Electronic Supplementary Material (ESI) for ChemComm.

Dinitrogen Extrusion from Enoldiazo Compounds under Thermal Conditions: Synthesis of Donor-Acceptor Cyclopropenes

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Supporting Information

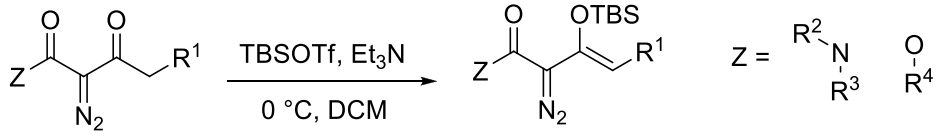
General Information

All reactions were performed in oven-dried (140 °C) glassware. DCM (dichloromethane), DCE (1,2-dichloroethane) and toluene were distilled prior to use and kept over activated 3 Å molecular sieves; $CHCl_3$ and $CDCl_3$ were purchased from Sigma Aldrich and used without further treatment. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates; visualization was accomplished with UV light (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (230-400 mesh). ^{1}H NMR spectra were recorded on an Inova™ (500 MHz) spectrometer, and chemical shifts were reported in ppm. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite; coupling constant(s) in Hz. ^{13}C NMR spectra were recorded on an Inova™ (125 MHz) spectrometer with complete proton decoupling. Enantioselectivity was determined on an Agilent 1200 Series HPLC using Daicel Chiralcel OD-H columns. High-resolution mass spectra (HRMS) were performed on a TOF-CS mass spectrometer using CsI as the standard.

Materials

Rh_2(*S*-NTTL)$_4$[1a,1b] and Rh_2(*S*-TCPTTL)$_4$[1c,1d] were prepared according to literature procedures. The diazoacetoacetamides **S-1** were prepared according to the literature procedures.[2] The diazoacetoacetates **S-3** were prepared according to the literature procedures.[3] All the other chemicals were obtained from commercial sources and used without further purification.

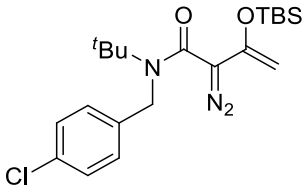
General Procedures for the Synthesis of Enoldiazoacetamides 1 and Enoldiazoacetates 3



To a 100 mL oven-dried round bottom flask containing a magnitic stirring bar, **S-1** or **S-3** (2.0 mmol) and Et_3N (1.5 eq, 3.0 mmol, 0.45 mL) in DCM (10 mL) were added TBSOTf (1.1 eq, 2.2 mmol, 0.5 mL) slowly at 0 ℃. After the reaction mixture was stirred for 0.5-1

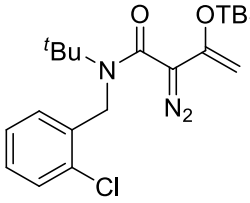
h under these conditions, hexanes (30 mL) were added, followed by saturated aqueous $NaHCO_3$ (40 mL). The organic phase was separated and washed two more times with saturated aqueous $NaHCO_3$ (40 mL X 2) and dried with anhydrous Na_2SO_4. After evaporating the solvents, enoldiazo compounds **1** and **3** were purified by flash chromatography (SiO_2 was treated with hexanes with 2% Et_3N for 30 min before use, hexanes 100%).

***N-tert*-Butyl-3-(*tert*-butyldimethylsilyloxy)-*N*-(4-chlorobenzyl)-2-diazobut-3-enamide**



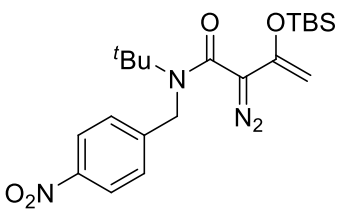
(1a). Red solid, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.54 (s, 2H), 4.40 (d, *J* = 2.1 Hz, 1H), 4.16 (d, *J* = 2.1 Hz, 1H), 1.37 (s, 9H), 0.88 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.07, 143.83, 138.00, 133.01, 128.72, 128.06, 89.09, 58.29, 50.26, 28.81, 25.55, 18.05, -4.80. This compound has been previously reported; the spectroscopic data are identical to those in reference 2a.

***N-tert*-Butyl-3-(*tert*-butyldimethylsilyloxy)-*N*-(2-chlorobenzyl)-2-diazobut-3-enamide**



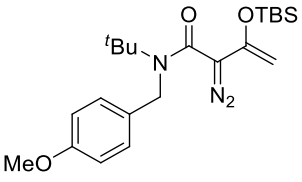
(1b). Red solid, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (comp, 2H), 7.27 – 7.20 (comp, 2H), 4.73 (s, 2H), 4.46 (d, *J* = 2.1 Hz, 1H), 4.19 (d, *J* = 2.1 Hz, 1H), 1.41 (s, 9H), 0.87 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.07, 143.97, 136.77, 132.03, 129.67, 128.32, 128.30, 126.68, 89.58, 58.57, 48.47, 28.68, 25.56, 18.05, -4.82. HRMS (ESI) calculated for $C_{21}H_{33}ClN_3O_2Si$ $[M+H]^+$: 422.2025; found: 422.2038.

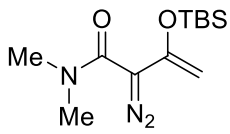
***N-tert*-Butyl-3-(*tert*-butyldimethylsilyloxy)-2-diazo-*N*-(4-nitrobenzyl)but-3-enamide**

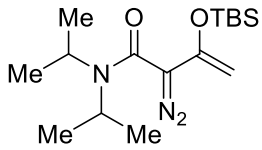


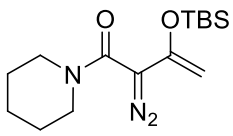
(1c). Red solid, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 4.66 (s, 2H), 4.40 (d, *J* = 2.2 Hz, 1H), 4.16 (d, *J* = 2.2 Hz, 1H), 1.40 (s, 9H), 0.86 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.21, 147.25, 147.21, 143.55, 127.34, 123.86,

89.53, 58.54, 50.17, 28.83, 25.51, 18.03, -4.82. This compound has been previously reported; the spectroscopic data are identical to those in reference 2a.

***N*-*tert*-Butyl-3-(*tert*-butyldimethylsilyloxy)-2-diazo-*N*-(4-methoxybenzyl)but-3-enamide (1d).**  Red solid, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.3 Hz, 2H), 6.86 (d, *J* = 7.3 Hz, 2H), 4.52 (s, 2H), 4.41 (d, *J* = 1.9 Hz, 1H), 4.15 (d, *J* = 1.9 Hz, 1H), 3.79 (s, 3H), 1.37 (s, 9H), 0.89 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.95, 158.80, 144.06, 131.28, 127.98, 113.93, 88.78, 58.09, 55.19, 50.46, 28.79, 25.57, 18.05, -4.79. This compound has been previously reported; the spectroscopic data are identical to those in reference 2a.

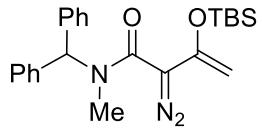
3-(*tert*-Butyldimethylsilyloxy)-2-diazo-*N*,*N*-dimethylbut-3-enamide (1e).  Red oil, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.42 (d, *J* = 3.7 Hz, 1H), 4.23 (d, *J* = 3.7 Hz, 1H), 2.95 (s, 6H), 0.89 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.81, 143.76, 90.55, 37.39, 25.52, 18.02, -4.85. HRMS (ESI) calculated for $C_{12}H_{23}N_3O_2SiNa$ $[M+Na]^+$: 292.1457; found: 292.1469.

3-(*tert*-Butyldimethylsilyloxy)-2-diazo-*N*,*N*-diisopropylbut-3-enamide (1f).  Red oil, 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (d, *J* = 2.0 Hz, 1H), 4.16 (d, *J* = 2.0 Hz, 1H), 3.76 – 3.68 (comp, 2H), 1.30 (d, *J* = 6.7 Hz, 12H), 0.91 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.43, 144.58, 89.65, 48.60, 25.58, 20.86, 18.09, -4.80. HRMS (ESI) calculated for $C_{16}H_{31}N_3O_2SiNa$ $[M+Na]^+$: 348.2083; found: 348.2072.

3-(*tert*-Butyldimethylsilyloxy)-2-diazo-1-(piperidin-1-yl)but-3-en-1-one (1g).  Red oil, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.39 (d, *J* = 2.1 Hz, 1H), 4.20 (d, *J* = 2.1 Hz, 1H), 3.42 – 3.40 (comp, 4H), 1.65 – 1.61 (comp, 2H), 1.58 – 1.53 (comp, 4H), 0.90 (s, 9H), 0.20 (s, 6H); ^{13}C NMR

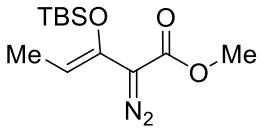
(125 MHz, $CDCl_3$) δ 164.00, 144.11, 90.01, 46.45, 25.77, 25.56, 24.51, 18.07, -4.80. HRMS (ESI) calculated for $C_{15}H_{27}N_3O_2SiNa$ $[M+Na]^+$: 332.1770; found: 332.1798.

***N*-Benzyl-3-(*tert*-butyldimethylsilyloxy)-2-diazo-*N*-methylbut-3-enamide (1h).** Red



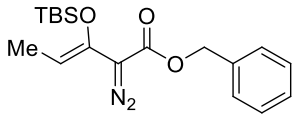
oil, 87% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (comp, 6H), 7.23 – 7.21 (comp, 4H), 6.81 (s, 1H), 4.52 (d, *J* = 2.1 Hz, 1H), 4.28 (d, *J* = 2.1 Hz, 1H), 2.80 (s, 3H), 0.93 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.36, 143.68, 138.48, 128.72, 128.50, 127.58, 91.17, 63.09, 33.13, 25.62, 18.12, -4.71. HRMS (ESI) calculated for $C_{24}H_{31}N_3O_2SiNa$ $[M+Na]^+$: 444.2083; found: 444.2071.

(*Z*)-Methyl 3-(*tert*-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3a). Red oil, 95%



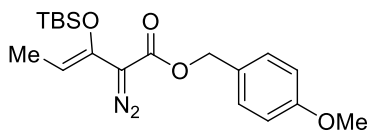
yield. ^1H NMR (500 MHz, $CDCl_3$) δ 5.27 (q, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 1.69 (d, *J* = 7.0 Hz, 3H), 0.97 (s, 9H), 0.16 (s, 6H). This compound has been previously reported; the spectroscopic data are identical to those in reference 3h.

(*Z*)-Benzyl 3-(*tert*-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3b). Red oil, 93%



yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (comp, 5H), 5.29 (q, *J* = 7.0 Hz, 1H), 5.24 (s, 2H), 1.69 (d, *J* = 7.0 Hz, 3H), 0.97 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.77, 135.94, 132.85, 128.50, 128.16, 128.10, 127.98, 108.20, 77.25, 77.00, 76.75, 66.29, 25.62, 18.17, 11.80, -4.66. HRMS (ESI) calculated for $C_{18}H_{26}N_2O_3SiNa$ $[M+Na]^+$: 369.1610; found: 369.1619.

(*Z*)-4-Methoxybenzyl 3-(*tert*-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3c). Red



oil, 90% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.27 (q, *J* = 7.0 Hz, 1H), 5.17 (s, 2H), 3.81 (s, 3H), 1.67 (d, *J* = 7.0 Hz,

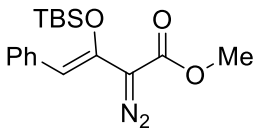
3H), 0.95 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.93, 159.62, 132.95, 129.98, 128.12, 113.90, 108.14, 66.21, 55.28, 25.66, 18.21, 11.84, -4.62. HRMS (ESI) calculated for $C_{19}H_{28}N_2O_3SiNa$ $[M+Na]^+$: 399.1716; found: 399.1708.

(*Z*)-2-Methoxybenzyl 3-(*tert*-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3d). Red oil, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.28 (comp, 2H), 6.97 – 6.93 (comp, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 5.29(s, 1H), 5.30 (q, *J* = 7.0 Hz, 1H), 3.84 (s, 3H), 1.68 (d, *J* = 7.0 Hz, 3H), 0.96 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.88, 157.35, 132.94, 129.37, 129.11, 124.33, 120.36, 110.36, 107.99, 61.92, 55.32, 25.65, 18.19, 11.83, -4.66. HRMS (ESI) calculated for $C_{19}H_{28}N_2O_3SiNa$ $[M+Na]^+$: 399.1716; found: 399.1719.

(*Z*)-Benzhydryl 3-(*tert*-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3e). Red oil, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (comp, 10H), 6.98 (s, 1H), 5.28 (q, *J* = 7.0 Hz, 1H), 1.68 (d, *J* = 7.0 Hz, 3H), 0.96 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.01, 140.13, 132.74, 128.50, 127.90, 126.94, 108.53, 77.13, 25.64, 18.19, 11.82, -4.66. HRMS (ESI) calculated for $C_{24}H_{30}N_2O_3SiNa$ $[M+Na]^+$: 445.1923; found: 445.1941.

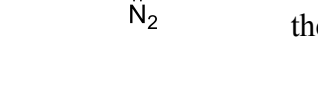
(Z)-2,6-Dichlorobenzyl 3-(*tert*-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3f). Red oil, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 5.49 (s, 2H), 5.27 (q, *J* = 7.0 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 9H), 0.14 (s, 6H);^{13}C NMR (125 MHz, $CDCl_3$) δ 164.44, 136.92, 132.72, 131.27, 130.45, 128.40, 108.24, 61.39, 25.62, 18.16, 11.81, -4.70. HRMS (ESI) calculated for $C_{18}H_{24}O_3N_2SiNaCl_2$ $[M+Na]^+$: 437.0831; found: 437.0803.

(*Z*)-Methyl 3-(*tert*-Butyldimethylsilyloxy)-2-diazo-4-phenylbut-3-enoate (3g). Red oil, 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz,

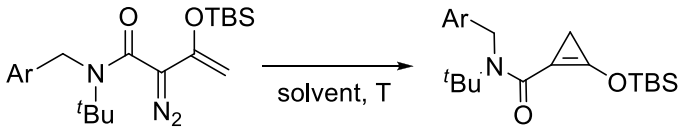


2H), 7.16 (t, J = 7.5 Hz, 1H), 6.40 (s, 1H), 3.86 (s, 3H), 0.97 (s, 9H), -0.07 (s, 6H). This compound has been previously reported; the spectroscopic data are identical to those in reference 3e.

(*Z*)-Benzyl 3-(*tert*-Butyldimethylsilyloxy)-2-diazo-4-phenylbut-3-enoate (3h). Red oil, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (comp, 2H), 7.45 – 7.34 (comp, 5H), 7.32 – 7.24 (comp, 2H), 7.17 (m, 1H), 6.42 (s, 1H), 5.31 (s, 2H), 0.97 (s, 9H), -0.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.29, 136.29, 135.82, 133.76, 129.02, 128.63, 128.33, 128.04, 127.90, 126.15, 111.42, 66.55, 25.75, 18.13, -4.80. HRMS (ESI) calculated for $C_{23}H_{28}O_3N_2SiNa$ $[M+Na]^+$: 431.1767; found: 431.1778.



Screening of Reaction Conditions for Preparation of Donor-Acceptor Cyclopropenes [a]

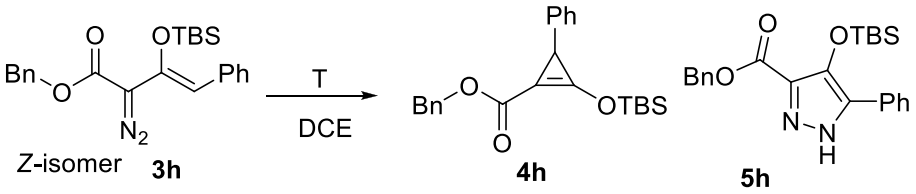


1a, Ar = 4-ClC$_6$H$_4$ **2a**

Entry	Solvent	T (°C)	Time (h)	Yield, %[b]
1	DCM	40	4	83
2	$CHCl_3$	50	3	quantitative
3	$CHCl_3$	refluxing	2	quantitative
4	DCE	50	3	87
5	Toluene	50	3	85
6	Hexane	50	4	75
7	CH_3CN	50	6	89
8	EtOAc	50	5	70

[a] Reactions were performed on a 0.4 mmol scale: 0.4 mmol **1a** in 4 mL solvent at indicated temperature. [b] The yield of cyclopropene was determined by ^{1}H NMR analysis using an internal standard (1,3,5-trimethoxybenzene).

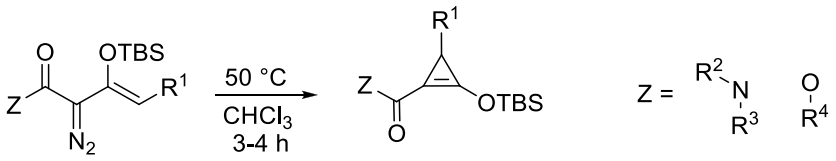
Temperature Effect on Thermal Reactions of 3h



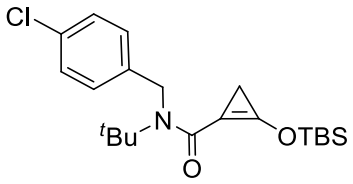
		4h : 5h
40 °C, DCE	9 h	39 : 61
60 °C, DCE	1.5 h	48 : 52
80 °C, DCE	25 min	58 : 42

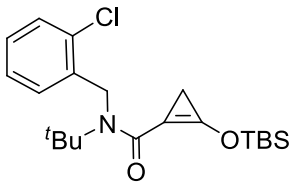
3h (0.4 mmol) at room temperature was added to a 10-mL oven-dried vial containing a magnetic stirring bar and 4 mL 1,2-dichloroethene (DCE), and then the vial was screwed close. The sealed reaction mixture was heated in oil bath at indicated temperature, during which time the diazo compound was converted to the corresponding cyclopropene. The color of the solution changed from orange to light yellow. After removing DCE under reduced pressure, the resulting reaction mixture was analyzed by ^{1}H NMR to determine the ratio of **4h** and **5h** by using an internal standard (1,3,5-trimethoxybenzene).

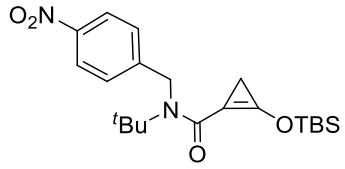
General Procedure for the Preparation of Donor-Acceptor Cyclopropenes 2 and 4

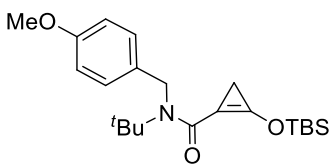


Enoldiazo compound (0.4 mmol) at room temperature was added to a 10-mL oven-dried vial containing a magnetic stirring bar and 4 mL $CHCl_3$, and then the vial was screwed close. The sealed reaction mixture was heated in oil bath at 50 °C for 3 to 4 hours, during which time the diazo compound was converted to the corresponding cyclopropene. The color of the solution changed from orange to colorless or light yellow. After removing $CHCl_3$ under reduced pressure, the resulting cyclopropenes were characterized directly without further purification.

***N-tert*-Butyl-2-(*tert*-butyldimethylsilyloxy)-*N*-(4-chlorobenzyl)cycloprop-1-enecarboxamide (2a).**  Colorless oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 4.73 (s, 2H), 1.79 (s, 2H), 1.42 (s, 9H), 0.72 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.32, 139.12, 134.59, 132.23, 128.45, 127.28, 72.09, 57.70, 49.07, 28.68, 24.93, 17.94, 17.51, -4.60. HRMS (ESI) calculated for $C_{21}H_{33}ClNO_2SiNa$ $[M+Na]^+$: 416.1789; found: 416.1767.

***N-tert*-Butyl-2-(*tert*-butyldimethylsilyloxy)-*N*-(2-chlorobenzyl)cycloprop-1-enecarboxamide (2b).**  Colorless oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (comp, 2H), 7.21– 7.12 (comp, 2H), 4.79 (s, 2H), 1.74 (s, 2H), 1.45 (s, 9H), 0.71 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.54, 137.74, 134.83, 131.51, 129.12, 127.64, 127.44, 126.65, 71.84, 57.62, 47.64, 28.50, 25.03, 17.81, 17.52, -4.65. HRMS (ESI) calculated for $C_{21}H_{33}ClNO_2SiNa$ $[M+Na]^+$: 416.1789; found: 416.1771.

***N-tert*-Butyl-2-(*tert*-butyldimethylsilyloxy)-*N*-(4-nitrobenzyl)cycloprop-1-enecarboxamide (2c).**  Colorless oil, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 4.86 (s, 2H), 1.80 (s, 2H), 1.44 (s, 9H), 0.69 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.28, 148.59, 146.89, 135.06, 126.69, 123.72, 71.89, 57.86, 49.39, 28.73, 24.89, 17.88, 17.48, -4.59. HRMS (ESI) calculated for $C_{21}H_{33}N_2O_4SiNa$ $[M+Na]^+$: 427.2029; found: 427.2031.

***N-tert*-Butyl-2-(*tert*-butyldimethylsilyloxy)-*N*-(4-methoxybenzyl)cycloprop-1-enecarboxamide (2d).**  Colorless oil, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 4.71 (s, 2H), 3.76 (s, 3H), 1.80 (s, 2H), 1.42 (s, 9H), 0.72 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.30, 158.33, 134.26,

132.41, 127.01, 113.73, 72.41, 57.59, 55.19, 49.01, 28.67, 25.00, 18.11, 17.55, -4.60. HRMS (ESI) calculated for $C_{22}H_{35}NO_3SiNa$ $[M+Na]^+$: 412.2284; found: 412.2291.

2-(*tert*-Butyldimethylsilyloxy)-*N*,*N*-dimethylcycloprop-1-enecarboxamide (2e). Light yellow oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.09 (s, 3H), 2.93 (s, 3H), 1.84 (s, 2H), 0.91 (s, 9H), 0.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.40, 135.82, 70.57, 37.16, 34.64, 25.24, 17.81, 17.77, -4.50. HRMS (ESI) calculated for $C_{12}H_{23}NO_2SiNa$ $[M+Na]^+$: 264.1396; found: 264.1377.

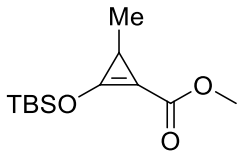
2-(*tert*-Butyldimethylsilyloxy)-*N*,*N*-diisopropylcycloprop-1-enecarboxamide (2f). Light yellow oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.38 – 4.33 (comp, 1H), 3.58 – 3.42 (comp, 1H), 1.84 (s, 2H), 1.40 (d, J = 6.7 Hz, 6H), 1.18 (d, J = 6.7 Hz, 6H), 0.94 (s, 9H), 0.27 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.87, 133.62, 71.96, 48.92, 45.38, 25.22, 20.98, 20.59, 17.79, 17.78, -4.43. HRMS (ESI) calculated for $C_{16}H_{31}NO_2SiNa$ $[M+Na]^+$: 320.2022; found: 320.2040.

(2-(*tert*-Butyldimethylsilyloxy)cycloprop-1-enyl)(piperidin-1-yl)methanone (2g). Light yellow oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58 – 3.54 (comp, 4H), 1.86 (s, 2H), 1.63 – 1.51 (comp, 6H), 0.93 (s, 9H), 0.28 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.83, 135.00, 70.65, 46.72, 42.57, 26.57, 25.63, 25.24, 24.70, 17.83, 17.81, -4.49. HRMS (ESI) calculated for $C_{15}H_{27}NO_2SiNa$ $[M+Na]^+$: 304.1709; found: 304.1706.

***N*-Benzhydryl-2-(*tert*-Butyldimethylsilyloxy)-*N*-methylcycloprop-1-enecarboxamide (2h).** Light yellow oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.20 (comp, 22H), 6.74 (s, 1H), 2.96 (s, 3H), 2.81 (s, 3H), 1.95 (s, 2H), 1.92 (s, 2H), 0.96 (s, 9H), 0.86 (s, 9H), 0.32 (s, 6H), 0.25 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.16, 160.91, 139.36, 139.13, 136.87,

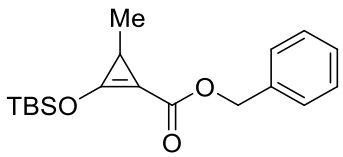
135.89, 128.85, 128.59, 128.38, 128.35, 127.47, 127.25, 70.71, 70.42, 64.49, 59.95, 25.30, 25.21, 17.91, 17.78, -4.34, -4.50. HRMS (ESI) calculated for $C_{24}H_{31}NO_2SiNa$ $[M+Na]^+$: 416.2022; found: 416.2029.

Methyl 2-(*tert*-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4a).



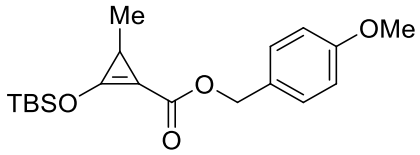
Light yellow oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 (s, 3H), 2.33 (q, J = 4.9 Hz, 1H), 1.23 (d, J = 4.9 Hz, 3H), 0.97 (s, 9H), 0.32 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 148.6, 77.2, 51.3, 25.3, 24.4, 19.4, 18.0, -5.1, -5.2. HRMS (ESI) calculated for $C_{12}H_{22}O_3SiNa$ $[M+Na]^+$: 265.1236; found: 265.1237.

Benzyl 2-(*tert*-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4b).



Light yellow oil, quantitative; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.44 (comp, 5 H), 5.21 (s, 2H), 2.38 (q, J = 4.8 Hz, 1H), 1.27 (d, J = 4.8 Hz, 3H), 0.98 (s, 9H), 0.32 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 148.8, 136.3, 128.4, 128.3, 128.0, 77.3, 65.9, 25.3, 24.4, 19.4, 18.0, -5.1, -5.2. HRMS (ESI) calculated for $C_{18}H_{26}O_3SiNa$ $[M+Na]^+$: 341.1549; found: 341.1550.

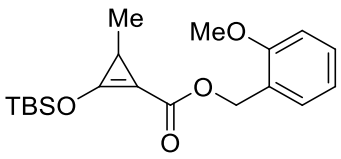
4-Methoxybenzyl 2-(*tert*-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4c).



Light yellow oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.12 (s, 2H), 3.80 (s, 3H), 2.33 (q, J = 4.8 Hz, 1H), 1.23 (d, J = 4.8 Hz, 3H), 0.95 (s, 9H), 0.29 (s, 3H), 0.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 159.5, 148.5, 130.1, 128.4, 113.8, 77.3, 65.8, 55.3, 25.3, 24.4, 19.4, 17.9, -5.1, -5.2. HRMS (ESI) calculated for $C_{19}H_{28}O_3SiNa$ $[M+Na]^+$: 371.1655; found: 371.1645.

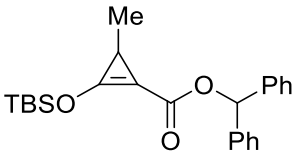
2-Methoxybenzyl 2-(*tert*-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4d).

Light yellow oil, quantitative; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.35 (d, J = 7.4 Hz, 1H), 7.27 – 7.32 (comp, 1H), 6.95 (t, J = 7.4 Hz, 1H), 6.88 (comp, 1H), 5.25 (s, 1H), 5.24



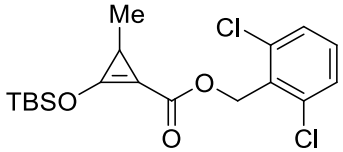
(s, 1H), 3.83 (s, 3H), 2.35 (q, J = 4.8 Hz, 1H), 1.25 (d, J = 4.8 Hz, 3H), 0.95 (s, 9H), 0.28 (s, 3H), 0.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 157.4, 148.2, 129.5, 129.3, 124.6, 120.3, 110.3, 77.4, 61.4, 55.3, 25.3, 24.3, 19.4, 17.9, -5.3, -5.3. HRMS (ESI) calculated for $C_{19}H_{28}O_3SiNa$ $[M+Na]^+$: 371.1655; found: 371.1648.

Benzhydryl 2-(*tert*-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4e).

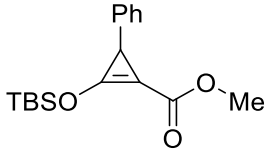


Light yellow oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.39 (comp, 8H), 7.27 – 7.31 (comp, 2H), 6.96 (s, 1H), 2.39 (q, J = 4.8 Hz, 1H), 1.29 (d, J = 4.8 Hz, 3H), 0.96 (s, 9H), 0.30 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 149.1, 140.5, 140.5, 128.4, 128.4, 127.8, 127.7, 127.4, 127.0, 77.3, 76.5, 25.3, 24.4, 19.4, 17.9, -5.1, -5.2. HRMS (ESI) calculated for $C_{24}H_{30}O_3SiNa$ $[M+Na]^+$: 417.1862; found: 417.1843.

2,6-Dichlorobenzyl 2-(*tert*-Butyldimethylsilyloxy)-3-methylcycloprop-1- enecarboxylate (4f). Light yellow oil, quantitative. ^{1}H NMR (500 MHz, $CDCl_3$) δ- 7.33 (d, J = 7.8 Hz, 2-H), 7.18 - 7.24 (t, J = 7.8 Hz, 1H), 5.37 - 5.48 (comp, 2H), 2.32 (q, J = 4.8 Hz, 1H), 1.21 (d, J = 4.8 Hz, 3H), 0.92 (s, 9H), 0.22 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 148.7, 137.1, 131.6, 130.3, 128.3, 76.9, 61.0, 25.3, 24.1, 19.2, 17.9, -5.4. HRMS (ESI) calculated for $C_{18}H_{24}O_3SiNaCl_2$ $[M+Na]^+$: 409.0769; found: 409.0770.

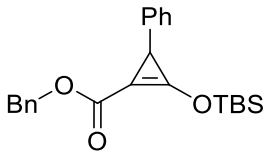


Methyl 2-(*tert*-Butyldimethylsilyloxy)-3-phenylcycloprop-1-enecarboxylate (4g).



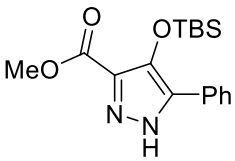
Light yellow oil, 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.29 (comp, 2H), 7.20 – 7.19 (comp, 3H), 3.75 (s, 3H), 3.41 (s, 1H), 0.95 (s, 9H), 0.30 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.55, 141.63, 140.93, 128.27, 126.31, 126.01, 71.67, 33.84, 25.29, 17.93, -5.02, -5.14. HRMS (ESI) calculated for $C_{17}H_{24}O_3SiNa$ $[M+Na]^+$: 327.1392; found: 327.1379.

Benzyl 2-(*tert*-Butyldimethylsilyloxy)-3-phenylcycloprop-1-enecarboxylate (4h).



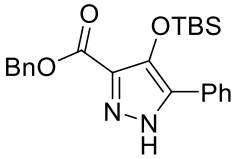
Light yellow oil, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (comp, 7H), 7.27 – 7.21 (comp, 3H), 5.25 (s, 2H), 3.47 (s, 1H), 0.97 (s, 9H), 0.32 (s, 3H), 0.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.97, 141.63, 141.25, 136.07, 128.45, 128.26, 128.21, 128.08, 126.30, 126.10, 109.99, 71.82, 66.18, 33.82, 25.30, 17.93, -5.01, -5.13. HRMS (ESI) calculated for $C_{23}H_{28}O_3SiNa$ $[M+Na]^+$: 403.1705; found: 403.1698.

Methyl 4-(*tert*-Butyldimethylsilyloxy)-5-phenyl-*1H*-pyrazole-3-carboxylate (5g).



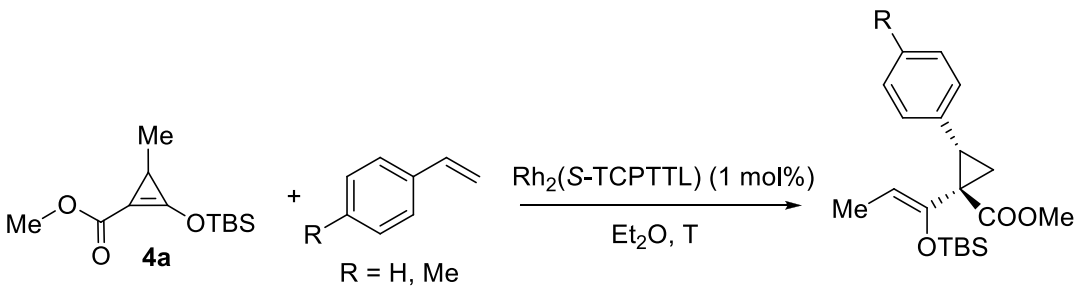
White solid, 23% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.40 (comp, 2H), 7.35 – 7.34 (comp, 1H), 3.92 (s, 3H), 0.97 (s, 9H), -0.11 (s, 6H). Purified by flash chromatography (SiO_2, Hexane:EtOAc = 80:20). This compound has been previously reported; the spectroscopic data are identical to those in reference 3e.

Benzyl 4-(*tert*-Butyldimethylsilyloxy)-5-phenyl-*1H*-pyrazole-3-carboxylate (5h).

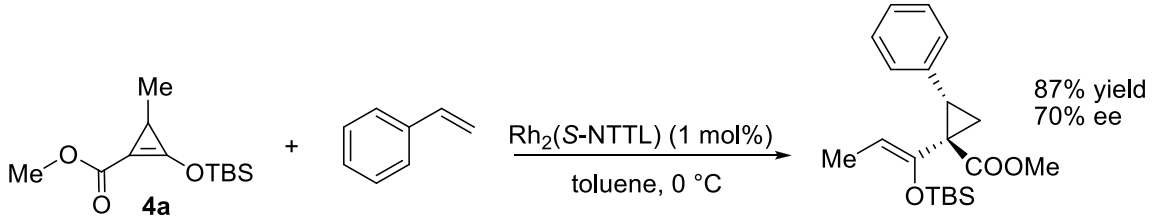


White solid, 33% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.72 (comp, 2H), 7.48 – 7.31 (comp, 8H), 5.36 (s, 2H), 0.90 (s, 9H), -0.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.91, 159.37, 139.25, 135.26, 131.18, 128.92, 128.62, 128.57, 128.36, 128.07, 127.50, 66.62, 25.53, 18.01, -4.86. HRMS (ESI) calculated for $C_{23}H_{28}O_3N_2SiNa$ $[M+Na]^+$: 431.1767; found: 431.1755. Purified by flash chromatography (SiO_2, Hexane:EtOAc = 80:20).

Procedures for the Asymmetric Cyclopropanation of Donor–Acceptor Cyclopropene 4a with Styrenes

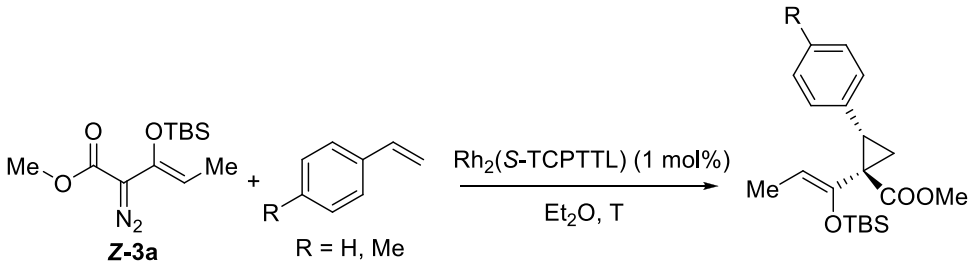


The catalyst Rh_2(*S*-TCPTTL)$_4$ (1 mol%, 5.4 mg, 0.003 mmol) was dissolved in Et_2O (1.0 mL). After addition of styrene (312 mg, 3.0 mmol) or 4-methylstyrene (354 mg, 3.0 mmol) the mixture was cooled to -20 °C or -40°C, and **4a** (0.3 mmol) which was generated from *Z*-**3a** (81.1 mg, 0.3 mmol) under thermal conditions, in Et_2O (1.0 mL) was added dropwise over 30 minutes. After the addition stirring was continued for 6 h. The solvent was evaporated and the residue was characterized by ^{1}H NMR spectral analysis to determine the diastereoselectivities. Then the reaction mixture was purified by flash chromatography (SiO_2, Hexane:EtOAc = 95:5) to afford **7** as colorless oil.

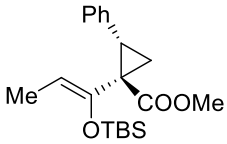


The same procedure was applied here as the cyclopropanation catalyzed by Rh_2(*S*-TCPTTL)$_4$, except the Rh_2(*S*-TCPTTL)$_4$ was replaced by Rh_2(*S*-NTTL)$_4$. And the solvent was replaced from Et_2O to toluene.

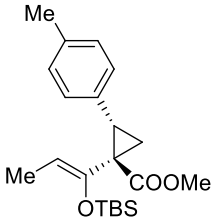
Procedures for the Asymmetric Cyclopropanation of Enoldiazoacetate *Z*-3a with Styrenes



The same procedure was applied here as the cyclopropanation of donor–acceptor cyclopropene **4a** with styrenes, except the donor–acceptor cyclopropene **4a** was replaced by enoldiazoacetate *Z*-**3a**.

(1*R*,2*S*)-Methyl 1-[(*Z*)-1-(*tert*-Butyldimethylsilyloxy)prop-1-enyl]-2 phenylcycloprop anecarboxylate (7). 

Following the procedures for the asymmetric cyclopropanation of donor–acceptor cyclopropene **4a** with styrenes from 0.3 mmol 4a (74 mg) and styrene 3.0 mol (312 mg). Colorless oil, 93 mg, 90% yield. $[\alpha]_D^{22}$ = -182° (c = 1.93, $CHCl_3$, pour 91% ee). 91% ee, HPLC condition for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, hexanes:IPA = 97:1, tr = 7.2, 7.8 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.13 (comp, 3H), 7.08 (comp, 2H), 4.52 (q, *J* = 6.5 Hz, 1H), 3.72 (s, 3H), 2.89 (dd, *J* = 9.3, 7.5 Hz, 1H), 1.79 (dd, *J* = 9.3, 4.7 Hz, 1H), 1.67 (dd, *J* = 7.5, 4.7 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 3H), 0.76 (s, 9H), 0.05 (s, 3H), -0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 143.6, 137.1, 127.9, 127.7, 126.3, 109.8, 52.2, 38.3, 33.2, 25.6, 22.5, 18.3, 10.8, -4.4, -4.5. The relative and absolute configurations were assigned following the reference 4.

(1*R*,2*S*)-Methyl 1-[(*Z*)-1-(*tert*-Butyldimethylsilyloxy)prop-1-enyl]-2-*p*-tolylcyclopro-panecarboxylate (8). 

Following the procedures for the asymmetric cyclopropanation of donor–acceptor cyclopropene **4a** with styrenes from 0.3 mmol **4a** (74 mg) and 4- methyl styrene 3.0 mol (354 mg). White solid, 92 mg, 86% yield, m.p. 41-43 °C. $[\alpha]_D^{22}$ = -145° (c = 1.54, CHCl3, pour 92% ee). 92% ee, HPLC condition for determination of enantiomeric excess: OD-H column, 230 nm, 0.5 mL/min, hexanes:methanol = 99:1, tr = 10.0, 10.8 min. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.50 (q, *J* = 6.6 Hz, 1H),3.71 (s, 3H), 2.85 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.29 (s, 3H), 1.77 (dd, *J* = 9.4, 4.6 Hz, 1H), 1.63 (dd, *J* = 7.5, 4.6 Hz, 1H), 1.41 (d, *J* = 6.6 Hz, 3H), 0.77 (s, 9H), 0.05 (s, 3H), -0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 143.6, 135.9, 134.0, 128.4, 127.8, 109.8, 52.1, 38.1, 33.1, 25.6,

22.4, 20.9, 18.3, 10.9, -4.4, -4.5. The relative and absolute configurations were assigned following reference 4.

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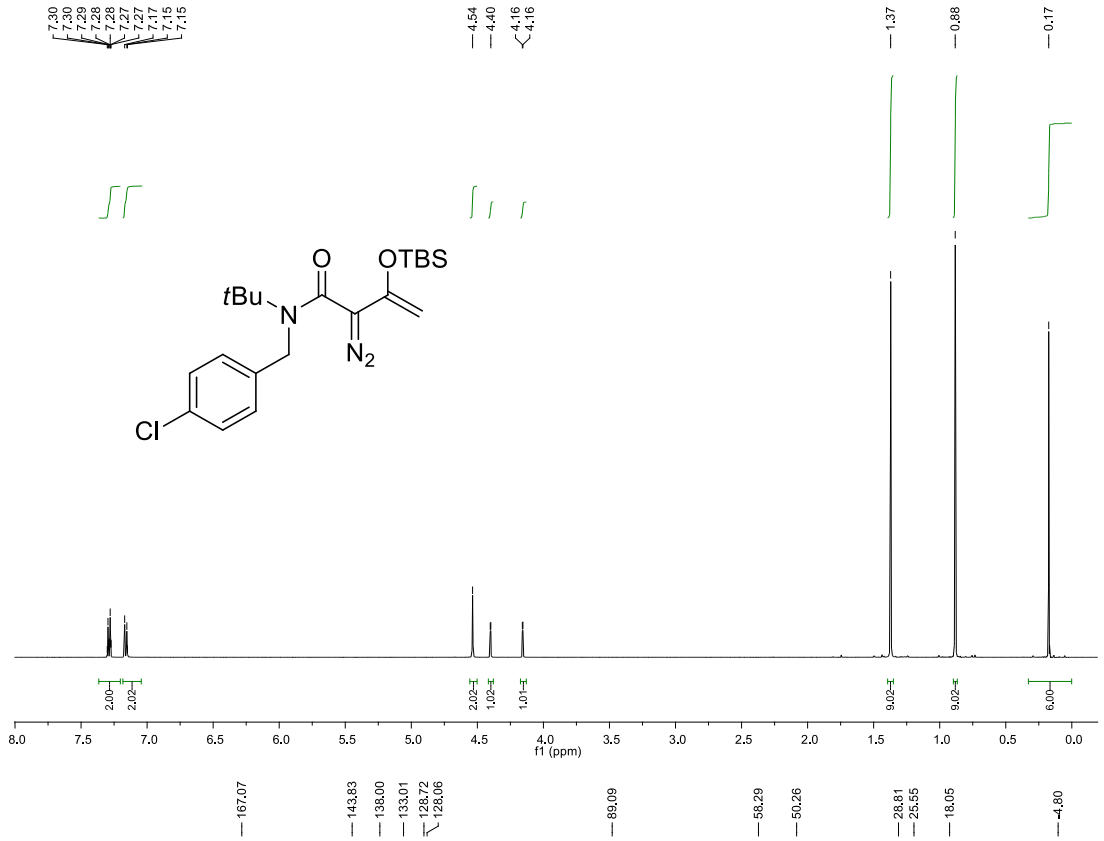
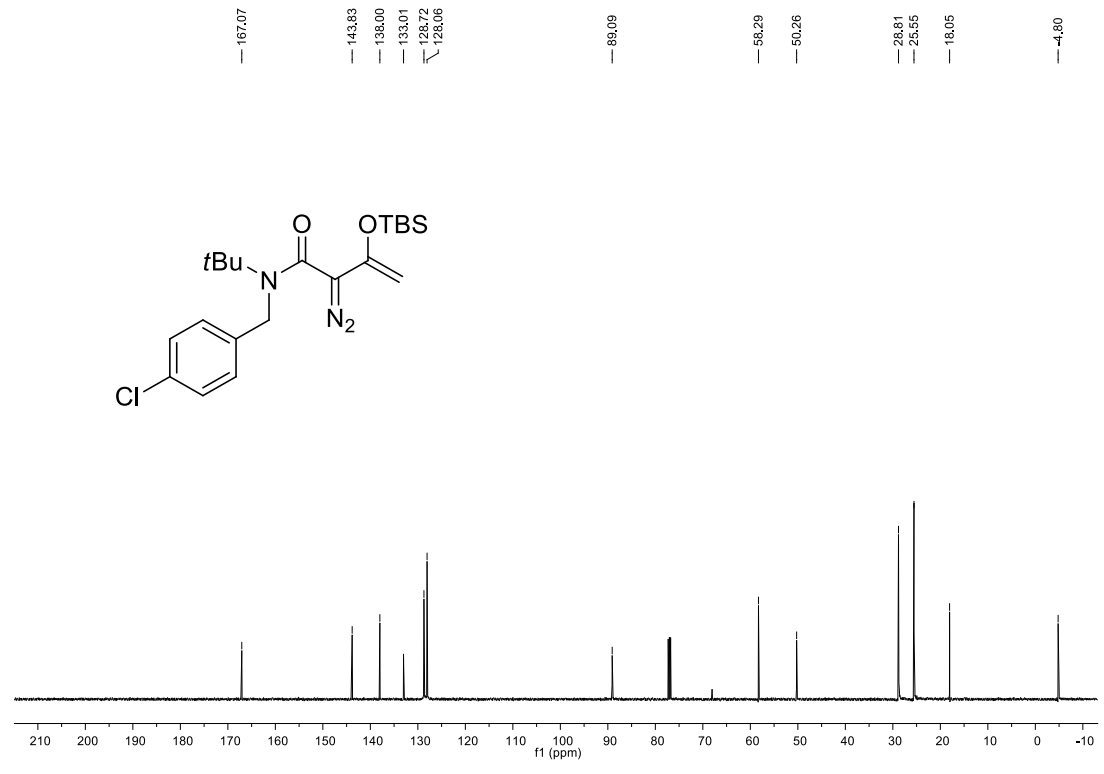
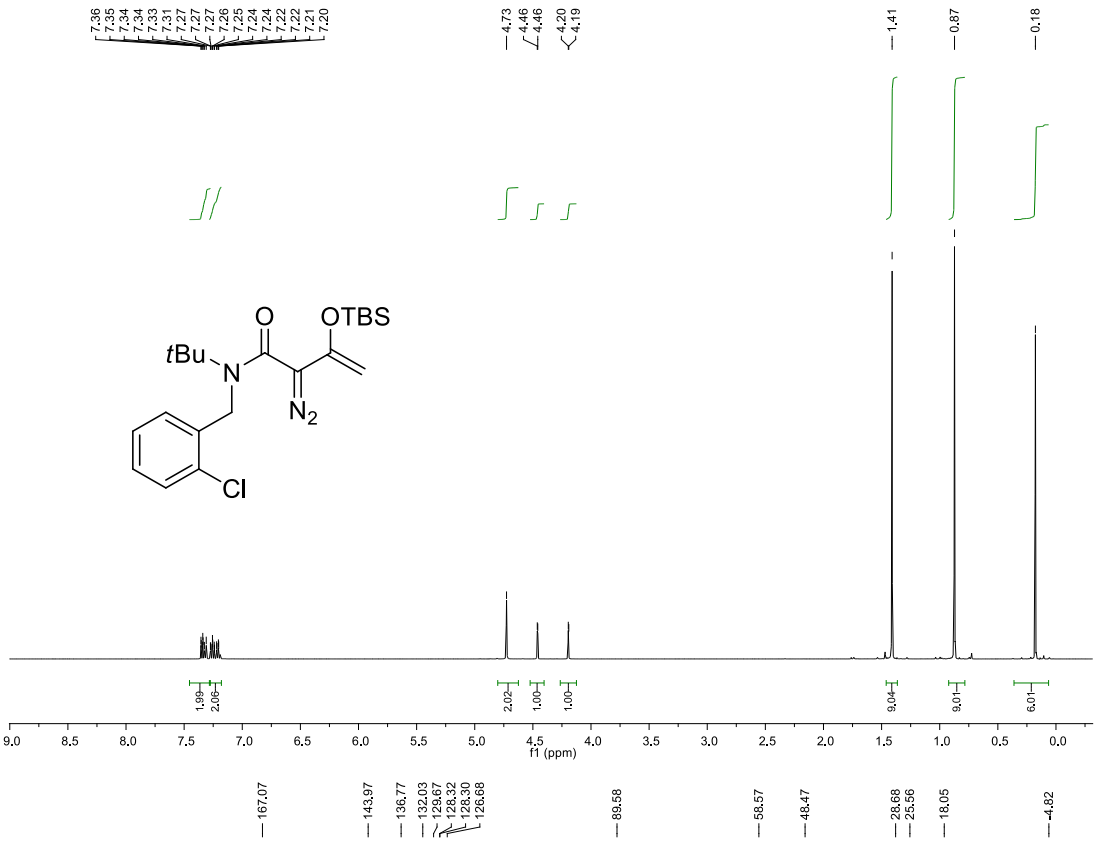
3. (a) H. M. L. Davies, Z.-Q. Peng and J. H. Houser, *Tetrahedron Lett.* **1994**, 35, 8939; (b) Y. Ueda, G. Roberge and V. Vinet, *Can. J. Chem.* **1984**, 62, 2936; (c) H. M. L. Davies, G. Ahmed and M. R. Churchill, *J. Am. Chem. Soc.* **1996**, 118, 10774; (d) K. Kundu and M. P. Doyle, *Tetrahedron: Asymmetry* **2006**, 17, 574; (e) Y. Qian, X. Xu, X. Wang, P. J. Zavalij, W. Hu and M. P. Doyle, *Angew. Chem. Int. Ed.* **2012**, 51, 5900; (f) X. Xu, P. J. Zavalij and M. P. Doyle, *Chem. Commun.* **2013**, *49*, 10287; (g) X. Xu, X. Wang, P. Y. Zavalij and M. P. Doyle, *Org. Lett*. **2015**, *17*, 790; (h). X. Xu, P. Y. Zavalij and M. P. Doyle, *J. Am. Chem. Soc*. **2013**, *135*, 12439.
4. P. Muller, G. Bernardinelli, Y. F. Allenbach, M. Ferri, H. D. Flack, *Org. Lett*. **2004**, *6*, 1725.

NMR Spectra of 1, 2, 3, 5, 7 and 8



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7.22
7.22
7.21
7.20
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4.20
4.19
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0.18
O
OTBS
tBu
N
N2
Cl
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2.02
1.00
1.00
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9.01
6.01
9.0
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7.0
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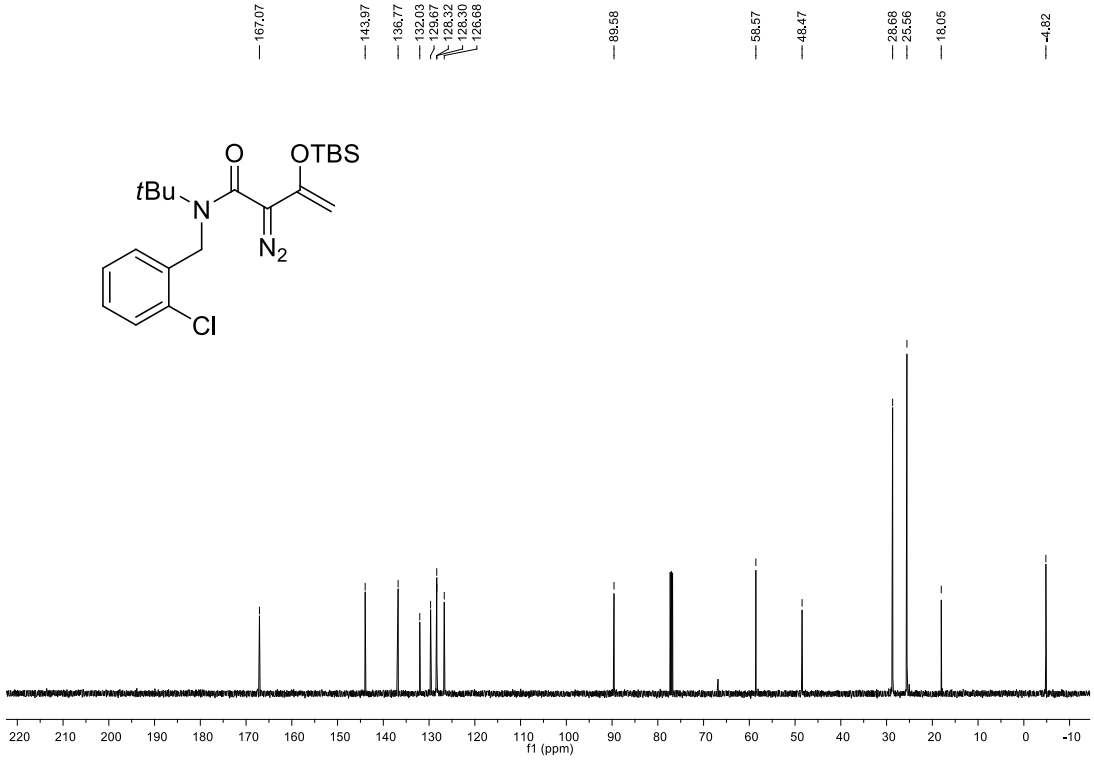
f1 (ppm)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18.05
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tBu
N
N2
Cl
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210
200
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180
170
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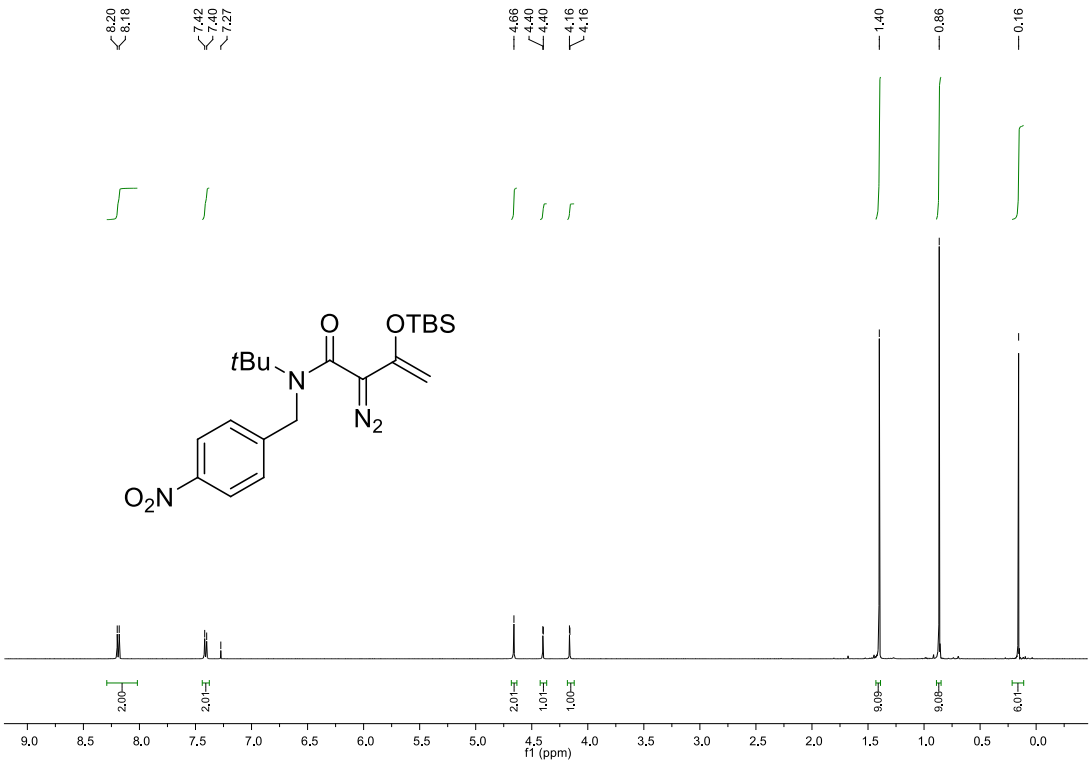
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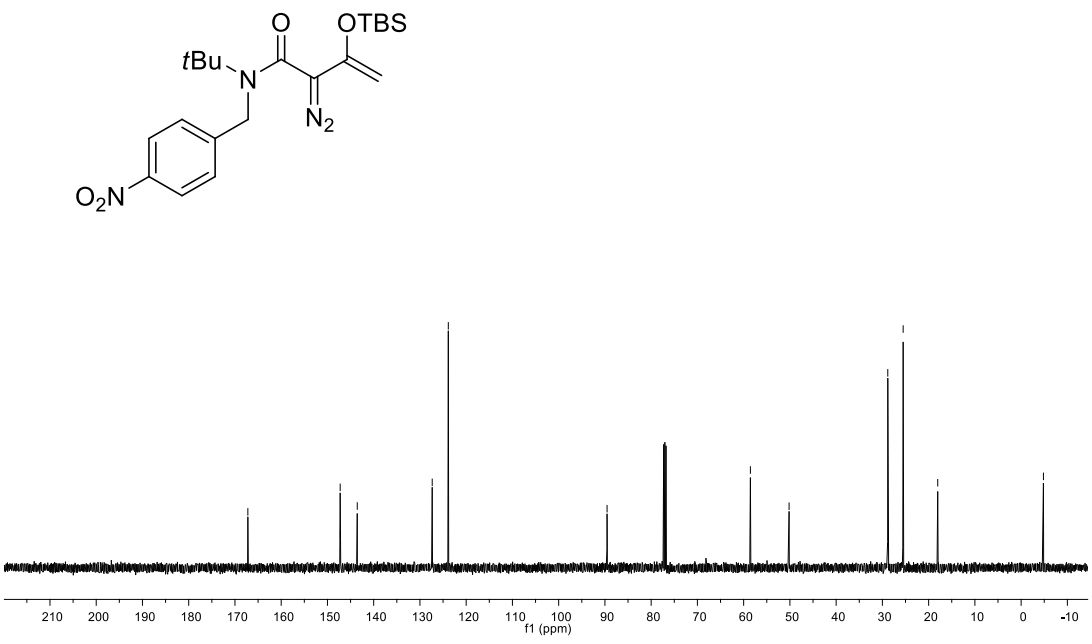
f1 (ppm)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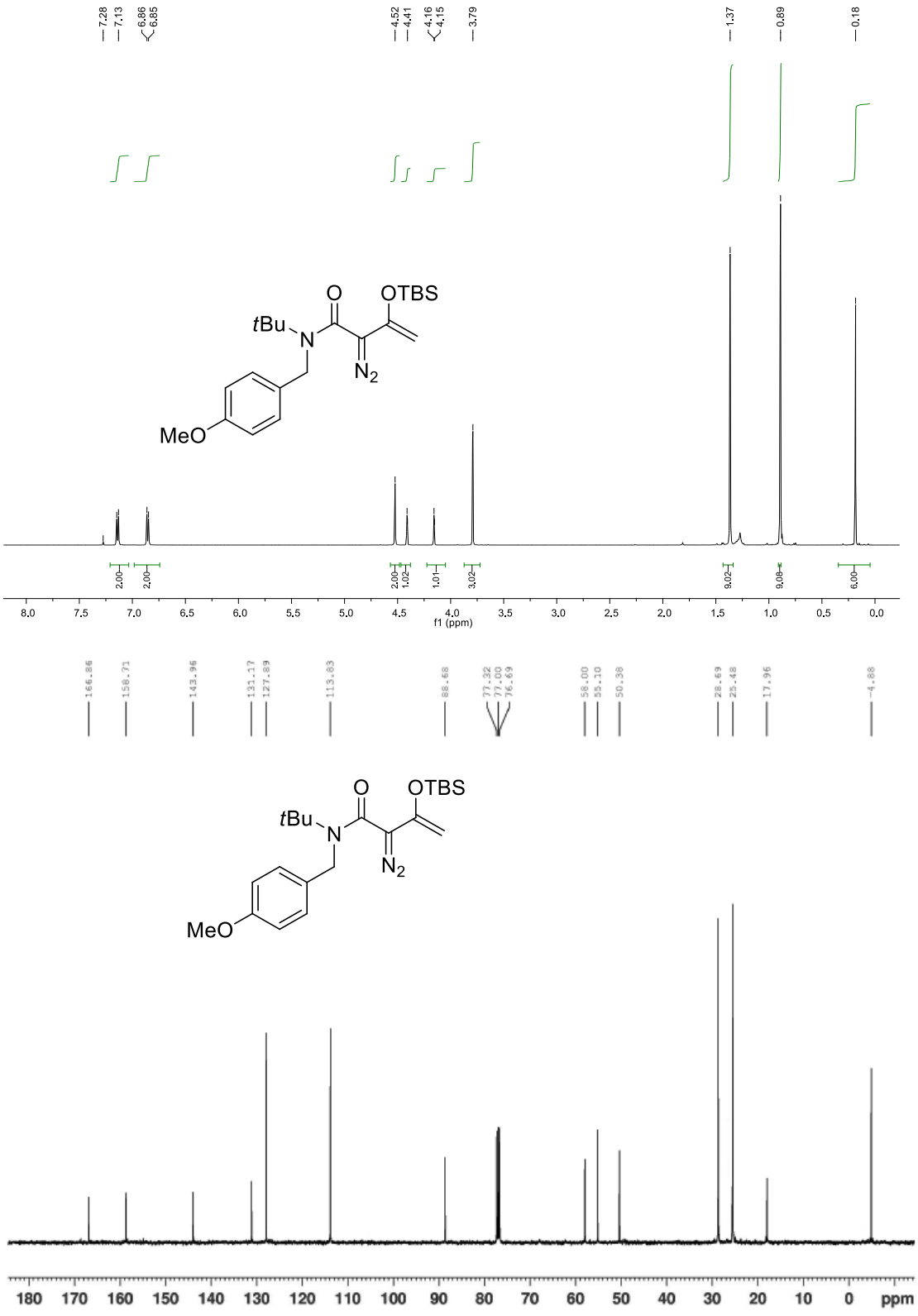
O2N
f1 (ppm)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tBu
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2.00
2.00
1.02
1.01
3.02
9.02
9.08
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1.5
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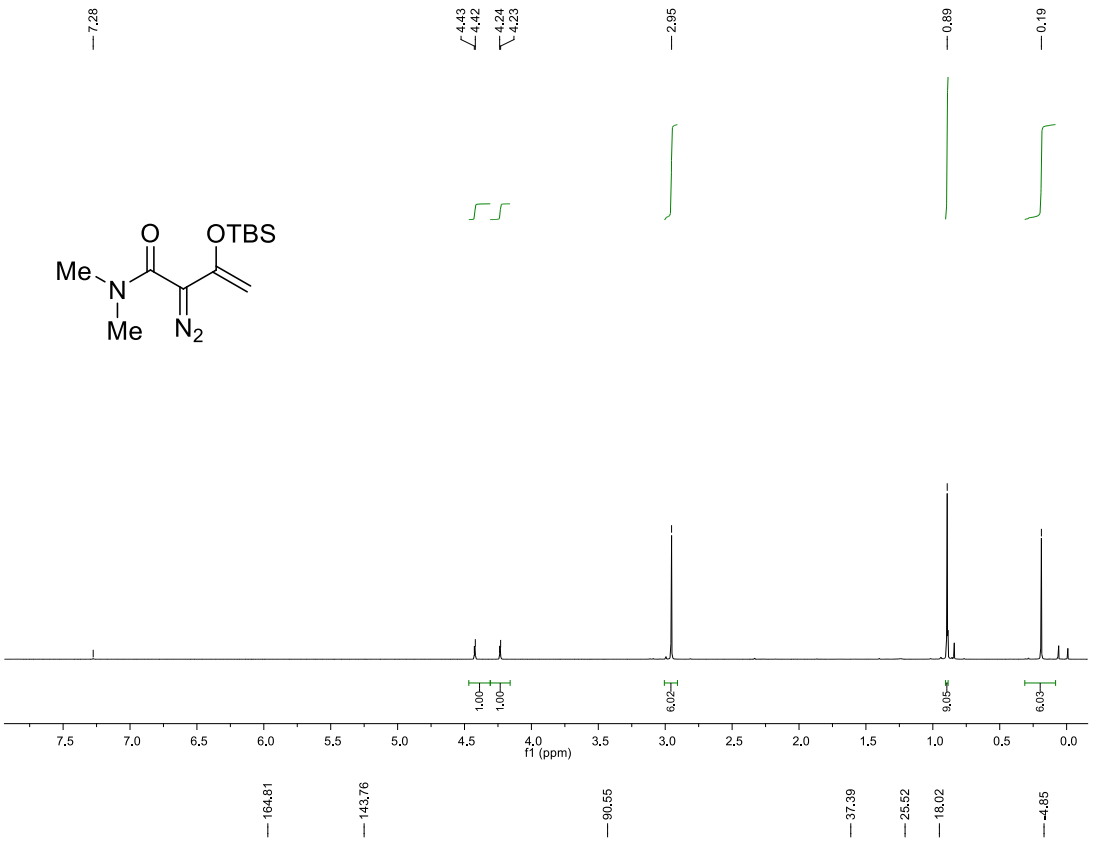
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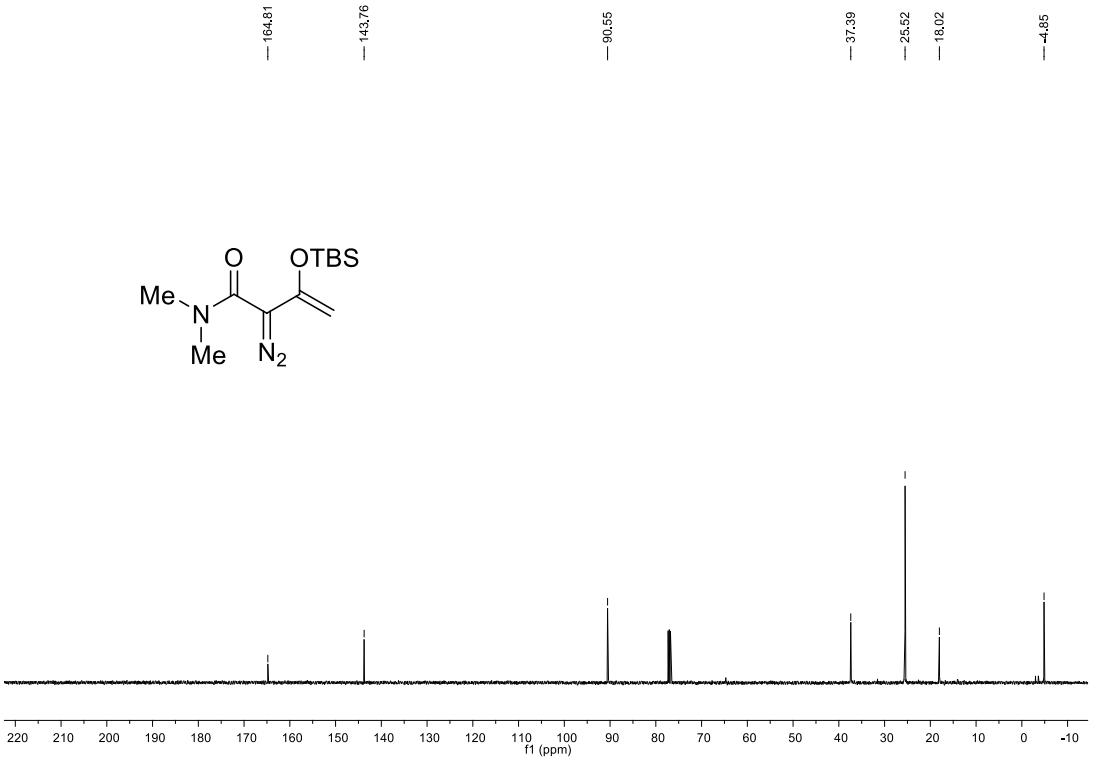
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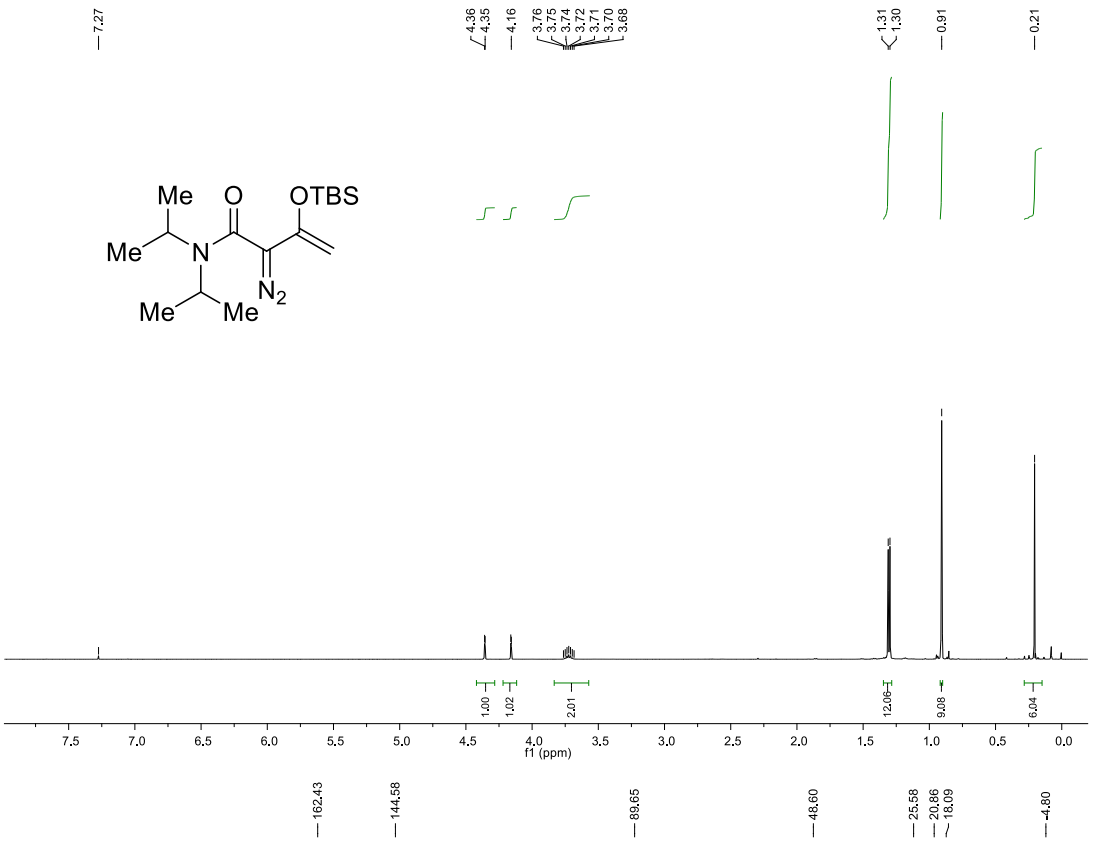
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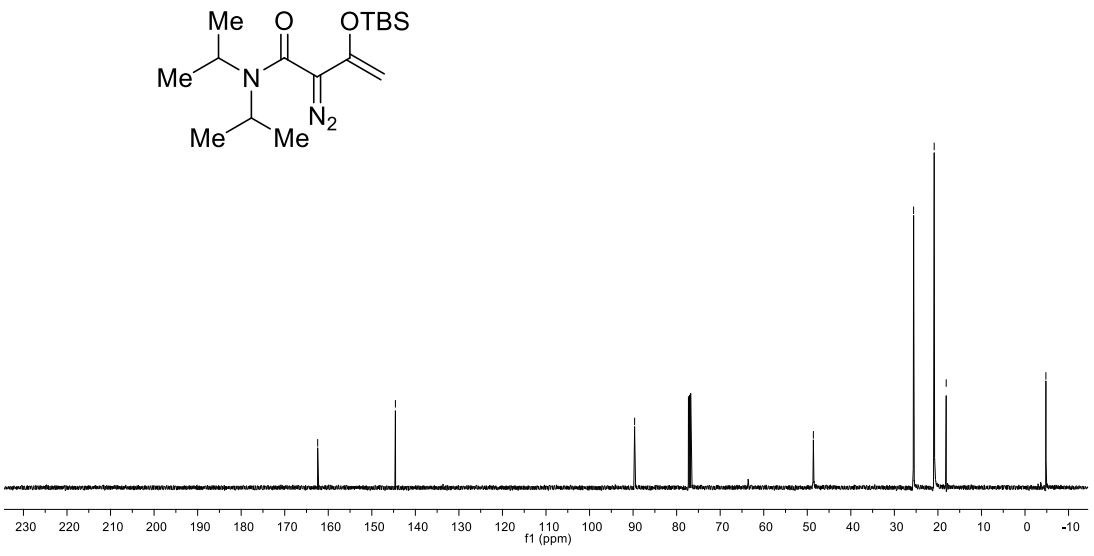
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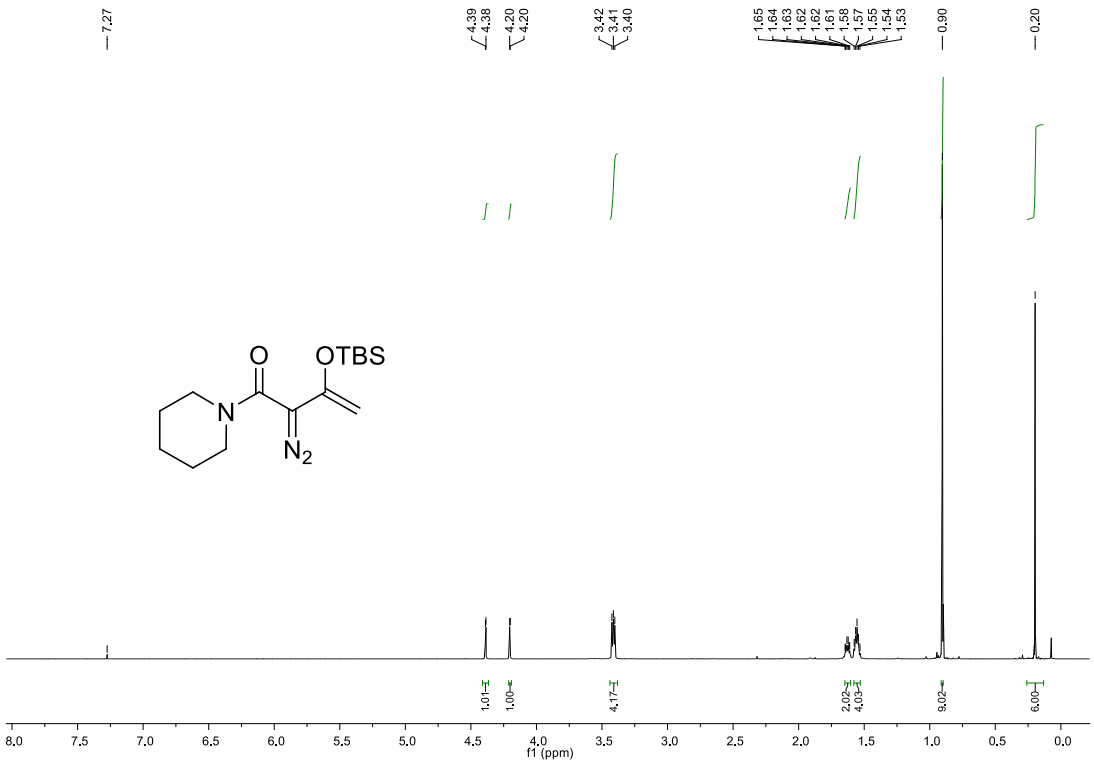
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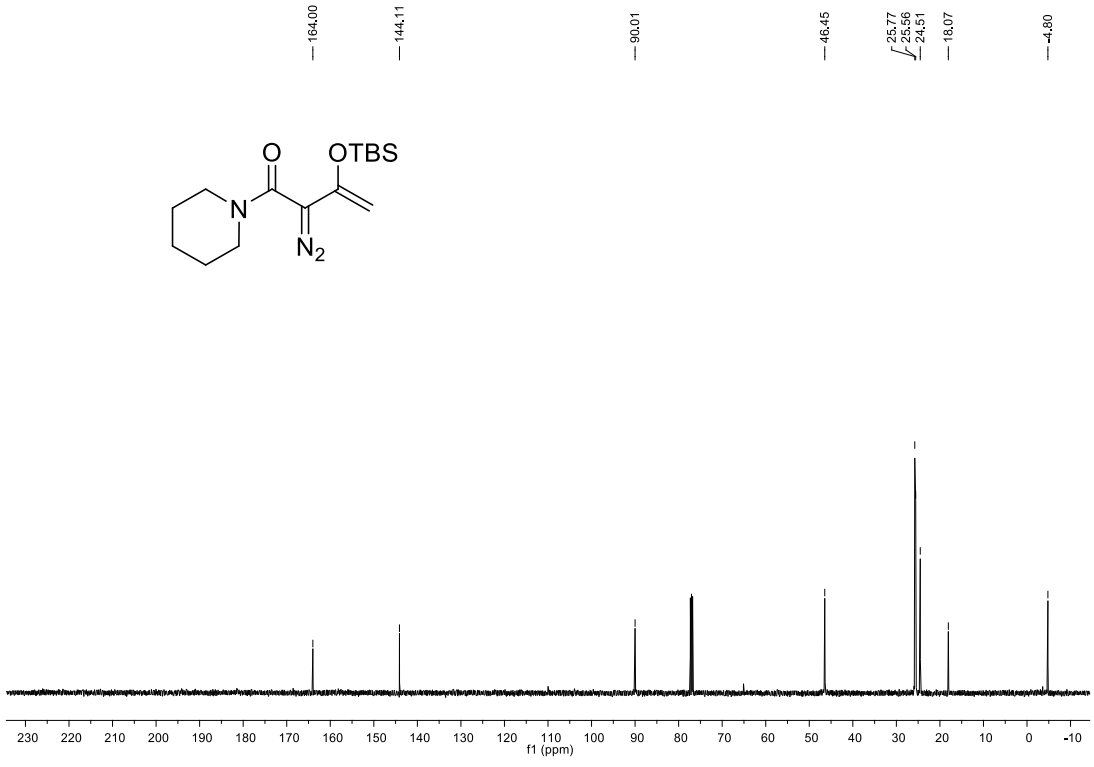
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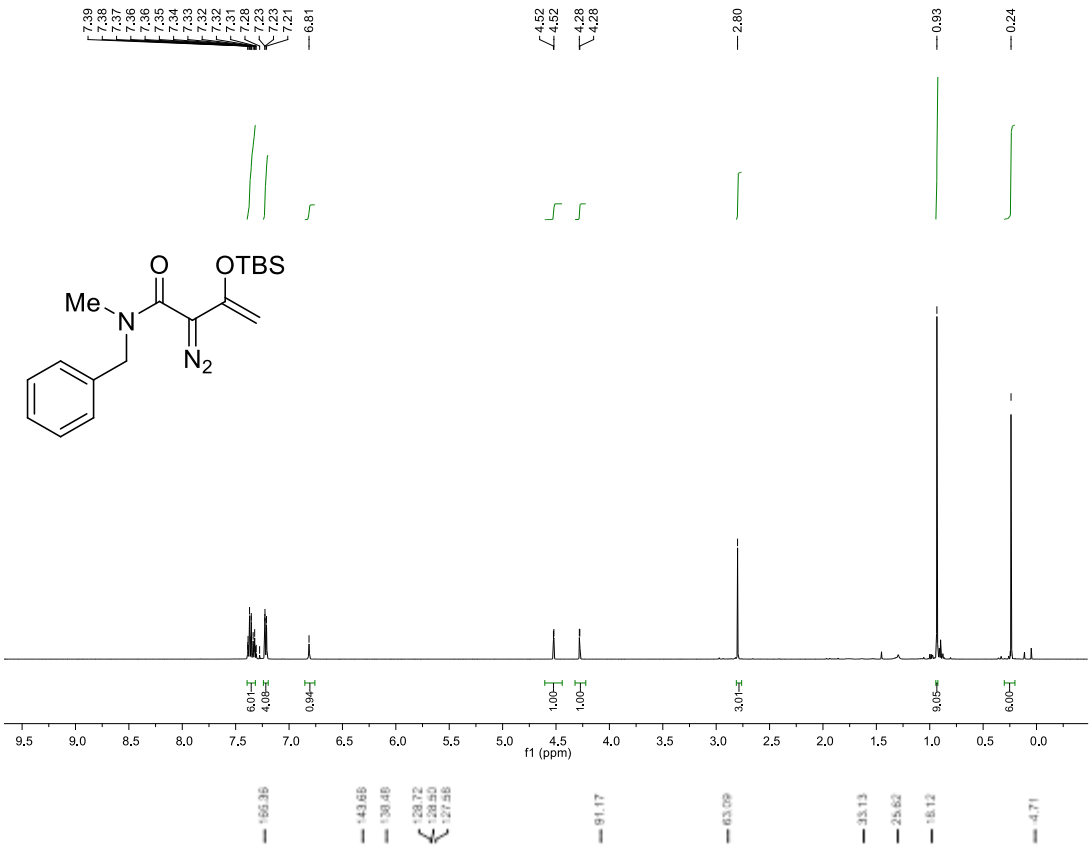
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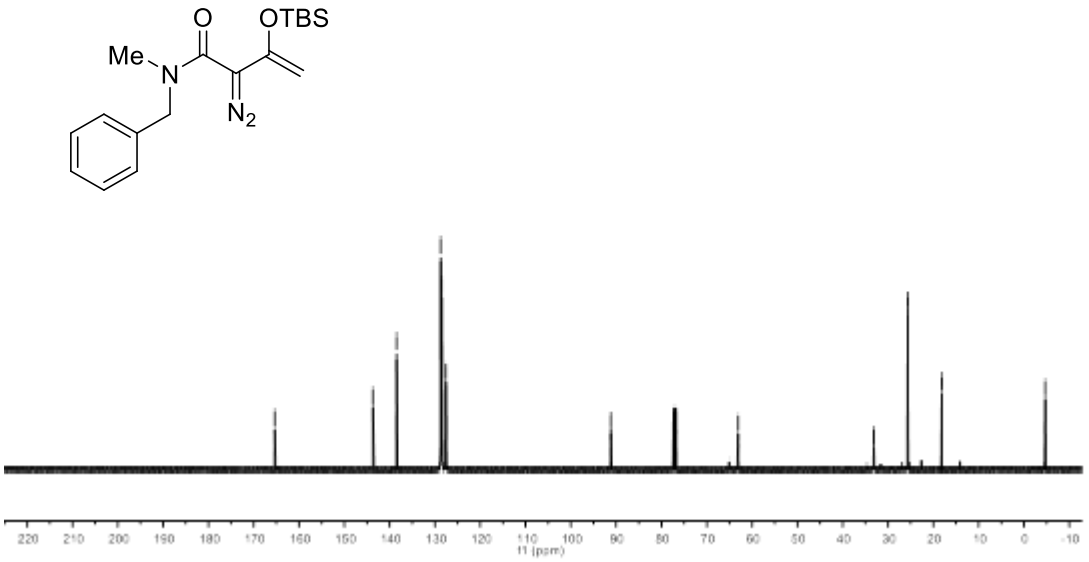
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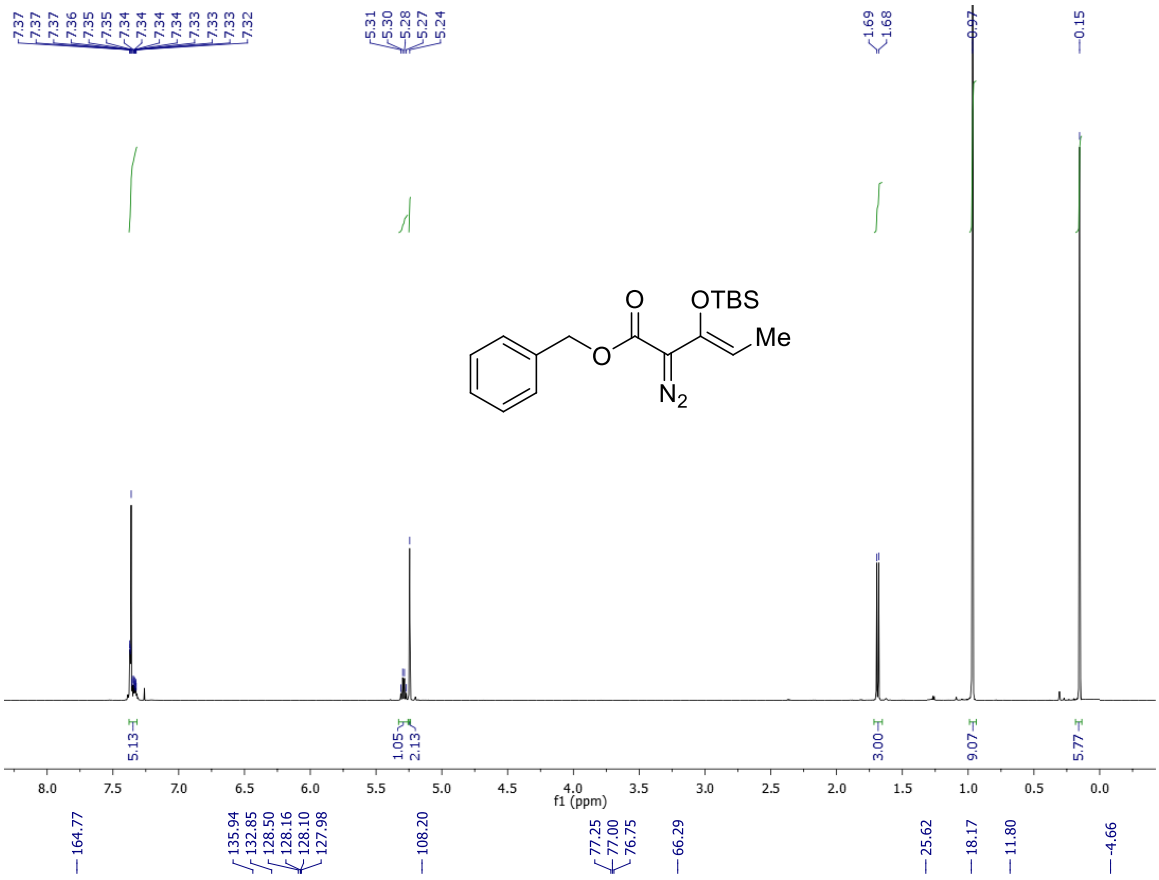
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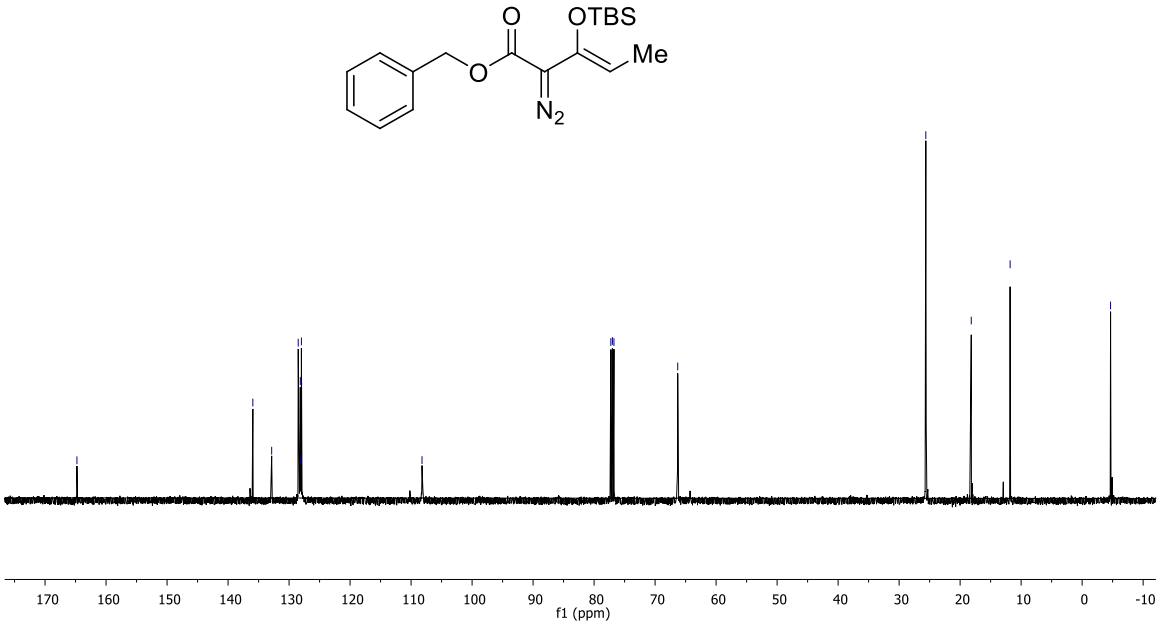
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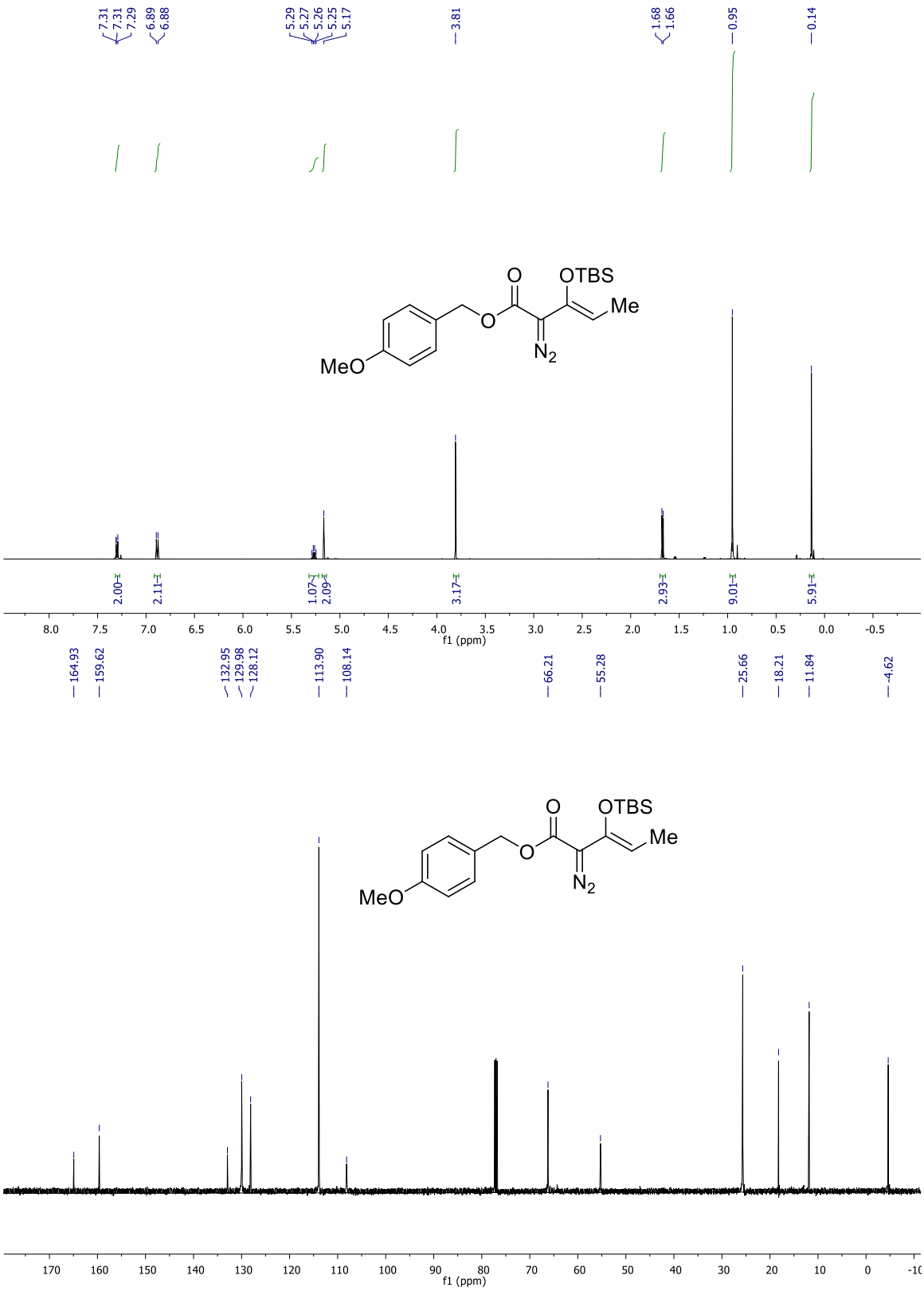
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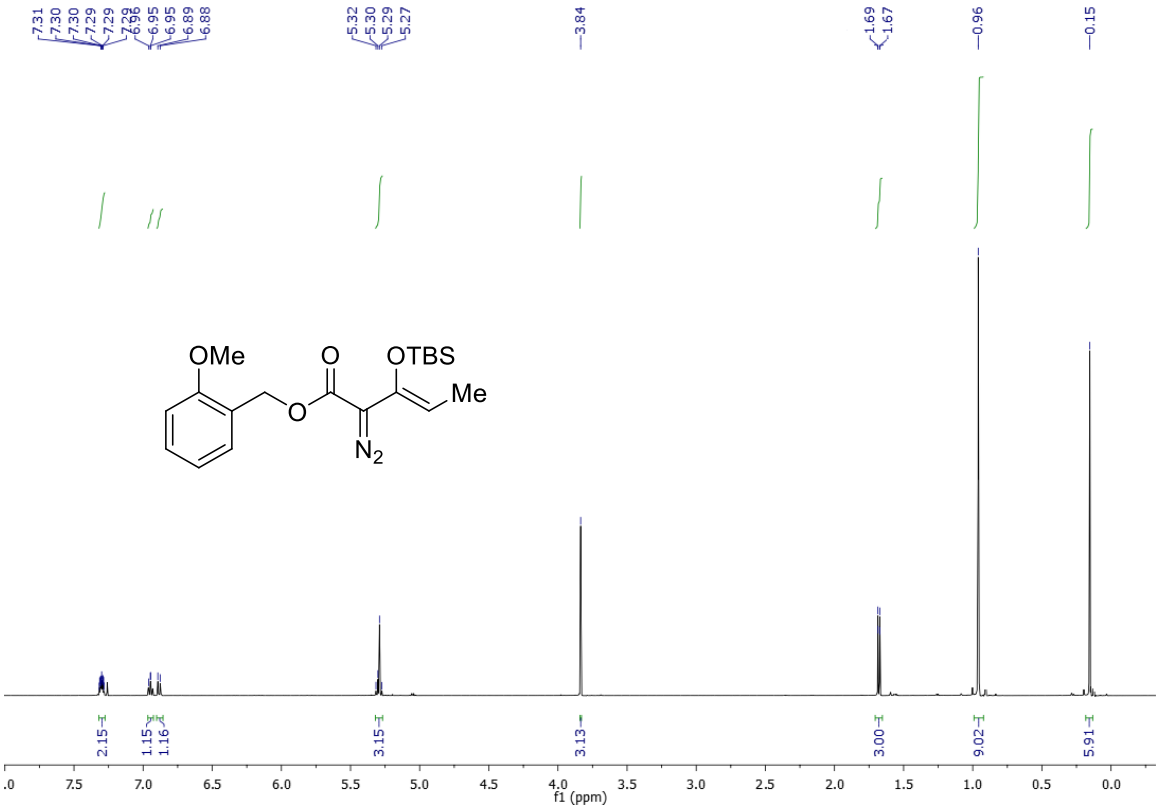
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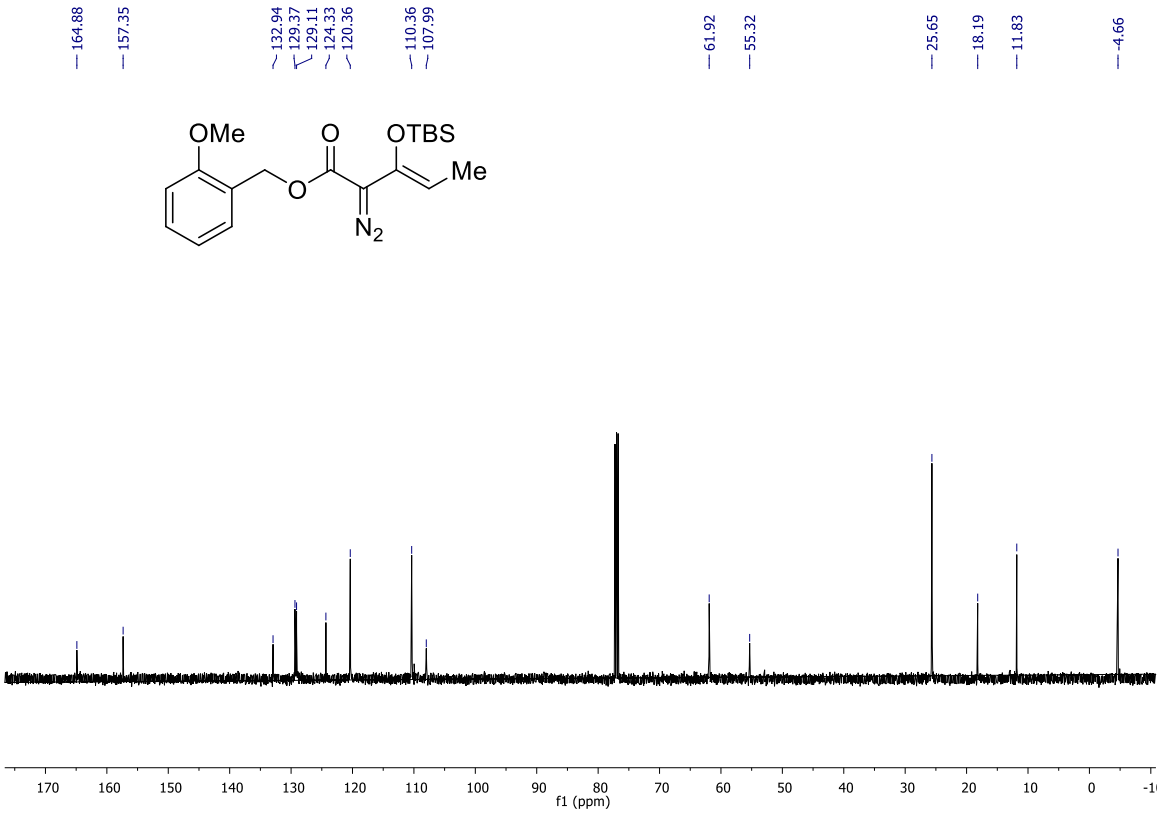
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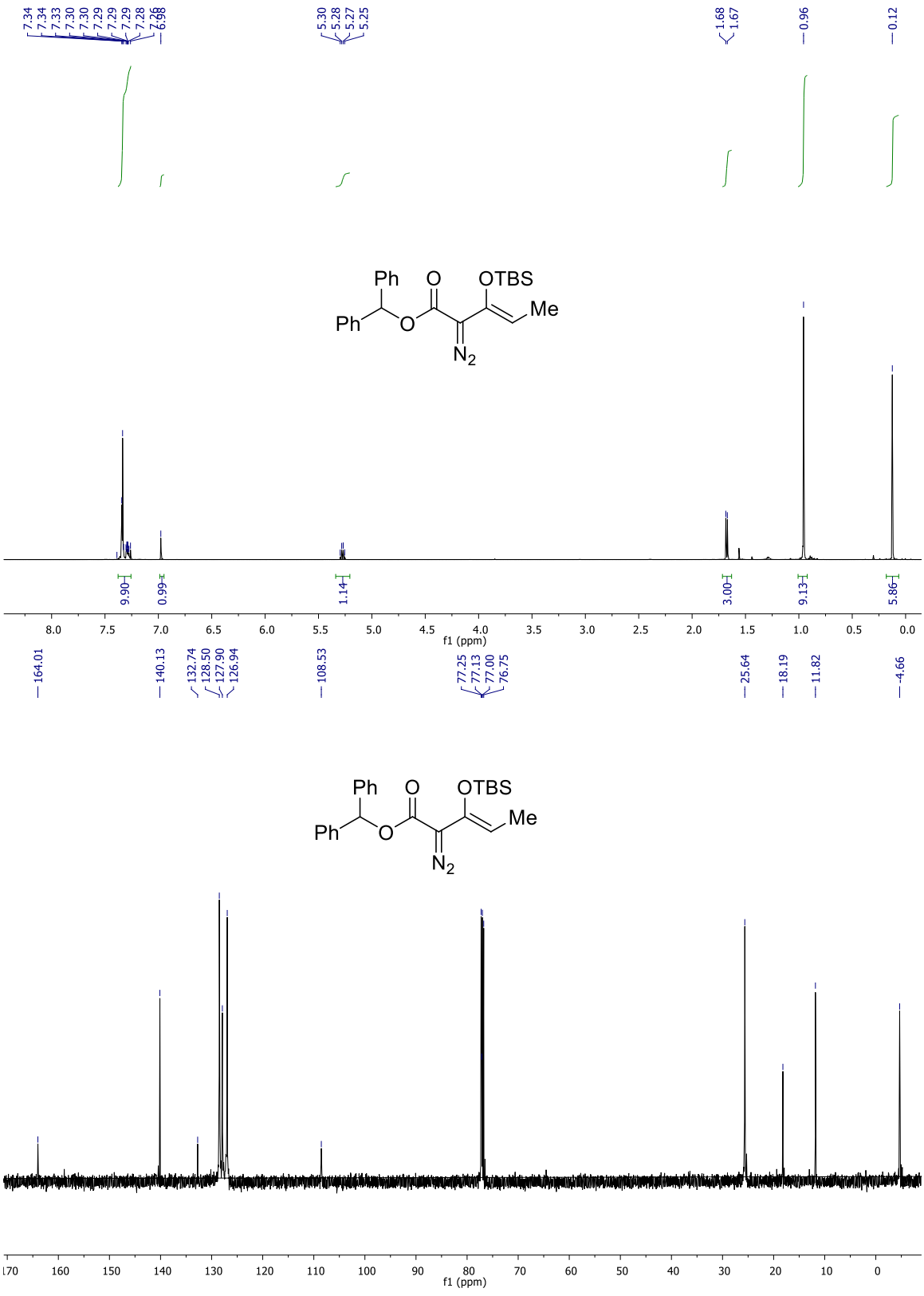
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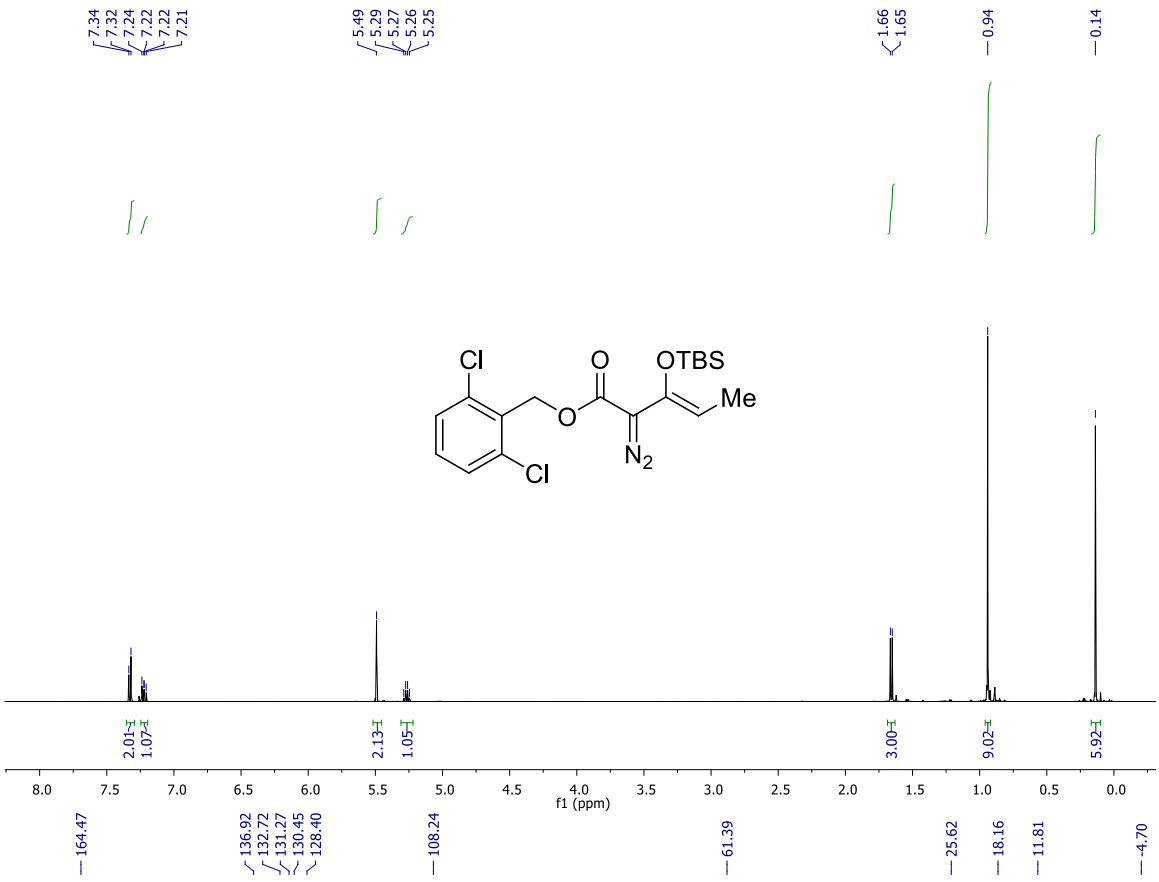
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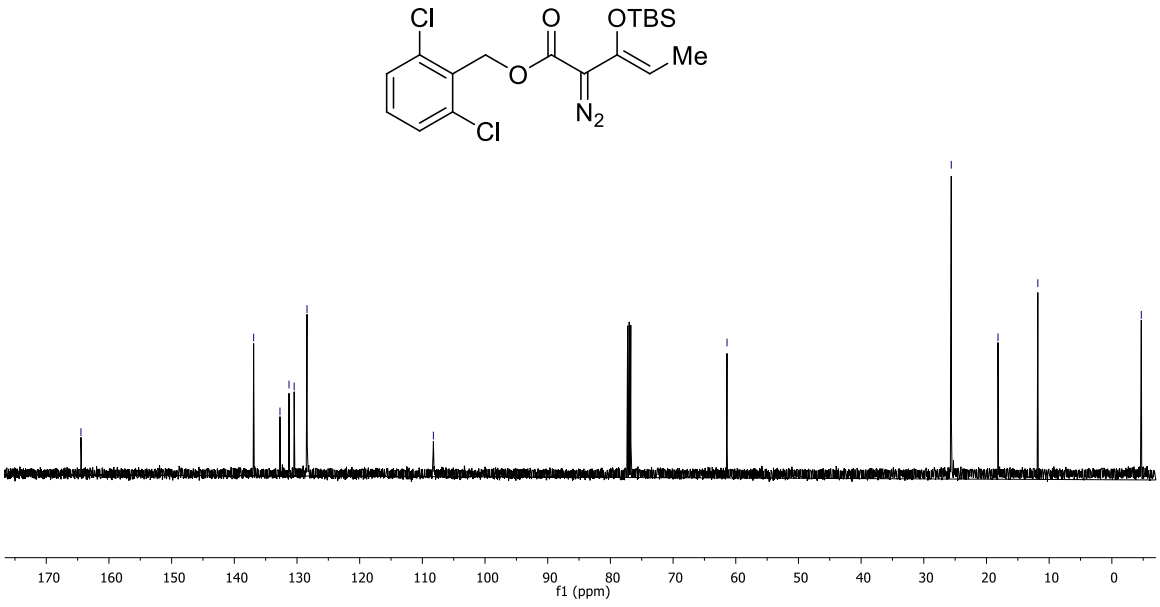
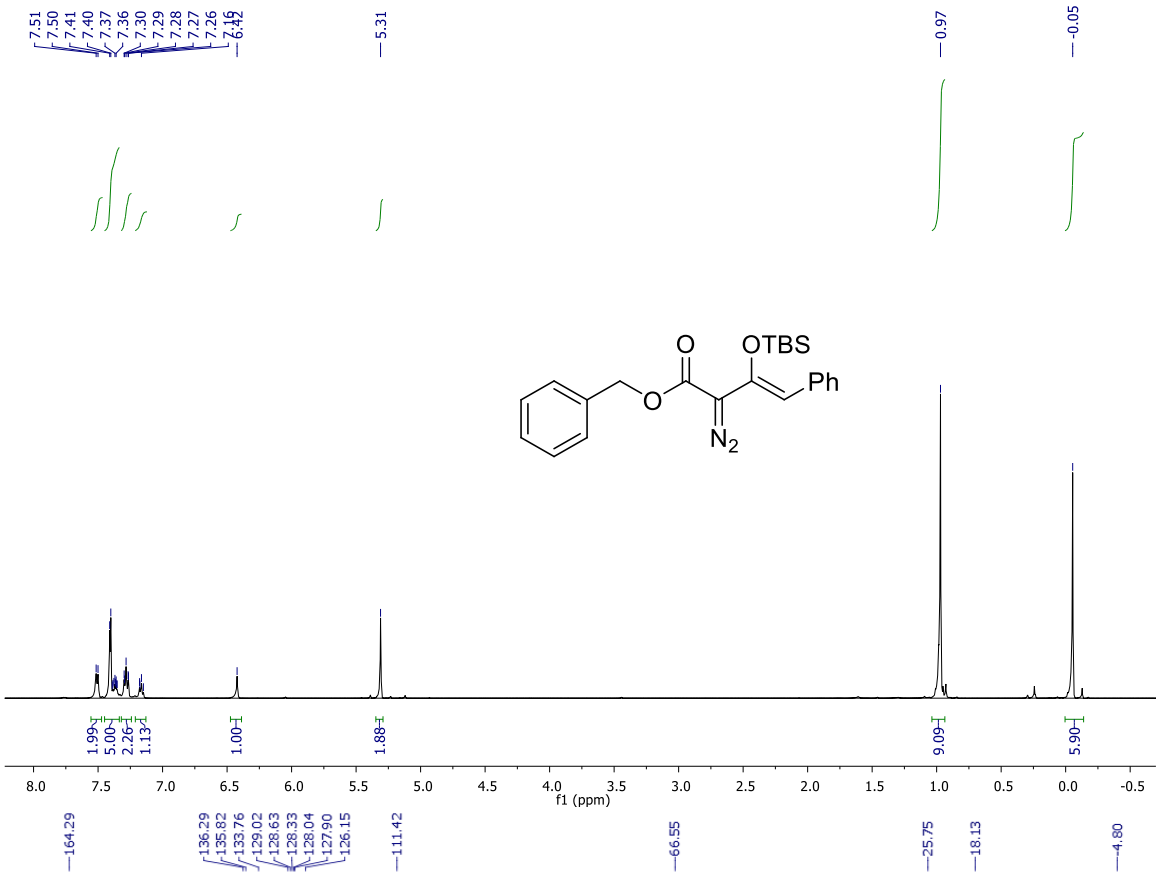
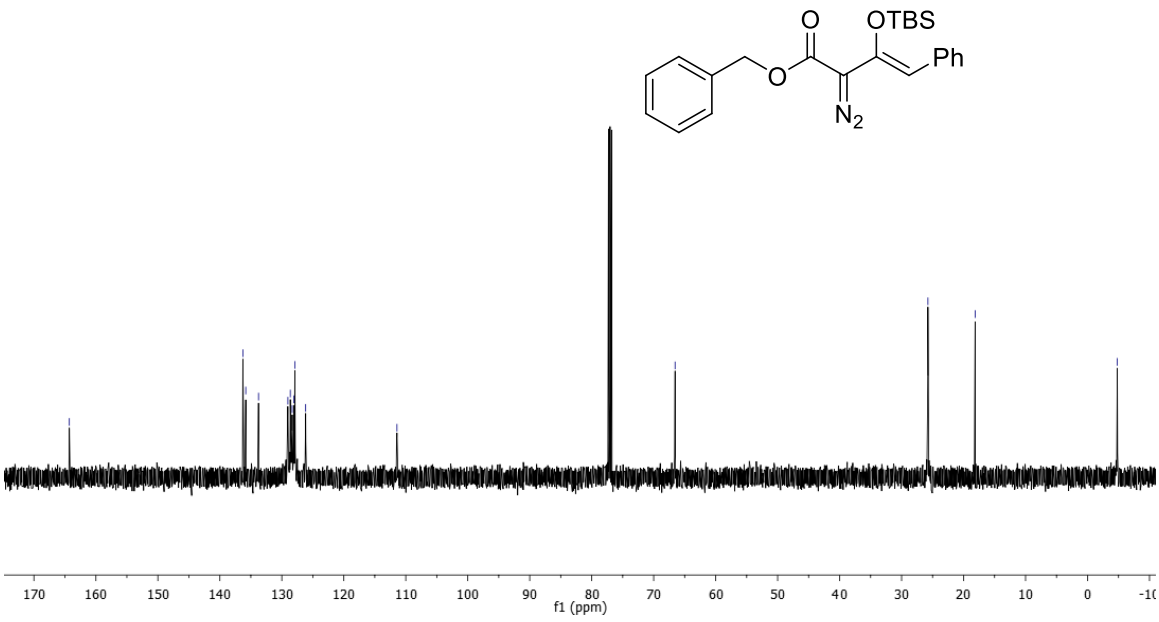
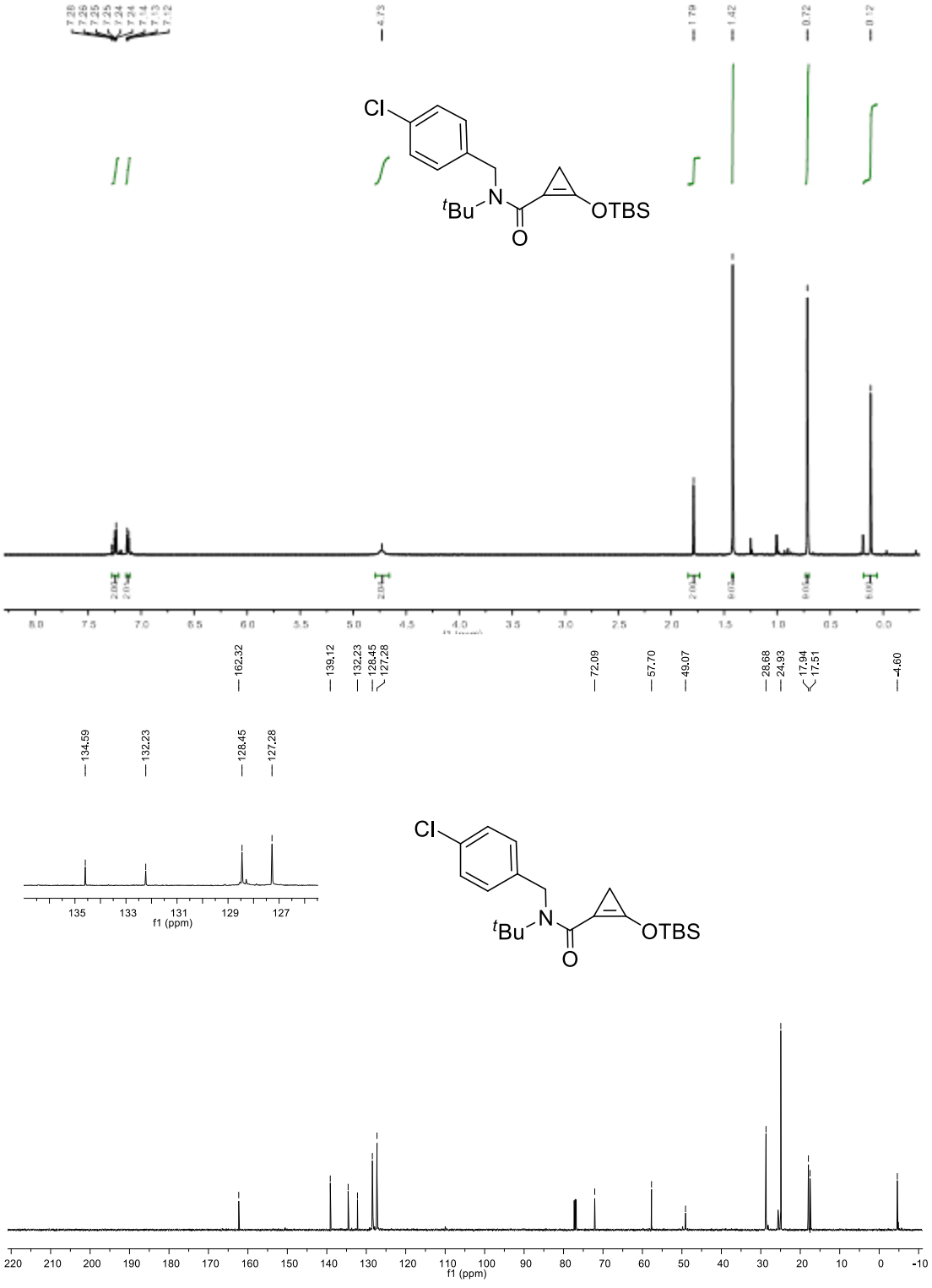
11.81
-4.70


Cl
O
OTBS
Me
O
N2
Cl
f1 (ppm)


7.51
7.50
7.41
7.40
7.37
7.36
7.30
7.29
7.28
7.27
7.26
6.42
5.31
0.97
-0.05
O
OTBS
Ph
O
N2
1.99
5.00
2.26
1.13
1.00
1.88
9.09
5.90
f1 (ppm)


164.29
136.29
135.82
133.76
129.02
128.63
128.33
128.04
127.90
126.15
111.42
66.55
25.75
18.13
4.80
O
OTBS
Ph
O
N2
f1 (ppm)


Cl
tBu
N
O
OTBS
162.32
139.12
132.23
128.45
127.28
72.09
57.70
49.07
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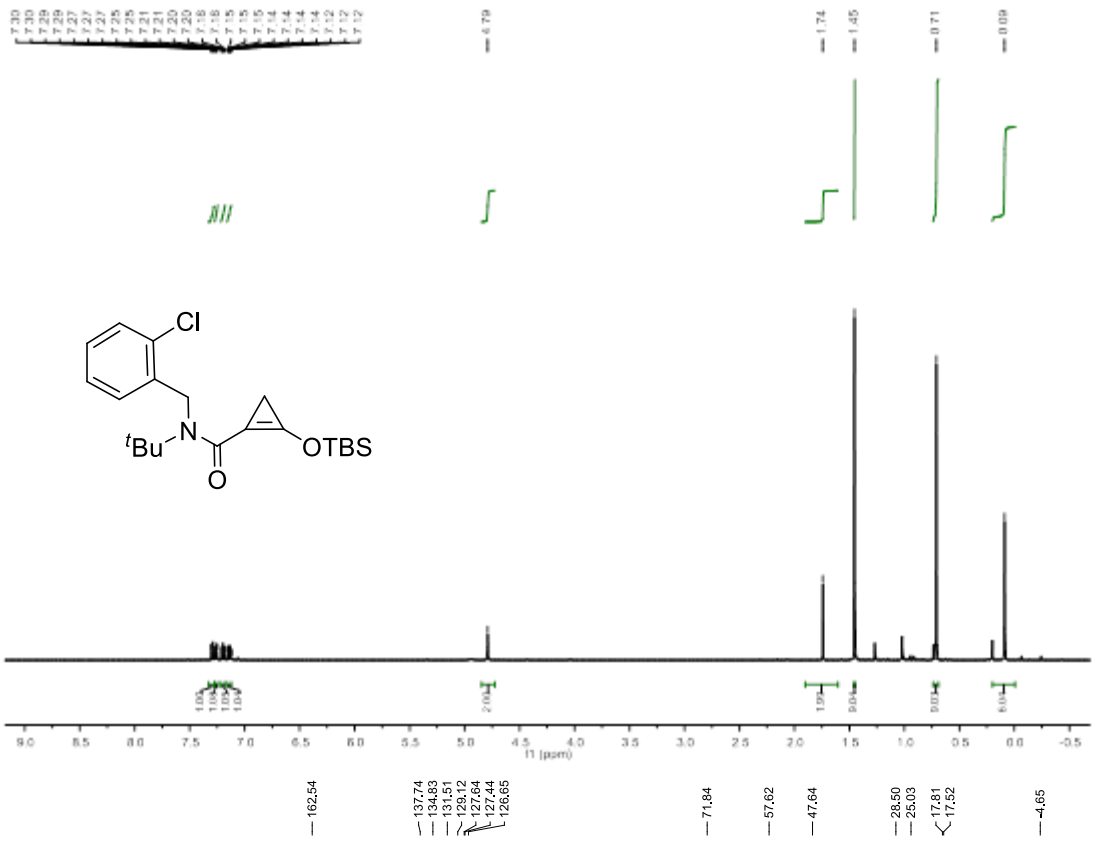
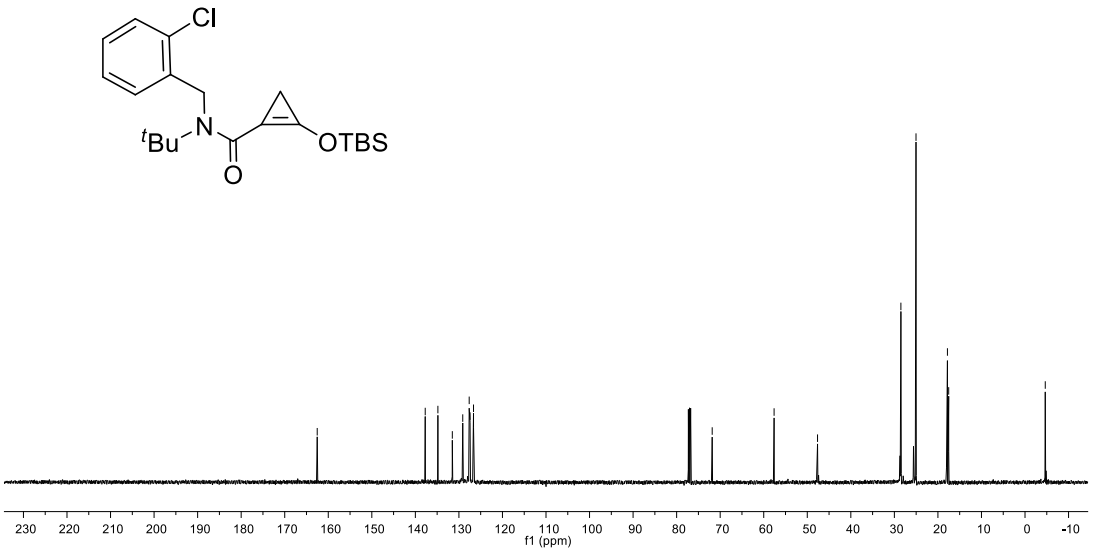
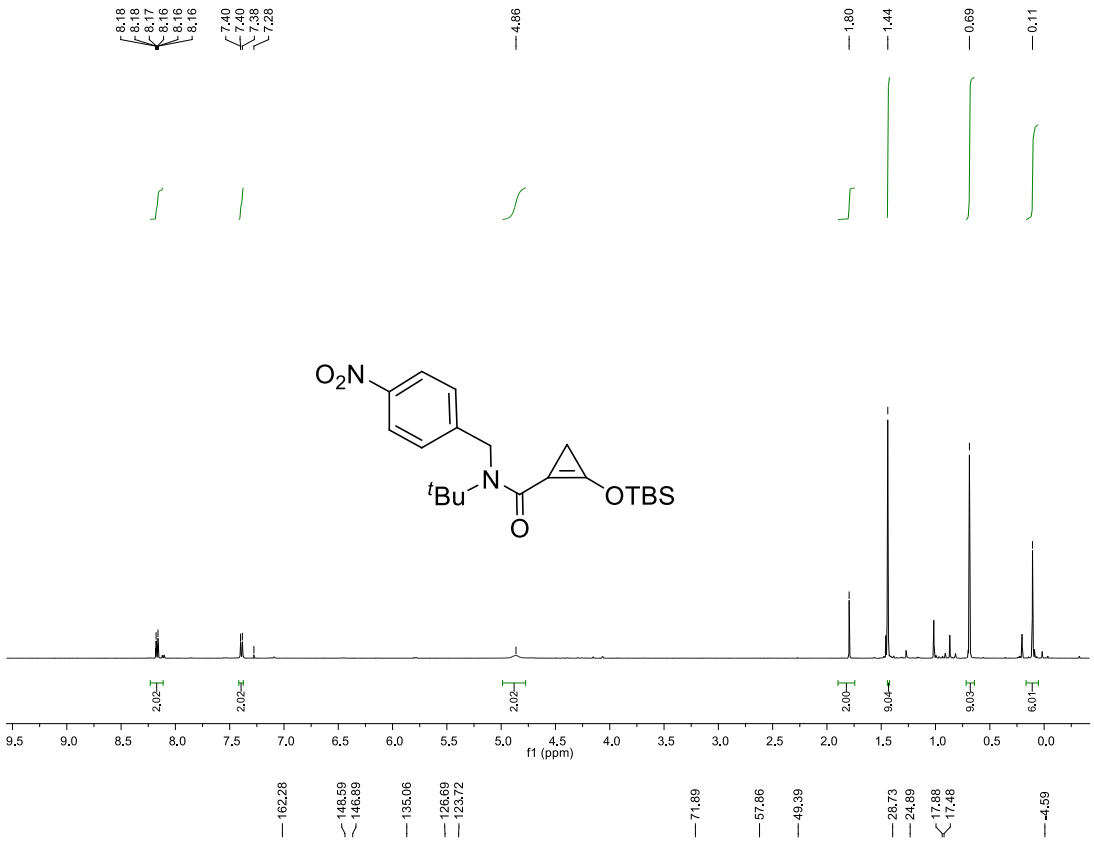
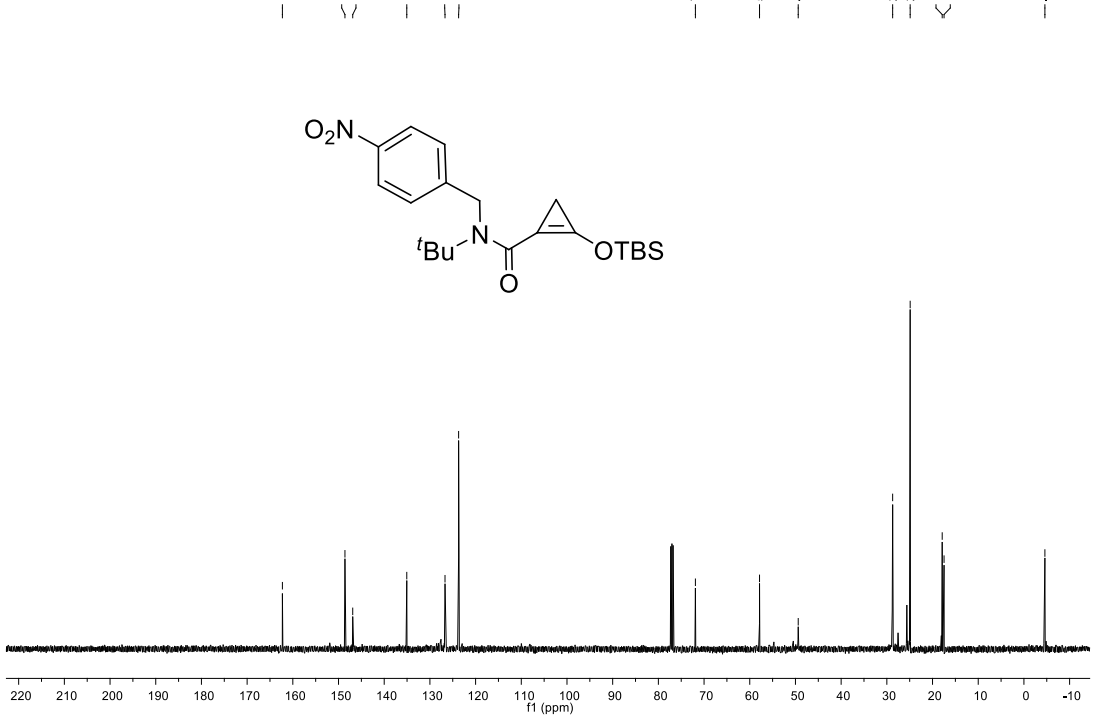
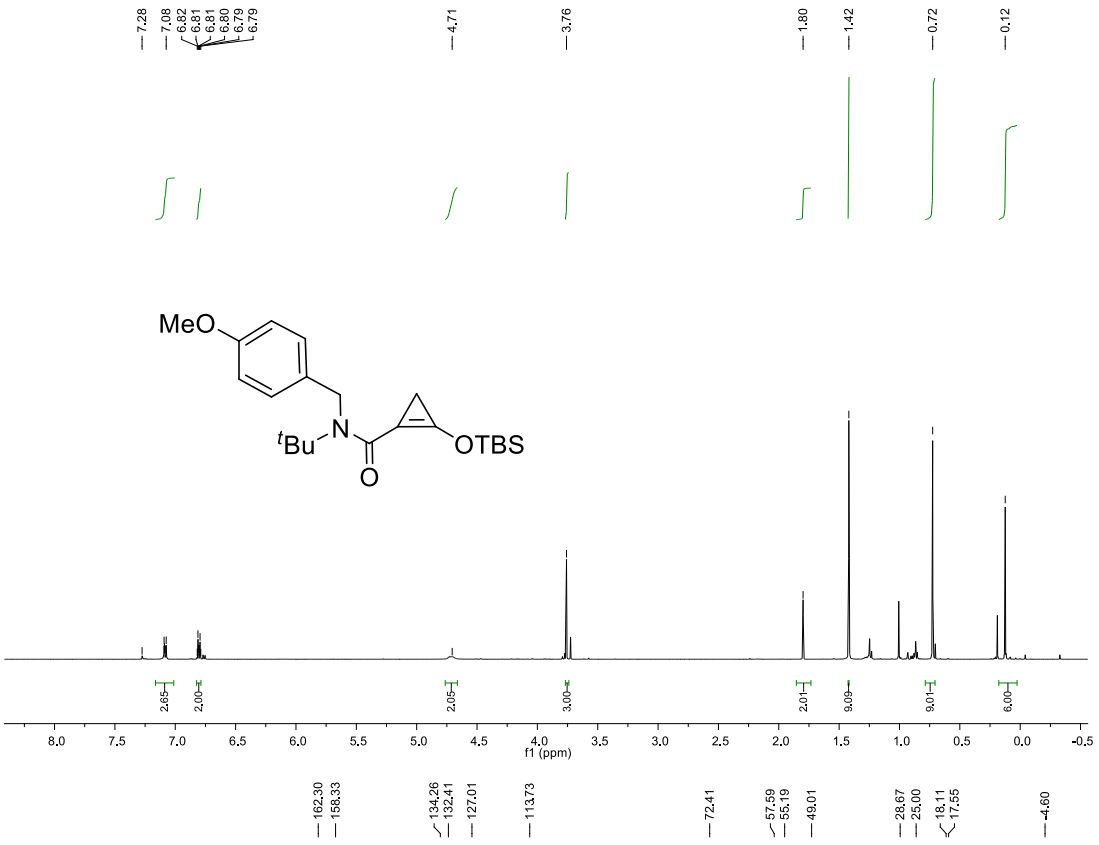
24.93
17.94
17.51
-4.80
134.59
f1 (ppm)

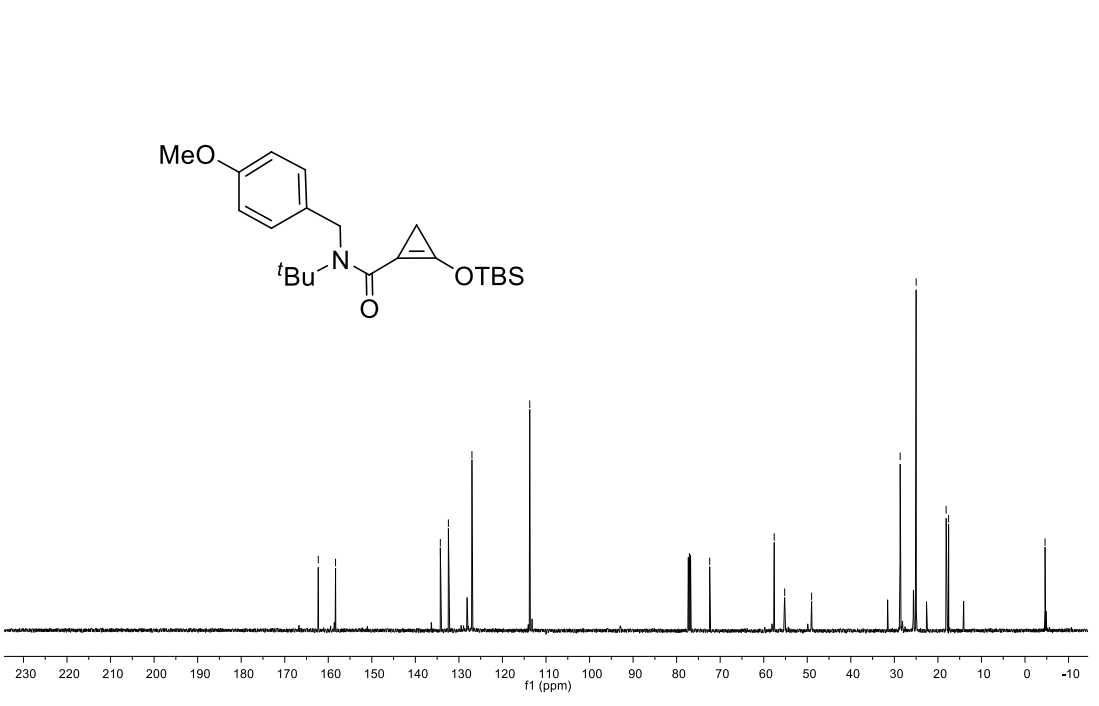

Cl
tBu
N
O
OTBS
f1 (ppm)

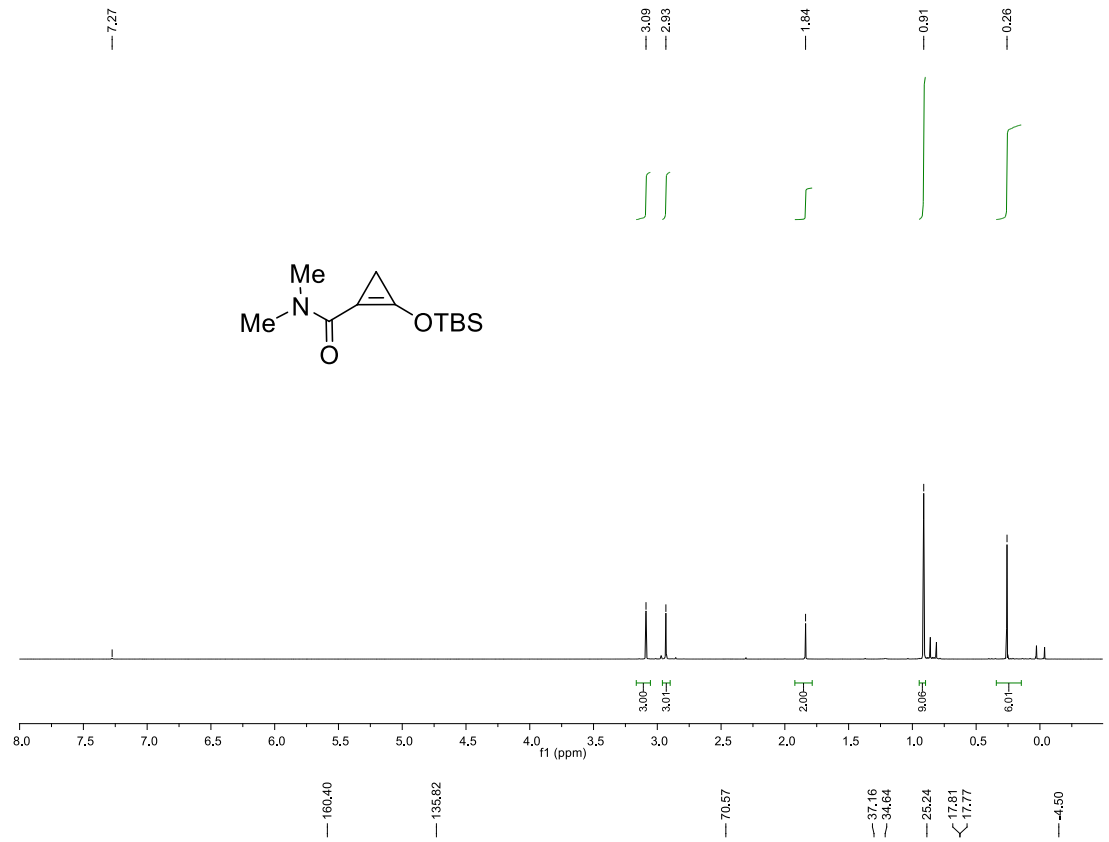

Cl
tBu
N
O
OTBS
f1 (ppm)

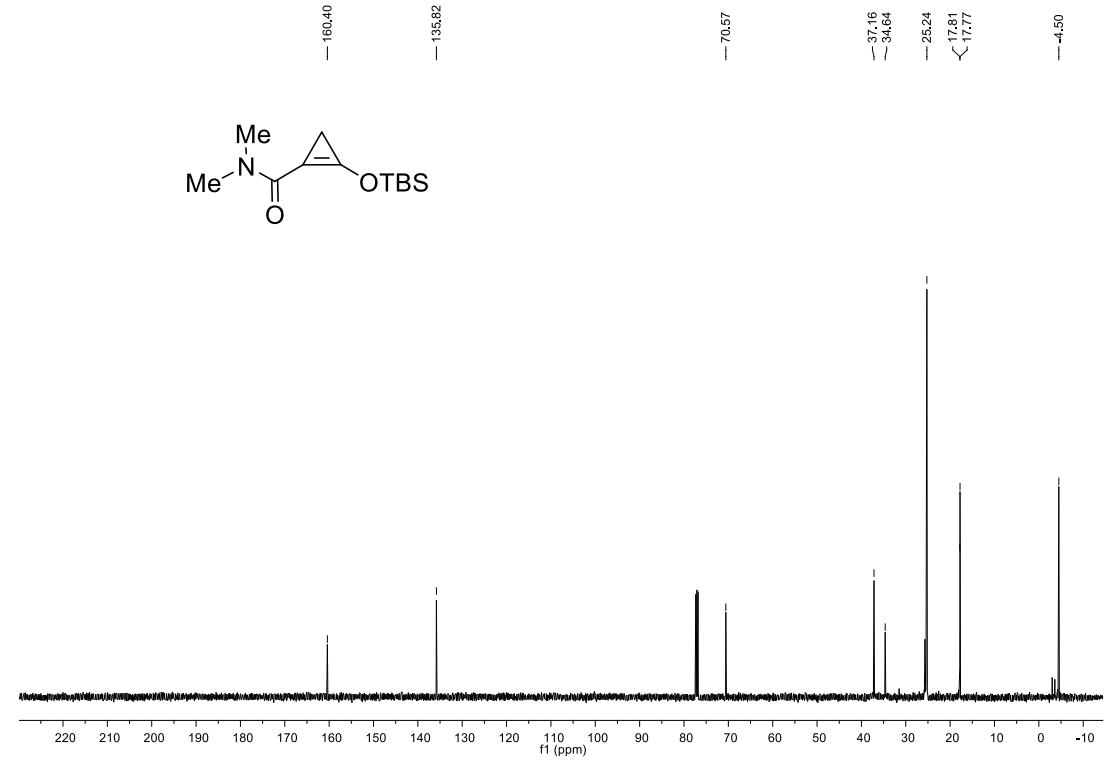

8.18
8.18
8.17
8.16
8.16
8.16
7.40
7.40
7.38
7.28
4.86
1.80
1.44
0.69
0.11
O2N
tBu
N
O
OTBS
2.02
2.02
2.02
2.00
9.04
9.03
6.01
f1 (ppm)

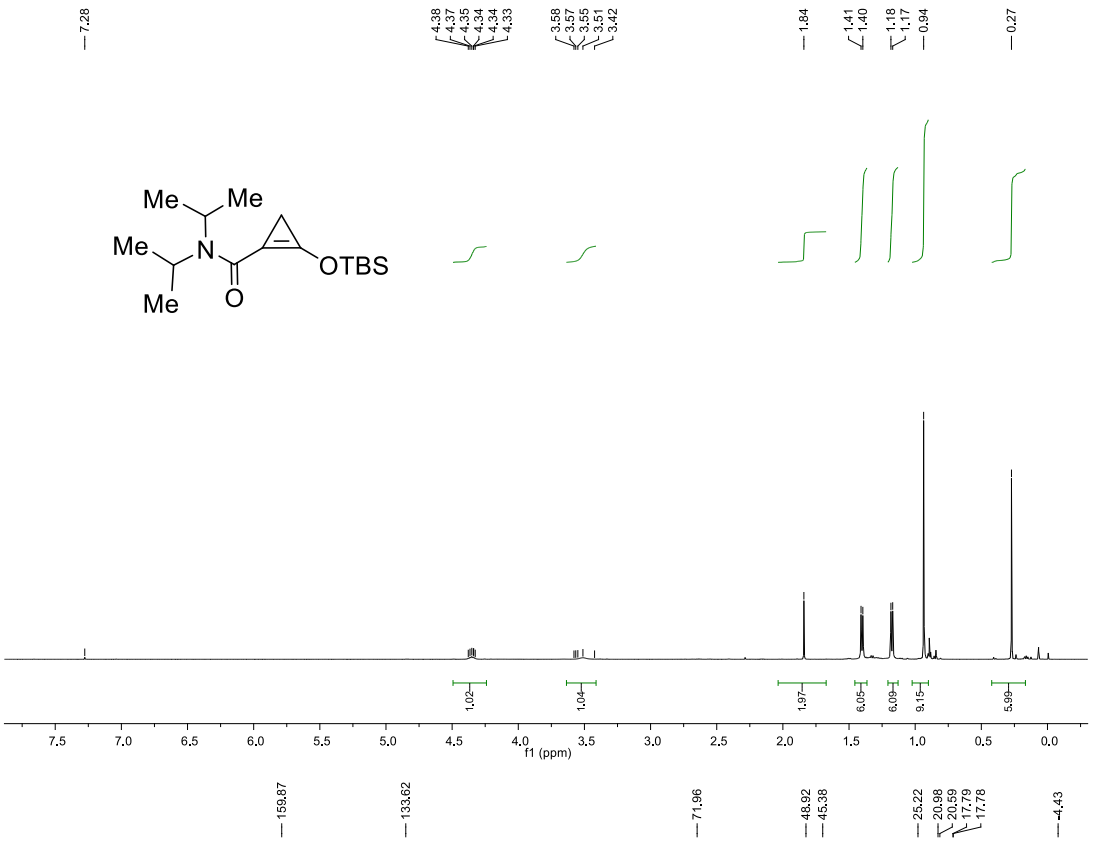

162.28
148.59
146.89
135.06
126.69
123.72
71.89
57.86
49.39
28.73
24.89
17.88
17.48
-4.59
O2N
tBu
N
O
OTBS
f1 (ppm)

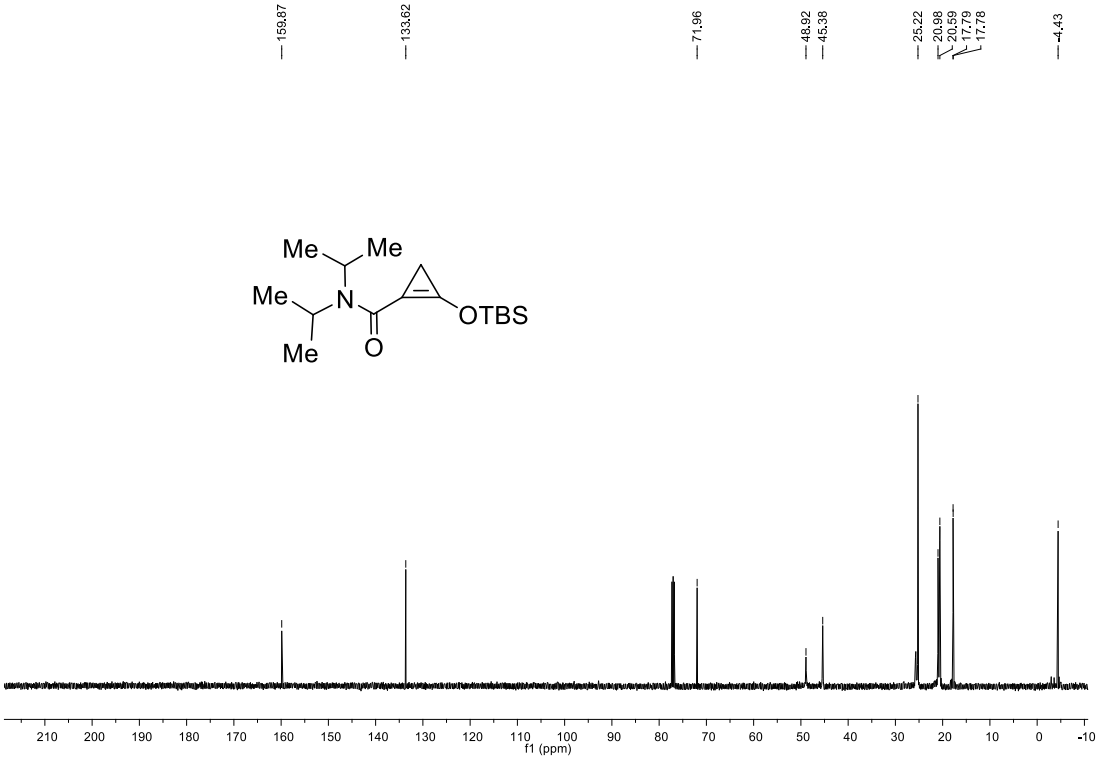

7.28
7.08
6.82
6.81
6.81
6.80
6.79
6.79
4.71
3.76
1.80
1.42
0.72
0.12
MeO
tBu
N
O
OTBS
2.65
2.00
2.05
3.00
2.01
9.09
9.01
6.00
f1 (ppm)

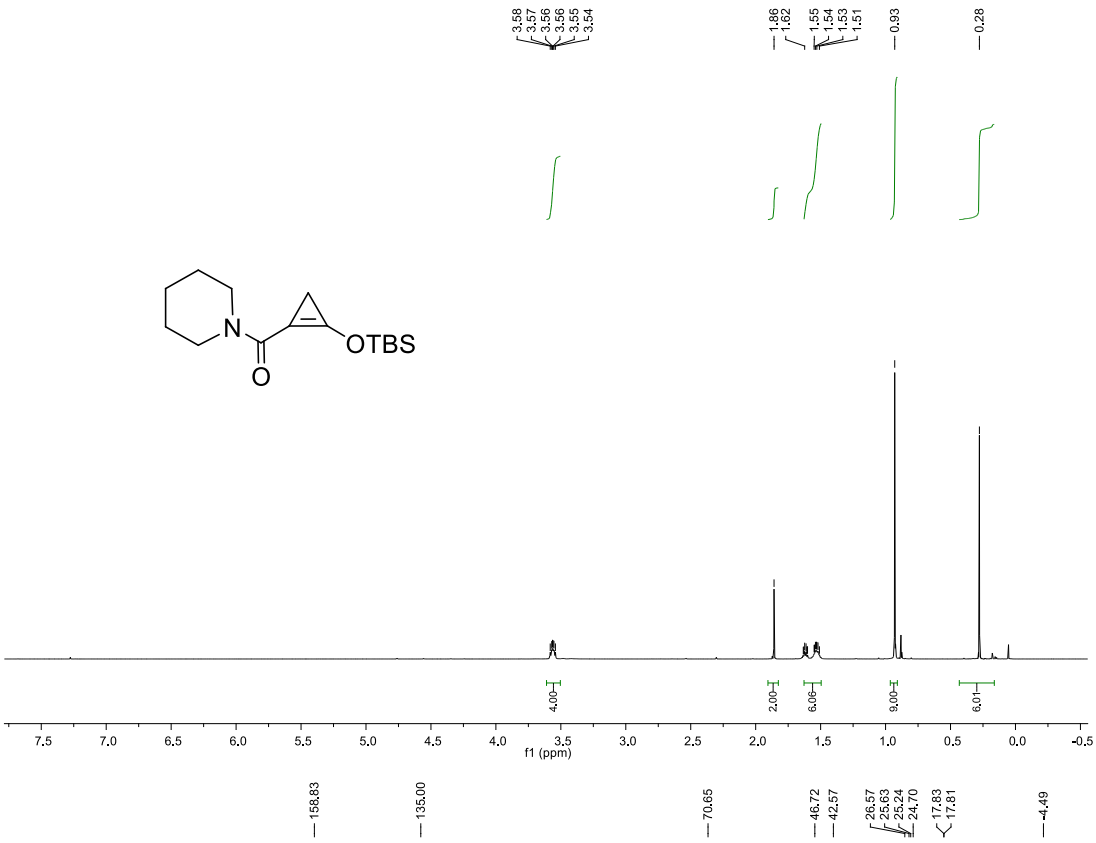

162.30
158.33
134.26
132.41
127.01
113.73
72.41
57.59
55.19
49.01
28.67
25.00
18.11
17.55
-4.60
MeO
tBu
N
O
OTBS
f1 (ppm)

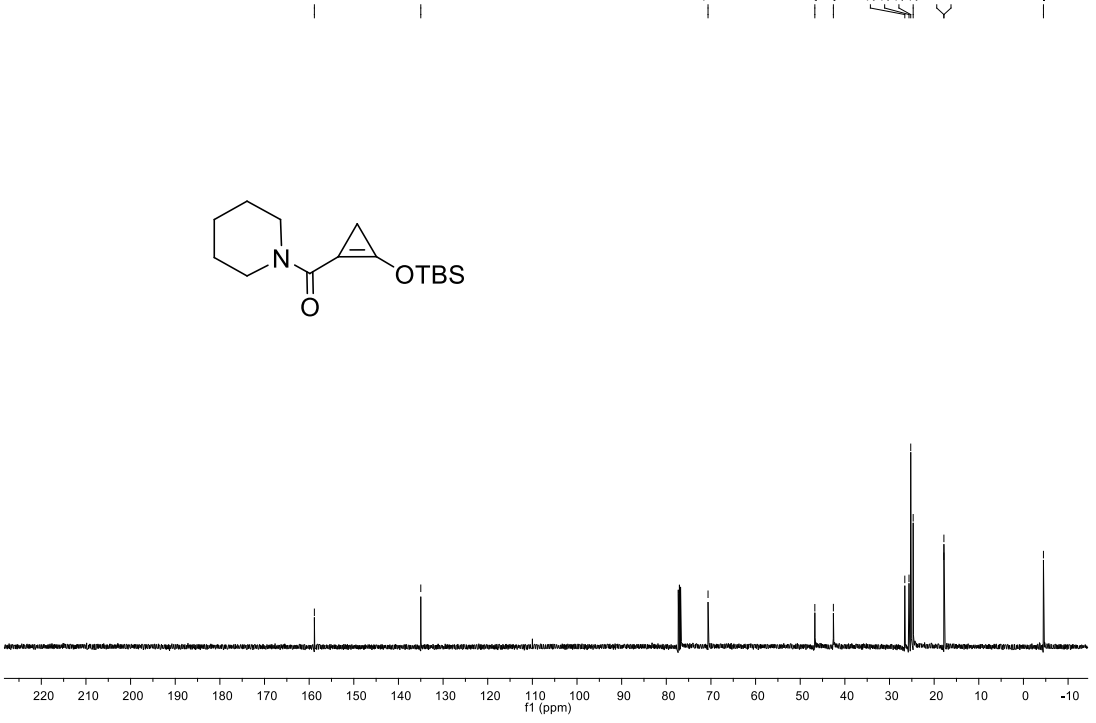

7.27
3.09
2.93
1.84
0.91
0.26
Me
N
Me
O
OTBS
3.00
3.01
2.00
9.06
6.01
f1 (ppm)


160.40
135.82
70.57
37.16
34.64
25.24
17.81
17.77
-4.50
Me
N
Me
O
OTBS
f1 (ppm)

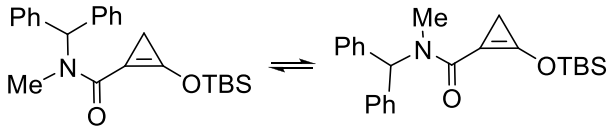

7.28
4.38
4.37
4.35
4.34
4.34
4.33
3.58
3.57
3.55
3.51
3.42
1.84
1.41
1.40
1.18
1.17
0.94
0.27
Me
Me
Me
N
OTBS
O
Me
1.02
1.04
1.97
6.05
6.09
9.15
5.99
f1 (ppm)

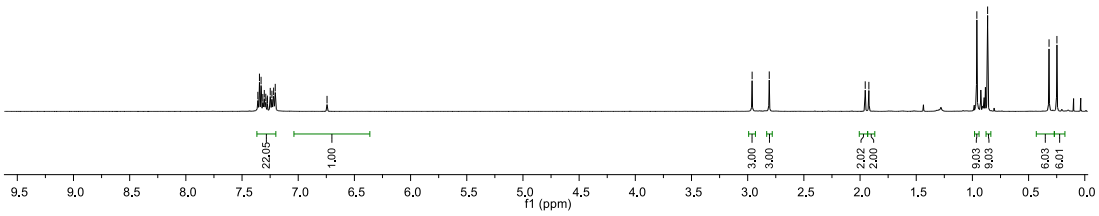

159.87
133.62
71.96
48.92
45.38
25.22
20.98
20.59
17.79
17.78
-4.43
Me
Me
Me
N
OTBS
O
Me
f1 (ppm)


3.58
3.57
3.56
3.56
3.55
3.54
1.86
1.62
1.55
1.54
1.53
1.51
0.93
0.28
N
O
OTBS
4.00
2.00
6.08
9.00
6.01
f1 (ppm)

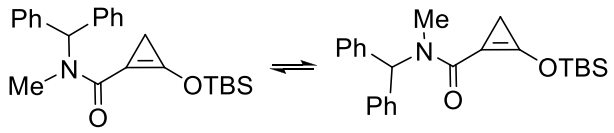

158.83
135.00
70.65
46.72
42.57
26.57
25.63
25.24
24.70
17.83
17.81
-4.49
N
O
OTBS
f1 (ppm)

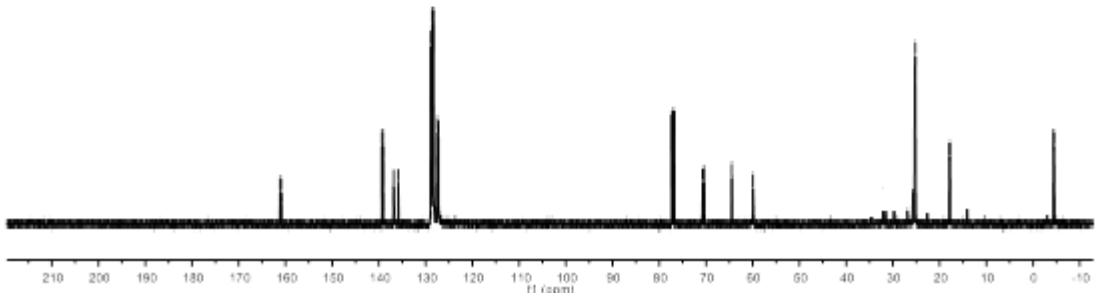

7.36
7.35
7.33
7.32
7.30
7.28
7.27
7.25
7.23
7.22
7.20
6.74
2.96
2.81
1.95
1.92
0.96
0.86
0.32
0.25

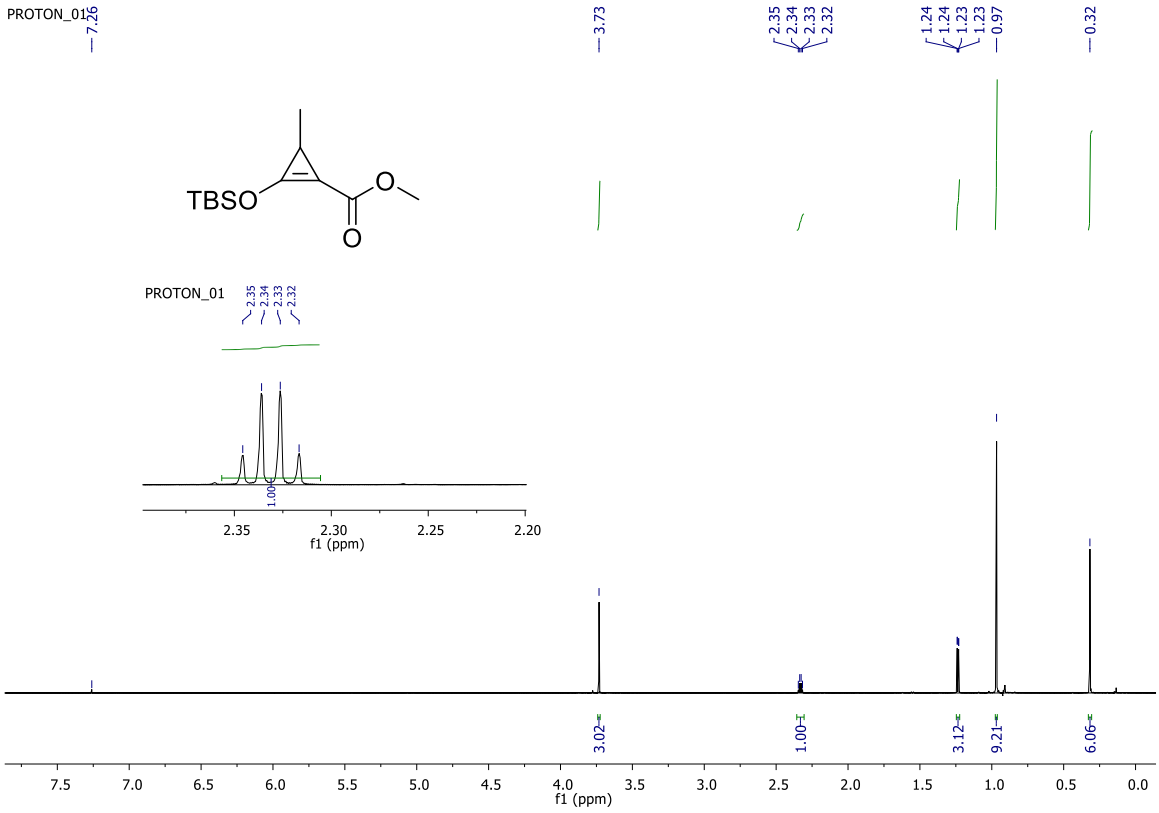

Ph
Ph
N
Me
O
OTBS
Me
N
Ph
Ph
O
OTBS

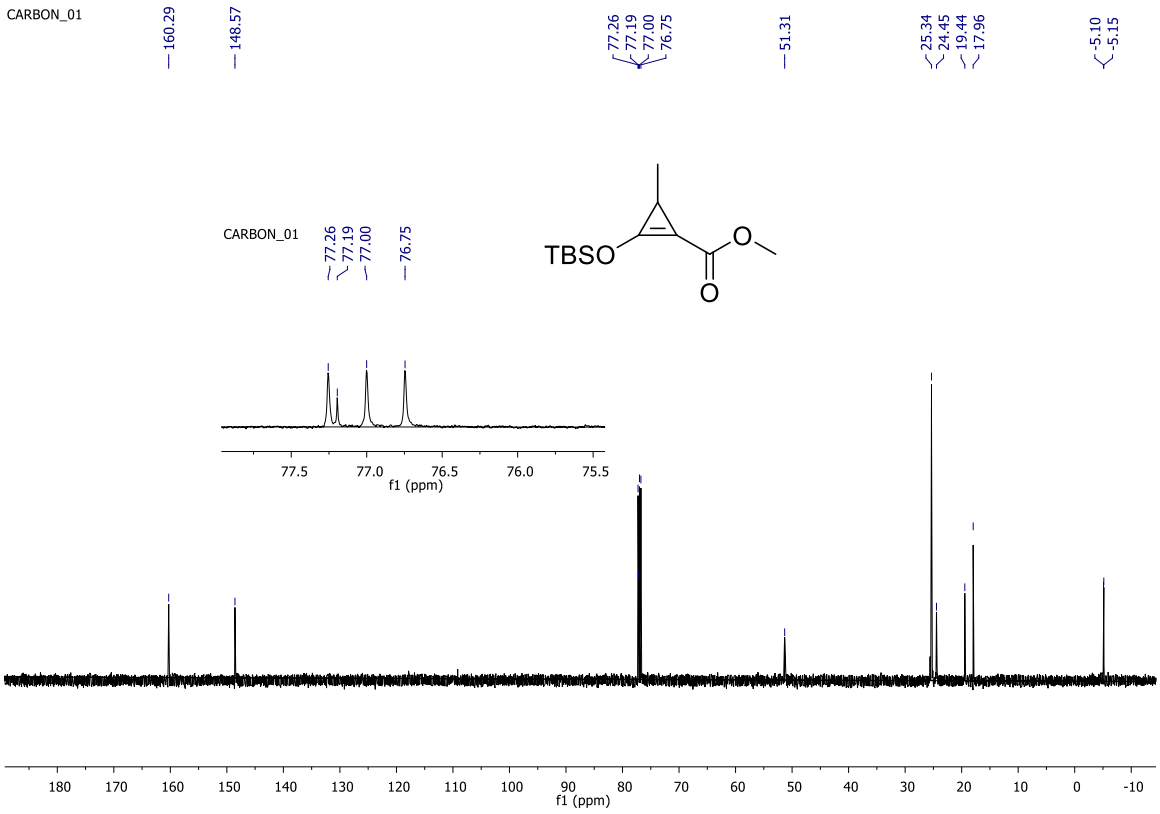

22.05
1.00
3.00
3.00
2.02
2.00
9.03
9.03
6.03
6.01
f1 (ppm)

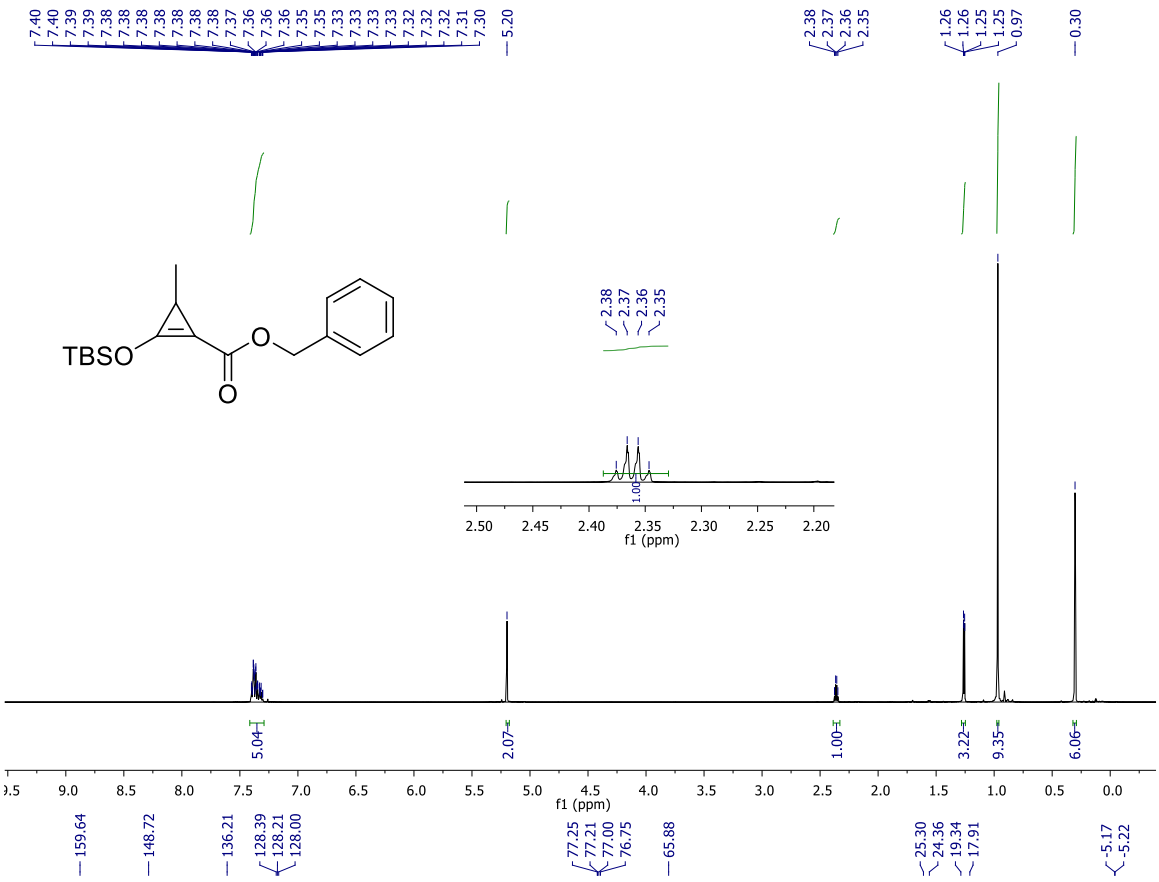

161.16
160.91
139.35
138.13
136.87
136.89
128.85
128.59
128.36
128.35
127.47
127.25
70.71
70.42
64.49
59.95
25.90
25.71
17.91
17.78
-4.34
-4.50

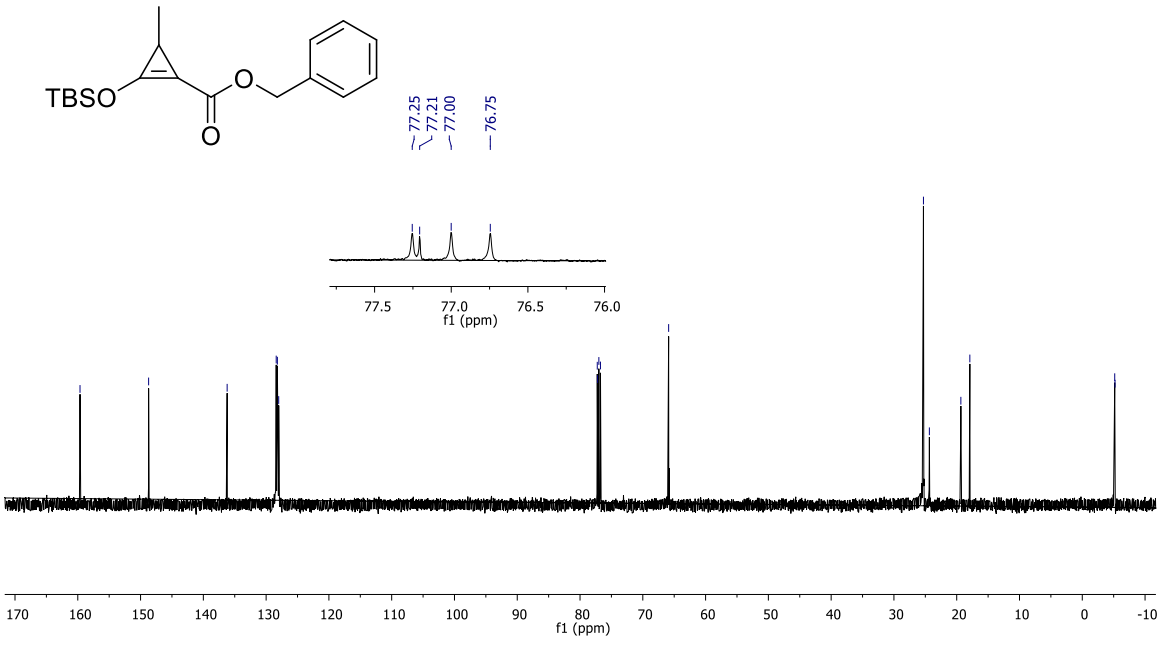

Ph
Ph
N
Me
O
OTBS
Me
N
Ph
Ph
O
OTBS

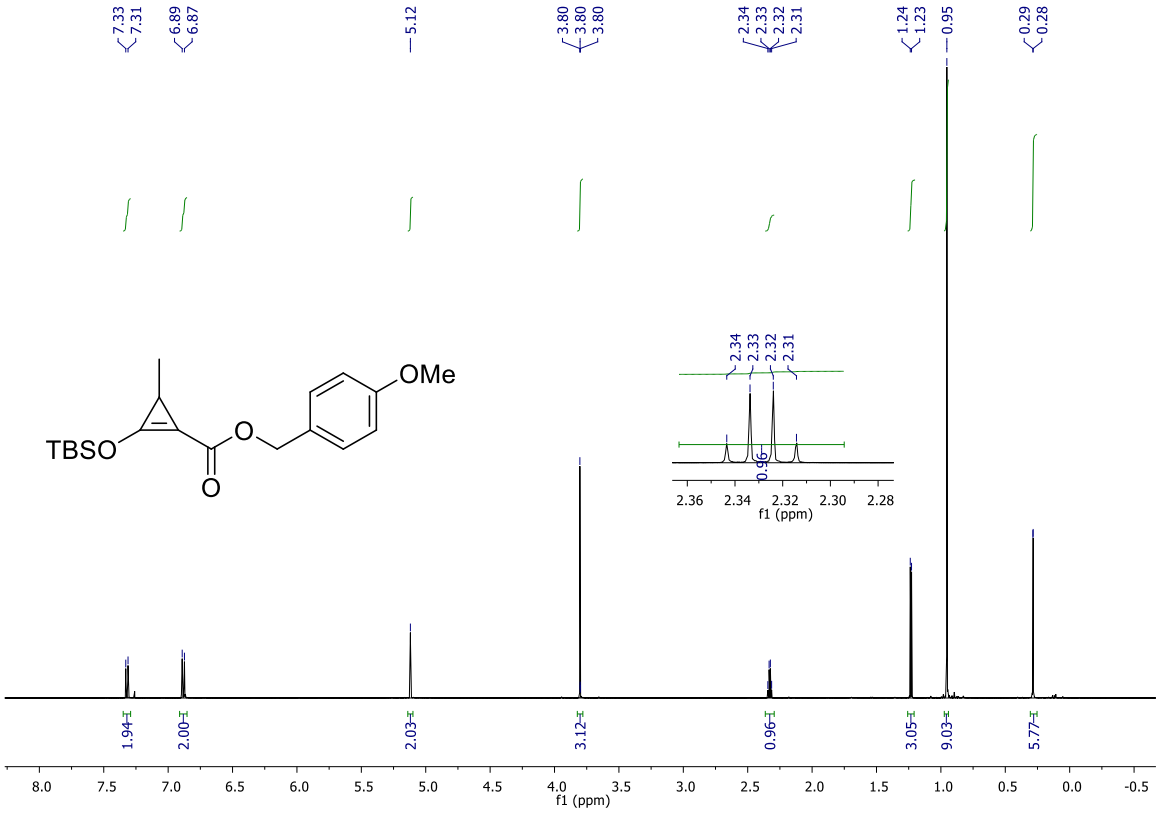

f1 (ppm)

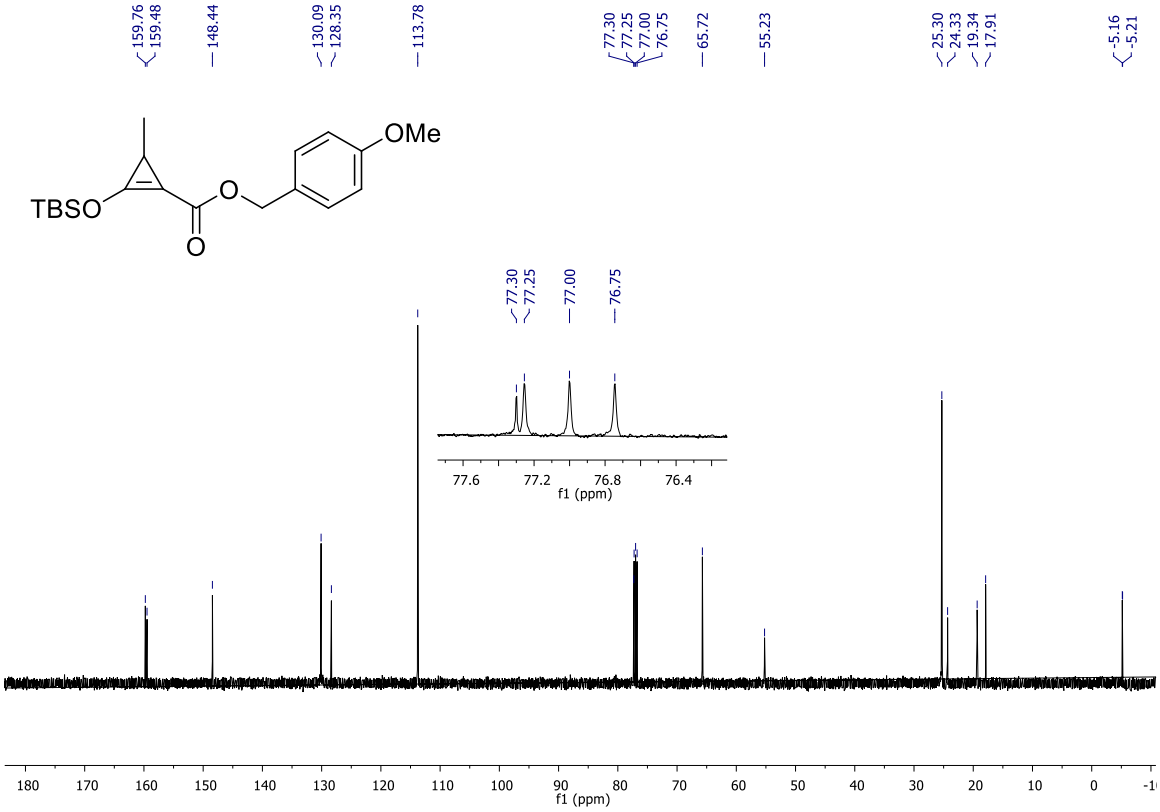

PROTON_01
7.26
3.73
2.35
2.34
2.33
2.32
1.24
1.24
1.23
1.23
0.97
0.32
TBSO
O
O
PROTON_01
2.35
2.34
2.33
2.32
1.00
2.35
2.30
2.25
2.20
f1 (ppm)
3.02
1.00
3.12
9.21
6.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

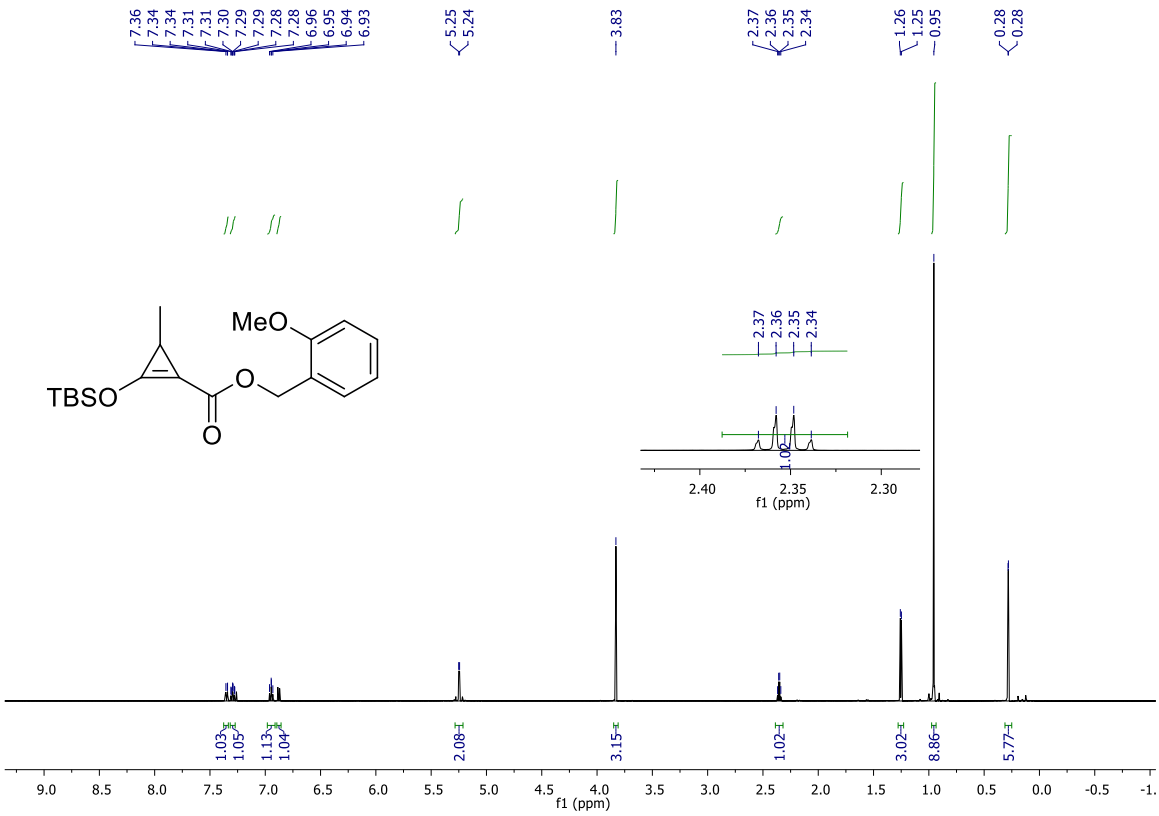

CARBON_01
160.29
148.57
77.26
77.19
77.00
76.75
51.31
25.34
24.45
19.44
17.96
-5.10
-5.15
CARBON_01
77.26
77.19
77.00
76.75
TBSO
O
O
77.5
77.0
76.5
76.0
75.5
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

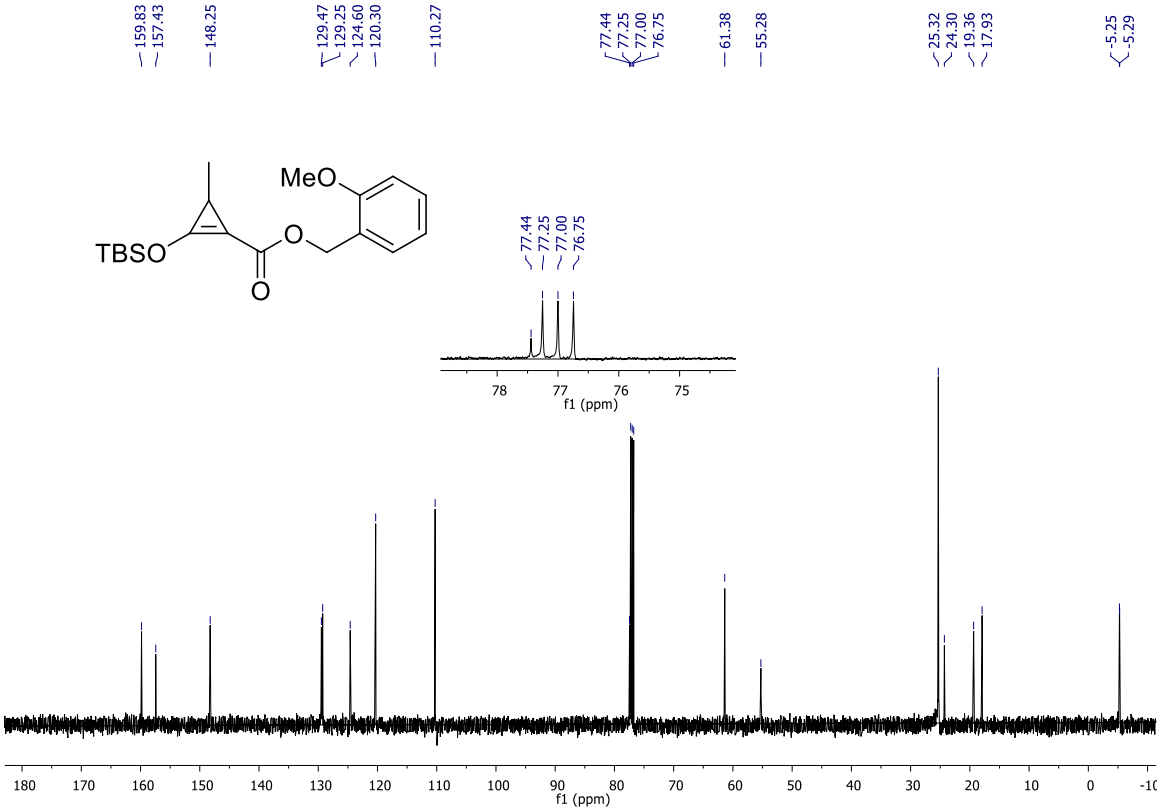

TBSO
O
O
f1 (ppm)

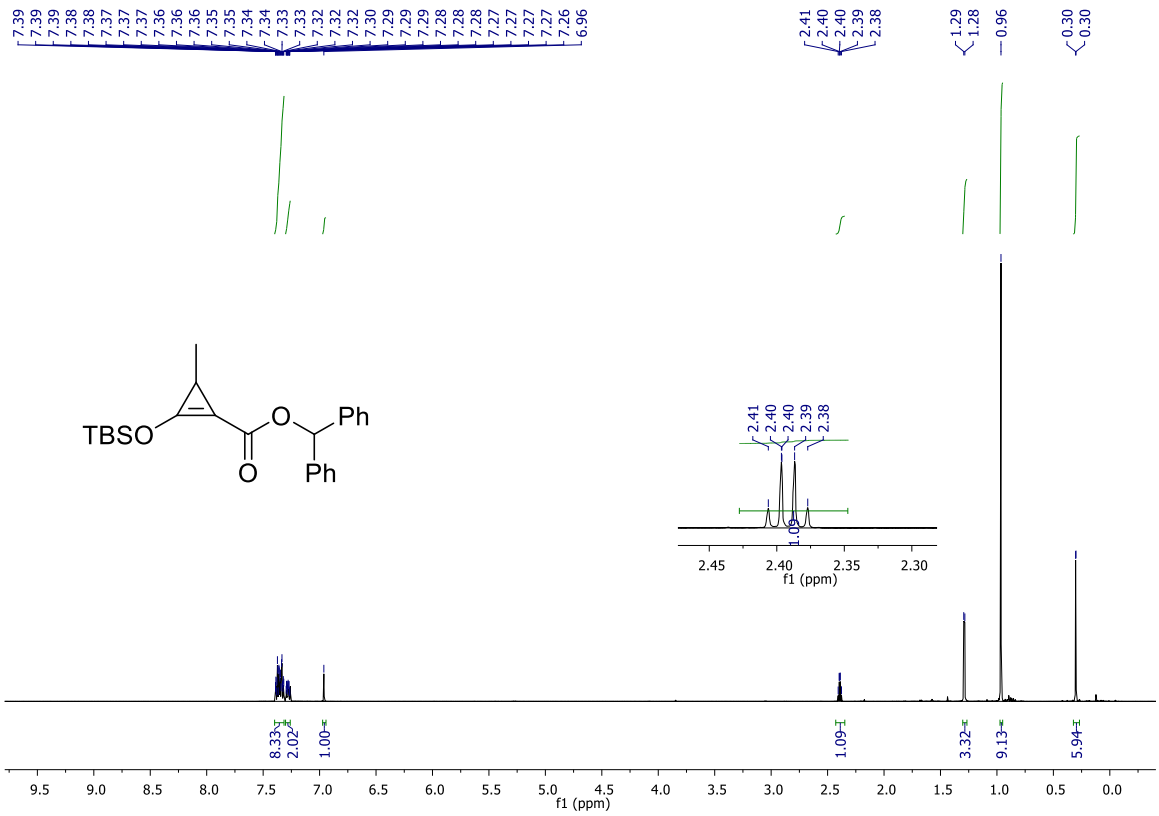

TBSO
O
O
f1 (ppm)

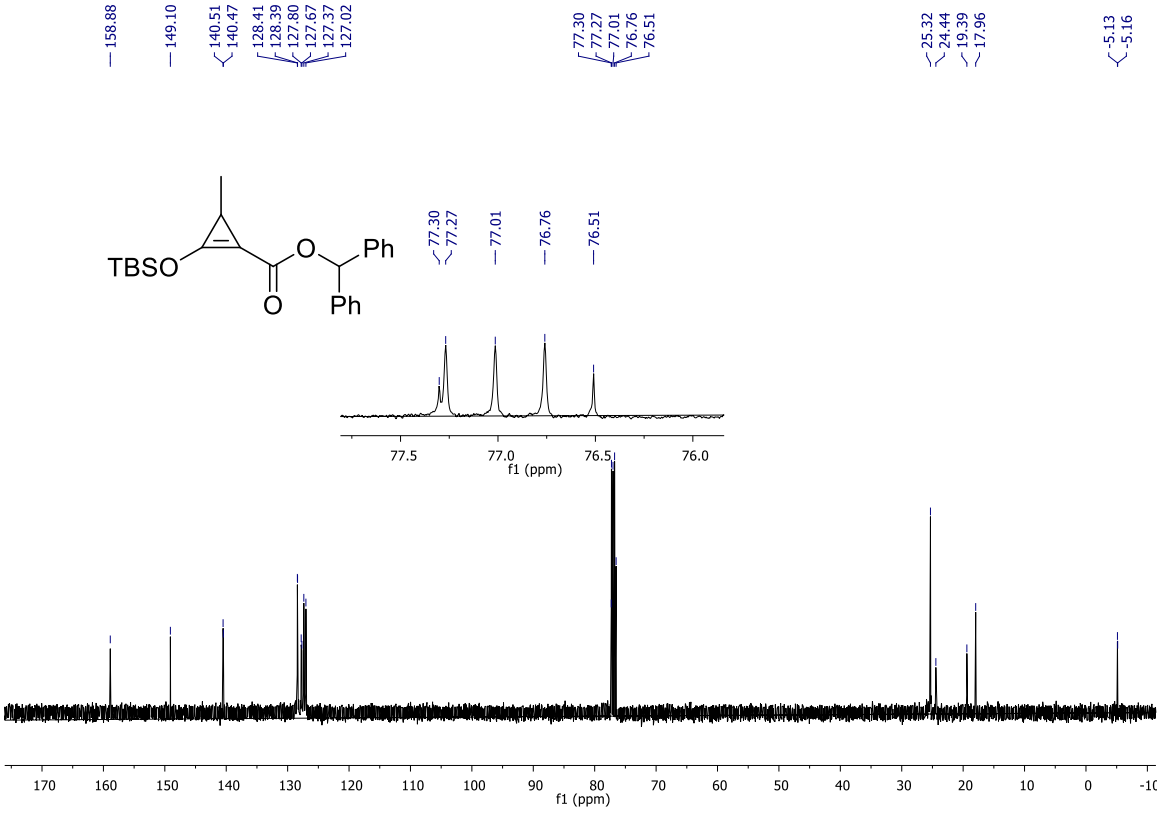

7.33
7.31
6.89
6.87
5.12
3.80
3.80
3.80
2.34
2.33
2.32
2.31
1.24
1.23
0.95
0.29
0.28
OMe
TBSO
O
O
0.96
2.36 2.34 2.32 2.30 2.28
f1 (ppm)
1.94
2.00
2.03
3.12
0.96
3.05
9.03
5.77
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

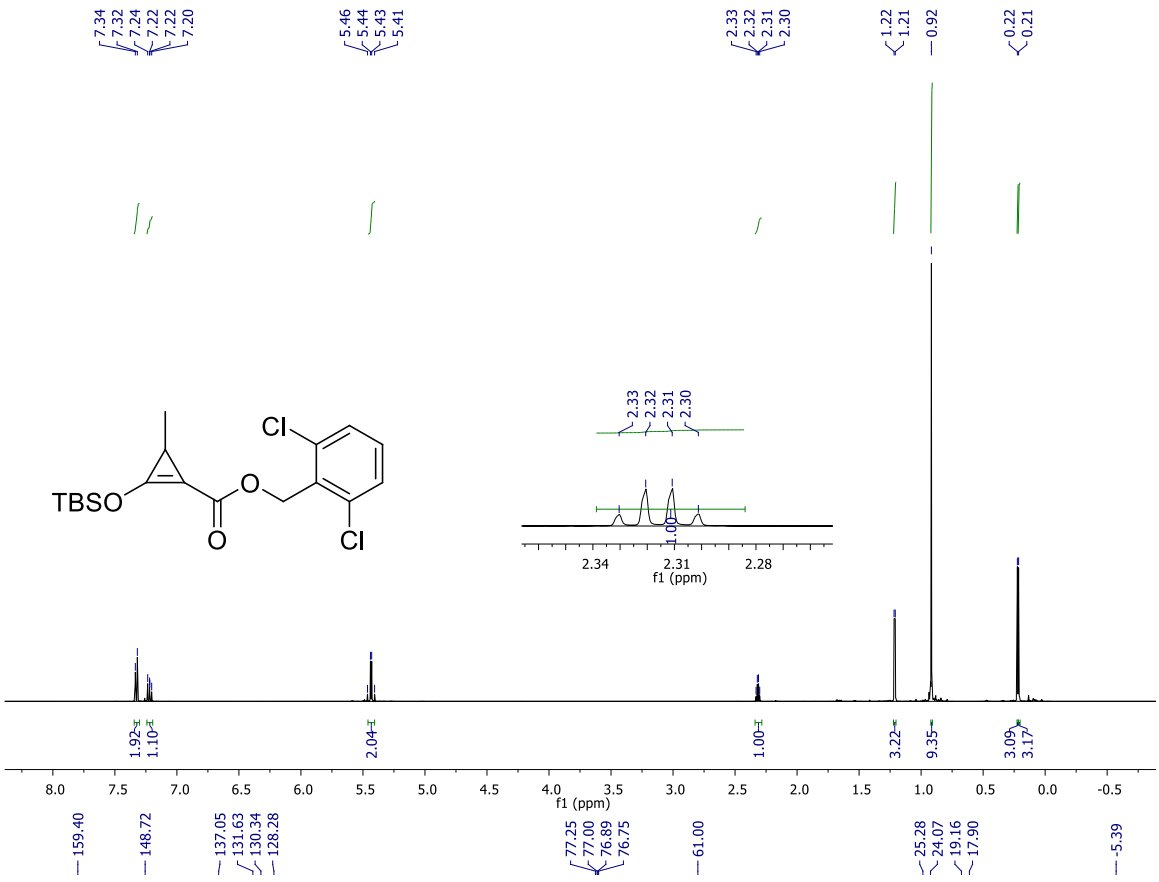

159.76
159.48
148.44
130.09
128.35
113.78
77.30
77.25
77.00
76.75
65.72
55.23
25.30
24.33
19.34
17.91
-5.16
-5.21
OMe
TBSO
O
O
77.6 77.2 76.8 76.4
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

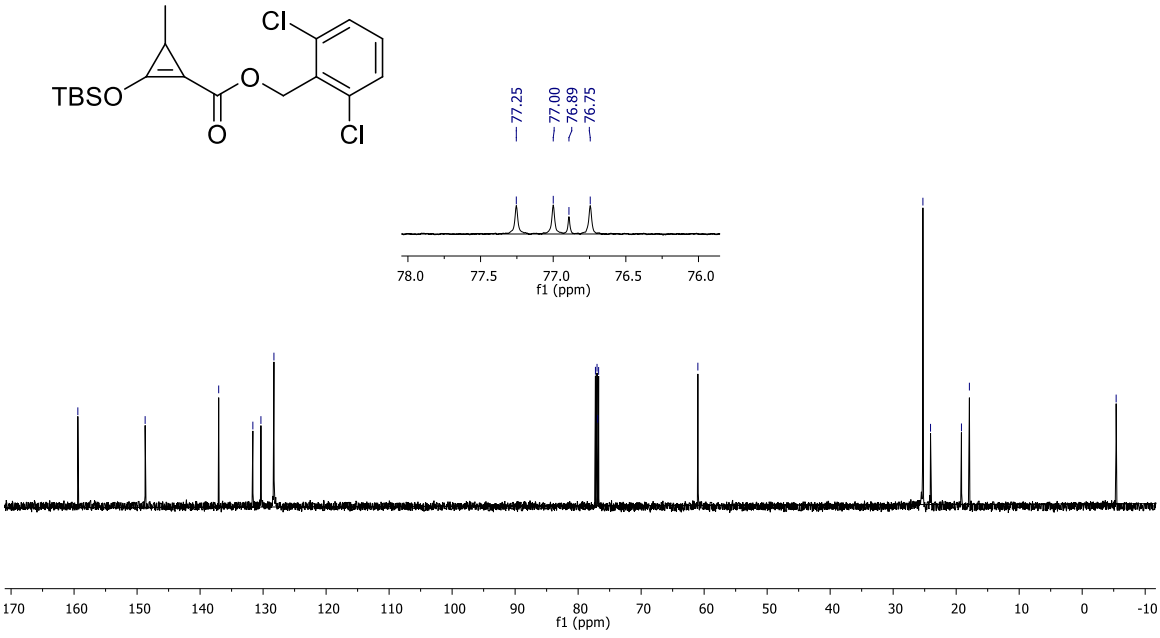

7.36
7.34
7.34
7.31
7.31
7.30
7.29
7.29
7.28
7.28
6.96
6.95
6.94
6.93
5.25
5.24
3.83
2.37
2.36
2.35
2.34
1.26
1.25
0.95
0.28
0.28
MeO
TBSO
O
O
2.37
2.36
2.35
2.34
1.00
2.40
2.35
2.30
f1 (ppm)
1.03
1.05
1.13
1.04
2.08
3.15
1.02
3.02
8.86
5.77
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

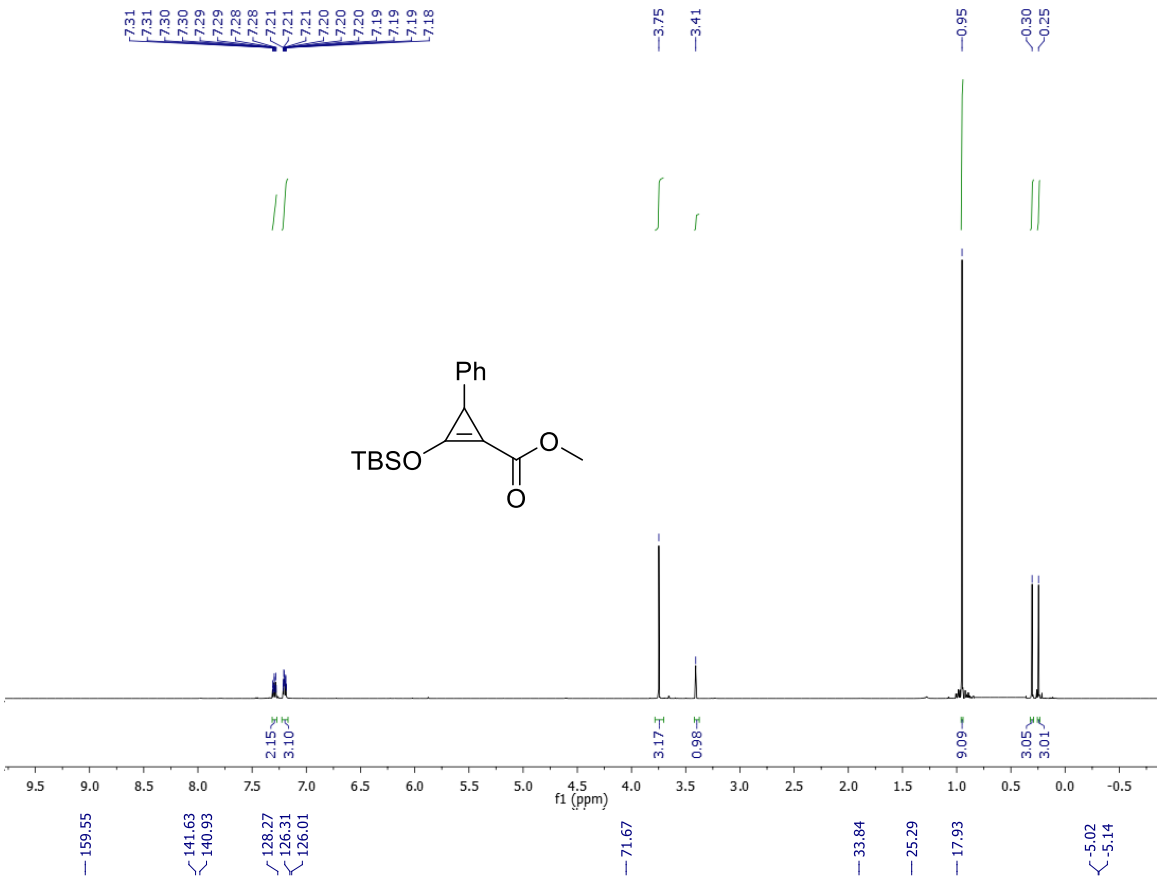

159.83
157.43
148.25
129.47
129.25
124.60
120.30
110.27
77.44
77.25
77.00
76.75
61.38
55.28
25.32
24.30
19.36
17.93
-5.25
-5.29
MeO
TBSO
O
O
77.44
77.25
77.00
76.75
78
77
76
75
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

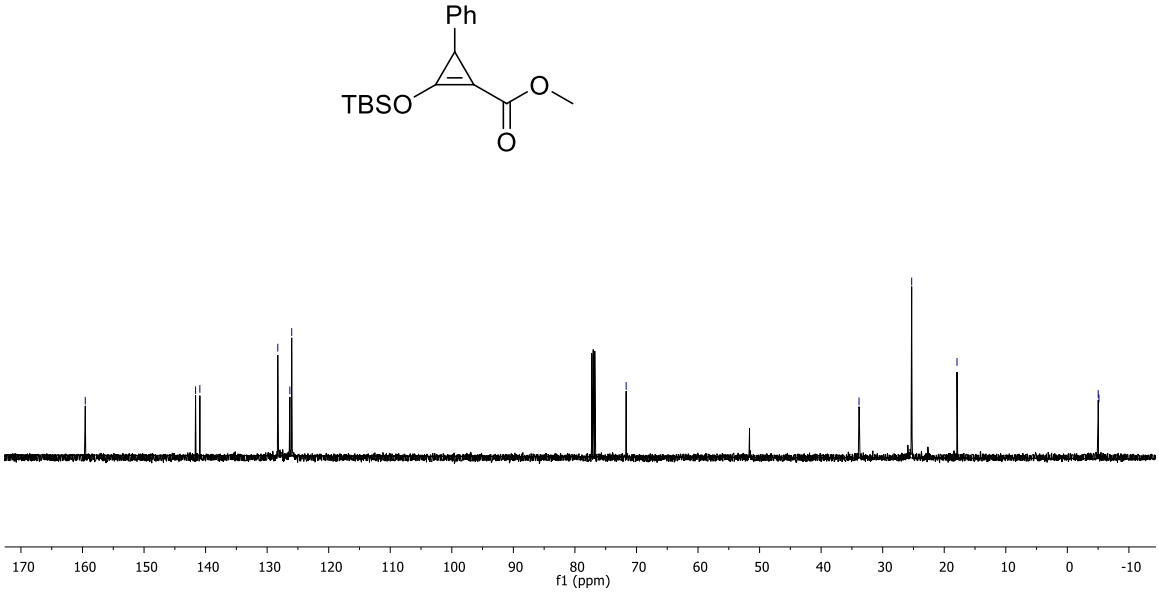

TBSO
O
O
Ph
Ph
f1 (ppm)

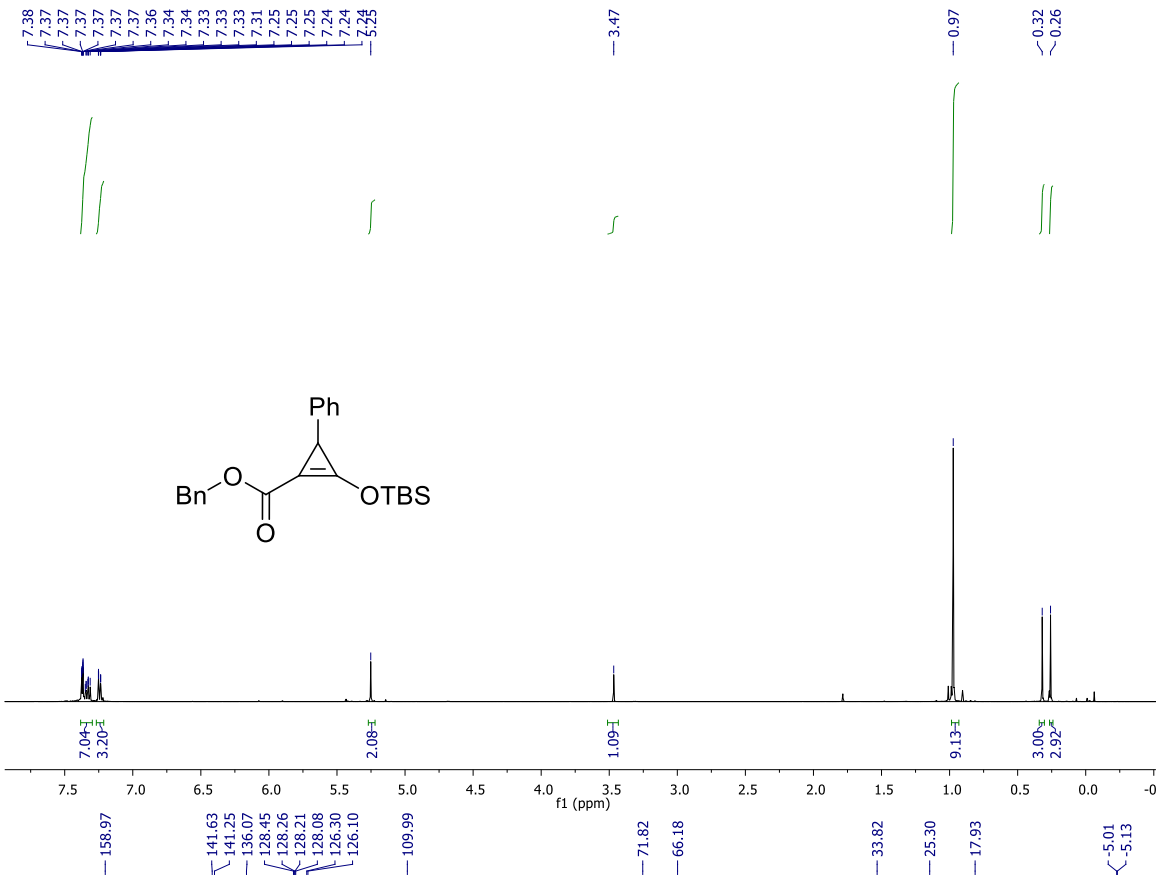

TBSO
O
O
Ph
Ph
f1 (ppm)


7.34
7.32
7.24
7.22
7.22
7.20
5.46
5.44
5.43
5.41
2.33
2.32
2.31
2.30
1.22
1.21
0.92
0.22
0.21
TBSO
O
O
Cl
Cl
2.34
2.31
2.28
f1 (ppm)
1.92
1.10
2.04
1.00
3.22
9.35
3.09
3.17
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
0.0
-0.5
f1 (ppm)
159.40
148.72
137.05
131.63
130.34
128.28
77.25
77.00
76.89
76.75
61.00
25.28
24.07
19.16
17.90
-5.39


TBSO
O
O
Cl
Cl
77.25
77.00
76.89
76.75
78.0
77.5
77.0
76.5
76.0
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.19
7.18
3.75
3.41
0.95
0.30
0.25
Ph
TBSO
O
O
2.15
3.10
3.17
0.98
9.09
3.05
3.01
f1 (ppm)
159.55
141.63
140.93
128.27
126.31
126.01
71.67
33.84
25.29
17.93
-5.02
-5.14


Ph
TBSO
O
O
f1 (ppm)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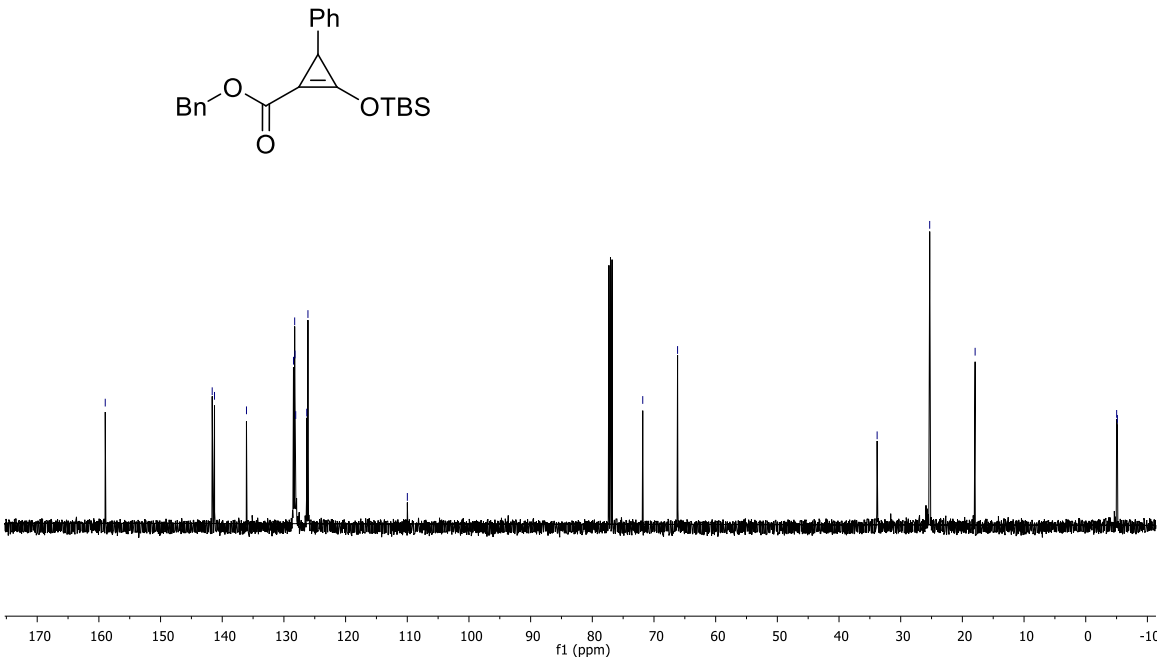
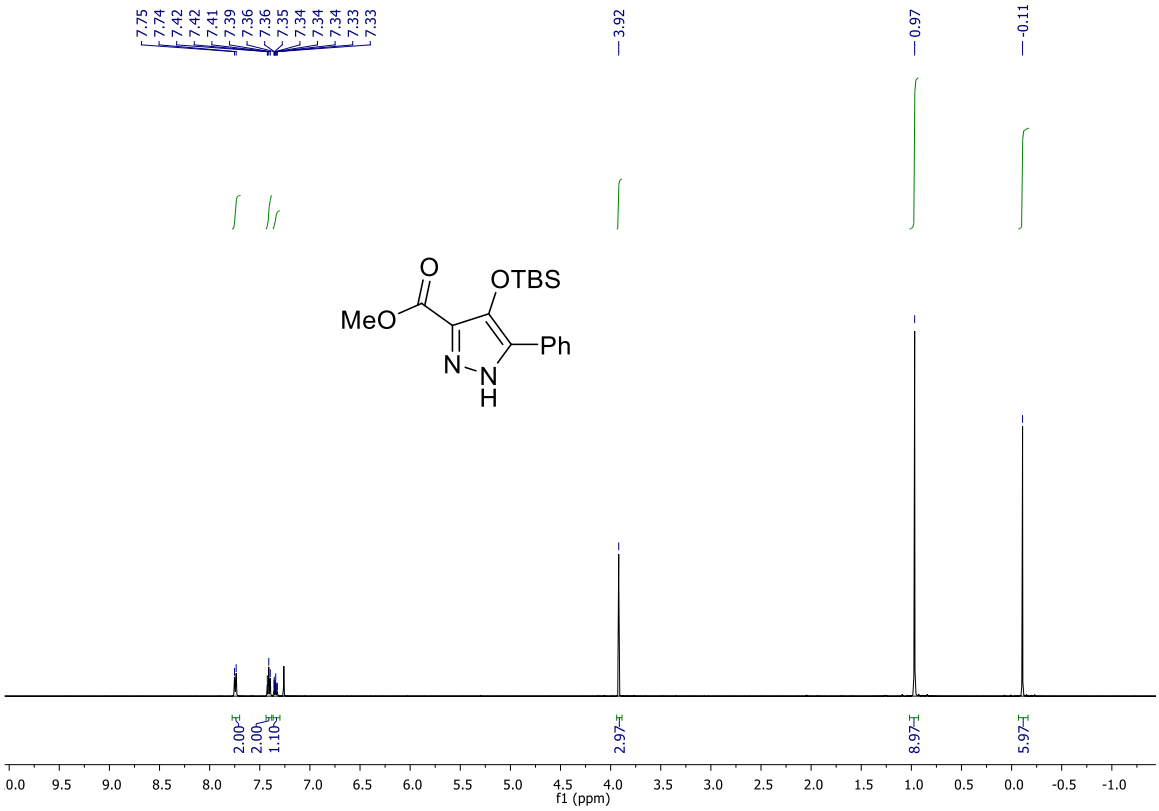
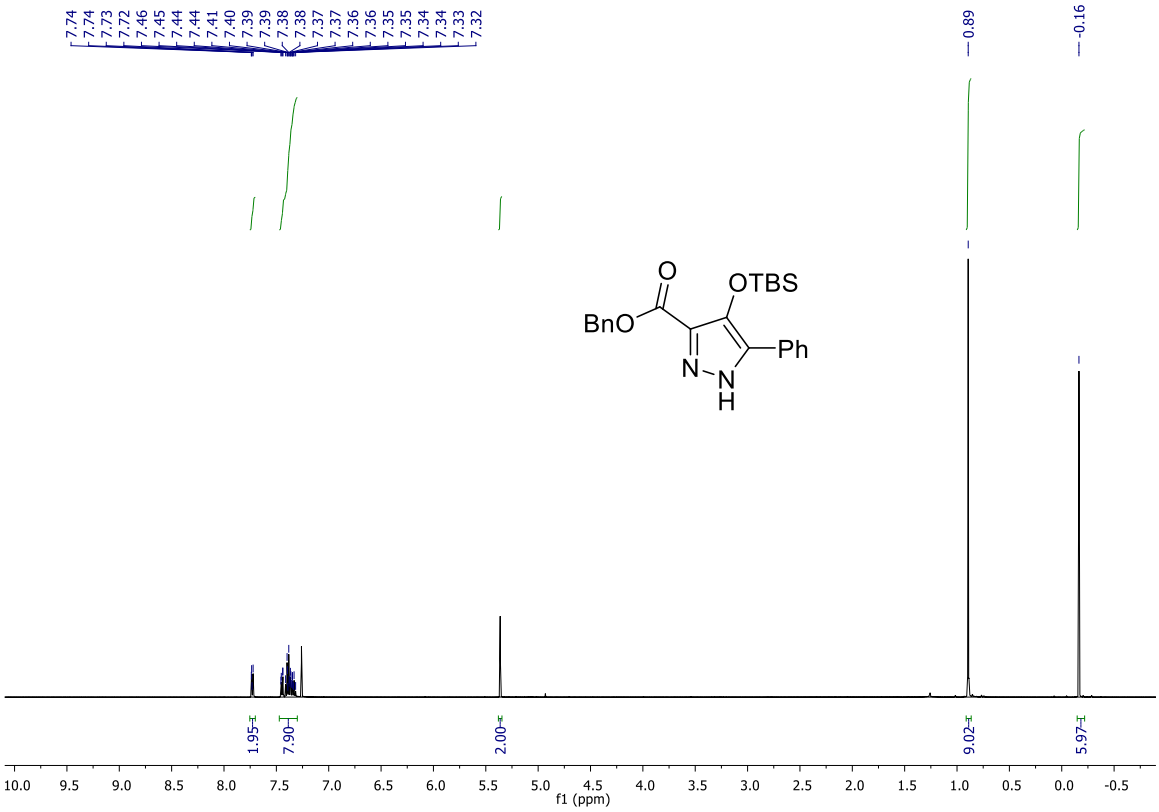
7.37
7.37
7.37
7.37
7.37
7.37
7.36
7.34
7.34
7.33
7.33
7.33
7.31
7.25
7.25
7.25
7.24
7.24
7.24
5.25
3.47
0.97
0.32
0.26
Ph
Bn
O
O
OTBS
7.04
3.20
2.08
1.09
9.13
3.00
2.92
f1 (ppm)


158.97
141.63
141.25
136.07
128.45
128.26
128.21
128.08
126.30
126.10
109.99
71.82
66.18
33.82
25.30
17.93
-5.01
-5.13
Ph
Bn
O
O
OTBS
f1 (ppm)


7.75
7.74
7.42
7.42
7.41
7.39
7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.33
3.92
0.97
-0.11
O
OTBS
MeO
Ph
N
N
H
2.00
2.00
1.10
2.97
8.97
5.97
0.0 9.5 9.0 8.5 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 0.0 -0.5 -1.0
f1 (ppm)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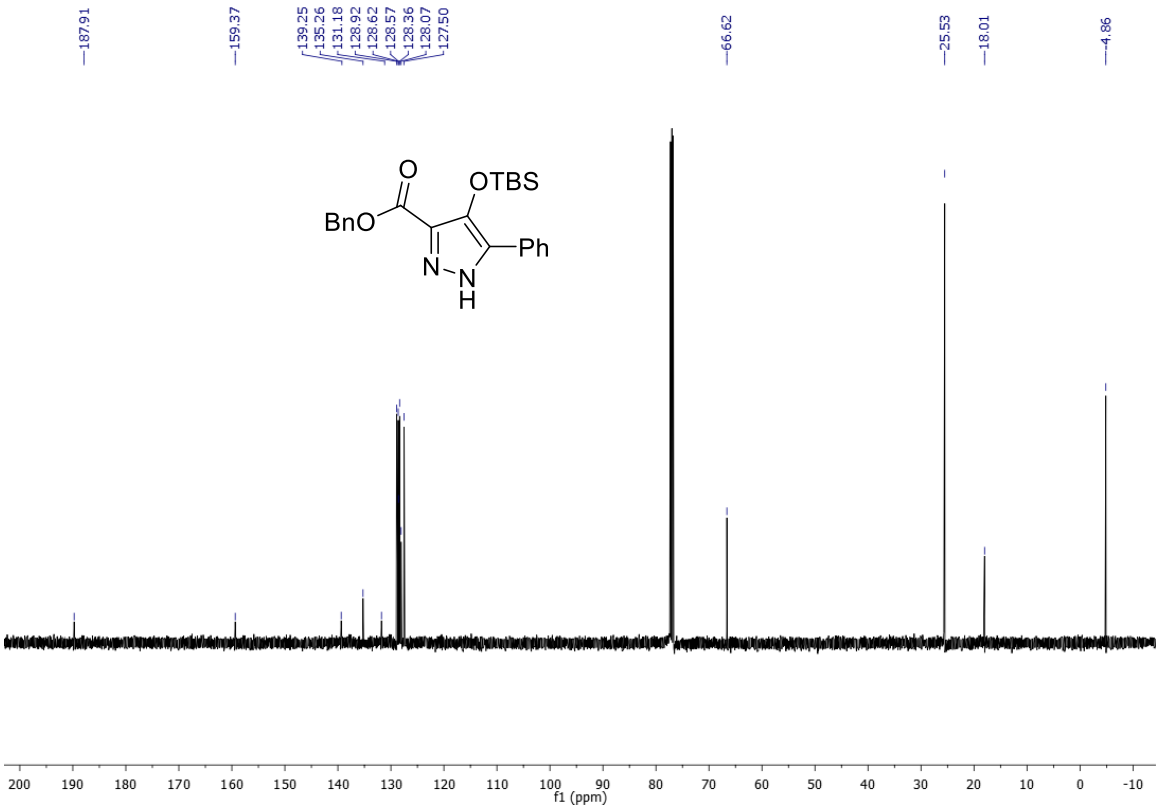
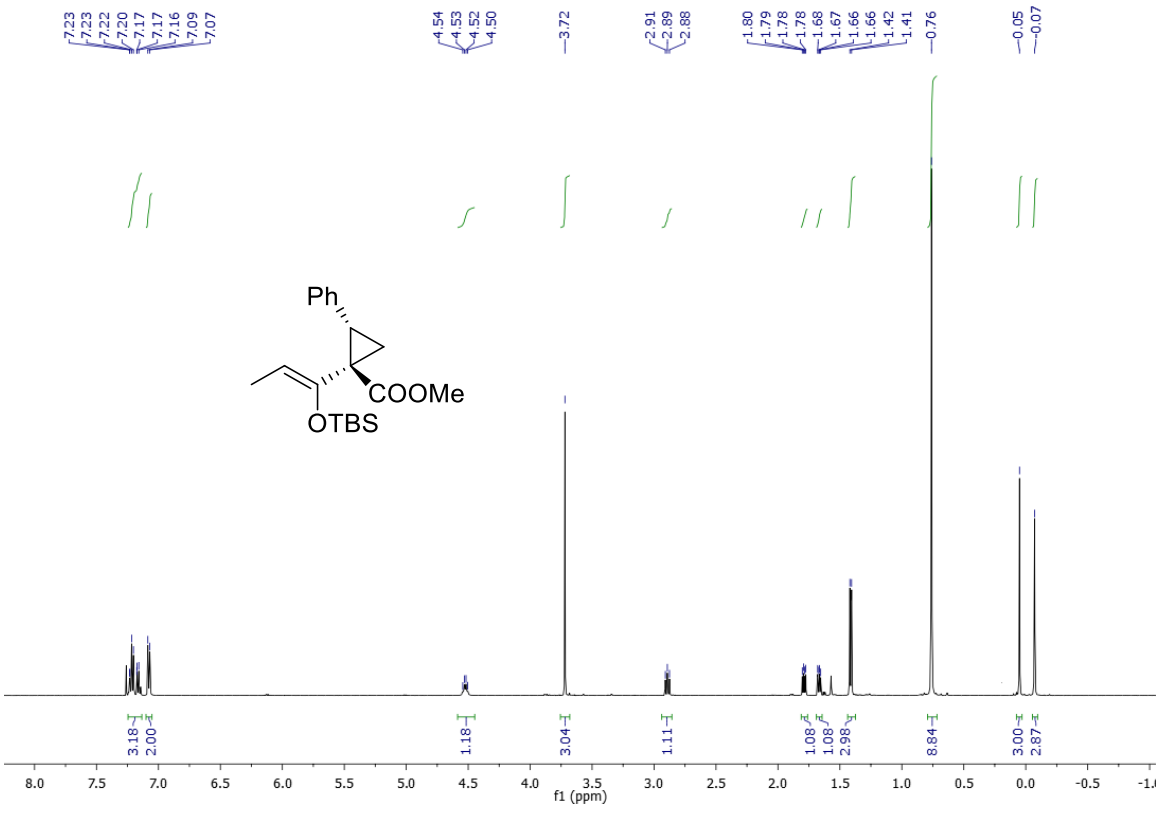
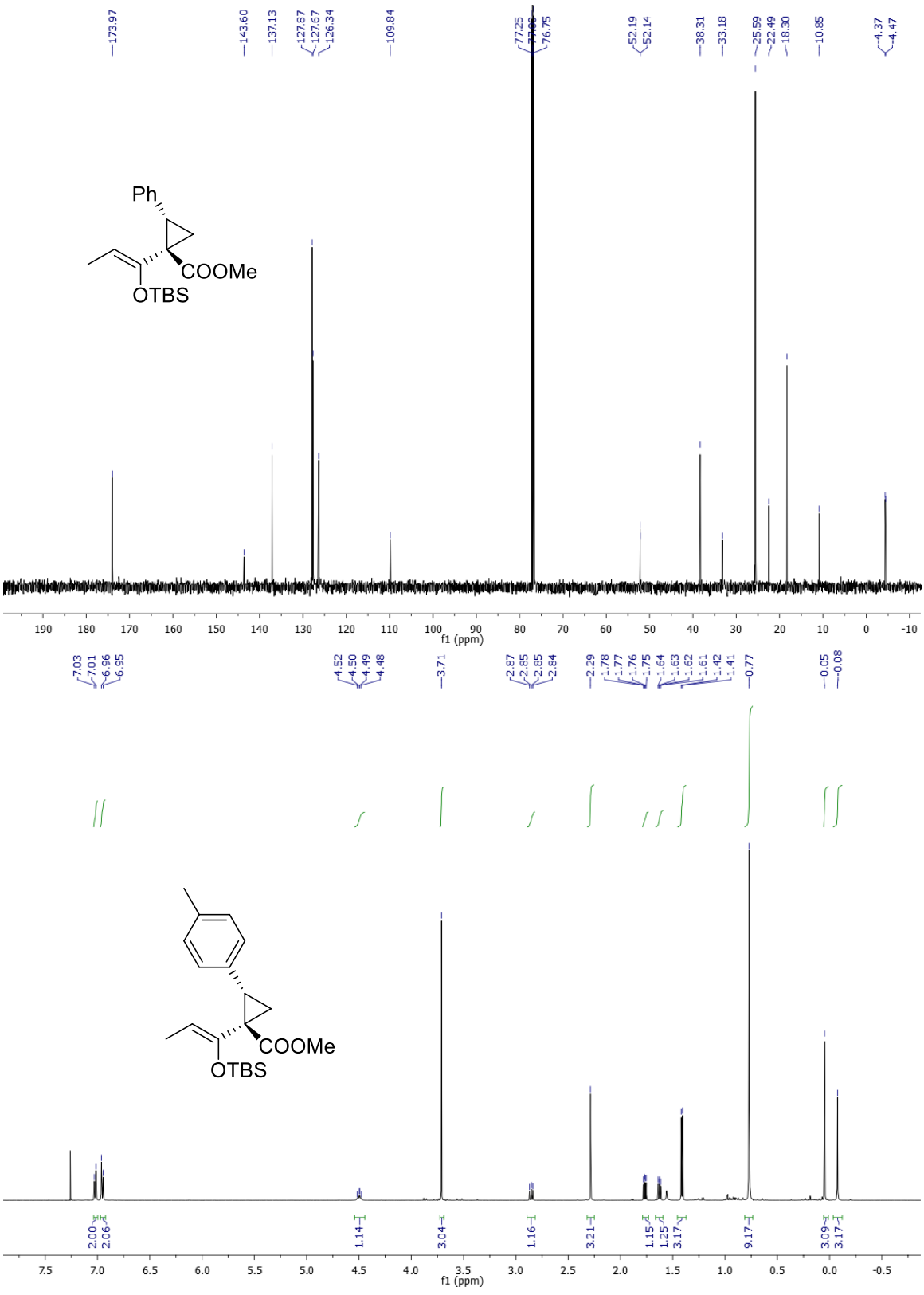
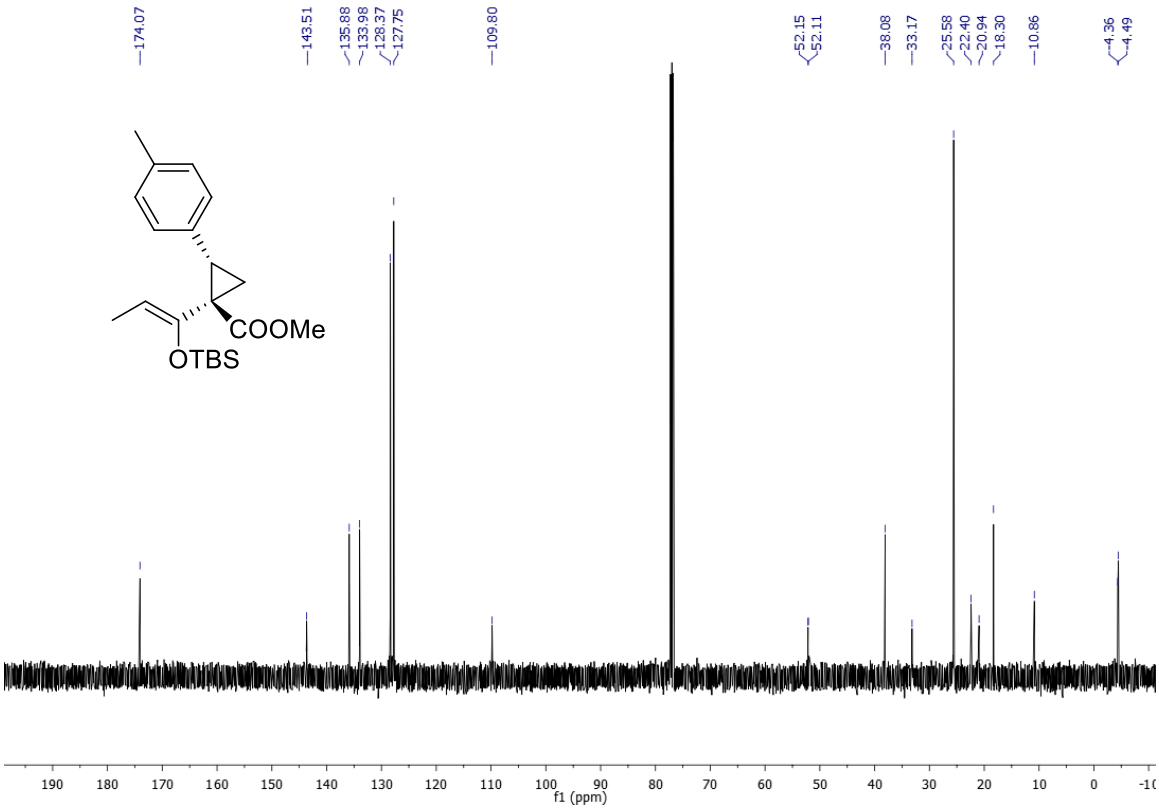
7.74
7.73
7.72
7.46
7.45
7.44
7.44
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
0.89
-0.16
O
OTBS
BnO
Ph
N
N
H
1.95
7.90
2.00
9.02
5.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

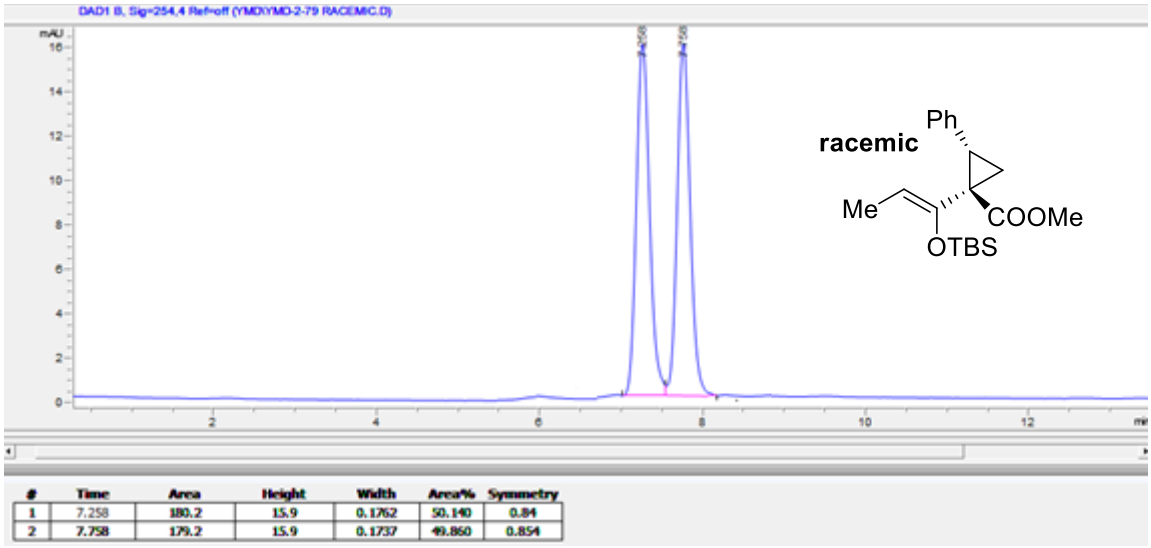

187.91
159.37
139.25
135.26
131.18
128.92
128.62
128.57
128.36
128.07
127.50
66.62
25.53
18.01
-4.86
O
OTBS
BnO
Ph
N
N
H
f1 (ppm)


7.23
7.23
7.22
7.20
7.17
7.17
7.16
7.09
7.07
4.54
4.53
4.52
4.50
3.72
2.91
2.89
2.88
1.80
1.79
1.78
1.78
1.68
1.67
1.66
1.66
1.42
1.41
0.76
0.05
0.07
Ph
COOMe
OTBS
3.18
2.00
1.18
3.04
1.11
1.08
1.08
2.98
8.84
3.00
2.87
f1 (ppm)

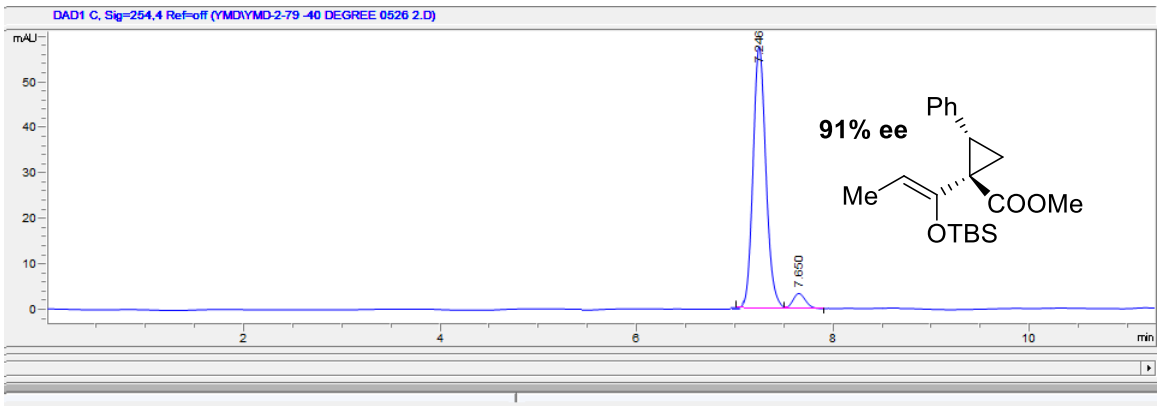

Ph
COOMe
OTBS
COOMe
OTBS
f1 (ppm)
f1 (ppm)



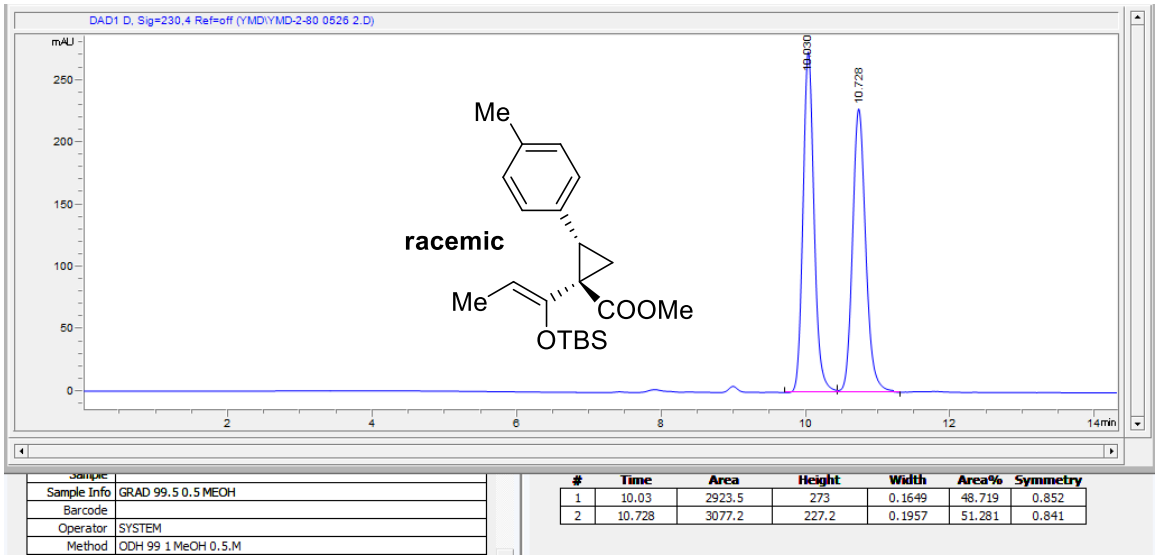
HPLC Analyses of 7 and 8



#	Time	Area	Height	Width	Area%	Symmetry
1	7.258	180.2	15.9	0.1762	50.140	0.84
2	7.758	179.2	15.9	0.1737	49.860	0.854

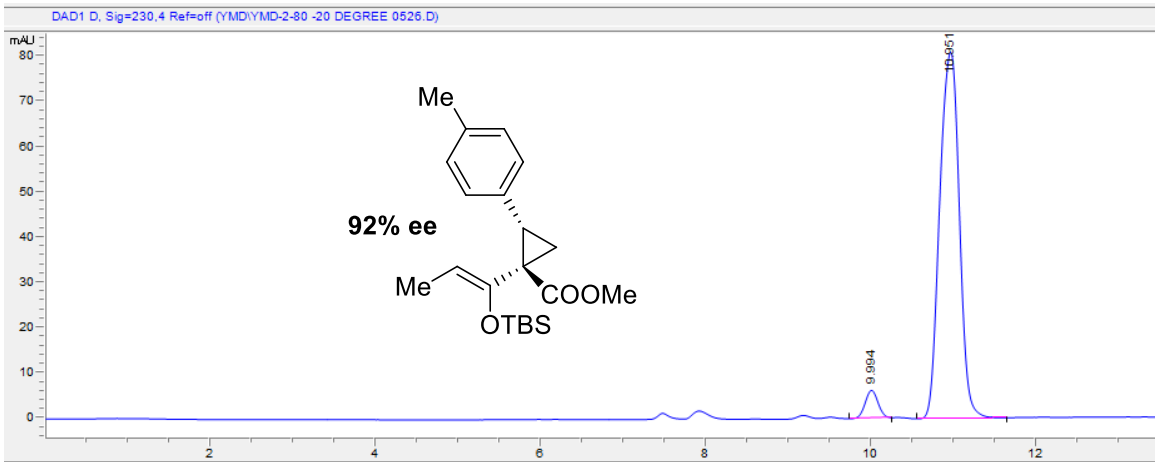


#	Time	Area	Height	Width	Area%	Symmetry
1	7.246	29.7	3.3	0.152	95.380	0.874
2	7.653	1.4	1.8E-1	0.1304	4.620	0.915



Sample Info	GRAD 99.5 0.5 MEOH
Barcode	
Operator	SYSTEM
Method	ODH 99 1 MeOH 0.5.M

#	Time	Area	Height	Width	Area%	Symmetry
1	10.03	2923.5	273	0.1649	48.719	0.852
2	10.728	3077.2	227.2	0.1957	51.281	0.841



Sample	
Sample Info	GRAD 99.5 0.5 MEOH
Barcode	
Operator	SYSTEM

#	Time	Area	Height	Width	Area%	Symmetry
1	9.994	66	6.1	0.1695	3.991	0.956
2	10.951	1588.5	81	0.2676	96.009	1.177