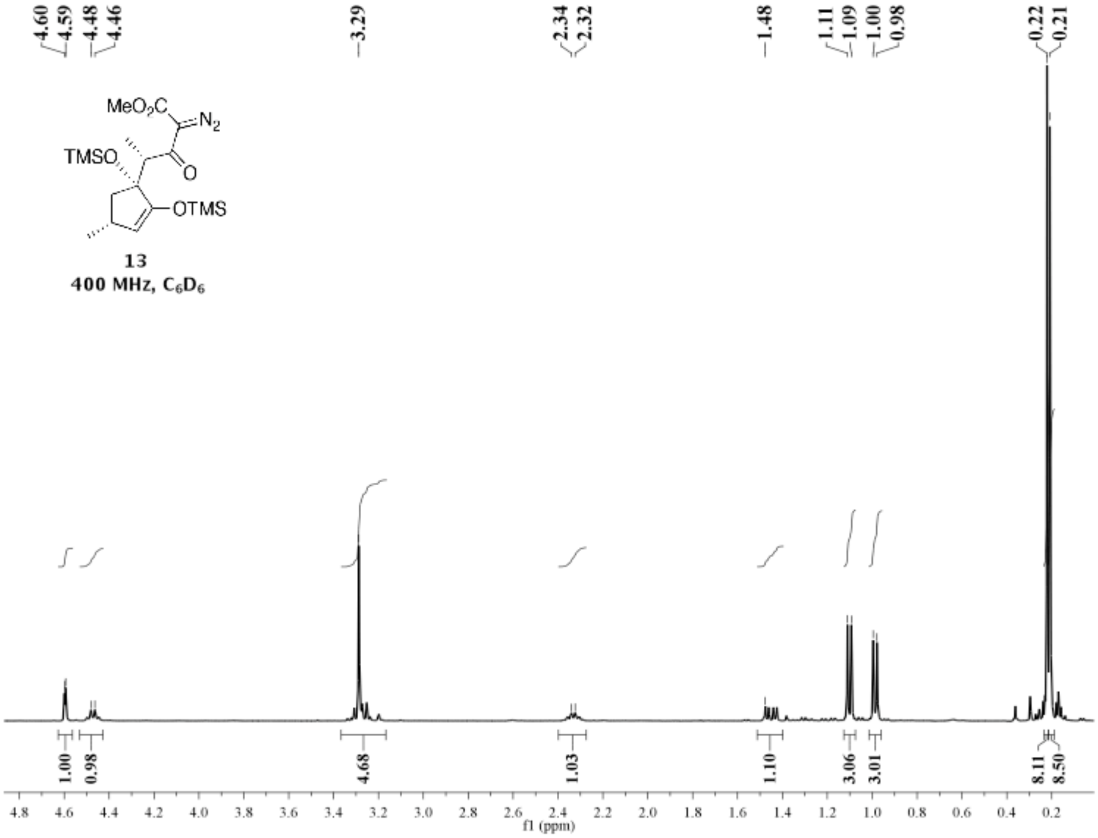
9
150 MHz, $CDCl_3$

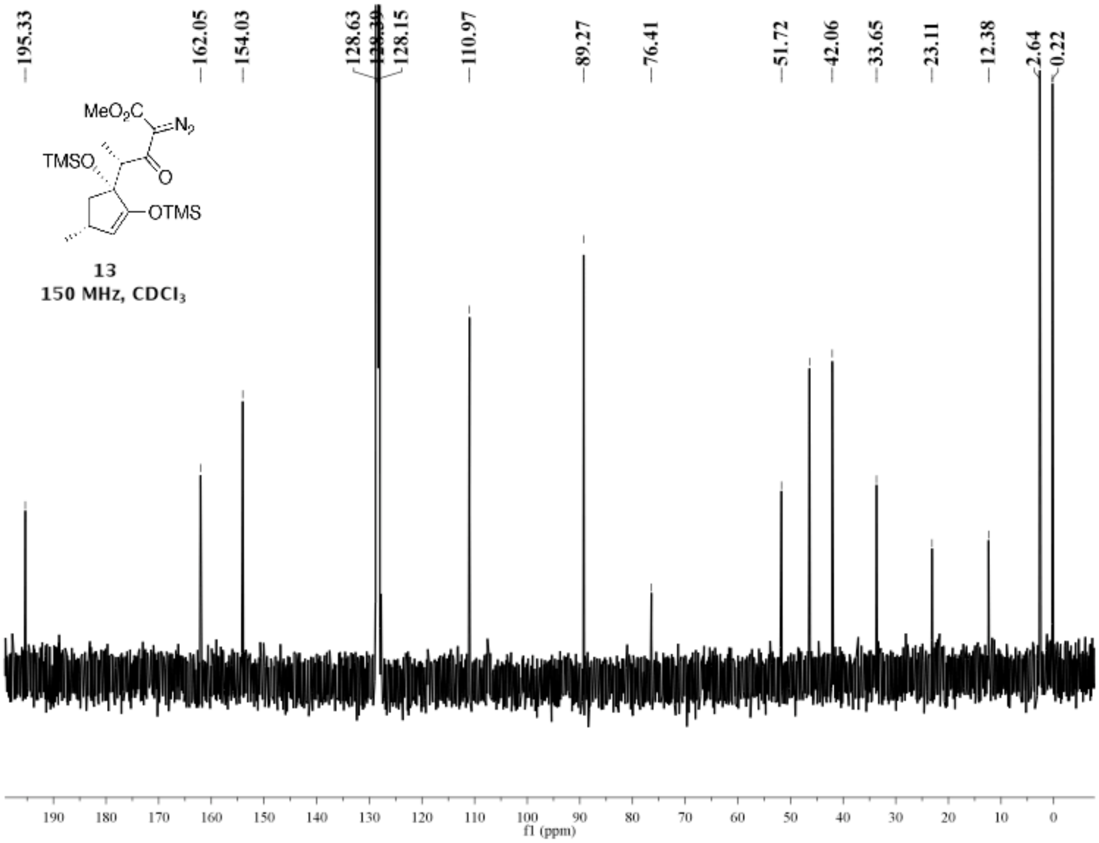

10
600 MHz, $CDCl_3$

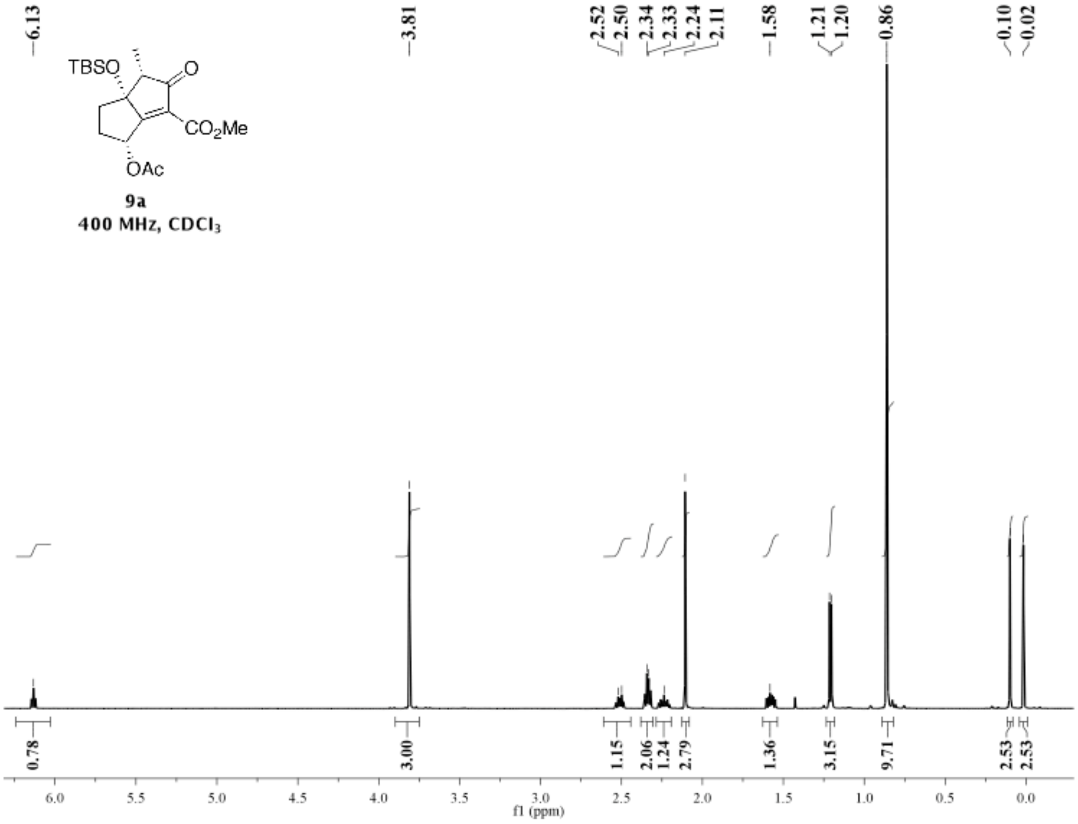

10
150 MHz, $CDCl_3$


5.10
4.81
4.79
4.26
3.74
3.58
3.18
1.99
1.20
1.19
CO_2Me
N_2
O
O
O
11
400 MHz, C_6D_6
0.94
1.00
1.10
1.26
2.47
4.15
3.45
3.14
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

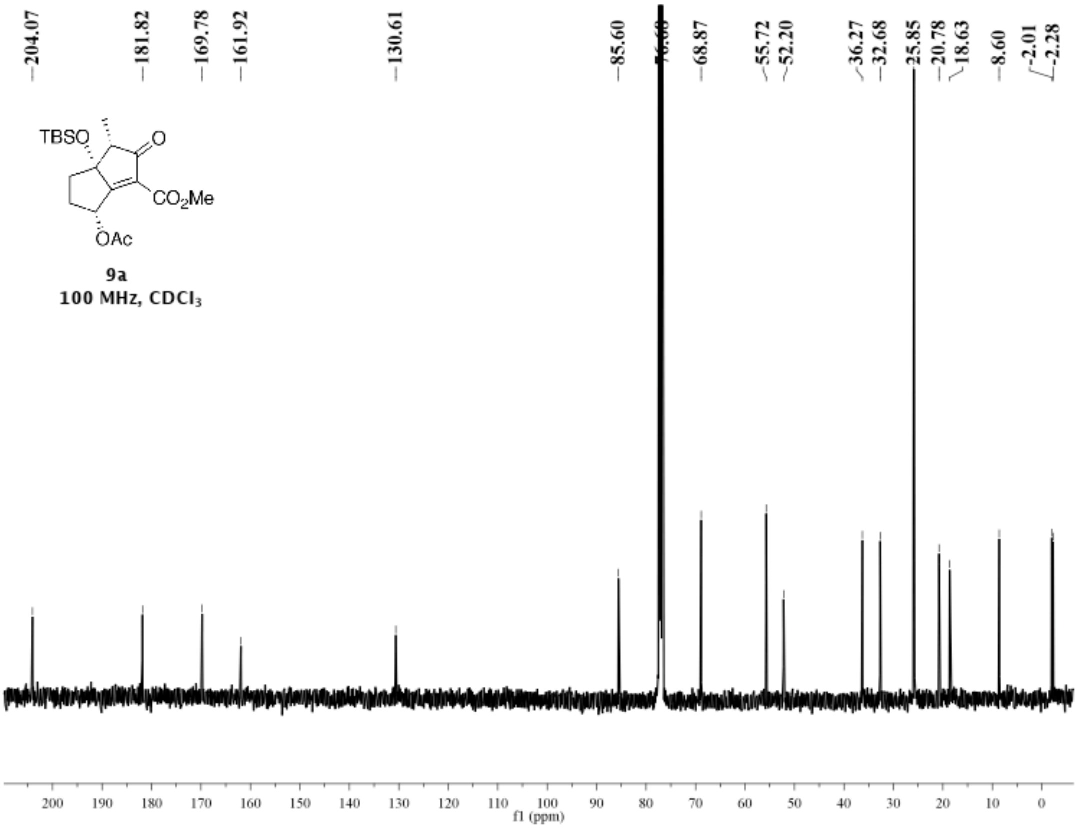

194.68
162.13
154.71
128.55
128.39
128.23
107.30
87.20
68.74
61.90
51.68
45.26
34.49
26.04
12.59
CO_2Me
N_2
O
O
O
11
150 MHz, C_6D_6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


4.60
4.59
4.48
4.46
3.29
2.34
2.32
1.48
1.11
1.09
1.00
0.98
0.22
0.21
MeO$_2$C
N$_2$
O
TMSO
OTMS
13
400 MHz, C$_6$D$_6$
1.00
0.98
4.68
1.03
1.10
3.06
3.01
8.11
8.50
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
f1 (ppm)

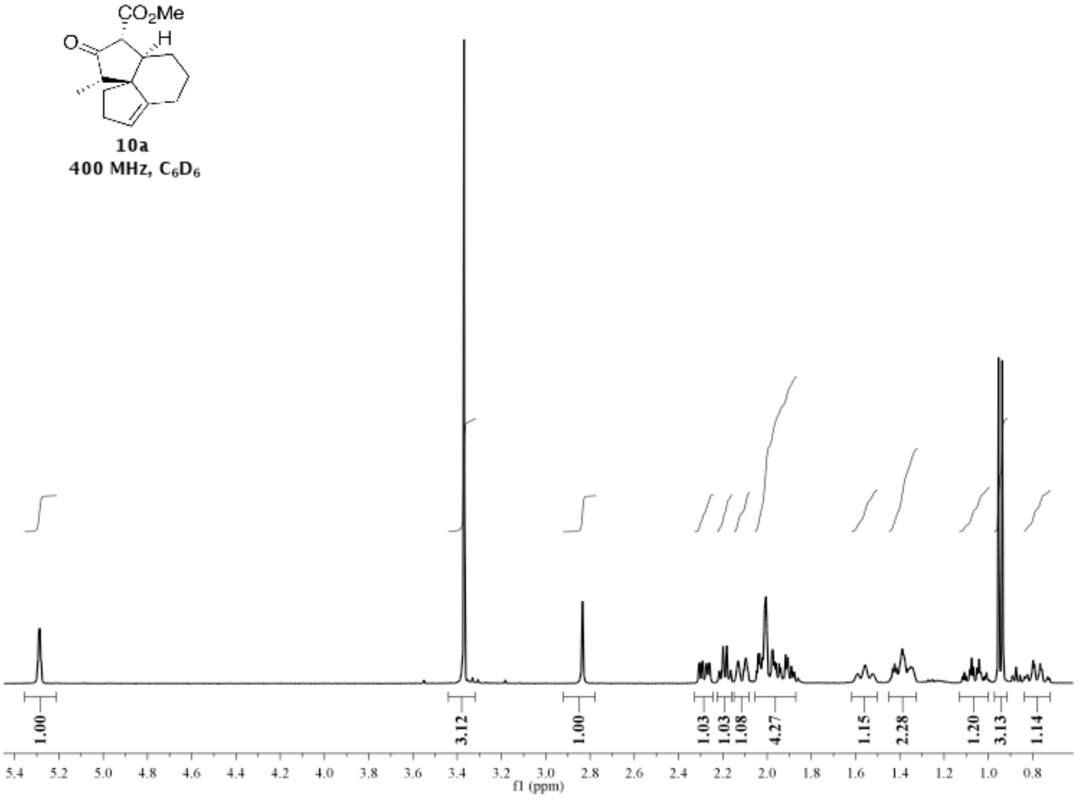

195.33
162.05
154.03
128.63
128.39
128.15
110.97
89.27
76.41
51.72
42.06
33.65
23.11
12.38
2.64
0.22
MeO$_2$C
N$_2$
O
TMSO
OTMS
13
150 MHz, CDCl$_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

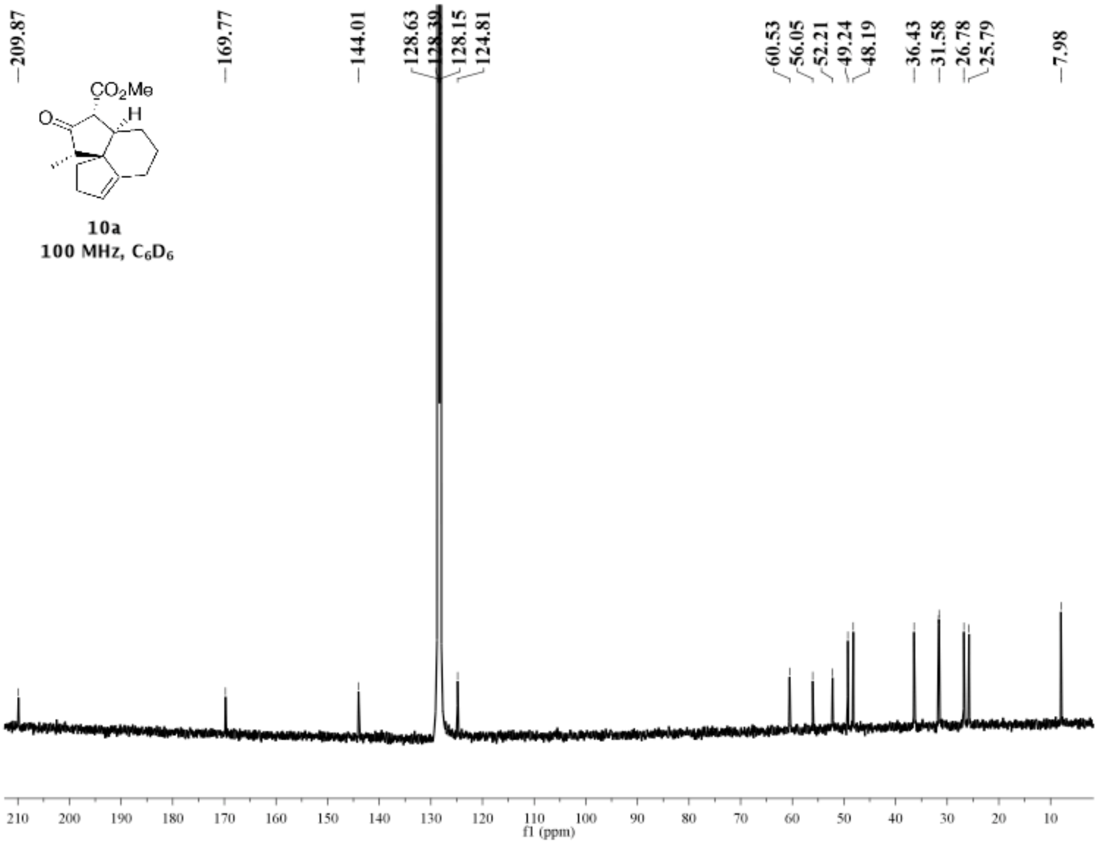


6.13
3.81
2.52
2.50
2.34
2.33
2.24
2.11
1.58
1.21
1.20
0.86
0.10
0.02
TBSO
O
CO2Me
OAc
9a
400 MHz, CDCl3
0.78
3.00
1.15
2.06
1.24
2.79
1.36
3.15
9.71
2.53
2.53
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



204.07
181.82
169.78
161.92
130.61
85.60
76.68
68.87
55.72
52.20
36.27
32.68
25.85
20.78
18.63
8.60
-2.01
-2.28
TBSO
O
CO2Me
OAc
9a
100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CO2Me
O
H
10a
400 MHz, C6D6
1.00
3.12
1.00
1.03
1.03
1.08
4.27
1.15
2.28
1.20
3.13
1.14
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)


209.87
169.77
144.01
128.63
128.39
128.15
124.81
60.53
56.05
52.21
49.24
48.19
36.43
31.58
26.78
25.79
7.98
CO2Me
O
H
10a
100 MHz, C6D6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)