Stereoselective Synthesis of Isochromanones by an Asymmetric Ortholithiation Strategy: Synthetic Access to the Isochromanone Core of the Ajudazols

Sebastian Essig[†] and Dirk Menche[‡*]

† Institut für Organische Chemie, Ruprecht-Karls Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany, present address: MRC Laboratory of Molecular Biology, Francis Crick Avenue, CB2 0QH Cambridge, U.K.

‡ Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

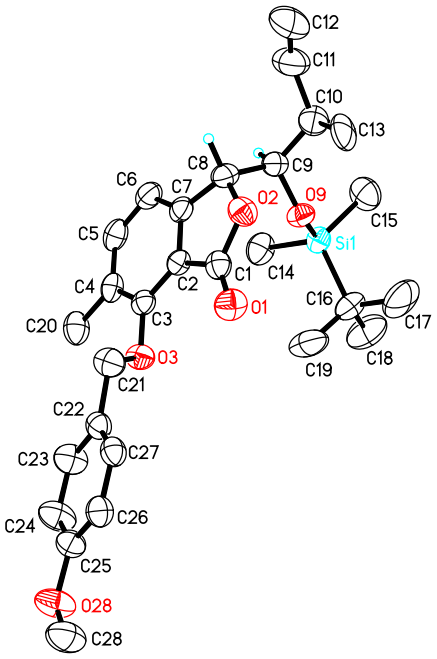
dirk.menche@uni-bonn.de

Table of Content

I X-Ray crystal structure analysis

X-ray crystal structure analysis of compound 54

Description: colourless crystal (needle), dimensions 1.18 x 0.15 x 0.13 mm^3, crystal system triclinic, space group P $\bar{1}$, Z = 2, a = 7.5558(10) Å, b = 13.3993(17) Å, c = 14.2195(18) Å, alpha = 83.276(3) deg, beta = 80.259(3) deg, gamma = 78.211(3) deg, V = 1383.8(3) $Å^3$, rho = 1.158 g/cm^3, T = 200(2) K, $Theta_{max}$ = 24.76 deg, radiation Mo Kalpha, lambda = 0.71073 Å, 0.3 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.1 and a completeness of 97.2% to a resolution of 0.84 Å, 18920 reflections measured, 4614 unique (R(int)=0.0381), 3709 observed (I > 2 σ (I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS, based on the Laue symmetry of the reciprocal space, mu = 0.12 mm^{-1}, T_{min} = 0.87, T_{max} = 0.98, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package,[1] 346 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.14 for observed reflections, final residual values R1(F) = 0.055, $wR(F^2)$ = 0.116 for observed reflections, residual electron density -0.23 to 0.17 $eÅ^{-3}$. CCDC 1440643 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



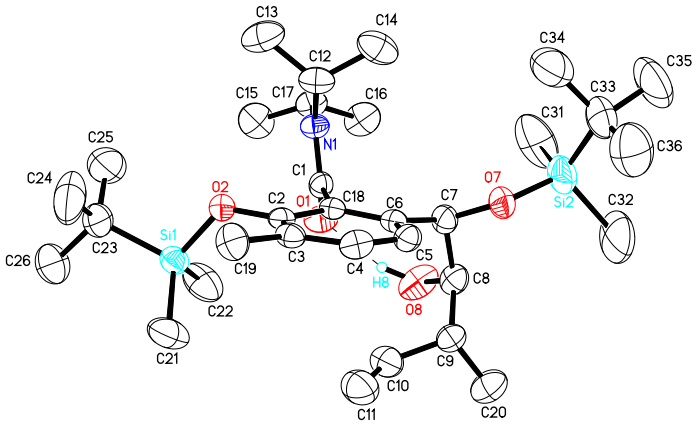
Thermal ellipsoid plots of compound **54** (50% probability).

Crystal data and structure refinement for **54**.

Identification code	CCDC 1440643	
Empirical formula	$C_{28}H_{38}O_5Si$	
Formula weight	482.67	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P $\bar{1}$	
Z	2	
Unit cell dimensions	a =7.5558(10) Å	α =83.276(3) deg.
	b = 13.3993(17) Å	β =80.259(3) deg.
	c = 14.2195(18) Å	γ =78.211(3) deg.
Volume	1383.8(3) $Å^3$	
Density (calculated)	1.16 g/cm^3	
Absorption coefficient	0.12 mm^{-1}	
Crystal shape	needle	
Crystal size	1.18 x 0.15 x 0.13 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.6 to 24.8 deg.	
Index ranges	-8≤h≤8, -15≤k≤15, 0≤ l≤16	
Reflections collected	4614	
Independent reflections	4614 (R(int) = 0.0000)	
Observed reflections	3709 (I >2 σ (I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.98 and 0.87	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4614 / 5 / 346	
Goodness-of-fit on F^2	1.14	
Final R indices (I>2σ (I))	R1 = 0.055, wR2 = 0.116	
Largest diff. peak and hole	0.17 and -0.23 $eÅ^{-3}$	

X-ray crystal structure analysis of compound 57

Description: colourless crystal (polyhedron), dimensions 0.48 x 0.37 x 0.11 mm^3, crystal system orthorhombic, space group $P2_12_12_1$, Z = 4, a = 11.406(3) Å, b = 13.239(3) Å, c = 23.993(7) Å, alpha = 90 deg, beta = 90 deg, gamma = 90 deg, V = 3623.0(18) $Å^3$, rho = 1.060 g/cm^3, T = 200(2) K, $Theta_{max}$ = 28.28 deg, radiation Mo Kalpha, lambda = 0.71073 Å, 0.3 deg omega-scans with CCD area detector, 500 frames covering the asymmetric unit in reciprocal space with a mean redundancy of 2.1 and 92.4% completeness for a resolution of 0.75 Å, 10573 reflections measured, 7549 unique (R(int) = 0.0522), 5056 observed (I >2 σ (I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu = 0.13mm^{-1}, T_{min} = 0.94, T_{max} = 0.99, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package,[1] 358 parameters refined, hydrogen atoms were treated using appropriate riding models, except of H8 of the hydroxy-group, which was refined isotropically, Flack absolute structure parameter 0.16(12), goodness of fit 0.89 for observed reflections, final residual values R1(F) = 0.053, wR(F^2) = 0.110 for observed reflections, residual electron density -0.23 to 0.24 $eÅ^{-3}$. CCDC 1440644 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Thermal ellipsoid plots of compound **57** (50% probability).

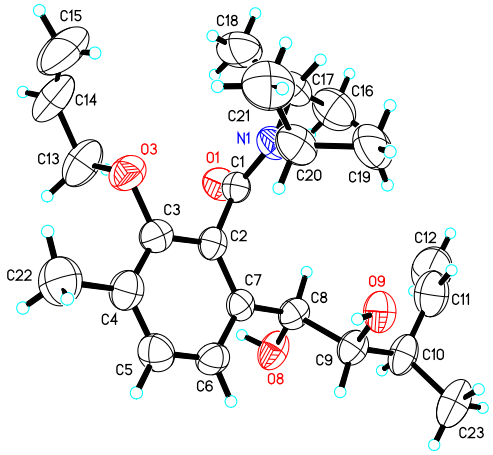
Table 10.12.1 Crystal data and structure refinement for **57**.

Identification code	CCDC 1440644	
Empirical formula	$C_{32}H_{59}NO_4Si_2$	
Formula weight	577.98	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Z	4	
Unit cell dimensions	a = 11.406(3) Å	α = 90 deg.
	b = 13.239(3) Å	β = 90 deg.
	c = 23.993(7) Å	γ = 90 deg.
Volume	3623.0(18) $Å^3$	
Density (calculated)	1.06 g/cm^3	
Absorption coefficient	0.13 mm^{-1}	
Crystal shape	polyhedron	
Crystal size	0.48 x 0.37 x 0.11 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.7 to 28.3 deg.	
Index ranges	-13≤h≤15, -9≤k≤15, -10≤l≤31	
Reflections collected	10573	
Independent reflections	7549 (R(int) = 0.0522)	
Observed reflections	5056 (I >2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.99 and 0.94	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	7549 / 0 / 358	
Goodness-of-fit on F^2	0.89	
Final R indices (I>2σ(I))	R1 = 0.053, wR2 = 0.110	
Absolute structure parameter	0.16(12)	
Largest diff. peak and hole	0.24 and -0.23 $eÅ^{-3}$	

X-ray crystal structure analysis of compound 67

Description: colourless crystal (needle), dimensions 1.40 x 0.11 x 0.05 mm^3, crystal system tetragonal, space group $P4_12_12$, Z = 8, a = 15.600(4) Å, b = 15.600(4) Å, c = 22.648(7) Å, alpha = 90 deg, beta = 90 deg, gamma = 90 deg, V = 5511(3) $Å^3$, rho = 1.043 g/cm^3, T = 200(2) K, $Theta_{max}$ = 23.00 deg, radiation Mo Kalpha, lambda = 0.71073 Å, 0.3 deg omega-scans with CCD area detector, covering a whole sphere in reciprocal space, 26690 reflections measured, 3839 unique (R (int)=0.0615), 3086

observed (I >2 σ (I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, mu = 0.07mm^{-1}, T_{min}= 0.91, T_{max}= 1.00, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package,[1] 283 parameters refined, hydrogen atoms were treated using appropriate riding models, Flack absolute structure parameter 2(2), goodness of fit 1.05 for observed reflections, final residual values R1(F) = 0.058, wR (F^2) = 0.150 for observed reflections, residual electron density -0.15 to 0.32 eÅ^{-3}. CCDC 907660 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



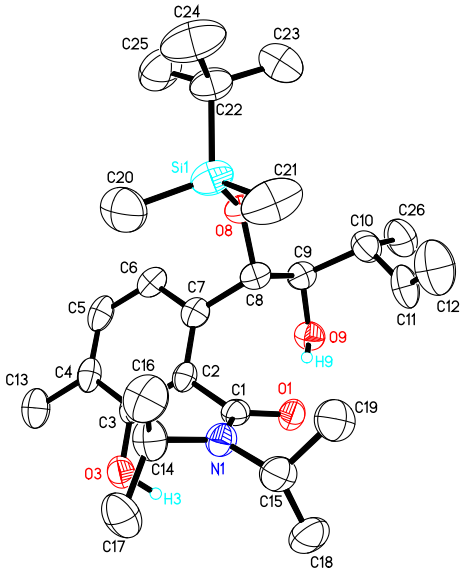
Thermal ellipsoid plots of compound **67** (50% probability).

Crystal data and structure refinement for **67**.

Identification code	CCDC 907660		
Empirical formula	$C_{26}H_{42}NO_4$		
Formula weight	432.61		
Temperature	200(2) K		
Wavelength	0.71073 Å		
Crystal system	tetragonal		
Space group	$P4_32_12$		
Z	8		
Unit cell dimensions	a = 15.600(4) Å	α =	90 deg.
	b = 15.600(4) Å	β =	90 deg.
	c = 22.648(7) Å	γ =	90 deg.
Volume	5511(3) Å^3		
Density (calculated)	1.04 g/cm^3		
Absorption coefficient	0.07 mm^{-1}		
Crystal shape	needle		
Crystal size	1.40 x 0.11 x 0.05 mm^3		
Crystal colour	colourless		
Theta range for data collection	1.6 to 23.0 deg.		
Index ranges	-16≤h≤17, -17≤k≤15, -24≤l≤23		
Reflections collected	26690		
Independent reflections	3839 (R(int) = 0.0615)		
Observed reflections	3086 (I >2σ(I))		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	1.00 and 0.91		
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	3839 / 0 / 283		
Goodness-of-fit on F^2	1.05		
Final R indices (I>2σ(I))	R1 = 0.058, wR2 = 0.150		
Absolute structure parameter	2(2)		
Largest diff. peak and hole	0.32 and -0.15 eÅ^{-3}		

X-ray crystal structure analysis of compound 41

Description: colourless crystal (plate), dimensions 0.27 x 0.18 x 0.05 mm^3, crystal system orthorhombic, space group $P2_12_12_1$, Z = 8, a = 11.4204(8) Å, b = 17.2635(13) Å, c = 33.066(3) Å, alpha = 90 deg, beta = 90 deg, gamma=90 deg, V = 6519.2(9) $Å^3$, rho = 1.033 g/cm^3, T = 200(2) K, $Theta_{max}$= 20.83 deg, radiation Mo Kalpha, lambda = 0.71073 Å, 0.3 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 7.31and a completeness of 99.6% to a resolution of 1.00 Å, 28366 reflections measured, 6816 unique (R(int)=0.0438), 5732 observed ($I > 2 \sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, mu = 0.10mm^{-1}, T_{min}= 0.97, T_{max} = 1.00, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package,[1] 649 parameters refined, hydrogen atoms were treated using appropriate riding models, except of H3 and H9 of the hydroxy groups, which were refined isotropically, Flack absolute structure parameter 0.07(17), goodness of fit 1.05 for observed reflections, final residual values R1(F) = 0.044, $wR(F^2)$ = 0.100 for observed reflections, residual electron density -0.18 to 0.24 $eÅ^{-3}$. CCDC 907658 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



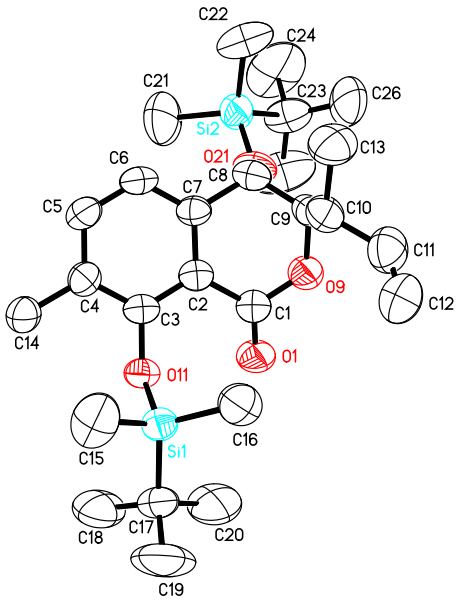
Thermal ellipsoid plots of compound **41** (50% probability).

Crystal data and structure refinement for **41**.

Identification code	CCDC 907658	
Empirical formula	$C_{29}H_{52}NO_4Si$	
Formula weight	506.81	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Z	8	
Unit cell dimensions	a = 11.4204(8) Å	α = 90 deg.
	b = 17.2635(13) Å	β = 90 deg.
	c = 33.066(3) Å	γ = 90 deg.
Volume	6519.2(9) $Å^3$	
Density (calculated)	1.03 g/cm^3	
Absorption coefficient	0.10 mm^{-1}	
Crystal shape	plate	
Crystal size	0.27 x 0.18 x 0.05 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.3 to 20.8 deg.	
Index ranges	-11≤h≤11, -17≤k≤17, -33≤l≤33	
Reflections collected	28366	
Independent reflections	6816 (R(int) = 0.0438)	
Observed reflections	5732 (I >2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.97	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6816 / 0 / 649	
Goodness-of-fit on F^2	1.05	
Final R indices (I>2σ (I))	R1 = 0.044, wR2 = 0.100	
Absolute structure parameter	0.07(17)	
Largest diff. peak and hole	0.24 and -0.18 $eÅ^{-3}$	

X-ray crystal structure analysis of compound 72

Description: colourless crystal (polyhedron), dimensions 0.27 x 0.15 x 0.12 mm^3, crystal system monoclinic, space group $P2_1$, Z = 8, a = 14.6819(6) Å, b = 27.0915(11) Å, c = 15.1614(7) Å, alpha = 90 deg, beta = 91.392(1) deg, gamma = 90 deg, V = 6028.7(4) $Å^3$, rho = 1.051 g/cm^3, T = 200(2) K, $Theta_{max}$= 23.26 deg, radiation Mo Kalpha, lambda = 0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 6.05 and a completeness of 99.8% to a resolution of 0.90Å, 53802 reflections measured, 17224 unique (R(int) = 0.0293), 12618 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS, based on the Laue symmetry of the reciprocal space, mu = 0.14mm^{-1} T_{min}= 0.96, T_{max}= 0.98, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package,[1] 1387 parameters refined, hydrogen atoms were treated using appropriate riding models, Flack absolute structure parameter -0.03(11), goodness of fit 1.01 for observed reflections, final residual values R1(F)=0.058, wR(F^2) = 0.143 for observed reflections, residual electron density -0.33 to 0.48 $eÅ^{-3}$. CCDC 907659 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Thermal ellipsoid plots of compound **72** (50% probability).

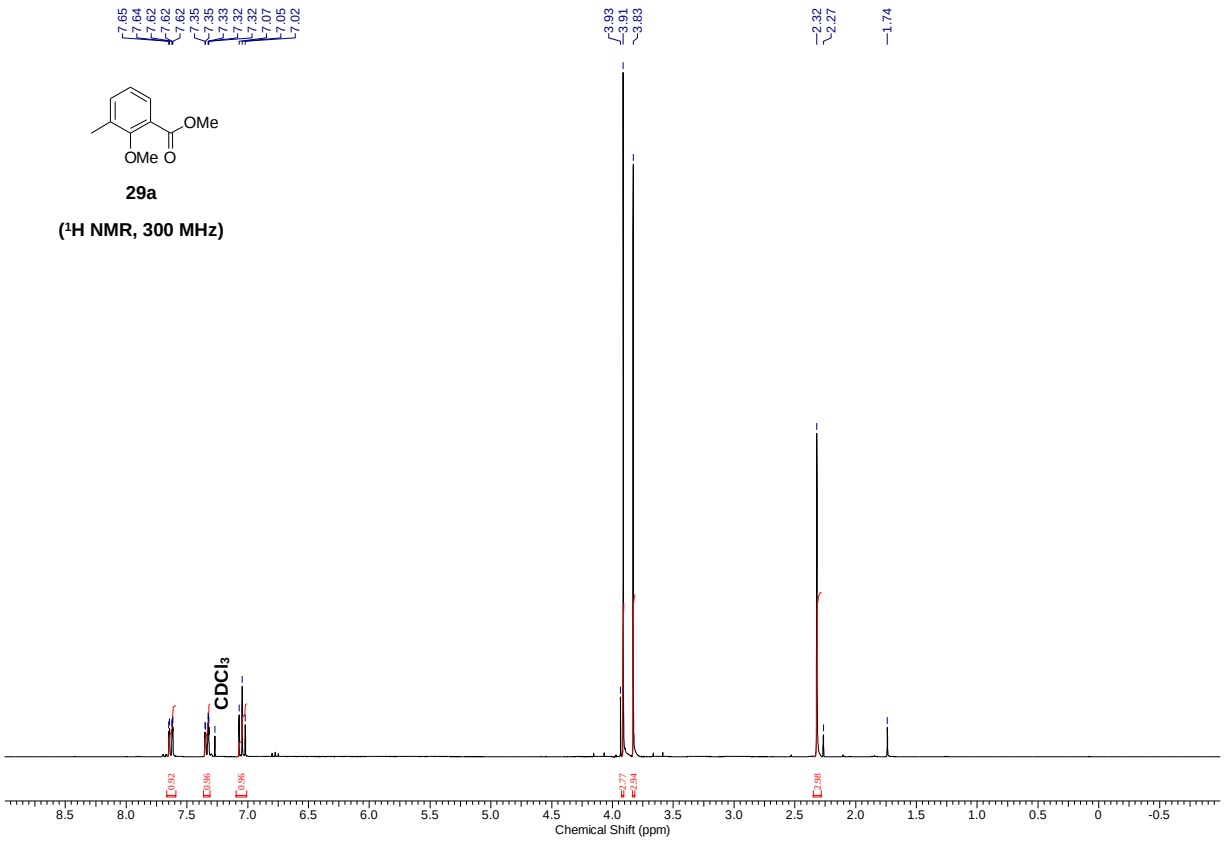
Crystal data and structure refinement for **72**.

Identification code	CCDC 907659	
Empirical formula	$C_{26}H_{44}O_4Si_2$	
Formula weight	476.79	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Z	8	
Unit cell dimensions	a = 14.6819(6) Å	α = 90 deg.
	b = 27.0915(11) Å	β = 91.392(1) deg.
	c = 15.1614(7) Å	γ = 90 deg.
Volume	6028.7(4) $Å^3$	
Density (calculated)	1.05 g/cm^3	
Absorption coefficient	0.14 mm^{-1}	
Crystal shape	polyhedron	
Crystal size	0.27 x 0.15 x 0.12 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.3 to 23.3 deg.	
Index ranges	-16≤h≤16, -30≤k≤30, -16≤l≤16	
Reflections collected	53802	
Independent reflections	17224 (R(int) = 0.0293)	
Observed reflections	12618 (I >2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.98 and 0.96	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	17224 / 3394 / 1387	
Goodness-of-fit on F^2	1.01	
Final R indices (I>2σ(I))	R1 = 0.058, wR2 = 0.143	
Absolute structure parameter	-0.03(11)	
Largest diff. peak and hole	0.48 and -0.33 $eÅ^{-3}$	

II References

(1) Sheldrick, G.M. *Acta Cryst.* **2008**, *A64*, 112-122.

III Copies of ^{1}H- and ^{13}C-NMR spectra



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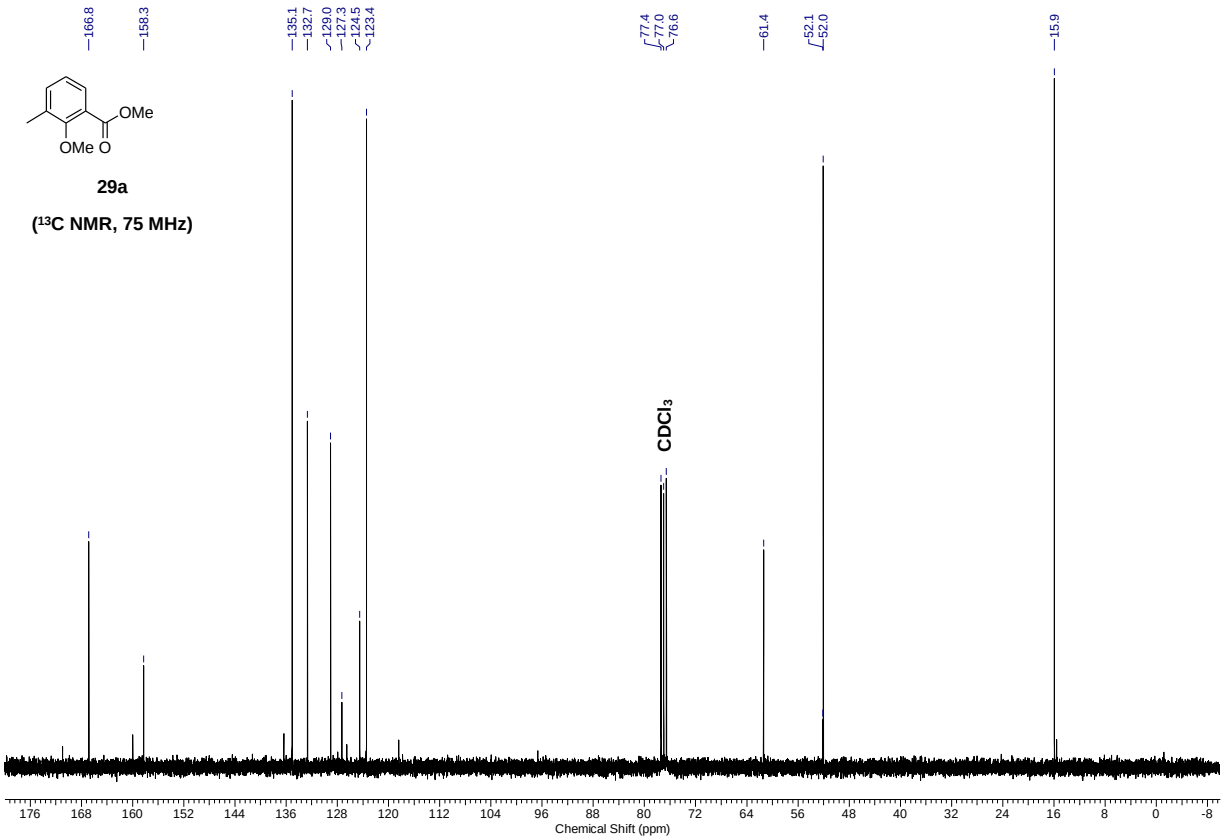
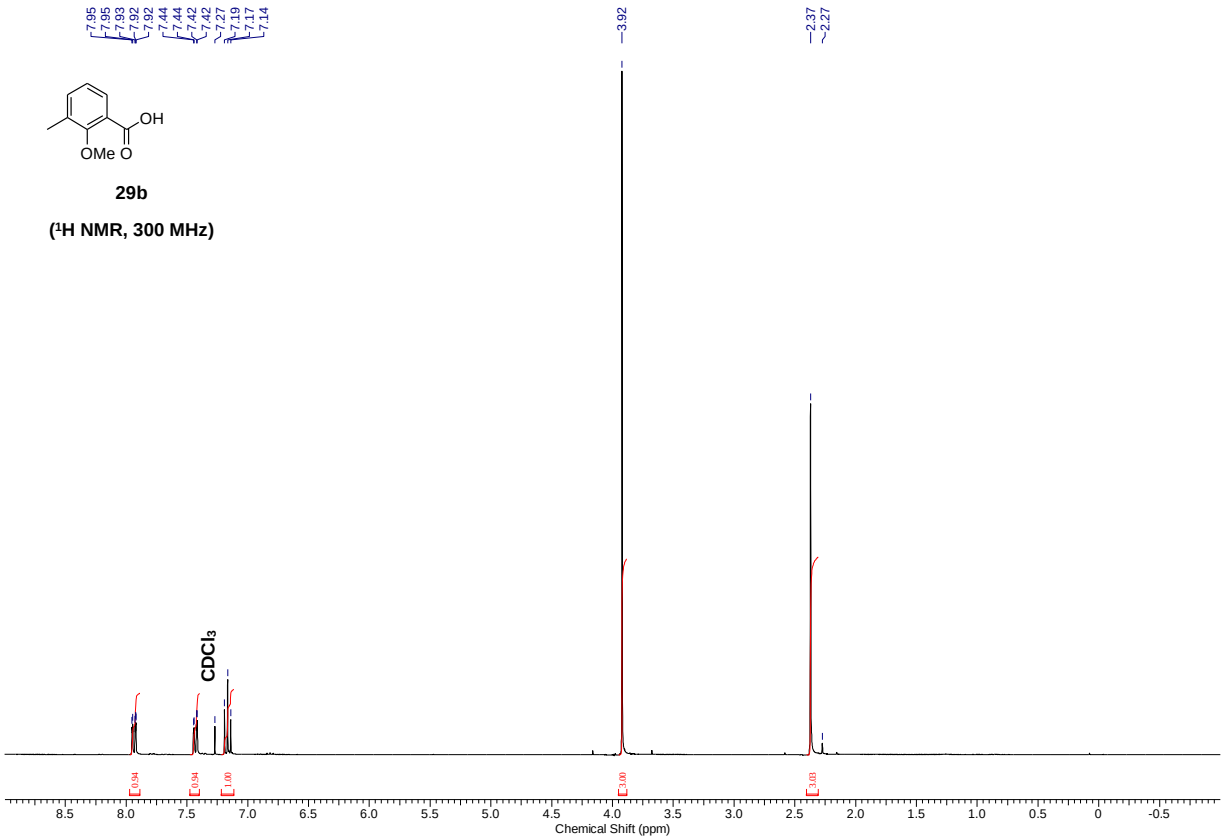
(^{1}H NMR, 300 MHz)



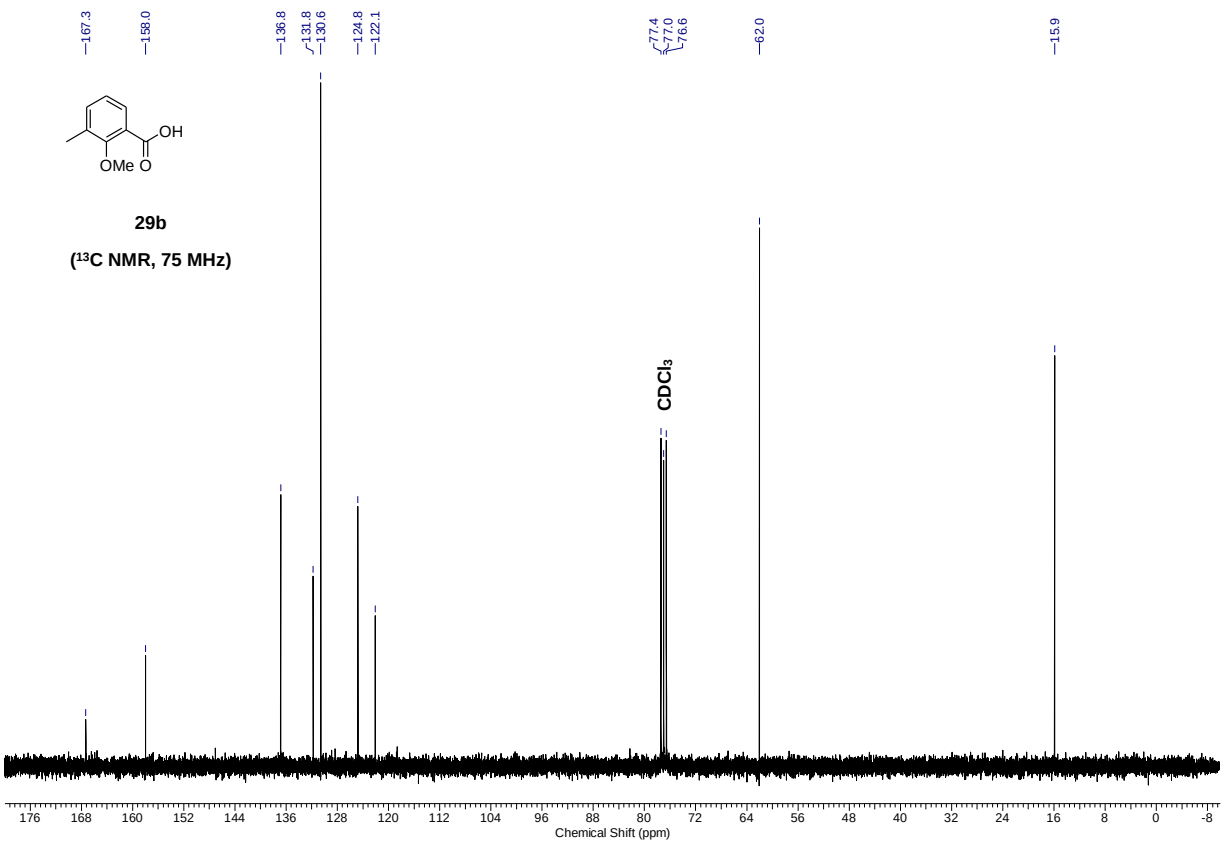
29a

(^{13}C NMR, 75 MHz)



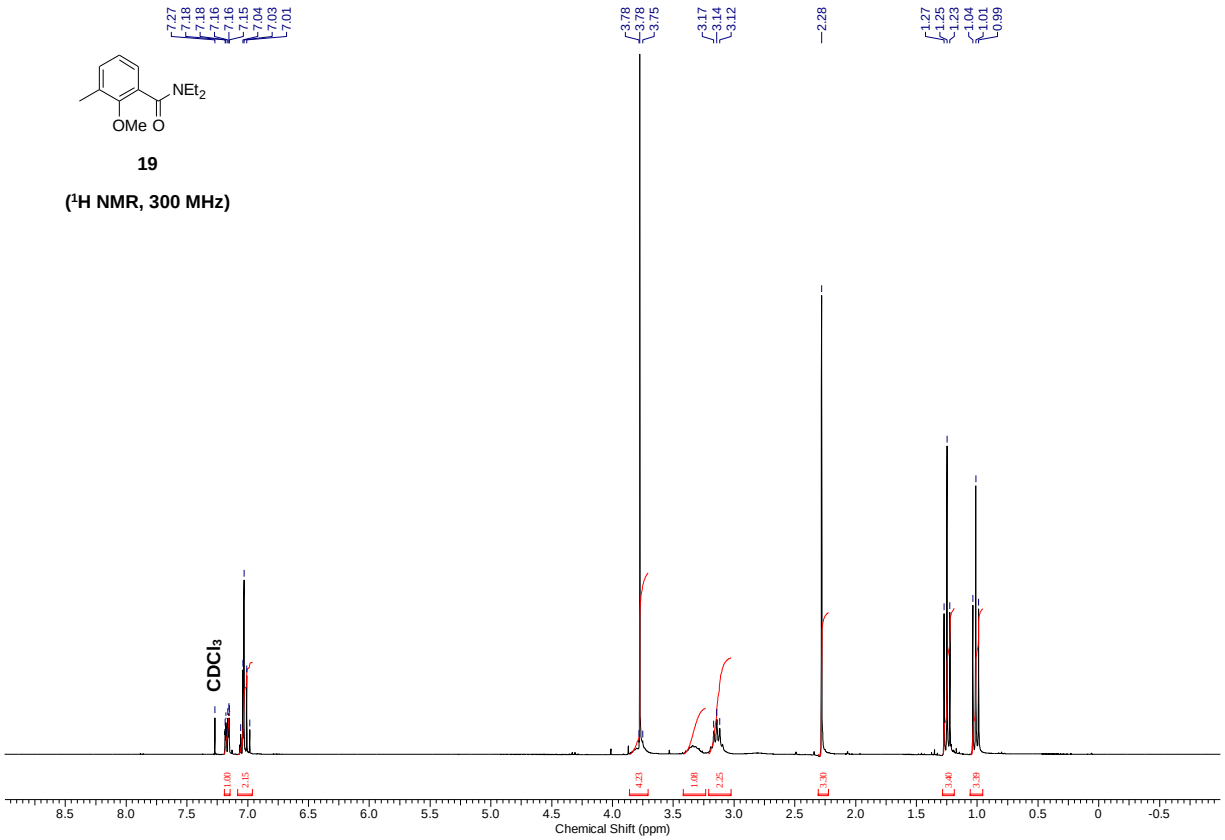
29b

(^{1}H NMR, 300 MHz)



29b

(^{13}C NMR, 75 MHz)



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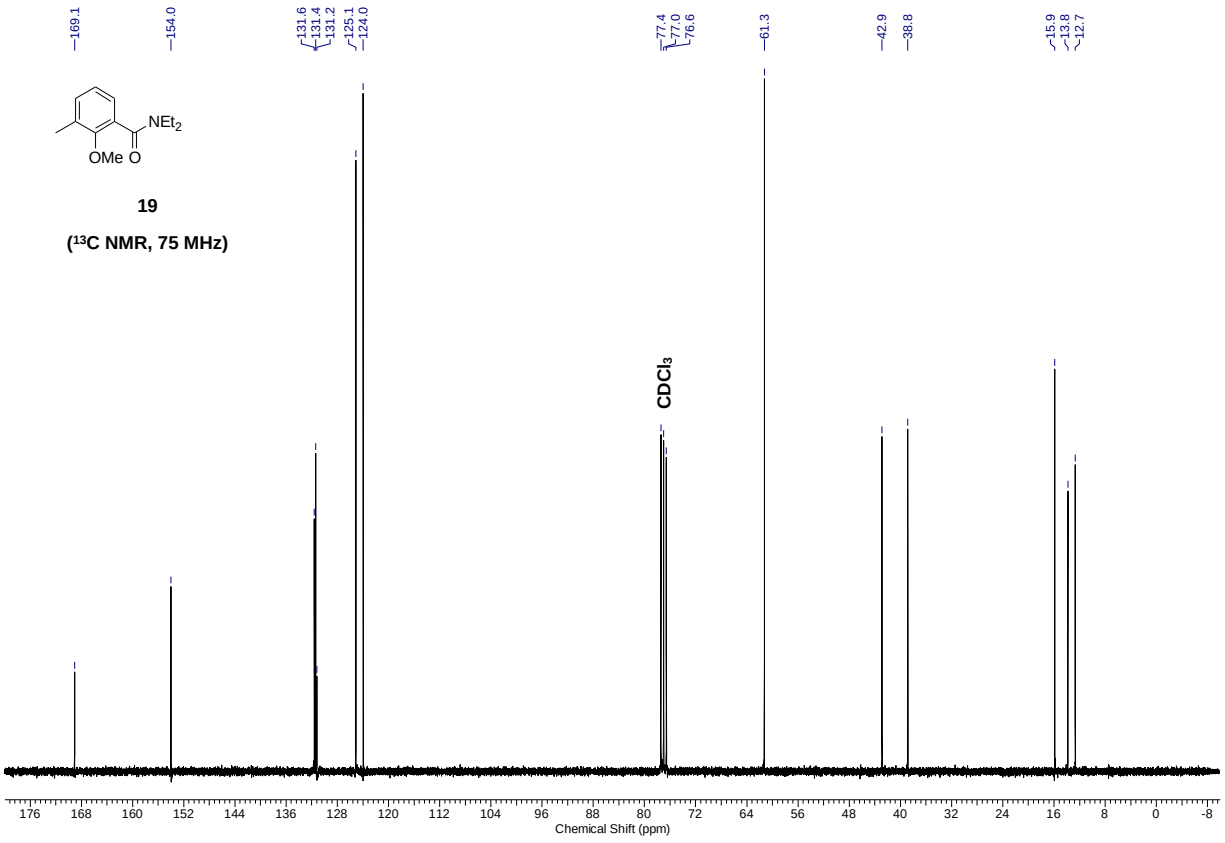
(^{1}H NMR, 300 MHz)



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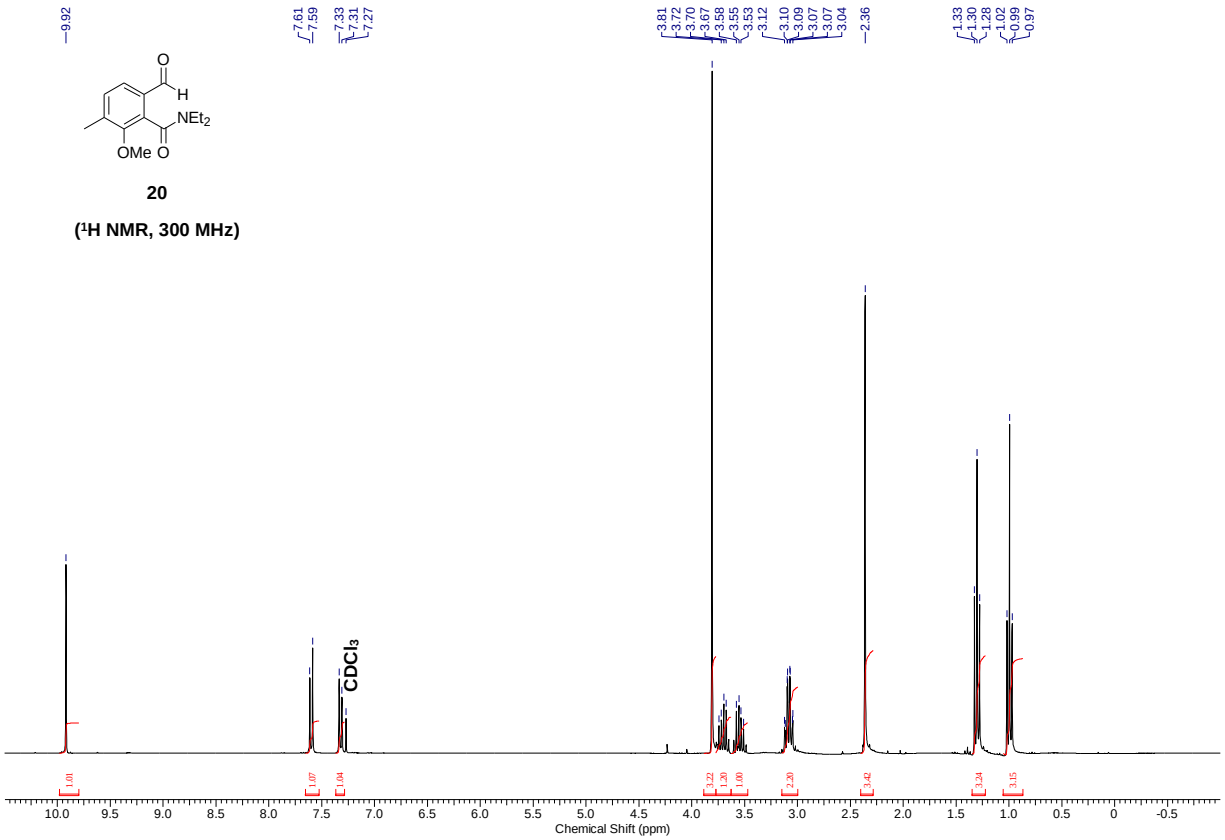
(^{13}C NMR, 75 MHz)



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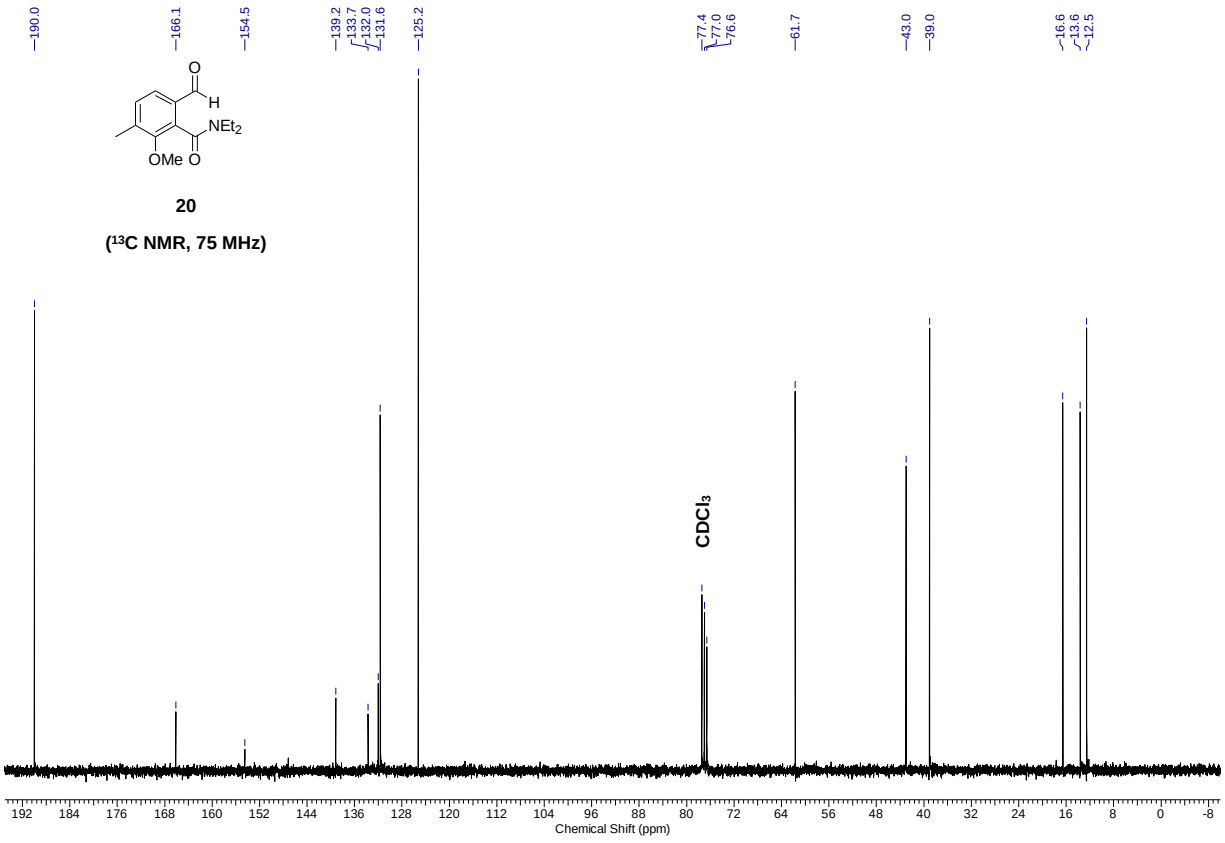
(^{1}H NMR, 300 MHz)



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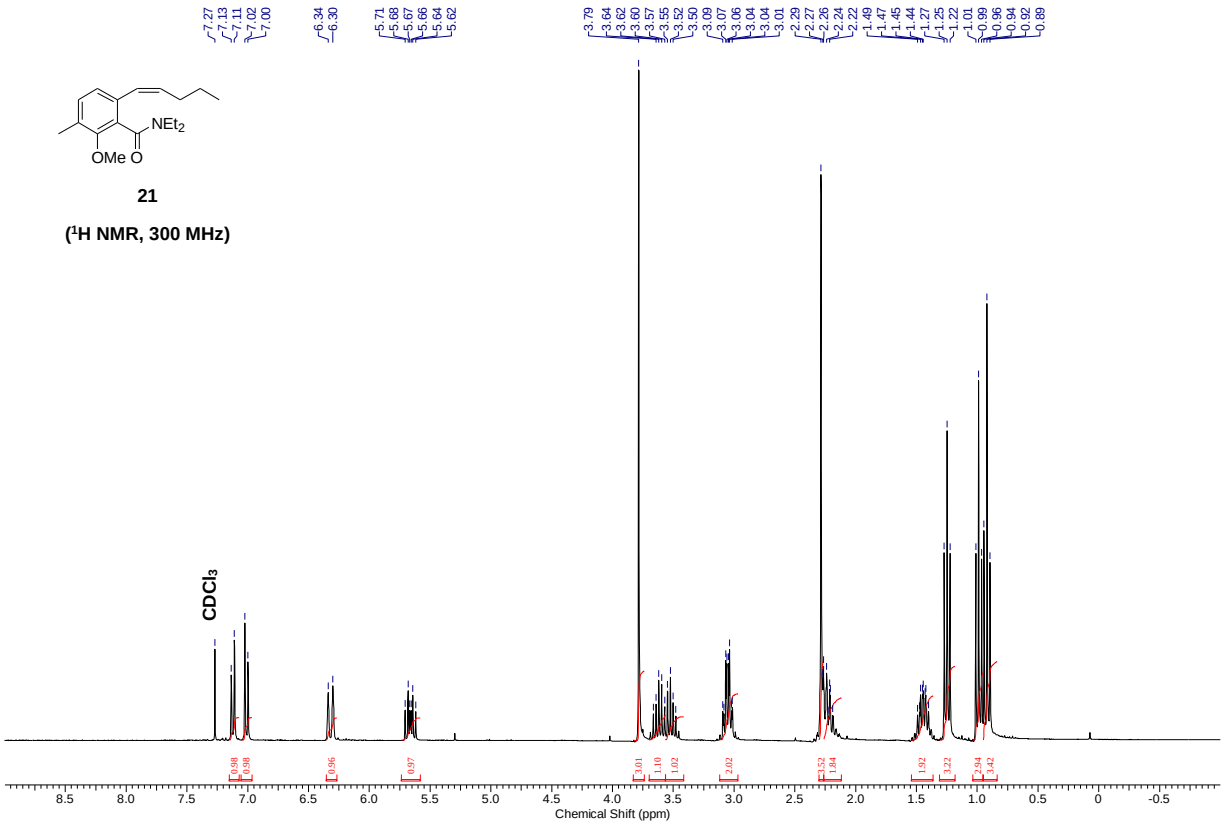
(^{13}C NMR, 75 MHz)



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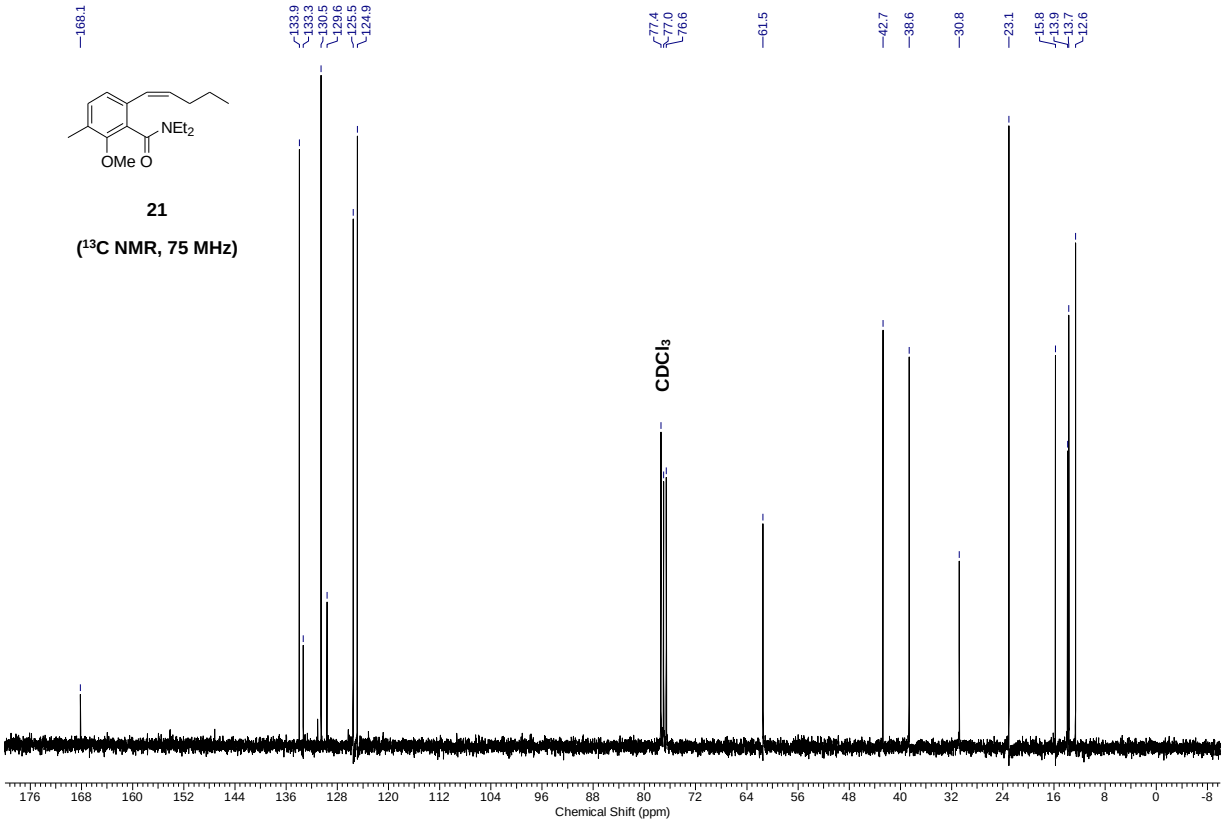
(^{1}H NMR, 300 MHz)



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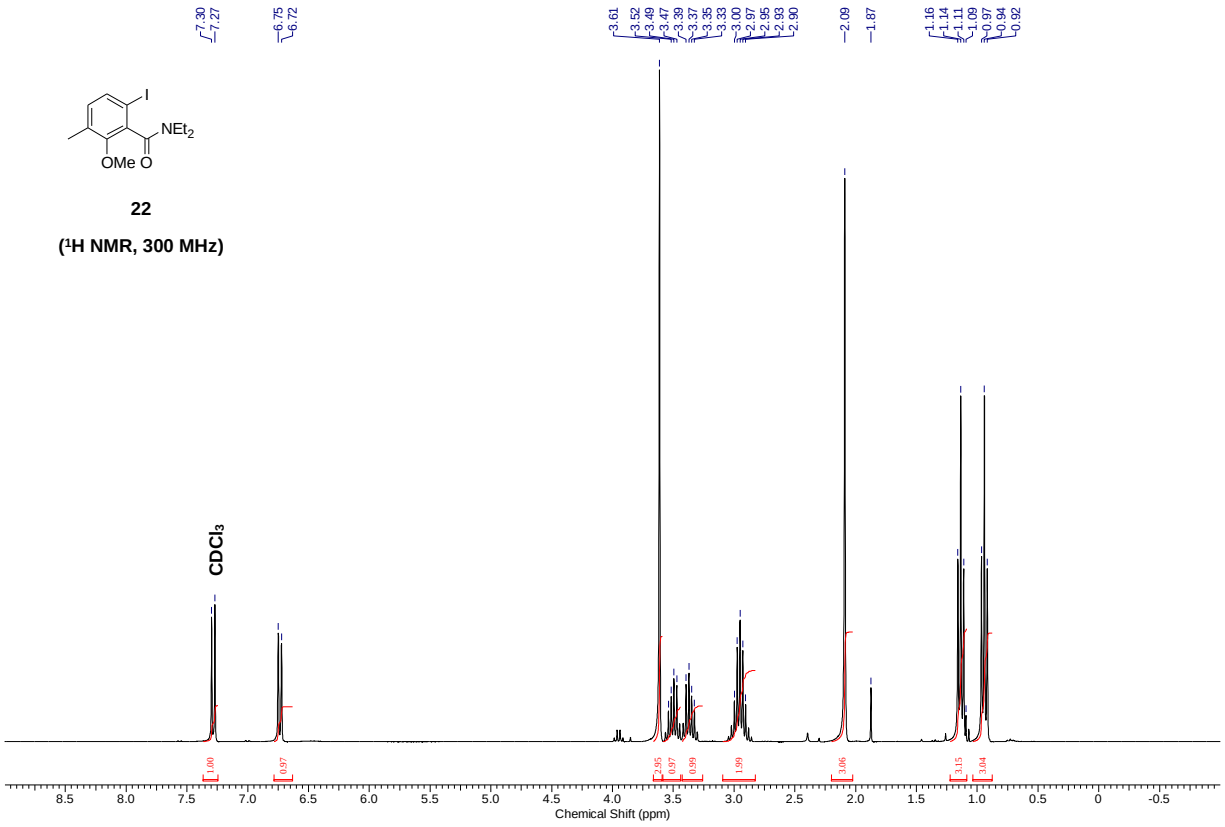
(^{13}C NMR, 75 MHz)



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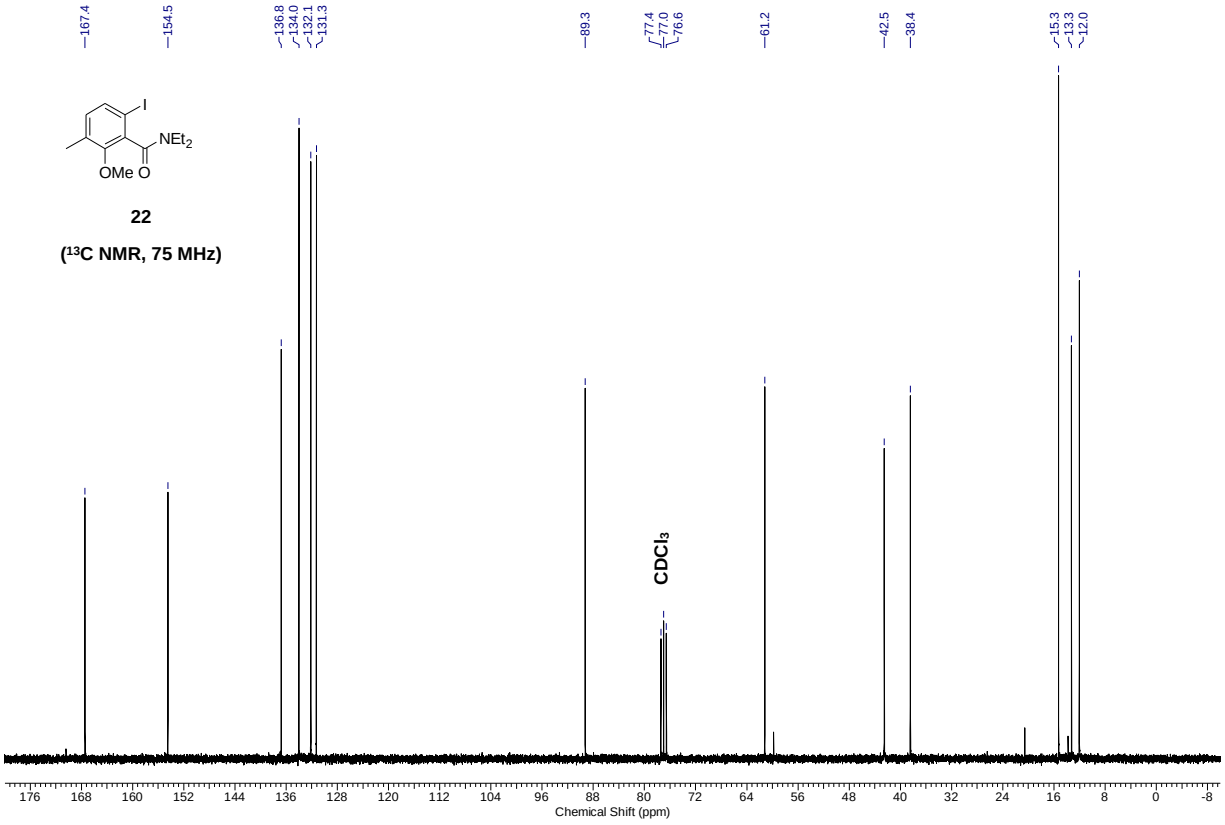
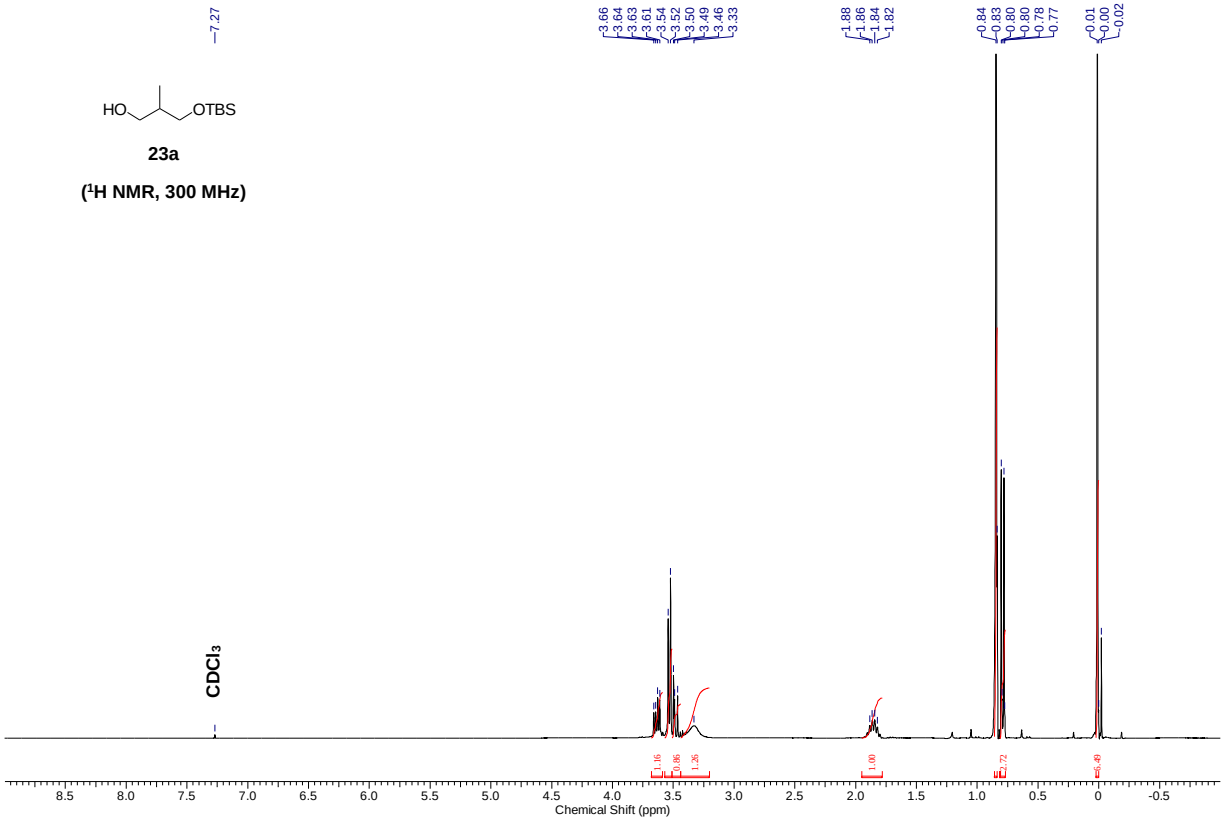
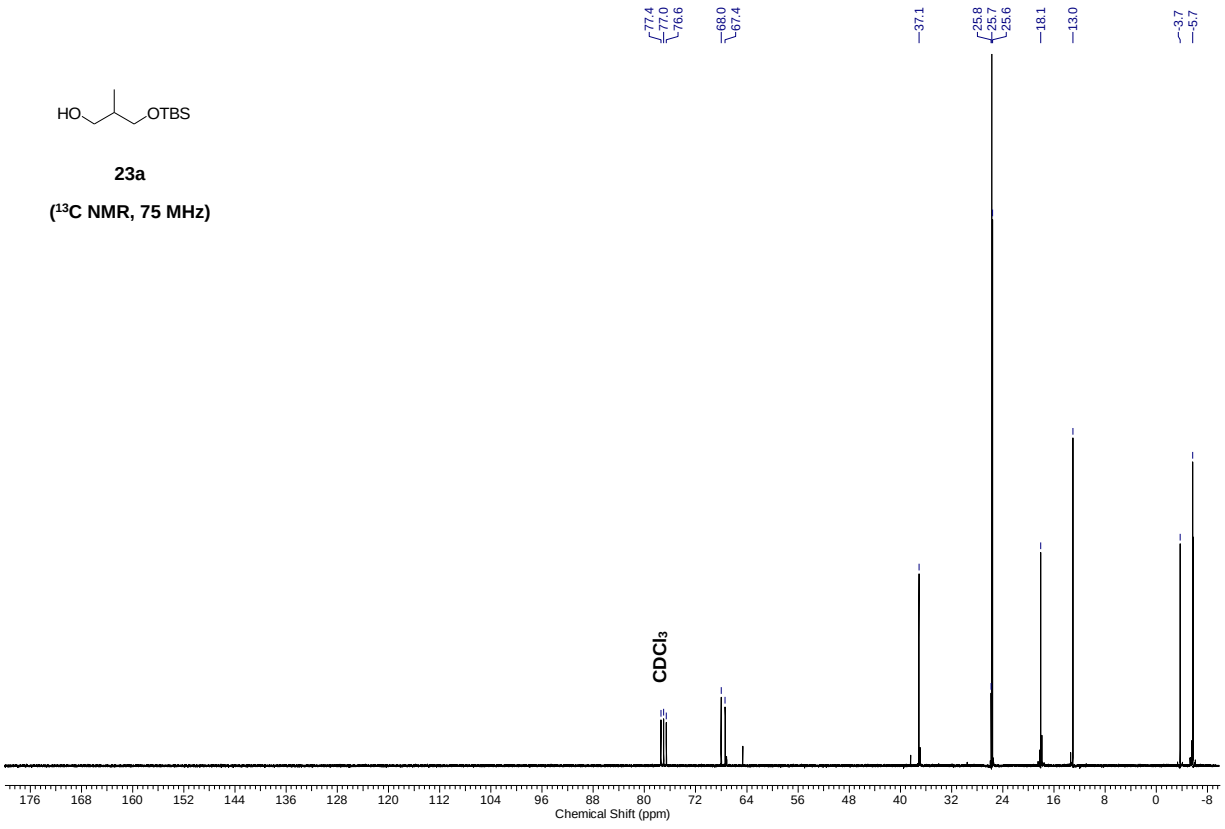
(^{1}H NMR, 300 MHz)

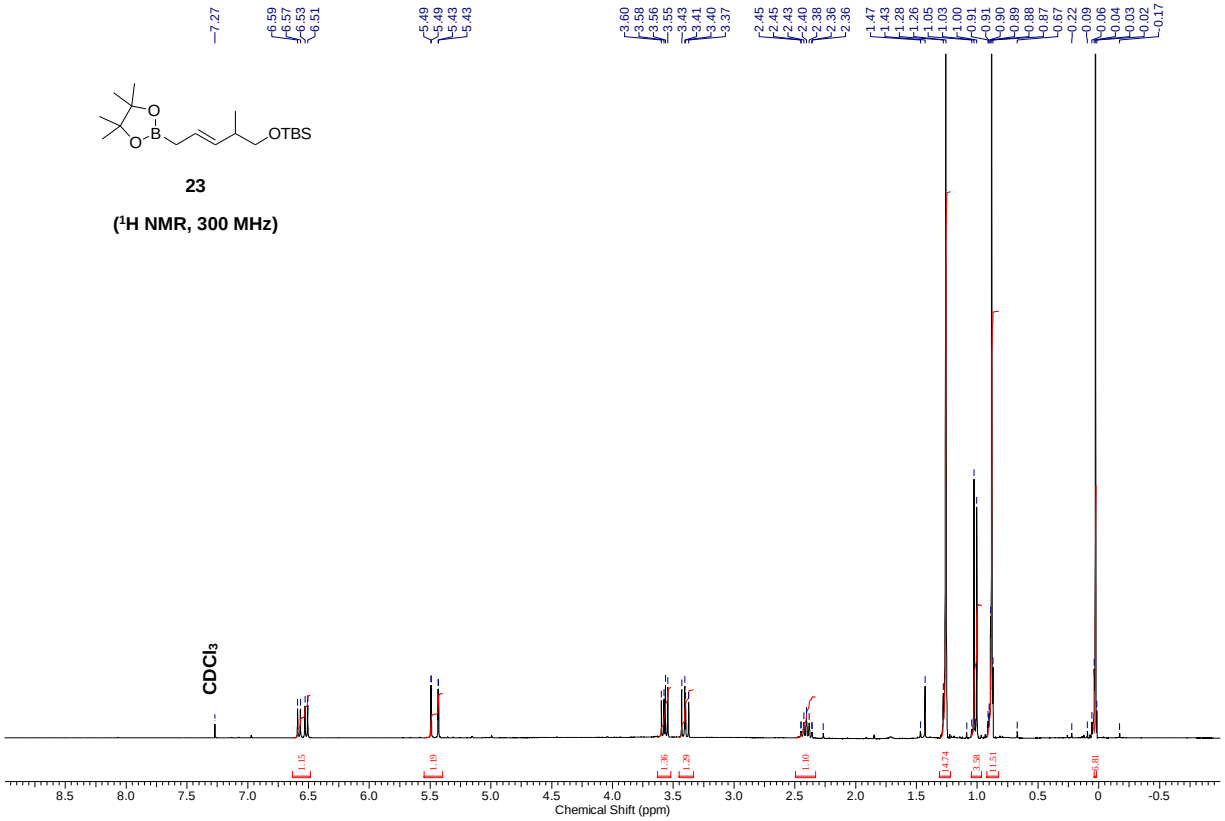


22

(^{13}C NMR, 75 MHz)

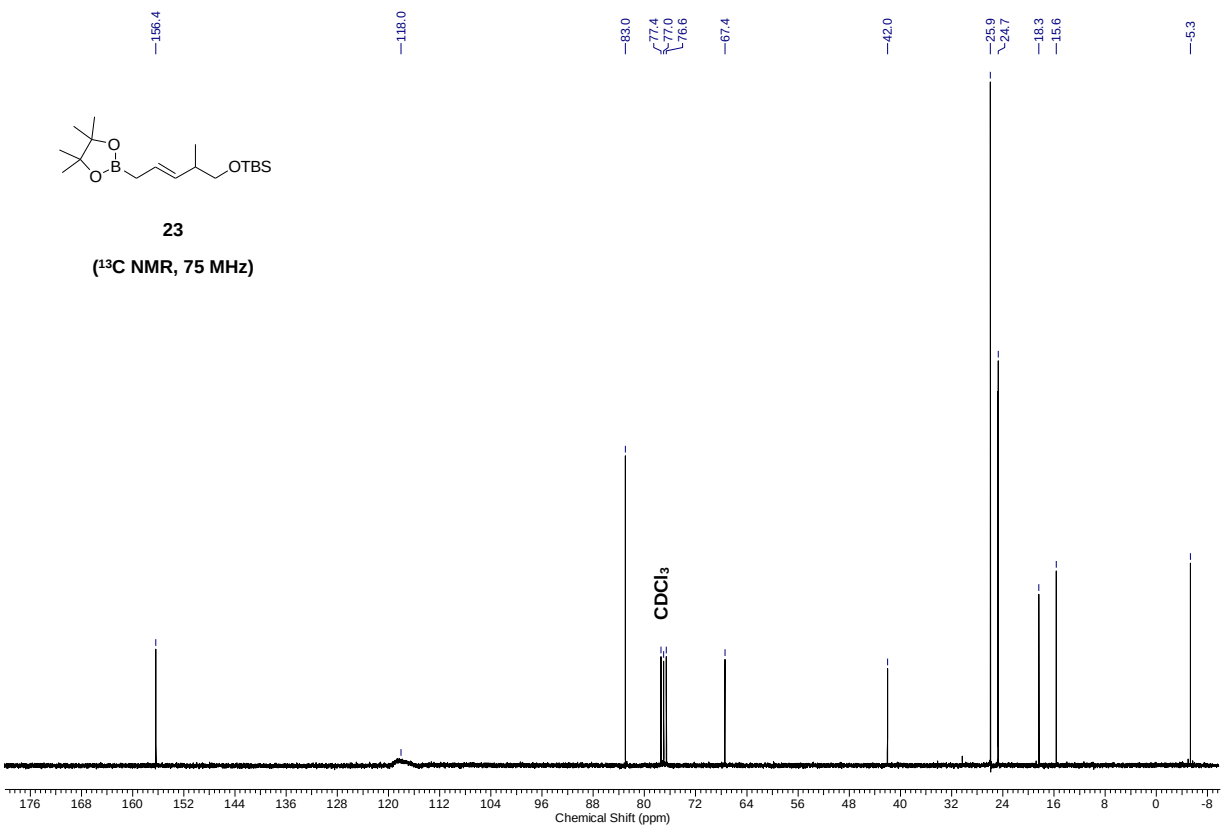

HO
OTBS
23a
(1H NMR, 300 MHz)
7.27
3.66
3.64
3.63
3.61
3.54
3.52
3.50
3.49
3.46
3.33
1.88
1.86
1.84
1.82
0.84
0.83
0.80
0.80
0.78
0.77
0.01
0.00
0.02
CDCl3
Chemical Shift (ppm)


HO
OTBS
23a
(13C NMR, 75 MHz)
77.4
77.0
76.6
68.0
67.4
37.1
25.8
25.7
25.6
18.1
13.0
-3.7
-5.7
CDCl3
Chemical Shift (ppm)



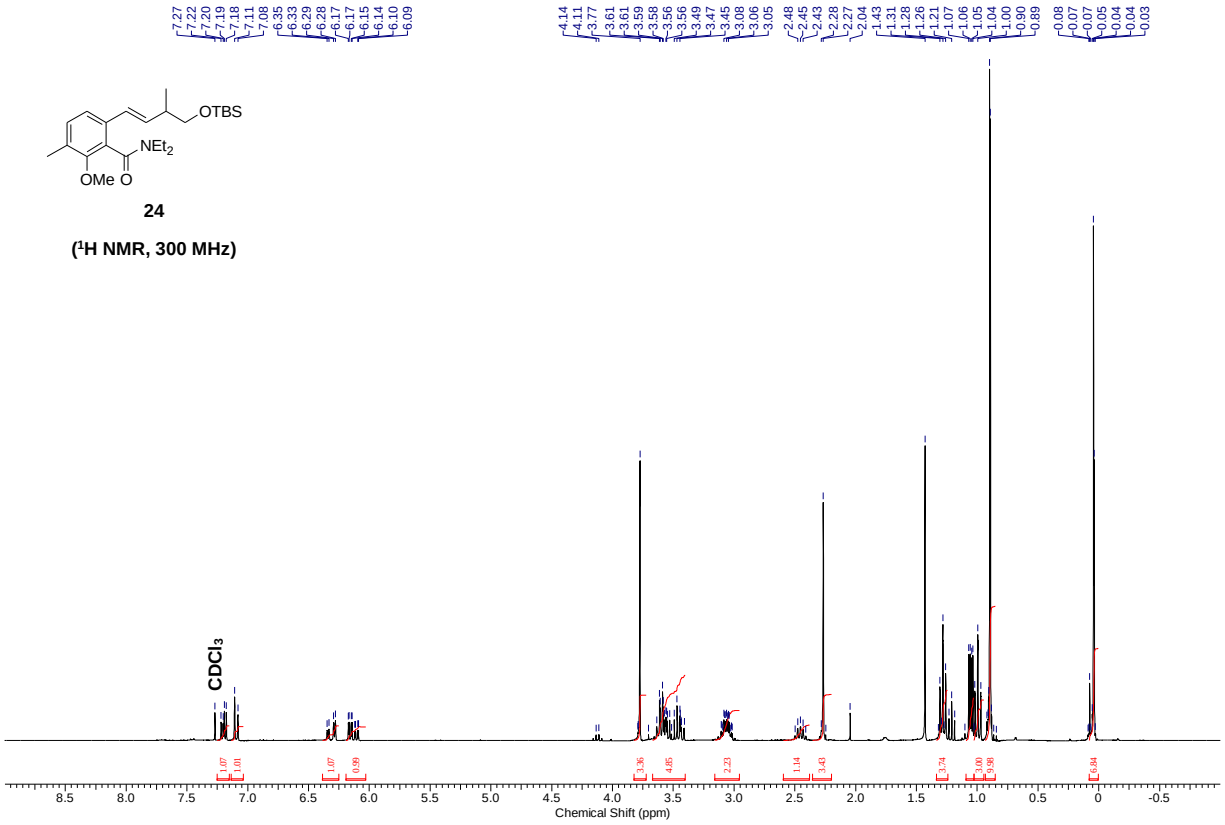
23

(^{1}H NMR, 300 MHz)



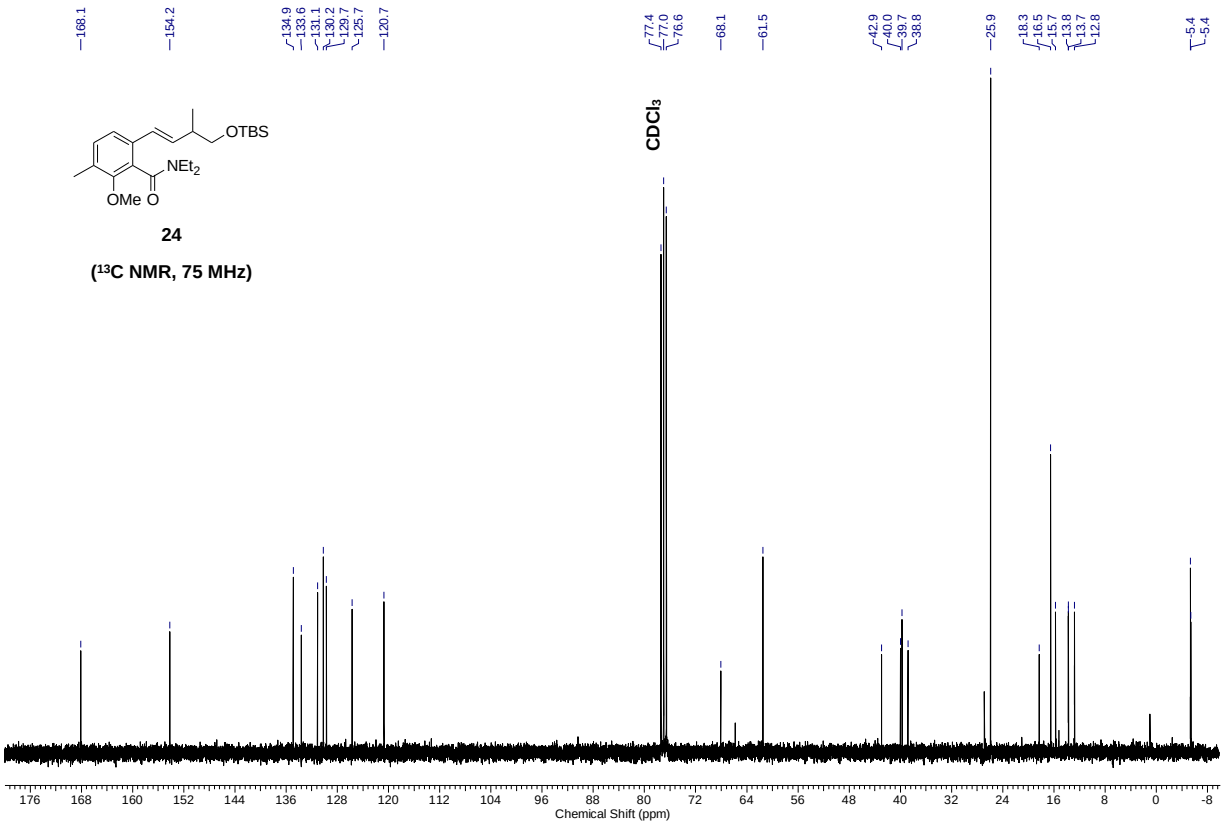
23

(^{13}C NMR, 75 MHz)



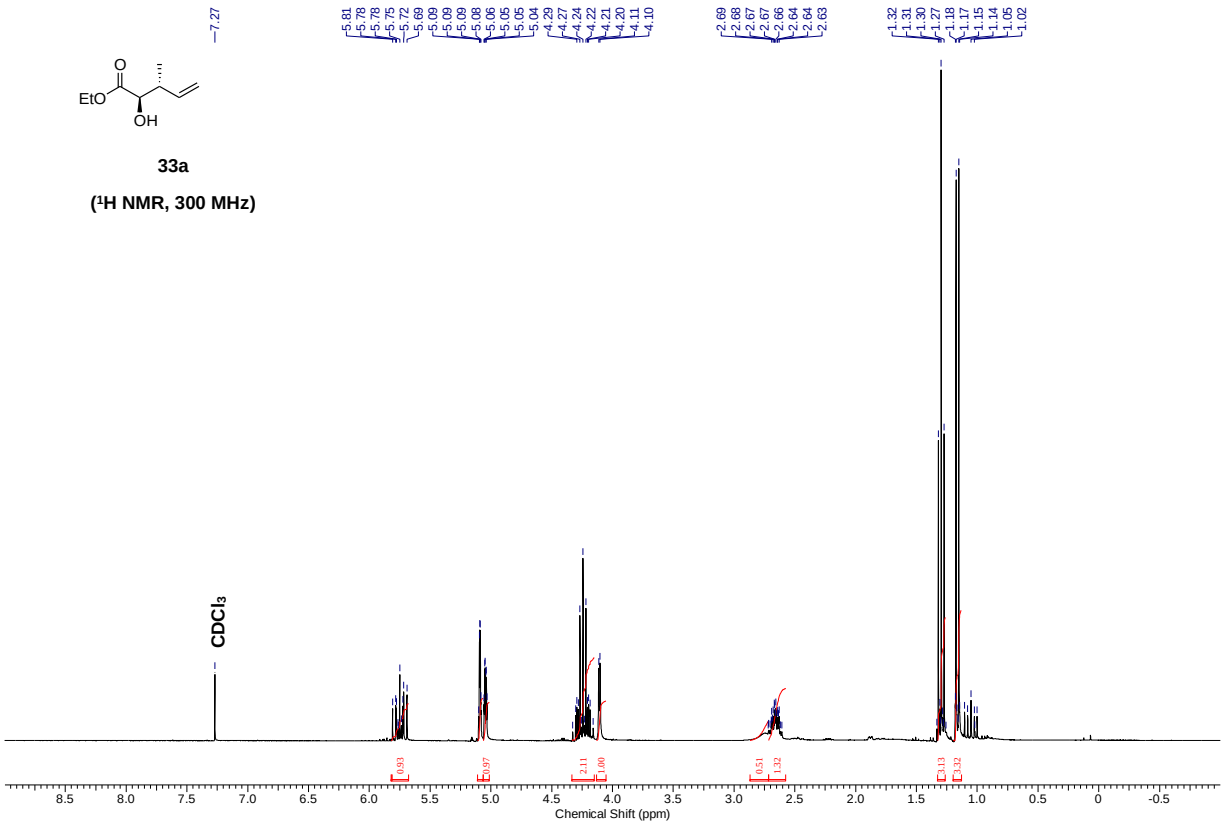
24

(^{1}H NMR, 300 MHz)



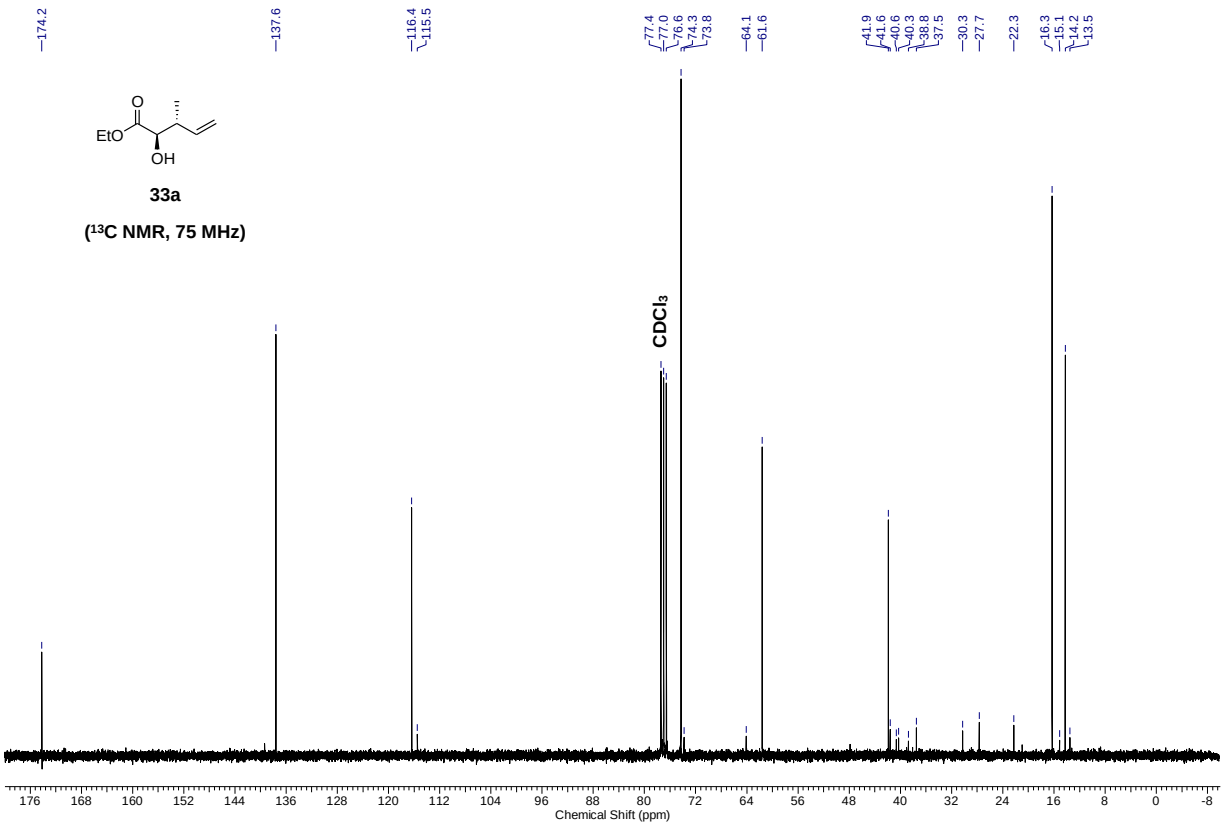
24

(^{13}C NMR, 75 MHz)



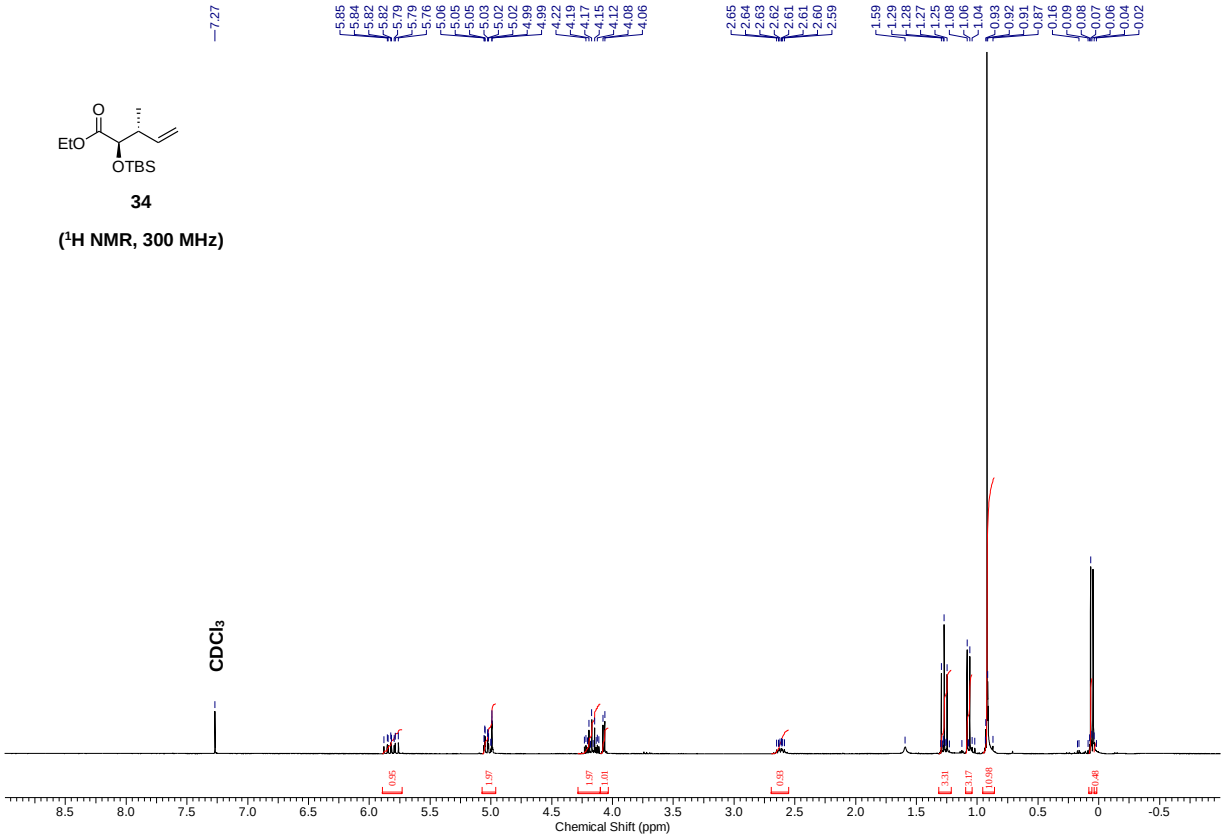
33a

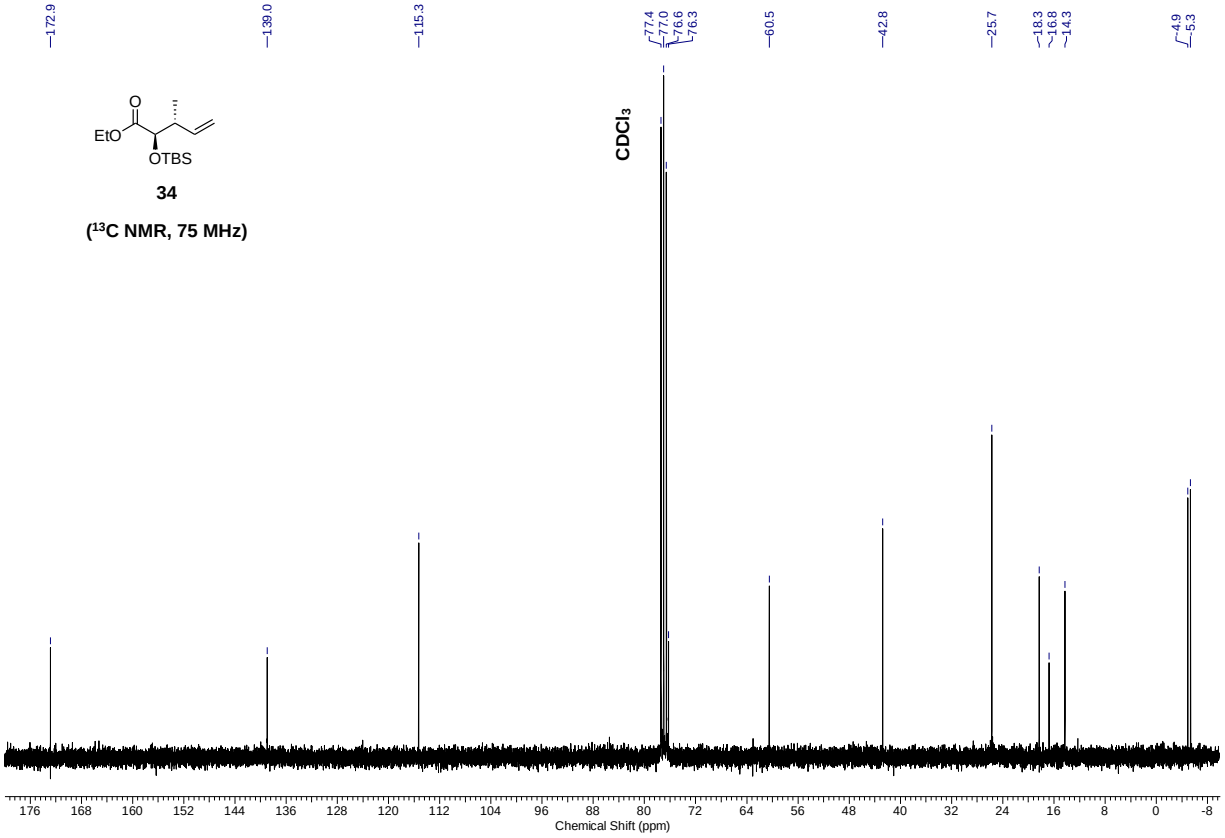
(^{1}H NMR, 300 MHz)

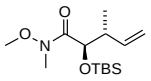


33a

(^{13}C NMR, 75 MHz)

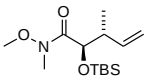

EtO
O
OTBS
34
(1H NMR, 300 MHz)
CDCl3
Chemical Shift (ppm)


EtO
O
OTBS
34
(13C NMR, 75 MHz)
CDCl3
Chemical Shift (ppm)



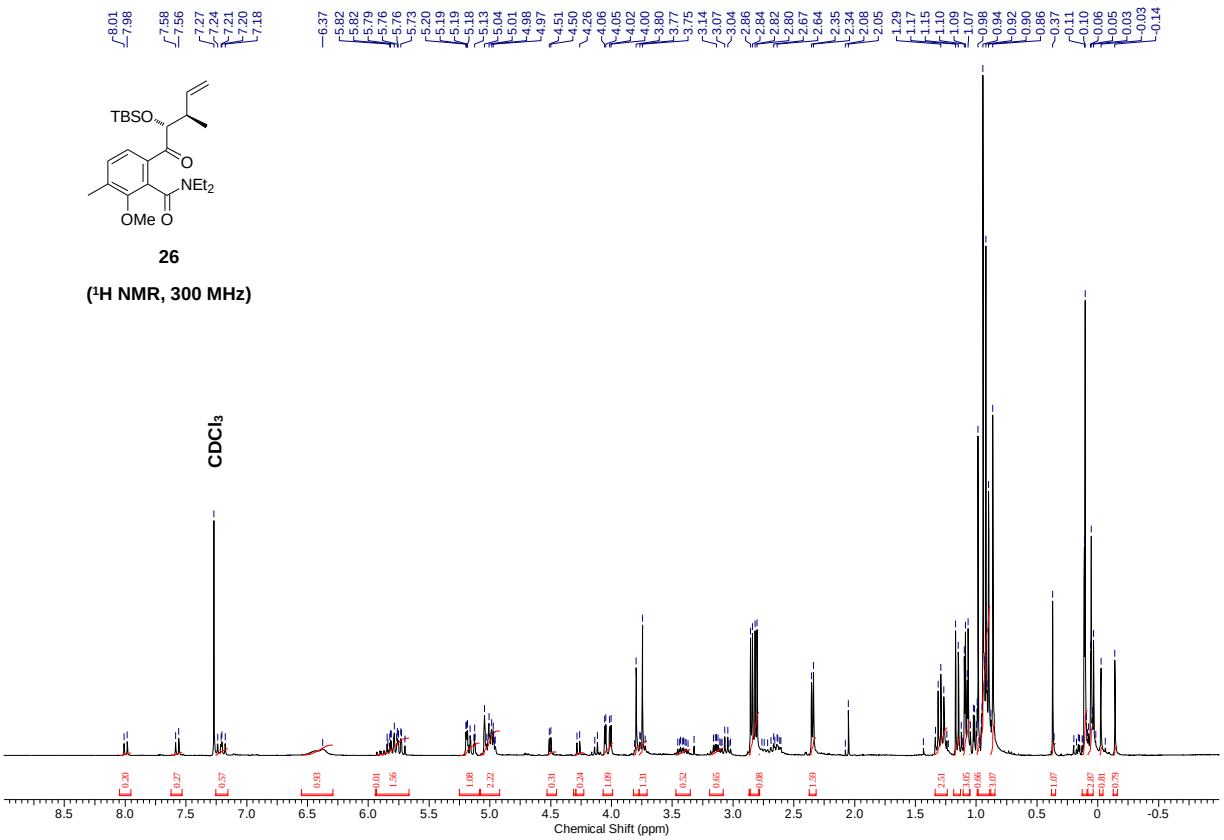
25

(^{1}H NMR, 300 MHz)



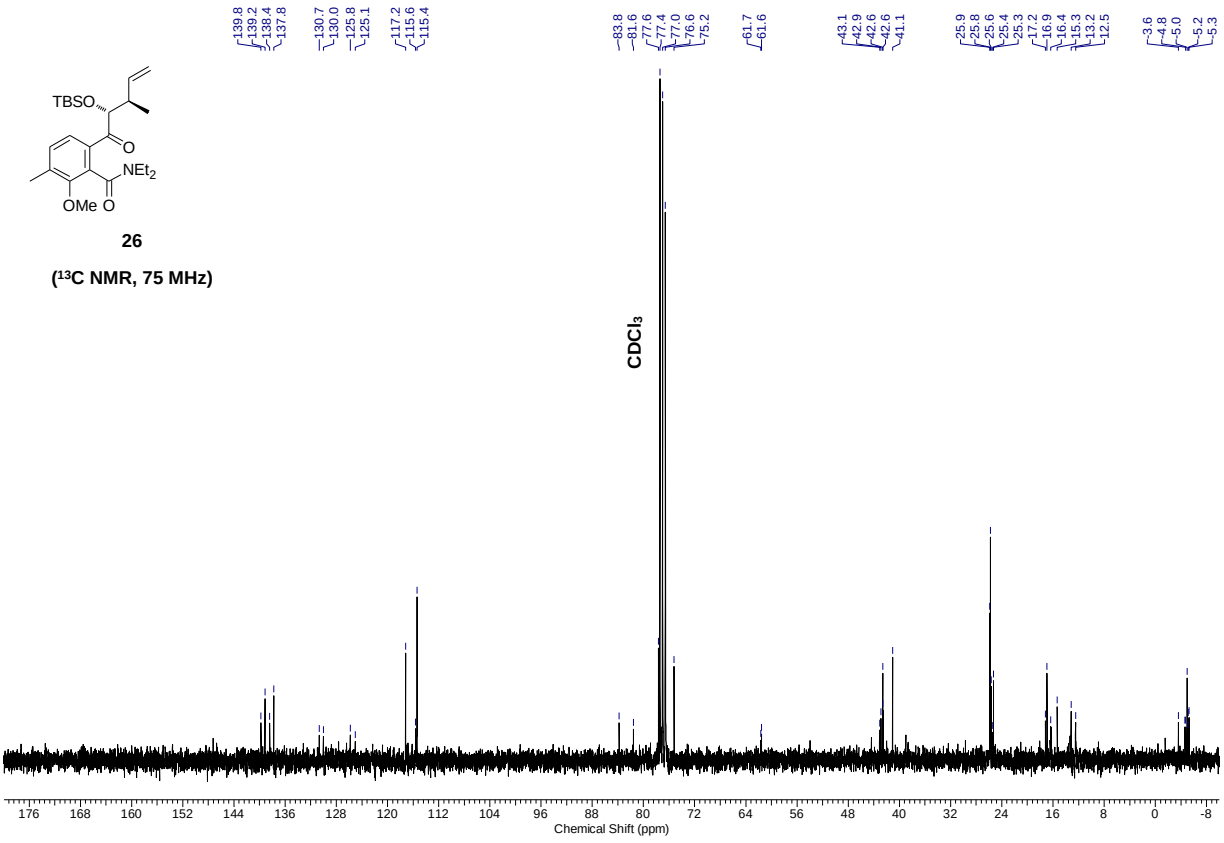
25

(^{13}C NMR, 75 MHz)



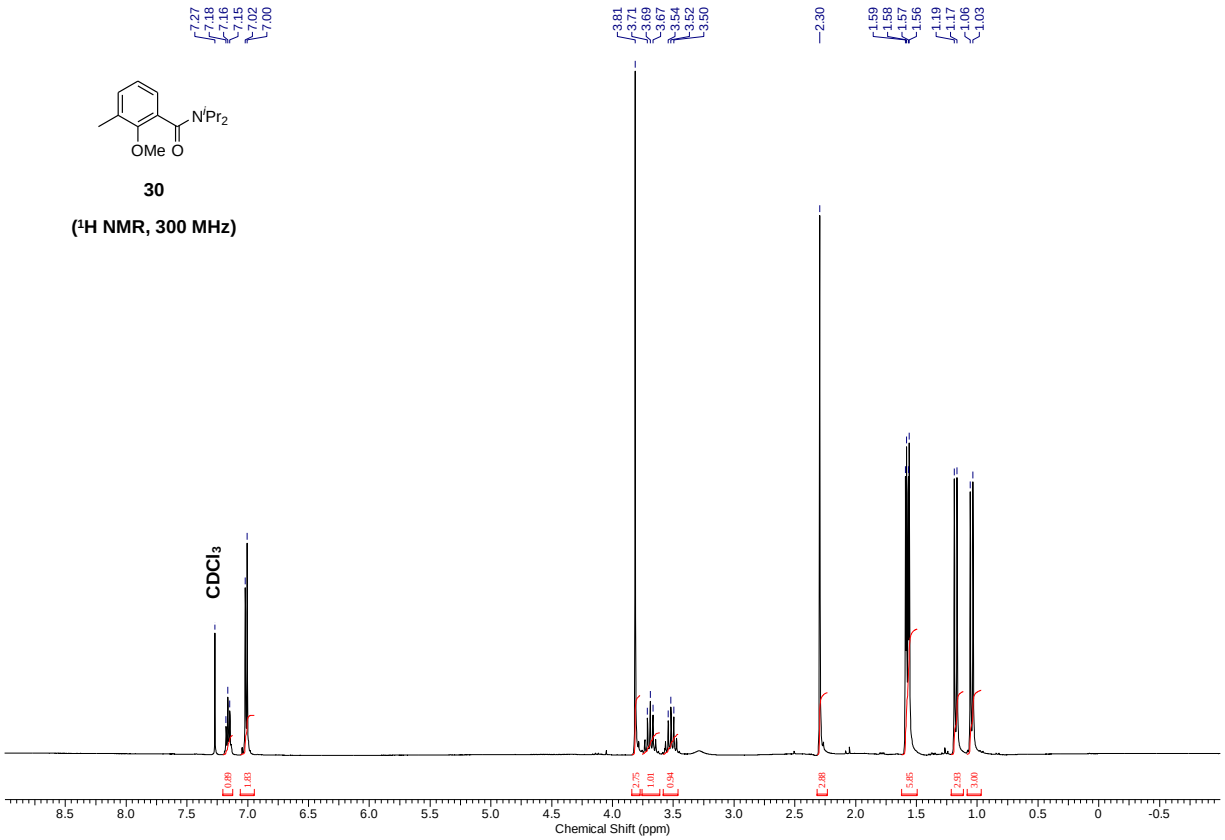
26

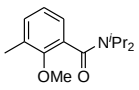
(^{1}H NMR, 300 MHz)



26

(^{13}C NMR, 75 MHz)



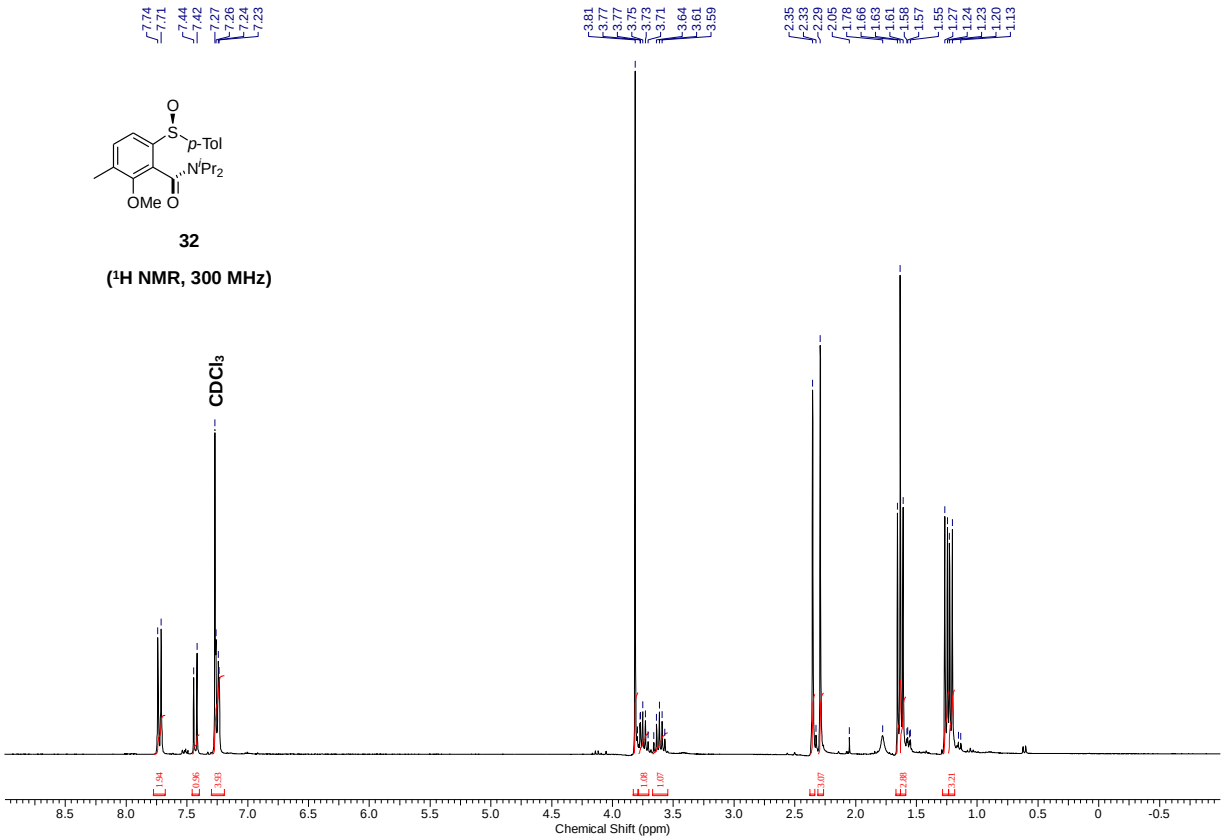


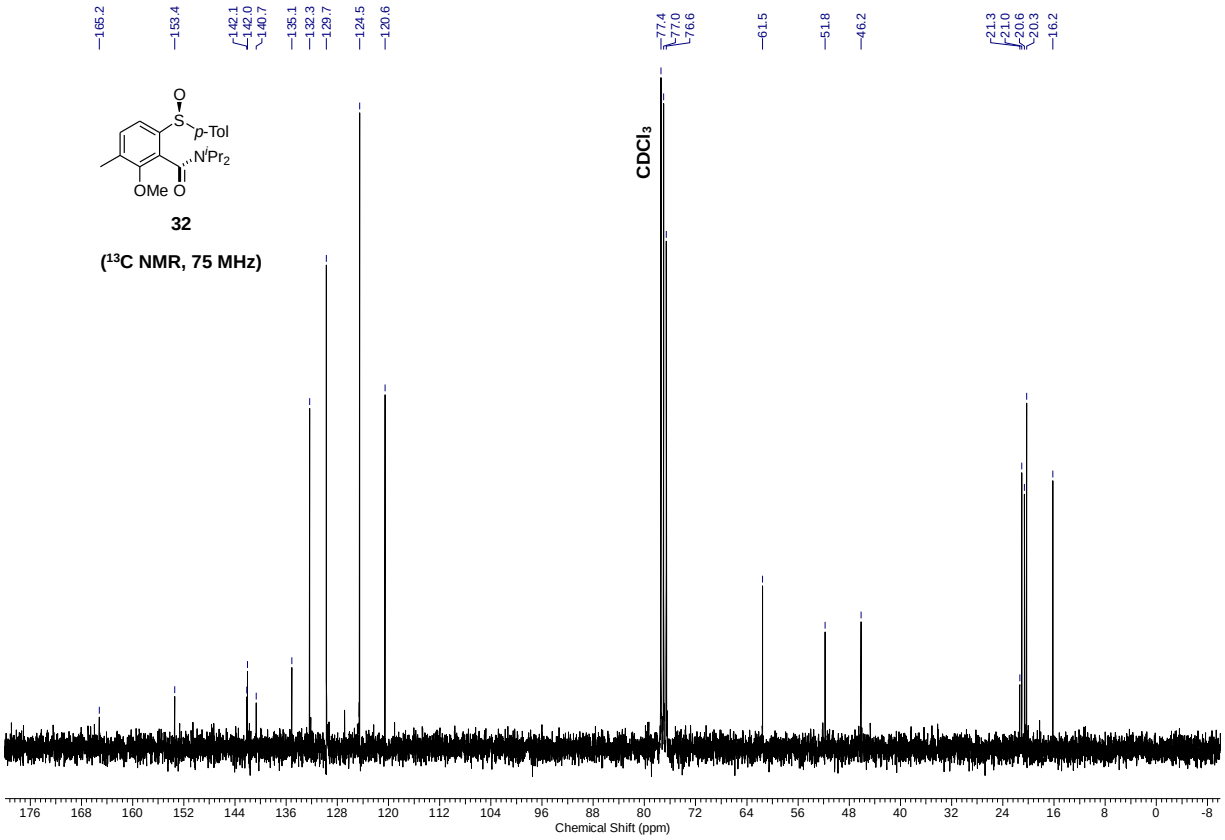
30

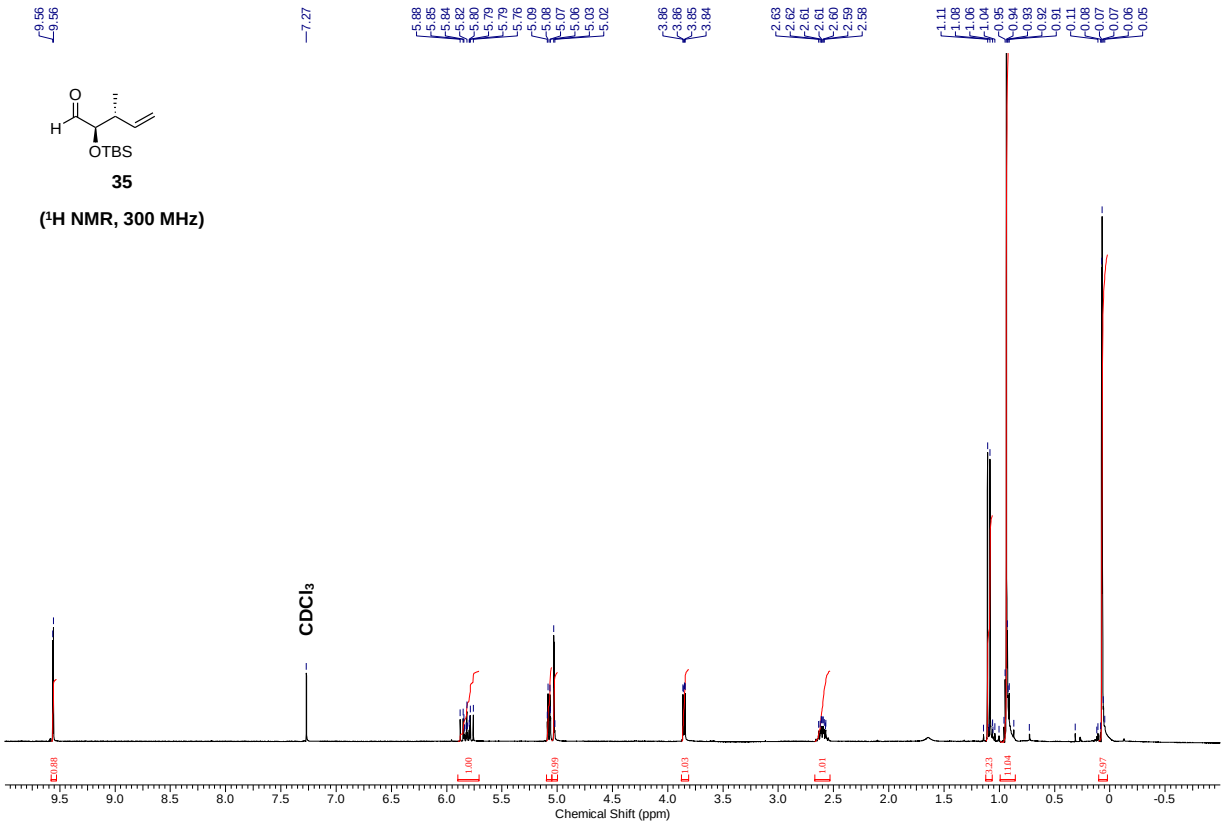
(^{1}H NMR, 300 MHz)

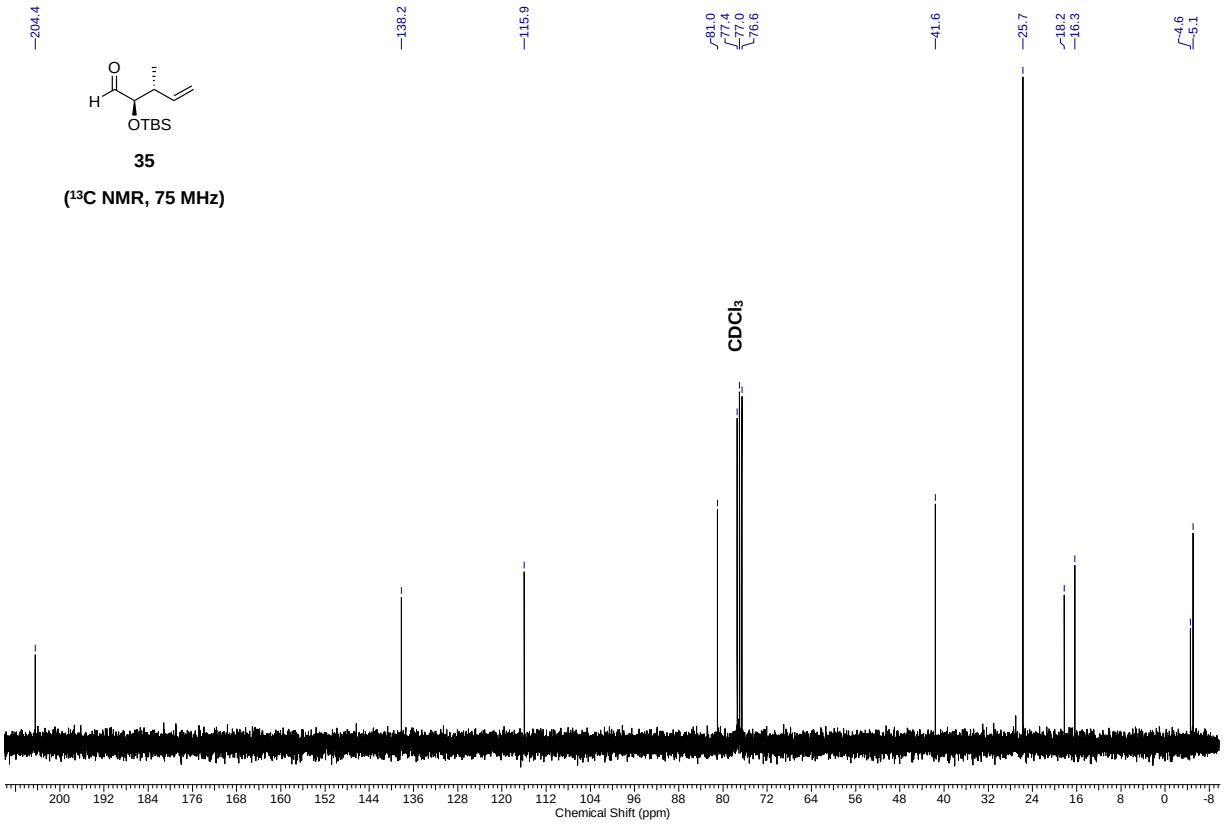
30

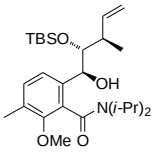
(^{13}C NMR, 75 MHz)


7.74
7.71
7.44
7.42
7.27
7.26
7.24
7.23
3.81
3.77
3.77
3.75
3.73
3.71
3.64
3.61
3.59
2.35
2.33
2.29
2.05
1.78
1.66
1.63
1.61
1.58
1.57
1.55
1.27
1.24
1.23
1.20
1.13
O
S
p-Tol
NiPr2
OMe O
32
(1H NMR, 300 MHz)
CDCl3
1.94
2.06
3.33
6.08
1.07
3.07
2.88
3.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)


165.2
153.4
142.1
142.0
140.7
135.1
132.3
129.7
124.5
120.6
77.4
77.0
76.6
61.5
51.8
46.2
21.3
21.0
20.6
20.3
16.2
O
S
p-Tol
NiPr2
OMe O
32
(13C NMR, 75 MHz)
CDCl3
176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

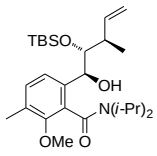

9.56
9.56
7.27
5.88
5.85
5.84
5.82
5.80
5.79
5.79
5.76
5.09
5.08
5.07
5.06
5.03
5.02
3.86
3.86
3.85
3.84
2.63
2.62
2.61
2.61
2.60
2.59
2.58
1.11
1.08
1.06
1.04
0.95
0.94
0.93
0.92
0.91
0.11
0.08
0.07
0.07
0.06
0.05
O
H
OTBS
35
(1H NMR, 300 MHz)
CDCl3
3.88
1.00
1.09
1.03
1.01
3.23
1.04
6.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)


204.4
138.2
115.9
81.0
77.4
77.0
76.6
41.6
25.7
18.2
16.3
4.6
5.1
O
H
OTBS
35
(13C NMR, 75 MHz)
CDCl3
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)



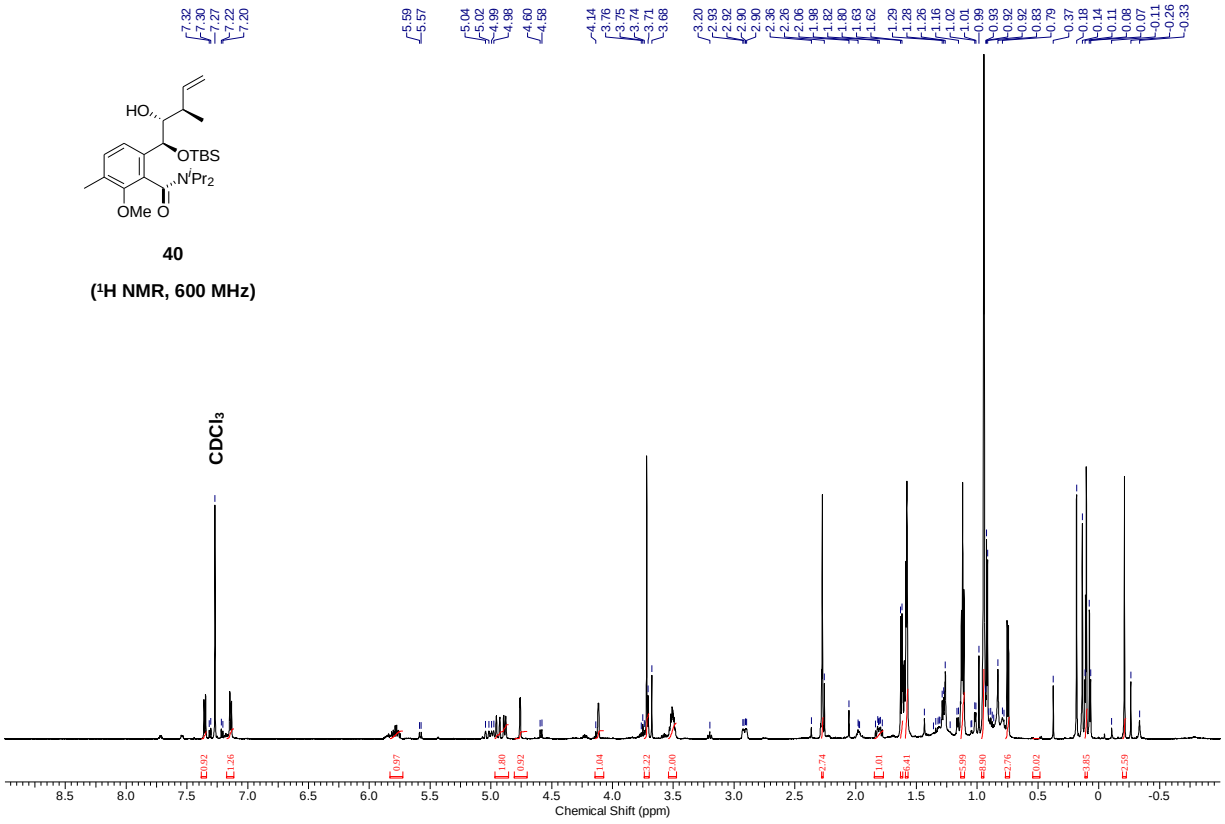
37

(^{1}H NMR, 300 MHz)



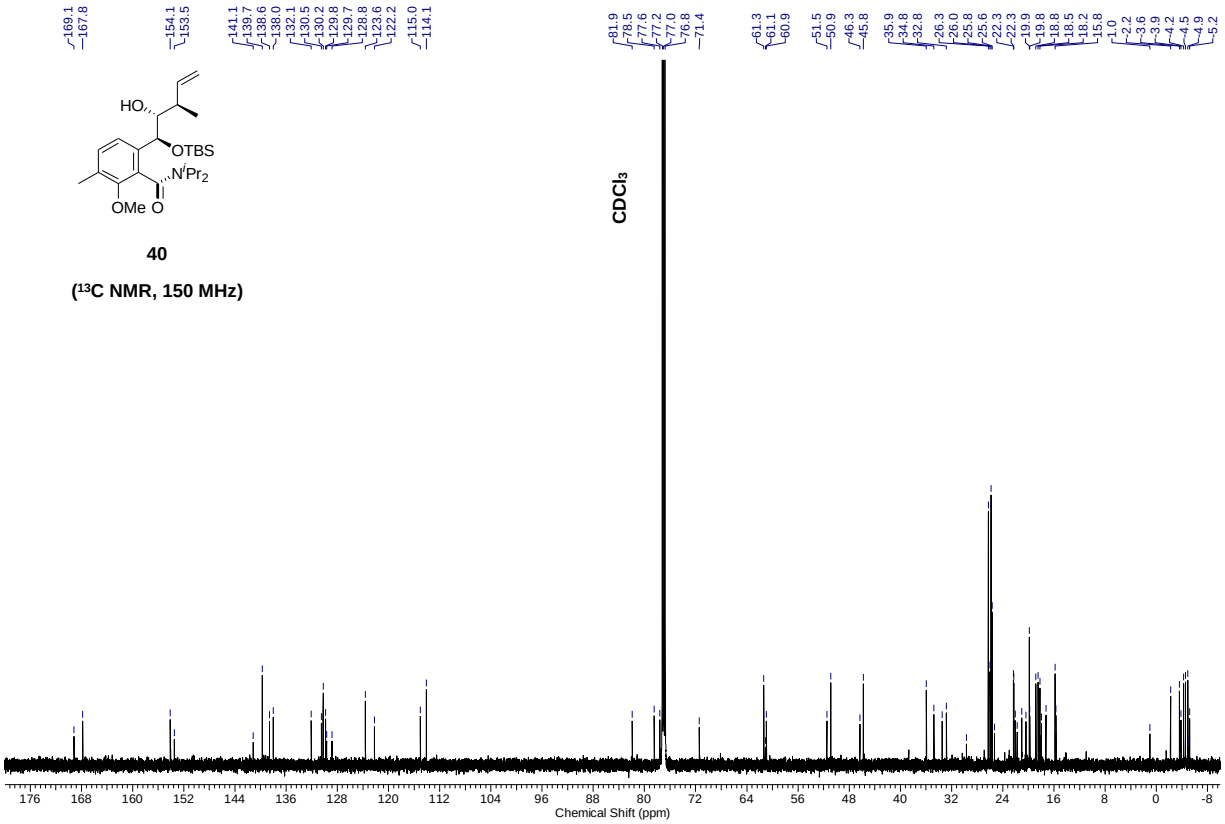
37

(^{13}C NMR, 125 MHz)



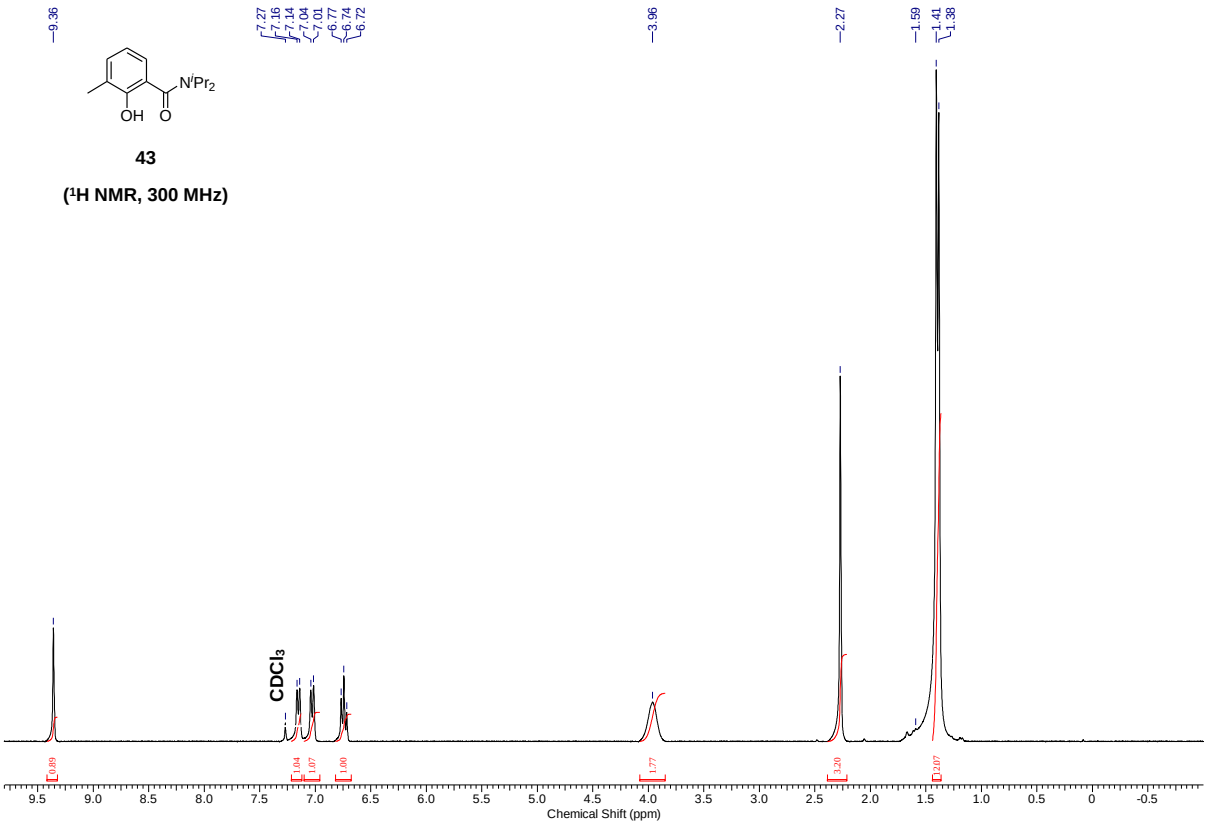
40

(^{1}H NMR, 600 MHz)



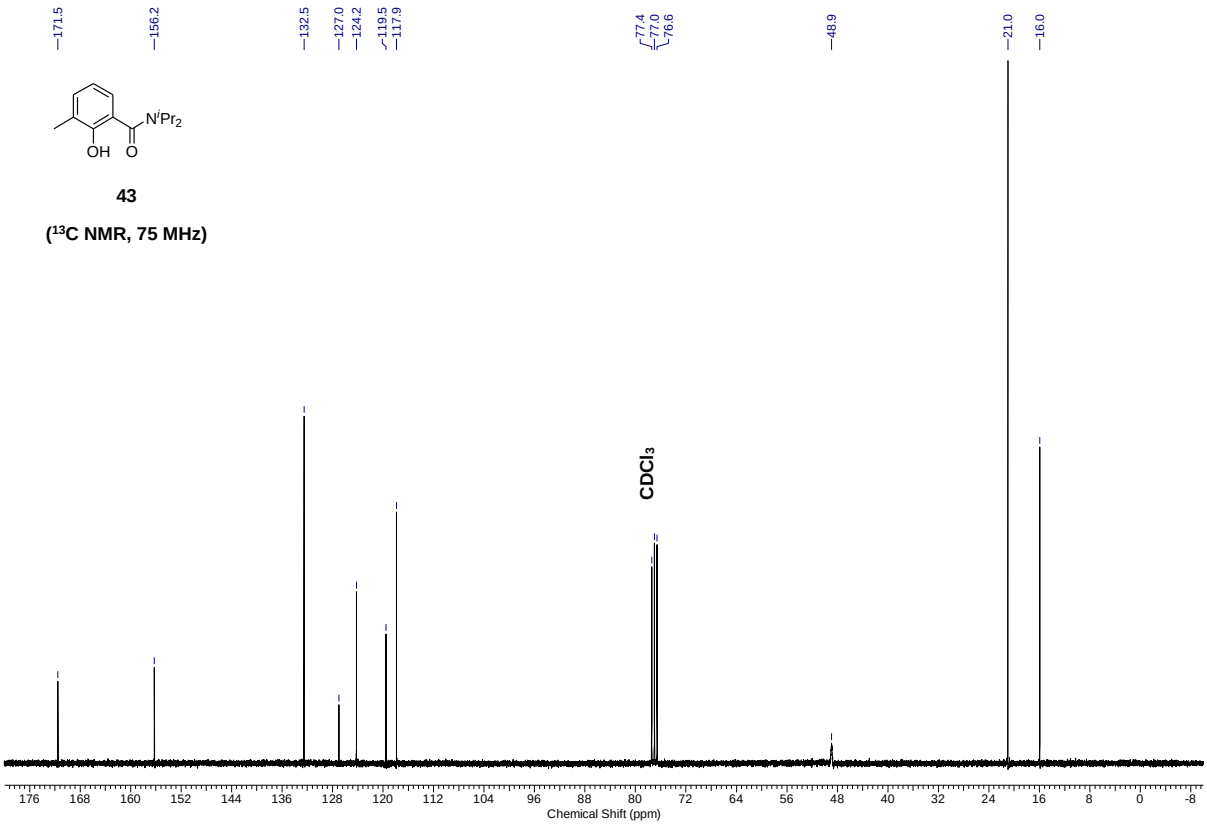
40

(^{13}C NMR, 150 MHz)



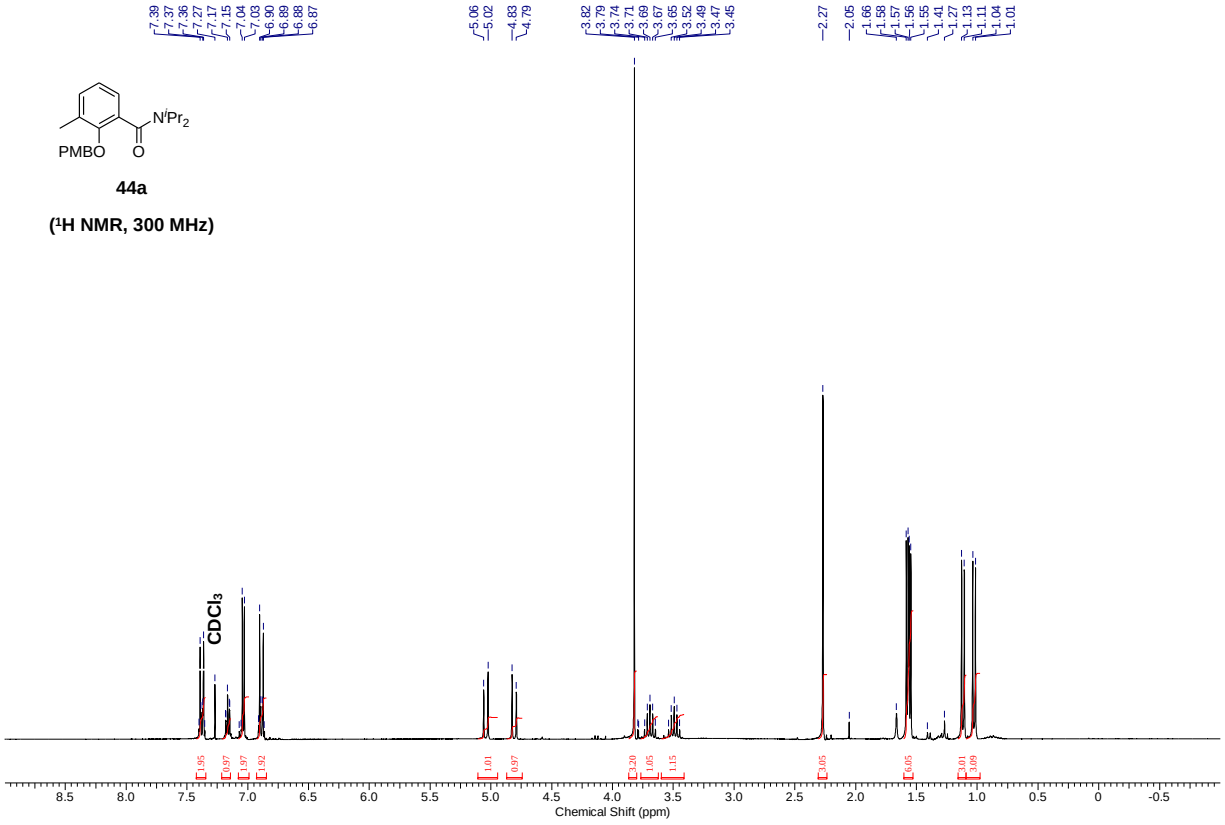
43

(^{1}H NMR, 300 MHz)



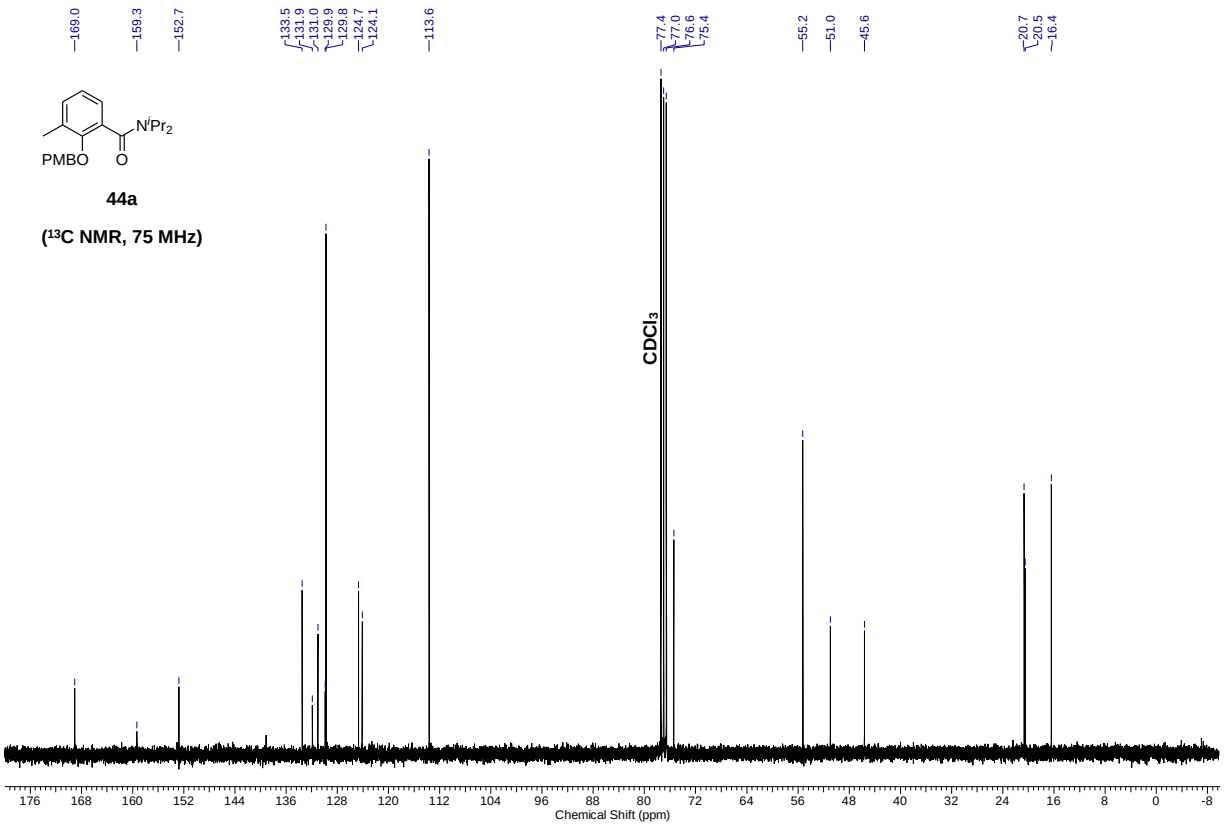
43

(^{13}C NMR, 75 MHz)



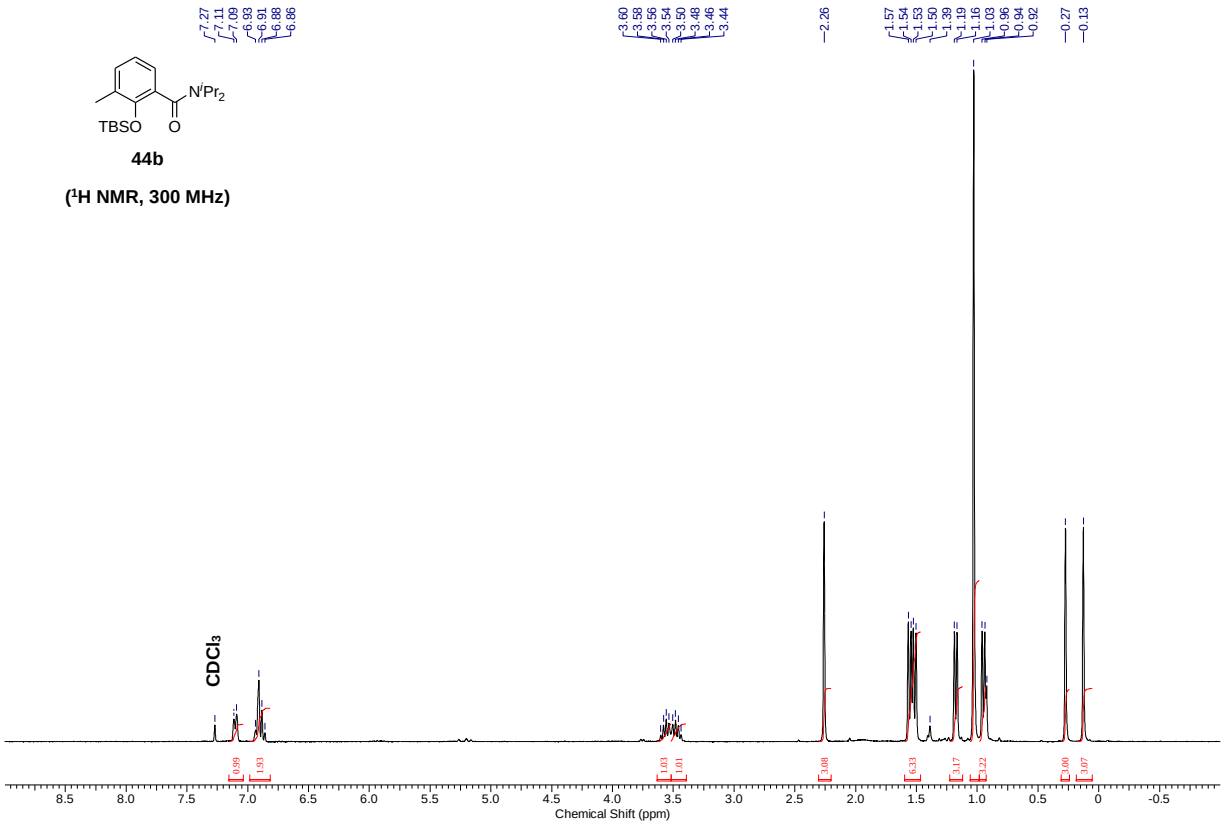
44a

(^{1}H NMR, 300 MHz)



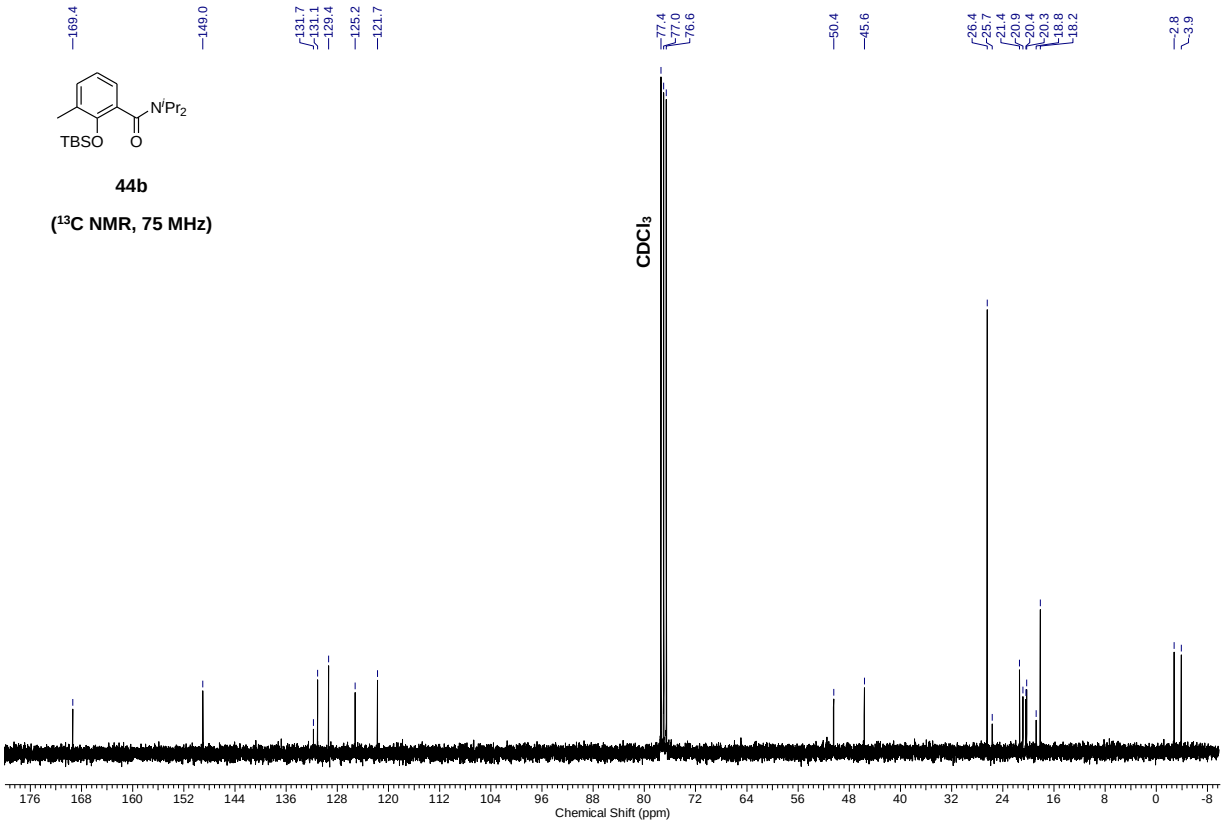
44a

(^{13}C NMR, 75 MHz)



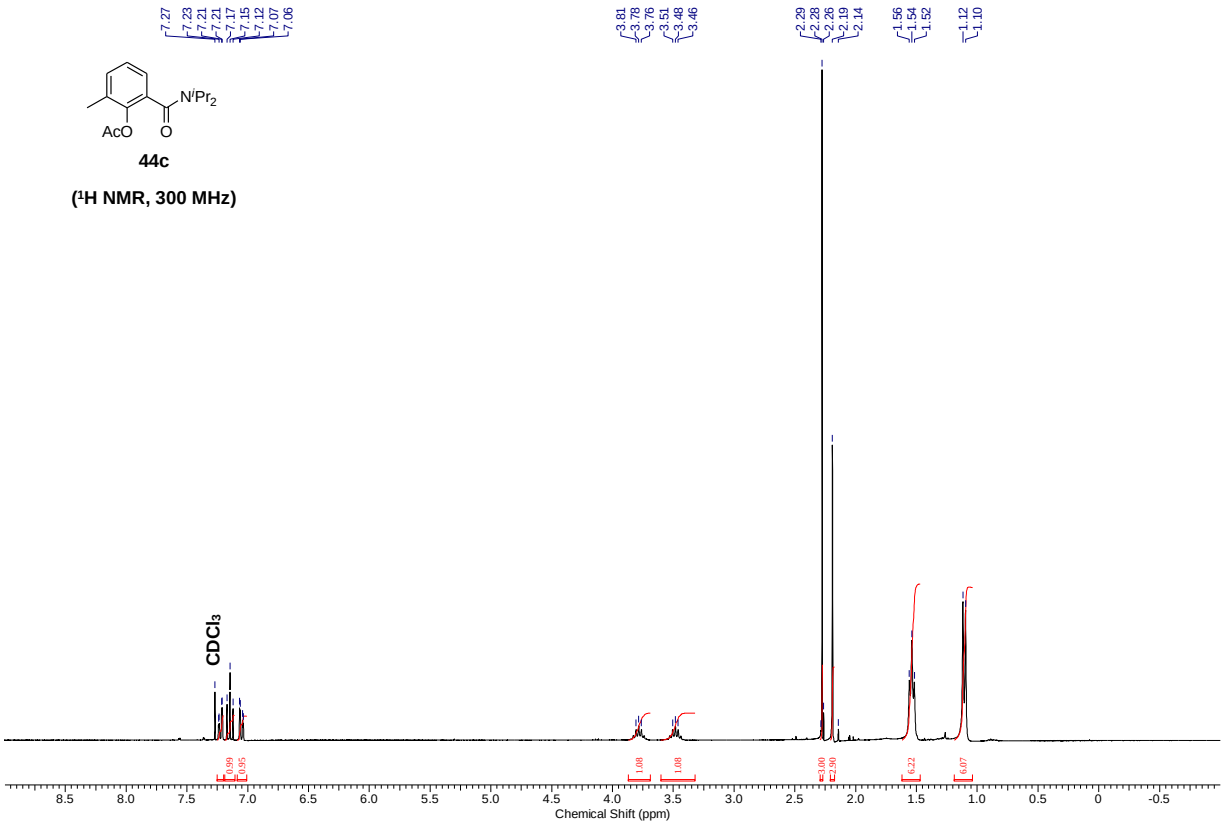
44b

(^{1}H NMR, 300 MHz)



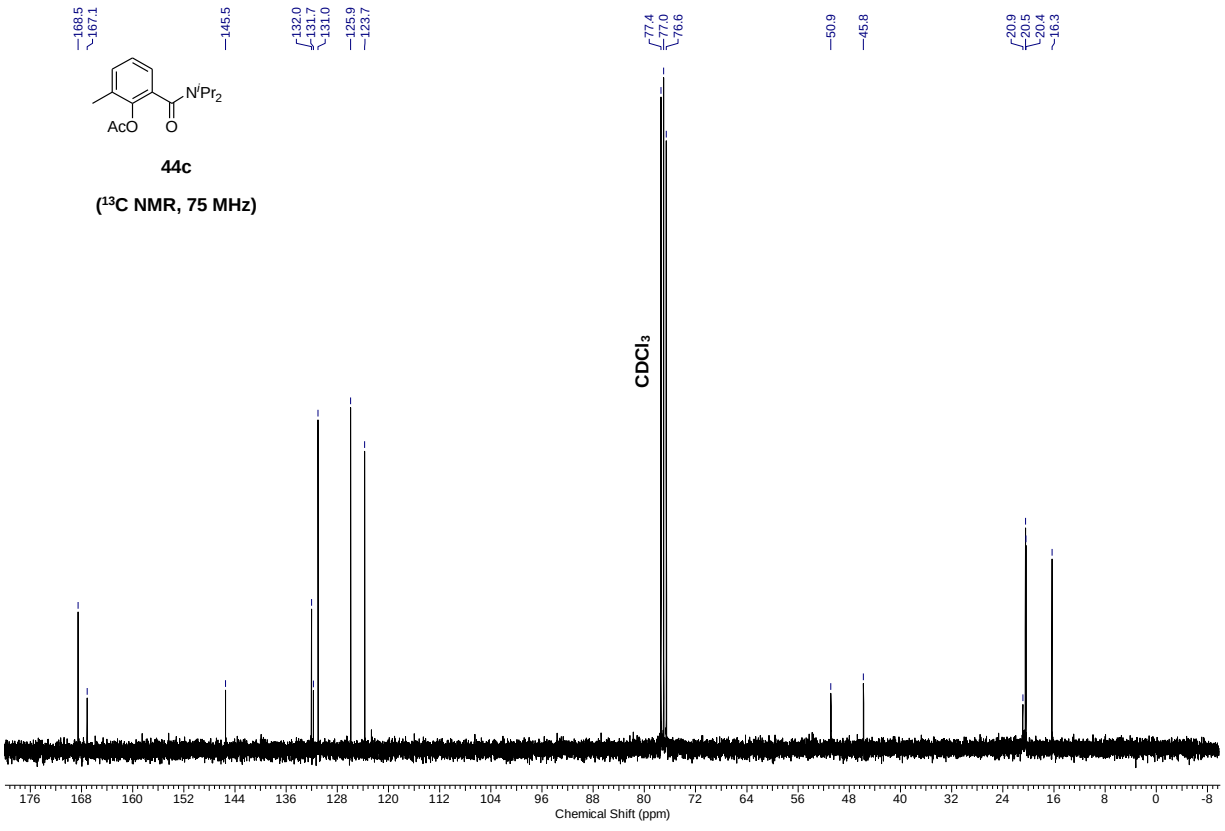
44b

(^{13}C NMR, 75 MHz)



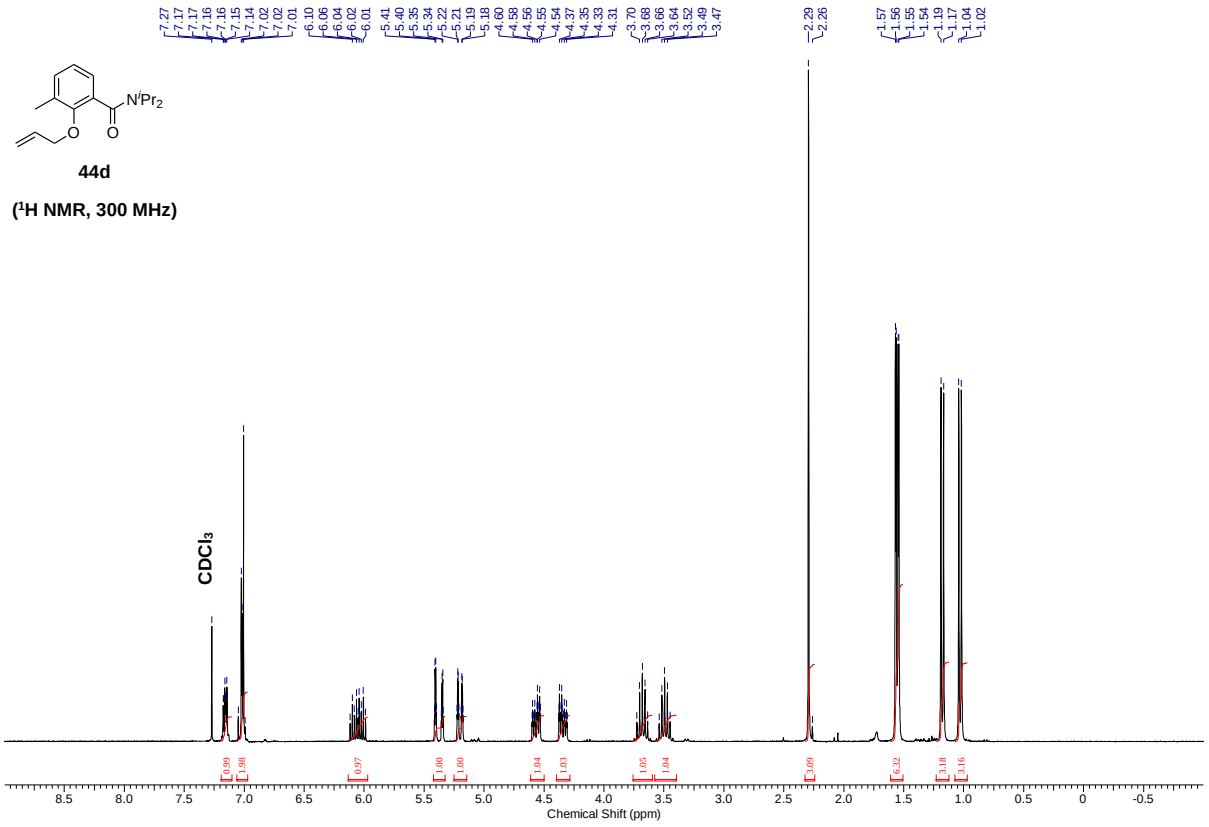
44c

(^{1}H NMR, 300 MHz)



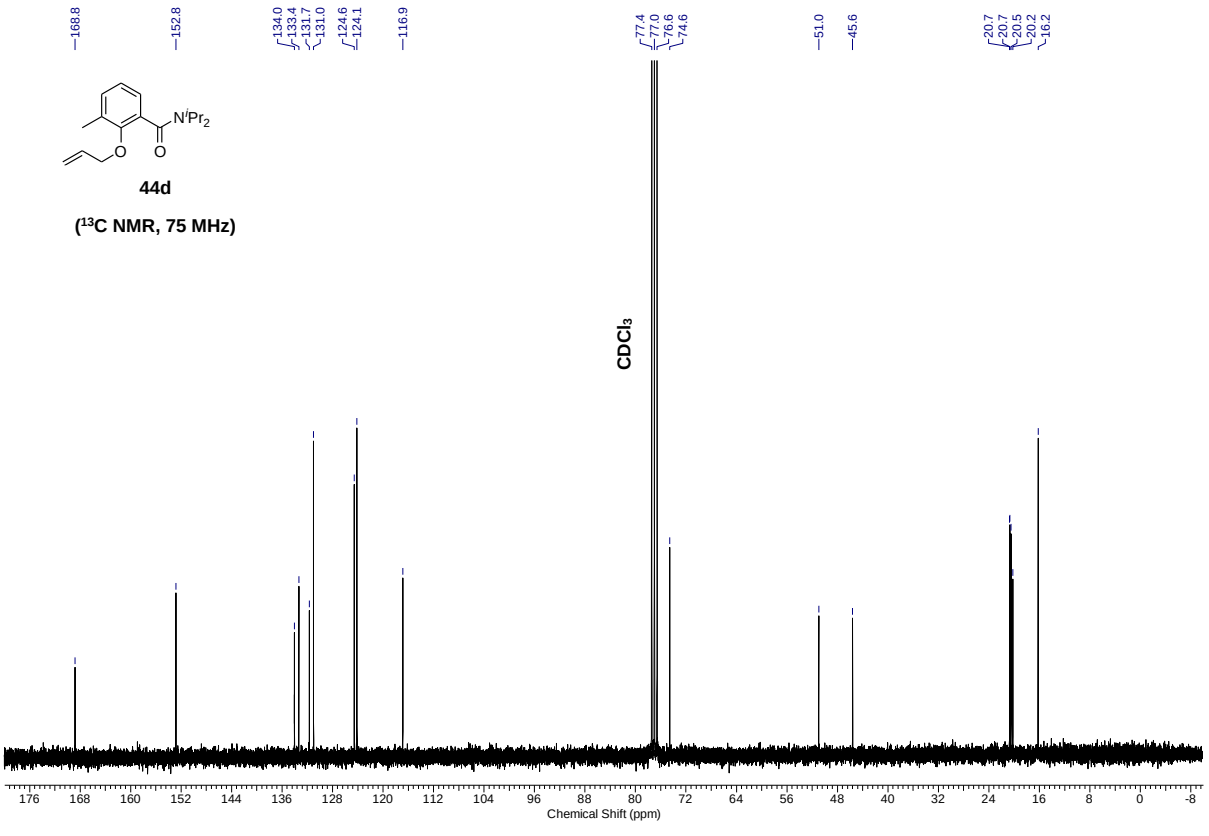
44c

(^{13}C NMR, 75 MHz)



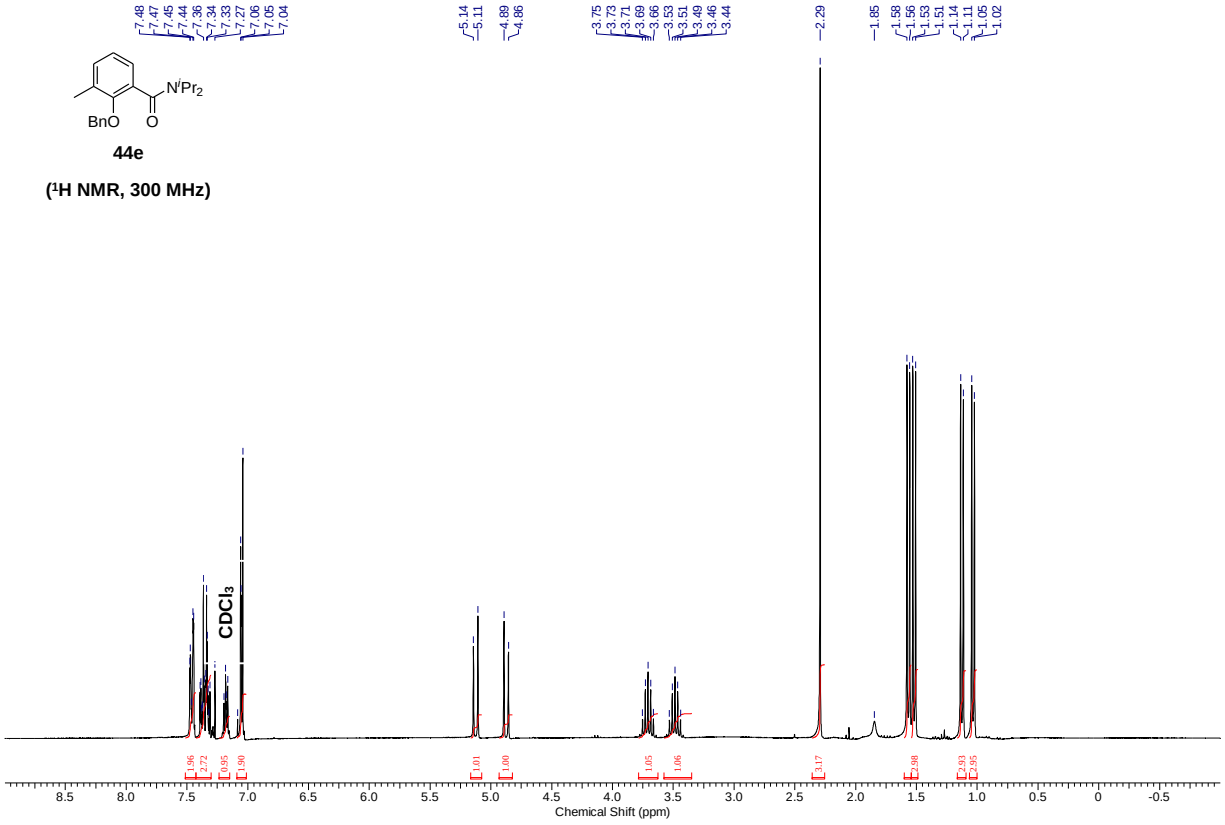
44d

(^{1}H NMR, 300 MHz)



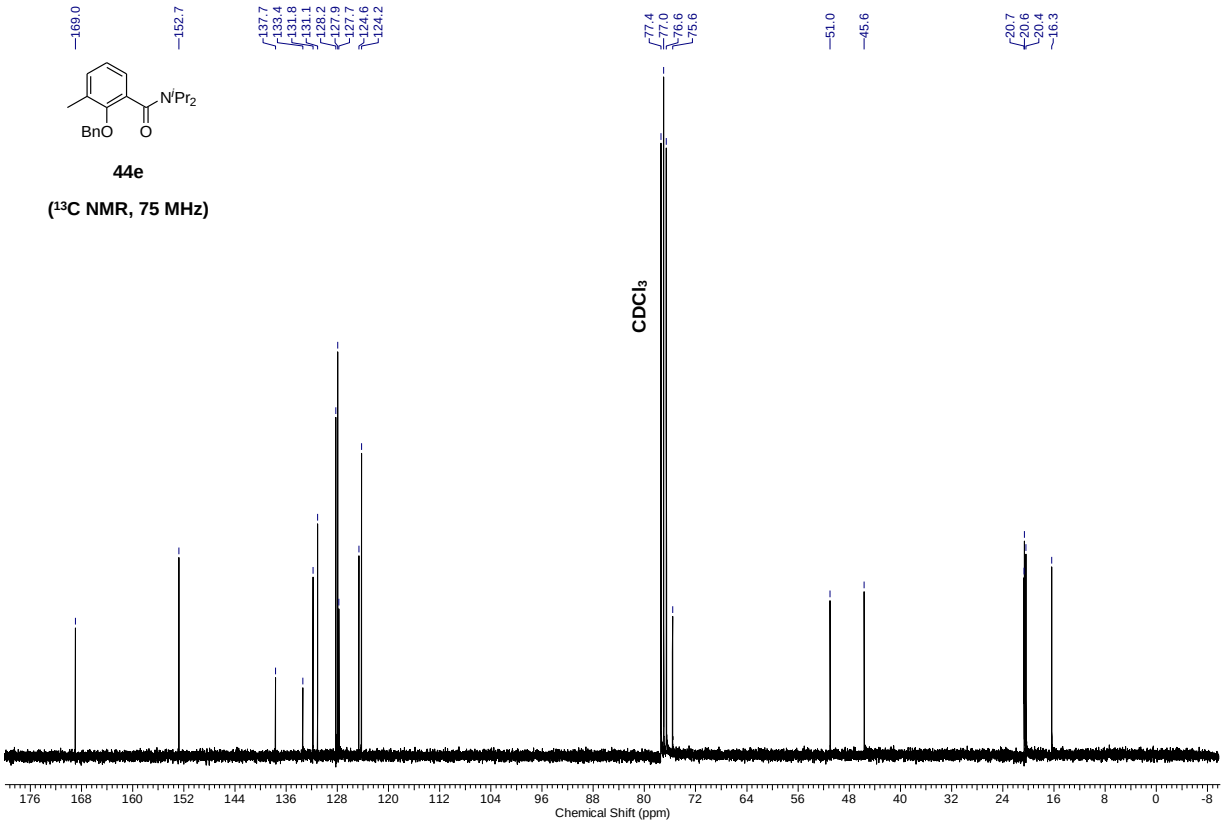
44d

(^{13}C NMR, 75 MHz)



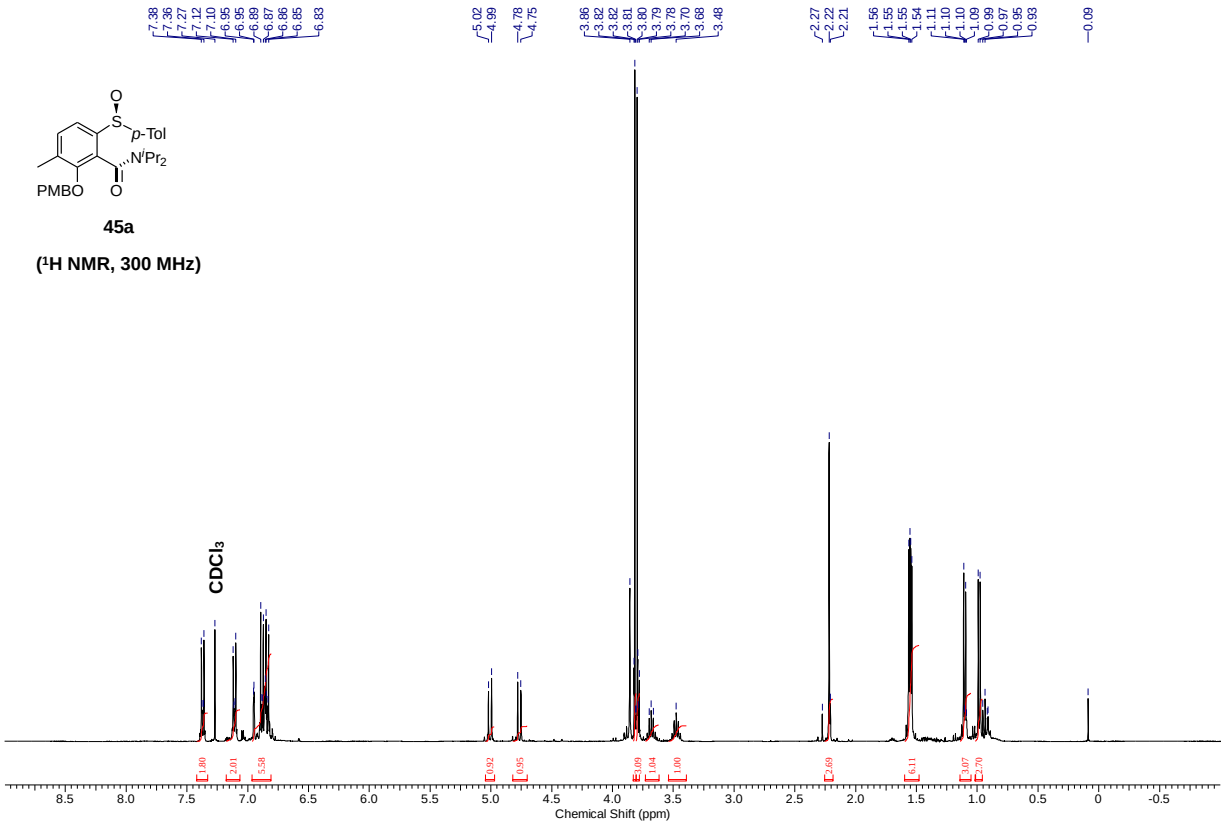
44e

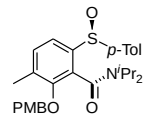
(^{1}H NMR, 300 MHz)



44e

(^{13}C NMR, 75 MHz)



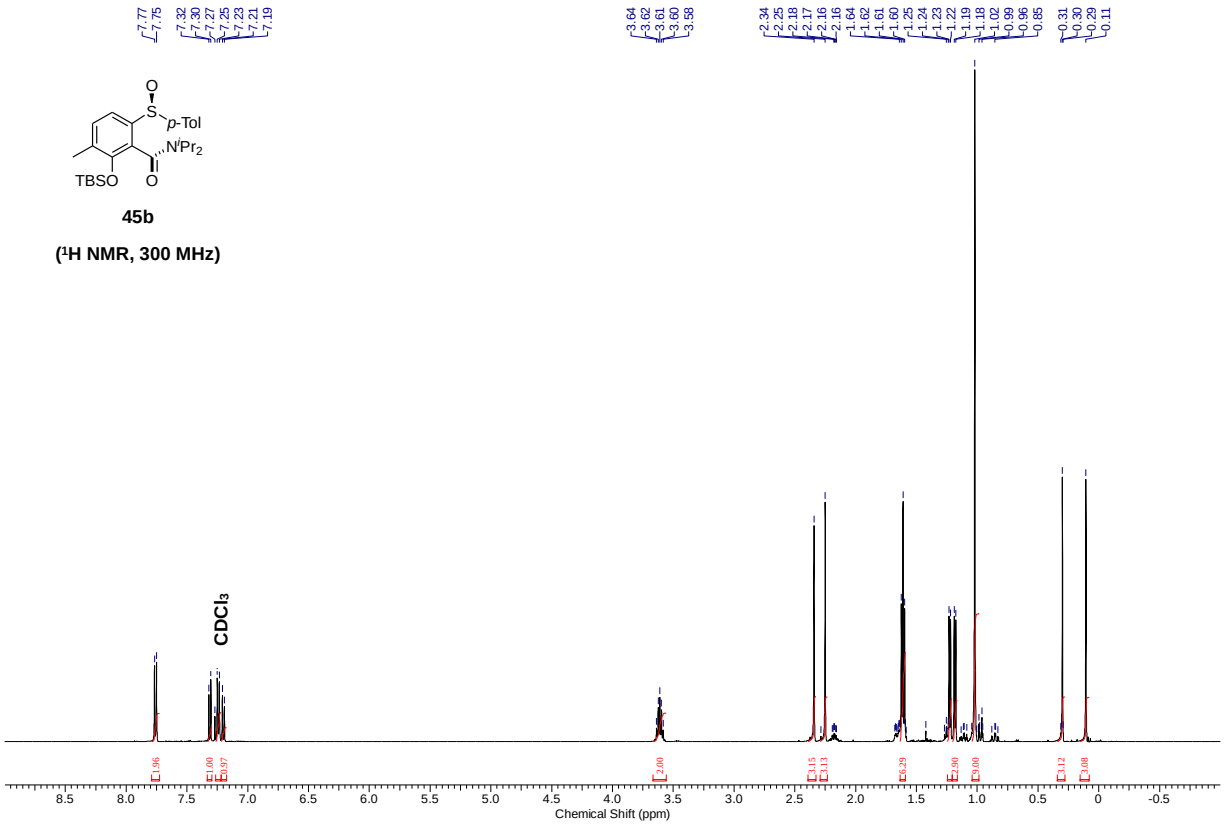


45a

(¹H NMR, 300 MHz)

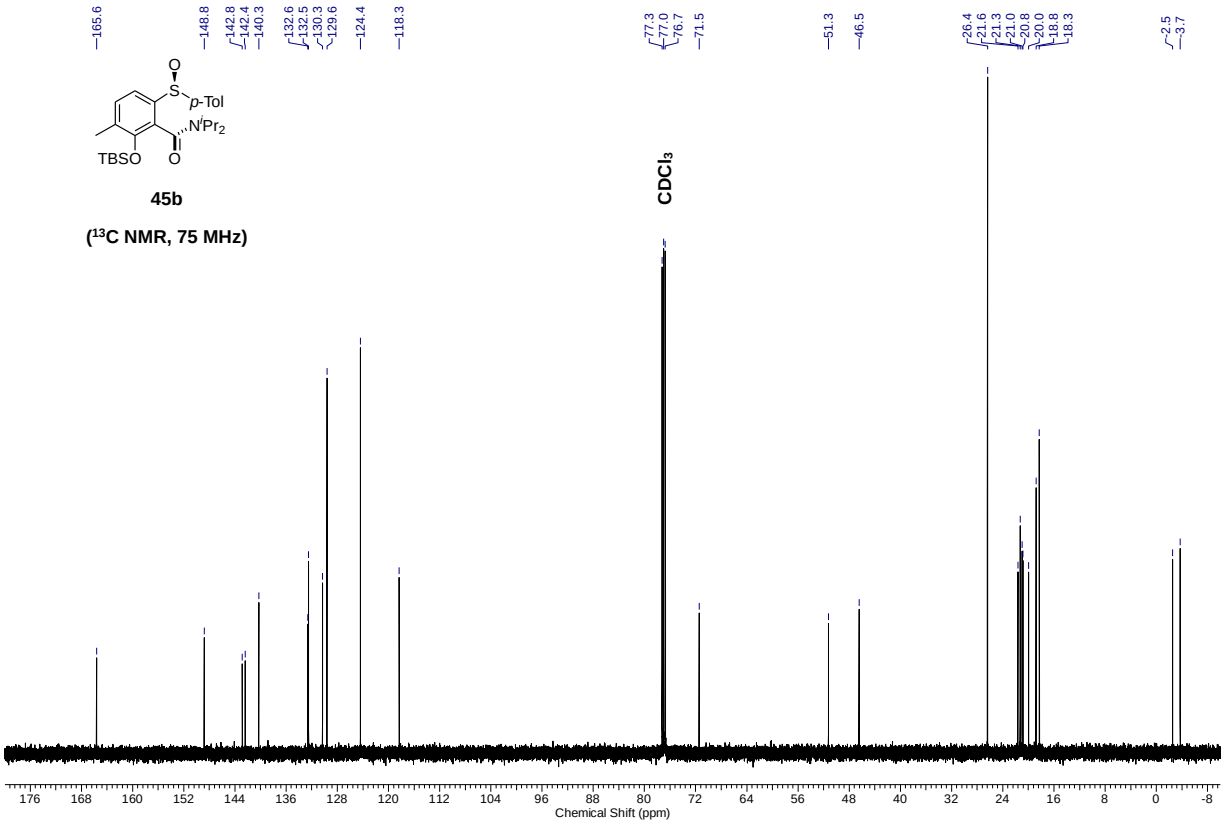
45a

(¹³C NMR, 101 MHz)



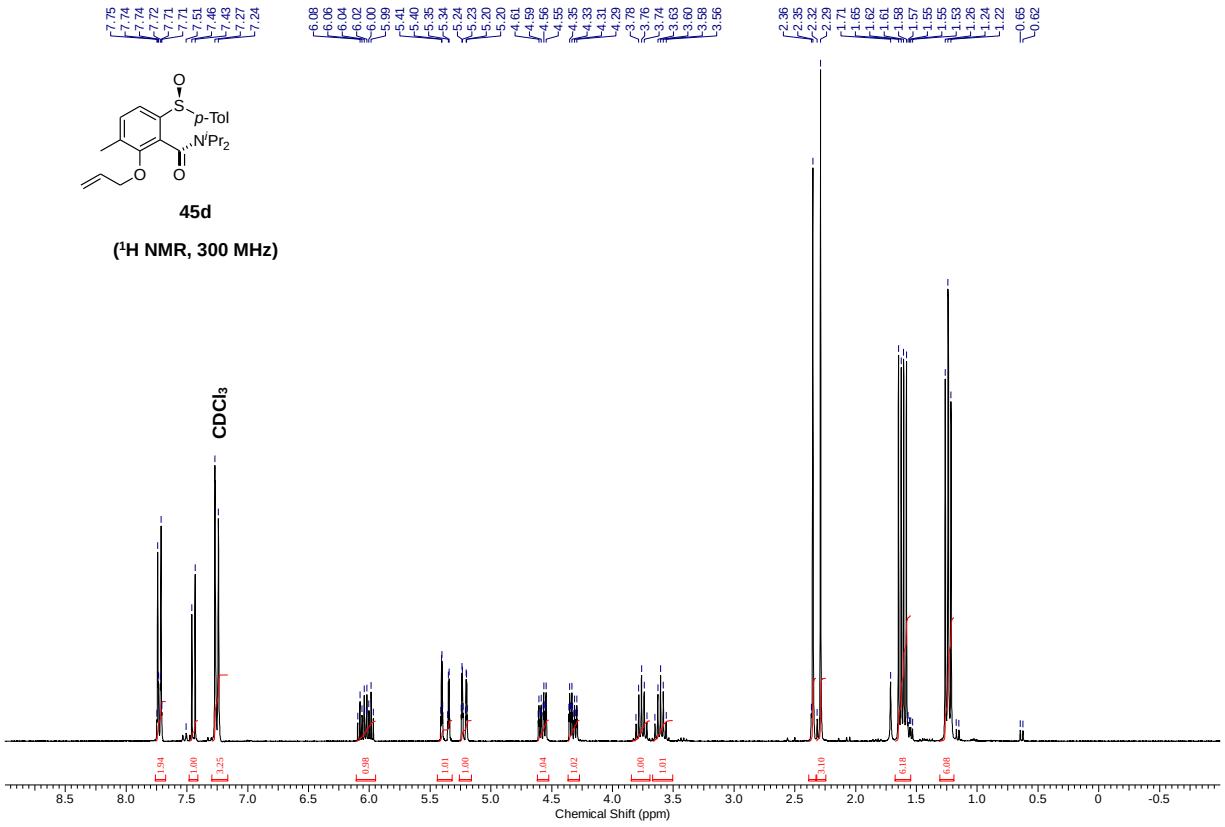
45b

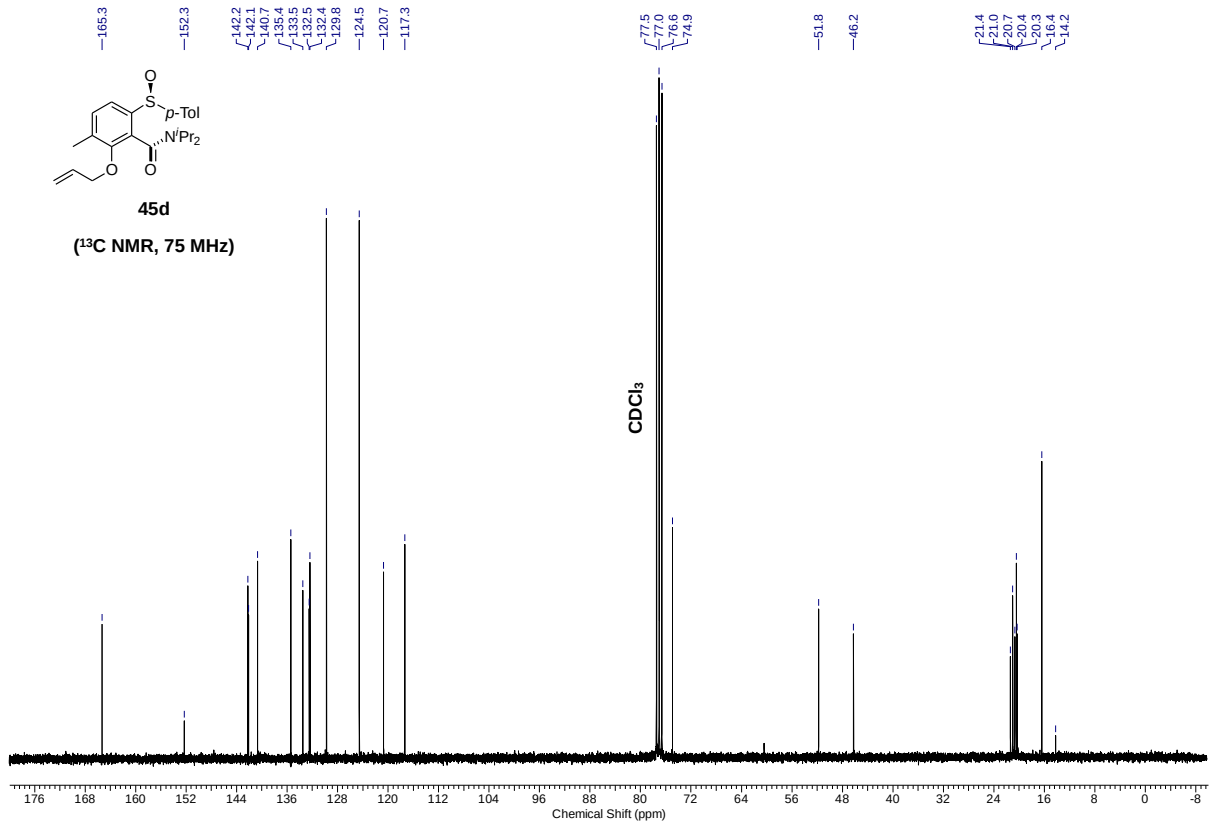
(¹H NMR, 300 MHz)

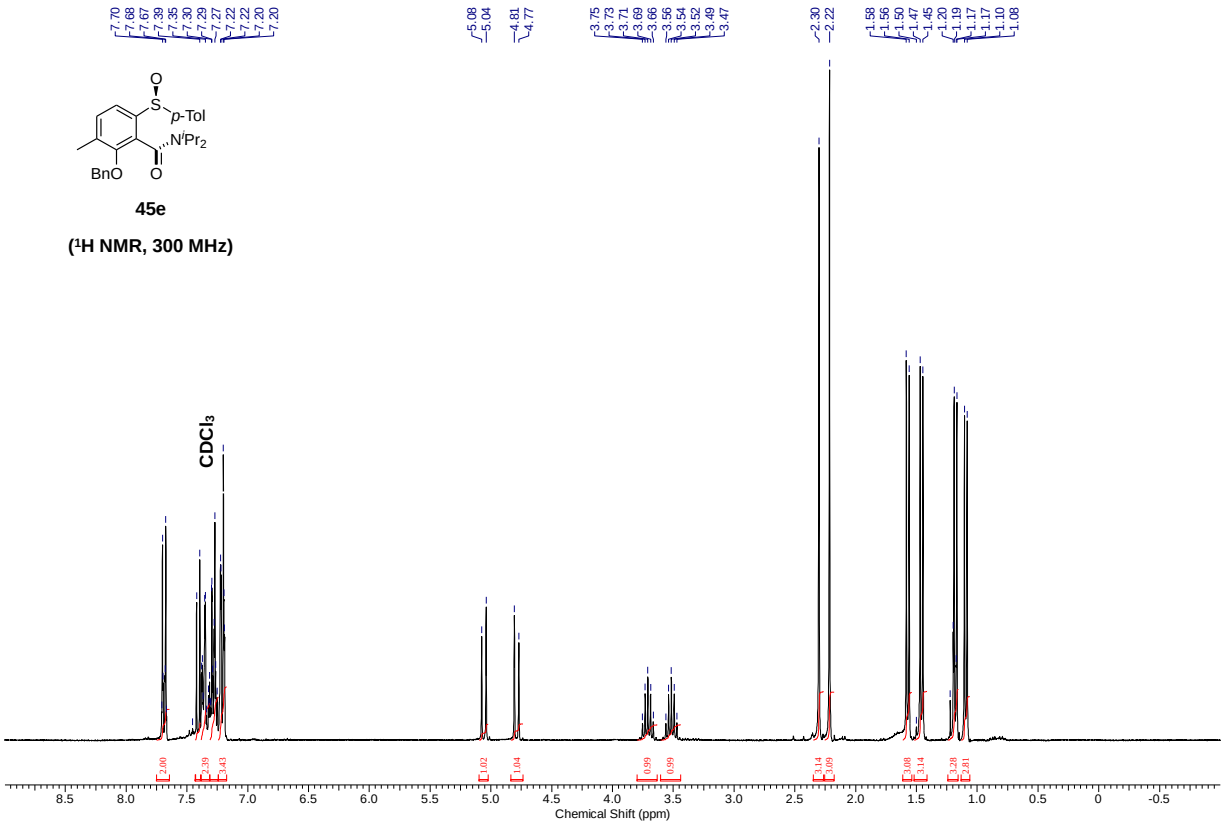


45b

(¹³C NMR, 75 MHz)

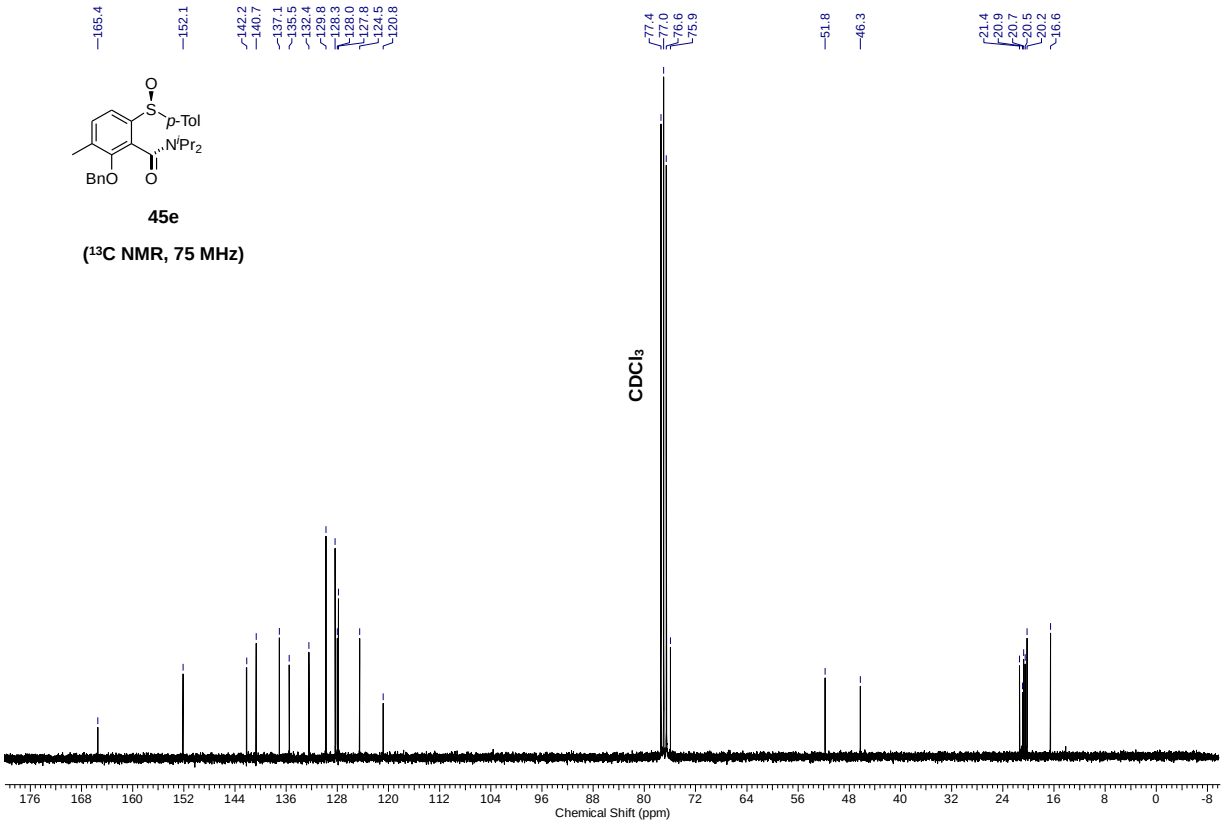

45d
(1H NMR, 300 MHz)
CDCl3
Chemical Shift (ppm)


45d
(13C NMR, 75 MHz)
CDCl3
Chemical Shift (ppm)



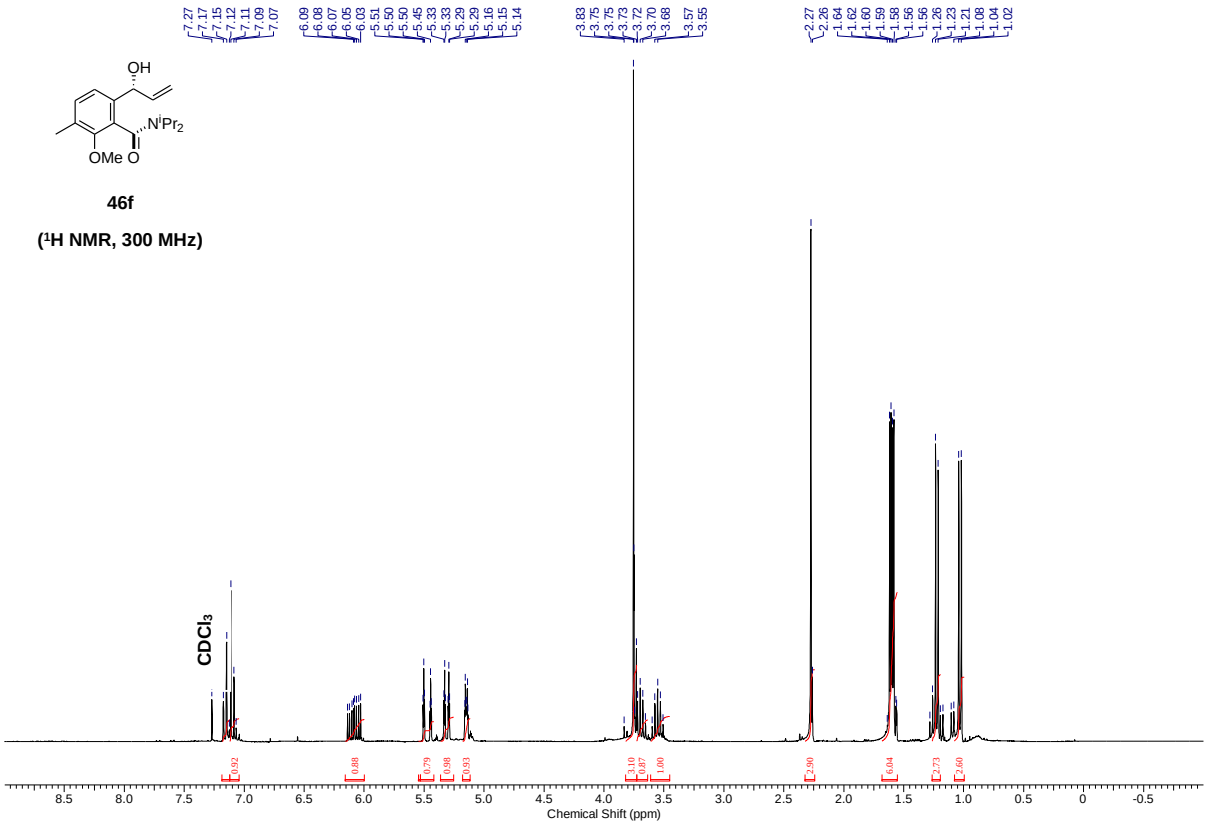
45e

(^{1}H NMR, 300 MHz)



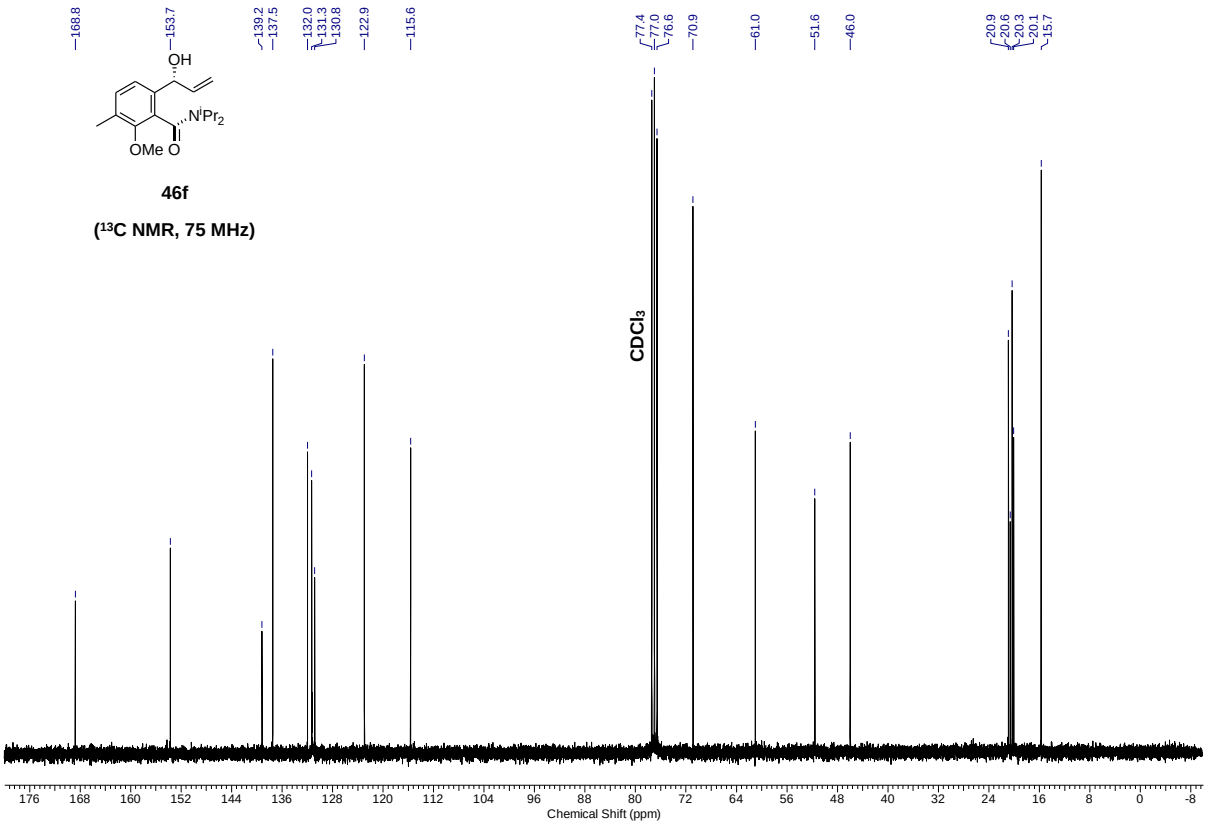
45e

(^{13}C NMR, 75 MHz)



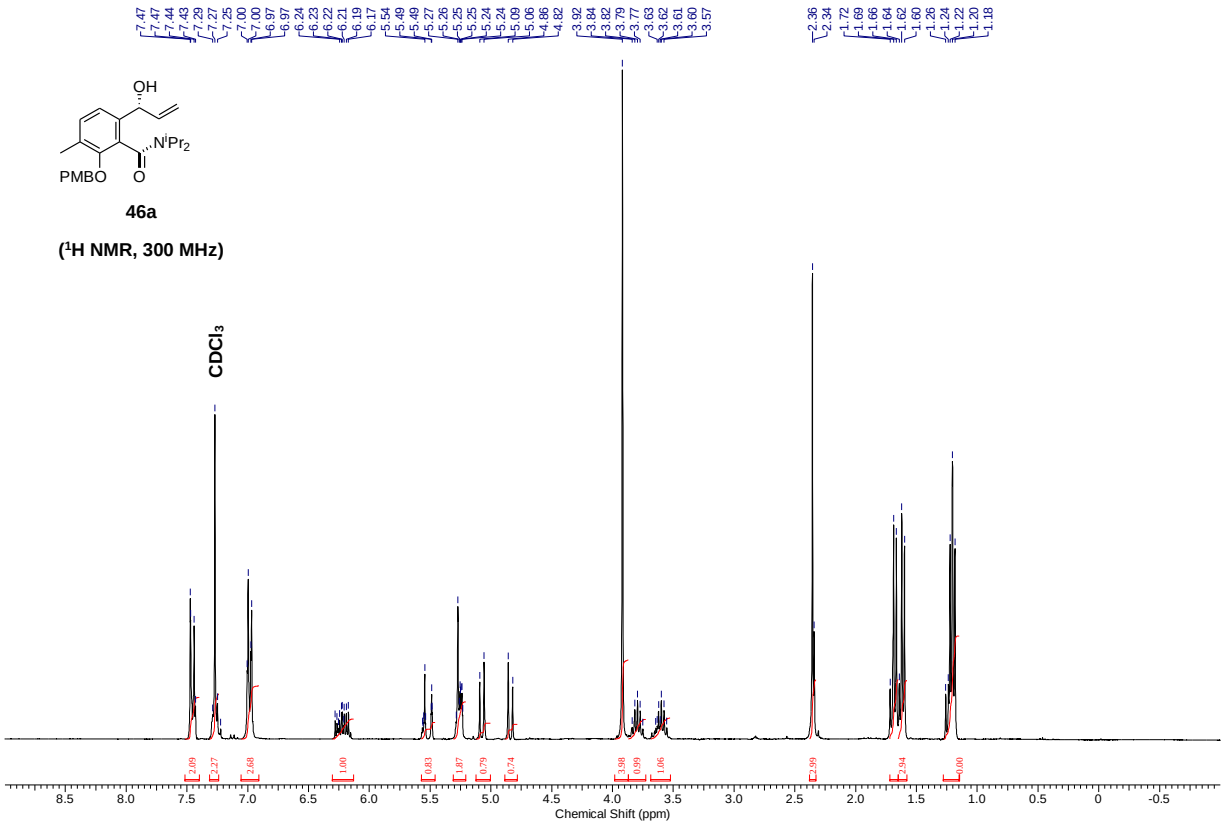
46f

(^{1}H NMR, 300 MHz)



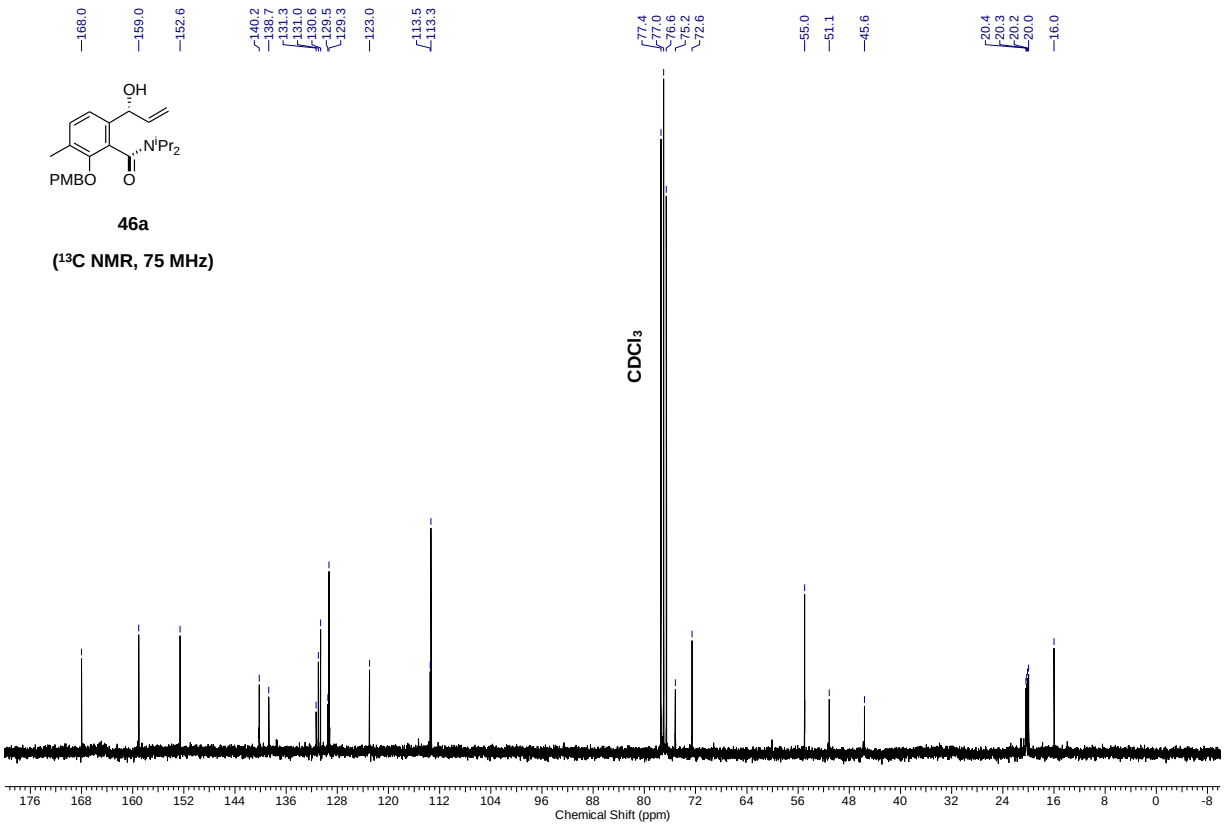
46f

(^{13}C NMR, 75 MHz)



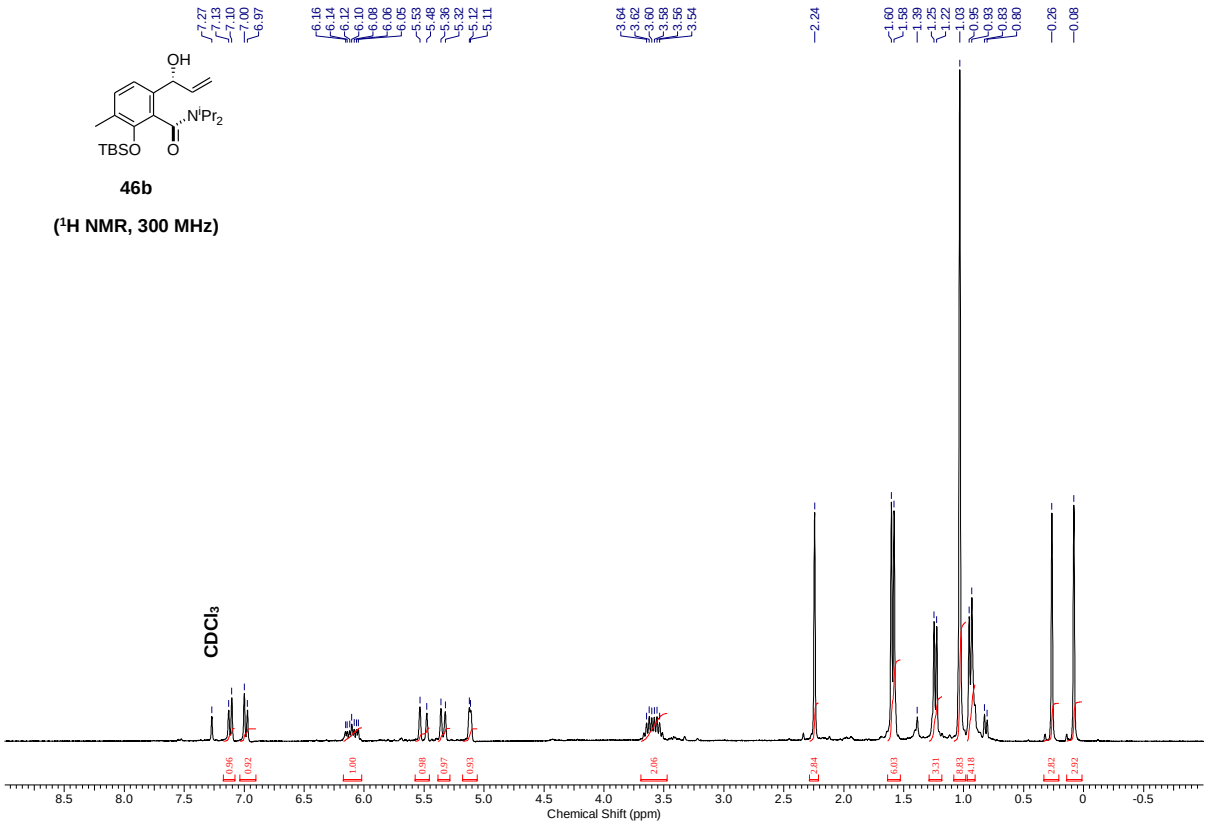
46a

(^{1}H NMR, 300 MHz)



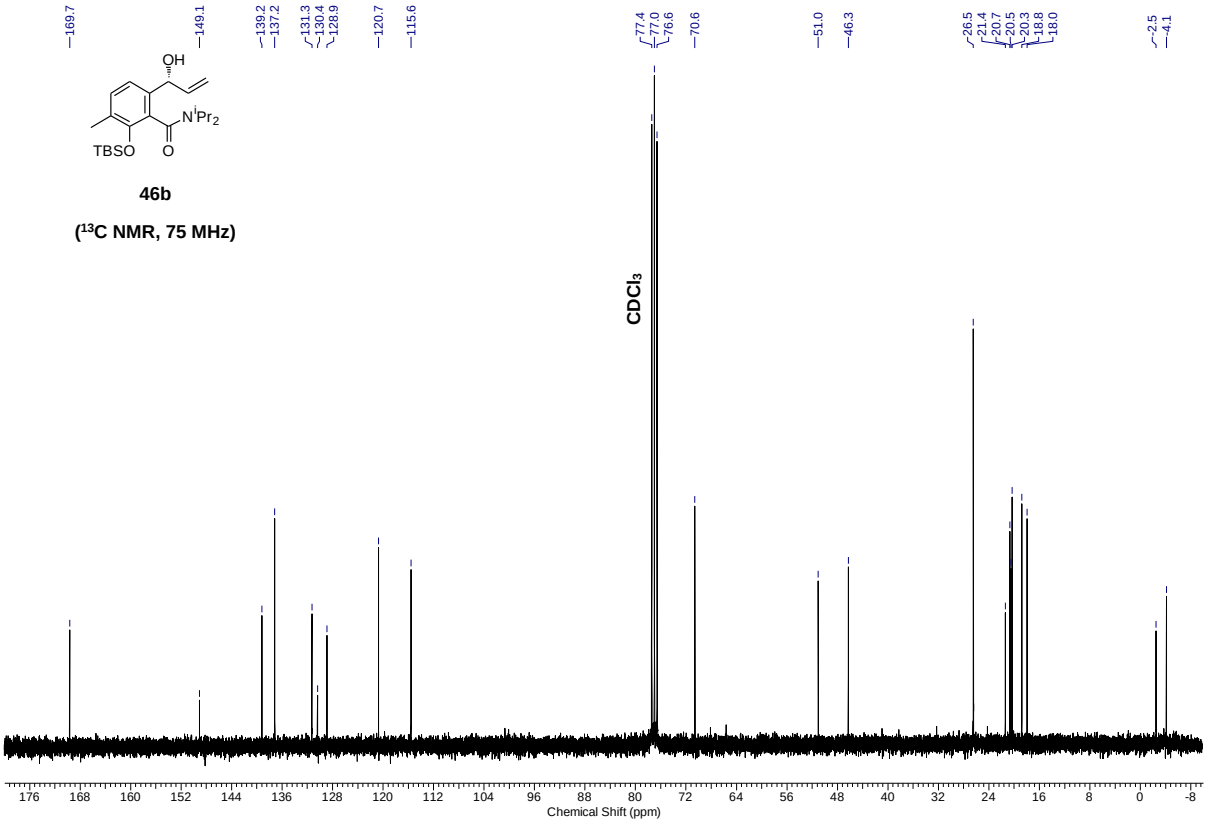
46a

(^{13}C NMR, 75 MHz)



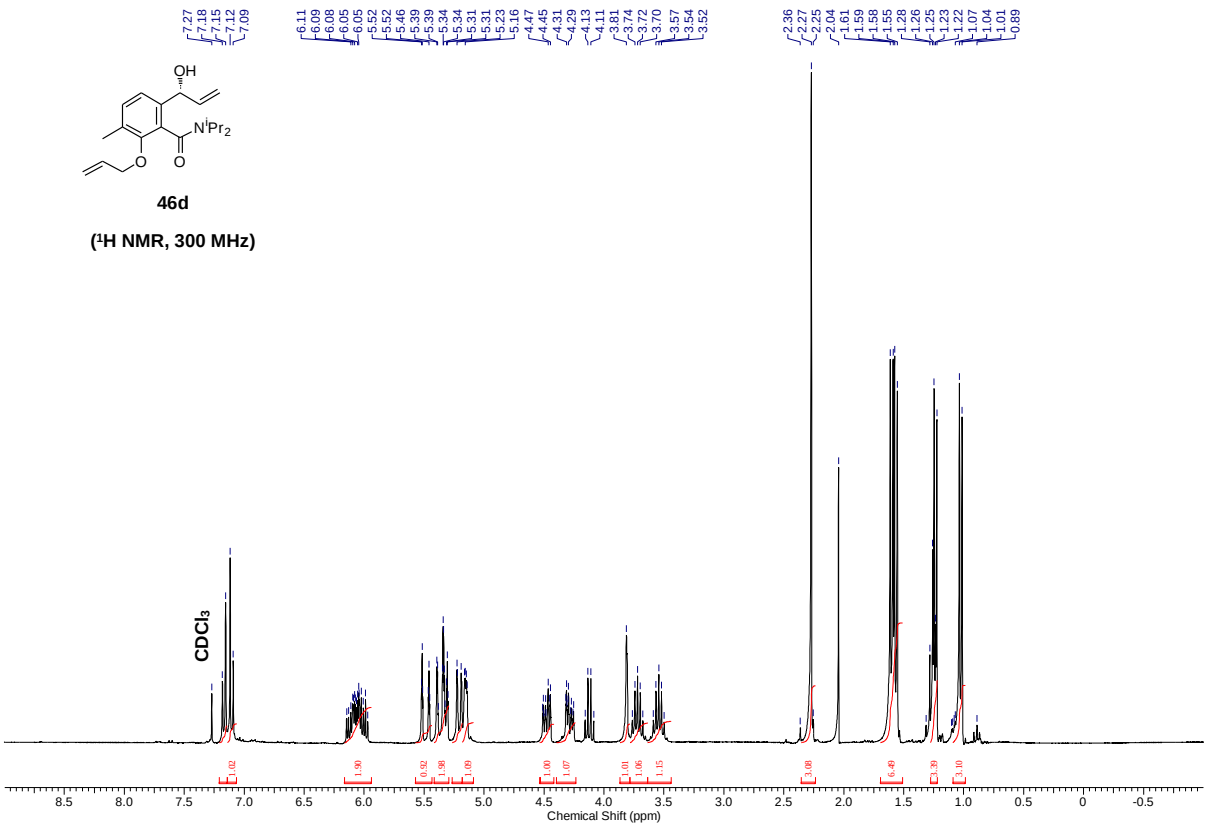
46b

(^{1}H NMR, 300 MHz)



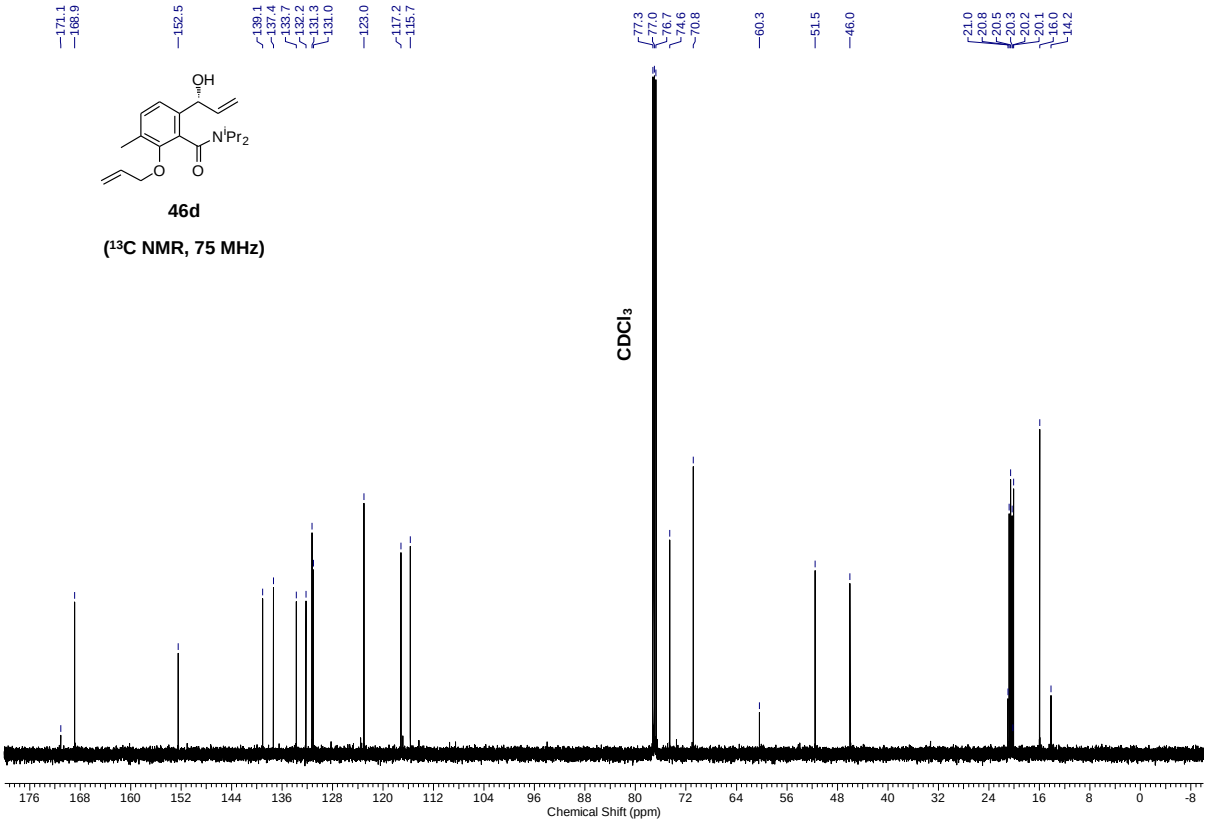
46b

(^{13}C NMR, 75 MHz)



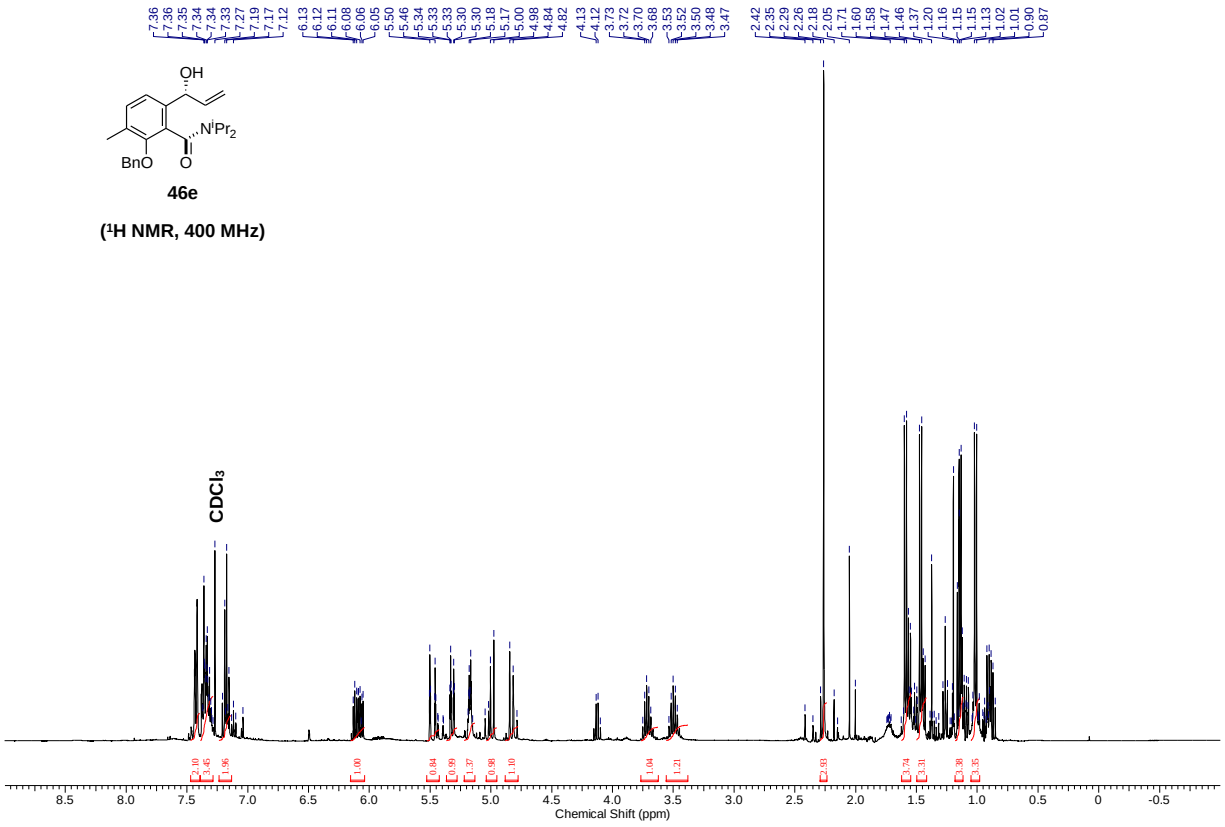
46d

(^{1}H NMR, 300 MHz)



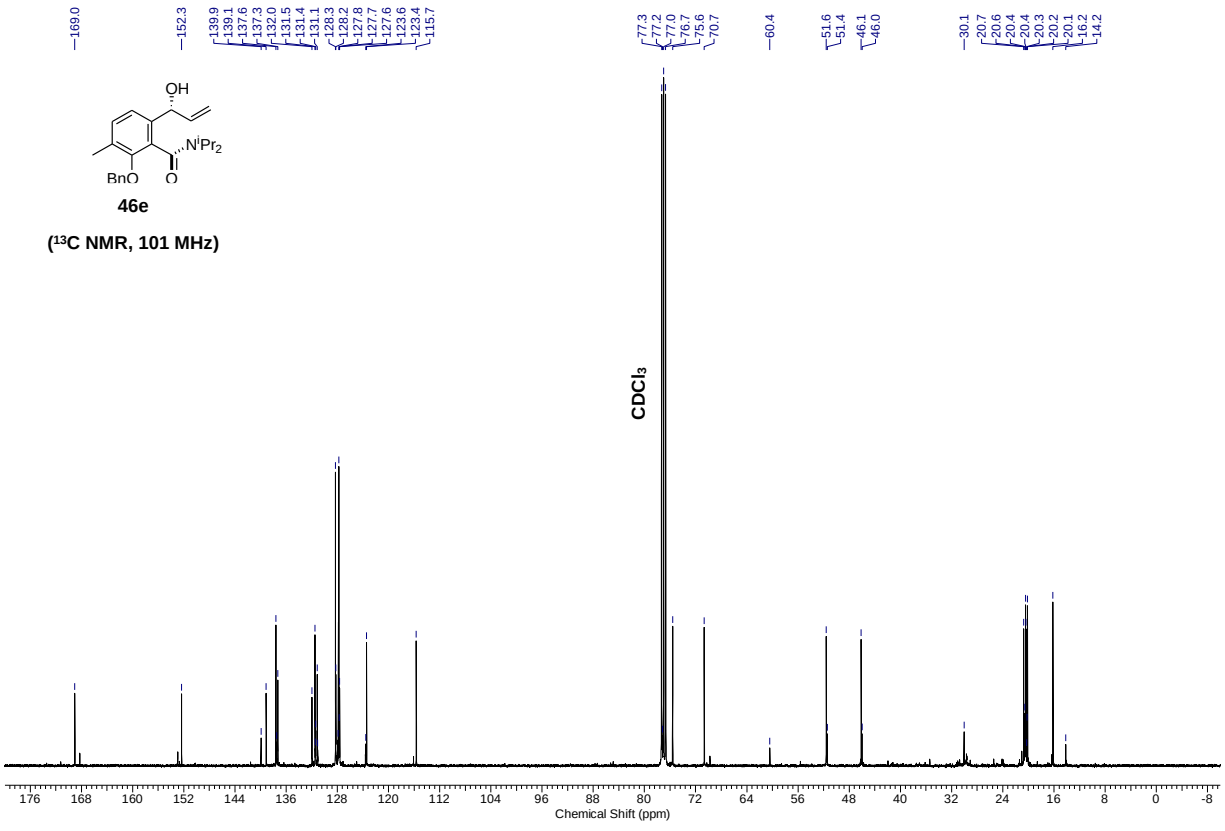
46d

(^{13}C NMR, 75 MHz)



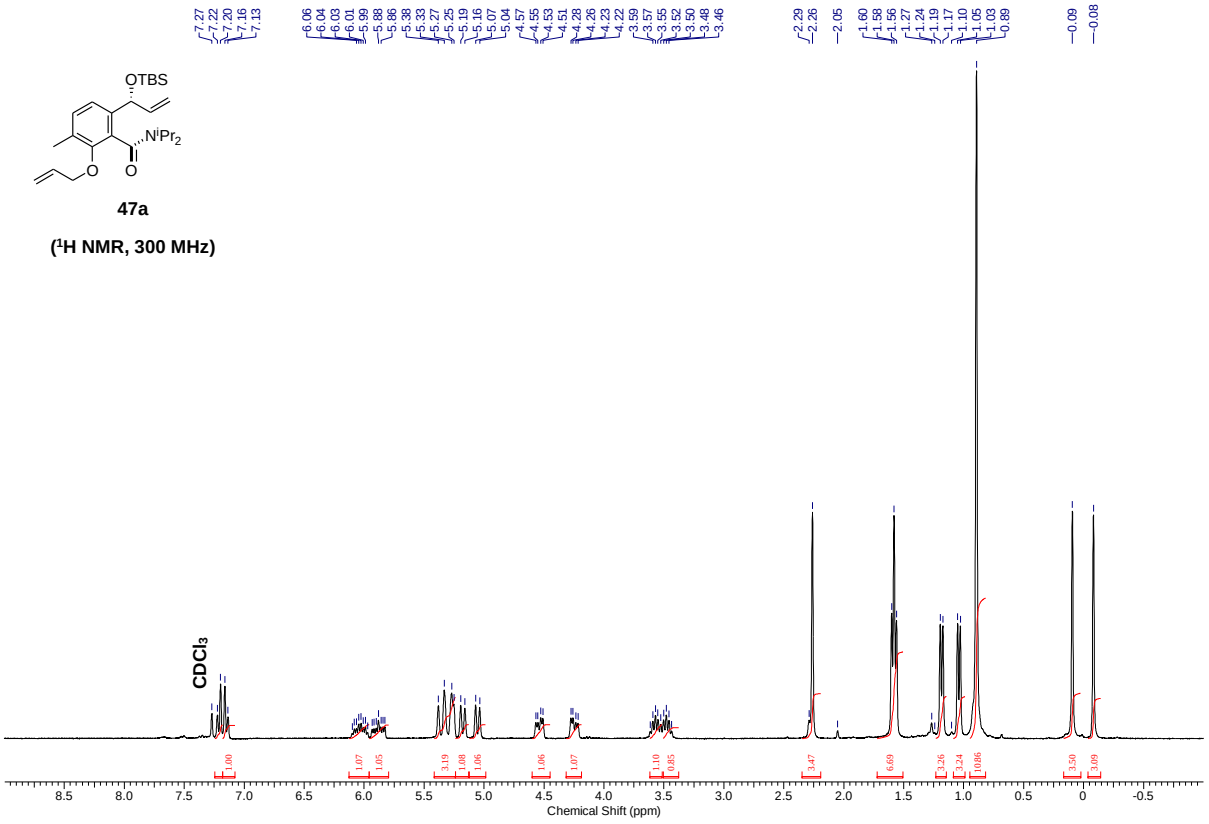
46e

(^{1}H NMR, 400 MHz)



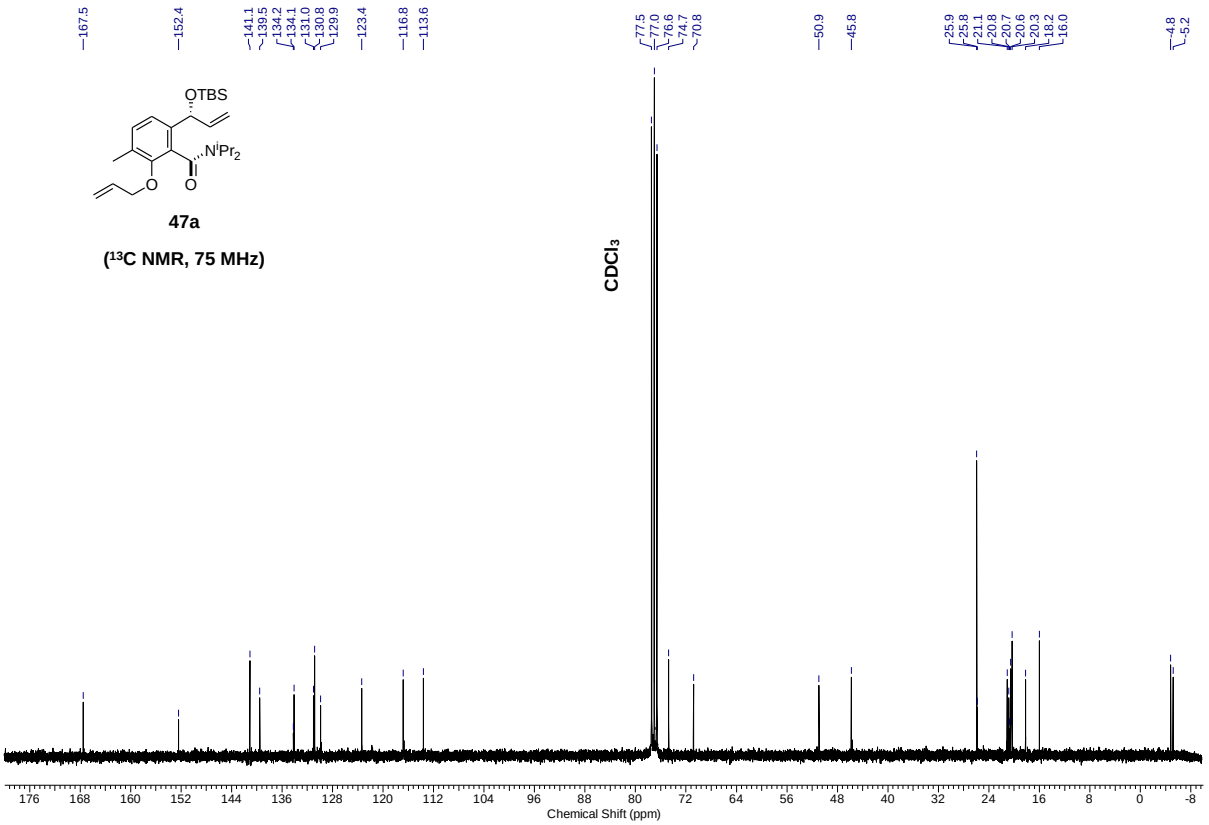
46e

(^{13}C NMR, 101 MHz)



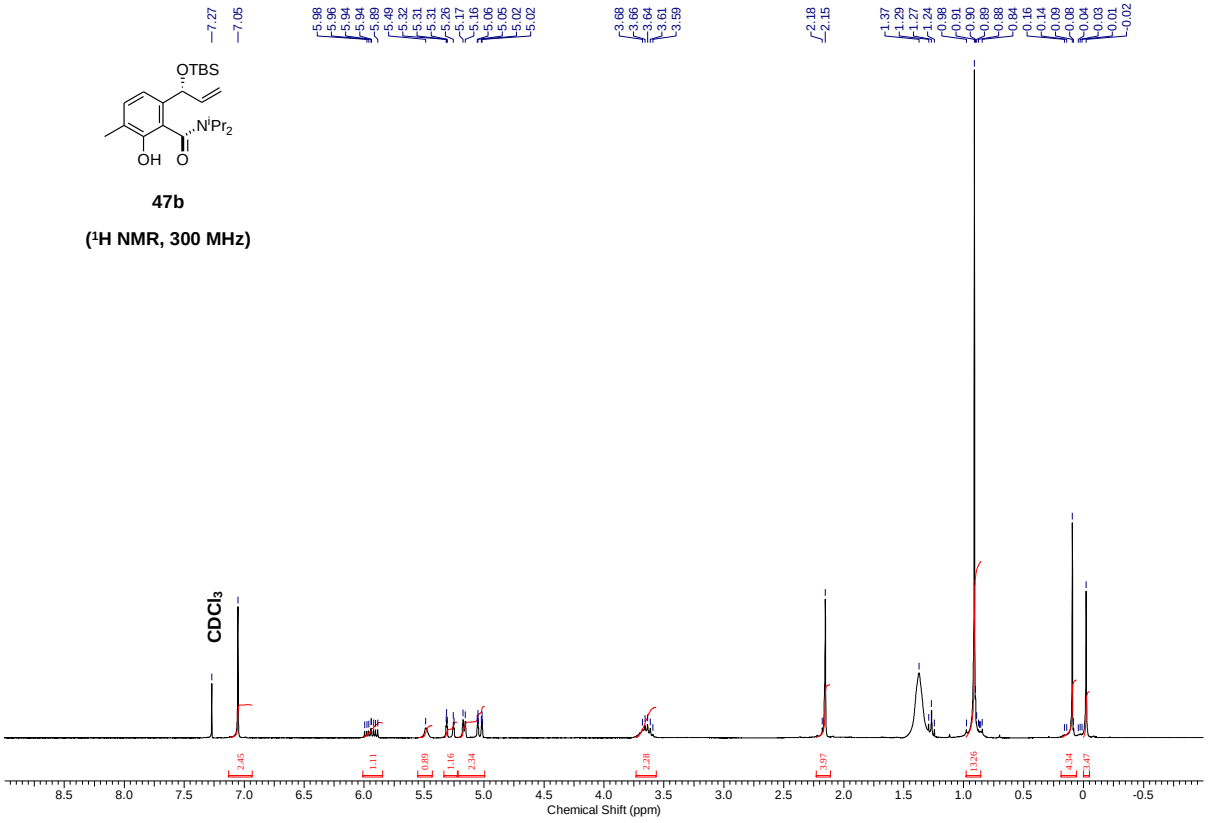
47a

(^{1}H NMR, 300 MHz)



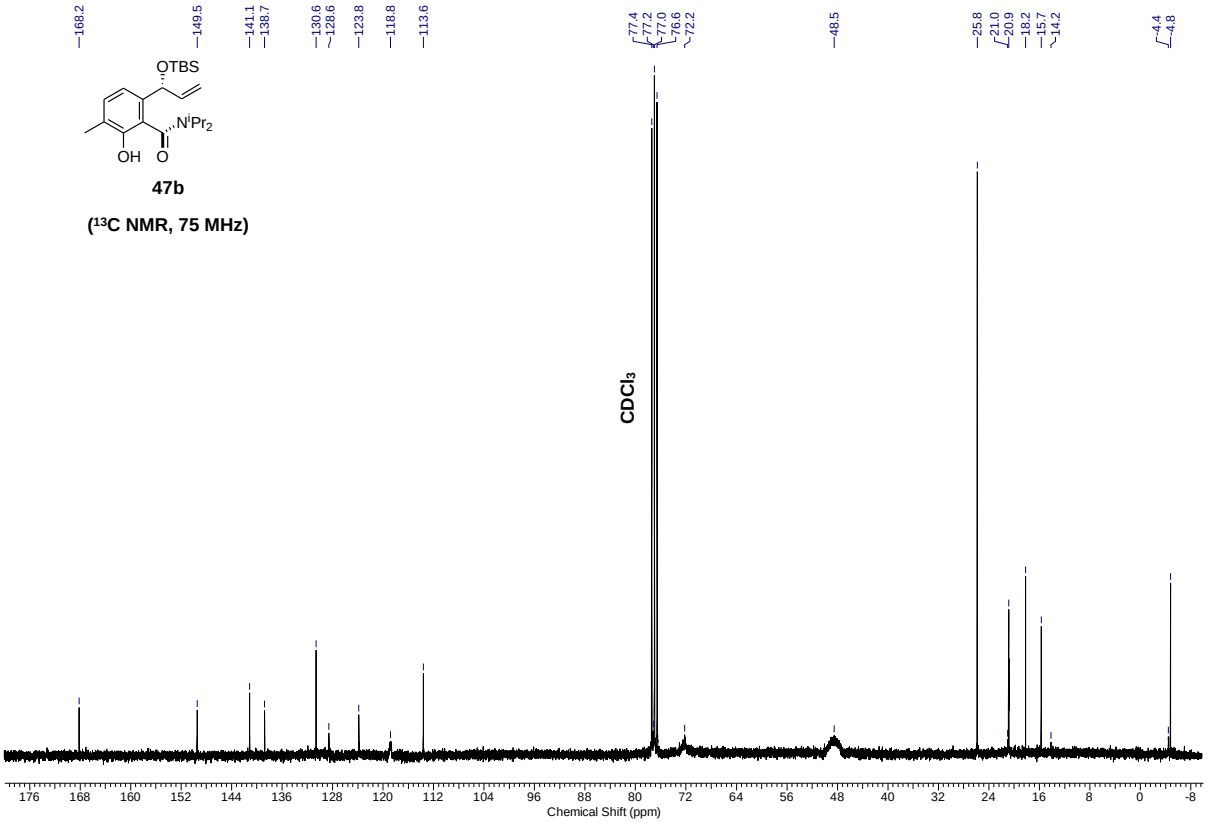
47a

(^{13}C NMR, 75 MHz)



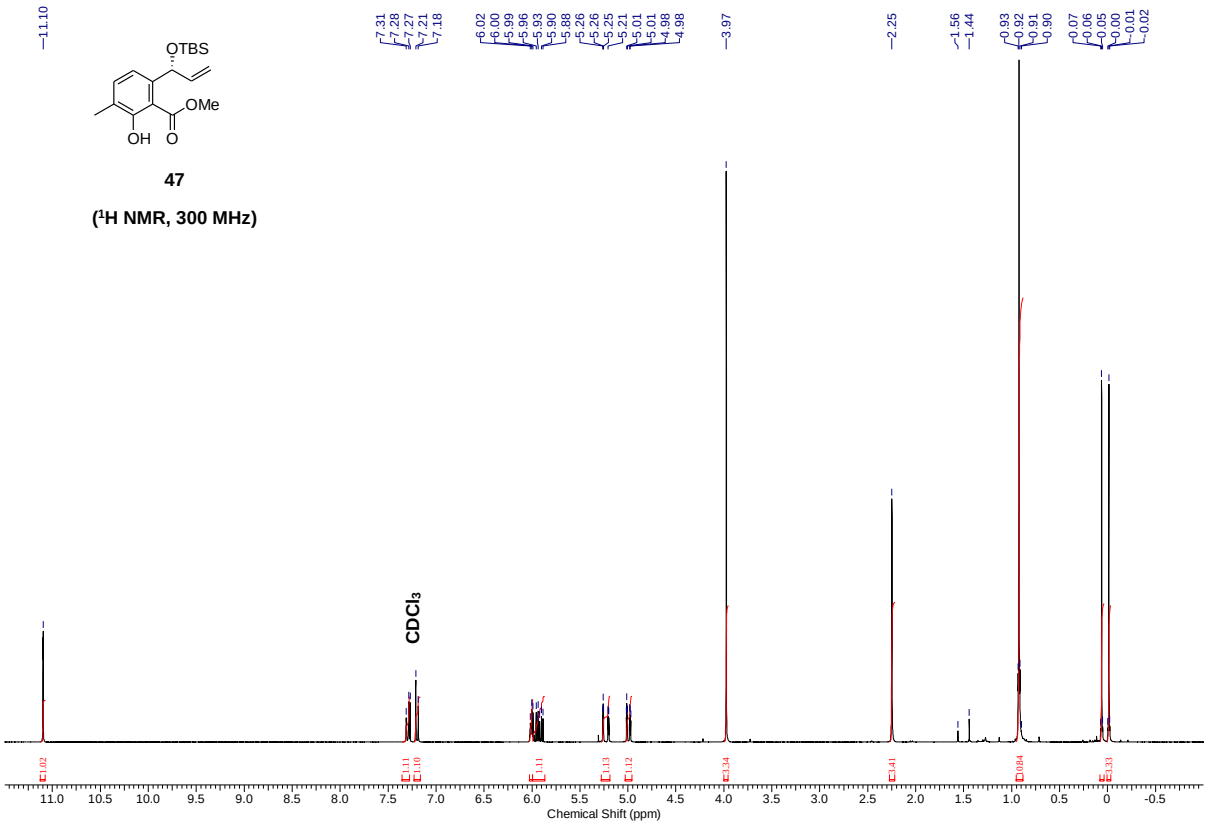
47b

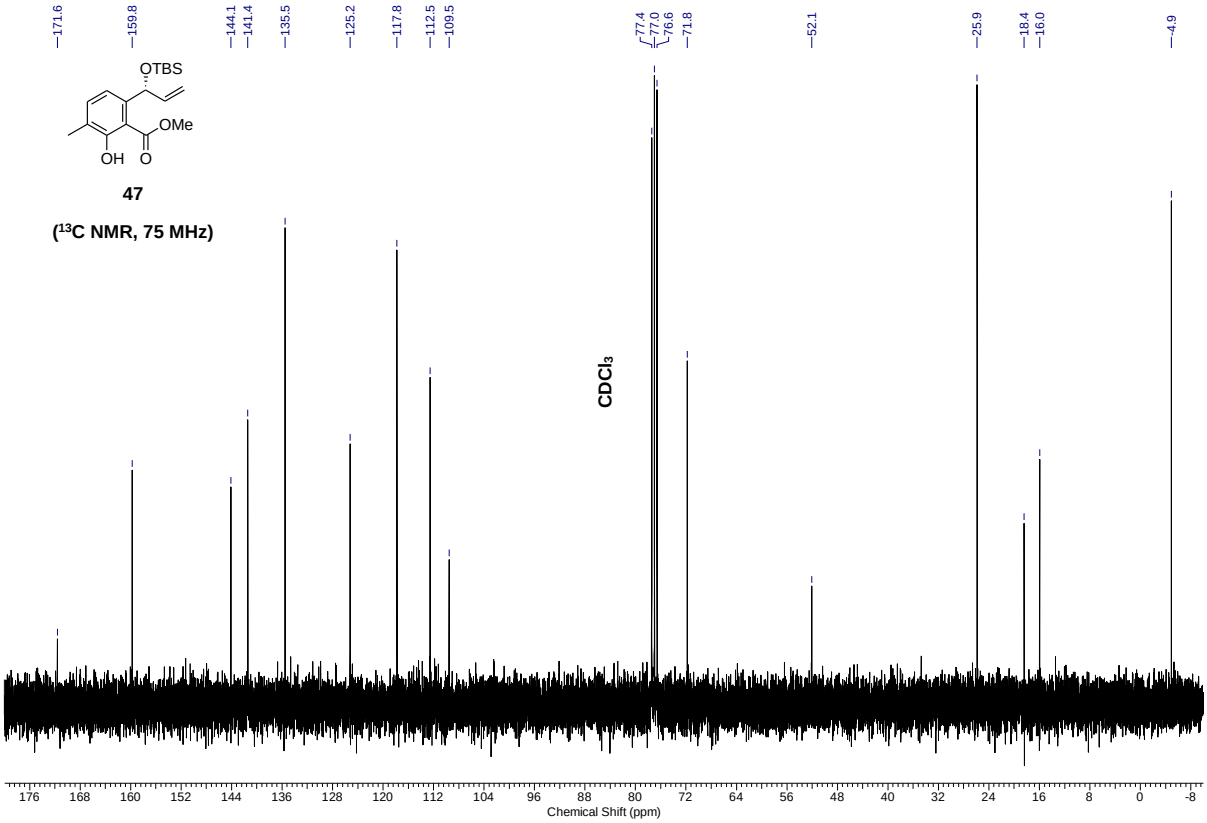
(^{1}H NMR, 300 MHz)

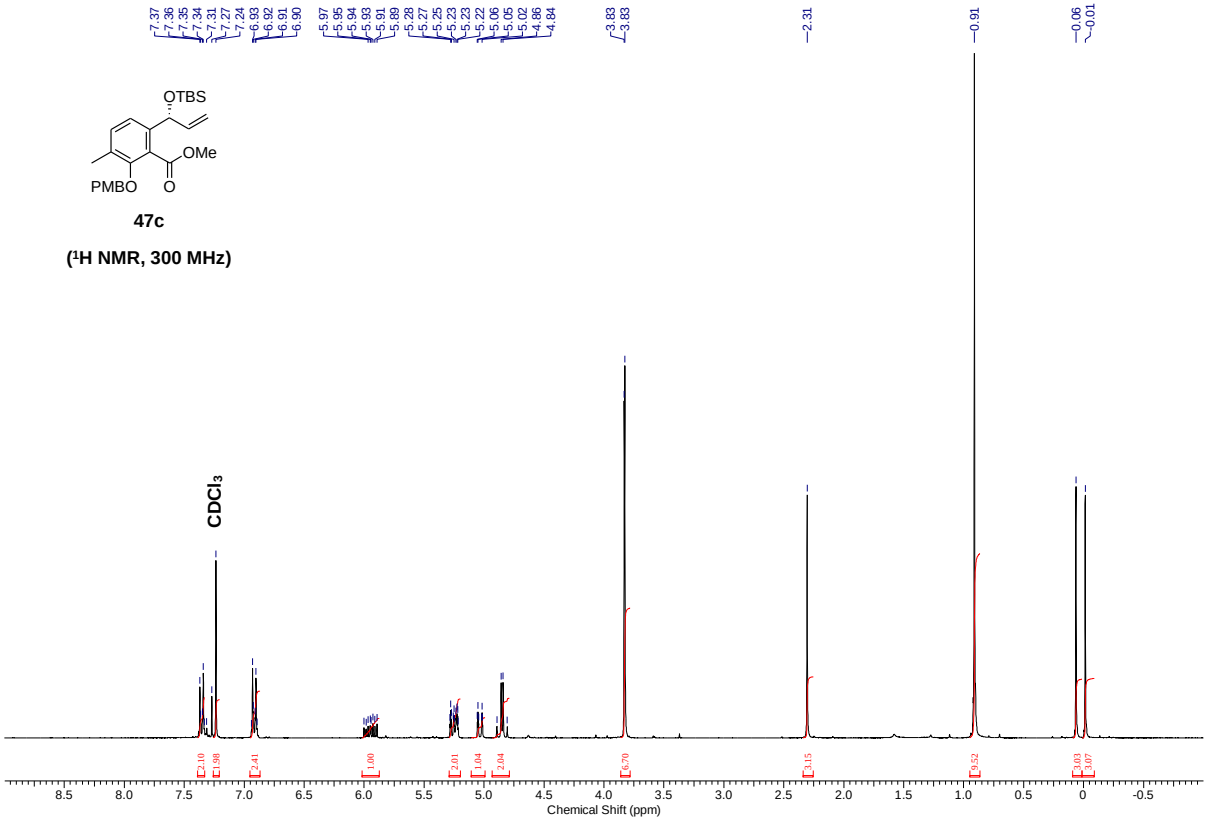


47b

(^{13}C NMR, 75 MHz)

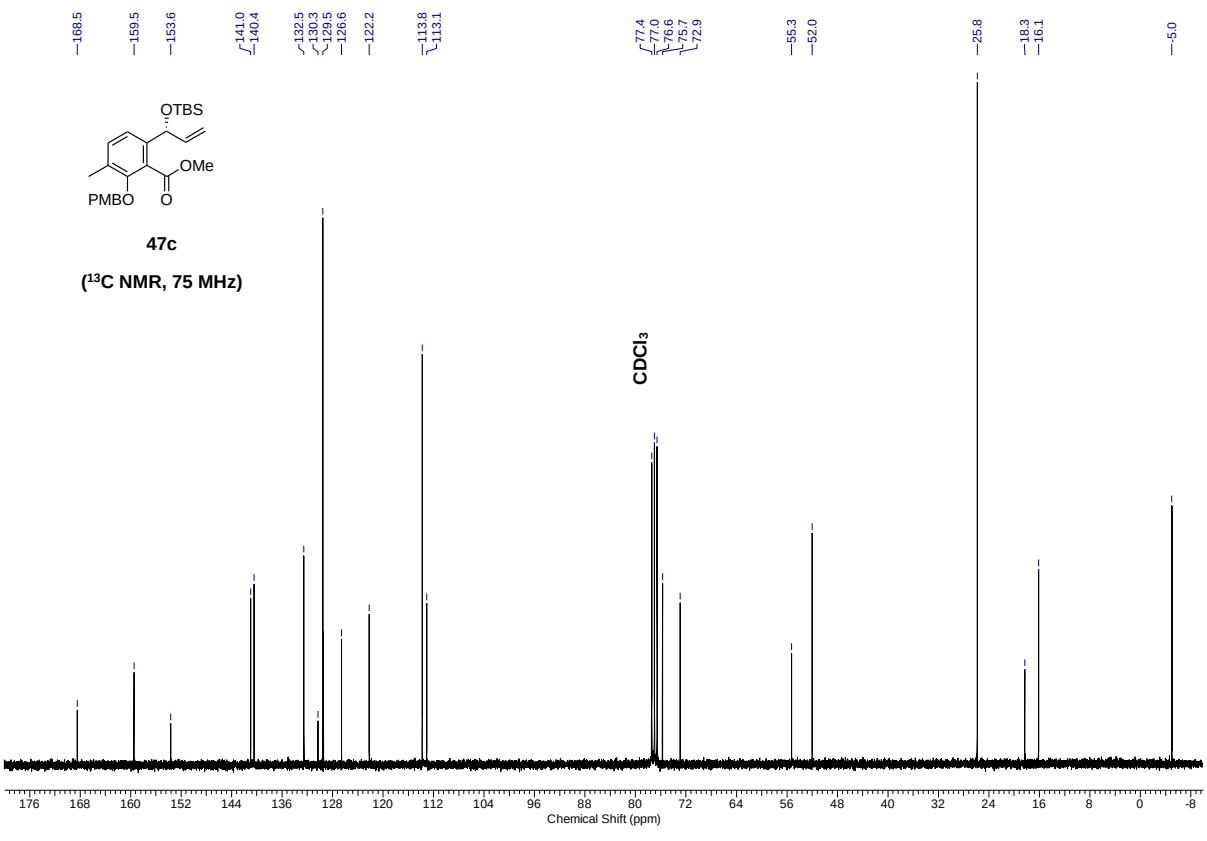

OTBS
OMe
OH O
47
(1H NMR, 300 MHz)
CDCl3
Chemical Shift (ppm)


OTBS
OMe
OH O
47
(13C NMR, 75 MHz)
CDCl3
Chemical Shift (ppm)



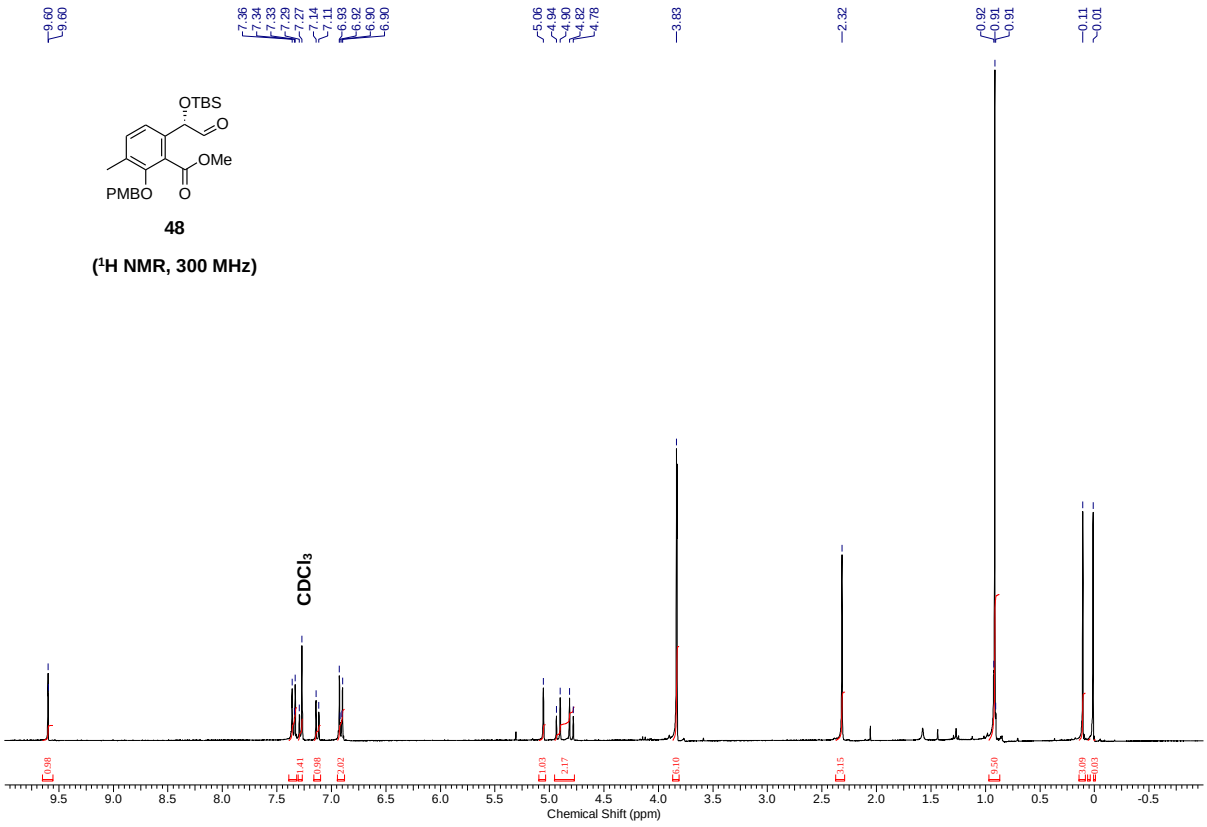
47c

(^{1}H NMR, 300 MHz)



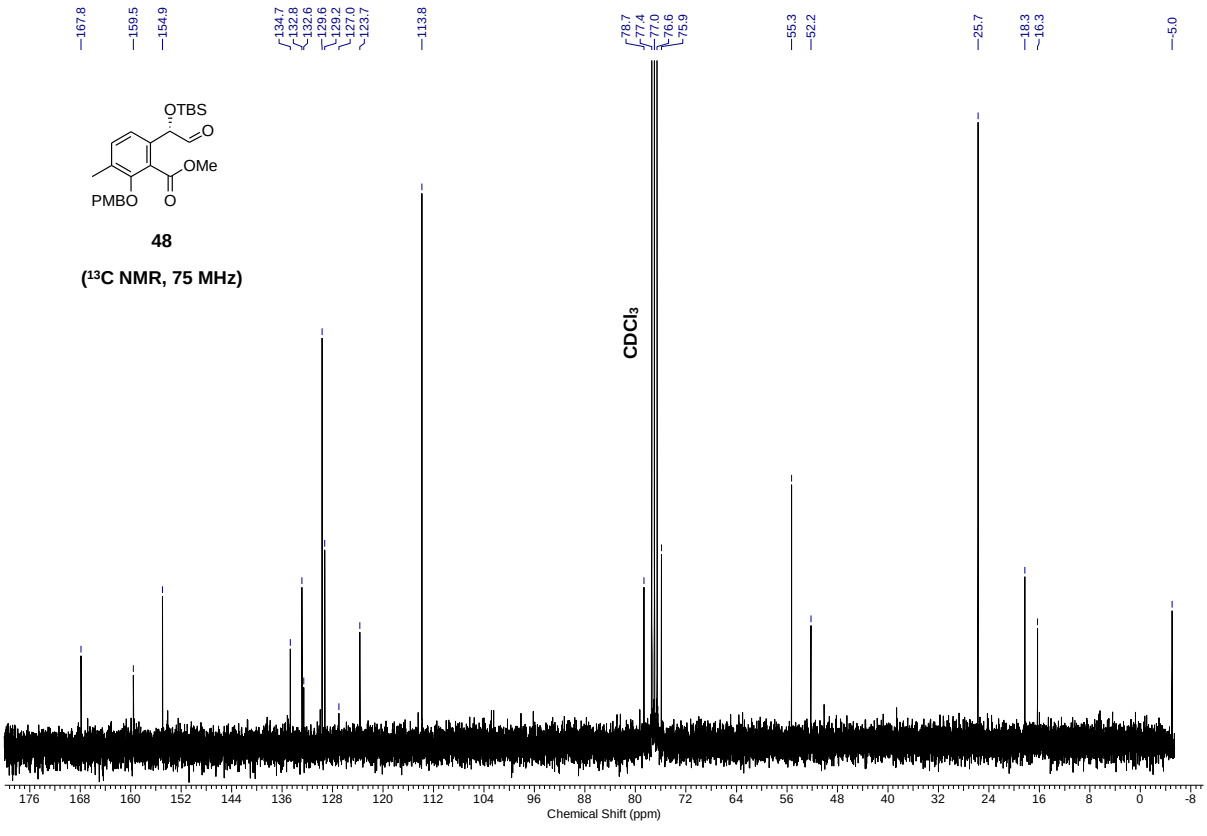
47c

(^{13}C NMR, 75 MHz)



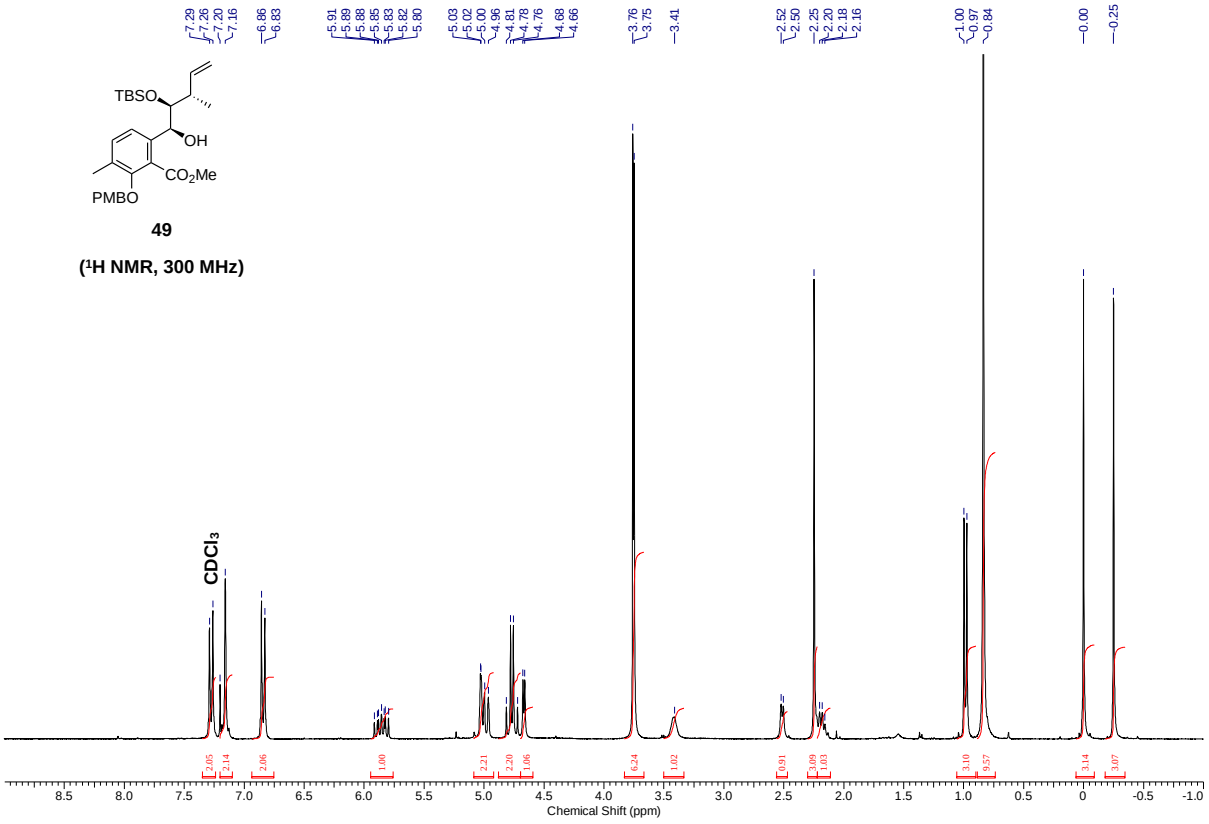
48

(^{1}H NMR, 300 MHz)



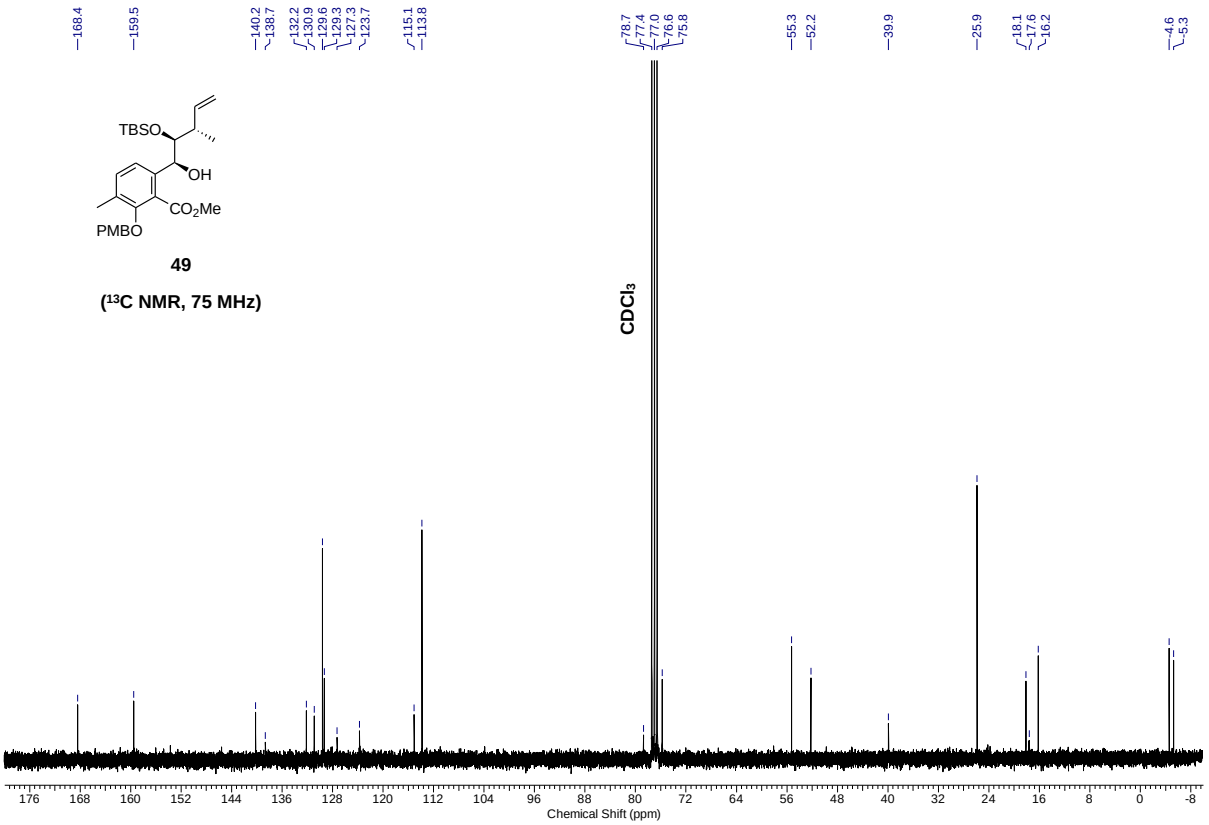
48

(^{13}C NMR, 75 MHz)



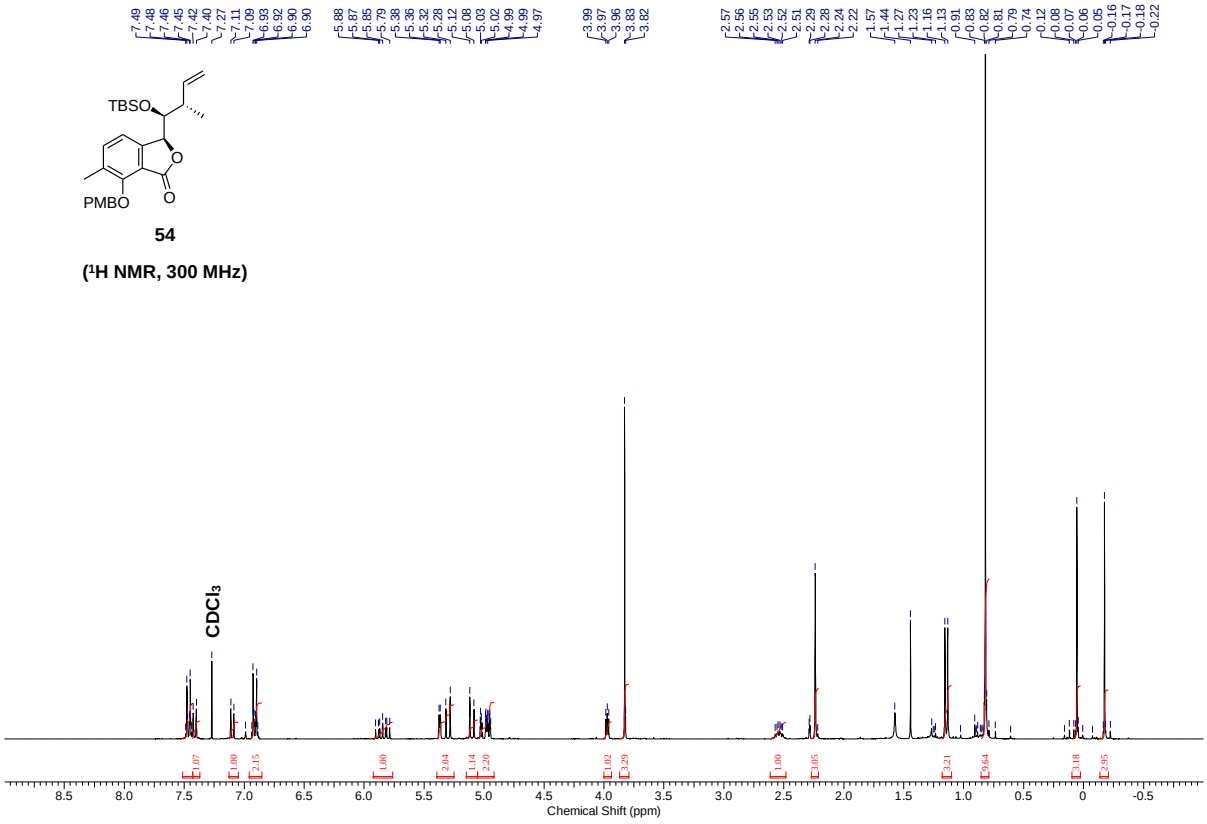
49

(^{1}H NMR, 300 MHz)



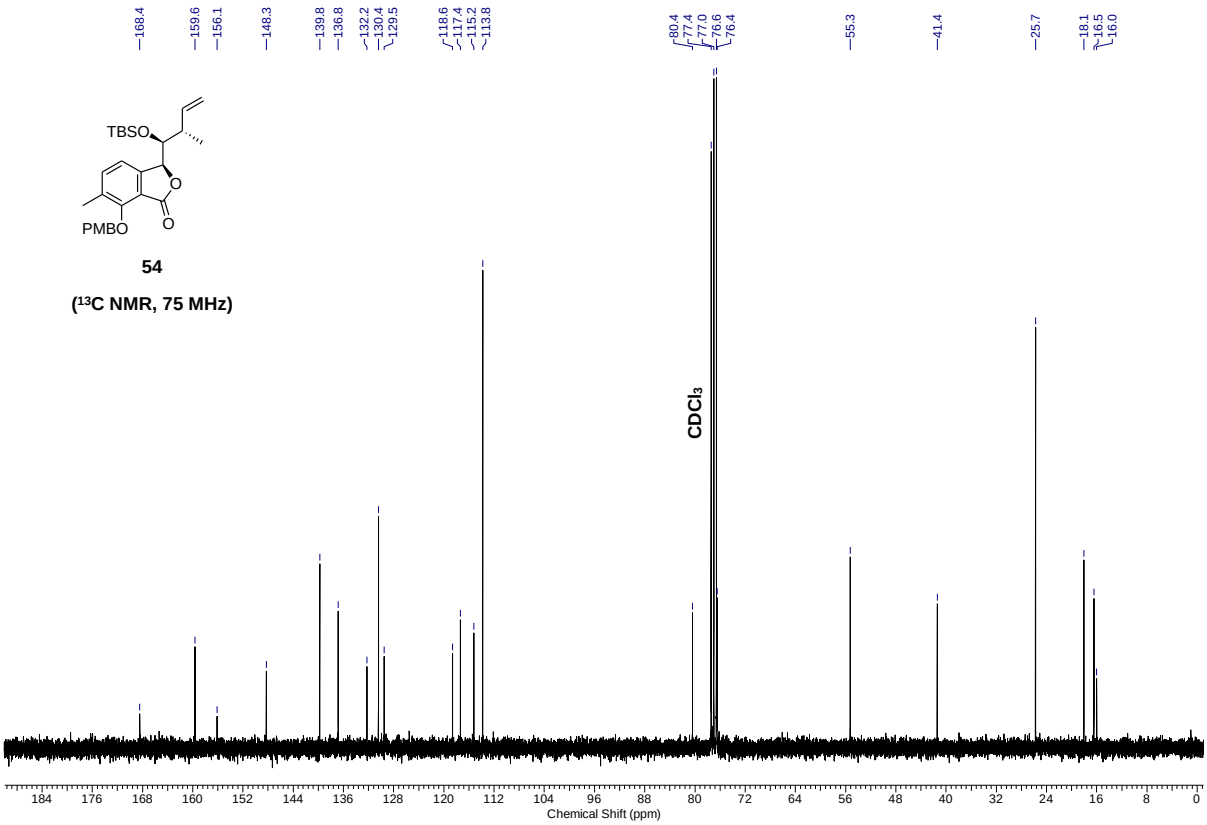
49

(^{13}C NMR, 75 MHz)



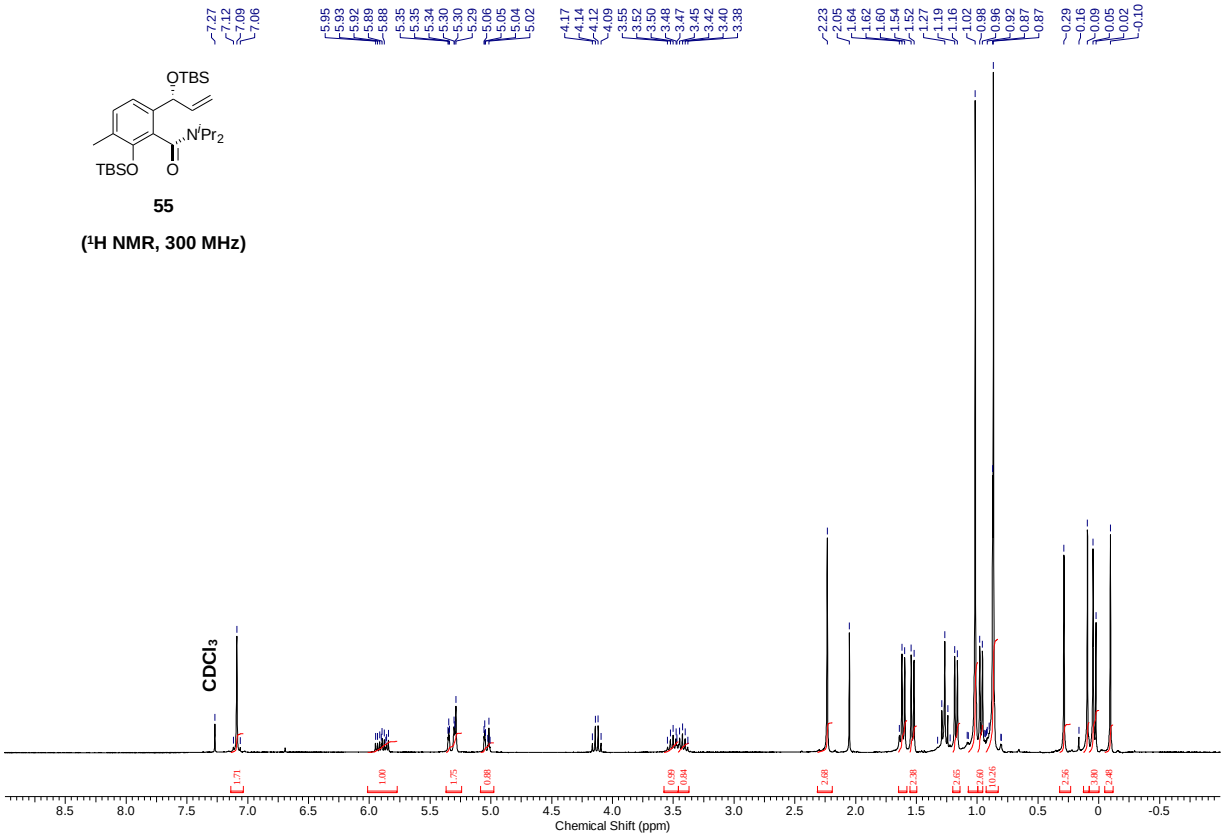
54

(^{1}H NMR, 300 MHz)



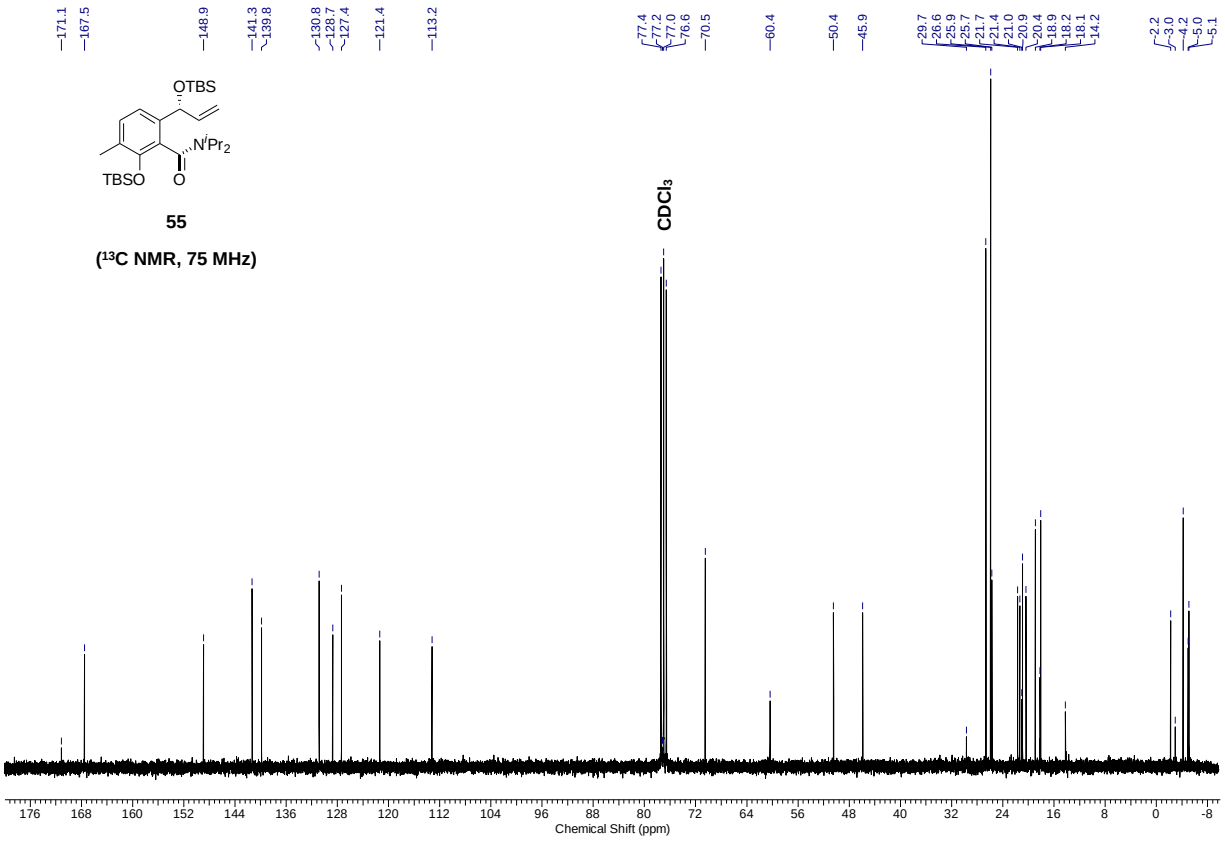
54

(^{13}C NMR, 75 MHz)



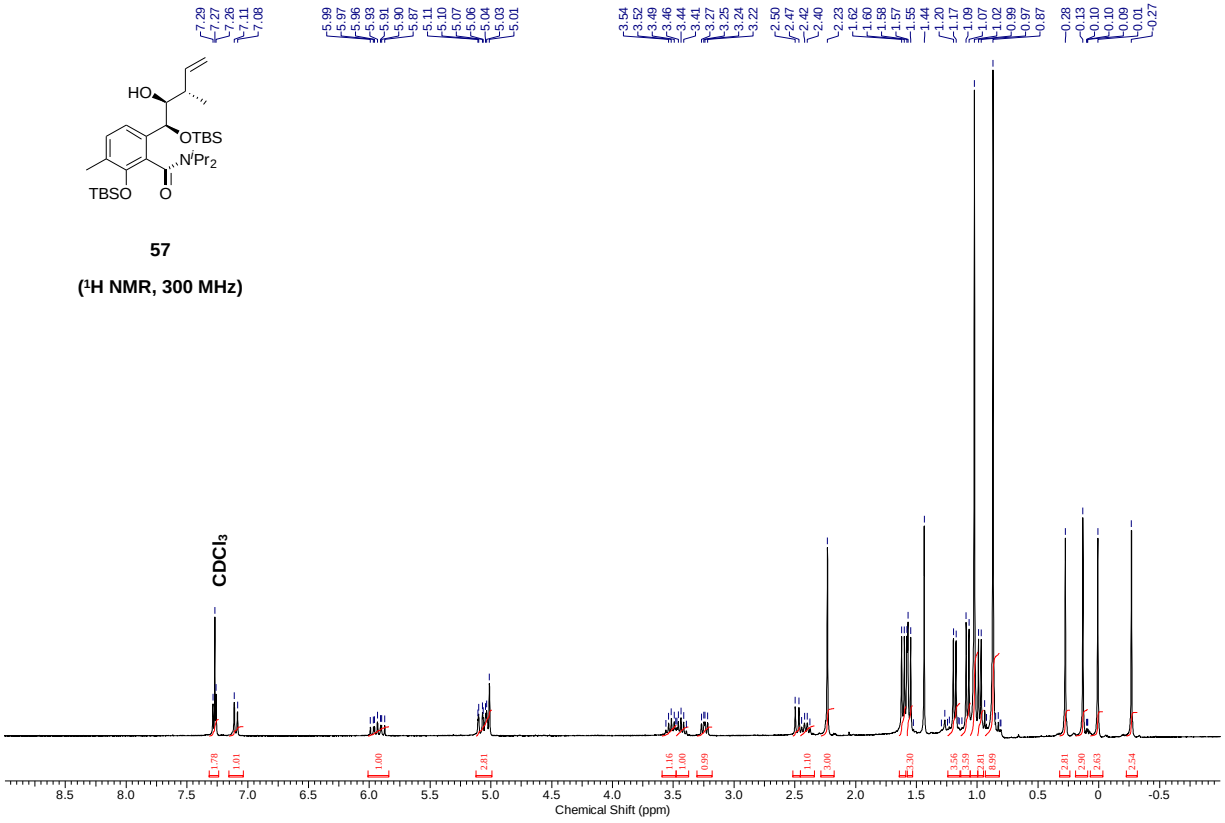
55

(^{1}H NMR, 300 MHz)



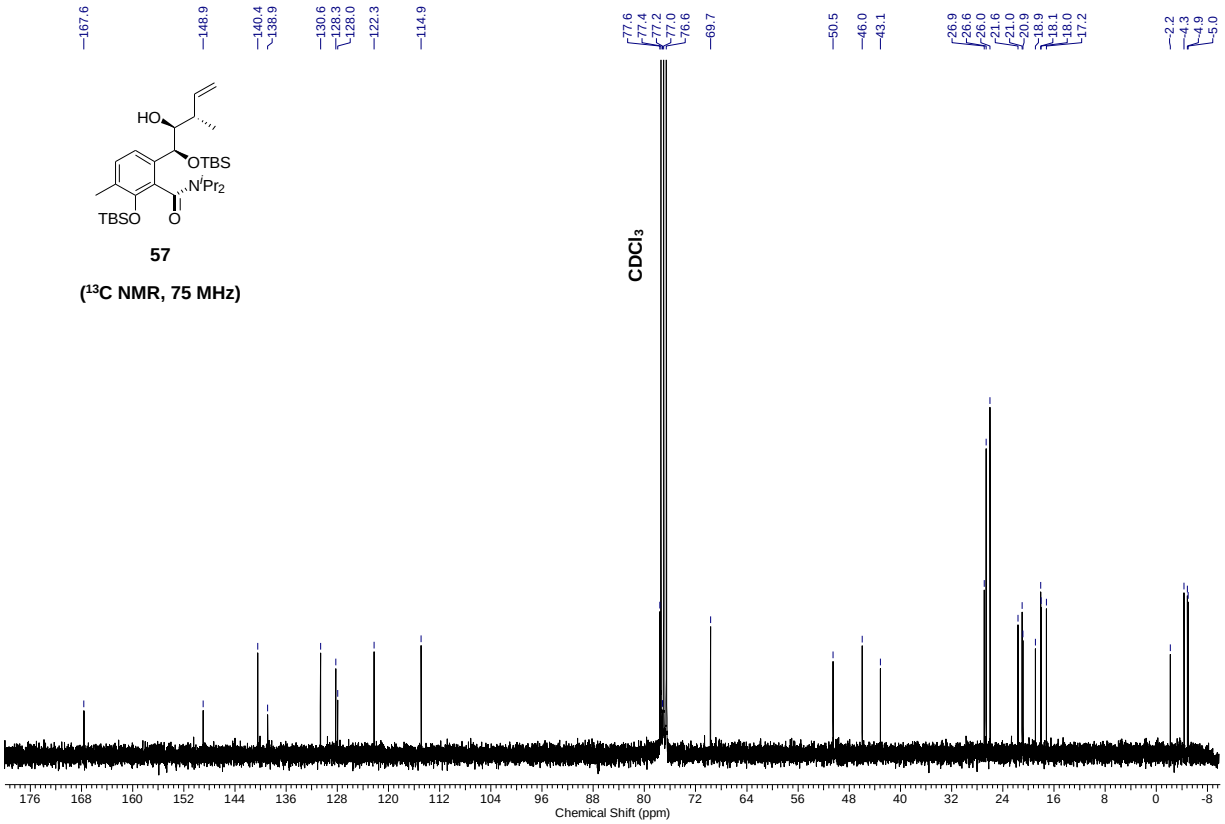
55

(^{13}C NMR, 75 MHz)



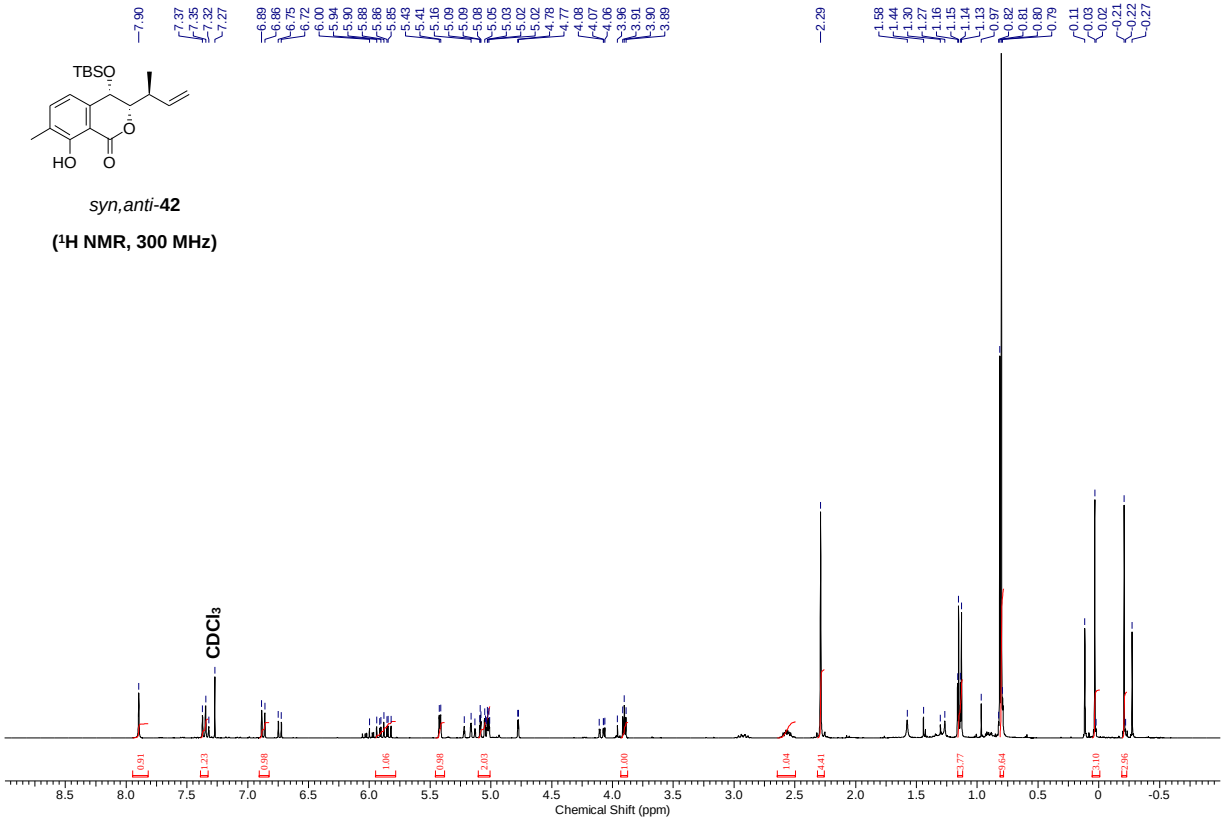
57

(^{1}H NMR, 300 MHz)



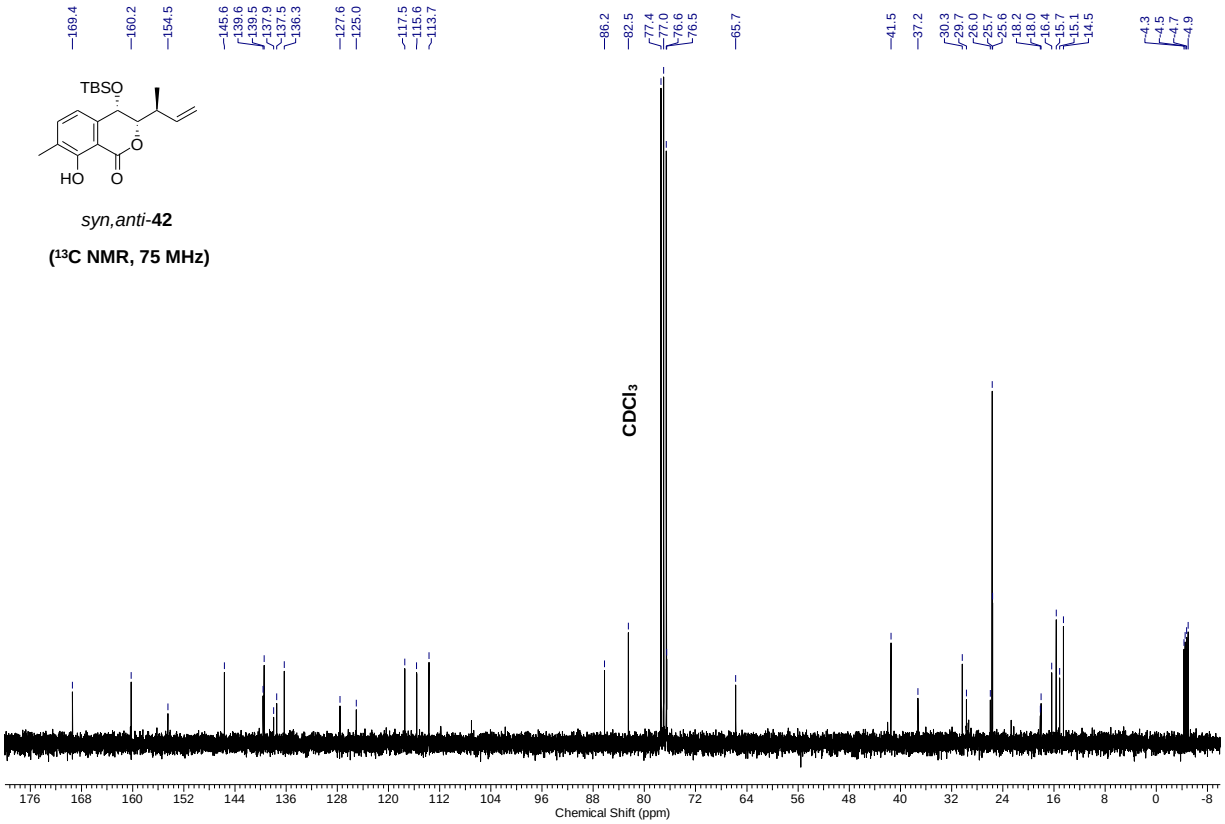
57

(^{13}C NMR, 75 MHz)



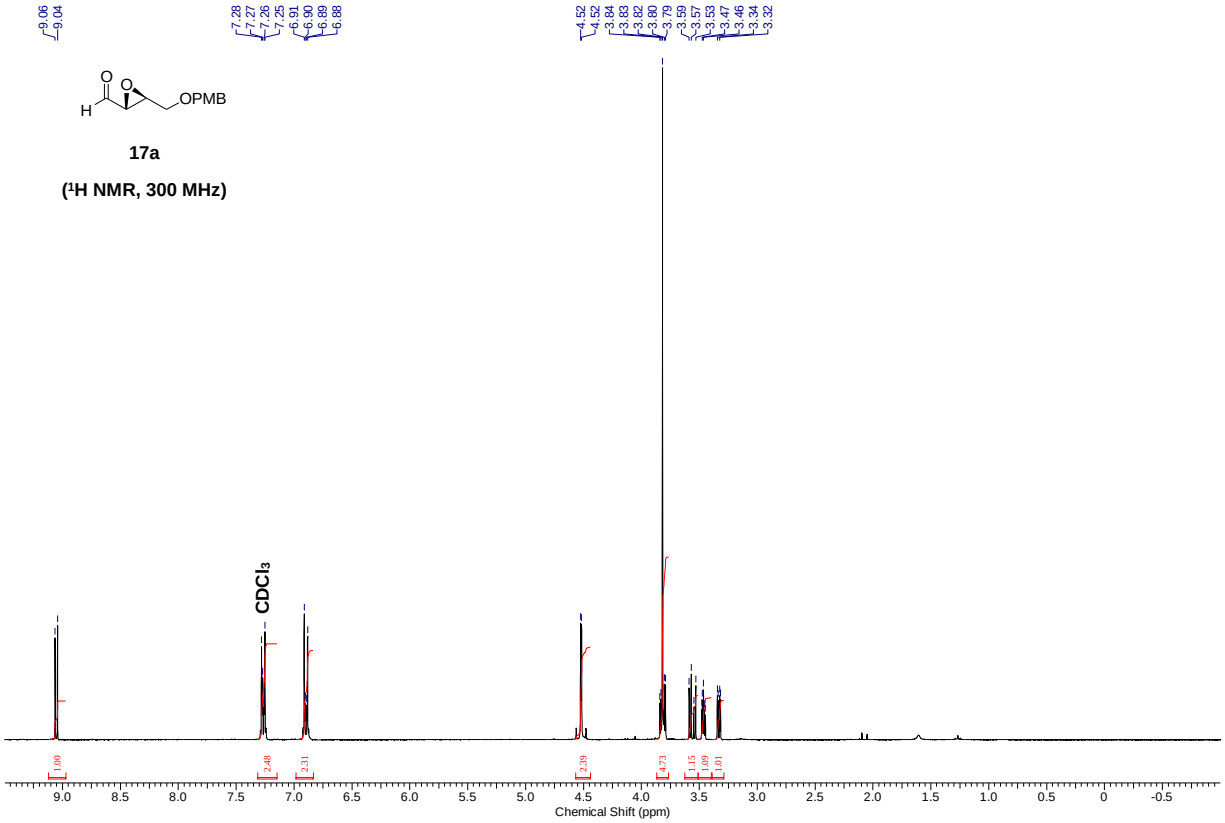
syn,anti-**42**

(^{1}H NMR, 300 MHz)



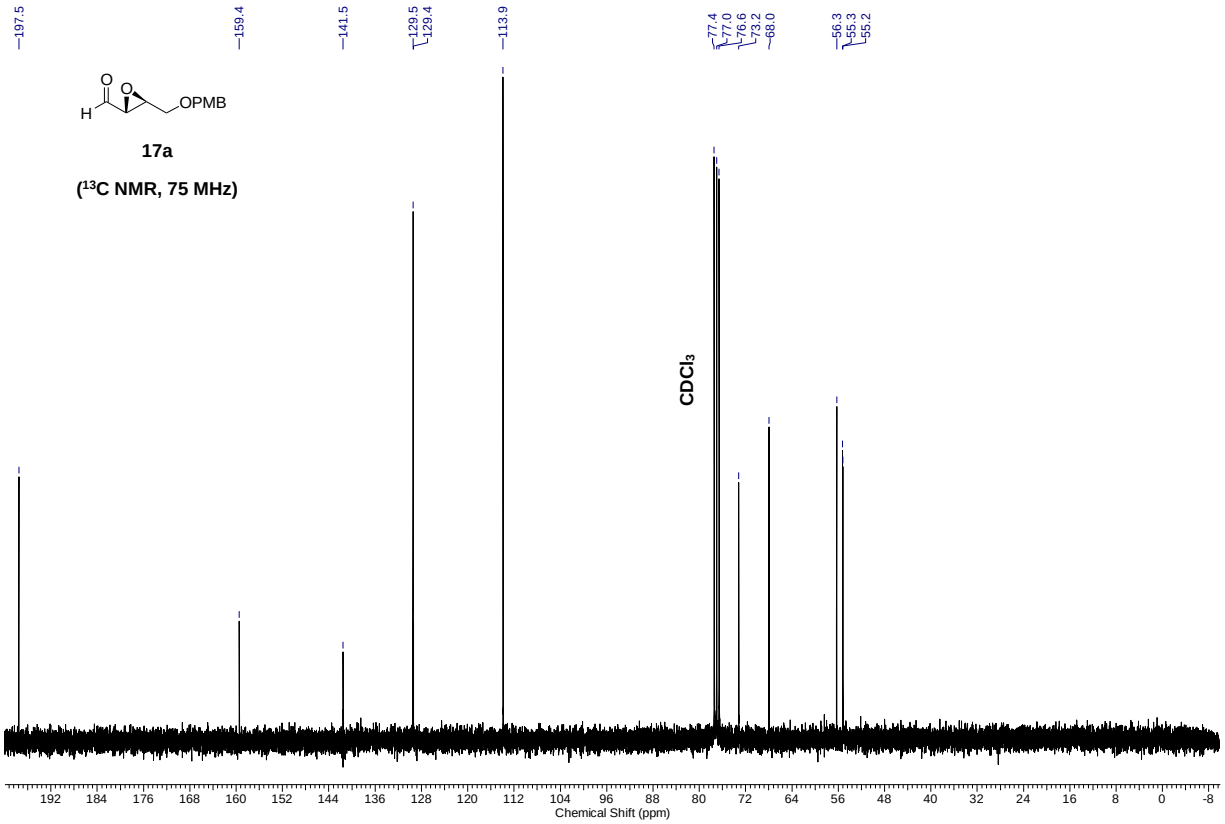
syn,anti-**42**

(^{13}C NMR, 75 MHz)



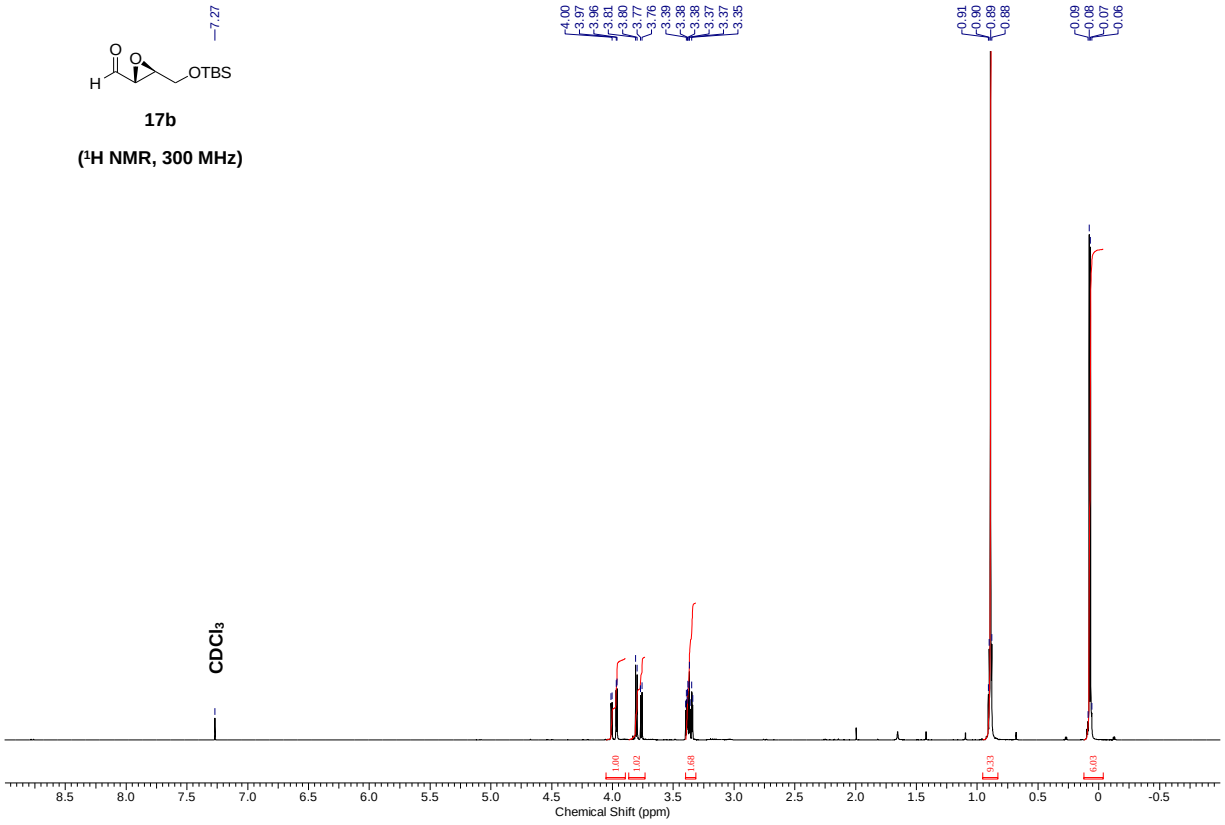
17a

(^{1}H NMR, 300 MHz)



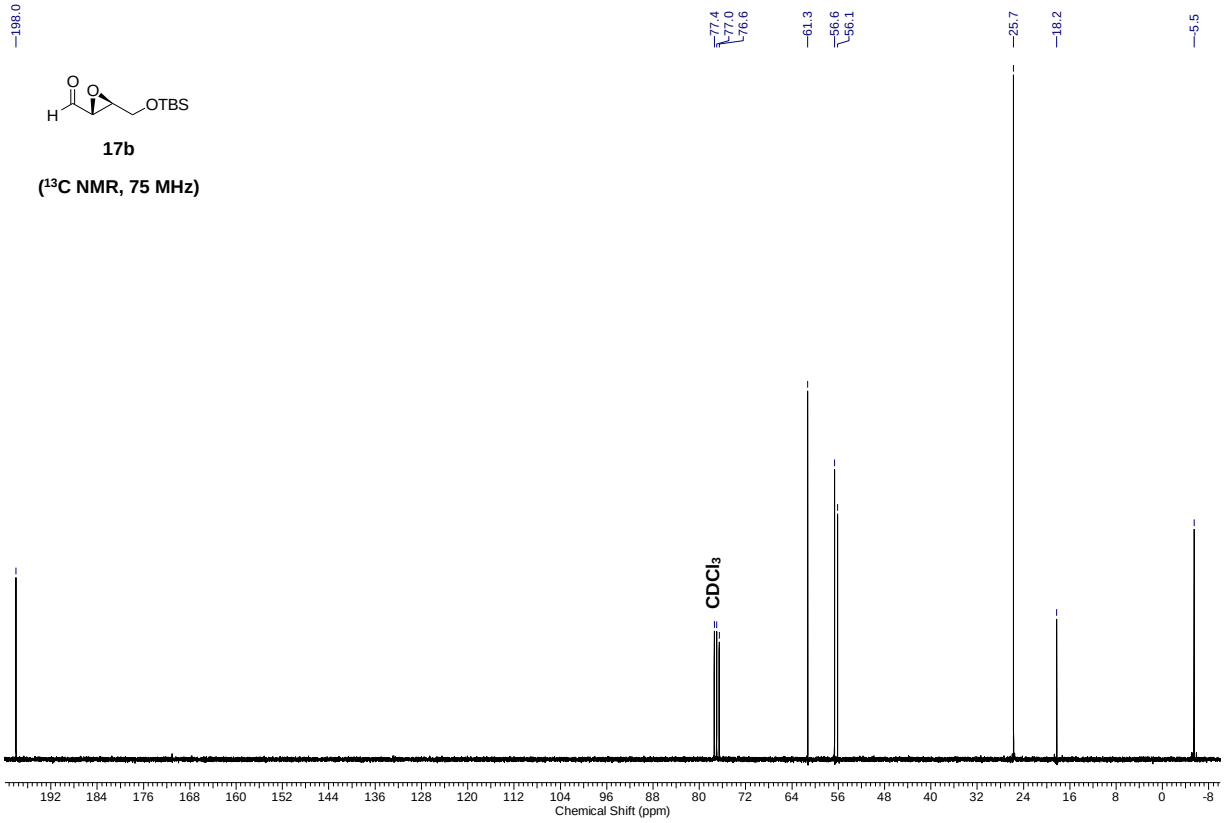
17a

(^{13}C NMR, 75 MHz)



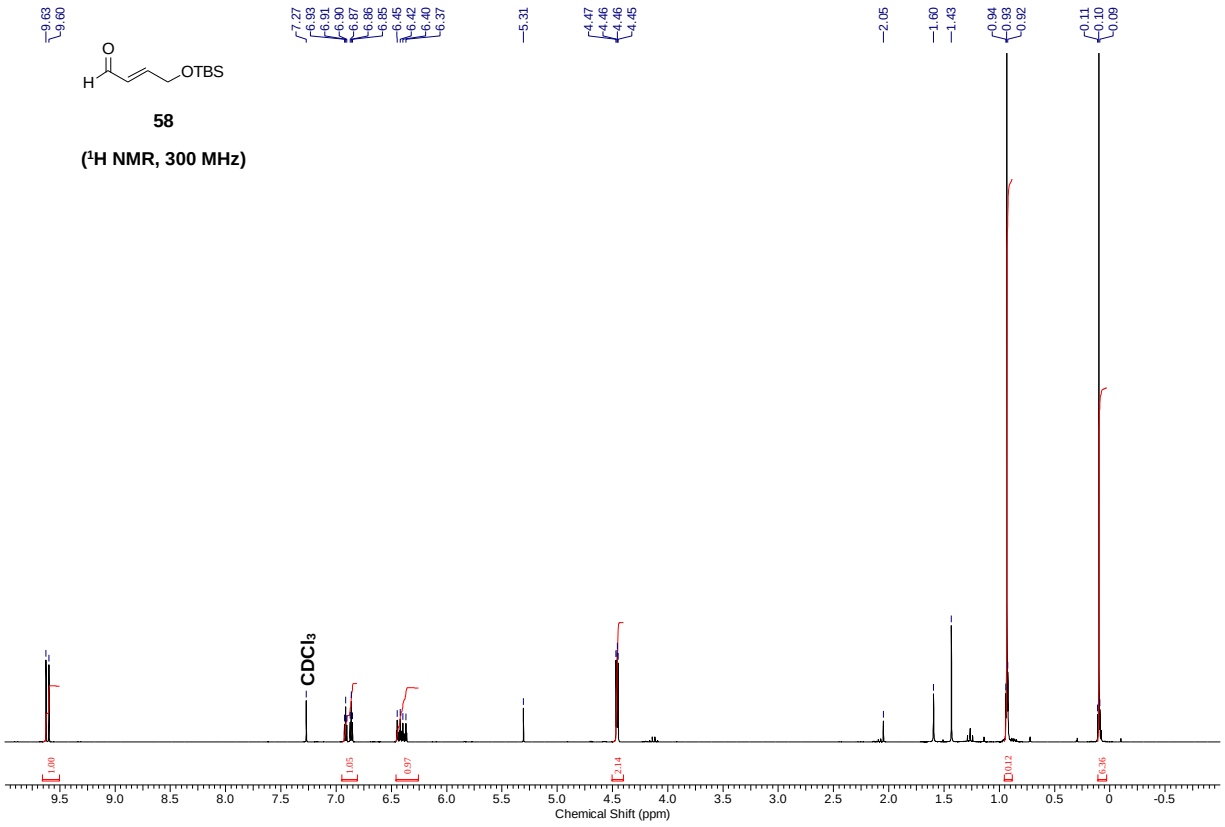
17b

(^{1}H NMR, 300 MHz)



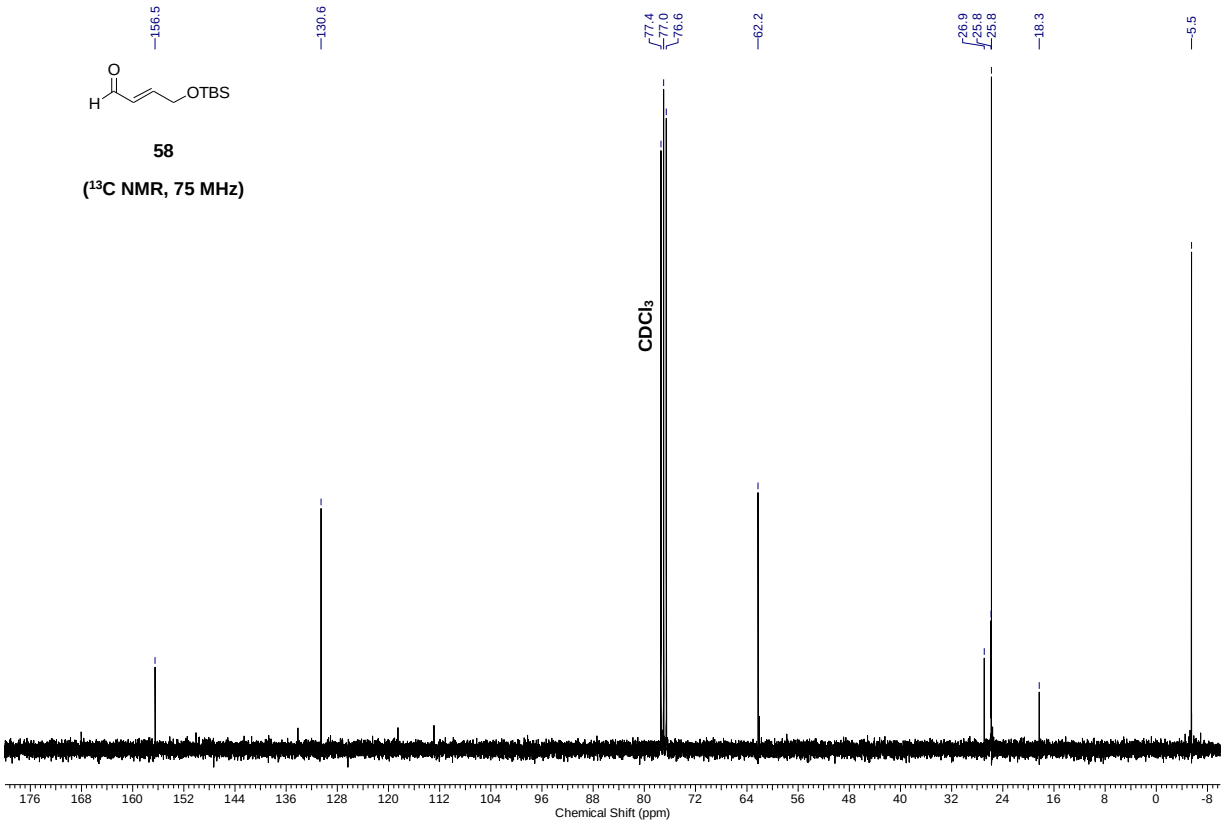
17b

(^{13}C NMR, 75 MHz)



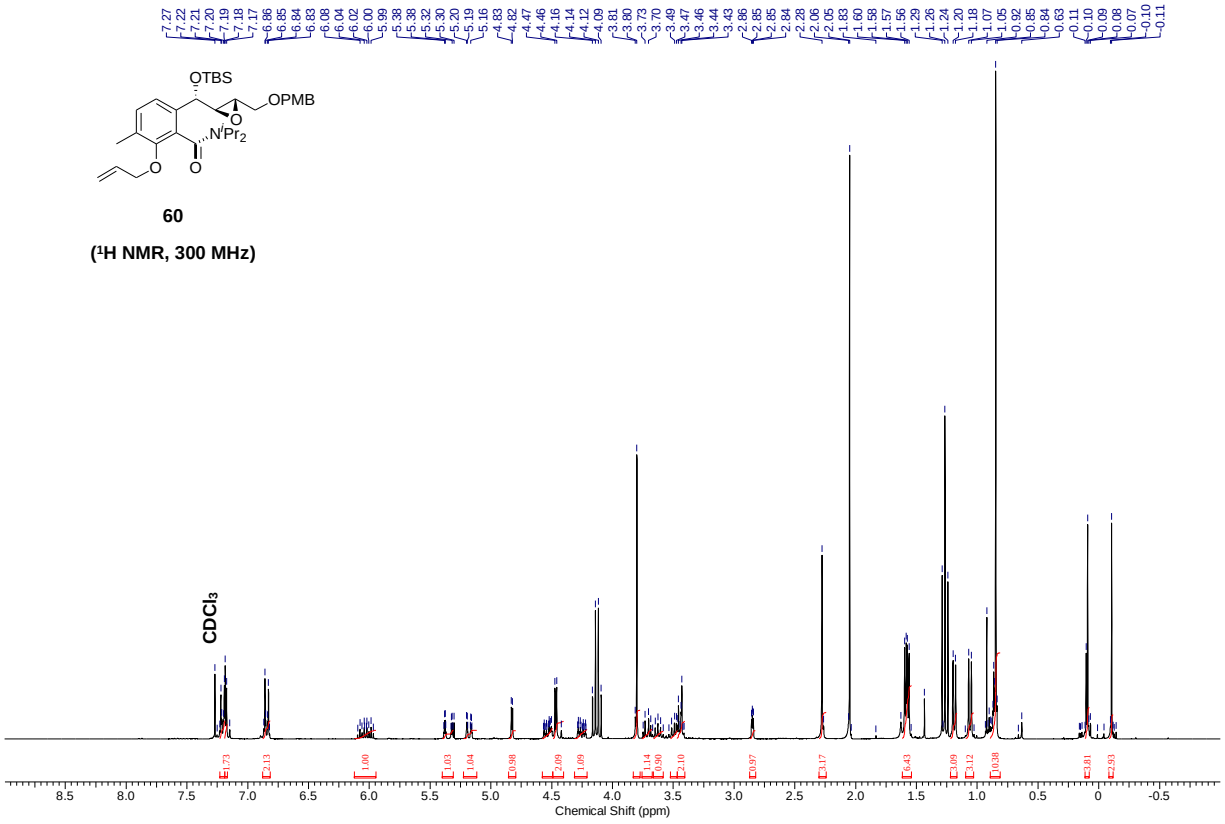
58

(^{1}H NMR, 300 MHz)



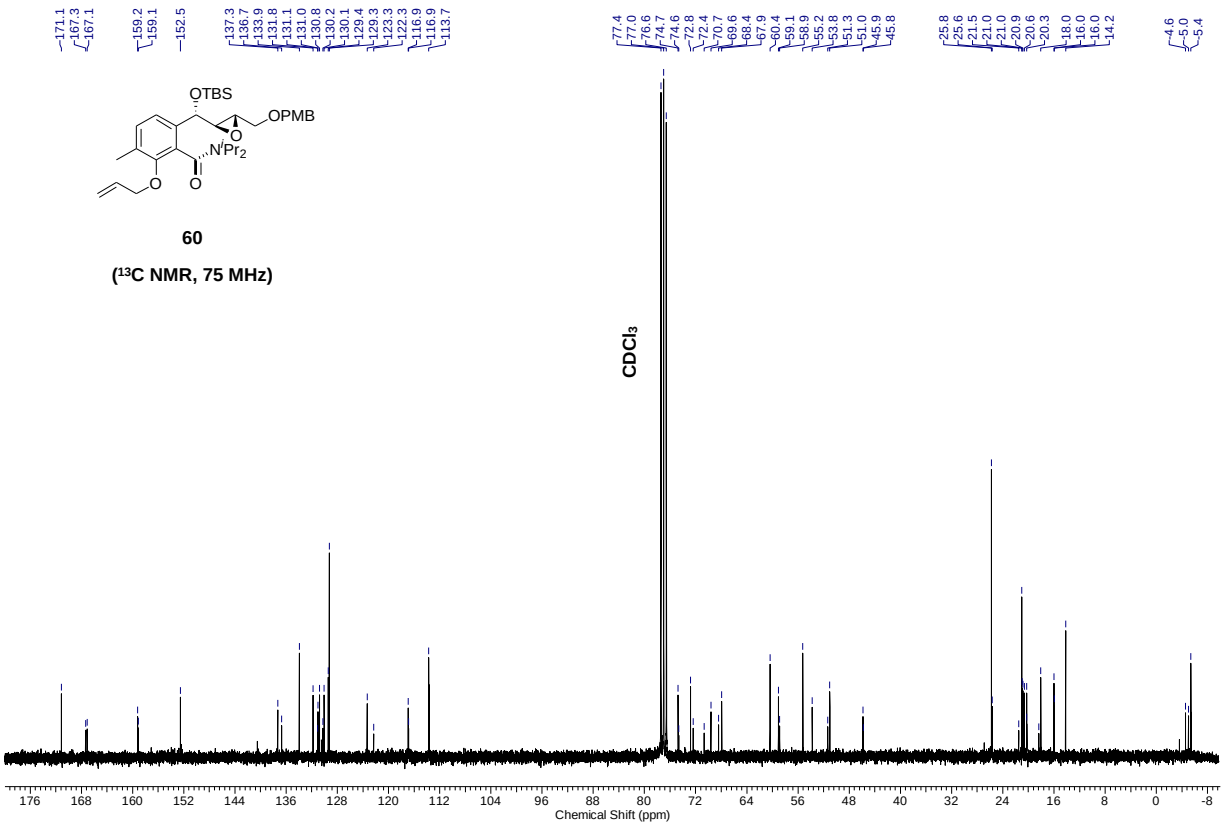
58

(^{13}C NMR, 75 MHz)



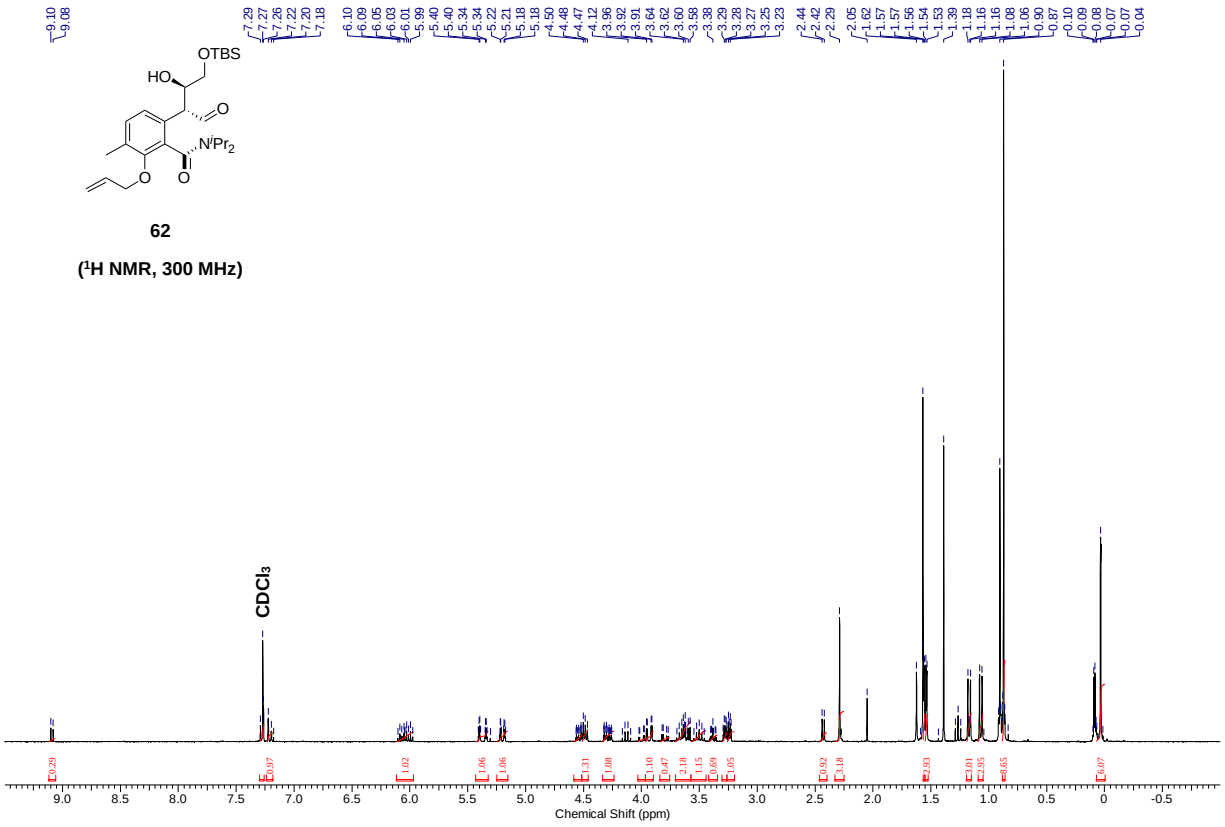
60

(^{1}H NMR, 300 MHz)



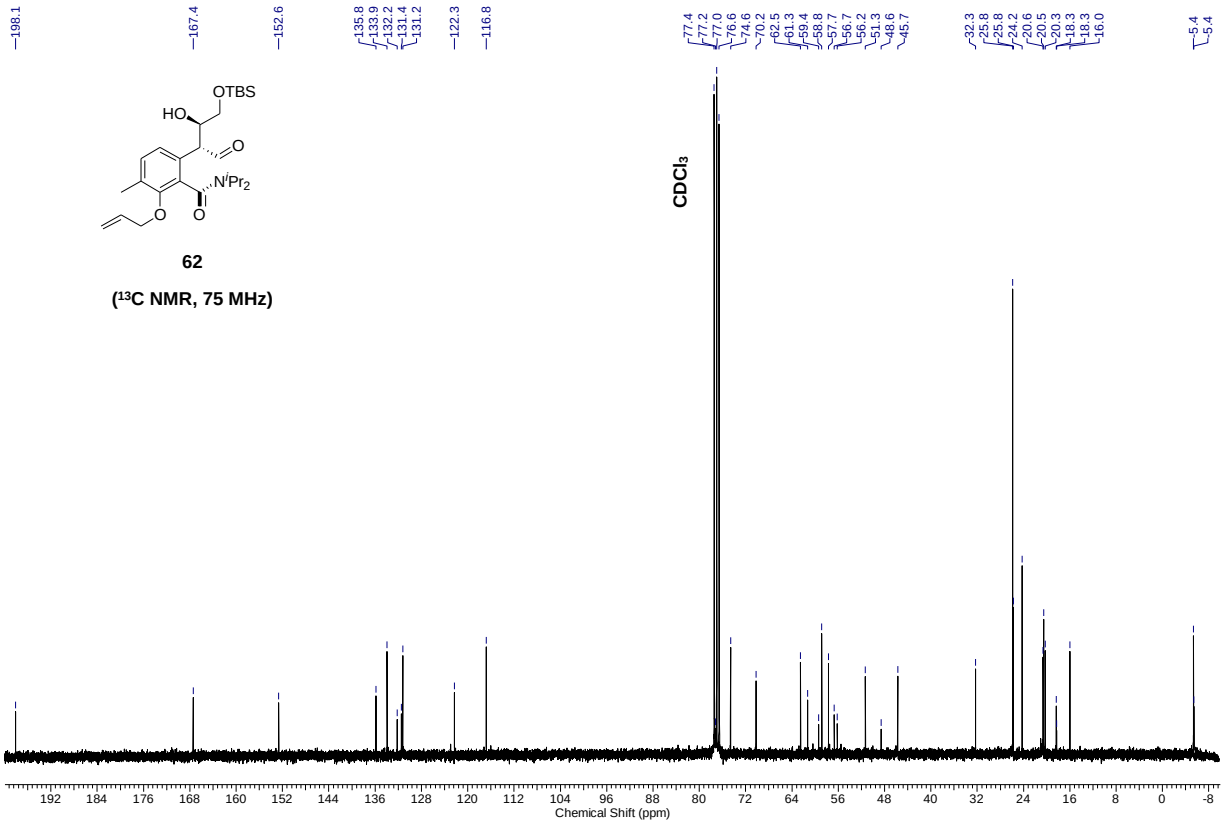
60

(^{13}C NMR, 75 MHz)



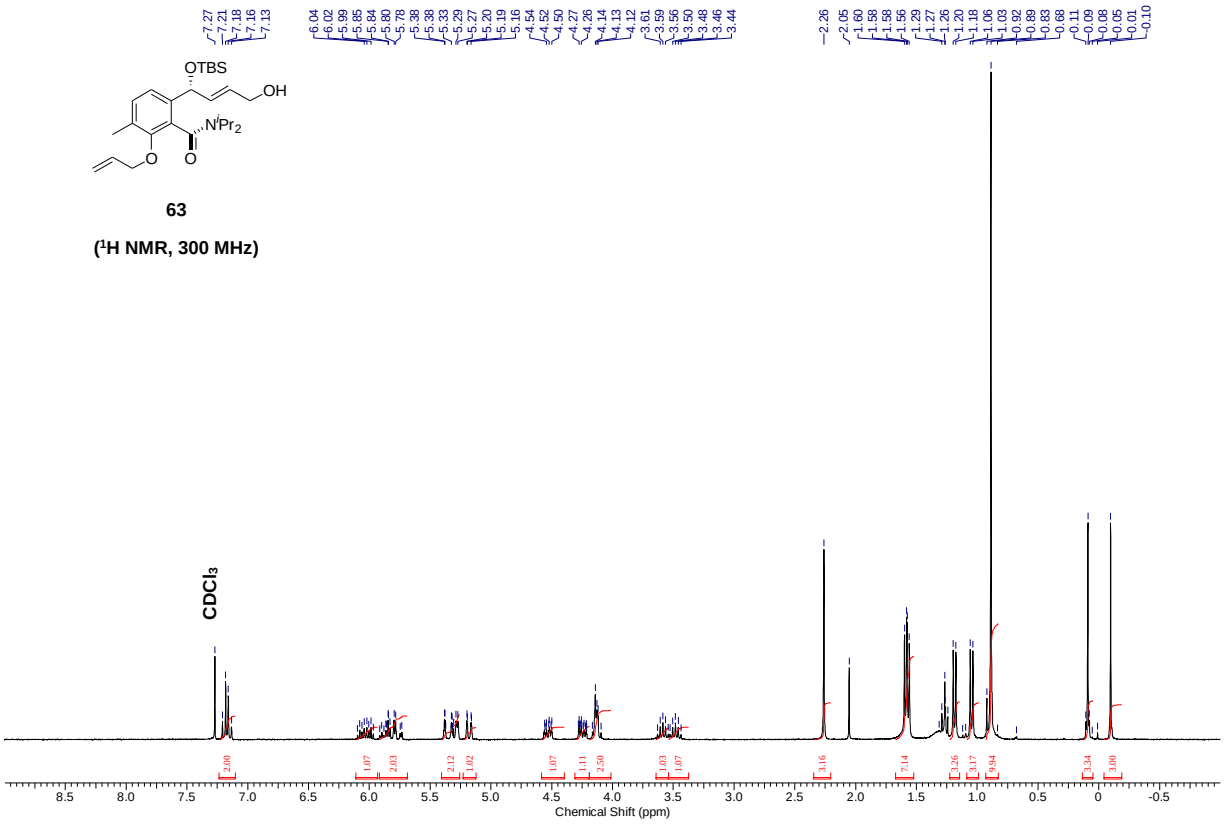
62

(^{1}H NMR, 300 MHz)



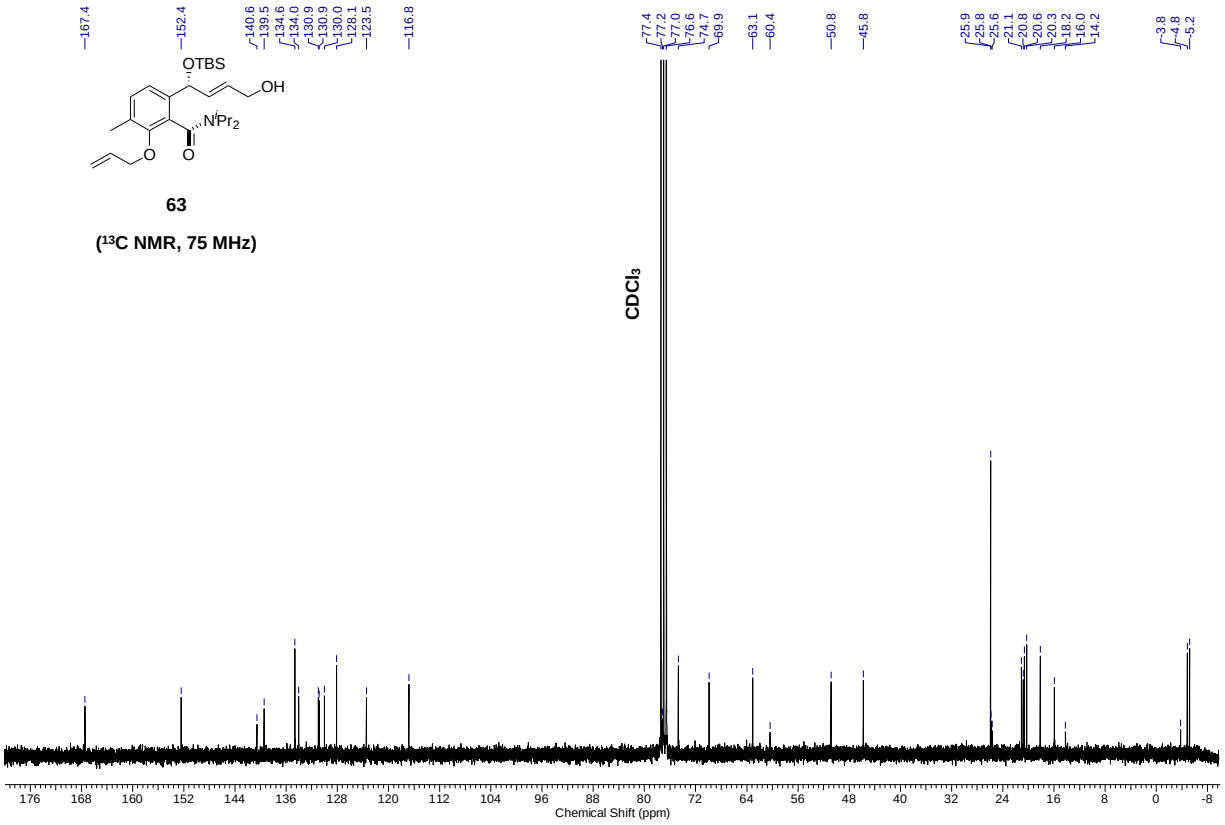
62

(^{13}C NMR, 75 MHz)



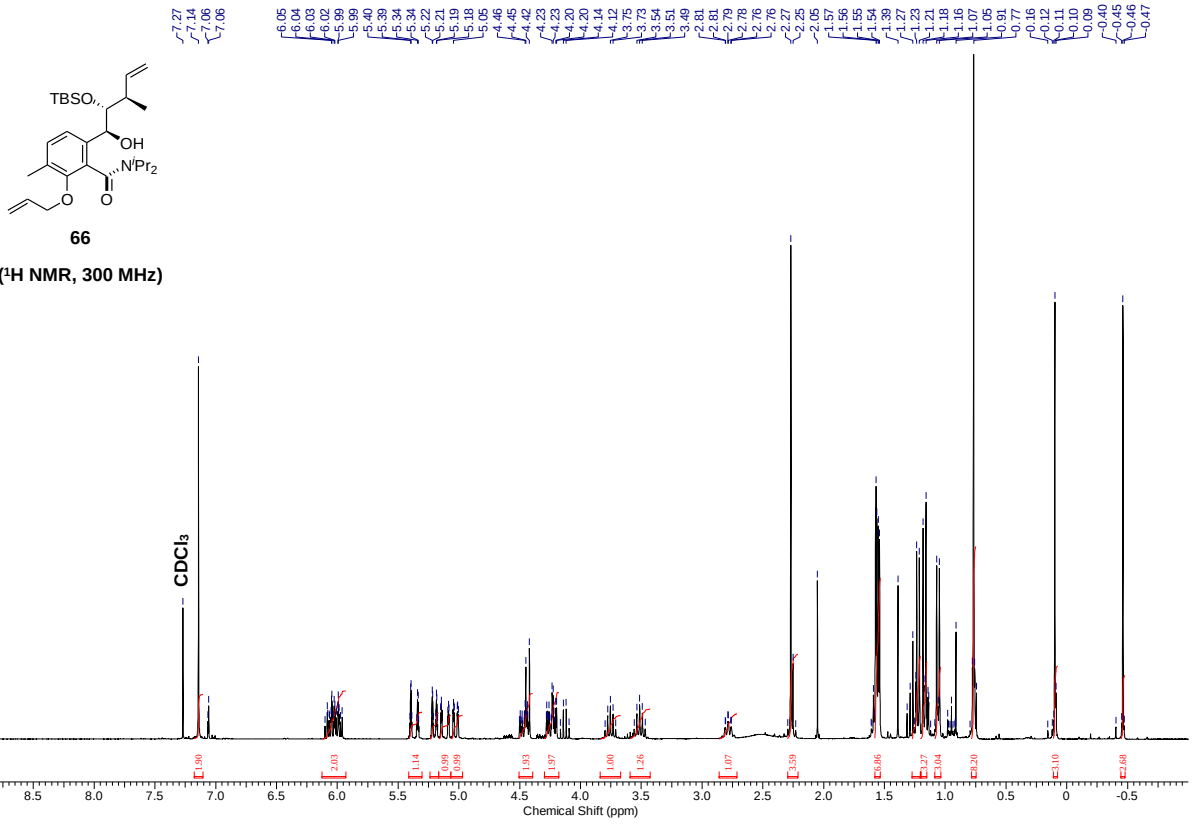
63

(^{1}H NMR, 300 MHz)



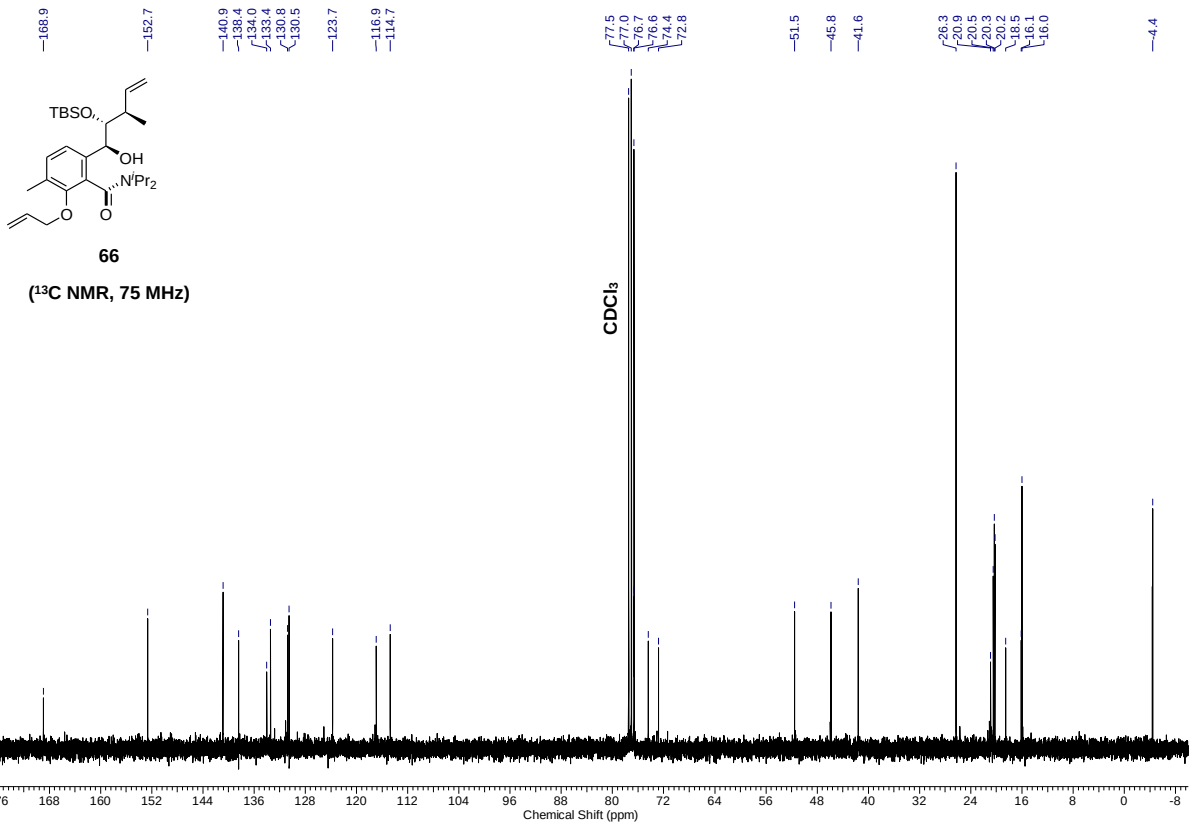
63

(^{13}C NMR, 75 MHz)



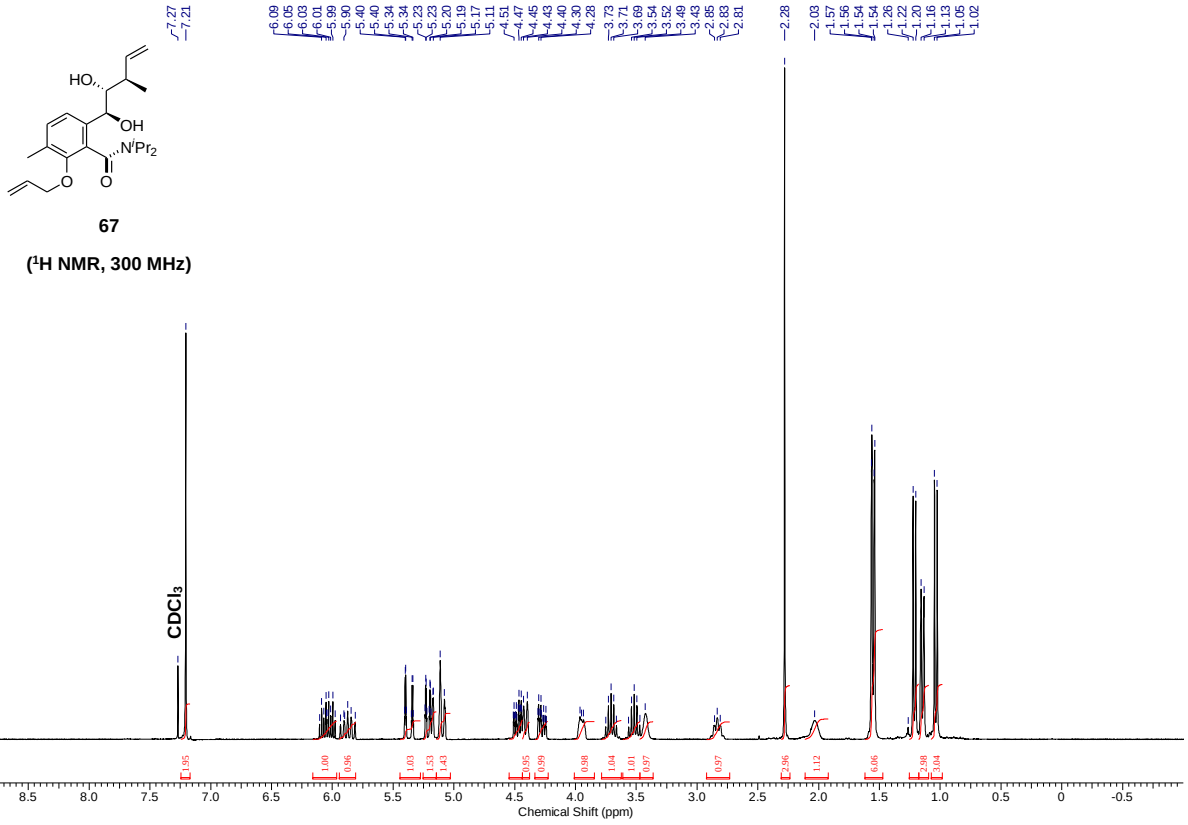
66

(^{1}H NMR, 300 MHz)



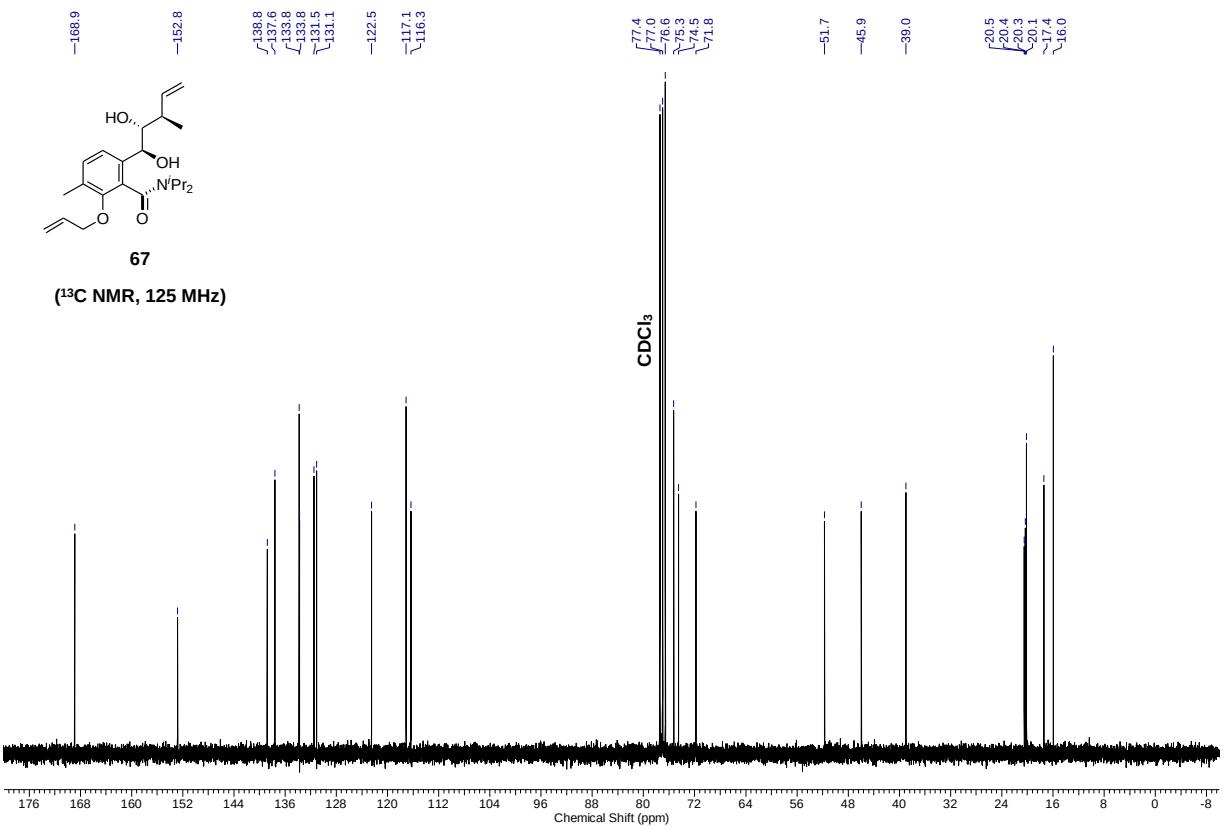
66

(^{13}C NMR, 75 MHz)



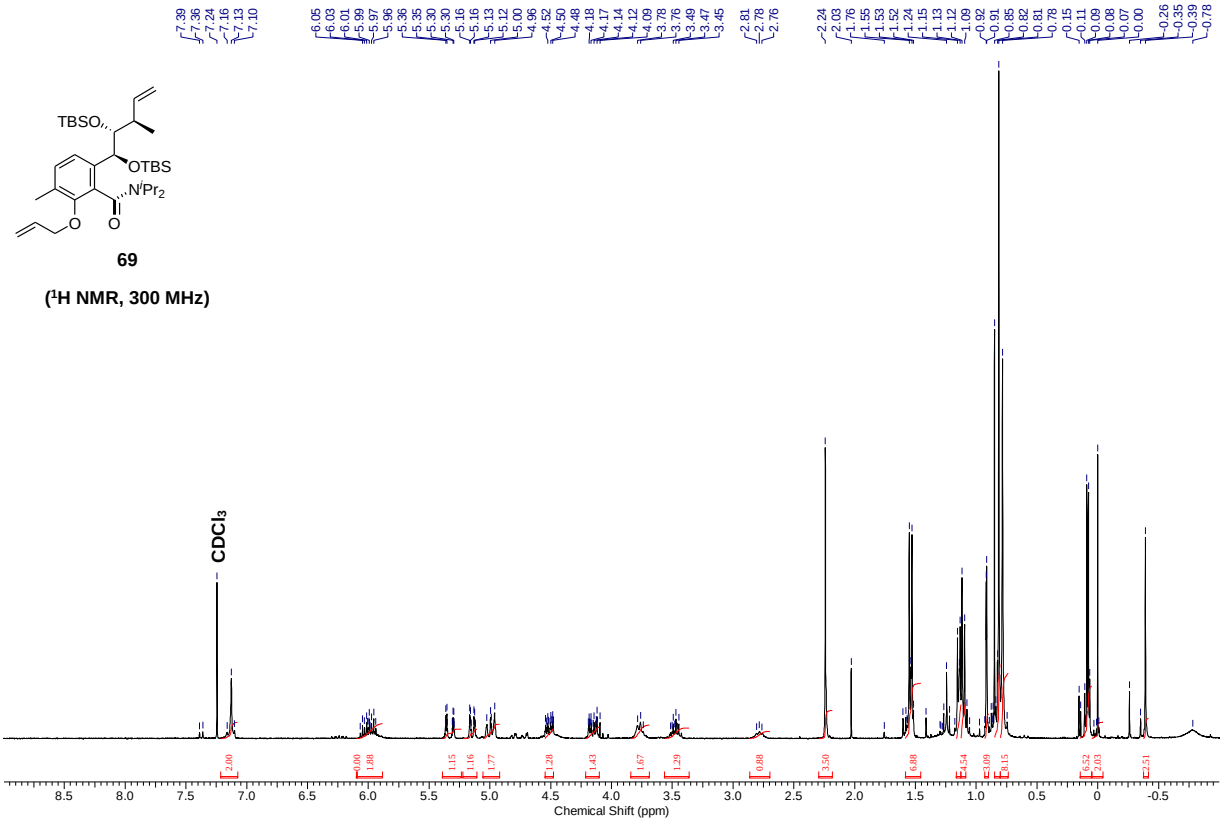
67

(^{1}H NMR, 300 MHz)



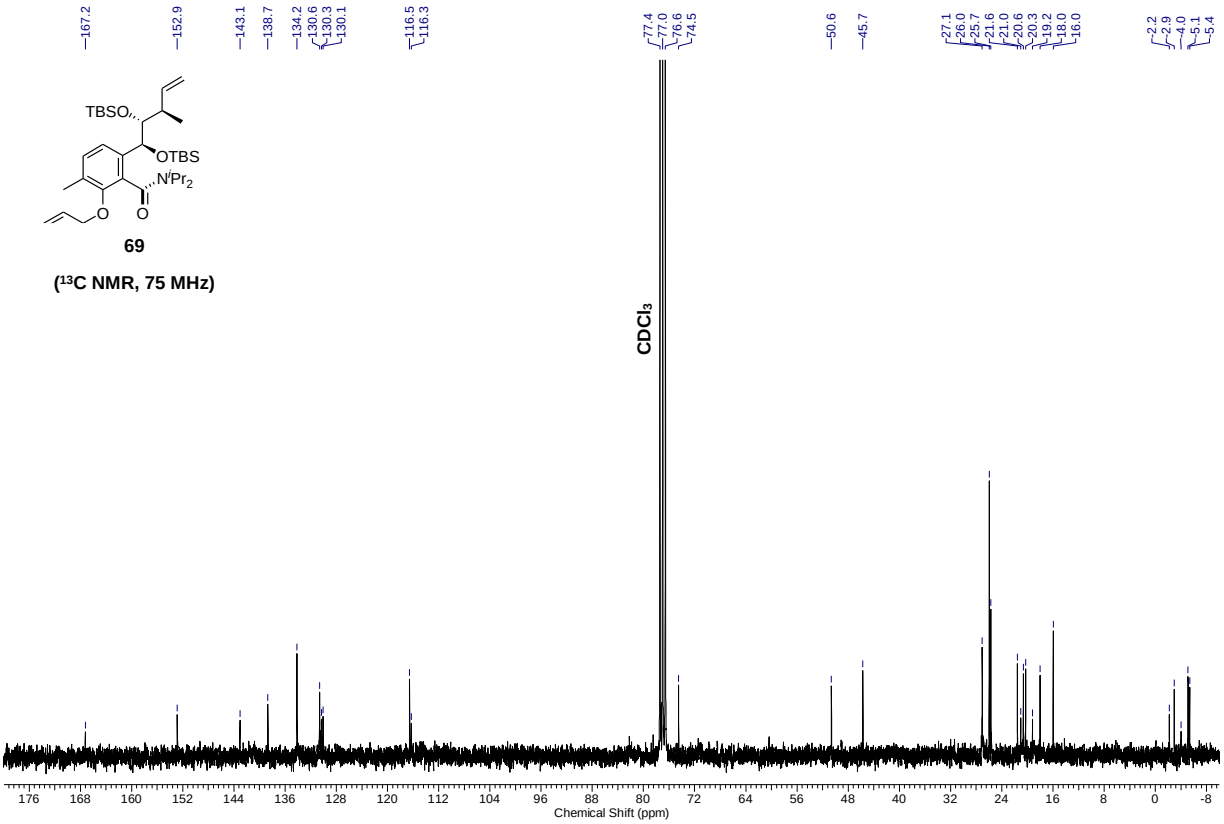
67

(^{13}C NMR, 125 MHz)



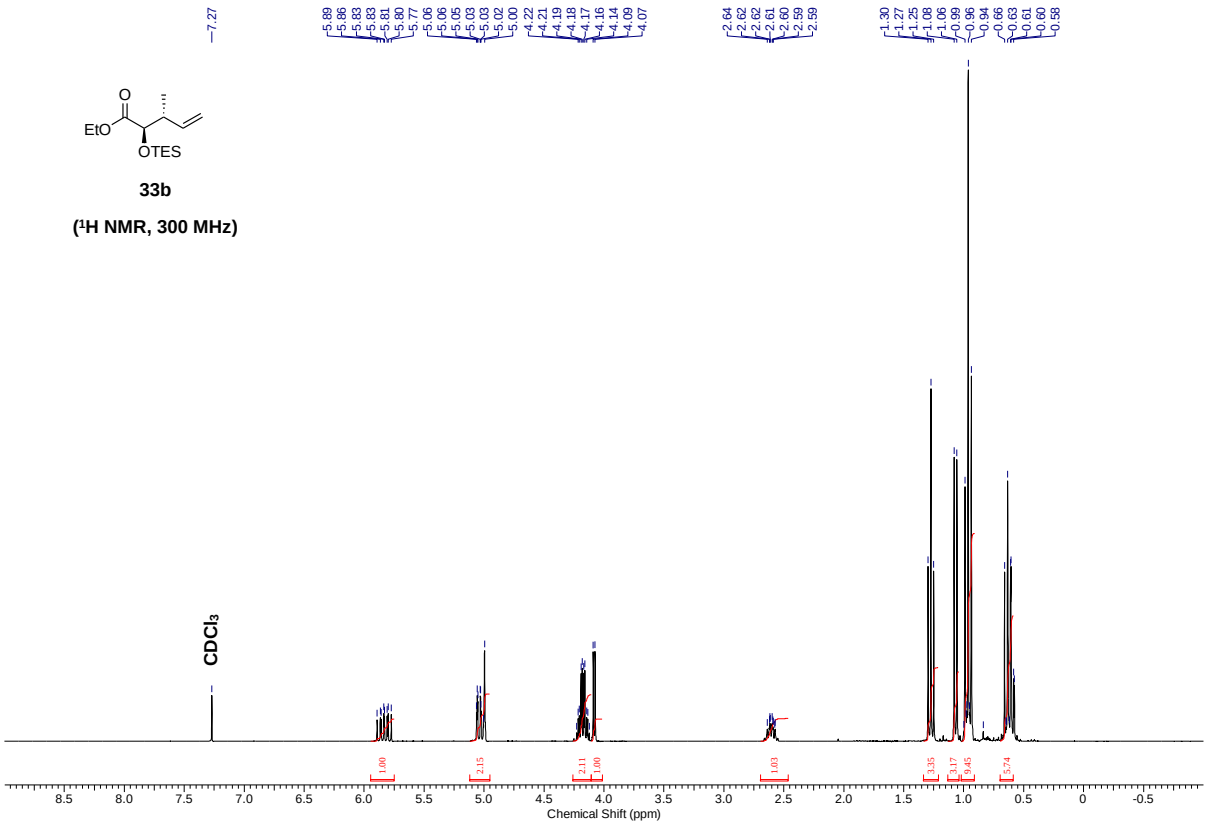
69

(^{1}H NMR, 300 MHz)



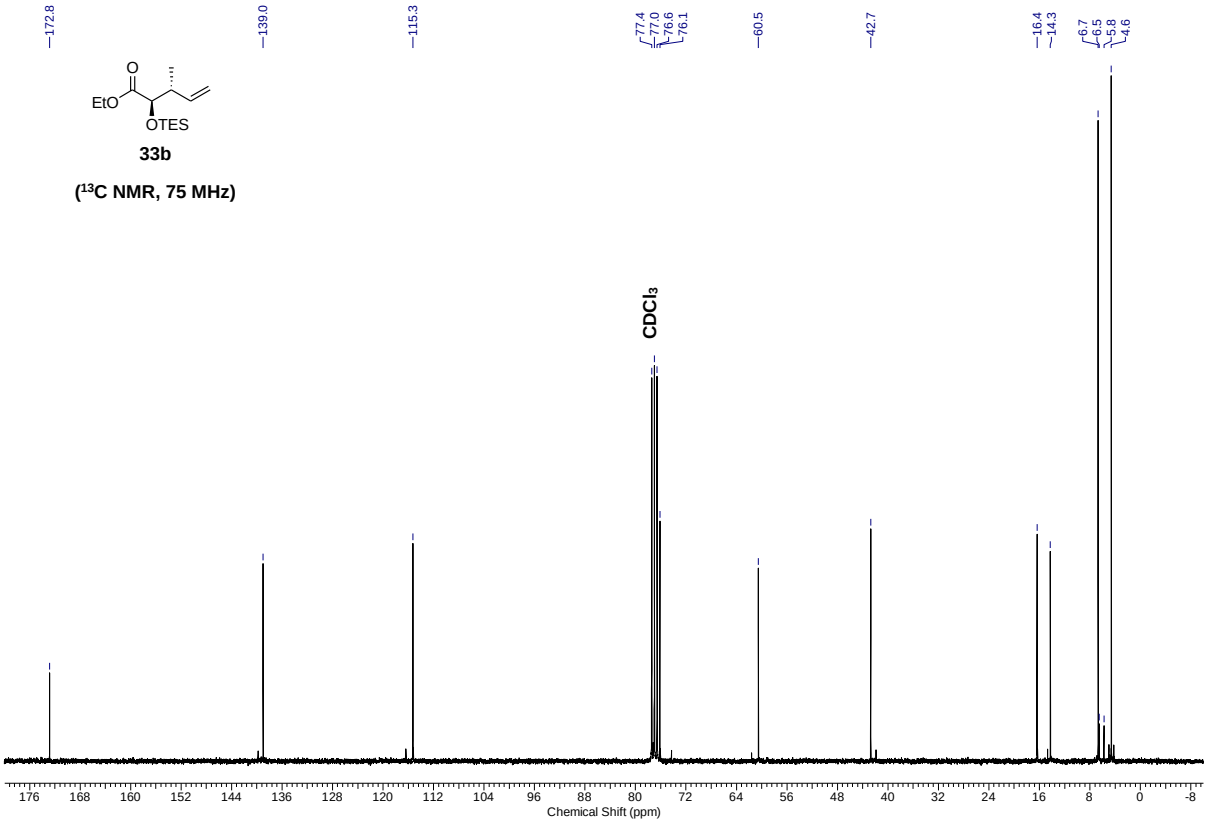
69

(^{13}C NMR, 75 MHz)



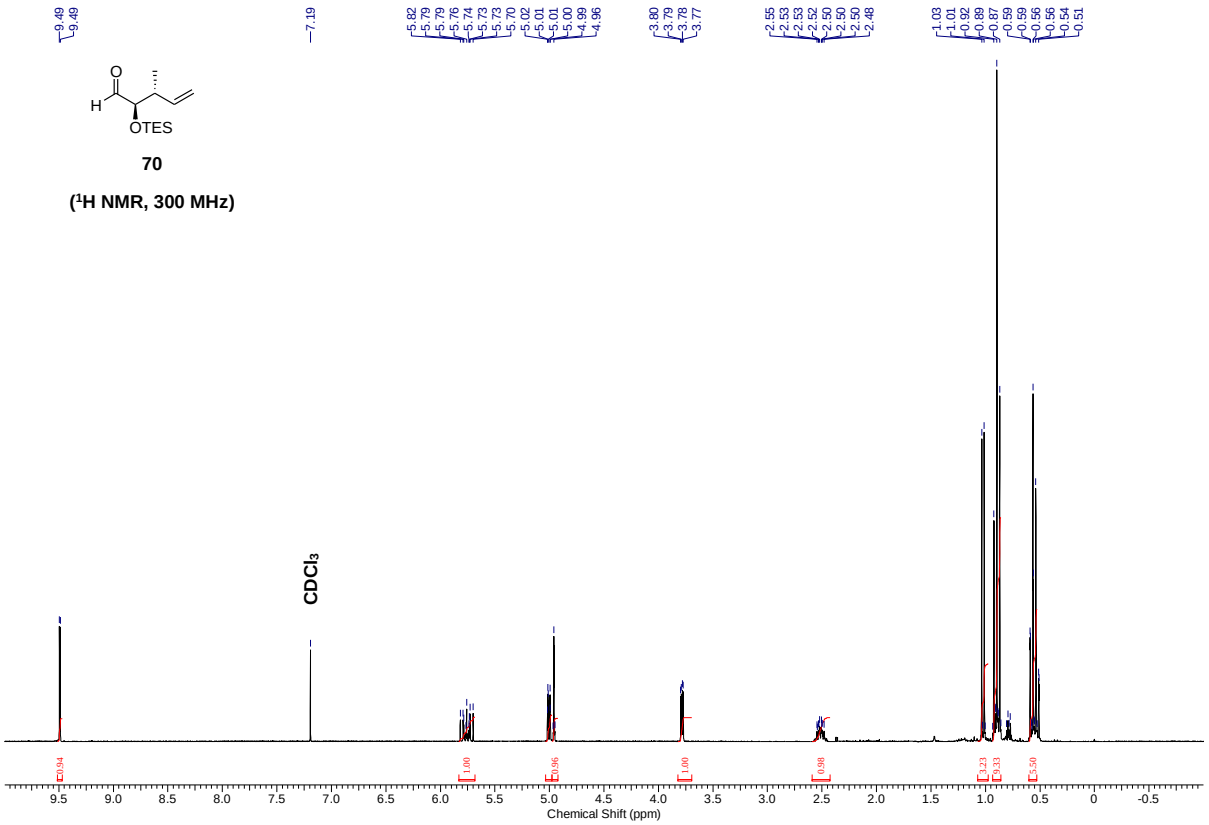
33b

(^{1}H NMR, 300 MHz)



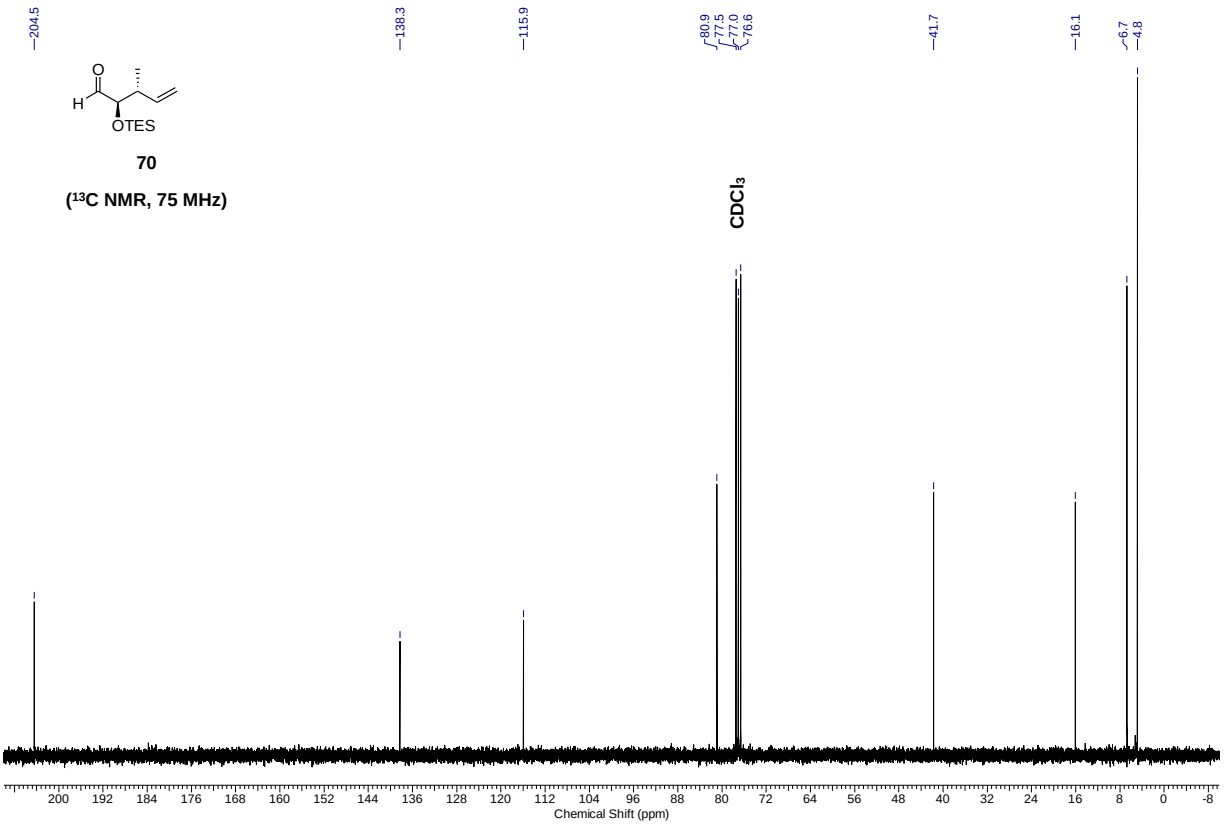
33b

(^{13}C NMR, 75 MHz)



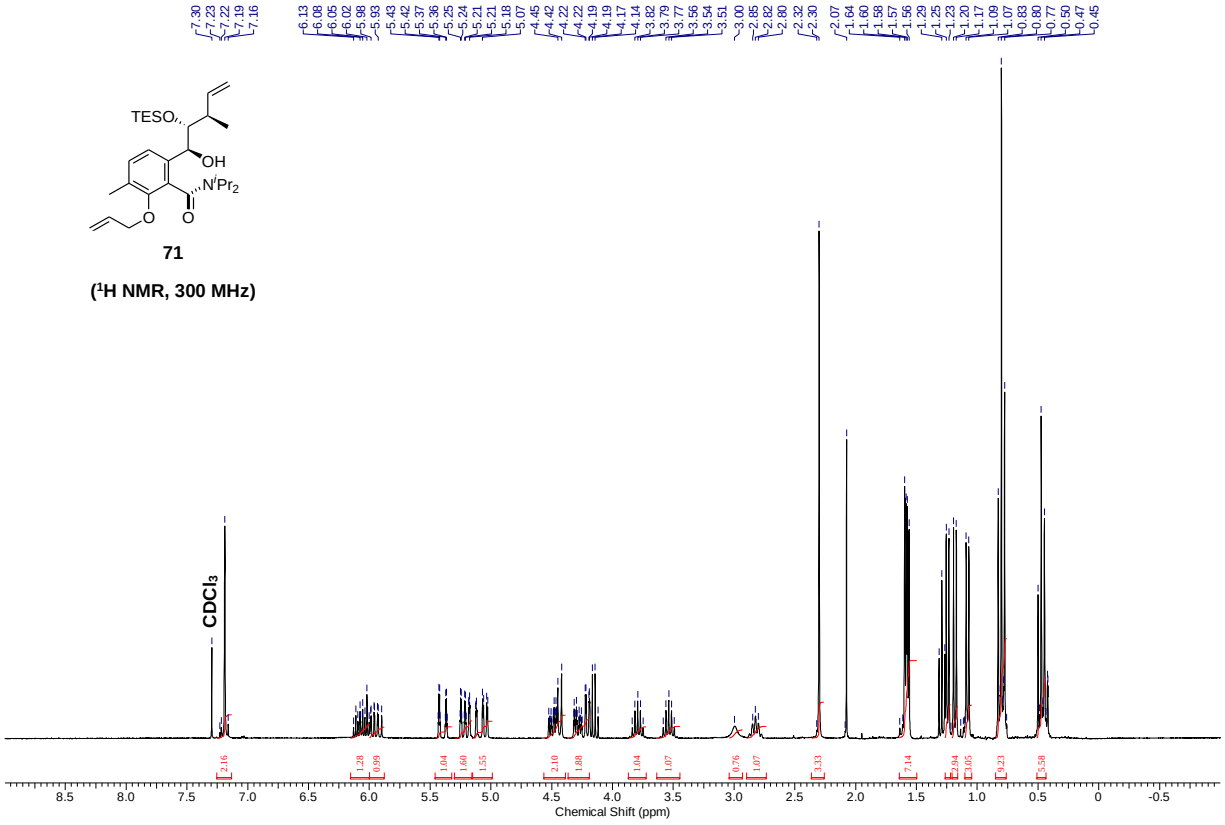
70

(^{1}H NMR, 300 MHz)



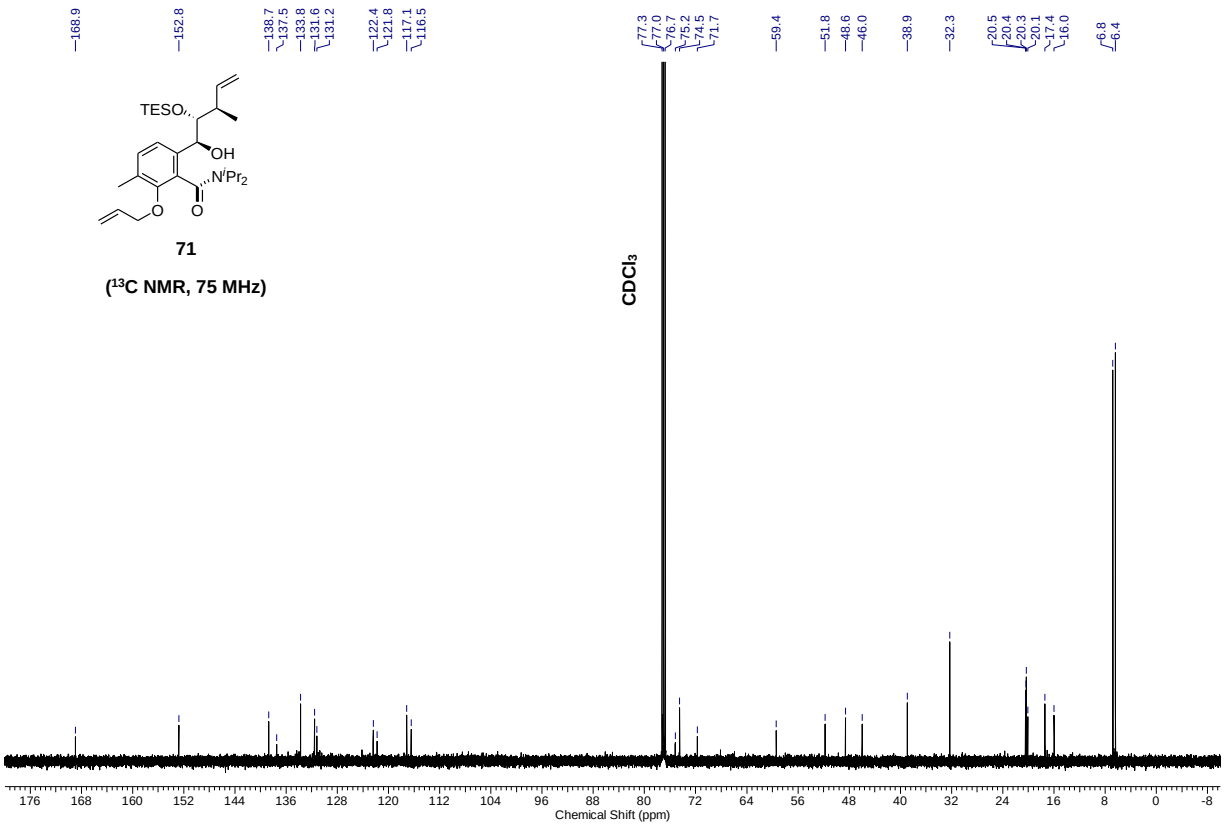
70

(^{13}C NMR, 75 MHz)



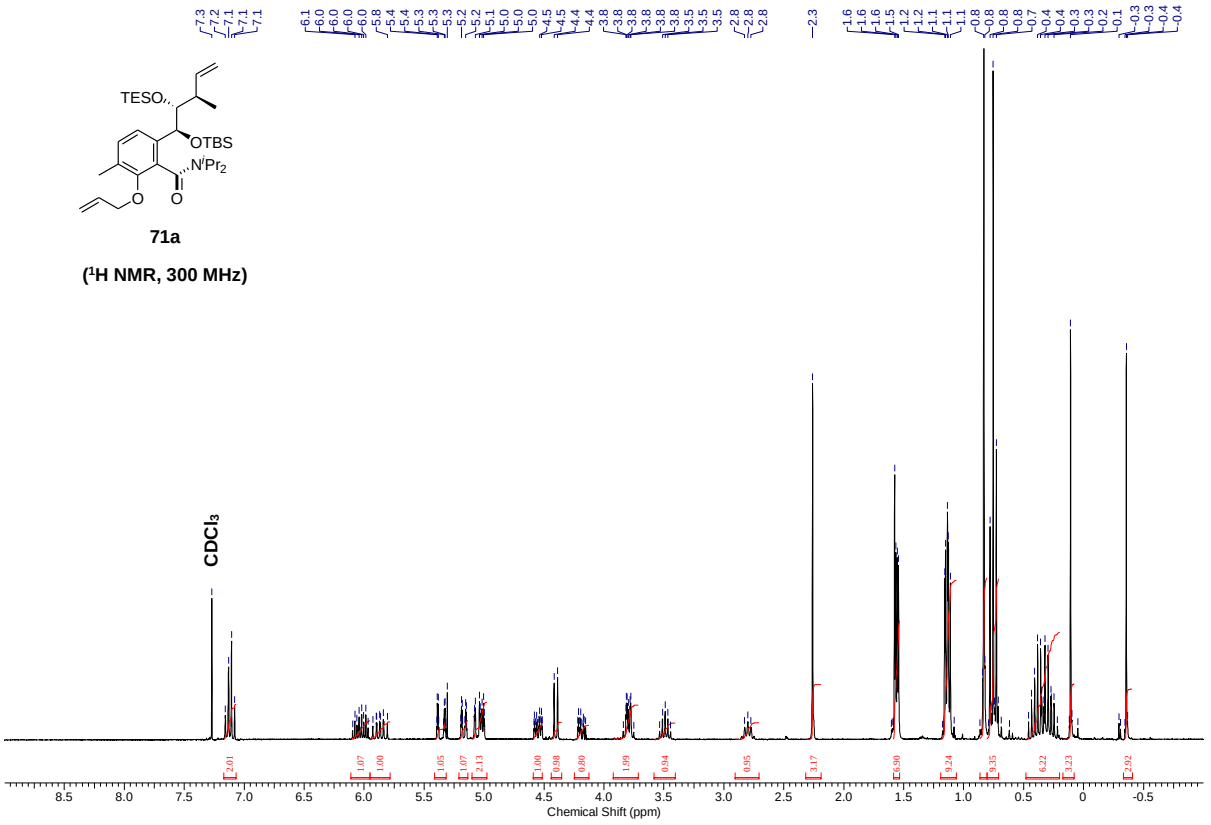
71

(^{1}H NMR, 300 MHz)



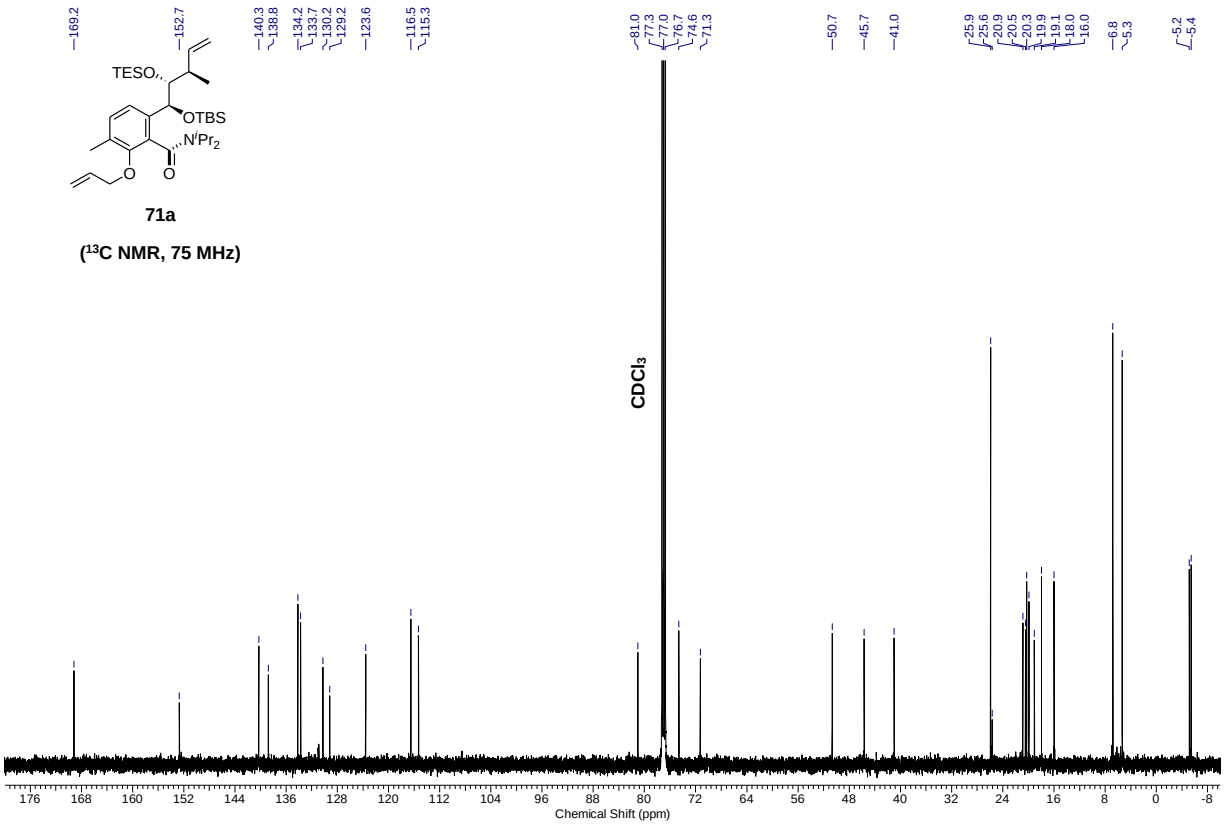
71

(^{13}C NMR, 75 MHz)



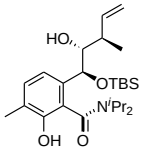
71a

(^{1}H NMR, 300 MHz)



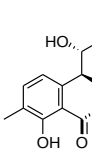
71a

(^{13}C NMR, 75 MHz)



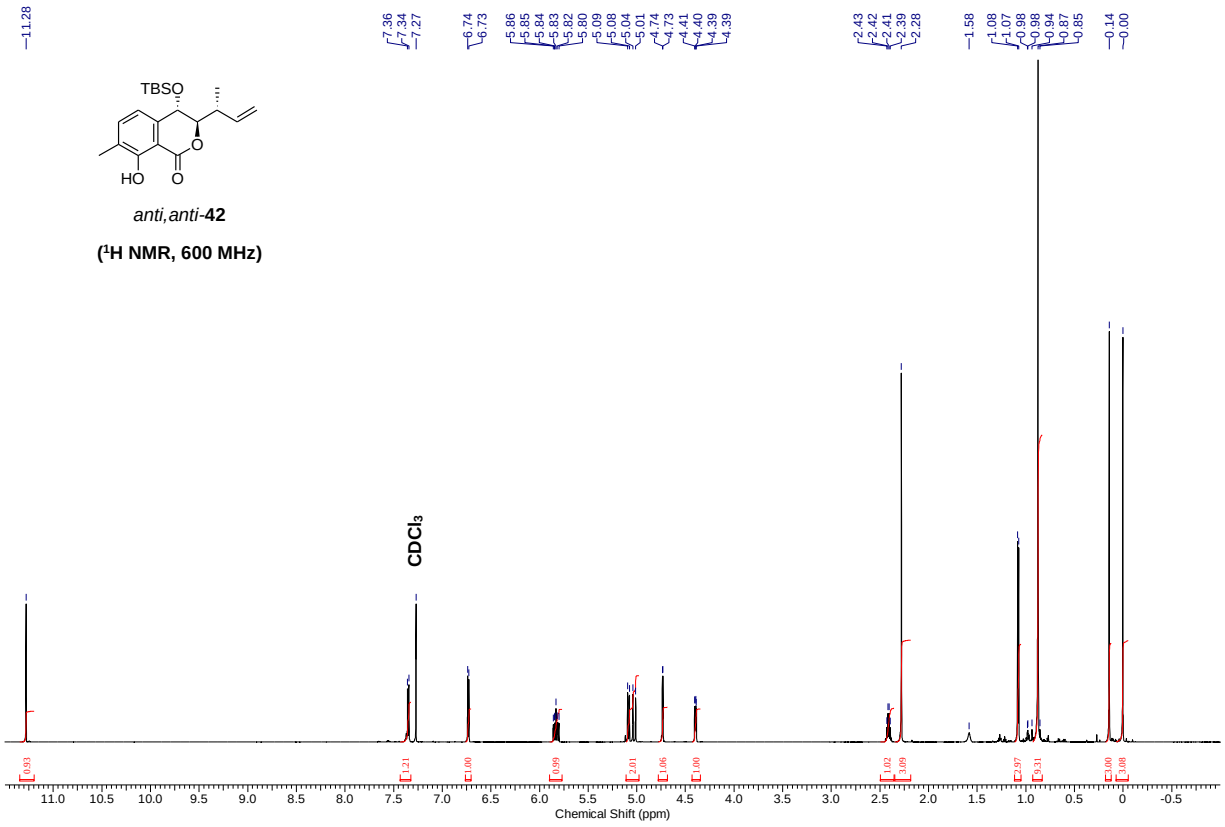
41

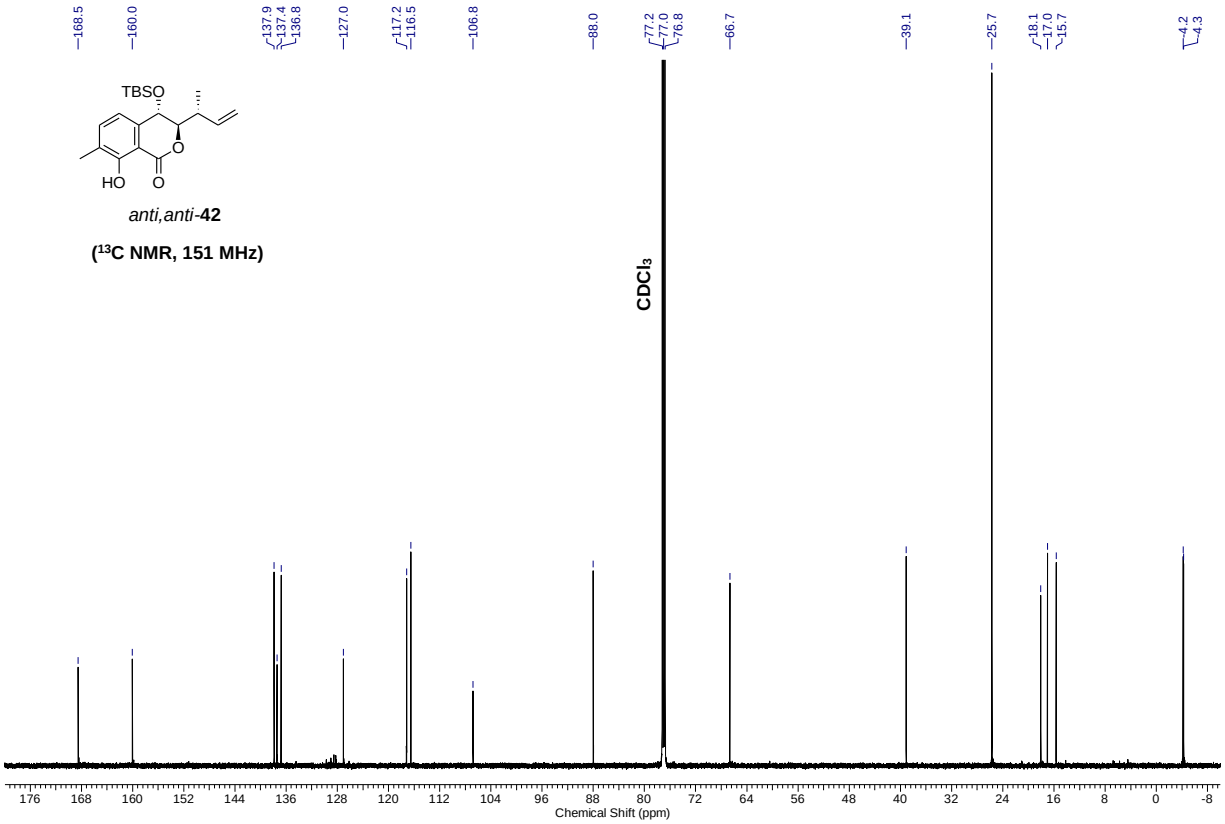
(^{1}H NMR, 300 MHz)

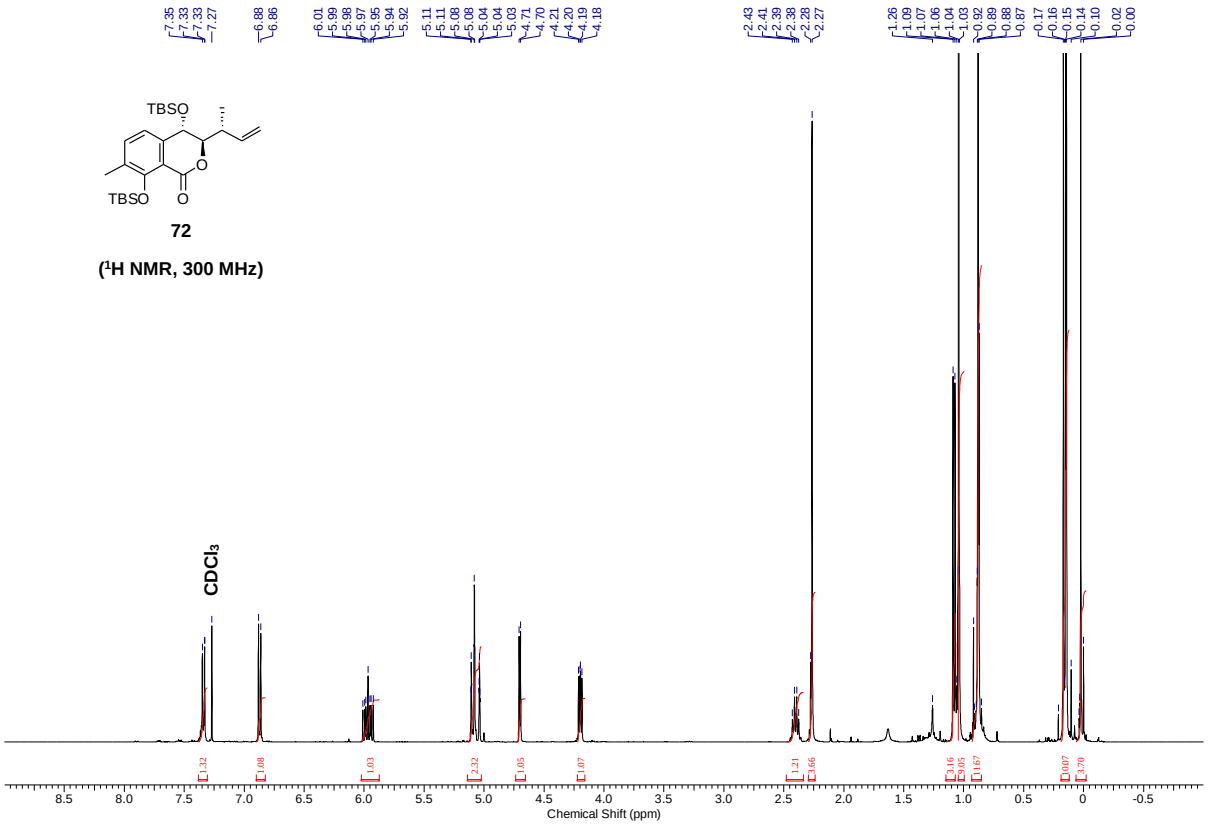


41

(^{13}C NMR, 75 MHz)

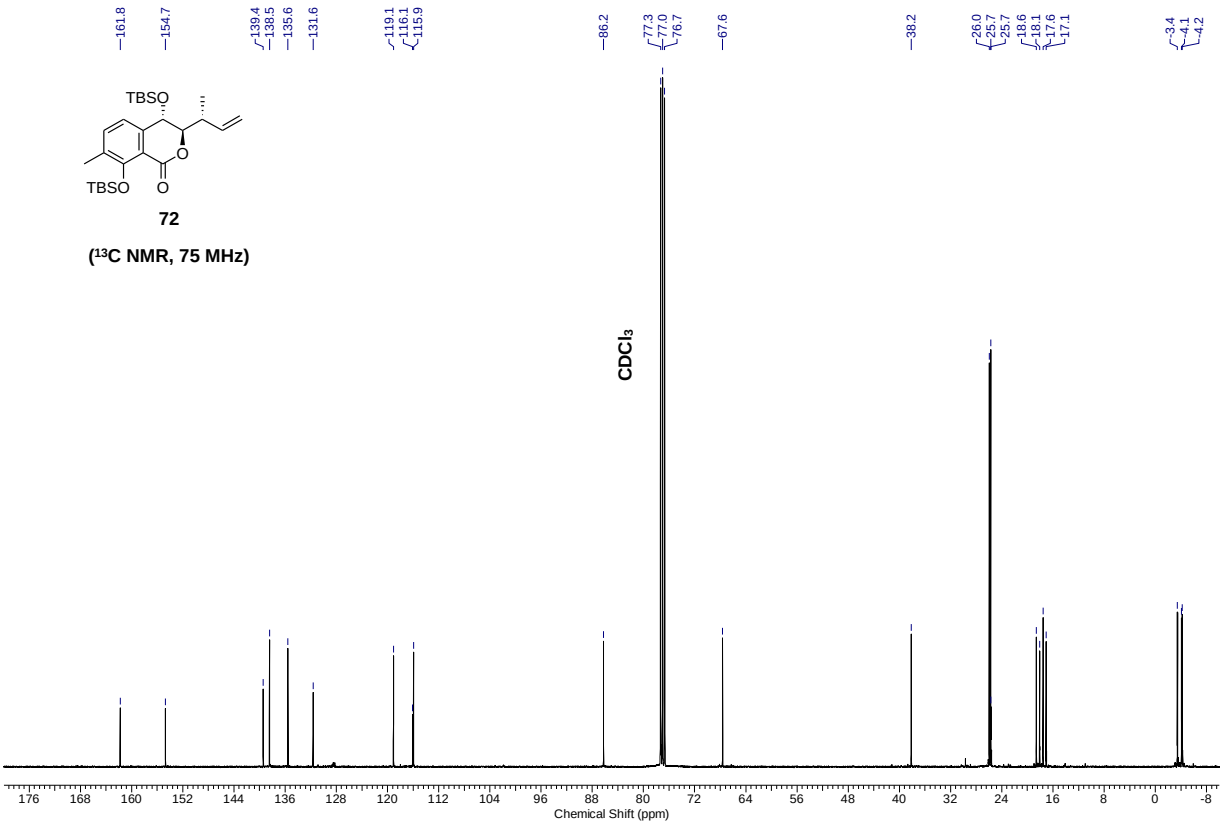

TBSO
HO
O
O
anti,anti-42
(1H NMR, 600 MHz)
CDCl3
Chemical Shift (ppm)


TBSO
HO
O
O
anti,anti-42
(13C NMR, 151 MHz)
CDCl3
Chemical Shift (ppm)



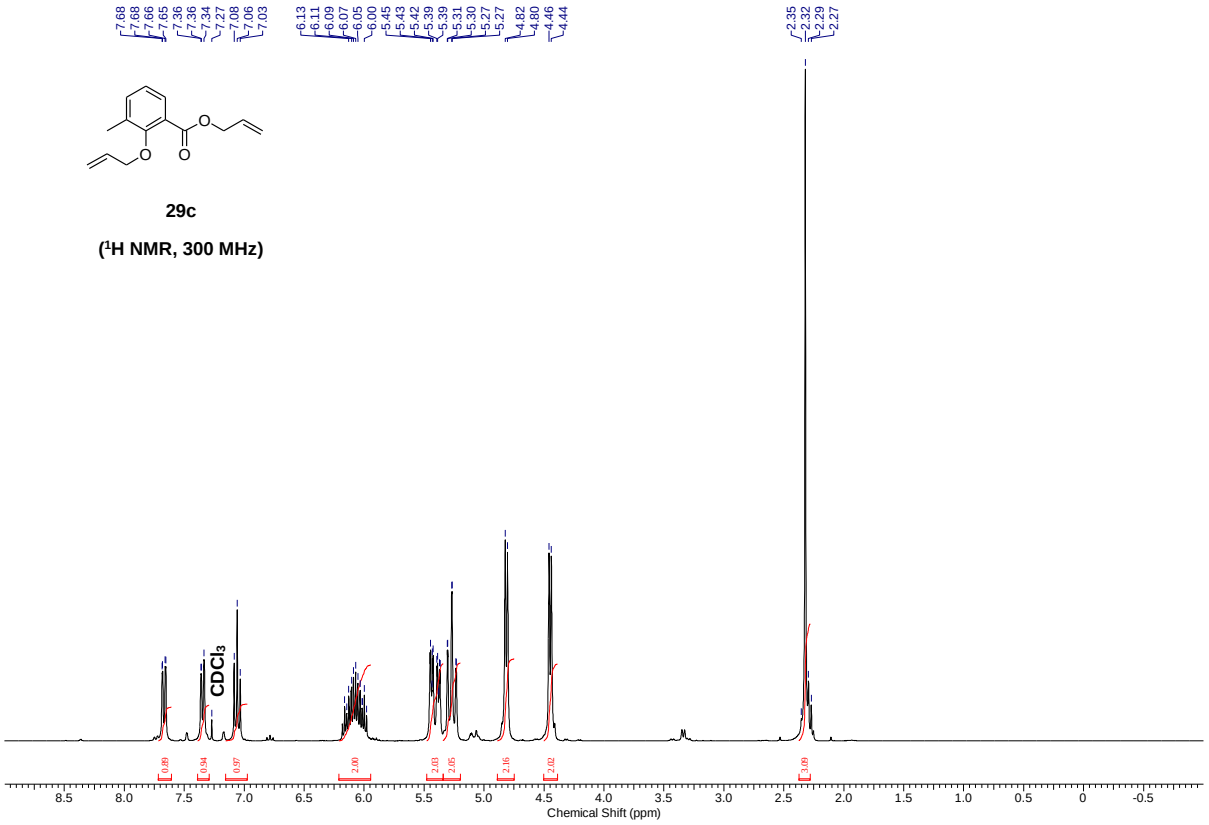
72

(^{1}H NMR, 300 MHz)



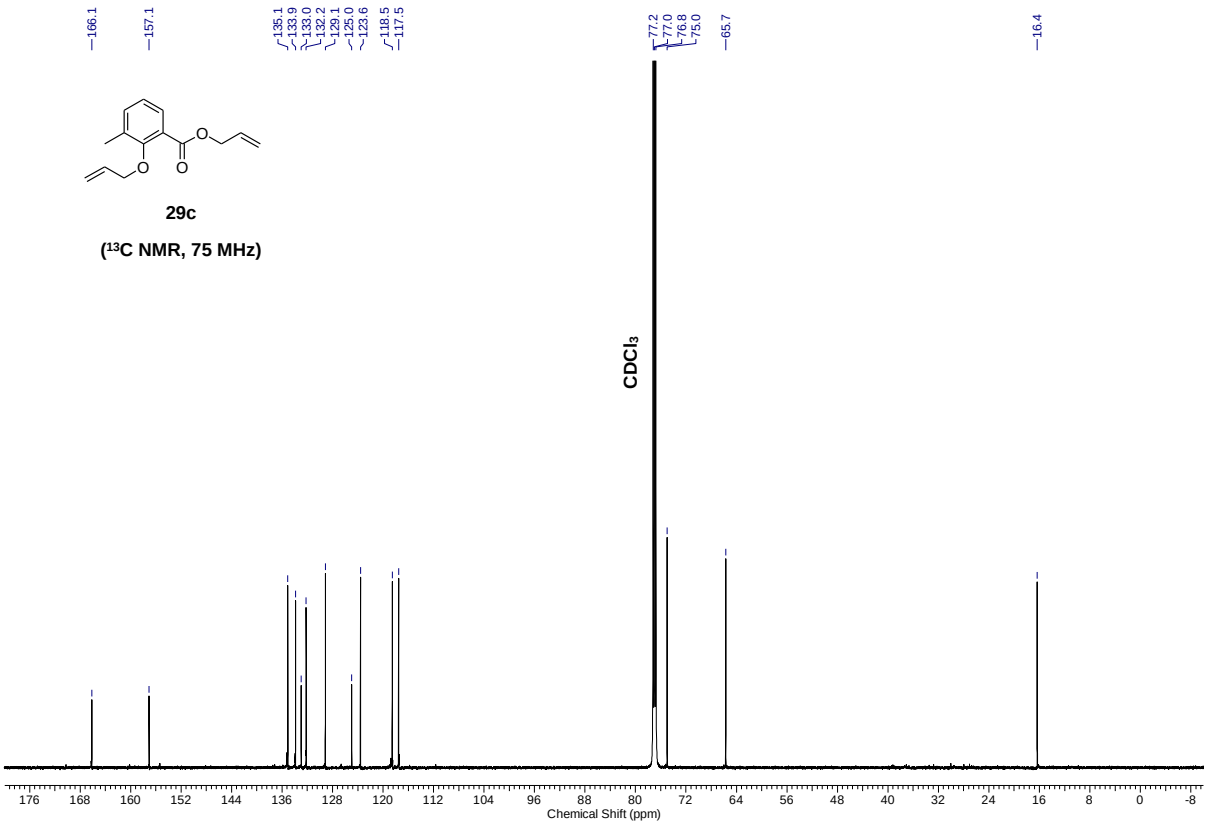
72

(^{13}C NMR, 75 MHz)



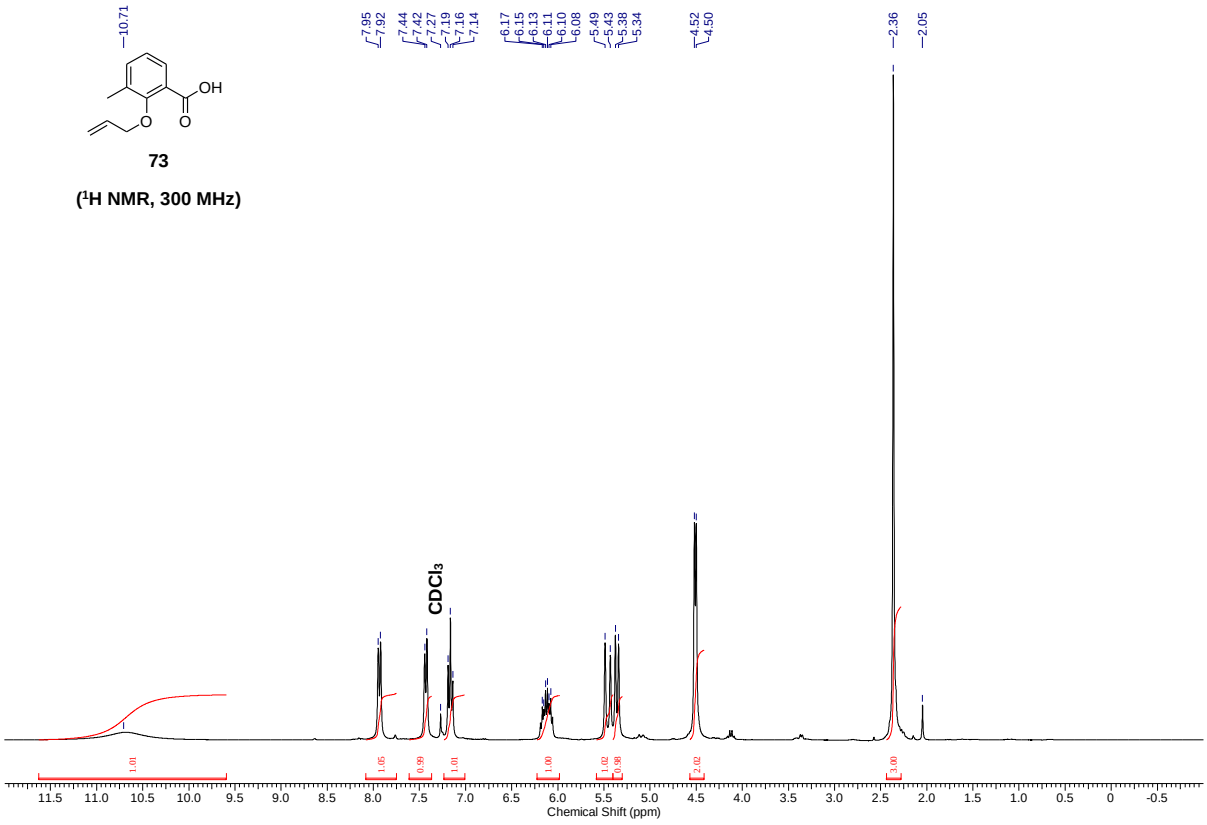
29c

(^{1}H NMR, 300 MHz)



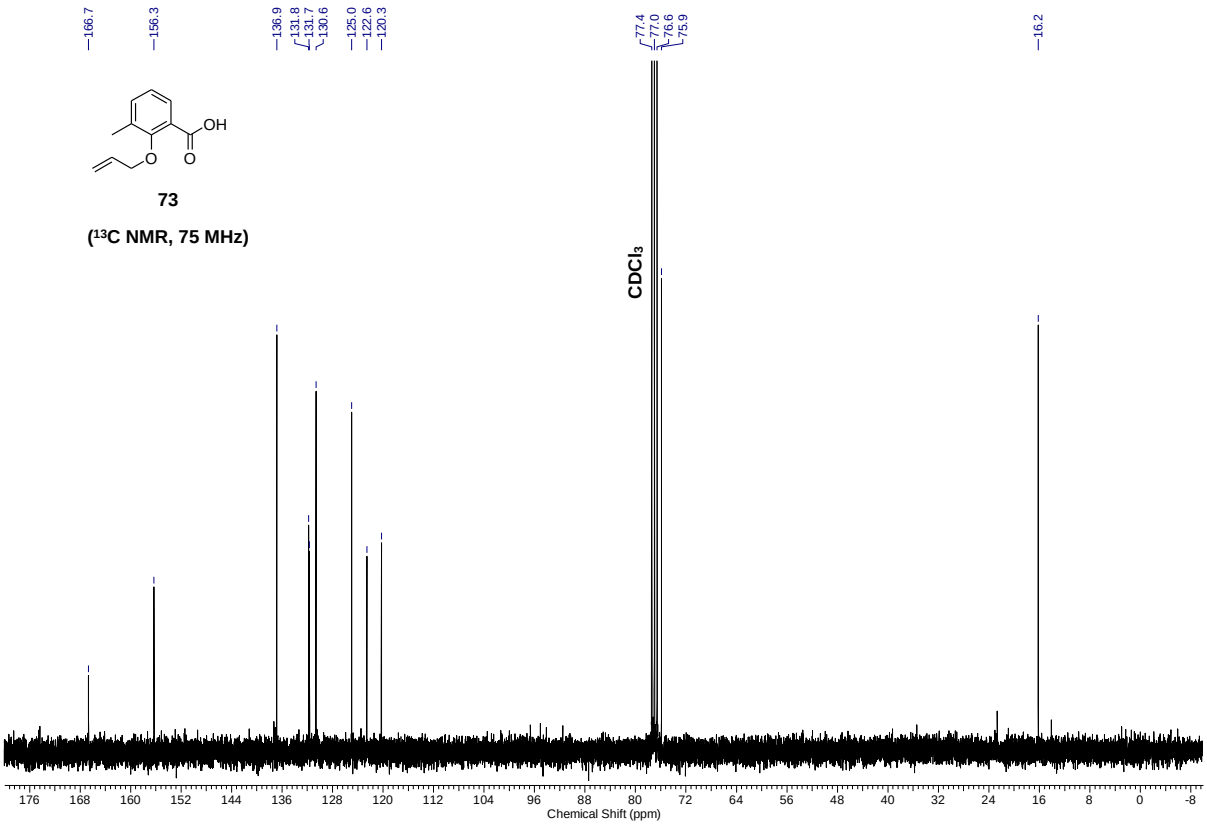
29c

(^{13}C NMR, 75 MHz)



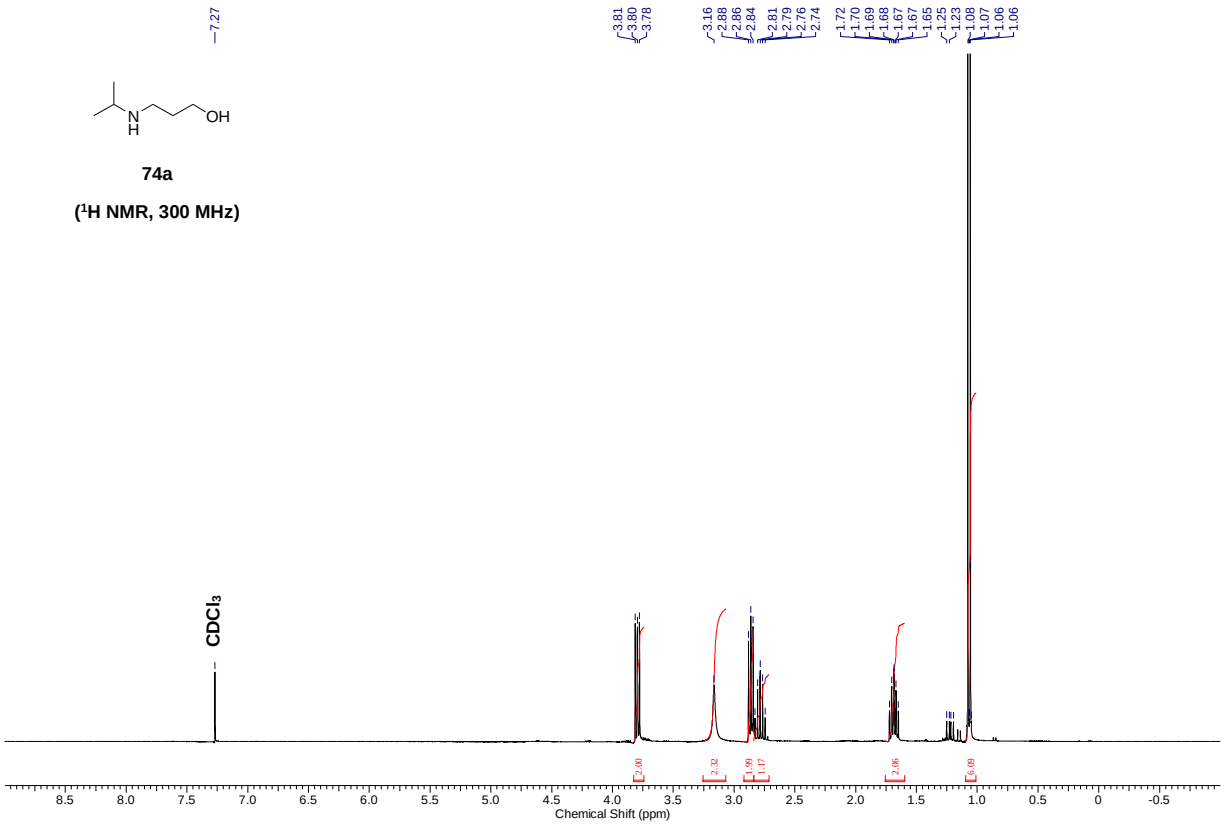
73

(^{1}H NMR, 300 MHz)



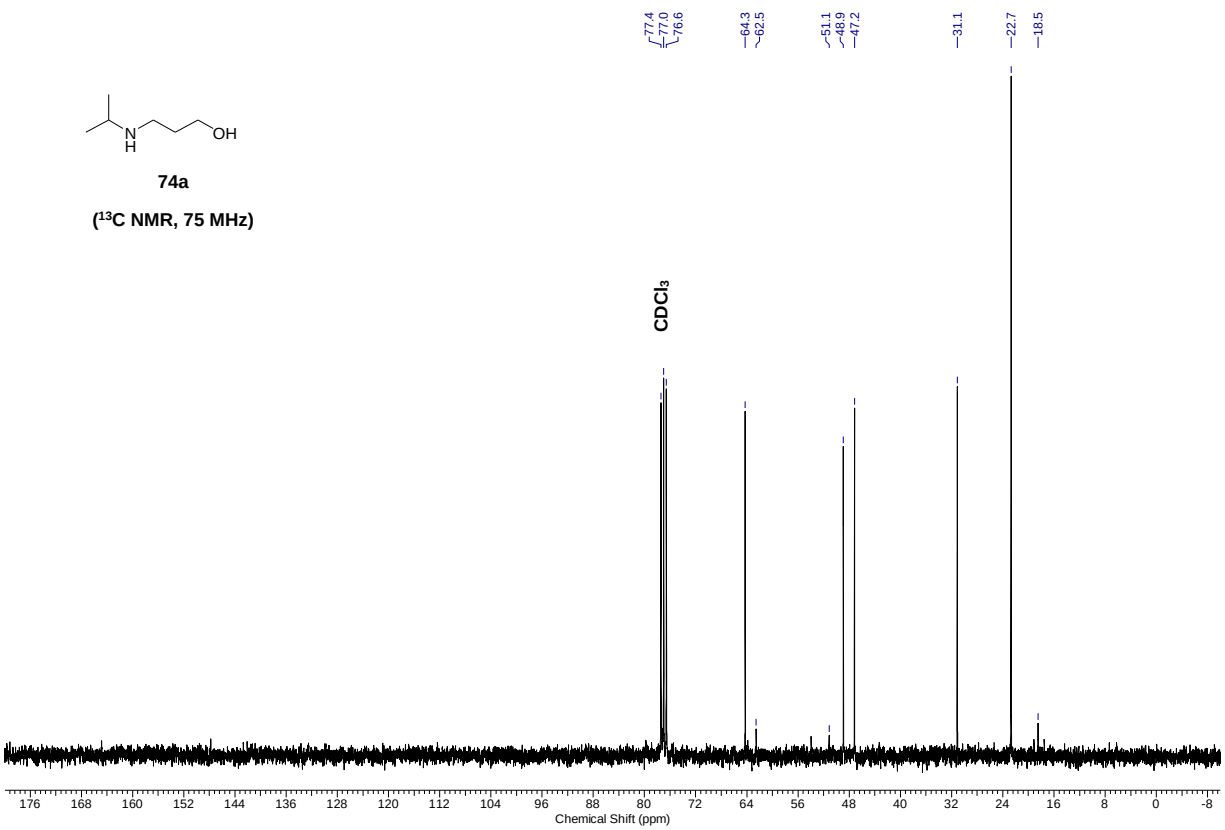
73

(^{13}C NMR, 75 MHz)



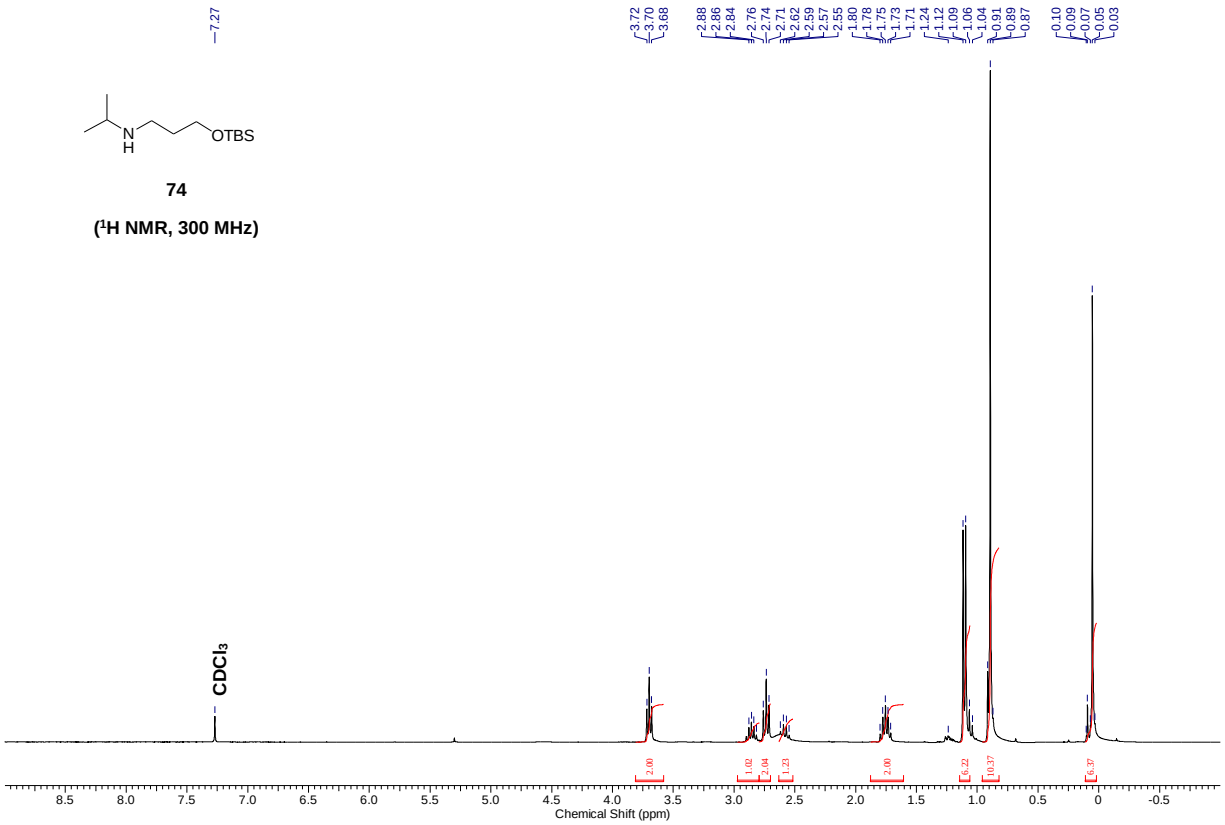
74a

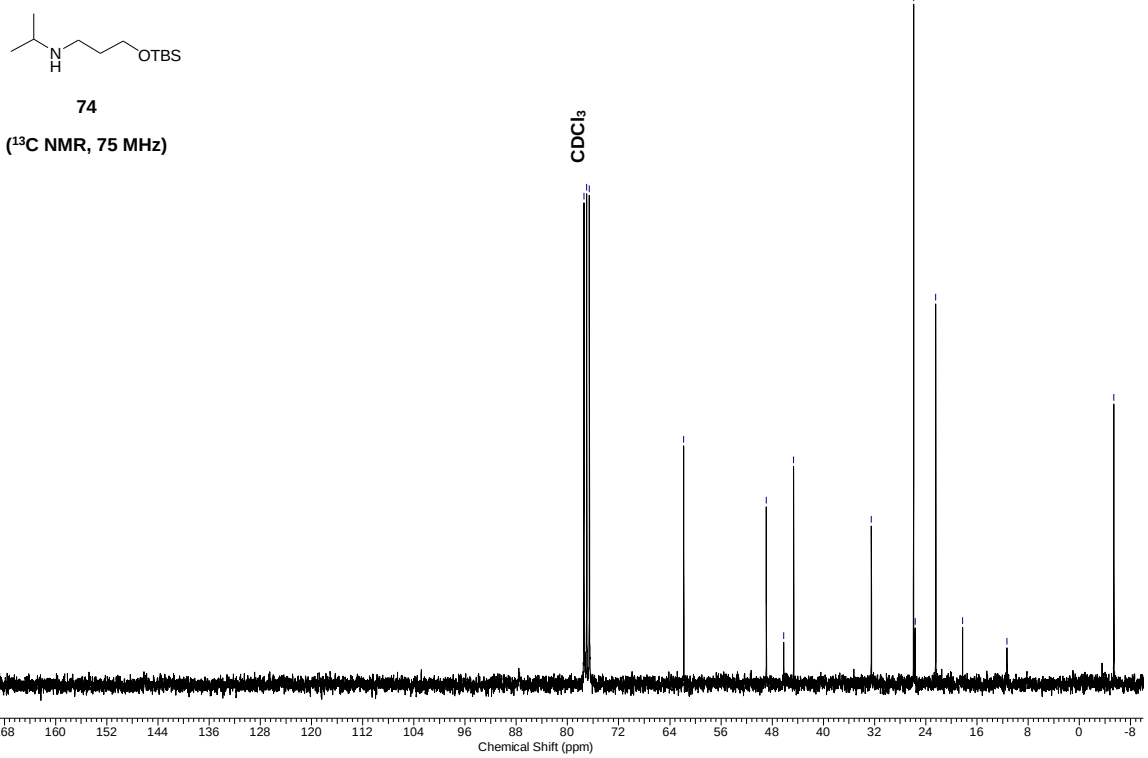
(^{1}H NMR, 300 MHz)



74a

(^{13}C NMR, 75 MHz)



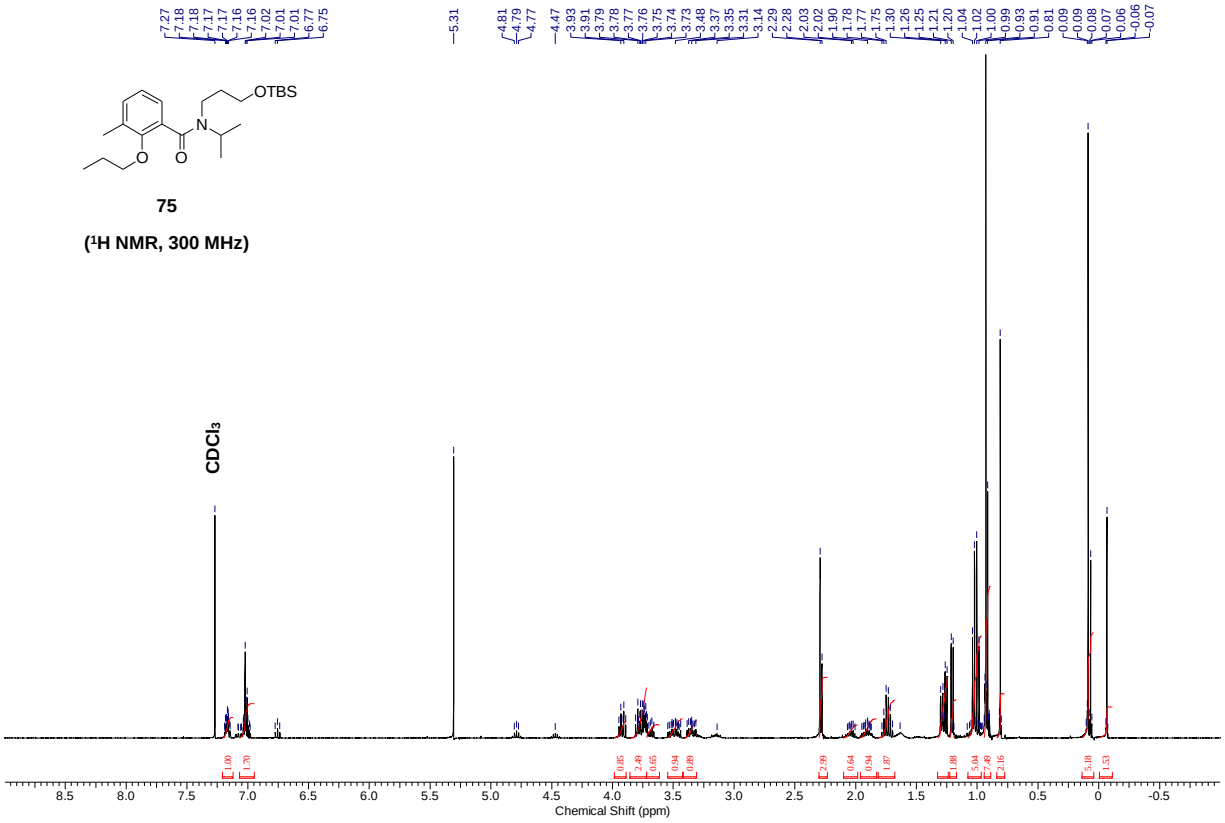


74

(^{1}H NMR, 300 MHz)

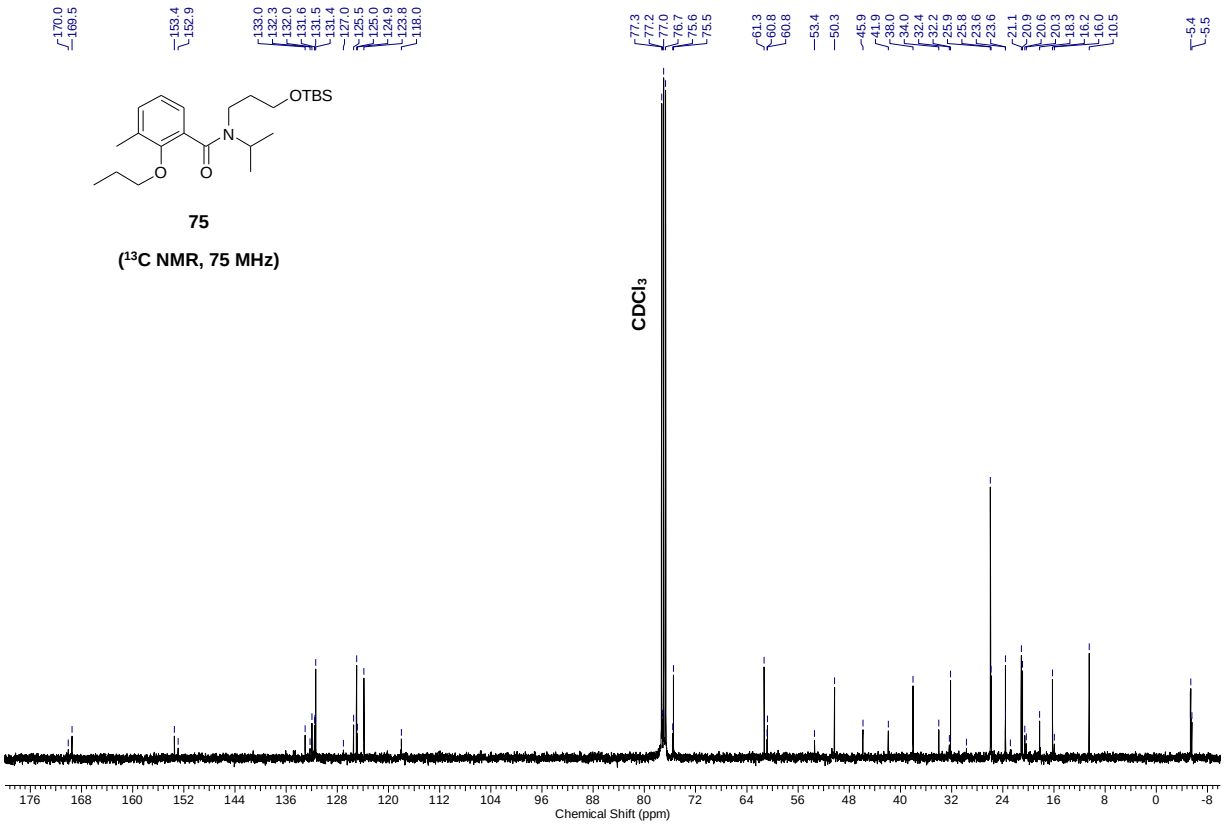
74

(^{13}C NMR, 75 MHz)



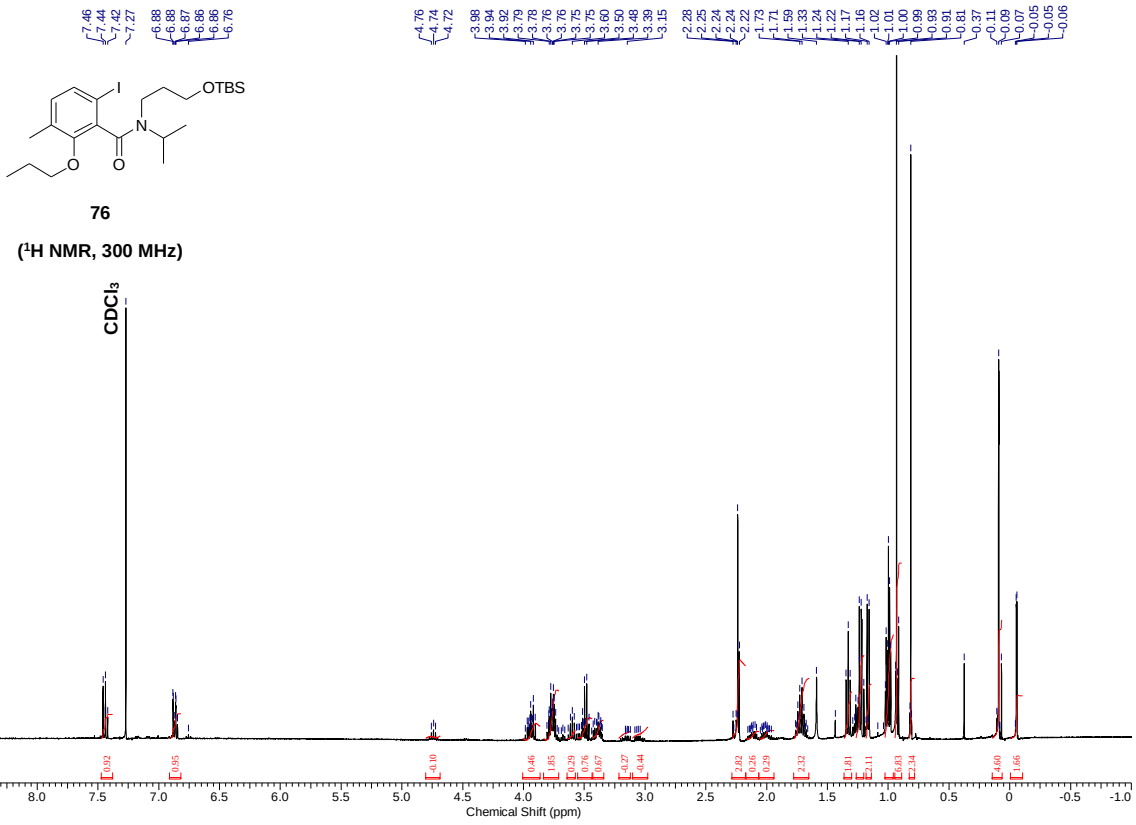
75

(^{1}H NMR, 300 MHz)



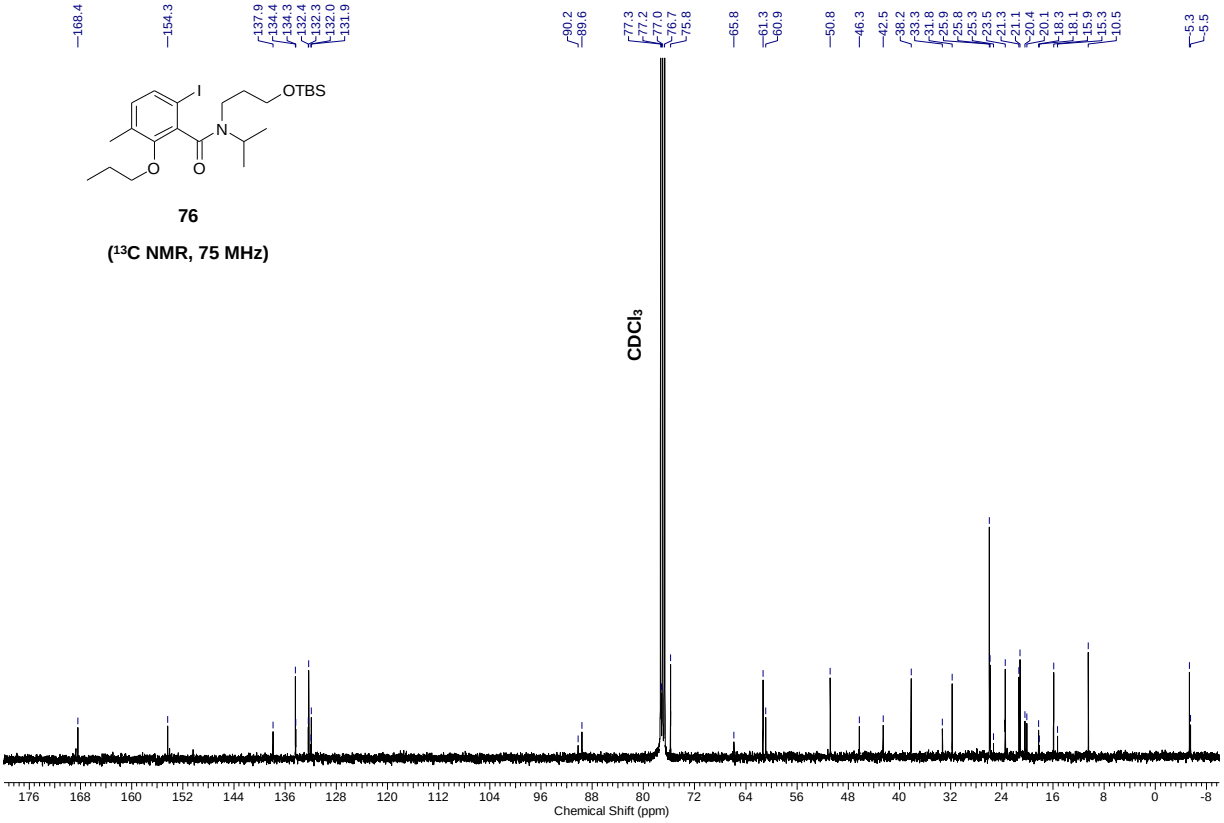
75

(^{13}C NMR, 75 MHz)



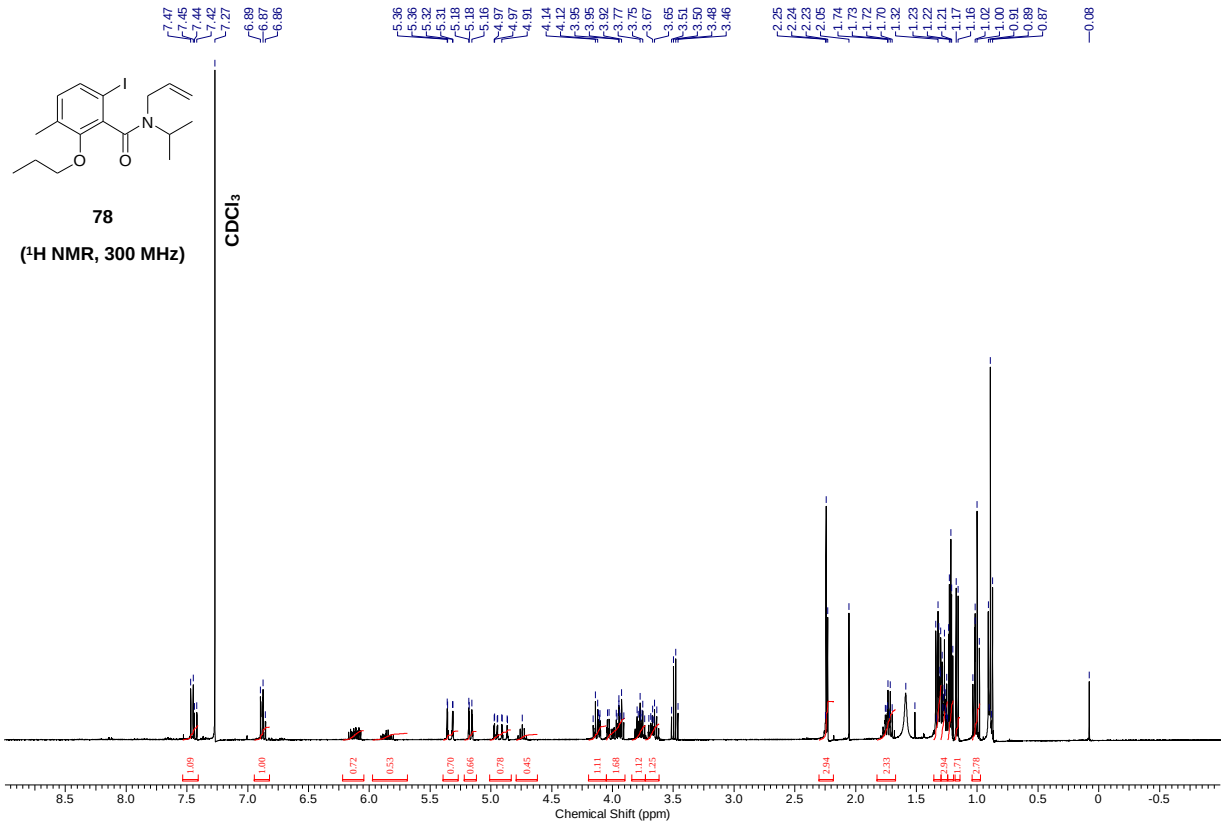
76

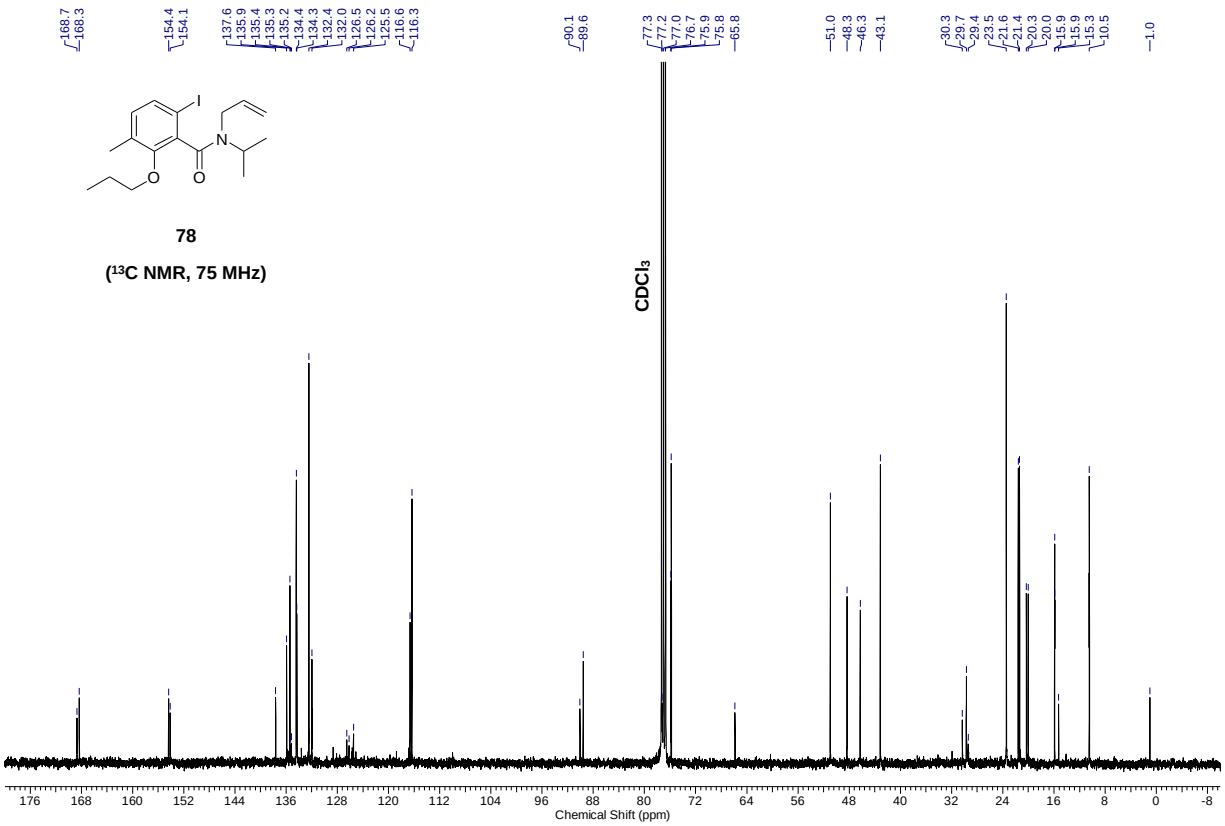
(^{1}H NMR, 300 MHz)



76

(^{13}C NMR, 75 MHz)


78
(1H NMR, 300 MHz)
CDCl3
Chemical Shift (ppm)


78
(13C NMR, 75 MHz)
CDCl3
Chemical Shift (ppm)