Supplementary Information

Regiodivergent Glycosylations of 6-deoxy-Erythronolide B and Oleandomycin-Derived Macrolides Enabled by Chiral Acid Catalysis

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Part I – Experimental Procedures, Results, Mechanistic Studies, Characterization Data and Supporting NMRs

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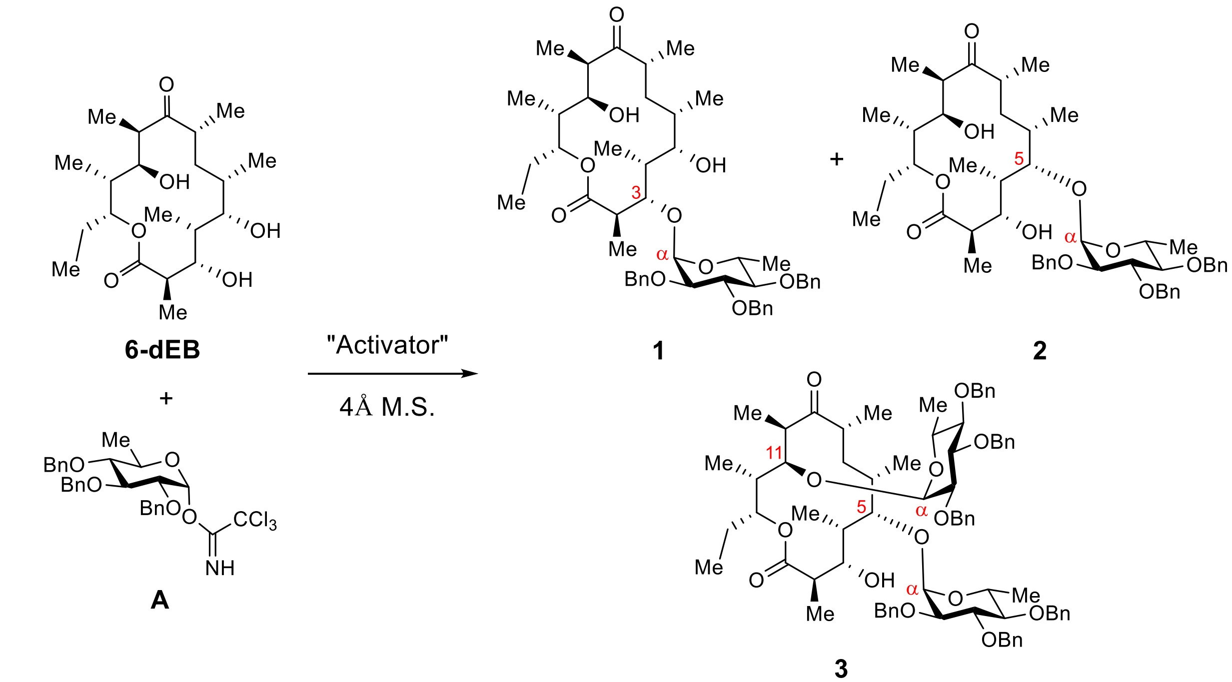
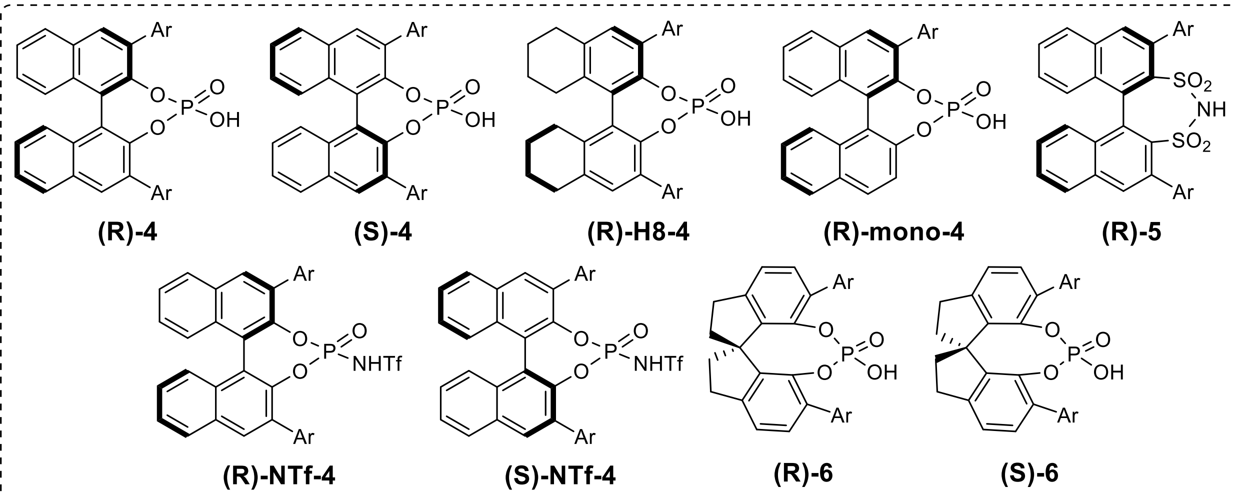
Summary of Experimental Results

SI-Table 1: Optimization for glycosylation of 6-dEB with donor A



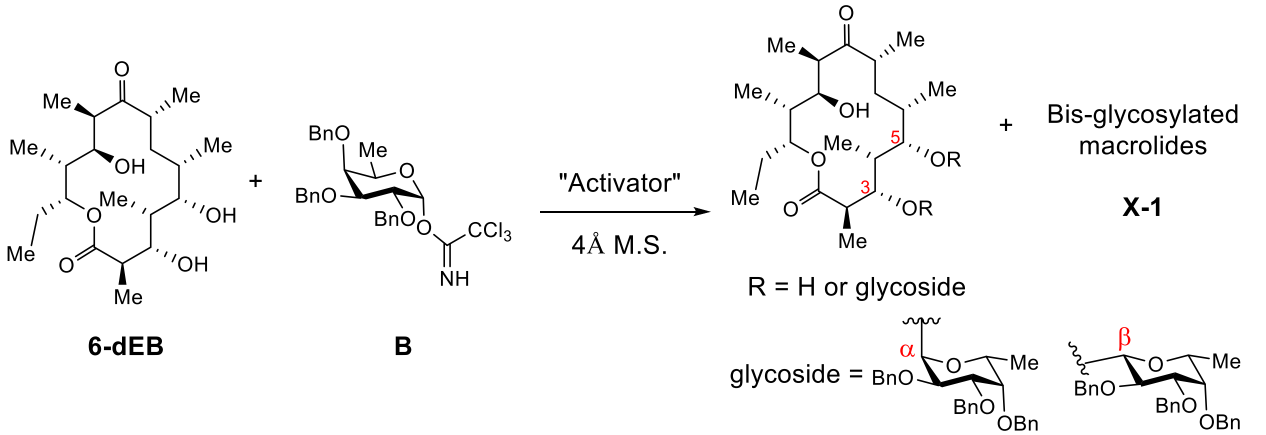


a : Ar = 2,6-iPr-4-Ad-Ph
b : Ar = 2,4,6-iPr-Ph
c : Ar = C_6F_5
d : Ar = 3,5-CF_3-Ph
e : Ar = 3,5-Cl-Ph
f : Ar = 3,5-F-Ph
g : Ar = 2,5-CF_3-Ph
h : Ar = 2,4-CF_3-Ph
i : Ar = 3,5-SF_5-Ph

Entry	Activator (mol%)	Solvent (conc.)	T (°C)	t (h)	Yield	1 : 2 : 3
1	TMS-OTf (20)	PhMe (0.05 M)	-20	17	57%	0 : 88 : 12
2	PhO_2PO_2H (50)	CH_2Cl_2 (0.05 M)	r.t.	26	30%	21 : 79 : 0
3	PhO_2PO_2H (50)	PhMe (0.05 M)	r.t.	26	35%	15 : 85 : 0
4	*p*-TsOH (20)	PhMe (0.05 M)	r.t.	26	<10%	17 : 83 : 0
5	BF_3•OEt_2 (20)	PhMe (0.05 M)	-20	24	59%	34 : (66)[a] : 0
6	**(R)-4a** (20)	CH_2Cl_2 (0.05 M)	r.t.	30	13%	13 : 87 : 0
7	**(R)-4b** (20)	CH_2Cl_2 (0.05 M)	r.t.	30	13%	17 : 83 : 0
8	**(R)-4c** (20)	PhMe (0.10 M)	r.t.	24	57%	25 : 75 : 0
9	**(R)-4d** (20)	PhMe (0.20 M)	r.t.	30	82%	35 : 65 : 0
10	**(R)-4d** (20)	CH_2Cl_2 (0.05 M)	r.t.	26	50%	50 : 50 : 0
11	**(S)-4d** (20)	PhMe (0.20 M)	r.t.	30	98%	1 : 99 : 0
12	**(R)-4e** (20)	PhMe (0.10 M)	r.t.	24	80%	52 : 48 : 0
13	**(R)-4f** (20)	CH_2Cl_2 (0.05 M)	r.t.	48	51%	69 : 31 : 0
14	**(R)-4g** (20)	PhMe (0.10 M)	r.t.	24	57%	40 : 60 : 0
15	**(R)-4h** (20)	PhMe (0.10 M)	r.t.	24	48%	21 : 79 : 0
16	**(R)-4i** (20)	PhMe (0.10 M)	r.t.	24	46%	6 : 94 : 0
17	**(S)-4i** (20)	PhMe (0.10 M)	r.t.	24	69%	3 : 97 : 0
18	**(R)-H8-4d** (20)	PhMe (0.10 M)	r.t.	24	57%	36 : 64 : 0
19	**(R)-H8-4g** (20)	PhMe (0.10 M)	r.t.	24	34%	37 : 63 : 0
20	**(R)-mono-4c** (20)	PhMe (0.10 M)	r.t.	24	50%	23 : 77 : 0
21	**(R)-NTf-4d** (20)	CH_2Cl_2 (0.05 M)	r.t.	24	95%	13 : 87 : 0
22	**(S)-NTf-4d** (20)	CH_2Cl_2 (0.05 M)	r.t.	24	51%	4 : 96 ; 0
23	**(R)-5d** (20)	PhMe (0.10M)	r.t.	24	71%	1 : 99 : 0
24	**(R)-6f** (20)	PhMe (0.10 M)	r.t.	48	75%	7 : 93 : 0
25	**(S)-6f** (20)	PhMe (0.10 M)	r.t.	48	54%	60 : 40 : 0
26	**(S)-6f** (20)	$PhCF_3$ (0.10 M)	r.t.	64	83%	63 : 37 : 0
27	**(S)-6f** (20)	CH_2Cl_2 (0.10 M)	r.t.	64	57%	71 : 29 : 0
28	**(S)-6f** (30)	CH_2Cl_2 (0.10 M)	r.t.	72	82%	73 : 27 : 0

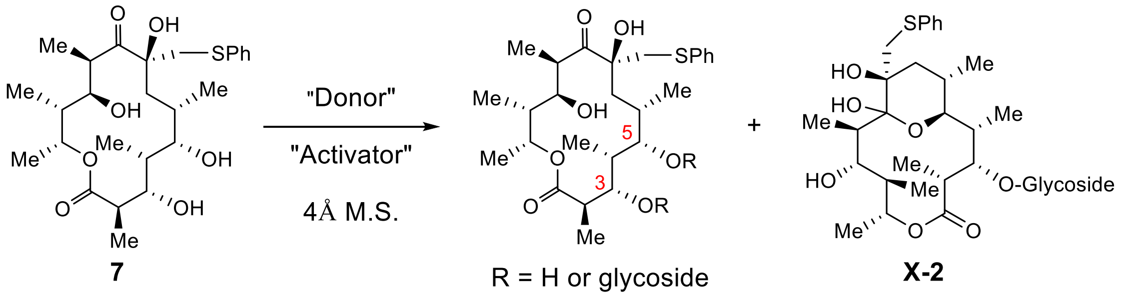
[a] mixture of $\alpha:\beta = 2.9:1$

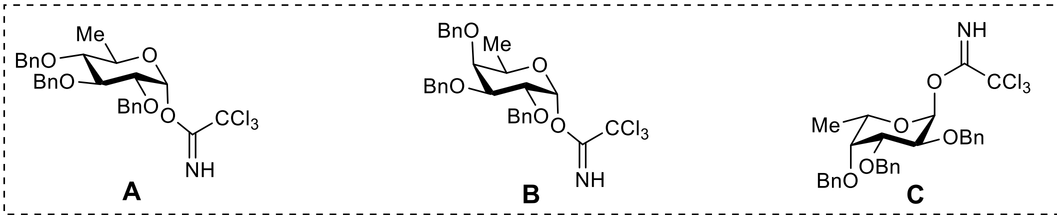
SI-Table 2: Glycosylation of 6-dEB with donor B



Entry	Activator (mol%)	Solvent (conc.)	T (°C)	t (h)	Yield	C_3-gly. (α:β)	:	C_5-gly. (α:β)	:	X-1
1	TMS-OTf (20)	PhMe (0.05 M)	-20	17	92%	0	:	69 (1.8:1)	:	31
2	**(S)-4d** (20)	PhMe (0.20 M)	r.t.	48	82%	1	:	99 (1.7:1)	:	0
3	**(S)-6f** (30)	CH_2Cl_2 (0.10 M)	r.t.	72	87%	56 (α-only)	:	44 (1:1.2)	:	0

SI-Table 3: Glycosylation of 6 with donor A, B or C

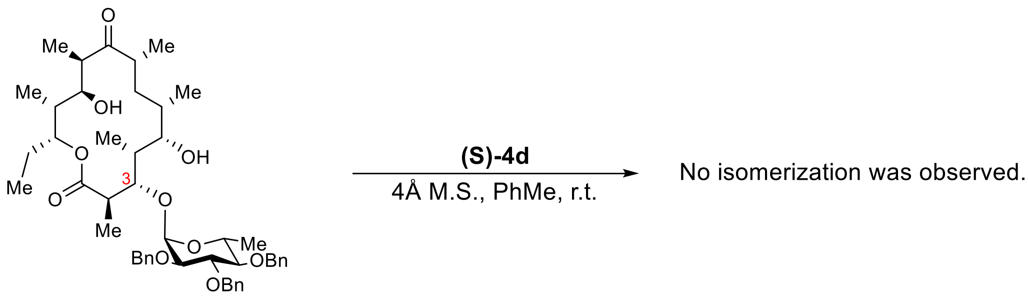




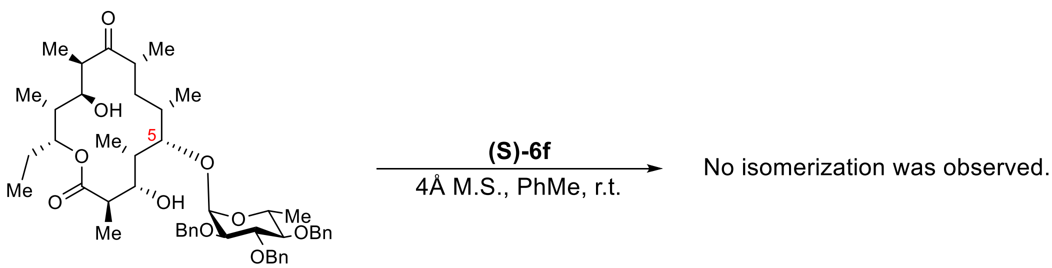
Entry	Donor	Activator (mol%)	Solvent (conc.)	T (°C)	t (h)	Yield	C_3-gly. (α:β)	C_5-gly. (α:β)	X-2 (α:β)
1	**A**	TMS-OTf (20)	PhMe (0.05 M)	-20	18	61%	0	51 (1.6:1)	49 (1:1)
2	**A**	**(R)-5d** (20)	PhMe (0.20 M)	r.t.	24	79%	30 (4:1)	70 (3.4:1)	0
3	**A**	**(S)-4d** (30)	DCM (0.20 M)	r.t.	48	52%	63 (1:1)	27 (3.5:1)	0
4	**A**	**(S)-6f** (30)	PhMe (0.30 M)	r.t.	48	60%	65 (3.4:1)	35 (1:1)	0
5	**A**	**(R)-6f** (20)	PhMe (0.30 M)	r.t.	48	80%	71 (1:1)	29 (1.9:1)	0
6	**B**	TMS-OTf (20)	PhMe (0.05 M)	-20	18	52%	0	54 (2.6:1)	46 (1.2:1)
7	**B**	**(R)-5d** (20)	PhMe (0.20 M)	r.t.	24	82%	29 (1.2:1)	71 (1:1.8)	0
8	**B**	**(S)-6f** (20)	PhMe (0.30 M)	r.t.	48	78%	64 (1.5:1)	36 (2.3:1)	0
9	**B**	**(R)-6f** (20)	PhMe (0.30 M)	r.t.	48	93%	91 (β-only)	9 (n.d.)	0
10	**C**	TMS-OTf (20)	PhMe (0.05 M)	-20	18	82%	0	53 (1.8:1)	47 (α-only)
11	**C**	**(R)-6f** (20)	PhMe (0.30 M)	r.t.	48	76%	88 (1:2)	12 (α-only)	0

Control Experiments

When pure C3-glycoside **1** was stirred with **(S)-4d**, which catalyzed the selective formation of C5-glycoside **2**, no isomerization was observed. Similarly, when pure **2** was stirred with **(S)-6f**, which catalyzed the selective formation of **1**, no reaction was observed.

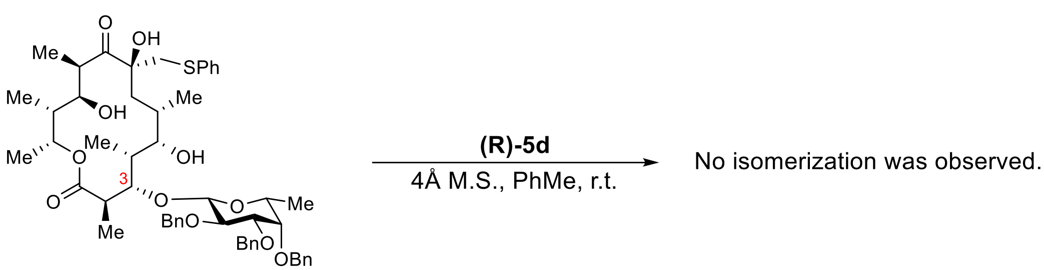


1

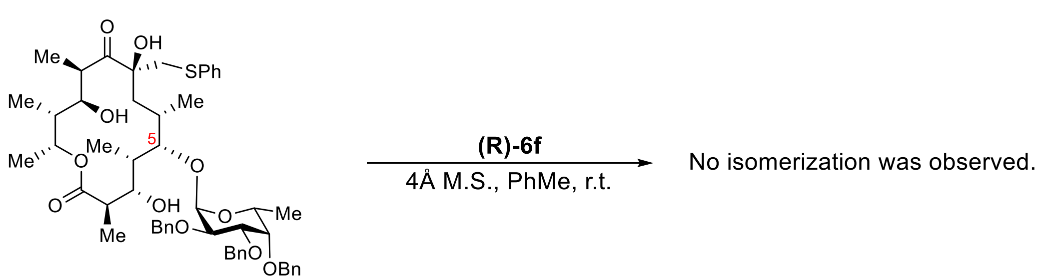


2

The same experiments were carried out with pure glycosides **8h** and **8i** generated from macrolide **7**. In both cases, we did not observe any isomerization of glycosides under the reaction condition with chiral acids.

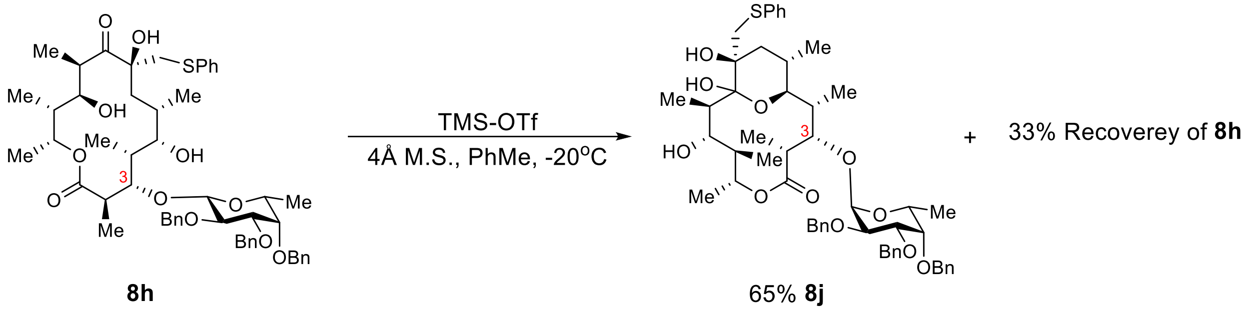


8h

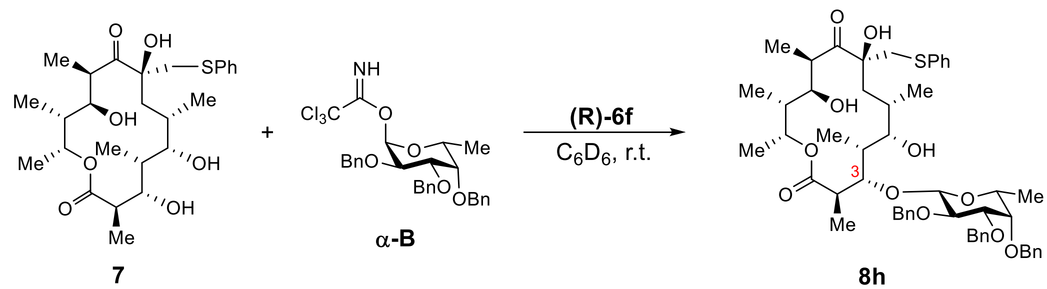


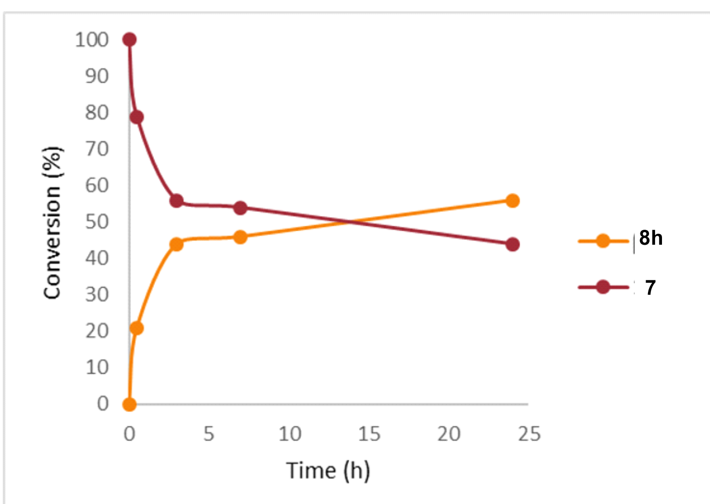
8i

When pure C3-glycoside **8h** was stirred with TMS-OTf, we observed hemiacetalization of **8h** to form **8j**, the same by-product isolated from glycosylation reaction catalyzed by TMS-OTf.

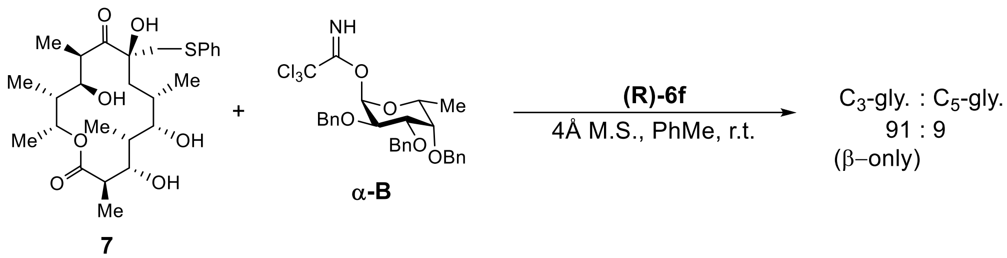


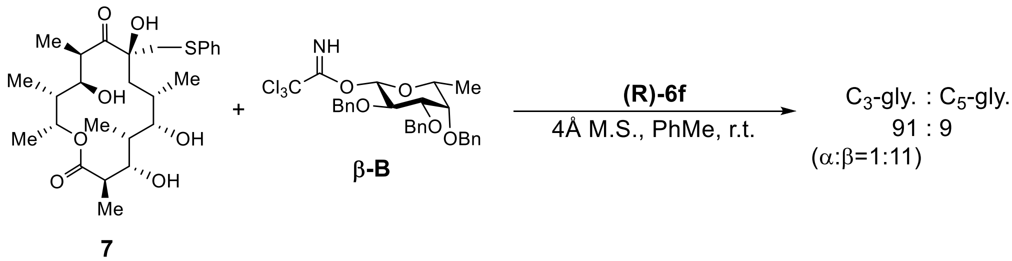
We were able to monitor the progress of CPA **(R)-6f** catalyzed glycosylation of **7** with donor **B** by ^{1}H NMR. As **7** was being consumed, we observed steady formation of C3-glycoside **8h**, without the formation of other isomers. (The reaction stalled at 50% conversion due to the absence of molecular sieves.)





When either α- or β-donor **B** was subjected to CPA catalyzed glycosylation of **7**, we observed the same regio- and stereoselectivity outcomes for both reactions.





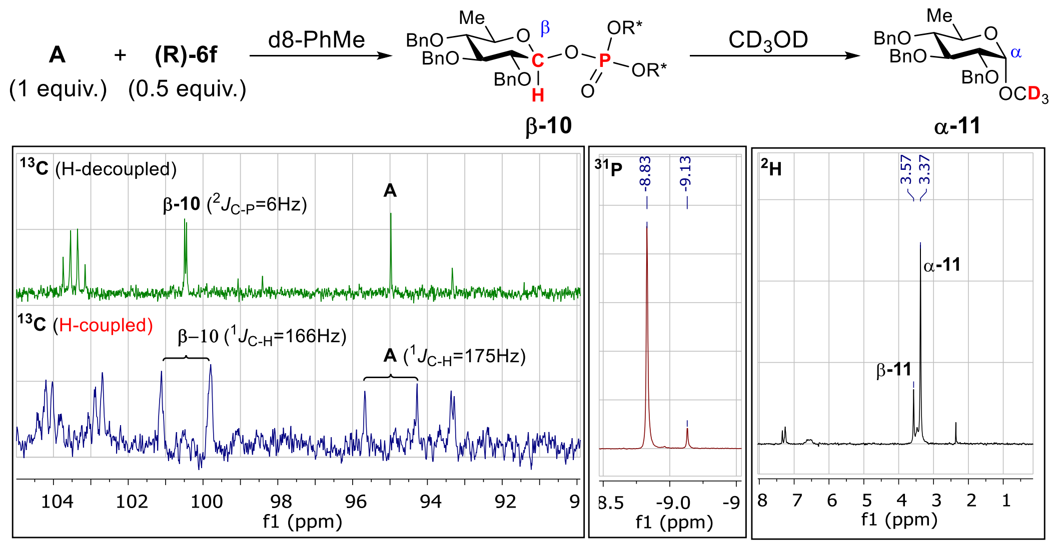
NMR Studies of Glycosyl Phosphate Intermediates

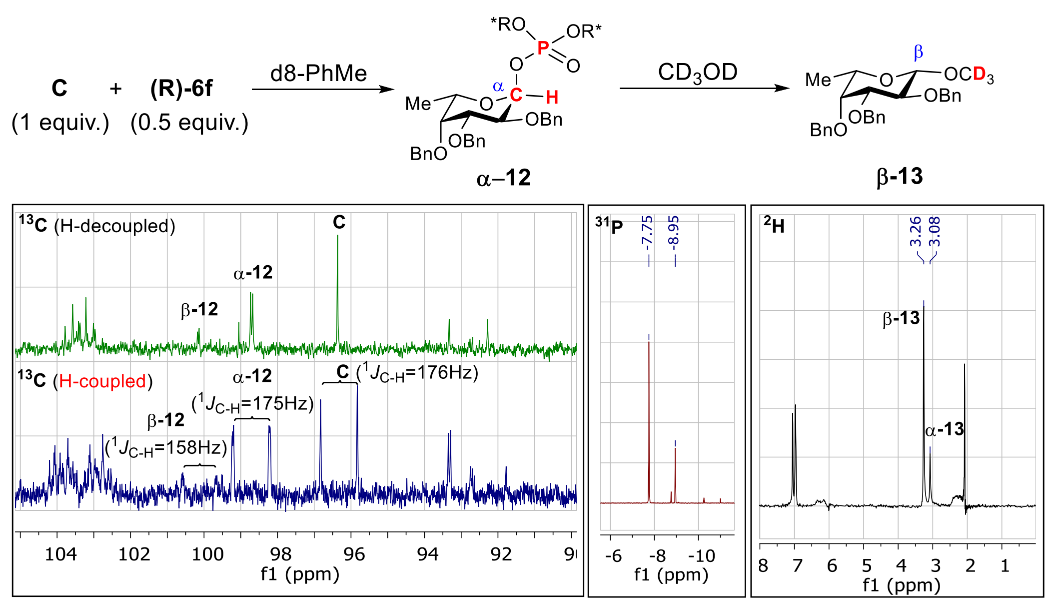
By mixing trichloroacetimidate donor (**A** or **C**) and chiral phosphoric acid **(R)-6f** in d_8-toluene, glycosyl phosphates (**10** and **12**) were generated *in-situ* and observed by NMR spectroscopy. The glycosyl phosphate intermediates are characterized by:

1. Disappearance of CPA's ^{31}P signal, and appearance of relatively more upfield ^{31}P signals.
2. Observation of 2-bonds P-C coupling ($^2J_{P\text{-}C}$ = ~ 6 – 7 Hz) in H-decoupled ^{13}C NMR.

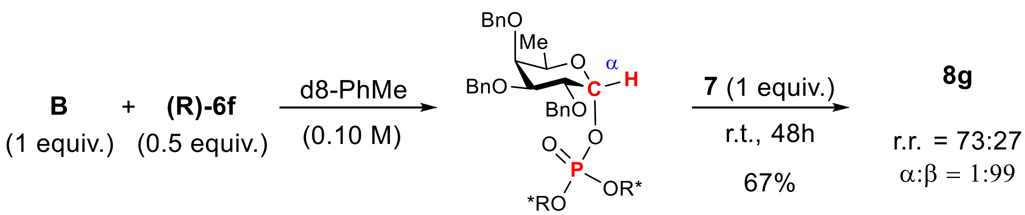
Stereochemistry of glycosyl phosphate intermediates are characterized by:

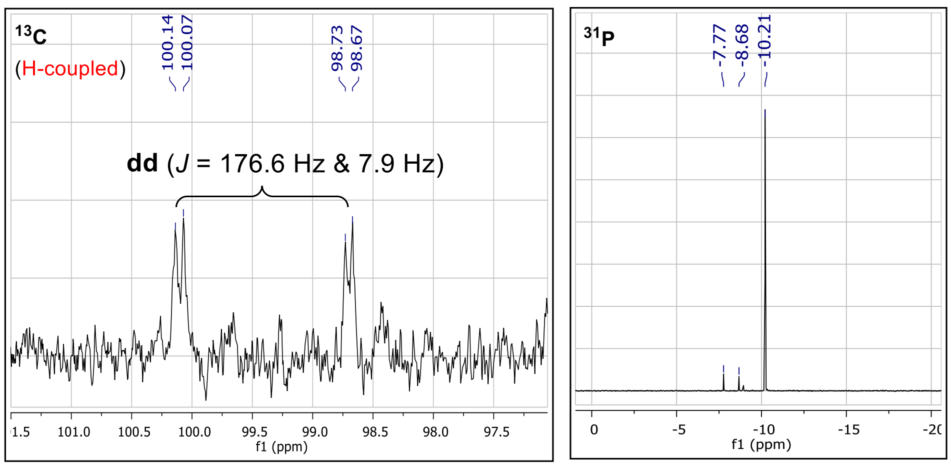
1. One-bond C-H coupling of anomeric carbon in H-coupled ^{13}C NMR; α-phosphate, $^1J_{C\text{-}H}$ = ~175 Hz and β-phosphate, $^1J_{C\text{-}H}$ = ~ 160 – 165 Hz.
2. Stereochemistry of methoxy ether (**11** and **13**) obtained from quenching of glycosyl phosphates with excess d_4-methanol.





The same experiment was repeated for trichloroacetimidate donor **B** and **(R)-6f**. The resulting α-phosphate was characterized by 2-bonds P-C coupling ($^{2}J_{P\text{-}C}$ = 7.9 Hz) and one-bond C-H coupling of anomeric carbon in H-coupled ^{13}C NMR ($^{1}J_{C\text{-}H}$ = 176.6 Hz). Next, macrolide **7** (1 equiv.) was added to the mixture, and the reaction was stirred at r.t. for 48h. The resulting glycosides were isolated in lower r.r, compared to standard reaction condition (see **SI-Table 3**), but the d.r. of the glycosides were essentially the same. The lower r,r. observed may be due to (1) lower concentration used in NMR studies (0.10M vs 0.30M), (2) absence of 4Å M.S., and (3) higher catalyst loading, which presumably have an effect on the overall acidity of the reaction medium.





Computational Studies

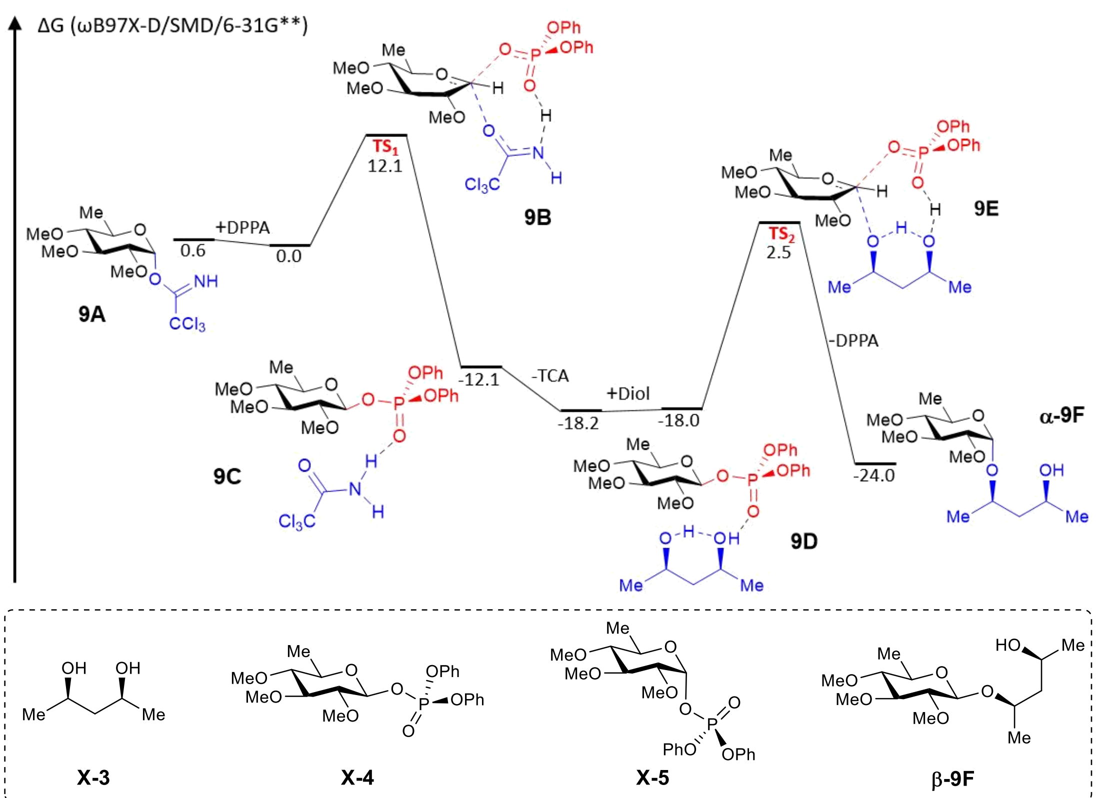
Al quantum chemical calculations were performed using the Q-Chem 4.3 package.[6] Geometry optimizations were evaluated using the B97-D density functional[7] using the double-ζ- quality basis set with polarization functions on all atoms, 6-31G**.[8] Pictorial representations of important stationary points were generated in Discovery Studio 4.1 Visualizer.[9]

For the growing string reaction path optimizations, between 7-15 nodes were used, including the end points. In the initial phase, termed growth phase, new nodes were added when the perpendicular gradient magnitude on the frontier node was less than 0.10 Hartree/Å for double-ended strings, or when the RMS gradient was less than 0.005 Hartree/Å for single-ended strings. Additionally, an initial maximum optimization step size of 0.1 Å-radians was used. When the total perpendicular gradient magnitude over all nodes, F, reached a value of less than 0.3, the climbing image search was initiated. When $F < 0.1$, or when the node of highest energy had a RMS gradient below double the nodal convergence criterion and $F < 0.2$, the exact transition state search was initiated. The string is considered fully converged when an RMS gradient < 0.0005 Hartree/Å was obtained for the node representing the transition state. Further detail regarding the growing string implementation developed in the Zimmerman group can be found in the references.[10]

The electronic Gibbs free energy values of all stationary points were computed through solvent corrected (dichloromethane) single point energies using the SMD model.[11] For these calculations the ωB97X-D exchange functional[12] was employed with a 6-31G** basis set. The final Gibbs free energy values were obtained by correcting the electronic free energy with the enthalpic and entropic contributions from vibrations, rotations, and translations at 298.15 K. These frequency computations were performed using the B97-D functional and 6-31G** basis set. Both TS described below were found to have two negative frequencies, one of them being numerically small and corresponding to a C3-O σ bond rotation. For the enthalpic and entropic corrections to the free energies from the harmonic oscillator approximation, all frequencies below 50 cm^{-1} were treated as if they were 50 cm^{-1}.

A model system consisting of diphenyl hydrogen phosphate (**DPPA**); 2,3,4-Tri-*O*-methyl-α-D-6-deoxyglucopyranosyl trichloroacetimidate **9A** and 2,4-*syn*-pentadiol (**X-3**) was utilized to explore various pathways leading to the overall conversion of the sugar donor to the respective *O*-glycoside. Single-ended growing string calculations were performed on optimized starting materials or intermediates as the fixed nodes with varying driving coordinates according to the pathways explored.[10d] To account for variation in conformations and binding complexes, the most stable conformations were sampled for the growing string calculations. These were obtained in part by manually sampling relevant torsions and angles of approach, and also by using an algorithm which allowed a thorough conformational analysis by ranking a vast number of unique conformers generated by the systematic variation of the torsional angles[13]. In the latter approach, 10,000 configurations were sampled and the lowest 100 energy structures at the semi-empirical PM6 level of theory were further investigated.

The interaction between **DPPA** and **9A** is estimated to be favorable (~0.6 kcal/mol), due to the formation of a hydrogen bond between the acidic proton of **DPPA** and the basic nitrogen of **9A**. An S_N2-like displacement of the trichloroacetimide moiety was modeled and found to be facile (**TS1**: 12.1 kcal/mol barrier). This was confirmed experimentally by the instantaneous formation of β-phosphates upon mixing dono**r A** with phosphoric acids **(R)-6f** (*cf*. SI-8). Following the exothermic release of trichloroacetamide (**TCA**), β-phosphate **X-4** would bind to the diol **X-3** (**9C to 9D**). Subsequently, a second SN_2-like displacement of the phosphate may occur to yield α-*O*-glycoside **α-9F**, with an estimated barrier of 20.7 kcal/mol (**TS2**). This double displacement mechanism supports the α-selectivity observed for the reaction of donor **A** with **6-dEB** catalyzed by a phosphoric acid. The increased β preference of glycosylations with fucose, or with the less reactive **7** may be due to a competing phosphate anomerization of the β-phosphate to the more stable α-form. A computed ΔG of 0.7 kcal/mol has been calculated between the β-phosphate **X-4** and the more stable α anomer **X-5**. This difference could be easily enhanced by the introduction of bulky groups in the phosphate. This hypothesis is backed-up by the fact that mostly α-phosphate is formed when benzyl protected 6-deoxyfucose-α-trichloroacetimidate is treated with various CPAs. Additionally, an analogous uncatalyzed SN_2-like reaction of the α-trichloroacetimidate **9A** with diol **X-3** to afford the β-glycoside (**β-9F)** was modelled but found to be high in energy (**TS3**: 34.8 kcal/mol barrier).



A summary of calculated values, including solvent corrected single point electronic energies, as well as enthalpic and entropic corrections associated with vibrational, rotational, and translational energy at 298.15 K are provided below.

	G_{SMD} (kcal/mol)[a]	H_{vrt} (kcal/mol)[b]	S_{vrt} (cal/mol.K)[b]	G_{corr} (kcal/mol)[c]
DPPA	-694020.3	139.1	124.1	-693918.2
6-deoxyglucose α-donor **9A**	-1406312.9	197.2	158.6	-1406163.0
Diol **X-3**	-218452.9	110.6	89.3	-218368.9
α-donor **9A** bound to **DPPA**	-2100349.7	337.5	233.7	-2100081.8
TS1: formation of β-phosphate **X-4**	-2100336.1	336.7	236.1	-2100069.7
β-phosphate **X-4** bound to **TCA**	-2100363.5	338.5	235.6	-2100095.2
β-phosphate **X-4**	-1103956.6	303.2	191.9	-1103710.6
TCA	-996395.8	33.4	90.4	-996389.3
β-phosphate **X-4** bound to diol **X-3**	-1322424.8	415.7	235.9	-1322079.4
TS2: formation of α-glycoside **α-9F**	-1322401.9	414.1	238.5	-1322058.9
α-glycoside **α-9F** bound to **DPPA**	-1322436.3	415.7	230.5	-1322089.2
α-glycoside **α-9F**	-628393.9	274.5	160.6	-628167.3
α-phosphate **X-5**	-1103958.0	303.4	190.6	-1103711.4
TS3: direct formation of β-glycoside **β-9F**	-1624742.1	305.9	206.6	-1624497.8

SI-Table 4. Calculated values for starting geometries, intermediates, and transition states. **a:** Solvent-corrected (dichloromethane) electronic energy (ωB97X-D/SMD/6-31G**). **b:** Vibrational, rotational, and translational entropic and enthalpic contributions (B97-D/6-31G**) at 298.15 K. **c:** Corrected free energy values at 298.15 K.

Cartesian coordinates for starting geometries, transition states, and products are described below.

- **DPPA**

28

C	-4.10738	1.21178	1.67082
C	-4.32407	0.40975	2.80231
C	-3.77138	-0.88019	2.85779
C	-3.01683	-1.37353	1.78490
C	-2.81599	-0.55925	0.66357
C	-3.34328	0.73714	0.59343
O	-2.02978	-1.09985	-0.36745
P	-2.48372	-1.12452	-1.93683
O	-4.11105	-1.20952	-1.89617
C	-4.74524	-2.28253	-1.23677
C	-4.44406	-3.61239	-1.55857
C	-5.13723	-4.63529	-0.89293
C	-6.11810	-4.32673	0.06254
C	-6.40610	-2.98501	0.36196
C	-5.71568	-1.95070	-0.28444
O	-2.35275	0.40615	-2.47481
O	-1.72116	-2.13225	-2.71372
H	-4.52731	2.21742	1.62366
H	-4.91706	0.78782	3.63560
H	-3.93622	-1.51166	3.73162
H	-2.59989	-2.37938	1.78978
H	-3.16652	1.35198	-0.28709
H	-3.67775	-3.82513	-2.30196
H	-4.91016	-5.67542	-1.12977
H	-6.65609	-5.12708	0.57176
H	-7.16379	-2.74004	1.10724
H	-5.89945	-0.90333	-0.05226
H	-1.69489	0.41669	-3.18923

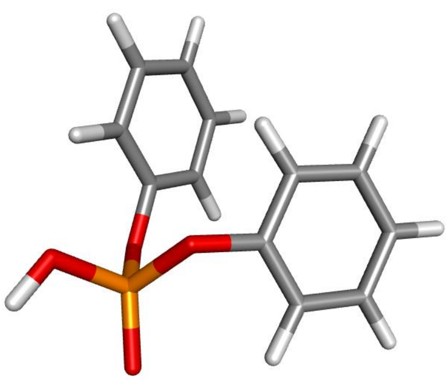


Figure C-1. Geometry of **DPPA.**

- 6-deoxyglucose α-donor **9A**

38

C	0.26331	-2.70561	-3.31594
C	1.12486	-1.77389	-2.39151
C	0.83283	0.14105	-0.91748
C	0.33207	-0.32343	0.47132
C	-1.20020	-0.21179	0.56065
C	-1.65131	1.19601	0.13065
C	-1.06267	1.58149	-1.24497
N	2.36918	-1.86436	-2.14021
C	-2.04257	-1.77266	2.17369
C	2.07803	-1.79458	1.15846
C	-3.74677	1.73744	1.15641
C	-1.32763	3.03770	-1.60114
O	0.31367	-0.82195	-1.91049
O	0.38560	1.41030	-1.25398
Cl	-0.43047	-1.72338	-4.67684
Cl	1.26779	-4.04275	-4.02500
Cl	-1.07781	-3.44810	-2.34439
O	0.70994	-1.66051	0.76014
O	-1.64413	-0.42623	1.90142
O	-3.07072	1.25688	-0.00736
H	1.92592	0.15063	-0.98444
H	0.76753	0.37456	1.21284
H	-1.65073	-0.94539	-0.12914
H	-1.29475	1.92492	0.88367
H	-1.50169	0.91534	-2.00422
H	2.79942	-2.65433	-2.62207
H	-2.41131	-1.78202	3.20887
H	-2.85860	-2.08785	1.49598
H	-1.19903	-2.47153	2.06930
H	2.20614	-2.83794	1.47562
H	2.76376	-1.58656	0.32023
H	2.30963	-1.12408	2.00779
H	-4.81851	1.73866	0.91373
H	-3.55537	1.08962	2.02465
H	-3.43061	2.77024	1.40149
H	-2.41087	3.21272	-1.58701
H	-0.84385	3.69992	-0.86778
H	-0.93211	3.26546	-2.59995

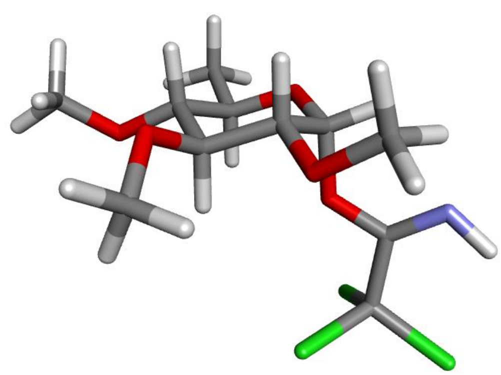


Figure C-2. Geometry of α-donor **9A.**

- Diol **X-3**

19

C	-1.90604	5.13988	-2.86560
O	-1.03433	5.00926	-1.74314
H	-0.13388	4.97374	-2.11551
C	-3.32347	4.83513	-2.37409
H	-3.57045	5.47818	-1.51755
H	-3.38942	3.78583	-2.04874
H	-4.05911	5.00882	-3.17400
H	-1.88167	6.18177	-3.25720
C	-1.49941	4.20385	-4.02516
H	-1.40502	3.17658	-3.63674
C	-0.19029	4.60734	-4.71435
H	-2.29241	4.20422	-4.79085
O	0.86545	4.51270	-3.72293
H	-0.28433	5.66112	-5.04361
C	0.14135	3.72443	-5.92298
H	1.65118	4.93464	-4.10026
H	0.22125	2.67401	-5.60777
H	1.09954	4.02732	-6.37481
H	-0.64019	3.80687	-6.69373

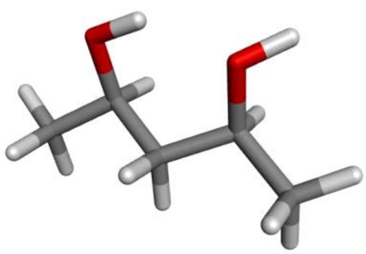


Figure C-3. Geometry of diol **X-3.**

- α-donor **9A** bound to **DPPA**

66

C	0.20014	-3.68847	-2.17462
C	1.45109	-2.75959	-1.97865
C	1.95514	-0.45788	-1.29579
C	1.70857	-0.34102	0.22655
C	0.35316	0.31857	0.52848
C	0.21117	1.61296	-0.28992
C	0.41719	1.32464	-1.79111
N	2.67172	-3.14982	-1.99431
C	-0.41053	-0.34124	2.69788
C	3.01837	-1.95136	1.42345
C	-1.19956	3.16568	0.85928
C	0.41680	2.58828	-2.63940
O	1.02355	-1.52249	-1.79205
O	1.70825	0.68639	-2.01543
Cl	-0.82839	-3.04214	-3.51532
Cl	0.68364	-5.39093	-2.58748
Cl	-0.72791	-3.70318	-0.62129
O	1.75210	-1.62756	0.83731
O	0.27212	0.64394	1.91764
O	-1.09631	2.16743	-0.15844
H	2.97533	-0.76155	-1.51920
H	2.49557	0.31909	0.62587
H	-0.46119	-0.36771	0.23788
H	0.98719	2.32784	0.04023
H	-0.37618	0.63726	-2.12701
H	2.75953	-4.14764	-2.18184
H	-0.39999	0.02272	3.73460
H	-1.45957	-0.45301	2.36377
H	0.09102	-1.31916	2.63788
H	2.90794	-2.95579	1.85355
H	3.82628	-1.95838	0.67661
H	3.27418	-1.23282	2.22192
H	-2.23772	3.52501	0.83729
H	-0.96239	2.75199	1.85075
H	-0.51896	4.01494	0.65318
H	-0.54700	3.09854	-2.51914
H	1.22323	3.26245	-2.31442
H	0.56987	2.33738	-3.69751
H	3.77943	2.57352	-1.94413
H	3.24927	3.82152	0.16536
C	4.12552	2.21740	-0.97675
C	3.82646	2.89686	0.20982
O	5.06918	0.41577	-2.16132
C	4.86249	1.02311	-0.92609
O	5.66205	-1.35575	-3.90524
H	9.48795	1.80251	-4.54860
C	4.25870	2.39257	1.44861
C	9.25651	1.49085	-3.52924
P	5.71233	-1.07931	-2.44921
H	7.86954	-0.07196	-4.15692
C	8.35111	0.43901	-3.32472
C	5.31525	0.51208	0.30156
H	4.01628	2.91774	2.37246
C	9.86459	2.13513	-2.44028
H	10.57007	2.94918	-2.60974
C	5.00541	1.20656	1.48279
C	8.05517	0.05341	-2.00895
O	5.02558	-2.09699	-1.43403
H	4.11374	-2.47109	-1.73639
C	9.55973	1.72790	-1.13181
H	5.88621	-0.41081	0.33982
O	7.18404	-1.01247	-1.72634
C	8.64914	0.68522	-0.90880
H	5.35215	0.80523	2.43608
H	10.02494	2.22438	-0.27907
H	8.38800	0.36158	0.09757

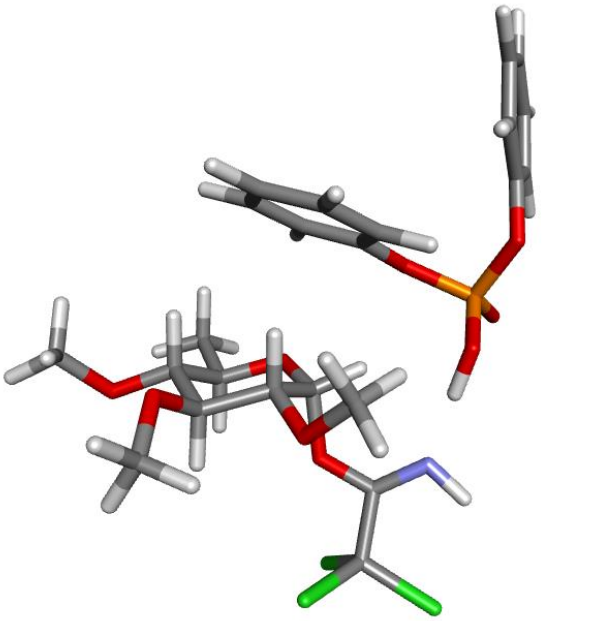


Figure C-4. Geometry of α-donor **9A** bound to **DPPA.**

- **TS1:** formation of β-phosphate **X-4**

66

C	0.96082	-3.58642	-2.70683
C	1.63722	-2.19861	-2.33866
C	1.47117	0.53729	-1.05649
C	1.02428	-0.03347	0.27739
C	-0.51054	-0.00491	0.43605
C	-1.01112	1.39719	0.05016
C	-0.61260	1.75035	-1.39429
N	2.95567	-2.18029	-2.17045
C	-1.16009	-1.61306	2.08987
C	2.77819	-1.44631	1.15690
C	-2.98067	1.97495	1.28565
C	-0.82511	3.21339	-1.74598
O	0.84652	-1.24255	-2.24242
O	0.82160	1.46016	-1.68150
Cl	0.08183	-3.38131	-4.26952
Cl	2.14111	-4.97564	-2.88195
Cl	-0.19486	-3.98835	-1.37775
O	1.49690	-1.34320	0.50643
O	-0.87357	-0.24174	1.78910
O	-2.43117	1.47683	0.05781
H	2.46353	0.35351	-1.46312
H	1.45156	0.67721	1.01056
H	-0.96096	-0.75050	-0.24025
H	-0.56437	2.13623	0.74173
H	-1.15374	1.08516	-2.08030
H	3.48671	-3.03535	-2.28628
H	-1.51015	-1.63079	3.13095
H	-1.95745	-2.00129	1.42967
H	-0.26419	-2.24208	1.98227
H	2.81979	-2.46204	1.57217
H	3.59866	-1.30463	0.44436
H	2.87695	-0.70456	1.96421
H	-4.06927	2.00314	1.14211
H	-2.72546	1.31763	2.12928
H	-2.61401	2.99801	1.49418
H	-1.88409	3.45216	-1.58610
H	-0.20750	3.85319	-1.10060
H	-0.56343	3.40185	-2.79515
H	7.19760	0.60233	2.70564
H	9.55958	-0.23773	2.71147
C	7.61998	0.10376	1.83434
C	8.93864	-0.36349	1.82328
O	5.51803	0.42260	0.79545
C	6.81992	-0.04918	0.68984
O	3.46327	1.76472	0.14547
H	5.96063	5.58130	1.90826
C	9.46615	-0.97820	0.67471
C	6.48928	4.85769	1.28462
P	4.66169	1.08284	-0.47816
H	4.66446	3.95746	0.49268
C	5.75241	3.96661	0.49234
C	7.32849	-0.67300	-0.46376
H	10.49708	-1.33498	0.66603
C	7.89375	4.82659	1.28078
H	8.45847	5.52484	1.89958
C	8.65592	-1.12721	-0.46141
C	6.44247	3.03342	-0.29804
O	4.42390	0.03979	-1.57461
H	3.47896	-1.31136	-1.88742
C	8.56732	3.88906	0.47956
H	6.69472	-0.78048	-1.34062
O	5.76677	2.13208	-1.12718
C	7.84430	2.98445	-0.31043
H	9.05555	-1.60286	-1.35936
H	9.65747	3.85130	0.47767
H	8.33958	2.22538	-0.91466

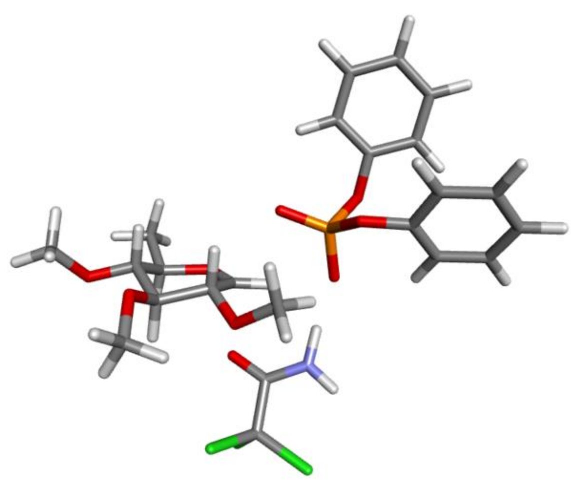


Figure C-5. Geometry of **TS1.**

- β-phosphate **X-4** bound to **TCA**

66

C	1.43608	-3.62307	-1.86648
C	1.89092	-2.13674	-2.23136
C	2.46391	0.93530	-0.42405
C	1.90763	0.14628	0.76743
C	0.36770	0.04724	0.63978
C	-0.28758	1.39451	0.23279
C	0.48667	2.09748	-0.90688
N	3.20988	-1.97316	-2.42871
C	-1.34408	-1.12341	1.85825
C	2.59595	-1.78467	2.01629
C	-2.00070	0.58546	-1.28226
C	-0.03644	3.50140	-1.17677
O	1.02606	-1.28238	-2.40309
O	1.87039	2.21146	-0.50240
Cl	1.30874	-4.52277	-3.44568
Cl	2.62109	-4.49629	-0.78418
Cl	-0.16544	-3.59904	-1.05352
O	2.52336	-1.14116	0.74299
O	-0.11445	-0.39507	1.91379
O	-1.68703	1.25416	-0.05378
H	2.29998	0.37833	-1.35724
H	2.16142	0.69230	1.69464
H	0.16886	-0.70977	-0.13531
H	-0.25112	2.05064	1.11546
H	0.43587	1.48126	-1.82189
H	3.89211	-2.66377	-2.13873
H	-1.50416	-1.53609	2.86446
H	-2.18865	-0.47453	1.58181
H	-1.27636	-1.95569	1.13337
H	3.18904	-2.69629	1.86431
H	3.10160	-1.13536	2.75665
H	1.59811	-2.04174	2.39793
H	-3.07457	0.36020	-1.23710
H	-1.80828	1.23165	-2.15706
H	-1.43911	-0.35291	-1.41947
H	-1.10695	3.44889	-1.41576
H	0.09043	4.12162	-0.27774
H	0.51194	3.96711	-2.00532
H	5.31053	-1.00083	0.95968
H	5.31798	-3.51284	0.94690
C	5.70102	-1.56023	0.11403
C	5.69574	-2.96161	0.08597
O	6.21627	0.53974	-0.97770
C	6.18377	-0.87128	-1.00396
O	3.87072	1.14944	-0.21213
H	3.11407	6.33217	0.20221
C	6.14954	-3.65259	-1.05020
C	3.33380	5.70111	-0.65957
P	4.85692	1.26298	-1.49729
H	4.70507	4.39693	0.42874
C	4.22609	4.62855	-0.52099
C	6.64186	-1.53497	-2.14767
H	6.13066	-4.74213	-1.06906
C	2.72077	5.95838	-1.89614
H	2.02612	6.79281	-1.99736
C	6.62065	-2.93841	-2.16501
C	4.48778	3.82978	-1.63690
O	4.28441	0.74675	-2.77824
H	3.54701	-1.03645	-2.67420
C	2.99661	5.13714	-3.00114
H	6.98797	-0.95479	-3.00118
O	5.42456	2.77831	-1.49071
C	3.88591	4.05890	-2.87864
H	6.96763	-3.47065	-3.05101
H	2.51925	5.33138	-3.96230
H	4.10827	3.39712	-3.71370

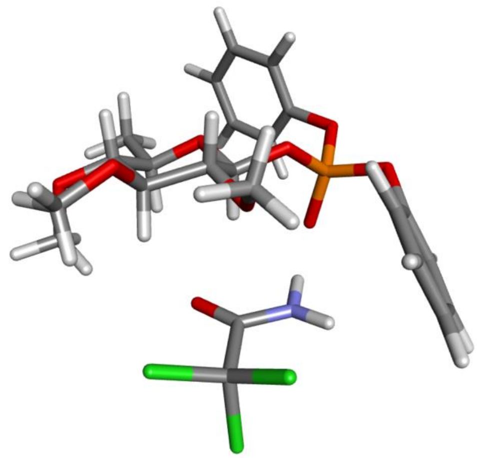


Figure C-6. Geometry of β-phosphate **X-4** bound to **TCA.**

- β-phosphate **X-4**

57

C	1.47686	0.75613	-0.54949
C	0.60932	0.36618	0.66051
C	-0.86324	0.73514	0.37630
C	-1.00333	2.18097	-0.14281
C	-0.02545	2.43035	-1.31339
C	-2.31227	-0.66424	1.67322
C	1.61514	-1.41230	1.91546
C	-3.20561	2.99100	0.33325
C	-0.03058	3.87609	-1.79068
O	1.31546	2.12708	-0.87737
O	0.67970	-1.03657	0.89632
O	-1.64261	0.59582	1.56532
O	-2.32105	2.42003	-0.63392
H	1.23038	0.11893	-1.41848
H	0.95245	0.94565	1.53535
H	-1.24101	0.06490	-0.41801
H	-0.74835	2.88240	0.67379
H	-0.30064	1.75337	-2.14541
H	-2.86896	-0.63841	2.62029

H	-3.02397	-0.80577	0.83778
H	-1.59549	-1.49908	1.68004
H	1.58628	-2.50732	1.97100
H	2.63833	-1.09617	1.67030
H	1.32055	-0.98370	2.89173
H	-4.17177	3.12707	-0.17215
H	-3.32455	2.33247	1.20662
H	-2.83489	3.97659	0.67644
H	-1.04481	4.14323	-2.11254
H	0.27303	4.54316	-0.96980
H	0.66921	4.00183	-2.62746
H	5.88937	-0.68770	1.84259
H	5.50414	-2.78178	3.18841
C	5.35922	-1.54314	1.42541
C	5.13228	-2.71296	2.16536
O	5.15204	-0.29037	-0.59106
C	4.87463	-1.46944	0.11407
O	2.84662	0.58362	-0.19009
H	3.87327	4.69951	2.16014
C	4.42318	-3.78431	1.59845
C	4.58426	4.10683	1.58268
P	3.97372	0.52854	-1.37607
H	3.10237	3.44143	0.12093
C	4.14125	3.41933	0.44265
C	4.17544	-2.53079	-0.47725
H	4.24466	-4.68940	2.17989
C	5.92851	4.03547	1.98240
H	6.26372	4.57291	2.87011
C	3.94646	-3.68810	0.28134
C	5.06969	2.66273	-0.28189
O	3.51296	0.01787	-2.68842
C	6.84073	3.27102	1.23707
H	3.81621	-2.43553	-1.50109
O	4.65564	1.99732	-1.45701
C	6.41426	2.57513	0.09569
H	3.39641	-4.51772	-0.16427
H	7.88625	3.21279	1.54245
H	7.09661	1.96801	-0.49663

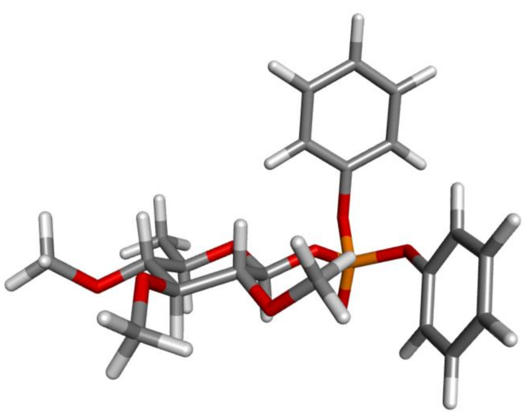


Figure C-7. Geometry of β-phosphate **X-4**

- **TCA**

9

O	-1.30869	-1.27960	-1.52241
C	-0.73985	-1.86867	-2.42298
H	0.40827	-3.12783	-1.31179
Cl	-2.13744	-0.13582	-4.08638
N	0.17868	-2.85558	-2.25794
Cl	-1.85601	-3.01396	-4.69634
C	-1.05625	-1.54373	-3.95653
H	0.63350	-3.31513	-3.03440
Cl	0.50310	-1.20288	-4.86013

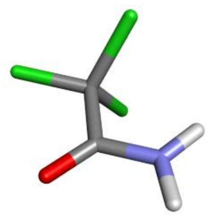


Figure C-8: Geometry of **TCA.**

- β-phosphate **X-4** bound to diol **X-3**

76

C	1.84302	0.53432	-1.24980
C	0.92078	-0.16624	-0.24088
C	-0.54694	0.13892	-0.60910
C	-0.76878	1.65713	-0.76925
C	0.27196	2.24318	-1.75070
C	-2.01106	-1.60483	0.10919
C	1.95007	-2.06691	0.79893
C	-3.07259	2.14640	-0.33068
C	0.19068	3.75726	-1.87658
O	1.60229	1.92888	-1.26381
O	1.12007	-1.57864	-0.26196
O	-1.40662	-0.34856	0.42637
O	-2.05504	1.94070	-1.31085
H	1.72489	0.10685	-2.25769
H	1.12443	0.25008	0.76135
H	-0.77719	-0.32768	-1.58127
H	-0.63706	2.14752	0.21551
H	0.12061	1.76035	-2.73134
H	-2.63151	-1.88121	0.97357
H	-2.65198	-1.52127	-0.78780
H	-1.24973	-2.38109	-0.06622
H	2.04668	-3.14903	0.64218
H	2.94739	-1.60767	0.78349
H	1.47461	-1.87953	1.77921
H	-3.97791	2.43674	-0.88180
H	-3.26267	1.23505	0.25601
H	-2.79514	2.96284	0.36503
H	-0.81712	4.03330	-2.21019
H	0.38792	4.22750	-0.90129
H	0.93235	4.11962	-2.60111

H	5.39579	0.50424	1.55101
H	5.23222	-1.21380	3.36711
C	5.40841	-0.55875	1.31973
C	5.31564	-1.53097	2.32696
O	5.66692	-0.02911	-1.03343
C	5.51082	-0.98166	-0.01108
O	3.19937	0.35082	-0.80056
H	3.40260	3.49806	2.85006
C	5.32618	-2.89790	2.00320
C	4.23258	3.30114	2.17005
P	4.45214	0.80499	-1.72611
H	2.94930	2.85612	0.45665
C	3.96344	2.94961	0.83857
C	5.52788	-2.33651	-0.35770
H	5.25190	-3.64732	2.79169
C	5.55633	3.39895	2.63008
H	5.75462	3.67151	3.66718
C	5.43336	-3.29642	0.66132
C	5.04507	2.69662	-0.01433
O	4.32097	0.63573	-3.19810
C	6.62389	3.15058	1.75188
H	5.61117	-2.62176	-1.40450
O	4.80474	2.34829	-1.35910
C	6.37257	2.79276	0.41851
H	5.44179	-4.35559	0.40139
H	7.65327	3.22564	2.10379
H	7.17857	2.57496	-0.28022
H	0.77238	-2.39868	-2.50333
H	3.12086	-2.16792	-2.14734
H	-1.76265	-2.56004	-2.71620
H	0.46166	-0.24397	-4.16246
O	-0.44336	-0.56372	-3.96612
O	2.20676	-0.75051	-4.34317
C	0.83784	-2.62252	-3.57847
C	3.32888	-2.58446	-3.14278
C	-1.68886	-2.59821	-3.81342
H	3.04308	-0.34220	-4.03368
H	0.77617	-3.71774	-3.69541
H	-2.53992	-2.04830	-4.23975
H	4.30479	-2.21414	-3.49054
C	-0.37397	-1.96659	-4.27286
C	2.21477	-2.17753	-4.11527
H	3.37582	-3.68058	-3.05535
H	-1.74663	-3.64949	-4.13319
H	-0.27272	-2.10035	-5.36969
H	2.38706	-2.66468	-5.09418

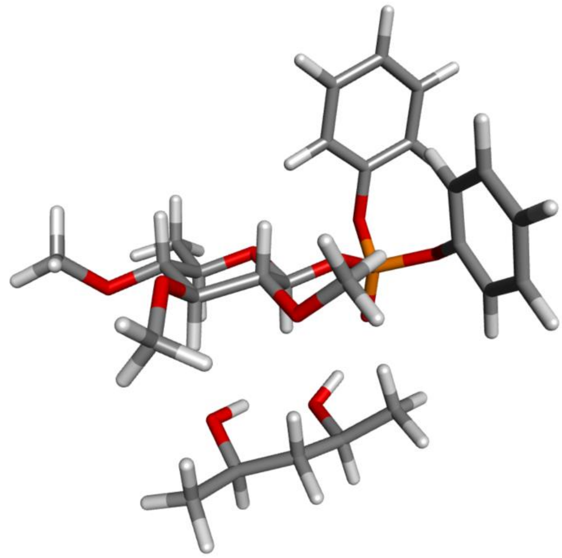


Figure C-9. Geometry of β-phosphate **X-4** bound to diol **X-3.**

- **TS2:** formation of α-glycoside **α-9F**

76

C	1.26956	1.61067	-1.65837
C	0.52545	0.73608	-0.68413
C	-0.93888	1.19047	-0.53350
C	-0.92647	2.68732	-0.18160
C	-0.17351	3.51796	-1.24489
C	-2.26913	-0.68969	0.09941
C	1.28432	-1.44626	-0.08258
C	-2.88332	3.20403	1.11090
C	0.18899	4.91426	-0.76595
O	1.09747	2.90155	-1.71070
O	0.64517	-0.61640	-1.07743
O	-1.56764	0.48383	0.53198
O	-2.22882	3.26424	-0.16353
H	2.17487	1.26615	-2.14478
H	1.03046	0.91899	0.27947
H	-1.47422	1.04078	-1.48528
H	-0.42905	2.80970	0.80059
H	-0.80352	3.55151	-2.14574
H	-2.73839	-1.11597	0.99636
H	-3.05322	-0.42922	-0.63591
H	-1.58505	-1.42166	-0.35498
H	1.40073	-2.43633	-0.53838
H	2.26920	-1.04341	0.18565
H	0.65019	-1.51869	0.81781
H	-3.79404	3.81019	1.01426
H	-3.13767	2.17039	1.38382
H	-2.24156	3.63353	1.90297
H	-0.73483	5.42525	-0.46855
H	0.86406	4.85200	0.09974
H	0.68020	5.48544	-1.56458

H	4.85598	-0.88050	2.17764
H	3.85864	-3.09634	2.82902
C	4.65441	-1.65063	1.43406
C	4.09331	-2.88767	1.78332
O	5.52715	-0.16988	-0.24868
C	4.95166	-1.38747	0.08758
O	3.34399	1.24582	-0.10411
H	4.41067	5.63850	1.70158
C	3.82713	-3.85227	0.79688
C	5.10151	4.82321	1.47728
P	4.51971	0.93375	-1.00920
H	4.01981	4.16562	-0.30125
C	4.87709	4.01506	0.35355
C	4.69083	-2.34306	-0.90869
H	3.39059	-4.81309	1.07487
C	6.20532	4.58703	2.31336
H	6.37531	5.21866	3.18657
C	4.12877	-3.57581	-0.54697
C	5.77035	2.96969	0.07258
O	4.28216	0.51250	-2.45442
C	7.08760	3.53421	2.02189
H	4.92016	-2.09308	-1.94317
O	5.59393	2.19159	-1.06914
C	6.87352	2.71891	0.90016
H	3.92443	-4.32016	-1.31852
H	7.94453	3.34383	2.67055
H	7.53585	1.88924	0.65724
H	0.66742	0.10119	-5.90071
H	2.82742	-1.18939	-6.50917
H	-1.44532	1.44155	-5.34813
H	0.95328	0.13848	-3.41018
O	0.26116	0.87973	-3.34025
O	2.37037	-0.47226	-3.94873
C	1.28891	0.94929	-5.56780
C	3.42096	-0.33829	-6.14251
C	-0.82210	2.27211	-4.98647
H	3.09014	-0.27359	-3.27894
H	1.45262	1.60698	-6.43461
H	-1.36443	2.78423	-4.17765
H	4.36018	-0.72090	-5.71833
C	0.52201	1.73978	-4.49125
C	2.64085	0.41643	-5.06410
H	3.66075	0.32229	-6.99038
H	-0.66630	2.98572	-5.80849
H	1.15265	2.57932	-4.14980
H	3.24652	1.26218	-4.69619

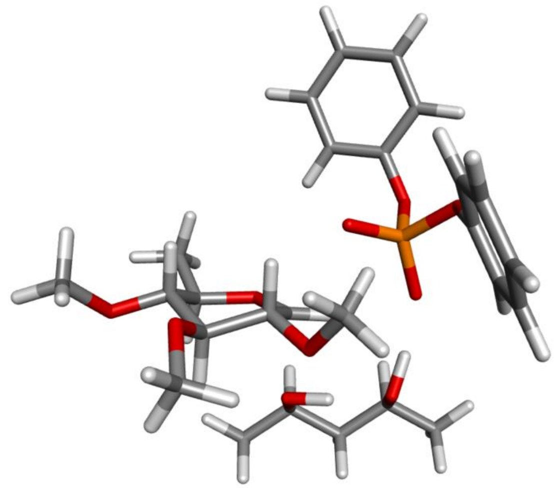


Figure C-10. Geometry of **TS2.**

- α-glycoside **α-9F** bound to **DPPA**

76

C	0.92283	1.79659	-1.16778
C	0.70724	0.29456	-0.86890
C	-0.78742	-0.04651	-0.97656
C	-1.59267	0.91134	-0.08129
C	-1.29048	2.38038	-0.43383
C	-1.89361	-2.12200	-1.39739
C	1.63426	-1.81999	-1.67090
C	-3.57610	-0.06086	0.83060
C	-1.98024	3.35814	0.50818
O	0.13380	2.61066	-0.31457
O	1.55243	-0.39430	-1.78856
O	-1.00601	-1.40018	-0.54614
O	-2.99813	0.68143	-0.24293
H	1.96255	2.07526	-0.96663
H	1.04207	0.10143	0.16287
H	-1.10535	0.08761	-2.02350
H	-1.28410	0.74505	0.96672
H	-1.60465	2.55863	-1.47579
H	-1.99113	-3.13021	-0.97080
H	-2.88450	-1.64144	-1.44698
H	-1.48657	-2.20506	-2.42388
H	2.59337	-2.09872	-2.12574
H	1.60675	-2.12855	-0.61699
H	0.80574	-2.31154	-2.20496
H	-4.64806	-0.15466	0.60705
H	-3.12341	-1.06233	0.91659
H	-3.45264	0.46735	1.79530
H	-3.06485	3.19367	0.46886
H	-1.62740	3.19798	1.53806
H	-1.75889	4.39469	0.21856
H	3.97430	2.17646	0.41278
H	2.47894	2.53528	2.37500
C	3.54200	1.33081	0.94042
C	2.70022	1.51926	2.04704

O	4.61610	-0.27326	-0.58797
C	3.79258	0.02374	0.49269
O	4.14825	1.95209	-1.96330
H	7.98020	4.29719	-0.05812
C	2.14322	0.42339	2.72454
C	7.96482	3.20854	-0.12614
P	4.75736	0.58611	-1.98920
H	6.53778	3.16377	-1.77832
C	7.16132	2.59016	-1.09553
C	3.27043	-1.08246	1.18057
H	1.48728	0.58271	3.58076
C	8.74546	2.43592	0.74860
H	9.37012	2.92281	1.49836
C	2.44688	-0.87913	2.29647
C	7.14861	1.18991	-1.16904
O	4.33372	-0.39646	-3.15081
C	8.71933	1.03479	0.65729
H	3.50791	-2.08320	0.82393
O	6.38472	0.54007	-2.15314
C	7.91534	0.40187	-0.30210
H	2.03266	-1.74204	2.81941
H	9.32045	0.43018	1.33780
H	7.86727	-0.68273	-0.38703
H	0.52179	2.49202	-5.07890
H	2.01061	1.31360	-6.87182
H	-0.70668	4.18214	-3.45604
H	1.66619	0.64425	-3.53418
O	0.62729	1.99005	-2.54865
O	2.25150	0.53317	-4.32044
C	1.45462	2.86094	-4.62121
C	2.90528	1.65830	-6.33235
C	0.25394	4.37965	-2.95602
H	3.48262	-0.05795	-3.64102
H	1.73054	3.79387	-5.13762
H	0.07264	4.54680	-1.88725
H	3.69985	0.90897	-6.45652
C	1.20055	3.19034	-3.14323
C	2.58771	1.84942	-4.85055
H	3.24525	2.60782	-6.77193
H	0.69473	5.28851	-3.39372
H	2.16627	3.38421	-2.64878
H	3.48152	2.21210	-4.31746

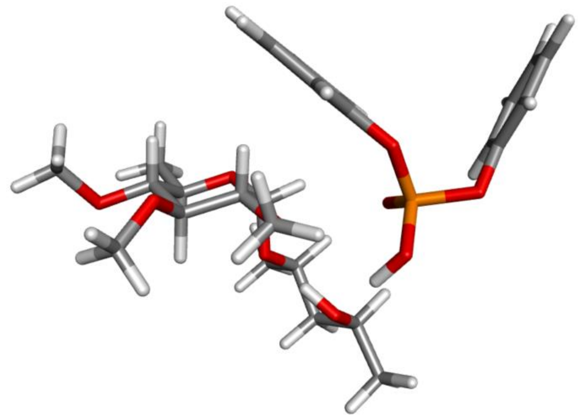


Figure C-11. Geometry of α-glycoside **α-9F** bound to **DPPA.**

- α-glycoside **α-9F**

48

C	0.69310	1.98582	-1.31233
C	0.68359	0.44556	-1.14161
C	-0.75412	-0.08825	-0.99956
C	-1.52925	0.71049	0.06699
C	-1.39866	2.23212	-0.16528
C	-0.80807	-2.38958	-1.68417
C	2.70452	-0.02425	-2.33336
C	-3.33923	-0.65817	0.86369
C	-2.01345	3.04657	0.96604
O	-0.00187	2.60888	-0.24311
O	1.29281	-0.22352	-2.24467
O	-0.75085	-1.46020	-0.59811
O	-2.92465	0.41345	0.01535
H	1.71897	2.38459	-1.23420
H	1.23168	0.21993	-0.20723
H	-1.27631	0.03726	-1.96470
H	-1.10911	0.46802	1.06165
H	-1.88928	2.47348	-1.12195
H	-0.90506	-3.38692	-1.23257
H	-1.68902	-2.19512	-2.32488
H	0.09989	-2.34530	-2.30383
H	3.05208	-0.63930	-3.17138
H	2.95654	1.02937	-2.54487
H	3.20519	-0.33556	-1.39762
H	-4.43607	-0.69402	0.80194
H	-2.91038	-1.61954	0.54380
H	-3.04315	-0.47152	1.91415
H	-3.06328	2.75208	1.08958
H	-1.47164	2.85665	1.90475
H	-1.96061	4.12067	0.74007
H	-0.42446	3.08538	-5.06313
H	1.05443	2.48512	-7.20798
H	-1.60049	4.27112	-3.05936
H	0.90618	0.94949	-4.05338
O	0.16010	2.26125	-2.58893

O	1.22896	1.05466	-4.96722
C	0.54669	3.41367	-4.65931
C	1.96603	2.60647	-6.60355
C	-0.60977	4.58695	-2.70051
H	0.76418	4.40967	-5.07882
H	-0.63019	4.66010	-1.60605
H	2.69857	1.85340	-6.92645
C	0.45123	3.57208	-3.13907
C	1.63304	2.41285	-5.12135
H	2.38074	3.60999	-6.78104
H	-0.38572	5.57809	-3.12340
H	1.44207	3.89048	-2.75776
H	2.55008	2.61574	-4.52225

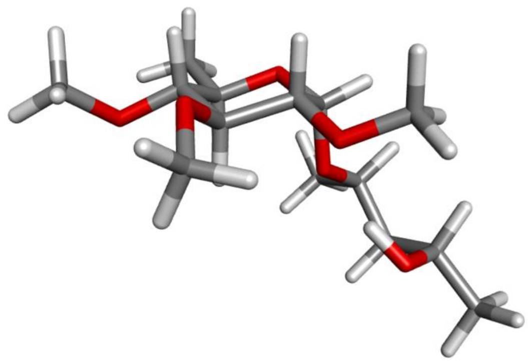


Figure SI-12. Geometry of α-glycoside **α-9F.**

- α-phosphate **X-5**

57

C	-0.24524	1.72159	-1.85611
C	0.34892	1.20370	-0.52633
C	0.63420	-0.30706	-0.60560
C	-0.61617	-1.05506	-1.11153
C	-1.15699	-0.42079	-2.41088
C	2.39226	-0.90709	0.89958
C	1.34838	3.18560	0.36803
C	-0.48588	-3.32814	-0.35234
C	-2.49752	-1.00821	-2.83189
O	-1.36996	1.01060	-2.24156
O	1.55093	1.88088	-0.18972
O	0.97952	-0.81892	0.68249
O	-0.31062	-2.41150	-1.43482
H	-0.53430	2.77849	-1.79492
H	-0.42278	1.36775	0.25017
H	1.44750	-0.47959	-1.32922
H	-1.40298	-1.00122	-0.33402
H	-0.40577	-0.57305	-3.20138
H	2.52409	-1.36661	1.88956
H	2.87274	-1.53929	0.13154
H	2.86429	0.08615	0.87934
H	2.33718	3.53851	0.68727
H	0.94838	3.88860	-0.37939
H	0.67348	3.13374	1.24248
H	-0.29017	-4.32934	-0.76118
H	0.20589	-3.11344	0.47526
H	-1.52306	-3.29203	0.03415
H	-2.38561	-2.09199	-2.96147
H	-3.25450	-0.81333	-2.05764
H	-2.83325	-0.55913	-3.77632
H	3.90082	1.07997	-5.97134
H	5.79193	2.03382	-7.31737
C	4.00845	2.15480	-6.10632
O	2.00384	2.44164	-4.81875
C	5.06374	2.69970	-6.85259
O	0.77734	1.58645	-2.91434
C	3.08199	3.02152	-5.51516
H	3.65529	-2.12141	-3.63708
C	5.18588	4.09078	-6.99745
H	2.63984	0.11572	-4.02344
P	1.82545	2.76653	-3.22282
C	3.95946	-1.27945	-3.01406
C	3.38232	-0.02009	-3.24160
H	5.35839	-2.44082	-1.83494
C	3.18083	4.41301	-5.64990
C	4.24586	4.94170	-6.39443
H	6.00933	4.50896	-7.57729
C	4.91377	-1.45947	-2.00184
O	1.44706	4.14833	-2.83371
C	3.76597	1.05966	-2.42883
H	2.44227	5.05119	-5.16799
O	3.27198	2.35518	-2.57678
C	5.28993	-0.36608	-1.20404
C	4.71605	0.89445	-1.41096
H	6.02914	-0.49396	-0.41225
H	4.33570	6.02314	-6.50366
H	4.98170	1.75271	-0.79598

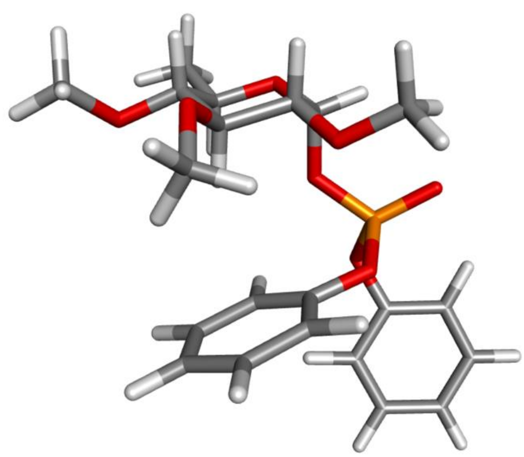


Figure C-13. Geometry of α-phosphate **X-5.**

- **TS3:** direct formation of β-glycoside **β-9F** from α-donor **9A**

57

C	0.18417	-3.63388	-3.10233
C	0.92248	-2.41207	-2.34934
C	1.24394	0.27515	-0.54510
C	0.50716	-0.14507	0.72777
C	-1.02167	0.06764	0.61034
C	-1.31433	1.45375	0.01084
C	-0.62421	1.59768	-1.35510
N	2.23908	-2.42859	-2.23480
C	-2.10451	-1.29628	2.25220
C	1.99584	-1.78077	1.66455
C	-3.43128	2.25686	0.79353
C	-0.73427	2.99188	-1.94935
O	0.10072	-1.56194	-1.93703
O	0.81904	1.30019	-1.27448
Cl	-0.76927	-2.96206	-4.49767
Cl	1.31108	-4.93661	-3.77191
Cl	-0.94117	-4.43406	-1.92052
O	0.73599	-1.50352	1.04725
O	-1.61964	0.00602	1.90012
O	-2.70308	1.61630	-0.25758
H	1.78118	-0.48072	-1.09048
H	0.86382	0.51588	1.54035
H	-1.43242	-0.70080	-0.06398
H	-0.94736	2.23888	0.69955
H	-1.03235	0.83112	-2.02681
H	2.65867	-3.25347	-2.65864
H	-2.62286	-1.18160	3.21378
H	-2.81657	-1.66882	1.49392
H	-1.27888	-2.01710	2.34968
H	1.92370	-2.80338	2.05530
H	2.82774	-1.73781	0.94471
H	2.19843	-1.08093	2.49644
H	-4.47222	2.31769	0.44924
H	-3.37443	1.68123	1.72876
H	-3.04884	3.27978	0.97377
H	-1.79726	3.24151	-2.05427
H	-0.25489	3.72723	-1.28529
H	-0.25411	3.02989	-2.93606
H	5.56720	1.07669	-0.57853
H	4.62606	2.77708	1.09124
H	6.43752	-0.76225	-2.22254
H	3.25974	-1.58183	-1.55454
O	4.00676	-0.94002	-1.08893
O	2.90412	0.87755	0.19728
C	4.78549	1.31985	-1.31673
C	3.89632	3.08841	0.33018
C	5.59429	-0.53150	-2.89049
H	3.38505	-0.00379	-0.15293
H	5.19616	2.07312	-2.00522
H	5.28530	-1.45766	-3.39498
H	2.98749	3.44137	0.83637
C	4.42666	0.02982	-2.07997
C	3.56330	1.92785	-0.60113
H	4.32243	3.92123	-0.24929
H	5.92698	0.19062	-3.65215
H	3.57478	0.23975	-2.75529
H	2.83306	2.25516	-1.35622

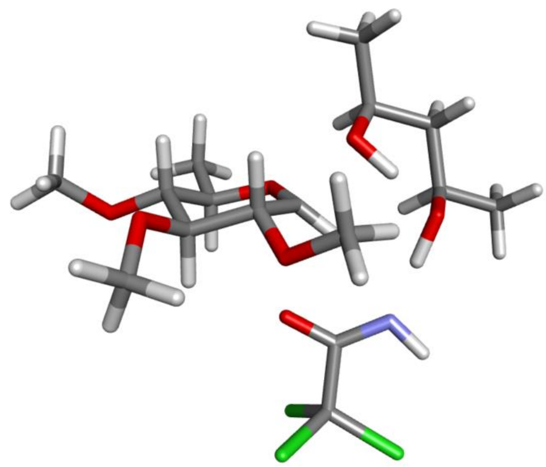


Figure C-14. Geometry of **TS3.**

General Methods

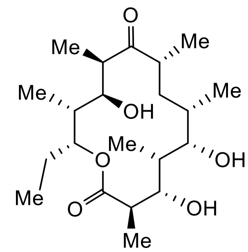
All reagents and solvents were purchased from Sigma-Aldrich, Fisher Scientific, and were used as received without further purification unless specified. 4Å molecular sieve was activated prior to use by heating under reduced pressure. Heating was achieved by use of a silicone bath with heating controlled by electronic contact thermometer. Cooling was achieved by use of cryocool machine. Deionized water was used in the preparation of all aqueous solutions and for all aqueous extractions. Solvents used for extraction and chromatography were ACS or HPLC grade. Purification of reactions mixtures was performed by flash chromatography using SiliCycle SiliaFlash P60 (230-400 mesh).

^{1}H NMR spectra were recorded on Varian vnmrs 700 (700 MHz), Varian vnmrs 500 (500 MHz), Varian INOVA 500 (500 MHz) or Varian MR400 (400 MHz) spectrometers and chemical shifts (δ) are reported in parts per million (ppm) with solvent resonance as the internal standard ($CDCl_3$ at δ 7.26, C_6D_6 at δ 7.16). Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). Proton-decoupled ^{13}C NMR spectra were recorded on Varian vnmrs 700 (700 MHz), Varian vnmrs 500 (500 MHz), Varian INOVA 500 (500 MHz) or Varian MR400 (400 MHz) spectrometers and chemical shifts (δ) are reported in ppm with solvent resonance as the internal standard ($CDCl_3$ at δ 77.16, C_6D_6 at 128.06). High resolution mass spectra (HRMS) were recorded on Micromass AutoSpec Ultima or VG (Micromass) 70-250-S Magnetic sector mass spectrometers in the University of Michigan mass spectrometry laboratory. Infrared (IR) spectra were recorded as thin film on a Perkin Elmer Spectrum BX FT-IR spectrometer. Absorption peaks were reported in wavenumbers (cm^{-1}). Optical rotations were measured in a solvent of choice on a JASCO P-2000 or Autopol III digital polarimeter at 589 nm (D-line).

Production of 6-deoxyErythronolide B (6-dEB)

Fermentation of 6-dEB:

The *E. coli* strain TB3 (pBP130/pBP144)[1] was generously provided as a gift from Dr. Blaine Pfeifer (SUNY Buffalo) and was used to access the macrolactone 6-deoxyerythronolide B (6-dEB) via fermentation. Individual colonies plated on LB-agar containing kanamycin (50 μg/mL) and ampicillin (100 μg/mL) were selected for overnight growth at 37 °C in 10 mL of LB supplemented with the same antibiotics. 6 x 1 L of 6-dEB production medium (2.8 L baffled Fernbach flasks) were inoculated with the 10 mL overnight seed cultures and incubated at 37 °C (180 rpm). When OD_{600} = 0.6-1.0, the cultures were allowed to cool at room temperature (~30 min) before IPTG (0.1 mL of 1 M stock solution), sodium propionate (20 mL of 1 M stock solution at pH 7.6), and Antifoam B (3 mL of 50% (v/v) stock solution) were added to initiate 6-dEB production. The cultures were subsequently incubated at 22 °C (180 rpm) for 5-7 days prior to centrifugation at 7550 x g for 15 min to remove cells. The resulting supernatant was extracted by incubating with Amberlite XAD16 resin (30 g of washed wet resin per 1 L of culture supernatant) overnight with shaking. The resin was collected, rinsed with water, and extracted with 3 x 100 mL of ethyl acetate (per 30 g of resin). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure to yield crude **6-dEB**, which was purified by flash column chromatography on silica gel (EtOAc:Hexanes, 30:70 v/v; followed by MeOH:CH_2Cl_2, 2:98 v/v).



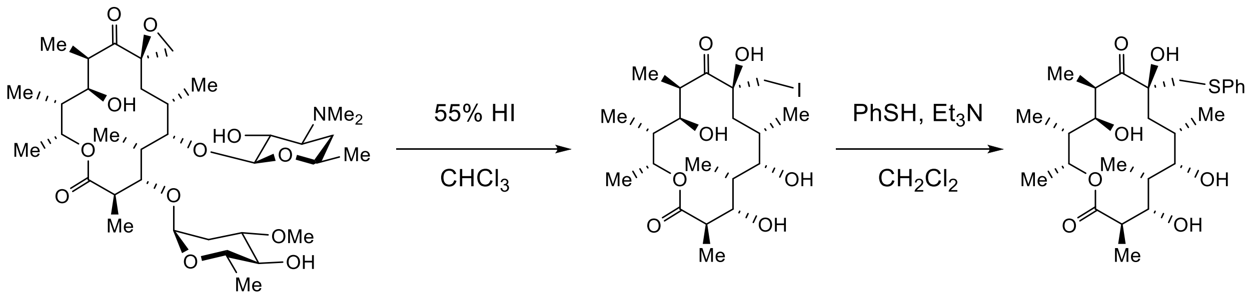
6-dEB

^{1}H NMR (700 MHz, $CDCl_3$) δ 5.15 (dd, *J* = 9.6, 2.7 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.92 (d, *J* = 10.4 Hz, 1H), 3.87 (s, 1H), 3.68 (d, *J* = 10.0 Hz, 1H), 2.86 (s, 1H), 2.82 – 2.72 (m, 2H), 2.62 (ddd, *J* = 12.9, 6.4, 3.5 Hz, 1H), 2.03 (dd, *J* = 11.9, 6.8 Hz, 2H), 1.87 (q, *J* = 6.4 Hz, 1H), 1.82 (ddd, *J* = 14.2, 9.6, 7.2 Hz, 1H), 1.77 – 1.71 (m, 1H), 1.67 (ddd, *J* = 14.3, 11.2, 3.5 Hz, 1H), 1.52 (dtd, *J* = 14.7, 7.4, 4.0 Hz, 1H), 1.30 (d, *J* = 6.7 Hz, 3H), 1.26 (td, *J* = 13.6, 4.2 Hz, 1H), 1.07 (d, *J* = 7.0 Hz, 3H), 1.06 (d, *J* = 4.1 Hz, 3H), 1.05 (d, *J* = 4.9 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (176 MHz, $CDCl_3$) δ 213.7, 178.5, 79.7, 76.6, 76.4, 71.1, 44.1, 43.6, 40.7, 39.4, 37.8, 37.6, 35.7, 25.5, 16.7, 14.9, 13.4, 10.8, 9.3, 7.0, 6.4.

<u>6-dEB Production Medium Recipe:</u>
This medium is the same as the "Enhanced Medium" previously described.[2] To 830 mL of Milli-Q water in a 2.8 L baffled Fernbach flask is added the following: 40 g tryptone, 14 g glycerol, 10 g NaCl, 1 g yeast extract. The pH of the medium is adjusted to 7.6 (NaOH) prior to autoclaving. After the medium has cooled, the following components are added: 100 mL of 1 M HEPES buffer (pH = 7.6, filter sterilized), 5.625 mL of trace metal solution, 1.875 mL of vitamin solution, 1.0 mL of kanamycin (50 mg/mL stock), and 1.0 mL of ampicillin (100 mg/mL stock). Trace metal solution contains the following components dissolved in water at a final volume of 1 L: 27.0 g $FeCl_3 \cdot 6H_2O$, 2.0 g $Na_2MoO_4 \cdot 2H_2O$, 1.9 g $CuSO_4 \cdot 5H_2O$, 1.3 g $ZnCl_2$, 1.0 g $CaCl_2$, 0.5 g H_3BO_3, 100 mL 12.1 M HCl. The solution is stored at room temperature and filter sterilized prior to addition to cultures. Vitamin solution contains the following components dissolved in water at a final volume of 1 L: 6.0 g nicotinic acid, 5.9 g pantothenic acid (hemicalcium salt), 1.7 g pyridoxine (HCl salt), 0.42 g riboflavin, 0.06 g biotin, 0.04 g folic acid. The pH of the solution is adjusted to 7.6 prior to filter sterilization and addition to cultures.

Synthesis of Substrates

Synthesis of Macrolide 7



X-7 was prepared from oleandomycin based on previously reported procedures.[3] **X-7** (300mg, 0.57mmol) was stirred in CH_2Cl_2 (0.1 M) with PhSH (0.24mL, 4 equiv.) and Et_3N (0.32mL, 4 equiv.) at room temperature. After 48h, reaction mixture was concentrated under reduced pressure. Crude was purified by flash column chromatography on silica gel (EtOAc:Hexanes, 30:70 to 50:50 v/v) to obtain 177 mg of **7** as yellow foamy solid (63% yield).

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.37 (d, J = 7.7 Hz, 2H), 7.33 – 7.25 (m, 2H), 7.19 (t, J = 7.3 Hz, 1H), 5.63 (q, J = 6.4 Hz, 1H), 4.07 (s, 1H), 3.66 – 3.53 (m, 3H), 3.39 (d, J = 13.1 Hz, 1H), 3.32 (d, J = 12.6 Hz, 2H), 3.10 (q, J = 6.6 Hz, 1H), 2.61 (dt, J = 14.1, 6.8 Hz, 1H), 2.37 (s, 1H), 2.02 (s, 1H), 2.01 – 1.89 (m, 3H), 1.72 – 1.62 (m, 2H), 1.52 (s, 1H), 1.26 (d, J = 6.6 Hz, 3H), 1.22 (d, J = 6.7 Hz, 3H), 1.12 (t, J = 6.6 Hz, 6H), 1.03 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 7.0 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$): δ 215.8, 176.0, 136.6, 129.9, 129.1, 126.6, 83.0, 79.4, 77.8, 70.0, 69.9, 44.3, 44.1, 41.8, 40.9, 40.3, 37.9, 36.2, 19.9, 18.7, 14.5, 9.2, 8.9, 7.9.

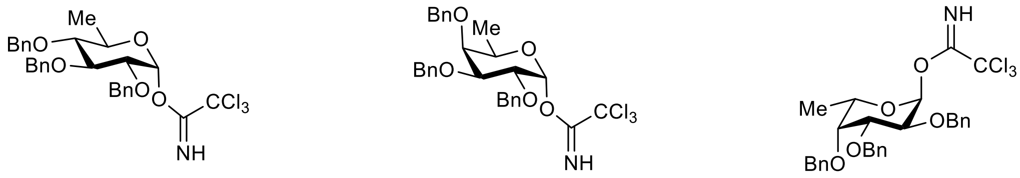
HRMS (m/z): $[M+Na]^+$ calcd. for $C_{26}H_{40}O_7$, 519.2392; found, 519.2379

TLC (EtOAc:Hexanes, 40:60 v/v): R_f = 0.2

IR (thin film, cm^{-1}): 3449, 2975, 2931, 2863, 1710, 1456, 1381, 1114

$[\alpha]_D$: -20.1 (c = 1.01 in $CHCl_3$)

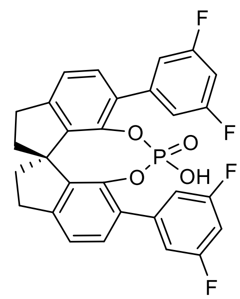
Synthesis of Sugar Donor A, B and C



A **B** **C**

Sugar donor **A**, **B** and **C** were synthesized based on previously reported procedures.[4]

Synthesis of Chiral Phosphoric Acid 6f



(R)-6f

(R)-6f was prepared based on previously reported methods.[5]

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.24 (m, 4H), 6.85 (d, J = 6.4 Hz, 4H), 6.19 (t, J = 8.1 Hz, 2H), 3.16 (ddd, J = 17.1, 11.4, 6.5 Hz, 2H), 2.98 (dd, J = 16.2, 7.8 Hz, 2H), 2.38 (dd, J = 12.1, 6.4 Hz, 2H), 2.21 (q, J = 11.4 Hz, 2H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 162.9 (dd, J = 246.7, 13.3 Hz), 146.4 (d, J = 2.3 Hz), 141.9, 140.8 (d, J = 3.1 Hz), 140.6, 133.3, 130.4 (d, J = 1.8 Hz), 123.1, 112.4 (dd, J = 19.8, 6.2 Hz), 102.3 (t, J = 25.5 Hz), 60.1, 38.8, 30.6.

^{19}F NMR (471 MHz, CDCl$_3$): δ -111.03.

^{31}P NMR (202 MHz, CDCl$_3$): δ -7.55.

HRMS (m/z): [M-H]$^-$ calcd. for $C_{29}H_{19}F_4O_4P$, 537.0879; found, 537.0935

IR (thin film, cm^{-1}): 2953, 1622, 1593, 1455, 1415, 1115, 985

[α]$_D$: +166.9 (c = 1.01 in $CHCl_3$)

General Procedures for Glycosylation Reactions

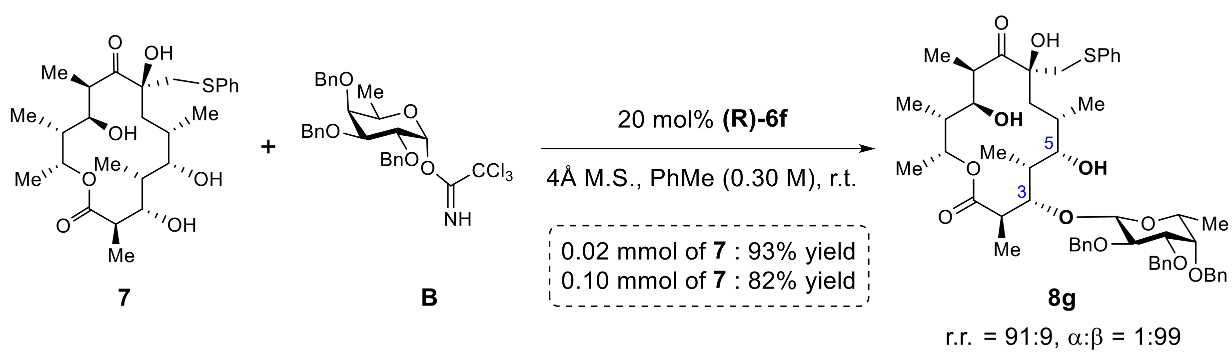
Glycosylation of Macrolide Catalyzed by TMS-OTf or BF_3•OEt_2

Macrolide (0.020mmol, 1.0 equiv.), sugar donor (0.024mmol, 1.2 equiv.) and 20mg of powdered 4Å molecular sieve were stirred in 400μL of dry toluene (0.05 M) at room temperature under N_2 for 10 min. Reaction mixture was then cooled to -20°C. After stirring for another 10 min., TMS-OTf or BF_3•OEt_2 (0.004mmol, 0.2 equiv.) in 20μL of dry toluene was added to the reaction. After 17 to 24h, reaction was quenched with Et_3N, filtered through a short pad of Celite with CH_2Cl_2 washing and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (pipette column) on silica gel (EtOAc:Hexanes, gradient) to obtain a mixture of glycosides. Each individual glycoside was isolated by separation on semi-prep HPLC (EtOAc:Hexanes) and characterized.

Glycosylation of Macrolide Catalyzed by Chiral Brønsted Acids

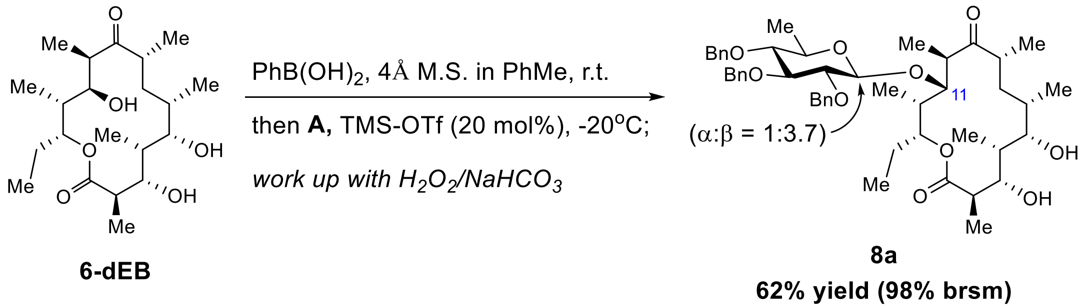
Macrolide (0.020mmol, 1.0 equiv.), sugar donor (0.024mmol, 1.2 equiv.), chiral Brønsted acid (0.004mmol, 0.2 equiv.) and 10mg of powdered 4Å molecular sieve were stirred in dry toluene (0.1 to 0.3 M) at room temperature. After 24 – 72h, reaction was quenched with Et_3N, filtered through a short pad of Celite with CH_2Cl_2 washing and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (pipette column) on silica gel (EtOAc:Hexanes, gradient) to obtain a mixture of glycosides. Each individual glycoside was isolated by separation on semi-prep HPLC (EtOAc:Hexanes) and characterized.

Large scale glycosylation of Macrolide 7 Catalyzed by Chiral Phosphoric Acids



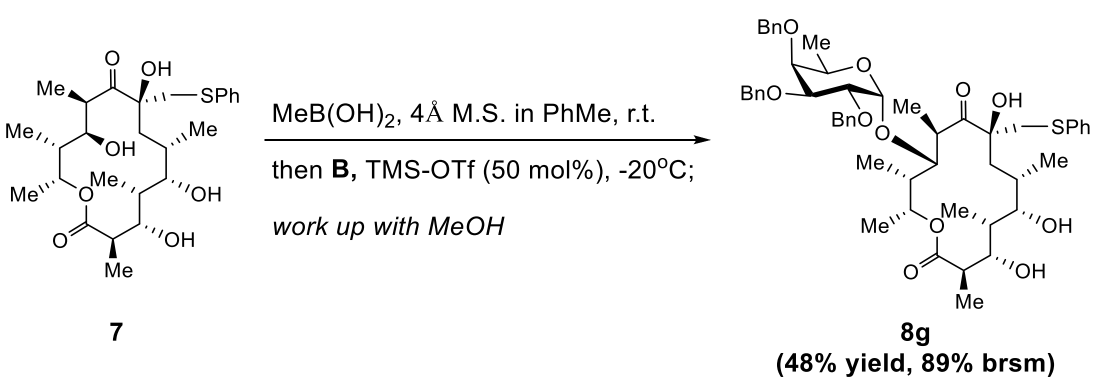
7 (50mg, 0.10mmol), donor **B** (70mg, 0.12mmol), **(R)-6f** (10.8mg, 0.02mmol) and 50mg of powdered 4Å molecular sieve were stirred in 340μL of dry toluene (0.30 M) at room temperature. After 48h, reaction was quenched with Et_3N, filtered through a short pad of Celite with CH_2Cl_2 washing and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel (EtOAc:Hexanes, 30:70 v/v) to obtain 75mg of **8g** as yellow foamy solid (82% yield, 91:9 r.r.).

C_{11}-Glycosylation of 6-dEB



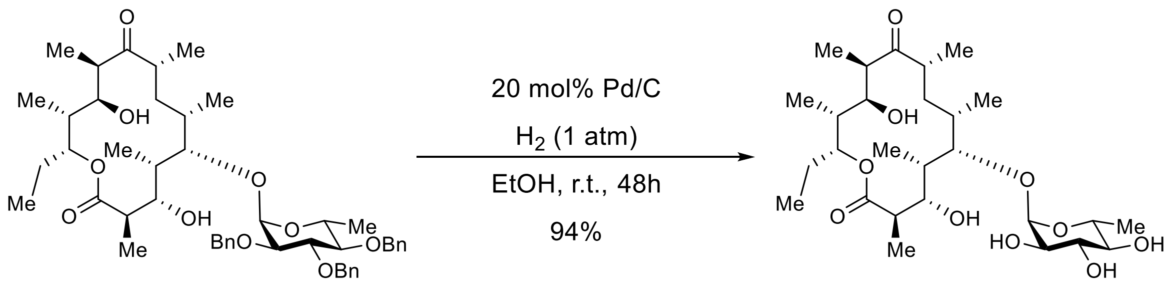
6-dEB (5mg, 0.010mmol), $PhB(OH)_2$ (1.2mg, 1 equiv.) and 10mg of powdered 4Å molecular sieve were stirred in 100µL of dry toluene at room temperature. After 3h, sugar donor **A** (17.4mg, 3 equiv.) in 100µL of dry toluene was added to the reaction, and the mixture was cooled to -20°C. TMS-OTf (0.36µL, 0.2 equiv.) in 20µL of dry toluene was added to the reaction. After 17h, the reaction was quenched with Et_3N, warmed up to room temperature and diluted with EtOAc. 30% H_2O_2, sat. $NaHCO_3$ and water were added to the solution, and the suspension was stirred at room temperature. After 2h, the reaction was extracted with CH_2Cl_2 twice. Combined organic was dried over Na_2SO_4, filtered through glass wool and concentrated under pressure. The crude mixture was purified by flash column chromatography (pipette column) on silica gel (EtOAc:Hexanes, 20:80 to 35:65 v/v) to obtain **8a** (5mg, 62% yield) as colorless oil and starting material **6-dEB** (1.5mg, 38% recovery). The diastereomeric glycosides were isolated by semi-prep HPLC (18mL/min, EtOAc:Hexanes, 25:75 v/v) and characterized.

C_{11}-Glycosylation of Macrolide 6



7 (10mg, 0.020mmol), $MeB(OH)_2$ (1.2mg, 1 equiv.) and 20mg of powdered 4Å molecular sieve were stirred in 200µL of dry toluene at room temperature. After 5h, sugar donor **B** (35mg, 3 equiv.) in 150µL of dry toluene was added to the reaction, and the mixture was cooled to -20°C. TMS-OTf (1.8µL, 0.5 equiv.) in 50µL of dry toluene was added to the reaction. After 17h, the reaction was quenched with Et_3N, warmed up to room temperature and stirred with MeOH for 30 minutes. Next, the reaction was filtered through a short pad of Celite with CH_2Cl_2 washing and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (pipette column) on silica gel (EtOAc:Hexanes, 20:80 to 60:40 v/v) to obtain **8g** (8.7mg, 48% yield) as yellow oil and starting material **7** (4.6mg, 46% recovery).

Procedure for Deprotection of Macrolide Glycoside



2

In a one dram vial, **1** (3.4mg, 4.2μmol) and Pd/C (0.9mg, 0.84μmol) were added, and the vial was sealed with rubber septum. The vial was evacuated and backfilled with N_2 three times, followed by H_2 for another three times. 200μL of EtOH was added to the vial, and the suspension was stirred with H_2 balloon on top for 48h at room temperature. At the end of the reaction, the suspension was filtered through a thin pad of Cealite with EtOAc washing. Combined organic layer was concentrated under reduced pressure, and the crude mixture was purified by flash column chromatography (pipette column) on silica gel (CH_2Cl_2:MeOH, 15:1 v/v) to obtain the debenzylated glycoside (2.1mg, 94% yield) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.13 (dd, *J* = 9.5, 3.0 Hz, 1H), 5.02 (d, *J* = 3.1 Hz, 1H), 3.92 (s, 2H), 3.87 (d, *J* = 10.2 Hz, 1H), 3.83 – 3.74 (m, 1H), 3.69 – 3.51 (m, 3H), 3.08 (q, *J* = 7.3 Hz, 2H), 2.84 – 2.67 (m, 2H), 2.67 – 2.56 (m, 1H), 2.42 – 2.23 (m, 1H), 1.93 (d, *J* = 5.8 Hz, 1H), 1.85 – 1.58 (m, 3H), 1.51 (ddd, *J* = 13.9, 7.2, 4.0 Hz, 1H), 1.32 (d, *J* = 5.4 Hz, 3H), 1.29 (d, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 6.9 Hz, 3H), 1.02 (m, 9H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 213.3, 178.5, 93.8, 79.0, 76.4, 76.1, 74.1, 72.4, 71.1, 68.8, 46.0, 44.9, 43.7, 40.6, 37.5, 32.1, 29.5, 25.6, 18.2, 16.3, 15.4, 13.0, 10.8, 9.3, 8.9, 8.0, 6.4.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{27}H_{48}O_{10}$, 555.3145; found, 555.3141.

TLC (CH_2Cl_2:MeOH, 10:1 v/v): R_f = 0.4

Characterization Data

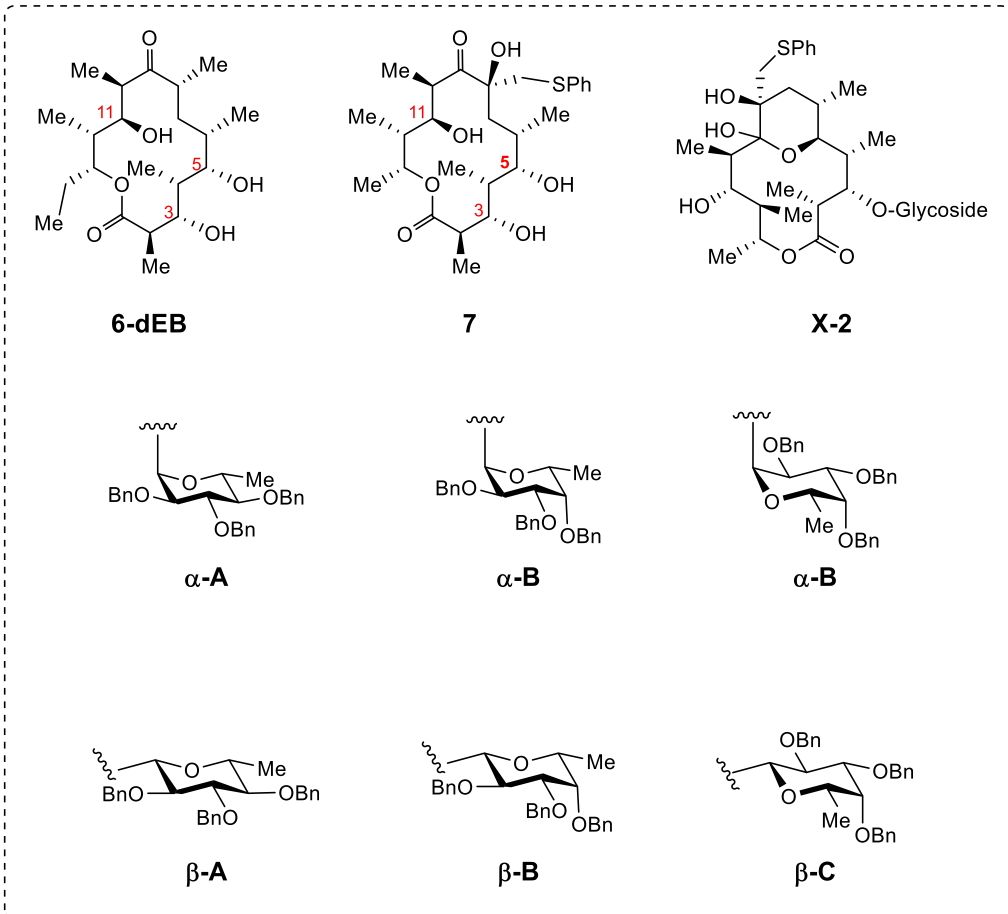
Nomenclature for compound labelling:

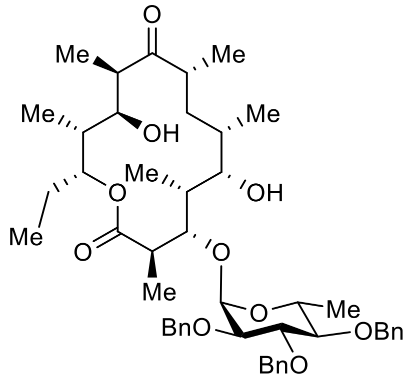
6-dEB-C_3-α-A

<u>6-dEB</u>-C_3-α-A: structure of macrolide (**6-dEB**, **7, or X-2**)

6-dEB-**<u>C_3</u>**-α-A: position of glycoside (C_3, C_5 or C_{11})

6-dEB-C_3-**<u>α-A</u>**: stereochemistry and structure of glycoside (α or β; A, B or C)





6-dEB-C_3-α-A (**1**)

^{1}H NMR (700 MHz, C_6D_6): δ 7.29 (d, J = 7.4 Hz, 2H), 7.26 (t, J = 7.2 Hz, 3H), 7.18 – 7.03 (m, 10H), 5.68 (dd, J = 9.8, 3.9 Hz, 1H), 4.89 – 4.79 (m, 3H), 4.75 (d, J = 3.1 Hz, 1H), 4.59 (d, J = 11.9 Hz, 1H), 4.55 (d, J = 11.9 Hz, 1H), 4.50 (d, J = 11.2 Hz, 1H), 4.13 (s, 1H), 4.10 (t, J = 9.4 Hz, 1H), 4.02 (dq, J = 12.3, 6.2 Hz, 1H), 3.92 (d, J = 4.0 Hz, 1H), 3.78 (d, J = 10.1 Hz, 1H), 3.68 (m, 2H), 3.48 (dd, J = 9.9, 3.2 Hz, 1H), 3.06 (t, J = 9.2 Hz, 1H), 2.83 (q, J = 6.7 Hz, 1H), 2.77 (dt, J = 13.5, 6.8 Hz, 1H), 2.71 – 2.63 (m, 1H), 1.81 – 1.74 (m, 2H), 1.65 (dt, J = 16.3, 7.3 Hz, 1H), 1.61 – 1.52 (m, 2H), 1.43 (d, J = 6.8 Hz, 3H), 1.43 – 1.35 (m, 1H), 1.34 (d, J = 6.9 Hz, 3H), 1.24 (d, J = 6.2 Hz, 3H), 1.19 (ddt, J = 14.7, 11.8, 7.3 Hz, 1H), 1.10 (d, J = 6.7 Hz, 3H), 1.08 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H), 0.79 (t, J = 7.3 Hz, 3H), 0.74 (d, J = 7.1 Hz, 3H).

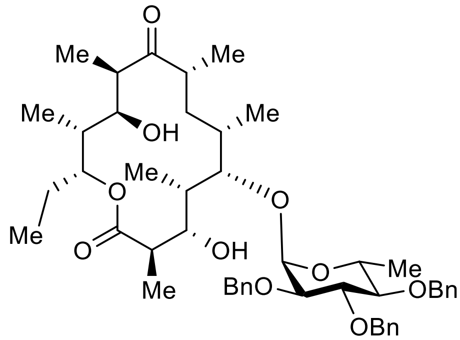
^{13}C NMR (176 MHz, C_6D_6): δ 217.8, 176.7, 139.3, 139.1, 137.5, 129.0, 128.9, 128.6, 128.6, 128.4, 128.3, 128.0, 127.8, 127.7, 100.6, 91.7, 84.6, 82.1, 80.6, 77.2, 75.6, 75.4, 75.4, 74.4, 71.1, 68.1, 45.4, 45.0, 42.4, 41.1, 39.8, 38.8, 35.0, 26.2, 18.1, 18.0, 16.0, 16.0, 10.7, 9.4, 9.2, 8.8.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{48}H_{66}O_{10}$, 820.5000; found, 820.4987

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.5

IR (thin film, cm^{-1}): 3500, 2971, 2927, 2971, 1725, 1701, 1454, 1069

$[\alpha]_D$: -10.0 (c = 0.24 in $CHCl_3$)



6-dEB-C_5-α-A (**2**)

^{1}H NMR (700 MHz, C_6D_6): δ 7.31 (d, J = 7.4 Hz, 2H), 7.29 (d, J = 7.4 Hz, 2H), 7.25 (d, J = 7.3 Hz, 2H), 7.17 (d, J = 7.3 Hz), 7.15 – 7.12 (m), 7.11 – 7.04 (m, 3H), 5.19 – 5.13 (m, 1H), 4.93 (d, J = 11.3 Hz, 1H), 4.89 (d, J = 3.7 Hz, 1H), 4.84 (d, J = 11.3 Hz, 1H), 4.78 (d, J = 11.2 Hz, 1H), 4.56 (d, J = 11.7 Hz, 1H), 4.52 (d, J = 2.9 Hz, 1H), 4.51 (d, J = 3.4 Hz, 1H), 4.31 (d, J = 3.4 Hz, 1H), 4.17 (d, J = 10.3 Hz, 1H), 4.10 (dq, J = 12.4, 6.2 Hz, 1H), 4.05 (t, J = 9.3 Hz, 1H), 3.93 (s, 1H), 3.79 (d, J = 9.5 Hz, 1H), 3.65 (s, 1H), 3.50 (dd, J = 9.7, 3.7 Hz, 1H), 3.10 (t, J = 9.2 Hz, 1H), 2.90 – 2.74 (m, 2H), 2.60 (d, J = 6.4 Hz, 1H), 2.24 (s, 1H), 2.03 (q, J = 6.3 Hz, 1H), 1.60 (td, J = 12.8, 11.1, 4.3 Hz, 1H), 1.55 (dt, J = 14.1, 7.1 Hz, 1H), 1.50 – 1.47 (m, 1H), 1.46 (d, J = 6.8 Hz, 3H), 1.26 (d, J = 7.1 Hz, 3H), 1.25 (d, J = 6.3 Hz, 3H), 1.21 (d, J = 6.9 Hz, 3H), 1.16 (d, J = 6.3 Hz, 3H), 1.13 (m, 1H), 1.03 (ddt, J = 13.9, 7.3, 3.9 Hz, 1H), 0.98 (d, J = 7.1 Hz, 3H), 0.66 (t, J = 7.3 Hz, 3H), 0.61 (d, J = 6.9 Hz, 3H).

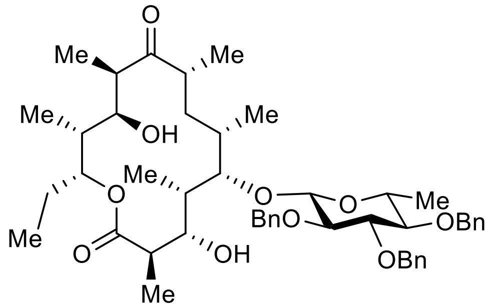
^{13}C NMR (126 MHz, C_6D_6): δ 212.4, 178.6, 139.5, 139.0, 138.6, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 95.9, 83.8, 82.4, 80.5, 79.2, 76.0, 75.6, 75.3, 73.6, 71.2, 69.1, 44.9, 43.4, 40.9, 39.9, 38.6, 37.6, 25.6, 18.3, 17.2, 15.5, 13.9, 10.6, 9.1, 8.3, 7.1.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{48}H_{66}O_{10}$, 820.5000; found, 820.4985

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.5

IR (thin film, cm^{-1}): 3468, 2971, 2925, 1704, 1453, 1070

[α]$_D$: +31.7 (c = 0.49 in $CHCl_3$)



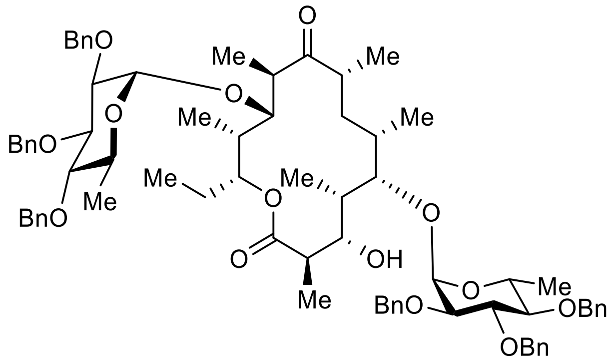
6-dEB-C_5-β-A

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.38 – 7.33 (m, 2H), 7.33 – 7.29 (m, 5H), 7.28 (m, 8H), 5.11 (dd, J = 9.6, 2.9 Hz, 1H), 4.91 (d, J = 11.3 Hz, 1H), 4.89 – 4.80 (m, 5H), 4.63 (d, J = 10.9 Hz, 1H), 4.50 (d, J = 7.8 Hz, 1H), 3.96 (d, J = 4.4 Hz, 1H), 3.89 (d, J = 10.3 Hz, 1H), 3.83 (dd, J = 4.8, 1.6 Hz, 1H), 3.69 – 3.64 (m, 2H), 3.44 – 3.38 (m, 2H), 3.26 (s, 1H), 3.20 (t, J = 9.2 Hz, 1H), 2.78 – 2.69 (m, 2H), 2.66 – 2.59 (m, 1H), 2.33 – 2.25 (m, 1H), 1.86 – 1.77 (m, 2H), 1.75 – 1.69 (m, 1H), 1.62 – 1.56 (m, 1H), 1.52 – 1.47 (m, 1H), 1.28 (d, J = 6.8 Hz, 3H), 1.27 (d, J = 6.2 Hz, 3H), 1.22 – 1.15 (m, 1H), 1.05 (d, J = 6.9 Hz, 3H), 1.03 (d, J = 6.5 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 7.2 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H), 0.87 (d, J = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 213.6, 179.2, 138.6, 138.1, 137.4, 129.7, 128.9, 128.6, 128.5, 128.4, 128.2, 128.0, 128.0, 127.7, 103.5, 84.8, 83.9, 81.0, 78.2, 76.3, 75.5, 75.4, 75.3, 71.7, 71.1, 44.7, 43.8, 40.7, 39.1, 38.2, 38.0, 35.5, 25.6, 18.0, 17.5, 15.5, 13.1, 10.8, 9.3, 8.3, 6.3.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{48}H_{66}O_{10}$, 820.5000; found, 820.4992

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.55



6-dEB-C$_5$-α-A-C$_{11}$-α-A (**3**)

^{1}H NMR (700 MHz, C_6D_6): δ 7.35 (d, J = 7.2 Hz, 2H), 7.31 (t, J = 6.4 Hz, 8H), 7.25 (dt, J = 12.5, 6.8 Hz, 6H), 7.14 – 7.03 (m, 20H), 5.81 (t, J = 7.5 Hz, 1H), 5.72 (d, J = 3.6 Hz, 1H), 5.02 (d, J = 11.4 Hz, 1H), 4.99 (d, J = 3.8 Hz, 1H), 4.93 (d, J = 11.2 Hz, 1H), 4.89 – 4.84 (m, 2H), 4.83 (d, J = 11.4 Hz, 1H), 4.77 (dd, J = 11.4, 1.9 Hz, 3H), 4.72 (d, J = 10.6 Hz, 1H), 4.57 (s, 2H), 4.51 (dd, J = 11.1, 9.2 Hz, 2H), 4.36 (d, J = 10.5 Hz, 1H), 4.31 (d, J = 9.4 Hz, 1H), 4.18 (dd, J = 4.9, 2.8 Hz, 1H), 4.17 – 4.14 (m, 1H), 4.08 (m, 3H), 3.82 (s, 1H), 3.56 (dd, J = 9.6, 3.8 Hz, 1H), 3.46 (dd, J = 10.1, 3.6 Hz, 1H), 3.25 (ddt, J = 13.1, 6.2, 3.4 Hz, 1H), 3.09 (m, 2H), 2.85 (dq, J = 10.2, 6.7 Hz, 1H), 2.68 (q, J = 6.3 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.01 (qd, J = 6.6, 6.1, 1.6 Hz, 1H), 1.88 – 1.80 (m, 1H), 1.59 (d, J = 6.7 Hz, 3H), 1.57 (m, 1H), 1.55 (d, J = 6.0 Hz, 3H), 1.46 (d, J = 6.2 Hz, 3H), 1.27 (d, J = 6.7 Hz, 3H), 1.26 – 1.23 (m, 1H), 1.22 (d, J = 7.0 Hz, 3H), 1.19 (d, J = 6.2 Hz, 3H), 1.18 – 1.15 (m, 1H), 1.15 – 1.08 (m, 1H), 0.95 (d, J = 7.1 Hz, 3H), 0.64 (d, J = 7.2 Hz, 3H), 0.47 (t, J = 7.4 Hz, 3H).

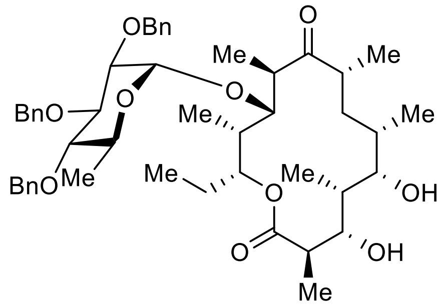
^{13}C NMR (126 MHz, C_6D_6): δ 211.0, 177.0, 139.9, 139.5, 139.4, 139.2, 139.1, 138.6, 128.7, 128.7, 128.5, 128.5, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 100.8, 93.7, 85.0, 83.7, 83.6, 82.5, 82.1, 81.8, 80.3, 80.2, 78.8, 75.6, 75.6, 75.4, 75.1, 74.9, 73.4, 69.1, 69.1, 44.9, 44.6, 41.4, 38.9, 38.1, 28.5, 26.0, 24.6, 18.3, 18.2, 17.0, 15.9, 15.6, 13.7, 13.6, 11.9, 10.1, 10.0, 9.8, 8.9, 8.8, 7.8, 7.4, 6.9.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{75}H_{94}O_{14}$, 1236.6987; found, 1239.6962

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.6

IR (thin film, cm^{-1}): 2921, 2854, 1713, 1454, 1070

[α]$_D$: +40.5 (c = 0.07 in $CHCl_3$)



6-dEB-C_{11}-α-A

^{1}H NMR (500 MHz, C_6D_6): δ 7.41 (d, J = 7.4 Hz, 2H), 7.32 (d, J = 7.4 Hz, 2H), 7.26 (d, J = 7.2 Hz, 2H), 7.11 – 7.01 (m, 3H), 5.83 (t, J = 7.3 Hz, 1H), 5.63 (d, J = 3.4 Hz, 1H), 5.01 (d, J = 11.5 Hz, 1H), 4.98 (d, J = 10.7 Hz, 1H), 4.86 (d, J = 11.2 Hz, 1H), 4.80 (t, J = 11.5 Hz, 2H), 4.53 (d, J = 11.2 Hz, 1H), 4.15 (m, 2H), 4.05 (dq, J = 12.0, 6.0 Hz, 1H), 3.99 (d, J = 10.4 Hz, 1H), 3.67 (m, 1H), 3.52 (dd, J = 10.1, 3.4 Hz, 1H), 3.09 (m, 2H), 2.96 (s, 1H), 2.73 (dq, J = 13.4, 6.7 Hz, 1H), 2.64 (q, J = 6.5 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.70 (m, 1H), 1.65 (m, 1H), 1.54 (d, J = 6.0 Hz, 3H), 1.49 (d, J = 6.7 Hz, 3H), 1.32 (d, J = 6.2 Hz, 3H), 1.26 (d, J = 6.6 Hz, 3H), 1.20 (m, 2H), 1.03 (d, J = 6.8 Hz, 3H), 1.00 – 0.93 (m, 1H), 0.81 (d, J = 7.1 Hz, 3H), 0.62 (d, J = 7.1 Hz, 3H), 0.48 (t, J = 7.3 Hz, 3H).

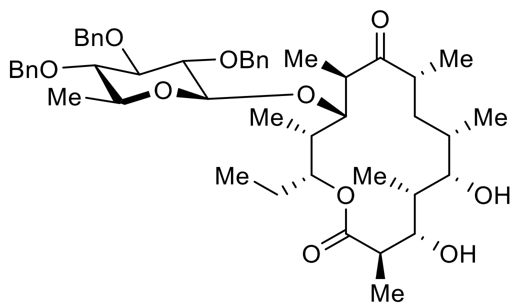
^{13}C NMR (126 MHz, C_6D_6): δ 211.0, 176.8, 139.9, 139.3, 139.3, 128.7, 128.5, 128.4, 128.2, 128.0, 127.8, 127.6, 127.5, 100.8, 85.0, 83.6, 82.0, 81.9, 79.0, 76.4, 75.6, 75.4, 75.4, 75.0, 69.1, 44.8, 44.2, 41.4, 39.3, 38.5, 38.0, 35.3, 26.1, 18.3, 16.7, 15.4, 13.9, 10.0, 9.9, 7.8, 7.4.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{48}H_{66}O_{10}$, 820.5000; found, 820.4979

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.3

IR (thin film, cm^{-1}): 3438, 2967, 2919, 2855, 1710, 1453, 1070

[α]$_D$: -3.2 (c = 0.10 in $CHCl_3$)



6-dEB-C_{11}-β-A (**8a**)

^{1}H NMR (700 MHz, C_6D_6): δ 7.46 (d, J = 7.5 Hz, 2H), 7.27 (d, J = 7.5 Hz, 2H), 7.19 (t, J = 7.6 Hz, 4H), 7.15 – 7.02 (m, 5H), 5.76 (dd, J = 8.3, 6.1 Hz, 1H), 5.07 (d, J = 11.4 Hz, 1H), 4.86 (d, J = 11.4 Hz, 1H), 4.76 (d, J = 11.4 Hz, 1H), 4.72 (d, J = 11.4 Hz, 1H), 4.67 (d, J = 11.4 Hz, 1H), 4.50 (d, J = 9.1 Hz, 1H), 4.40 (d, J = 7.3 Hz, 1H), 4.39 (d, 1H), 3.91 (d, J = 10.1 Hz, 1H), 3.78 – 3.71 (m, 1H), 3.55 (dd, J = 9.2, 7.4 Hz, 1H), 3.48 (t, J = 9.0 Hz, 1H), 3.35 (dq, J = 9.6, 6.1 Hz, 1H), 3.29 (ddt, J = 12.3, 9.3, 6.0 Hz, 1H), 3.14 (t, J = 9.1 Hz, 1H), 2.76 – 2.67 (m, 2H), 2.65 (s, 1H), 1.89 (q, J = 6.7 Hz, 1H), 1.80 – 1.76 (m, 1H), 1.74 (m, 1H), 1.64 – 1.58 (m, 1H), 1.57 – 1.52 (m, 1H), 1.40 (d, J = 6.8 Hz, 3H), 1.36 (d, J = 6.1 Hz, 3H), 1.33 (m, 1H), 1.28 (d, J = 6.7 Hz, 3H), 1.17 (d, J = 6.3 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H), 1.04 (td, J = 13.6, 3.5 Hz, 1H), 0.87 (d, J = 7.1 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H), 0.79 (d, J = 7.2 Hz, 3H).

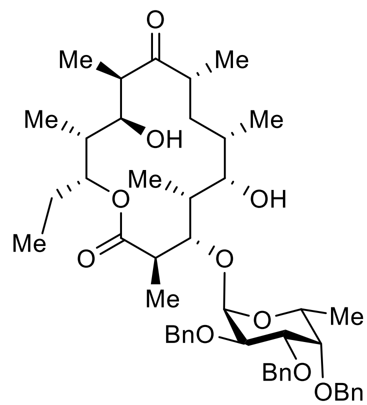
^{13}C NMR (126 MHz, C_6D_6): δ 214.1, 174.8, 139.8, 139.4, 139.3, 128.5, 128.5, 128.4, 128.4, 128.3, 127.8, 127.7, 127.7, 127.5, 99.4, 84.8, 83.6, 83.2, 78.3, 76.1, 75.8, 75.5, 75.2, 75.1, 74.9, 71.6, 44.0, 43.9, 41.0, 39.6, 39.0, 38.7, 35.5, 26.7, 18.2, 17.2, 15.1, 14.3, 10.7, 10.2, 8.0, 7.5.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{48}H_{66}O_{10}$, 820.5000; found, 820.4989

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.4

IR (thin film, cm^{-1}): 3489, 2971, 2928, 2880, 1733, 1702, 1453, 1071

$[\alpha]_D$: -42.3 (c = 0.23 in $CHCl_3$)



6-dEB-C_3-α-B (**8b**)

[1]H NMR (500 MHz, C_6D_6): δ 7.39 (d, J = 7.3 Hz, 3H), 7.34 – 7.18 (m, 8H), 7.14 – 6.96 (m, 4H), 5.65 (dd, J = 9.9, 3.8 Hz, 1H), 4.96 (d, J = 11.3 Hz, 1H), 4.85 (d, J = 3.5 Hz, 1H), 4.64 (dd, J = 11.8, 4.3 Hz, 2H), 4.57 (d, J = 11.9 Hz, 1H), 4.49 (t, J = 11.6 Hz, 2H), 4.20 (dd, J = 10.4, 3.4 Hz, 1H), 4.14 (d, J = 2.4 Hz, 1H), 4.03 – 3.91 (m, 2H), 3.86 – 3.79 (m, 2H), 3.70 (d, J = 9.8 Hz, 1H), 3.66 (s, 1H), 3.34 (s, 1H), 2.91 – 2.75 (m, 2H), 2.70 – 2.60 (m, 1H), 1.83 – 1.72 (m, 1H), 1.68 – 1.62 (m, 1H), 1.62 – 1.57 (m, 1H), 1.55 (td, J = 7.3, 2.5 Hz, 1H), 1.47 (d, J = 6.8 Hz, 3H), 1.34 (d, J = 6.9 Hz, 3H), 1.25 – 1.18 (m, 1H), 1.15 (d, J = 6.5 Hz, 3H), 1.10 (d, J = 6.8 Hz, 3H), 1.07 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H), 0.94 – 0.89 (m, 1H), 0.79 (t, J = 7.4 Hz, 3H), 0.74 (d, J = 7.1 Hz, 3H).

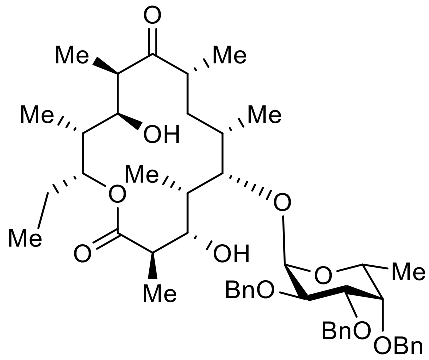
[13]C NMR (176 MHz, C_6D_6): δ 217.3, 176.8, 139.4, 139.1, 137.7, 130.3, 130.2, 129.1, 128.7, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 101.3, 90.6, 79.1, 78.6, 77.3, 76.7, 75.5, 75.3, 74.8, 73.0, 71.0, 67.7, 45.2, 45.0, 42.3, 41.1, 40.1, 38.6, 35.2, 26.2, 18.0, 16.8, 16.0, 15.9, 14.4, 10.7, 9.4, 9.2, 8.6.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{48}H_{66}O_{10}$, 825.4554; found, 825.4535

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.5

IR (thin film, cm^{-1}): 3494, 2961, 2919, 2873, 2849, 1725, 1705, 1453

$[α]_D$: +8.8 (c = 0.07 in $CHCl_3$)



6-dEB-C_5-α-B (**8c**)

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.38 – 7.27 (m, 21H), 5.13 (d, J = 3.8 Hz, 2H), 4.97 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 11.7 Hz, 1H), 4.77 – 4.68 (m, 3H), 4.65 (d, J = 11.5 Hz, 1H), 4.10 (dd, J = 9.9, 3.7 Hz, 1H), 3.89 (m, 2H), 3.85 – 3.84 (m, 1H), 3.83 – 3.81 (m, 1H), 3.79 (d, J = 10.4 Hz, 1H), 3.69 (s, 1H), 3.65 (d, J = 9.7 Hz, 1H), 3.41 (s, 1H), 2.82 – 2.69 (m, 2H), 2.64 – 2.53 (m, 1H), 2.32 (m, 1H), 1.90 (q, J = 6.3 Hz, 1H), 1.82 (tt, J = 14.8, 7.3 Hz, 1H), 1.73 (dt, J = 15.7, 6.9 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.52 (ddt, J = 14.6, 11.8, 7.5 Hz, 1H), 1.31 (d, J = 6.7 Hz, 3H), 1.24 (m, 1H), 1.18 (d, J = 6.4 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 6.7 Hz, 3H), 1.00 – 0.97 (m, 6H), 0.93 (t, J = 7.3 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H).

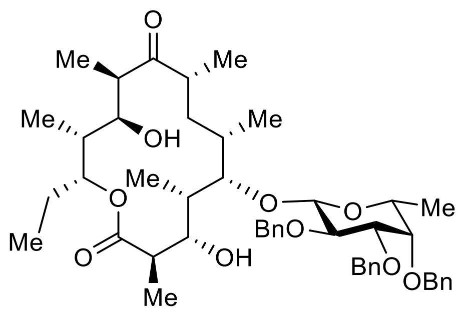
^{13}C NMR (176 MHz, $CDCl_3$): δ 213.5, 178.7, 138.7, 138.6, 128.5, 128.5, 128.4, 128.4, 127.8, 127.8, 127.8, 127.7, 127.7, 94.2, 79.5, 79.0, 76.3, 75.9, 74.8, 73.5, 73.5, 71.1, 68.2, 44.4, 43.6, 40.7, 39.2, 37.8, 37.5, 29.9, 25.6, 22.8, 16.9, 16.7, 15.2, 14.3, 13.0, 10.8, 9.3, 8.0, 6.4.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{48}H_{66}O_{10}$, 825.4554; found, 825.4534

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.5

IR (thin film, cm^{-1}): 3508, 2924, 2851, 1704, 1454, 1095, 1044

$[\alpha]_D$: +19.0 (c = 0.05 in $CHCl_3$)



6-dEB-C_5-β-B

^{1}H NMR (500 MHz, C_6D_6): δ 7.48 (d, J = 7.3 Hz, 2H), 7.31 (d, J = 7.0 Hz, 3H), 7.27 (d, J = 7.2 Hz, 2H), 7.23 – 7.17 (m, 5H), 7.15 – 6.97 (m, 7H), 5.09 (dd, J = 9.6, 3.1 Hz, 1H), 4.94 (d, J = 11.3 Hz, 1H), 4.85 (d, J = 12.0 Hz, 2H), 4.48 (d, J = 11.5 Hz, 1H), 4.42 (s, 2H), 4.39 (d, J = 4.4 Hz, 1H), 4.32 (d, J = 7.7 Hz, 1H), 4.27 (d, J = 4.6 Hz, 2H), 4.01 (dd, J = 9.7, 7.8 Hz, 1H), 3.95 (d, J = 3.7 Hz, 1H), 3.91 – 3.80 (m, 2H), 3.25 (dd, J = 9.8, 2.8 Hz, 1H), 3.13 (d, J = 2.4 Hz, 1H), 3.03 – 2.90 (m, 1H), 2.91 – 2.78 (m, 2H), 2.68 – 2.53 (m, 2H), 2.00 (q, J = 6.8 Hz, 1H), 1.63 – 1.52 (m, 2H), 1.49 (d, J = 6.7 Hz, 3H), 1.47 – 1.42 (m, 1H), 1.37 (d, J = 6.3 Hz, 3H), 1.31 (d, J = 6.7 Hz, 3H), 1.21 (d, J = 6.9 Hz, 3H), 1.13 (dd, J = 13.7, 3.7 Hz, 1H), 1.10 (d, J = 6.4 Hz, 3H), 1.06 (d, J = 7.2 Hz, 3H), 0.99 (ddt, J = 15.0, 7.6, 3.1 Hz, 1H), 0.66 (t, J = 7.3 Hz, 3H), 0.59 (d, J = 6.9 Hz, 3H).

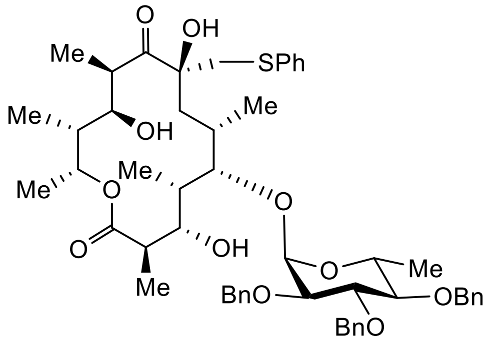
^{13}C NMR (176 MHz, C_6D_6): δ 211.8, 179.4, 139.2, 138.8, 138.3, 129.1, 128.8, 128.5, 128.4, 128.4, 128.3, 128.1, 128.00, 127.9, 127.8, 104.9, 85.8, 83.8, 78.5, 78.5, 77.0, 76.3, 75.7, 75.2, 72.8, 71.3, 70.9, 45.2, 44.1, 41.0, 39.2, 38.5, 38.5, 35.8, 25.5, 17.8, 17.0, 15.7, 13.6, 10.7, 9.1, 8.6, 6.7.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{48}H_{66}O_{10}$, 820.5000; found, 820.4984

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.5

IR (thin film, cm^{-1}): 3464, 2971, 2927, 2877, 1701, 1598, 1454, 1064

$[\alpha]_D$: -13.1 (c = 0.31 in $CHCl_3$)



7-C_5-α-A (**8d**)

^{1}H NMR (700 MHz, C_6D_6): δ 7.40 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.24 (m, 4H), 7.23 – 7.17 (m, 4H), 7.14 – 7.03 (m, 5H), 6.99 (dd, J = 8.4, 7.1 Hz, 2H), 6.96 – 6.87 (m, 1H), 5.86 (q, J = 6.4 Hz, 1H), 4.98 (d, J = 11.4 Hz, 1H), 4.95 (d, J = 3.7 Hz, 1H), 4.89 (d, J = 11.2 Hz, 1H), 4.82 (d, J = 11.3 Hz, 1H), 4.60 (d, J = 11.3 Hz, 1H), 4.57 – 4.49 (m, 2H), 4.21 (dq, J = 9.5, 6.1 Hz, 1H), 4.12 (dd, J = 9.9, 8.9 Hz, 1H), 4.09 (s, 1H), 3.79 (dd, J = 9.9, 3.6 Hz, 1H), 3.68 (d, J = 9.3 Hz, 1H), 3.51 (s, 1H), 3.46 (dd, J = 9.9, 3.7 Hz, 1H), 3.40 (d, J = 2.6 Hz, 1H), 3.28 (d, J = 13.3 Hz, 1H), 3.12 (t, J = 9.3 Hz, 1H), 3.08 (d, J = 13.3 Hz, 1H), 2.98 (q, J = 7.0 Hz, 1H), 2.71 (d, J = 3.8 Hz, 1H), 2.65 (dq, J = 9.8, 6.7 Hz, 1H), 2.14 (m, 1H), 2.00 (dd, J = 14.8, 2.8 Hz, 1H), 1.84 (dd, J = 8.3, 6.0 Hz, 1H), 1.62 – 1.55 (m, 1H), 1.46 – 1.40 (m, 3H), 1.39 (d, J = 6.7 Hz, 3H), 1.36 (d, J = 6.2 Hz, 3H), 1.30 (d, J = 6.8 Hz, 3H), 1.20 (d, J = 7.1 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 0.63 (d, J = 7.1 Hz, 3H).

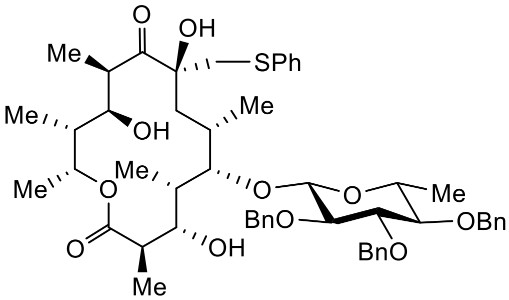
^{13}C NMR (176 MHz, C_6D_6): δ 216.0, 175.5, 139.6, 139.0, 138.6, 137.6, 130.0, 129.2, 128.8, 128.6, 128.5, 128.4, 128.4, 128.3, 127.7, 127.7, 127.7, 127.6, 126.4, 99.9, 90.1, 84.1, 83.7, 82.0, 81.1, 78.3, 75.5, 75.4, 74.3, 70.4, 69.6, 68.9, 44.8, 44.0, 42.1, 41.8, 40.7, 37.5, 21.2, 18.7, 18.3, 14.5, 9.3, 8.8, 8.8.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 930.4826; found, 930.4796

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.2

IR (thin film, cm^{-1}): 3406, 2918, 2853, 1718, 1597, 1454, 1369, 1069

$[\alpha]_D$: +15.0 (c = 0.24 in $CHCl_3$)



7-C_5-β-A

^{1}H NMR (700 MHz, C_6D_6): δ 7.45 (d, J = 7.5 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.19 – 7.12 (m, 4H), 7.09 (d, J = 6.5 Hz, 5H), 7.05 (s, 1H), 6.99 (t, J = 7.4 Hz, 2H), 6.90 (t, J = 7.2 Hz, 1H), 5.80 (q, J = 6.5 Hz, 1H), 5.08 (d, J = 11.7 Hz, 1H), 4.91 (d, J = 11.2 Hz, 1H), 4.86 (d, J = 11.5 Hz, 1H), 4.81 (d, J = 11.7 Hz, 2H), 4.68 (d, J = 7.6 Hz, 1H), 4.49 (d, J = 11.4 Hz, 1H), 4.02 (s, 1H), 3.89 (s, 1H), 3.79 (d, J = 9.6 Hz, 1H), 3.66 (t, J = 9.0 Hz, 1H), 3.59 – 3.52 (m, 3H), 3.40 (d, J = 13.3 Hz, 1H), 3.37 – 3.32 (m, 1H), 3.26 (d, J = 13.2 Hz, 1H), 3.21 – 3.13 (m, 2H), 2.99 – 2.94 (m, 1H), 2.55 (p, J = 6.4 Hz, 1H), 2.16 – 2.03 (m, 2H), 1.94 – 1.89 (m, 1H), 1.73 – 1.68 (m, 1H), 1.50 – 1.45 (m, 1H), 1.44 (d, J = 6.6 Hz, 3H), 1.27 (d, J = 6.0 Hz, 3H), 1.19 (t, J = 7.8 Hz, 6H), 0.95 (d, J = 6.3 Hz, 3H), 0.61 (d, J = 7.0 Hz, 3H).

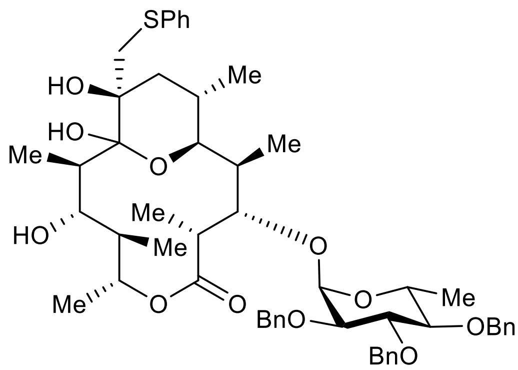
^{13}C NMR (176 MHz, C_6D_6): δ 214.7, 175.7, 139.5, 139.2, 139.1, 137.8, 130.2, 130.2, 129.2, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.6, 126.5, 102.3, 86.2, 85.5, 84.2, 83.5, 82.8, 77.3, 75.5, 75.1, 71.4, 70.3, 69.5, 44.4, 44.0, 42.1, 41.2, 37.8, 32.4, 29.6, 20.6, 18.6, 18.3, 14.8, 14.4, 9.1, 8.8, 8.7.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 930.4826; found, 930.4757

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.3

IR (thin film, cm^{-1}): 3382, 3240, 2957, 2912, 2851, 1694, 1617, 1453, 1069

$[\alpha]_D$: -2.5 (c = 0.25 in $CHCl_3$)



X-2-α-A (**8e**)

^{1}H NMR (700 MHz, C_6D_6): δ 7.52 (dd, J = 8.3, 1.0 Hz, 3H), 7.40 – 7.28 (m, 6H), 7.13 (t, J = 7.5 Hz, 3H), 7.11 – 7.03 (m, 7H), 6.95 (t, J = 7.4 Hz, 1H), 5.27 (d, J = 3.4 Hz, 1H), 5.26 – 5.22 (m, 1H), 5.04 (d, J = 11.3 Hz, 1H), 4.93 (dd, J = 20.5, 11.3 Hz, 2H), 4.68 (d, J = 11.6 Hz, 1H), 4.64 (d, J = 11.4 Hz, 2H), 4.54 (dq, J = 12.0, 5.9 Hz, 1H), 4.40 (d, J = 9.2 Hz, 1H), 4.35 – 4.27 (m, 1H), 3.90 (m, 2H), 3.60 (dd, J = 10.0, 3.4 Hz, 1H), 3.49 – 3.36 (m, 2H), 3.27 – 3.14 (m, 2H), 2.59 (q, J = 7.5, 6.9 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.01 (s, 1H), 1.96 (dd, J = 13.7, 3.7 Hz, 1H), 1.83 – 1.68 (m, 2H), 1.50 (d, J = 6.1 Hz, 3H), 1.43 (d, J = 7.2 Hz, 3H), 1.25 (d, J = 7.1 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 7.2 Hz, 3H), 0.48 (d, J = 7.0 Hz, 3H), 0.39 (d, J = 6.6 Hz, 3H).

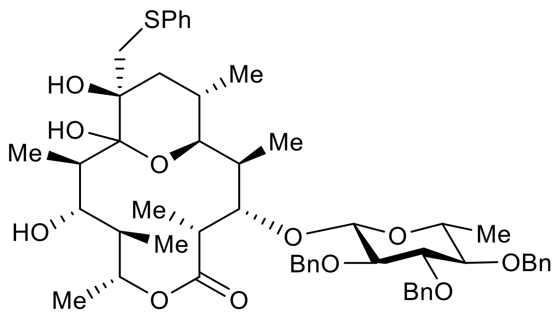
^{13}C NMR (176 MHz, C_6D_6): δ 175.1, 139.8, 139.4, 138.9, 138.6, 129.9, 129.3, 128.6, 128.5, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 126.3, 107.4, 98.2, 84.9, 82.3, 81.8, 76.6, 75.6, 75.3, 74.3, 73.0, 72.9, 68.4, 44.1, 43.1, 42.2, 39.6, 37.9, 34.9, 32.4, 27.7, 23.2, 18.8, 16.0, 14.5, 14.4, 13.6, 9.9, 9.4, 7.6.

HRMS (m/z): $[M+Na-H_2O]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 912.4720; found, 912.4690

TLC (EtOAc:Hexanes, 20:80 v/v): R_f = 0.3

IR (thin film, cm^{-1}): 3463, 2923, 2851, 1734, 1454, 1377, 1071

$[\alpha]_D$: +4.0 (c = 0.12 in $CHCl_3$)



X-2-β-A

^{1}H NMR (700 MHz, C_6D_6): δ 7.54 (d, J = 7.3 Hz, 2H), 7.43 (d, J = 7.4 Hz, 2H), 7.30 (d, J = 7.4 Hz, 2H), 7.24 (d, J = 7.3 Hz, 2H), 7.20 – 7.13 (m, 4H), 7.12 – 7.02 (m, 7H), 6.96 (t, J = 7.4 Hz, 1H), 5.31 (d, J = 7.9 Hz, 1H), 5.17 (m, 2H), 4.95 (d, J = 11.4 Hz, 1H), 4.82 (dd, J = 27.1, 11.5 Hz, 2H), 4.71 (d, J = 11.4 Hz, 1H), 4.57 (dd, J = 10.7, 1.8 Hz, 1H), 4.48 (d, J = 11.6 Hz, 1H), 3.98 – 3.83 (m, 2H), 3.70 (t, J = 9.0 Hz, 1H), 3.65 – 3.54 (m, 2H), 3.51 – 3.38 (m, 2H), 3.26 – 3.13 (m, 2H), 2.80 – 2.71 (m, 1H), 2.51 – 2.40 (m, 1H), 2.05 – 1.94 (m, 2H), 1.85 – 1.75 (m, 1H), 1.77 – 1.69 (m, 1H), 1.54 – 1.45 (m, 1H), 1.43 (d, J = 7.3 Hz, 3H), 1.31 (d, J = 6.2 Hz, 3H), 1.22 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H), 1.11 (d, J = 7.2 Hz, 3H), 0.46 (d, J = 2.7 Hz, 3H), 0.45 (d, J = 3.1 Hz, 3H).

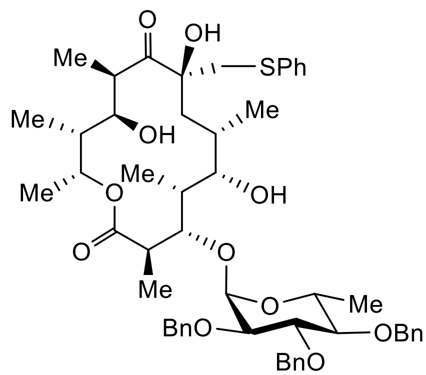
^{13}C NMR (176 MHz, C_6D_6): δ 177., 139.9, 139.5, 139.4, 138.7, 129.9, 129.3, 128.5, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6, 127.6, 127.5, 126.3, 107.2, 101.1, 85.3, 84.1, 83.6, 80.8, 75.7, 74.9, 74.8, 73.9, 73.4, 73.4, 73.0, 71.6, 43.3, 43.0, 40.0, 39.5, 37.6, 34.9, 27.7, 18.2, 16.2, 14.4, 13.3, 10.8, 10.0, 7.6.

HRMS (m/z): $[M+Na-H_2O]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 912.4720; found, 912.4703

TLC (EtOAc:Hexanes, 20:80 v/v): R_f = 0.4

IR (thin film, cm^{-1}): 2919, 2851, 1720, 1379, 1068

$[\alpha]_D$: -+15.4 (c = 0.07 in $CHCl_3$)



7-C_3-α-A (**8f**)

^{1}H NMR (500 MHz, C_6D_6): δ 7.42 – 7.24 (m, 5H), 7.19 - 7.04 (m, 6H), 6.95 (m, 4H), 5.99 (q, J = 6.6 Hz, 1H), 4.89 – 4.75 (m, 3H), 4.68 (d, J = 3.3 Hz, 1H), 4.62 (d, J = 12.1 Hz, 1H), 4.55 (d, J = 12.1 Hz, 1H), 4.48 (d, J = 11.2 Hz, 1H), 4.20 (s, 1H), 4.06 (t, J = 9.4 Hz, 1H), 3.98 (dq, J = 10.3, 6.3 Hz, 1H), 3.80 (d, J = 4.3 Hz, 1H), 3.67 (d, J = 9.7 Hz, 1H), 3.63 (d, J = 10.1 Hz, 1H), 3.52 – 3.44 (m, 3H), 3.27 (d, J = 13.5 Hz, 1H), 3.12 (d, J = 13.5 Hz, 1H), 3.06 – 2.97 (m, 2H), 2.67 (dq, J = 9.8, 6.5 Hz, 1H), 2.15 (dd, J = 14.5, 10.6 Hz, 1H), 2.06 (d, J = 13.8 Hz, 1H), 1.48 (m, 1H), 1.40 (d, J = 6.7 Hz, 3H), 1.38 – 1.28 (m, 7H), 1.21 (dd, J = 6.4, 4.3 Hz, 6H), 1.00 (d, J = 6.7 Hz, 3H), 0.67 (d, J = 7.1 Hz, 3H).

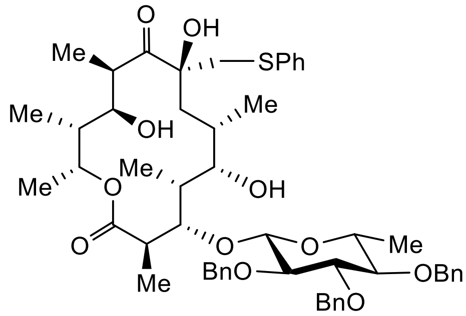
^{13}C NMR (176 MHz, C_6D_6): δ 217.4, 175.5, 139.2, 139.0, 137.7, 137.4, 129.9, 129.2, 129.2, 129.1, 128.9, 128.8, 128.6, 128.4, 128.4, 127.7, 127.7, 126.3, 100.9, 92.3, 84.6, 84.4, 82.0, 80.5, 80.0, 75.6, 75.4, 74.2, 70.4, 69.4, 67.9, 44.7, 44.5, 43.1, 42.3, 40.1, 39.2, 36.9, 21.0, 18.8, 18.0, 15.4, 9.9, 9.7, 8.7.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 935.4380; found, 935.4362

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.4

IR (thin film, cm^{-1}): 3439, 2926, 1720, 1454, 1328, 1069

$[\alpha]_D$: +9.1 (c = 0.07 in $CHCl_3$)



7-C_3-β-A

^{1}H NMR (500 MHz, C_6D_6): δ 7.39 – 7.28 (m, 7H), 7.23 (d, J = 7.1 Hz, 2H), 7.09 (q, J = 7.1 Hz, 3H), 7.01 (t, J = 7.6 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 5.96 (q, J = 6.7 Hz, 1H), 4.92 (t, J = 11.4 Hz, 2H), 4.82 – 4.58 (m, 3H), 4.40 (d, J = 11.3 Hz, 1H), 4.30 (d, J = 7.9 Hz, 1H), 4.16 (s, 1H), 3.72 (d, J = 9.5 Hz, 1H), 3.67 (m, 1H), 3.64 (d, J = 10.1 Hz, 1H), 3.48 (t, J = 9.1 Hz, 1H), 3.36 – 3.24 (m, 3H), 3.17 (d, J = 13.5 Hz, 1H), 3.10 – 2.97 (m, 2H), 2.86 (t, J = 9.2 Hz, 1H), 2.84 – 2.74 (m, 2H), 2.25 – 2.03 (m, 2H), 1.77 (t, J = 6.9 Hz, 1H), 1.53 – 1.42 (m, 5H), 1.39 (d, J = 6.7 Hz, 3H), 1.35 (d, J = 6.9 Hz, 3H), 1.20 (d, J = 6.8 Hz, 3H), 1.12 (d, J = 6.1 Hz, 3H), 1.03 (d, J = 6.6 Hz, 3H), 0.69 (d, J = 7.1 Hz, 3H).

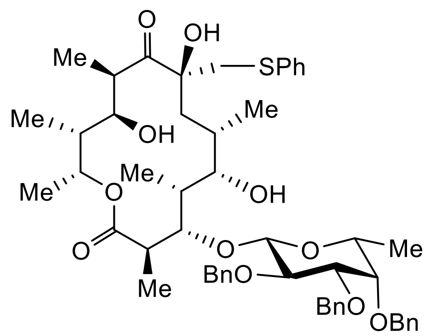
^{13}C NMR (176 MHz, C_6D_6): δ 217.4, 174.7, 139.5, 139.0, 138.9, 137.6, 129.8, 129.2, 128.6, 128.6, 128.6, 128.4, 128.3, 127.9, 127.7, 127.7, 126.4, 104.5, 88.3, 84.7, 84.5, 83.4, 82.6, 80.7, 75.5, 75.2, 75.1, 71.6, 70.5, 69.7, 45.4, 44.3, 42.1, 41.6, 40.4, 38.3, 37.6, 20.8, 18.8, 17.7, 14.4, 9.6, 9.6, 8.8.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 935.4380; found, 935.4368

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.45

IR (thin film, cm^{-1}): 3485, 2973, 2925, 2855, 1725, 1454, 1380, 1117, 1067

[α]$_D$: +2.5 (c = 0.29 in $CHCl_3$)



7-C_3-β-B (**8g**)

^{1}H NMR (700 MHz, C_6D_6): δ 7.36 (d, J = 7.5 Hz, 2H), 7.34 – 7.24 (m, 6H), 7.21 – 7.17 (m, 4H), 7.12 (dt, J = 15.3, 7.4 Hz, 4H), 7.08 – 6.89 (m, 4H), 5.96 (q, J = 6.5 Hz, 1H), 4.89 (d, J = 11.4 Hz, 1H), 4.86 (d, J = 11.7 Hz, 1H), 4.73 (d, J = 11.3 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 12.4 Hz, 2H), 4.30 (d, J = 7.7 Hz, 1H), 4.16 (s, 1H), 3.98 – 3.89 (m, 1H), 3.75 (s, 1H), 3.72 (d, J = 9.9 Hz, 2H), 3.32 (s, 1H), 3.27 (d, J = 13.6 Hz, 1H), 3.23 (dd, J = 9.8, 2.6 Hz, 1H), 3.13 (d, J = 13.5 Hz, 1H), 3.10 (d, J = 2.1 Hz, 1H), 3.03 (m, 2H), 2.84 (q, J = 6.3 Hz, 1H), 2.78 (dt, J = 13.5, 6.8 Hz, 1H), 2.17 – 2.10 (m, 1H), 2.07 (d, J = 14.8 Hz, 1H), 1.76 (q, J = 6.7 Hz, 1H), 1.48 (s, 3H), 1.46 (m, 2H), 1.43 (d, J = 6.7 Hz, 3H), 1.32 (d, J = 6.8 Hz, 3H), 1.20 (d, J = 6.8 Hz, 3H), 1.06 (d, J = 6.3 Hz, 3H), 1.02 (d, J = 6.6 Hz, 3H), 0.66 (d, J = 7.1 Hz, 3H).

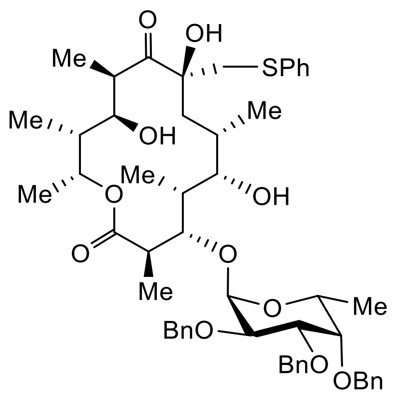
^{13}C NMR (176 MHz, C_6D_6): δ 217.6, 175.0, 139.3, 139.2, 139.1, 137.7, 129.8, 129.2, 128.7, 128.5, 128.5, 128.3, 127.8, 127.8, 127.7, 126.3, 104.7, 87.8, 84.5, 82.7, 80.6, 80.2, 76.7, 75.5, 75.0, 73.2, 70.8, 70.5, 69.6, 45.4, 44.3, 42.1, 41.9, 40.3, 38.4, 37.6, 20.9, 18.8, 16.6, 14.5, 9.7, 9.6, 8.8.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 930.4826; found, 930.4801

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.25

IR (thin film, cm^{-1}): 3447, 2919, 2855, 1720, 1454, 1378, 1064

$[\alpha]_D$: -2.3 (c = 0.69 in $CHCl_3$)



7-C_3-α-B

^{1}H NMR (500 MHz, C_6D_6): δ 7.36 (t, J = 7.7 Hz, 5H), 7.34 – 7.27 (m, 4H), 7.26 – 7.17 (m, 4H), 7.14 – 7.05 (m, 3H), 7.03 – 6.86 (m, 4H), 6.01 (q, J = 6.5 Hz, 1H), 4.93 (d, J = 11.3 Hz, 1H), 4.76 (d, J = 3.4 Hz, 1H), 4.67 – 4.51 (m, 5H), 4.48 (d, J = 11.3 Hz, 1H), 4.24 – 4.16 (m, 4H), 3.91 (dd, J = 10.4, 2.8 Hz, 1H), 3.84 (d, J = 4.4 Hz, 1H), 3.78 (q, J = 6.6 Hz, 1H), 3.68 (d, J = 9.7 Hz, 1H), 3.64 (d, J = 10.1 Hz, 1H), 3.44 (t, J = 2.9 Hz, 2H), 3.33 (d, J = 2.4 Hz, 1H), 3.27 (d, J = 13.5 Hz, 1H), 3.13 (d, J = 13.5 Hz, 1H), 3.03 (q, J = 6.8 Hz, 1H), 2.73 (dq, J = 10.3, 6.9 Hz, 1H), 2.14 (dd, J = 14.8, 10.6 Hz, 1H), 2.05 (d, J = 14.6 Hz, 1H), 1.75 (q, J = 7.8 Hz, 1H), 1.53 – 1.43 (m, 1H), 1.43 (d, J = 6.8 Hz, 3H), 1.36 (d, J = 7.0 Hz, 5H), 1.30 (d, J = 5.7 Hz, 3H), 1.21 (d, J = 6.7 Hz, 3H), 1.14 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 6.7 Hz, 3H), 0.68 (d, J = 7.1 Hz, 3H).

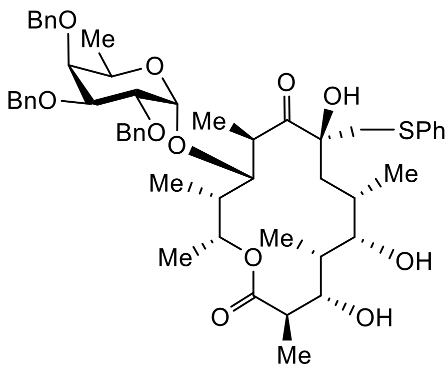
^{13}C NMR (176 MHz, C_6D_6): δ 217.4, 175.4, 139.4, 139.1, 137.7, 137.7, 129.8, 129.2, 129.2, 128.8, 128.7, 128.5, 128.5, 128.4, 128.4, 128.3, 127.9, 127.8, 127.8, 127.7, 126.3, 101.8, 91.3, 84.4, 80.2, 79.1, 78.5, 76.6, 75.2, 74.6, 72.8, 70.4, 69.3, 67.5, 44.8, 44.5, 43.1, 42.3, 40.1, 39.1, 37.0, 21.0, 18.9, 16.8, 15.4, 9.9, 9.7, 8.8.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 935.4380; found, 935.4353

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.4

IR (thin film, cm^{-1}): 3399, 2920, 2851, 1723, 1453, 1380, 1099

$[\alpha]_D$: +12.8 (c = 0.09 in $CHCl_3$)



7-C_{11}-α-B (**8h**)

¹H NMR (700 MHz, $CDCl_3$): δ 7.43 – 7.27 (m, 17H), 7.23 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 5.50 (d, J = 6.1 Hz, 1H), 5.06 (d, J = 3.2 Hz, 1H), 4.96 (d, J = 11.6 Hz, 1H), 4.85 (t, J = 12.0 Hz, 2H), 4.77 (d, J = 11.7 Hz, 1H), 4.69 (d, J = 11.1 Hz, 1H), 4.67 (s, 1H), 4.61 (d, J = 11.4 Hz, 1H), 4.39 (d, J = 6.8 Hz, 1H), 4.03 (dd, J = 9.8, 2.9 Hz, 1H), 3.97 – 3.90 (m, 1H), 3.89 (d, J = 10.5 Hz, 1H), 3.82 (q, J = 6.5 Hz, 1H), 3.77 – 3.71 (m, 1H), 3.65 (s, 1H), 3.36 – 3.25 (m, 3H), 2.51 – 2.44 (m, 1H), 2.38 – 2.29 (m, 1H), 1.97 – 1.91 (m, 1H), 1.81 – 1.68 (m, 3H), 1.29 (d, J = 6.7 Hz, 3H), 1.07 (d, J = 5.1 Hz, 3H), 1.02 (d, J = 7.1 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H), 0.91 (d, J = 4.4 Hz, 3H), 0.65 (d, J = 7.1 Hz, 3H).

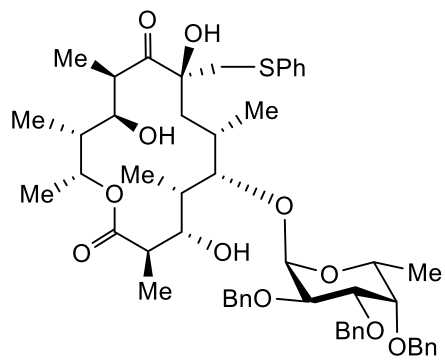
¹³C NMR (176 MHz, $CDCl_3$): δ 213.2, 176.0, 139.1, 138.9, 138.8, 137.6, 130.0, 129.00, 128.6, 128.5, 128.5, 128.3, 128.2, 128.2, 127.7, 127.6, 127.6, 127.5, 126.2, 99.3, 82.7, 79.8, 79.5, 79.4, 78.0, 76.8, 76.2, 75.1, 74.5, 72.9, 71.3, 67.8, 44.9, 44.7, 44.5, 42.8, 40.5, 39.3, 33.8, 18.7, 17.5, 16.9, 15.4, 9.3, 8.4, 8.0.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 935.4380; found, 935.4363

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.2

IR (thin film, cm^{-1}): 3411, 2973, 2919, 2852, 1721, 1453, 1379, 1096

$[\alpha]_D$: +8.6 (c = 0.93 in $CHCl_3$)



7-C_5-α-B (**8i**)

^{1}H NMR (500 MHz, C_6D_6): δ 7.39 (dd, J = 7.5, 5.9 Hz, 4H), 7.36 – 7.29 (m, 3H), 7.26 – 7.18 (m, 6H), 7.14 – 7.07 (m, 2H), 7.02 – 6.88 (m, 5H), 5.88 (q, J = 6.6 Hz, 1H), 5.05 (d, J = 3.8 Hz, 1H), 4.96 (d, J = 11.4 Hz, 1H), 4.75 – 4.43 (m, 5H), 4.18 (dd, J = 10.2, 3.8 Hz, 1H), 4.13 – 4.05 (m, 1H), 4.00 (s, 1H), 3.96 (dd, J = 10.2, 2.8 Hz, 1H), 3.83 – 3.76 (m, 1H), 3.72 (d, J = 9.8 Hz, 1H), 3.54 (s, 1H), 3.40 (s, 1H), 3.38 (d, J = 2.6 Hz, 1H), 3.25 (d, J = 13.2 Hz, 1H), 3.07 (d, J = 13.1 Hz, 1H), 2.99 – 2.89 (m, 2H), 2.74 (dq, J = 10.6, 6.6 Hz, 1H), 2.14 (dd, J = 14.7, 10.4 Hz, 1H), 1.98 (dd, J = 14.8, 3.1 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.64 – 1.55 (m, 1H), 1.45 (d, J = 6.7 Hz, 3H), 1.43 (m, 1H), 1.30 (d, J = 6.4 Hz, 3H), 1.27 (d, J = 7.1 Hz, 3H), 1.25 (d, J = 6.8 Hz, 3H), 1.18 (d, J = 6.7 Hz, 3H), 0.98 (d, J = 6.7 Hz, 3H), 0.66 (d, J = 7.1 Hz, 3H).

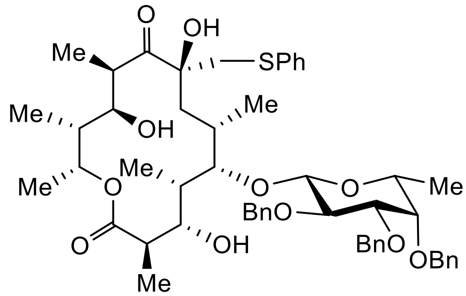
^{13}C NMR (176 MHz, C_6D_6): δ 216.3, 175.4, 139.4, 139.3, 139.0, 129.9, 129.2, 128.8, 128.7, 128.5, 128.4, 128.3, 127.4, 127.4, 127.1, 126.4, 100.6, 89.0, 83.7, 79.7, 78.7, 78.2, 77.0, 75.2, 74.5, 72.9, 70.4, 69.6, 68.6, 44.6, 44.0, 42.1, 41.5, 40.7, 37.5, 20.7, 18.7, 17.0, 14.8, 9.3, 8.7.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 935.4380; found, 935.4337

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.2

IR (thin film, cm^{-1}): 3472, 2920, 2880, 2852, 1707, 1455, 1106

$[\alpha]_D$: +38.0 (c = 0.07 in $CHCl_3$)



7-C_5-β-B

^{1}H NMR (700 MHz, C_6D_6): δ 7.46 (d, J = 7.5 Hz, 2H), 7.38 (t, J = 7.4 Hz, 4H), 7.30 (d, J = 7.5 Hz, 2H), 7.21 – 7.18 (m, 5H), 7.10 (m, 4H), 7.01 (t, J = 7.7 Hz, 2H), 6.91 (t, J = 7.4 Hz, 1H), 5.74 (q, J = 6.2 Hz, 1H), 4.98 (d, J = 11.3 Hz, 1H), 4.91 (t, J = 12.7 Hz, 2H), 4.57 – 4.47 (m, 4H), 4.26 (s, 1H), 4.05 (dd. J = 9.6, 7.9 Hz, 1H), 3.99 (s, 1H), 3.96 (s, 1H), 3.90 (d, J = 9.8 Hz, 1H), 3.80 (dd, J = 9.6, 4.1 Hz, 1H), 3.63 (s, 1H), 3.39 (d, J = 13.2 Hz, 1H), 3.34 (dd, J = 9.6, 2.6 Hz, 1H), 3.24 (d, J = 13.2 Hz, 1H), 3.20 – 3.15 (m, 1H), 3.07 (q, J = 6.1 Hz, 1H), 2.91 (q, J = 6.9 Hz, 1H), 2.60 (dt, J = 13.2, 6.7 Hz, 1H), 2.49 (s, 1H), 2.05 – 1.90 (m, 4H), 1.47 – 1.41 (m, 1H), 1.33 (d, J = 6.5 Hz, 3H), 1.30 (d, J = 6.7 Hz, 3H), 1.20 (d, J = 7.1 Hz, 3H), 1.18 (d, J = 6.8 Hz, 3H), 1.17 (d, J = 6.3 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H), 0.61 (d, J = 7.1 Hz, 3H).

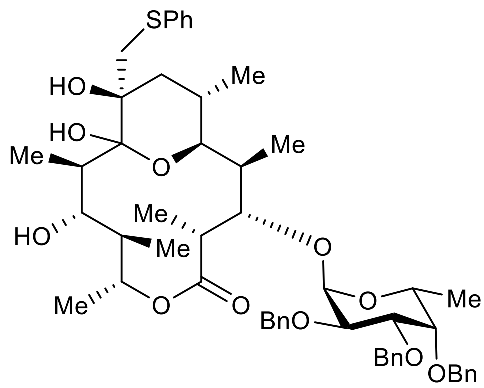
^{13}C NMR (176 MHz, C_6D_6): δ 213.8, 176.1, 139.4, 139.2, 139.1, 137.9, 130.1, 129.2, 128.7, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.8, 127.7, 126.4, 103.7, 87.7, 83.8, 83.4, 79.6, 77.7, 77.2, 75.5, 75.2, 72.9, 70.6, 70.4, 69.7, 44.7, 43.2, 42.1, 41.8, 40.4, 38.3, 37.0, 20.1, 18.6, 17.2, 14.8, 8.8, 8.6.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 930.4826; found, 930.4716

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.2

IR (thin film, cm^{-1}): 3525, 2925, 1705, 1453, 1362, 1067

$[\alpha]_D$: -15.4 (c = 0.08 in $CHCl_3$)



X-2-α-B (**8j**)

^{1}H NMR (700 MHz, C_6D_6): δ 7.52 (d, J = 7.3 Hz, 2H), 7.41 (dd, J = 16.9, 7.4 Hz, 4H), 7.32 (d, J = 7.4 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.15 – 7.02 (m, 9H), 6.95 (t, J = 7.4 Hz, 1H), 5.34 – 5.26 (m, 1H), 5.24 (d, J = 3.5 Hz, 1H), 5.04 (d, J = 11.2 Hz, 1H), 4.71 (t, J = 11.2 Hz, 2H), 4.63 (d, J = 11.8 Hz, 1H), 4.53 (dd, J = 20.0, 11.3 Hz, 2H), 4.47 – 4.41 (m, 2H), 4.30 (dd, J = 10.4, 3.5 Hz, 1H), 4.17 (dd, J = 10.4, 2.7 Hz, 1H), 3.92 (dd, J = 10.6, 8.3 Hz, 1H), 3.87 (d, J = 10.5 Hz, 1H), 3.52 (s, 1H), 3.48 (d, J = 13.3 Hz, 1H), 3.42 (d, J = 13.3 Hz, 1H), 3.22 (p, J = 7.2 Hz, 1H), 2.61 – 2.51 (m, 2H), 2.01 (s, 1H), 1.98 (dd, J = 13.7, 3.7 Hz, 1H), 1.82 – 1.68 (m, 2H), 1.46 (d, J = 6.3 Hz, 3H), 1.43 (m, 1H), 1.38 (d, J = 7.1 Hz, 3H), 1.19 (d, J = 6.8 Hz, 6H), 1.10 (d, J = 7.2 Hz, 3H), 0.50 (d, J = 7.0 Hz, 3H), 0.38 (d, J = 6.6 Hz, 3H).

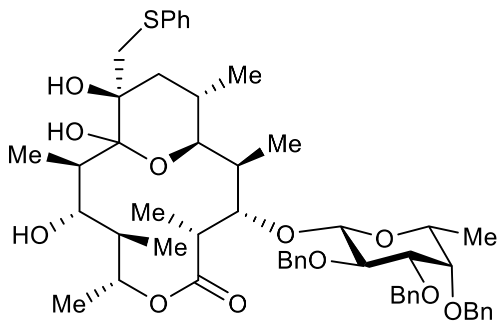
^{13}C NMR (176 MHz, C_6D_6): δ 175.0, 139.8, 139.6, 139.4, 138.7, 129.9, 129.3, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.6, 126.3, 107.5, 98.8, 81.1, 79.7, 79.2, 77.7, 75.5, 74.6, 74.4, 73.1, 73.1, 73.1, 72.8, 68.0, 44.2, 43.0, 42.4, 39.8, 38.0, 35.0, 27.7, 17.4, 15.9, 14.5, 13.7, 9.4, 9.0, 7.6.

HRMS (m/z): $[M+Na-H_2O]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 912.4720; found, 912.4676

TLC (EtOAc:Hexanes, 20:80 v/v): R_f = 0.3

IR (thin film, cm^{-1}): 2923, 2853, 1726, 1455, 1377, 1100

$[\alpha]_D$: +9.0 (c = 0.08 in $CHCl_3$)



X-2-β-B

^{1}H NMR (500 MHz, C_6D_6): δ 7.54 (dd, J = 8.3, 1.1 Hz, 2H), 7.46 (d, J = 7.1 Hz, 2H), 7.35 (t, J = 7.5 Hz, 4H), 7.22 – 7.17 (m, 4H), 7.16 – 7.08 (m, 4H), 7.10 – 7.01 (m, 3H), 7.00 – 6.90 (m, 1H), 5.23 – 5.11 (m, 3H), 4.99 (d, J = 11.7 Hz, 1H), 4.80 (d, J = 11.4 Hz, 1H), 4.71 (d, J = 11.9 Hz, 1H), 4.59 – 4.47 (m, 3H), 4.27 (s, 1H), 4.08 (dd, J = 9.7, 7.8 Hz, 1H), 3.94 – 3.84 (m, 2H), 3.53 – 3.40 (m, 3H), 3.27 (q, J = 6.2 Hz, 1H), 3.25 – 3.18 (m, 1H), 3.19 (d, J = 2.6 Hz, 1H), 2.76 (qd, J = 7.2, 1.7 Hz, 1H), 2.47 (dtd, J = 14.0, 7.0, 1.8 Hz, 1H), 2.04 – 1.91 (m, 2H), 1.78 – 1.64 (m, 2H), 1.46 (d, J = 7.3 Hz, 3H), 1.23 (d, J = 6.4 Hz, 3H), 1.20 – 1.15 (m, 6H), 1.13 (d, J = 7.2 Hz, 3H), 0.48 (d, J = 7.0 Hz, 3H), 0.41 (d, J = 6.4 Hz, 3H).

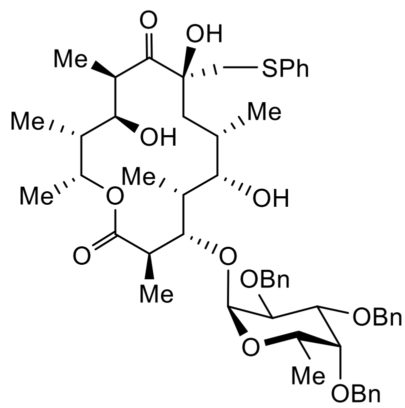
^{13}C NMR (176 MHz, C_6D_6): δ 177.2, 140.0, 139.7, 139.7, 138.8, 129.9, 129.2, 128.6, 128.4, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.4, 126.2, 107.2, 101.7, 83.3, 80.8, 80.7, 78.0, 75.3, 75.2, 73.8, 73.7, 73.4, 73.4, 73.0, 70.7, 43.5, 42.9, 40.2, 39.3, 37.5, 34.9, 34.3, 32.4, 27.7, 27.3, 23.2, 17.2, 16.2, 14.6, 14.4, 13.3, 11.0, 10.1, 7.7.

HRMS (m/z): $[M+Na-H_2O]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 912.4720; found, 912.4699

TLC (EtOAc:Hexanes, 20:80 v/v): R_f = 0.3

IR (thin film, cm^{-1}): 2920, 2851, 1718, 1461, 1378, 1086

$[\alpha]_D$: -4.4 (c = 0.28 in $CHCl_3$)



7-C_3-α-C (**8k**)

^{1}H NMR (500 MHz, C_6D_6): δ 7.43 – 7.26 (m, 8H), 7.24 – 7.18 (m, 5H), 7.14 – 6.86 (m, 7H), 5.92 (q, J = 6.7 Hz, 1H), 4.98 (d, J = 11.3 Hz, 1H), 4.84 (d, J = 3.5 Hz, 1H), 4.73 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 12.1 Hz, 1H), 4.49 (dd, J = 19.3, 11.3 Hz, 2H), 4.34 (d, J = 11.5 Hz, 1H), 4.21 (s, 1H), 4.08 (dd, J = 10.2, 3.6 Hz, 1H), 3.96 (q, J = 7.2 Hz, 1H), 3.83 (dd, J = 10.3, 2.6 Hz, 1H), 3.73 (d, J = 10.0 Hz, 1H), 3.67 – 3.54 (m, 3H), 3.44 (s, 1H), 3.37 – 3.28 (m, 2H), 3.19 (d, J = 13.6 Hz, 1H), 3.06 (q, J = 6.5 Hz, 1H), 2.86 – 2.71 (m, 1H), 2.24 (dd, J = 14.7, 10.6 Hz, 1H), 2.00 (d, J = 14.6 Hz, 1H), 1.88 – 1.74 (m, 1H), 1.51 (d, J = 6.8 Hz, 3H), 1.46 (s, 3H), 1.44 (m, 1H), 1.22 (d, J = 6.8 Hz, 3H), 1.19 (d, J = 6.4 Hz, 6H), 0.96 (d, J = 6.6 Hz, 3H), 0.64 (d, J = 7.1 Hz, 3H).

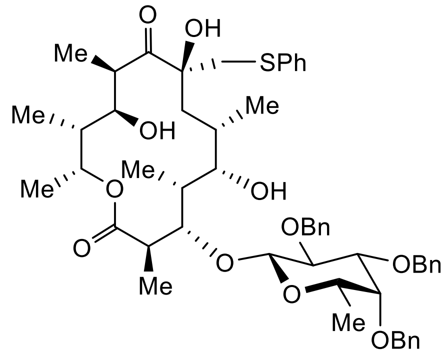
^{13}C NMR (126 MHz, C_6D_6): δ 216.2, 175.2, 139.1, 139.0, 138.9, 138.5, 129.5, 129.1, 128.8, 128.8, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.7, 127.6, 127.3, 127.1, 126.0, 125.6, 100.8, 89.5, 83.9, 80.6, 78.1, 77.9, 77.4, 74.9, 74.1, 73.7, 72.7, 72.3, 71.5, 69.9, 68.9, 68.5, 67.2, 45.1, 44.4, 42.6, 41.7, 40.0, 38.9, 20.5, 18.3, 16.9, 16.2, 15.2, 12.6, 9.1, 9.1, 8.5.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 930.4826; found, 930.4797

TLC (EtOAc:Hexanes, 40:60 v/v): R_f = 0.36

IR (thin film, cm^{-1}): 3351, 2924, 2850, 1723, 1454, 1377, 1097

$[\alpha]_D$: -27.8 (c = 0.11 in $CHCl_3$)



7-C_3-β-C

^{1}H NMR (500 MHz, C_6D_6): δ 7.39 (d, J = 7.3 Hz, 2H), 7.35 (d, J = 7.1 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.19 - 7.13 (m, 6H), 7.09 (t, J = 7.4 Hz, 3H), 7.00 (t, J = 7.6 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 5.94 (q, J = 6.6 Hz, 1H), 4.94 – 4.78 (m, 3H), 4.49 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 7.7 Hz, 1H), 4.41 – 4.29 (m, 2H), 4.16 (s, 1H), 4.03 – 3.93 (m, 2H), 3.71 (d, J = 11.3 Hz, 2H), 3.31 (s, 1H), 3.23 – 2.95 (m, 7H), 2.79 (dq, J = 9.9, 6.5 Hz, 1H), 2.12 – 1.91 (m, 2H), 1.83 (q, J = 7.2 Hz, 1H), 1.58 (d, J = 6.8 Hz, 3H), 1.49 – 1.39 (m, 2H), 1.35 (d, J = 6.4 Hz, 3H), 1.26 (d, J = 6.9 Hz, 3H), 1.20 (d, J = 2.5 Hz, 3H), 1.18 (d, J = 3.0 Hz, 3H), 0.98 (d, J = 6.6 Hz, 3H), 0.67 (d, J = 7.1 Hz, 3H).

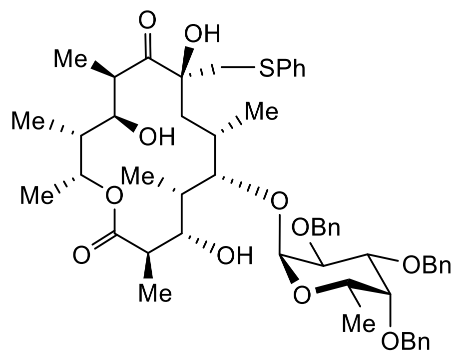
^{13}C NMR (126 MHz, C_6D_6): δ 217.2, 175.6, 139.3, 138.9, 138.5, 137.7, 129.9, 129.2, 128.7, 128.6, 128.5, 128.5, 128.4, 128.2, 128.0, 127.8, 126.4, 103.9, 86.5, 84.2, 84.0, 80.0, 79.8, 77.0, 76.1, 75.3, 73.0, 70.8, 70.4, 69.6, 44.5, 44.3, 42.7, 42.2, 40.3, 38.5, 37.3, 20.8, 18.7, 17.0, 16.0, 9.6, 9.1, 8.8.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 930.4826; found, 930.4806

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.3

IR (thin film, cm^{-1}): 3479, 2972, 2921, 2854, 1727, 1453, 1378, 1069

$[\alpha]_D$: -6.2 (c = 0.13 in $CHCl_3$)



7-C_5-α-C

^{1}H NMR (700 MHz, C_6D_6): δ 7.43 – 7.32 (m, 6H), 7.21 (dt, J = 19.7, 7.7 Hz, 5H), 7.14 – 7.10 (m, 4H), 7.10 – 7.03 (m, 2H), 7.00 (t, J = 7.8 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 5.64 (q, J = 6.5 Hz, 1H), 4.99 (d, J = 11.4 Hz, 1H), 4.97 (d, J = 3.6 Hz, 1H), 4.75 – 4.64 (m, 2H), 4.62 – 4.47 (m, 3H), 4.20 (dd, J = 10.2, 3.7 Hz, 1H), 4.05 (d, J = 9.0 Hz, 1H), 4.00 (d, J = 3.6 Hz, 1H), 3.97 – 3.89 (m, 3H), 3.86 (d, J = 10.4 Hz, 1H), 3.69 – 3.61 (m, 2H), 3.45 (d, J = 13.2 Hz, 1H), 3.40 – 3.34 (m, 1H), 3.22 (d, J = 13.3 Hz, 1H), 2.92 (q, J = 5.9 Hz, 1H), 2.75 (dq, J = 10.2, 6.8 Hz, 1H), 2.24 – 2.16 (m, 1H), 2.03 – 1.94 (m, 2H), 1.78 (dd, J = 14.5, 6.5 Hz, 1H), 1.50 – 1.41 (m, 1H), 1.38 (d, J = 6.7 Hz, 3H), 1.26 (d, J = 7.0 Hz, 3H), 1.21 (d, J = 6.7 Hz, 3H), 1.17 (d, J = 6.5 Hz, 3H), 1.12 (d, J = 7.0 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H), 0.68 (d, J = 7.0 Hz, 3H).

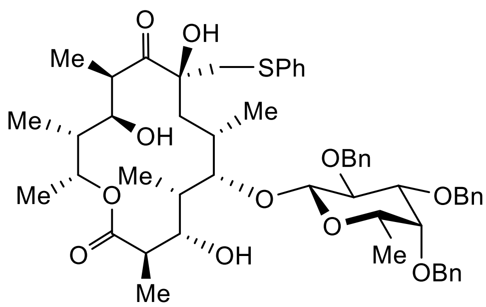
^{13}C NMR (176 MHz, C_6D_6): δ 211.0, 177.1, 139.4, 139.3, 138.3, 137.8, 130.2, 129.4, 129.0, 128.7, 128.7, 128.6, 128.4, 128.4, 127.8, 126.5, 100.4, 89.7, 82.5, 79.7, 78.4, 78.3, 77.4, 75.2, 74.8, 73.2, 70.5, 69.7, 68.0, 44.9, 43.2, 42.3, 38.9, 35.9, 18.8, 18.6, 17.1, 15.3, 8.9, 8.6, 8.0.

HRMS (m/z): $[M+Na]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 935.4380; found, 935.4365

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.36

IR (thin film, cm^{-1}): 3334, 2923, 2852, 1716, 453, 1178, 1047

$[\alpha]_D$: -34.4 (c = 0.19 in $CHCl_3$)



7-C_5-β-C

^{1}H NMR (700 MHz, C_6D_6): δ 7.58 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H), 7.31 (d, J = 7.4 Hz, 4H), 7.28 – 7.18 (m, 4H), 7.13 (t, J = 7.4 Hz, 4H), 7.06 (dd, J = 16.3, 8.9 Hz, 2H), 7.00 (t, J = 7.6 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 5.92 (q, J = 6.6 Hz, 1H), 5.09 (d, J = 10.5 Hz, 1H), 4.90 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 10.5 Hz, 1H), 4.64 (d, J = 11.9 Hz, 1H), 4.53 (dd, J = 15.1, 12.1 Hz, 2H), 4.36 (d, J = 7.7 Hz, 1H), 4.28 (s, 1H), 4.15 (s, 1H), 4.05 – 4.02 (m, 1H), 3.99 (d, J = 10.2 Hz, 1H), 3.64 (d, J = 9.5 Hz, 1H), 3.54 (s, 1H), 3.48 (s, 1H), 3.20 (dd, J = 10.0, 2.3 Hz, 1H), 3.15 (d, J = 13.5 Hz, 1H), 3.10 – 3.02 (m, 2H), 2.98 (q, J = 7.2, 6.8 Hz, 1H), 2.87 (q, J = 6.2 Hz, 1H), 2.84 – 2.76 (m, 1H), 2.17 – 2.07 (m, 1H), 2.00 (d, J = 14.5 Hz, 1H), 1.78 (d, J = 7.0 Hz, 1H), 1.60 (d, J = 6.7 Hz, 3H), 1.51 – 1.40 (m, 2H), 1.34 (d, J = 6.5 Hz, 3H), 1.30 (d, J = 7.1 Hz, 3H), 1.19 (d, J = 6.7 Hz, 3H), 1.13 (d, J = 6.2 Hz, 3H), 0.96 (d, J = 6.4 Hz, 3H), 0.62 (d, J = 7.1 Hz, 3H).

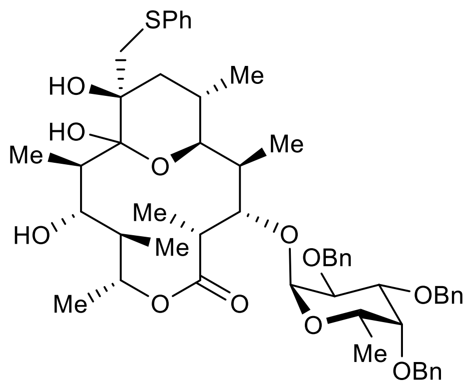
^{13}C NMR (176 MHz, C_6D_6): δ 216.3, 175.9, 139.2, 139.1, 137.5, 130.1, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.8, 127.8, 126.5, 106.5, 89.7, 84.1, 82.6, 80.0, 79.7, 76.6, 76.0, 75.0, 73.4, 71.2, 70.3, 69.0, 45.0, 44.6, 42.2, 41.9, 40.3, 40.0, 36.7, 20.4, 18.8, 16.6, 15.1, 9.6, 8.9.

HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 930.4826; found, 930.4774

TLC (EtOAc:Hexanes, 30:70 v/v): R_f = 0.2

IR (thin film, cm^{-1}): 3441, 2920, 2825, 1723, 1454, 1378, 1084

$[\alpha]_D$: -7.0 (c = 0.11 in $CHCl_3$)



X-2-α-C

^{1}H NMR (700 MHz, C_6D_6): δ 7.52 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 7.37 (dd, J = 15.7, 7.7 Hz, 4H), 7.23 – 7.18 (m, 5H), 7.15 – 7.03 (m, 6H), 6.95 (t, J = 7.0 Hz, 1H), 5.90 (d, J = 3.5 Hz, 1H), 5.26 (q, J = 6.6 Hz, 1H), 5.09 (d, J = 11.3 Hz, 1H), 4.76 (d, J = 11.9 Hz, 1H), 4.66 (d, J = 11.2 Hz, 1H), 4.63 – 4.51 (m, 3H), 4.46 (d, J = 10.5 Hz, 1H), 4.32 (dd, J = 10.4, 3.4 Hz, 1H), 4.13 – 4.05 (m, 2H), 3.97 (d, J = 10.4 Hz, 1H), 3.90 – 3.84 (m, 1H), 3.53 – 3.39 (m, 2H), 3.18 (p, J = 7.4 Hz, 1H), 2.76 (q, J = 7.2 Hz, 1H), 2.45 (p, J = 8.1, 7.5 Hz, 1H), 2.02 – 1.94 (m, 2H), 1.86 – 1.74 (m, 2H), 1.51 – 1.40 (m, 4H), 1.33 (d, J = 6.4 Hz, 3H), 1.20 – 1.14 (m, 6H), 1.12 (d, J = 7.1 Hz, 3H), 0.44 (d, J = 6.8 Hz, 3H), 0.38 (d, J = 6.9 Hz, 3H).

^{13}C NMR (176 MHz, C_6D_6): δ 176.7, 139.7, 139.7, 139.5, 138.6, 129.9, 129.3, 128.6, 128.5, 128.4, 128.4, 128.3, 127.7, 127.7, 127.5, 126.3, 107.3, 96.6, 81.0, 79.6, 79.1, 77.4, 75.2, 74.4, 73.3, 73.3, 73.2, 73.0, 67.5, 43.6, 43.1, 40.5, 39.6, 38.0, 34.9, 27.7, 17.1, 16.1, 14.4, 13.5, 10.4, 10.2, 7.7.

HRMS (m/z): $[M+Na-H_2O]^+$ calcd. for $C_{53}H_{68}O_{11}S$, 912.4720; found, 912.4700

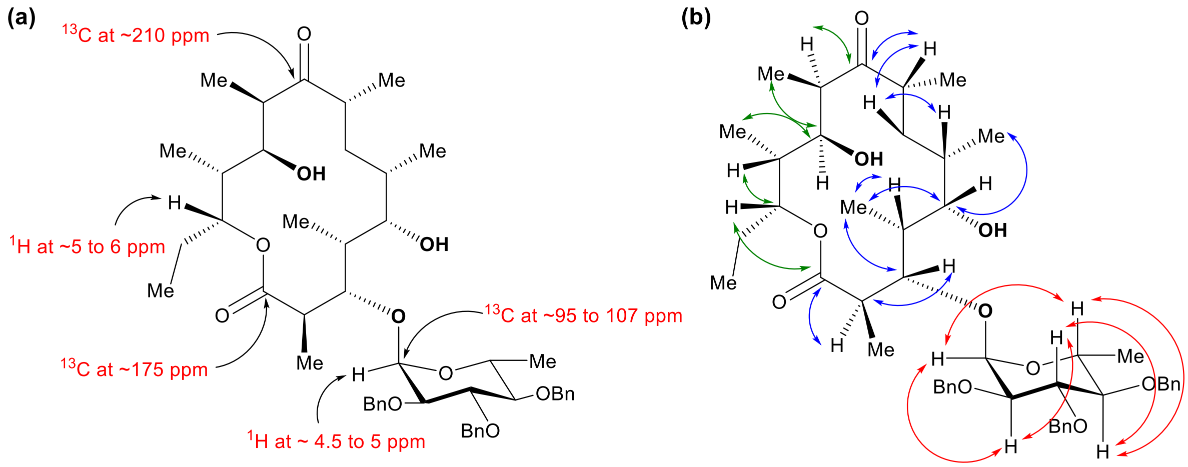
TLC (EtOAc:Hexanes, 20:80 v/v): R_f = 0.36

IR (thin film, cm^{-1}): 3477, 2959, 2923, 2852, 1725, 1454, 1374, 1098

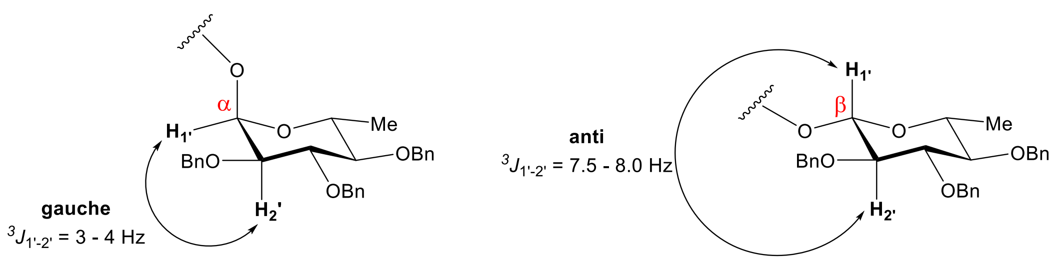
$[\alpha]_D$: -36.7 (c = 0.17 in $CHCl_3$)

Structural Elucidation of Glycosides

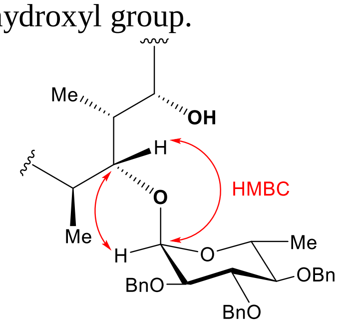
The structure of each isolated glycoside was characterized and assigned based on 1D and 2D NMR experiments. Each proton signal on ^{1}H NMR was assigned by analyzing cross-peaks on COSY, HSQC, and HMBC spectra. Figure below shows **(a)** easily identifiable starting points for NMR assignments, and **(b)** propagation of frequently observed COSY or HMBC correlations for each isolated spin systems.



The stereochemical configuration of glycosidic linkage (α or β) was assigned based on the ^{3}J coupling constant between anomeric proton **$H_{1'}$** and its vicinal proton **$H_{2'}$**. For α-anomer, **$H_{1'}$** and **$H_{2'}$** are in *gauche* conformation; for β-anomer, **$H_{1'}$** and **$H_{2'}$** are in *anti* conformation. According to Karplus equation, the ^{3}J coupling constant between **$H_{1'}$** and **$H_{2'}$** in α-anomer should be smaller (~ 3 to 4 Hz) compared to the ^{3}J coupling constant between **$H_{1'}$** and **$H_{2'}$** in β-anomer (~7.5 to 8.0 Hz).



The site of glycosylation on macrolide was assigned based on the observation of HMBC cross-peak between anomeric carbon and proton geminal to hydroxyl group or cross-peak between anomeric proton and carbon with hydroxyl group.

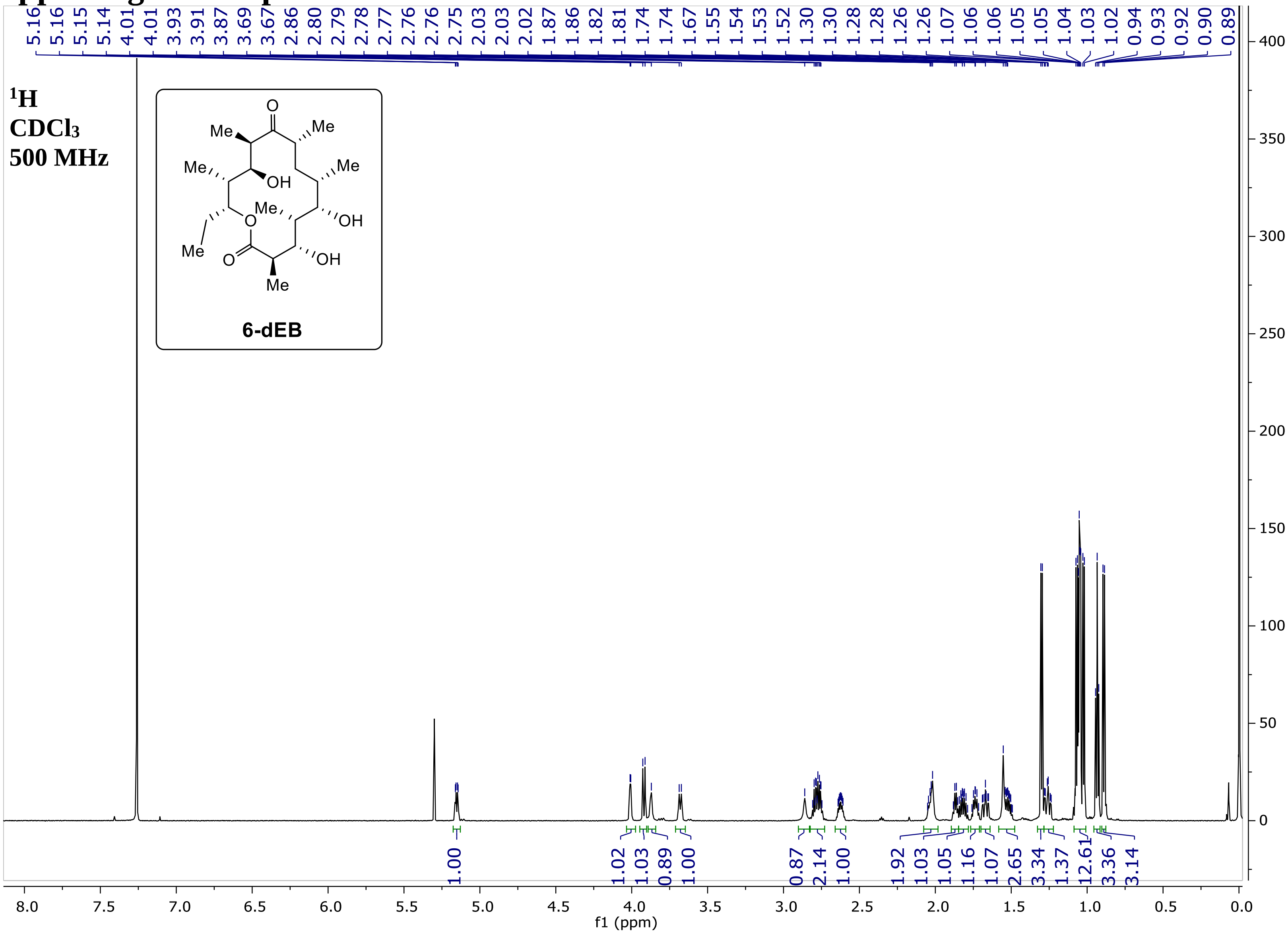


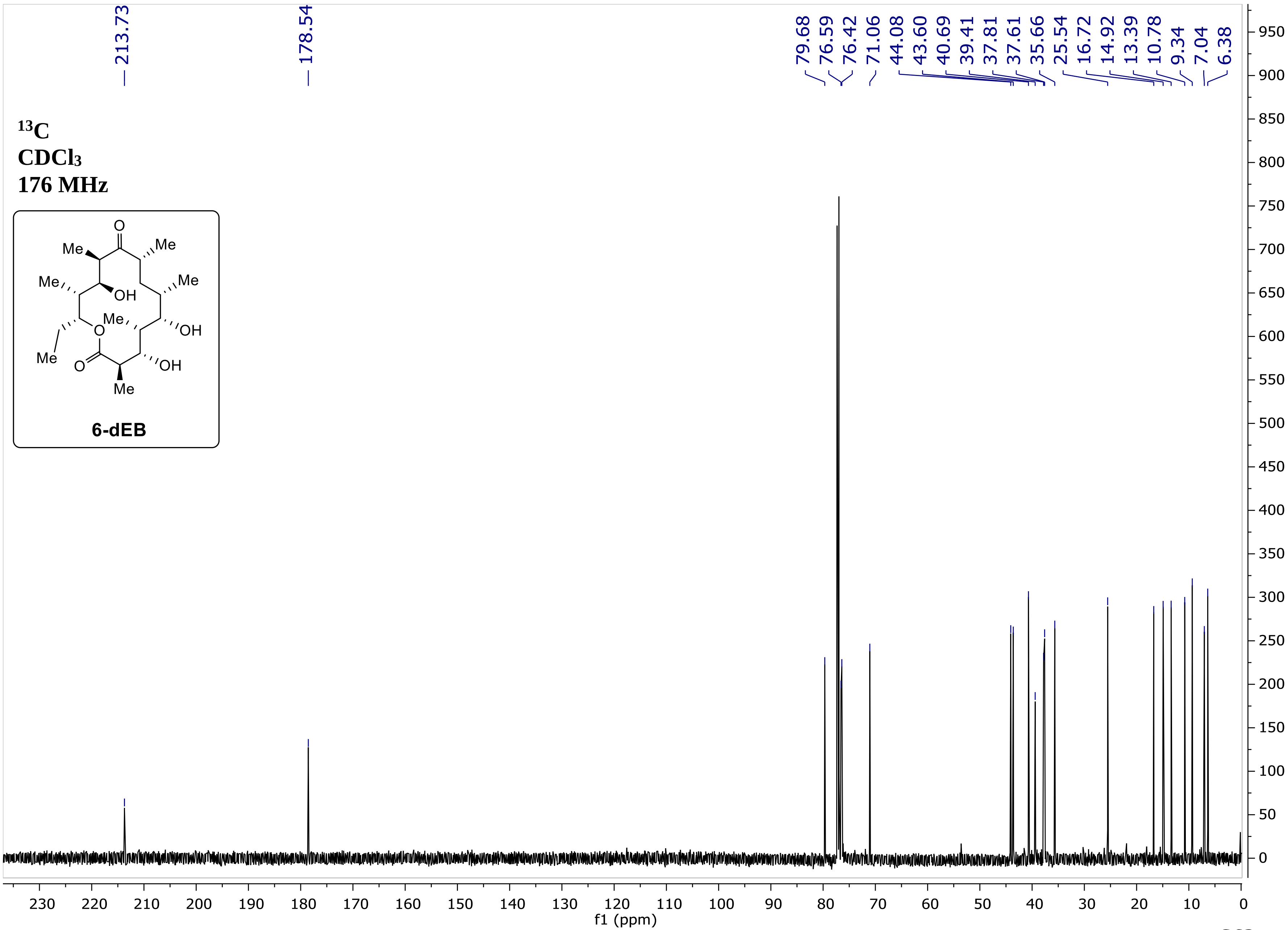
The table below summarizes ^{3}J coupling constants and key HMBC correlations used to assign the stereochemical configuration of glycosidic linkages and sites of glycosylation for each glycoside:

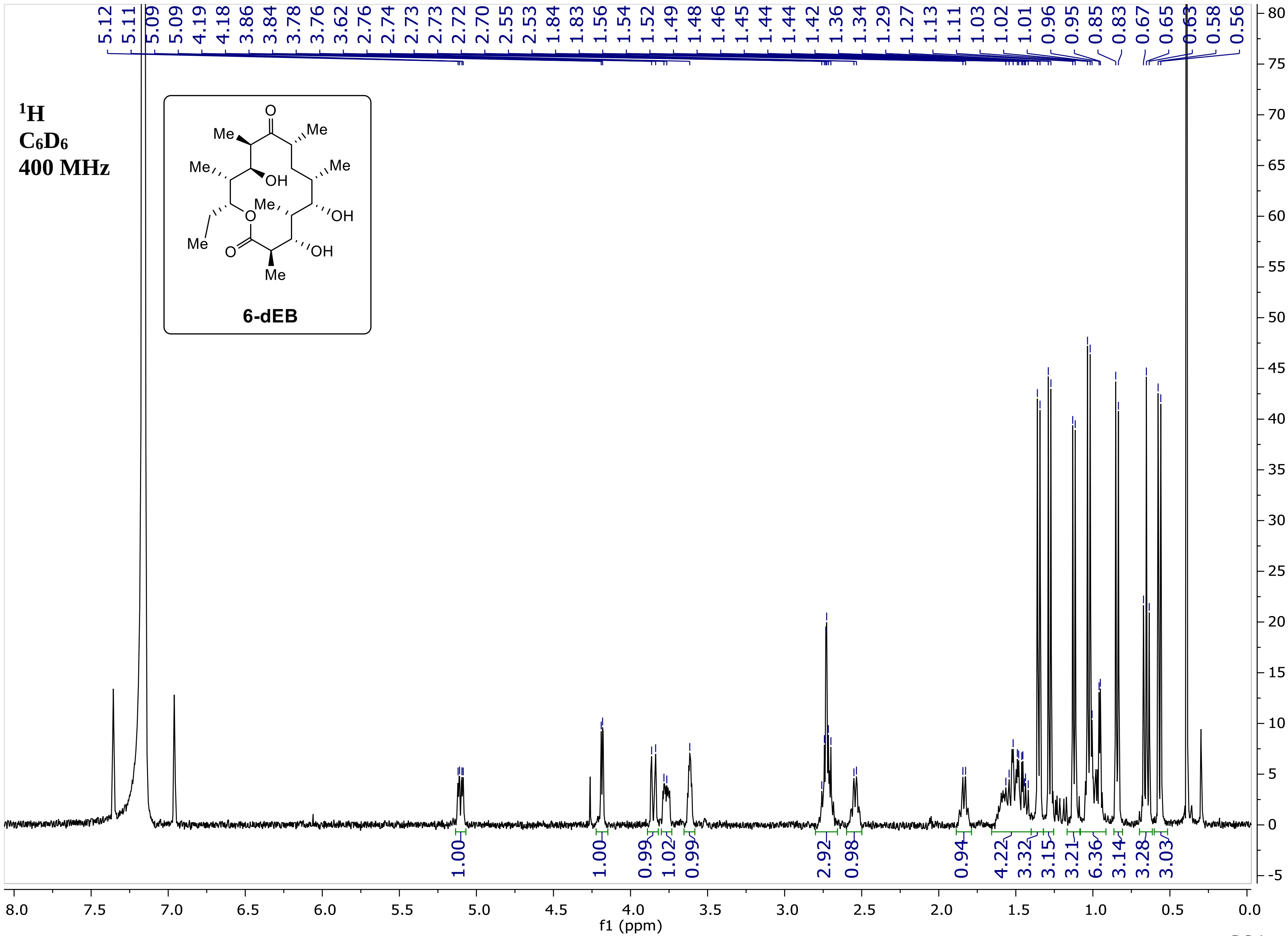
Compounds	^{3}J **(H$_{1'}$-H$_{2'}$)**	**HMBC Correlations**
6-dEB-C$_3$-α-A (**1**)	3.1 Hz	H$_{1'}$ (δ 4.74) - C$_3$ (δ 91.8) H$_3$ (δ 3.77) - C$_{1'}$ (δ 100.6)
6-dEB-C$_5$-α-A (**2**)	3.7 Hz	H$_{1'}$ (δ 4.92) - C$_5$ (δ 82.5) H$_5$ (δ 3.94) - C$_{1'}$ (δ 95.9)
6-dEB-C$_5$-α-A-C$_{11}$-α-A (**3**)	3.8 Hz 3.6 Hz	H$_{1'}$ (δ 4.99) - C$_5$ (δ 80.3) H$_{1'}$ (δ 5.71) - C$_{11}$ (δ 83.7) H$_{11}$ (δ 4.30) - C$_{1'}$ (δ 100.9)
6-dEB-C$_{11}$-α-A	3.6 Hz	H$_{1'}$ (δ 5.65) - C$_{11}$ (δ 83.5) H$_{11}$ (δ 4.15) - C$_{1'}$ (δ 100.8)
6-dEB-C$_{11}$-β-A (**8a**)	7.3 Hz	H$_{1'}$ (δ 4.41) - C$_{11}$ (δ 75.7) H$_{11}$ (δ 4.49) - C$_{1'}$ (δ 99.5)
6-dEB-C$_3$-α-B (**8b**)	3.5 Hz	H$_{1'}$ (δ 4.86) - C$_3$ (δ 89.8) H$_3$ (δ 3.80) - C$_{1'}$ (δ 100.8)
6-dEB-C$_5$-α-B (**8c**)	3.8 Hz	H$_5$ (δ 3.85) - C$_{1'}$ (δ 94.2)
6-dEB-C$_5$-β-B	7.7 Hz	H$_{1'}$ (δ 4.32) - C$_5$ (δ 85.8) H$_5$ (δ 3.95) - C$_{1'}$ (δ 104.9)
7-C$_5$-α-A (**8d**)	3.6 Hz	H$_{1'}$ (δ 4.95) - C$_5$ (δ 90.1) H$_5$ (δ 3.52) - C$_{1'}$ (δ 99.9)
7-C$_5$-β-A	7.8 Hz	H$_{1'}$ (δ 4.68) - C$_5$ (δ 86.2)
X-2-α-A (**8e**)	3.4 Hz	H$_3$ (δ 4.39) - C$_{1'}$ (δ 98.2) H$_5$ (δ 3.92) - C$_9$ (δ 107.5) H$_{11}$ (δ 3.36) - C$_9$ (δ 107.5)
X-2-β-A	7.9 Hz	H$_3$ (δ 4.55) - C$_{1'}$ (δ 101.1) H$_5$ (δ 3.88) - C$_9$ (δ 107.3)
7-C$_3$-α-A (**8f**)	3.3 Hz	H$_{1'}$ (δ 4.67) - C$_3$ (δ 92.4) H$_3$ (δ 3.62) - C$_{1'}$ (δ 101.0)
7-C$_3$-β-A	7.9 Hz	H$_{1'}$ (δ 4.31) - C$_3$ (δ 88.3) H$_3$ (δ 3.64) - C$_{1'}$ (δ 104.4)
7-C$_3$-β-B (**8g**)	7.7 Hz	H$_{1'}$ (δ 4.29) - C$_3$ (δ 87.5) H$_3$ (δ 3.71) - C$_{1'}$ (δ 104.4)
7-C$_3$-α-B	3.4 Hz	H$_{1'}$ (δ 4.76) - C$_3$ (δ 91.3) H$_3$ (δ 3.63) - C$_{1'}$ (δ 101.7)
7-C$_{11}$-α-B (**8h**)	2.9 Hz	H$_{11}$ (δ 4.39) - C$_{1'}$ (δ 99.3)
7-C$_5$-α-B (**8i**)	3.8 Hz	H$_{1'}$ (δ 5.05) - C$_5$ (δ 89.1) H$_5$ (δ 3.53) - C$_{1'}$ (δ 100.4)
7-C$_5$-β-B	7.9 Hz	H$_{1'}$ (δ 4.51) - C$_5$ (δ 87.7)
X-2-α-B (**8j**)	3.5 Hz	H$_{1'}$ (δ 5.24) - C$_3$ (δ 74.5) H$_3$ (δ 4.43) - C$_{1'}$ (δ 98.8) H$_5$ (δ 3.90) - C$_9$ (δ 107.5) H$_{11}$ (δ 3.93) - C$_9$ (δ 107.5)

X-2-β-B	7.8 Hz	$H_{1'}$ (δ 5.17) - C_3 (δ 73.9) H_3 (δ 4.56) - $C_{1'}$ (δ 101.7) H_5 (δ 3.91) - C_9 (δ 107.3) H_{11} (δ 3.88) - C_9 (δ 107.3)
7-C_3-α-C (**8k**)	3.5 Hz	$H_{1'}$ (δ 4.84) - C_3 (δ 89.6) H_3 (δ 3.73) - $C_{1'}$ (δ 100.8)
7-C_3-β-C	7.7 Hz	$H_{1'}$ (δ 4.41) - C_3 (δ 86.5) H_3 (δ 3.99) - $C_{1'}$ (δ 103.8)
7-C_5-α-C	3.7 Hz	$H_{1'}$ (δ 4.97) - C_5 (δ 89.6) H_5 (δ 4.01) - $C_{1'}$ (δ 100.5)
7-C_5-β-C	7.7 Hz	$H_{1'}$ (δ 4.35) - C_5 (δ 89.7) H_5 (δ 3.54) - $C_{1'}$ (δ 107.4)
X-2-α-C	3.5 Hz	H_3 (δ 4.45) - $C_{1'}$ (δ 96.9) H_5 (δ 3.96) - C_9 (δ 107.2) H_{11} (δ 3.87) - C_9 (δ 107.2)

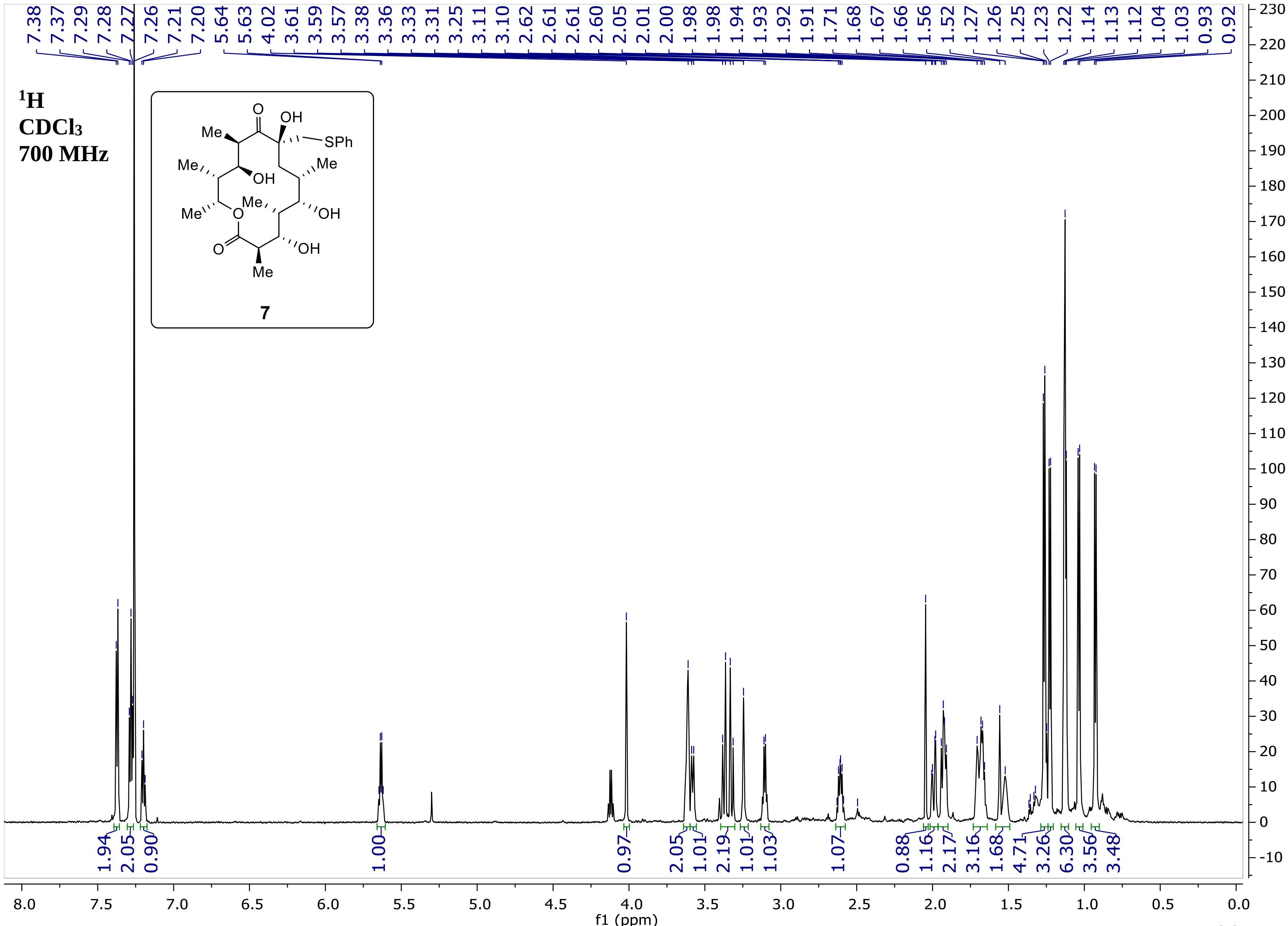
Supporting NMR Spectra



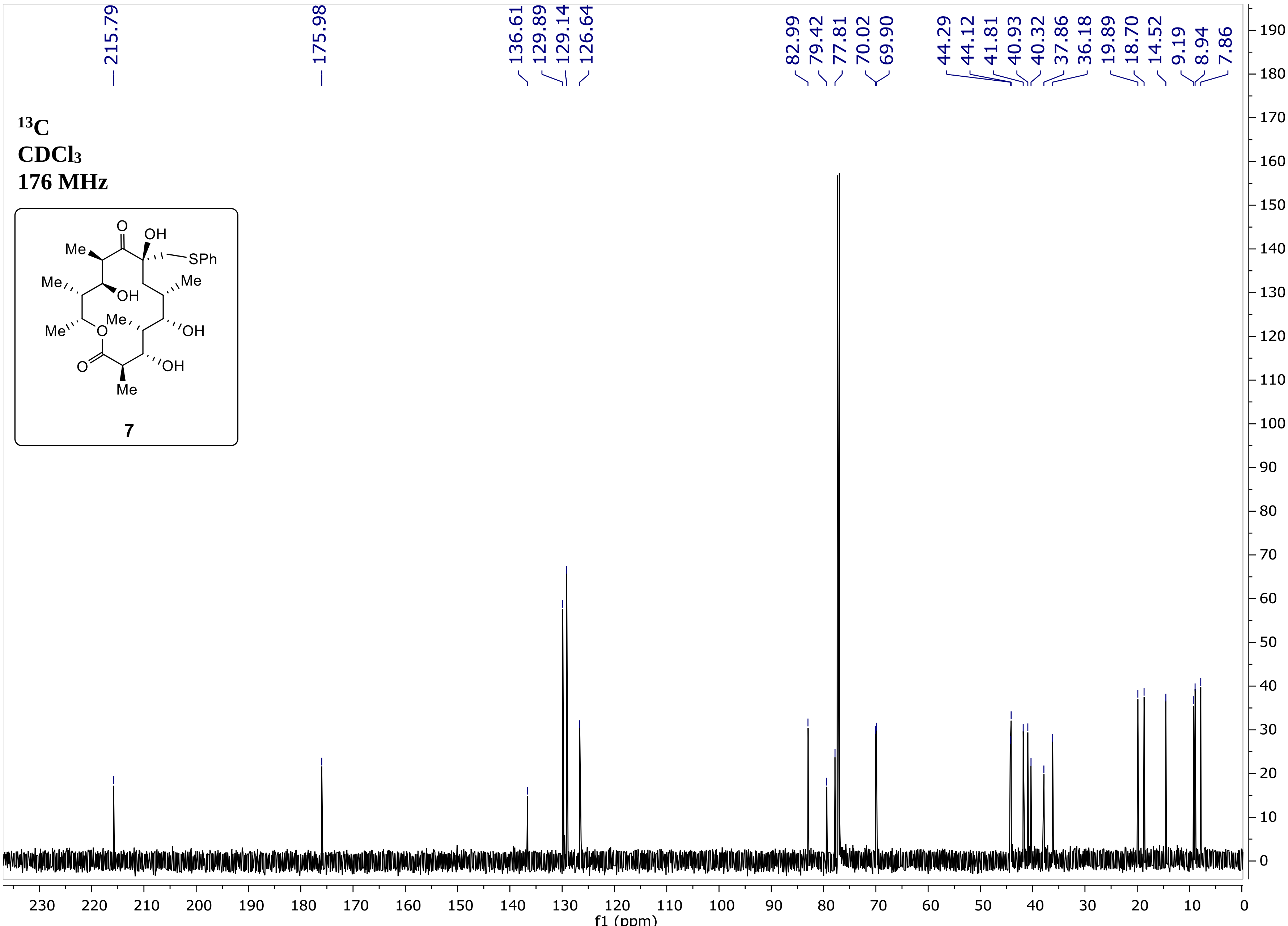

213.73
178.54
79.68
76.59
76.42
71.06
44.08
43.60
40.69
39.41
37.81
37.61
35.66
25.54
16.72
14.92
13.39
10.78
9.34
7.04
6.38
^{13}C
$CDCl_3$
176 MHz
O
Me
Me
Me
OH
Me
Me
O
OH
Me
O
OH
Me
6-dEB
f1 (ppm)

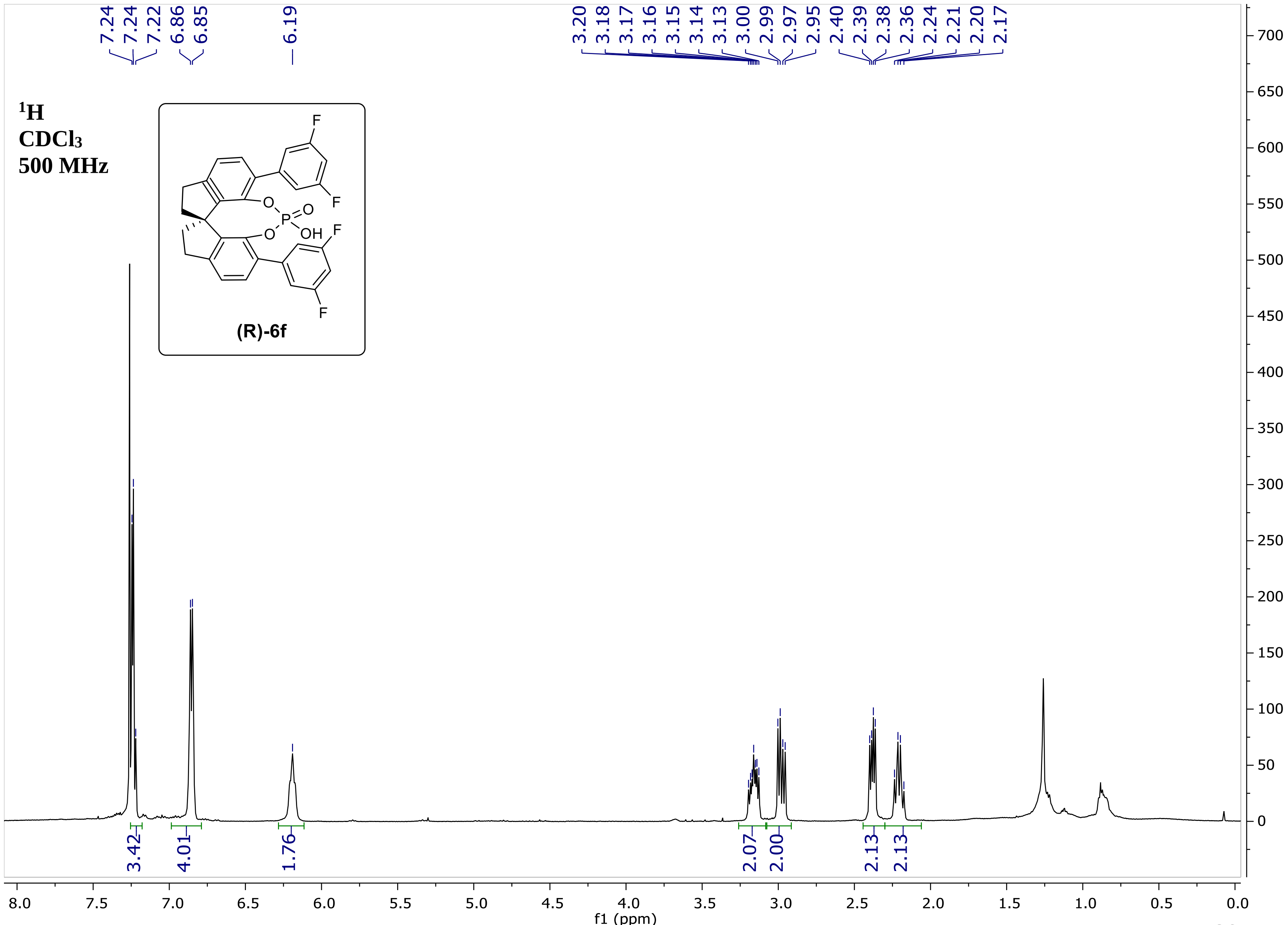


5.12 5.11 5.09 5.09 4.19 4.18 3.86 3.84 3.78 3.76 3.62 2.76 2.74 2.73 2.73 2.72 2.70 2.55 2.53 1.84 1.83 1.56 1.54 1.52 1.49 1.48 1.46 1.45 1.44 1.44 1.42 1.36 1.34 1.29 1.27 1.13 1.11 1.03 1.02 1.01 0.96 0.95 0.85 0.83 0.67 0.65 0.63 0.58 0.56
¹H
C_6D_6
400 MHz
Me
Me
Me
OH
Me
Me
OH
Me
OH
Me
O
O
O
Me
6-dEB
1.00 1.00 0.99 1.02 0.99 2.92 0.98 0.94 4.22 3.32 3.15 3.21 6.36 3.14 3.28 3.03
f1 (ppm)

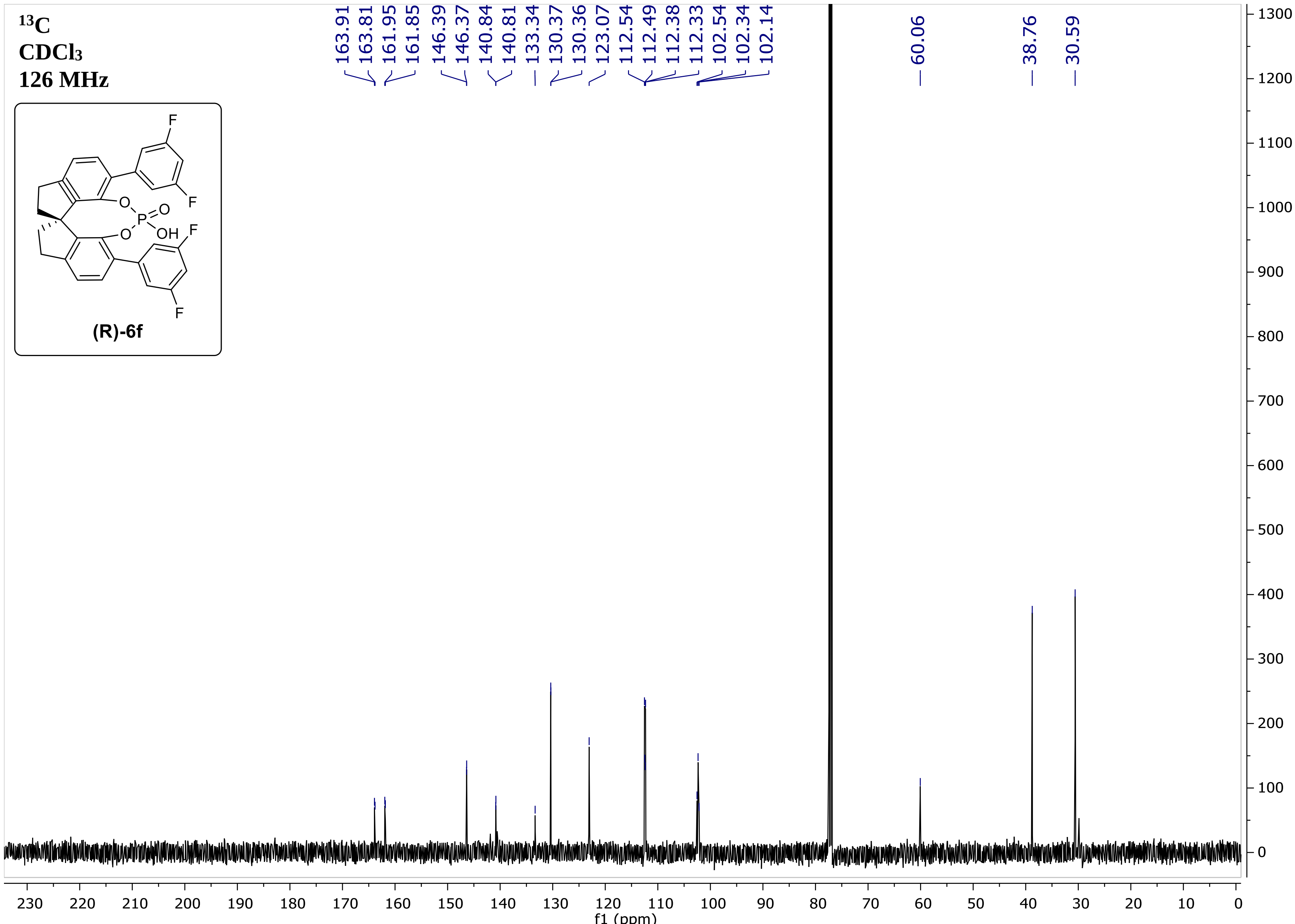


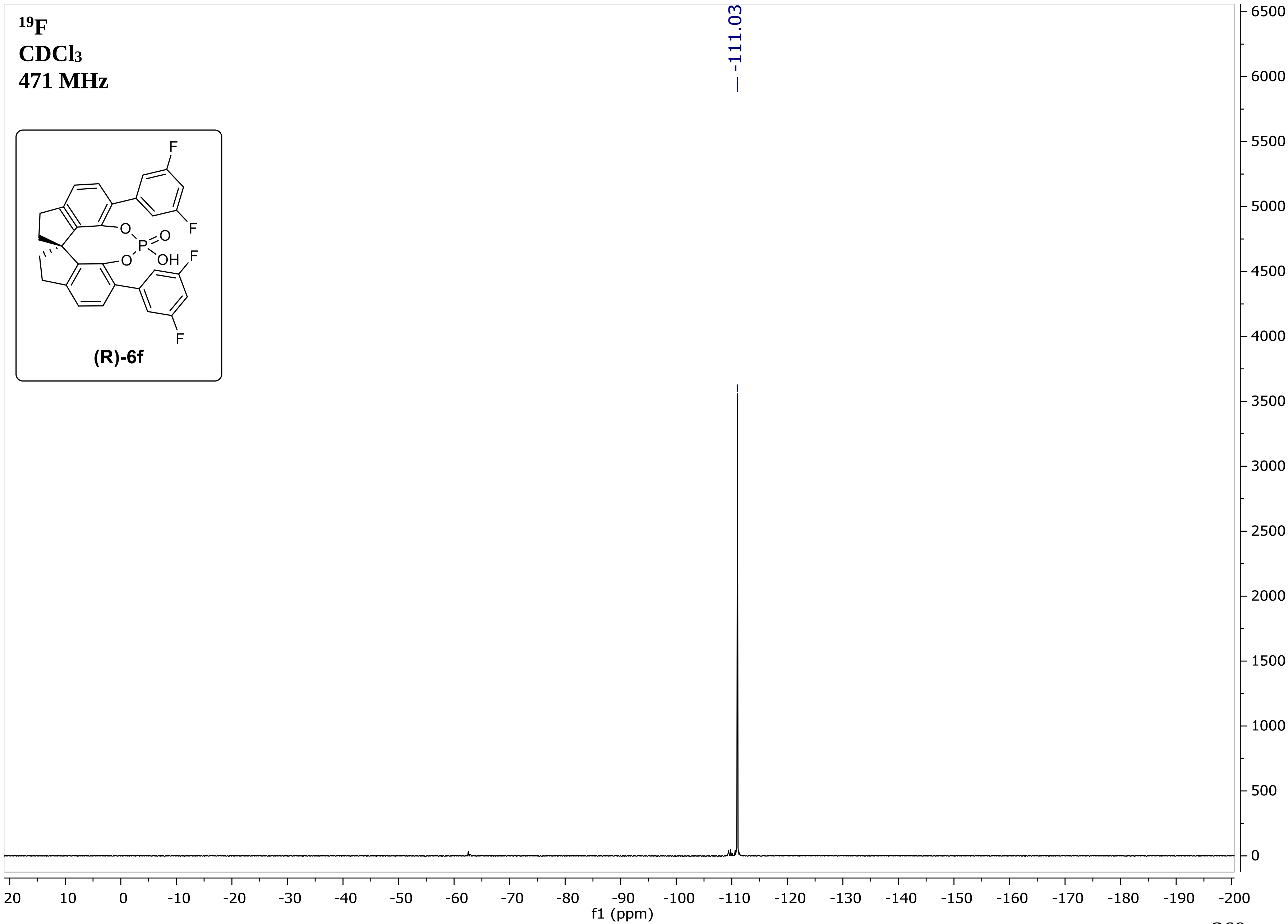
^{1}H
$CDCl_3$
700 MHz
7
7.38 7.37 7.29 7.28 7.27 7.26 7.21 7.20 5.64 5.63 4.02 3.61 3.59 3.57 3.38 3.36 3.33 3.31 3.25 3.11 3.10 2.62 2.61 2.61 2.60 2.05 2.01 2.00 1.98 1.98 1.94 1.93 1.92 1.91 1.71 1.68 1.67 1.66 1.56 1.52 1.27 1.26 1.25 1.23 1.22 1.14 1.13 1.12 1.04 1.03 0.93 0.92
1.94 2.05 0.90 1.00 0.97 2.05 1.01 2.19 1.01 1.03 1.07 0.88 1.16 2.17 3.16 1.68 4.71 3.26 6.30 3.56 3.48
f1 (ppm)


215.79
175.98
136.61
129.89
129.14
126.64
82.99
79.42
77.81
70.02
69.90
44.29
44.12
41.81
40.93
40.32
37.86
36.18
19.89
18.70
14.52
9.19
8.94
7.86
13C
CDCl3
176 MHz
O
OH
Me
SPh
Me
OH
Me
Me
O
Me
OH
O
OH
Me
7
f1 (ppm)

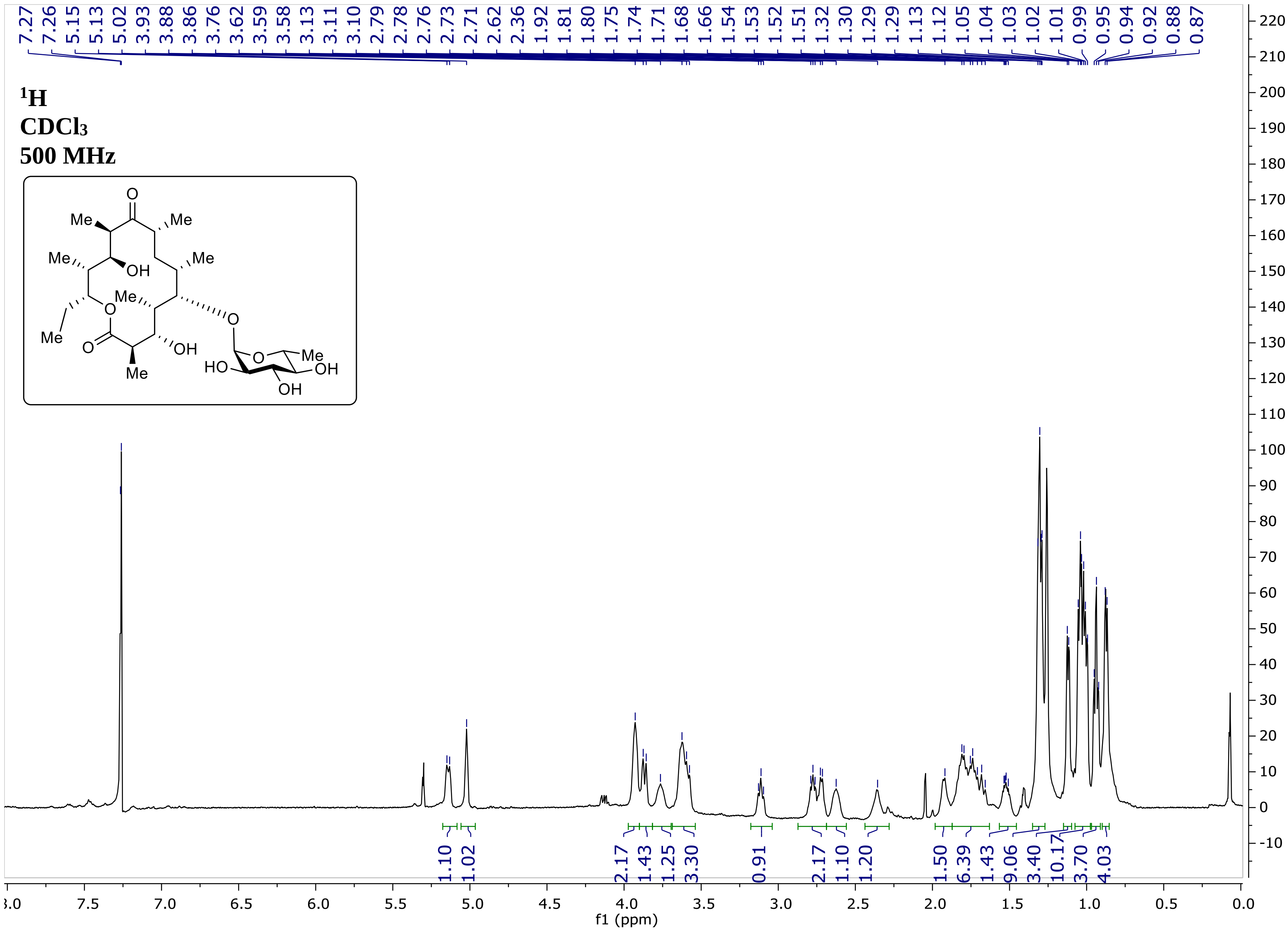


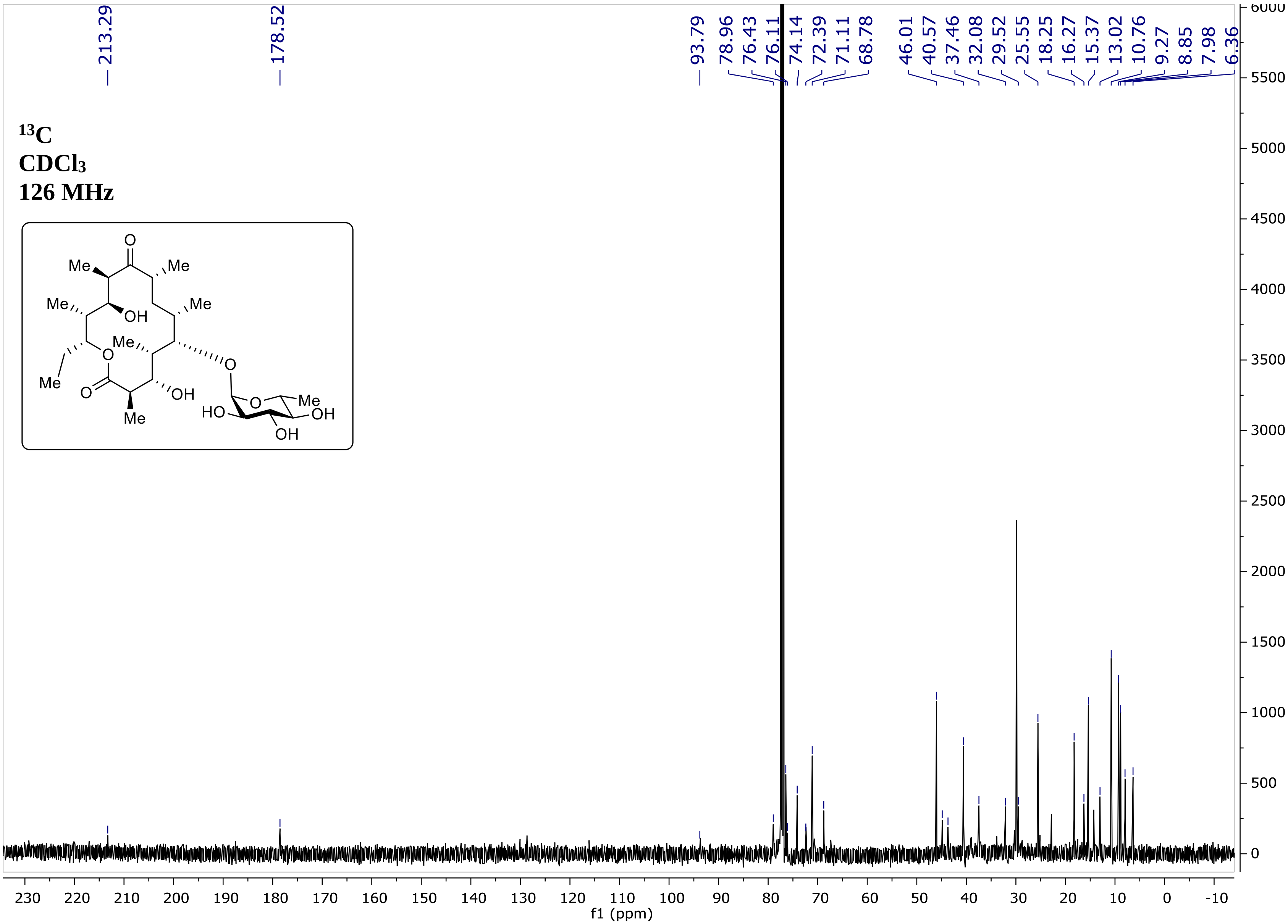
^{1}H
$CDCl_3$
500 MHz
(R)-6f
7.24
7.24
7.22
6.86
6.85
6.19
3.20
3.18
3.17
3.16
3.15
3.14
3.13
3.00
2.99
2.97
2.95
2.40
2.39
2.38
2.36
2.24
2.21
2.20
2.17
3.42
4.01
1.76
2.07
2.00
2.13
2.13
f1 (ppm)


13C
CDCl3
126 MHz
163.91
163.81
161.95
161.85
146.39
146.37
140.84
140.81
133.34
130.37
130.36
123.07
112.54
112.49
112.38
112.33
102.54
102.34
102.14
60.06
38.76
30.59
(R)-6f
f1 (ppm)

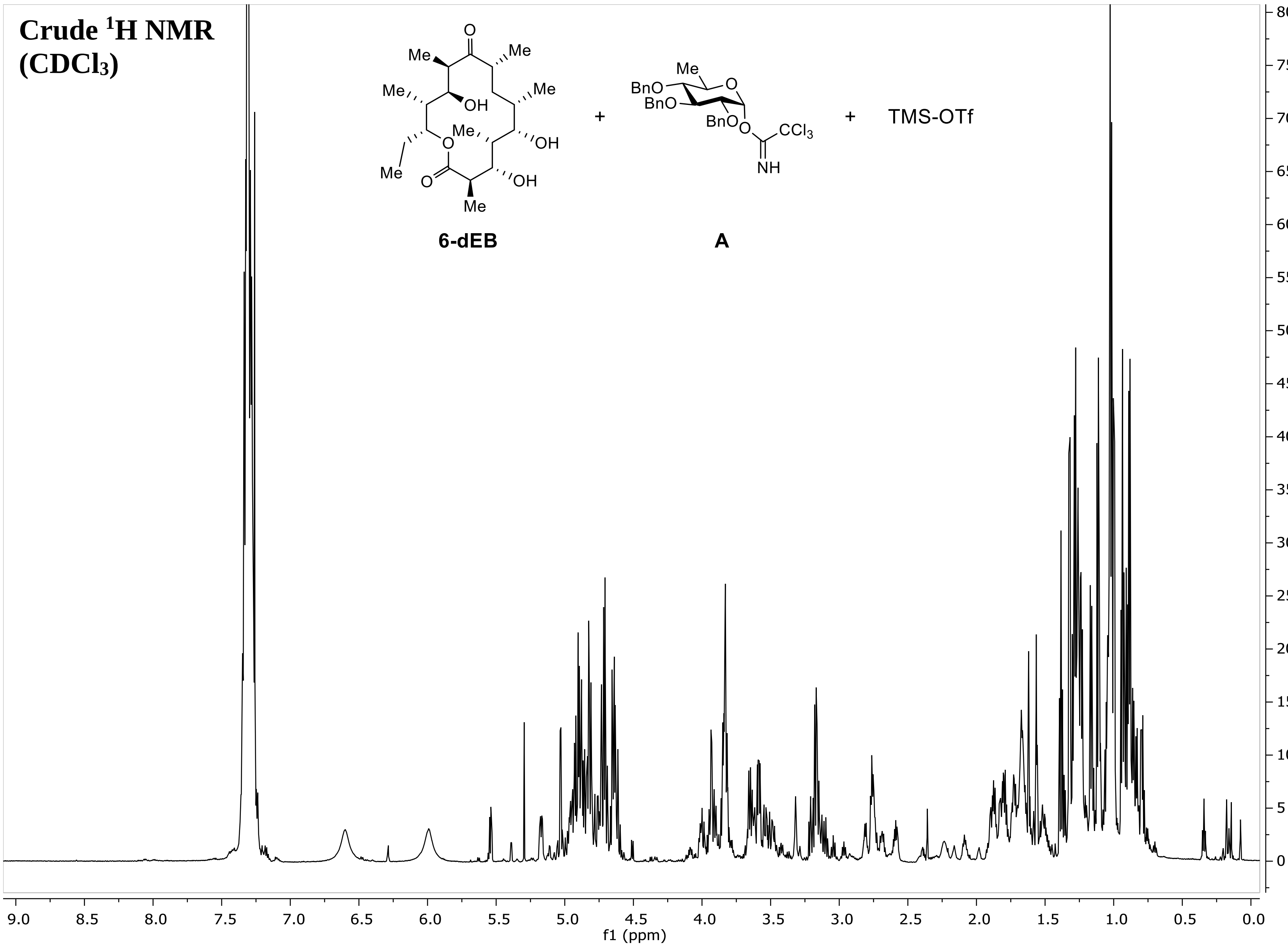


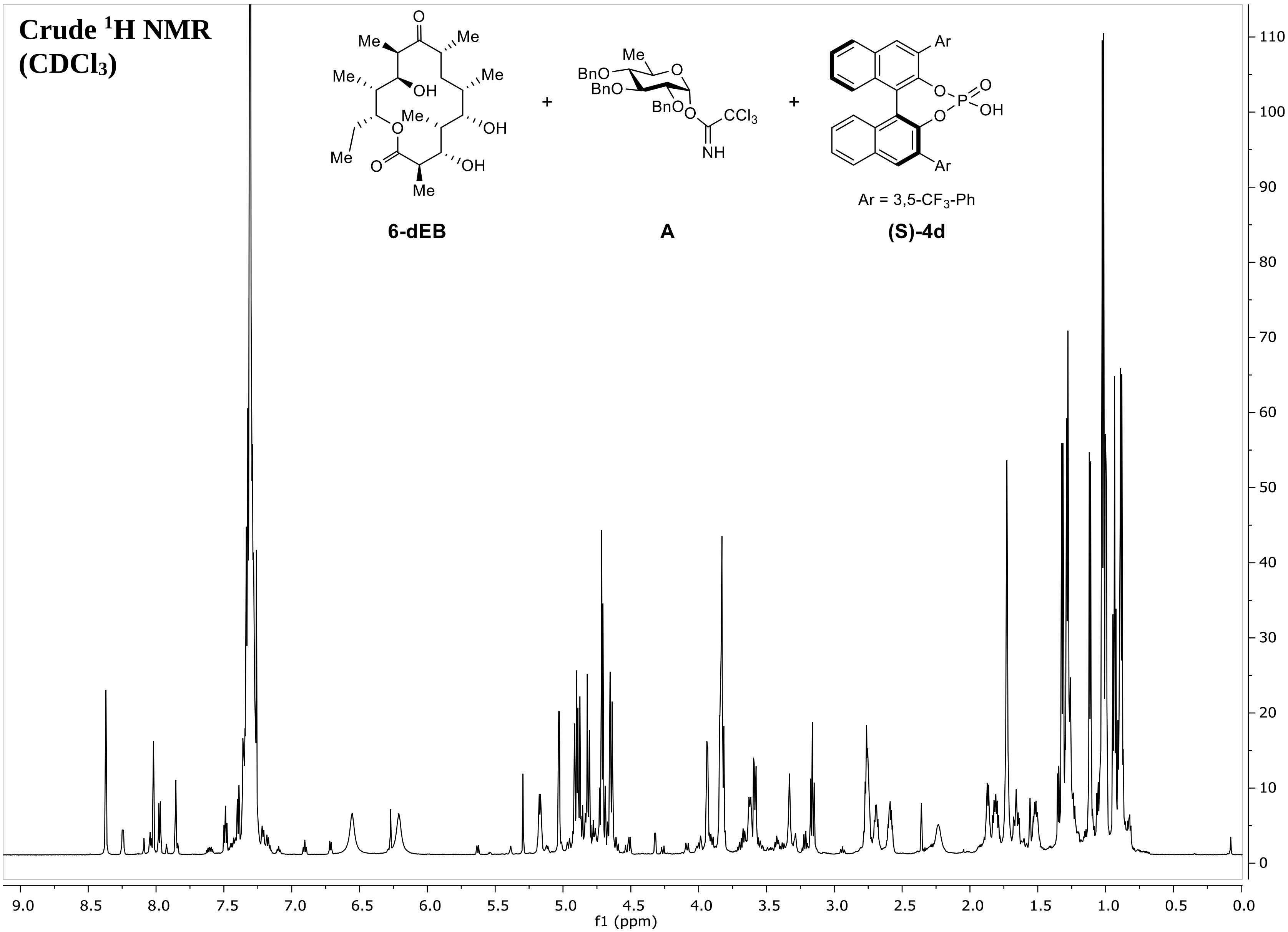
19F
CDCl3
471 MHz
-111.03
F
F
O
P
O
OH
O
F
F
(R)-6f
f1 (ppm)


^{1}H
$CDCl_3$
500 MHz
7.27 7.26 5.15 5.13 5.02 3.93 3.88 3.86 3.76 3.62 3.59 3.58 3.13 3.11 3.10 2.79 2.78 2.76 2.73 2.71 2.62 2.36 1.92 1.81 1.80 1.75 1.74 1.71 1.68 1.66 1.54 1.53 1.52 1.51 1.32 1.30 1.29 1.29 1.13 1.12 1.05 1.04 1.03 1.02 1.01 0.99 0.95 0.94 0.92 0.88 0.87
1.10 1.02 2.17 1.43 1.25 3.30 0.91 2.17 1.10 1.20 1.50 6.39 1.43 9.06 3.40 10.17 3.70 4.03
f1 (ppm)
Me
O
Me
OH
HO
OH
OH
Me

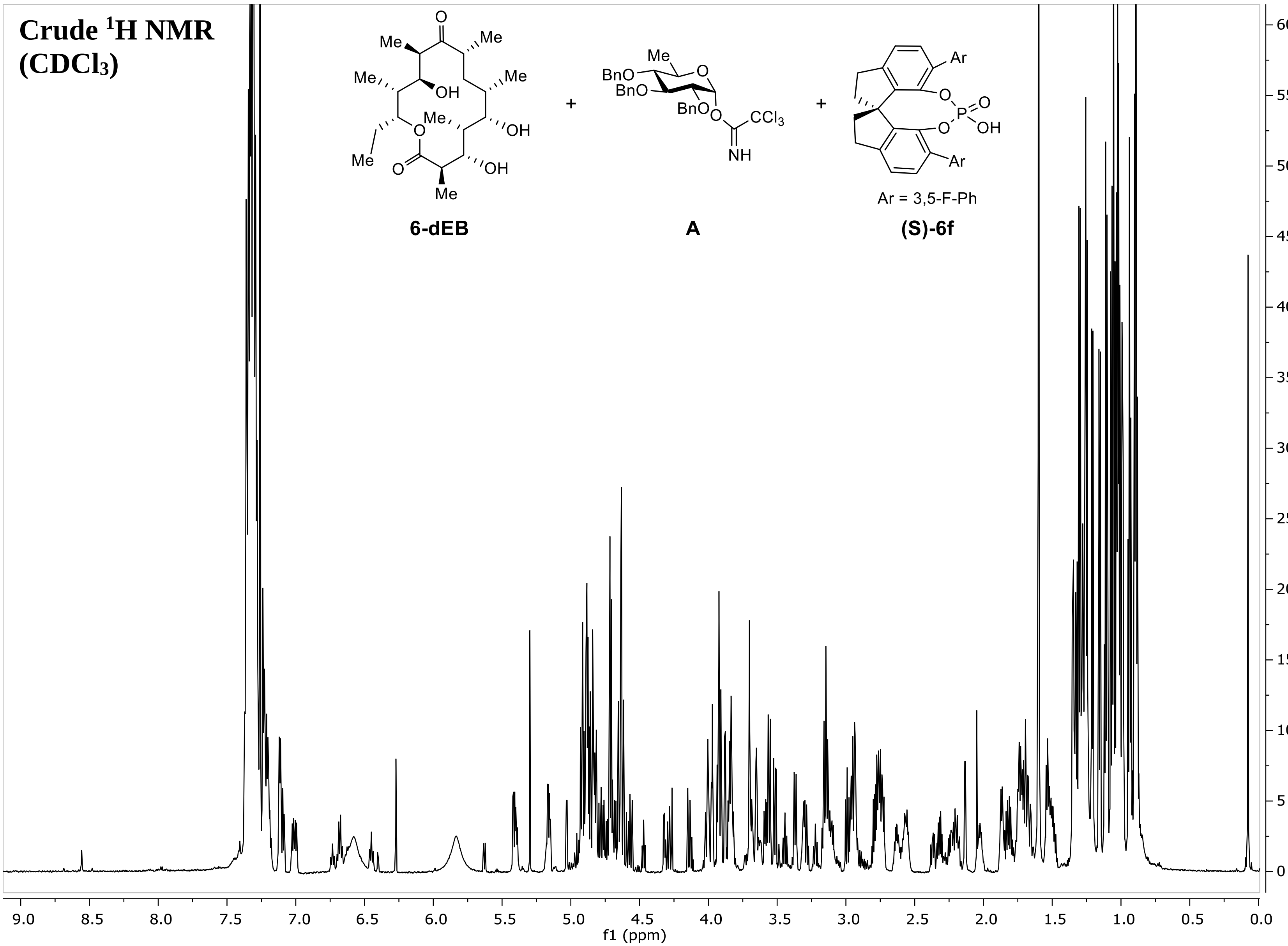


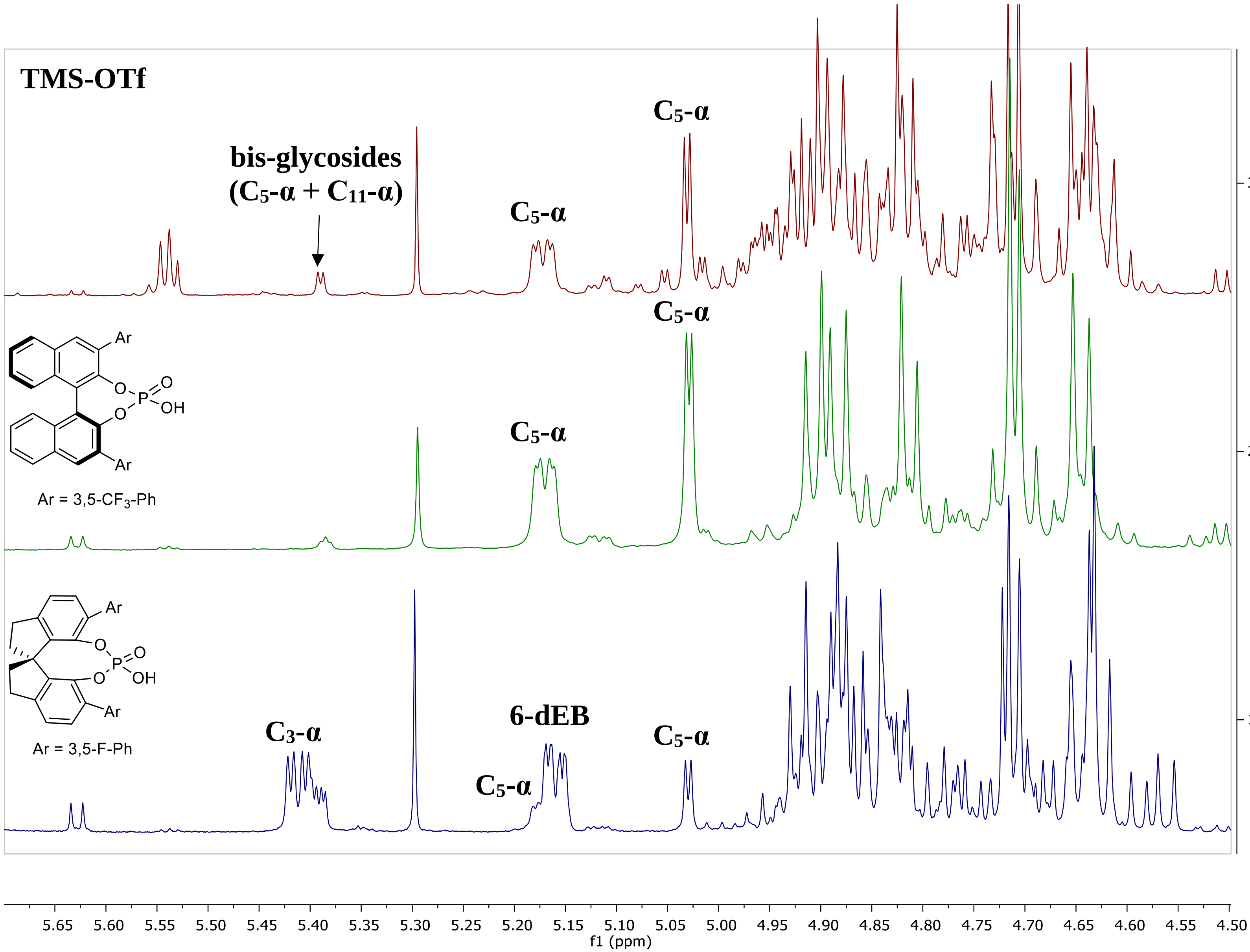
213.29
178.52
93.79
78.96
76.43
76.11
74.14
72.39
71.11
68.78
46.01
40.57
37.46
32.08
29.52
25.55
18.25
16.27
15.37
13.02
10.76
9.27
8.85
7.98
6.36
13C
CDCl3
126 MHz
f1 (ppm)


Crude ¹H NMR
(CDCl3)
6-dEB
A
TMS-OTf
f1 (ppm)

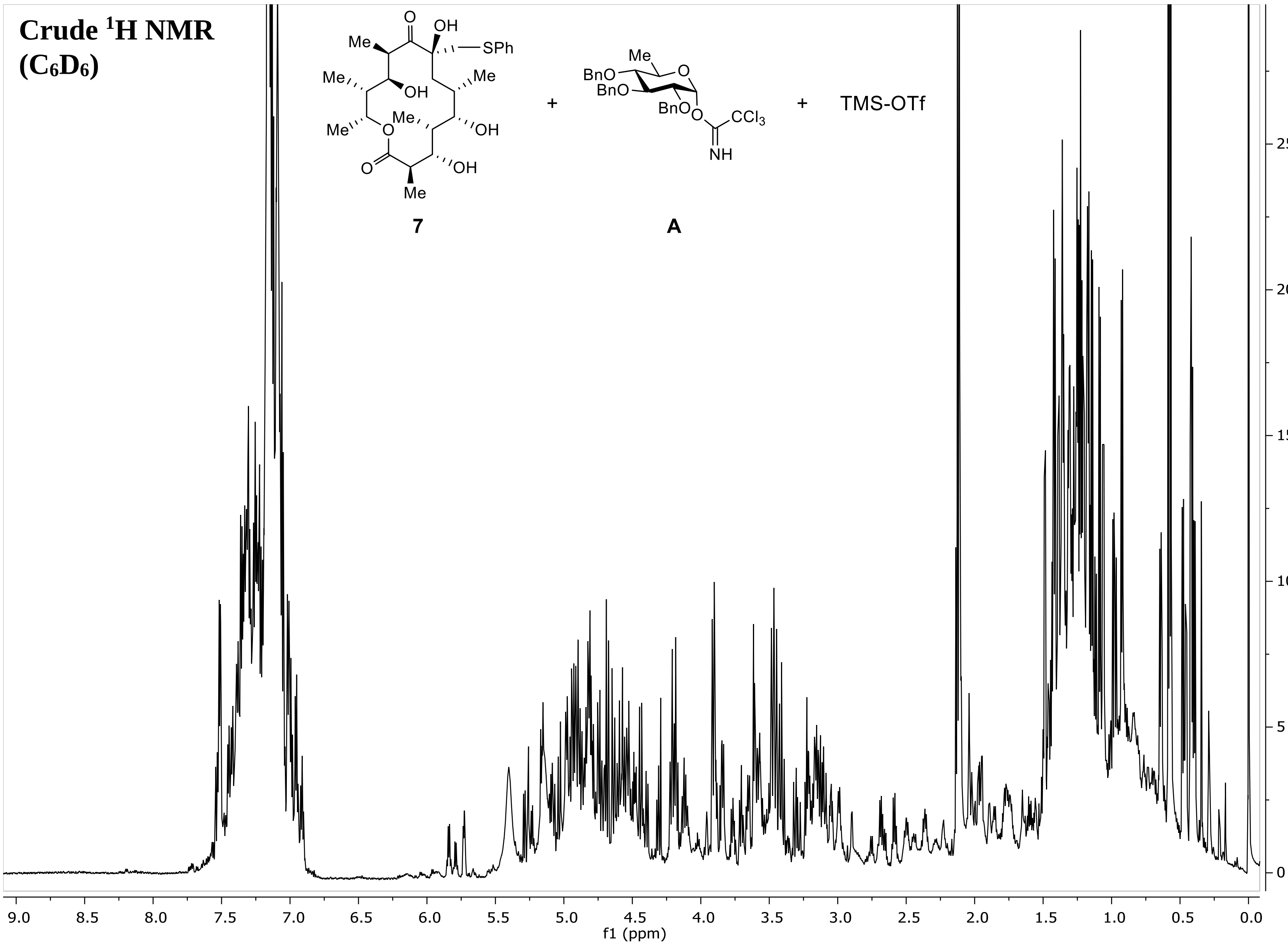

Crude ¹H NMR
(CDCl₃)
6-dEB
A
(S)-4d
Ar = 3,5-CF₃-Ph
f1 (ppm)

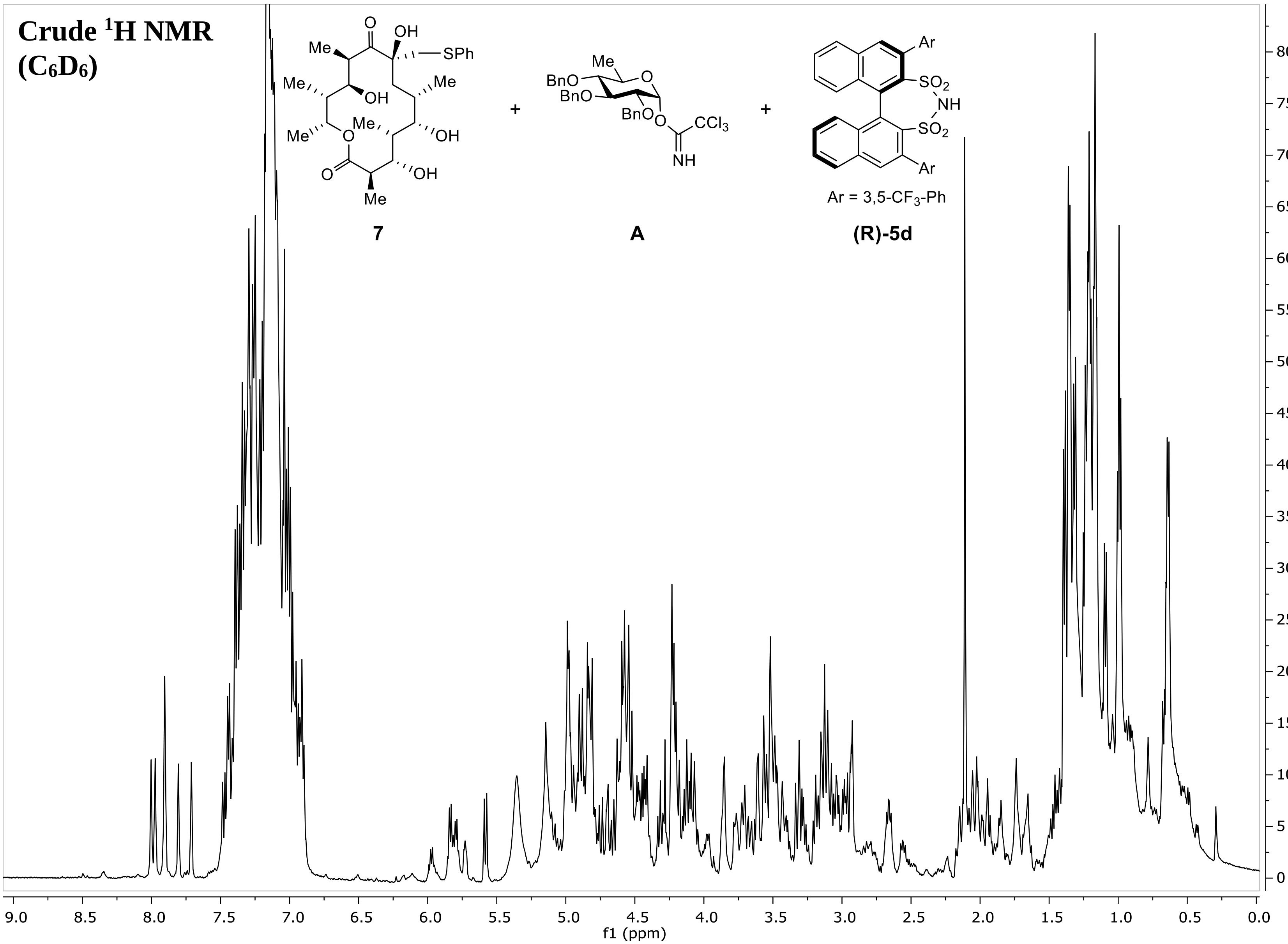
Crude ^{1}H NMR ($CDCl_3$)



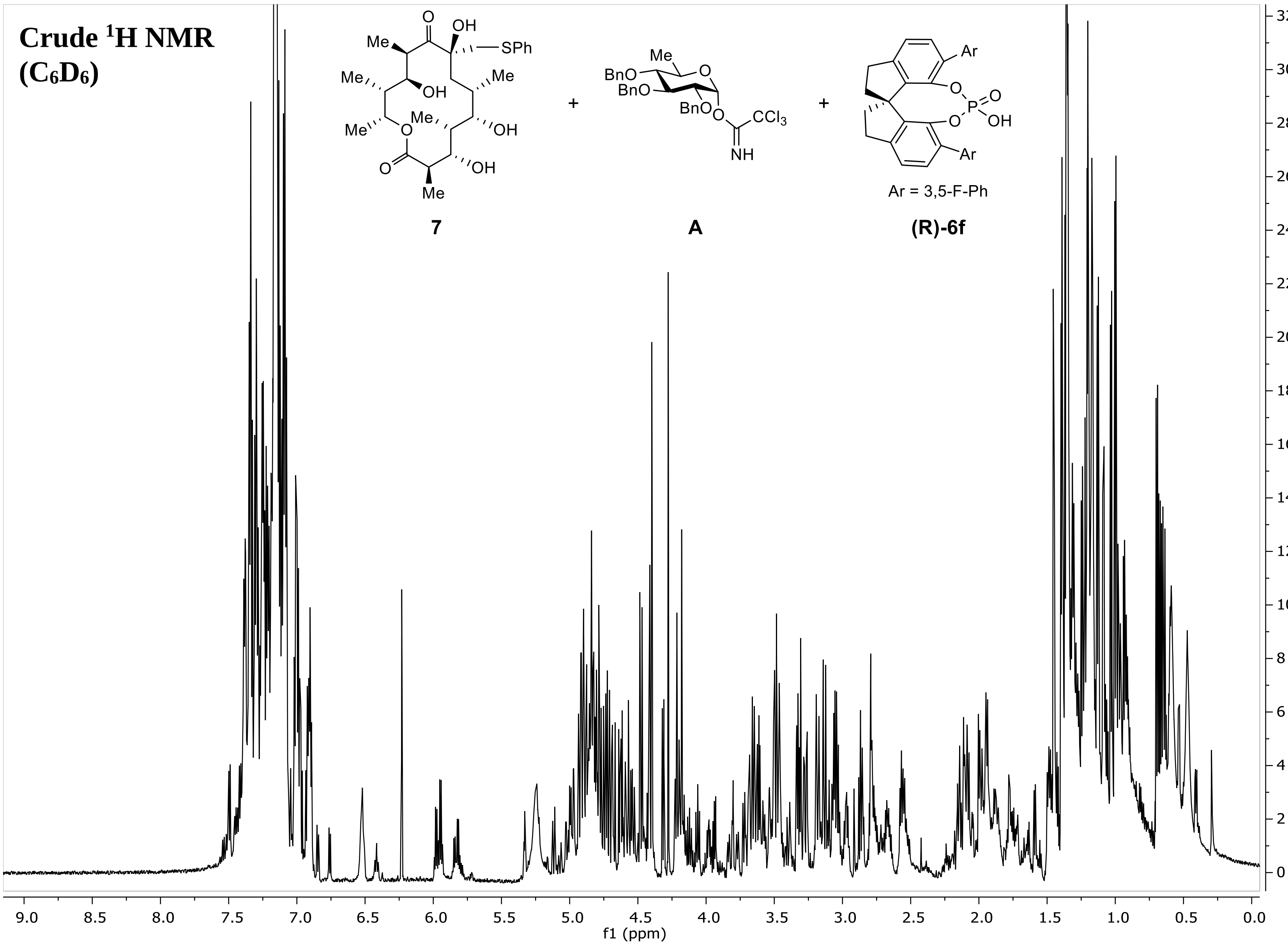

TMS-OTf
bis-glycosides
(C5-α + C11-α)
C5-α
C5-α
C5-α
C5-α
Ar
O
O
P
O
OH
Ar
Ar = 3,5-CF3-Ph
Ar
O
P
O
O
OH
Ar
Ar = 3,5-F-Ph
C3-α
6-dEB
C5-α
C5-α
3
2
1
5.65 5.60 5.55 5.50 5.45 5.40 5.35 5.30 5.25 5.20 5.15 5.10 5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50
f1 (ppm)

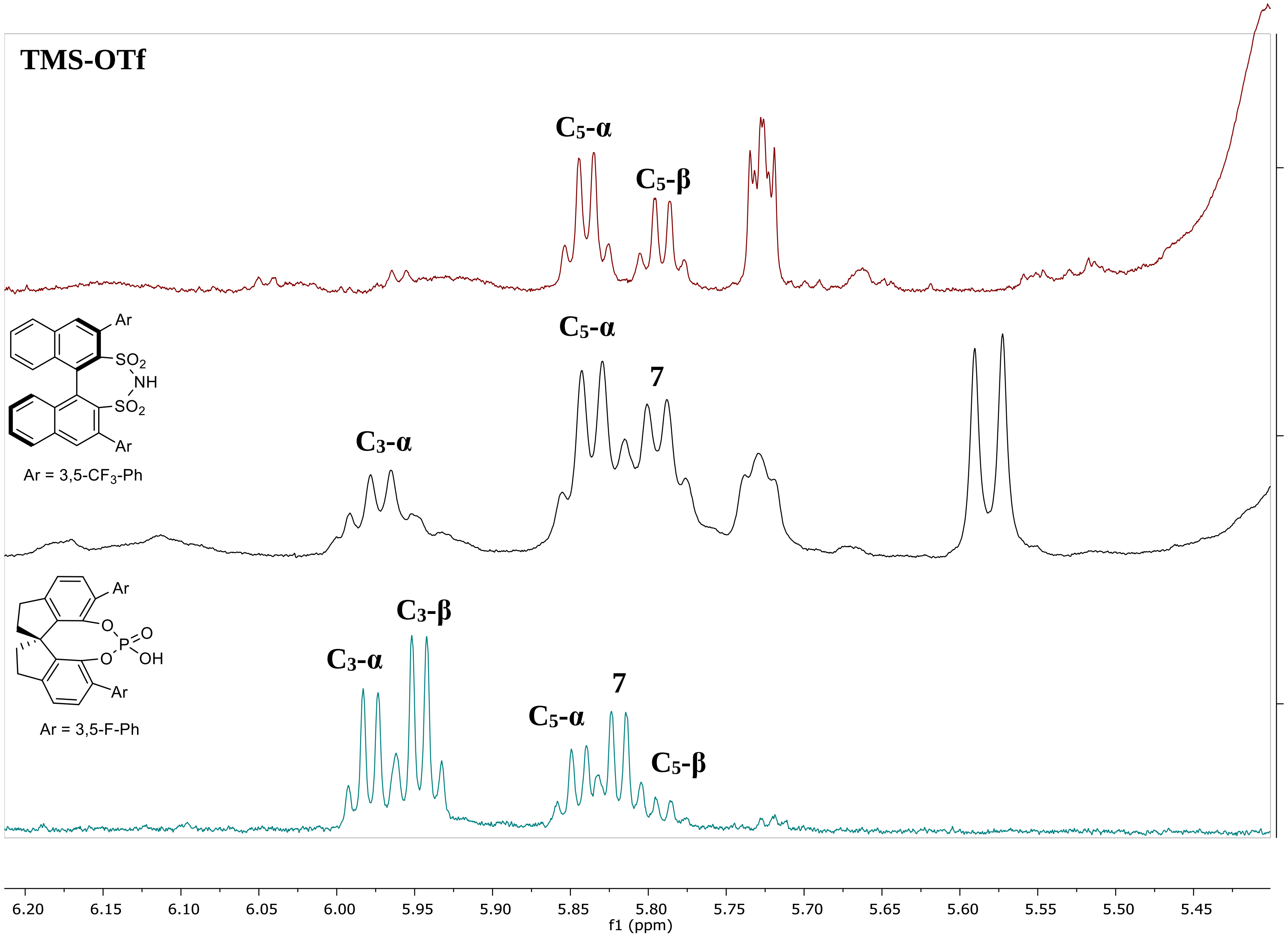
Crude ^{1}H NMR
(C_6D_6)





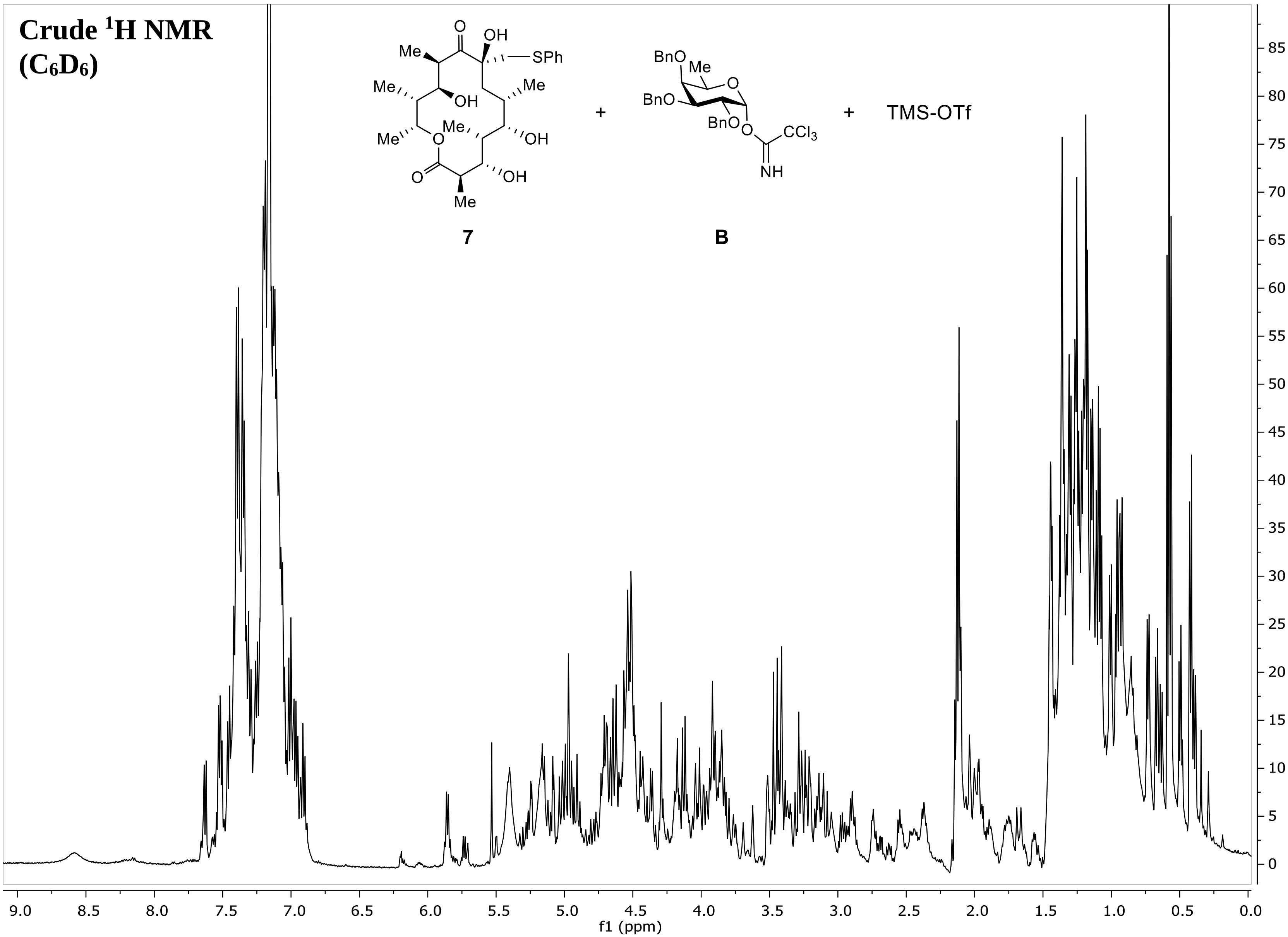
Crude ¹H NMR
(C6D6)
7
A
(R)-5d
Ar = 3,5-CF3-Ph
f1 (ppm)

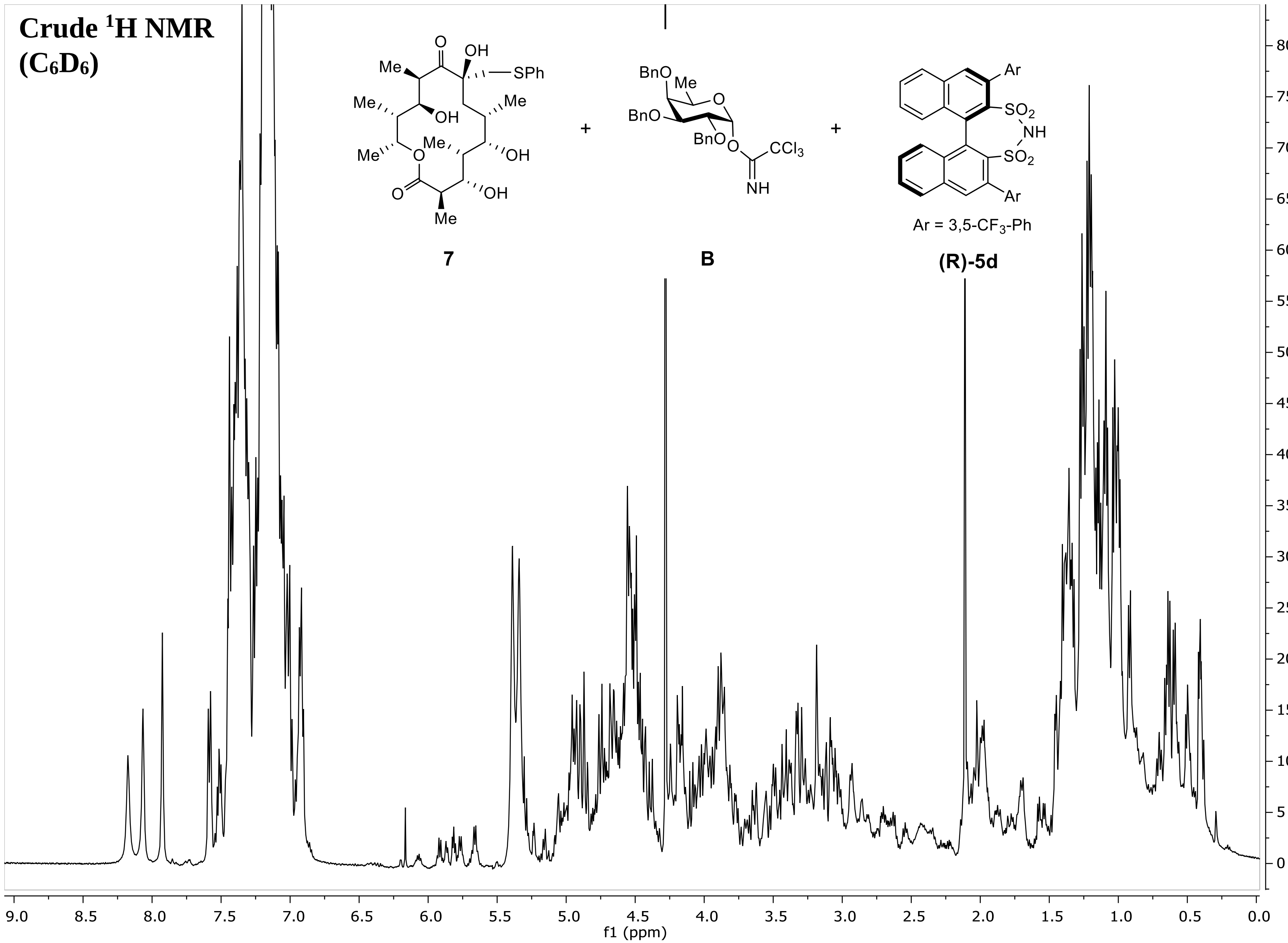

Crude ^{1}H NMR
(C_6D_6)
7
A
(R)-6f
Ar = 3,5-F-Ph
f1 (ppm)

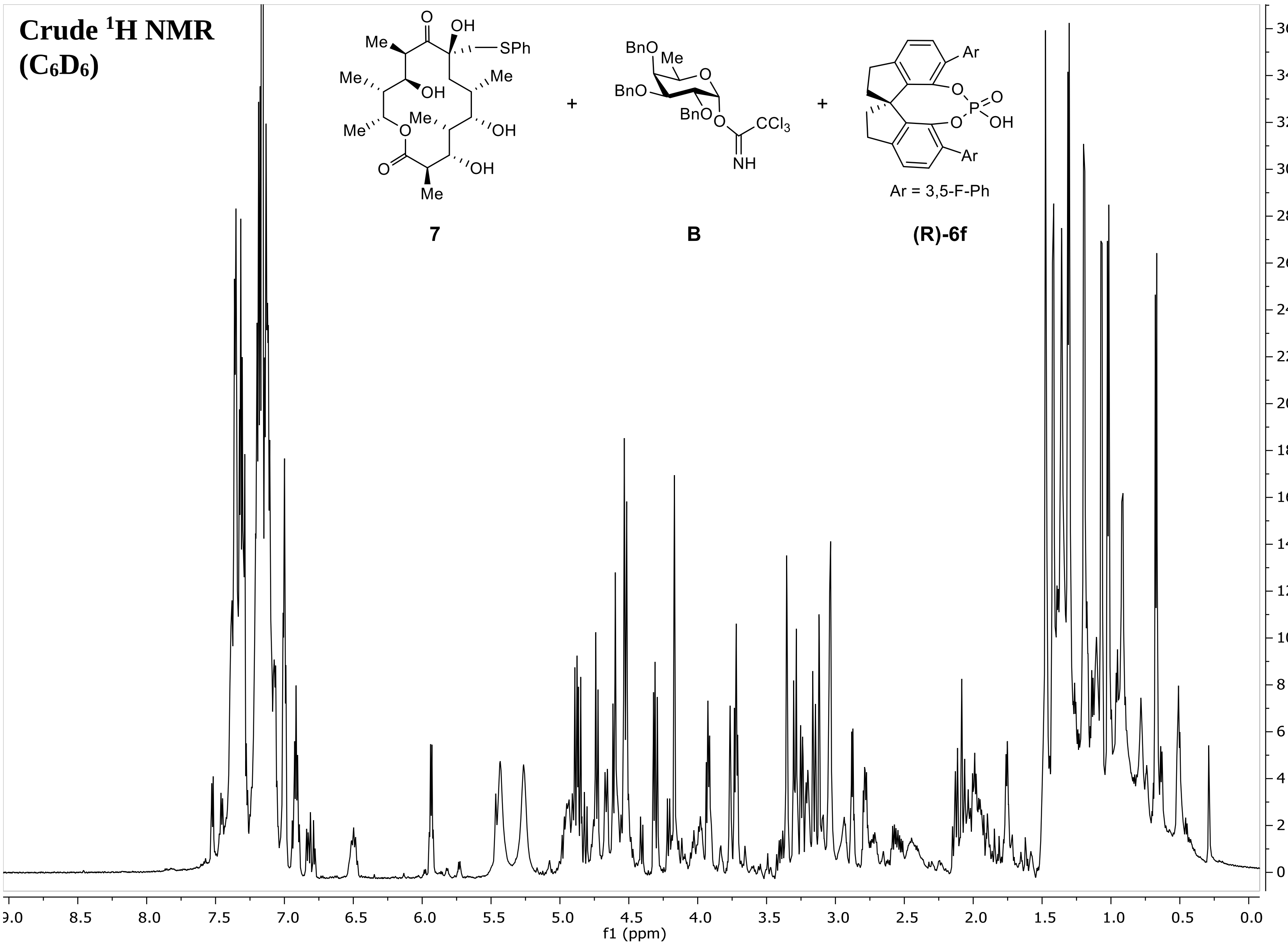


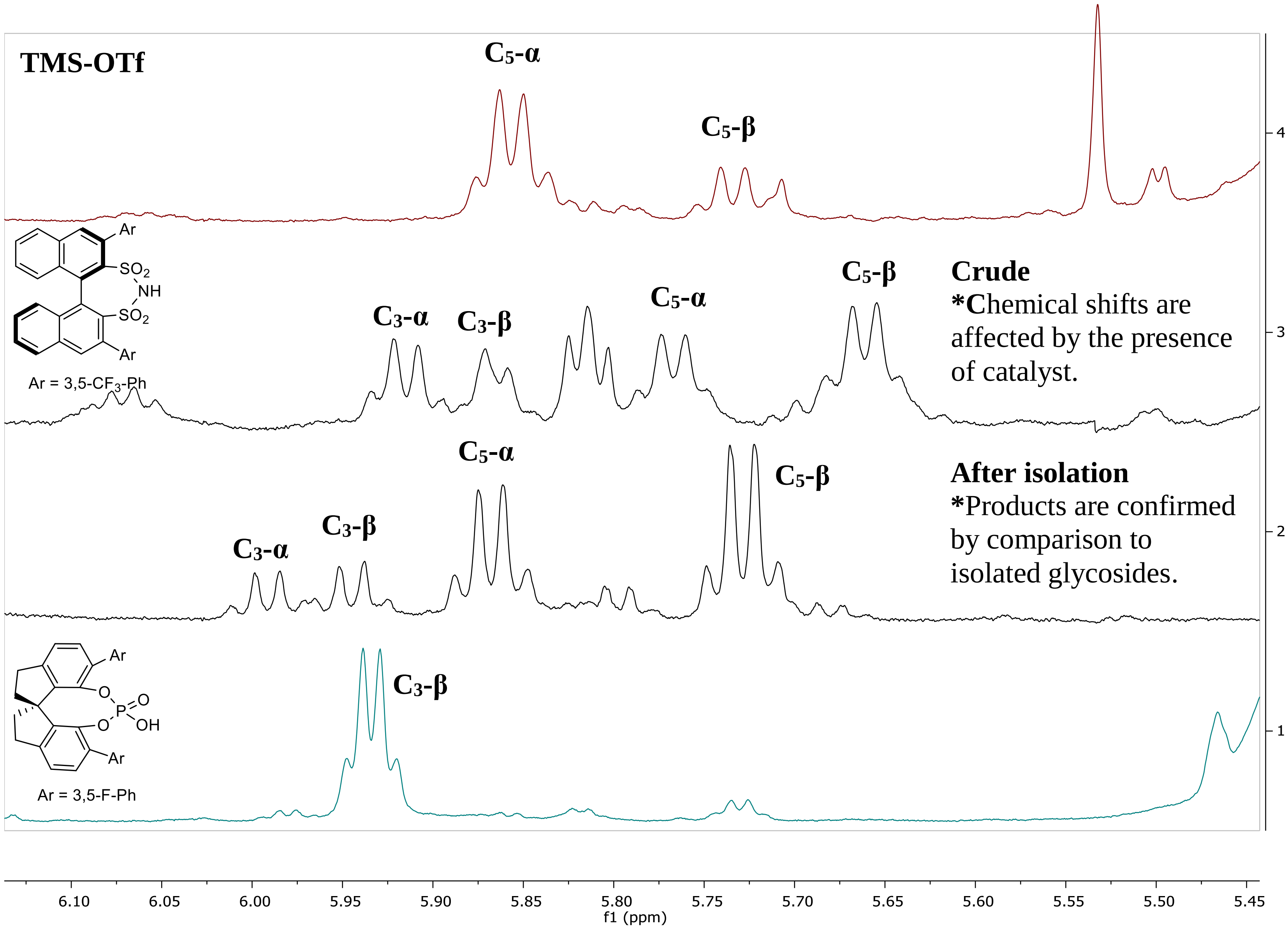
TMS-OTf
C5-α
C5-β
C5-α
7
C3-α
Ar
SO2
NH
SO2
Ar
Ar = 3,5-CF3-Ph
C3-β
C3-α
C5-α
7
C5-β
Ar
O
P
O
OH
O
Ar
Ar = 3,5-F-Ph
3
2
1
6.20 6.15 6.10 6.05 6.00 5.95 5.90 5.85 5.80 5.75 5.70 5.65 5.60 5.55 5.50 5.45
f1 (ppm)

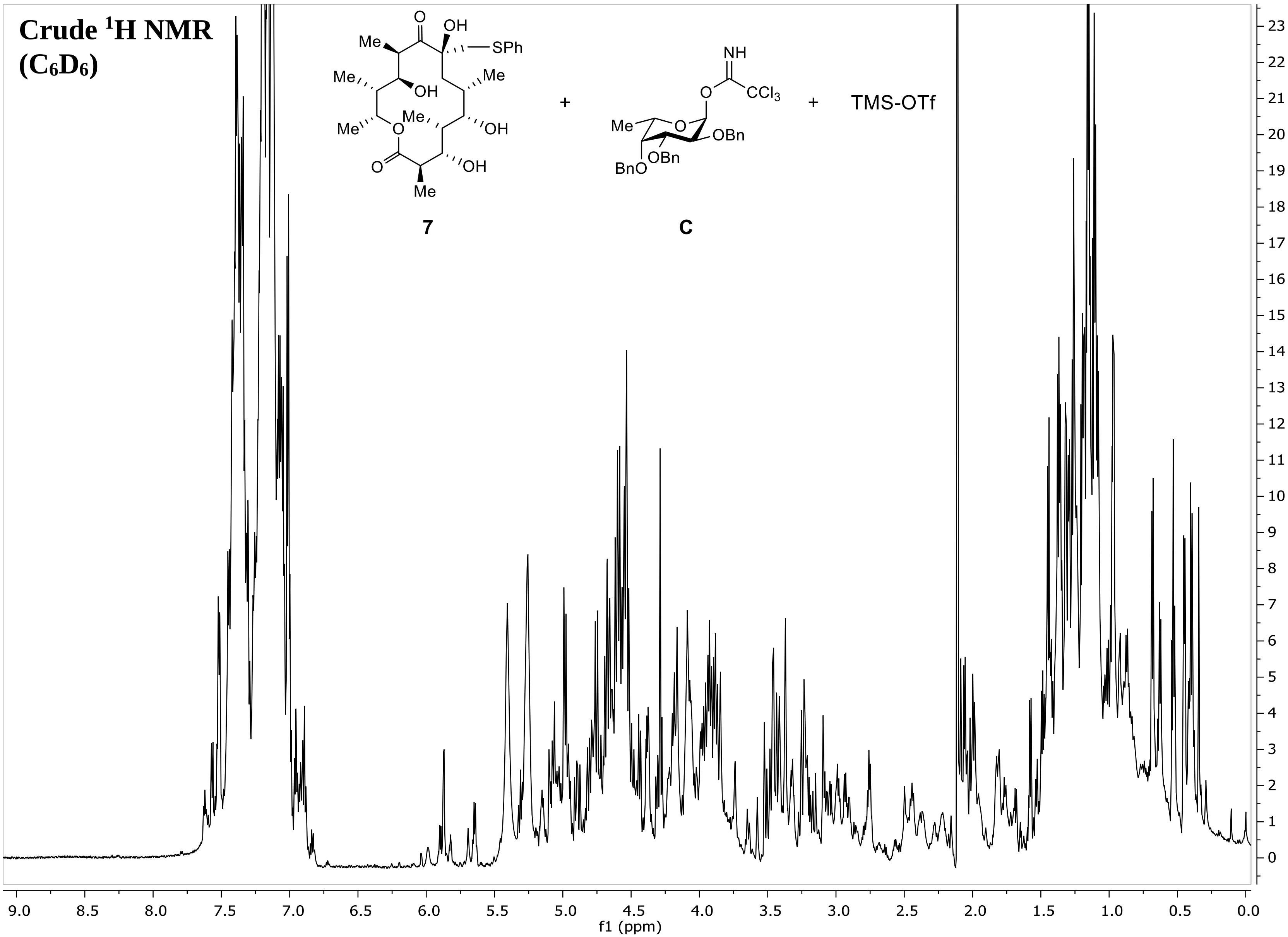
Crude ¹H NMR (C_6D_6)




Crude ¹H NMR
(C6D6)
7
B
(R)-5d
Ar = 3,5-CF3-Ph
f1 (ppm)

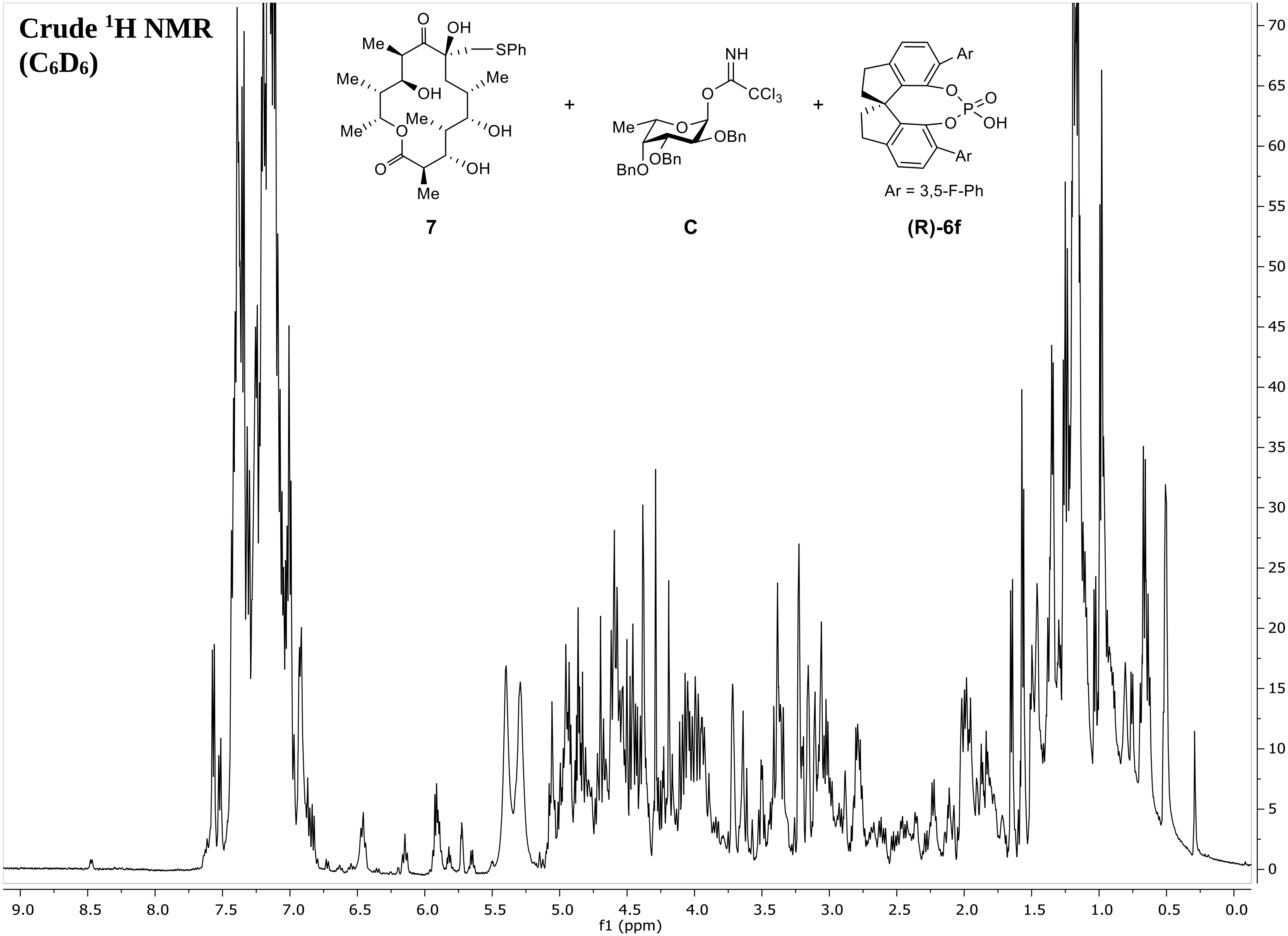

Crude ¹H NMR
(C6D6)
Me
OH
SPh
Me
OH
Me
Me
Me
OH
OH
Me
BnO
Me
BnO
BnO
CCl3
NH
Ar
OH
Ar
Ar = 3,5-F-Ph
7
B
(R)-6f
f1 (ppm)

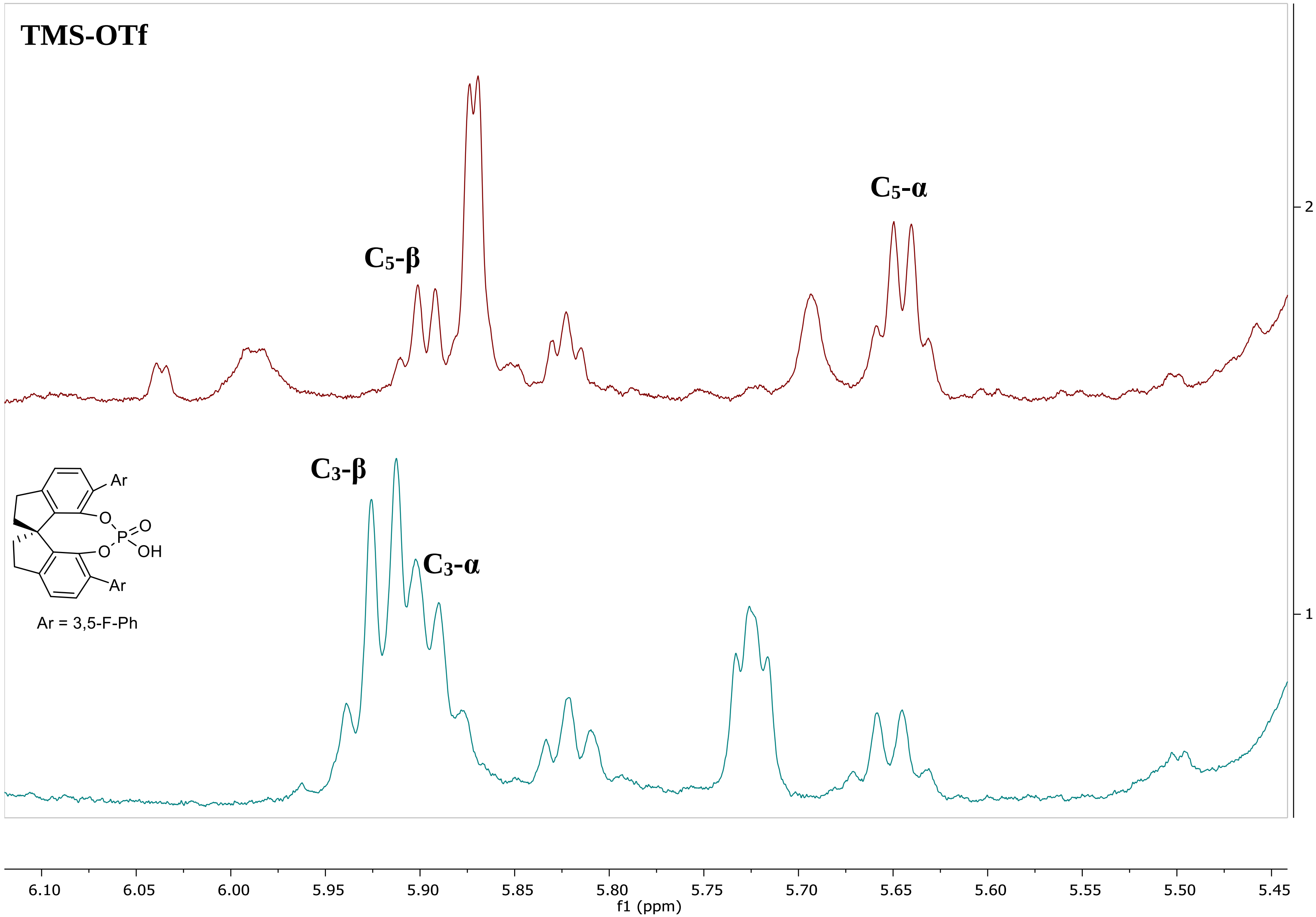

TMS-OTf
C5-α
C5-β
Ar
SO2
NH
SO2
Ar
Ar = 3,5-CF3-Ph
C3-α
C3-β
C5-α
C5-β
Crude
*Chemical shifts are affected by the presence of catalyst.
C5-α
C3-β
C3-α
C5-β
After isolation
*Products are confirmed by comparison to isolated glycosides.
Ar
O
P
O
OH
O
Ar
Ar = 3,5-F-Ph
C3-β
6.10
6.05
6.00
5.95
5.90
5.85
5.80
5.75
5.70
5.65
5.60
5.55
5.50
5.45
f1 (ppm)
4
3
2
1

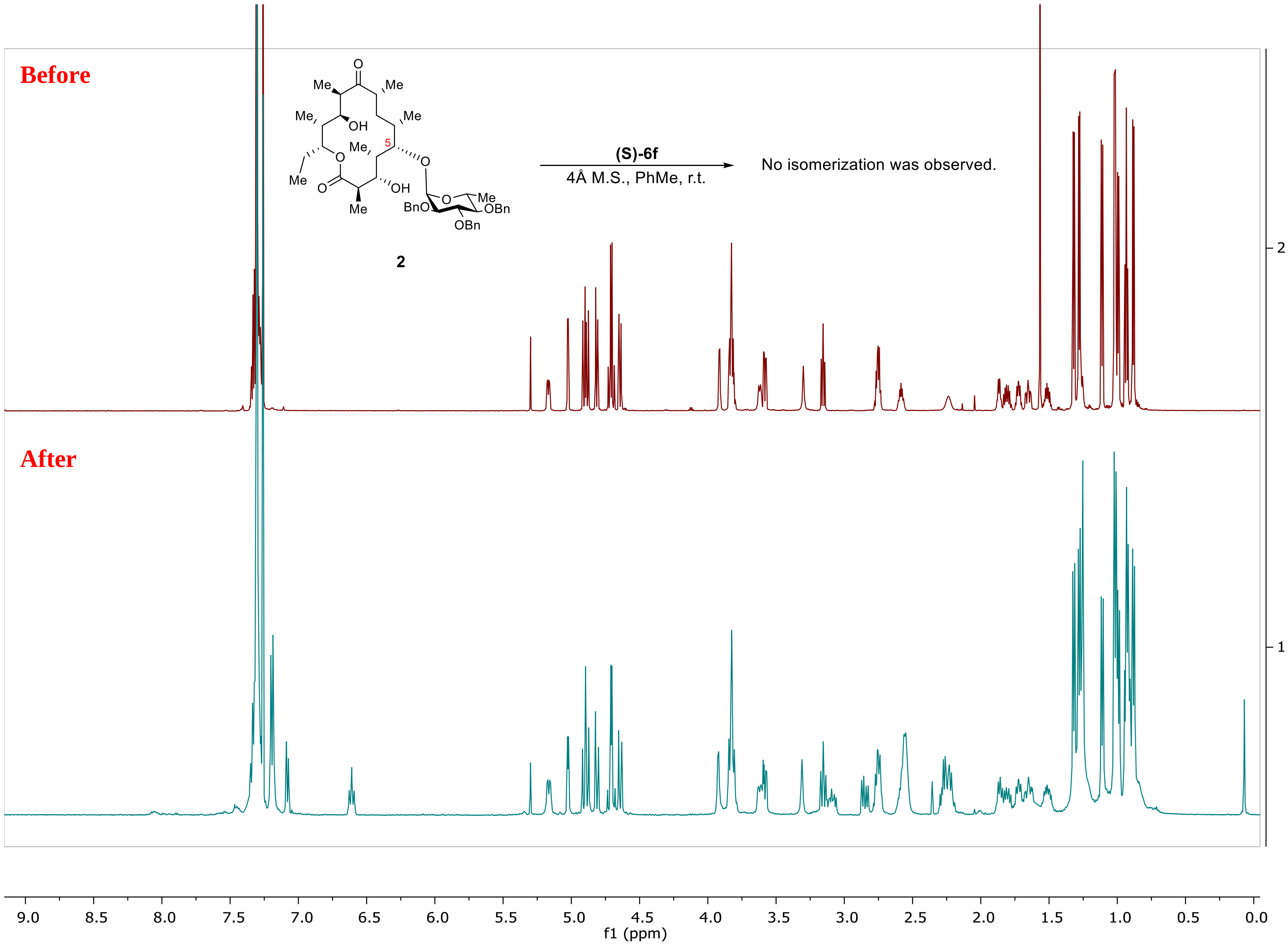


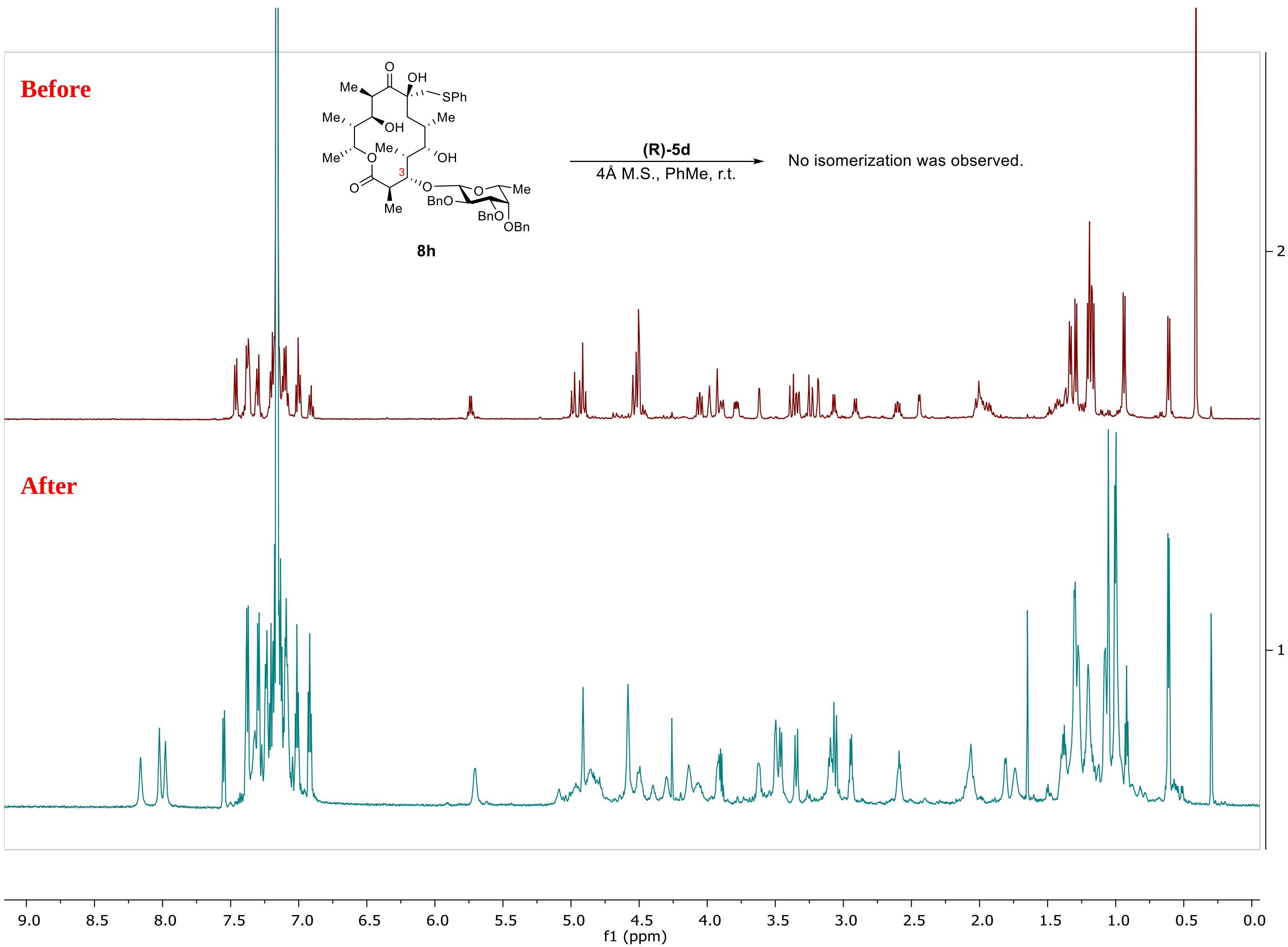
Crude ¹H NMR
(C6D6)
Me
O
OH
SPh
Me
Me
OH
Me
Me
O
OH
O
OH
Me
7
+
NH
O
CCl3
Me
O
OBn
BnO
OBn
C
+
TMS-OTf
f1 (ppm)

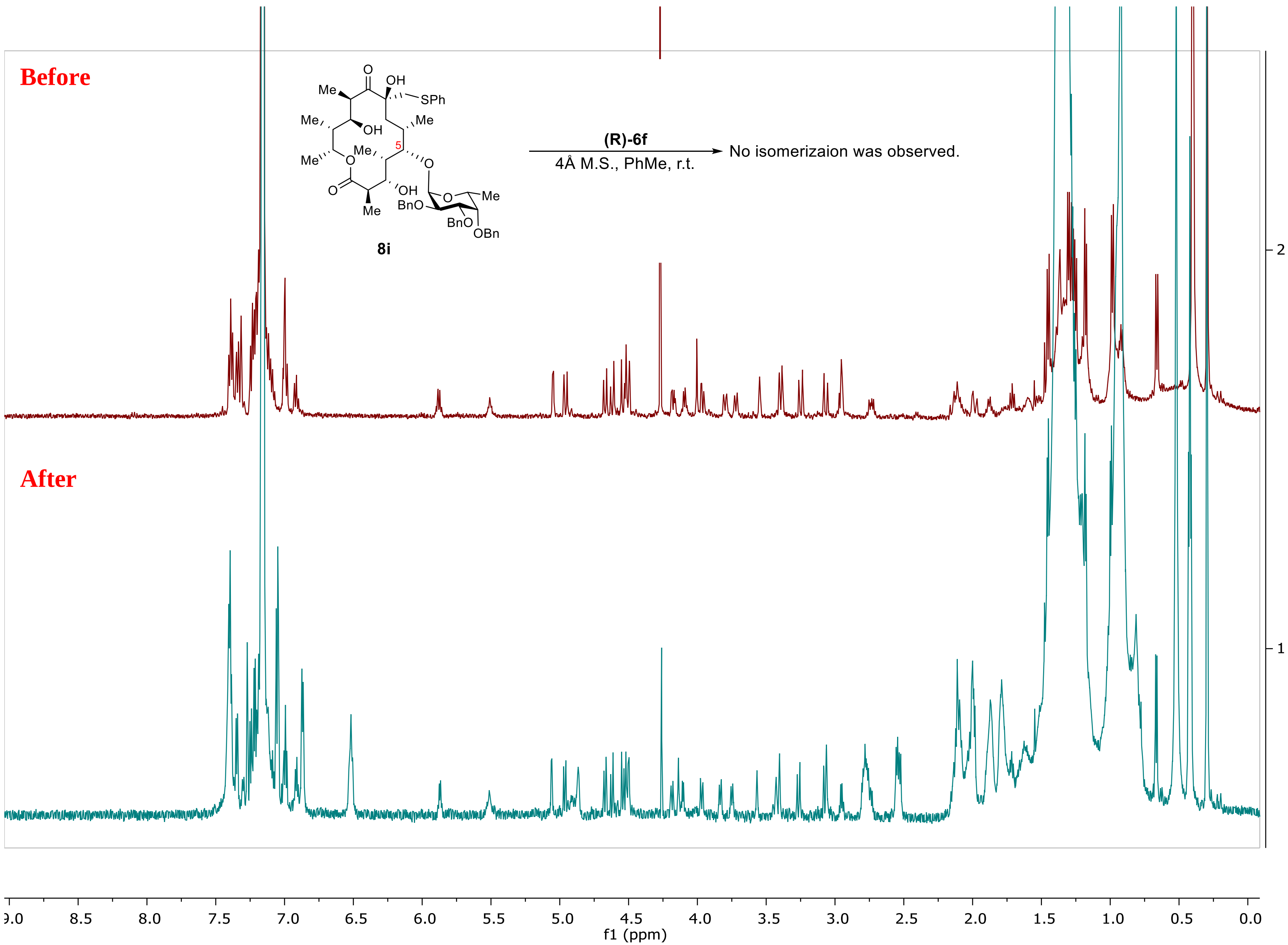
Crude ^{1}H NMR (C_6D_6)



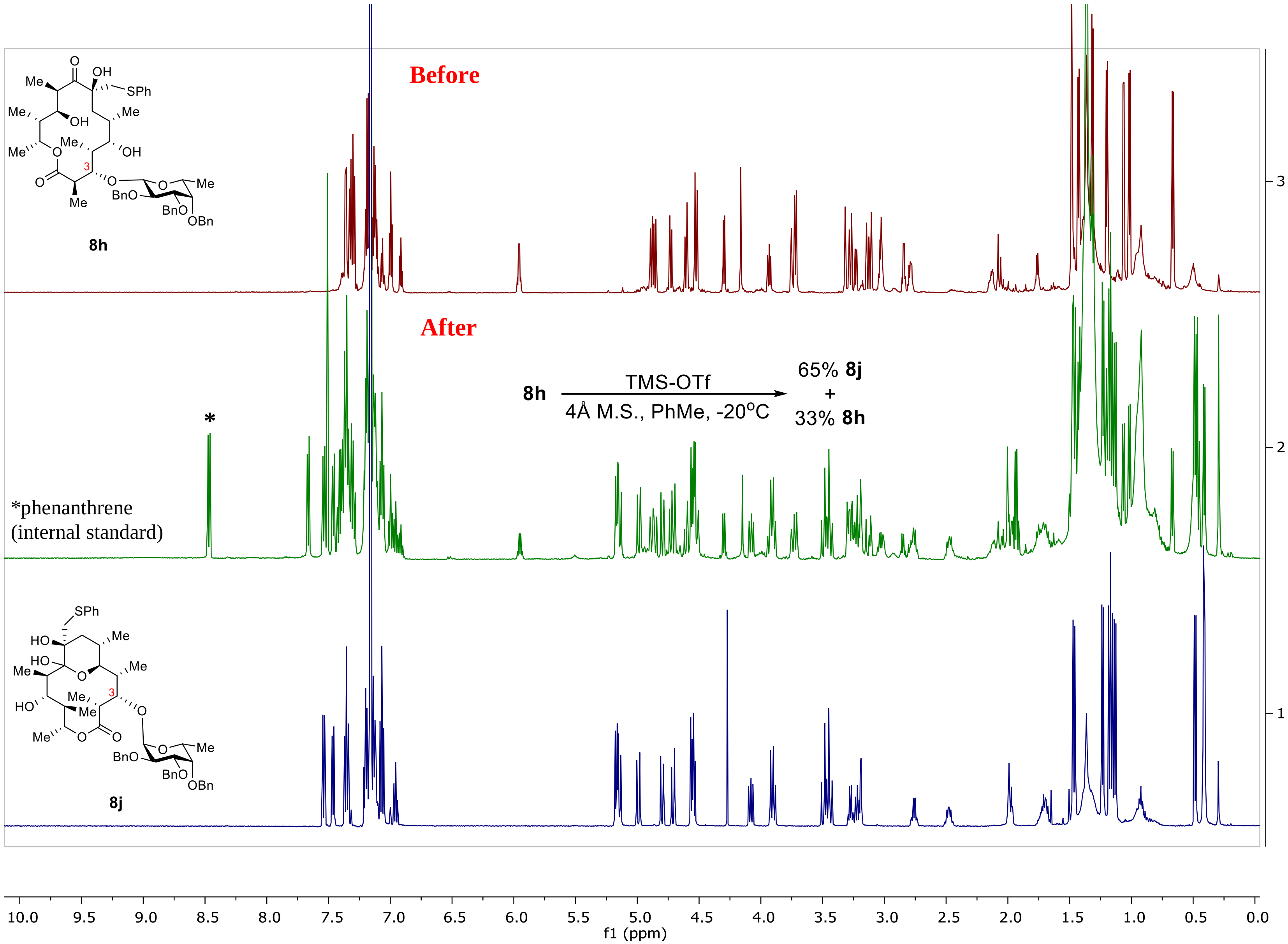

TMS-OTf
C5-β
C5-α
C3-β
C3-α
Ar
O
P
O
OH
O
Ar
Ar = 3,5-F-Ph
2
1
6.10
6.05
6.00
5.95
5.90
5.85
5.80
5.75
5.70
5.65
5.60
5.55
5.50
5.45
f1 (ppm)

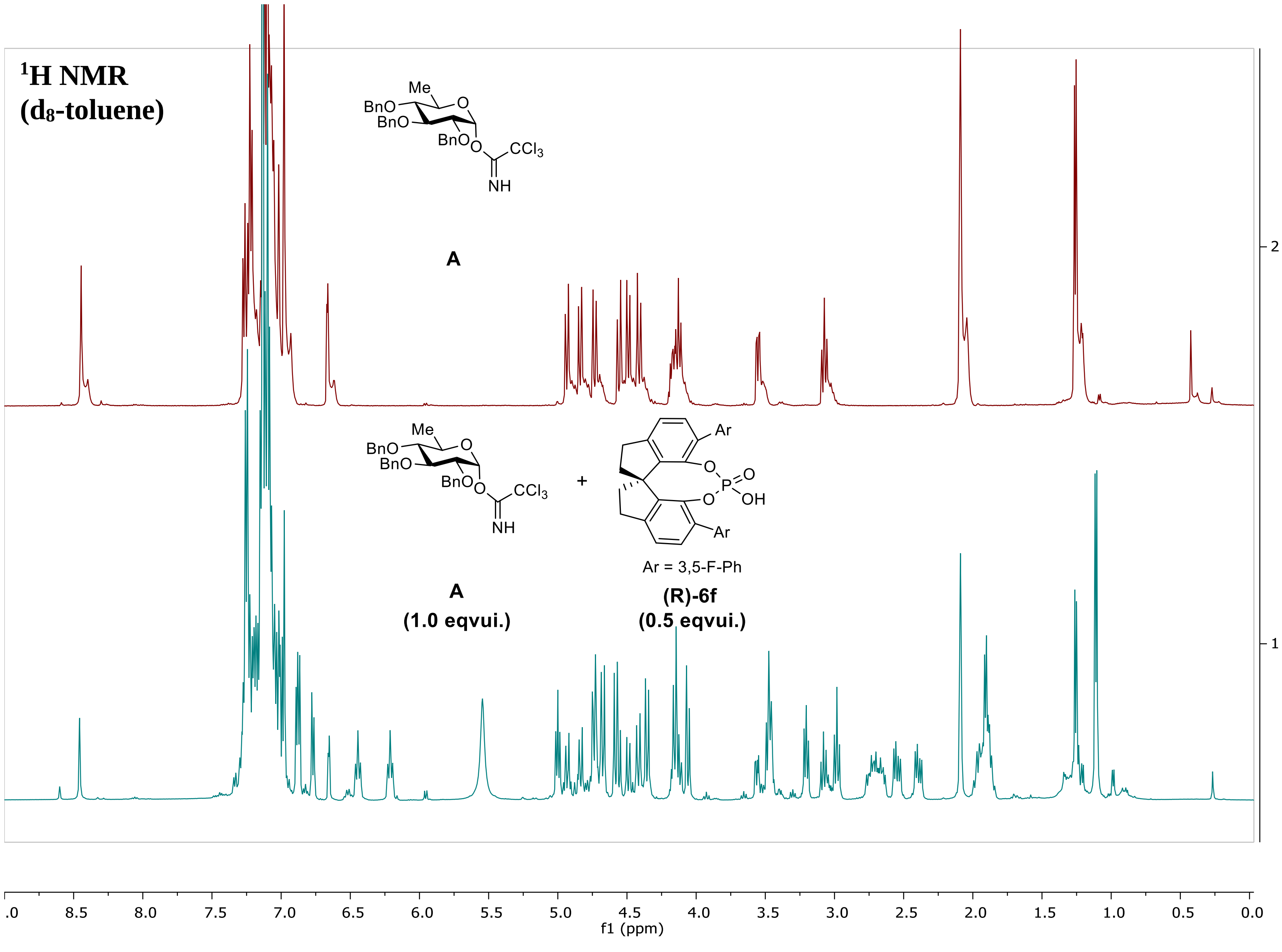

Before
After
2
(S)-6f
4Å M.S., PhMe, r.t.
No isomerization was observed.
f1 (ppm)


Before
After
(R)-5d
4Å M.S., PhMe, r.t.
No isomerization was observed.
8h
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
2
1

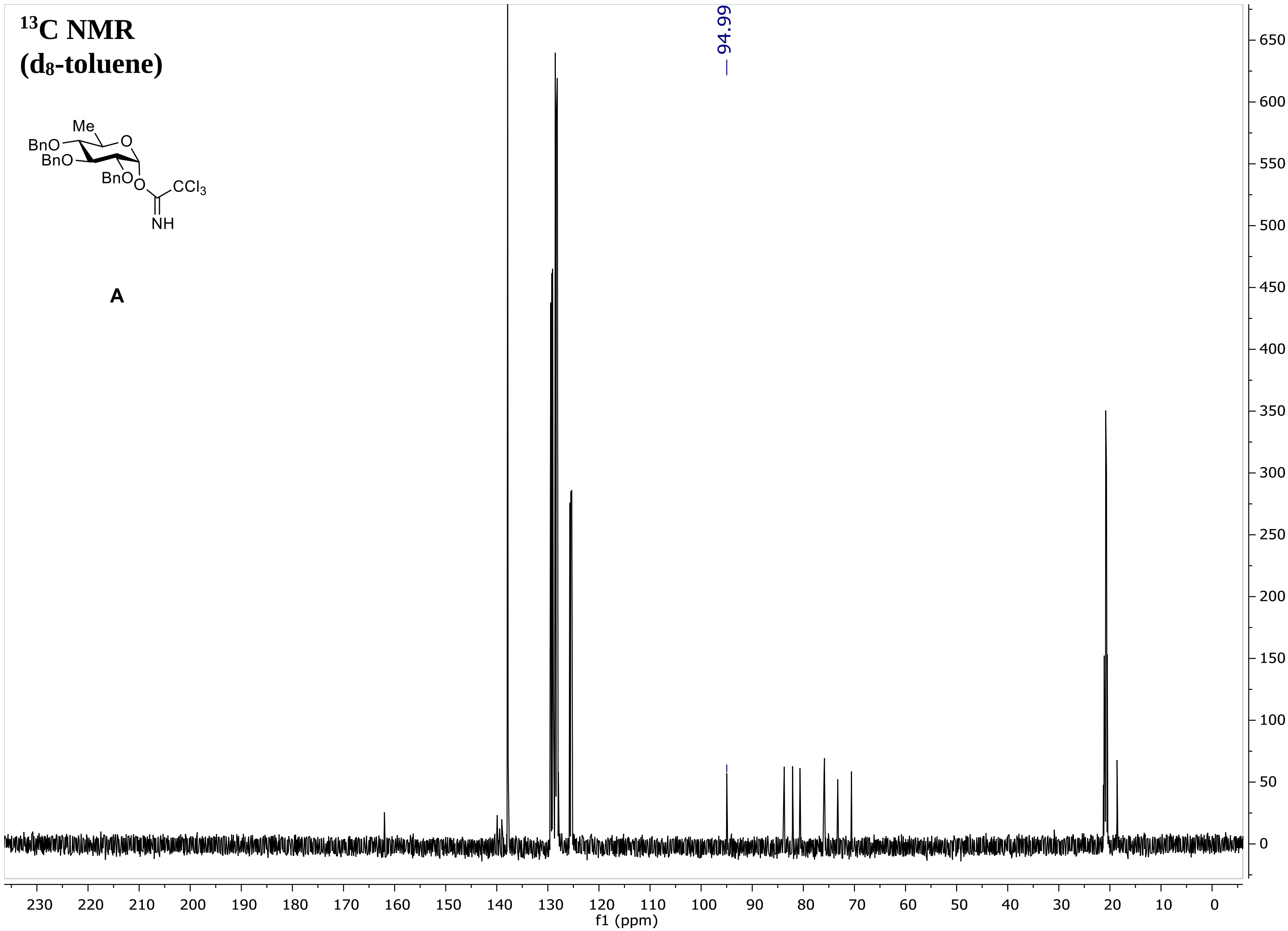


Before
After
(R)-6f
4Å M.S., PhMe, r.t.
No isomerizaion was observed.
8i
f1 (ppm)

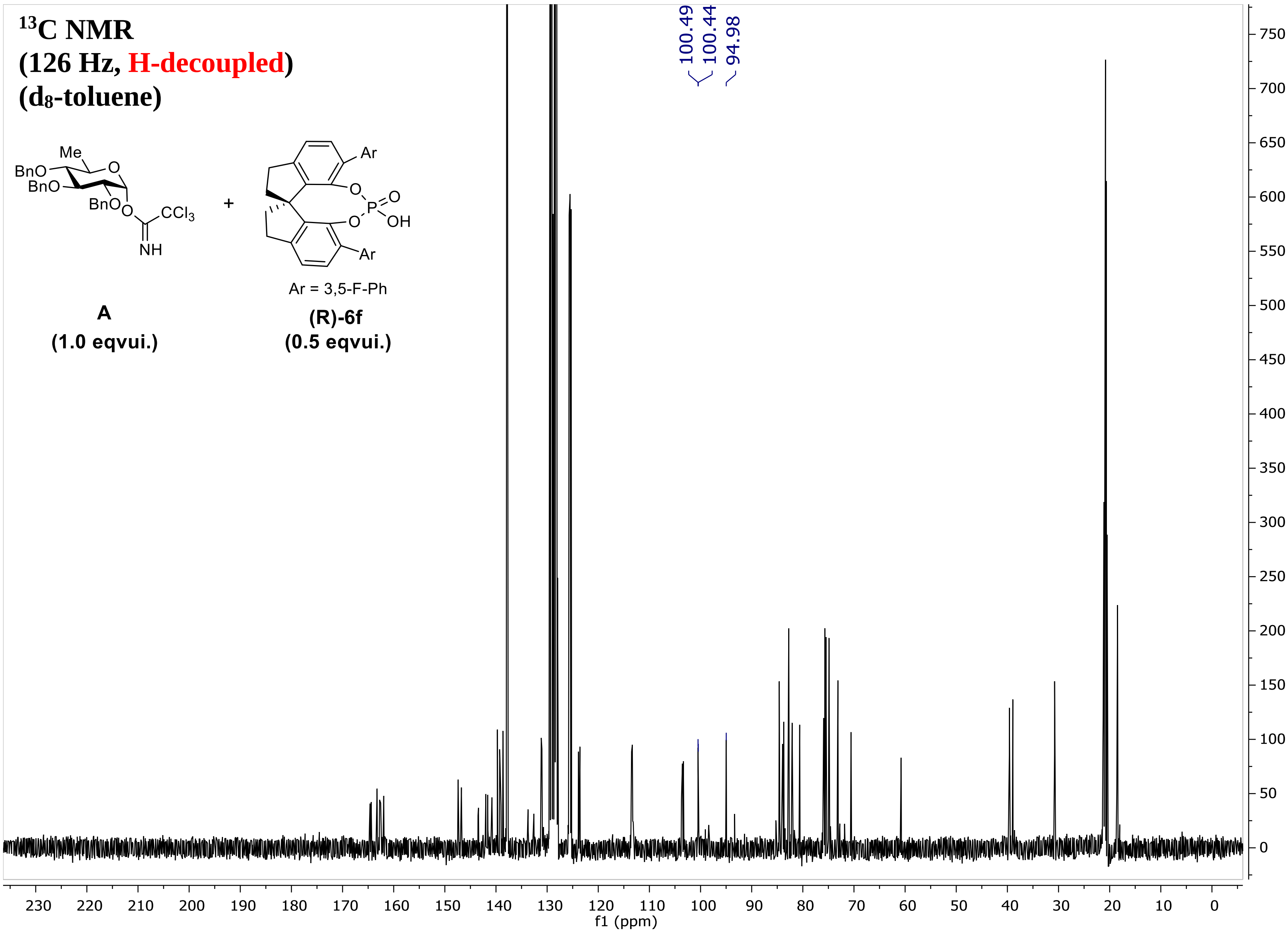

Before
After
8h
TMS-OTf
4Å M.S., PhMe, -20°C
65% 8j
+
33% 8h
*phenanthrene
(internal standard)
8j
f1 (ppm)



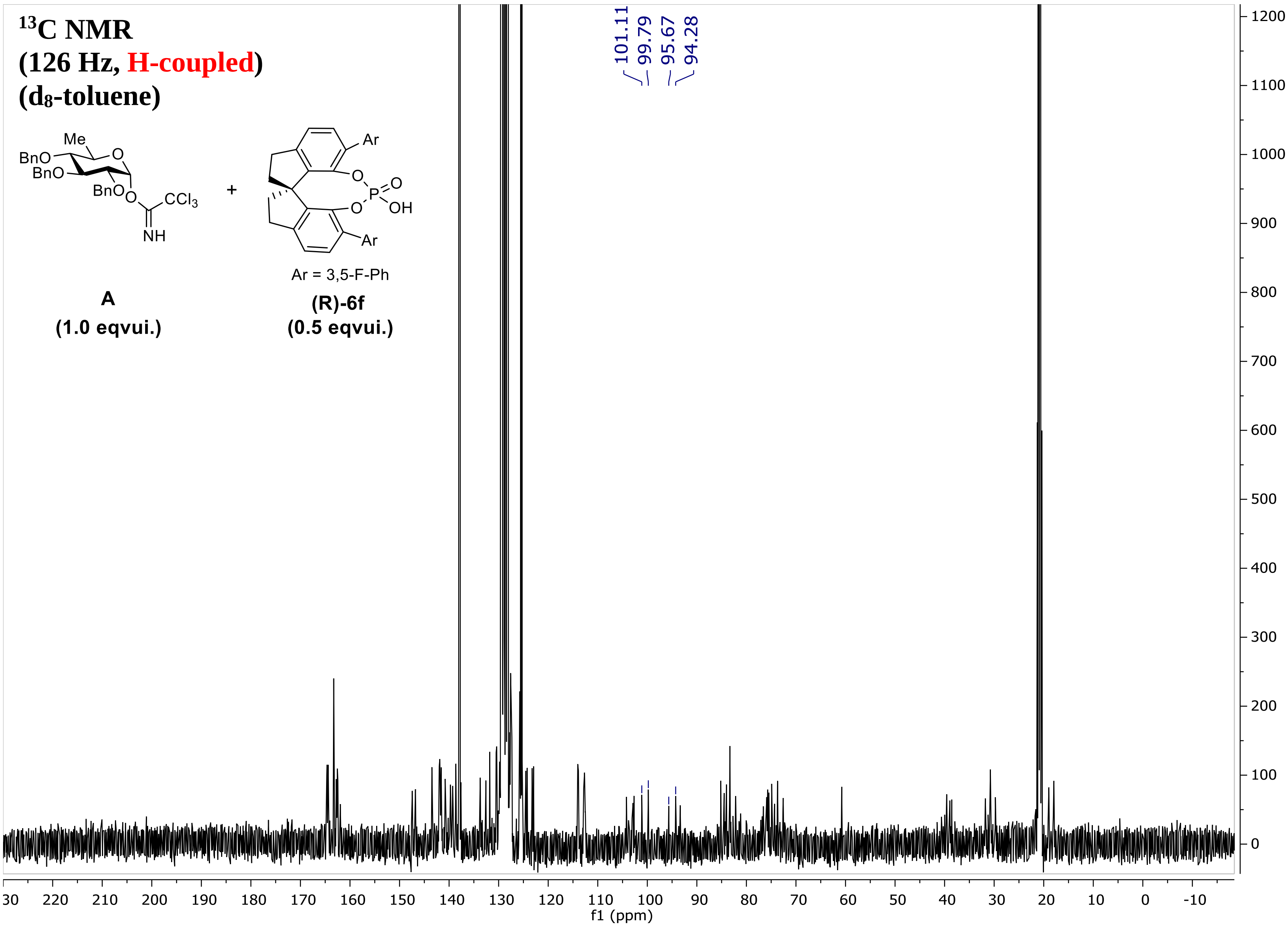
1H NMR
(d8-toluene)
Me
BnO
BnO
BnO
O
O
CCl3
NH
A
+
Ar
O
P
O
OH
Ar
Ar = 3,5-F-Ph
A
(1.0 eqvui.)
(R)-6f
(0.5 eqvui.)
2
1
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

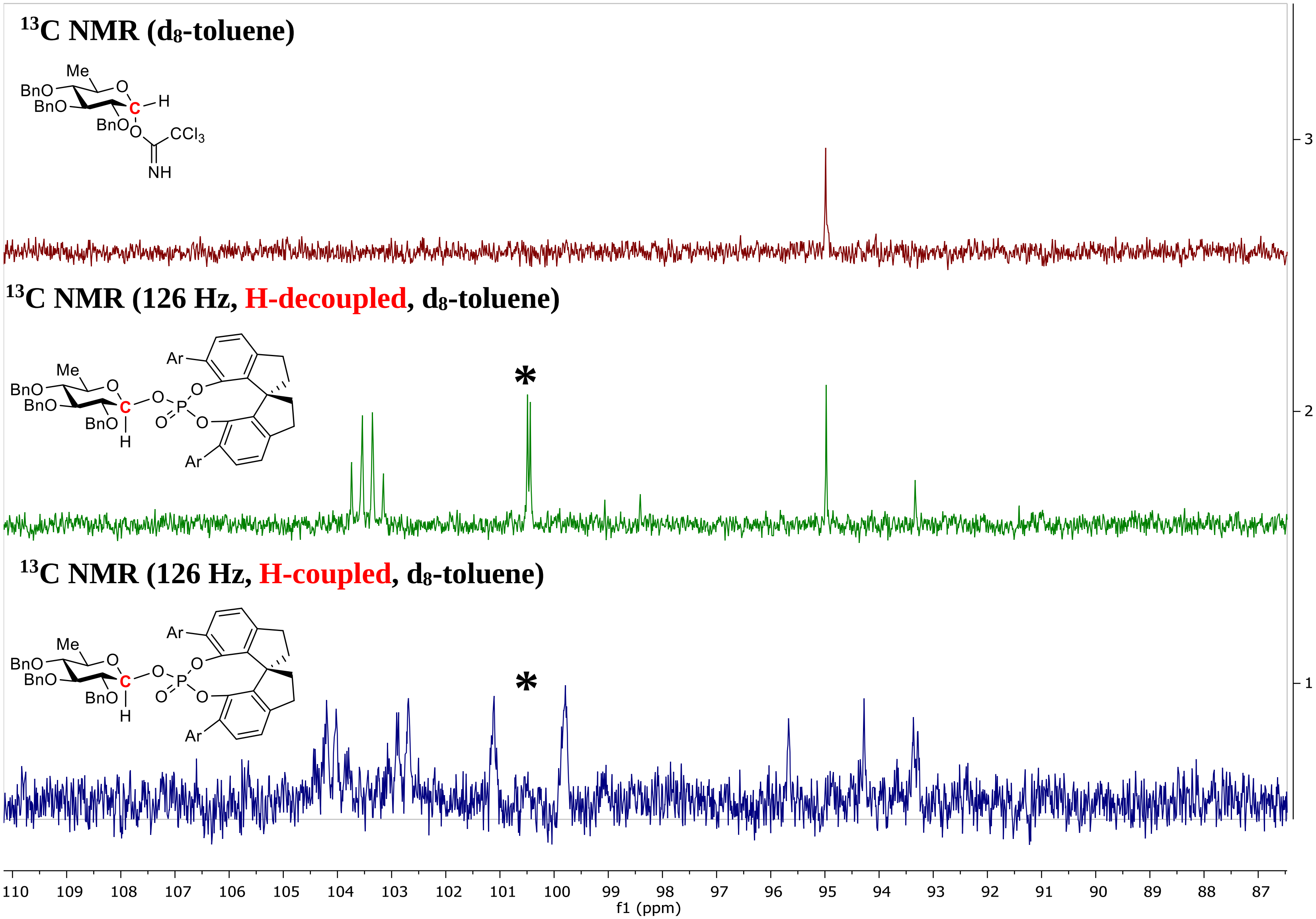


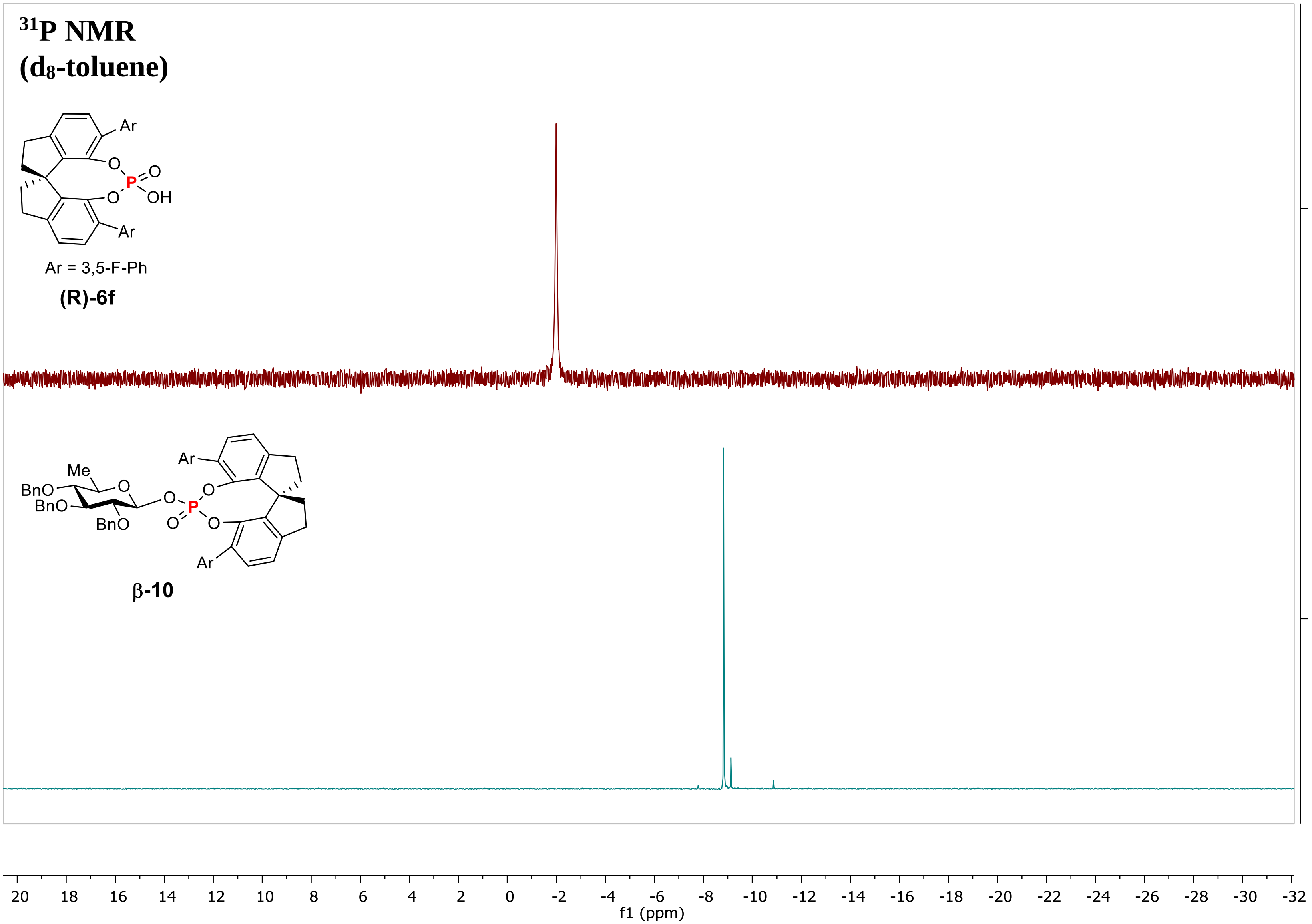
13C NMR
(d8-toluene)
Me
BnO
BnO
O
BnO
O
CCl3
NH
A
94.99
f1 (ppm)



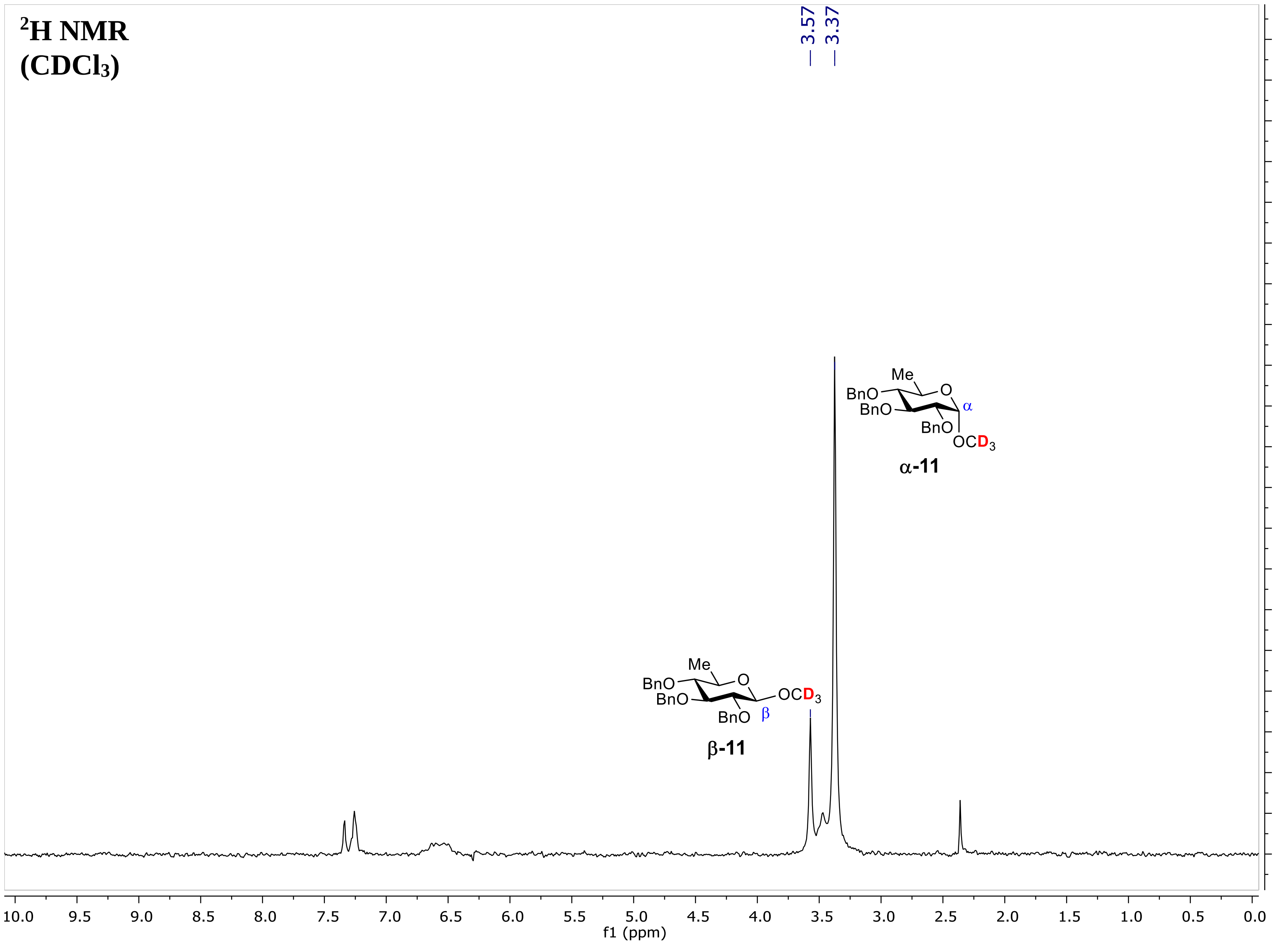
^{13}C NMR
(126 Hz, H-decoupled)
(d$_8$-toluene)
Me
BnO
BnO
BnO
O
O
CCl$_3$
NH
+
Ar
O
P
O
OH
O
Ar
Ar = 3,5-F-Ph
A
(1.0 eqvui.)
(R)-6f
(0.5 eqvui.)
100.49
100.44
94.98
f1 (ppm)


13C NMR
(126 Hz, H-coupled)
(d8-toluene)
Me
BnO
BnO
BnO
O
O
CCl3
NH
+
Ar
O
P
O
O
OH
Ar
Ar = 3,5-F-Ph
A
(1.0 eqvui.)
(R)-6f
(0.5 eqvui.)
101.11
99.79
95.67
94.28
f1 (ppm)

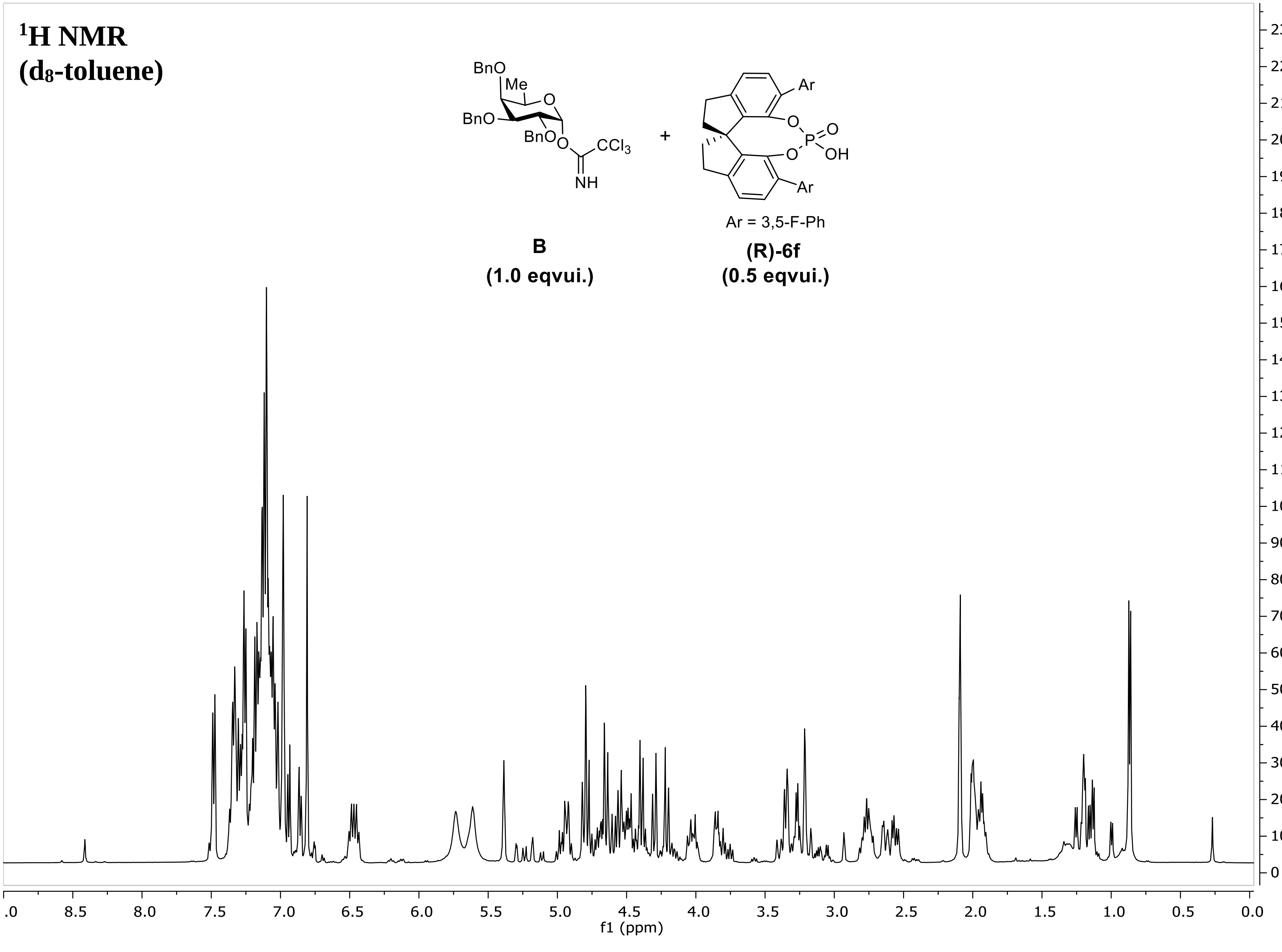

13C NMR (d8-toluene)
13C NMR (126 Hz, H-decoupled, d8-toluene)
13C NMR (126 Hz, H-coupled, d8-toluene)
*
*
f1 (ppm)



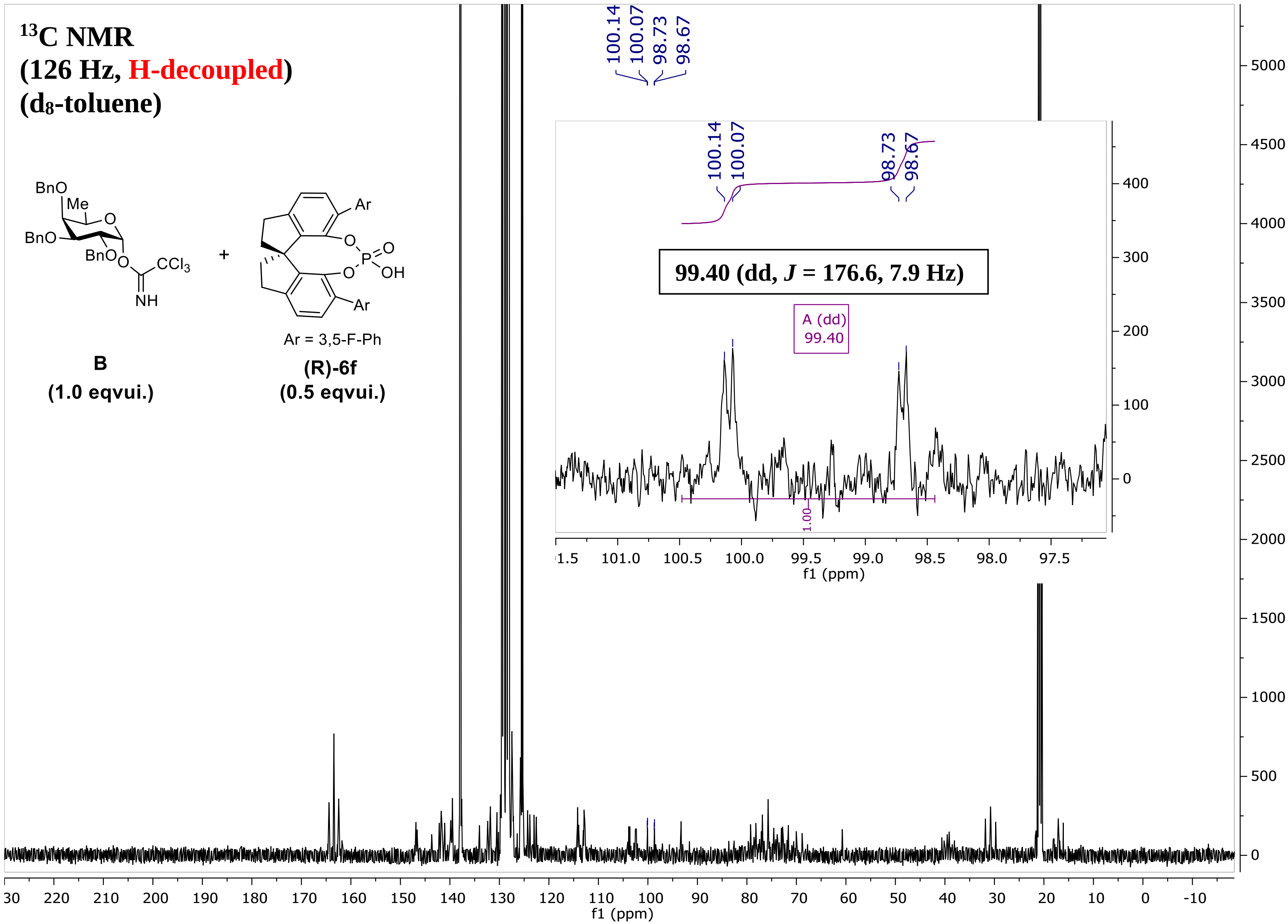
31P NMR
(d8-toluene)
Ar
O
P
O
OH
Ar
Ar = 3,5-F-Ph
(R)-6f
Me
BnO
BnO
BnO
O
O
O
P
O
O
Ar
Ar
β-10
2
1
20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32
f1 (ppm)



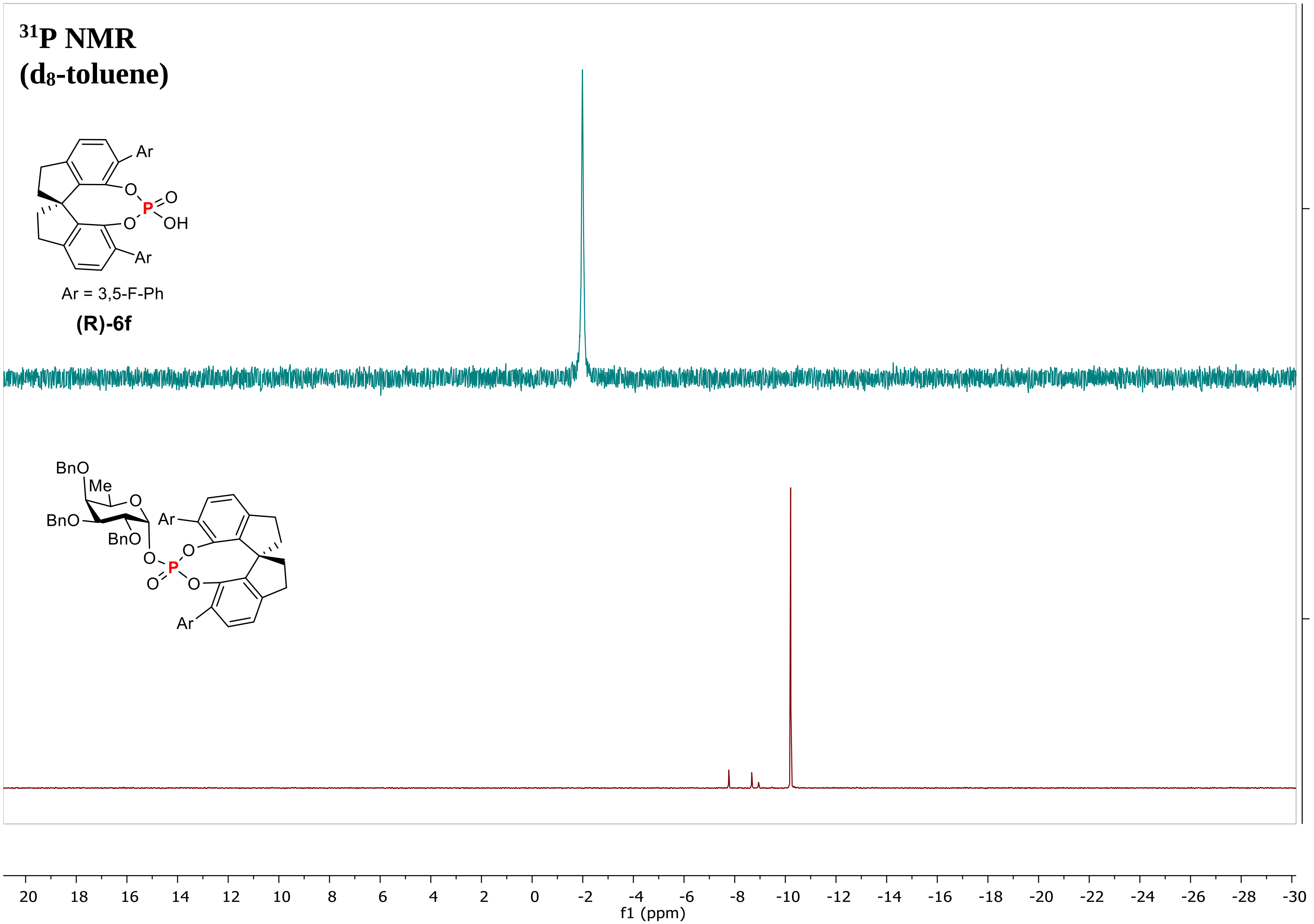
²H NMR
(CDCl₃)
3.57
3.37
Me
BnO
BnO
BnO
O
OCD₃
α
α-11
β
β-11
f1 (ppm)



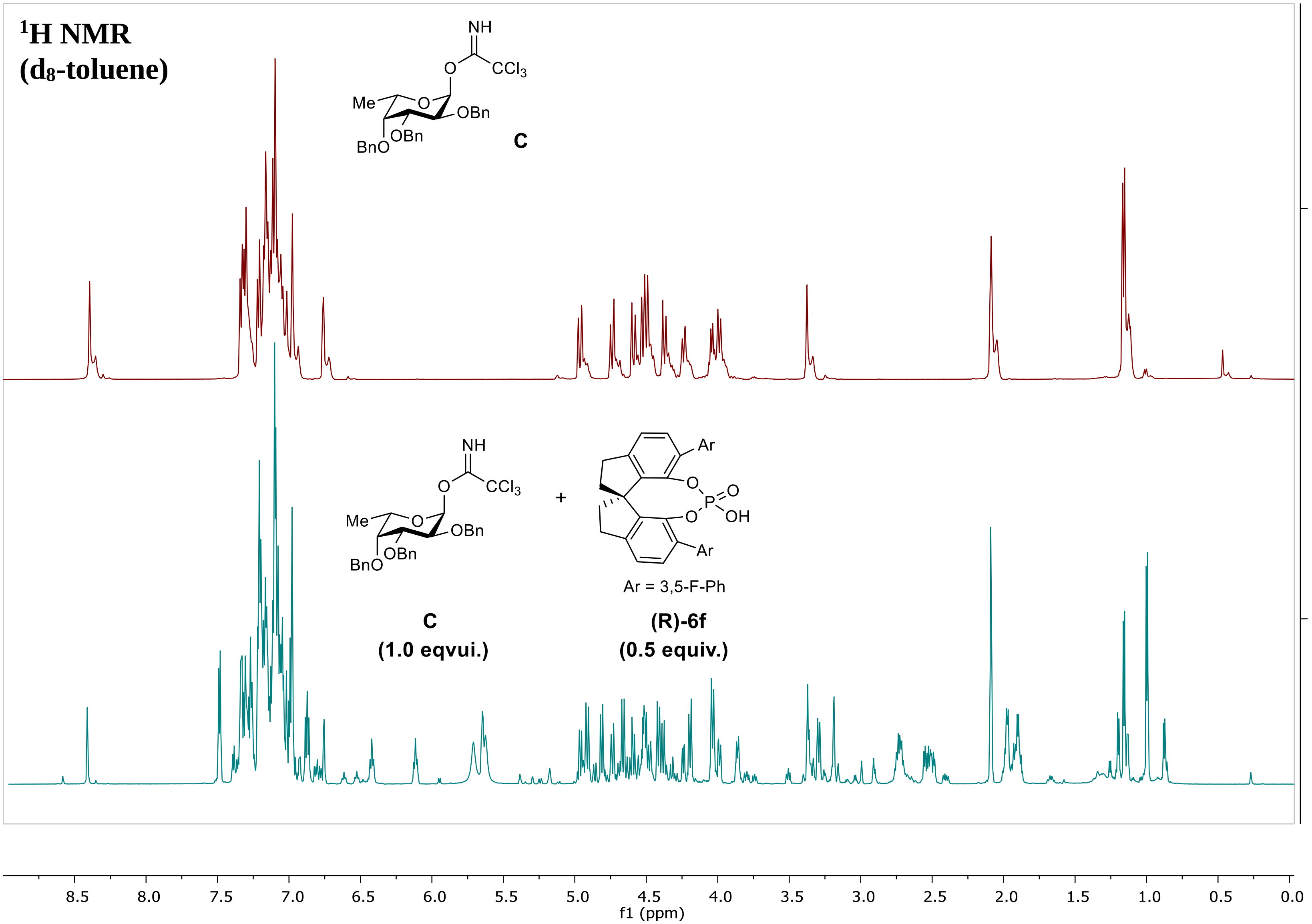
1H NMR
(d8-toluene)
BnO
Me
O
BnO
BnO
O
CCl3
NH
+
Ar
O
P
O
OH
O
Ar
Ar = 3,5-F-Ph
B
(1.0 eqvui.)
(R)-6f
(0.5 eqvui.)
f1 (ppm)



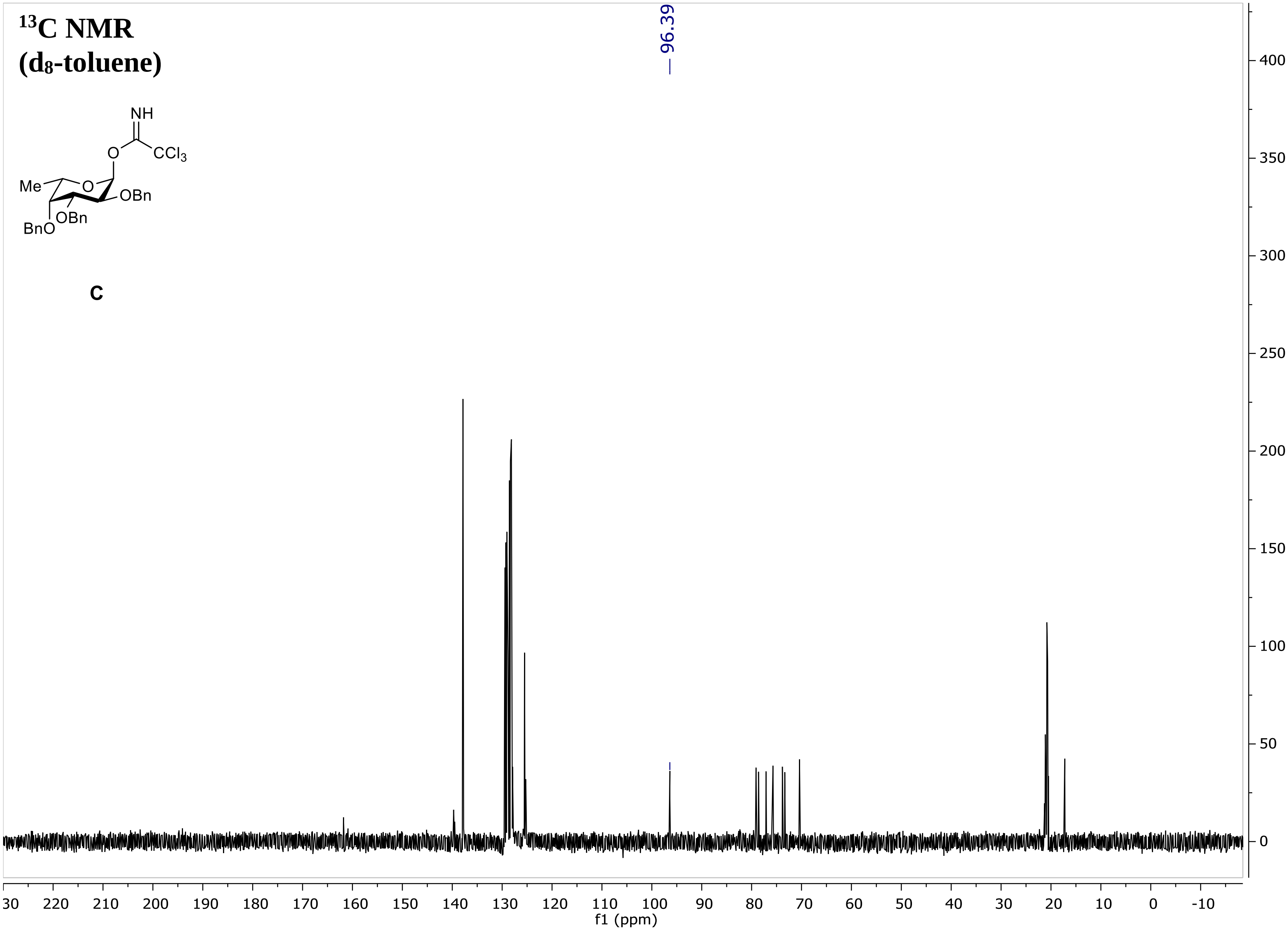
^{13}C NMR
(126 Hz, H-decoupled)
(d$_8$-toluene)
BnO
Me
BnO
BnO
CCl$_3$
NH
+
Ar
OH
Ar
Ar = 3,5-F-Ph
B
(1.0 eqvui.)
(R)-6f
(0.5 eqvui.)
100.14
100.07
98.73
98.67
99.40 (dd, J = 176.6, 7.9 Hz)
A (dd)
99.40
1.00
f1 (ppm)

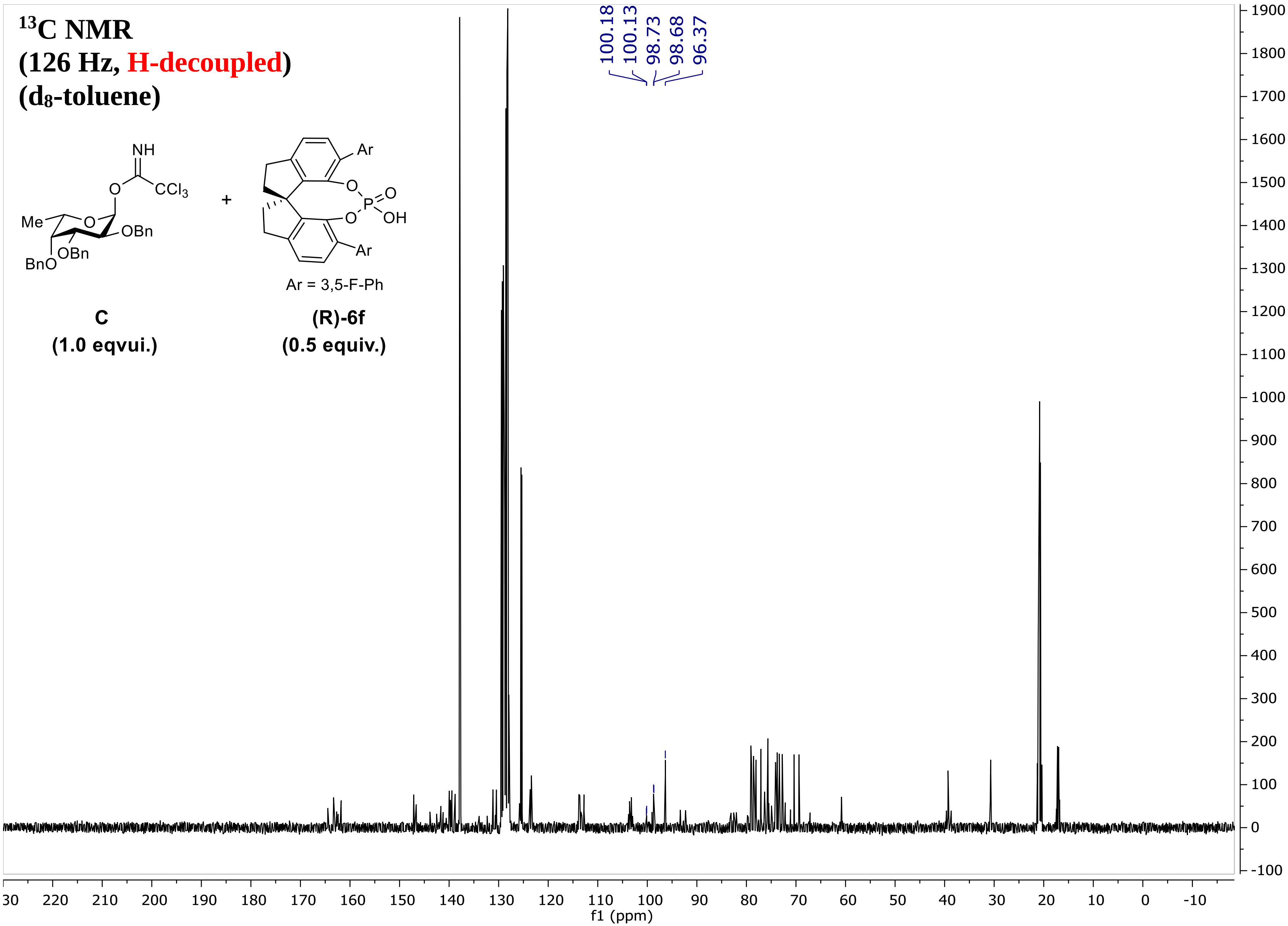


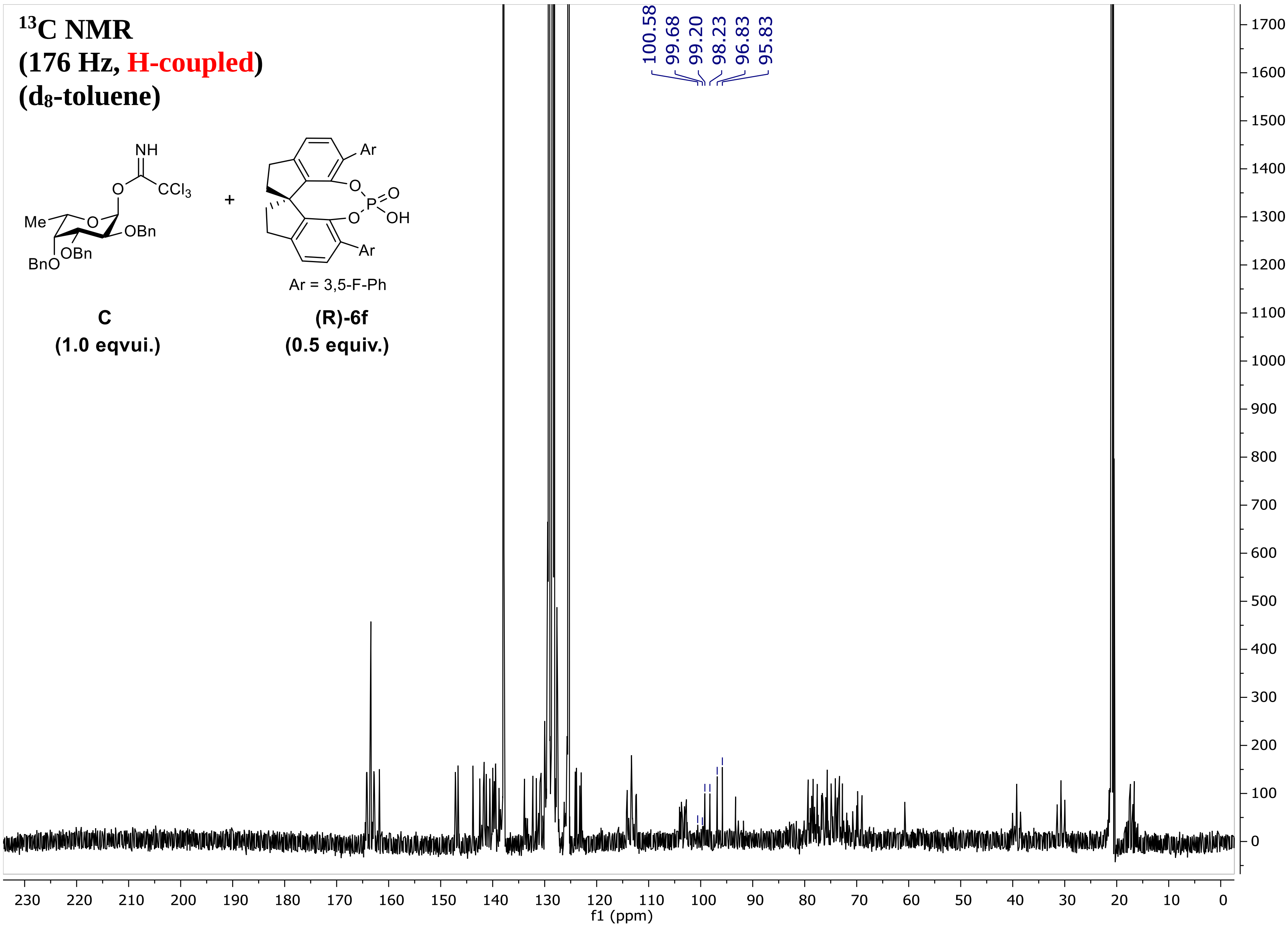
31P NMR
(d8-toluene)
Ar
O
P
O
O
OH
Ar
Ar = 3,5-F-Ph
(R)-6f
BnO
Me
O
BnO
BnO
Ar
O
O
P
O
O
Ar
2
1
20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30
f1 (ppm)



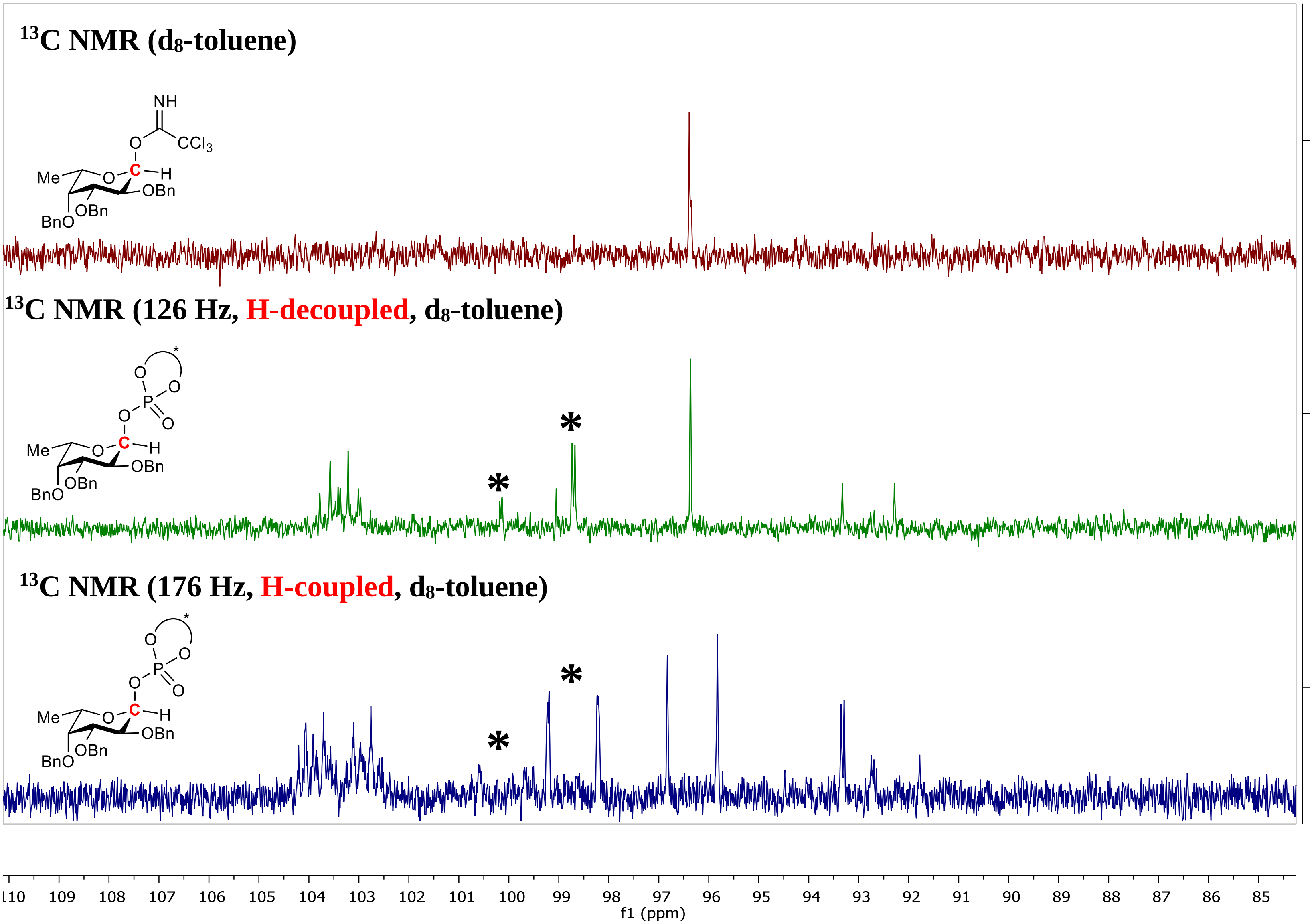
^{1}H NMR
(d$_8$-toluene)
NH
O
CCl$_3$
Me
O
OBn
BnO
OBn
C
+
Ar
O
P
O
OH
Ar = 3,5-F-Ph
C
(1.0 eqvui.)
(R)-6f
(0.5 equiv.)
2
1
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

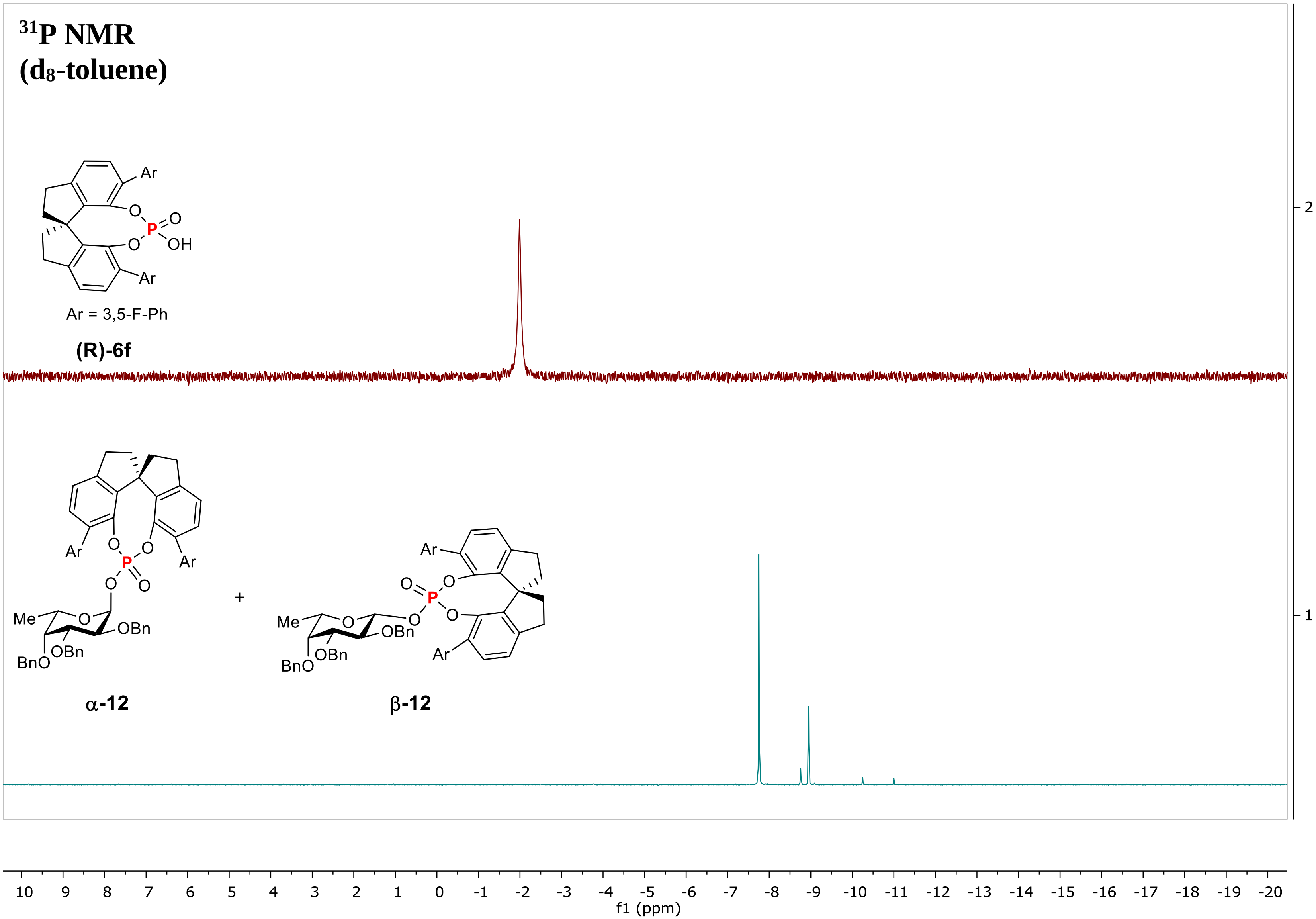

13C NMR
(d8-toluene)
NH
O
CCl3
Me
O
OBn
OBn
BnO
C
96.39
f1 (ppm)


13C NMR
(126 Hz, H-decoupled)
(d8-toluene)
NH
O
CCl3
Me
OBn
BnO
+
Ar
O
P
OH
Ar = 3,5-F-Ph
C
(1.0 eqvui.)
(R)-6f
(0.5 equiv.)
100.18
100.13
98.73
98.68
96.37
f1 (ppm)

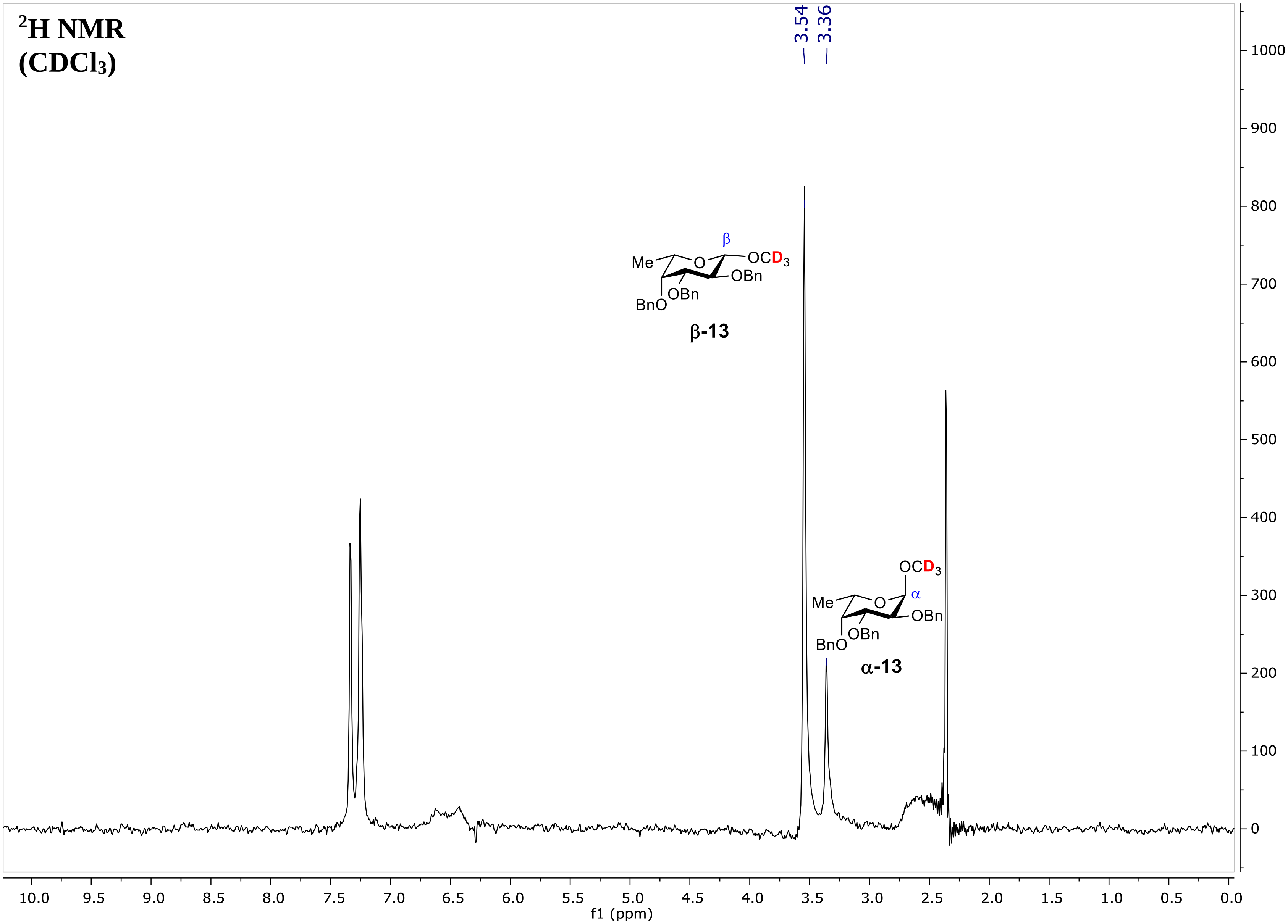


13C NMR
(176 Hz, H-coupled)
(d8-toluene)
NH
CCl3
O
Me
O
OBn
OBn
BnO
+
Ar
O
P
O
O
OH
Ar
Ar = 3,5-F-Ph
C
(1.0 eqvui.)
(R)-6f
(0.5 equiv.)
100.58
99.68
99.20
98.23
96.83
95.83
f1 (ppm)


13C NMR (d8-toluene)
NH
O
CCl3
Me
C
H
OBn
OBn
BnO
13C NMR (126 Hz, H-decoupled, d8-toluene)
O
P
O
H
C
Me
OBn
OBn
BnO
13C NMR (176 Hz, H-coupled, d8-toluene)
3
2
1
110 109 108 107 106 105 104 103 102 101 100 99 98 97 96 95 94 93 92 91 90 89 88 87 86 85
f1 (ppm)



31P NMR
(d8-toluene)
Ar
O
P
O
OH
Ar
Ar = 3,5-F-Ph
(R)-6f
Ar
O
P
O
O
Ar
O
Me
O
OBn
OBn
BnO
α-12
+
Ar
O
P
O
O
O
Ar
Me
O
OBn
OBn
BnO
β-12
2
1
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14 -15 -16 -17 -18 -19 -20
f1 (ppm)



²H NMR
(CDCl3)
3.54
3.36
Me
O
β
OCD3
OBn
OBn
BnO
β-13
OCD3
Me
O
α
OBn
OBn
BnO
α-13
f1 (ppm)

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