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Synthesis of Axially Chiral Biaryl Thioglycosides through Thiosugar-Directed Pd-Catalyzed Asymmetric C–H Activation.

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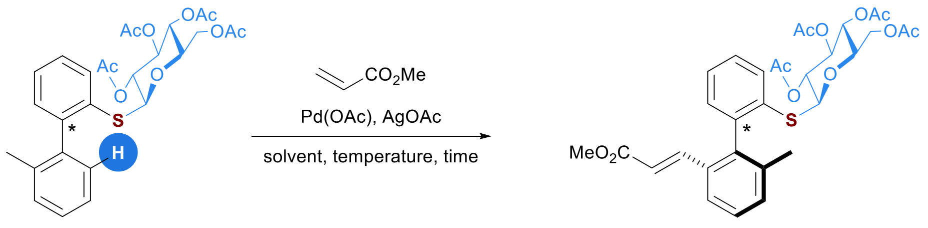
General information

Air sensitive reactions are conducted under an argon atmosphere. For the catalytic C-H-activation, $Pd(OAc)_2$ (99.9%, Aldrich) and AgOAc (99%, Alfa Aesar) were used. Other solvents and reagents were used as obtained from suppliers. Analytical TLC was performed using Merck pre-coated silica gel 60F plates and analyzed by UV light or by vanillin staining solution upon heating. For silica gel chromatography, CombiFlash® Rf Systems was used, with Biotage® SNAP Ultra Cartridges or by packed column using VWR chemicals (40-63 mesh). NMR-spectra were recorded on Bruker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75MHz), Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100MHz), and Bruker Avance 200 (^{19}F: 188 MHz) using a suitable deuterated solvent. The chemical shifts are reported in ppm relative to the solvent residual peak in $CDCl_3$ (δ 7.26) or CD_3OD (δ 3.31) for ^{1}H NMR spectra. For the ^{13}C NMR spectra, the solvent signals of $CDCl_3$ (δ 77.16) or CD_3OD (δ 49.00 ±0.01) were used as the internal standards. Multiplicities were abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants were given in Hz. Mass spectrometric data were recorded on a Micromass Spectrometer and m/z values were reported in Daltons. High resolution mass spectrometric data (HR-MS) were recorded using LCT Premier-(Waters) or QTOF 6500 series (Agilent Technologies). HPLC-Mass (LC-Ms) were recorded on LCT Premier - (Waters) Alliance 2695, PDA diodes, positive and negative electrospray ESI, TOF analyser or LC-MS : QTOF 6500 series (Agilent Technologies) 1260 Infinity, PDA diodes, ESI or APCI electrospray, Q-TOF analyser. Melting points were recorded in open capillaries on a Büchi B-540 apparatus and are uncorrected. Optical rotations were obtained with a Perkin-Elmer 343 polarimeter using sodium light (D line 589 nm) and denoted as specific rotations: $[\alpha]_D^{20}$. Yields were calculated based on the collected products. Some unknown and non-separable impurities are found in several products. Several ways have been used to detect diastereomeric ratio (dr) including chiral HPLC, HPLC-Mass and ^{1}H- and ^{19}F-NMR.

1. Optimization of the olefination reaction on model substrate 7a



7a (dr = 1:1)　**8a**

Table S1: Optimization of reaction conditions.

entry	oxidant	acrylate (equiv)	Pd(OAc)$_2$	solvent	time	temp.	yield	dr	notes
1	AgOAc (6 equiv)	2	10%	DCE/HFIP (2 :1)	17h	80°C	10%	1.3:1	Ar
2	AgOAc (6 equiv)	9	20%	DCE/HFIP (2 :1)	24h	80°C	55%	1.5:1	Ar
3	AgOAc (2 equiv)	6	20%	DCE	17h	120°C	20%	1.6:1	Ar
3	AgNO$_3$ (2 equiv)	6	20%	DCE	17h	120°C	18%	1.6:1	Ar
4	AgOAc (6 equiv)	6	20%+Cu(OAc)$_2$ (2 equiv)	DCE/HFIP (1 :1)	2d	80°C	50%	1.1:1	Ar
5	AgOAc (6 equiv)	8	20%	DCE/HFIP (2 :1)	4h	110°C (4h),MV	57%	1.4:1	Ar
6	AgOAc (6eq.)	6	20%	DCE/HFIP (2 :1)	4h	120°C	70%	1.4:1	**Air, 5ml tube**
7	AgOAc (6 equiv)	6	20%	DCE/HFIP (2 :1)	6h	120°C	69%	1.4:1	Air, 20ml tube
8	AgOAc (6 equiv)	6	20%	DCE/HFIP (2 :1)	4h	80°C	73%	1.5:1	Air, 20ml tube
9	AgOAc (6 equiv)	6	20%	DCE/HFIP (2 :1)	4h	80°C	73%	1.4:1	O2, 20ml tube
10	AgOAc (6 equiv)	2	20%	DCE/HFIP (2 :1)	4h	80°C(1h), 120°C(3h)	57%	1.3: 1	Air, 20ml tube
11	AgOAc (6 equiv)	6	10%	DCE/HFIP (2 :1)	4h	80°C (1h), 120°C(3h)	48%	1.2: 1	Air, 20ml tube
12	AgOAc (6 equiv)	4	20%	DCE/HFIP (2 :1)	4h	80°C	78%	1.5: 1	Air, 20ml tube
13	AgOAc (6 equiv)	**2**	**20%**	**DCE/HFIP (2 :1)**	**4h**	80°C	**76%**	**1.6: 1**	**Air, 20ml tube**

Reaction conditions: substituted thioglycoside **7a** (0.15 mmol), solvent (0.1 M), dr ratio is determined by LC-Ms spectroscopy.

Table S2: Effect of catalyst loading.

entry	oxidant	Acrylate (equiv)	$Pd(OAc)_2$	solvent	time	temp.	yield	dr	notes
1	AgOAc	2	20%	DCE/HFIP	4h	80°C	76%	1.6:1	Air, 20ml tube
2	AgOAc	2	10%	DCE/HFIP	4h	80°C	35%	1.1:1	Air, 20ml tube

Reaction conditions: substituted thioglycoside **7a** (0.15 mmol), AgOAc (6 equiv), solvent (DCE/HFIP, 2 :1, 0.1 M), dr ratio is determined using LC-Ms spectroscopy.

Table S3: Solvent effect.

entry	oxidant	Acrylate (equiv)	$Pd(OAc)_2$	solvent	time	temp.	yield	dr	notes
1	AgOAc	2	20%	DCE/HFIP (2 :1)	4h	80°C	76%	1.6:1	Air, 20ml tube
2	AgOAc	2	20%	HFIP	4h	80°C	66%	0.9:1	Air, 20ml tube
3	AgOAc	2	20%	DCE	4h	80°C	50%	2.1:1	Air, 20ml tube

Reaction conditions: substituted thioglycoside **7a** (0.15 mmol), AgOAc (6equiv), solvent (0.1M), dr ratio is determined using LC-Ms spectroscopy.

Table S4: Effect of AgOAc loading.

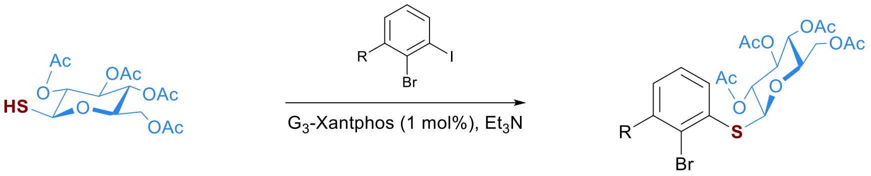
entry	AgOAc (equiv)	Acrylate (equiv)	$Pd(OAc)_2$	solvent	time	temp.	yield	dr	notes
1	6	2	20%	DCE/HFIP	4h	80°C	76%	1.6:1	Air, 20ml tube
2	-	2	20%	DCE/HFIP	4h	80°C	16%	1.2:1	Air, 20ml tube
3	2	2	20%	DCE/HFIP	4h	80°C	76%	1.4:1	Air, 20ml tube
4	4	2	20%	DCE/HFIP	4h	80°C	71%	1.1:1	Air, 20ml tube

Reaction conditions: substituted thioglycoside **7a** (0.15 mmol), solvent (DCE/HFIP, 2:1, 0.1 M), dr ratio is determined using LC-Ms.

2. Synthesis of starting materials

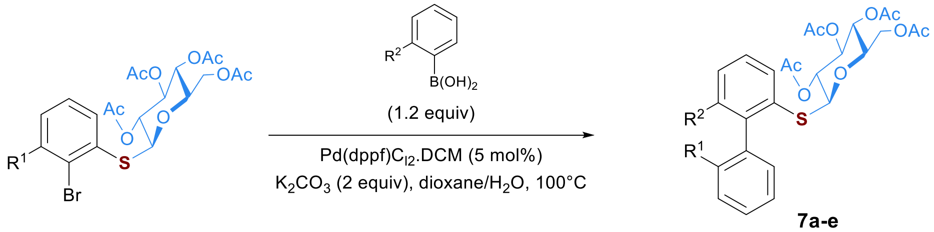
a) General procedure A for coupling of acetylated thioglycoside with aryl iodides.

Adapted from a previously published procedure.[1]



To a round bottom flask charged with G$_3$-Xantphos pre-catalyst (1 mol %), acetylated thioglycoside[1] (1 equiv) and aryl halide (1 equiv) were added. After Ar flushing, THF (0.25M) was added and the mixture left stirred for 5 min before NEt$_3$ (1 equiv) was added. The reaction mixture was stirred at room temperature under Ar until TLC showed the disappearance of starting thiol. The suspended solid was filtered off whereas the filtrate was diluted with EtOAc and extracted twice with water. The collected organic layers were washed with brine, dried over MgSO$_4$ then concentrated under reduced pressure. After completion and solvent evaporation, the residue was purified by column chromatography, unless otherwise noted, to give the desired product.

b) General procedure B for Suzuki coupling of aryl thioglycosides with boronic acids.

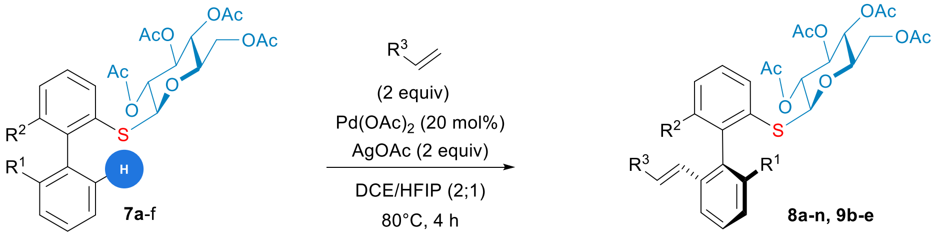


7a-e

A reaction tube was charged with Pd(dppf)Cl$_2$.DCM (5 mol%), bromo thioglycoside (1 equiv), arylboronic acid (1.2 equiv) and K$_2$CO$_3$ (2 equiv). The reaction vessel was purged with Ar and sealed, then a dioxane-water mixture (9:1, 0.23 M) was added. The reaction mixture was warmed in preheated oil bath at 100°C for relevant time. The reaction mixture was then allowed to cool to room temperature, diluted with EtOAc and filtered over celite. The crude reaction mixture was concentrated under reduced pressure and purified by column chromatography.

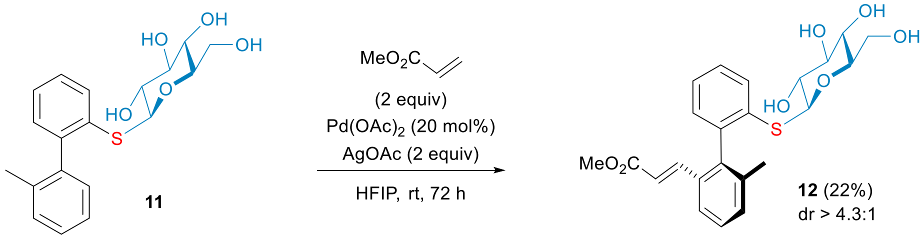
3. C–H olefination

a) General procedure C for C-H activation



A reaction tube equipped with a magnetic stir bar was charged with thiosugar **7a-f**, AgOAc (2 equiv), Pd(OAc)$_2$ (20 mol %) methyl acrylate (2 equiv) and a DCE-HFIP mixture (2:1, 0.1M) under air atmosphere. The tube was sealed and heated in preheated oil bath at 80 ºC for 4 hours unless otherwise described. The reaction mixture was cooled to room temperature, diluted with EtOAc and filtered through a pad of Celite. The solvent was evaporated under reduced pressure. The crude was purified by column chromatography. Otherwise specified, traces (less than 3% of *Z* isomers are detectable in some ^{1}H NMR spectra.

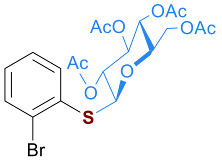
b) Special procedure C for C-H activation of unprotected thioglycoside 11 at room temperature



A reaction tube equipped with a magnetic stir bar was charged with thiosugar **11**, AgOAc (2 equiv), Pd(OAc)$_2$ (20 mol %), methyl acrylate (2 equiv) and HFIP (0.1M) under air atmosphere. The tube was sealed and stirred at room temperature for 72 hours. The reaction mixture was diluted with EtOAc and filtered through a pad of Celite. The solvent was evaporated under reduced pressure. The crude was purified by column chromatography to give **12**.

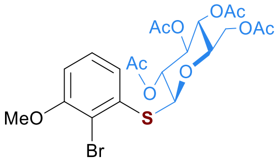
4. Characterization of starting thioglycosides and their precursors

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-bromophenyl)thio)tetrahydro-2H-pyran-3,4,5 triyl triacetate:



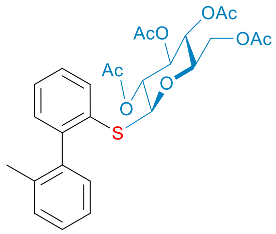
Following general procedure A, the title compound (2.3 g, 81 %) was obtained as a white powder separated upon washing the EtOAc residue with Et$_2$O; reaction time: 2h; R$_f$ = 0.4 (40% EtOAc in cyclohexane); mp:150.3-151.1°C; $[\alpha]_D^{20}$ - 42 (c, 0.5 in CHCl$_3$). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.69-7.54 (m, 2H, Ph), 7.34- 7.28 (m, 1H, Ph), 7.22-7.14 (m, 1H, Ph), 5.28 (td, *J* = 9.3, 0.9 Hz, 1H, H3′), 5.17-5.05 (m, 2H, H4′+ H2′), 4.81 (dd, *J* = 10.1, 0.9 Hz, 1H, H1′), 4.32-4.12 (m, 2H, H6′), 3.82-3.73 (m, 1H, H-5′), 2.16-2.00 (m, 12H, 4 x CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.5 (CO), 169.1 (CO), 168.3 (CO), 133.2, 132.3, 131.8, 128.13, 126.9, 125.4 (Ph), 84.4 (C1′), 74.9 (C5′), 72.9 (C3′), 68.7, 67.3(C2′+C4′), 61.2 (C6′), 19.7 (CH$_3$), 19.5 (CH$_3$). HRMS (ESI): m/z calcd for $C_{20}H_{23}BrO_9S$ [M+Na]+ 541.0144; found 541.0142.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-bromo-3-methoxyphenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate:



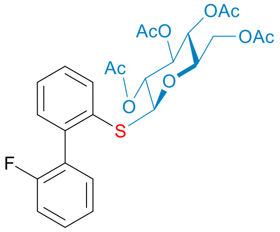
Following general procedure A, the title compound (335 mg, 89%) was obtained as crystals; reaction time: 2h; R$_f$ = 0.3 (40% EtOAc in cyclohexane); mp = 112.8-113.3°C; $[\alpha]_D^{20}$ -50 (c, 0.5 in CHCl$_3$). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.31-7.16 (m, 2H, Ph), 6.83 (dt, *J* = 7.9, 1.2 Hz, 1H, Ph), 5.28 (td, *J* = 9.2, 0.9 Hz, 1H, H3′), 5.18-5.05 (m, 2H, H4′+ H2′), 4.84 (dd, *J* = 10.2, 0.9 Hz, 1H, H1′), 4.26 (dd, *J* = 12.3, 5.5 Hz, 1H, H6′), 4.16 (dd, *J* = 12.4, 2.4 Hz, 1H, H6′), 3.90 (d, *J* = 0.8 Hz, 3H, OCH$_3$), 3.78 (ddd, *J* = 9.8, 5.4, 2.3 Hz, 1H, H5′), 2.16-1.99 (m, 12H, 4 x CH$_3$).^{13}C NMR (75 MHz, CDCl$_3$) δ 170.4 (CO), 170.1 (CO), 169.3 (CO), 169.3 (CO), 156.6 (Ph), 136.4 (Ph), 128.2 (Ph), 123.3 (Ph), 115.0 (Ph), 110.7 (Ph), 85.3 (C1′), 75.8 (C5′), 73.9 (C3′), 69.7 (C2′), 68.3 (C4′), 62.2 (C6′), 56.5 (OCH$_3$), 20.7 (CH$_3$), 20.5 (CH$_3$). HRMS (ESI): m/z calcd for $C_{21}H_{25}BrO_{10}S$ $[M+Na]^+$ 548.0352; found 548.0350.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **7a**:



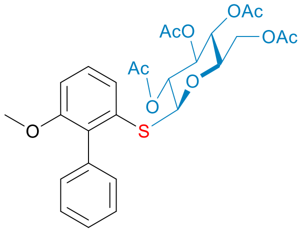
Following general procedure B, the title compound (1.2 g, 80%) was obtained as a white powder as a 1:1 mixture of two atropisomers detected by ^{1}H NMR (two different methyl groups at 1.75 and 1.84 ppm for 1.5 H each); The equatorial configuration (C1') was determined by the observed coupling constants of the doublets at 4.63 and 4.55 ppm (^3J = 10.0 Hz and 10.4 Hz respectively) corresponding to both atropisomer; reaction time: 4h; R$_f$ = 0.15 (25% EtOAc in cyclohexane); mp = 164.5-165.3°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73-7.67 (m, 1H, Ph), 7.39-7.30 (m, 2H, Ar), 7.27-7.14 (m, 4H, Ph), 7.06 (bd, *J* = 7.5, Hz, 1H, Ph), 5.20-5.10 (m, 1H, H3′), 5.90-5.00 (m, 1H, H4′), 4.93 (t, *J* = 10.4 Hz, 0.5H, H2′), 4.91 (t, *J* = 10.4 Hz, 0.5H, H2′), 4.63 (d, *J* = 10.0 Hz, 0.5H, H*1′*), 4.55 (d, *J* = 10.4 Hz, 0.5H, H*1′*), 4.26-4.09 (m, 2H, H6′), 3.72-3.63 (m, 1H, H5′), 2.11 (s, 1.5H, COCH$_3$), 2.09 (s, 1.5H, COCH$_3$), 2.07 (s, 1.5H, COCH$_3$), 2.04 (s, 1.5H, COCH$_3$), 2.02 (s, 1.5H, COCH$_3$), 2.01 (s, 1.5H, COCH$_3$), 1.97 (s, 1.5H, COCH$_3$), 1.95 (s, 1.5H, COCH$_3$), 1.84 (s, 1.5H, CH$_3$), 1.75 (s, 1.5H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.7, 170.3, 170.2, 169.5, 169.4, 169.2, 144.3, 143.5, 140.6, 140.3, 136.6, 135.6, 133.3, 132.8, 132.6, 131.2, 130.3, 130.1, 130.0, 129.7, 129.2, 128.2, 128.1, 128.10, 128.0, 127.9, 127.6, 125.6, 125.4, 86.9, 86.6, 75.9, 75.8, 74.0, 73.9, 70.0, 69.9, 68.6, 68.5, 62.5, 62.5, 20.9, 20.7, 20. 5, 20.2, 20.1. HRMS (ESI): m/z calcd for $C_{27}H_{30}O_9S$ $[M+NH_4]^+$ 548.1954; found 548.1951.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-fluoro-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **7b**:



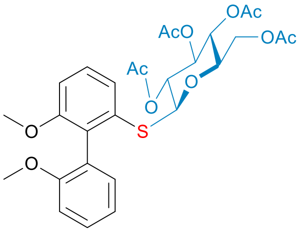
Following general procedure B, the title compound (0.42 g, 81%) was obtained as white crystal. The equatorial configuration (C1’) was determined by the observed coupling constant of the corresponding doublet (^3J = 10.4 Hz at 4.55 ppm); reaction time: 4 h; R_f = 0.34 (2:3 EtOAc/cyclohexane); mp = 143.2-143.6°C; $[\alpha]_D^{20}$ -68 (c, 0.5 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.74 (m, 1H, Ph), 7.41-7.27 (m, 4H, Ph), 7.25-7.06 (m, 3H, Ph), 5.14 (t, *J* = 9.3 Hz, 1H, H3′), 5.03 (t, *J* = 9.3 Hz, 1H, H4′), 4.91 (t, *J* = 9.1 Hz, 1H, H2′), 4.79 (d, *J* = 10.4 Hz, 0.05H, H1′), 4.56 (bd, *J* = 10.0 Hz, 0.99H, H1′), 4.21 (dd, *J* = 12.4, 5.6 Hz, 1H, H6′), 4.13 (dd, *J* = 12.4, 2.4 Hz, 1H, H6′), 3.67-3.62 (m, 1H H5′), 2.10 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$), 1.78 (bs, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.2, 159.61 (d, *J* = 327 Hz), 139.0, 133.6, 132.9, 131.9, 130.9, 129.7, 129.6, 128.7, 128.5, 128.4, 123.9, 123.8, 115.4 (d, *J* = 30 Hz), 86.8, 75.8, 74.0, 70.0, 69.5, 62.4, 20.6, 20.5. ^{19}F NMR (188 MHz, $CDCl_3$) δ -113.95. HRMS (ESI): m/z calcd for $C_{26}H_{27}FO_9S$ $[M+Na]^+$ 557.1258; found 557.1248.

(2*S*,3*S*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-((6-methoxy-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **7c**:



Following general procedure B, the title compound (112 mg, 70%) was obtained as white crystals. The equatorial configuration (C1’) was determined by the observed coupling constant of the corresponding doublet (^3J = 10.2 Hz at 4.55 ppm); reaction time: 4 h; R_f = 0.1 (20% EtOAc in cyclohexane); mp = 128.9-130.1; $[\alpha]_D^{20}$ -60 (c, 0.5 in $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.24 (m, 5H, Ph), 7.17 (bd, *J* = 7.1 Hz, 2H, Ph), 6.89 (dd, *J* = 8.1, 1.3 Hz, 1H, Ph), 5.12 (t, *J* = 9.3 Hz, 1H, H3′), 5.02 (t, *J* = 9.7 Hz, 1H, H4′), 4.90 (dd, *J* = 10.2, 9.2 Hz, 1H, H2′), 4.55 (d, *J* = 10.2 Hz, 1H, H*1′*), 4.21 (dd, *J* = 12.4, 5.6 Hz, 1H, H6′), 4.11 (dd, *J* = 12.4, 2.4 Hz, 1H, H6′), 3.70-3.62 (m, 1H, H5′), 3.68 (s, 3H, OCH_3), 2.08 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 1.94 (s, 3H, $COCH_3$), 1.76 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 169.4, 169.1, 157.2, 136.4, 134.5, 133.0, 130.8, 130.1, 128.8, 127.9, 127.8, 127.4, 123.8, 110.6, 86.6, 75.8, 74.0, 69.9, 68.5, 62.4, 56.0, 20.8, 20.6, 20.5. HRMS (ESI): m/z calcd for $C_{27}H_{30}O_{10}S$ $[M+Na]^+$ 569.1457; found 569.1453.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2',6-dimethoxy-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **7d**:

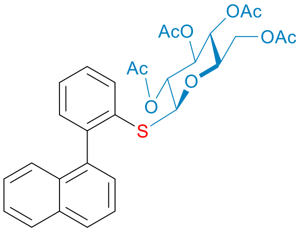


Following general procedure B, the title compound was synthesized using 1.7 equiv. of 2-methoxyphenyl boronic acid and 2.5 equiv. of K_2CO_3. Purification by flash chromatography afforded a major atropisomer (50 mg, 30%) as creamy white crystals along with a minor atropisomer (17 mg, 10%) as white powder; the equatorial configurations (C1') of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^3J = 10.0 Hz at 4.52 ppm for major and ^3J = 10.3 Hz at 4.58 ppm for minor); reaction time: 8 h;

Major atropisomer: R_f = 0.3 (20% EtOAc in cyclohexane); mp = 111.9-112.5°C; $[\alpha]_D^{20}$ -120 (c, 0.3 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.24 (m, 3H, Ph), 7.00 (dd, *J* = 7.2, 1.6 Hz, 1H, Ph), 6.99-6.90 (m, 3H, Ph), 5.12 (t, *J* = 9.6 Hz, 1H, H3′), 5.03 (t, *J* = 9.6 Hz, 1H, H4′), 4.88 (dd, *J* = 10.4, 9.2 Hz, 1H, H2′), 4.52 (d, *J* = 10.0 Hz, 1H, H1′), 4.23 (dd, *J* = 12.0, 5.6 Hz, 1H, H6′), 4.15 (dd, *J* = 12.0, 2.4 Hz, 1H, H6′), 3.72 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.70-3.63 (m, 1H, H5′), 2.11 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$), 1.68 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.3, 169.5, 169.4, 157.5, 157.4, 136.0, 131.3, 129.6, 129.2, 128.7, 125.4, 124.2, 120.1, 111.0, 87.5, 75.7, 73.9, 70.0, 69.6, 62.5, 56.1, 55.7, 20.9, 20.7, 20.5. HRMS (ESI): m/z calcd for $C_{28}H_{32}O_{11}S$ $[M+Na]^+$ 599.1563; found 599.1558.

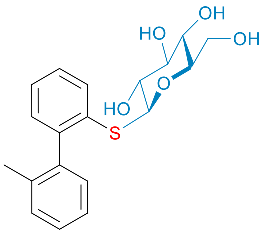
Minor atropisomer: R_f = 0.24 (20% EtOAc in cyclohexane); mp = 162.9-164.1°C; $[\alpha]_D^{16}$ -30 (c, 0.5 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 3H, Ph), 7.00 (dd, *J* = 7.4, 1.8 Hz, 1H, Ph), 6.95-6.87 (m, 3H, Ph), 5.07 (t, *J* = 9.3 Hz, 1H, H3′), 4.99 (t, *J* = 9.7 Hz, 1H, H4′), 4.87 (dd, *J* = 10.3, 9.2 Hz, 1H, H2′), 4.58 (d, *J* = 10.3 Hz, 1H, H-1′), 4.17 (dd, *J* = 12.0, 5.2 Hz, 1H, H6′), 4.09 (dd, *J* = 12.0, 2.4 Hz, 1H, H6′), 3.71 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.55 (ddd, *J* = 9.9, 5.4, 2.5 Hz, 1H, H5′), 2.05 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$), 1.91 (s, 3H, $COCH_3$), 1.72 (s, 3H, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 169.5, 169.3, 157.7, 157.0, 134.2, 132.1, 130.6, 129.1, 128.7, 125.9, 125.4, 120.5, 111.1, 110.9, 86.4, 75. 8, 74.2, 69.8, 68.6, 62.5, 56.2, 55.7, 20.9, 20.7, 20.7. HRMS (ESI): m/z calcd for $C_{28}H_{32}O_{11}S$ $[M+Na]^+$ 599.1563; found 599.1562.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(naphthalen-1-yl)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **7e**:



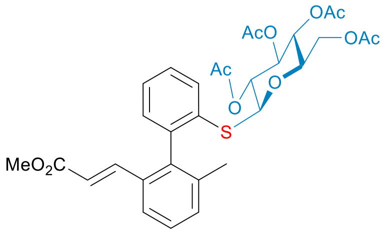
Following general procedure B, the title compound (0.46 g, 84%) was obtained as white foam as a mixture of two atropisomers detected by ^{1}H NMR (1.4:1); the equatorial configurations (C1') of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^3J = 10.0 Hz at 4.54 ppm for major and ^3J = 10.0 Hz at 4.49 ppm for minor); reaction time: 4 h; R$_f$ = 0.11 (20% EtOAc in cyclohexane); mp = 72.5-72.9 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92-7.84 (m, 2H, Ar), 7.83-7.77 (m, 1H, Ar), 7.54-7.37 (m, 6H, Ar), 7.36-7.28 (m, 2H, Ar), 5.11-4.95 (m, 2H, H3′ and H4′), 4.81 (ddd, *J* = 10.1, 8.9, 6.6 Hz, 1H, H2′), 4.54 (d, *J* = 10.0 Hz, 0.57H, H1′), 4.49 (d, *J* = 10.0 Hz, 0.43H, H1′), 4.25-3.97 (m, 2H, H6′), 3.70-3.63 (m, 0.57H, H5′), 3.53-3.46 (m, 0.44H, H5′), 2.13 (s, 1.74H, COCH$_3$), 2.09 (s, 1.41H, COCH$_3$), 2.00 (s, 1.80H, COCH$_3$),. 1.99 (s, 1.39H, COCH$_3$), 1.93 (s, 1.33H, COCH$_3$), 1.91 (s, 1.69H, COCH$_3$), 1.62 (bs, 0.59H, COCH$_3$), 1.57 (s, 1.36H, COCH$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 170.7, 170.2, 170.15, 169.5, 169.4, 169.11, 169.10, 143.1, 142.3, 138.6, 138.2, 134.3, 133.6, 133.5, 133.4, 133.2, 132.3, 131.9, 131.5, 131.2, 128.6, 128.5, 128.4, 128.2, 128.2, 128.16, 127.8, 127.5, 126.9, 126.4, 126.2, 126.1, 126.0, 125.9, 125.8, 125.3, 125.1, 86.9, 86.7, 75.8, 75.7, 73.9, 73.9, 69.9, 69.6, 68.5, 68.4, 62.5, 62.3, 20.9, 20.84, 20.6, 20.3, 19.9. HRMS (ESI): m/z calcd for $C_{30}H_{30}O_9S$ [M+Na]+ 589.1508; found 589.1499.

(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(hydroxymethyl)-6-((2'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triol **11**:



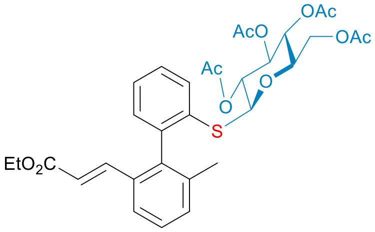
Following published procedure^2, the title compound (110 mg, 100%) was obtained as white crystals as a mixture of two atropisomers (1.3:1) detected by ^{1}H NMR; the equatorial configurations (C1') of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^3J = 9.8 Hz at 4.74 ppm); R$_f$ = 0.0 (20% EtOAc in cyclohexane); mp = 124.3-125.6°C; ^{1}H NMR (400 MHz, MeOD) δ 7.74 (dd, *J* = 8.0, 0.8 Hz, 0.5H, Ph), 7.71 (dd, *J* = 8.0, 0.8 Hz, 0.5H, Ph), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H, Ph), 7.34-7.20 (m, 4H, Ph), 7.15-7.08 (m, 2H, Ph), 4.74 (d, *J* = 9.8 Hz, 1H, H1′), 3.96 (dd, *J* = 4.8, 2.4 Hz, 0.46H, H6′), 3.93 (dd, *J* = 4.4, 2.0 Hz, 0.46H, H6′), 3.74 (bd, *J* = 6.0 Hz, 0.63H,), 3.71 (bd, *J* = 5.6 Hz, 0.63H,), 3.48-3.38 (m, 3H, H5′, H4′, H3′), 3.28-3.19 (m, 1H, H2′), 2.14 (s, 1.53H, CH$_3$), 2.13 (s, 1.36H, CH$_3$). ^{13}C NMR (100 MHz, MeOD) δ 142.7, 142.6, 141.7, 141.6, 137.6, 137.4, 136.5, 136.4, 130.9, 130.8, 130.74, 130.7, 129.2, 129.1, 129.0, 128.9, 128.8, 126.8, 126.75, 126.6, 126.5, 88.3, 87.9, 81.9, 79.7, 79.66, 74.0, 73.9, 71.4, 62.82, 62.8, 20.1, 20.0. HRMS (ESI): m/z calcd for $C_{19}H_{22}O_5S$ [M+Na]$^+$ 385.1080; found 385.1082.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8a**:



Following general procedure C, the title compound (70 mg, 76%) was obtained as white powder as a mixture of two atropisomers detected by ^{1}H NMR (1.3:1); the equatorial configurations (C1') of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^3J = 10.4 Hz at 4.70 ppm for major and ^3J = 10.0 Hz at 4.69 ppm for minor); reaction time: 4 h; R_f = 0.35 (40% EtOAc in Cyclohexane); upon further purification we get atropoenriched product (dr 7.8:1 detected by LC mass and 6:1 by ^{1}H NMR); mp = 195.4-196.7°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.78 (m, 0.43H, Ar), 7.78-7.73 (m, 0.57H, Ar), 7.59-7.53 (m, 1H, Ar), 7.45-7.37 (m, 2H, Ar), 7.35-7.25 (m, 2.42H, Ar + *H*C=$CHCO_2Me$), 7.21 (d, *J* = 15.6 Hz, 1H, *H*C=$CHCO_2Me$), 7.14-7.07 (m, 1H, Ar), 6.34 (d, *J* = 16.0 Hz, 0.42H, HC=C*H*CO_2Me), 6.27 (d, *J* = 16.0 Hz, 0.54H, HC=C*H*CO_2Me), 5.24-5.02 (m, 2H, H3′, H4′), 4.98-4.87 (m, 1H, H2′), 4.70 (d, *J* = 10.4 Hz, 0.57H, H1′), 4.69 (d, *J* = 10.0 Hz, 0.42H, H1′), 4.36-4.09 (m, 2H, H6′), 3.81-3.66 (m, 1H, H5′), 3.77 (s, 1.29H, OCH_3), 3.69 (s, 1.71H, OCH_3), 2.14 (2s, 3H, $COCH_3$), 2.04 (2s, 3H, $COCH_3$), 2.02 (s, 1.67H, $COCH_3$), 2.00 (s, 1.75H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.89 (s, 1.81H, CH_3), 1.76 (s, 1.81H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 170.2, 170.1, 169.5, 169.5, 169.3, 169.0, 169.0, 167.4, 167.2, 143.6, 143.1, 141.2, 141.0, 140.8, 140.3, 137.8, 136.6, 134.3, 134.0, 133.3, 132.9, 132.7, 131.9, 131.3, 131.2, 130.4, 130.3, 129.0, 128.8, 128.6, 128.3, 128.1, 124.1, 123.4, 119.2, 118.7, 91.8, 87.0, 86.4, 72.9, 72.9, 70.4, 70.1, 69.9, 68.6, 68.4, 67.9, 62.4, 61.6, 51.8, 51.6, 20.8, 20.8, 20.7, 20.6, 20.5, 20.5, 20.4. HRMS (ESI): m/z calcd for $C_{31}H_{34}O_{11}S$ $[M+NH_4]^+$ 632.2166; found 632.2166.

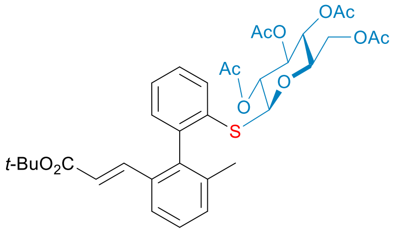
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8b**:



Following general procedure C, the title compound (70 mg, 74%) was obtained as yellowish powder as a mixture of two atropisomers (1.4:1 detected by ^{1}H NMR); the equatorial configurations (C1') of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^3J = 10.3 Hz at 4.66 ppm for major and ^3J = 10.0 Hz at 4.65 ppm for minor); reaction time: 4 h; R_f = 0.38 (40% EtOAc in cyclohexane); mp = 137.2-138.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 0.41H, Ar), 7.74-7.69 (m, 0.57H, Ar), 7.59-7.49 (m, 1H, Ar), 7.43-7.33 (m, 2H, Ar), 7.32-7.22 (m, 3H, Ar + *H*C=$CHCO_2Et$), 7.17 (d, *J* = 16 Hz, *H*C=$CHCO_2Me$), 7.11-7.04 (m, 1H, Ar), 6.30 (d, *J* = 16.0 Hz, 0.40H, HC=C*H*CO_2Et), 6.24 (d, *J* = 16.0 Hz, 0.55H, HC=C*H*CO_2Et), 5.21-4.99 (m, 2H, H3′, H4′), 4.94-4.86 (m, 1H, H2′), 4.66 (d, *J* = 10.4 Hz, 0.55H, H1′), 4.65 (d, *J* = 10.0 Hz, 0.40H, H1′), 4.27-4.06 (m, 4H, H-6′ and C*H*$_2CH_3$), 3.76-3.65 (m, 1H, H5′), 2.11 (2s, 3H, $COCH_3$), 2.01-2.00-

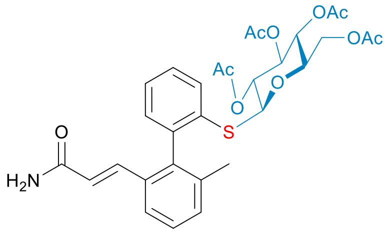
1.98-1.96-1.95-1.94 (6s, 9H, 3 x $COCH_3$), 1.85 (s, 1.70H, CH_3), 1.73 (s, 1.30H, CH_3), 1.28 (t, *J* = 7.2 Hz, 1.2H, CH_2CH_3), 1.22 (t, *J* = 7.2 Hz, 1.65H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1, 169.9, 169.4, 169.3, 169.2, 168.9, 166.9, 166.6, 143.3, 142.8, 141.1, 140.9, 140.6, 140.2, 137.65, 136.5, 134.1, 133.9, 133.1, 132.8, 132.7, 131.6, 131.15, 131.1, 130.3, 130.2, 128.8, 128.6, 128.4, 128.1, 127.98, 123.9, 123.2, 119.4, 119.0 86.9, 86.2, 75.7, 75.6, 73.8, 73.8, 70.0, 69.7, 68.4, 68.3, 62.3, 60.4, 60.2, 20.7, 20.5, 20.3, 20.3, 14.2, 14.2. HRMS (ESI): m/z calcd for $C_{32}H_{36}O_{11}S$ $[M+Na]^+$ 651.1876; found 651.1875.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((2'-((E)-3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8c**:



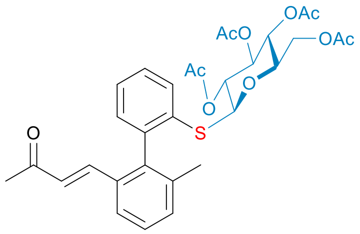
Following general procedure C, the title compound (46 mg, 54%) was obtained as creamy-white powder as a mixture of two atropisomers (10:1 detected by ^1H NMR); the equatorial configurations (C1') of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^3J = 10.0 Hz at 4.65 ppm for major and ^3J = 10.4 Hz at 4.73 ppm for minor); reaction time: 24h; R_f = 0.12 (20% EtOAc in Cyclohexane); m.p.=173.8-174.5°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79-7.68 (m, 1H, Ar), 7.56-7.50 (m, 1H, Ar), 7.40-7.33 (m, 2H, Ar), 7.31-7.20 (m, 2H, Ar), 7.16 (d, *J* = 16.0 Hz, 0.09H, *H*C=CHCO₂ *t*Bu), 7.08 (d, *J* = 15.6 Hz, 0.91H, *H*C=CHCO₂*t*Bu), 7.12-7.02 (m, 1H, Ar), 6.28 (d, *J* = 16.0 Hz, 0.09H, HC=C*H*CO₂*t*Bu), 6.20 (d, *J* = 16.0 Hz, 0.91H, HC=C*H*CO₂*t*Bu), 5.16 (t, *J* = 9.3 Hz, 1H, H3′), 5.04 (dd, *J* = 10.0, 9.4 Hz, 1H, H4′), 4.90 (dd, *J* = 10.3, 9.2 Hz, 1H, H2′), 4.73 (d, *J* = 10.4 Hz, 0.09H, H1′), 4.65 (d, *J* = 10.0 Hz, 0.91H, H1′), 4.28 (dd, *J* = 12.4, 4.4 Hz, 0.09H, H6′), 4.23 (dd, *J* = 12.4, 5.6 Hz, 1H, H6′), 3.83 (ddd, *J* = 10.0, 5.1, 2.3 Hz, 0.09H, H5′), 3.72 (ddd, *J* = 10.0, 5.1, 2.3 Hz, 0.91H, H5′), 2.11 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$), 1.85 (s, 3H, CH_3), 1.46 (s, 0.7H, *t*Bu), 1.41 (s, 8.3H, *t*Bu). ^{13}C NMR (101 MHz, $CDCl_3$) δ (major atropisomer) 170.7, 170.3, 169.5, 169.1, 166.1, 141.8, 140.8, 140.5, 136.5, 134.3, 134.1, 131.4, 131.0, 130.4, 128.9, 128.2, 128.2, 124.2, 123.8, 87.1, 80.3, 75.9, 74.0, 70.1, 68.4, 62.4, 28.3, 20.9, 20.7, 20.5. HRMS (ESI): m/z calcd for $C_{34}H_{40}O_{11}S$ $[M+Na]^+$ 679.2189; found 679.2189.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-((*E*)-3-amino-3-oxoprop-1-en-1-yl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8d**:



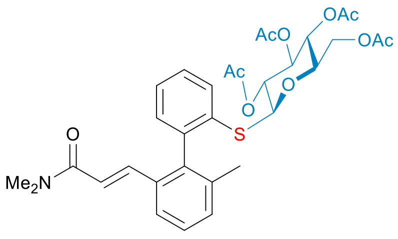
Following general procedure C, the title compound (50.1 mg, 56%) was obtained as creamy-white crystals as a mixture of two atropisomers (2:1 detected by ^{1}H NMR); the equatorial configurations (C1’) of both atropisomers were determined by the observed coupling constant of the corresponding doublets (^{3}J = 10.0 Hz at 4.66 ppm for major and ^{3}J = 10.4 Hz at 4.64 ppm for minor); reaction time: 4 h; R_f = 0.4 (100% EtOAc); mp = 118.9-120.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.66 (m, 1H, Ar), 7.56-6.95 (m, 7H, Ar and C*H*=CHCONH$_2$), 6.37-6.18 (m, 1H, CH=C*H*CONH$_2$), 6.06-5.59 (bs, 2H, NH$_2$), 5.23-4.78 (m, 3H, H3′, H4′, H2′), 4.66 (bd, *J* = 10.0 Hz, 0.65H, H1′), 4.64 (bd, *J* = 10.4 Hz, 0.35H, H1′), 4.31-4.06 (m, 2H, H6′), 3.80-3.69 (m, 0.63H, H5′), 3.69-3.60 (m, 0.35H, H5′), 2.10 (2s, 3H, COCH$_3$), 2.01 (s, 2H, COCH$_3$), 1.98 (s, 3H, COCH$_3$), 1.96 (s, 2H, COCH$_3$), 1.95 (s, 1H, COCH$_3$), 1.92 (s, 1H, COCH$_3$), 1.85 (s, 2H, CH$_3$), 1.70 (s, 1H, CH$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.4, 170.2, 169.5, 169.4, 168.2, 167.1, 141.8, 141.6, 141.3, 140.4, 140.2, 139.9, 137.7, 136.9, 134.3, 134.0, 133.4, 132.8, 130.6, 130.5, 130.3, 129.1, 129.0, 128.7, 128.3, 128.0, 127.9, 127.8, 124.1, 123.5, 86.5, 86.3, 75.9, 75.8, 73.9, 73.8, 70.0, 69.8, 68., 68.3, 62.4, 20.9, 20.7, 20.6, 20.5. HRMS (ESI): m/z calcd for $C_{30}H_{34}NO_{10}S$ $[M+H]^+$ 600.1903; found 600.1903.

(2*S*,3*S*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)-6-((2'-methyl-6'-((*E*)-3-oxobut-1-en-1-yl)-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8e**:



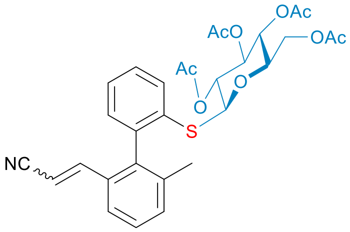
Following general procedure C, the title compound (44 mg, 49%) was obtained as creamy-white solid as a mixture of two atropisomers (2:1 detected by ^{1}H NMR); the equatorial configurations (C1’) of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^{3}J = 10.2 Hz at 4.70 ppm for major and ^{3}J = 9.9 Hz at 4.68 ppm for minor); reaction time: 4 h; R_f = 0.23 (40% EtOAc in cyclohexane); mp = 137.8-139.1°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.73 (m, 1H, Ar), 7.59-7.63 (m, 1H, Ar), 7.47-7.23 (m, 4H, Ar), 7.15-7.04 (m, 2H, Ar and C*H*=CHCOMe), 6.98 (d, *J* = 16.2 Hz, 0.91H, *H*C=CHCOMe), 6.60 (d, *J* = 16.2 Hz, 0.32H, CH=C*H*COMe), 6.53 (d, *J* = 16.2 Hz, 0.66H, CH=C*H*COMe), 5.32-4.84 (m, 3H, H3′, H4′, H2′), 4.70 (bd, *J* = 10.2 Hz, 0.66H, H1′), 4.68 (bd, *J* = 9.9 Hz, 0.32H, H1′), 4.36-4.10 (m, 2H, H6′), 3.82-3.65 (m, 2H, H5′), 2.18-2.13-2.12-2.10-2.03-1.98-1.97-1.85-1.75 (9s, 18H, 2 x CH$_3$ and 4 x COCH$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 198.1, 170.6, 170.2, 170.1, 169.5, 169.2, 169.1, 141.9, 141.8, 140.9, 140.8, 140.0, 137.9, 136.7, 134.3, 134.0, 133.5, 132.3, 132.1, 131.5, 130.8, 130.5, 129.0, 128.9, 128.7, 128.4, 128.2, 127.9, 127.6, 124.0, 123.4, 86.5, 86.3, 76.0, 75.9, 73.9, 73.8, 70.0, 70.0, 68.5, 68.5, 62.4, 28.0, 27.0, 20.8, 20.7, 20.6, 20.5. HRMS (ESI): m/z calcd for $C_{31}H_{34}O_{10}S$ $[M+Na]^+$ 621.1770; found 621.1769.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-((*E*)-3-(dimethylamino)-3-oxoprop-1-en-1-yl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8f**:



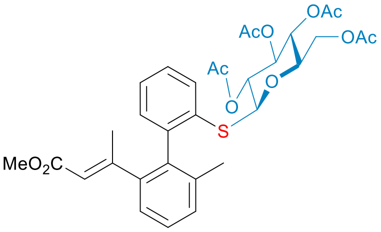
Following general procedure C, the title compound (56 mg, 69%) was obtained as white crystals as a mixture of two atropisomers (1.5:1 detected by ^{1}H NMR); the equatorial configurations (C1') of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^{3}J = 10.4 Hz at 4.64 ppm for major and ^{3}J = 10.0 Hz at 4.73 ppm for minor); reaction time: 4 h; R$_f$ = 0.57 (100% EtOAc); mp = 78.8-80.1 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81-7.76 (m, 0.4H, Ar), 7.70-7.65 (m, 0.6H, Ar), 7.55-7.50 (m, 0.4H, Ar), 7.48-7.43 (m, 0.6H, Ar), 7.41-7.16 (m, 5H, Ar and Ar and C*H*=CHNMe$_2$), 7.15-7.04 (m, 2H, Ar and C*H*=CHNMe$_2$), 6.70 (d, *J* = 15.6 Hz, 0.4H, HC=C*H*CONMe$_2$), 6.54 (d, *J* = 15.6 Hz, 0.6H, CH=C*H*CONMe$_2$), 5.15 (t, *J* = 9.6 Hz, 1H, H3′), 5.02 (t, *J* = 10.0 Hz, 1H, H4′), 4.93-4.81 (m, 1H, H2′), 4.73 (d, *J* = 10.0 Hz, 0.4H, H1′), 4.64 (d, *J* = 10.4 Hz, 0.6H, H1′), 4.19 (bdd, *J* = 12.4, 6.0 Hz, 1H, H6′), 4.13 (dd, *J* = 12.4, 2.4 Hz, 1H, H6′), 3.80-3.67 (m, 1H, H5′), 3.11 (s, 1.2H, NMe$_2$), 2.99 (s, 3H, NMe$_2$), 2.92 (s, 1.8H, NMe$_2$), 2.10-2.09-1.99-1.98-1.97-1.95-1.93-1.84 (8s, 15H, CH$_3$ and 4 x COCH$_3$).^{13}C NMR (75 MHz, CDCl$_3$) δ 170.7, 170.7, 170.2, 170.1, 169., 169.4, 169.4, 169.1, 166.6, 166.3, 142.1, 141.3, 140.8, 140.4, 140.2, 137.6, 136.4, 135.1, 134.6, 134.3, 133.8, 132.7, 131.3, 131.0, 130.5, 130.2, 130.1, 129.1, 128.8, 128.5, 128.2, 128.1, 127.8, 124.4, 123.1, 119.7, 118.8, 87.2, 86.3, 75.7, 75.4, 73.9, 73.8, 70.0, 69.9, 68.6, 68.4, 62.4, 62.3, 37.5, 37.4, 35.8, 35.8, 20.9, 20.9, 20.7, 20.5. HRMS (ESI): m/z calcd for C$_{32}$H$_{37}$NO$_{10}$S [M+H]$^+$ 628.2216; found 628.2218.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-((*E*,*Z*)-2-cyanovinyl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8g**:



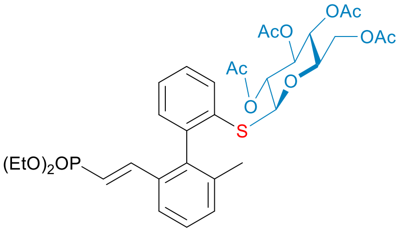
Following general procedure C, the title compound (35 mg, 40%) was obtained as white powder as a mixture of two *E* atropisomers and one *Z* atropisomer (1.8:1:1.1 (Z)) detected by ^{1}H NMR; the equatorial configurations (C1') of atropisomers were determined by the observed coupling constant of the corresponding doublet (^{3}J = 10.0 Hz at 4.72 ppm for major, ^{3}J = 10.4 Hz at 4.67 ppm for minor and ^{3}J = 10.0 at 4.71 ppm for the *Z* compound); reaction time: 24 h; R$_f$ = 0.1 (20% EtOAc in Pentane); mp = 74.7-75.3°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (bdd, *J* = 13.6, 7.6 Hz, 0.27H, Ar), 7.76-7.66 (m, 1H, Ar), 7.47-7.26 (m, 4.76H, Ar), 7.08-7.01 (m, 1H, Ar), 6.95 (d, *J* = 16.4 Hz, 0.24H, *H*C=CHCN), 6.91 (d, *J* = 16.4 Hz, 0.44H, *H*C=CHCN), 6.67 (d, *J* = 12.0 Hz, 0.27H, *H*C=CHCN *Z* compound), 5.71 (d, *J* = 16.4 Hz, 0.24H, HC=C*H*CN), 5.69 (d, *J* = 16.4 Hz, 0.44H, HC=C*H*CN), 5.24 (d, *J* = 12.0 Hz, 0.27H, HC=C*H*CN *Z* compound), 5.22-5.00 (m, 2H, H3′,H4′), 4.97-4.87 (m, 1H, H2′), 4.72 (d, *J* = 10 Hz, 0.44H, H1′), 4.71 (d, *J* = 10 Hz, 0.27H, H1′, *Z* compound), 4.67 (d, *J* = 10.4 Hz, 0.24H, H1′), 4.32-4.07 (m, 2H, H6′), 3.80-3.69 (m, 1H, H5′), 2.12-2.11-2.09-2.08-2.07-2.03-2.02-2.01-1.99-1.98-1.97-1.96 (12s, 12H, 12 x $COCH_3$), 1.86-1.85-1.80 (4s, 3H, 2 CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.6, 170.6, 170.2, 170.2, 170.1, 169.5, 169.4, 169.3, 169.2, 169.1, 169.0, 149.5, 149.1, 148.0, 147.8, 140.5, 140.3, 139.9, 139.5, 139.2, 138.2, 137.8, 137.1, 136.6, 134.4, 133.9, 133.7, 133.6, 133.1, 132.8, 132.5, 132.2, 132.1, 132.0, 131.1, 130.8, 130.7, 130.5, 130.3, 130.2, 129.3, 129.2, 129.0, 128.5, 128.5, 128.2, 128.0, 125.3, 124.9, 123.2, 122.7, 118.4, 118.3, 117.3, 97.3, 96.9, 96.5, 86.5, 86.1, 85.9, 76.0, 76.0, 73.9, 70.0, 68.5, 68.4, 62.4, 20.9, 20.8, 20.7, 20.5, 20.4. HRMS (ESI): m/z calcd for $C_{30}H_{31}NO_9S$ $[M+Na]^+$ 604.1720; found 604.1613.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-((*E*)-4-methoxy-4-oxobut-2-en-2-yl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8h**:



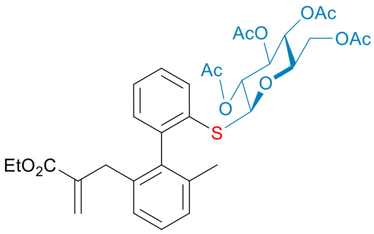
Following general procedure C, the title compound (19 mg, 32% using 4 equiv. of methyl crotonate) was obtained as colorless oil as a mixture of two atropisomers 2.1:1 detected by ^1H NMR; the equatorial configurations (C1’) of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^3J = 10.4 Hz at 4.74 ppm for minor and ^3J = 10.4 Hz at 4.67 ppm for major); reaction time: 24 h; R_f = 0.39 (40% EtOAc in Pentane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.65 (m, 1H, Ar), 7.34-7.15 (m, 4H, Ar), 7.10-6.98 (m, 2H, Ar), 5.77 (bq, *J* = 1.6 Hz, 0.33H, C=C*H*CO_2Me), 5.69 (bq, *J* = 1.2 Hz, 0.69H, C=C*H*CO_2Me), 5.26-5.14 (m, 1H, H3′), 5.10-4.90 (m, 2H, H4′,H2′), 4.74 (d, *J* = 10.4 Hz, 0.33H, H1′), 4.67 (d, *J* = 10.4 Hz, 0.69H, H1′), 4.28-4.15 (m, 2H, H6′), 3.79-3.70 (m, 1H, H5′), 3.69 (s, 1.00H, $COOCH_3$), 3.63 (s, 2.0H, $COOCH_3$), 2.13-2.12-2.11 (3s, 3H, 3 x CH_3), 2.03-2.02-2.01-2.00-1.98-1.97-1.97-1.96 (8s, 12H, 4 x CH_3), 1.86 (s, 2H, CH_3), 1.71 (s, 1H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 170.2, 169.5, 169.3, 169.1, 166.9, 158.8, 158.4, 144.5, 143.1, 141.3, 141.0, 137.8, 137.3, 136.3, 134.6, 131.0, 130.8, 130.7, 130.3, 129.7, 129.3, 128.5, 128.0, 127.9, 127.7, 125.5, 124.8, 119.9, 119.4, 87.2, 86.9, 76.0, 75.9, 74.0, 73.9, 70.1, 69.8, 68.8, 68.6, 62.6, 51.0, 20.9, 20.8, 20.7, 20.5, 20.4. HRMS (ESI): m/z calcd for $C_{32}H_{36}O_{11}S$ $[M+Na]^+$ 651.1871; found 651.1870.

(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-6-((2'-((*E*)-2-(diethoxyphosphoryl)vinyl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8i**:



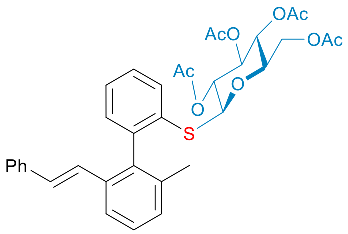
Following general procedure C, the title compound (37 mg, 57%) was obtained as colorless oil as a mixture of two atropisomers (2.6:1 detected by ^1H NMR); the equatorial configurations (C1’) of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^{3}J = 10.0 Hz at 4.67 ppm for minor and ^{3}J = 10.4 Hz at 4.62 ppm for major); reaction time: 4 h; R_f = 0.4 (90% EtOAc in cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.74 (m, 0.27H, Ar), 7.24-7.65 (m, 0.69H, Ar), 7.55-7.18 (m, 5H, Ar), 7.14-6.79 (m, 1H, Ar), 6.92 (d, J = 17.2 Hz, 0.27H, *H*C=CHPO(OEt)$_2$), 6.22 (d, J = 17.6 Hz, 0.69H, *H*C=CHPO(OEt)$_2$), 6.07 (d, J = 17.6 Hz, 0.69H, HC=C*H*PO(OEt)$_2$), 6.03 (d, J = 17.2 Hz, 0.27H, HC=C*H*PO(OEt)$_2$), 5.22-5.09 (m, 1H, H3′), 5.09-4.98 (m, 1H, H4′), 4.95-4.84 (m, 1H, H2′), 4.67 (d, J = 10.0 Hz, 0.27H, H1′), 4.62 (d, J = 10.4 Hz, 0.69H, H1′), 4.29-4.06 (m, 2H, H6′), 4.06-3.84 (m, 4H, 2 x C*H*$_2$CH$_3$), 3.81-3.68 (m, 2H, 1H, H5′), 2.10 (s, 3H, $COCH_3$), 2.00-1.99-1.98-1.96-1.95-1.94 (6s, 9H, 3 x $COCH_3$), 1.83 (s, 2.07H, CH_3), 1.74 (s, 0.81H, CH_3), 1.29-1.13 (m, 6H, 2 x CH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.6, 170.2, 170.1, 169.5, 169., 169.1, 146.8, 146.7, 146.5, 146.4, 141.2, 140.8, 140.3, 140.2, 139.7, 136.4, 134.8, 134.6, 134.4, 133.2, 133.1, 131.7, 131.3, 131.2, 130.3, 130.3, 128.9, 128.6, 128.8, 128.3, 128.2, 123.8, 123.3, 116.9, 116.4, 115.0, 114.5, 86.9, 86.2, 75.9, 75.6, 73.9, 70.0, 69.9, 68.6, 68.5, 62.5, 62.4, 62.1, 62.0, 62.0, 61.9, 20.8, 20.6, 20.7, 20.5, 16.5, 16.4,16.4, 16.3. HRMS (ESI): m/z calcd for $C_{33}H_{41}O_{12}PS$ $[M+H]^+$ 693.2135; found 693.2145.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-(2-(ethoxycarbonyl)allyl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8j**:



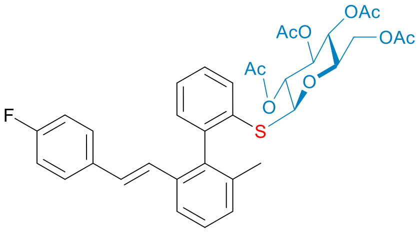
Following general procedure C, the title compound (46 mg, 47%) was obtained as a colorless oil as a mixture of two atropisomers (1.7:1 detected by ^{1}H NMR); the equatorial configurations (C1’) of both atropisomers were determined by the observed coupling constant of the corresponding doublet (^{3}J = 10.0 Hz at 4.78 ppm for minor and ^{3}J = 10.0 Hz at 4.68 ppm for major); reaction time: 4 h; R_f = 0.1 (20% EtOAc in cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.64 (m, 1H, Ar), 7.37-7.27 (m, 2H, Ar), 7.24-6.99 (m, 4H, Ar), 6.18-6.10 (m, 1H, =CH*H*), 5.27-5.14 (m, 2H, H3′ + =C*H*H), 5.06 (t, J = 9.7 Hz, 1H, H4′), 4.98-4.88 (m, 1H, H2′), 4.78 (d, J = 10.0 Hz, 0.34H, H*1′*), 4.68 (d, J = 10.0 Hz, 0.56H, H*1′*), 4.28-4.16 (m, 2H, H6′), 4.16-4.03 (m, 2H, C*H*HCH$_3$), 3.80-3.71 (m, 1H, H5′), 3.37-3.14 (m, 2H, CH_2), 2.11-2.10 (2s, 3H, $COCH_3$), 2.02-2.01 (2s, 3H, $COCH_3$), 1.98-1.97 (2s, 3H, $COCH_3$), 1.95-1.94 (2s, 3H, $COCH_3$), 1.84-1.83 (2s, 3H, CH_3), 1.24-1.17 (m, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 170.2, 169.5, 169.3, 169.2, 167.0, 166.9, 141.5, 141.3, 140.0, 139.9, 139.8, 137.6, 137.2, 136.4, 135.9, 134.3, 133.7, 131.2, 130.7, 130.4, 130.4, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.3, 126.9, 126.8, 126.6, 87.0, 86.2, 75.9, 75.8, 74.0, 70.1, 70.0, 68.7, 68.6, 62.6, 60.8, 60.7, 35.7, 35.7, 20.9, 20.8, 20.7, 20.6, 20.6, 20.5, 14.3, 14.3. HRMS (ESI): m/z calcd for $C_{33}H_{38}O_{11}S$ $[M+Na]^+$ 665.2033; found 665.2045.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-methyl-6'-((*E*)-styryl)-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8k**:



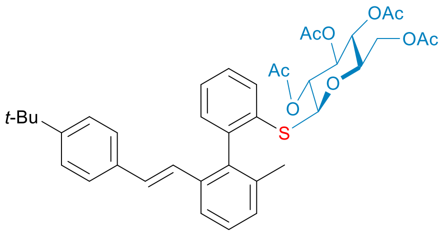
Following general procedure C, the title compound (14 mg, 15%) was obtained as a white solid; the equatorial configuration (C1') of the major atropisomer (> 20:1) was determined by the observed coupling constant of the corresponding doublet (^3J = 10.3 Hz at 4.72 ppm); reaction time: 4 h; R_f = 0.67 (1:4:1 EtOAc/cyclohexane/Et_2O); mp = 199.3-200.7 °C; $[\alpha]_D^{20}$ -204 (c, 0.3 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.78 (m, 1H, Ar), 7.63 (bd, *J* = 7.6 Hz, 1H, Ar), 7.46-7.13 (m, 10H, Ar), 6.97 (d, *J* = 16.2 Hz, 1H, *H*C=CHPh), 6.59 (d, *J* = 16.2 Hz, 1H, HC=C*H*Ph), 5.21 (t, *J* = 9.3 Hz, 1H, H3′), 5.09 (dd, *J* = 10.0, 9.4 Hz, 1H, H4′), 4.98 (dd, *J* = 10.3, 9.1 Hz, 1H, H2′), 4.72 (d, *J* = 10.3 Hz, 1H, H1′), 4.34 – 4.08 (m, 2H, H-6′), 3.77 (ddd, *J* = 10.0, 5.5, 2.6 Hz, 1H, H5′), 2.15 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 1.87 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 169.5, 169.2, 141.2, 139.2, 137.6, 136.7, 136.1, 134.5, 130.9, 130.7, 130.0, 128.9, 128.6, 128.5, 128.1, 128.0, 127.6, 127.1, 126.7, 122.9, 75.9, 74.0, 70.0, 68.5, 62.5, 20.9, 20.8, 20.7, 20.5. HRMS (ESI): m/z calcd for $C_{35}H_{36}O_9S$ $[M+Na]^+$ 655.1972; found 655.1971

<u>(2*S*,3*S*,4*R*,5*S*,6*R*)-2-(acetoxymethyl)-6-((2'-((*E*)-4-fluorostyryl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8l**:</u>



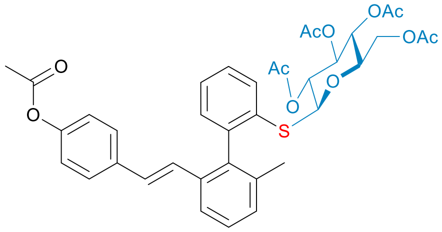
Following general procedure C, the title compound (28 mg, 38% using 4 equiv. of 4-fluorostyrene) was obtained as a colorless oil; the equatorial configuration (C1') of the major atropisomer (> 20:1) was determined by the observed coupling constant of the corresponding doublet (^3J = 10.1 Hz at 4.58 ppm); reaction time: 48 h; R_f = 0.33 (30% EtOAc in cyclohexane) ; $[\alpha]_D^{16}$ +55.6 (c, 0.27 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (bd, *J* = 7.6 Hz, 1H, Ar), 7.56 (bd, *J* = 7.8 Hz, 1H, Ar), 7.46-7.35 (m, 2H, Ar), 7.29 (bt, *J* = 7.7 Hz, 1H, Ar), 7.25-7.21 (m, 2H, Ar), 7.18 (bd, *J* = 7.4 Hz, 2H, Ar), 6.97 (bt, *J* = 8.7 Hz, 2H, Ar), 6.90 (bd, *J* = 16.2 Hz, 1H, *H*C=CHPhF), 6.52 (d, *J* = 16.3 Hz, 1H, HC=C*H*PhF), 4.98-4.88 (m, 2H H4′, H3′), 4.86-4.79 (m, 1H, H2′), 4.58 (d, *J* = 10.1 Hz, 1H, H1′), 4.09 (dd, *J* = 12, 5.6 Hz, 1H, H6′), 3.98 (dd, *J* = 12.4, 2.8 Hz, 1H, H6′), 3.23 (ddd, *J* = 8.4, 5.9, 2.6 Hz, 1H, H5′), 2.07 (s, 3H, $COCH_3$), 1.96 (s, 6H, 2 x $COCH_3$), 1.94 (s, 3H, $COCH_3$), 1.70 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.2, 169.5, 162.5 (d, *J* = 246 Hz), 142.7, 139.6, 137.2, 135.6, 133.9, 133.0, 130.5, 129.4, 128.9, 128.8, 128.4, 128.1, 128.1, 128.0, 127.7, 122.5, 116.0, 115.8, 86.3, 75.7, 73.8, 69.9, 68.6, 62.4, 20.8, 20.7, 20.6, 20.5. ^{19}F NMR (188 MHz) δ -113.98. HRMS (ESI): m/z calcd for $C_{35}H_{35}FO_9S$ $[M+NH_4]^+$ 668.2324; found 668.2320.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((-2'-((*E*)-4-(tert-butyl)styryl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8m**:



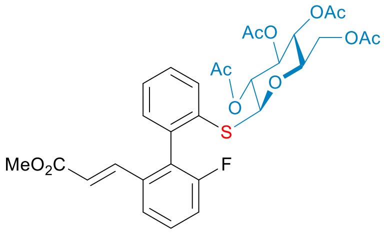
Following general procedure C, the title compound (23 mg, 22%) was obtained as colorless oil; the equatorial configuration (C1’) of the major atropisomer (> 20:1) was determined by the observed coupling constant of the corresponding doublet (^3J = 10.0 Hz at 4.60 ppm); reaction time: 24 h; R_f = 0.23 (20% EtOAc in cyclohexane). $[\alpha]_D^{16}$ +1.03 (c, 0.11 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (bd, *J* = 6.4 Hz, 1H, Ar), 7.58 (bd, *J* = 7.6 Hz, 1H, Ar), 7.44-7.30 (m, 2H, Ar), 7.30 (t, *J* = 7.7 Hz, 3H, Ar), 7.22-7.14 (m, 4H, Ar), 6.91 (d, *J* = 16.3 Hz, 1H, *H*C=CHPh*t*-Bu), 6.57 (d, *J* = 16.3 Hz, 1H, HC=C*H*Ph*t*-Bu), 4.98-4.89 (m, 2H, H4′,H3′), 4.88-4.77 (m, 1H, H2′), 4.60 (d, *J* = 10.1 Hz, 1H, H1′), 4.05 (dd, *J* = 12.4, 5.6 Hz, 1H, H6′), 3.96 (dd, *J* = 12.4, 2.4 Hz, 1H, H6′), 3.25-3.17 (m, 1H, H5′) , 2.07 (s, 3H, $COCH_3$), 1.96 (s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$), 1.94 (s, 3H, $COCH_3$), 1.72 (s, 3H, CH_3), 1.29 (s, 9H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 170.2, 169.5, 169.4, 151.1, 142.8, 139.6, 137.0, 136.0, 133.9, 133.0, 130.6, 130.0, 129.1, 128.7, 128.3, 128.0, 127.2, 126.3, 125.8, 122.5, 86.1, 75.5, 73.9, 69.9, 68.5, 62.2, 34.8, 31.4, 29.8, 20.9, 20.7, 20.7, 20.6, 20.5. HRMS (ESI): m/z calcd for $C_{39}H_{44}O_9S$ $[M+Na]^+$ 711.2604; found 711.2596.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-((*E*)-4-acetoxystyryl)-6'-methyl-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **8n**:



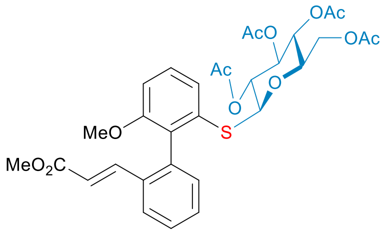
Following general procedure C, the title compound (45 mg, 44%) was obtained as a white powder as a 1:1 mixture of two atropisomers detected by ^1H NMR; the equatorial configurations (C1’) of both atropisomers were determined by the observed coupling constant of the corresponding doublets (^3J = 10.0 Hz at 4.67 ppm and ^3J = 10.0 Hz at 4.61 ppm); reaction time: 24 h; R_f = 0.23 (20% EtOAc in cyclohexane); mp = 83.7-85.3°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.70 (m, 1H, Ar), 7.56 (bd, *J* = 7.8 Hz, 1H, Ar), 7.46-7.08 (m, 7H, Ar), 7.02 (d, *J* = 10.8 Hz, 1H, Ar), 6.97 (d, *J* = 9.6 Hz, 1H, Ar), 6.92 (d, *J* = 16.0 Hz, 0.5H, HC=C*H*PhCOMe), 6.90 (d, *J* = 16.4 Hz, 0.5H, HC=C*H*PhCOMe), 6.55 (d, *J* = 16.4 Hz, 0.5H, *H*C=CHPhCOMe), 6.48 (d, *J* = 16.0 Hz, 0.5H, *H*C=CHPhCOMe), 5.17 (t, *J* = 9.2 Hz, 0.5H,H3’), 5.05 (t, *J* = 9.6 Hz, 0.5H,H3’), 5.00-4.77 (m, 2H, H4’ and H2’), 4.67 (d, *J* = 10.0 Hz, 0.5H, H1′), 4.61 (d, *J* = 10.0 Hz, 0.5H, H1′), 4.28- 3.95 (m, 2H, H6′), 3.78-3.68 (m, 0.5H, H5′), 3.33-3.24 (m, 0.5H, H5′), 2.26 (s, 1.5H, $PhCOCH_3$), 2.25 (s, 1.5H, $PhCOCH_3$), 2.10 (s, 1.5H, $COCH_3$), 2.06 (s, 1.5H, $COCH_3$), 2.01 (s, 1.5H, $COCH_3$), 1.99 (s, 1.5H, $COCH_3$), 1.96-1.95-1.94 (3s, 6H, 2 x $COCH_3$), 1.83 (s, 1.5H, CH_3), 1.71 (s, 1.5H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.6, 170.2, 170.1, 169.4, 169.3, 169. 1, 150.2, 150.0, 142.5, 141.0, 139.6, 139.1, 137.1, 136.5, 136.1, 135.6, 135.4, 135.2, 134.4, 133.8, 133.0, 130.8, 130.6, 130.5, 129.3, 129.1, 128.9, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 127.4, 127.4, 122.8, 122.6, 122.0, 121.7, 86.7, 86.2, 75.9, 75.6, 73.9, 73.8, 69.9, 69.9, 68.5, 68.4, 62.5, 62.3, 21.2, 20.8, 20.7, 20.6, 20.5, 20.4. HRMS (ESI): m/z calcd for $C_{37}H_{38}O_{11}S$ $[M+Na]^+$ 713.2027; found 713.2026.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2'-fluoro-6'-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **9b**:



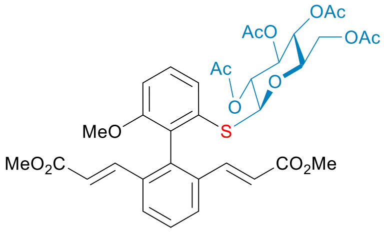
Following general procedure C, the title compound (28 mg, 30%) was obtained as white crystals as a mixture of two atropisomers (1.5:1 and 1.6:1 respectively detected by ^{1}H NMR and ^{19}F); the equatorial configurations (C1') of both atropisomers were determined by the observed coupling constant of the corresponding doublets (^3J = 10.3 Hz at 4.58 ppm and ^3J = 10.4 Hz at 4.53 ppm); reaction time: 4 h; R_f = 0.17 (30% EtOAc in cyclohexane); mp = 81.5-82.9°C. $[\alpha]_D^{16}$ -56 (c, 0.5 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.68 (m, 1H, Ar), 7.47-7.01 (m, 7H, Ar, HC=C*H*COMe), 6.29 (d, *J* = 16.0 Hz, 0.4H, *H*C=CHCOMe), 6.21 (d, *J* = 16.0 Hz, 0.6H, *H*C=CHCOMe), 5.13-4.92 (m, 2H, H3′, H4′), 4.84 (t, *J* = 9.4 Hz, 1H, H2′), 4.58 (d, *J* = 10.3 Hz, 0.6H, H1′), 4.53 (d, *J* = 10.4 Hz, 0.4H, H1′), 4.12-4.01 (m, 2H, H6′), 3.69 (s, 1.2H, CH_3), 3.62 (s, 1.8H, CH_3), 3.64-3.56 (m, 1H, H5′), 2.04 (s, 1.2H, $COCH_3$), 2.03 (s, 1.8H, $COCH_3$),. 1.93 (s, 3H, $COCH_3$), 1.90 (s, 1.8H, $COCH_3$), 1.88 (s, 1.2H, $COCH_3$), 1.77 (s, 1.8H, $COCH_3$), 1.69 (s, 1.2H, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7,170.3, 170.2, 169.5, 169.3, 169.2, 167.1, 166.8, 160.3 (d, *J* = 244.5 Hz), 159.8 (d, *J* = 243.3 Hz), 141.7 (d, *J* = 3.3 Hz), 141.4 (d, *J* = 3.3 Hz), 135.8, 134.0, 133.8, 133.7, 133.6, 131.4, 131.3, 129.6, 129.5, 128.7, 128.5, 122.3, 122.2, 121.6, 121.6, 120.7, 120.3, 117.0 (d, *J* = 22.7 Hz), 116.4 (d, *J* = 22.8 Hz), 86.9, 86., 75.9, 75.8, 74.0, 73.9, 70.1, 70.0, 68.5, 68.5, 62.4, 62.3, 52.0, 51.8, 20.9, 20.7, 20.6, 20.5. ^{19}F NMR (188 MHz) δ -111.63, -112.14. HRMS (ESI): m/z calcd for $C_{30}H_{31}FO_{11}S$ $[M+Na]^+$ 641.1469; found 641.1465.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((6-methoxy-2'-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **9c**:



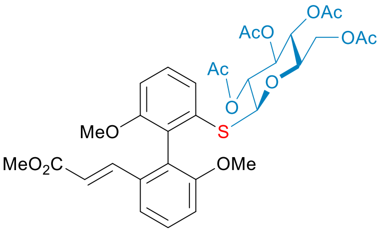
Following general procedure C, the title compound (34 mg, 59%) was obtained as a white powder as a mixture of two atropisomers 1:2.1 detected by ^{1}H NMR; The achiral byproduct **10**, resulting from a decoupling reaction was also generated (17 mg, 26%) as creamy crystals in the reaction (see below its description); the equatorial configurations (C1’) of both atropisomers **9c** were determined by the observed coupling constant of the corresponding doublets (^3J = 10.4 Hz at 4.64 ppm for the minor compound and ^3J = 10.0 Hz at 4.62 ppm for the major compound); reaction time: 4 h; R_f = 0.1 (30% EtOAc in cyclohexane); mp = 67.9-69.3°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.65 (m, 1H, Ar), 7.42-7.23 (m, 5H, Ar, HC=C*H*CO_2Me), 7.16-7.08 (m, 1H, Ar), 6.95-6.88 (m, 1H, Ar), 6.32 (d, *J* = 16.0 Hz, 0.46H, *H*C=CHCO_2Me), 6.28 (d, *J* = 16.0 Hz, 0.54H, *H*C=CHCO_2Me), 5.18-5.00 (m, 2H, H3′, H4′), 4.90 (dd, *J* = 10.0, 9.2 Hz, 1H, H2′), 4.64 (d, *J* = 10.4 Hz, 0.46H, H1′), 4.62 (d, *J* = 10.0 Hz, 0.46H, H1′), 4.30-4.06 (m, 2H, H6′), 3.73 (s, 1.38H, OMe), 3.68 (s, 1.62H, OMe), 3.67 (s, 1.62H, OMe), 3.66 (s, 1.38H, OMe), 3.76-3.64 (m, 1H, H5′), 2.11 (s, 1.38H, $COCH_3$), 2.09 (s, 1.62H, $COCH_3$), 2.00 (s, 1.38H, $COCH_3$), 1.99 (s, 1.62H, $COCH_3$), 1.96 (s, 1.62H, $COCH_3$), 1.94 (s, 1.38H, $COCH_3$), 1.82 (s, 1.62H, $COCH_3$), 1.74 (s, 1.38H, $COCH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 170.3, 170.41, 169.5, 169.4, 169.2, 169.1, 167.6, 167.4, 157.3, 157.3, 143.4, 143.0, 137.7, 137.6, 135.1, 135.1, 134.2, 133.1, 131.9, 131.1, 130.2, 130.1, 129.7, 129.6, 128.3, 128.2, 126.3, 125.8, 123.8, 118.8, 118.4, 110.6, 86.7, 86.2, 75.8, 74.0, 73.9, 70.1, 69.8, 68.5, 68.4, 62.4, 62.3, 56.0, 51.7, 51.6, 20.8, 20.7, 20.4. HRMS (ESI): m/z calcd for $C_{31}H_{34}O_{12}S$ $[M+NH_4]^+$ 648.2115; found 648.2109.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((6-methoxy-2',6'-bis((*E* *or* *Z*)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **10**:



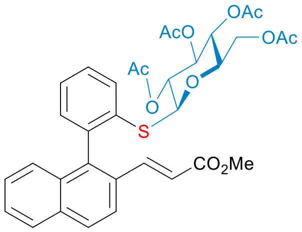
Compound **10** was obtained as a 91:9 mixture of *E* and *Z* diastereomers detected by ^{1}H NMR. Traces (< 2%) of *ZE* product are partially detectable on the ^{1}H NMR spectra; the equatorial configuration (C1’) of compound *E*-**10** was determined by the observed coupling constant of the corresponding doublet (^3J = 10.3 Hz at 4.66 ppm); R_f = 0.06 (30% EtOAc in cyclohexane); mp = 81.8-83.2°C; $[\alpha]_D^{20}$ -12 (c, 0.5 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.65 (m, 2H, Ar), 7.46-7.35 (m, 3H, Ar), 7.23 (d, *J* = 16.0 Hz, 1H, HC=C*H*CO_2Me), 7.16 (d, *J* = 15.6 Hz, 1H, HC=C*H*CO_2Me), 6.95 (dd, *J* = 7.4, 2.0 Hz, 1H, Ar), 6.49 (d, *J* = 12.0 Hz, 0.09H, HC=C*H*CO_2Me), 6.47 (d, *J* = 12.4 Hz, 0.09H, HC=C*H*CO_2Me), 6.32 (d, *J* = 16.0 Hz, 1H, *H*C=CHCO_2Me), 6.27 (d, *J* = 16.0 Hz, 1H, *H*C=CHCO_2Me), 5.76 (d, *J* = 12.4 Hz, 0.09H, *H*C=CHCO_2Me), 5.72 (d, *J* = 12.4 Hz, 0.09H, *H*C=CHCO_2Me), 5.09 (t, *J* = 9.2 Hz, 1H, H3′), 5.02 (t, *J* = 9.6 Hz, 1H, H4′), 4.85 (dd, *J* = 10.3, 9.0 Hz, 1H, H2′), 4.66 (d, *J* = 10.3 Hz, 1H, H1′), 4.25-4.08 (m, 2H, H6′), 3.75 (s, 3H, OMe), 3.68 (s, 3H, OMe), 3.65 (s, 3H, OMe), 3.73-3.63 (m, 1H, H5’), 2.16 (s, 0.27H, $COCH_3$), 2.11 (s, 3H, $COCH_3$), 2.04 (s, 0.27H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 1.94 (s, 3H, $COCH_3$), 1.76 (s, 3H, $COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.2, 169.5, 169.1, 167.3, 167.1, 157.2, 142.9, 142.5, 138.3, 135.6, 135.5, 134.1, 130.6, 128.5, 128.41, 127.3, 127.0, 124.1, 120.0, 119.4, 110.9, 86.4, 75.8, 73.9, 69.9, 68.5, 62.3, 56.1, 51.9, 51.7, 20.9, 20.7, 20.5. HRMS (ESI): m/z calcd for $C_{35}H_{38}O_{14}S$ $[M+NH_4]^+$ 732.2326; found 732.2317.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2',6-dimethoxy-6'-((*E*,*Z*)-3-methoxy-3-oxoprop-1-en-1-yl)-[1,1'-biphenyl]-2-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **9d**:



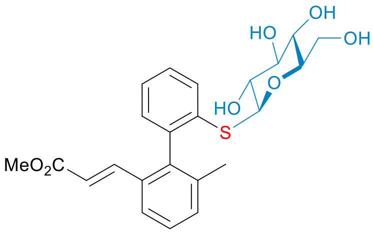
Starting with the atropoenriched isomer **7e** (dr> 20:1) and following general procedure C, the title compound (14 mg, 49%) was obtained as white crystals as a *E*/*Z* = 6:1 mixture of diastereomers detected by ^{1}H NMR; the equatorial configuration (C1') of the major *E* diastereomer and the minor *Z* diastereomer were determined by the observed coupling constants of the corresponding doublets (^3J = 10.4 Hz at 4.58 ppm and 4.54 ppm); reaction time: 4 h; R$_f$ = 0.1 (30% EtOAc in cyclohexane); mp = 72.7-73.5°C; [α]$_D^{20}$ -32.5 (c, 0.4 in CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42-7.29 (m, 4H, Ar), 7.26 (d, *J* = 16.0 Hz, 1H, *H*C=CHCO$_2$Me), 6.98-6.86 (m, 2H, Ar), 6.48 (d, *J* = 12.4 Hz, 1H, *H*C=CHCO$_2$Me, compound *Z*), 6.32 (d, *J* = 16.0 Hz, 1H, HC=C*H*CO$_2$Me), 5.75 (d, *J* = 12.4 Hz, 0.17H, HC=C*H*CO$_2$Me, compound *Z*), 5.34 (t, *J* = 10.0 Hz, 0.34H, H3′, compound *Z*), 5.30-5.12 (m, 0.51H, compound *Z*), 5.46 (d, *J* = 3.6 Hz, 1H, H4′), 5.11-4.99 (m, 2H, H3′,H4′), 4.93 (dd, *J* = 8.8, 5.2 Hz, 0.17H, H2′, compound *Z*), 4.84 (dd, *J* = 10.4, 8.8 Hz, 0.17H, H2′), 4.58 (d, *J* = 10.4 Hz, 1H, H1′), 4.54 (d, *J* = 10.4 Hz, 1H, H1′, compound *Z*), 4.27-4.20 (m, 1H, H6′), 4.19-4.11 (m, 1H, H6′), 3.74 (s, 3H, OCH$_3$), 3.69 (s, 3H, OCH$_3$), 3.67 (s, 3H, OCH$_3$), 3.71-3.65 (m, 1H, H5′), 3.67 (s, 3H, OCH$_3$), 2.12 (s, 3H, COCH$_3$), 2.00 (s, 3H, COCH$_3$), 1.94 (s, 3H, COCH$_3$), 1.67 (s, 3H, COCH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) compound *E*: δ 170.7, 170.2, 169.5, 167.6, 167.40, 158.0, 157.4, 143.5, 135.9, 134.2, 129.6, 129.2, 126.9, 126.5, 124.6, 118.8, 118.0, 112.5, 111.1, 86.9, 75.8, 73.9, 69.9, 68.6, 62.5, 56.1, 51.8, 20.9, 20.7, 20.4. compound *Z*: δ 170.8, 170.2, 169.7, 169.4, 142.2, 129.3, 128.3, 124.3, 121.8, 119.9, 111.3, 111.0, 90.4, 72.3, 71.2, 70.1, 68.7, 67.5, 62.1, 56.0, 20.8, 20.8, 20.5. HRMS (ESI): m/z calcd for $C_{32}H_{36}O_{13}S$ [M+NH$_4$]$^+$ 678.2220; found 678.2226.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((2-(2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)naphthalen-1-yl)phenyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate **9f**:



Following general procedure C, the title compound (55 mg, 60%) was obtained as white powder as a 2:1 mixture of two atropisomers detected by ^{1}H NMR; the equatorial configurations (C1') of both atropisomers **9d** were determined by the observed coupling constant of the corresponding doublets (^3J = 10.0 Hz at 4.65 ppm for the minor compound and ^3J = 10.4 Hz at 4.54 ppm for the major compound); reaction time: 4 h; R$_f$ = 0.27 (40% EtOAc in cyclohexane); mp = 76.8-77.7°C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93-7.75 (m, 4H, Ar), 7.53-7.32 (m, 5H, Ar), 7.28-7.17 (m, 2H, Ar), 6.49 (d, *J* = 16.0 Hz, 0.33H, HC=C*H*CO$_2$Me), 6.43 (d, *J* = 16.0 Hz, 0.66H, HC=C*H*CO$_2$Me), 5.08-4.93 (m, 2H, H3′, H4′), 4.81 (dd, *J* = 10.4, 9.2 Hz, 0.33H, H2′), 4.74 (dd, *J* = 10.0, 8.8 Hz, 0.66H, H2′), 4.65 (d, *J* = 10.0 Hz, 0.33H, H1′), 4.54 (d, *J* = 10.4 Hz, 0.66H, H1′), 4.24-4.05 (m, 2H, H6′), 3.77 (s, 1.98H, OCH$_3$), 3.70 (s, 0.99H, OCH$_3$), 3.69-3.58 (m, 1H, H5′), 2.13 (s, 1.98H, COCH$_3$), 2.11 (s, 0.99H, COCH$_3$), 1.99 (s, 3H, COCH$_3$), 1.92 (s, 0.99H, COCH$_3$), 1.90 (s, 1.98H, COCH$_3$), 1.62 (s, 0.99H, COCH$_3$), 1.19 (s, 1.98H, COCH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.7, 170.2, 170.1, 169.5, 169.4, 169.2, 169.1, 167.5, 167.2, 143.3, 142.6, 140.2, 139.9, 139.5, 139.1, 135.4, 134.2, 134.2, 134.1, 133.5, 133.0, 132.4, 131.7, 131.6, 131.4, 131.2, 129.7, 129.4, 129.2, 128.8, 128.7, 128.6, 128.2, 128.1, 128.0, 127.4, 127.3, 127.2, 127.1, 126.9, 126.9, 123.1, 122.3, 119.6, 118.9, 87.0, 86.4, 75.8, 73.9, 73.8, 69.9, 69.7, 68.5, 62.5, 62.3, 51.9, 51.7, 20.9, 20.6, 20.3, 20.7. HRMS (ESI): m/z calcd for $C_{34}H_{34}O_{11}S$ [M+Na]$^+$ 673.1714; found 673.1719.

methyl (*E*)-3-((*S*)-6-methyl-2'-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)thio)-[1,1'-biphenyl]-2-yl)acrylate **12**:



Following general procedure D, the title compound (8 mg, 13%) was obtained as a yellow oil as a mixture of two atropisomers (4.3:1 detected by ^{1}H NMR); the equatorial configurations (C1') of the major and minor atropisomers were determined by the observed coupling constants of the corresponding doublets (^3J = 10.0 Hz at 4.72 and 4.68 ppm); reaction time: 72 h; R$_f$ = 0.1 (80% EtOAc in cyclohexane. ^{1}H NMR (400 MHz, MeOD) δ 7.78-7.72 (m, 1H, Ar), 7.63-7.67 (m, 1H, Ar), 7.42 (td, *J* = 7.7, 1.5 Hz, 1H, Ar), 7.35-7.21 (m, 4H, Ar), 7.26 (d, *J* = 16.0 Hz, 1H, *H*C=CHCO$_2$Me), 6.98 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar), 6.32 (d, *J* = 16.0 Hz, 0.8H, HC=C*H*CO$_2$Me), 6.31 (d, *J* = 16.0 Hz, 0.2H, HC=C*H*CO$_2$Me), 4.72 (d, *J* = 10.0 Hz, 0.8H, H1′), 4.68 (d, *J* = 10.0 Hz, 0.8H, H1′), 3.74-3.66 (m, 2H, H6′), 3.66 (s, 3H, OCH$_3$), 3.42-3.31 (m, 1H, H5′,H4′,H3′), 3.16 (dd, *J* = 9.8, 8.3 Hz, 1H, H2′), 2.08 (s, 3H, CH$_3$). ^{13}C NMR (101 MHz, MeOD) δ (major atropisomer) 169.00, 145.0, 142.2, 139.3, 138.7, 137.4, 134.7, 132.9, 131.1, 131.0, 130.8, 129.9, 129.2, 129.1, 127.1, 124.9, 119.3, 88.50, 81.9, 79.7, 73.9, 71.3, 62.8, 52.0, 20.5. HRMS (ESI): m/z calcd for $C_{23}H_{30}O_7S$ [M+Na]$^+$ 469.1291; found 469.1296.

DFT Calculations

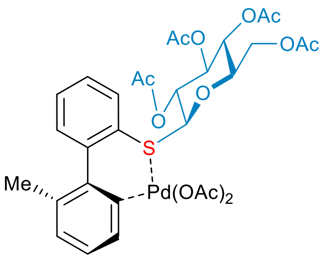
Quantum chemical calculations were carried out with Gaussian 09 software package revision D.01.[3] Geometries were optimized employing the B3LYP [4]functional coupled with the basis sets LANL2DZ for Pd and 6-31+G(d,p) for the other elements. The temperature was considered using the same level of theory, at 353.15 K for the reaction of protected sugar (**7a**) and 273.15 K for **11a**. To include the solvent effect, the parameters had to be independently defined since HFIP is not defined as a solvent in Gaussian 09. The employed parameters are summarized in Table S1, HFIP for **11a** and a mixture 2:1 DCE/HFIP for **7a**. Those values were included in the Gibbs free energy profiles via single point calculations with the SMD [5]continuum solvation model, employing the wB97xD [6] functional and the basis sets 6-311+(d,p) for C, H, O, and S, and SDD for Pd. Structures were plotted using CYLview 2.0. [7]

Table S1: Solvent parameters[a]

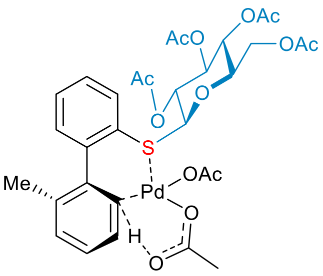
Parameter	HFIP	DCE:HFIP (2:1)
Eps	16.70	12.32
EpsInf	1.63	1.93
HbondAcidity	1.96	0.72
HbondBasicity	0.00	0.07
SurfaceTensionAtInterface	23.23	38.32
CarbonAromaticity	0.00	0.00
ElectronegativeHalogenicity	0.60	0.53

[a] keyword: scrf = (SMD, solvent = generic,read)

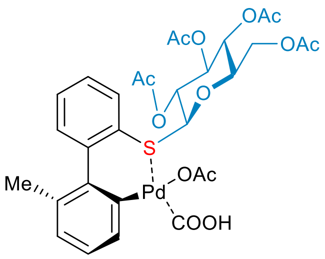
Depiction of structures corresponding to following the Cartesian coordinates



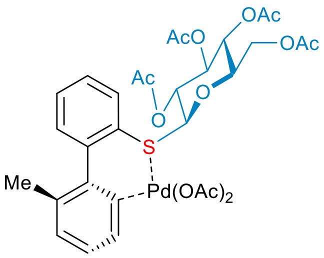
SM-OAc_*aR*



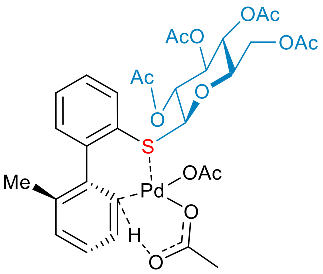
TS-OAc_*aR*



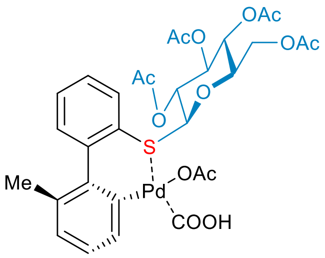
Pdt-OAc_*aR*



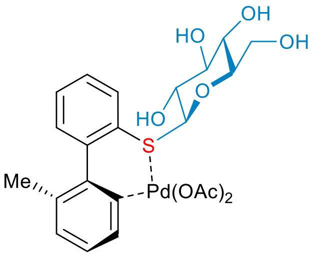
SM-OAc_*aS*



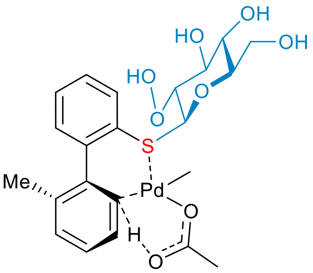
TS-OAc_*aS*



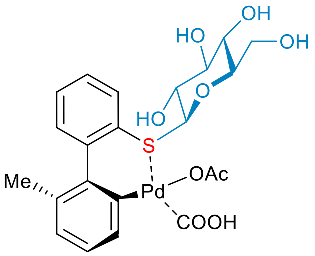
Pdt-OAc_*aS*



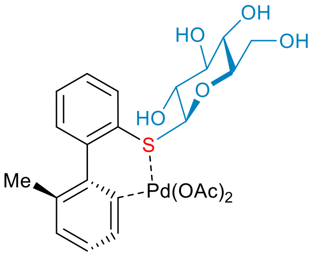
SM-OH_*aR*



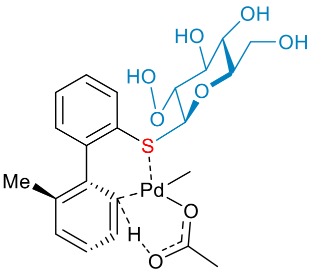
TS-OH_*aR*



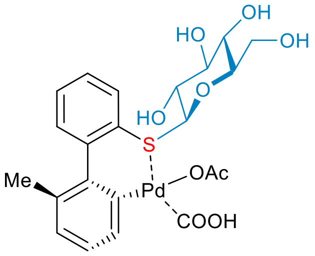
Pdt-OH_*aR*



SM-OH_*aS*



TS-OH_*aS*



Pdt-OH_*aS*

Cartesian Coordinates

SM_OH_*aS*

Imaginary frequencies = 0
E(ωB97xD, HFIP) = -2095.99962
$E_{\text{Thermal correction}}$ = 0.417376

C	-3.525737	-2.172870	1.866108
C	-2.693383	-1.656722	0.866297
C	-1.305086	-1.890636	0.952639
C	-0.761739	-2.588377	2.036409
C	-1.612804	-3.092522	3.022309
C	-2.992449	-2.893341	2.936812
H	-4.594336	-1.985828	1.810798
H	-1.189270	-3.629586	3.865624
H	-3.649252	-3.278307	3.710776
C	-3.218153	-0.822531	-0.255078
C	-3.818229	-1.396682	-1.388725
C	-3.026868	0.583641	-0.183446
C	-4.201340	-0.542257	-2.439498
C	-3.417573	1.407938	-1.255873
C	-3.998152	0.837369	-2.388857
H	-4.653445	-0.980102	-3.326086
H	-3.267860	2.479294	-1.183663
H	-4.295958	1.461075	-3.226188
Pd	-0.660320	1.085927	-0.217269
O	1.329721	1.484969	-0.055556
H	-2.770617	1.040172	0.783129
C	-1.535347	3.424245	1.182159
O	-1.028399	3.082979	0.018399
O	-1.971359	2.630147	2.018936
C	2.018912	2.400747	-0.687451
O	3.171181	2.651737	-0.300312
S	-0.340594	-1.293587	-0.450201
C	-4.021167	-2.889904	-1.509929
H	-3.077258	-3.430634	-1.381874
H	-4.712203	-3.267654	-0.748826
H	-4.428347	-3.148442	-2.490858
H	0.309400	-2.711794	2.134908
C	1.392691	-1.852008	-0.078014
C	2.194793	-1.736831	-1.387630
H	1.294178	-2.923271	0.158302
C	3.681868	-1.885980	-1.082853
H	2.042480	-0.745025	-1.835939
C	3.300476	-1.021876	1.225441
C	4.071420	-0.811936	-0.084335
H	3.873764	-2.884359	-0.656188
H	3.633106	-1.973628	1.666790
H	3.818490	0.166569	-0.506656
O	1.869489	-1.103572	0.997408
C	3.522411	0.151251	2.223161
H	2.537558	0.563962	2.467995
H	3.980882	-0.228407	3.140734
O	5.472842	-0.899886	0.140292
H	5.701744	-0.094702	0.638655
O	4.369695	-1.755457	-2.321220
H	5.302600	-1.592337	-2.115146
O	1.725013	-2.756360	-2.256361
H	2.335978	-2.795139	-3.007037
O	4.395449	1.156979	1.730156
H	3.909896	1.742388	1.102466
C	-1.528333	4.926544	1.420542
H	-1.730143	5.476938	0.498381
H	-2.260311	5.180387	2.189144
H	-0.532216	5.217692	1.772041
C	1.430581	3.089561	-1.899154
H	1.119527	2.343050	-2.638391
H	0.542051	3.654166	-1.605634
H	2.173979	3.755041	-2.339837

SM_OH_*aR*

Imaginary frequencies = 0
E(ωB97xD, HFIP) = -2096.00121
$E_{\text{Thermal correction}}$ = 0.416225

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C	0.407864	-2.250547	1.544232
C	0.197192	-1.003499	2.169877
C	0.169575	-0.902368	3.569762
C	0.339579	-2.033768	4.366217
C	0.556247	-3.273513	3.761117
H	0.772856	-4.337180	1.906270
H	0.315872	-1.942807	5.447781
H	0.711260	-4.160325	4.368462
C	0.467751	-2.427592	0.064811
C	-0.474408	-3.233160	-0.603537
C	1.523897	-1.827542	-0.669821
C	-0.351980	-3.383826	-1.996056
C	1.611103	-1.994625	-2.065176
C	0.661718	-2.766339	-2.728981
H	-1.085418	-3.994692	-2.517312
H	2.427790	-1.529290	-2.603430
H	0.714459	-2.899211	-3.805226
Pd	1.705719	0.541460	-0.391059
O	2.300869	2.474165	-0.026503
H	2.428102	-1.496322	-0.128238
C	4.369692	0.098878	-1.267484
O	4.476667	-0.564738	-0.231697
O	3.246221	0.598885	-1.722969
C	-1.614973	-3.925176	0.112332
H	-1.291212	-4.864432	0.575938
H	-2.034614	-3.303783	0.907787
H	-2.417936	-4.171273	-0.587879
C	1.542423	3.459213	0.322328

O	0.309740	3.414543	0.473058
S	0.042728	0.573999	1.302372
H	0.019036	0.070587	4.027164
C	-1.738231	0.596617	0.759163
C	-2.219249	2.044476	0.522374
H	-2.262115	0.166530	1.627253
C	-3.716912	1.978990	0.209321
H	-1.683839	2.449742	-0.342412
C	-3.343071	-0.317617	-0.738837
C	-3.947817	1.071851	-0.988599
H	-4.249350	1.570540	1.084131
H	-3.880017	-0.806475	0.088941
H	-3.449094	1.519703	-1.861368
O	-1.947175	-0.184857	-0.396774
C	-3.430646	-1.216908	-1.977011
H	-2.778465	-2.078449	-1.832893
H	-3.068150	-0.664320	-2.857220
O	-4.741699	-1.719573	-2.177011
H	-5.353498	-0.966330	-2.174241
O	-5.339612	0.900632	-1.264470
H	-5.740906	1.780671	-1.313543
O	-4.238342	3.260326	-0.113685
H	-3.940367	3.872740	0.575964
O	-2.051633	2.882048	1.645481
H	-1.179449	3.309349	1.530393
C	5.571007	0.422915	-2.143179
H	6.328238	-0.355766	-2.032064
H	5.284689	0.540469	-3.190594
H	5.996231	1.372909	-1.800639
C	2.295545	4.765959	0.538801
H	3.371328	4.638088	0.416394
H	1.926210	5.503991	-0.180125
H	2.073463	5.141008	1.542434

TS_OH_*aS*

Imaginary frequencies = 1 (-1059.9662)
E(ωB97xD, HFIP) = -2095.98743
$E_{\text{Thermal correction}}$ = 0.414074

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C	-2.575136	-1.578927	0.815849
C	-1.191305	-1.848002	0.878945
C	-0.637373	-2.527441	1.969586
C	-1.468587	-2.960319	3.004120
C	-2.841471	-2.707053	2.959041
H	-4.446332	-1.797838	1.848313
H	-1.034861	-3.482335	3.851779
H	-3.484543	-3.028289	3.772733
C	-3.141454	-0.810626	-0.328811
C	-4.113012	-1.387646	-1.177743
C	-2.669277	0.513100	-0.569524
C	-4.586950	-0.629654	-2.259820
C	-3.182022	1.232659	-1.670224
C	-4.136963	0.668703	-2.509950
H	-5.319684	-1.076709	-2.927282
H	-2.839507	2.249011	-1.844401
H	-4.528764	1.227390	-3.355113
Pd	-0.570991	1.026710	-0.248954
O	1.437009	1.475124	-0.052260
H	-2.612961	1.267093	0.507344
C	-1.991107	3.161672	1.097020
O	-1.039902	3.010782	0.260241
O	-2.800645	2.238277	1.419604
C	2.097845	2.495478	-0.516823
O	3.228779	2.763001	-0.071384
S	-0.232619	-1.304630	-0.549793
C	-4.626657	-2.799980	-0.991489
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H	-5.398020	-2.854212	-0.214534
H	-5.073044	-3.168253	-1.919450
H	0.430602	-2.689916	2.034867
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C	2.329045	-1.642819	-1.450966
H	1.430277	-2.916932	0.028349
C	3.814936	-1.761108	-1.128501
H	2.153911	-0.638322	-1.860389
C	3.374348	-1.001783	1.204530
C	4.159233	-0.717617	-0.082283
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H	3.732781	-1.958626	1.613614
H	3.887845	0.270563	-0.468788
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H	5.752204	0.000523	0.714568
O	4.517357	-1.561434	-2.349680
H	5.440643	-1.375022	-2.121357
O	1.901802	-2.640133	-2.366762
H	2.515622	-2.621339	-3.115703
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H	-1.576085	5.274047	1.202488
H	-3.204533	4.789509	1.792199
H	-1.769819	4.456412	2.769609
C	1.498162	3.330022	-1.633281
H	1.168696	2.684498	-2.454649
H	0.620186	3.864142	-1.259814
H	2.236881	4.044569	-1.998925

TS_OH_*aR*

Imaginary frequencies = 1 (-903.7946)
E(ωB97xD, HFIP) = -2095.99165
$E_{\text{Thermal correction}}$ = 0.411954

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C	0.664431	-2.067846	1.427419
C	0.383484	-0.861620	2.107084

C	0.490530	-0.777653	3.503201
C	0.884605	-1.886817	4.250532
C	1.199087	-3.077813	3.593220
H	1.349993	-4.085762	1.704883
H	0.965269	-1.811980	5.330601
H	1.540815	-3.940824	4.157034
C	0.538718	-2.219076	-0.051640
C	-0.273454	-3.243793	-0.592034
C	1.257183	-1.349674	-0.920542
C	-0.381192	-3.344959	-1.987521
C	1.104319	-1.488575	-2.318394
C	0.288188	-2.477686	-2.852601
H	-1.021351	-4.119583	-2.403117
H	1.666663	-0.832783	-2.976785
H	0.176349	-2.584213	-3.927764
Pd	1.686389	0.705670	-0.399279
O	2.277172	2.647661	0.043911
H	2.510947	-1.257236	-0.626738
C	4.208665	-0.276793	-1.376023
O	3.904164	-1.308535	-0.703964
O	3.407546	0.692945	-1.592859
C	-1.075252	-4.210636	0.256770
H	-0.469581	-5.058645	0.596360
H	-1.488522	-3.731581	1.148183
H	-1.905422	-4.625374	-0.322178
C	1.485791	3.651587	0.189325
O	0.241844	3.611260	0.100531
S	0.048432	0.702021	1.275846
H	0.277472	0.166040	3.995828
C	-1.763046	0.631100	0.849489
C	-2.244641	2.012153	0.351629
H	-2.223363	0.405938	1.825102
C	-3.752283	1.910946	0.097127
H	-1.730232	2.242017	-0.589107
C	-3.477983	-0.543824	-0.293452
C	-4.054250	0.764059	-0.852858
H	-4.258739	1.724031	1.058371
H	-3.963381	-0.778473	0.666644
H	-3.574378	0.971983	-1.821103
O	-2.058188	-0.377013	-0.089215
C	-3.676217	-1.732084	-1.239825
H	-3.065479	-2.565015	-0.889631
H	-3.331445	-1.459263	-2.248775
O	-5.020450	-2.184644	-1.248919
H	-5.592403	-1.418853	-1.416789
O	-5.461048	0.592688	-1.038426
H	-5.836595	1.458432	-1.256376
O	-4.259229	3.102809	-0.486872
H	-3.937695	3.842757	0.050453
O	-2.045715	3.041896	1.292781
H	-1.190506	3.465869	1.056052
C	5.599722	-0.174534	-1.962472
H	5.853376	-1.105977	-2.475054
H	5.671742	0.673952	-2.643059
H	6.312953	-0.042441	-1.142214
C	2.180845	4.974165	0.484492
H	3.265533	4.862892	0.507857
H	1.896847	5.701783	-0.281936
H	1.825912	5.356609	1.447010

Pdt_OH_*aS*

Imaginary frequencies = 0

E(ωB97xD, HFIP) = -2096.01588

$E_{\text{Thermal correction}}$ = 0.418344

C	-3.260577	-2.118377	1.787097
C	-2.510162	-1.663623	0.690091
C	-1.142472	-2.017036	0.649547
C	-0.572490	-2.824377	1.638057
C	-1.355911	-3.284783	2.698360
C	-2.699818	-2.921149	2.780769
H	-4.299887	-1.819300	1.868600
H	-0.903586	-3.906051	3.465432
H	-3.308061	-3.249418	3.618238
C	-3.130211	-0.800153	-0.359506
C	-4.383695	-1.143994	-0.941109
C	-2.460640	0.370062	-0.800663
C	-4.950406	-0.280165	-1.887558
C	-3.057213	1.204435	-1.755552
C	-4.310361	0.892634	-2.284294
H	-5.904342	-0.548039	-2.334689
H	-2.540918	2.098934	-2.093880
H	-4.771858	1.546455	-3.019575
Pd	-0.558334	0.906582	-0.329131
O	1.442566	1.491833	0.116173
H	-2.663739	1.443967	1.184027
C	-1.970452	3.197031	1.129122
O	-1.152540	2.931734	0.241960
O	-2.779489	2.294389	1.665664
C	2.152874	2.520379	-0.204361
O	3.219244	2.796201	0.386691
S	-0.196706	-1.378124	-0.751815
C	-5.120589	-2.435187	-0.639422
H	-4.438535	-3.258896	-0.415520
H	-5.802515	-2.335349	0.213585
H	-5.728830	-2.723336	-1.501912
H	0.480690	-3.069171	1.613039
C	1.564334	-1.847633	-0.361984
C	2.411764	-1.462119	-1.587768
H	1.550682	-2.947918	-0.295605
C	3.889543	-1.561173	-1.222838
H	2.203281	-0.421552	-1.872150
C	3.330453	-1.092715	1.163211
C	4.156716	-0.639910	-0.047030
H	4.132834	-2.600951	-0.948148
H	3.710184	-2.075853	1.481150
H	3.870375	0.379239	-0.326580
O	1.924129	-1.235647	0.835182
C	3.400021	-0.067657	2.333312
H	2.386870	0.323128	2.475305
H	3.716888	-0.574468	3.250193
O	5.546294	-0.695428	0.252023

H	5.685650	0.009083	0.912437
O	4.626060	-1.190000	-2.382813
H	5.531314	-0.996510	-2.095633
O	2.061498	-2.352055	-2.637063
H	2.705416	-2.221208	-3.348616
O	4.323878	0.984320	2.105041
H	3.888464	1.683754	1.548631
C	-2.128320	4.575259	1.697743
H	-1.455670	5.265344	1.190591
H	-3.166620	4.902931	1.591627
H	-1.898076	4.550011	2.767652
C	1.708142	3.387445	-1.375725
H	1.777927	2.805660	-2.302606
H	0.666254	3.695190	-1.255328
H	2.350159	4.265625	-1.461109

Pdt_OH_*aR*

Imaginary frequencies = 0
E(ωB97xD, HFIP) = -2096.02202
$E_{\text{Thermal correction}}$ = 0.415872

C	0.570375	-3.430570	1.947205
C	0.269732	-2.217676	1.299657
C	0.129705	-1.083010	2.133380
C	0.211215	-1.182205	3.528443
C	0.457269	-2.412584	4.138096
C	0.662356	-3.535000	3.335732
H	0.753347	-4.311382	1.342889
H	0.519721	-2.481483	5.219666
H	0.902309	-4.493978	3.785840
C	0.129154	-2.176968	-0.188947
C	-0.620649	-3.186029	-0.860958
C	0.705127	-1.128594	-0.947497
C	-0.716657	-3.143838	-2.258605
C	0.578159	-1.118116	-2.343779
C	-0.115748	-2.132457	-3.003929
H	-1.296225	-3.911664	-2.765011
H	1.019614	-0.310014	-2.921123
H	-0.206702	-2.120455	-4.087002
Pd	1.640208	0.502458	-0.207151
O	2.733395	2.182570	0.537793
H	2.882334	-1.783883	-0.748981
C	4.048991	-0.646348	-1.701872
O	3.783516	-1.821234	-1.142548
O	3.307001	0.334328	-1.605723
C	-1.401592	-4.280934	-0.155987
H	-0.801936	-5.184369	0.008376
H	-1.782586	-3.962828	0.817217
H	-2.255907	-4.576910	-0.772102
C	2.256527	3.371578	0.568442
O	1.089294	3.695856	0.243453
S	0.086273	0.597536	1.497886
H	0.105649	-0.285391	4.131270
C	-1.679910	0.892313	0.983261
C	-1.774261	2.240686	0.237805
H	-2.206971	0.961977	1.948622
C	-3.242291	2.449779	-0.153485
H	-1.163203	2.177657	-0.673784
C	-3.587352	-0.025264	-0.080265
C	-3.778537	1.247708	-0.916691
H	-3.830643	2.577425	0.769944
H	-4.155706	0.062150	0.858932
H	-3.210694	1.138419	-1.853023
O	-2.183242	-0.168880	0.212467
C	-4.035412	-1.300137	-0.801856
H	-3.681593	-2.165328	-0.235759
H	-3.575595	-1.337089	-1.800600
O	-5.448918	-1.403172	-0.868608
H	-5.792419	-0.571305	-1.231352
O	-5.170045	1.392497	-1.209611
H	-5.298085	2.269152	-1.600968
O	-3.396957	3.594909	-0.980710
H	-2.939175	4.327618	-0.540709
O	-1.384844	3.330330	1.034458
H	-0.440365	3.546615	0.817854
C	5.336841	-0.615697	-2.469955
H	5.294818	-1.346333	-3.283699
H	5.505793	0.384045	-2.867393
H	6.160942	-0.904433	-1.810565
C	3.217046	4.462315	1.026341
H	4.190533	4.052392	1.300341
H	3.337087	5.192375	0.219305
H	2.781594	4.992048	1.879590

SM_OAc_*aS*

Imaginary frequencies = 0
E(ωB97xD, DCE-HFIP) = -2706.558703
$E_{\text{Thermal correction}}$ = 0.510342

C	3.372594	2.589567	-2.493973
C	2.869225	1.419251	-1.909907
C	1.475418	1.294942	-1.740508
C	0.618267	2.335380	-2.117551
C	1.145005	3.491000	-2.696672
C	2.521096	3.620406	-2.891347
H	4.447254	2.691064	-2.614851
H	0.471418	4.292125	-2.985469
H	2.930565	4.523146	-3.334281
C	3.795376	0.350528	-1.433909
C	4.411857	-0.543391	-2.329345
C	4.037182	0.244803	-0.041041
C	5.259996	-1.530575	-1.799015
C	4.894989	-0.752986	0.455144
C	5.501439	-1.643200	-0.428717
H	5.728520	-2.235941	-2.481134
H	5.064125	-0.827892	1.522812
H	6.151433	-2.428028	-0.054596
Pd	1.970745	-0.476705	1.033381
O	0.377334	-1.392990	1.933734
H	3.701574	1.048185	0.631124

C	3.174410	0.624790	3.344756
O	2.850738	-0.550964	2.870649
O	3.150602	1.678806	2.697332
C	0.639311	-2.668215	2.168304
O	1.539276	-3.310305	1.634209
S	0.899730	-0.301833	-1.104785
C	4.170267	-0.471576	-3.820985
H	3.102698	-0.405215	-4.054434
H	4.648315	0.408468	-4.266268
H	4.573569	-1.356485	-4.320812
H	-0.447221	2.275934	-1.945959
C	-0.915703	-0.033233	-0.967287
C	-1.651945	-1.343056	-0.609372
H	-1.227578	0.315876	-1.958268
C	-3.160824	-1.014659	-0.638187
H	-1.338467	-1.635878	0.392296
C	-2.569700	1.343799	0.035472
C	-3.443882	0.113209	0.373791
H	-3.436872	-0.681745	-1.638150
H	-2.838637	1.741419	-0.950498
H	-3.186851	-0.229202	1.376505
O	-1.195182	0.919787	0.031036
O	-1.320430	-2.482790	-1.424058
C	-1.473352	-2.450259	-2.773672
O	-1.841545	-1.469394	-3.388156
O	-3.995040	-2.179439	-0.458952
C	-3.993344	-2.878547	0.706848
O	-3.334339	-2.574063	1.678312
O	-4.855261	0.412770	0.482610
C	-5.563090	0.870515	-0.584804
O	-5.073376	1.120414	-1.666898
C	-4.904087	-4.076493	0.611504
H	-5.862630	-3.802093	0.163791
H	-4.441115	-4.830754	-0.033800
H	-5.051121	-4.496662	1.606432
C	-1.120856	-3.784039	-3.378473
H	-0.142193	-4.115185	-3.020147
H	-1.854857	-4.533492	-3.064797
H	-1.123906	-3.700873	-4.465130
C	-7.021033	1.017421	-0.229986
H	-7.451875	0.029698	-0.036446
H	-7.134960	1.608537	0.683061
H	-7.547701	1.491859	-1.057743
C	-2.697040	2.429526	1.085695
H	-3.747286	2.658561	1.283135
H	-2.223884	2.114961	2.020948
O	-2.032427	3.602413	0.580632
C	-2.131756	4.716184	1.350499
O	-2.783782	4.756436	2.373099
C	-1.327673	5.852718	0.772114
H	-1.554425	5.983760	-0.289678
H	-1.547359	6.767577	1.322270
H	-0.260781	5.621291	0.857750
C	-0.298915	-3.273791	3.202682
H	-0.001273	-2.907594	4.191458
H	-1.333827	-2.972264	3.029299
H	-0.208147	-4.361342	3.181315
C	3.586814	0.594710	4.809143
H	4.003189	-0.375457	5.088601
H	4.302291	1.396076	5.005813
H	2.695216	0.771505	5.421300

SM_OAc_*aR*

Imaginary frequencies = 0
E(ωB97xD, DCE-HFIP) = -2706.563461
$E_{\text{Thermal correction}}$ = 0.515077

C	-2.731110	-1.244863	3.675473
C	-2.195767	-0.845439	2.440771
C	-1.823272	-1.848919	1.524439
C	-2.014068	-3.203689	1.830425
C	-2.560532	-3.577512	3.058200
C	-2.915729	-2.593253	3.983533
H	-3.030232	-0.481806	4.388052
H	-2.709615	-4.628357	3.287333
H	-3.347666	-2.872821	4.939918
C	-2.066922	0.603373	2.114281
C	-1.135693	1.423103	2.777270
C	-2.925187	1.158185	1.127534
C	-1.068341	2.780370	2.413611
C	-2.839815	2.523870	0.800457
C	-1.898804	3.329787	1.437339
H	-0.324113	3.413411	2.886870
H	-3.509808	2.931709	0.053210
H	-1.805774	4.380284	1.180180
Pd	-2.577062	0.146835	-1.022966
O	-2.456533	-0.721166	-2.865931
H	-3.816950	0.596959	0.805254
C	-5.149494	1.234329	-1.586287
O	-5.534859	0.511686	-0.660066
O	-3.899013	1.420324	-1.923370
C	-0.205311	0.900813	3.852344
H	-0.702769	0.868699	4.829528
H	0.151089	-0.112066	3.645012
H	0.665974	1.553715	3.953453
C	-1.318468	-1.136279	-3.344969
O	-0.237126	-1.147934	-2.745786
S	-1.144728	-1.506348	-0.116369
H	-1.735344	-3.957172	1.100011
C	0.529746	-0.761921	0.278570
C	1.629563	-1.686241	-0.293948
H	0.597388	-0.702207	1.368036
C	3.000208	-1.001381	-0.145750
H	1.412518	-1.862746	-1.347694
C	1.837328	1.204517	-0.146181
C	2.919467	0.359528	-0.854893
H	3.230610	-0.845193	0.907479
H	2.065956	1.319463	0.919331
H	2.610494	0.219067	-1.891275
O	0.586157	0.515121	-0.312458
C	1.605422	2.581044	-0.776461
H	0.663338	2.984241	-0.403098

H	1.580101	2.512875	-1.865750
O	1.615815	-3.010839	0.289938
C	1.859183	-3.202506	1.611013
O	1.997821	-2.304230	2.417453
O	4.091887	-1.842254	-0.579441
C	4.230044	-2.210691	-1.882828
O	3.486894	-1.859372	-2.772201
O	4.214078	0.986502	-0.984261
C	4.916959	1.381564	0.102209
O	4.513813	1.298590	1.245540
O	2.687783	3.484101	-0.462742
C	2.544716	4.289261	0.620278
O	1.552601	4.307418	1.320205
C	1.948939	-4.673511	1.930668
H	2.946611	-5.033591	1.655524
H	1.804190	-4.820364	3.001290
H	1.218103	-5.247160	1.356379
C	5.422409	-3.121193	-2.048922
H	5.622616	-3.260501	-3.111280
H	6.299682	-2.707683	-1.544403
H	5.205204	-4.091785	-1.590424
C	6.256780	1.938580	-0.310811
H	6.113956	2.784400	-0.990050
H	6.808224	2.254616	0.574673
H	6.826669	1.177674	-0.852558
C	3.776833	5.129162	0.842275
H	4.522648	4.522146	1.367473
H	4.209068	5.456778	-0.105920
H	3.522073	5.986834	1.465610
C	-6.131201	1.997792	-2.465000
H	-7.046309	2.201694	-1.905237
H	-5.692933	2.923979	-2.843688
H	-6.383109	1.367711	-3.325422
C	-1.437804	-1.625648	-4.784332
H	-2.252978	-2.349308	-4.872291
H	-1.678961	-0.779009	-5.435021
H	-0.494463	-2.074304	-5.099022

TS_OAc_*aS*

Imaginary frequencies = 1 (-1110.1380)
E(ωB97xD, DCE-HFIP) = -2706.543979
$E_{\text{Thermal correction}}$ = 0.508102

C	3.552197	2.246758	-2.375714
C	2.964997	1.097192	-1.826106
C	1.560501	1.067850	-1.695624
C	0.777114	2.154045	-2.101250
C	1.390238	3.279142	-2.654966
C	2.778734	3.330201	-2.790137
H	4.633932	2.291057	-2.455259
H	0.775600	4.118088	-2.967211
H	3.258036	4.212352	-3.203826
C	3.804782	-0.044621	-1.364766
C	4.628752	-0.745706	-2.275870
C	3.754386	-0.428192	0.004560
C	5.389431	-1.821410	-1.793519
C	4.538980	-1.517418	0.438350
C	5.356117	-2.207280	-0.451696
H	6.011915	-2.374915	-2.492671
H	4.502334	-1.813307	1.483049
H	5.955631	-3.046739	-0.111139
Pd	1.868758	-0.460067	1.106847
O	0.141030	-0.817579	2.181835
H	3.777580	0.567946	0.880151
C	3.676720	0.869966	2.930808
O	2.819768	-0.068230	2.944598
O	4.144312	1.394254	1.868163
C	0.258577	-1.939273	2.862370
O	1.111450	-2.800618	2.640117
S	0.871249	-0.468735	-1.031054
C	4.691700	-0.409182	-3.751800
H	3.710865	-0.137146	-4.151845
H	5.364621	0.433083	-3.951406
H	5.066375	-1.265018	-4.320795
H	-0.295196	2.152596	-1.965277
C	-0.937247	-0.130798	-0.995547
C	-1.704665	-1.399580	-0.558589
H	-1.201271	0.140445	-2.025016
C	-3.207748	-1.058507	-0.643200
H	-1.417583	-1.624175	0.468910
C	-2.602836	1.335985	-0.142186
C	-3.491848	0.142158	0.279832
H	-3.459103	-0.793952	-1.669584
H	-2.856905	1.657593	-1.159523
H	-3.248054	-0.125548	1.308169
O	-1.231619	0.907644	-0.092942
O	-1.368385	-2.597869	-1.283148
C	-1.500672	-2.663251	-2.634380
O	-1.864032	-1.731962	-3.323732
O	-4.060784	-2.197433	-0.400321
C	-4.085294	-2.817424	0.809209
O	-3.435080	-2.457857	1.767268
O	-4.901288	0.462623	0.350394
C	-5.594694	0.842770	-0.756058
O	-5.093683	1.001284	-1.850045
C	-5.015892	-4.003502	0.780530
H	-5.982903	-3.724865	0.353283
H	-4.587822	-4.786012	0.145297
H	-5.141356	-4.386915	1.792962
C	-1.125620	-4.033080	-3.136574
H	-0.108541	-4.280962	-2.818668
H	-1.794456	-4.783890	-2.704564
H	-1.197458	-4.051743	-4.223790
C	-7.053291	1.036046	-0.426265
H	-7.495904	0.076406	-0.140593
H	-7.165390	1.713778	0.424876
H	-7.570498	1.434775	-1.298702
C	-2.734072	2.500112	0.820158
H	-3.784453	2.740066	1.002574
H	-2.255233	2.260494	1.774305
O	-2.077670	3.634716	0.221316
C	-2.174468	4.803603	0.902764
O	-2.802007	4.918527	1.935167

C	-1.406285	5.902578	0.212205
H	-1.725531	5.993113	-0.830301
H	-1.570042	6.843116	0.737863
H	-0.338685	5.660279	0.211527
C	-0.775636	-2.085722	3.968955
H	-0.711688	-1.230419	4.649204
H	-1.782855	-2.102968	3.544105
H	-0.593293	-3.011181	4.518020
C	4.177954	1.387047	4.261363
H	3.731935	0.829227	5.084682
H	5.268384	1.307476	4.293955
H	3.922595	2.447674	4.348650

TS_OAc_*aR*

Imaginary frequencies = 1 (-1154.8451)
E(ωB97xD, DCE-HFIP) = -2706.542312
$E_{\text{Thermal correction}}$ = 0.515681

C	-3.043846	-0.672981	3.475303
C	-2.340341	-0.462907	2.277440
C	-1.903133	-1.599765	1.568819
C	-2.168164	-2.891963	2.043247
C	-2.868999	-3.073682	3.235476
C	-3.310571	-1.957379	3.949807
H	-3.410606	0.188999	4.023764
H	-3.074810	-4.076874	3.596566
H	-3.872360	-2.084905	4.870557
C	-2.098531	0.920617	1.778572
C	-1.374480	1.842774	2.571175
C	-2.603236	1.305235	0.505317
C	-1.169943	3.137161	2.070339
C	-2.380286	2.625262	0.057683
C	-1.673544	3.538084	0.832376
H	-0.581080	3.839849	2.653287
H	-2.781180	2.929225	-0.905490
H	-1.488219	4.546478	0.476015
Pd	-2.534950	-0.056630	-1.178655
O	-2.366723	-1.173169	-2.907397
H	-3.860853	0.951330	0.221637
C	-5.154847	1.127390	-1.387399
O	-5.148134	1.004361	-0.118944
O	-4.138669	0.931056	-2.125748
C	-0.767996	1.483146	3.913710
H	-1.497334	1.569221	4.728071
H	-0.381436	0.460491	3.935327
H	0.057677	2.161424	4.147188
C	-1.218434	-1.646969	-3.290520
O	-0.154657	-1.571474	-2.657648
S	-1.105595	-1.514800	-0.048667
H	-1.830348	-3.748932	1.468115
C	0.549034	-0.718069	0.326733
C	1.663671	-1.721327	-0.050459
H	0.556151	-0.497692	1.398349
C	3.034410	-1.035159	0.091810
H	1.503163	-2.031333	-1.083979
C	1.904524	1.160599	-0.274474
C	3.024400	0.226700	-0.785801
H	3.203782	-0.750073	1.129363
H	2.054920	1.414783	0.781207
H	2.790775	-0.042232	-1.816477
O	0.662892	0.454999	-0.442614
C	1.734497	2.443682	-1.092971
H	0.777307	2.899108	-0.837365
H	1.778347	2.232425	-2.163587
O	1.593872	-2.958717	0.697244
C	1.759648	-2.979316	2.044061
O	1.874941	-1.985885	2.733561
O	4.135352	-1.935465	-0.165252
C	4.345453	-2.465132	-1.401144
O	3.663839	-2.221412	-2.372264
O	4.333867	0.826072	-0.896136
C	4.960551	1.350715	0.182233
O	4.477846	1.404692	1.295841
O	2.809562	3.368597	-0.821901
C	2.572793	4.384082	0.048630
O	1.501963	4.580238	0.584744
C	1.795955	-4.397623	2.555737
H	2.787875	-4.819405	2.359019
H	1.617390	-4.398554	3.631258
H	1.062229	-5.020686	2.039248
C	5.531868	-3.398224	-1.378564
H	5.774138	-3.695922	-2.398697
H	6.392438	-2.916648	-0.906253
H	5.286590	-4.286939	-0.787674
C	6.330404	1.855603	-0.198605
H	6.244121	2.599999	-0.995680
H	6.813191	2.292126	0.675718
H	6.937480	1.031477	-0.585615
C	3.815923	5.209940	0.265483
H	4.475457	4.676423	0.958841
H	4.357908	5.359018	-0.671477
H	3.541100	6.168455	0.706441
C	-6.445601	1.547571	-2.054391
H	-6.747898	2.526677	-1.670406
H	-6.325120	1.588104	-3.136925
H	-7.232480	0.834667	-1.790866
C	-1.279995	-2.350667	-4.641966
H	-1.920186	-3.235709	-4.563934
H	-1.728017	-1.689489	-5.389501
H	-0.277609	-2.648658	-4.953097

Pdt_OAc_*aS*

Imaginary frequencies = 0
E(ωB97xD, DCE-HFIP) = -2706.56858
$E_{\text{Thermal correction}}$ = 0.511523

C	3.612007	2.254764	-2.142656
C	2.997989	1.053456	-1.749970
C	1.585174	1.014097	-1.773076
C	0.837233	2.106555	-2.221248
C	1.483306	3.272654	-2.636276
C	2.874279	3.353509	-2.582876

H	4.692246	2.329254	-2.083127
H	0.891633	4.115475	-2.980678
H	3.384772	4.266633	-2.874315
C	3.820729	-0.105787	-1.290156
C	4.960492	-0.529670	-2.032893
C	3.464719	-0.804072	-0.108521
C	5.737433	-1.582788	-1.533389
C	4.262790	-1.861742	0.352687
C	5.411662	-2.235502	-0.344393
H	6.604159	-1.908735	-2.103310
H	3.971806	-2.399977	1.252114
H	6.032304	-3.049652	0.020672
Pd	1.730121	-0.673443	0.937058
O	-0.053462	-0.883373	2.094780
H	4.065403	0.773393	1.226943
C	3.641217	0.638269	3.060736
O	2.741088	-0.178857	2.876797
O	4.344658	1.191098	2.074466
C	0.141151	-1.944886	2.827879
O	1.079804	-2.738507	2.643554
S	0.819172	-0.525743	-1.207500
C	5.352199	0.054653	-3.377550
H	4.486449	0.398206	-3.948880
H	6.035702	0.906726	-3.278509
H	5.871651	-0.702954	-3.972139
H	-0.243403	2.078870	-2.227539
C	-0.971099	-0.099914	-1.122763
C	-1.776670	-1.346460	-0.688923
H	-1.258476	0.206634	-2.135894
C	-3.263666	-0.935046	-0.693323
H	-1.456477	-1.615878	0.318925
C	-2.530563	1.404063	-0.127418
C	-3.439474	0.227288	0.302302
H	-3.546006	-0.604157	-1.691852
H	-2.838432	1.779495	-1.111000
H	-3.140697	-0.099003	1.298994
O	-1.176416	0.928522	-0.186363
O	-1.523630	-2.531999	-1.468040
C	-1.732409	-2.549350	-2.810640
O	-2.095599	-1.583944	-3.451580
O	-4.163166	-2.041968	-0.472913
C	-4.167166	-2.730661	0.699230
O	-3.456545	-2.463972	1.643893
O	-4.826763	0.601701	0.478528
C	-5.573188	1.057060	-0.562216
O	-5.140716	1.238979	-1.681647
C	-5.165597	-3.860089	0.646806
H	-6.145708	-3.490553	0.332494
H	-4.842132	-4.601618	-0.090791
H	-5.232691	-4.326906	1.629301
C	-1.441127	-3.916078	-3.373931
H	-0.420609	-4.215796	-3.117723
H	-2.118609	-4.652926	-2.931396
H	-1.568825	-3.895717	-4.455987
C	-6.994868	1.305813	-0.124404
H	-7.447964	0.369902	0.216892
H	-7.013940	2.003577	0.718153
H	-7.564034	1.710997	-0.960760
C	-2.552440	2.528389	0.889702
H	-3.577843	2.791012	1.161409
H	-2.010824	2.232705	1.792909
O	-1.907871	3.669425	0.288252
C	-1.893368	4.803814	1.028736
O	-2.410423	4.889723	2.123818
C	-1.159857	5.911385	0.313459
H	-1.607517	6.088350	-0.669244
H	-1.203904	6.820392	0.913105
H	-0.116748	5.621015	0.153188
C	-0.868025	-2.156149	3.945312
H	-0.918198	-1.261078	4.574412
H	-1.862690	-2.317719	3.519934
H	-0.582136	-3.018778	4.550287
C	4.050668	1.105871	4.428214
H	3.424131	0.630249	5.181517
H	5.102793	0.859171	4.600685
H	3.953651	2.194348	4.487519

Pdt_OAc_*aR*

Imaginary frequencies = 0
E(ωB97xD, DCE-HFIP) = -2706.577732
$E_{\text{Thermal correction}}$ = 0.512612

C	-2.529833	2.119949	3.481810
C	-1.939844	1.499342	2.364419
C	-1.623038	0.129709	2.502729
C	-1.821326	-0.549585	3.712333
C	-2.361633	0.110001	4.815875
C	-2.737624	1.447396	4.685999
H	-2.852347	3.150777	3.392524
H	-2.510145	-0.422787	5.750041
H	-3.202185	1.969173	5.517881
C	-1.705944	2.282200	1.115591
C	-1.146110	3.591174	1.190725
C	-2.032618	1.754452	-0.153101
C	-1.014170	4.343895	0.016018
C	-1.902547	2.536090	-1.304304
C	-1.409531	3.838808	-1.220513
H	-0.578487	5.338161	0.075502
H	-2.185916	2.132126	-2.270722
H	-1.301085	4.441540	-2.118136
Pd	-2.569108	-0.128745	-0.567048
O	-3.175400	-2.135368	-1.227751
H	-4.327027	-1.780425	-1.962847
C	-5.016492	-0.025297	-2.484729
O	-5.124224	-1.322957	-2.488956
O	-4.125137	0.616470	-1.890942
C	-0.610815	4.213726	2.469408
H	-1.369761	4.802743	2.998614
H	-0.229384	3.469625	3.172517
H	0.207552	4.898768	2.226640
C	-2.329920	-3.124149	-1.422699
O	-1.142264	-3.074745	-1.107797
S	-1.169007	-0.920358	1.113625

H	-1.564305	-1.601936	3.779048
C	0.642922	-0.578434	0.853193
C	1.361139	-1.856391	0.359624
H	1.013168	-0.266411	1.835251
C	2.855122	-1.517897	0.175732
H	0.907315	-2.164282	-0.582573
C	2.183808	0.882781	-0.214124
C	3.003149	-0.305459	-0.761278
H	3.290628	-1.278505	1.145158
H	2.552592	1.195469	0.769939
H	2.603859	-0.560073	-1.743004
O	0.821142	0.434156	-0.110361
C	2.131480	2.089242	-1.148130
H	1.273271	2.711918	-0.886832
H	2.038171	1.791531	-2.196788
O	1.189864	-3.018161	1.197971
C	1.539671	-3.011124	2.504568
O	1.943346	-2.031443	3.101324
O	3.626585	-2.667866	-0.241618
C	3.433640	-3.245074	-1.458264
O	2.660656	-2.832251	-2.295844
O	4.386279	0.005051	-1.044744
C	5.234055	0.383697	-0.055225
O	4.914285	0.506791	1.108875
O	3.352365	2.837722	-0.962180
C	3.459082	3.987819	-1.670055
O	2.598555	4.386995	-2.426948
C	1.360653	-4.382374	3.107366
H	2.136318	-5.050736	2.718495
H	1.451344	-4.316976	4.191738
H	0.392478	-4.802773	2.823203
C	4.302896	-4.469858	-1.604901
H	4.303368	-4.787817	-2.647582
H	5.321296	-4.268521	-1.262843
H	3.896593	-5.274815	-0.983056
C	6.619167	0.613174	-0.607217
H	6.579161	1.304909	-1.453178
H	7.260628	1.010806	0.179141
H	7.030410	-0.332188	-0.975718
C	4.778184	4.673010	-1.406318
H	5.044468	4.618756	-0.347974
H	5.565905	4.168728	-1.977056
H	4.717147	5.710791	-1.735034
C	-6.068220	0.702920	-3.280842
H	-7.061789	0.360631	-2.977604
H	-5.976004	1.778985	-3.136358
H	-5.948437	0.459341	-4.341696
C	-2.939207	-4.365684	-2.057329
H	-3.723466	-4.767863	-1.407090
H	-3.408007	-4.112412	-3.014329
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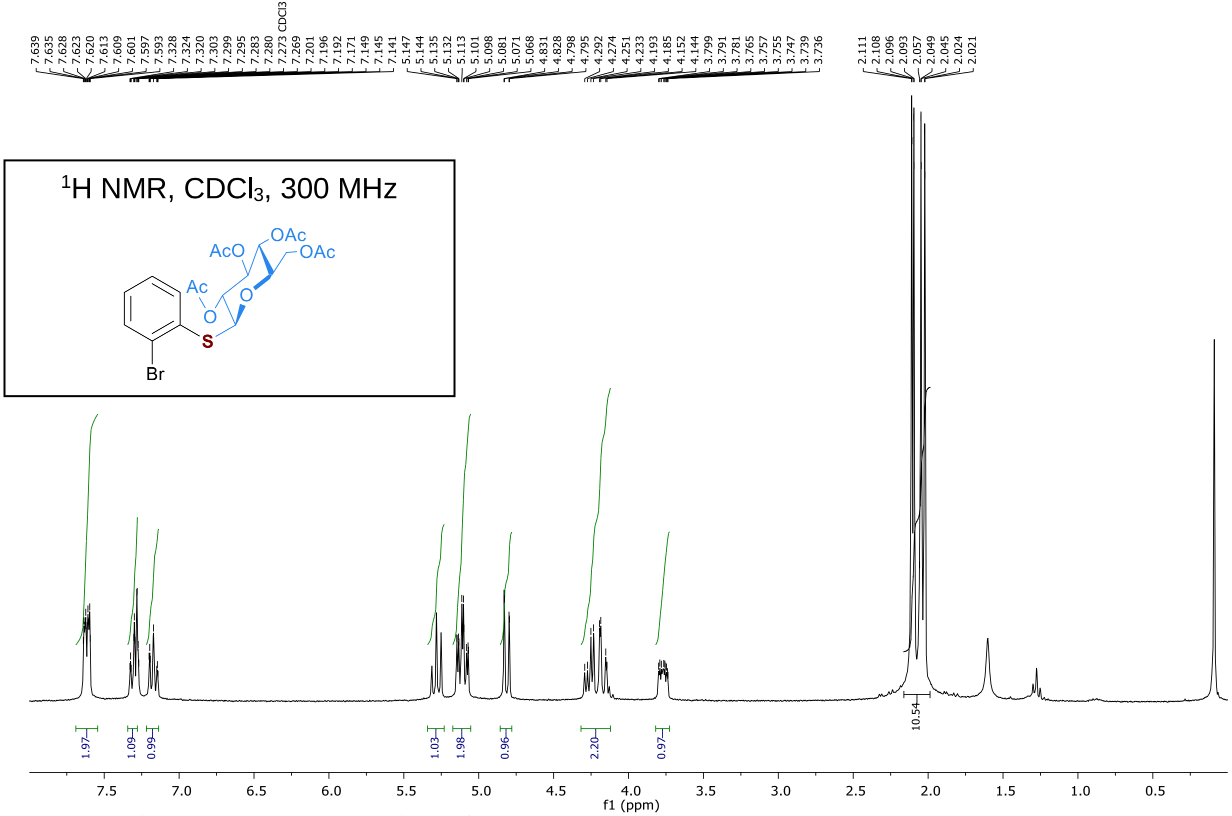
NMR spectra.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¹H NMR, CDCl₃, 300 MHz
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OAc
OAc
Ac
O
O
S
Br
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1.09
0.99
1.03
1.98
0.96
2.20
0.97
10.54
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7.0
6.5
6.0
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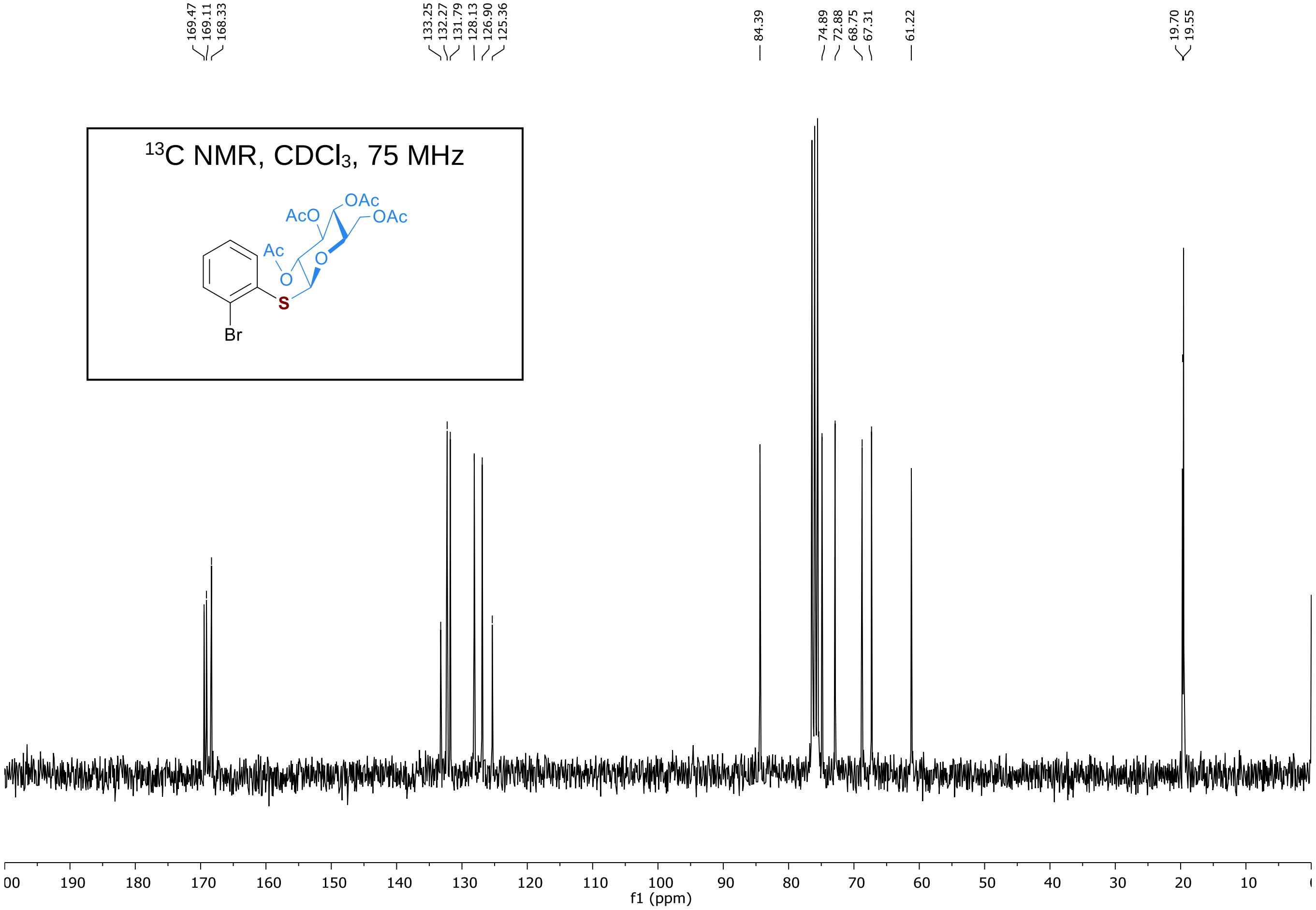
0.5
f1 (ppm)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67.31
61.22
19.70
19.55
¹³C NMR, CDCl₃, 75 MHz
AcO
OAc
OAc
Ac
O
O
S
Br
00
190
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100
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20
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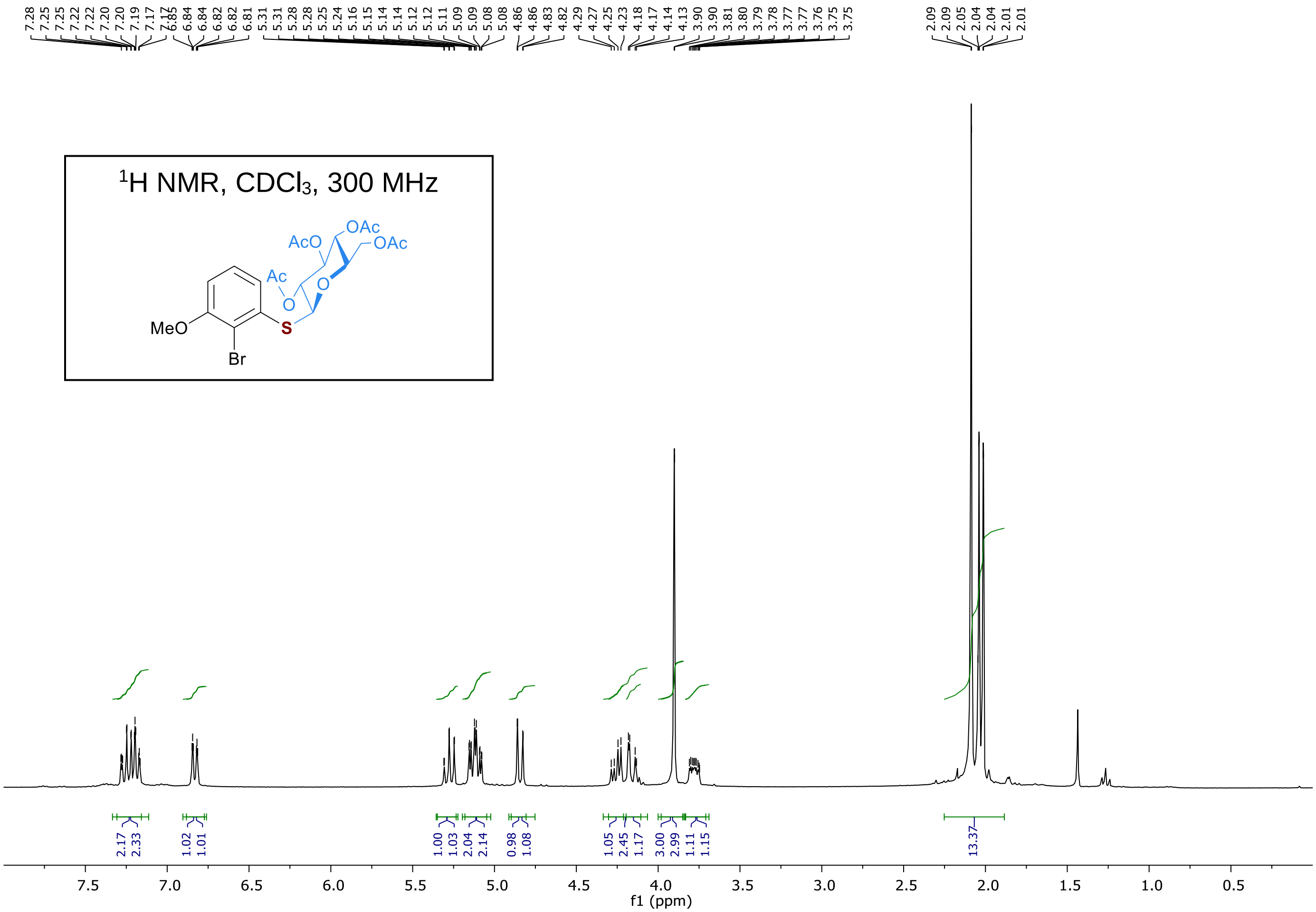
f1 (ppm)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2.09
2.05
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2.04
2.01
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OAc
OAc
Ac
O
O
S
MeO
Br
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1.00
1.03
2.04
2.14
0.98
1.08
1.05
2.45
1.17
3.00
2.99
1.11
1.15
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2.5
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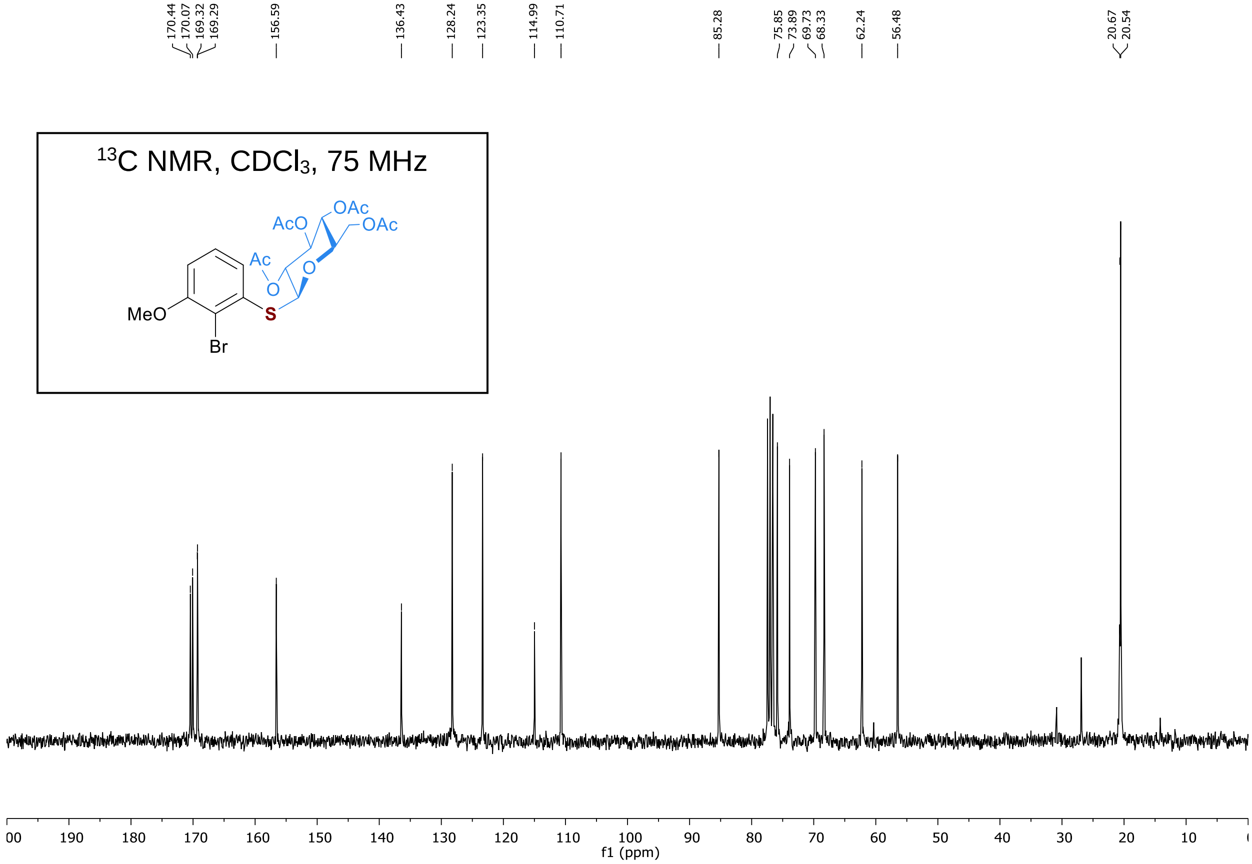
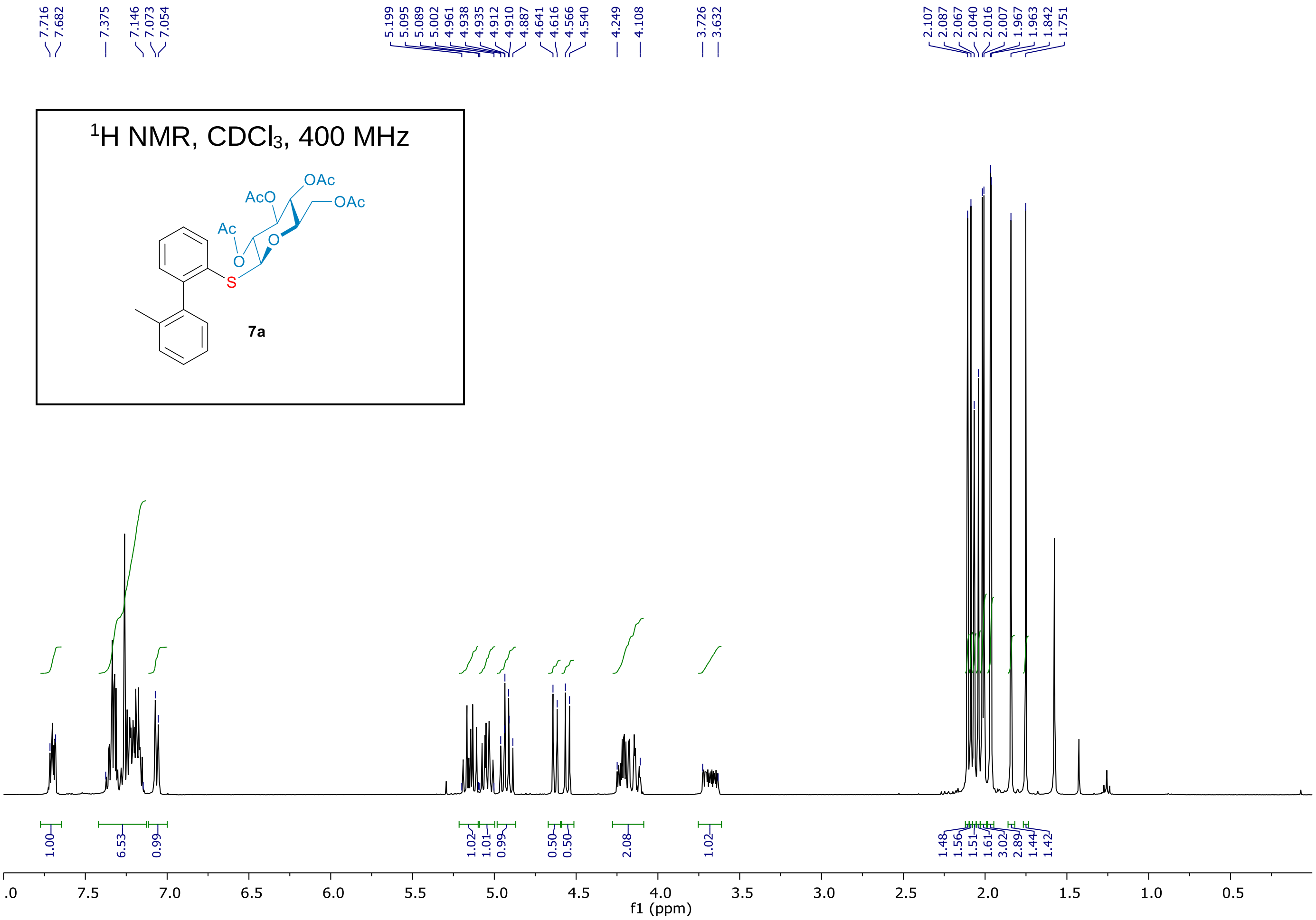
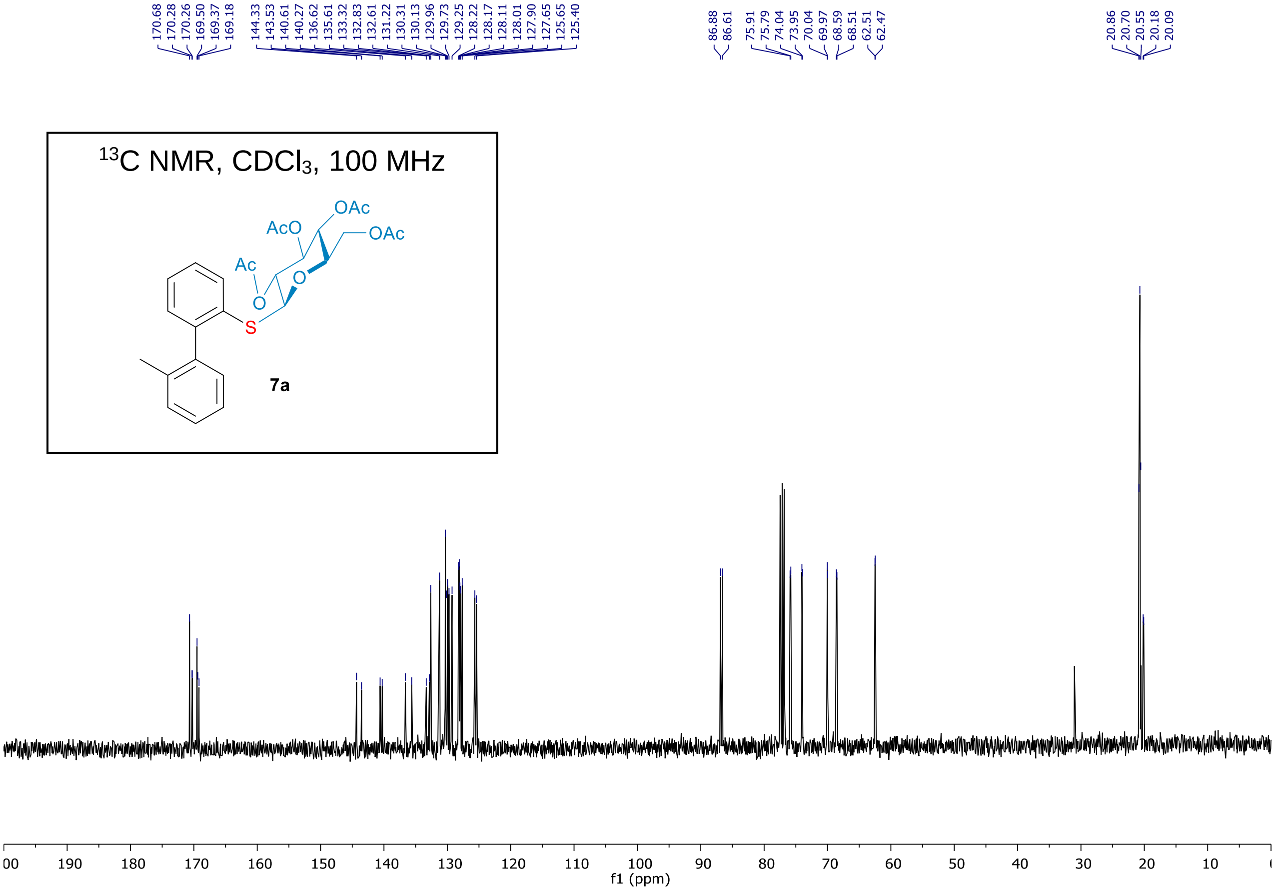
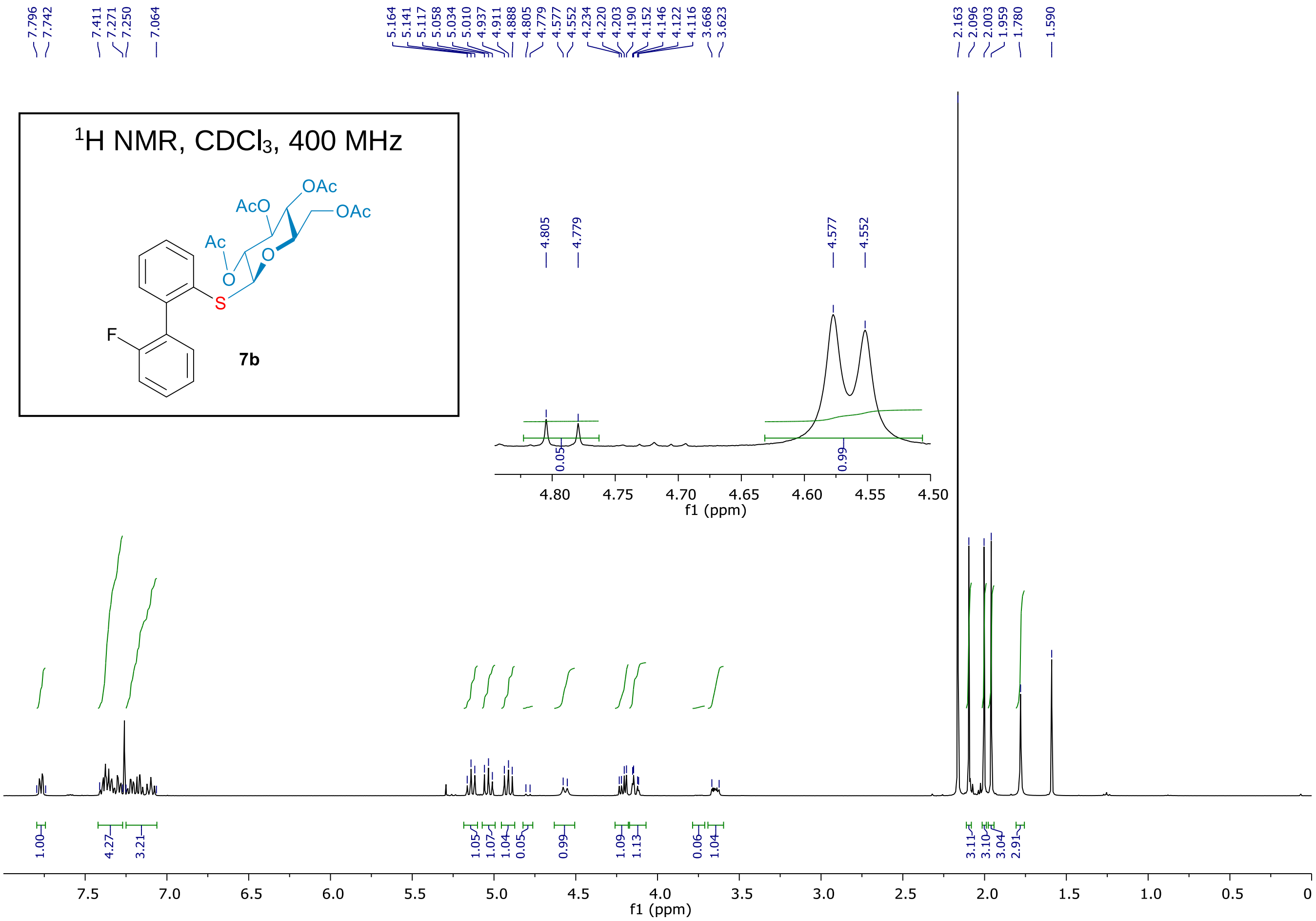
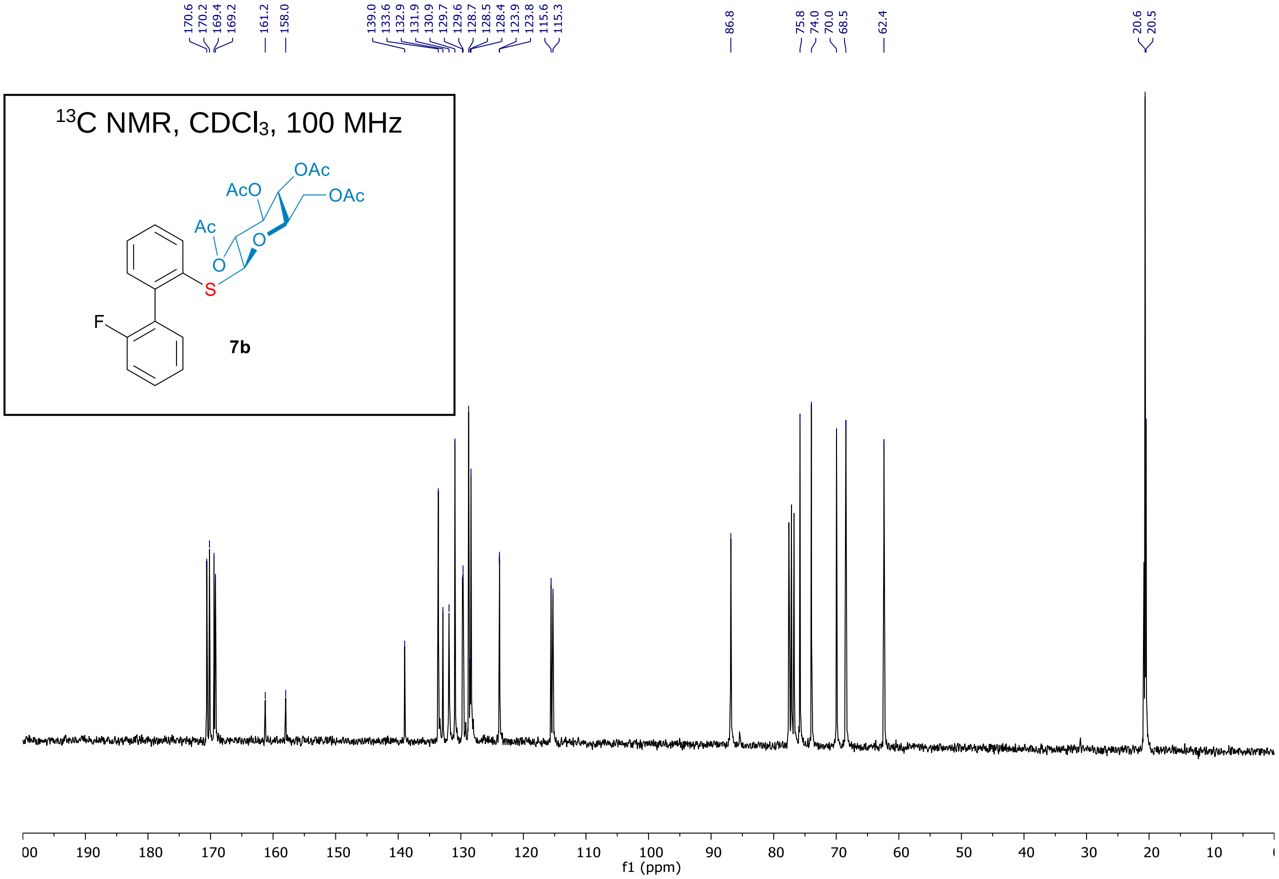
1.5
1.0
0.5
f1 (ppm)

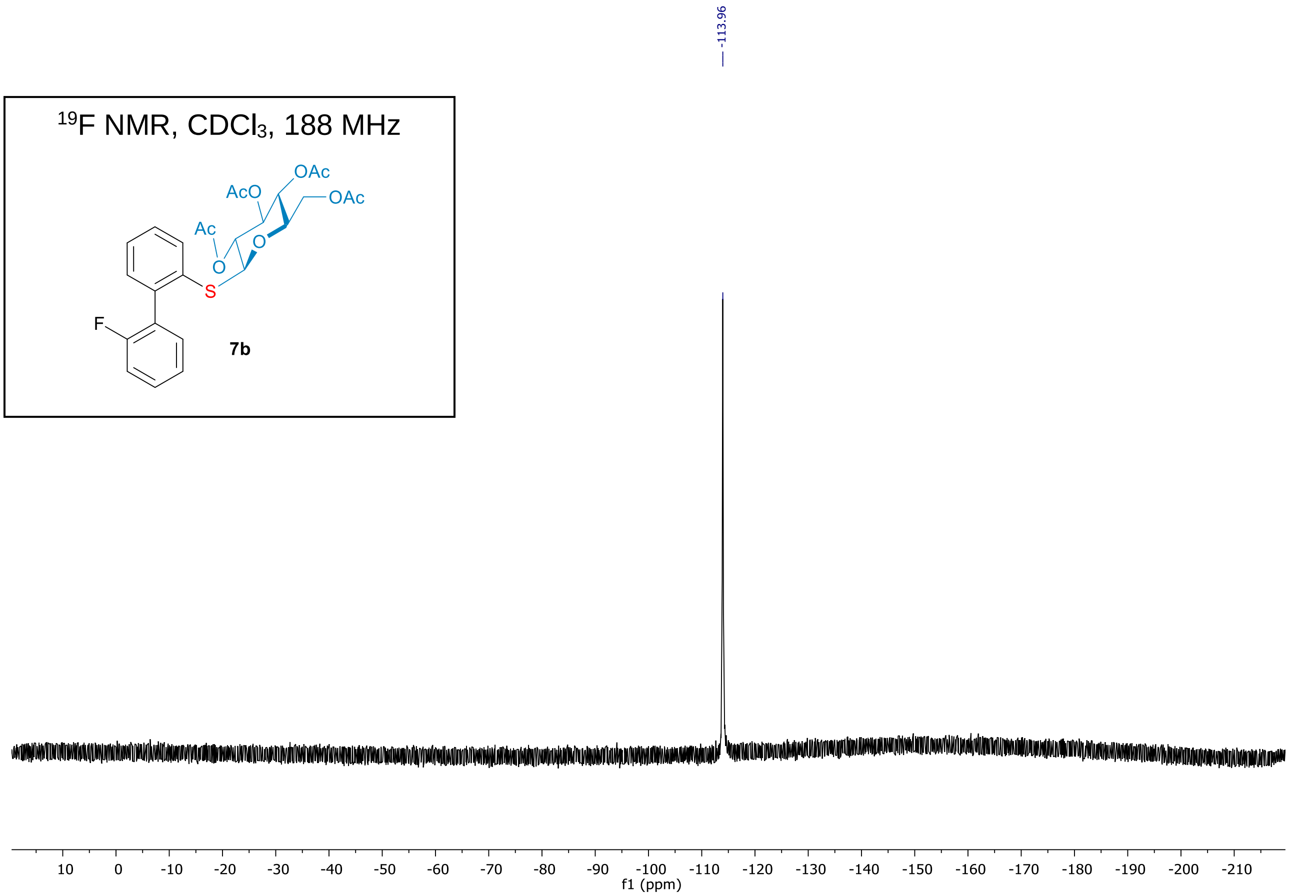

170.44
170.07
169.32
169.29
156.59
136.43
128.24
123.35
114.99
110.71
85.28
75.85
73.89
69.73
68.33
62.24
56.48
20.67
20.54
^{13}C NMR, CDCl$_3$, 75 MHz
AcO
OAc
OAc
Ac
O
O
S
MeO
Br
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

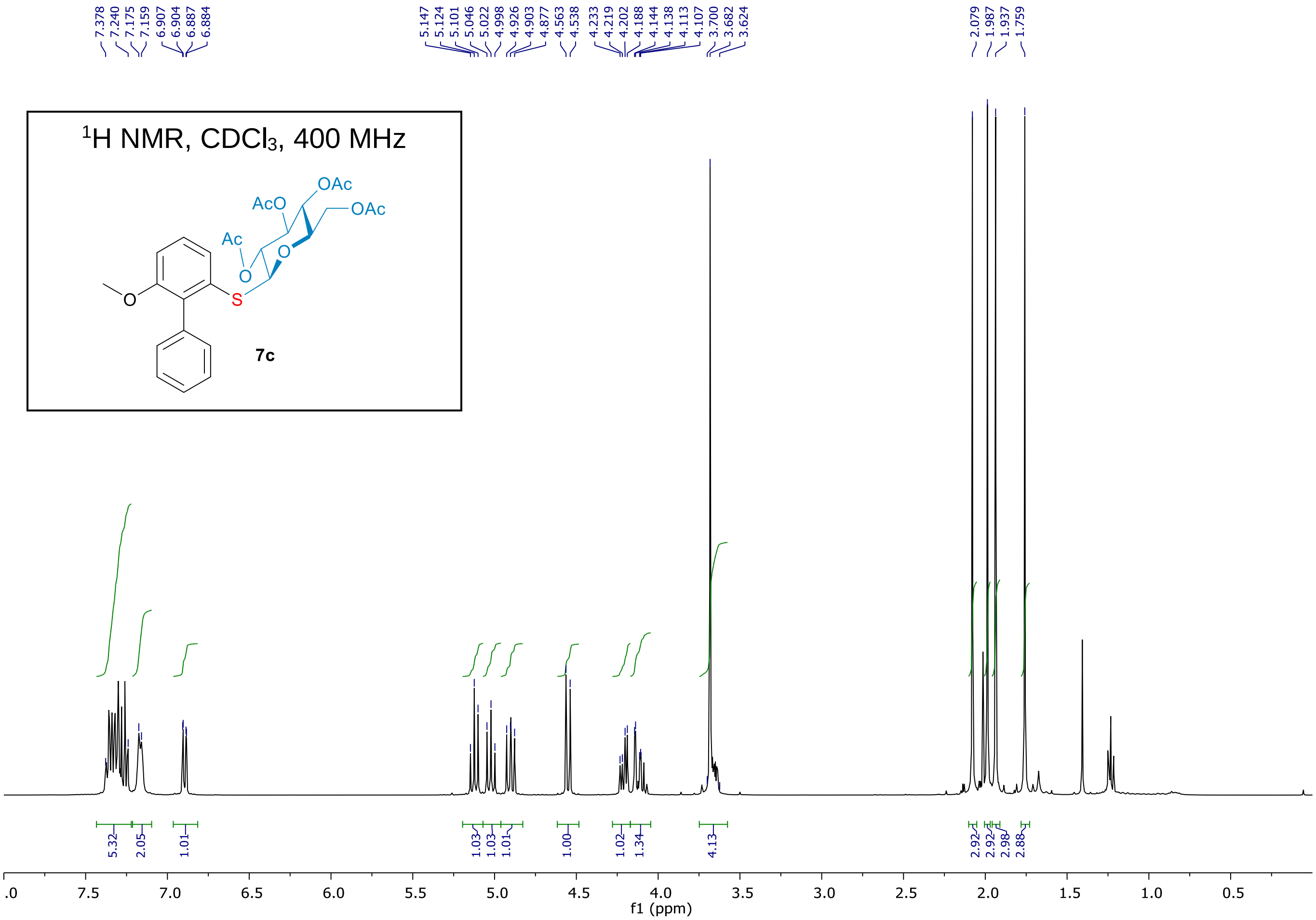

7.716
7.682
7.375
7.146
7.073
7.054
5.199
5.095
5.089
5.002
4.961
4.938
4.935
4.912
4.910
4.887
4.641
4.616
4.566
4.540
4.249
4.108
3.726
3.632
2.107
2.087
2.067
2.040
2.016
2.007
1.967
1.963
1.842
1.751
1H NMR, CDCl3, 400 MHz
AcO
OAc
OAc
Ac
O
O
S
7a
1.00
6.53
0.99
1.02
1.01
0.99
0.50
0.50
2.08
1.02
1.48
1.56
1.51
1.61
3.02
2.89
1.44
1.42
f1 (ppm)

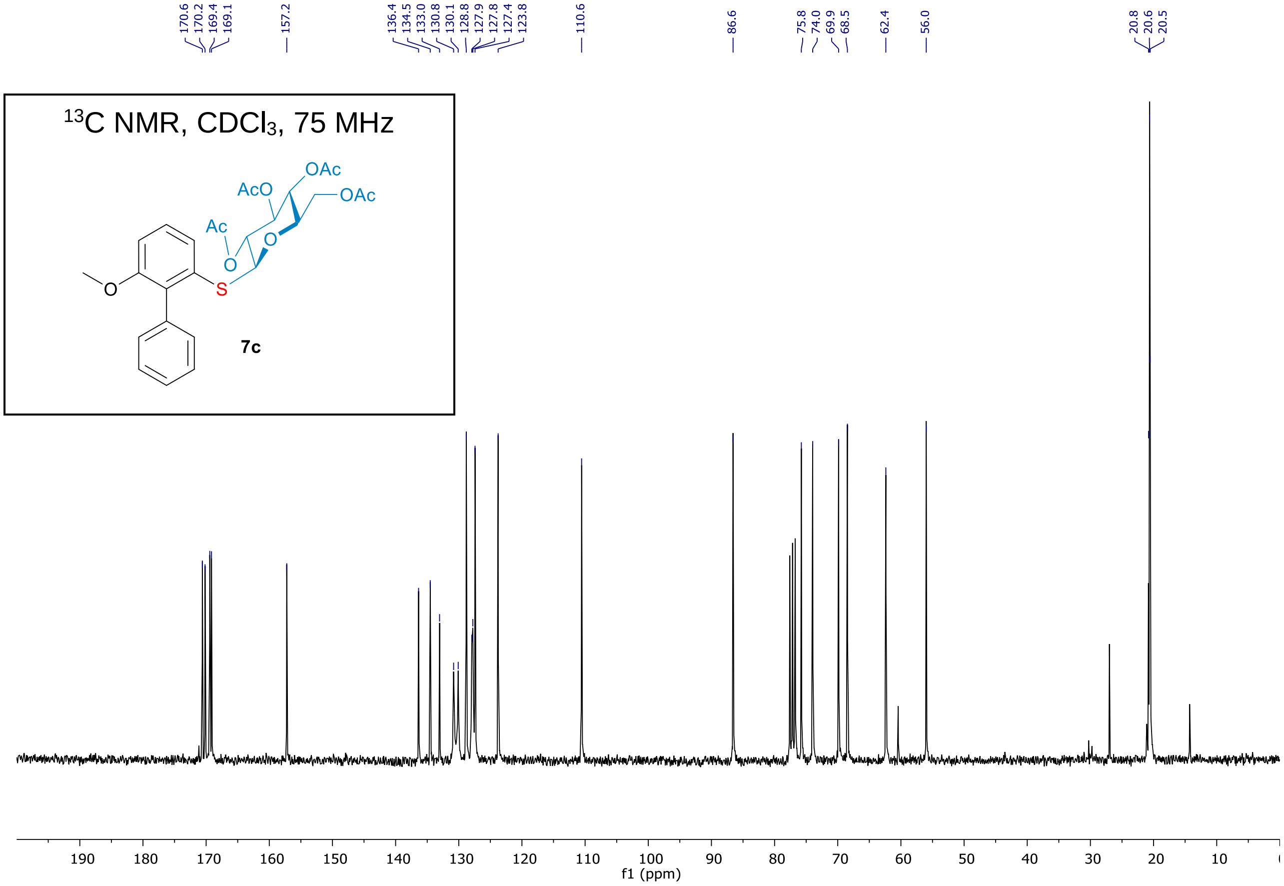

170.68
170.28
170.26
169.50
169.37
169.18
144.33
143.53
140.61
140.27
136.62
135.61
133.32
132.83
132.61
131.22
130.31
130.13
129.96
129.73
129.25
128.22
128.17
128.11
128.01
127.90
127.65
125.65
125.40
86.88
86.61
75.91
75.79
74.04
73.95
70.04
69.97
68.59
68.51
62.51
62.47
20.86
20.70
20.55
20.18
20.09
13C NMR, CDCl3, 100 MHz
AcO
OAc
OAc
Ac
O
O
S
7a
f1 (ppm)

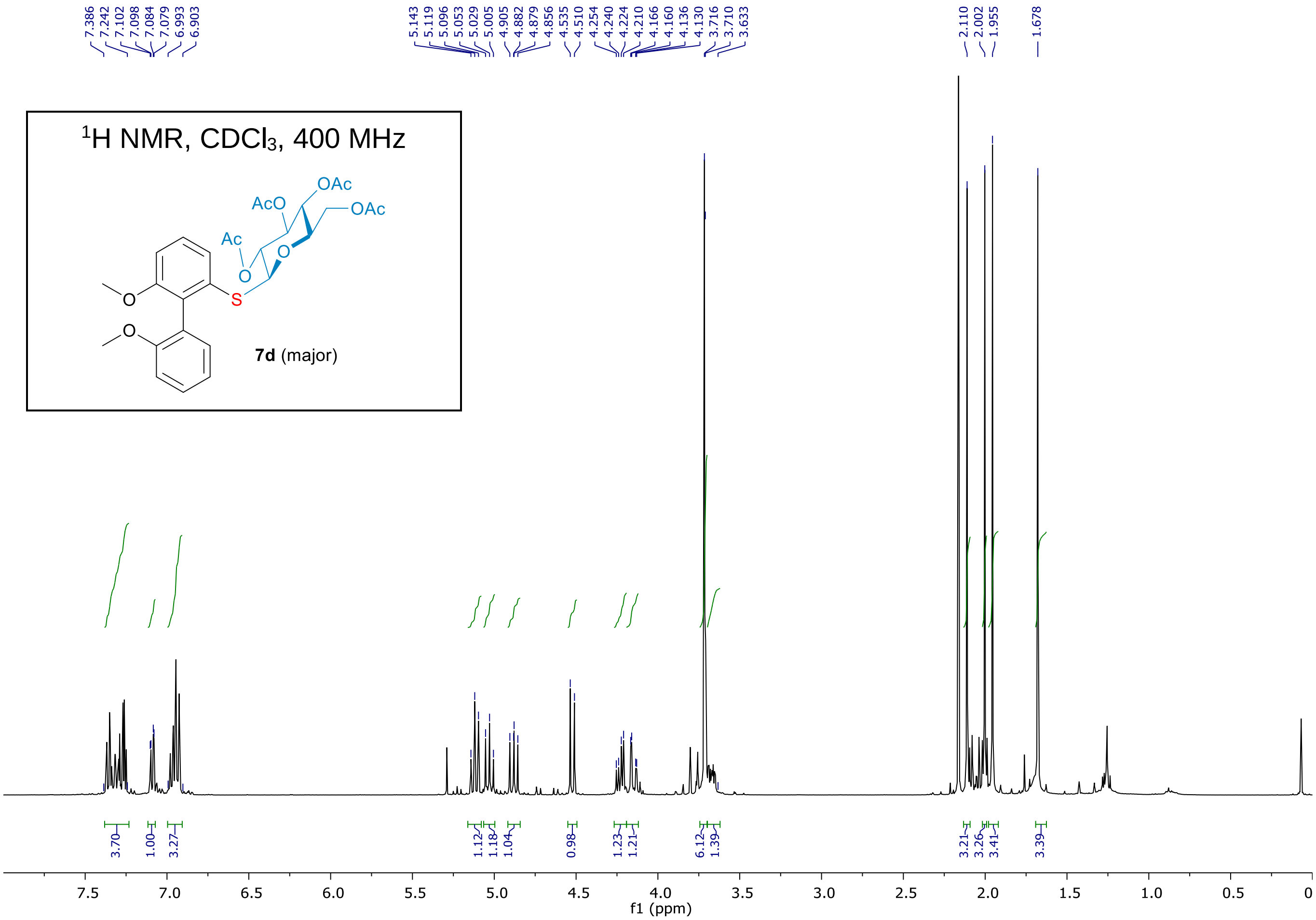

7.796
7.742
7.411
7.271
7.250
7.064
5.164
5.141
5.117
5.058
5.034
5.010
4.937
4.911
4.888
4.805
4.779
4.577
4.552
4.234
4.220
4.203
4.190
4.152
4.146
4.122
4.116
3.668
3.623
2.163
2.096
2.003
1.959
1.780
1.590
^{1}H NMR, $CDCl_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
F
7b
4.805
4.779
4.577
4.552
0.05
0.99
4.80
4.75
4.70
4.65
4.60
4.55
4.50
f1 (ppm)
1.00
4.27
3.21
1.05
1.07
1.04
0.05
0.99
1.09
1.13
0.06
1.04
3.11
3.10
3.04
2.91
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
f1 (ppm)

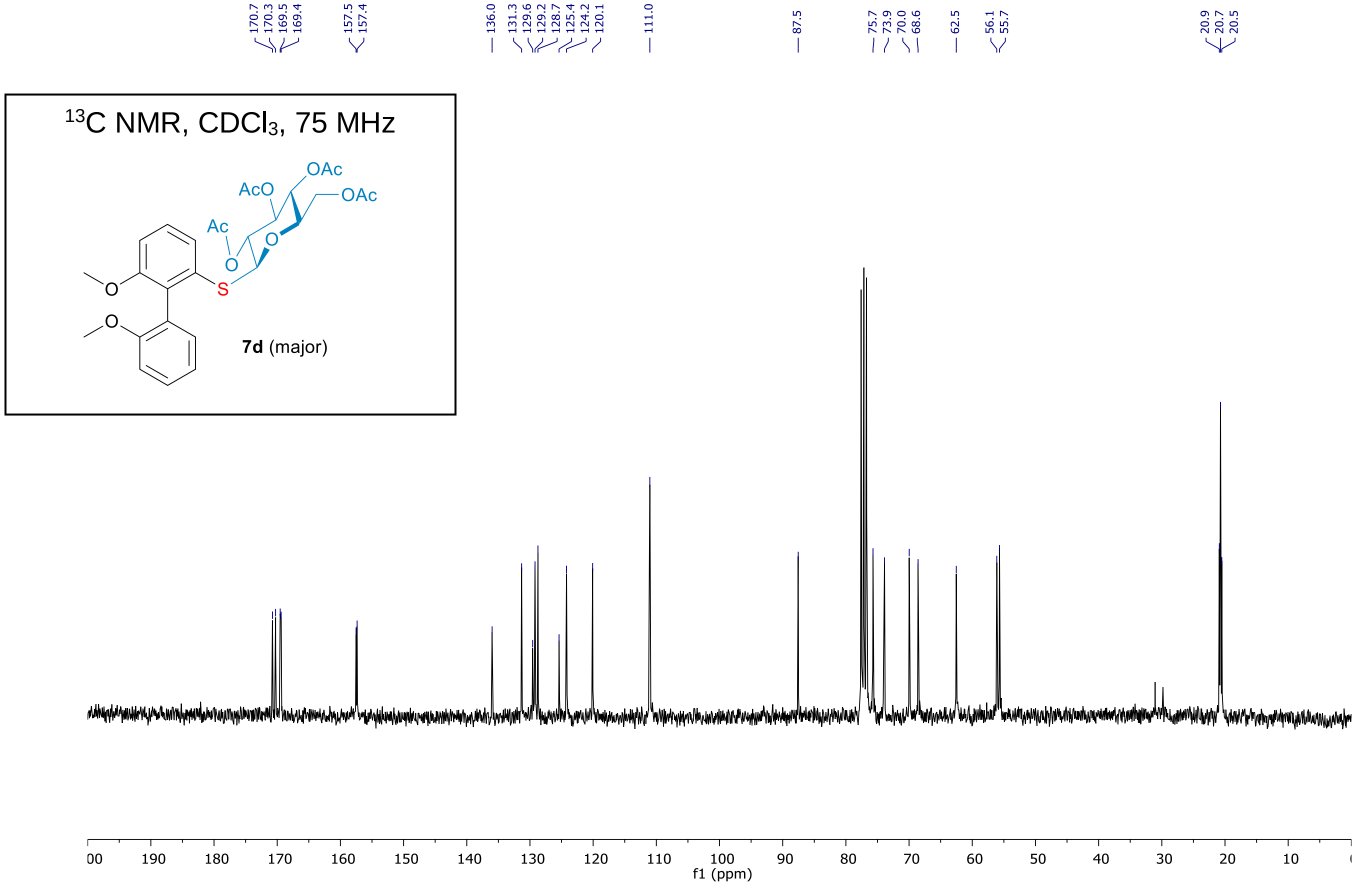

170.6
170.2
169.4
169.2
161.2
158.0
139.0
133.6
132.9
131.9
130.9
129.7
129.6
128.7
128.5
128.4
123.9
123.8
115.6
115.3
86.8
75.8
74.0
70.0
68.5
62.4
20.6
20.5
^{13}C NMR, $CDCl_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
F
7b
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

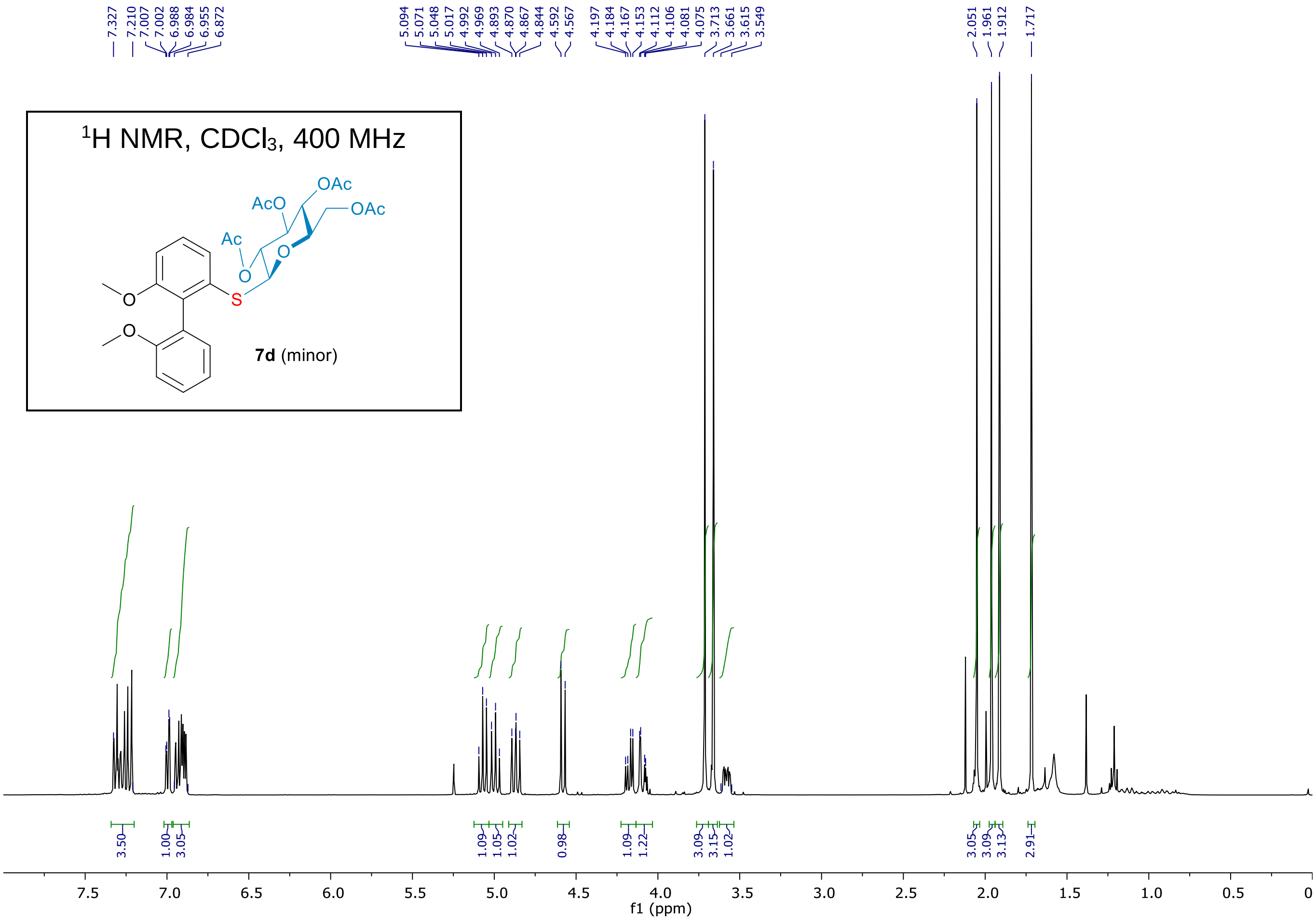

-113.96
^{19}F NMR, CDCl$_3$, 188 MHz
OAc
AcO
OAc
Ac
O
O
S
F
7b
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

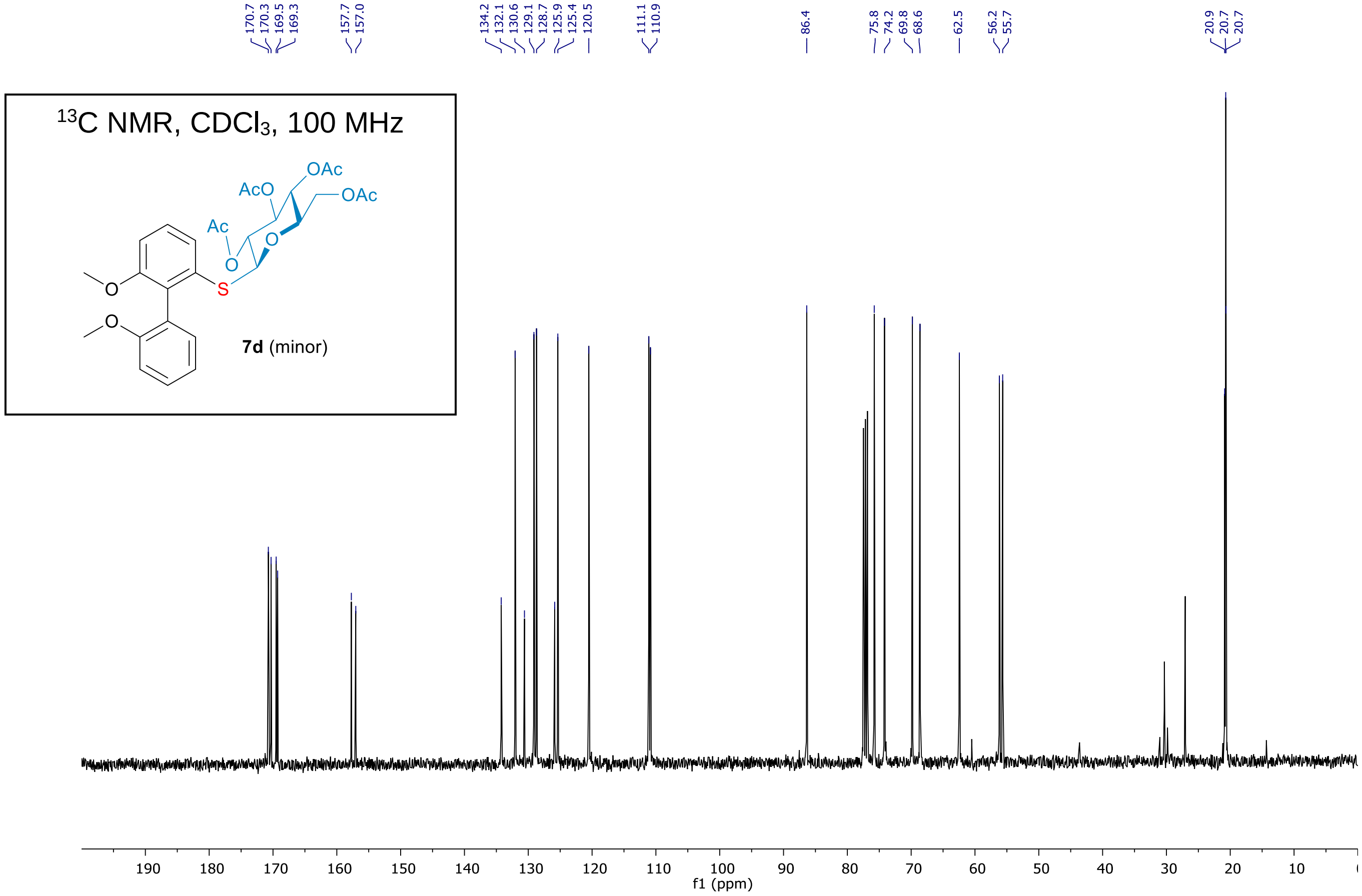

7.378
7.240
7.175
7.159
6.907
6.904
6.887
6.884
5.147
5.124
5.101
5.046
5.022
4.998
4.926
4.903
4.877
4.563
4.538
4.233
4.219
4.202
4.188
4.144
4.138
4.113
4.107
3.700
3.682
3.624
2.079
1.987
1.937
1.759
1H NMR, CDCl3, 400 MHz
OAc
AcO
OAc
Ac
O
O
O
S
7c
5.32
2.05
1.01
1.03
1.03
1.01
1.00
1.02
1.34
4.13
2.92
2.92
2.98
2.88
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

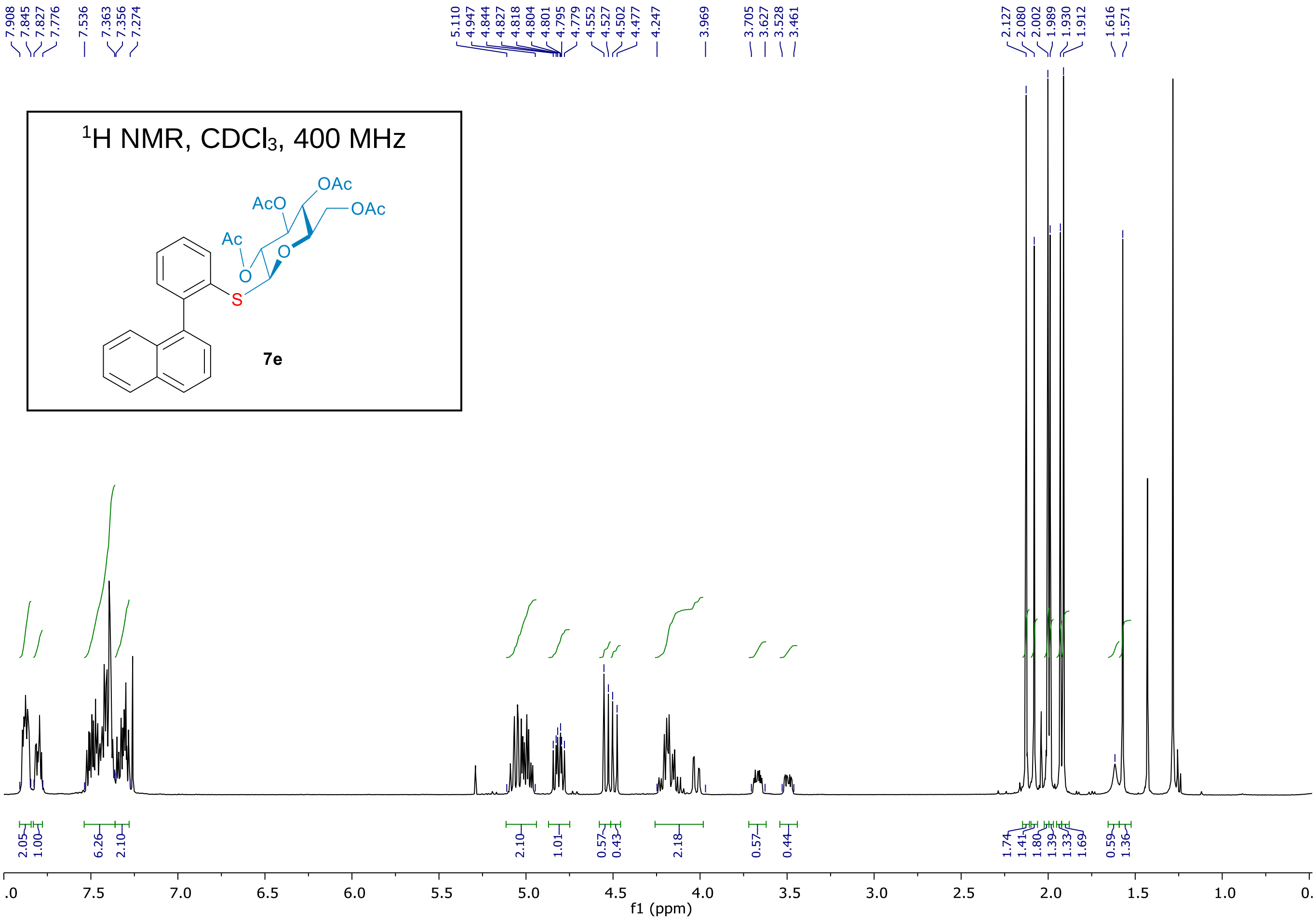

170.6
170.2
169.4
169.1
157.2
136.4
134.5
133.0
130.8
130.1
128.8
127.9
127.8
127.4
123.8
110.6
86.6
75.8
74.0
69.9
68.5
62.4
56.0
20.8
20.6
20.5
13C NMR, CDCl3, 75 MHz
OAc
AcO
OAc
Ac
O
O
O
S
7c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

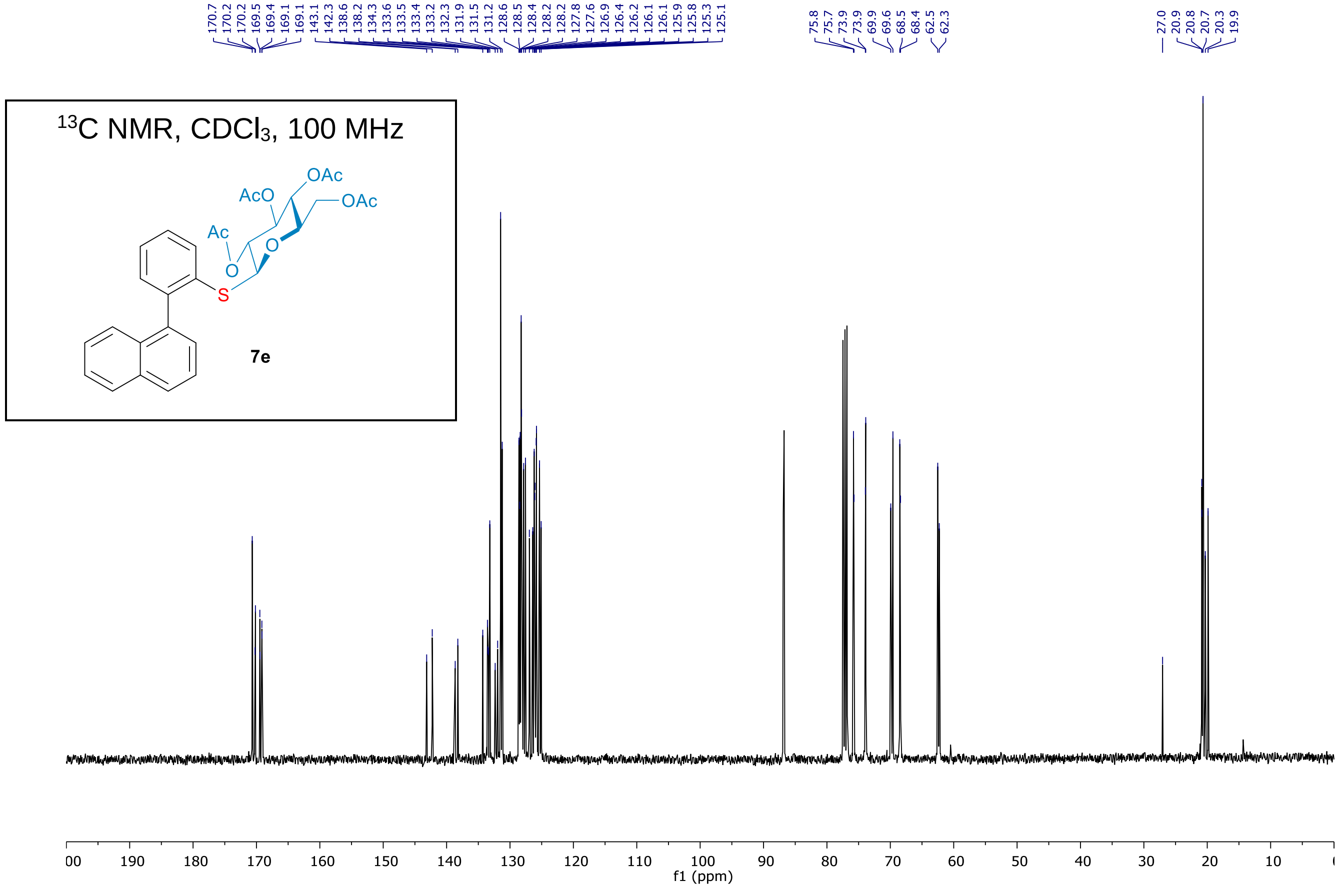

7.386
7.242
7.102
7.098
7.084
7.079
6.993
6.903
5.143
5.119
5.096
5.053
5.029
5.005
4.905
4.882
4.879
4.856
4.535
4.510
4.254
4.240
4.224
4.210
4.166
4.160
4.136
4.130
3.716
3.710
3.633
2.110
2.002
1.955
1.678
1H NMR, CDCl3, 400 MHz
OAc
AcO
OAc
Ac
O
O
O
S
O
7d (major)
3.70
1.00
3.27
1.12
1.18
1.04
0.98
1.23
1.21
6.12
1.39
3.21
3.26
3.41
3.39
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
f1 (ppm)

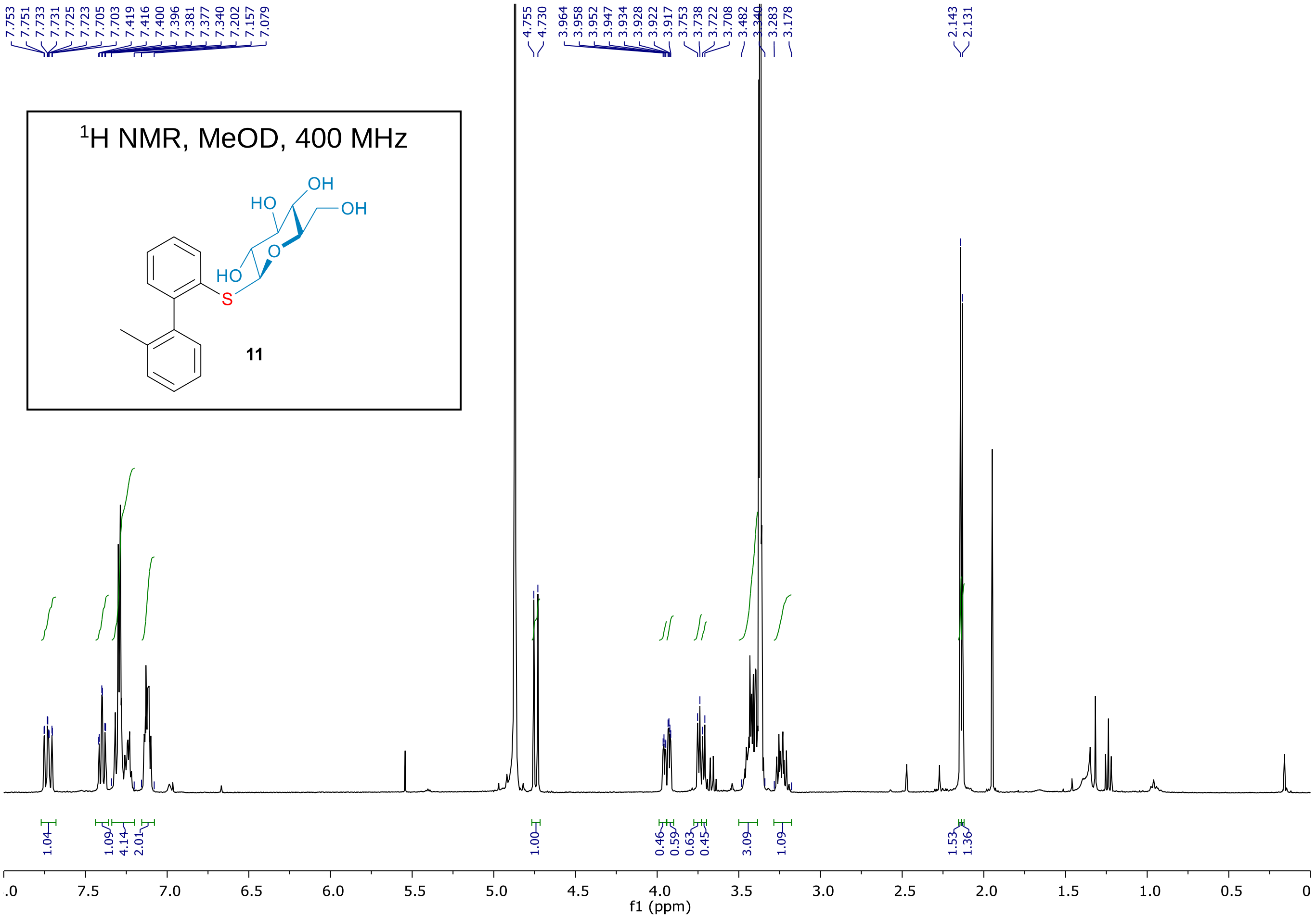

170.7
170.3
169.5
169.4
157.5
157.4
136.0
131.3
129.6
129.2
128.7
125.4
124.2
120.1
111.0
87.5
75.7
73.9
70.0
68.6
62.5
56.1
55.7
20.9
20.7
20.5
13C NMR, CDCl3, 75 MHz
OAc
AcO
OAc
Ac
O
O
O
S
O
7d (major)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

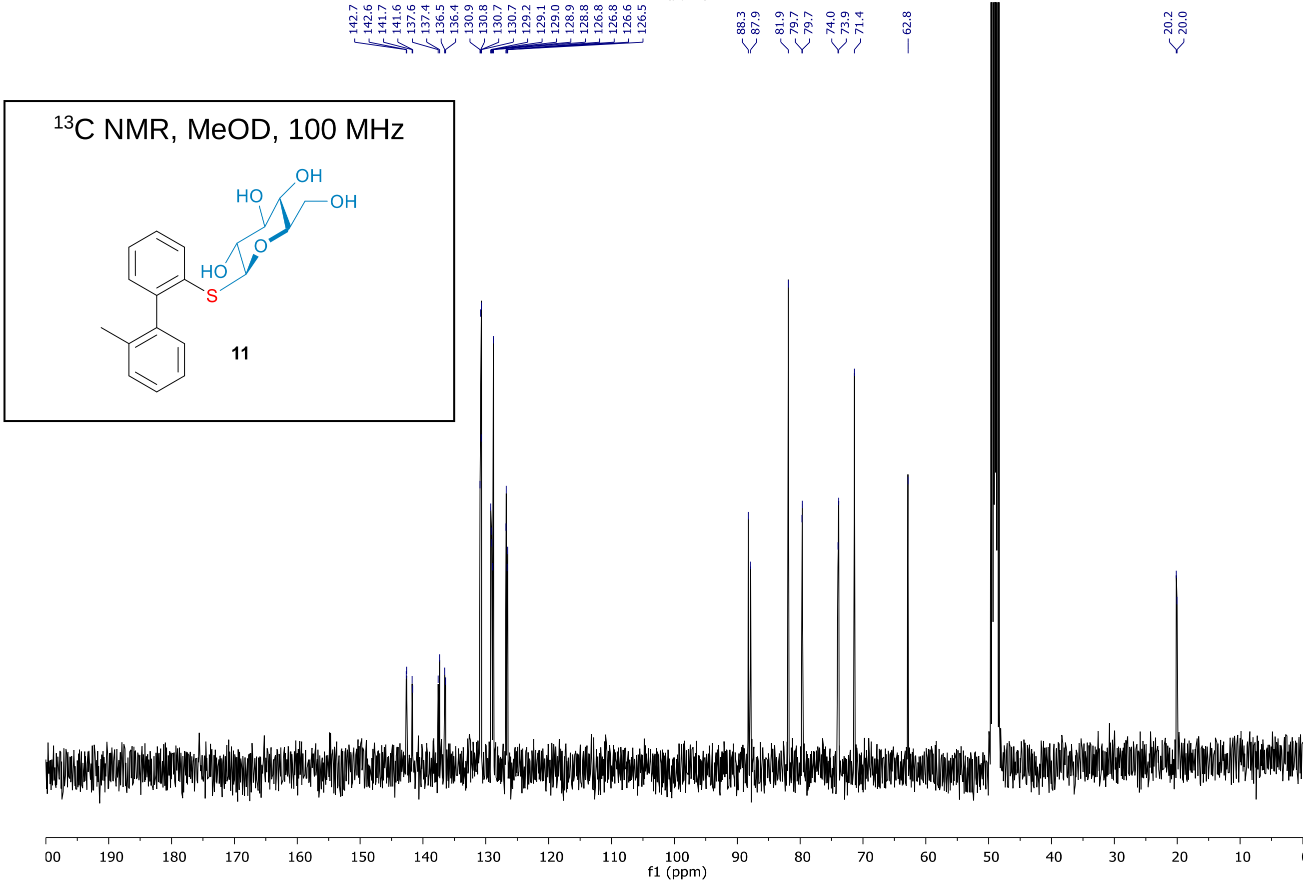

7.327
7.210
7.007
7.002
6.988
6.984
6.955
6.872
5.094
5.071
5.048
5.017
4.992
4.969
4.893
4.870
4.867
4.844
4.592
4.567
4.197
4.184
4.167
4.153
4.112
4.106
4.081
4.075
3.713
3.661
3.615
3.549
2.051
1.961
1.912
1.717
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
O
S
O
7d (minor)
3.50
1.00
3.05
1.09
1.05
1.02
0.98
1.09
1.22
3.09
3.15
1.02
3.05
3.09
3.13
2.91
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
f1 (ppm)

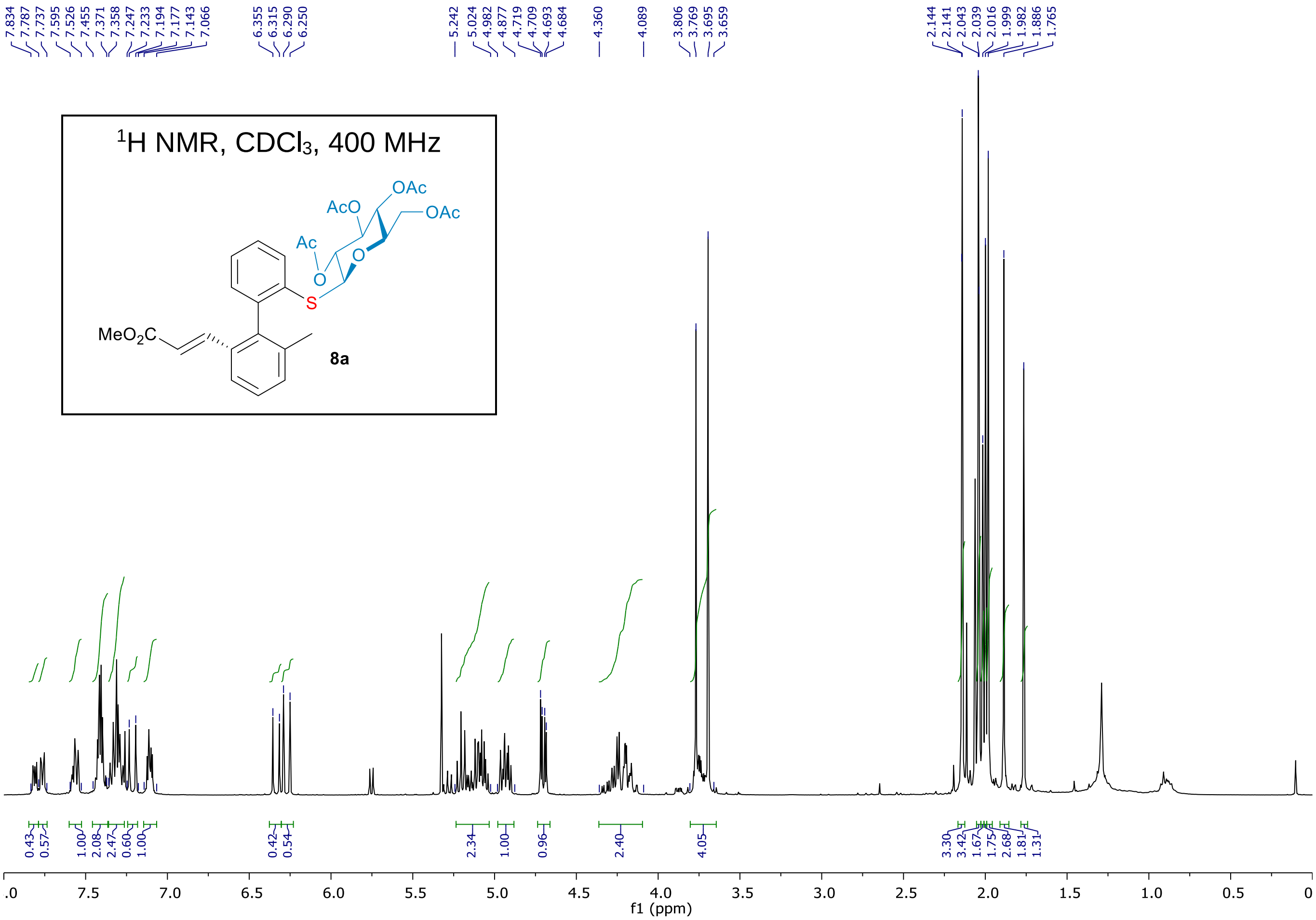

170.7
170.3
169.5
169.3
157.7
157.0
134.2
132.1
130.6
129.1
128.7
125.9
125.4
120.5
111.1
110.9
86.4
75.8
74.2
69.8
68.6
62.5
56.2
55.7
20.9
20.7
20.7
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
O
S
O
7d (minor)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

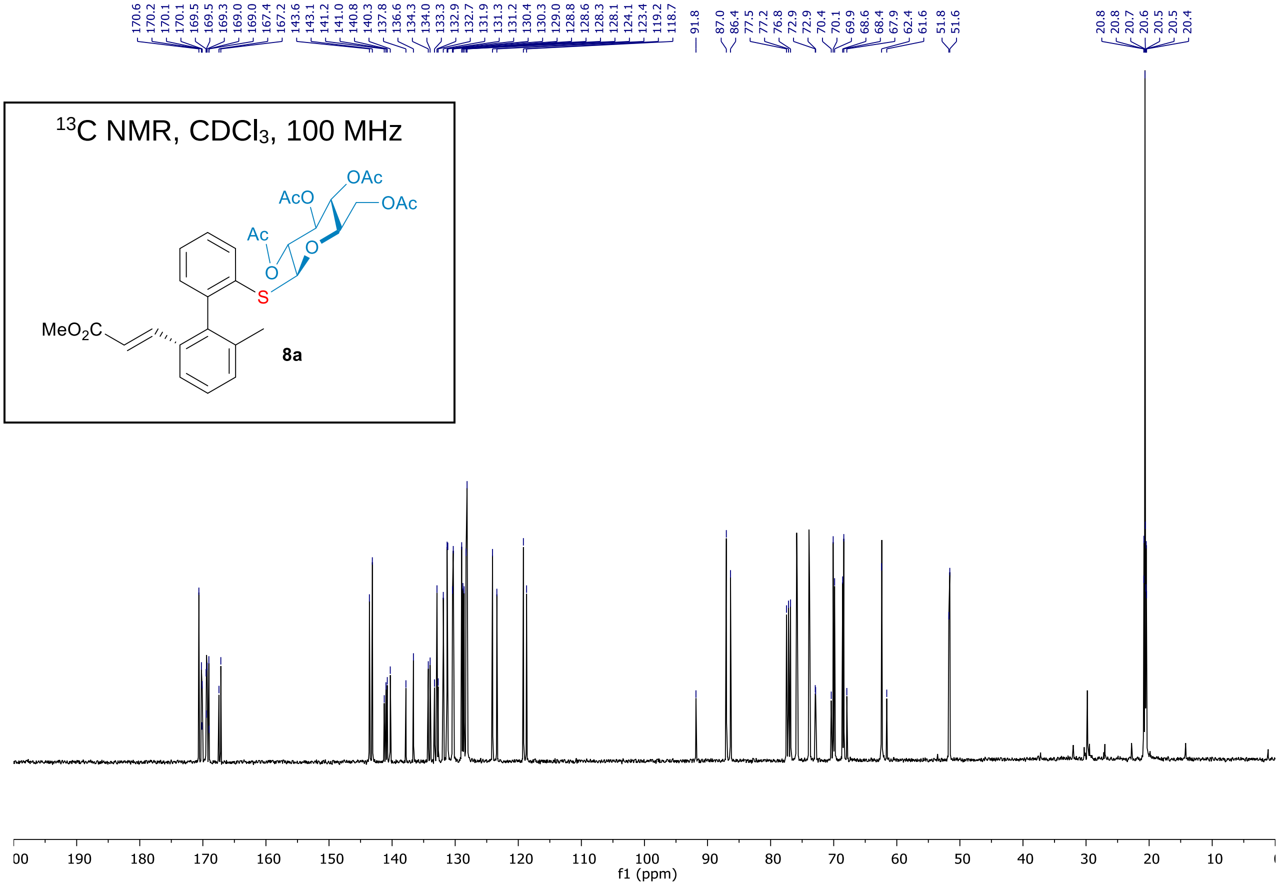

1H NMR, CDCl3, 400 MHz
7e
AcO
OAc
OAc
Ac
O
O
S
7.908
7.845
7.827
7.776
7.536
7.363
7.356
7.274
5.110
4.947
4.844
4.827
4.818
4.804
4.801
4.795
4.779
4.552
4.527
4.502
4.477
4.247
3.969
3.705
3.627
3.528
3.461
2.127
2.080
2.002
1.989
1.930
1.912
1.616
1.571
2.05
1.00
6.26
2.10
2.10
1.01
0.57
0.43
2.18
0.57
0.44
1.74
1.41
1.80
1.39
1.33
1.69
0.59
1.36
f1 (ppm)

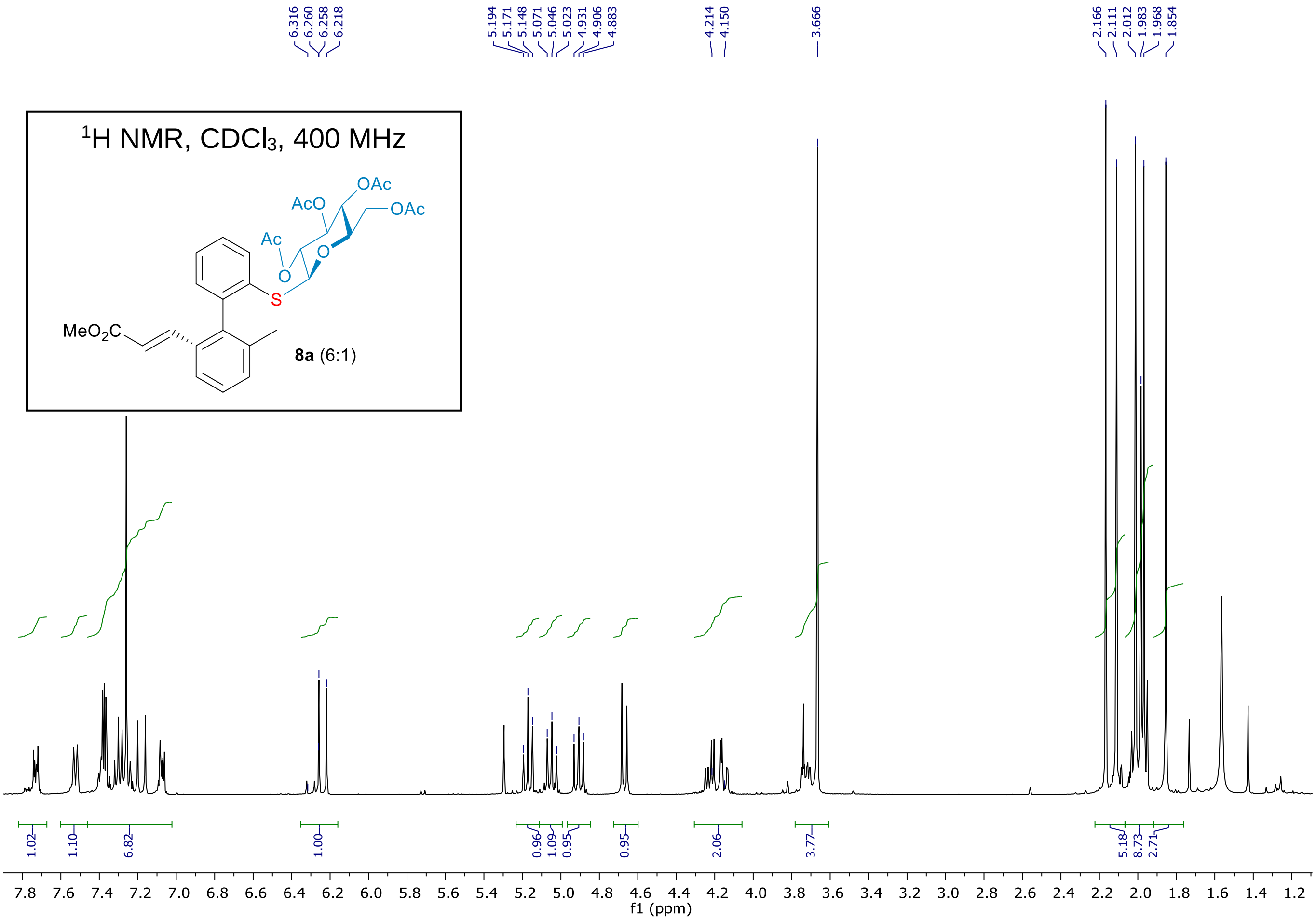

13C NMR, CDCl3, 100 MHz
7e
AcO
OAc
OAc
Ac
O
O
S
170.7
170.2
170.2
169.5
169.4
169.1
169.1
143.1
142.3
138.6
138.2
134.3
133.6
133.5
133.4
133.2
132.3
131.9
131.5
131.2
128.6
128.5
128.4
128.2
128.2
127.8
127.6
126.9
126.4
126.2
126.1
126.1
125.9
125.8
125.3
125.1
75.8
75.7
73.9
73.9
69.9
69.6
68.5
68.4
62.5
62.3
27.0
20.9
20.8
20.7
20.3
19.9
f1 (ppm)

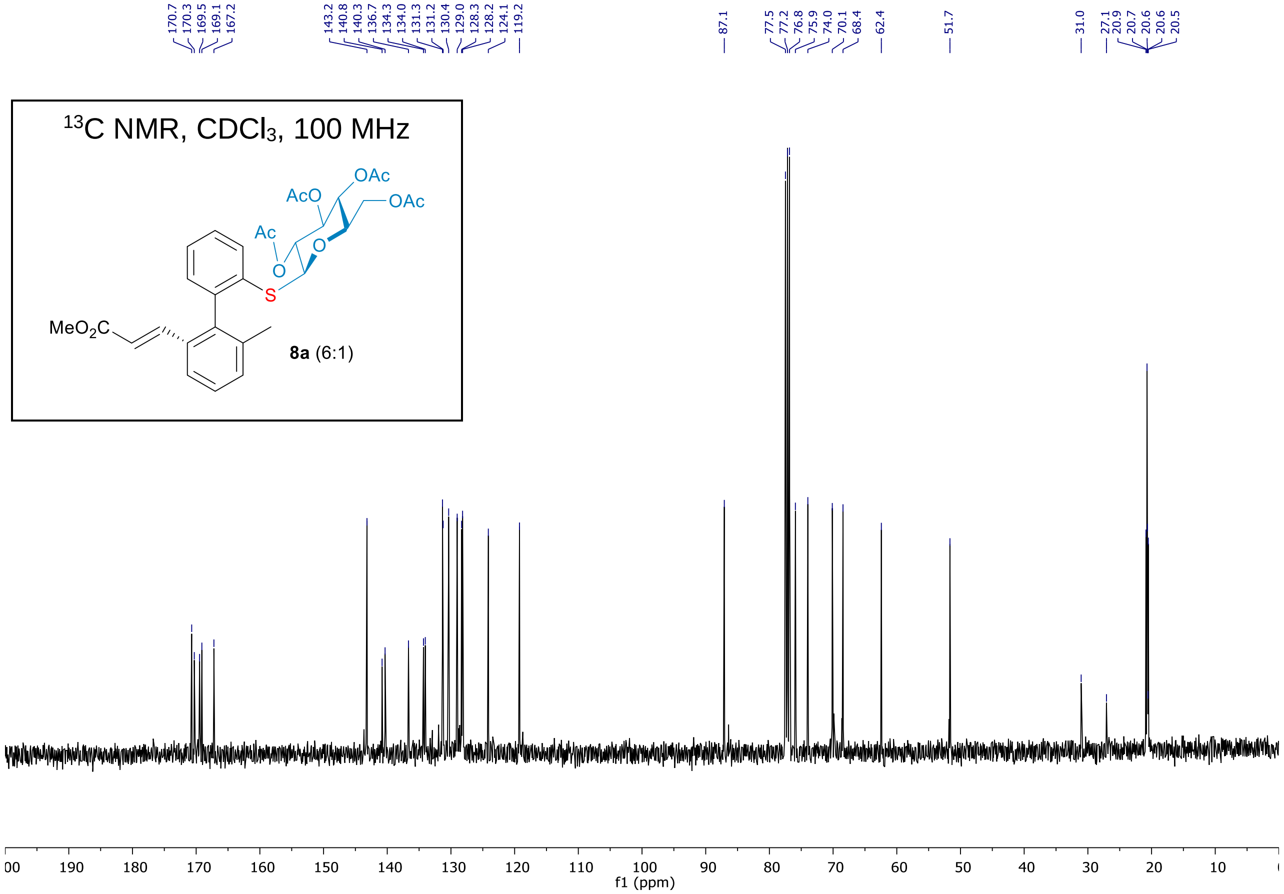

7.753
7.751
7.733
7.731
7.725
7.723
7.705
7.703
7.419
7.416
7.400
7.396
7.381
7.377
7.340
7.202
7.157
7.079
4.755
4.730
3.964
3.958
3.952
3.947
3.934
3.928
3.922
3.917
3.753
3.738
3.722
3.708
3.482
3.340
3.283
3.178
2.143
2.131
^{1}H NMR, MeOD, 400 MHz
HO
OH
OH
O
HO
S
11
1.04
1.09
4.14
2.01
1.00
0.46
0.59
0.63
0.45
3.09
1.09
1.53
1.36
.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
f1 (ppm)


142.7
142.6
141.7
141.6
137.6
137.4
136.5
136.4
130.9
130.8
130.7
130.7
129.2
129.1
129.0
128.9
128.8
126.8
126.8
126.6
126.5
88.3
87.9
81.9
79.7
79.7
74.0
73.9
71.4
62.8
20.2
20.0
^{13}C NMR, MeOD, 100 MHz
HO
OH
OH
O
HO
S
11
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

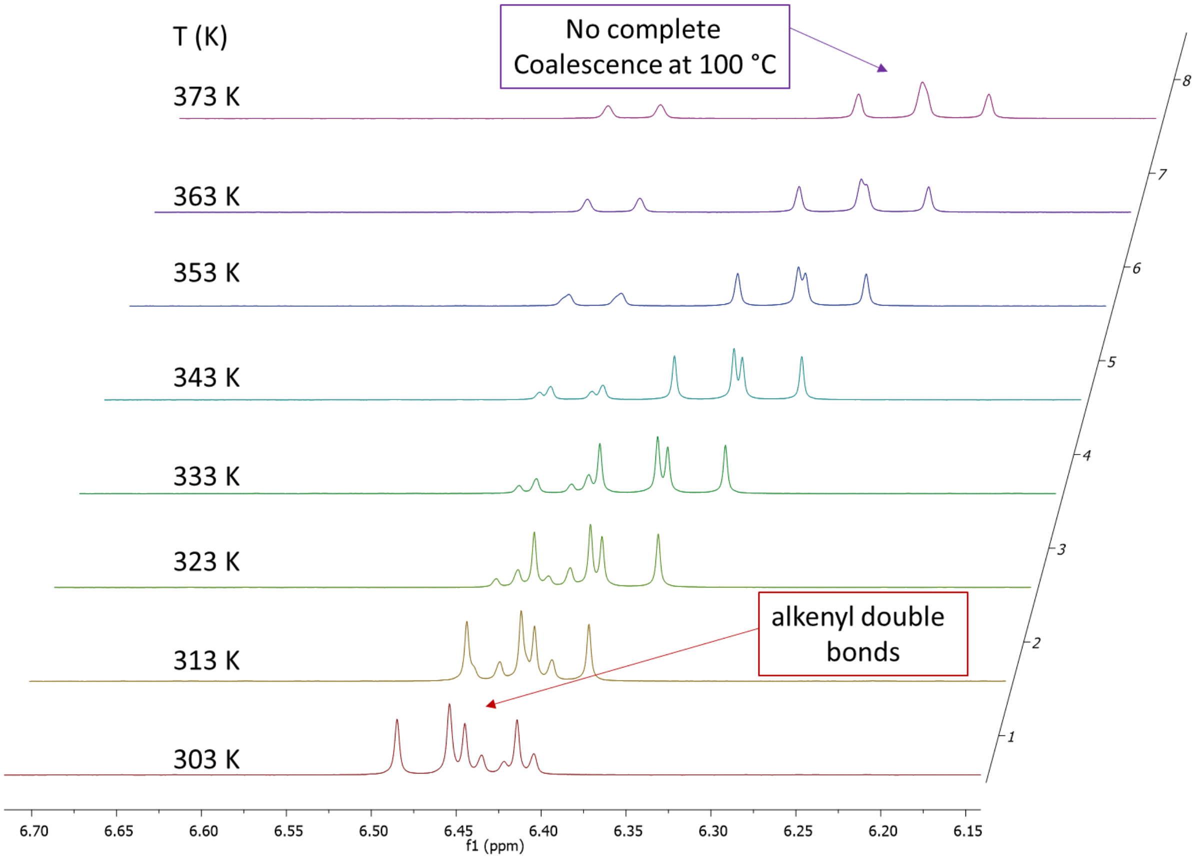

7.834
7.787
7.737
7.595
7.526
7.455
7.371
7.358
7.247
7.233
7.194
7.177
7.143
7.066
6.355
6.315
6.290
6.250
5.242
5.024
4.982
4.877
4.719
4.709
4.693
4.684
4.360
4.089
3.806
3.769
3.695
3.659
2.144
2.141
2.043
2.039
2.016
1.999
1.982
1.886
1.765
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
MeO$_2$C
8a
0.43
0.57
1.00
2.08
2.47
0.60
1.00
0.42
0.54
2.34
1.00
0.96
2.40
4.05
3.30
3.42
1.67
1.75
2.68
1.81
1.31
.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
f1 (ppm)


170.6
170.2
170.1
170.1
169.5
169.5
169.3
169.0
169.0
167.4
167.2
143.6
143.1
141.2
141.0
140.8
140.3
137.8
136.6
134.3
134.0
133.3
132.9
132.7
131.9
131.3
131.2
130.4
130.3
129.0
128.8
128.6
128.3
128.1
124.1
123.4
119.2
118.7
91.8
87.0
86.4
77.5
77.2
76.8
72.9
72.9
70.4
70.1
69.9
68.6
68.4
67.9
62.4
61.6
51.8
51.6
20.8
20.8
20.7
20.6
20.5
20.5
20.4
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
MeO$_2$C
8a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


6.316
6.260
6.258
6.218
5.194
5.171
5.148
5.071
5.046
5.023
4.931
4.906
4.883
4.214
4.150
3.666
2.166
2.111
2.012
1.983
1.968
1.854
^{1}H NMR, CDCl$_3$, 400 MHz
AcO
OAc
OAc
Ac
O
O
S
MeO$_2$C
8a (6:1)
1.02
1.10
6.82
1.00
0.96
1.09
0.95
0.95
2.06
3.77
5.18
8.73
2.71
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)


170.7
170.3
169.5
169.1
167.2
143.2
140.8
140.3
136.7
134.3
134.0
131.3
131.2
130.4
129.0
128.3
128.2
124.1
119.2
87.1
77.5
77.2
76.8
75.9
74.0
70.1
68.4
62.4
51.7
31.0
27.1
20.9
20.7
20.6
20.6
20.5
^{13}C NMR, CDCl$_3$, 100 MHz
AcO
OAc
OAc
Ac
O
O
S
MeO$_2$C
8a (6:1)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

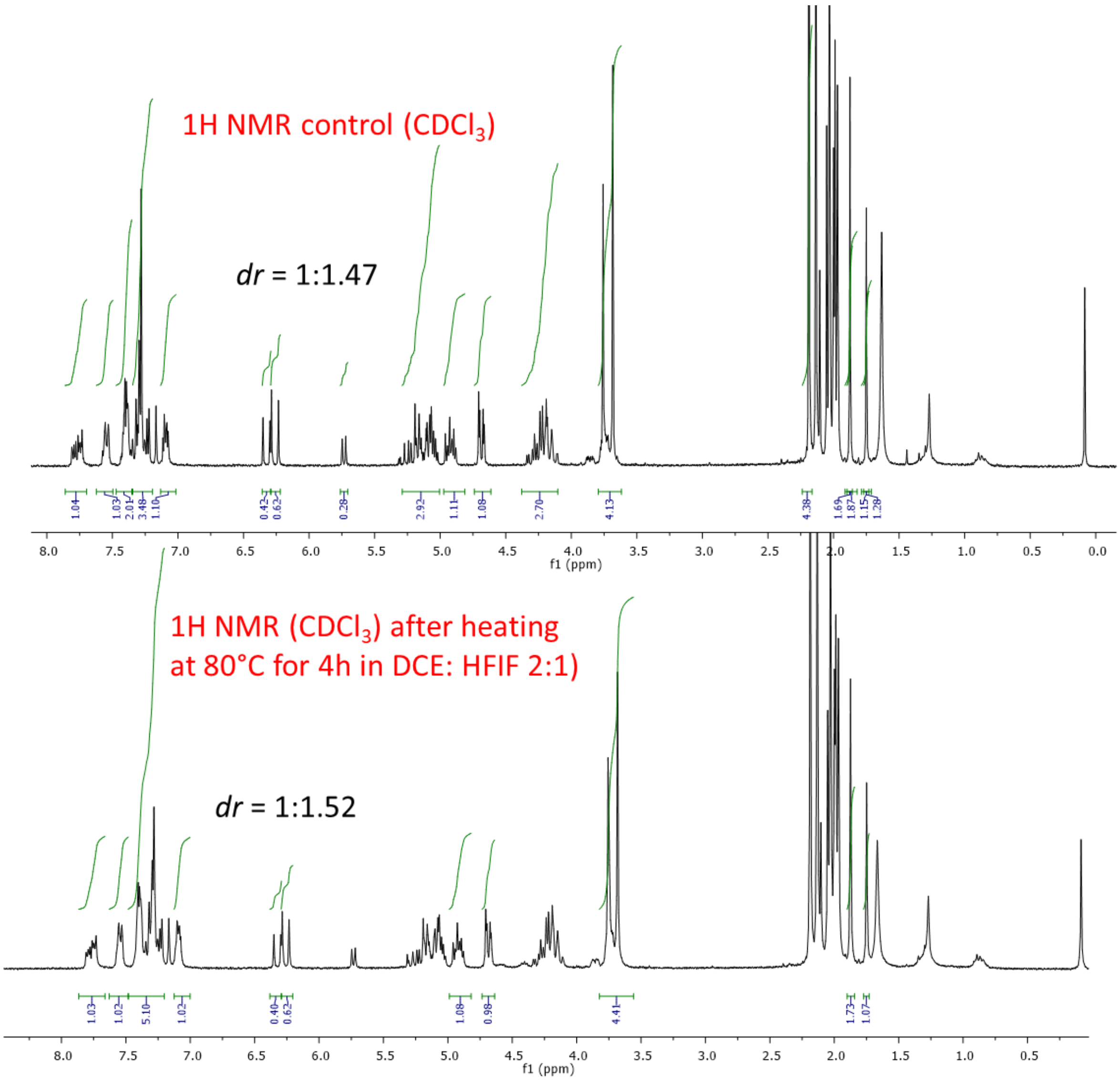
Variable temperature 1H NMR studies (solvant: DMSO D-6, T = 303 to 373K)
(tentative to determine the coalescence temperature and calculate de energy barrier)



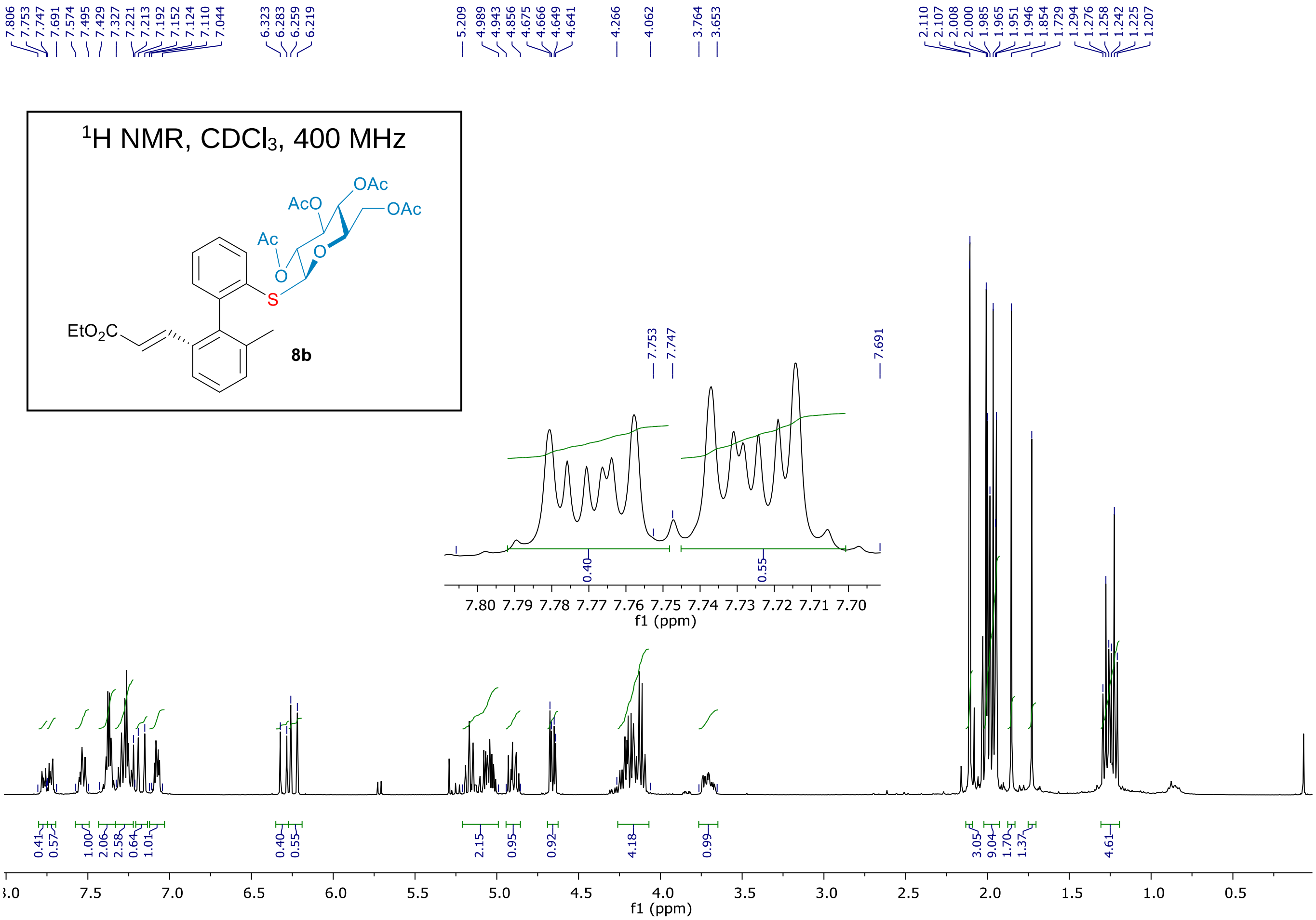
Conclusion: Since no complete coalescence was observed at 100°C, we can conclude that the biarylthioglycoside **8a** is configurationally stable at this reaction temperature.

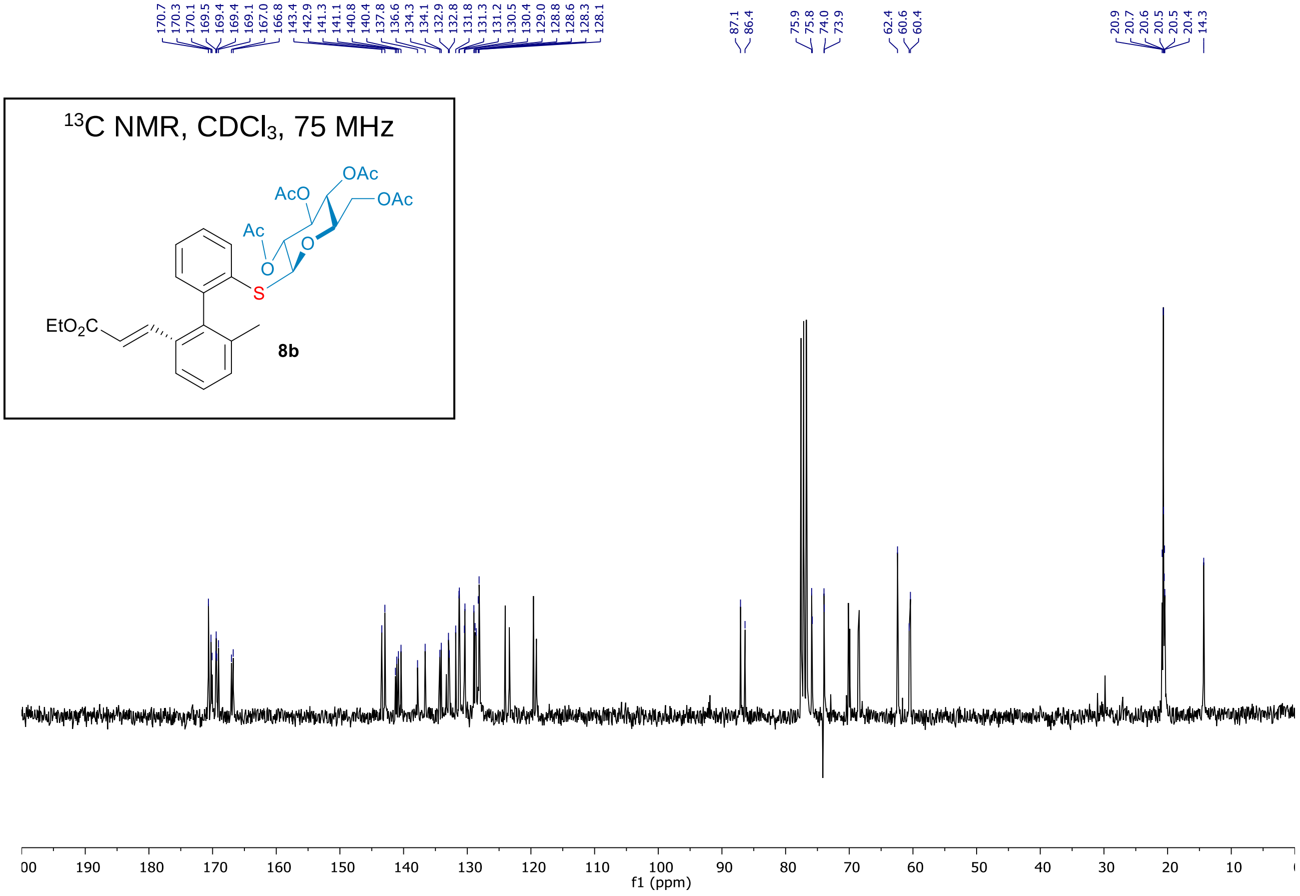
Atropo-stability experiment of 8a at 80 °C

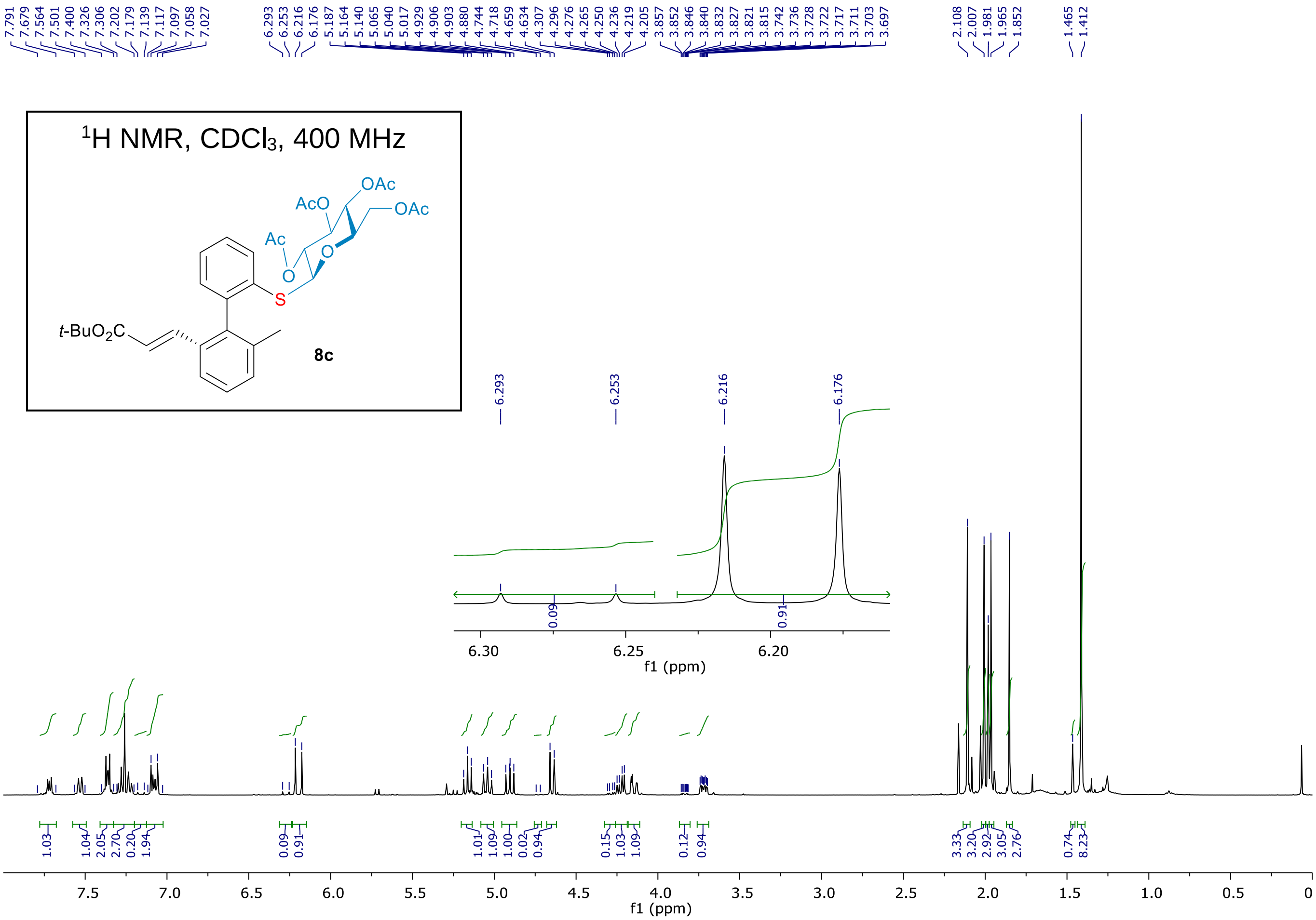
*A solution of **8a** was heated at 80 °C for 4h. 1H NMR was recorded before and after heating*

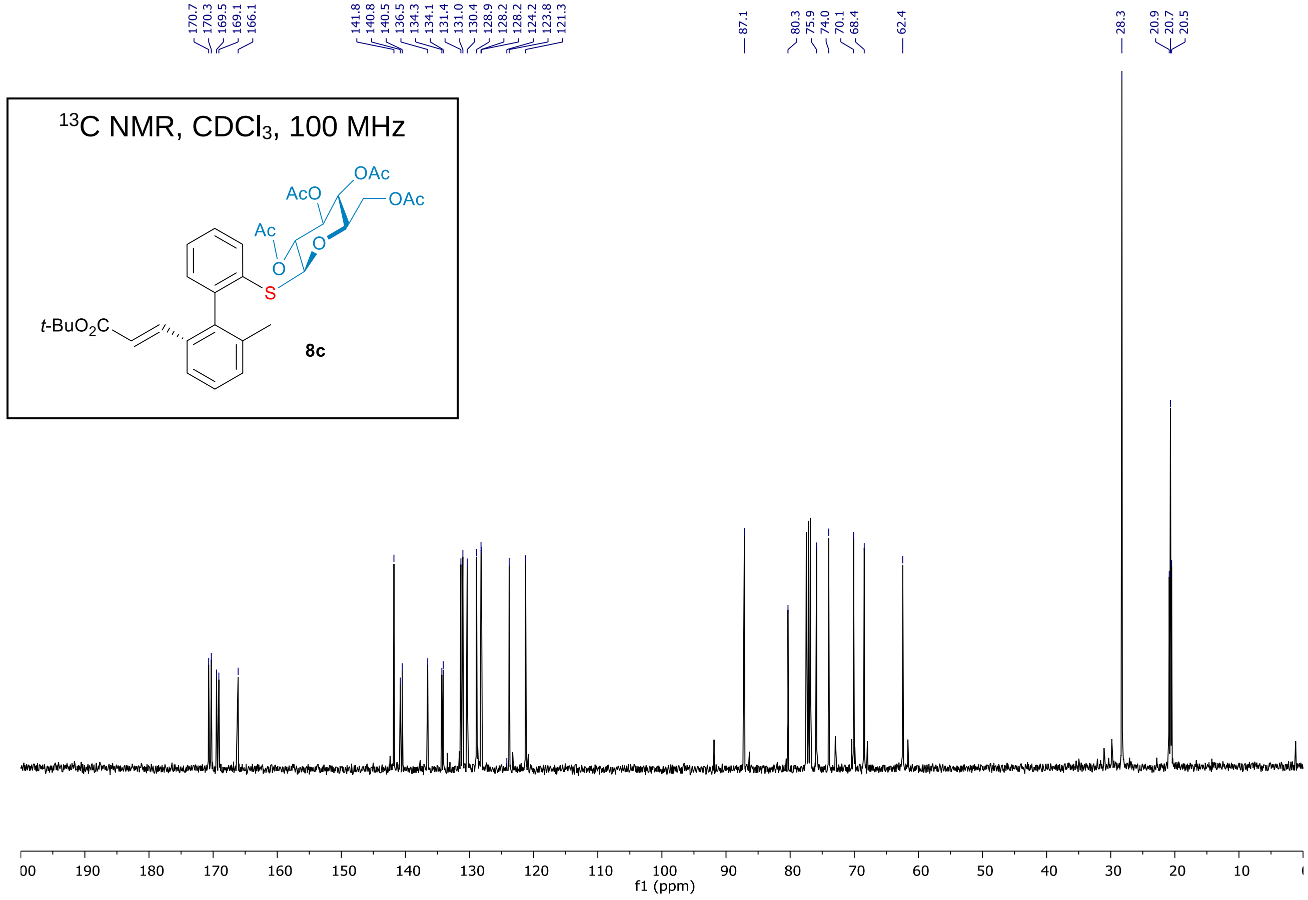


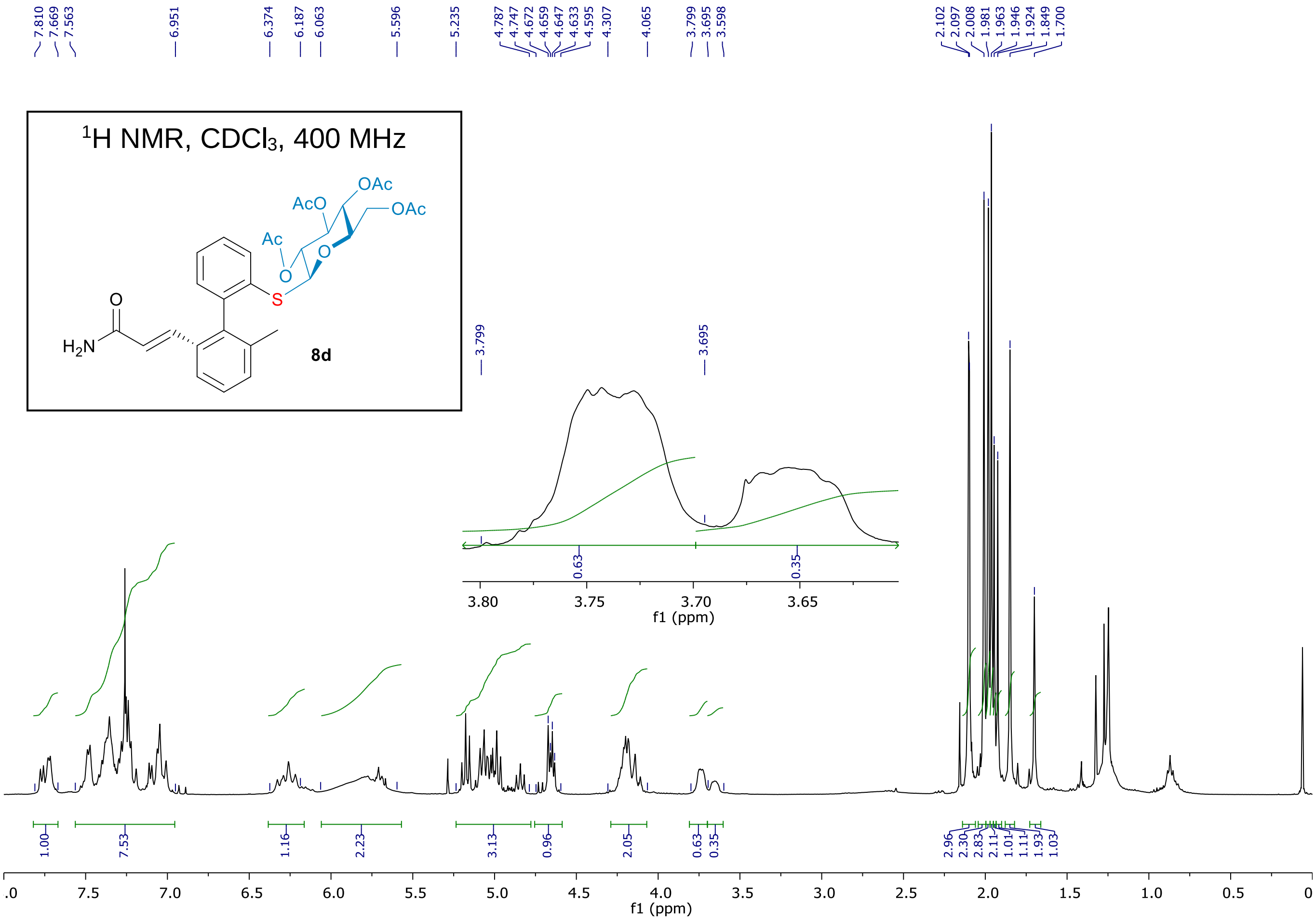
Conclusion: Since no variation of the *dr* ratio was observed, we can conclude that the biarylthioglycoside **8a** is configurationally stable at the reaction temperature of 80°C.

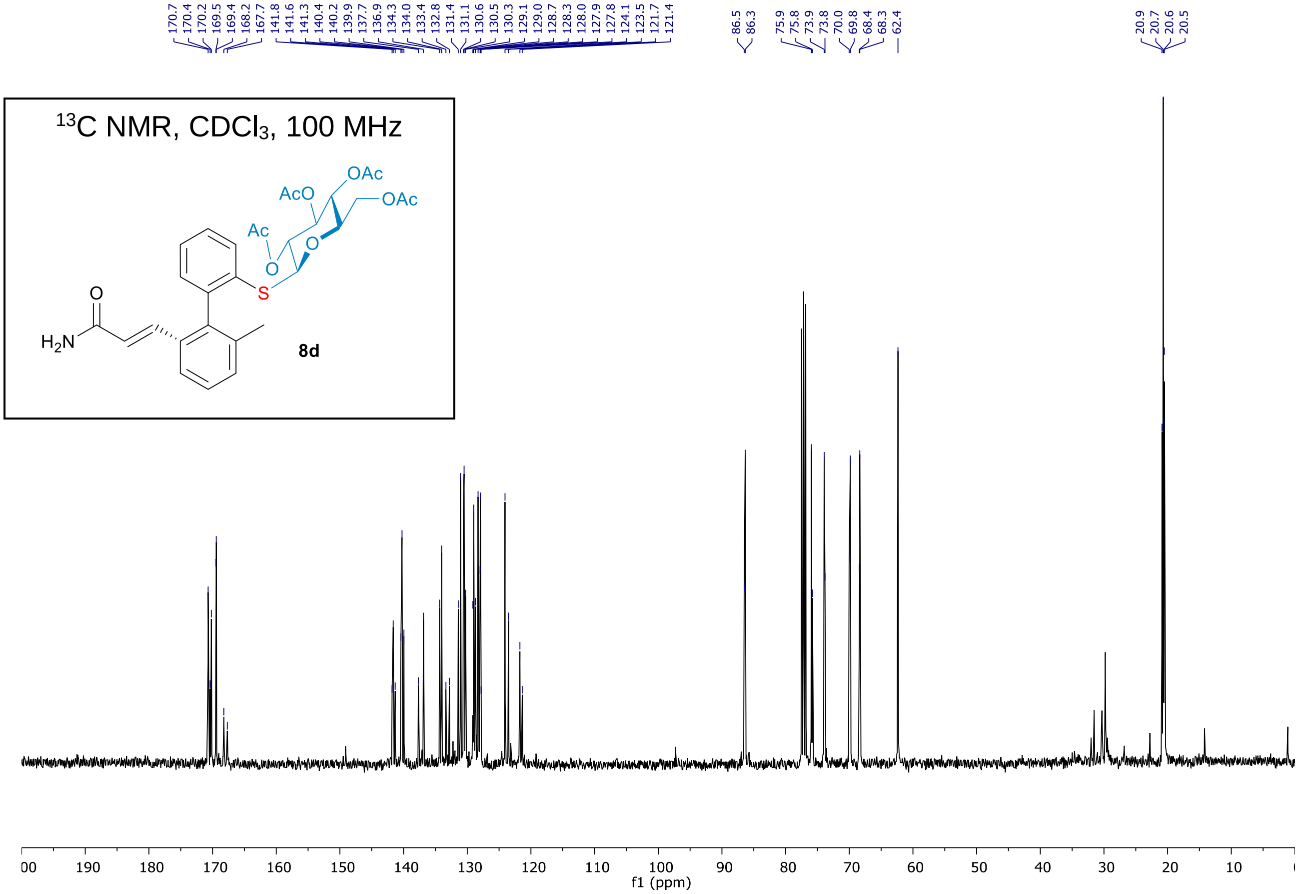

7.806
7.753
7.747
7.691
7.574
7.495
7.429
7.327
7.221
7.213
7.192
7.152
7.124
7.110
7.044
6.323
6.283
6.259
6.219
5.209
4.989
4.943
4.856
4.675
4.666
4.649
4.641
4.266
4.062
3.764
3.653
2.110
2.107
2.008
2.000
1.985
1.965
1.951
1.946
1.854
1.729
1.294
1.276
1.258
1.242
1.225
1.207
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
EtO$_2$C
8b
7.753
7.747
7.691
0.40
0.55
7.80 7.79 7.78 7.77 7.76 7.75 7.74 7.73 7.72 7.71 7.70
f1 (ppm)
0.41
0.57
1.00
2.06
2.58
0.64
1.01
0.40
0.55
2.15
0.95
0.92
4.18
0.99
3.05
9.04
1.70
1.37
4.61
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

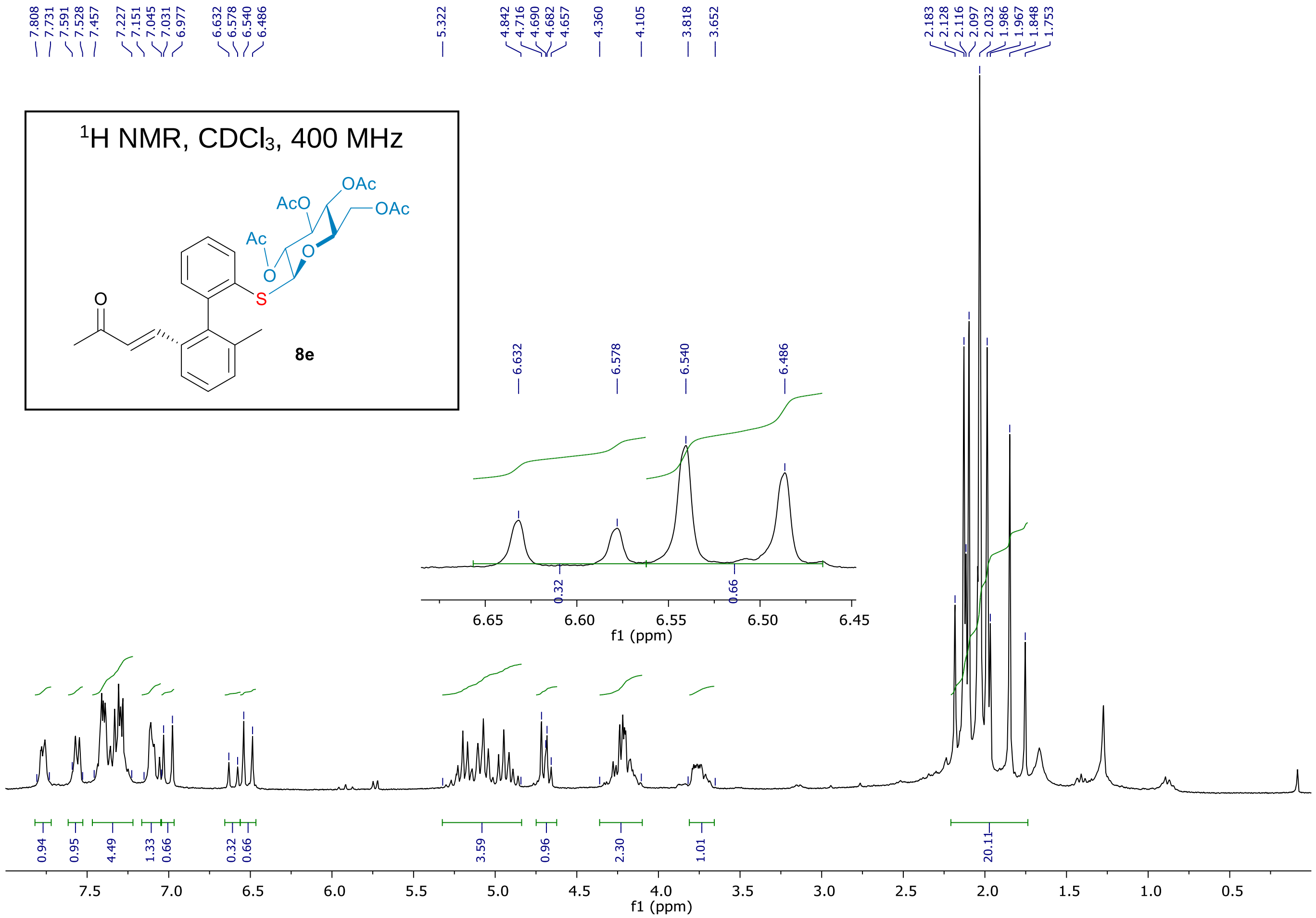

170.7
170.3
170.1
169.5
169.4
169.4
169.1
167.0
166.8
143.4
142.9
141.3
141.1
140.8
140.4
137.8
136.6
134.3
134.1
132.9
132.8
131.8
131.3
131.2
130.5
130.4
129.0
128.8
128.6
128.3
128.1
87.1
86.4
75.9
75.8
74.0
73.9
62.4
60.6
60.4
20.9
20.7
20.6
20.5
20.5
20.4
14.3
^{13}C NMR, CDCl$_3$, 75 MHz
OAc
AcO
OAc
Ac
O
O
S
EtO$_2$C
8b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.791
7.679
7.564
7.501
7.400
7.326
7.306
7.202
7.179
7.139
7.117
7.097
7.058
7.027
6.293
6.253
6.216
6.176
5.187
5.164
5.140
5.065
5.040
5.017
4.929
4.906
4.903
4.880
4.744
4.718
4.659
4.634
4.307
4.296
4.276
4.265
4.250
4.236
4.219
4.205
3.857
3.852
3.846
3.840
3.832
3.827
3.821
3.815
3.742
3.736
3.728
3.722
3.717
3.711
3.703
3.697
2.108
2.007
1.981
1.965
1.852
1.465
1.412
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
t-BuO$_2$C
8c
6.293
6.253
6.216
6.176
0.09
0.91
6.30
6.25
6.20
f1 (ppm)
1.03
1.04
2.05
2.70
0.20
1.94
0.09
0.91
1.01
1.09
1.00
0.02
0.94
0.15
1.03
1.09
0.12
0.94
3.33
3.20
2.92
3.05
2.76
0.74
8.23
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
f1 (ppm)

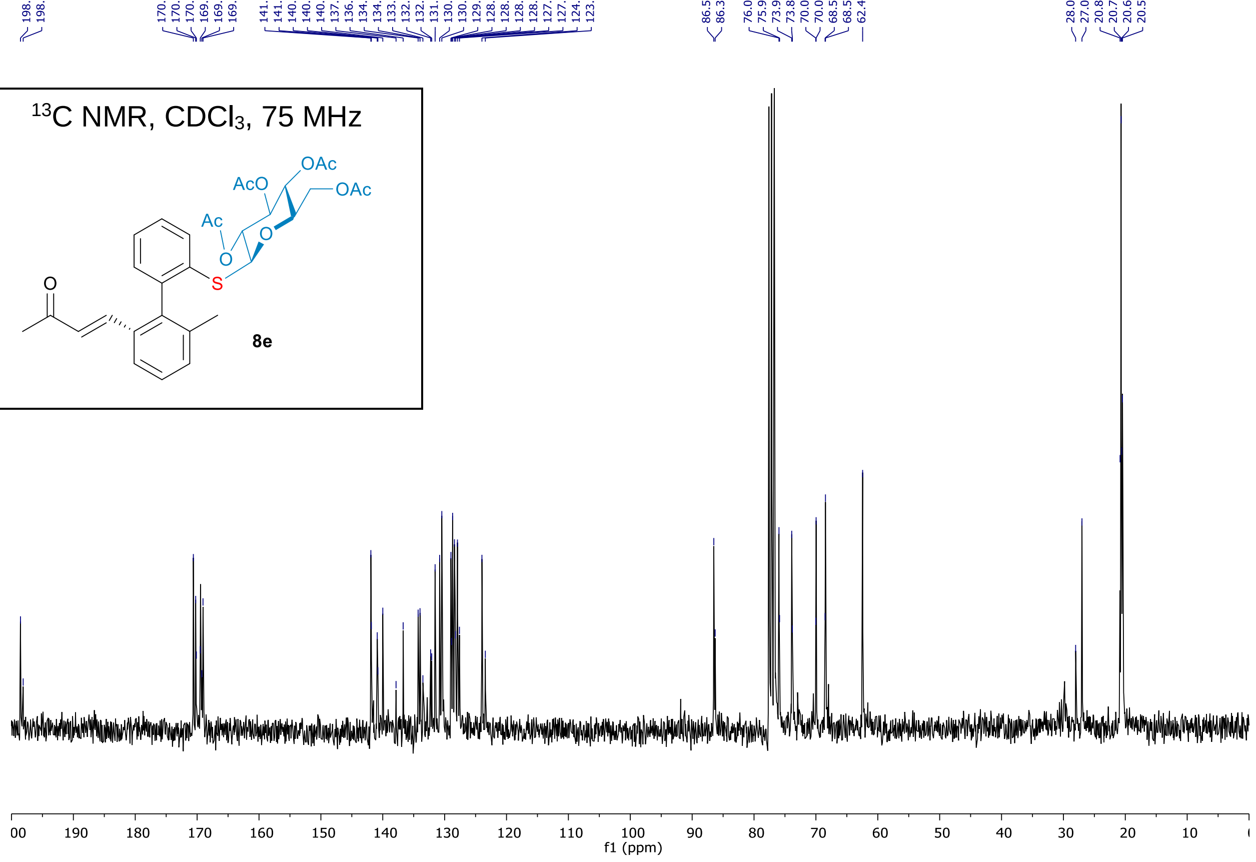

170.7
170.3
169.5
169.1
166.1
141.8
140.8
140.5
136.5
134.3
134.1
131.4
131.0
130.4
128.9
128.2
128.2
124.2
123.8
121.3
87.1
80.3
75.9
74.0
70.1
68.4
62.4
28.3
20.9
20.7
20.5
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
t-BuO$_2$C
8c
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.810
7.669
7.563
6.951
6.374
6.187
6.063
5.596
5.235
4.787
4.747
4.672
4.659
4.647
4.633
4.595
4.307
4.065
3.799
3.695
3.598
2.102
2.097
2.008
1.981
1.963
1.946
1.924
1.849
1.700
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
O
H_2N
8d
3.799
3.695
0.63
0.35
3.80
3.75
3.70
3.65
f1 (ppm)
1.00
7.53
1.16
2.23
3.13
0.96
2.05
0.63
0.35
2.96
2.30
2.83
2.11
1.01
1.11
1.93
1.03
.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
f1 (ppm)

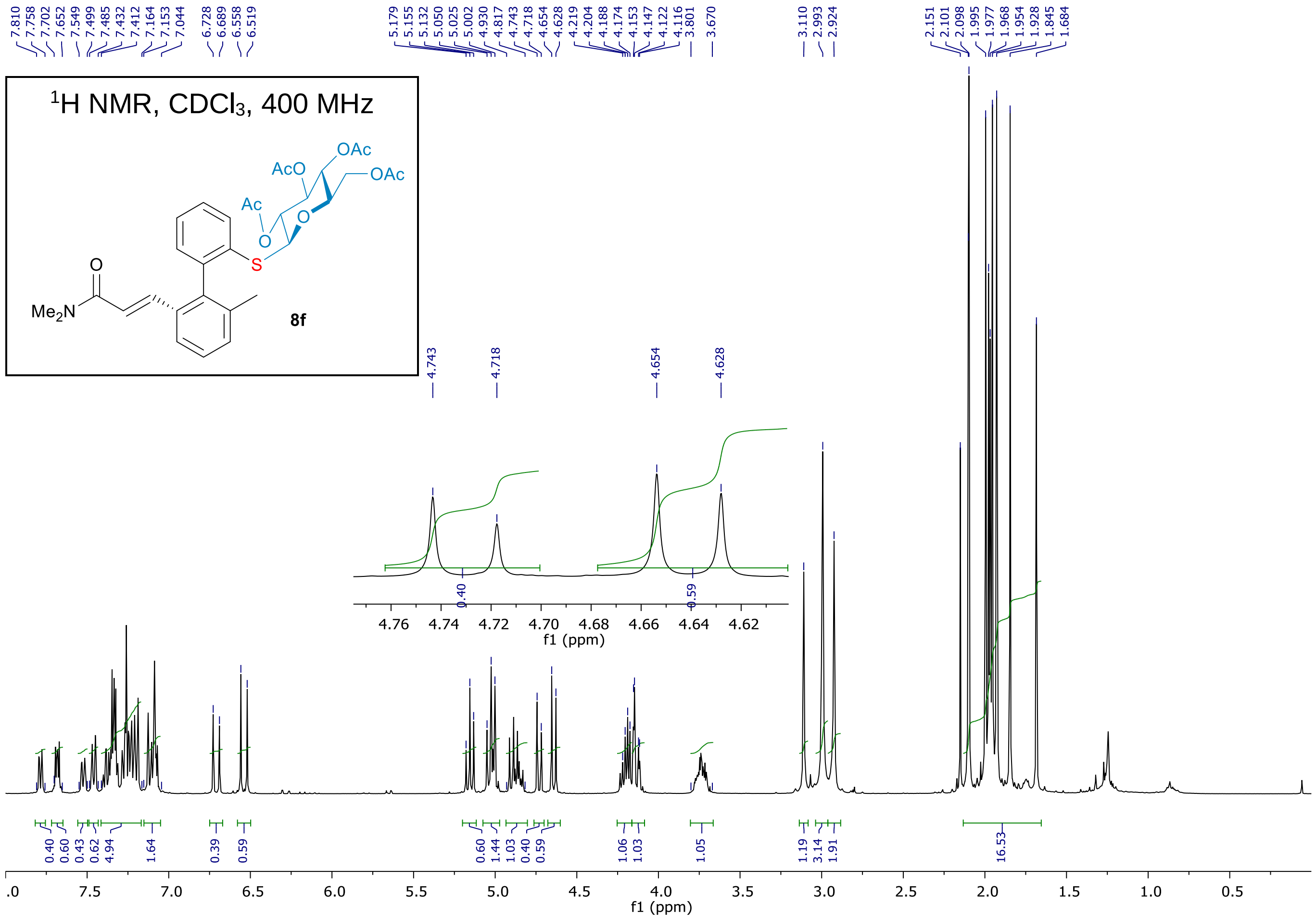

170.7
170.4
170.2
169.5
169.4
168.2
167.7
141.8
141.6
141.3
140.4
140.2
139.9
137.7
136.9
134.3
134.0
133.4
132.8
131.4
131.1
130.6
130.5
130.3
129.1
129.0
128.7
128.3
128.0
127.9
127.8
124.1
123.5
121.7
121.4
86.5
86.3
75.9
75.8
73.9
73.8
70.0
69.8
68.4
68.3
62.4
20.9
20.7
20.6
20.5
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
O
H_2N
8d
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

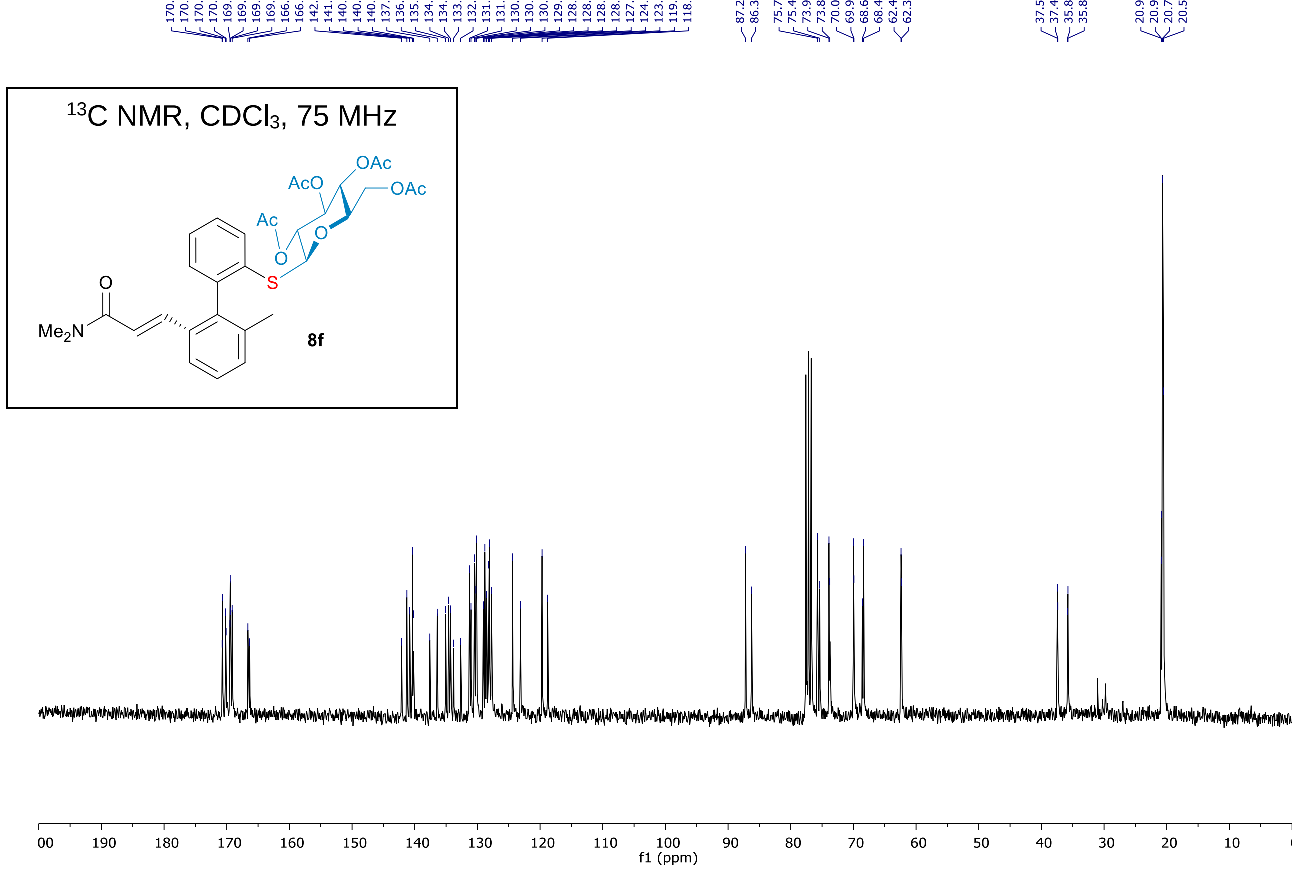


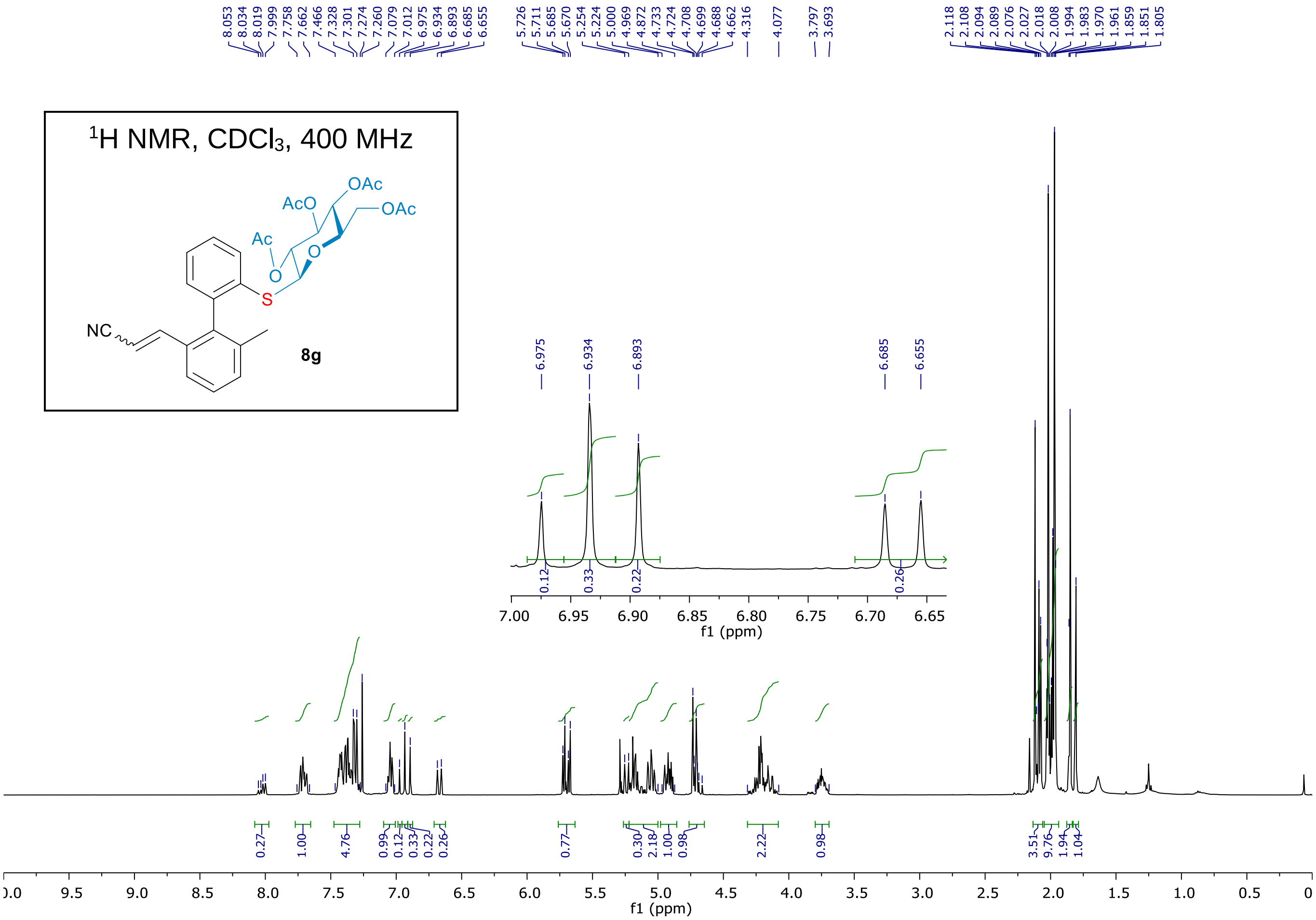
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
O
S
8e
7.808
7.731
7.591
7.528
7.457
7.227
7.151
7.045
7.031
6.977
6.632
6.578
6.540
6.486
5.322
4.842
4.716
4.690
4.682
4.657
4.360
4.105
3.818
3.652
2.183
2.128
2.116
2.097
2.032
1.986
1.967
1.848
1.753
0.94
0.95
4.49
1.33
0.66
0.32
0.66
3.59
0.96
2.30
1.01
20.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
6.632
6.578
6.540
6.486
0.32
0.66
6.65
6.60
6.55
6.50
6.45
f1 (ppm)

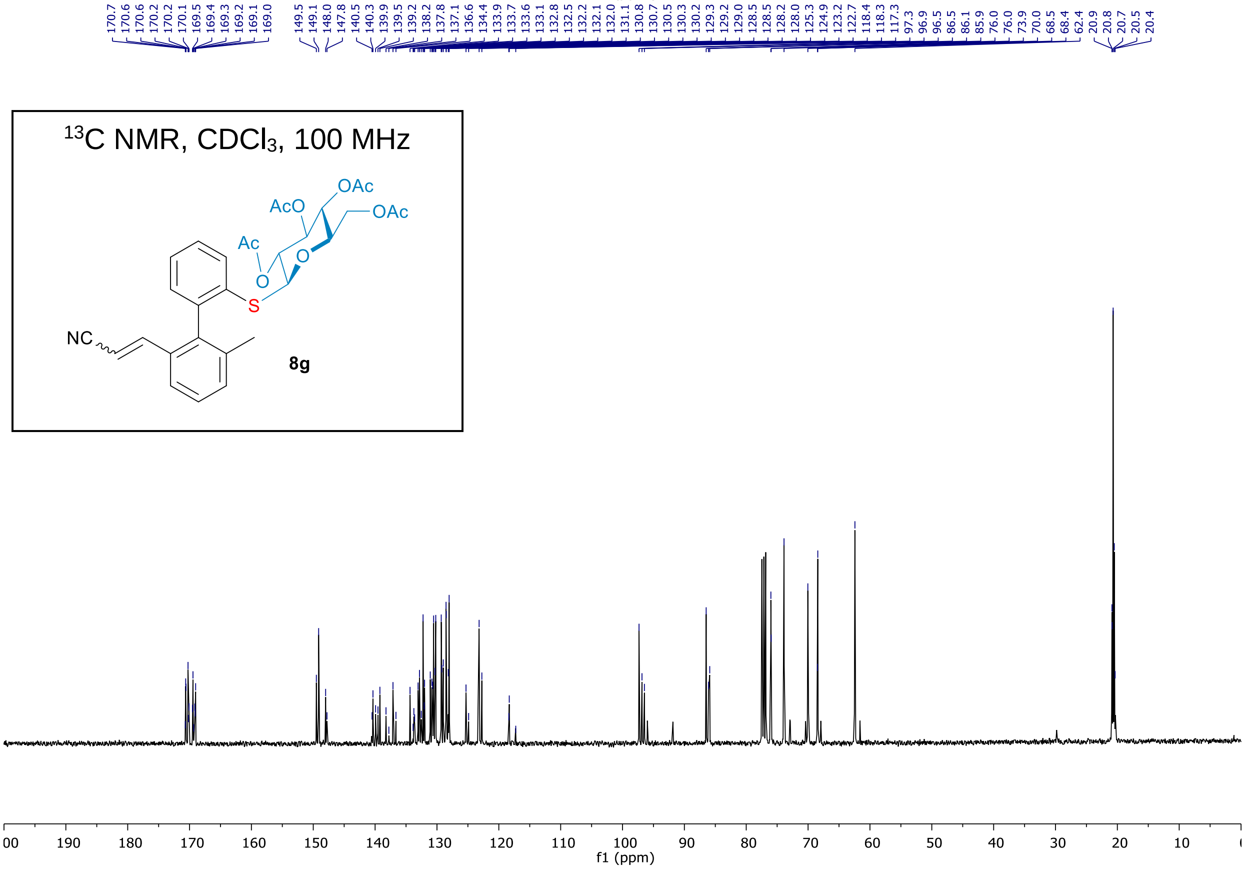


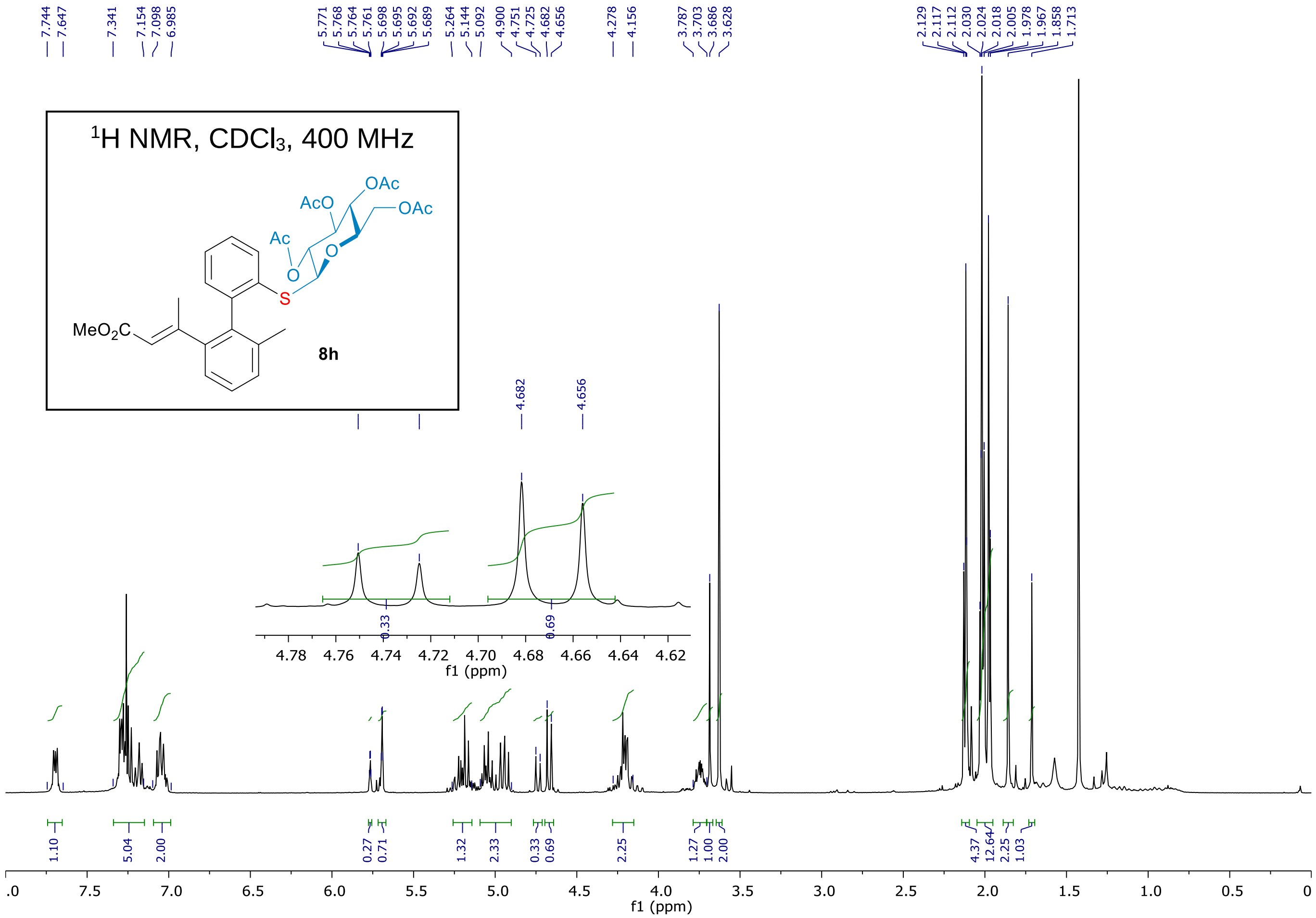
^{13}C NMR, CDCl$_3$, 75 MHz
OAc
AcO
OAc
Ac
O
O
O
S
8e
198.5
198.1
170.6
170.2
170.1
169.5
169.2
169.1
141.9
141.8
140.9
140.8
140.0
137.9
136.7
134.3
134.0
133.5
132.3
132.1
131.5
130.8
130.5
129.0
128.9
128.7
128.4
128.2
127.9
127.6
124.0
123.4
86.5
86.3
76.0
75.9
73.9
73.8
70.0
70.0
68.5
68.5
62.4
28.0
27.0
20.8
20.7
20.6
20.5
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


1H NMR, CDCl3, 400 MHz
AcO
OAc
OAc
Ac
O
O
S
O
Me2N
8f
7.810 7.758 7.702 7.652 7.549 7.499 7.485 7.432 7.412 7.164 7.153 7.044
6.728 6.689 6.558 6.519
5.179 5.155 5.132 5.050 5.025 5.002 4.930 4.817 4.743 4.718 4.654 4.628 4.219 4.204 4.188 4.174 4.153 4.147 4.122 4.116 3.801 3.670
3.110 2.993 2.924
2.151 2.101 2.098 1.995 1.977 1.968 1.954 1.928 1.845 1.684
4.743 4.718 4.654 4.628
0.40 0.59
4.76 4.74 4.72 4.70 4.68 4.66 4.64 4.62
f1 (ppm)
0.40 0.60 0.43 0.62 4.94 1.64 0.39 0.59 0.60 1.44 1.03 0.40 0.59 1.06 1.03 1.05 1.19 3.14 1.91 16.53
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

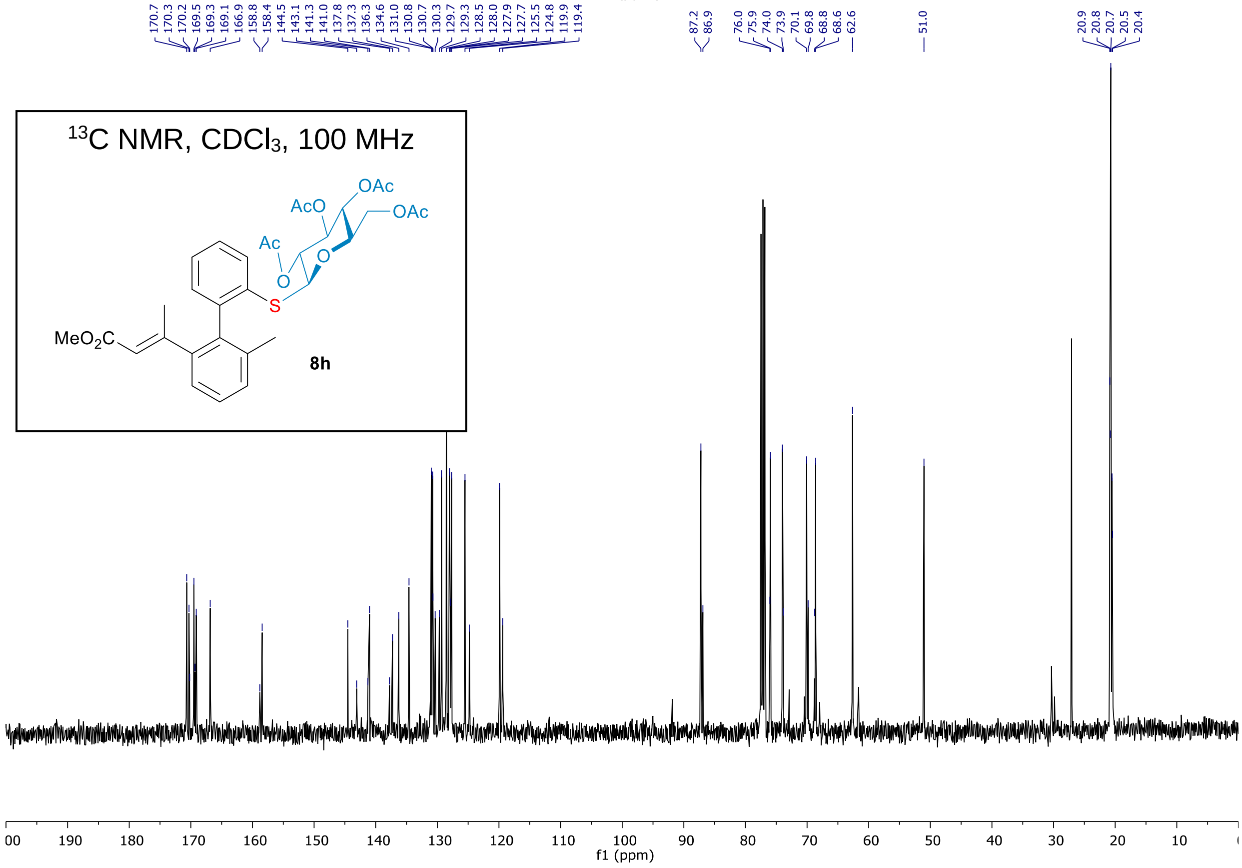

170.7 170.7 170.2 170.1 169.5 169.4 169.4 169.1 166.6 166.3 142.1 141.3 140.8 140.4 140.2 137.6 136.4 135.1 134.6 134.3 133.8 132.7 131.3 131.0 130.5 130.2 130.1 129.1 128.8 128.5 128.2 128.1 127.8 124.4 123.1 119.7 118.8
87.2 86.3 75.7 75.4 73.9 73.8 70.0 69.9 68.6 68.4 62.4 62.3
37.5 37.4 35.8 35.8
20.9 20.9 20.7 20.5
13C NMR, CDCl3, 75 MHz
AcO
OAc
OAc
Ac
O
O
S
O
Me2N
8f
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.053
8.034
8.019
7.999
7.758
7.662
7.466
7.328
7.301
7.274
7.260
7.079
7.012
6.975
6.934
6.893
6.685
6.655
5.726
5.711
5.685
5.670
5.254
5.224
5.000
4.969
4.872
4.733
4.724
4.708
4.699
4.688
4.662
4.316
4.077
3.797
3.693
2.118
2.108
2.094
2.089
2.076
2.027
2.018
2.008
1.994
1.983
1.970
1.961
1.859
1.851
1.805
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
NC
8g
6.975
6.934
6.893
6.685
6.655
0.12
0.33
0.22
0.26
7.00
6.95
6.90
6.85
6.80
6.75
6.70
6.65
f1 (ppm)
0.27
1.00
4.76
0.99
0.12
0.33
0.22
0.26
0.77
0.30
2.18
1.00
0.98
2.22
0.98
3.51
9.76
1.94
1.04
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
f1 (ppm)

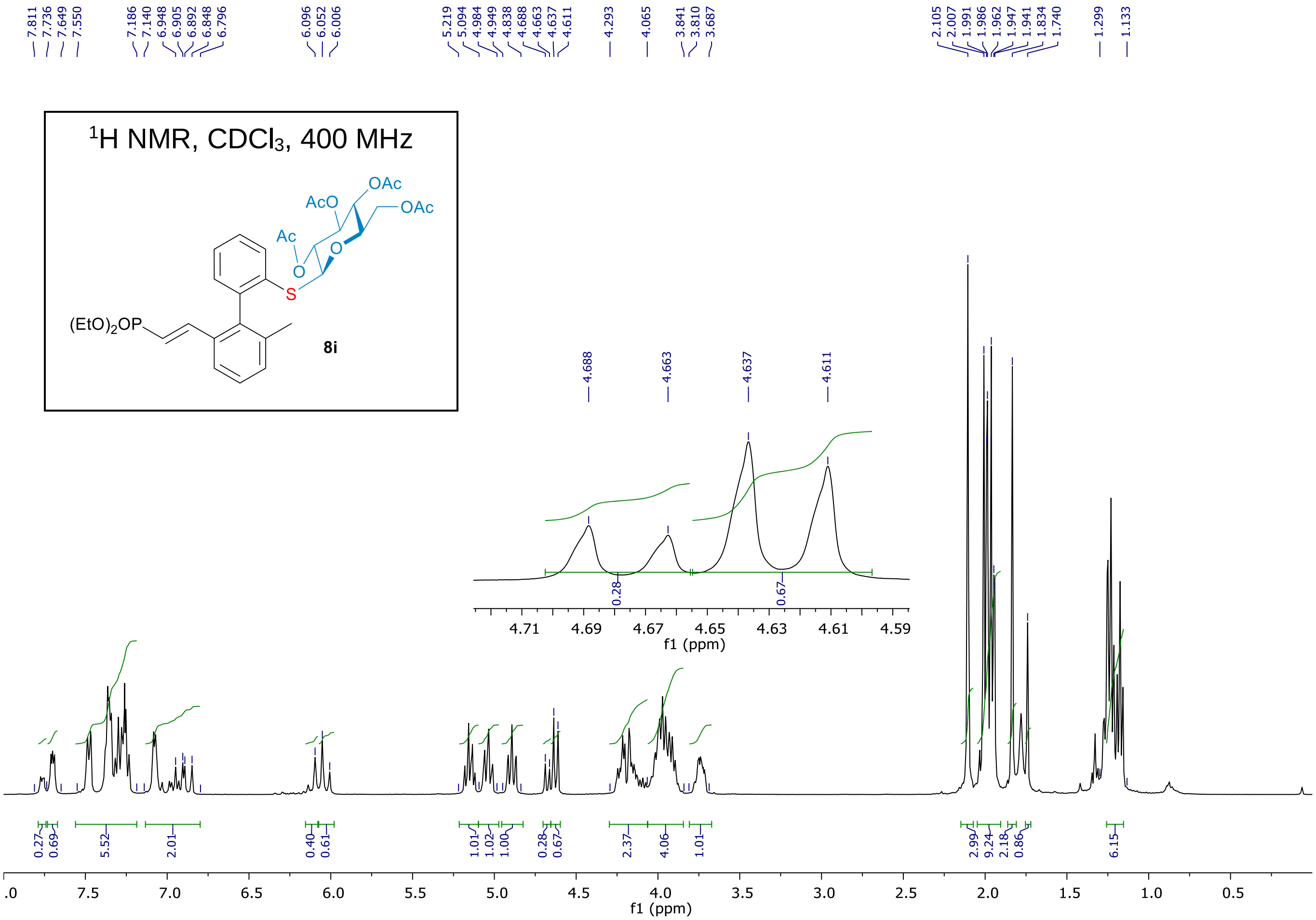

170.7
170.6
170.6
170.2
170.2
170.1
169.5
169.4
169.3
169.2
169.1
169.0
149.5
149.1
148.0
147.8
140.5
140.3
139.9
139.5
139.2
138.2
137.8
137.1
136.6
134.4
133.9
133.7
133.6
133.1
132.8
132.5
132.2
132.1
132.0
131.1
130.8
130.7
130.5
130.3
130.2
129.3
129.2
129.0
128.5
128.5
128.2
128.0
125.3
124.9
123.2
122.7
118.4
118.3
117.3
97.3
96.9
96.5
86.5
86.1
85.9
76.0
73.9
70.0
68.5
68.4
62.4
20.9
20.8
20.7
20.5
20.4
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
NC
8g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

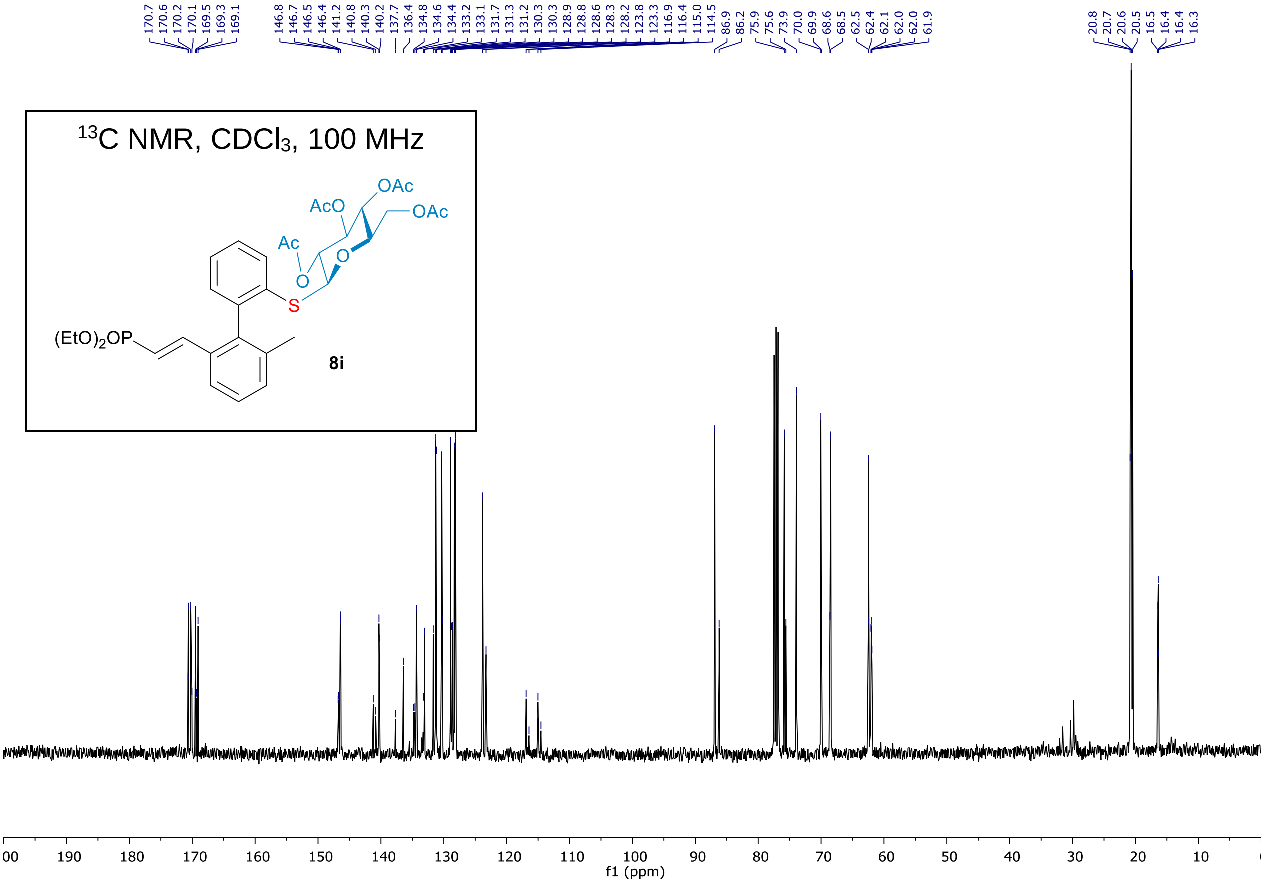


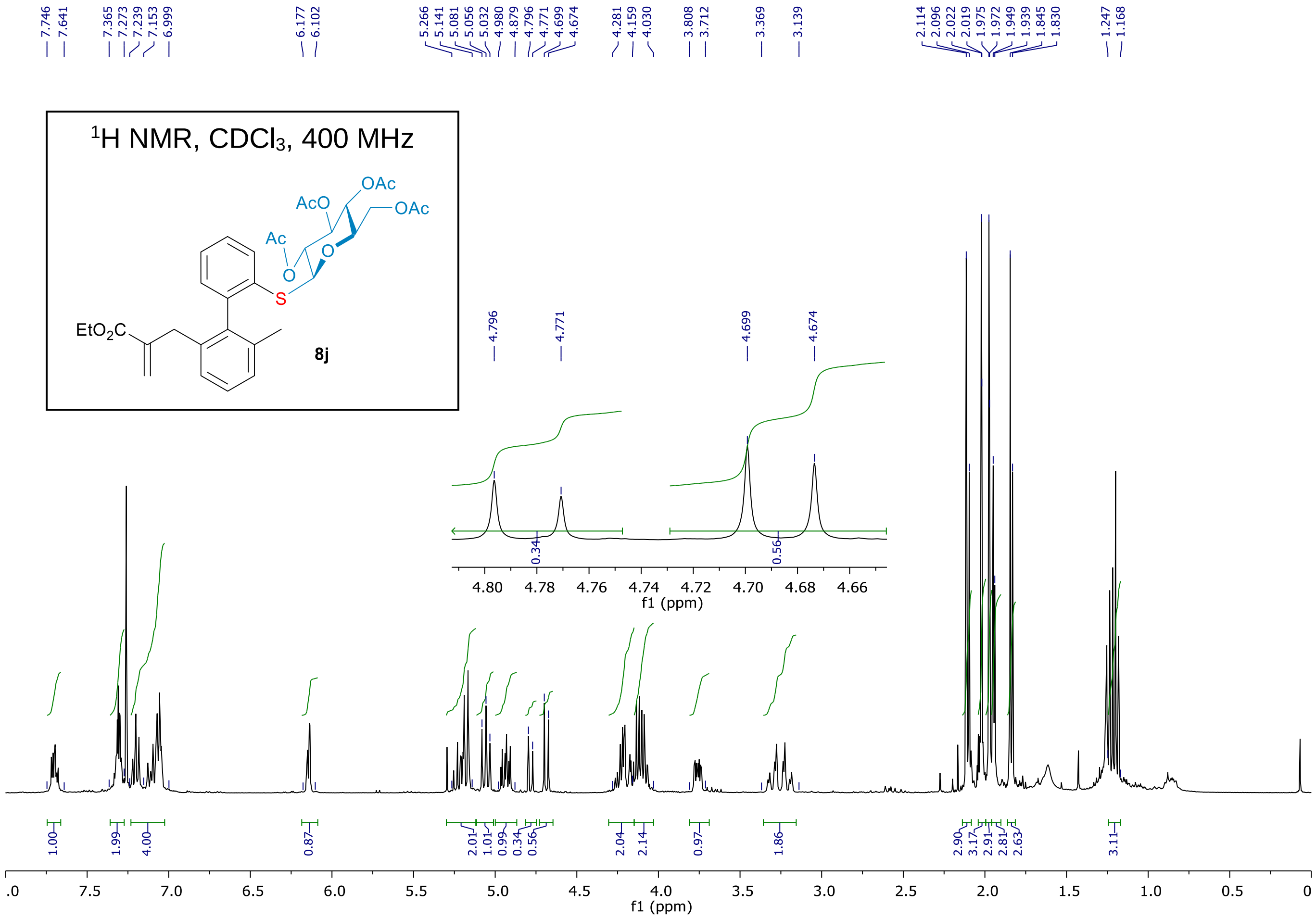
7.744
7.647
7.341
7.154
7.098
6.985
5.771
5.768
5.764
5.761
5.698
5.695
5.692
5.689
5.264
5.144
5.092
4.900
4.751
4.725
4.682
4.656
4.278
4.156
3.787
3.703
3.686
3.628
2.129
2.117
2.112
2.030
2.024
2.018
2.005
1.978
1.967
1.858
1.713
1H NMR, CDCl3, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
MeO2C
8h
4.682
4.656
0.33
0.69
4.78 4.76 4.74 4.72 4.70 4.68 4.66 4.64 4.62
f1 (ppm)
1.10
5.04
2.00
0.27
0.71
1.32
2.33
0.33
0.69
2.25
1.27
1.00
2.00
4.37
12.64
2.25
1.03
.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
f1 (ppm)

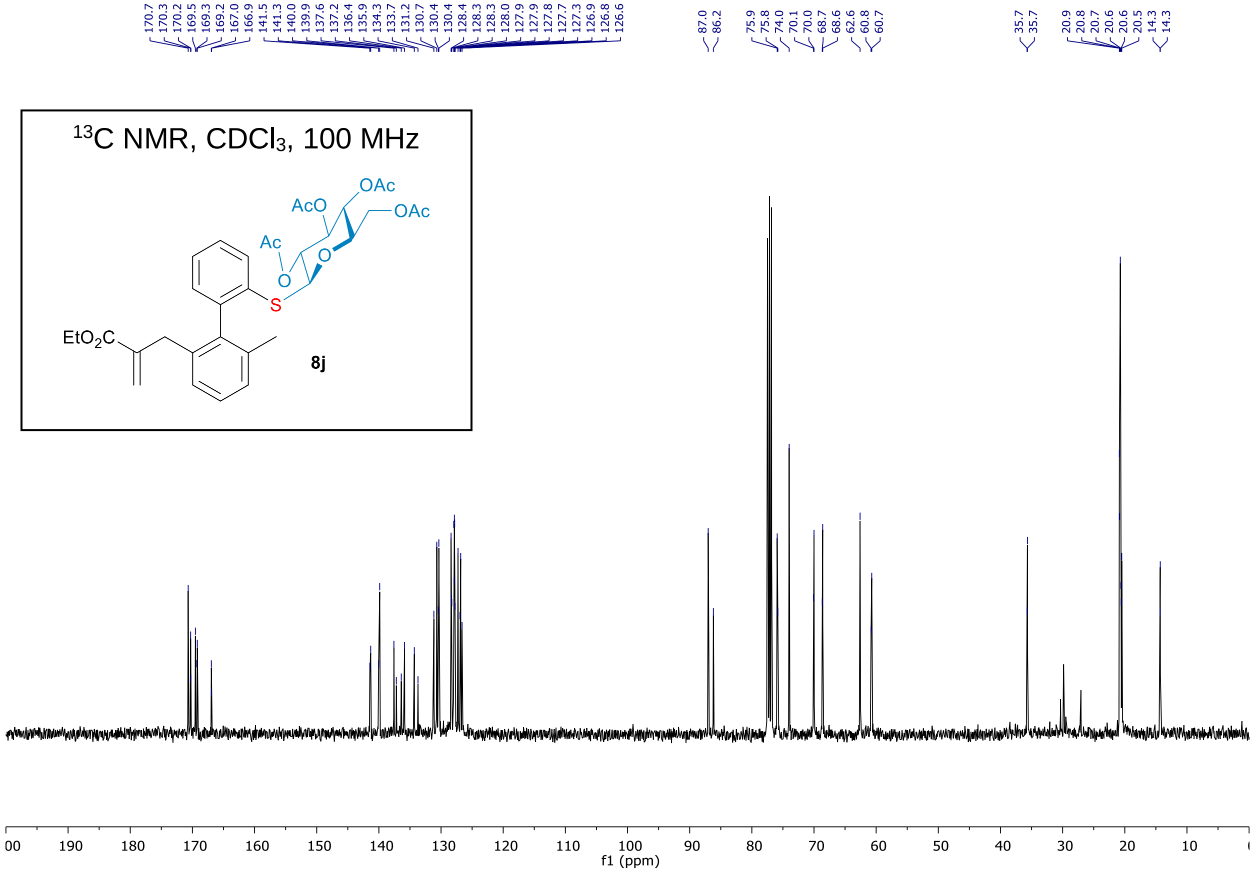


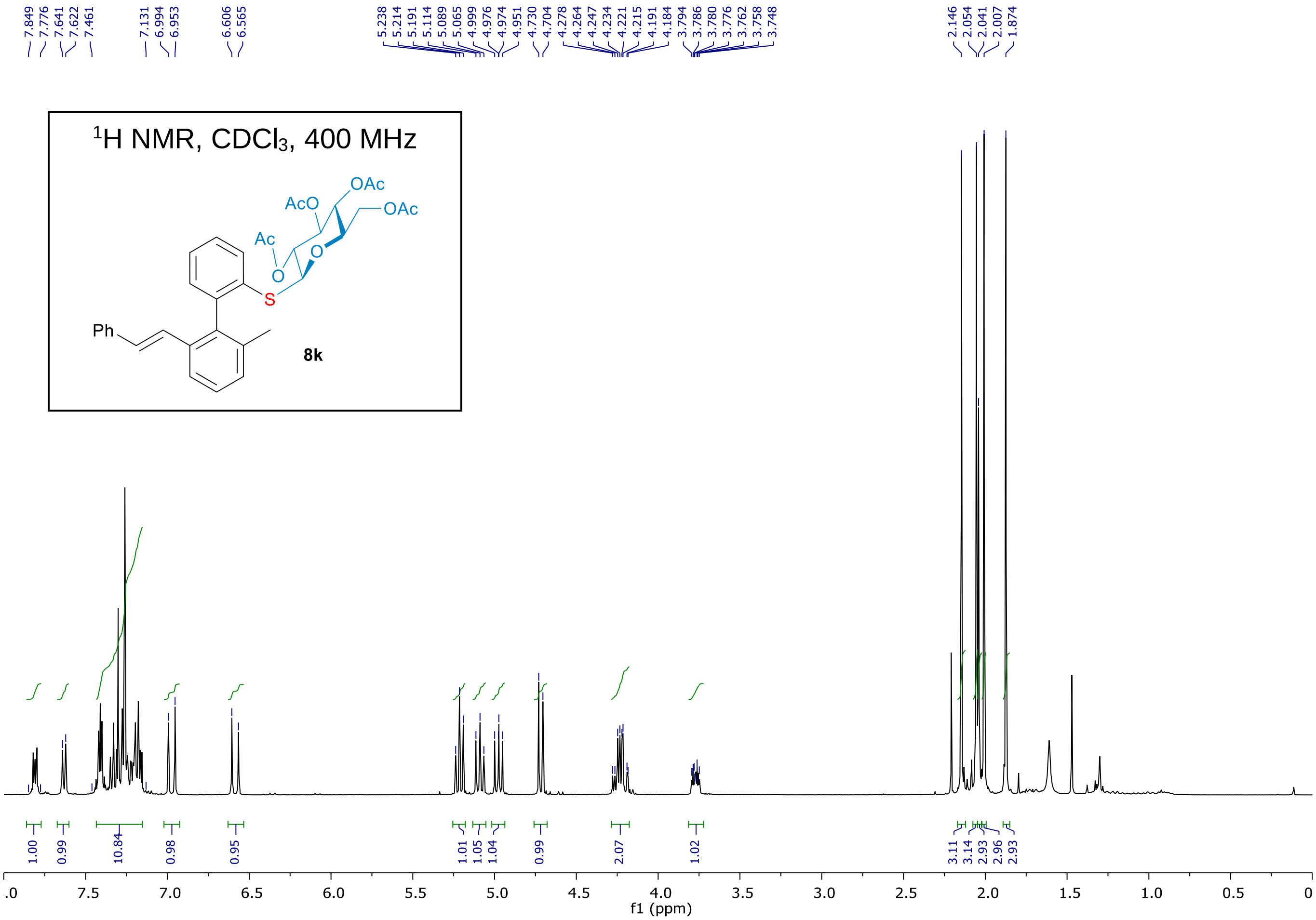
170.7
170.3
170.2
169.5
169.3
169.1
166.9
158.8
158.4
144.5
143.1
141.3
141.0
137.8
137.3
136.3
134.6
131.0
130.8
130.7
130.3
129.7
129.3
128.5
128.0
127.9
127.7
125.5
124.8
119.9
119.4
87.2
86.9
76.0
75.9
74.0
73.9
70.1
69.8
68.8
68.6
62.6
51.0
20.9
20.8
20.7
20.5
20.4
13C NMR, CDCl3, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
MeO2C
8h
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

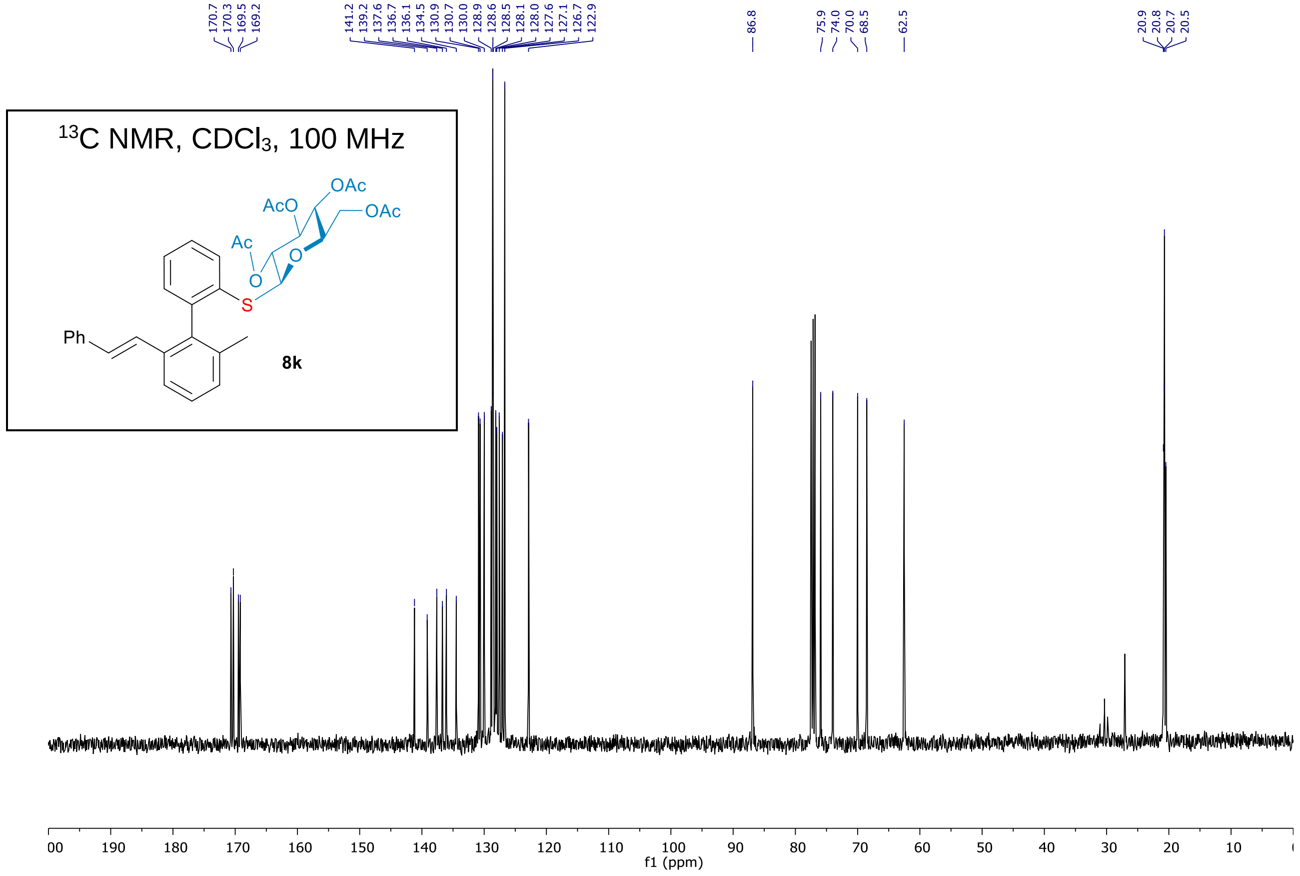

1H NMR, CDCl3, 400 MHz
8i
(EtO)2OP
AcO
OAc
OAc
Ac
O
O
S
7.811 7.736 7.649 7.550 7.186 7.140 6.948 6.905 6.892 6.848 6.796 6.096 6.052 6.006 5.219 5.094 4.984 4.949 4.838 4.688 4.663 4.637 4.611 4.293 4.065 3.841 3.810 3.687 2.105 2.007 1.991 1.986 1.962 1.947 1.941 1.834 1.740 1.299 1.133
4.688 4.663 4.637 4.611
0.28 0.67
4.71 4.69 4.67 4.65 4.63 4.61 4.59
f1 (ppm)
0.27 0.69 5.52 2.01 0.40 0.61 1.01 1.02 1.00 0.28 0.67 2.37 4.06 1.01 2.99 9.24 2.18 0.86 6.15
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

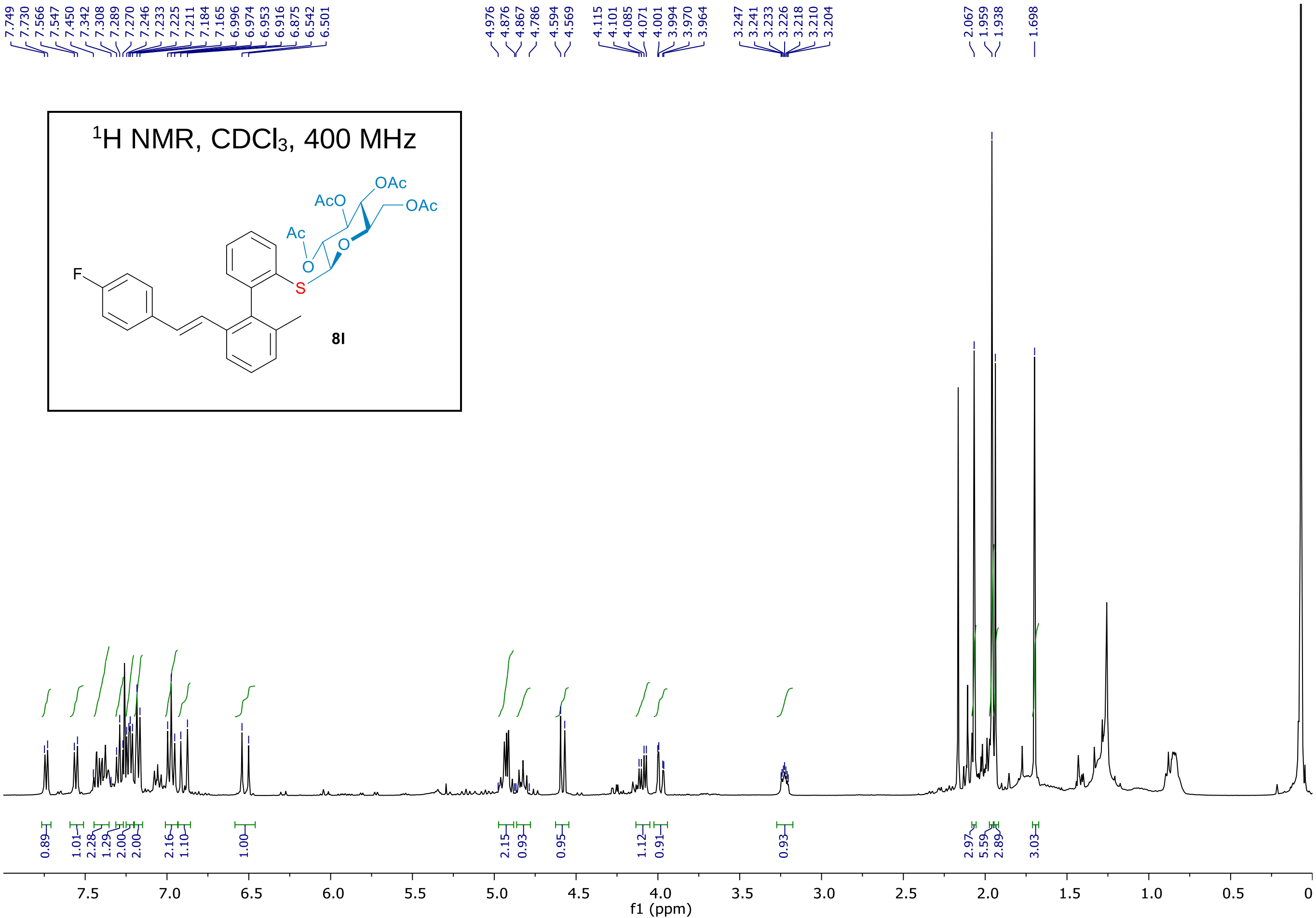

13C NMR, CDCl3, 100 MHz
8i
(EtO)2OP
AcO
OAc
OAc
Ac
O
O
S
170.7 170.6 170.2 170.1 169.5 169.3 169.1 146.8 146.7 146.5 146.4 141.2 140.8 140.3 140.2 137.7 136.4 134.8 134.6 134.4 133.2 133.1 131.7 131.3 131.2 130.3 130.3 128.9 128.8 128.6 128.3 128.2 123.8 123.3 116.9 116.4 115.0 114.5 86.9 86.2 75.9 75.6 73.9 70.0 69.9 68.6 68.5 62.5 62.4 62.1 62.0 62.0 61.9 20.8 20.7 20.6 20.5 16.5 16.4 16.4 16.3
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

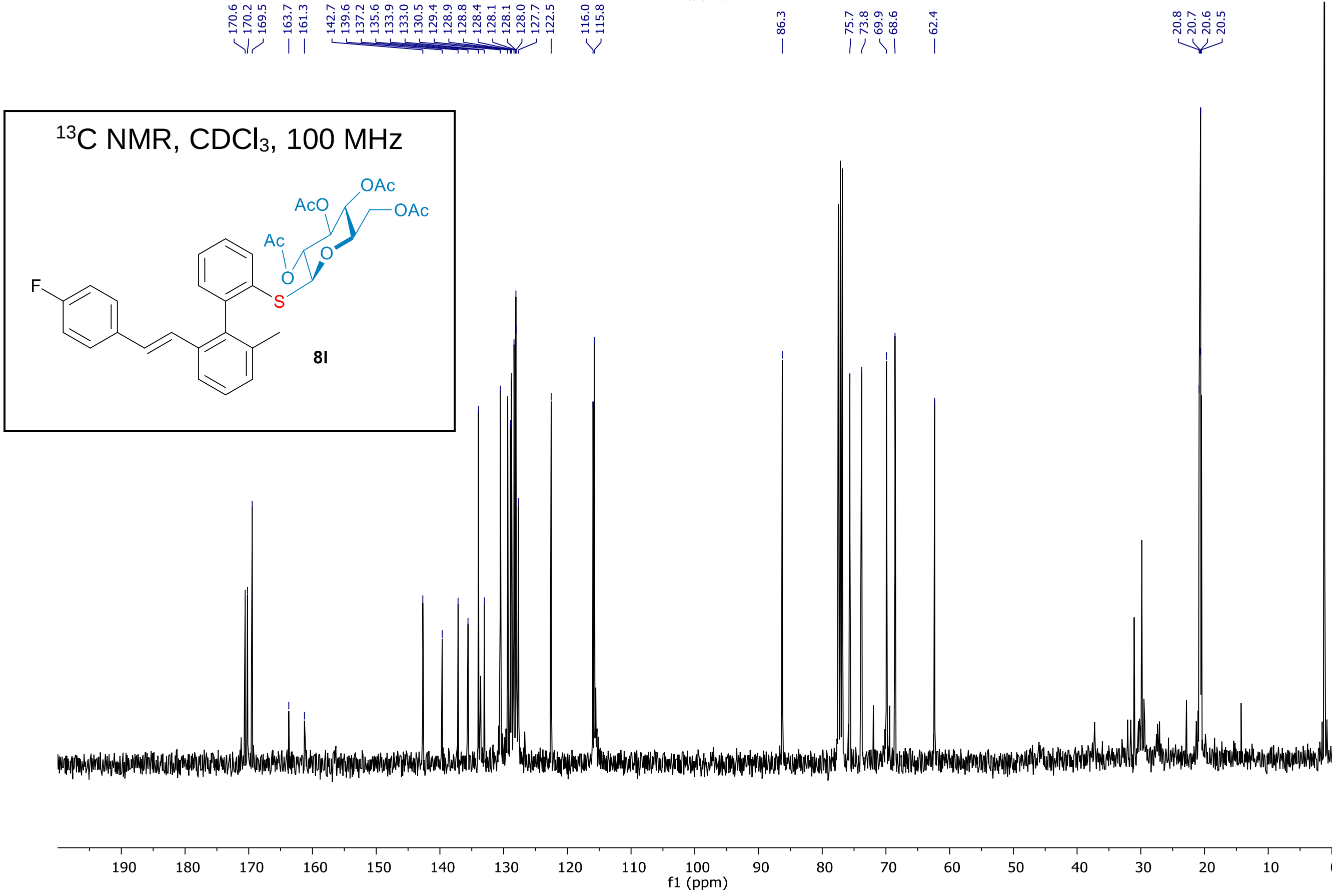

7.746
7.641
7.365
7.273
7.239
7.153
6.999
6.177
6.102
5.266
5.141
5.081
5.056
5.032
4.980
4.879
4.796
4.771
4.699
4.674
4.281
4.159
4.030
3.808
3.712
3.369
3.139
2.114
2.096
2.022
2.019
1.975
1.972
1.949
1.939
1.845
1.830
1.247
1.168
1H NMR, CDCl3, 400 MHz
AcO
OAc
OAc
Ac
O
O
S
EtO2C
8j
4.796
4.771
4.699
4.674
0.34
0.56
4.80
4.78
4.76
4.74
4.72
4.70
4.68
4.66
f1 (ppm)
1.00
1.99
4.00
0.87
2.01
1.01
0.99
0.34
0.56
2.04
2.14
0.97
1.86
2.90
3.17
2.91
2.81
2.63
3.11
.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
f1 (ppm)

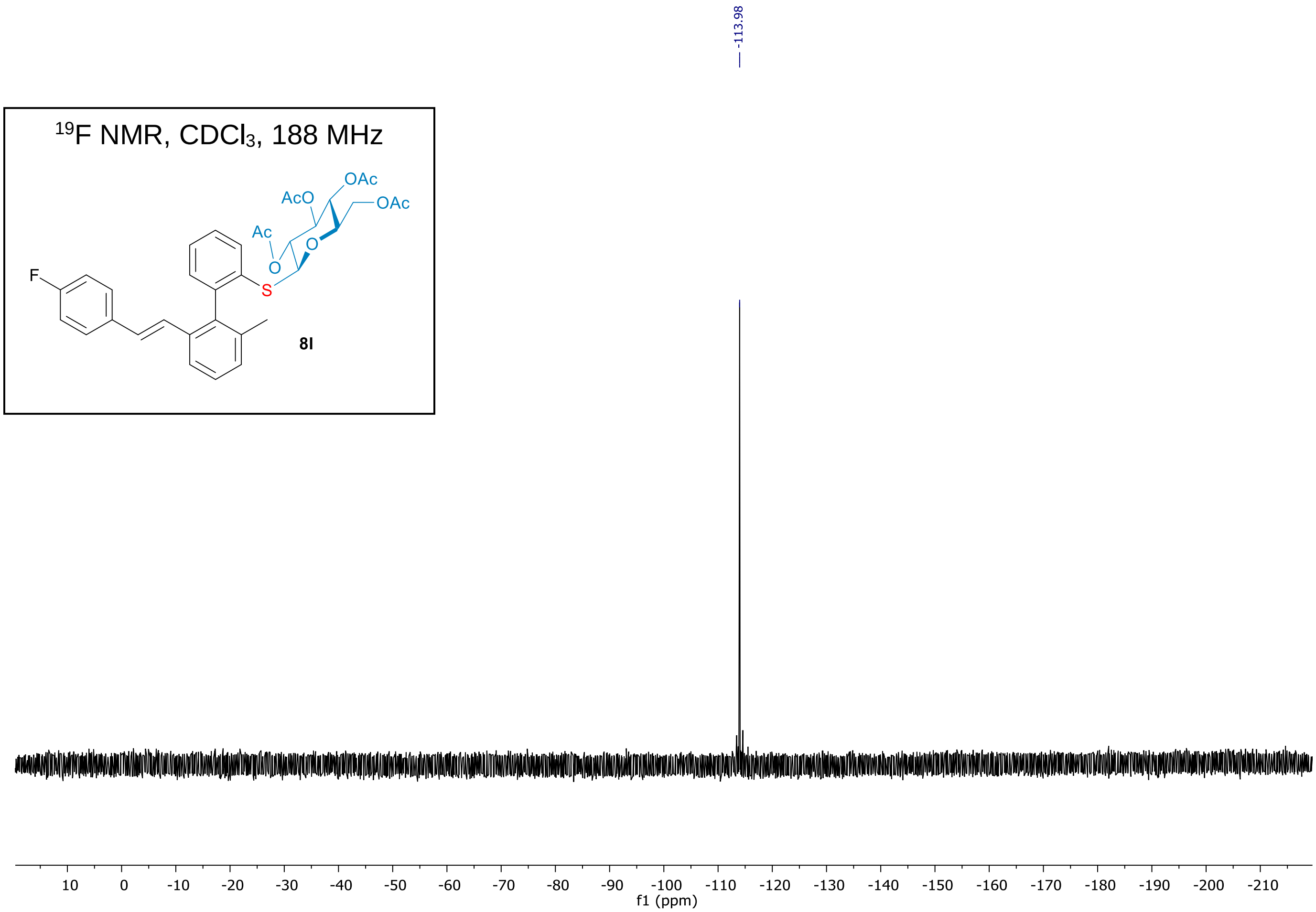

170.7
170.3
170.2
169.5
169.3
169.2
167.0
166.9
141.5
141.3
140.0
139.9
137.6
137.2
136.4
135.9
134.3
133.7
131.2
130.7
130.4
130.4
128.4
128.3
128.3
128.0
127.9
127.9
127.8
127.7
127.3
126.9
126.8
126.6
87.0
86.2
75.9
75.8
74.0
70.1
70.0
68.7
68.6
62.6
60.8
60.7
35.7
35.7
20.9
20.8
20.7
20.6
20.6
20.5
14.3
14.3
13C NMR, CDCl3, 100 MHz
AcO
OAc
OAc
Ac
O
O
S
EtO2C
8j
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

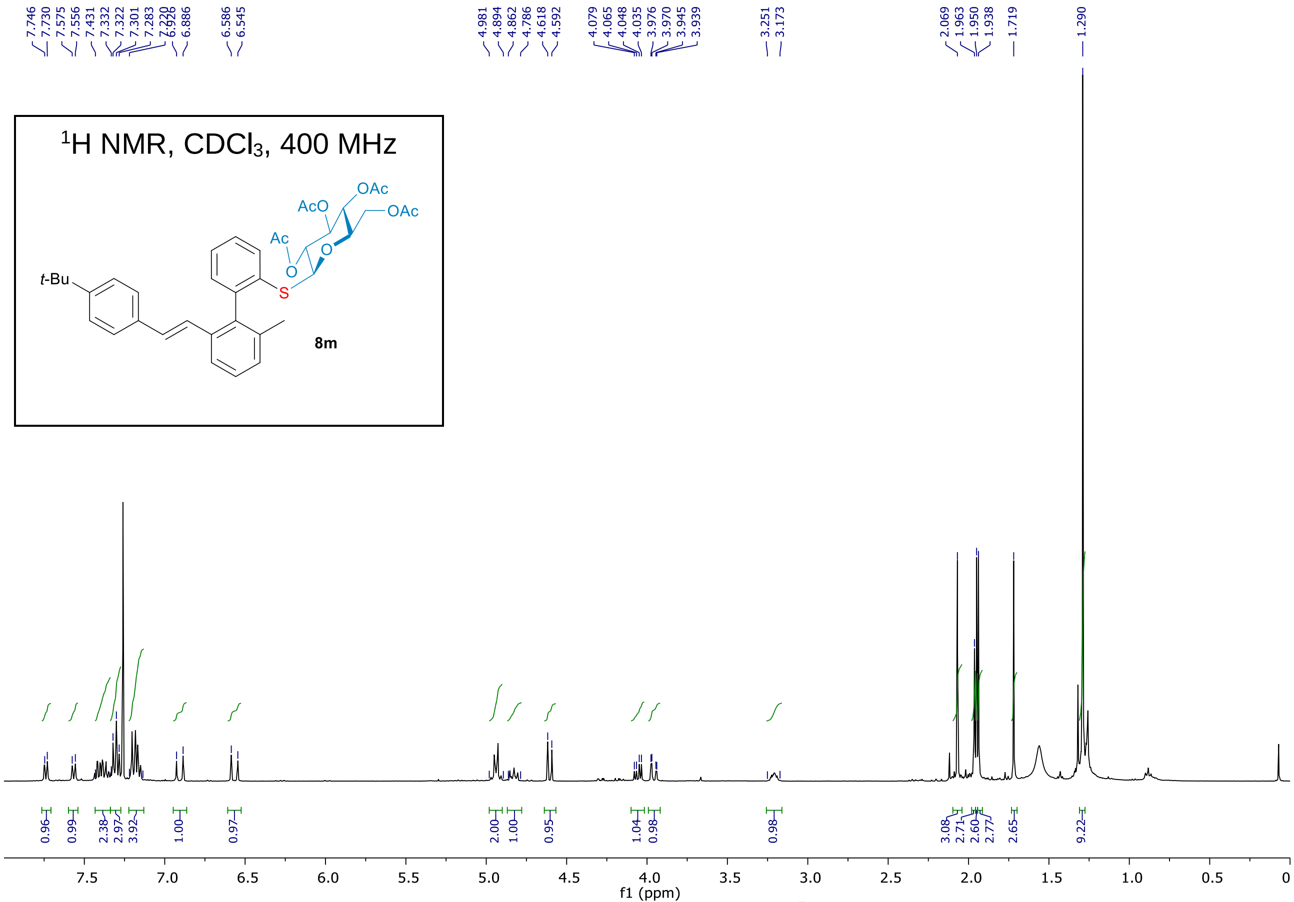

7.849
7.776
7.641
7.622
7.461
7.131
6.994
6.953
6.606
6.565
5.238
5.214
5.191
5.114
5.089
5.065
4.999
4.976
4.974
4.951
4.730
4.704
4.278
4.264
4.247
4.234
4.221
4.215
4.191
4.184
3.794
3.786
3.780
3.776
3.762
3.758
3.748
2.146
2.054
2.041
2.007
1.874
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
Ph
8k
1.00
0.99
10.84
0.98
0.95
1.01
1.05
1.04
0.99
2.07
1.02
3.11
3.14
2.93
2.96
2.93
.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
f1 (ppm)

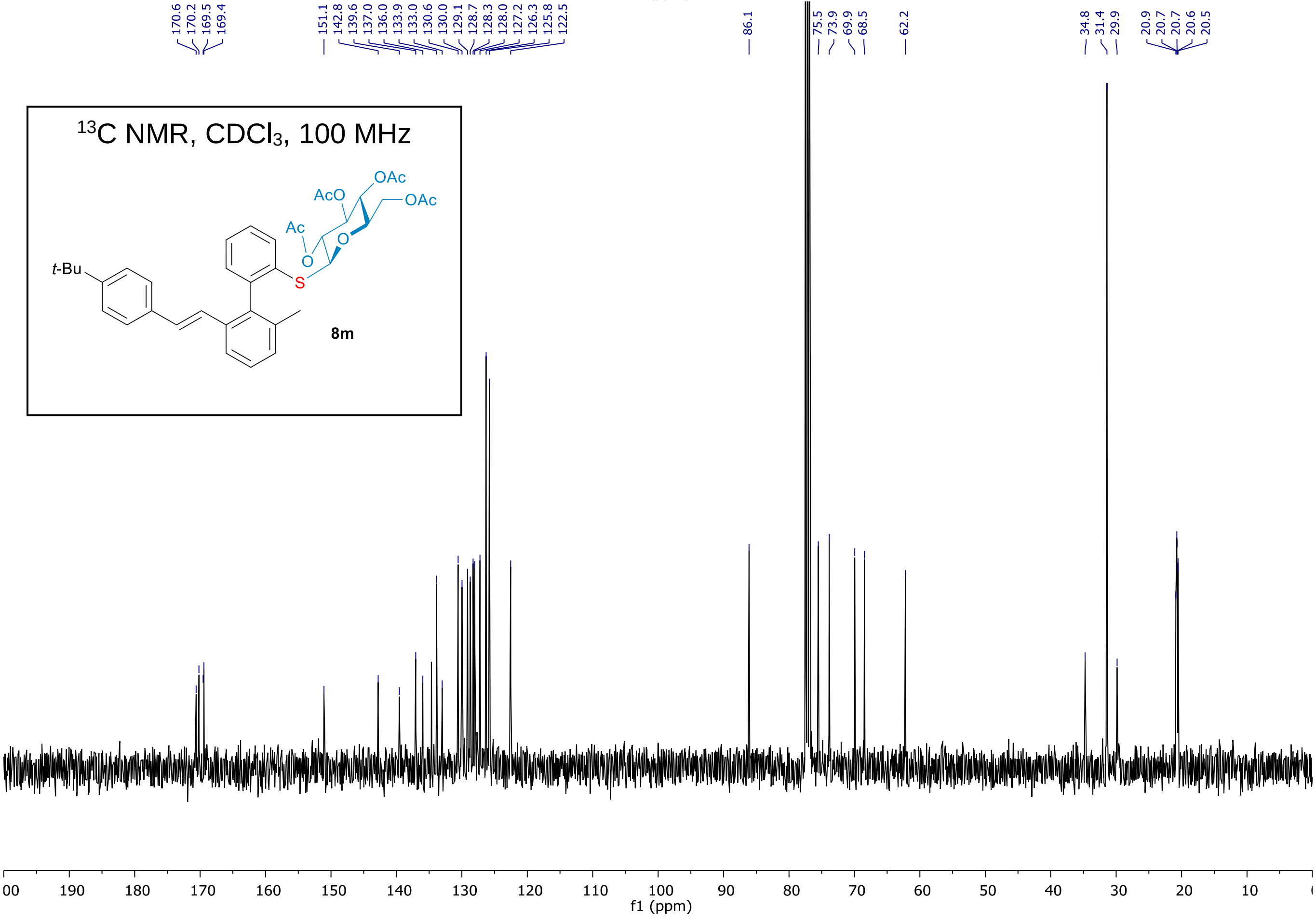

170.7
170.3
169.5
169.2
141.2
139.2
137.6
136.7
136.1
134.5
130.9
130.7
130.0
128.9
128.6
128.5
128.1
128.0
127.6
127.1
126.7
122.9
86.8
75.9
74.0
70.0
68.5
62.5
20.9
20.8
20.7
20.5
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
Ph
8k
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

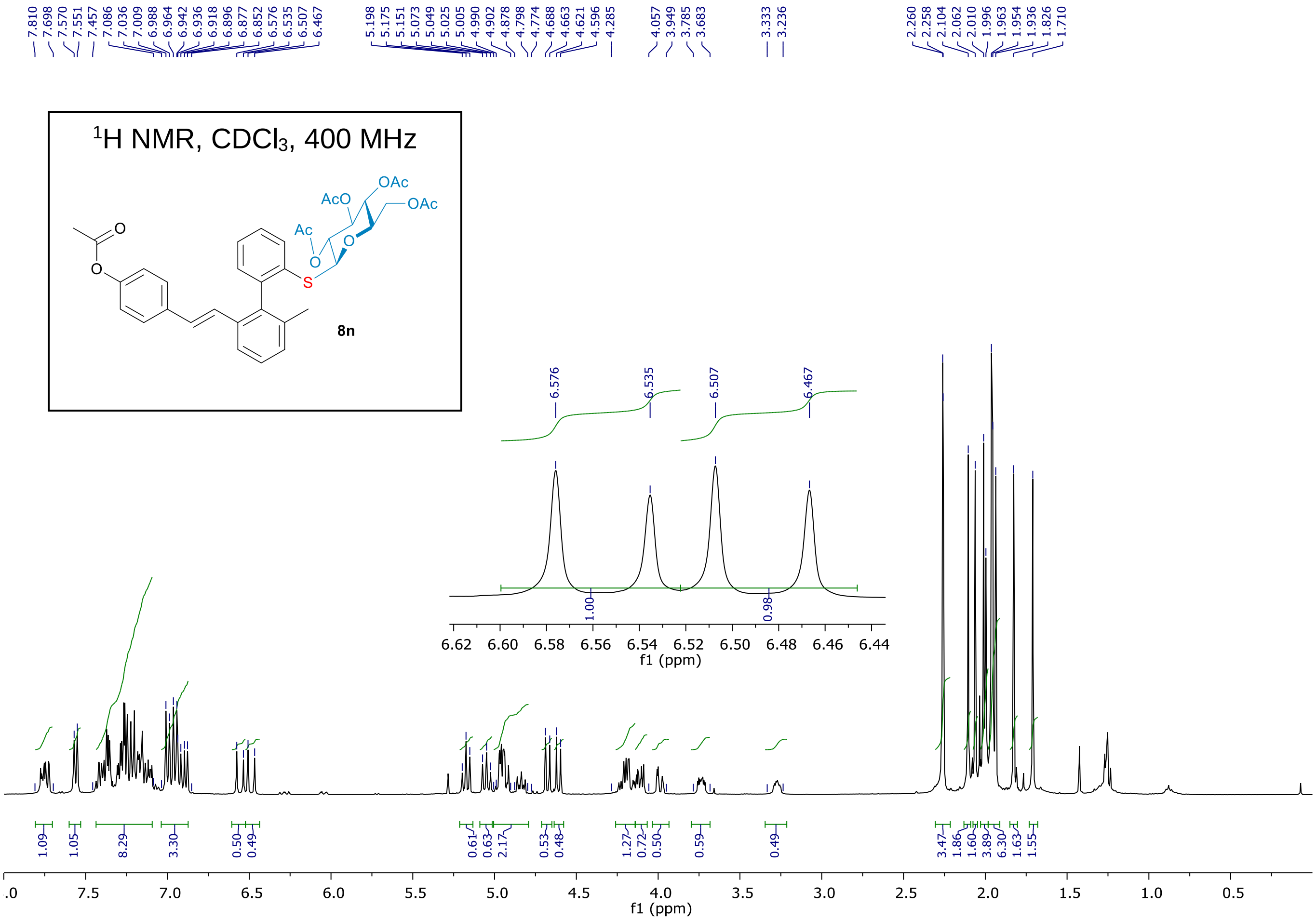

7.749
7.730
7.566
7.547
7.450
7.342
7.308
7.289
7.270
7.246
7.233
7.225
7.211
7.184
7.165
6.996
6.974
6.953
6.916
6.875
6.542
6.501
4.976
4.876
4.867
4.786
4.594
4.569
4.115
4.101
4.085
4.071
4.001
3.994
3.970
3.964
3.247
3.241
3.233
3.226
3.218
3.210
3.204
2.067
1.959
1.938
1.698
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
F
S
8l
0.89
1.01
2.28
1.29
2.00
2.00
2.16
1.10
1.00
2.15
0.93
0.95
1.12
0.91
0.93
2.97
5.59
2.89
3.03
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
f1 (ppm)

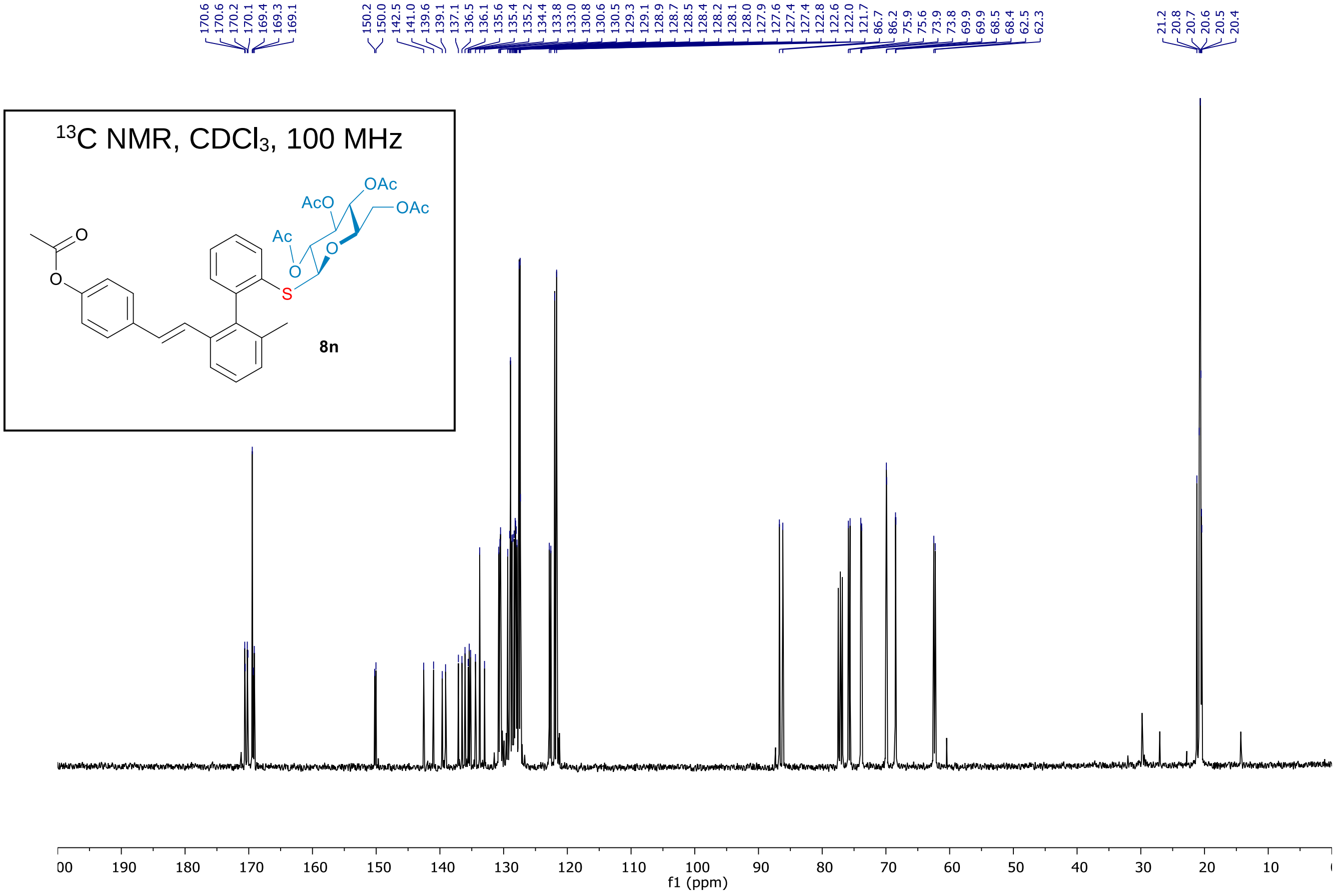

170.6
170.2
169.5
163.7
161.3
142.7
139.6
137.2
135.6
133.9
133.0
130.5
129.4
128.9
128.8
128.4
128.1
128.0
127.7
122.5
116.0
115.8
86.3
75.7
73.8
69.9
68.6
62.4
20.8
20.7
20.6
20.5
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
F
S
8l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

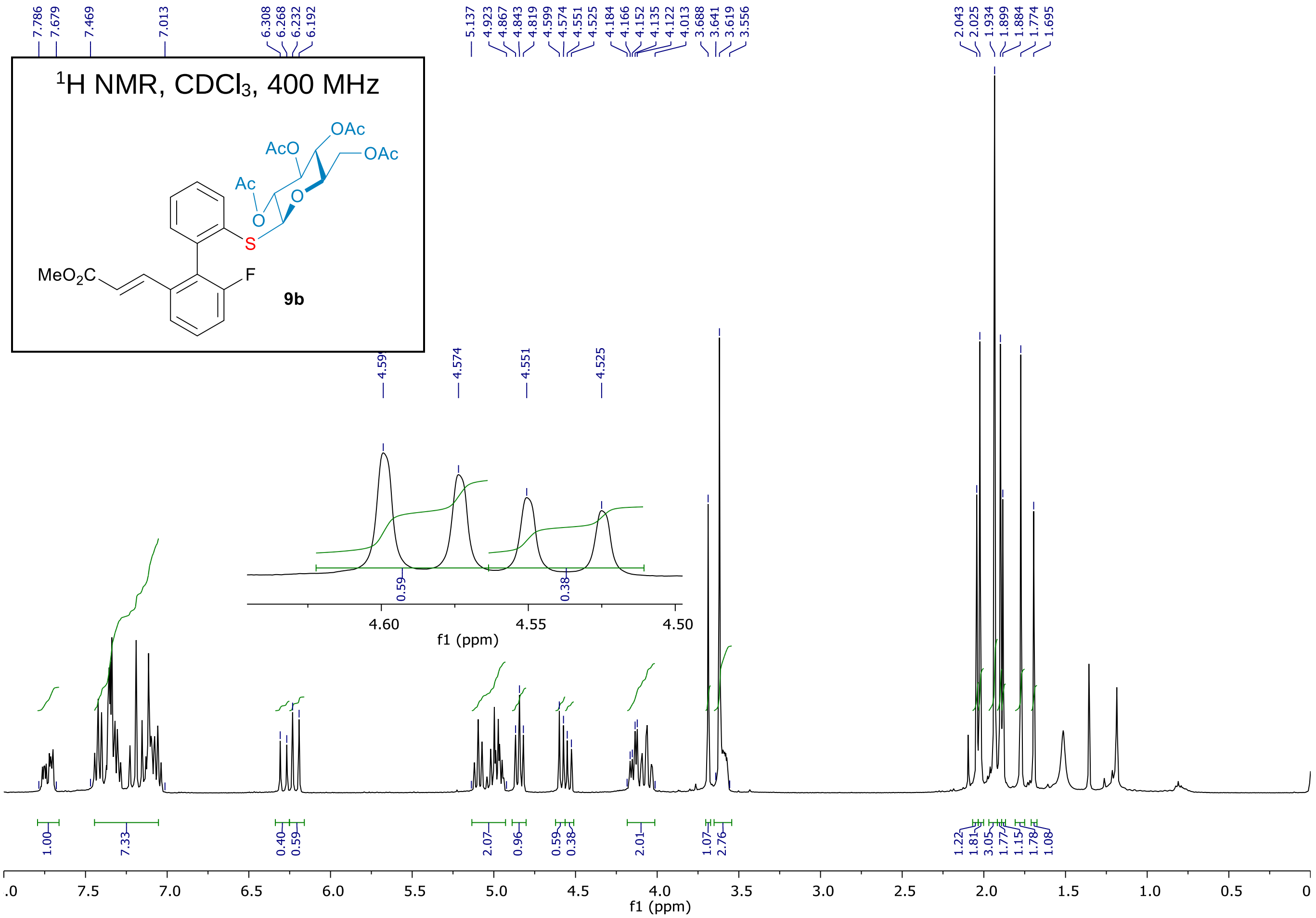

^{19}F NMR, CDCl$_3$, 188 MHz
F
Ac
O
AcO
OAc
OAc
O
S
8l
-113.98
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.746
7.730
7.575
7.556
7.431
7.332
7.322
7.301
7.283
7.220
6.926
6.886
6.586
6.545
4.981
4.894
4.862
4.786
4.618
4.592
4.079
4.065
4.048
4.035
3.976
3.970
3.945
3.939
3.251
3.173
2.069
1.963
1.950
1.938
1.719
1.290
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
t-Bu
S
8m
0.96
0.99
2.38
2.97
3.92
1.00
0.97
2.00
1.00
0.95
1.04
0.98
0.98
3.08
2.71
2.60
2.77
2.65
9.22
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
f1 (ppm)

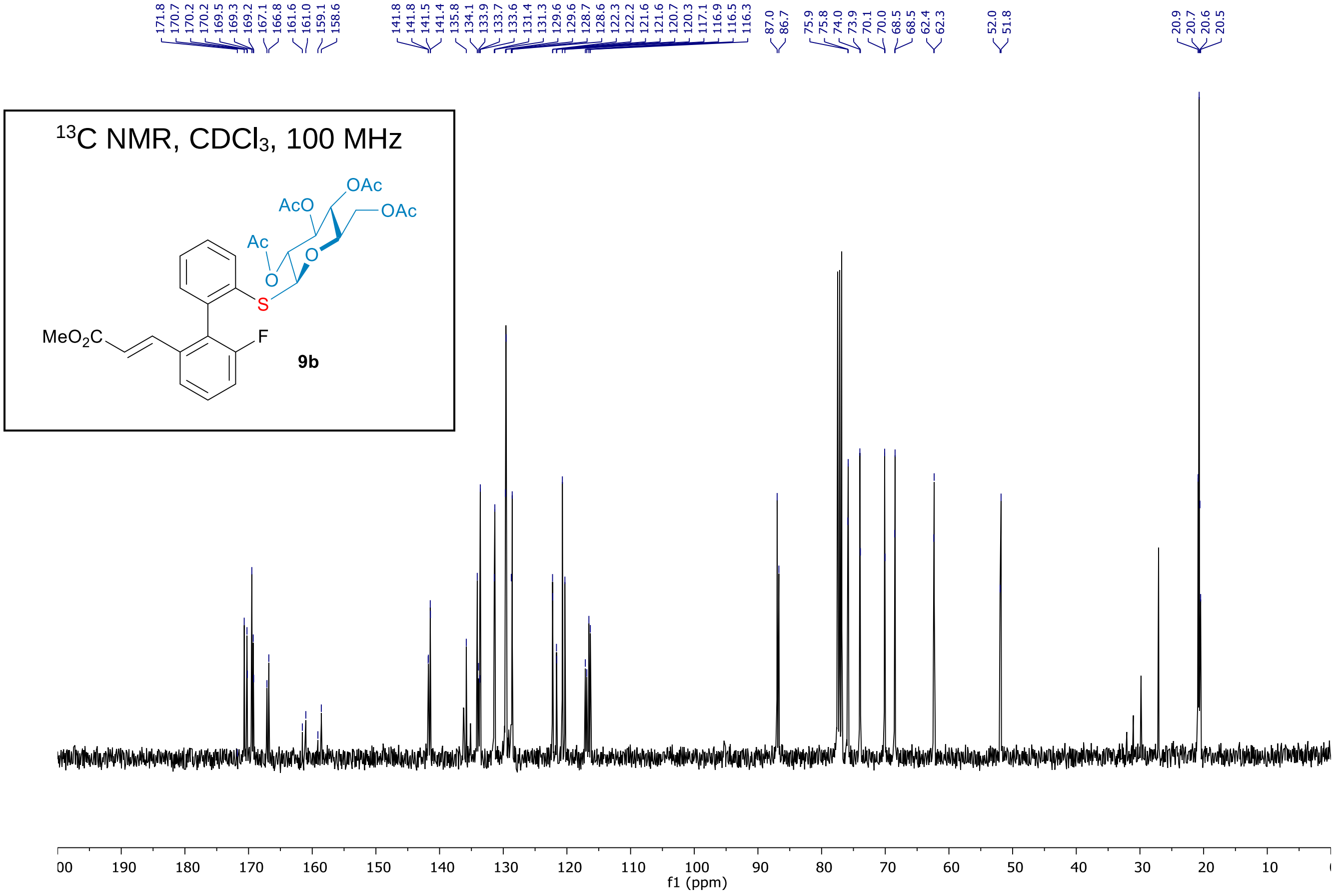

170.6
170.2
169.5
169.4
151.1
142.8
139.6
137.0
136.0
133.9
133.0
130.6
130.0
129.1
128.7
128.3
128.0
127.2
126.3
125.8
122.5
86.1
75.5
73.9
69.9
68.5
62.2
34.8
31.4
29.9
20.9
20.7
20.7
20.6
20.5
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
t-Bu
S
8m
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.810
7.698
7.570
7.551
7.457
7.086
7.036
7.009
6.988
6.964
6.942
6.936
6.918
6.896
6.877
6.852
6.576
6.535
6.507
6.467
5.198
5.175
5.151
5.073
5.049
5.025
5.005
4.990
4.902
4.878
4.798
4.774
4.688
4.663
4.621
4.596
4.285
4.057
3.949
3.785
3.683
3.333
3.236
2.260
2.258
2.104
2.062
2.010
1.996
1.963
1.954
1.936
1.826
1.710
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
O
O
S
8n
6.576
6.535
6.507
6.467
1.00
0.98
6.62 6.60 6.58 6.56 6.54 6.52 6.50 6.48 6.46 6.44
f1 (ppm)
1.09
1.05
8.29
3.30
0.50
0.49
0.61
0.63
2.17
0.53
0.48
1.27
0.72
0.50
0.59
0.49
3.47
1.86
1.60
3.89
6.30
1.63
1.55
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

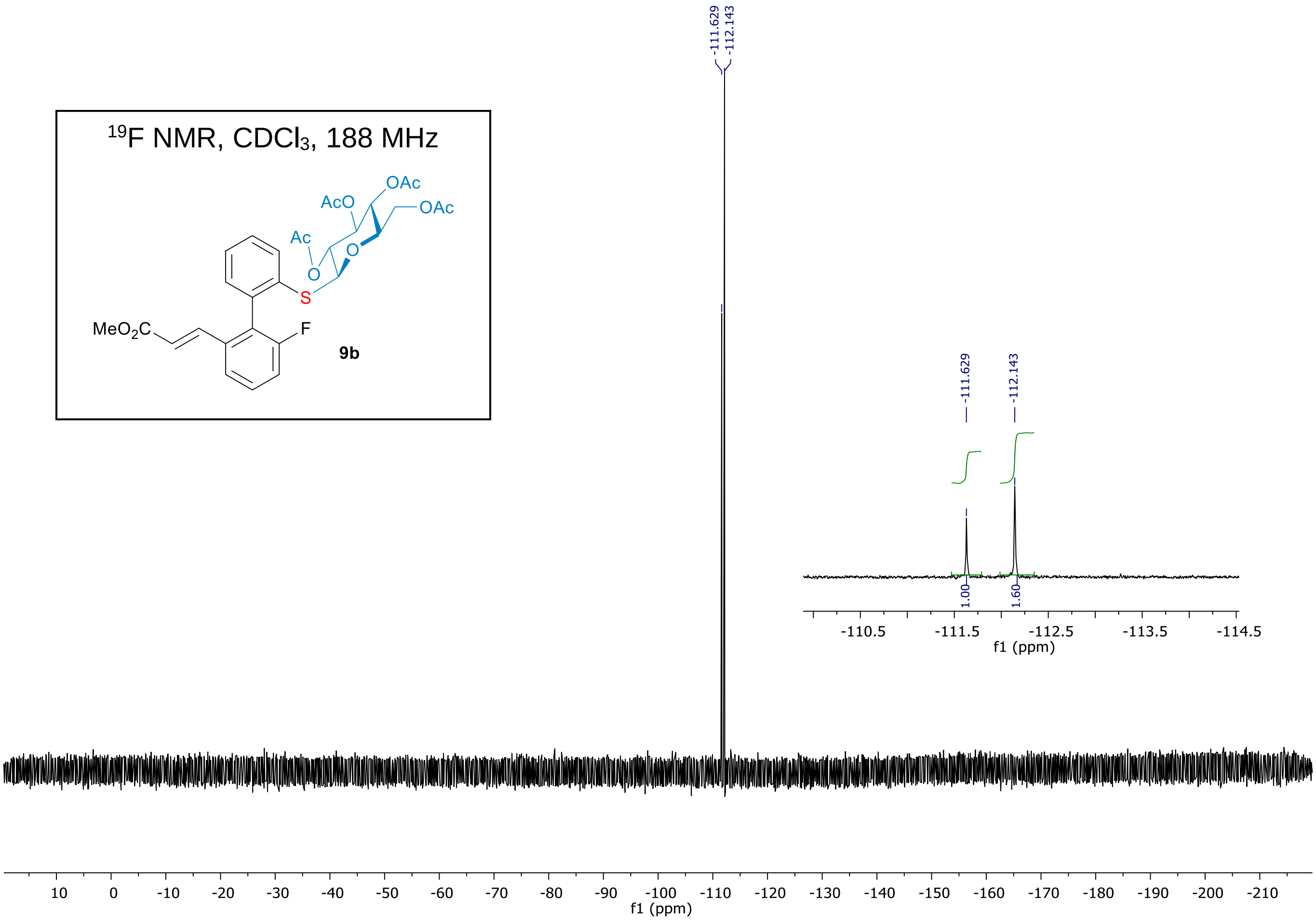

170.6
170.6
170.2
170.1
169.4
169.3
169.1
150.2
150.0
142.5
141.0
139.6
139.1
137.1
136.5
136.1
135.6
135.4
135.2
134.4
133.8
133.0
130.8
130.6
130.5
129.3
129.1
128.9
128.7
128.5
128.4
128.2
128.1
128.0
127.9
127.6
127.4
127.4
122.8
122.6
122.0
121.7
86.7
86.2
75.9
75.6
73.9
73.8
69.9
69.5
68.4
62.5
62.3
21.2
20.8
20.7
20.6
20.5
20.4
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
O
O
S
8n
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



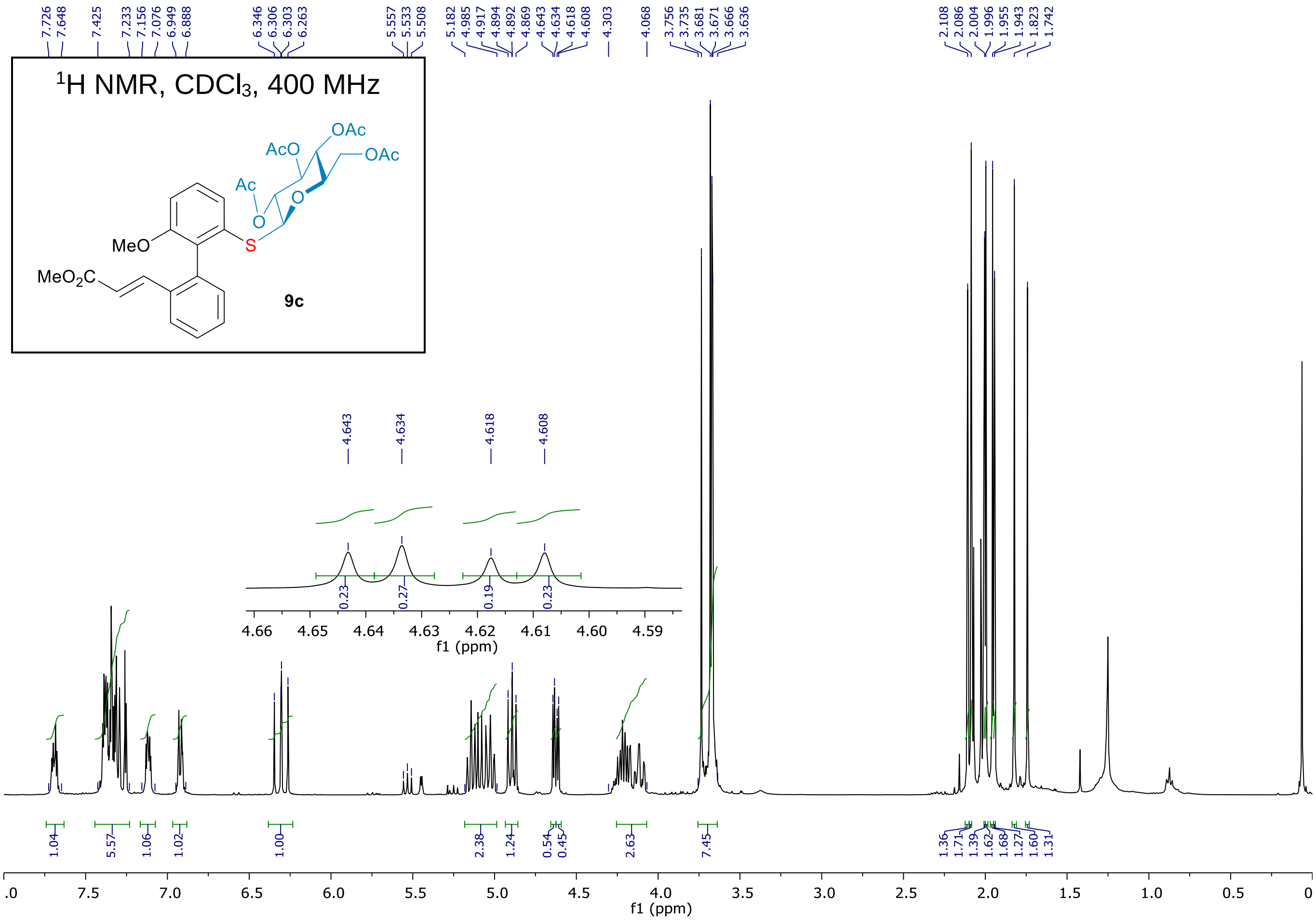
1H NMR, CDCl3, 400 MHz
9b
MeO2C
F
S
AcO
OAc
OAc
Ac
O
O
7.786
7.679
7.469
7.013
6.308
6.268
6.232
6.192
5.137
4.923
4.867
4.843
4.819
4.599
4.574
4.551
4.525
4.184
4.166
4.152
4.135
4.122
4.013
3.688
3.641
3.619
3.556
2.043
2.025
1.934
1.899
1.884
1.774
1.695
0.59
0.38
4.60
4.55
4.50
f1 (ppm)
1.00
7.33
0.40
0.59
2.07
0.96
0.59
0.38
2.01
1.07
2.76
1.22
1.81
3.05
1.77
1.15
1.78
1.08
.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
f1 (ppm)

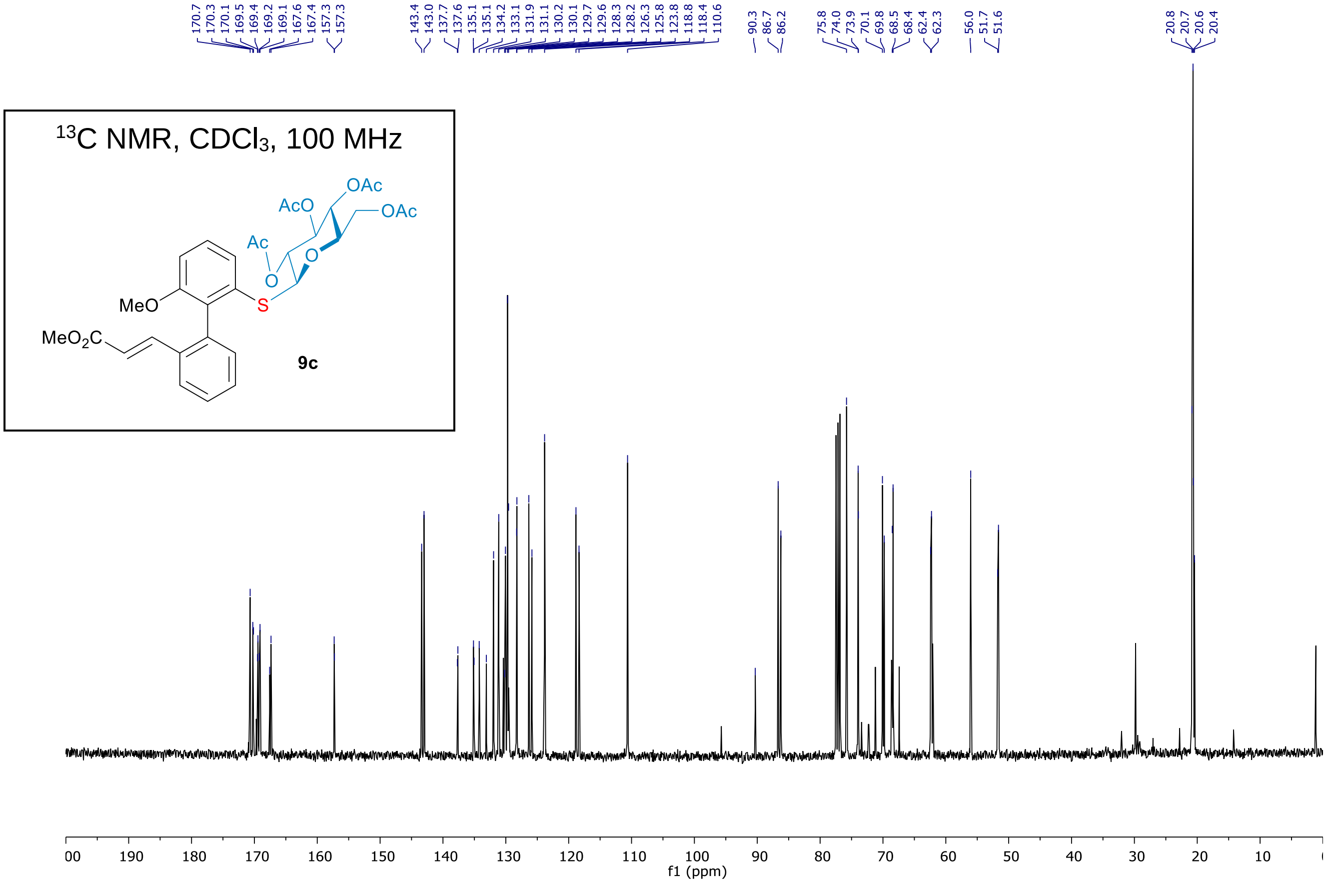


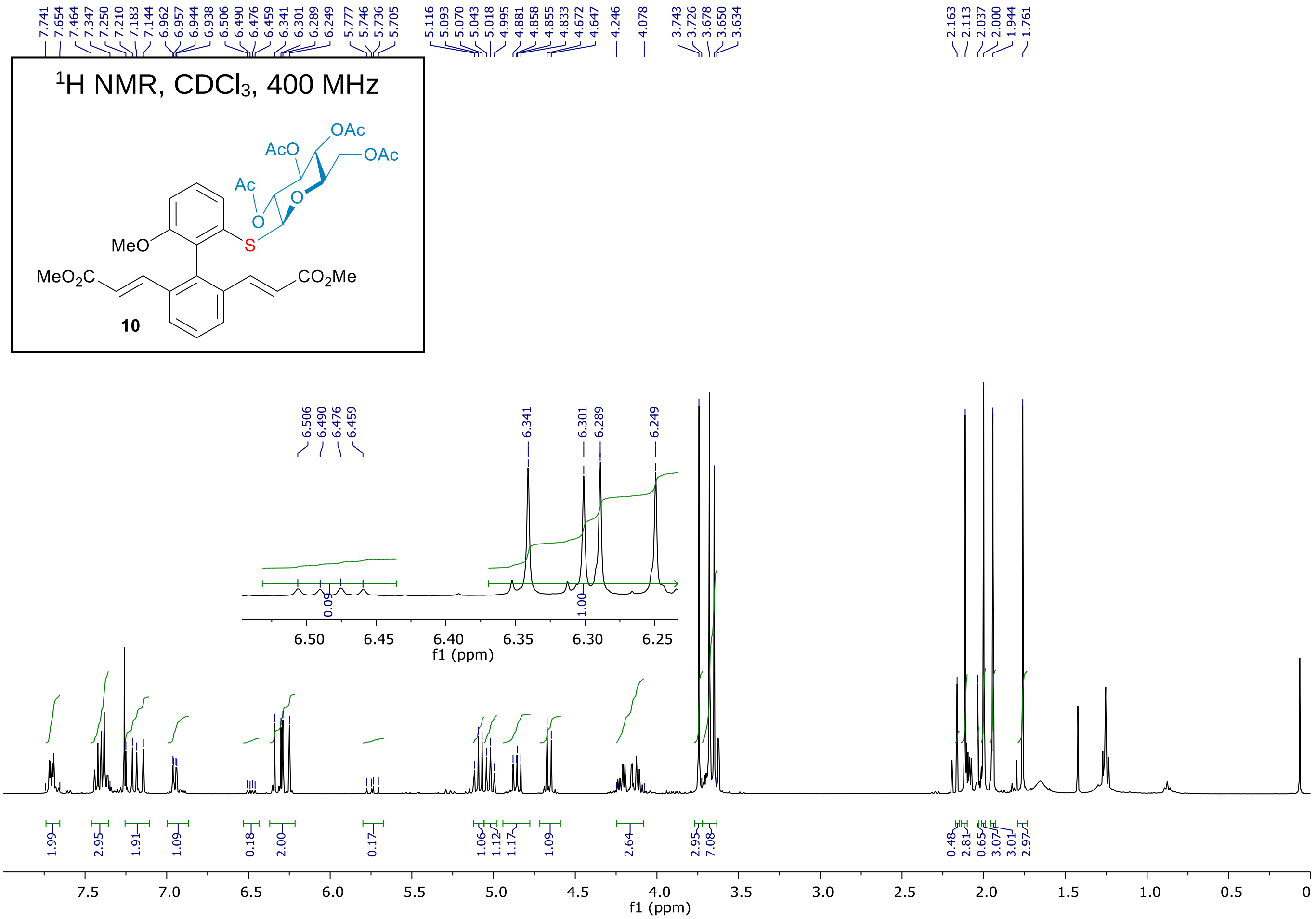
13C NMR, CDCl3, 100 MHz
9b
MeO2C
F
S
AcO
OAc
OAc
Ac
O
O
171.8
170.7
170.2
169.5
169.3
169.2
167.1
166.8
161.6
161.0
159.1
158.6
141.8
141.8
141.5
141.4
135.8
134.1
133.9
133.7
133.6
131.4
131.3
129.6
129.6
128.7
128.6
122.3
122.2
121.6
120.7
120.3
117.1
116.9
116.5
116.3
87.0
86.7
75.9
75.8
74.0
73.9
70.1
70.0
68.5
62.4
62.3
52.0
51.8
20.9
20.7
20.6
20.5
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



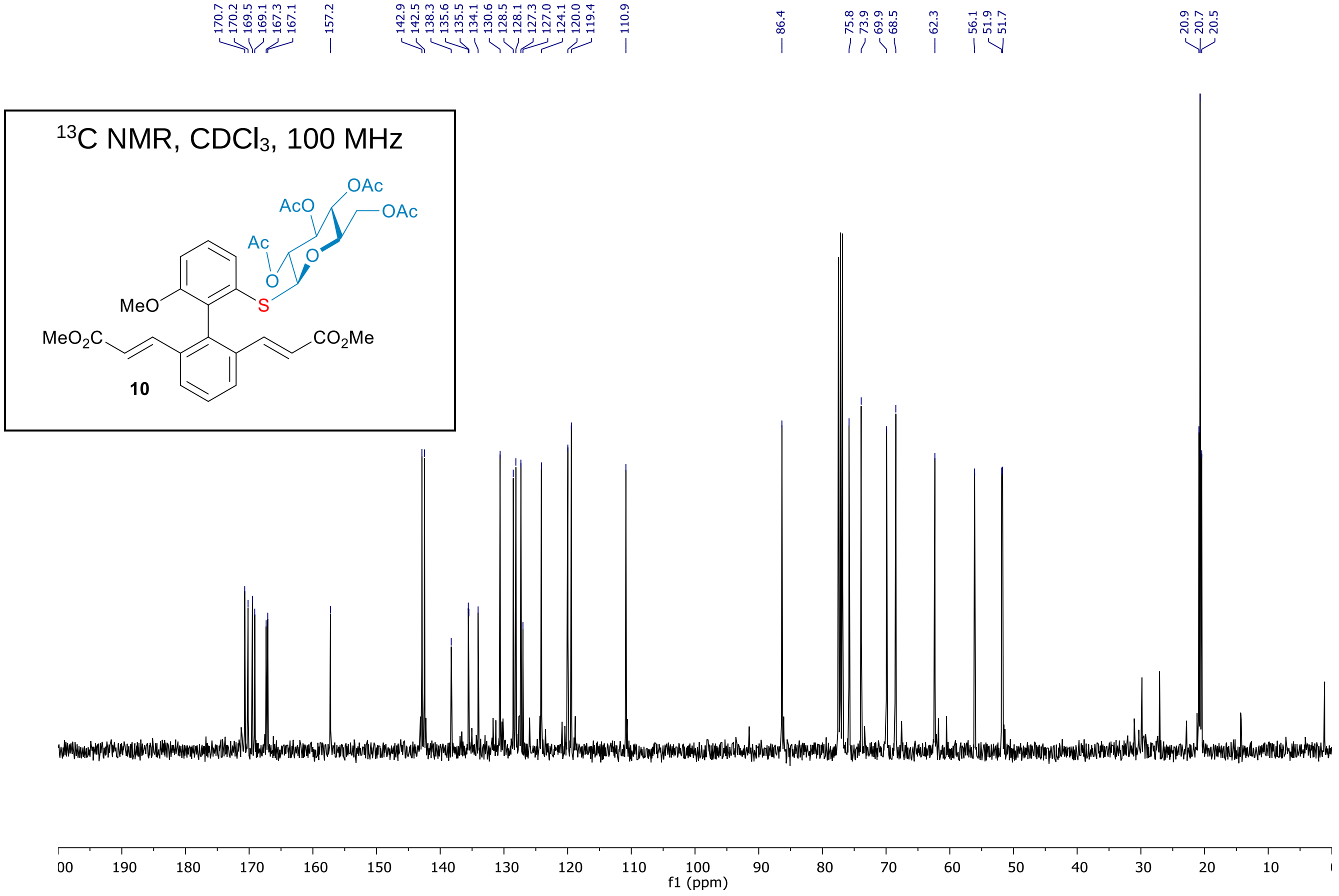
19F NMR, CDCl3, 188 MHz
OAc
AcO
OAc
Ac
O
O
S
MeO2C
F
9b
-111.629
-112.143
1.00
1.60
-110.5
-111.5
-112.5
-113.5
-114.5
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.726
7.648
7.425
7.233
7.156
7.076
6.949
6.888
6.346
6.306
6.303
6.263
5.557
5.533
5.508
5.182
4.985
4.917
4.894
4.892
4.869
4.643
4.634
4.618
4.608
4.303
4.068
3.756
3.735
3.681
3.671
3.666
3.636
2.108
2.086
2.004
1.996
1.955
1.943
1.823
1.742
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
MeO
MeO$_2$C
9c
4.643
4.634
4.618
4.608
0.23
0.27
0.19
0.23
4.66
4.65
4.64
4.63
4.62
4.61
4.60
4.59
f1 (ppm)
1.04
5.57
1.06
1.02
1.00
2.38
1.24
0.54
0.45
2.63
7.45
1.36
1.71
1.39
1.62
1.68
1.27
1.60
1.31
.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
f1 (ppm)

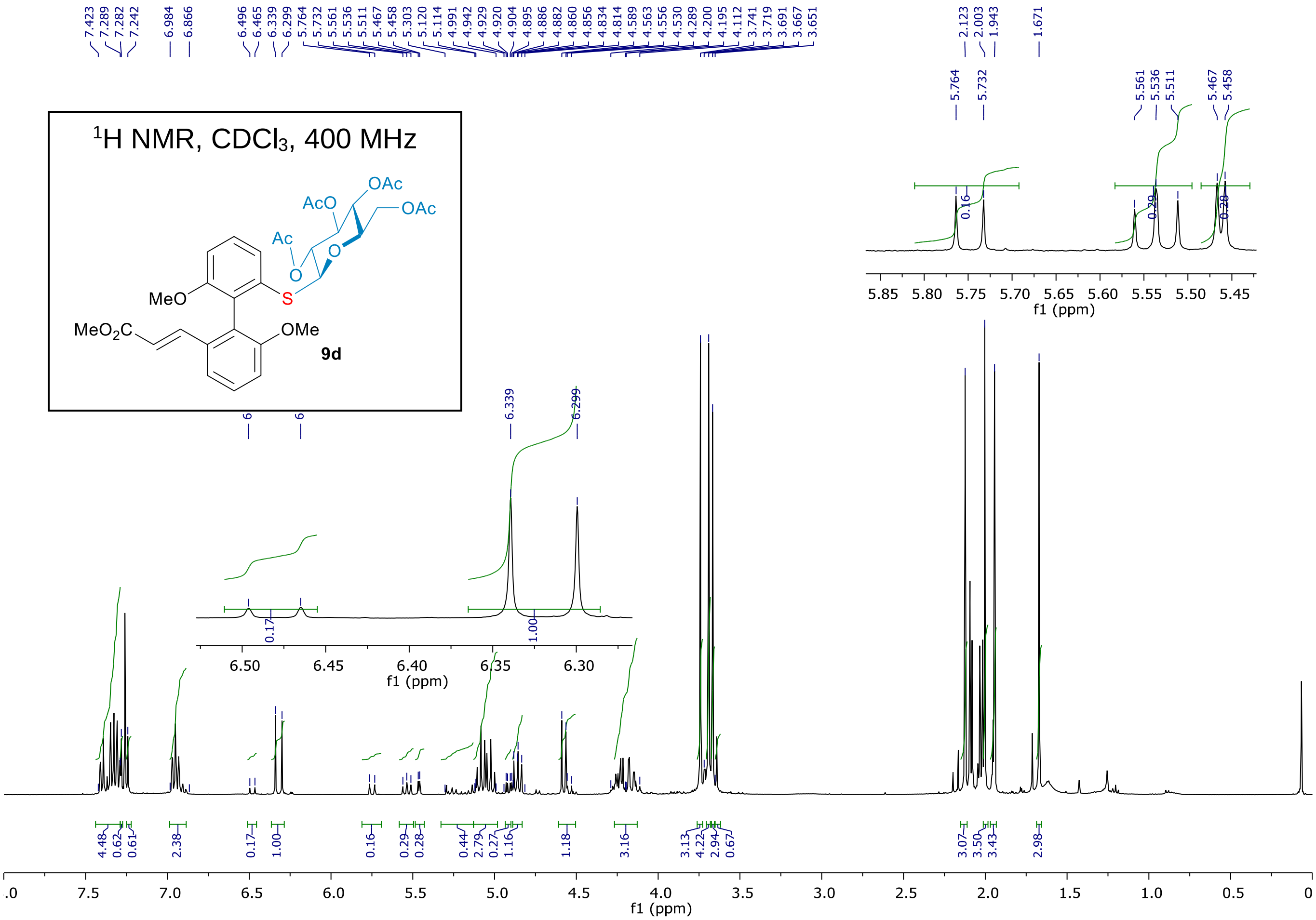

170.7
170.3
170.1
169.5
169.4
169.2
169.1
167.6
167.4
157.3
157.3
143.4
143.0
137.7
137.6
135.1
135.1
134.2
133.1
131.9
131.1
130.2
130.1
129.7
129.6
128.3
128.2
126.3
125.8
123.8
118.8
118.4
110.6
90.3
86.7
86.2
75.8
74.0
73.9
70.1
69.8
68.5
68.4
62.4
62.3
56.0
51.7
51.6
20.8
20.7
20.6
20.4
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
MeO
MeO$_2$C
9c
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



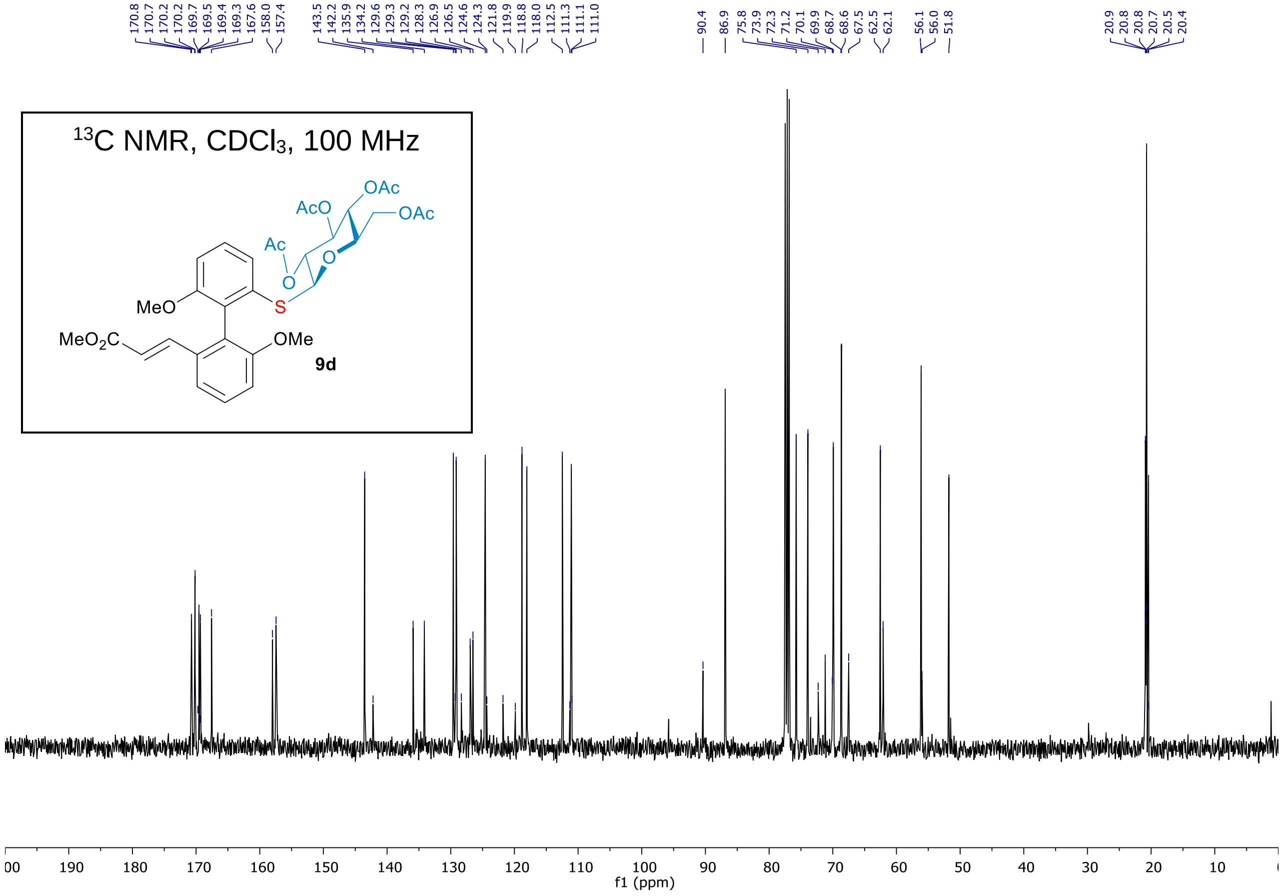
7.741
7.654
7.464
7.347
7.250
7.210
7.183
7.144
6.962
6.957
6.944
6.938
6.506
6.490
6.476
6.459
6.341
6.301
6.289
6.249
5.777
5.746
5.736
5.705
5.116
5.093
5.070
5.043
5.018
4.995
4.881
4.858
4.855
4.833
4.672
4.647
4.246
4.078
3.743
3.726
3.678
3.650
3.634
2.163
2.113
2.037
2.000
1.944
1.761
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
MeO
S
MeO$_2$C
CO$_2$Me
10
6.506
6.490
6.476
6.459
6.341
6.301
6.289
6.249
0.09
1.00
6.50
6.45
6.40
6.35
6.30
6.25
f1 (ppm)
1.99
2.95
1.91
1.09
0.18
2.00
0.17
1.06
1.12
1.17
1.09
2.64
2.95
7.08
0.48
2.81
0.65
3.07
3.01
2.97
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
f1 (ppm)



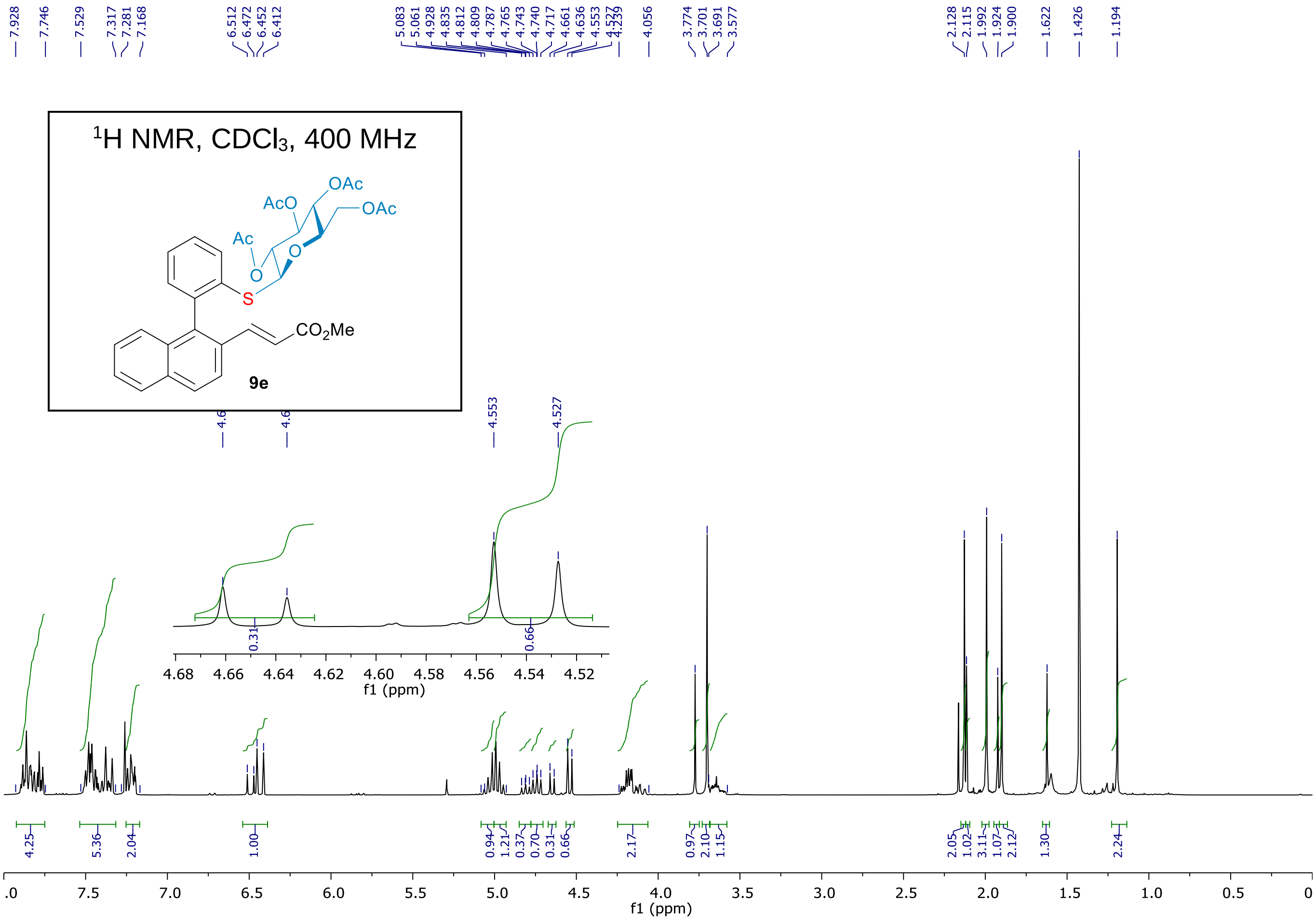
170.7
170.2
169.5
169.1
167.3
167.1
157.2
142.9
142.5
138.3
135.6
135.5
134.1
130.6
128.5
128.1
127.3
127.0
124.1
120.0
119.4
110.9
86.4
75.8
73.9
69.9
68.5
62.3
56.1
51.9
51.7
20.9
20.7
20.5
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
MeO
S
MeO$_2$C
CO$_2$Me
10
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

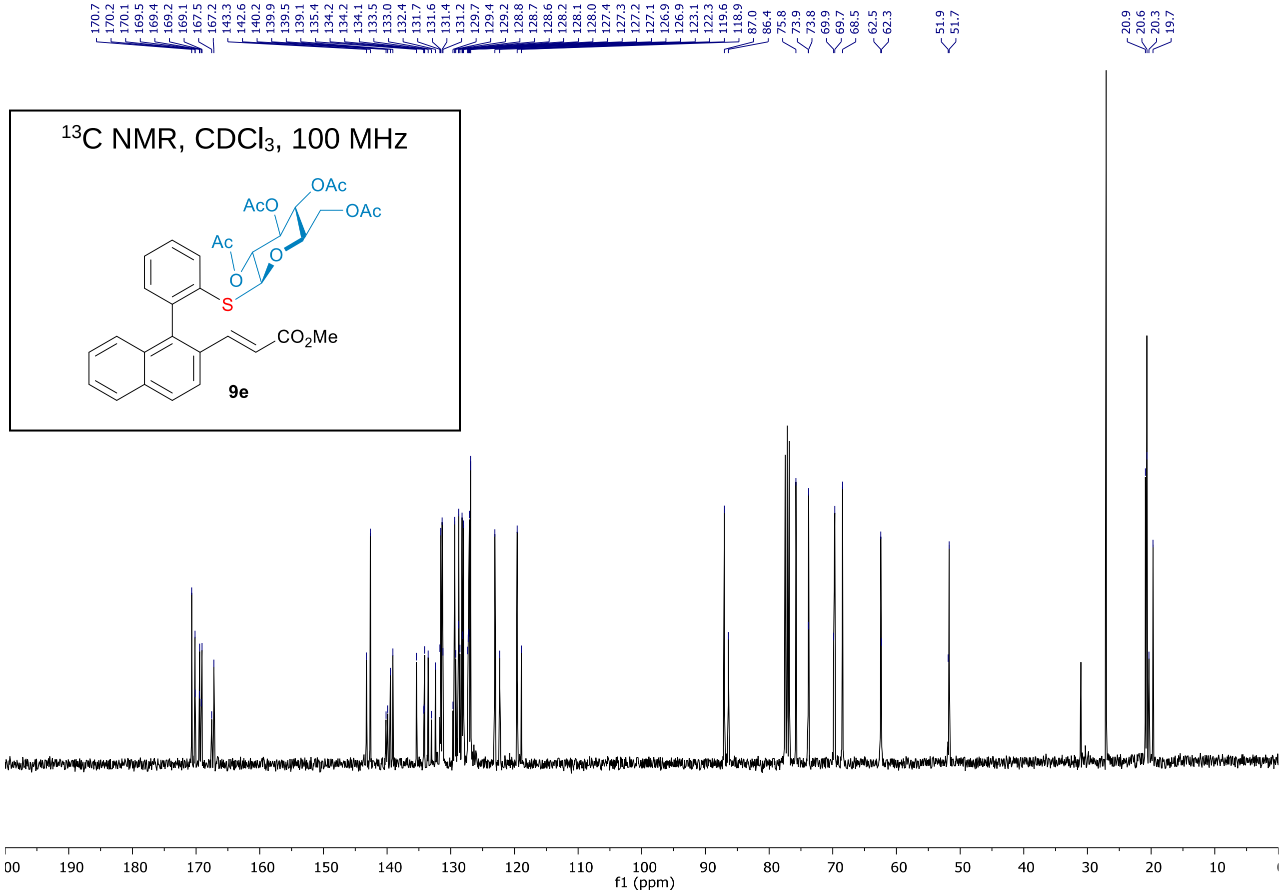


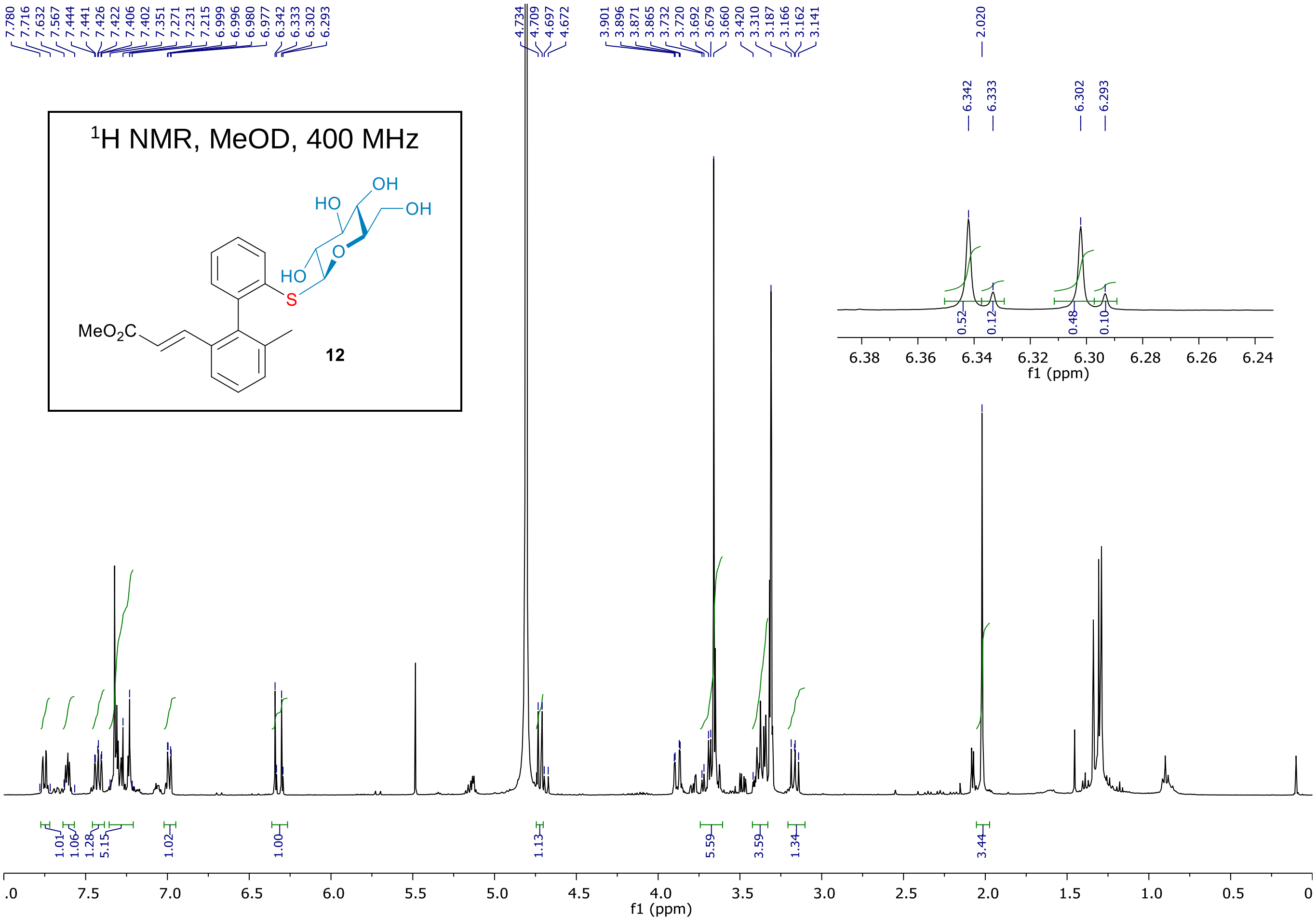
1H NMR, CDCl3, 400 MHz
AcO
OAc
OAc
Ac
O
O
S
MeO
MeO2C
OMe
9d
7.423 7.289 7.282 7.242 6.984 6.866 6.496 6.465 6.339 6.299 5.764 5.732 5.561 5.536 5.511 5.467 5.458 5.303 5.120 5.114 4.991 4.942 4.929 4.920 4.904 4.895 4.886 4.882 4.860 4.856 4.834 4.814 4.589 4.563 4.556 4.530 4.289 4.200 4.195 4.112 3.741 3.719 3.691 3.667 3.651 2.123 2.003 1.943 1.671
4.48 0.62 0.61 2.38 0.17 1.00 0.16 0.29 0.28 0.44 2.79 0.27 1.16 1.18 3.16 3.13 4.22 2.94 0.67 3.07 3.50 3.43 2.98
f1 (ppm)



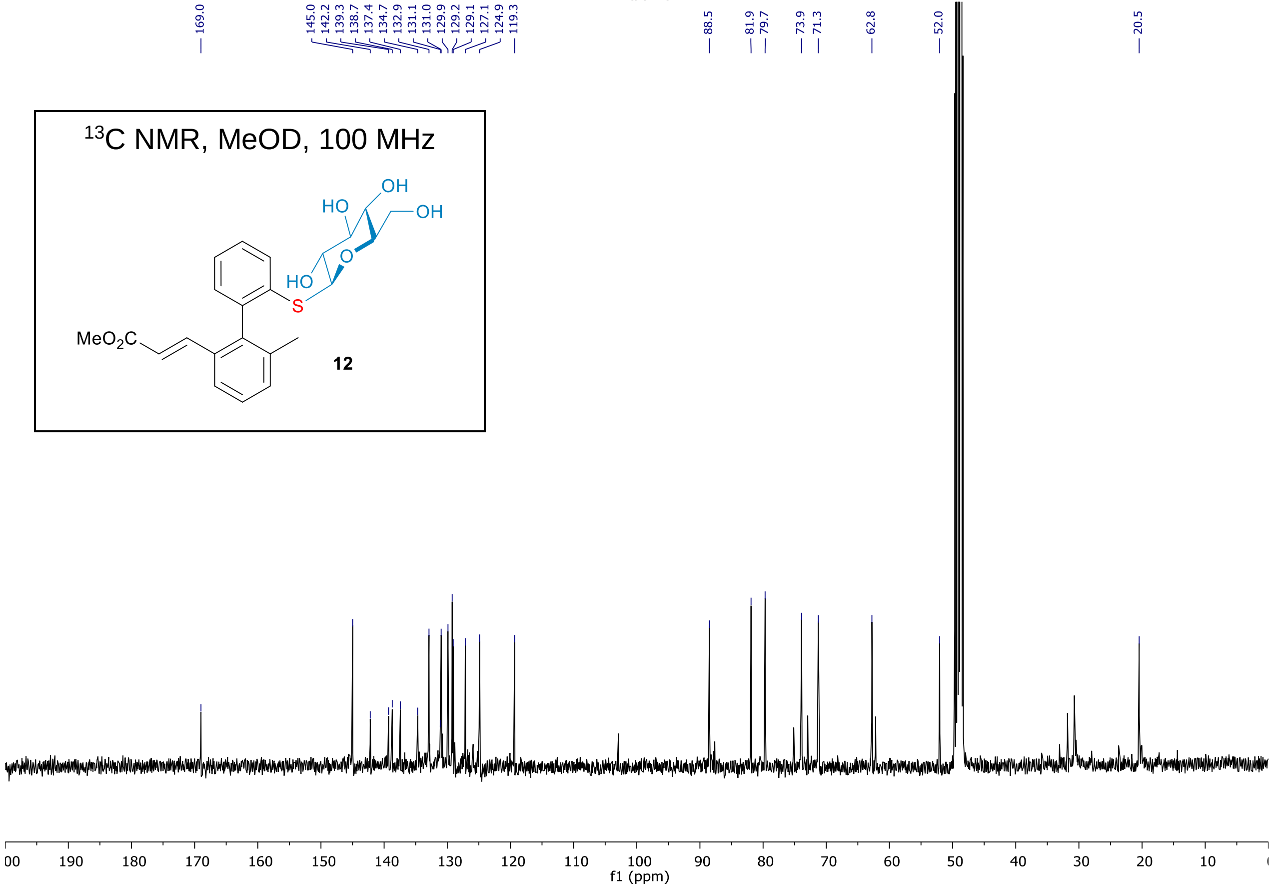
13C NMR, CDCl3, 100 MHz
AcO
OAc
OAc
Ac
O
O
S
MeO
MeO2C
OMe
9d
170.8 170.7 170.2 170.2 169.7 169.5 169.4 169.3 167.6 158.0 157.4 143.5 142.2 135.9 134.2 129.6 129.3 129.2 128.3 126.9 126.5 124.6 124.3 121.8 119.9 118.8 118.0 112.5 111.3 111.1 111.0 90.4 86.9 75.8 73.9 72.3 71.2 70.1 69.9 68.7 68.6 67.5 62.5 62.1 56.1 56.0 51.8 20.9 20.8 20.8 20.7 20.5 20.4
f1 (ppm)


7.928
7.746
7.529
7.317
7.281
7.168
6.512
6.472
6.452
6.412
5.083
5.061
4.928
4.835
4.812
4.809
4.787
4.765
4.743
4.740
4.717
4.661
4.636
4.553
4.527
4.239
4.056
3.774
3.701
3.691
3.577
2.128
2.115
1.992
1.924
1.900
1.622
1.426
1.194
^{1}H NMR, CDCl$_3$, 400 MHz
OAc
AcO
OAc
Ac
O
O
S
CO$_2$Me
9e
4.553
4.527
0.31
0.66
4.68
4.66
4.64
4.62
4.60
4.58
4.56
4.54
4.52
f1 (ppm)
4.25
5.36
2.04
1.00
0.94
1.21
0.37
0.70
0.31
0.66
2.17
0.97
2.10
1.15
2.05
1.02
3.11
1.07
2.12
1.30
2.24
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
f1 (ppm)


170.7
170.2
170.1
169.5
169.4
169.2
169.1
167.5
167.2
143.3
142.6
140.2
139.9
139.5
139.1
135.4
134.2
134.1
133.5
133.0
132.4
131.7
131.6
131.4
131.2
129.7
129.4
129.2
128.8
128.7
128.6
128.2
128.1
128.0
127.4
127.3
127.2
127.1
126.9
126.9
123.1
122.3
119.6
118.9
87.0
86.4
75.8
73.9
73.8
69.9
69.7
68.5
62.5
62.3
51.9
51.7
20.9
20.6
20.3
19.7
^{13}C NMR, CDCl$_3$, 100 MHz
OAc
AcO
OAc
Ac
O
O
S
CO$_2$Me
9e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



^{1}H NMR, MeOD, 400 MHz
HO
OH
OH
O
HO
S
MeO$_2$C
12
7.780 7.716 7.632 7.567 7.444 7.441 7.426 7.422 7.406 7.402 7.351 7.271 7.231 7.215 6.999 6.996 6.980 6.977 6.342 6.333 6.302 6.293
4.734 4.709 4.697 4.672
3.901 3.896 3.871 3.865 3.732 3.720 3.692 3.679 3.660 3.420 3.310 3.187 3.166 3.162 3.141
2.020
6.342 6.333 6.302 6.293
0.52 0.12 0.48 0.10
6.38 6.36 6.34 6.32 6.30 6.28 6.26 6.24
f1 (ppm)
1.01 1.06 1.28 5.15 1.02 1.00 1.13 5.59 3.59 1.34 3.44
.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
f1 (ppm)



^{13}C NMR, MeOD, 100 MHz
HO
OH
OH
O
HO
S
MeO$_2$C
12
169.0
145.0 142.2 139.3 138.7 137.4 134.7 132.9 131.1 131.0 129.9 129.2 129.1 127.1 124.9 119.3
88.5
81.9 79.7
73.9 71.3
62.8
52.0
20.5
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

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