# Supporting Information

# Stereoselective Synthesis of Fused Vinylcyclopropanes by Intramolecular Tsuji-Trost Cascade Cyclization

John Braun,[a] Maxim I. Ariëns,[a] Bianca T. Matsuo,[a] Steven de Vries,[a] Ellen D. H. van Wordragen,[a] Brecht D. Ellenbroek,[a] Christophe M. L. Vande Velde,[b] Romano V. A. Orru[a] and Eelco Ruijter*[a]

[a] *Department of Chemistry & Pharmaceutical Sciences and Amsterdam Institute for Molecules, Medicines & Systems (AIMMS), Vrije Universiteit Amsterdam, De Boelelaan 1108, 1081 HZ Amsterdam, The Netherlands*

[b] *Faculty of Applied Engineering, Advanced Reactor Technology, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium*

Email: e.ruijter@vu.nl

# Contents

# General information

Commercially available reagents were purchased from Sigma-Aldrich, Fischer, Strem Chemicals or Fluorochem and were used as purchased unless mentioned otherwise. Solvents were purchased from VWR Chemicals or Sigma-Aldrich and used without purification, unless stated otherwise. Anhydrous, air-free solvents were obtained from a PureSolv MD 5 solvent purification system. Infrared (IR) spectra were recorded neat using a Shimadzu FTIR-8400s spectrophotometer and wavelengths are reported in $cm^{-1}$. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600 (150.90 MHz for $^{13}C$), Bruker Avance 500 (125.78 MHz for $^{13}C$) or Bruker Avance 300 () using the residual $CHCl_3$ as internal standard ($^{1}H$: δ 7.26 ppm, $^{13}C\{^{1}H\}$: δ 77.16 ppm). Chemical shifts (δ) are given in ppm and coupling constants (*J*) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet), br (broad singlet) and m (multiplet) or combinations thereof. Electrospray Ionization (ESI) high-resolution mass spectrometry was carried out using a Bruker micrOTOF-Q instrument in positive ion mode (capillary potential of 4500 V). Flash chromatography was performed on Silicycle Silica-P Flash Silica Gel (particle size 40-63 µm, pore diameter 60 Å) using the indicated eluent. Thin Layer Chromatography (TLC) was performed using TLC plates from Merck ($SiO_2$, Kieselgel 60 F254 neutral, on aluminium with fluorescence indicator) and compounds were visualized by UV detection (254 nm) and/or $KMnO_4$ stain. SFC-MS analysis was conducted using a Shimadzu Nexera SFC-MS equipped with a Nexera X2 SIL-30AC autosampler, Nexera UC LC-30AD SF $CO_2$ pump, Nexera X2 LC-30AD liquid chromatograph, Nexera UC SFC-30A back pressure regulator, prominence SPD-M20A diode array detector, prominence CTO-20AC column oven and CBM-20A system controller. Enantiomeric excess was determined by SFC-MS analysis using a Lux® 3 µm Cellulose-3 column (cellulose tris(4-methylbenzoate), 150 x 4.6 mm). A gradient of supercritical $CO_2$ (A) and methanol (B) was used. Method 1: 0% B/100% A → 30% B/70% A over the course of 15 min. and was maintained at 30% B/70% A for 2 min. Method 2: 0% B/100% A → 20% B/80% A over the course of 15 min. and was maintained at 20% B/80% A for 2 min. Method 3: 0% B/100% A → 30% B/70% A over the course of 20 min. and was maintained at 30% B/70% A for 2 min. Method 4: 0% B/100% A → 20% B/80% A over the course of 20 min. and was maintained at 20% B/80% A for 2 min. The flow was maintained at 1.0 mL/min and the sample injection volume was 5 µL. Mass spectrometry analyses were performed using a Shimadzu LCMS-2020 mass spectrometer. The data were acquired in full-scan APCI mode (MS) from *m/z* 100 to 800 in positive ionisation mode. Data was processed using Shimadzu Labsolutions 5.82. Specific rotations were measured with an automatic AA-10 polarimeter.

# General procedures

**Procedure A: Appel reaction of allylic alcohol to allylic bromide**

The corresponding allylic alcohol (1.0 equiv) was dissolved in anhydrous $CH_2Cl_2$ (0.24 M) and cooled to 0 °C. Subsequently, tetrabromomethane (1.1 equiv) and triphenylphosphine (1.1 equiv) were added and the reaction mixture was stirred for 3 h at 0 °C. The reaction mixture was concentrated and purified by silica gel column chromatography as described in the corresponding synthetic procedure**.**

**Procedure B: Formation of allylic amine ($S_N2$ substitution of the allylic bromide)**

To a suspension of the corresponding amine (2.0 equiv) and cesium carbonate (2.0 equiv) in anhydrous DMF (0.2 M) was added a solution of the corresponding allylic bromide (1.0 equiv) in anhydrous DMF (1.0 M). The reaction mixture was heated to 65 °C and was stirred for 2 h. The reaction mixture was diluted with EtOAc and washed with sat. aq. $NaHCO_3$ (5×), dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The crude was used directly in the next reaction without purification.

**Procedure C: Amide formation from allylic amine and ester**

To a solution of the corresponding allylic amine (1.0 equiv) in dry toluene (0.2 M) was added 4-dimethylaminopyridine (0.2 equiv) and the corresponding ester (1.2 equiv). The reaction mixture was heated to 80 °C and was stirred for 16 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography as described in the corresponding synthetic procedure.

**Procedure D: Amide formation from allylic amine and carboxylic acid**

To a solution of the corresponding allylic amine (1.0 equiv) in dry $CH_2Cl_2$ (0.1 M) at 0 °C was added 4-dimethylaminopyridine (0.1 equiv), EDC·HCl (1.3 equiv) and the corresponding carboxylic acid (1.3 equiv). The reaction mixture was stirred overnight at room temperature. The organic layer was washed with $H_2O$ (3x) and brine, and the organic layer was dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography as described in the corresponding synthetic procedure.

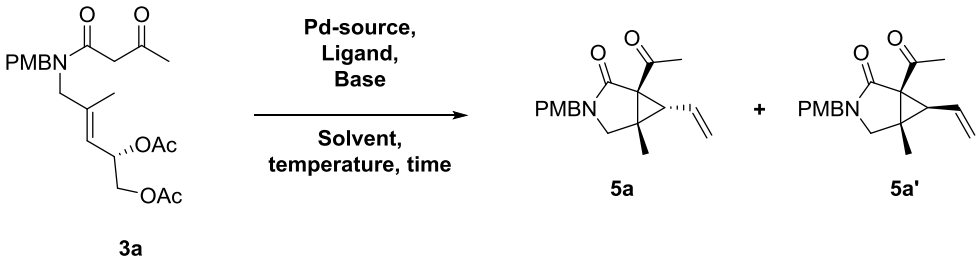
**Procedure E: Acetal deprotection**

The corresponding acetal protected diol (1.0 equiv) was dissolved in THF (0.8 M) and an aqueous solution of AcOH (80% v/v, 44 equiv) was added. The reaction mixture was stirred at 65 °C for 12 h. The reaction mixture was concentrated and co-evaporated with toluene (3x). The crude product (1.0 equiv) was subsequently dissolved in pyridine (0.2 M) and acetic anhydride (2.3 equiv) was added dropwise. The reaction mixture was stirred overnight at room temperature. The reaction mixture was concentrated and co-evaporated with toluene (3x). The crude product was purified by silica gel column chromatography as described in the corresponding synthetic procedure.

**Procedure F: Tsuji-Trost cascade cyclization**

To a flamedried flask, containing a solution of the corresponding diacetate (1.0 equiv) in anhydrous and degassed DMF (0.1 M) was added $Pd(PPh_3)_4$ (0.1 equiv) and *N*,*N*,*N*,*N*'-tetramethylguanidine (2.0 equiv). The reaction mixture was heated to 80 °C and stirred for 5 - 8 h. The reaction mixture was cooled to room temperature, diluted with EtOAc and quenched with sat. aq. $NH_4Cl$ solution. The organic phase was washed with sat. aq. $NH_4Cl$ (2x) and brine, dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography as described in the corresponding synthetic procedure.

# Optimization of the Tsuji-Trost cyclization cascade



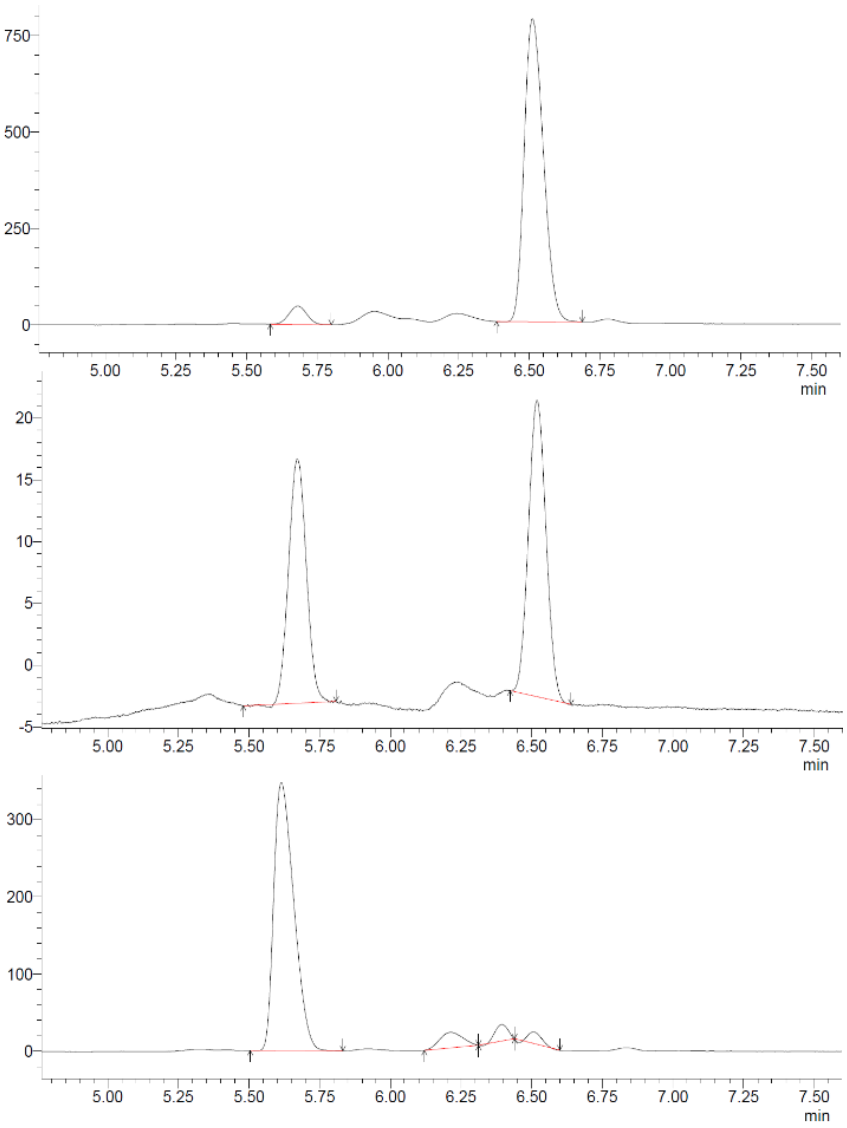

**Optimization table**[a]

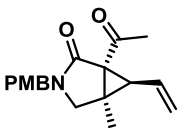
| | Pd-source | ligand | base | solvent | temp. (°C) | time (h) | Yield[b] (%) | *dr* (5a / 5a') |
|---|---|---|---|---|---|---|---|---|
| 1 | $Pd(PPh_3)_4$ | - | DBU | PhMe | 20 | 16 | 0[c] | |
| 2 | $Pd(PPh_3)_4$ | - | DBU | PhMe | 80 | 16 | 52 | 3 : 1 |
| 3 | $Pd(PPh_3)_4$ | - | DBU | THF | 65 | 16 | 45 | 3 : 1 |
| 4 | $Pd(PPh_3)_4$ | - | DBU | $CH_2Cl_2$ | 40 | 16 | 45 | 3 : 1 |
| 5 | $Pd(PPh_3)_4$ | - | DBU | $C_2H_4Cl_2$ | 85 | 16 | 40 | 3 : 1 |
| 6 | $Pd(PPh_3)_4$ | - | DBU | DMF | 80 | 16 | 65 | 9 : 1 |
| 7 | $Pd(OAc)_2$ | $PPh_3$ | DBU | DMF | 80 | 16 | 65 | 9 : 1 |
| 8 | $Pd(OAc)_2$ | XantPhos | DBU | DMF | 80 | 16 | 0[c] | |
| 9 | $Pd(OAc)_2$ | DPEPhos | DBU | DMF | 80 | 16 | 35 | 3 : 7 |
| **10** | **$Pd(PPh_3)_4$** | **-** | **TMG** | **DMF** | **80** | **5** | **75** | **9 : 1** |
| 11 | $Pd(PPh_3)_4$ | - | TMG | THF | 80 | 16 | 45 | 3 : 1 |
| 12 | $Pd(PPh_3)_4$ | - | TMG | $CH_2Cl_2$ | 80 | 16 | 45 | 3 : 1 |

[a] Reaction conditions: **3a** (0.2 mmol, 1.0 equiv), Pd-source (0.02 mmol, 10 mol%), ligand (monodentate ligand: 0.10 mmol, 50 mol% / bidentate ligand: 0.05 mmol, 25mol%), solvent (0.2 M). [b] Isolated yield. [c] No conversion.

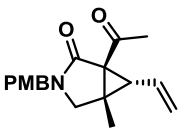
# Structural analysis of vinylcyclopropanes

## SFC-MS analysis of enantiomeric excess



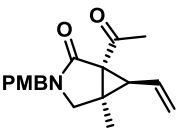




***ent*-5a**

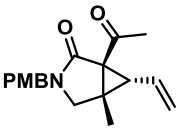



**5a**

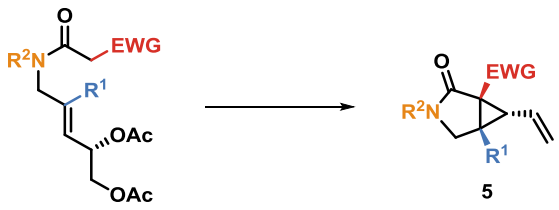
\+

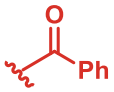
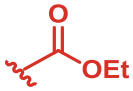



**ent-5a**




**5a**

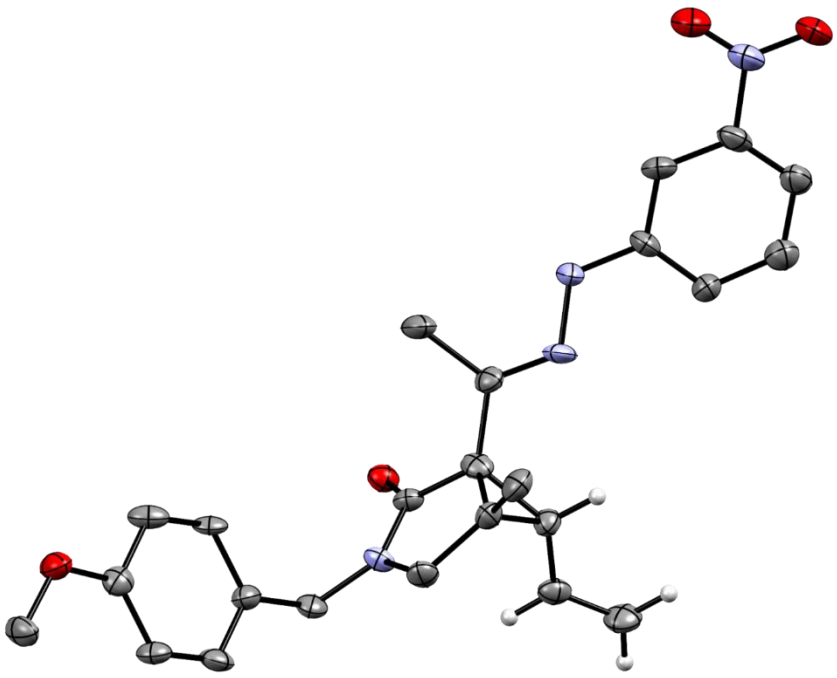



| | $R^2$ | $R^1$ | EWG | ee **3** (%) | ee **5** (%) | es (%) |
|---|---|---|---|---|---|---|
| **a** | PMB | Me |  | 92 | 90 | 98 |
| **b** | PMB | Me |  | 87 | 89 | >99 |
| **c** | PMB | Me |  | 100 | 96 | 96 |
| **d** | PMB | Me |  | 97 | 93 | 96 |
| **g** | Me | Me |  | 95 | 89 | 94 |
| **h** | *i*-Pr | Me |  | 94 | 89 | 95 |
| **i** | PMB | Et |  | 90 | 88 | 98 |

## X-ray analysis

Crystals of (**7**) suitable for x-ray diffraction were grown by slow evaporation from ethanol solution. A fragment of a needle 0.11 x 0.06 x 0.04 mm was mounted on a kapton loop and flash-cooled in the 106K cold stream on the Agilent SuperNova diffractometer with Cu K(α) microsource, mirror monochromator and Atlas CCD detector. Data were collected via w scans, up to 75.337° in q, and were reduced and corrected for absorption with CrysAlisPro, Agilent Technologies, Version 1.171.38.41r (Rigaku OD, 2015). The structure was solved with SHELXT-2017/1 and refined with SHELXL-2017/1 and the ShelxLE graphical interface.[1] All other details of the crystallographic experiment and refinement can be found under CSD reference nr. 1856030, which is available for download at the Cambridge Crystallographic Data Centre.

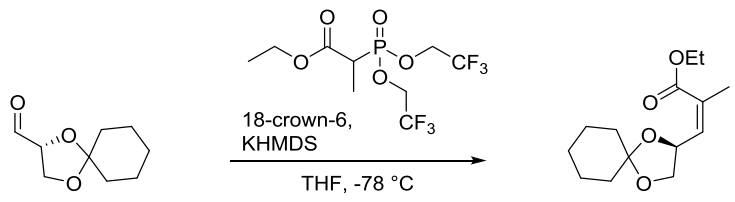
The structure is monoclinic, space group $P2_1$, with two independent molecules in the asymmetric unit. Both symmetry independent molecules display a hydrogen bond with the hydrazone H as donor, and the amide oxygen as acceptor. Even though they are stereochemically identical, and very similar in conformation, there is no crystallographic symmetry between them.



# Synthetic procedures

## Esters

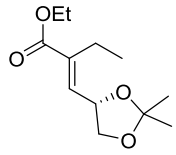
**ethyl (*S,Z*)-2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)acrylate (S01)**




**S01**

A solution of ethyl 2-[bis(2,2,2-trifluoroethoxy)phosphoryl]propanoate (1.5 g, 4.33 mmol, 1.1 equiv) and 18-crown-6 (5.2 g, 19.7 mmol, 5.0 equiv) in THF (100 mL) was cooled to -78 °C after which a 1 M solution of KHMDS in THF (4.0 mL, 4.0 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred for 30 min. at -78 °C and a solution of 2,3-O-cyclohexylidene-D-glyceraldehyde (804 mg, 4.73 mmol, 1.2 equiv) in THF (5 mL) was added dropwise at -78 °C. The reaction mixture was stirred for 1 h at -78 °C, after which the reaction mixture was quenched by the addition of a sat. aq. $NH_4Cl$ solution. The reaction mixture was extracted with $Et_2O$ (3x) and the combined organic phases were dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (1% → 5% EtOAc/cHex), providing the title compound as a colorless oil in 58% yield (590 mg, 2.32 mmol). $\mathbf{R_F}$ = 0.4 (EtOAc/cHex = 1:9). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 6.07 (d, *J* = 7.0 Hz, 1H), 5.26 (q, *J* = 7.0 Hz, 1H), 4.29 (t, *J* = 7.4 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.59 (t, *J* = 7.5 Hz, 1H), 1.92 (s, 3H), 1.70 – 1.53 (m, 8H), 1.46 – 1.36 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 167.17, 142.66, 129.43, 110.21, 73.77, 69.41, 60.79, 36.44, 35.15, 25.31, 24.00, 20.15, 14.37. **IR (neat)**: υmax ($cm^{-1}$): 2933, 2862, 2341, 1716, 1656, 1450, 1367, 1342, 2339, 1207, 1099, 1070, 1041, 929. **HRMS (ESI)**: m/z calculated for $C_{14}H_{22}O_4Na^+$ ($[M+Na]^+$) = 277.1410, found = 277.1396. $\mathbf{[\alpha]_D^{20}}$ = + 62.86 (c = 1.05, $CHCl_3$).

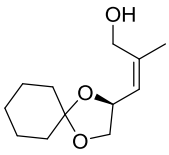
**ethyl (*S*,*E*)-2-((2,2-dimethyl-1,3-dioxolan-4-yl)methylene)butanoate (S02)**



Ethyl 2-bromobutyrate (18 mL, 122 mmol, 1.2 equiv) was added to a suspension of $PPh_3$ (26.7 g, 102 mmol, 1.0 equiv) in $H_2O$ (100 mL). The reaction mixture was stirred at 100 °C for 16 h after which the reaction mixture was cooled to room temperature and extracted with $CH_2Cl_2$ (3x 20 mL). The organic phases were dried ($Na_2SO_4$) and concentrated under reduced pressure. The crude phosphonium bromide intermediate (18.4 g, 40.5 mmol, 1.0 equiv) was subsequently dissolved in anhydrous THF (200 mL) and cooled to 0 °C after which KO*t*Bu (4.1 g, 36.5 mmol, 0.90 equiv) was added in portions. The reaction mixture was stirred for 1 h at 0 °C after which a solution of (*R*)-(+)-2,2-dimethyl-1,3-dioxolane-4-carboxaldehyde (5 g, 38.5 mmol, 0.95 equiv) in $CH_2Cl_2$ (10 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature. The reaction was quenched by addition of sat. aq. $NH_4Cl$ solution (20 mL) and the reaction mixture was stirred for 10 min. at room temperature, diluted with EtOAc (50 mL) and transferred to a separation funnel. The aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organics were washed with brine, dried ($Na_2SO_4$) and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (2% → 10% EtOAc/cHex) which provided the title compound in 36% yield (3.28 g, 14.4 mmol). $\mathbf{R_F}$ = 0.7 (EtOAc/cHex = 1:9). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 6.62 (d, *J* = 8.3 Hz, 1H), 4.85 (ddd, *J* = 8.4, 7.7, 6.2 Hz, 1H), 4.25 – 4.17 (m, 2H), 4.14 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.63 (t, *J* = 7.9 Hz, 1H), 2.41 – 2.28 (m, 2H), 1.45 (s, 3H), 1.41 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 167.12, 137.61, 137.59, 109.99, 72.60, 69.19, 60.91, 26.78, 26.01, 20.86, 14.69, 14.36. **IR (neat):** vmax ($cm^{-1}$): 2983, 1712, 1369, 1305, 1271, 1232, 1213, 1141, 1114, 1056, 1029. **HRMS (ESI)**: *m/z* calculated for $C_{12}H_{20}O_4Na$ $[M+Na]^+$ = 251.1254, found = 251.1254. $\mathbf{[\alpha]_D^{20}}$ = + 15.7 (c = 3.95, $CHCl_3$).

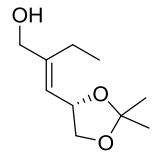
## Alcohols

**(*S,Z*)-2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)prop-2-en-1-ol (S03)**



Allylic ester **S01** (590 mg, 2.32 mmol, 1.0 equiv) was dissolved in anhydrous THF (0.3 M) and the reaction mixture was cooled to 0 °C after which a solution of DIBAL-H (1.0 M in heptane, 5.1 mL, 5.1 mmol 2.2 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was cooled to 0 °C, quenched by the dropwise addition of MeOH (20 mL) and stirred for 3 h at room temperature. The white suspension was filtered over Celite® and the residue was washed with MeOH. The filtrate was concentrated under reduced pressure after which the title compound was obtained as a colorless liquid in 97% yield (480 mg, 2.26 mmol). The product was directly used in the next reaction without purification. $\mathbf{R_F}$ = 0.3 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.34 (d, *J* = 8.1 Hz, 1H), 4.86 (q, *J* = 7.5 Hz, 1H), 4.17 (dd, *J* = 68.7, 13.7 Hz, 2H), 4.06 (t, *J* = 7.0 Hz, 1H), 3.53 (t, *J* = 8.0 Hz, 1H), 1.84 (s, 3H), 1.67 – 1.33 (m, 10H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 141.38, 125.49, 109.94, 71.84, 69.52, 62.18, 36.54, 35.62, 25.24, 24.12, 24.05, 21.88. **IR (neat)**: υmax ($cm^{-1}$): 3380, 2910, 2551, 1550, 1432, 1344, 1250, 1190, 1080, 1050, 1030, 910. **HRMS (ESI)**: m/z calculated for $C_{12}H_{20}NaO_3$ ($[M+Na]^+$) = 235.1305, found = 235.1305.

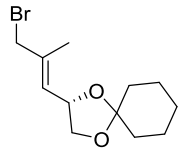
**(*S,E*)-2-((2,2-dimethyl-1,3-dioxolan-4-yl)methylene)butan-1-ol (S04)**



Allylic ester **S02** (3.28 g, 14.4 mmol, 1.0 equiv) was dissolved in anhydrous THF (70 mL) and the reaction mixture was cooled to 0 °C after which a solution of DIBAL-H (1.0 M in heptane, 35 mL, 35 mmol 2.4 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was cooled to 0 °C, quenched by the dropwise addition of MeOH (100 mL) and stirred for 3 h at room temperature. The white suspension was filtered over Celite® and the residue was extracted with MeOH. The filtrate was concentrated under reduced pressure after which the title compound was obtained as a colorless liquid in 96% yield (2.56 g, 13.8 mmol). The product was directly used in the next reaction without purification. $\mathbf{R_F}$ = 0.2 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.44 (d, *J* = 8.7 Hz, 1H), 4.83 (td, *J* = 8.4, 6.0 Hz, 1H), 4.10 – 4.04 (m, 3H), 3.55 (t, *J* = 8.1 Hz, 1H), 2.26 – 2.16 (m, 1H), 2.16 – 2.08 (m, 1H), 1.42 (s, 3H), 1.41 (s, 3H), 1.03 (t, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 146.98, 121.92, 109.22, 72.31, 69.70, 65.83, 26.92, 26.16, 21.73, 14.19. **HRMS (ESI)**: *m/z* calculated for $C_{10}H_{18}O_3Na$ $[M+Na]^+$ = 209.1148, found = 209.1155. **$[\alpha]_D^{20}$** = + 16.00 (c = 0.50, $CHCl_3$).

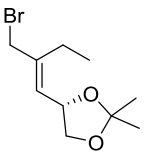
## Bromides

**(*S*,*E*)-2-(3-bromo-2-methylprop-1-en-1-yl)-1,4-dioxaspiro[4.5]decane (S05)**



Allylic alcohol **6** (3.85 g, 18.2 mmol, 1.0 equiv) – as prepared according to literature procedure reported by Kiyotsuka *et al.*[2] – was used in general procedure A. After TLC analysis indicated complete conversion, the reaction mixture was concentrated and the crude product was purified by silica gel column chromatography (1% EtOAc/cHex), providing the pure product as a colorless liquid in 94% yield (4.7 g, 17.2 mmol). The product appears relatively unstable and is often used directly without purification in the next steps. $\mathbf{R_F}$ = 0.2 (EtOAc/cHex = 3:97). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.61 (d, *J* = 8.3 Hz, 1H), 4.75 (td, *J* = 8.0, 6.1 Hz, 1H), 4.09 (dd, *J* = 8.1, 6.1 Hz, 1H), 3.96 – 3.91 (m, 2H), 3.54 (t, *J* = 7.9 Hz, 1H), 1.85 (d, *J* = 1.3 Hz, 3H), 1.66 – 1.59 (m, 10H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.13, 128.69, 110.30, 72.69, 68.99, 40.08, 36.65, 35.77, 25.44, 24.29, 24.22, 15.66. **IR (neat)**: νmax ($cm^{-1}$): 2933, 2858, 2358, 2345, 2327, 1448, 1382, 1365, 1330, 1280, 1249, 1230, 1209, 1163, 1103, 1068, 1041, 1004, 929. **HRMS (ESI)**: calculated for $C_{12}H_{19}BrNaO_2$ ($[M+Na]^+$) = 297.0461, found = 297.0462. $\mathbf{[\alpha]_D^{20}}$ = + 46.0 (c = 1.00, $CHCl_3$).

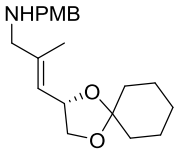
**(*S*,*E*)-4-(2-(bromomethyl)but-1-en-1-yl)-2,2-dimethyl-1,3-dioxolane (S06)**



Allylic alcohol **S04** (2.56 g, 13.8 mmol) was used in general procedure A. After TLC analysis indicated complete conversion, the reaction mixture was concentrated and the crude product was purified by silica gel column chromatography (1% EtOAc/cHex), providing the pure product as a colorless liquid in 91% yield (3.84 g, 12.6 mmol). $\mathbf{R_F}$ = 0.75 (EtOAc/cHex = 1:9). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.57 (d, *J* = 8.5 Hz, 1H), 4.83 – 4.71 (m, 1H), 4.08 (dd, *J* = 8.2, 6.1 Hz, 1H), 3.98 (q, *J* = 10.3 Hz, 2H), 3.54 (t, *J* = 8.0 Hz, 1H), 2.37 – 2.22 (m, 2H), 1.42 (s, 3H), 1.40 (s, 3H), 1.06 (t, *J*= 7.6 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 142.86, 128.08, 109.49, 72.47, 69.35, 37.19, 26.88, 26.05, 22.15, 13.60. **IR (neat):** νmax ($cm^{-1}$): 1712, 1436, 1380, 1311, 1245, 1157, 1118, 1085, 1070, 1043, 1026, 1012.

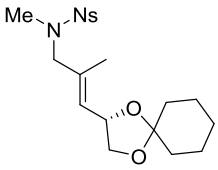
## Amines

**(*S*,*E*)-*N*-(4-methoxybenzyl)-2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)prop-2-en-1-amine (S07)**



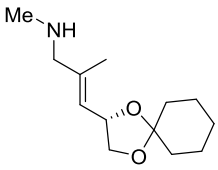

Allylic bromide **S05** (4.7 g, 17.2 mmol, 1.0 equiv) was used in general procedure B, providing the pure title compound as a yellow oil in 91% yield (5.18 g, 15.6 mmol). $\mathbf{R_F}$ = 0.3 (EtOAc/cHex = 9:1). The NMR spectra contain double alkylated amine as a minor impurity (7.4 mol%). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.43 – 5.37 (m, 1H), 4.83 (td, *J* = 8.3, 6.0 Hz, 1H), 4.06 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 2H), 3.51 (t, *J* = 8.1 Hz, 1H), 3.17 (s, 2H), 1.75 (d, *J* = 1.2 Hz, 3H), 1.67 – 1.53 (m, 10H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 158.95, 139.94, 132.63 , 129.68, 123.63, 114.09, 109.86, 72.74, 69.38, 56.60, 55.61, 52.85, 36.73, 35.94, 25.49, 24.31, 24.25, 15.87. **IR (neat)**: νmax ($cm^{-1}$): 2935, 2862, 2852, 2837, 1610, 1512, 1463, 1448, 1363, 1299, 1278, 1245, 1172, 1163, 1105, 1070, 1035, 931, 908, 846, 829. **HRMS (ESI)**: calculated for $C_{20}H_{30}NO_3$ ($[M+H]^+$) = 332.2220, found = 332.2227. $\mathbf{[\alpha]_D^{20}}$ = + 4.85 (c = 1.65, $CHCl_3$).

**(*S*,*E*)-*N*-methyl-*N*-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-4-nitrobenzenesulfonamide (S08)**



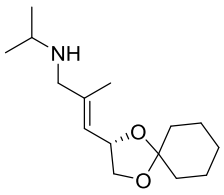

A solution of *N*-methyl-4-nitrobenzenesulfonamide (393 mg, 1.82 mmol, 1.0 equiv) in anhydrous THF (5 mL) was cooled to 0 °C. NaH (110 mg, 60 wt%, 2.73 mmol, 1.5 equiv) was added portionwise, after which the reaction mixture was allowed to warm to room temperature. After 30 minutes, the reaction mixture was cooled to 0 °C and a solution of allylic bromide **S05** (500 mg, 1.82 mmol, 1.0 equiv) in anhydrous THF (2 mL) was added dropwise. The reaction mixture was stirred at room temperature for 6 h, after which TLC analysis indicated complete conversion. The reaction mixture was diluted with EtOAc and washed with sat. aq. $NH_4Cl$, sat. aq. $NaHCO_3$ and brine. The organic phase was dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The crude product was directly used in the next reaction. $\mathbf{R_F}$ = 0.4 (EtOAc/cHex = 2:3). **$^1$H NMR** (300 MHz, $CDCl_3$) δ 8.44 – 8.29 (m, 2H), 8.10 – 7.89 (m, 2H), 5.61 (dd, *J* = 8.5, 1.5 Hz, 1H), 4.87 – 4.65 (m, 2H), 4.12 – 4.03 (m, 1H), 3.93 (s, 2H), 3.59 – 3.49 (m, 1H), 2.73 (s, 1H), 2.72 (s, 2H), 1.84 (s, 1H), 1.83 (s, 2H), 1.72 – 1.50 (m, 10H). Some rotameric signals were observed.

**(*S*,*E*)-*N*,2-dimethyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)prop-2-en-1-amine (S09)**



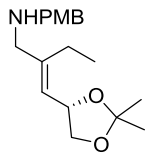

To a solution of crude **S08** (theor. 1.82 mmol, 1.0 equiv) in DMF (5 mL) was added $Cs_2CO_3$ (2.37 g, 7.28 mmol, 4.0 equiv) and thiophenol (0.4 mL, 3.7 mmol, 2.0 equiv). The reaction mixture was stirred overnight at room temperature and subsequently filtered and concentrated under reduced pressure. The crude product was used directly in the next reaction. $\mathbf{R_F}$ = 0.1 (EtOAc/cHex = 2:3).

**(*S,E*)-*N*-isopropyl-2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)prop-2-en-1-amine (S10)**



To a suspension of isopropylamine (1.3 mL, 14.6 mmol, 2.0 equiv) and cesium carbonate (4.8 g, 14.6 mmol, 2.0 equiv) in dry DMF (70 mL) was added a solution of allylic bromide **S05** (2 g,7.3 mmol, 1.0 equiv) in dry DMF (5 mL). The reaction mixture was heated to 65 °C and was stirred for 3 h. The reaction mixture was diluted with EtOAc (100 mL) and washed with sat. aq. $NaHCO_3$ (2×), dried ($Na_2SO_4$), filtered and concentrated under reduced pressure affording the crude title compound in 54% yield (1.00 g, 3.95 mmol). The crude product was used directly in the next reaction. $\mathbf{R_F}$ = 0.2 (EtOAc/cHex = 2:3). **$^1$H NMR** (300 MHz, $CDCl_3$) δ 5.38 (d, *J* = 8.5, 1.5 Hz, 1H), 4.82 (q, *J* = 8.3, 6.0 Hz, 1H), 4.05 (dd, *J* = 8.0, 5.9 Hz, 1H), 3.51 (t, *J* = 8.1 Hz, 1H), 3.17 (s, 2H), 2.85 – 2.68 (m, 1H), 1.75 (s, 3H), 1.61 (s, 11H), 1.06 (d, *J* = 6.2 Hz, 6H). **IR (neat):** vmax ($cm^{-1}$): 2931, 2862, 1672, 1448, 1363, 1332, 1278, 1249, 1230, 1141, 1163, 1099, 1068, 1039, 1020. **HRMS (ESI):** *m/z* calculated for $C_{15}H_{28}NO_2^+$ $[M+H]^+$ 254.2108, found: 254.2124. $\mathbf{[\alpha]_D^{20}}$ = + 7.16 (c = 1.68, $CHCl_3$).

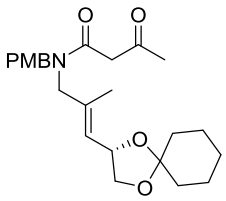
**(*S,E*)-2-((2,2-dimethyl-1,3-dioxolan-4-yl)methylene)-*N*-(4-methoxybenzyl)butan-1-amine (S11)**



To a suspension of 4-methoxybenzylamine (3.5 mL, 25.2 mmol, 2.0 equiv) and cesium carbonate (8.2 g, 25.2 mmol, 2.0 equiv) in anhydrous DMF (80 mL) was added a solution of allylic bromide **S06** (3.84 g, 12.6 mmol, 1.0 equiv) in dry DMF (10 mL). The reaction mixture was heated to 65 °C and was stirred for 3 h. The reaction mixture was cooled to room temperature, diluted with EtOAc (100 mL) and washed with sat. aq. $NaHCO_3$ (5×), dried ($Na_2SO_4$), filtered and concentrated under reduced pressure affording the crude title compound in 87% yield (3.31 g, 10.95 mmol). The crude product was used directly in the next reaction. $\mathbf{R_F}$ = 0.50 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.7, 7.1 Hz, 2H), 6.96 – 6.83 (m, 2H), 5.37 (dd, *J* = 8.7, 1.4 Hz, 1H), 4.84 (td, *J* = 8.4, 5.9 Hz, 1H), 4.05 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.81 – 3.77 (m, 3H), 3.73 – 3.67 (m, 2H), 3.53 (t, *J* = 8.1 Hz, 1H), 3.21 (s, 2H), 2.24 – 2.10 (m, 2H), 1.43 (s, 3H), 1.40 (s, 3H), 1.01 (t, *J* = 7.6 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 132.66, 129.92, 129.39, 129.28, 122.38, 114.08, 113.88, 109.06, 72.63, 69.79, 64.53, 55.40, 53.94, 52.82, 26.98, 26.20, 22.87, 14.24. **IR (neat):** vmax ($cm^{-1}$): 2952, 1610, 1510, 1454, 1442, 1369, 1299, 1244, 1211, 1174, 1155, 1054, 1033. **HRMS (ESI)**: *m/z* calculated for $C_{18}H_{28}NO_3$ $[M+H]^+$ = 306.2064, found = 306.2074. $\mathbf{[\alpha]_D^{20}}$= + 7.67 (c = 4.95, $CHCl_3$).

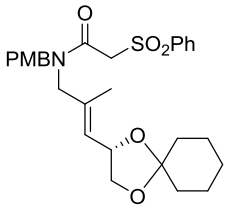
## Acetals

**(*S,E*)-*N*-(4-methoxybenzyl)-*N*-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-3-oxobutanamide (S12)**



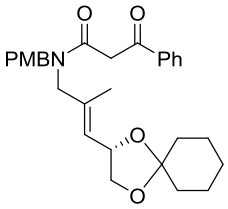
Allylic amine **S07** (5.18 g, 15.6 mmol, 1.0 equiv) was used in general procedure C using ethyl acetoacetate. The crude product was purified by silica gel column chromatography (30% → 45% EtOAc/cHex) providing the title compound as yellow oil in 89% yield (5.78 g, 13.9 mmol). $\mathbf{R_F}$ = 0.7 (EtOAc/cHex = 4:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.23 – 6.99 (m, 2H), 6.96 – 6.77 (m, 2H), 5.25 (d, *J* = 8.1 Hz, 1H), 4.81 (td, *J* = 8.0, 6.0 Hz, 1H), 4.64 – 4.24 (m, 2H), 4.09 – 4.03 (m, 1H), 3.81 – 3.77 (m, 3H), 3.67 (s, 1H), 3.56 (m, 1H), 3.47 (m, 1H), 2.27 (m, 2H), 1.68 – 1.30 (m, 10H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.10, 134.99, 129.57, 128.93, 127.64, 125.95, 124.20, 114.47, 114.09, 110.00, 109.81, 72.32, 72.11, 69.03, 55.45, 55.39, 53.50, 51.56, 50.16, 49.74, 48.08, 36.47, 35.64, 25.21, 24.00, 15.09, 14.33. Multiple rotameric signals were observed. **IR (neat)**: νmax ($cm^{-1}$): 2931, 2860, 1718, 1633, 1612, 1585, 1512, 1487, 1446, 1419, 1384, 1361, 1330, 1301, 1278, 1244, 1207, 1161, 1099, 1070, 1031, 927, 910, 846, 825, 754, 607, 541. **HRMS (ESI)**: calculated for $C_{24}H_{33}NO_5Na$ ($[M+Na]^+$) = 438.2251, found = 438.2247. $\mathbf{[\alpha]_D^{20}}$ = + 9.14 (c = 1.75, $CHCl_3$).

**(*S,E*)-*N*-(4-methoxybenzyl)-N-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-2-(phenylsulfonyl)acetamide (S13)**



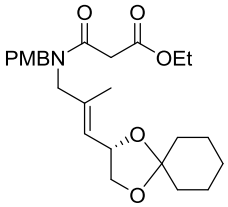
Prepared from allylic amine **S07** (506 mg, 1.50 mmol, 1.0 equiv) and (phenylsulfonyl)acetic acid (300 mg, 1.95 mmol, 1.3 equiv), according to general procedure D. Purification of the crude material by silica gel column chromatography (30% EtOAc/cHex) afforded the title compound as a yellow oil in 86% yield (658 mg, 1.28 mmol). $\mathbf{R_F}$ = 0.55 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 21.6, 7.8 Hz, 2H), 7.72 – 7.51 (m, 3H), 7.19 – 7.01 (m, 2H), 6.92 – 6.78 (m, 2H), 5.30 (dd, *J* = 97.8, 8.3 Hz, 1H), 4.82 (dq, *J* = 15.3, 7.7, 7.2 Hz, 1H), 4.72 – 4.60 (m, 1H), 4.46 (dd, *J* = 54.3, 14.3 Hz, 1H), 4.25 – 4.15 (m, 2H), 4.13 – 4.00 (m, 1H), 3.99 – 3.86 (m, 2H), 3.84 – 3.75 (m, 3H), 3.48 (dt, *J* = 50.6, 8.0 Hz, 1H), 1.73 – 1.66 (m, 3H), 1.66 – 1.32 (m, 10H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.25, 162.12, 159.38, 159.21, 138.89, 138.77, 135.20, 134.81, 134.35, 129.51, 129.26, 129.24, 128.64, 128.63, 128.47, 127.47, 127.44, 124.12, 114.62, 114.12, 110.01, 109.89, 72.33, 72.03, 69.08, 68.98, 60.02, 59.93, 55.45, 55.40, 53.70, 52.28, 50.22, 48.82, 36.43, 35.66, 35.58, 25.23, 25.18, 24.08, 24.02, 23.96, 15.27, 14.86. Multiple rotameric signals were observed. **IR (neat)**: νmax ($cm^{-1}$): 2931, 2858, 1649, 1612, 1512, 1446, 1363, 1321, 1247, 1155, 1101, 1033, 927. **HRMS (ESI)**: *m/z* calculated for $C_{28}H_{35}NO_6SNa^+$ $[M+Na]^+$ 536.2077, found: 536.2073. $\mathbf{[\alpha]_D^{20}}$ = + 13.15 (c = 0.76, $CHCl_3$).

**(*S,E*)-*N*-(4-methoxybenzyl)-*N*-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-3-oxo-3-phenylpropanamide (S14)**



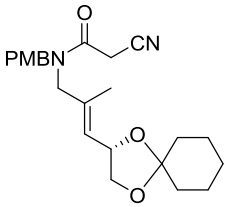

Prepared from allylic amine **S07** (990 mg, 3.0 mmol, 1.0 equiv) and ethyl benzoylacetate (0.6 mL, 3.6 mmol, 1.2 equiv), according to general procedure C. Purification of the crude material by silica gel column chromatography (30% EtOAc/cHex) afforded the title compound as a yellow oil in 75% yield (1.08 g, 2.26 mmol). $\mathbf{R_F}$ = 0.80 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 15.25 (d, *J* = 9.0 Hz, 0.3H), 7.98 (dd, *J* = 23.2, 7.8 Hz, 1H), 7.81 – 7.69 (m, 1H), 7.59 (q, *J* = 8.0 Hz, 1H), 7.52 – 7.33 (m, 2H), 7.21 (dd, *J* = 8.3, 5.9 Hz, 1H), 7.11 (dd, *J* = 28.4, 8.2 Hz, 1H), 6.87 (dd, *J* = 20.3, 8.2 Hz, 2H), 5.87 (s, 0.2H), 5.72 (s, 0.2H), 5.36 (d, *J* = 8.5 Hz, 0H), 5.29 (d, *J* = 8.0 Hz, 1H), 4.82 (p, *J* = 8.0 Hz, 1H), 4.73 – 4.32 (m, 2H), 4.20 – 3.88 (m, 3H), 3.84 – 3.78 (m, 3H), 3.75 (s, 1H), 3.52 – 3.41 (m, 1H), 1.72 – 1.69 (m, 3H), 1.61 (q, *J* = 14.0, 11.9 Hz, 10H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 194.09, 194.01, 172.73, 172.66, 172.05, 171.84, 167.86, 167.65, 159.16, 159.10, 159.01, 158.94, 136.17, 136.08, 136.02, 135.93, 135.19, 134.91, 134.79, 133.76, 130.77, 130.74, 129.53, 129.40, 128.78, 128.75, 128.69, 128.61, 128.45, 127.87, 127.62, 125.99, 125.98, 125.73, 125.37, 124.91, 124.07, 114.36, 114.28, 113.97, 109.88, 109.67, 84.99, 84.80, 72.27, 72.22, 72.03, 68.97, 68.90, 55.35, 55.28, 53.53, 53.24, 51.52, 51.13, 49.74, 49.12, 48.01, 47.74, 45.97, 45.76, 36.37, 36.29, 35.57, 35.51, 25.15, 25.11, 23.98, 23.97, 23.90, 15.02, 14.94, 14.89, 14.64. Multiple rotameric and tautomeric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2931, 2858, 2364, 2331, 1623, 1614, 1573, 1512, 1479, 1446, 1375, 1247, 1217, 1174, 1101, 1033, 927. **HRMS (ESI):** *m/z* calculated for $C_{29}H_{35}NO_5Na^+$ $[M+Na]^+$ 500.2407, found: 500.2395. $\mathbf{[\alpha]_D^{20}}$ = + 10.64 (c = 0.47, $CHCl_3$).

**ethyl (*S,E*)-3-((4-methoxybenzyl)(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)amino)-3-oxopropanoate (S15)**



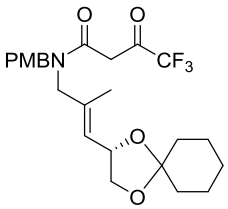

To a solution of allylic amine **S07** (500 mg, 1.50 mmol, 1.0 equiv) in anhydrous $CH_2Cl_2$ (15 mL) was added $Et_3N$ (313 µL, 2.25 mmol, 1.5 equiv) and 4-dimethylaminopyridine (18 mg, 0.15 mmol, 0.1 equiv). The reaction mixture was cooled to 0 °C and ethyl malonyl chloride (230 µL, 1.80 mmol, 1.2 equiv) was added, after which the reaction mixture was stirred overnight at room temperature. TLC analysis indicated complete conversion and the reaction mixture was concentrated to ± 5 mL, diluted with EtOAc (20 mL) and washed with sat. aq. $NH_4Cl$ (3x) and brine. The organic layer was dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (30% EtOAc/cHex) providing the title compound as a yellow oil in 97% yield (646 mg, 1.45 mmol). $\mathbf{R_F}$ = 0.75 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 58.4, 8.2 Hz, 2H), 6.84 (dd, *J* = 22.1, 8.2 Hz, 2H), 5.29 – 5.21 (m, 1H), 4.80 (q, *J* = 7.6 Hz, 1H), 4.48 (dd, *J* = 101.5, 14.4 Hz, 1H), 4.45 – 4.22 (m, 1H), 4.18 (p, *J* = 6.9 Hz, 2H), 4.09 – 3.85 (m, 2H), 3.79 (s, 1H), 3.77 (s, 2H), 3.68 (s, 1H), 3.52 – 3.40 (m, 3H), 1.71 – 1.62 (m, 3H), 1.62 – 1.33 (m, 10H), 1.26 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 167.69, 166.95, 166.78, 159.27, 159.05, 135.82, 134.79, 129.54, 128.89, 127.67, 125.88, 124.41, 114.43, 114.00, 109.97, 109.75, 72.30, 72.05, 69.01, 68.95, 61.64, 55.33, 53.51, 51.48, 49.73, 47.95, 41.44, 41.26, 36.41, 36.40, 35.60, 35.56, 25.19, 25.17, 23.96, 23.95, 15.03, 14.70, 14.20, 14.13. **IR (neat):** vmax ($cm^{-1}$): 2931, 1733, 1647, 1512, 1446, 1245, 1161, 1099, 1031, 927. Rotameric signals were observed. **HRMS (ESI):** *m/z* calculated for $C_{25}H_{35}NO_6Na^+$ $[M+Na]^+$ 468.2356, found: 468.2356. $\mathbf{[\alpha]_D^{20}}$ = + 8.00 (c = 1.00, $CHCl_3$).

**(*S,E*)-2-cyano-*N*-(4-methoxybenzyl)-*N*-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)acetamide (S16)**



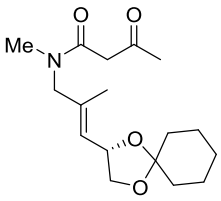
Prepared from allylic amine **S07** (662 mg, 2.0 mmol, 1.0 equiv) and cyanoacetic acid (221 mg, 2.6 mmol, 1.3 equiv), according to general procedure D. Purification of the crude material by silica gel column chromatography (35% EtOAc/cHex) afforded the title compound as a yellow oil in 90% yield (713 mg, 1.79 mmol). $\mathbf{R_F}$ = 0.60 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 162.6, 8.2 Hz, 2H), 6.98 (dd, *J* = 73.5, 8.1 Hz, 2H), 5.25 (d, *J* = 8.3 Hz, 1H), 4.80 (q, *J* = 7.5 Hz, 1H), 4.63 – 4.29 (m, 2H), 4.09 – 3.96 (m, 2H), 3.80 (s, 1H), 3.79 (s, 2H), 3.70 (s, 1H), 3.52 – 3.45 (m, 3H), 1.74 – 1.64 (m, 3H), 1.63 – 1.25 (m, 10H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.51, 162.48, 159.51, 159.35, 135.15, 134.09, 129.98, 128.17, 127.39, 126.71, 126.63, 124.63, 114.76, 114.18, 114.04, 110.14, 109.93, 72.17, 71.90, 68.96, 68.90, 55.49, 55.41, 53.48, 52.74, 49.79, 49.08, 36.42, 36.40, 35.58, 35.54, 25.43, 25.19, 25.17, 25.14, 24.05, 24.03, 23.97, 15.16, 14.89. Multiple rotameric signals were observed. **IR (neat):** νmax ($cm^{-1}$): 2933, 1658, 1512, 1446, 1247, 1176, 1163, 1107, 1033, 927. **HRMS (ESI):** *m/z* calculated for $C_{23}H_{30}N_2O_4Na^+$ $[M+Na]^+$ 421.2098, found: 421.2096. $\mathbf{[\alpha]_D^{20}}$ = + 4.22 (c = 0.71, $CHCl_3$).

**(*S,E*)-4,4,4-trifluoro-*N*-(4-methoxybenzyl)-*N*-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-3-oxobutanamide (S17)**



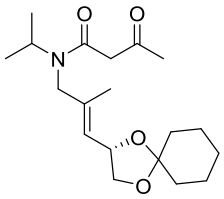
Prepared from allylic amine **S07** (990 mg, 3.0 mmol, 1.0 equiv) and methyl 4,4,4-trifluoroacetoacetate (460 µL, 3.6 mmol, 1.2 equiv), according to Procedure C. Purification of the crude material by silica gel column chromatography (20% EtOAc/cHex) afforded the title compound as a yellow oil in 95% yield (1.34 g, 2.86 mmol). $\mathbf{R_F}$ = 0.30 (EtOAc/cHex = 1:4). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 15.21 (s, 0.2H), 7.17 (dd, *J* = 11.5, 8.3 Hz, 1H), 7.11 – 7.03 (m, 1H), 6.92 – 6.84 (m, 2H), 5.91 (s, 0.2H), 5.83 (s, 0.2H), 5.66 – 5.60 (m, 0.4H), 5.50 (s, 0.2H), 5.32 – 5.25 (m, 1H), 4.81 (q, *J* = 7.9 Hz, 1H), 4.66 (dd, *J* = 47.0, 14.6 Hz, 0.5H), 4.51 – 4.33 (m, 1.2H), 4.09 – 4.04 (m, 1H), 4.00 – 3.91 (m, 0.4H), 3.81 (s, 1H), 3.80 (s, 2H), 3.74 (d, *J* = 7.1 Hz, 1H), 3.52 – 3.46 (m, 1H), 2.83 (q, *J* = 15.1 Hz, 0.4H), 2.72 (s, 0.4H), 1.70 – 1.63 (m, 3H), 1.63 – 1.51 (m, 10H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 171.51, 171.27, 171.22, 159.52, 159.50, 159.40, 159.34, 134.99, 134.84, 134.11, 134.08, 129.83, 129.62, 128.22, 128.16, 128.02, 127.81, 127.04, 126.55, 126.24, 125.76, 124.89, 123.64, 121.37, 120.02, 117.78, 114.61, 114.57, 114.25, 110.10, 109.96, 72.25, 72.22, 72.03, 69.03, 69.00, 68.94, 68.88, 55.46, 55.41, 53.26, 53.18, 51.79, 51.37, 49.85, 49.24, 48.46, 48.06, 36.48, 36.42, 35.62, 35.56, 33.51, 33.34, 25.22, 24.09, 24.00, 23.99, 15.07, 15.01, 14.83. Multiple rotameric and tautomeric signals were observed. **IR (neat)**: νmax ($cm^{-1}$): 2933, 1612, 1512, 1448, 1282, 1247, 1174, 1099, 1031, 925, 908. **HRMS (ESI)**: *m/z* calculated for $C_{24}H_{30}NO_5F_3Na^+$ $[M+Na]^+$ 492.1968, found: 492.1964. $\mathbf{[\alpha]_D^{20}}$ = + 14.5 (c = 1.93, $CHCl_3$).

**(*S,E*)-*N*-methyl-N-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-3-oxobutanamide (S18)**



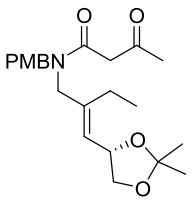
Crude allylic amine **S09** (theor. 1.82 mmol, 1.0 equiv) was used in general procedure C using ethyl acetoacetate. The crude product was purified by silica gel column chromatography (50% → 80% EtOAc/cHex) providing the title compound as a yellow oil in 20% yield (115 mg, 0.37 mmol) over 3 steps. $\mathbf{R_F}$ = 0.15 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 14.70 (d, *J* = 64.2 Hz, 0.2H), 5.35 – 5.22 (m, 1H), 4.80 (q, *J* = 7.4 Hz, 1H), 4.06 (dd, *J* = 8.1, 6.0 Hz, 1H), 3.97 (dd, *J* = 48.0, 14.4 Hz, 1H), 3.78 (s, 1H), 3.59 (s, 1H), 3.53 – 3.44 (m, 2H), 2.91 (s, 1H), 2.86 (s, 2H), 2.27 (d, *J* = 4.5 Hz, 3H), 1.68 – 1.64 (m, 3H), 1.64 – 1.17 (m, 10H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 202.60 ($C_q$), 202.35 ($C_q$), 167.18 ($C_q$), 166.90 ($C_q$), 135.96 ($C_q$), 135.08 ($C_q$), 125.90 (CH), 124.45 (CH), 110.02 ($C_q$), 109.83 ($C_q$), 72.34 (CH), 72.09 (CH), 69.08 ($CH_2$), 69.02 ($CH_2$), 57.05 ($CH_2$), 54.13 ($CH_2$), 36.46 ($CH_2$), 35.61 ($CH_2$), 35.09 ($CH_3$), 34.13 ($CH_3$), 30.41 ($CH_3$), 25.23 ($CH_2$), 25.20 ($CH_2$), 24.08 ($CH_2$), 24.05 ($CH_2$), 23.99 ($CH_2$), 14.91 ($CH_3$), 14.58 ($CH_3$). The NMR spectra contain 18 mol% of enol tautomer and multiple rotameric signals. **IR (neat):** vmax ($cm^{-1}$): 2941, 2925, 2858, 1720, 1639, 1631, 1575, 1514, 1475, 1440, 1334, 1163, 1095, 1024, 927. **HRMS (ESI)**: calculated for $C_{17}H_{27}NO_4Na$ ($[M+Na]^+$) = 332.1832, found = 332.1823. $\mathbf{[\alpha]_D^{20}}$ = + 7.8 (c = 1.28, $CHCl_3$).

**(*S,E*)-N-isopropyl-*N*-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-3-oxobutanamide (S19)**



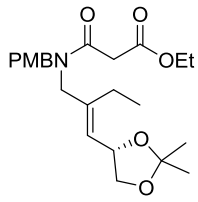
The crude allylic amine **S10** (1.0 g, 3.95 mmol, 1.0 equiv) was subjected to general procedure C using ethyl acetoacetate. The crude material was purified by silica gel column chromatography (30% → 40% EtOAc/cHex) providing the pure title compound as a yellow oil in 61% yield (815 mg, 2.41 mmol). $\mathbf{R_F}$ = 0.55 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.33 – 5.18 (m, 1H), 4.86 – 4.66 (m, 2H), 4.05 (dt, *J* = 8.1, 5.5 Hz, 1H), 4.01 – 3.74 (m, 1H), 3.62 (dd, *J* = 9.1, 5.1 Hz, 2H), 3.50 – 3.45 (m, 1H), 3.45 – 3.31 (m, 1H), 2.26 (d, *J* = 15.2 Hz, 2H), 1.70 (d, *J* = 3.9 Hz, 3H), 1.59 (m, 10H), 1.17 (d, *J* = 6.6 Hz, 2H), 1.09 (dd, *J* = 17.6, 6.8 Hz, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 203.09, 167.70, 137.25, 136.58, 123.75, 123.05, 109.97, 109.61, 72.45, 72.18, 69.05, 68.97, 50.71, 50.66, 49.98, 49.09, 46.83, 45.97, 36.47, 35.67, 25.28, 25.22, 24.07, 24.04, 24.02, 21.29, 21.19, 20.15, 20.04, 15.35, 15.07. Multiple rotameric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2933, 1718, 1631, 1587, 1099. **HRMS (ESI):** *m/z* calculated for $C_{19}H_{31}NO_4Na^+[M+Na]^+$ 360.2137, found: 360.2150. $\mathbf{[\alpha]_D^{20}}$ = + 10.43 (c = 1.15, $CHCl_3$).

**(*S*,*E*)-*N*-(2-((2,2-dimethyl-1,3-dioxolan-4-yl)methylene)butyl)-*N*-(4-methoxybenzyl)-3-oxobutanamide (S20)**



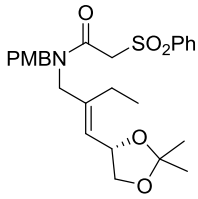
Allylic amine **S11** (1.02 g, 3.34 mmol, 1.0 equiv) was used in general procedure C using ethyl acetoacetate. After purification by silica gel column chromatography (10% → 50% EtOAc/cHex), the title compound and the starting material were isolated as a yellow oil in 41% yield (357 mg, 1.08 mmol) and 21% yield (218 mg, 0.71 mmol, 21%), respectively. $\mathbf{R_F}$ = 0.50 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 14.76 (s, 0.14H), 14.71 (s, 0.14H), 7.22 – 7.03 (m, 2H), 6.92 – 6.80 (m, 2H), 5.39 – 5.15 (m, 1H), 4.82 (tt, *J* = 8.3, 5.6 Hz, 1H), 4.63 – 4.36 (m, 2H), 4.32 (m, 1H), 4.12 – 3.94 (m, 2H), 3.81 – 3.78 (m, 3H), 3.74 – 3.65 (m, 1H), 3.59 (s, 1H), 3.55 – 3.44 (m, 2H), 2.28 (s, 1H), 2.26 (s, 1H), 2.17 – 1.96 (m, 2H), 1.94 (d, *J* = 6.8 Hz, 1H), 1.56 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.06 – 0.96 (m, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 202.56, 167.57, 167.30, 159.37, 159.23, 141.84, 141.15, 129.64, 129.07, 127.97, 127.65, 124.52, 123.13, 122.56, 122.40, 114.57, 114.20, 113.90, 109.47, 109.28, 87.07, 72.49, 72.24, 69.64, 55.43, 53.94, 52.83, 51.17, 50.08, 49.27, 48.81, 48.30, 47.41, 30.52, 30.45, 26.99, 26.16, 26.12, 22.68, 22.25, 22.16, 14.09, 14.02. Multiple rotameric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2979, 2937, 1722, 1635, 1612, 1585, 1512, 1488, 1440, 1417, 1369, 1301, 1244, 1211, 1174, 1155, 1110, 1054, 1031. **HRMS (ESI)**: *m/z* calculated for $C_{22}H_{32}O_5N$ $[M+H]^+$ = 390.2275, found = 390.2271. $\mathbf{[\alpha]_D^{20}}$ = + 9.41 (c = 0.85, $CHCl_3$).

**ethyl (*S*,*E*)-3-((2-((2,2-dimethyl-1,3-dioxolan-4-yl)methylene)butyl)(4-methoxybenzyl)amino)-3-oxopropanoate (S21)**



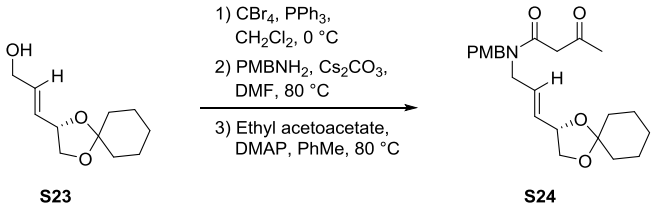
To a solution of allylic amine **S11** (1.3 g, 4.26 mmol, 1.0 equiv) in anhydrous $CH_2Cl_2$ (50 mL) was added $Et_3N$ (0.89 mL, 6.39 mmol, 1.5 equiv) and 4-dimethylaminopyridine (52 mg, 0.43 mmol, 0.1 equiv). The reaction mixture was cooled to 0 °C and ethyl malonyl chloride (0.65 mL, 5.11 mmol, 1.2 equiv) was added, after which the reaction mixture was stirred overnight at room temperature. TLC analysis indicated complete conversion and the reaction mixture was concentrated to ± 5 mL, diluted with EtOAc (50 mL) and washed with sat. aq. $NH_4Cl$ (3x) and brine. The organic layer was dried ($Na_2SO_4$), filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (5% → 50% EtOAc/cHex) providing the title compound as a yellow oil in 65% yield (1.19 g, 2.8 mmol). $\mathbf{R_F}$ = 0.70 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.24 – 7.01 (m, 2H), 6.94 – 6.76 (m, 2H), 5.29 – 5.11 (m, 1H), 4.87 – 4.77 (m, 1H), 4.67 – 4.33 (m, 2H), 4.20 (dq, *J* = 8.4, 7.1 Hz, 2H), 4.10 – 3.99 (m, 2H), 3.83 – 3.78 (m, 4H), 3.75 – 3.72 (m, 1H), 3.53 – 3.46 (m, 2H), 3.42 (d, *J* = 2.1 Hz, 1H), 2.18 – 1.93 (m, 2H), 1.60 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.28 (td, *J* = 7.1, 1.3 Hz, 3H), 1.06 – 0.90 (m, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 167.75, 167.70, 167.25, 167.01, 166.71, 165.77, 164.50, 160.99, 160.33, 159.36, 159.22, 159.19, 141.92, 140.99, 129.63, 129.32, 129.09, 128.51, 127.84, 127.71, 126.18, 125.04, 122.76, 114.54, 114.12, 109.46, 109.23, 108.88, 88.35, 72.51, 72.23, 69.69, 69.62, 61.67, 61.36, 60.53, 55.41, 51.15, 49.77, 49.18, 48.20, 46.16, 46.04, 41.54, 41.29, 39.09, 26.97, 26.16, 22.63, 22.12, 21.19, 14.28, 14.02. Multiple rotameric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2983, 1735, 1649, 1612, 1512, 1442, 1417, 1369, 1321, 1301, 1245, 1213, 1174, 1155, 1108, 1054, 1027. **HRMS (ESI)**: *m/z* calculated for $C_{23}H_{34}O_6N$ $[M+H]^+$ = 420.2381, found = 420.2384. $\mathbf{[\alpha]_D^{20}}$ = + 7.38 (c = 1.63, $CHCl_3$).

**(*S*,*E*)-*N*-(2-((2,2-dimethyl-1,3-dioxolan-4-yl)methylene)butyl)-*N*-(4-methoxybenzyl)-2-(phenylsulfonyl)acetamide (S22)**



Prepared from allylic amine **S11** (990 mg, 3.25 mmol, 1.0 equiv) and (phenylsulfonyl)acetic acid (844 mg, 4.22 mmol, 1.3 equiv), according to general procedure D. Purification of the crude material by silica gel column chromatography (10% → 50% EtOAc/cHex) afforded the title compound as a yellow oil in 61% yield (962 mg, 1.98 mmol). $\mathbf{R_F}$ = 0.20 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.99 – 7.83 (m, 2H), 7.72 – 7.65 (m, 1H), 7.62 – 7.51 (m, 2H), 7.19 – 7.02 (m, 2H), 6.94 – 6.84 (m, 2H), 5.42 – 5.09 (m, 1H), 4.89 – 4.77 (m, 1H), 4.66 (s, 1H), 4.48 (dd, *J* = 78.4, 15.6 Hz, 1H), 4.25 – 4.07 (m, 2H), 4.06 – 3.96 (m, 3H), 3.82 – 3.80 (m, 3H), 3.64 – 3.38 (m, 1H), 2.22 – 1.94 (m, 2H), 1.57 (s, 3H), 1.46 – 1.37 (m, 6H), 1.07 – 1.00 (m, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 162.36, 162.11, 159.48, 159.34, 141.19, 141.10, 139.01, 138.94, 134.38, 129.61, 129.29, 128.67, 128.60, 127.61, 127.52, 124.87, 122.55, 114.71, 114.22, 109.48, 109.38, 72.51, 72.19, 69.73, 69.61, 60.14, 55.46, 51.43, 50.26, 49.98, 49.06, 26.97, 26.20, 26.12, 22.82, 22.19, 14.00, 13.96. Multiple rotameric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2985, 2343, 1649, 1612, 1512, 1446, 1419, 1371, 1321, 1309, 1245, 1222, 1176, 1085, 1054, 1027. **HRMS (ESI)**: *m/z* calculated for $C_{26}H_{34}O_6NS$ $[M+H]^+$ = 488.2101, found = 488.2102. $\mathbf{[\alpha]_D^{20}}$ = + 6.25 (c = 1.60, $CHCl_3$).

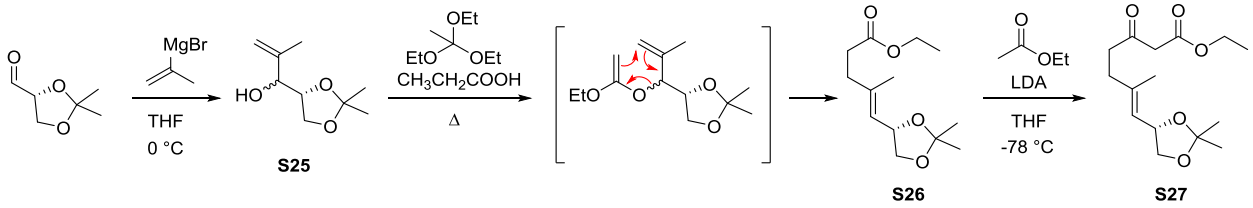
**(*S*,*E*)-*N*-(3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-*N*-(4-methoxybenzyl)-3-oxobutanamide (S24)**



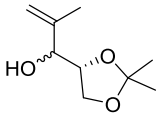

**S23** **S24**

Allylic alcohol **S23** (366 mg, 1.87 mmol, 1.0 equiv) was prepared as reported by Iwabuchi *et al.*[3] and subjected to general procedure A, affording the pure allylic bromide in 60% yield (296 mg, 1.13 mmol) after silica gel column chromatography (1% → 8% EtOAc/cHex). $\mathbf{R_F}$ = 0.7 (EtOAc/cHex = 3:7). **$^1$H NMR** (300 MHz, $CDCl_3$) δ 6.09 – 5.93 (m, 1H), 5.75 (dd, *J* = 15.2, 7.1 Hz, 1H), 4.53 (q, *J* = 6.9 Hz, 1H), 4.10 (dd, *J* = 8.2, 6.2 Hz, 1H), 4.03 – 3.86 (m, 2H), 3.60 (t, *J* = 7.8 Hz, 1H), 1.70 – 1.31 (m, 10H). The allylic bromide (296 mg, 1.13 mmol) was subsequently used in general procedure B, providing the crude allylic amine (331 mg, *theor.* 1.04 mmol, 92%) which was directly converted to the allylic amide in general procedure C using ethyl acetoacetate. Purification of the crude material by silica gel column chromatography (5% → 65% EtOAc/cHex) afforded the title compound as a yellow oil in 45% yield (187 mg, 0.47 mmol). $\mathbf{R_F}$ = 0.3 (EtOAc/cHex = 2:3). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.20 – 7.05 (m, 2H), 6.90 – 6.81 (m, 2H), 5.78 – 5.62 (m, 1H), 5.60 – 5.49 (m, 1H), 4.57 – 4.44 (m, 3H), 4.41 – 4.35 (m, 1H), 4.09 – 4.02 (m, 1H), 4.00 – 3.95 (m, 1H), 3.80 (s, 1H), 3.79 (s, 2H), 3.58 – 3.54 (m, 1H), 3.54 – 3.49 (m, 1H), 2.28 (s, 1H), 2.26 (s, 1H), 1.96 – 1.90 (m, 1H), 1.68 (s, 1H), 1.64 – 1.34 (m, 10H). Multiple rotameric and keto-enol signals were observed. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 202.59, 202.49, 167.01, 159.35, 159.16, 131.58, 131.03, 130.75, 129.63, 128.98, 128.25, 127.93, 127.90, 127.81, 114.49, 114.31, 114.13, 114.07, 110.33, 110.12, 87.10, 76.08, 75.84, 75.74, 69.13, 69.09, 55.39, 50.54, 50.03, 49.57, 48.54, 48.01, 47.53, 46.77, 46.20, 36.35, 35.47, 30.53, 25.20, 24.07, 22.20. **IR (neat)**: vmax ($cm^{-1}$): 2933, 2856, 1718, 1612, 1488, 1363, 1301, 1278, 1207, 1161, 1033 973, 927. **HRMS (ESI)**: *m/z* calculated for $C_{23}H_{31}O_5NNa^+$ $[M+Na]^+$ 424.2086, found: 424.2080. $\mathbf{[\alpha]_D^{20}}$ = + 15.4 (c = 0.91, $CHCl_3$).

**Synthesis of carbon analogous acetal**

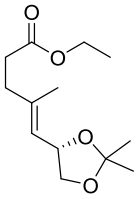



**1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2-methylprop-2-en-1-ol (S25)**



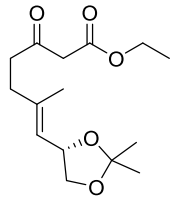
A solution of isopropenylmagnesium bromide in THF (0.5 M, 30 mL, 15 mmol, 1.5 equiv) was cooled to 0 °C after which a solution of (*R*)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (1.3 g, 10 mmol, 1.0 equiv) in $CH_2Cl_2$ (2.0 mL) was added dropwise. The resulting suspension was stirred for 5 hours at room temperature. The reaction mixture was quenched by the addition of sat. aq. $NH_4Cl$ solution (20 mL). The aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organics were dried ($Na_2SO_4$) and concentrated under reduced pressure, affording the crude title compound (1.72 g, 10 mmol, quantitative), which was directly used in the next reaction. $\mathbf{R_F}$ = 0.3 (EtOAc/cHex = 1:4). **$^1$H NMR** (300 MHz, $CDCl_3$) δ 5.15 – 5.04 (m, 1H), 4.97 (h, *J* = 1.3 Hz, 1H), 4.32 – 4.12 (m, 1H), 4.04 – 3.90 (m, 2H), 3.83 – 3.70 (m, 1H), 1.79 (q, *J* = 1.4 Hz, 3H), 1.48 (s, 3H), 1.40 (s, 3H). **IR (neat):** vmax ($cm^{-1}$): 2995, 1736, 1418, 1247, 1159, 1058, 975, 863, 846, 415. **HRMS (ESI)**: *m/z* calculated for $C_9H_{16}O_3Na$ $[M+Na]^+$ = 195.0997, found = 195.0994.

**ethyl (*S*,*E*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-methylpent-4-enoate (S26)**



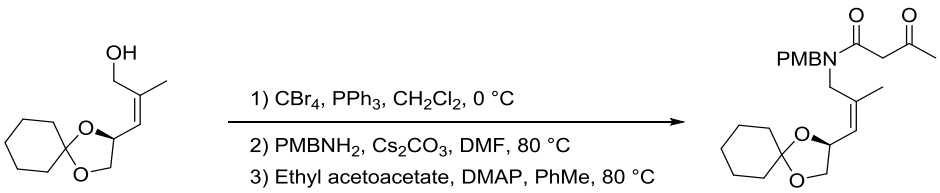
A flamedried flask was charged with **S25** (1.8 g, 10.5 mmol, 1.0 equiv), triethyl ortoacacetate (9.6 ml, 52 mmol, 5.0 equiv) and propionic acid (233 µl, 3.2 mmol, 0.3 equiv). The reaction mixture was heated to 150 °C and was stirred for 2 h. After TLC analysis indicated full conversion, the reaction mixture was allowed to cool to room temperature and was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (10% EtOAc/cHex), providing the title compound in 70% yield (1.75 g, 7.35 mmol). $\mathbf{R_F}$ = 0.30 (EtOAc/cHex = 1:5). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.23 (dq, *J* = 8.5, 1.4 Hz, 1H), 4.80 (td, *J* = 8.3, 5.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.06 (dd, *J* = 8.0, 6.0 Hz, 1H), 3.49 (t, *J* = 8.1 Hz, 1H), 2.56 – 2.32 (m, 4H), 1.75 (s, 3H), 1.42 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 173.18, 140.25, 122.89, 109.01, 72.94, 72.60, 69.55, 60.54, 34.58, 32.79, 26.95, 26.14, 16.83, 14.37. **IR (neat):** vmax ($cm^{-1}$): 2987, 1735, 1371, 1236, 1157, 1043, 864, 848, 603, 401. **HRMS (ESI)**: *m/z* calculated for $C_{13}H_{22}O_4Na$ $[M+Na]^+$ = 265.1410, found = 265.1399. $\mathbf{[\alpha]_D^{20}}$ = + 11.42 (c = 1.75, $CHCl_3$).

**ethyl (*S*,*E*)-7-(2,2-dimethyl-1,3-dioxolan-4-yl)-6-methyl-3-oxohept-6-enoate (S27)**



A solution of lithium bis(trimethylsilyl)amide (1.0 M in THF, 12.4 mL, 12.4 mmol, 2.0 equiv) was cooled to −78 °C, after which anhydrous ethyl acetate (1.2 mL, 12.4 mmol, 2.0 equiv) was added dropwise. The reaction mixture was stirred at -78 °C for 1h, after which a solution of **S26** (1.5 g, 6.2 mmol, 1.0 equiv) in THF (5.0 mL) was added dropwise. The reaction mixture was slowly warmed to room temperature and was stirred for 16 hours. Subsequently, the reaction mixture was quenched by the addition of sat. aq. $NH_4Cl$ solution (20 mL). The aqueous phase was extracted with EtOAc (3 x 50 mL), dried ($Na_2SO_4$) and concentrated under reduced pressure. After purification by silica gel column chromatography (5% → 10% EtOAc/cHex), the pure title compound was obtained in 50% yield (0.88 g, 3.1 mmol). $\mathbf{R_F}$ = 0.30 (EtOAc/cHex = 1:5). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.16 – 5.10 (m, 1H), 4.76 – 4.65 (m, 1H), 4.18 – 4.07 (m, 2H), 4.07 – 4.00 (m, 1H), 3.98 (dd, *J* = 8.1, 6.0 Hz, 1H), 3.37 (s, 2H), 2.65 – 2.59 (m, 2H), 2.34 – 2.20 (m, 2H), 1.66 (s, 3H), 1.38 – 1.30 (m, 6H), 1.21 (td, *J* = 7.2, 3.3 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 201.90, 171.88, 167.09, 140.06, 128.00, 122.73, 108.90, 89.32, 76.81, 72.69, 69.40, 61.44, 60.67, 49.34, 44.93, 41.08, 32.78, 26.83, 26.01, 16.87, 14.12. **IR (neat):** νmax ($cm^{-1}$): 2985, 2935, 2337, 1317, 1305, 1116, 1056, 1024, 850, 513, 493, 403. **HRMS (ESI)**: *m/z* calculated for $C_{15}H_{24}O_5Na$ $[M+Na]^+$ = 307.1521, found = 307.1516. $\mathbf{[\alpha]_D^{20}}$ = + 15 (c = 0.8, $CHCl_3$).

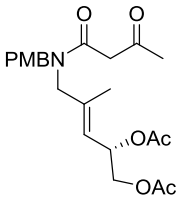
**(*S*,*Z*)-*N*-(4-methoxybenzyl)-*N*-(2-methyl-3-(1,4-dioxaspiro[4.5]decan-2-yl)allyl)-3-oxobutanamide (S28)**




Allylic alcohol **S03** (635 mg, 2.31 mmol, 1.0 equiv) was subjected to general procedure A, affording the crude allylic bromide (559 mg, 2.04 mmol) which was subsequently used in general procedure B. The obtained crude allylic amine (660 mg, *theor.* 1.99 mmol) was used in general procedure C using ethyl acetoacetate. Purification of the crude material by silica gel column chromatography (10% → 40% EtOAc/cHex) afforded the pure title compound as a yellow oil in 74% yield (610 mg, 1.47 mmol). $\mathbf{R_F}$ = 0.3 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.15 (m, 2H), 6.86 (m, 2H), 5.48 – 5.38 (m, 1H), 4.61 – 4.47 (m, 1H), 4.46 – 4.39 (m, 1H), 3.96 – 3.83 (m, 2H), 3.80 (s, 2H), 3.79 (s, 1H), 3.68 – 3.56 (m, 2H), 3.49 – 3.39 (m, 1H), 2.29 (s, 0.8H), 2.27 (s, 1.2H), 1.75 (s, 1H), 1.72 (s, 2H), 1.66 – 1.31 (m, 10H). Multiple rotameric and keto-enol signals were observed. **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 202.47, 202.35, 175.81, 172.59, 167.33, 167.19, 159.43, 159.20, 137.29, 137.01, 135.98, 131.76, 129.65, 129.61, 129.23, 128.86, 128.76, 128.48, 128.10, 128.05, 127.79, 127.69, 114.56, 114.36, 114.15, 110.09, 109.82, 71.64, 71.60, 71.08, 69.20, 69.11, 55.46, 55.39, 50.39, 50.13, 49.44, 48.31, 47.16, 47.11, 43.90, 36.54, 36.52, 35.61, 35.56, 30.55, 30.44, 25.25, 25.23, 24.09, 24.06, 24.03, 24.00, 21.50, 21.11. **IR (neat)**: υmax ($cm^{-1}$): 3348, 2974, 2933, 1722, 1639, 1512, 1444, 1247, 1174, 1108, 931. **HRMS (ESI)**: m/z calculated for $C_{24}H_{33}NO_5Na^+$ ($[M+Na]^+$) = 438.2251, found = 438.2264. $\mathbf{[\alpha]_D^{20}}$ = + 28.57 (c = 1.89, $CHCl_3$).

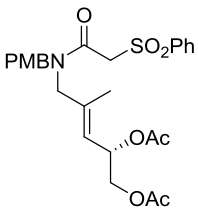
## Diacetates

**(*S,E*)-5-(*N*-(4-methoxybenzyl)-3-oxobutanamido)-4-methylpent-3-ene-1,2-diyl diacetate (3a)**



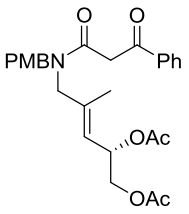

Cyclohexylidene protected diol **S12** (531 mg, 1.28 mmol, 1.0 equiv) was subjected to general procedure E and the crude material was purified by silica gel column chromatography (30% → 50% EtOAc/cHex), providing the pure title compound as a yellow oil in 89% yield (478 mg, 1.14 mmol) over 2 steps. $\mathbf{R_F}$ = 0.3 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 1H), 7.05 (dd, *J* = 12.1, 8.3 Hz, 1H), 6.93 – 6.80 (m, 2H), 5.79 – 5.63 (m, 1H), 5.22 – 5.07 (m, 1H), 4.58 – 4.31 (m, 2H), 4.20 – 3.91 (m, 4H), 3.85 – 3.77 (m, 3H), 2.27 (d, *J* = 6.1 Hz, 2H), 2.11 – 2.05 (m, 6H), 2.04 (s, 3H), 1.77 – 1.67 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 202.46, 170.88, 170.84, 170.37, 167.51, 167.28, 159.34, 159.17, 137.61, 136.71, 129.60, 128.78, 127.92, 127.74, 127.68, 121.67, 120.27, 114.50, 114.13, 68.87, 64.95, 60.55, 55.39, 53.27, 52.67, 51.16, 49.87, 48.12, 47.56, 30.53, 21.23, 20.95, 15.35, 15.13, 14.33. Multiple rotameric signals were observed. **IR (neat)**: νmax ($cm^{-1}$): 1739, 1639, 1514, 1438, 1371, 1299, 1244, 1224, 1176, 1039. HRMS (ESI): calculated for $C_{22}H_{29}NO_7Na$ ($[M+Na]^+$) = 442.1836, found = 442.1829. $\mathbf{[\alpha]_D^{20}}$ = + 26.12 (c = 2.45, $CHCl_3$). **SFC-MS (method 1):** 92% ee: $t_{ret.}$ (major) = 4.65 min. (96%), $t_{ret.}$ (minor) = 4.49 min. (4%).

**(*S,E*)-5-(*N*-(4-methoxybenzyl)-2-(phenylsulfonyl)acetamido)-4-methylpent-3-ene-1,2-diyl diacetate (3b)**



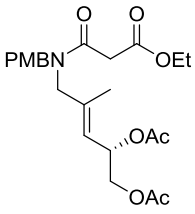

Prepared from acetal **S13** (384 mg, 0.75 mmol, 1.0 equiv), according to general procedure E. Purification of the crude material by silica gel column chromatography (50% EtOAc/cHex) afforded the title compound as a yellow oil in 91% yield (354 mg, 0.68 mmol) over 2 steps. $\mathbf{R_F}$ = 0.36 (cyclohexane/EtOAc = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.73 – 7.64 (m, 1H), 7.61 – 7.55 (m, 2H), 7.19 – 7.03 (m, 2H), 6.92 – 6.84 (m, 2H), 5.81 – 5.66 (m, 1H), 5.35 – 5.07 (m, 1H), 4.68 – 4.38 (m, 2H), 4.24 – 4.13 (m, 2H), 4.21 – 4.02 (m, 2H), 3.99 – 3.93 (m, 2H), 3.81 (s, 1.5H), 3.81 (s, 1.5H), 2.10 – 2.07 (m, 3H), 2.07 (s, 3H), 1.75 (s, 1H), 1.74 (s, 2H). Multiple rotameric signals were observed. **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 170.94, 170.79, 170.32, 170.30, 162.35, 162.20, 159.53, 159.36, 138.99, 138.90, 137.20, 136.75, 134.43, 134.39, 129.65, 129.32, 129.29, 128.71, 128.65, 128.39, 127.57, 127.42, 121.39, 120.66, 114.72, 114.22, 68.85, 68.73, 64.99, 64.79, 60.07, 59.99, 55.51, 55.46, 53.66, 52.00, 50.48, 48.99, 21.29, 21.20, 20.97, 20.92, 15.48, 15.28. **IR (neat)**: νmax ($cm^{-1}$): 2931, 1735, 1649, 1514, 1446, 1369, 1321, 1309, 1244, 1224, 1157, 1033. **HRMS** (ESI): *m/z* calculated for $C_{26}H_{31}NO_8SNa^+$ $[M+Na]^+$ 540.1662, found: 540.1644. $\mathbf{[\alpha]_D^{20}}$ = + 30.0 (c = 0.40, $CHCl_3$). **SFC-MS (method 1):** 87% ee: $t_{ret.}$ (major) = 8.75 min. (93.4%), $t_{ret.}$ (minor) = 7.64 min. (6.5%).

**(*S,E*)-5-(*N*-(4-methoxybenzyl)-3-oxo-3-phenylpropanamido)-4-methylpent-3-ene-1,2-diyl diacetate (3c)**



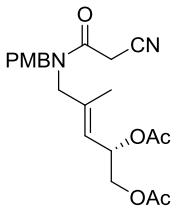

Prepared from acetal **S14** (1.0 g, 2.1 mmol, 1.0 equiv), according to general procedure E. Purification of the crude material by silica gel column chromatography (25% EtOAc/cHex) afforded the title compound as a yellow oil in 75% yield (757 mg, 1.57 mmol) over 2 steps. $\mathbf{R_F}$ = 0.80 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.03 – 7.89 (m, 1H), 7.78 – 7.67 (m, 1H), 7.66 – 7.35 (m, 3H), 7.24 – 7.04 (m, 2H), 6.91 – 6.82 (m, 2H), 5.79 – 5.66 (m, 1H), 5.27 – 5.12 (m, 1H), 4.62 – 4.33 (m, 2H), 4.21 – 3.94 (m, 4H), 3.81 (s, 1H), 3.80 – 3.78 (m, 2H), 3.76 (s, 1H), 2.10 – 1.94 (m, 6H), 1.79 – 1.73 (m, 2H), 1.70 (s, 1H). Multiple romateric and keto-enol tautomeric signals were observed. **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 194.14, 194.06, 172.94, 172.80, 172.33, 172.00, 170.86, 170.81, 170.34, 170.31, 168.01, 167.74, 159.38, 159.33, 159.24, 159.16, 137.99, 137.82, 137.06, 136.85, 136.35, 136.26, 134.92, 133.89, 130.93, 129.72, 129.57, 129.22, 128.92, 128.90, 128.86, 128.81, 128.73, 128.62, 128.59, 128.24, 128.05, 128.01, 127.85, 126.14, 126.06, 121.72, 121.54, 120.50, 120.46, 114.52, 114.46, 114.17, 114.15, 85.06, 84.83, 68.93, 68.90, 64.99, 64.90, 64.85, 55.48, 55.46, 55.41, 53.48, 53.11, 51.27, 50.98, 50.02, 49.27, 48.19, 48.14, 46.09, 45.78, 21.27, 21.23, 21.11, 20.93, 20.84, 15.39, 15.36, 15.26, 15.11.**IR (neat)**: vmax ($cm^{-1}$): 1735, 1623, 1612, 1512, 1479, 1369, 1242, 1220, 1176, 1033. **HRMS (ESI)**: *m/z* calculated for $C_{27}H_{31}NO_7Na^+$ $[M+Na]^+$ 504.1993, found: 504.1976. $\mathbf{[\alpha]_D^{20}}$ = + 20.0 (c = 1.00, $CHCl_3$). **SFC-MS (method 1):** 100% ee: $t_{ret.}$ = 5.48 min. (100%).

**(*S,E*)-5-(3-ethoxy-*N*-(4-methoxybenzyl)-3-oxopropanamido)-4-methylpent-3-ene-1,2-diyl diacetate (3d)**



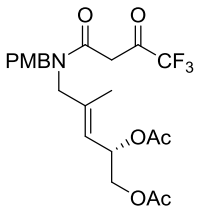

Prepared from acetal **S15** (463 mg, 1.04 mmol, 1.0 equiv), according to general procedure E. Purification of the crude material by silica gel column chromatography (45% EtOAc/cHex) afforded the title compound as a yellow oil in 60% yield (280 mg, 0.62 mmol) over 2 steps. $\mathbf{R_F}$ = 0.50 (EtOAc/cHex = 3:2). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 60.1, 8.4 Hz, 2H), 6.86 (dd, *J* = 20.5, 8.6 Hz, 2H), 5.78 – 5.65 (m, 1H), 5.15 (d, *J* = 8.4 Hz, 1H), 4.49 (s, 1H), 4.35 (s, 1H), 4.25 – 4.01 (m, 4H), 4.00 – 3.93 (m, 1H), 3.80 (s, 1H), 3.79 (s, 2H), 3.70 (s, 1H), 3.51 (s, 1H), 3.39 (s, 1H), 2.07 (d, 6H), 1.72 (d, *J* = 14.3 Hz, 3H), 1.32 – 1.25 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 170.87, 170.85, 170.38, 170.30, 167.70, 167.67, 166.99, 166.71, 159.36, 159.17, 137.73, 136.58, 129.63, 128.81, 127.76, 127.62, 121.84, 120.43, 114.50, 114.09, 68.90, 68.83, 64.95, 64.85, 61.73, 61.71, 55.47, 55.40, 53.27, 51.12, 49.80, 48.11, 41.50, 41.22, 21.26, 21.21, 20.94, 15.35, 15.05, 14.26. Multiple rotameric and tautomeric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2981, 1731, 1647, 1512, 1456, 1367, 1240, 1218, 1174, 1031. **HRMS (ESI):** *m/z* calculated for $C_{23}H_{31}NO_8Na^+$ $[M+Na]^+$ 472.1942, found: 472.1935. $\mathbf{[\alpha]_D^{20}}$ = + 26.7 (c = 0.60, $CHCl_3$). **SFC-MS (method 1):** 97% ee: $t_{ret.}$ (major) = 3.47 min. (98.6%), $t_{ret.}$ (minor) = 3.91 min. (1.4%).

**(*S,E*)-5-(2-cyano-*N*-(4-methoxybenzyl)acetamido)-4-methylpent-3-ene-1,2-diyl diacetate (3e)**



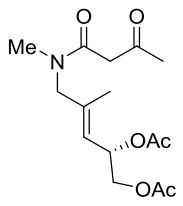

Prepared from acetal **S16** (175 mg, 0.44 mmol, 1.0 equiv), according to general procedure E. Purification of the crude material by silica gel column chromatography (50% EtOAc/cHex) afforded the title compound as a yellow oil in 83% yield (146 mg, 0.36 mmol) over 2 steps. $\mathbf{R_F}$ = 0.30 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 156.2, 8.6 Hz, 2H), 6.97 (dd, *J* = 67.9, 8.6 Hz, 2H), 5.70 (ddd, *J* = 8.7, 7.4, 3.9 Hz, 0.33H), 5.65 (ddd, *J* = 8.7, 7.1, 3.8 Hz, 0.67H), 5.15 – 5.08 (m, 1H), 4.52 – 4.43 (m, 1.33H), 4.38 – 4.30 (m, 0.67H), 4.19 – 4.11 (m, 1H), 4.08 – 3.91 (m, 2H) 3.81 (s, 1H), 3.79 (s, 2H), 3.69 (s, 1H), 3.52 (s, 1H), 3.45 (d, *J* = 2.3 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 1.74 – 1.70 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 170.84, 170.44, 170.28, 162.63, 162.49, 159.62, 159.48, 137.00, 135.77, 130.01, 128.84, 128.06, 127.53, 127.36, 126.59, 122.67, 120.78, 114.81, 114.26, 113.99, 113.96, 68.84, 68.77, 64.76, 64.67, 55.49, 55.41, 53.27, 51.97, 49.95, 49.33, 25.40, 25.06, 21.22, 21.19, 20.91, 15.36, 15.17. Rotamers were observed in a 1:2 ratio. **IR (neat)**: vmax ($cm^{-1}$): 2923, 1733, 1658, 1512, 1440, 1369, 1242, 1176, 1031, 960. Mass could not be observed by HRMS. $\mathbf{[\alpha]_D^{20}}$ = + 21.7 (c = 1.20, $CHCl_3$).

**(*S,E*)-4-methyl-5-(4,4,4-trifluoro-*N*-(4-methoxybenzyl)-3-oxobutanamido)pent-3-ene-1,2-diyl diacetate (3f)**



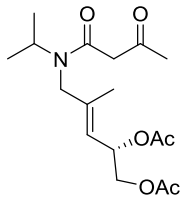

Prepared from acetal **S17** (563 mg, 1.2 mmol, 1.0 equiv), according to general procedure E. Purification of the crude material by silica gel column chromatography (35% EtOAc/cHex) afforded the title compound as a yellow oil in 92% yield (524 mg, 1.1 mmol) over 2 steps. $\mathbf{R_F}$ = 0.60 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.19 – 7.04 (m, 2H), 6.93 – 6.83 (m, 2H), 5.74 – 5.65 (m, 1H), 5.20 – 5.09 (m, 1H), 4.61 – 4.36 (m, 2H), 4.22 – 3.91 (m, 3H), 3.81 (s, 1H), 3.80 (s, 2H), 3.76 – 3.68 (m, 1H), 2.91 – 2.77 (m, 1H), 2.68 (s, 1H), 2.10 – 2.01 (m, 6H), 1.73 (s, 3H). Multiple rotameric and keto-enol tautomeric signals were observed. **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 171.59, 171.26, 170.96, 170.87, 170.37, 170.31, 159.60, 159.47, 136.92, 135.86, 129.90, 129.74, 128.11, 127.88, 126.98, 123.44, 122.46, 121.97, 121.55, 121.34, 120.88, 114.68, 114.64, 114.31, 68.79, 68.74, 68.66, 64.76, 64.73, 55.49, 55.44, 53.05, 51.55, 51.10, 50.05, 49.33, 48.76, 48.44, 33.59, 33.30, 21.23, 21.10, 20.93, 20.87, 15.34, 15.17. **IR (neat):** vmax ($cm^{-1}$): 1735, 1612, 1514, 1461, 1442, 1371, 1245, 1222, 1174, 1107, 1033. **HRMS (ESI):** *m/z* calculated for $C_{22}H_{26}NO_7F_3Na^+$ $[M+Na]^+$ 496.1553, found: 496.1554. $\mathbf{[\alpha]_D^{20}}$ = + 30.0 (c = 1.00, $CHCl_3$).

**(*S*,*E*)-4-methyl-5-(*N*-methyl-3-oxobutanamido)pent-3-ene-1,2-diyl diacetate (3g)**



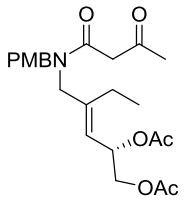
Acetal **S18** (107 mg, 0.34 mmol, 1.0 equiv) was subjected to general procedure E. The crude product was purified by silica gel column chromatography (1% → 2% MeOH/$CH_2Cl_2$) providing the title compound as a yellow oil in 83% yield (88 mg, 0.28 mmol) over 2 steps. $\mathbf{R_F}$ = 0.1 (MeOH/$CH_2Cl_2$ = 1:99). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.78 – 5.63 (m, 1H), 5.24 – 5.06 (m, 1H), 4.22 – 3.99 (m, 2H), 3.95 (s, 1H), 3.77 (s, 1H), 3.58 (s, 1H), 3.43 (s, 1H), 2.93 – 2.78 (m, 3H), 2.30 – 2.20 (m, 3H), 2.06 – 2.00 (m, 6H), 1.69 (t, *J* = 12.3 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 202.31, 202.14, 170.76, 170.73, 170.24, 170.20, 137.72, 136.77, 133.87, 131.66, 129.48, 124.06, 123.60, 121.66, 121.54, 121.03, 120.34, 120.15, 86.79, 68.75, 68.10, 65.11, 64.87, 64.75, 56.72, 53.85, 50.23, 49.63, 35.07, 34.08, 30.34, 21.14, 20.82, 15.13, 14.87. Multiple rotameric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2935, 2864, 1739, 1676, 1639, 1444, 1407, 1367, 1224, 1163, 1097, 1039, 925. **HRMS (ESI)**: calculated for $C_{15}H_{23}NO_6Na$ ([M+Na]$^+$) = 336.1418, found = 336.1403. **$[\alpha]_D^{20}$** = + 15.45 (c = 2.2, $CHCl_3$). **SFC-MS (method 1):** 95% ee: $t_{ret.}$ (major) = 5.97 min. (97.5%), $t_{ret.}$ (minor) = 9.59 min. (2.5%).

**(*S*,*E*)-5-(*N*-isopropyl-3-oxobutanamido)-4-methylpent-3-ene-1,2-diyl diacetate (3h)**



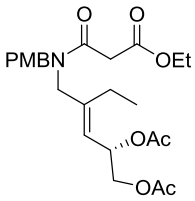
Acetal **S19** (793 mg, 2.35 mmol, 1.0 equiv) was subjected to general procedure E. The crude product was purified by silica gel column chromatography (0.5% MeOH/$CH_2Cl_2$) providing the pure title compound as a yellow oil in 56% yield (450 mg, 1.32 mmol) over 2 steps. $\mathbf{R_F}$ = 0.1 (EtOAc/cHex = 3:7). **$^1$H NMR** (500 MHz, $CDCl_3$, rotamers observed in 3:7 ratio) δ 14.92 (s, 0.06H), 14.70 (s, 0.17H), 5.74 (td, *J* = 8.2, 3.7 Hz, 0.3H), 5.68 (td, *J* = 8.0, 3.7 Hz, 0.7H), 5.22 – 5.15 (m, 0.7H), 5.15 – 5.07 (m, 0.3H), 4.83 – 4.68 (m, 0.7H), 4.18 – 4.08 (m, 1H), 4.08 – 3.99 (m, 1H), 3.94 (p, *J* = 6.7 Hz, 0.3H), 3.88 – 3.83 (m, 0.3H), 3.66 – 3.58 (m, 2H), 3.33 (s, 1H), 2.27 (s, 0.7H), 2.23 (s, 1.3H), 2.06 – 2.00 (m, 6H), 1.79 – 1.73 (m, 3H), 1.17 – 1.11 (m, 2H), 1.09 – 1.04 (m, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 202.86, 202.51, 174.84, 172.80, 170.86, 170.83, 170.80, 170.37, 170.33, 170.28, 167.71, 166.33, 139.13, 138.45, 137.90, 119.85, 119.75, 118.78, 88.45, 86.94, 69.13, 69.03, 68.89, 65.04, 64.90, 64.82, 50.56, 50.26, 49.93, 48.70, 48.22, 48.10, 46.49, 46.13, 45.75, 44.52, 30.62, 30.34, 22.00, 21.21, 21.14, 21.05, 20.90, 20.88, 20.05, 19.93, 15.58, 15.49, 15.40. Multiple rotameric signals were observed. **IR (neat): vmax ($cm^{-1}$):** 2923, 1735, 1631, 1589, 1433, 1367, 1220, 1163, 1128, 1112, 1076, 1041. **HRMS (ESI):** *m/z* calculated for $C_{17}H_{27}NO_6Na^+$ [M+Na]$^+$ 364.1723, found: 364.1738. **$[\alpha]_D^{20}$** = + 40.04 (c = 1.15, $CHCl_3$). **SFC-MS (method 1):** 94% ee: $t_{ret.}$ (major) = 2.35 min. (96.9%), $t_{ret.}$ (minor) = 5.20 min. (3.1%).

**(*S*,*E*)-4-((*N*-(4-methoxybenzyl)-3-oxobutanamido)methyl)hex-3-ene-1,2-diyl diacetate (3i)**



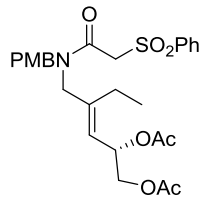
Isopropylidene protected diol **S20** (311 mg, 0.79 mmol, 1.0 equiv) was subjected to general procedure E and the crude material was purified by silica gel column chromatography (10% → 40% EtOAc/cHex), providing the pure title compound as a yellow oil in 73% yield (251 mg, 0.58 mmol) over 2 steps. $\mathbf{R_F}$ = 0.25 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, Chloroform-d) δ 7.18 – 7.01 (m, 2H), 6.94 – 6.79 (m, 2H), 5.83 – 5.65 (m, 1H), 5.29 – 4.87 (m, 1H), 4.59 – 4.35 (m, 1H), 4.30 (d, *J* = 5.2 Hz, 1H), 4.18 – 4.08 (m, 1H), 4.08 – 3.95 (m, 2H), 3.81 – 3.76 (m, 4H), 3.71 (d, *J* = 1.7 Hz, 1H), 3.60 (s, 1H), 3.45 (s, 1H), 2.28 – 2.24 (m, 2H), 2.24 – 2.12 (m, 1H), 2.08 – 2.04 (m, 7H), 1.92 (s, 1H), 1.07 – 0.97 (m, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 202.34, 175.88, 175.50, 172.47, 170.75, 170.27, 167.58, 167.20, 159.36, 159.23, 159.13, 144.09, 143.20, 142.35, 129.65, 128.85, 127.95, 127.78, 127.70, 121.02, 119.05, 114.52, 114.15, 87.08, 68.48, 68.47, 65.22, 65.12, 55.36, 50.94, 50.10, 49.77, 48.81, 48.32, 47.62, 30.49, 22.82, 22.42, 21.25, 21.20, 13.25. Multiple rotameric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2966, 1733, 1637, 1612, 1585, 1512, 1488, 1421, 1367, 1238, 1174, 1157, 1031. **HRMS (ESI)**: *m/z* calculated for $C_{23}H_{32}NO_7$ $[M+H]^+$ = 434.2173, found = 434.2176. **$[\alpha]_D^{20}$** = + 17.3 (c = 1.85, $CHCl_3$). **SFC-MS (method 3):** 90% ee: $t_{ret.}$ (major) = 6.40 min. (95%), $t_{ret.}$ (minor) = 5.81 min. (5%).

**(*S*,*E*)-4-((3-ethoxy-*N*-(4-methoxybenzyl)-3-oxopropanamido)methyl)hex-3-ene-1,2-diyl diacetate (3j)**



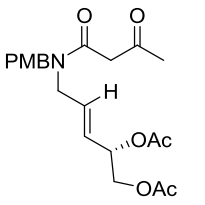
Isopropylidene protected diol **S21** (1.0 g, 2.38 mmol, 1.0 equiv) was subjected to general procedure E and the crude material was purified by silica gel column chromatography (30% → 40% EtOAc/cHex), providing the pure title compound as a yellow oil in 61% yield (676 mg, 1.46 mmol) over 2 steps. $\mathbf{R_F}$ = 0.35 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.23 – 7.04 (m, 2H), 6.90 – 6.80 (m, 2H), 5.84 – 5.68 (m, 1H), 5.13 – 5.05 (m, 1H), 4.49 (s, 1H), 4.35 (s, 1H), 4.23 – 4.11 (m, 3H), 4.09 – 3.96 (m, 2H), 3.82 – 3.77 (m, 3H), 3.74 (s, 1H), 3.51 (s, 1H), 3.37 (d, *J* = 2.6 Hz, 1H), 2.27 – 2.16 (m, 1H), 2.09 – 2.03 (m, 7H), 1.32 – 1.22 (m, 3H), 1.09 – 0.96 (m, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 170.82, 170.80, 170.32, 170.23, 167.66, 167.07, 166.65, 159.40, 159.24, 143.36, 142.24, 137.23, 132.12, 129.70, 129.23, 128.90, 127.68, 127.48, 121.20, 119.21, 114.53, 114.13, 68.55, 68.48, 65.26, 65.18, 61.67, 55.47, 55.40, 50.94, 49.85, 48.77, 48.32, 43.20, 41.53, 41.16, 22.84, 22.37, 21.27, 21.22, 20.91, 14.26, 13.36, 13.30. Multiple rotameric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2972, 1731, 1643, 1512, 1442, 1369, 1303, 1244, 1218, 1174, 1031, 746. **HRMS (ESI)**: *m/z* calculated for $C_{24}H_{34}NO_8$ $[M+H]^+$ = 464.2279, found = 464.2283. **$[\alpha]_D^{20}$** = + 14.86 (c = 1.48, $CHCl_3$). **SFC-MS (method 2):** 92% ee: $t_{ret.}$ (major) = 5.33 min. (96%), $t_{ret.}$ (minor) = 6.11 min. (4%).

**(*S*,*E*)-4-((*N*-(4-methoxybenzyl)-2-(phenylsulfonyl)acetamido)methyl)hex-3-ene-1,2-diyl diacetate (3k)**



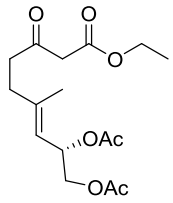

Isopropylidene protected diol **S22** (739 mg, 1.52 mmol, 1.0 equiv) was subjected to general procedure E and the crude material was purified by silica gel column chromatography (30% → 50% EtOAc/cHex), providing the pure title compound as a yellow oil in 87% yield (701 mg, 1.32 mmol) over 2 steps. $\mathbf{R_F}$ = 0.30 (EtOAc/cHex = 2:3). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.95 – 7.84 (m, 2H), 7.72 – 7.65 (m, 1H), 7.61 – 7.52 (m, 2H), 7.10 (dd, *J* = 63.5, 8.6 Hz, 2H), 6.90 – 6.83 (m, 2H), 5.83 – 5.69 (m, 1H), 5.14 (dd, *J* = 158.0, 9.0 Hz, 1H), 4.62 (s, 1H), 4.48 – 4.40 (m, 1H), 4.25 – 4.19 (m, 1H), 4.16 – 4.06 (m, 2H), 4.04 – 3.96 (m, 3H), 3.80 (d, *J* = 3.4 Hz, 3H), 2.21 (dt, *J* = 14.1, 7.9 Hz, 1H), 2.10 – 2.06 (m, 3H), 2.06 – 2.04 (m, 4H), 1.03 (dt, *J* = 14.9, 7.6 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 170.90, 170.73, 170.22, 162.39, 162.09, 159.50, 159.36, 142.72, 142.47, 138.91, 134.38, 134.36, 129.69, 129.27, 128.66, 128.60, 128.40, 127.59, 127.43, 120.74, 119.31, 114.69, 114.20, 68.49, 68.30, 65.26, 65.05, 60.06, 60.01, 55.48, 55.43, 51.26, 50.44, 49.55, 49.11, 22.91, 22.53, 21.31, 21.20, 20.89, 13.31. Multiple rotameric signals were observed. **IR (neat):** vmax ($cm^{-1}$): 2972, 1737, 1265, 1245, 1224, 1157, 730. **HRMS (ESI)**: *m/z* calculated for $C_{27}H_{34}NO_8S[M+H]^+$ = 532.2000, found = 532.1998. $\mathbf{[\alpha]_D^{20}}$ = + 14.13 (c = 2.69, $CHCl_3$). **SFC-MS (method 1):** 94% ee: $t_{ret.}$ (major) = 8.79 min. (97%), $t_{ret.}$ (minor) = 7.64 min. (3%).

**(*S*,*E*)-5-(*N*-(4-methoxybenzyl)-3-oxobutanamido)pent-3-ene-1,2-diyl diacetate (3l)**



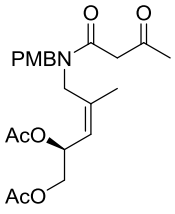

Acetal **S24** (177 mg, 0.44 mmol, 1.0 equiv) was subjected to general procedure E. After purification of the crude material by silica gel column chromatography (10% → 60% EtOAc/cHex), the title compound was obtained as a yellow oil in 68% yield (120 mg, 0.30 mmol) over 2 steps. $\mathbf{R_F}$ = 0.1 (EtOAc/cHex = 1:2). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.18 – 7.00 (m, 2H), 6.89 – 6.79 (m, 2H), 5.76 – 5.61 (m, 1H), 5.57 – 5.41 (m, 2H), 4.55 – 4.44 (m, 2H), 4.35 (s, 1H), 4.20 – 4.13 (m, 1H), 4.06 – 3.95 (m, 2H), 3.79 – 3.75 (m, 4H), 3.58 – 3.48 (m, 2H), 2.34 – 2.21 (m, 2H), 2.08 – 2.02 (m, 6H). Multiple rotameric and keto-enol signals were observed. **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 202.43, 175.74, 172.21, 170.66, 170.04, 166.96, 159.32, 159.13, 129.70, 129.57, 129.21, 129.13, 129.09, 128.79, 127.90, 127.81, 127.73, 127.46, 127.25, 127.10, 126.70, 114.44, 114.27, 114.09, 114.03, 87.04, 71.22, 71.12, 64.82, 64.70, 55.39, 55.32, 50.54, 49.92, 49.51, 48.41, 47.93, 47.66, 47.50, 46.53, 46.07, 30.53, 30.48, 21.15, 21.10, 20.85. **IR (neat)**: vmax ($cm^{-1}$): 2937, 1737, 1637, 1612, 1585, 1512, 1448, 1440, 1421, 1365, 1301, 1218, 1174, 1159, 1110, 1031, 975, 948. **HRMS (ESI)**: m/z calculated for $C_{21}H_{28}NO_7^+$ ($[M+H]^+$) = 406.1860, found = 406.1873. $\mathbf{[\alpha]_D^{20}}$ = + 21.88 (c = 1.92, $CHCl_3$).

**(*S*,*E*)-9-ethoxy-4-methyl-7,9-dioxonon-3-ene-1,2-diyl diacetate (3m)**



Isopropylidene protected diol **S27** (360 mg, 1.27 mmol, 1.0 equiv) was subjected to general procedure E and the crude material was purified by silica gel column chromatography (10% → 20% EtOAc/cHex), providing the pure title compound as a yellow oil in 64% yield (267 mg, 0.81 mmol) over 2 steps. $\mathbf{R_F}$ = 0.60 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.74 (dddd, *J* = 15.2, 12.3, 7.6, 3.6 Hz, 1H), 5.14 (m, 1H), 4.23 – 4.12 (m, 3H), 4.04 (ddd, *J* = 11.9, 7.8, 4.5 Hz, 1H), 3.45 (s, 2H), 2.73 – 2.61 (m, 2H), 2.37 – 2.13 (m, 2H), 2.08 (s, 6H), 1.79 (s, 3H), 1.29 (t, *J* = 6.9, 3.4 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 201.65, 171.79, 170.67, 170.15, 142.85, 141.27, 135.78, 123.22, 119.49, 118.82, 88.16, 77.16, 71.33, 68.98, 65.06, 63.87, 61.37, 60.67, 49.27, 42.81, 40.90, 37.64, 33.08, 31.66, 25.80, 21.08, 17.04, 14.08. **IR (neat):** νmax ($cm^{-1}$): 2979, 1731, 1440, 1369, 1218, 1164, 1093, 960, 865, 605, 470. **HRMS (ESI)**: *m/z* calculated for $C_{16}H_{24}O_7Na$ $[M+Na]^+$ = 351.1402, found = 351.1414. $\mathbf{[\alpha]_D^{20}}$ = + 18 (c = 2.66, $CHCl_3$).

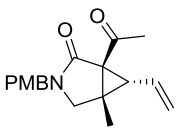
**(*S*,*Z*)-5-(*N*-(4-methoxybenzyl)-3-oxobutanamido)-4-methylpent-3-ene-1,2-diyl diacetate (*Z*-3a)**



Acetal **S28** (550 mg, 1.33 mmol, 1.0 equiv) was subjected to general procedure E, furnishing the pure title compound as a yellow oil in 69% yield (387 mg, 0.92 mmol) over 2 steps after purification by silica gel column chromatography (20% → 40% EtOAc/cHex). $\mathbf{R_F}$ = 0.35 (EtOAc/cHex = 2:3). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.25 – 7.07 (m, 2H), 6.91 – 6.72 (m, 2H), 5.58 – 5.41 (m, 1H), 5.32 – 5.25 (m, 1H), 4.47 – 4.26 (m, 2H), 4.14 – 3.95 (m, 3H), 3.80 (s, 2H), 3.78 (s, 1H), 3.68 – 3.52 (m, 2H), 2.29 (s, 1H), 2.24 (s, 2H), 2.09 – 1.95 (m, 6H), 1.80 – 1.65 (m, 3H). Multiple rotameric and keto-enol signals were observed. **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 202.61, 202.45, 170.66, 170.20, 170.10, 167.65, 159.34, 159.17, 138.97, 138.10, 129.52, 128.72, 127.94, 127.88, 127.53, 123.94, 123.70, 123.52, 122.83, 114.59, 114.35, 114.20, 114.17, 68.40, 68.28, 68.11, 68.05, 65.09, 65.00, 64.91, 55.43, 55.38, 50.17, 50.06, 49.93, 49.35, 48.46, 47.94, 47.88, 47.09, 45.42, 44.69, 30.58, 21.42, 21.15, 21.09, 20.87, 20.82. **IR (neat)**: υmax ($cm^{-1}$): 2947, 1735, 1637, 1512, 1438, 1367, 1240, 1220, 1176, 1031, 945. **HRMS (ESI)**: m/z calculated for $C_{22}H_{29}NO_7Na^+$ ($[M+Na]^+$) = 442.1849, found = 442.1836. $\mathbf{[\alpha]_D^{20}}$ = + 17.78 (c = 0.9, $CHCl_3$).

## Vinylcyclopropanes

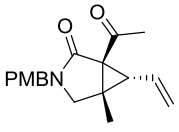
**(1*R*,5*S*,6*R*)-1-acetyl-3-(4-methoxybenzyl)-5-methyl-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (5a)**




Allylic acetate **3a** (109 mg, 0.26 mmol, 1.0 equiv) was used in general procedure G. The reaction mixture was concentrated under reduced pressure to give the crude product as a 9:1 mixture of diastereomers as judged by $^1$H NMR. The crude material was purified by silica gel column chromatography (30% EtOAc/cHex) providing the title compound as a slightly yellow oil in 75% yield (53 mg, 0.19 mmol). **0.65 mmol scale experiment:** allylic acetate **3a** (274 mg, 0.65 mmol, 1.0 equiv) was used in general procedure G. The reaction mixture was concentrated and the crude material was purified by silica gel column chromatography (30% EtOAc/cHex) providing the title compound as a slightly yellow oil in 71% yield (137 mg, 0.46 mmol). $\mathbf{R_F}$ = 0.6 (EtOAc/cHex = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 6.89 – 6.85 (m, 2H), 5.36 – 5.07 (m, 3H), 4.45 – 4.24 (m, 2H), 3.81 (s, 3H), 3.23 – 3.15 (m, 2H), 2.79 – 2.74 (m, 1H), 2.52 (s, 3H), 1.27 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 201.85, 169.91, 159.63, 130.42, 129.21, 128.26, 121.17, 114.42, 55.64, 50.25, 46.13, 39.79, 38.90, 31.30, 30.04, 16.16. **IR (neat)**: νmax ($cm^{-1}$): 2923, 1685, 1514, 1442, 1419, 1357, 1247, 1215, 1176, 1033. **HRMS (ESI)**: calculated for $C_{18}H_{21}NO_3Na$ ($[M+Na]^+$) = 322.1314, found = 322.1398. $\mathbf{[\alpha]_D^{20}}$ = + 84.9 (c = 1.06, $CHCl_3$). **SFC-MS (method 2):** 90% ee: $t_{ret.}$ (major enantiomer) = 5.61 min. (95%), $t_{ret.}$ (minor enantiomer) = 6.21 min. (5%).

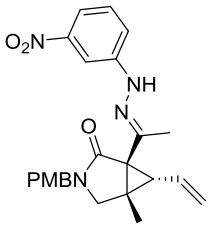
### 1.0 mmol scale experiment

**(1*R*,5*S*,6*R*)-1-acetyl-3-(4-methoxybenzyl)-5-methyl-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (5a)**



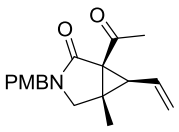

Allylic acetate **3a** (420 mg, 1.00 mmol, 1.0 equiv) was used in general procedure G. The reaction mixture was concentrated under reduced pressure to give the crude product as a 9:1 mixture of diastereomers as judged by $^1$H NMR. The crude material was purified by silica gel column chromatography (30% EtOAc/cHex) providing the title compound as a slightly yellow oil in 62% yield (185 mg, 0.62 mmol). **SFC-MS (method 2):** 88% ee: $t_{ret.}$ (major enantiomer) = 5.59 min. (94%), $t_{ret.}$ (minor enantiomer) = 6.20 min. (6%), e.s. = 97% (based on **3a** in 91% ee ).

**(1*R*,5*S*,6*R*)-3-(4-methoxybenzyl)-5-methyl-1-((*E*)-1-(2-(3-nitrophenyl)hydrazineylidene)ethyl)-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (7)**



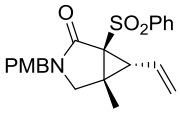
Vinylcyclopropane **5a** (30 mg, 0.1 mmol, 1.0 equiv) was dissolved in EtOH (2.0 mL). Next, 3-nitrophenylhydrazine hydrochloride (18 mg, 0.095 mmol , 0.95 equiv) was added and the reaction mixture was stirred for 3 h at room temperature. The reaction mixture was filtered and the yellow precipitate was concentrated under reduced pressure to afford the pure title compound (44 mg, 0.1 mmol) in quantitative yield. $\mathbf{R_F}$ = 0.7 (EtOAc/cHex = 3:7). **$^1$H NMR** (500 MHz, MeOD) δ 7.97 – 7.95 (m, 1H), 7.61 – 7.56 (m, 1H), 7.47 – 7.42 (m, 1H), 7.42 – 7.36 (m, 1H), 7.29 – 7.20 (m, 2H), 6.98 – 6.87 (m, 2H), 5.44 – 5.36 (m, 1H), 5.32 – 5.21 (m, 1H), 5.14 – 5.10 (m, 1H), 4.45 – 4.30 (m, 2H), 3.80 (s, 3H), 3.39 – 3.35 (m, 1H), 3.30 – 3.26 (m, 1H), 2.62 (d, *J* = 8.1 Hz, 1H), 2.04 (s, 3H), 1.23 (s, 3H). **$^{13}$C NMR** (126 MHz, MeOD) δ 173.98, 160.91, 150.57, 148.83, 141.65, 131.47, 131.11, 130.82, 129.42, 121.02, 120.02, 119.50, 115.09, 114.21, 107.86, 55.70, 51.55, 51.07, 35.67, 34.21, 16.89, 16.35. **HRMS (ESI)**: calculated for $C_{24}H_{27}N_4O_4$ ([M+H]$^+$) = 435.2027, found = 435.2045. $\mathbf{[\alpha]_D^{20}}$ = + 7.69 (c = 0.5, MeOH).

**(1*R*,5*S*,6*S*)-1-acetyl-3-(4-methoxybenzyl)-5-methyl-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (5a')**



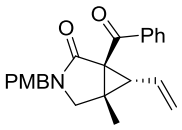
$\mathbf{R_F}$ = 0.7 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.17 – 7.13 (m, 2H), 6.89 – 6.84 (m, 2H), 6.02 – 5.92 (m, 1H), 5.26 – 5.11 (m, 2H), 4.34 (dd, *J* = 98.0, 14.5 Hz, 2H), 3.81 (s, 3H), 3.25 – 3.15 (m, 2H), 2.55 (s, 3H), 2.01 (d, *J* = 9.6 Hz, 1H), 1.40 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 202.46, 171.67, 159.38, 135.73, 135.19, 130.18, 129.79, 129.68, 128.46, 124.99, 120.95, 119.24, 114.34, 66.64, 57.42, 55.44, 53.69, 50.07, 47.09, 45.95, 44.17, 34.21, 31.84, 29.85, 11.93. **HRMS (ESI)**: calculated for $C_{18}H_{22}NO_3$ ([M+H]$^+$) = 300.1594, found = 300.1595. $\mathbf{[\alpha]_D^{20}}$ = + 100 (c = 0.3, $CHCl_3$).

**(1*S*,5*R*,6*R*)-3-(4-methoxybenzyl)-5-methyl-1-(phenylsulfonyl)-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (5b)**



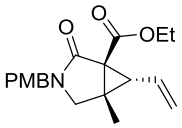
Prepared from precursor **3b** (176 mg, 0.34 mmol, 1.0 equiv), according to general procedure G. Purification of the crude material by silica gel column chromatography (15% → 35% EtOAc/cHex) afforded the title compound as a yellow oil in 75% yield (101 mg, 0.26 mmol). $\mathbf{R_F}$ = 0.30 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.70 – 7.62 (m, 1H), 7.62 – 7.51 (m, 2H), 7.07 – 6.98 (m, 2H), 6.84 – 6.74 (m, 2H), 5.38 – 5.27 (m, 1H), 5.16 – 5.03 (m, 2H), 4.24 (q, *J* = 14.4 Hz, 2H), 3.78 (s, 3H), 3.16 – 3.04 (m, 2H), 2.92 (d, *J* = 7.6 Hz, 1H), 1.72 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 164.78, 159.43, 140.37, 133.75, 130.03, 128.84, 127.40, 127.35, 122.18, 114.18, 56.15, 55.40, 49.19, 45.87, 38.20, 36.80, 16.96. **IR (neat):** vmax (cm$^{-1}$): 2929, 2839, 1689, 1610, 1512, 1481, 1446, 1419, 1305, 1288, 1245, 1218, 1201, 1176, 1147, 1108, 1087, 1072, 1029, 991, 968, 926. **HRMS (ESI)**: *m/z* calculated for $C_{22}H_{24}NO_4S^+$ [M+H]$^+$ 398.1421, found: 398.1407. $\mathbf{[\alpha]_D^{20}}$ = + 104.94 (c = 1.62, $CHCl_3$). **SFC-MS (method 1):** 89% ee: $t_{ret.}$ (major) = 6.61 min. (94.6%), $t_{ret.}$ (minor) = 6.47 min. (5.4%).

**(1*R*,5*S*,6*R*)-1-benzoyl-3-(4-methoxybenzyl)-5-methyl-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (5c)**



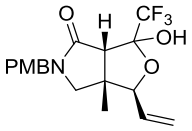
Prepared from precursor **3c** (88 mg, 0.18 mmol, 1.0 equiv), according to general procedure G. Purification of the crude material by silica gel column chromatography (5% → 45% EtOAc/cHex) afforded the title compound as a yellow oil in 65% yield (43 mg, 0.12 mmol). $\mathbf{R_F}$ = 0.30 (EtOAc/cHex = 1:4). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.60 – 7.54 (m, 1H), 7.47 – 7.39 (m, 2H), 7.30 – 7.24 (m, 2H), 6.98 – 6.86 (m, 2H), 5.47 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.40 – 5.31 (m, 1H), 5.24 (dd, *J* = 10.4, 1.9 Hz, 1H), 4.37 (dd, *J* = 340.4, 14.3 Hz, 2H), 3.85 (s, 3H), 3.39 (dd, *J* = 51.4, 11.2 Hz, 2H), 2.78 (d, *J* = 7.9 Hz, 1H), 1.24 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 194.16, 169.92, 159.48, 137.71, 133.17, 130.32, 129.16, 128.62, 121.09, 114.23, 55.47, 50.14, 49.53, 45.78, 36.05, 35.17, 17.21. **IR (neat):** vmax ($cm^{-1}$): 2930, 1679, 1610, 1512, 1448, 1419, 1340, 1303, 1245, 1218, 1203, 1176, 1109, 1032, 916. **HRMS (ESI):** *m/z* calculated for $C_{23}H_{23}NO_3Na^+$ $[M+Na]^+$ 384.1570, found: 384.1564. $\mathbf{[\alpha]_D^{20}}$ = − 16.22 (c = 1.11, $CHCl_3$). **SFC-MS (method 2):** 96% ee: $t_{ret.}$ (major) = 5.46 min. (98.3%), $t_{ret.}$ (minor) = 8.44 min. (1.7%).

**ethyl (1*S*,5*S*,6*R*)-3-(4-methoxybenzyl)-5-methyl-2-oxo-6-vinyl-3-azabicyclo[3.1.0]hexane-1-carboxylate (5d)**



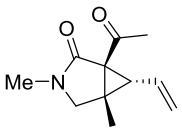
Prepared from precursor **3d** (107 mg, 0.24 mmol, 1.0 equiv), according to general procedure G. Purification of the crude material by silica gel column chromatography (30% EtOAc/cHex) afforded the title compound as a yellow oil in 60% yield (48 mg, 0.15 mmol). $\mathbf{R_F}$ = 0.42 (EtOAc/cHex = 2:3). **$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 2H), 6.90 – 6.80 (m, 2H), 5.39 – 5.27 (m, 1H), 5.22 – 5.06 (m, 2H), 4.39 – 4.18 (m, 4H), 3.79 (s, 3H), 3.21 – 3.07 (m, 2H), 2.65 – 2.58 (m, 1H), 1.35 – 1.24 (m, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 167.84, 167.44, 159.31, 130.48, 130.29, 129.79, 128.86, 128.02, 120.97, 119.10, 114.20, 114.07, 61.65, 61.34, 55.39, 53.56, 49.73, 45.84, 43.32, 40.42, 37.52, 35.04, 16.68, 14.48, 12.22. **IR (neat)**: vmax ($cm^{-1}$): 2952, 2360, 1733, 1693, 1647, 1612, 1512, 1440, 1245, 1174, 1031. **HRMS (ESI)**: *m/z* calculated for $C_{19}H_{23}NO_4Na^+$ $[M+Na]^+$ 352.1519, found: 352.1508. $\mathbf{[\alpha]_D^{20}}$ = + 89.3 (c = 1.03, $CHCl_3$). **SFC-MS (method 2):** 93% ee: $t_{ret.}$ (major) = 5.88 min. (96.5%), $t_{ret.}$ (minor) = 7.08 min. (3.5%).

**(1*S*,3a*S*,6a*S*)-3-hydroxy-5-(4-methoxybenzyl)-6a-methyl-3-(trifluoromethyl)-1-vinylhexahydro-4*H*-furo[3,4-c]pyrrol-4-one (11)**



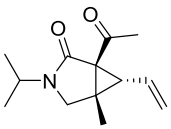
Precursor **3f** (524 mg, 1.1 mmol, 1.0 equiv) was dissolved in anhydrous toluene (8 mL) and subsequently DBU (328 µL, 2.2 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (127 mg, 0.11 mmol, 0.1 equiv) were added. The reaction mixture was stirred overnight at 80 °C. Purification of the crude material by silica gel column chromatography (10% → 30% EtOAc/cHex) afforded the title compound as a yellow oil in 20% yield (73 mg, 0.21 mmol). $\mathbf{R_F}$ = 0.46 (EtOAc/cHex = 3:7). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 2H), 6.93 – 6.87 (m, 2H), 6.28 (s, 1H), 5.74 (ddd, *J* = 17.5, 10.3, 7.5 Hz, 1H), 5.33 – 5.07 (m, 2H), 4.44 (dd, *J* = 199.1, 14.4 Hz, 2H), 4.15 (d, *J* = 7.3 Hz, 1H), 3.81 (d, *J* = 1.2 Hz, 3H), 3.11 (s, 1H), 3.07 – 2.86 (m, 1H), 1.59 (s, 3H), 1.12 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 171.35, 159.63, 131.12, 129.81, 126.91, 121.81 (q, *J* = 285.6 Hz), 120.63, 114.46, 100.54 (q, *J* = 34.5 Hz), 86.74, 57.45, 55.45, 51.92, 47.99, 46.48, 29.83, 18.11. **IR (neat):** vmax ($cm^{-1}$): 2921, 1666, 1612, 1514, 1458, 1269, 1245, 1172, 1143, 1049, 1031, 1002, 939. **HRMS (ESI):** *m/z* calculated for $C_{18}H_{21}NO_4F_3^+$ $[M+H]^+$ 372.1417, found: 372.1421. $\mathbf{[\alpha]_D^{20}}$ = − 4.35 (c = 1.15, $CHCl_3$).

**(1*R*,5*S*,6*R*)-1-acetyl-3,5-dimethyl-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (5g)**



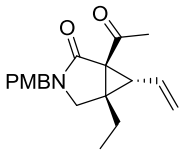
Precrusor **3g** (80 mg, 0.25 mmol, 1.0 equiv) was subjected to general procedure G. The crude material was purified by silica gel column chromatography (1% → 4% MeOH/$CH_2Cl_2$) providing the title compound as a yellow oil in 68% yield (33 mg, 0.17 mmol). $\mathbf{R_F}$ = 0.3 (MeOH/$CH_2Cl_2$ = 2:98). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.43 – 5.34 (m, 1H), 5.31 – 5.20 (m, 2H), 3.32 (dd, *J* = 67.9, 10.9 Hz, 2H), 2.82 (s, 3H), 2.78 (d, *J* = 7.1 Hz, 1H), 2.49 (s, 3H), 1.32 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 201.66 ($C_q$), 170.04 ($C_q$), 129.06 (CH), 121.04 ($CH_2$), 52.77 ($CH_2$), 39.20 (CH), 30.72 ($CH_3$), 28.98 ($CH_3$), 15.88 ($CH_3$). **IR (neat):** vmax ($cm^{-1}$): 2923, 1677, 1639, 1494, 1431, 1402, 1358, 1339, 1215, 1182, 1093, 1045, 916. **HRMS (ESI)**: calculated for $C_{11}H_{16}NO_2$ ($[M+H]^+$) = 194.1176, found = 194.1179. $\mathbf{[\alpha]_D^{20}}$ = + 46.15 (c = 1.04, $CHCl_3$). **SFC-MS (method 2):** 89% ee: $t_{ret.}$ (major) = 4.66 min. (94.6%), $t_{ret.}$ (minor) = 5.43 min. (5.4%).

**(1*R*,5*S*,6*R*)-1-acetyl-3-isopropyl-5-methyl-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (5h)**



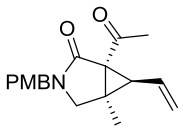
Precursor **3h** (93 mg, 0.27 mmol, 1.0 equiv) was subjected to general procedure F. The crude material was purified by silica gel column chromatography (15% → 65% EtOAc/cHex) providing the title compound as a yellow oil in 69% yield (20 mg, 0.09 mmol) based on recovered starting material (48 mg, 0.14 mmol, 52%). Diastereomeric ratio = 10 : 1 as indicated by $^1$H NMR. $\mathbf{R_F}$ = 0.30 (*major*) and 0.35 (*minor*) (EtOAc/cHex = 3:7). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.43 – 5.33 (m, 2H), 5.24 – 5.19 (m, 1H), 4.41 – 4.32 (m, 1H), 3.28 (dd, *J* = 35.6, 10.6 Hz, 2H), 2.78 – 2.74 (m, 1H), 2.48 (s, 3H), 1.32 (s, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 201.90, 172.21, 171.61, 170.72, 170.05, 169.84, 169.06, 136.81, 136.33, 136.13, 134.44, 134.30, 133.28, 132.91, 132.78, 132.70, 132.22, 132.01, 129.09, 125.44, 125.37, 125.19, 125.14, 124.60, 124.11, 123.64, 121.02, 119.23, 119.05, 117.60, 117.14, 116.24, 115.91, 103.76, 85.68, 84.10, 81.46, 68.03, 67.61, 67.59, 65.47, 63.70, 62.02, 49.85, 48.93, 45.58, 45.42, 42.93, 42.82, 39.01, 31.58, 30.76, 30.34, 30.29, 29.85. **IR (neat)**: vmax ($cm^{-1}$): 2974, 2927, 1747, 1672, 1643, 1481, 1427, 1359, 1338, 1240, 1228, 1209, 1184, 1163, 1126, 1091, 1054. **HRMS (ESI)**: *m/z* calculated for $C_{13}H_{19}NO_2Na^+[M+Na]^+$ 244.1303, found: 244.1320. $\mathbf{[\alpha]_D^{20}}$ = + 113.33 (c = 0.8, $CHCl_3$). **SFC-MS (method 2):** 89% ee: $t_{ret.}$ (major) = 4.65 min. (94.7%), $t_{ret.}$ (minor) = 8.69 min. (5.3%).

**(1*R*,5*S*,6*R*)-1-acetyl-5-ethyl-3-(4-methoxybenzyl)-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (5i)**



Allylic acetate **3i** (102 mg, 0.24 mmol, 1.0 equiv) was used in general procedure G. The reaction mixture was concentrated under reduced pressure to give the crude product as a 9:1 mixture of diastereomers as judged by $^1$H NMR. The crude material was purified by silica gel column chromatography (0% → 30% EtOAc/cHex) providing the title compound as a yellow oil in 41% yield (23 mg, 0.07 mmol) based on recovered starting material (23 mg, 0.05 mmol, 21%). $\mathbf{R_F}$ = 0.50 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 2H), 6.91 – 6.82 (m, 2H), 5.33 – 5.29 (m, 1H), 5.21 – 5.06 (m, 2H), 4.36 (dd, *J* = 75.4, 14.3 Hz, 2H), 3.80 (s, 3H), 3.20 (dd, *J* = 101.3, 10.9 Hz, 2H), 2.80 (d, *J* = 7.8 Hz, 1H), 2.53 (s, 3H), 1.66 – 1.47 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 201.61, 169.78, 159.42, 130.12, 129.69, 129.24, 128.09, 120.76, 114.22, 55.42, 47.71, 46.00, 44.46, 44.02, 39.07, 30.69, 23.15, 11.30. **IR (neat):** vmax ($cm^{-1}$): 2987, 1679, 1512, 2358, 1215, 1174, 746. **HRMS (ESI)**: *m/z* calculated for $C_{19}H_{24}NO_3$ $[M+H]^+$ = 314.1751, found = 314.1760. $\mathbf{[\alpha]_D^{20}}$ = + 63.49 (c = 1.26, $CHCl_3$). **SFC-MS (method 4):** 88% ee: $t_{ret.}$ (major) = 6.76 min. (94%), $t_{ret.}$ (minor) = 6.63 min. (6%).

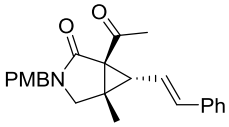
**(1*S*,5*R*,6*S*)-1-acetyl-3-(4-methoxybenzyl)-5-methyl-6-vinyl-3-azabicyclo[3.1.0]hexan-2-one (*ent*-5a)**




Upon submission of precursor ***Z*-3a** (109 mg, 0.26 mmol, 1.0 equiv) to general procedure G, no full conversion of starting material was observed over the course of 8 h. Silica gel column chromatography (5% → 40% EtOAc/cHex) provided the title compound as a yellow oil (40 mg, 0.13 mmol, 50%) and recovered starting material (20 mg, 0.05 mmol, 20%). $\mathbf{R_F}$ = 0.6 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.21 – 7.19 (m, 2H), 6.89 – 6.85 (m, 2H), 5.34 – 5.30 (m, 1H), 5.19 – 5.09 (m, 2H), 4.35 (dd, *J* = 99.3, 14.3 Hz, 2H), 3.80 (s, 3H), 3.19 (q, *J* = 11.0 Hz, 2H), 2.76 (d, *J* = 7.8 Hz, 1H), 2.51 (s, 3H), 1.27 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 201.61, 169.70, 159.45, 150.02, 130.21, 129.03, 128.08, 120.94, 114.23, 55.43, 50.06, 45.93, 39.56, 38.67, 30.77, 15.96. **IR (neat)**: υmax ($cm^{-1}$): 2923, 1676, 1610, 1512, 1483, 1440, 1419, 1357, 1336, 1303, 1244, 1215, 1174, 1108, 1031, 991. **HRMS (ESI)**: m/z calculated for $C_{18}H_{22}NO_3^+$ ($[M+H]^+$) = 300.1594, found = 300.1597. $\mathbf{[\alpha]_D^{20}}$ = − 82.5 (c = 0.8, $CHCl_3$).

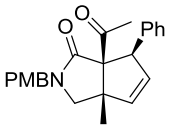
## Vinylcyclopropane rearrangement

**(1*R*,5*S*,6*R*)-1-acetyl-3-(4-methoxybenzyl)-5-methyl-6-((*E*)-styryl)-3-azabicyclo[3.1.0]hexan-2-one (14)**




Vinylcyclopropane **5a** (50 mg, 0.12 mmol, 1.0 equiv) and styrene (41 µL, 0.36 mmol, 3.0 equiv) were dissolved in anhydrous $CH_2Cl_2$ (2 mL). The solution was degassed with argon followed by the addition of Grubbs II generation catalyst (100 µg, 0.01 mmol, 0.1 equiv). The reaction mixture was heated to reflux and was stirred for 16 h, after which TLC analysis indicated complete conversion. The reaction mixture was concentrated under reduced pressure and the crude material was purified by silica gel column chromatography (20% EtOAc/cHex), providing the pure product as an off-white solid in 44% yield (26 mg, 0.05 mmol). $\mathbf{R_F}$ = 0.3 (EtOAc/cHex = 3:7). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 6.95 (dd, *J* = 91.9, 7.8 Hz, 4H), 6.65 (d, *J* = 15.7 Hz, 1H), 5.46 (dd, *J* = 15.7, 8.8 Hz, 1H), 4.43 (dd, *J* = 387.1, 14.2 Hz, 2H), 3.83 (s, 3H), 3.36 (dd, *J* = 32.7, 10.7 Hz, 2H), 2.96 (d, *J* = 8.8 Hz, 1H), 2.59 (s, 3H), 1.38 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 201.63, 169.50, 159.44, 136.53, 135.84, 130.42, 128.49, 128.21, 127.75, 126.29, 120.43, 114.42, 55.34, 50.22, 46.12, 40.16, 39.27, 30.83, 16.11. **IR (neat)**: υmax ($cm^{-1}$): 2820, 2181, 1743, 1674, 1510, 1446, 1269, 1242, 1199, 1176, 966. **HRMS (ESI)**: calculated for $C_{24}H_{26}NO_3$ ($[M+H]^+$) = 376.1907, found = 376.1905. $\mathbf{[\alpha]_D^{20}}$ = + 165.4 (c = 1.33, $CHCl_3$). m.p.: 102 – 105 °C.

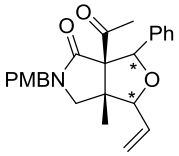
**(3a*S*,6*R*,6a*R*)-6a-acetyl-2-(4-methoxybenzyl)-3a-methyl-6-phenyl-3,3a,6,6a-tetrahydrocyclopenta[c]pyrrol-1(2*H*)-one (15)**



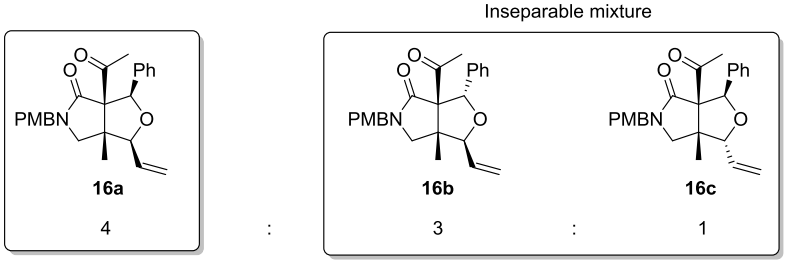

To a solution of styrylcyclopropane **14** (26 mg, 0.1 mmol, 1.0 equiv) and $SnCl_4$ (13.2 µL, 0.11 mmol, 1.1 equiv) in anhydrous $CH_2Cl_2$ (2 mL) were added freshly dried 4 Å MS (50 mg). The reaction mixture was heated to reflux and was stirred for 2 h, after which TLC analysis indicated complete conversion. The reaction mixture was poured into a sat. aq. $NaHCO_3$ solution at 0 °C which was subsequently transferred to a separation funnel. The phases were separated and the aqueous phase was extracted 3x with $CH_2Cl_2$. The organics were combined and washed with brine, dried ($Na_2SO_4$) and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography (50% EtOAc/cHex), providing the pure cyclopentene as a grey solid in 58% yield (15 mg, 0.06 mmol). $\mathbf{R_F}$ = 0.6 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 5H), 6.96 (dd, *J* = 135.9, 8.5 Hz, 4H), 5.75 (dd, *J* = 5.7, 2.7 Hz, 1H), 5.50 (d, *J* = 5.7 Hz, 1H), 4.74 (s, 1H), 4.43 (dd, *J* = 115.1, 14.7 Hz, 2H), 3.80 (s, 3H), 3.19 (dd, *J* = 119.9, 9.8 Hz, 2H), 1.95 (s, 3H), 1.51 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 204.69, 173.28, 159.23, 140.00, 137.24, 132.79, 129.32, 129.15, 128.78, 127.97, 127.43, 114.22, 58.22, 56.00, 55.40, 52.62, 46.57, 30.71, 21.42. **IR (neat)**: υmax ($cm^{-1}$): 2920, 1681, 1512,1440, 1353, 1282, 1245, 1215, 1174, 1029. **HRMS (ESI)**: calculated for $C_{24}H_{26}NO_3$ ($[M+H]^+$) = 376.1907, found = 376.1905. $\mathbf{[\alpha]_D^{20}}$ = + 235.6 (c = 0.73, $CHCl_3$). m.p.: 109 – 113 °C.

## Vinylcyclopropane cycloaddition

**(3a*S*,6a*S*)-3a-acetyl-5-(4-methoxybenzyl)-6a-methyl-3-phenyl-1-vinylhexahydro-4*H*-furo[3,4-c]pyrrol-4-one (16)**




To vinylcyclopropane **5a** (100 mg, 0.35 mmol, 1.0 equiv) in anhydrous $CH_2Cl_2$ (1 mL) was added $Sn(OTf)_2$ (32 µL, 0.17 mmol, 0.5 equiv) and benzaldehyde (120 µL, 1.05 mmol, 3.0 equiv). The reaction mixture was stirred overnight at room temperature. TLC analysis indicated complete conversion and the reaction mixture was concentrated. Column chromatography (20% EtOAc/cHex) provided **16a** (30 mg, 0.07 mmol, 21%) as a colorless oil and an inseparable mixture of **16b** and **16c** (30 mg, 0.07 mmol, 21%) as a colorless oil in a 4:3:1 ratio.




**<u>16a</u>: $R_F$** = 0.7 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.26 – 7.23 (m, 2H), 6.93 – 6.86 (m, 2H), 5.89 (ddd, *J* = 17.5, 10.5, 7.2 Hz, 1H), 5.33 (s, 1H), 5.29 – 5.11 (m, 2H), 4.50 (dd, *J* = 108.5, 14.4 Hz, 2H), 3.81 (s, 3H), 3.04 (dd, *J* = 26.0, 10.6 Hz, 2H), 1.68 (s, 3H), 1.09 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 203.34, 173.25, 159.51, 138.38, 132.64, 129.91, 128.40, 127.99, 127.84, 126.90, 119.81, 114.39, 87.01, 85.02, 55.45, 53.03, 51.93, 46.61, 31.37, 17.02. **IR (neat)**: υmax ($cm^{-1}$): 2927, 2837, 1670, 1510, 1448, 1357, 1242, 1228, 1193, 1176, 966. **HRMS (ESI)**: calculated for $C_{25}H_{28}NO_4$ ($[M+H]^+$) = 406.2013, found = 406.1994. **$[\alpha]_D^{20}$** = + 45.71 (c = 0.7, $CHCl_3$).

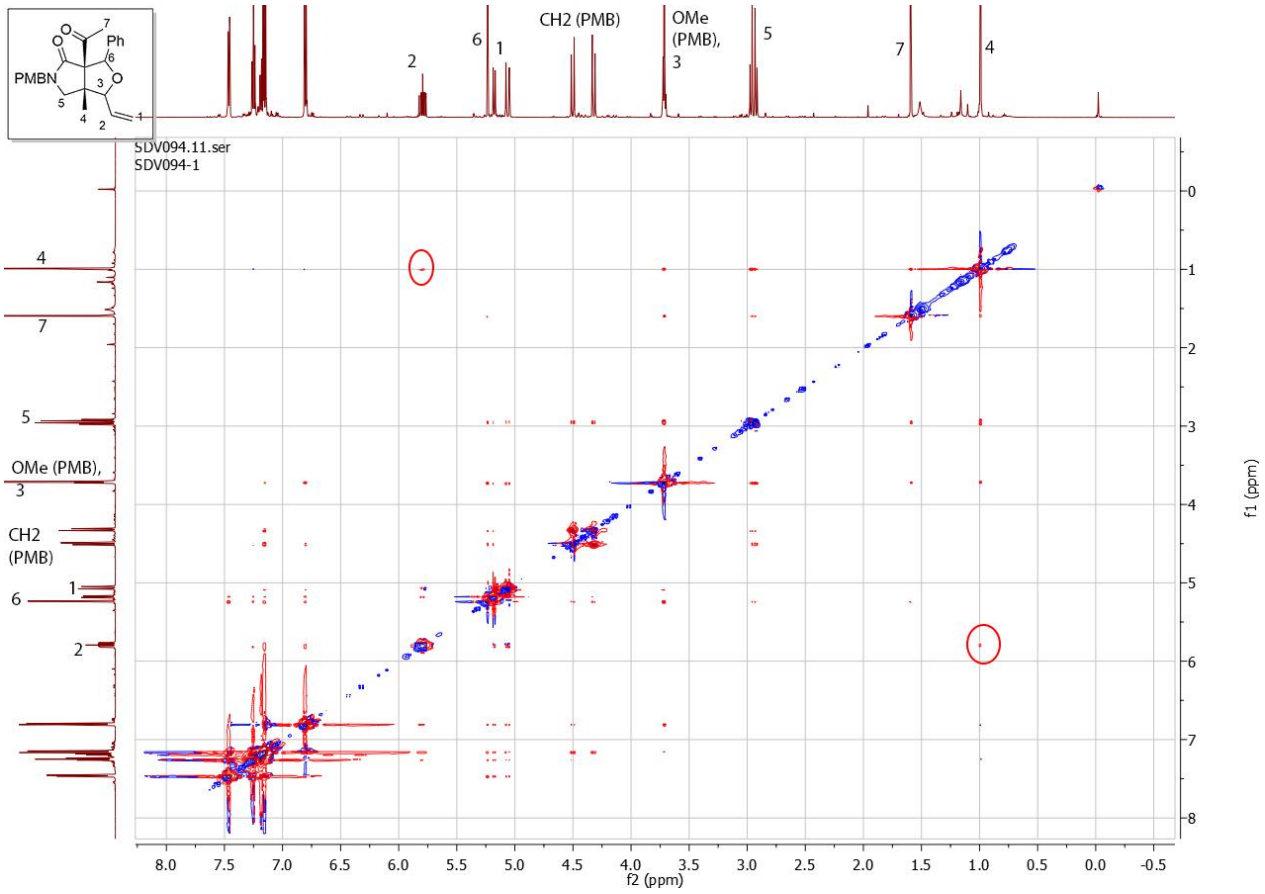
**<u>16b</u>: $R_F$** = 0.6 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.04 (m, 5H), 7.13 – 6.73 (m, 4H), 6.06 (s, 1H), 6.03 – 5.94 (m, 1H), 5.30 – 5.18 (m, 2H), 4.39 – 4.22 (m, 3H), 3.80 (s, 3H), 3.19 (dd, *J* = 139.1, 9.9 Hz, 2H), 2.15 (s, 3H), 1.01 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 204.17, 159.43, 133.59, 131.81, 130.18, 129.96, 127.99, 127.78, 126.38, 119.65, 114.21, 89.73, 84.61, 56.93, 55.42, 46.42, 30.29, 18.25.

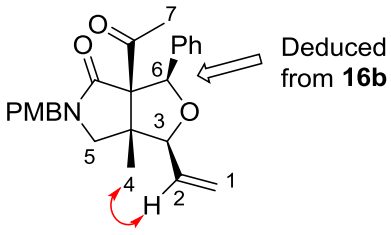
**<u>16c:</u> $R_F$** = 0.6 (EtOAc/cHex = 1:1). **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.03 (m, 5H), 6.95 (m, 4H), 5.80 – 5.73 (m, 2H), 5.49 – 5.30 (m, 2H), 4.16 – 4.08 (m, 1H), 3.80 (s, 3H), 3.11 (dd, *J* = 474.0, 9.9 Hz, 2H), 2.29 (s, 3H), 1.10 (s, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 205.83, 170.20, 159.43, 137.21, 133.59, 131.81, 129.96, 129.14, 128.40, 127.30, 126.38, 119.97, 113.92, 89.73, 85.84, 84.61, 55.42, 52.57, 52.33, 30.99, 19.93.

**<u>16b+16c</u>**: **IR (neat)**: υmax ($cm^{-1}$): 2912, 1685, 1610, 1585, 1512, 1490, 1440, 1421, 1382, 1353, 1323, 1301, 1271, 1244, 1205, 1174, 1128, 1110, 1081, 1066, 1029, 993.

**NOESY analysis of 16a:**

All relevant correlations are indicated by a red outline.



**NOESY analysis of 16b + 16c:**

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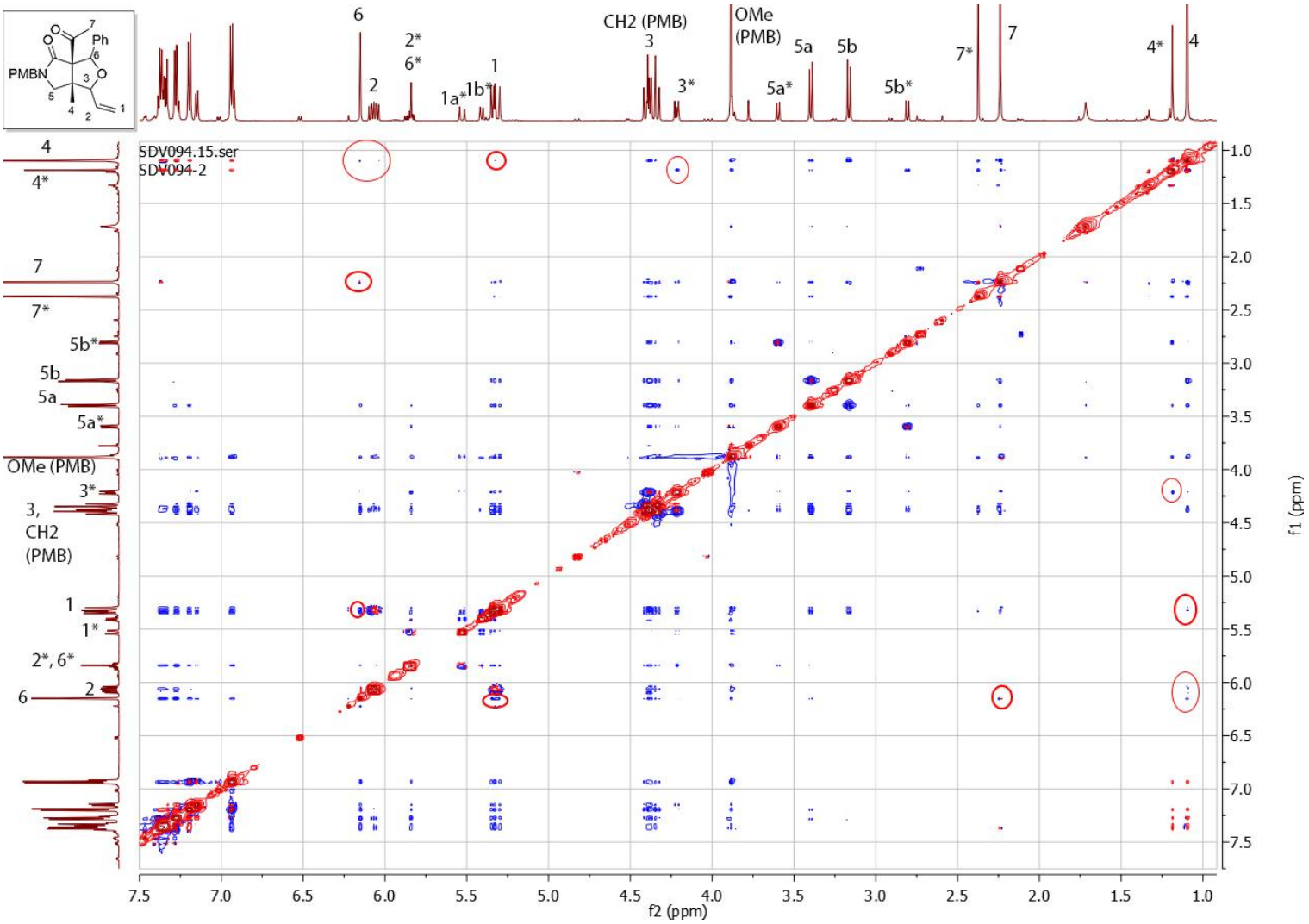
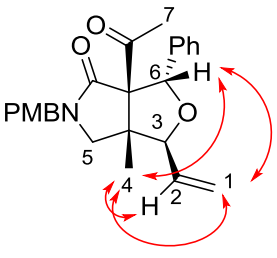
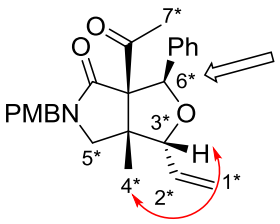


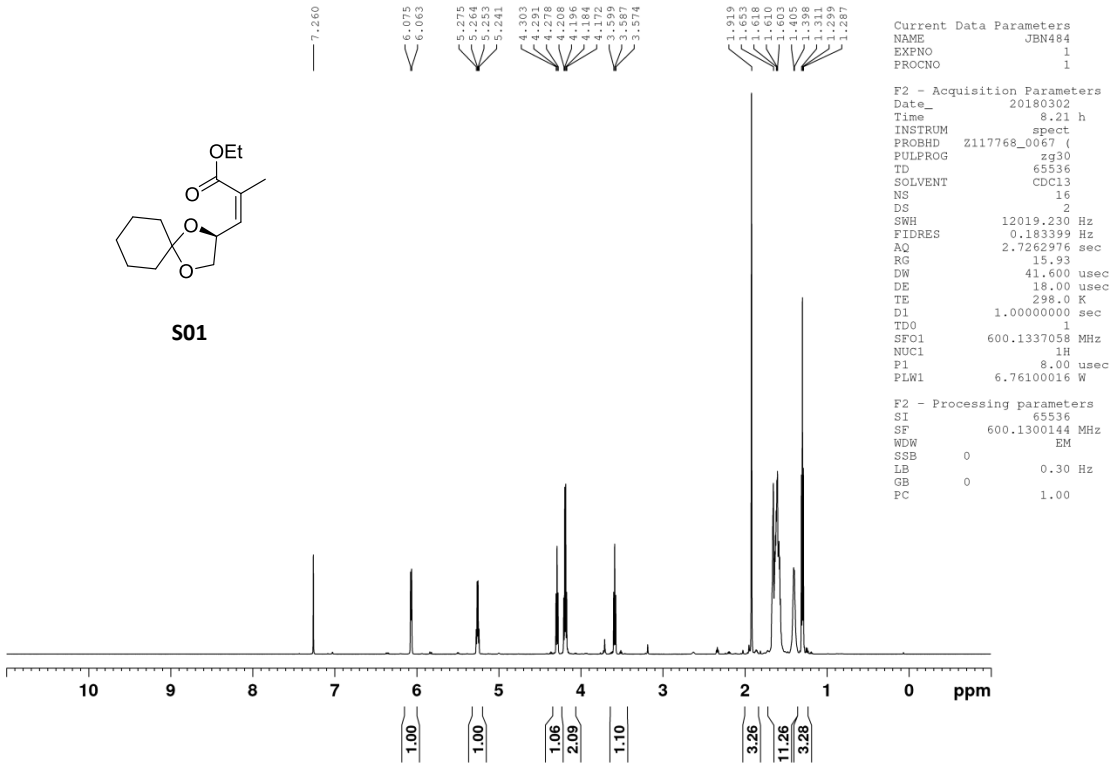

**16b**

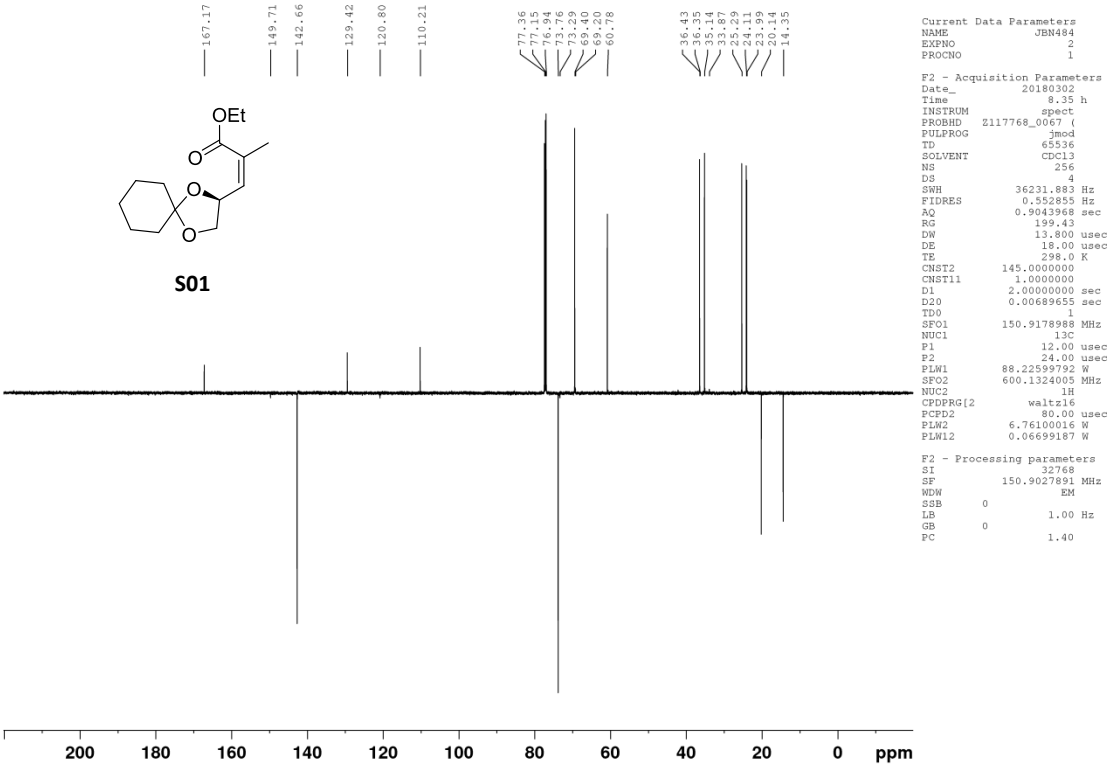


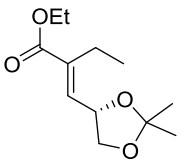

**16c**

# NMR spectra

## Esters

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**S02**


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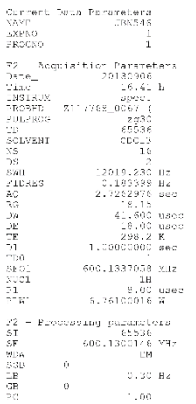
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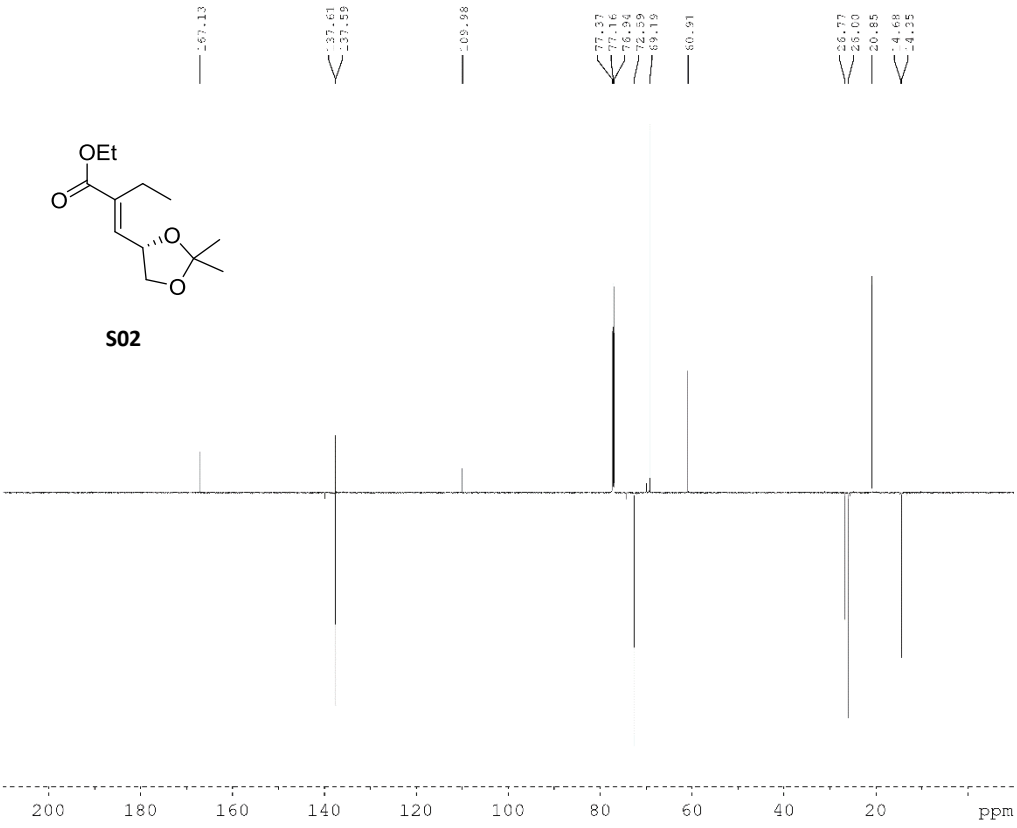
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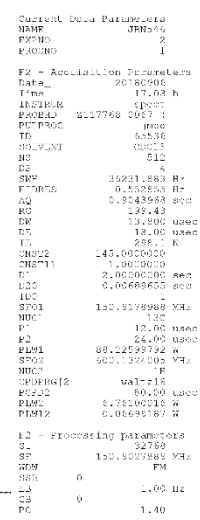
**S02**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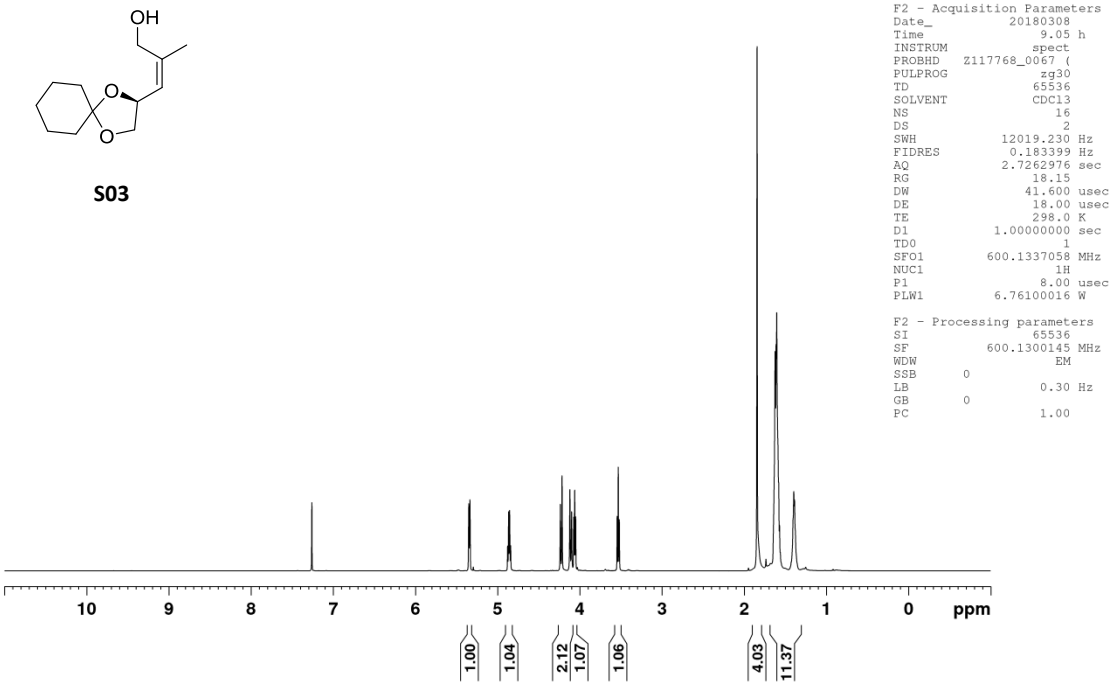
## Alcohols

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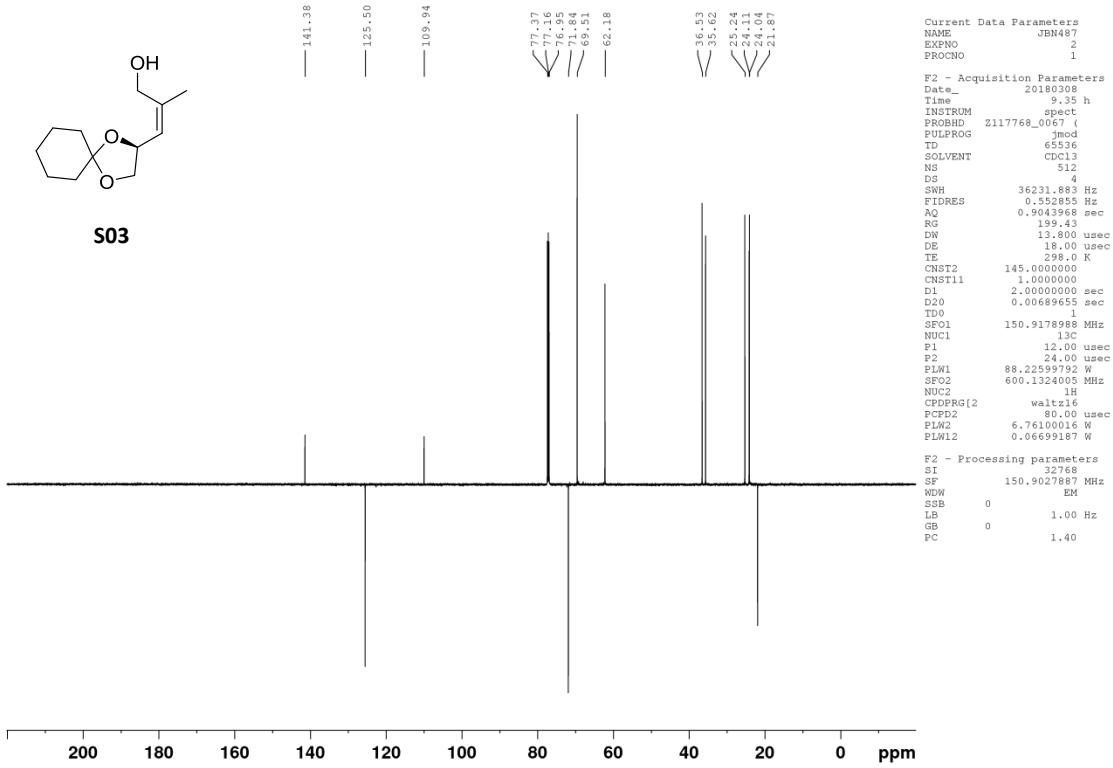


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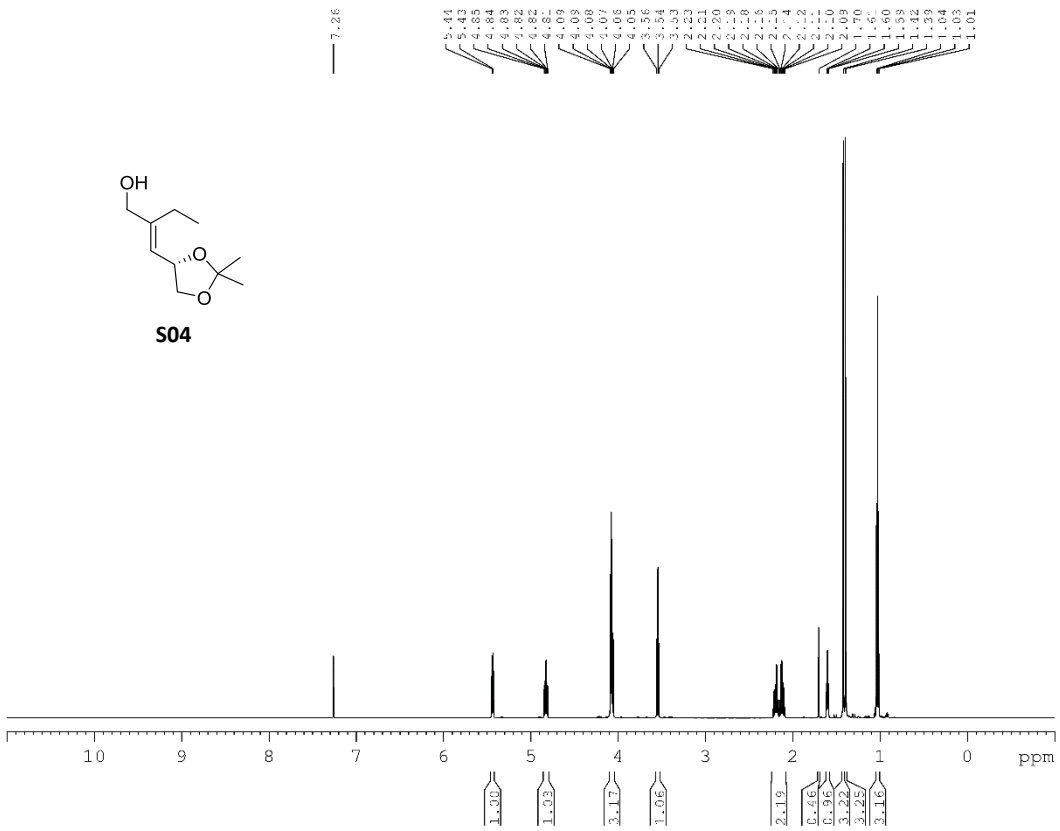
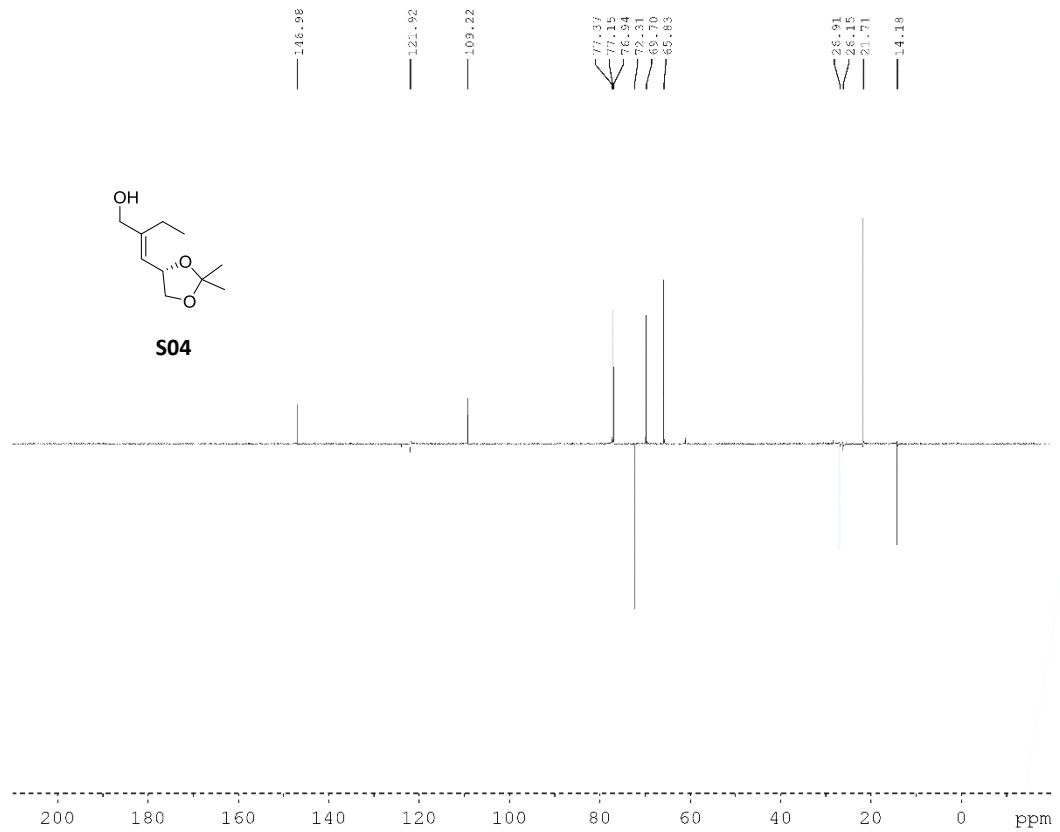
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

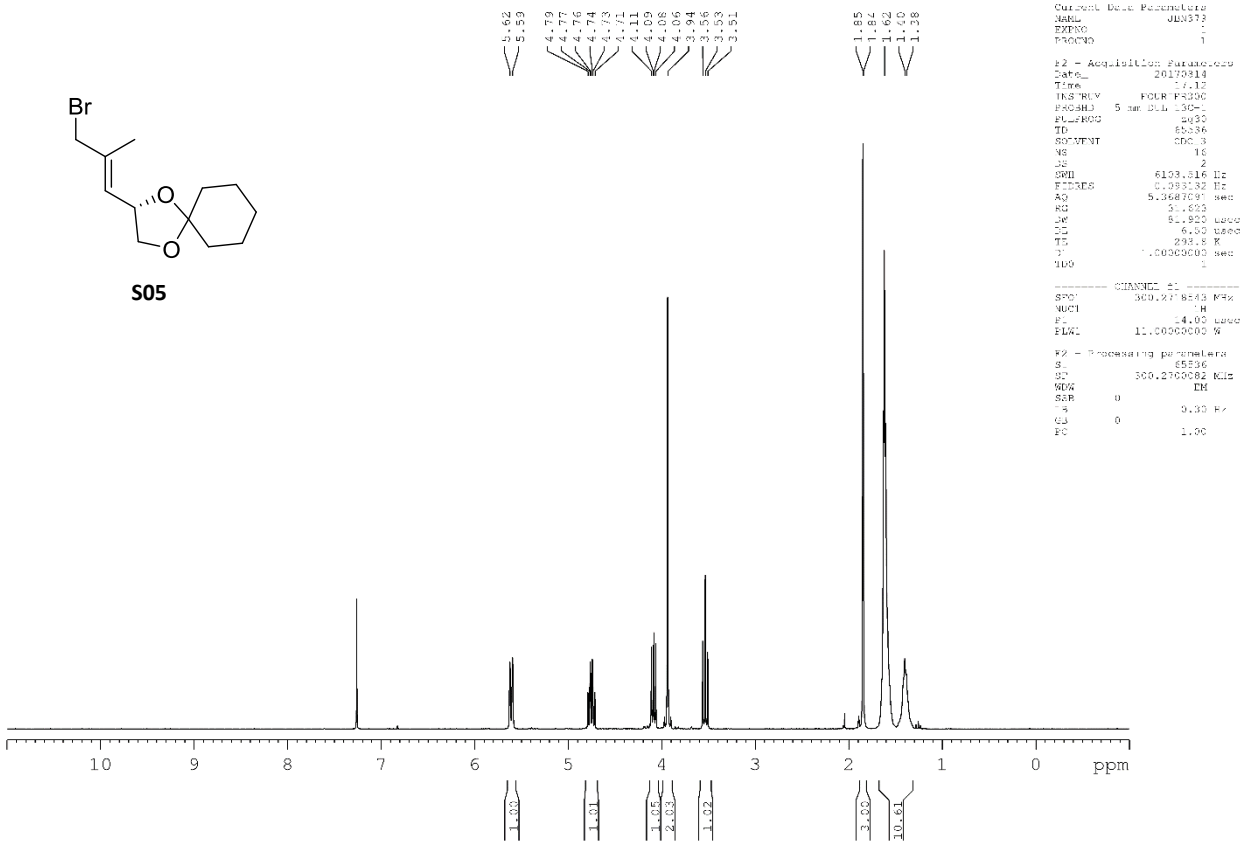

OH
7.26
5.44
5.43
4.85
4.84
4.83
4.82
4.82
4.81
4.09
4.08
4.07
4.06
4.05
3.56
3.54
3.53
2.23
2.21
2.20
2.19
2.18
2.16
2.15
2.14
2.12
2.11
2.10
2.09
1.70
1.60
1.59
1.42
1.39
1.04
1.03
1.01
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
3.17
1.06
2.19
0.46
0.96
3.22
3.25
3.16

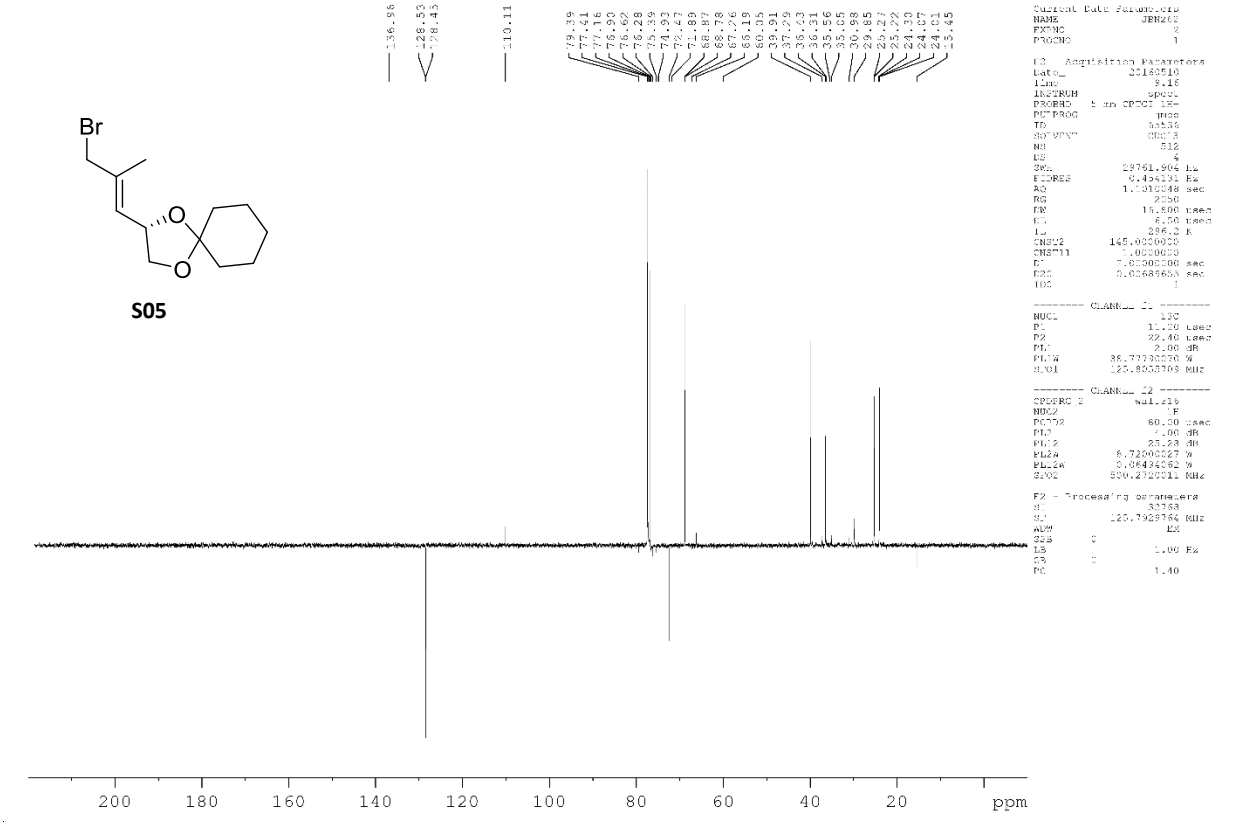
**S04**

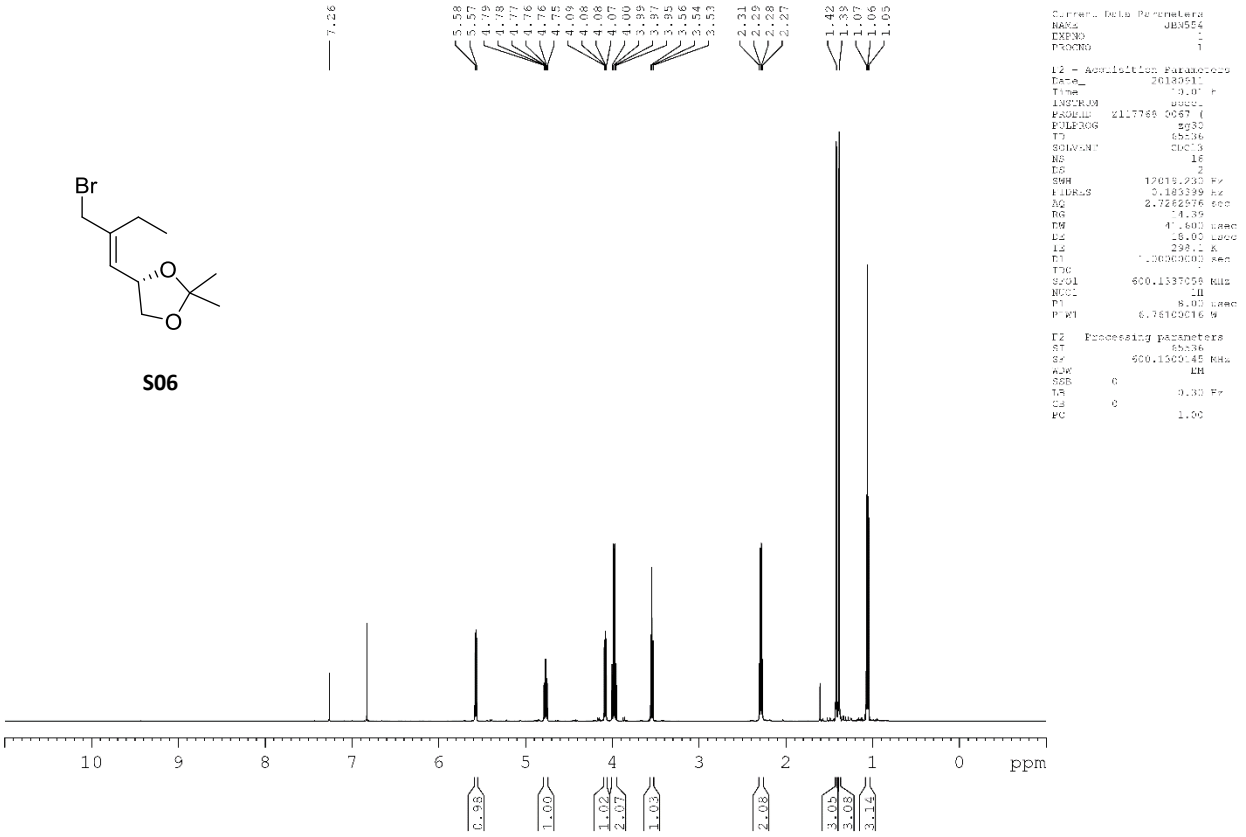

OH
146.98
121.92
109.22
77.37
77.15
76.94
72.31
69.70
65.83
26.91
26.15
21.71
14.18
200
180
160
140
120
100
80
60
40
20
0
ppm

**S04**

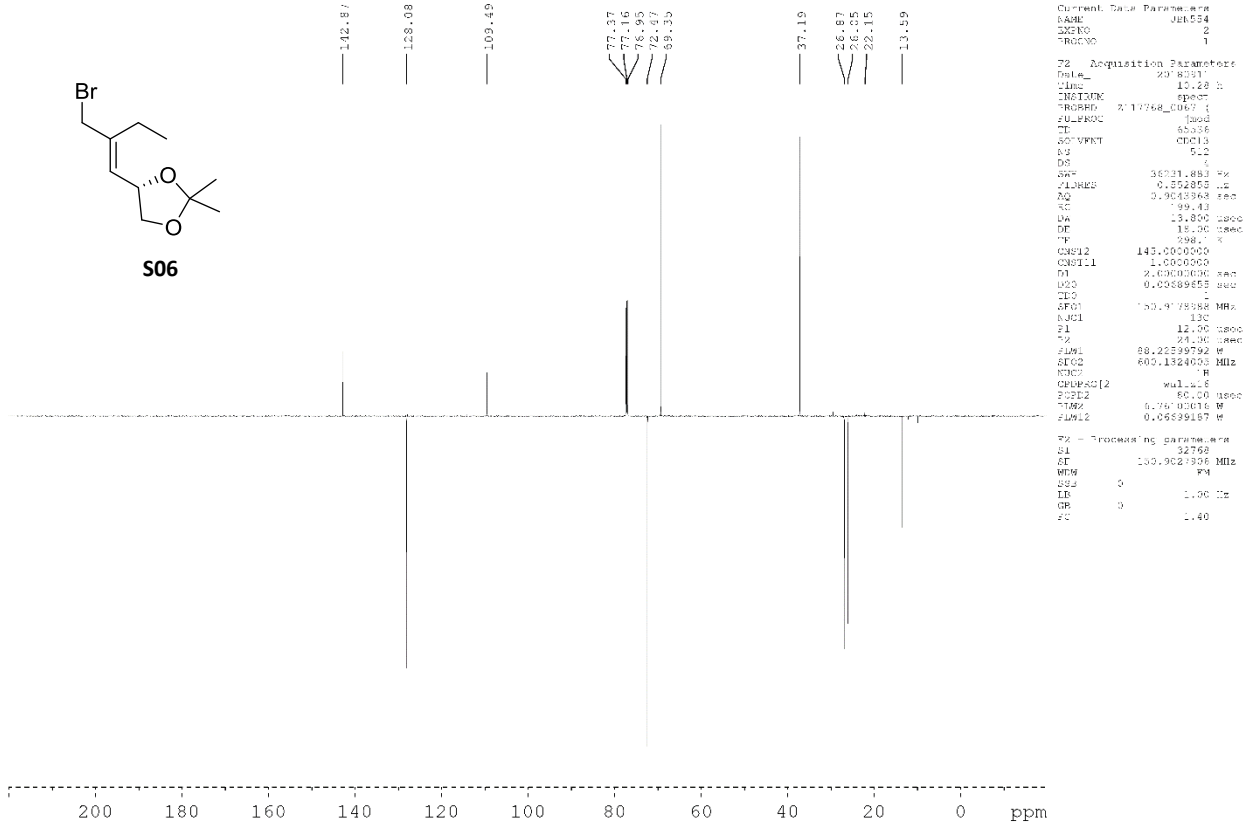
## Bromides


Br
O
O
S05
5.62
5.59
4.79
4.77
4.76
4.74
4.73
4.71
4.11
4.09
4.08
4.06
3.94
3.56
3.53
3.51
1.85
1.84
1.62
1.40
1.38
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.05
2.03
1.02
3.03
10.61


Br
O
O
S05
136.96
128.53
128.43
110.11
79.39
77.41
77.16
76.90
76.62
76.28
75.39
74.93
72.47
71.89
68.87
68.78
67.26
65.19
60.05
39.91
37.29
36.43
36.31
35.56
35.55
30.98
29.85
25.27
25.22
24.38
24.07
24.01
15.45
200
180
160
140
120
100
80
60
40
20
ppm

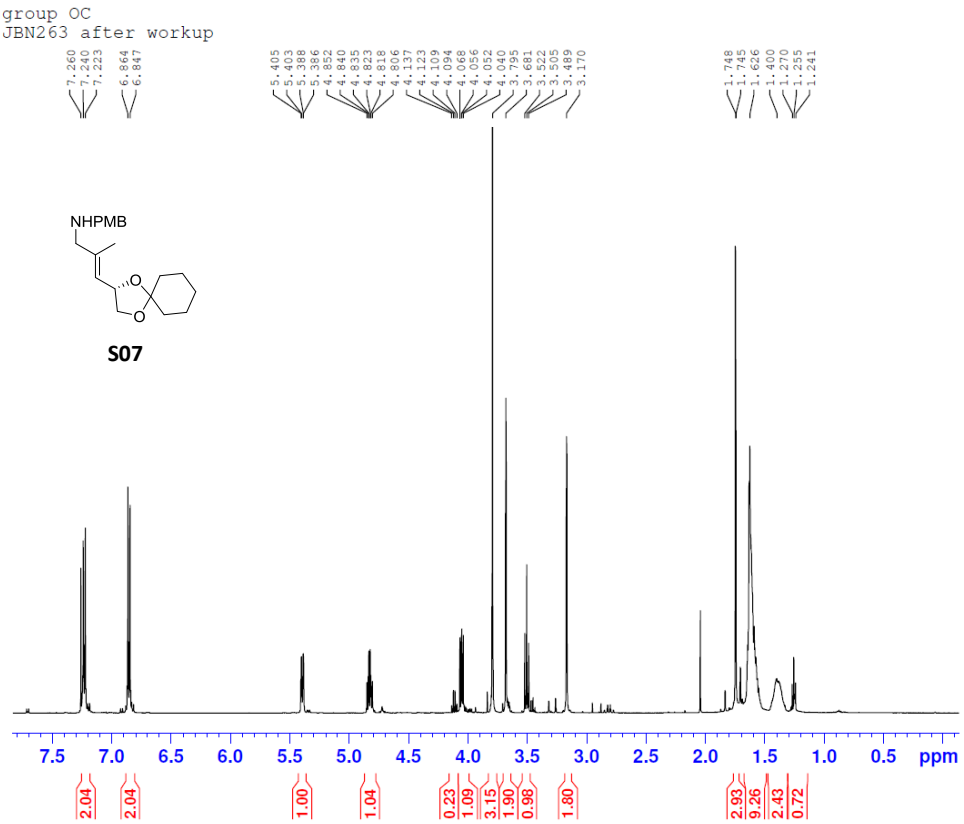

Br
O
O
7.26
5.58
5.57
4.79
4.78
4.77
4.76
4.76
4.75
4.09
4.08
4.08
4.07
4.00
3.99
3.97
3.95
3.56
3.54
3.53
2.31
2.29
2.28
2.27
1.42
1.38
1.07
1.06
1.05
0.98
1.00
1.02
2.07
1.03
2.08
3.01
3.08
3.14
10
9
8
7
6
5
4
3
2
1
0
ppm

**S06**


Br
O
O
142.87
128.08
109.49
77.37
77.16
76.95
72.47
69.35
37.19
26.87
26.35
22.15
13.59
200
180
160
140
120
100
80
60
40
20
0
ppm

**S06**

## Amines

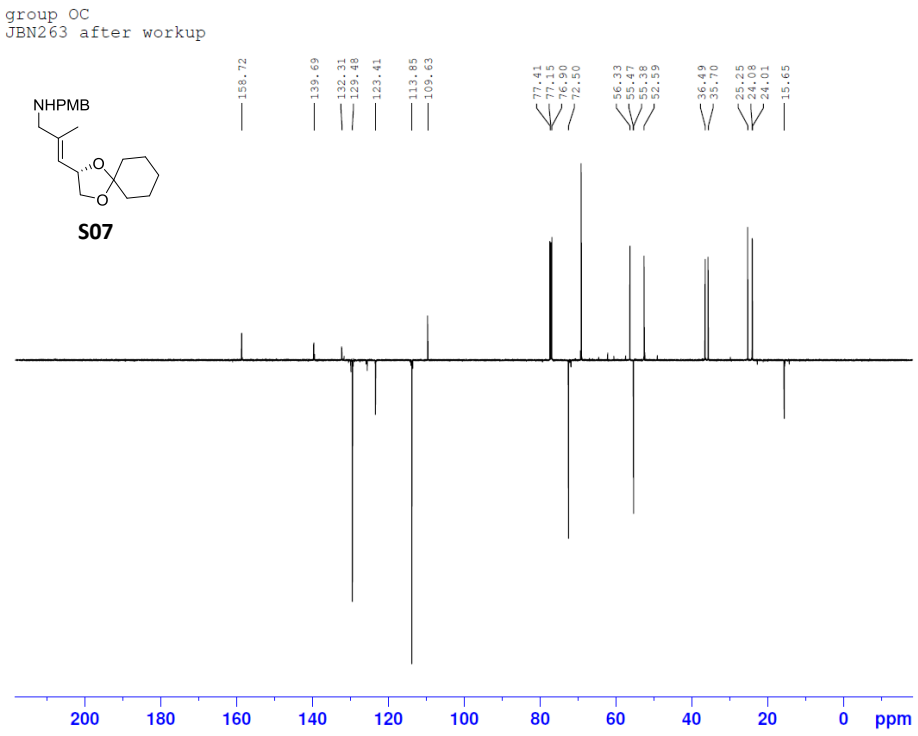



```
Current Data Parameters
NAME                  JBN263
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160510
Time                 18.18
INSTRUM              spect
PROBHD    5 mm CPTCI 1H-
PULPROG              zg30
TD                  65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719425 sec
RG                      18
DW                 48.400 usec
DE                  6.50 usec
TE                 296.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   6.70 usec
PL1                  4.00 dB
PL1W           8.72000027 W
SFO1          500.2730894 MHz

F2 - Processing parameters
SI                   32768
SF            500.2700081 MHz
WDW                     EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```



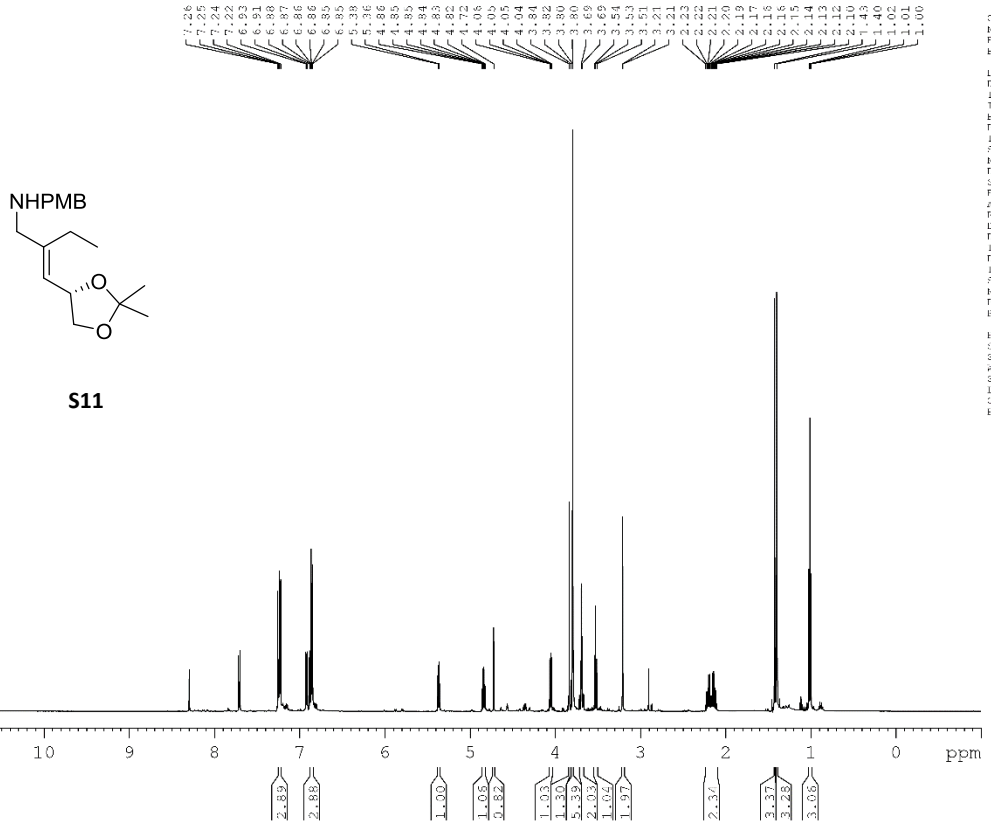

```
Current Data Parameters
NAME                  JBN263
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160510
Time                 20.20
INSTRUM              spect
PROBHD    5 mm CPTCI 1H-
PULPROG             jmod
TD                  65536
SOLVENT              CDCl3
NS                     512
DS                       4
SWH             29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010048 sec
RG                    2050
DW                 16.800 usec
DE                  6.50 usec
TE                 296.2 K
CNST2         145.0000000
CNST11          1.0000000
D1              2.00000000 sec
D20             0.00689655 sec
TD0                      1

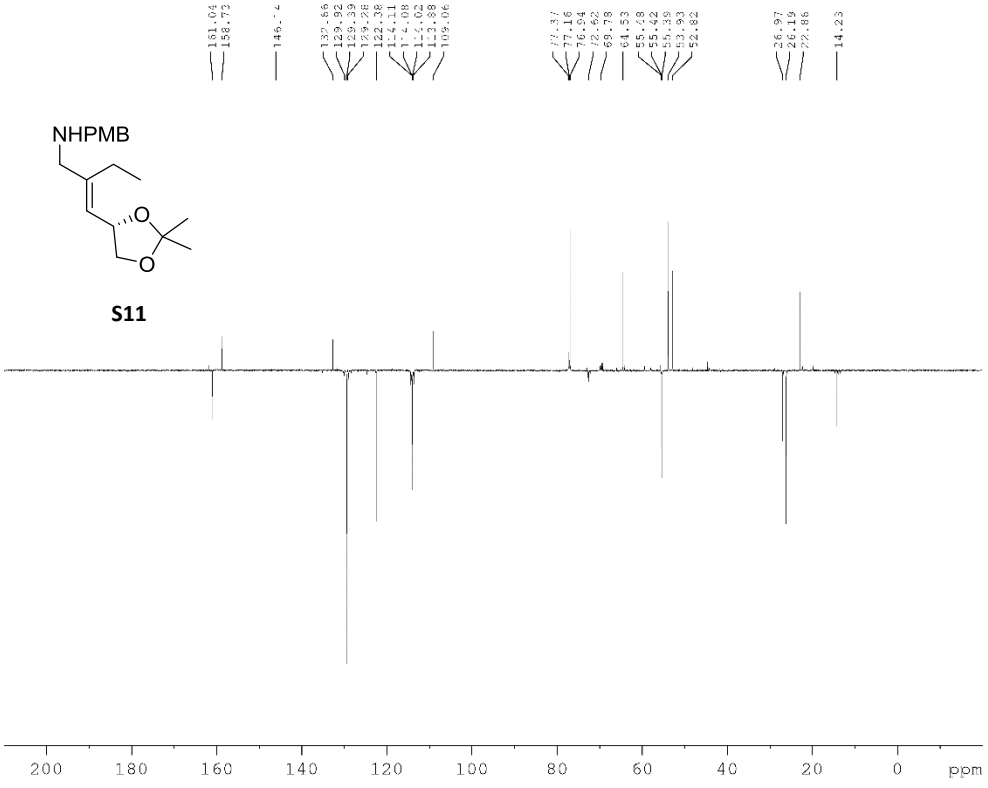
======== CHANNEL f1 ========
NUC1                   13C
P1                  11.20 usec
P2                  22.40 usec
PL1                 -2.00 dB
PL1W           88.77790070 W
SFO1          125.8055709 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  4.00 dB
PL12                25.28 dB
PL2W           8.72000027 W
PL12W          0.06494062 W
SFO2          500.2720011 MHz

F2 - Processing parameters
SI                   32768
SF            125.7929791 MHz
WDW                     EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

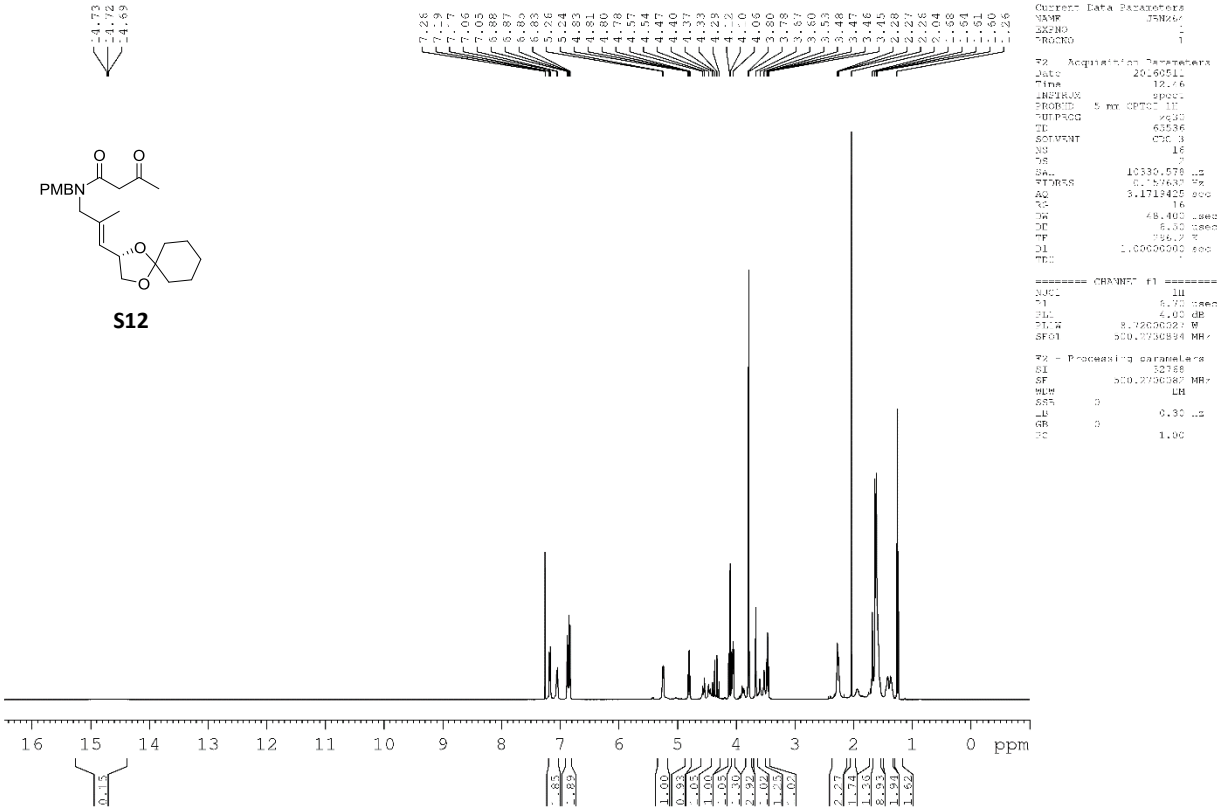


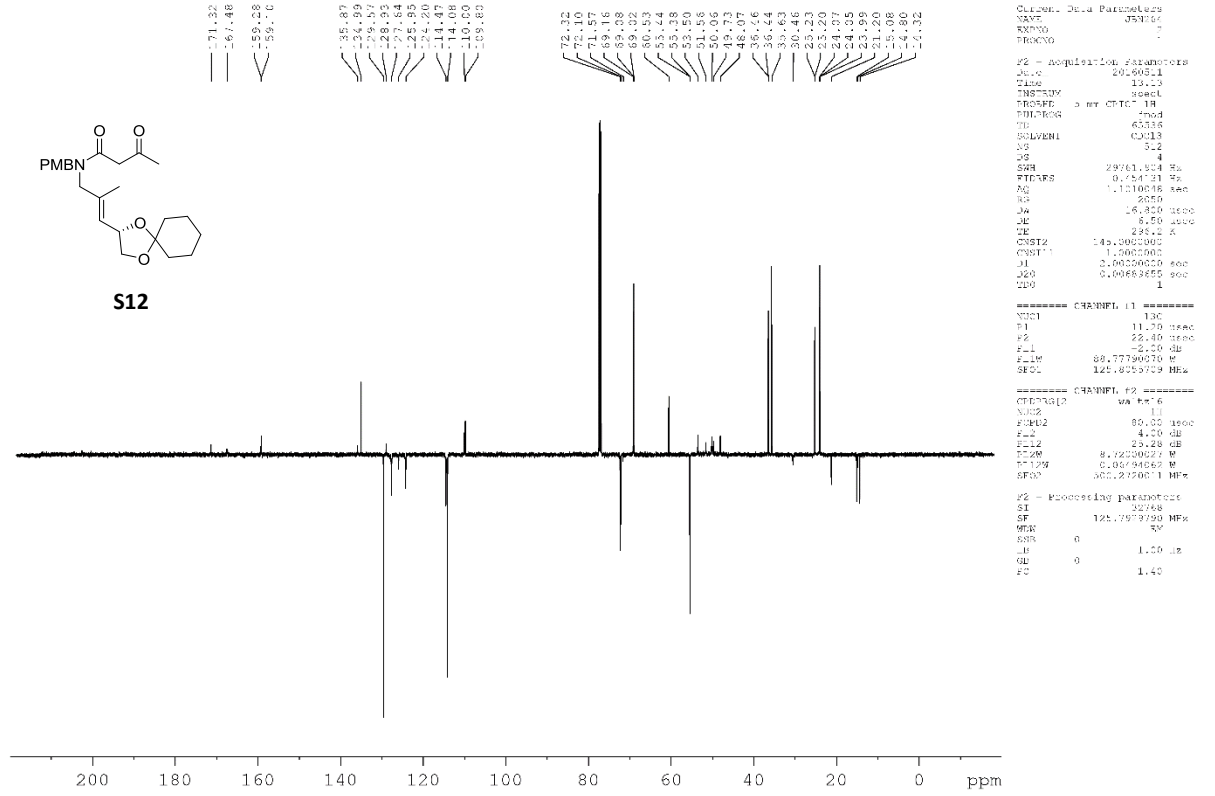

**S11**

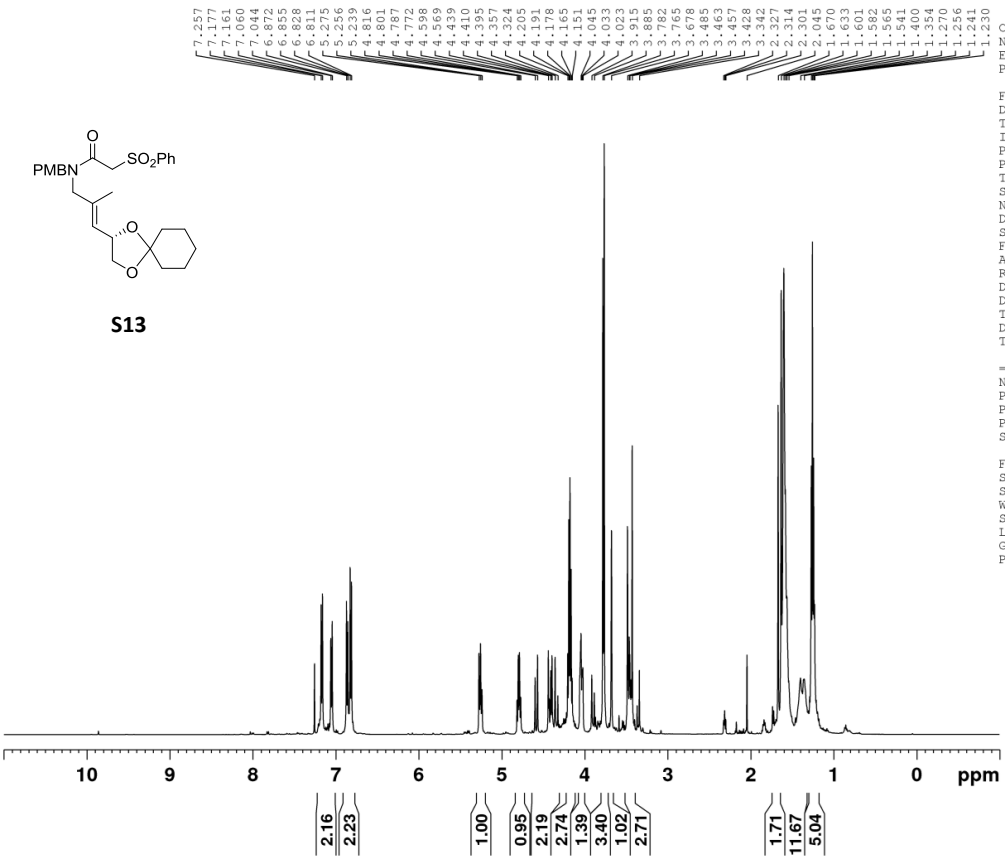



**S11**

## Acetals





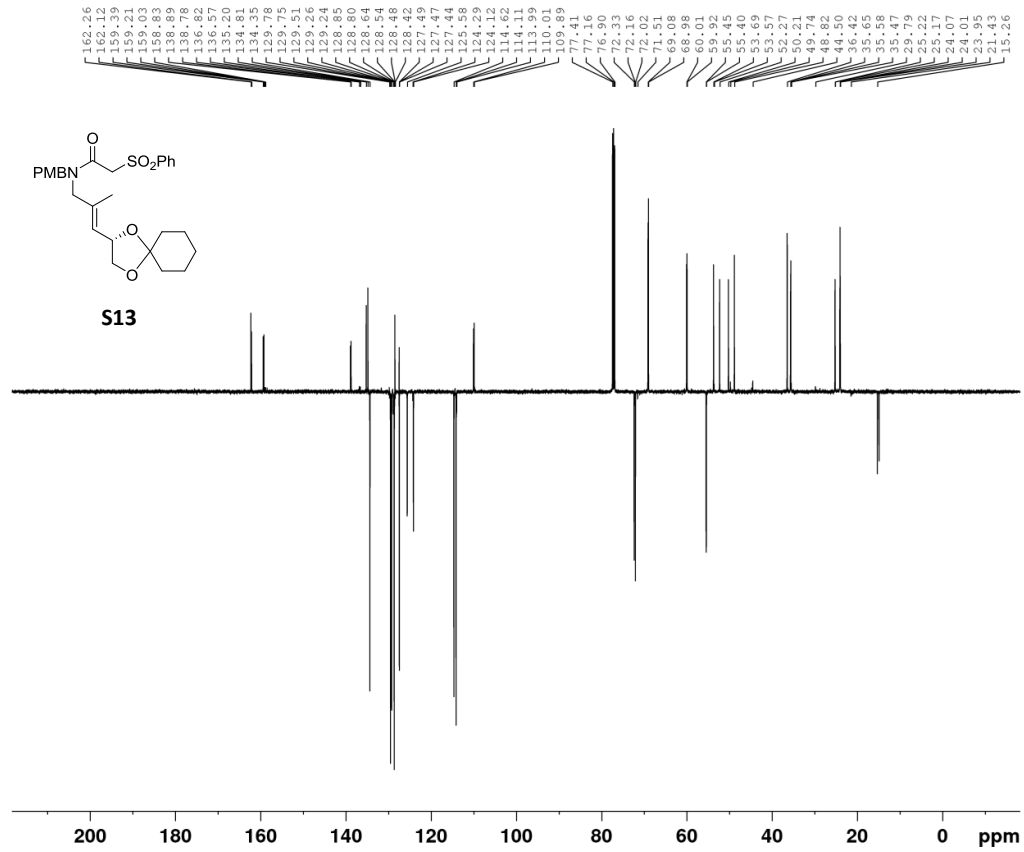

**S13**

```
Current Data Parameters
NAME                  BM008f
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20161031
Time                   16.12
INSTRUM                spect
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                3.1719425 sec
RG                     11.3
DW                   48.400 usec
DE                    6.50 usec
TE                   298.3 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     6.70 usec
PL1                    4.00 dB
PL1W            8.72000027 W
SFO1           500.2730894 MHz

F2 - Processing parameters
SI                        32768
SF               500.2700096 MHz
WDW                        EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```




**S13**

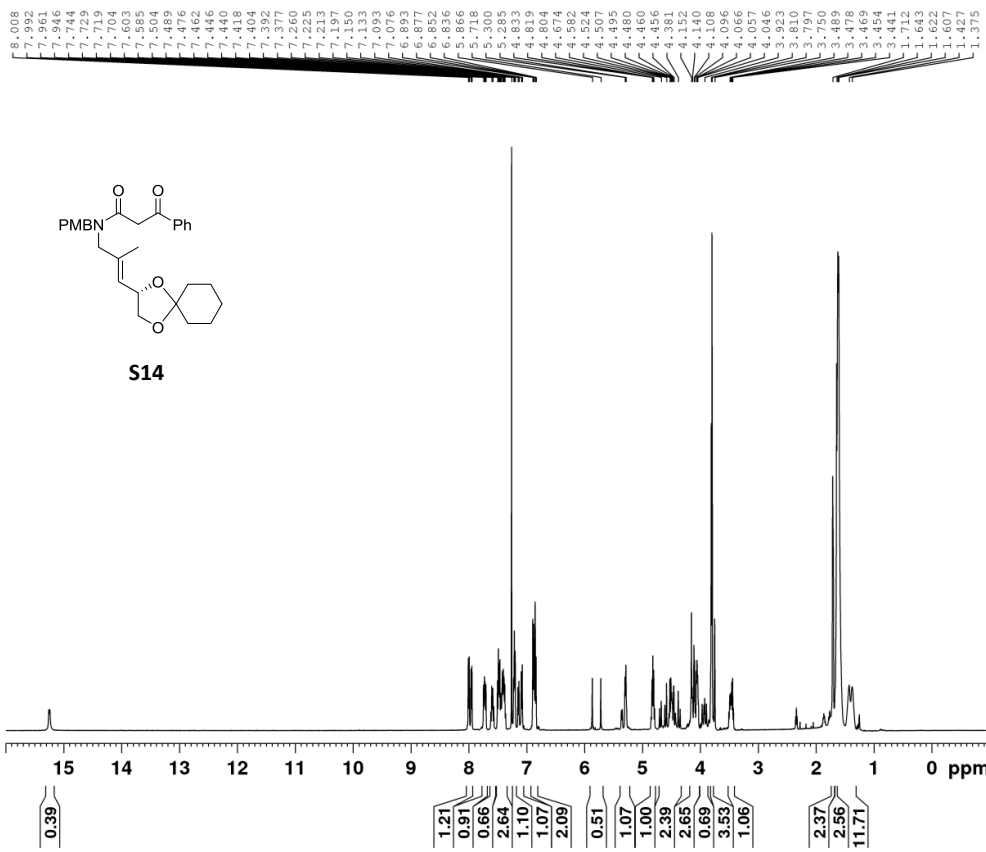
```
Current Data Parameters
NAME      BM039purefinal
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_               20160826
Time                   11.26
INSTRUM                spect
PROBHD    5 mm CPTCI 1H-
PULPROG                jmod
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010048 sec
RG                     2050
DW                   16.800 usec
DE                    6.50 usec
TE                   298.2 K
CNST2             145.0000000
CNST11              1.0000000
D1                  2.00000000 sec
D20                 0.00689655 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                    11.20 usec
P2                    22.40 usec
PL1                   -2.00 dB
PL1W           88.77790070 W
SFO1          125.8055709 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                      1H
PCPD2                 80.00 usec
PL2                    4.00 dB
PL12                  25.28 dB
PL2W            8.72000027 W
PL12W           0.06494062 W
SFO2          500.2720011 MHz

F2 - Processing parameters
SI                        32768
SF               125.7929818 MHz
WDW                        EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



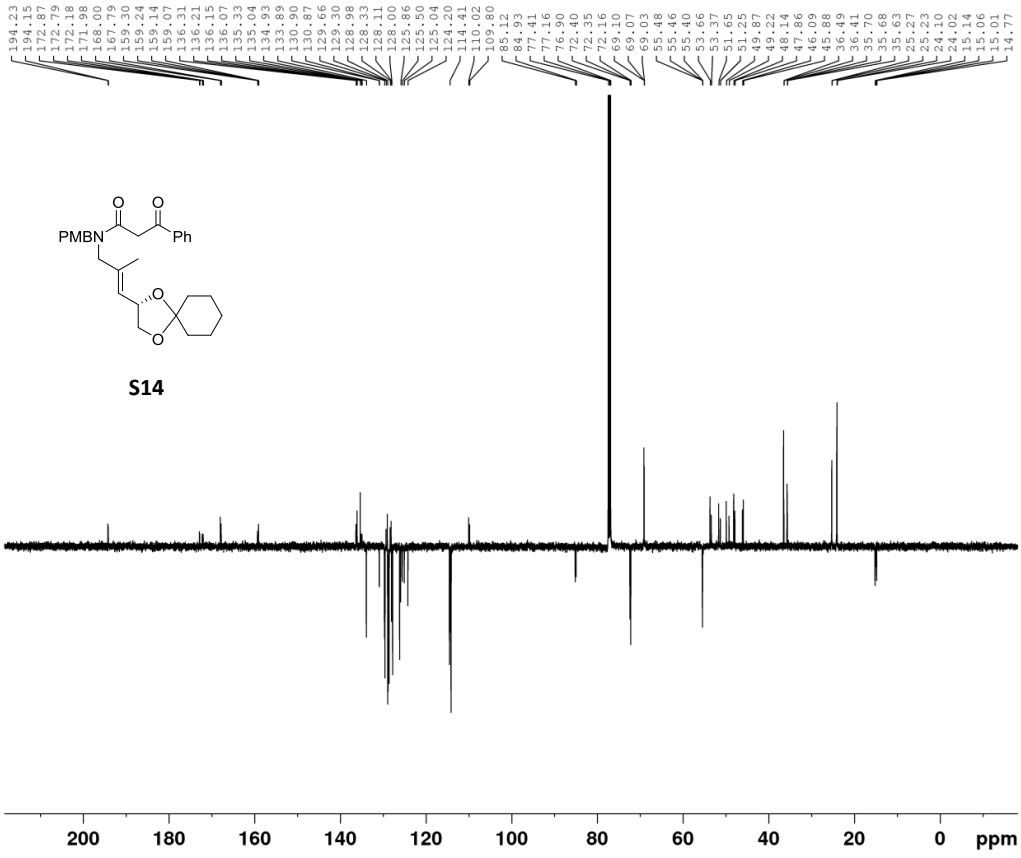

Current Data Parameters
NAME BMO030
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160813
Time 17.31
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 12.7
DW 48.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 6.70 usec
PL1 4.00 dB
PL1W 8.72000027 W
SFO1 500.2730894 MHz

F2 - Processing parameters
SI 32768
SF 500.2700076 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

**S14**




Current Data Parameters
NAME BMO030
EXPNO 2
PROCNO 1

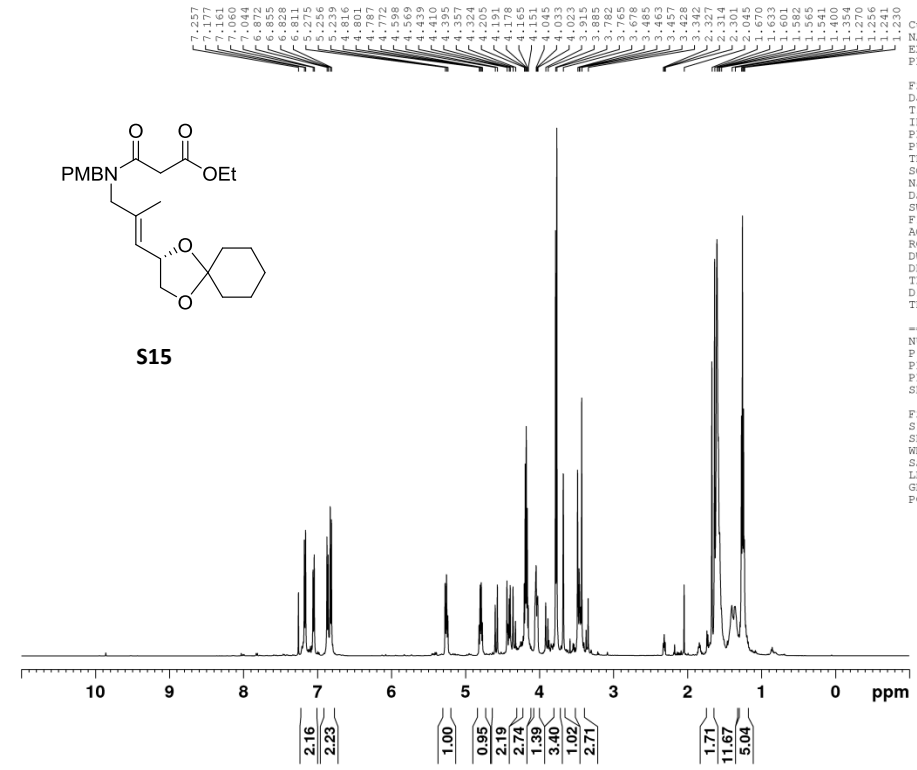
F2 - Acquisition Parameters
Date_ 20160813
Time 18.26
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 11.20 usec
P2 22.40 usec
PL1 -2.00 dB
PL1W 88.77790070 W
SFO1 125.8055709 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 25.28 dB
PL2W 8.72000027 W
PL12W 0.06494062 W
SFO2 500.2720011 MHz

F2 - Processing parameters
SI 32768
SF 125.7929764 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

**S14**



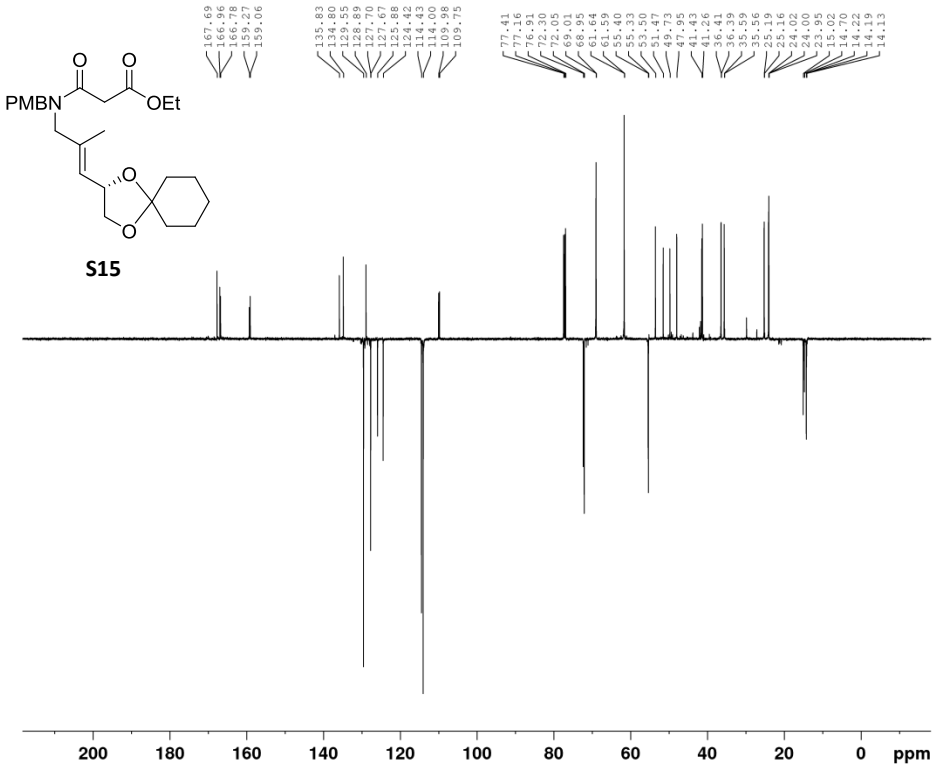

**S15**

```
Current Data Parameters
NAME                  BM008f
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20161031
Time                  16.12
INSTRUM               spect
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719425 sec
RG                     11.3
DW                48.400 usec
DE                 6.50 usec
TE                 298.3 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                   1H
P1                  6.70 usec
PL1                 4.00 dB
PL1W          8.72000027 W
SFO1        500.2730894 MHz

F2 - Processing parameters
SI                    32768
SF            500.2700096 MHz
WDW                      EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```




**S15**

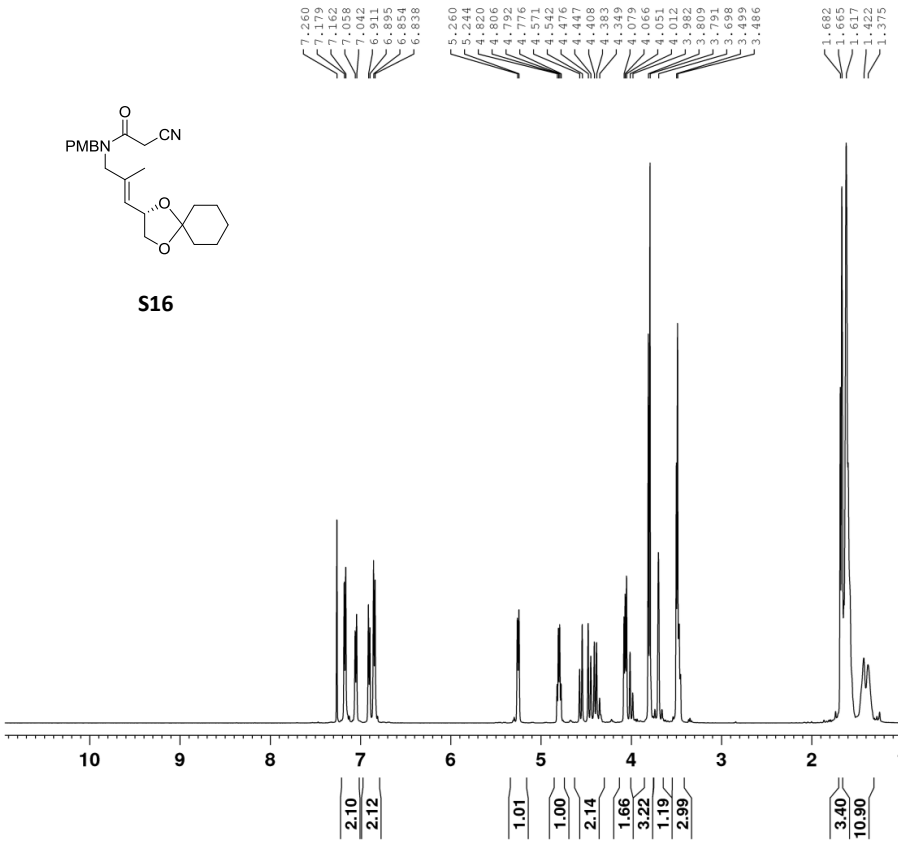
```
Current Data Parameters
NAME                  BM008C
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20161101
Time                  17.39
INSTRUM               spect
PROBHD    5 mm CPTCI 1H-
PULPROG               jmod
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010048 sec
RG                     2050
DW                16.800 usec
DE                 6.50 usec
TE                 298.2 K
CNST2         145.0000000
CNST11          1.0000000
D1              2.00000000 sec
D20             0.00689655 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                  13C
P1                 11.20 usec
P2                 22.40 usec
PL1                -2.00 dB
PL1W         88.77790070 W
SFO1        125.8055709 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 4.00 dB
PL12               25.28 dB
PL2W          8.72000027 W
PL12W         0.06494062 W
SFO2        500.2720011 MHz

F2 - Processing parameters
SI                    32768
SF            125.7929827 MHz
WDW                      EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

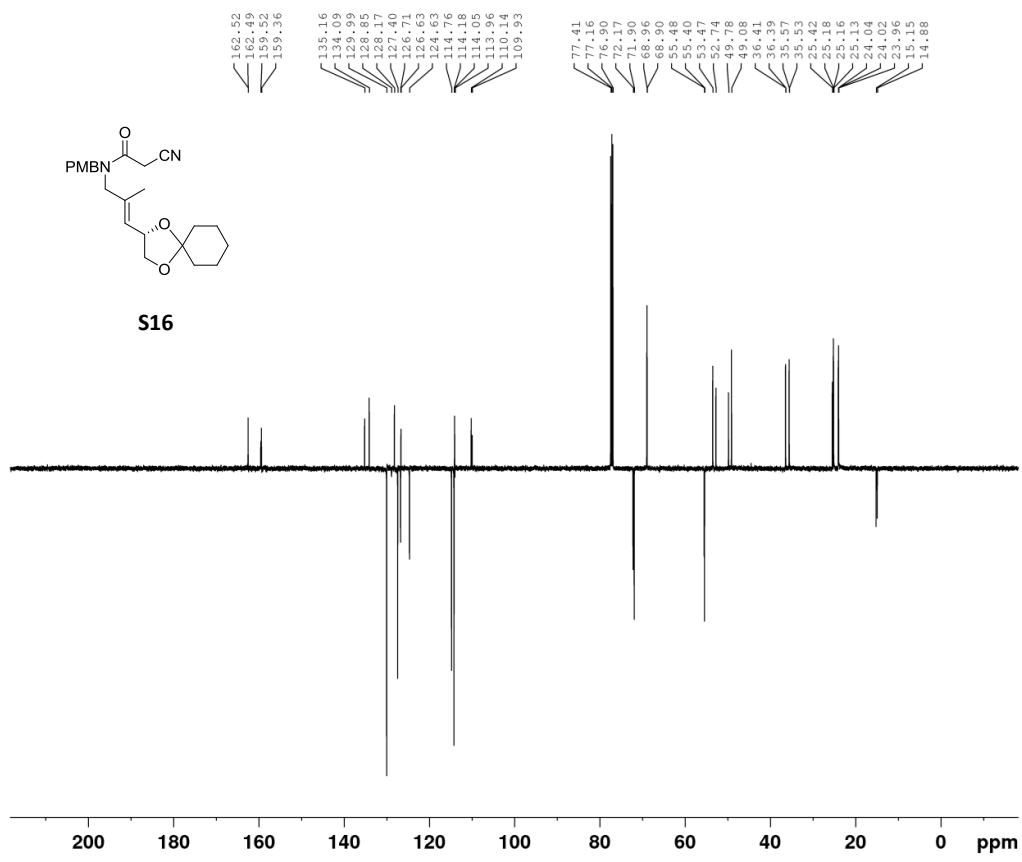



```
Current Data Parameters
NAME              BM040pure
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_           20160826
Time              11.44
INSTRUM           spect
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                 14.2
DW               48.400 usec
DE                6.50 usec
TE                298.3 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                6.70 usec
PL1               4.00 dB
PL1W         8.72000027 W
SFO1        500.2730894 MHz

F2 - Processing parameters
SI                32768
SF           500.2700069 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



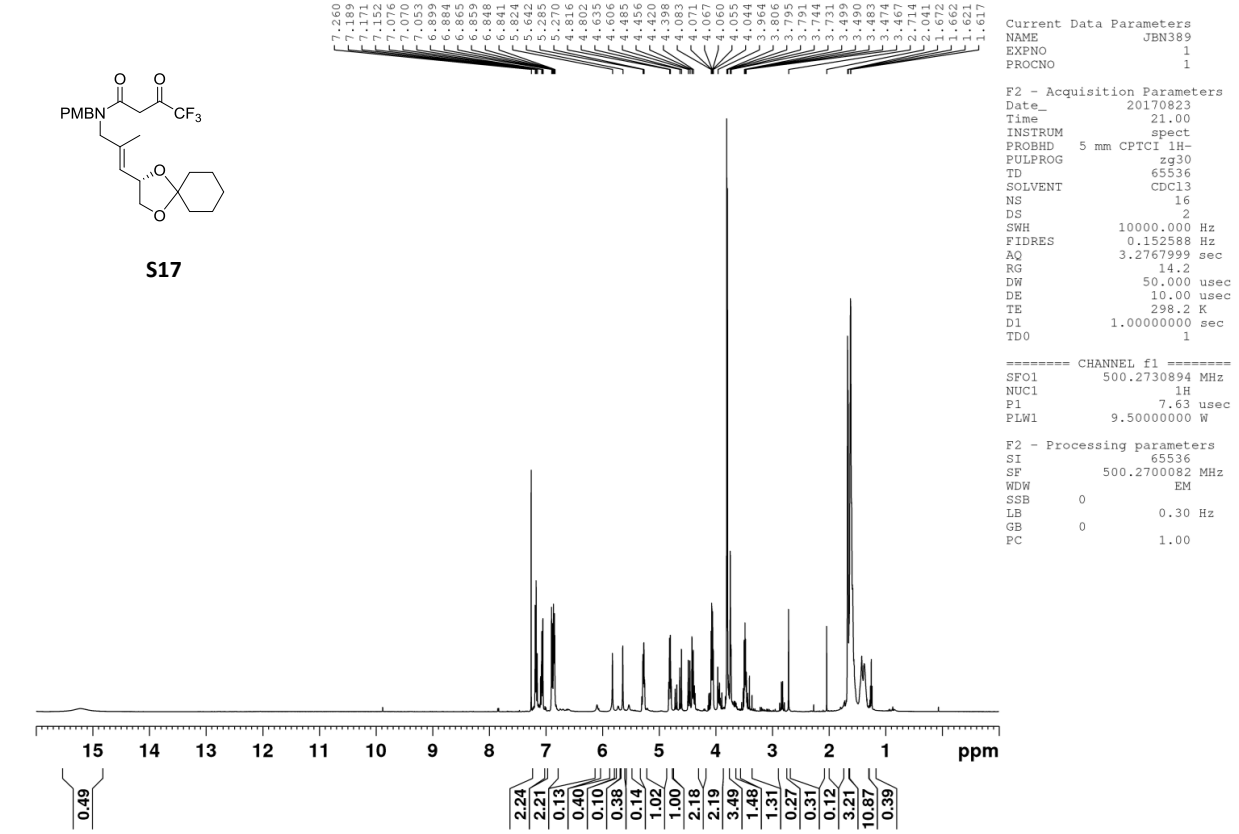

```
Current Data Parameters
NAME      BM040pureCarbon
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_           20160826
Time              14.24
INSTRUM           spect
PROBHD   5 mm CPTCI 1H-
PULPROG           jmod
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG                 2050
DW               16.800 usec
DE                6.50 usec
TE                287.6 K
CNST2        145.0000000
CNST11         1.0000000
D1             2.00000000 sec
D20            0.00689655 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1               11.20 usec
P2               22.40 usec
PL1               -2.00 dB
PL1W         88.77790070 W
SFO1        125.8055709 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                4.00 dB
PL12              25.28 dB
PL2W          8.72000027 W
PL12W         0.06494062 W
SFO2        500.2720011 MHz

F2 - Processing parameters
SI                32768
SF           125.7929828 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

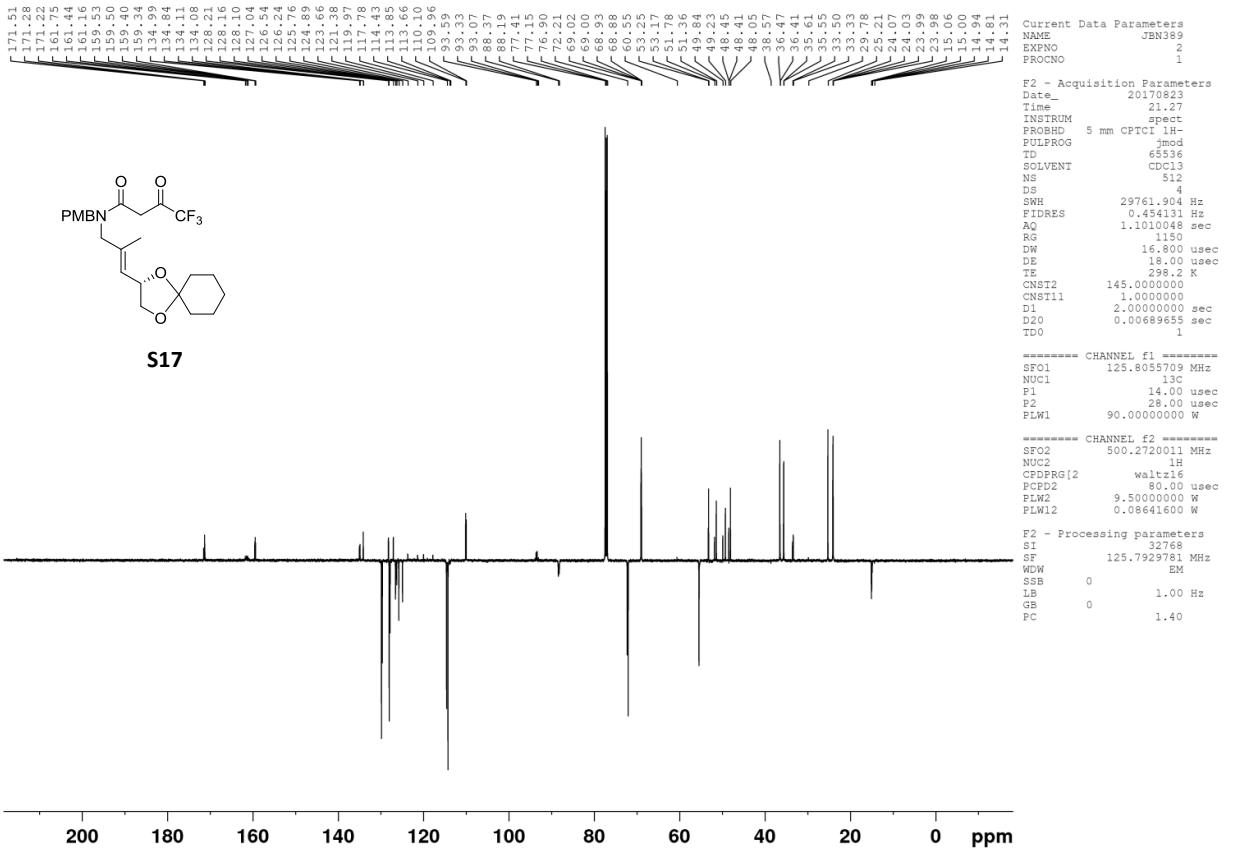



```
Current Data Parameters
NAME                  JBN389
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170823
Time                  21.00
INSTRUM                spect
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2767999 sec
RG                       14.2
DW                    50.000 usec
DE                    10.00 usec
TE                    298.2 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           500.2730894 MHz
NUC1                     1H
P1                     7.63 usec
PLW1            9.50000000 W

F2 - Processing parameters
SI                    65536
SF             500.2700082 MHz
WDW                      EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```



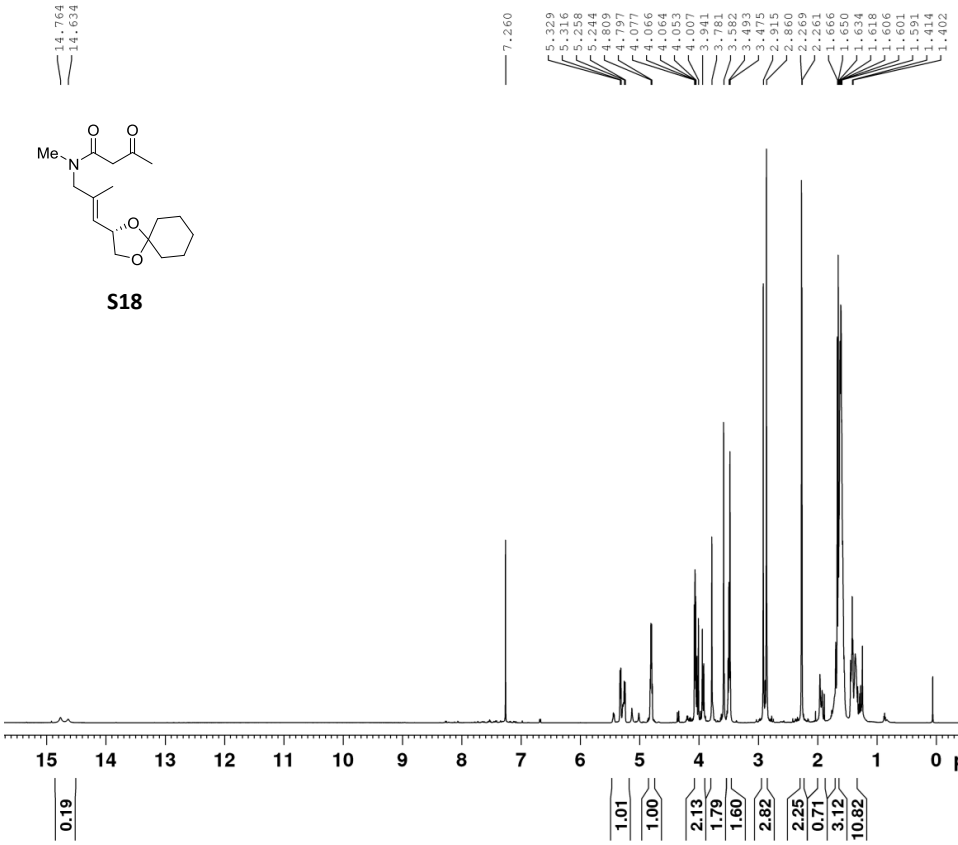

```
Current Data Parameters
NAME                  JBN389
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170823
Time                  21.27
INSTRUM                spect
PROBHD    5 mm CPTCI 1H-
PULPROG               zgmod
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH              29761.904 Hz
FIDRES               0.454131 Hz
AQ                1.1010048 sec
RG                     1150
DW                    16.800 usec
DE                    18.00 usec
TE                    298.2 K
CNST2           145.0000000
CNST11            1.0000000
D1                2.00000000 sec
D20               0.00689655 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           125.8055709 MHz
NUC1                     13C
P1                    14.00 usec
P2                    28.00 usec
PLW1            90.00000000 W

======== CHANNEL f2 ========
SFO2           500.2720011 MHz
NUC2                     1H
CPDPRG[2          waltz16
PCPD2                 80.00 usec
PLW2             9.50000000 W
PLW12            0.08641600 W

F2 - Processing parameters
SI                    32768
SF             125.7929781 MHz
WDW                      EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```

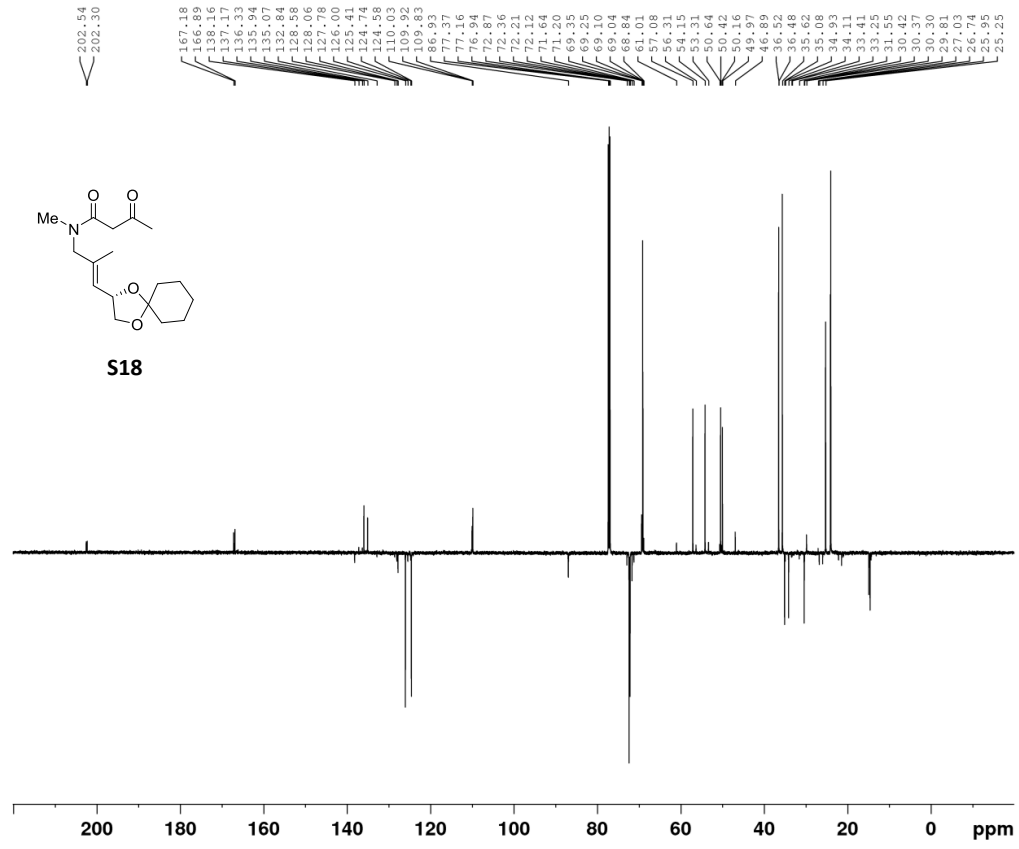



**S18**

```
Current Data Parameters
NAME                  JBN460
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20171208
Time                 10.03 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               12019.230 Hz
FIDRES             0.183399 Hz
AQ                2.7262976 sec
RG                    14.39
DW                   41.600 usec
DE                   18.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                        1
SFO1            600.1337058 MHz
NUC1                    1H
P1                    8.00 usec
PLW1             6.76100016 W

F2 - Processing parameters
SI                    65536
SF              600.1300154 MHz
WDW                      EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```

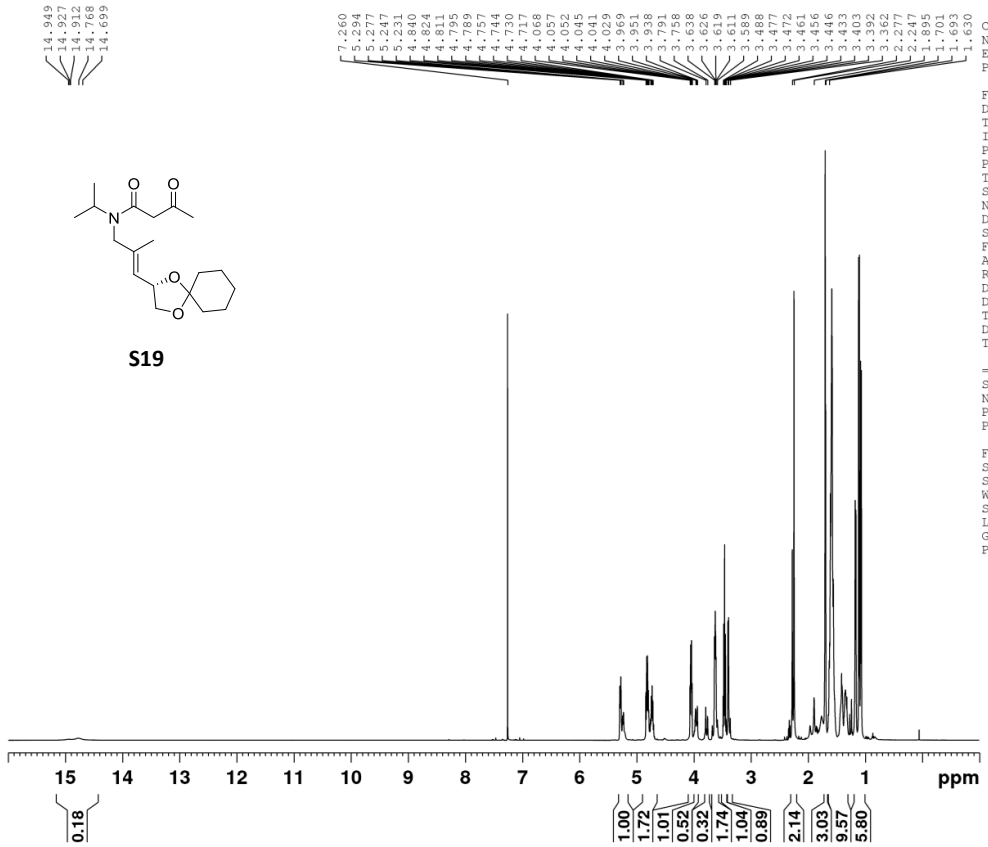



**S18**

```
Current Data Parameters
NAME                  JBN460
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20171208
Time                 10.29 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                jmod
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               36231.883 Hz
FIDRES             0.552855 Hz
AQ                0.9043968 sec
RG                   199.43
DW                   13.800 usec
DE                   18.00 usec
TE                   298.0 K
CNST2           145.0000000
CNST11            1.0000000
D1                2.00000000 sec
D20               0.00689655 sec
TD0                        1
SFO1            150.9178988 MHz
NUC1                    13C
P1                   12.00 usec
P2                   24.00 usec
PLW1            88.22599792 W
SFO2            600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                80.00 usec
PLW2             6.76100016 W
PLW12            0.06699187 W

F2 - Processing parameters
SI                    32768
SF              150.9027912 MHz
WDW                      EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```



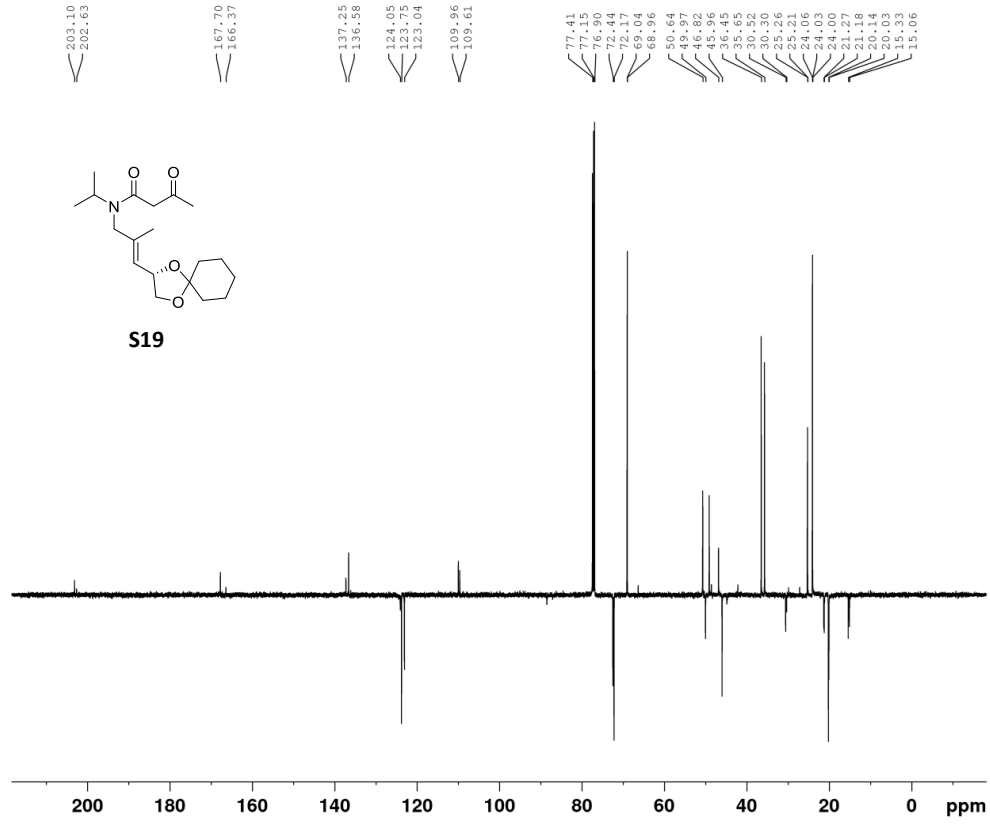

**S19**

```
Current Data Parameters
NAME                  JBN396
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170824
Time                   2.20
INSTRUM               spect
PROBHD   5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                3.2767999 sec
RG                     14.2
DW                   50.000 usec
DE                   10.00 usec
TE                    298.2 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           500.2730894 MHz
NUC1                     1H
P1                     7.63 usec
PLW1           9.50000000 W

F2 - Processing parameters
SI                    65536
SF              500.2700083 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```




**S19**

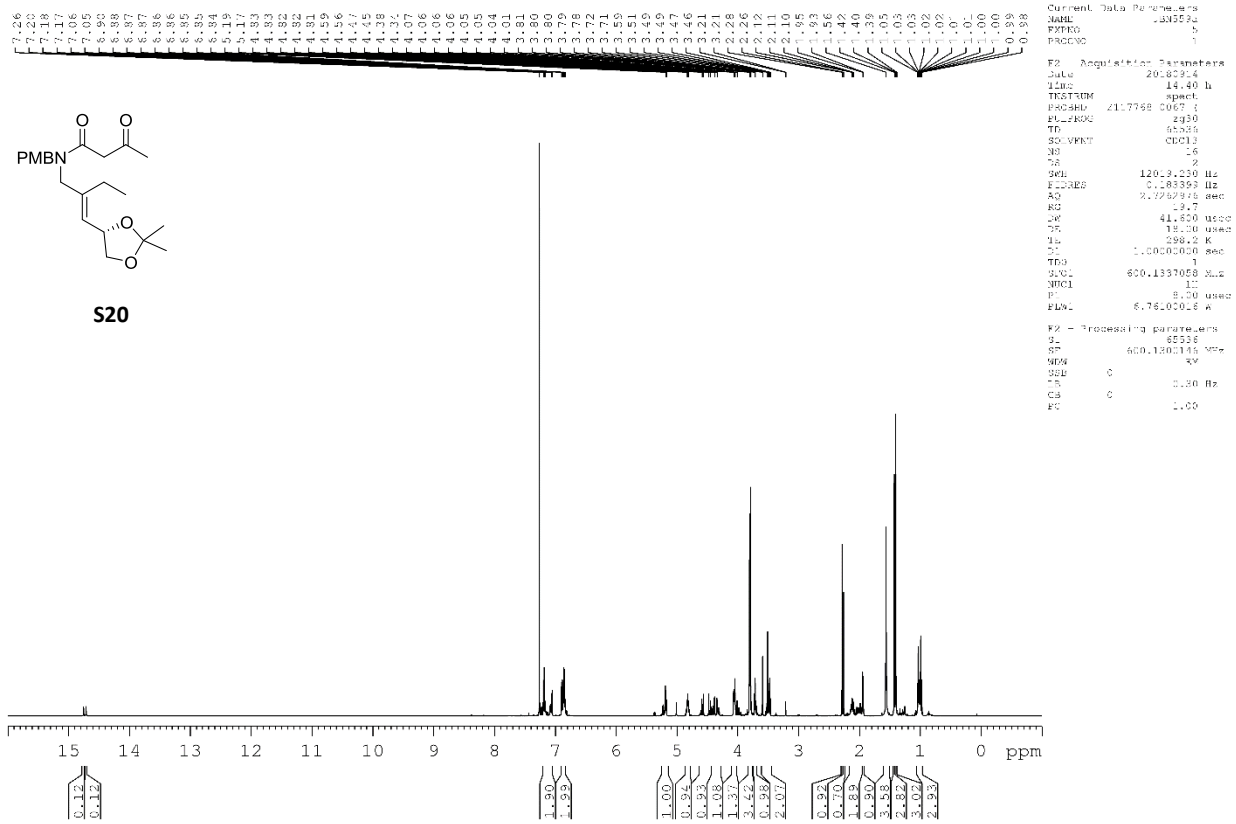
```
Current Data Parameters
NAME                  JBN396
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170824
Time                   2.47
INSTRUM               spect
PROBHD   5 mm CPTCI 1H-
PULPROG               jmod
TD                    65536
SOLVENT               CDCl3
NS                       512
DS                         4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                1.1010048 sec
RG                     1150
DW                   16.800 usec
DE                   18.00 usec
TE                    298.2 K
CNST2          145.0000000
CNST11           1.0000000
D1               2.00000000 sec
D20              0.00689655 sec
TD0                        1

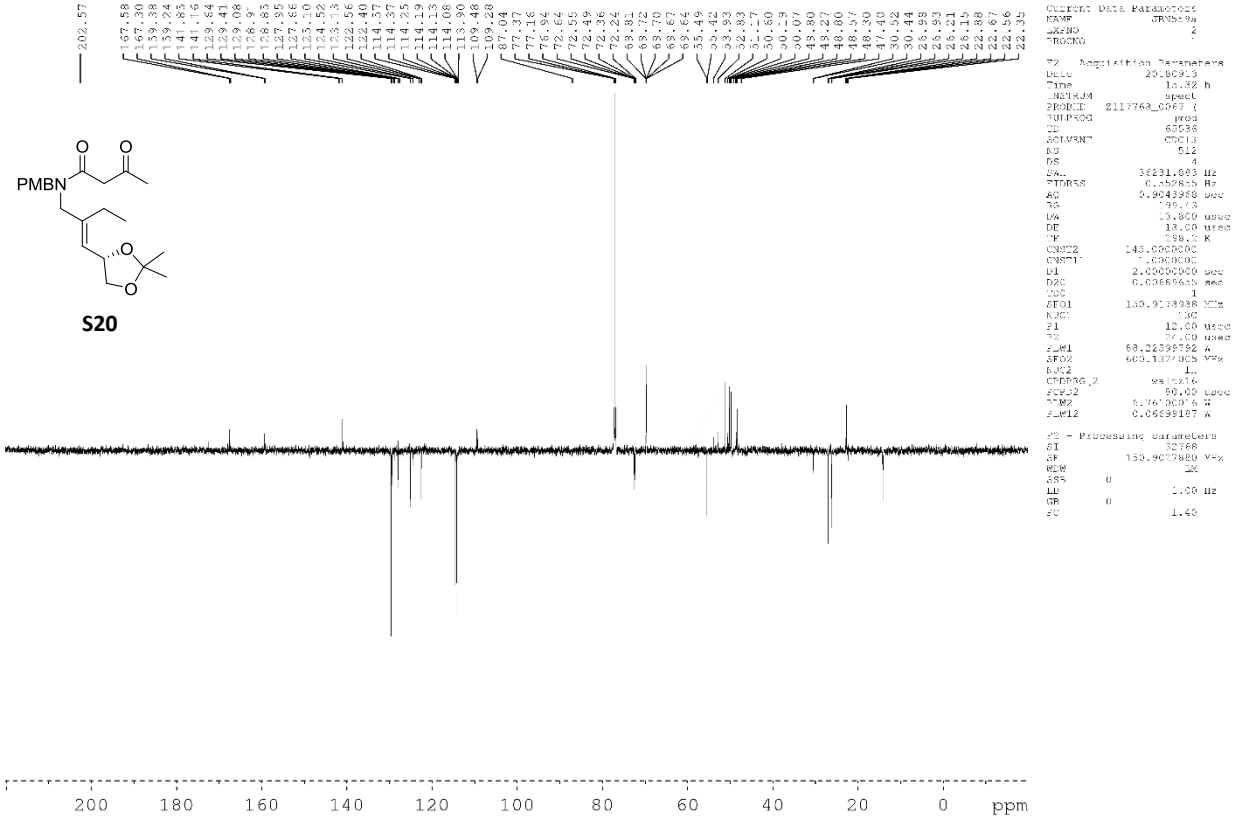
======== CHANNEL f1 ========
SFO1           125.8055709 MHz
NUC1                    13C
P1                   14.00 usec
P2                   28.00 usec
PLW1           90.00000000 W

======== CHANNEL f2 ========
SFO2           500.2720011 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                80.00 usec
PLW2            9.50000000 W
PLW12           0.08641600 W

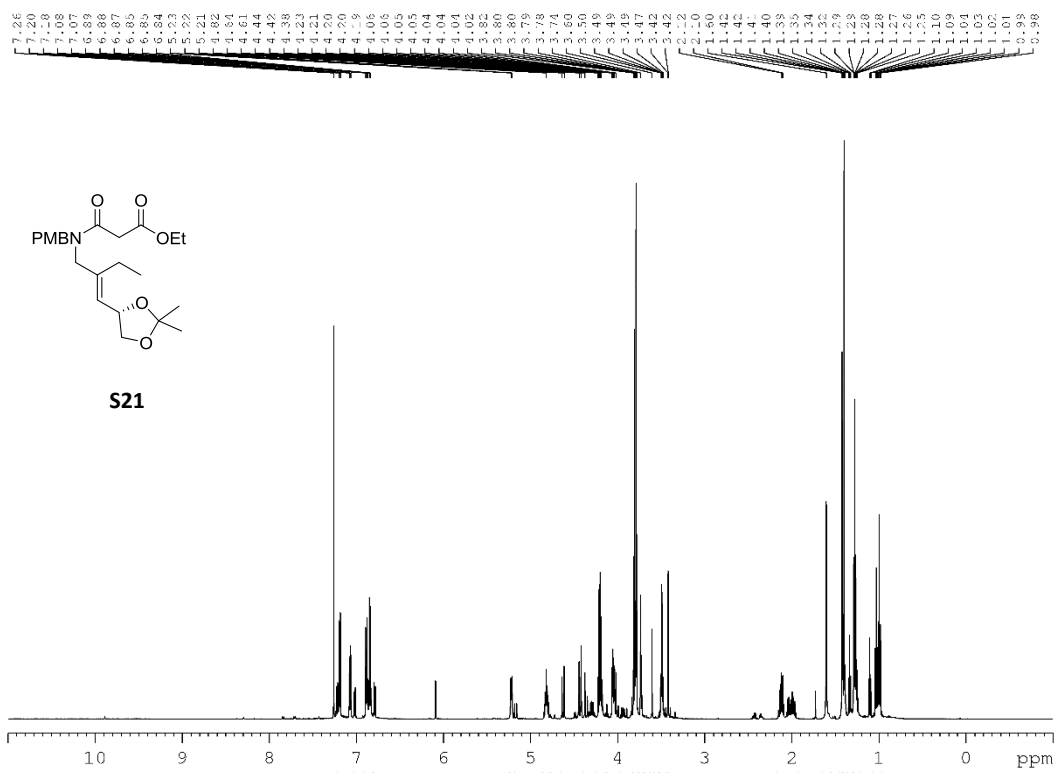
F2 - Processing parameters
SI                    32768
SF             125.7929780 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```


PMBN
O
O
O
O
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

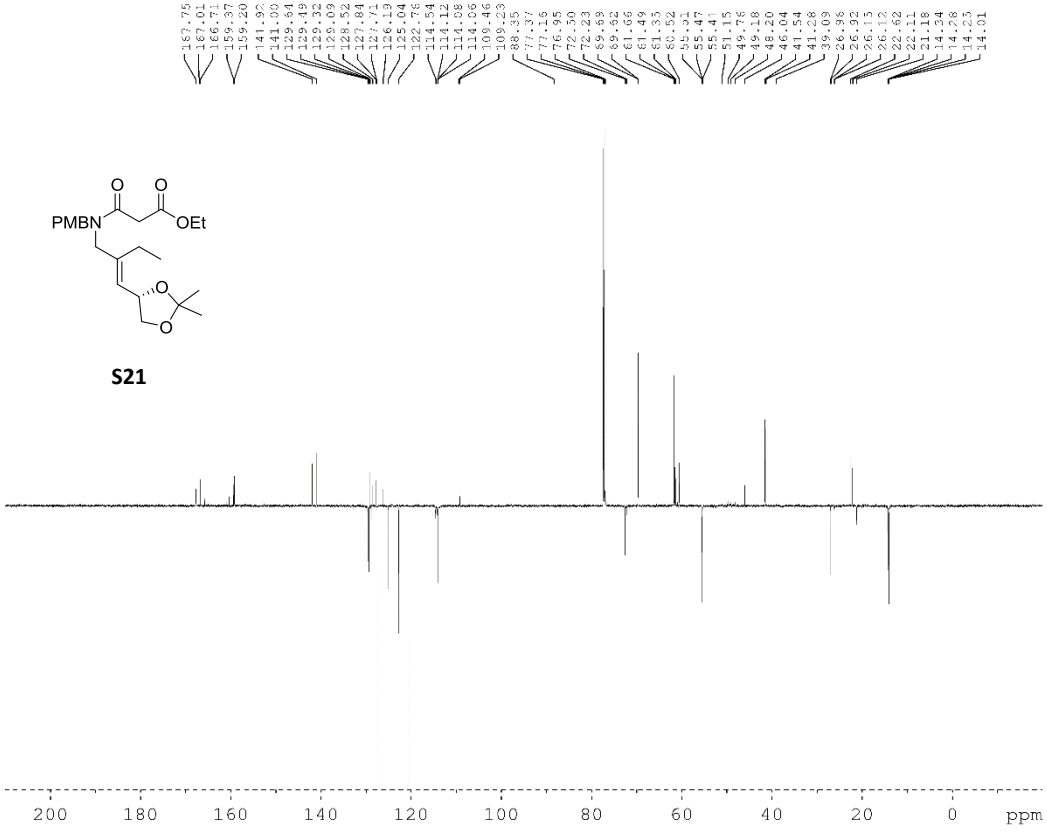
**S20**


PMBN
O
O
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm

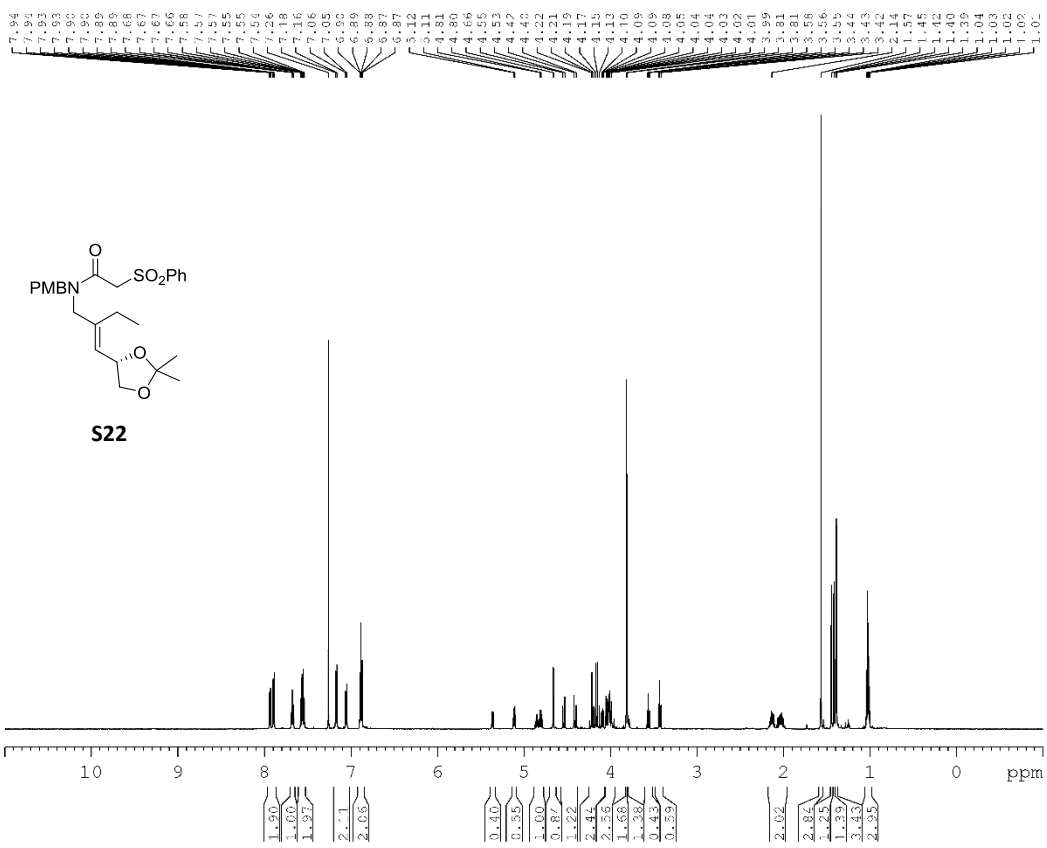
**S20**



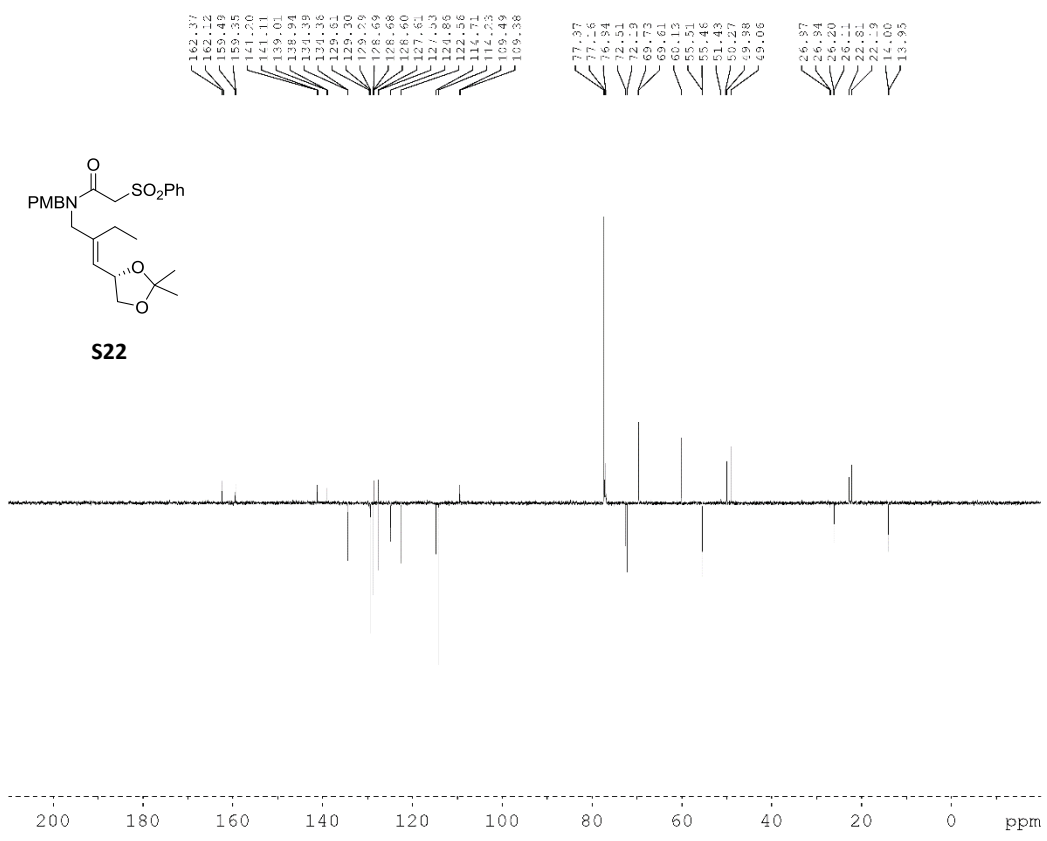

**S21**



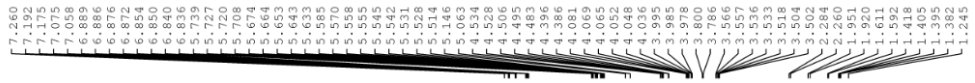

**S21**

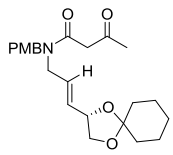



**S22**




**S22**






**S24**

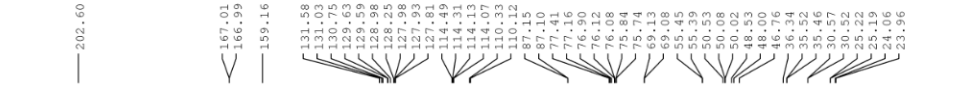


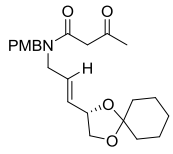

```
Current Data Parameters
NAME                  JBN394
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170824
Time                   0.33
INSTRUM               spect
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                 3.2767999 sec
RG                       16
DW                   50.000 usec
DE                   10.00 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            500.2730894 MHz
NUC1                    1H
P1                    7.63 usec
PLW1           9.50000000 W

F2 - Processing parameters
SI                    65536
SF              500.2700081 MHz
WDW                     EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```






**S24**



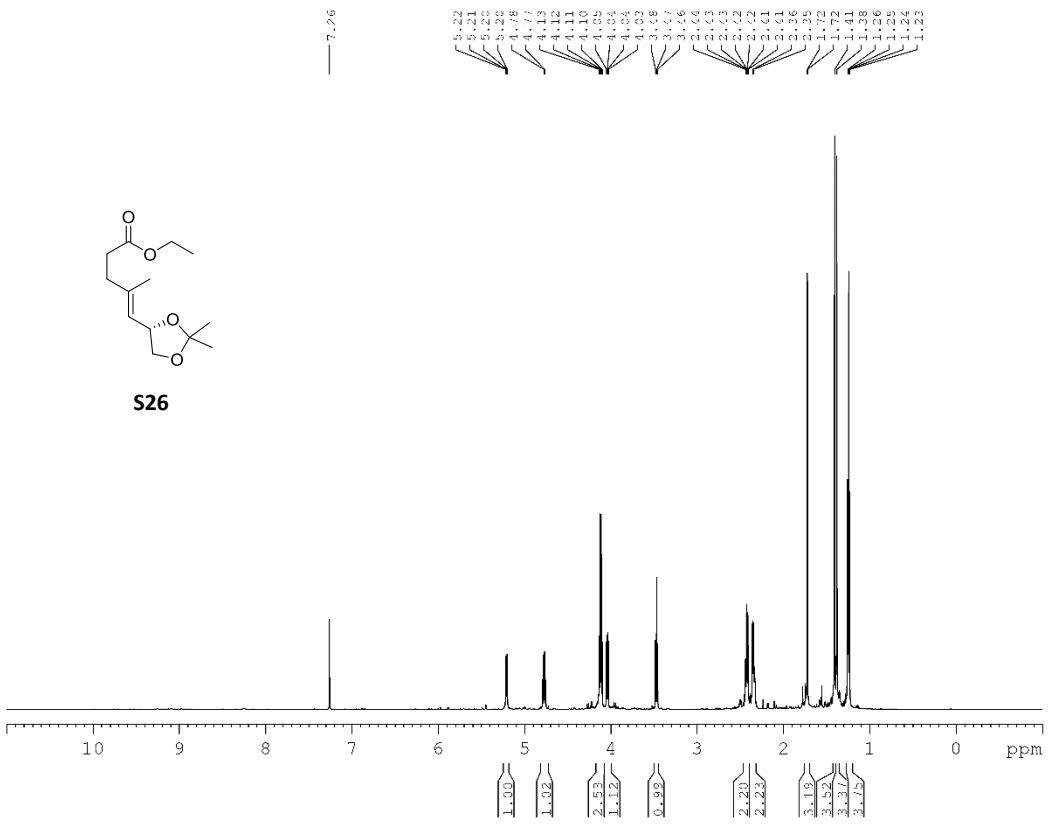

```
Current Data Parameters
NAME                  JBN394
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170824
Time                   1.01
INSTRUM               spect
PROBHD    5 mm CPTCI 1H-
PULPROG               jmod
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010048 sec
RG                     1030
DW                   16.800 usec
DE                   18.00 usec
TE                   298.2 K
CNST2           145.0000000
CNST11            1.0000000
D1                2.00000000 sec
D20               0.00689655 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            125.8055709 MHz
NUC1                    13C
P1                   14.00 usec
P2                   28.00 usec
PLW1           90.00000000 W

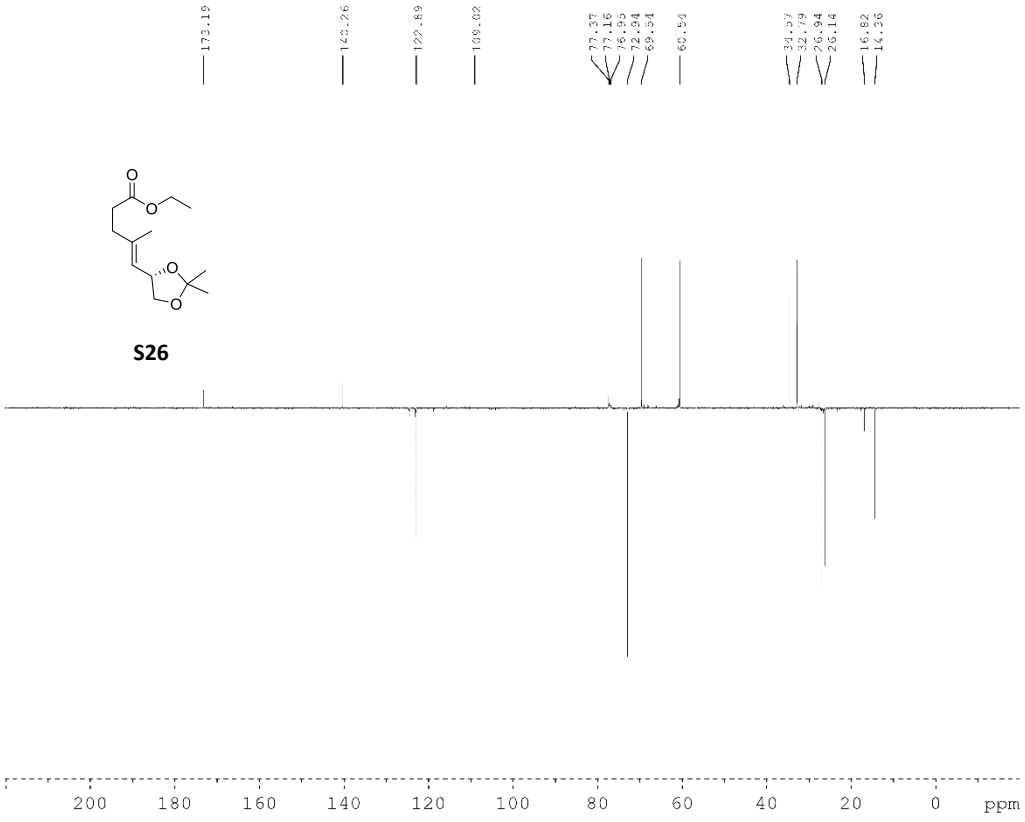
======== CHANNEL f2 ========
SFO2            500.2720011 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                80.00 usec
PLW2           9.50000000 W
PLW12          0.08641600 W

F2 - Processing parameters
SI                    32768
SF              125.7929782 MHz
WDW                     EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```


7.26
5.22
5.21
5.20
4.78
4.77
4.13
4.12
4.11
4.10
4.05
4.04
4.04
4.03
3.48
3.47
3.46
2.43
2.43
2.42
2.42
2.41
2.41
2.36
2.35
1.72
1.72
1.41
1.38
1.26
1.25
1.24
1.23
1.00
1.02
2.53
1.12
0.98
2.20
2.22
3.19
3.52
3.37
3.17
10
9
8
7
6
5
4
3
2
1
0
ppm

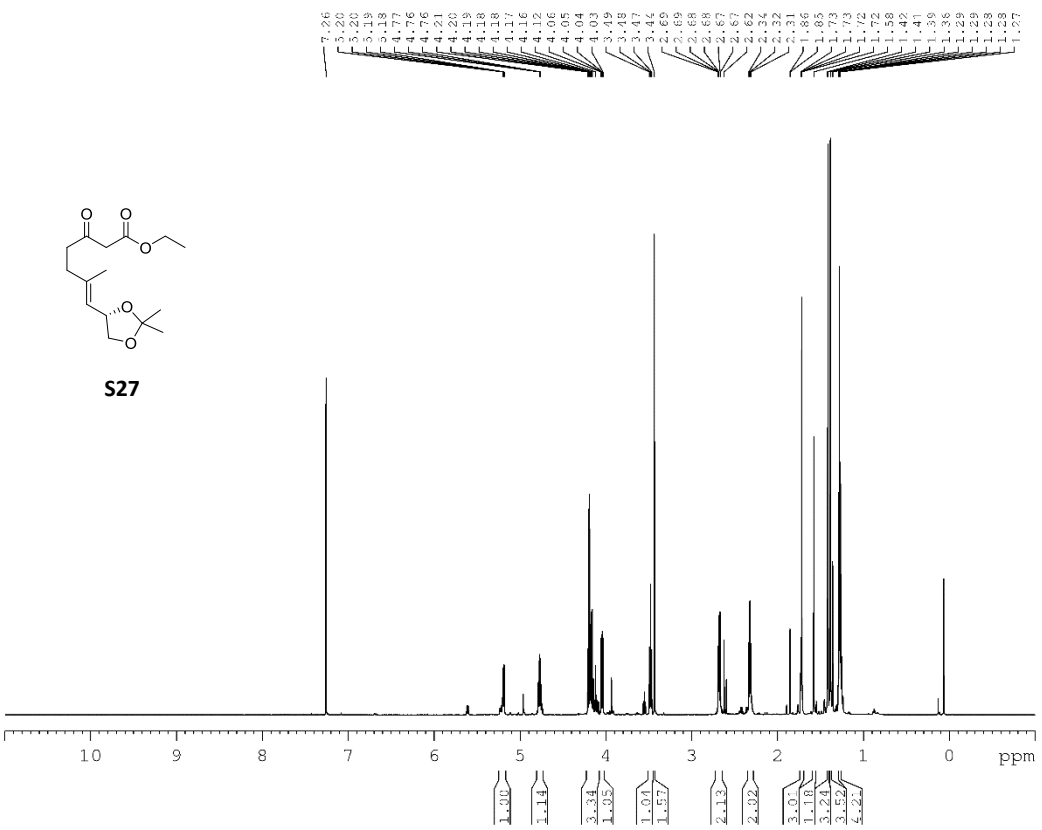


**S26**

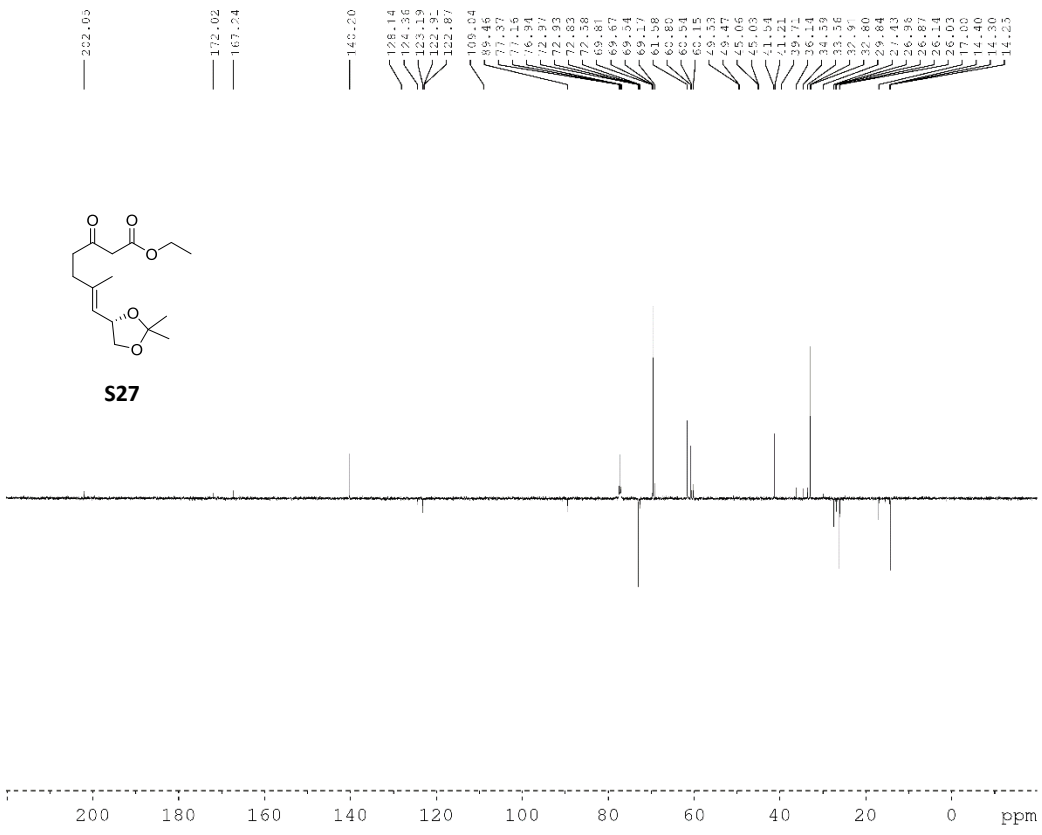

173.19
143.26
122.89
109.02
77.37
77.16
76.95
72.94
69.54
60.54
34.97
32.79
26.94
26.14
16.82
14.26
200
180
160
140
120
100
80
60
40
20
0
ppm



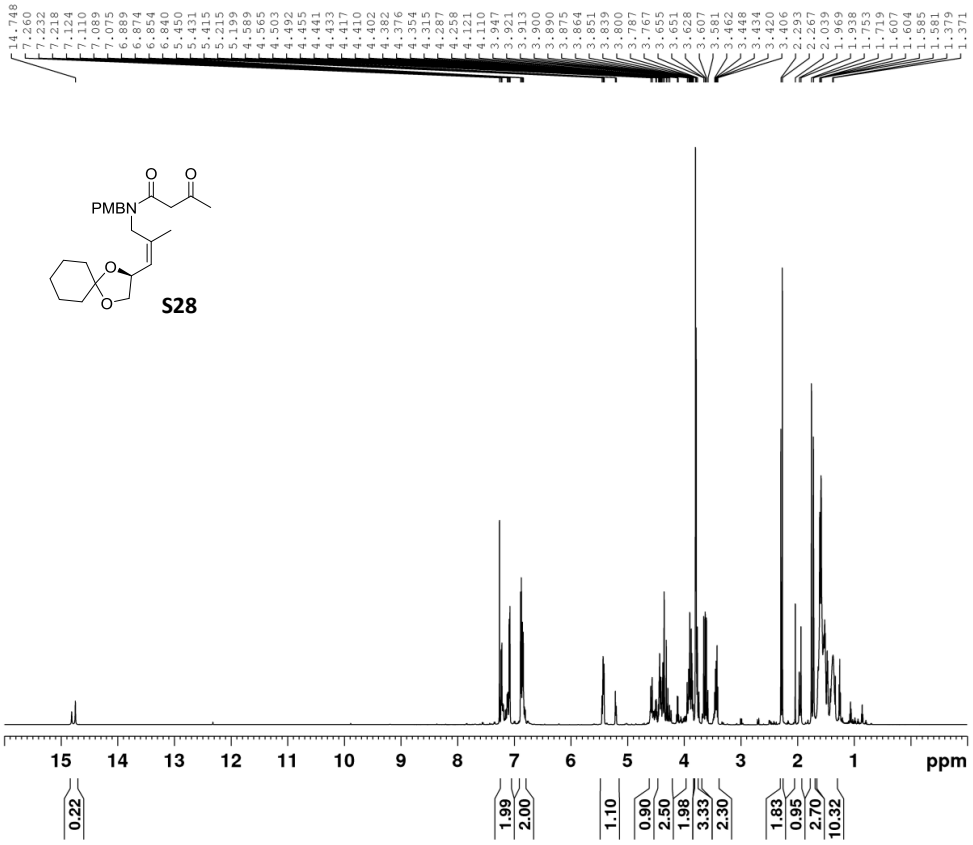
**S26**

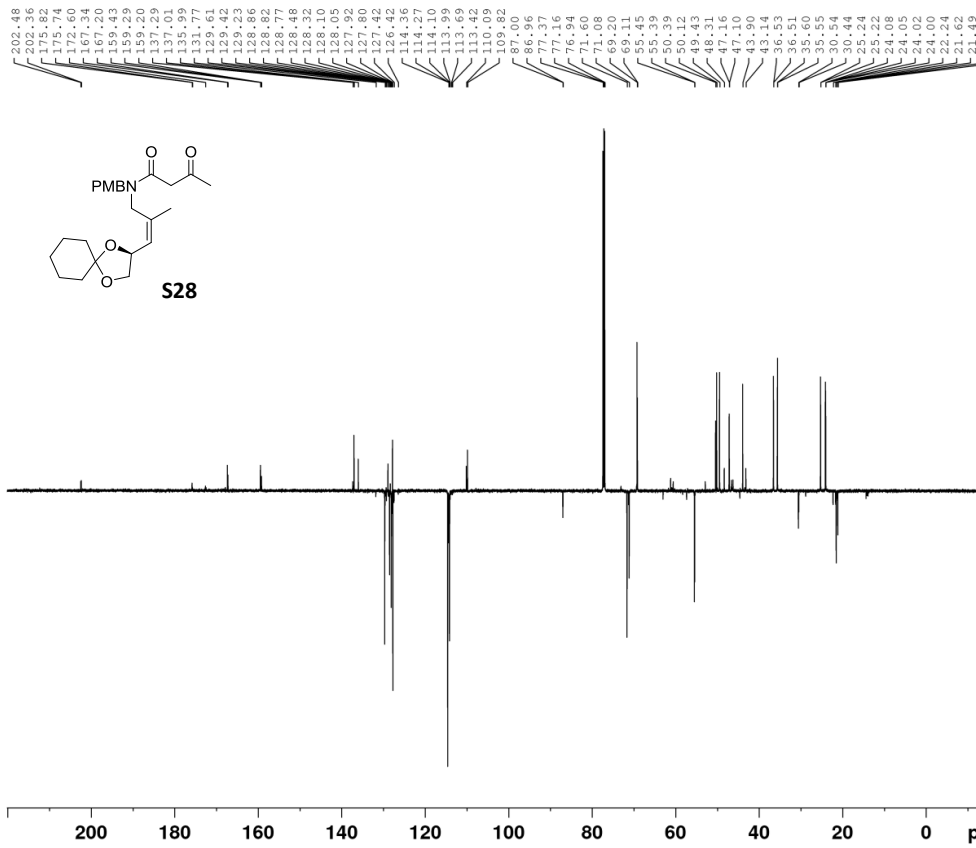


**S27**

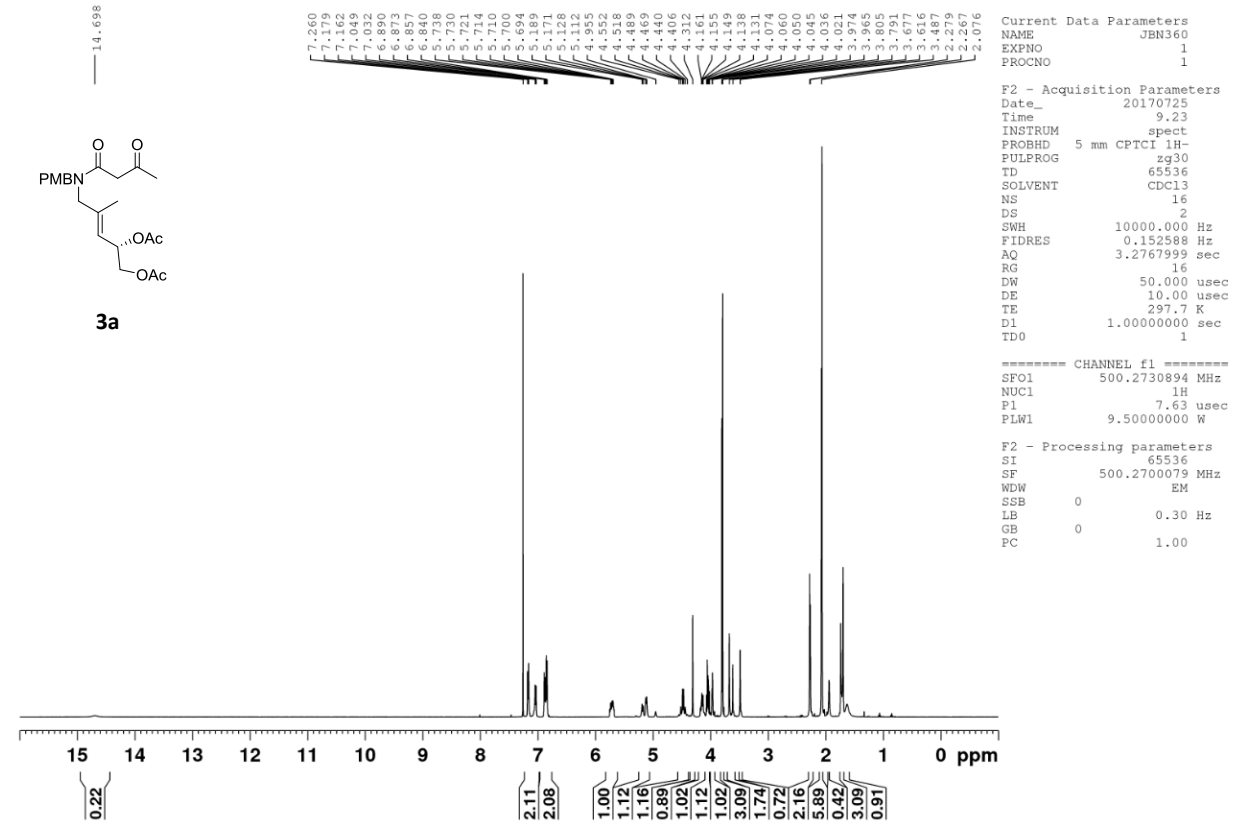


**S27**


PMBN
S28


PMBN
S28

## Diacetates

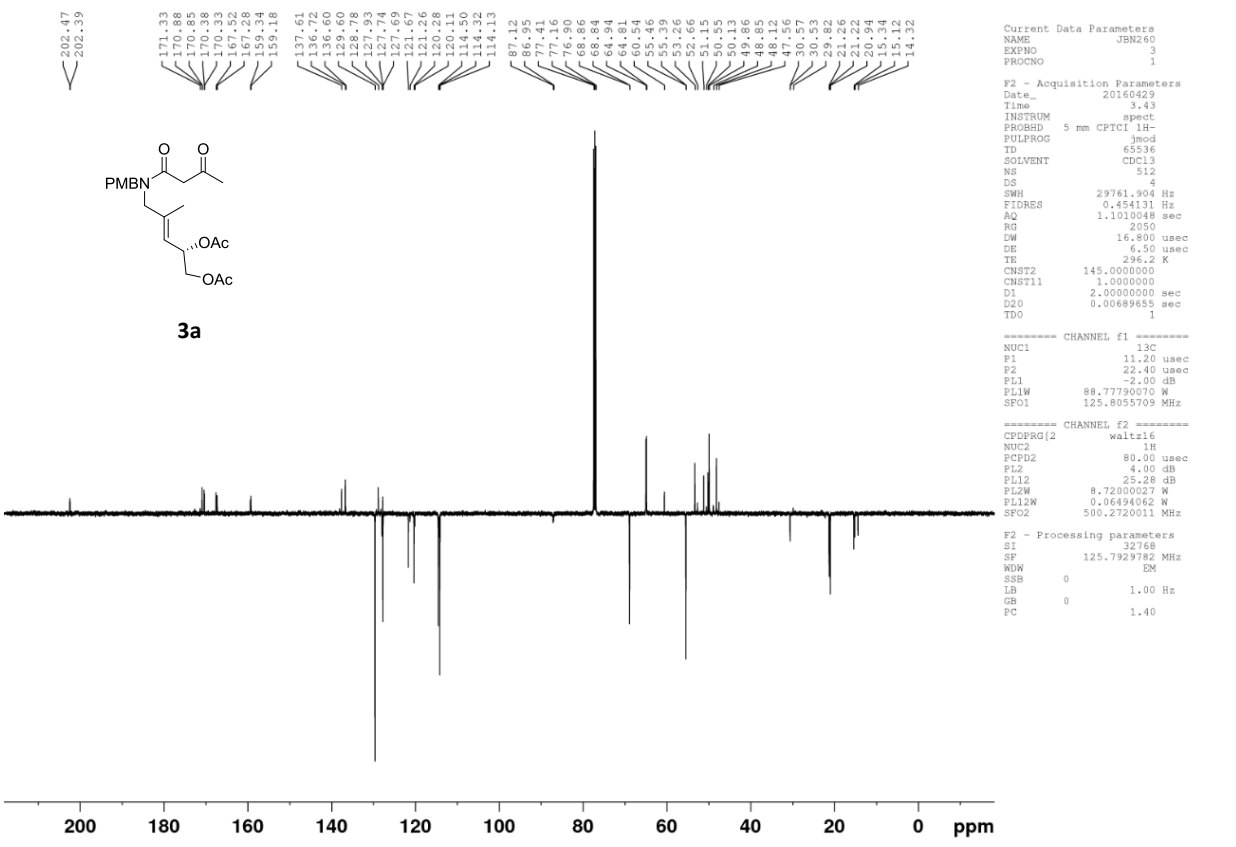



```
Current Data Parameters
NAME                  JBN360
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20170725
Time                    9.23
INSTRUM                spect
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2767999 sec
RG                       16
DW                  50.000 usec
DE                  10.00 usec
TE                  297.7 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            500.2730894 MHz
NUC1                      1H
P1                     7.63 usec
PLW1            9.50000000 W

F2 - Processing parameters
SI                        65536
SF              500.2700079 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



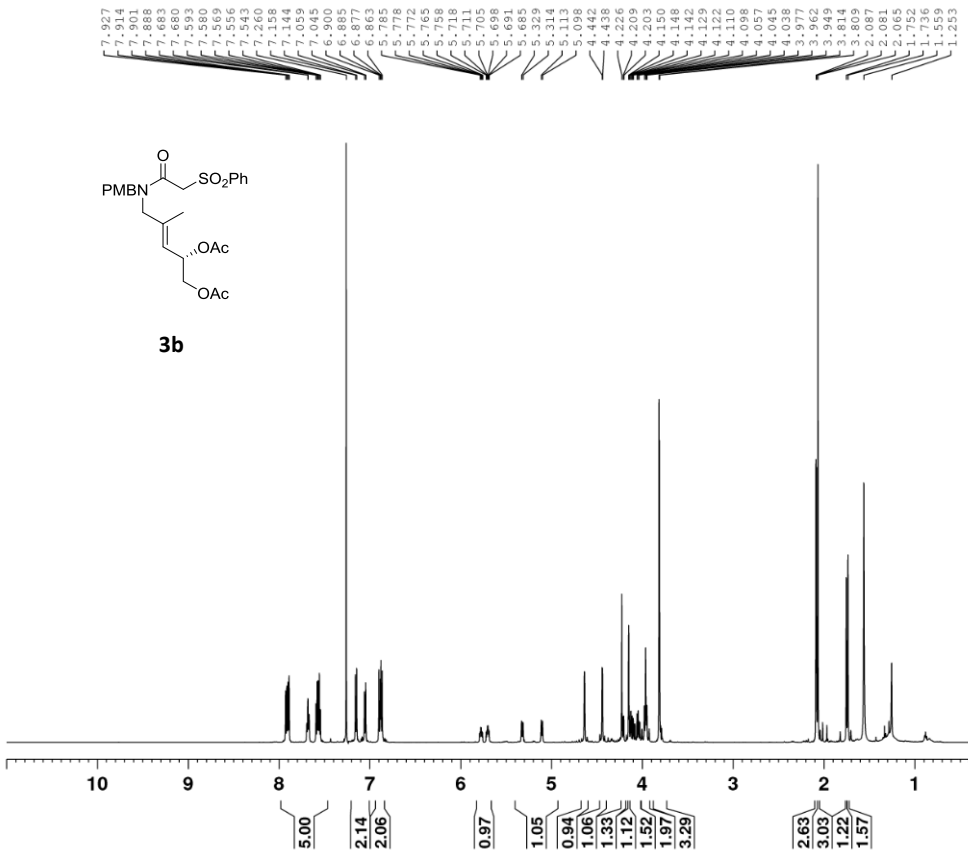

```
Current Data Parameters
NAME                  JBN260
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_               20160429
Time                    3.43
INSTRUM                spect
PROBHD    5 mm CPTCI 1H-
PULPROG                jmod
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH              29761.904 Hz
FIDRES               0.454131 Hz
AQ                1.1010048 sec
RG                     2050
DW                  16.800 usec
DE                   6.50 usec
TE                  296.2 K
CNST2          145.0000000
CNST11           1.0000000
D1               2.00000000 sec
D20              0.00689655 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                  11.20 usec
P2                  22.40 usec
PL1                 -2.00 dB
PL1W           88.77790070 W
SFO1          125.8055709 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                      1H
PCPD2               80.00 usec
PL2                  4.00 dB
PL12                25.28 dB
PL2W            8.72000027 W
PL12W           0.06494062 W
SFO2          500.2720011 MHz

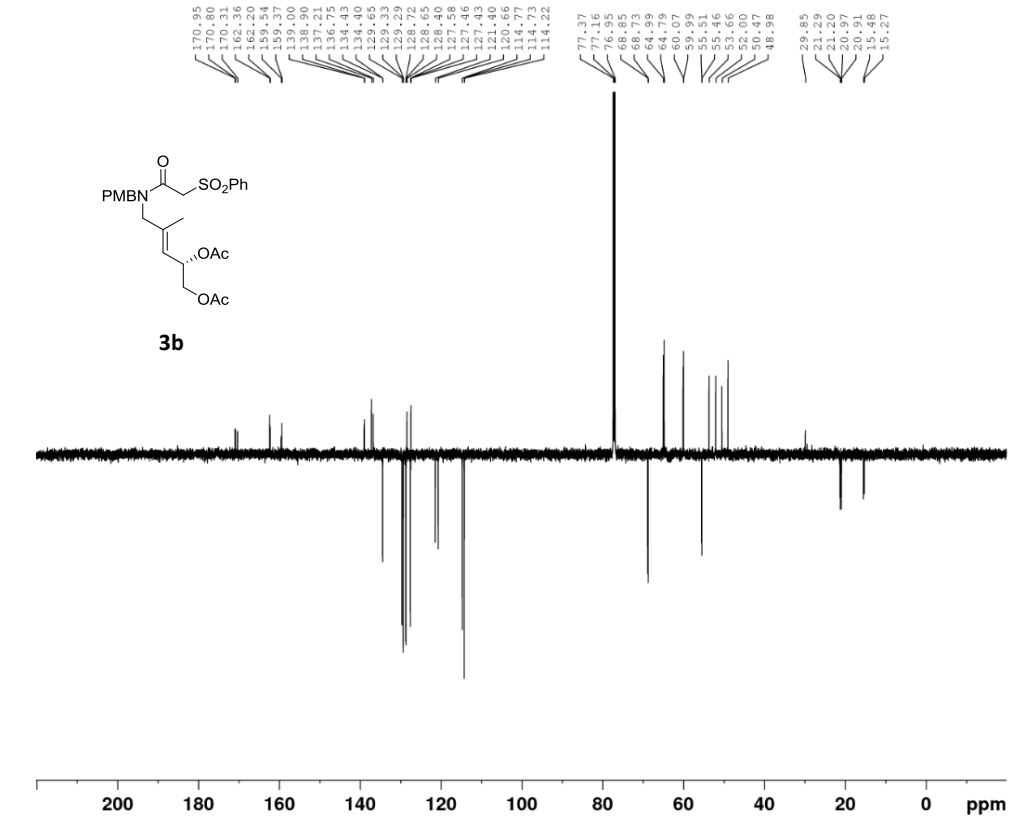
F2 - Processing parameters
SI                        32768
SF              125.7929782 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```




```
Current Data Parameters
NAME                  BMO-046
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180316
Time                   11.57 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               12019.230 Hz
FIDRES                0.183399 Hz
AQ                 2.7262976 sec
RG                     22.37
DW                    41.600 usec
DE                    18.00 usec
TE                    298.0 K
D1                1.00000000 sec
TD0                         1
SFO1           600.1337058 MHz
NUC1                       1H
P1                     8.00 usec
PLW1           6.76100016 W

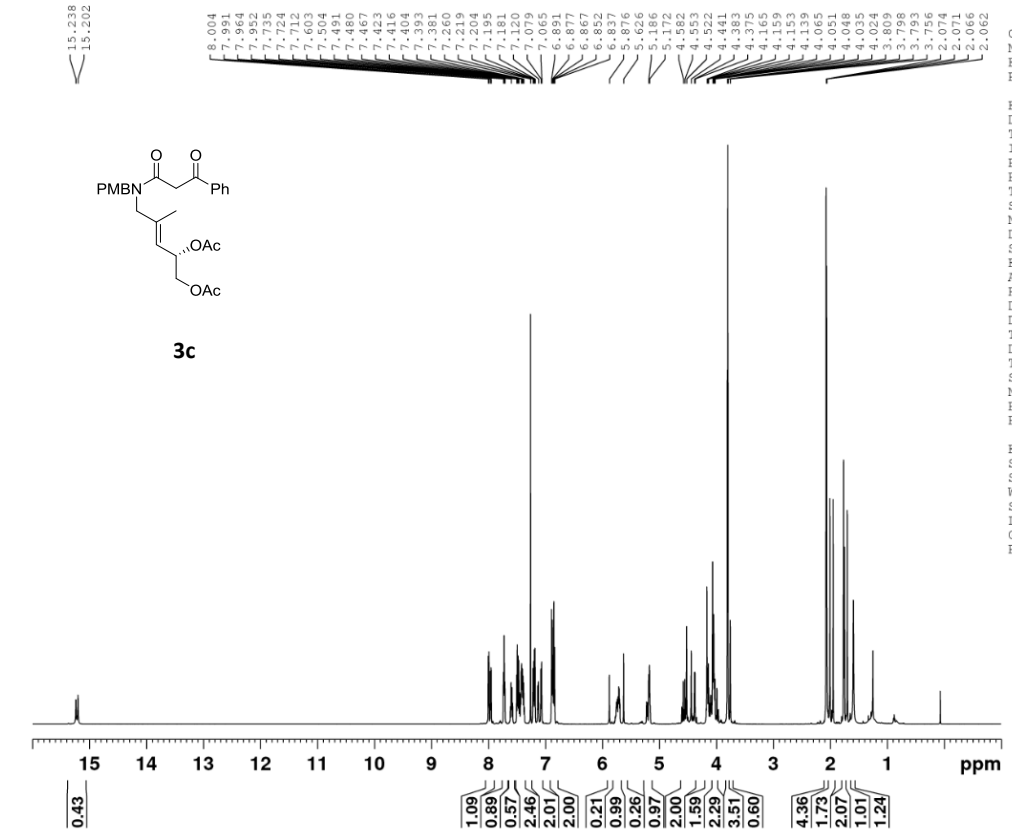
F2 - Processing parameters
SI                    65536
SF              600.1300149 MHz
WDW                       EM
SSB         0
LB                     0.30 Hz
GB          0
PC                     1.00
```




```
Current Data Parameters
NAME                  BMO-046
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180316
Time                   12.23 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG              jmod
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               36231.883 Hz
FIDRES                0.552855 Hz
AQ                 0.9043968 sec
RG                     199.43
DW                    13.800 usec
DE                    18.00 usec
TE                    298.0 K
CNST2             145.0000000
CNST11              1.0000000
D1                 2.00000000 sec
D20                0.00689655 sec
TD0                         1
SFO1           150.9178988 MHz
NUC1                       13C
P1                    12.00 usec
P2                    24.00 usec
PLW1           88.22599792 W
SFO2           600.1324005 MHz
NUC2                       1H
CPDPRG[2           waltz16
PCPD2                 80.00 usec
PLW2           6.76100016 W
PLW12          0.06699187 W

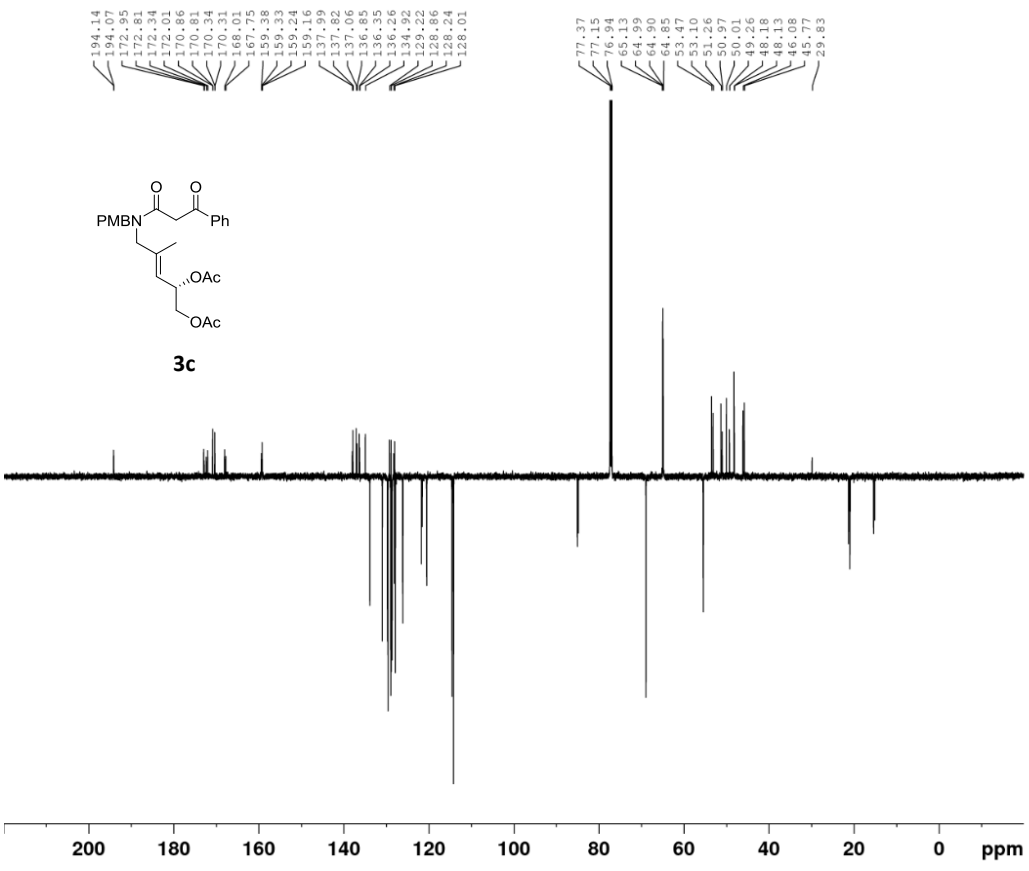
F2 - Processing parameters
SI                    32768
SF              150.9027878 MHz
WDW                       EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```




```
Current Data Parameters
NAME                  BMO-033
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180316
Time                   10.56 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                12019.230 Hz
FIDRES             0.183399 Hz
AQ                 2.7262976 sec
RG                     22.37
DW                    41.600 usec
DE                    18.00 usec
TE                    298.0 K
D1              1.00000000 sec
TD0                        1
SFO1           600.1337058 MHz
NUC1                      1H
P1                     8.00 usec
PLW1            6.76100016 W

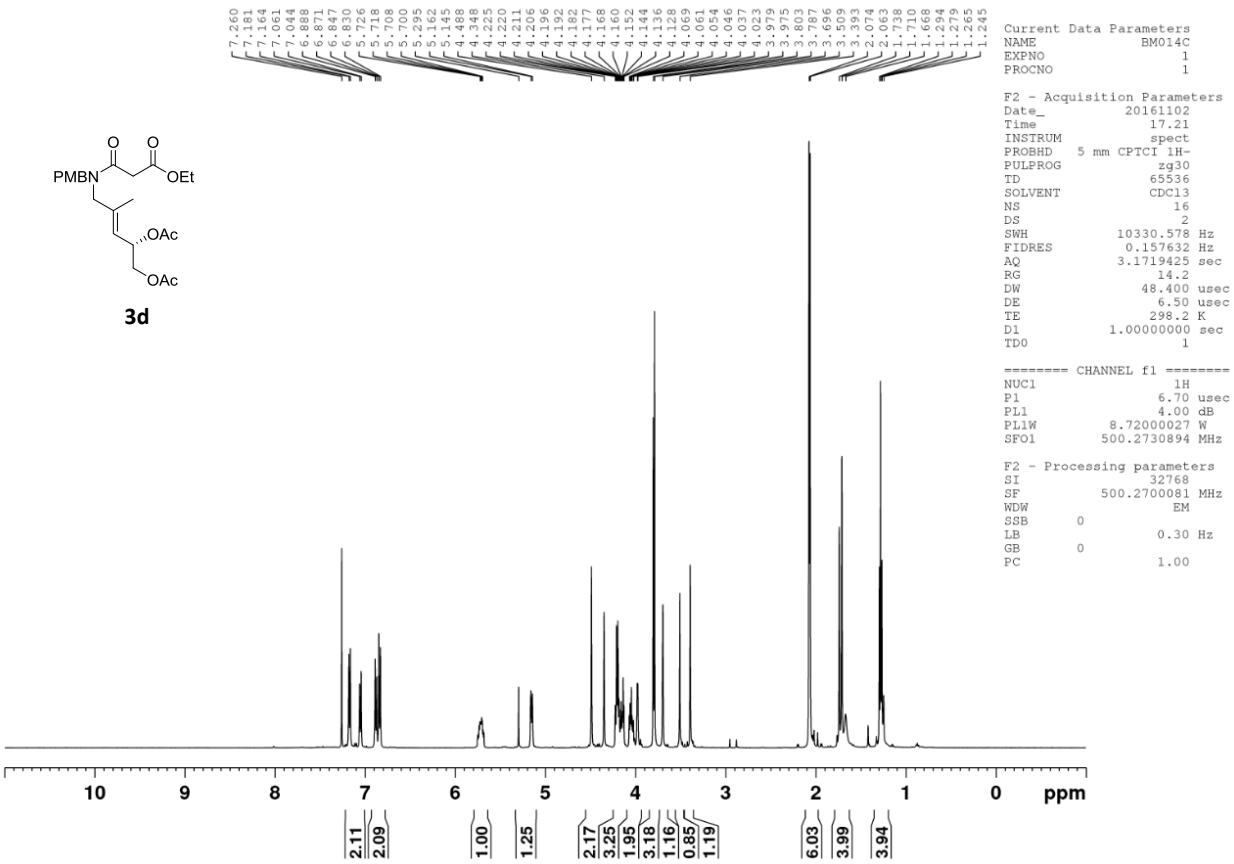
F2 - Processing parameters
SI                     65536
SF             600.1300147 MHz
WDW                       EM
SSB         0
LB                     0.30 Hz
GB          0
PC                     1.00
```

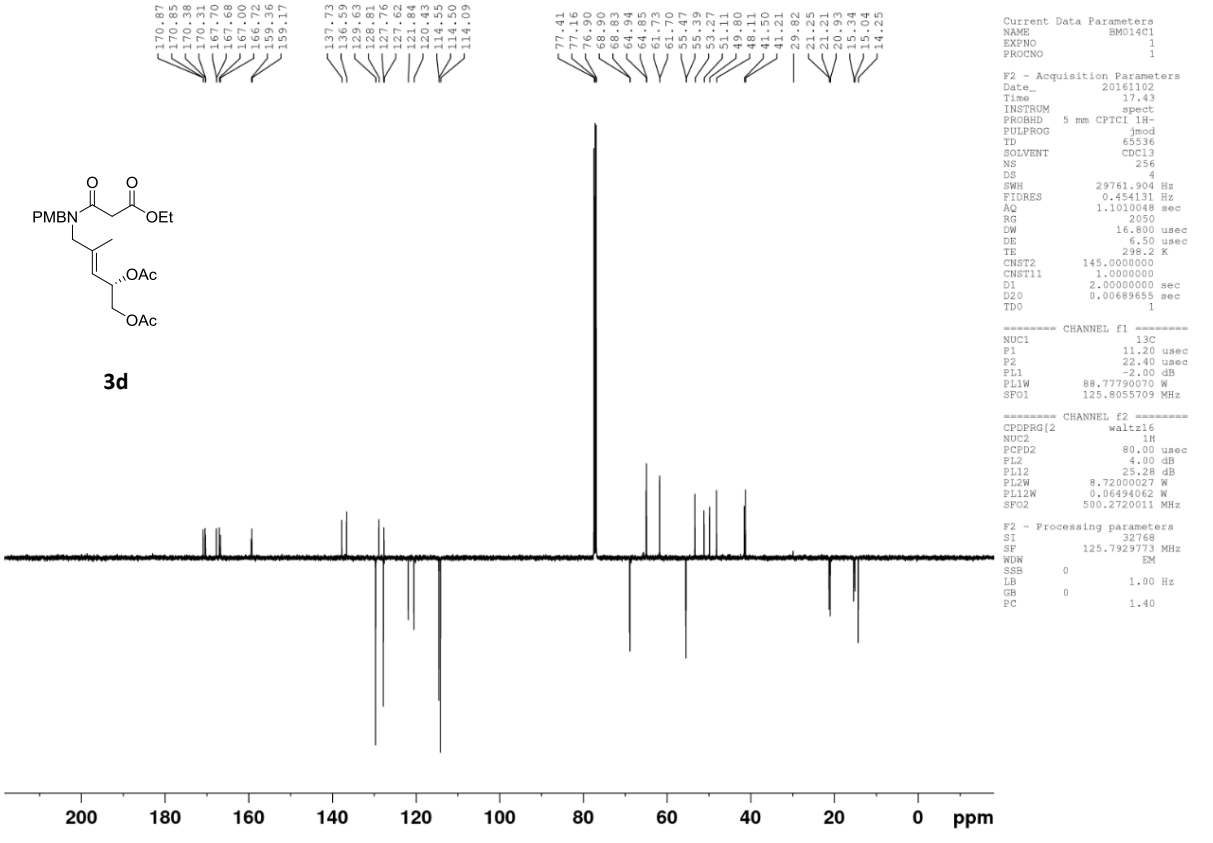


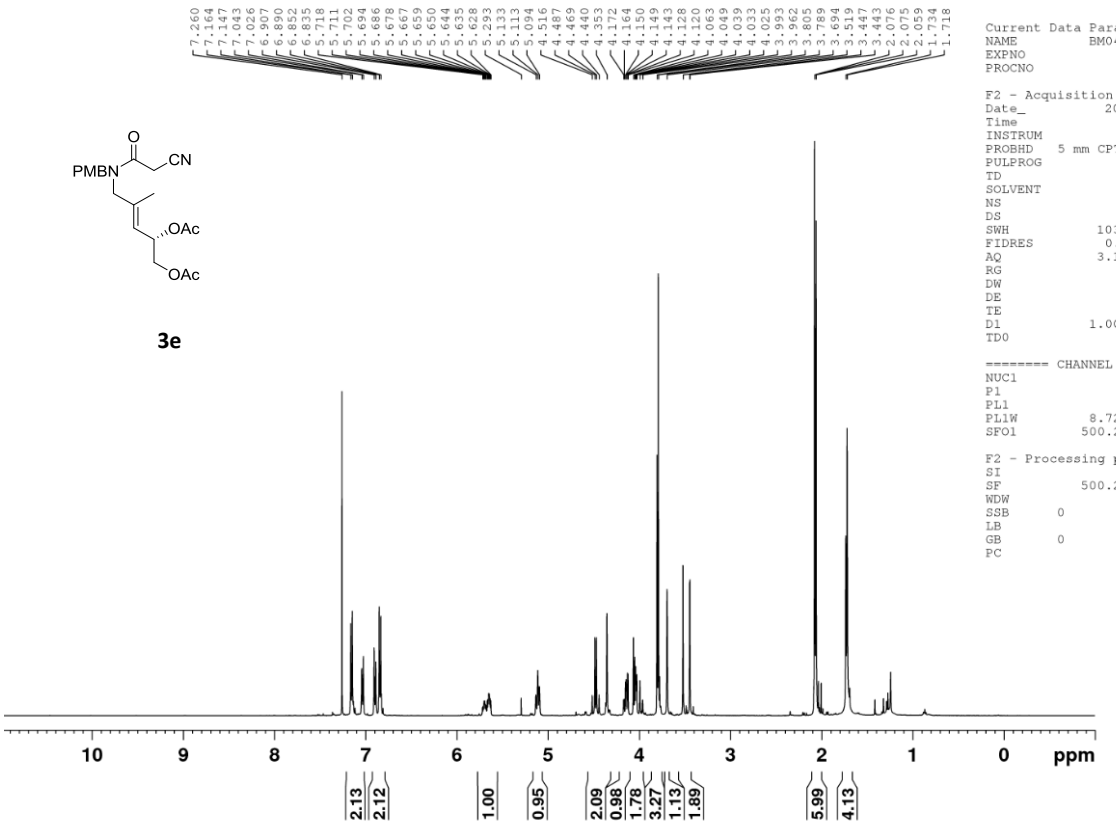

```
Current Data Parameters
NAME                  BMO-033
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180316
Time                   11.23 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                 jmod
TD                     65536
SOLVENT                CDCl3
NS                       512
DS                         4
SWH                36231.883 Hz
FIDRES             0.552855 Hz
AQ                 0.9043968 sec
RG                     199.43
DW                    13.800 usec
DE                    18.00 usec
TE                    298.0 K
CNST2             145.0000000
CNST11              1.0000000
D1                  2.00000000 sec
D20                 0.00689655 sec
TD0                        1
SFO1           150.9178988 MHz
NUC1                      13C
P1                    12.00 usec
P2                    24.00 usec
PLW1           88.22599792 W
SFO2           600.1324005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2            6.76100016 W
PLW12           0.06699187 W

F2 - Processing parameters
SI                     32768
SF             150.9027900 MHz
WDW                       EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```


PMBN
OEt
OAc
OAc
3d
7.260 7.181 7.164 7.061 7.044 6.888 6.871 6.847 6.830 5.726 5.718 5.708 5.700 5.295 5.162 5.145 4.488 4.348 4.225 4.220 4.211 4.206 4.196 4.192 4.182 4.177 4.168 4.160 4.152 4.144 4.136 4.128 4.069 4.061 4.054 4.046 4.037 4.023 3.979 3.975 3.803 3.787 3.696 3.509 3.393 2.074 2.063 1.738 1.710 1.668 1.294 1.279 1.265 1.245
Current Data Parameters
NAME BM014C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161102
Time 17.21
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 14.2
DW 48.400 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 6.70 usec
PL1 4.00 dB
PL1W 8.72000027 W
SFO1 500.2730894 MHz
F2 - Processing parameters
SI 32768
SF 500.2700081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
2.11 2.09 1.00 1.25 2.17 3.25 1.95 3.18 1.16 0.85 1.19 6.03 3.99 3.94


PMBN
OEt
OAc
OAc
3d
170.87 170.85 170.38 170.31 167.70 167.68 167.00 166.72 159.36 159.17 137.73 136.59 129.63 128.81 127.76 127.62 121.84 120.43 114.55 114.50 114.09 77.41 77.16 76.90 68.90 68.83 64.94 64.85 61.73 61.70 55.47 55.39 53.27 53.11 49.80 48.11 41.50 41.21 29.82 21.25 21.21 20.93 15.34 15.04 14.25
Current Data Parameters
NAME BM014C1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20161102
Time 17.43
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.20 usec
P2 22.40 usec
PL1 -2.00 dB
PL1W 88.77790070 W
SFO1 125.8055709 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 25.28 dB
PL2W 8.72000027 W
PL12W 0.06494062 W
SFO2 500.2720011 MHz
F2 - Processing parameters
SI 32768
SF 125.7929773 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

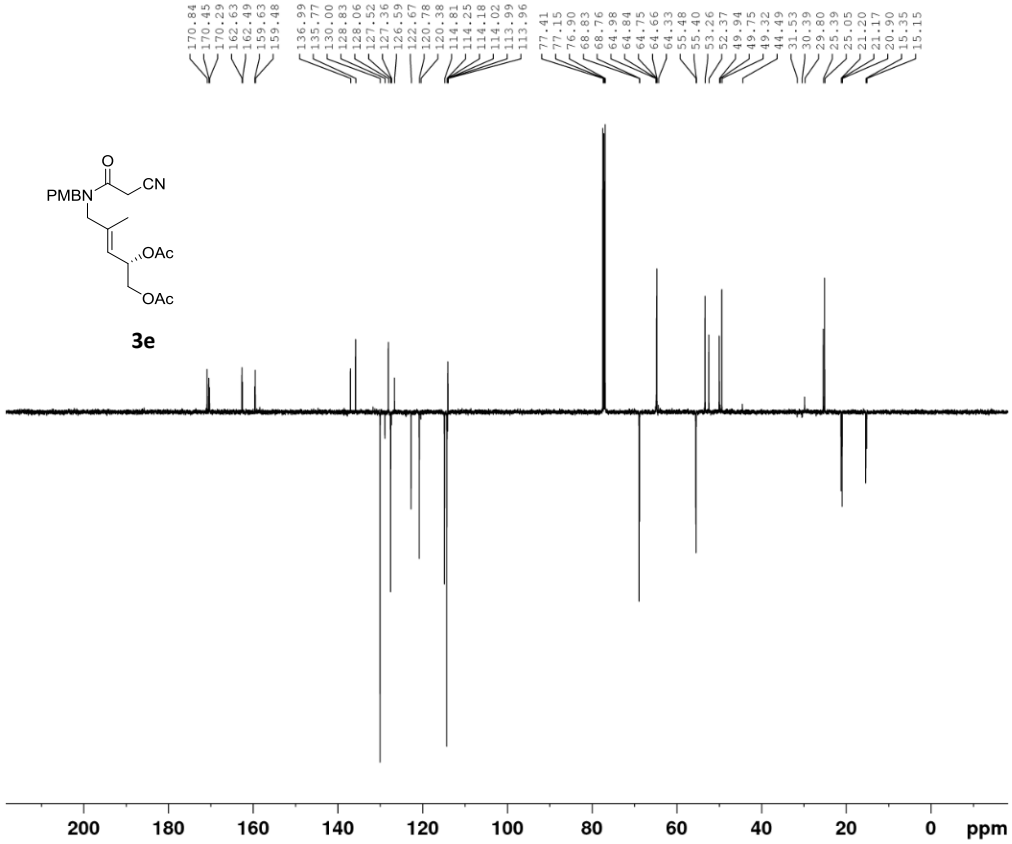



```
Current Data Parameters
NAME          BM047FINAL
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160913
Time               11.07
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                12.7
DW               48.400 usec
DE                6.50 usec
TE              298.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 6.70 usec
PL1                4.00 dB
PL1W         8.72000027 W
SFO1         500.2730894 MHz

F2 - Processing parameters
SI                 32768
SF           500.2700081 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



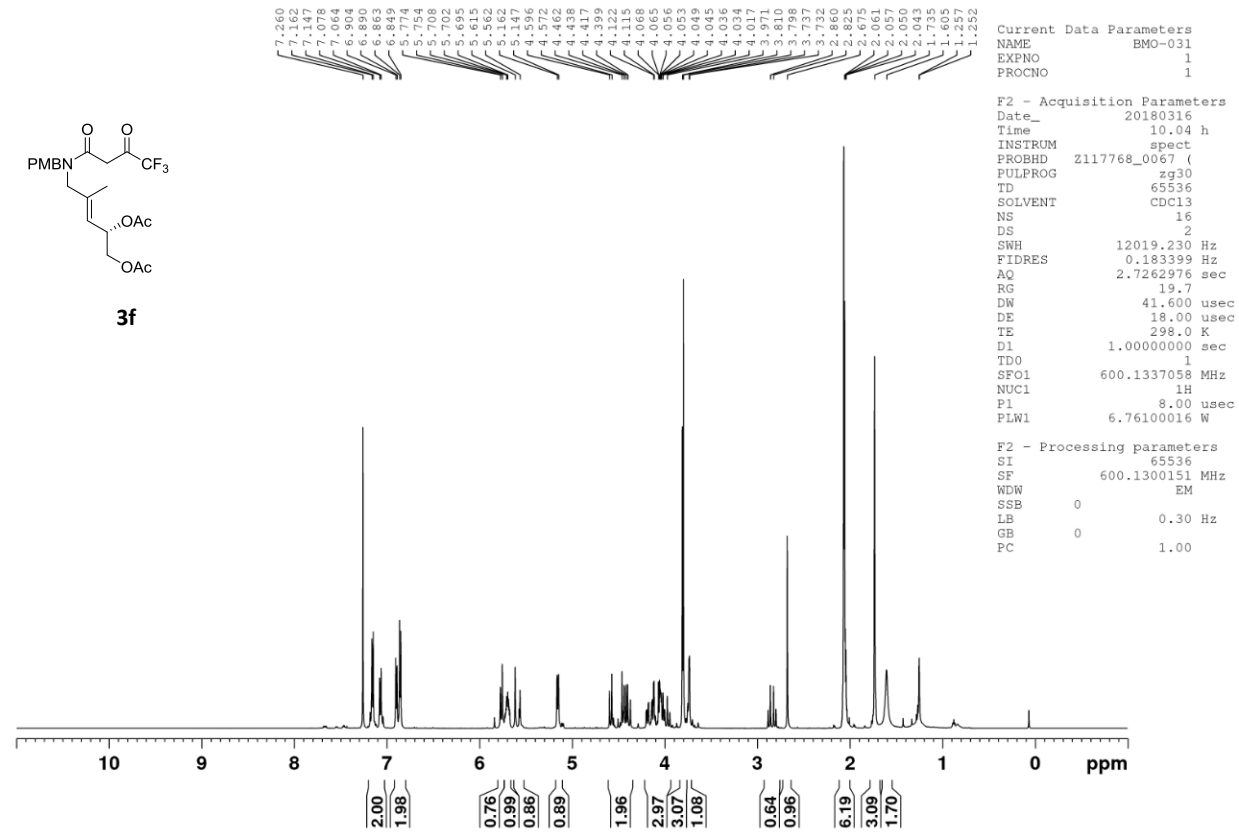

```
Current Data Parameters
NAME                BM047C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160913
Time                 11.55
INSTRUM              spect
PROBHD   5 mm CPTCI 1H-
PULPROG              jmod
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010048 sec
RG                   2050
DW                 16.800 usec
DE                  6.50 usec
TE                298.2 K
CNST2         145.0000000
CNST11          1.0000000
D1              2.00000000 sec
D20             0.00689655 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  11.20 usec
P2                  22.40 usec
PL1                 -2.00 dB
PL1W         88.77790070 W
SFO1         125.8055709 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  4.00 dB
PL12                25.28 dB
PL2W          8.72000027 W
PL12W         0.06494062 W
SFO2         500.2720011 MHz

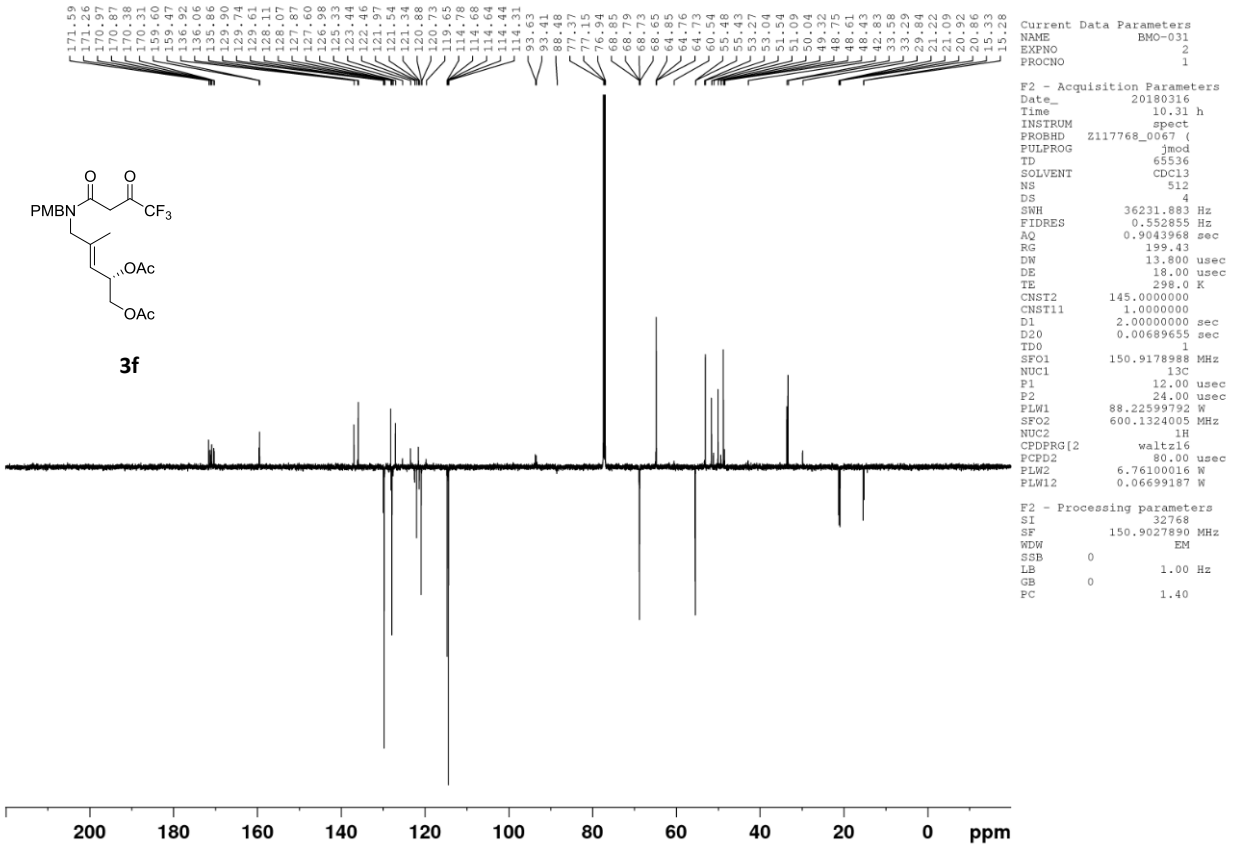
F2 - Processing parameters
SI                   32768
SF           125.7929799 MHz
WDW                     EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```




```
Current Data Parameters
NAME                  BMO-031
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180316
Time                   10.04 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               12019.230 Hz
FIDRES                0.183399 Hz
AQ                 2.7262976 sec
RG                       19.7
DW                     41.600 usec
DE                     18.00 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                         1
SFO1           600.1337058 MHz
NUC1                       1H
P1                     8.00 usec
PLW1           6.76100016 W

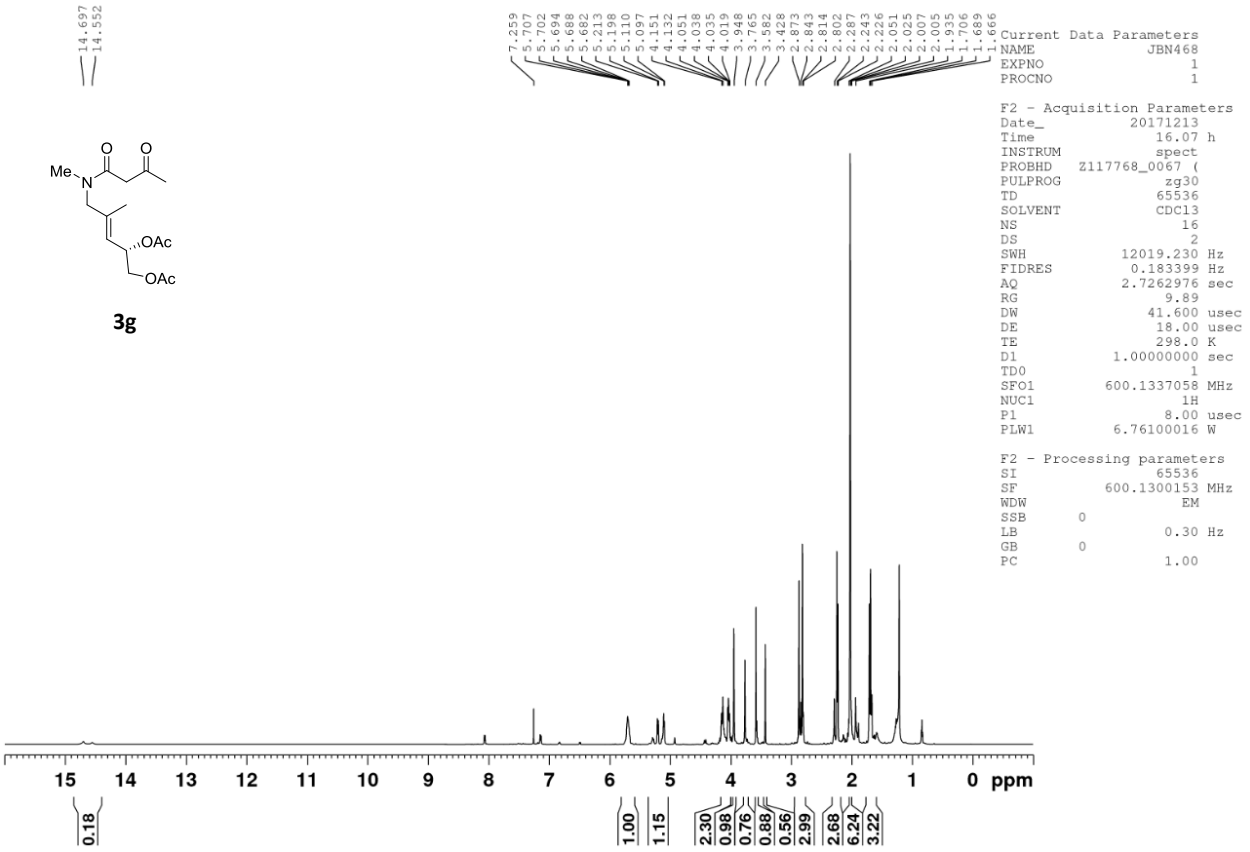
F2 - Processing parameters
SI                         65536
SF                600.1300151 MHz
WDW                           EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```




```
Current Data Parameters
NAME                  BMO-031
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180316
Time                   10.31 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                jmod
TD                    65536
SOLVENT               CDCl3
NS                       512
DS                         4
SWH               36231.883 Hz
FIDRES                0.552855 Hz
AQ                 0.9043968 sec
RG                     199.43
DW                     13.800 usec
DE                     18.00 usec
TE                     298.0 K
CNST2             145.0000000
CNST11              1.0000000
D1                 2.00000000 sec
D20                0.00689655 sec
TD0                         1
SFO1           150.9178988 MHz
NUC1                       13C
P1                     12.00 usec
P2                     24.00 usec
PLW1           88.22599792 W
SFO2           600.1324005 MHz
NUC2                       1H
CPDPRG[2            waltz16
PCPD2                  80.00 usec
PLW2           6.76100016 W
PLW12          0.06699187 W

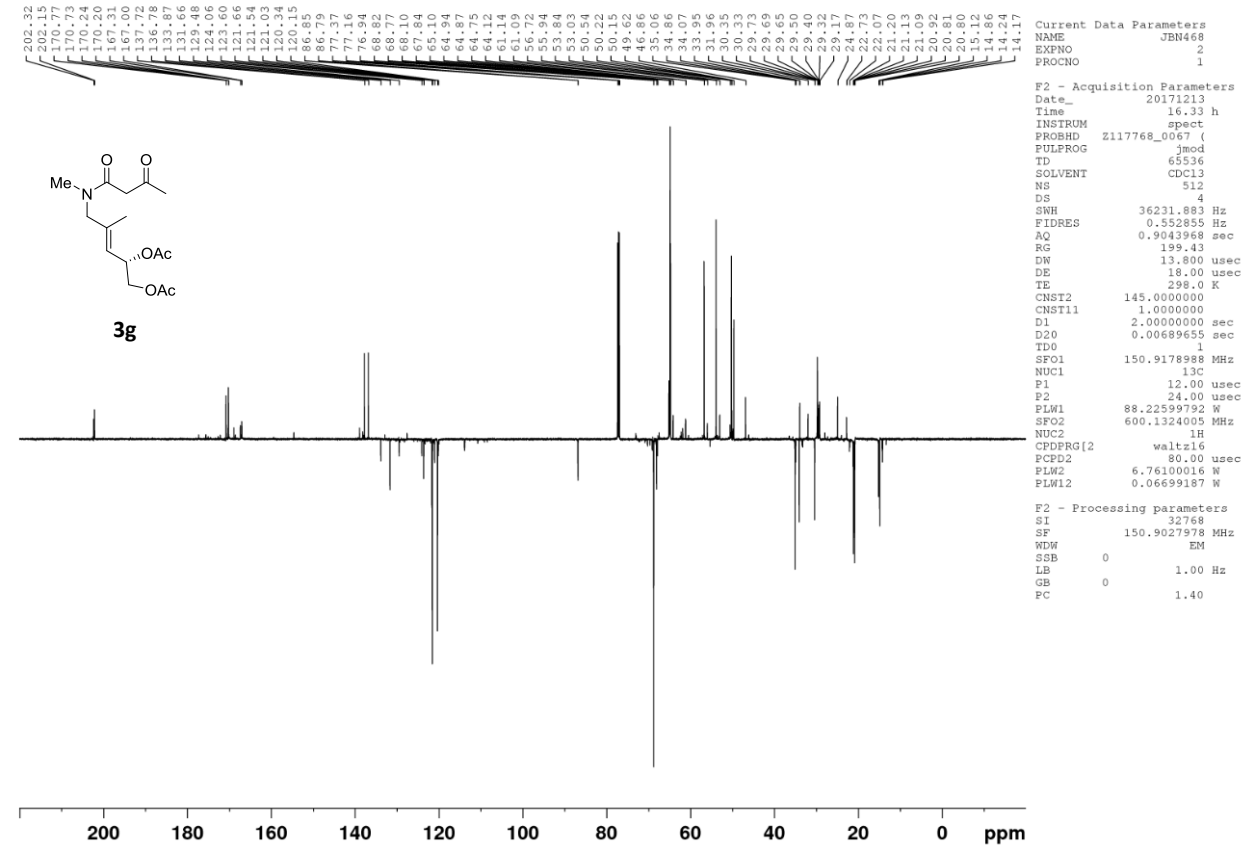
F2 - Processing parameters
SI                         32768
SF                150.9027890 MHz
WDW                           EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```




```
Current Data Parameters
NAME                  JBN468
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20171213
Time                 16.07 h
INSTRUM              spect
PROBHD   Z117768_0067 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             12019.230 Hz
FIDRES              0.183399 Hz
AQ                2.7262976 sec
RG                     9.89
DW                   41.600 usec
DE                   18.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                        1
SFO1           600.1337058 MHz
NUC1                    1H
P1                     8.00 usec
PLW1            6.76100016 W

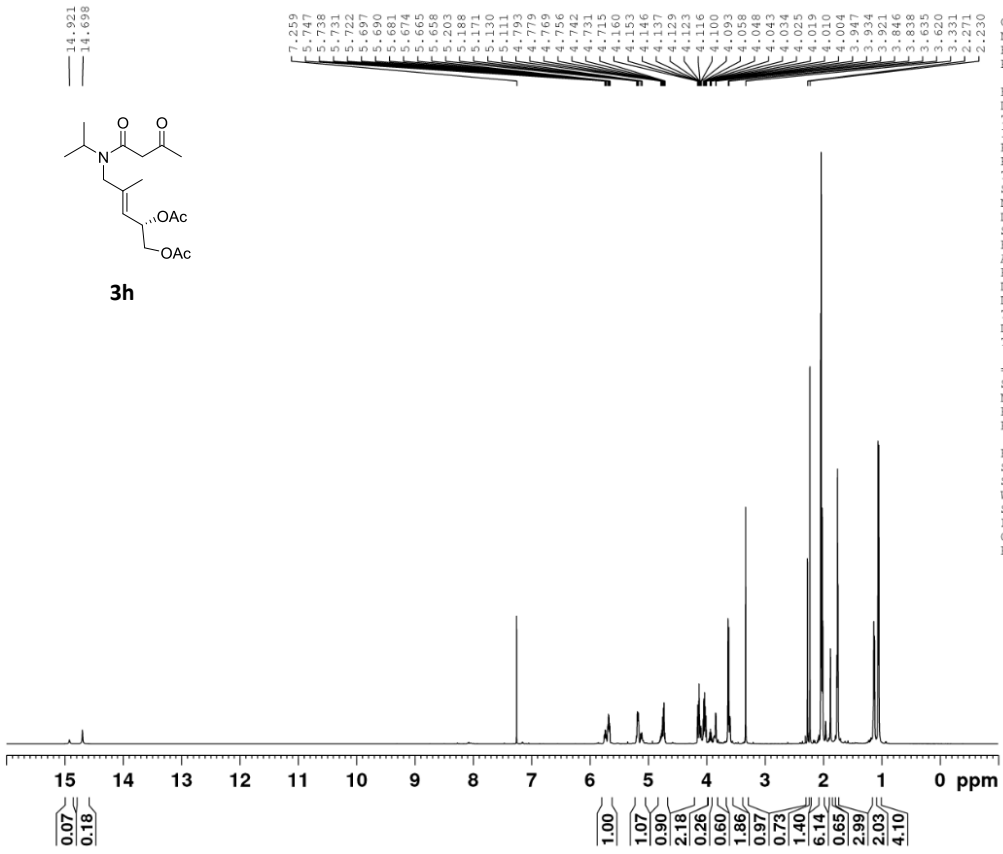
F2 - Processing parameters
SI                     65536
SF              600.1300153 MHz
WDW                    EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```




```
Current Data Parameters
NAME                  JBN468
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20171213
Time                 16.33 h
INSTRUM              spect
PROBHD   Z117768_0067 (
PULPROG              jmod
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH             36231.883 Hz
FIDRES              0.552855 Hz
AQ                0.9043968 sec
RG                   199.43
DW                   13.800 usec
DE                   18.00 usec
TE                   298.0 K
CNST2          145.0000000
CNST11           1.0000000
D1               2.00000000 sec
D20              0.00689655 sec
TD0                        1
SFO1           150.9178988 MHz
NUC1                   13C
P1                   12.00 usec
P2                   24.00 usec
PLW1           88.22599792 W
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2                80.00 usec
PLW2            6.76100016 W
PLW12           0.06699187 W

F2 - Processing parameters
SI                     32768
SF              150.9027978 MHz
WDW                    EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

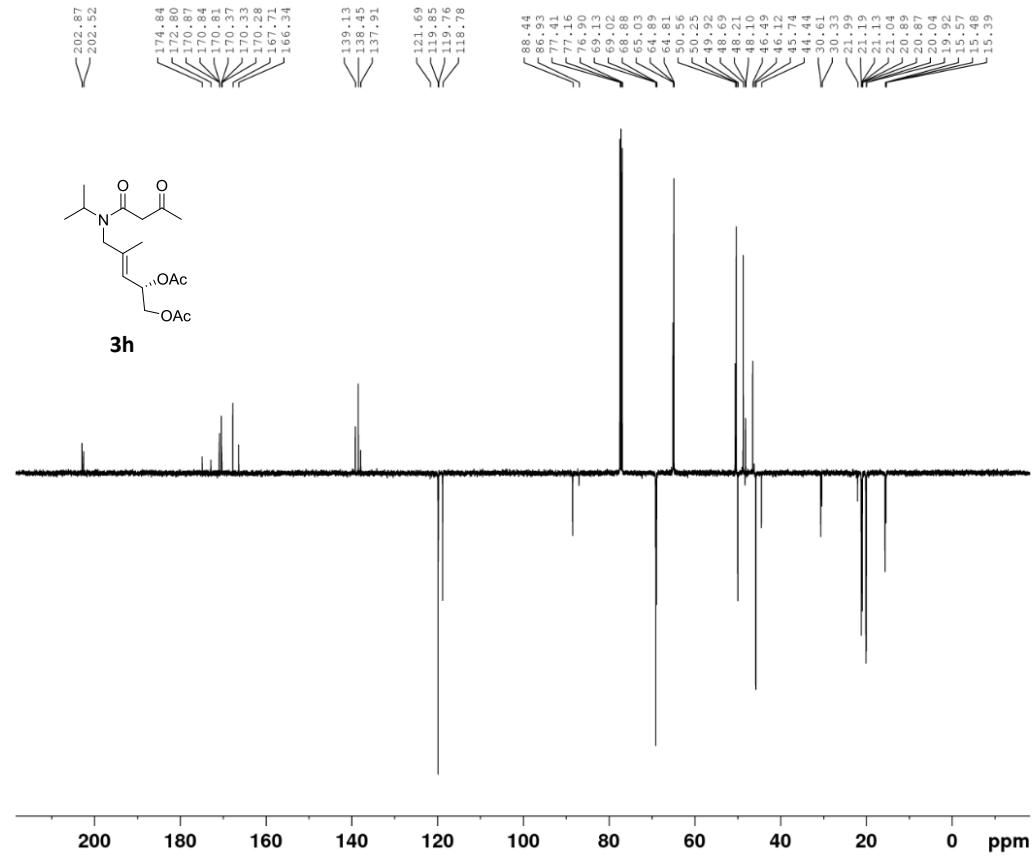



```
Current Data Parameters
NAME                  JBN359
EXPNO                      7
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170801
Time                   9.52
INSTRUM               spect
PROBHD   5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2767999 sec
RG                      12.7
DW                    50.000 usec
DE                    10.00 usec
TE                    298.2 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           500.2730894 MHz
NUC1                     1H
P1                    7.63 usec
PLW1           9.50000000 W

F2 - Processing parameters
SI                    65536
SF             500.2700080 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```



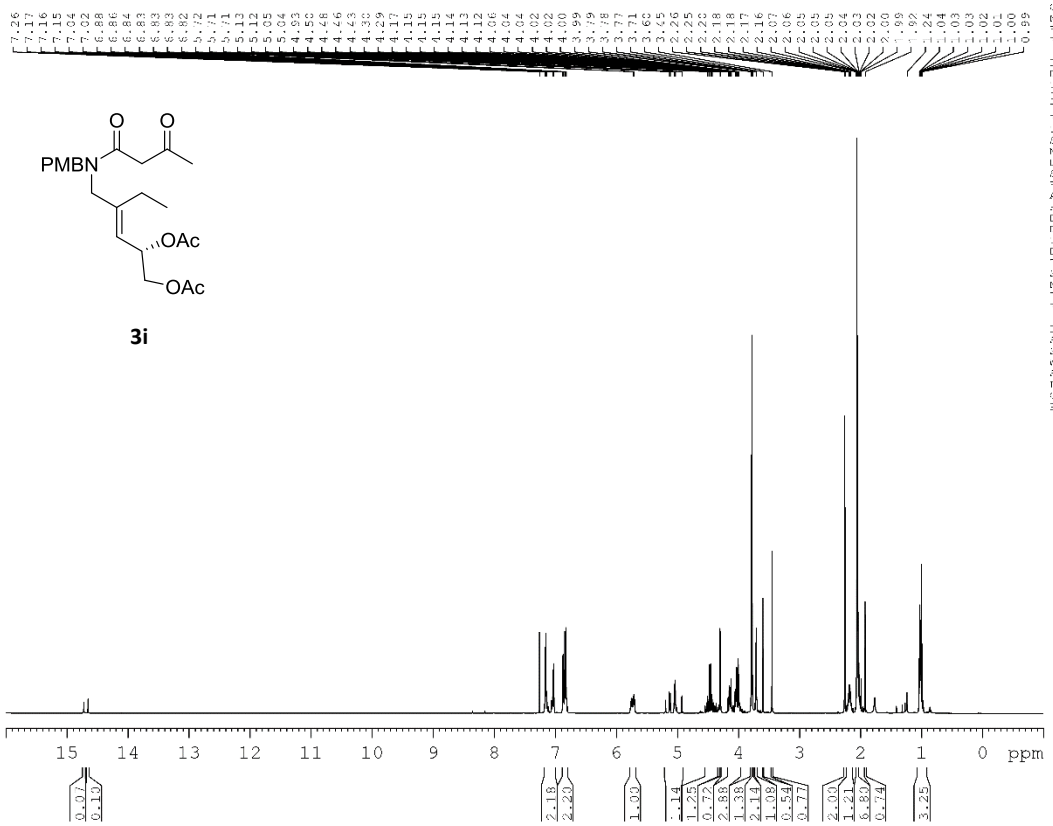

```
Current Data Parameters
NAME                  JBN359
EXPNO                      9
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170801
Time                  10.12
INSTRUM               spect
PROBHD   5 mm CPTCI 1H-
PULPROG               jmod
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        4
SWH              29761.904 Hz
FIDRES               0.454131 Hz
AQ                1.1010048 sec
RG                     1030
DW                    16.800 usec
DE                    18.00 usec
TE                    298.2 K
CNST2           145.0000000
CNST11            1.0000000
D1               2.00000000 sec
D20              0.00689655 sec
TD0                        1

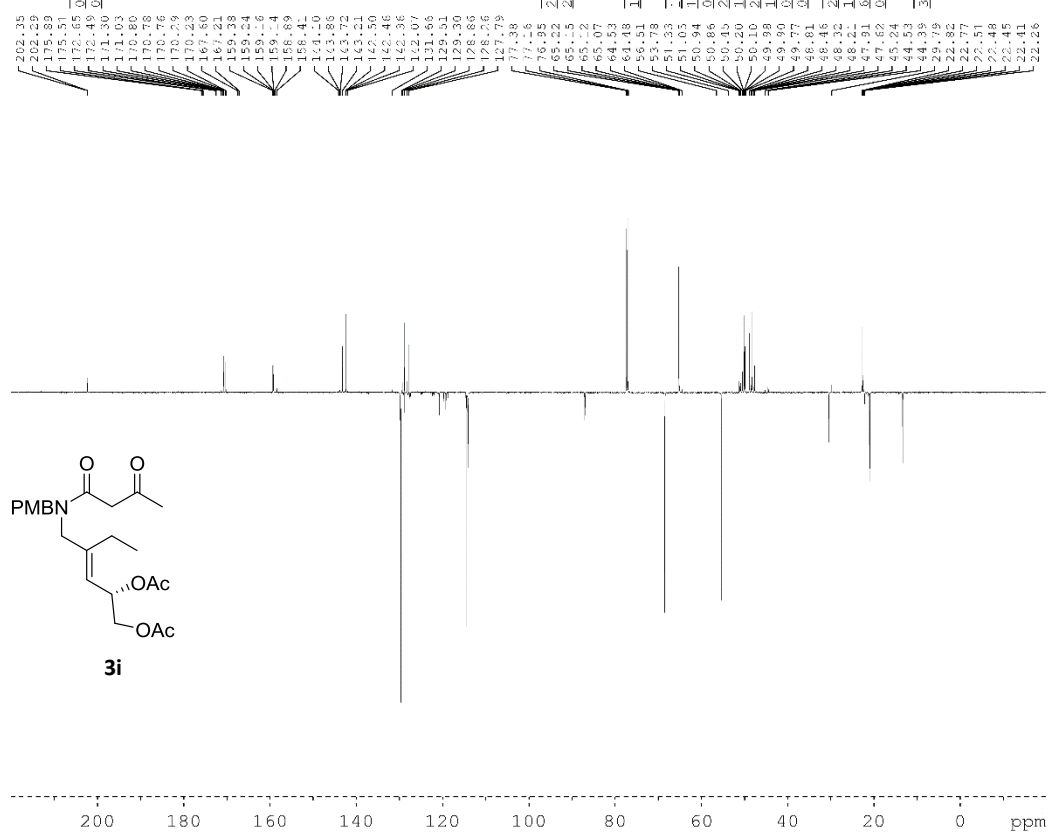
======== CHANNEL f1 ========
SFO1           125.8055709 MHz
NUC1                    13C
P1                    14.00 usec
P2                    28.00 usec
PLW1            90.00000000 W

======== CHANNEL f2 ========
SFO2           500.2720011 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            9.50000000 W
PLW12           0.08641600 W

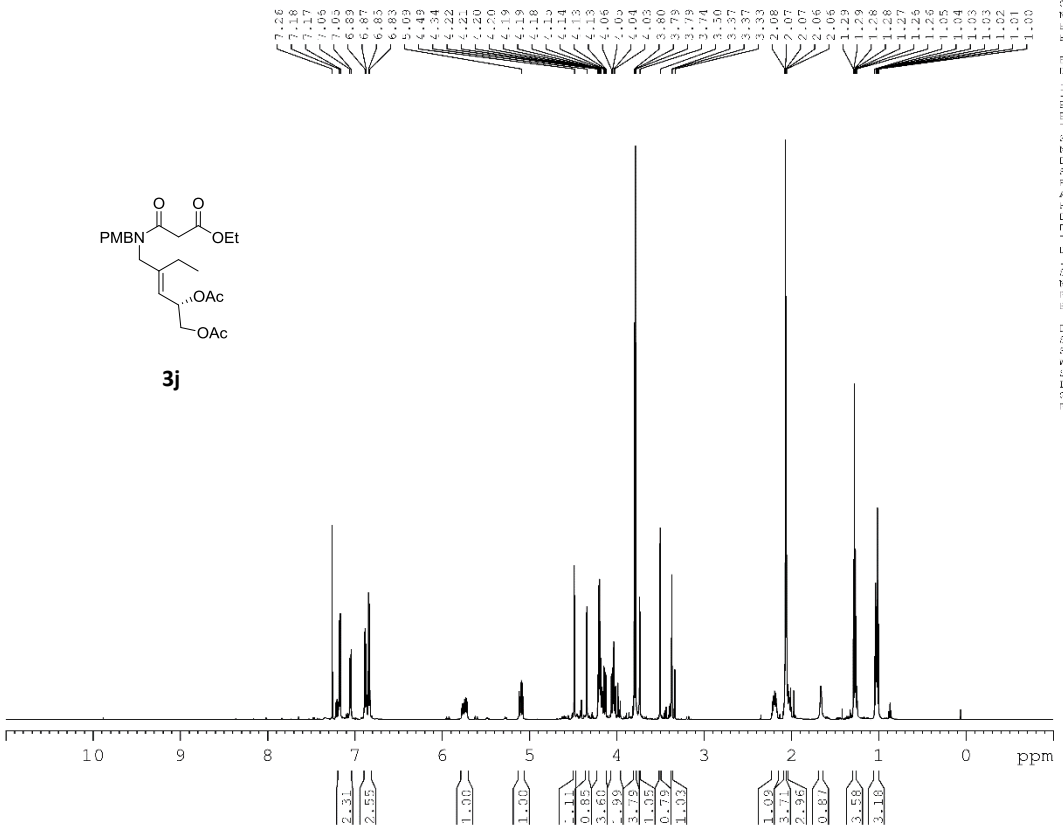
F2 - Processing parameters
SI                    32768
SF             125.7929791 MHz
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

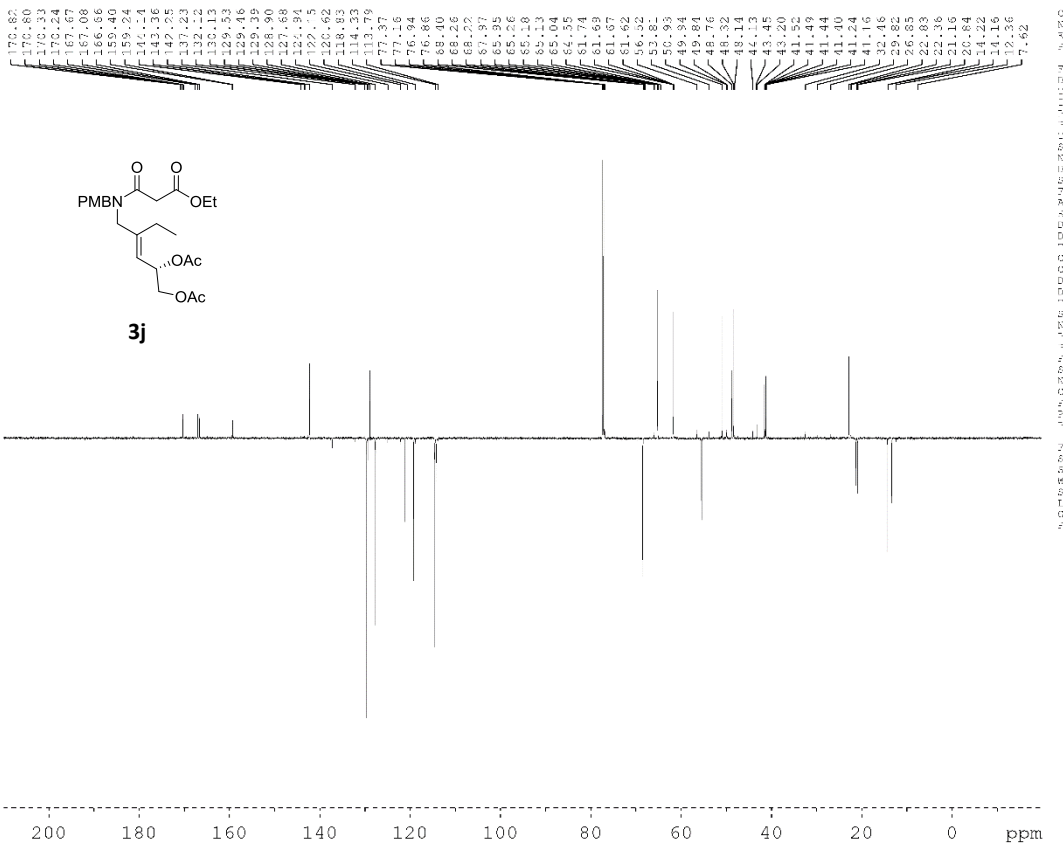


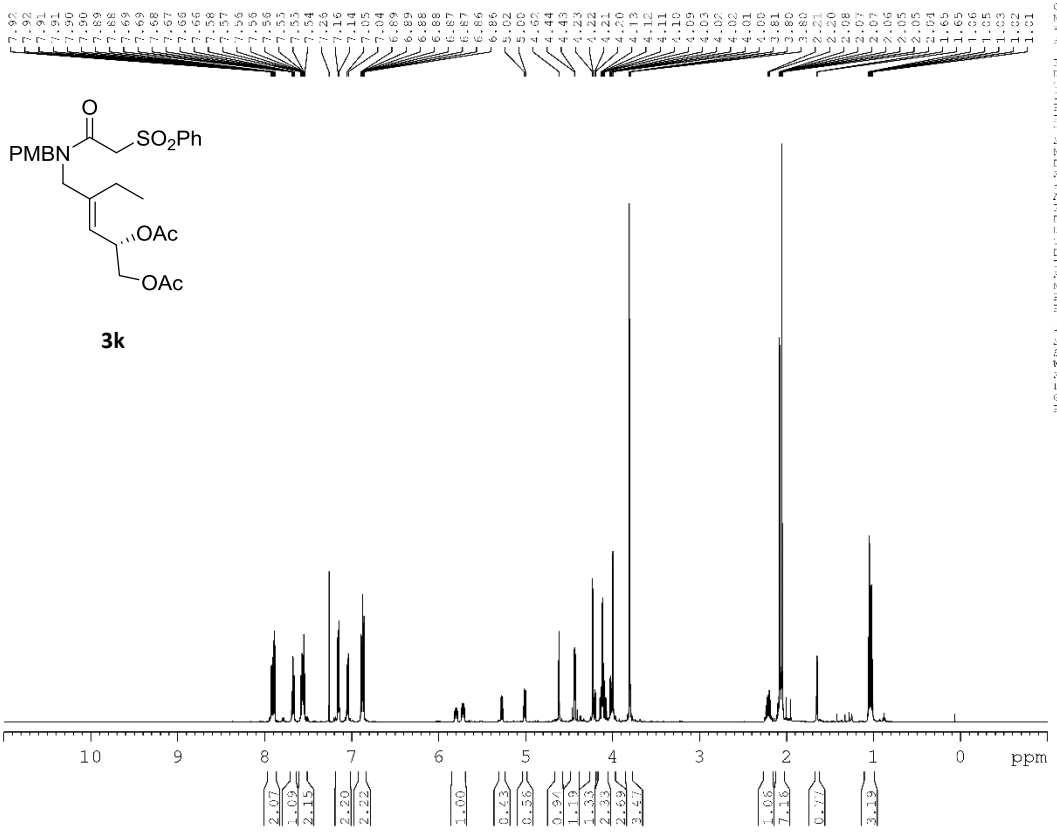

**3i**



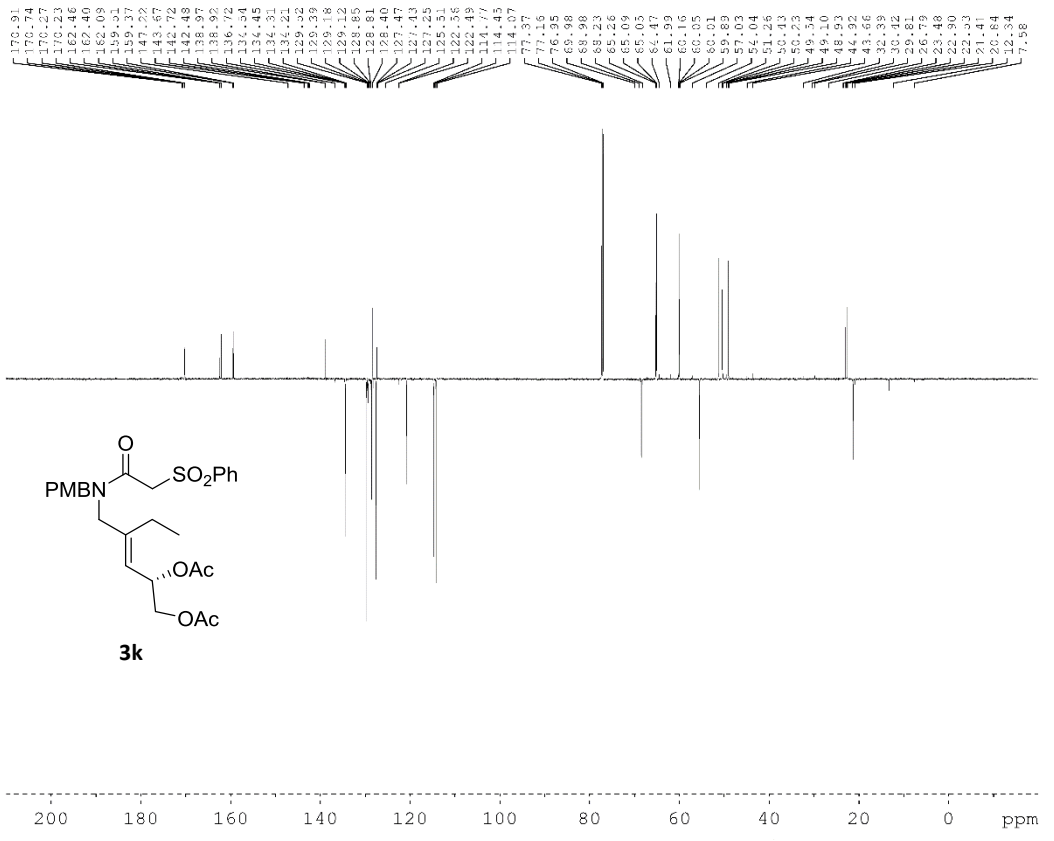

**3i**


PMBN
O
O
OEt
OAc
OAc
3j
ppm

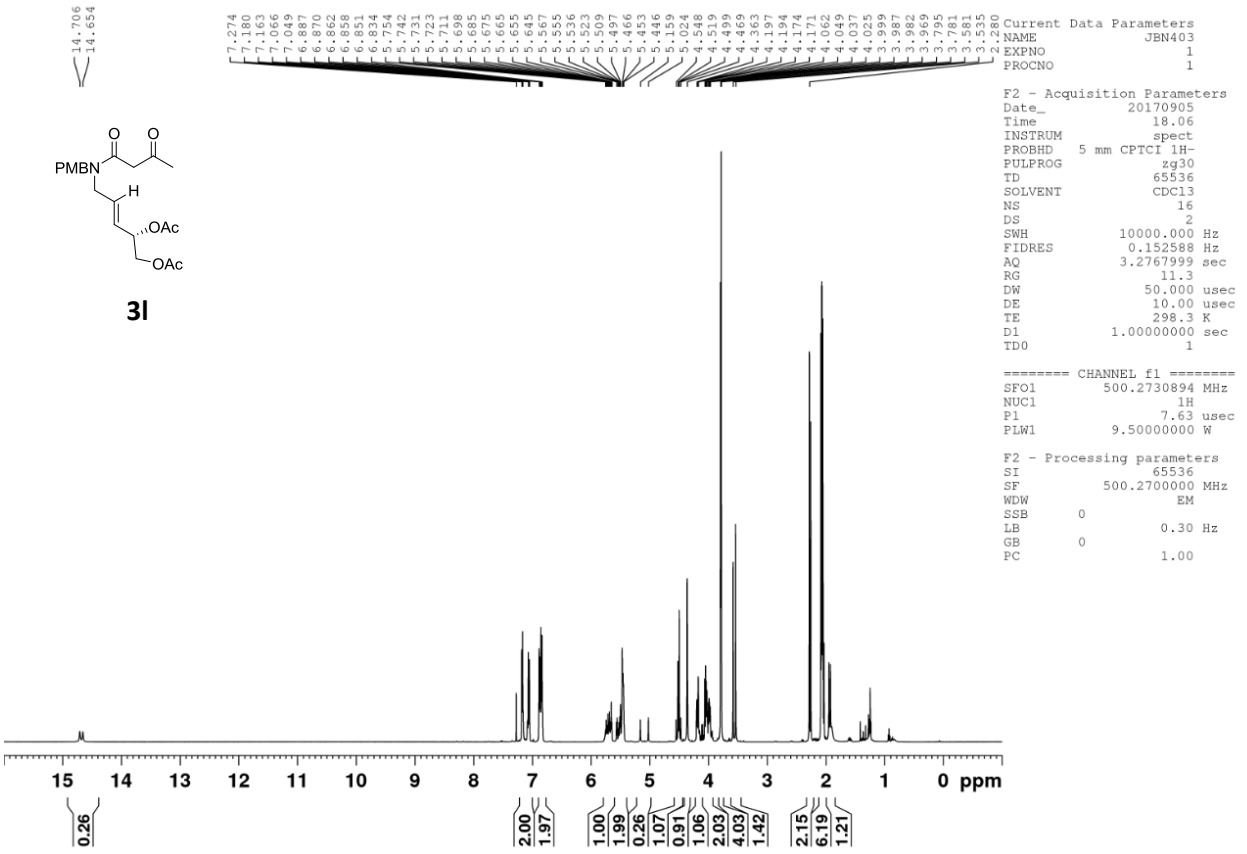

PMBN
O
O
OEt
OAc
OAc
3j
ppm




**3k**




**3k**

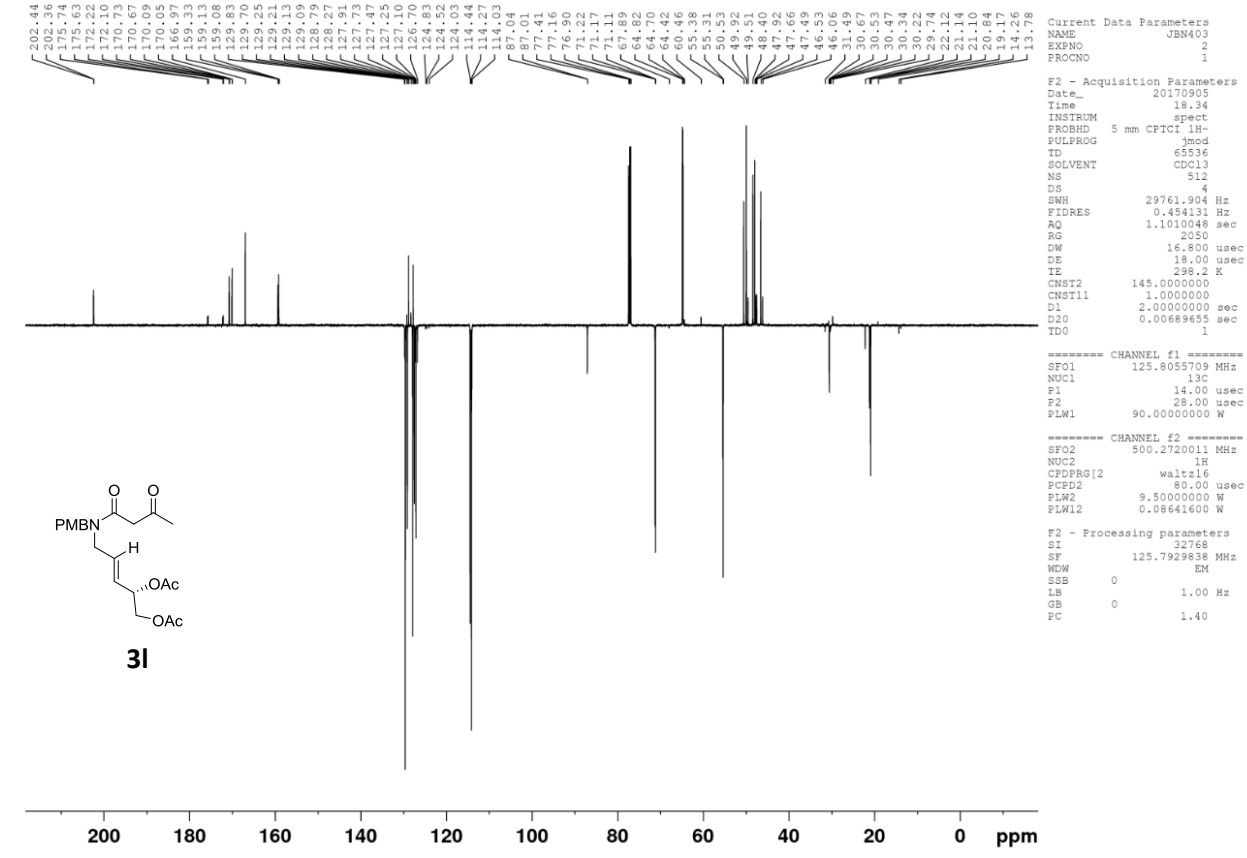



```
Current Data Parameters
NAME                  JBN403
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170905
Time                  18.06
INSTRUM               spect
PROBHD    5 mm CPTCI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10000.000 Hz
FIDRES                0.152588 Hz
AQ                3.2767999 sec
RG                       11.3
DW                    50.000 usec
DE                    10.00 usec
TE                    298.3 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            500.2730894 MHz
NUC1                      1H
P1                     7.63 usec
PLW1            9.50000000 W

F2 - Processing parameters
SI                        65536
SF              500.2700000 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```



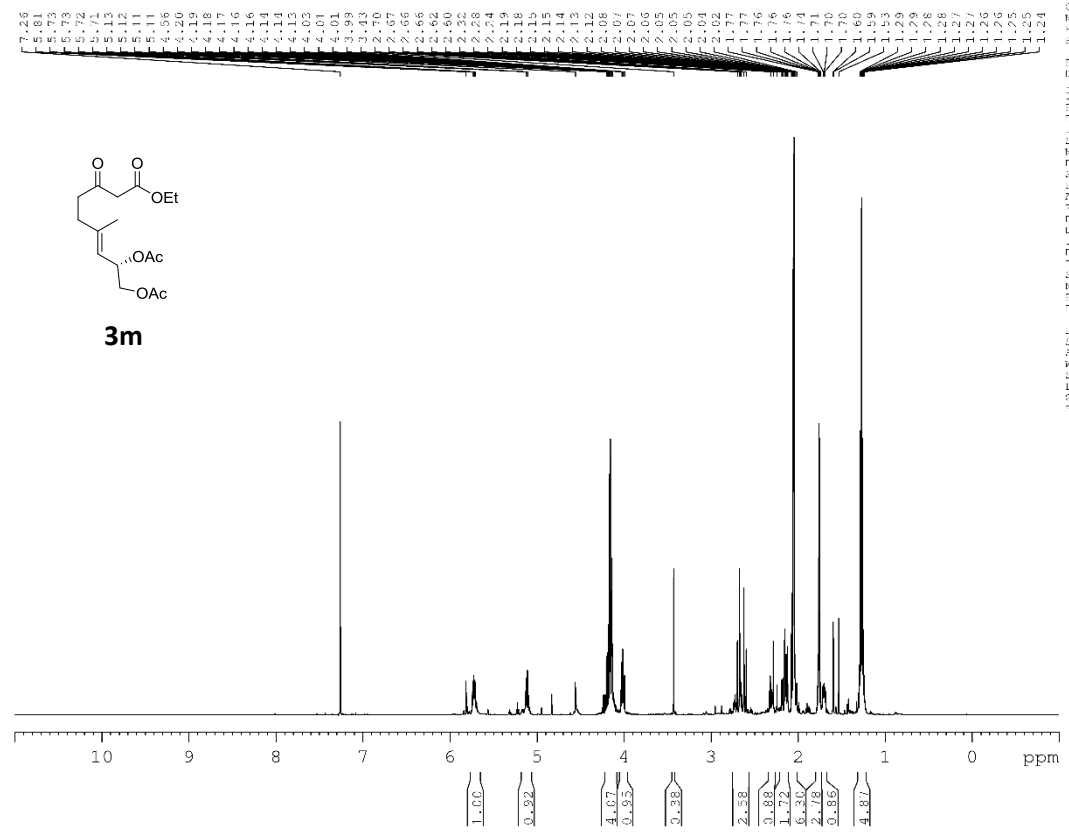

```
Current Data Parameters
NAME                  JBN403
EXPNO                      2
PROCNO                     1

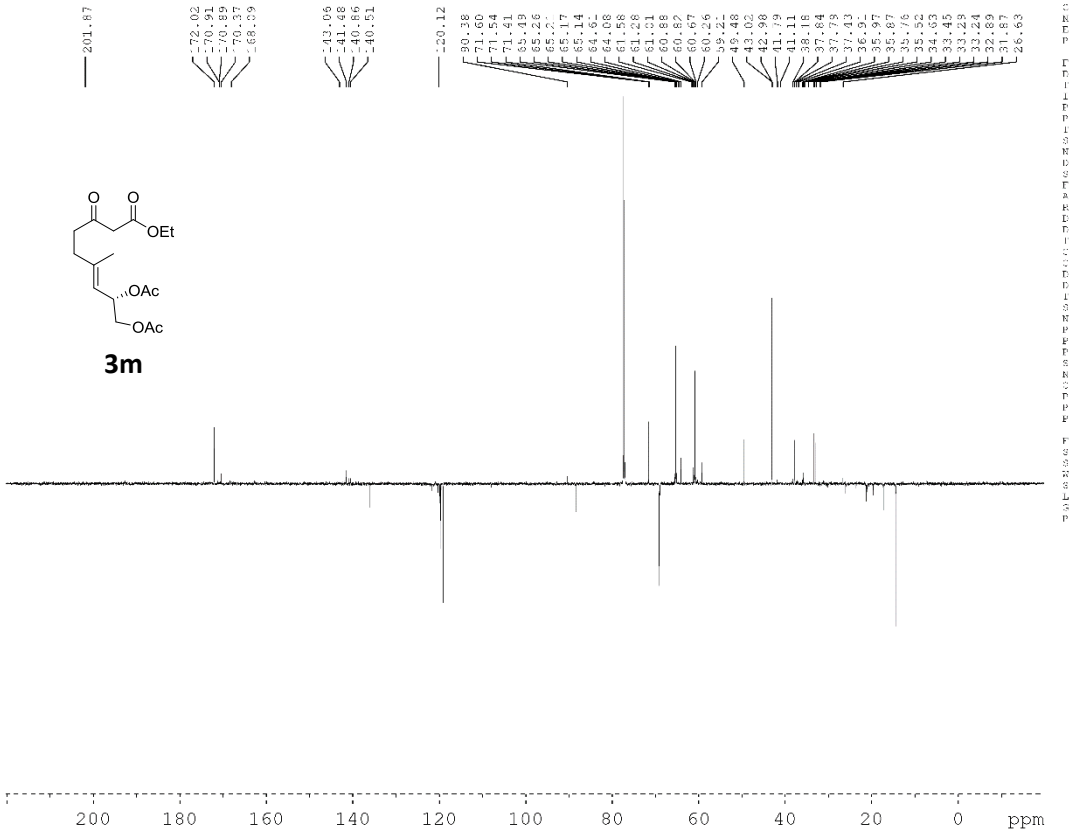
F2 - Acquisition Parameters
Date_              20170905
Time                  18.34
INSTRUM               spect
PROBHD    5 mm CPTCI 1H-
PULPROG               jmod
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                1.1010048 sec
RG                     2050
DW                    16.800 usec
DE                    18.00 usec
TE                    298.2 K
CNST2           145.0000000
CNST11            1.0000000
D1                2.00000000 sec
D20               0.00689655 sec
TD0                        1

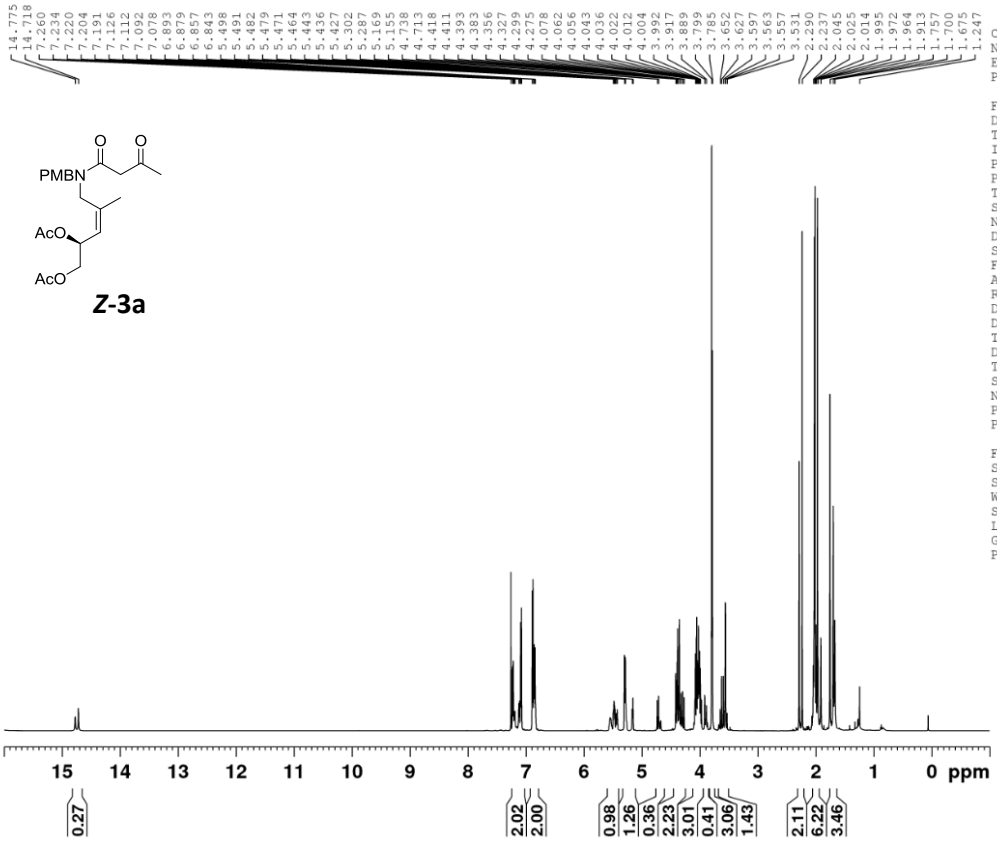
======== CHANNEL f1 ========
SFO1            125.8055709 MHz
NUC1                      13C
P1                    14.00 usec
P2                    28.00 usec
PLW1            90.00000000 W

======== CHANNEL f2 ========
SFO2            500.2720011 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2             9.50000000 W
PLW12            0.08641600 W

F2 - Processing parameters
SI                        32768
SF              125.7929838 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```


OEt
OAc
OAc
3m
ppm

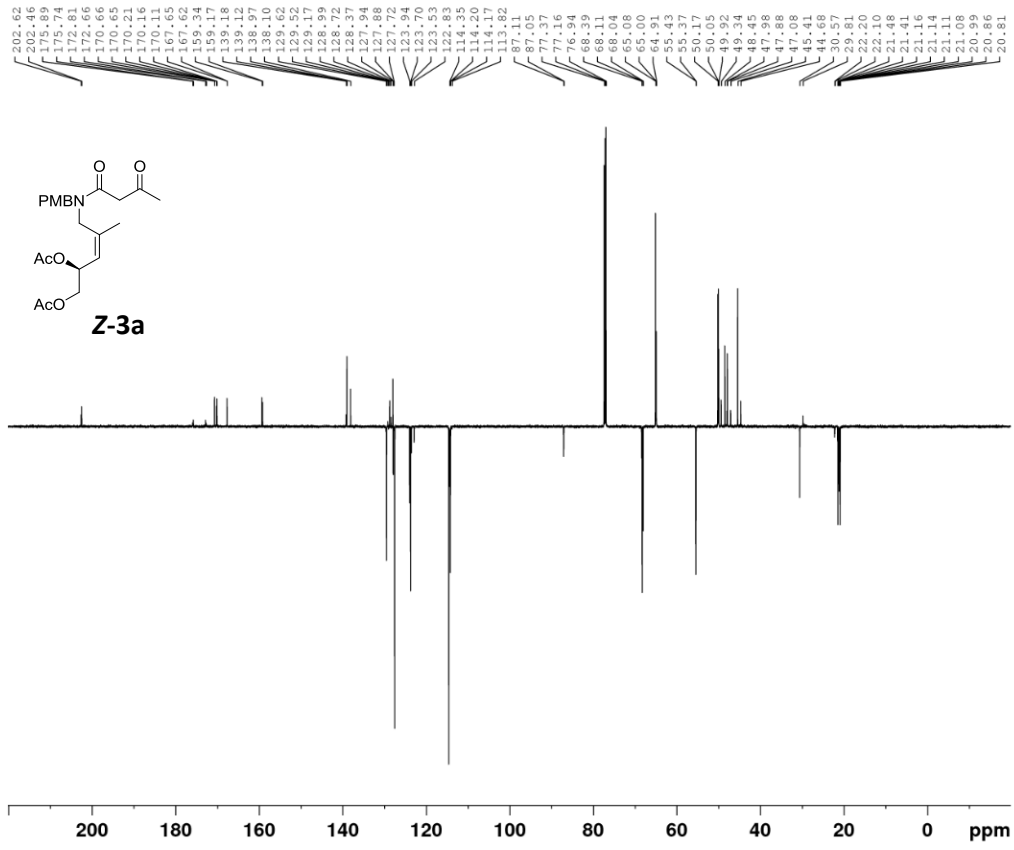

OEt
OAc
OAc
3m
ppm




```
Current Data Parameters
NAME                  JBN492
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20180326
Time                  9.44 h
INSTRUM               spect
PROBHD    Z117768_0067 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12019.230 Hz
FIDRES               0.183399 Hz
AQ                2.7262976 sec
RG                    14.39
DW                   41.600 usec
DE                   18.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                       1
SFO1           600.1337058 MHz
NUC1                    1H
P1                    8.00 usec
PLW1           6.76100016 W

F2 - Processing parameters
SI                    65536
SF             600.1300153 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

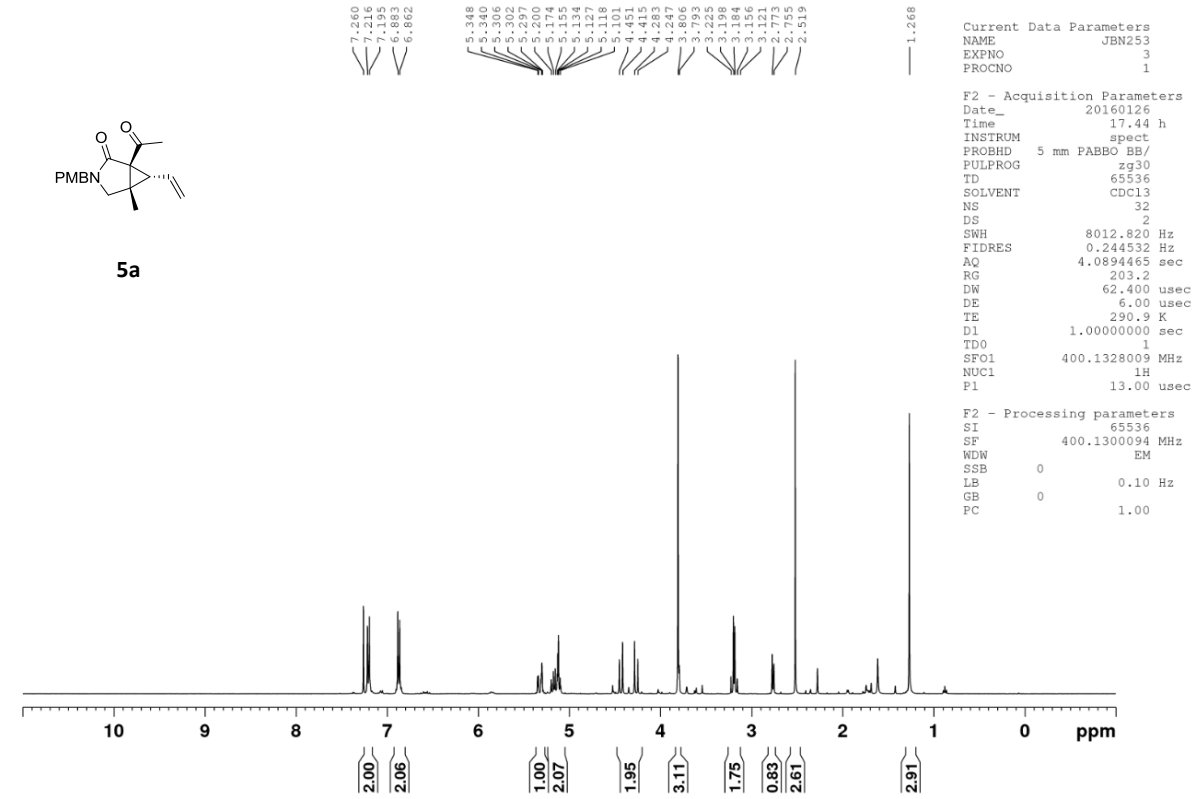


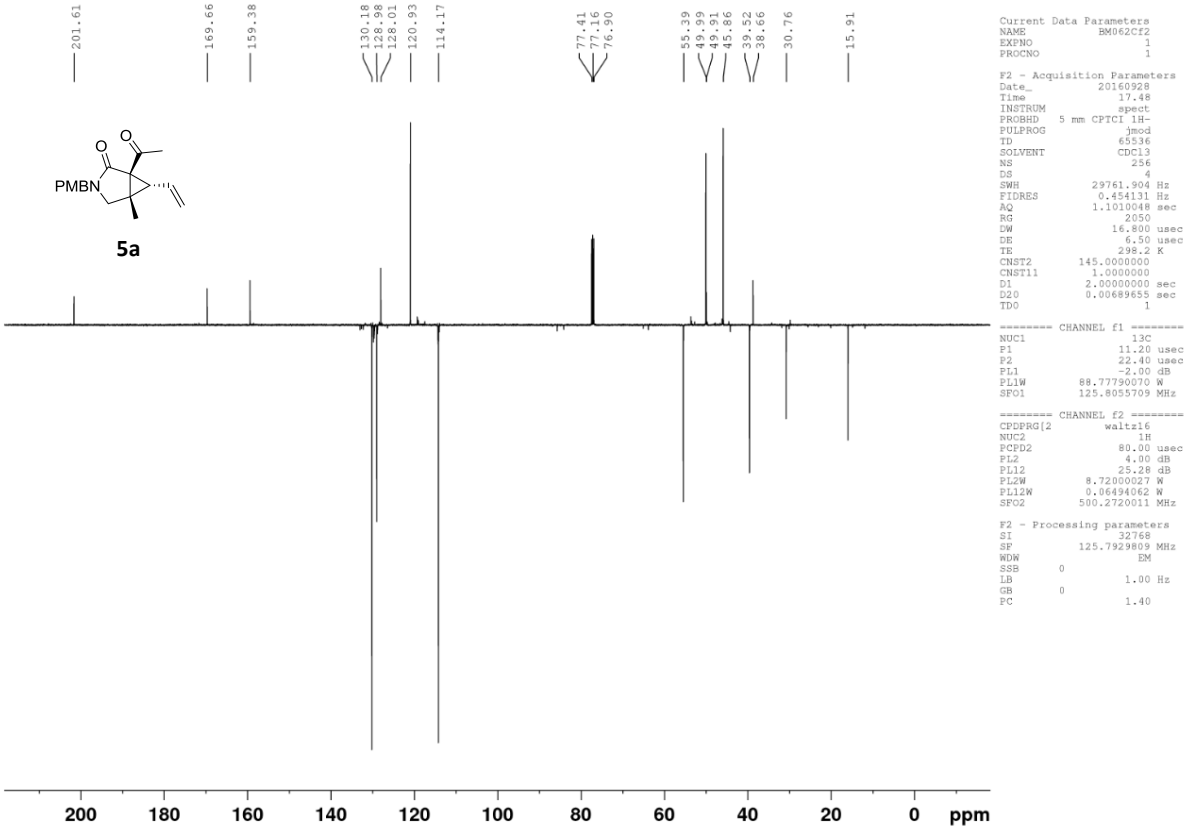

```
Current Data Parameters
NAME                  JBN492
EXPNO                      2
PROCNO                     1

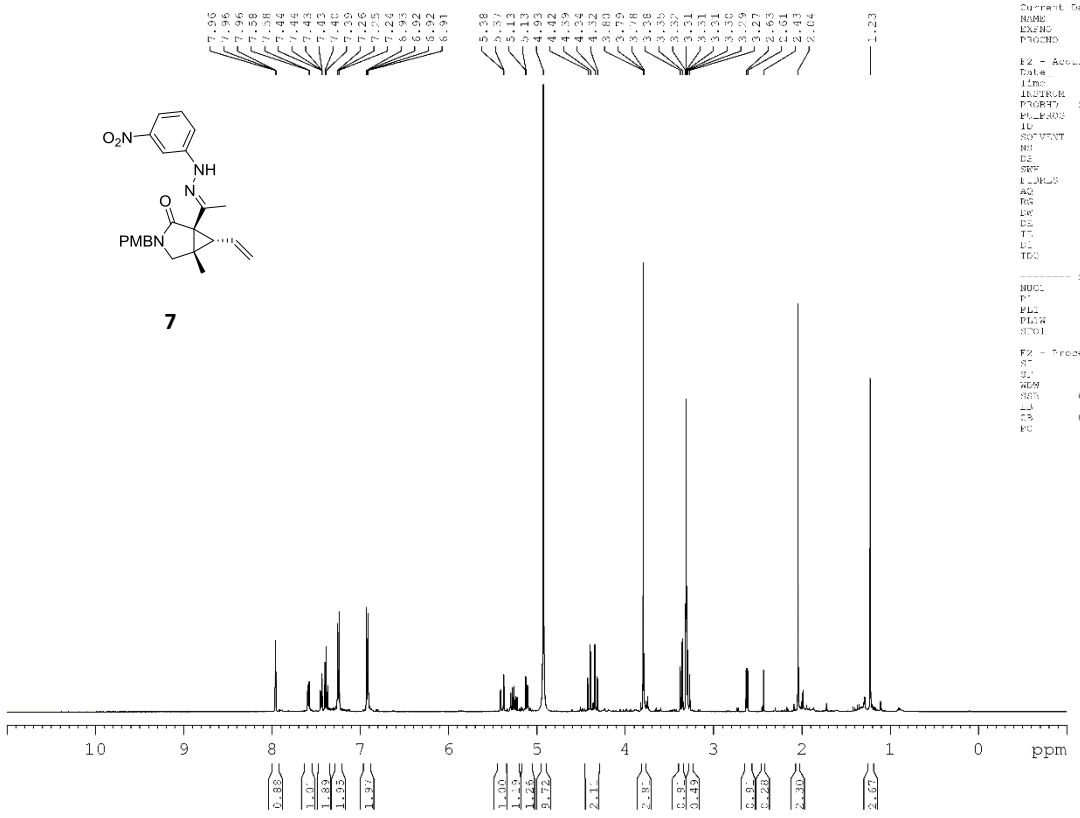
F2 - Acquisition Parameters
Date_              20180326
Time                 10.10 h
INSTRUM               spect
PROBHD    Z117768_0067 (
PULPROG                jmod
TD                    65536
SOLVENT               CDCl3
NS                       512
DS                         4
SWH              36231.883 Hz
FIDRES               0.552855 Hz
AQ                0.9043968 sec
RG                    199.43
DW                   13.800 usec
DE                   18.00 usec
TE                   298.0 K
CNST2           145.0000000
CNST11            1.0000000
D1              2.00000000 sec
D20             0.00689655 sec
TD0                       1
SFO1           150.9178988 MHz
NUC1                    13C
P1                   12.00 usec
P2                   24.00 usec
PLW1           88.22599792 W
SFO2           600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                80.00 usec
PLW2            6.76100016 W
PLW12           0.06699187 W

F2 - Processing parameters
SI                    32768
SF             150.9027917 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

## Vinylcyclopropanes



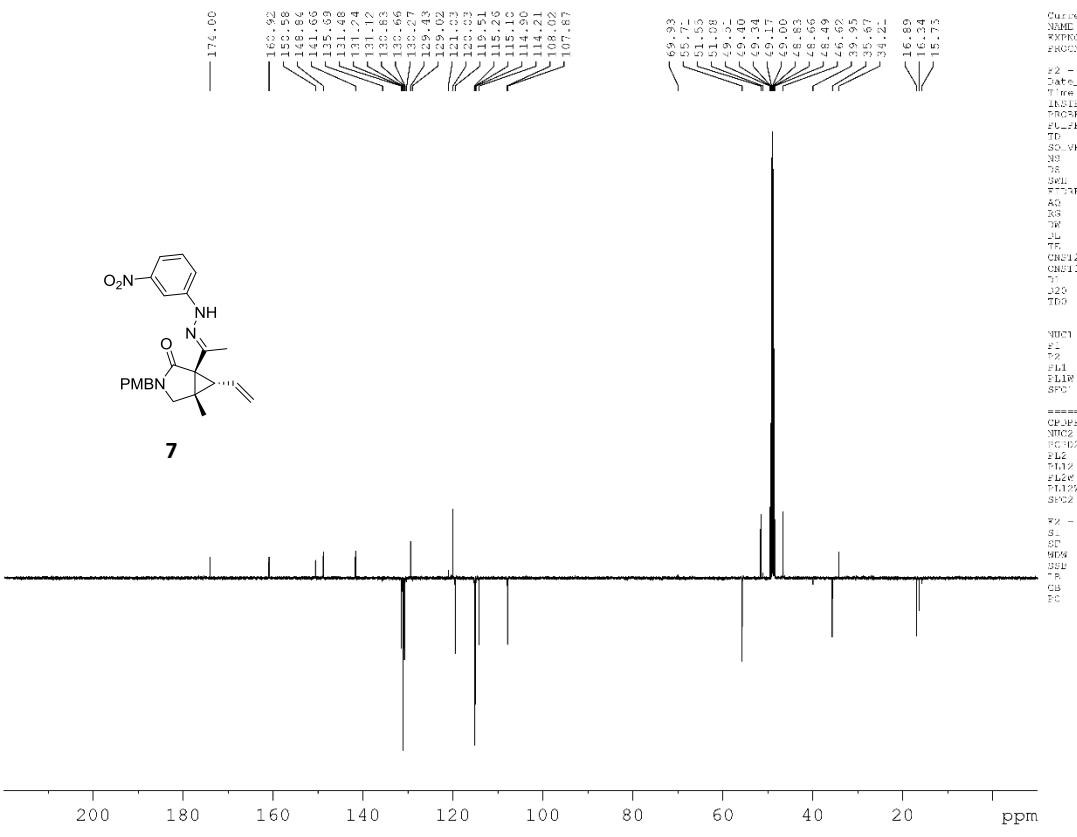



```
Current Data Parameters
NAME                  JSN256
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160323
Time                   9.44
INSTRUM                spoc
PROBHD   5 mm CPTCI 1H
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                        32
DS                         2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719428 sec
RG                      71.7
DW                   48.400 usec
DE                    6.50 usec
TE                   300.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    8.70 usec
PL1                   4.00 dB
PL1W          8.72000027 W
SFO1          500.2730890 MHz

F2 - Processing parameters
SI                     32768
SF            500.2700055 MHz
WDW                       EM
SSB                  0
LB                    0.30 Hz
GB                   0
PC                    1.00
```



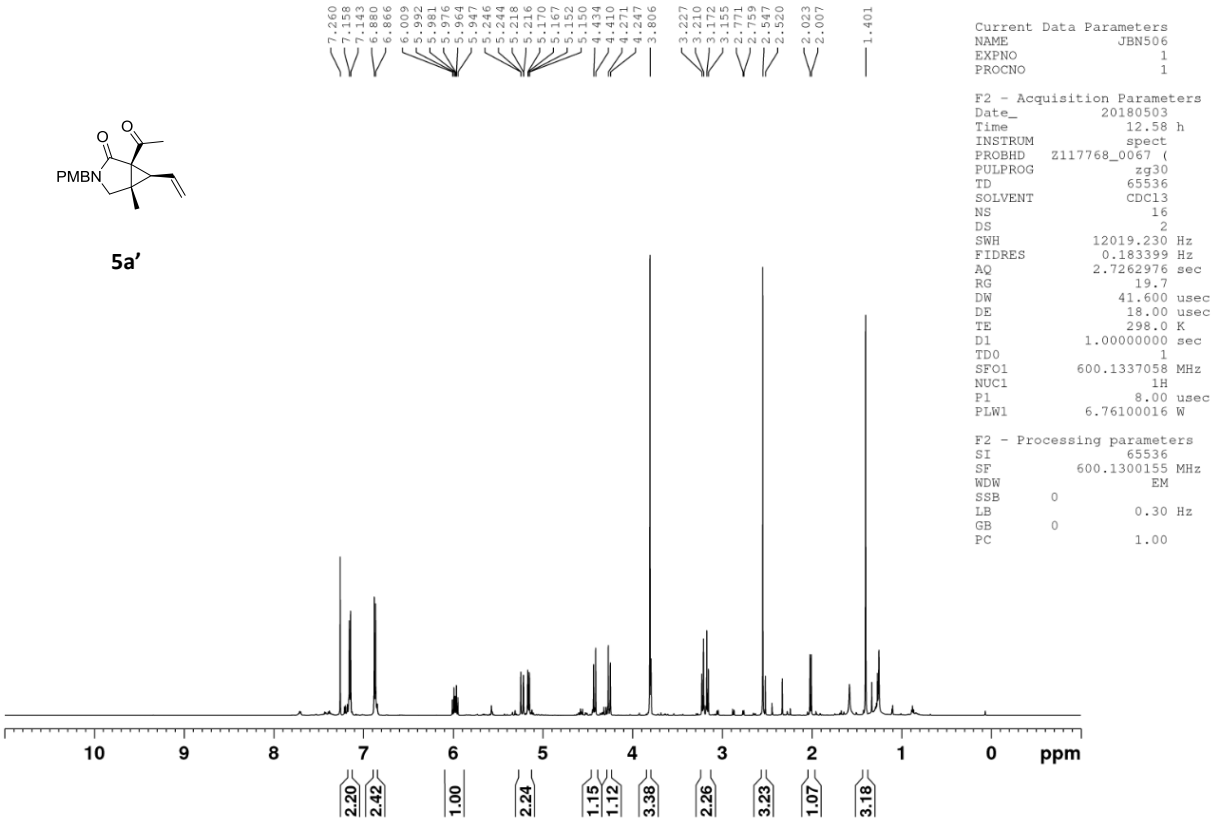

```
Current Data Parameters
NAME                  JSN256
EXPNO                      2
PROCNO                     1

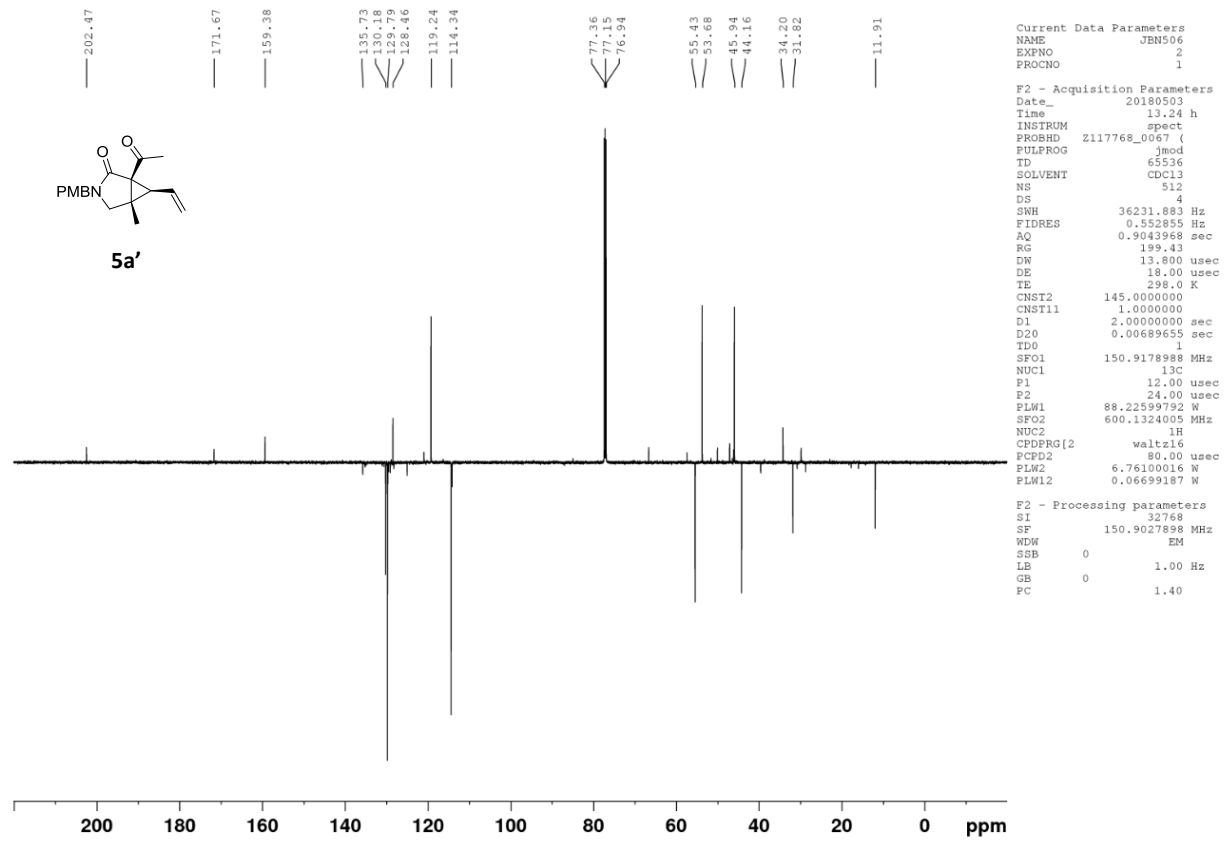
F2 - Acquisition Parameters
Date_              20160323
Time                  10.14
INSTRUM                spoc
PROBHD   5 mm CPTCI 1H
PULPROG                jmod
TD                    65536
SOLVENT                MeOD
NS                      512
DS                        4
SWH               23781.904 Hz
FIDRES             0.362911 Hz
AQ                 1.3762048 sec
RG                     2050
DW                   16.800 usec
DE                    6.50 usec
TE                   300.0 K
CNST12          145.0000000
CNST11            1.0000000
D1                2.0000000 sec
D20               0.03333635 sec
TD0                        1

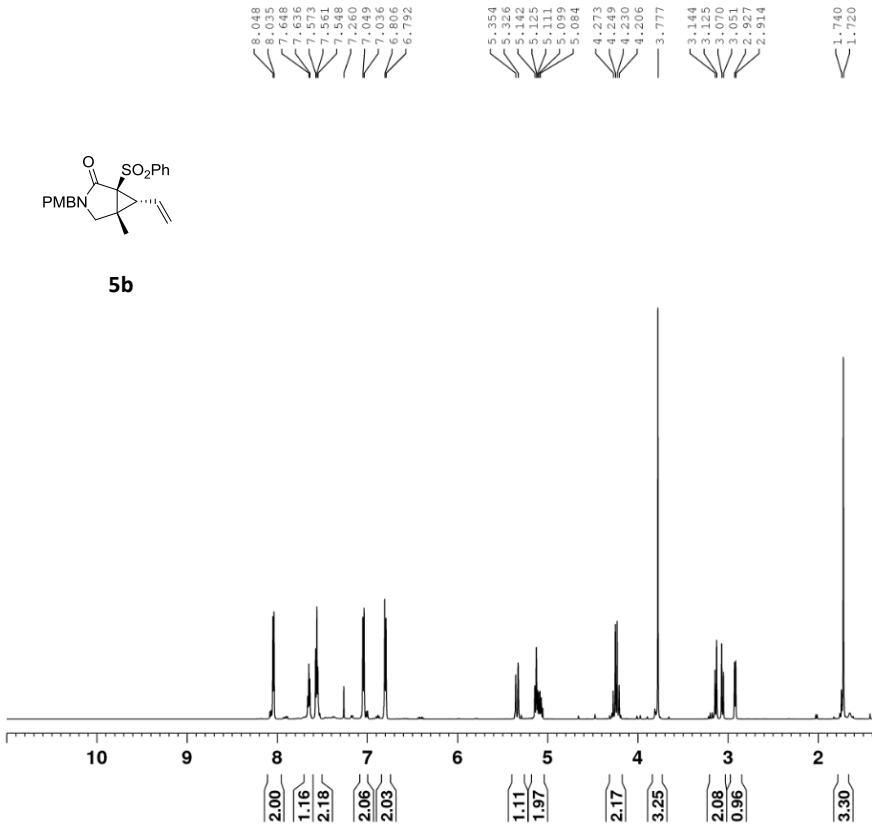
======== CHANNEL f1 ========
NUC1                      13C
P1                   11.20 usec
P2                   22.70 usec
PL1                  -2.00 dB
PL1W          88.77790070 W
SFO1          125.7855709 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                      1H
PCPD2                80.00 usec
PL2                   4.00 dB
PL12                 23.98 dB
PL2W          8.72000027 W
PL12W         0.06479062 W
SFO2          500.2720011 MHz

F2 - Processing parameters
SI                     32768
SF            125.7928145 MHz
WDW                       EM
SSB                  0
LB                    1.00 Hz
GB                   0
PC                    1.40
```


7.260
7.158
7.143
6.880
6.866
6.009
5.992
5.981
5.976
5.964
5.947
5.246
5.244
5.218
5.216
5.170
5.167
5.152
5.150
4.434
4.410
4.271
4.247
3.806
3.227
3.210
3.172
3.155
2.771
2.759
2.547
2.520
2.023
2.007
1.401
PMBN
5a'
Current Data Parameters
NAME JBN506
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180503
Time 12.58 h
INSTRUM spect
PROBHD Z117768_0067 (
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 19.7
DW 41.600 usec
DE 18.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P1 8.00 usec
PLW1 6.76100016 W
F2 - Processing parameters
SI 65536
SF 600.1300155 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
2.20 2.42 1.00 2.24 1.15 1.12 3.38 2.26 3.23 1.07 3.18

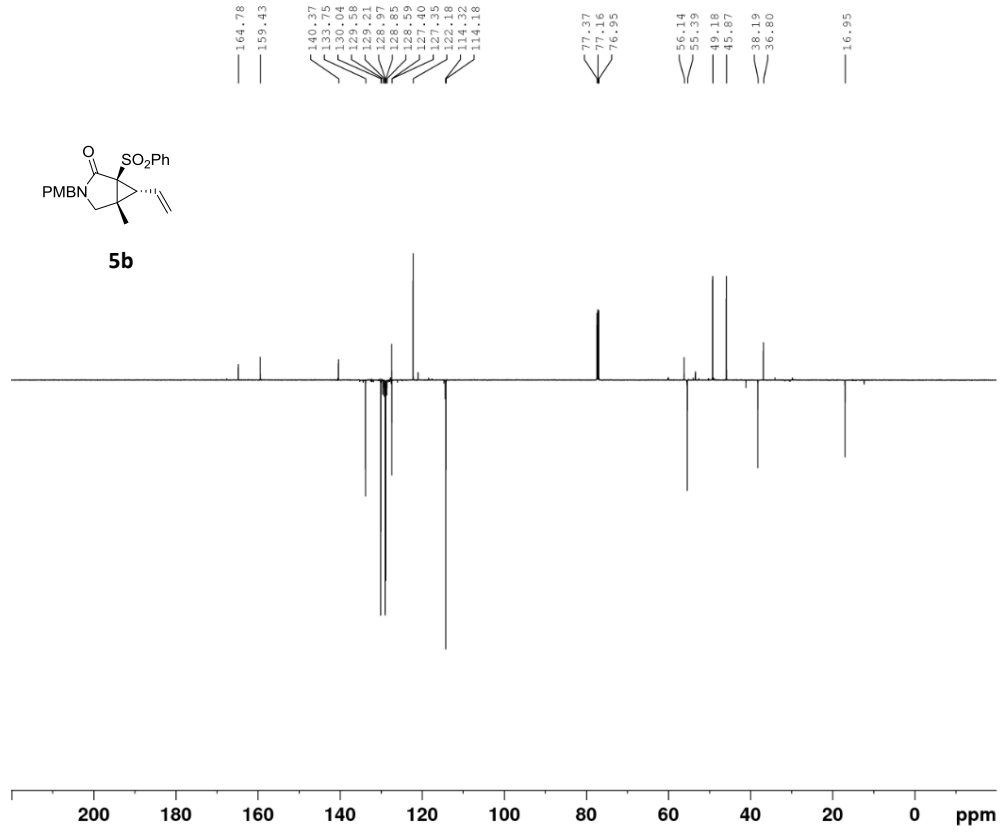

202.47
171.67
159.38
135.73
130.18
129.79
128.46
119.24
114.34
77.36
77.15
76.94
55.43
53.68
45.94
44.16
34.20
31.82
11.91
PMBN
5a'
Current Data Parameters
NAME JBN506
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180503
Time 13.24 h
INSTRUM spect
PROBHD Z117768_0067 (
PULPROG jmod
TD 65536
SOLVENT CDC13
NS 512
DS 4
SWH 36231.883 Hz
FIDRES 0.552855 Hz
AQ 0.9043968 sec
RG 199.43
DW 13.800 usec
DE 18.00 usec
TE 298.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 12.00 usec
P2 24.00 usec
PLW1 88.22599792 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 6.76100016 W
PLW12 0.06699187 W
F2 - Processing parameters
SI 32768
SF 150.9027898 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm




```
Current Data Parameters
NAME                  JBN410
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20180223
Time                  15.39 h
INSTRUM               spect
PROBHD    Z117768_0067 (
PULPROG               zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12019.230 Hz
FIDRES               0.183399 Hz
AQ                2.7262976 sec
RG                       14.39
DW                    41.600 usec
DE                    18.00 usec
TE                    298.0 K
D1               1.00000000 sec
TD0                        1
SFO1            600.1337058 MHz
NUC1                      1H
P1                     8.00 usec
PLW1             6.76100016 W

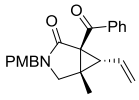
F2 - Processing parameters
SI                    65536
SF              600.1300146 MHz
WDW                      EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```




```
Current Data Parameters
NAME                  JBN410
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20180223
Time                  16.05 h
INSTRUM               spect
PROBHD    Z117768_0067 (
PULPROG               jmod
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH              36231.883 Hz
FIDRES               0.552855 Hz
AQ                0.9043968 sec
RG                      199.43
DW                    13.800 usec
DE                    18.00 usec
TE                    298.0 K
CNST2           145.0000000
CNST11            1.0000000
D1                2.00000000 sec
D20               0.00689655 sec
TD0                        1
SFO1            150.9178988 MHz
NUC1                      13C
P1                    12.00 usec
P2                    24.00 usec
PLW1             88.22599792 W
SFO2            600.1324005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2              6.76100016 W
PLW12             0.06699187 W

F2 - Processing parameters
SI                    32768
SF              150.9027943 MHz
WDW                      EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



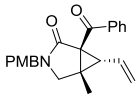

**5c**




Current Data Parameters
NAME JBN413
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180123
Time 17.78 h
INSTRUM spect
PROBHD Z117768_0067 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183398 Hz
AQ 2.7262976 sec
RG 9.7
DW 41.600 usec
DE 18.00 usec
TE 298.0 K
D1 1.00000000 sec
D20 0.00689655 sec
TD0 1
SFO1 600.1333058 MHz
NUC1 1H
P1 9.90 usec
PLW1 8.76100016 W

F2 - Processing parameters
SI 65536
SF 600.1300146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



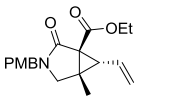

**5c**




Current Data Parameters
NAME JBN413
EXPNO 2
PROCNO 1

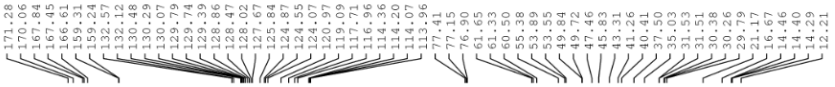
F2 - Acquisition Parameters
Date_ 20180123
Time 18.19 h
INSTRUM spect
PROBHD Z117768_0067 (
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 36231.883 Hz
FIDRES 0.552855 Hz
AQ 0.9043968 sec
RG 199.43
DW 13.800 usec
DE 18.00 usec
TE 298.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 12.00 usec
P2 24.00 usec
PLW1 88.22599792 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 6.76100016 W
PLW12 0.06699187 W

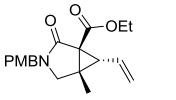
F2 - Processing parameters
SI 32768
SF 150.9027899 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


O
OEt
PMBN

**5d**

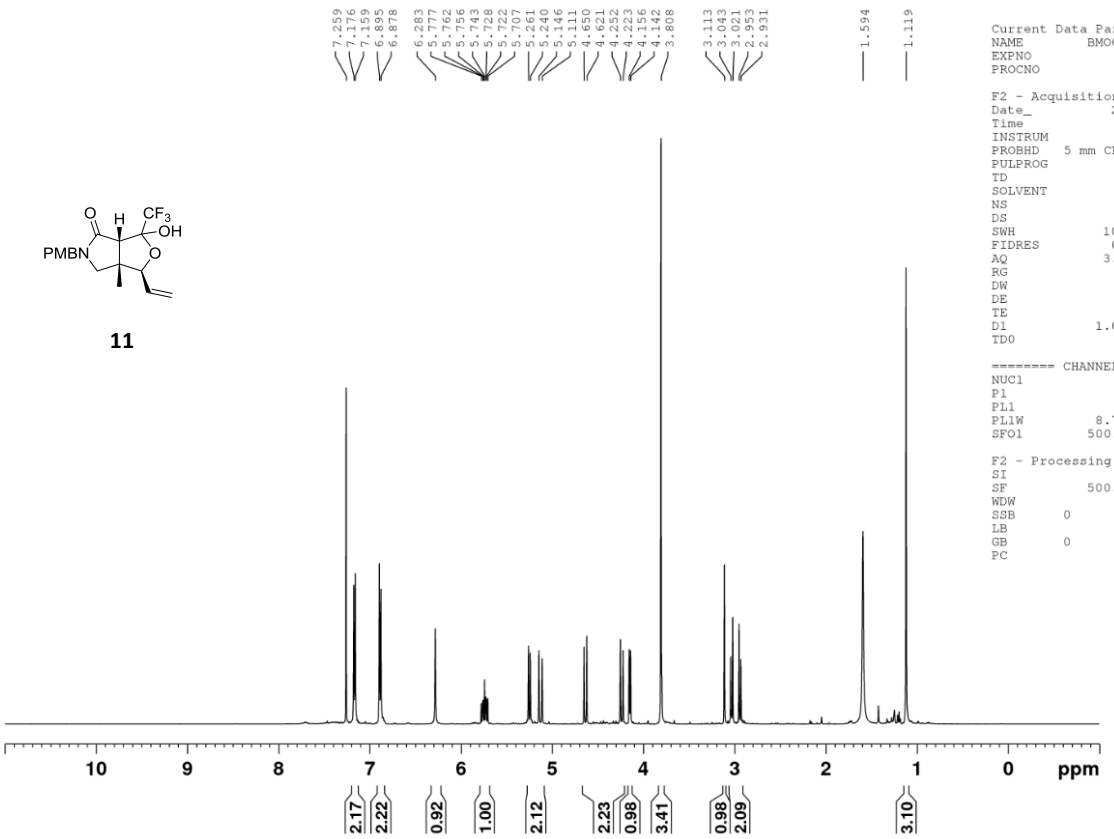

10
9
8
7
6
5
4
3
2
1
0
ppm




O
OEt
PMBN

**5d**


200
180
160
140
120
100
80
60
40
20
0
ppm







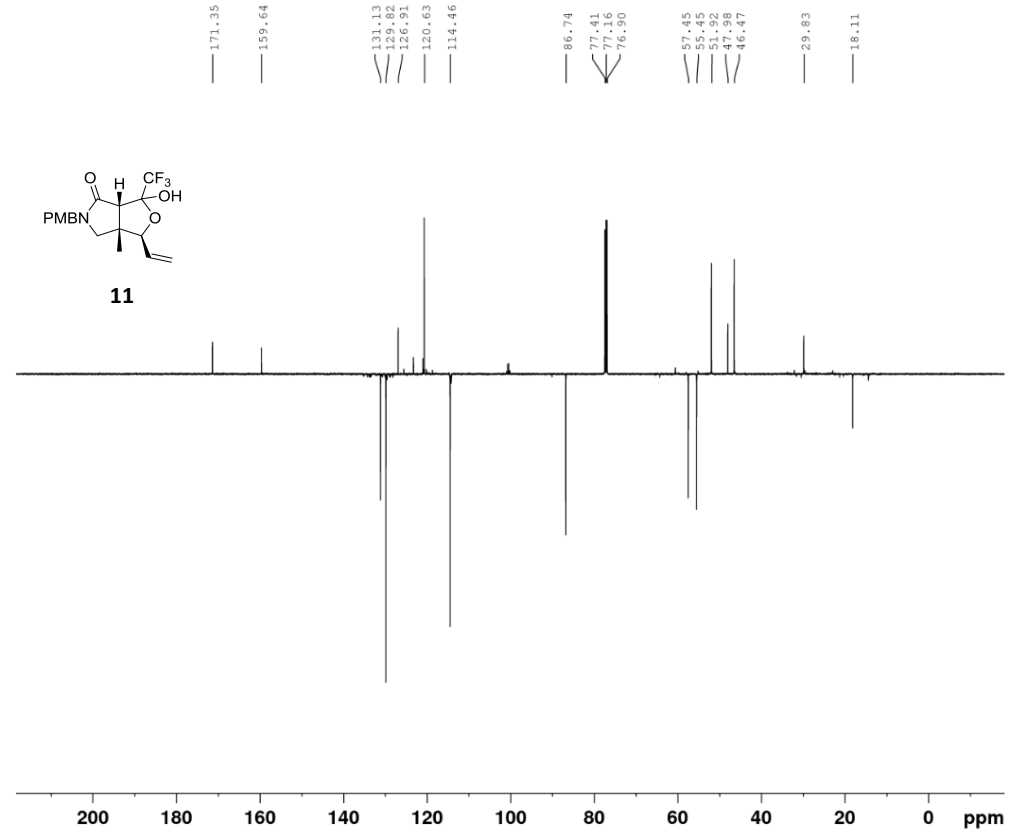
**11**

```
Current Data Parameters
NAME         BM0035-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160812
Time               17.08
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                12.7
DW              48.400 usec
DE               6.50 usec
TE              298.2 K
D1          1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 6.70 usec
PL1                4.00 dB
PL1W         8.72000027 W
SFO1        500.2730894 MHz

F2 - Processing parameters
SI                 32768
SF          500.2700076 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```







**11**

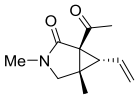
```
Current Data Parameters
NAME          BM0035-3C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20160812
Time               12.28
INSTRUM            spect
PROBHD   5 mm CPTCI 1H-
PULPROG            jmod
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG                2050
DW              16.800 usec
DE               6.50 usec
TE              298.2 K
CNST2       145.0000000
CNST11        1.0000000
D1          2.00000000 sec
D20         0.00689655 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                11.20 usec
P2                22.40 usec
PL1               -2.00 dB
PL1W        88.77790070 W
SFO1       125.8055709 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                4.00 dB
PL12              25.28 dB
PL2W         8.72000027 W
PL12W        0.06494062 W
SFO2        500.2720011 MHz

F2 - Processing parameters
SI                 32768
SF          125.7929781 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```




**5g**




```
Current Data Parameters
NAME                  JBN469
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
Date_              20180124
Time                 17.40 h
INSTRUM              spect
PROBHD    Z117768_0067 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             12019.230 Hz
FIDRES              0.183399 Hz
AQ                2.7262976 sec
RG                     19.7
DW                   41.600 usec
DE                   18.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                     1
SFO1           600.1337058 MHz
NUC1                   1H
P1                    8.00 usec
PLW1            6.76100016 W

F2 - Processing parameters
SI                    65536
SF              600.1300145 MHz
WDW                    EM
SSB         0
LB                    0.30 Hz
GB          0
PC                    1.00
```



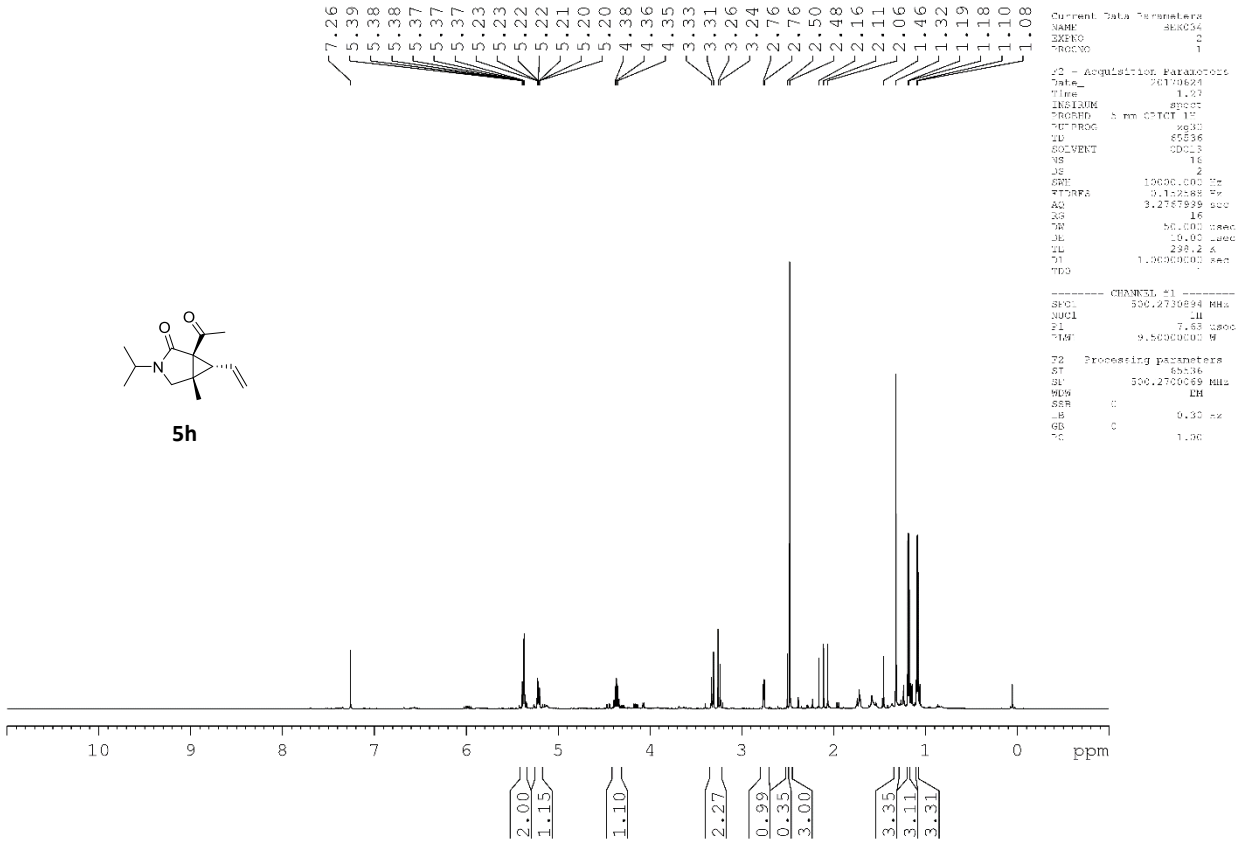

**5g**



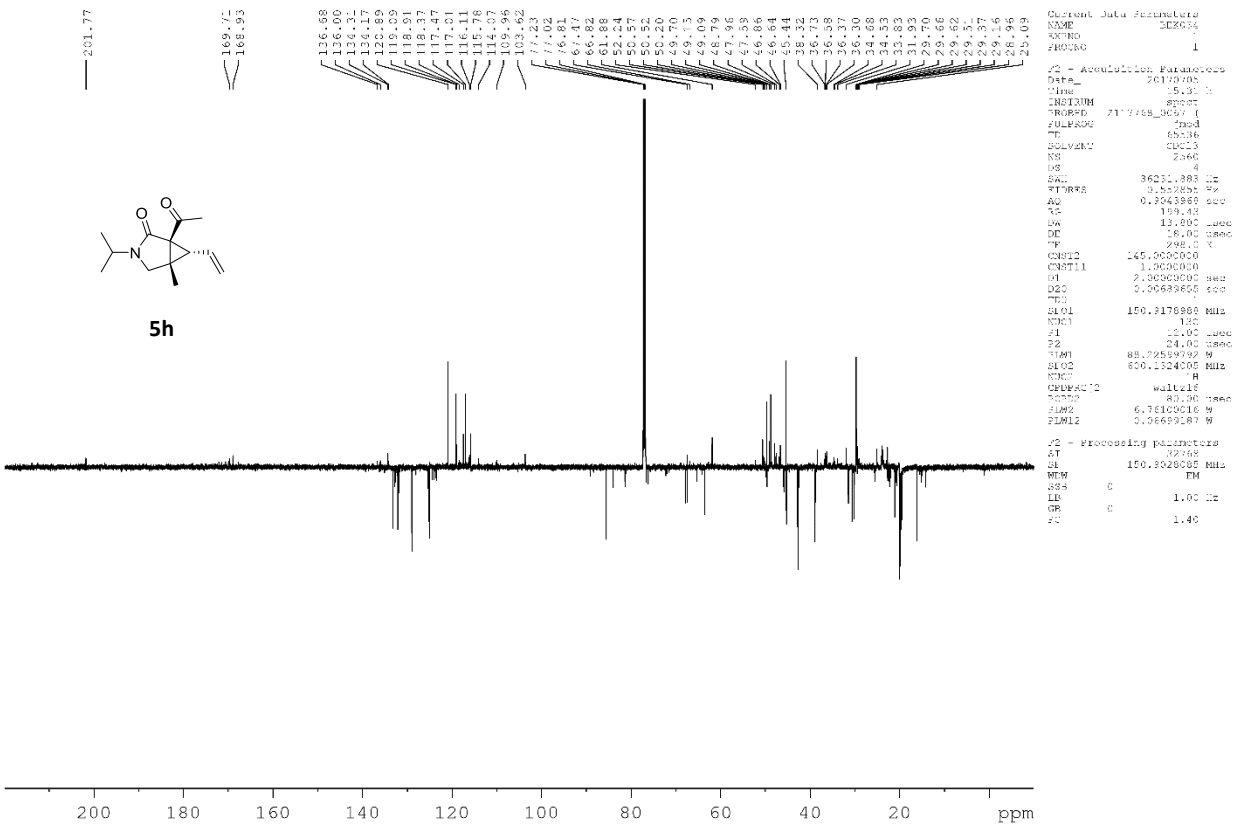

```
Current Data Parameters
NAME                  JBN469
EXPNO                      6
PROCNO                     1

F2 - Acquisition Parameters
Date_              20180124
Time                 19.34 h
INSTRUM              spect
PROBHD    Z117768_0067 (
PULPROG              jmod
TD                  65536
SOLVENT             CDCl3
NS                   2048
DS                      4
SWH             36231.883 Hz
FIDRES              0.552855 Hz
AQ                0.9043968 sec
RG                   199.43
DW                   13.800 usec
DE                   18.00 usec
TE                   298.0 K
CNST2          145.0000000
CNST11           1.0000000
D1               2.00000000 sec
D20              0.00689655 sec
TD0                     1
SFO1           150.9178988 MHz
NUC1                   13C
P1                   12.00 usec
P2                   24.00 usec
PLW1           88.22599792 W
SFO2           600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            6.76100016 W
PLW12           0.06699187 W

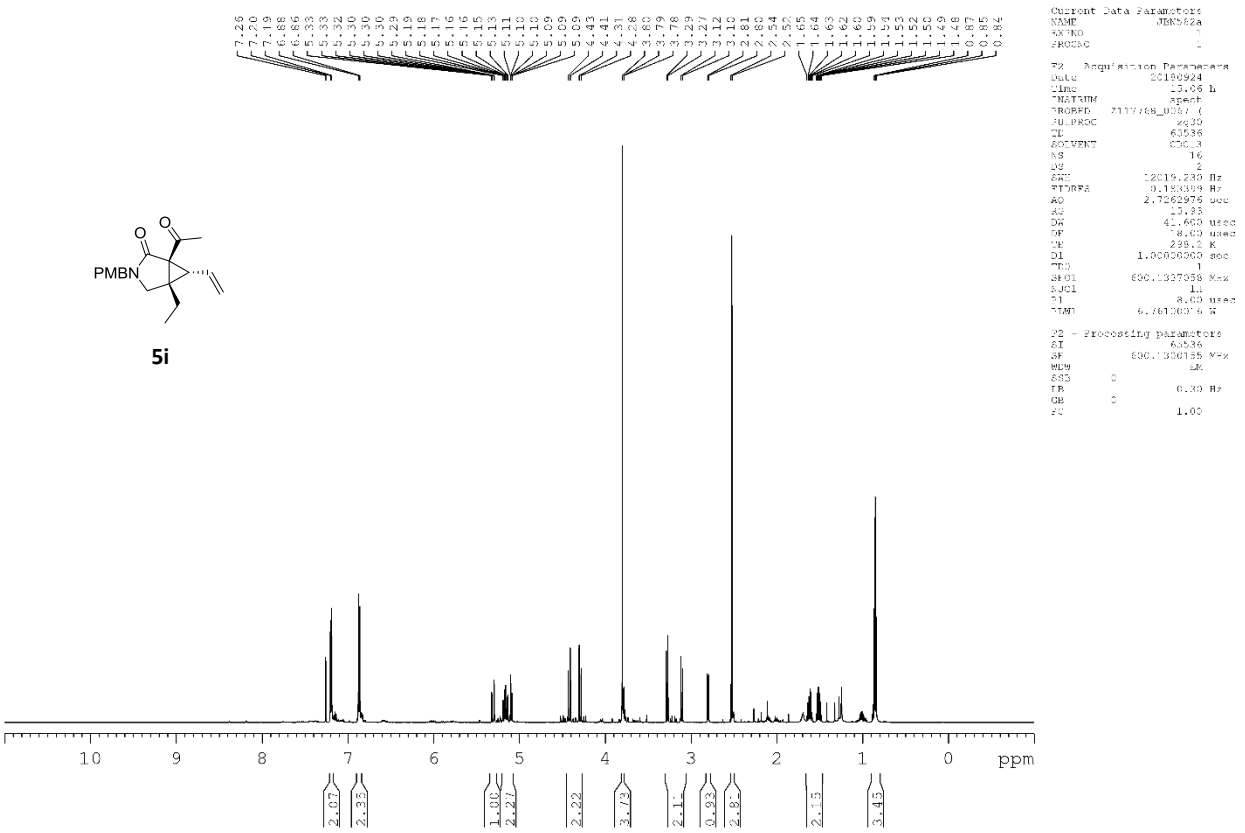
F2 - Processing parameters
SI                    32768
SF              150.9027887 MHz
WDW                    EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```

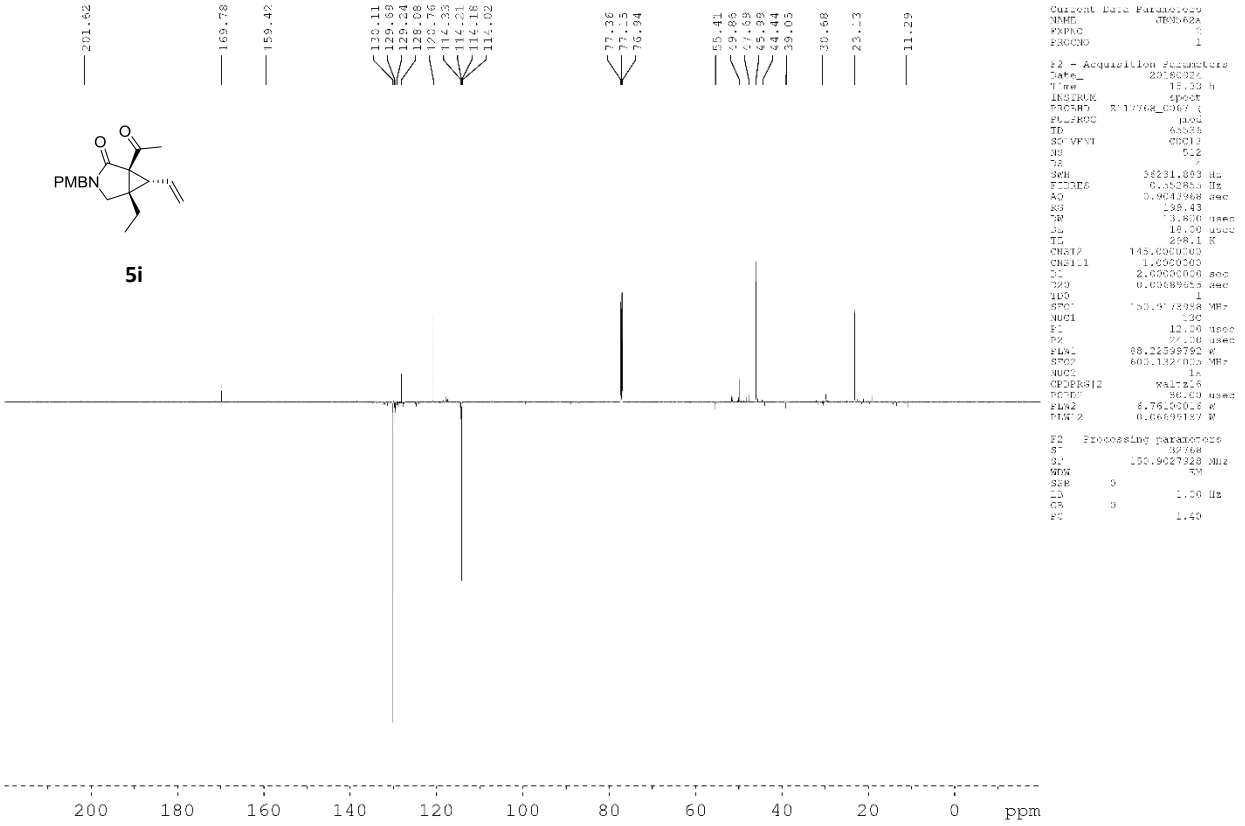


**5h**



**5h**





Current Data Parameters
NAME JMB562a
EXPNO 1
PROCNO 1

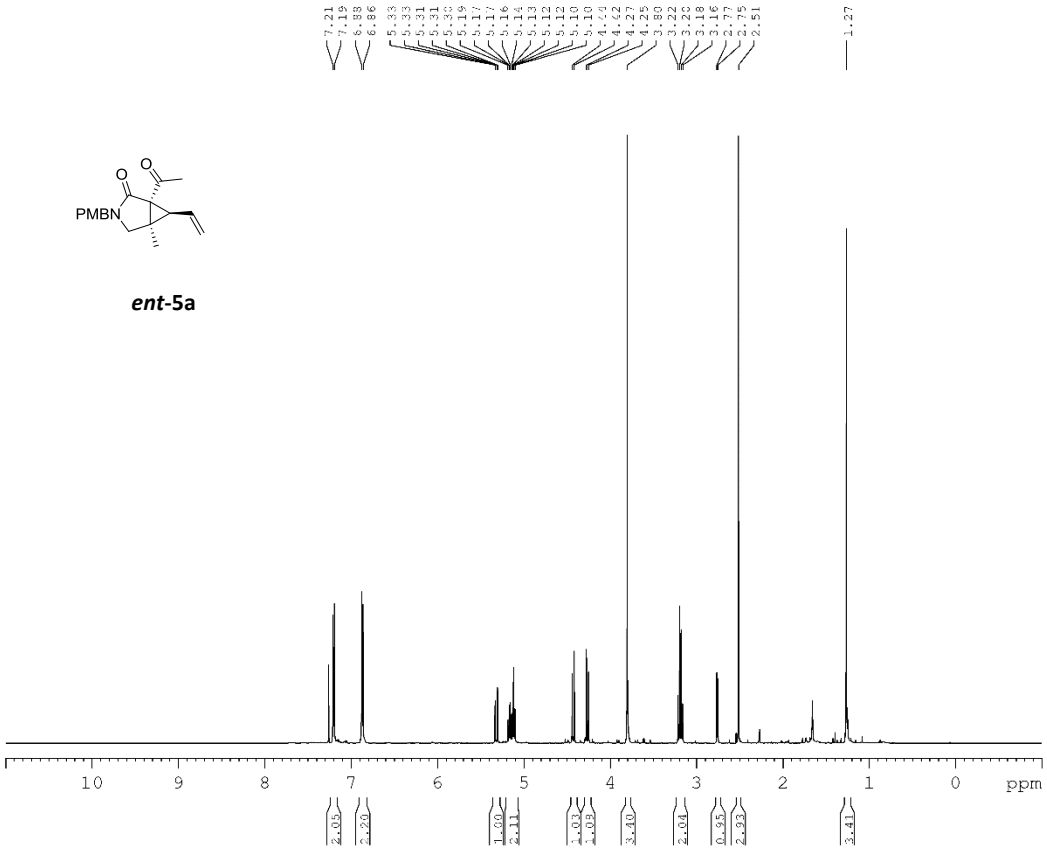
F2 - Acquisition Parameters
Date_ 20180924
Time 15.06 h
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183459 Hz
AQ 2.7262976 sec
RG 15.83
DW 41.600 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P1 8.00 usec
PLW1 6.76100076 W

F2 - Processing parameters
SI 65536
SF 600.1300135 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

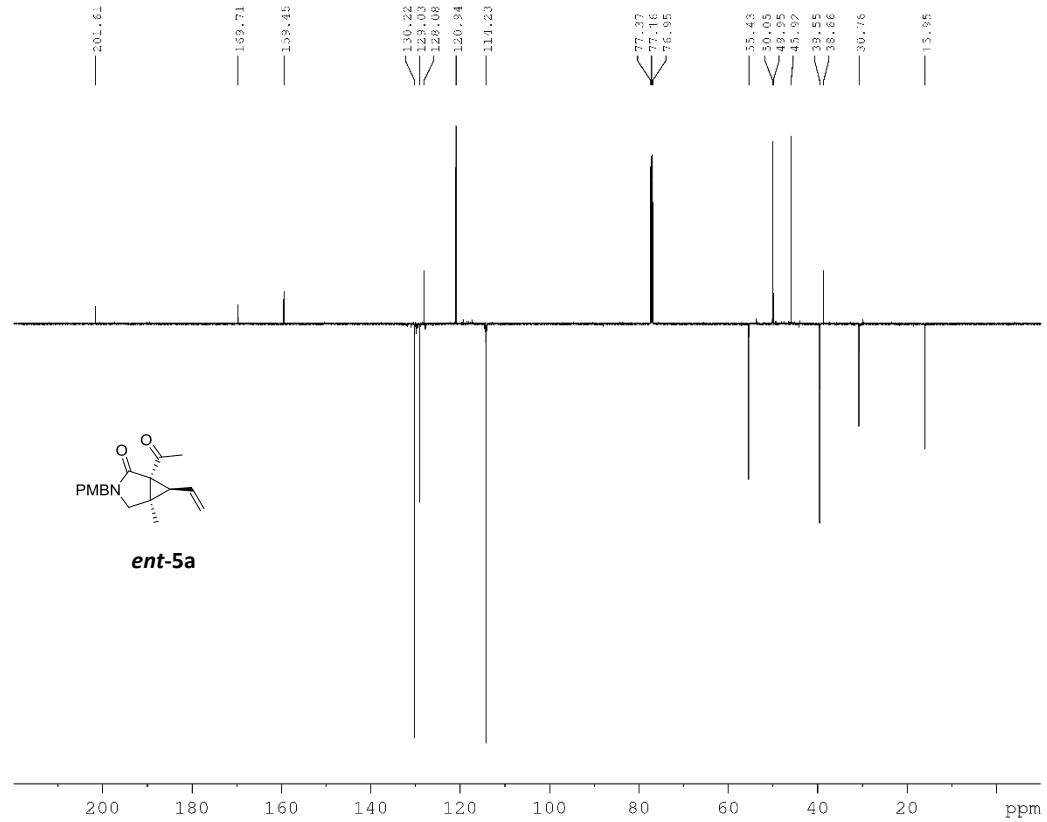
Current Data Parameters
NAME JMB562a
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180924
Time 15.33 h
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 36231.883 Hz
FIDRES 0.552850 Hz
AQ 0.9043968 sec
RG 199.43
DW 13.800 usec
DE 10.00 usec
TE 298.1 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9778998 MHz
NUC1 13C
P1 12.50 usec
P2 27.20 usec
PLW1 88.22598792 W
SFO2 600.1320005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 8.76100018 W
PLW12 0.66699187 W

F2 - Processing parameters
SI 32768
SF 150.9027928 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

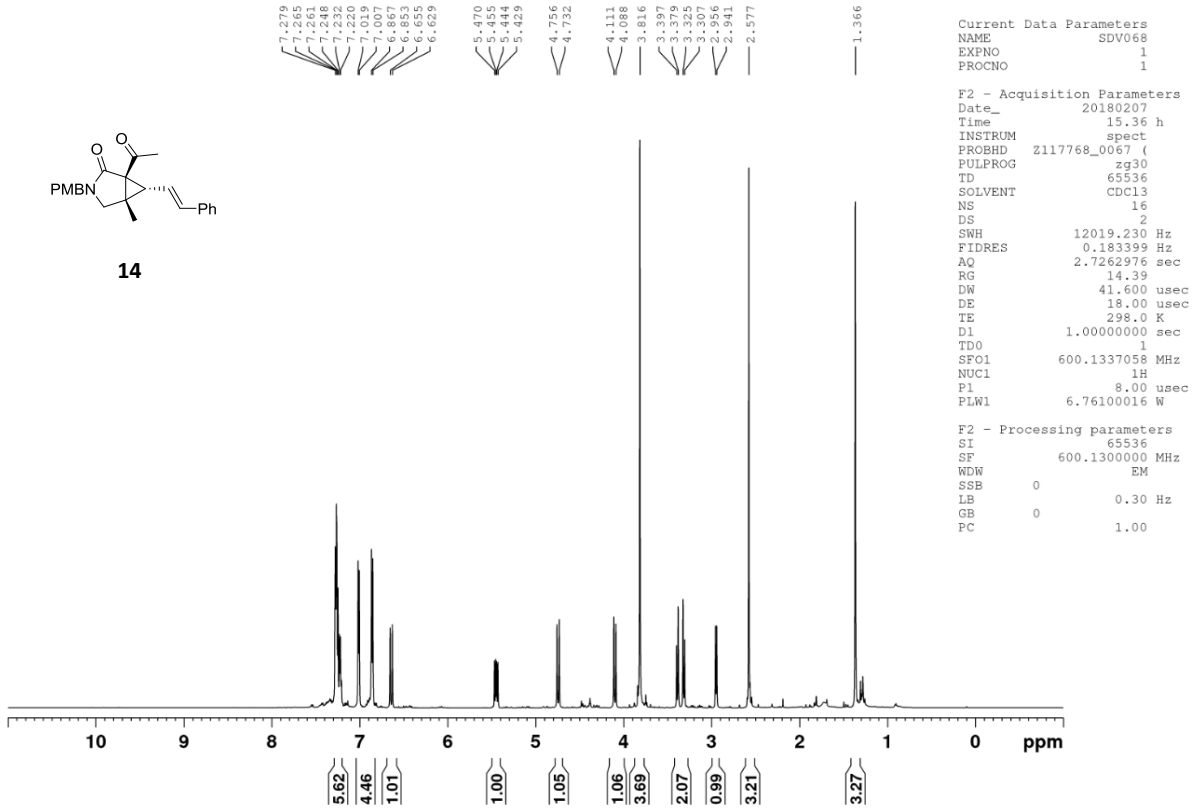

7.21
7.19
6.88
6.86
5.33
5.33
5.31
5.31
5.30
5.19
5.17
5.17
5.16
5.14
5.13
5.12
5.12
5.10
5.10
4.44
4.42
4.27
4.25
3.80
3.22
3.20
3.18
3.16
2.77
2.75
2.51
1.27
PMBN
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
2.20
1.00
2.11
1.03
1.09
3.40
2.04
0.95
2.93
3.41

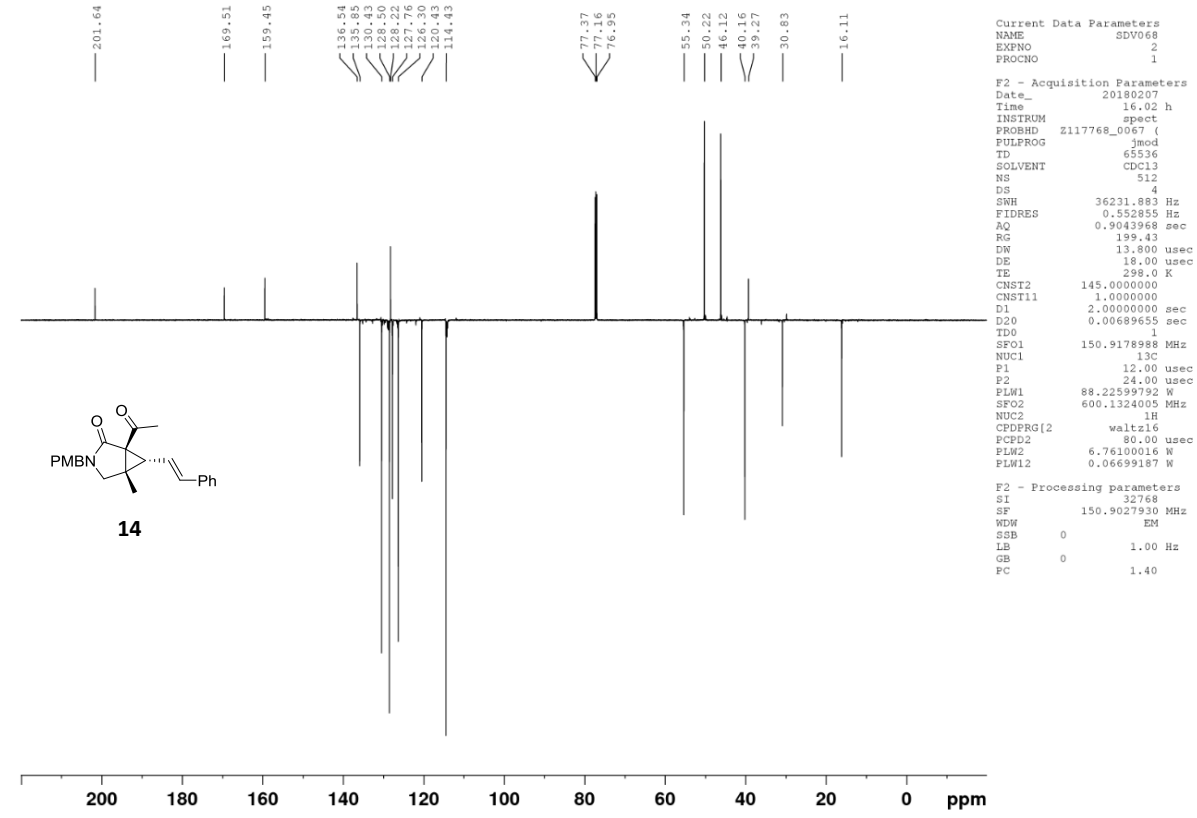
***ent*-5a**

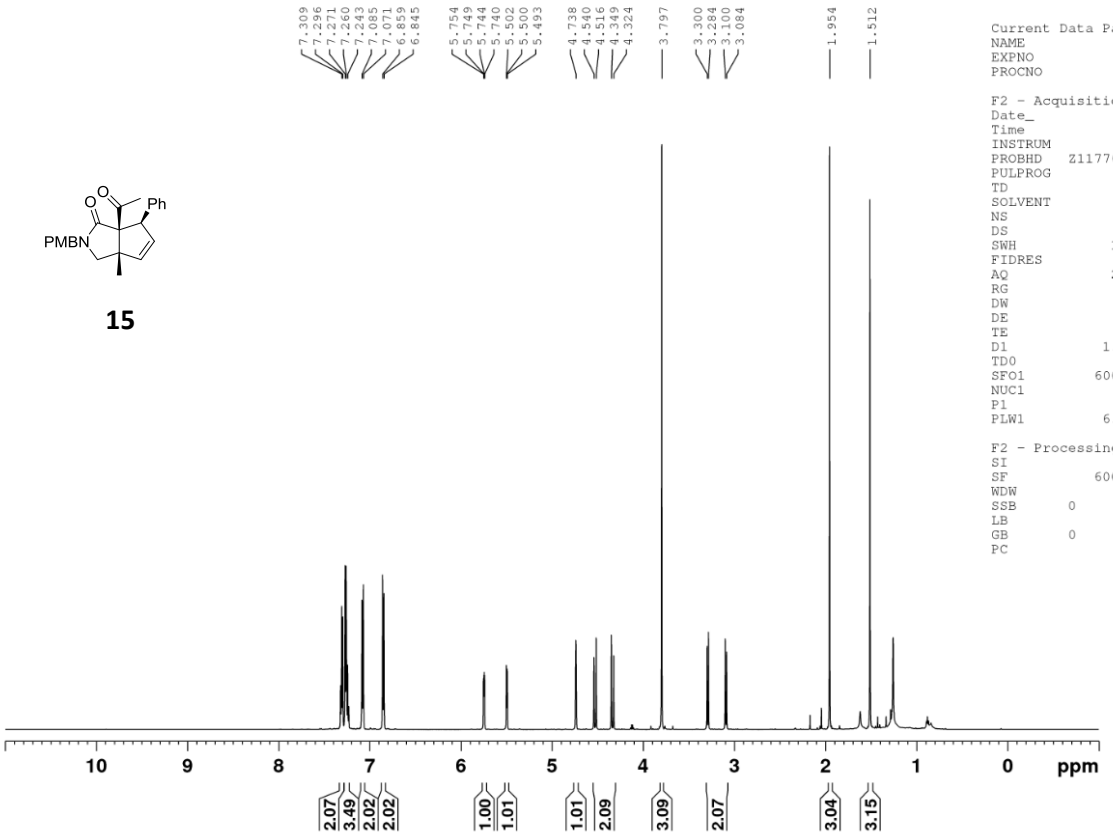

201.61
169.71
168.45
130.22
129.03
128.08
120.94
114.23
77.37
77.16
76.95
35.43
30.05
29.95
29.92
28.55
28.66
30.76
15.95
PMBN
O
O
200
180
160
140
120
100
80
60
40
20
ppm

***ent*-5a**

## Vinylcyclopentane rearrangement







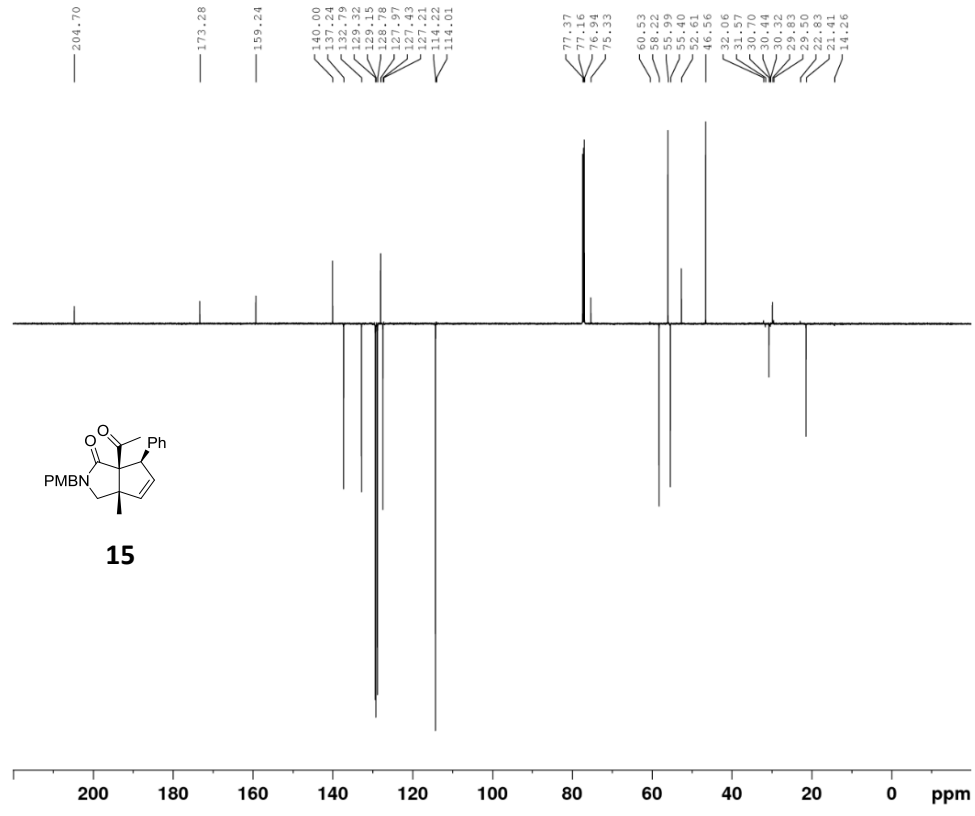


**15**

```
Current Data Parameters
NAME                  SDV075
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20180130
Time                  16.30 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12019.230 Hz
FIDRES               0.183399 Hz
AQ                2.7262976 sec
RG                    15.93
DW                   41.600 usec
DE                   18.00 usec
TE                   298.0 K
D1               1.00000000 sec
TD0                        1
SFO1           600.1337058 MHz
NUC1                      1H
P1                     8.00 usec
PLW1            6.76100016 W

F2 - Processing parameters
SI                    65536
SF             600.1300139 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```







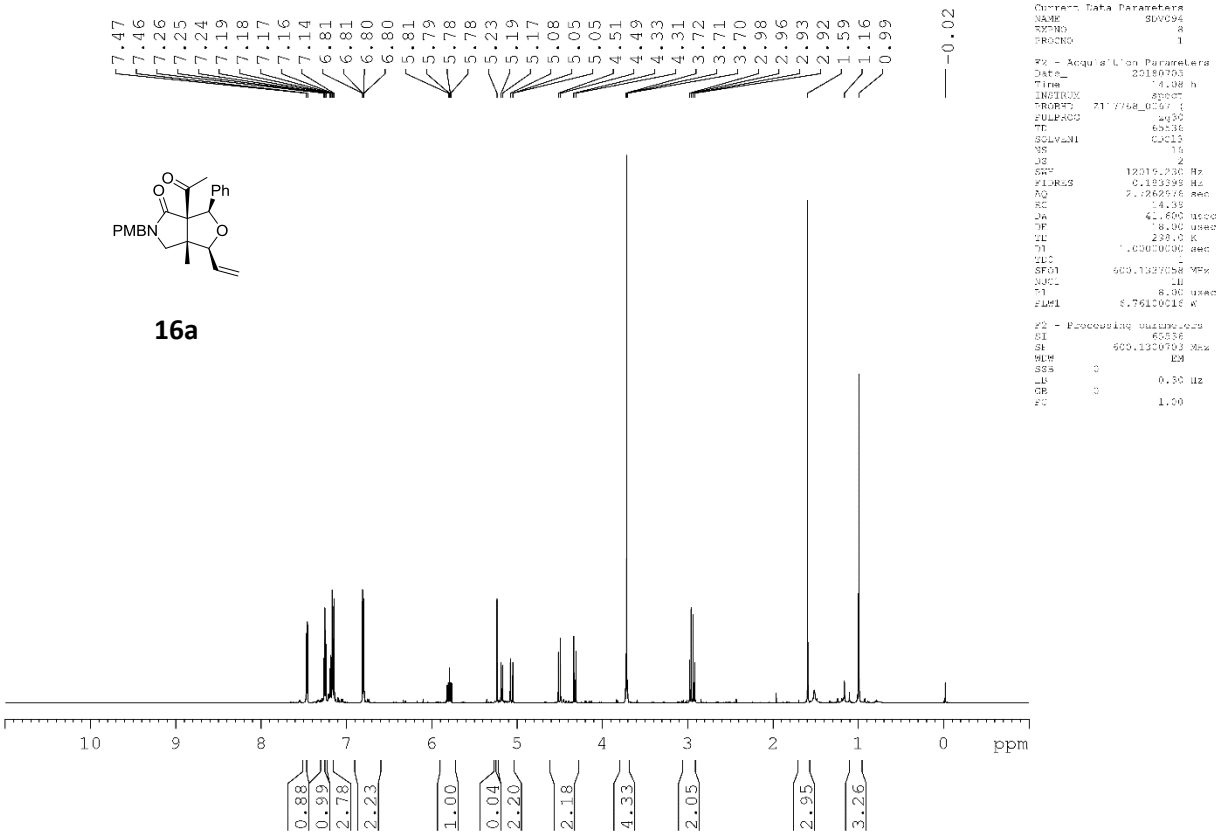
**15**

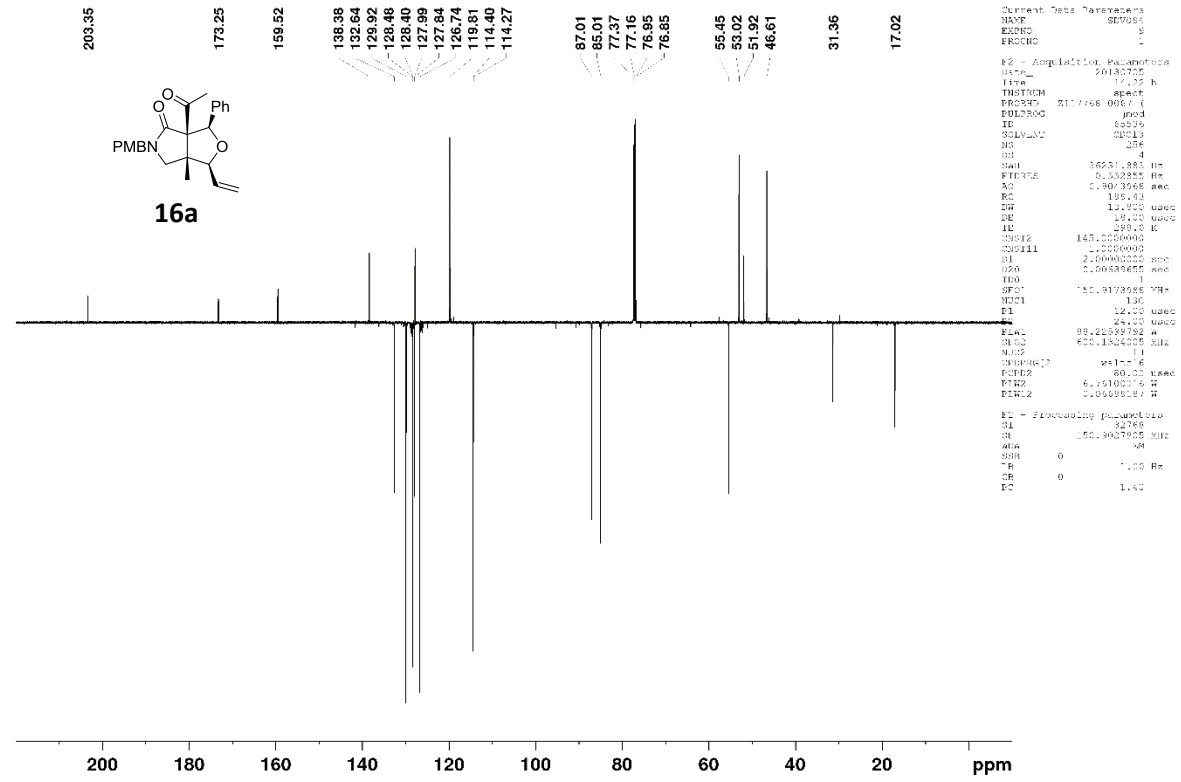
```
Current Data Parameters
NAME                  SDV075
EXPNO                      2
PROCNO                     1

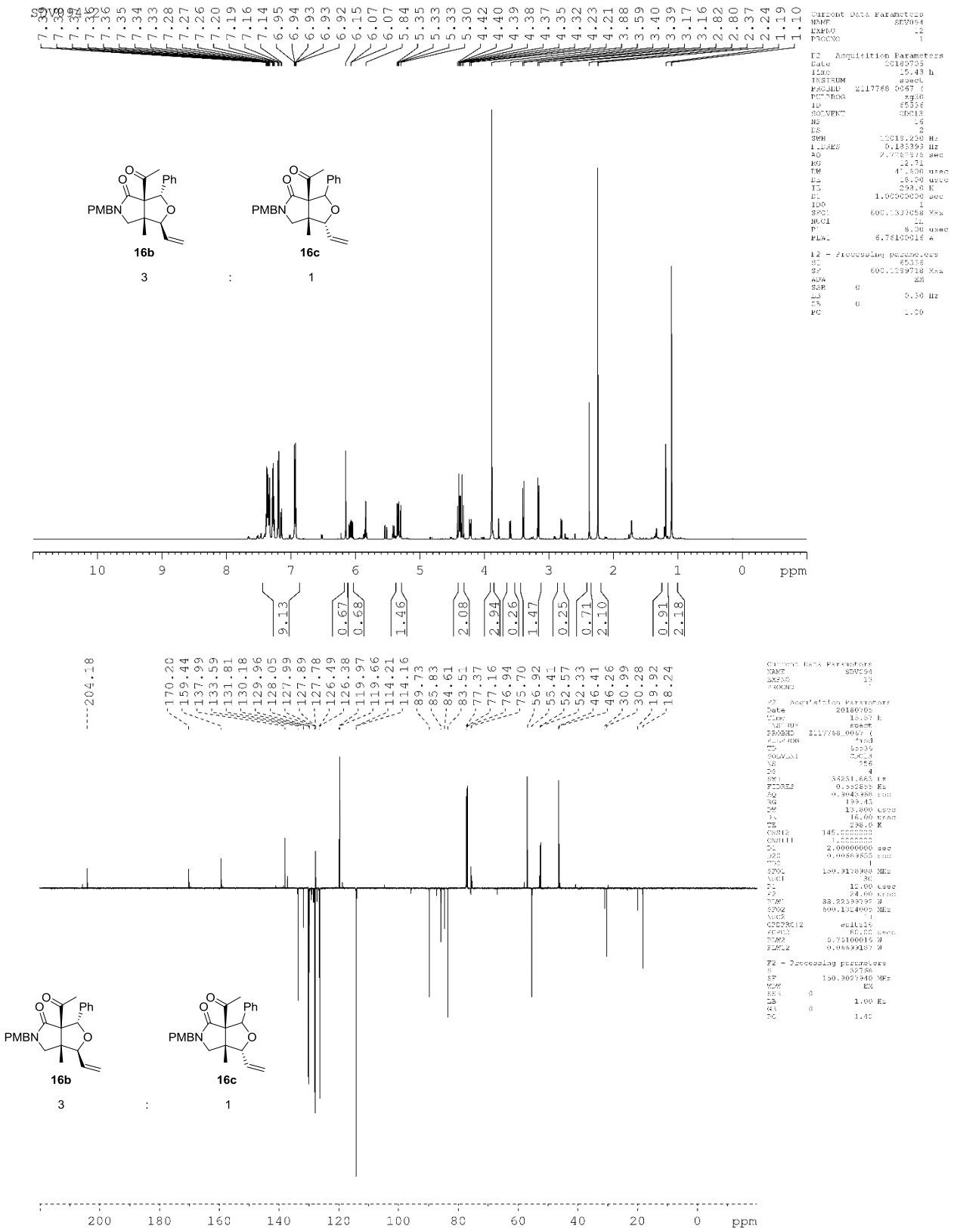
F2 - Acquisition Parameters
Date_               20180130
Time                  16.56 h
INSTRUM                spect
PROBHD    Z117768_0067 (
PULPROG                jmod
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH              36231.883 Hz
FIDRES               0.552855 Hz
AQ                0.9043968 sec
RG                   199.43
DW                   13.800 usec
DE                   18.00 usec
TE                   298.0 K
CNST2           145.0000000
CNST11            1.0000000
D1                2.00000000 sec
D20               0.00689655 sec
TD0                        1
SFO1           150.9178988 MHz
NUC1                      13C
P1                    12.00 usec
P2                    24.00 usec
PLW1           88.22599792 W
SFO2           600.1324005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2            6.76100016 W
PLW12           0.06699187 W

F2 - Processing parameters
SI                    32768
SF             150.9027905 MHz
WDW                      EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

## Vinylcyclopropane cycloaddition




SDV094
7.37 7.36 7.36 7.35 7.34 7.33 7.28 7.27 7.26 7.20 7.19 7.16 7.14 6.95 6.94 6.93 6.93 6.92 6.15 6.07 6.07 5.84 5.35 5.33 5.30 4.42 4.40 4.39 4.38 4.37 4.35 4.32 4.23 4.21 3.88 3.59 3.40 3.39 3.17 3.16 2.82 2.80 2.37 2.24 1.19 1.10
Current Data Parameters
NAME SDV094
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date 20180705
Time 15.43 h
INSTRUM spect
PROBHD 2117768_0067 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183393 Hz
AQ 2.7262976 sec
RG 2.71
DW 41.600 usec
DE 18.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1337058 MHz
NUC1 1H
P1 8.00 usec
PLW1 6.76100016 W
F2 - Processing parameters
SI 65536
SF 600.1299710 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
O
PMBN
16b
16c
3 : 1
10 9 8 7 6 5 4 3 2 1 0 ppm
9.13 0.67 0.68 1.46 2.08 2.94 0.26 1.47 0.25 0.71 2.10 0.91 2.18
204.18 170.20 159.44 137.99 133.59 131.81 130.18 129.96 128.05 127.99 127.89 127.78 126.49 126.38 119.97 119.66 114.21 114.16 89.73 85.83 84.61 83.51 77.37 77.16 76.94 75.70 56.92 55.41 52.57 52.33 46.41 46.26 30.99 30.28 19.92 18.24
Current Data Parameters
NAME SDV094
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date 20180705
Time 16.57 h
INSTRUM spect
PROBHD 2117768_0067 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 54231.663 Hz
FIDRES 0.992895 Hz
AQ 0.9043968 sec
RG 199.45
DW 13.800 usec
DE 18.00 usec
TE 298.0 K
CNST12 145.0000000
CNST13 1.0000000
D1 2.00000000 sec
D20 0.00884858 sec
TD0 1
SFO1 150.9178980 MHz
NUC1 13C
P1 10.00 usec
P2 24.00 usec
PLW1 88.82399597 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 5.76100016 W
PLW12 0.08899187 W
F2 - Processing parameters
SI 32768
SF 150.9027940 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

## References


(1) (a) Sheldrick, G.M., *Acta Cryst.* **2008**, *A64*, 112. (b) Hübschle, C.B.; Sheldrick, G. M.; Dittrich B., *J. Appl. Cryst.* **2011**, *44*, 1281.

(2) Kiyotsuka, Y.; Katayama, Y.; Acharya, H. P.; Hyodo, T.; Kobayashi, Y., *J. Org. Chem.* **2009,** *74*, 1939-1951.

(3) Ikeda, S.; Shibuya, M.; Kanoh, N.; Iwabuchi, Y., *Org. Lett.* **2009,** *11*, 1833-1836.