Supporting Information

Asymmetric Palladium-Catalyzed Umpolung Cyclization of Allylic Acetate-Aldehyde using Formate as a Reductant

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Contents:

General Information

Reactions were carried out in clean, dry glassware under argon atmosphere using high quality solvents. Reagents were purchased at the highest commercial quality and used without further purification. Reactions were monitored by thin layer chromatography separations carried out on 0.2 mm E. Merck silica gel plates (60 F254) using UV light as a visualizing agent and phosphomolybdic acid, *p*-anisaldehyde, or potassium permanganate solutions and heat as developing agents. Preparative TLC was performed on 0.75 mm Wakogel® B-5F PLC plate. ^{1}H-NMR spectra (400 and 600 MHz) and ^{13}C-NMR spectra (100 and 150 MHz) were recorded on JEOL JNM-Al400 and JEOL JNM-ECA600 spectrometers, respectively. Chemical shifts (δ) are given from TMS (0 ppm) as internal standard for ^{1}H-NMR and $^{13}CDCl_3$ (77.0 ppm) for ^{13}C-NMR. The following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet), ddd (double double doublet), br.s (broad singlet), br.d (broad doublet). Mass spectra and high resolution mass spectra were measured on JEOL JMS-DX303 and MS-AX500 (for EI) or Thermo Scientific™ Exactive™ Plus Orbitrap Mass Spectrometer (for ESI), responsively. IR spectra were recorded on a Shimazu JASCO FT/IR-4100. Melting points were measured with a Round Science melting point meter RFS-10 and are uncorrected. Analytical HPLC was performed using Daicel Chiralpak AD-H, OD-H or AS-H. Optical rotations ($[\alpha]_D$) were measured on JASCO P-1010 polarimeter.

Experimental Procedures

Palladium-Catalyzed Umpolung Cyclization of Allylic Acetate-Aldehyde

General procedure for Table 1

To a test tube containing a solution of **13** (1 eq., see Table 1S) in anhydrous MeCN (0.05 M) were added Pd catalyst (10 mol% , $Pd(dppe)_2$, $Pd(PPh_3)_4$, Pd_2dba_3-dppe, $PdCp(\eta^3$-allyl)-dppe, $Pd(OAc)_2$-dppe, $Pd[P(o\text{-tolyl})_3]_2$-dppe, $Pd[P(o\text{-tolyl})_3]_2$-(*S*)-SEGPHOS (**12a**)) and reductant (3 eq., HCO_2H/Et_3N, HCO_2H/Bu_3N, $HSiEt_3$, HCO_2H) under argon. The resulting mixture was sealed with a screw cap and stirred at 50 ℃ (Entries 1, 3-14) or 80 ℃ (Entry 2) for the time described in Table 1. Then concentrated *in vacuo*. The residue was purified by preparative TLC eluting with 1:1 EtOAc/hexane to afford **11a**.

Table 1S

Entry	Pd cat. (mg, mol%)	Ligand (mg, mol%)	Reductant (μL, mmol)	**13** (mg, mmol)	**11a** (mg, mmol, %, %ee)
1	$Pd(dppe)_2$ (45.2, 100)	-	-	**13a**; 19.9, 0.050	5.2, 0.015, 31
2	$Pd(dppe)_2$ (5.0, 10)	-	-	**13a**; 22.3, 0.055	trace
3	$Pd(PPh_3)_4$ (62.7, 100)	-	-	**13a**; 21.8, 0.054	trace
4	$Pd(dppe)_2$ (3.1, 10)	-	HCO_2H/Et_3N (3.9/14.4, 0.10)	**13a**; 13.8, 0.034	5.3, 0.015, 45
5	$Pd(dppe)_2$ (4.2, 10)	-	HCO_2H/Bu_3N (5.2/32.1, 0.14)	**13a**; 18.3, 0.046	7.7, 0.022, 49
6	$Pd(dppe)_2$ (4.0, 10)	-	$HSiEt_3$ (21.2, 0.13)	**13a**; 17.8, 0.044	6.9, 0.020, 45

7	Pd_2dba_3 (2.1, 5)	dppe (1.3, 7.5)	HCO_2H/Bu_3N (5.1/31.9, 0.14)	**13a**; 18.2, 0.045	9.2, 0.027, 59
8	$PdCp(\eta^3\text{-allyl})$ (0.9, 10)	dppe (2.6, 15)	HCO_2H/Bu_3N (4.9/30.5, 0.13)	**13a**; 17.4, 0.043	8.9, 0.026, 60
9	$Pd(OAc)_2$ (0.8, 10)	dppe (2.1, 15)	HCO_2H/Bu_3N (4.1/25.2, 0.11)	**13a**; 14.4, 0.036	8.5, 0.025 69
10	$Pd[P(o\text{-tolyl})_3]_2$ (2.5, 10)	dppe (2.1, 15)	HCO_2H/Bu_3N (4.0/24.7, 0.11)	**13a**; 14.1, 0.035	9.4, 0.027, 78
11	$Pd[P(o\text{-tolyl})_3]_2$ (3.3, 10)	-	HCO_2H/Bu_3N (4.0/25.1, 0.11)	**13a**; 14.3, 0.036	0, 0, 0
12	$Pd[P(o\text{-tolyl})_3]_2$ (4.2, 10)	(*S*)-SEGPHOS (5.4, 15)	HCO_2H/Bu_3N (6.7/44.2, 0.18)	**13a**; 23.7, 0.059	17.7, 0.052, 86, 95
13	$Pd[P(o\text{-tolyl})_3]_2$ (2.0, 10)	(*S*)-SEGPHOS (5.4, 15)	HCO_2H (1.1, 0.028)	**13b**; 12.2, 0.028	6.8, 0.020, 70, 90
14	$Pd[P(o\text{-tolyl})_3]_2$ (2.2, 10)	(*S*)-SEGPHOS (2.9, 15)	-	**13c**; 12.1, 0.031	5.9, 0.017, 60, 91

General procedure for the Table 2

To a test tube containing a solution of **13** (1 eq., see Table 2S) in anhydrous MeCN (0.05 M) were added $Pd[P(o\text{-tolyl})_3]_2$ (10 mol%), Ligand (15 mol%, (*S*)-SEGPHOS, (*S*)-DM-SEGPHOS), and HCO_2H-Bu_3N (3 eq.) or HCO_2H (1 eq.) under argon. The resulting mixture was sealed with a screw cap and stirred at 50 °C (Entries 1-6, 9-12) or 80 °C (Entries 7, 8) for the time described in Table 2. Then concentrated *in vacuo*. The residue was purified by preparative TLC to afford **11**. The corresponding racemate was also prepared by the same procedure using dppe as a

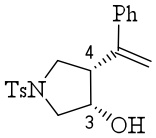
ligand in place of SEGPHOS.

Table 2S

Entry	**13** (mg, mmol)	Pd (mg, mol%)	Ligand (mg, mol%)	Reductant (μl, mmol)	**11** (mg, mmol, %, %ee)
1	**(±)-13d**; 21.1, 0.061	4.3, 10	(*S*)-SEGPHOS (5.6, 15)	HCO_2H/Bu_3N (6.9/45.7, 0.182)	**(3*S*, 4*S*)-11d**; 8.8, 0.030 50, 90
2	**(±)-13d**; 15.2, 0.044	3.1, 10	(*S*)-DM-SEGPHOS (4.7, 15)	HCO_2H-Bu_3N (4.9/32.8, 0.131)	**(3*S*, 4*S*)-11d**; 10.3, 0.033 75, 90
3	**(±)-13e**; 15.6, 0.063	4.5, 10	(*S*)-DM-SEGPHOS (6.8, 15)	HCO_2H-Bu_3N (7.1/47.1, 0.188)	**(3*S*, 4*S*)-11e**; 8.6, 0.045, 72, 97
4	**(±)-13f**; 11.5, 0.024	1.7, 10	(*S*)-DM-SEGPHOS (2.6, 15)	HCO_2H-Bu_3N (2.7/17.7, 0.071)	**(1*R*, 2*R*)-11f**; 7.1, 0.017 70, 93 **(1*R*, 2*S*)-11f'**; 2.9, 0.007 29, 94
5	**(*Z*)-13f'**; 12.7, 0.027	2.0, 10	(*S*)-DM-SEGPHOS (3.0, 15)	HCO_2H-Bu_3N (3.1/20.3, 0.082)	**(1*R*, 2*R*)-11f**; 5.7, 0.013, 49, 97 **(1*R*, 2*S*)-11f'**; 1.3, 0.003, 11, 76

6	**(*E*)-13f'**; 16.3, 0.033	2.4, 10	(*S*)-DM-SEGPHOS (3.6, 15)	HCO_2H-Bu_3N (3.8/22.9, 0.100)	**(1*R*, 2*R*)-11f**; 3.3, 0.008 23, 71 **(1*R*, 2*S*)-11f'**; 7.8, 0.018 54, 99
7	**(±)-13g**; 24.3, 0.116	8.3, 10	(*S*)-DM-SEGPHOS (12.5, 15)	HCO_2H-Bu_3N (13.1/81.4, 0.347)	**(1*R*, 5*R*)-11g**; 10.1, 0.066 57, 86
8	**(±)-13h**; 50.0, 0.223	15.9, 10	(*S*)-DM-SEGPHOS (24.2, 15)	HCO_2H-Bu_3N (25.2/157, 0.669)	**(1*R*, 5*R*)-11h**; 28.6 0.172 77, 91
9	**(±)-13i**; 14.1, 0.045	3.2, 10	(*S*)-DM-SEGPHOS (4.9, 15)	HCO_2H (1.7, 0.045)	**(3*S*, 4*S*)-11i** 7.5, 0.028, 62, 69 **(3*S**, 4*R**)-11i'**; 1.9, 0.007, 16, 60
10	**(±)-13j**; 17.0, 0.052	3.7, 10	(*S*)-SEGPHOS (4.8, 15)	HCO_2H (2.0, 0.052)	**(3*S*, 4*S*)-11j**; 12.7, 0.045, 86, 76
11	**(±)-13k**; 11.0, 0.029	2.1, 10	(*S*)-DM-SEGPHOS (3.1, 15)	HCO_2H (1.1, 0.029)	**(3*S*, 4*S*)-11k**; 4.9, 0.015, 51, 88
12	**13l (*E*:*Z*=1:2.5)**; 8.3, 0.023	1.7, 10	(*S*)-DM-SEGPHOS (2.5, 15)	HCO_2H-Bu_3N (2.6/16.0, 0.070)	**(3*S*, 4*S*)-11l**; 4.5, 0.015, 64, 87

(3*S*,4*S*)-1-[(4-Methylphenyl)sulfonyl]-4-(1-phenylethenyl)-3-pyrrolidinol (11a)[1)]



Yellow oil.

R_f = 0.53 (1:4 EtOAc/toluene).

IR ν (neat, cm^{-1}): 3515, 2948, 1339, 1161.

^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, 2H, *J* = 7.6 Hz), 7.35-7.27 (m, 7H), 5.46 (s, 1H), 5.06 (s, 1H), 4.18 (m, 1H), 3.75 (dd, 1H, *J* = 8.4, 8.0 Hz), 3.62 (dd, 1H, *J* = 11.4, 3.6 Hz), 3.42-3.37 (m, 2H), 3.30 (m, 1H), 2.44 (s, 3H), 1.33 (br.s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 143.2, 140.5, 134.0, 129.7, 128.7, 128.2, 127.5, 126.1, 116.1, 70.4, 55.8, 48.7, 48.5, 21.5.

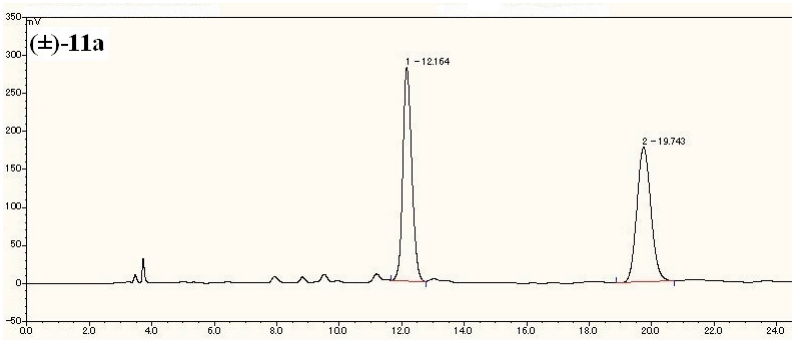
LRMS (EI) m/z (relative intensity): 343 $[M]^+$ (42), 299 (11), 279 (15), 226 (10), 188 (100), 130 (25).

HRMS (EI, $[M]^+$]): calcd for $C_{19}H_{21}NO_3S$, 343.1242; found, 343.1248.

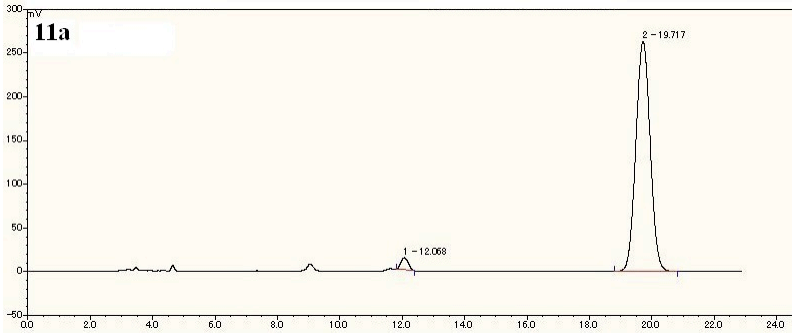
$[\alpha]^{24}_D$ = +23.1 (*c* 1.05 in $CHCl_3$).

Chiral HPLC: (Daicel Chiralpak AD-H, *i*-propanol/hexane = 20:80, 1.0 mL/min, λ = 254 nm): t_R(3*R*, 4*R*) = 12.3 min (minor enantiomer), t_R(3*S*, 4*S*) = 19.9 min (major enantiomer).

HPLC chromatographs of **11a**

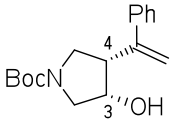


Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	12.16	280.482	92.564	50.11
2	19.74	176.853	92.151	49.89



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	12.07	14.071	3.875	2.71
2	19.72	262.730	139.035	97.29

(3*S*, 4*S*)-*tert*-Butyl 3-hydroxy-4-(1-phenylethenyl)pyrrolidine-1-carboxylate (11d)



White solid.

mp = 119-121 °C

IR ν (neat, cm^{-1}): 3423, 2976, 1679, 1418, 1173, 1133, 894, 777, 700.

^{1}H NMR (400 MHz, $CDCl_3$) mixture of rotamers: δ 7.37-7.29 (m, 5H), 5.51 (s, 1H), 5.21 (s, 0.5H), 5.20 (s, 0.5H), 4.20 (s, 1H), 3.78 (dd, 0.5H, *J* = 8.0, 7.6 Hz), 3.71 (dd, 0.5H, *J* = 10.0, 8.0 Hz), 3.61-3.51 (m. 3H), 3.38-3.33 (m, 1H), 1.66 (s, 1H), 1.47 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) mixture of rotamers: δ 154.6, 144.0, 143.9, 141.0, 128.6, 128.0, 126.2, 116.2, 115.8, 79.4, 70.7, 69.9, 54.1, 53.8, 48.7, 48.0, 46.7, 46.2, 28.5.

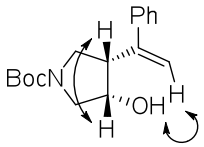
LRMS (EI) m/z (relative intensity): 289 $[M]^+$ (4), 233 (100), 215 (19).

HRMS (EI, $[M]^+$]): calcd for $C_{17}H_{23}NO_3$, 289.1678; found, 289.1672.

$[\alpha]^{24}_D$ = +30.8 (*c* 1.01 in CHCl3).

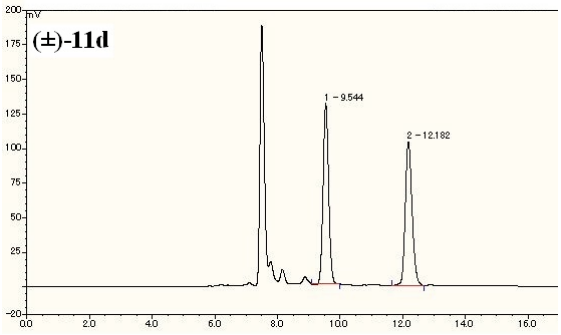
Chiral HPLC: (Daicel Chiralpak AD-H, *i*-propanol/hexane =20:80, 0.5 mL/min, λ = 254 nm): t_R(3*R*, 4*R*) = 9.4 min (minor enantiomer), t_R(3*S*, 4*S*) = 12.1 min (major enantiomer).

The relative stereochemistry was determined by NOESY correlation as shown below.

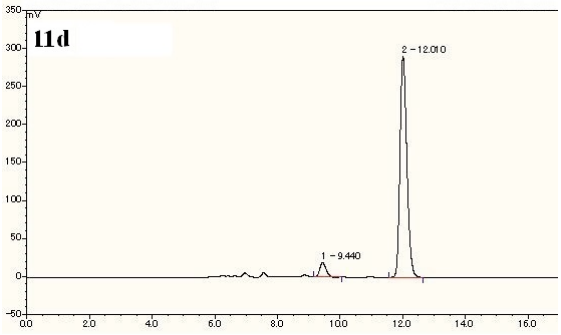


NOESY correlation of **11d**

HPLC chromatographs of **11d**



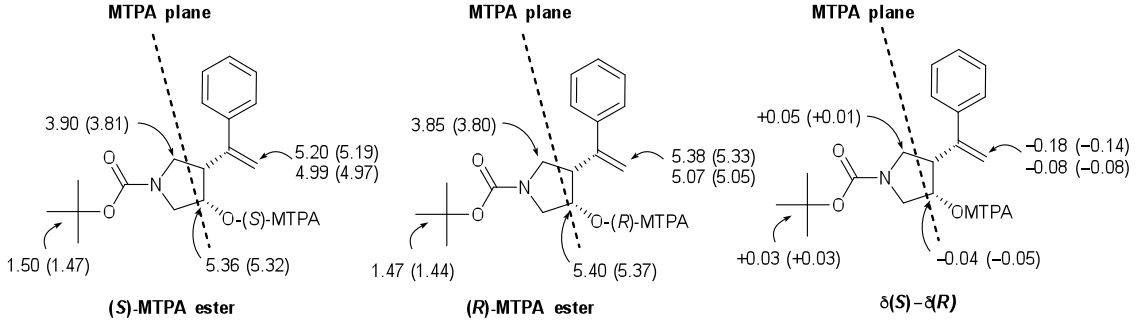
Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	9.54	130.26	26.634	50.33
2	12.18	104.011	26.282	49.67



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	9.44	18.894	4.134	5.29
2	12.01	290.960	73.971	94.71

Determination of the absolute configurations of 11d

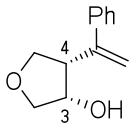
11d was converted into both (*R*)- and (*S*)-MTPA esters ((*R*)- or (*S*)-Mosher's acid, DCC, DMAP, CH_2Cl_2) and then the absolute configurations were determined by Mosher's ester analysis as (3*S*, 4*S*).[2)]



(*R*)-MTPA-(3*S*,4*S*)-**11d**: ^{1}H NMR (600 M Hz, $CDCl_3$): mixture of rotamers δ 7.43-7.35 (m, 10H), 5.40 (5.37) (m, 1H), 5.38 (5.33) (s, 1H), 5.07 (5.05) (s, 1H), 3.85 (3.80) (m, 1H), 3.72-3.65 (m, 1H), 3.60-3.46 (m, 3H), 3.40 (3.42) (s, 3H), 1.47 (1.44) (s, 9H).

(*S*)-MTPA-(3*S*,4*S*)-**11d**: ^{1}H NMR (600 M Hz, $CDCl_3$): mixture of rotamers δ 7.43-7.35 (m, 10H), 5.36 (5.32) (m, 1H), 5.20 (5.19) (s, 1H), 4.99 (4.97) (s, 1H), 3.90 (3.81) (dd, 1H, *J* = 9.6, 7.8 Hz), 3.74-3.57 (m, 3H), 3.50 (m, 1H), 3.44 (s, 3H), 1.50 (1.47) (s, 9H).

(3*S*, 4*S*)-4-(1-Phenylethenyl)oxolan-3-ol (11e)



Yellow oil

IR ν (neat, cm^{-1}): 3421, 2926, 1071, 906, 777, 701.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.26 (m, 5H), 5.54 (s, 1H), 5.13 (s, 1H), 4.31 (m, 1H), 4.13 (dd, 2H, *J* = 8.0, 8.0 Hz), 4.08 (dd, 1H, *J* = 10.0, 4.0 Hz), 3.99 (dd, 1H, *J* = 10.4, 8.0 Hz), 3.89 (dd, 1H, *J* = 10.0, 1.2 Hz), 3.39 (m, 1H), 1.68 (d, 1H, *J* = 2.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.4, 128.6, 128.0, 126.1, 115.9, 75.8, 71.5, 69.2, 49.8.

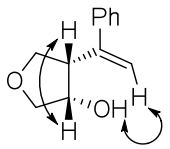
LRMS (EI) m/z (relative intensity): 190 $[M]^+$ (3), 172 (5), 159 (13), 131 (100).

HRMS (EI, $[M]^+$]): calcd for $C_{12}H_{14}O_2$, 190.0994; found, 190.0979.

$[\alpha]^{24}_D$ = +6.76 (*c* 0.80 in $CHCl_3$).

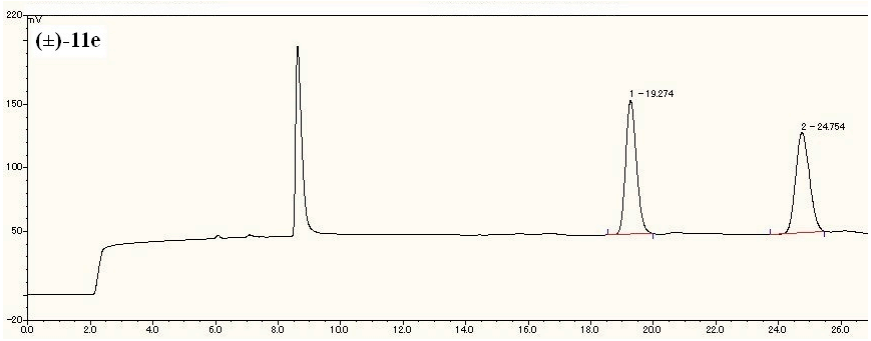
Chiral HPLC: (Daicel Chiralpak OD-H, *i*-propanol/hexane =1:10, 1.0 mL/min, λ = 254 nm): t_R(3*R*, 4*R*) = 19.3 min (minor enantiomer), t_R(3*S*, 4*S*) = 24.9 min (major enantiomer).

The relative stereochemistry was determined by NOESY correlation as shown below.

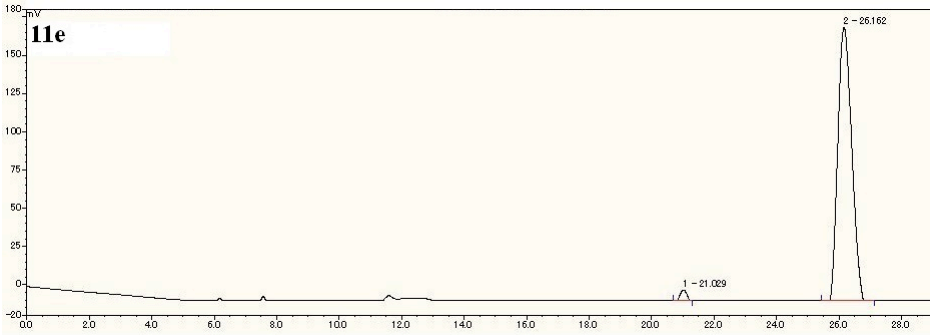


NOESY correlation of **11e**

HPLC chromatographs of **11e**



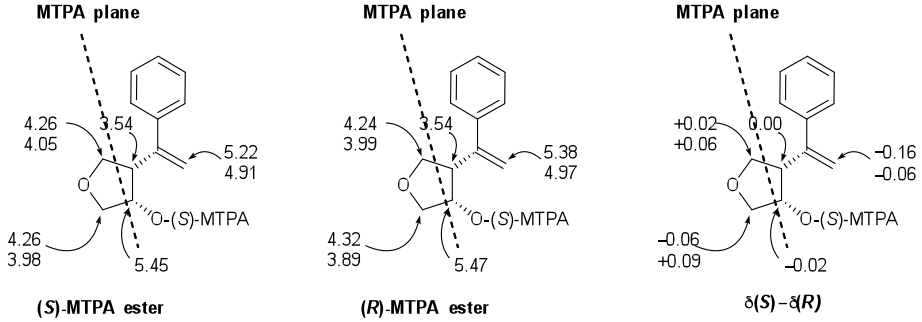
Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	19.27	105.214	42.328	51.40
2	24.75	78.592	40.026	48.60



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	21.03	6.521	1.475	1.59
2	26.16	178.224	91.135	98.41

Determination of the absolute configurations of 11e

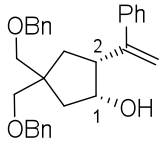
11e was converted into both (*R*)- and (*S*)-MTPA esters ((*R*)- or (*S*)-Mosher's acid, DCC, DMAP, CH_2Cl_2) and then the absolute configurations were determined by Mosher's ester analysis as (3*S*, 4*S*).[2)]



(*R*)-MTPA-(3*S*,4*S*)-**11e**: ^{1}H NMR (600 M Hz, $CDCl_3$): δ 7.39-7.38 (m, 1H), 7.34-7.31 (m, 9H), 5.47 (dd, 1H, *J* = 4.2, 4.2 Hz), 5.38 (s, 1H), 4.97 (s, 1H), 4.32 (dd, 1H, *J* = 11.4, 4.2 Hz), 4.24 (dd, 1H, *J* = 7.8, 7.8 Hz), 3.99 (dd, 1H, *J* = 11.4, 7.8 Hz), 3.89 (d, 1H, *J* = 11.4 Hz), 3.56-3.52 (m, 1H), 3.41 (s, 3H).

(*S*)-MTPA-(3*S*,4*S*)-**11e**: ^{1}H NMR (600 M Hz, $CDCl_3$): δ 7.39 (m, 3H), 7.36-7.32 (m, 2H), 7.26 (m, 3H), 7.19-7.17 (m, 2H), 5.45 (dd, 1H, *J* = 4.2, 4.2 Hz), 5.22 (d, 1H, *J* =1.2 Hz), 4.91 (d, 1H, *J* =1.2 Hz), 4.28-4.26 (m, 2H), 4.05 (dd, 1H, *J* = 11.4, 7.8 Hz), 3.98 (d, 1H, *J* = 11.4 Hz), 3.54 (m, 1H), 3.45 (s, 3H).

(1*R*, 2*R*)-4,4-Bis[(benzyloxy)methyl]-2-(1-phenylethenyl)cyclopentan-1-ol (11f)



Yellow oil

IR ν (neat, cm^{-1}): 3467, 3029, 2856, 1454, 1094, 735, 698.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.22 (m, 15H), 5.35 (s, 1H), 5.15 (s, 1H), 4.61 (d, 1H, *J* = 10.8 Hz), 4.54 (d, 1H, *J* = 10.8 Hz), 4.51 (s, 2H), 4.01 (m, 1H), 3.47 (s, 2H), 3.36 (s, 2H), 3.08 (m, 1H), 2.69 (d, 1H, *J* = 7.2 Hz), 2.02 (dd, 1H, *J* = 7.2, 6.0 Hz), 1.86-1.75 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ147.7, 142.6, 138.5, 138.0, 128.4, 128.3, 128.2, 127.7, 127.6, 127.5, 127.4, 127.2, 126.4, 114.1, 75.8, 75.6, 73.5, 73.3, 73.3, 50.1, 45.7, 41.5, 33.0.

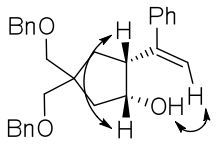
LRMS (EI) m/z (relative intensity): 428 $[M]^+$ (5), 410 (3), 320 (25), 319 (43).

HRMS (EI, $[M]^+$]): calcd for $C_{29}H_{32}O_3$, 428.2351; found, 428.2341.

$[\alpha]^{26}_D$ = +22.0 (*c* 0.98 in $CHCl_3$).

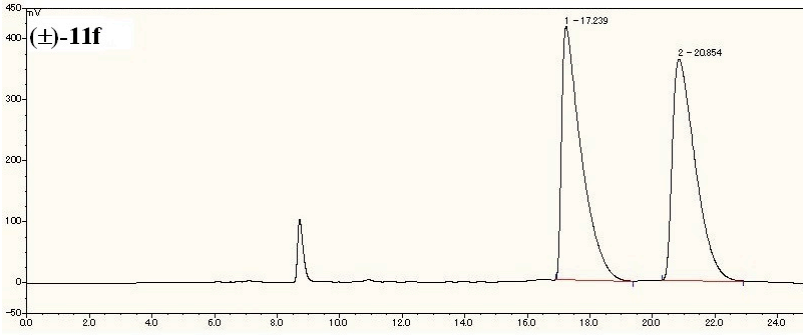
Chiral HPLC: (Daicel Chiralpak OD-H, *i*-propanol/hexane =1:10, 0.5 mL/min, λ = 254 nm): t_R(1*S*, 2*S*) = 11.6 min (minor enantiomer), t_R(1*R*, 2*R*) = 50.7 min (major enantiomer).

The relative stereochemistry was determined by NOESY correlation as shown below.

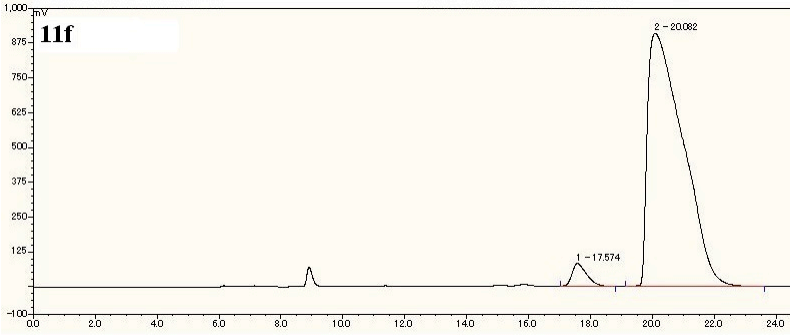


NOESY correlation of **11f**

HPLC chromatographs of **11f**



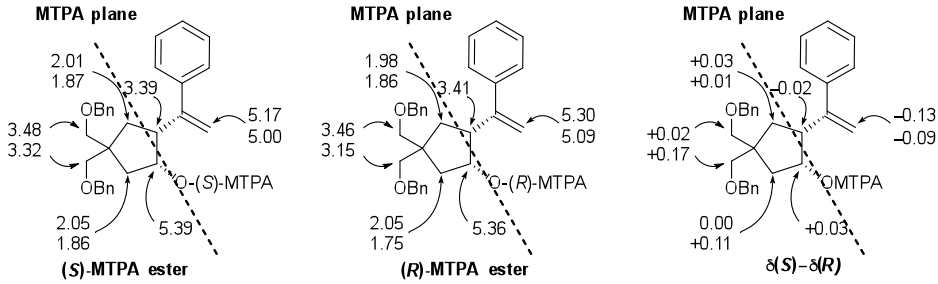
Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	17.24	415.054	302.559	49.70
2	20.85	362.402	306.171	50.30



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	17.57	81.085	44.322	3.55
2	20.08	909.609	1203.237	96.45

Determination of the absolute configurations of 11f

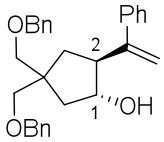
11f was converted into both (*R*)- and (*S*)-MTPA esters ((*R*)- or (*S*)-Mosher's acid, DCC, DMAP, CH_2Cl_2) and then the absolute configurations were determined by Mosher's ester analysis as (1*R*, 2*R*).[2)]



(*R*)-MTPA-(1*R*, 2*R*)-**11f**: ^{1}H NMR (600 M Hz, $CDCl_3$): δ 7.42-7.24 (m, 20H), 5.36 (dd, 1H, *J* = 4.8, 4.8 Hz), 5.30 (s, 1H), 5.09 (s, 1H), 4.53 (s, 2H), 4.31 (s, 2H), 3.46 (s, 2H), 3.44 (s, 3H), 3.41 (m, 1H), 3.16 (d, 1H, *J* = 9.0 Hz), 3.14 (d, 1H, *J* = 9.0 Hz), 2.05 (dd, 1H, *J* = 15.6, 4.8 Hz), 1.98 (dd, 1H, *J* = 13.2, 6.6 Hz), 1.86 (dd, 1H, *J* = 13.2, 13.2 Hz), 1.75 (d, 1H, *J* = 15.6 Hz).

(*S*)-MTPA-(1*R*, 2*R*)-**11f**: ^{1}H NMR (600 M Hz, $CDCl_3$): δ 7.43-7.25 (m, 18H), 7.19-7.17 (m, 2H), 5.39 (dd, 1H, *J* = 4.2, 4.2 Hz), 5.17 (s, 1H), 5.00 (s, 1H), 4.54 (s, 2H), 4.46 (d, 1H, *J* = 12.0 Hz), 4.43 (d, 1H, *J* = 12.0 Hz), 3.48 (s, 2H), 3.39 (m, 1H), 3.33 (m, 5H), 2.05 (dd, 1H, *J* = 15.6, 4.8 Hz), 2.01 (dd, 1H, *J* = 13.2, 6.6 Hz), 1.87 (dd, 1H, *J* = 13.2, 13.2 Hz), 1.86 (d, 1H, *J* = 15.6 Hz).

(1*R*, 2*S*)-4,4-Bis[(benzyloxy)methyl]-2-(1-phenylethenyl)cyclopentan-1-ol (11f')



Yellow oil.

IR ν (neat, cm^{-1}): 3417, 3029, 2855, 1495, 1453, 1363, 1095, 735, 698.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 15H), 5.21 (s, 1H), 5.10 (s, 1H), 4.54 (s, 2H), 4.46 (s, 2H), 4.18 (m, 1H), 3.44 (d, 1H, *J* = 8.8 Hz), 3.41 (d, 1H, *J* = 8.8 Hz), 3.30 (d, 1H, *J* = 8.8 Hz), 3.27 (d, 1H, *J* = 8.8 Hz), 3.02 (m, 1H), 2.34 (brs, 1H), 2.08 (dd, 1H, *J* = 13.6, 7.2 Hz), 2.00 (dd, 1H, *J* = 13.6, 8.0 Hz), 1.63 (dd, 1H, *J* = 13.6, 7.2 Hz), 2.00 (dd, 1H, *J* = 13.6, 9.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 142.2, 138.6, 138.3, 128.4, 128.3, 128.2, 127.6, 127.5, 127.4, 127.4, 127.3, 126.7, 111.6, 76.2, 75.8, 75.6, 73.4, 73.2, 51.9, 44.4, 40.7, 36.2.

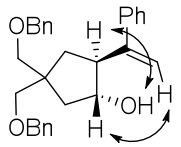
LRMS (EI) m/z (relative intensity): 428 $[M]^+$ (4), 410 (3), 337 (29), 319 (51), 302 (28).

HRMS (EI, $[M]^+$]): calcd for $C_{29}H_{32}O_3$, 428.2351; found, 428.2336.

$[\alpha]^{26}_D$ = −18.7 (*c* 0.96 in $CHCl_3$).

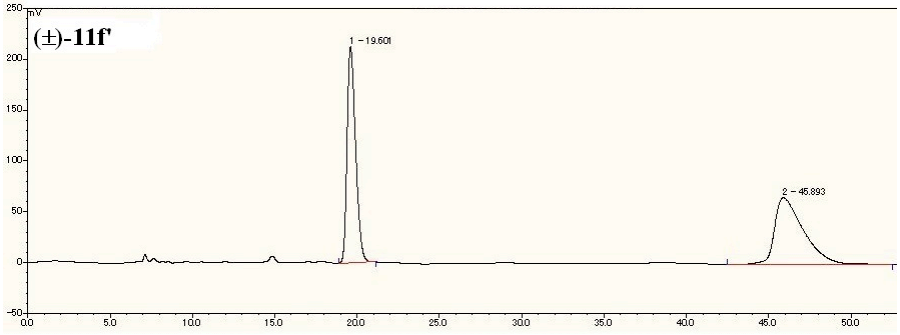
Chiral HPLC: (Daicel Chiralpak OD-H, *i*-propanol/hexane =1:10, 0.5 mL/min, λ = 254 nm): t_R(1*R*, 2*S*) = 18.8 min (major enantiomer), t_R(1*S*, 2*R*) = 43.7 min (minor enantiomer).

The relative stereochemistry was determined by NOESY correlation as shown below.

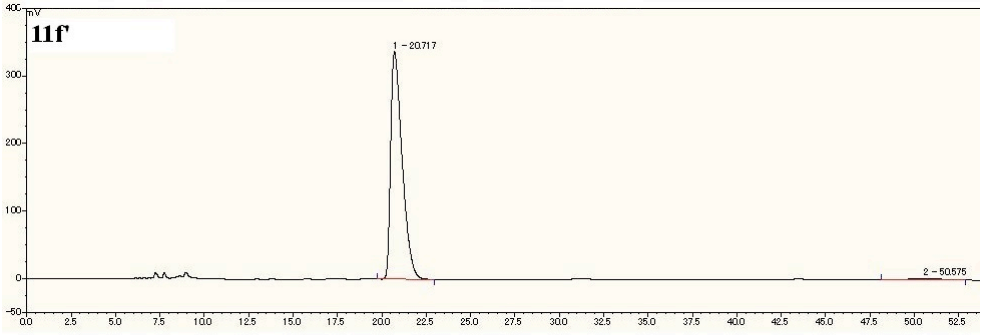


NOESY correlation of **11f**

HPLC chromatographs of **11f'**



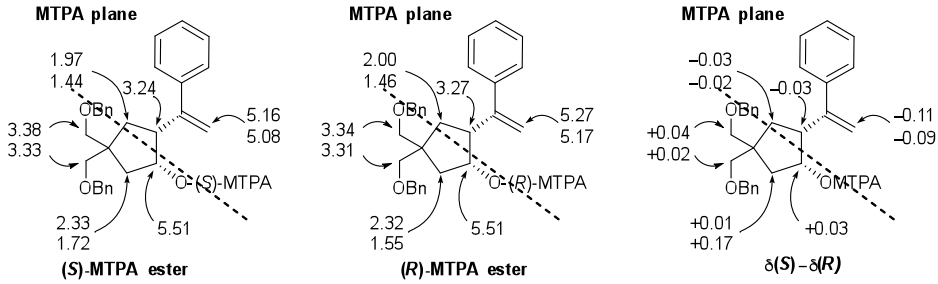
Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	19.60	212.165	127.568	49.24
2	45.89	65.493	131.520	50.76



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	20.72	336.382	243.303	97.20
2	50.58	2.576	6.996	2.80

Determination of the absolute configurations of 11f'

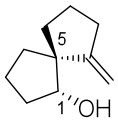
11f' was converted into both (*R*)- and (*S*)-MTPA esters ((*R*)- or (*S*)-Mosher's acid, DCC, DMAP, CH_2Cl_2) and then the absolute configurations were determined by Mosher's ester analysis as (1*R*, 2*S*).[2)]



(*R*)-MTPA-(3*S*,4*S*)-**11f'**: ^{1}H NMR (400 M Hz, $CDCl_3$): δ 7.48-7.46 (m, 2H), 7.37-7.23 (m, 18H), 5.51 (m, 1H), 5.27 (s, 1H), 5.17 (s, 1H), 4.50 (s, 2H), 4.44 (s, 2H), 3.46 (s, 3H), 3.36-3.27 (m, 5H), 2.32 (dd, 1H, *J* = 13.6, 7.6 Hz), 2.00 (dd, 1H, *J* = 13.2, 8.0 Hz), 1.58-1.53 (m, 1H), 1.46 (dd, 1H, *J* = 13.2, 12.0 Hz).

(*S*)-MTPA-(3*S*,4*S*)-**11f'**: ^{1}H NMR (400 M Hz, $CDCl_3$): δ 7.48-7.47 (m, 2H), 7.34-7.20 (m, 18H), 5.51 (m, 1H), 5.16 (s, 1H), 5.08 (s, 1H), 4.49 (s, 2H), 4.48 (s, 2H), 3.46 (s, 3H), 3.39 (d, 1H, *J* = 8.8 Hz), 3.36 (d, 1H, *J* = 8.8 Hz), 3.35 (d, 1H, *J* = 8.8 Hz), 3.31 (d, 1H, *J* = 8.8 Hz), 3.27-3.20 (m, 1H), 2.33 (dd, 1H, *J* = 13.6, 7.6 Hz), 1.97 (dd, 1H, *J* = 13.6, 8.4 Hz), 1.72 (dd, 1H, *J* = 13.6, 7.6 Hz), 1.44 (dd, 1H, *J* = 13.6, 11.6 Hz).

(1*R*,5*R*)-6-Methylenespiro[4.4]nonan-1-ol (11g)



Colorless oil.

IR ν (neat, cm^{-1}): 3449, 2959, 2868, 1730, 1448, 1404, 1261, 1162, 1069, 802.

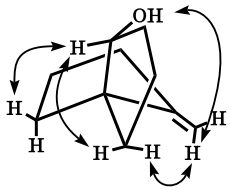
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.14 (s, 1H), 4.93 (s, 1H), 3.55 (d, 1H, *J* = 4.8 Hz), 2.45-2.40 (m, 1H), 2.01-1.73 (m, 5H), 1.67-1.44 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 107.4, 76.8, 58.9, 38.8, 35.7, 34.1, 32.6, 22.7, 21.4.

MS: structurally significant fragment peaks were not observed in EI, ESI and FAB mass spectrum.

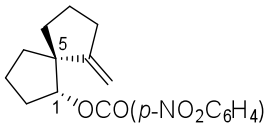
$[\alpha]^{20}_D$ = –37.7 (*c* 0.55 in $CHCl_3$).

The relative stereochemistry was determined by NOESY correlation as shown below.



NOESY correlation of **11g**

Determination of the enantiomeric excess of 11g



11g was converted into its *p*-nitrobenzoyl ester (*p*-NO_2BzCl, Et_3N, DMAP, DCM) and then enatiomeric excess was determined by chiral HPLC.

IR ν (neat, cm^{-1}): 2956, 1722, 1527, 1276, 718.

^1H NMR (400 MHz, $CDCl_3$): δ 8.28-8.26 (m, 2H), 8.16-8.14 (m, 2H), 5.14 (m, 1H), 486 (s, 1H), 4.79 (s, 1H), 2.49-2.43 (m, 1H), 2.38-2.26 (m, 2H), 2.12-2.05 (m, 1H), 1.971.89 (m, 2H), 1.81-1.57 (m, 6H).

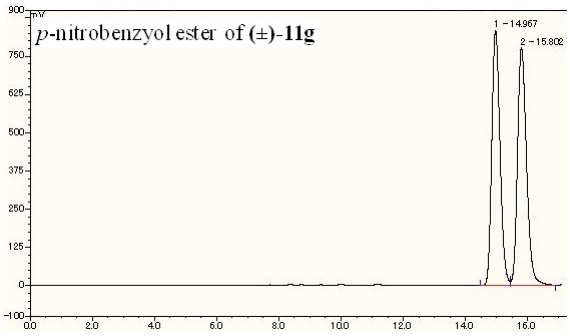
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 163.9, 153.9, 136.6, 130.5, 123.5, 107.5, 82.0, 57.6, 39.2, 36.8, 33.8, 31.5, 22.6, 21.7.

LRMS (EI) m/z (relative intensity): 301 $[M]^+$ (0.2), 283 (1.6), 257 (4.2), 150 (18), 134 (100).

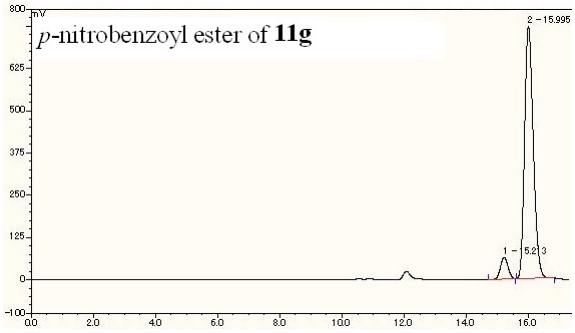
HRMS (EI, $[M]^+$]): calcd for $C_{17}H_{19}NO_4$, 301.1314; found, 301.1344.

Chiral HPLC: (Daicel Chiralpak OD-H, *i*-propanol/hexane =1:100, 0.5 mL/min, λ = 254 nm): t_R(1*S*, 5*S*) = 15.2 min (minor enantiomer), t_R(1*R*, 5*R*) = 16.0 min (major enantiomer).

HPLC chromatographs of *p*-nitrobenzoyl ester of **11g**

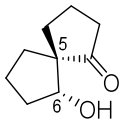


Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	14.97	833.461	255.050	49.32
2	15.80	776.156	262.055	50.68



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	15.21	63.807	17.997	6.95
2	16.00	746.775	241.106	93.05

Determination of the absolute configurations of 11g



To the solution of **11g** (7.9 mg, 0.051 mmol) in THF/H_2O/^{t}BuOH (1/1/1, 1 mL) was added solution of OsO_4 (0.05 M in THF, 51.9 μL, 0.003 mmol). The mixture was stirred at room temerature for 30 min before addition of $NaIO_4$ (27.7 mg, 0.130 mmol). The mixture was stirred at room temerature for 6 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (14:1)] to afford (5*R*, 6*R*)-6-hydroxyspiro[4.4]nonan-1-one[3)] (5.8 mg, 73%) as a colorless oil.

R_f = 0.19 (4:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3445, 2957, 2869, 1732.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (br s, 1H), 3.42 (br s, 1H), 2.34-2.30 (m, 2H), 2.02-1.56 (m, 10H).

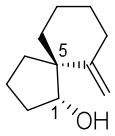
^{13}C NMR (100 MHz, $CDCl_3$): δ 225.4, 80.4, 58.8, 39.1, 35.6, 34.4, 33.9, 21.3, 19.3.

LRMS (EI) m/z (relative intensity): 154 $[M]^+$ (24), 136 (50), 110 (56), 97 (100).

HRMS (EI, $[M]^+$]): calcd for $C_9H_{14}O_2$, 154.0994; found, 154.0991.

$[\alpha]^{26}_D$ =+34.6 (*c* 1.05 in $CHCl_3$). (lit. [3)] $[\alpha]^{26}_D$ =+47.7 (*c* 2.00 in $CHCl_3$))

(1*R*, 5*R*)-6-Methylenespiro[4.5]decan-1-ol (11h)



Colorless oil.

IR ν (neat, cm^{-1}): 3453, 2932, 2857, 1639, 1445, 1040, 876.

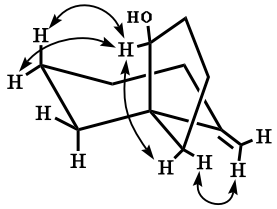
^1H NMR (400 MHz, $CDCl_3$): δ 4.97 (s, 1H), 4.84 (s, 1H), 4.19 (m, 1H), 2.35-2.30 (m, 1H), 2.18-2.08 (m, 2H), 2.04-1.95 (m, 1H), 1.87-1.74 (m, 3H), 1.69-1.49 (m, 4H), 1.41-1.33 (m, 2H), 1.29-1.16 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 110.5, 74.2, 54.8, 35.9, 34.9, 32.8, 31.6, 28.3, 22.6, 20.0.

HRMS (EI, $[M]^+$]): calcd for $C_{11}H_{18}O$, 166.1358; found, 166.1342.

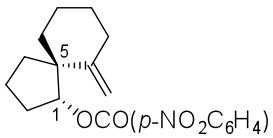
$[\alpha]^{21}_D$ = −20.0 (*c* 0.38 in $CHCl_3$).

The relative stereochemistry was determined by NOESY correlation as shown below.



NOESY correlation of **11h**

Determination of the enantiomeric excess of 11h



11h was converted into its *p*-nitrobenzoyl ester (*p*-NO_2BzCl, Et_3N, DMAP, DCM) and then enatiomeric excess was determined by chiral HPLC.

IR ν (neat, cm^{-1}): 2934, 2858, 1721, 1527, 1347, 1279, 1120, 719.

^1H NMR (400 MHz, $CDCl_3$): δ 8.26-8.24 (m, 2H), 8.14-8.11 (m, 2H), 5.57 (m, 1H), 4.81 (m, 2H), 2.34-2.28 (m, 2H), 2.25-2.20 (m, 1H), 2.02 (dt, 1H, *J* = 13.2, 4.4 Hz), 1.89-1.75 (m, 5H), 1.69-1.56 (m, 2H), 1.49-1.47 (m, 1H), 1.38-1.29 (m, 1H), 1.25-1.21 (m, 1H).

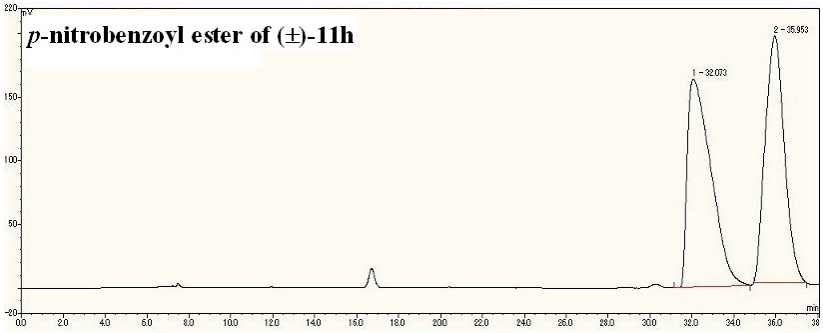
^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 151.1, 150.4, 136.3, 130.6, 123.4, 107.9, 79.8, 53.3, 36.2, 34.9, 34.2, 31.0, 28.6, 22.7, 20.2.

LRMS (EI) m/z (relative intensity): 315 $[M]^+$ (0.5), 297 (8.7), 271 (2.5), 148 (100).

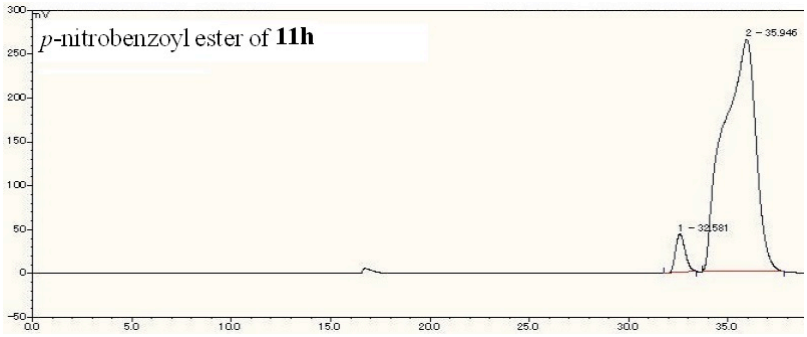
HRMS (EI, $[M]^+$]): calcd for $C_{18}H_{21}NO_4$, 315.1471; found, 315.1463.

Chiral HPLC: (Daicel Chiralpak AD-H, *i*-propanol/hexane =1:500, 0.5 mL/min, λ = 254 nm): t_R(1*S*, 5*S*) = 32.6 min (minor enantiomer), t_R(1*R*, 5*R*) = 35.9 min (major enantiomer).

HPLC chromatographs of *p*-nitrobenzoyl ester of **11h**

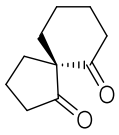


Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	32.07	163.513	213.920	50.98
2	35.95	193.856	205.711	49.02



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	32.58	43.427	24.452	4.74
2	35.95	264.205	491.254	95.26

Determination of the absolute configurations of 11h



To a solution of **11h** (33.4 mg, 0.201 mmol) in anhydrous DCM (1 mL) was added DMP (170 mg, 0.402 mmol). The mixture was stirred at room temperature for 3 h, and then treated with aqueous $Na_2S_2O_3$ and aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was dissolved in THF/H_2O/^{t}BuOH (1/1/1, 5 mL), and treated with a solution of OsO_4 (0.05 M in THF, 201 μL, 0.010 mmol). The mixture was

stirred at room temperature for 30 min before addition of $NaIO_4$ (107 mg, 0.502 mmol). The mixture was stirred at room temperature for 6 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (14:1)] to afford (*R*)-spiro[4.5]decane-1,6-dione[3] (20.1 mg, 60%) as a colorless oil.

R_f = 0.43 (4:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2944, 2864, 1747, 173, 1698, 1447.

^1H NMR (400 MHz, $CDCl_3$): δ 2.73-2.64 (m, 2H), 2.44 (dt, 1H, *J* = 14.4, 5.2 Hz), 2.33-2.29 (m, 2H), 2.17-2.10 (m, 1H), 2.09-1.99 (m, 2H), 1.97-1.85 (m, 2H), 1.80-1.55 (m, 4H).

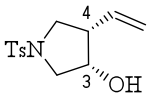
^{13}C NMR (100 MHz, $CDCl_3$): δ 215.7, 208.1, 64.4, 39.8, 38.5, 35.9, 33.7, 26.7, 21.0, 19.0.

LRMS (EI) m/z (relative intensity): 166 $[M]^+$ (69), 148 (21), 138 (64), 121 (23), 111 (100).

HRMS (EI, $[M]^+$]): calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.0973.

$[\alpha]^{26}_D$ = +132 (*c* 0.575 in $CHCl_3$). (lit.[3] $[\alpha]^{26}_D$ = +185 (*c* 0.40 in $CHCl_3$))

(3*S*, 4*S*)-1-[(4-Methylphenyl)sulfonyl]-4-vinyl-3-pyrrolidinol (11i)[4]



Yellow oil.

IR ν (neat, cm^{-1}): 3508, 2925, 1725, 1598, 1340, 1162, 1092, 1056, 815, 757, 669.

^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 5.74 (ddd, 1H, *J* = 17.6, 10.4, 7.2), 5.23 (d, 1H, *J* = 10.4 Hz), 5.14 (d, 1H, *J* = 17.6 Hz), 4.20 (m, 1H), 3.58-3.50 (m, 2H), 3.34 (dd, 1H, *J* = 11.4, 1.6 Hz), 3.21 (dd, 1H, *J* = 10.0, 10.0 Hz), 2.75-2.68 (m, 1H), 2.42 (s, 3H), 1.46 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 134.0, 132.4, 129.7, 127.5, 119.5, 72.5, 55.7, 49.1, 47.8, 21.5.

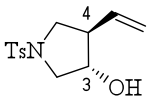
LRMS (EI) m/z (relative intensity): 267 $[M]^+$ (76), 184 (72), 155 (42), 112 (100).

HRMS (EI, $[M]^+$]): calcd for $C_{13}H_{17}NO_3S$, 267.0929; found, 267.0919.

$[\alpha]^{24}_D$ = +4.46 (*c* 0.50 in $CHCl_3$).

Chiral HPLC: (Daicel Chiralpak AD-H, *i*-propanol/hexane =10:90, 1.0 mL/min, λ = 254 nm): t_R(3*S*, 4*S*) = 24.4 min (major enantiomer), t_R(3*R*, 4*R*) = 47.1 min (minor enantiomer).

(3*S, 4*R**)-1-[(4-Methylphenyl)sulfonyl]-4-vinyl-3-pyrrolidinol (11i')**[5)]



Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 5.55 (ddd, 1H, *J* = 18.4, 10.8, 8.0), 5.12 (m, 1H), 5.08 (m, 1H), 3.99 (m, 1H), 3.59-3.53 (m, 2H), 3.18-3.12 (m, 1H), 2.59(m, 1H), 2.42 (s, 3H), 1.70 (m, 1H).

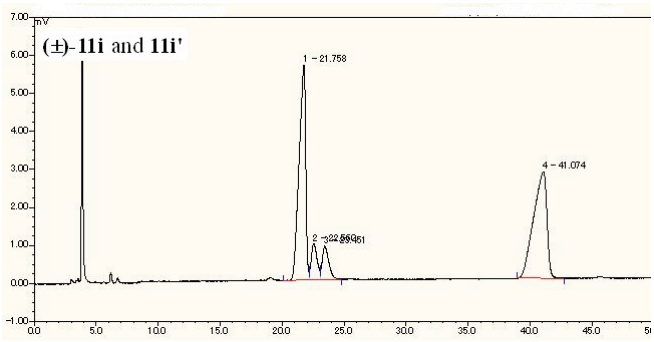
^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 129.7, 127.9, 127.5, 121.8, 117.9, 74.8, 53.7, 50.6, 50.4, 21.5.

$[\alpha]^{25}_D = -13.3$ (*c* 0.14 in $CHCl_3$).

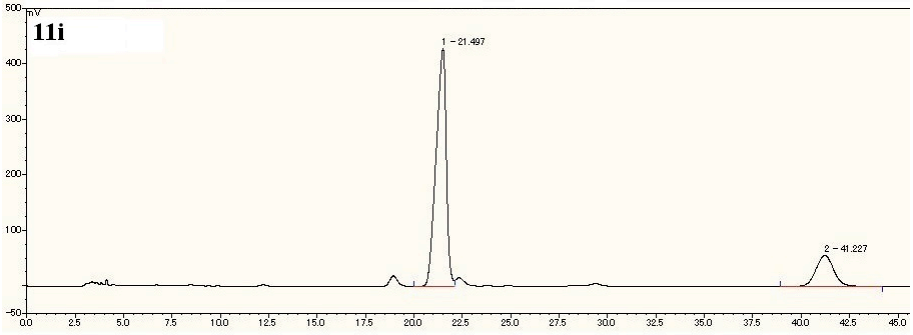
Chiral HPLC: (Daicel Chiralpak AD-H, *i*-propanol/hexane =10:90, 1.0 mL/min, λ = 254 nm): t_R(3*S*, 4*R*) = 23.9 min (major enantiomer), t_R(3*R*, 4*S*) = 25.4 min (minor enantiomer).

The absolute configurations of major enantiomer of **11i'** have not yet been assigned.

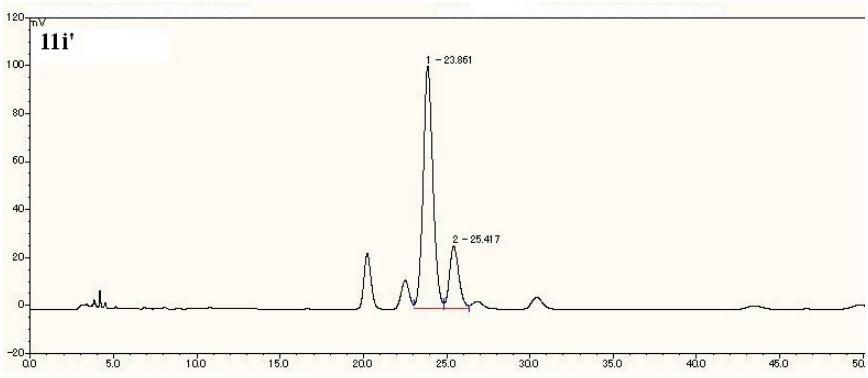
HPLC chromatographs of **11i** and **11i'**



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	21.76	5.652	3.505	43.43
2	22.56	0.943	0.525	6.51
3	23.45	0.881	0.543	6.72
4	41.07	2.795	3.498	43.34

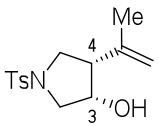


Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	21.50	428.445	261.429	81.85
2	41.23	55.446	57.984	18.15



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	23.86	101.018	68.628	80.12
2	25.42	26.056	17.031	19.88

(3*S*, 4*S*)-4-(Prop-1-en-2-yl)-1-tosylpyrrolidin-3-ol (11j)



Yellow oil

IR ν (neat, cm^{-1}): 3509, 2920, 1339, 1161, 1091, 671, 605.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 5.03 (s, 1H), 4.73 (s, 1H), 4.28-426 (m, 1H), 3.58-3.51 (m, 2H), 3.44 (d, 1H, *J* = 11.6 Hz), 3.31 (dd, 1H, *J* = 11.6, 9.2 Hz), 2.66-2.61 (m, 1H), 2.43 (s, 3H), 1.77 (s, 3H), 1.42 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 139.5, 134.0, 129.6, 127.5, 113.9, 70.2, 55.9, 50.5, 47.7,

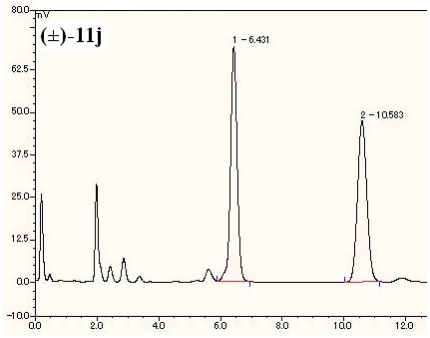
22.9, 21.5.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{14}H_{19}NO_3SNa$, 304.0983; found, 304.0972.

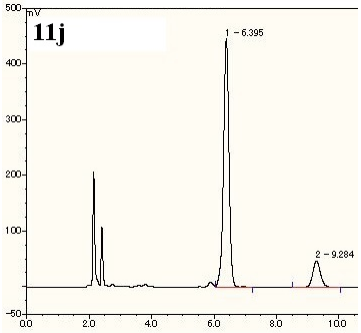
$[\alpha]^{26}_D$ = +4.58 (*c* = 1.00 in $CHCl_3$).

Chiral HPLC: (Daicel Chiralpak AD-H, *i*-propanol/hexane =20:80, 1.0 mL/min, λ = 254 nm): t_R(3*S*, 4*S*) = 9.7 min (major enantiomer), t_R(3*R*, 4*R*) = 13.1 min (minor enantiomer).

HPLC chromatographs of **11j**

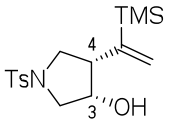


Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	6.43	69.106	16.990	50.81
2	10.58	47.232	16.448	49.19



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	6.39	445.930	92.832	87.97
2	9.28	47.076	12.692	12.03

(3*S*, 4*S*)-1-Tosyl-4-{1-(trimethylsilyl)vinyl}pyrrolidin-3-ol (11k)



Brown solid

Mp = 113-4 °C.

IR ν (neat, cm^{-1}): 3523, 2954, 1340, 1250, 1161, 839, 668.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, 2H, *J* = 8.4 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 5.65 (m , 2H), 4.12 (m, 1H), 3.60 (ddd, 1H, *J* = 12.0, 4.4, 1.2 Hz), 3.50 (dd, 1H, *J* = 9.2, 6.8 Hz), 3.42 (d, 1H, *J* = 11.6 Hz), 3.34 (dd, 1H, *J* = 11.6, 9.2 Hz), 2.87 (m, 1H), 2.43 (m, 4H), 0.11 (s, 9H).

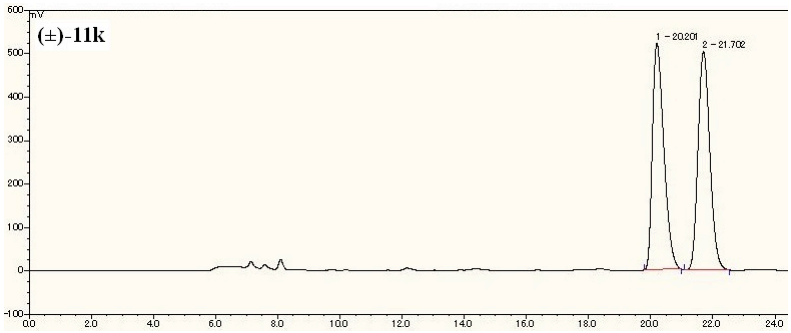
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 143.4, 14.1, 129.6, 128.2, 127.5, 70.5, 55.9, 48.5, 48.1, 21.5, −1.62.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{16}H_{25}NO_3SSiNa$, 362.1222; found, 362.1211.

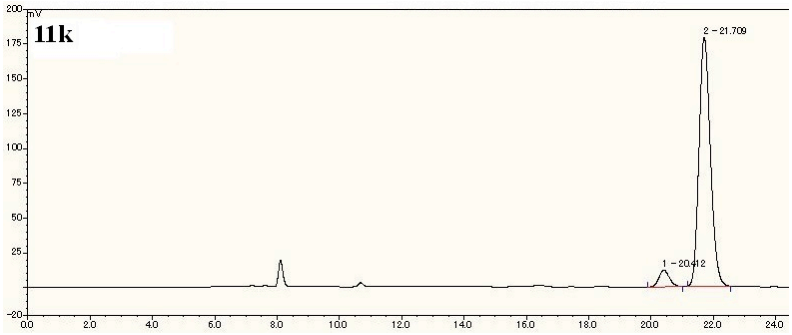
$[\alpha]^{29}_D$ = −11.2 (*c* = 0.10 in $CHCl_3$).

Chiral HPLC: (Daicel Chiralpak AD-H, *i*-propanol/hexane =10:90, 0.5 mL/min, λ = 254 nm): t_R(3*R*, 4*R*) = 20.4 min (minor enantiomer), t_R(3*S*, 4*S*) = 21.7 min (major enantiomer).

HPLC chromatographs of **11k**

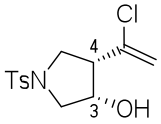


Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	20.20	520.842	221.367	49.96
2	21.70	502.952	221.692	50.04



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	20.41	11.997	4.664	5.79
2	21.71	179.048	75.941	94.21

(3*S*, 4*S*)-4-(1-Chlorovinyl)-1-tosylpyrrolidin-3-ol (11l)



Yellow oil

IR ν (neat, cm^{-1}): 3507, 2928, 1340, 1161, 669, 605.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 5.43 (s, 1H), 5.17 (s, 1H), 4.48 (m, 1H), 3.65 (dd, 1H, *J* = 8.8, 7.2 Hz), 3.56 (dd, 1H, *J* = 11.6, 4.4 Hz), 3.41 (d, 1H, *J* = 11.6 Hz), 3.33 (dd, 1H, *J* = 11.6, 8.8 Hz), 2.93-2.88 (m, 1H), 2.43 (s, 3H), 1.61 (brd, 1H, *J* = 3.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 136.4, 133.8, 129.8, 127.5, 115.6, 70.9, 55.3, 52.2, 47.6, 21.5.

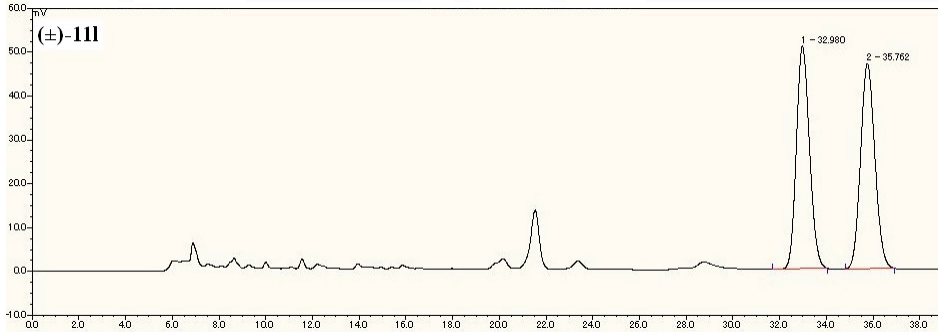
LRMS (EI) m/z (relative intensity): 301 $[M]^+$ (14), 266 (97), 244 (13), 184 (100).

HRMS (EI, $[M]^+$]): calcd for $C_{13}H_{16}ClNO_3S$, 301.0539 (-)-11k; found, 301.0553.

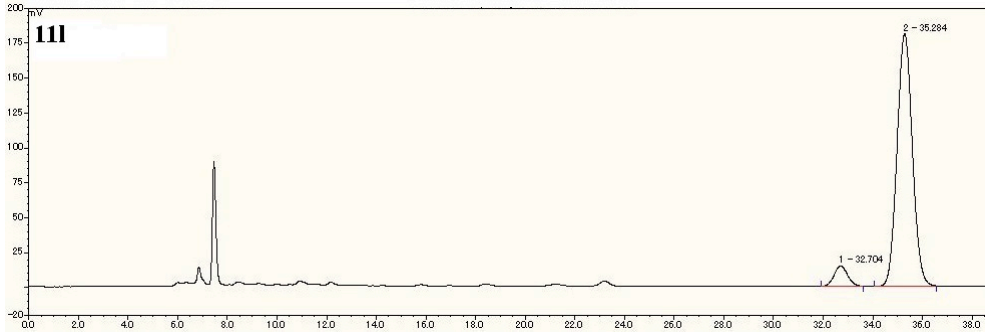
$[\alpha]^{28}_D$ = −8.91 (*c* = 0.81 in $CHCl_3$).

Chiral HPLC: (Daicel Chiralpak AD-H, *i*-propanol/hexane =10:90, 0.5 mL/min, λ = 254 nm): t_R(3*R* 4*R*) = 20.4 min (minor enantiomer), t_R(3*S*, 4*S*) = 21.7 min (major enantiomer).

HPLC chromatographs of **11l**



Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	32.98	50.694	33.001	49.85
2	35.76	46.730	33.203	50.15

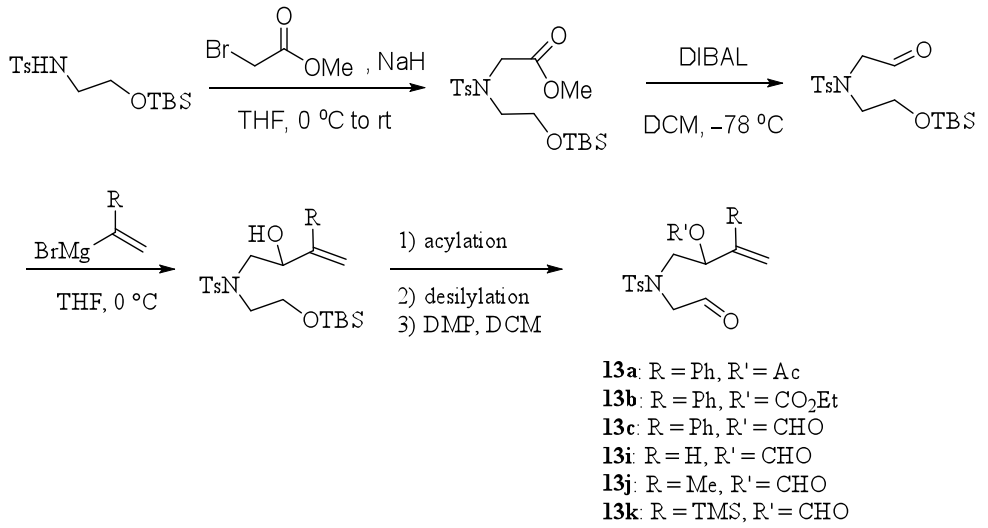


Peak	RT (time)	Hight (mV)	Area (mV*time)	Area%
1	32.70	14.610	9.150	6.62
2	35.28	180.647	129.056	93.38

Pd(II) catalyzed cyclization of allene-aldehyde to give (1*R*, 5*R*)-11f

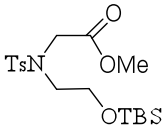
To a test tube containing a solution of 3,3-Bis[(benzyloxy)methyl]hepta-5,6-dienal (12.6 mg, 0.036 mmol) in anhydrous MeCN (360 μL) were added $Pd(OAc)_2$ (0.8 mg, 10 mol%), (*S*)-SEGPHOS (2.2 mg, 10 mol%) and $PhB(OH)_2$ (6.6 mg, 1.5 eq.) under argon. The resulting mixture was sealed with a screw cap and stirred at 50 °C for 2 h. Then the mixture were added $CHCl_3$ and *N*,*N*-diethanolaminomethylpolystyrene (PS-DEAM^{TM}, 1.8 mmol/g, 3 eq.). The mixture was agitated for 2 h and then filtered and washed with $CHCl_3$. The filtrate was concentrated in vacuo and the residue was purified by preparative TLC to afford **(1*R*, 5*R*)-11f** (12.3 mg, 80%).

Preparation of Substrates



13a: R = Ph, R' = Ac
13b: R = Ph, R' = CO_2Et
13c: R = Ph, R' = CHO
13i: R = H, R' = CHO
13j: R = Me, R' = CHO
13k: R = TMS, R' = CHO

{[2-(*tert*-Butyldimethylsilanyloxy)ethyl](toluene-4-sulfonyl)amino}acetic acid methyl ester



To a solution of *N*-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-4-methylbenzenesulfonamide[6] (3.00 g, 9.10 mmol) in anhydrous THF (120 mL) was added a suspension of NaH (262 mg, 10.9 mmol) in anhydrous THF (30 mL) at 0 °C, and stirred for 15 min at room temperature. Then methyl bromoacetate (0.92 mL, 10 mmol) was added to the mixture at 0 °C. The mixture was stirred at room temperature for 8 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (10:1)] to afford [[2-(*tert*-butyldimethylsilanyloxy)ethyl](toluene-4-sulfonyl) amino]acetic acid methyl ester (3.43 g, 94%) as a colorless oil.

R_f = 0.63 (9:1 toluene/EtOAc).

IR ν (neat, cm^{-1}): 2954, 2857, 1756, 1343, 1160, 1091, 937, 837, 779.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, 2H, *J* = 8.4 Hz), 7.28 (d, 2H, *J* = 8.4 Hz), 4.24 (s, 2H), 3.76 (t, 2H, *J* = 5.6 Hz), 3.61 (s, 3H), 3.36 (t, 2H, *J* = 5.6 Hz), 2.41 (s, 3H), 0.83 (s, 9H), 0.03 (s, 6H).

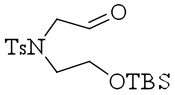
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 143.3, 137.0, 129.4, 127.4, 62.9, 51.9, 50.1, 49.5, 25.6, 21.5, 18.1, –5.6.

LRMS (EI) m/z (relative intensity): 386 $[M\text{-}CH_3]^+$ (3), 344 (100), 286 (8), 272 (9), 256 (7), 255

(7), 155 (16).

HRMS (EI, $[M\text{-}CH_3]^+$]): calcd for $C_{17}H_{28}NO_5SSi$,386.1457; found, 386.1440.

_N_-[2-(_tert_-Butyldimethylsilanyloxy)ethyl]-4-methyl-_N_-(2-oxoethyl)benzenesulfonamide



To a solution of [[2-(*tert*-butyldimethylsilanyloxy)ethyl](toluene-4-sulfonyl)amino]acetic acid methyl ester (3.30 g, 8.22 mmol) in anhydrous DCM (30 mL) was added DIBAL (12.3 mL of a 1.01 M solution in toluene, 12.4 mmol) dropwise at −78 °C. The mixture was stirred for 2 h at −78 °C. The mixture was allowed to warm up to room temperature, and then diluted with Et_2O, quenched with pH 6.86 phosphate buffer. The precipitate was removed by filtration through a Celite® pad, washed with Et_2O, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (9:1)] to afford *N*-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (2.47 g, 81%) as a white solid.

Mp = 62-65 °C.

R_f = 0.54 (9:1 toluene/EtOAc).

IR ν (neat, cm^{-1}): 2954, 2929, 2857, 1736, 1346, 1258, 1161, 1091, 997, 837, 780.

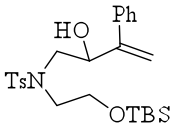
^1H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 7.74 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 3.94 (s, 2H), 3.79 (t, 2H, *J* = 5.0 Hz), 3.31 (t, 2H, *J* = 5.0 Hz), 2.42 (s, 1H), 0.86 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 143.9, 136.0, 129.9, 127.2, 63.5, 58.7, 52.0, 25.8, 21.5, 18.2, −5.6.

LRMS (EI) m/z (relative intensity): 371 $[M]^+$ (0.2), 356 (2), 342 (19), 314 (72), 272 (8), 155 (11).

HRMS (EI, $[M]^+$)): calcd for $C_{17}H_{29}NO_4SSi$, 371.1587; found, 371.1591.

_N_-[2-(_tert_-Butyldimethylsilanyloxy)ethyl]-_N_-(2-hydroxy-3-phenyl-but-3-enyl)-4-methylbenzenesulfonamide



To a solution of magnesium turnings (303 mg, 12.5 mmol) and iodine (1 crystal) in anhydrous THF (15 mL) was added 1-phenylvinyl bromide (0.81 mL, 6.24 mmol) dropwise at 0 °C. The mixture was stirred for 1 h at room temperature, before addition of a solution of *N*-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (1.16 g,

3.12 mmol) in anhydrous THF (30 mL) dropwise at −78 °C. The mixture was stirred for 1 h at −78 °C. The mixture was allowed to warm up to room temperature for 2 h, and then treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (15:1)] to afford *N*-[2-(*tert*-butyl-dimethyl-silanyloxy)ethyl]-*N*-(2-hydroxy-3-phenyl-but-3-enyl)-4-methylbenze-nesulfonamide (1.20 g, 81%) as a yellow oil.

R_f = 0.54 (9:1 toluene/EtOAc).

IR ν (neat, cm^{-1}): 3414, 2954, 2928, 2857, 1344, 1161, 1090, 837, 714.

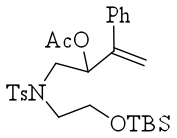
^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8.4 Hz), 7.43-7.26 (m, 5H), 7.22 (d, 2H, *J* = 8.4 Hz), 5.54 (s, 1H), 5.42 (s, 1H), 4.99 (m, 1H), 4.24 (d, 1H, *J* = 1.6 Hz), 3.99-3.94 (m, 1H), 3.83-3.78 (m, 1H), 3.46 (ddd, 1H, *J* = 14.8, 5.0, 5.0 Hz), 3.33 (d, 1H, 14.4 Hz), 3.14 (ddd, 1H, *J* = 14.8, 7.2, 4.4), 2.80 (dd, 1H, *J* = 14.4, 9.6 Hz), 2.38 (s, 3H), 0.91 (s, 9H), 0.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 143.4, 139.2, 135.5, 129.6, 128.4, 127.7, 127.3, 126.5, 113.7, 72.5, 63.1, 57.0, 52.9, 25.9, 21.4, 18.4, −5.5.

LRMS (EI) m/z (relative intensity): 475 $[M]^+$ (11), 418 (26), 342 (100), 272 (44).

HRMS (EI, $[M]^+$)): calcd for $C_{25}H_{37}NO_4SSi$, 475.2213; found, 475.2220.

1-(*N*-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-phenylbut-3-en-2-yl acetate



To a solution of *N*-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-*N*-(2-hydroxy-3-phenyl-but-3-enyl)-4-methylbenzenesulfonamide (1.10 g, 2.31 mmol) in anhydrous THF (15 mL) were added Et_3N (0.64 mL, 4.6 mmol), DMAP (25 mg, 0.23 mmol), and acetic anhydride (0.44 mL, 4.6 mmol). The mixture was stirred at room temperature for 1 h, and then partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (9:1)] to afford 1-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-phenylbut-3-en-2-yl acetate (1.08 g, 90%) as a pale yellow oil.

R_f = 0.70 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2954, 2929, 2857, 1747, 1348, 1230, 1162, 1091, 837, 779.

^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, 2H, *J* = 8.4 Hz), 7.46-7.29 (m, 5H), 7.23 (d, 2H, *J* = 8.4 Hz), 5.91 (dd, 1H, *J* = 9.4, 3.2 Hz), 5.38 (s, 1H), 5.32 (s, 1H), 3.66 (t, 2H, *J* = 6.4 Hz), 3.53-3.25

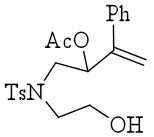
(m, 4H), 2.39 (s, 3H), 2.11 (s, 3H), 0.82 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 146.0, 143.2, 138.4, 137.0, 129.6, 128.5, 128.1, 127.1, 126.7, 114.5, 73.6, 61.8, 52.1, 50.6, 25.8, 21.4, 21.0, 18.1, −5.6.

LRMS (EI) m/z (relative intensity): 502 $[M\text{-}CH_3]^+$ (1.6), 460 (55), 342 (100), 314 (9), 272 (12).

HRMS (EI, $[M\text{-}CH_3]^+$]): calcd for $C_{26}H_{36}NO_5SSi$, 502.2083; found, 502.2086.

1-[*N*-(2-Hydroxyethyl)(4-methylbenzene)sulfonamide]-3-phenylbut-3-en-2-yl acetate



To a solution of 1-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-phenylbut-3-en-2-yl acetate (1.00 mg, 1.93 mmol) in anhydrous THF (20 mL) were added AcOH (0.11 mL, 1.9 mmol), and Bu_4NF (2.1 mL 1.0 M solution in THF, 2.1 mmol) successively. The mixture was stirred at room temperature for 3 h, and then partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (2:1)] to afford 1-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]-3-phenylbut-3-en-2-yl acetate (743 mg, 95%) as a colorless oil.

R_f = 0.39 (1:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3534, 3026, 29.32, 1743, 1598, 1338, 1232, 1159, 1046, 755, 658.

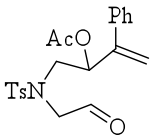
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, 2H, J = 8.4 Hz), 7.46-7.32 (m, 5H), 7.24 (d, 2H, J = 8.4 Hz), 6.07 (brd, 2H, J = 8.0 Hz), 5.40 (s, 1H), 5.36 (s, 1H), 3.81-3.69 (m, 2H), 3.37 (dd, 1H, J = 15.4, 9.6 Hz), 3.29-3.16 (m, 3H), 2.42 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 145.4, 143.6, 138.2, 135.4, 129.7, 128.6, 128.2, 127.2, 126.6, 114.4, 73.7, 61.1, 53.5, 53.1, 21.4, 21.1.

LRMS (EI) m/z (relative intensity): 403 $[M]^+$ (2), 342 (2), 329 (2), 269 (15), 227 (100), 155 (11).

HRMS (EI, $[M]^+$]): calcd for $C_{21}H_{25}O_5S$, 403.1453; found: 403.1442.

1-[*N*-(2-Oxoethyl)(4-methylbenzene)sulfonamide]-3-phenylbut-3-en-2-yl acetate (13a)



To a solution of 1-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]-3-phenyl but-3-en-2-yl acetate (200 mg, 0.496 mmol) in anhydrous DCM (10 mL) was added Dess-Martin periodinane

(315 mg, 0.74 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h, and then treated with saturated aqueous Na_2SO_3, and $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (3:1)] to afford **13a** (163 mg, 82%) as a colorless oil.

R_f = 0.41 (1:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 1740, 1346, 1229, 1159, 713.

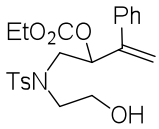
^1H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.57 (d, 2H, *J* = 8.4 Hz), 7.42-7.33 (m, 5H), 7.26 (d, 2H, *J* = 8.4 Hz), 5.87 (dd, 1H, *J* = 8.4, 2.8 Hz), 5.41 (s, 1H), 5.32 (s,1H), 3.92 (d, 1H, *J* = 18.4 Hz), 3.75 (d, 2H, 18.4 Hz), 3.48 (dd, 1H, *J* = 15.4, 2.8 Hz), 3.22 (dd, 1H, *J* = 15.4, 8.4 Hz), 2.43 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 169.7, 145.2, 144.1, 138.0, 135.2, 129.9, 128.7, 128.4, 127.4, 126.6, 114.8, 74.0, 58.5, 52.7, 21.5. 21.1.

LRMS (EI) m/z (relative intensity): 401 $[M]^+$ (4), 372 (7), 359 (20), 330 (24), 246 (45), 226 (100), 155 (60).

HRMS (EI, $[M]^+$)): calcd for $C_{21}H_{23}NO_5S$, 401.1297; found, 401.1289.

_N_-{2-[(Ethoxycarbonyl)oxy]-3-phenylbut-3-en-1-yl}-2-hydroxy-_S_-(4-methylphenyl)ethane-1-sulfonamide



To a solution of *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-hydroxy-*S*-(4-methylphenyl)-3-phenylbut-3-ene-1-sulfonamide (1.50 g, 3.15 mmol) in anhydrous DCM (10 mL) were added pyridine (1.52 mL, 18.9 mmol) and ethyl chloroformate (908 μL, 9.46 mmol) at 0 °C. The mixture was stirred for 2 h at the same temperature, and then treated with aqueous 3 M HCl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was dissolved in MeOH (20 mL). To this solution was added *p*-toluenesulfonic acid monohydrate (137 mg, 0.721 mmol). The mixture was stirred at room temperature for 1 h, and then basified with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (1:1)] to afford *N*-{2-[(ethoxycarbonyl)oxy]-3-phenylbut-3-en-1-yl}-2-hydroxy-*S*-(4-methylphenyl)ethane-1-sulfonamide (1.10 g, 88%) as a yellow oil.

R_f = 0.21 (2:1 hexane/EtOAc).

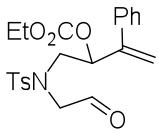
IR ν (neat, cm^{-1}): 3533, 2984, 2932, 1749, 1341, 1261, 1159, 1023, 714, 657.

^1H NMR (400 MHz, $CDCl_3$): 7.56 (d, 2H, *J* = 8.4 Hz), 7.46 (m, 2H), 7.39-7.33 (m, 3H), 7.23 (d, 2H, *J* = 8.4 Hz), 5.91 (dd, 1H, *J* = 9.6, 2.8 Hz), 5.43 (s, 1H), 5.40 (s, 1H), 4.23 (q, 2H, *J* = 7.6 Hz), 3.83-3.70 (m, 2H), 3.39-3.30 (m, 2H), 3.22 (dd, 1H, *J* = 15.6, 9.6 Hz), 3.17-3.12 (m, 1H), 2.78 (t, 1H, *J* = 5.6 Hz), 2.39 (s, 3H), 1.33 (t, 3H, *J* = 7.6 Hz)

^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 145.3, 143.6, 138.0, 135.3, 129.7, 128.7, 128.3, 127.4, 126.6, 114.6, 78.0, 64.5, 61.2, 53.4, 53.3, 21.4, 14.2.

HRMS (ESI, $[M+Na]^+$)): calcd for $C_{26}H_{37}NO_5SSiNa$, 456.1457; found, 456.1450.

_N_-{2-[(Ethoxycarbonyl)oxy]-3-phenylbut-3-en-1-yl}-_S_-(4-methylphenyl)-2-oxoethane-1-sulfonamide (13b)



To a solution of *N*-{2-[(ethoxycarbonyl)oxy]-3-phenylbut-3-en-1-yl}-2-hydroxy-*S*-(4-methyl-phenyl)ethane-1-sulfonamide (250 mg, 0.645 mmol) in anhydrous DCM (5.0 mL) was added Dess-Martin periodinane (328 mg, 0.774 mmol). The mixture was stirred at room temperature for 2 h, and then treated with saturated aqueous $Na_2S_2O_3$, and $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (3:1)] to afford *N*-{2-[(ethoxycarbonyl)oxy]-3-phenylbut-3-en-1-yl}-*S*-(4-methylphenyl)-2-oxoethane-1-sulfonamide (**13b**) (172 mg, 62%) as a yellow oil.

R_f = 0.64 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2983, 1749, 1598, 1346, 1261, 1160, 759.

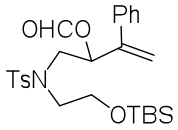
^1H NMR (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 7.55 (d, 2H, *J* = 8.4 Hz), 7.43-7.35 (m, 5H), 7.24 (d, 2H, *J* = 8.4 Hz), 5.73 (m, 1H), 5.43 (s, 1H), 5.35 (s, 1H), 4.21 (q, 2H, *J* = 7.2 Hz), 4.03 (d, 1H, *J* = 19.2 Hz), 3.87 (d, 1H, *J* = 19.2 Hz), 3.55 (dd, 1H, *J* = 15.6, 2.4 Hz), 3.12 (dd, 1H, *J* = 15.6, 8.8 Hz), 2.41 (s, 3H), 1.32 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 153.9, 145.1, 144.1, 137.8, 135.3, 129.8, 128.7, 128.4, 127.4, 126.6, 114.8, 78.5, 64.5, 58.9, 52.8, 21.5, 14.2.

LRMS (EI) m/z (relative intensity): 431 $[M]^+$ (1), 418 (4), 402 (6), 387 (11), 330 (17), 276 (36), 226 (98).

HRMS (EI, $[M-CHO]^+$)): calcd for $C_{21}H_{24}NO_5S$, 402.1375; found, 402.1360.

1-(_N_-{2-[(_tert_-Butyldimethylsilyl)oxy]ethyl}4-methylbenzenesulfonamide)-3-phenylbut-3-en-2-yl formate



To a solution of *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-hydroxy-*S*-(4-methylphenyl)-3-phenylbut-3-ene-1-sulfonamide (500 mg, 1.05 mmol) in anhydrous DCM (5.0 mL) were added DMAP (1 crystal) and *N*-formyl benzotriazole[7] (232 mg, 1.58 mmol). The mixture was stirred for 2 h at room temperature, and then treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (8:1)] to afford 1-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}4-methylbenzene-sulfonamide)-3-phenylbut-3-en-2-yl formate (529 mg, quant.) as a colorless oil.

R_f = 0.74 (1:1 hexane/EtOAc).

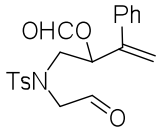
IR ν (neat, cm^{-1}): 2954, 2929, 2853, 1730, 1345, 1161, 836, 778.

^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.60 (d, 2H, *J* =8.4 Hz), 7.43 (m, 2H), 7.35 (m, 3H), 7.23 (d, 2H, *J* = 8.4 Hz), 6.01 (m, 1H), 5.41 (s, 1H), 5.35 (s, 1H), 3.68 (dd, 2H, *J* = 6.4, 6.4 Hz), 3.57 (dd, 1H, *J* = 14.8, 9.2 Hz), 3.45 (dd, 1H, *J* = 14.8, 2.8 Hz), 3.76 (ddd, 1H, *J* = 15.2, 6.4, 6.4 Hz), 3.27 (ddd, 1H, *J* = 15.2, 6.4, 6.4 Hz), 2.39 (s, 3H), 0.80 (s, 9H), −0.02 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 145.4, 143.3, 138.2, 137.0, 129.6, 128.6, 128.3, 127.3, 127.2, 126.7, 73.6, 62.0, 52.2, 50.8, 25.9, 25.7, 18.1, −5.58.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{26}H_{37}NO_5SSiNa$, 526.2059; found, 526.2045.

1-[*N*-(2-Oxoethyl)4-methylbenzenesulfonamide]-3-phenylbut-3-en-2-yl formate (13c)



To a solution of 1-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}4-methylbenzenesulfonamide)-3-phenylbut-3-en-2-yl formate (170 mg, 0.439 mmol) in THF (18 mL) were added H_2O (3.0 mL) and formic acid (9.0 mL). The mixture was stirred for 8 h at room temperature, and then treated with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was dissolved in anhydrous DCM (5.0 mL). Dess-Martin periodinane (223 mg, 0.527 mmol). The mixture was stirred at room temperature for 2 h, and then treated with saturated aqueous $Na_2S_2O_3$, and $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (3:1)] to afford 1-[*N*-(2-oxoethyl)4-methylbenzenesulfonamide]-3-phenylbut-3-en-2-yl formate (**13c**) (79.1 mg,

47%) as a yellow oil.

R_f = 0.21 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3027, 2977, 2929, 1729, 1598, 1495, 1344, 1162, 1090, 757.

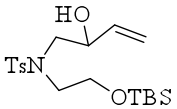
^1H NMR (400 MHz, $CDCl_3$): δ 9.53 (s, 1H), 8.07 (s, 1H), 7.56 (d, 2H, *J* = 8.4 Hz), 7.41-7.33 (m, 5H), 7.25 (d, 2H, *J* = 8.4 Hz), 5.99 (dd, 1H, *J* = 8.8, 2.8 Hz), 3.97 (d, 1H, *J* = 18.8 Hz), 3.83 (d, 1H, *J* = 18.8 Hz), 3.49 (dd, 1H, *J* = 15.2, 2.8 Hz), 3.28 (dd, 1H, *J* = 15.2, 8.8 Hz), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 159.6, 144.5, 144.2, 137.7, 135.1, 129.8, 128.7, 128.5, 127.4, 126.6, 115.4, 73.9, 58.5, 52.6, 21.4.

LRMS (EI) m/z (relative intensity): 374 (4), 358 (4), 312 (14), 226 (91).

HRMS (EI, $[M-CHO]^+$)): calcd for $C_{19}H_{20}NO_4S$, 358.1113; found, 358.1120.

_N_-[2-(_tert_-Butyldimethylsilanyloxy)ethyl]-_N_-(2-hydroxybut-3-enyl)-4-methylbenzene-sulfonamide



To a solution of *N*-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-4-methyl-*N*-(2-oxoethyl)-benzene-sulfonamide (1.00 g, 2.69 mmol) in anhydrous THF (20 mL) was added vinylmagnesium bromide (6.7 mL of a 1.0 M solution in THF, 6.7 mL) dropwise at −78 °C, and the resulting mixture was stirred for 30 min. The mixture was allowed to warm up to room temperature for 2 h, and treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (10:1)] to afford *N*-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-*N*-(2-hydroxybut-3-enyl)-4-methyl-benzenesulfonamde (909 mg, 84%) as a white solid.

R_f = 0.44 (9:1 toluene/EtOAc).

Mp 44-47 °C.

IR ν (neat, cm^{-1}): 3430, 2954, 2858, 1341, 1161, 1090, 837, 778.

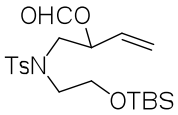
^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, 2H, *J* = 8.0 Hz), 7.31 (d, 2H, *J* = 8.0 Hz), 5.81 (ddd, 1H, *J* = 17.2, 10.8, 5.6 Hz), 5.37 (d, 2H, *J* = 17.2 Hz), 5.18 (d, 2H, *J* = 10.8 Hz), 4.44-4.36 (m, 1H), 4.03 (d, 1H, *J* = 2.8 Hz), 3.98-3.93 (m, 1H), 3.87-3.80 (m, 1H), 3.38-3.22 (m, 3H), 2.43 (s, 3H), 0.91 (s, 9H), 0.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.2, 129.9, 129.8, 127.3, 116.3, 71.9, 63.4, 56.9, 52.6, 25.9, 21.5, 18.4, −5.5.

LRMS (EI) m/z (relative intensity): 384 $[M-CH_3]^+$ (1), 342 (100), 314 (8), 286 (3), 187 (21), 155 (9).

HRMS (EI, $[M-CH_3])^+$)): calcd for $C_{18}H_{30}NO_4SSi$, 384.1665; found, 384.1648.

1-(*N*-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)but-3-en-2-yl formate



Acylation of *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-hydroxy-*S*-(4-methylphenyl)but-3-ene-1-sulfonamide (505 mg, 1.26 mmol) with *N*-formyl benzotriazole[7] gave 1-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)but-3-en-2-yl formate (415 mg, 77%).

Column: hexane – EtOAc (15:1). Colorless oil.

R_f = 0.69 (2:1 hexane/EtOAc).

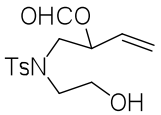
IR ν (neat, cm^{-1}): 2954, 2929, 2857, 1728, 134, 1257, 1161, 1091, 837, 779.

^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.69 (d, 2H, *J* = 8.4 Hz), 7.28 (d, 2H, *J* = 8.4 Hz), 5.77 (ddd, 1H, *J* = 17.2, 10.0, 6.0 Hz), 5.58 (m, 1H), 5.35 (d, 1H, *J* = 17.2 Hz), 5.27 (d, 1H, *J* = 10.0 Hz), 3.72 (t, 2H, *J* = 5.6 Hz), 3.57 (dd, 1H, *J* = 14.8, 8.8 hz), 3.47 (dd, 1H, *J* = 14.8, 4.8 Hz), 3.40-3.25 (m, 2H), 2.41 (s, 3H), 0.85 (s, 9H), 0.01 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 143.4, 137.1, 132.9, 129.6, 127.3, 119.1, 72.3, 62.3, 51.8, 50.7, 25.9, 21.5, 18.1, −5.5.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{20}H_{33}NO_5SSiNa$, 450.1746; found, 450.1731.

1-[*N*-(2-Hydroxyethyl)(4-methylbenzene)sulfonamide]but-3-en-2-yl formate



Desilylation of 1-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]but-3-en-2-yl formate (400 mg, 0.935 mmol) with HCO_2H/THF/H_2O gave 1-[*N*-(2-hydroxyethyl)(4-methylbenzene) sulfonamide]but-3-en-2-yl formate (93.8 mg, 32%).

Column: hexane – EtOAc (3:1). Pale yellow oil.

R_f = 0.63 (1:1 hexane/EtOAc).

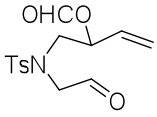
IR ν (neat, cm^{-1}): 3527, 2929, 1724, 1598, 1337, 1159, 1090, 985, 661.

^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.70 (d, 2H, *J* = 8.4 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 5.79 (ddd, 1H, *J* = 17.2, 10.4, 6.4 Hz), 5.63 (m, 1H), 5.37 (d, 1H, *J* = 17.2 Hz), 5.30 (d, 1H, *J* = 10.4 Hz), 3.77 (brs, 2H), 3.47 (dd, 1H, *J* = 14.8, 8.8 Hz), 3.36-3.26 (m, 3H), 2.80 (brs, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 143.8, 135.6, 132.6, 129.7, 127.2, 119.4, 72.6, 60.9, 52.6, 52.2, 21.4.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{14}H_{19}NO_5SNa$, 336.0882; found, 336.0875.

1-[*N*-(2-Oxoethyl)(4-methylbenzene)sulfonamide]but-3-en-2-yl formate (13i)



Dess-Martin oxidation of 1-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]but-3-en-2-yl formate (93.0 mg, 0.297 mmol) with *N*-formyl benzotriazole gave **13i** (55.8 mg, 60%).

Column: hexane – EtOAc (3:1). Yellow oil.

R_f = 0.43 (1:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2951, 2932, 1728, 1345, 1231, 1161, 1090, 758.

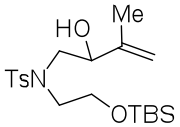
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.98 (s, 1H), 7.68 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 5.80 (ddd, 1H, *J* = 17.2, 10.8, 6.0 Hz), 5.33 (m, 1H), 5.37 (d, 1H, *J* = 17.2 Hz), 5.33 (d, 1H, *J* = 10.8 Hz), 3.96 (d, 1H, *J* = 18.8 Hz), 3.94 (d, 1H, *J* = 18.8 Hz), 3.47 (dd, 1H, *J* = 15.2, 8.0 Hz), 3.45 (dd, 1H, *J* = 15.2, 4.0 Hz), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 197.9, 159.6, 144.3, 135.4, 132.3, 129.9, 127.4, 119.8, 72.9, 58.3, 52.5, 21.5.

LRMS (EI) m/z (relative intensity): 282 (1), 254 (29), 226 (91), 198 (8), 184 (14).

HRMS (EI, $[M-CHO]^+$)): calcd for $C_{13}H_{16}NO_4S$, 282.0800; found, 282.0779.

***N*-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}-2-hydroxy-3-methyl-*S*-(4-methylphenyl)but-3-ene-1-sulfonamide**



To a solution of *N*-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (400 mg, 1.08 mmol) in anhydrous THF (10 mL) was added isopropenylmagnesium bromide solution (0.5 M in THF, 3.9 mL, 2.0 mmol) dropwise at 0 °C. The mixture was allowed to warm up to room temperature for 2 h, and then treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (8:1)] to afford *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-hydroxy-3-methyl-*S*-(4-methylphenyl)but-3-ene-1-sulfonamide (420 mg, 94%) as a colorless oil.

R_f = 0.58 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3511, 2954, 2929, 2858, 1342, 1257, 1160, 1090, 996, 837.

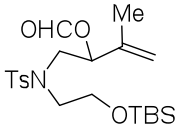
^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 5.05 (s, 1H), 4.89 (s, 1H), 4.30 (d, 2H, *J* = 9.6 Hz), 3.98-3.90 (m, 2H), 3.82 (ddd, 1H, *J* = 10.4, 5.2, 5.2 Hz), 3.44-3.34 (m, 2H), 3.25 (ddd, 1H, *J* = 14.8, 7.2, 4.4 Hz), 2.98 (dd, 1H, *J* = 14.4, 9.6 Hz), 2.43 (s, 3H), 1.74 (s, 3H), 0.93 (s, 9H), 0.12 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 143.5, 136.0, 129.8, 127.3, 112.0, 74.4, 63.2, 56.2, 52.5, 25.9, 21.5, 18.6, 18.4, 14.2, −5.48, −5.46.

LRMS (EI) m/z (relative intensity): 413 $[M]^+$ (1), 398 (1), 356 (28), 342 (100).

HRMS (EI, $[M]^+$)): calcd for $C_{20}H_{35}NO_4SSi$, 413.2056; found, 413.2048.

1-(*N*-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-methylbut-3-en-2-yl formate



Acylation of *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-hydroxy-3-methyl-*S*-(4-methylphenyl) but-3-ene-1-sulfonamide (658 mg, 1.59 mmol) with *N*-formyl benzotriazole[7] gave 1-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-methylbut-3-en-2-yl formate (649 mg, 92%).

Column: hexane – EtOAc (8:1). Colorless oil.

R_f = 0.70 (2:1 hexane/EtOAc).

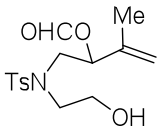
IR ν (neat, cm^{-1}): 2954, 2929, 2857, 1730, 1343, 1257, 1161, 1091, 837.

^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.69 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 2H, *J* = 8.4 Hz), 5.43 (dd, 1H, *J* = 8.4, 4.4 Hz), 5.01 (s, 1H), 4.97 (s, 1H), 3.71 (dd, 2H, *J* = 6.4, 6.4 Hz), 3.58 (dd, 1H, *J* = 15.2, 8.4 Hz), 3.51 (dd, 1H, *J* = 15.2, 4.4 Hz), 3.37 (dt, 1H, *J* = 14.8, 6.4 Hz), 3.28 (dt, 1H, *J* = 14.8, 6.4 Hz), 2.40 (s, 3H), 1.75 (s, 3H), 0.84 (s, 9H), 0.01 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 143.4, 140.3, 137.3, 129.6, 127.2, 114.7, 75.1, 62.3, 51.1, 50.4, 25.8, 21.4, 12.4, 18.2, −5.5.

HRMS (ESI, $[M+Na]^+$)): calcd for $C_{21}H_{35}NO_5SSiNa$, 464.1903; found, 464.1886.

1-[*N*-(2-Hydroxyethyl)(4-methylbenzene)sulfonamide]-3-methylbut-3-en-2-yl formate



Desilylation of 1-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-

methylbut-3-en-2-yl formate (630 mg, 1.42 mmol) with $HCO_2H/THF/H_2O$ gave 1-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]-3-methylbut-3-en-2-yl formate (384 mg, 82%).

Column: hexane – EtOAc (2:1). Colorless oil.

R_f = 0.09 (2:1 hexane/EtOAc).

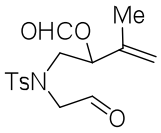
IR ν (neat, cm^{-1}): 3530, 2932, 1726, 1597, 1338, 1160, 1090, 754, 655.

^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.70 (d, 2H, *J* = 8.4 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 5.51 (dd, 1H, *J* = 8.8, 4.0 Hz), 5.06 (s, 1H), 5.01 (s, 1H), 3.83-3.74 (m, 2H), 3.46 (dd, 1H, *J* = 15.2, 8.8 Hz), 3.38 (dd, 1H, *J* = 15.2, 4.0 Hz), 3.32-3.30 (m, 2H),2.43 (s, 3H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 143.8, 140.1, 135.7, 129.7, 127.3, 114.9, 75.4, 61.1, 52.3, 52.1, 21.5, 18.4.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{15}H_{21}NO_5SNa$, 350.1038 found, 350.1022.

3-Methyl-1-[*N*-(2-oxoethyl)(4-methylbenzene)sulfonamide]but-3-en-2-yl formate (13j)



Dess-Martin oxidation of 1-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]-3-methylbut-3-en-2-yl formate (281 mg, 0.857 mmol) gave **13j (**177 mg, 64%).

Column: hexane – EtOAc (3:1). Pale yellow oil.

R_f = 0.63 (1:1 hexane/EtOAc).

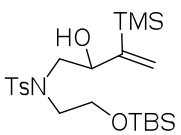
IR ν (neat, cm^{-1}): 2925, 1728, 1344, 1160, 1090, 657.

^1H NMR (400 MHz, $CDCl_3$): δ 9.58 (dd, 1H, *J* = 1.2, 1.2 Hz), 7.97 (s, 1H), 7.68 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 5.38 (dd, 1H, *J* = 8.0, 4.0 Hz), 5.03 (s, 1H), 5.02 (s, 1H), 3.97 (dd, 1H, *J* = 19.2, 1.2 Hz), 3.86 (dd, 1H, *J* = 19.2, 1.2 Hz), 3.47 (dd, 1H, *J* = 15.2, 4.0 Hz), 3.40 (dd, 1H, 15.2, 8.0 Hz), 2.44 (s, 3H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 159.6, 144.3, 139.7, 135.3, 130.0, 127.4, 115.0, 75.5, 58.1, 51.6, 21.6, 18.5.

HRMS (ESI, $[M+Na]^+$)): calcd for $C_{15}H_{19}NO_5SNa$, 348.0882; found, 348.0868.

***N*-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}-2-hydroxy-*S*-(4-methylphenyl)-3-(trimethylsilyl)-but-3-ene-1-sulfonamide**



To a suspension of magnesium turnings (78.5 mg, 3.23 mmol) and 1,2-dibromoethane (13.7 μL,

0.161 mmol) in anhydrous THF (5.0 mL) was added (1-bromovinyl)trimethylsilane (0.33 mL, 2.2 mmol) dropwise at 0 °C. The mixture was refluxed for 10 min with stirring and left to stir at room temperature for 2 h. To the mixture was added *N*-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide solution (400 mg, 1.08 mmol) in anhydrous THF (10 mL) slowly. The mixture was stirred for 1 h at room temperature, and then treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (15:1)] to afford *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-hydroxy-*S*-(4-methylphenyl)-3-(trimethylsilyl)but-3-ene-1-sulfonamide (452 mg, 89%) as a pale yellow oil.

R_f = 0.76 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3413, 2954, 2929, 2860, 1344, 1251, 1160, 1090, 838.

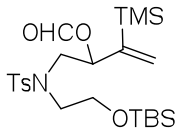
^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 5.84 (dd, 1H, *J* = 2.4, 1.2 Hz), 5.46 (dd, 1H, *J* = 2.4, 1.2 Hz), 4.55 (m, 1H), 4.01 (brs, 1H), 3.97 (m, 1H), 3.82 (ddd, 1H, *J* = 10.0, 5.2, 4.4 Hz), 3.40 (ddd, 1H, *J* = 15.2, 5.2, 4.8. Hz), 3.28 (dd, 1H, *J* = 14.4, 2.0 Hz), 2.81 (dd, 1H, *J* = 14.4, 10.0 Hz), 2.42 (s, 3H), 0.90 (s, 9H), 0.14 (s, 9H), 0.10 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 144.3, 136.7, 130.5, 128.1, 126.1, 75.2, 64.1, 58.7, 53.5, 26.7, 22.3, 19.2, 0.00, –4.64, –4.68.

LRMS (EI) m/z (relative intensity): 456 $[M\text{-}CH_3]^+$ (7), 414 (27), 342 (100).

HRMS (EI, $[M\text{-}CH_3]^+$)): calcd. for $C_{21}H_{38}NO_4SSi_2$, 456.2060; found, 456.2060.

1-(*N*-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-(trimethylsilyl)but-3-en-2-yl formate



Acylation of *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-hydroxy-*S*-(4-methylphenyl)-3-(trimethylsilyl)but-3-ene-1-sulfonamide (600 mg, 1.27 mmol) with *N*-formyl benzotriazole[7] gave 1-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-(trimethylsilyl) but-3-en-2-yl formate (532 mg, 84%).

Column: hexane – EtOAc (8:1). White solid.

R_f = 0.79 (2:1 hexane/EtOAc).

mp = 40-41 °C.

IR ν (neat, cm^{-1}): 2955, 2929, 2857, 1730, 1343, 1252, 1159, 1091, 839.

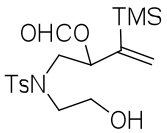
^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.69 (d, 2H, *J* = 8.4 Hz), 7.28 (d, 2H, *J* = 8.4 Hz), 5.82 (s,1H), 5.63 (dd, 1H, *J* = 9.6, 4.0 Hz), 5.51 (s, 1H), 3.57 (dd, 2H, *J* = 6.4, 6.4 Hz),

3.52-3.31 (m, 4H), 2.41 (s, 3H), 0.86 (s, 9H), 0.17 (s, 9H), 0.02 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 148.3, 143.3, 137.5, 129.6, 127.6, 127.2, 76.0, 62.2, 53.0, 50.8, 25.8, 21.5, 18.2, −1.03, −5.49.

HRMS (ESI, $[M+Na]^+$)): calcd for $C_{23}H_{41}NO_5SSi_2Na$, 522.2142; found, 522.2120.

1-[*N*-(2-Hydroxyethyl)(4-methylbenzene)sulfonamide]-3-(trimethylsilyl)but-3-en-2-yl formate



Desilylation of 1-(*N*-{2-[(*tert*-Butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-3-(trimethylsilyl)but-3-en-2-yl formate (510 mg, 1.02 mmol) with HCO_2H/THF/H_2O gave 1-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]-3-(trimethylsilyl)but-3-en-2-yl formate (367 mg, 93%).

Column: hexane – EtOAc (4:1). Colorless oil.

R_f = 0.32 (2:1 hexane/EtOAc).

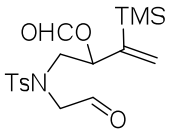
IR ν (neat, cm^{-1}): 3518, 2954, 1726, 1338, 1250, 1159, 1089, 841.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.68 (d, 2H, *J* = 8.4 Hz), 7.30 (d, 2H, *J* = 8.4 Hz), 5.85 (s, 1H), 5.72 (dd, 1H, *J* = 9.6, 2.0 Hz), 5.53 (s, 1H), 3.84-3.73 (m, 2H), 3.40-3.26 (m, 4H), 2.63 (brs, 1H), 2.41 (s, 3H), 0.17 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 148.0, 143.8, 136.0, 129.8, 127.8, 127.3, 75.9, 61.2, 53.9, 52.5, 21.5, −1.1.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{17}H_{27}NO_5SSiNa$, 408.1277; found, 408.1259.

1-[*N*-(2-Oxoethyl)(4-methylbenzene)sulfonamide]-3-(trimethylsilyl)but-3-en-2-yl formate (13k)



Dess-Martin oxidation of 1-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]-3-(trimethylsilyl)but-3-en-2-yl formate (340 mg, 0.882 mmol) gave **13k** (272 mg, 80%).

Column: hexane – EtOAc (2:1). Colorless oil.

R_f = 0.65 (1:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2951, 1728, 1346, 1251, 1160, 842.

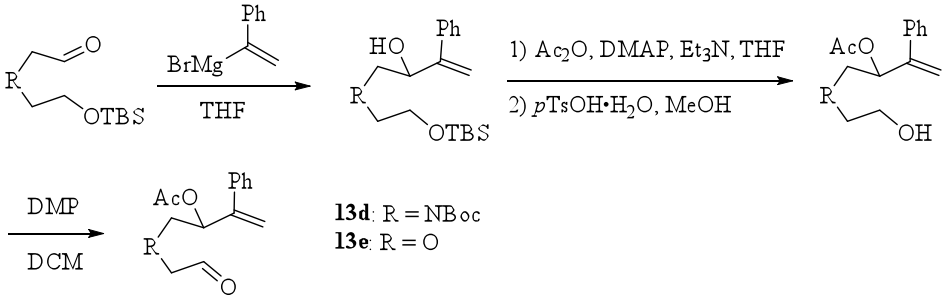
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.94 (s, 1H), 7.67 (d, 2H, *J* = 8.4 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 5.81 (s, 1H), 5.91 (brd, 1H, *J* = 10.0 Hz), 5.54 (s, 1H), 4.06 (d, 1H, *J* = 18.8 Hz),

3.89 (d, 1H, J = 18.8 Hz), 3.44 (dd, 1H, J = 15.2, 2.4 Hz), 3.18 (dd, 1H, J = 15.2, 10.0 Hz), 2.44 (s, 3H), 0.18 (s, 9H).

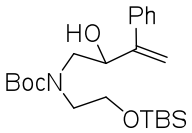
^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 159.6, 147.7, 144.2, 135.6, 129.9, 127.7, 127.3, 76.1, 58.4, 53.5, 21.5, −1.2.

LRMS (EI) m/z (relative intensity): 368 (4), 354 (14), 326 (4), 248 (24), 226 (100).

HRMS (EI, $[M-CHO]^+$]): calcd for $C_{16}H_{24}NO_5SSi$, 354.1195; found, 354.1187.



***tert*-Butyl *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-*N*-(2-hydroxy-3-phenylbut-3-en-1-yl) carbamate**



Alkenylation of *tert*-butyl *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-*N*-(2-oxoethyl)carbamate[82] (1.16 g, 3.12 mmol) with α-styryl Grignard reagent gave *tert*-butyl *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-*N*-(2-hydroxy-3-phenylbut-3-en-1-yl)carbamate (794 mg, 50%). Column: hexane – EtOAc (15:1). Yellow oil.

R_f = 0.44 (4:1 toluene/EtOAc).

IR ν (neat, cm^{-1}): 3428, 2956, 2929, 2858, 1698, 1674, 1472, 1409, 1366, 1252, 1173, 1104, 836, 778.

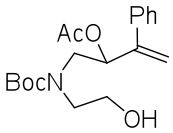
^{1}H NMR (400 MHz, $CDCl_3$): mixture of rotamers: δ 7.38-7.33 (m, 2H), 7.32-7.26 (m, 3H), 5.51 (brs, 1H), 5.39 (s, 1H), 4.88 (brs, 1H), 4.75 (brs, 0.6H), 4.45 (brs, 0.4H), 4.07 (m, 0.4H), 3.75-3.64 (m, 2.6H), 3.44 (m, 0.6H), 3.32 (dd, 0.6H, J = 14.4, 8.0 Hz), 3.19 (m, 1.4H), 2.85 (dd, 0.4H, J = 14.4, 9.6 Hz), 1.47 (s, 5.4H), 1.42 (s, 3.6H), 0.91 (s, 3.6H), 0.83 (s, 5.4H), 0.10 (s, 2.4H), 0.07 (s, 3.6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 155.5, 149.1, 139.8, 128.4, 128.3, 127.6, 126.7, 126.6, 113.7, 113.4, 80.5, 80.2, 73.5, 72.9, 61.9, 61.7, 57.0, 55.7, 52.3, 51.7, 28.4, 25.9, 25.9, −5.5, −5.5.

LRMS (EI) m/z (relative intensity): 322 $[M]^+$ (0.1), 279 (1), 265 (13).

HRMS (EI, $[M]^+$]): calcd for $C_{18}H_{30}NO_3Si$, 322.1964; found, 322.1954.

1-{[*(tert*-Butoxy)carbonyl](2-hydroxyethyl)amino}-3-phenylbut-3-en-2-yl acetate



To a solution of *tert*-butyl *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-*N*-(2-hydroxy-3-phenylbut-3-en-1-yl)carbamate (400 mg, 1.24 mmol) in anhydrous THF (5.0 mL) were added Et_3N (345 μL, 2.48 mmol), DMAP (1 crystal) and Ac_2O (234 μl, 2.48 mmol). The mixture was stirred at room temperature for 1 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was dissolved in DCM/MeOH (9:1, 10 mL). To this solution was added CSA (110 mg, 0.47 mmol). The mixture was stirred at room temperature for 1 h, and then treated with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (2:1)] to afford 1-{[*(tert*-butoxy)carbonyl](2-hydroxyethyl)amino}-3-phenylbut-3-en-2-yl acetate (266 mg, 80%) as a colorless oil.

R_f = 0.23 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3480, 2977, 1739, 1691, 1409, 1363, 1232, 773.

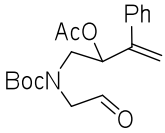
^1H NMR (400 MHz, $CDCl_3$): mixture of rotamers: δ 7.46 (d, 2H, *J* = 6.0 Hz), 7.36-7.29 (m, 3H), 6.07 (brs, 0.3H), 5.90 (d, 0.7H, *J* = 7.6 Hz), 5.42-5.36 (m, 1.3H), 5.31 (s, 0.7H), 3.71 (m, 2.0H), 3.59-3.50 (m, 1.3H), 3.39-3.37 (m, 1H), 3.26-3.20 (m, 1H), 3.08 (m, 0.7H), 2.14 (s, 3H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): mixture of rotamers: δ 169.9, 156.8, 146.6, 138.8, 128.5, 128.1, 126.7, 114.2, 80.8, 74.5, 73.6, 62.2, 52.4, 51.8, 28.2, 21.1.

LRMS (EI) m/z (relative intensity): 349 $[M]^+$ (1), 293 (3), 249 (21), 233 (42).

HRMS (EI, $[M]^+$]): calcd for $C_{19}H_{27}NO_5$, 349.1889; found, 349.1880.

1-{[(*tert*-Butoxy)carbonyl](2-oxoethyl)amino}-3-phenylbut-3-en-2-yl acetate (13d)



Dess-Martin oxidation of 1-{[*(tert*-butoxy)carbonyl](2-hydroxyethyl)amino}-3-phenylbut-3-en-2-yl acetate (100 mg, 0.286 mmol) gave **13d (**80.9 mg, 82%).

Column: hexane – EtOAc (6:1). Pale yellow oil.

R_f = 0.67 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2981, 2936, 1743, 1699, 1369, 1230, 1165, 1147, 1036, 762.

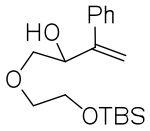
^1H NMR (400 MHz, $CDCl_3$): mixture of rotamers: δ 9.51 (s, 0.6H), 9.48 (s, 0.4H), 7.46-7.45 (m, 2H), 7.37-7.27 (m, 3H), 5.89 (dd, 0.4H, *J* = 8.8, 3.6 Hz), 5.83 (dd, 0.6H, *J* = 8.8, 3.6 Hz), 5.04 (s, 0.4H), 5.36 (s, 0.6H), 5.35 (s, 0.4H), 5.28 (s, 6H), 3.99 (s, 1H), 3.90-3.66 (m, 2H), 3.39 (dd, 0.4H, *J* = 14.8, 8.8 Hz), 3.15 (dd, 0.4H, *J* = 14.8, 8.8 Hz), 2.12 (s, 1.8H), 2.10 (s, 1.2H), 1.40 (s, 3.6H), 1.37 (s, 5.4H).

^{13}C NMR (100 MHz, $CDCl_3$): mixture of rotamers: δ 199.1, 198.8, 169.9, 169.8, 155.3, 154.7, 146.3, 145.9, 138.6, 138.5, 128.6, 128.5, 128.2, 128.2, 126.7, 126.6, 114.6, 114.1, 81.3, 81.2, 74.9, 73.9, 58.7, 52.3, 52.0, 28.1, 28.1, 21.1.

LRMS (EI) m/z (relative intensity): 347 $[M]^+$ (1), 303 (2), 291 (20), 249 (50), 231 (50).

HRMS (EI, $[M]^+$]): calcd for $C_{19}H_{25}NO_5$, 347.1733; found, 347.1729.

1-{2-[(*tert*-Butyldimethylsilyl)oxy]ethoxy}-3-phenylbut-3-en-2-ol



Alkenylation of 2-{2-[(*tert*-butyldimethylsilyl)oxy]ethoxy}acetaldehyde[2] (960 mg, 4.36 mmol) with α-styryl Grignard reagen gave 1-{2-[(*tert*-butyldimethylsilyl)oxy]ethoxy}-3-phenylbut-3-en-2-ol (733 mg, 52%).

Column: hexane – EtOAc (15:1). Yellow oil.

R_f = 0.46 (4:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3447, 2954, 2928, 2857, 1472, 1255, 1138, 1105, 836, 777.

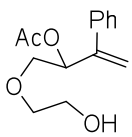
^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.26 (m, 5H), 5.51 (s, 1H), 5.39 (s, 1H), 4.85 (d, 1H, *J* = 8.4 Hz), 3.75 (t, 2H, *J* = 8.4 Hz), 3.61-3.54 (m, 4H), 3.32 (dd, 1H, *J* = 10.0, 8.4 Hz), 0.89 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 139.8, 128.3, 127.6, 126.6, 113.8, 75.0, 72.7, 72.1, 62.7, 25.9, 18.3, −5.3.

LRMS (EI) m/z (relative intensity): 322 $[M]^+$ (0.1), 279 (1), 265 (13).

HRMS (EI, $[M]^+$]): calcd for $C_{18}H_{30}O_3Si$, 322.1964 found, 322.1954.

1-(2-Hydroxyethoxy)-3-phenylbut-3-en-2-yl acetate



To a solution of 1-{2-[(*tert*-butyldimethylsilyl)oxy]ethoxy}-3-phenylbut-3-en-2-ol (400 mg,

0.949 mmol) in anhydrous THF (5 mL) were added Et_3N (264 μl, 1.90 mmol), DMAP (1 crystal) and Ac_2O (179 μl, 1.90 mmol). The mixture was stirred at room temperature for 1 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was dissolved in MeOH (10 mL). Then to this solution was added *p*-toluenesulfonic acid monohydrate (59.0 mg, 0.310 mmol). The mixture was stired at room temperature for 1 h, and then basified with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (2:1)] to afford 1-(2-hydroxyethoxy)-3-phenylbut-3-en-2-yl acetate (196 mg, 63%) as a colorless oil.

R_f = 0.25 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3447, 2933, 2870, 1742, 1374, 1236, 1132, 1052, 779.

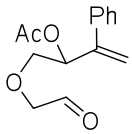
^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, 2H, *J* = 6.8 Hz), 7.37-7.31 (m, 3H), 5.91 (dd, 1H, *J* = 7.6, 3.2 Hz), 5.38 (s, 1H), 5.35 (s, 1H), .3.65-3.47 (m, 6H), 2.16 (s, 3H), 2.04 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 145.4, 139.0, 128.5, 128.1, 126.7, 114.7, 74.1, 72.4, 72.2, 61.6, 21.2.

LRMS (EI) m/z (relative intensity): 251 $[M+H]^+$ (0.1), 219 (1), 190 (60).

HRMS (EI, $[M]^+$]): calcd for $C_{24}H_{18}O_4$, 250.1205; found, 250.1329.

1-(2-Oxoethoxy)-3-phenylbut-3-en-2-yl acetate (13e)



Dess-Martin oxidation of 1-(2-hydroxyethoxy)-3-phenylbut-3-en-2-yl acetate (100 mg, 0.403 mmol) gave **13e** (57.0 mg, 58%).

Column: hexane – EtOAc (6:1). Colorless oil.

R_f = 0.31 (2:1 hexane/EtOAc).

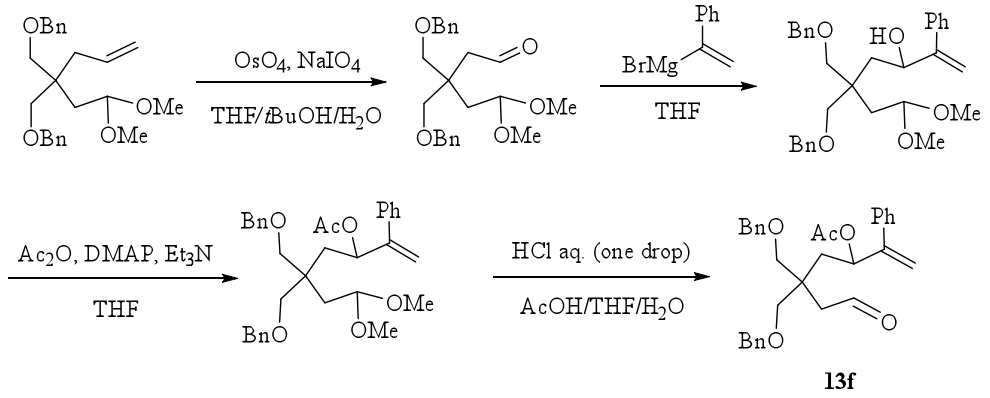
IR ν (neat, cm^{-1}): 2928, 2871, 1739, 1375, 1234, 1139, 1051, 780, 702.

^1H NMR (400 MHz, $CDCl_3$): δ 9.64 (dd, 1H, *J* = 0.8, 0.8 Hz), 7.45-7.41 (m, 2H), 7.37- 7.29 (m, 3H), 5.94 (m, 1H), 5.39 (s, 1H), 5.36 (s, 1H), 4.08 (dd, 2H, *J* = 17.6, 0.8 Hz), 4.02 (dd, 2H, *J* = 17.6, 0.8 Hz), 3.64 (m, 2H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 170.1, 145.0, 138.8, 128.5, 128.2, 126.7, 114.9, 76.4, 74.0, 72.7, 21.1.

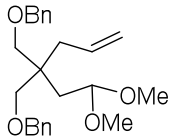
LRMS (EI) m/z (relative intensity):248 $[M]^+$ (0.1), 219 (1), 188 (100).

HRMS (EI, $[M]^+$]): calcd for $C_{14}H_{16}O_4$, 248.1049; found, 248.1020.



13f

[({2-[(Benzyloxy)methyl]-2-(2,2-dimethoxyethyl)pent-4-en-1-yl}oxy)methyl]benzene



[({2-[(Benzyloxy)methyl]-2-(2,2-dimethoxyethyl)pent-4-en-1-yl}oxy)methyl]benzene was prepared according to the modified literature procedure[9] using allyl bromide instead of 1-bromo-2-butyne.

Colorless oil.

R_f = 0.50 (4:1 hexane/EtOAc).

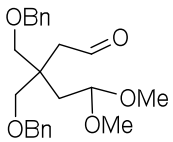
IR ν (neat, cm^{-1}): 2928, 2858, 1454, 1364, 1116, 1100, 1076, 736, 698.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 10H), 5.80 (ddt, 1H, *J* = 17.2, 10.4, 7.2 Hz), 5.07-5.02 (m, 2H), 4.57 (t, 1H, *J* = 5.2 Hz), 4.47 (s, 4H), 3.36 (s, 4H), 3.25 (s, 6H), 2.21 (d, 2H, *J* = 7.2 Hz), 1.68 (d, 2H, *J* = 5.2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 134.4, 128.2, 127.4, 127.3, 117.8, 102.3, 73.1, 72.9, 52.5, 40.6, 37.4, 35.1.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{24}H_{32}O_4Na$, 407.2198; found, 407.2181.

3,3-Bis(benzyloxymethyl)-5,5-dimethoxypentanal



To a solution of [({2-[(benzyloxy)methyl]-2-(2,2-dimethoxyethyl)pent-4-en-1-yl}oxy)methyl] benzene (1.50 g, 3.90 mmol) in THF/*t*-BuOH/H_2O (1:1:1, 60 mL) was added OsO_4 solution (0.05 M in THF, 3.90 mL, 0.195 mmol). The mixture was stirred for 30 min at room

temperature before addition of $NaIO_4$ (2.09 g, 9.75 mmol). The mixture was stirred for 1.5 h at room temperature, and then diluted with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (8:1)] to afford 3,3-bis(benzyloxymethyl)-5,5-dimethoxy-pentanal (932 mg, 60%) as a colorless oil.

R_f = 0.47 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2932, 2860, 1708, 1454, 1114, 1098, 1076, 737, 698.

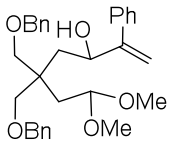
^1H NMR (400 MHz, $CDCl_3$): δ 9.78 (t, 1H, *J* = 2.4 Hz), 7.34-7.25 (m, 10H), 4.50 (t, 1H, *J* = 5.6 Hz), 4.46 (s, 4H), 3.48 (d, 2H, *J* = 9.2 Hz), 3.43 (d, 2H, *J* = 9.2 Hz), 3.24 (s, 6H), 2.48 (d, 2H, *J* = 2.4 Hz), 1.84 (d, 2H, *J* = 5.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 138.1, 128.3, 127.5, 127.5, 102.1, 73.3, 73.2, 52.6, 47.4, 41.0, 35.8.

LRMS (EI) m/z (relative intensity):354 (2), 323 (4), 278 (23).

HRMS (EI, $[M\text{-}MeOH]^+$]): calcd for $C_{22}H_{26}O_4$, 354.1831; found, 354.1826.

5,5-Bis(benzyloxymethyl)-7,7-dimethoxy-2-phenylhept-1-en-3-ol



Alkenylation of 3,3-bis(benzyloxymethyl)-5,5-dimethoxy-pentanal (930 mg, 2.41 mmol) with α-styryl Grignard reagent gave 5,5-bis(benzyloxymethyl)-7,7-dimethoxy-2-phenylhept-1-en-3-ol (916 mg, 67%).

Column: hexane – EtOAc (8:1). Yellow oil.

R_f = 0.50 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3433, 2929, 2861, 1454, 1365, 1115, 1075, 1028, 737, 698.

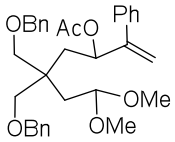
^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.21 (m, 15H), 5.41 (s, 1H), 5.24 (s, 1H), 4.77 (m, 1H), 4.51 (m, 1H), 4.47-4.45 (m, 4H), 4.38 (dd, 1H, *J* = 6.4, 4.4 Hz), 3.47 (d, 1H, *J* = 9.2 Hz), 3.40 (d, 1H, *J* = 9.2 Hz), 3.19 (s, 3H), 3.16 (s, 3H), 1.83 (dd, 1H, *J* = 14.8, 6.4 Hz), 1.72 (m, 2H), 1.46 (dd, 2H, *J* = 14.8, 10.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 140.4, 137.9, 128.3, 128.3, 128.1, 127.6, 127.6, 127.6, 127.2, 126.9, 111.8, 102.1, 73.7, 73.4, 73.3, 73.3, 69.4, 53.1, 52.0, 41.1, 40.2, 35.5.

LRMS (EI) m/z (relative intensity): 458 $[M\text{-}MeOH]^+$ (11), 426 (14), 335(64).

HRMS (EI, $[M\text{-}MeOH]^+$]): calcd for $C_{30}H_{34}O_4$, 458.2457; found, 458.2463.

5,5-Bis(benzyloxymethyl)-7,7-dimethoxy-2-phenylhept-1-en-3-yl acetate



Acetylation of 5,5-bis(benzyloxymethyl)-7,7-dimethoxy-phenylhept-1-en-3-ol (400 mg, 0.815mmol) with Ac_2O from gave 5,5-bis(benzyloxymethyl)-7,7-dimethoxy-2-phenylhept-1-en-3-yl acetate (391 mg, 90%).

Column: hexane – EtOAc (8:1). Yellow oil.

R_f = 0.63 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2931, 2858, 1739, 1454, 1367, 1237, 1119, 1099, 1076, 698.

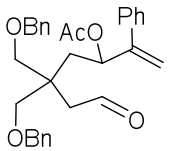
^1H NMR (400 MHz, $CDCl_3$): δ 7.43-7.41 (m, 2H), 7.31-7.20 (m, 13H), 5.91 (d, 1H, *J* = 9.6 Hz), 5.21 (s, 1H), 5.20 (s, 1H), 4.49 (t, 1H, *J* = 5.2 Hz), 4.46-4.38 (m, 4H), 3.41-3.31 (m, 4H), 3.19 (s, 3H), 3.14 (s, 3H), 2.00 (s, 3H), 1.91 (dd, 1H, *J* = 15.2, 9.6 Hz), 1.74-1.70 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 150.3, 139.2, 138.5, 138.5, 128.2, 128.2, 127.6, 127.4, 127.3, 127.0, 112.4, 102.0, 73.1,73.1, 73.1, 72.8, 72.7, 52.4, 51.9, 40.3, 37.4, 35.2, 21.3.

LRMS (EI) m/z (relative intensity):532 $[M]^+$ (0.3), 500 (2), 442 (41).

HRMS (EI, $[M]^+$]): calcd for $C_{33}H_{40}O_6$, 532.2825; found, 532.2811.

5,5-Bis(benzyloxymethyl)-7-oxo-2-phenylhept-1-en-3-yl acetate (13f)



To a solution of 5,5-bis(benzyloxymethyl)-7,7-dimethoxy-2-phenylhept-1-en-3-yl acetate (150 mg, 0.282 mmol) in AcOH/THF/H_2O (1:1:1, 1.2 mL) was added 3 M HCl aq. (one drop). The mixture was stirred at room temperature for 4 h, and then basified with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (3:1)] to afford 5,5-bis(benzyloxymethyl)-7-oxo-2-phenylhept-1-en-3-yl acetate (**13f**) (128 mg, 94%) as a yellow oil.

R_f = 0.69 (4:1 toluene/EtOAc).

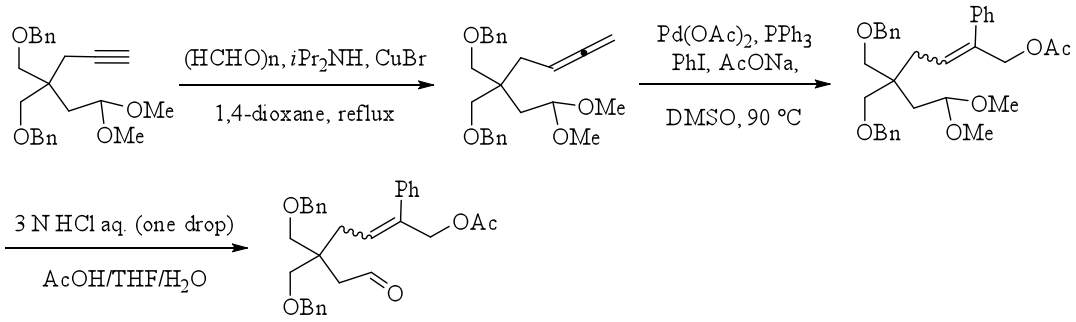
IR ν (neat, cm^{-1}): 3030, 2859, 1740, 1717, 1368, 1233, 1096, 1027, 698.

^1H NMR (400 MHz, $CDCl_3$): δ 9.74 (t, 1H, *J* = 2.4 Hz), 7.40-7.38 (m, 2H), 7.33-7.20 (m, 13H), 5.87 (dd, 1H, *J* = 10.0, 1.6 Hz), 5.24 (s, 1H), 5.19 (s, 1H), 4.41 (m, 4H), 3.47-3.37 (m, 4H), 2.45 (dd, 1H, *J* = 15.6, 2.4 Hz), 2.40 (dd, 1H, 15.6, 2.4 Hz), 2.01 (s, 3H), 1.97 (dd, 1H, *J* = 15.2, 10.0 Hz), 1.83 (dd, 1H, *J* = 15.2, 1.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): 201.6, 175.1, 169.9, 149.7, 138.9, 138.0, 128.4, 128.3, 127.9, 127.6, 127.5, 127.5, 126.9, 112.7, 73.3, 73.1, 73.1, 72.6, 72.5, 47.6, 41.9, 37.7, 21.3.

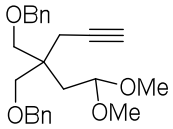
LRMS (EI) m/z (relative intensity): 486 $[M]^+$ (0.1), 426 (11), 395 (7), 335 (37).

HRMS (EI, $[M]^+$]): calcd for $C_{31}H_{34}O_5$, 486.2406; found, 48602419.



13f'

[({2-[(Benzyloxy)methyl]-2-(2,2-dimethoxyethyl)pent-4-yn-1-yl}oxy)methyl]benzene



[({2-[(Benzyloxy)methyl]-2-(2,2-dimethoxyethyl)pent-4-yn-1-yl}oxy)methyl]benzene was prepared according to the modified literature procedureエラー! 参照元が見つかりません。 using 3-bromo-1-propyne instead of 1-bromo-2-butyne.

Colorless oil.

R_f = 0.45 (4:1 hexane/EtOAc).

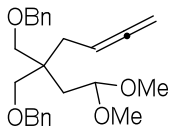
IR ν (neat, cm^{-1}): 3292, 2928, 2905, 2862, 1454, 1365, 1099, 698.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.31 (m, 10H), 4.57 (t, 1H, *J* = 6.0 Hz), 4.50 (s, 4H), 3.45 (s, 4H), 3.26 (s, 6H), 2.39 (d, 2H, *J* = 2.4 Hz), 1.94 (t, 1H, *J* = 2.4 Hz), 1.80 (d, 2H, *J* = 6.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 128.2, 127.4, 127.3, 102.1, 81.4, 70.3, 52.5, 40.4, 34.5, 22.9.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{24}H_{30}O_4Na$, 405.2042; found, 405.2023.

[({2-[(Benzyloxy)methyl]-2-(2,2-dimethoxyethyl)hexa-4,5-dien-1-yl}oxy)methyl]benzene



To a solution of [({2-[(benzyloxy)methyl]-2-(2,2-dimethoxyethyl)pent-4-yn-1-yl}oxy)methyl] benzene (2.50 g, 6.54 mmol) in anhydrous 1,4-dioxane (65 mL) were added paraformaldehyde

(393 mg, 13.1 mmol), CuBr (281 mg, 1.96 mmol) and diisopropylamine (1.8 mL, 13 mmol). The mixture was refluxed for 9 h with stirring, and then treated with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (14:1)] to afford [({2-[(benzyloxy)methyl]-2-(2,2-dimethoxy-ethyl)hexa-4,5-dien-1-yl}oxy)methyl]benzene (930 mg, 37%) as a yellow oil.

R_f = 0.50 (4:1 hexane/EtOAc).

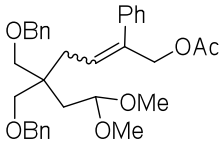
IR ν (neat, cm^{-1}): 2928, 2858, 1954, 1454, 1364, 1116, 1098, 1076, 698.

^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 10 H), 5.06 (tt, 1H, *J* = 7.6, 7.6 Hz), 4.61-4.55 (m, 3H), 4.49 (s, 4H), 3.38 (s, 4H), 3.26 (s, 6H), 2.17 (dt, 2H, *J* = 7.6, 2.4 Hz), 1.70 (d, 2H, 2.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.9, 138.7, 128.2, 127.4, 127.3, 102.3, 85.5, 73.5, 73.1, 72.7, 52.5, 41.0, 34.9, 32.4.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{25}H_{32}O_4Na$, 419.2198 found, 419.2180.

5,5-Bis[(benzyloxy)methyl]-7,7-dimethoxy-2-phenylhept-2-en-1-yl acetate[10)]



To a solution of [({2-[(benzyloxy)methyl]-2-(2,2-dimethoxyethyl)hexa-4,5-dien-1-yl}oxy)methyl]benzene (80.0 mg, 0.232 mmol) in anhydrous DMSO (3.5 mL) were added $Pd(OAc)_2$ (5.2 mg, 0.023 mmol), PPh_3 (12.1 mg, 0.046 mmol), iodobenzene (38.7 μL, 0.347 mmol) and sodium acetate (94.9 mg, 1.16 mmol). The mixture was stirred at 90 °C for 10 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (10:1)] to afford 5,5-bis[(benzyloxy)methyl]-7,7-dimethoxy-2-phenylhept-2-en-1-yl acetate (85.1 mg, 69%, *E*:*Z* = 3:1) as a yellow oil.

R_f = 0.33 (4:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2931, 2858, 1738, 1496, 1454, 1366, 1230, 1120, 1099, 1076, 699.

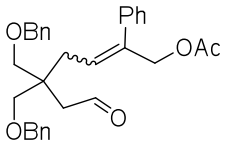
^1H NMR (400 MHz, $CDCl_3$): *E* isomer: δ 7.31-7.17 (m, 15H), 6.10 (t, 1H, *J* = 8.0 Hz), 5.03 (s, 2H), 4.55 (t, 1H, *J* = 5.6 Hz), 4.48 (s, 4H), 3.40 (s, 4H), 3.25 (s, 6H), 2.46 (d, 2H, *J* = 8.0 Hz), 1.93 (s, 3H), 1.74 (d, 2H, *J* = 5.6 Hz). *Z* isomer: δ 7.31-7.17 (m, 15H), 5.86 (t, 1H, *J* = 8.0 Hz), 4.73 (s, 2H), 4.42 (s, 4H), 4.38 (t, 1H, *J* = 5.6 Hz), 3.32 (s, 4H), 3.15 (s, 6H), 2.21 (d, 2H, *J* = 8.0 Hz), 1.96 (s, 3H), 1.63 (d, 2H, *J* = 5.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): *E* + *Z* mixture: δ 171.0, 170.7, 140.9, 138.7, 138.5, 138.0, 137.2,

136.0, 130.8, 128.7, 128.2, 128.2, 128.1, 127.7, 127.5, 127.4, 127.3, 127.3, 127.0, 127.0, 126.1, 102.4, 102.2, 73.2, 73.1, 72.9, 72.7, 69.2, 61.1, 52.7, 52.4, 41.3, 40,9, 35.2, 35.2, 32.0, 31.8, 20.9, 20.9.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{33}H_{40}O_6Na$, 555.2723; found, 555.2709.

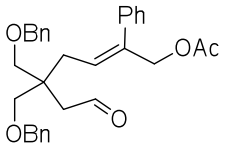
5,5-Bis[(benzyloxy)methyl]-7-oxo-2-phenylhept-2-en-1-yl acetate (13f')



13f' (102 mg, 74%, *E*:*Z* = 3.2:1) was prepared from 5,5-bis[(benzyloxy)methyl]-7,7-dimethoxy-2-phenylhept-2-en-1-yl acetate (150 mg, 0.282 mmol) through deperotection with acid.

PTLC: toluene – EtOAc (9:1) 2 times. Pale yellow oil.

(*E*)-13f'



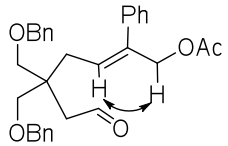
R_f = 0.21 (9:1 toluene/EtOAc).

IR ν (neat, cm^{-1}): 2859, 1738, 1717, 1454, 1366, 1227, 1097, 1027, 738, 700.

^1H NMR (400 MHz, $CDCl_3$): δ 9.62 (t, 1H, *J* = 2.8 Hz), 7.31-7.20 (m, 15H), 5.78 (t, 1H, *J* = 8.0 Hz), 4.72 (s, 2H), 4.41 (s, 4H), 3.40 (d, 2H, *J* = 8.8 Hz), 3.33 (d, 2H, *J* = 8.8 Hz), 2.31 (d, 2H, *J* = 2.8 Hz), 2.27 (d, 2H, *J* = 8.0 Hz), 1.98 (s, 3H).

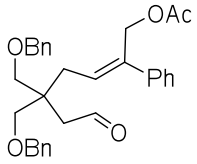
^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 170.6, 138.6 138.1 137.6, 128.6, 128.3, 127.5, 127.5, 127.4, 127.3, 126.0, 73.2, 72.7, 68.9, 47.5, 43.0, 32.1, 20.9.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{31}H_{34}O_5Na$, 509.2304; found, 509.2292.



NOESY correlation of **(*E*)-13f'**

(*Z*)-13f'



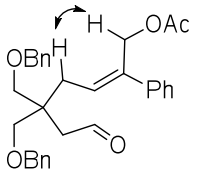
R_f = 0.22 (9:1 toluene/EtOAc).

IR ν (neat, cm^{-1}): 2859, 1737, 1717, 1496, 1454, 1366, 1237, 1098, 1027, 739, 698.

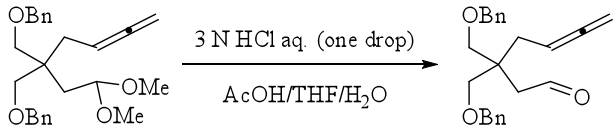
^1H NMR (400 MHz, $CDCl_3$): δ 9.81 (t, 1H, *J* = 2.8 Hz), 7.32-7.23 (m, 15H), 5.98 (t, 1H, *J* = 8.0 Hz), 5.00 (s, 2H), 4.47 (s, 4H), 3.49 (d, 2H, *J* = 9.2 Hz), 3.45 (d, 2H, *J* = 9.2 Hz), 2.53 (d, 2H, *J* = 8.0 Hz), 2.47 (d, 2H, *J* = 2.8 Hz), 1.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 170.9, 140.5, 138.0, 137.0, 129.3, 128.3, 128.3, 127.6, 127.6, 127.3, 126.1, 73.4, 72.6, 60.8, 47.5, 43.3, 32.3, 20.8.

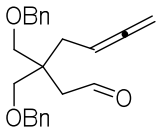
HRMS (ESI, $[M+Na]^+$]): calcd for $C_{31}H_{34}O_5Na$, 509.2304; found, 509.2292.



NOESY correlation of **(*Z*)-13f'**



3,3-Bis[(benzyloxy)methyl]hepta-5,6-dienal



Deacetalization of [({2-[(benzyloxy)methyl]-2-(2,2-dimethoxyethyl)hexa-4,5-dien-1-yl}oxy) methyl]benzene (90.0 mg, 0.229 mmol) with 3 M HCl aq. and AcOH/THF/H_2O gave 3,3-Bis[(benzyloxy)methyl]hepta-5,6-dienal (79.0 mg, quant.).

Column: toluene – EtOAc (14:1). Colorless oil.

R_f = 0.58 (9:1 toluene/EtOAc).

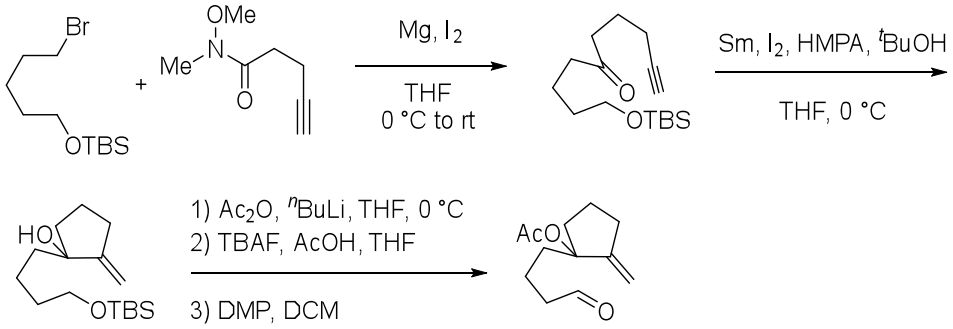
IR ν (neat, cm^{-1}): 3030, 2917, 2860, 1954, 1717, 1496, 1454, 1365, 1205, 1097, 850, 698.

^1H NMR (400 MHz, $CDCl_3$): δ 9.80 (t, 1H, *J* = 2.8 Hz), 7.33-7.24 (m, 10H), 5.00 (dddd, 1H, *J* = 8.4, 8.4, 6.8, 6.8 Hz), 4.62 (dd, 1H, *J* = 6.8, 2.4 Hz), 4.61 (dd, 1H, *J* = 6.8, 2.4 Hz), 4.48 (m, 4H), 3.47 (d, 2H, *J* = 9.2 Hz), 3.43 (d, 2H, *J* = 9.2 Hz), 2.43 (d, 2H, *J* = 2.8 Hz), 2.26 (dd, 1H, *J* = 8.4,

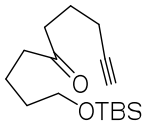
2.4 Hz), 2.25 (dd, 1H, J = 8.4, 2.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.1, 202.1, 138.2, 128.3, 127.6, 127.5, 84.7, 74.1, 73.3, 72.6, 47.3, 43.2, 32.8.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{23}H_{26}O_3Na$, 373.1780; found, 373.1765.



1-[(*tert*-Butyldimethylsilyl)oxy]dec-9-yn-5-one



A slurry of magnesium turnings (546 mg, 22.4 mmol) in THF (10 mL) was treated with a few crystals of iodine. A solution of {(5-bromopentyl)oxy}(*tert*-butyl)dimethylsilane[11] (4.0 g, 15.0 mmol) in THF (5 mL) was added dropwise to the magnesium slurry. The mixture was refluxed for 1 h with stirring before addition of Weinreb amide[12] (928 mg, 5.99 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature for 9 h, and then treated with aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (30:1)] to afford 1-((*tert*-butyldimethylsilyl)oxy)dec-9-yn-5-one (1.42 g, 84%) as a colorless oil.

R_f = 0.51 (4:1 hexane/EtOAc).

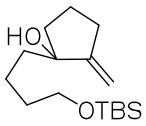
IR ν (neat, cm^{-1}): 3308, 2954, 2929, 2858, 1716, 1472, 1463, 1361, 1256, 1101, 837, 776.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (t, 2H, J = 6.0 Hz), 2.55 (t, 2H, J = 7.2 Hz), 2.44 (t, 2H, J = 7.2 Hz), 2.23 (dt, 2H, J = 7.2, 2.8 Hz), 1.95 (t, 1H, J = 2.8 Hz), 1.79 (tt, 2H, J = 7.2, 7.2 Hz), 1.67-1.60 (m, 2H), 1.54-1.47 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.0, 83.4, 68.9, 62.6, 42.5, 40.8, 32.1, 25.8, 22.1, 20.2, 18.2, 17.6, −5.5.

HRMS (ESI, $[M+Na]^+$)): calcd for $C_{16}H_{30}O_2SiNa$, 305.1913; found, 305.1905.

1-{4-[(*tert*-Butyldimethylsilyl)oxy]butyl}-2-methylenecyclopentan-1-ol



SmI_2 was prepared according to the literature procedure[13]; Samarium powder (3.00 g, 20.0 mmol) was stirred under argon for 24 h before 75 mL of THF was added. To the slurry were added iodine (2.53 g, 9.98 mmol) dissolved in THF (25 mL), and then the resulting mixture was stirred at 60 °C for 18 h. To the SmI_2 solution was added HMPA (6.9 mL, 40 mmol), and a solution of 1-((*tert*-butyldimethylsilyl)oxy)dec-9-yn-5-one (939 mg, 3.33 mol) and *tert*-butyl alcohol (0.95 mL, 9.98 mmol) in THF (30 mL) successively at 0 °C. The mixture was stirred at 0 °C for 1.5 h, and then treated with water. The aqueous layer was extracted with Et_2O twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (20:1)] to afford 1-{4-[(*tert*-butyldimethylsilyl)oxy]butyl}-2-methylenecyclopentanol (626 mg, 66%) as a yellow oil.

R_f = 0.40 (4:1 hexane/EtOAc).

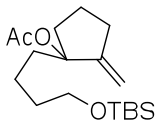
IR ν (neat, cm^{-1}): 3406, 2954, 2929, 2858, 1472, 1255, 1101, 836, 773.

^1H NMR (400 MHz, $CDCl_3$): δ 5.04 (s, 1H), 4.96 (s, 1H), 3.63 (t, 2H, J = 6.0 Hz), 2.55-2.48 (m, 1H), 2.36-2.28 (m, 1H), 1.75 (m, 3H), 1.69-1.61 (m, 2H), 1.59-1.36 (m, 6H), 0.90 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 105.8, 80.5, 63.1, 39.3, 39.2, 33.3, 31.7, 26.0, 21.5, 20.7, 18.3, −5.3.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{16}H_{32}O_2SiNa$, 307.2069; found, 307.2062.

1-{4-[(*tert*-Butyldimethylsilyl)oxy]butyl}-2-methylenecyclopentyl acetate



To the solution of 1-{4-[(*tert*-butyldimethylsilyl)oxy]butyl}-2-methylenecyclopentanol (86.8 mg, 0.306 mmol) in anhydrous THF (1.5 mL) was added *n*-BuLi (2.6 M in THF, 0.18 mL, 0.46 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h before addition of Ac_2O (46 μL, 0.489 mmol). The mixture was stirred at room temperature for 1 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (24:1)] to afford 1-{4-[(*tert*-butyldimethylsilyl)oxy]butyl}-2-methylenecyclopentyl acetate (40.8 mg, 41%, 98% b.r.s.m.) as a colorless oil.

R_f = 0.67 (4:1 hexane/EtOAc).

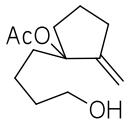
IR ν (neat, cm^{-1}): 2954, 2930, 2858, 1740, 1366, 1250, 1102, 836, 775.

^1H NMR (400 MHz, $CDCl_3$): δ 4.98 (s, 2H), 3.56 (t, 2H, *J* = 6.0 Hz), 2.55-2.47 (m, 1H), 2.30-2.23 (m, 1H), 2.15 (dt, 1H, *J* = 13.2, 7.6 Hz), 1.96-1.65 (m, 6H), 1.58-1.21 (m, 6H), 0.84 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 153.2, 107.5, 89.0, 62.9, 37.7, 36.6, 33.0, 31.4, 25.9, 22.1, 22.0, 20.2, 18.3, –5.3.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{18}H_{34}O_3SiNa$, 349.2175; found, 349.2168.

1-(4-Hydroxybutyl)-2-methylenecyclopentyl acetate



To a solution of 1-{4-[(*tert*-butyldimethylsilyl)oxy]butyl}-2-methylenecyclopentyl acetate (39.9 mg, 0.123 mmol) in anhydrous THF (1 mL) were added TBAF (1.0 M in THF, 0.25 mL, 0.245 mmol) and AcOH (21 μL, 0.368 mmol). The mixture was stirred at room temperature for 20 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (4:1)] to afford 1-(4-hydroxybutyl)-2-methylenecyclopentyl acetate (21.6 mg, 83%) as a yellow oil.

R_f = 0.11 (4:1 hexane/EtOAc).

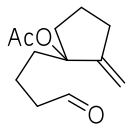
IR ν (neat, cm^{-1}): 3422, 2947, 2872, 1733, 1659, 1434, 1368, 1251, 1181, 1020, 893.

^1H NMR (400 MHz, $CDCl_3$): δ 5.04 (m, 2H), 3.65 (t, 2H, *J* = 6.4 Hz), 2.60-2.52 (m, 1H), 2.36-2.28 (m, 1H), 2.19 (dt, 1H, *J* = 13.2 7.6 Hz), 2.00-1.91 (m, 4H), 1.89-1.74 (m, 2H), 1.59-1.33 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 153.1, 107.6, 88.9, 62.7, 37.5, 36.7, 32.9, 31.4, 22.2, 21.9, 20.2.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{12}H_{20}O_3Na$, 235.1310; found, 235.1304.

2-Methylene-1-(4-oxobutyl)cyclopentyl acetate (13g)



Dess-Martin oxidation of 1-(4-hydroxybutyl)-2-methylenecyclopentyl acetate (130.1 mg, 0.612 mmol) gave **13g** (79.4 mg, 61%).

Column: hexane – EtOAc (14:1). Colorless oil.

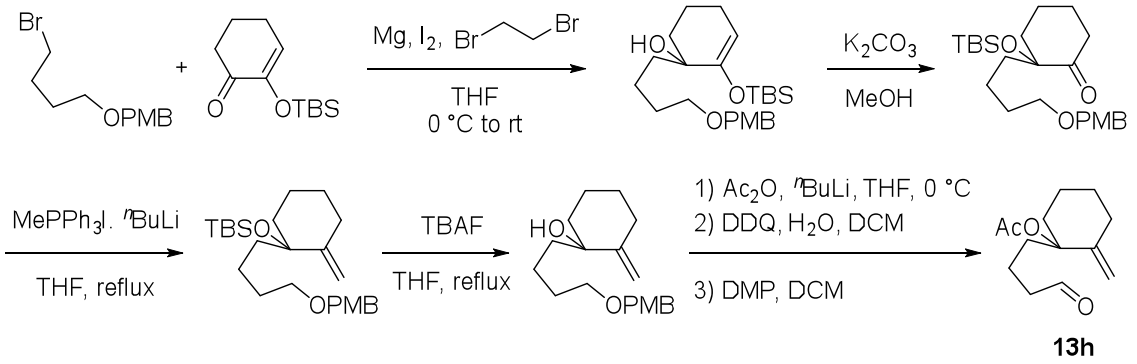
R_f = 0.40 (4:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2956, 1735, 1434, 1368, 1249, 1183, 1018, 894.

^1H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 5.05 (s, 1H), 5.05 (s, 1H), 2.61-2.53 (m, 1H), 2.46 (t, 2H, *J* = 7.2 Hz), 2.38-2.29 (m, 1H), 2.19 (dt, 1H, *J* = 13.2, 8.0 Hz), 2.01-1.55 (m, 10H).

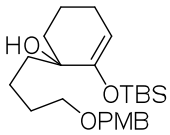
^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 169.8, 152.8, 107.8, 88.5, 43.9, 37.1, 36.6, 31.3, 22.1, 21.9, 16.6.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{12}H_{18}O_3Na$, 233.1154; found, 233.1149.



13h

2-[(*tert*-Butyldimethylsilyl)oxy]-1-{4-[(4-methoxybenzyl)oxy]butyl}cyclohex-2-en-1-ol[14)]



To a stirred mixture of magnesium turnings (678 mg, 27.9 mmol) and iodine (1 crystal) in anhydrous THF (8.0 mL) under reflux, a solution of 1-[(4-bromobutoxy)methyl]-4-methoxybenzene[15)] (5.70 g, 20.9 mmol) in anhydrous THF (2.0 mL) was added. Then a catalystic amount of 1,2-dibromoethane was added, and the reaction mixture was stirred for 2 h under reflux. To a solution of Grignard reagent was added a solution of 2-{(*tert*-butyldimethylsilyl)oxy}cyclohex-2-en-1-one[14)] (3.16 g, 13.9 mmol) in anhydrous THF (10 mL) at 0 °C. The mixture was stirred for 9 h, and then treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (20:1)] to afford 2-[(*tert*-butyldimethylsilyl)oxy]-1-{4-[(4-methoxybenzyl)oxy]butyl}cyclohex-2-en-1-ol (3.97 g, 68%) as a colorless oil.

R_f = 0.41 (4:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3485, 2932, 2857, 1513, 1248, 1180, 1098, 838, 780.

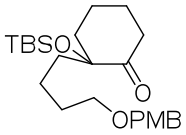
^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 2H, *J* = 8.8 Hz), 6.86 (d, 2H, *J* = 8.8 Hz), 4.80 (dd, 1H, *J* = 4.8, 3.6 Hz), 4.42 (s, 2H), 3.79 (s, 3H), 3.43 (t, 2H, *J* = 6.8 Hz), 2.09-1.92 (m, 3H),

1.79-1.46 (m, 8H), 1.48-1.23 (m, 2H), 0.93 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 152.3, 130.7, 129.1, 113.6, 103.8, 72.4, 72.3, 70.0, 55.1, 39.1, 34.1, 30.3, 25.7, 24.3, 20.6, 19.3, 18.1, –4.6.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{24}H_{40}O_4SiNa$, 443.2594; found, 443.2581.

2-[(*tert*-Butyldimethylsilyl)oxy]-2-{4-[(4-methoxybenzyl)oxy]butyl}cyclohexan-1-one[14)]



To a solution of silyl enol ether (3.97 g, 9.44 mmol) in anhydrous MeOH (20 mL) was added K_2CO_3 (261 mg, 1.89 mmol). The mixture was stirred for 1 h, and then diluted with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (25:1)] to afford 2-[(*tert*-butyldimethylsilyl)oxy]-2-{4-[(4-methoxybenzyl)oxy]butyl}cyclohexan-1-one (3.77 g, 95%) as a colorless oil.

R_f = 0.56 (4:1 hexane/EtOAc).

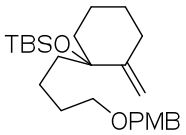
IR ν (neat, cm^{-1}): 2951, 2935, 2855, 1723, 1616, 1513, 1248, 1099, 836, 777.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.8 Hz), 4.41 (s, 2H), 3.78 (s, 3H), 3.42 (ddd, 2H, *J* = 6.0, 6.0, 1.2 Hz), 2.48 (dt, 1H, *J* = 13.6, 4.8 Hz), 2.37-2.29 (m, 1H), 1.92-1.84 (m, 2H), 1.82-1.71 (m, 3H), 1.69-1.56 (m, 5H), 1.50-1.39 (m, 1H), 1.26-1.18 (m, 1H), 0.87 (s, 9H), 0.16 (s, 3H), 0.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 159.0, 130.6, 129.1, 113.6, 81.8, 72.4, 69.8, 55.1, 40.8, 39.4, 37.8, 29.9, 27.3, 25.9, 22.4, 19.7, 18.5, –2.5, –3.0.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{24}H_{40}O_4SiNa$, 443.2594; found, 443.2579.

***tert*-Butyl{(1-[4-{(4-methoxybenzyl)oxy}butyl]-2-methylenecyclohexyl)oxy}dimethylsilane**



To a solution of methyltriphenylphosphonium iodide (21.2 g, 52.3 mmol) in anhydrous THF (80 mL) was added *n*-BuLi (2.6 M in THF, 20 ml, 52 mmol) at 0 °C. The mixture was stirred for 1 h at same temperature, and then a solution of 2-[(*tert*-butyldimethylsilyl)oxy]-2-{4-[(4-methoxybenzyl)oxy]butyl}cyclohexan-1-one (3.67 g, 8.72 mmol) in anhydrous THF (10 mL) was added. The mixture was refluxed for 12 h with stirring, and then treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was

purified by silica gel chromatography [toluene – hexane (1:4)] to afford *tert*-butyl {(1-[4-{(4-methoxybenzyl)oxy}butyl]-2-methylenecyclohexyl)oxy}dimethylsilane (2.34 g, 64%) as a colorless oil.

R_f = 0.71 (4:1 hexane/EtOAc).

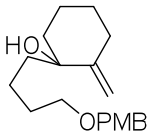
IR ν (neat, cm^{-1}): 2933, 2856, 1612, 1513, 1465, 835, 772.

^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 2H, *J* = 8.0 Hz), 6.86 (d, 2H, *J* = 8.0 Hz), 4.98 (s, 1H), 4.71 (s, 1H), 4.42 (s, 2H), 3.80 (s, 3H), 3.42 (m, 2H), 2.28 (d, 1H, *J* = 13.2 Hz), 1.97 (t, 1H, *J* = 13.2 Hz), 1.86-1.26 (m, 11H), 1.23-.15 (m, 1H), 0.91 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 159.1, 152.4, 130.8, 129.2, 113.7, 107.4, 78.3, 72.5, 70.3, 55.2, 41.7, 37.9, 33.9, 30.1, 27.8, 26.1, 24.0, 19.8, 18.7, –1.6, –2.0.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{25}H_{42}O_3SiNa$, 441.2801; found, 441.2794.

1-{4-[(4-Methoxybenzyl)oxy]butyl}-2-methylenecyclohexan-1-ol



To a solution of *tert*-butyl{(1-[4-{(4-methoxybenzyl)oxy}butyl]-2-methylenecyclohexyl)oxy} dimethylsilane (1.20 g, 2.87 mmol) in anhydrous THF (15 mL) was added TBAF (1.0 M in THF, 28.6 mL, 28.6 mmol). The mixture was refluxed for 6 d with stirring, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (4:1)] to afford 1-{4-[(4-methoxybenzyl)oxy]butyl}-2-methylenecyclohexan-1-ol (820 mg, 94%) as a colorless oil.

R_f = 0.24 (4:1 hexane/EtOAc).

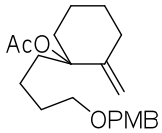
IR ν (neat, cm^{-1}): 3457, 2934, 2857, 1642, 1613, 1586, 1515, 1247, 1097, 1034, 820.

H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 2H, *J* = 8.0 Hz), 6.86 (d, 2H, *J* = 8.0 Hz), 4.89 (s, 1H), 4.77 (s, 1H), 4.42 (s, 2H), 3.80 (s, 3H), 3.44 (t, 2H, *J* = 6.4 Hz), 2.32 (d, 1H, *J* = 13.2 Hz), 2.02 (m, 1H), 1.81 (m, 1H), 1.74-1.69 (m, 3H), 1.62-1.26 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 59.1, 153.4, 130.7, 129.2, 113.7, 106.2, 75.2, 72.5, 70.0, 55.2, 4103, 36.8, 33.8, 30.0, 27.9, 23.8, 19.7.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{19}H_{28}O_3Na$, 327.1936; found, 327.1925.

1-{4-[(4-Methoxybenzyl)oxy]butyl}-2-methylenecyclohexyl acetate



To a solution of 1-{4-[(4-methoxybenzyl)oxy]butyl}-2-methylenecyclohexan-1-ol (761 mg, 2.50 mmol) in anhydrous THF (25 mL) was added *n*-BuLi (2.6 M in THF, 1.4 mL, 3.8 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h before addition of Ac_2O (378 μL, 4.00 mml). The mixture was stirred at room temerature for 1 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (14:1)] to afford 1-{4-[(4-methoxybenzyl)oxy]butyl}-2-methylenecyclohexyl acetate (335 mg, 39%, 98% b.r.s.m.) as a colorless oil.

R_f = 0.39 (4:1 hexane/EtOAc).

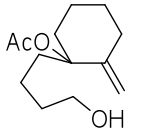
IR ν (neat, cm^{-1}): 2935, 2860, 1734, 1513, 1367, 1239, 1102, 1035.

^1H NMR (400 MHz, $CDCl_3$): 7.25 (d, 2H, *J* = 8.4 Hz), 6.87 (d, 2H, *J* = 8.4 Hz), 4.90 (s, 1H), 4.88 (s, 1H), 3.80 (s, 3H), 3.43 (t, 2H, *J* = 6.4 Hz), 2.25-2.07 (m, 3H), 2.05-1.99 (m, 5H), 1.90-1.84 (m, 1H), 1.72-1.67 (m, 1H), 1.64-1.54 (m, 5H), 1.39-1.21 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): 169.6, 159.1, 148.6, 130.7, 129.2, 113.7, 108.4, 85.0, 72.5, 69.9, 55.2, 37.2, 33.5, 33.2, 29.8, 28.0, 22.5, 22.1, 19.8.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{21}H_{30}O_4Na$, 369.2042; found, 369.2033.

1-(4-Hydroxybutyl)-2-methylenecyclohexyl acetate



To the solution of 1-{4-[(4-methoxybenzyl)oxy]butyl}-2-methylenecyclohexyl acetate (768 mg, 2.22 mmol) in DCM (10 mL) was added DDQ (755 mg, 3.33 mmol) and water (1.1 mL). The mixture was stirred at room temerature for 1 h, and then treated with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (4:1)] to afford 1-(4-hydroxybutyl)-2-methylenecyclohexyl acetate (318 mg, 63%) as a pale yellow oil.

R_f = 0.24 (2:1 hexane/EtOAc).

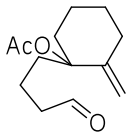
IR ν (neat, cm^{-1}): 3428, 2936, 2864, 1735, 1368, 1256, 1239, 1026.

^1H NMR (400 MHz, $CDCl_3$): δ 4.91 (s, 1H), 4.89 (s, 1H), 3.64 (t, 2H, *J* = 6.4 Hz), 2.27-2.11 (m, 3H), 2.09-1.99 (m, 5H), 1.93-1.87 (m, 1H), 1.76-1.78 (m, 1H), 1.60-1.53 (m, 5H), 1.36-1.26 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 148.5, 108.5, 85.1, 62.7, 37.3, 33.5, 33.1, 32.7, 27.9, 22.5, 22.1, 19.3.

HRMS (ESI, $[M+Na]^+$)): calcd for $C_{13}H_{22}O_3Na$, 249.1467; found, 249.1461.

2-Methylene-1-(4-oxobutyl)cyclohexyl acetate (13h)



Dess-Martin oxidation of 1-(4-hydroxybutyl)-2-methylenecyclohexyl acetate (318 mg, 1.47 mmol) gave **13h (**284 mg, 86%).

Column: hexane – EtOAc (9:1). Colorless oil.

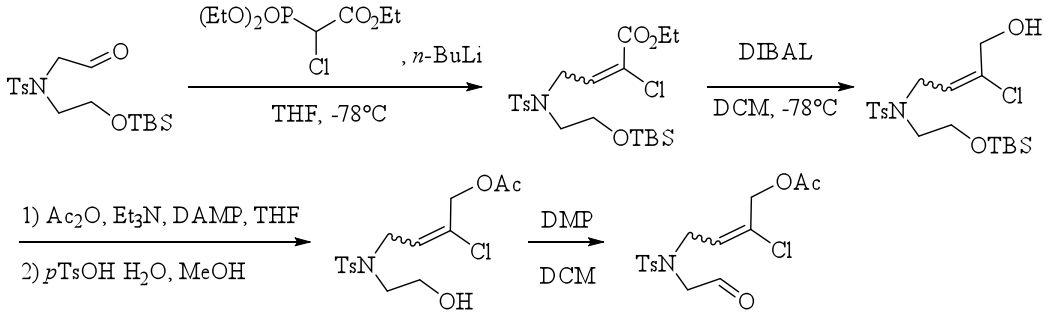
R_f = 0.58 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2937, 2863, 1734, 1368, 1256, 1238.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, 1H, *J* = 1.6 Hz), 4.92 (s, 1H), 4.90 (s, 1H), 2.45 (m, 2H), 2.27-2.22 (m, 1H), 2.15-1.91 (m, 8H), 1.71 (m, 1H), 1.56 (m, 5H).

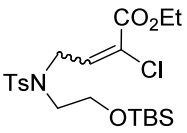
^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 169.5, 148.0, 108.6, 84.7, 43.7, 37.0, 33.3, 32.6, 27.7, 22.4, 21.9, 15.7.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{13}H_{20}O_3Na$, 247.1310; found, 247.1305.



13l

Ethyl 4-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-2-chloro-but-2-enoate



To a solution of triethyl 2-chloro-2-phosphonoacetate (0.69 mL, 3.23 mmol) in anhydrous THF (10 mL) was added *n*-BuLi solution (2.6 M in THF, 1.24 mL, 3.23 mmol). The mixture was stirred for 20 min at room temperature before slow addition of a solution of

N-[2-(*tert*-butyldimethylsilanyloxy)ethyl]-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (1.00 g, 2.69 mmol) in anhydrous THF (10 mL) at −78 °C. The mixture was stirred at −78 °C for 5 h, and then treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (8:1)] to afford ethyl 4-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene)sulfonamide)-2-chlorobut-2-enoate (1.28 g, quant.) as a pale yellow oil.

R_f = 0.60 (2:1 hexane/EtOAc).

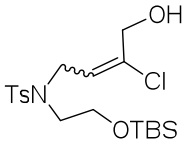
IR ν (neat, cm^{-1}): 2955, 2929, 2857, 1733, 1716, 1348, 1231, 1162, 1091, 837, 779.

^1H NMR (400 MHz, $CDCl_3$): major isomer: δ 7.64 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 2H, *J* = 8.4 Hz), 6.45 (t, 1H, *J* = 5.6 Hz), 4.32 (d, 2H, *J* = 5.6 Hz), 4.22 (q, 2H, 7.2 Hz), 3.72 (t, 2H, *J* = 5.6 Hz), 3.22 (t, 2H, *J* = 5.6 Hz), 2.39 (s, 3H), 1.29 (t, 3H, *J* = 7.2 Hz), 0.82 (s, 9H), 0.00 (s, 6H). minor isomer: δ 7.66 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 2H, *J* = 8.4 Hz), 6.94 (t, 1H, *J* = 5.6 Hz), 4.22 (q, 2H, 7.2 Hz), 4.13 (d, 2H, *J* = 5.6 Hz), 3.72 (t, 2H, *J* = 5.6 Hz), 3.24 (t, 2H, *J* = 5.6 Hz), 2.39 (s, 3H), 1.27 (t, 3H, *J* = 7.2 Hz), 0.82 (s, 9H), 0.00 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): mixture: 162.2, 161.5, 143.6, 142.7, 138.1, 136.4, 129.8, 127.2, 127.1, 125.5, 122.8, 62.6, 62.4, 62.3, 51.2, 50.9, 49.1, 48.4, 25.8, 21.5, 18.2, 14.1, 14.0, −5.54.

HRMS (ESI, $[M+Na]^+$)): calcd for $C_{21}H_{34}ClNO_5SSiNa$, 498.1513; found, 498.1500.

_N_-{2-[(_tert_-Butyldimethylsilyl)oxy]ethyl}-3-chloro-4-hydroxy-S-(4-methylphenyl)but-2-ene-1-sulfonamide



To a solution of ethyl 4-(*N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}(4-methylbenzene) sulfonamide)-2-chlorobut-2-enoate (1.28 g, 2.69 mmol) in anhydrous DCM (15 mL) was added DIBAL solution (1.0 M in toluene, 8.1 mL, 8.1 mmol) at −78 °C. The mixture was allowed to warm up to 0 °C and stirred for 2 h, and then treated with MeOH and aqueous Rochelle salt. The mixture was stirred for 1.5 h, and then aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography [hexane – EtOAc (6:1)] to afford *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-3-chloro-4-hydroxy-*S*-(4-methylphenyl)but-2-ene-1-sulfonamide (941 mg, 81%) as a colorless oil.

R_f = 0.39 (2:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 3470, 2958, 2932, 2857, 1342, 1159, 1090, 836.

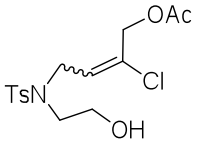
^1H NMR (400 MHz, $CDCl_3$): major isomer: δ 7.63 (d, 2H, *J* = 8.4 Hz), 7.26 (d, 2H, *J* = 8.4 Hz),

5.68 (t, 1H, J = 7.6 Hz), 4.24 (brs, 2H), 3.98 (d, 2H, J = 7.6 Hz), 3.70 (t, 2H, J = 6.0 Hz), 3.21 (t, 2H, J = 6.0 Hz), 2.63 (br s, 1H), 2.38 (s, 3H), 0.82 (s, 9H), 0.03 (s, 6H). minor isomer: δ 7.65 (d, 2H, J = 8.4 Hz), 7.26 (d, 2H, J = 8.4 Hz), 5.78 (t, 1H, J = 6.4 Hz), 4.08 (m, 2H), 4.00 (d, 2H, J = 6.4 Hz), 3.69 (t, 2H, J = 4.0 Hz), 3.20 (t, 2H, J = 4.0 Hz), 2.63 (br s, 1H), 2.38 (s, 3H), 0.82 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): mixture: 143.6, 143.4, 137.0, 136.9, 136.8, 135.6, 129.8, 129.7 127.2, 127.1, 125.3, 122.4, 66.1, 63.0, 62.1, 61.8, 50.0, 49.9, 47.1, 46.6, 25.8, 25.8, 21.5, 18.2, 14.2, −5.49, −5.52.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{19}H_{32}ClNO_4SSiNa$, 456.1407; found, 456.1401.

2-Chloro-4-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]but-2-en-1-yl acetate



2-Chloro-4-[*N*-(2-hydroxyethyl)(4-methylbenzene)sulfonamide]but-2-en-1-yl acetate (89.3 mg, 78%) was prepared from *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-3-chloro-4-hydroxy-*S*-(4-methylphenyl)but-2-ene-1-sulfonamide (136 mg, 1.96 mmol) through acetylation with Ac_2O and desilylation with *p*-toluenesulfonic acid monohydrate.

Column: hexane – EtOAc (2:1). Colorless oil.

R_f = 0.41 (1:1 hexane/EtOAc).

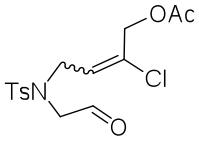
IR ν (neat, cm^{-1}): 3530, 2954, 2928, 2860, 1744, 1339, 1227, 1160, 1090, 1035.

^{1}H NMR (400 MHz, $CDCl_3$): major isomer: δ 7.70 (d, 2H, J = 8.4 Hz), 7.33 (d, 2H, J = 8.4 Hz), 5.78 (t, 1H, J = 7.2 Hz), 4.71 (s, 2H), 4.07 (d, 2H, J = 7.2 Hz), 3.75 (br s, 2H), 3.28 (m, 2H), 2.44 (s, 3H), 2.21 (brs, 1H), 2.07 (s, 3H). minor isomer: δ 7.70 (d, 2H, J = 8.4 Hz), 7.33 (d, 2H, J = 8.4 Hz), 5.83 (t, 1H, J = 6.8 Hz), 4.60 (s, 2H), 4.04 (d, 2H, J = 6.8 Hz), 3.75 (br s, 2H), 3.25 (m, 2H), 2.44 (s, 3H), 2.21 (brs, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): mixture: δ: 170.6, 143.8, 136.4, 131.6, 131.3, 130.0, 128.6, 127.3, 127.1, 124.8, 66.3, 61.9, 61.5, 60.9, 50.7, 49.9, 47.0, 46.7, 21.5, 20.7.

HRMS (ESI, $[M+Na]^+$]): calcd for $C_{15}H_{20}ClNO_5SNa$, 384.0648; found, 384.0638.

2-Chloro-4-[*N*-(2-oxoethyl)(4-methylbenzene)sulfonamide]but-2-en-1-yl acetate (13l)



Dess-Martin oxidation of *N*-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-3-chloro-4-hydroxy-*S*-(4-methylphenyl)but-2-ene-1-sulfonamide (80.0 mg, 0.221 mmol) gave **13l** (63.5 mg, 79%).

Column: hexane – EtOAc (2:1). Yellow oil.

R_f = 0.49 (1:1 hexane/EtOAc).

IR ν (neat, cm^{-1}): 2977, 2932, 1743, 1601, 1342, 1227, 1160, 1091, 1035.

^1H NMR (400 MHz, $CDCl_3$): major isomer: δ 9.57 (s, 1H), 7.70 (d, 2H, *J* = 8.4 Hz), 7.34 (d, 2H, *J* = 8.4 Hz), 5.80 (t, 1H, *J* = 7.6 Hz), 4.61 (s, 2H), 4.02 (d, 2H, *J* = 7.6 Hz), 3.95 (s, 2H), 2.45 (s, 3H), 2.08 (s, 3H). minor isomer: δ 9.58 (s, 1H), 7.71 (d, 2H, *J* = 8.4 Hz), 7.35 (d, 2H, *J* = 8.4 Hz), 5.84 (t, 1H, *J* = 6.8 Hz), 4.61 (s, 2H), 4.01 (d, 2H, *J* = 6.8 Hz), 3.86 (s, 2H), 2.45 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): mixture: δ 197.3, 170.4, 144.2, 135.5, 132.9, 130.0, 127.5, 127.4, 127.3, 123.0, 66.0, 61.6, 56.7, 56.2, 46.8, 46.3, 21.5, 20.6

LRMS (EI) m/z (relative intensity): 330$[M-CHO]^+$ (67), 299 (6), 155 (36), 147 (100).

HRMS (EI, $[M-CHO]^+$)): calcd for $C_{14}H_{17}ClNO_4S$, 330.0567; found, 330.0562.

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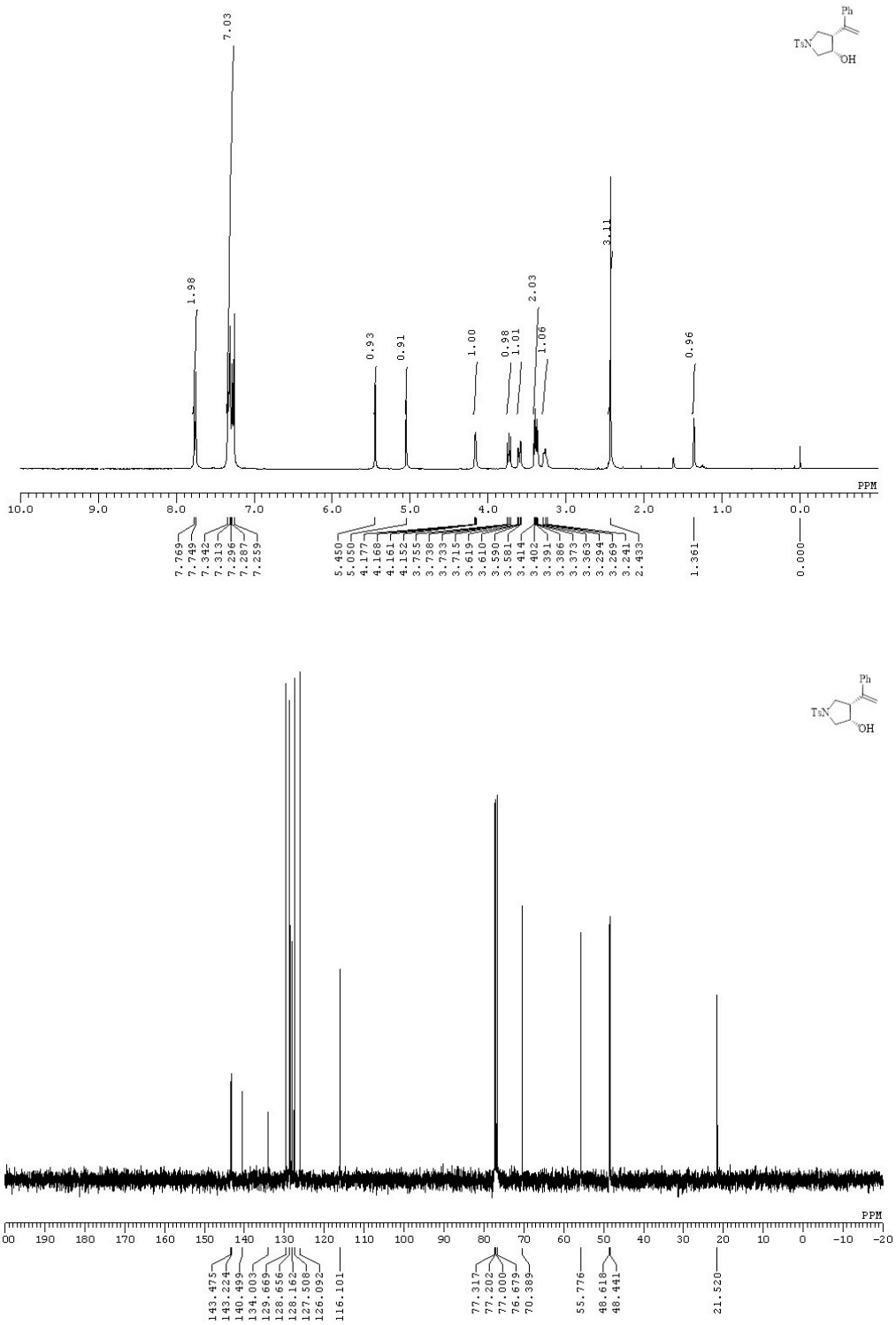
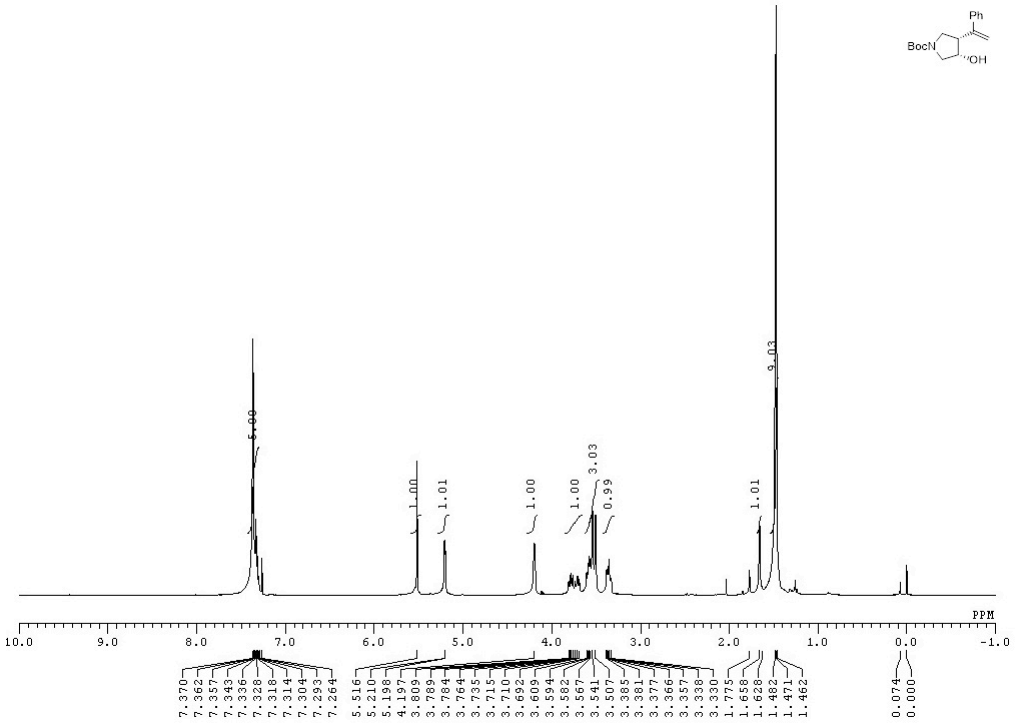
^{1}H and ^{13}C NMR spectra

11a



11d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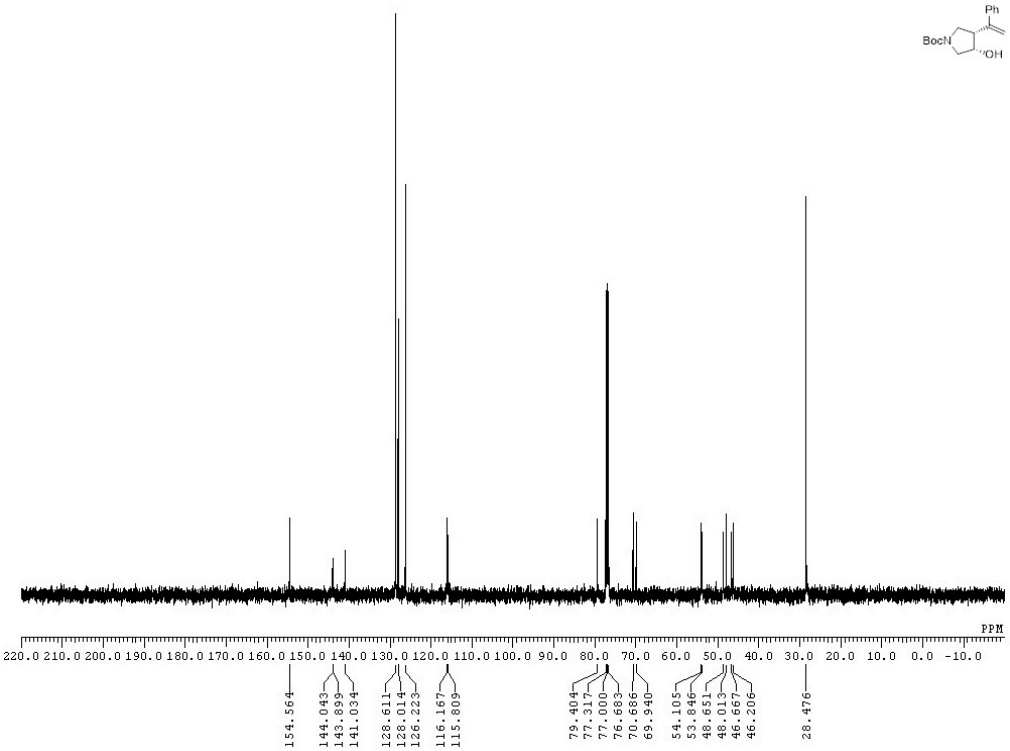
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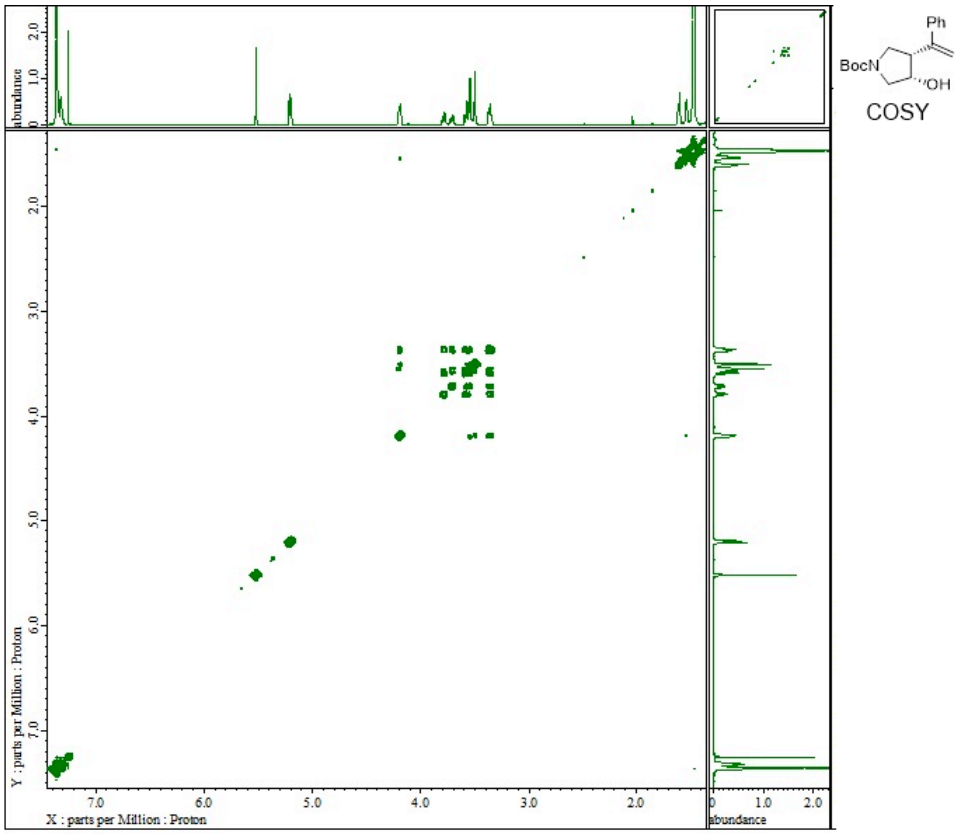
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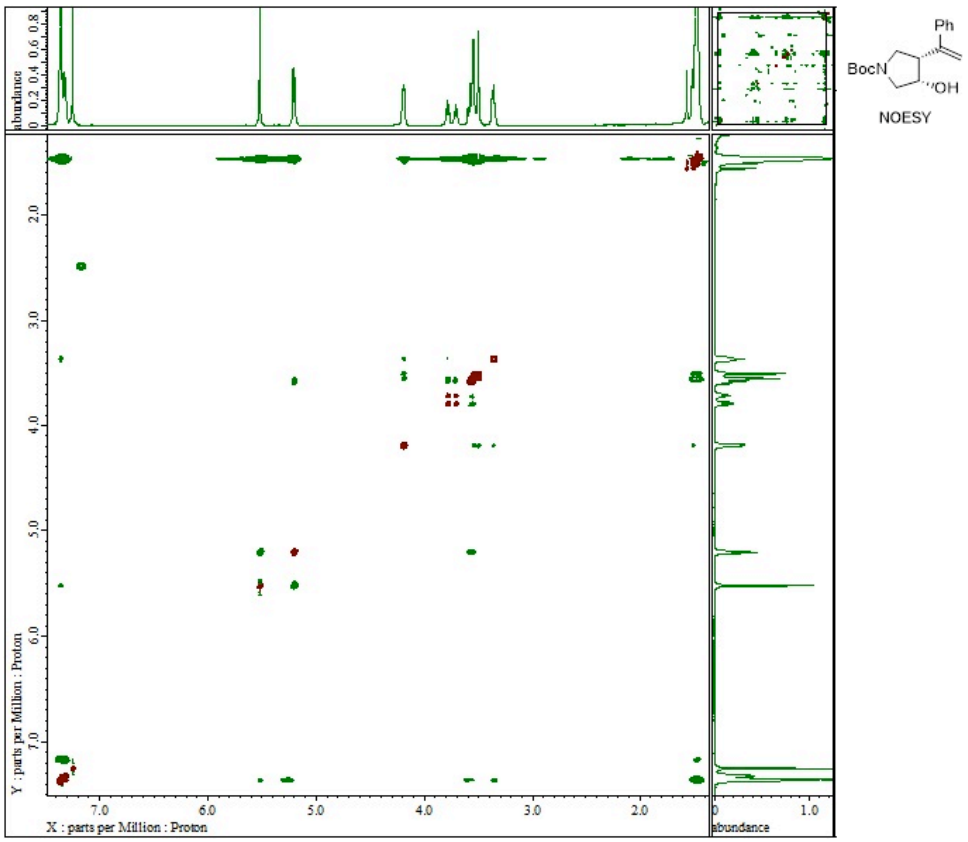
X : parts per Million : Proton
Abundance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BocN
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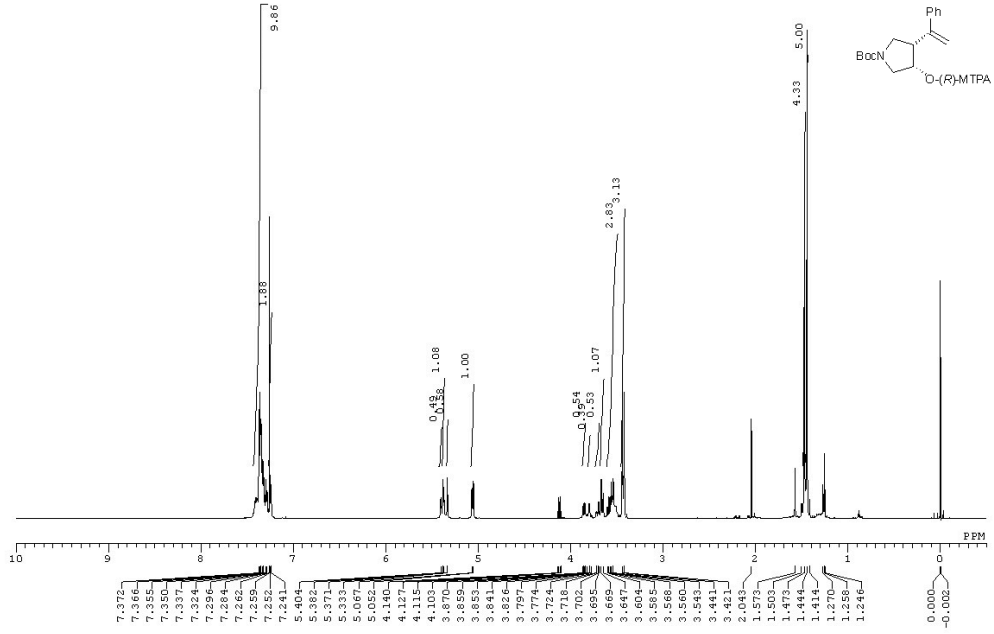
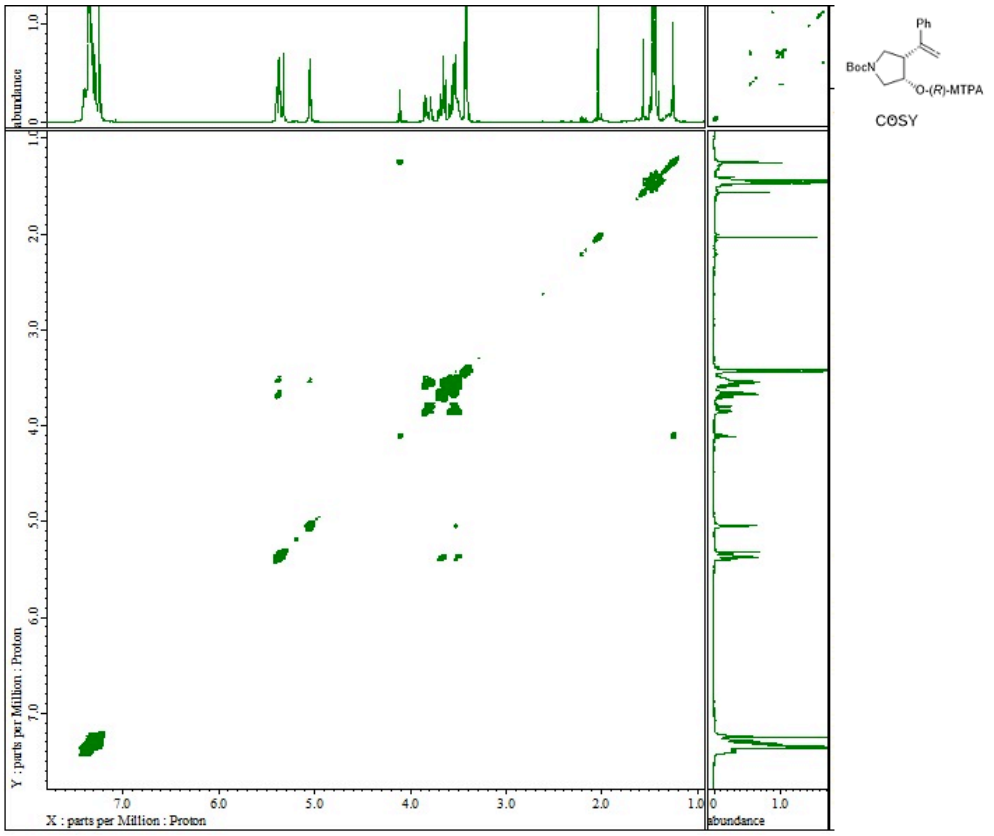
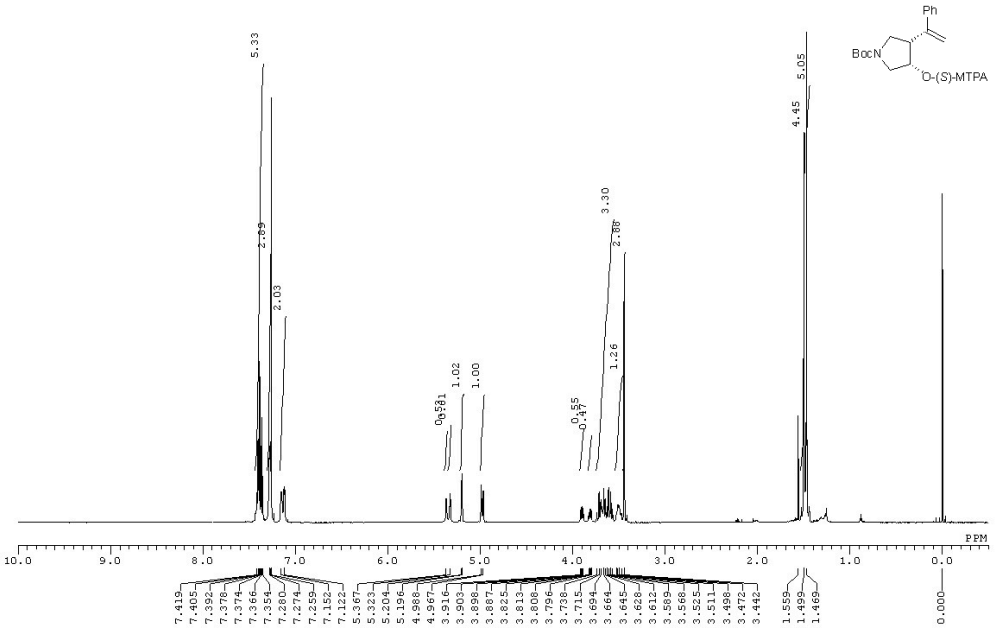
Y : parts per Million : Proton
X : parts per Million : Proton
Abundance

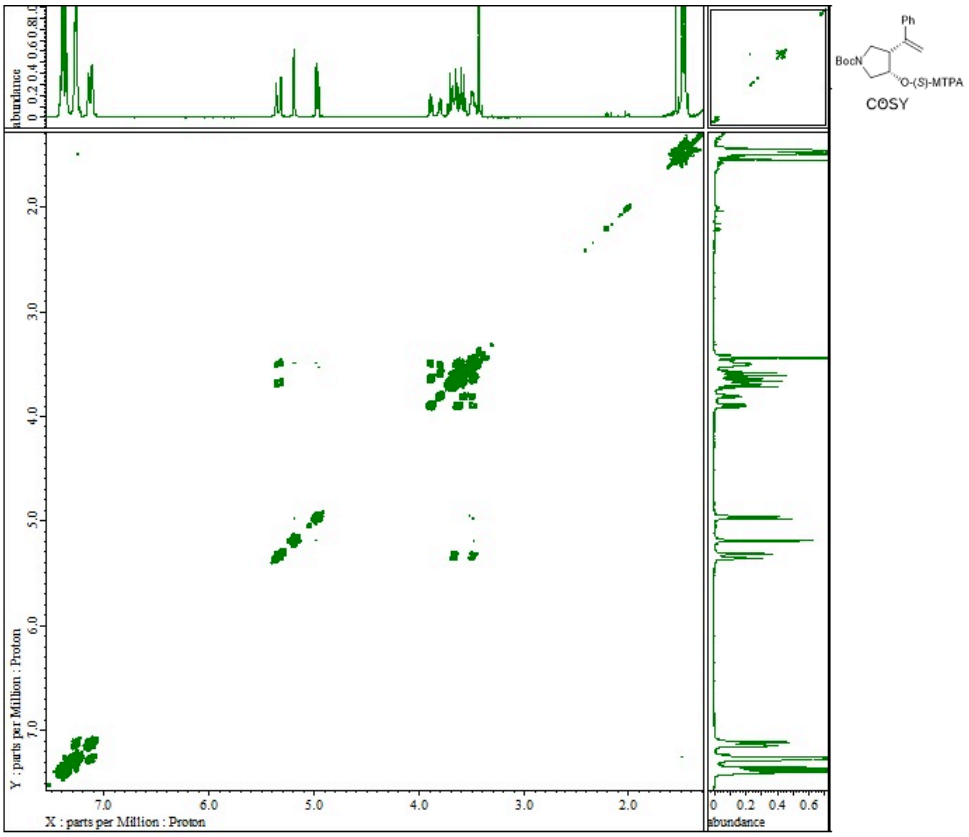
(*R*)-MTPA ester of (3*S*,4*S*)-**11d**



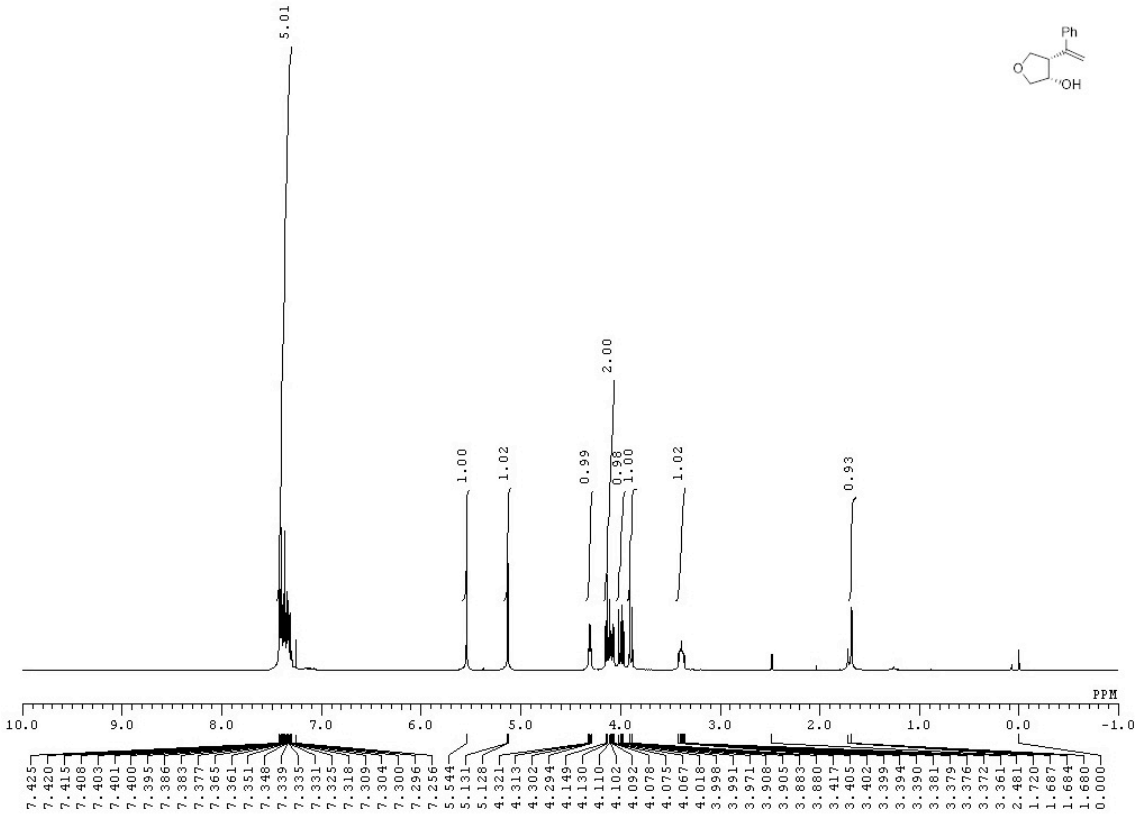


(*S*)-MTPA ester of (3*S*,4*S*)-**11d**





11e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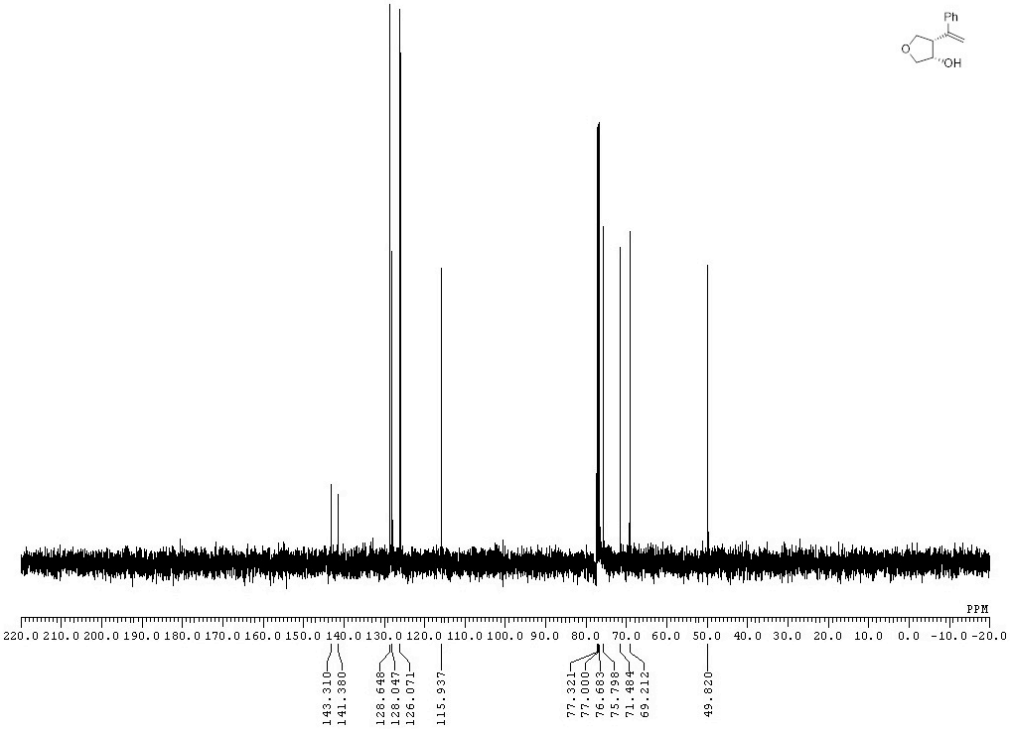
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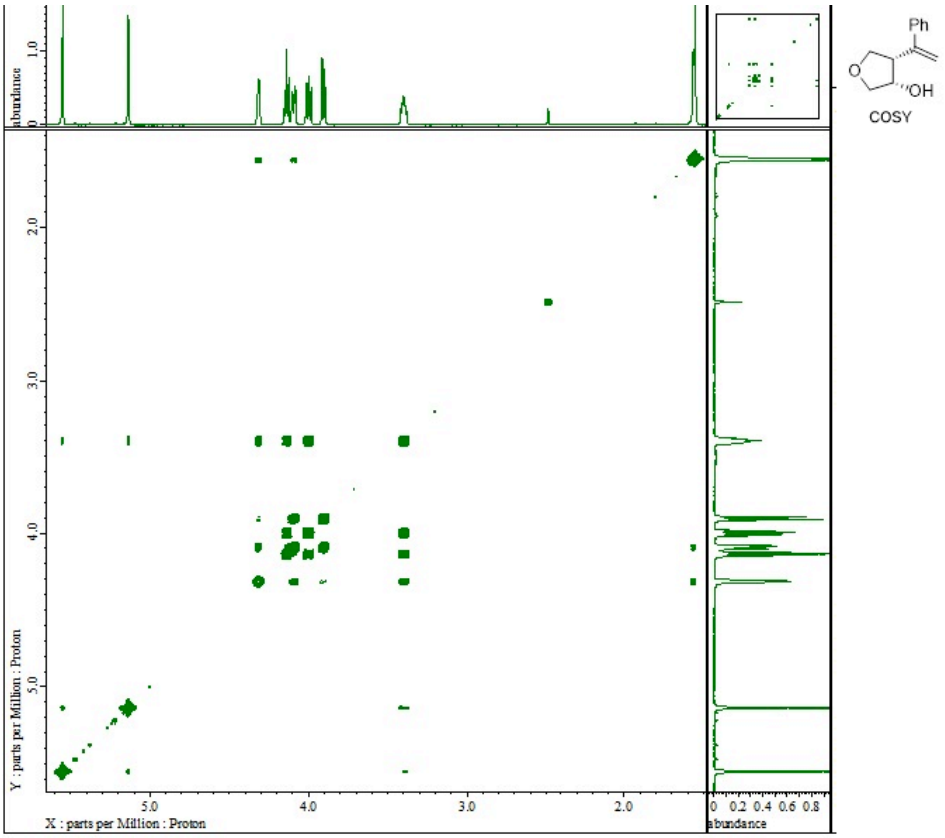
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Y : parts per Million : Proton
X : parts per Million : Proton
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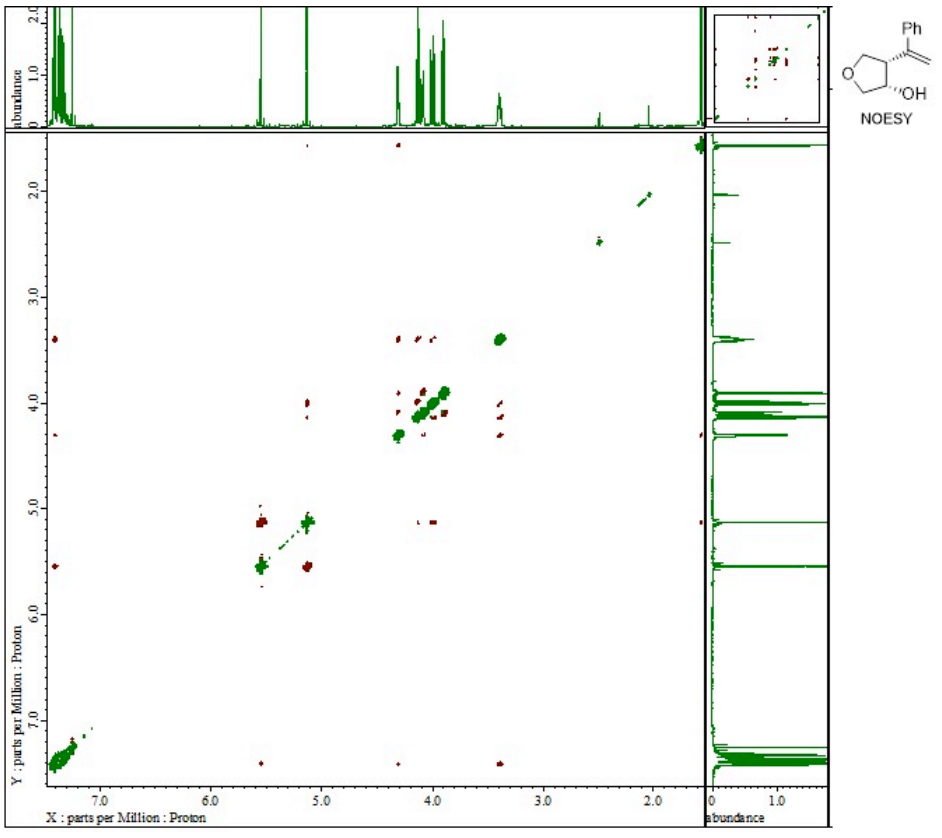
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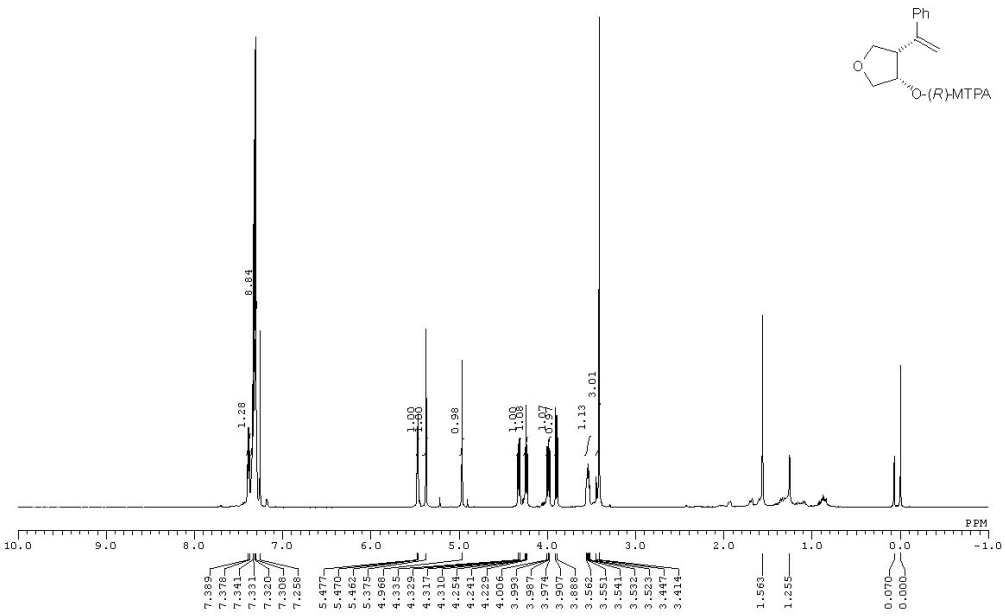
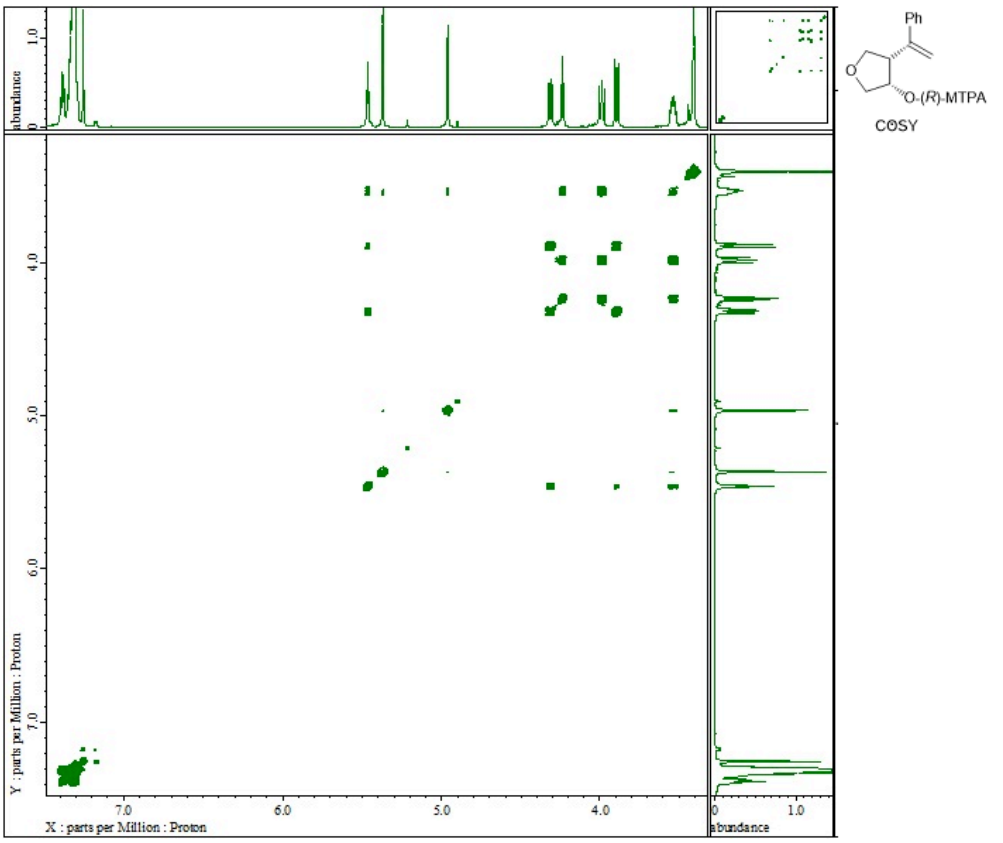
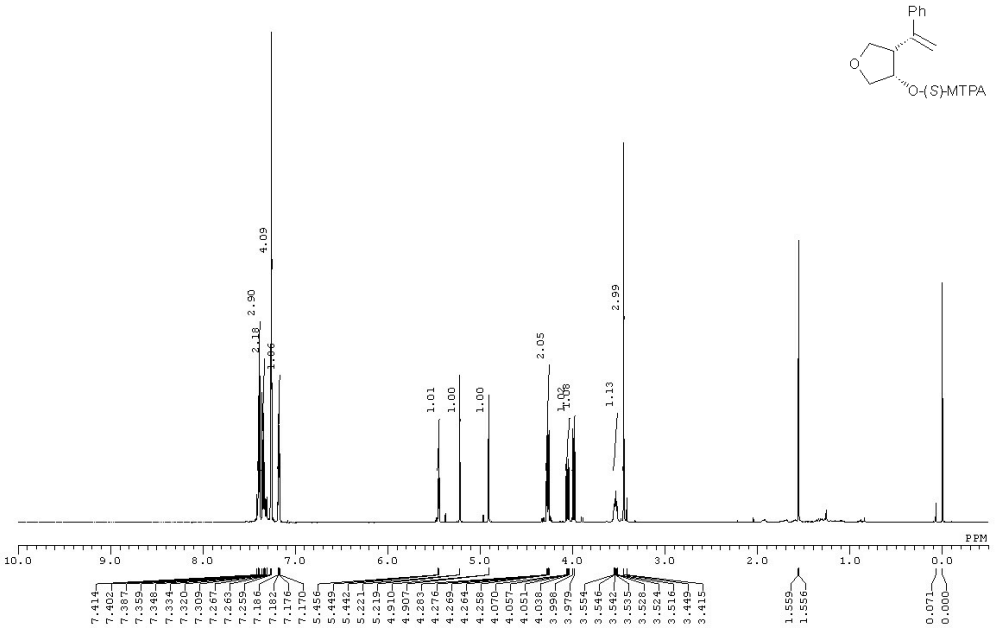
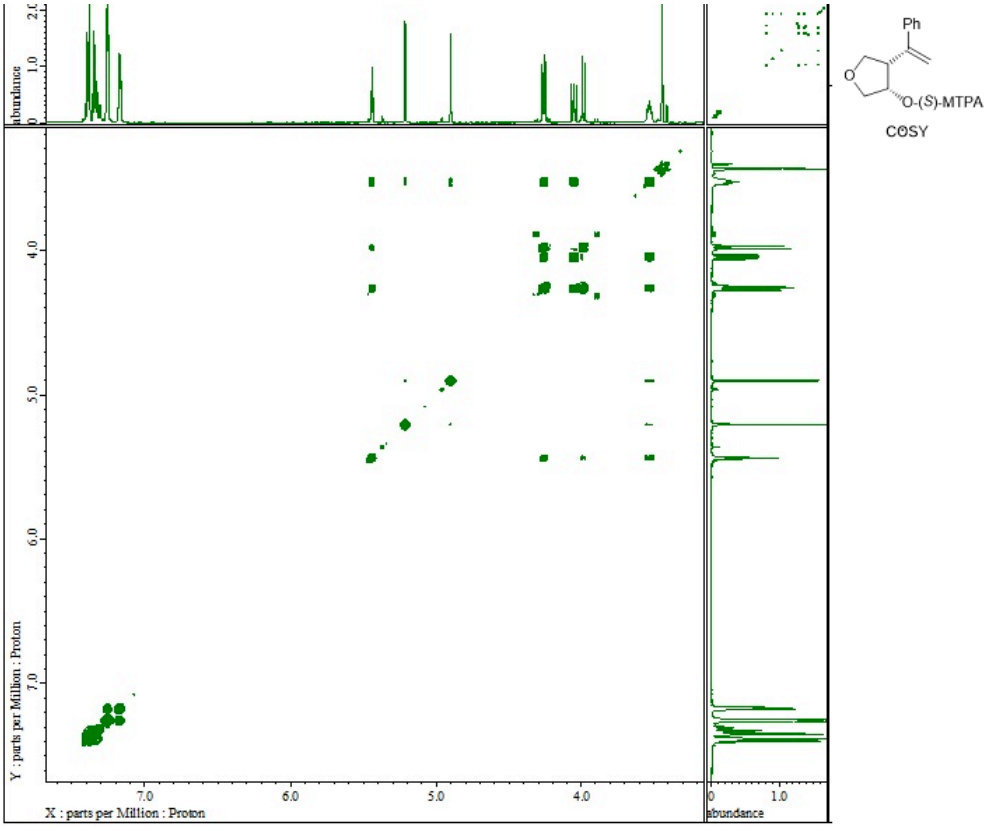
(*R*)-MTPA ester of (3*S*,4*S*)-**11e**



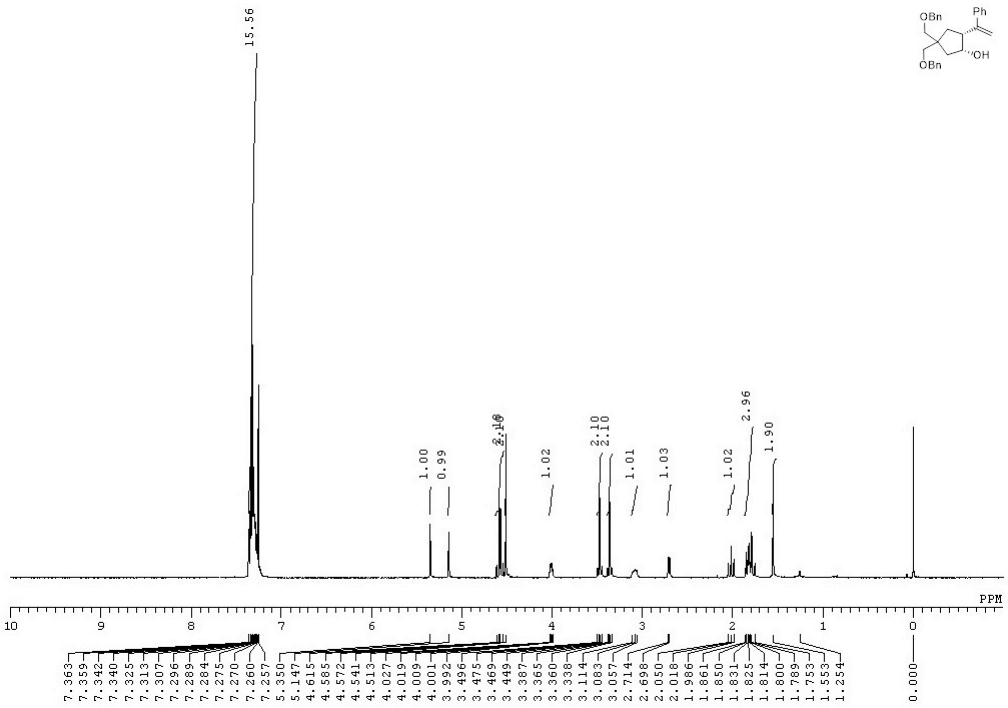


(*S*)-MTPA ester of (3*S*,4*S*)-**11e**





11f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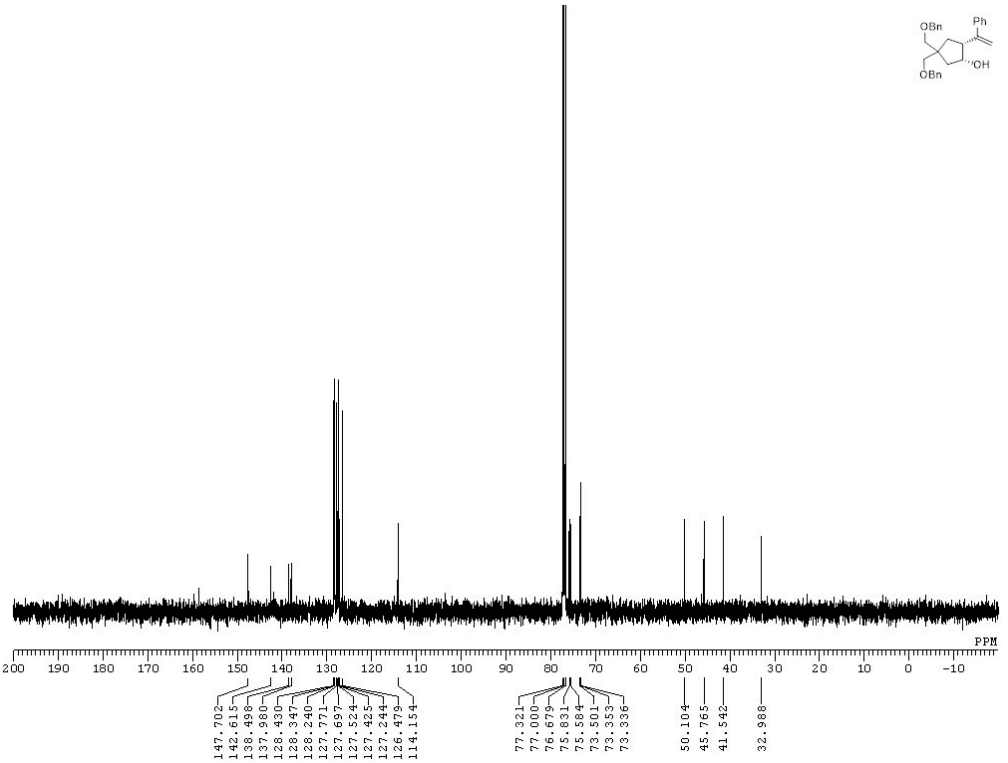
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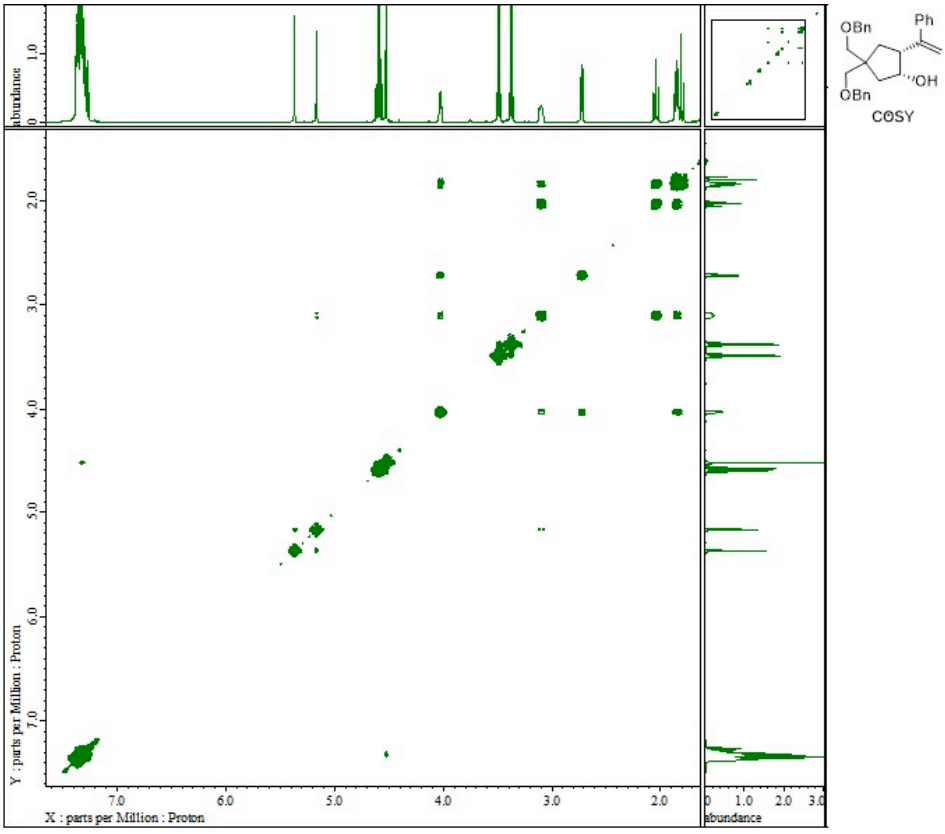
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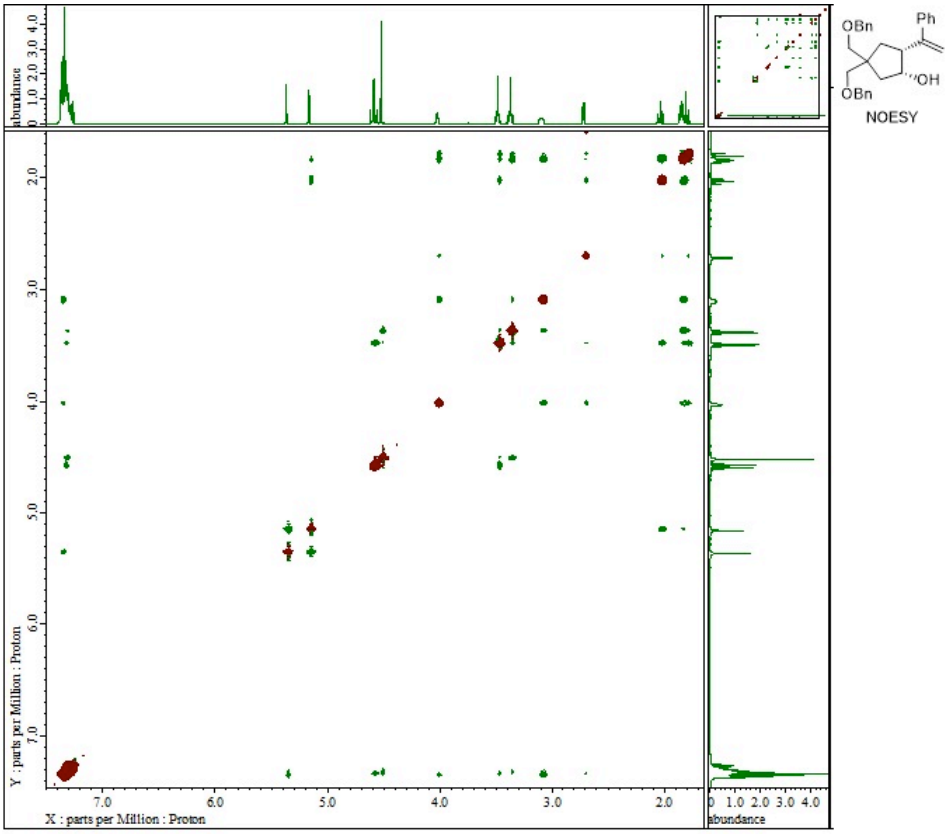
abundance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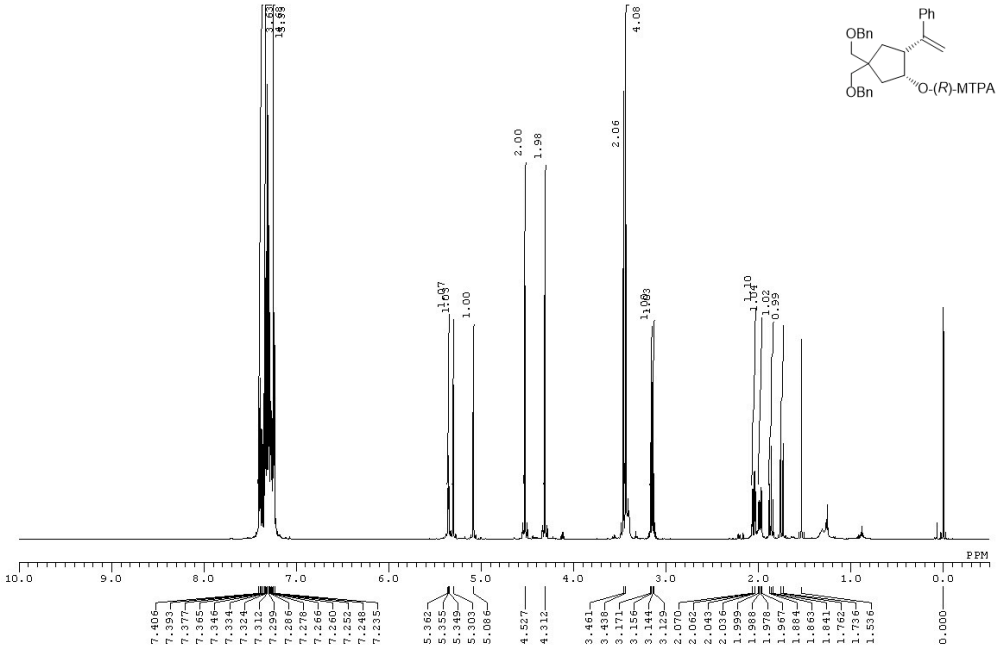
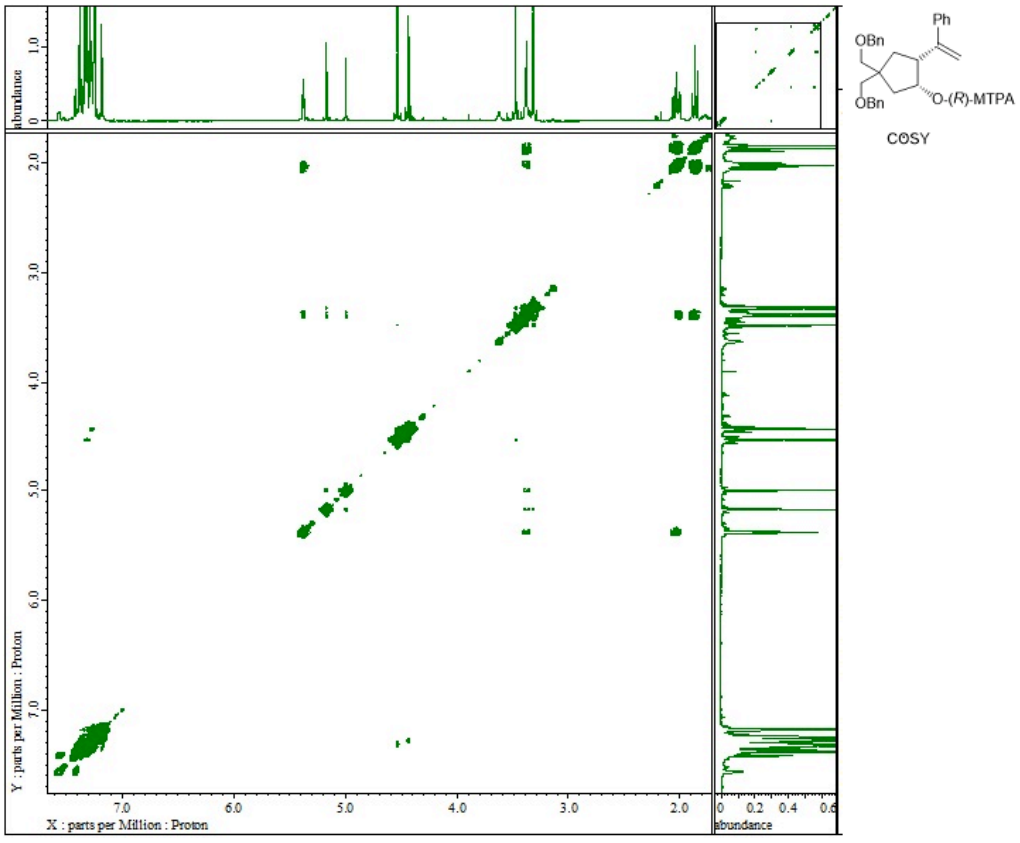
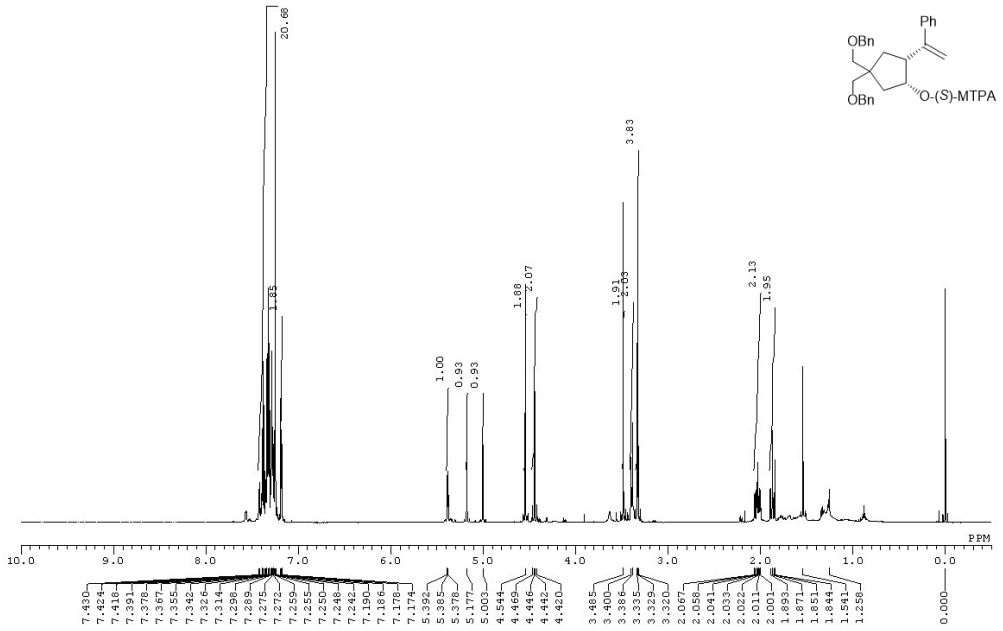
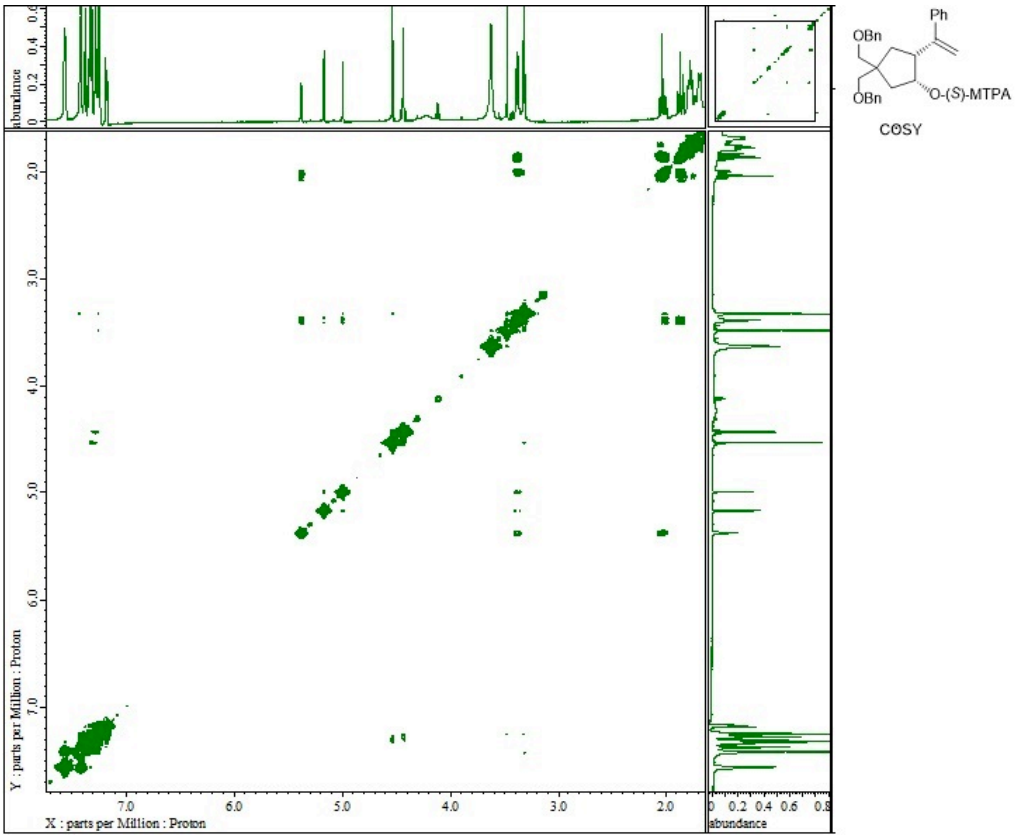
(*R*)-MTPA ester of (1*R*,2*R*)-**11f**



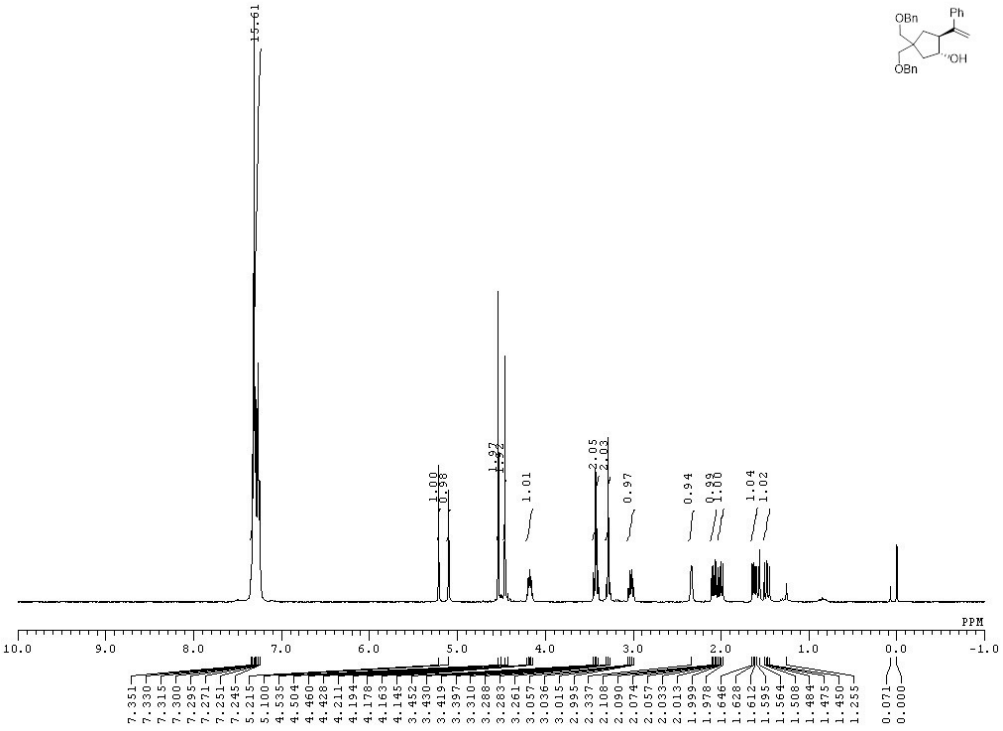


(*S*)-MTPA ester of (1*R*,2*R*)-**11f**





11f'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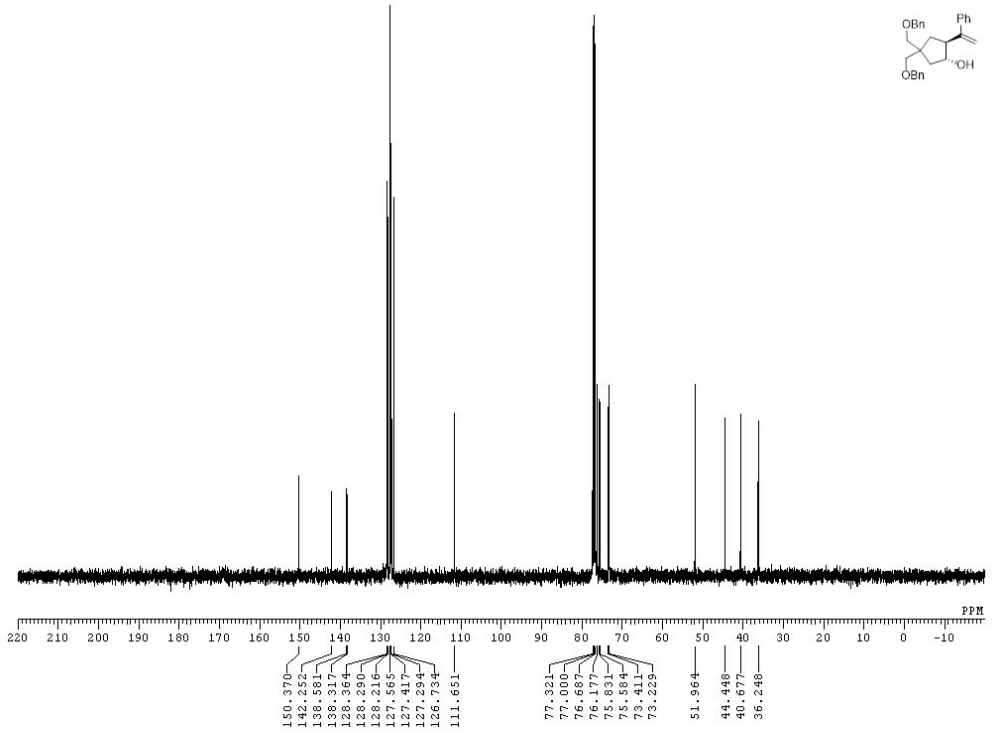
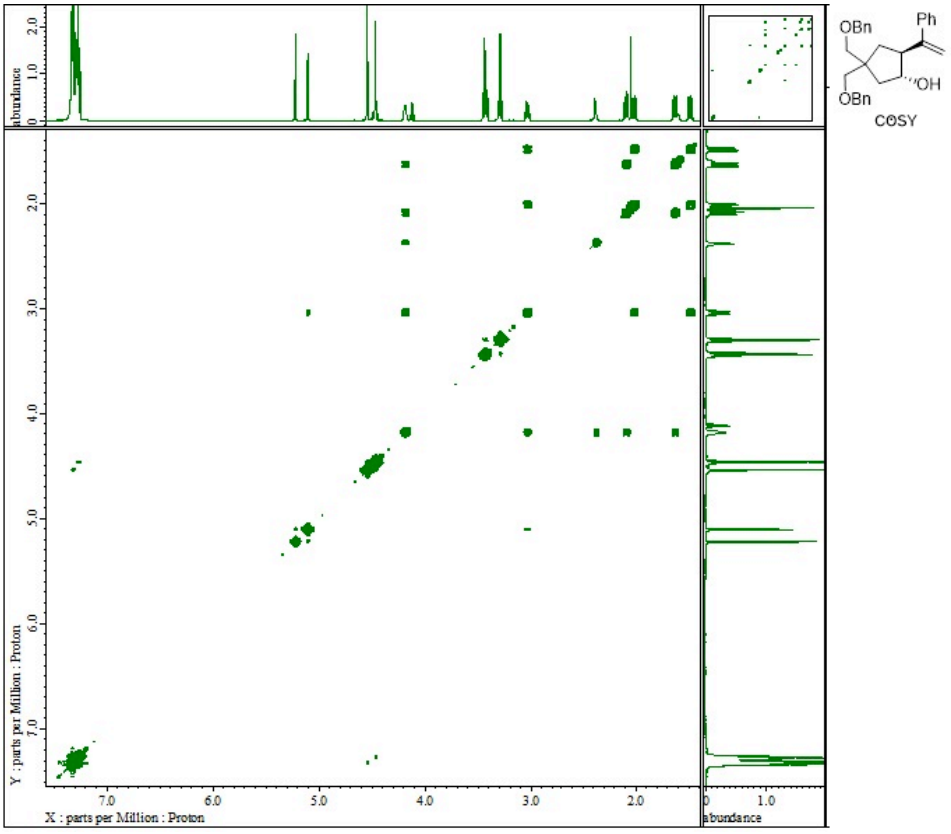
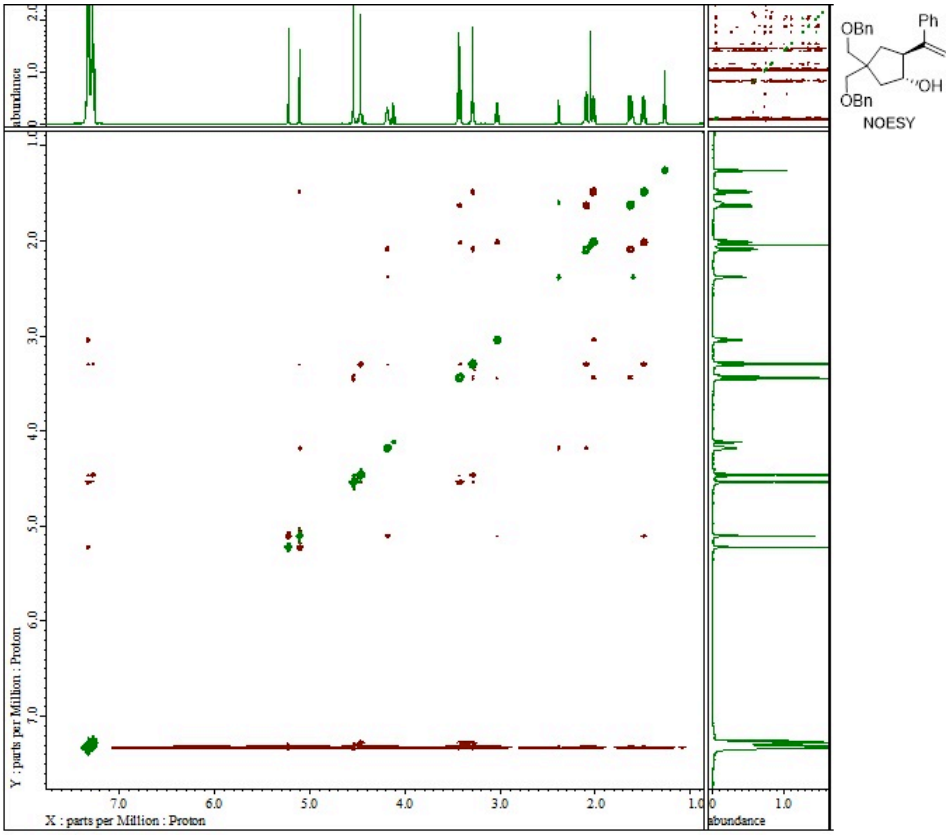
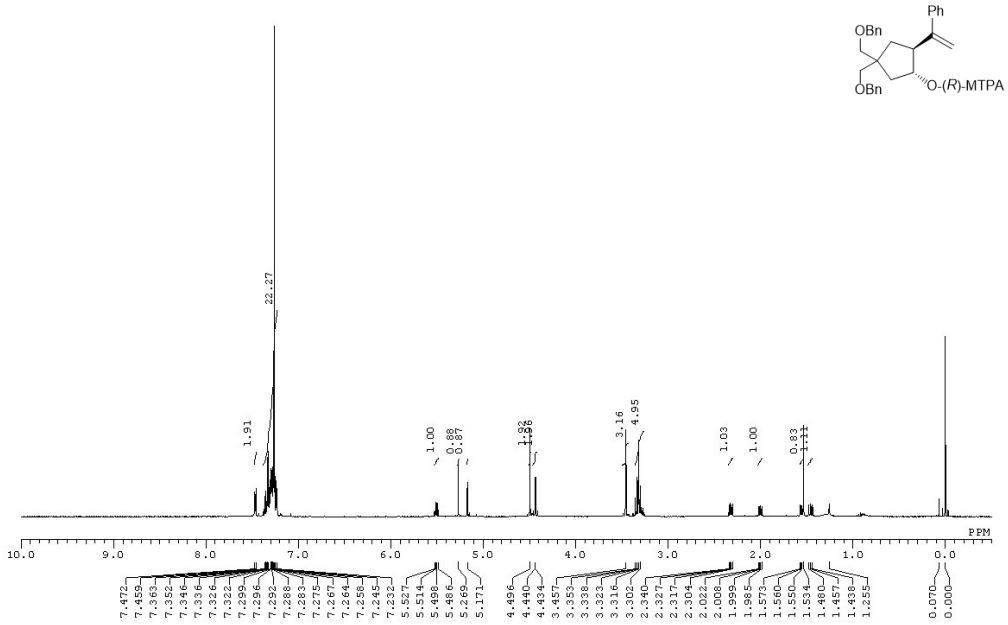
1.612
1.595
1.564
1.508
1.484
1.475
1.450
1.255
0.071
0.000

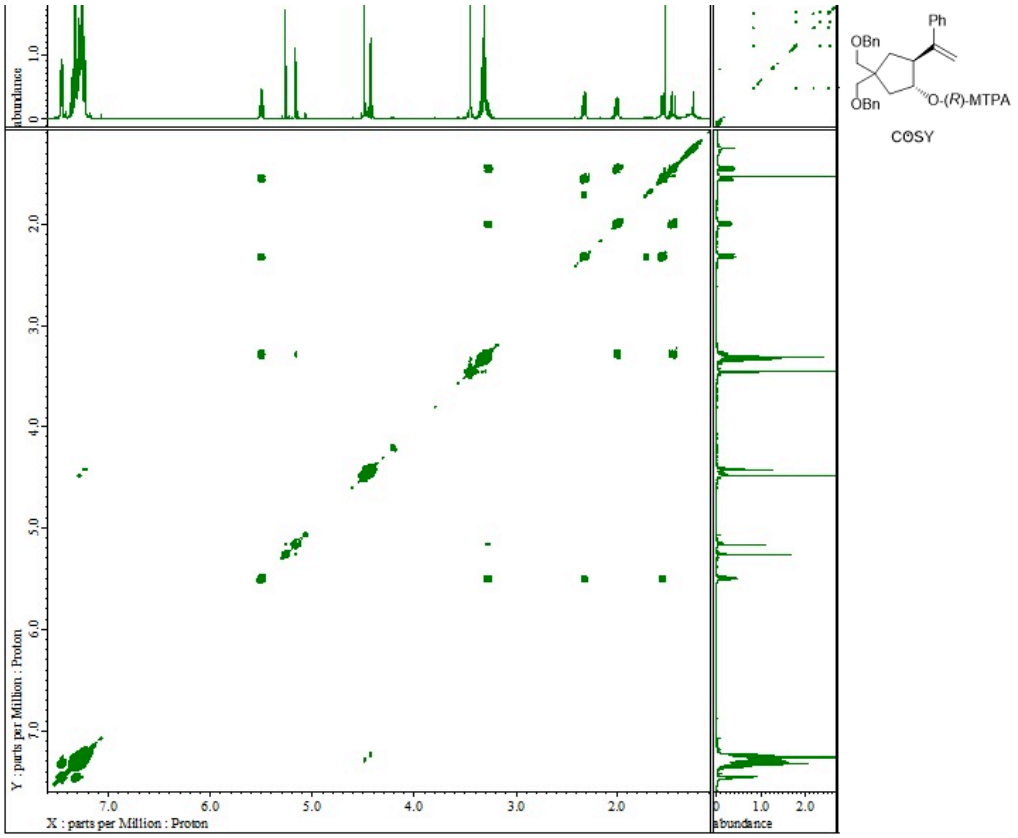

OBn
Ph
OBn
OH
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
150.370
142.252
138.581
138.317
128.364
128.290
128.216
127.565
127.417
127.294
126.734
111.651
77.321
77.000
76.687
76.177
75.831
75.584
73.411
73.229
51.964
44.448
40.677
36.248


OBn
Ph
OH
OBn
COSY
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

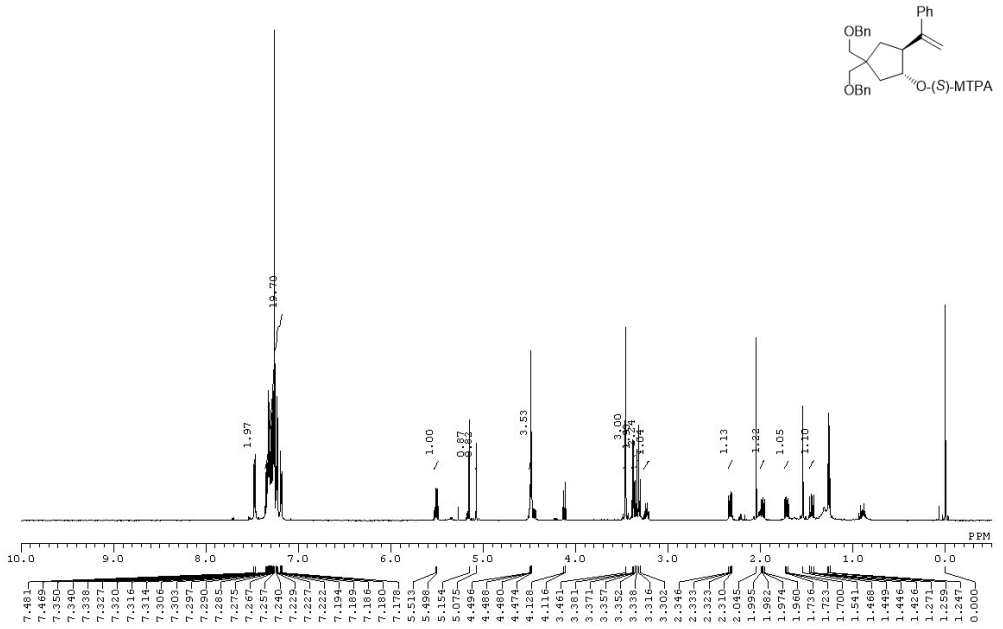

OBn
Ph
OH
OBn
NOESY
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

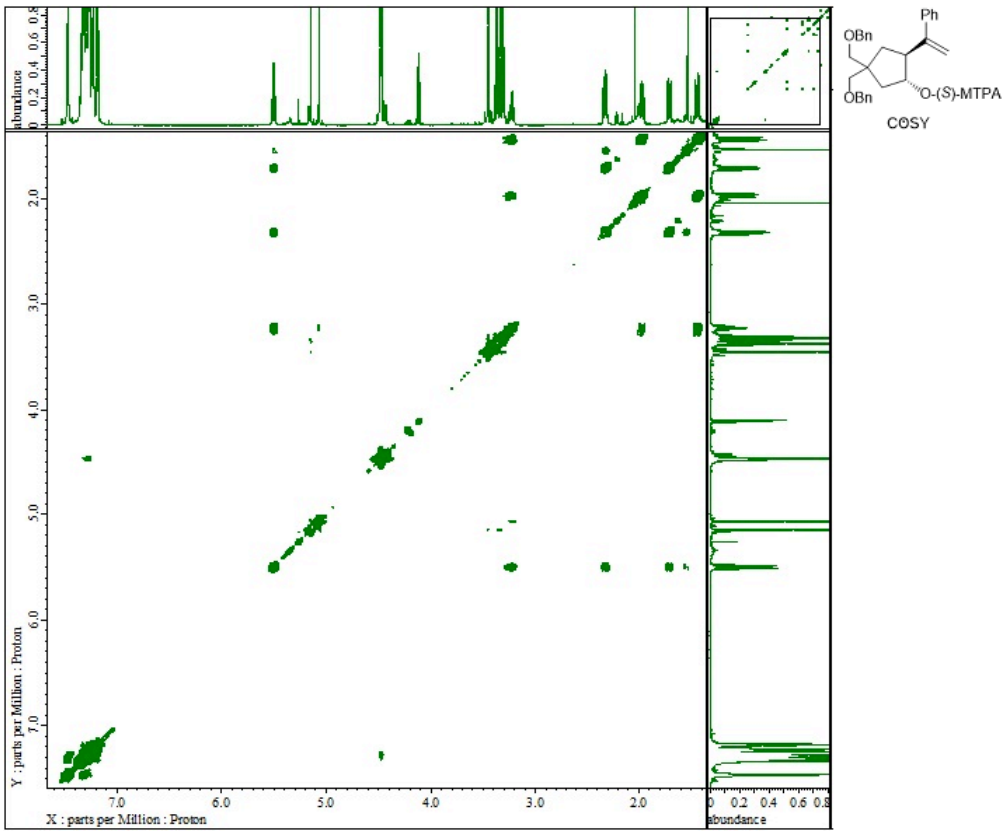
(*R*)-MTPA ester of (1*R*,2*S*)-**11f'**



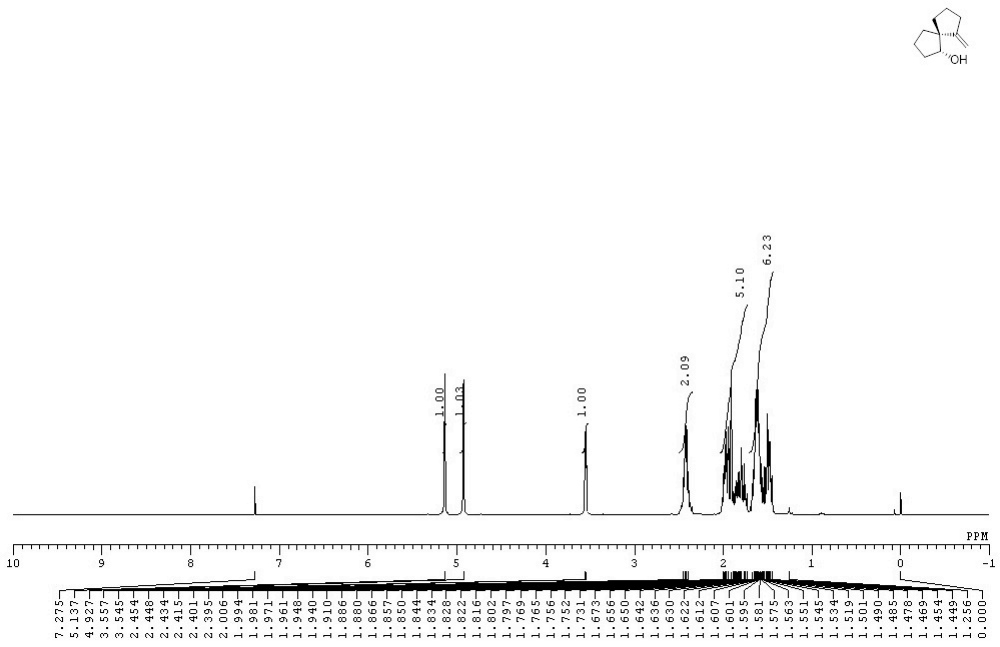


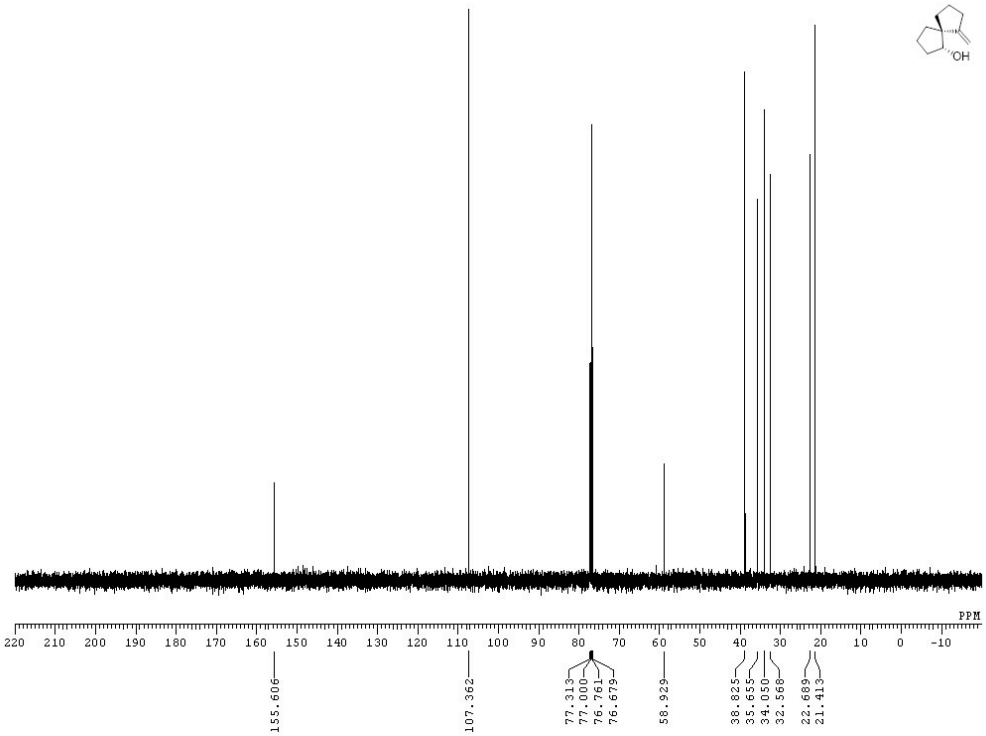
(*S*)-MTPA ester of (1*R*,2*S*)-**11f'**

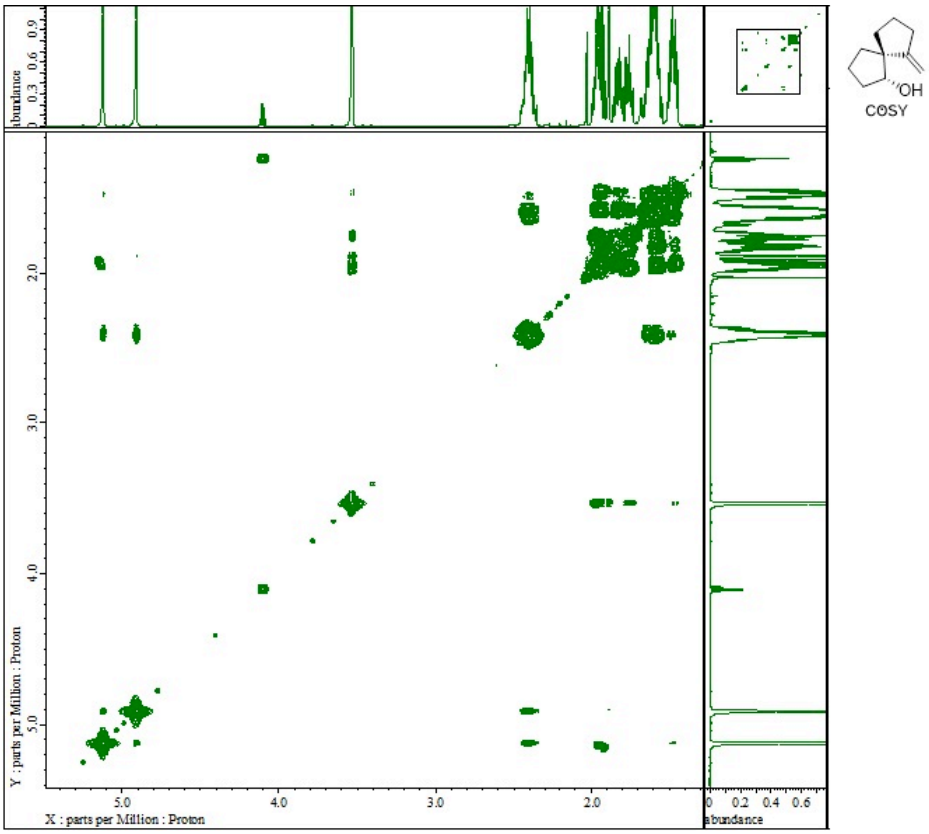


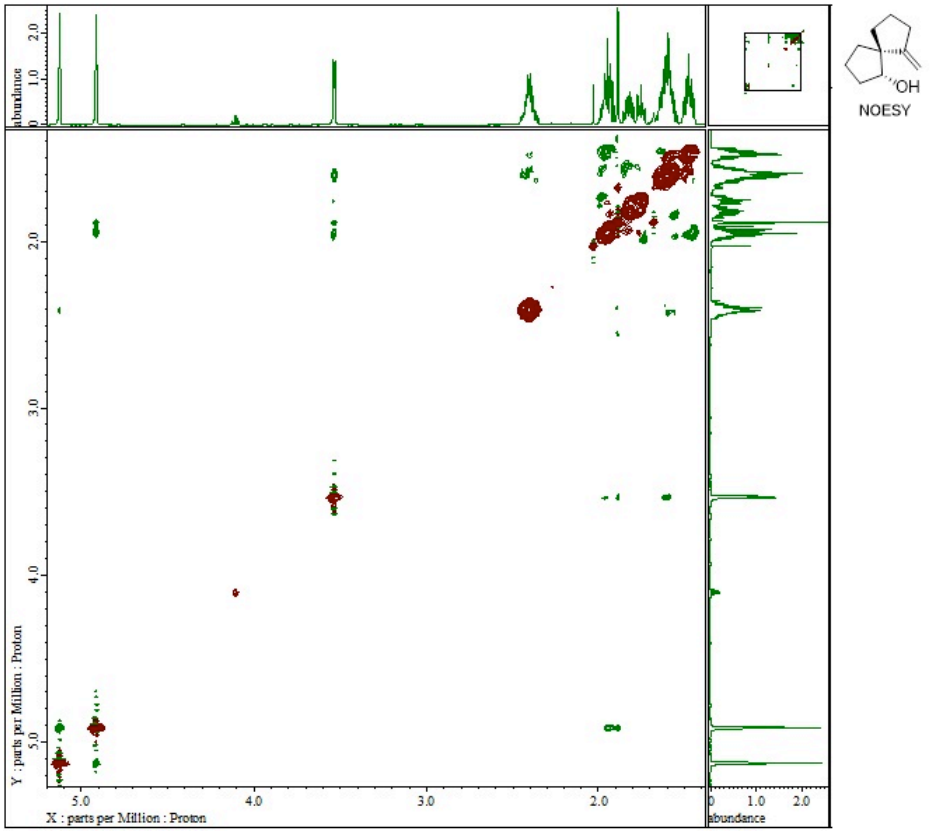


11g

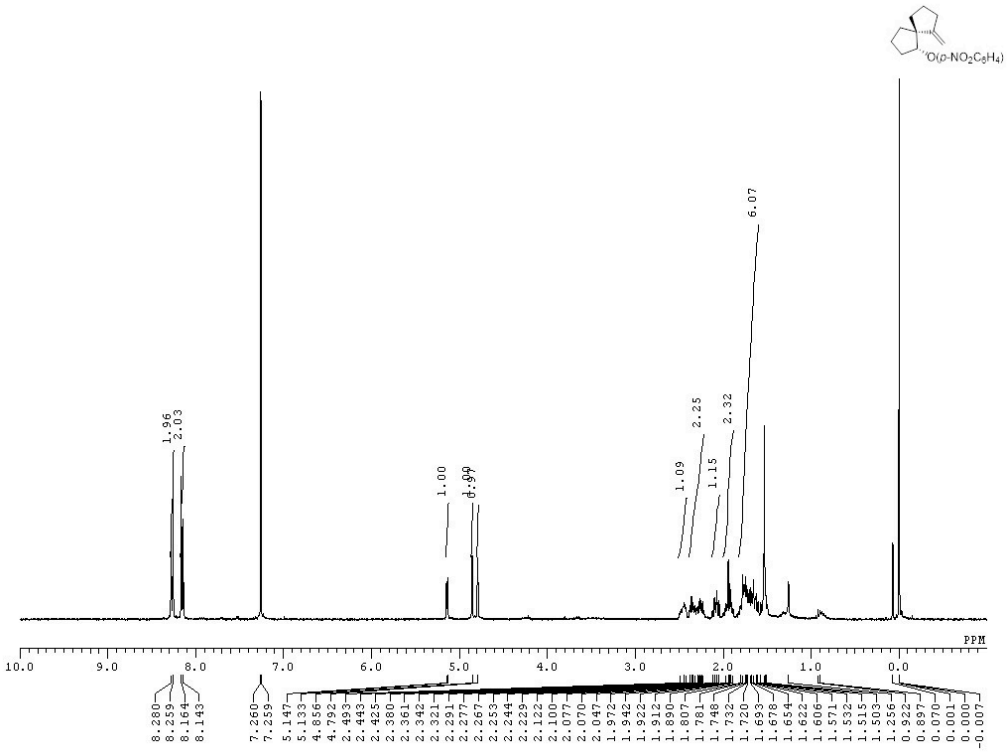

OH
1.00
1.02
1.00
2.09
5.10
6.23
PPM
10 9 8 7 6 5 4 3 2 1 0 -1
7.275
5.137
4.927
3.557
3.545
2.454
2.448
2.434
2.415
2.401
2.395
2.006
1.994
1.981
1.971
1.961
1.948
1.940
1.910
1.886
1.880
1.866
1.857
1.850
1.844
1.834
1.828
1.822
1.816
1.802
1.797
1.769
1.765
1.756
1.752
1.731
1.673
1.656
1.650
1.642
1.636
1.630
1.622
1.612
1.607
1.601
1.595
1.581
1.575
1.563
1.551
1.545
1.534
1.519
1.501
1.490
1.485
1.478
1.469
1.454
1.449
1.256
0.000

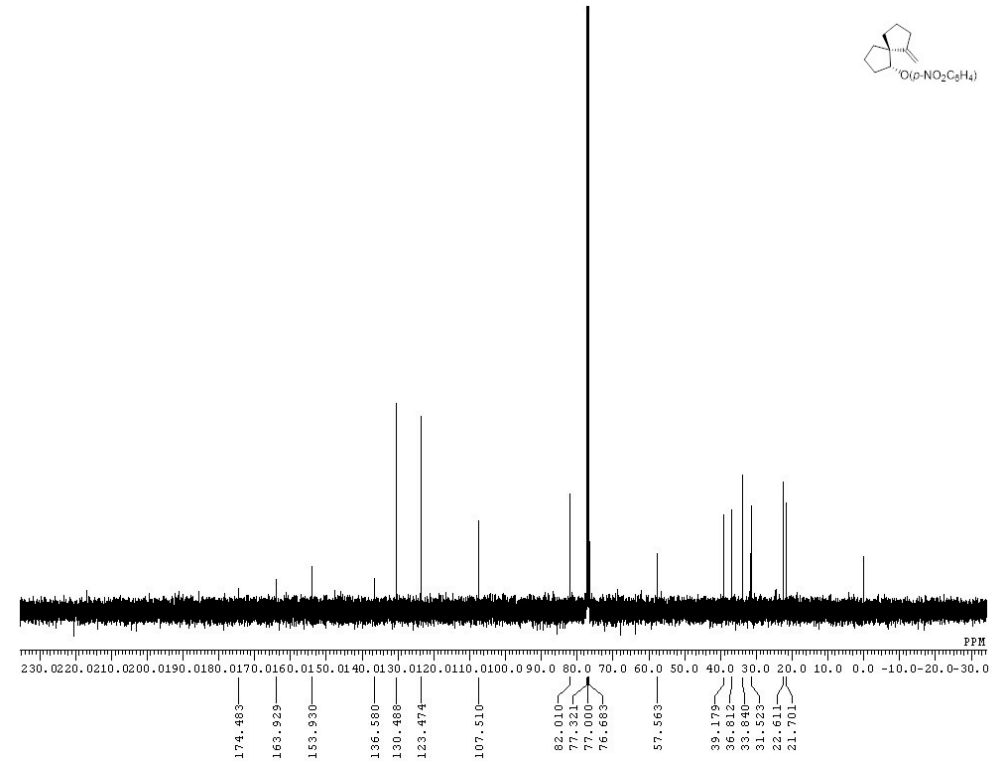

OH
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
155.606
107.362
77.313
77.000
76.761
76.679
58.929
38.825
35.655
34.050
32.560
22.689
21.413


OH
COSY
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

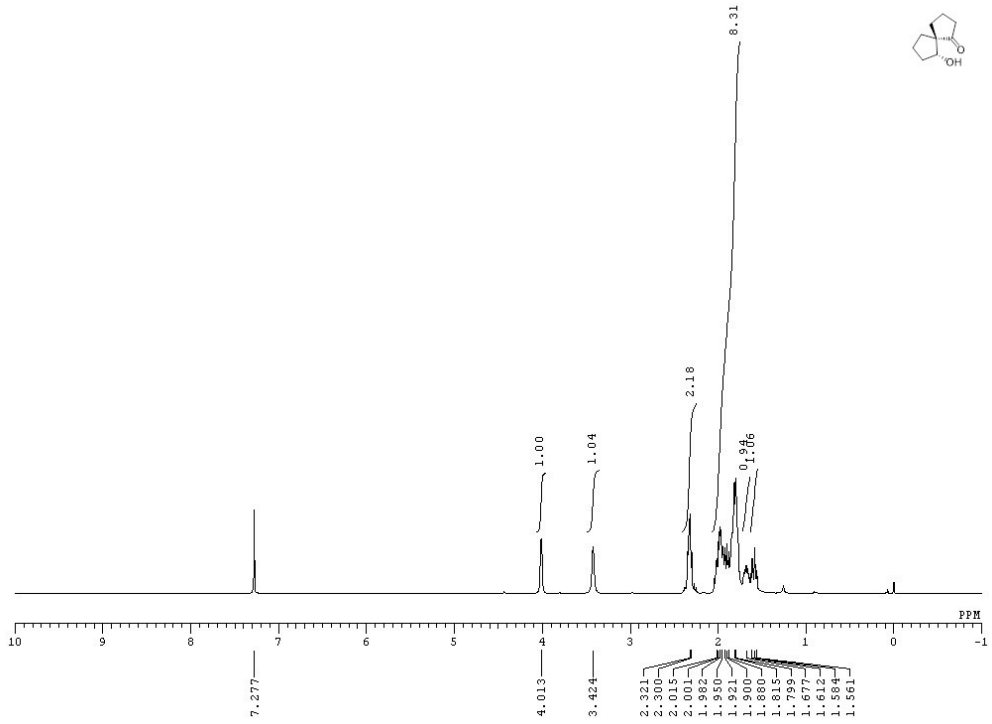

OH
NOESY
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

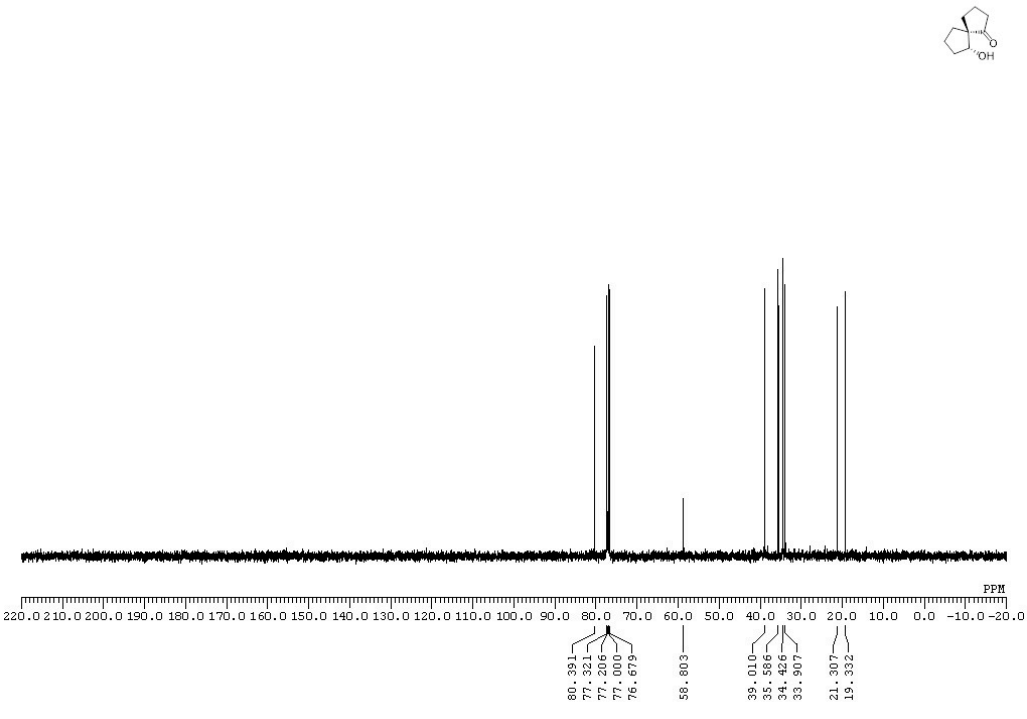
***p*-nitrobenzoate of 11g**



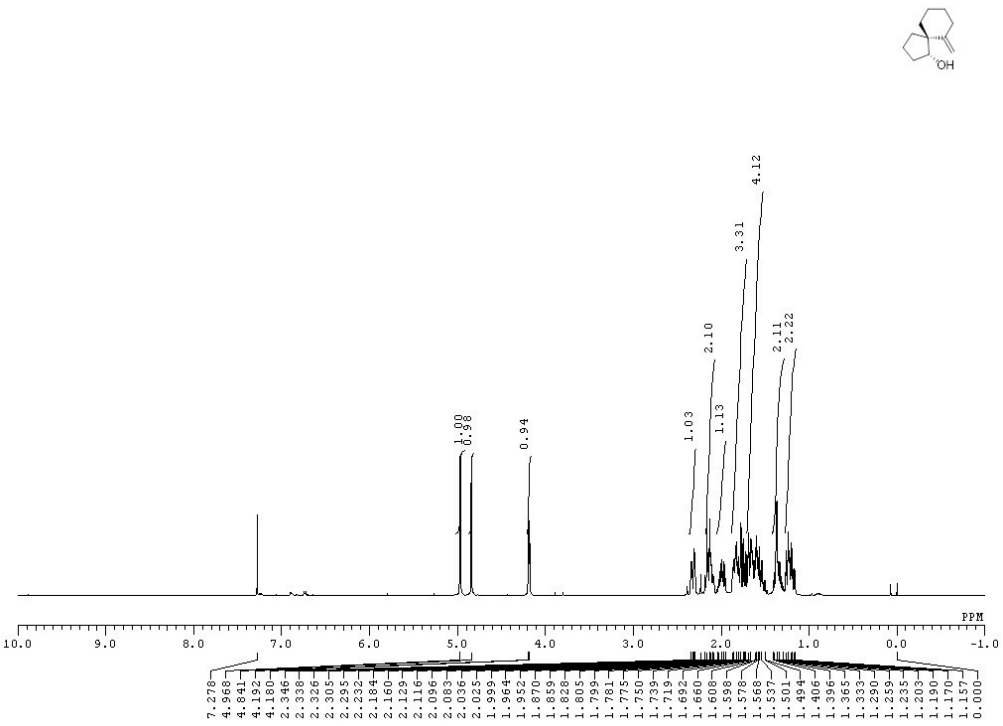


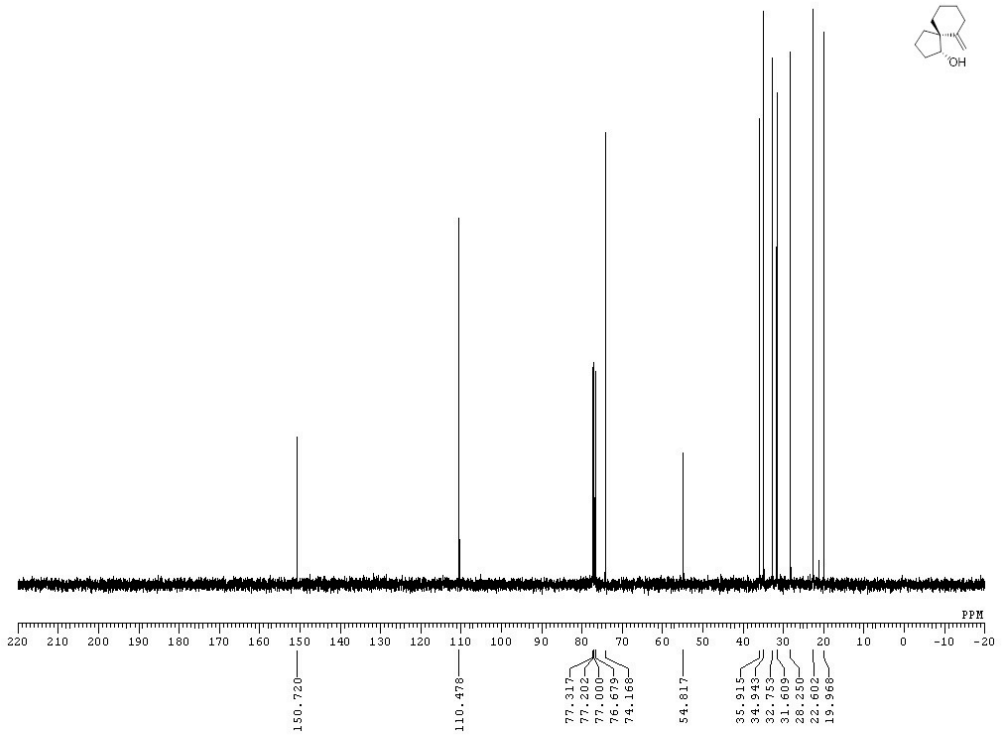
(5*R*, 6*R*)-6-Hydroxyspiro[4.4]nonan-1-one

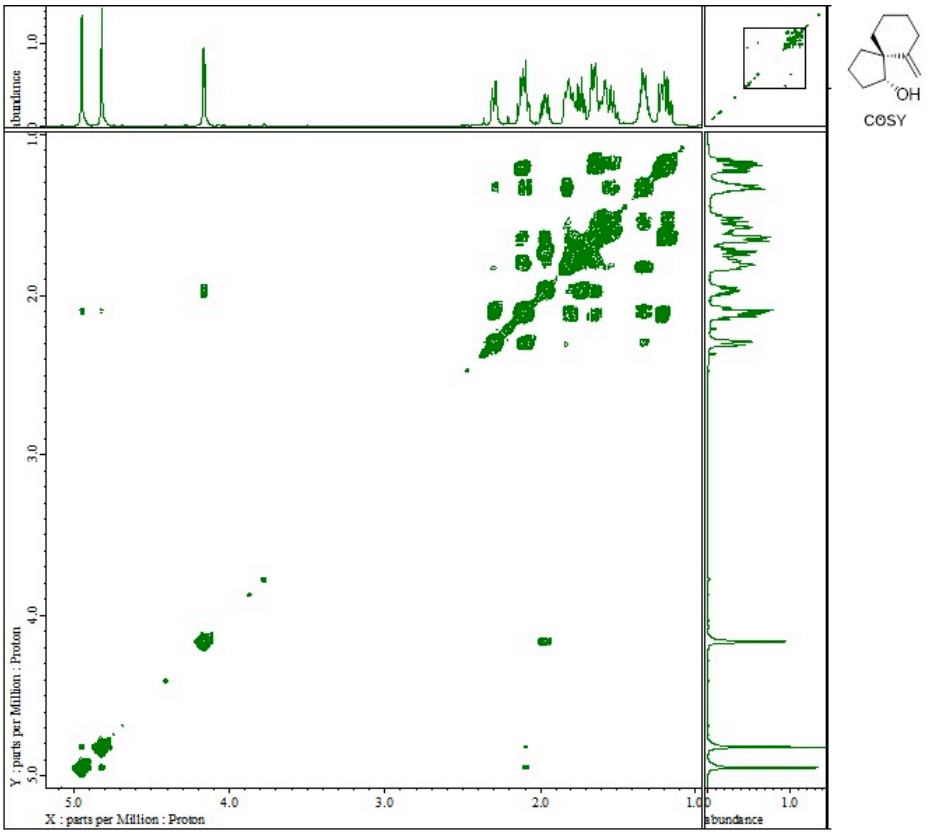


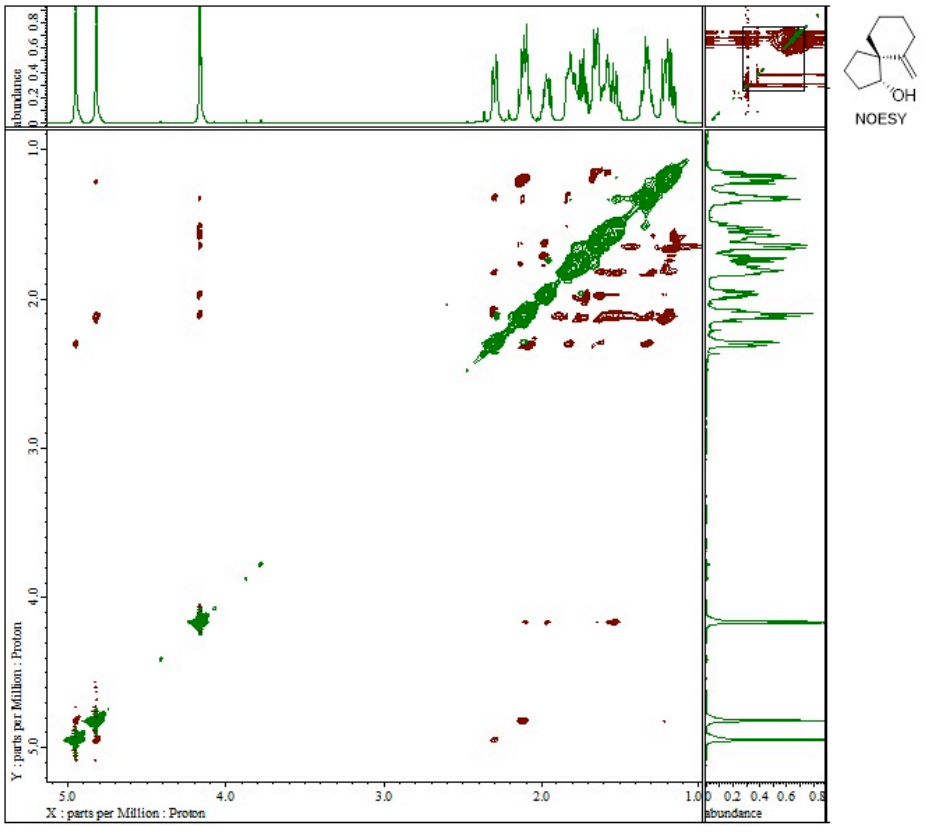


11h

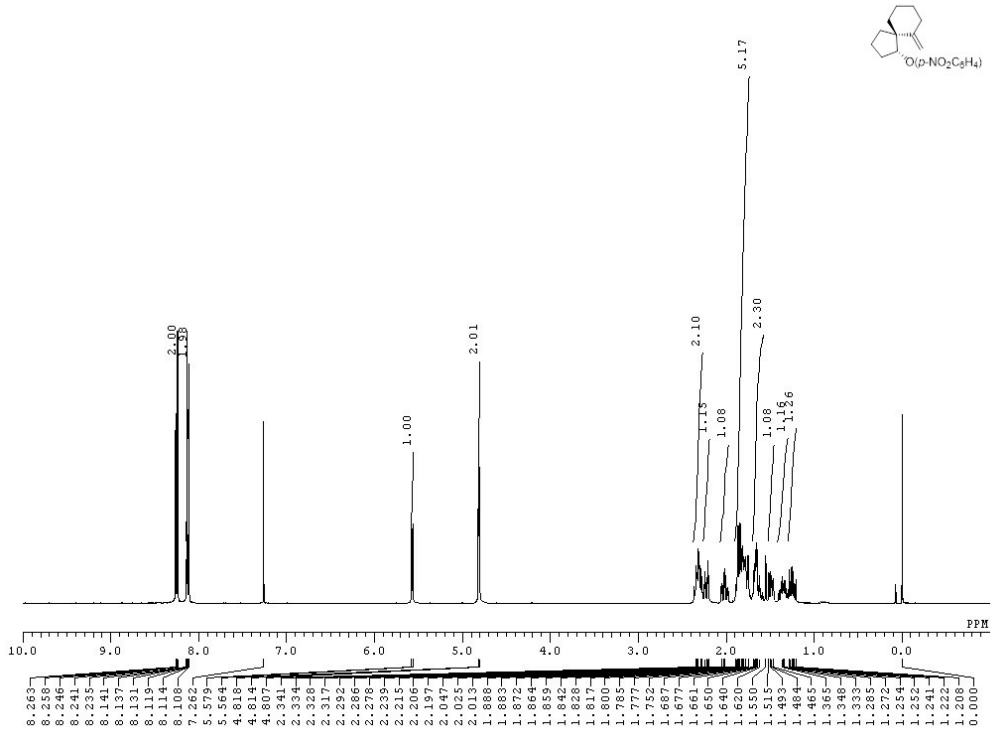

OH
4.12
3.31
2.10
2.11
2.22
1.03
1.13
1.00
0.98
0.94
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

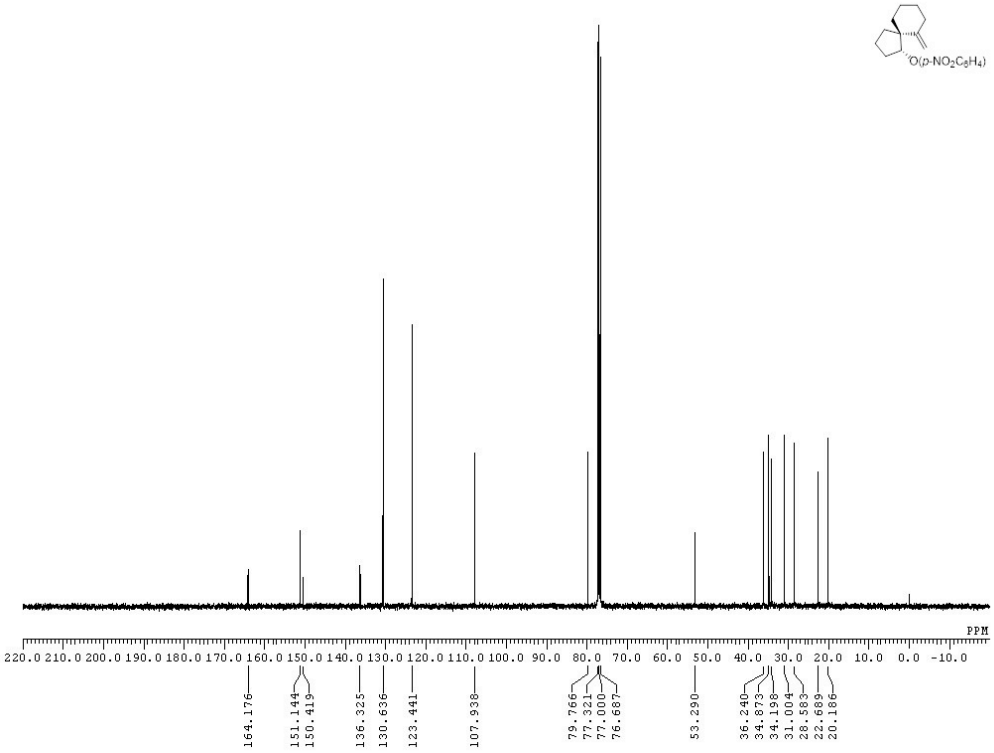

OH
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
150.720
110.478
77.317
77.202
77.000
76.679
74.168
54.817
35.915
34.943
32.753
31.609
28.250
22.602
19.968


Abundance
Y : parts per Million : Proton
X : parts per Million : Proton
Abundance
OH
COSY

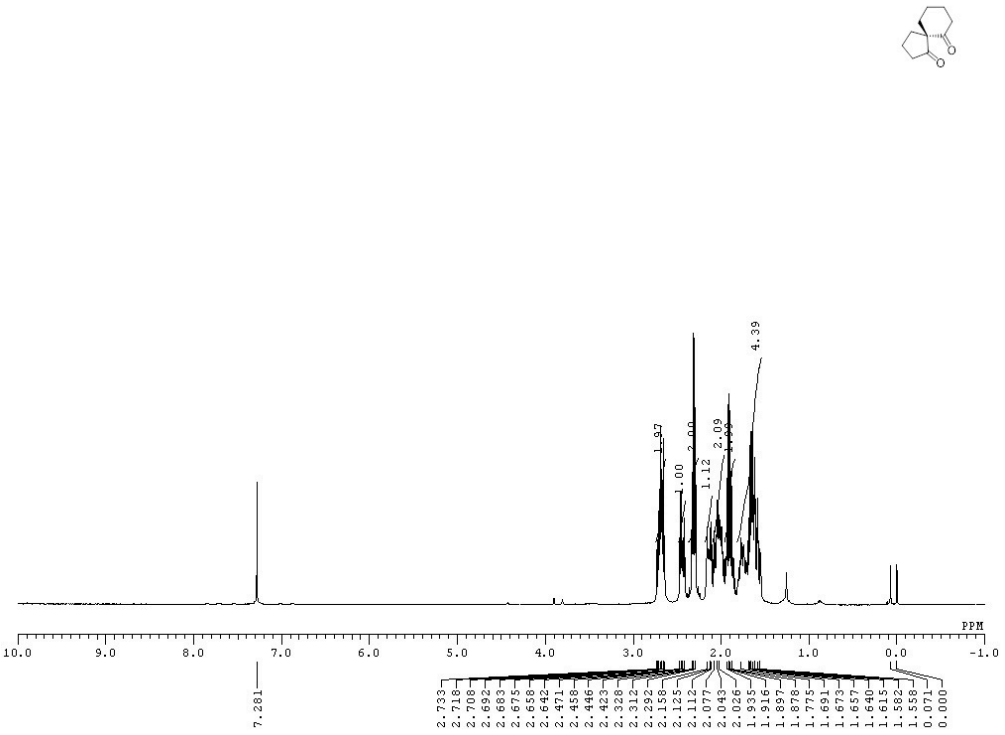

Abundance
Y : parts per Million : Proton
X : parts per Million : Proton
Abundance
OH
NOESY

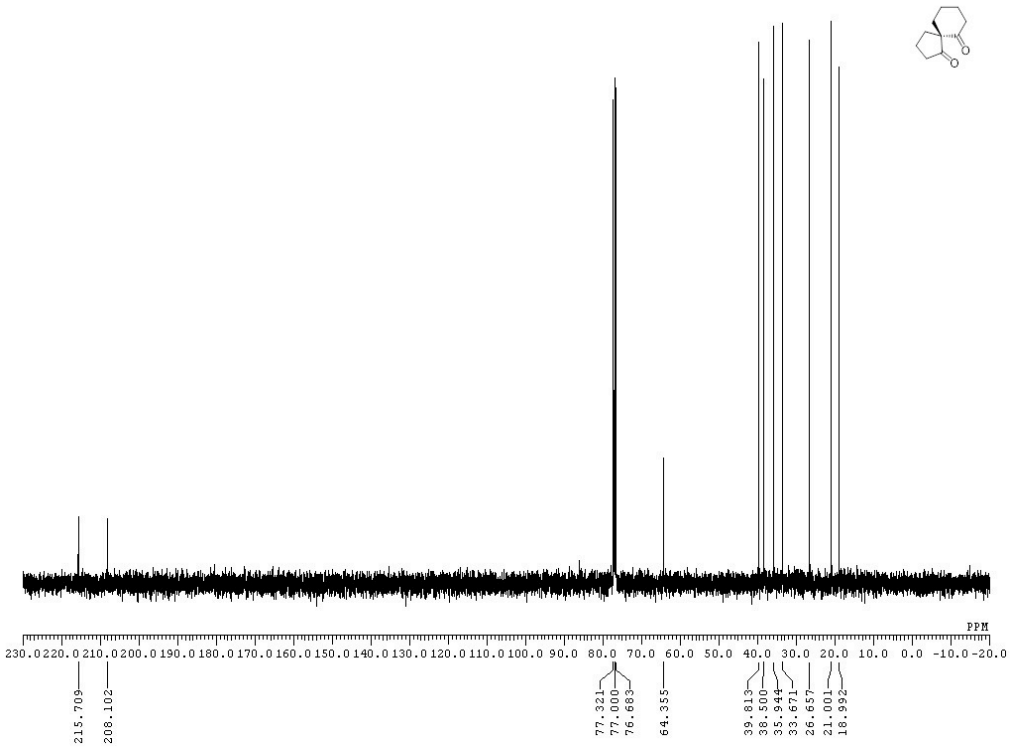
***p*-nitorobenzoate of 11h**



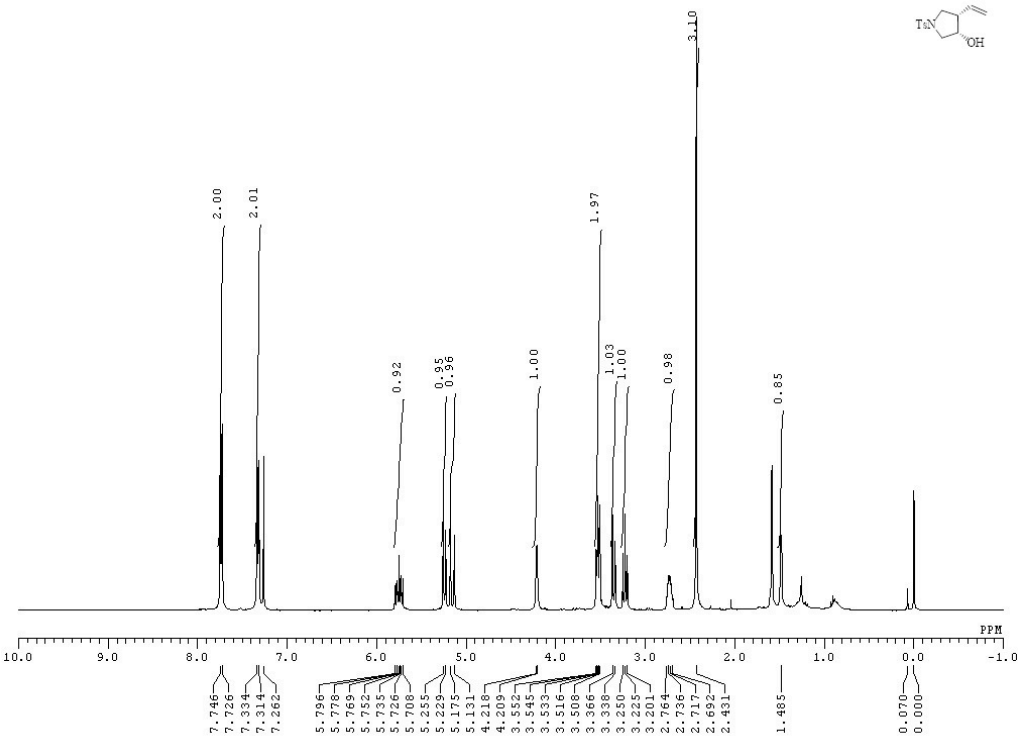


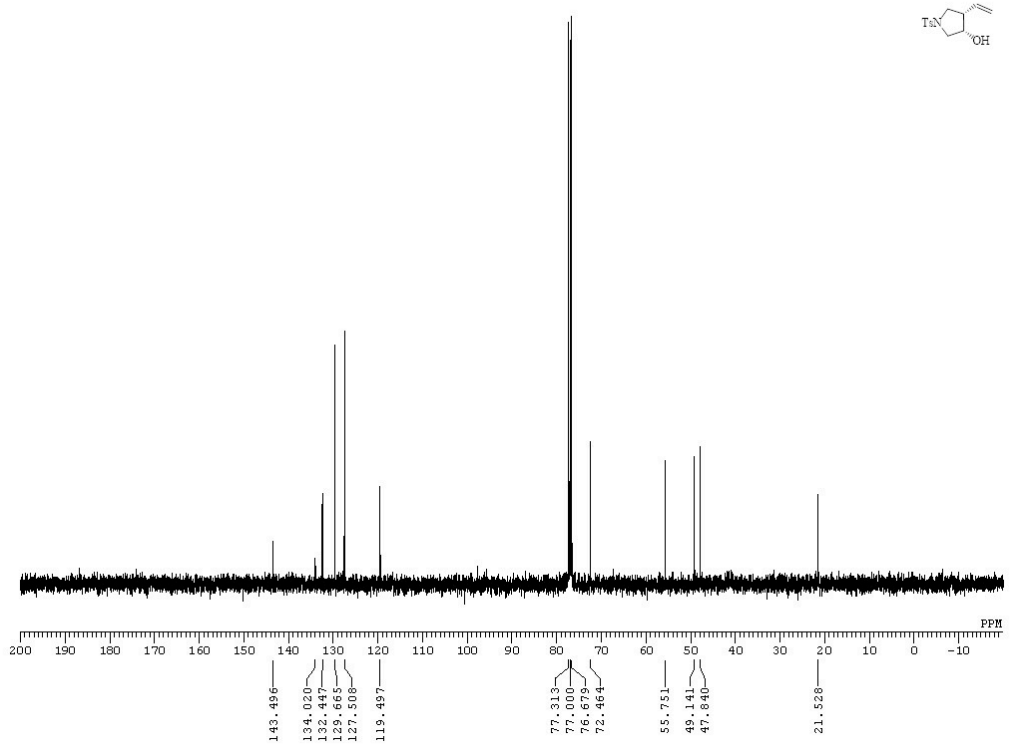
(*R*)-Spiro[4.5]decane-1,6-dione



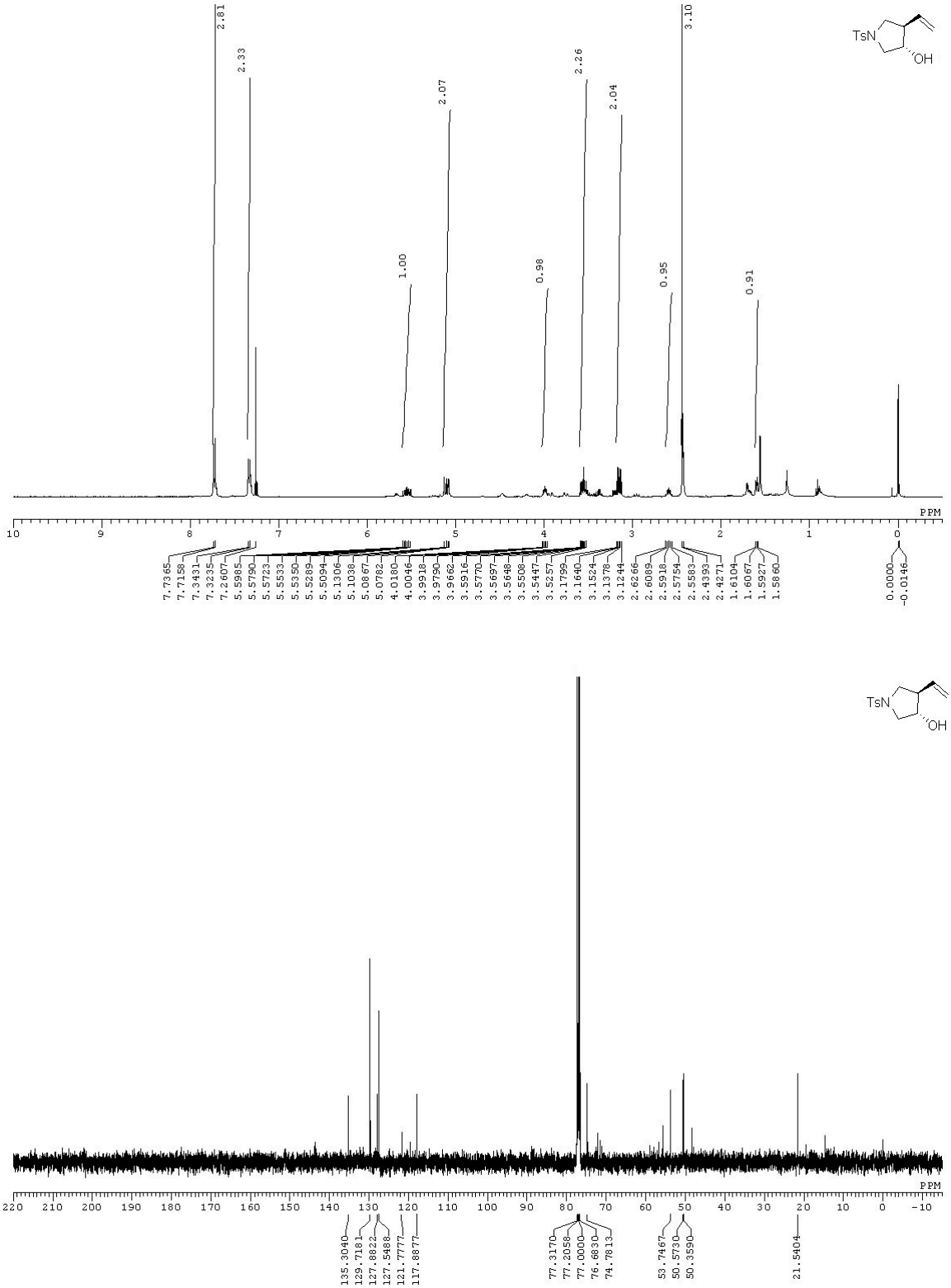


11i

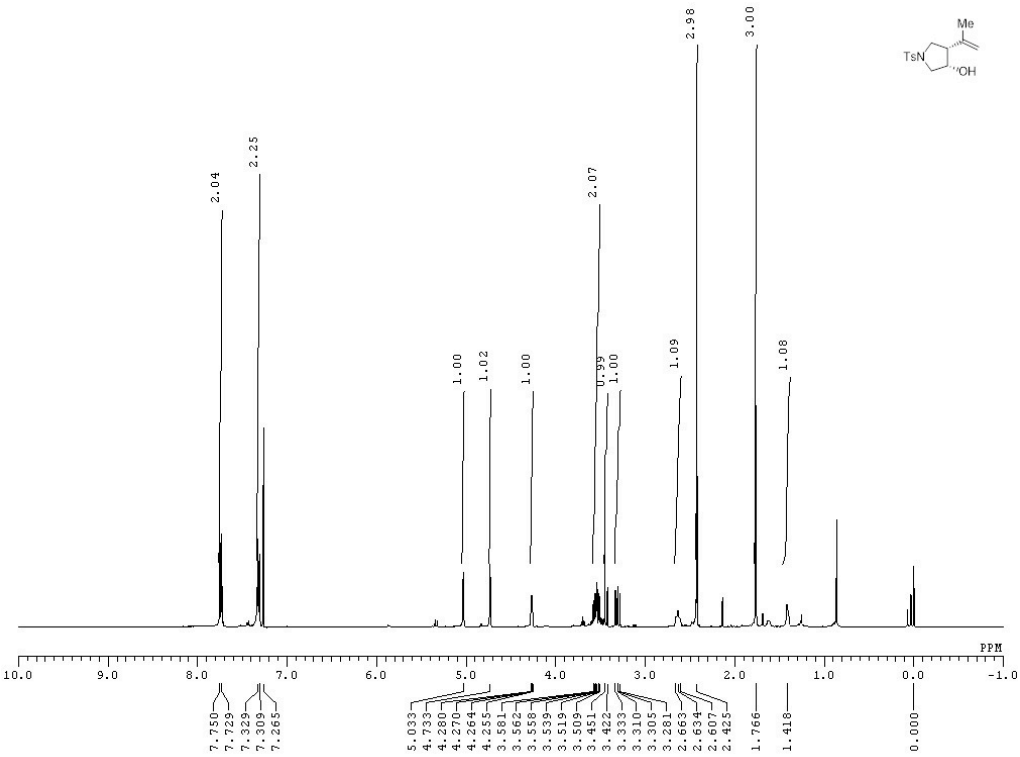

Ts
N
OH
2.00
2.01
0.92
0.95
0.96
1.00
1.97
1.03
1.00
0.98
3.10
0.85
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.746
7.726
7.334
7.314
7.262
5.796
5.778
5.769
5.752
5.735
5.726
5.708
5.255
5.229
5.175
5.131
4.218
4.209
3.552
3.545
3.533
3.516
3.508
3.366
3.338
3.250
3.225
3.201
2.764
2.736
2.717
2.692
2.431
1.485
0.070
0.000

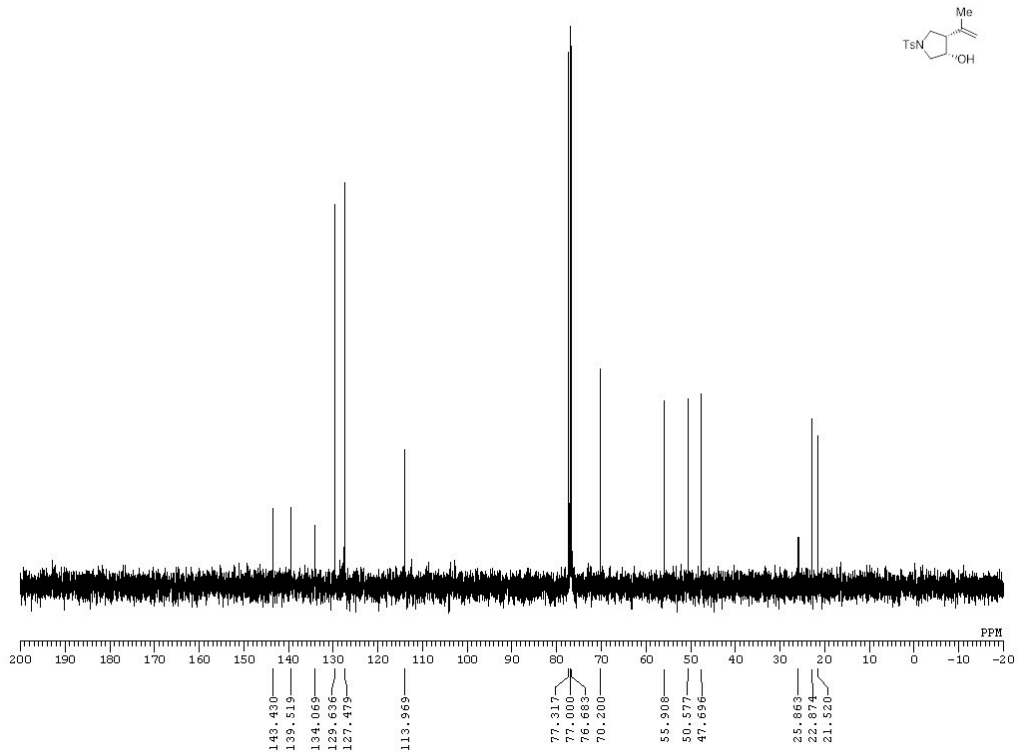

Ts
N
OH
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
143.496
134.020
132.447
129.665
127.508
119.497
77.313
77.000
76.679
72.464
55.751
49.141
47.840
21.528

11i'

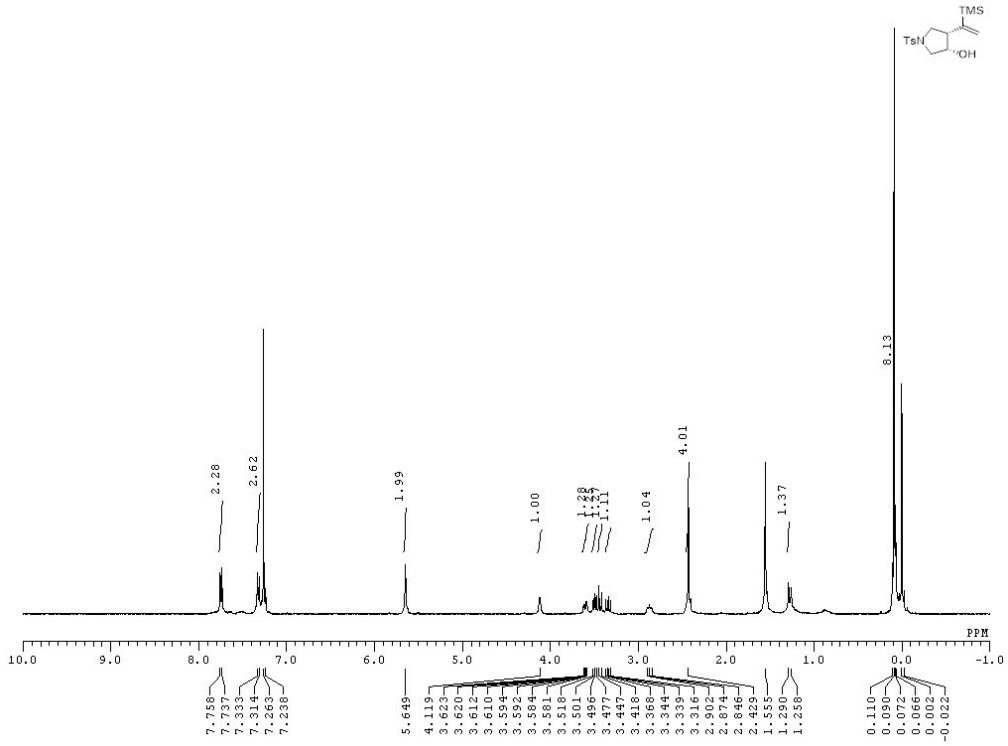

TsN
OH
2.81
2.33
2.07
1.00
0.98
2.26
2.04
0.95
3.10
0.91
PPM
10 9 8 7 6 5 4 3 2 1 0
7.7365 7.7158 7.3431 7.3235 7.2607 5.5985 5.5790 5.5723 5.5533 5.5350 5.5289 5.5094 5.1306 5.1038 5.0867 5.0782 4.0180 4.0046 3.9918 3.9790 3.9662 3.5916 3.5770 3.5697 3.5648 3.5508 3.5447 3.5257 3.1799 3.1640 3.1524 3.1378 3.1244 2.6266 2.6089 2.5918 2.5754 2.5583 2.4393 2.4271 1.6104 1.6067 1.5927 1.5860 0.0000 -0.0146
TsN
OH
PPM
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
135.3040 129.7181 127.8822 127.5488 121.7777 117.8877 77.3170 77.2058 77.0000 76.6830 74.7813 53.7467 50.5730 50.3590 21.5404

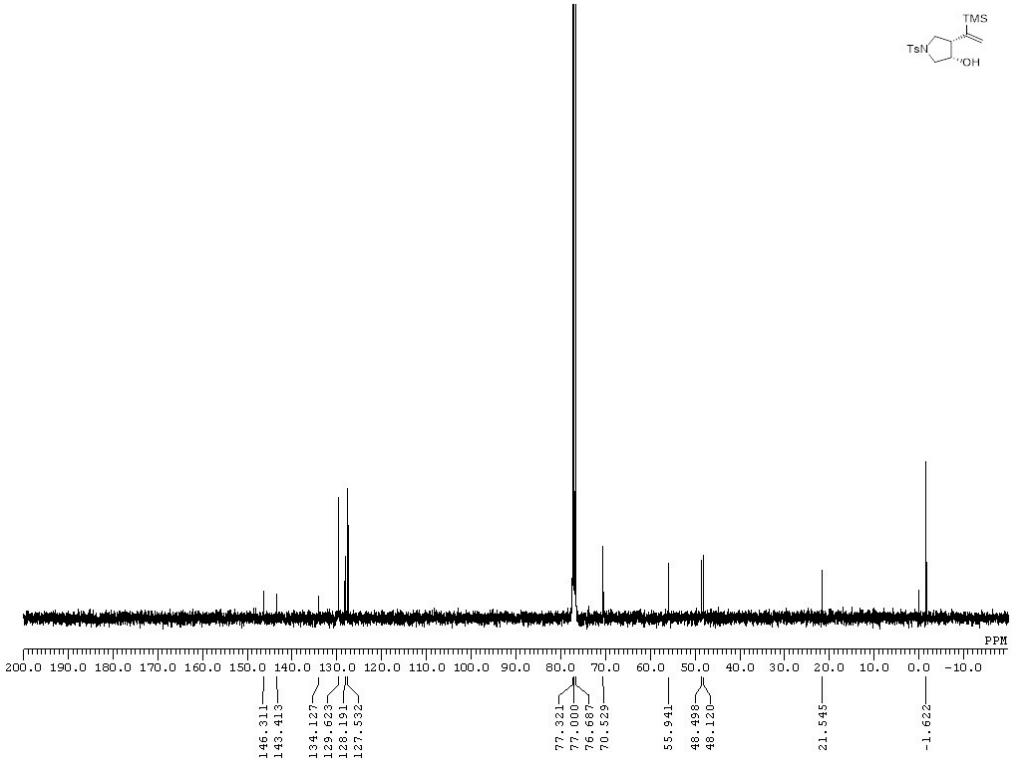
11j


Me
TsN
OH
2.98
3.00
2.04
2.25
2.07
1.00
1.02
1.00
0.99
1.00
1.09
1.08
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.750
7.729
7.329
7.309
7.265
5.033
4.733
4.280
4.270
4.264
4.255
3.581
3.562
3.558
3.539
3.519
3.509
3.451
3.422
3.333
3.310
3.305
3.281
2.683
2.634
2.607
2.425
1.766
1.418
0.000

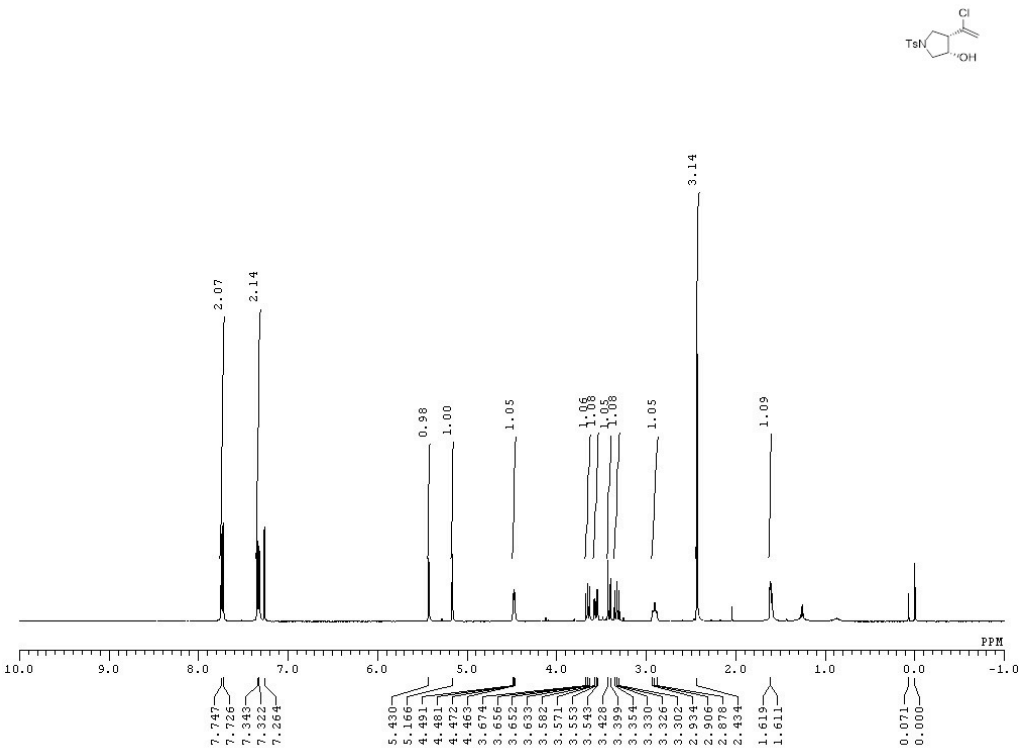

Me
TsN
OH
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
143.430
139.519
134.069
129.636
127.479
113.969
77.317
77.000
76.683
70.200
55.908
50.577
47.696
25.863
22.874
21.520

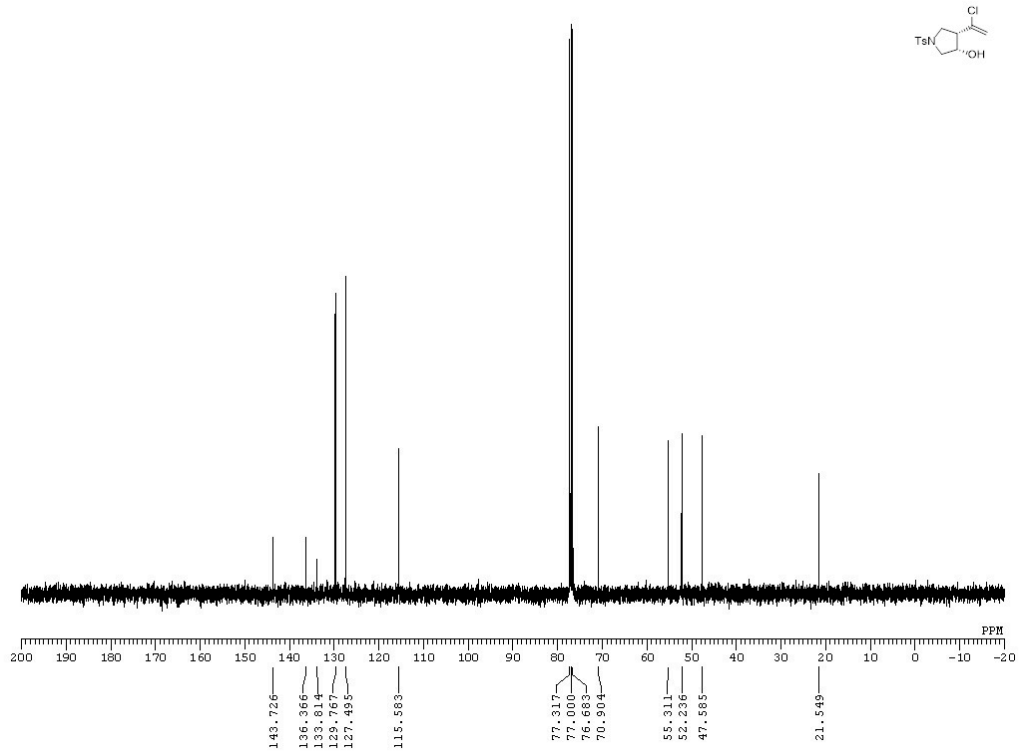
11k


TMS
TsN
OH
2.28
2.62
1.99
1.00
1.28
1.27
1.11
1.04
4.01
1.37
8.13
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.758 7.737 7.333 7.314 7.263 7.238
5.649 4.119 3.623 3.620 3.612 3.610 3.594 3.592 3.584 3.581 3.518 3.501 3.496 3.477 3.447 3.418 3.368 3.344 3.339 3.316 2.902 2.874 2.846 2.429 1.555 1.290 1.258
0.110 0.090 0.072 0.066 0.002 -0.022

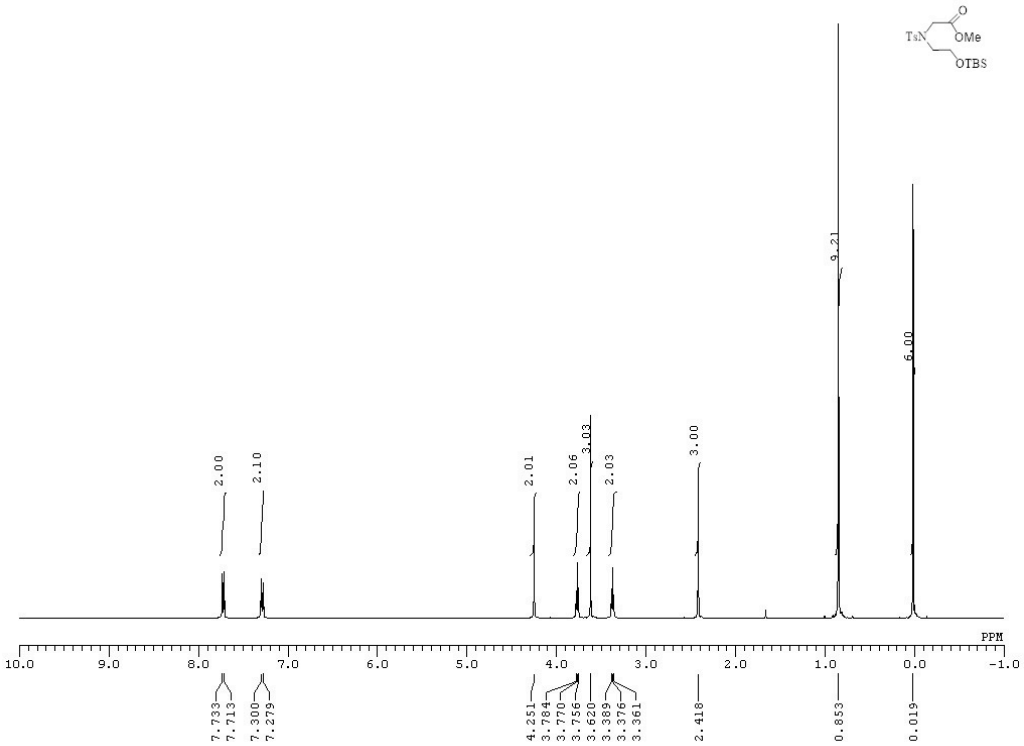

TMS
TsN
OH
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
146.311 143.413 134.127 129.623 128.191 127.532
77.321 77.000 76.687 70.529 55.941 48.498 48.120 21.545 -1.622

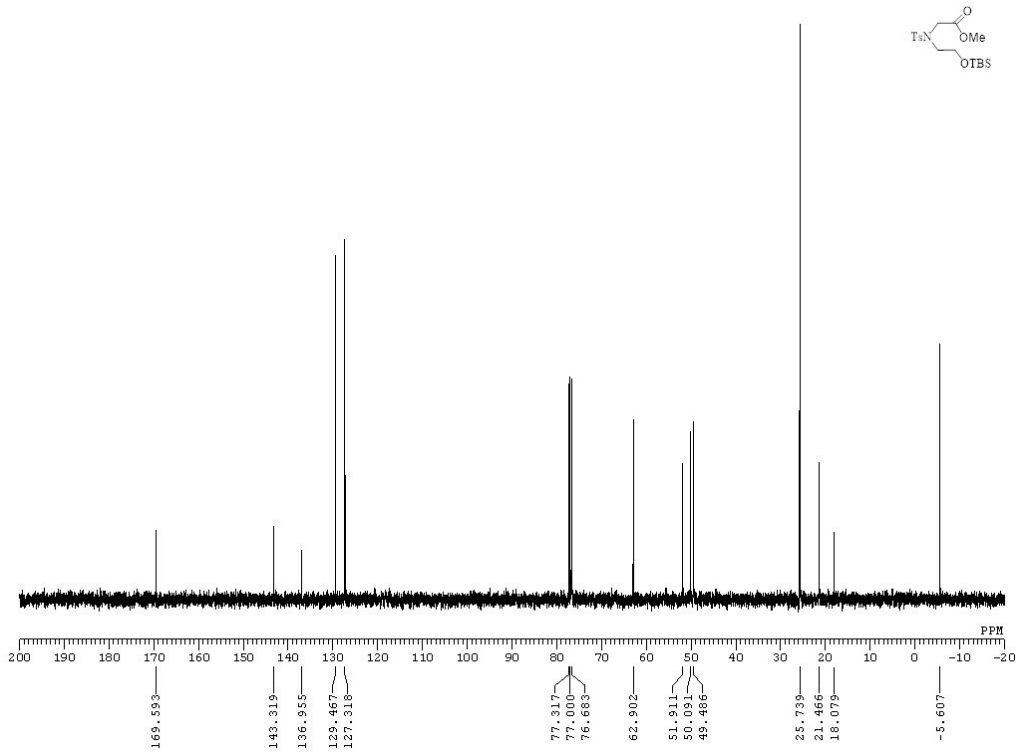
11l

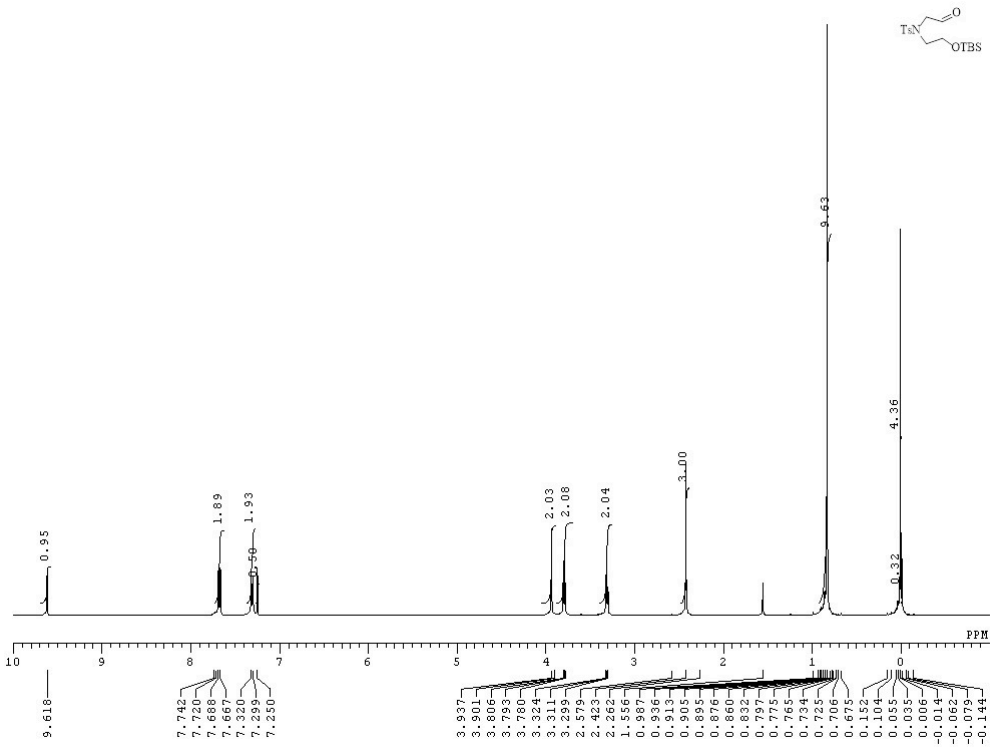

Cl
TsN
OH
3.14
2.07
2.14
0.98
1.00
1.05
1.06
1.08
1.03
1.08
1.05
1.09
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.747
7.726
7.343
7.322
7.264
5.430
5.166
4.491
4.481
4.472
4.463
3.674
3.656
3.652
3.633
3.582
3.571
3.553
3.543
3.428
3.399
3.354
3.330
3.326
3.302
2.934
2.906
2.878
2.494
1.619
1.611
0.071
0.000

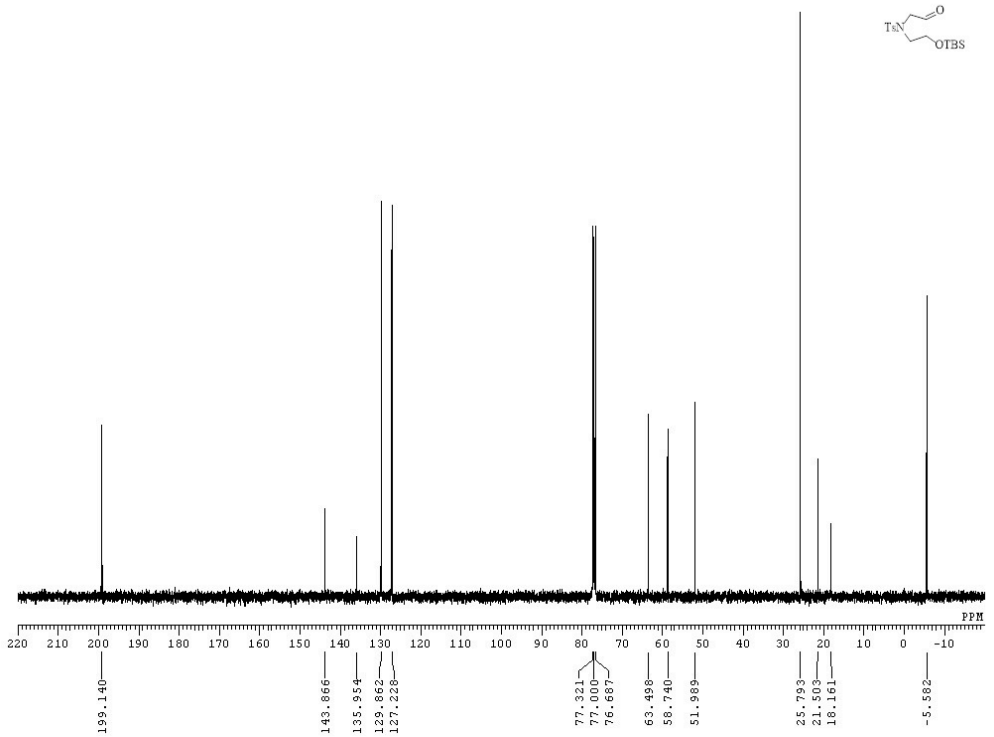

Cl
TsN
OH
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
143.726
136.366
133.814
129.767
127.495
115.583
77.317
77.000
76.683
70.904
55.311
52.236
47.585
21.549

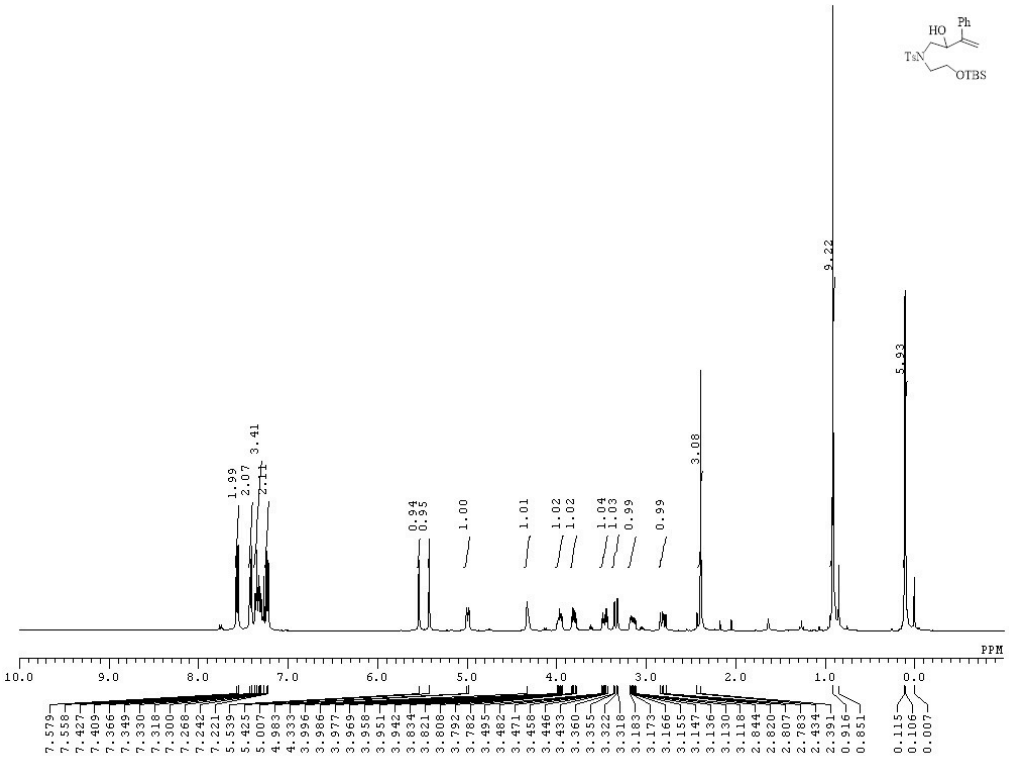
Substrate

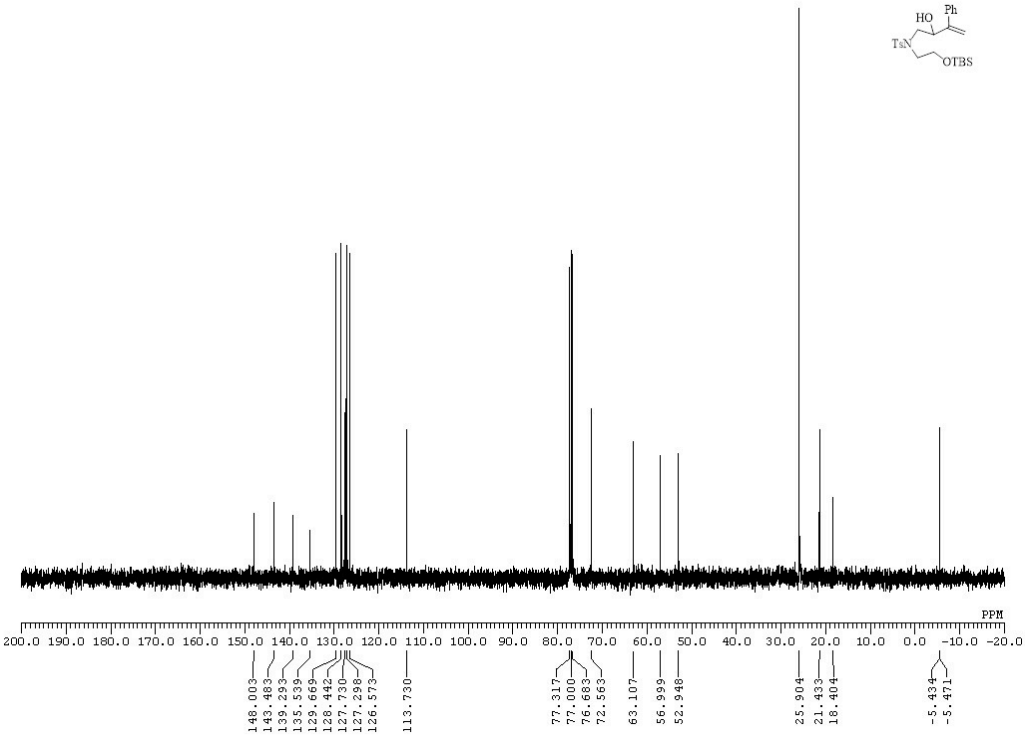

TsN
O
OMe
OTBS
2.00
2.10
2.01
2.06
3.03
2.03
3.00
9.21
6.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.733
7.713
7.300
7.279
4.251
3.784
3.770
3.756
3.620
3.389
3.376
3.361
2.418
0.853
0.019

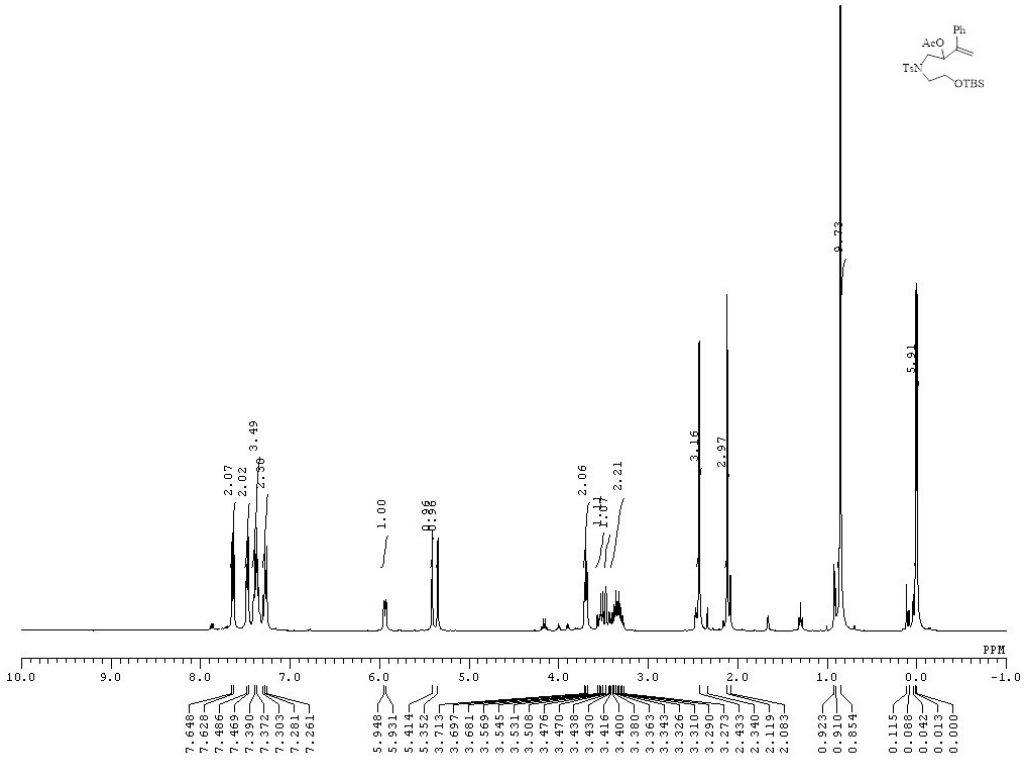

TsN
O
OMe
OTBS
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
169.593
143.319
136.955
129.467
127.318
77.317
77.000
76.683
62.902
51.911
50.091
49.486
25.739
21.466
18.079
-5.607

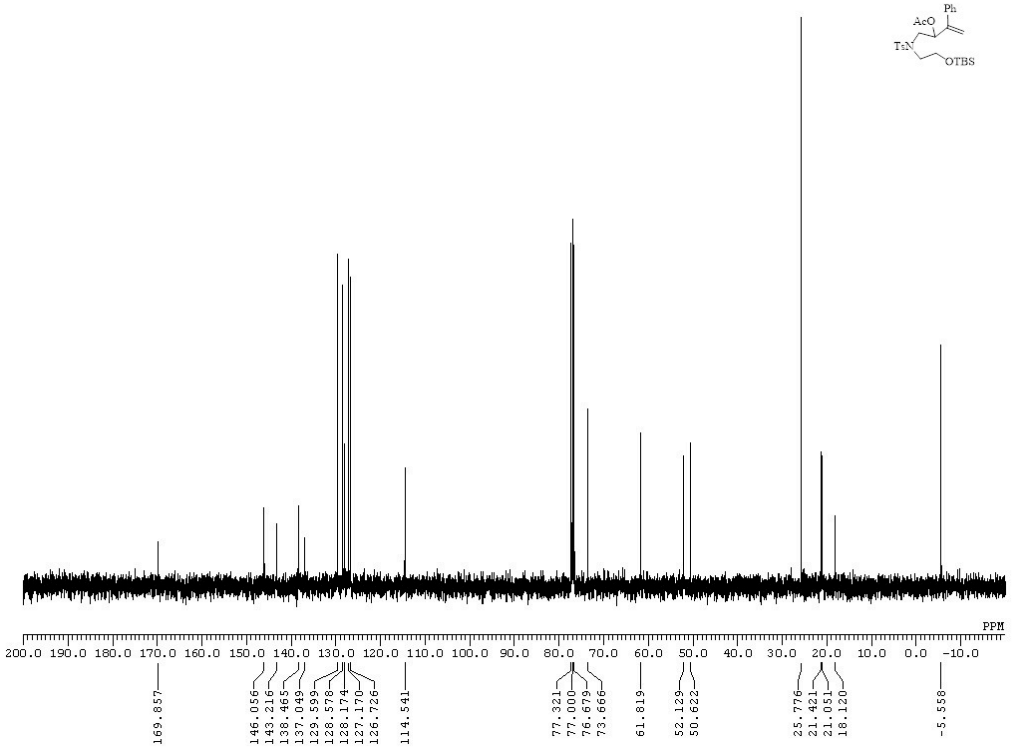

TsN
O
OTBS
0.95
1.89
1.93
0.50
2.03
2.08
2.04
3.00
9.63
4.36
0.32
PPM
9.618
7.742
7.720
7.688
7.667
7.320
7.299
7.250
3.937
3.901
3.806
3.793
3.780
3.324
3.311
3.299
2.579
2.423
2.262
1.556
0.987
0.936
0.913
0.905
0.895
0.876
0.860
0.832
0.797
0.775
0.765
0.734
0.725
0.706
0.675
0.152
0.104
0.055
0.035
0.006
-0.014
-0.062
-0.079
-0.144

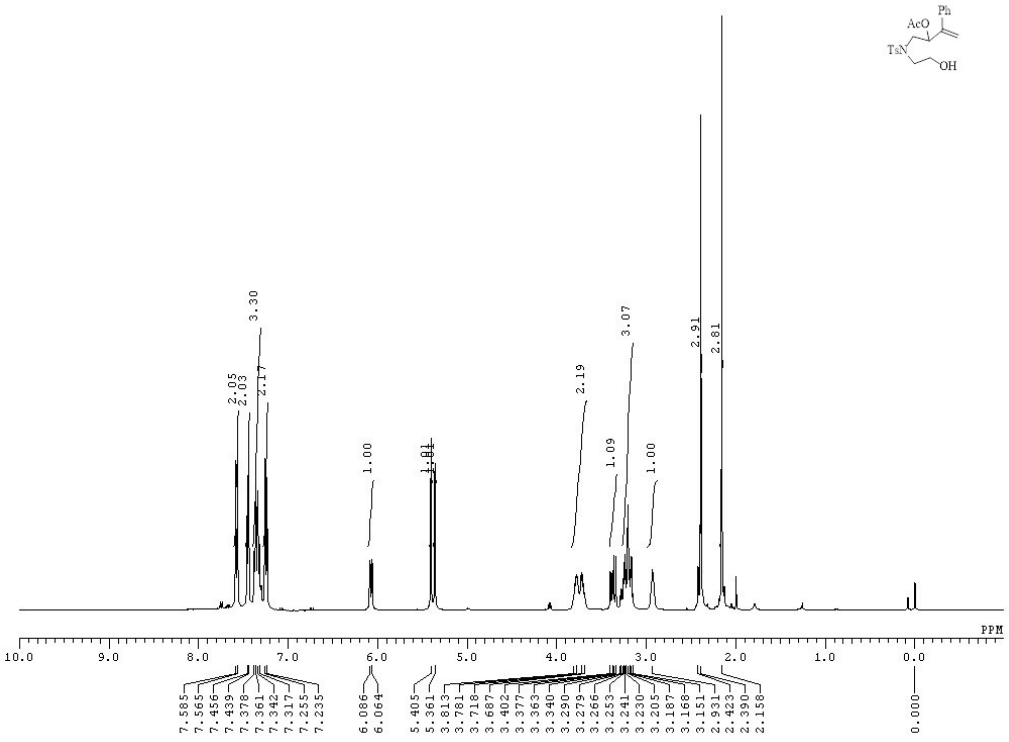

TsN
O
OTBS
PPM
199.140
143.866
135.954
129.862
127.228
77.321
77.000
76.687
63.498
58.740
51.989
25.793
21.503
18.161
-5.582

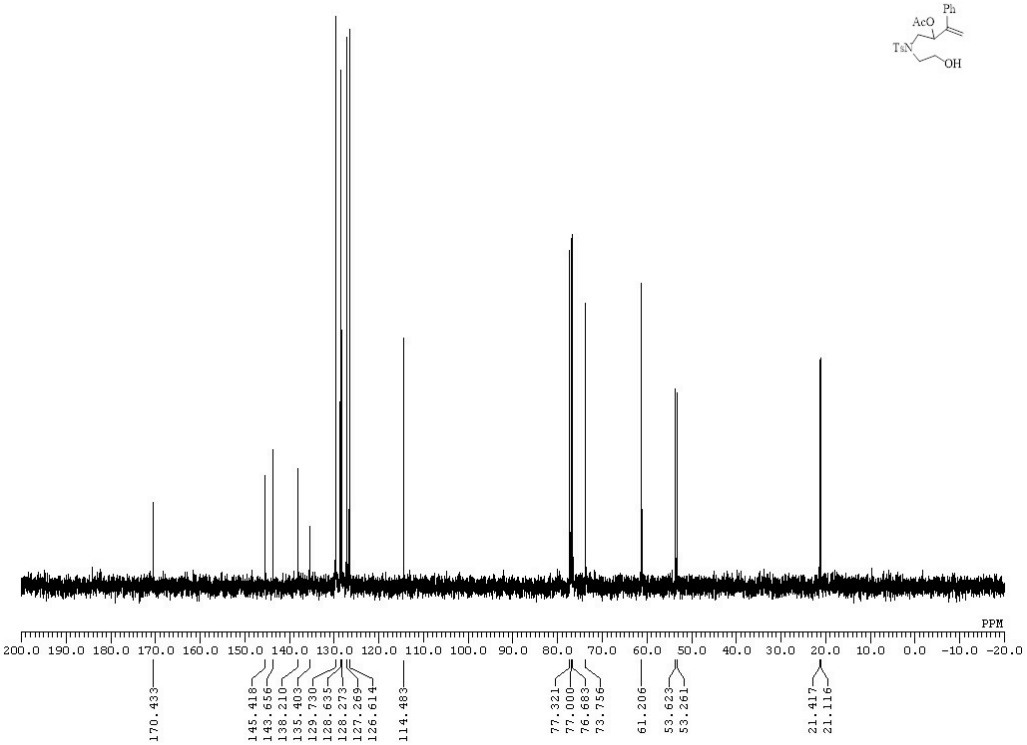

HO
Ph
TsN
OTBS
9.22
5.93
3.08
1.99
2.07
3.41
2.11
0.94
0.95
1.00
1.01
1.02
1.02
1.04
1.03
0.99
0.99
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.579
7.558
7.427
7.409
7.366
7.349
7.330
7.318
7.300
7.268
7.242
7.221
5.539
5.425
5.007
4.983
4.333
3.996
3.986
3.977
3.969
3.958
3.951
3.942
3.834
3.821
3.808
3.792
3.782
3.495
3.482
3.471
3.458
3.446
3.433
3.360
3.355
3.322
3.318
3.183
3.173
3.166
3.155
3.147
3.136
3.130
3.118
2.844
2.820
2.807
2.783
2.434
2.391
0.916
0.851
0.115
0.106
0.007


HO
Ph
TsN
OTBS
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
148.003
143.483
139.293
135.539
129.669
128.442
127.730
127.298
126.573
113.730
77.317
77.000
76.683
72.563
63.107
56.999
52.948
25.904
21.433
18.404
-5.434
-5.471

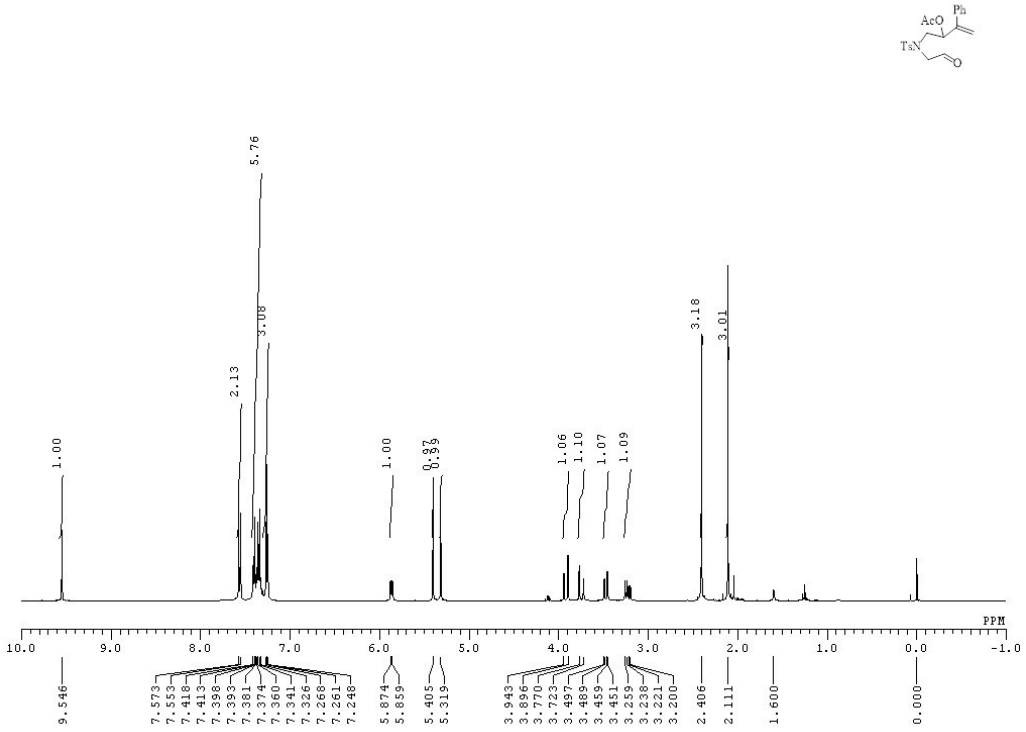

Ph
AcO
TsN
OTBS
9.73
5.81
3.16
2.97
2.07
2.02
2.30
3.49
1.00
0.98
2.06
1.07
2.21
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.648 7.628 7.486 7.469 7.390 7.372 7.303 7.281 7.261
5.948 5.931 5.414 5.352 3.713 3.697 3.681 3.569 3.545 3.531 3.508 3.476 3.470 3.438 3.430 3.416 3.400 3.380 3.363 3.343 3.326 3.310 3.290 3.273 2.433 2.340 2.119 2.083
0.923 0.910 0.854
0.115 0.088 0.042 0.013 0.000

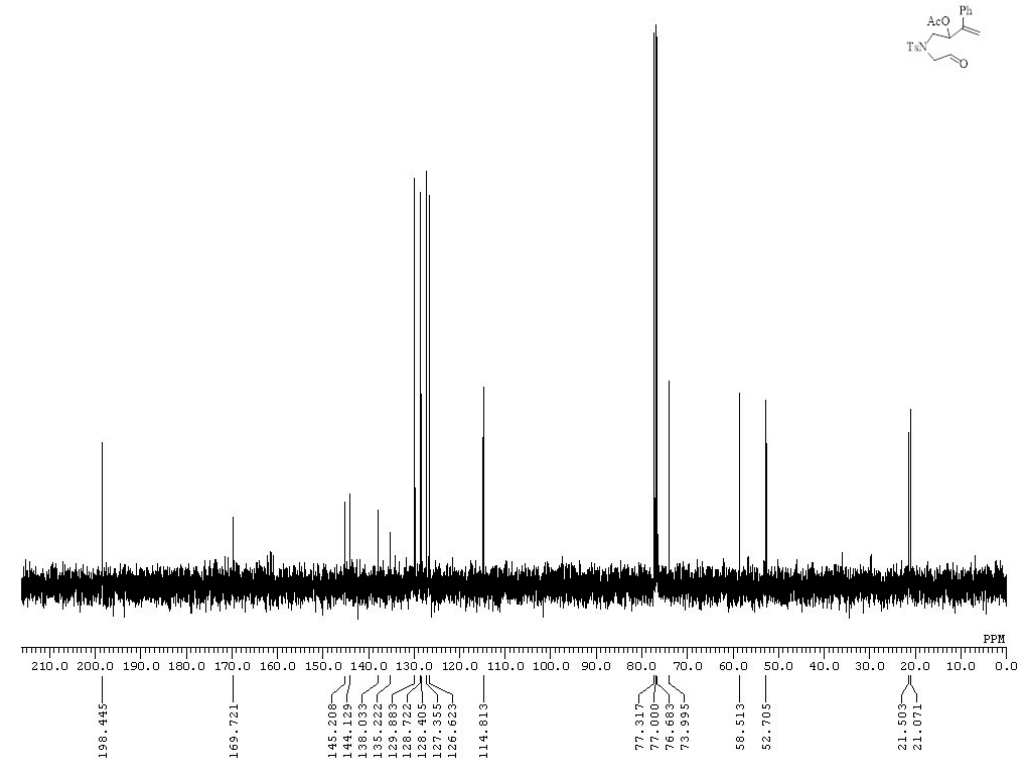

Ph
AcO
TsN
OTBS
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
169.857
146.056 143.216 138.465 137.049 129.599 128.578 128.174 127.170 126.726
114.541
77.321 77.000 76.679 73.666
61.819
52.129 50.622
25.776 21.421 21.051 18.120
-5.558

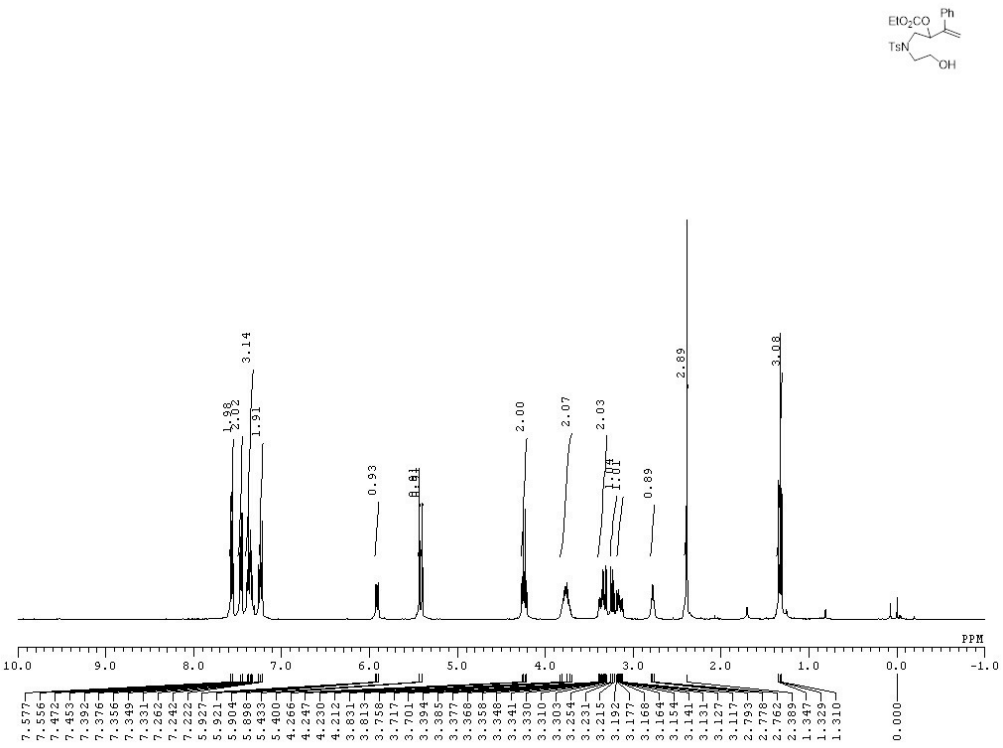

Ph
AcO
TsN
OH
2.05
2.03
3.30
2.17
1.00
1.01
1.01
2.19
1.09
3.07
1.00
2.91
2.81
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.585
7.565
7.456
7.439
7.378
7.361
7.342
7.317
7.255
7.235
6.086
6.064
5.405
5.361
3.813
3.781
3.718
3.687
3.402
3.377
3.363
3.340
3.290
3.279
3.266
3.253
3.241
3.230
3.205
3.187
3.168
3.151
2.931
2.423
2.390
2.158
0.000

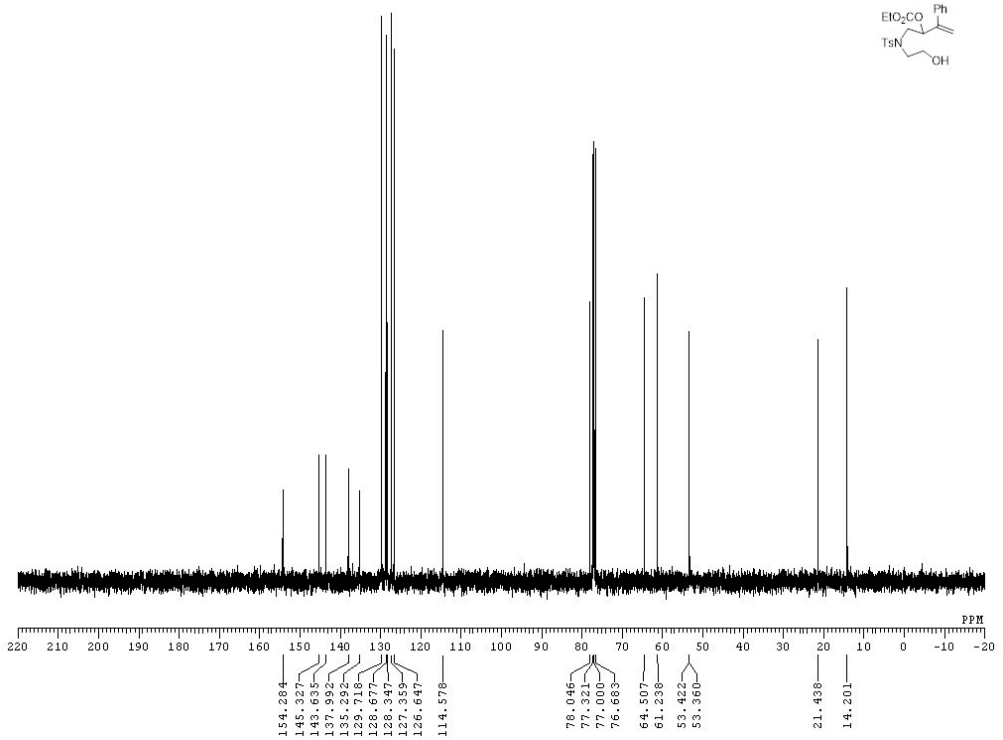

Ph
AcO
TsN
OH
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
170.433
145.418
143.656
138.210
135.403
129.730
128.635
128.273
127.269
126.614
114.483
77.321
77.000
76.683
73.756
61.206
53.623
53.261
21.417
21.116

13a

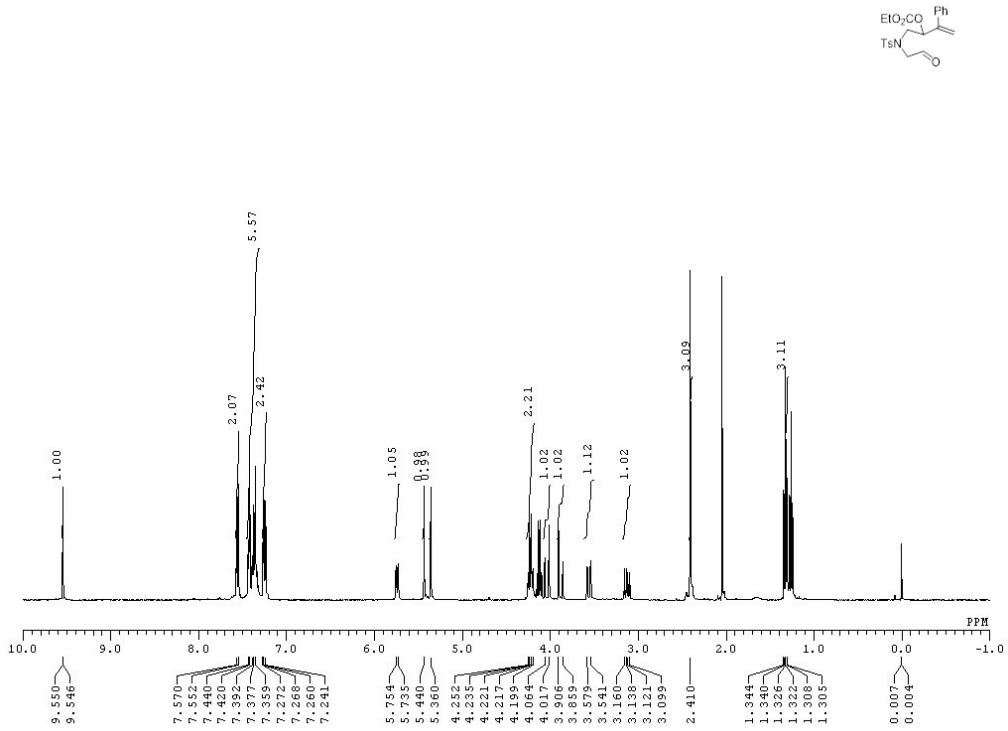

AcO
Ph
TsN
O
5.76
3.08
2.13
1.00
1.00
0.97
0.99
1.06
1.10
1.07
1.09
3.18
3.01
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
9.546
7.573 7.553 7.418 7.413 7.398 7.393 7.381 7.374 7.360 7.341 7.326 7.268 7.261 7.248
5.874 5.859
5.405 5.319
3.943 3.896 3.770 3.723 3.497 3.489 3.459 3.451 3.259 3.238 3.221 3.200
2.406
2.111
1.600
0.000

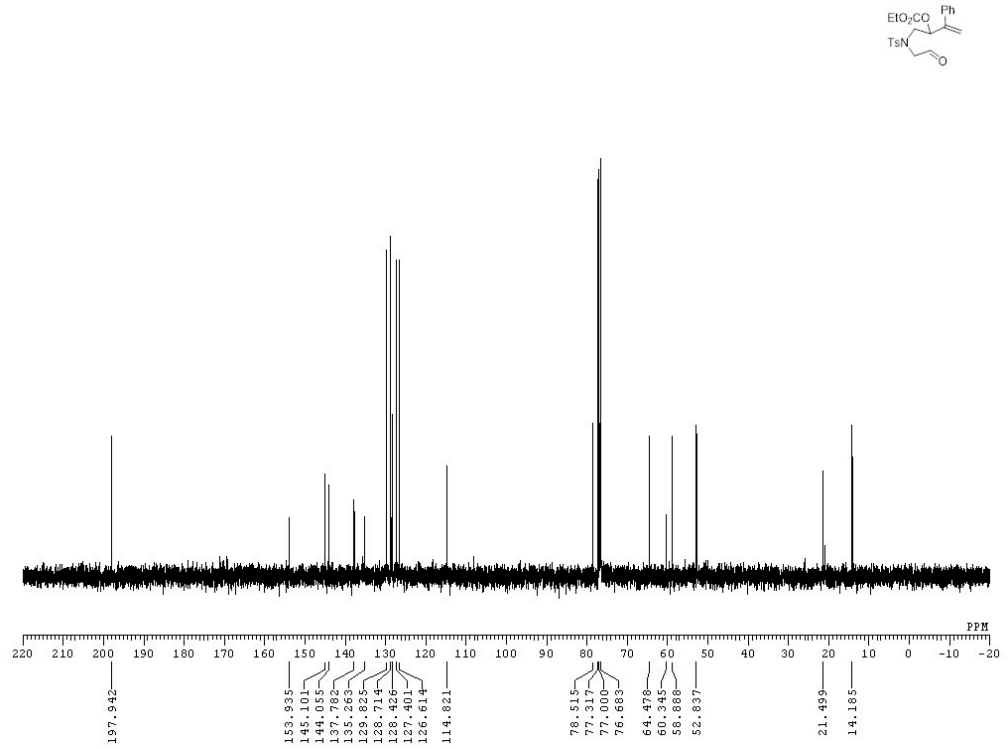

AcO
Ph
TsN
O
PPM
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
198.445
169.721
145.208
144.129
138.033
135.222
129.883
128.722
128.405
127.355
126.623
114.813
77.317
77.000
76.683
73.995
58.513
52.705
21.503
21.071

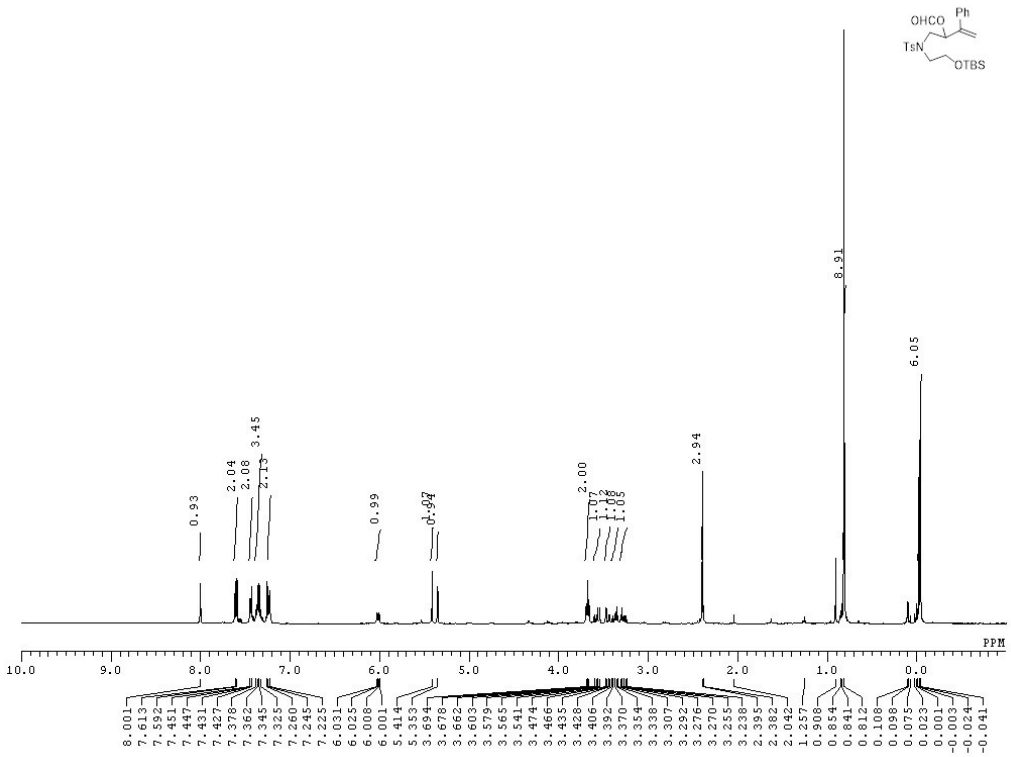

EtO2CO
Ph
TsN
OH
3.14
2.02
1.91
0.93
2.00
2.07
2.03
1.01
0.89
2.89
3.08
PPM

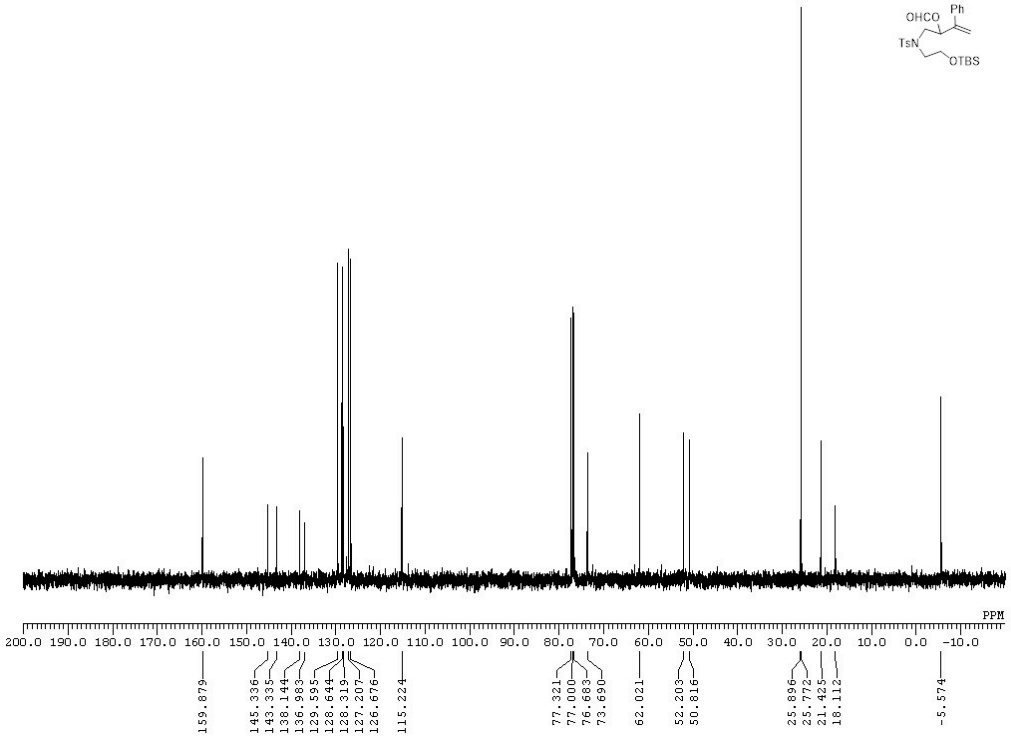

EtO2CO
Ph
TsN
OH
PPM

13b

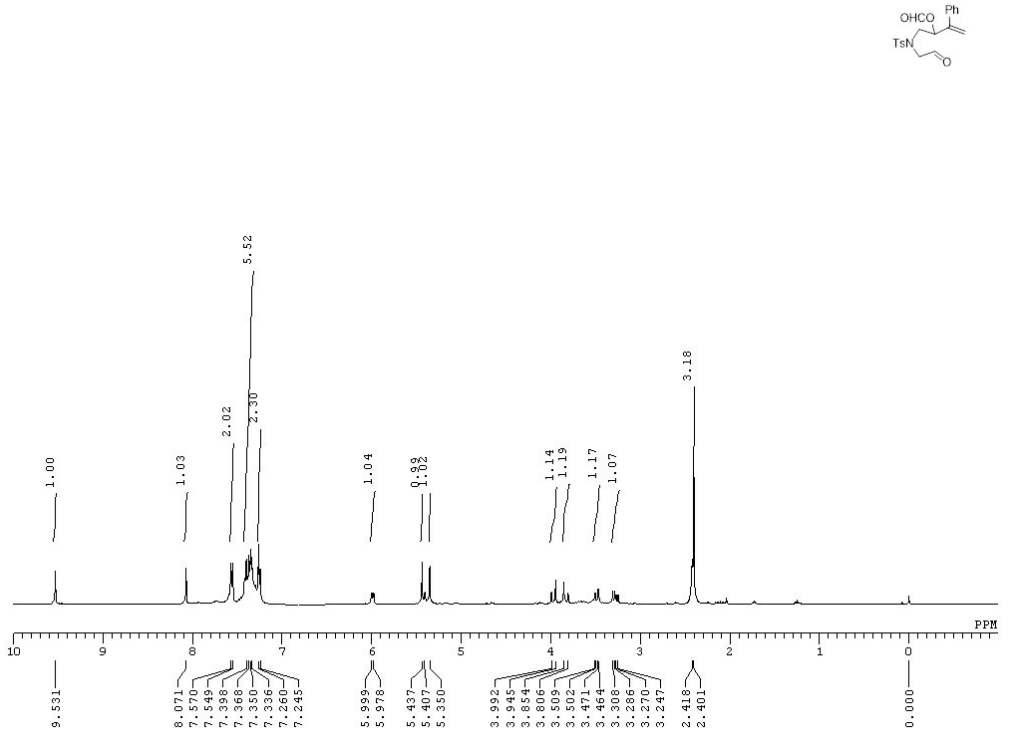

EtO2CO
Ph
TsN
O
1.00
2.07
5.57
2.42
1.05
0.88
0.99
2.21
1.02
1.02
1.12
1.02
3.09
3.11
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
9.550
9.546
7.570
7.552
7.440
7.420
7.392
7.377
7.359
7.272
7.268
7.260
7.241
5.754
5.735
5.440
5.360
4.252
4.235
4.221
4.217
4.199
4.064
4.017
3.906
3.859
3.579
3.541
3.160
3.138
3.121
3.099
2.410
1.344
1.340
1.326
1.322
1.308
1.305
0.007
0.004


EtO2CO
Ph
TsN
O
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
197.942
153.935
145.101
144.055
137.782
135.263
129.825
128.714
128.426
127.401
126.614
114.821
78.515
77.317
77.000
76.683
64.478
60.345
58.888
52.837
21.499
14.185


OHCO
Ph
TsN
OTBS
0.93
2.04
2.08
3.45
2.13
0.99
0.97
2.00
1.07
1.08
1.05
2.94
8.91
6.05
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.001
7.613
7.592
7.451
7.447
7.431
7.427
7.378
7.362
7.345
7.325
7.260
7.245
7.225
6.031
6.025
6.008
6.001
5.414
5.353
3.694
3.678
3.662
3.603
3.579
3.565
3.541
3.474
3.466
3.435
3.428
3.406
3.392
3.370
3.354
3.338
3.307
3.292
3.276
3.270
3.255
3.238
2.395
2.382
2.042
1.257
0.908
0.854
0.841
0.812
0.108
0.098
0.075
0.023
0.001
-0.003
-0.024
-0.041


OHCO
Ph
TsN
OTBS
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
159.879
145.336
143.335
138.144
136.983
129.595
128.644
128.319
127.207
126.676
115.224
77.321
77.000
76.683
73.690
62.021
52.203
50.816
25.896
25.772
21.425
18.112
-5.574

13c


OHCO
Ph
TsN
O
5.52
3.18
2.02
2.30
1.00
1.03
1.04
0.98
1.02
1.14
1.19
1.17
1.07
PPM
10
9
8
7
6
5
4
3
2
1
0
9.531
8.071
7.570
7.549
7.398
7.368
7.350
7.336
7.260
7.245
5.999
5.978
5.437
5.407
5.350
3.992
3.945
3.854
3.806
3.509
3.502
3.471
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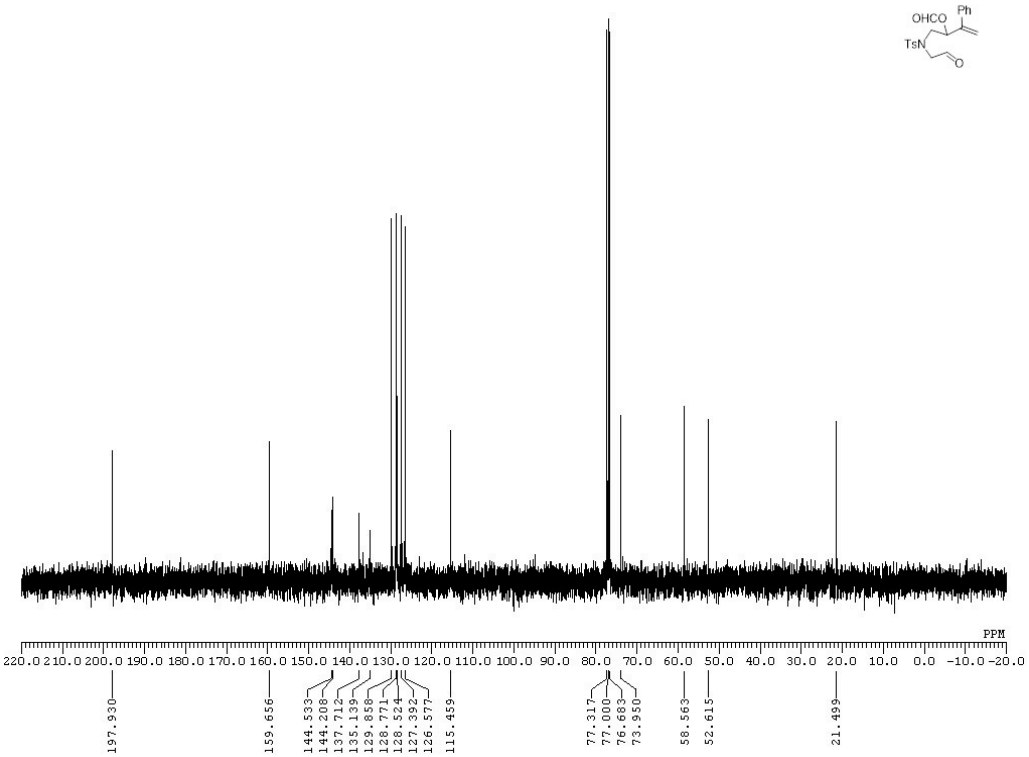
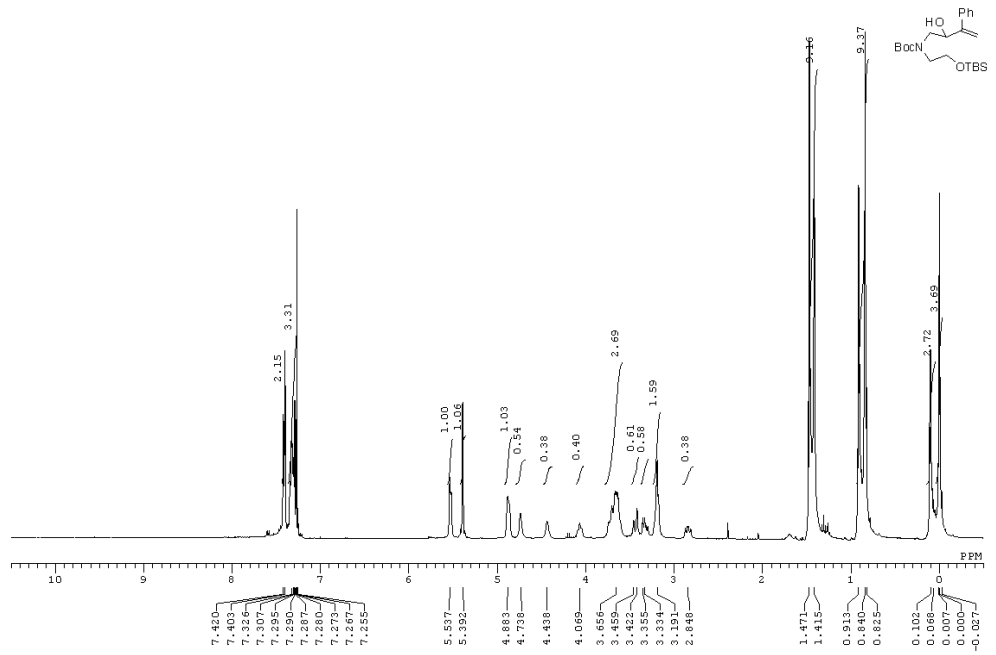
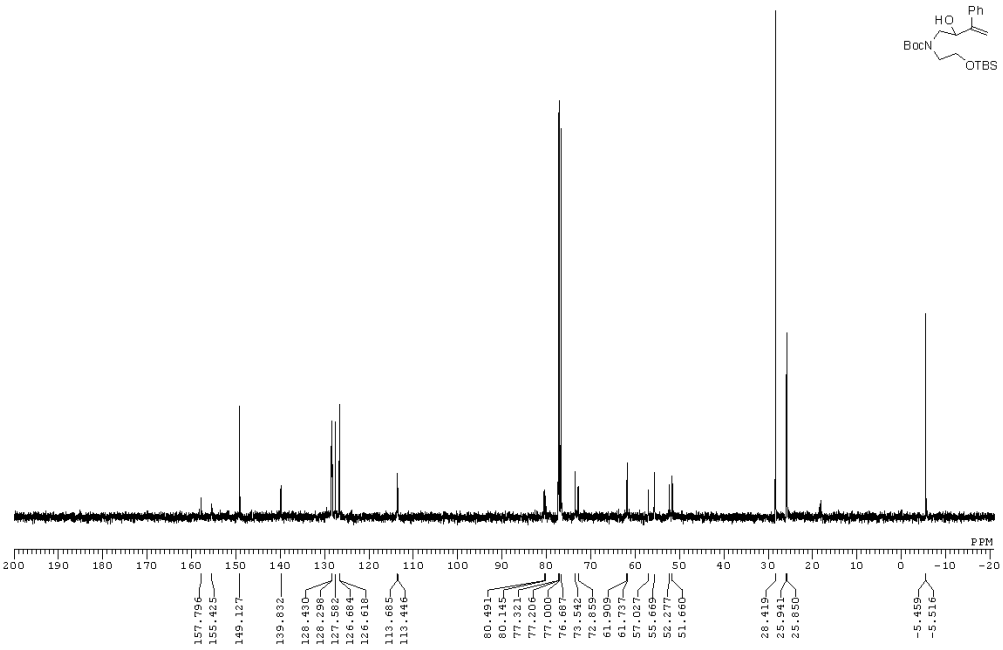
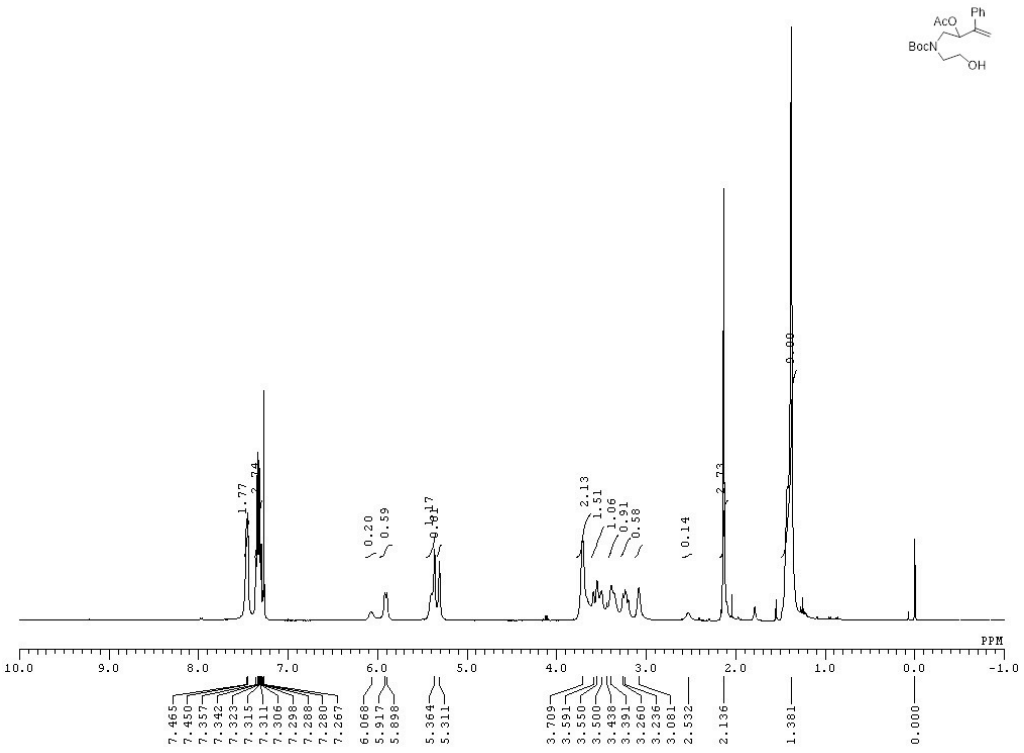
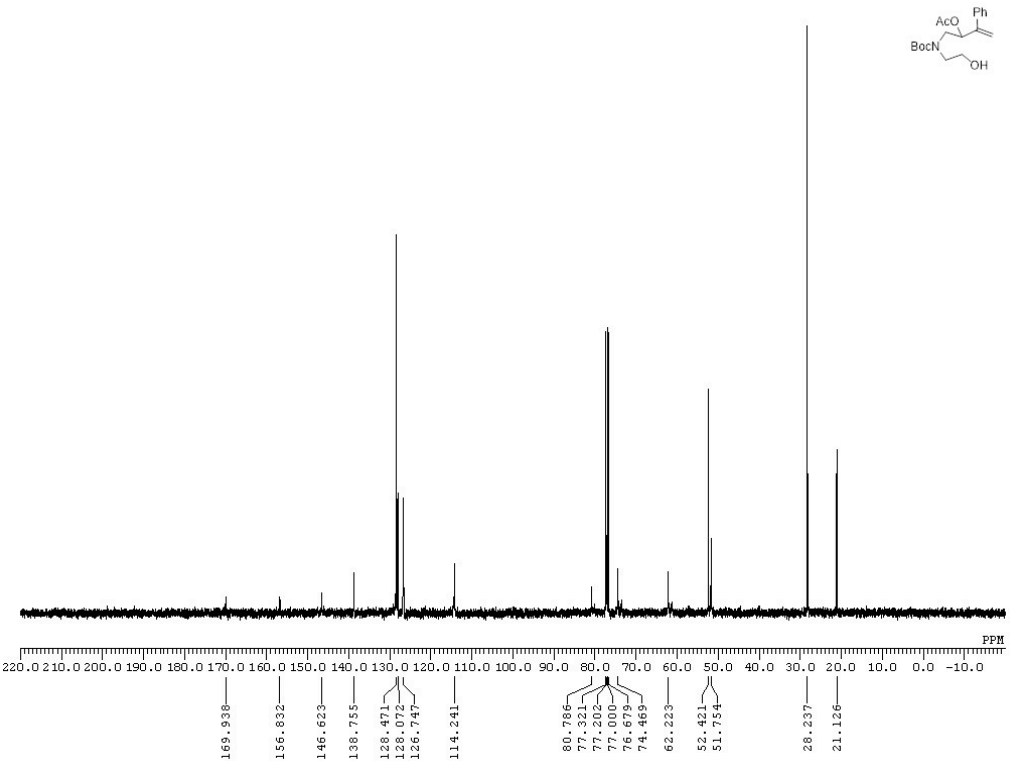
3.308
3.286
3.270
3.247
2.418
2.401
0.000


OHCO
Ph
TsN
O
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
197.930
159.656
144.533
144.208
137.712
135.139
129.858
128.771
128.524
127.392
126.577
115.459
77.317
77.000
76.683
73.950
58.563
52.615
21.499

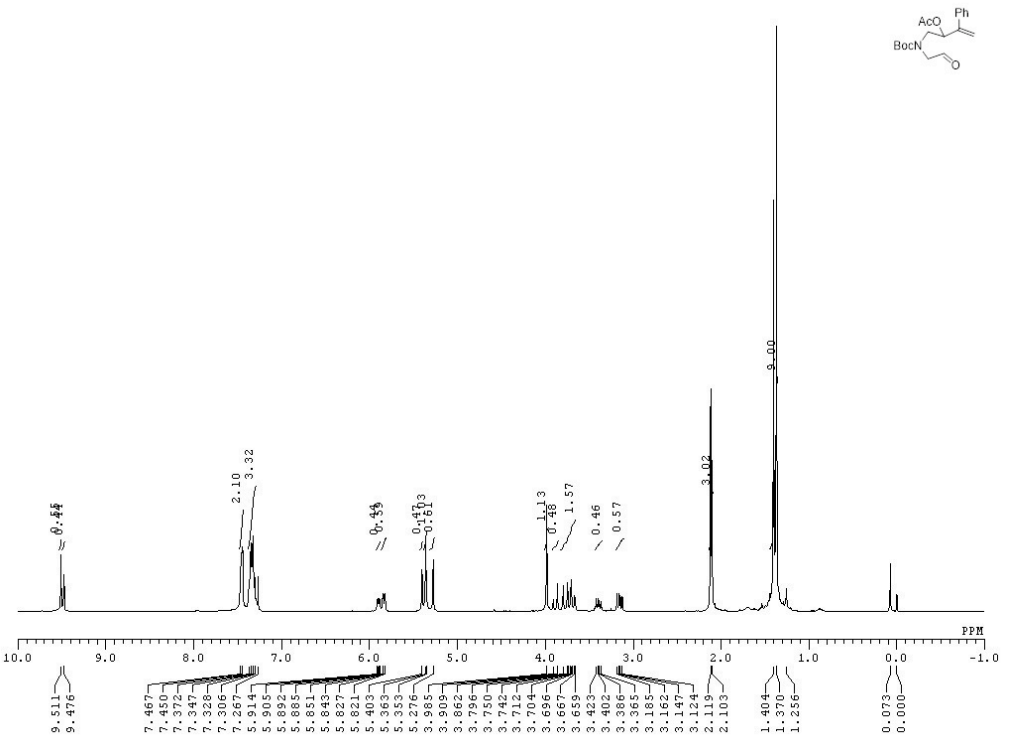

HO
Ph
BocN
OTBS
9.16
9.37
3.31
2.15
2.72
3.69
2.69
1.59
1.00
1.08
1.03
0.54
0.38
0.40
0.61
0.58
0.38
PPM
7.420
7.403
7.326
7.307
7.295
7.290
7.287
7.280
7.273
7.267
7.255
5.537
5.392
4.883
4.738
4.438
4.069
3.656
3.459
3.422
3.355
3.334
3.191
2.848
1.471
1.415
0.913
0.840
0.825
0.102
0.066
0.007
0.000
-0.027


HO
Ph
BocN
OTBS
PPM
157.796
155.425
149.127
139.832
128.430
128.298
127.582
126.684
126.618
113.685
113.446
80.491
80.145
77.321
77.206
77.000
76.667
73.542
72.859
61.909
61.737
57.027
55.669
52.277
51.660
28.419
25.941
25.850
-5.459
-5.516


AcO
Ph
BocN
OH
1.77
2.74
0.20
0.59
1.17
2.13
1.51
1.06
0.91
0.58
0.14
2.73
9.00
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.465 7.450 7.357 7.342 7.323 7.315 7.311 7.306 7.298 7.288 7.280 7.267
6.068 5.917 5.898
5.364 5.311
3.709 3.591 3.550 3.500 3.438 3.391 3.260 3.236 3.081
2.532
2.136
1.381
0.000


AcO
Ph
BocN
OH
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
169.938
156.832
146.623
138.755
128.471
128.072
126.747
114.241
80.786
77.321
77.202
77.000
76.679
74.469
62.223
52.421
51.754
28.237
21.126

13d


AcO
Ph
BocN
O
PPM
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
0.44
2.10
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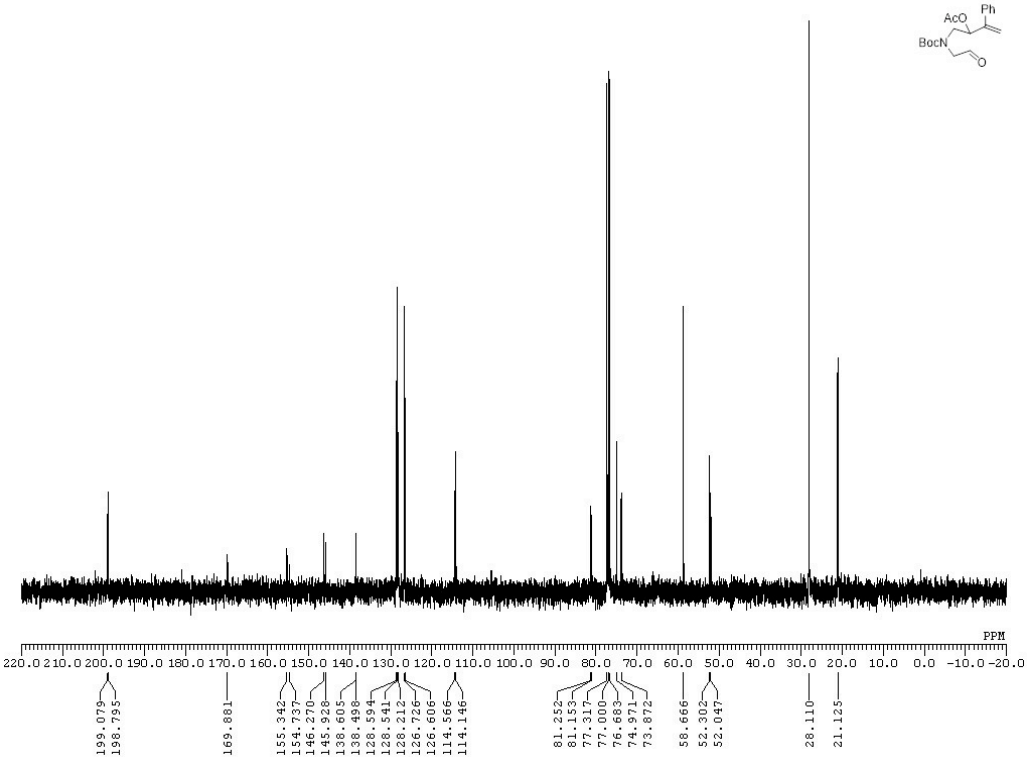
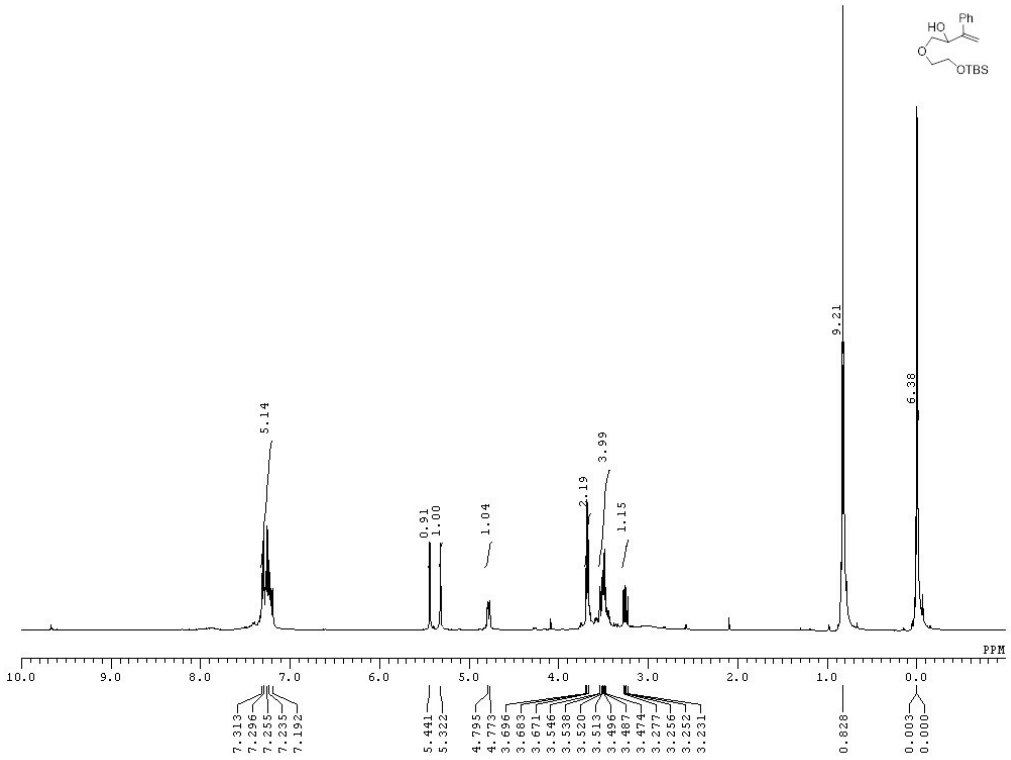
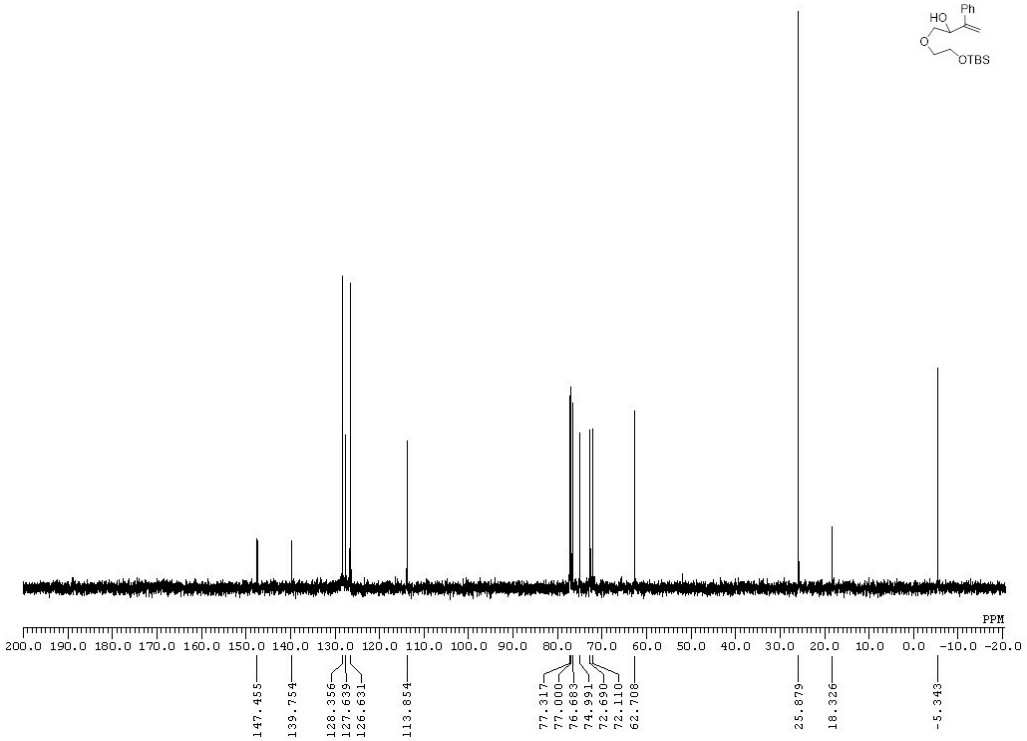
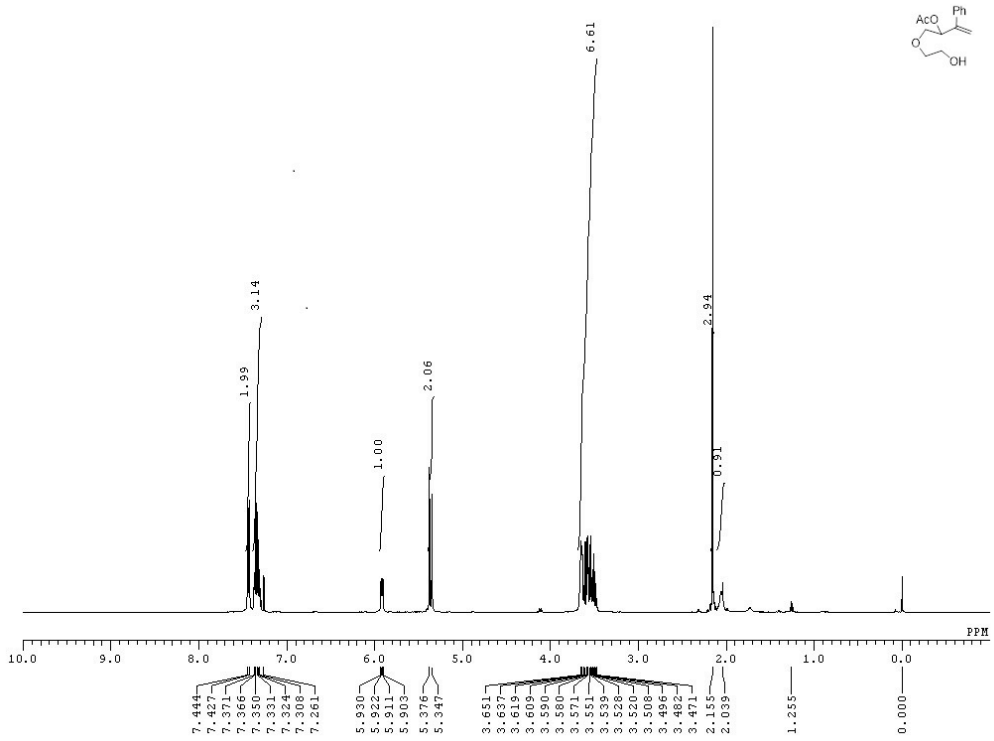
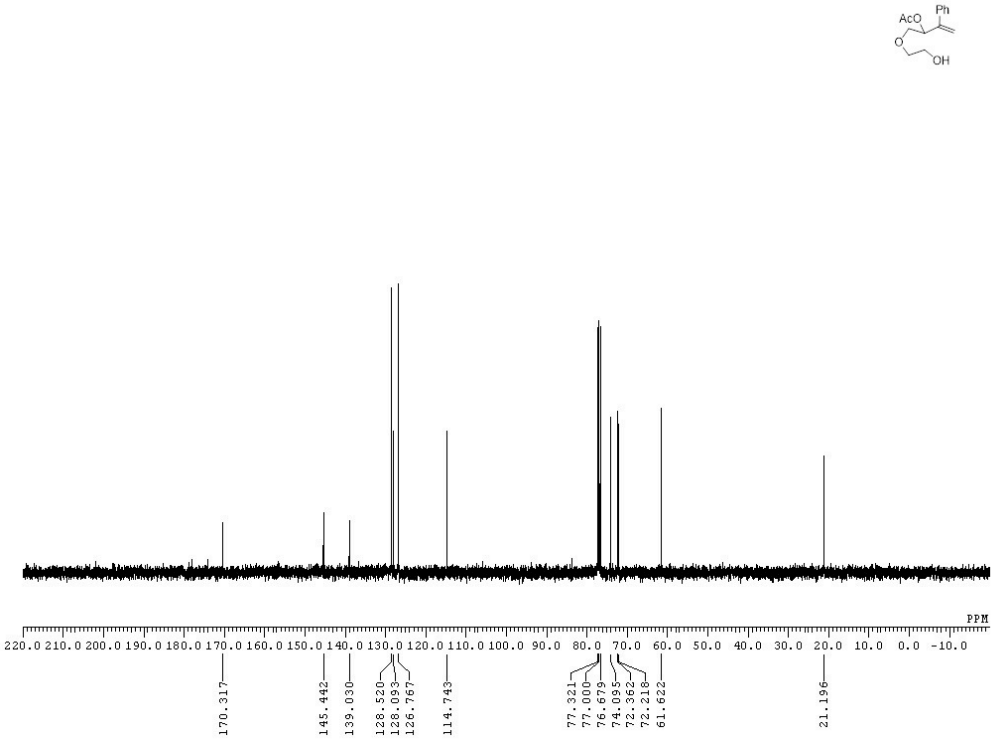
0.47
0.61
1.13
0.48
1.57
0.46
0.57
3.02
9.00


AcO
Ph
BocN
O
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
-20.0

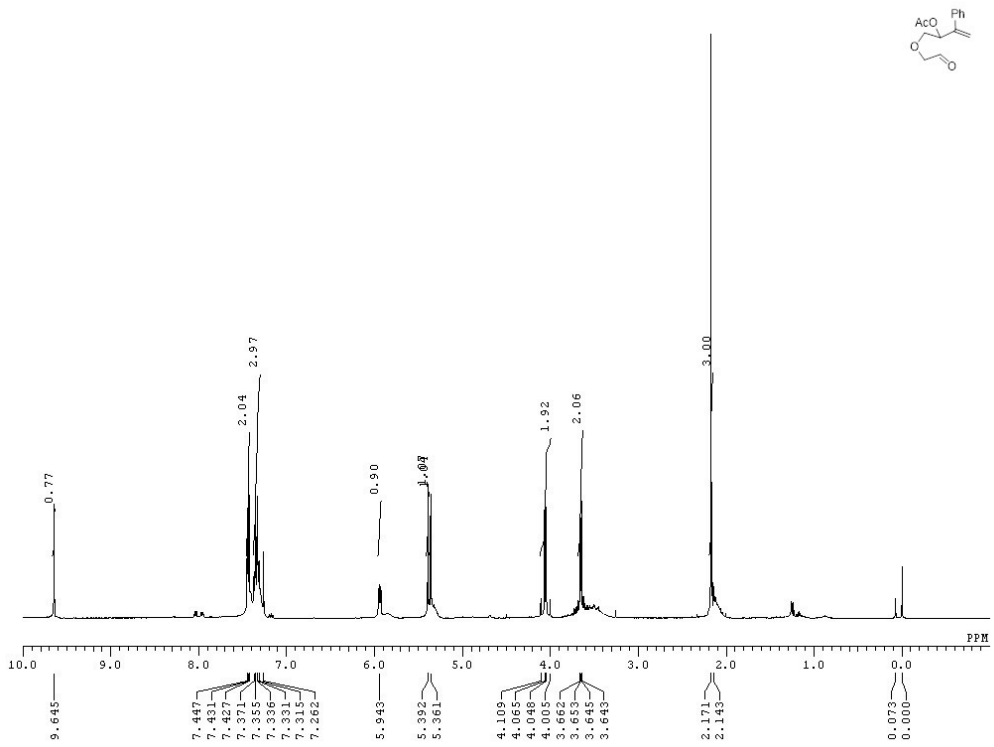

HO
Ph
O
OTBS
9.21
6.38
5.14
3.99
2.19
1.15
0.91
1.00
1.04
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
7.313 7.296 7.255 7.235 7.192
5.441 5.322
4.795 4.773
3.696 3.683 3.671 3.546 3.538 3.520 3.513 3.496 3.487 3.474 3.277 3.256 3.252 3.231
0.828
0.003 0.000

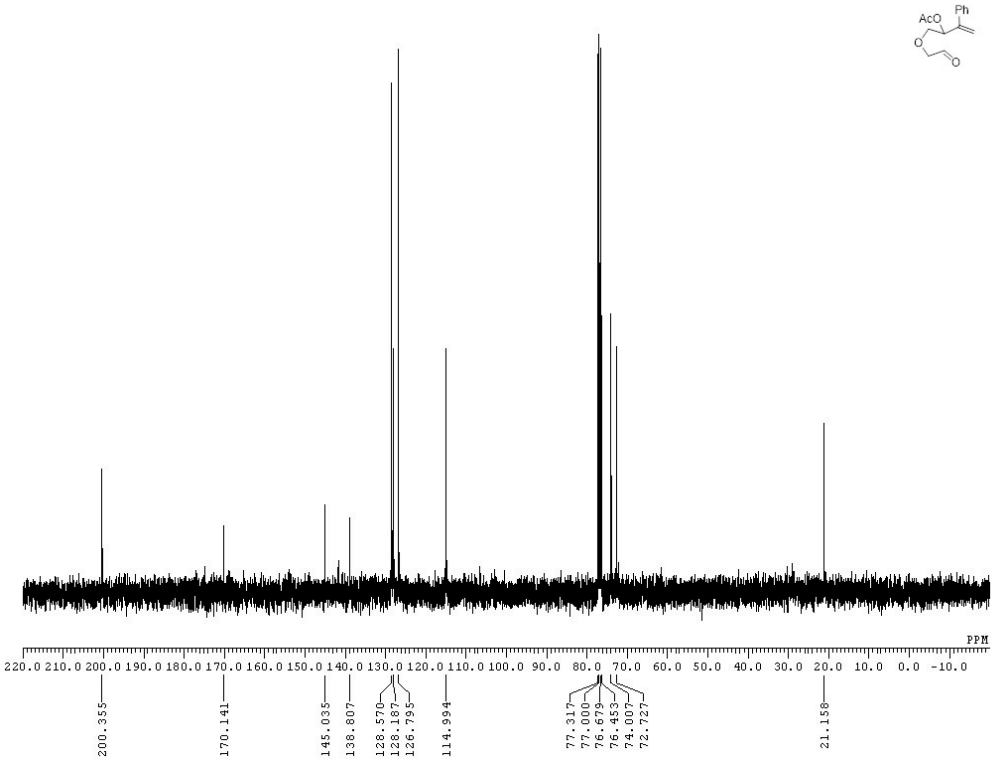

HO
Ph
O
OTBS
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
147.455
139.754
128.356 127.639 126.631
113.854
77.317 77.000 76.683 74.991 72.690 72.110
62.708
25.879
18.326
-5.343

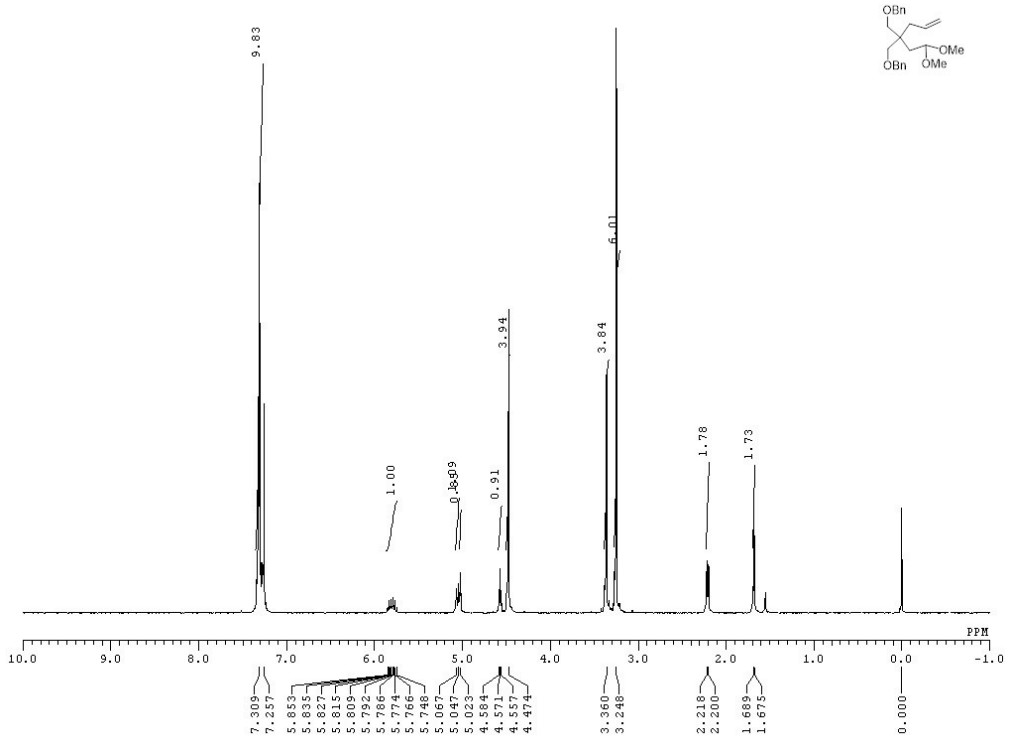

AcO
Ph
O
OH
6.61
3.14
2.94
1.99
2.06
1.00
0.91
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
7.444 7.427 7.371 7.366 7.350 7.331 7.324 7.308 7.261
5.930 5.922 5.911 5.903 5.376 5.347
3.651 3.637 3.619 3.609 3.590 3.580 3.571 3.551 3.539 3.528 3.520 3.508 3.496 3.482 3.471
2.155 2.039
1.255
0.000

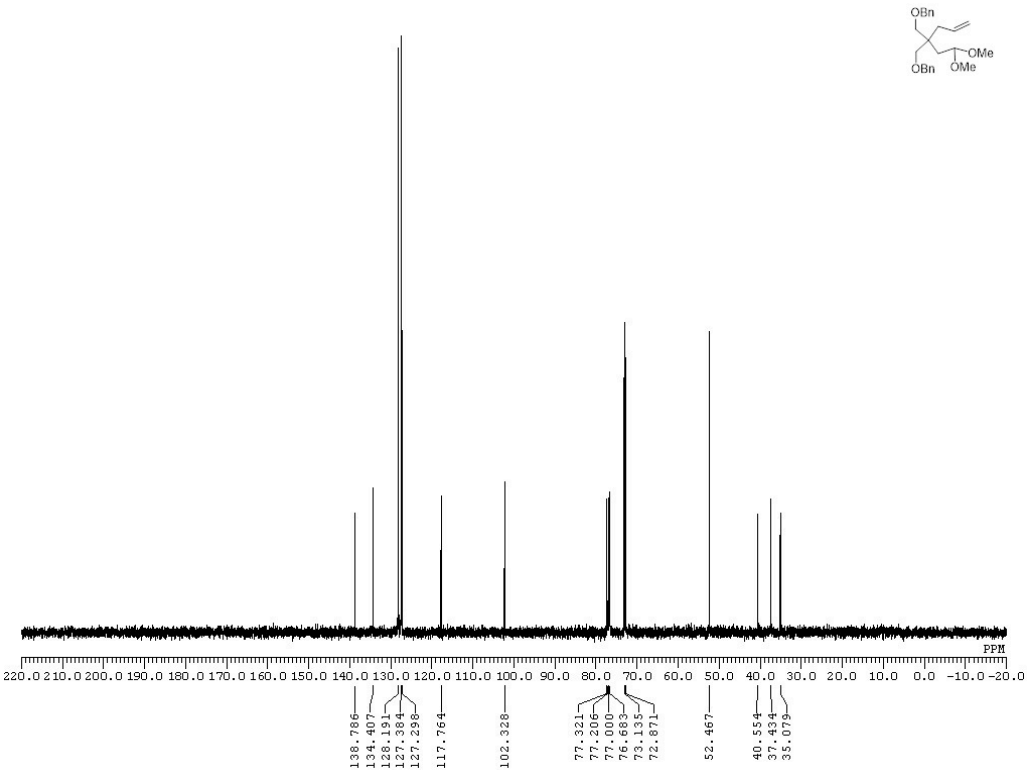

AcO
Ph
O
OH
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
170.317
145.442
139.030
128.520
128.093
126.767
114.743
77.321
77.000
76.679
74.095
72.362
72.218
61.622
21.196

13e


AcO
Ph
O
O
0.77
2.04
2.97
0.90
1.00
1.92
2.06
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
9.645
7.447
7.431
7.427
7.371
7.355
7.336
7.331
7.315
7.262
5.943
5.392
5.361
4.109
4.065
4.048
4.005
3.662
3.653
3.645
3.643
2.171
2.143
0.073
0.000


AcO
Ph
O
O
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
200.355
170.141
145.035
138.807
128.570
128.187
126.795
114.994
77.317
77.000
76.679
76.453
74.007
72.727
21.158


OBn
OBn
OMe
OMe
9.83
6.01
3.94
3.84
1.78
1.73
1.00
0.91
PPM
7.309
7.257
5.853
5.835
5.827
5.815
5.809
5.792
5.786
5.774
5.766
5.748
5.067
5.047
5.023
4.584
4.571
4.557
4.474
3.360
3.248
2.218
2.200
1.689
1.675
0.000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OBn
OMe
OMe
PPM
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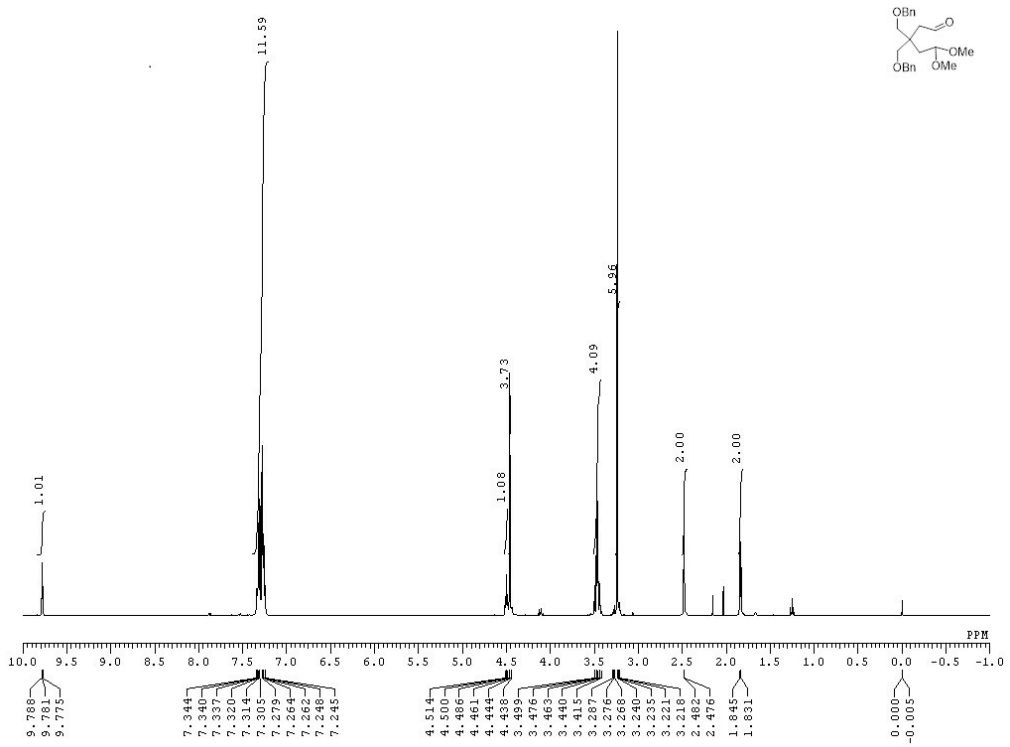
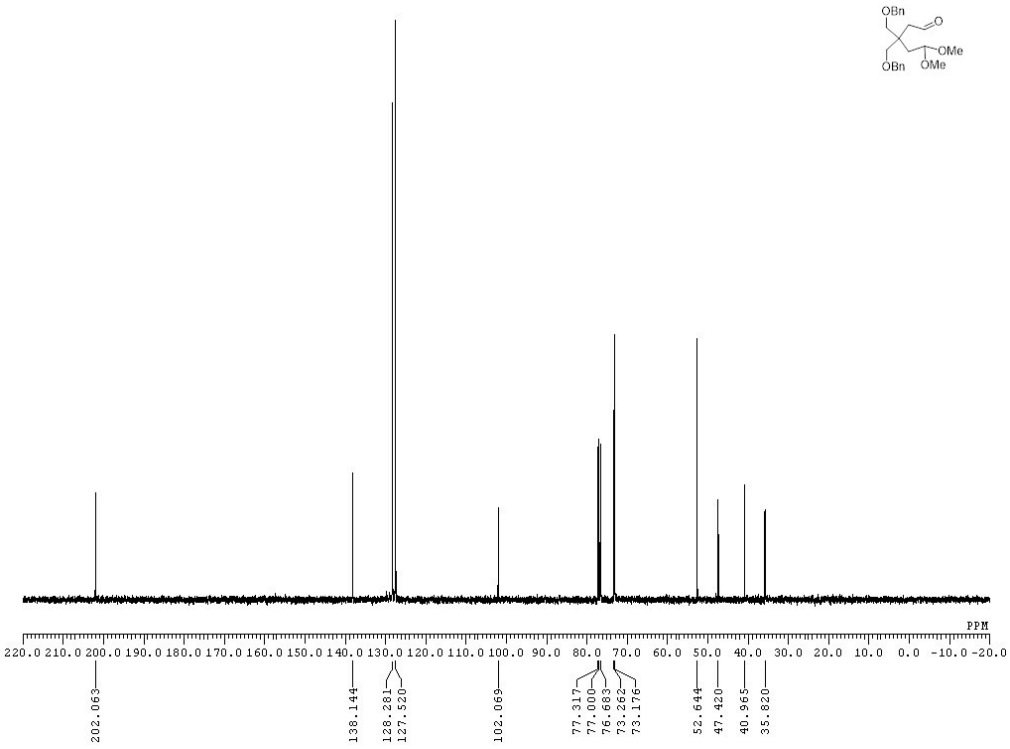
134.407
128.191
127.384
127.298
117.764
102.328
77.321
77.206
77.000
76.683
73.135
72.871
52.467
40.554
37.434
35.079


OBn
OBn
OMe
OMe
1.01
11.59
1.08
3.73
4.09
5.96
2.00
2.00
PPM
9.788
9.781
9.775
7.344
7.340
7.337
7.320
7.314
7.305
7.279
7.264
7.262
7.248
7.245
4.514
4.500
4.486
4.461
4.444
4.438
3.499
3.476
3.463
3.440
3.415
3.287
3.276
3.268
3.240
3.235
3.221
3.218
2.482
2.476
1.845
1.831
0.000
-0.005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OBn
OMe
OMe
PPM
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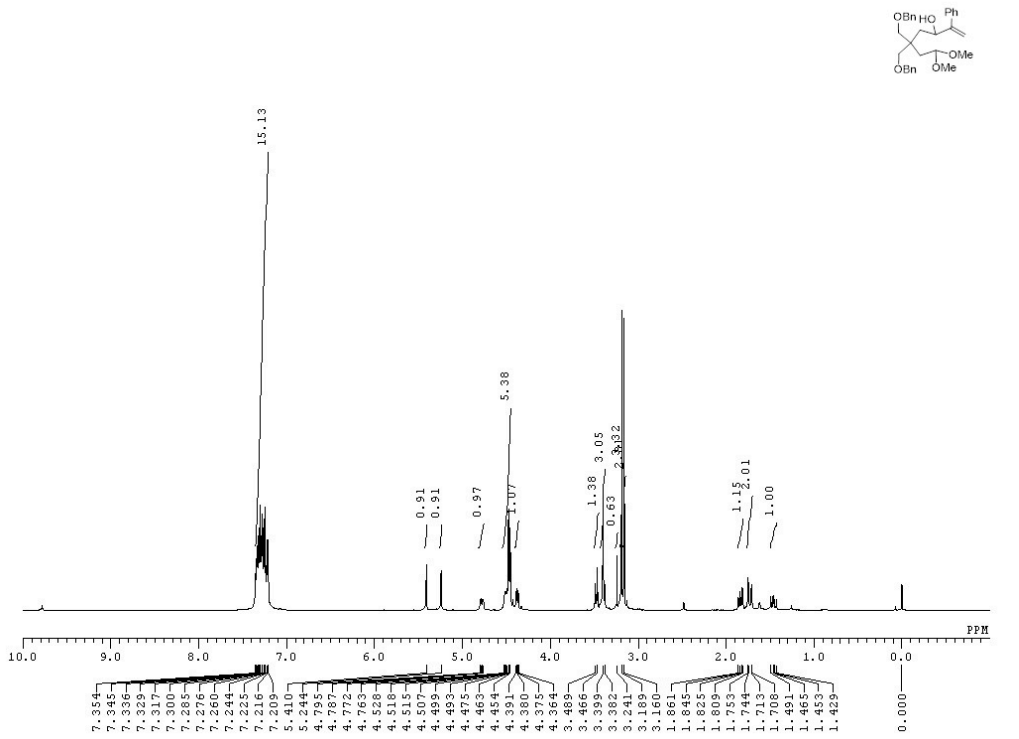
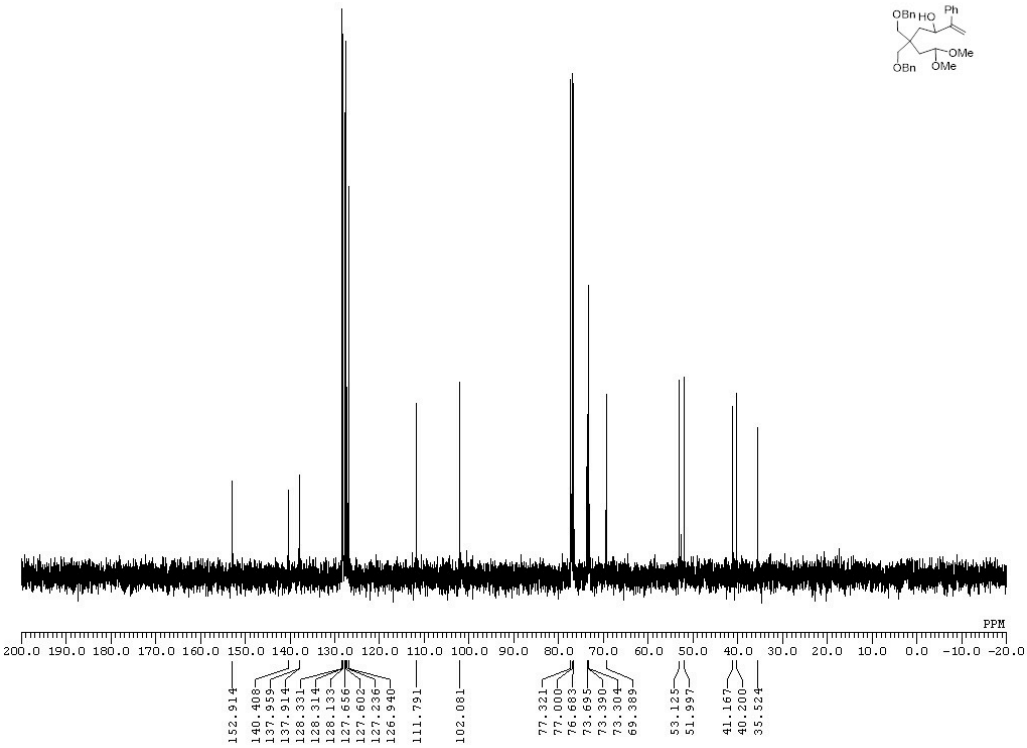
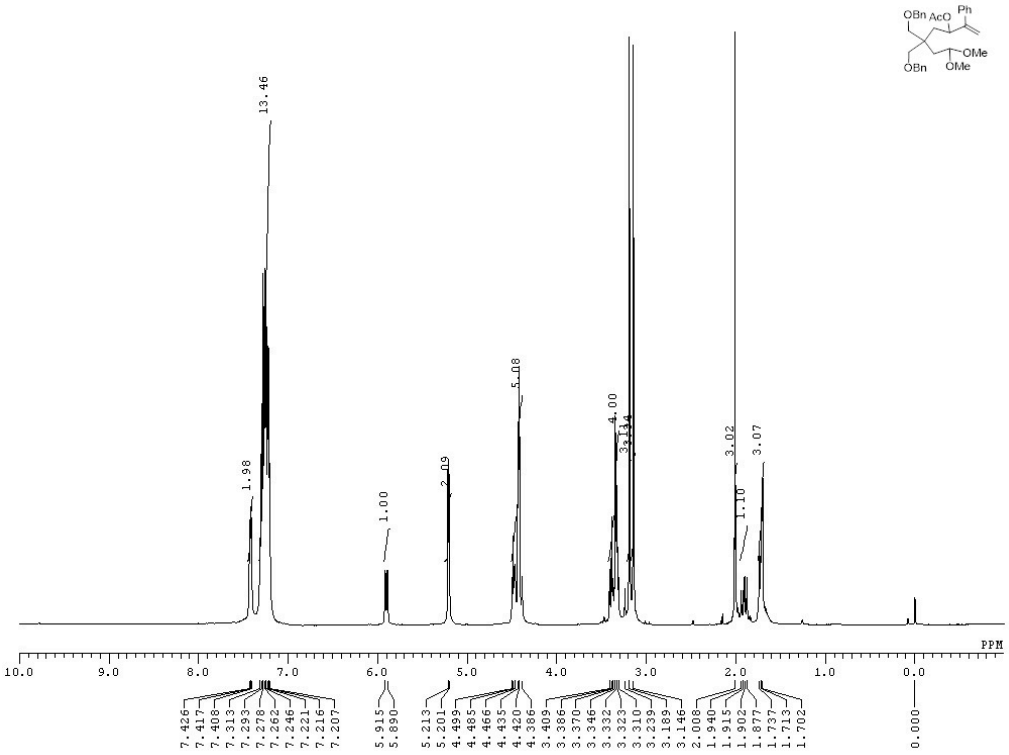
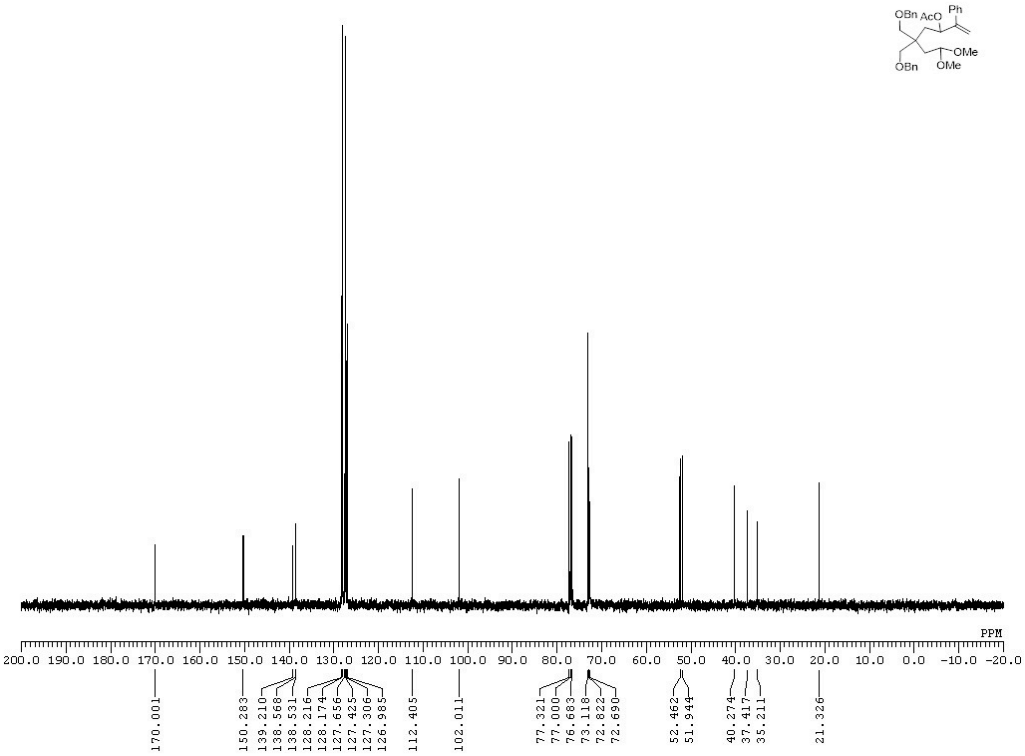
138.144
128.281
127.520
102.069
77.317
77.000
76.683
73.262
73.176
52.644
47.420
40.965
35.820

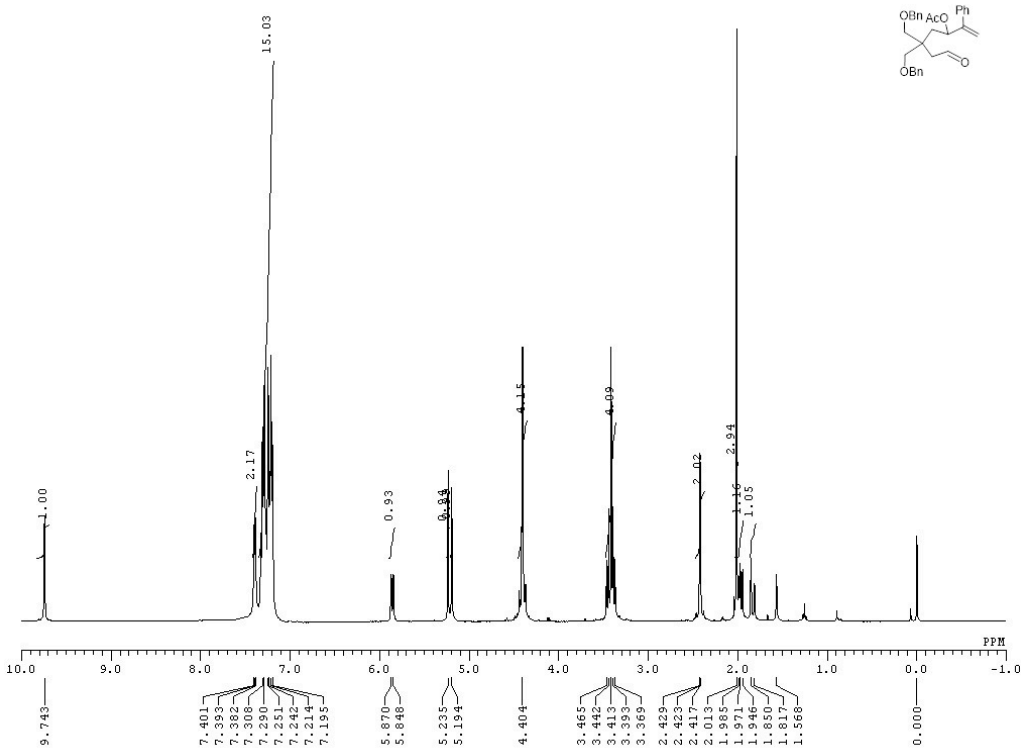

OBn
HO
Ph
OMe
OBn
OMe
15.13
0.91
0.91
0.97
1.07
5.38
1.38
3.05
2.32
0.63
1.15
2.01
1.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.354
7.345
7.336
7.329
7.317
7.300
7.285
7.276
7.260
7.244
7.225
7.216
7.209
5.410
5.244
4.795
4.787
4.772
4.763
4.528
4.518
4.515
4.507
4.499
4.493
4.475
4.463
4.454
4.391
4.380
4.375
4.364
3.489
3.466
3.399
3.382
3.241
3.189
3.160
1.861
1.845
1.825
1.809
1.753
1.744
1.713
1.708
1.491
1.465
1.453
1.429
0.000


OBn
HO
Ph
OMe
OBn
OMe
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
152.914
140.408
137.959
137.914
128.331
128.314
128.133
127.656
127.602
127.236
126.940
111.791
102.081
77.321
77.000
76.683
73.695
73.390
73.304
69.389
53.125
51.997
41.167
40.200
35.524


OBn AcO Ph
OBn
OMe
OMe
13.46
1.98
1.00
2.09
5.08
4.00
3.14
3.02
1.10
3.07
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
7.426 7.417 7.408 7.313 7.293 7.278 7.262 7.246 7.221 7.216 7.207
5.915 5.890
5.213 5.201 4.499 4.485 4.466 4.435 4.420 4.386
3.409 3.386 3.370 3.346 3.332 3.323 3.310 3.239 3.189 3.146
2.008 1.940 1.915 1.902 1.877 1.737 1.713 1.702
0.000


OBn AcO Ph
OBn
OMe
OMe
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
170.001
150.283 139.210 138.568 138.531 128.216 128.174 127.656 127.425 127.306 126.985
112.405
102.011
77.321 77.000 76.683 73.118 72.822 72.690
52.462 51.944
40.274 37.417 35.211
21.326

13f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AcO
Ph
OBn
O
15.03
2.17
1.00
0.93
4.15
4.09
2.02
2.94
1.16
1.05
PPM
9.743
7.401
7.393
7.382
7.308
7.290
7.231
7.242
7.214
7.195
5.870
5.848
5.235
5.194
4.404
3.465
3.442
3.413
3.393
3.369
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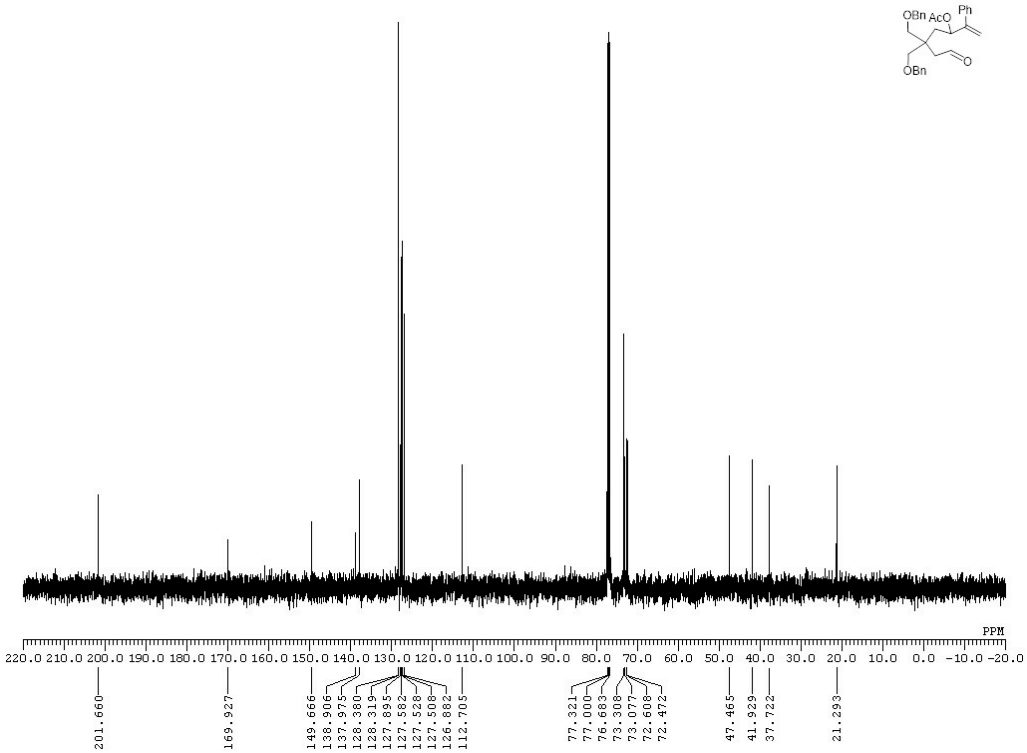
2.423
2.417
2.013
1.985
1.971
1.946
1.850
1.817
1.568
0.000


OBn
AcO
Ph
OBn
O
PPM
201.660
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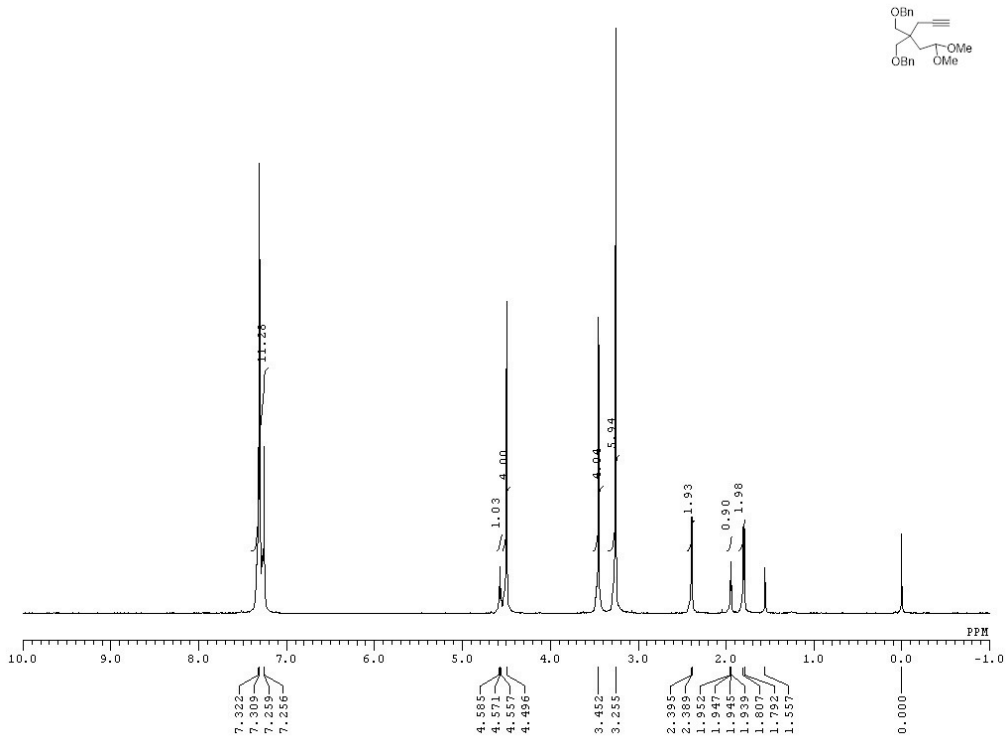
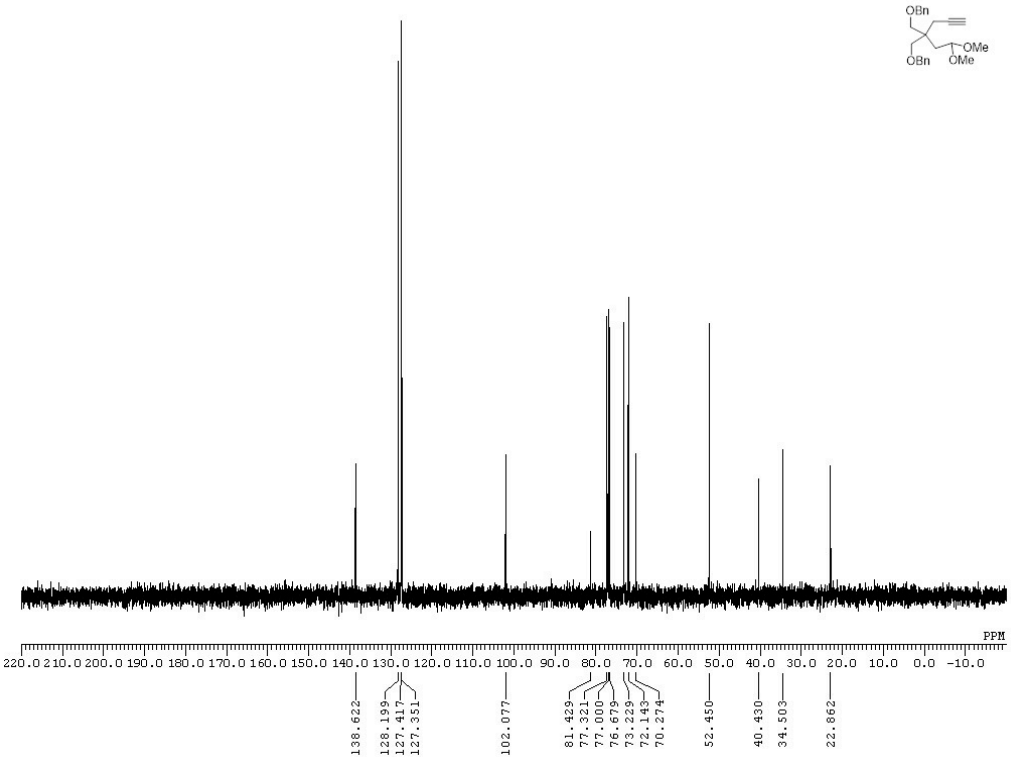
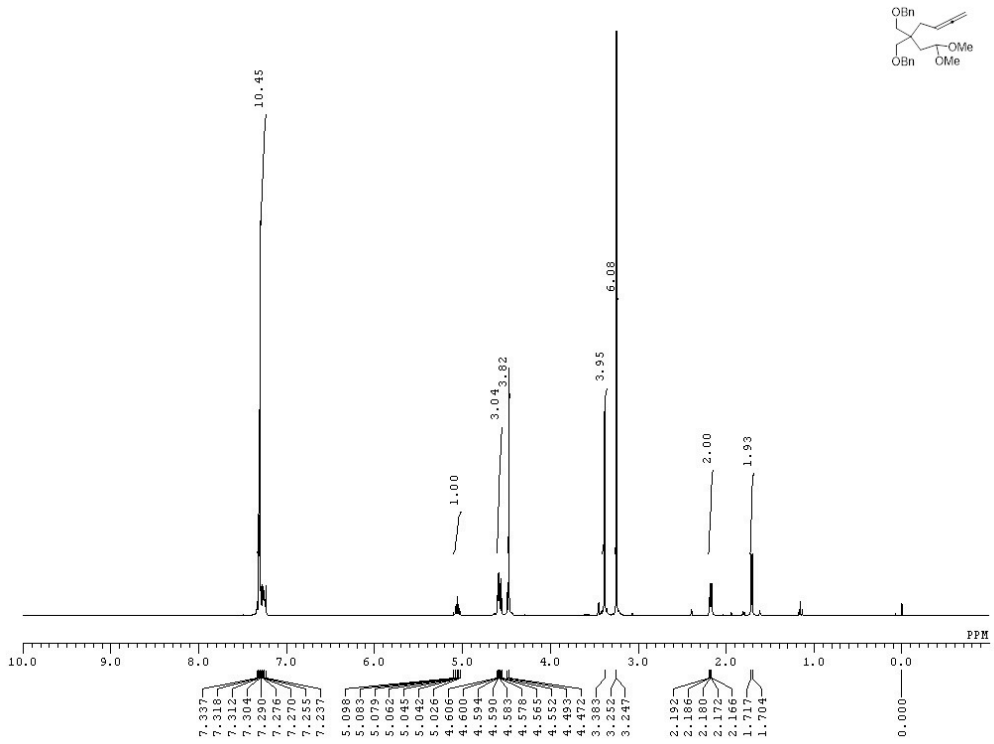
149.666
138.906
137.975
128.380
128.319
127.895
127.582
127.528
127.500
126.882
112.705
77.321
77.000
76.683
73.308
73.077
72.608
72.472
47.465
41.929
37.722
21.293


OBn
OBn
OMe
OMe
11.28
1.03
4.00
4.04
5.94
1.93
0.90
1.98
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.322
7.309
7.259
7.256
4.585
4.571
4.557
4.496
3.452
3.255
2.395
2.389
1.952
1.947
1.945
1.939
1.807
1.792
1.557
0.000


OBn
OBn
OMe
OMe
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
138.622
128.199
127.417
127.351
102.077
81.429
77.321
77.000
76.679
73.229
72.143
70.274
52.450
40.430
34.503
22.862


OBn
OBn
OMe
OMe
10.45
6.08
3.95
3.82
3.04
1.00
2.00
1.93
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.337
7.318
7.312
7.304
7.290
7.276
7.270
7.255
7.237
5.098
5.083
5.079
5.062
5.045
5.042
5.026
4.606
4.600
4.594
4.590
4.583
4.578
4.565
4.552
4.493
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3.247
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2.186
2.180
2.172
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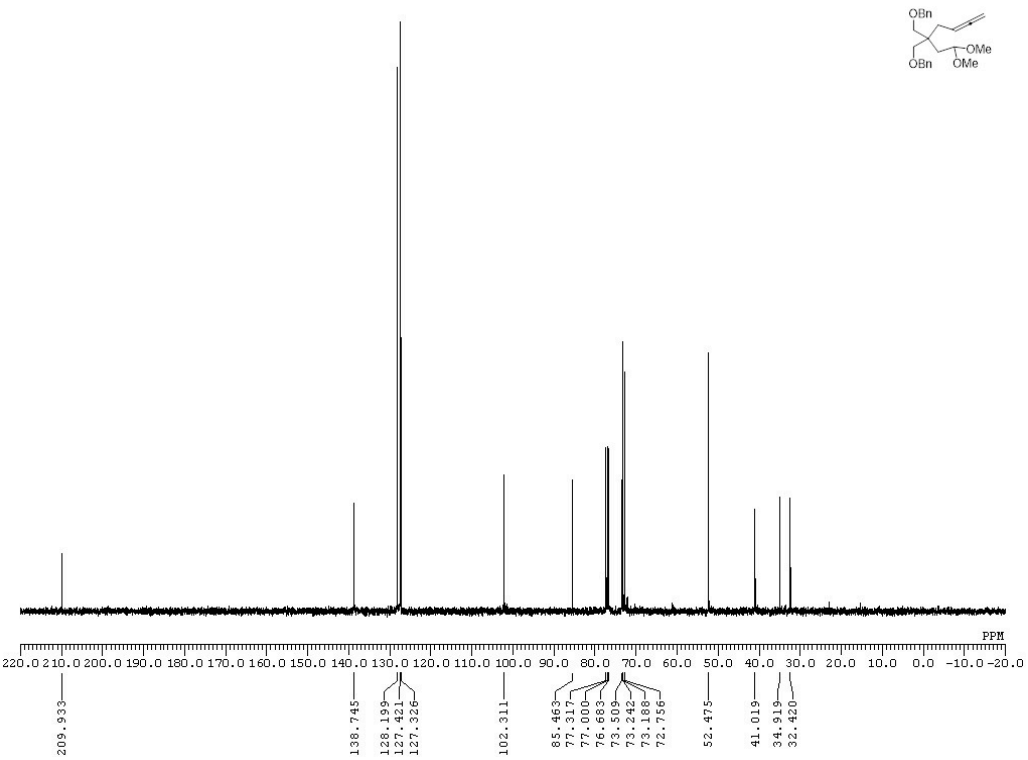
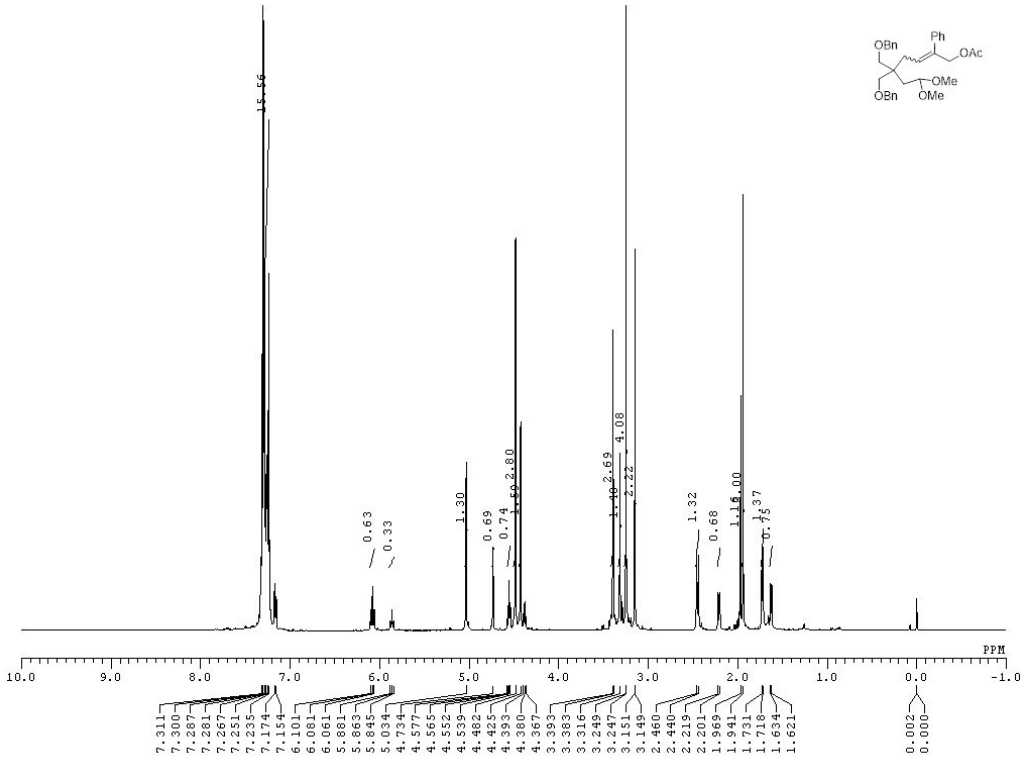
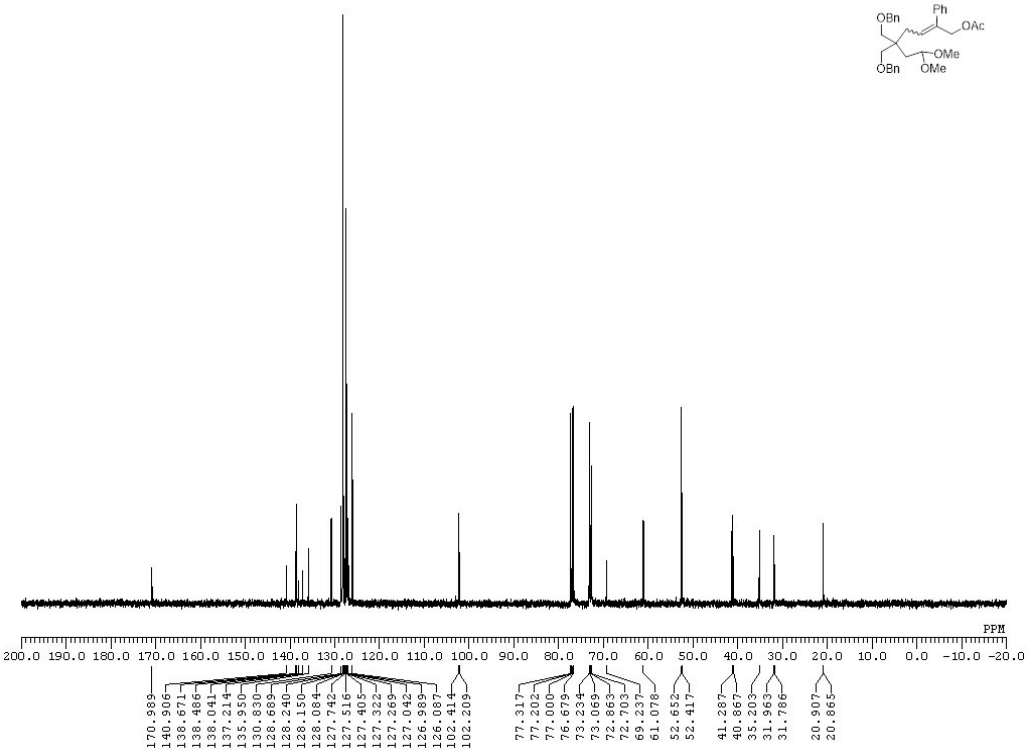
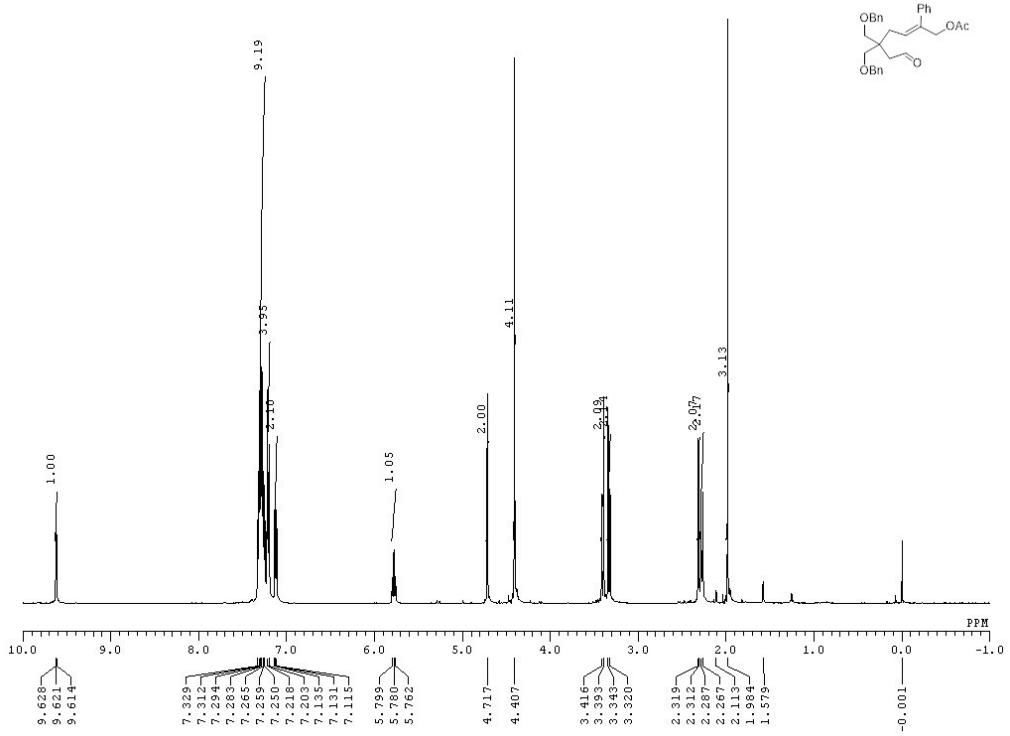
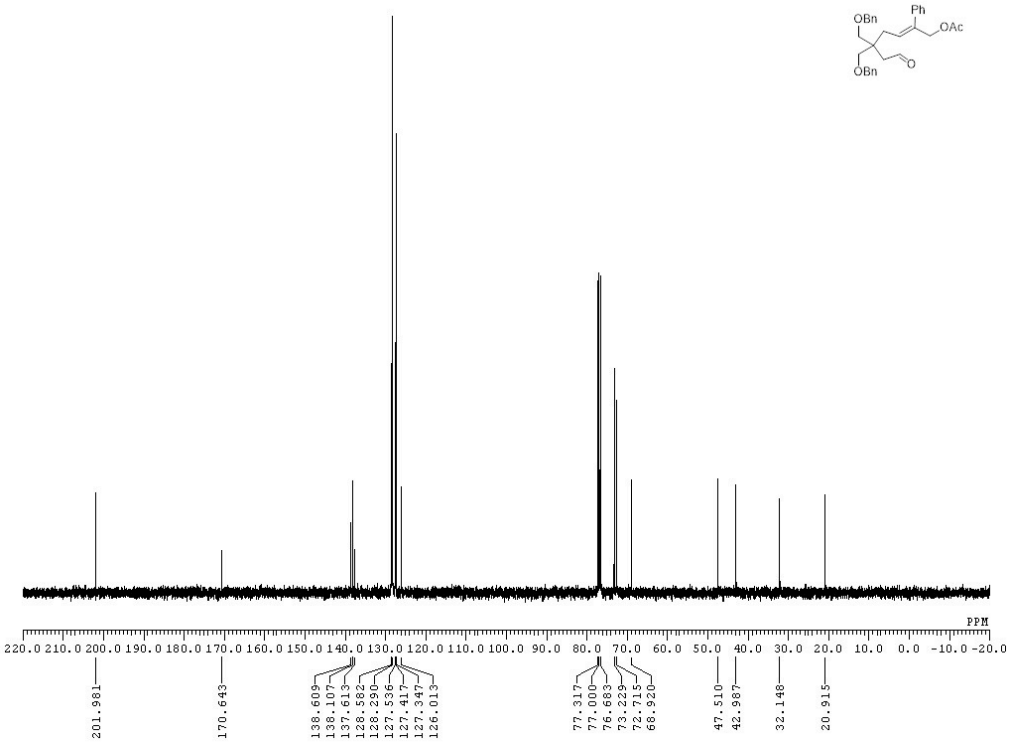

OBn
OBn
OMe
OMe
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
-20.0
209.933
138.745
128.199
127.421
127.326
102.311
85.463
77.317
77.000
76.683
73.509
73.242
73.188
72.756
52.475
41.019
34.919
32.420

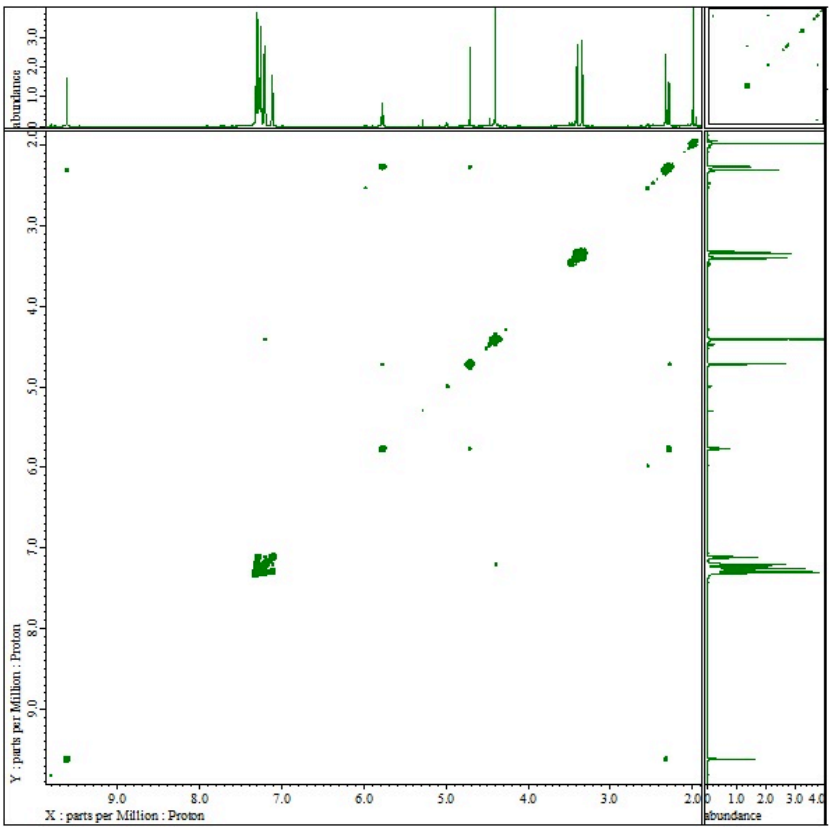

OBn
Ph
OAc
OMe
OBn
OMe
15.56
0.63
0.33
1.30
0.69
0.74
2.80
2.69
4.08
2.22
1.32
0.68
16.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0

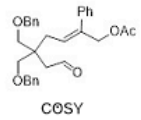

OBn
Ph
OAc
OMe
OBn
OMe
PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
-20.0

(*E*)-13f'

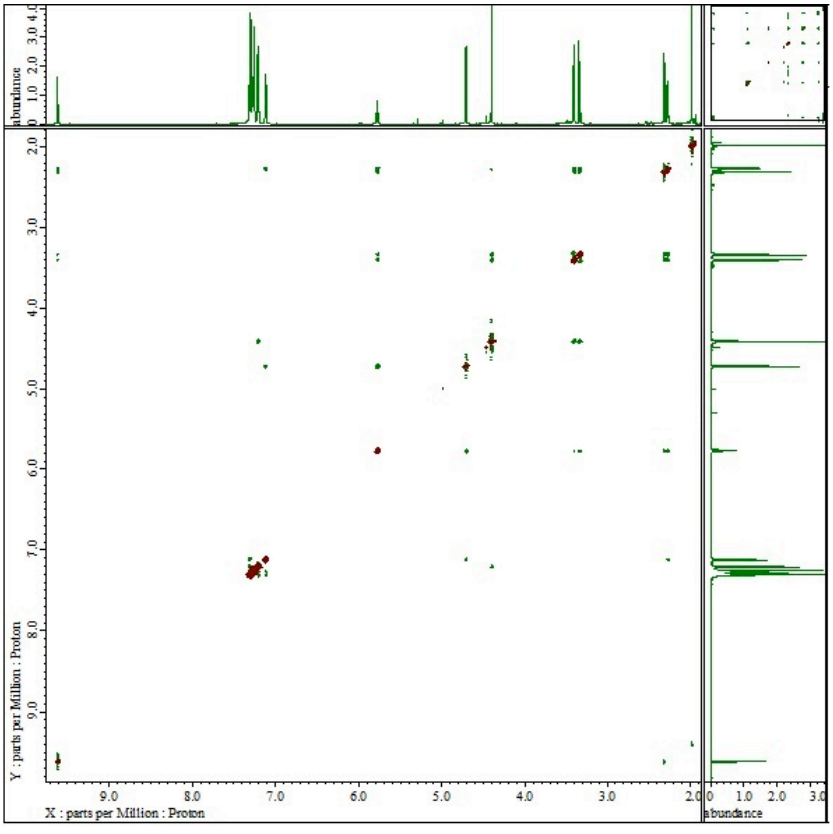

OBn
Ph
OAc
OBn
O
1.00
9.19
3.95
2.10
1.05
2.00
4.11
2.09
2.07
3.13
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
9.628 9.621 9.614
7.329 7.312 7.294 7.283 7.265 7.259 7.250 7.218 7.203 7.135 7.131 7.115
5.799 5.780 5.762
4.717 4.407
3.416 3.393 3.343 3.320
2.319 2.312 2.287 2.267 2.113 1.984 1.579
-0.001

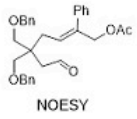

OBn
Ph
OAc
OBn
O
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
201.981
170.643
138.609 138.107 137.613 128.582 128.290 127.536 127.417 127.347 126.013
77.317 77.000 76.683 73.229 72.715 68.920
47.510 42.987 32.148 20.915


Abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance


OBn
Ph
OAc
O
OBn

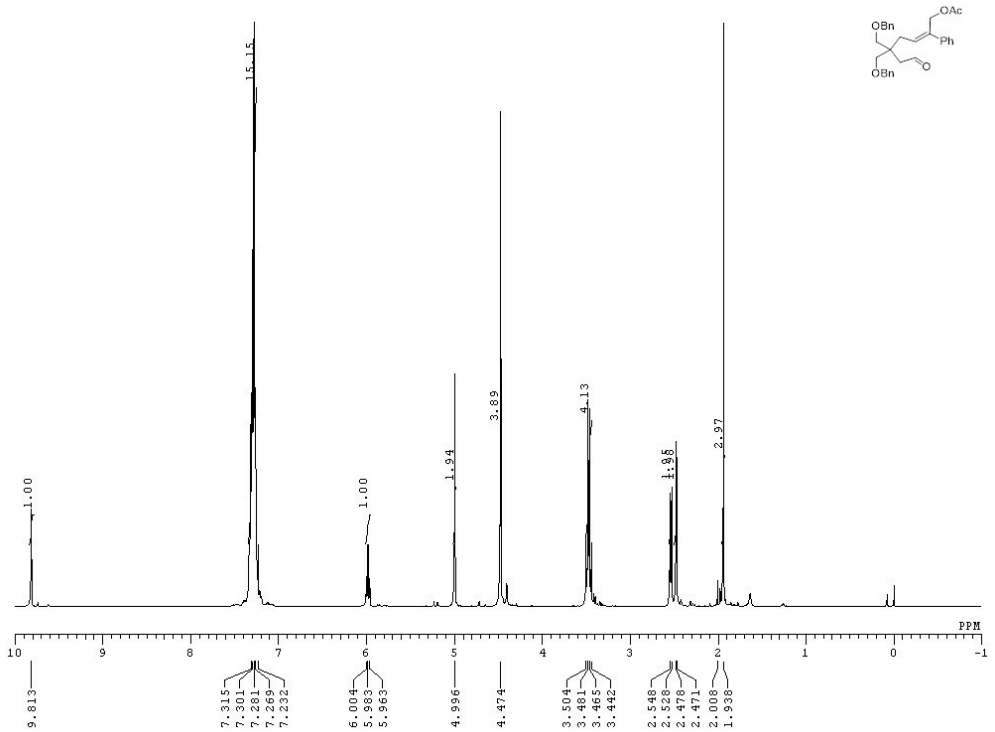
COSY

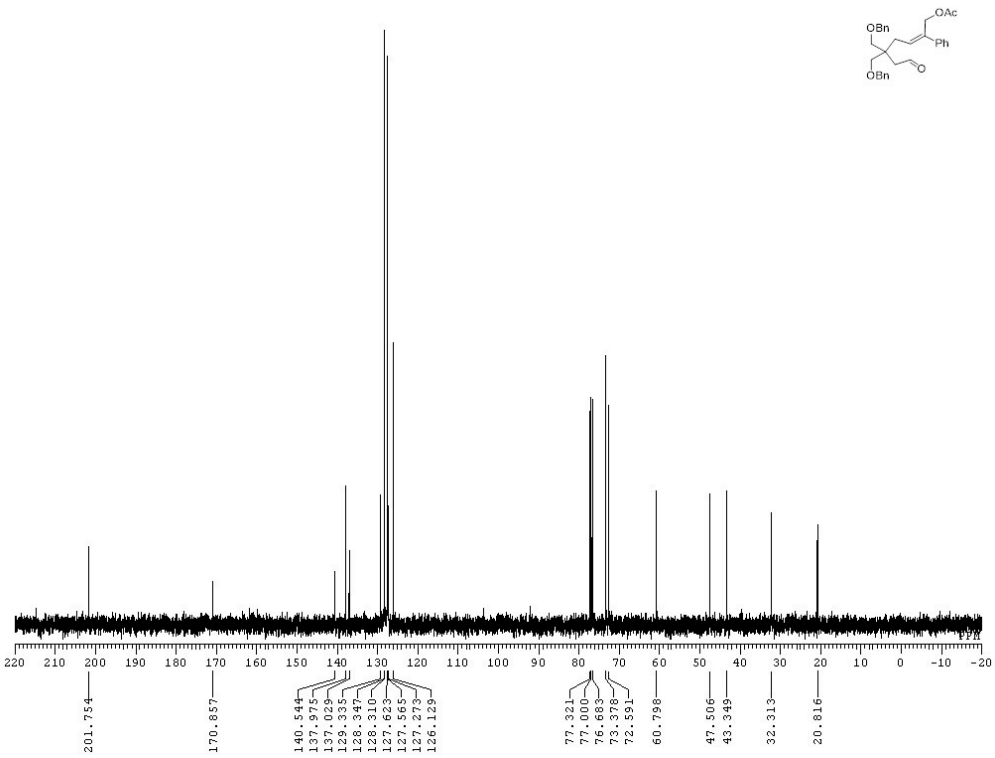

Abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance


OBn
Ph
OAc
O
OBn

NOESY

(*Z*)-13f'


OAc
OBn
Ph
OBn
O
15.15
1.00
1.00
1.94
3.89
4.13
1.95
2.97
PPM
9.813
7.315
7.301
7.281
7.269
7.232
6.004
5.983
5.963
4.996
4.474
3.504
3.481
3.465
3.442
2.548
2.528
2.478
2.471
2.008
1.938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OBn
Ph
OBn
O
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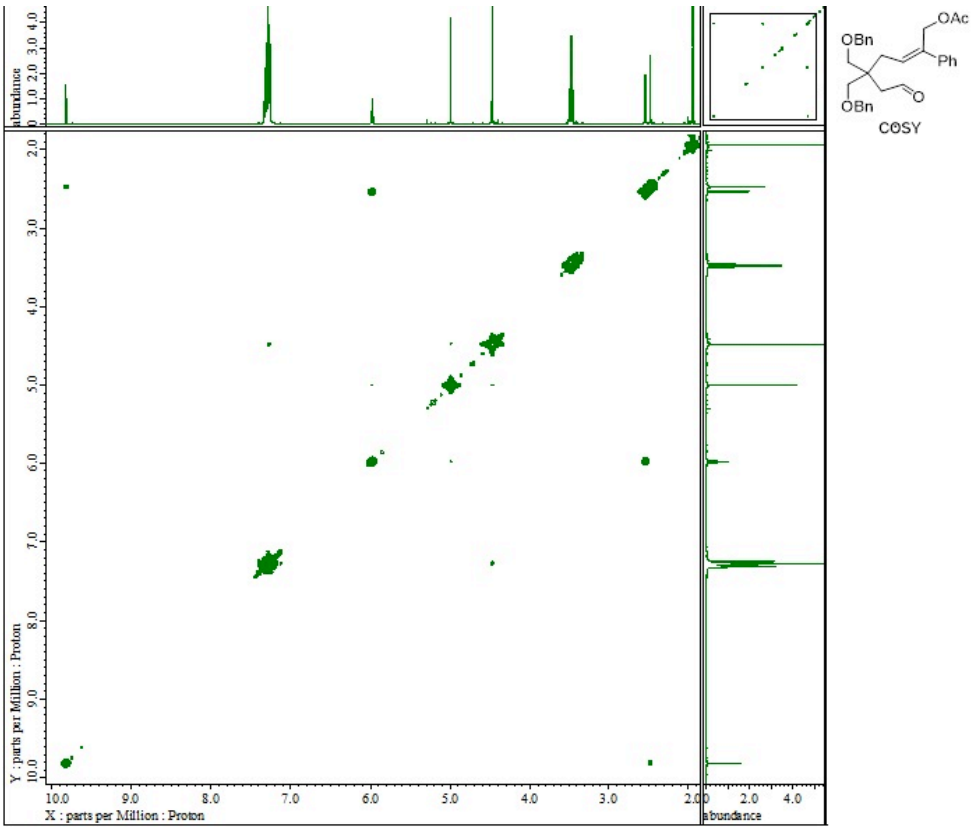
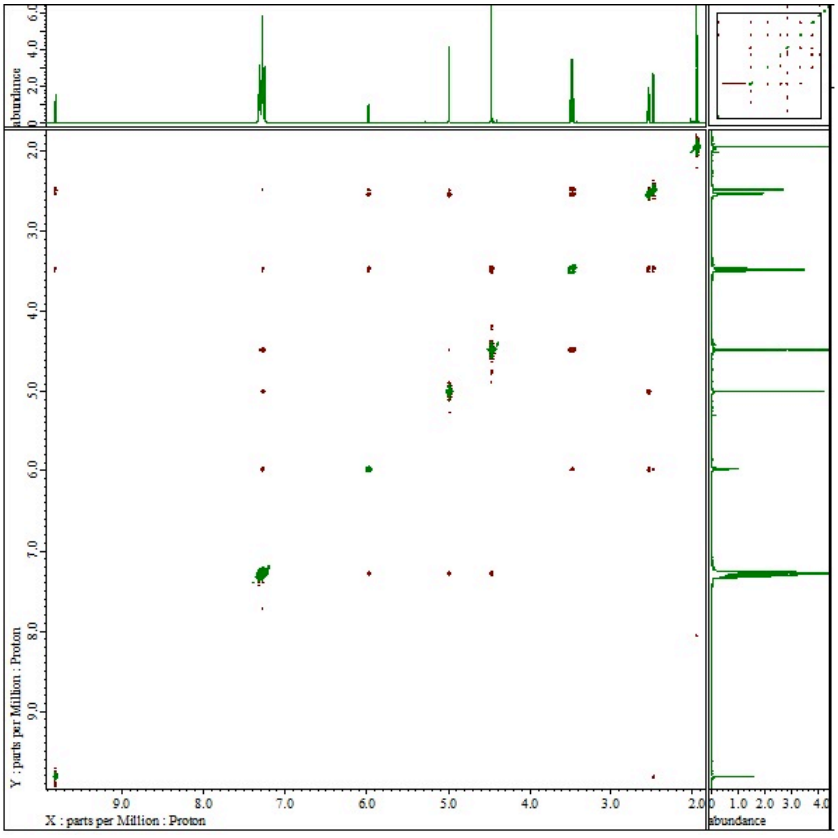
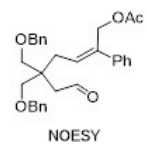
170.857
140.544
137.975
137.029
129.335
128.347
128.310
127.623
127.565
127.273
126.129
77.321
77.000
76.683
73.378
72.591
60.798
47.506
43.349
32.313
20.816


abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

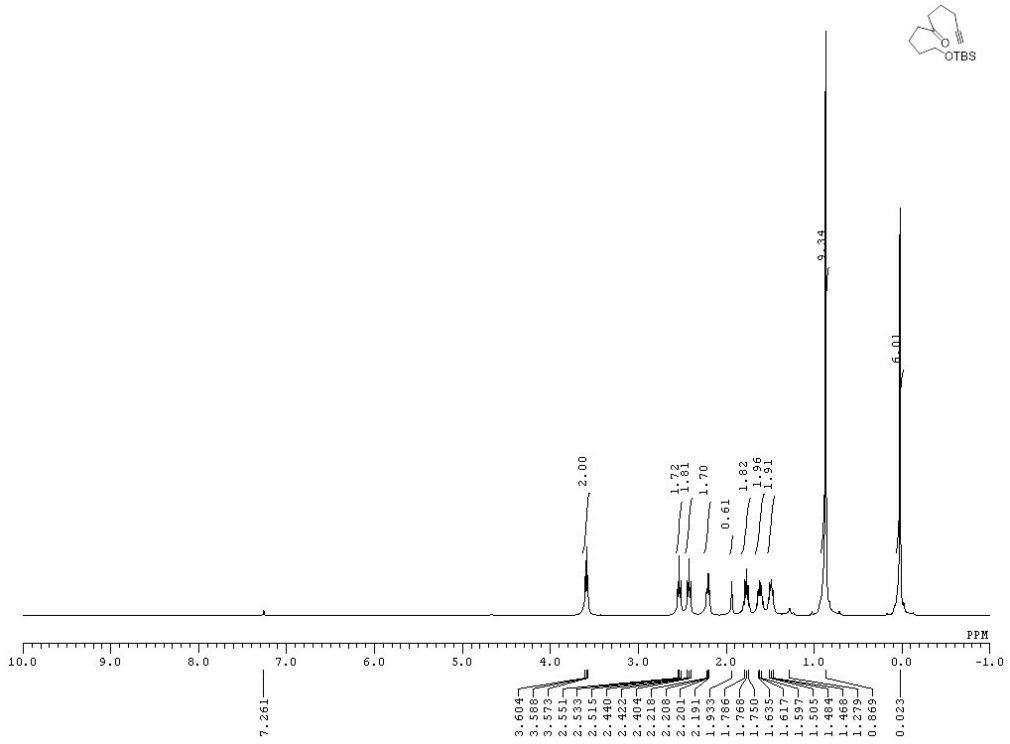
OAc
OBn
Ph
OBn
O

COSY


abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance


OAc
OBn
Ph
OBn
O

NOESY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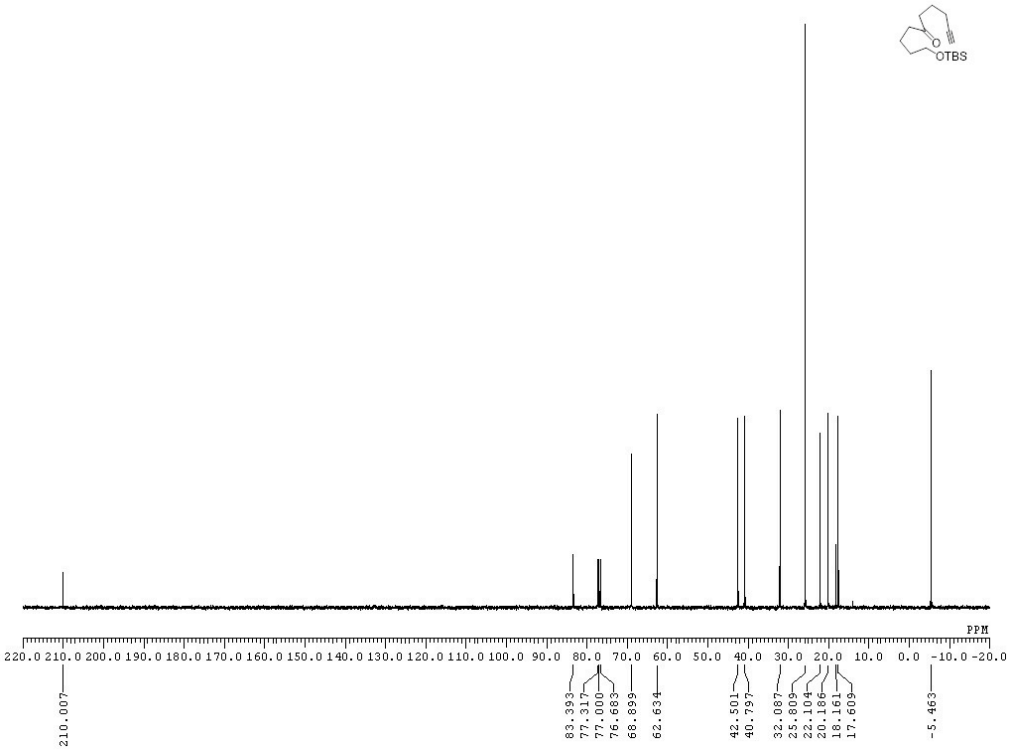
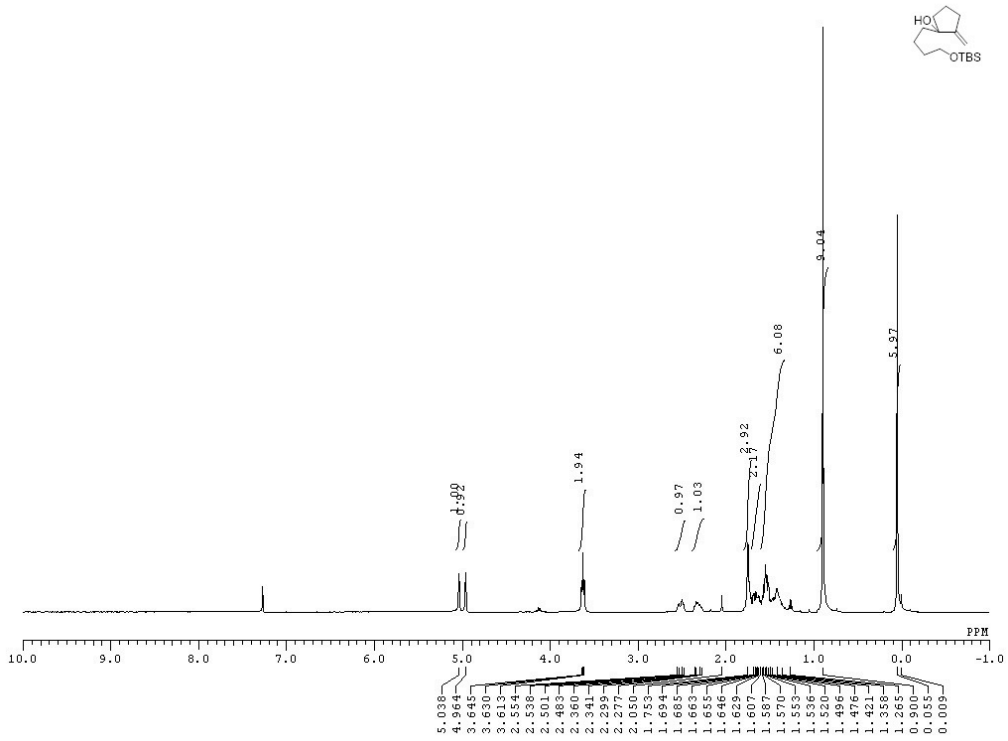
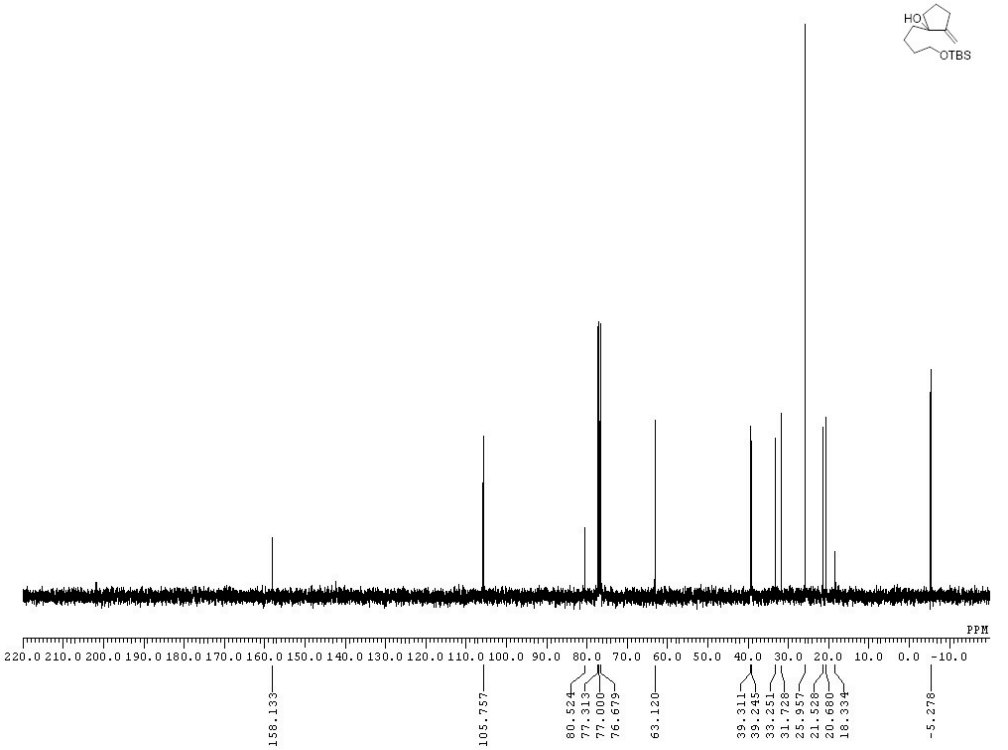
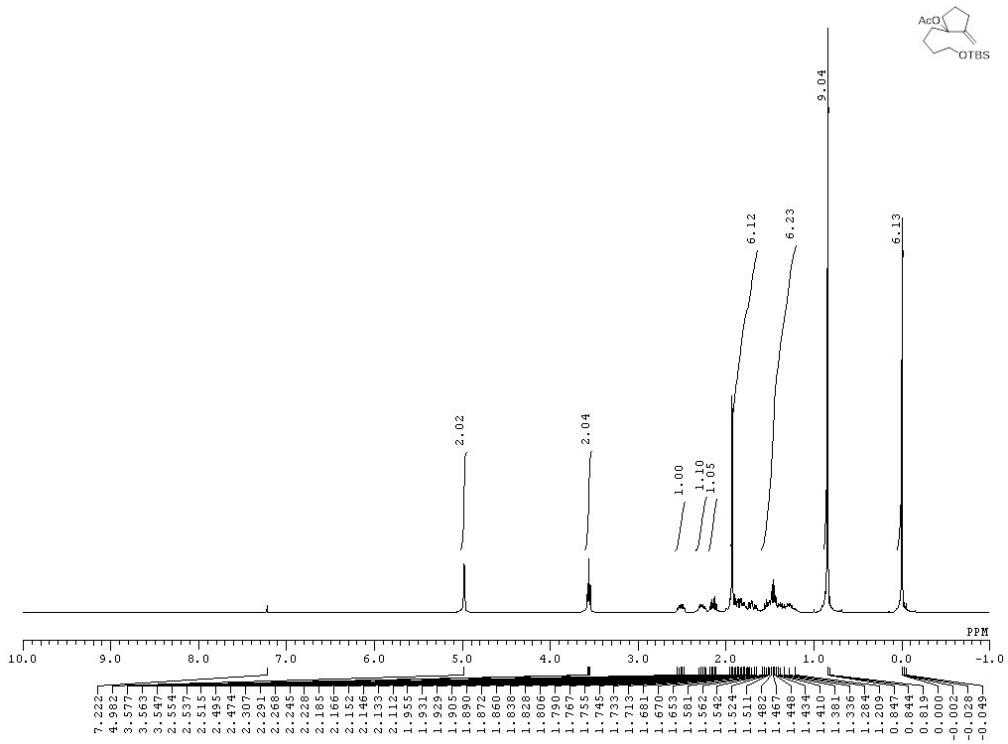
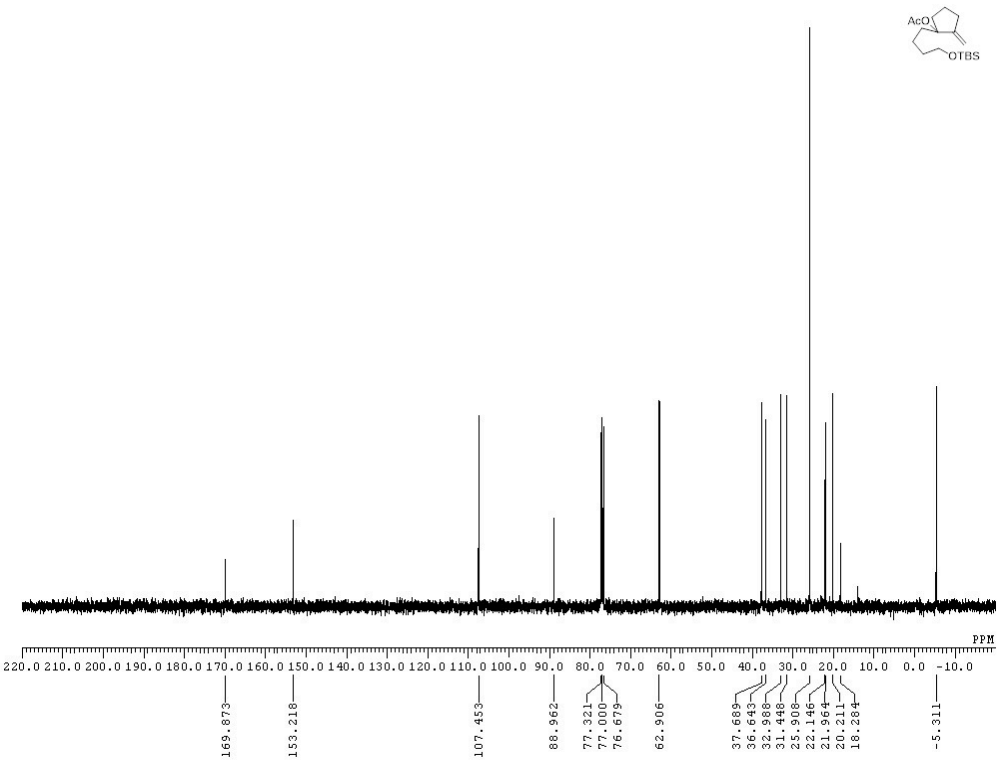
9.34
6.01
2.00
1.72
1.81
1.70
0.61
1.82
1.96
1.91
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.261
3.604 3.588 3.573 3.551 2.533 2.515 2.440 2.422 2.404 2.218 2.208 2.201 2.191 1.933 1.786 1.768 1.750 1.635 1.617 1.597 1.505 1.484 1.468 1.279 0.869
0.023


OTBS
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
210.007
83.393 77.317 77.000 76.683 68.899 62.634 42.501 40.797 32.087 25.809 22.104 20.186 18.161 17.609 -5.463


HO
OTBS
1.00
1.00
1.94
0.97
1.03
2.92
2.19
6.08
9.04
5.97
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
5.038
4.964
3.645
3.630
3.613
2.554
2.538
2.501
2.483
2.360
2.341
2.299
2.277
2.050
1.753
1.694
1.685
1.663
1.655
1.646
1.629
1.607
1.587
1.570
1.553
1.536
1.520
1.496
1.476
1.421
1.358
1.265
0.900
0.055
0.009


HO
OTBS
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
158.133
105.757
80.524
77.313
77.000
76.679
63.120
39.311
39.245
33.251
31.728
25.957
21.528
20.680
18.394
-5.278


AcO
OTBS
9.04
6.12
6.23
6.13
2.02
2.04
1.00
1.10
1.05
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.222 4.982 3.577 3.563 3.547 3.534 2.537 2.515 2.495 2.474 2.307 2.291 2.268 2.245 2.228 2.185 2.166 2.152 2.146 2.133 2.112 1.955 1.931 1.929 1.905 1.890 1.872 1.860 1.838 1.828 1.806 1.790 1.767 1.755 1.745 1.733 1.713 1.681 1.670 1.653 1.581 1.562 1.542 1.524 1.511 1.482 1.467 1.448 1.434 1.410 1.381 1.336 1.284 1.209 0.847 0.844 0.819 0.000 -0.002 -0.028 -0.049


AcO
OTBS
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
169.873
153.218
107.453
88.962
77.321
77.000
76.679
62.906
37.689
36.643
32.988
31.448
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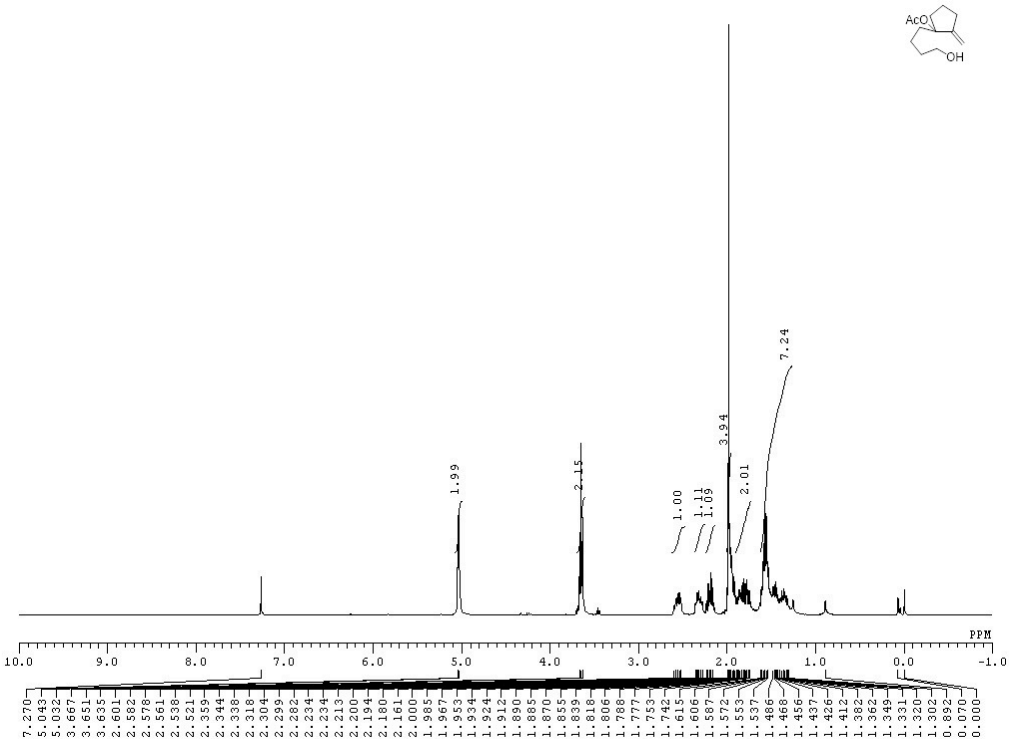
22.146
21.964
20.211
18.284
-5.311


AcO
OH
1.99
2.15
1.00
1.11
1.09
3.94
2.01
7.24
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.270
5.043
5.032
3.667
3.651
3.635
2.601
2.582
2.578
2.561
2.538
2.521
2.359
2.344
2.338
2.318
2.304
2.299
2.282
2.234
2.234
2.213
2.200
2.194
2.180
2.161
2.000
1.985
1.967
1.953
1.934
1.924
1.912
1.890
1.885
1.870
1.855
1.839
1.818
1.806
1.788
1.777
1.753
1.742
1.615
1.606
1.587
1.572
1.553
1.537
1.486
1.468
1.456
1.437
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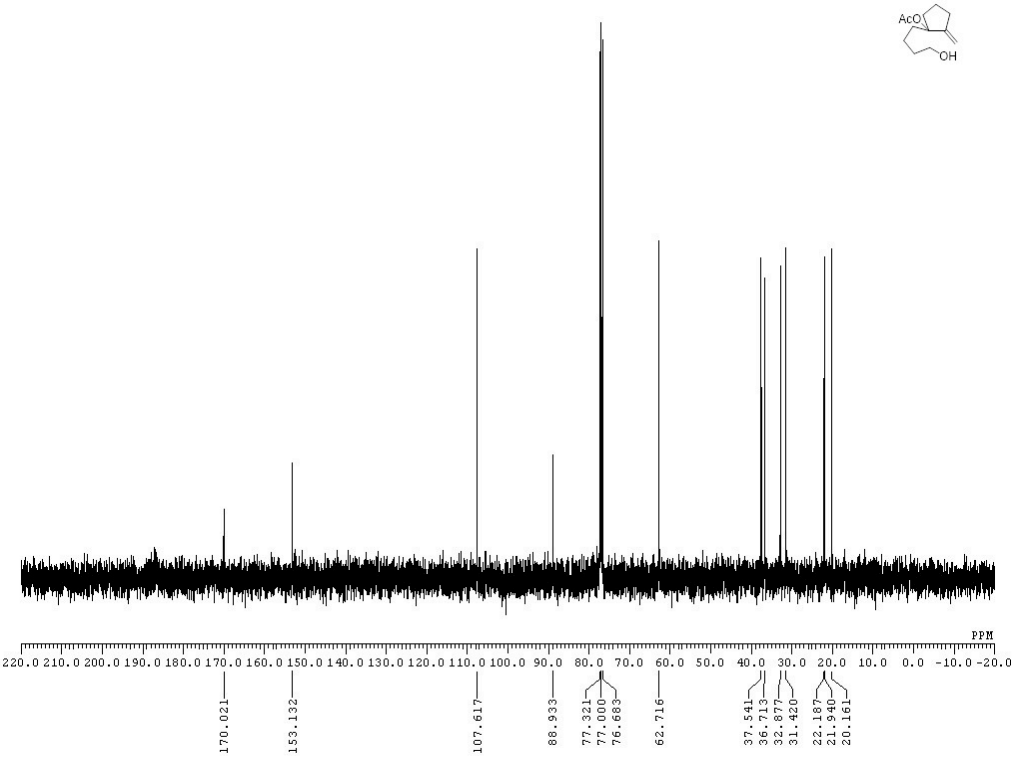
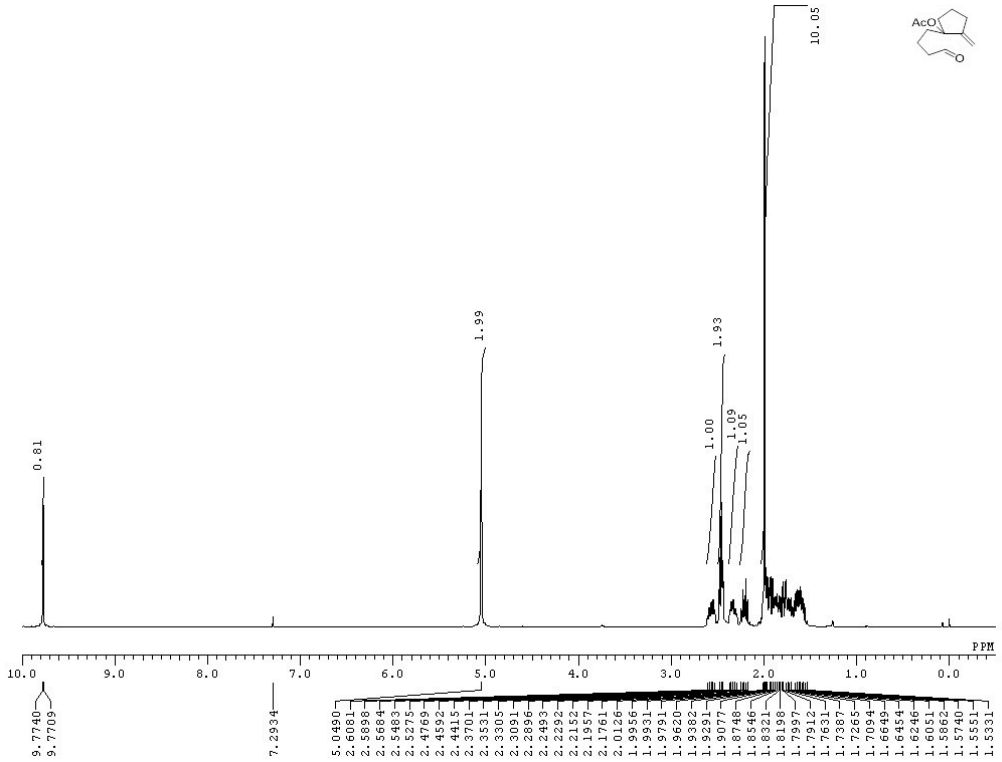
1.412
1.382
1.362
1.349
1.331
1.320
1.302
0.892
0.070
0.000


AcO
OH
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
170.021
153.132
107.617
88.933
77.321
77.000
76.683
62.716
37.541
36.713
32.877
31.420
22.187
21.940
20.161

13g


AcO
O
10.05
1.99
1.93
1.00
1.09
1.05
0.81
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
9.7740
9.7709
7.2934
5.0490
2.6081
2.5898
2.5684
2.5483
2.5275
2.4769
2.4592
2.4415
2.3701
2.3531
2.3305
2.3091
2.2896
2.2493
2.2292
2.2152
2.1957
2.1761
2.0126
1.9956
1.9931
1.9791
1.9620
1.9382
1.9291
1.9077
1.8748
1.8546
1.8321
1.8198
1.7997
1.7912
1.7631
1.7387
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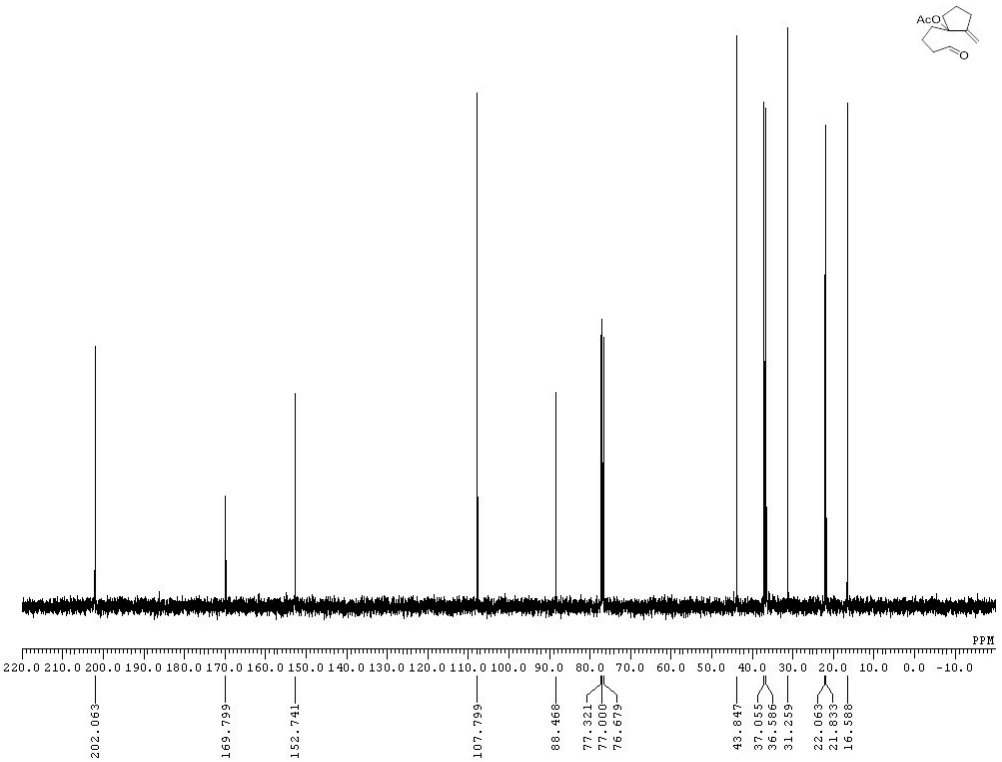
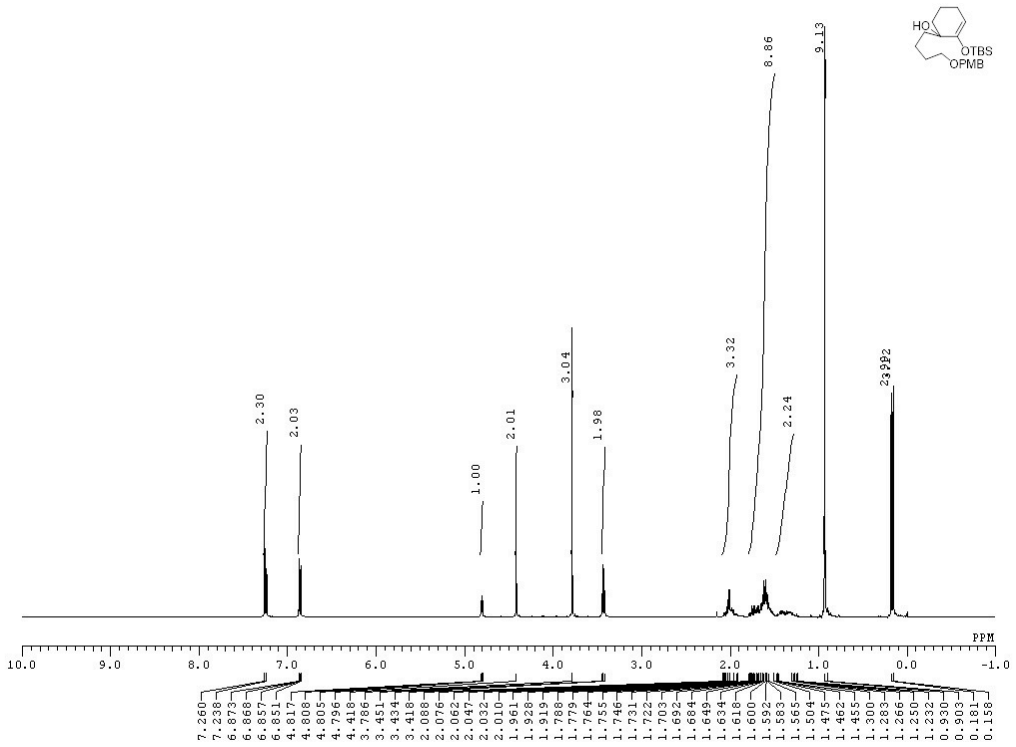
1.6051
1.5862
1.5740
1.5551
1.5331


AcO
O
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
202.063
169.799
152.741
107.799
88.468
77.321
77.000
76.679
43.847
37.055
36.586
31.259
22.063
21.833
16.588


HO
OTBS
OPMB
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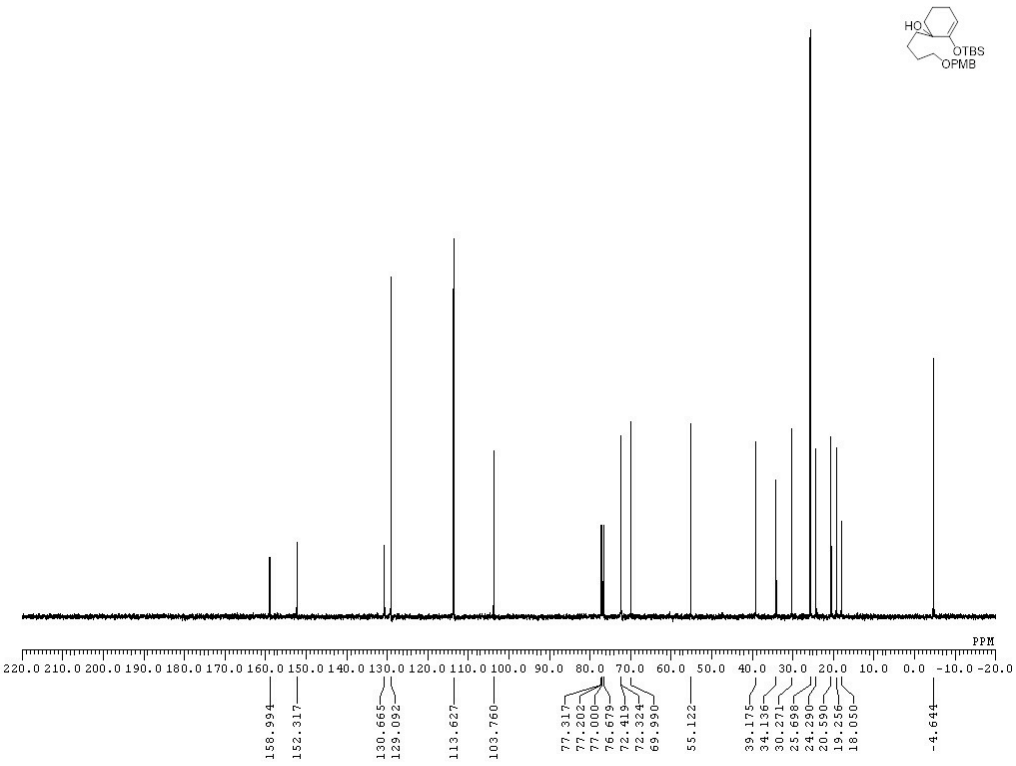
8.86
3.32
3.04
2.30
2.03
2.01
1.98
2.24
1.00
PPM


HO
OTBS
OPMB
PPM
158.994
152.317
130.665
129.092
113.627
103.760
77.317
77.202
77.000
76.679
72.419
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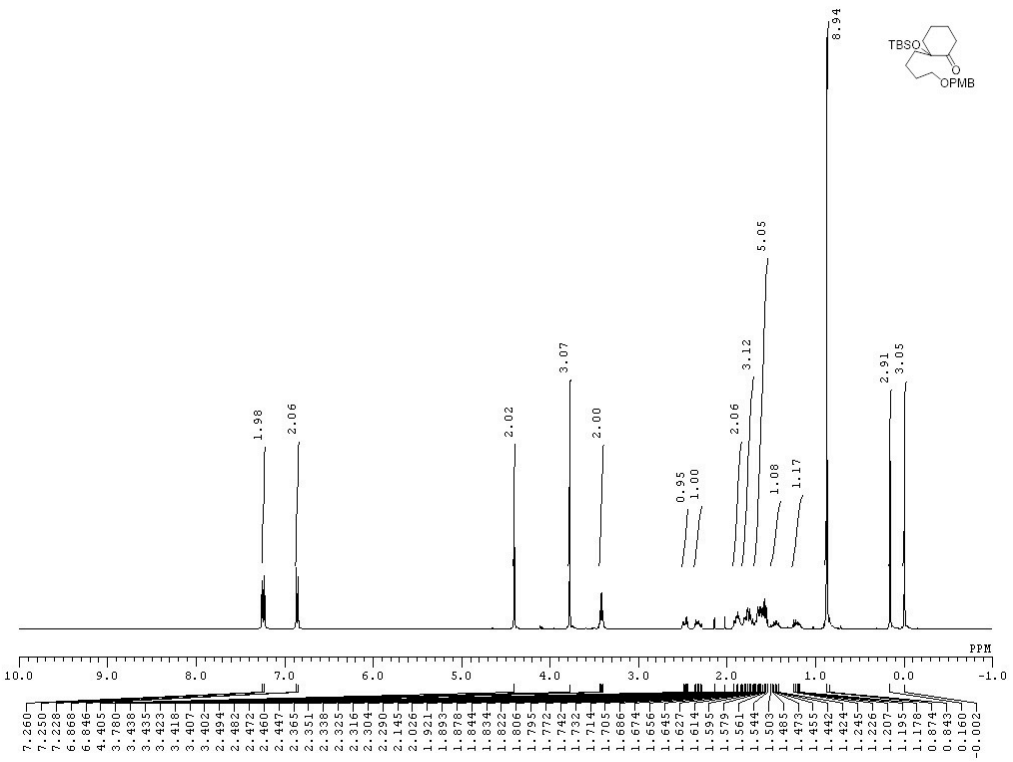
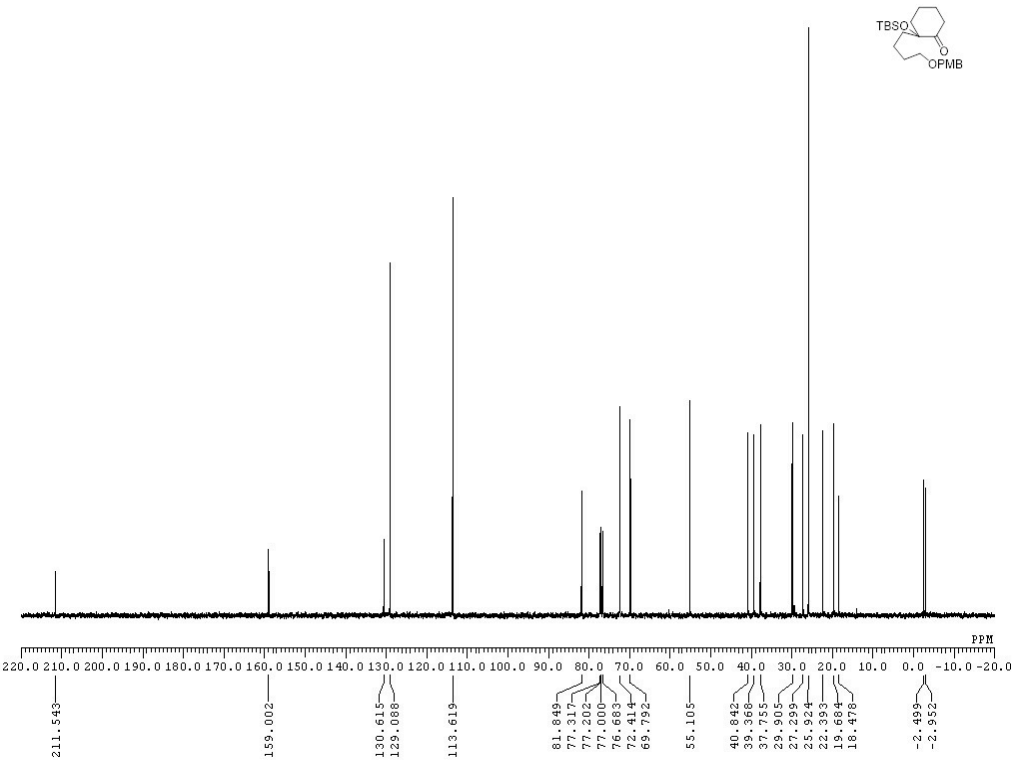
24.290
20.590
19.256
18.050
-4.644


TBSO
OPMB
8.94
5.05
3.12
3.07
2.91
3.05
2.06
2.02
2.00
1.98
2.06
1.08
1.17
0.95
1.00
PPM


TBSO
OPMB
PPM
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159.002
130.615
129.088
113.619
81.849
77.317
77.202
77.000
76.683
72.414
69.792
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22.393
19.684
18.478
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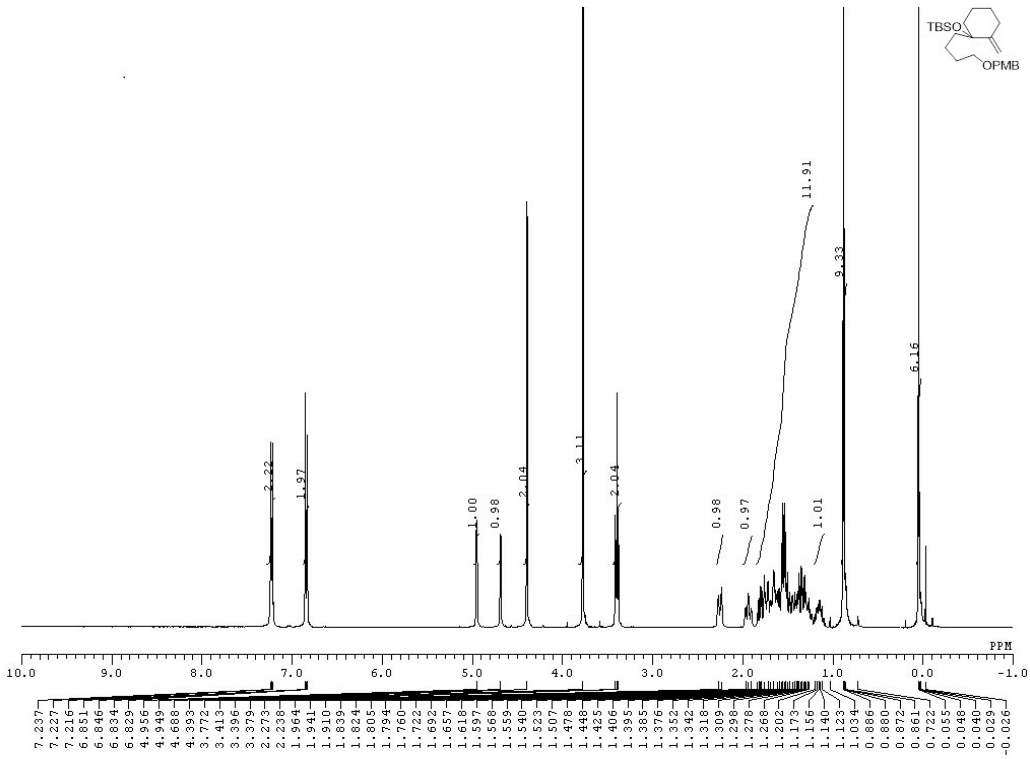
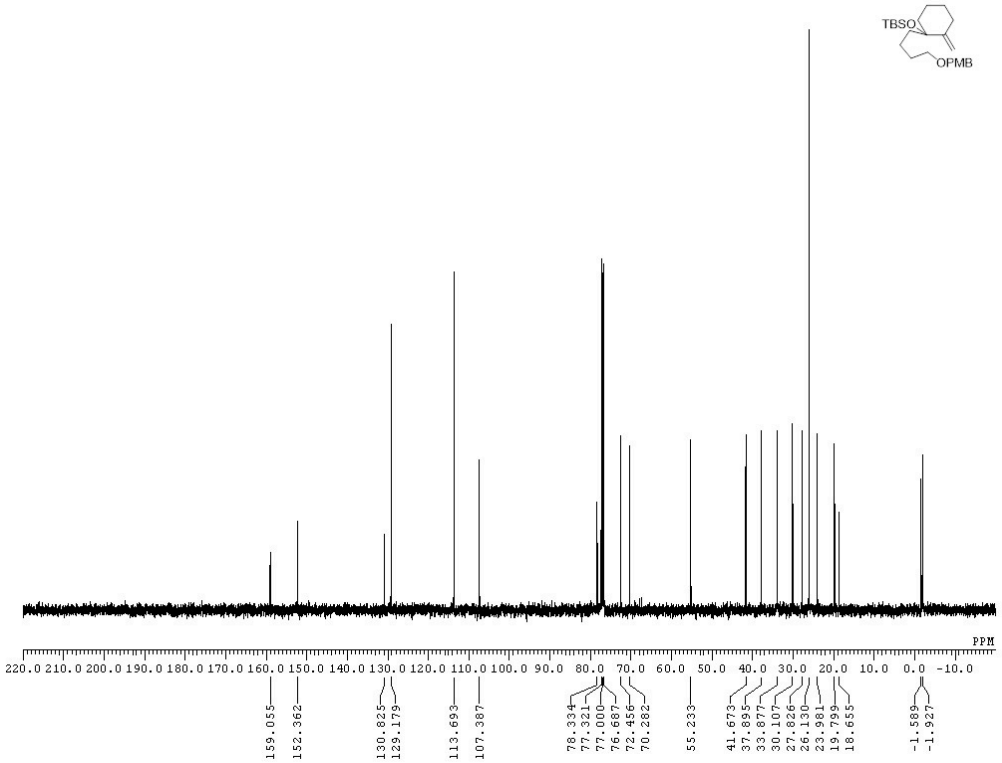
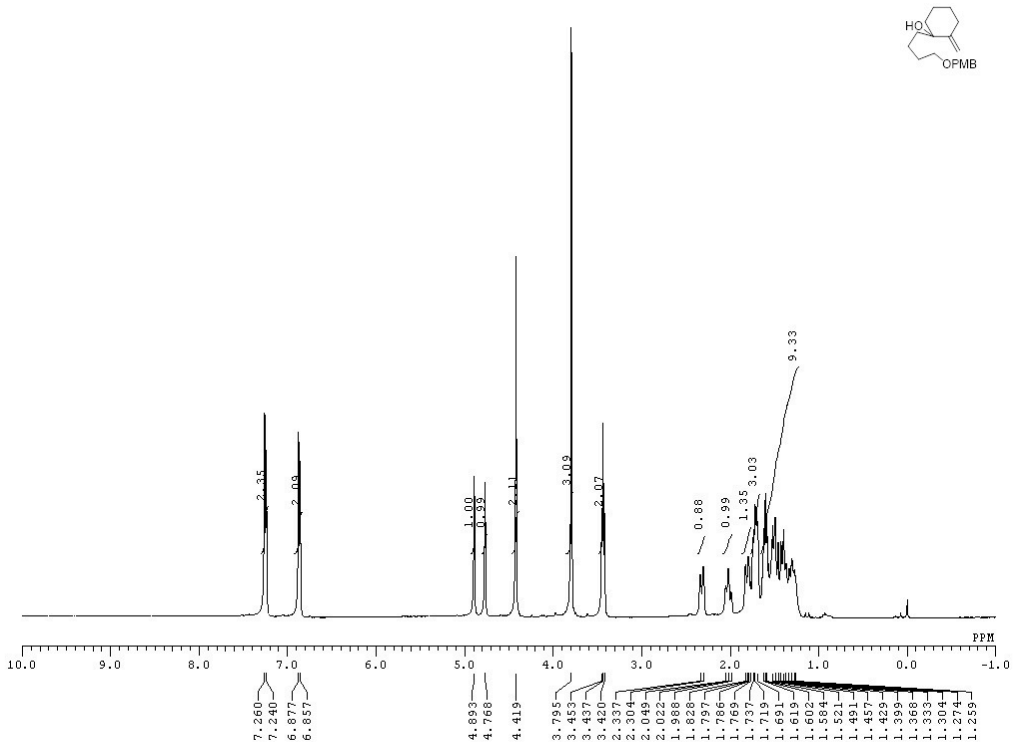
-2.952


TBSO
OPMB
2.22
1.97
1.00
0.98
2.04
3.11
2.04
0.98
0.97
11.91
1.01
9.33
6.16
PPM


TBSO
OPMB
PPM


HO
OPMB
2.35
2.09
1.00
0.99
2.11
3.09
2.07
0.88
0.99
1.35
3.03
9.33
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.260
7.240
6.877
6.857
4.693
4.768
4.419
3.795
3.453
3.437
3.420
2.337
2.304
2.049
2.022
1.988
1.828
1.797
1.786
1.769
1.737
1.719
1.691
1.619
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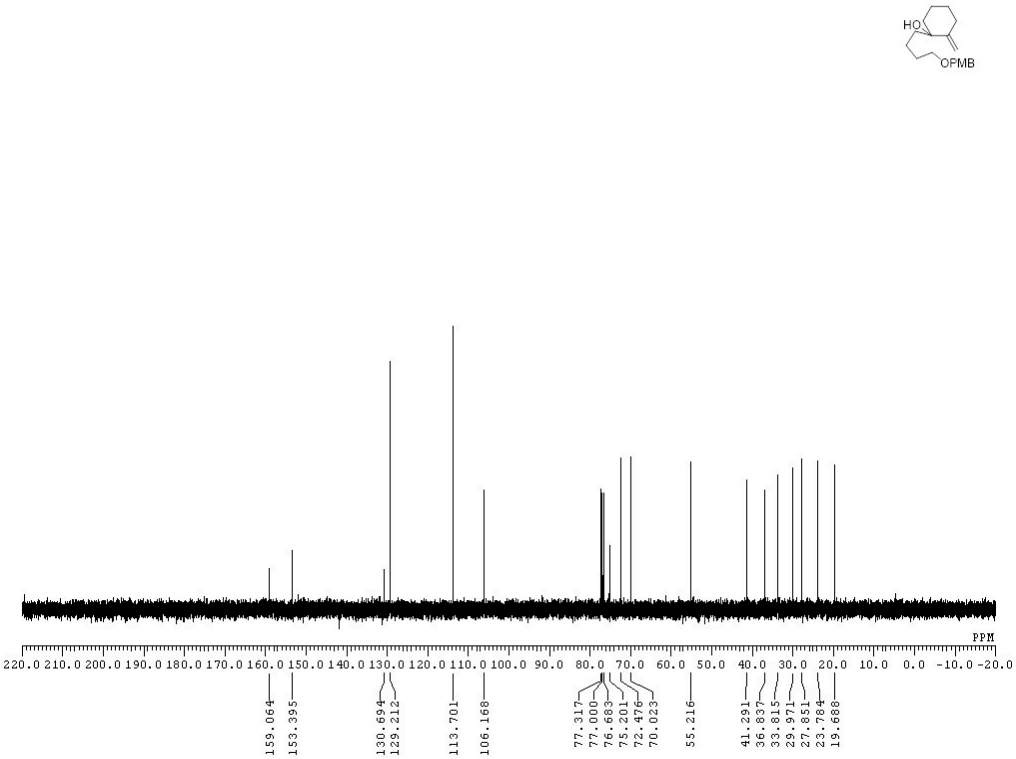
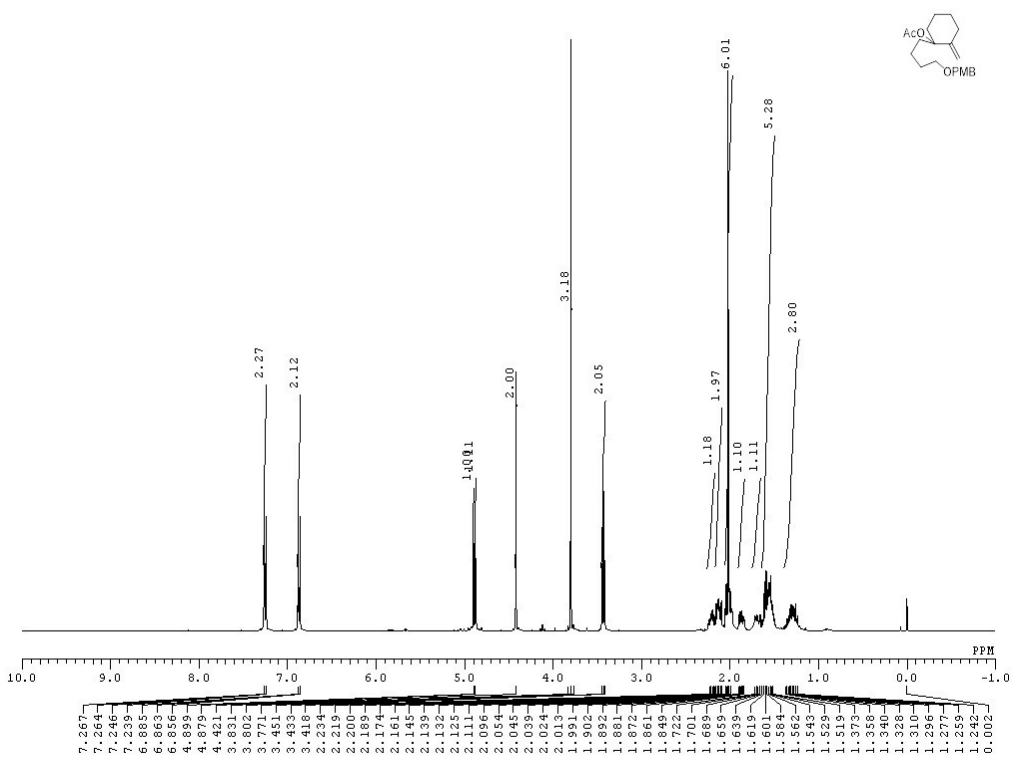
1.259


HO
OPMB
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
159.064
153.395
130.694
129.212
113.701
106.168
77.317
77.000
76.683
75.201
72.476
70.023
55.216
41.291
36.837
33.815
29.971
27.351
23.784
19.688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OPMB
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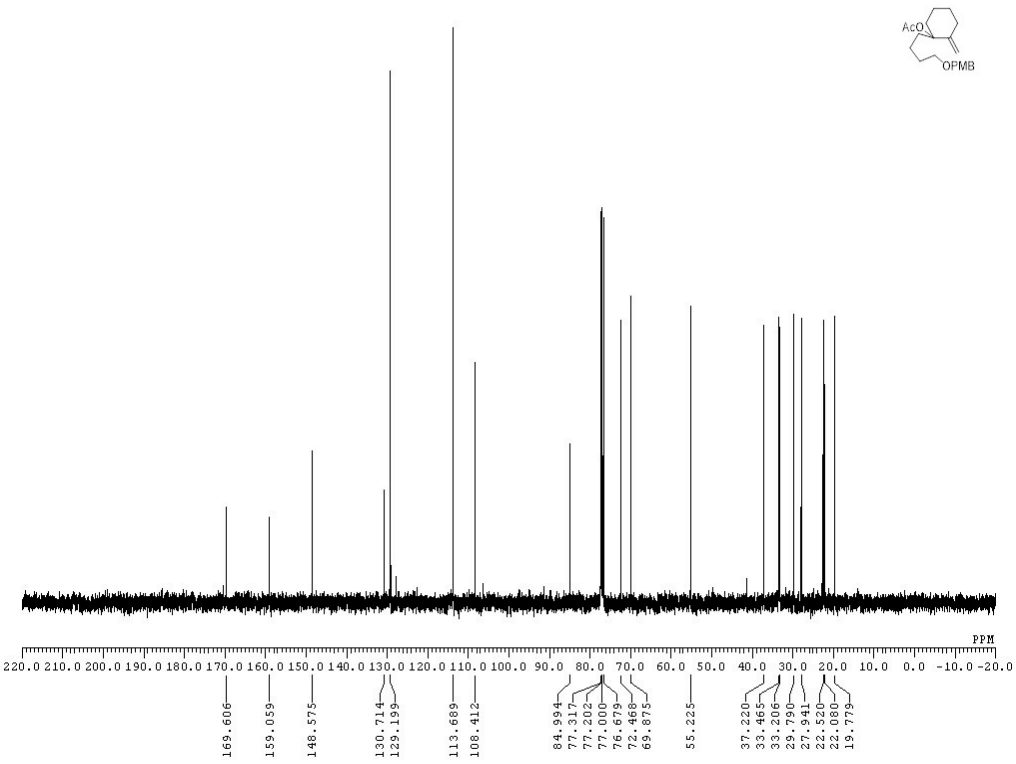
2.80
2.27
2.12
2.00
2.05
1.97
1.18
1.10
1.11
PPM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PPM
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129.199
113.689
108.412
84.994
77.317
77.202
77.000
76.679
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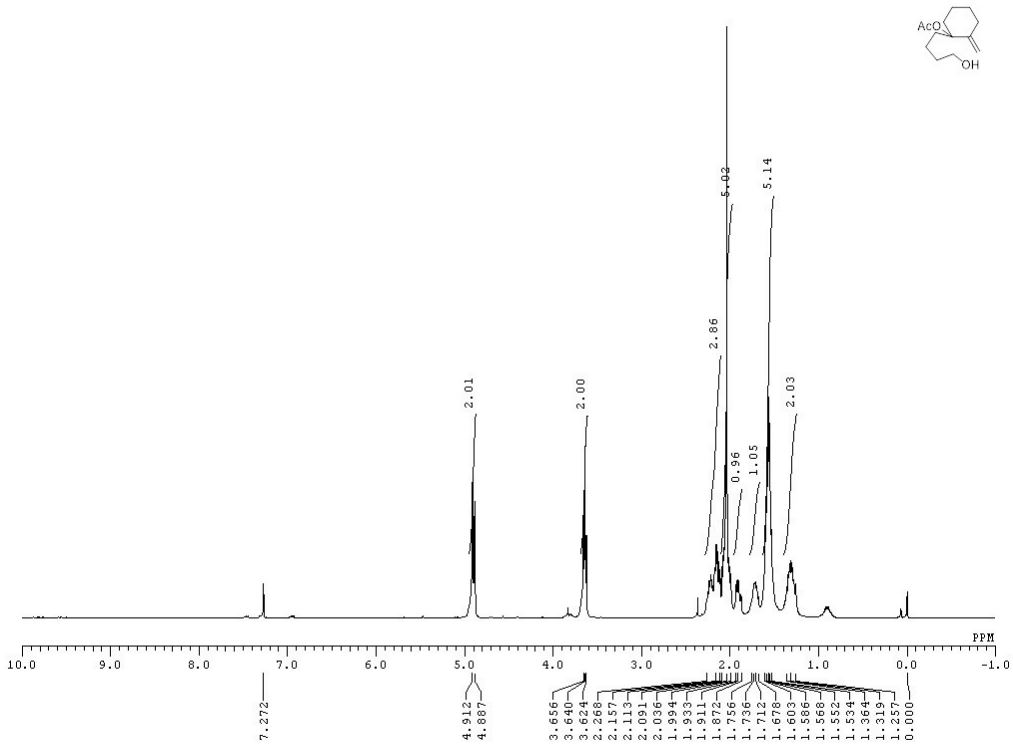
69.875
55.225
37.220
33.465
33.206
29.790
27.941
22.320
22.080
19.779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OH
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5.14
2.86
2.01
2.00
2.03
0.96
1.05
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.272
4.912
4.887
3.656
3.640
3.624
2.268
2.157
2.113
2.091
2.036
1.994
1.933
1.911
1.872
1.756
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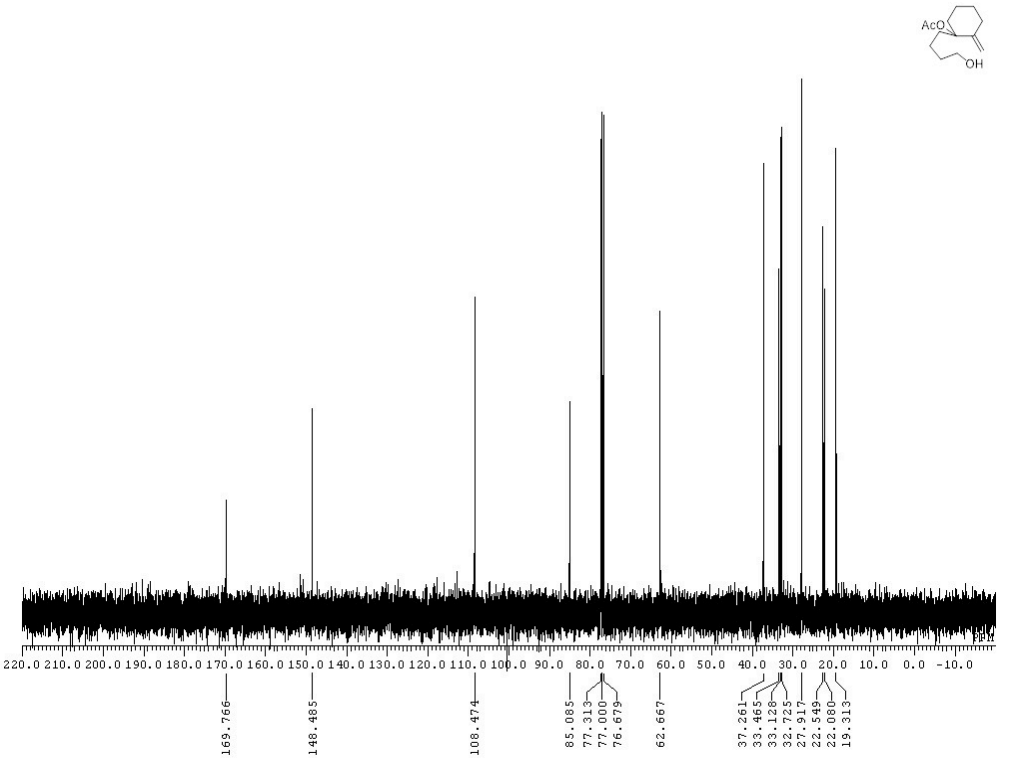
1.678
1.603
1.586
1.568
1.552
1.534
1.364
1.319
1.257
0.000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OH
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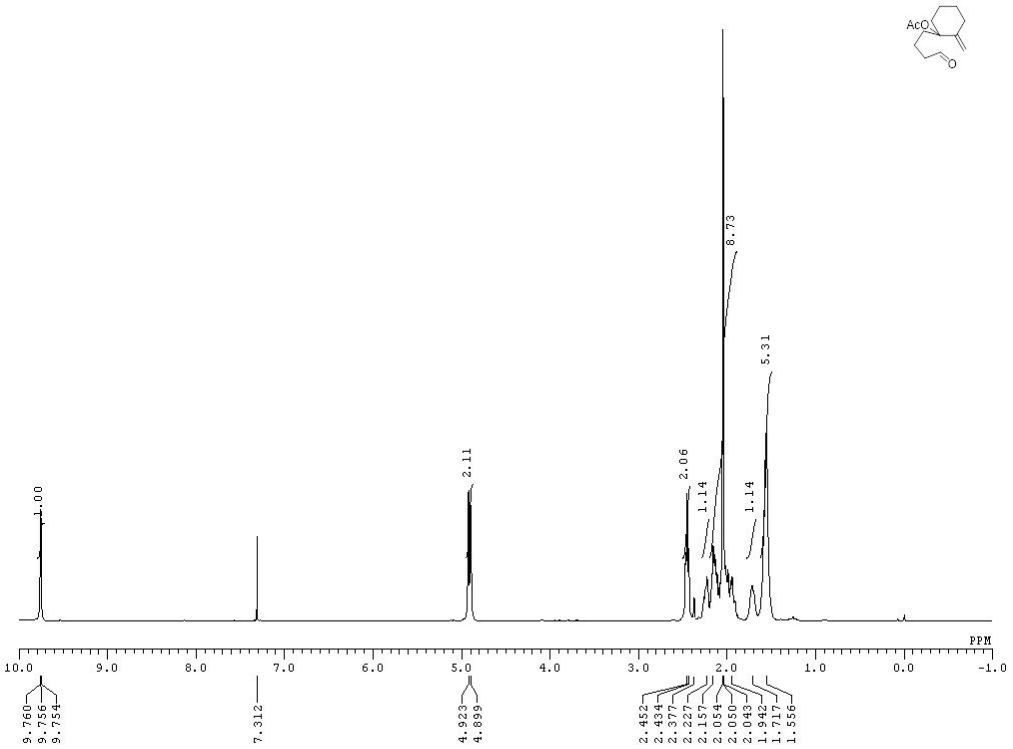
169.766
148.485
108.474
85.085
77.313
77.000
76.679
62.667
37.261
33.465
33.128
32.725
27.917
22.549
22.080
19.313

13h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O
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2.11
2.06
1.14
1.14
8.73
5.31
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
9.760
9.756
9.754
7.312
4.923
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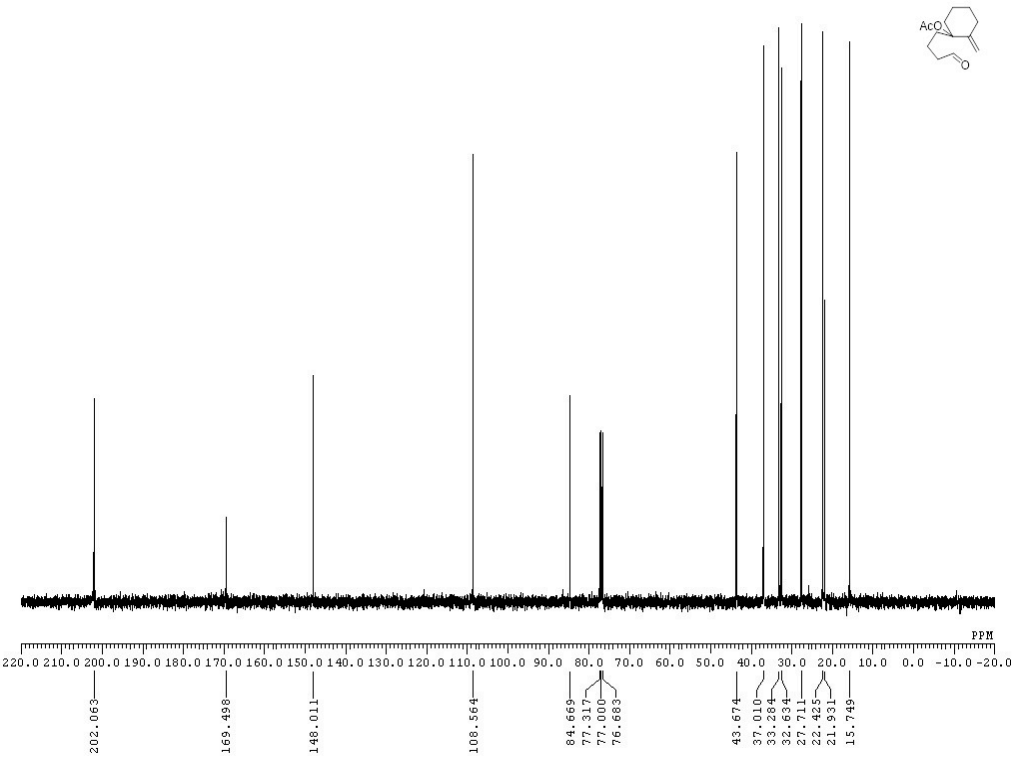
2.377
2.227
2.157
2.054
2.050
2.043
1.942
1.717
1.556


AcO
O
PPM
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202.063
169.498
148.011
108.564
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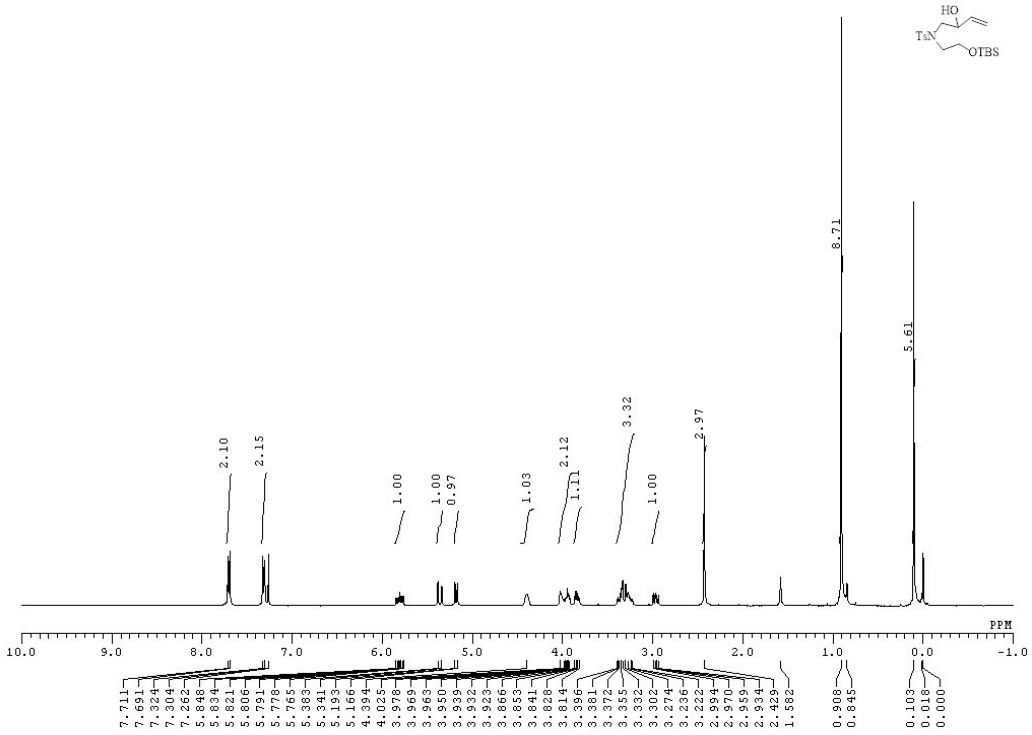
77.000
76.683
43.674
37.010
33.284
32.634
27.711
22.425
21.931
15.749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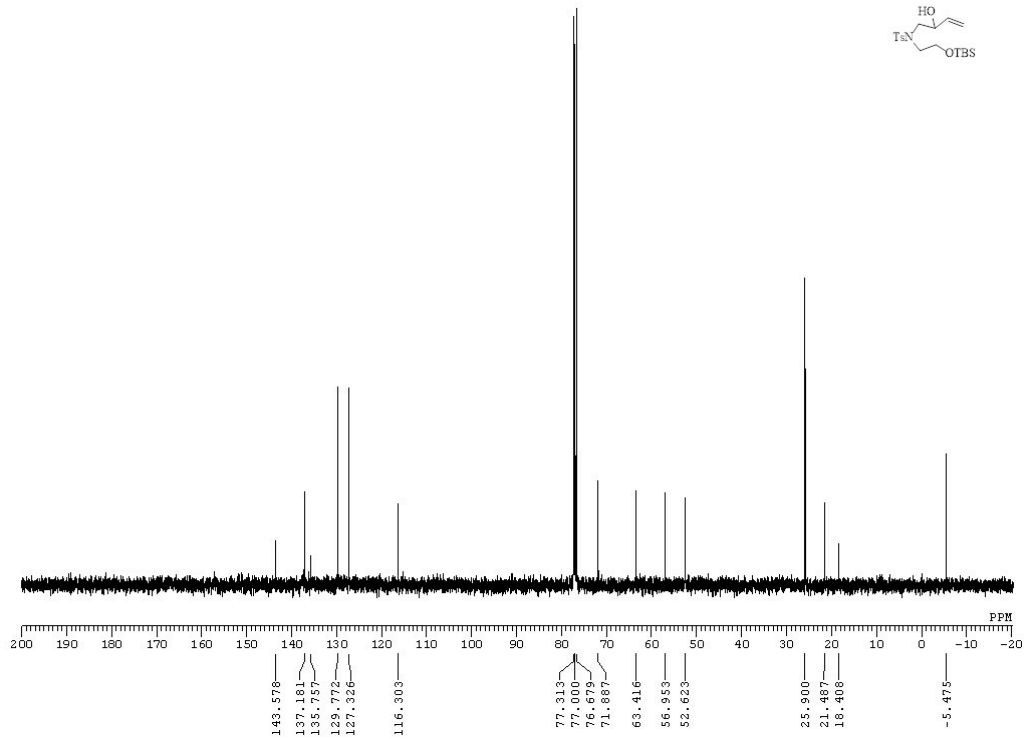
TsN
OTBS
8.71
5.61
3.32
2.97
2.10
2.15
2.12
1.00
1.00
0.97
1.03
1.11
1.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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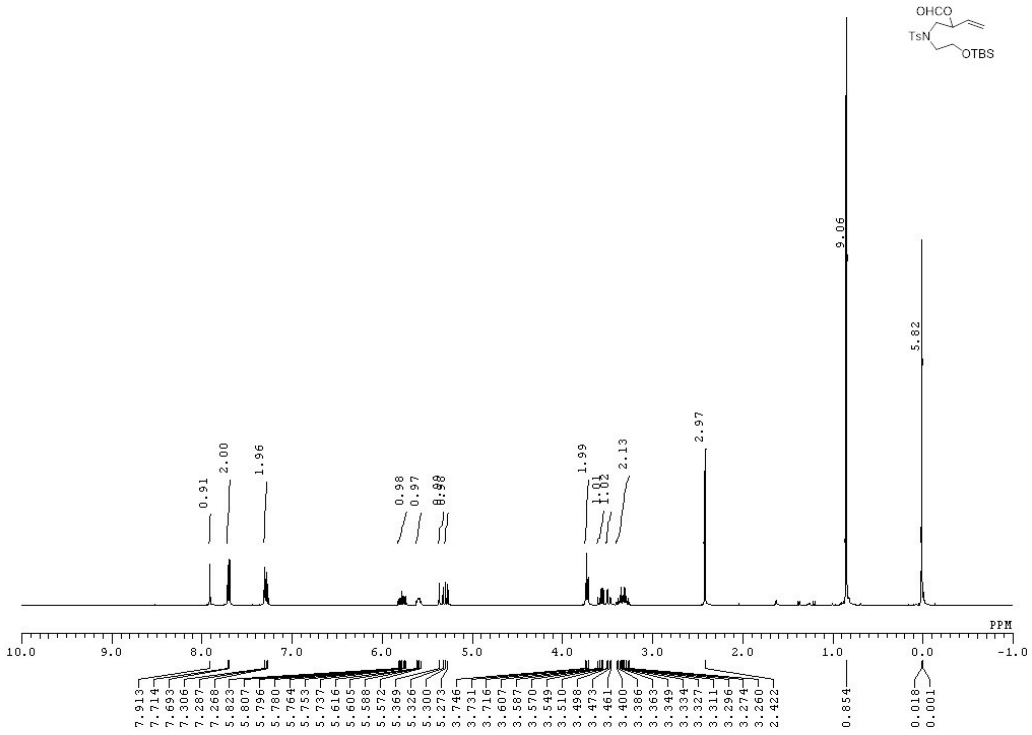
TsN
OTBS
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
143.578
137.181
135.757
129.772
127.326
116.303
77.313
77.000
76.679
71.887
63.416
56.953
52.623
25.900
21.487
18.408
-5.475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OTBS
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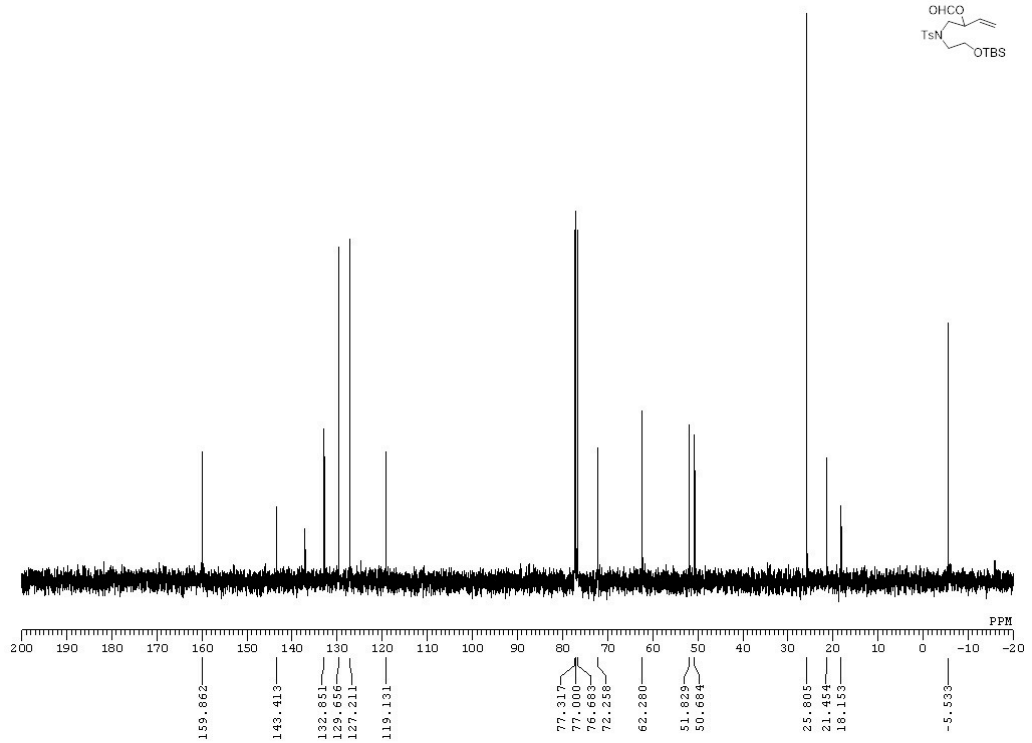
5.82
2.97
2.13
2.00
1.99
1.96
1.02
1.01
0.98
0.97
0.91
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
0.854
0.018
0.001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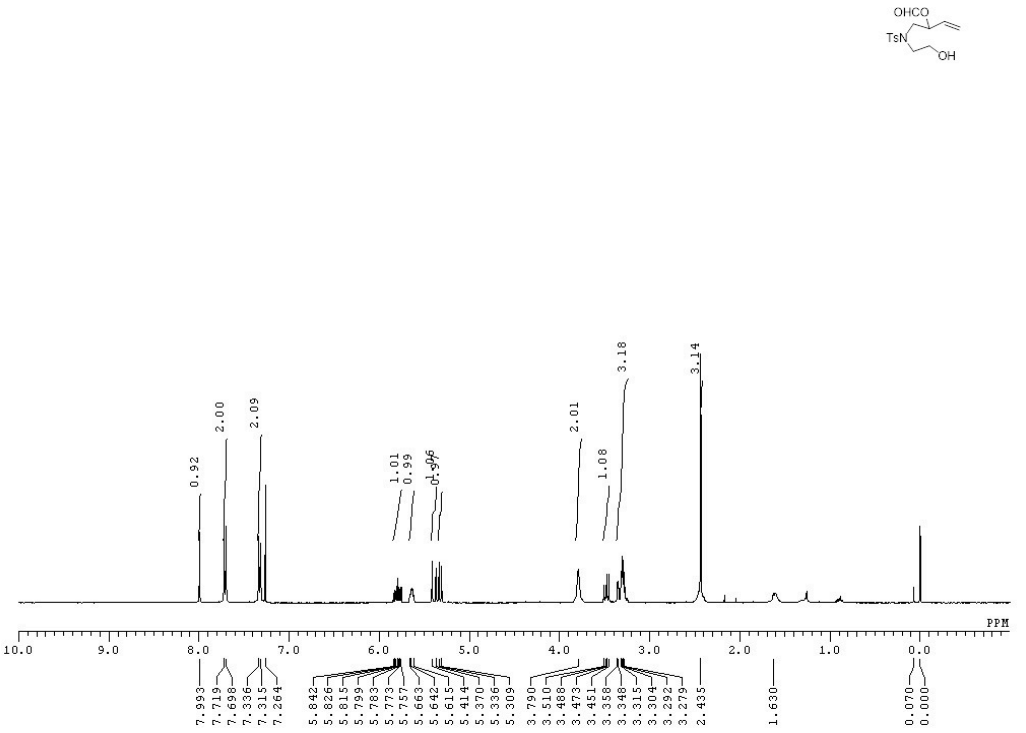
TsN
OTBS
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
159.862
143.413
132.851
129.656
127.211
119.131
77.317
77.000
76.683
72.258
62.280
51.829
50.684
25.805
21.454
18.153
-5.533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TsN
OH
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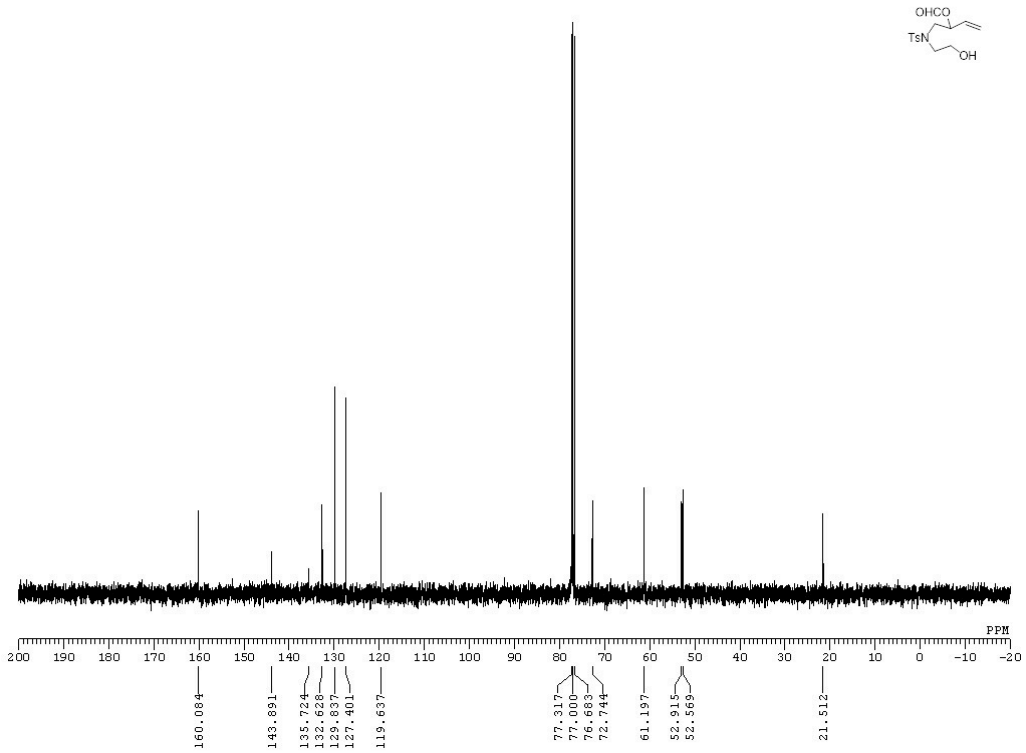
2.09
1.01
0.99
1.06
2.01
1.08
3.18
3.14
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.993
7.719
7.698
7.336
7.315
7.264
5.842
5.826
5.815
5.799
5.783
5.773
5.757
5.663
5.642
5.615
5.414
5.370
5.336
5.309
3.790
3.510
3.488
3.473
3.451
3.358
3.348
3.315
3.304
3.292
3.279
2.435
1.630
0.070
0.000


OHCO
TsN
OH
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
160.084
143.891
135.724
132.628
129.837
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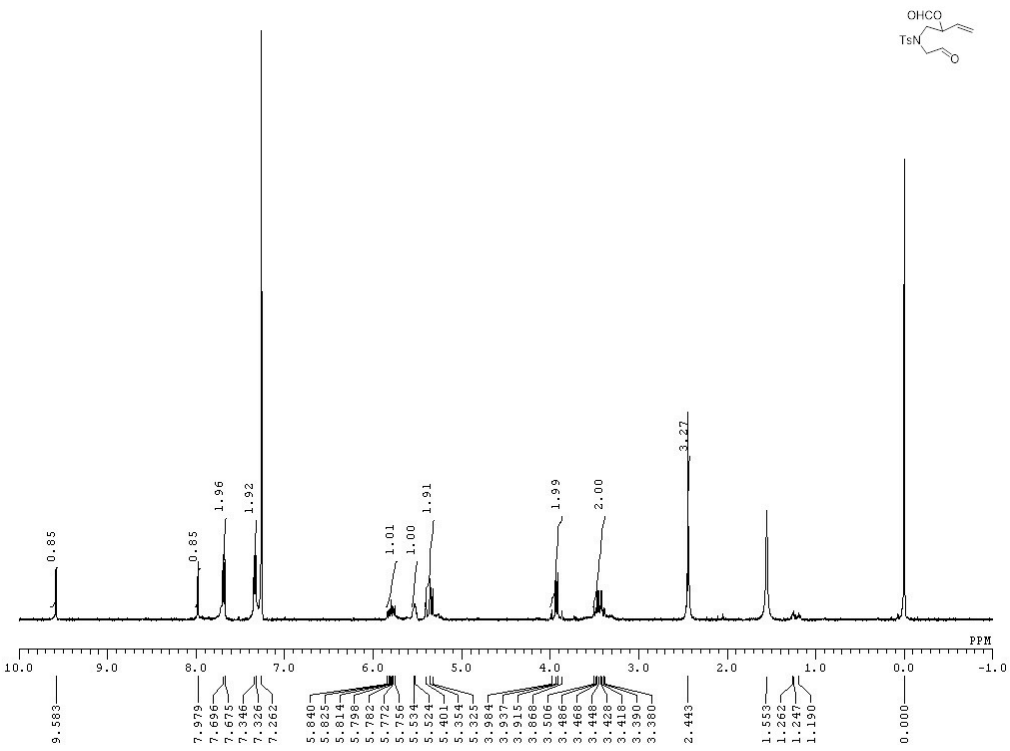
119.637
77.317
77.000
76.683
72.744
61.197
52.915
52.569
21.512

13i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TsN
O
0.85
0.85
1.96
1.92
1.01
1.00
1.91
1.99
2.00
3.27
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
9.583
7.979
7.696
7.675
7.346
7.326
7.262
5.840
5.825
5.814
5.798
5.782
5.772
5.756
5.534
5.524
5.401
5.354
5.325
3.984
3.937
3.915
3.868
3.506
3.486
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3.448
3.428
3.418
3.390
3.380
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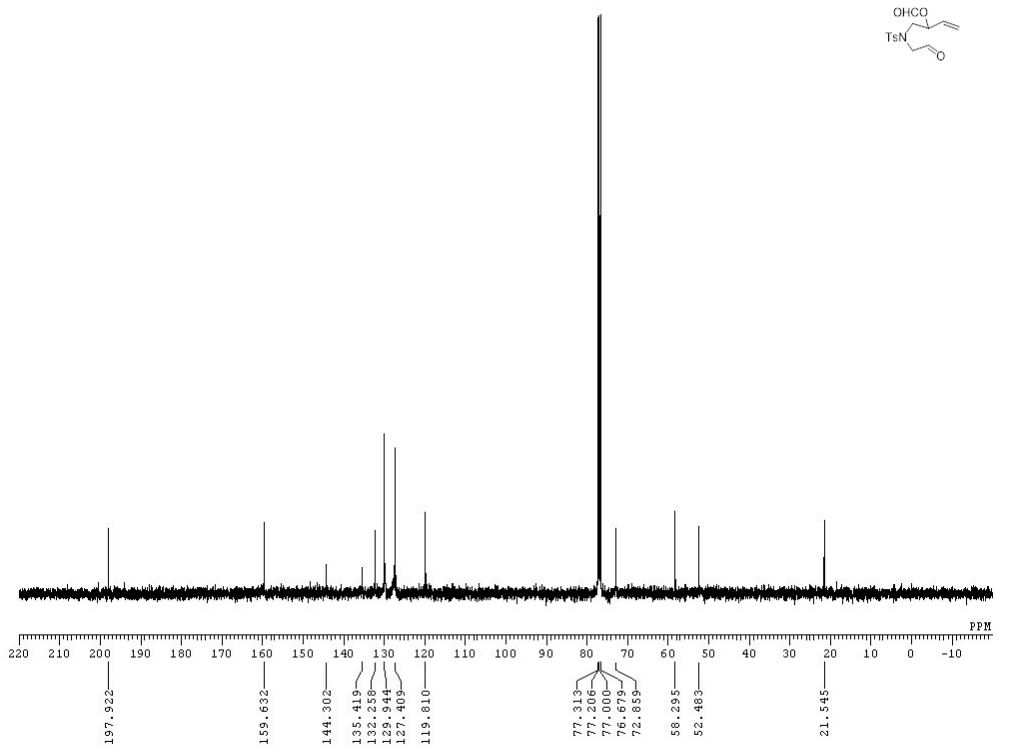
1.553
1.262
1.247
1.190
0.000


OHCO
TsN
O
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
197.922
159.632
144.302
135.419
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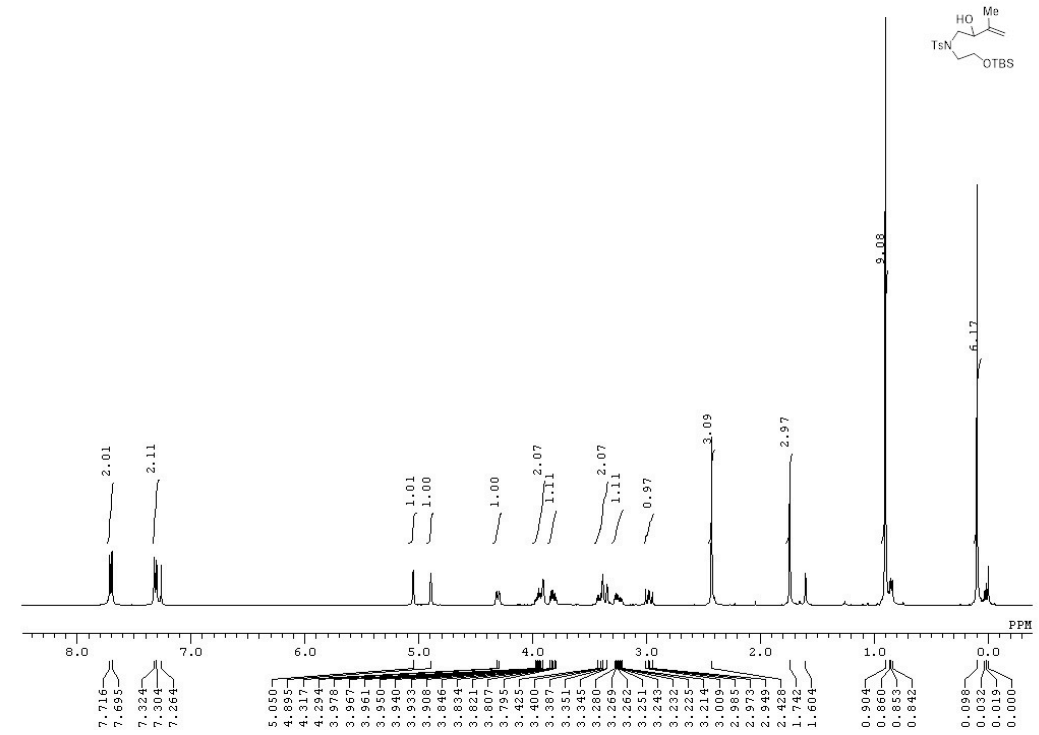
127.409
119.810
77.313
77.206
77.000
76.679
72.859
58.295
52.483
21.545


HO
Me
TsN
OTBS
2.01
2.11
1.01
1.00
1.00
2.07
1.11
2.07
1.11
0.97
3.09
2.97
9.08
6.17
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.716
7.695
7.324
7.304
7.264
5.050
4.895
4.317
4.294
3.978
3.967
3.961
3.950
3.940
3.933
3.908
3.846
3.834
3.821
3.807
3.795
3.425
3.400
3.387
3.351
3.345
3.280
3.269
3.262
3.251
3.243
3.232
3.225
3.214
3.009
2.985
2.973
2.949
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0.842
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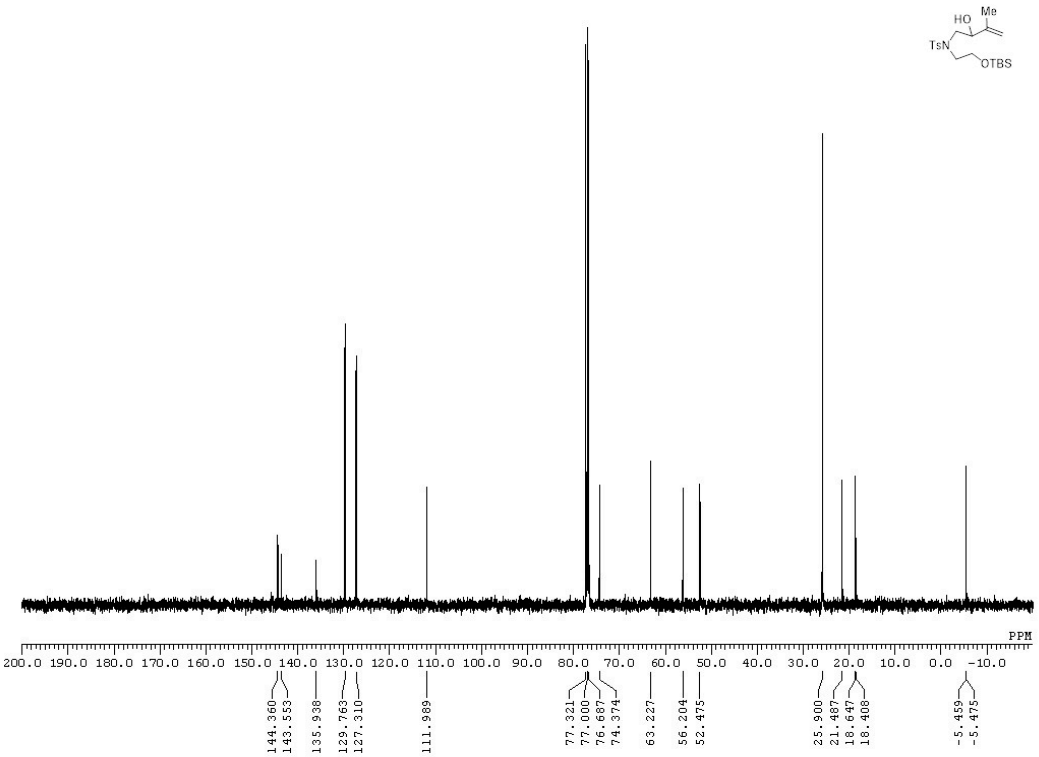
0.032
0.019
0.000


HO
Me
TsN
OTBS
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
144.360
143.553
135.938
129.763
127.310
111.989
77.321
77.000
76.687
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63.227
56.204
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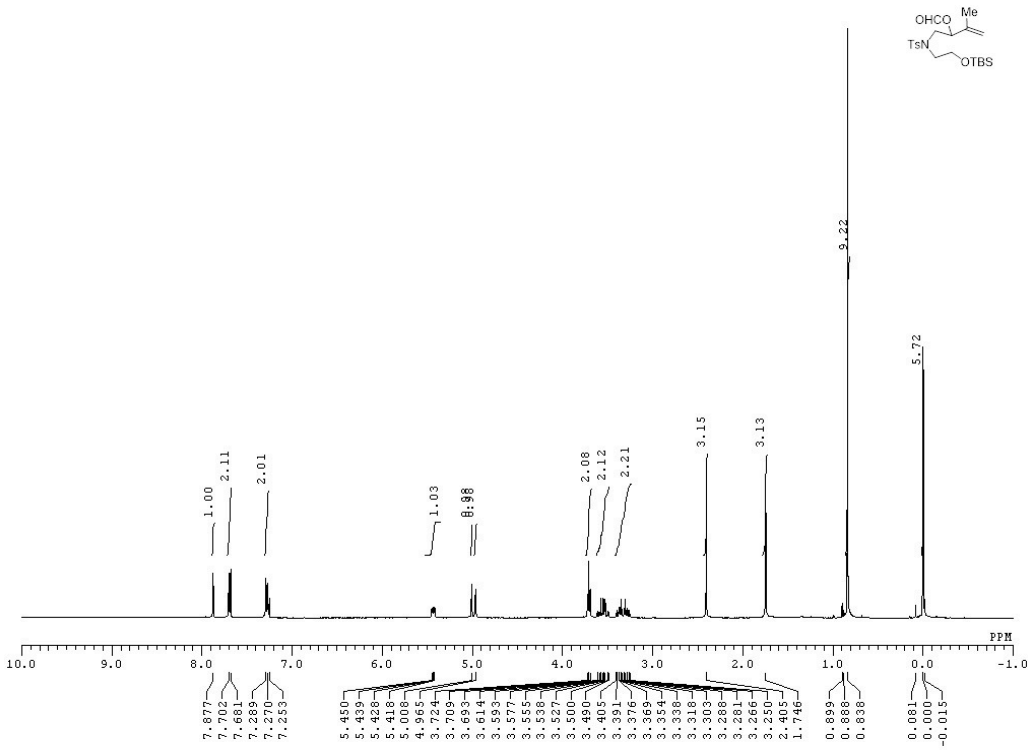
21.487
18.647
18.408
-5.459
-5.475


OHCO
Me
TsN
OTBS
1.00
2.11
2.01
1.03
8.98
2.08
2.12
2.21
3.15
3.13
9.22
5.72
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.877
7.702
7.681
7.289
7.270
7.253
5.450
5.439
5.428
5.418
5.008
4.965
3.724
3.709
3.693
3.614
3.593
3.577
3.555
3.538
3.527
3.500
3.490
3.405
3.391
3.376
3.369
3.354
3.338
3.318
3.303
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2.405
1.746
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0.888
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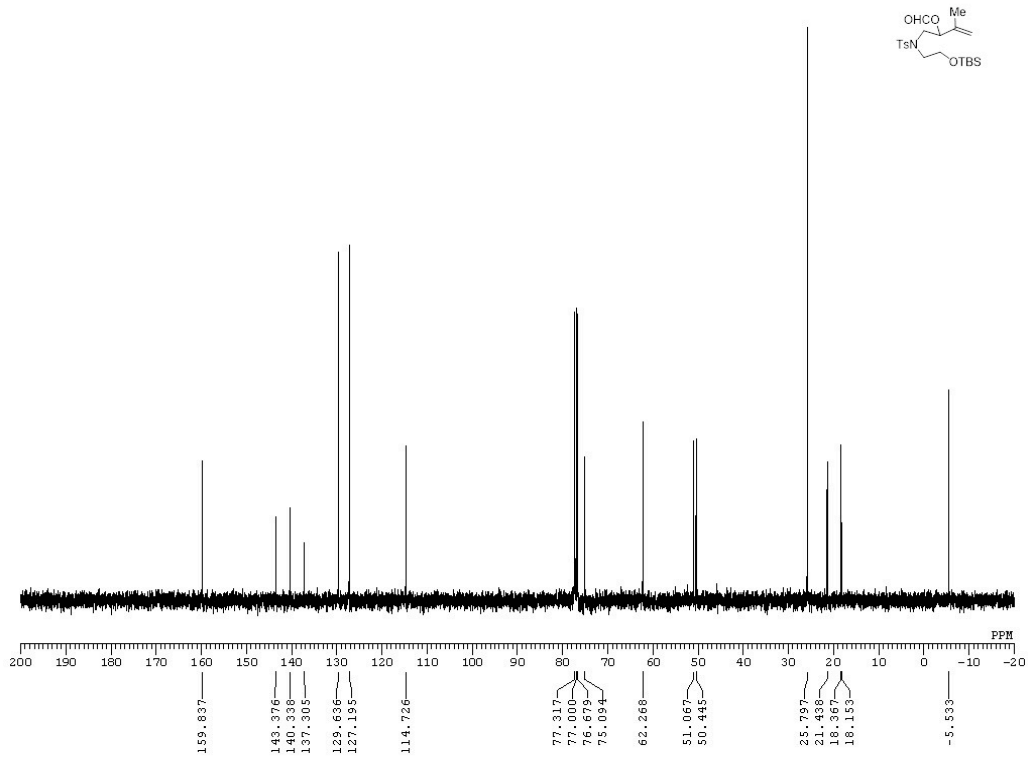
0.000
-0.015


OHCO
Me
TsN
OTBS
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
159.837
143.376
140.338
137.305
129.636
127.195
114.726
77.317
77.000
76.679
75.094
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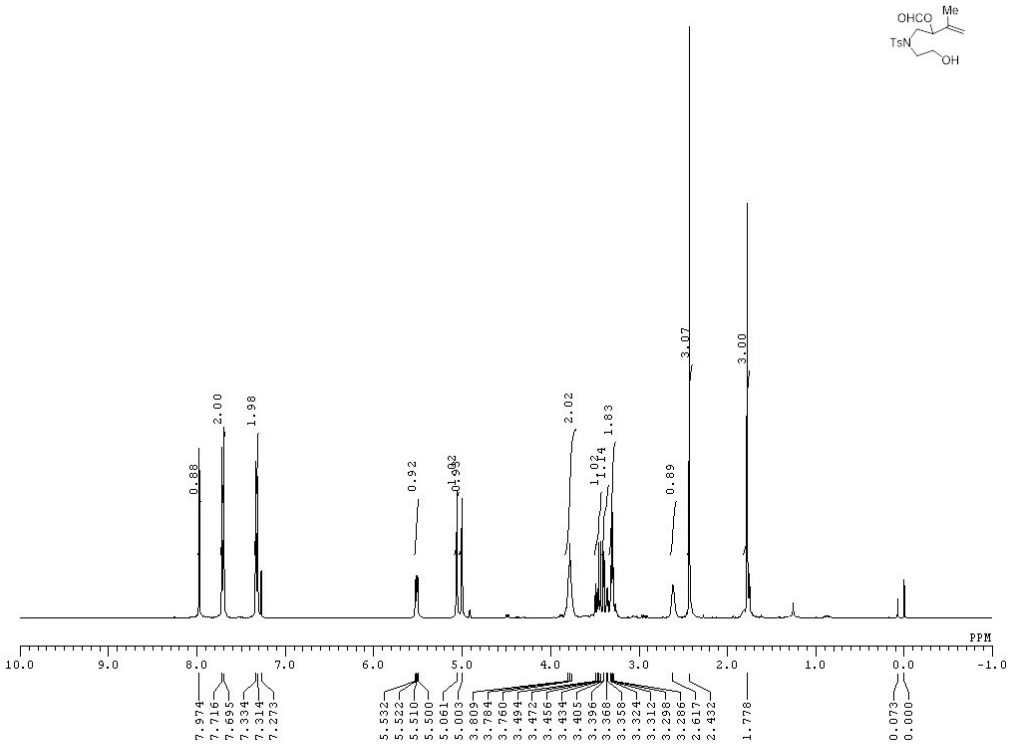
25.797
21.438
18.367
18.153
-5.533


OHCO
Me
TsN
OH
0.88
2.00
1.98
0.92
1.00
2.02
1.83
1.02
1.14
0.89
3.07
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.974
7.716
7.695
7.334
7.314
7.273
5.532
5.522
5.510
5.500
5.061
5.003
3.809
3.784
3.760
3.494
3.472
3.456
3.434
3.405
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3.298
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2.617
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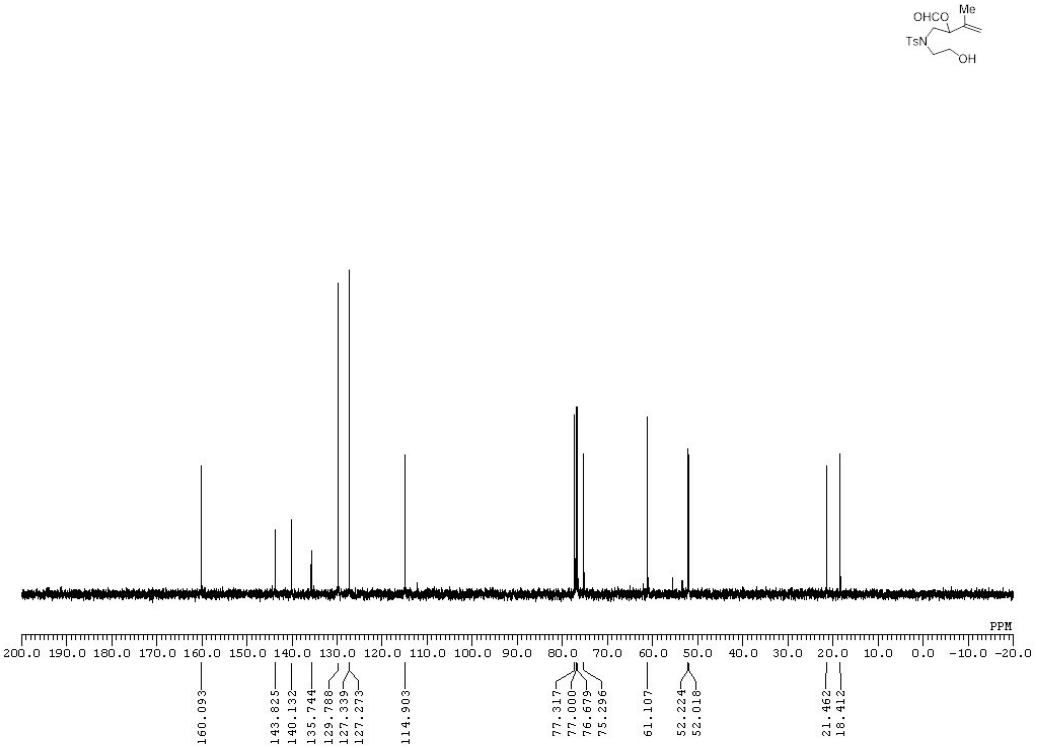
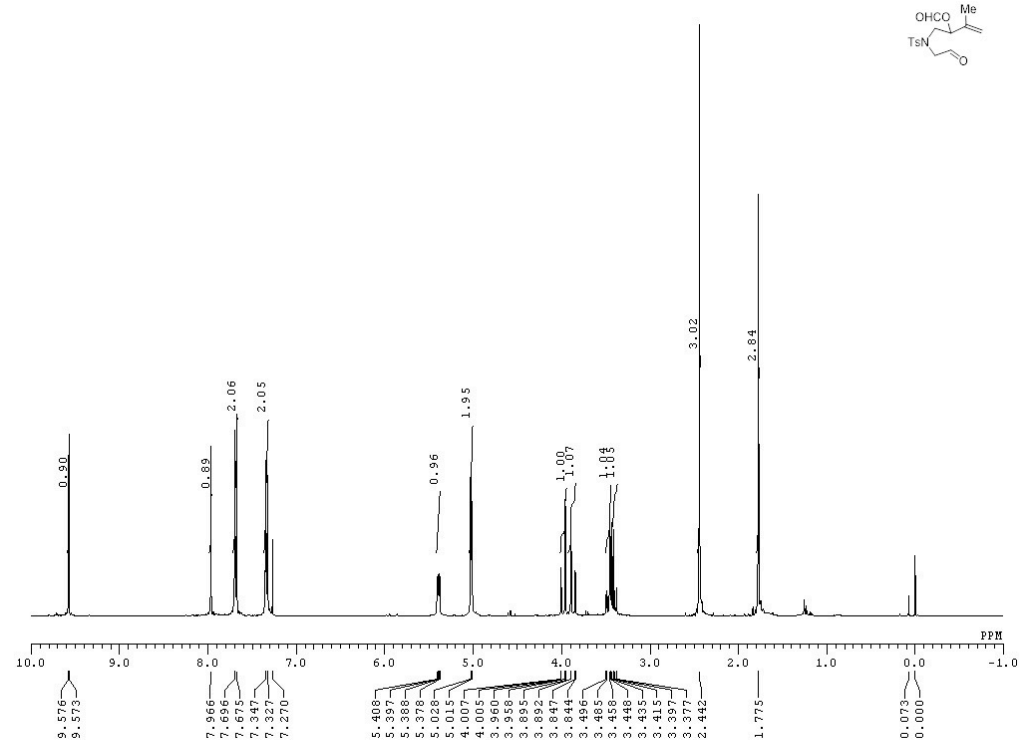
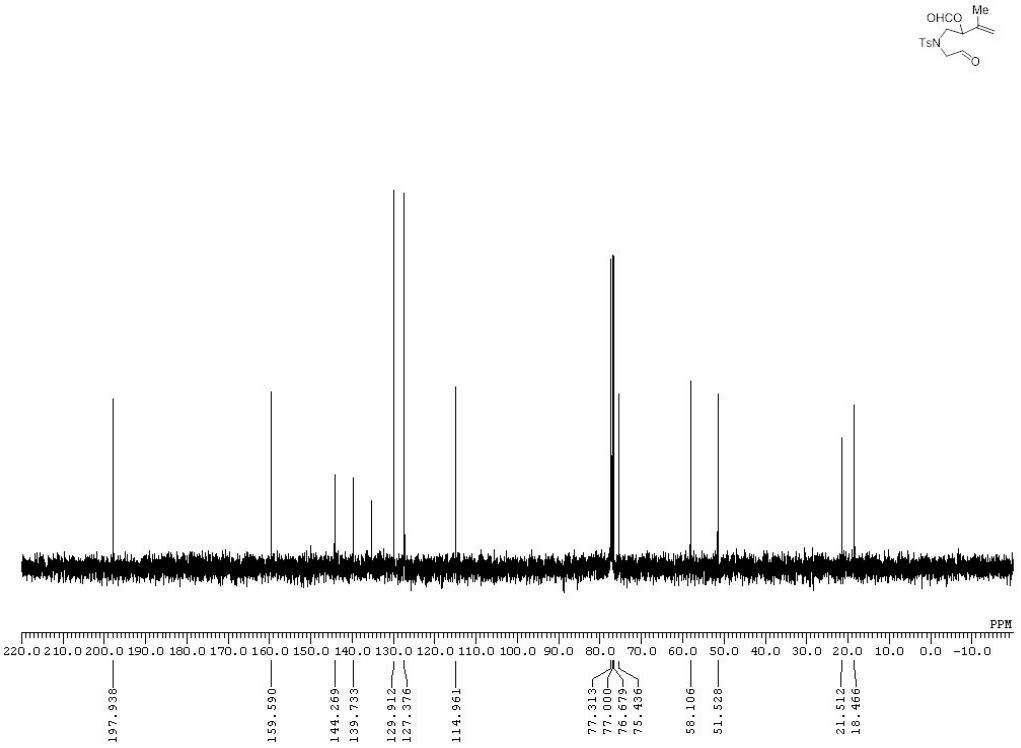
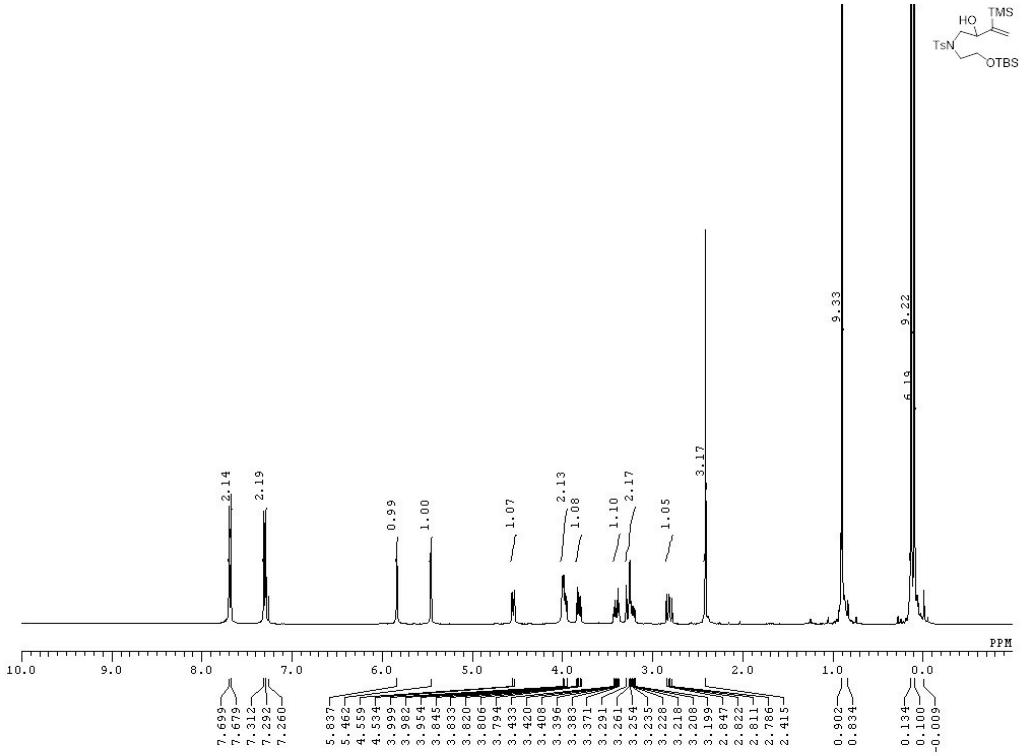
0.073
0.000


OHCO
Me
TsN
OH
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
160.093
143.825
140.132
135.744
129.788
127.339
127.273
114.903
77.317
77.000
76.679
75.296
61.107
52.224
52.018
21.462
18.412

13j


OHCO
Me
TsN
O
0.90
0.89
2.06
2.05
0.96
1.95
1.00
1.07
1.04
1.03
3.02
2.84
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
9.576 9.573 7.966 7.696 7.675 7.347 7.327 7.270 5.408 5.397 5.388 5.378 5.028 5.015 4.007 4.005 3.960 3.958 3.895 3.892 3.847 3.844 3.496 3.485 3.458 3.448 3.435 3.415 3.397 3.377 2.442 1.775 0.073 0.000


OHCO
Me
TsN
O
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
197.938 159.590 144.269 139.733 129.912 127.376 114.961 77.313 77.000 76.679 75.436 58.106 51.528 21.512 18.466


HO
TMS
TsN
OTBS
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2.19
0.99
1.00
1.07
2.13
1.08
1.10
2.17
1.05
3.17
9.33
9.22
6.19
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.699
7.679
7.312
7.292
7.260
5.837
5.462
4.559
4.534
3.999
3.982
3.954
3.845
3.833
3.820
3.806
3.794
3.433
3.420
3.408
3.396
3.383
3.371
3.291
3.261
3.254
3.235
3.228
3.218
3.208
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2.811
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0.834
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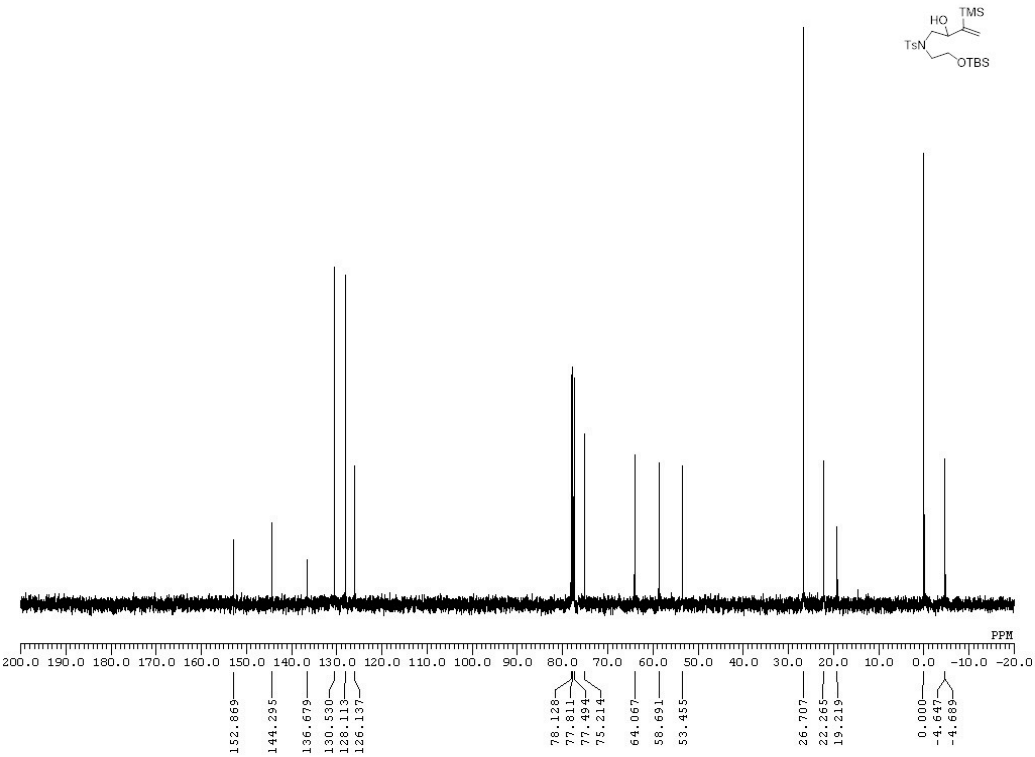
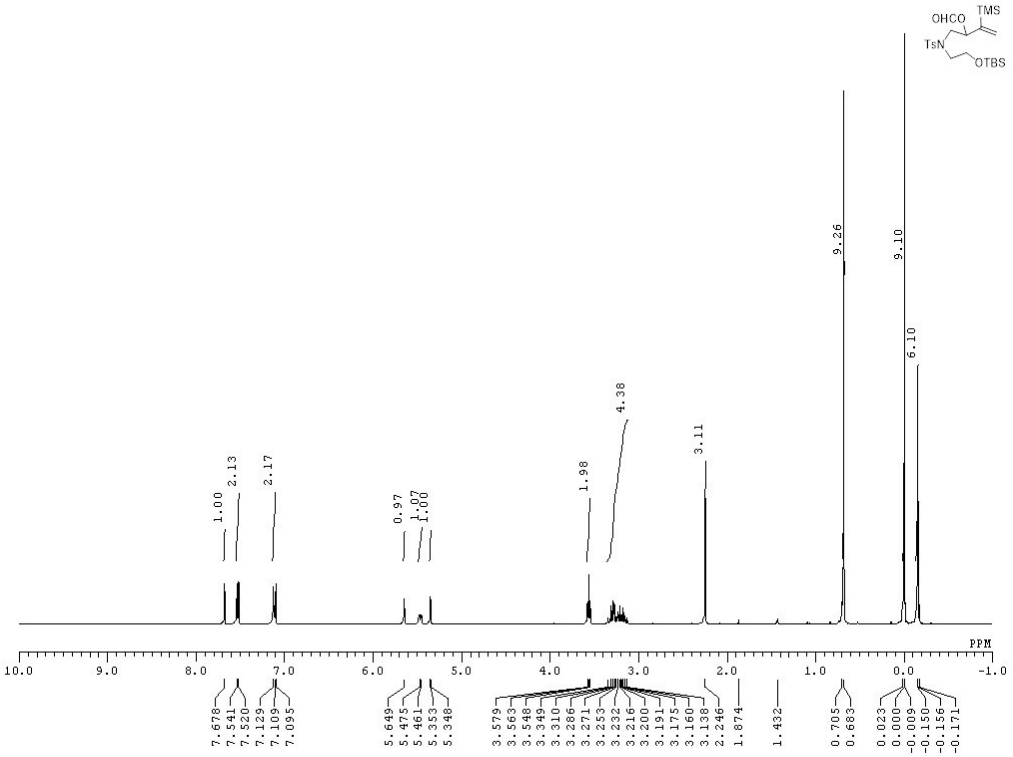
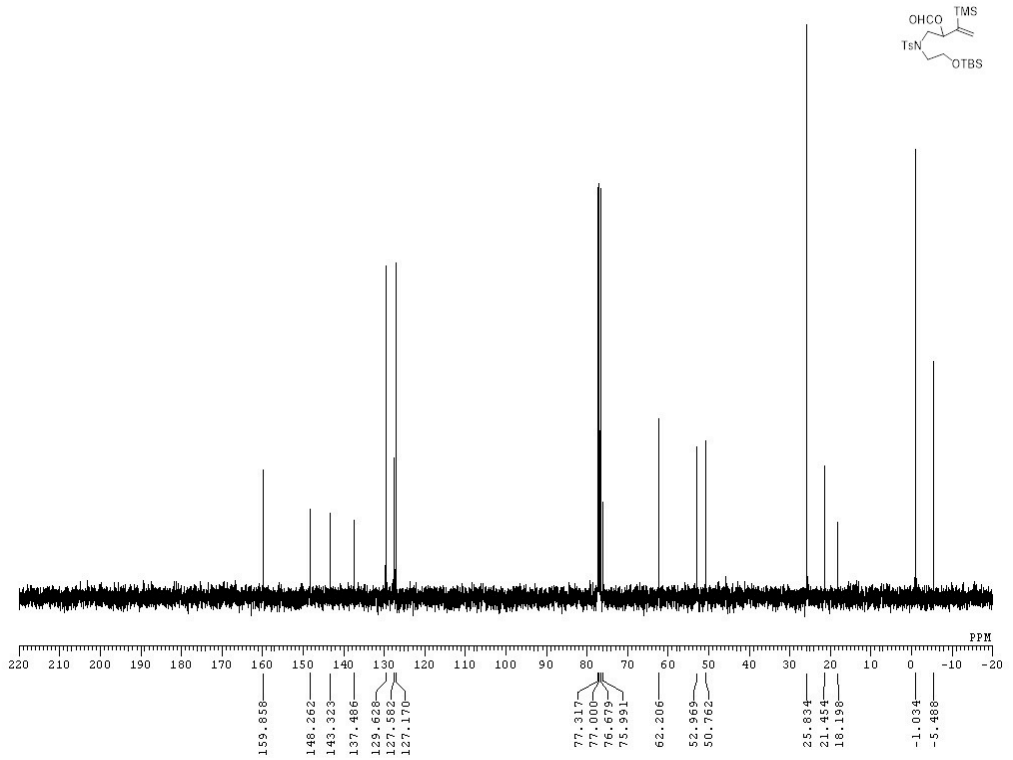
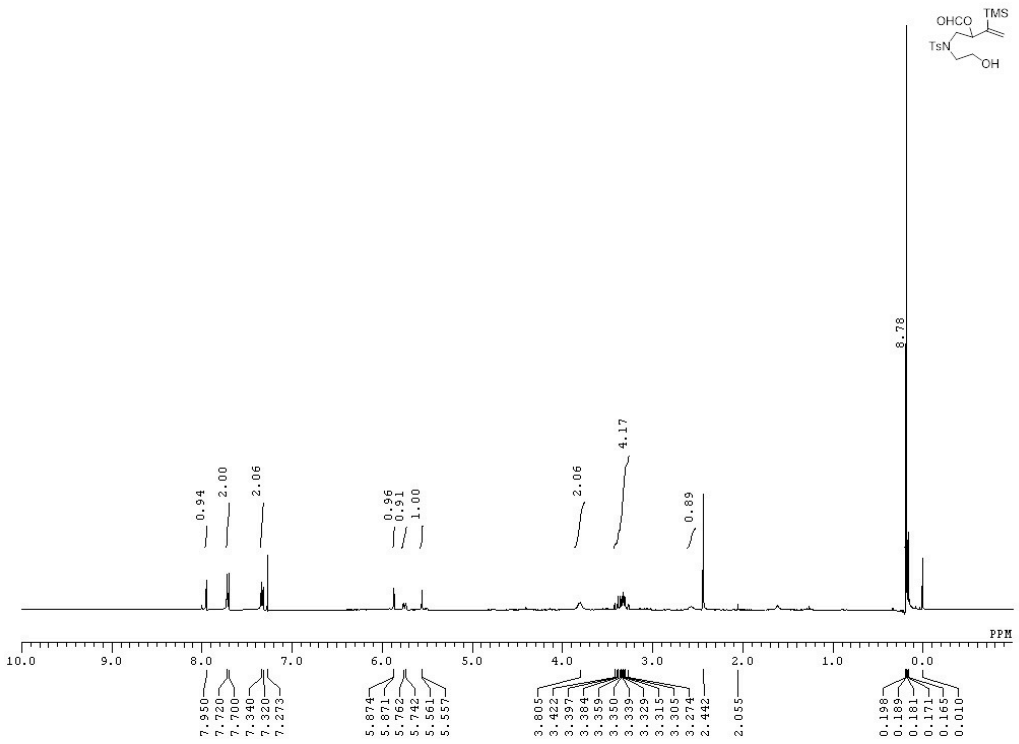
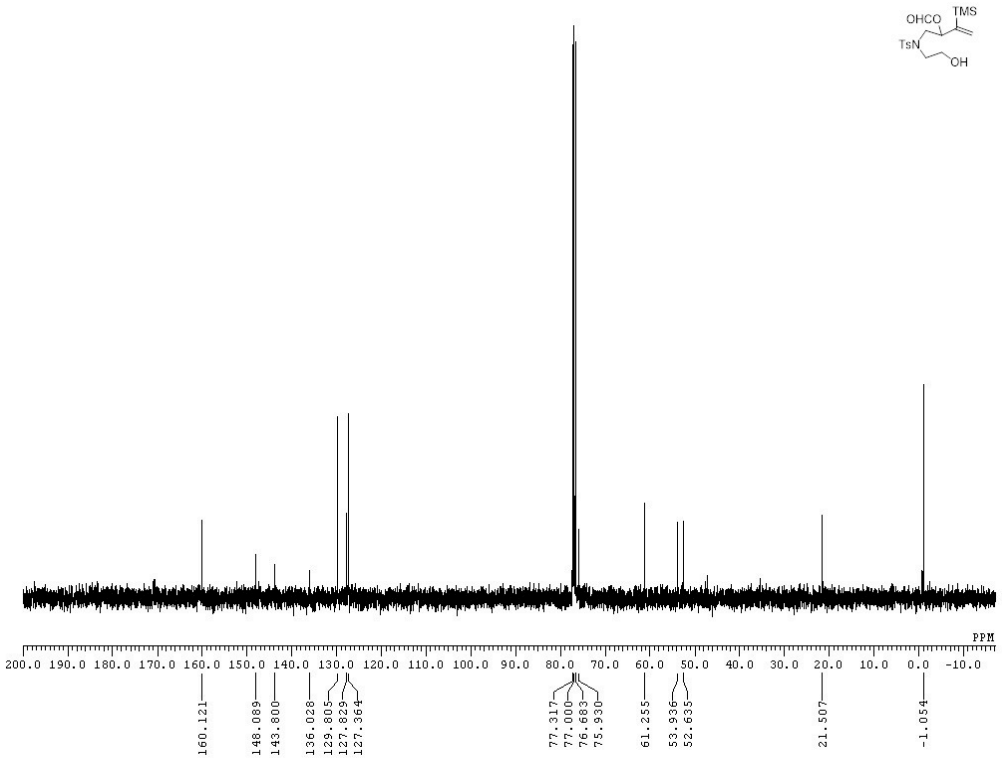
0.100
-0.009


HO
TMS
TsN
OTBS
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
152.869
144.295
136.679
130.530
128.113
126.137
78.128
77.811
77.494
75.214
64.067
58.691
53.455
26.707
22.265
19.219
0.000
-4.647
-4.689

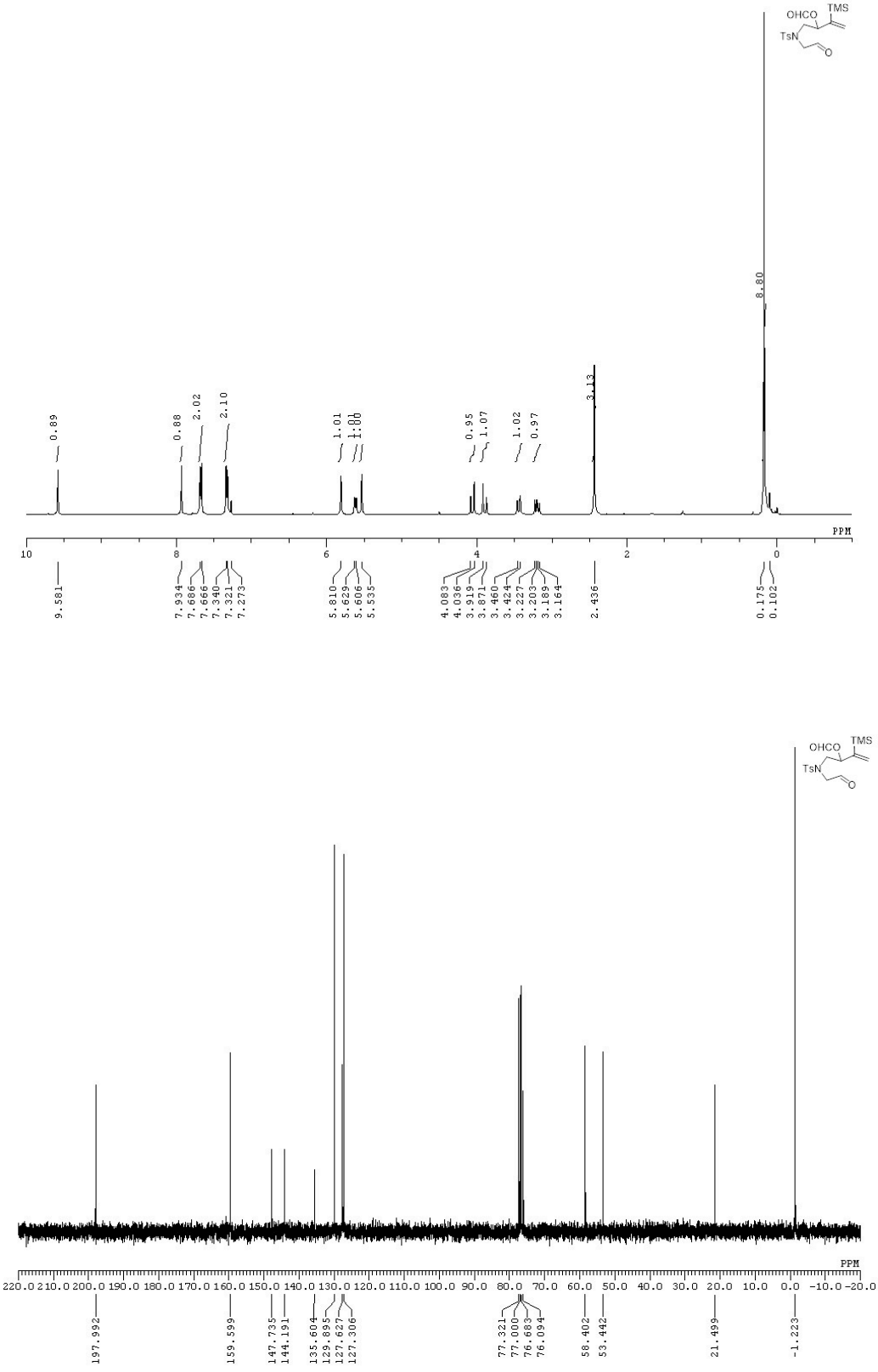

OHCO
TMS
TsN
OTBS
9.26
9.10
6.10
4.38
3.11
1.98
2.17
2.13
1.00
0.97
1.07
1.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.678
7.541
7.520
7.129
7.109
7.095
5.649
5.475
5.461
5.353
5.348
3.579
3.563
3.548
3.349
3.310
3.286
3.271
3.253
3.232
3.216
3.200
3.191
3.175
3.160
3.138
2.246
1.874
1.432
0.705
0.683
0.023
0.000
-0.009
-0.150
-0.156
-0.171

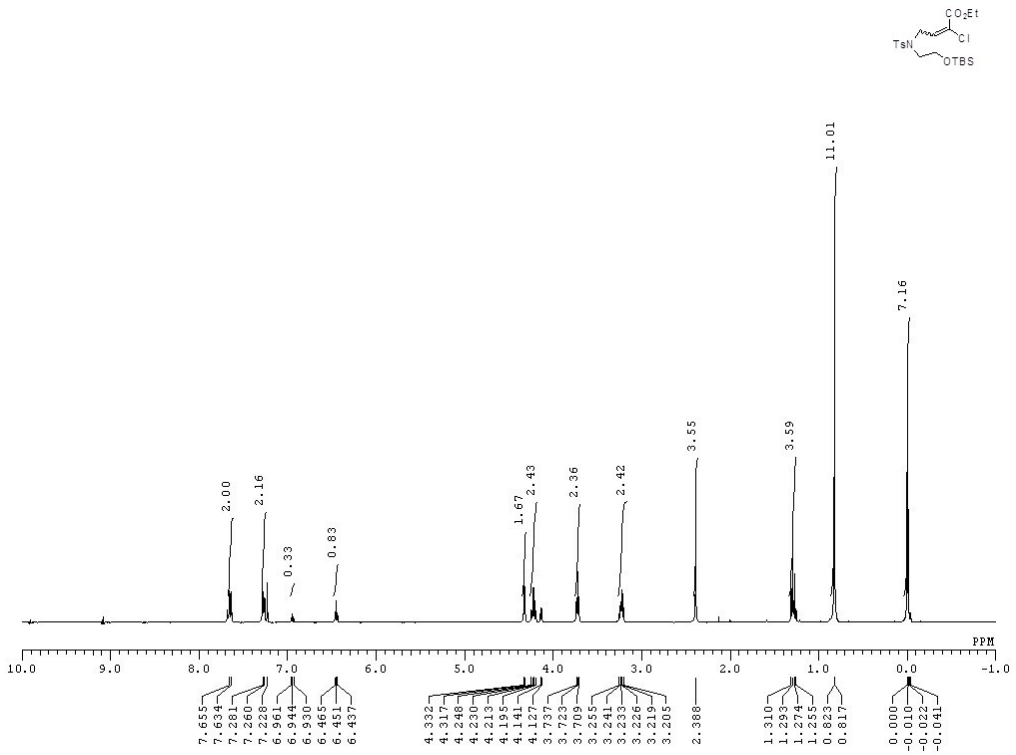

OHCO
TMS
TsN
OTBS
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
159.858
148.262
143.323
137.486
129.628
127.582
127.170
77.317
77.000
76.679
75.991
62.206
52.969
50.762
25.834
21.454
18.198
-1.034
-5.488

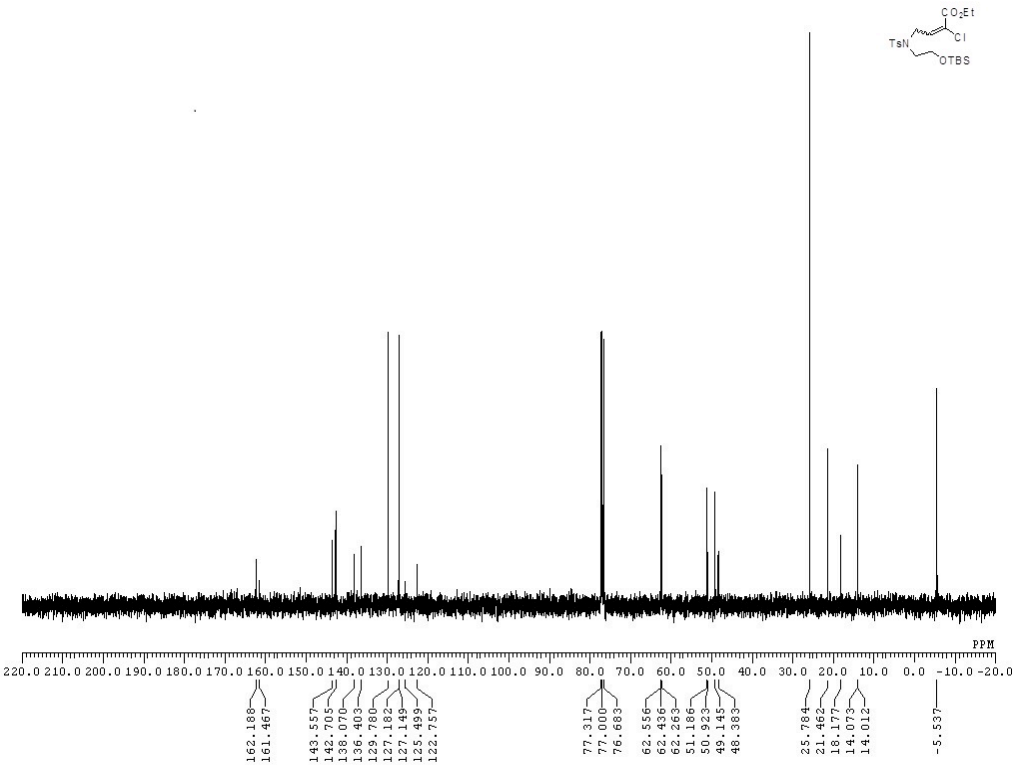

OHCO
TMS
TsN
OH
8.78
4.17
2.06
2.06
2.00
0.94
0.96
0.91
1.00
0.89
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.950
7.720
7.700
7.340
7.320
7.273
5.874
5.871
5.762
5.742
5.561
5.557
3.805
3.422
3.397
3.384
3.359
3.350
3.339
3.329
3.315
3.305
3.274
2.442
2.055
0.198
0.189
0.181
0.171
0.165
0.010

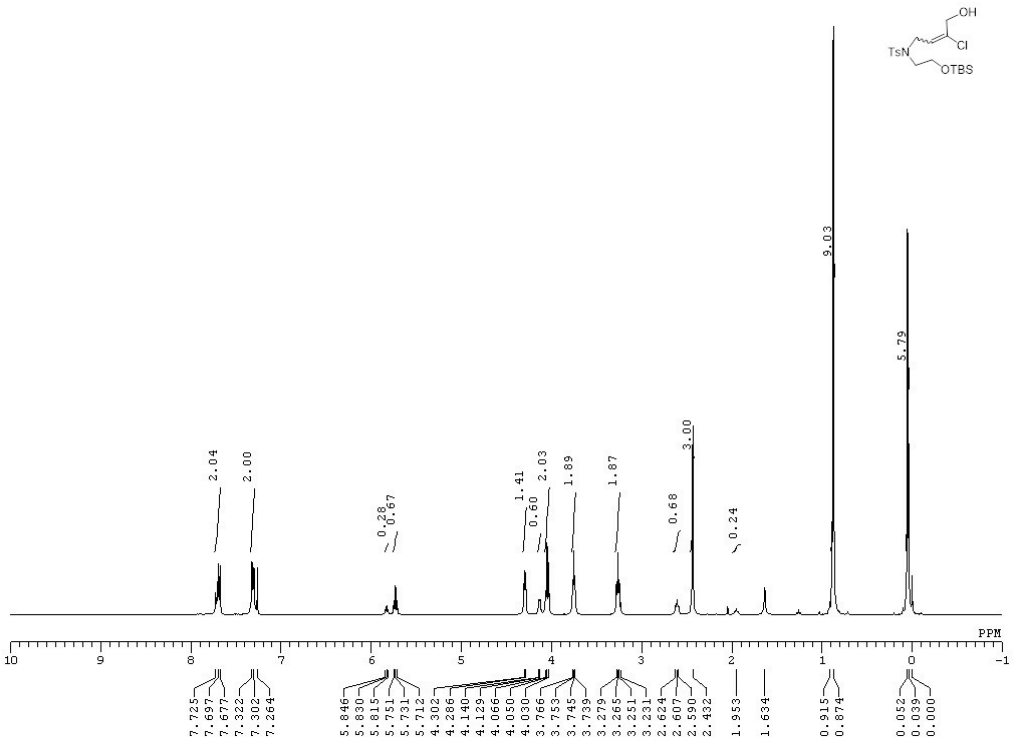

OHCO
TMS
TsN
OH
PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
160.121
148.089
143.800
136.028
129.805
127.829
127.364
77.317
77.000
76.683
75.930
61.255
53.936
52.635
21.507
-1.054

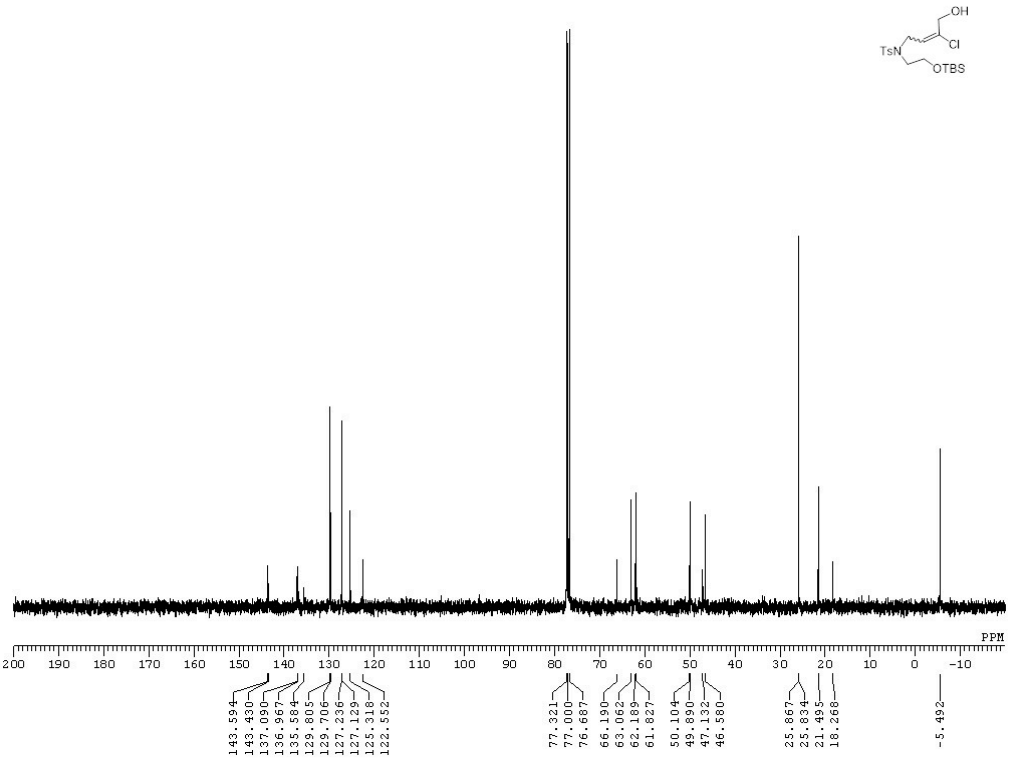
13k

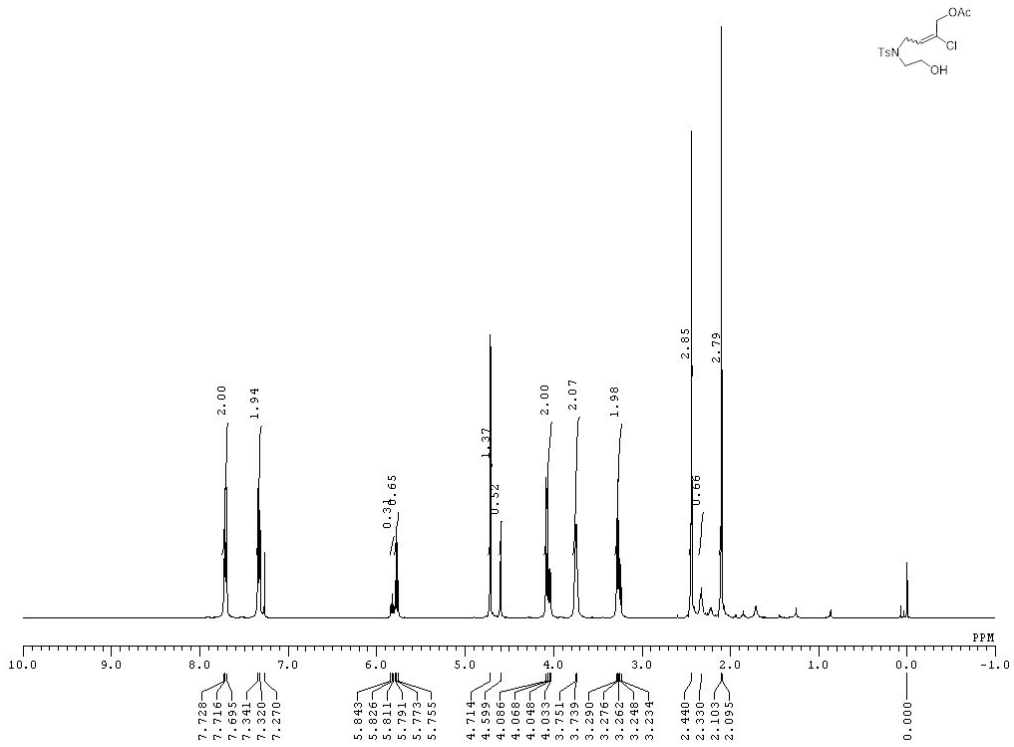

OHCO
TMS
TsN
O
0.89
0.88
2.02
2.10
1.01
1.00
0.95
1.07
1.02
0.97
3.13
8.80
PPM
10
8
6
4
2
0
9.581
7.934
7.666
7.666
7.340
7.321
7.273
5.810
5.629
5.606
5.535
4.083
4.036
3.919
3.871
3.460
3.424
3.227
3.203
3.189
3.164
2.436
0.175
0.102
197.992
159.599
147.735
144.191
135.604
129.895
127.627
127.306
77.321
77.000
76.683
76.094
58.402
53.442
21.499
-1.223

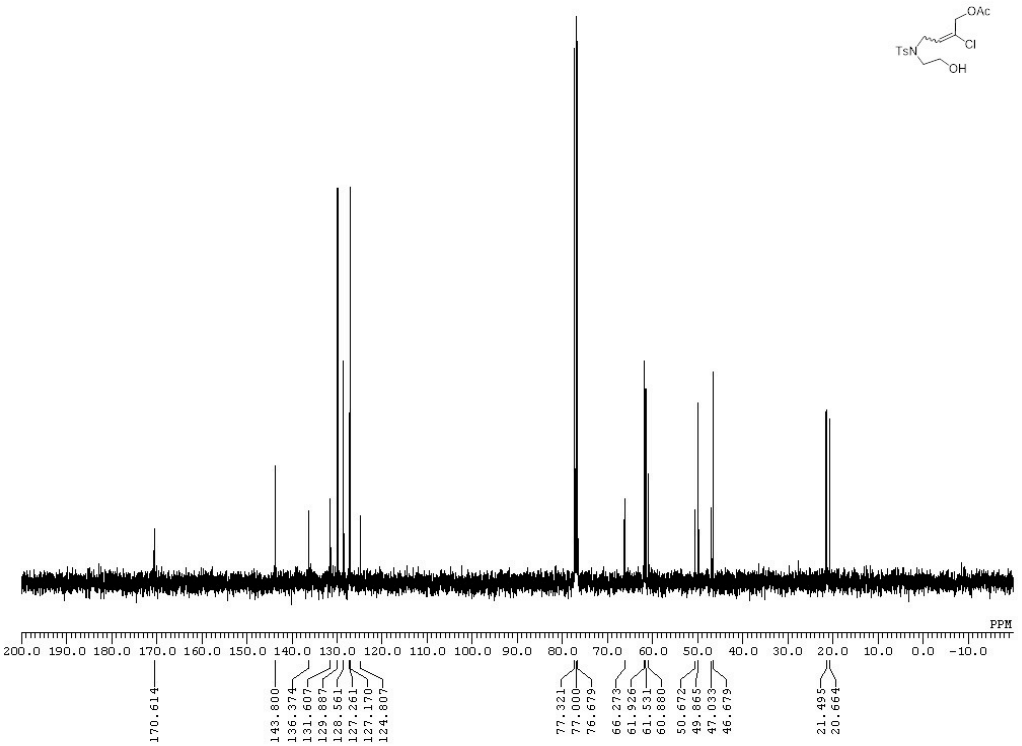

CO2Et
Cl
TsN
OTBS
11.01
7.16
3.55
3.59
2.00
2.16
0.33
0.83
1.67
2.43
2.36
2.42
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.655 7.634 7.281 7.260 7.228 6.961 6.944 6.930 6.465 6.451 6.437
4.332 4.317 4.248 4.230 4.213 4.195 4.141 4.127 3.737 3.723 3.709 3.255 3.241 3.233 3.226 3.219 3.205
2.388
1.310 1.293 1.274 1.255 0.823 0.817
0.000 -0.010 -0.022 -0.041


CO2Et
Cl
TsN
OTBS
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
162.188 161.467
143.557 142.705 138.070 136.403 129.780 127.182 127.149 125.499 122.757
77.317 77.000 76.683
62.556 62.436 62.263
51.186 50.923 49.145 48.383
25.784 21.462 18.177 14.073 14.012
-5.537

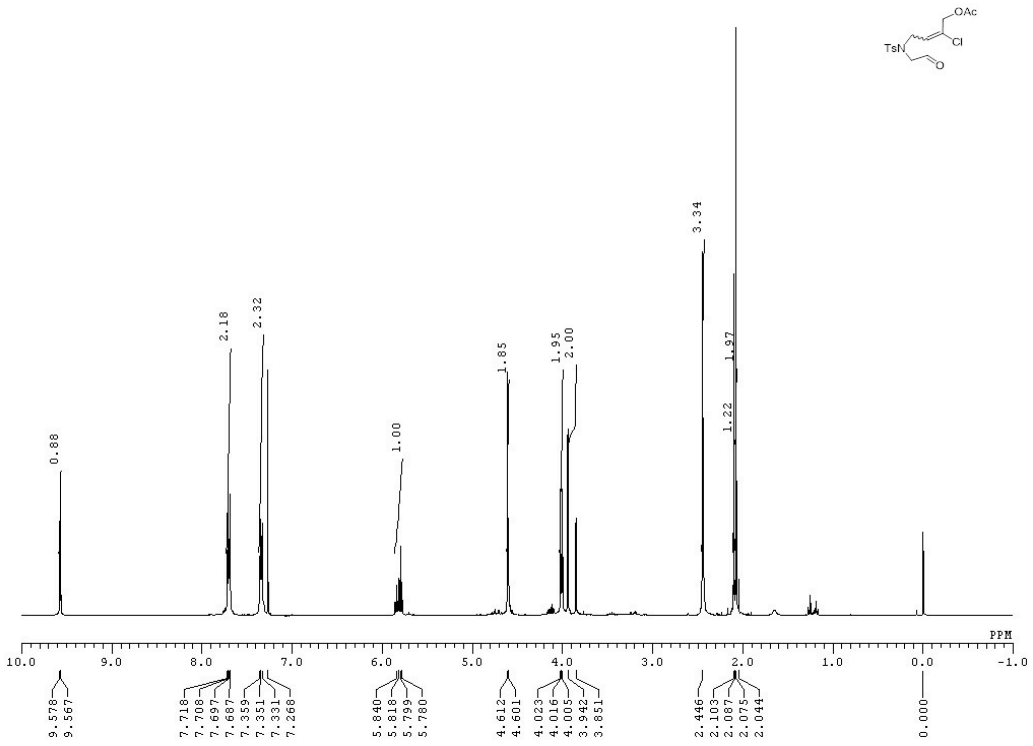

OH
Cl
TsN
OTBS
2.04
2.00
0.28
0.67
1.41
0.60
2.03
1.89
1.87
0.68
3.00
0.24
9.03
5.79
PPM
7.725
7.697
7.677
7.322
7.302
7.264
5.846
5.830
5.815
5.751
5.731
5.712
4.302
4.286
4.140
4.129
4.066
4.050
4.030
3.766
3.753
3.745
3.739
3.279
3.265
3.251
3.231
2.624
2.607
2.590
2.432
1.953
1.634
0.915
0.874
0.052
0.039
0.000

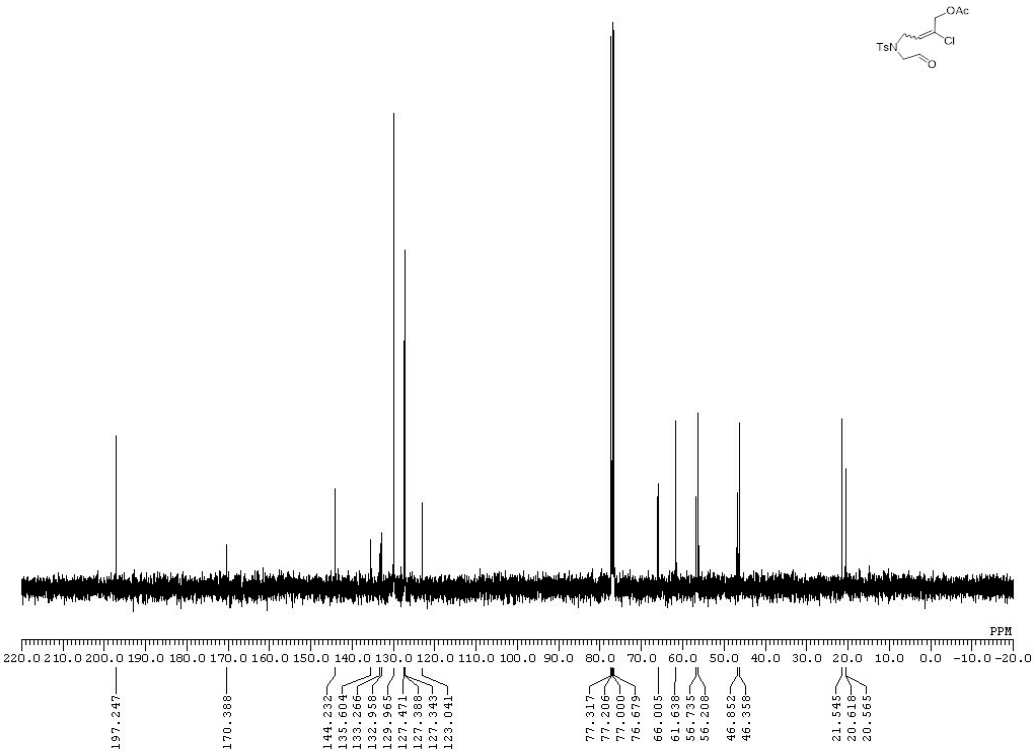

OH
Cl
TsN
OTBS
PPM
143.594
143.430
137.090
136.967
135.584
129.805
129.706
127.236
127.129
125.318
122.552
77.321
77.000
76.687
66.190
63.062
62.189
61.827
50.104
49.890
47.132
46.580
25.867
25.834
21.495
18.268
-5.492


OAc
Cl
TsN
OH
2.00
1.94
0.38
0.65
1.37
0.52
2.00
2.07
1.98
2.85
2.79
0.66
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.728 7.716 7.695 7.341 7.320 7.270
5.843 5.826 5.811 5.791 5.773 5.755
4.714 4.599 4.086 4.068 4.048 4.033 3.751 3.739 3.290 3.276 3.262 3.248 3.234
2.440 2.330 2.103 2.095
0.000


OAc
Cl
TsN
OH
PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
170.614
143.800 136.374 131.607 129.887 128.561 127.261 127.170 124.807
77.321 77.000 76.679
66.273 61.926 61.531 60.880
50.672 49.865 47.033 46.679
21.495 20.664

13l


OAc
Cl
TsN
O
0.88
2.18
2.32
1.00
1.85
1.95
2.00
3.34
1.97
1.22
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
9.578 9.567 7.718 7.708 7.697 7.687 7.359 7.351 7.331 7.268 5.840 5.818 5.799 5.780 4.612 4.601 4.023 4.016 4.005 3.942 3.851 2.446 2.103 2.087 2.075 2.044 0.000


OAc
Cl
TsN
O
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0
197.247 170.388 144.232 135.604 133.266 132.958 129.965 127.471 127.388 127.343 123.041 77.317 77.206 77.000 76.679 66.005 61.638 56.735 56.208 46.852 46.358 21.545 20.618 20.565