Supporting Information

Catalytic and Photochemical Strategies to Stabilized Radicals Based on Anomeric Nucleophiles

Feng Zhu,[a] Shuo-qing Zhang,[b] Zhenhao Chen,[a] Jinyan Rui,[a] Xin Hong,[b]* Maciej A. Walczak[a]*

[a]Department of Chemistry, University of Colorado, Boulder, CO 80309, United States
[b]Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, P. R. China

*hxchem@zju.edu.cn
*maciej.walczak@colorado.edu

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1. General Information

All chemicals were purchased as reagent grade and used without further purification unless otherwise noted. Solvents were filtered through a column of activated alumina prior to use. All reactions were carried out under anhydrous N_2 in ove*n*-dried glassware. *m*-Xylene was distilled under nitrogen over sodium and degassed prior to use. Anhydrous 1,4-dioxane, 4,4′-di-tert-butyl-2,2′-dipyridyl and CuCl were purchased from Sigma-Aldrich. Aldrich® Micro Photochemical Reactors (5 W blue LED strips) were purchased from Sigma-Aldrich. Anhydrous KF was purchased from Strem Chemicals, Inc. Visualizations were performed with UV light and/or Hanessian stain and/or sulfuric acid stain (5% H_2SO_4 in MeOH). Column chromatography was performed on silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker/Varian 300/400/500 MHz instruments and are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. The residual solvent reference peaks were used from published literature. 2D NMR experiments were performed using standard parameters (*200 and More NMR Experiments,* S. Berger, S. Braun, Wiley-VCH, **2004**). IR measurements were performed on Agilent Cary 630 FT/IR instrument and optical rotations were measured on JASCO P-1030 and are reported as average of five data points. High-resolution mass spectra (HR-MS) were recorded on a Waters Synapt G2 HDMS q-TOF hybrid mass spectrometer. UV-vis spectra were recorded on Cary 5000 UV/Vis Spectrometer.

2. General Procedures

General Procedure A for Cross-Coupling Reactions

Anomeric stannane (1.50 equiv), disulfide (1.00 equiv), and CuCl (300 mol%) were added to a one-dram vial with a screw-top septum, and the vial was then evacuated and refilled with N_2 (3x). Anhydrous m-xylene and 1,2-dichloroethane (2:1, 3.00 mL) were added and the reaction mixture was heated in an oil bath (130 °C) for the indicated period of time, cooled to rt, filtered through a pad of Celite®, and concentrated. ^{1}H NMR spectra were recorded using this mixture to evaluate diastereoselectivity. The crude material was purified by column chromatography on SiO_2.

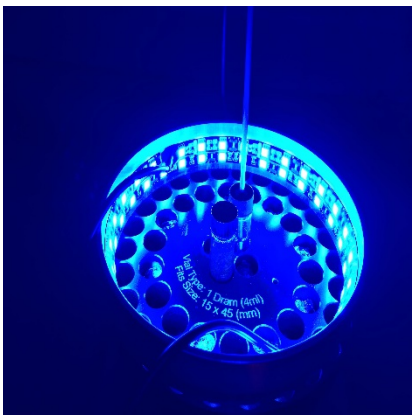
General Procedure B for Cross-Coupling Reactions

Anomeric stannane (1.50 equiv), disulfide or *N*-arylthiosuccinimide (1.00 equiv), KF (3.00 equiv), 4,4′-di-*tert*-butyl-2,2′-dipyridyl or 2,2′:6′,2″-terpyridine (25 - 45 mol%), and CuCl (20 - 40 mol%) were added to a one-dram vial with a screw-top septum, and the vial was then evacuated and refilled with N_2 (3x). After anhydrous 1,4-dioxane (2.00 mL) were added, the reaction mixture was stirred at 120 °C under 5W blue LED irradiation for the indicated period of time. The resulting mixture was cooled to rt, filtered through a pad of Celite®, and concentrated. ^{1}H NMR spectra were recorded using this mixture to evaluate diastereoselectivity. The crude material was purified by column chromatography on SiO_2.

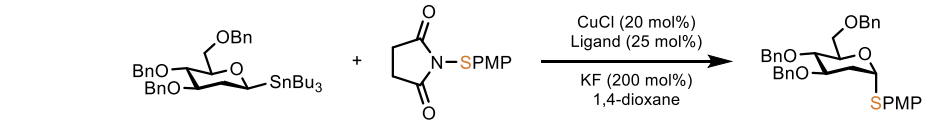
General Procedure C for Cross-Coupling Reactions

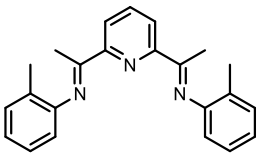
Anomeric stannane (1.50 equiv), disulfide (1.00 equiv), KF (3.00 equiv), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (45 mol%) were added to a one-dram vial with a screw-top septum, and the vial was then evacuated and refilled with N_2 (3x). After anhydrous 1,4-dioxane (2.00 mL) were added, the reaction mixture was stirred at 120 °C under 5W blue LED irradiation for the indicated period of time. The resulting mixture was cooled to rt, filtered through a pad of Celite®, and concentrated. ^{1}H NMR spectra were recorded using this mixture to evaluate diastereoselectivity. The crude material was purified by column chromatography on SiO_2.

Reaction set-up for photochemical thioglycosylations:

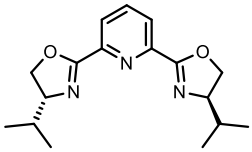


3. Additional Reaction Optimization Conditions

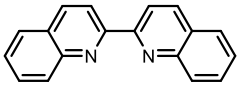




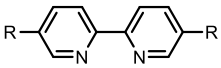
L12
24% α:β 6.5:1



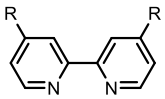
L13
20%, only α



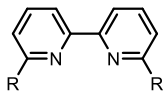
L14
25%, only α



L15, R = H, 28% α:β 4.9:1
L16, R = OPiv, 41% α:β 7.1:1

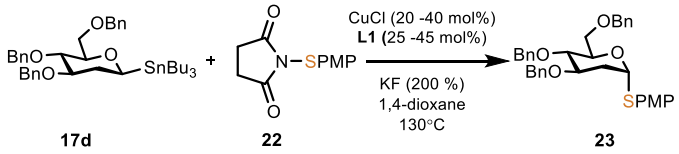


L17, R = Me, 30%, only α
L18, R = *t*Bu, 31% only α
L19, R = OMe, 25% α:β 9.1:1
L20, R = COO*i*Pr, 31% α:β 7.1:1
L21, R = CF_3, 21% α:β 3.4:1



L22, R = Me, 29%, only α
L23, R = OMe, 32% α:β 2.8:1
L24, R = OPiv, 25% only α
L25, R = COO*i*Pr, 31% α:β 7.1:1

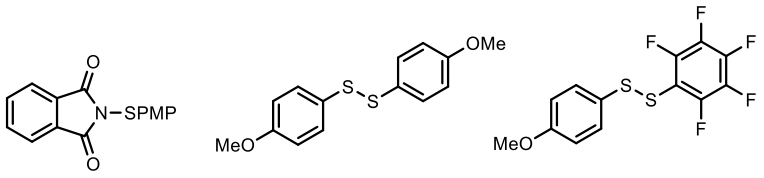
Reaction conditions: **22** (0.100 mmol, 1.0 equiv), **17d** (1.5 equiv), CuCl (20 mol%), Ligand (25 mol%) and 1,4-dioxane (2.0 mL) under N_2, 130 °C, 24h, yield of isolated product. Anomeric selectivities determined by ^{1}H NMR analysis of unpurified reaction mixtures.



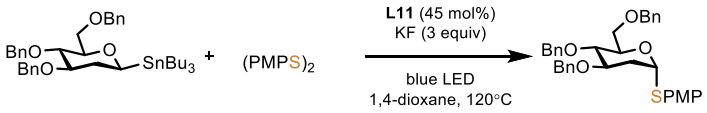
17d **22** **23**

Entry	Catalyst	Additives	Solvent	Yield	α:β
1 [a]	CuCl (20 mol%)	KF (300 mol%)	Dioxane	31%	Only α
2 [a]	CuCl (20 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	32%	Only α
3 [a]	CuCl (20 mol%)	LiF (300 mol%)	Dioxane/Xylene(1:1)	36%	Only α
4 [a]	CuCl (20 mol%)	CsF (300mol%)	Dioxane/Xylene(1:1)	19%	Only α
5	CuCl (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	52%	Only α
6	CuCl (40 mol%)	LiF (300 mol%)	Dioxane/Xylene(1:1)	44%	Only α
7	CuBr (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	41%	Only α
8	CuI (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	<5%	Only α
9	CuTc (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	38%	Only α
10	$CuOP(O)Ph_2$ (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	27%	Only α
11	$CuCl_2$ (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	N.D.	N.A.
12 [b]	CuCl (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	28%	Only α
13 [c]	CuCl (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	50%	Only α
14 [c,d]	CuCl (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	50%	>30:1
15 [e]	CuCl (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	36%	Only α
16	CuCl (50 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	50%	Only α
17 [f]	CuCl (40 mol%)	KF (300 mol%)	Dioxane/Xylene(1:1)	52%	Only α
18 [f,g]	CuCl (40 mol%)	KF (300 mol%)	Dioxane	21%	Only α
19 [c,f,g]	CuCl (40 mol%)	KF (300 mol%)	Dioxane	54%	Only α
20 [g,h]	CuCl (40 mol%)	KF (300 mol%)	Dioxane	73%	Only α
21 [g,i]	CuCl (20 mol%)	KF (300 mol%)	Dioxane	74%	Only α
22 [i,j]		KF (300 mol%)	Dioxane	N.D.	N.A.
23 [k]	CuCl (40 mol%)	KF (300 mol%)	Dioxane	52%	Only α

General reaction conditions: β-D-glucose **17d** (1.5 equiv), sulfur electrophile (1 equiv), CuCl (20 - 40 mol%), terpyridine **L1** (25 – 45 mol%), 1,4-dioxane/*m*-xylene (1:1, 2.0 mL) under N_2, 130 °C, 96 h, yield of isolated product, anomeric selectivities determined by ^{1}H NMR using unpurified reactions mixtures. [a] 24 h. [b]Sulfur electrophile **24** (1 equiv) was used. [c]Sulfur electrophile **18** (1 equiv) was used. [d]Terpyridine **L1** (40 mol%) were used. [e]Sulfur electrophile **25** was used. [f]Terpyridine **L1** (45 mol%),120 °C, 96 h. [g]Blue LED irradiation was used. [h]Sulfur electrophile **18** (1 equiv), dtbbpy **L11** (45 mol%), 130 °C, 96 h. [i]Sulfur electrophile **18** (1 equiv), dtbbpy **L11** (25 mol%),120 °C, 96 h. [j]Without CuCl and blue LED irradiation. [k]Sulfur electrophile **18** (1 equiv), dtbbpy **L11** (45 mol%), 120 °C, 96 h, without blue LED irradiation.



24 **18** **25**

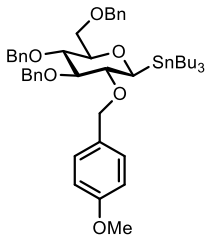


17d **18** **23**

Entry	Variation from standard conditions	Yield	α:β
1	none	72%	Only α
2	no blue LED	N.D.	------
3	no **L11**	50%	Only α
4	no KF	61%	Only α
5	no blue KF and **L11**	50%	Only α
6	DMAP instead of **L11**	46%	Only α
7	toluene as solvent	43%	Only α
8	MeCN as solvent	50%	Only α
9	*t*BuOH as solvent	38%	Only α
10	DMF as solvent	N.D.	N.A.
11	room temperature was employed	15%	Only α
12	*t*BuOH as solvent	38%	Only α
13	4-Methoxybenzenethiol was employed	N.D.	------
14	**22** was employed	N.D.	------
15	390 nm was employed	33%	Only α

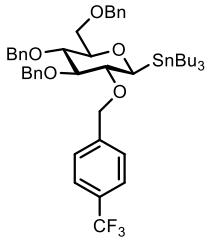
General reaction conditions: disulfide (0.100 mmol, 1 equiv), anomeric stannanes (1.5 equiv), **L11** (45 mol%), KF (3 equiv), blue LED (5W), 1,4-dioxane (2 mL), 120 °C, 48 h, yield of isolated product, anomeric selectivities determined by ^{1}H NMR using unpurified reactions mixtures.

4. Detailed Experimental Procedures for Compounds 17a-51



17a

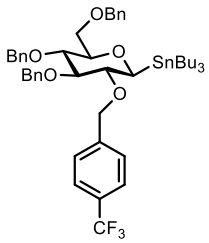
(2-*O*-(4-Methoxybenzyl)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane (17a). To a solution of (3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane (300 mg, 0.41 mmol) in THF (3.00 mL) KHMDS (1.00 mL, 0.500 mmol, 0.5 M in PhMe) was added under N_2 at rt. After stirring for 0.5 h, 4-methoxybenzyl chloride (0.82 mmol, 0.110 mL) was added to the reaction mixture and stirred 12 h. The crude mixture was purified by chromatographic purification on SiO_2 (Hexanes:EtOAc, 15:1) to afford product **17a** (304.4 mg, 88%) as a light yellow oil: $[\alpha]_D^{25}$ = -4.0 (c = 0.40, $CHCl_3$); IR (ATR) ν = 3029, 2959, 2921, 2863, 1733, 1490, 1458, 1360, 1240, 1094, 730, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 - 7.26 (m, 13H), 7.25 - 7.16 (m, 4H), 6.87 - 6.79 (m, 2H), 4.99 – 4.94 (m, 2H), 4.88 - 4.81 (m, 2H), 4.68 - 4.53 (m, 4H), 3.79 (s, 3H), 3.75 - 3.59 (m, 5H), 3.49 (d, *J* = 10.8 Hz, 1H), 3.30 - 3.26 (m, 1H), 1.54 - 1.37 (m, 6H), 1.33 - 1.20 (m, 6H), 0.96 - 0.73 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 138.9, 138.6, 130.9, 129.3, 128.6, 128.5, 128.4, 128.1, 127.8 (2), 127.7, 127.6, 127.5, 113.8, 89.7, 83.4, 81.6, 79.4, 75.5, 75.2, 74.9, 74.2, 73.6, 69.7, 55.4, 29.3, 27.6, 13.8, 9.3; HRMS (ESI) *m/z* calcd for $C_{47}H_{64}O_6SnNa$ $[M + Na]^+$ 867.3617, found 867.3623.



17b

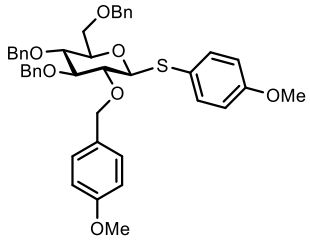
(2-*O*-(4-(Trifluoromethyl)benzyl)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane (17b). To a solution of (3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane (300 mg, 0.41 mmol) in THF (3.00 mL) KHMDS (1.00 mL, 0.500 mmol, 0.5 M in PhMe) was added under N_2 at rt. After stirring for 0.5 h, 4-(trifluoromethyl)benzyl chloride (0.82 mmol, 0.120 mL) was added to the reaction mixture and stirred 12 h. The crude mixture was purified by chromatographic purification on SiO_2 (Hexanes:EtOAc, 20:1) to afford the product **17b** (202 mg, 56%) as a light yellow oil: $[\alpha]_D^{25}$ = -4.2 (c = 0.30, $CHCl_3$); IR (ATR) ν = 3032, 2960, 2920, 2863, 1743, 1480, 1458, 1367, 1250, 1102, 730, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.37 - 7.23 (m, 17H), 5.11 (d, *J* = 12.3 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.9 Hz,

1H), 4.73 (d, *J* = 11.1 Hz, 1H), 4.70 - 4.57 (m, 4H), 3.79 - 3.60 (m, 5H), 3.52 (d, *J* = 10.7 Hz, 1H), 3.35 - 3.26 (m, 1H), 1.53 - 1.37 (m, 6H), 1.30 - 1.19 (m, 6H), 0.94 - 0.77 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 138.8, 138.6, 138.5, 128.6 (2), 128.5, 128.0, 127.9 (2), 127.8, 127.7, 127.6 (2), 127.2, 125.4, 125.4 -125.2 (m), 89.6, 83.4, 81.9, 79.4, 75.5, 75.2, 74.7, 73.6, 73.4, 72.3, 69.6, 29.2, 27.5, 13.8, 9.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.49; HRMS (ESI) *m/z* calcd for $C_{47}H_{61}O_5FSnNa$ $[M + Na]^+$ 905.3391, found 905.3380.



17c

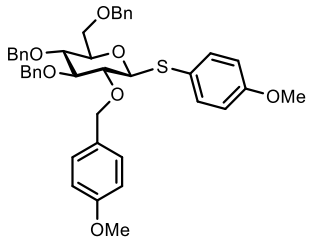
(2-*O*-Methyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane (17c). To a solution of (3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane (300 mg, 0.41 mmol) in THF (3.00 mL) was added KHMDS (1.00 mL, 0.500 mmol, 0.5 M in PhMe) under N_2 at rt. After stirring for 0.5 h, CH_3I (0.82 mmol, 0.052mL) was added to the reaction mixture and stirred for 8 h. The crude mixture was purified by chromatography on SiO_2 (Hexanes:EtOAc, 20:1) to afford the product **17c** (303 mg, 99%) as a colorless liquid: $[\alpha]_D^{23}$ = -1.0 (c = 2.40, $CHCl_3$); IR (ATR) ν = 3033, 2959, 2929, 2873, 1733, 1499, 1458, 1365, 1275, 1097, 739, 702, 601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.24 (m, 15H), 4.97 - 4.77 (m, 3H), 4.68 - 4.50 (m, 3H), 3.72 - 3.65 (m, 2H), 3.62 - 3.36 (m, 7H), 3.28 - 3.23 (m, 1H), 1.60 - 1.47 (m, 6H), 1.42 - 1.21 (m, 6H), 1.07 - 0.82 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9 (2), 138.6 (2), 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 89.6, 83.7, 83.4, 79.1, 75.4, 75.2, 74.9, 73.6, 69.6, 60.5, 29.2, 27.6, 13.9, 9.1; HRMS (ESI) *m/z* calcd for $C_{40}H_{58}O_5SnNa$ $[M + Na]^+$ 761.3204, found 761.3220.



21a

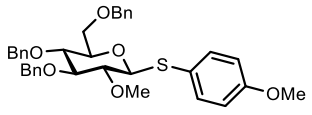
4-Methoxyphenyl 2-*O*-(4-methoxybenzyl)-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (21a). According to the general protocol A, (2-*O*-(4-methoxybenzyl)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane **17a** (127 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), and CuCl (30.0 mg, 0.300 mmol) were added to anhydrous *m*-xylene and 1,2-dichloroethane (2:1, 3.00 mL). The reaction mixture was heated under N_2 at 130 ºC for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **21a** (55.4 mg, 80%) as a light yellow oil: $[\alpha]_D^{25}$ = +0.9 (c = 16.3, $CHCl_3$); IR (ATR) ν = 3033, 2906, 2866, 1596, 1517, 1495, 1458, 1361, 1290, 1249, 1067, 1033, 914, 828, 739, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 - 7.54 (m, 2H), 7.38 - 7.27 (m, 15H), 7.24 - 7.20 (m, 2H), 6.91 - 6.87 (m, 2H), 6.80 - 6.74 (m, 2H), 4.95 - 4.82 (m, 4H), 4.70 (d, *J* = 9.9 Hz, 1H), 4.65 - 4.53 (m, 4H), 3.83 - 3.60 (m, 10H), 3.50 - 3.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 159.5, 138.6, 138.5, 138.2, 135.2, 130.5, 130.0, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9 (2), 127.8, 127.6, 123.7, 114.5, 114.0, 88.1, 86.9, 80.7, 79.1,

78.0, 75.9, 75.1 (2), 73.5, 69.2, 55.4 (2); HRMS (ESI) *m/z* calcd for $C_{42}H_{44}O_7SNa$ [M + Na]$^+$ 715.2705, found 715.2715.



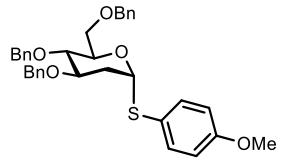
21b

4-Methoxyphenyl 2-*O*-(4-(trifluoromethyl)benzyl)-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (21b). According to the general protocol A, (2-*O*-(4-(trifluoromethyl)benzyl)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane **17b** (132.2 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), and CuCl (30.0 mg, 0.300 mmol) were added to anhydrous *m*-xylene and 1,2-dichloroethane (2:1, 3.00 mL). The reaction mixture was heated under N_2 at 130 ºC for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **21b** (53.3 mg, 73%, α:β > 50:1) as a light yellow oil: $[\alpha]_D^{24}$ = -1.3 (c = 13.7, $CHCl_3$); IR (ATR) ν = 3033, 2903, 2866, 1596, 1499, 1458, 1327, 1290, 1249, 1164, 1126, 1067, 823, 739, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 - 7.58 (m, 2H), 7.55 - 7.48 (m, 4H), 7.38 - 7.30 (m, 15H), 6.79 - 6.74 (m, 2H), 4.95 - 4.77 (m, 5H), 4.65 - 4.53 (m, 4H), 3.83 - 3.62 (m, 7H), 3.51 - 3.41 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 142.4 (2), 138.5, 138.4, 138.1, 135.2, 130.6 - 129.3 (m), 128.6 (2), 128.5, 128.1, 128.0, 127.9, 127.8 (2), 127.7, 125.5 - 125.4 (m), 123.4, 114.6, 87.9, 86.9, 81.0, 79.2, 78.0, 75.9, 75.2, 74.5, 73.6, 69.2, 55.4; ^{19}F NMR (282 MHz $CDCl_3$) δ -62.47; HRMS (ESI) *m/z* calcd for $C_{42}H_{41}O_6F_3SNa$ [M + Na]$^+$ 753.2474, found 753.2472.



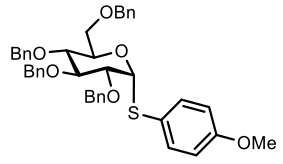
21c

4-Methoxyphenyl 2-*O*-methyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (21c). According to the general protocol A, (2-*O*-methyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane **S3** (110.7 mg, 0.150 mmol), 1-((4-methoxyphenyl)thio)pyrrolidine-2,5-dione (23.7 mg, 0.100 mmol), and CuCl (30.0 mg, 0.300 mmol) were added to anhydrous *m*-xylene and 1,2-dichloroethane (2:1, 3.00 mL). The reaction mixture was heated under N_2 at 130 ºC for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **17c** (39.9 mg, 68%, α:β = 1:17) as a light yellow oil: $[\alpha]_D^{24}$ = -1.7 (c = 16.3, $CHCl_3$); IR (ATR) ν = 3033, 1903, 2866, 1596, 1495, 1458, 1365, 1286, 1249, 1074, 1033, 914, 832, 739, 702, 646, 527 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 - 7.52 (m, 2H), 7.37 - 7.27 (m, 13H), 7.23 - 7.20 (m, 2H), 6.80 - 6.73 (m, 2H), 4.92 - 4.81 (m, 3H), 4.62 - 4.51 (m, 3H), 4.43 (d, *J* = 9.8 Hz, 1H), 3.80 - 3.69 (m, 5H), 3.65 (s, 3H), 3.62 - 3.54 (m, 2H), 3.44 (ddt, *J* = 8.5, 3.9, 1.9 Hz, 1H), 3.18 - 3.12 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 138.6, 138.5, 138.3, 135.3, 128.6, 128.5 (2), 128.1, 128.0, 127.9 (2), 127.8, 127.6, 123.5, 114.5, 87.8, 86.9, 82.7, 79.1, 77.8, 75.8, 75.1, 73.5, 69.3, 61.1, 55.4; HRMS (ESI) *m/z* calcd for $C_{35}H_{38}O_6SNa$ [M + Na]$^+$ 609.2287, found 609.2295.



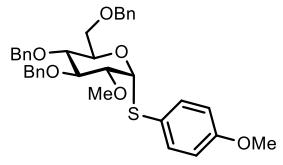
23

4-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (23). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] **17d** (106 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (23.7 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (6.70 mg, 0.025 mmol), and CuCl (2.00 mg, 0.020 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **23** (41.2 mg, 74%) as a colorless oil. Characterization data matched the literature report.[1]



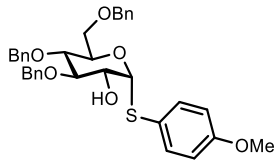
27a

4-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (27). According to the general protocol B, (2,3,4,6-tetra-*O*-benzyl-2-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (122.1 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (23.7 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (6.70 mg, 0.025 mmol), and CuCl (2.00 mg, 0.020 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **23** (31.8 mg, 48%, α:β = 2.7:1) as a colorless oil. Characterization data matched the literature report.[2]



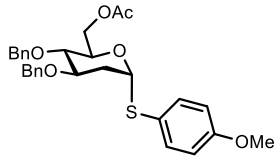
27b

4-Methoxyphenyl 2-*O*-methyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-glucopyranoside (27b). According to the general protocol B, (2-*O*-methyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane **S3** (110.6 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (23.7 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 2,2′:6′,2″-terpyridine (5.80 mg, 0.025 mmol), and CuCl (2.00 mg, 0.020 mmol) were added to anhydrous *m*-xylene and 1,4-dioxane (1:1, 2.00 mL). The reaction mixture was stirred at 130 °C for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **27b** (51.6 mg, 88%, α:β = 3.9:1) as a light yellow oil: $[\alpha]_D^{23}$ = +17.8 (c = 1.35, $CHCl_3$); IR (ATR) ν = 3033, 2925, 2858, 1596, 1499, 1458, 1361, 1290, 1249, 1093, 1033, 832, 743, 702, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 - 7.42 (m, 2H), 7.40 - 7.27 (m, 13H), 7.17 (dd, *J* = 7.2, 2.4 Hz, 2H), 6.87 - 6.72 (m, 2H), 5.60 (d, *J* = 5.3 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.82 (dd, *J* = 22.6, 10.9 Hz, 2H), 4.63 - 4.49 (m, 2H), 4.48 - 4.37 (m, 2H), 3.87 - 3.78 (m, 2H), 3.76 (s, 3H), 3.70 - 3.60 (m, 3H), 3.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 139.0, 138.4, 138.2, 134.9, 128.5, 128.5, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 124.5, 114.7, 87.7, 82.7, 82.5, 77.7, 75.8, 75.3, 73.6, 71.2, 69.0, 58.3, 55.5; HRMS (ESI) *m/z* calcd for $C_{35}H_{38}O_6SNa$ $[M + Na]^+$ 609.2287, found 609.2288.



27c

4-Methoxyphenyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-glucopyranoside (27c). According to the general protocol B, (3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (109 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **27c** (25.8 mg, 45%, α:β = 3.9:1) as a light yellow oil: $[\alpha]_D^{22}$ = +26.9 (c = 1.05, $CHCl_3$); IR (ATR) ν = 3402, 3033, 2910, 2869, 1596, 1499, 1458, 1365, 1290, 1249, 1178, 1074, 1033, 832, 743, 702, 646 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 - 7.42 (m, 2H), 7.39 - 7.27 (m, 13H), 7.21 - 7.18 (m, 2H), 6.81 - 6.76 (m, 2H), 5.46 (d, *J* = 5.3 Hz, 1H), 4.89 (s, 2H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 10.8 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.40 - 4.38 (m, 1H), 3.95 (q, *J* = 6.5 Hz, 1H), 3.82 (dd, *J* = 10.8, 4.3 Hz, 4H), 3.77 (s, 3H), 3.73 - 3.63 (m, 3H), 2.33 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 138.5, 138.2, 138.1, 135.0, 128.7, 128.6, 128.5, 128.1, 128.0 (3), 127.8, 124.1, 114.8, 91.1, 83.6, 77.9, 75.6, 75.1, 73.6, 72.6, 72.0, 68.8, 55.5; HRMS (ESI) *m/z* calcd for $C_{34}H_{36}O_6SNa$ $[M + Na]^+$ 595.2130, found 595.2135.

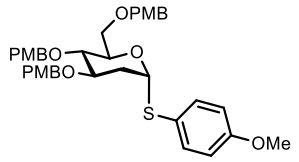


27d

4-Methoxyphenyl 3,4-di-*O*-benzyl-6-*O*-acetyl-2-deoxy-1-thio-α-D-glucopyranoside (27d). According to the general protocol B, (3,4-di-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)tri-*n*-butylstannane **S1** (98.9 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **27d** (24.4 mg, 48%) as a colorless oil: $[\alpha]_D^{24}$ = +24.9 (c = 1.60, $CHCl_3$); IR (ATR) ν = 3033, 2955, 1745, 1596, 1499, 1458, 1368, 1290, 1249, 1182, 1097, 1033, 832, 743, 702, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.29 (m, 12H), 6.85 - 6.80 (m, 2H), 5.47 (d, *J* = 5.5 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.72 - 4.60 (m, 3H), 4.44 - 4.22 (m, 3H), 4.01 (ddd, *J* = 11.5, 8.6, 4.8 Hz, 1H), 3.79 (s, 3H), 3.46 (dd, *J* = 9.6, 8.6 Hz, 1H), 2.46 (ddd, *J* = 13.5, 4.9, 1.4 Hz, 1H), 2.11 - 2.03 (m, 1H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 159.8, 138.3, 138.2, 134.8, 128.6 (2), 128.3, 128.0, 127.9, 124.7, 114.7, 84.9, 78.2, 78.0, 75.1, 72.0, 70.0, 63.7, 55.5, 35.9, 21.0; HRMS (ESI) *m/z* calcd for $C_{29}H_{32}O_6SNa$ $[M + Na]^+$ 531.1817, found 531.1823.

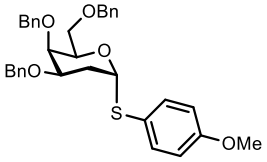
According to the general protocol C, (3,4-di-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane **S1** (98.9 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h

and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **27d** (36.6 mg, 72%) as a colorless oil.



27e

4-Methoxyphenyl 3,4,6-tri-*O*-(4-methoxybenzyl)-2-deoxy-1-thio-α-D-glucopyranoside (27e). According to the general protocol B, (3,4,6-tri-*O*-(4-methoxybenzyl)-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane **S2** (123.1 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (6.70 mg, 0.025 mmol), and CuCl (2.00 mg, 0.020 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **27e** (38.8 mg, 60%) as a light yellow oil: $[\alpha]_D^{24}$ = +17.7 (c = 7.65, $CHCl_3$); IR (ATR) ν = 3033, 2906, 2839, 1614, 1514, 1465, 1365, 1305, 1246, 1178, 1089, 1033, 825, 761, 646, 523 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.21 (m, 6H), 7.13 - 7.09 (m, 2H), 6.91 - 6.73 (m, 8H), 5.49 (d, *J* = 5.3 Hz, 1H), 4.81 (d, *J* = 10.4 Hz, 1H), 4.64 - 4.54 (m, 3H), 4.45 - 4.37 (m, 2H), 4.32 (ddd, *J* = 9.8, 4.4, 1.9 Hz, 1H), 3.94 (ddd, *J* = 11.3, 8.6, 4.7 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.75 - 3.69 (m, 1H), 3.63 (dd, *J* = 10.5, 2.1 Hz, 1H), 3.54 (dd, *J* = 9.8, 8.7 Hz, 1H), 2.40 (ddd, *J* = 13.5, 4.9, 1.4 Hz, 1H), 2.05 (ddd, *J* = 13.4, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 159.4, 159.3 (2), 134.6, 130.8, 130.7, 130.4, 129.7 (2), 129.5, 125.2, 114.6, 114.0, 113.9, 113.8, 85.1, 78.4, 77.7, 74.7, 73.1, 71.7, 71.7, 68.7, 55.4, 55.3, 36.2; HRMS (ESI) *m/z* calcd for $C_{37}H_{42}O_8SNa$ $[M + Na]^+$ 669.2498, found 669.2503.

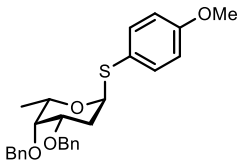


27f

4-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-galactopyranoside (27f). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)tri-*n*-butylstannane **S3** (106 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **27f** (29.5 mg, 53%) as a light yellow oil: $[\alpha]_D^{24}$ = +17.4 (c = 4.15, $CHCl_3$); IR (ATR) ν = 3033, 2869, 1596, 1495, 1458, 1368, 1286, 1249, 1178, 1093, 1063, 1033, 832, 739, 702, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.27 (m, 17H), 6.74 - 6.69 (m, 2H), 5.55 (d, *J* = 5.5 Hz, 1H), 4.94 (d, *J* = 11.6 Hz, 1H), 4.67 - 4.61 (m, 3H), 4.50 - 4.40 (m, 3H), 3.95 - 3.89 (m, 2H), 3.74 (s, 3H), 3.62 (dd, *J* = 6.3, 0.9 Hz, 2H), 2.58 (ddd, *J* = 12.8, 11.7, 5.7 Hz, 1H), 2.19 - 2.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 139.0, 138.4, 138.4, 134.7, 128.6, 128.5, 128.4, 128.2, 127.8 (2), 127.7 (2), 127.5, 125.1, 114.6, 85.5, 75.5, 74.5, 73.6, 73.6, 70.9, 70.7, 69.9, 55.4, 31.8. Characterization data matched the literature report.[2]

According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)tri-*n*-butylstannane **S3** (106 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300

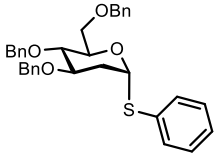
mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **27f** (33.6 mg, 64%) as a light yellow oil.



27g

4-Methoxyphenyl 3,4-di-*O*-benzyl-2-deoxy-1-thio-α-L-fucopyranoside (27g). According to the general protocol B, (3,4-di-*O*-benzyl-2-deoxy-β-L-fucopyranosyl)tri-*n*-butylstannane **S4** (90.2 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (6.70 mg, 0.025 mmol), and CuCl (2.00 mg, 0.020 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **27g** (23.9 mg, 53%) as a light yellow oil: $[\alpha]_D^{23}$ = -12.9 (c = 7.60, $CHCl_3$); IR (ATR) ν = 3033, 2936, 2869, 1596, 1495, 1458, 1365, 1286, 1249, 1175, 1104, 1059, 1030, 962, 832, 739, 702, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41- 7.27 (m, 12H), 6.88 - 6.81 (m, 2H), 5.57 (d, *J* = 5.4 Hz, 1H), 4.99 (d, *J* = 11.7 Hz, 1H), 4.72 - 4.58 (m, 3H), 4.34 - 4.28 (m, 1H), 3.93 (ddd, *J* = 12.2, 4.4, 2.4 Hz, 1H), 3.79 (s, 3H), 3.67 - 3.66 (m, 1H), 2.56 (td, *J* = 12.6, 5.7 Hz, 1H), 2.18 - 2.12 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 139.0, 138.5, 134.8, 134.1, 128.6, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 127.4, 125.6, 114.6, 85.5, 76.2, 76.0, 74.6, 70.6, 67.8, 55.4, 31.4, 17.3; HRMS (ESI) *m/z* calcd for $C_{27}H_{30}O_4SNa$ $[M + Na]^+$ 473.1762, found 473.1753.

According to the general protocol C, (3,4-di-*O*-benzyl-2-deoxy-β-L-fucopyranosyl)tri-*n*-butylstannane **S4** (90.2 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **27g** (35.2 mg, 78%) as a light yellow oil.

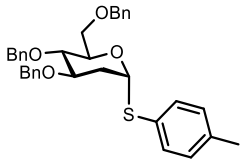


27h

Phenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (27h). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane (106 mg, 0.150 mmol), 1,2-diphenyldisulfane (21.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **27h** (24.2 mg, 46%, α/β > 15:1) as a colorless oil: $[\alpha]_D^{23}$ = +11.8 (c = 2.60, $CHCl_3$); IR (ATR) ν = 3033, 2921, 2866, 1588, 1458, 1365, 1100, 1030, 739, 698, 642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 - 7.43 (m, 2H), 7.36 - 7.27 (m, 13H), 7.25 - 7.19 (m, 5H), 5.69 (d, *J* = 5.8 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.72 - 4.58 (m, 3H), 4.55 (d, *J* = 10.8 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.31 (ddd, *J* = 9.9, 4.2, 2.1 Hz, 1H), 4.02 - 3.94 (m, 1H), 3.83 (dd, *J* = 10.7, 4.1 Hz, 1H), 3.74 - 3.62 (m, 2H), 2.46 (ddd, *J* = 13.4, 4.9, 1.4 Hz, 1H), 2.13 (ddd, *J* = 13.5, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 138.6, 138.5, 138.3, 135.2, 131.3, 129.0, 128.6, 128.5 (2), 128.1, 128.0, 127.9 (2), 127.8, 127.7, 127.2, 84.2, 78.6, 78.1, 75.1, 73.5, 72.1, 71.9, 69.0, 36.4; HRMS (ESI) *m/z* calcd for $C_{33}H_{34}O_4SNa$ [M + Na]$^+$ 549.2075, found 549.2078.

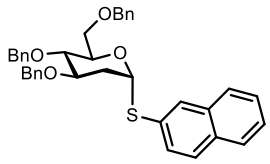
According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-diphenyldisulfane (21.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **27h** (33.7 mg, 64%) as a colorless oil.



27i

4-Methylphenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (27i). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(4-methylphenyl)disulfane (24.6 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **27i** (32.5 mg, 60%) as a colorless oil: $[\alpha]_D^{23}$ = +17.3 (c = 5.80, $CHCl_3$); IR (ATR) ν = 3033, 2921, 2866, 1499, 1458, 1365, 1193, 1089, 1030, 814, 739, 702, 650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.28 (m, 15H), 7.23 -7.20 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.62 (d, *J* = 5.7, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.72 - 4.53 (m, 4H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.33 (ddd, *J* = 9.8, 4.2, 2.0 Hz, 1H), 3.98 (ddd, *J* = 11.6, 5.8, 3.3 Hz, 1H), 3.83 (dd, *J* = 10.6, 4.2 Hz, 1H), 3.73 - 3.61 (m, 2H), 2.46 (ddd, *J* = 13.4, 4.9, 1.4 Hz, 1H), 2.31 (s, 3H), 2.11 (ddd, *J* = 13.4, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6 (2), 138.3, 137.4, 132.0, 131.3, 129.8, 128.6, 128.5, 128.4, 128.0 (2), 127.9, 127.8 (2), 127.7, 84.5, 78.6, 78.1, 75.1, 73.5, 72.0, 71.8, 69.1, 36.3, 21.2; HRMS (ESI) *m/z* calcd for $C_{34}H_{36}O_4SNa$ [M + Na]$^+$ 563.2232, found 563.2241.

According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), bis(4-methylphenyl)disulfane (24.6 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **27i** (28.7 mg, 53%) as a colorless oil.

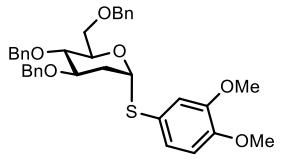


27j

2-Naphthyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (27j). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-di(naphthalen-2-yl)disulfane (31.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane

(2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **27j** (26.0 mg, 45%, α:β > 20:1) as a colorless oil: $[\alpha]_D^{25}$ = +18.6 (c = 2.50, $CHCl_3$); IR (ATR) ν = 3033, 2921, 2866, 1587, 1499, 1458, 1365, 1193, 1097, 1030, 948, 858, 817, 739, 702, 638 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.79 - 7.68 (m, 3H), 7.53 - 7.41 (m, 3H), 7.39 - 7.27 (m, 12H), 7.23 - 7.20 (m, 2H), 5.82 (d, *J* = 5.4 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.74 - 4.54 (m, 4H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.36 (ddd, *J* = 9.7, 4.0, 1.9 Hz, 1H), 4.03 (ddd, *J* = 11.5, 8.7, 4.9 Hz, 1H), 3.83 (dd, *J* = 10.7, 4.1 Hz, 1H), 3.68 (ddd, *J* = 8.8, 5.0, 3.0 Hz, 2H), 2.5 - 2.45 (m, 1H), 2.17 (ddd, *J* = 13.4, 11.5, 5.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.5, 138.2, 133.9, 132.5, 132.4, 129.7, 128.7, 128.6, 128.5 (2), 128.1, 128.0, 127.9 (3), 127.8, 127.7, 127.6, 126.6, 126.1, 84.1, 78.6, 78.1, 75.2, 73.6, 72.1, 72.0, 69.1, 36.4; HRMS (ESI) *m/z* calcd for $C_{37}H_{36}O_4SNa$ $[M + Na]^+$ 599.2232, found 599.2239.

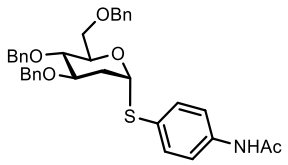
According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-di(naphthalen-2-yl)disulfane (31.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **27j** (31.8 mg, 55%) as a colorless oil.



27k

3,4-Dimethoxyphenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (27k). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(3,4-dimethoxyphenyl)disulfane (33.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **27k** (31.1 mg, 53%) as a colorless oil: $[\alpha]_D^{23}$ = +13.2 (c = 1.45, $CHCl_3$); IR (ATR) ν = 3033, 2906, 2866, 1588, 1506, 1458, 1398, 1365, 1320, 1257, 1234, 1182, 1093, 1030, 951, 914, 884, 854, 739, 702, 653, 609 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 - 7.27 (m, 13H), 7.24 - 7.20 (m, 2H), 7.06 - 6.98 (m, 2H), 6.70 (d, *J* = 8.3 Hz, 1H), 5.56 (d, *J* = 5.4 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.72 - 4.53 (m, 4H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.36 (ddd, *J* = 9.8, 4.5, 2.0 Hz, 1H), 3.97 (ddd, *J* = 11.5, 8.8, 4.9 Hz, 1H), 3.88 - 3.76 (m, 7H), 3.69 - 3.56 (m, 2H), 2.45 (ddd, *J* = 13.7, 4.6, 1.0 Hz, 1H) 2.09 (ddd, *J* = 13.3, 11.6, 5.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 149.1, 138.6, 138.5, 138.2, 128.6, 128.5 (2), 128.1, 128.0, 127.9 (2), 127.8 (2), 125.8, 125.6, 116.0, 111.6, 85.1, 78.7, 78.0, 75.2, 73.6, 72.0, 71.8, 69.3, 56.1, 56.0, 36.2; HRMS (ESI) *m/z* calcd for $C_{35}H_{38}O_6SNa$ $[M + Na]^+$ 609.2287, found 609.2289.

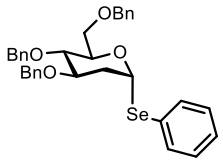
According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(3,4-dimethoxyphenyl)disulfane (33.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **27k** (33.4 mg, 60%) as a colorless oil.



27l

4-Acetylaminophenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (27l). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(4-acetylaminophenyl)disulfane (33.2 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 1:1) **27l** (47.3 mg, 81%) as a colorless foam: $[\alpha]_D^{24}$ = +18.5 (c = 3.50, $CHCl_3$); IR (ATR) ν = 3316, 3033, 2918, 2869, 1674, 1596, 1532, 1499, 1458, 1402, 1372, 1316, 1257, 1097, 1033, 836, 743, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 - 7.27 (m, 17H), 7.22 -7.19 (m, 2H), 7.11 (s, 1H), 5.59 (d, *J* = 5.4 Hz, 1H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.71 - 4.52 (m, 4H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.30 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.96 (ddd, *J* = 11.5, 8.6, 4.8 Hz, 1H), 3.82 (dd, *J* = 10.6, 4.1 Hz, 1H), 3.68 - 3.60 (m, 2H), 2.44 (dd, *J* = 13.4, 4.9 Hz, 1H), 2.16 - 2.05 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 138.6, 138.5, 138.3, 137.4, 132.9, 129.8, 128.6, 128.5(2), 128.1, 128.0, 127.9 (2), 127.8, 127.7, 120.3, 84.6, 78.6, 78.0, 75.1, 73.6, 72.1, 71.9, 69.1, 36.3, 24.9; HRMS (ESI) *m/z* calcd for $C_{35}H_{37}O_5SNa$ $[M + Na]^+$ 606.2292, found 606.2292.

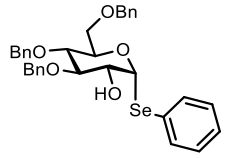
According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(4-acetamidophenyl)disulfane (33.2 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 1:1) **27l** (40.8 mg, 70%) as a colorless foam.



27m

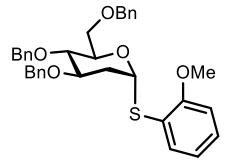
Phenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-seleno-α-D-glucopyranoside (27m). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-diphenyldiselane (31.2 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 2,2′:6′,2″-terpyridine (5.8 mg, 0.025 mmol), and CuCl (2.00 mg, 0.020 mmol) were added to anhydrous *m*-xylene and 1,4-dioxane (1:1, 2.00 mL). The reaction mixture was stirred at 130 °C for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **27m** (29.8 mg, 48%, α:β = 5:1) as a light yellow oil: $[\alpha]_D^{25}$ = +17.3 (c = 5.00, $CHCl_3$); IR (ATR) ν = 3063, 3033, 2910, 2866, 1581, 1458, 1365, 1190, 1097, 1030, 951, 735, 698, 624, 568 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59 - 7.54 (m, 2H), 7.38 - 7.19 (m, 18H), 6.00 (d, *J* = 5.4, 1H), 4.91 (d, *J* = 10.8, 1H), 4.71 - 4.45 (m, 5H), 4.24 (ddd, *J* = 9.9, 4.1, 2.1 Hz, 1H), 3.96 - 3.75 (m, 2H), 3.71 - 3.63 (m, 2H), 2.55 (ddd, *J* = 13.6, 4.9, 1.4 Hz, 1H), 2.19 (ddd, *J* = 13.5, 11.5, 5.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.5, 138.2, 133.8, 129.2, 128.6, 128.5 (2), 128.1, 128.0, 127.9 (2), 127.8 (2), 127.5, 82.5, 78.7, 78.4, 75.2, 73.6, 73.5, 72.0, 68.9, 37.5; HRMS (ESI) *m/z* calcd for $C_{33}H_{34}O_4SeNa$ $[M + Na]^+$ 597.1520, found 597.1521.

According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-diphenyldiselane (31.2 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **27m** (35.4 mg, 57%) as a light yellow oil.



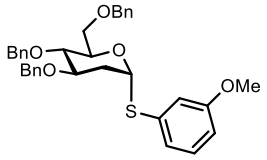
27n

Phenyl 3,4,6-tri-*O*-benzyl-1-seleno-α-D-glucopyranoside (27n). According to the general protocol B, (3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (109 mg, 0.150 mmol), 1,2-diphenyldiselane (31.2 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), 2,2′:6′,2″-terpyridine (5.80 mg, 0.025 mmol), and CuCl (2.00 mg, 0.020 mmol) were added to anhydrous *m*-xylene and 1,4-dioxane (1:1, 2.00 mL). The reaction mixture was stirred at 130 °C for 96 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **27n** (38.9 mg, 66%, α:β = 4:1) as a light yellow oil: $[\alpha]_D^{23}$ = +24.2 (c = 11.2, $CHCl_3$); IR (ATR) ν = 3450, 3063, 3033, 2869, 1581, 1499, 1458, 1361, 1212, 1074, 1048, 914, 735, 298, 620, 575, 553 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 - 7.60 (m, 2H), 7.40 - 7.27 (m, 14H), 7.26 - 7.18 (m, 4H), 5.95 (d, *J* = 5.1 Hz, 1H), 4.94 - 4.82 (m, 3H), 4.65 - 4.50 (m, 2H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.24 (ddd, *J* = 9.7, 3.8, 2.1 Hz, 1H), 3.91 (dt, *J* = 9.2, 5.4 Hz, 1H), 3.83 (dd, *J* = 10.9, 3.8 Hz, 1H), 3.78 - 3.58 (m, 3H), 2.39 (d, *J* = 5.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 138.1, 138.0, 134.4, 129.2 (2), 128.7, 128.6, 128.5, 128.1, 128.0 (2), 127.9, 127.8, 89.8, 84.4, 77.3, 75.5, 75.1, 73.9, 73.6, 72.8, 68.5; HRMS (ESI) *m/z* calcd for $C_{33}H_{34}O_5SeNa$ $[M + Na]^+$ 613.1469, found 613.1475.



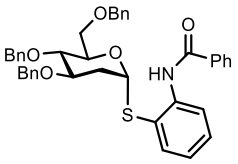
46a

2-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (46a). According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(2-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **46a** (25.1 mg, 45%) as a colorless oil: $[\alpha]_D^{29}$ = +17.8 (c = 5.05, $CHCl_3$); IR (ATR) ν = 3067, 3033, 2921, 2866, 1585, 1480, 1458, 1365, 1275, 1249, 1194, 1097, 1074, 1030, 952, 851, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.41 - 7.26 (m, 13H), 7.24 - 7.16 (m, 3H), 6.92 - 6.82 (m, 2H), 5.82 (d, *J* = 5.5 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.73 - 4.50 (m, 4H), 4.42 (d, *J* = 12.1 Hz, 1H), 4.31 - 4.24 (m, 1H), 4.13 - 4.01 (m, 1H), 3.87 (s, 3H), 3.84 - 3.77 (m, 1H), 3.72 - 3.54 (m, 2H), 2.51 (ddd, *J* = 13.4, 5.0, 1.4 Hz, 1H), 2.14 (ddd, *J* = 13.5, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 138.7, 138.6, 138.3, 132.5, 128.6, 128.5 (2), 128.4, 128.0, 127.8 (2), 127.7 (2), 122.8, 121.4, 110.7, 81.9, 78.6, 78.2, 75.1, 73.5, 72.0, 71.9, 68.9, 55.9, 36.2; HRMS (ESI) *m/z* calcd for $C_{34}H_{36}O_5SNa$ $[M + Na]^+$ 579.2181, found 579.2185.



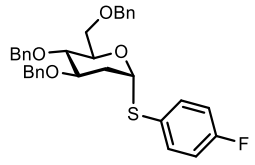
46b

3-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (46b). According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(3-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **46b** (29.0 mg, 52%) as a colorless oil: $[\alpha]_D^{28}$ = +19.5 (c = 5.20, $CHCl_3$); IR (ATR) ν = 3061, 3033, 2921, 2869, 1592, 1480, 1458, 1369, 1287, 1253, 1194, 1097, 1048, 1033, 955, 866, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.13 (m, 16H), 7.07 - 7.01 (m, 2H), 6.77 (ddd, *J* = 8.2, 2.4, 1.2 Hz, 1H), 5.73 (d, *J* = 5.6, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.74 - 4.52 (m, 4H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.29 (ddd, *J* = 9.7, 4.1, 2.0 Hz, 1H), 3.97 (ddd, *J* = 11.5, 8.7, 4.8 Hz, 1H), 3.83 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.75 (s, 3H), 3.71 - 3.57 (m, 2H), 2.46 (ddd, *J* = 13.4, 4.9, 1.4 Hz, 1H), 2.14 (ddd, *J* = 13.5, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 138.6, 138.5, 138.2, 136.4, 129.8, 128.6, 128.5 (2), 128.1, 128.0, 127.9 (2), 127.8, 127.7, 123.3, 116.1, 113.2, 84.1, 78.5, 78.1, 75.1, 73.5, 72.1, 71.9, 69.0, 55.4, 36.4; HRMS (ESI) *m/z* calcd for $C_{34}H_{36}O_5SNa$ $[M + Na]^+$ 579.2181, found 579.2190.



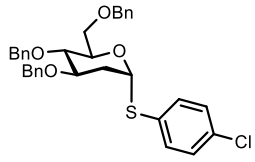
46c

2-Benzamidopheny 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (46c). According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), *N,N′*-(disulfanediylbis(2,1-phenylene))dibenzamide (45.6 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **46c** (51.6 mg, 80%, α:β = 10:1) as a colorless oil: $[\alpha]_D^{29}$ = +11.3 (c = 15.1, $CHCl_3$); IR (ATR) ν = 3361, 3029, 2866, 1681, 1581, 1514, 1495, 1436, 1365, 1305, 1249, 1194, 1097, 1030, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.57 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.99 - 7.90 (m, 2H), 7.61 - 7.27 (m, 17H), 7.22 - 7.16 (m, 2H), 7.08 - 6.93 (m, 1H), 5.42 (dd, *J* = 5.3, 2.2 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.75 - 4.48 (m, 4H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.28 - 4.18 (m, 1H), 4.00 (tdd, *J* = 10.9, 5.0, 3.0 Hz, 1H), 3.74 - 3.32 (m, 3H), 2.42 (ddd, *J* = 13.6, 4.8, 2.2 Hz, 1H), 2.17 - 2.01 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 139.8, 138.4, 138.3, 138.0, 136.1, 135.2, 132.5, 132.2, 132.0, 130.5, 129.0, 128.6, 128.5 (2), 128.1 (2), 128.0 (2), 127.9, 127.8 (3), 127.7, 127.2, 124.5, 122.2, 120.6, 85.5, 77.8, 77.5, 74.8, 73.6, 73.3, 72.1, 68.5, 36.4; HRMS (ESI) *m/z* calcd for $C_{40}H_{39}O_5SNNa$ $[M + Na]^+$ 668.2447, found 668.2474.



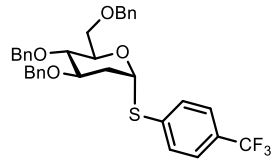
46d

4-Fluorophenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (46d). According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(4-fluorophenyl)disulfane (25.4 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **46d** (30.5 mg, 55%) as a colorless oil: $[\alpha]_D^{29}$ = +19.2 (c = 6.40, $CHCl_3$); IR (ATR) ν = 3033, 2921, 2866, 1592, 1495, 1458, 1369, 1231, 1160, 1093, 1033, 952, 836, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 - 7.40 (m, 2H), 7.39 - 7.26 (m, 13H), 7.25 - 7.19 (m, 2H), 6.97 - 6.79 (m, 2H), 5.57 (d, *J* = 5.7 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.73 - 4.52 (m, 4H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.37 - 4.28 (m, 1H), 4.03 - 3.90 (m, 1H), 3.81 (dd, *J* = 10.6, 4.6 Hz, 1H), 3.74 - 3.49 (m, 2H), 2.44 (ddd, *J* = 13.5, 5.0, 1.4 Hz, 1H), 2.11 (ddd, *J* = 13.5, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 160.9, 138.5 (2), 138.2, 134.4, 134.2, 129.8 (2), 128.6, 128.5 (2), 128.1, 128.0, 127.9 (2), 127.8 (2), 116.2, 115.9, 84.7, 78.6, 78.0, 75.2, 73.6, 72.1, 71.8, 69.1, 36.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.28; HRMS (ESI) *m/z* calcd for $C_{33}H_{33}O_4SFNa$ $[M + Na]^+$ 567.1981, found 567.1995.



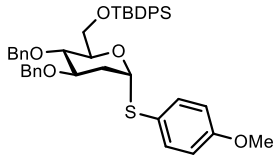
46e

4-Chlorophenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (46e). According to the general protocol A, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(4-chlorophenyl)disulfane (28.7 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 9:1) **46e** (25.2 mg, 45%) as a colorless oil: $[\alpha]_D^{29}$ = +19.3 (c = 5.50, $CHCl_3$); IR (ATR) ν = 3033, 2921, 2862, 1499, 1480, 1458, 1365, 1194, 1093, 1030, 1015, 952, 821, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 - 7.18 (m, 19H), 5.64 (d, *J* = 5.7, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.72 - 4.41 (m, 5H), 4.28 (ddd, *J* = 9.8, 4.4, 2.0 Hz, 1H), 3.96 (ddd, *J* = 11.6, 8.7, 4.9 Hz, 1H), 3.80 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.70 - 3.55 (m, 2H), 2.44 (ddd, *J* = 13.5, 4.9, 1.4 Hz, 1H), 2.13 (ddd, *J* = 13.5, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 138.4, 138.1, 133.5, 133.4, 132.8, 129.2, 129.1, 128.6, 128.5 (2), 128.1, 128.0, 127.9, 127.8 (2), 84.2, 78.5, 77.9, 75.2, 73.6, 72.1, 71.9, 69.0, 36.2; HRMS (ESI) *m/z* calcd for $C_{33}H_{33}O_4ClSNa$ $[M + Na]^+$ 583.1686, found 583.1702.



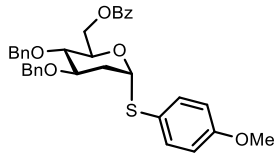
46f

4-(Trifluoromethyl)phenyl 3,4,6-tri-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (46f). According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (106 mg, 0.150 mmol), 1,2-bis(4-(trifluoromethyl)phenyl)disulfane (35.4 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **46f** (37.8 mg, 67%) as a white foam: $[\alpha]_D^{29}$ = +15.2 (c = 3.40, $CHCl_3$);IR (ATR) ν = 3033, 2925, 2869, 1611, 1499, 1458, 1406, 1328, 1167, 1127, 1093, 1067, 1019, 1033, 955, 836, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 - 7.52 (m, 2H), 7.49 - 7.42 (m, 2H), 7.40 - 7.26 (m, 13H), 7.24 - 7.15 (m, 2H), 5.78 (d, *J* = 6.4 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.73 - 4.51 (m, 4H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.24 (ddd, *J* = 9.7, 4.3, 2.0 Hz, 1H), 3.96 (ddd, *J* = 11.6, 8.6, 4.9 Hz, 1H), 3.81 (dd, *J* = 10.7, 4.3 Hz, 1H), 3.72 - 3.59 (m, 2H), 2.44 (ddd, *J* = 13.6, 4.9, 1.4 Hz, 1H), 2.17 (ddd, *J* = 13.6, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 138.4 (2), 138.1, 130.0, 128.6, 128.5 (2), 128.1, 128.0, 127.9, 127.9, 127.9, 125.8 - 125.7 (m), 122.4, 83.3, 78.4, 77.9, 75.2, 73.6, 72.1, 72.1, 69.0, 36.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.6; HRMS (ESI) *m/z* calcd for $C_{34}H_{33}O_4SF_3Na$ $[M + Na]^+$ 617.1949, found 617.1971.



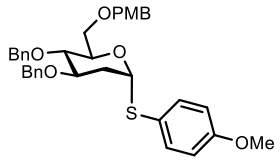
47a

4-Methoxyphenyl 3,4-di-*O*-benzyl-6-*tert*-butydiphenylsilyl-2-deoxy-1-thio-α-D-glucopyranoside (47a). According to the general protocol C, (3,4-di-*O*-benzyl-6-*tert*-butydiphenylsilyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane **S5** (128.3 mg, 0.150 mmol), 1,2-bis(2-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 20:1) **47a** (63.4 mg, 90%) as a colorless oil: $[\alpha]_D^{29}$ = +9.9 (c = 19.5, $CHCl_3$); IR (ATR) ν = 3070, 3033, 2933, 2858, 1696, 1462, 1499, 1462, 1432, 1365, 1290, 1249, 1182, 1156, 1093, 1033, 948, 829, 743, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 - 7.64 (m, 4H), 7.47 - 7.20 (m, 18H), 6.82 - 6.71 (m, 2H), 5.55 (dd, *J* = 5.8, 1.3 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.77 - 4.66 (m, 3H), 4.29 (ddd, *J* = 9.6, 4.0, 1.8 Hz, 1H), 4.10 - 3.89 (m, 3H), 3.77 (s, 3H), 3.75 - 3.66 (m, 1H), 2.50 (ddd, *J* = 13.3, 4.9, 1.4 Hz, 1H), 2.11 (ddd, *J* = 13.4, 11.6, 5.7 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 138.6, 138.5, 136.0, 135.7, 134.1, 134.0, 133.3, 129.7, 129.6, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8 (2), 127.6, 125.8, 114.6, 85.1, 78.7, 78.1, 75.3, 73.1, 72.2, 63.2, 55.4, 36.5, 27.0, 19.5; HRMS (ESI) *m/z* calcd for $C_{43}H_{48}O_5SSiNa$ $[M + Na]^+$ 727.2889, found 727.2927.



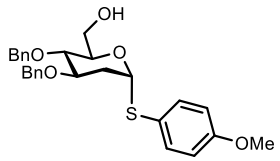
47b

4-Methoxyphenyl 3,4-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (47b). According to the general protocol C, (3,4-di-*O*-benzyl-6-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)tri-*n*-butylstannane **S7** (108.2 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **47b** (49.6 mg, 87%) as a light yellow oil: $[\alpha]_D^{29}$ = +15.7 (c = 13.7, $CHCl_3$); IR (ATR) ν = 3033, 2925, 1722, 1596, 1499, 1458, 1279, 1249, 1179, 1093, 1030, 832, 717, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 - 7.95 (m, 2H), 7.61 - 7.52 (m, 1H), 7.48 -7.30 (m, 14H), 6.73 - 6.62 (m, 2H), 5.51 (dd, *J* = 5.6, 1.4 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.81 - 4.49 (m, 6H), 4.06 (ddd, *J* = 11.4, 8.5, 4.8 Hz, 1H), 3.72 (s, 3H), 3.57 (td, *J* = 9.1, 4.7 Hz, 1H), 2.51 (ddd, *J* = 13.4, 4.9, 1.4 Hz, 1H), 2.11 (ddd, *J* = 13.4, 11.6, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 159.7, 138.3, 138.1, 134.5, 133.1, 130.2, 129.9, 128.7, 128.6, 128.4, 128.3, 128.0 (2), 127.9, 127.1, 124.7, 114.7, 84.9, 78.6, 78.0, 75.2, 72.0, 70.3, 64.2, 55.4, 36.1; HRMS (ESI) *m/z* calcd for $C_{34}H_{34}O_6SNa$ $[M + Na]^+$ 593.1974, found 593.1980.



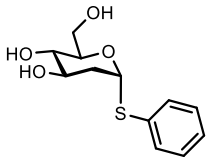
47c

4-Methoxyphenyl 3,4-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-2-deoxy-1-thio-α-D-glucopyranoside (47c). According to the general protocol C, (3,4-di-*O*-benzyl-6-*O*-(4-methoxybenzyl)-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane **S9** (110.7 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 6:1) **47c** (41.0 mg, 70%) as a light yellow oil: $[\alpha]_D^{29}$ = +9.0 (c = 2.15, $CHCl_3$); IR (ATR) ν = 3448, 2929, 2836, 1614, 1596, 1581, 1499, 1458, 1369, 1290, 1249, 1179, 1097, 1033, 832, 743, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 - 7.26 (m, 11H), 7.25 - 7.17 (m, 3H), 6.88 - 6.79 (m, 2H), 6.79 - 6.71 (m, 2H), 5.50 (d, *J* = 5.3 Hz, 1H), 4.89 (d, *J* = 10.9 Hz, 1H), 4.72 - 4.46 (m, 4H), 4.43 - 4.29 (m, 2H), 3.96 (ddd, *J* = 11.6, 8.7, 4.9 Hz, 1H), 3.82 - 3.71 (m, 7H), 3.68 - 3.50 (m, 2H), 2.49 - 2.37 (m, 1H), 2.14 -2.00 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 159.3, 138.6 (2), 134.7, 132.8, 130.4, 130.1, 129.8, 129.7, 128.6, 128.5 (2), 128.0, 127.9, 127.8 (2), 125.1, 114.8, 114.6, 113.9, 113.8, 85.1, 78.7, 78.0, 75.1, 73.2, 72.0, 71.7, 68.7, 55.4, 55.4, 36.2; HRMS (ESI) *m/z* calcd for $C_{35}H_{38}O_6SNa$ $[M + Na]^+$ 609.2287, found 609.2303.



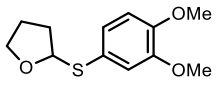
47d

4-Methoxyphenyl 3,4-di-*O*-benzyl-2-deoxy-1-thio-α-D-glucopyranoside (47d). According to the general protocol C, (3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)tri-*n*-butylstannane **S6** (92.5 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **47d** (41.0 mg, 88%) as a light yellow oil: $[\alpha]_D^{29}$ = +21.3 (c = 16.1, $CHCl_3$); IR (ATR) ν = 3461, 3033, 2921, 2873, 1596, 1495, 1458, 1369, 1290, 1249, 1179, 1093, 1033, 948, 832, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 - 7.28 (m, 12H), 6.91 - 6.80 (m, 2H), 5.49 - 5.41 (m, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.76 - 4.59 (m, 3H), 4.23 (dtt, *J* = 9.3, 3.3, 1.6 Hz, 1H), 4.09 - 3.94 (m, 1H), 3.79 (m, 5H), 3.52 (dd, *J* = 9.7, 8.7 Hz, 1H), 2.46 (ddd, *J* = 13.5, 4.9, 1.4 Hz, 1H), 2.03 (ddd, *J* = 13.5, 11.5, 5.7 Hz, 1H), 1.71 (q, *J* = 5.0, 3.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 138.5, 138.4, 135.1, 128.6, 128.2, 128.0, 127.9, 124.6, 114.8, 85.0, 78.6, 77.8, 75.1, 72.2, 72.0, 62.3, 55.4, 36.0; HRMS (ESI) *m/z* calcd for $C_{27}H_{30}O_5SNa$ $[M + Na]^+$ 489.1712, found 489.1703.



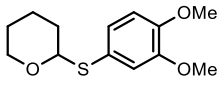
47e

4-Phenyl 2-deoxy-1-thio-α-D-glucopyranoside (47e). According to the general protocol B, (2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[4] (65.6 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (CH_2Cl_2:MeOH, 10:1) **47e** (23.5 mg, 82%) as a colorless oil: $[\alpha]_D^{29}$ = +30.8 (c = 11.9, MeOH); IR (ATR) ν = 3342, 3065, 2925, 2884, 1588, 1484, 1443, 1235, 1186, 1071, 1045, 955, 851, 773, 743, 695 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 7.58 - 7.46 (m, 2H), 7.41 - 7.16 (m, 3H), 5.64 (ddt, *J* = 5.6, 1.2, 0.6 Hz, 1H), 4.07 (dddd, *J* = 9.7, 3.8, 3.2, 0.6 Hz, 1H), 3.96 - 3.76 (m, 3H), 3.39 - 3.33 (m, 1H), 2.30 (ddd, *J* = 13.3, 5.0, 1.2 Hz, 1H), 2.06 (ddd, *J* = 13.5, 11.9, 5.6 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 136.5, 132.7, 129.9, 128.2, 85.7, 74.8, 73.3, 70.6, 62.4, 49.0, 39.7; HRMS (ESI) *m/z* calcd for $C_{12}H_{16}O_4SNa$ $[M + Na]^+$ 279.0667, found 279.0664.



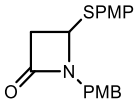
48a

2-(3,4-Dimethoxyphenyl)tetrahydrofuran (48a). According to the general protocol C, 1tributyl(tetrahydrofuran-2-yl)stannane (54.2 mg, 0.150 mmol), 1,2-bis(3,4-dimethoxyphenyl)disulfane (33.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **48a** (17.1 mg, 82%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 - 7.04 (m, 2H), 6.85 - 6.76 (m, 1H), 5.55 - 5.48 (m, 1H), 4.07 - 3.90 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.43 - 2.25 (m, 1H), 2.07 - 1.78 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0 (2), 126.1, 125.8, 116.1, 111.6, 88.3, 67.4, 56.1, 56.0, 32.6, 25.0. Characterization data matched the literature report.[2]



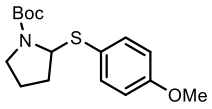
48b

2-(3,4-Dimethoxyphenyl)tetrahydro-2*H*-pyran (48b). According to the general protocol C, tributyl(tetrahydro-2*H*-pyran-2-yl)stannane (56.3 mg, 0.150 mmol), 1,2-bis(3,4-dimethoxyphenyl)disulfane (33.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **48b** (15.5 mg, 70%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 - 7.04 (m, 2H), 6.86 - 6.75 (m, 1H), 5.04 (dd, *J* = 6.3, 3.7 Hz, 1H), 4.27 - 4.10 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.65 - 3.48 (m, 1H), 2.09 - 1.94 (m, 1H), 1.91 - 1.55 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0 (2), 125.8, 125.6, 116.1, 111.5, 86.4, 65.0, 56.1, 56.0, 31.7, 25.7, 22.0. Characterization data matched the literature report.[2]



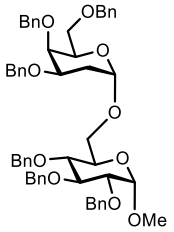
48c

1-(4-Methoxybenzyl)-4-((4-methoxyphenyl)thio)azetidin-2-one (48c). According to the general protocol C, 1-(4-methoxybenzyl)-4-(tributylstannyl)azetidin-2-one (72.2 mg, 0.150 mmol), 1,2-bis(4-methoxyphenyl)disulfane (27.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 2:1) **48c** (29.0 mg, 88%) as a colorless oil: IR (ATR) ν = 2955, 2840, 1756, 1614, 1596, 1514, 1499, 1465, 1391, 1290, 1249, 1179, 1108, 1033, 948, 832 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.28 (m, 2H), 7.17 - 7.04 (m, 2H), 6.97 - 6.67 (m, 4H), 4.78 - 4.57 (m, 2H), 4.05 (d, *J* = 14.9 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.17 (dd, *J* = 14.9, 4.8 Hz, 1H), 2.75 (ddd, *J* = 14.9, 2.3, 1.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 160.7, 159.3, 137.2, 129.9, 127.7, 119.9, 115.1, 114.3, 58.2, 55.5, 55.4, 44.0, 43.8; HRMS (ESI) *m/z* calcd for $C_{18}H_{19}O_3SNa$ $[M + Na]^+$ 352.0983, found 352.0984.



48d

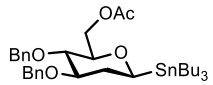
***tert*-Butyl 2-((4-methoxyphenyl)thio)pyrrolidine-1-carboxylate (48d).** According to the general protocol C, *tert*-butyl 2-(tri-*n*-butylstannyl)pyrrolidine-1-carboxylate (69.0 mg, 0.150 mmol), 1,2-bis(3,4-dimethoxyphenyl)disulfane (33.8 mg, 0.100 mmol), KF (17.4 mg, 0.300 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 19:1) **48d** (25.9 mg, 84%) as a colorless oil: H NMR (300 MHz, $CDCl_3$) δ 7.54 - 7.34 (m, 2H), 6.98 - 6.63 (m, 2H), 5.20 (d, *J* = 26.4 Hz, 1H), 3.79 (s, 3H), 3.34 (d, *J* = 26.7 Hz, 2H), 2.14 - 1.77 (m, 4H), 1.54 - 1.28 (m, 9H);^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 153.7, 137.2, 124.4, 114.6, 80.1, 67.1, 55.4, 45.6, 33.6, 28.4, 22.3. Characterization data matched the literature report.[4]



51

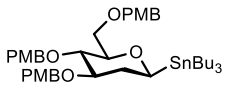
Methyl 6-*O*-(2-deoxy-3,4,6-tris-*O*-benzyl-α-D-galactopyranosyl)-2,3,4-tris-*O*-benzyl-α-D-glucopyranoside (51). According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)tri-*n*-butylstannane (159 mg, 0.225 mmol), 1,2-bis(4-methoxyphenyl)disulfane (41.7 mg, 0.150 mmol), KF (26.1 mg, 0.450 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (18.2 mg, 0.068 mmol) were added to anhydrous 1,4-dioxane (3.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 48 h and filtered through Celite® to obtain a crude mixture for next step. A solution of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **50** (46.4 mg, 0.100 mmol) and the crude mixture in dry CH_2Cl_2 (5 mL) was stirred with powdered molecular sieves (4Å) under N_2 for 30 min. NIS (45 mg, 0.200 mmol) was added and stirring was continued for further 30 min, when after addition of a catalytic amount of AgOTf (2.6 mg, 0.010 mmol) the color of the reaction mixture turned deep yellow brown. The mixture was stirred for 10h, then Et_3N was added to quench the mixture. After stirring for additional 20 min, the mixture was concentrated and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 6:1) **51** (63.4 mg, 72%, α:β =5:1) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 -7.22 (m, 30H), 5.04 (d, *J* = 3.6 H, 1H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.96 - 4.76 (m, 4H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.65 - 4.50 (m, 5H), 4.39 (q, *J* = 11.8 Hz, 2H), 4.00 (dd, *J* = 9.6, 8.8 Hz, 1H), 3.94 - 3.69 (m, 5H), 3.68 - 3.42 (m, 5H), 3.33 (s, 3H), 2.22 (td, *J* = 12.5, 3.6 Hz, 1H), 2.03 (dd, *J* = 12.6, 4.5 Hz, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 138.9, 138.5, 138.4, 138.3 (2), 128.6, 128.5, 128.4, 128.3, 128.2 (2), 128.0, 127.8 (2), 127.7, 127.6, 127.5, 98.4, 98.0, 82.3, 80.1, 78.0, 77.4, 75.9, 75.1, 74.4, 74.3, 73.5, 73.4, 73.0, 70.4, 70.2, 69.9, 69.5, 66.2, 55.1, 31.1. Characterization data matched the literature report.[5]

5. Detailed Experimental Procedures for Compounds S1- S13



S1

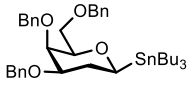
(3,4-Di-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane (S1). To a solution of *i*-Pr_2NH (1.45 mL, 10.3 mmol) in anhydrous THF (15.0 mL), *n*-BuLi (6.20 mL, 9.95 mmol, 1.6 M in hexane) was added at 0 °C. After stirring for 15 min, Bu_3SnH (3.00 mL, 10.6 mmol) was added, and the reaction mixture was stirred at -78 °C for another 15 min. The solution of Bu_3SnLi in THF was warmed up to 0 °C. To a solution of 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-D-glucose (2.00 g, 3.43 mmol) in $CHCl_3$/PhMe (2:1, 15.0 mL) was added $SOCl_2$ (1.80 mL, 24.8 mmol). The resulting solution was stirred at rt for 0.5 h and concentrated under vacuum. The residue was dissolved in THF (20.0 mL) and added dropwise via syringe to the above freshly prepared solution of Bu_3SnLi (9.95 mmol) in THF (15.0 mL) at 0 °C. The resulted reaction mixture was stirred at 0 °C for 1.5 h, quenched with water, and extracted with EtOAc (3 x 50.0 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and was purified by short column on SiO_2 (Hexanes:EtOAc, 25:1) to obtain the crude product (117 mg, 4.0%) as a colorless oil. To a solution of the above product (117 mg, 0.137 mmol) in anhydrous THF (3.00 mL), TBAF solution (0.40 mL, 4.0 mmol, 1.00 M in THF) was added under N_2. The reaction mixture was stirred at rt 12 h and concentrated under vacuum. The residue was dissolved in pyridine/Ac_2O mixture (3:1, 4.00 mL) and stirred 12 h. After removal of the volatiles, the crude mixture was quenched with water, extracted with EtOAc (3 x 50.0 mL) and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 50:1) to obtain **S1** (49.0 mg, 54%) as a colorless oil: $[\alpha]_D^{22}$ = -0.7 (c = 3.90, $CHCl_3$); IR (ATR) ν = 3033, 2955, 1745, 1596, 1499, 1458, 1368, 1290, 1249, 1097, 1033, 832, 743, 702, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 - 7.27 (m, 10H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.75 - 4.59 (m, 3H), 4.31 (dd, *J* = 11.6, 2.2 Hz, 1H), 4.16 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.67 - 3.54 (m, 2H), 3.38 (dd, *J* = 9.6, 8.5 Hz, 1H), 3.26 (ddd, *J* = 9.6, 5.2, 2.1 Hz, 1H), 2.15 (ddd, *J* = 13.0, 5.0, 2.0 Hz, 1H), 2.01 (s, 3H), 1.82 (td, *J* = 13.2, 10.7 Hz, 1H), 1.61 - 1.42 (m, 6H), 1.37 - 1.25 (m, 6H), 1.01 - 0.78 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 138.8, 138.5, 134.9, 129.8, 128.6 (2), 128.3, 127.9, 127.8 (2), 83.0, 80.4, 79.0, 75.3, 71.6, 70.7, 64.4, 36.8, 29.2, 27.5, 21.0, 13.8, 8.8; HRMS (ESI) *m/z* calcd for $C_{34}H_{52}O_5SnNa$ $[M + Na]^+$ 683.2742, found 683.2750.



S2

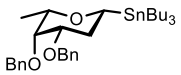
(3,4,6-Tri-*O*-(4-methoxybenzyl)-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane (S2). To a solution of (2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane (72.0 mg, 0.165 mmol) in THF (2.00 mL) was added KHMDS (1.50 mL, 0.750 mmol, 0.5 M in PhMe) under N_2 at room temperature. After stirring for 0.5 h, 4-methoxybenzyl chloride (0.660 mmol, 0.089mL) was added. The resulted reaction mixture was stirred at r.t. for 8 h, quenched with water, and extracted with EtOAc (3 x 50.0 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and was purified by short column on SiO_2 (Hexanes:EtOAc, 20:1) to afford **S2** (109 mg, 83%) as a white foam: $[\alpha]_D^{23}$ = -1.16 (c = 1.50, $CHCl_3$); IR (ATR) ν = 2955, 2929, 2854, 1614, 1517, 1465, 1361, 1305, 1253, 1176, 1097, 1041, 825 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 3H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.19 - 7.12 (m, 2H), 6.90 - 6.80 (m, 6H), 4.81 (d, *J* = 10.5 Hz, 1H), 4.67 - 4.59 (m, 2H), 4.59 - 4.52 (m, 2H), 4.47 (d, *J* = 11.8 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.66 - 3.48

(m, 4H), 3.42 (t, J = 9.0 Hz, 1H), 3.20 (dt, J = 9.4, 3.3 Hz, 1H), 2.15 - 2.06 (m, 1H), 1.81 (td, J = 13.2, 10.5 Hz, 1H), 1.50 (ddd, J = 6.7, 4.9, 3.4 Hz, 6H), 1.36 - 1.25 (m, 6H), 1.02 - 0.80 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 131.2, 129.8, 129.4, 129.2, 113.9 (2), 113.8, 83.3, 82.8, 79.1, 77.4, 74.8, 73.2, 71.4, 70.8, 69.9, 55.4, 55.4, 37.2, 29.3, 27.5, 13.9, 8.8; HRMS (ESI) *m/z* calcd for $C_{42}H_{62}O_7SnNa$ $[M + Na]^+$ 821.3425, found 821.3441.



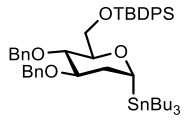
S3

(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)tri-*n*-butylstannane (S3). To a solution of *i*-Pr_2NH (1.9 mL, 13.8 mmol) in anhydrous and degassed THF (13.8 mL) was added *n*-BuLi (5.34 mL, 13.3 mmol, 2.5 M in hexanes) at -78°C. After stirring for 15 min, to the reaction mixture Bu_3SnH (3.84 mL, 4.16 g, 14.3 mmol) was added and stirred for another 15 min, then allowed to warm up to 0 °C. A solution of 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-galactopyranosyl chloride (2.08 g, 4.60 mmol) in anhydrous THF (27.6 mL) was added at 0 °C. After stirring at 0 °C for 1.5 h, the reaction was quenched with H_2O (50.0 mL) and extracted with EtOAc (3 × 30.0 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 to 30:1) to afford **S3** (1.03 g, 31.1%) as a colorless oil: $[\alpha]_D^{23}$ = -1.0 (c = 38.1, $CHCl_3$); IR (ATR) ν = 3033, 2959, 2925, 2854, 1499, 1458, 1361, 1208, 1100, 1030, 881, 735, 698, 601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.27 (m, 15H), 5.03 (d, J = 11.8 Hz, 1H), 4.69 - 4.63 (m, 3H), 4.55 - 4.45 (m, 2H), 3.95 - 3.92 (m, 1H), 3.80 - 3.70 (m, 1H), 3.64 - 3.51 (m, 3H), 3.44 -3.39 (m, 1H), 2.50 - 2.38 (m, 1H), 1.86 - 1.80 (m, 1H), 1.64 - 1.50 (m, 6H), 1.39 - 1.32 (m, 6H), 0.98 - 0.89 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 138.9, 138.5, 128.5, 128.4, 128.1, 127.9, 127.7, 127.6(2), 127.4, 127.2, 80.9, 80.3, 77.6, 76.7, 74.1, 73.9, 73.6, 71.7, 70.2, 70.0, 32.5, 29.2, 27.5, 13.8, 8.7; HRMS (ESI) *m/z* calcd for $C_{39}H_{56}O_4SnNa$ $[M + Na]^+$ 731.3107, found 731.3118.



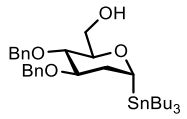
S4

(2,3,4-Tri-*O*-benzyl-β-L-fucopyranosyl)tri-*n*-butylstannane (S4). To a solution of *i*-Pr_2NH (1.56mL, 11.13 mmol) in anhydrous THF (15.0 mL) was added *n*-BuLi (4.30 mL, 10.8 mmol, 2.5 M in hexane) at -78 °C. After stirring for 15 min, Bu_3SnH (3.26 mL, 11.5 mmol) was added at -78 °C. The reaction mixture was stirred another 15 min, then warmed up to 0 °C. To a solution of 3,4-di-*O*-benzyl-L-fucal (1.22 mg, 3.71 mmol) in $CHCl_3$/PhMe (2:1, 15.0 mL) was added $SOCl_2$ (0.5 mL). The resulting solution was stirred at room temperature for 0.5 h and concentrated under vacuum. The residue was dissolved in anhydrous THF and added dropwise to the above stannane mixture at 0 °C. After stirring for 1.5 h, the reaction mixture was quenched with water (30.0 mL) and extracted with EtOAc (3 × 20.0 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 25:1) to afford **S4** (320 mg, 14%) as a colorless oil: $[\alpha]_D^{23}$ = +1.3 (c = 2.55, $CHCl_3$); IR (ATR) ν = 3033, 2959, 2925, 2854, 1499, 1458, 1380, 1361, 1212, 1182, 1111, 1059, 1033, 962, 843, 739, 702, 601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$)δ 7.45 - 7.29 (m, 10H), 5.02 (d, J = 11.9 Hz, 1H), 4.69 (d, J = 11.9 Hz, 1H), 4.64 (d, J = 2.4 Hz, 2H), 3.69 (dd, J = 13.2, 2.0 Hz, 1H), 3.62 - 3.57 (m, 1H), 3.50 (ddd, J = 11.4, 4.6, 2.5 Hz, 1H), 3.29 - 3.20 (m, 1H), 2.36 (td, J = 12.9, 11.4 Hz, 1H), 1.82 - 1.72 (m, 1H), 1.56 - 1.48 (m, 6H), 1.36 - 1.28 (m, 6H), 1.15 (d, J = 6.4 Hz, 3H), 0.91 (q, J = 7.1 Hz, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 139.1, 128.5, 128.2, 127.8, 127.6, 127.4, 127.2, 81.0, 78.0, 76.9, 74.3, 71.5, 70.0, 32.1, 29.2, 27.5, 18.2, 13.9, 8.8; HRMS (ESI) *m/z* calcd for $C_{32}H_{50}O_3SnNa$ $[M + Na]^+$ 625.2686, found 625.2689.



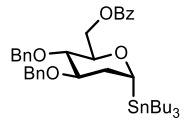
S5

(3,4-Di-*O*-benzyl-6-(*tert*-butyldiphenylsilyl)-2-deoxy-α-D-glucopyranosyl)tri-*n*-butylstannane (S5). To a solution of *i*-Pr_2NH (1.45 mL, 10.3 mmol) in anhydrous THF (15.0 mL), *n*-BuLi (6.20 mL, 9.95 mmol, 1.6 M in hexane) was added at 0 °C. After stirring for 15 min, Bu_3SnH (3.00 mL, 10.6 mmol) was added, and the reaction mixture was stirred at -78 °C for another 15 min. The solution of Bu_3SnLi in THF was warmed up to 0 °C. To a solution of 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-D-glucose (2.00 g, 3.43 mmol) in $CHCl_3$/PhMe (2:1, 15.0 mL) was added $SOCl_2$ (1.80 mL, 24.8 mmol). The resulting solution was stirred at rt for 0.5 h and concentrated under vacuum. The residue was dissolved in THF (20.0 mL) and added dropwise via syringe to the above freshly prepared solution of Bu_3SnLi (9.95 mmol) in THF (15.0 mL) at 0 °C. The resulted reaction mixture was stirred at 0 °C for 1.5 h, quenched with water, and extracted with EtOAc (3 x 50.0 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and was purified by short column on SiO_2 (Hexanes:EtOAc, 20:1) to afford **S5** (879 mg, 33%) as a colorless oil: $[\alpha]_D^{30}$ = +16.0 (c = 6.95, $CHCl_3$); IR (ATR) ν = 3033, 2959, 2929, 2858, 1458, 1432, 1365, 1115, 1093, 1030, 870, 743, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 - 7.62 (m, 4H), 7.46 - 7.26 (m, 13H), 7.25 - 7.16 (m, 3H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.76 - 4.49 (m, 4H), 3.88 (d, *J* = 3.2 Hz, 2H), 3.63 - 3.48 (m, 2H), 3.14 (dt, *J* = 7.7, 3.2 Hz, 1H), 2.28 - 2.08 (m, 2H), 1.55 - 1.34 (m, 6H), 1.33 - 1.20 (m, 6H), 1.05 (d, *J* = 3.7 Hz, 9H), 0.97 - 0.74 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 139.0, 138.8, 136.0, 135.8, 134.0, 133.6, 129.6, 129.6, 128.6, 128.4, 127.9, 127.8, 127.7, 127.6, 127.5, 80.9, 80.6, 78.7, 74.9, 71.6, 71.5, 63.8, 36.4, 29.3, 27.5, 27.0, 19.4, 13.8, 10.1; HRMS (ESI) *m/z* calcd for $C_{48}H_{68}O_4SiSnNa$ $[M + Na]^+$ 879.3807, found 879.3813.



S6

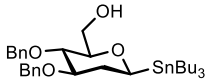
(3,4-Di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)tri-*n*-butylstannane (S6). To a solution of the **S5** (800 mg, 0.936 mmol) in anhydrous THF (3.00 mL), TBAF solution (3.70 mL, 3.70 mmol, 1.00 M in THF) was added under N_2. The reaction mixture was stirred at rt 12 h. The crude mixture purified by column chromatography on SiO_2 (Hexanes:EtOAc, 20:1) to obtain **S6** (450 mg, 78%) as a colorless oil: $[\alpha]_D^{30}$ = +4.1 (c = 18.9, $CHCl_3$); IR (ATR) ν = 3469, 3033, 2959, 2921, 2854, 1499, 1458, 1365, 1179, 1089, 1030, 966, 877, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.27 (m, 10H), 4.95 (d, *J* = 11.3 Hz, 1H), 4.74 - 4.46 (m, 4H), 3.81 - 3.51 (m, 3H), 3.39 (t, *J* = 8.8 Hz, 1H), 3.08 (ddd, *J* = 9.1, 4.8, 3.1 Hz, 1H), 2.24 - 2.06 (m, 2H), 1.83 (m, 1H), 1.54 - 1.37 (m, 6H), 1.35 - 1.24 (m, 6H), 0.96 - 0.80 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.6, 128.6, 128.5, 128.1, 127.8, 127.8, 80.6, 79.5, 79.0, 75.0, 71.9, 71.4, 62.9, 36.3, 29.3, 27.6, 13.8, 10.1; HRMS (ESI) *m/z* calcd for $C_{32}H_{50}O_4SnNa$ $[M + Na]^+$ 641.2635, found 641.2653.



S7

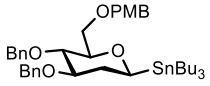
(3,4-Di-*O*-benzyl-6-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl)tri-n-butylstannane (S7). To a solution of (3,4-Di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)tri-*n*-butylstannane **S6** (224 mg, 0.36 mmol) in pyridine (3

ml), benzoyl chloride (0.085 ml, 0.73 mmol) was added. The reaction mixture was stirred at rt 12 h. After removal of solvents, the crude mixture was quenched with water, extracted with EtOAc (3 x 50.0 mL) and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 20:1) to obtain **S7** (142 mg, 55%) as a colorless oil:$[\alpha]_D^{29}$ = +4.2 (c = 2.50, $CHCl_3$); IR (ATR) ν = 3067, 3033, 2959, 2925, 2973, 1726, 1458, 1275, 1182, 1097, 1074, 1030, 968, 739, 717, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 - 7.99 (m, 2H), 7.58 - 7.50 (m, 1H), 7.41 - 7.19 (m, 12H), 4.96 (d, *J* = 11.1 Hz, 1H), 4.77 - 4.46 (m, 6H), 3.70 - 3.58 (m, 1H), 3.54 - 3.35 (m, 2H), 2.31 - 2.11 (m, 2H), 1.54 - 1.38 (m, 6H), 1.34 - 1.17 (m, 6H), 1.07 - 0.62 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 138.5, 138.4, 133.1, 129.9, 128.6, 128.5, 128.4, 128.2, 127.9 (2), 80.6, 78.5, 74.9, 71.5, 64.6, 36.1, 29.2, 27.6, 13.8, 10.1; HRMS (ESI) *m/z* calcd for $C_{39}H_{54}O_5SnNa$ $[M + Na]^+$ 745.2891, found 745.2899.



S8

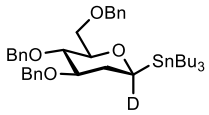
(3,4-Di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane (S8). To a solution of *i*-Pr_2NH (1.45 mL, 10.3 mmol) in anhydrous THF (15.0 mL), *n*-BuLi (6.20 mL, 9.95 mmol, 1.6 M in hexane) was added at 0 °C. After stirring for 15 min, Bu_3SnH (3.00 mL, 10.6 mmol) was added, and the reaction mixture was stirred at -78 °C for another 15 min. The solution of Bu_3SnLi in THF was warmed up to 0 °C. To a solution of 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-D-glucose (2.00 g, 3.43 mmol) in $CHCl_3$/PhMe (2:1, 15.0 mL) was added $SOCl_2$ (1.80 mL, 24.8 mmol). The resulting solution was stirred at rt for 0.5 h and concentrated under vacuum. The residue was dissolved in THF (20.0 mL) and added dropwise via syringe to the above freshly prepared solution of Bu_3SnLi (9.95 mmol) in THF (15.0 mL) at 0 °C. The resulted reaction mixture was stirred at 0 °C for 1.5 h, quenched with water, and extracted with EtOAc (3 x 50.0 mL). The combined organic layer was dried over Na_2SO_4, concentrated, and was purified by short column on SiO_2 (Hexanes:EtOAc, 30:1) to obtain the crude product (117 mg, 4.0%) as a colorless oil. To a solution of the above product (117 mg, 0.137 mmol) in anhydrous THF (3.00 mL), TBAF solution (0.40 mL, 4.0 mmol, 1.00 M in THF) was added under N_2. After stirring at rt for 12 h, the reaction was quenched with H_2O (50.0 mL) and extracted with EtOAc (3 × 30.0 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 to 20:1) to afford **S8** (84 mg, 98%) as a colorless oil: $[\alpha]_D^{29}$ = -1.4 (c = 4.60, $CHCl_3$); IR (ATR) ν = 3591, 3461, 3033, 3067, 2959, 2929, 2858, 1458, 1365, 1212, 1104, 1078, 1033, 870, 825, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 - 7.30 (m, 10H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.79 - 4.61 (m, 3H), 3.82 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.72 - 3.53 (m, 3H), 3.40 (t, *J* = 9.1 Hz, 1H), 3.16 (ddd, *J* = 9.4, 5.1, 3.1 Hz, 1H), 2.15 (ddd, *J* = 13.1, 5.0, 2.0 Hz, 1H), 1.81 (td, *J* = 13.3, 10.7 Hz, 2H), 1.61 - 1.44 (m, 6H), 1.37 - 1.24 (m, 6H), 1.01 - 0.77 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 138.6, 134.9, 129.8, 128.6, 128.2, 127.9, 127.8, 127.7, 82.7, 82.4, 79.5, 75.3, 71.7, 70.9, 63.1, 37.0, 29.3, 27.5, 13.8, 8.8; HRMS (ESI) *m/z* calcd for $C_{32}H_{50}O_4SnNa$ $[M + Na]^+$ 641.2635, found 641.2650.



S9

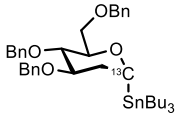
(3,4-Di-*O*-benzyl-6-(4-methoxybenzyl)-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane (S9). To a solution of (3,4-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane **S8** (124 mg, 0.2 mmol) in anhydrous THF (10.0 mL), KHMDS (0.60 mL, 0.300 mmol, 0.5 M in PhMe) was added under N_2 at rt. After stirring for 0.5 h, 4-methoxybenzyl chloride (0.400 mmol, 0.054 mL) was added to the reaction mixture and stirred 12 h. The crude mixture was purified by chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1)

to afford product **S9** (129.9 mg, 88%) as a light yellow oil: $[\alpha]_D^{28}$ = -0.7 (c = 3.95, $CHCl_3$); IR (ATR) ν = 3033, 2955, 2925, 2854, 1614, 1518, 1458, 1365, 1305, 1249, 1179, 1104, 825, 739, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.20 (m, 13H), 6.92 - 6.80 (m, 2H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.75 - 4.44 (m, 5H), 3.79 (s, 3H), 3.71 - 3.42 (m, 5H), 3.23 (dt, *J* = 9.3, 3.2 Hz, 1H), 2.13 (ddd, *J* = 13.2, 4.9, 2.0 Hz, 1H), 1.84 (td, *J* = 13.2, 10.4 Hz, 1H), 1.57 - 1.45 (m, 6H), 1.39 - 1.22 (m, 6H), 1.09 - 0.74 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 139.0, 138.9, 131.1, 129.2, 128.5, 128.4, 128.1, 127.8, 127.7, 113.8, 83.3, 83.0, 79.4, 75.2, 73.2, 71.7, 70.8, 69.8, 55.4, 37.1, 29.2, 27.5, 13.9, 8.8; HRMS (ESI) *m/z* calcd for $C_{40}H_{58}O_5SnNa$ $[M + Na]^+$ 761.3213, found 761.3231.



S10

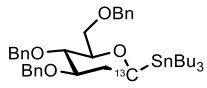
(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-(1-D)glucopyranosyl)tri-*n*-butylstannane (S10). To a solution of *i*-Pr_2NH (0.88 mL, 6.33 mmol) in anhydrous THF (15.0 mL) *n*-BuLi (2.5 mL, 6.12 mmol, 2.5 M in hexane) was added at -78 ºC. The reaction mixture was stirred at -78 °C for 15 min followed by Bu_3SnH (1.8 5 mL, 6.54 mmol) and stirred at -78 °C for another 15 min, then allowed to warm up to 0 °C. A solution of 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl chloride (920 mg, 2.11 mmol) in anhydrous THF (30.0 mL) was added at 0 °C. After stirring at 0 °C for 1.5 h, the reaction was quenched with H_2O (30.0 mL) and extracted with EtOAc (3 × 20.0 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 25:1) to afford **S10** (603 mg, 40%) as a colorless oil: $[\alpha]_D^{23}$ = -1.0 (c = 2.10, $CHCl_3$); IR (ATR) ν = 3033, 2959, 2925, 2854, 1499, 1458, 1365, 1201, 1097, 873, 739, 702, 601 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 - 7.26 (m, 15H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.76 - 4.59 (m, 4H), 4.55 (d, *J* = 12.3 Hz, 1H), 3.71 (d, *J* = 3.3 Hz, 2H), 3.62 - 3.45 (m, 2H), 3.24 (dt, *J* = 9.1, 3.2 Hz, 1H), 2.20 - 2.04 (m, 1H), 1.84 (dd, *J* = 13.1, 10.3 Hz, 1H), 1.57 - 1.48 (m, 6H), 1.37 - 1.25 (m, 6H), 1.02 - 0.83 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ139.1, 139.0, 138.9, 128.5, 128.5, 128.4, 128.2, 127.8, 127.7, 127.6, 127.4, 83.2, 83.0, 79.4, 77.4, 75.3, 73.5, 71.7, 70.2, 37.0, 29.3, 27.5, 13.9, 8.8; HRMS (ESI) *m/z* calcd for $C_{39}H_{55}DO_4SnNa$ $[M + Na]^+$ 732.3170, found 732.3180.



S11

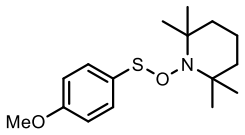
(3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-(1-^{13}C)glucopyranosyl)tri-*n*-butylstannane (S11). To a solution of *i*-Pr_2NH (1.05 mL, 7.50 mmol) in anhydrous and degassed THF (7.50 mL), *n*-BuLi (4.50 mL, 11.25 mmol, 2.5 M in hexanes) was added dropwise at -78°C. The reaction mixture was stirred at -78 °C for 15 min followed by Bu_3SnH (2.09 mL, 2.26 g, 7.75 mmol) and stirred at -78 °C for another 15 min, then allowed to warm up to 0 °C. A solution of 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-(1-^{13}C)glucopyranosyl chloride (1.13 g, 2.50 mmol) in anhydrous THF (15 mL) was added to the above stannane mixture at 0 °C. After stirring at 0 °C for 1.5 h, the reaction was quenched with H_2O (30.0 mL) and extracted with EtOAc (3 × 20.0 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 to 10:1) to afford **S11** (0.669 g, 38%) as a light yellow oil: $[\alpha]_D^{24}$ = +5.3 (c = 12.3, $CHCl_3$); IR (ATR) ν = 3033, 2959, 2921, 2854, 1499, 1458, 1363, 1074, 1030, 881, 735, 698, 598 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 - 7.20 (m, 15H), 4.93 (d, *J* = 11.1 Hz, 1H), 4.75 - 4.45 (m, 5H), 3.81 - 3.45 (m, 4H), 3.22 - 3.16 (m, 1H), 2.23 - 2.19 (m, 2H), 1.60 - 1.42 (m, 6H), 1.37 - 1.25 (m, 6H), 1.00 - 0.70 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 138.8, 138.4, 128.5, 128.4, 127.9, 127.8, 127.6, 80.8, 79.4, 78.9,

74.3, 74.2, 73.6, 72.0, 69.8, 69.7, 64.9, 29.2, 27.6, 13.8, 10.1; HRMS (ESI) *m/z* calcd for $C_{38}{}^{13}CCH_{56}O_4SnNa$ $[M + Na]^+$ 732.3133, found 732.3143.



S12

(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-(1-^{13}C)glucopyranosyl)tri-*n*-butylstannane (S12). To a solution of *i*-Pr_2NH (1.05 mL, 7.50 mmol) in anhydrous THF (7.50 mL) was added *n*-BuLi (2.90 mL, 7.25 mmol, 2.5 M in hexanes) by dropwise at -78°C. After stirring at for 15 min, Bu_3SnH (2.09 mL, 2.26 g, 7.75 mmol) was added at -78 °C. The reaction mixture was stirred for another 15 min, then allowed to warm up to 0 °C. A solution of 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-(1-^{13}C)glucopyranosyl chloride (1.13 g, 2.50 mmol) in anhydrous THF (15 mL) was added to the above stannane mixture at 0 °C. After stirring at 0 °C for 1.5 h, the reaction mixture was quenched with H_2O (30.0 mL) and extracted with EtOAc (3 × 20.0 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 to 30:1) to afford **S12** (0.298 g, 17%) as a colorless oil: $[\alpha]_D^{25}$ = -0.9 (c = 4.70, $CHCl_3$); IR (ATR) ν = 3033, 2959, 2925, 2854, 1499, 1458, 1361, 1208, 1100, 1030, 881, 735, 698, 601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 - 7.27 (m, 15H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.81 - 4.44 (m, 5H), 3.75 - 3.73 (d, *J* = 3.2 Hz, 2H), 3.68 (ddd, *J* = 137.2, 13.2, 1.7 Hz, 1H), 3.63 - 3.48 (m, 2H), 3.33 - 3.18 (m, 1H), 2.19 -2.13 (m, 1H), 1.98 - 1.82 (m, 1H), 1.70 - 1.46 (m, 6H), 1.47 - 1.32 (m, 6H), 1.12 - 0.75 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 139.0, 138.9, 128.5, 128.4 (2), 128.1, 127.8, 127.7, 127.6, 127.4, 83.3-83.2 (d), 83.0 (d), 79.3, 75.2, 73.5-73.3 (m), 71.7, 70.8, 68.3 - 68.2 (m), 29.2, 27.5, 13.9, 8.8 - 8.7 (d); HRMS (ESI) *m/z* calcd for $C_{38}{}^{13}CCH_{56}O_4SnNa$ $[M + Na]^+$ 732.3133, found 732.3146.

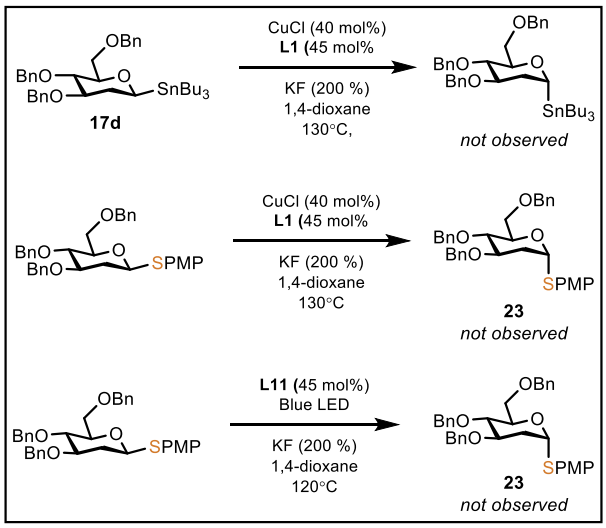


S13

1-(((4-Methoxyphenyl)thio)oxy)-2,2,6,6-tetramethylpiperidine (S13). 1,2-Bis(4-methoxyphenyl)disulfane **18** (27.8 mg, 0.100 mmol) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (31.3 mg, 0.200 mmol) were added to a one-dram vial with a screw-top septum, and the vial was then evacuated and refilled with N_2 (3x). Anhydrous dioxane (2.00 mL) were added and the reaction mixture was stirred at room temperature under 5W blue LED irradiation for 12 h and afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **S13** (14.5 mg, 49%) as a light yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 - 7.55 (m, 2H), 6.98 - 6.93 (m, 2H), 3.84 (s, 3H), 1.72 - 1.53 (m, 15H), 0.93 - 0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 141.6, 127.6, 114.1, 55.6, 43.7, 41.6, 35.5, 32.6, 28.9, 28.1, 17.4. Characterization data matched the literature report.[7]

6. Additional Mechanistic Experiments

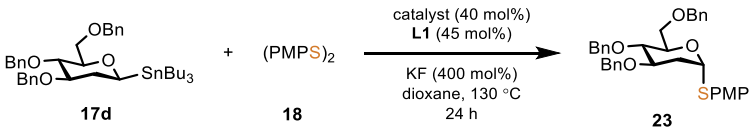
6.1. Anomerization experiments with thioglycosdies and anomeric stannanes



Reaction conditions: **22** (0.100 mmol, 1.0 equiv), **17d** (1.5 equiv), CuCl (40 mol%), **L1** (45 mol%) and 1,4-dioxane (2.0 mL) under N_2, 120 or 130 °C, 24 h, blue LED or without blue LED, yield of isolated product. Anomeric selectivities determined by ^{1}H NMR analysis of unpurified reaction mixtures.

No change in anomeric purity was observed for anomeric stannanes and thioglycosides upon exposure to the optimized reaction conditions.

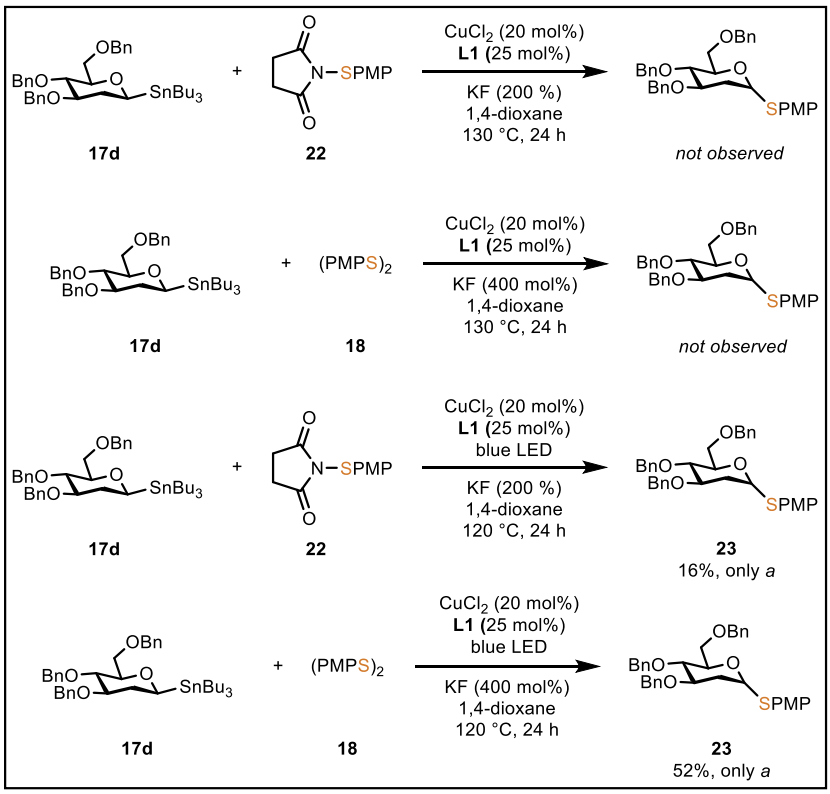
6.2. Thioglycosylations with late transition metals



Entry	Metal	Light	Yield	α:β
1	$NiCl_2(DME)$	No	23%	Only α
2	$PdCl_2(MeCN)_2$	No	28%	Only α
3	$AuCl(PPh_3)_3$	No	16%	Only α
4	$CoCl_2(PPh_3)_2$	No	N.D.	N.A.
5	$NiCl_2(DME)$	Yes	18%	Only α
6	$PdCl_2(MeCN)_2$	Yes	16%	Only α
7	$AuCl(PPh_3)_3$	Yes	45%	Only α
8	$CoCl_2(PPh_3)_2$	Yes	N.D.	N.A.

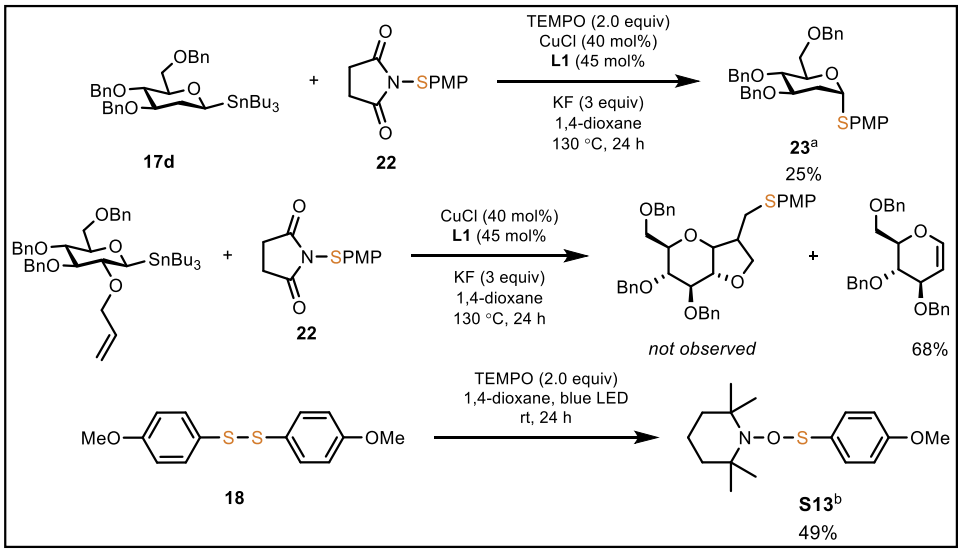
Reaction conditions: **18** (0.100 mmol, 1.0 equiv), **17d** (1.5 equiv), Catalyst (40 mol%), **L1** (45 mol%) and 1,4-dioxane (2.0 mL) under N_2, 130 °C, 24 h, blue LED or without blue LED, yield of isolated product. Anomeric selectivities determined by ^{1}H NMR analysis of unpurified reaction mixtures.

6.3. Probing the role of Cu(II) in thermal and photochemical thioglycosylations



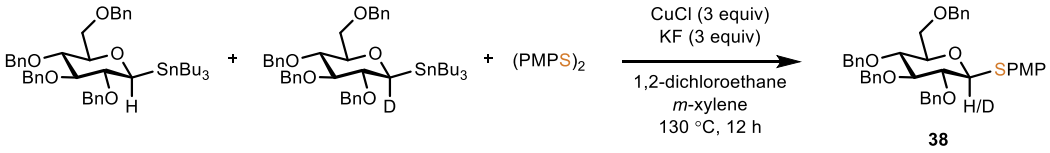
General reaction conditions: sulfur electrophile (0.100 mmol, 1.0 equiv), **17d** (1.5 equiv), $CuCl_2$ (20 - 40 mol%), **L1** (25 - 45 mol%) and 1,4-dioxane (2.0 mL) under N_2, blue LED or without blue LED, 130 °C, 24 h, yield of isolated product. Anomeric selectivities determined by ^{1}H NMR analysis of unpurified reaction mixtures.

6.4. Radical trapping experiments

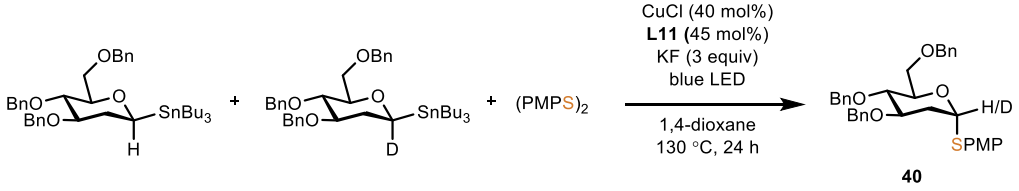


General reaction conditions: **22** (0.100 mmol, 1.0 equiv), stannanes (1.5 equiv), CuCl (40 mol%), **L1** (45 mol%), KF (3 equiv), and 1,4-dioxane (2.0 mL) under N_2, 130 °C, 24 h, yield of isolated product. Anomeric selectivities determined by ^{1}H NMR analysis of unpurified reaction mixtures. [a] (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (2 equiv) was used. [b] **18** (0.100 mmol, 1.0 equiv), (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (2 equiv), and 1,4-dioxane (2.0 mL) under N_2, 23 °C, 24 h.

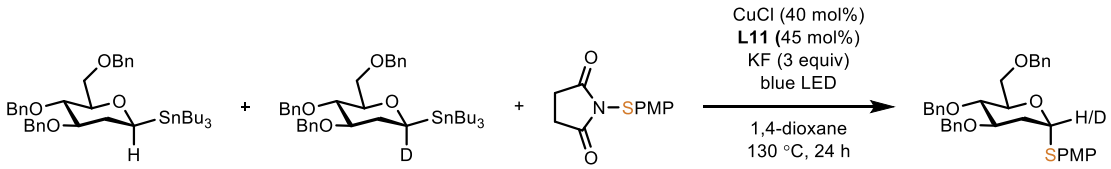
6.5. KINETIC ISOTOPE EFFECT EXPERIMENTS



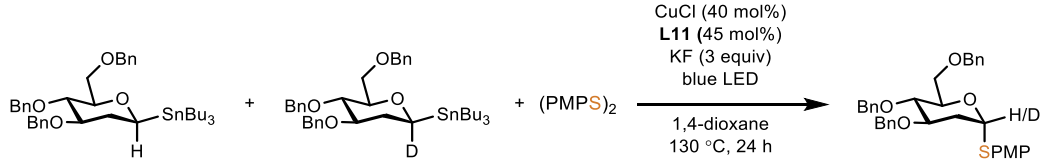
According to the general protocol A, (2,3,4,6-tri-*O*-benzyl-β-D)glucopyranosyl)tri-*n*-butylstannane[1] (81.4 mg, 0.100 mmol), (2,3,4,6-tri-*O*-benzyl-β-D-(1-D)glucopyranosyl)tri-*n*-butylstannane[1] (81.5 mg, 0.100 mmol), 1,2-bis(4-methoxyphenyl)disulfane **18** (83.4 mg, 0.300 mmol), KF (17.4 mg, 0.300 mmol), and CuCl (30.0 mg, 0.300 mmol) were added to anhydrous 1,2-dichloroethane and *m*-xylene (2:1, 3.00 mL). The reaction mixture was stirred under N_2 at 130 °C for 12 h. The KIE value represents the average of two separate runs. Based on the ^{1}H NMR results, an average KIE value of 1.03 was determined.



According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D)glucopyranosyl)tri-*n*-butylstannane[1] (70.7 mg, 0.100 mmol), (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-(1-D)glucopyranosyl)tri-*n*-butylstanne **S10** (70.8 mg, 0.100 mmol), 1,2-bis(4-methoxyphenyl)disulfane **18** (83.4 mg, 0.300 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred under N_2 at 130 °C for 24 h. The KIE value represents the average of two separate runs. Based on the ^{1}H NMR results, an average KIE value of 0.83 was determined.

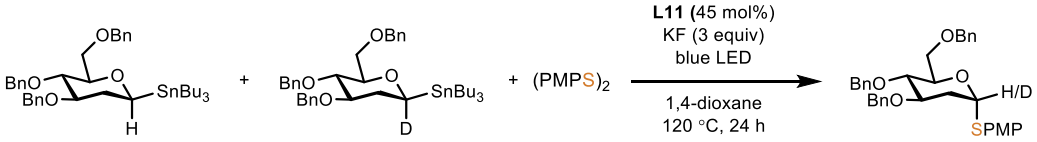


According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D)glucopyranosyl)tri-*n*-butylstannane[1] (70.7 mg, 0.100 mmol), (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-(1-D)glucopyranosyl)tri-*n*-butylstanne **S10** (70.8 mg, 0.100 mmol), 1-((4-methoxyphenyl)thio)pyrrolidine-2,5-dione **22** (71.1 mg, 0.300 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred under N_2 at 130 °C for 24 h. The KIE value represents the average of two separate runs. Based on the ^{1}H NMR results, an average KIE value of 0.90 was determined.

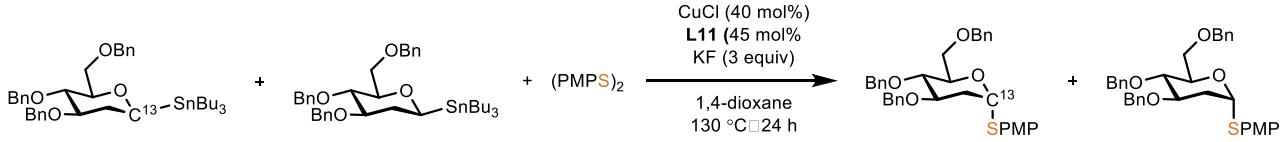


According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D)glucopyranosyl)tri-*n*-butylstannane[1] (70.7 mg, 0.100 mmol), (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-(1-D)glucopyranosyl)tri-*n*-butylstanne **S10** (70.8

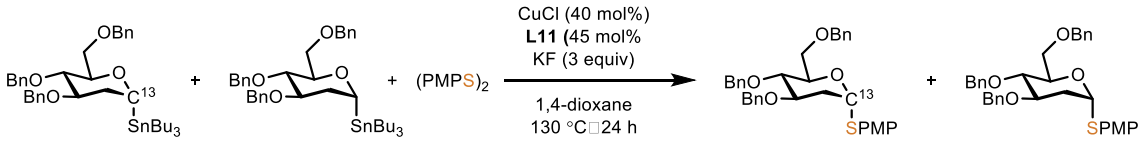
mg, 0.100 mmol), 1,2-bis(4-methoxyphenyl)disulfane **18** (83.4 mg, 0.300 mmol), KF (17.4 mg, 0.300 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 24 h. The KIE value represents the average of two separate runs. Based on the ^{1}H NMR results, an average KIE value of 0.92 was determined.



According to the general protocol C, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D)glucopyranosyl)tri-*n*-butylstannane[1] (70.7 mg, 0.100 mmol), (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-(1-D)glucopyranosyl)tri-*n*-butylstananne **S10** (70.8 mg, 0.100 mmol), 1,2-bis(4-methoxyphenyl)disulfane **18** (83.4 mg, 0.300 mmol), KF (17.4 mg, 0.300 mmol), 24,4′-di-*tert*-butyl-2,2′-dipyridyl (12.1 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred at 120 °C under 5W blue LED irradiation for 24 h. The KIE value represents the average of two separate runs. Based on the ^{1}H NMR results, an average KIE value of 0.74 was determined.

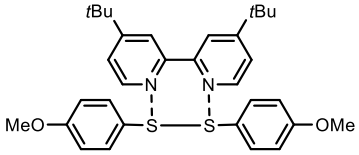


According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)tri-*n*-butylstannane[1] (70.7 mg, 0.100 mmol), (3,4,6-tri-*O*-benzyl-2-deoxy-β-D-(1-^{13}C)glucopyranosyl)tri-*n*-butylstannane **S11** (70.8 mg, 0.100 mmol), 1,2-bis(4-methoxyphenyl)disulfane **18** (83.4 mg, 0.300 mmol), KF (17.4 mg, 0.300 mmol), 2,2′:6′,2″-terpyridine (18.7 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred under N_2 at 130 °C for 12 h. The KIE value represents the average of two separate runs. Based on the ^{1}H NMR results, an average KIE value of 1.031 was determined.



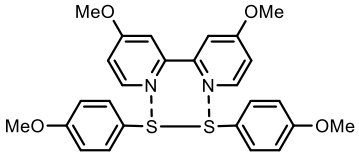
According to the general protocol B, (3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)tri-*n*-butylstannane[1] (70.7 mg, 0.100 mmol), (3,4,6-tri-*O*-benzyl-2-deoxy-α-D-(1-^{13}C)glucopyranosyl)tri-*n*-butylstannane **S12** (70.8 mg, 0.100 mmol), 1,2-bis(4-methoxyphenyl)disulfane **18** (83.4 mg, 0.300 mmol), KF (17.4 mg, 0.300 mmol), 2,2′:6′,2″-terpyridine (18.7 mg, 0.045 mmol), and CuCl (4.00 mg, 0.040 mmol) were added to anhydrous 1,4-dioxane (2.00 mL). The reaction mixture was stirred under N_2 at 130 °C for 12 h. The KIE value represents the average of two separate runs. Based on the ^{1}H NMR results, an average KIE value of 1.033 was determined.

6.6. NMR ANALYSIS OF DISULFIDE-BIPYRIDINE MIXTURES



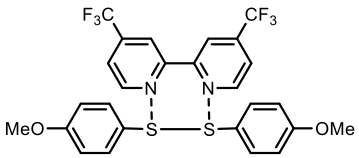
Ratio of 2,2'-bipyridine to **18**	^{1}H NMR shift of *Me*O in disulfide*
0	3.8238
25:1	3.8181
50:1	3.8123
75:1	3.8069
100:1	3.8008
200:1	3.7778
300:1	3.7520
400:1	3.7265
500:1	3.7046
750:1	3.6500
1000:1	3.5929

*300 MHz NMR, $CDCl_3$, 23 °C



Ratio of 2,2'-bipyridine to **18**	^{1}H NMR shift of *Me*O in disulfide
0	3.8238
25:1	3.8165
50:1	3.8096
75:1	3.8015
100:1	3.7941

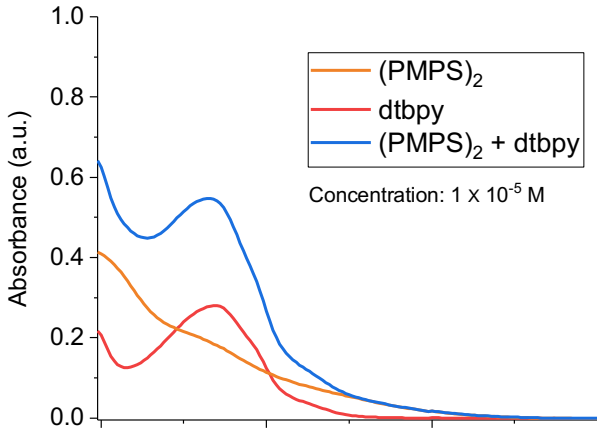
*300 MHz NMR, $CDCl_3$, 23 °C



Ratio of 2,2'-bipyridine to **18**	^{1}H NMR shift of *Me*O in disulfide
0	3.8238
25:1	3.8220
50:1	3.8196
75:1	3.8169

*300 MHz NMR, $CDCl_3$, 23 °C

6.7. UV-vis Absorption Spectra



Solutions in $CHCl_3$, 23 °C

7. Computational Details

All DFT calculations were performed with the Gaussian 16 software package.[7] Geometry optimizations of all the minima and transition states were carried out at the B3LYP[8] level of theory with additional Grimme's D3 dispersion correction (Becke-Johnson damping)[9] using the def2-SVP basis set.[10] Vibrational frequencies were computed at the same level to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K, as well as to check whether each optimized structure is a transition state or not. The single-point energies were computed at the same level of theory, combined with def2-TZVPP basis set and SMD solvation model[11] for 1,4-dioxane using the optimized structures. The 3D diagrams of molecules were generated using CYLView.[12] In addition, to correct the Gibbs free energies under pressure of 1 atm to the standard state in solution (1 mol/L), a correction of $RT\ln(c_s/c_g)$ (about 1.89 kcal/mol) is added to energies of all species. c_s is the standard molar concentration in solution (1 mol/L), c_g is the standard molar concentration in gas phase (0.0446 mol/L), and R is the gas constant.

Table S1. Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures for all the figures calculated at the B3LYP-D3(BJ)/def2-TZVPP-SMD(1,4-dioxane)//B3LYP-D3(BJ)/def2-SVP level of theory.*

Structures	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
int1 (*doublet*)	0.402938	0.432857	0.338549	−3373.739683	−3373.306826	−3373.401134	
int2 (*doublet*)	0.257714	0.273516	0.214856	−654.293904	−654.020388	−654.079048	
TS3 (*triplet*)	0.661809	0.706908	0.581810	−4028.045108	−4027.338200	−4027.463298	283.9*i*
int4 (*CSS*)	0.309719	0.332599	0.256694	−2743.737570	−2743.404971	−2743.480876	
P_{Ax} (*CSS*)	0.353818	0.375738	0.302092	−1284.348409	−1283.972671	−1284.046317	

TS5 (*triplet*)	0.662605	0.708128	0.579847	−4028.051988	−4027.343860	−4027.472141	24.0*i*
int6 (*CSS*)	0.665717	0.710865	0.586529	−4028.063258	−4027.352393	−4027.476729	
TS7 (*CSS*)	0.663411	0.708761	0.582261	−4028.043643	−4027.334882	−4027.461382	73.3*i*
TS8 (*triplet*)	0.660577	0.706156	0.577217	−4028.027753	−4027.321597	−4027.450536	385.8*i*
$\mathbf{P_{Eq}}$ (*CSS*)	0.353496	0.375504	0.301627	−1284.346847	−1283.971343	−1284.045220	
TS9 (*triplet*)	0.662364	0.707645	0.579510	−4028.022330	−4027.314685	−4027.442820	45.6*i*
int10 (*CSS*)	0.665186	0.710433	0.584677	−4028.055108	−4027.344675	−4027.470431	
TS11 (*CSS*)	0.663781	0.709101	0.581988	−4028.048124	−4027.339023	−4027.466136	162.9*i*

* Only the most stable spin states are listed here. CSS = closed-shell singlet.

Coordinates

int1 (*doublet*)

Cu	-0.14851400	1.71160700	2.29728000
S	2.10799700	1.42559000	2.41293900
C	2.58126200	1.98454000	0.80241300
C	3.38921100	3.12836400	0.64889300
C	2.14456900	1.31098700	-0.35638000
C	3.73695000	3.59101600	-0.62110500
H	3.72514500	3.65582600	1.54412600
C	2.49181400	1.77887300	-1.62430500
H	1.49262700	0.44350300	-0.25095600
C	3.28886000	2.92031300	-1.76497900
H	4.35983600	4.48433600	-0.71973100
H	2.12550300	1.25172800	-2.50879600
H	3.55948100	3.28488100	-2.75907700
N	-1.92345900	1.21404800	1.57273900
C	-2.07350600	1.05502600	0.22131600
C	-3.11239000	1.08908300	2.24577800
C	-3.53790000	0.73744200	-0.11017800
O	-1.17756000	1.16090300	-0.60402700
C	-4.23258800	0.73850700	1.25181500
O	-3.27788700	1.23199300	3.44665500
H	-3.58364000	-0.22566000	-0.64148600
H	-3.91524800	1.50211900	-0.80691400
H	-4.66296200	-0.23457900	1.53579300
H	-5.03888400	1.48175200	1.34811600
N	-0.69446200	3.03995000	3.93223800
C	-0.78079300	4.33905200	3.66822800
C	-1.05260000	2.51118500	5.09787700
C	-1.25026100	5.22984900	4.64554800
C	-0.38240700	4.71798000	2.28180600
C	-1.53347100	3.33359600	6.12606400
C	-1.62637200	4.70579500	5.88402300
C	-0.26612400	6.04693300	1.85947900
N	-0.15752800	3.69714000	1.43004400
H	-1.83565300	2.92330200	7.08921200
H	-2.00223300	5.37113100	6.66427500
C	0.07749800	6.30957500	0.53203000
C	0.14430400	3.94128900	0.15404800
H	0.18301200	7.34056200	0.18668700
C	0.27734900	5.24166000	-0.34010800
H	0.26612400	3.06521400	-0.48450700
H	0.53941300	5.39683400	-1.38735800
H	-0.43343500	6.86670100	2.55826500
H	-1.33844600	6.29818300	4.44879300

C	-0.88242400	1.03352900	5.18735300
C	-1.20823000	0.28943700	6.32658400
C	-0.16230600	-0.87390300	4.08169500
C	-1.00445800	-1.09047300	6.31364400
H	-1.62159100	0.77581000	7.20994100
C	-0.46908200	-1.68999400	5.17320000
H	0.27819100	-1.27650300	3.16454200
H	-1.26001100	-1.69075000	7.18972400
H	-0.28855600	-2.76514900	5.12529300
N	-0.37260800	0.43819900	4.09670300

int2 (*doublet*)

C	-0.02842900	-2.23280300	0.22050300
C	0.30903400	-1.38447700	1.40480400
O	0.15597300	-1.71512400	-1.02553900
H	0.13479200	-3.31357700	0.24048400
C	-0.20085600	0.04425700	1.22443000
H	1.40902200	-1.32012100	1.55533600
C	-0.28995600	-0.37847900	-1.24894100
C	0.22174800	0.56515800	-0.14919800
O	0.31142200	0.87325500	2.25098300
H	-1.30639100	0.04565200	1.24943800
C	0.17098800	0.03920500	-2.62862300
H	-1.39564700	-0.36129300	-1.23418900
O	-0.30285300	1.85851600	-0.37799000
H	1.32805800	0.58261500	-0.18517300
C	-0.63749900	1.70396200	2.87610400
O	-0.56342800	-0.66056800	-3.59628800
H	1.25732700	-0.17097400	-2.72123400
H	0.02230800	1.13202600	-2.72958500
C	0.62693400	2.90996100	-0.24976500
H	-1.43038100	1.11577100	3.37858700
H	-1.12023400	2.39533100	2.16219800
H	-0.10765700	2.29260500	3.63961100
C	-0.16755100	-0.37617100	-4.90830700
H	0.07803400	3.85227100	-0.39207700
H	1.10432000	2.91625400	0.74518700
H	1.42131500	2.84829200	-1.01945000
H	-0.80639000	-0.95844700	-5.58811000
H	0.89033400	-0.65512500	-5.09291500
H	-0.27979800	0.70060100	-5.15356500
H	-0.10348700	-1.82433500	2.32652800

TS3 (*triplet*)

Cu	-0.31242900	2.11887600	2.73299500

S	1.99535700	1.35762300	2.47070200
C	2.58047000	2.24935600	1.05293500
C	3.20542400	3.50622100	1.18173700
C	2.41975800	1.70467700	-0.23563000
C	3.66587400	4.18379600	0.05110700
H	3.32611500	3.95510300	2.16720700
C	2.88357200	2.39066400	-1.36058600
H	1.89524300	0.75500300	-0.34351800
C	3.51397800	3.63138100	-1.22507500
H	4.14732200	5.15844900	0.17175100
H	2.74494100	1.95068500	-2.35201600
H	3.87774400	4.16598500	-2.10641700
N	-1.72636000	1.08746500	1.76295800
C	-1.65414000	0.57595500	0.49436300
C	-2.92214000	0.78128100	2.37490000
C	-2.90357900	-0.26602400	0.19722100
O	-0.74752600	0.75902900	-0.30446700
C	-3.78131700	-0.07637000	1.43298300
O	-3.25852600	1.12975900	3.49246300
H	-2.58891900	-1.30859000	0.03150300
H	-3.35455300	0.08256200	-0.74402900
H	-4.05345800	-1.00950300	1.94961000
H	-4.72131400	0.46071900	1.23189400
N	-0.32070500	3.59652800	4.11896700
C	-0.15276100	4.85563300	3.69353900
C	-0.47513500	3.26719900	5.41090200
C	-0.15866600	5.90467600	4.61549200
C	0.03352400	4.95256600	2.23323400
C	-0.49350700	4.27079900	6.38242000
C	-0.33751600	5.59845500	5.97023900
C	0.37236300	6.12914500	1.55870000
N	-0.13805300	3.78852400	1.55588200
H	-0.61119200	4.02862500	7.43777900
H	-0.34913700	6.40075500	6.71053200
C	0.52839100	6.09608800	0.17419300
C	0.00492200	3.75084800	0.22572900
H	0.80597400	7.00211100	-0.36872400
C	0.33718500	4.89068900	-0.50444800
H	-0.14485600	2.77341600	-0.24103500
H	0.46323400	4.81790600	-1.58447900
H	0.52345700	7.05397000	2.11566400
H	-0.02611400	6.93689300	4.29272600
C	-0.55985300	1.81451700	5.62985000
C	-0.65799900	1.20292700	6.88597900
C	-0.54512900	-0.26609600	4.57146600

C	-0.70920200	-0.18441200	6.96389200
H	-0.68564900	1.81108300	7.78916700
C	-0.65687400	-0.93938700	5.78435800
H	-0.49087700	-0.79248900	3.61551400
H	-0.78467400	-0.67742100	7.93526000
H	-0.70068900	-2.02921300	5.80347600
N	-0.49469000	1.06412800	4.50296400
C	4.37402000	1.71071700	3.81554500
C	4.26315500	0.67532800	4.87945700
O	4.29085800	3.01357200	4.18514900
H	5.00964700	1.56129100	2.94171300
C	3.14267100	0.99632900	5.88076400
H	5.20642200	0.60209300	5.46642900
C	3.19778800	3.34628300	5.03571700
C	3.21695200	2.46751200	6.29505900
O	3.22473900	0.21157000	7.05617600
H	2.16431500	0.83703700	5.39138200
C	3.28788600	4.82743200	5.32208300
H	2.26706400	3.14141600	4.47909700
O	2.12594400	2.85892600	7.10350300
H	4.16915900	2.63119400	6.83945800
C	2.97081100	-1.15868400	6.87340200
O	2.94516600	5.52892600	4.14824500
H	4.32208600	5.07433100	5.63663100
H	2.59894800	5.08268900	6.14724500
C	2.27868600	2.67081800	8.49138700
H	3.77758600	-1.66837800	6.31452500
H	2.01901400	-1.32766200	6.33631600
H	2.90044100	-1.61755600	7.87065400
C	3.17992400	6.90549700	4.22530700
H	1.41122400	3.14154800	8.97959000
H	2.32276500	1.60446300	8.75974800
H	3.19646500	3.16460900	8.86580800
H	2.88575000	7.35050400	3.26344700
H	4.24929500	7.13334600	4.40606000
H	2.58978600	7.38323500	5.03445400
H	4.09768600	-0.30440400	4.40696200

int4 (*CSS*)

Cu	-0.52341300	2.03335900	3.04072000
N	-1.33299600	1.10101600	1.52815700
C	-1.23243600	-0.23615100	1.25149000
C	-2.08199400	1.76115300	0.57998300
C	-1.99453200	-0.57138200	-0.03946300
O	-0.63143100	-1.06781600	1.91858000

C	-2.56405300	0.77110800	-0.49226200
O	-2.32609300	2.95598600	0.57311000
H	-2.75775300	-1.33144400	0.18950300
H	-1.29588600	-1.03151500	-0.75549000
H	-3.66375700	0.80335100	-0.53535700
H	-2.19945700	1.10821500	-1.47527900
N	-0.47678300	3.46274900	4.51293900
C	-0.15303800	4.72561500	4.18769600
C	-0.52035300	3.06564200	5.79559000
C	0.04739000	5.69427900	5.17820600
C	0.01278700	4.95439800	2.73393700
C	-0.32578700	3.98009300	6.83805200
C	-0.05570100	5.31248700	6.51800300
C	-0.14967100	6.20347500	2.12214700
N	0.33223400	3.84914000	2.03090500
H	-0.35621300	3.65423600	7.87817600
H	0.11152300	6.04384900	7.31152000
C	0.02732300	6.30094200	0.74252500
C	0.48260900	3.94609400	0.70921800
H	-0.10462500	7.25933200	0.23552500
C	0.35364100	5.15134100	0.02007600
H	0.71309400	3.01515000	0.18397800
H	0.49209000	5.18161900	-1.06195800
H	-0.43711500	7.07584600	2.71092600
H	0.31079000	6.71762100	4.90835100
C	-0.73616300	1.61035200	5.97373800
C	-1.17462300	1.03178000	7.17177600
C	-0.61846000	-0.46489300	4.93443400
C	-1.31980800	-0.35372400	7.23382900
H	-1.41699300	1.65526600	8.03341800
C	-1.03463400	-1.11593600	6.09818500
H	-0.42162700	-0.99431900	3.99556100
H	-1.66310800	-0.83046200	8.15487000
H	-1.13666700	-2.20269600	6.10480200
N	-0.46511500	0.86425200	4.88097100

P_{Ax} (*CSS*)

C	0.09443800	-1.98186300	1.16471100
C	0.52561300	-0.74791100	1.95697000
O	0.36082800	-1.81203800	-0.19860800
H	0.66362700	-2.86935700	1.47091500
C	-0.06255000	0.54182400	1.37073700
H	1.62385800	-0.67347500	1.89776000
C	-0.26600500	-0.68938000	-0.80366900
C	0.19332100	0.61592500	-0.13671600

O	0.50420600	1.68968600	1.97318400
H	-1.16143400	0.55508800	1.50858200
C	0.04501800	-0.74181500	-2.28280400
H	-1.36127800	-0.76793200	-0.68161500
O	-0.52619300	1.66919400	-0.73688100
H	1.28280100	0.74241200	-0.29824000
C	-0.03656900	2.03009300	3.22510400
O	-0.66924700	-1.80950900	-2.85540600
H	1.13769300	-0.87665300	-2.42109300
H	-0.24834000	0.22155700	-2.73994200
C	0.14676600	2.90555700	-0.82569700
H	0.14558000	1.25385800	3.99252400
H	-1.12896900	2.20279200	3.16510400
H	0.45014000	2.95941200	3.55416400
C	-0.41347400	-1.99305500	-4.22035300
H	-0.52822700	3.60468000	-1.34073900
H	0.40407400	3.30597500	0.16732800
H	1.07836400	2.81624500	-1.41944600
H	-1.02884600	-2.83540300	-4.56793700
H	0.65262500	-2.22893500	-4.41450600
H	-0.67627700	-1.09403100	-4.81410200
H	0.25451300	-0.86185300	3.01664700
S	-1.69122100	-2.35770700	1.54347500
C	-1.84645300	-3.98838200	0.82833100
C	-2.31831500	-5.02586900	1.64714500
C	-1.55608600	-4.24035500	-0.52297900
C	-2.50283300	-6.30660700	1.12152400
H	-2.53346600	-4.82236700	2.69837200
C	-1.72204900	-5.53157300	-1.03043900
H	-1.19843400	-3.44208300	-1.17348700
C	-2.19919500	-6.56447400	-0.21801200
H	-2.87464900	-7.10754200	1.76548000
H	-1.48650900	-5.72586000	-2.07994400
H	-2.33548200	-7.56814400	-0.62803900

TS5 (*triplet*)

Cu	0.17489900	1.75278600	2.50937300
S	1.48282200	0.12030900	1.55546800
C	0.39957100	-0.64707100	0.37990600
C	-0.19585600	0.09307700	-0.65988900
C	0.11627000	-2.02065600	0.47014700
C	-1.04445200	-0.52425300	-1.57837300
H	-0.01013500	1.16547800	-0.73060300
C	-0.72425700	-2.63875000	-0.45766000
H	0.55057400	-2.59539700	1.28971800

C	-1.31099900	-1.89535000	-1.48586900
H	-1.50214400	0.07146000	-2.37268600
H	-0.93451900	-3.70757400	-0.36626200
H	-1.97535900	-2.37820100	-2.20667200
N	-1.70969800	1.21708100	1.87459400
C	-2.39940300	1.99948200	0.99124200
C	-2.30745700	-0.00667300	2.04286900
C	-3.60665800	1.23214900	0.43146000
O	-2.10779800	3.14685500	0.67624100
C	-3.52342900	-0.13075500	1.11363300
O	-1.94010200	-0.88809200	2.80461700
H	-3.50801700	1.18881400	-0.66401200
H	-4.52696500	1.79559000	0.65165400
H	-3.32266300	-0.95819800	0.41655800
H	-4.41090400	-0.40488400	1.70417500
N	-0.48200400	3.35068200	3.60447900
C	-0.44733600	4.55736100	3.03175200
C	-0.93697000	3.14300600	4.84383500
C	-0.93558300	5.67139400	3.72311800
C	0.22948200	4.58402200	1.71435200
C	-1.42490400	4.21645500	5.59744200
C	-1.42792700	5.48635300	5.01576200
C	0.28062900	5.70858800	0.88903100
N	0.84333300	3.43732700	1.37313500
H	-1.77240400	4.07210200	6.62000200
H	-1.79613900	6.34278400	5.58450000
C	0.99161900	5.63186900	-0.30648600
C	1.53356100	3.35958800	0.23793100
H	1.04023800	6.49531700	-0.97370300
C	1.63947700	4.44084200	-0.63779800
H	1.99957000	2.38867000	0.04171700
H	2.21333500	4.34266300	-1.56070300
H	-0.23547700	6.62583800	1.17108000
H	-0.89946600	6.66454200	3.27846400
C	-0.84203800	1.73327900	5.29933100
C	-1.46393500	1.24317400	6.45084900
C	-0.02591200	-0.37502400	4.76047700
C	-1.33678800	-0.11509100	6.75311900
H	-2.05414000	1.90120100	7.08906100
C	-0.61117400	-0.94030000	5.89655100
H	0.54225400	-0.96198300	4.03536500
H	-1.81791600	-0.52416400	7.64443600
H	-0.50976500	-2.00956300	6.08699900
N	-0.12153800	0.92559000	4.49607800
C	3.55913500	2.41274700	3.02329700

C	3.83921300	1.55362700	4.20823100
O	3.55317000	3.76492400	3.19898700
C	3.04776300	2.01712500	5.43679300
H	4.91668200	1.58622500	4.48247300
C	2.79994700	4.24136700	4.30802700
C	3.15889900	3.52847800	5.62040400
O	3.49751500	1.38907900	6.62461200
H	1.97910600	1.80036600	5.27623700
C	2.98091100	5.74079000	4.38590300
H	1.73810100	4.02987000	4.12535200
O	2.23038700	3.99688400	6.58170600
H	4.19535000	3.78120400	5.92072300
C	2.91074400	0.13674800	6.87718900
O	2.23974500	6.34655700	3.35284000
H	4.05942900	5.97895300	4.28753800
H	2.63191800	6.09099000	5.37502800
C	2.69659800	4.05586700	7.91104500
H	3.05325100	-0.57367600	6.04119400
H	1.82416400	0.22436900	7.06636000
H	3.39332900	-0.28184800	7.77251000
C	2.42425800	7.73006600	3.26334900
H	1.87007900	4.44052400	8.52707400
H	3.00431700	3.06598600	8.28175400
H	3.55587200	4.74906700	8.00790800
H	1.80882800	8.09848700	2.42905300
H	3.48147600	7.99552200	3.06171100
H	2.11448800	8.25357800	4.19148000
H	3.60133100	0.50753000	3.96118400
H	3.86786200	2.11664700	2.02006000

int6 (*CSS*)

Cu	0.30745000	1.86224500	2.22008700
S	1.44471000	0.03294000	1.39446000
C	0.27439000	-0.96571300	0.51910300
C	0.46414700	-1.20634100	-0.85307700
C	-0.82919200	-1.56102400	1.15943900
C	-0.40791100	-2.03853300	-1.55786400
H	1.29561400	-0.71634600	-1.36141200
C	-1.70815000	-2.37846900	0.44920700
H	-1.01195300	-1.35826700	2.21424100
C	-1.49937000	-2.62748300	-0.91246000
H	-0.24217100	-2.21409400	-2.62397000
H	-2.56297500	-2.82481300	0.96423200
H	-2.18719300	-3.27042100	-1.46712600
N	-1.40221500	1.48935700	1.21683200

C	-1.45195700	1.49356900	-0.16093500
C	-2.60463000	1.11234100	1.75797800
C	-2.81602600	0.98922100	-0.64130400
O	-0.55245200	1.82794800	-0.91235800
C	-3.60603100	0.77896900	0.64426500
O	-2.87571100	1.03891800	2.94793100
H	-2.64290200	0.06051000	-1.20554300
H	-3.25128400	1.72210800	-1.33727200
H	-3.95179300	-0.25498600	0.79344800
H	-4.48527300	1.43374300	0.74940900
N	-0.77383000	3.28173400	3.43146900
C	-0.90892500	4.52272300	2.94918900
C	-1.30283600	2.93290400	4.61328400
C	-1.54776900	5.52072100	3.69857100
C	-0.34568400	4.78263400	1.59569800
C	-1.96085600	3.88075300	5.40744100
C	-2.06809800	5.19088400	4.94527400
C	-0.61509400	5.95352500	0.87281600
N	0.42780000	3.82066400	1.08537900
H	-2.36198600	3.60696700	6.38170300
H	-2.55293600	5.95283200	5.55896600
C	-0.03200900	6.11343500	-0.38423800
C	0.98401900	3.96003000	-0.11348100
H	-0.22738500	7.01648500	-0.96724200
C	0.79570400	5.10934800	-0.88614200
H	1.57985000	3.11772600	-0.46955200
H	1.26776600	5.19615800	-1.86600900
H	-1.27261000	6.72408500	1.27368600
H	-1.60640100	6.54214700	3.32840400
C	-1.14238600	1.51347800	5.03506800
C	-1.84843700	0.96005800	6.11222300
C	-0.11820500	-0.50697200	4.58719400
C	-1.66380900	-0.38891800	6.41201900
H	-2.55530500	1.55493400	6.68924800
C	-0.78509200	-1.14629800	5.63558300
H	0.57953100	-1.03863000	3.93077200
H	-2.21331000	-0.84654600	7.23788100
H	-0.62131900	-2.20776400	5.83037900
N	-0.29115200	0.78080400	4.31317400
C	2.24328800	2.38364600	2.88659000
C	2.87608300	1.44963900	3.89667500
O	2.29501300	3.71026100	3.23406900
C	2.60255200	1.81336500	5.35602100
H	3.97309500	1.50832800	3.75970700
C	2.08145100	4.12452100	4.57949600

C	2.87987700	3.29210200	5.58908500
O	3.42202500	1.05819000	6.23035200
H	1.54247800	1.64425500	5.60431600
C	2.43106600	5.60452400	4.66438300
H	1.01819100	4.00146000	4.82908500
O	2.46040300	3.72417200	6.86600100
H	3.96449900	3.47623400	5.45109200
C	2.95709700	-0.24414300	6.48592900
O	1.66084100	6.41208900	3.80613600
H	3.51177700	5.73293600	4.46019500
H	2.23909900	5.92182700	5.69970200
C	3.42158800	3.62845500	7.89469200
H	2.90758000	-0.86295200	5.57066500
H	1.94901600	-0.23578500	6.94383300
H	3.66240000	-0.71580000	7.18529700
C	2.26640700	6.71056600	2.56770600
H	2.95451500	4.01971200	8.81040800
H	3.74351400	2.58864000	8.05855800
H	4.31637900	4.24161900	7.66814500
H	1.60716400	7.41465200	2.04191800
H	2.40220600	5.81375300	1.94235100
H	3.25288500	7.19441100	2.71051300
H	2.58918800	0.41461600	3.67367100
H	2.67613700	2.29442000	1.88556200

TS7 (*CSS*)

Cu	0.23246900	1.50423500	2.63533100
S	1.65017000	-0.24403400	2.05369600
C	0.68407100	-0.86162100	0.69653100
C	1.15146300	-0.76799500	-0.62326200
C	-0.54356100	-1.50546500	0.93764200
C	0.40867800	-1.29676300	-1.67941700
H	2.10016500	-0.26221700	-0.81346400
C	-1.27650600	-2.04612500	-0.11789500
H	-0.92407100	-1.56171800	1.95846700
C	-0.80723700	-1.93891700	-1.43233500
H	0.77867900	-1.19994800	-2.70323400
H	-2.22753900	-2.54564000	0.08565200
H	-1.38997300	-2.35158500	-2.25956600
N	-1.51162600	1.29358600	1.58739300
C	-1.62648000	1.43578000	0.22806300
C	-2.69613500	0.90180000	2.14854700
C	-3.05747200	1.11004700	-0.22668000
O	-0.73804800	1.77627700	-0.53923800
C	-3.74846200	0.65584100	1.05402700

O	-2.91391900	0.73993900	3.34231000
H	-3.00763800	0.34791200	-1.01764800
H	-3.50023900	2.01524600	-0.67228400
H	-3.99063300	-0.41938200	1.05835400
H	-4.67488900	1.19510600	1.30316000
N	-0.63598700	3.12085000	3.85663900
C	-0.70487500	4.33692300	3.30195600
C	-1.19049300	2.86445300	5.04688900
C	-1.31033700	5.40402000	3.97793400
C	-0.09951000	4.45955600	1.94907200
C	-1.81641700	3.88334000	5.77806700
C	-1.86130600	5.16727300	5.23619600
C	-0.36686700	5.53544900	1.09251600
N	0.69611900	3.44765300	1.57519100
H	-2.24954500	3.68383100	6.75752000
H	-2.32524800	5.98282500	5.79517200
C	0.22035600	5.54783900	-0.17308400
C	1.23662400	3.44656000	0.35959600
H	0.02215100	6.37208400	-0.86225700
C	1.04328900	4.48759300	-0.55014800
H	1.83910200	2.57282500	0.10159900
H	1.50254200	4.44520900	-1.53881200
H	-1.03460300	6.34058800	1.39908100
H	-1.32464000	6.40262700	3.54327100
C	-1.12210600	1.44941300	5.50030400
C	-1.88189600	0.95898800	6.57074500
C	-0.29628900	-0.65813400	5.04296400
C	-1.83420700	-0.40333000	6.86076000
H	-2.53006500	1.61844700	7.14736400
C	-1.03456100	-1.23731100	6.07711400
H	0.35256400	-1.24908700	4.38622900
H	-2.43187800	-0.81182700	7.67893400
H	-0.98690400	-2.31322900	6.25568500
N	-0.33208200	0.64437900	4.78024500
C	3.30357000	1.80054300	2.80196300
C	3.71331300	0.88250300	3.89626000
O	3.15045300	3.07950100	3.06509000
C	2.99962200	1.18223500	5.21520700
H	4.80425700	1.01890800	4.04822800
C	2.56982500	3.49389200	4.31975300
C	3.05990500	2.67374400	5.52152000
O	3.59142800	0.47529700	6.28612600
H	1.93580300	0.92040800	5.10869000
C	2.82442000	4.98107700	4.50870400
H	1.49377200	3.30334300	4.21278600

O	2.19281200	3.03350400	6.57522600
H	4.10741700	2.94279400	5.76993200
C	3.11737000	-0.84358100	6.44241400
O	2.16459500	5.81023000	3.58954400
H	3.91745300	5.16809300	4.50379600
H	2.43918500	5.22687000	5.50870500
C	2.72911600	2.95252000	7.87871400
H	3.24847200	-1.44788600	5.52558700
H	2.04571000	-0.86113600	6.71252800
H	3.69848200	-1.30796700	7.25190000
C	2.87545100	6.09271500	2.40400600
H	1.94497400	3.29527400	8.56897200
H	3.02729900	1.92507400	8.13636500
H	3.61154100	3.61267800	7.99164000
H	2.28361700	6.82439200	1.83778100
H	3.02236000	5.19825100	1.77884500
H	3.86614500	6.53500000	2.62878200
H	3.56562600	-0.15899400	3.57949200
H	3.62478600	1.61825400	1.77759500

TS8 (*triplet*)

Cu	-0.26257700	1.52643500	2.58678900
S	1.73069600	0.31502600	1.80060000
C	2.40590500	1.28222800	0.47588800
C	3.45709000	2.19333500	0.69030500
C	1.87459300	1.15869500	-0.82225300
C	3.96617300	2.95002300	-0.36658000
H	3.84349600	2.32681900	1.69854900
C	2.38720500	1.92314200	-1.87196200
H	1.02740900	0.49375100	-0.98934400
C	3.43831100	2.82015800	-1.65477800
H	4.77960300	3.65661200	-0.17705100
H	1.95290200	1.81816700	-2.86981800
H	3.83768300	3.41511600	-2.47998500
N	-1.99046000	1.28315700	1.60821900
C	-2.18462800	1.20185200	0.25620900
C	-3.17439200	1.17456000	2.30612700
C	-3.66573700	0.93384100	-0.04755300
O	-1.32429500	1.33484400	-0.60283000
C	-4.33472500	0.94420100	1.32578200
O	-3.29326300	1.24497800	3.51577200
H	-3.74670100	-0.02753800	-0.57871800
H	-4.03179000	1.70871400	-0.73825600
H	-4.84085900	0.00335200	1.59180000
H	-5.07307000	1.74997000	1.45847600

N	0.31833200	2.42120300	4.29514200
C	0.86675900	3.64225300	4.21183100
C	0.18308500	1.75225300	5.45376700
C	1.28409900	4.29906600	5.36859400
C	0.96399300	4.13750700	2.82477600
C	0.58790800	2.35558100	6.65100500
C	1.13272200	3.64101500	6.59847800
C	1.61464600	5.31764400	2.45225000
N	0.37946700	3.34693100	1.88951700
H	0.48675000	1.83541400	7.60415100
H	1.45685700	4.13186800	7.51797700
C	1.66467800	5.66705200	1.10399300
C	0.41593400	3.67968500	0.59503600
H	2.18221400	6.57763500	0.79355300
C	1.05709600	4.83873300	0.15813800
H	-0.07403400	2.98246300	-0.09019900
H	1.08846600	5.06681000	-0.90717600
H	2.08783000	5.93671500	3.21070300
H	1.74429200	5.28211600	5.32137100
C	-0.37088900	0.40174500	5.28231500
C	-0.63362900	-0.49694600	6.32781800
C	-1.10967500	-1.15769600	3.70763100
C	-1.14515500	-1.75506800	6.03106100
H	-0.43997000	-0.20546300	7.36060700
C	-1.38847100	-2.10020800	4.69339300
H	-1.28313000	-1.35875800	2.64753700
H	-1.35666800	-2.46456000	6.83398400
H	-1.79124500	-3.07640100	4.42050000
N	-0.61786300	0.04668700	3.99443200
C	3.10796100	0.84211400	3.91252200
C	4.21703700	-0.14494600	3.77199000
O	3.47179900	2.16266300	3.88539600
H	2.26349400	0.61260500	4.56945400
C	5.34330400	0.15709400	4.77275600
H	4.65305200	-0.09382600	2.75876000
C	4.59731500	2.58049200	4.66640500
C	5.78851900	1.60494400	4.58987300
O	6.47799400	-0.66617900	4.58677000
H	4.96913900	0.04682200	5.81155600
C	5.03336000	3.95087100	4.18599800
H	4.29405500	2.65304500	5.72704000
O	6.69165800	2.01964200	5.59189700
H	6.25648600	1.68234300	3.58776500
C	6.33511100	-1.98763300	5.04118800
O	4.14882800	4.95579400	4.62085300

H	5.09653500	3.93772600	3.07904900
H	6.04493300	4.13990600	4.59010800
C	8.06085600	1.83538100	5.30325200
H	5.57499500	-2.55375600	4.47096400
H	6.05799200	-2.02357200	6.11370600
H	7.30539900	-2.48835300	4.91205700
C	4.59050700	6.24471500	4.29319300
H	8.62677700	2.23045700	6.15966500
H	8.30900400	0.77339600	5.15475400
H	8.36062200	2.39691800	4.39589100
H	3.86704600	6.96693700	4.70091400
H	4.65882100	6.39371100	3.19651200
H	5.58614200	6.46292400	4.72863100
H	3.81735000	-1.16030300	3.90309800

P_{Eq} (*CSS*)

C	-0.25080900	-1.93371000	1.01294100
C	0.27820400	-0.80435200	1.89134400
O	0.20130900	-1.75525100	-0.31161100
H	-1.35793100	-1.94871700	1.02531900
C	-0.13043500	0.55794700	1.31029800
H	1.37858200	-0.85683100	1.92083100
C	-0.32414400	-0.58656500	-0.91483200
C	0.19887600	0.65857200	-0.18349200
O	0.51364000	1.62752900	1.97273300
H	-1.23011300	0.67849400	1.39668200
C	0.04850200	-0.62385500	-2.38032800
H	-1.43076600	-0.58907900	-0.84824200
O	-0.40766400	1.78576100	-0.77395800
H	1.30041700	0.69914900	-0.29410100
C	-0.01845700	1.95909800	3.23073900
O	-0.67098900	-1.66238000	-2.99582400
H	1.14171300	-0.79038500	-2.46915500
H	-0.19256800	0.35556400	-2.83479800
C	0.36130800	2.96856800	-0.78561200
H	0.10627600	1.14820000	3.97291500
H	-1.09712700	2.20349600	3.16616800
H	0.52203900	2.84442600	3.59491400
C	-0.34166700	-1.85195100	-4.34451500
H	-0.22717500	3.73129200	-1.31622600
H	0.58923600	3.32096100	0.23247100
H	1.31675900	2.82291700	-1.32751100
H	-0.96096200	-2.67450300	-4.73030700
H	0.72584300	-2.12125900	-4.47622600
H	-0.54079900	-0.94458100	-4.95054500

H	-0.09626300	-0.91847600	2.91928000
S	0.31997500	-3.54358700	1.63987000
C	-0.78598700	-4.66790000	0.80049800
C	-1.20057000	-4.47852800	-0.52882200
C	-1.21132900	-5.80283000	1.50878500
C	-2.05416200	-5.41286400	-1.12093400
H	-0.85396500	-3.61467000	-1.09681600
C	-2.04162800	-6.74241400	0.89484600
H	-0.89728800	-5.93980500	2.54620600
C	-2.47299700	-6.54747900	-0.42034000
H	-2.38193300	-5.25335600	-2.15139000
H	-2.36510300	-7.62361900	1.45461600
H	-3.13210400	-7.27716100	-0.89660300

TS9 (*triplet*)

Cu	0.41066300	1.80185200	2.71192000
S	1.62512900	0.16531300	1.29408000
C	0.46648600	-0.75918800	0.37566100
C	0.68402600	-0.95969500	-1.00690900
C	-0.70829800	-1.28975600	0.95825400
C	-0.23522400	-1.66898000	-1.77556400
H	1.57787600	-0.52906800	-1.46098800
C	-1.62112000	-2.00196600	0.18541800
H	-0.91100700	-1.11511900	2.01316400
C	-1.39108500	-2.19381800	-1.18337800
H	-0.05644500	-1.80857200	-2.84447100
H	-2.52486500	-2.40178800	0.65163400
H	-2.11357800	-2.74733200	-1.78810300
N	-1.27210600	1.63092600	1.51458900
C	-1.15869900	1.89637300	0.17497300
C	-2.53251100	1.21127200	1.83715400
C	-2.48076100	1.59780600	-0.54359700
O	-0.14427100	2.27759900	-0.39123800
C	-3.42159500	1.18171300	0.58342200
O	-2.92176300	0.88458200	2.95187100
H	-2.28929800	0.79653500	-1.27376100
H	-2.80209000	2.48557500	-1.10910500
H	-3.83328300	0.16716400	0.47254600
H	-4.27492100	1.86157100	0.73395800
N	-0.80774800	2.87210200	4.18691900
C	-1.05180100	4.16167700	3.94723500
C	-1.50606000	2.17059300	5.07865600
C	-2.05898100	4.83944800	4.64930200
C	-0.20108100	4.78280400	2.89475000
C	-2.52872700	2.77890600	5.81968900

C	-2.79980100	4.12766800	5.59374300
C	-0.10307100	6.16685900	2.70428000
N	0.49474400	3.92716200	2.12768900
H	-3.11851800	2.21173300	6.53862600
H	-3.60084800	4.62361900	6.14616600
C	0.74902800	6.64967000	1.70855300
C	1.29135700	4.37762700	1.16257100
H	0.85627000	7.72583400	1.55407700
C	1.46070600	5.74391800	0.92327600
H	1.78610800	3.61896400	0.56429900
H	2.14707100	6.07471300	0.14284000
H	-0.66207000	6.85778500	3.33592200
H	-2.27693000	5.88846900	4.44976300
C	-1.10753100	0.74267700	5.21817800
C	-1.60957500	-0.09460300	6.22253800
C	0.22807300	-0.95939100	4.39498500
C	-1.16349800	-1.41451900	6.28930800
H	-2.33634300	0.27508600	6.94545900
C	-0.22361800	-1.86263600	5.36061900
H	0.96222700	-1.24392200	3.63282900
H	-1.54610300	-2.08441600	7.06277100
H	0.15411800	-2.88633900	5.37770300
N	-0.20622800	0.29415800	4.33137500
C	2.24664300	2.24891500	3.62244900
C	2.80819900	1.29172100	4.64550600
O	3.12673900	2.37407400	2.53051900
C	4.19333400	1.77442400	5.10833000
H	2.92056400	0.28469300	4.21149500
C	4.38671800	2.92736000	2.85644000
C	5.10044100	2.06439100	3.91065200
O	4.86059800	0.82583000	5.92736700
H	4.08024200	2.72516700	5.66953800
C	5.21511100	3.03167200	1.58017800
H	4.24469000	3.94372800	3.27740900
O	6.27288800	2.76026700	4.28563800
H	5.35836000	1.09144600	3.44681700
C	4.33810500	0.68737600	7.22115000
O	4.56146000	3.75643800	0.56383000
H	5.46518500	2.01079100	1.23471800
H	6.15769700	3.54199500	1.83275200
C	7.38234300	1.96265300	4.62843700
H	3.32213000	0.24802000	7.22734200
H	4.29168800	1.65944400	7.75262200
H	5.00597000	0.01507100	7.77982100
C	3.99689400	2.95324500	-0.44921500

H	8.22238200	2.64414800	4.83020100
H	7.18748300	1.34444500	5.51915100
H	7.67035700	1.29059700	3.79533900
H	3.47948100	3.62286700	-1.15232700
H	3.27311400	2.21949000	-0.05505100
H	4.77777300	2.40275900	-1.01184900
H	2.12464600	1.21301300	5.50377900
H	2.04866300	3.24125800	4.07240400

int10 (*CSS*)

Cu	0.35296900	1.70694200	2.51622400
S	1.50061200	0.03683400	1.45089200
C	0.28528400	-0.80293500	0.47075100
C	0.44415000	-0.80688800	-0.92672400
C	-0.80561600	-1.49682900	1.02742100
C	-0.44396600	-1.51118500	-1.74269800
H	1.26303100	-0.23258300	-1.36185800
C	-1.70314300	-2.18068900	0.20813000
H	-0.96893100	-1.46974000	2.10378000
C	-1.52306100	-2.19908300	-1.18040700
H	-0.30196600	-1.50543100	-2.82645000
H	-2.55073300	-2.70399600	0.65837400
H	-2.22572400	-2.73948300	-1.81944000
N	-1.31140700	1.53888400	1.46090500
C	-1.28485300	1.83523000	0.11350200
C	-2.53948800	1.07373400	1.85388900
C	-2.62056100	1.45221600	-0.52821900
O	-0.34106200	2.30572200	-0.49572900
C	-3.48530800	1.01254800	0.64806900
O	-2.86740900	0.75040800	2.98626800
H	-2.41730400	0.63964100	-1.24189200
H	-3.01329000	2.30534500	-1.10111500
H	-3.86854700	-0.01502900	0.56386100
H	-4.34868100	1.66815200	0.84272800
N	-0.76897600	2.82609800	4.11409500
C	-0.94829800	4.13550700	3.89919000
C	-1.47847800	2.17636900	5.04605900
C	-1.88652900	4.87408400	4.63356900
C	-0.11041400	4.74869900	2.83170700
C	-2.43287000	2.85468900	5.81905000
C	-2.63778100	4.21411700	5.60307800
C	0.10723400	6.12893000	2.72273800
N	0.44759600	3.88952000	1.97193900
H	-3.01963100	2.32732700	6.56875300
H	-3.38772400	4.75610200	6.18321200

C	0.93744000	6.59438900	1.70067600
C	1.21781500	4.32453500	0.97877300
H	1.14265500	7.66333700	1.60693200
C	1.50352500	5.68187400	0.81081900
H	1.58610000	3.55941500	0.30067900
H	2.16927200	6.00108200	0.00840200
H	-0.33460800	6.82511300	3.43587300
H	-2.04300300	5.93327700	4.43237400
C	-1.19424900	0.72408600	5.22471500
C	-1.83339100	-0.06071700	6.19615700
C	0.03238600	-1.08613200	4.48396600
C	-1.51114800	-1.41441800	6.28457900
H	-2.57742000	0.36419100	6.86849300
C	-0.55921400	-1.94620800	5.41351600
H	0.78222900	-1.43297500	3.76429400
H	-2.00299700	-2.04725200	7.02695900
H	-0.28062500	-3.00106100	5.44695200
N	-0.28217300	0.20224600	4.40214200
C	2.13991600	2.08128600	3.35047900
C	2.71031000	1.10609900	4.34500000
O	3.04695900	2.35144900	2.33171000
C	4.00646000	1.70260300	4.92970000
H	2.94860900	0.14982000	3.85401500
C	4.22713800	3.00434800	2.76717300
C	4.95591700	2.15312700	3.81877400
O	4.70280800	0.77483600	5.74020500
H	3.75789800	2.60087000	5.53243800
C	5.11195100	3.25071800	1.54678900
H	3.95900700	3.97758600	3.22618900
O	6.02102600	2.93941000	4.31036100
H	5.33991700	1.24069000	3.32172300
C	4.11202900	0.50754200	6.98536100
O	4.43621400	3.89050800	0.49306100
H	5.53278300	2.28360000	1.21151200
H	5.95075200	3.88716500	1.86826600
C	7.18443900	2.23763500	4.68779000
H	3.14792800	-0.02744700	6.89329800
H	3.93487600	1.43717200	7.56252900
H	4.80658500	-0.13013700	7.55119900
C	3.97008200	3.01267400	-0.51301900
H	7.92965100	2.98694200	4.99334400
H	6.99542400	1.54423800	5.52243300
H	7.59872500	1.65735000	3.83963400
H	3.43908300	3.62171100	-1.25927900
H	3.28391400	2.24488000	-0.11796000

H	4.81378500	2.50486000	-1.02121200
H	1.98684200	0.91385800	5.14556800
H	1.81904000	3.01356800	3.84831100

TS11 (*CSS*)

Cu	-0.58992000	1.32378300	2.69080700
S	0.42212200	-0.58155900	2.02989300
C	1.17864800	-0.45042900	0.43660600
C	2.48779500	-0.93637600	0.26490600
C	0.46644300	0.02721800	-0.67680500
C	3.07048200	-0.95925600	-1.00220300
H	3.03833100	-1.29517400	1.13619600
C	1.06008700	0.00435700	-1.94128600
H	-0.54112100	0.42632700	-0.54101100
C	2.35701900	-0.49090900	-2.11104900
H	4.08681700	-1.34217600	-1.12559900
H	0.49843200	0.37669800	-2.80190500
H	2.81359100	-0.50942100	-3.10384800
N	-2.57116600	1.27998200	2.14952300
C	-2.90852100	1.44462700	0.83633700
C	-3.68933700	1.18609500	2.93698500
C	-4.43168300	1.39343700	0.65206200
O	-2.12544300	1.62037400	-0.09117300
C	-4.96068400	1.22375700	2.07180000
O	-3.71577600	1.09800400	4.15636500
H	-4.67534400	0.55908700	-0.02408800
H	-4.76239000	2.31607800	0.15045300
H	-5.52605300	0.29326200	2.23617700
H	-5.60057600	2.04981600	2.41906600
N	-1.03105900	2.76361900	4.42131000
C	-0.96144000	4.06933900	4.13593700
C	-1.49270900	2.33717800	5.60201400
C	-1.36935500	5.03887600	5.06506900
C	-0.44832600	4.42929700	2.78133000
C	-1.89244800	3.25221400	6.58865500
C	-1.83224600	4.61463500	6.30815900
C	-0.10514000	5.74208500	2.42768800
N	-0.33628900	3.42205300	1.90159700
H	-2.23949300	2.90778200	7.56154700
H	-2.14907400	5.34503100	7.05584400
C	0.35259800	5.99343800	1.13397600
C	0.07986800	3.66043500	0.65944400
H	0.63995500	7.00562700	0.84082900
C	0.44214700	4.93862600	0.22851500
H	0.10825100	2.79886700	-0.00682600

H	0.79816300	5.09339800	-0.79010500
H	-0.17560700	6.55478700	3.15020700
H	-1.33907900	6.09979700	4.82092300
C	-1.55584900	0.86352100	5.81574000
C	-2.30133300	0.30247500	6.86330700
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C	1.51684200	1.34103600	3.06845200
C	2.27658300	0.56356200	4.10753400
O	2.32095200	1.69567900	1.99654100
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O	4.25954900	0.83262900	5.53069600
H	2.89645100	2.34812300	5.18960600
C	4.15509200	3.01170400	1.16648700
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O	5.01155100	3.15655100	3.94789100
H	4.81623400	1.26921900	3.09588900
C	3.72930600	0.53028600	6.79594500
O	3.43412500	3.63560200	0.13618200
H	4.66105600	2.09750200	0.80065300
H	4.92717000	3.71234300	1.51887500
C	6.30791700	2.80798200	4.38071500
H	2.90762400	-0.20871800	6.74728000
H	3.34470900	1.43643500	7.30524300
H	4.54162100	0.10386800	7.40197900
C	2.98617100	2.75539500	-0.87276500
H	6.82498800	3.74372400	4.63944700
H	6.28405400	2.14445400	5.25939700
H	6.87929100	2.30294400	3.57672700
H	2.44304800	3.35450200	-1.61817500
H	2.31785500	1.97741800	-0.48051600
H	3.83440800	2.25798100	-1.38092100
H	1.59657200	0.24150300	4.90468800
H	1.10658000	2.24879700	3.53758300

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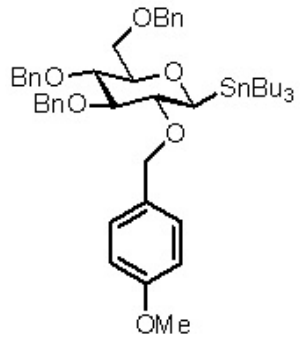
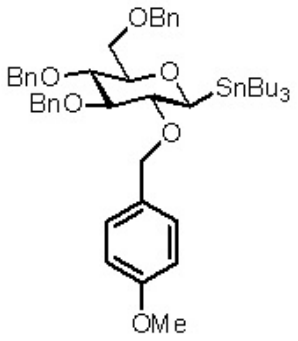
9. Copies of 1D and 2D NMR Spectra

17a (^{1}H NMR, 300MHz, $CDCl_3$)

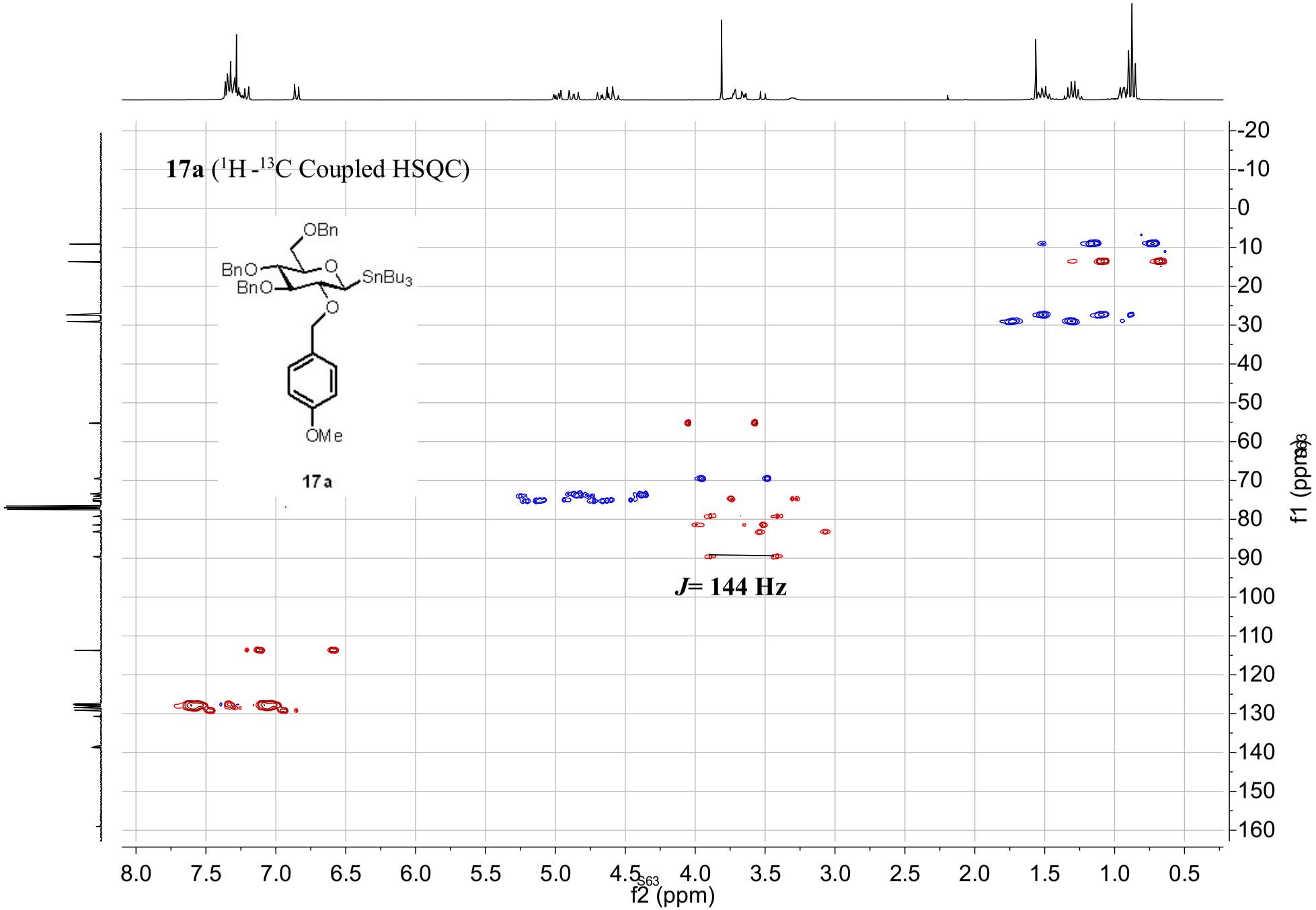


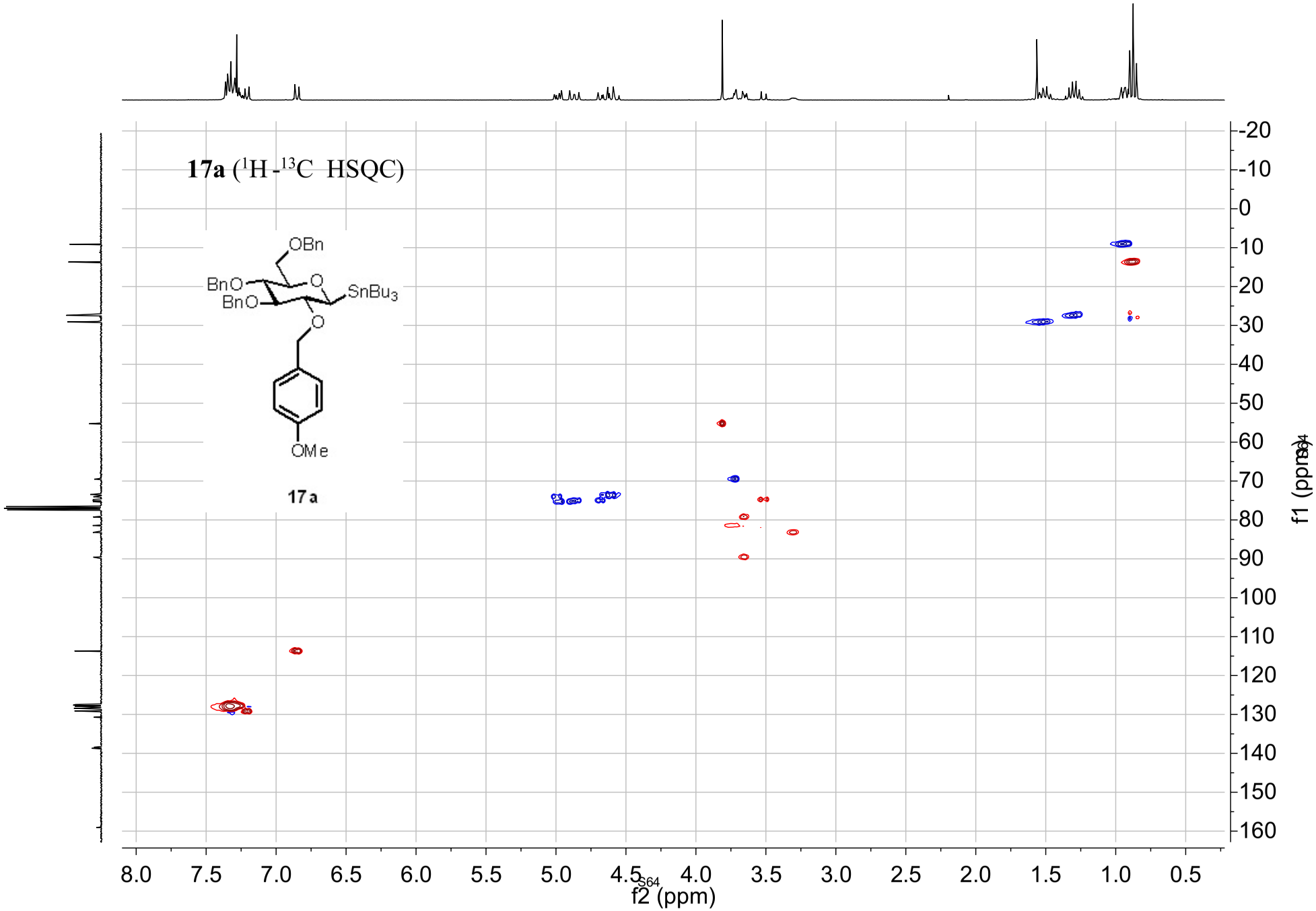
17a

17a (^{13}C NMR, 75MHz, $CDCl_3$)

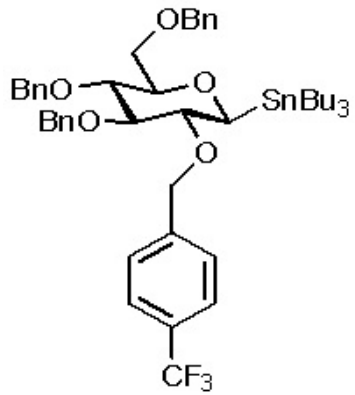


17a


17a (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
SnBu3
O
OMe
17a
J= 144 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

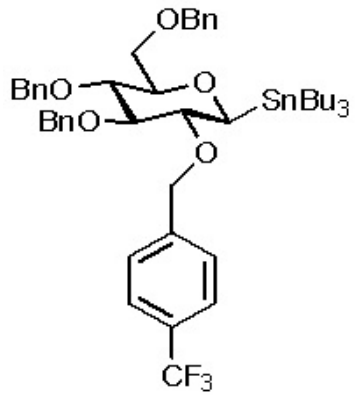

17a (1H -13C HSQC)
OBn
BnO
BnO
O
SnBu3
O
OMe
17a
f2 (ppm)
f1 (ppm)

17b (^{1}H NMR, 300MHz, $CDCl_3$)



17b

17b (^{13}C NMR, 75MHz, $CDCl_3$)

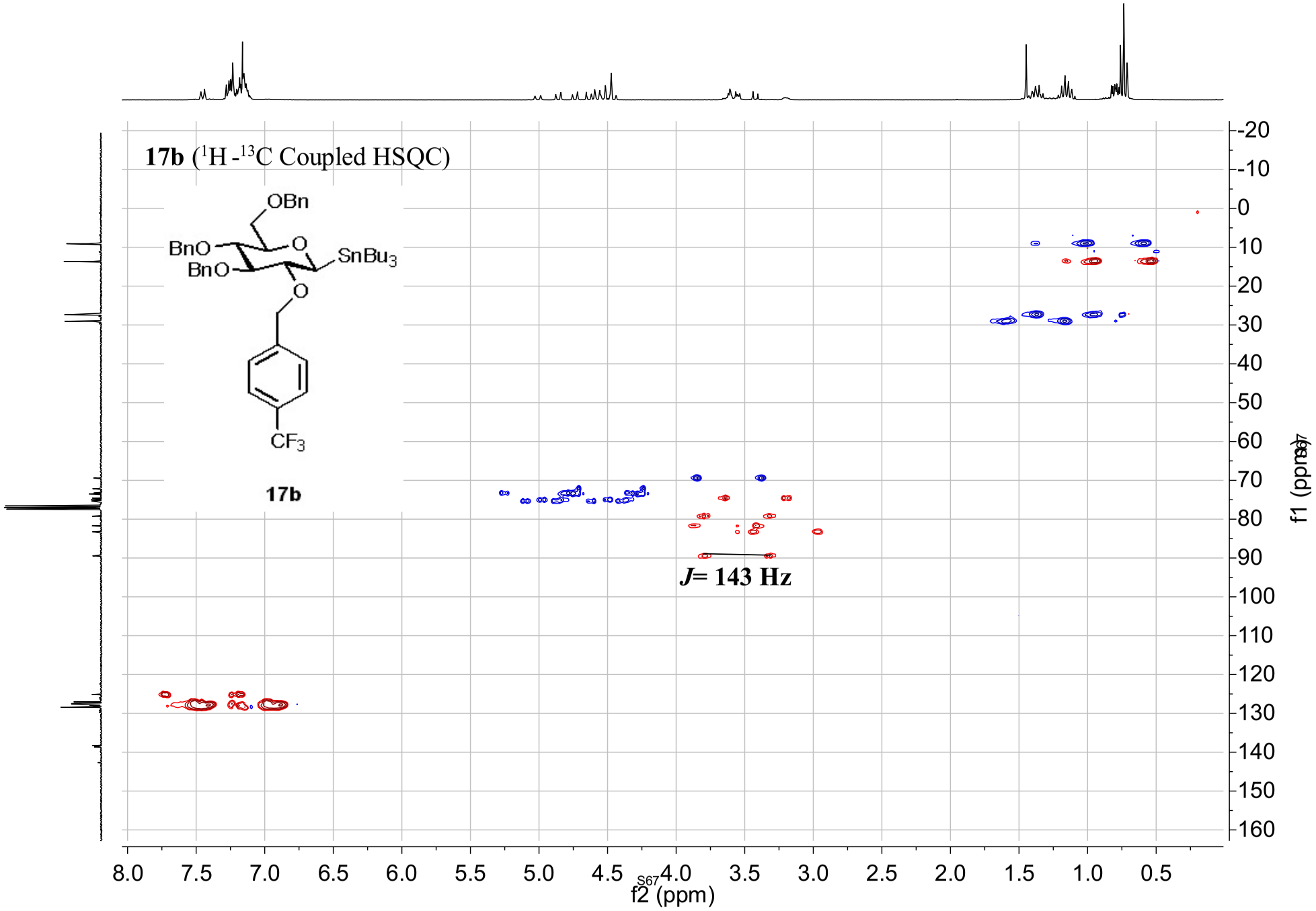


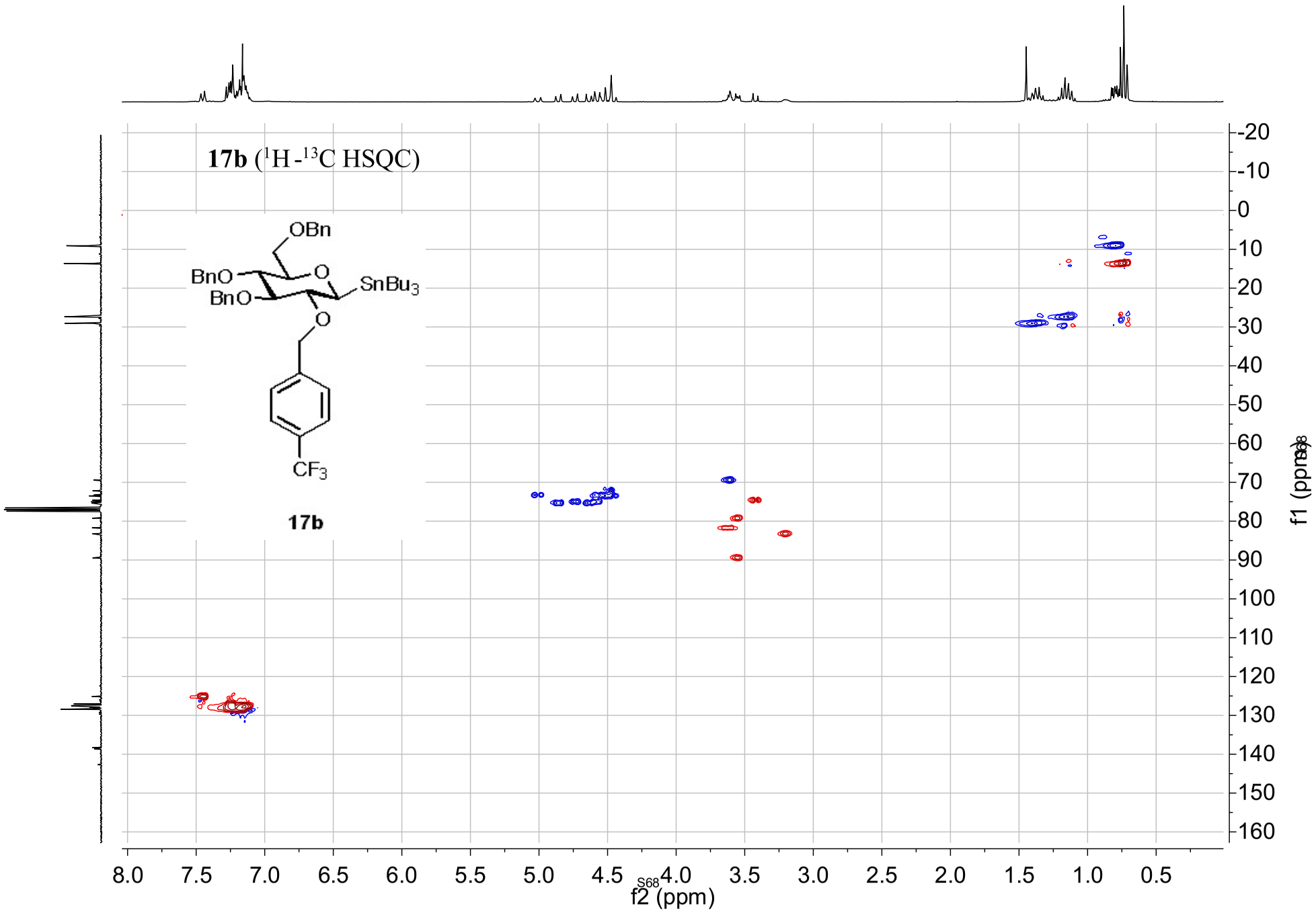
17b

142.87
138.79
138.62
138.47
128.58
128.56
128.45
128.04
127.94
127.87
127.78
127.75
127.61
127.56
127.17
125.35
125.30
125.25
125.20
89.60
83.39
81.88
79.38
77.16
75.51
75.18
74.72
73.64
73.43
72.28
69.58
29.21
27.54
13.78
9.23

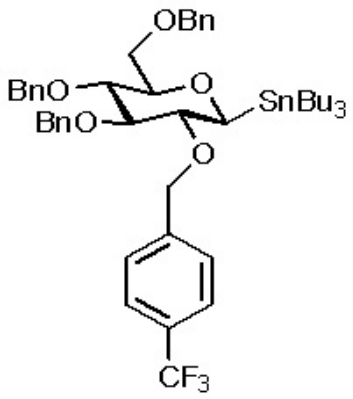
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)


17b (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
SnBu3
O
CF3
17b
J= 143 Hz
f2 (ppm)
f1 (ppm)

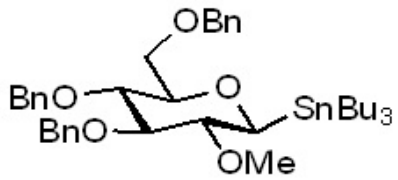

17b (1H -13C HSQC)
OBn
BnO
BnO
O
SnBu3
O
CF3
17b
f2 (ppm)
f1 (ppm)

17b (^{19}F NMR, 282 MHz, $CDCl_3$)

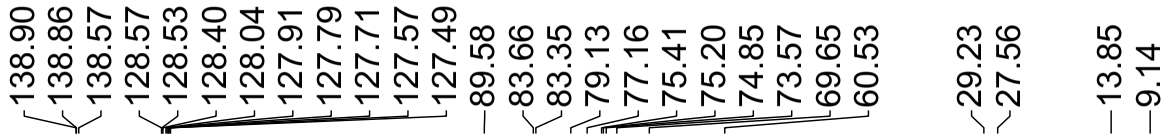


17b

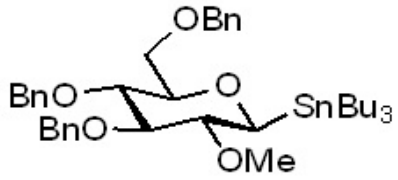
17c (^{1}H NMR, 300MHz, $CDCl_3$)



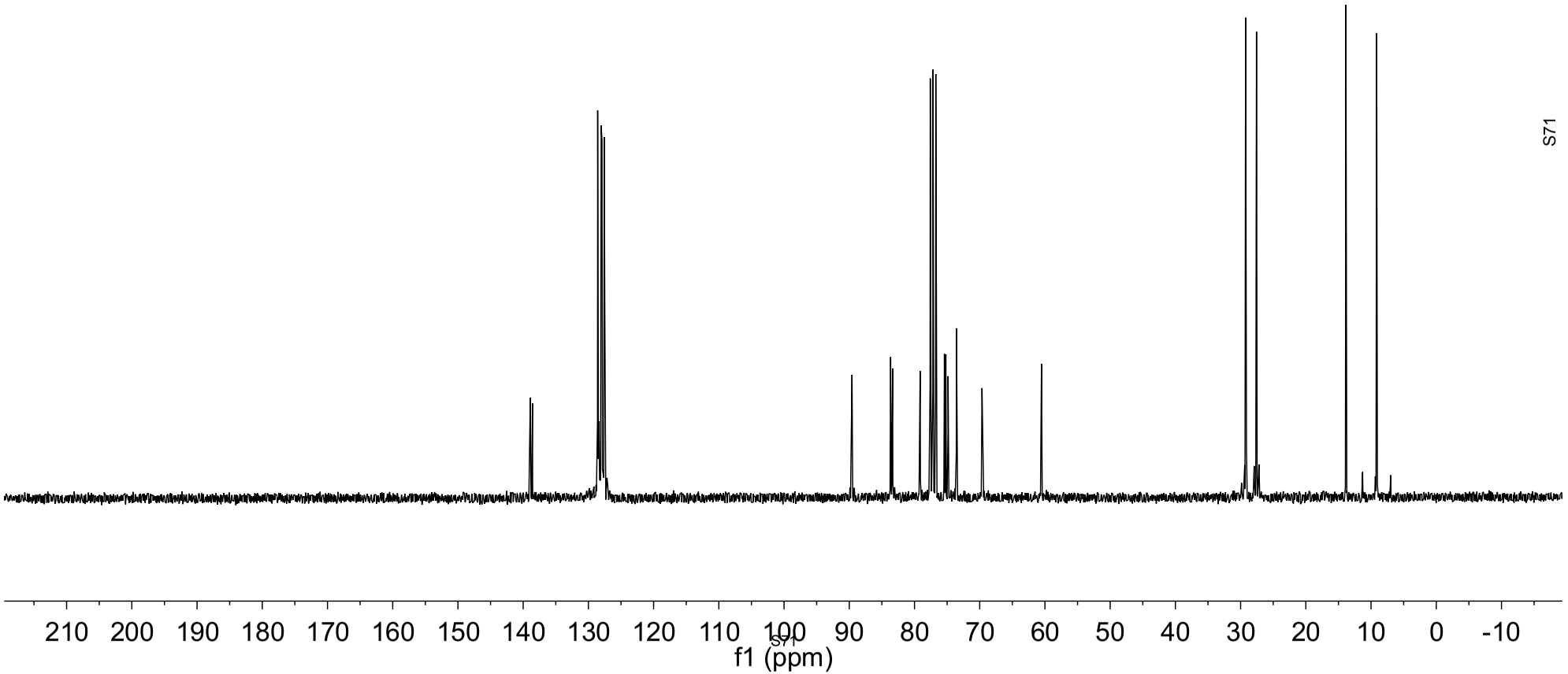
17c

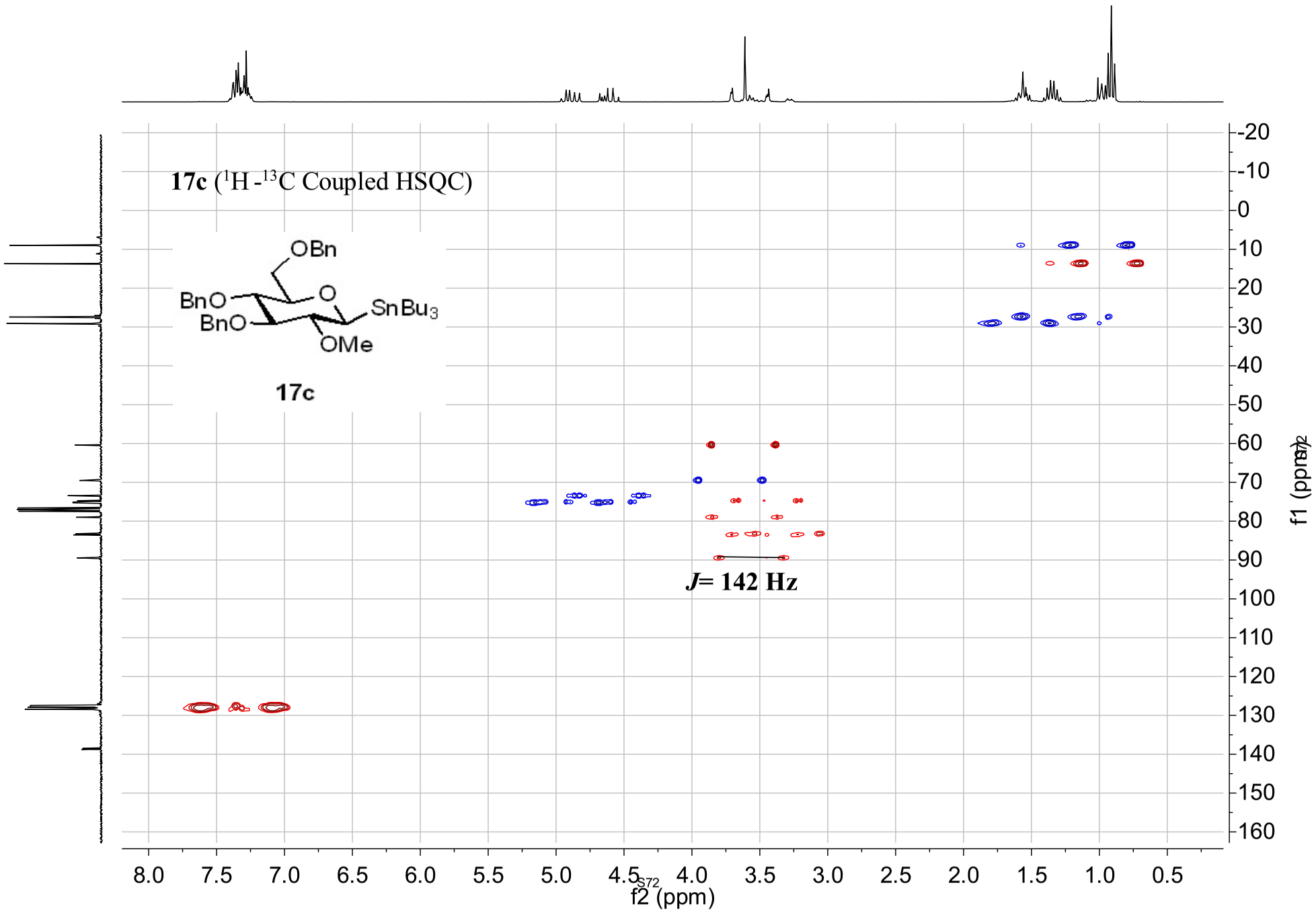


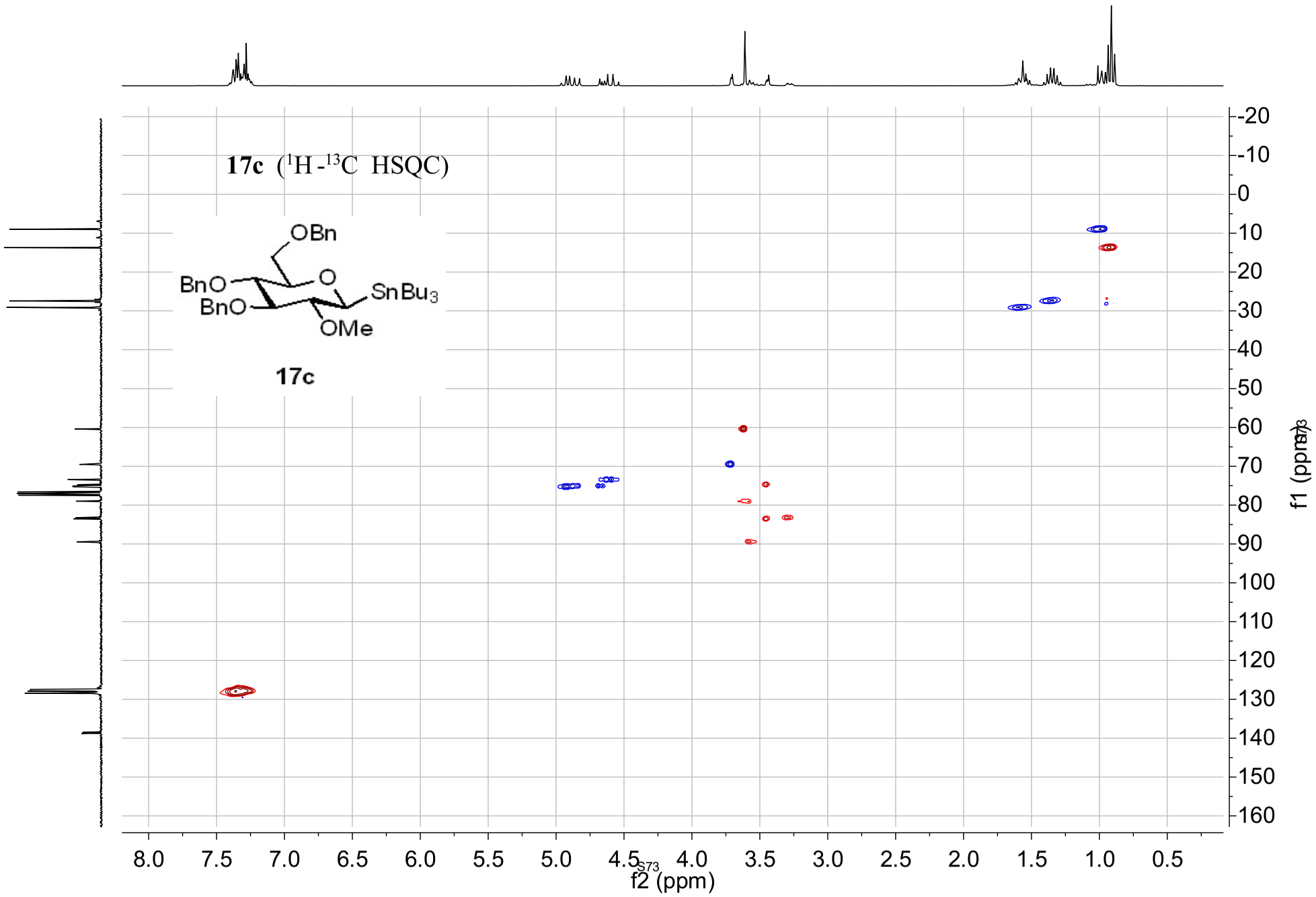
17c (^{13}C NMR, 75MHz, $CDCl_3$)



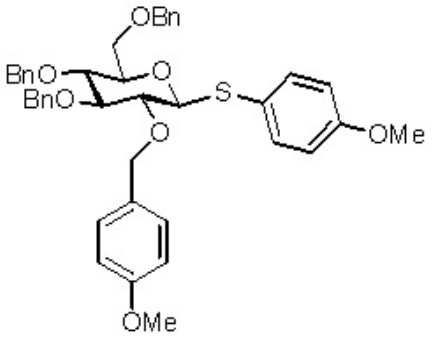
17c




17c (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
SnBu3
OMe
17c
J= 142 Hz
f2 (ppm)
f1 (ppm)

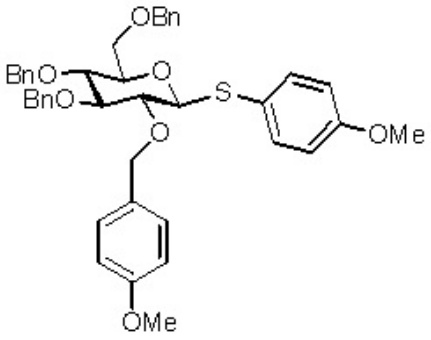

17c (^{1}H-^{13}C HSQC)
OBn
BnO
BnO
O
SnBu3
OMe
17c
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

21a (^{1}H NMR, 300MHz, $CDCl_3$)



21a

21a (^{13}C NMR, 75MHz, $CDCl_3$)

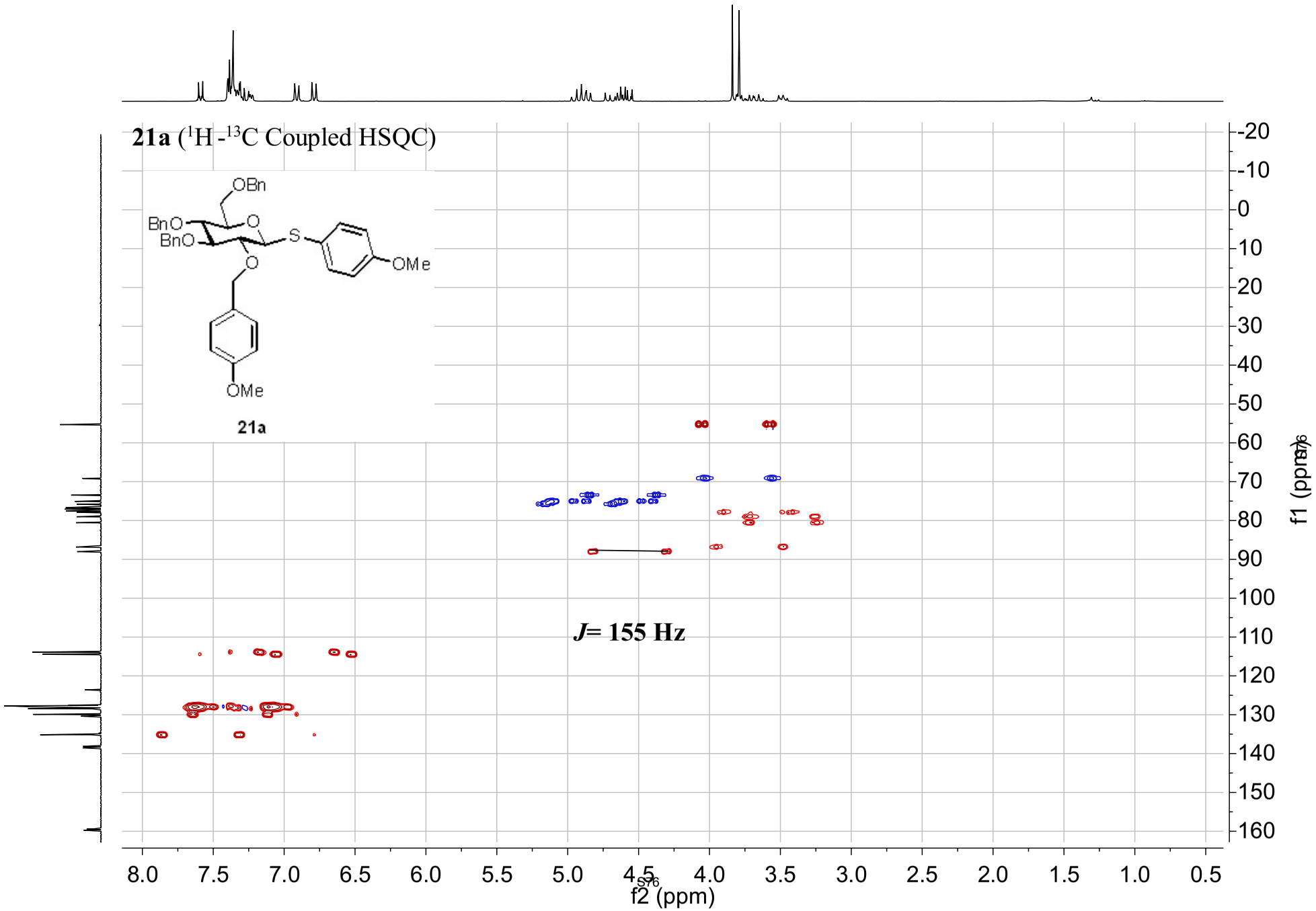


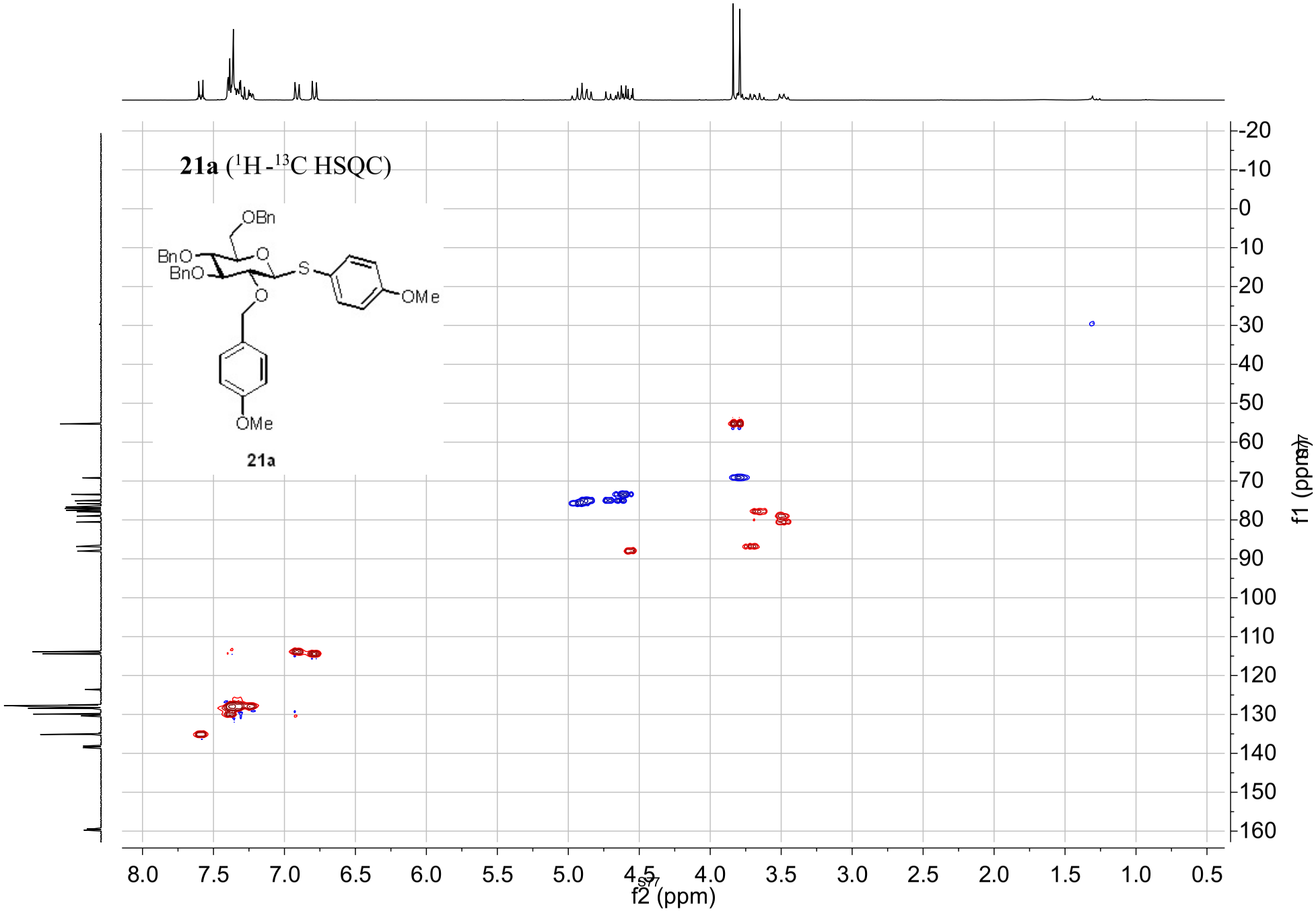
21a

159.83
159.51
138.63
138.51
138.21
135.23
130.47
130.00
128.56
128.53
128.45
128.05
127.97
127.90
127.85
127.78
127.64
123.69
114.53
113.98
88.09
86.90
80.65
79.11
77.97
77.16
75.88
75.15
75.11
73.54
69.24
55.40
55.39

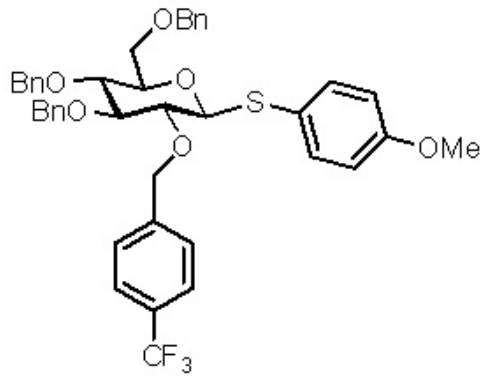
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)


21a (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
S
OMe
O
OMe
21a
J= 155 Hz
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
f2 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)

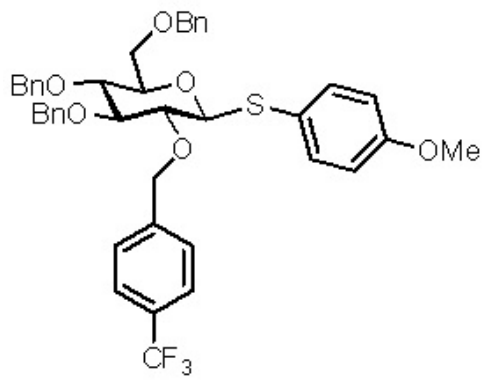

21a (1H-13C HSQC)
OBn
BnO
BnO
O
S
OMe
O
OMe
21a
f2 (ppm)
f1 (ppm)

21b (^{1}H NMR, 300MHz, $CDCl_3$)

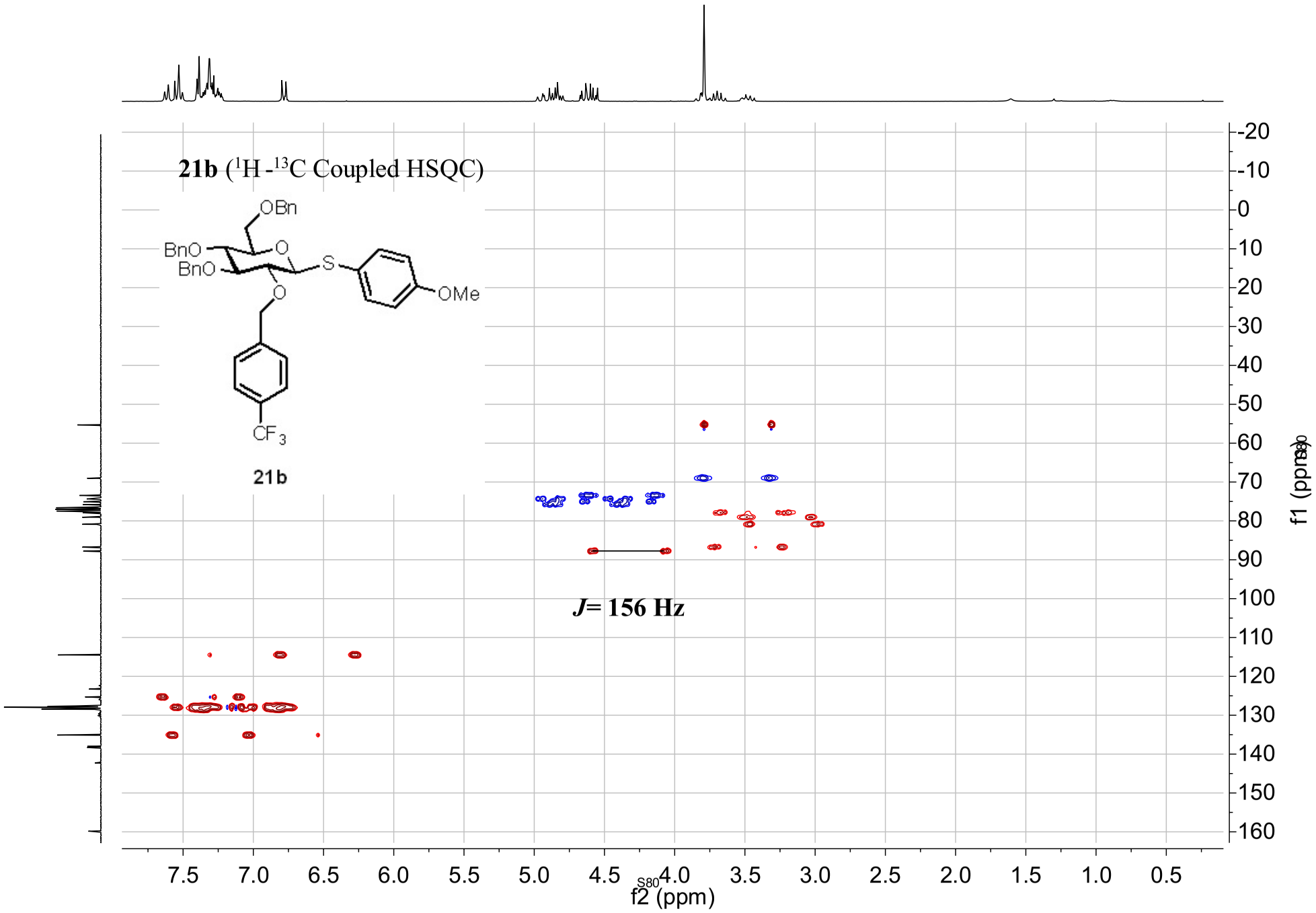


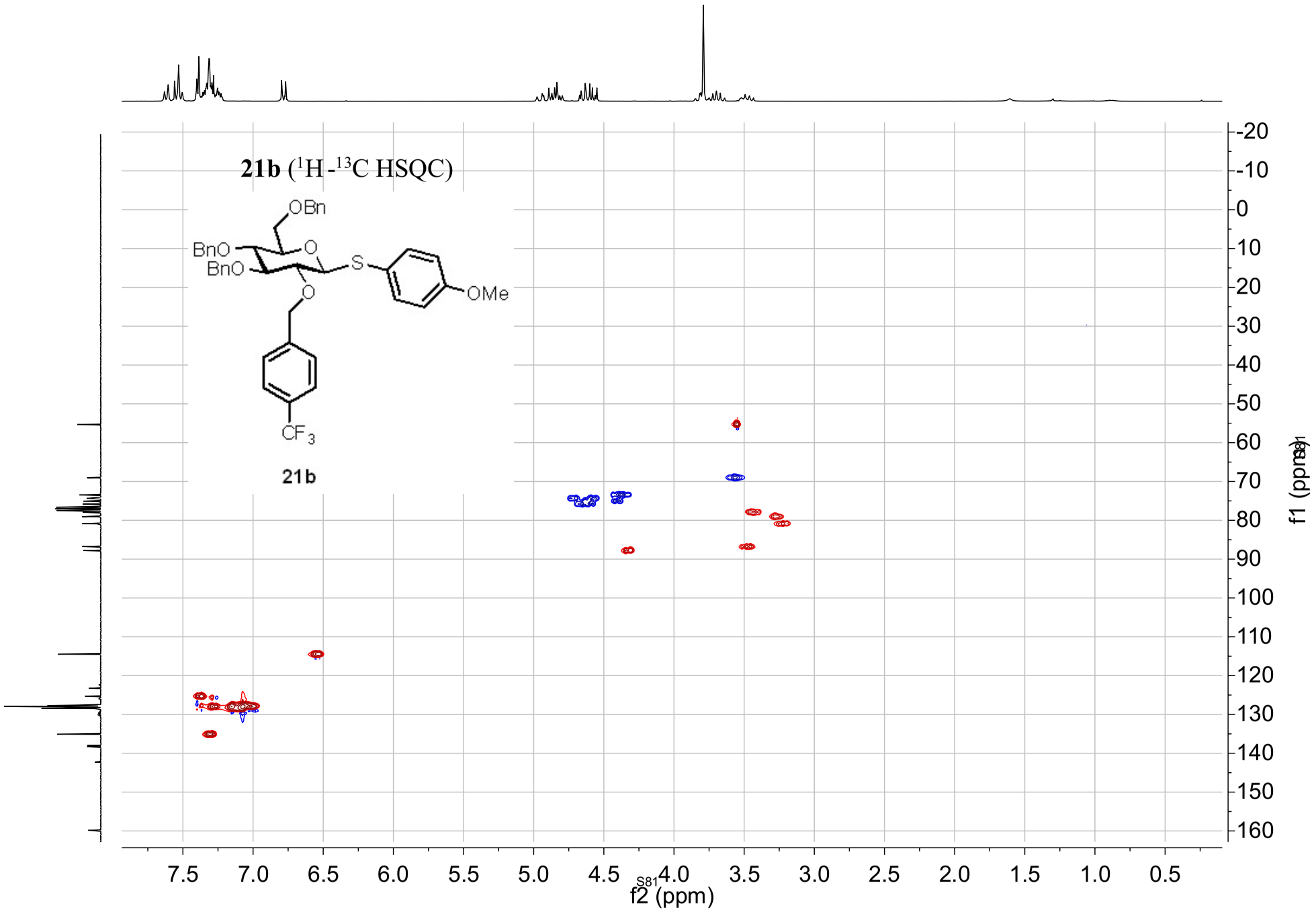
21b

21b (^{13}C NMR, 75MHz, $CDCl_3$)

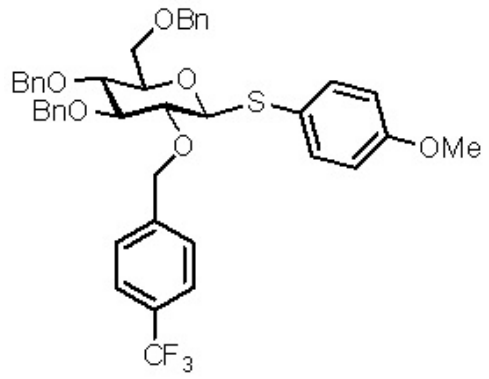


21b


21b (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
S
OMe
O
CF3
21b
J= 156 Hz
f2 (ppm)
f1 (ppm)

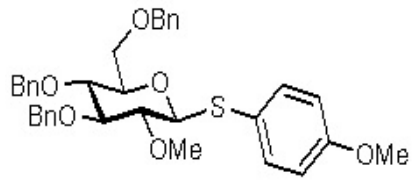

21b (1H-13C HSQC)
OBn
BnO
BnO
O
S
OMe
O
CF3
21b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)

21b (^{19}F NMR, 282 MHz, $CDCl_3$)



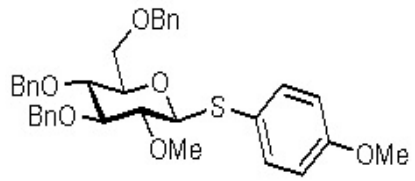
21b

21c (^{1}H NMR, 300MHz, $CDCl_3$)



21c

21c (^{13}C NMR, 75MHz, $CDCl_3$)

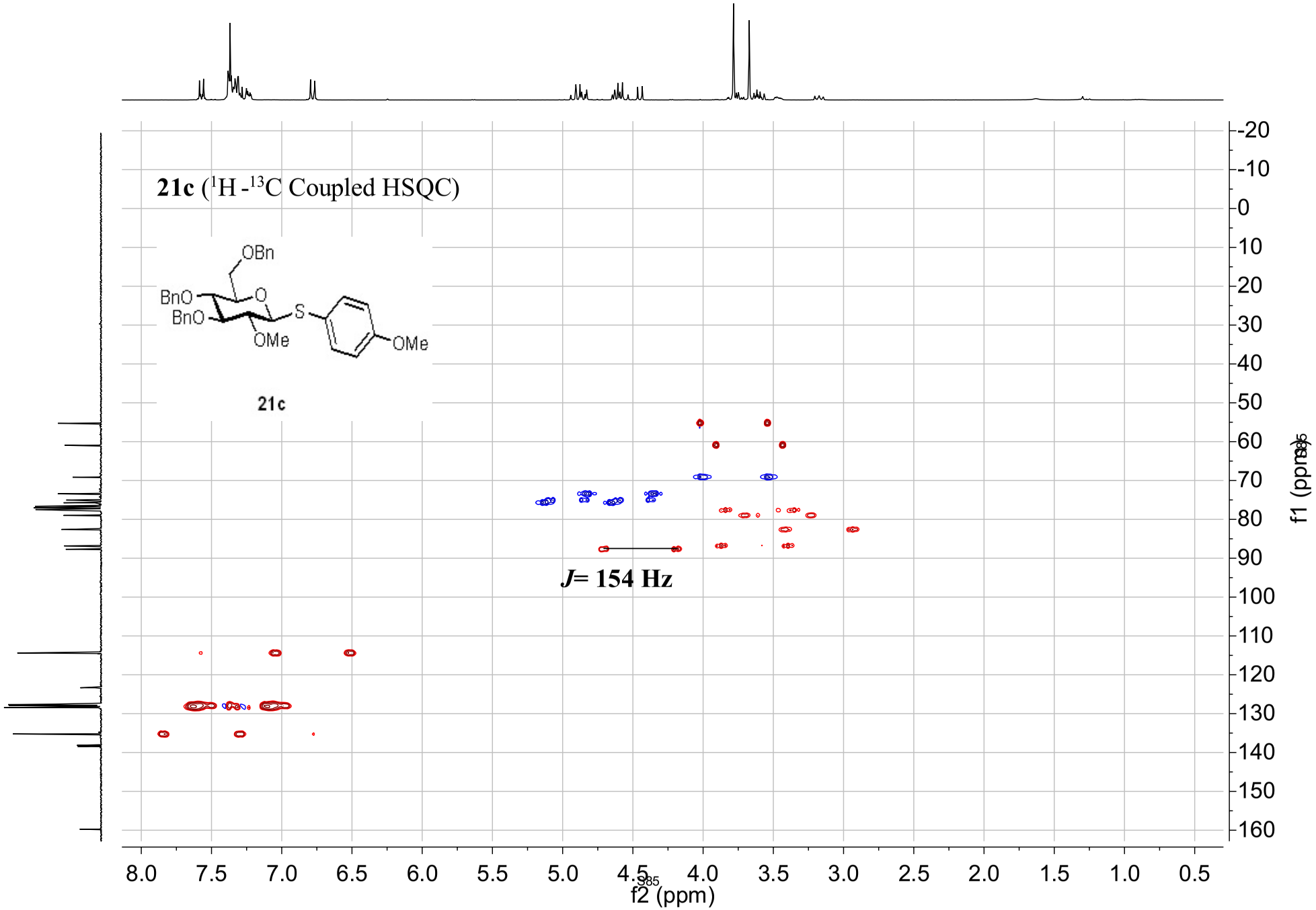


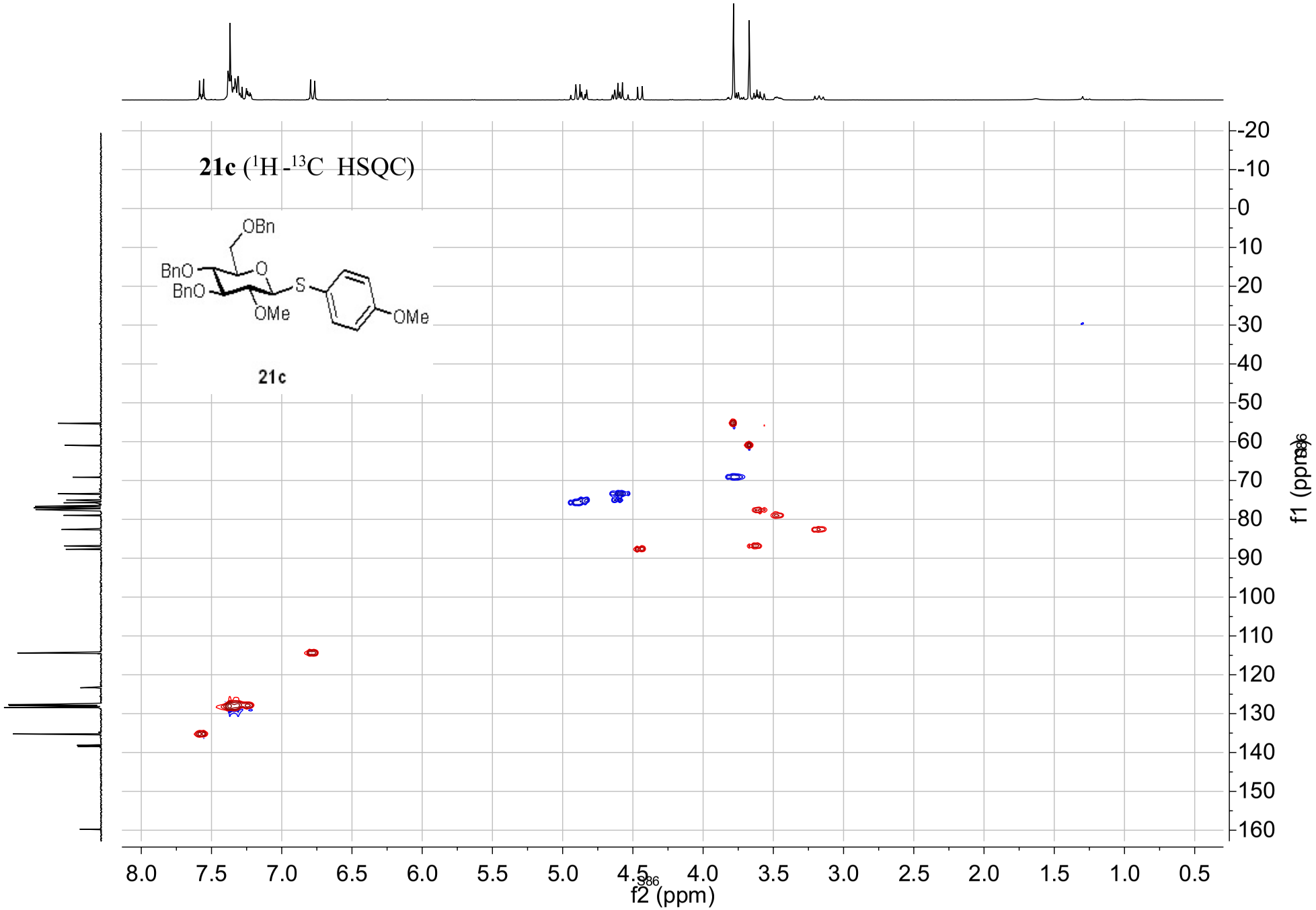
21c

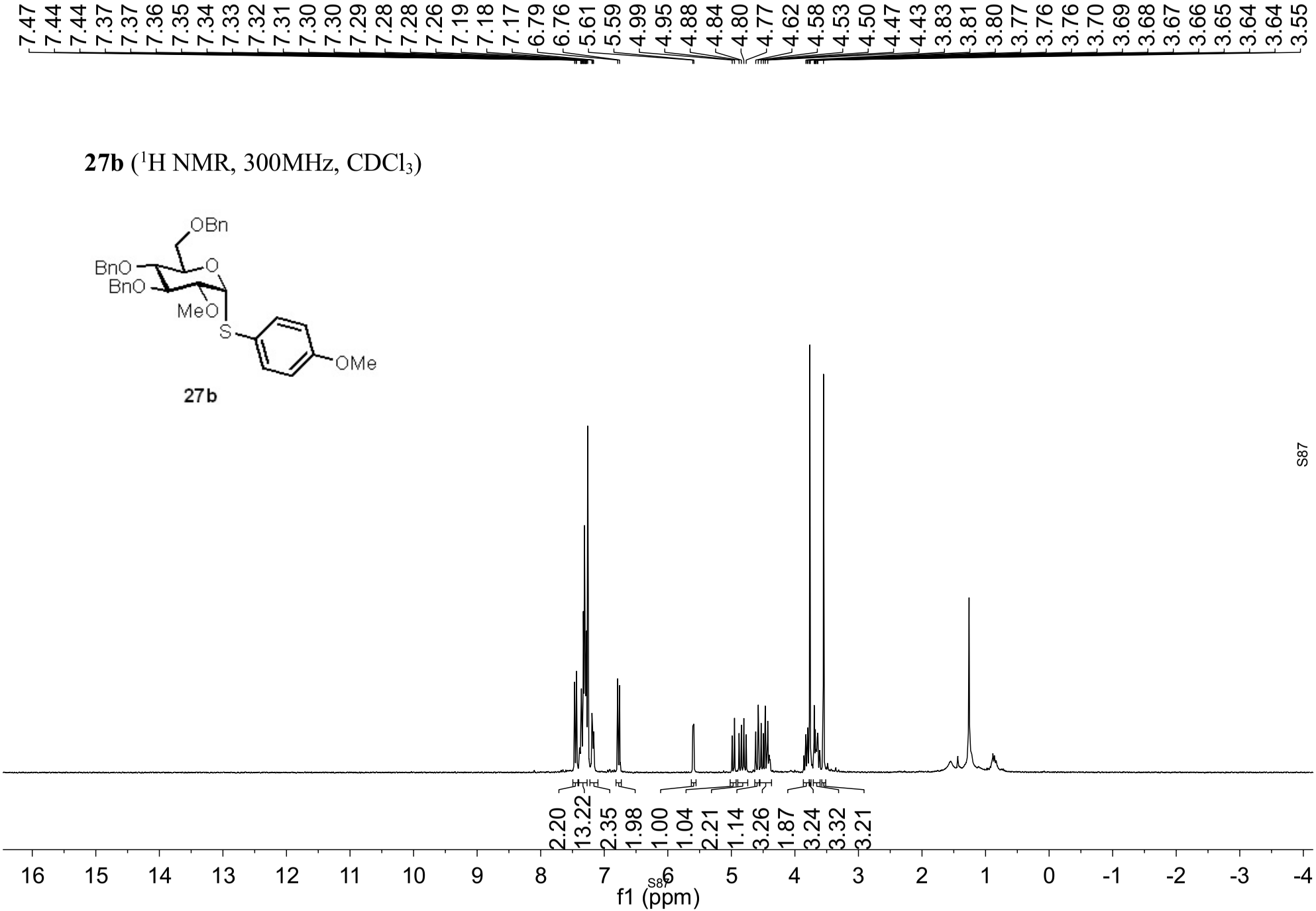
159.86
138.57
138.52
138.26
135.35
128.57
128.54
128.45
128.11
128.04
127.90
127.86
127.78
127.65
123.45
114.50
87.81
86.93
82.74
79.11
77.79
77.16
75.85
75.14
73.53
69.26
61.06
55.40

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

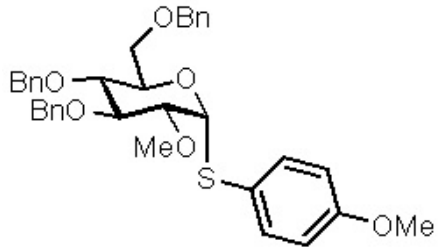
f1 (ppm)


21c (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
S
OMe
OMe
21c
J= 154 Hz
f2 (ppm)
f1 (ppm)

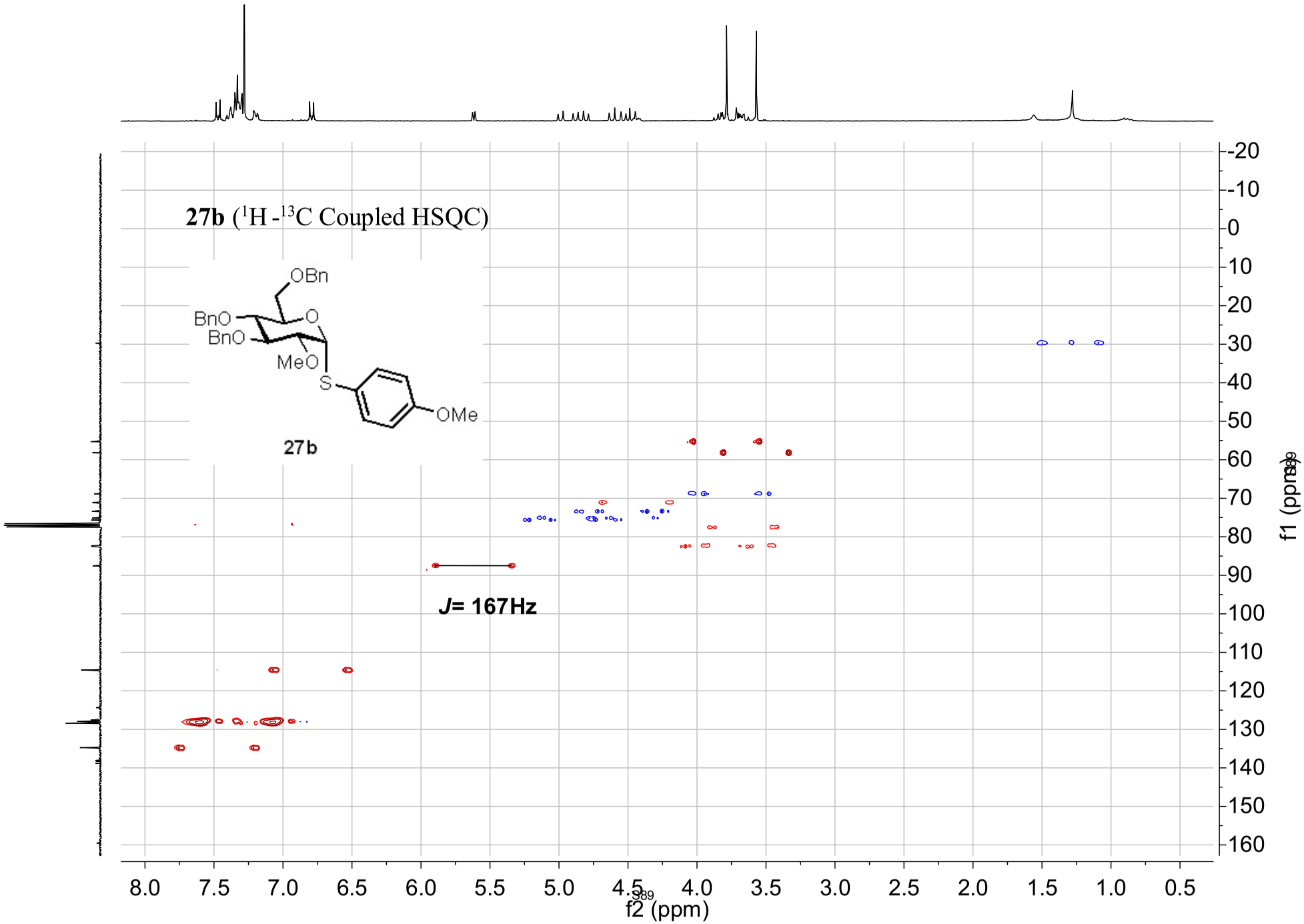

21c (^{1}H-^{13}C HSQC)
OBn
BnO
BnO
O
S
OMe
OMe
21c
f2 (ppm)
f1 (ppm)

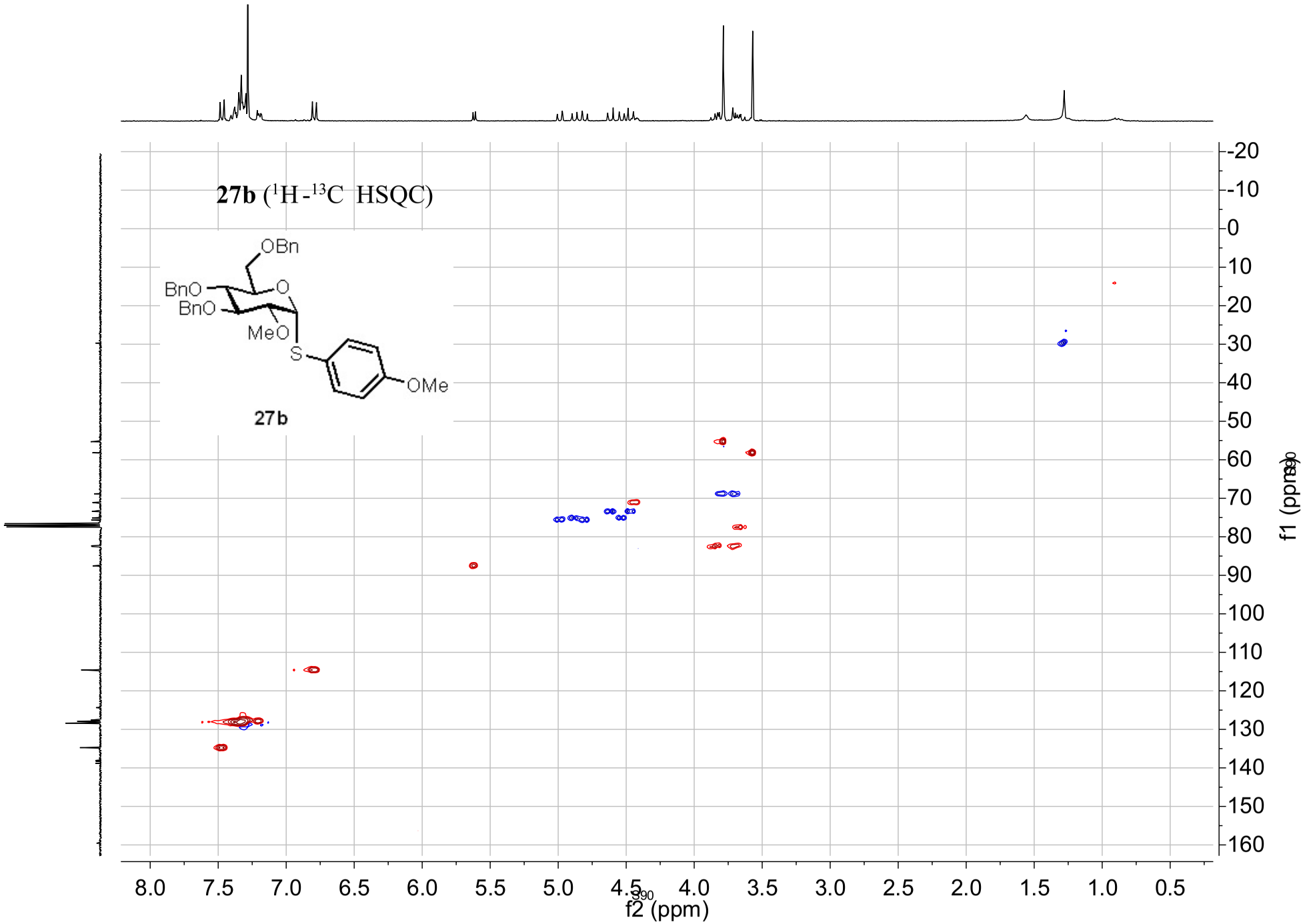

7.47
7.44
7.44
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.26
7.19
7.18
7.17
6.79
6.76
5.61
5.59
4.99
4.95
4.88
4.84
4.80
4.77
4.62
4.58
4.53
4.50
4.47
4.43
3.83
3.81
3.80
3.77
3.76
3.76
3.70
3.69
3.68
3.67
3.66
3.65
3.64
3.64
3.55
27b (1H NMR, 300MHz, CDCl3)
OBn
BnO
BnO
O
MeO
S
OMe
27b
S87
2.20
13.22
2.35
1.98
1.00
1.04
2.21
1.14
3.26
1.87
3.24
3.32
3.21
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

27b (^{13}C NMR, 75MHz, $CDCl_3$)

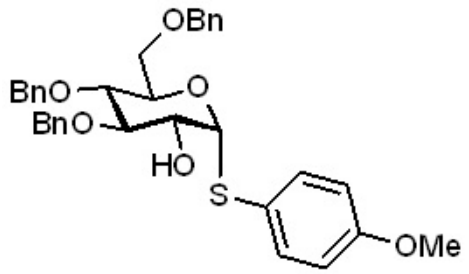


27b

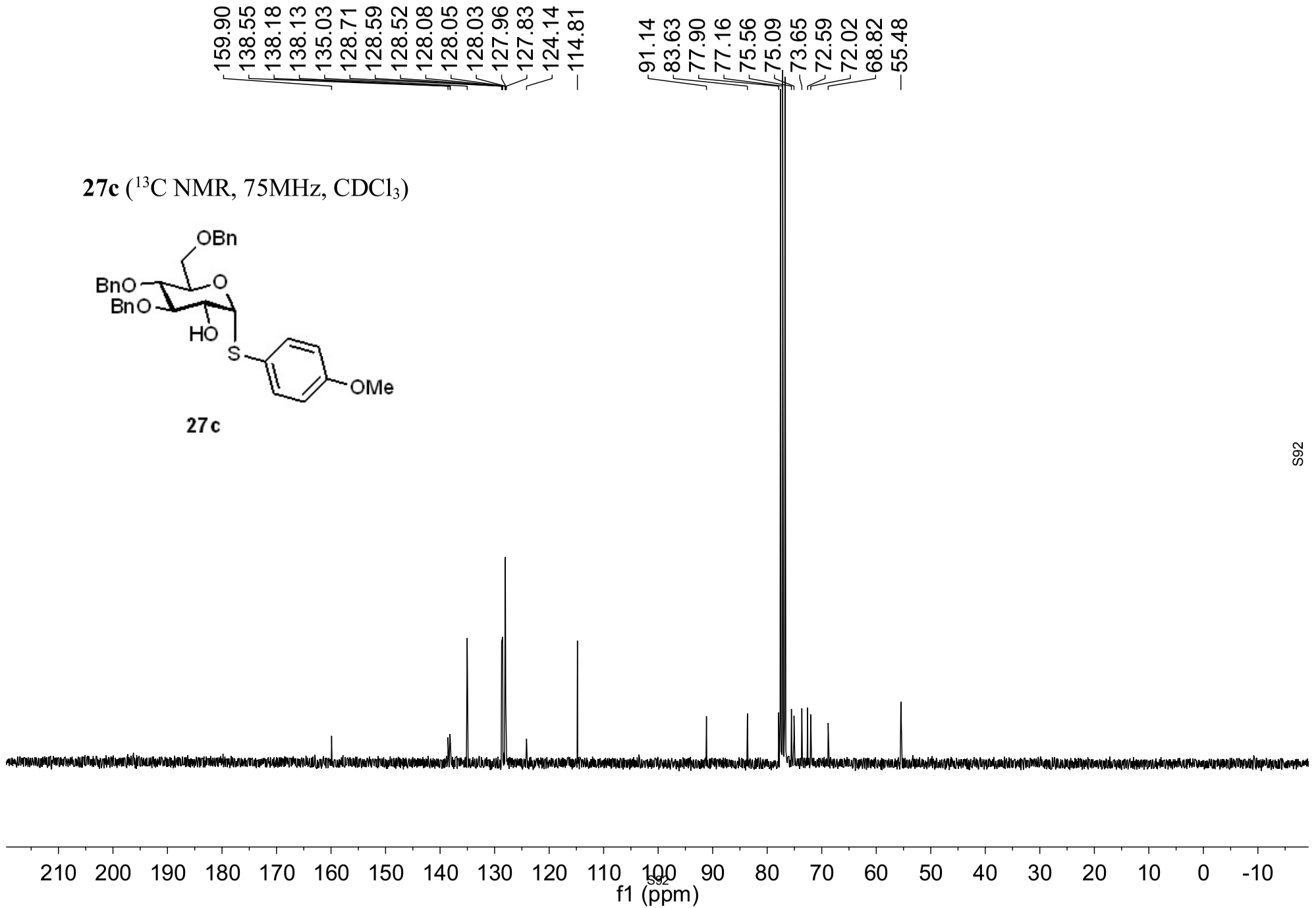

27b (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
MeO
S
OMe
27b
J= 167Hz
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160


27b (1H -13C HSQC)
OBn
BnO
O
BnO
MeO
S
OMe
27b
f2 (ppm)
f1 (ppm)

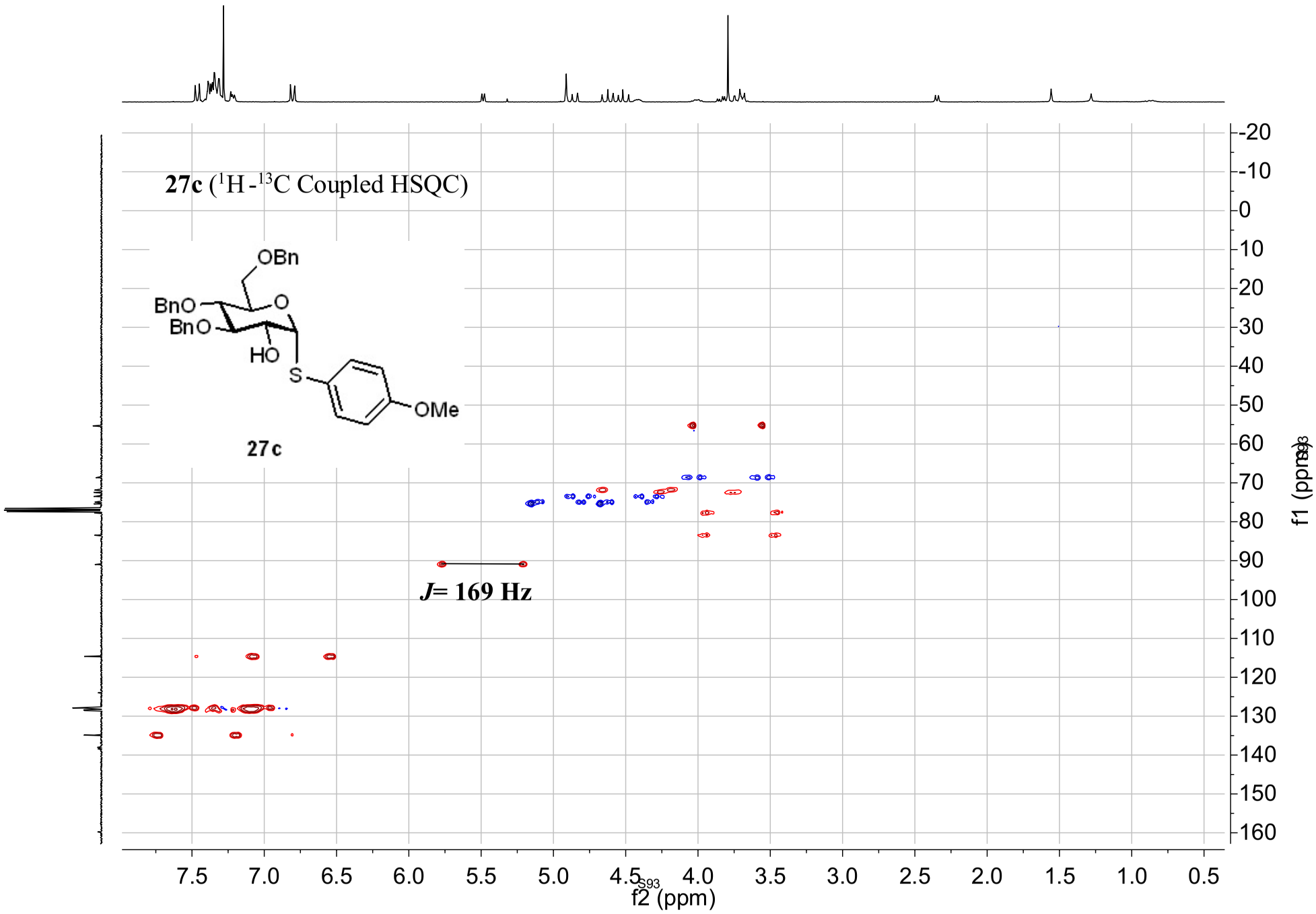
27c (^{1}H NMR, 300MHz, $CDCl_3$)

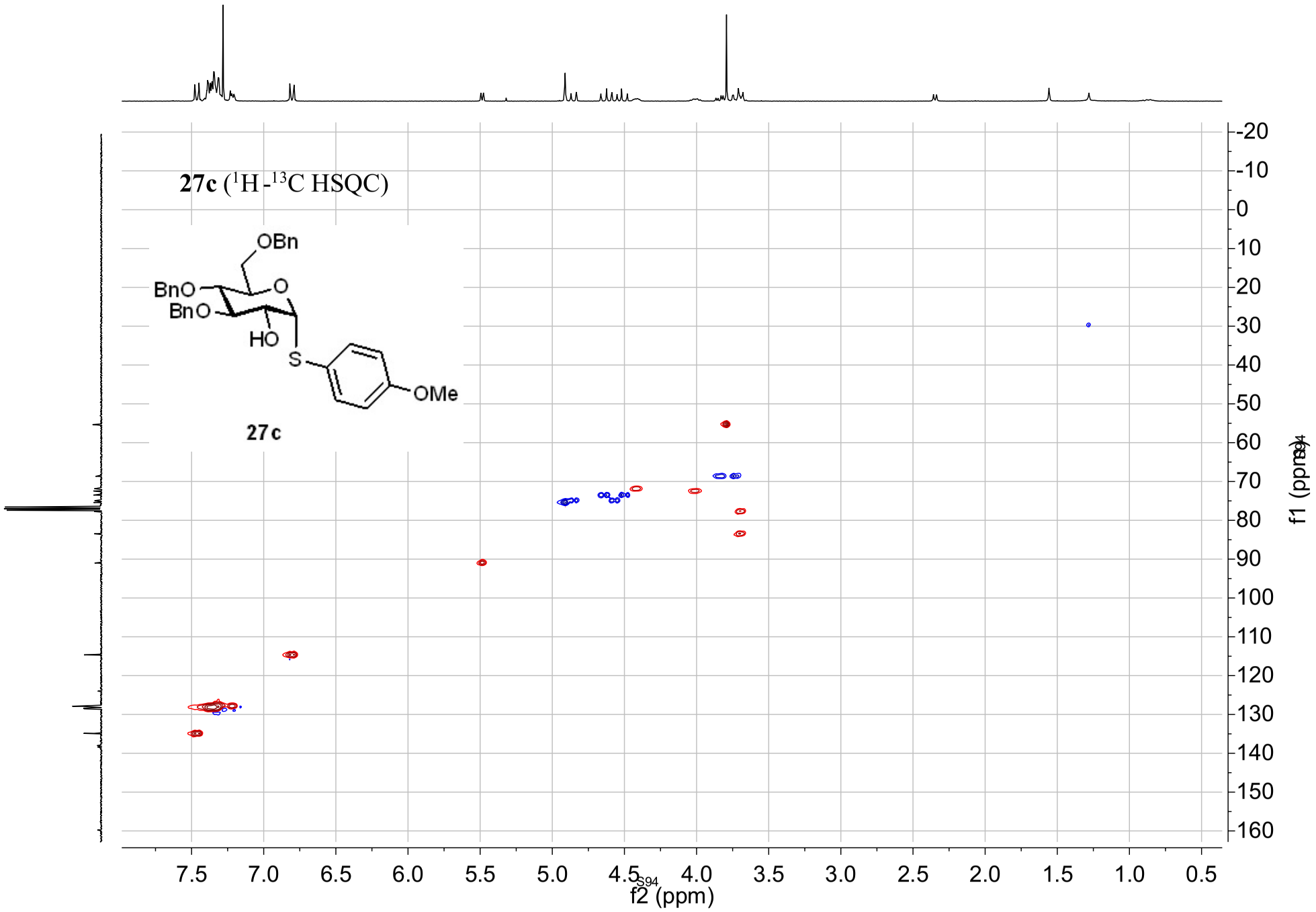


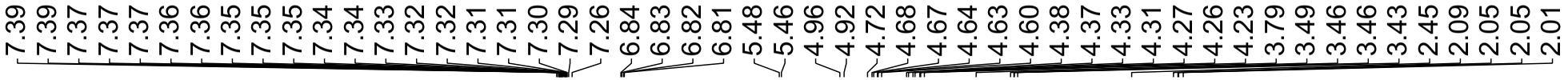
27c



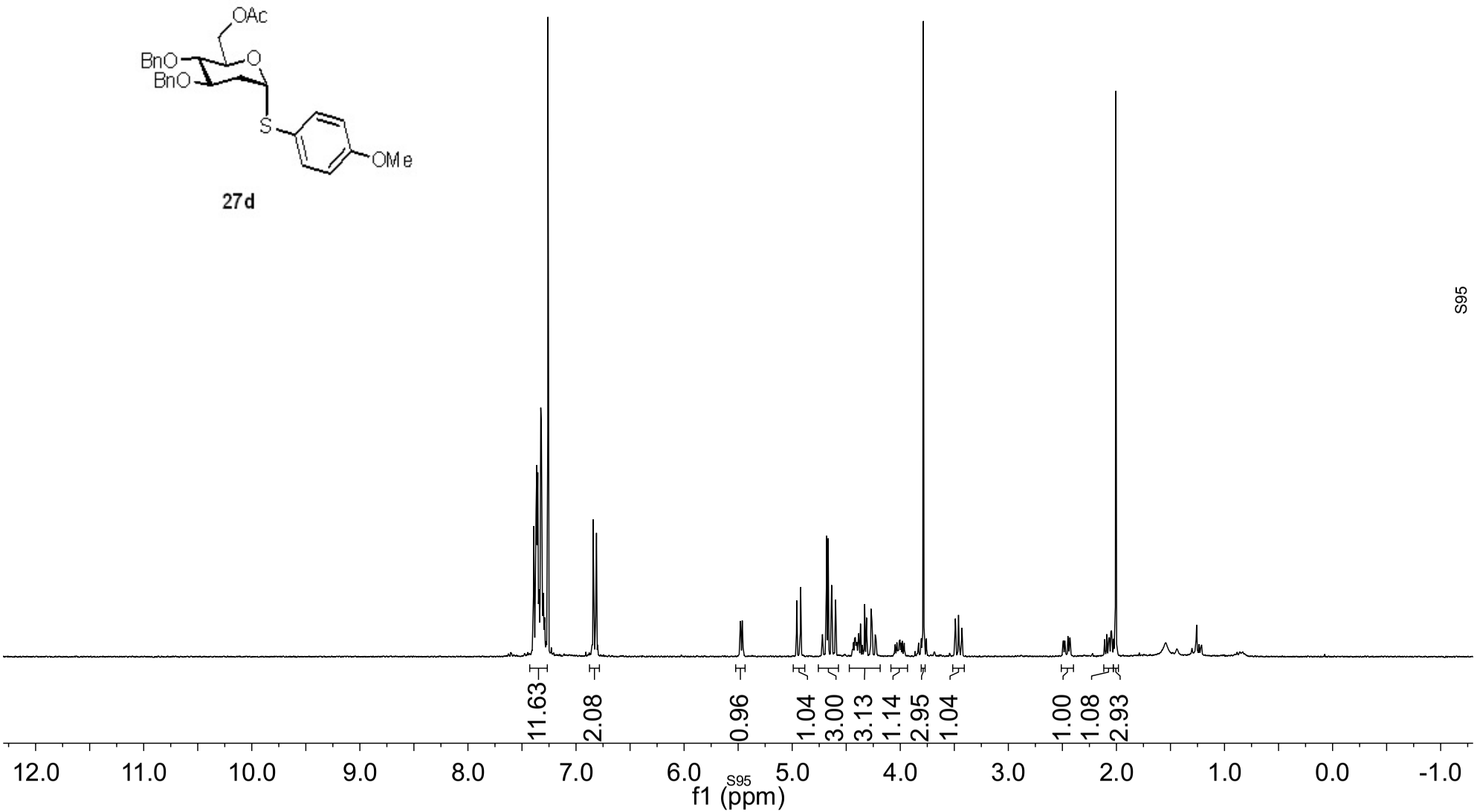
27c (^{13}C NMR, 75MHz, $CDCl_3$)


27c (1H -13C Coupled HSQC)
OBn
BnO
O
BnO
HO
S
OMe
27c
J= 169 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

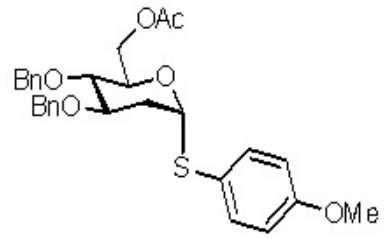

27c (1H-13C HSQC)
OBn
BnO
O
BnO
HO
S
OMe
27c
f2 (ppm)
f1 (ppm)



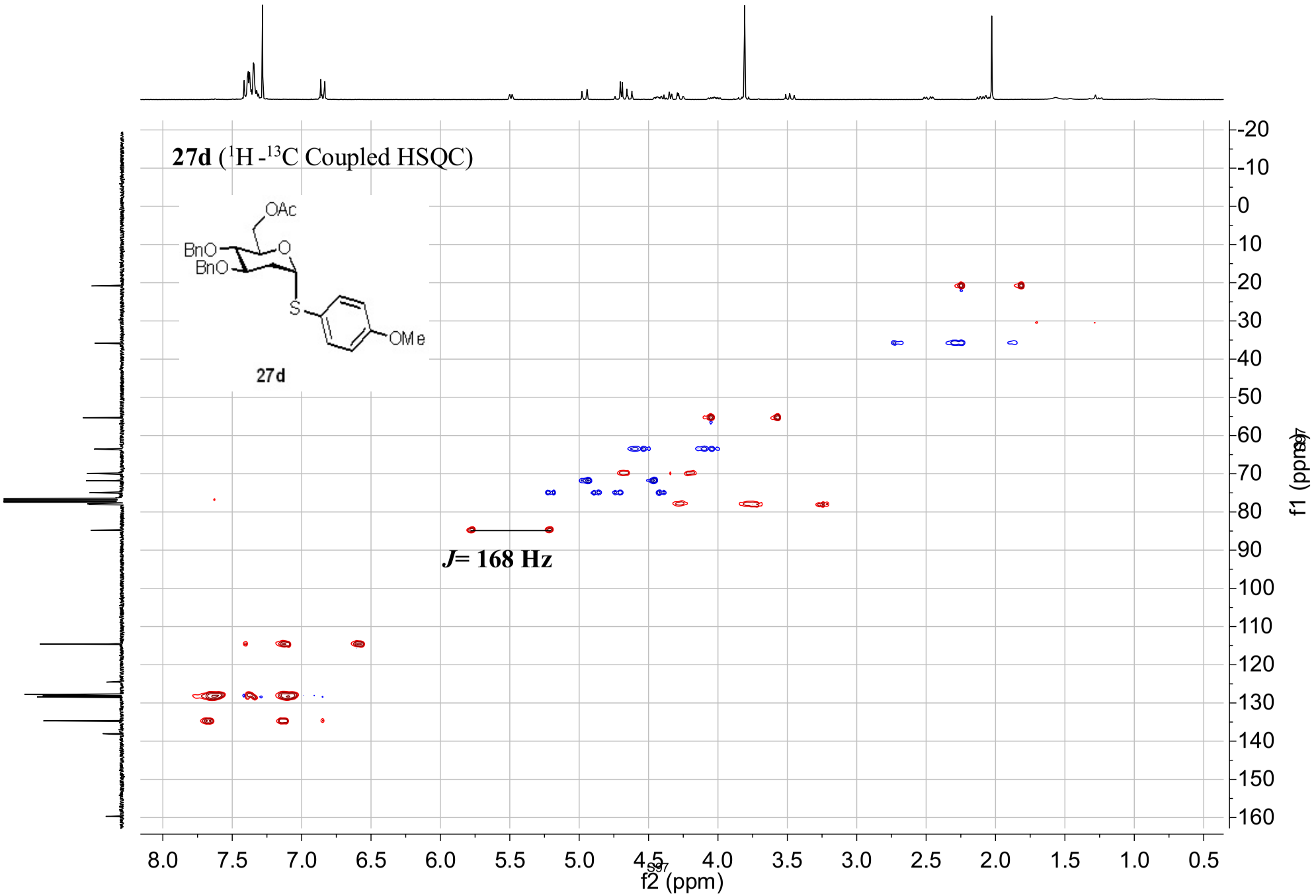
27d (^{1}H NMR, 300MHz, $CDCl_3$)

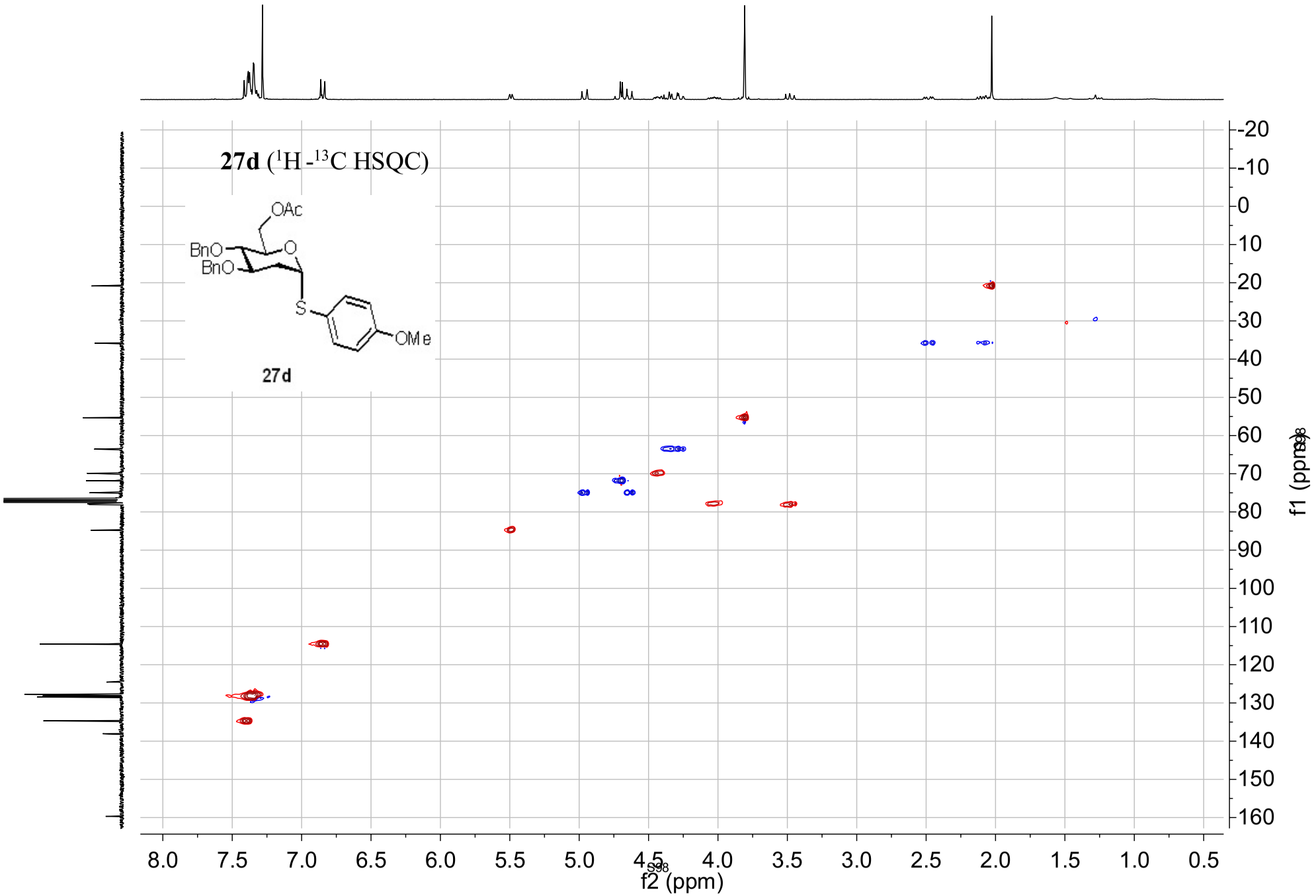


27d (^{13}C NMR, 75MHz, $CDCl_3$)



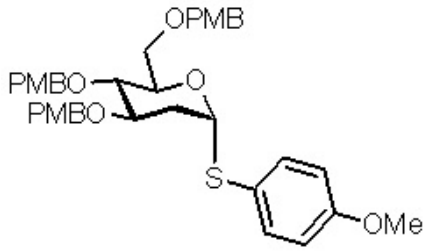
27d


27d (1H -13C Coupled HSQC)
OAc
BnO
BnO
O
S
OMe
27d
J= 168 Hz
f2 (ppm)
f1 (ppm)


27d (1H -13C HSQC)
OAc
BnO
BnO
O
S
OMe
27d
f2 (ppm)
f1 (ppm)

7.39 7.37 7.36 7.30 7.28 7.28 7.27 7.26 7.25 7.24 7.12 7.10 7.10 6.90 6.89 6.88 6.87 6.86 6.86 6.85 6.84 6.84 6.83 6.82 6.77 6.77 6.75 6.74 5.48 4.82 4.79 4.61 4.60 4.60 4.58 4.54 4.45 4.42 4.41 4.37 3.82 3.81 3.80 3.80 3.79 3.78 3.76 3.75 3.65 3.54 3.54

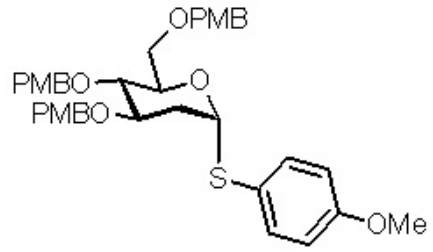
27e (^{1}H NMR, 300MHz, $CDCl_3$)



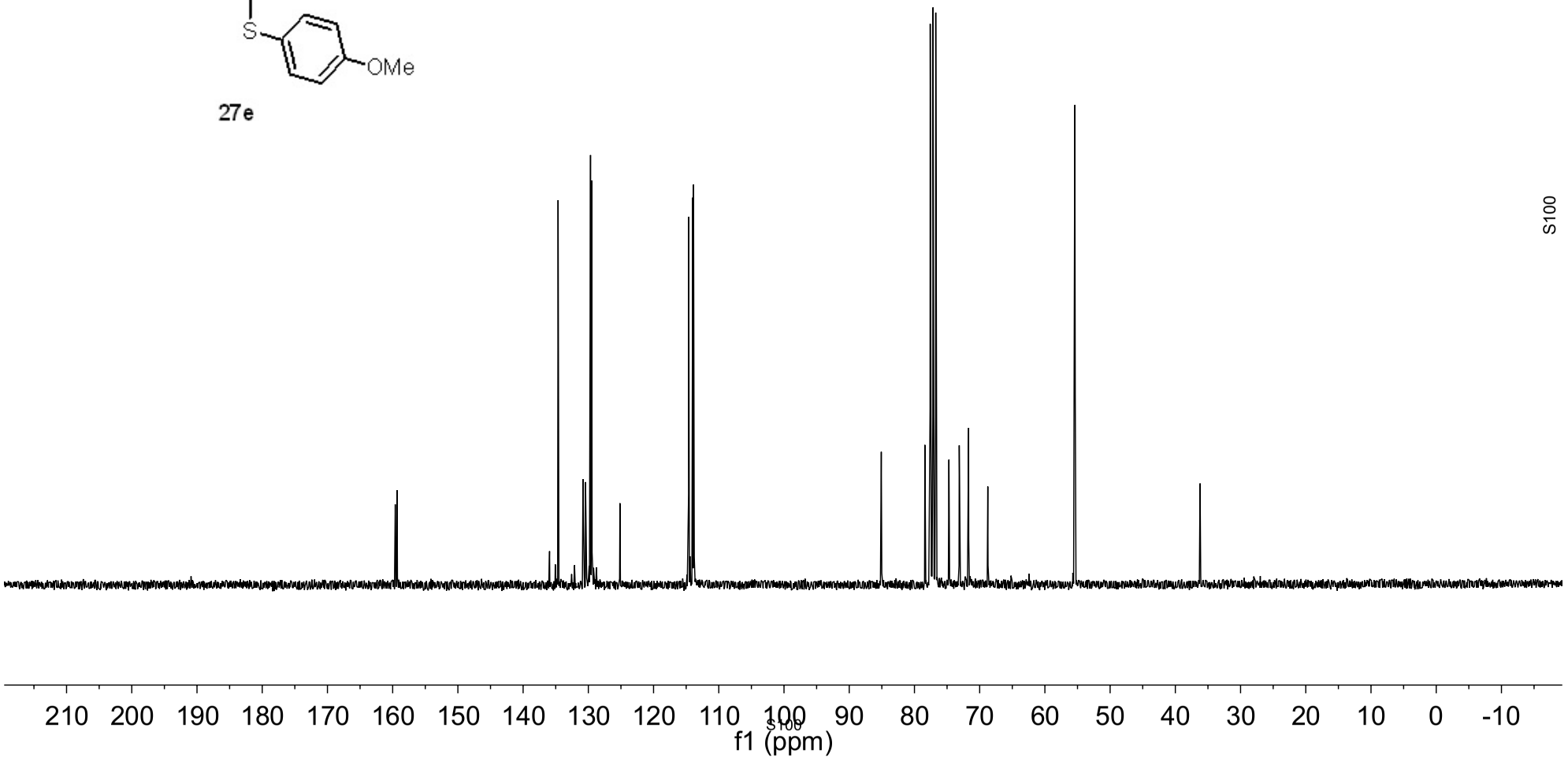
27e

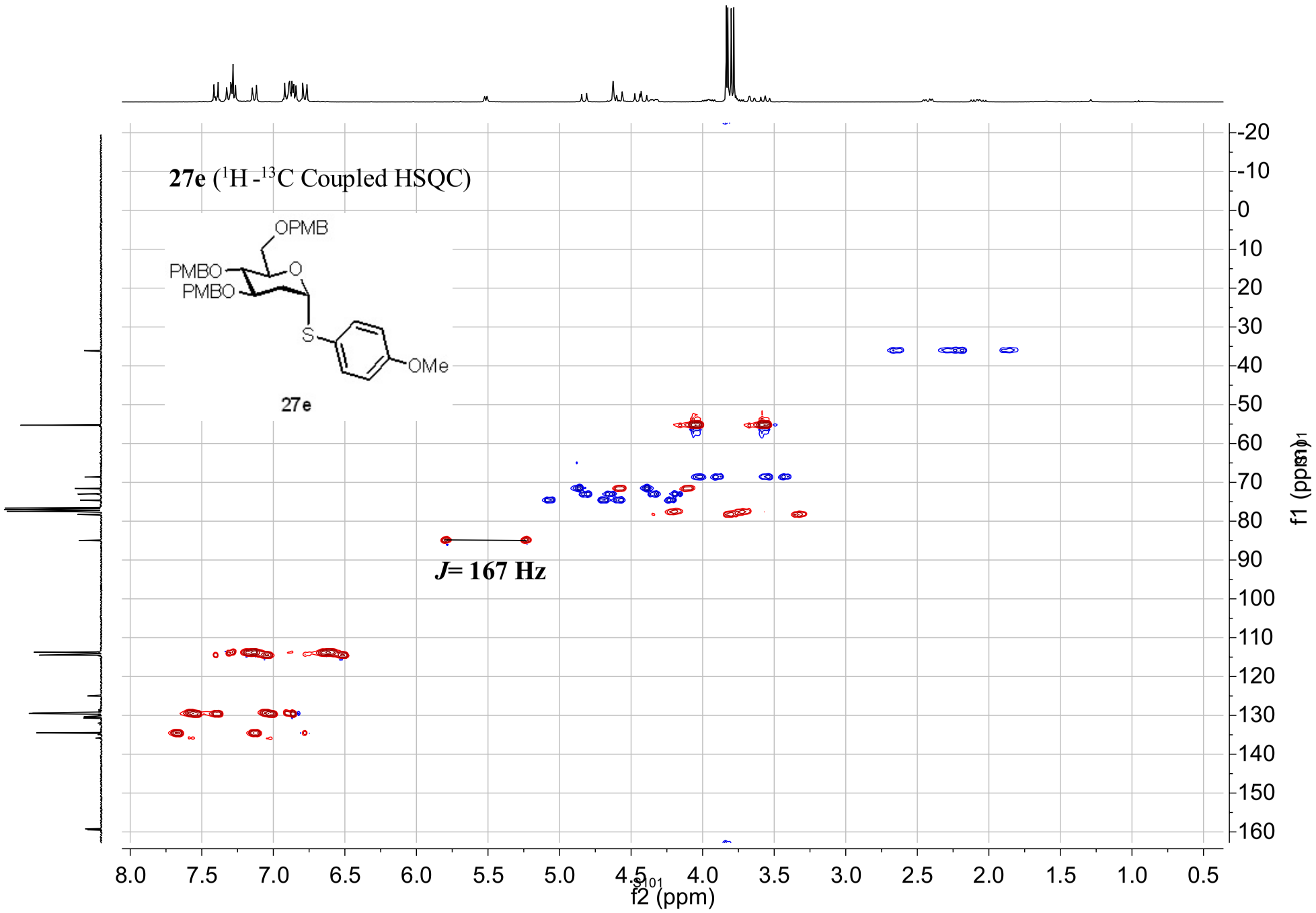
159.60
159.36
159.34
159.32
134.63
130.82
130.74
130.43
129.68
129.66
129.48
125.15
114.61
113.99
113.87
113.83
85.08
78.40
77.72
77.16
74.71
73.13
71.74
71.69
68.75
55.41
55.35
36.21

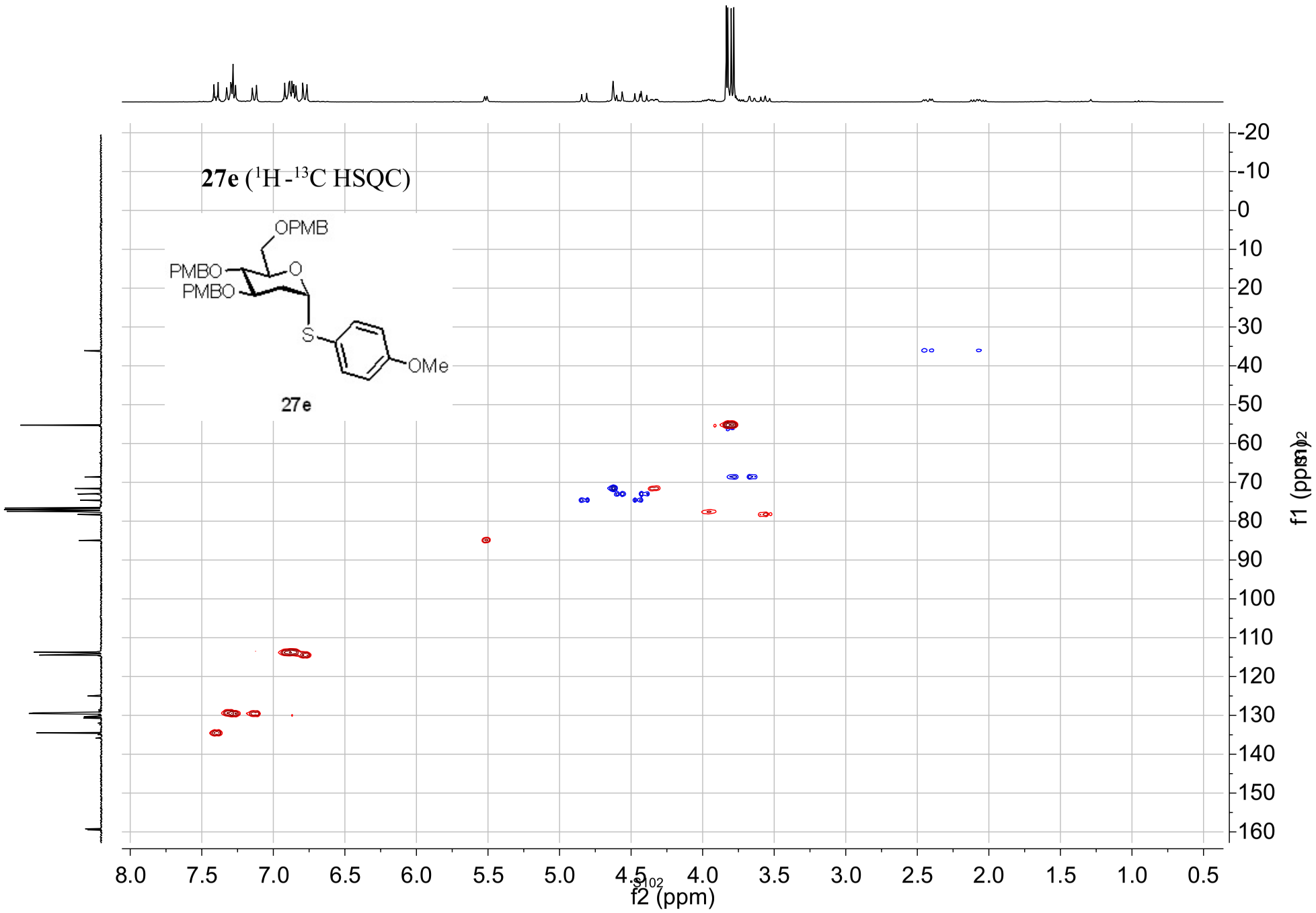
27e (^{13}C NMR, 75MHz, $CDCl_3$)



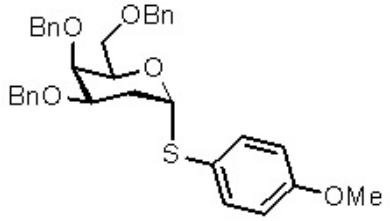
27e




27e (^{1}H -^{13}C Coupled HSQC)
OPMB
PMBO
PMBO
O
S
OMe
27e
J= 167 Hz
f2 (ppm)
f1 (ppm)

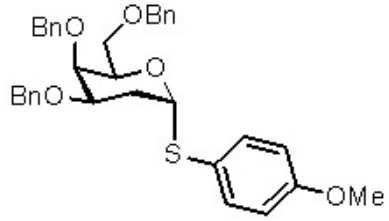

27e (1H -13C HSQC)
OPMB
PMBO
PMBO
O
S
OMe
27e
f2 (ppm)
f1 (ppm)

27f (^{1}H NMR, 300MHz, $CDCl_3$)

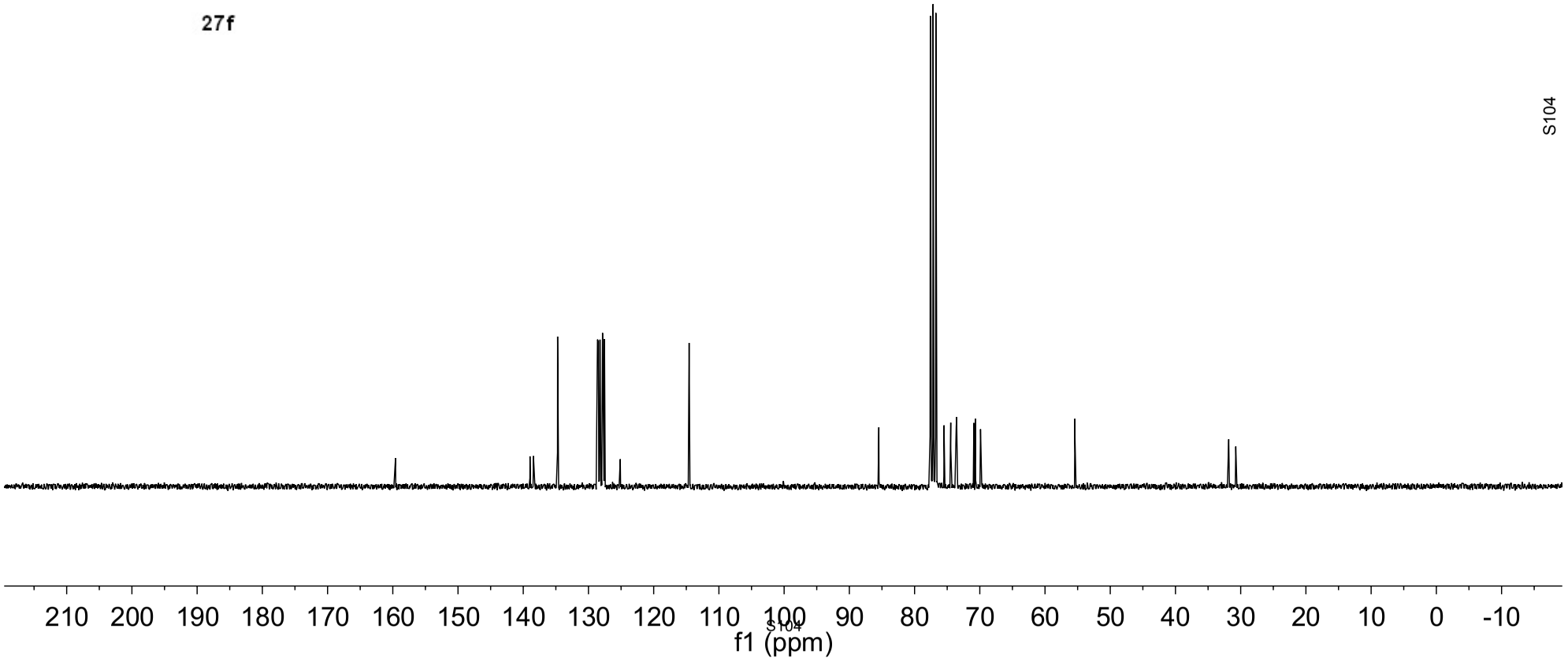


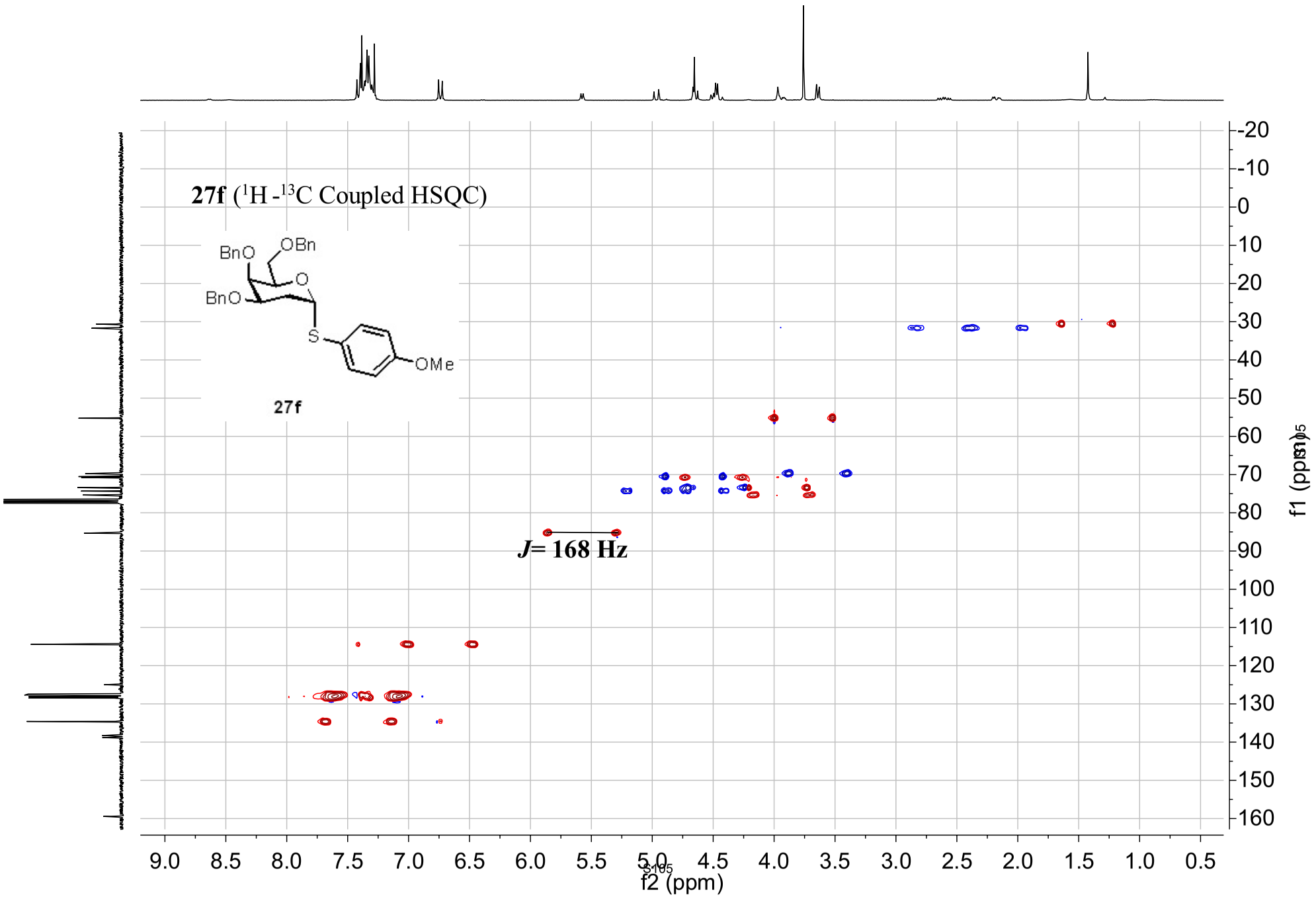
27f

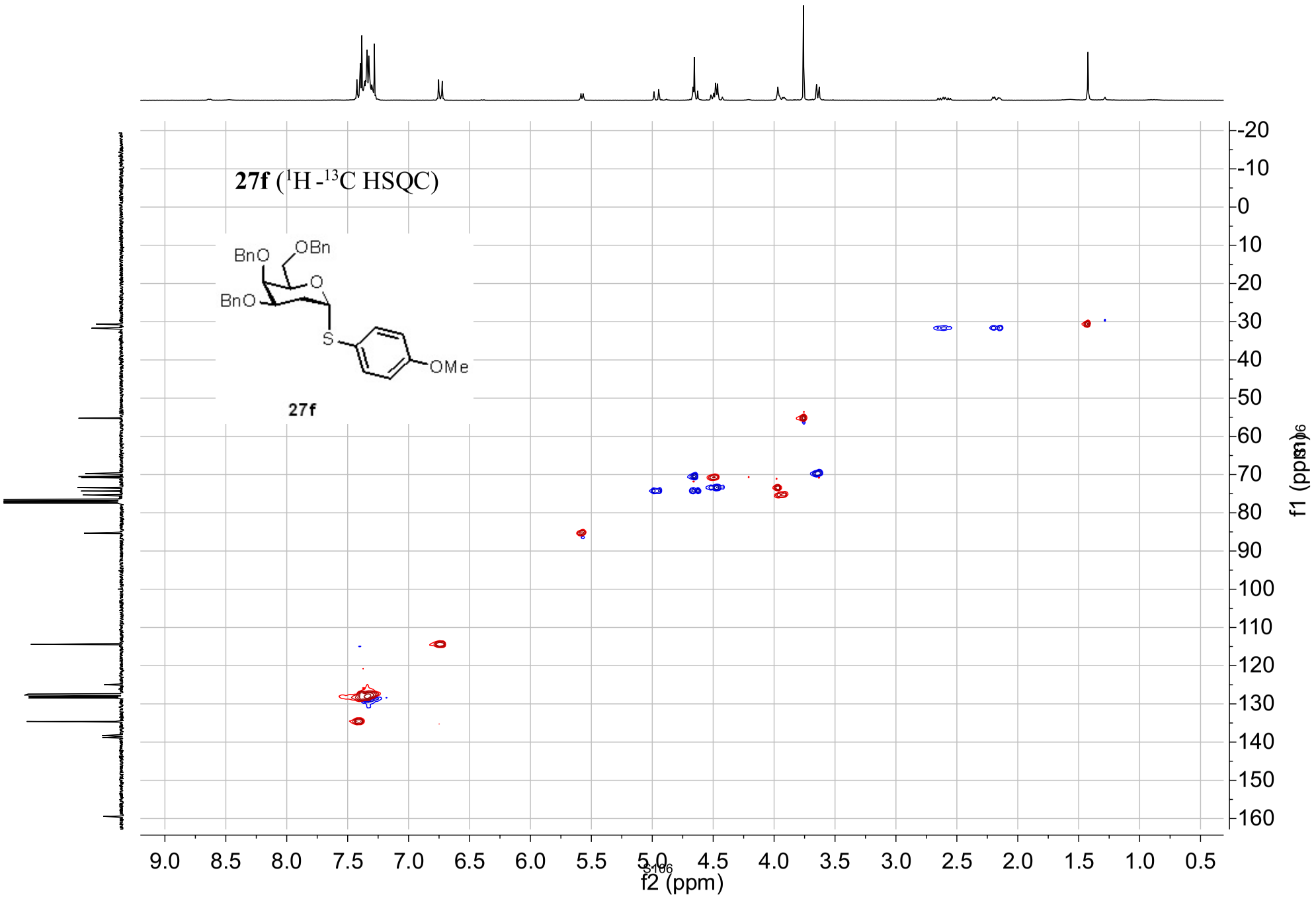
27f (^{13}C NMR, 75MHz, $CDCl_3$)



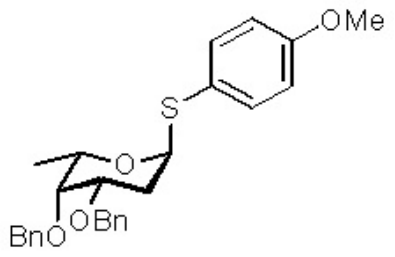
27f



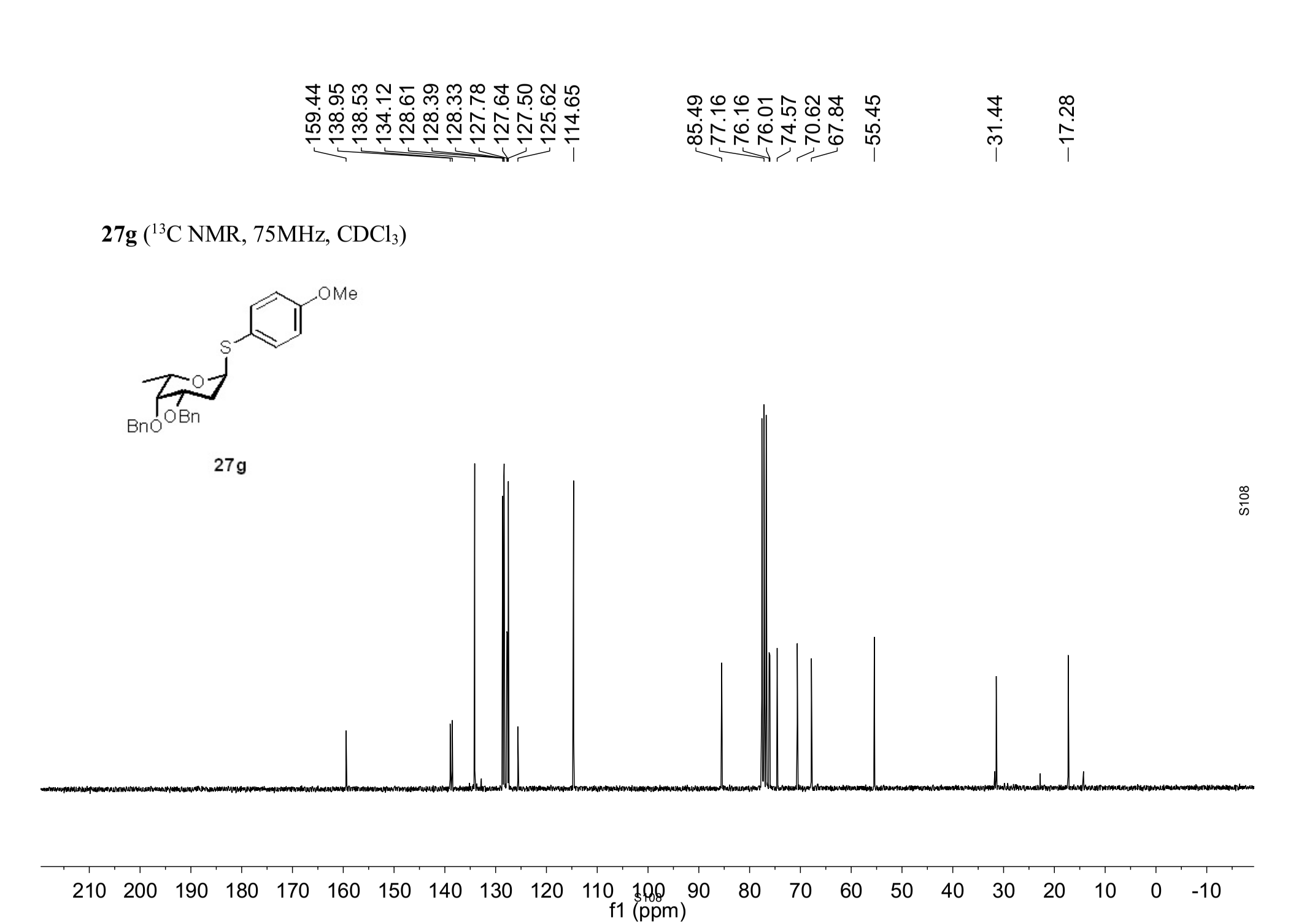

27f (1H -13C Coupled HSQC)
BnO
OBn
O
BnO
S
OMe
27f
J= 168 Hz
f2 (ppm)
f1 (ppm)


27f (1H -13C HSQC)
BnO
OBn
O
BnO
S
OMe
27f
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

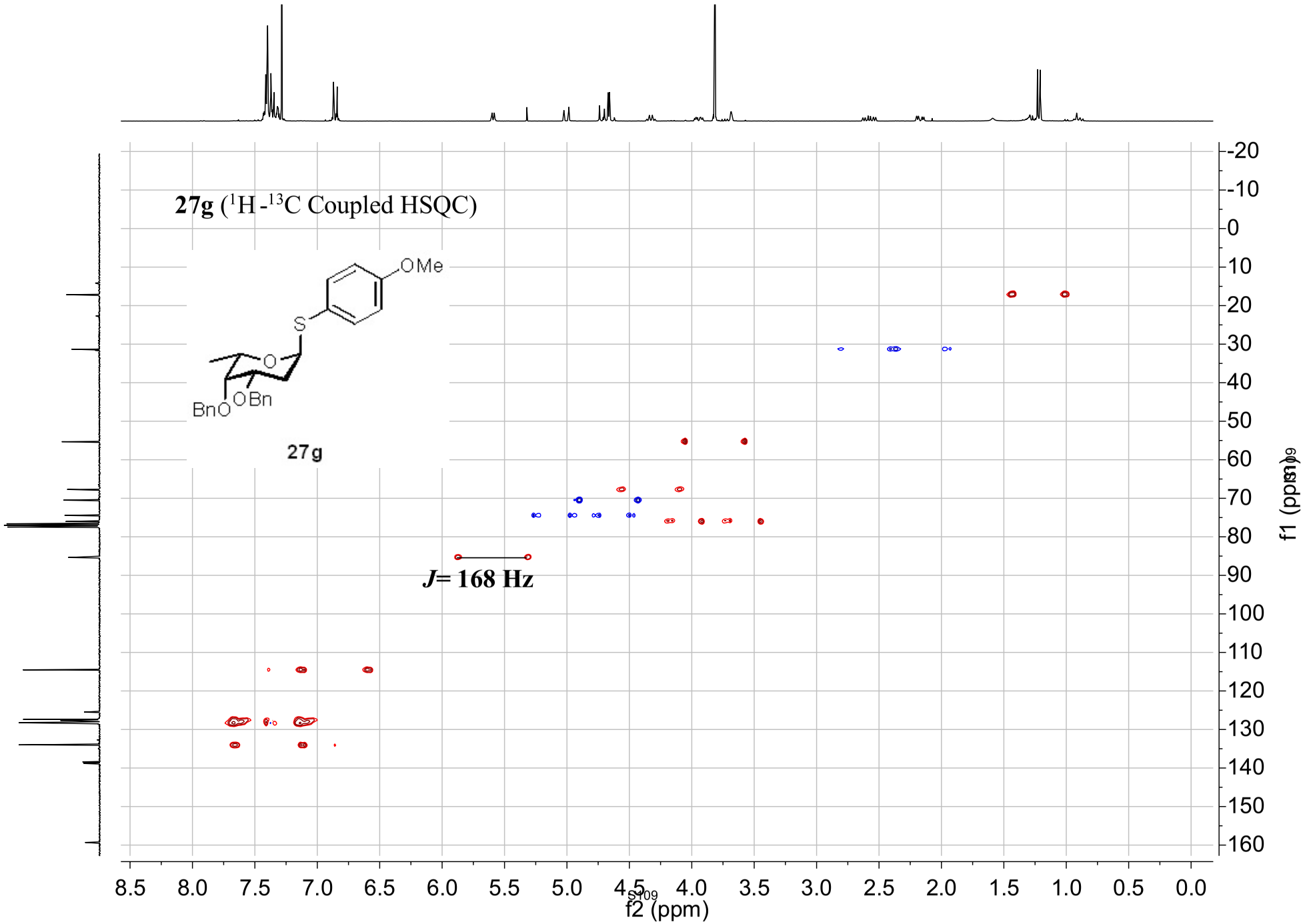
27g (^{1}H NMR, 300MHz, $CDCl_3$)

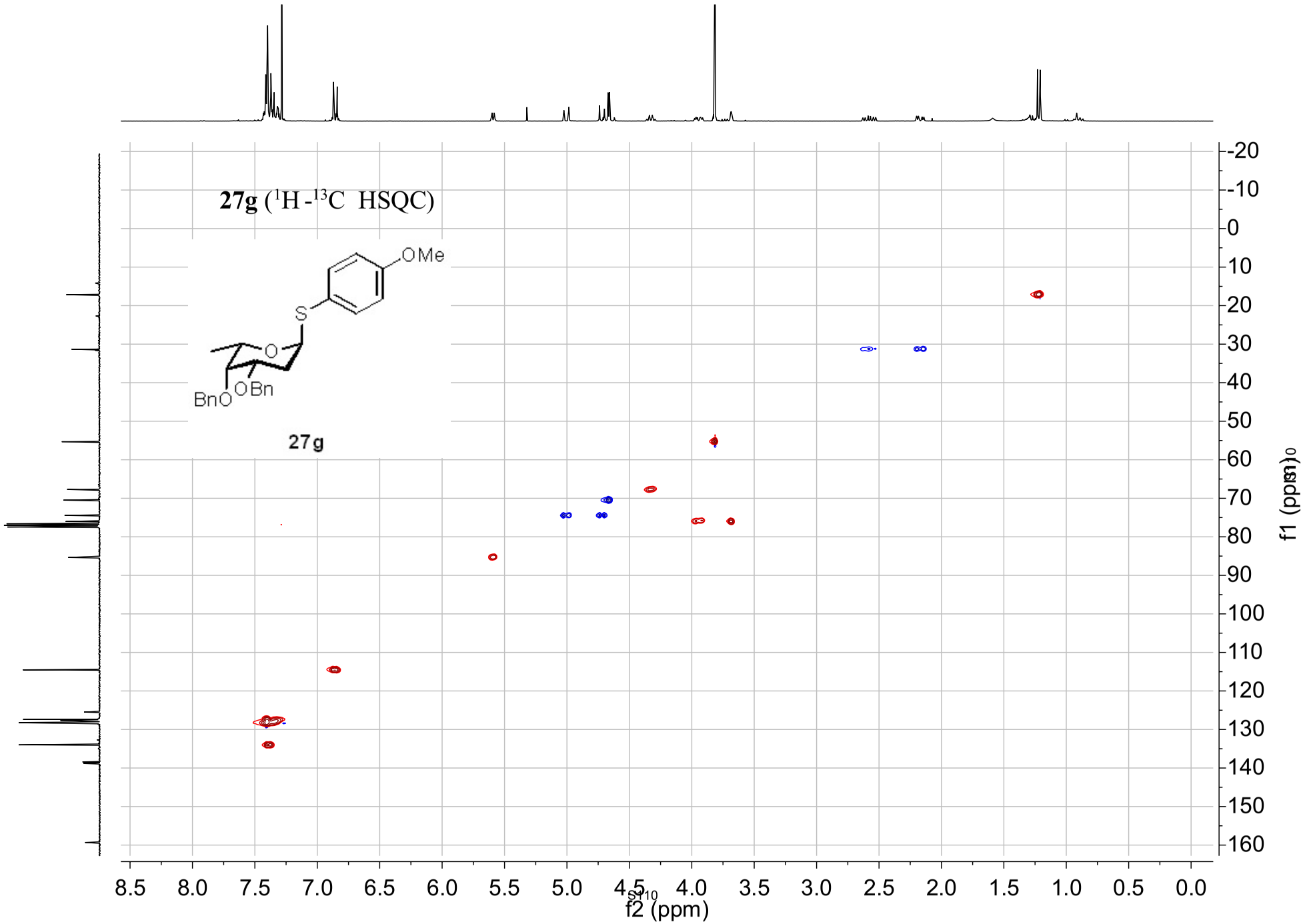


27g

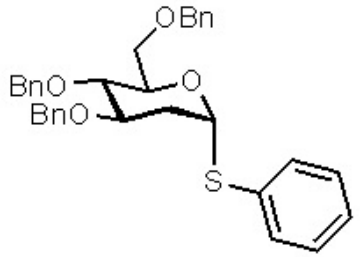


27g (^{13}C NMR, 75MHz, $CDCl_3$)


27g (1H -13C Coupled HSQC)
OMe
S
O
BnO
OBn
27g
J= 168 Hz
f2 (ppm)
f1 (ppm)
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
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160

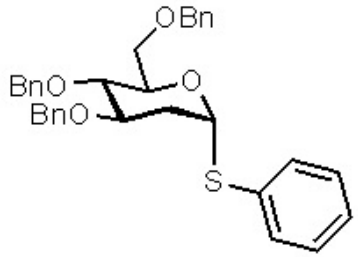

27g (1H -13C HSQC)
OMe
S
O
BnO
OBn
27g
f2 (ppm)
f1 (ppm)

27h (^{1}H NMR, 300MHz, $CDCl_3$)

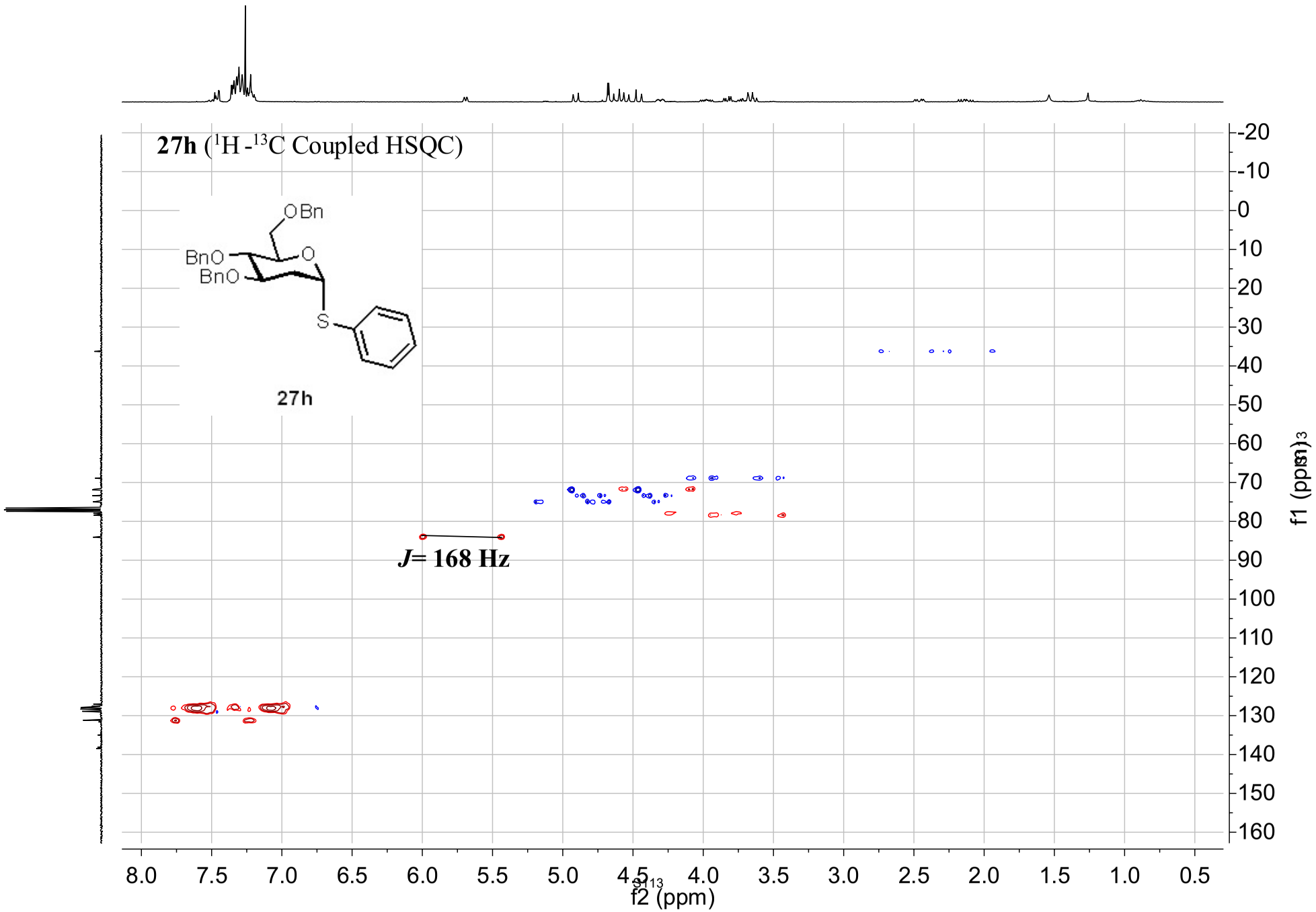


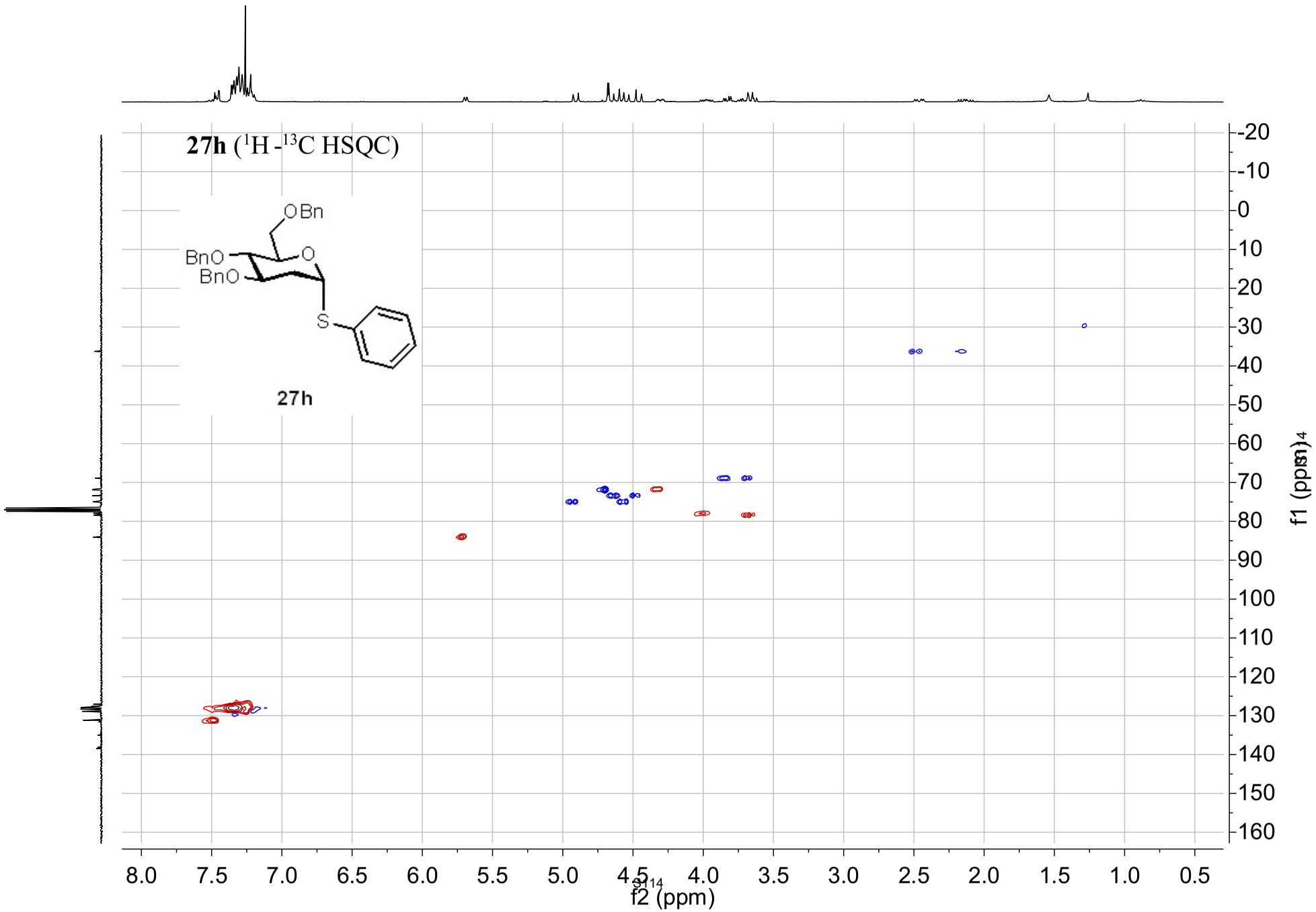
27h

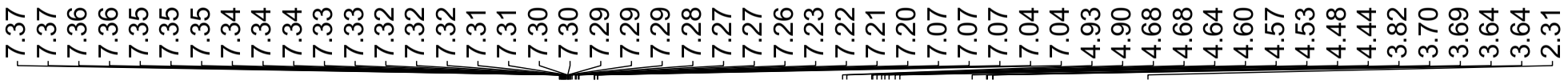
27h (^{13}C NMR, 75MHz, $CDCl_3$)



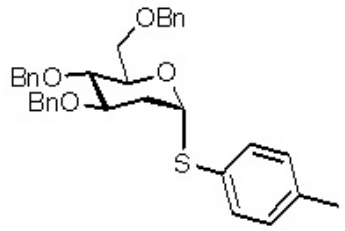
27h


27h (^{1}H -^{13}C Coupled HSQC)
OBn
BnO
BnO
O
S
27h
J= 168 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

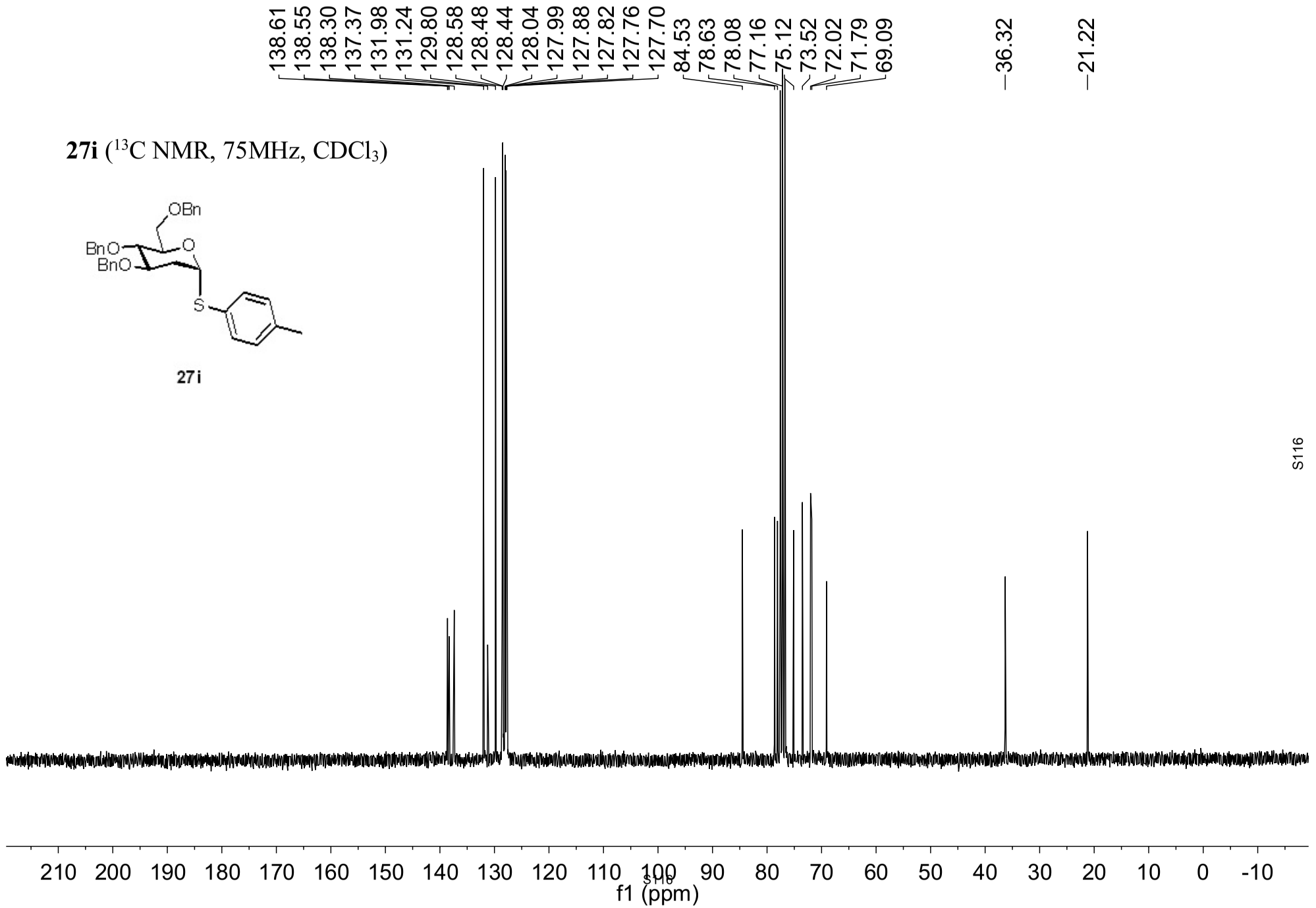

27h (1H -13C HSQC)
OBn
BnO
BnO
O
S
27h
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160



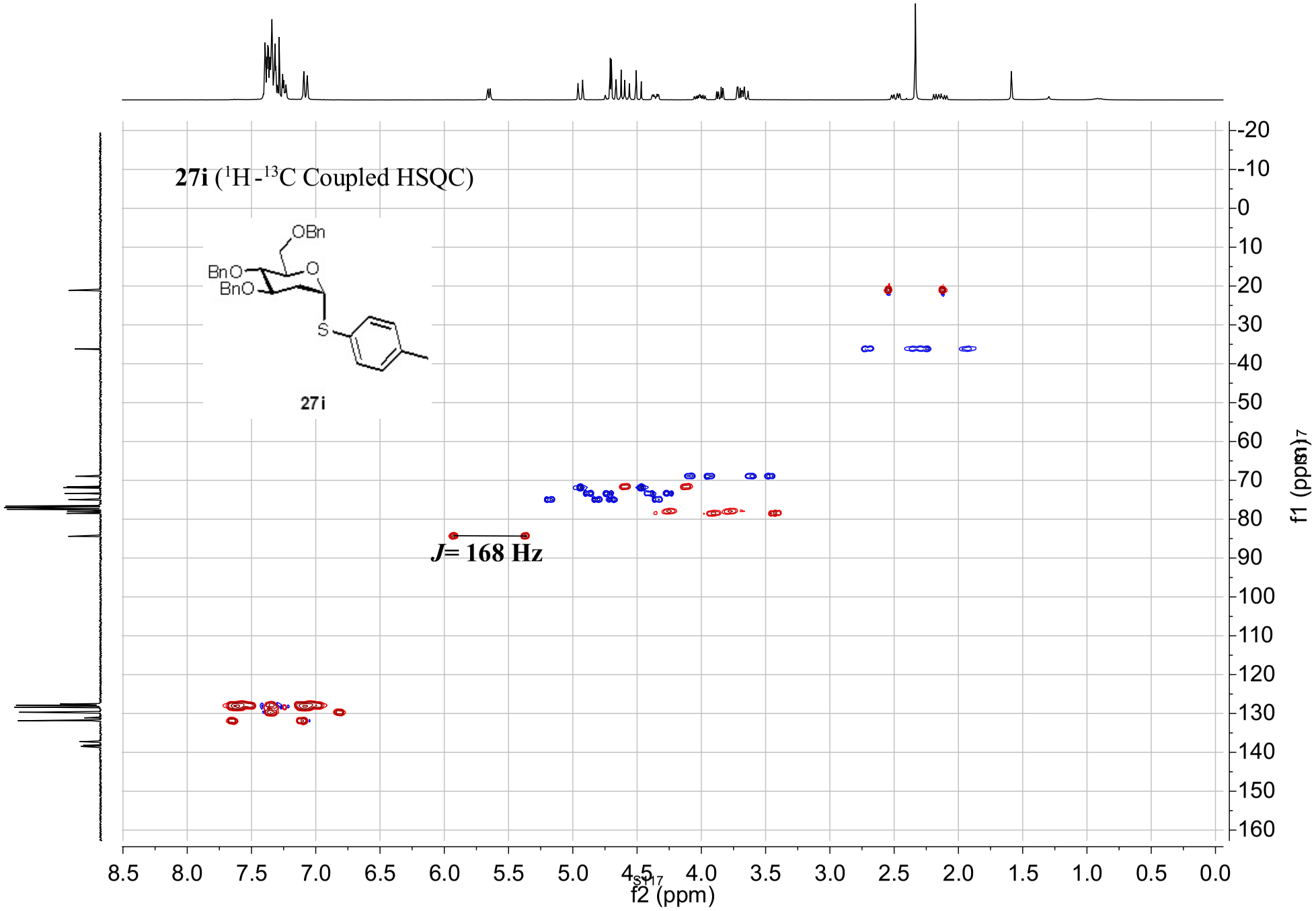
27i (^{1}H NMR, 300MHz, $CDCl_3$)

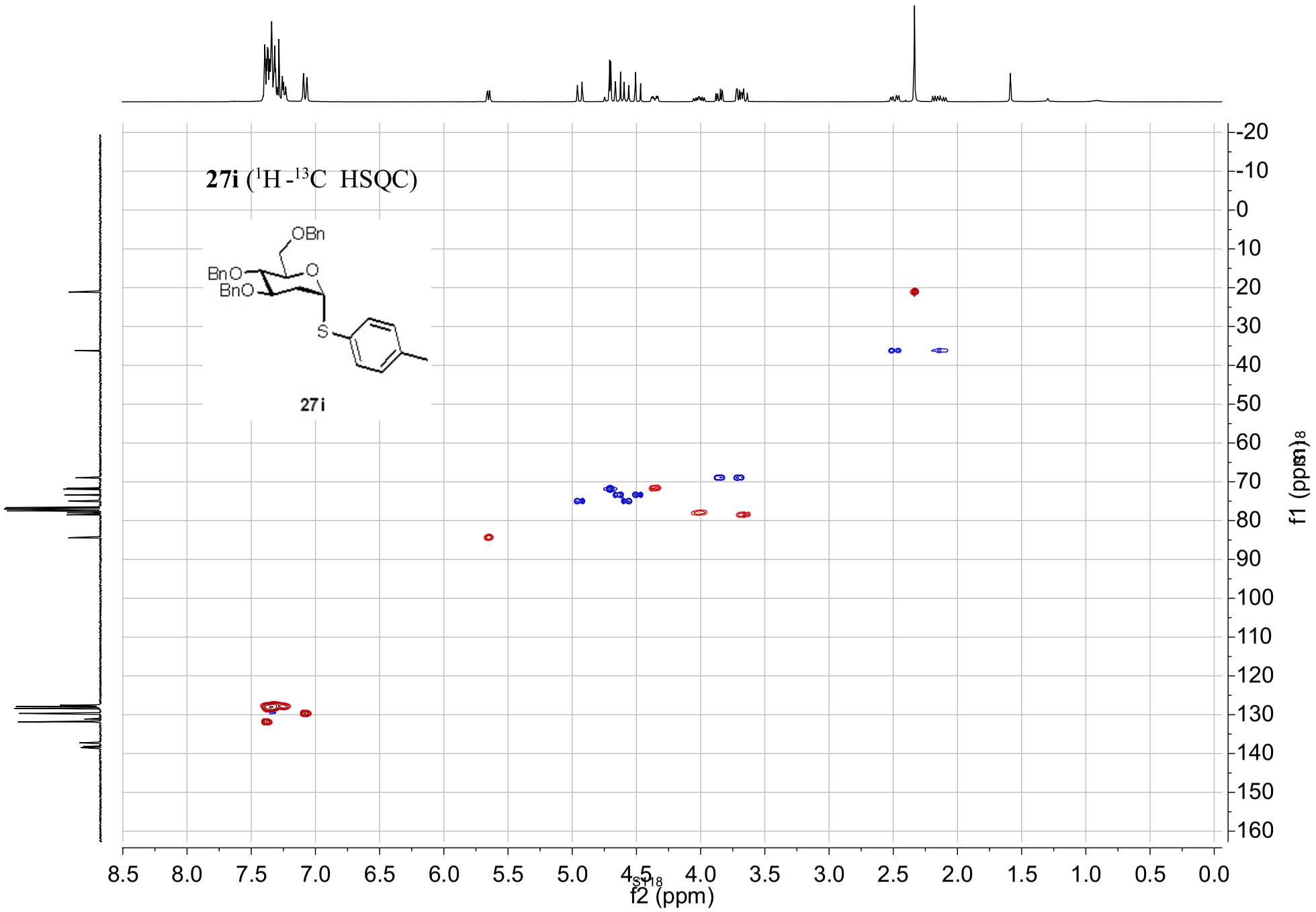


27i

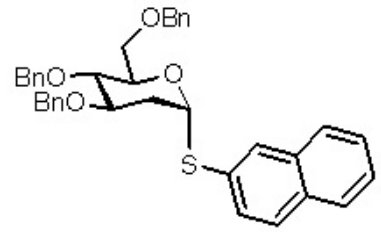


27i (^{13}C NMR, 75MHz, $CDCl_3$)

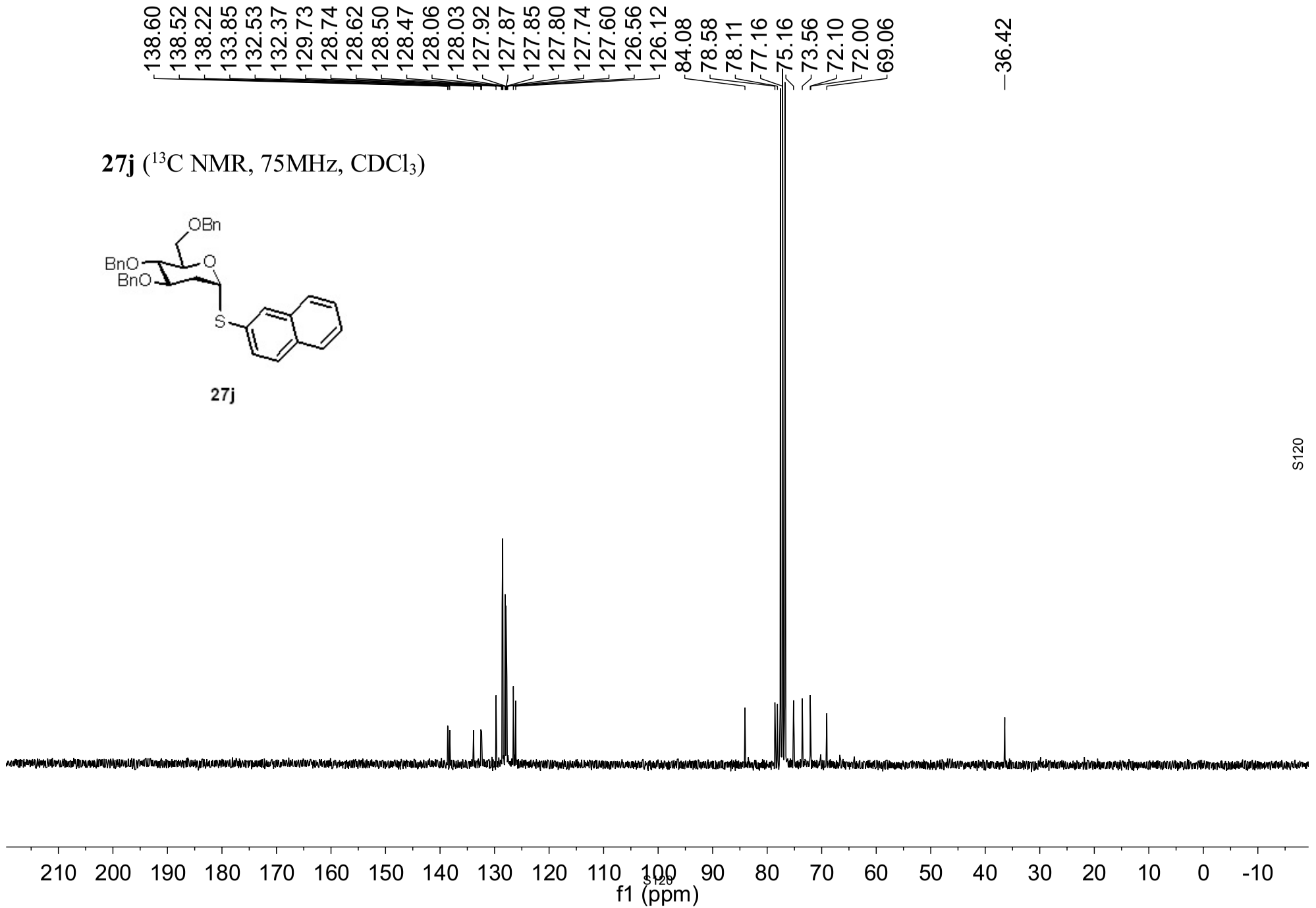

27i (1H-13C Coupled HSQC)
OBn
BnO
BnO
O
S
27i
J= 168 Hz
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
f1 (ppm)


27i (1H -13C HSQC)
OBn
BnO
BnO
O
S
27i
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

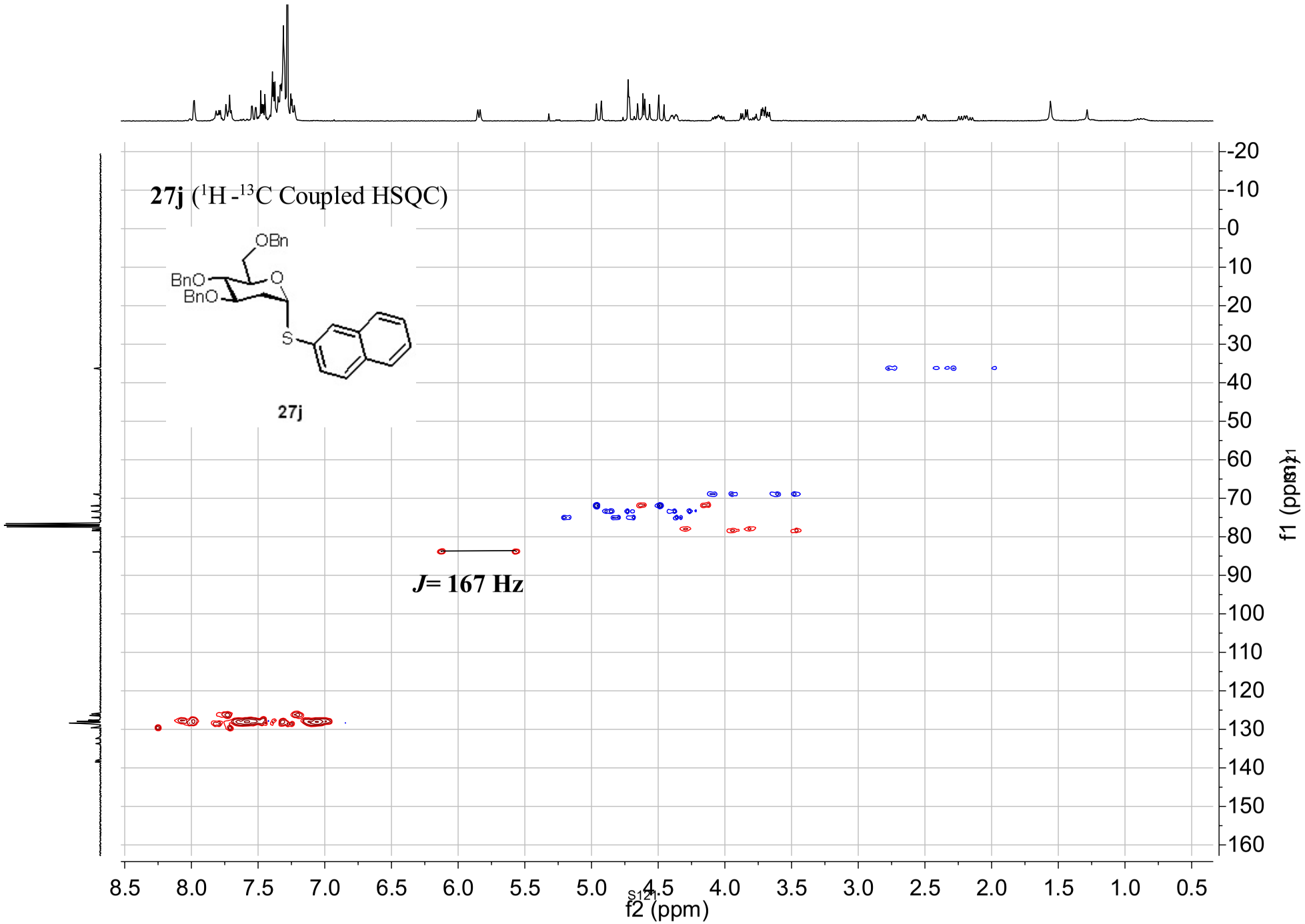
27j (^{1}H NMR, 300MHz, $CDCl_3$)

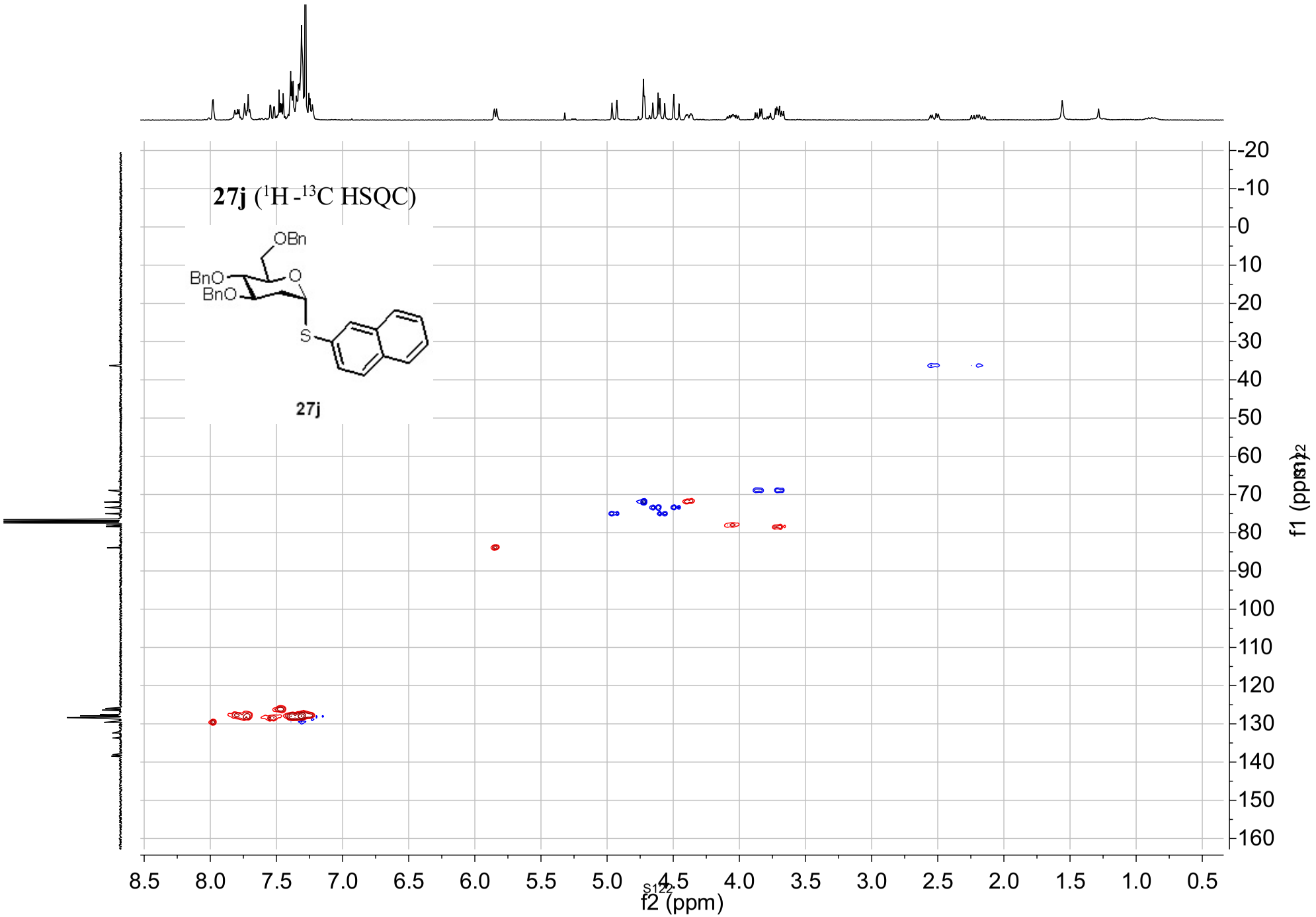


27j

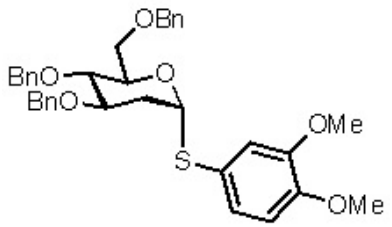


27j (^{13}C NMR, 75MHz, $CDCl_3$)


27j (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
S
27j
J= 167 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

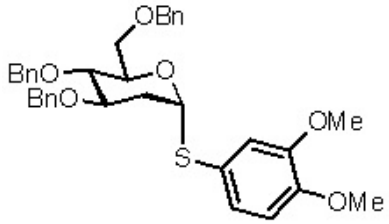

27j (1H -13C HSQC)
OBn
BnO
BnO
O
S
27j
f2 (ppm)
f1 (ppm)

27k (^{1}H NMR, 300MHz, $CDCl_3$)

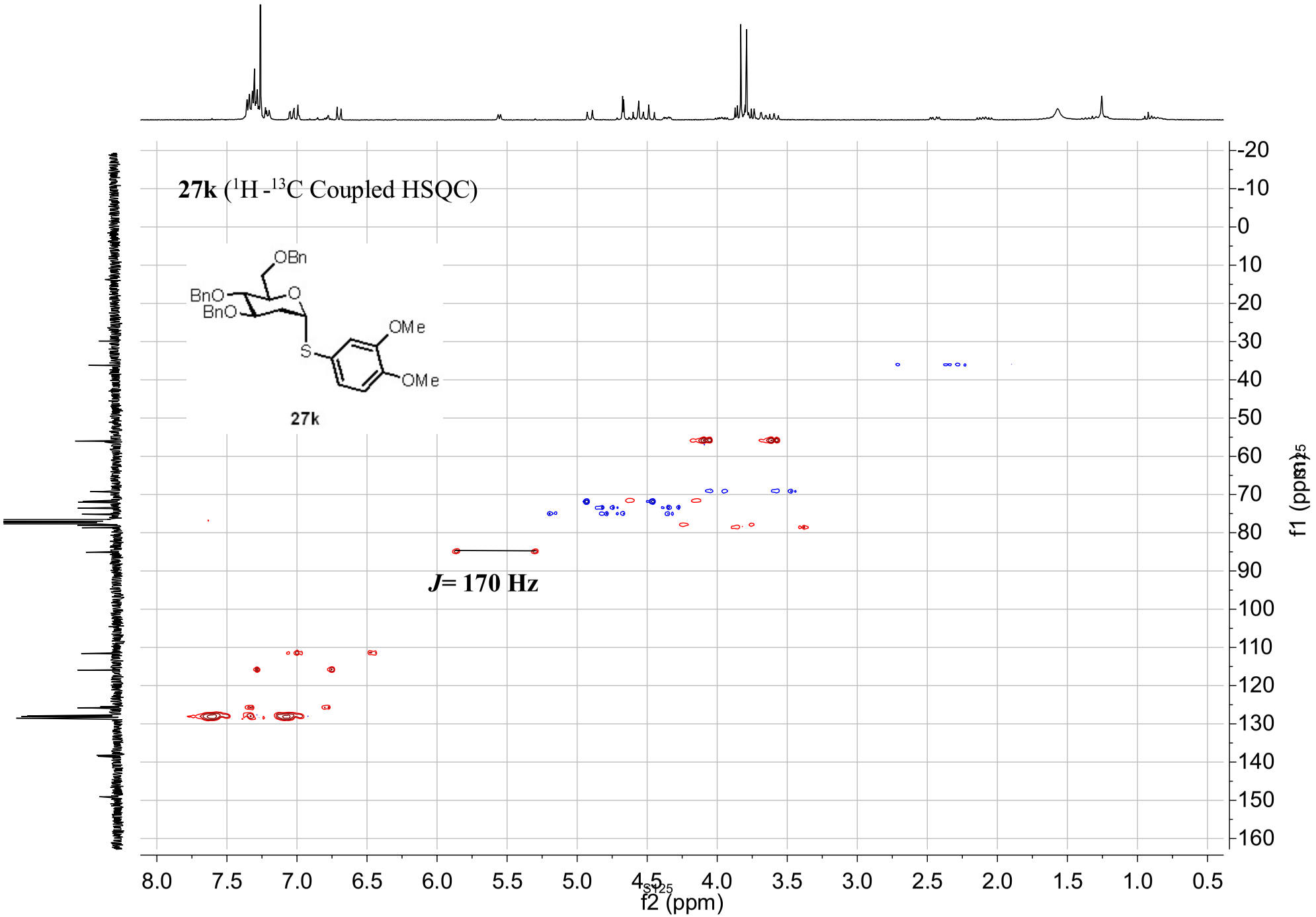


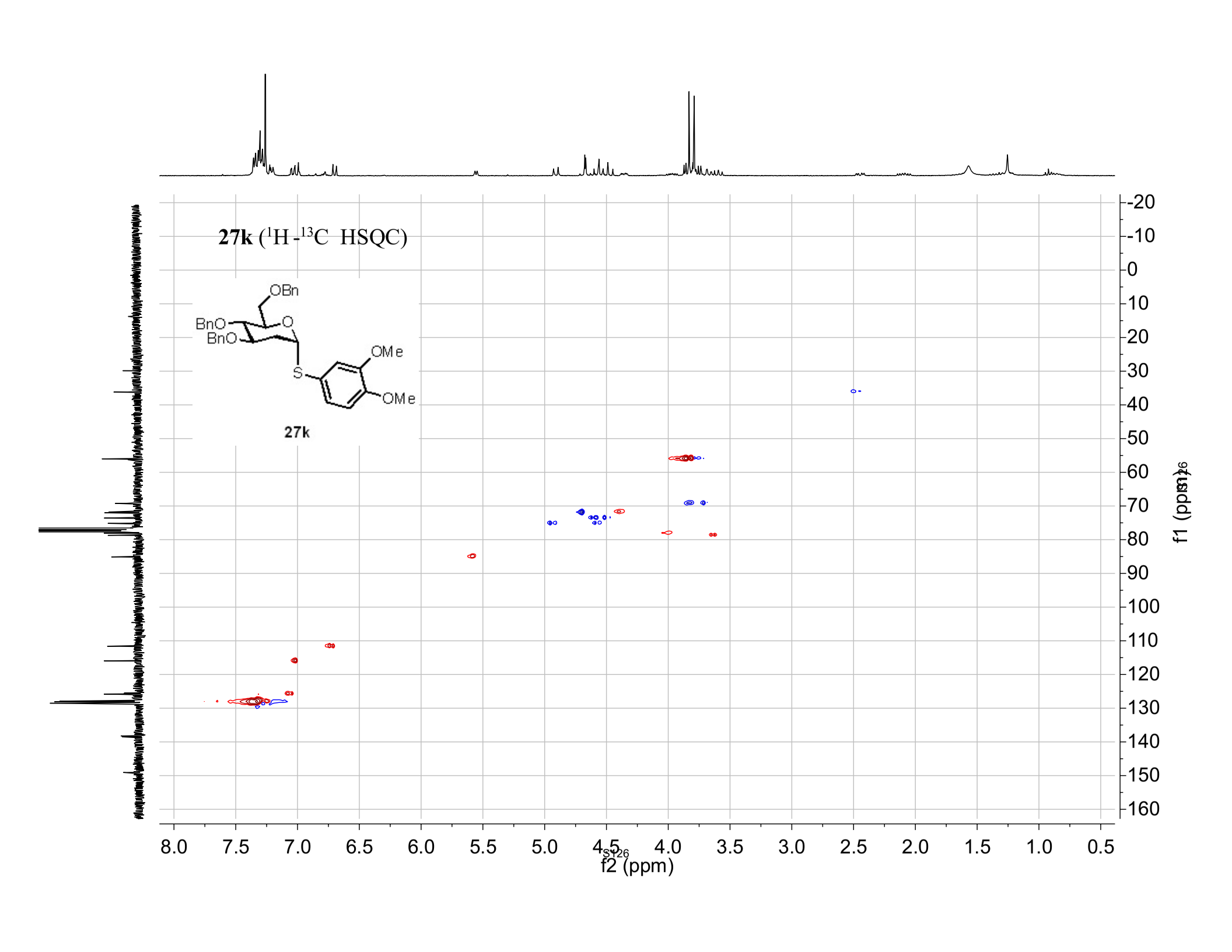
27k

27k (^{13}C NMR, 75MHz, $CDCl_3$)

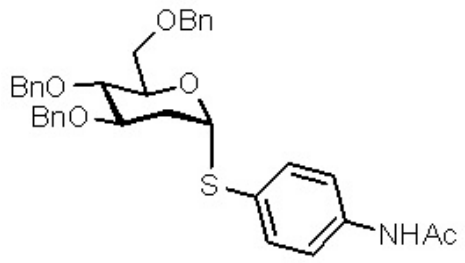


27k


27k (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
S
OMe
OMe
27k
J= 170 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

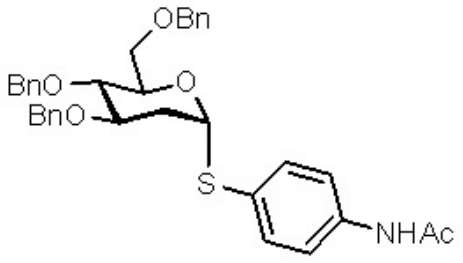

27k (^{1}H -^{13}C HSQC)
OBn
BnO
BnO
O
S
OMe
OMe
27k
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

27l (^{1}H NMR, 300MHz, $CDCl_3$)

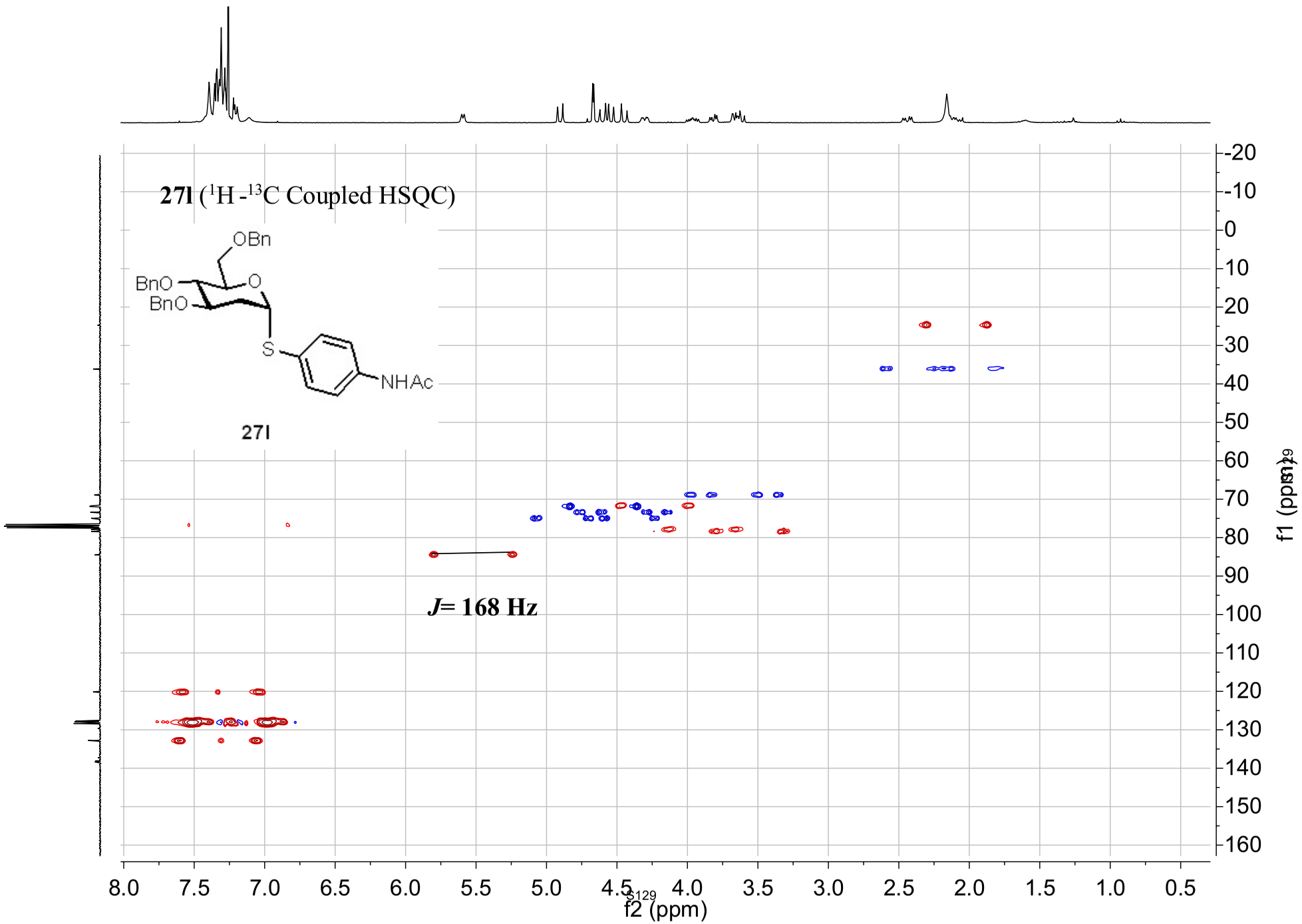


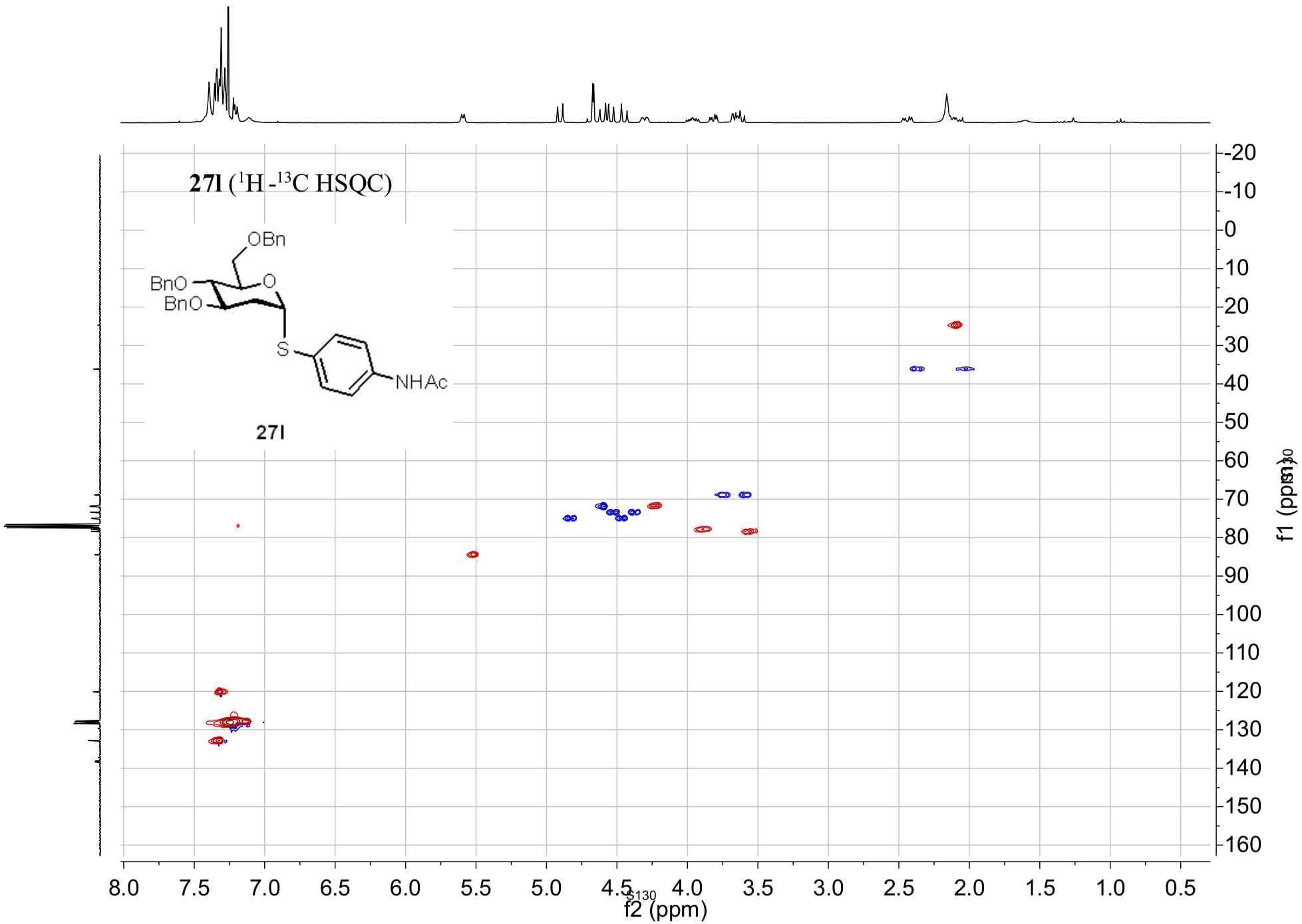
27l

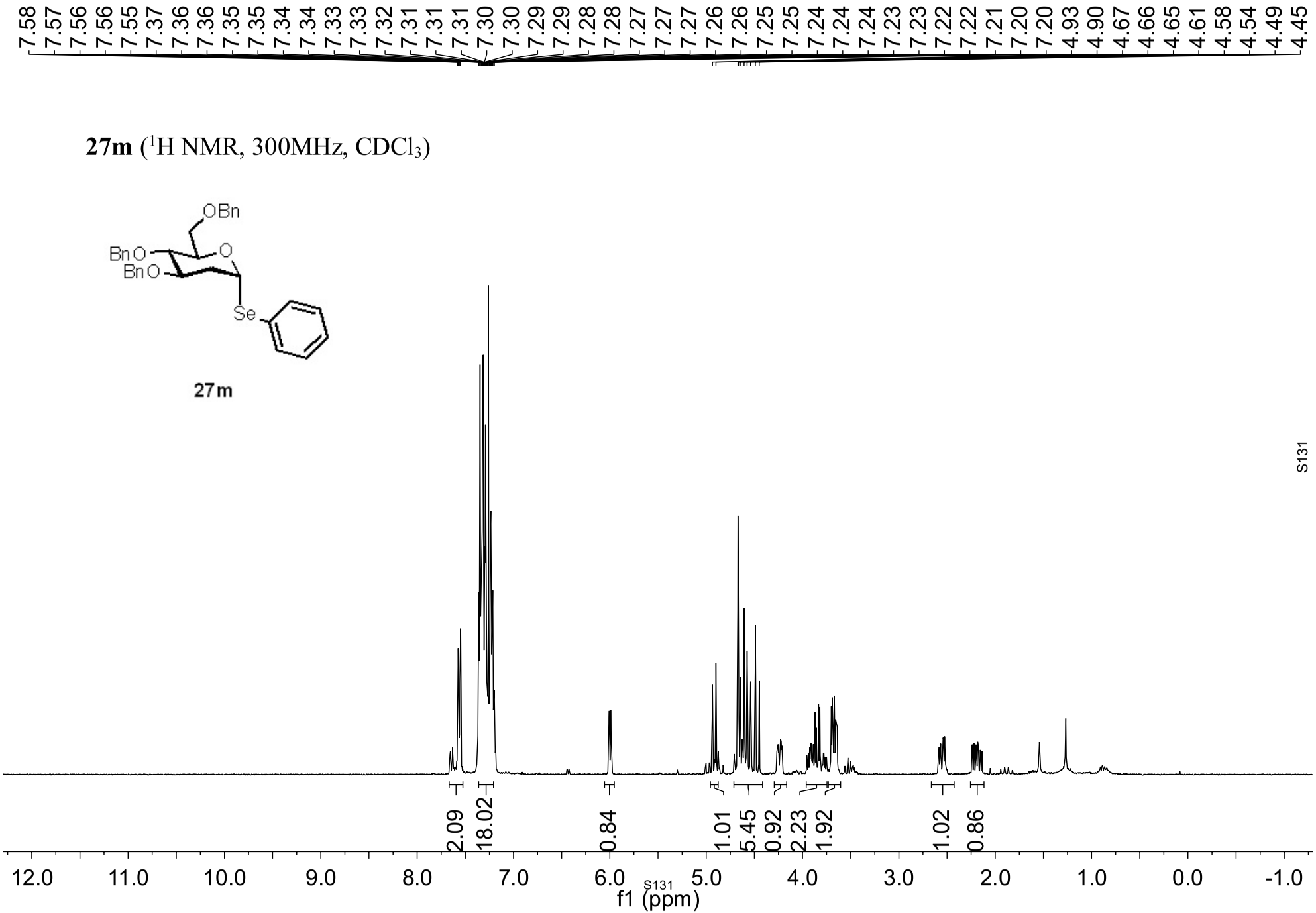
27l (^{13}C NMR, 75MHz, $CDCl_3$)



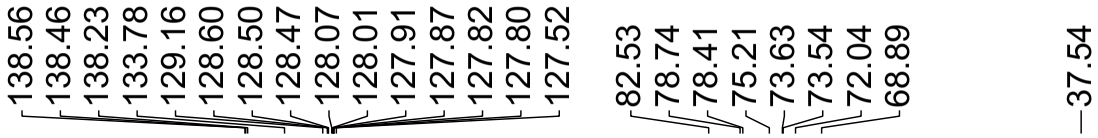
27l


27l (^{1}H -^{13}C Coupled HSQC)
OBn
BnO
BnO
O
S
NHAc
27l
J= 168 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

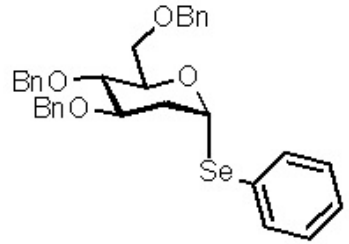

27l (1H -13C HSQC)
OBn
BnO
BnO
O
S
NHAc
27l
f2 (ppm)
f1 (ppm)



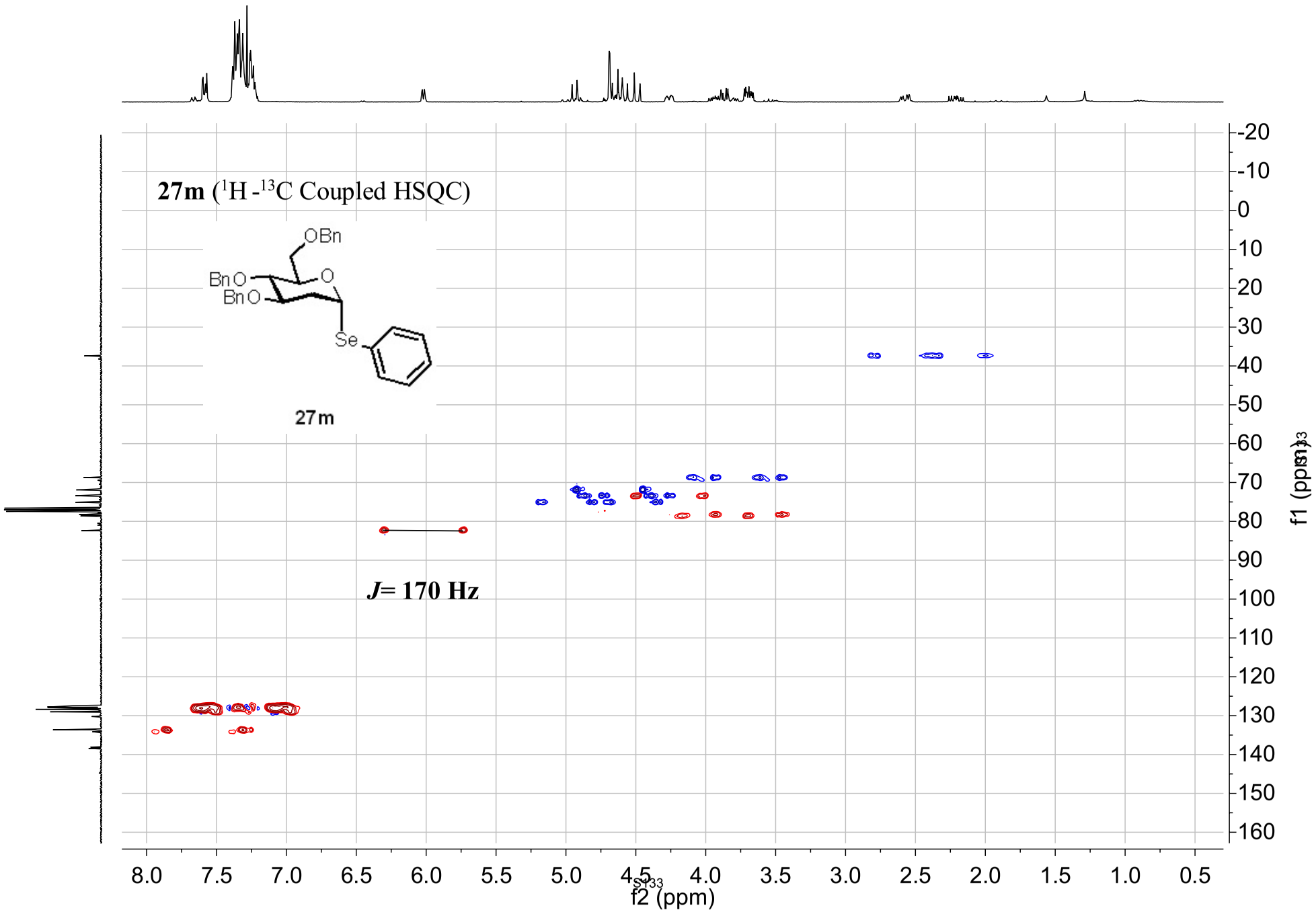
27m (^{1}H NMR, 300MHz, $CDCl_3$)

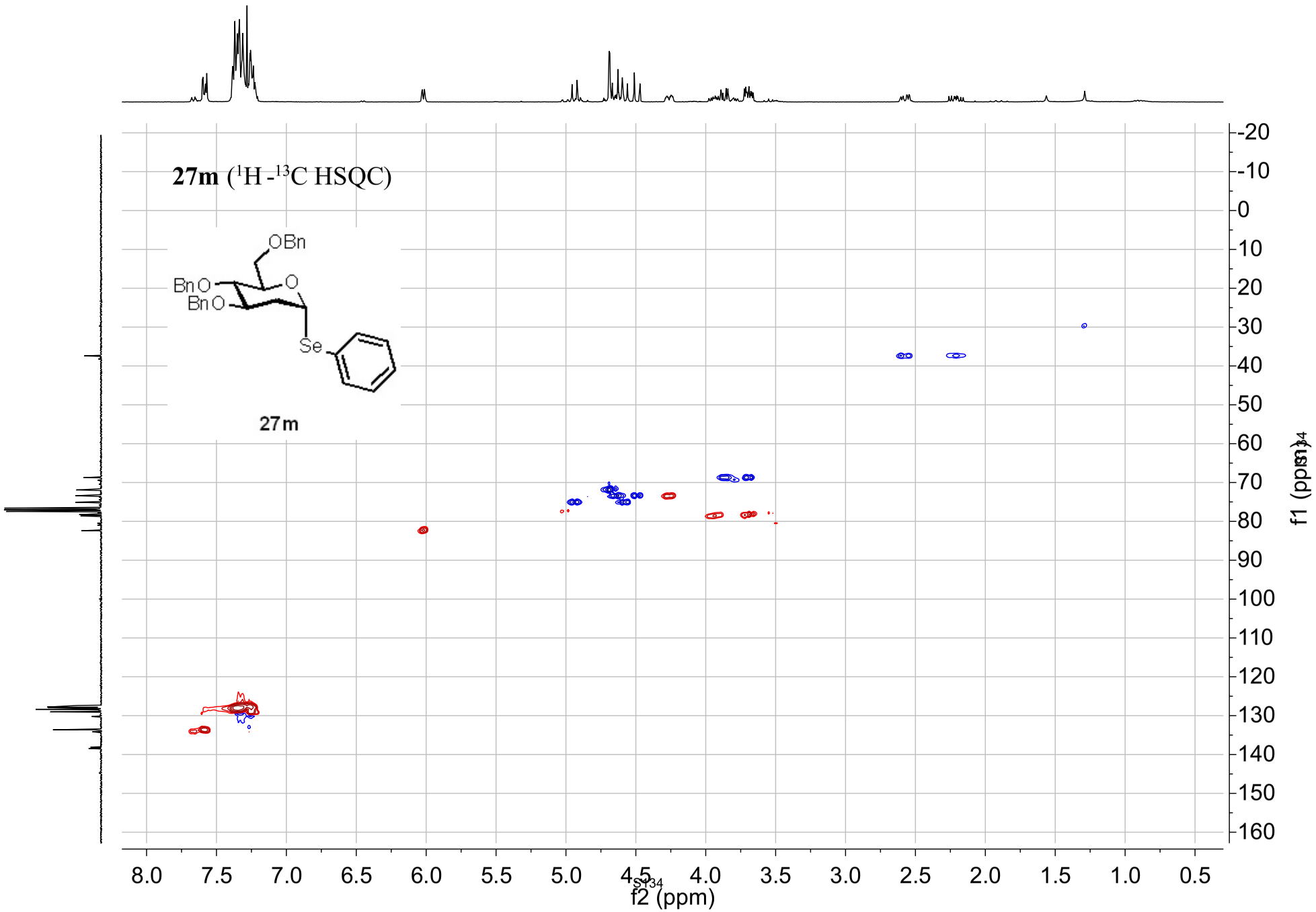


27m (^{13}C NMR, 75MHz, $CDCl_3$)

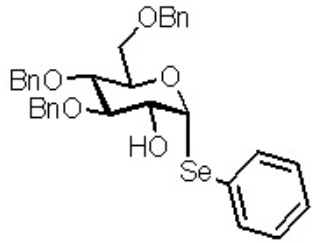


27m


27m (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
Se
27m
J= 170 Hz
f2 (ppm)
f1 (ppm)

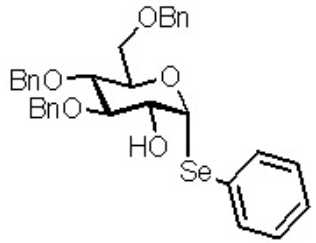

27m (1H -13C HSQC)
OBn
BnO
BnO
O
Se
27m
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

27n (^{1}H NMR, 300MHz, $CDCl_3$)

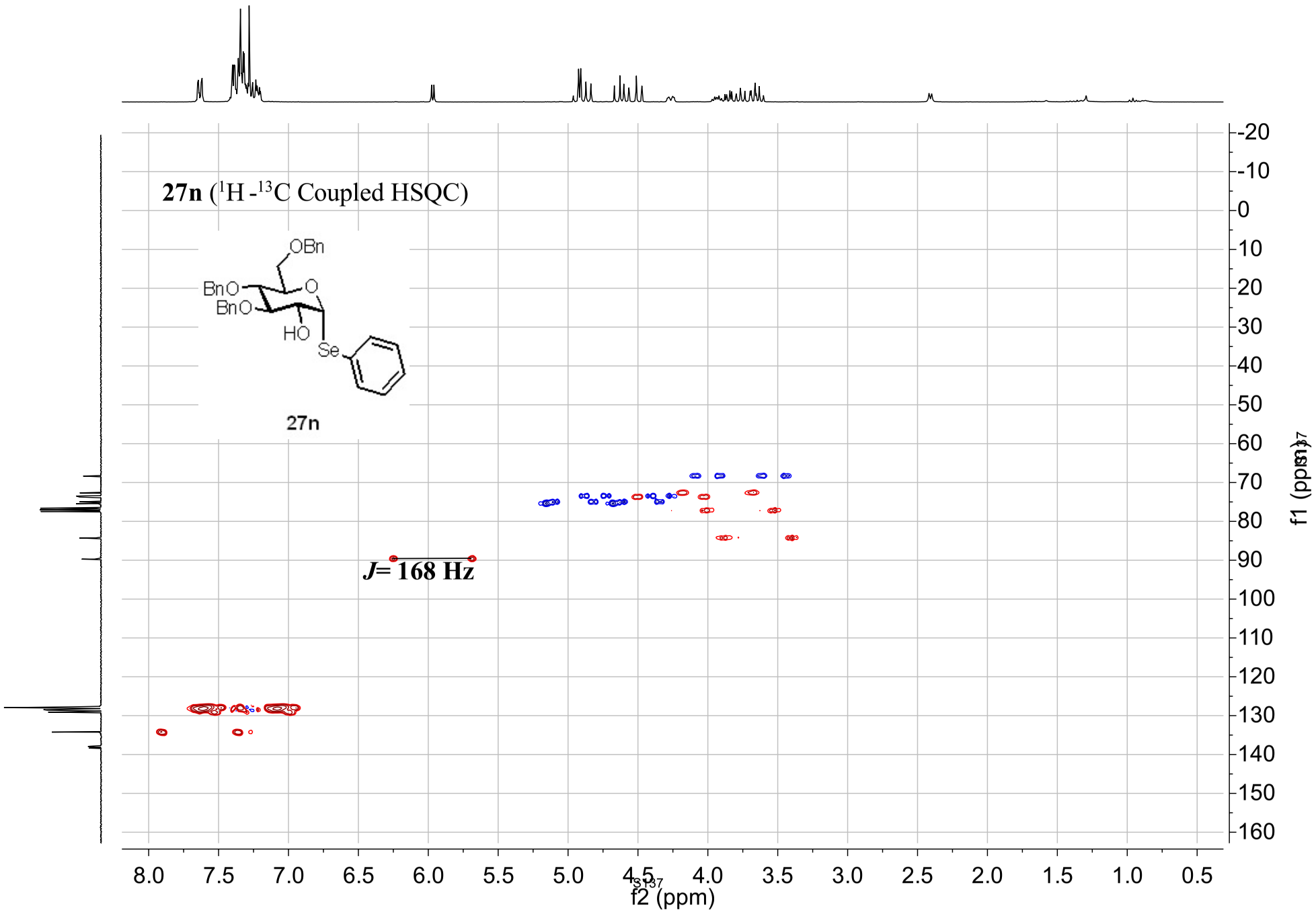


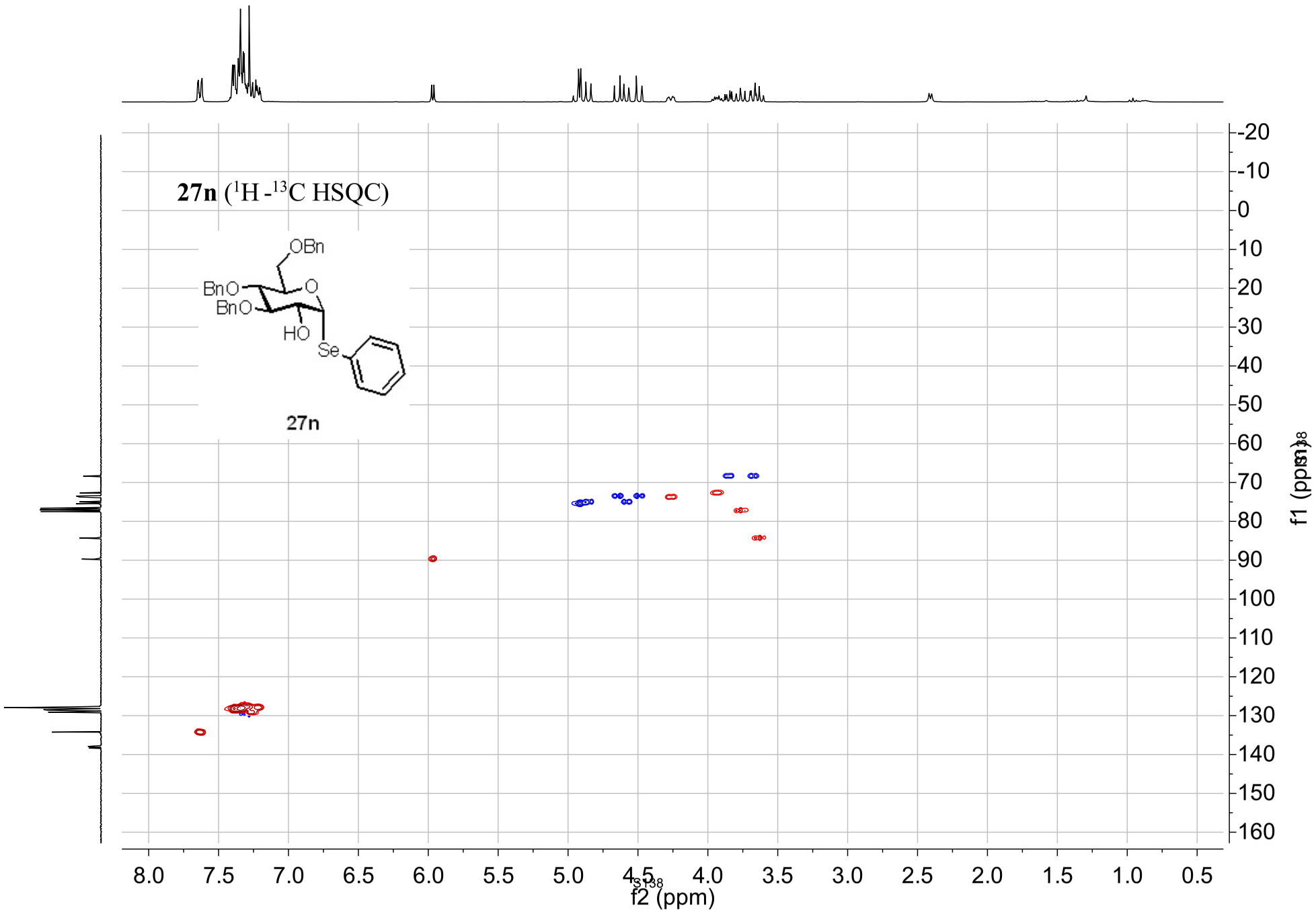
27n

27n (^{13}C NMR, 75MHz, $CDCl_3$)

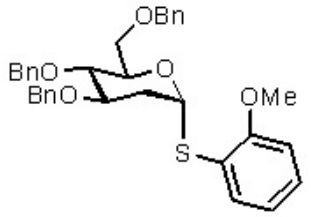


27n


27n (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
HO
Se
27n
J= 168 Hz
f2 (ppm)
f1 (ppm)


27n (1H -13C HSQC)
OBn
BnO
BnO
O
HO
Se
27n
f2 (ppm)
f1 (ppm)

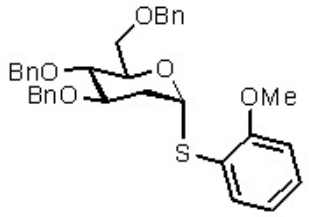
46a (^{1}H NMR, 300MHz, $CDCl_3$)



46 a

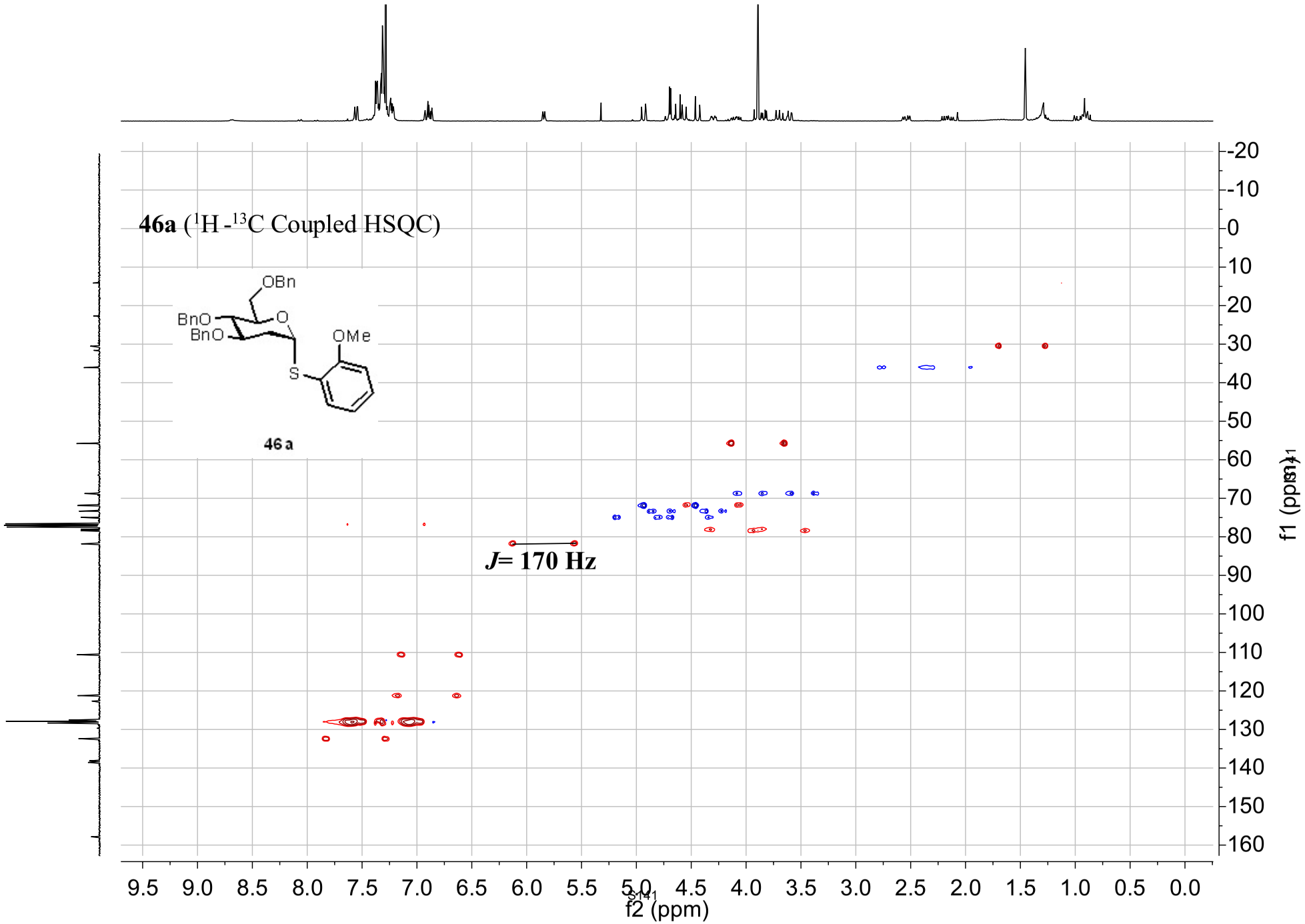
157.97
138.69
138.60
138.26
132.51
128.57
128.49
128.46
128.42
127.99
127.84
127.78
127.71
127.70
122.75
121.36
110.72
81.95
78.56
78.22
77.16
75.09
73.47
72.03
71.89
68.90
55.94
36.22

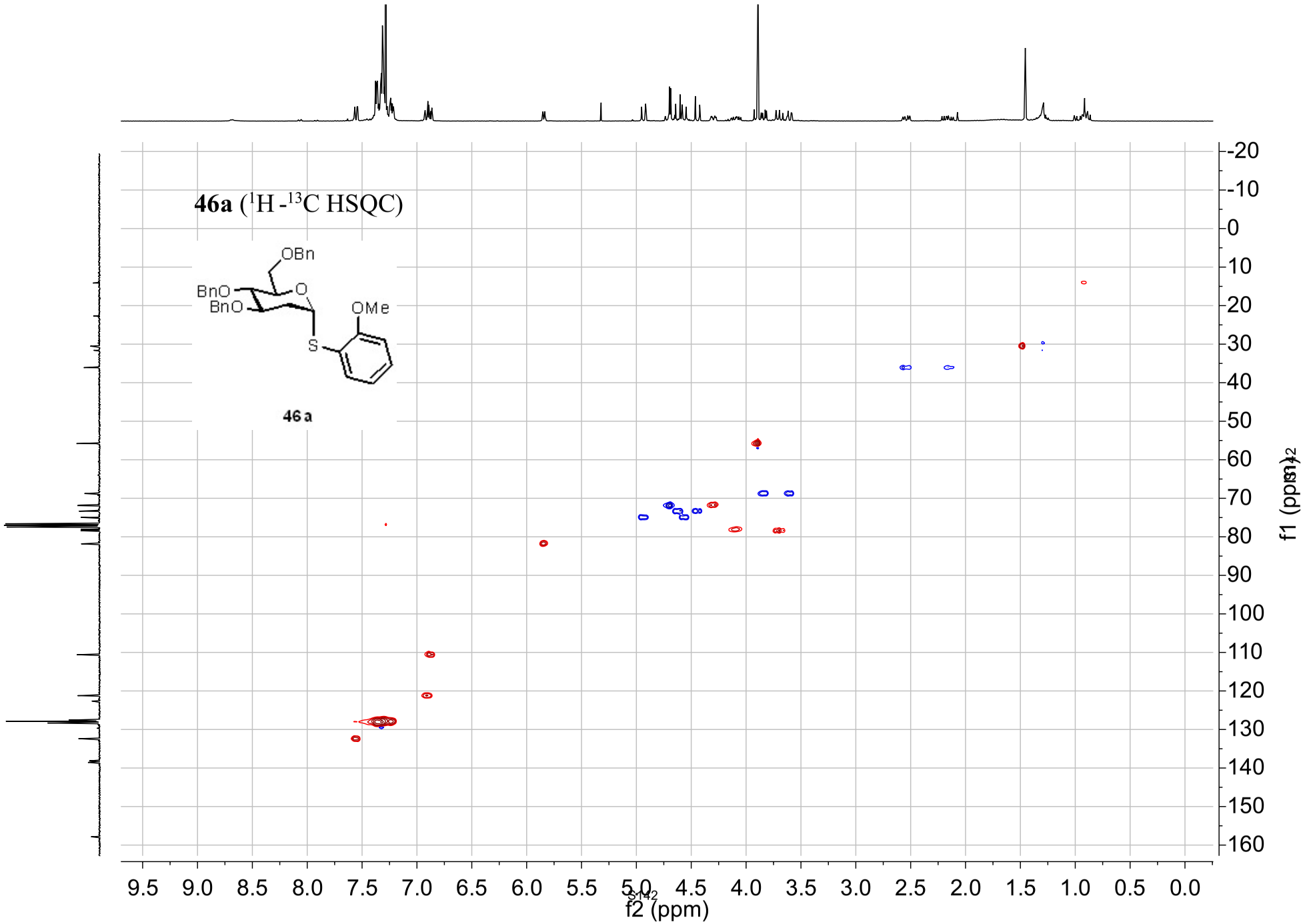
46a (^{13}C NMR, 75MHz, $CDCl_3$)



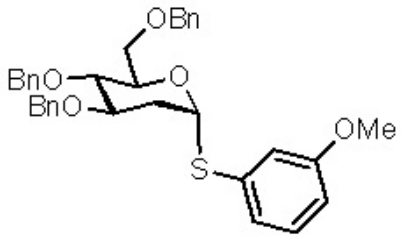
46 a

S140


46a (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
OMe
S
46a
J= 170 Hz
f2 (ppm)
f1 (ppm)


46a (1H -13C HSQC)
OBn
BnO
BnO
O
OMe
S
46a
f2 (ppm)
f1 (ppm)

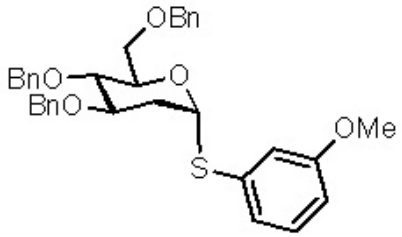
46b (^{1}H NMR, 300MHz, $CDCl_3$)



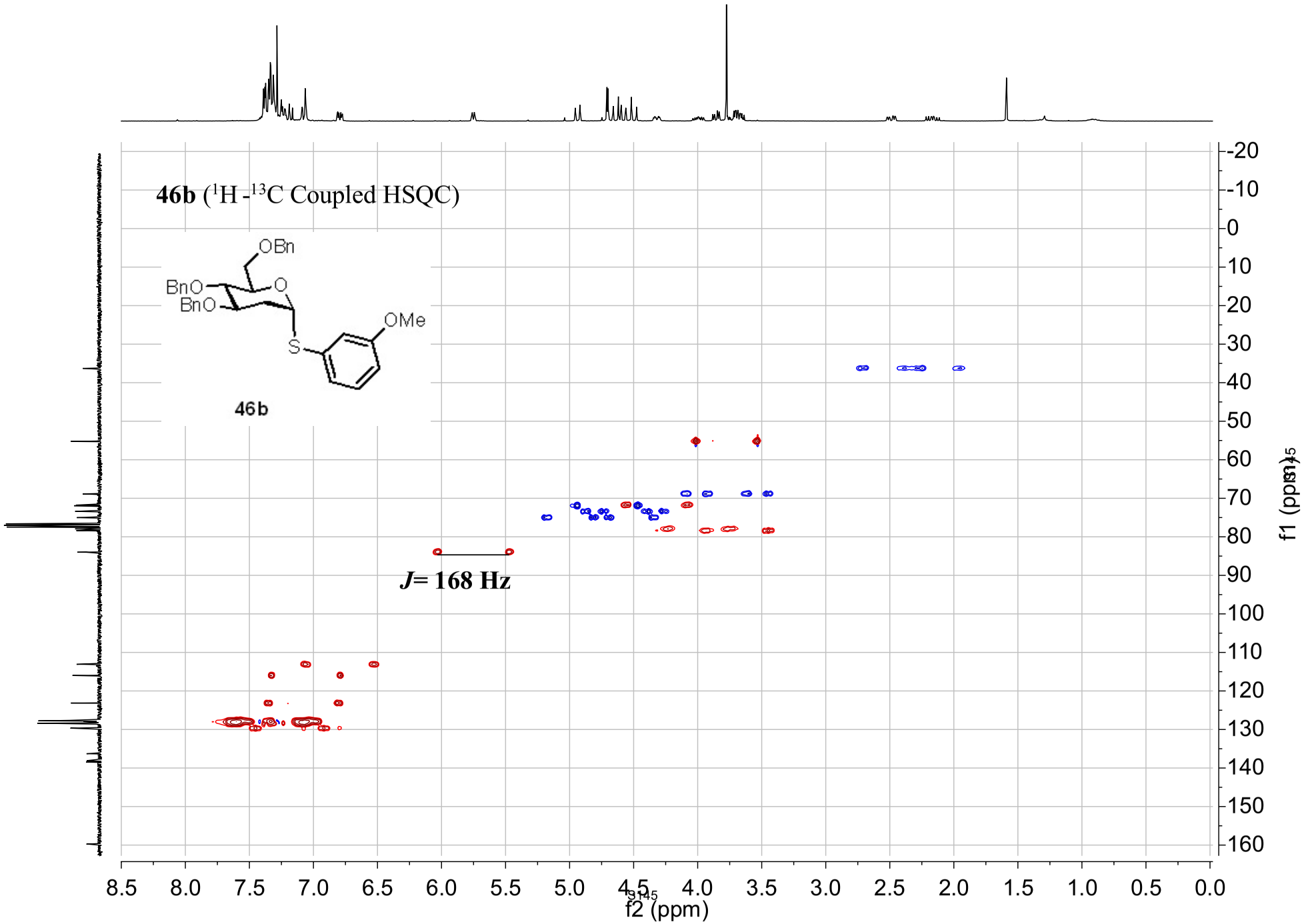
46b

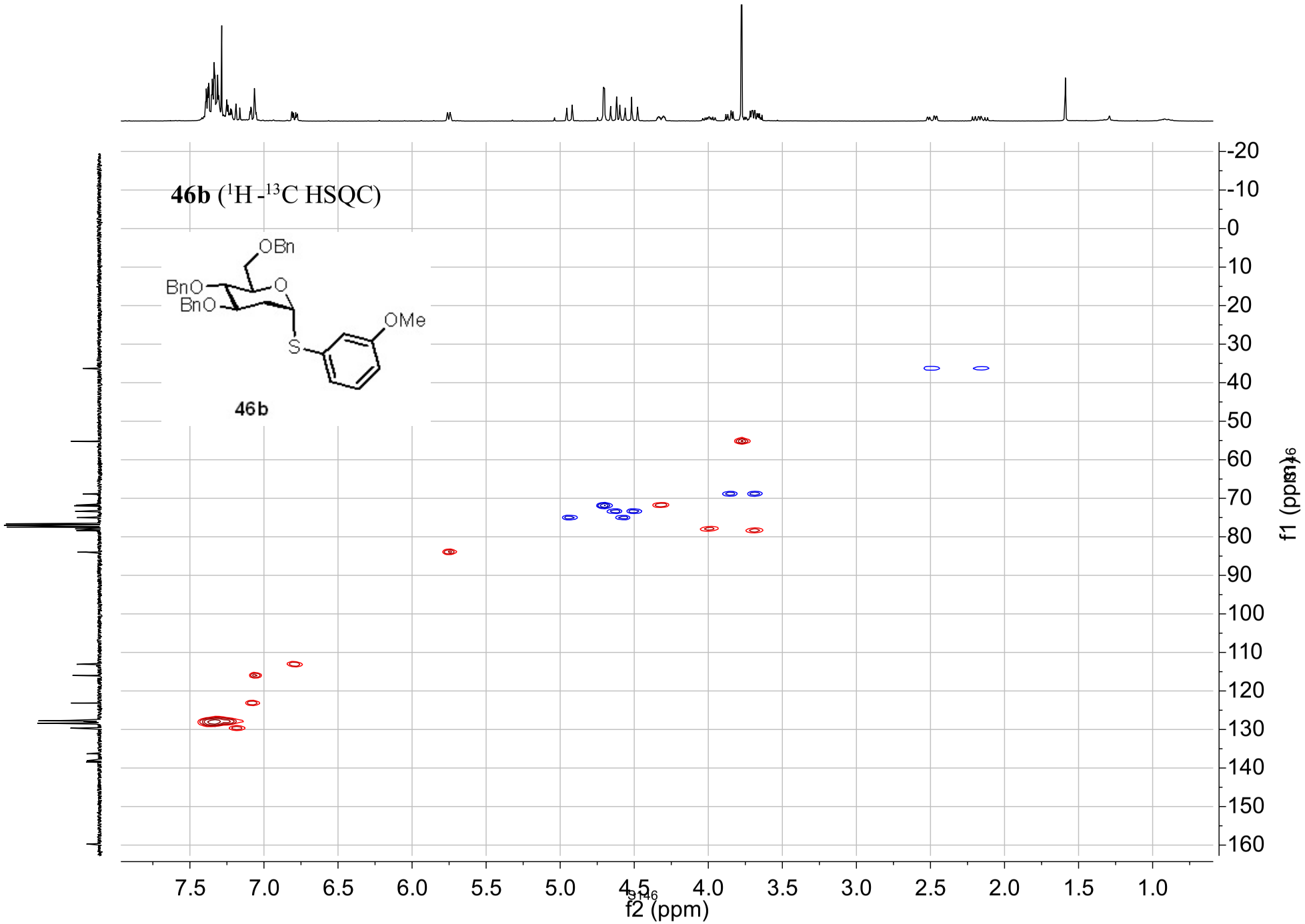
159.88
138.57
138.49
138.20
136.41
129.78
128.60
128.49
128.46
128.05
128.01
127.89
127.85
127.78
127.74
123.26
116.11
113.21
84.12
78.50
78.07
77.16
75.15
73.52
72.05
71.89
68.98
55.38
36.41

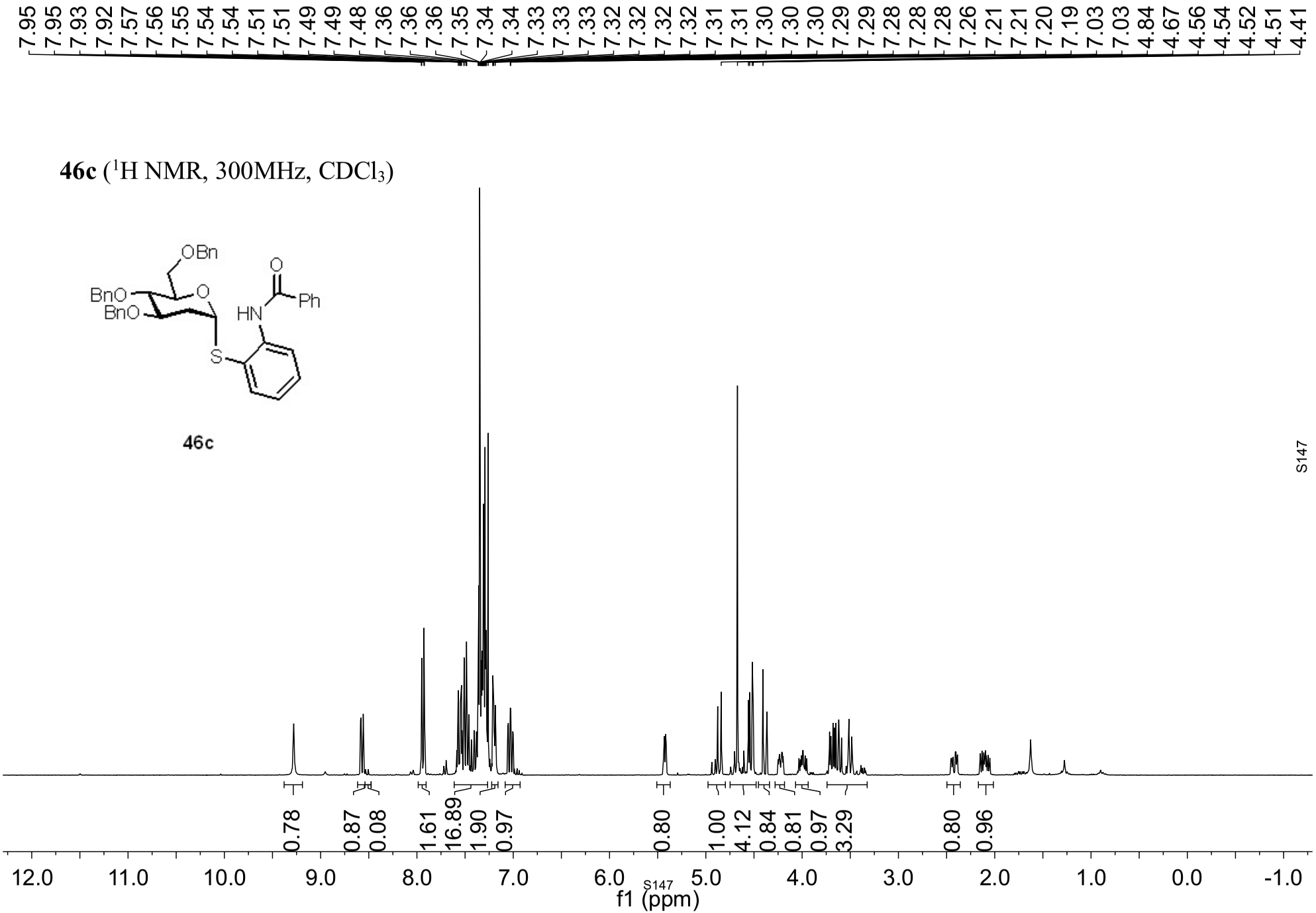
46b (^{13}C NMR, 75MHz, $CDCl_3$)



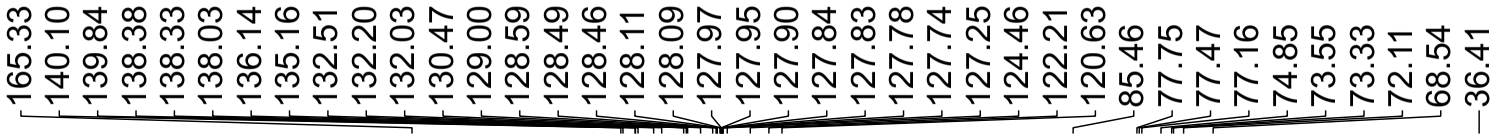
46b


46b (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
OMe
S
46b
J= 168 Hz
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
f2 (ppm)
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
f1 (ppm)

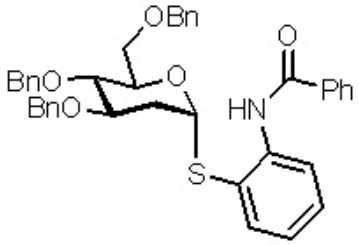

46b (1H -13C HSQC)
OBn
BnO
BnO
O
S
OMe
46b
f2 (ppm)
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160



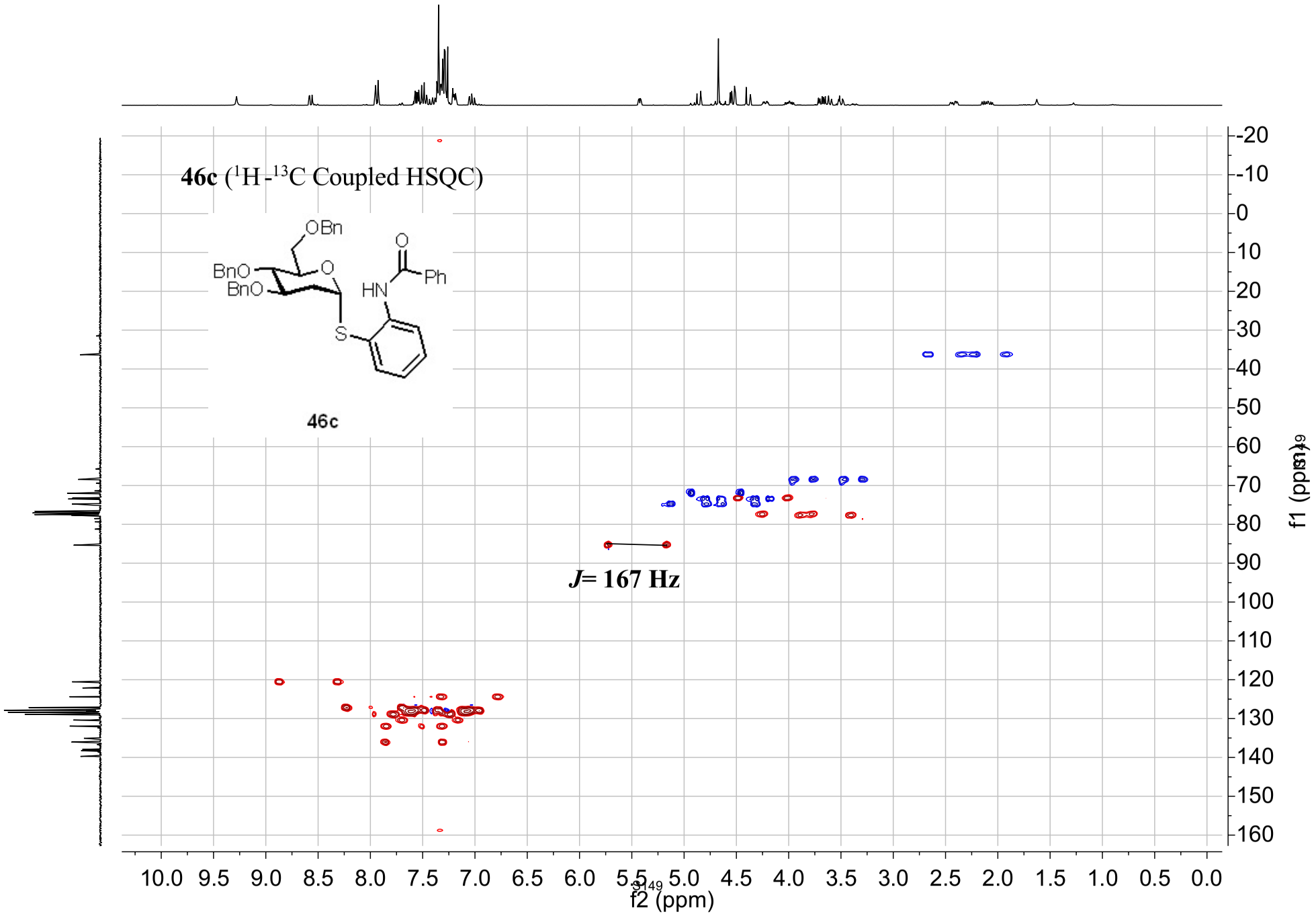
46c (^{1}H NMR, 300MHz, $CDCl_3$)

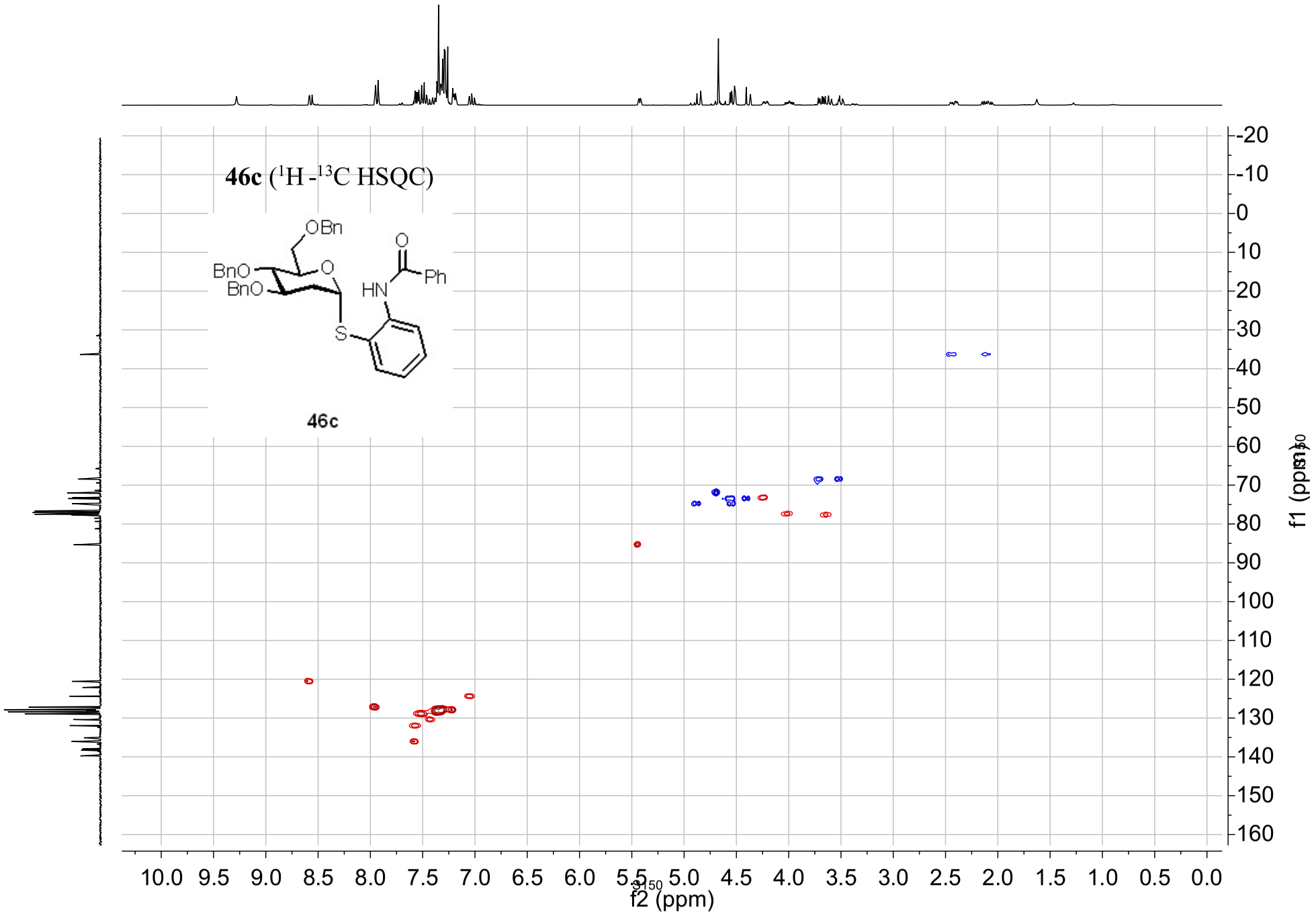


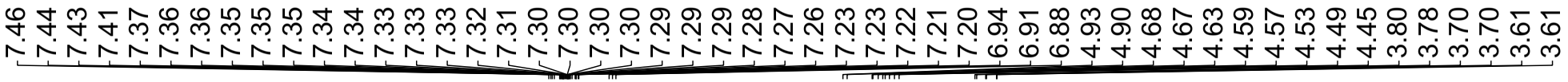
46c (^{13}C NMR, 75MHz, $CDCl_3$)



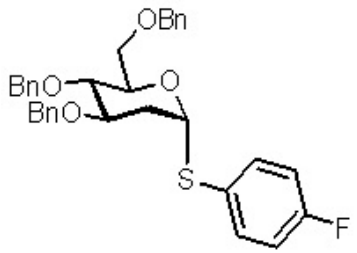
46c


46c (1H-13C Coupled HSQC)
OBn
BnO
BnO
O
HN
O
Ph
S
46c
J= 167 Hz
f2 (ppm)
f1 (ppm)

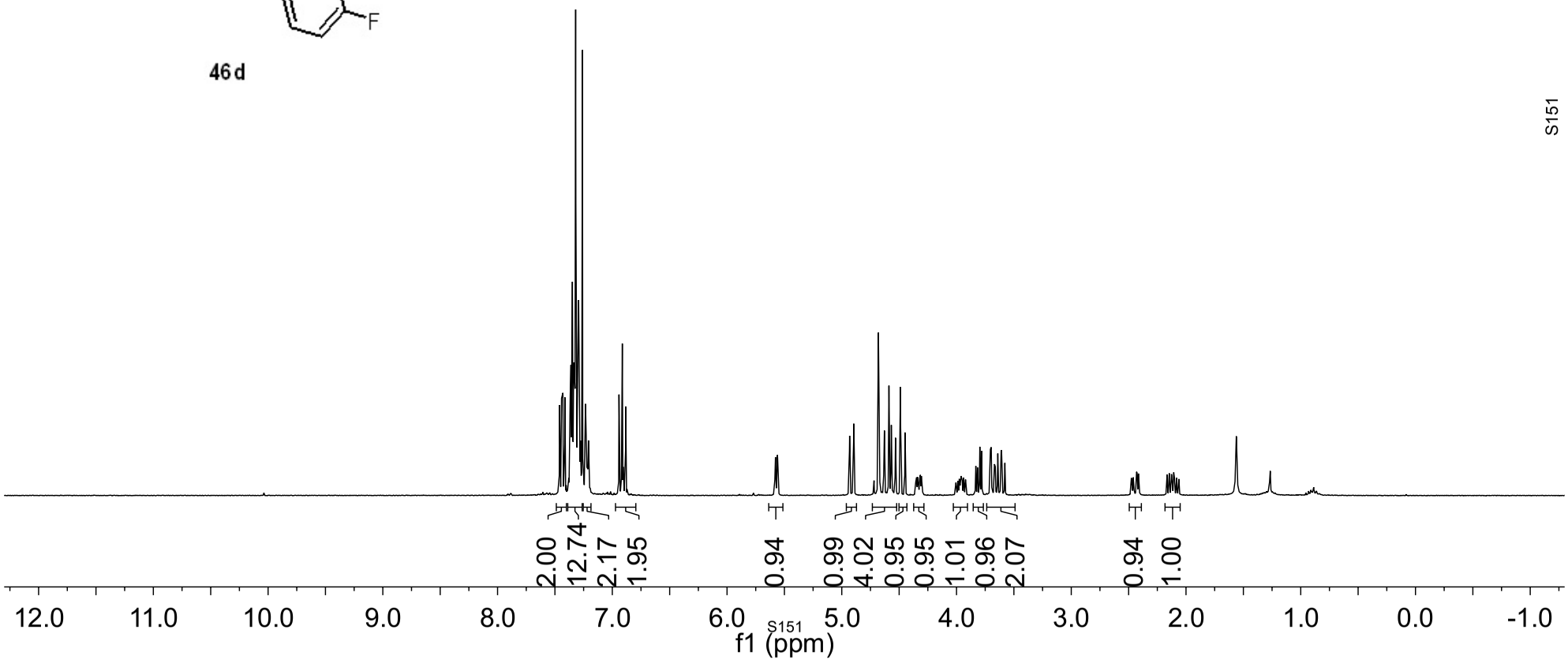

46c (1H -13C HSQC)
OBn
BnO
BnO
O
HN
O
Ph
S
46c
f2 (ppm)
f1 (ppm)

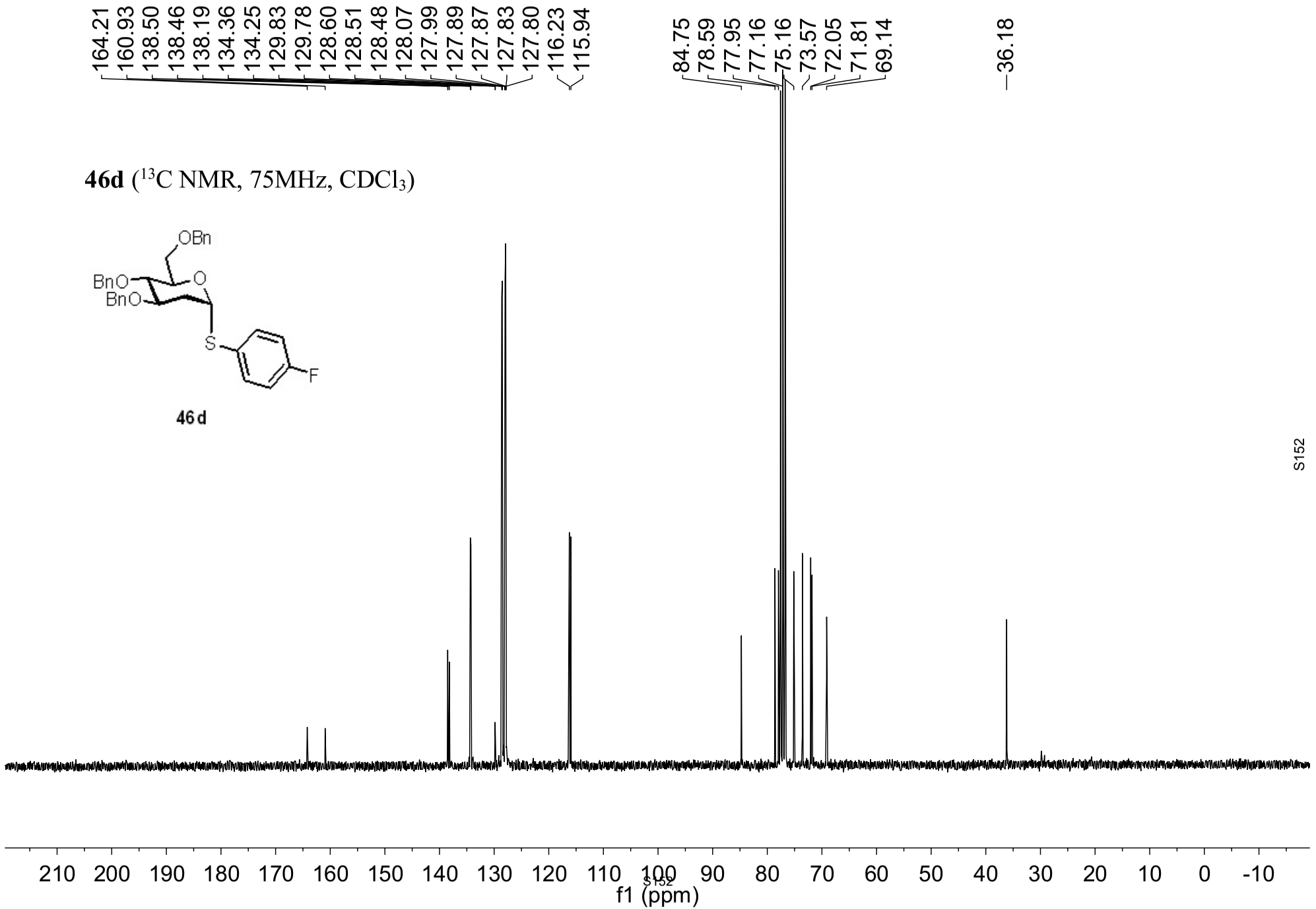


46d (^{1}H NMR, 300MHz, $CDCl_3$)

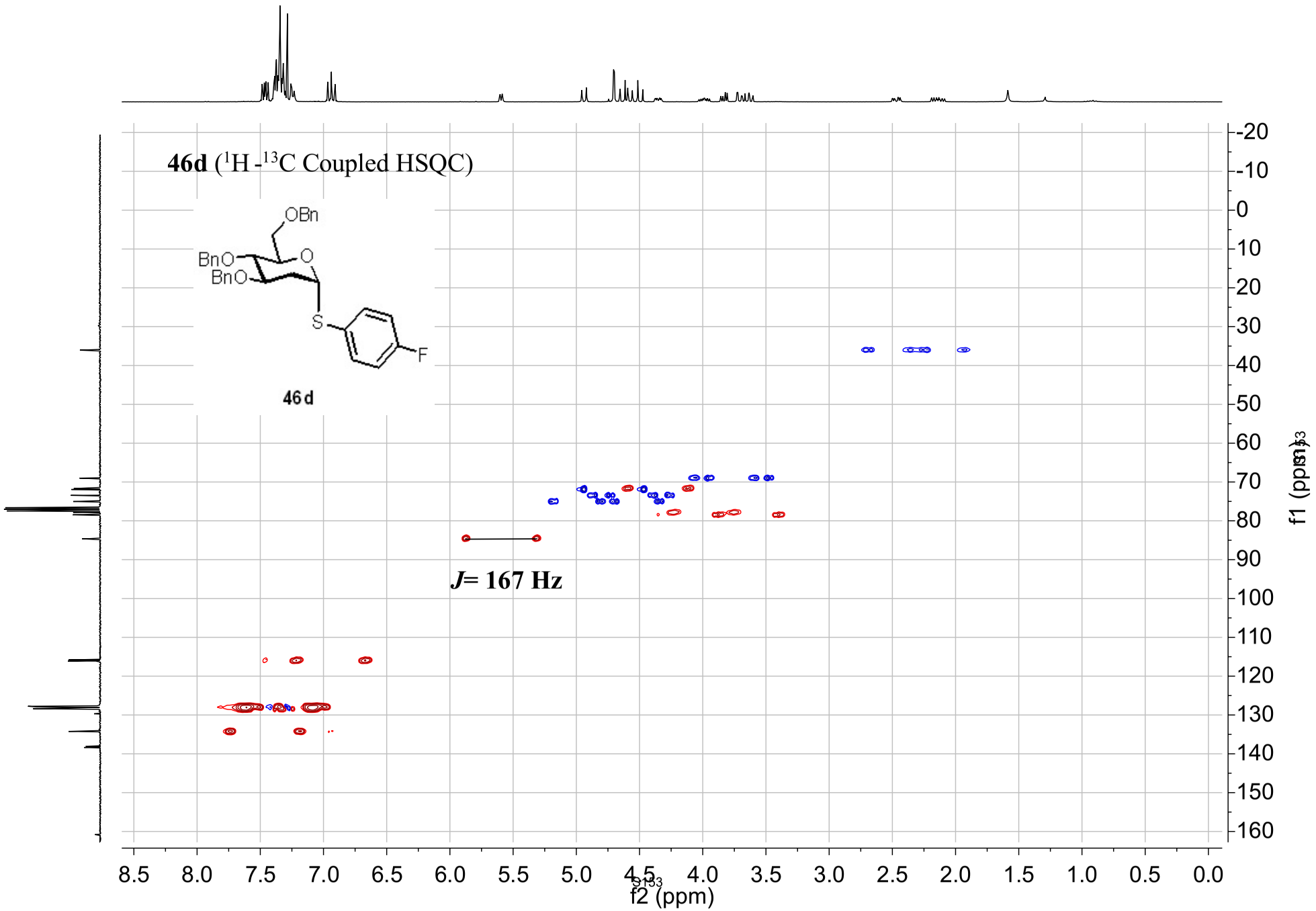


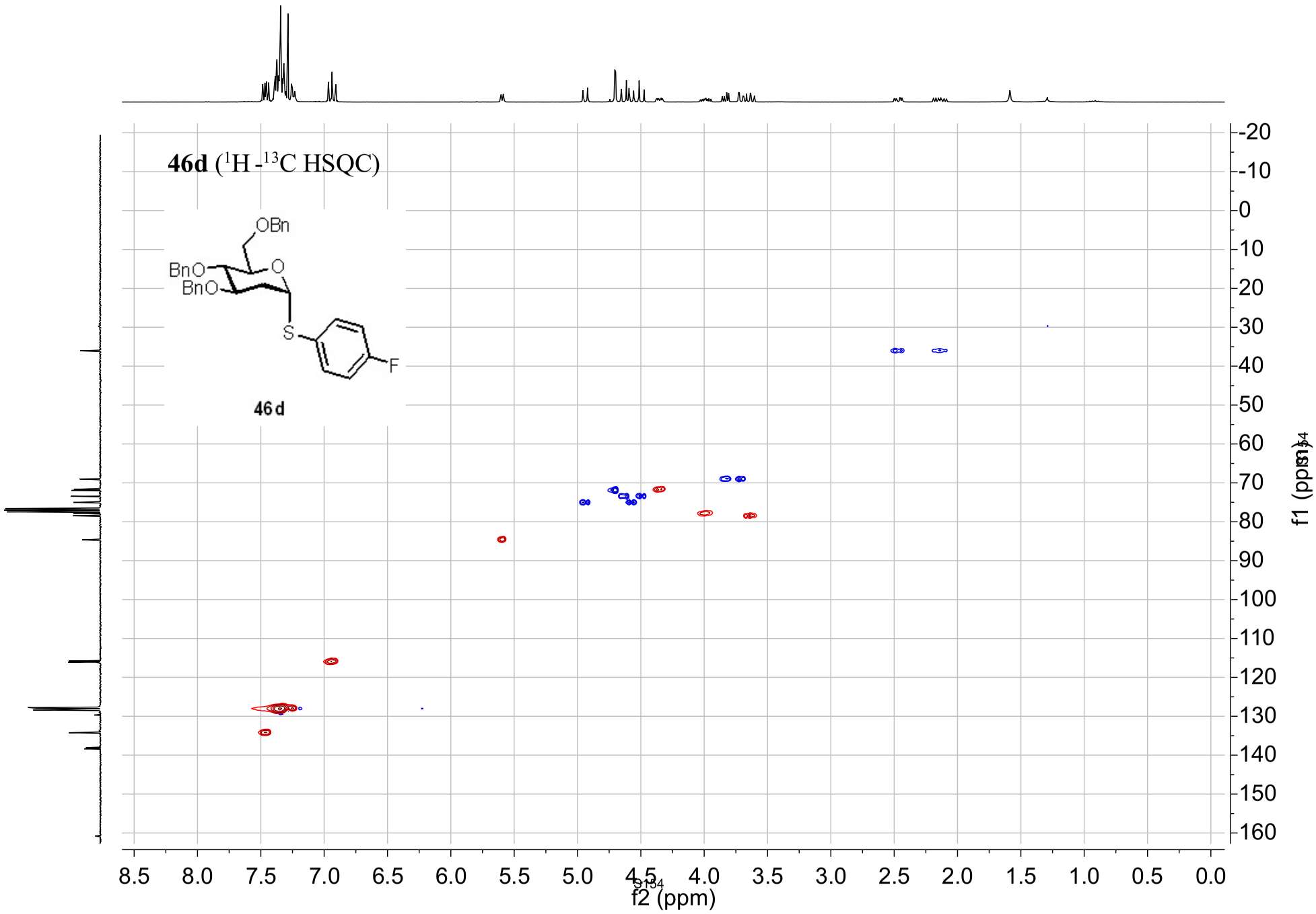
46 d



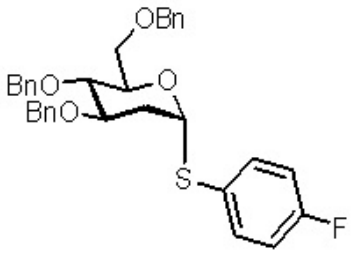


46d (^{13}C NMR, 75MHz, $CDCl_3$)


46d (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
S
F
46 d
J= 167 Hz
f2 (ppm)
f1 (ppm)
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
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160


46d (1H -13C HSQC)
OBn
BnO
BnO
O
S
F
46 d
f2 (ppm)
f1 (ppm)

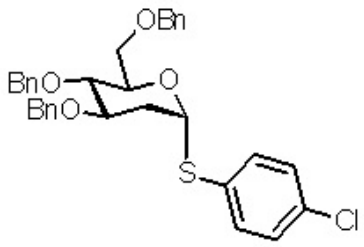
46d (^{19}F NMR, 282MHz, $CDCl_3$)



46 d

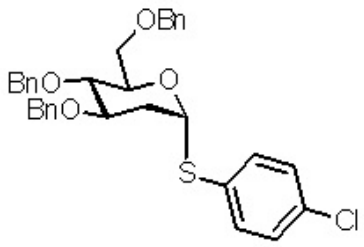
S155

46e (^{1}H NMR, 300MHz, $CDCl_3$)

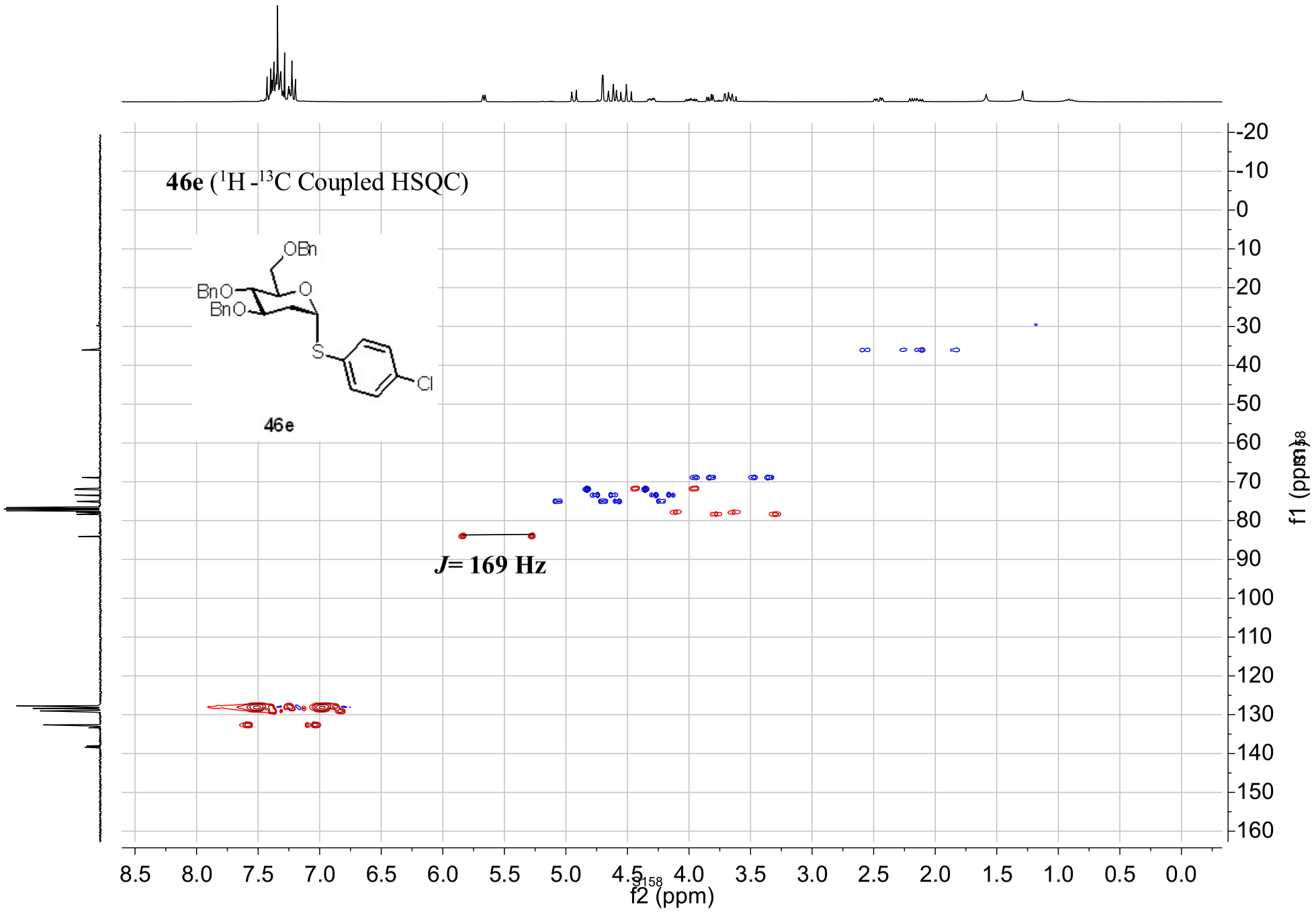


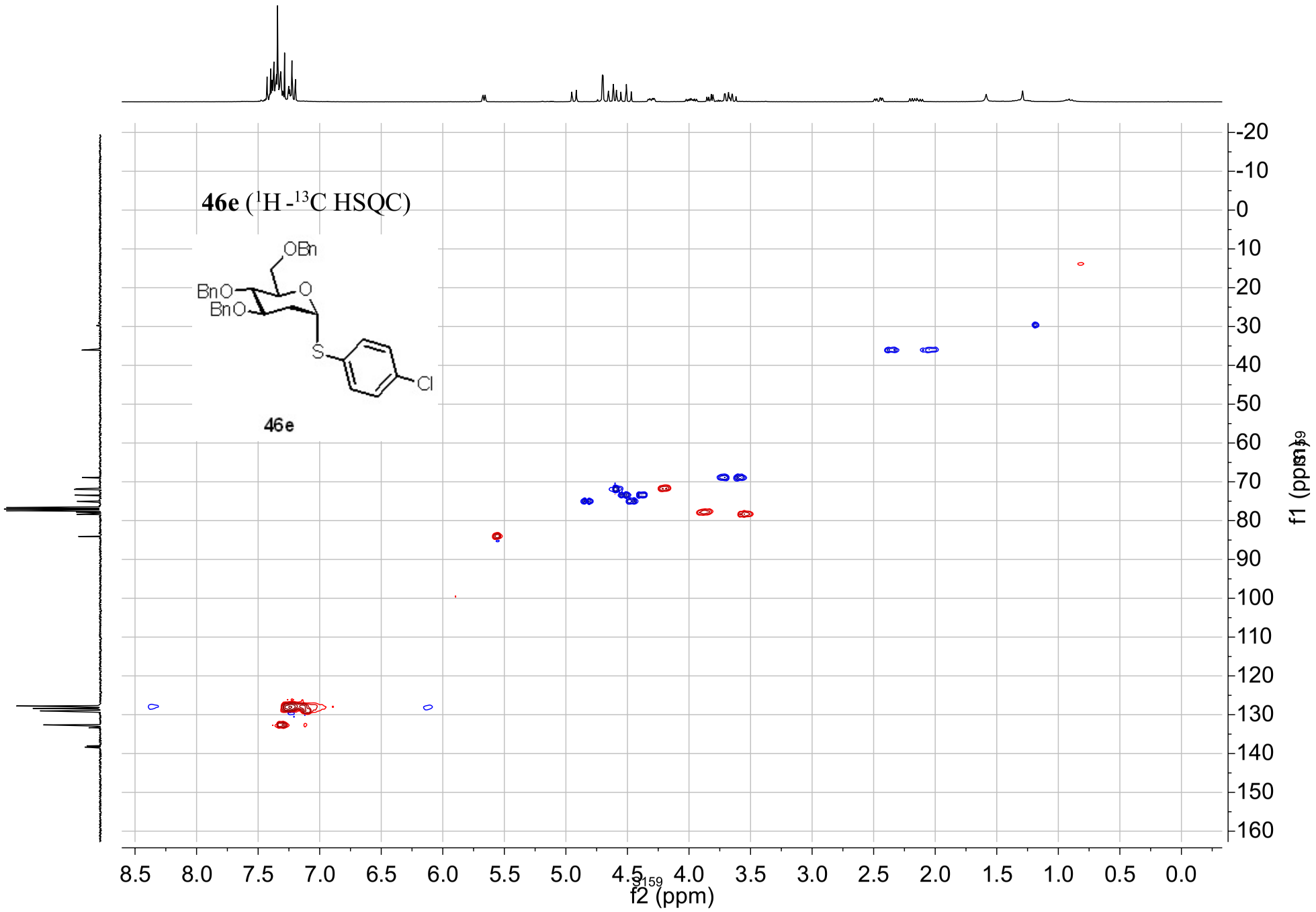
46e

46e (^{13}C NMR, 75MHz, $CDCl_3$)

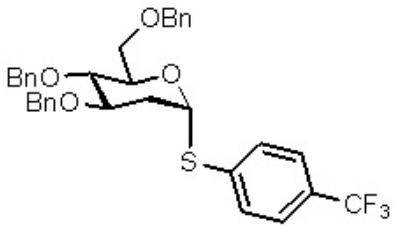


46e

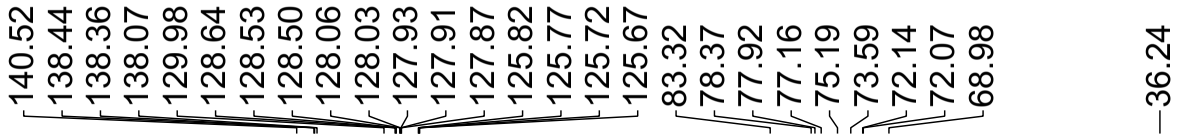

46e (^{1}H -^{13}C Coupled HSQC)
OBn
BnO
BnO
O
S
Cl
46e
J= 169 Hz
f2 (ppm)
f1 (ppm)


46e (1H -13C HSQC)
OBn
BnO
BnO
O
S
Cl
46e
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
f2 (ppm)
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
f1 (ppm)

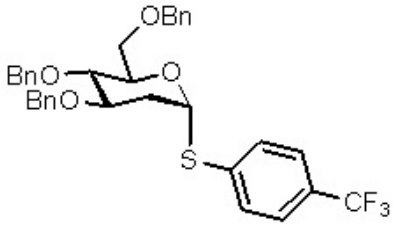
46f (^{1}H NMR, 300MHz, $CDCl_3$)



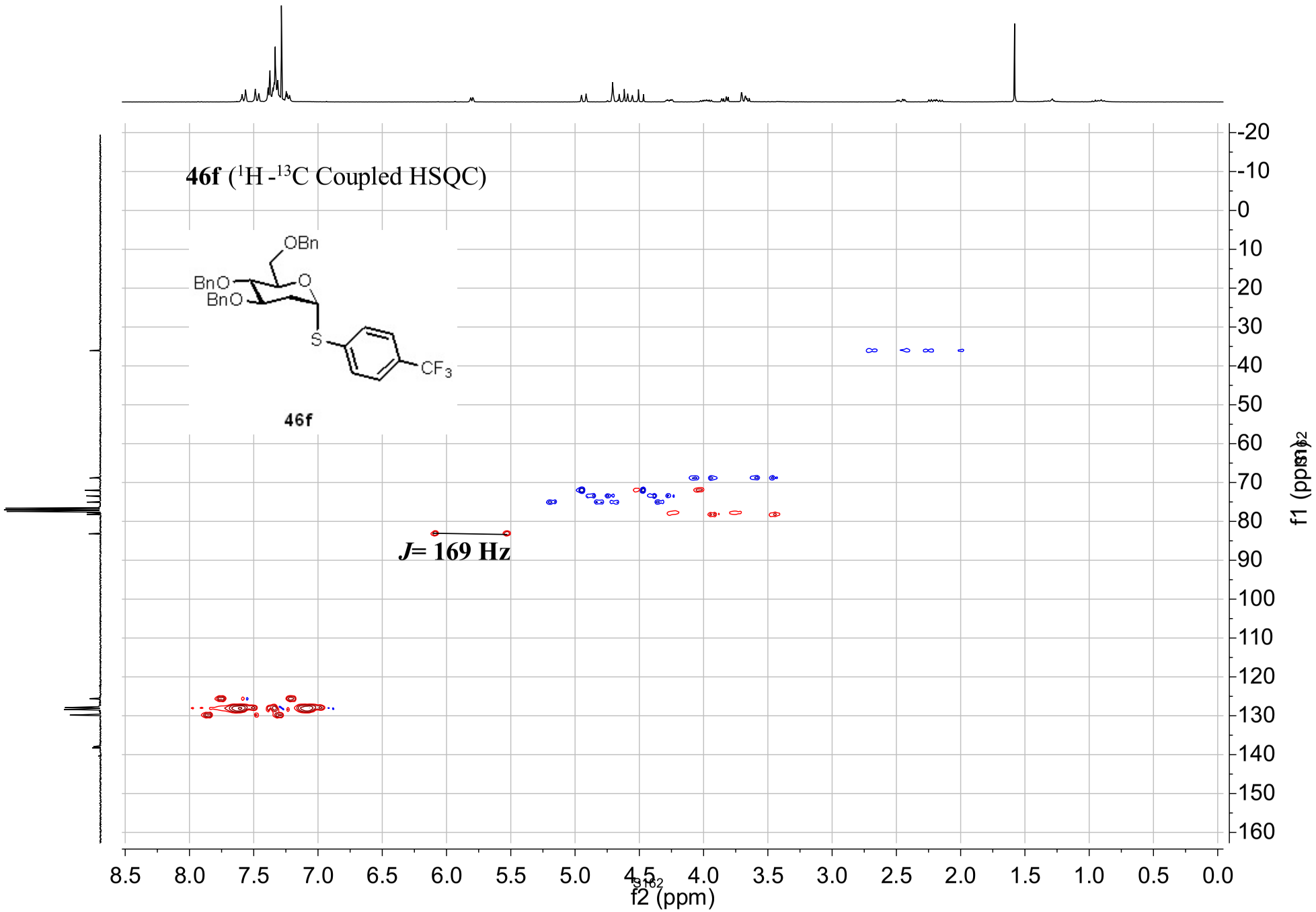
46f

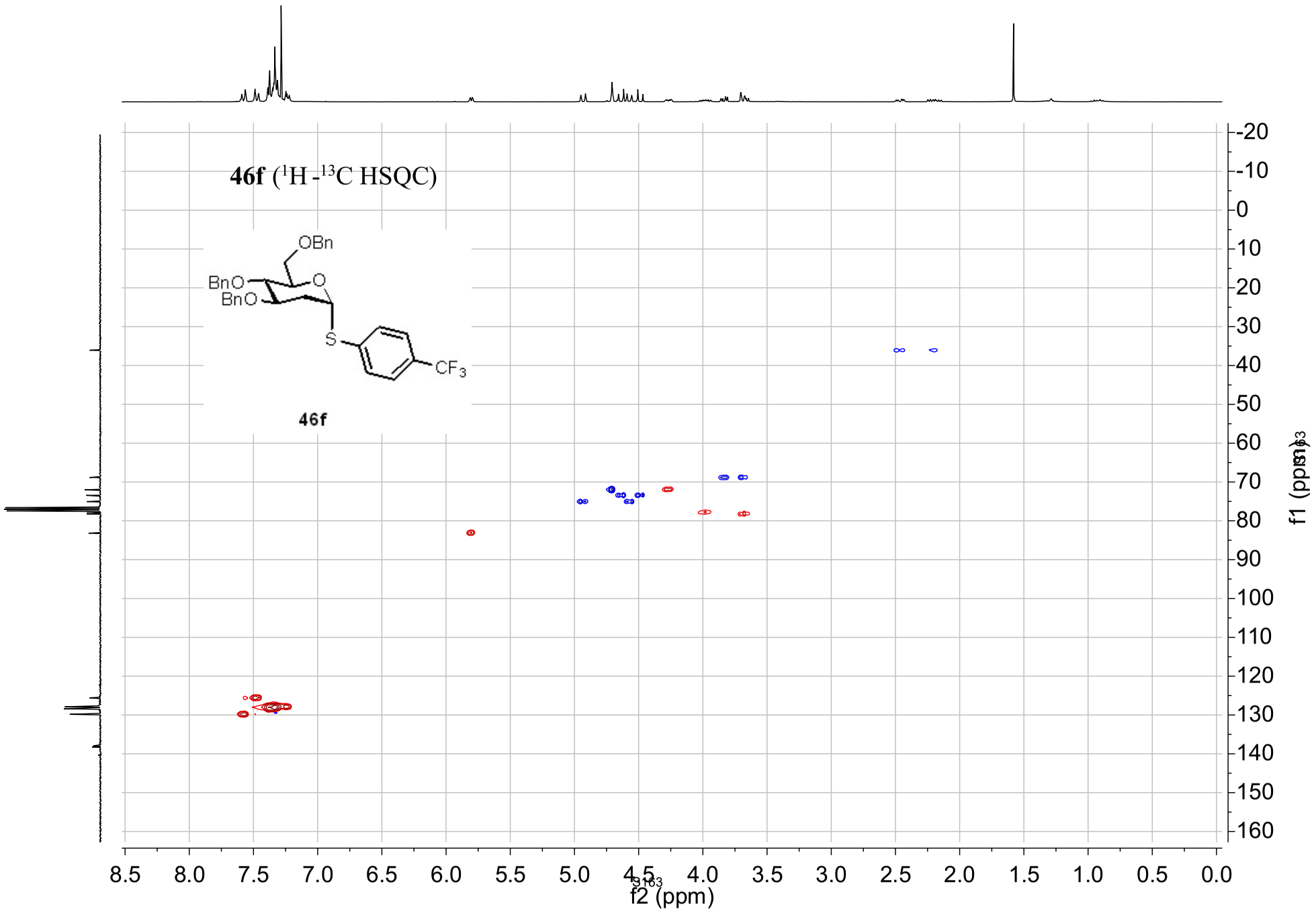


46f (^{13}C NMR, 75MHz, $CDCl_3$)

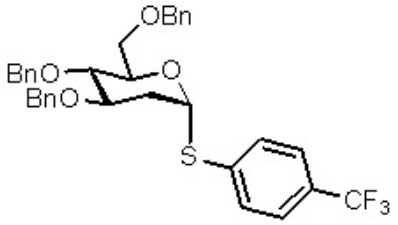


46f


46f (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
S
CF3
46f
J= 169 Hz
f2 (ppm)
f1 (ppm)


46f (^{1}H -^{13}C HSQC)
OBn
BnO
BnO
O
S
CF3
46f
f2 (ppm)
f1 (ppm)

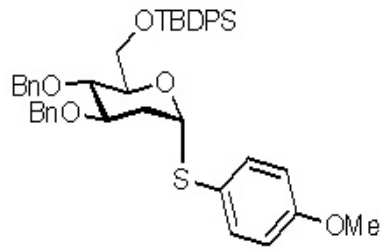
46f (^{19}F NMR, 282MHz, $CDCl_3$)



46f

S164

47a (^{1}H NMR, 300MHz, $CDCl_3$)



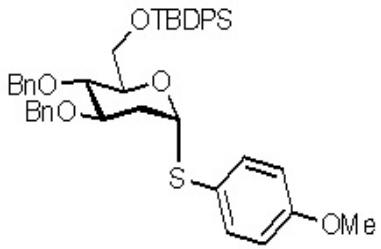
47a

159.38
138.63
138.54
136.03
135.72
134.06
133.99
133.30
129.67
129.60
128.61
128.52
128.07
127.95
127.86
127.79
127.75
127.64
125.82
114.58

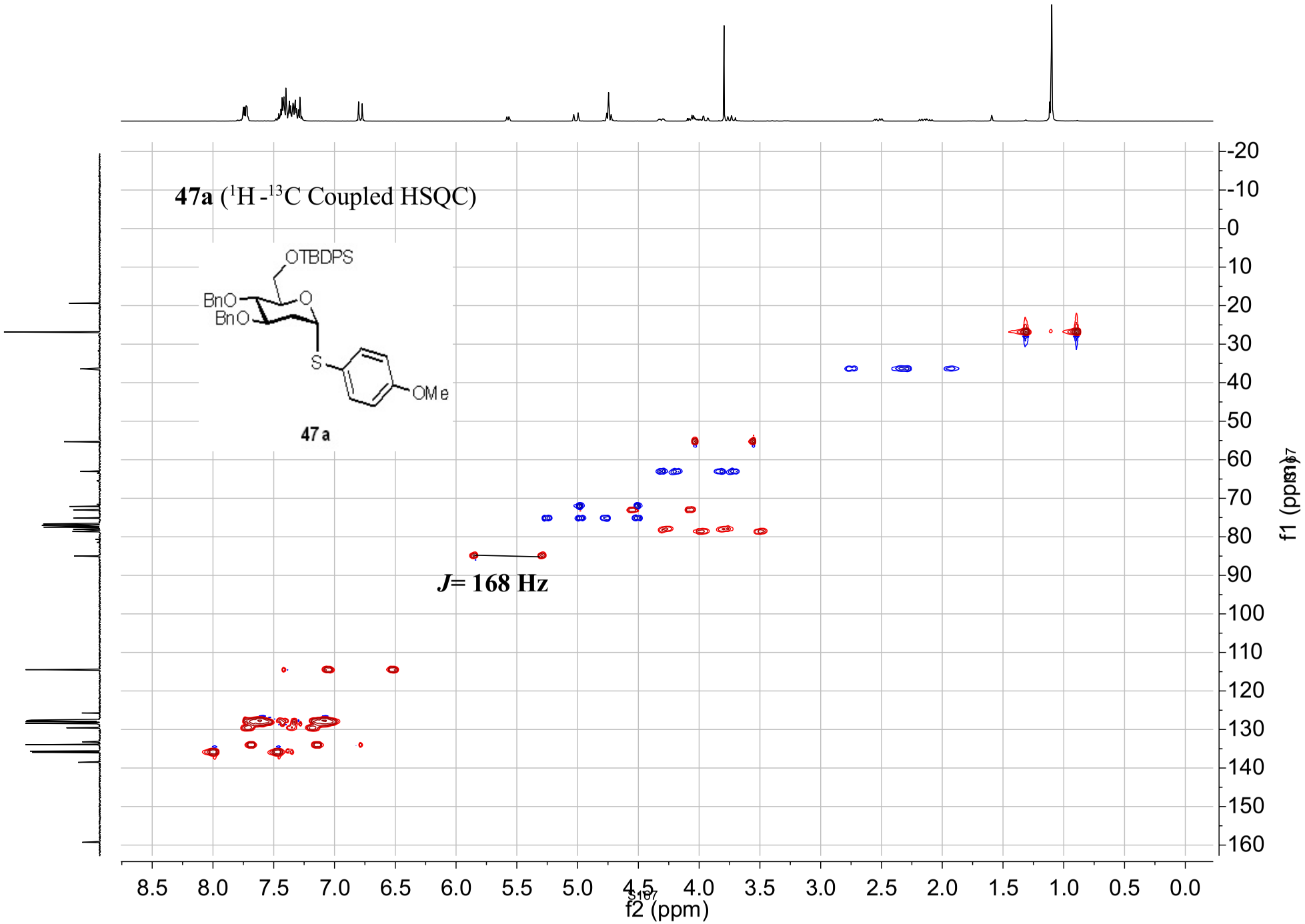
85.05
78.73
78.12
77.16
75.27
73.10
72.22
63.16
55.41

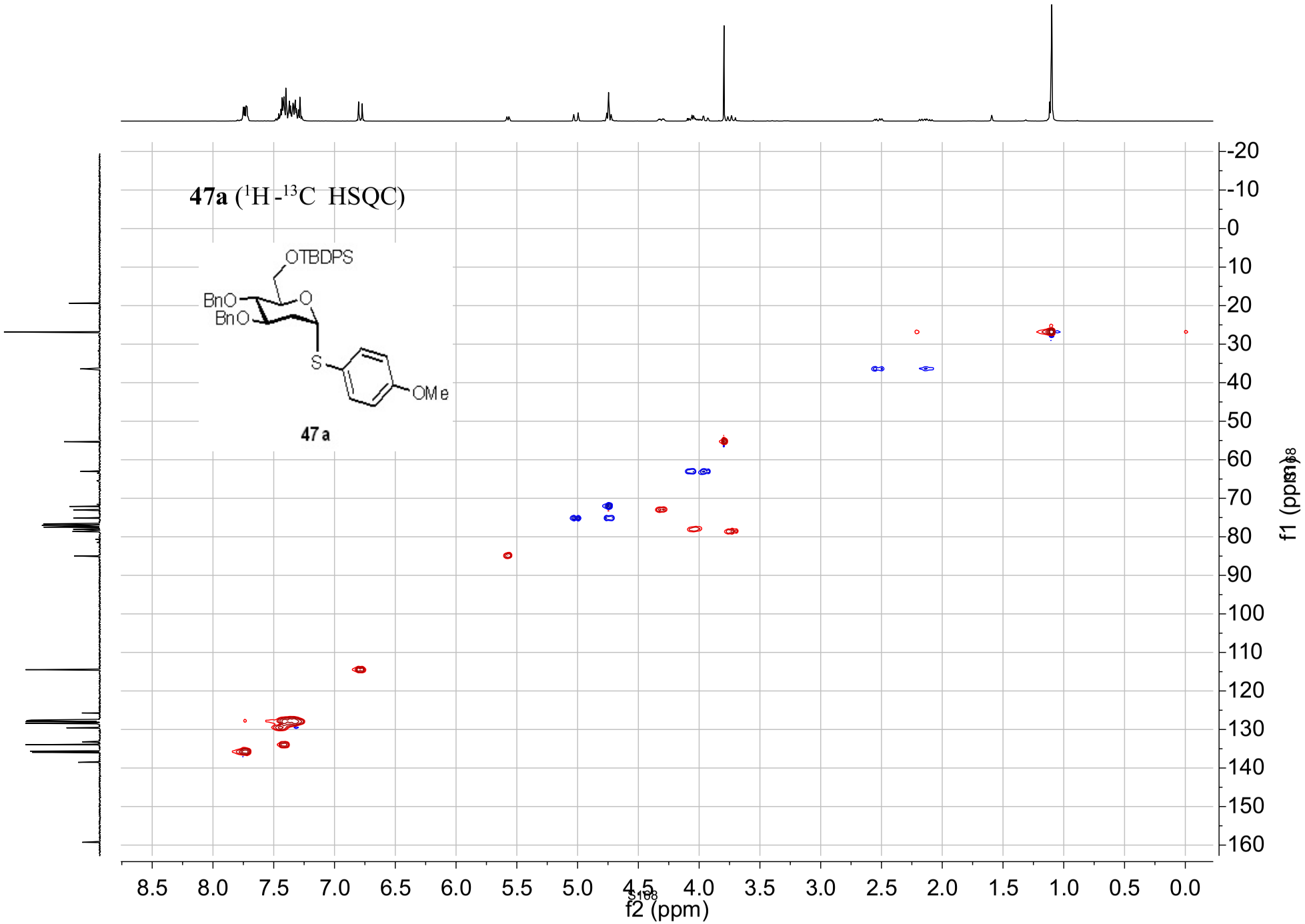
36.53
26.95
19.47

47a (^{13}C NMR, 75MHz, $CDCl_3$)

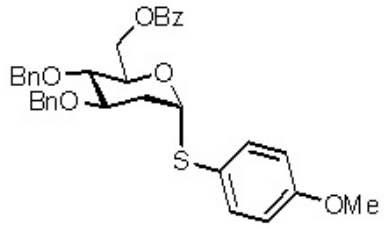


47a


47a (1H -13C Coupled HSQC)
OTBDPS
BnO
BnO
O
S
OMe
47a
J= 168 Hz
f2 (ppm)
f1 (ppm)


47a (1H -13C HSQC)
OTBDPS
BnO
BnO
O
S
OMe
47a
f2 (ppm)
f1 (ppm)
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
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160

47b (^{1}H NMR, 300MHz, $CDCl_3$)



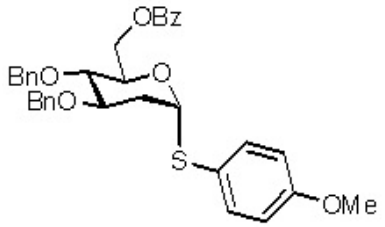
47b

166.44
159.67
138.27
138.09
134.54
133.10
130.18
129.87
128.66
128.60
128.45
128.26
128.00
127.98
127.89
127.11
124.72
114.68

84.85
78.62
78.00
77.16
75.23
72.05
70.28
64.23
55.37

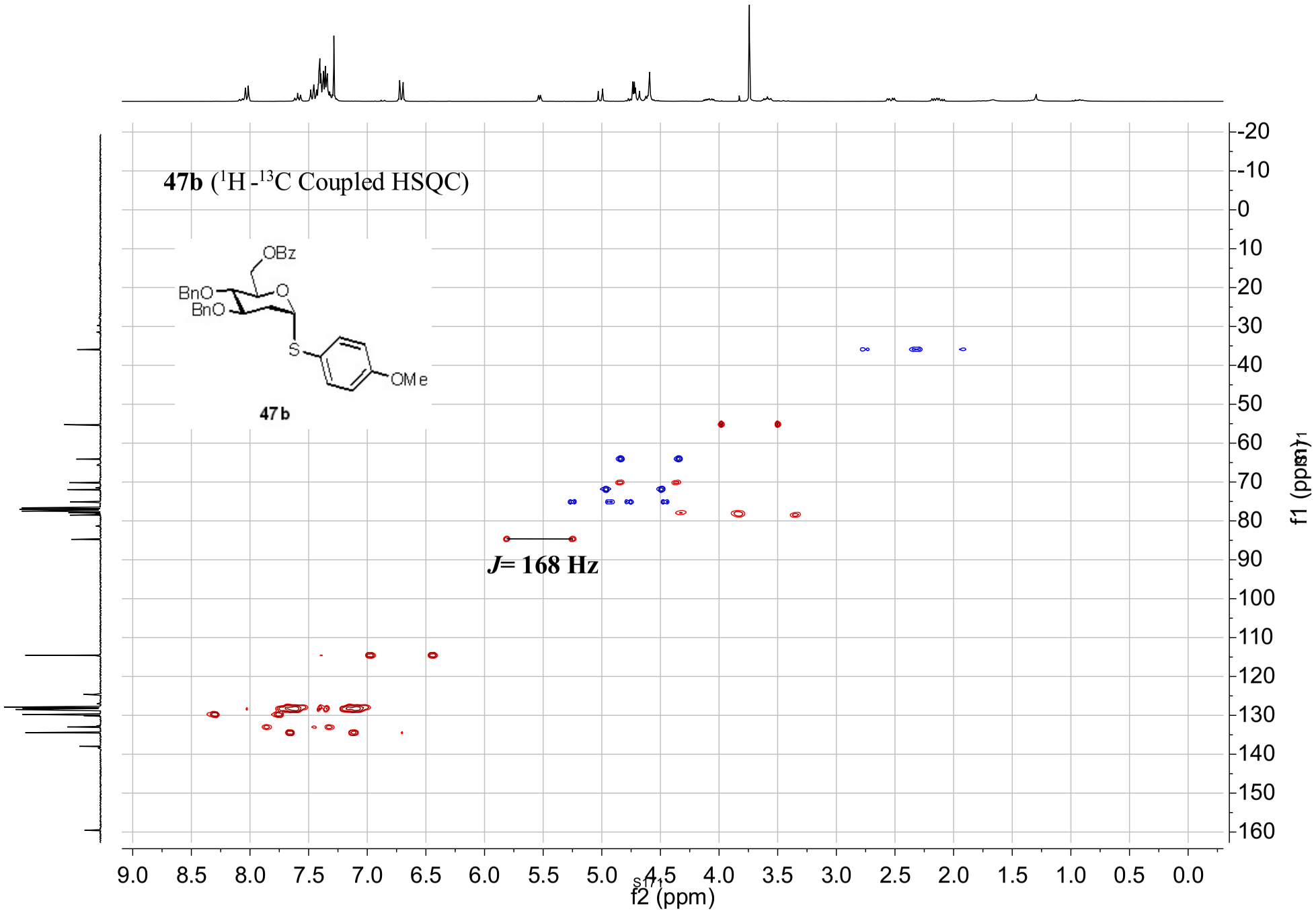
36.05

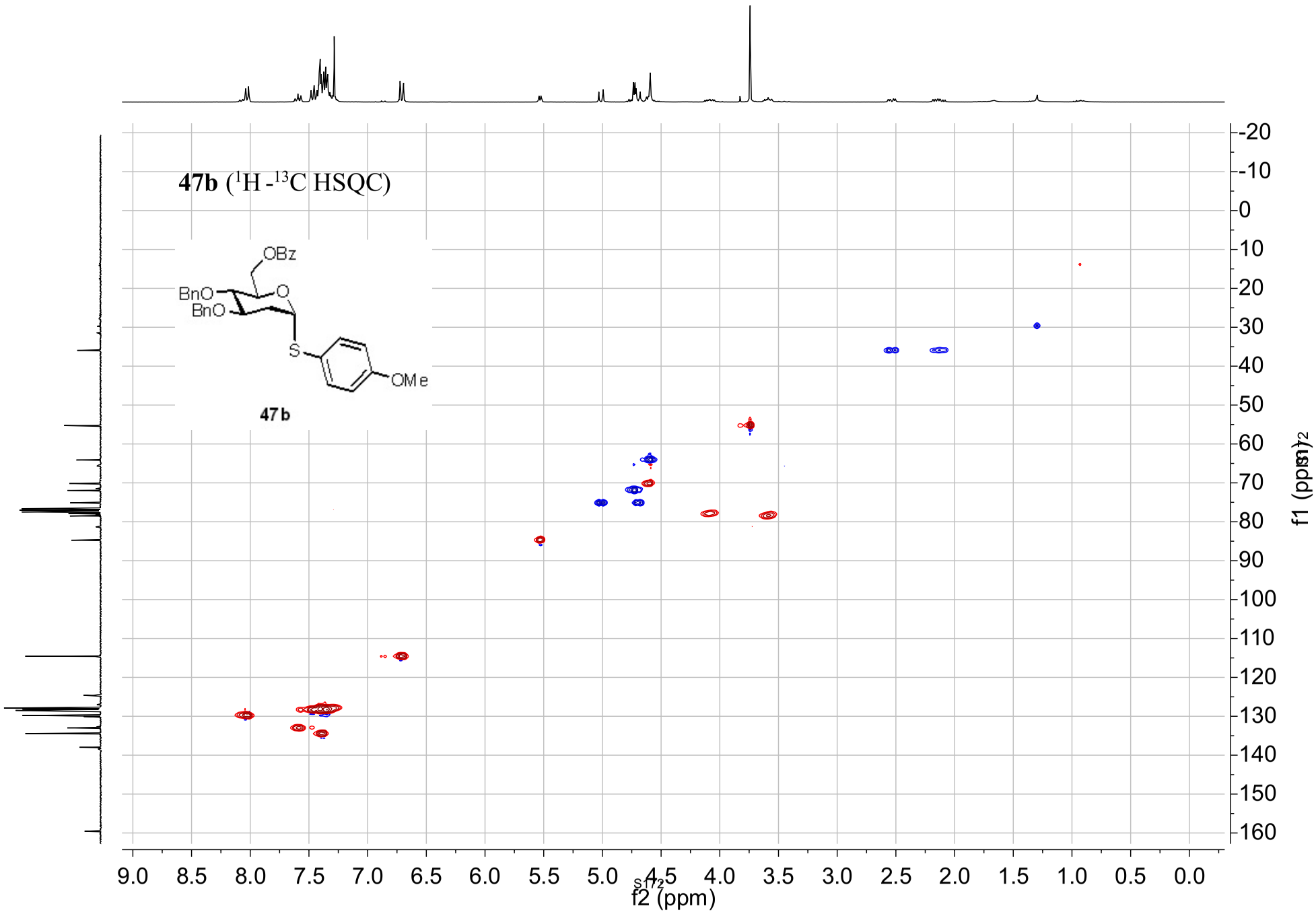
47b (^{13}C NMR, 75MHz, $CDCl_3$)



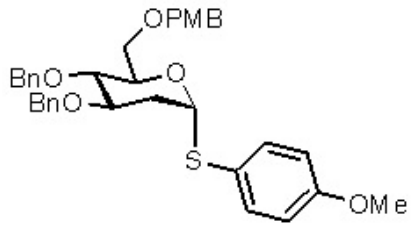
47b

S170

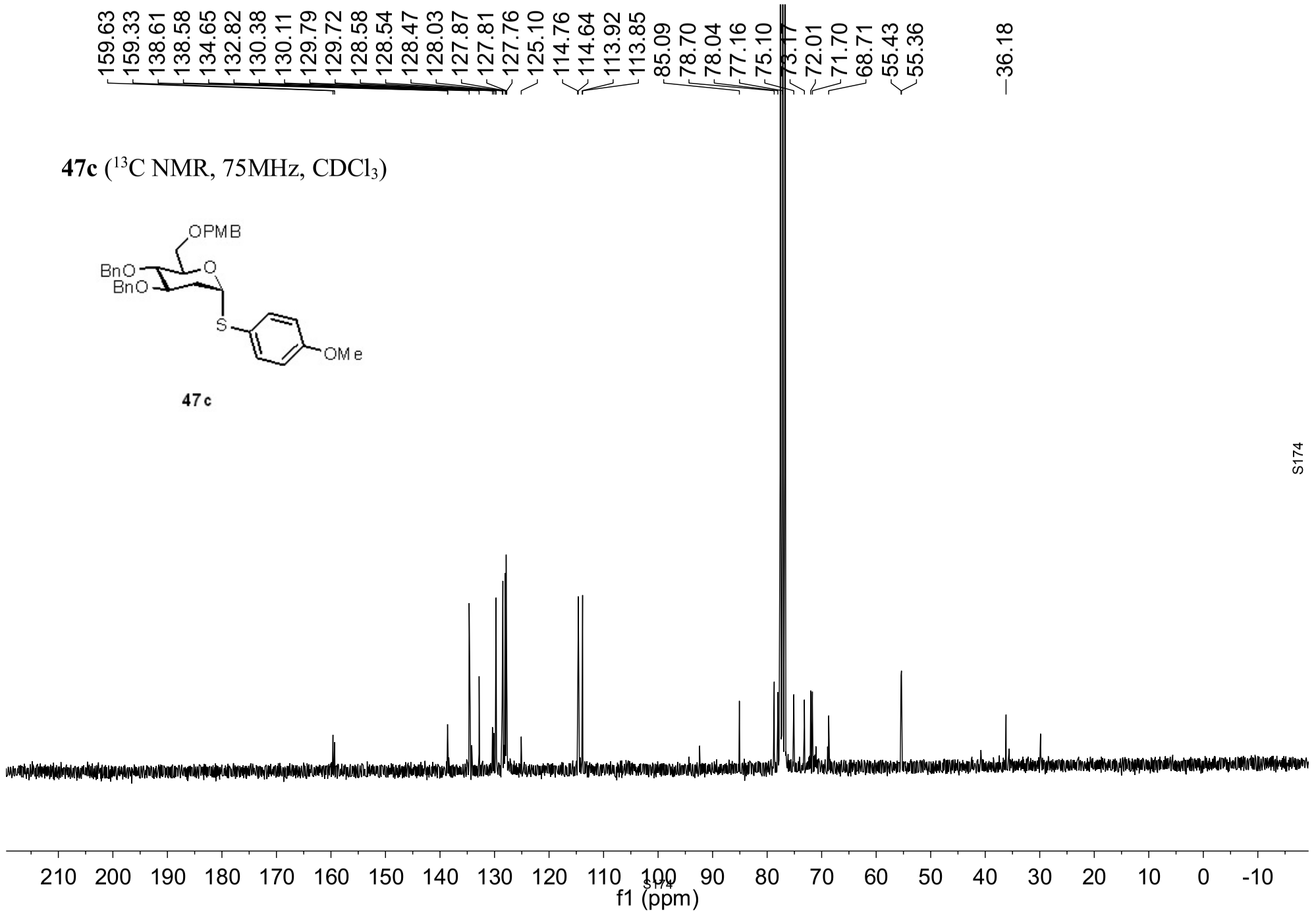

47b (1H -13C Coupled HSQC)
OBz
BnO
BnO
O
S
OMe
47b
J= 168 Hz
f2 (ppm)
f1 (ppm)

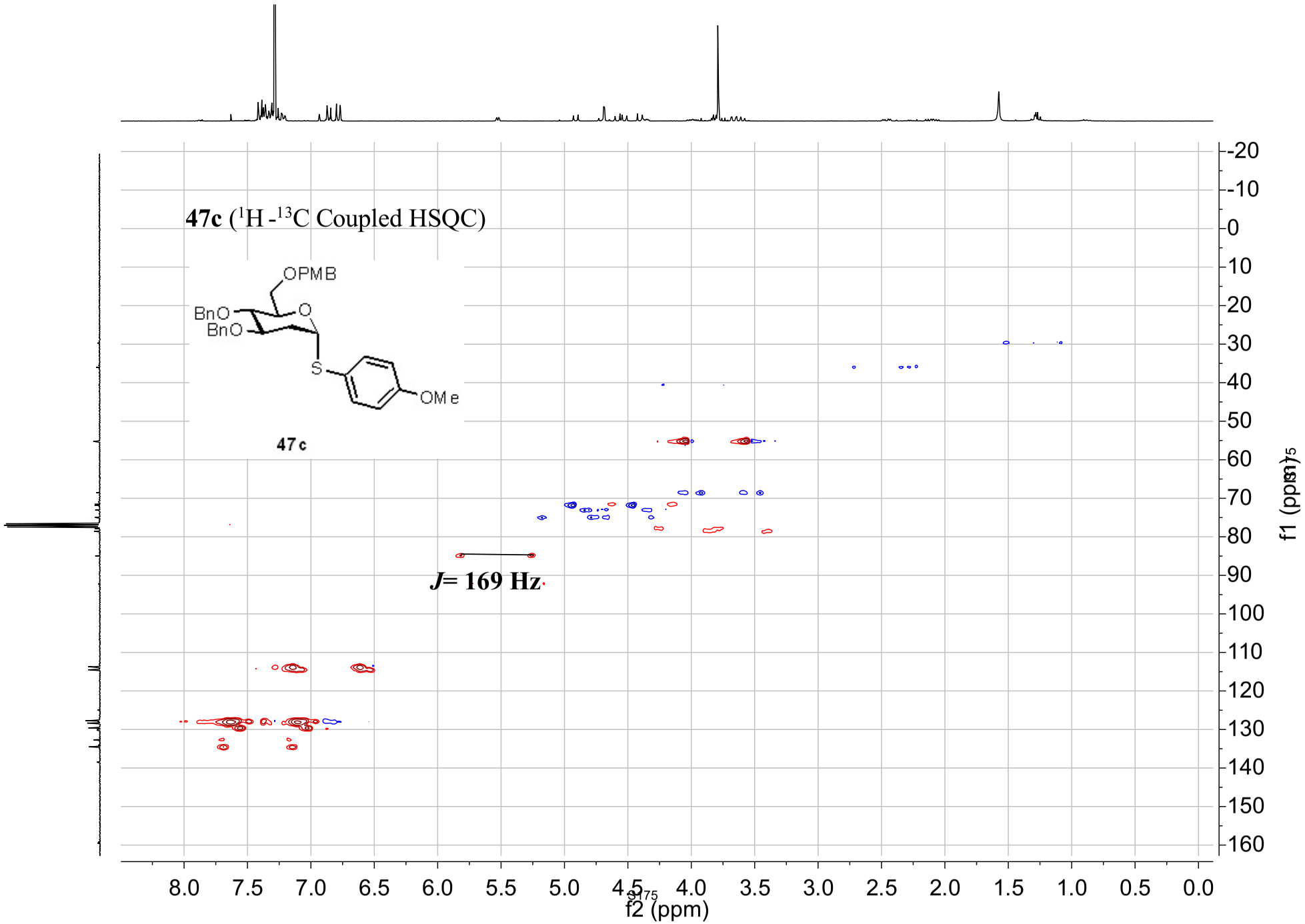

47b (1H -13C HSQC)
OBz
BnO
BnO
O
S
OMe
47b
f2 (ppm)
f1 (ppm)

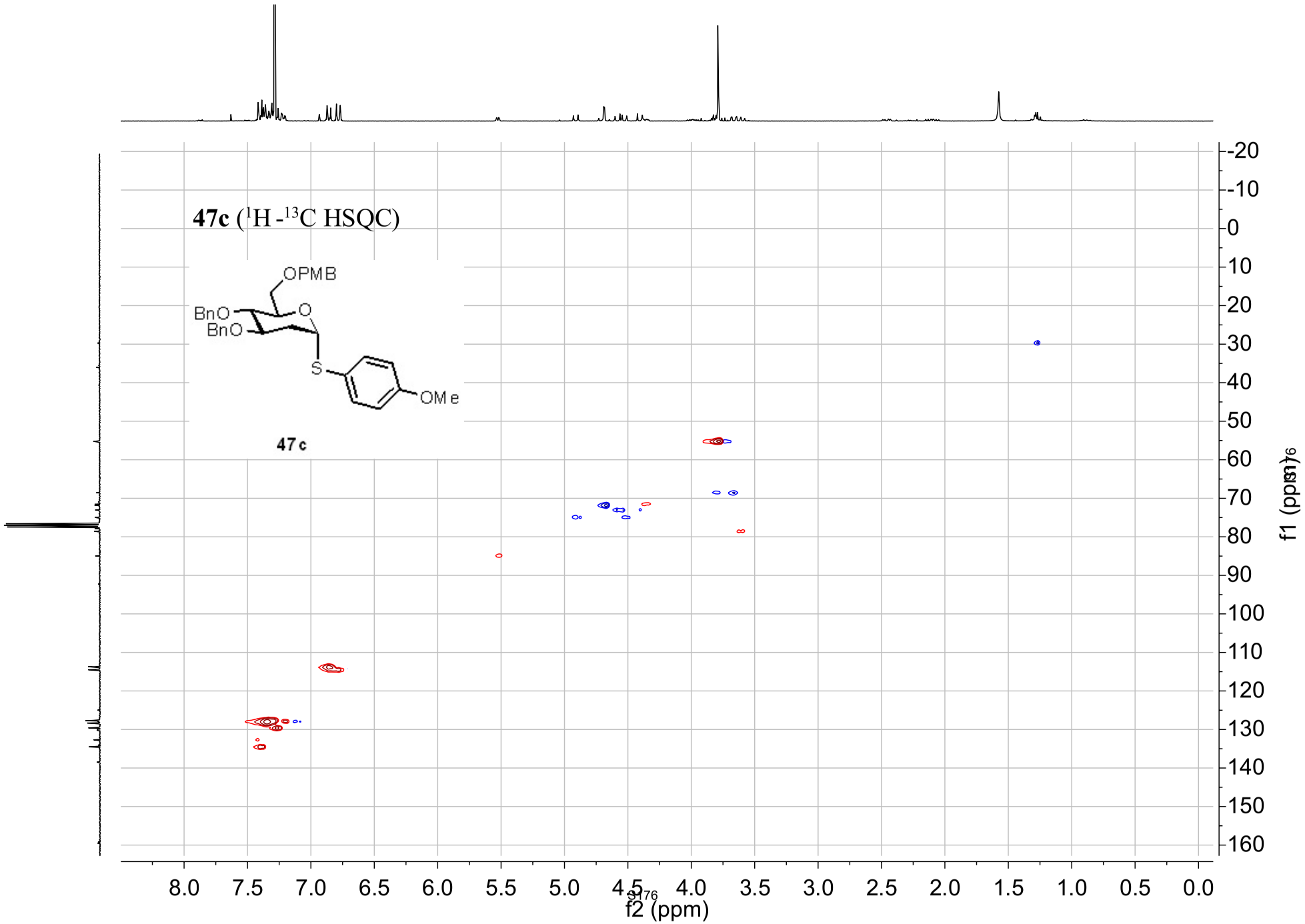
47c (^{1}H NMR, 300MHz, $CDCl_3$)



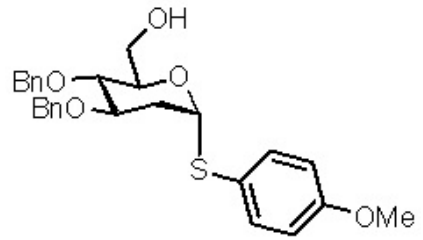
47c


159.63
159.33
138.61
138.58
134.65
132.82
130.38
130.11
129.79
129.72
128.58
128.54
128.47
128.03
127.87
127.81
127.76
125.10
114.76
114.64
113.92
113.85
85.09
78.70
78.04
77.16
75.10
73.17
72.01
71.70
68.71
55.43
55.36
36.18
47c (^{13}C NMR, 75MHz, $CDCl_3$)
OPMB
BnO
BnO
O
S
OMe
47c
S174
S174
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


47c (1H -13C Coupled HSQC)
OPMB
BnO
BnO
O
S
OMe
47c
J= 169 Hz
f2 (ppm)
f1 (ppm)

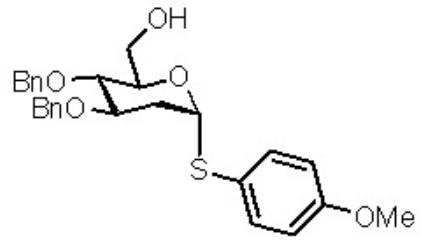

47c (1H -13C HSQC)
OPMB
BnO
BnO
O
S
OMe
47c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)

47d (^{1}H NMR, 300MHz, $CDCl_3$)

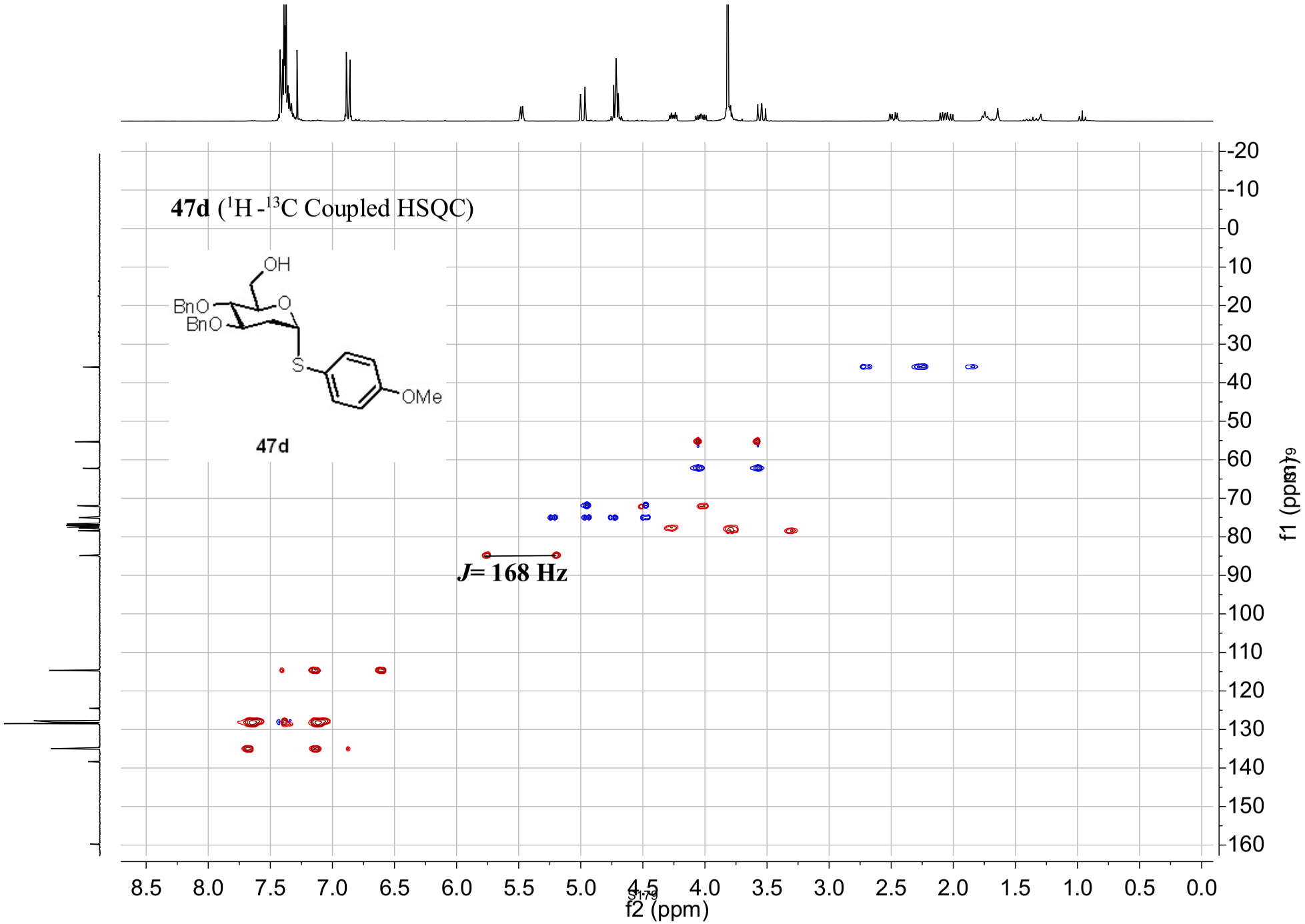


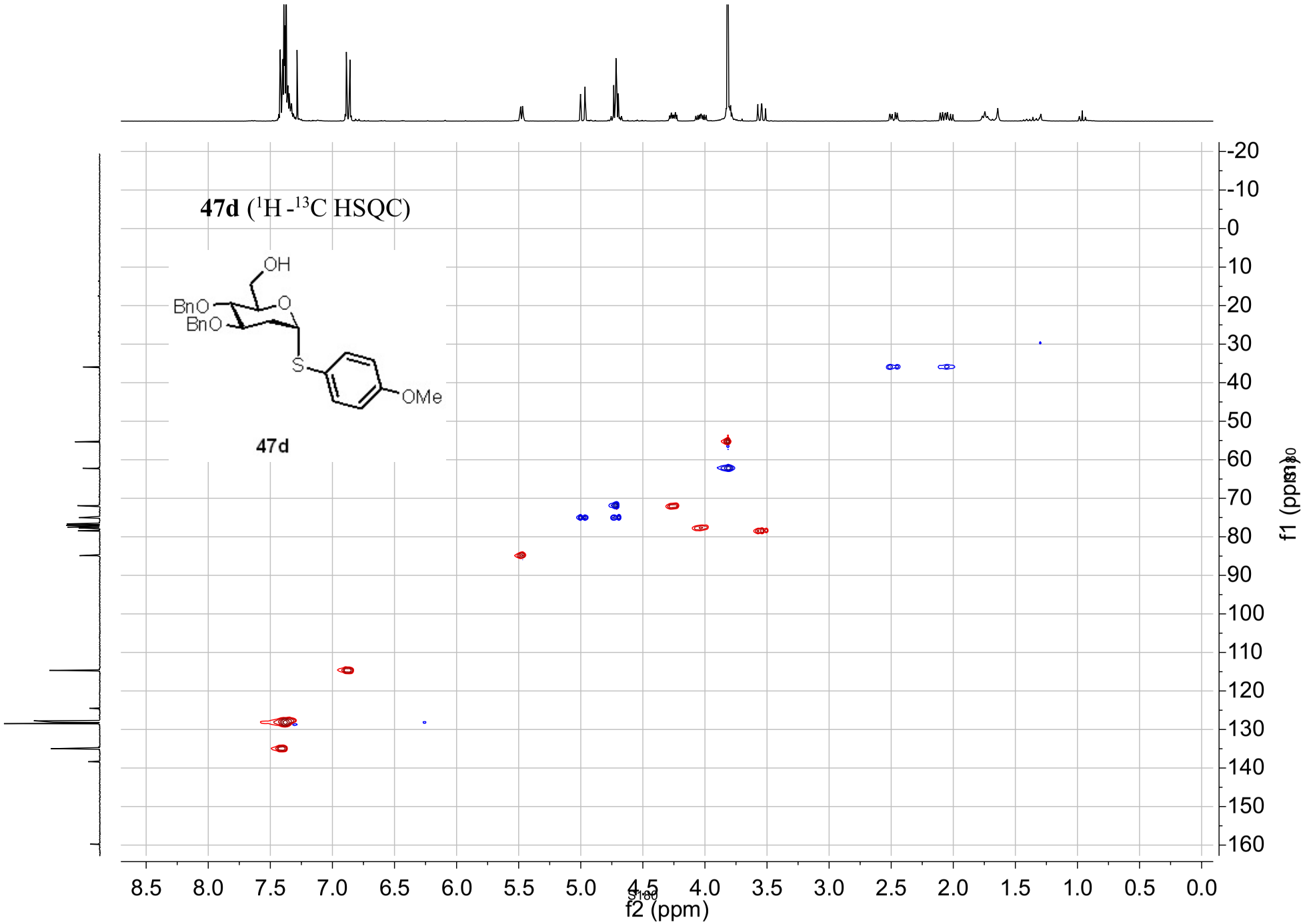
47d

47d (^{13}C NMR, 75MHz, $CDCl_3$)

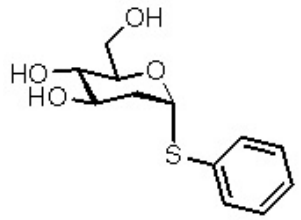


47d


47d (1H -13C Coupled HSQC)
OH
BnO
BnO
O
S
OMe
47d
J= 168 Hz
f2 (ppm)
f1 (ppm)

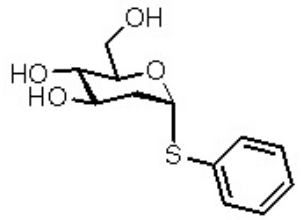

47d (1H -13C HSQC)
OH
BnO
BnO
O
S
OMe
47d
f2 (ppm)
f1 (ppm)

47e (^{1}H NMR, 300MHz, CD_3OD)

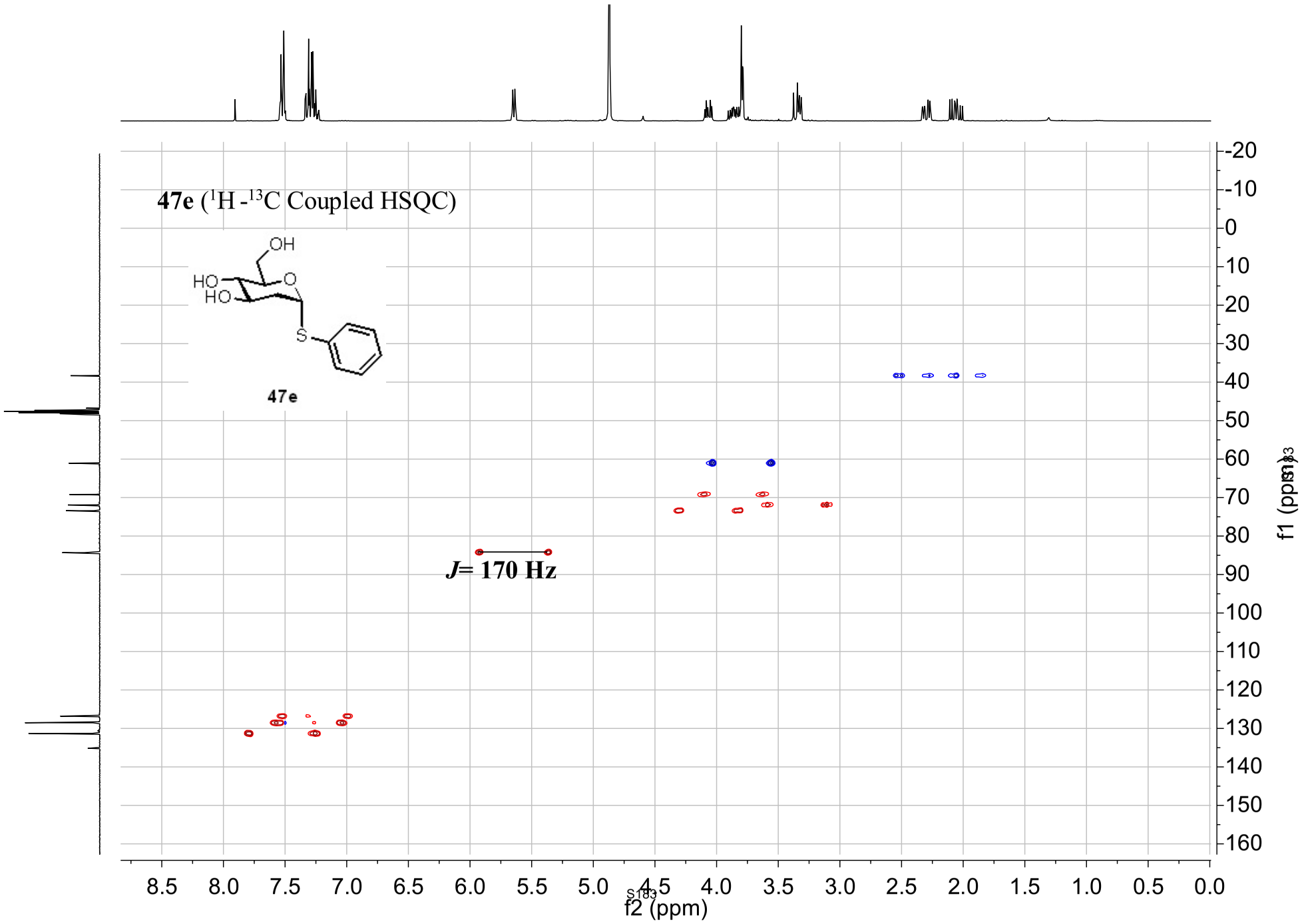


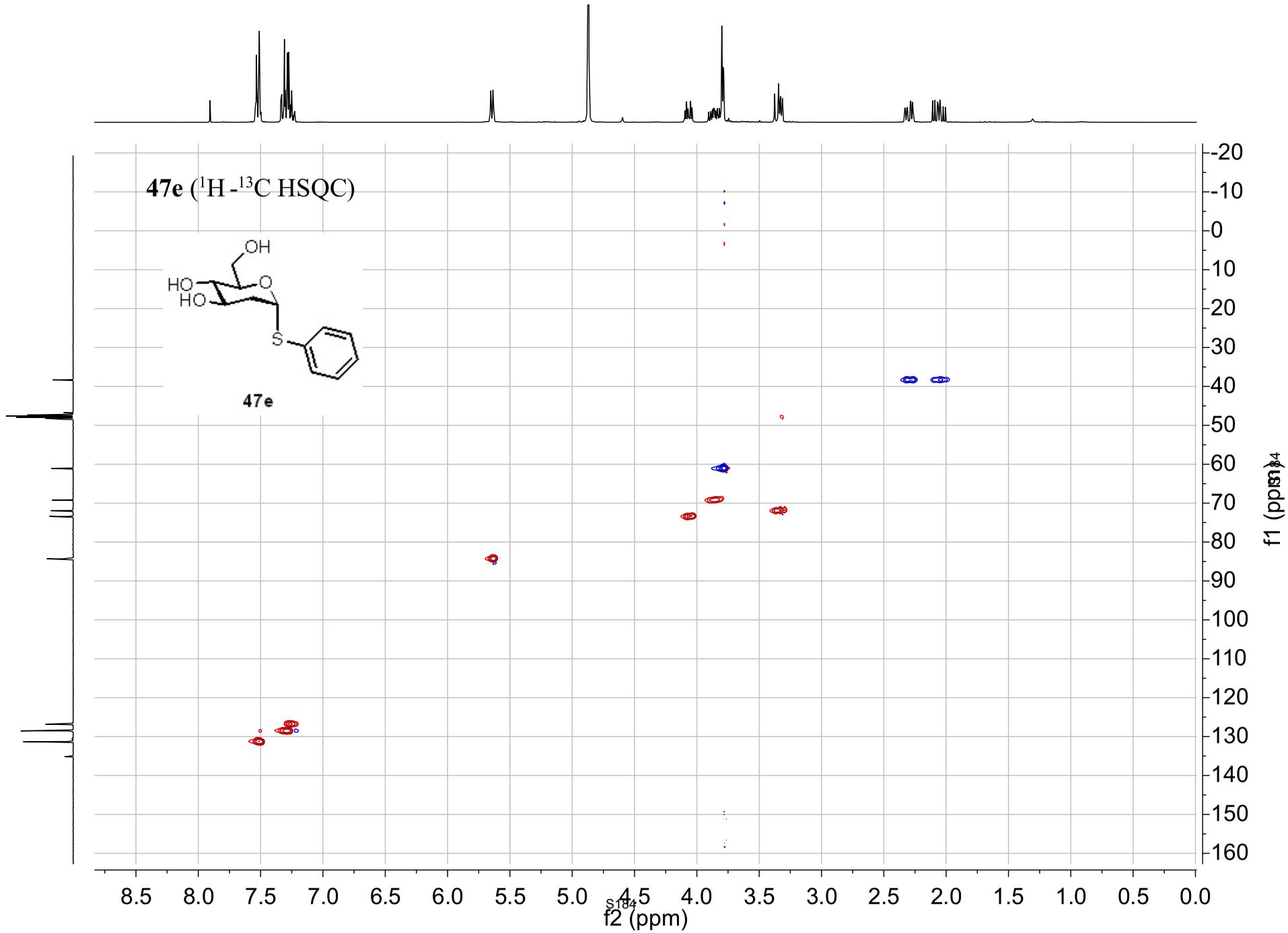
47e

47e (^{13}C NMR, 75MHz, CD_3OD)

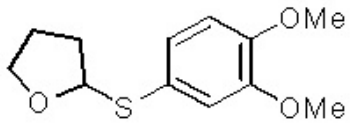


47e


47e (1H -13C Coupled HSQC)
OH
HO
HO
O
S
47e
J= 170 Hz
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
f2 (ppm)
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
f1 (ppm)

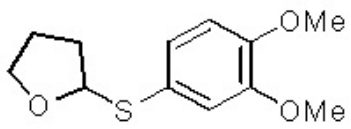

47e (1H -13C HSQC)
OH
HO
HO
O
S
47e
f2 (ppm)
f1 (ppm)

48a (^{1}H NMR, 300MHz, $CDCl_3$)



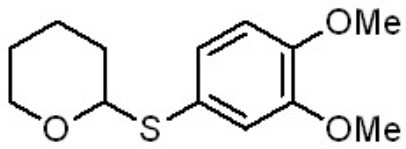
48a

48a (^{13}C NMR, 75MHz, $CDCl_3$)

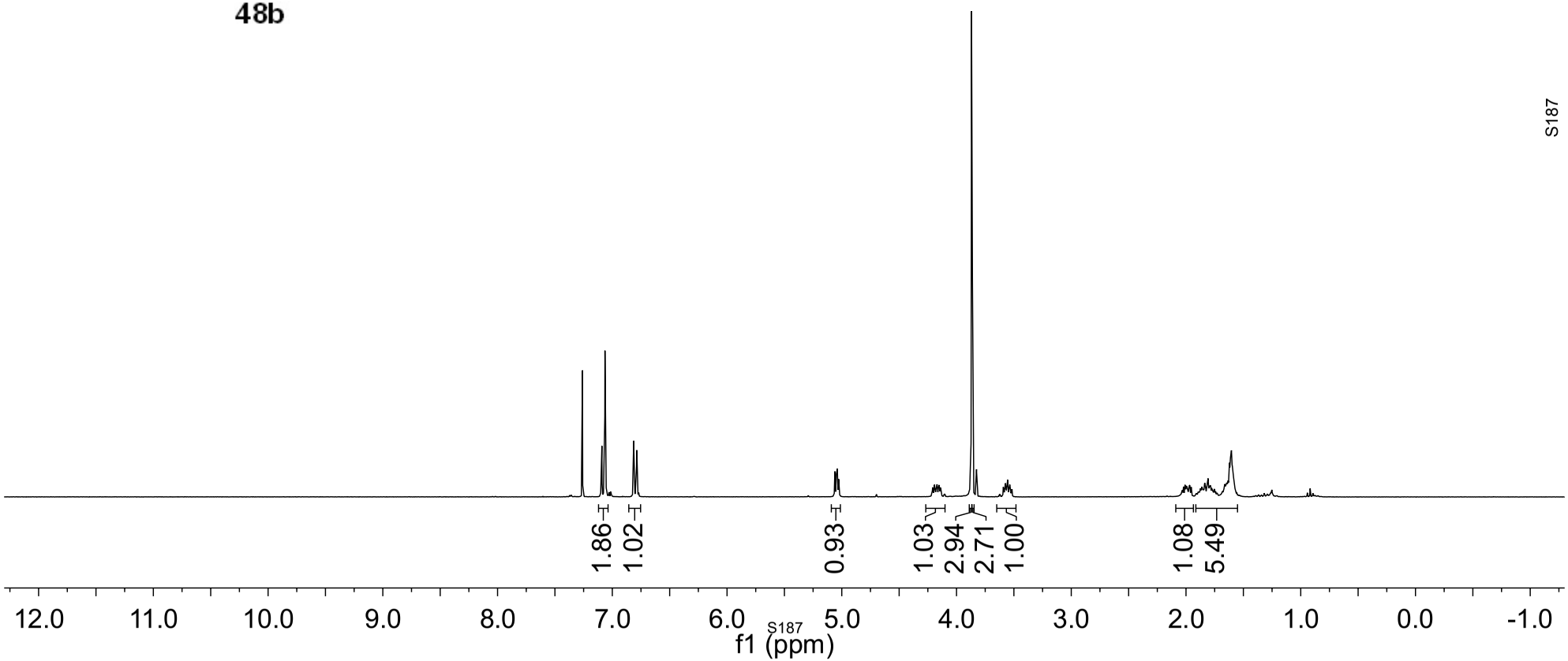


48a

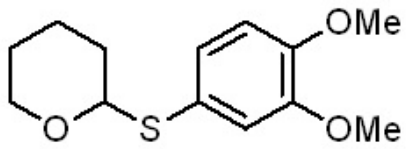
48b (^{1}H NMR, 300MHz, $CDCl_3$)



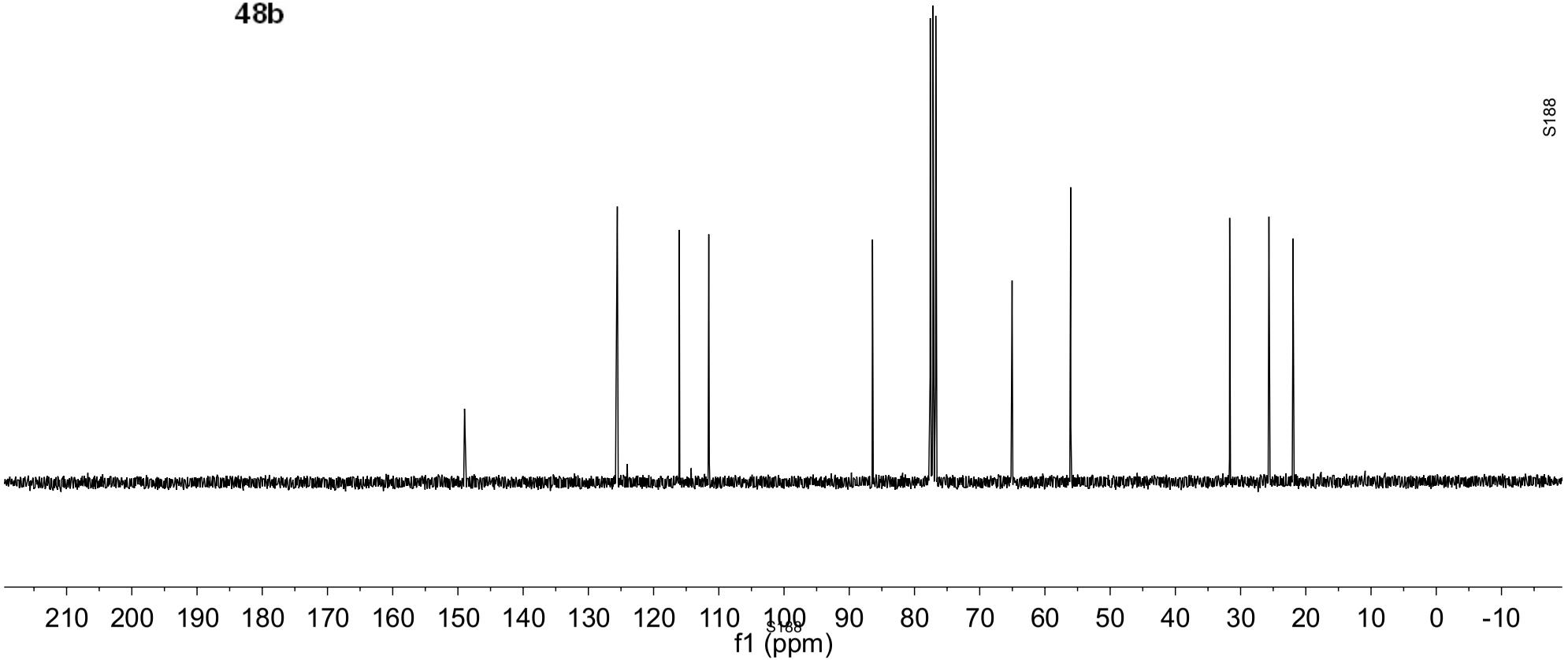
48b



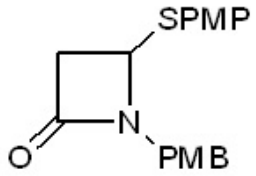
48b (^{13}C NMR, 75MHz, $CDCl_3$)



48b

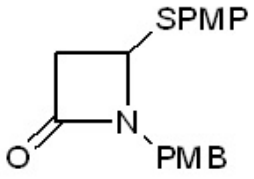


48c (^{1}H NMR, 300MHz, $CDCl_3$)



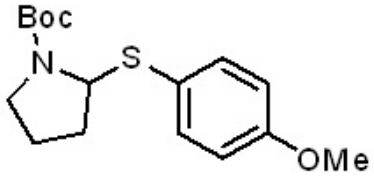
48c

48c (^{13}C NMR, 75MHz, $CDCl_3$)



48c

48d (^{1}H NMR, 300MHz, $CDCl_3$)

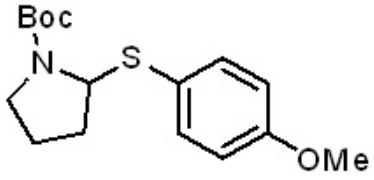


48d

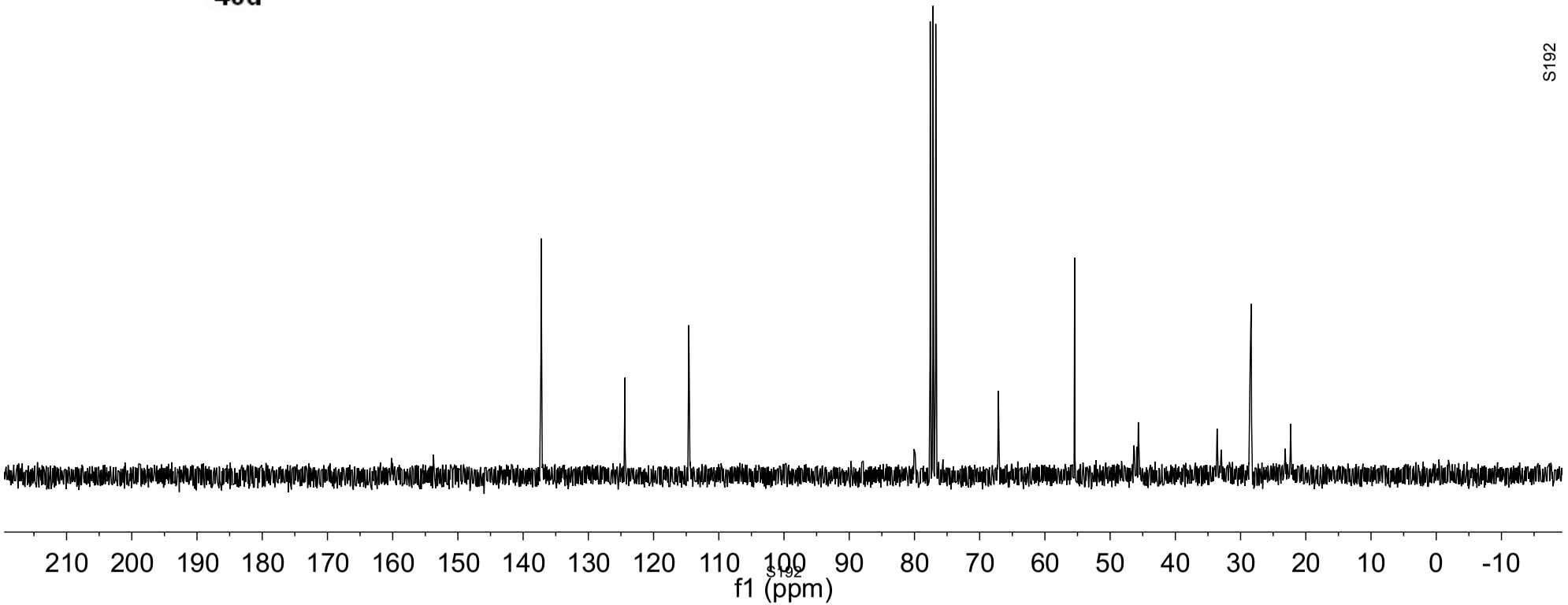
^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 28.4, 33.6, 45.6, 55.4, 67.1, 80.1, 114.6, 124.4, 137.2, 153.7, 199.1.

199.13
153.68
137.24
124.48
114.60
80.06
67.14
55.44
45.59
33.62
28.38
22.28

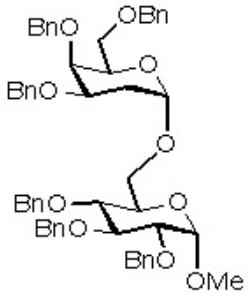
48d (^{13}C NMR, 75MHz, $CDCl_3$)



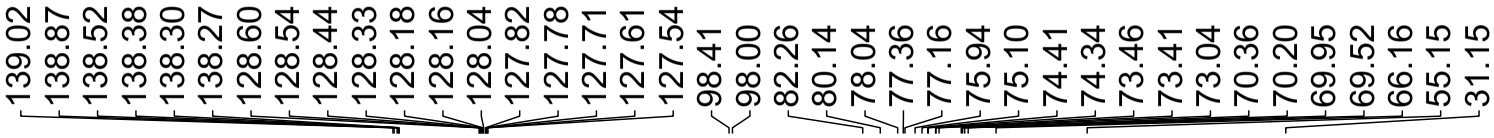
48d



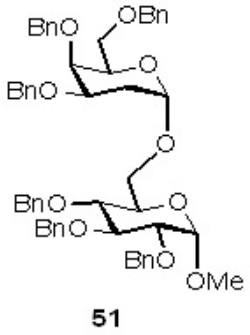
51 (^{1}H NMR, 300MHz, $CDCl_3$)



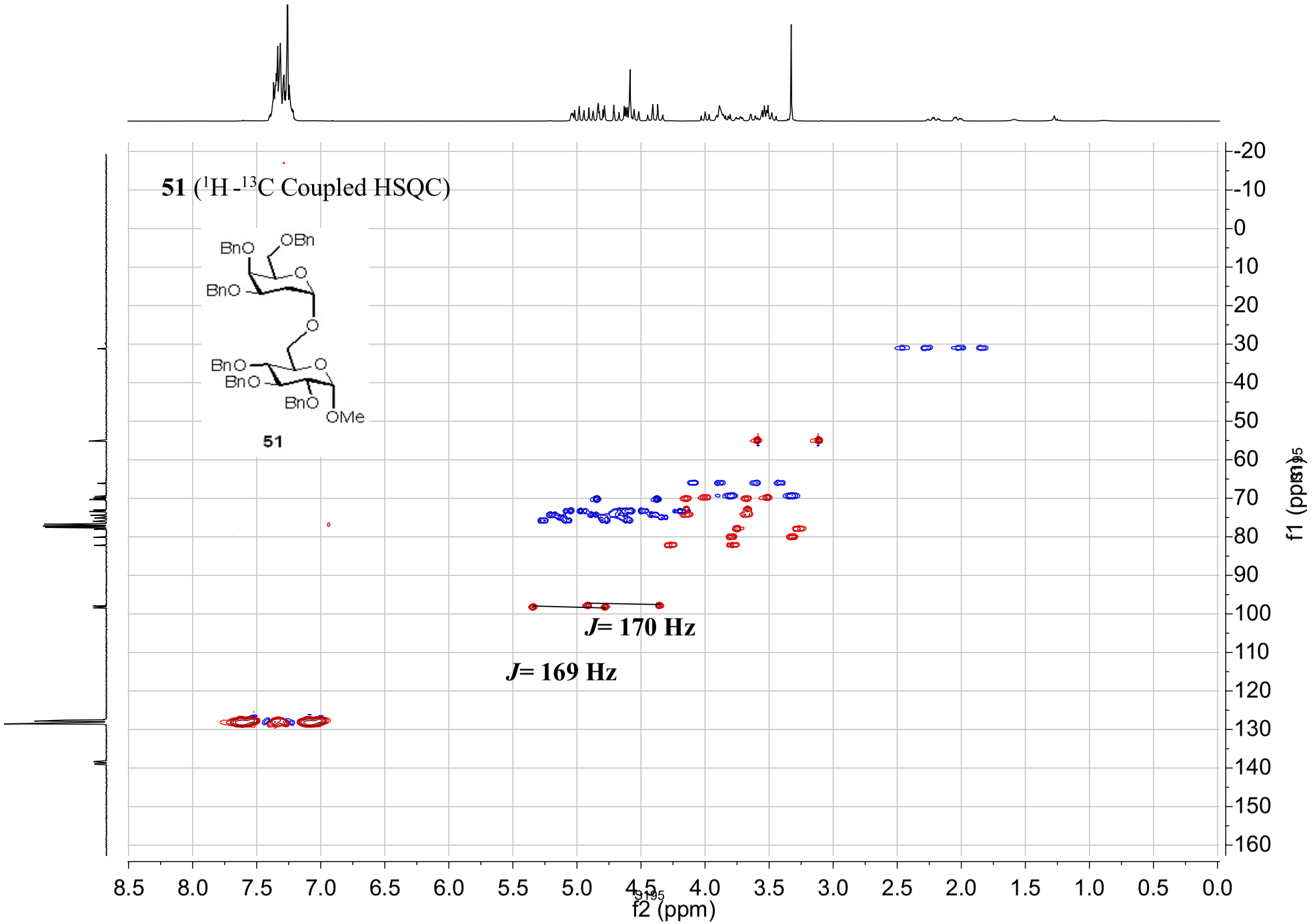
51

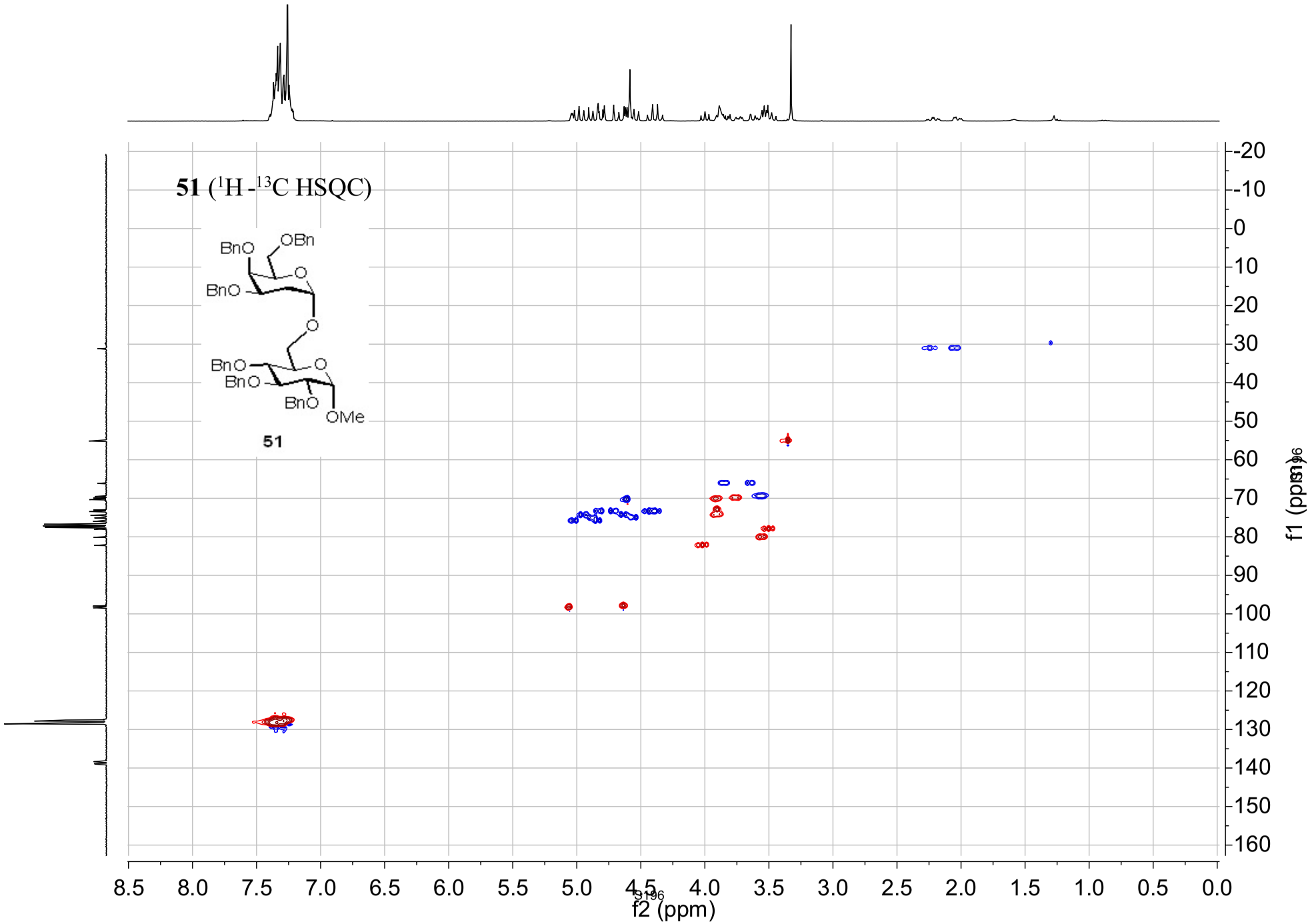


51 (^{13}C NMR, 75MHz, $CDCl_3$)

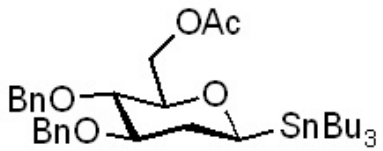


51

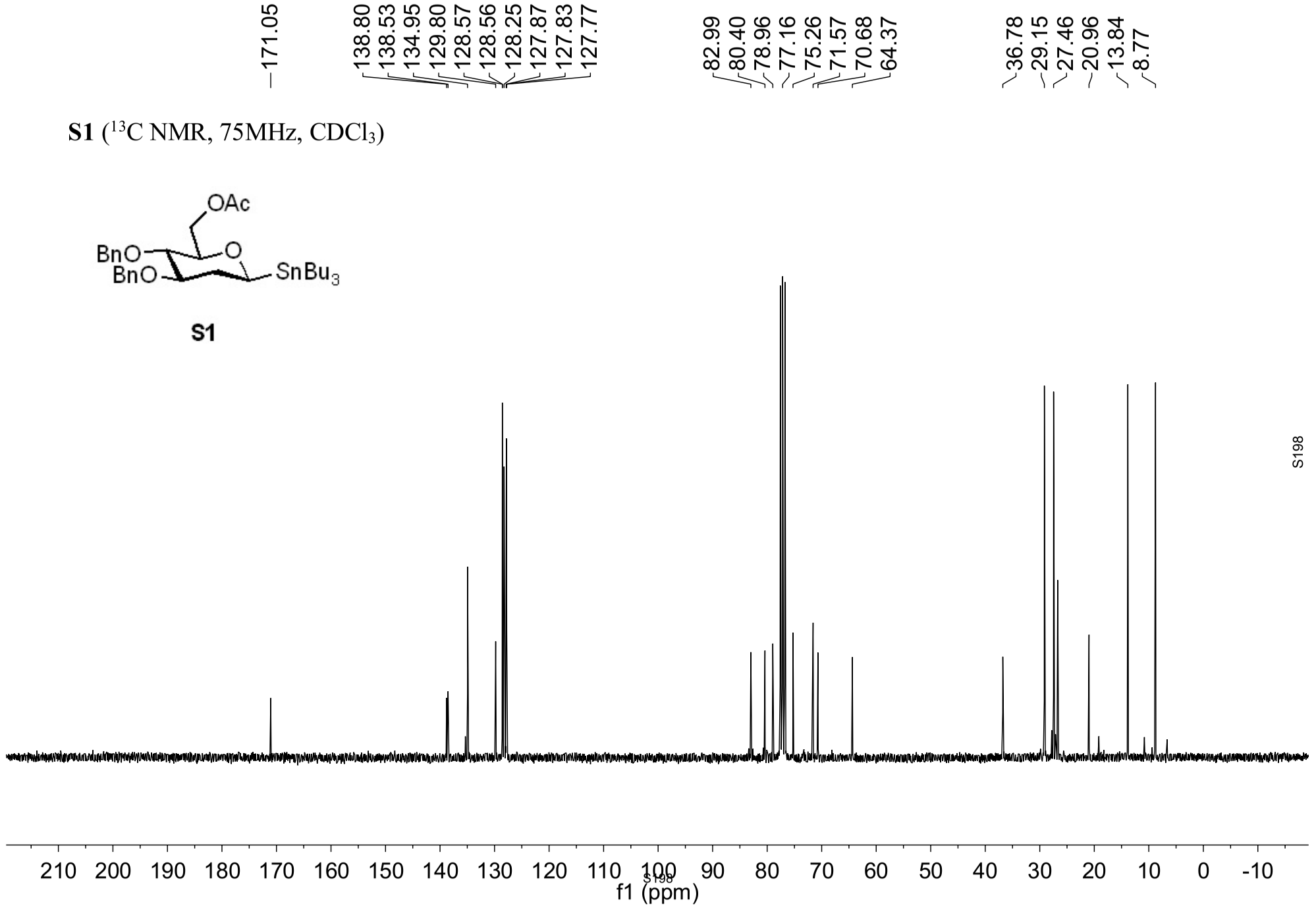

51 (1H -13C Coupled HSQC)
BnO
OBn
BnO
O
O
BnO
O
BnO
BnO
OMe
51
J= 170 Hz
J= 169 Hz
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
f1 (ppm)


51 (1H -13C HSQC)
BnO
OBn
BnO
O
O
BnO
O
BnO
BnO
OMe
51
f2 (ppm)
f1 (ppm)

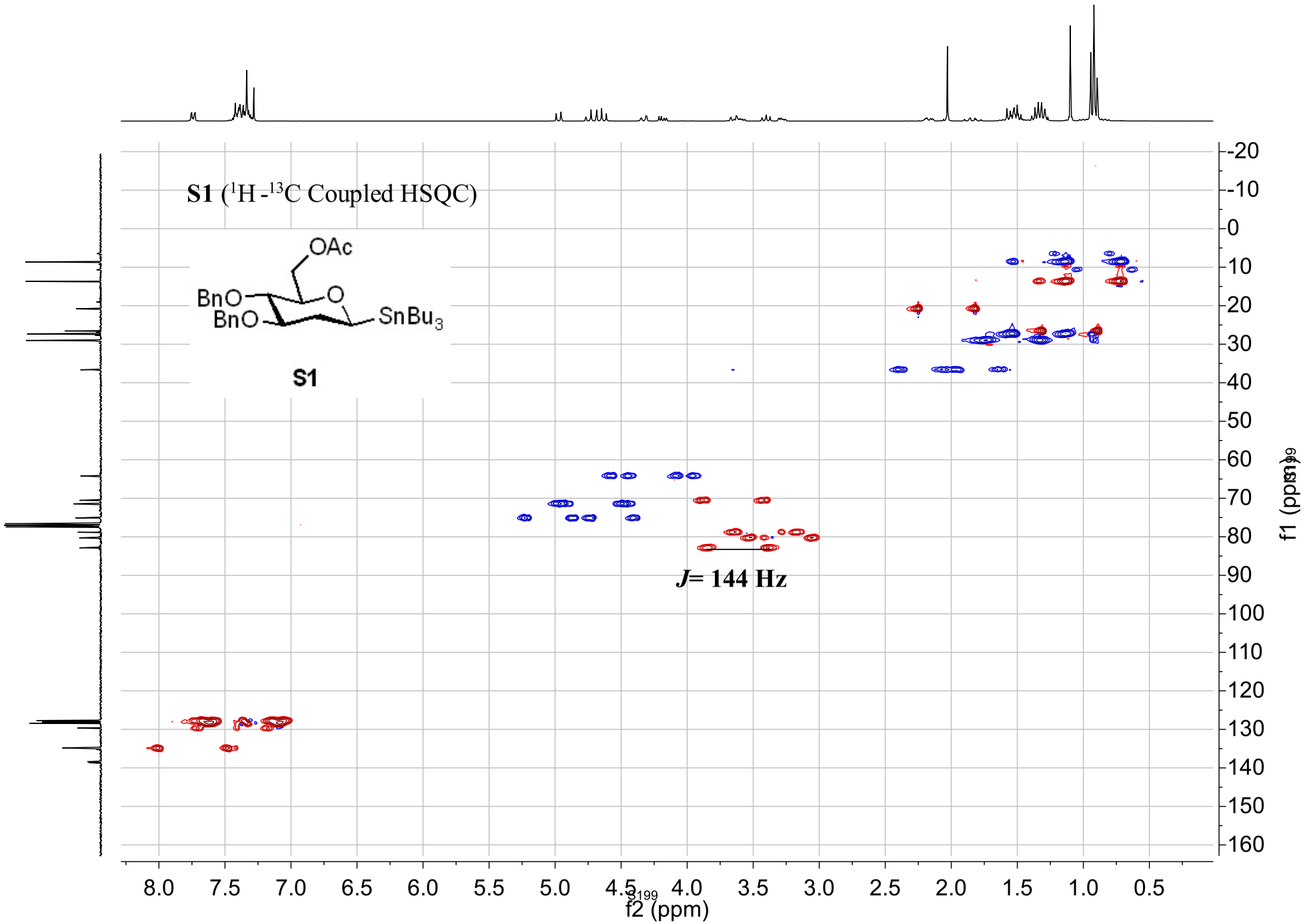
S1 (^{1}H NMR, 300MHz, $CDCl_3$)

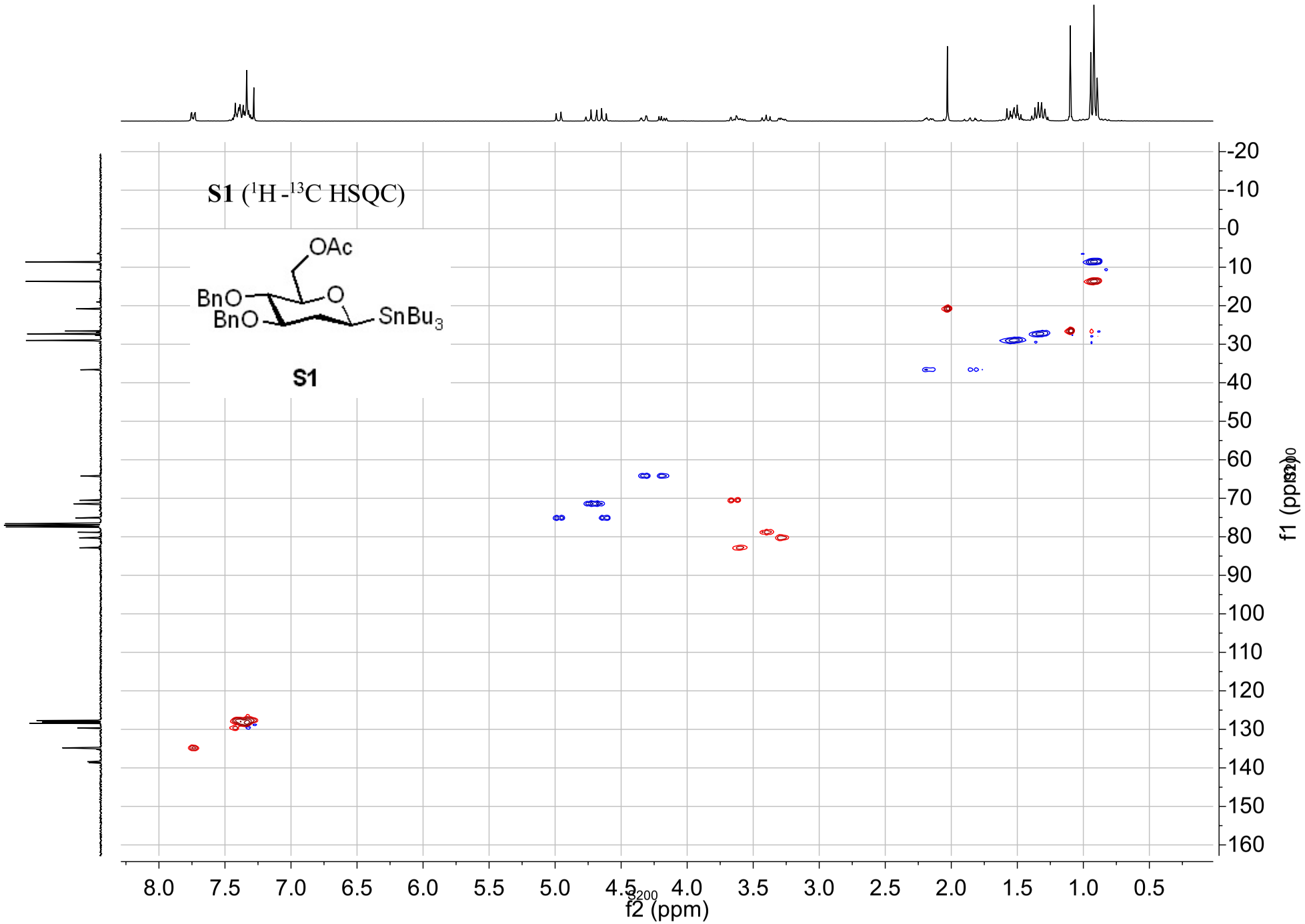


S1

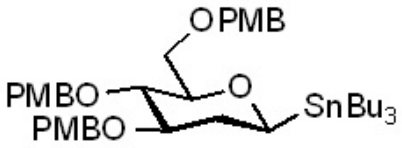


S1 (^{13}C NMR, 75MHz, $CDCl_3$)


S1 (1H -13C Coupled HSQC)
OAc
BnO
BnO
O
SnBu3
S1
J= 144 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

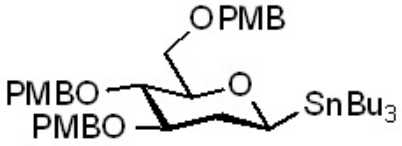

S1 (1H -13C HSQC)
OAc
BnO
BnO
O
SnBu3
S1
f2 (ppm)
f1 (ppm)

S2 (^{1}H NMR, 300MHz, $CDCl_3$)

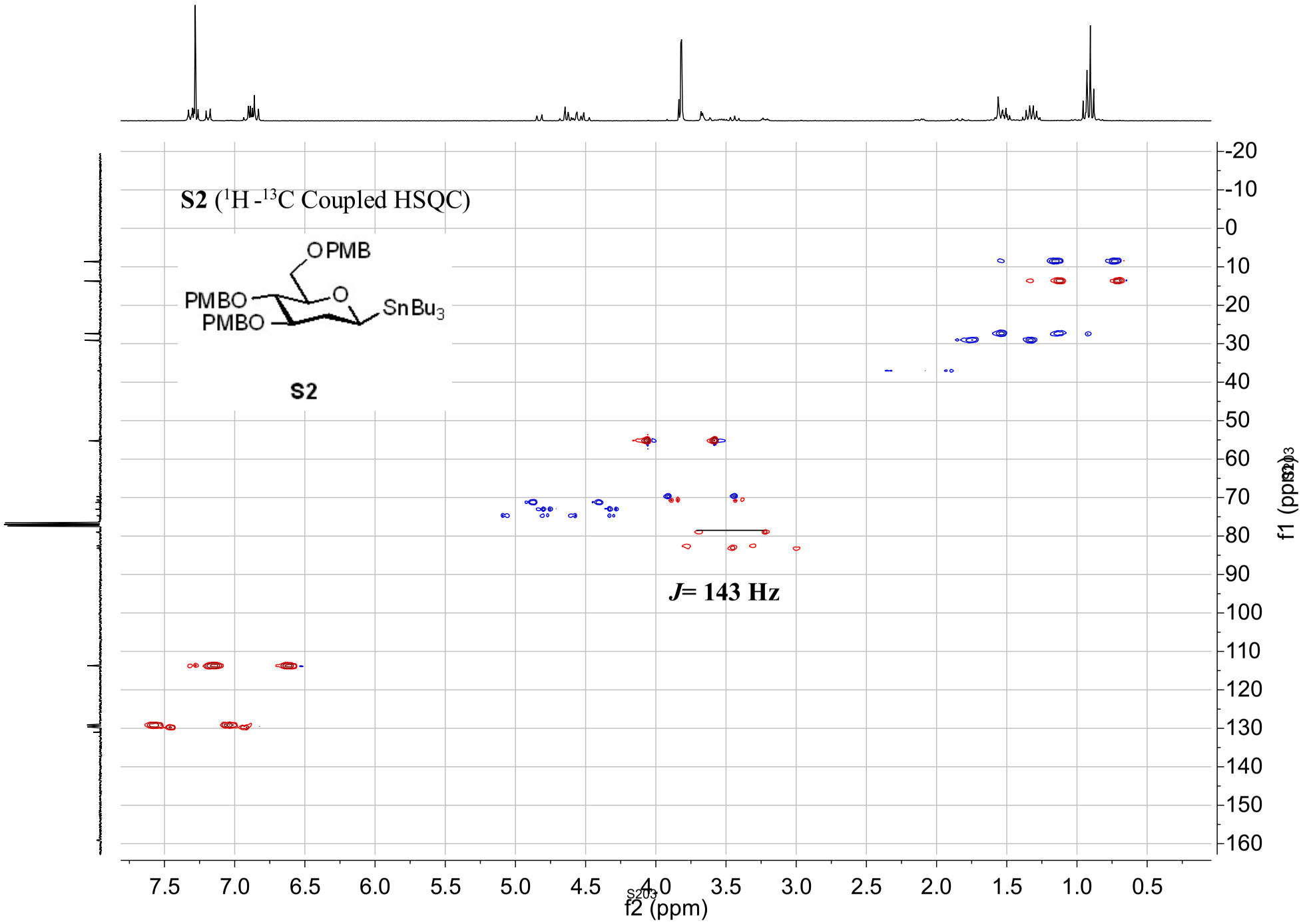


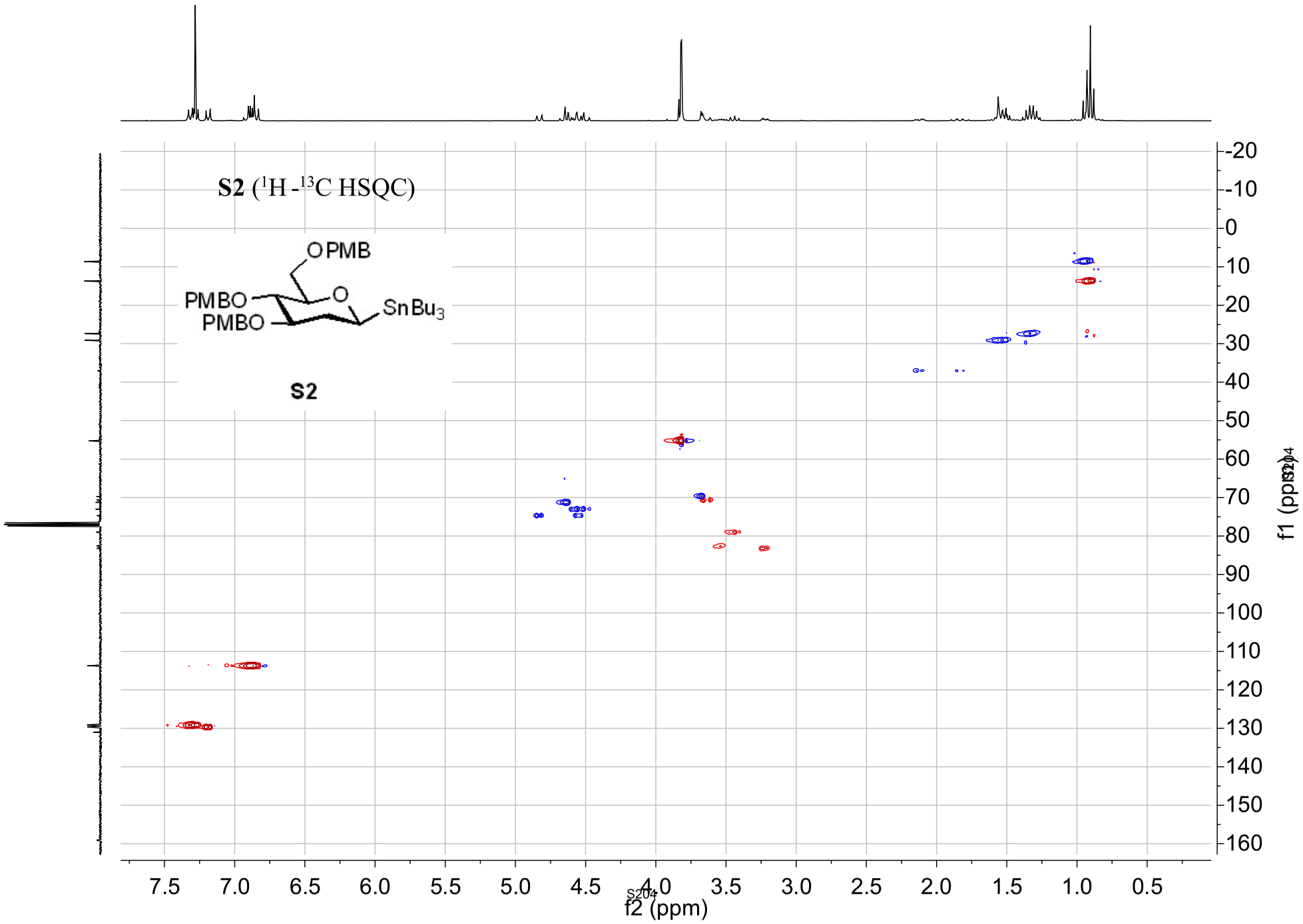
S2

S2 (^{13}C NMR, 75MHz, $CDCl_3$)

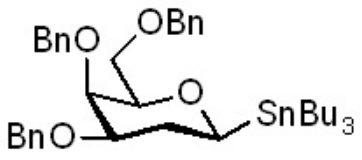


S2


S2 (1H -13C Coupled HSQC)
OPMB
PMBO
O
SnBu3
PMBO
S2
J= 143 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

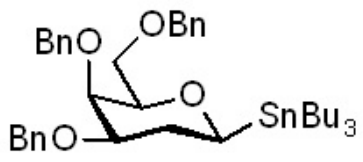

S2 (1H -13C HSQC)
OPMB
PMBO
O
SnBu3
PMBO
S2
f2 (ppm)
f1 (ppm)
S204

S3 (^{1}H NMR, 300MHz, $CDCl_3$)

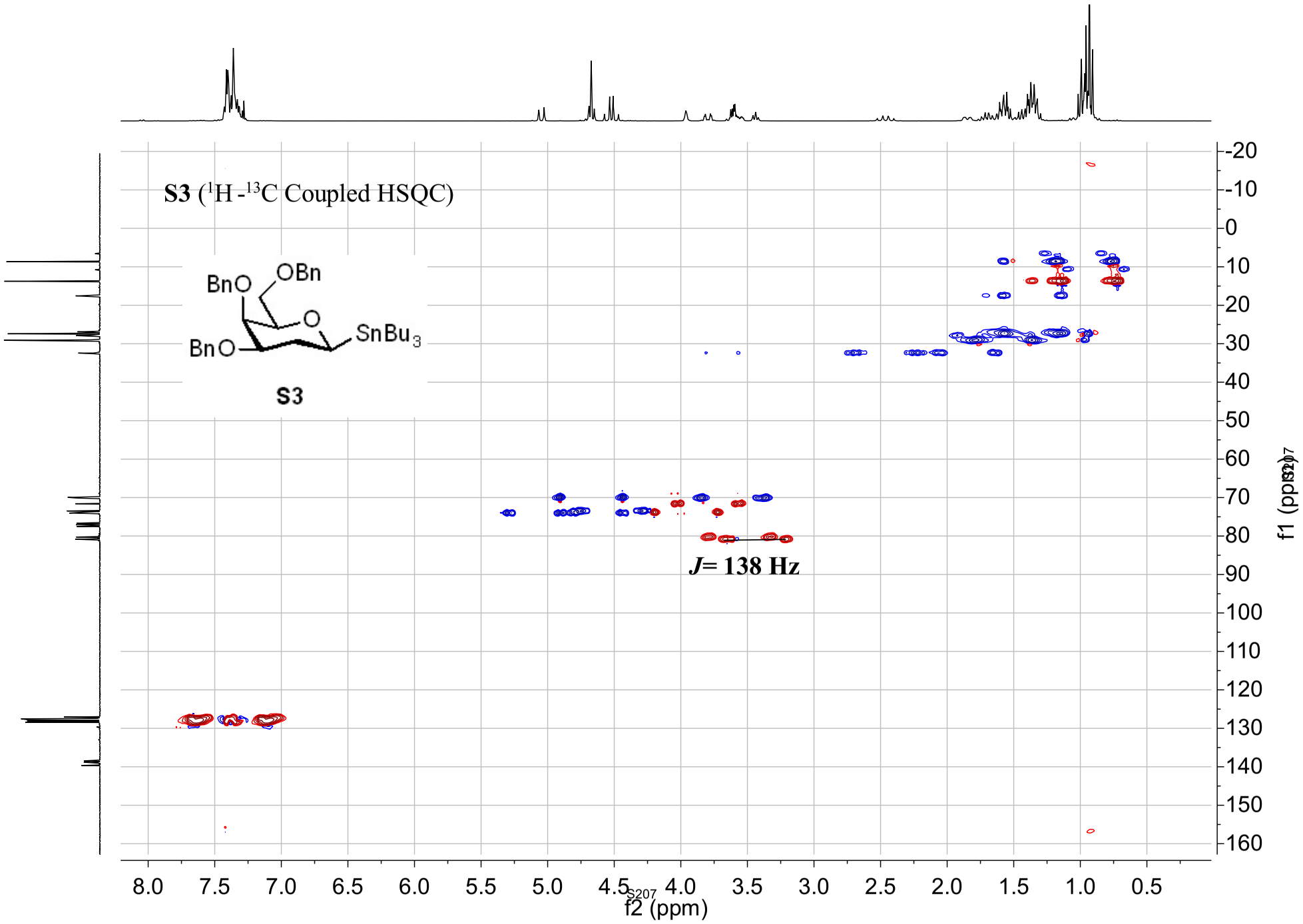


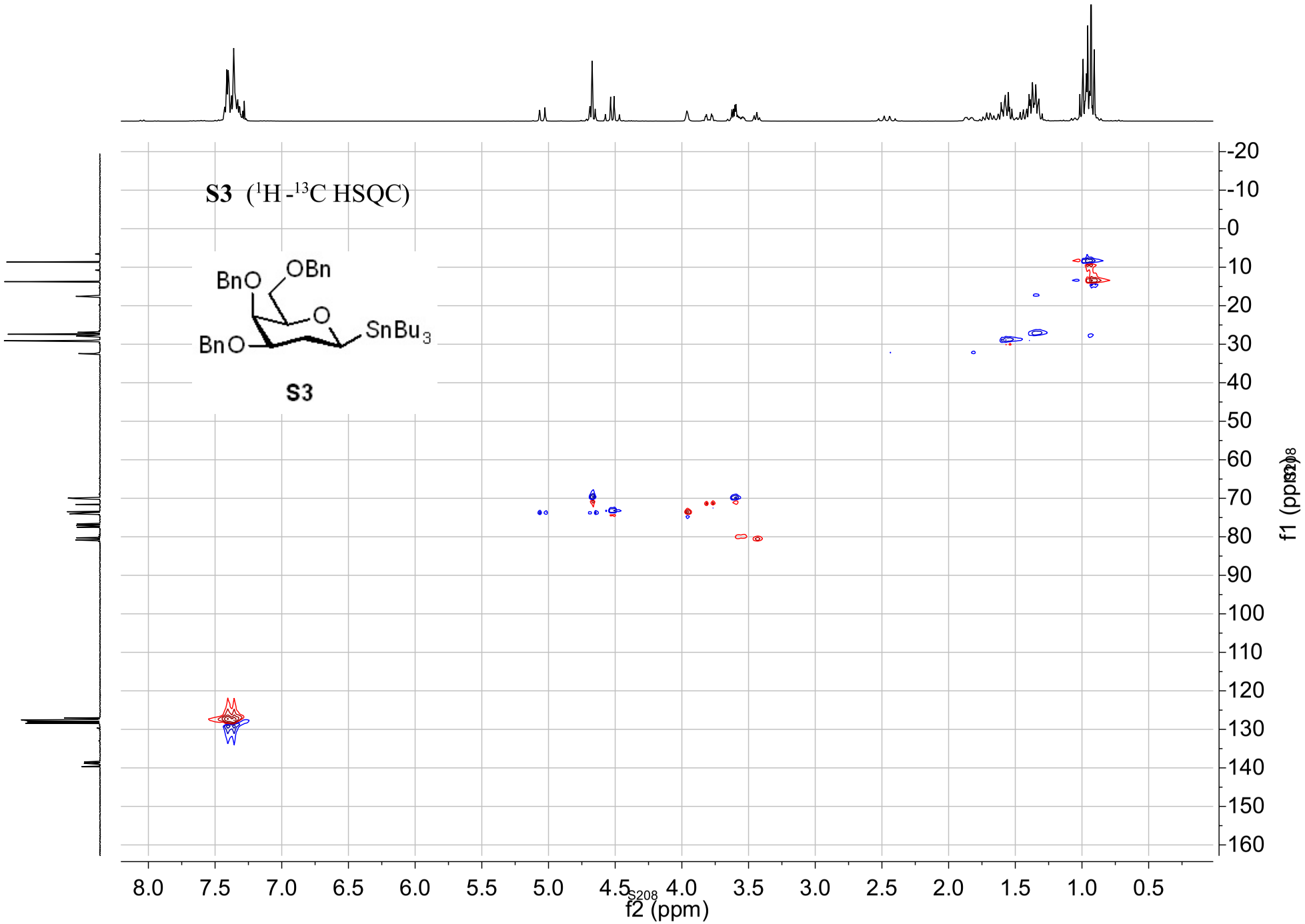
S3

S3 (^{13}C NMR, 75MHz, $CDCl_3$)

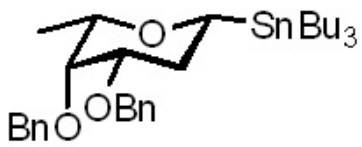


S3


S3 (1H -13C Coupled HSQC)
BnO
OBn
O
SnBu3
BnO
S3
J= 138 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

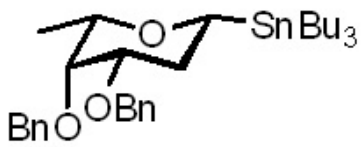

S3 (1H -13C HSQC)
BnO
OBn
O
SnBu3
BnO
S3
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

S4 (^{1}H NMR, 300MHz, $CDCl_3$)

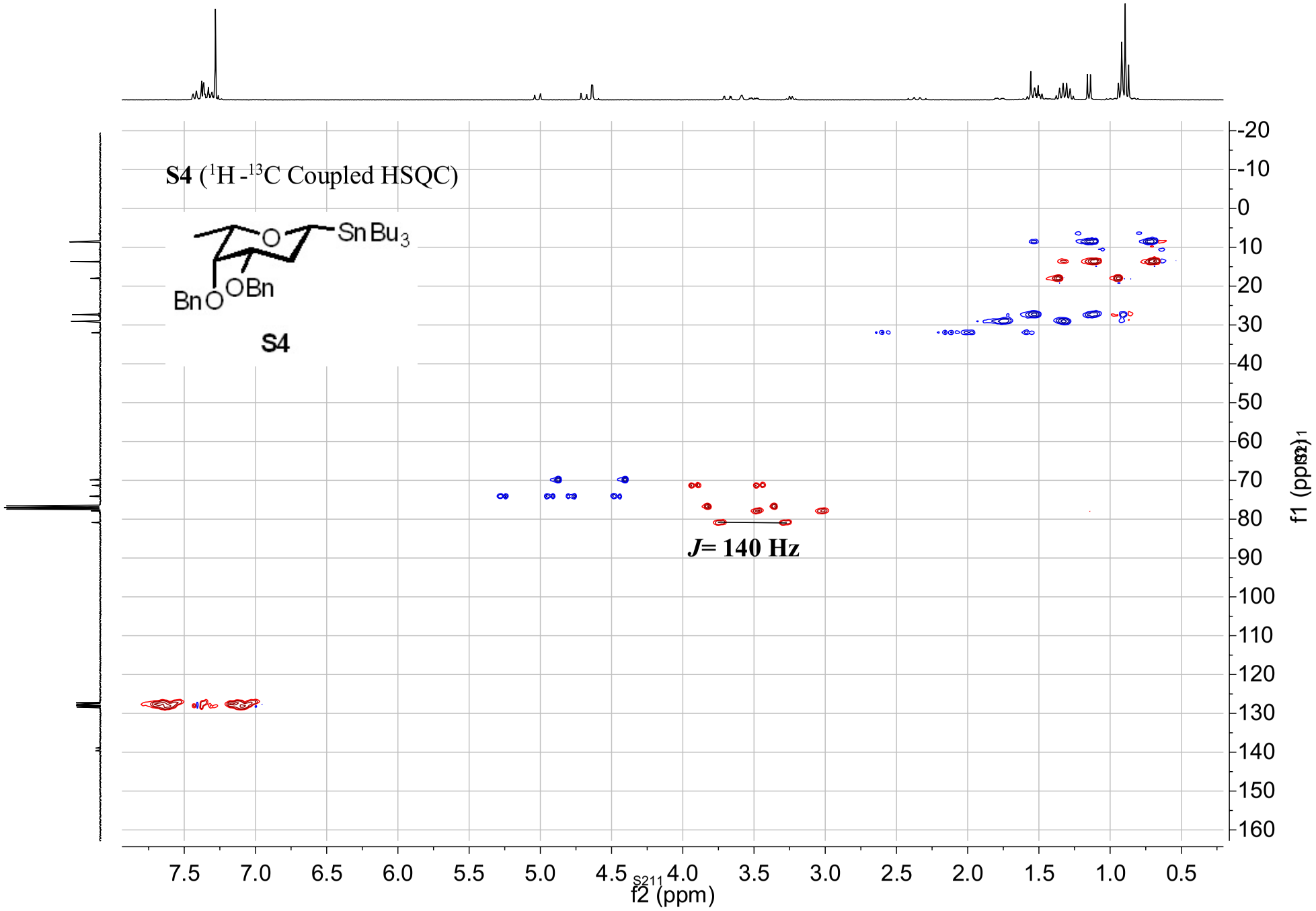


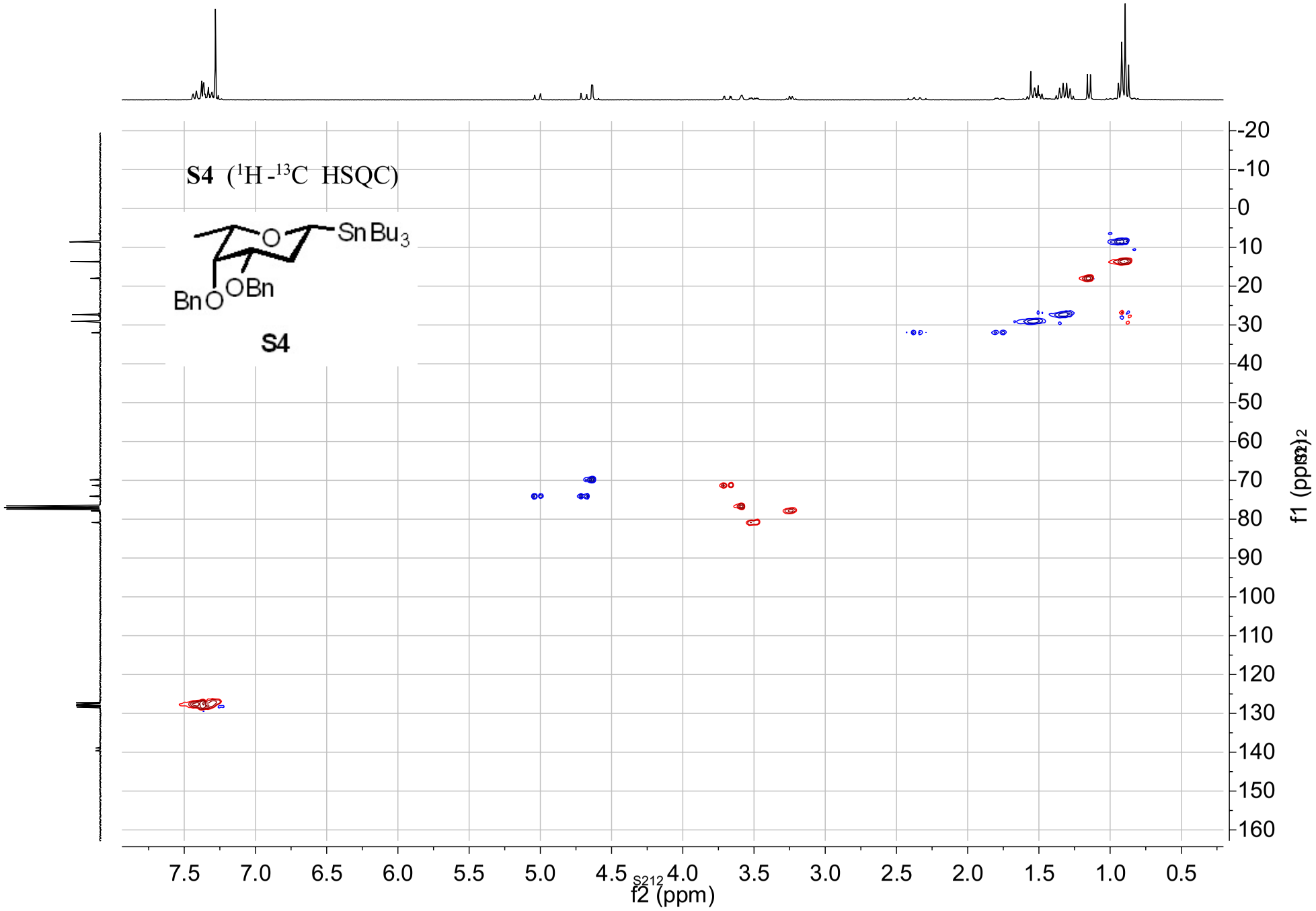
S4

S4 (^{13}C NMR, 75MHz, $CDCl_3$)

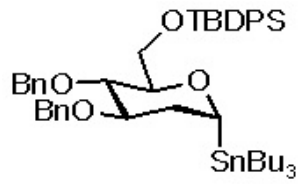


S4


S4 (1H -13C Coupled HSQC)
Sn Bu3
O
Bn O OBn
S4
J= 140 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

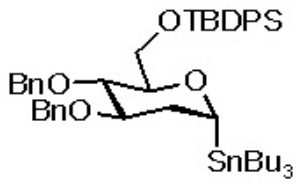

S4 (1H -13C HSQC)
Sn Bu3
O
Bn O OBn
S4
f2 (ppm)
f1 (ppm)

S5 (^{1}H NMR, 300MHz, $CDCl_3$)

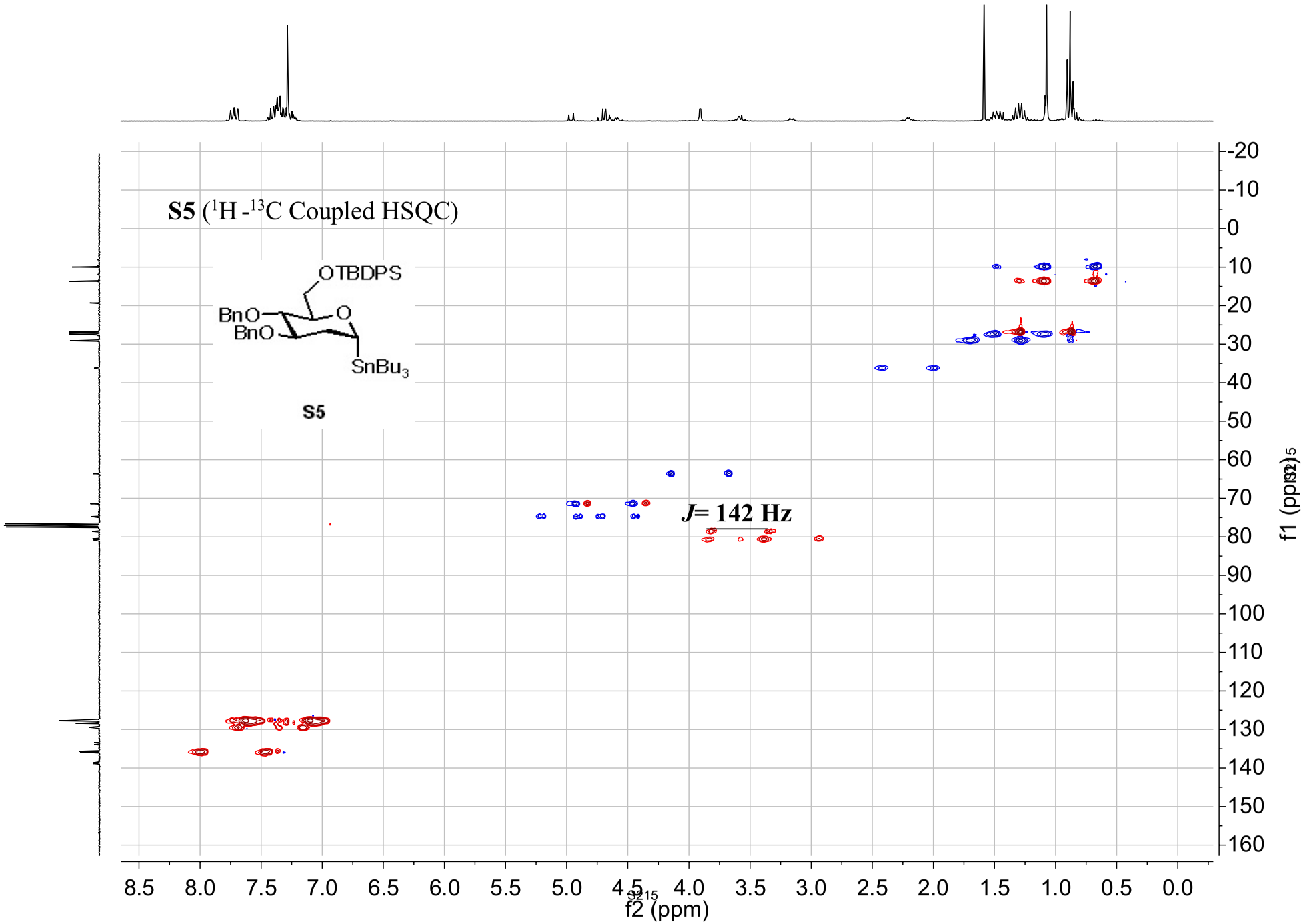


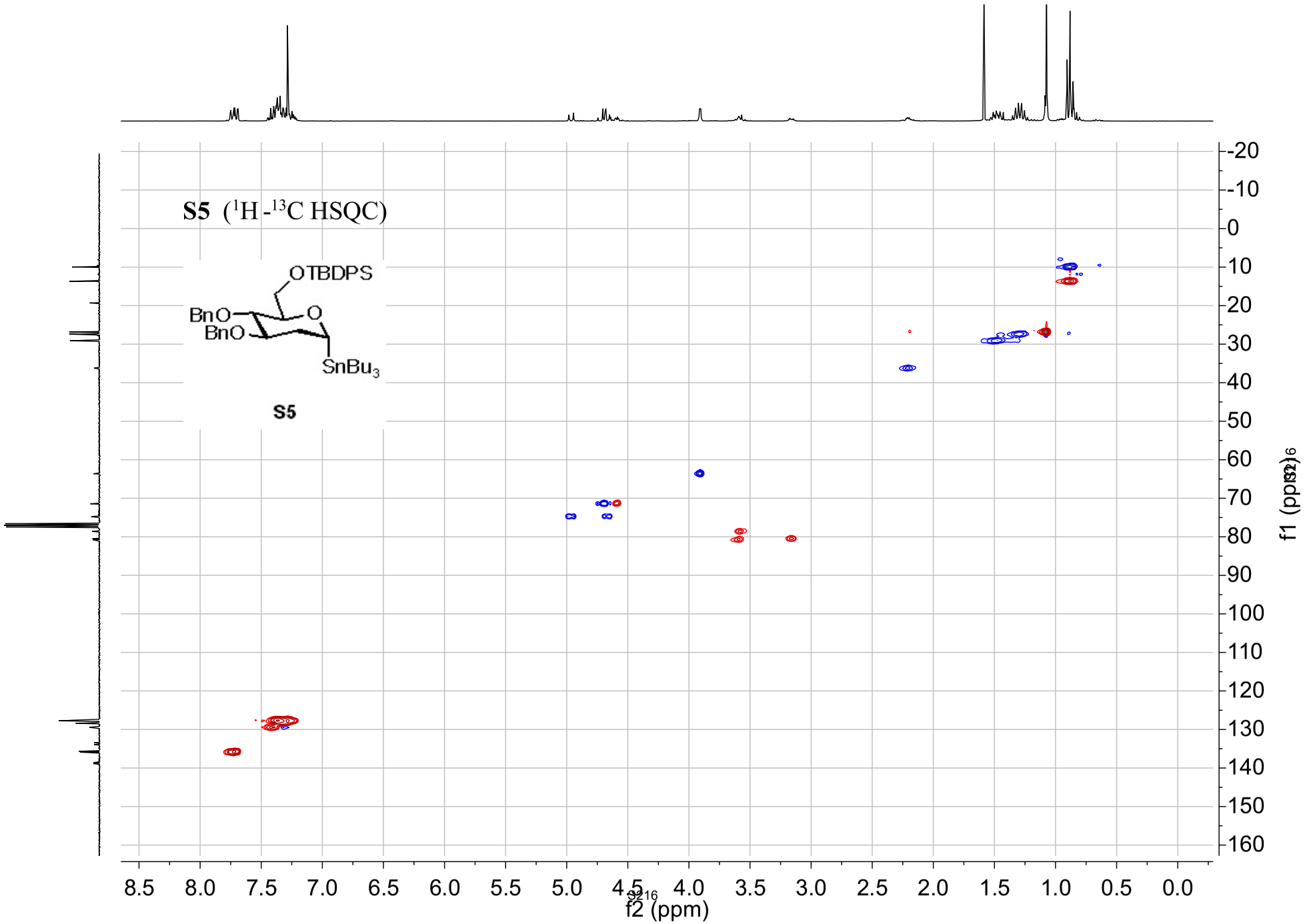
S5

S5 (^{13}C NMR, 75MHz, $CDCl_3$)

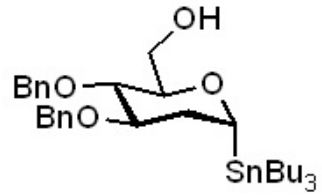


S5


S5 (1H -13C Coupled HSQC)
OTBDPS
BnO
BnO
O
SnBu3
S5
J= 142 Hz
f2 (ppm)
f1 (ppm)

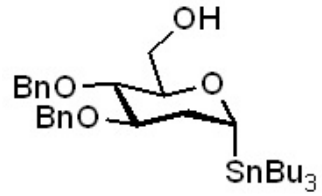

S5 (1H-13C HSQC)
OTBDPS
BnO
BnO
O
SnBu3
S5
f2 (ppm)
f1 (ppm)

S6 (^{1}H NMR, 300MHz, $CDCl_3$)

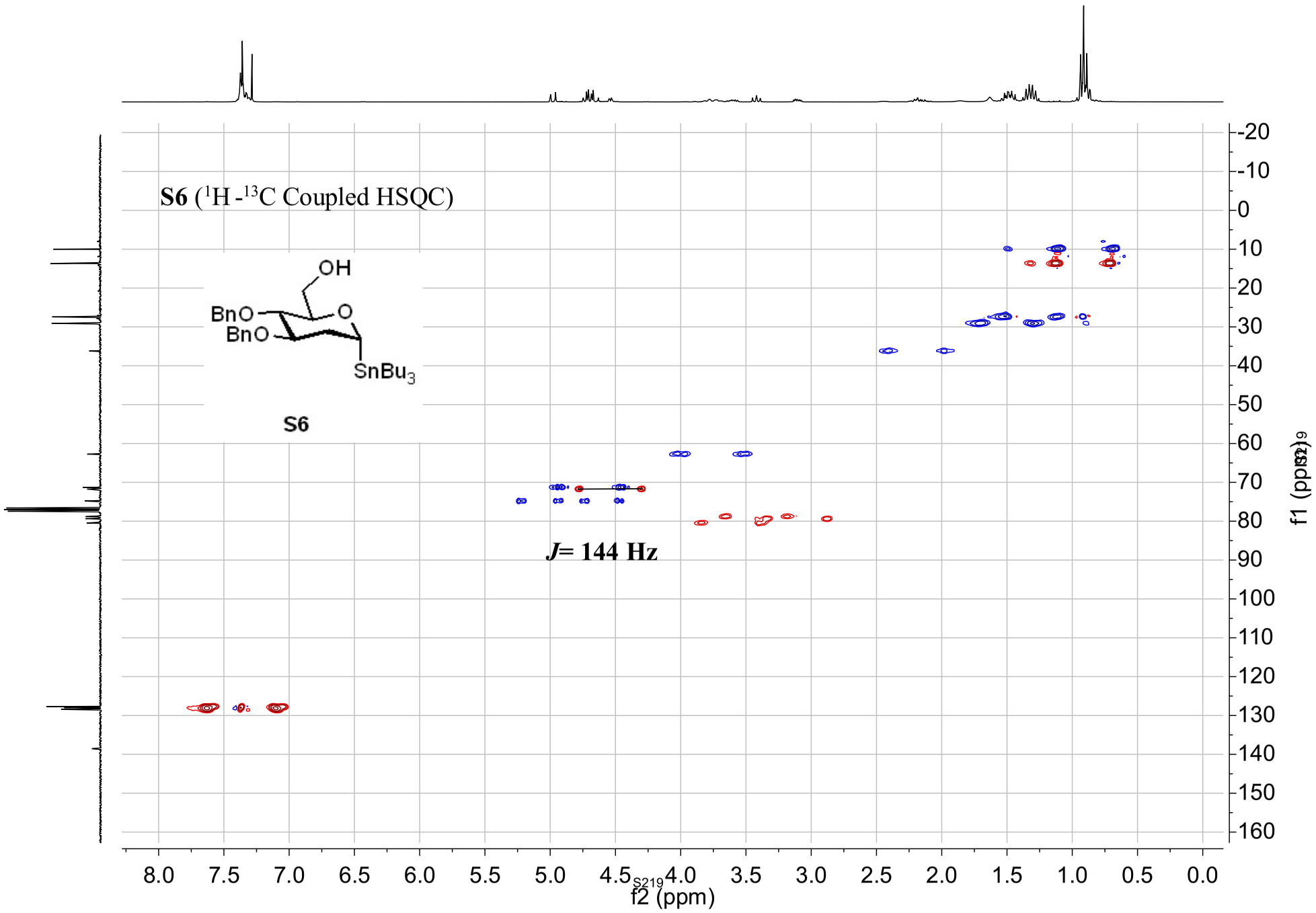


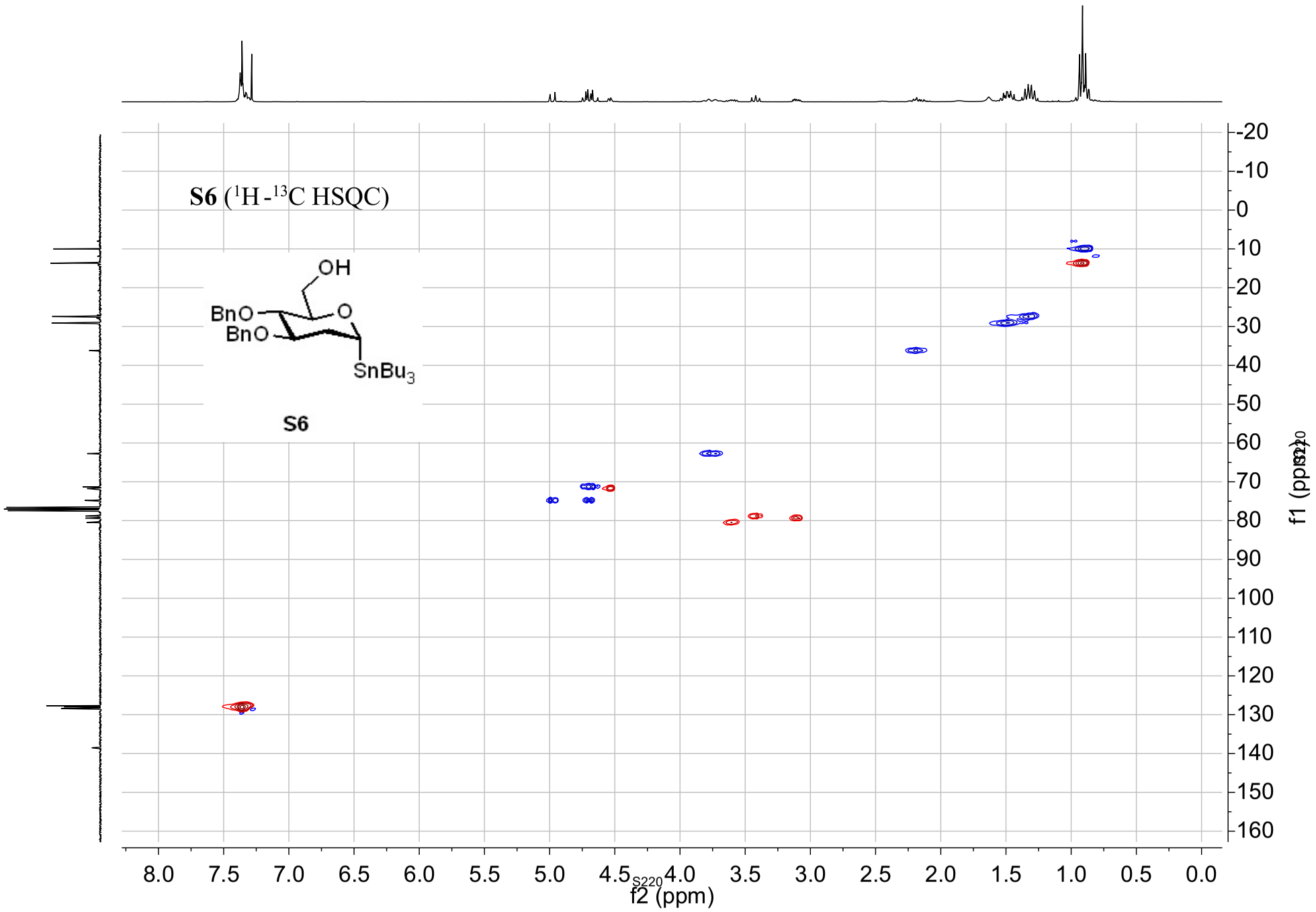
S6

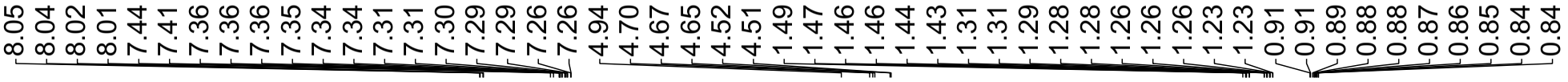
S6 (^{13}C NMR, 75MHz, $CDCl_3$)



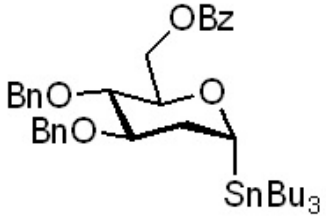
S6


S6 (1H -13C Coupled HSQC)
OH
BnO
BnO
O
SnBu3
S6
J= 144 Hz
f2 (ppm)
f1 (ppm)

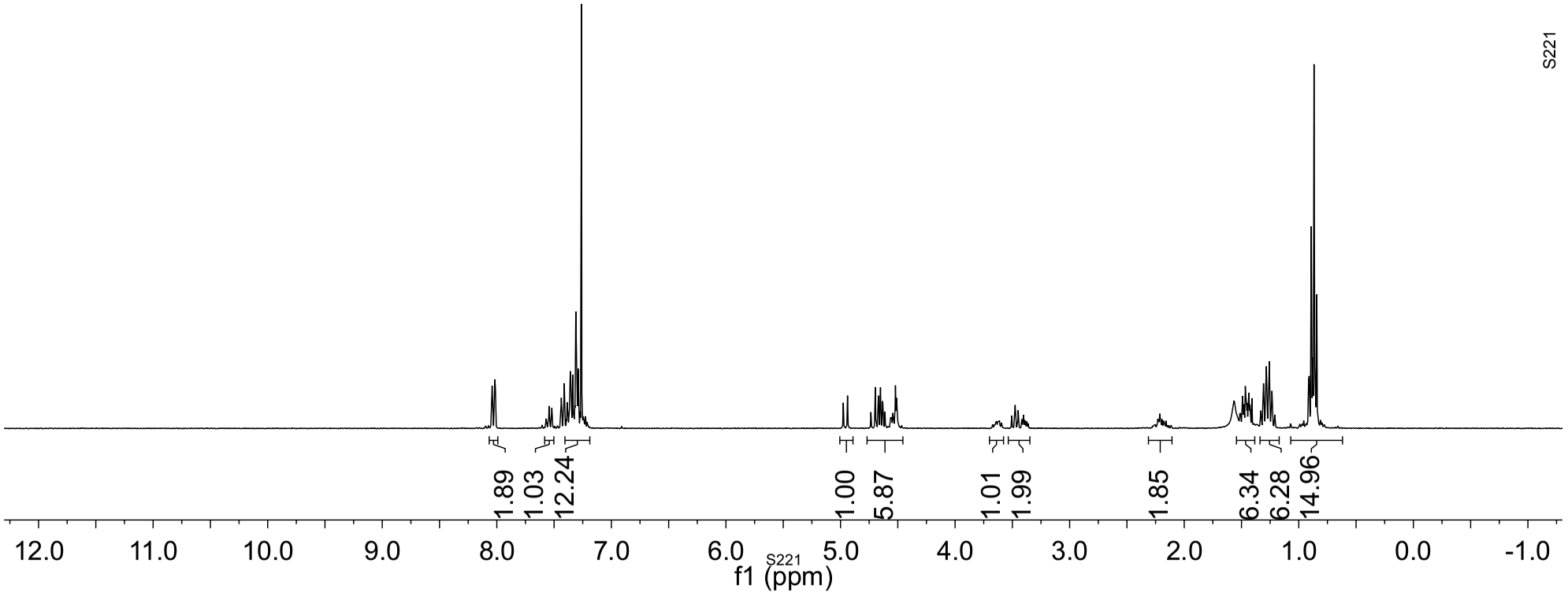

S6 (1H-13C HSQC)
OH
BnO
BnO
O
SnBu3
S6
f2 (ppm)
f1 (ppm)



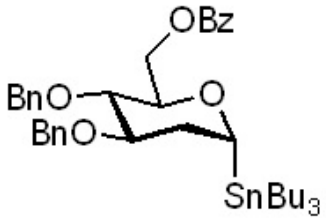
S7 (^{1}H NMR, 300MHz, $CDCl_3$)



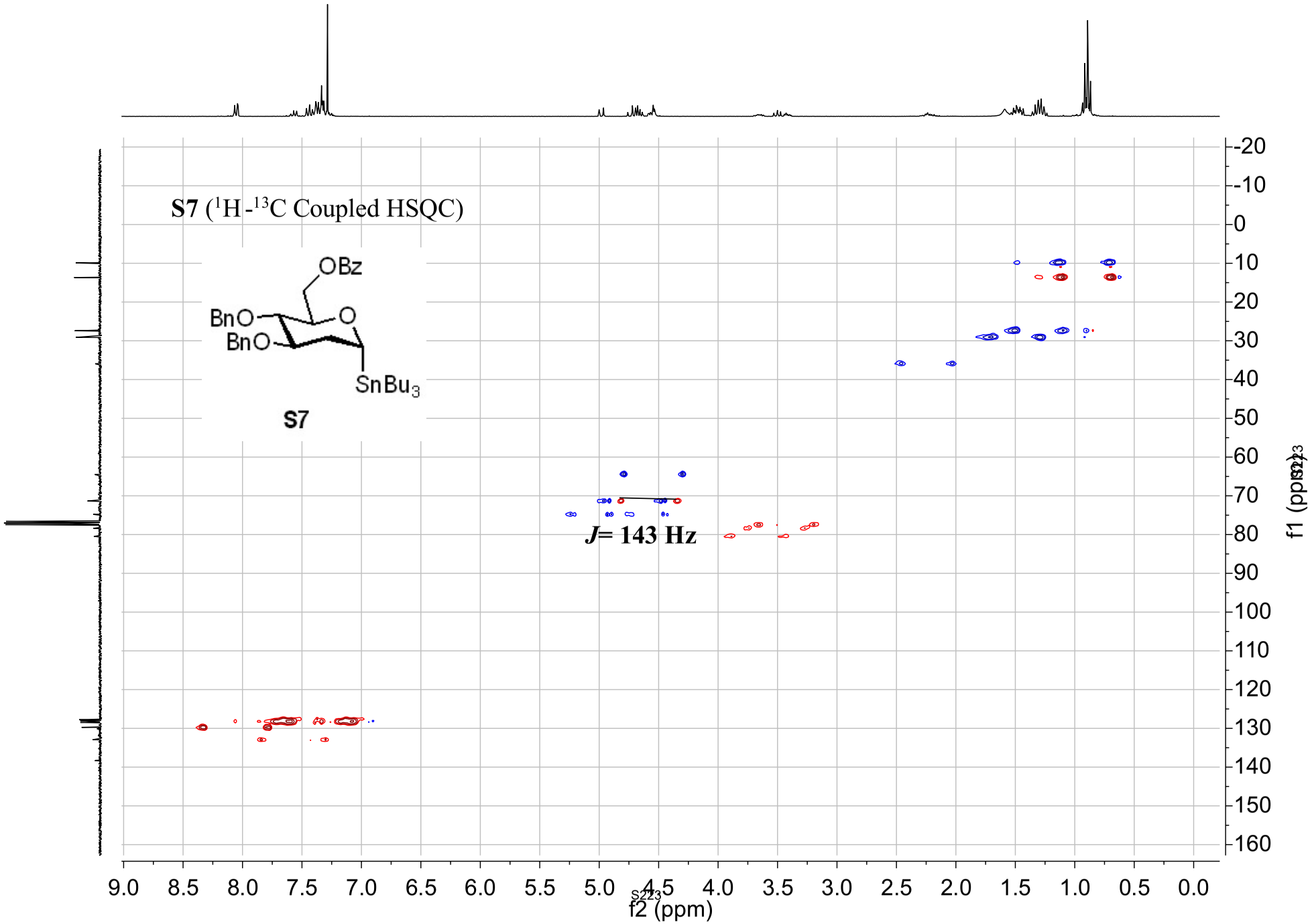
S7

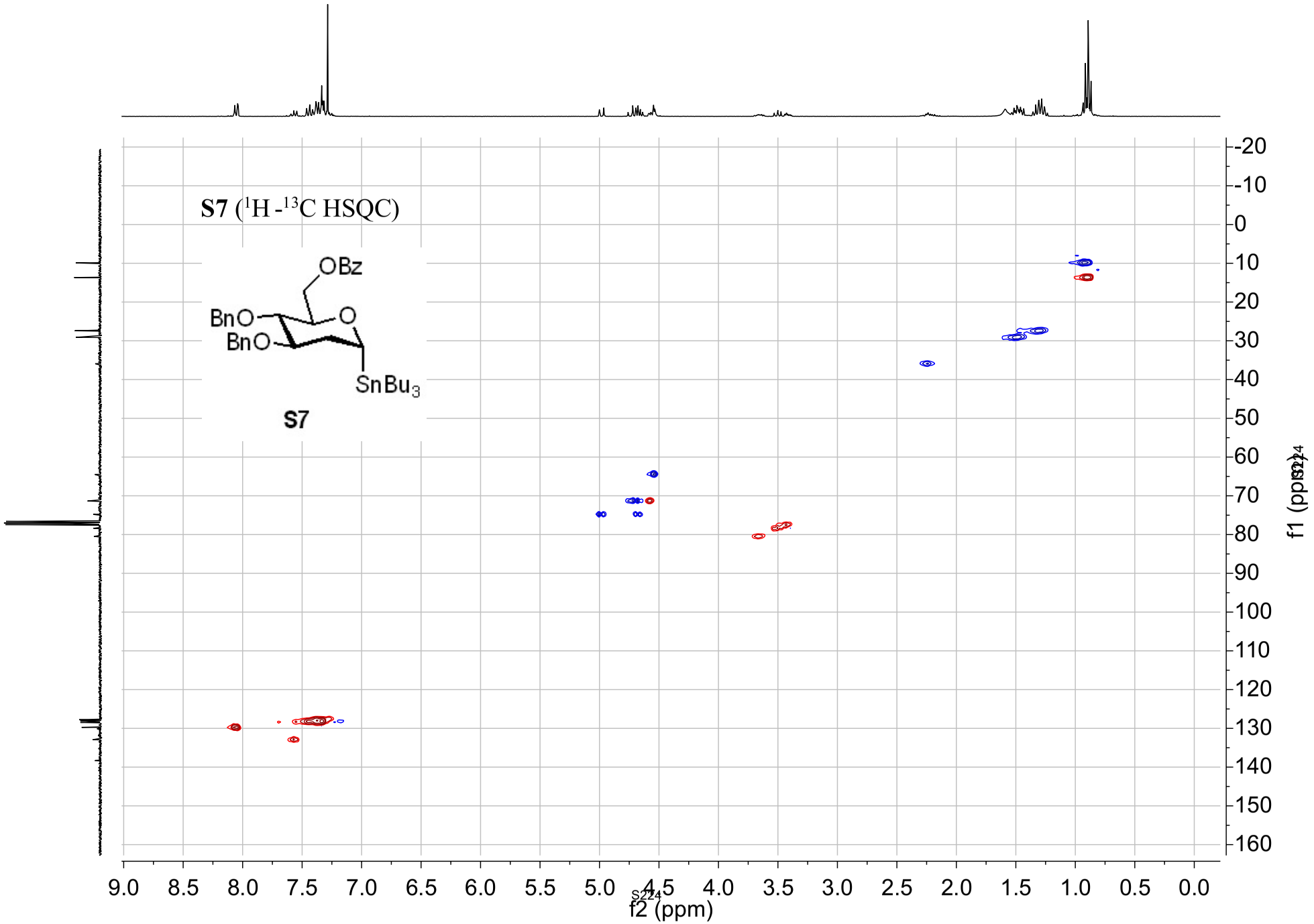


S7 (^{13}C NMR, 75MHz, $CDCl_3$)

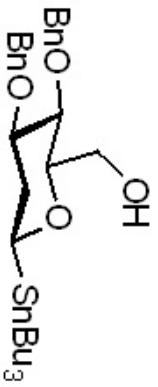


S7

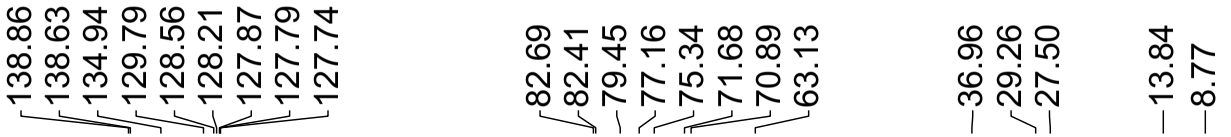

S7 (1H-13C Coupled HSQC)
OBz
BnO
BnO
O
SnBu3
S7
J= 143 Hz
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160


S7 (^{1}H -^{13}C HSQC)
OBz
BnO
BnO
O
SnBu$_3$
S7
f2 (ppm)
f1 (ppm)
S224

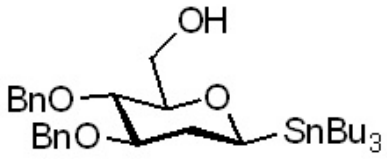
S8 (^{1}H NMR, 300MHz, $CDCl_3$)



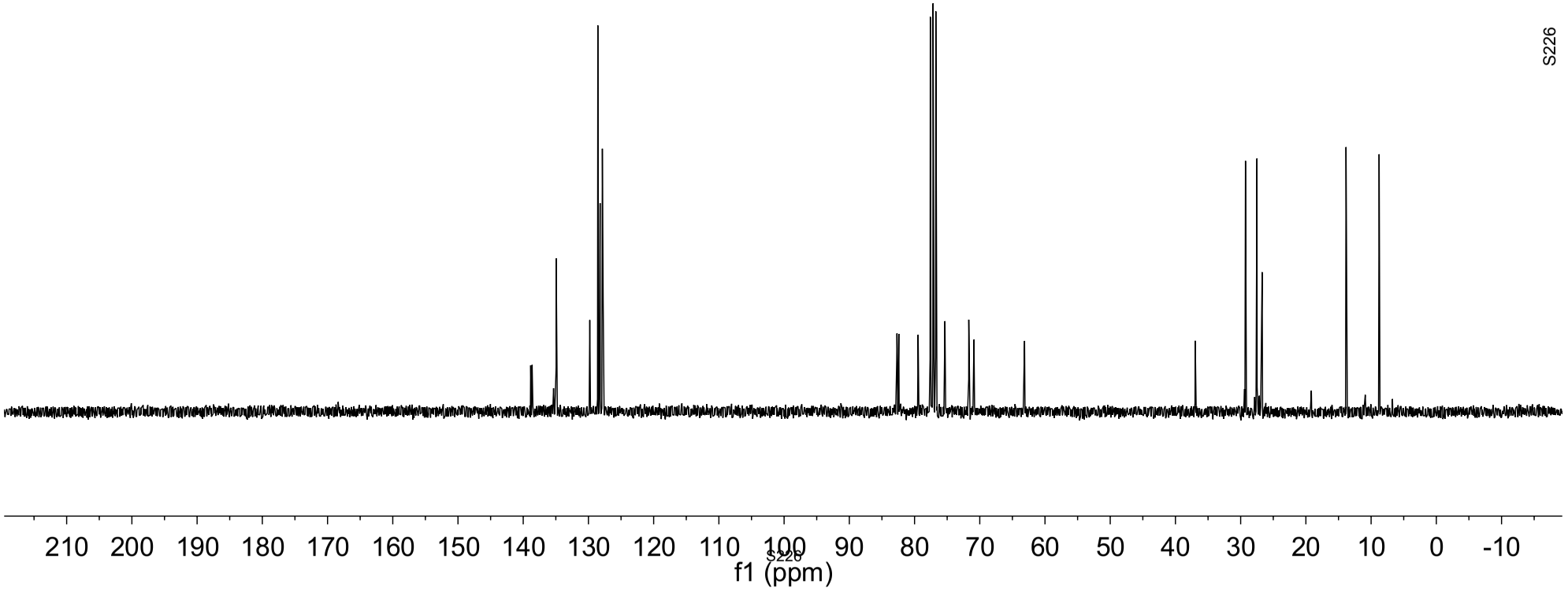
S8

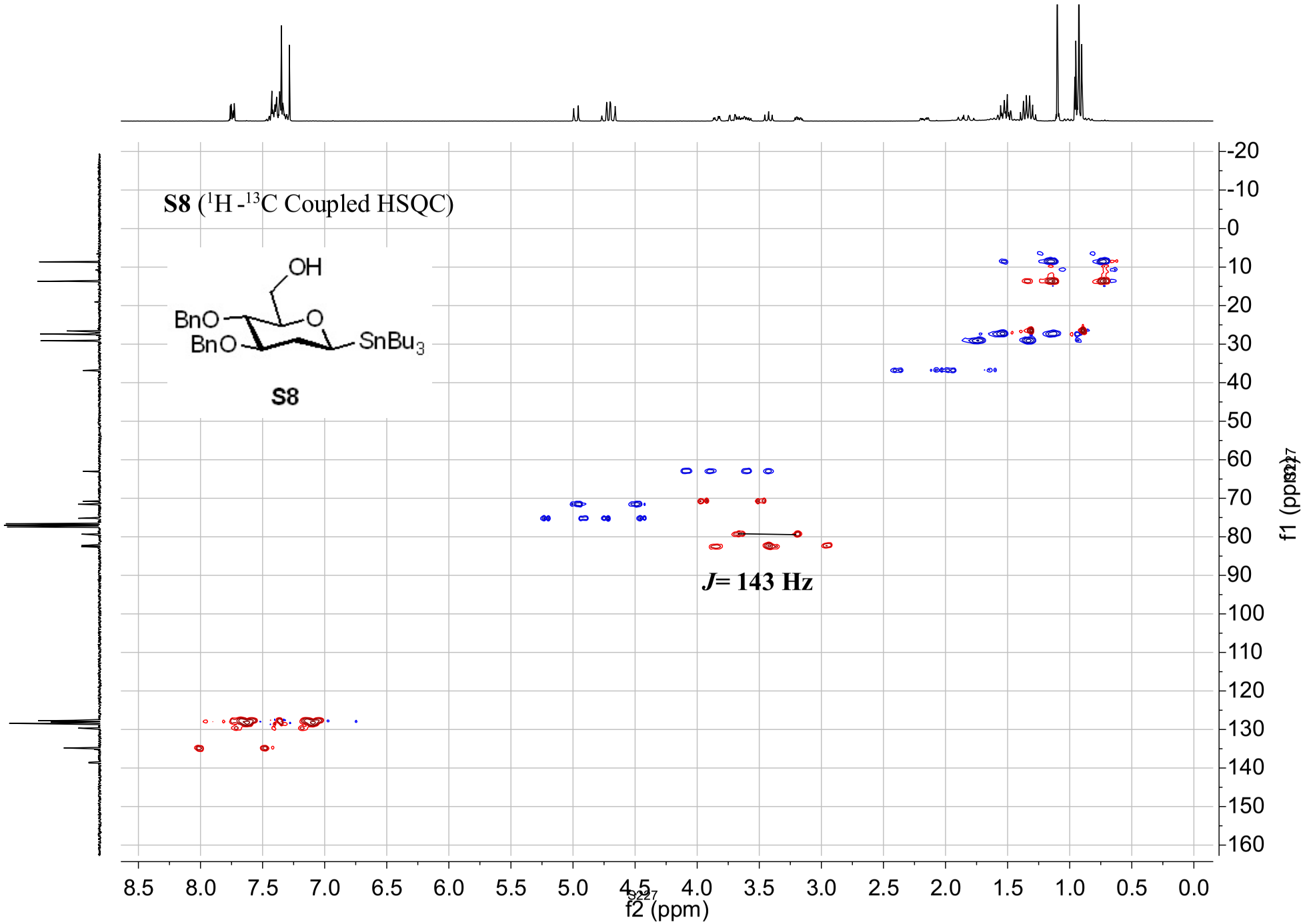


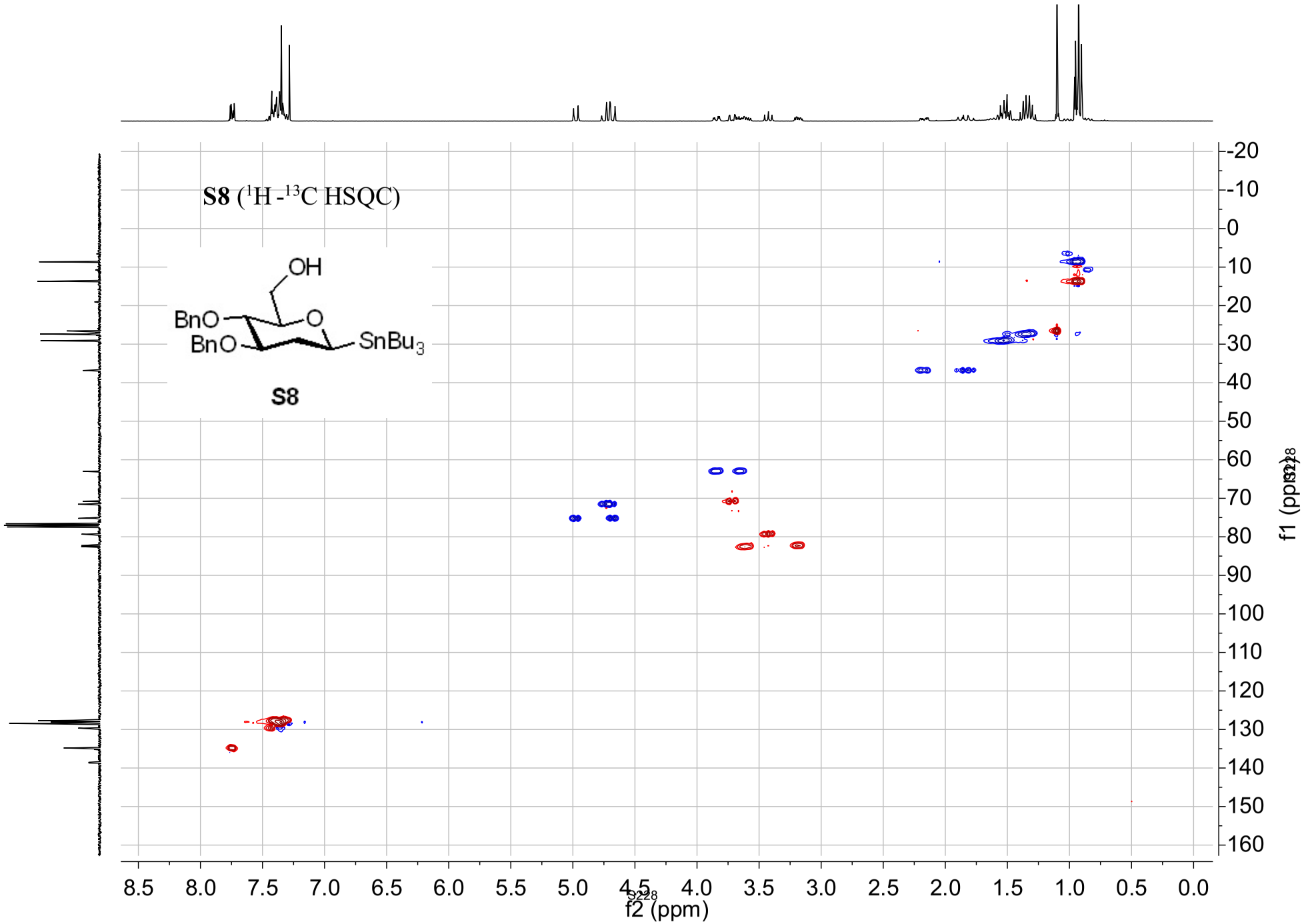
S8 (^{13}C NMR, 75MHz, $CDCl_3$)

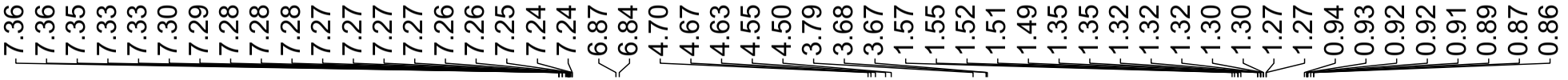


S8

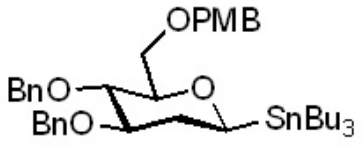



S8 (1H -13C Coupled HSQC)
OH
BnO
O
BnO
SnBu3
S8
J= 143 Hz
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

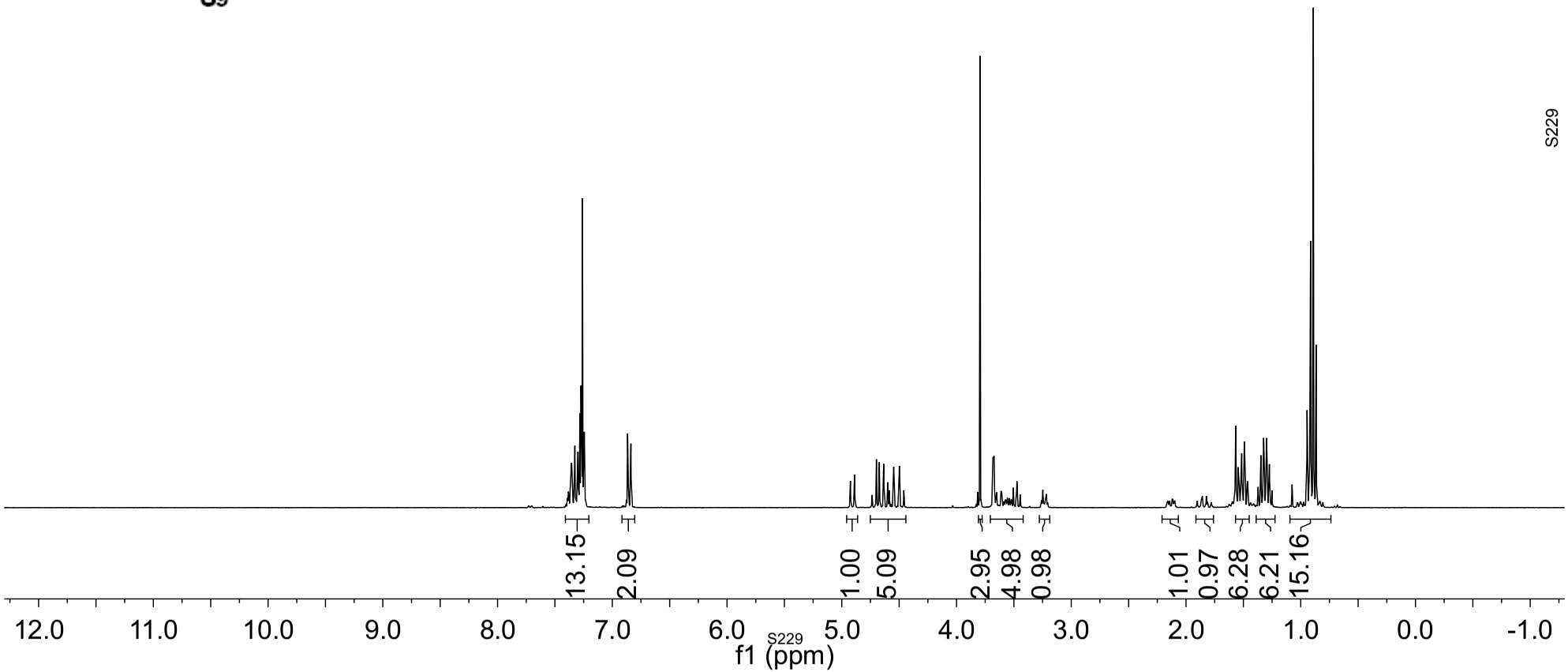

S8 (1H -13C HSQC)
OH
BnO
O
BnO
SnBu3
S8
f2 (ppm)
f1 (ppm)
S228



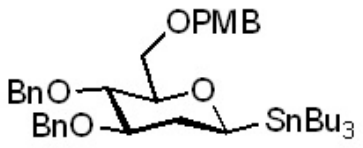
S9 (^{1}H NMR, 300MHz, $CDCl_3$)



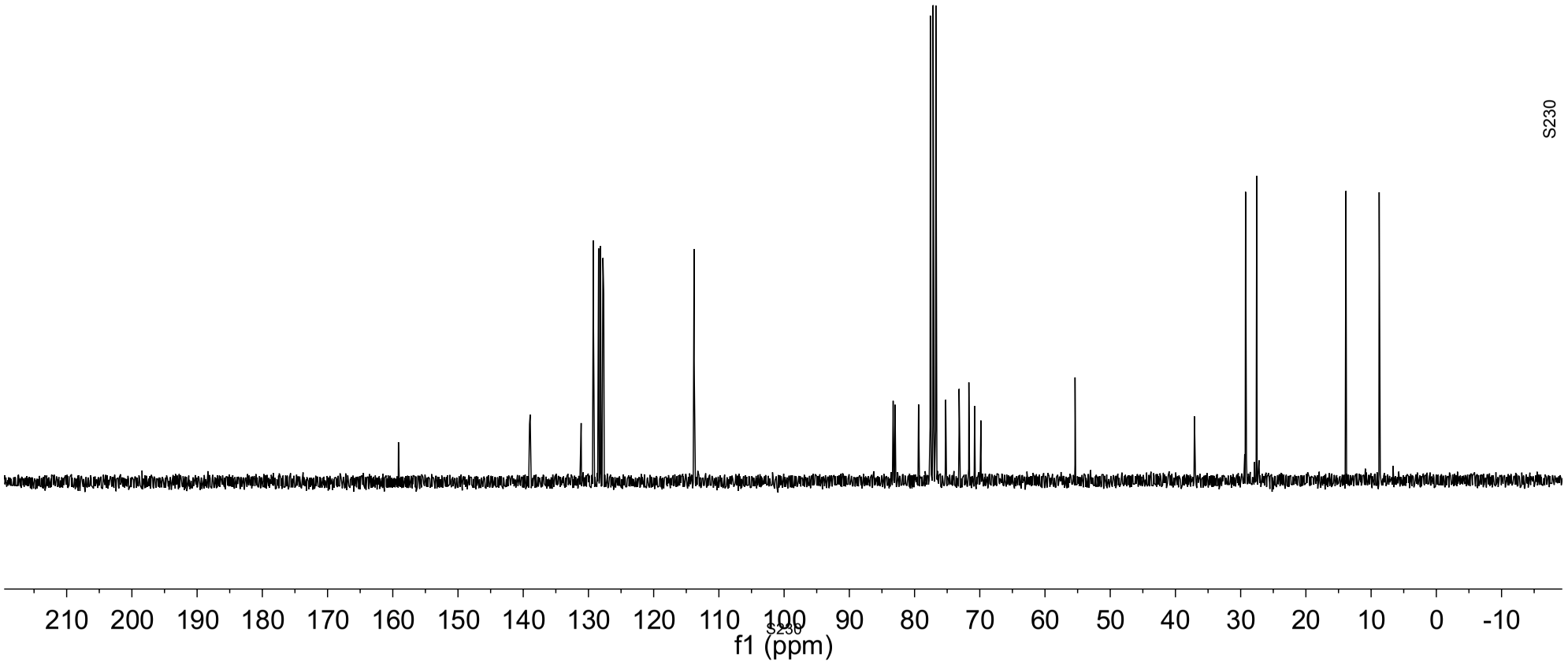
S9

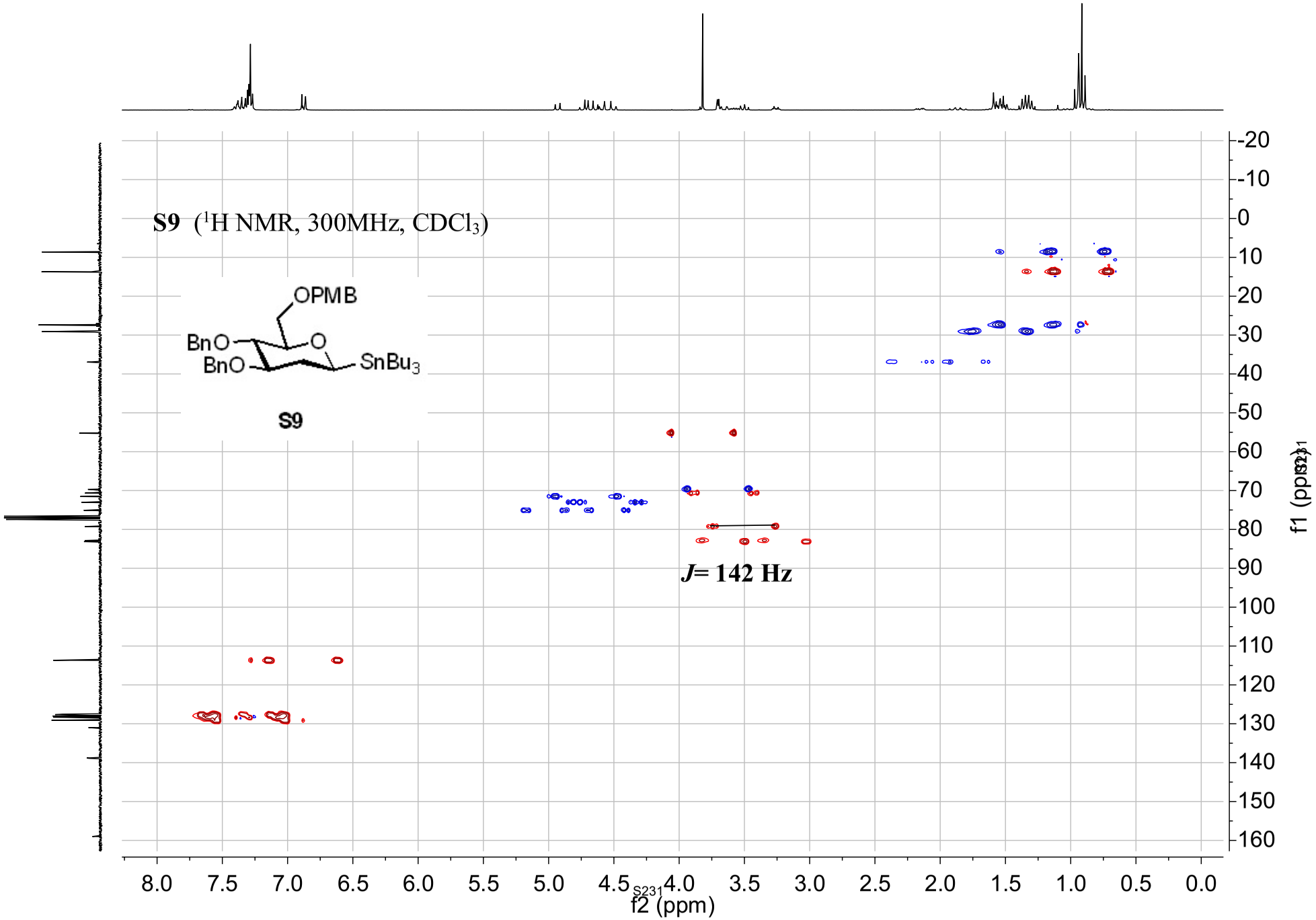


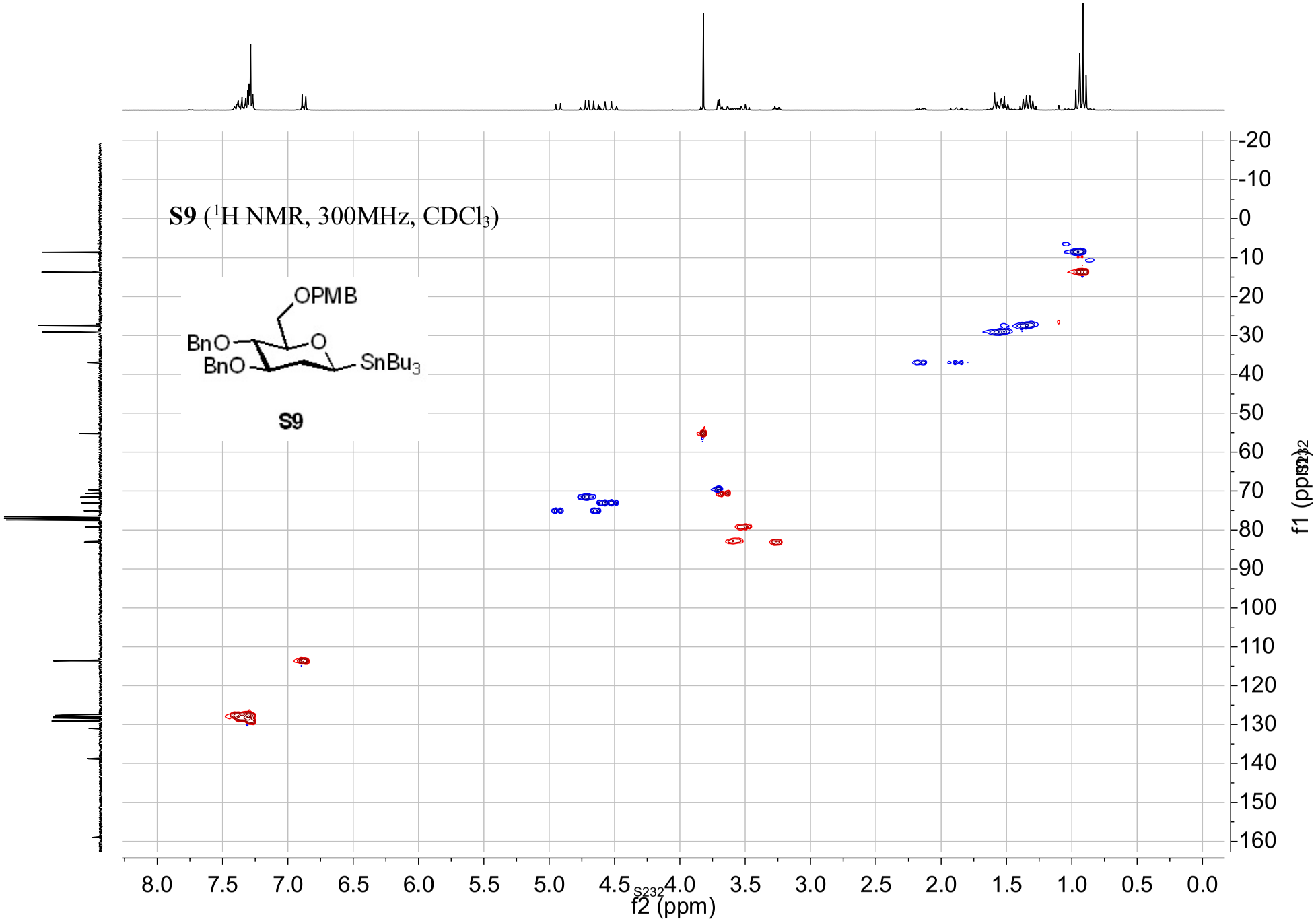
S9 (^{1}H NMR, 300MHz, $CDCl_3$)



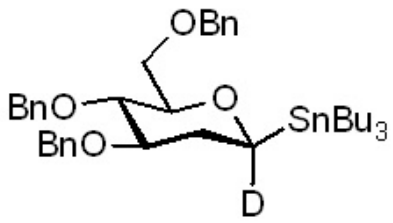
S9




S9 (1H NMR, 300MHz, CDCl3)
OPMB
BnO
BnO
O
SnBu3
S9
J= 142 Hz
f2 (ppm)
f1 (ppm)

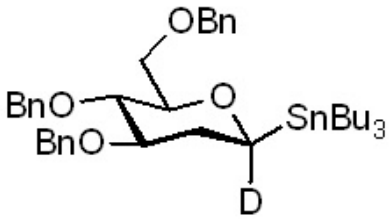

S9 (1H NMR, 300MHz, CDCl3)
OPMB
BnO
BnO
O
SnBu3
S9
f2 (ppm)
f1 (ppm)

S10 (^{1}H NMR, 300MHz, $CDCl_3$)

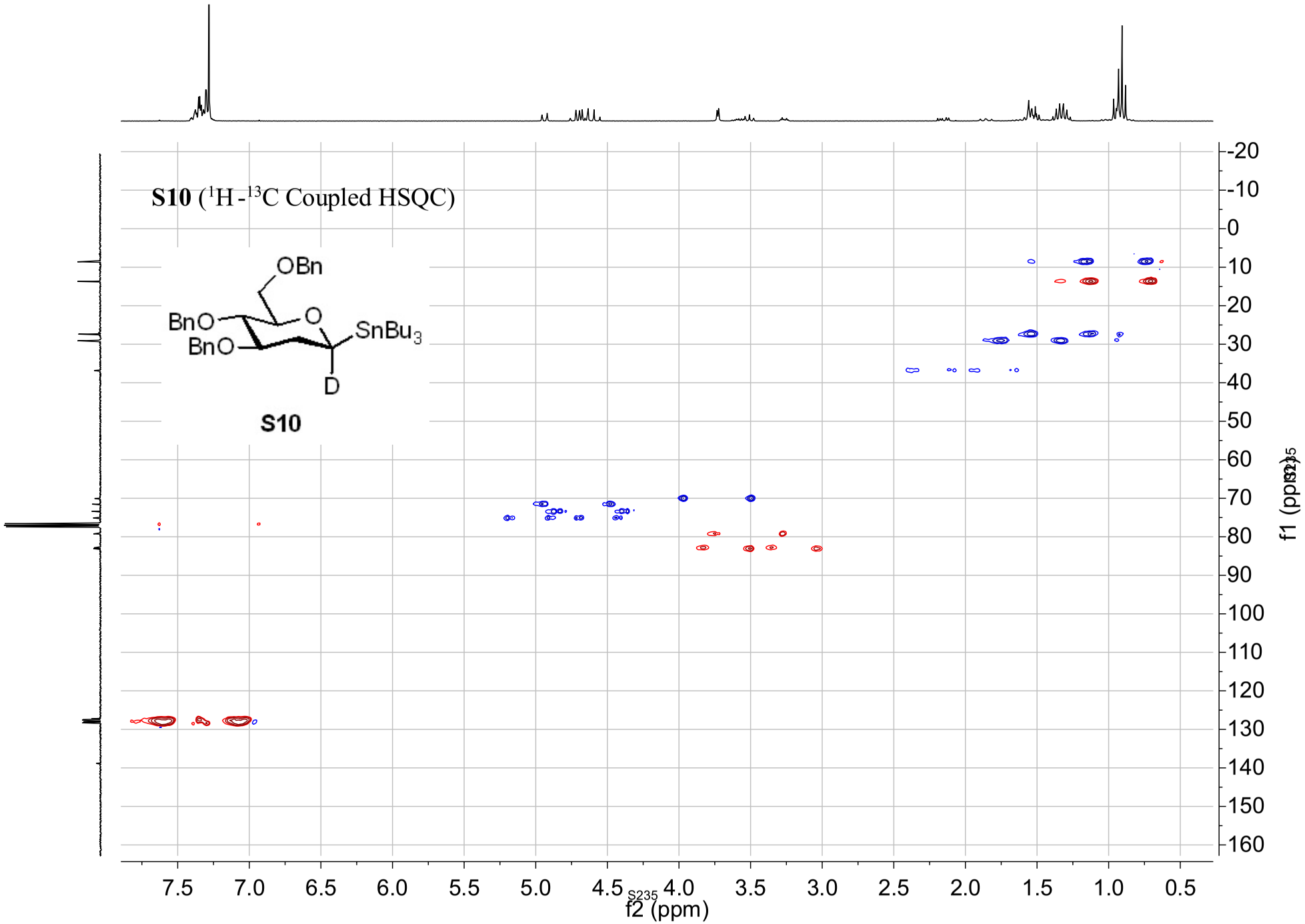


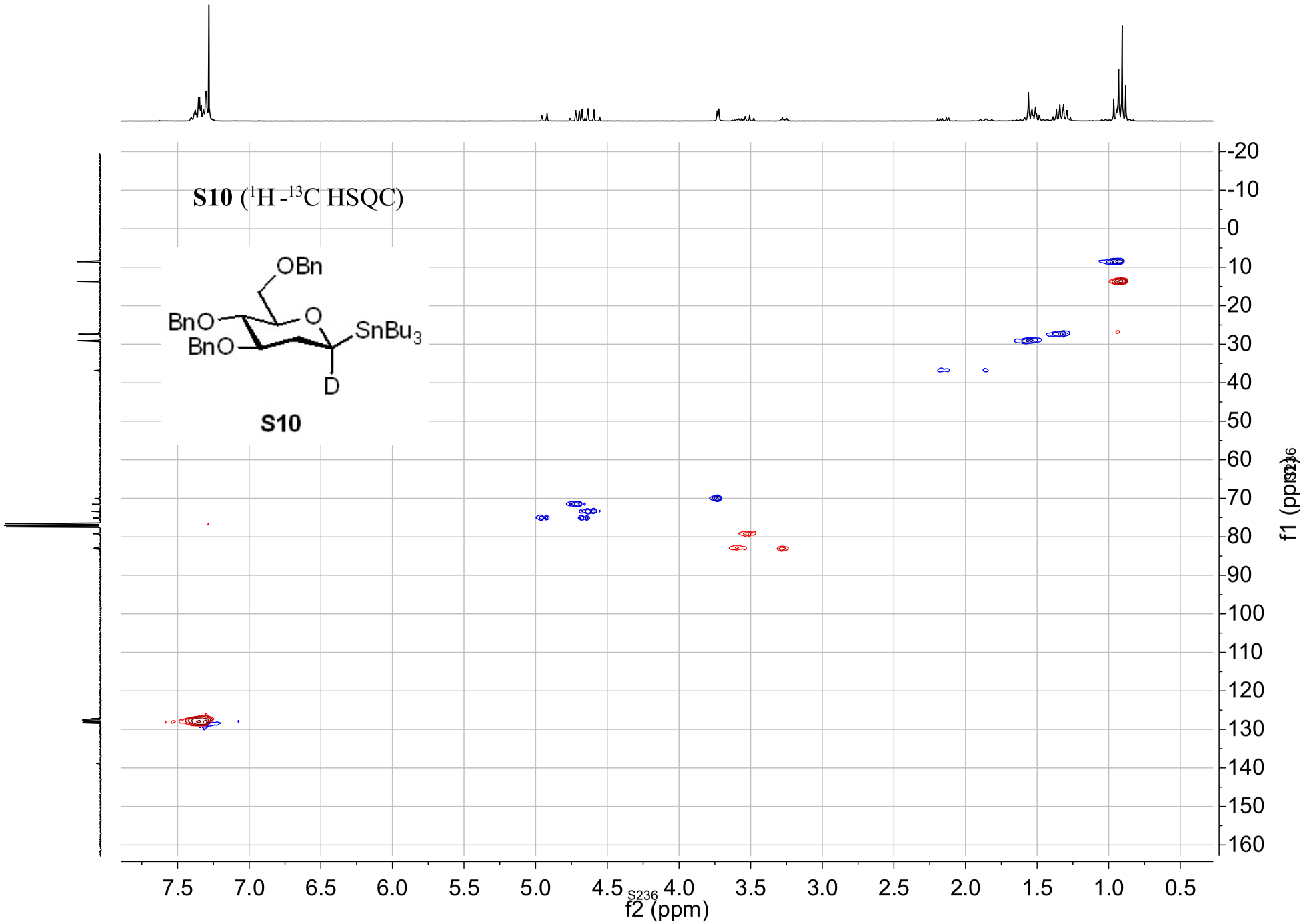
S10

S10 (^{13}C NMR, 75MHz, $CDCl_3$)

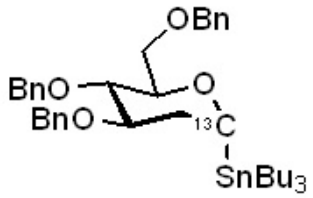


S10


S10 (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
SnBu3
D
S10
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

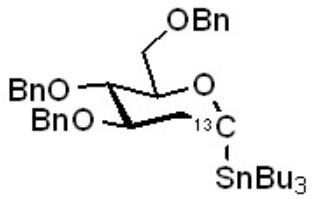

S10 (1H -13C HSQC)
OBn
BnO
BnO
O
SnBu3
D
S10
f2 (ppm)
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

S11 (^{1}H NMR, 300MHz, $CDCl_3$)

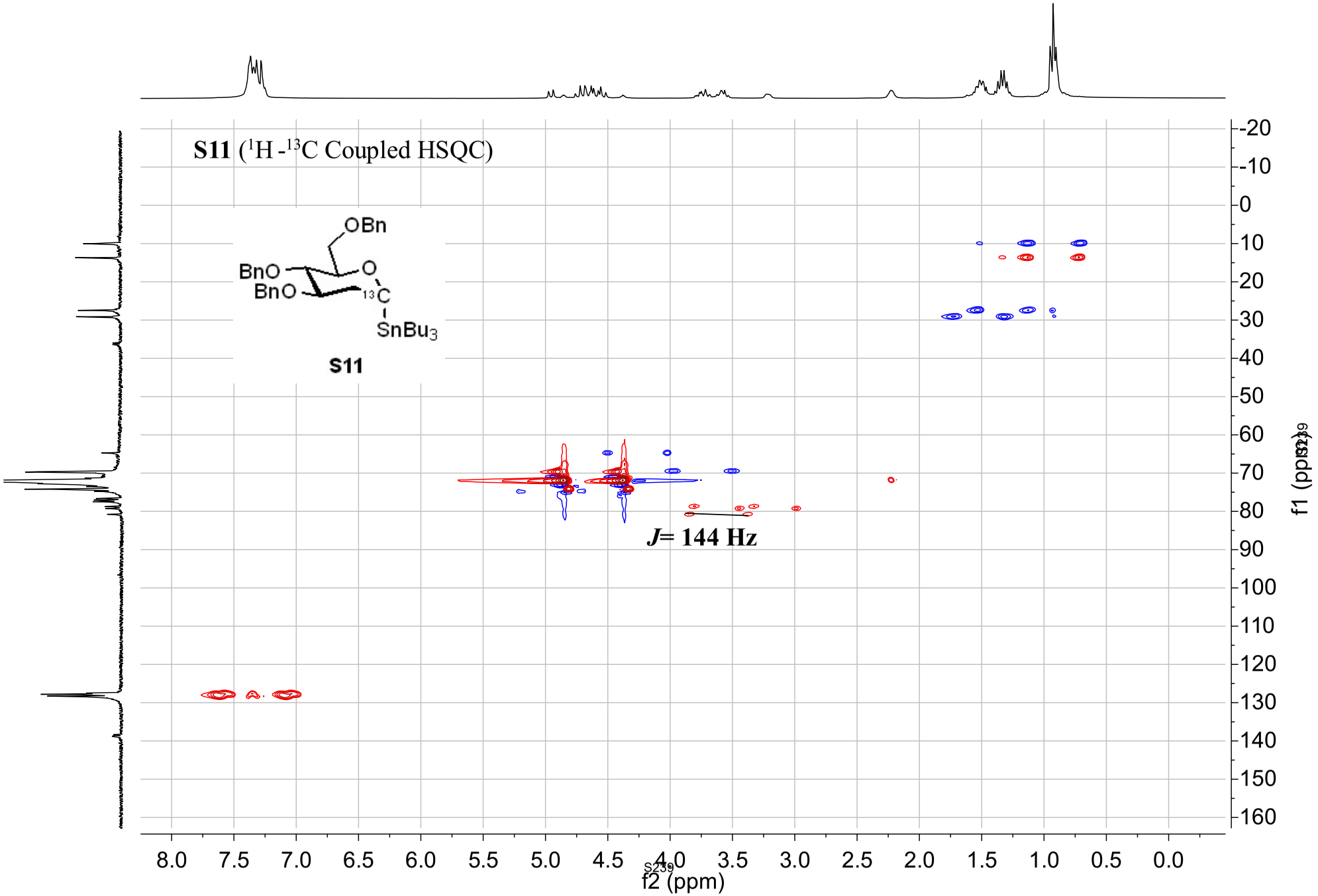


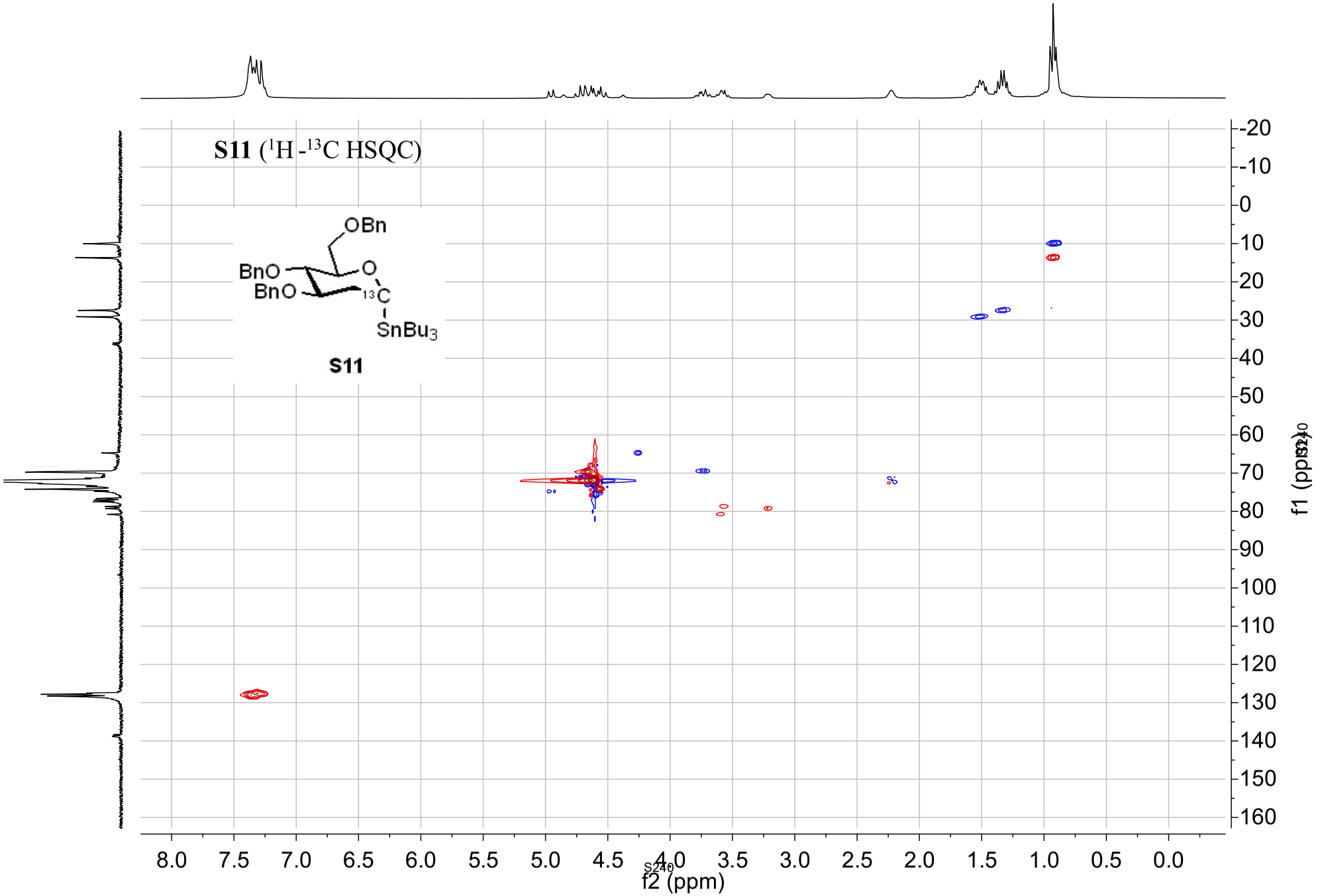
S11

S11 (^{13}C NMR, 75MHz, $CDCl_3$)

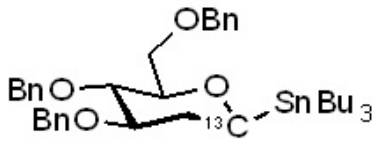


S11


S11 (1H -13C Coupled HSQC)
OBn
BnO
BnO
O
13C
SnBu3
S11
J= 144 Hz
f2 (ppm)
f1 (ppm)
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
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

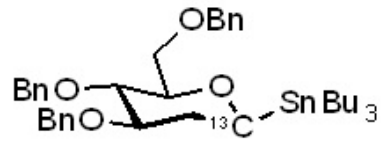

S11 (1H -13C HSQC)
OBn
BnO
BnO
O
13C
SnBu3
S11
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

S12 (^{1}H NMR, 300MHz, $CDCl_3$)

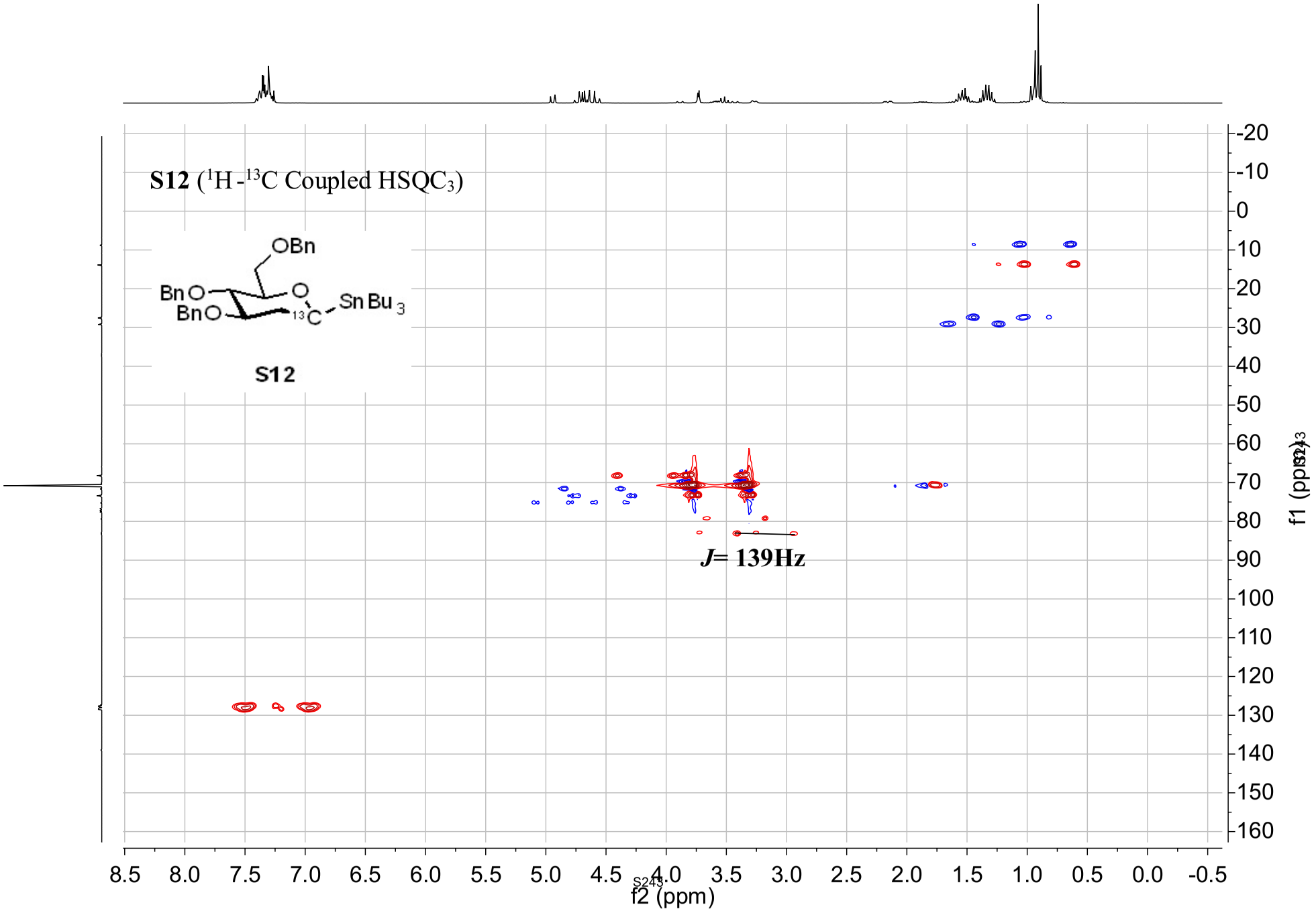


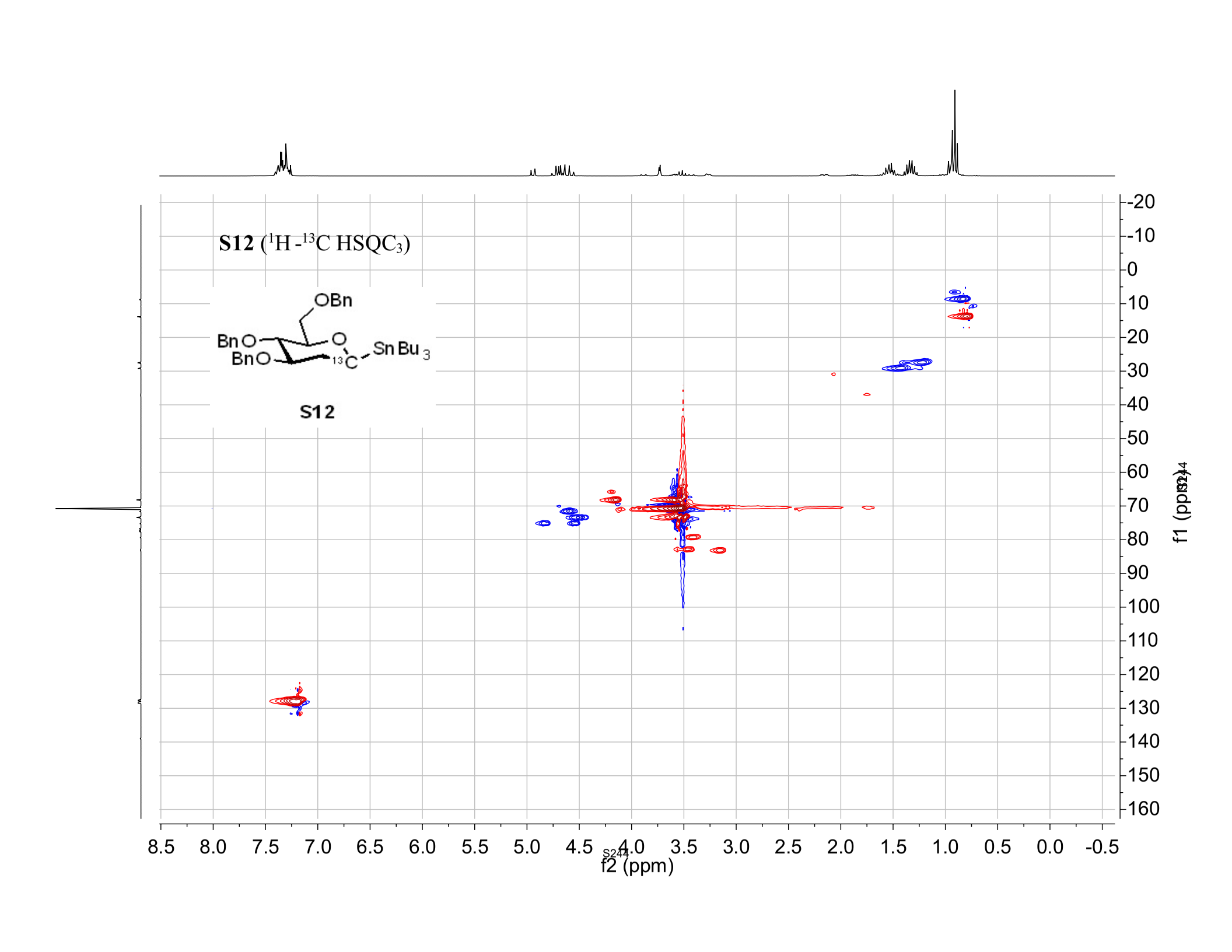
S12

S12 (^{13}C NMR, 75MHz, $CDCl_3$)

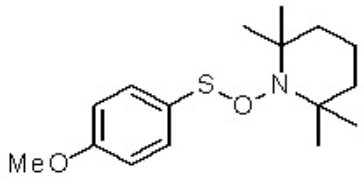


S12


S12 (1H -13C Coupled HSQC3)
OBn
Bn O
Bn O
O
13C
Sn Bu 3
S12
J= 139Hz
f2 (ppm)
f1 (ppm)

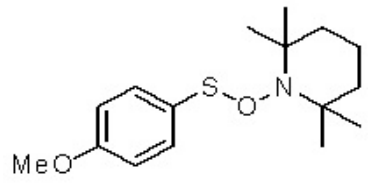

S12 (1H -13C HSQC3)
OBn
BnO
BnO
O
13C
Sn Bu 3
S12
f2 (ppm)
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
-20 -10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160

S13 (^{1}H NMR, 300MHz, $CDCl_3$)



S13

S13 (^{13}C NMR, 75MHz, $CDCl_3$)



S13