Supporting Information

Pd-Catalyzed Stereoretentive Synthesis of Reversed *C*-Acyl Glycosides: Access to Rare L-Sugars and Higher-Carbon Sugars

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1. General Information

Commercially available materials were used as received without further purification unless otherwise noted. All reactions were carried out under anhydrous N_2 in oven-dried glassware. $Pd_2(dba)_3$ (98% purity) were purchased from Leyan. CuCl were purchased from Sigma-Aldrich. Anhydrous 1,4-dioxane (99.5% purity) were purchased from Adamas. 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 (200-400 mesh). Automated column chromatography was performed on a Biotage Selekt using Silicycle high-resolution SiO_2 cartridges unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on Bruker 400/500 MHz instruments and were 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**). High-resolution mass spectra (HR-MS) were recorded on a Waters Micromass Q-Tof Premier mass spectrometer. Optical rotations were measured on an Anton Paar MCP 5500 automatic polarimeter using a 100 mm path-length cell at 589 nm and were reported as an average of five data points. Thin layer chromatography was used to monitor reaction progress and analyze fractions from column chromatography.

2. General Procedures

General Procedure A for Cross-Coupling Reactions.

To a solution of non-classical anomeric stannane (2.0 equiv) and thioester (1.0 equiv) in anh.1,4-dioxane (2.00 mL), $Pd_2(dba)_3$ (2.5 mol%), ligand **L6** (10 mol%), CuCl (1.0 equiv) were added. The reaction mixture was placed under Ar, heated at 90 °C using a metal heating block 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 Preparation of Thioesters

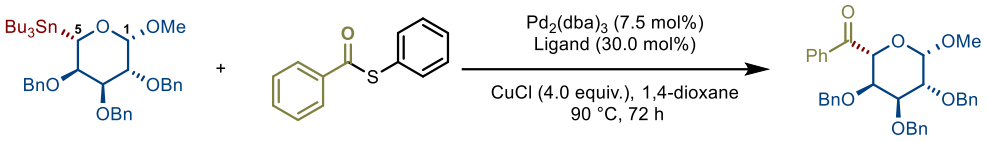
Under N_2, RCOOH (1.00 equiv), Ph_2S_2 (1.10 equiv), and anh. CH_2Cl_2 were successively added into a flame-dried glassware. The mixture was cooled to 0 °C, P(*n*-Bu)$_3$ (1.20 equiv) was added drop-wise. After stirring for the time indicated at rt, the reaction was concentrated and directly purified by column chromatography on SiO_2 to yield the thioester product.

General Procedure C for Preparing Pyranosyl Stannanes

To a solution of 4-deoxypentenoside (1.0 equiv) in a cooled (0 °C), vigorously stirring biphasic solution of DCM, saturated aq. $NaHCO_3$, and acetone, a solution of Oxone® (4.0 equiv) in H_2O was added dropwise over 15 min. The mixture was stirred at 0 °C for 0.5 h, then at rt for 2 h. The organic phase was then separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and concentrated to afford the crude epoxide. The crude epoxide (1.0 equiv) was dissolved in anhydrous and degassed THF, cooled to -15 °C, and a solution of $MeMgSnBu_3$ (1.5 equiv) in THF was added. The reaction was stirred at -15 °C for 1.5 h, then warmed to -10 °C and stirred for 1 h, quenched with H_2O, filtered twice through Celite®, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2, and the combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography on SiO_2.

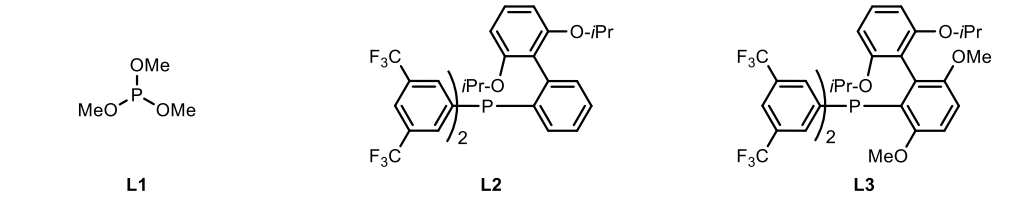
3. Additional Reaction Optimization Conditions

Table 1 Screening of ligands



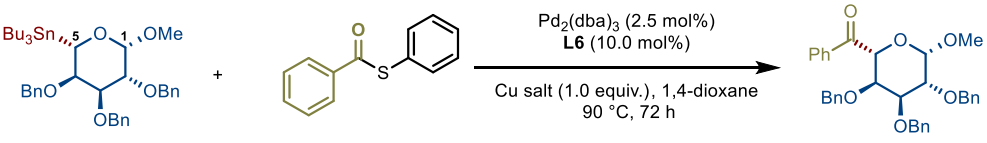
9a, L type, β only **10a** **12a**, L type, β only

Entry	Ligand	NMR yield
1	**L1**	32%
2	**L2**	63%
3	**L3**	71%
4	**L4**	72%
5	**L5**	82%
6	**L6**	86%



L1 **L2** **L3** **L4** **L5** **L6**

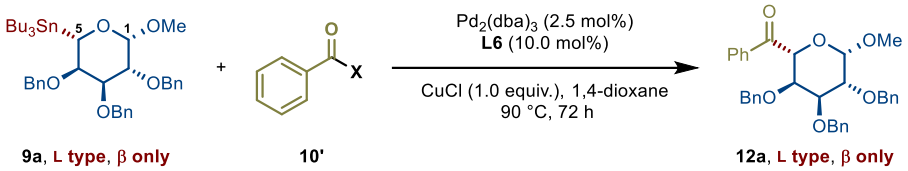
Table 2 Screening of copper salts



9a, L type, β only **10a** **12a**, L type, β only

Entry	Cu salts	NMR yield
1	**CuCl**	85%
2	CuBr	60%
3	CuI	9%
4	----	None

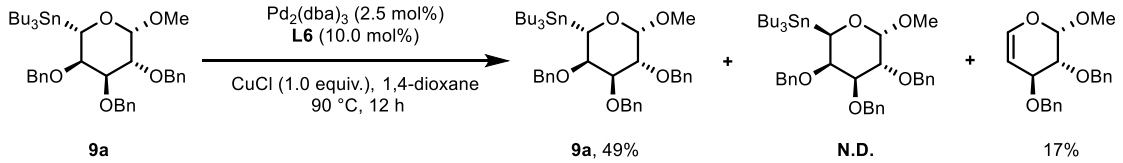
Table 3 Screening of acylating reagents



9a, **L type**, **β only** **10'** **12a**, **L type**, **β only**

Entry	Acylating reagents	NMR yield
1	**X = SPh**	85%
2	X = Cl	42%
3	X = OCOPh	67%

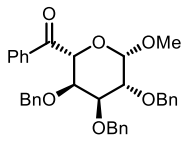
4. Stereochemical Integrity of the Reversed Glycosyl Stannane



To a solution of tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane **9a**[1] (72.4 mg, 0.100 mmol) in anh.1,4-dioxane (2.00 mL), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) were added. The reaction mixture was placed under Ar, heated at 90 °C using a metal heating block for 12 h, 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 (Hexanes:EtOAc, 1:0 then 15:1) to afford **9a** (35.1 mg, 49%) as a colorless oil and (2*S*,3*R*,4*S*)-3,4-bis(benzyloxy)-2-methoxy-3,4-dihydro-2*H*-pyran[2] (5.60 mg, 17%) as a colorless oil.

No evidence of configurational inversion at the anomeric center was observed, indicating that the stereochemical configuration of **9a** remains intact under the transmetalation conditions. Although a minor β-O elimination side reaction was detected, this pathway does not compromise the stereochemical integrity of the anomeric center.

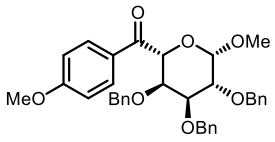
5. Detailed Experimental Procedures for Compounds 12-42



12a

Phenyl((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12a).

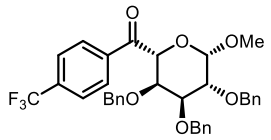
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl benzothioate (21.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 6:1) **12a** (43.3 mg, 80%) as a colorless oil: $[a]_D^{20}$ = +29.3 (c = 2.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.27 (m, 17H), 5.01 (d, *J* = 4.3 Hz, 1H, H-5), 4.79 – 4.71 (m, 6H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.54 – 4.53 (m, 1H), 4.13 (dd, *J* = 8.4, 2.3 Hz, 1H), 3.97 (dd, *J* = 8.4, 2.2 Hz, 1H), 2.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.0, 138.8, 138.7, 138.3, 135.5, 133.1, 129.4, 128.5, 128.4 (2), 128.1, 128.0, 127.9, 127.8, 127.7 (2), 101.8, 75.9, 75.6, 75.5, 74.3, 73.8, 73.4, 73.3, 57.8; HRMS (ESI) *m/z* calcd for $C_{34}H_{34}O_6Na$ $[M + Na]^+$ 561.2253, found 561.2250.



12b

(4-Methoxyphenyl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12b).

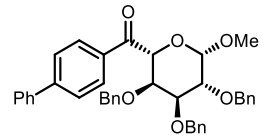
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **12b** (54.4 mg, 96%) as a colorless oil: $[a]_D^{20}$ = +32.7 (c = 2.10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.26 (m, 15H), 6.93 (d, *J* = 8.3 Hz, 2H), 4.97 (d, *J* = 4.1 Hz, 1H, H-5), 4.78 – 4.71 (m, 6H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.52 – 4.50 (m, 1H), 4.13 (d, *J* = 8.1 Hz, 1H), 3.95 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 2.96 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.4, 163.4, 138.8 (2), 138.4, 131.7, 128.6, 128.4 (2), 128.1, 128.0, 127.8, 127.7 (2), 127.6, 113.6, 101.7, 75.9, 75.6, 75.5, 74.3, 73.7, 73.3, 73.2, 57.8, 55.5; HRMS (ESI) *m/z* calcd for $C_{35}H_{36}O_7Na$ $[M + Na]^+$ 591.2359, found 591.2354.



12c

(4-(Trifluoromethyl)phenyl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12c).

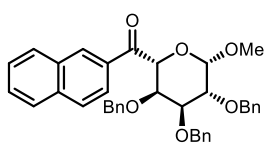
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-(trifluoromethyl)benzothioate (28.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 6:1) **12c** (56.0 mg, 92%) as a colorless oil: $[a]_D^{20}$ = +24.0 (c = 2.17, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.29 (m, 15H), 4.98 (d, *J* = 4.8 Hz, 1H, H-5), 4.77 – 4.72 (m, 6H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.50 – 4.48 (m, 1H), 4.08 (dd, *J* = 8.2, 2.9 Hz, 1H), 3.95 (dd, *J* = 8.1, 2.7 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.0, 138.6 (2) , 138.2, 138.0, 134.3 (q, *J* = 32.5 Hz), 129.7, 128.5 (2), 128.2, 128.0, 127.9 (2), 127.8, 125.5 (q, *J* = 3.5 Hz), 123.7 (q, *J* = 272.7 Hz), 101.9, 75.9, 75.8, 75.1, 74.0, 73.9, 73.5, 73.2, 58.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -63.1; HRMS (ESI) *m/z* calcd for $C_{35}H_{33}O_6F_3Na$ $[M + Na]^+$ 629.2127, found 629.2121.



12d

[1,1'-Biphenyl]-4-yl((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12d).

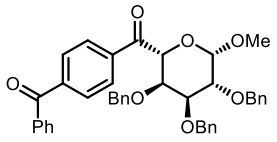
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl [1,1'-biphenyl]-4-carbothioate (29.0 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **12d** (39.3 mg, 64%) as a colorless oil: $[a]_D^{20}$ = +25.8 (c = 1.77, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.29 (m, 18H), 5.04 (d, *J* = 4.4 Hz, 1H, H-5), 4.77 – 4.72 (m, 6H), 4.66 (d, *J* = 11.8 Hz, 1H), 4.55 – 4.53 (m, 1H), 4.14 (d, *J* = 8.1 Hz, 1H), 3.97 (d, *J* = 8.2 Hz, 1H), 2.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.6, 145.6, 139.9, 138.8 (2), 138.3, 134.3, 130.0, 129.1, 128.5 (3), 128.4, 128.2, 128.0, 127.9, 127.8 (2), 127.7, 127.3, 127.1, 101.8, 76.0, 75.8, 75.5, 74.4, 73.8, 73.4, 73.3, 57.9; HRMS (ESI) *m/z* calcd for $C_{40}H_{38}O_6Na$ $[M + Na]^+$ 637.2566, found 637.2562.



12e

Naphthalen-2-yl((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12e).

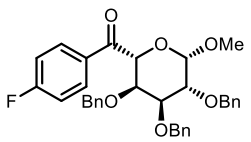
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl naphthalene-2-carbothioate (26.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **12e** (53.1 mg, 90%) as a colorless oil: $[a]_D^{20}$ = +21.9 (c = 2.70, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.08 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.95 – 7.87 (m, 3H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.26 (m, 15H), 5.17 (d, *J* = 4.4 Hz, 1H, H-5), 4.81 – 4.73 (m, 6H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.61 – 4.59 (m, 1H), 4.20 (dd, *J* = 8.3, 2.8 Hz, 1H), 4.01 (dd, *J* = 8.3, 2.7 Hz, 1H), 2.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.0, 138.8 (2), 138.3, 135.6, 132.8, 132.5, 131.4, 129.8, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8 (2), 127.7 (2), 126.8, 124.8, 101.8, 76.0, 75.8, 75.6, 74.4, 73.8, 73.4, 73.3, 57.9; HRMS (ESI) *m/z* calcd for $C_{38}H_{36}O_6Na$ $[M + Na]^+$ 611.2410, found 611.2402.



12f

(4-Benzoylphenyl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12f).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-benzoylbenzothioate **S1** (31.8 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **12f** (59.5 mg, 93%) as a colorless oil: $[a]_D^{20}$ = +19.4 (c = 3.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.53 – 7.28 (m, 17H), 5.03 (d, *J* = 4.7 Hz, 1H, H-5), 4.77 – 4.72 (m, 6H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.53 – 4.51 (m, 1H), 4.09 (dd, *J* = 8.1, 2.9 Hz, 1H), 3.95 (dd, *J* = 8.2, 2.7 Hz, 1H), 2.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.4, 196.0, 141.1, 138.6, 138.1 (2), 137.0, 133.1, 130.1, 129.9, 129.2, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8 (2), 127.7, 101.8, 75.8 (2), 75.2, 74.1, 73.9, 73.4, 73.2, 58.0; HRMS (ESI) *m/z* calcd for $C_{41}H_{38}O_7Na$ $[M + Na]^+$ 665.2515, found 665.2507.

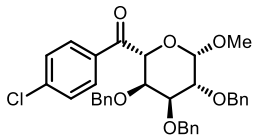


12g

(4-Fluorophenyl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12g).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-

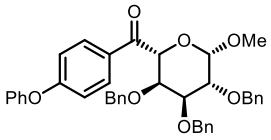
fluorobenzothioate (23.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **12g** (54.3 mg, 98%) as a colorless oil: $[a]_D^{20}$ = +26.2 (c = 2.78, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.06 (m, 2H), 7.40 – 7.28 (m, 15H), 7.14 – 7.11 (m, 2H), 4.96 (d, *J* = 4.7 Hz, 1H, H-5), 4.77 – 4.71 (m, 6H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.50 – 4.49 (m, 1H), 4.10 (dd, *J* = 8.2, 3.0 Hz, 1H), 3.95 (dd, *J* = 8.2, 2.9 Hz, 1H), 2.96 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.3, 165.6 (d, *J* = 255.0 Hz), 138.7, 138.2, 132.1 (d, *J* = 9.2 Hz), 131.9 (d, *J* = 2.9 Hz), 128.5, 128.1, 128.0, 127.9, 127.8 (2), 127.7, 115.6 (d, *J* = 21.8 Hz), 101.8, 75.8, 75.7, 75.3, 74.2, 73.8, 73.4, 73.2, 57.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ = -104.8; HRMS (ESI) *m/z* calcd for $C_{34}H_{33}O_6FNa$ $[M + Na]^+$ 579.2159, found 579.2159.



12h

(4-Chlorophenyl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12h).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-chlorobenzothioate (24.9 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **12h** (53.4 mg, 93%) as a colorless oil: $[a]_D^{20}$ = +27.5 (c = 1.98, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.27 (m, 17H), 4.94 (d, *J* = 4.8 Hz, 1H, H-5), 4.76 – 4.71 (m, 6H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.48 (dd, *J* = 4.8, 3.0 Hz, 1H), 4.08 (dd, *J* = 8.1, 3.0 Hz, 1H), 3.94 (dd, *J* = 8.1, 2.7 Hz, 1H), 2.97 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.7, 139.5, 138.7, 138.2, 133.9, 130.8, 128.8, 128.5, 128.1, 128.0, 127.9, 127.8 (2), 127.7, 101.8, 75.8 (2), 75.3, 74.2, 73.8, 73.4, 73.2, 57.9; HRMS (ESI) *m/z* calcd for $C_{34}H_{33}O_6ClNa$ $[M + Na]^+$ 595.1863, found 595.1856.

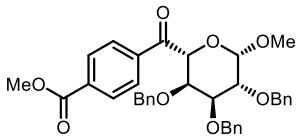


12i

(4-Phenoxyphenyl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12i).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-phenoxybenzothioate **S2** (30.6 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **12i** (59.1 mg, 94%) as a colorless oil: $[a]_D^{20}$ = +31.4 (c = 2.97, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.43 – 7.28 (m, 17H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 4.98 (d, *J* = 4.8 Hz, 1H, H-5), 4.79 – 4.72 (m, 6H), 4.65 (d, *J* = 11.9 Hz,

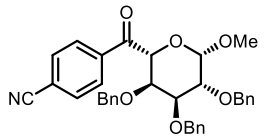
1H), 4.52 – 4.51 (m, 1H), 4.13 (dd, *J* = 8.1, 3.0 Hz, 1H), 3.96 (dd, *J* = 8.1, 2.7 Hz, 1H), 3.03 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.4, 161.9, 155.5, 138.7, 138.3, 131.7, 130.2, 130.1, 128.4 (3), 128.1, 127.9, 127.8 (2), 127.7 (2), 124.7, 120.3, 117.2, 101.7, 75.9, 75.7, 75.4, 74.3, 73.8, 73.4, 73.2, 57.8; HRMS (ESI) *m/z* calcd for $C_{40}H_{38}O_7Na$ [M + Na]$^+$ 653.2515, found 653.2509.



12j

Methyl 4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbonyl)benzoate (12j).

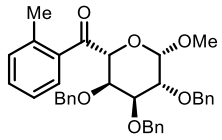
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), methyl 4-((phenylthio)carbonyl)benzoate (27.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **12j** (52.8 mg, 88%) as a colorless oil: $[\alpha]_D^{20}$ = +24.0 (c = 2.48, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 4H), 7.40 – 7.27 (m, 15H), 4.99 (d, *J* = 4.1 Hz, 1H, H-5), 4.77 – 4.70 (m, 6H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.51 – 4.50 (m, 1H), 4.08 (d, *J* = 8.2 Hz, 1H), 3.96 – 3.94 (m, 4H), 2.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.5, 166.3, 138.8, 138.6 (2), 138.2, 133.7, 129.7, 129.3, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8 (2), 127.7, 101.9, 75.8 (2), 75.3, 74.2, 73.8, 73.4, 73.3, 57.9, 52.5; HRMS (ESI) *m/z* calcd for $C_{36}H_{36}O_8Na$ [M + Na]$^+$ 619.2308, found 619.2303.



12k

4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbonyl)benzonitrile (12k).

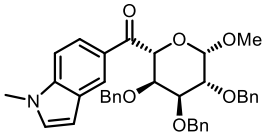
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-cyanobenzothioate (23.9 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **12k** (53.7 mg, 95%) as a white solid: $[\alpha]_D^{20}$ = +23.4 (c = 2.44, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.28 (m, 15H), 4.95 (d, *J* = 5.2 Hz, 1H, H-5), 4.74 – 4.69 (m, 6H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.45 (dd, *J* = 5.0, 3.0 Hz, 1H), 4.04 (dd, *J* = 7.9, 2.9 Hz, 1H), 3.92 (dd, *J* = 7.9, 2.5 Hz, 1H), 2.97 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.6, 138.5 (2), 137.9, 132.3, 129.7, 128.5 (2), 128.1, 128.0, 127.9 (3), 127.8, 118.0, 116.2, 101.8, 75.9, 75.7, 74.9, 73.9 (2), 73.4, 73.1, 58.0; HRMS (ESI) *m/z* calcd for $C_{35}H_{33}NO_6Na$ [M + Na]$^+$ 586.2206, found 586.2200.



12l

***o*-Tolyl((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12l).**

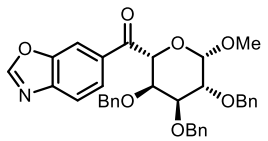
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 2-methylbenzothioate (22.8 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **12l** (47.0 mg, 85%) as a colorless oil: $[a]_D^{20}$ = +33.1 (c = 2.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.23 (m, 18H), 4.98 (d, *J* = 3.8 Hz, 1H, H-5), 4.80 – 4.76 (m, 4H), 4.70 – 4.66 (m, 2H), 4.64 – 4.62 (m, 1H), 4.60 (d, *J* = 3.0 Hz, 1H), 4.07 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.97 (dd, *J* = 9.0, 2.9 Hz, 1H), 2.78 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 200.2, 140.1, 138.8, 138.7, 138.4, 135.1, 132.1, 131.7, 130.5, 128.5 (2), 128.4, 128.1, 127.8, 127.6, 125.4, 101.9, 76.4, 75.8, 75.3, 74.4, 74.0, 73.4, 73.2, 57.7, 21.5; HRMS (ESI) *m/z* calcd for $C_{35}H_{36}O_6Na$ [M + Na]$^+$ 575.2410, found 575.2407.



12m

(1-Methyl-1*H*-indol-5-yl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12m).

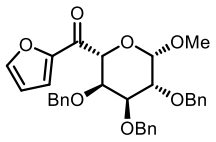
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 1-methyl-1*H*-indole-5-carbothioate **S3** (26.7 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 2:1) **12m** (47.1 mg, 80%) as a yellow oil: $[a]_D^{20}$ = +33.1 (c = 1.41, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.26 (m, 16H), 7.10 (s, 1H), 6.59 (s, 1H), 5.13 (br, 1H, H-5), 4.78 – 4.66 (m, 7H), 4.58 – 4.55 (m, 1H), 4.21 (d, *J* = 8.2 Hz, 1H), 3.98 (d, *J* = 8.3 Hz, 1H), 3.81 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.9, 139.2, 139.0, 138.9, 138.6, 130.4, 128.4 (2), 128.1, 128.0, 127.9, 127.7, 127.6, 124.4, 122.9, 109.1, 103.3, 101.7, 76.1, 75.8, 75.7, 74.7, 73.7, 73.4, 73.3, 57.8, 33.1; HRMS (ESI) *m/z* calcd for $C_{37}H_{37}NO_6Na$ [M + Na]$^+$ 614.2519, found 614.2513.



12n

Benzo[*d*]oxazol-6-yl((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12n).

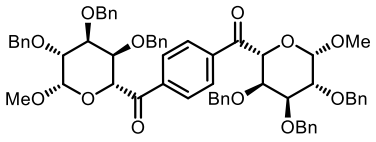
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl benzo[*d*]oxazole-6-carbothioate **S4** (25.5 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 2:1) **12n** (44.8 mg, 77%) as a yellow oil: $[a]_D^{20}$ = +25.8 (c = 2.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.23 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.26 (m, 15H), 5.04 (d, *J* = 4.6 Hz, 1H, H-5), 4.76 – 4.71 (m, 6H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.52 – 4.50 (m, 1H), 4.11 (d, *J* = 8.0 Hz, 1H), 3.95 (d, *J* = 8.0 Hz, 1H), 2.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.7, 155.3, 149.9, 143.8, 138.7, 138.6, 138.2, 133.3, 128.5, 128.4 (2), 128.1, 128.0, 127.9, 127.8 (2), 127.7, 126.3, 120.4, 112.5, 101.8, 75.9 (2), 75.3, 74.3, 73.8, 73.4, 73.2, 57.9; HRMS (ESI) *m/z* calcd for $C_{35}H_{33}NO_7Na$ [M + Na]$^+$ 602.2155, found 602.2152.



12o

Furan-2-yl((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12o).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl furan-2-carbothioate (20.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 2:1) **12o** (48.7 mg, 92%) as a white solid: $[a]_D^{20}$ = +36.9 (c = 2.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.37 – 7.23 (m, 16H), 6.51 – 6.50 (m, 1H), 4.81 – 4.65 (m, 6H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.33 (dd, *J* = 6.2, 2.5 Hz, 1H), 4.01 (dd, *J* = 7.0, 2.8 Hz, 1H), 3.84 (dd, *J* = 6.8, 2.2 Hz, 1H), 3.24 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 185.1, 151.1, 146.8, 138.7, 138.5, 138.0, 128.4 (3), 128.1, 127.9 (2), 127.8 (2), 127.7, 119.9, 112.2, 101.4, 75.8, 75.7, 74.9, 74.1, 73.8, 73.4, 72.8, 57.6; HRMS (ESI) *m/z* calcd for $C_{32}H_{32}O_7Na$ [M + Na]$^+$ 551.2046, found 551.2042.

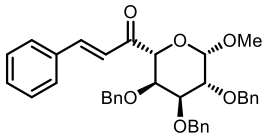


12p

1,4-Phenylenebis(((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone) (12p).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (289 mg, 0.400 mmol), *S*,*S*-diphenyl benzene-1,4-bis(carbothioate) (35.0 mg, 0.100 mmol), $Pd_2(dba)_3$ (4.60 mg, 0.005 mmol), ligand **L6** (15.90 mg, 0.020 mmol), CuCl (19.80 mg, 0.200 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 2:1) **12p** (83.9 mg,

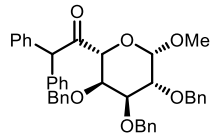
84%) as a colorless oil: $[a]_D^{20}$ = +28.2 (c = 3.62, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 4H), 7.42 – 7.28 (m, 30H), 5.01 (d, *J* = 4.8 Hz, 2H, H-5), 4.77 – 4.69 (m, 12H), 4.66 (d, *J* = 11.8 Hz, 2H), 4.50 (dd, *J* = 4.6, 3.1 Hz, 2H), 4.08 (dd, *J* = 8.0, 2.8 Hz, 2H), 3.95 (dd, *J* = 8.1, 2.5 Hz, 2H), 2.93 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.3, 138.6, 138.5, 138.1, 129.3, 128.5, 128.4, 128.1, 127.9 (2), 127.8 (2), 127.7, 101.8, 75.7, 75.6, 75.2, 74.1, 73.8, 73.4, 73.2, 57.8; HRMS (ESI) *m/z* calcd for $C_{62}H_{62}O_{12}Na$ $[M + Na]^+$ 1021.4139, found 1021.4118.



12q

(*E*)-3-Phenyl-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)prop-2-en-1-one (12q).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-(*p*-tolyl) (*E*)-3-phenylprop-2-enethioate (25.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **12q** (38.8 mg, 69%) as a pale yellow oil: $[a]_D^{20}$ = +5.53 (c = 1.62, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 16.1 Hz, 1H), 7.57 – 7.56 (m, 2H), 7.40 – 7.23 (m, 18H), 7.07 (d, *J* = 16.1 Hz, 1H), 4.80 – 4.67 (m, 5H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 5.9 Hz, 1H, H-5), 4.32 (dd, *J* = 5.4, 2.5 Hz, 1H), 3.97 (dd, *J* = 7.3, 2.8 Hz, 1H), 3.88 (dd, *J* = 7.3, 2.3 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.3, 143.3, 138.7, 138.6, 138.1, 134.7, 130.6, 129.0, 128.6, 128.5 (2), 128.2, 128.0, 127.9, 127.8 (3), 123.0, 101.5, 78.0, 75.8, 74.9, 74.2, 73.8, 73.3, 72.9, 58.3; HRMS (ESI) *m/z* calcd for $C_{36}H_{36}O_6Na$ $[M + Na]^+$ 587.2410, found 587.2408.

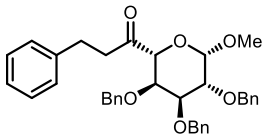


12r

2,2-Diphenyl-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-one (12r).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 2,2-diphenylethanethioate (30.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **12r** (60.6 mg, 96%) as a white solid: $[a]_D^{20}$ = +60.8 (c = 2.31, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 25H), 5.68 (s, 1H), 4.77 (d, *J* = 12.4 Hz, 1H), 4.70 (d, *J* = 1.9 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 7.8 Hz, 1H, H-5), 4.26 (d, *J* = 11.5 Hz, 1H), 4.21 (d, *J* = 11.5 Hz, 1H), 4.09 (dd, *J* = 7.8, 2.7 Hz, 1H), 3.76 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.67 (dd, *J* = 5.8, 1.8 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 204.9, 138.6 (2), 138.3 (2), 138.0, 129.5, 129.3, 128.8, 128.5 (2), 128.4, 128.0, 127.9 (2), 127.8 (2), 127.7,

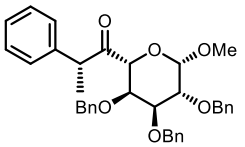
127.2, 127.1, 101.0, 76.7, 75.7, 74.3, 74.2, 73.8, 73.2, 72.4, 59.9, 57.9; HRMS (ESI) *m/z* calcd for $C_{41}H_{40}O_6Na$ [M + Na]$^+$ 651.2723, found 651.2720.



12s

3-Phenyl-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)propan-1-one (12s).

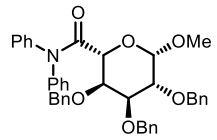
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 3-phenylpropanethioate (24.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 6:1) **12s** (52.8 mg, 93%) as a colorless oil: $[a]_D^{20}$ = +50.2 (c = 2.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 20H), 4.78 (d, *J* = 12.4 Hz, 1H), 4.76 (d, *J* = 1.8 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.58 (d, *J* = 12.4 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.38 (d, *J* = 11.8 Hz, 1H), 4.23 (d, *J* = 7.8 Hz, 1H, H-5), 4.06 (dd, *J* = 7.8, 2.9 Hz, 1H), 3.80 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.71 (dd, *J* = 5.8, 1.7 Hz, 1H), 3.50 (s, 3H), 2.98 – 2.86 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.5, 141.2, 138.6, 138.3, 137.9, 128.5 (3), 128.3, 128.0, 127.9, 127.8, 126.1, 101.1, 77.7, 75.5, 74.3, 73.9, 73.7, 73.2, 72.3, 57.9, 40.9, 29.4; HRMS (ESI) *m/z* calcd for $C_{36}H_{38}O_6Na$ [M + Na]$^+$ 589.2566, found 589.2560.



12t

(*R*)-2-Phenyl-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)propan-1-one (12t).

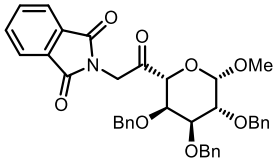
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl (*R*)-2-phenylpropanethioate (24.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **12t** (47.7 mg, 84%) as a colorless oil: $[a]_D^{20}$ = +11.5 (c = 2.09, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.13 (m, 20H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.61 (s, 1H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 12.4 Hz, 1H), 4.41 – 4.37 (m, 2H), 4.32 – 4.28 (m, 1H), 4.00 (s, 2H), 3.84 (d, *J* = 9.6 Hz, 1H), 3.62 (s, 1H), 3.55 (d, *J* = 4.4 Hz, 1H), 3.37 (s, 3H), 1.44 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.9, 140.0, 138.7, 138.1, 137.9, 128.8, 128.7, 128.5, 128.4 (2), 128.0, 127.9 (2), 127.8, 127.7, 127.1, 100.5, 76.2, 75.5, 75.0, 73.9, 73.8, 73.1, 72.0, 57.4, 50.0, 18.2; HRMS (ESI) *m/z* calcd for $C_{36}H_{38}O_6Na$ [M + Na]$^+$ 589.2566, found 589.2559.



12u

(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-6-methoxy-*N*,*N*-diphenyltetrahydro-2*H*-pyran-2-carboxamide (12u).

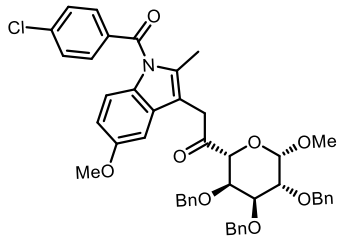
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-(*p*-tolyl) diphenylcarbamothioate (31.9 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **12u** (23.6 mg, 37%) as a colorless oil: $[\alpha]_D^{20}$ = +49.7 (c = 0.97, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.19 (m, 23H), 7.11 – 7.10 (m, 2H), 4.77 (d, *J* = 12.6 Hz, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.60 – 4.54 (m, 2H), 4.46 – 4.41 (m, 3H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.33 (s, 1H), 3.67 (s, 1H), 3.47 – 3.45 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 167.9, 142.9, 142.3, 138.7 (2), 138.4, 129.4, 129.0, 128.5 (2), 128.4, 127.8 (2), 127.7, 127.6 (2), 126.3, 101.0, 75.6, 74.7, 74.6, 73.6, 73.2 (2), 70.8, 57.8; HRMS (ESI) *m/z* calcd for $C_{40}H_{39}NO_6Na$ $[M + Na]^+$ 652.2675, found 652.2670.



12v

2-(2-Oxo-2-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethyl)isoindoline-1,3-dione (12v).

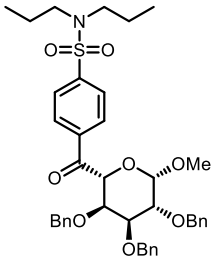
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 2-(1,3-dioxoisoindolin-2-yl)ethanethioate[3] (29.7 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **12v** (51.5 mg, 83%) as a colorless oil: $[\alpha]_D^{20}$ = +75.7 (c = 2.36, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.75 – 7.71 (m, 2H), 7.37 – 7.21 (m, 15H), 4.90 (d, *J* = 18.5 Hz, 1H), 4.83 – 4.79 (m, 2H), 4.73 (d, *J* = 12.4 Hz, 1H), 4.65 – 4.61 (m, 2H), 4.55 – 4.48 (m, 3H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.14 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.73 (dd, *J* = 5.2, 2.8 Hz, 1H), 3.67 (dd, *J* = 5.4, 1.7 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 199.6, 167.8, 138.3, 138.2, 137.9, 134.1, 132.3, 128.5 (3), 127.9 (2), 127.8, 123.5, 100.8, 77.3, 75.4, 74.7, 73.8, 73.7, 73.4, 73.1, 58.1, 44.7; HRMS (ESI) *m/z* calcd for $C_{37}H_{35}NO_8Na$ $[M + Na]^+$ 644.2260, found 644.2253.



12w

2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-one (12w).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)ethanethioate[4] (45.0 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **12w** (57.1 mg, 74%) as a yellow solid: $[\alpha]_D^{20}$ = +43.6 (c = 2.03, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.19 (m, 15H), 6.96 (s, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 1H), 4.83 – 4.77 (m, 2H), 4.63 – 4.59 (m, 2H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.43 – 4.37 (m, 3H), 4.10 (d, *J* = 7.7 Hz, 1H), 4.05 (d, *J* = 15.9 Hz, 1H), 3.87 (d, *J* = 16.0 Hz, 1H), 3.81 – 3.73 (m, 5H), 3.59 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 203.5, 168.3, 156.2, 139.2, 138.5, 138.2, 137.9, 136.3, 134.0, 131.2, 130.9, 129.2, 128.5 (2), 128.4, 128.1, 127.9 (3), 115.0, 112.4, 111.8, 101.5, 101.3, 76.8, 75.5, 74.3, 73.9, 73.8, 73.2, 72.5, 58.1, 55.7, 35.3, 13.7; HRMS (ESI) *m/z* calcd for $C_{46}H_{44}NO_8ClNa$ $[M + Na]^+$ 796.2653, found 796.2649.

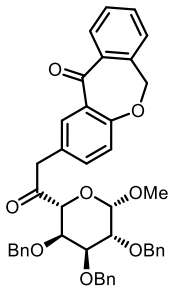


12x

***N*,*N*-Dipropyl-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbonyl)benzenesulfonamide (12x)**

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzothioate[5, 6] (37.8 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **12x** (63.6 mg, 91%) as a colorless oil: $[\alpha]_D^{20}$ = +16.3 (c = 3.45, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.29 (m, 15H), 4.96 (d, *J* = 4.8 Hz, 1H, H-5), 4.75 – 4.70 (m, 6H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.48 – 4.45 (m, 1H), 4.04 (d, *J* = 7.8 Hz, 1H), 3.92 (d, *J* = 7.9 Hz, 1H), 3.10 (t, *J* = 7.7 Hz, 4H), 2.93 (s, 3H), 1.57 – 1.50 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.8, 144.1, 138.5, 138.1, 138.0, 129.9,

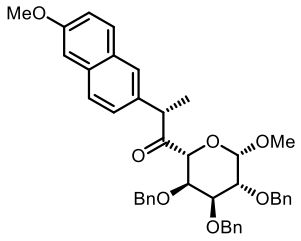
128.5, 128.1, 128.0, 127.9 (2), 127.8 (2), 127.1, 101.8, 75.9, 75.7, 75.0, 73.9 (2), 73.4, 73.2, 57.9, 49.8, 21.9, 11.2; HRMS (ESI) *m/z* calcd for $C_{40}H_{47}NO_8SNa$ [M + Na]$^+$ 724.2920, found 724.2912.



12y

2-(2-Oxo-2-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethyl)dibenzo[*b*,*e*]oxepin-11(6*H*)-one (12y).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)ethanethioate[4] (36.0 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **12y** (50.3 mg, 73%) as a pale yellow oil: $[a]_D^{20}$ = +53.6 (c = 1.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.25 (m, 17H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 2H), 4.82 – 4.77 (m, 2H), 4.61 (t, *J* = 13.1 Hz, 2H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.35 (d, *J* = 7.6 Hz, 1H, H-5), 4.12 (dd, *J* = 7.6, 2.4 Hz, 1H), 3.98 (d, *J* = 16.7 Hz, 1H), 3.88 (d, *J* = 16.7 Hz, 1H), 3.80 (dd, *J* = 5.5, 2.5 Hz, 1H), 3.73 (d, *J* = 5.9 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 204.4, 190.9, 160.4, 140.6, 138.5, 138.2, 137.9, 137.0, 135.6, 132.9, 132.8, 129.5, 129.3, 128.5 (3), 128.3, 128.0, 127.9 (2), 127.8 (2), 127.7, 125.2, 121.0, 101.2, 77.2, 75.5, 74.3, 73.9, 73.7, 73.6, 73.2, 72.5, 58.2, 44.7; HRMS (ESI) *m/z* calcd for $C_{43}H_{40}O_8Na$ [M + Na]$^+$ 707.2621, found 707.2610.

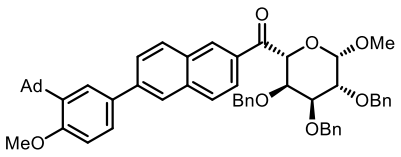


12z

(*S*)-2-(6-Methoxynaphthalen-2-yl)-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)propan-1-one (12z).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanethioate[5, 6] (32.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 2:1) **12z** (60.2 mg, 93%) as a white solid: $[a]_D^{20}$ = +154 (c = 2.41, $CHCl_3$); ^{1}H

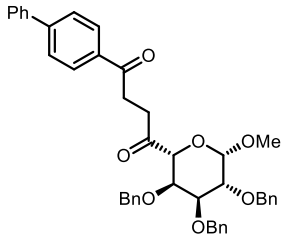
NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.61 (s, 1H), 7.38 – 7.26 (m, 11H), 7.19 – 7.12 (m, 7H), 4.76 (d, *J* = 2.4 Hz, 1H), 4.73 (s, 2H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.61 – 4.48 (m, 4H), 4.22 (dd, *J* = 5.2, 2.9 Hz, 1H), 4.18 (d, *J* = 5.3 Hz, 1H, H-5), 3.94 – 3.90 (m, 4H), 3.83 (dd, *J* = 7.7, 2.3 Hz, 1H), 3.58 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 207.5, 157.8, 138.7, 138.5, 138.1, 135.5, 133.8, 129.4, 129.2, 128.5, 128.4, 128.3, 128.0 (2), 127.8 (2), 127.6 (2), 126.8, 126.6, 119.1, 105.7, 101.8, 75.9, 75.2, 75.0, 73.9, 73.4, 73.1, 73.0, 58.5, 55.4, 47.9, 17.2; HRMS (ESI) *m/z* calcd for $C_{41}H_{42}O_7Na$ $[M + Na]^+$ 669.2828, found 669.2819.



12aa

(6-(3-(Adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (12aa).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 6-(3-(adamantan-1-yl)-4-methoxyphenyl)naphthalene-2-carbothioate[7] (50.5 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **12aa** (81.2 mg, 98%) as a pale yellow solid: $[\alpha]_D^{20}$ = +25.0 (c = 3.71, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.09 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.01 (s, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.80 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.56 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.44 – 7.27 (m, 14H), 7.23 (s, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 5.18 (d, *J* = 4.3 Hz, 1H, H-5), 4.81 – 4.78 (m, 5H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.60 (t, *J* = 3.7 Hz, 1H), 4.20 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.01 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.90 (s, 3H), 2.89 (s, 3H), 2.21 (s, 6H), 2.13 (s, 3H), 1.83 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.9, 159.0, 141.8, 139.1, 138.8 (2), 138.4, 136.0, 132.6, 132.4, 131.2 (2), 130.2, 128.5, 128.4 (3), 128.1, 128.0, 127.9, 127.7 (3), 126.6, 126.1, 125.8, 125.2, 124.8, 112.2, 101.8, 77.4, 76.0, 75.8, 75.6, 74.5, 73.8, 73.4, 73.3, 57.9, 55.2, 40.7, 37.3, 37.2, 29.2; HRMS (ESI) *m/z* calcd for $C_{55}H_{56}O_7Na$ $[M + Na]^+$ 851.3924, found 851.3915.

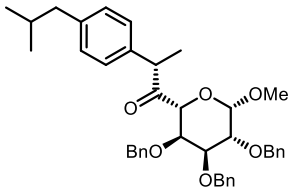


12ab

1-([1,1'-Biphenyl]-4-yl)-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)butane-1,4-dione (12ab).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanethioate **S5** (34.6 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under

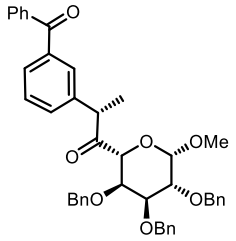
Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **12ab** (55.7 mg, 83%) as a pale yellow solid: $[\alpha]_D^{20}$ = +51.9 (c = 2.21, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.43 – 7.28 (m, 16H), 4.83 – 4.79 (m, 2H), 4.68 – 4.53 (m, 5H), 4.46 (d, *J* = 7.6 Hz, 1H, H-5), 4.21 (dd, *J* = 7.5, 2.1 Hz, 1H), 3.84 (dd, *J* = 5.4, 2.2 Hz, 1H), 3.76 (d, *J* = 5.8 Hz, 1H), 3.57 (s, 3H), 3.38 – 3.27 (m, 2H), 3.21 – 3.07 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.4, 198.1, 145.8, 140.0, 138.6, 138.3, 138.1, 135.5, 129.0, 128.7, 128.5, 128.4, 128.3 (2), 127.9 (2), 127.8 (3), 127.3 (2), 101.1, 77.9, 75.6, 74.5, 73.9, 73.8, 73.2, 72.5, 57.9, 33.3, 32.3; HRMS (ESI) *m/z* calcd for $C_{43}H_{42}O_7Na$ $[M + Na]^+$ 693.2828, found 693.2821.



12ac

(*S*)-2-(4-Isobutylphenyl)-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)propan-1-one (12ac).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl (*S*)-2-(4-isobutylphenyl)propanethioate **S6** (29.8 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **12ac** (60.8 mg, 98%) as a colorless oil: $[\alpha]_D^{20}$ = +134 (c = 1.60, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 13H), 7.19 – 7.17 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.70 (dd, *J* = 11.2, 2.4 Hz, 3H), 4.63 – 4.49 (m, 4H), 4.36 – 4.31 (m, 1H), 4.19 – 4.16 (m, 2H), 3.86 (dd, *J* = 7.6, 2.1 Hz, 1H), 3.78 (dd, *J* = 7.6, 2.5 Hz, 1H), 3.52 (s, 3H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.88 – 1.80 (m, 1H), 1.37 (d, *J* = 7.0 Hz, 3H), 0.90 – 0.89 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 207.6, 140.7, 138.7, 138.6, 138.3, 137.6, 129.8, 128.5, 128.4 (2), 128.1, 128.0, 127.9, 127.8 (2), 127.7 (2), 101.8, 75.9, 75.2 (2), 73.9, 73.4, 73.2, 72.9, 58.4, 47.7, 45.1, 30.3, 22.5 (2), 17.2; HRMS (ESI) *m/z* calcd for $C_{40}H_{46}O_6Na$ $[M + Na]^+$ 645.3192, found 645.3189.

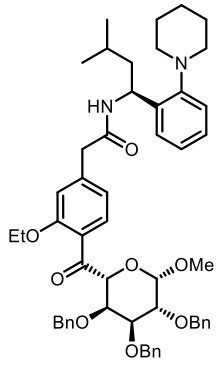


12ad

(*S*)-2-(3-benzoylphenyl)-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)propan-1-one (12ad).

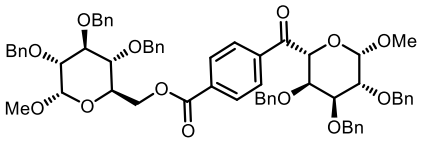
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl (*S*)-2-(3-benzoylphenyl)propanethioate **S7** (34.6 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated

under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **12ad** (59.9 mg, 89%) as a colorless oil: $[a]_D^{20}$ = +110 (c = 2.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.73 (s, 1H), 7.69 (d, *J* = 7.3 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.35 – 7.23 (m, 15H), 4.73 (d, *J* = 12.8 Hz, 2H), 4.66 – 4.62 (m, 2H), 4.57 – 4.45 (m, 4H), 4.18 (s, 2H), 3.83 (d, *J* = 6.7 Hz, 1H), 3.76 (d, *J* = 6.7 Hz, 1H), 3.52 (s, 3H), 1.44 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 206.7, 196.4, 140.7, 138.5, 138.4, 138.2, 138.1, 137.5, 132.6, 132.0, 130.1, 129.9, 129.0, 128.9, 128.4 (4), 128.1, 127.9, 127.8 (3), 127.7, 101.6, 75.7, 75.4, 74.8, 73.9, 73.4, 73.2, 72.9, 58.3, 47.9, 17.3; HRMS (ESI) *m/z* calcd for $C_{43}H_{42}O_7Na$ $[M + Na]^+$ 693.2828, found 693.2823.



12ae

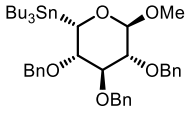
2-(3-ethoxy-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbonyl)phenyl)-*N*-((*S*)-3-methyl-1-(2-(piperidin-1-yl)phenyl)butyl)acetamide (12ae).
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl (*S*)-2-ethoxy-4-(2-((3-methyl-1-(2-(piperidin-1-yl)phenyl)butyl)amino)-2-oxoethyl)benzothioate[7] (54.5 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 2:1) **12ae** (80.4 mg, 93%) as a yellow oil: $[a]_D^{20}$ = +4.93 (c = 2.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.19 (m, 17H), 7.07 – 7.03 (m, 2H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.83 (s, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 5.42 – 5.37 (m, 1H), 5.26 (d, *J* = 4.2 Hz, 1H, H-5), 4.76 – 4.66 (m, 6H), 4.63 (d, *J* = 2.4 Hz, 1H), 4.52 – 4.51 (m, 1H), 4.08 – 3.91 (m, 4H), 3.52 (s, 2H), 2.98 – 2.92 (m, 2H), 2.84 (s, 3H), 2.64 – 2.61 (m, 2H), 1.77 – 1.71 (m, 2H), 1.68 – 1.37 (m, 10H), 0.92 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 199.2, 168.8, 158.2, 152.6, 141.4, 138.9, 138.8, 138.7, 138.6, 132.2, 128.4, 128.0 (2), 127.8, 127.7, 127.6, 127.5, 126.2, 125.1, 122.8, 121.4, 113.0, 101.7, 78.0, 75.9, 75.4, 74.6, 73.8, 73.1, 73.0, 64.4, 57.7, 49.7, 46.7, 44.3, 26.8, 25.4, 24.2, 22.8, 22.6, 14.7; HRMS (ESI) *m/z* calcd for $C_{54}H_{65}N_2O_8$ $[M + H]^+$ 869.4741, found 869.4734.



12af

((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methyl 4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbonyl)benzoate (12af)

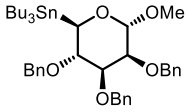
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), ((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methyl 4-((phenylthio)carbonyl)benzoate **S10** (70.5 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 3:1) **12af** (81.6 mg, 79%) as a colorless oil: $[\alpha]_D^{20}$ = +42.4 (c = 3.62, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 4H), 7.38 – 7.19 (m, 30H), 5.03 (d, *J* = 10.7 Hz, 1H), 4.97 (d, *J* = 4.6 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.85 (d, *J* = 10.7 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.75 – 4.67 (m, 7H), 4.63 – 4.61 (m, 3H), 4.54 (dd, *J* = 12.0, 2.2 Hz, 1H), 4.50 – 4.46 (m, 2H), 4.08 – 4.05 (m, 2H), 3.97 – 3.92 (m, 2H), 3.61 – 3.57 (m, 2H), 3.39 (s, 3H), 2.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.4, 165.4, 138.9, 138.6 (2), 138.5, 138.2, 138.1, 137.8, 133.4, 129.7, 129.2, 128.6 (3), 128.4 (2), 128.2 (2), 128.1 (2), 128.0, 127.9 (3), 127.8 (2), 127.7, 101.8, 98.1, 82.2, 80.1, 77.5, 76.0, 75.8, 75.7, 75.3, 75.1, 74.1, 73.8, 73.5, 73.4, 73.3, 68.7, 64.0, 58.0, 55.3; HRMS (ESI) *m/z* calcd for $C_{63}H_{64}O_{13}Na$ $[M + Na]^+$ 1051.4245, found 1051.4252.



9e'

Tributyl((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane (9e')

A solution of (2*S*,3*S*,4*S*,5*R*,6*R*)-4,5-bis(benzyloxy)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-ol[1] (311 mg, 0.491 mmol) in anh. THF (3.00 mL) was cooled to 0 °C, and a solution of KHMDS (0.983 mL, 0.983 mmol, 1.0 M in THF) was added at 0 °C. After stirring for 0.5 h, BnBr (0.117 mL, 0.983 mmol) was added, and the reaction mixture was stirred at 0 °C for additional 0.5 h and then at rt overnight. The resulting solution was concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 then 20:1) to afford **9e'** (262 mg, 74%) as a colorless oil: $[\alpha]_D^{20}$ = -38.9 (c = 0.95, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 15H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.83 (t, *J* = 11.9 Hz, 2H), 4.71 (t, *J* = 11.8 Hz, 2H), 4.58 (d, *J* = 11.4 Hz, 1H), 4.48 (d, *J* = 6.1 Hz, 1H, H-5), 4.41 (d, *J* = 6.1 Hz, 1H), 3.81 (t, *J* = 6.6 Hz, 1H), 3.71 (dd, *J* = 9.3, 7.4 Hz, 1H), 3.47 – 3.44 (m, 4H), 1.49 – 1.43 (m, 6H), 1.31 – 1.23 (m, 6H), 0.92 – 0.82 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.9, 138.7, 138.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6 (2), 105.5, 83.3, 82.5, 82.2, 75.1, 74.1, 73.2, 70.8, 55.9, 29.2, 27.6, 13.8, 10.4; HRMS (ESI) *m/z* calcd for $C_{39}H_{56}O_5SnNa$ $[M + Na]^+$ 747.3047, found 747.3062.

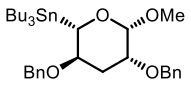


9f

Tributyl((2*R*,3*S*,4*R*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane (9f)

A solution of (2*R*,3*S*,4*S*,5*S*,6*S*)-4,5-bis(benzyloxy)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-ol[1] (506 mg, 0.799 mmol) in anh. THF (5.00 mL) was cooled to 0 °C, and a solution of KHMDS (1.60 mL, 1.60 mmol, 1.0 M in THF) was added at 0 °C. After stirring for 0.5 h, BnBr (0.200 mL, 1.60 mmol) was added, and the reaction mixture was stirred at 0 °C for additional 0.5

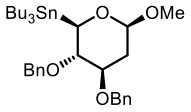
h and then at rt overnight. The resulting solution was concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 then 20:1) to afford **9f** (546 mg, 94%) as a colorless oil: $[a]_D^{20}$ = +19.3 (c = 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.39 (m, 2H), 7.34 – 7.26 (m, 13H), 5.10 (d, *J* = 11.1 Hz, 1H), 4.76 (d, *J* = 12.4 Hz, 1H), 4.71 (d, *J* = 12.4 Hz, 1H), 4.67 (s, 1H), 4.63 – 4.61 (m, 2H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.14 – 4.10 (m, 1H), 3.85 – 3.82 (m, 3H), 3.30 (s, 3H), 1.56 – 1.45 (m, *J* = 7.5 Hz, 6H), 1.32 – 1.25 (m, 6H), 1.01 – 0.85 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.1, 138.8, 138.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6 (2), 127.4, 100.0, 82.5, 77.6, 75.2, 74.4, 72.7, 71.8, 65.1, 54.7, 29.3, 27.6, 13.8, 9.2; HRMS (ESI) *m/z* calcd for $C_{39}H_{56}O_5SnNa$ $[M + Na]^+$ 747.3042, found 747.3040.



9h

((2*S*,3*R*,5*R*,6*S*)-3,5-Bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)tributylstannane (9h).

A solution of (2*S*,3*R*,5*R*,6*S*)-5-(benzyloxy)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-ol[1] (611 mg, 1.16 mmol) in anh. THF (7.20 mL) was cooled to 0 °C, and a solution of KHMDS (2.30 mL, 2.30 mmol, 1.0 M in THF) was added at 0 °C. After stirring for 0.5 h, BnBr (0.300 mL, 2.53 mmol) was added, and the reaction mixture was stirred at 0 °C for additional 0.5 h and then at rt overnight. The resulting solution was concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 then 20:1) to afford **9h** (590 mg, 83%) as a colorless oil: $[a]_D^{20}$ = -2.29 (c = 0.88, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 10H), 4.77 (d, *J* = 12.7 Hz, 1H), 4.60 (d, *J* = 12.7 Hz, 1H), 4.43 (d, *J* = 11.6 Hz, 1H), 4.37 – 4.34 (m, 2H), 3.88 – 3.84 (m, 1H), 3.80 – 3.76 (m, 2H), 3.50 (s, 3H), 2.33 – 2.29 (m, 1H), 1.58 – 1.44 (m, 7H), 1.32 – 1.25 (m, 6H), 0.96 – 0.84 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.3, 138.6, 128.4 (2), 127.9, 127.8, 127.6 (2), 104.0, 74.8, 73.7, 72.6, 72.3, 70.5, 57.3, 33.1, 29.3, 27.6, 13.8, 9.4; HRMS (ESI) *m/z* calcd for $C_{32}H_{50}O_4SnNa$ $[M + Na]^+$ 641.2629, found 641.2628.

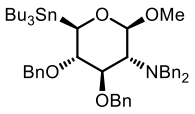


9i

((2*R*,3*S*,4*R*,6*R*)-3,4-bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)tributylstannane (9i).

A solution of (2*R*,3*S*,4*R*,6*R*)-4-(benzyloxy)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-ol[1] (171 mg, 0.324 mmol) in anh. THF (2.00 mL) was cooled to 0 °C, and a solution of KHMDS (0.650 mL, 0.650 mmol, 1.0 M in THF) was added at 0 °C. After stirring for 0.5 h, BnBr (0.100 mL, 0.842 mmol) was added, and the reaction mixture was stirred at 0 °C for additional 0.5 h and then at rt overnight. The resulting solution was concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 then 30:1) to afford **9i** (196 mg, 98%) as a colorless oil: $[a]_D^{20}$ = -11.5 (c = 1.47, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 10H), 5.13 (d, *J* = 11.1 Hz, 1H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.61 (d, *J* = 11.1 Hz, 1H), 4.53 (d, *J* = 11.4 Hz, 1H), 4.17 (d, *J* = 9.5 Hz, 1H), 3.67 – 3.59 (m, 2H), 3.46 – 3.41 (m, 4H), 2.36 (dd, *J* = 12.2, 4.1 Hz, 1H), 1.55 – 1.43 (m, 7H), 1.30 – 1.23 (m, 6H), 0.96 – 0.84 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.9, 138.4, 128.6, 128.3, 128.0, 127.8 (2), 127.5, 103.9, 81.8, 81.0, 74.5, 71.0, 69.4, 56.6, 36.6,

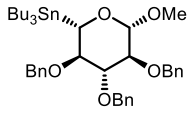
29.2, 27.6, 13.8, 9.2; HRMS (ESI) *m/z* calcd for $C_{32}H_{50}O_4SnNa$ [M + Na]$^+$ 641.2629, found 641.2625.



9j

(2*R*,3*R*,4*R*,5*S*,6*R*)-*N*,*N*-Dibenzyl-4,5-bis(benzyloxy)-2-methoxy-6-(tributylstannyl)tetrahydro-2*H*-pyran-3-amine (9j).

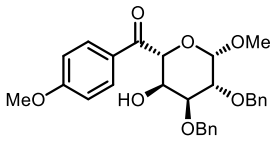
A solution of (2*R*,3*S*,4*R*,5*R*,6*R*)-4-(benzyloxy)-5-(dibenzylamino)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-ol[1] (511 mg, 0.707 mmol) in anh. THF (4.40 mL) was cooled to 0 °C, and a solution of KHMDS (1.40 mL, 1.40 mmol, 1.0 M in THF) was added at 0 °C. After stirring for 0.5 h, BnBr (0.200 mL, 1.68 mmol) was added, and the reaction mixture was stirred at 0 °C for additional 0.5 h and then at rt overnight. The resulting solution was concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 then 40:1) to afford **9j** (557 mg, 97%) as a colorless oil: $[a]_D^{20}$ = -13.9 (c = 2.81, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.21 (m, 20H), 5.14 (d, *J* = 11.1 Hz, 1H), 4.96 (d, *J* = 11.1 Hz, 1H), 4.82 (d, *J* = 11.1 Hz, 1H), 4.60 – 4.56 (m, 1H), 4.36 (d, *J* = 8.4 Hz, 1H), 4.09 (d, *J* = 13.8 Hz, 2H), 3.93 (d, *J* = 13.8 Hz, 2H), 3.74 – 3.66 (m, 2H), 3.59 (s, 3H), 3.46 (d, *J* = 10.8 Hz, 1H, H-5), 2.92 (t, *J* = 9.0 Hz, 1H), 1.54 – 1.44 (m, 6H), 1.33 – 1.25 (m, 6H), 0.99 – 0.87 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 140.1, 139.2, 138.6, 129.0, 128.5, 128.3 (2), 128.2, 127.9, 127.8, 127.5, 127.4, 127.3, 126.8, 106.7, 83.8, 82.6, 74.4, 74.2, 72.3, 69.0, 63.7, 56.3, 55.2, 29.2, 27.6, 13.8, 9.2; HRMS (ESI) *m/z* calcd for $C_{46}H_{64}NO_4Sn$ [M + H]$^+$ 814.3857, found 814.3864.



9l

Tributyl((2*S*,3*R*,4*S*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane (9l).

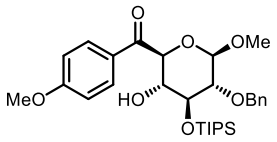
A solution of (2*S*,3*R*,4*R*,5*S*,6*S*)-4,5-bis(benzyloxy)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-ol **S8** (1.00 g, 1.58 mmol) in anh. THF (9.90 mL) was cooled to 0 °C, and a solution of KHMDS (3.20 mL, 3.20 mmol, 1.0 M in THF) was added at 0 °C. After stirring for 0.5 h, BnBr (0.400 mL, 3.37 mmol) was added, and the reaction mixture was stirred at 0 °C for additional 0.5 h and then at rt overnight. The resulting solution was concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 then 30:1) to afford **9l** (1.02 g, 89%) as a colorless oil: $[a]_D^{20}$ = -8.75 (c = 0.82, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 15H), 5.05 (d, *J* = 11.0 Hz, 1H), 4.97 – 4.93 (m, 2H), 4.75 – 4.69 (m, 2H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.14 (d, *J* = 7.1 Hz, 1H), 3.71 (t, *J* = 9.8 Hz, 1H), 3.59 (t, *J* = 8.2 Hz, 1H), 3.55 (s, 3H), 3.47 (d, *J* = 10.5 Hz, 1H, H-5), 3.41 (t, *J* = 8.0 Hz, 1H), 1.53 – 1.41 (m, 6H), 1.31 – 1.23 (m, 6H), 0.99 – 0.85 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.9, 138.7, 138.6, 128.5 (2), 128.4, 128.2, 128.1, 127.7, 127.6 (2), 107.9, 87.1, 83.1, 81.1, 75.6, 74.9, 74.4, 69.1, 57.0, 29.2, 27.6, 13.8, 9.2; HRMS (ESI) *m/z* calcd for $C_{39}H_{56}O_5SnNa$ [M + Na]$^+$ 747.3047, found 747.3050.



13a

((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-Bis(benzyloxy)-3-hydroxy-6-methoxytetrahydro-2*H*-pyran-2-yl)(4-methoxyphenyl)methanone (13a).

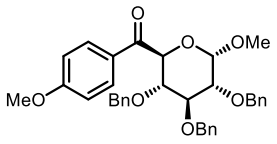
According to the general protocol A, (2*S*,3*R*,4*S*,5*R*,6*S*)-4,5-bis(benzyloxy)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-ol[1] (127 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 2:1) **13a** (29.5 mg, 62%) as a colorless oil: $[a]_D^{20}$ = +7.99 (c = 1.41, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.27 (m, 10H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.93 (d, *J* = 4.3 Hz, 1H, H-5), 4.77 – 4.67 (m, 6H), 4.13 (dd, *J* = 7.8, 3.0 Hz, 1H), 3.86 (s, 3H), 3.83 (dd, *J* = 7.9, 2.4 Hz, 1H), 2.98 (s, 3H), 2.86 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.1, 163.6, 138.5, 138.3, 131.8, 128.6, 128.5, 128.4, 128.0 (2), 127.9, 113.7, 101.6, 76.1, 75.4, 73.7, 73.5, 67.2, 57.9, 55.5; HRMS (ESI) *m/z* calcd for $C_{28}H_{30}O_7Na$ $[M + Na]^+$ 501.1889, found 501.1884.



13b

((2*S*,3*R*,4*S*,5*R*,6*R*)-5-(Benzyloxy)-3-hydroxy-6-methoxy-4-((triisopropylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)(4-methoxyphenyl)methanone (13b).

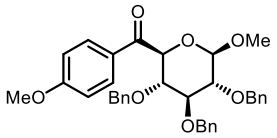
According to the general protocol A, (2*R*,3*S*,4*S*,5*R*,6*R*)-5-(benzyloxy)-6-methoxy-2-(tributylstannyl)-4-((triisopropylsilyl)oxy)tetrahydro-2*H*-pyran-3-ol[1] (140 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **13b** (28.9 mg, 53%) as a colorless oil: $[a]_D^{20}$ = +15.3 (c = 1.37, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.36 – 7.27 (m, 5H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.51 (d, *J* = 7.7 Hz, 1H), 4.36 (d, *J* = 9.2 Hz, 1H, H-5), 4.00 (t, *J* = 9.0 Hz, 1H), 3.93 (t, *J* = 8.6 Hz, 1H), 3.88 (s, 3H), 3.48 (s, 3H), 3.32 (t, *J* = 8.1 Hz, 1H), 2.82 (s, 1H), 1.19 – 1.15 (m, 3H), 1.09 – 1.07 (m, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.7, 164.2,139.1, 131.9, 128.4, 128.2, 127.7, 127.4, 113.9, 105.8, 82.6, 76.9, 75.4, 74.5, 72.1, 57.3, 55.6, 18.4 (2), 13.1; HRMS (ESI) *m/z* calcd for $C_{30}H_{44}O_7SiNa$ $[M + Na]^+$ 567.2754, found 567.2748.



13c

(4-Methoxyphenyl)((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (13c).

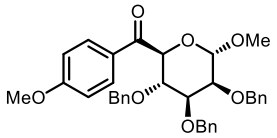
According to the general protocol A, tributyl((2*R*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **13c** (12.5 mg, 22%) as a colorless oil: $[a]_D^{20}$ = -2.87 (c = 0.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.28 (m, 10H), 7.19 – 7.13 (m, 3H), 6.93 – 6.90 (m, 4H), 5.08 (d, *J* = 9.7 Hz, 1H, H-5), 4.99 (d, *J* = 10.9 Hz, 1H), 4.87 – 4.82 (m, 2H), 4.70 – 4.65 (m, 3H), 4.41 (d, *J* = 10.4 Hz, 1H), 4.11 (t, *J* = 9.3 Hz, 1H), 3.92 – 3.87 (m, 4H), 3.64 (dd, *J* = 9.7, 3.4 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.6, 164.2, 138.8, 138.2, 137.9, 131.6, 129.5, 128.7, 128.5, 128.3, 128.2 (2), 128.0, 127.8, 127.7, 114.0, 99.5, 81.9, 80.0, 79.6, 76.0, 75.3, 73.8, 69.4, 56.4, 55.7; HRMS (ESI) *m/z* calcd for $C_{35}H_{36}O_7Na$ $[M + Na]^+$ 591.2359, found 591.2351.



13d

(4-Methoxyphenyl)((2*S*,3*S*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (13d).

According to the general protocol A, tributyl((2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **13d** (42.0 mg, 74%) as a white solid: $[a]_D^{20}$ = -11.5 (c = 2.17, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.40 – 7.30 (m, 10H), 7.22 – 7.21 (m, 3H), 7.07 – 7.05 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.99 – 4.95 (m, 2H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.78 – 4.75 (m, 2H), 4.67 (d, *J* = 9.4 Hz, 1H, H-5), 4.63 (d, *J* = 10.4 Hz, 1H), 4.53 (d, *J* = 7.6 Hz, 1H), 4.10 (t, *J* = 9.2 Hz, 1H), 3.89 (s, 3H), 3.83 (t, *J* = 9.1 Hz, 1H), 3.59 – 3.55 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 192.6, 164.1, 138.6, 138.5, 138.0, 131.6, 129.0, 128.5, 128.3, 128.2, 127.9, 127.8, 127.7, 113.9, 105.4, 84.5, 82.0, 79.0, 75.9, 75.1, 74.9, 74.7, 57.3, 55.6; HRMS (ESI) *m/z* calcd for $C_{35}H_{36}O_7Na$ $[M + Na]^+$ 591.2359, found 591.2355.

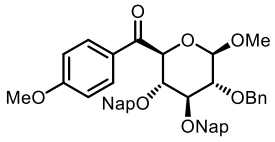


13e

(4-Methoxyphenyl)((2*S*,3*S*,4*S*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (13e).

According to the general protocol A, tributyl((2*R*,3*S*,4*R*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane **9f** (145 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **13e** (49.6 mg, 87%) as a white solid: $[a]_D^{20}$ = +27.2 (c = 1.90, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15

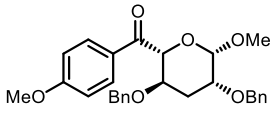
(d, *J* = 8.4 Hz, 2H), 7.44 – 7.30 (m, 10H), 7.23 – 7.20 (m, 3H), 7.11 – 7.09 (m, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 4.87 – 4.67 (m, 7H), 4.52 – 4.46 (m, 2H), 4.04 (dd, *J* = 9.1, 2.3 Hz, 1H), 3.88 – 3.86 (m, 4H), 3.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.1, 163.8, 138.6, 138.4, 138.2, 132.0, 128.9, 128.5, 128.2, 128.0, 127.8, 127.7, 127.6, 113.8, 100.2, 79.7, 76.2, 74.9, 73.9, 73.0, 72.5, 55.8, 55.5; HRMS (ESI) *m/z* calcd for $C_{35}H_{36}O_7Na$ [M + Na]$^+$ 591.2359, found 591.2354.



13f

((2*S*,3*S*,4*S*,5*R*,6*R*)-5-(Benzyloxy)-6-methoxy-3,4-bis(naphthalen-2-ylmethoxy)tetrahydro-2*H*-pyran-2-yl)(4-methoxyphenyl)methanone (13f).

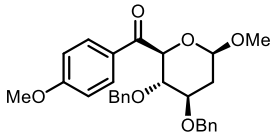
According to the general protocol A, ((2*R*,3*S*,4*R*,5*R*,6*R*)-5-(benzyloxy)-6-methoxy-3,4-bis(naphthalen-2-ylmethoxy)tetrahydro-2*H*-pyran-2-yl)tributylstannane[1] (165 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **13f** (52.5 mg, 79%) as a white solid: $[\alpha]_D^{20}$ = -64.5 (c = 2.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 2H), 7.86 – 7.75 (m, 5H), 7.65 – 7.58 (m, 2H), 7.52 – 7.31 (m, 11H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.17 (d, *J* = 11.3 Hz, 1H), 5.06 (d, *J* = 11.3 Hz, 1H), 5.01 (d, *J* = 11.1 Hz, 1H), 4.94 (d, *J* = 10.7 Hz, 1H), 4.82 (d, *J* = 11.1 Hz, 1H), 4.78 (d, *J* = 10.7 Hz, 1H), 4.74 (d, *J* = 9.5 Hz, 1H, H-5), 4.58 (d, *J* = 7.6 Hz, 1H), 4.19 (t, *J* = 9.2 Hz, 1H), 3.94 (t, *J* = 9.1 Hz, 1H), 3.84 (s, 3H), 3.68 – 3.65 (m, 1H), 3.58 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 192.8, 164.0, 138.5, 136.1, 135.4, 133.4, 133.2, 133.1, 133.0, 131.7, 128.9, 128.5, 128.2 (2), 128.0 (2), 127.8 (2), 127.6, 126.9, 126.6, 126.2, 126.1, 126.0, 125.9 (2), 125.8, 113.9, 105.4, 84.5, 82.0, 79.2, 75.9, 75.2, 74.9, 74.8, 57.3, 55.5; HRMS (ESI) m/z calcd for $C_{43}H_{40}O_7Na$ [M + Na]$^+$ 691.2672, found 691.2662.



13g

((2*R*,3*R*,5*R*,6*S*)-3,5-Bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)(4-methoxyphenyl)methanone (13g).

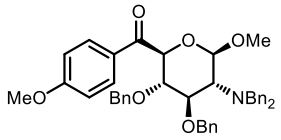
According to the general protocol A, ((2*S*,3*R*,5*R*,6*S*)-3,5-bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)tributylstannane **9h** (123 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **13g** (44.8 mg, 97%) as a colorless oil: $[\alpha]_D^{20}$ = +39.3 (c = 1.76, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.26 (m, 10H), 6.93 (d, *J* = 8.3 Hz, 2H), 4.77 (br, 1H, H-5), 4.62 – 4.51 (m, 5H), 4.41 – 4.39 (m, 1H), 3.92 – 3.89 (m, 1H), 3.86 (s, 3H), 2.88 (s, 3H), 2.30 – 2.24 (m, 1H), 2.08 – 2.03 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.9, 163.3, 138.6, 138.3, 131.7, 128.7, 128.5 (2), 127.9 (2), 127.8 (2), 113.6, 101.1, 76.0, 72.8, 71.7, 71.5, 71.3, 57.7, 55.5, 26.9; HRMS (ESI) *m/z* calcd for $C_{28}H_{30}O_6Na$ [M + Na]$^+$ 485.1940, found 485.1937.



13h

((2*S*,3*S*,4*R*,6*R*)-3,4-Bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)(4-methoxyphenyl)methanone (13h).

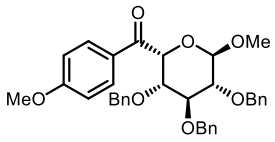
According to the general protocol A, ((2*R*,3*S*,4*R*,6*R*)-3,4-bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)tributylstannane **9i** (61.7 mg, 0.100 mmol), *S*-phenyl 4-methoxybenzothioate (48.9 mg, 0.200 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **13h** (38.2 mg, 83%) as a white solid: $[a]_D^{20}$ = -19.3 (c = 1.48, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.29 (m, 5H), 7.24 – 7.19 (m, 3H), 7.13 – 7.09 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.83 (d, *J* = 10.5 Hz, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.65 (d, *J* = 10.4 Hz, 1H), 4.59 (d, *J* = 9.3 Hz, 1H, H-5), 4.56 (dd, *J* = 9.6, 1.6 Hz, 1H), 4.01 (t, *J* = 9.0 Hz, 1H), 3.88 (s, 3H), 3.85 – 3.80 (m, 1H), 3.46 (s, 3H), 2.41 – 2.38 (m, 1H), 1.79 – 1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 192.8, 163.9, 138.4, 138.3, 131.7, 129.1, 128.6, 128.3, 128.2, 127.8 (2), 127.7, 113.9, 101.8, 79.1, 79.0, 75.1, 75.0, 71.8, 56.8, 55.6, 36.4; HRMS (ESI) *m/z* calcd for $C_{28}H_{30}O_6Na$ $[M + Na]^+$ 485.1940, found 485.1932.



13i

((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4-Bis(benzyloxy)-5-(dibenzylamino)-6-methoxytetrahydro-2*H*-pyran-2-yl)(4-methoxyphenyl)methanone (13i).

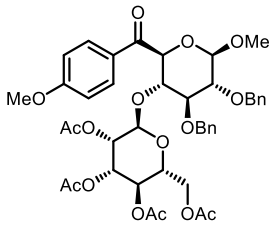
According to the general protocol A, (2*R*,3*R*,4*R*,5*S*,6*R*)-*N*,*N*-dibenzyl-4,5-bis(benzyloxy)-2-methoxy-6-(tributylstannyl)tetrahydro-2*H*-pyran-3-amine **9j** (163 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **13i** (65.1 mg, 99%) as a colorless oil: $[a]_D^{20}$ = -22.5 (c = 2.79, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.40 (m, 8H), 7.36 – 7.16 (m, 10H), 7.02 – 7.00 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.68 – 4.62 (m, 3H), 4.59 (d, *J* = 10.4 Hz, 1H), 4.14 (t, *J* = 9.0 Hz, 1H), 4.04 (d, *J* = 13.8 Hz, 2H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.86 – 3.83 (m, 5H), 3.40 (s, 3H), 3.09 (dd, *J* = 9.6, 6.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 193.3, 163.9, 139.7, 139.0, 138.1, 131.6, 129.0 (2), 128.4, 128.3 (2), 128.2, 127.7, 127.4, 127.0, 113.9, 103.7, 80.8, 79.4, 75.3, 74.8, 74.4, 63.8, 56.4, 55.6, 55.1; HRMS (ESI) *m/z* calcd for $C_{42}H_{43}NO_6Na$ $[M + Na]^+$ 680.2988, found 680.2980.



13j

(4-Methoxyphenyl)((2*R*,3*S*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (13j)

According to the general protocol A, tributyl((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane **9e'** (145 mg, 0.200 mmol), *S*-phenyl 4-methoxybenzothioate (24.4 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **13j** (8.10 mg, 14%) as a colorless oil: $[\alpha]_D^{20}$ = -6.5 (c = 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 7.35 – 7.27 (m, 10H), 7.20 – 7.13 (m, 3H), 6.99 – 6.97 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.25 (d, *J* = 4.8 Hz, 1H, H-5), 4.87 (d, *J* = 5.3 Hz, 1H), 4.83 (d, *J* = 11.3 Hz, 1H), 4.77 (d, *J* = 11.7 Hz, 1H), 4.67 (dd, *J* = 11.5, 3.6 Hz, 2H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.33 (d, *J* = 11.8 Hz, 1H), 4.09 (dd, *J* = 7.6, 6.2 Hz, 1H), 3.98 (dd, *J* = 6.2, 4.8 Hz, 1H), 3.87 (s, 3H), 3.52 (dd, *J* = 7.5, 5.4 Hz, 1H), 3.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.5, 163.7, 138.5 (2), 137.8, 131.1, 129.2, 128.5 (2), 128.3, 128.1, 128.0 (2), 127.9, 127.8, 127.7, 113.8, 102.6, 80.2, 79.2, 78.5, 74.5, 73.7, 73.4, 72.9, 56.5, 55.6; HRMS (ESI) *m/z* calcd for $C_{35}H_{36}O_7Na$ $[M + Na]^+$ 591.2359, found 591.2359.

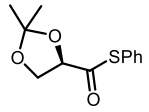


13k

(2*R*,3*R*,4*S*,5*S*,6*R*)-2-(Acetoxymethyl)-6-(((2*S*,3*S*,4*S*,5*R*,6*R*)-4,5-bis(benzyloxy)-6-methoxy-2-(4-methoxybenzoyl)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (13k)

According to the general protocol A, (2*R*,3*R*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)-6-(((2*R*,3*S*,4*R*,5*R*,6*R*)-4,5-bis(benzyloxy)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate[1] (771 mg, 0.080 mmol), *S*-phenyl 4-methoxybenzothioate (9.80 mg, 0.040 mmol), $Pd_2(dba)_3$ (0.900 mg, 0.0010 mmol), ligand **L6** (3.20 mg, 0.0040 mmol), CuCl (4.00 mg, 0.040 mmol) in 1,4-dioxane (0.800 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 1:1) **13k** (27.2 mg, 84%) as a colorless oil: $[\alpha]_D^{20}$ = +28.5 (c = 1.43, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.9 Hz, 2H), 7.30 – 7.21 (m, 8H), 7.19 – 7.16 (m, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 5.41 (d, *J* = 1.8 Hz, 1H), 5.21 (dd, *J* = 3.3, 1.6 Hz, 1H), 5.03 – 4.98 (m, 2H), 4.91 (d, *J* = 11.1 Hz, 1H), 4.85 (dd, *J* = 10.1, 3.4 Hz, 1H), 4.72 (d, *J* = 9.4 Hz, 1H), 4.68 (d, *J* = 11.1 Hz, 1H), 4.61 (d, *J* = 11.1 Hz, 1H), 4.49 (d, *J* = 7.5 Hz, 1H), 4.25 (t, *J* = 9.2 Hz, 1H), 4.00 (dd, *J* = 12.4, 4.4 Hz, 1H), 3.88 (s, 3H), 3.83 – 3.77 (m, 2H), 3.57 (dd, *J* = 9.0, 7.6 Hz, 1H), 3.50 (s, 3H), 3.21 – 3.18 (m, 1H), 2.10 (s, 3H), 1.91 – 1.89 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 192.2, 171.0, 170.0, 169.7, 169.6, 164.4, 138.2, 138.1, 131.6, 128.7, 128.5, 128.3, 128.2, 127.9, 127.5, 127.4, 114.3, 105.3, 98.1, 84.7, 82.0, 75.3 (2), 74.6, 73.7,

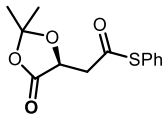
69.2, 69.0 (2), 65.3, 61.7, 57.4, 55.7, 20.9, 20.8, 20.7, 20.6; HRMS (ESI) *m/z* calcd for $C_{42}H_{48}O_{16}Na$ $[M + Na]^+$ 831.2840, found 831.2850.



15

***S*-Phenyl (*R*)-2,2-dimethyl-1,3-dioxolane-4-carbothioate (15).**

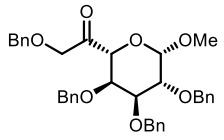
At room temperature, (*S*)-(2,2-dimethyl-1,3-dioxolan-4-yl)methanol (396 mg, 3.00 mmol) was dissolved in CH_2Cl_2 (18.0 mL) and H_2O (6.00 mL), then treated with TEMPO (70.3 mg, 0.450 mmol) and BAIB (1.93 g, 6.00 mmol). After vigorous stirring overnight, the reaction mixture was quenched with saturated $Na_2S_2O_3$ solution, extracted with CH_2Cl_2 (3 × 20.0 mL), washed once with brine, dried over Na_2SO_4, concentrated under reduced pressure, and used for next step without further purification. According to the general protocol *B*, this crude product, Ph_2S_2 (720 mg, 3.30 mmol), and P(*n*-Bu)$_3$ (0.816 mL, 3.30 mmol) were dissolved in anh. CH_2Cl_2 (30.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) afforded **15** (155 mg, 22%) as a white solid: $[\alpha]_D^{20}$ = +105.6 (c = 0.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 5H), 4.68 – 4.66 (m, 1H), 4.29 (t, *J* = 8.2 Hz, 1H), 4.18 (dd, *J* = 8.9, 4.4 Hz, 1H), 1.68 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 200.8, 134.8, 129.6, 129.4, 127.3, 112.3, 80.5, 68.2, 26.1, 25.2; HRMS (ESI) *m/z* calcd for $C_{12}H_{14}O_3SNa$ $[M + Na]^+$ 261.0561, found 261.0569.



16

***S*-Phenyl (*S*)-2-(2,2-dimethyl-5-oxo-1,3-dioxolan-4-yl)ethanethioate (16).**

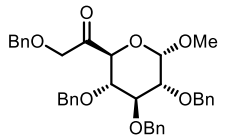
According to the general protocol B, (*S*)-2-(2,2-dimethyl-5-oxo-1,3-dioxolan-4-yl)acetic acid (348 mg, 2.00 mmol), Ph_2S_2 (480 mg, 2.20 mmol), and P(*n*-Bu)$_3$ (0.544 mL, 2.20 mmol) were dissolved in anh. CH_2Cl_2 (20.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) afforded **16** (446 mg, 84%) as a white solid: $[\alpha]_D^{20}$ = -17.5 (c = 0.82, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 5H), 4.77 (dd, *J* = 6.8, 3.5 Hz, 1H), 3.27 (dd, *J* = 16.7, 3.4 Hz, 1H), 3.11 (dd, *J* = 16.7, 6.9 Hz, 1H), 1.61 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 193.3, 172.0, 134.6, 129.9, 129.4, 126.9, 111.5, 70.6, 44.6, 27.0, 25.9; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_4SNa$ $[M + Na]^+$ 289.0510, found 289.0506.



17

2-(Benzyloxy)-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-one (17).

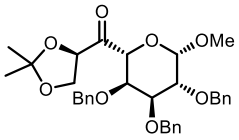
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 2-(benzyloxy)ethanethioate **14** (25.8 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **17** (52.0 mg, 89%) as a colorless oil: $[a]_D^{20}$ = +47.6 (c = 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 20H), 4.78 – 4.75 (m, 2H), 4.64 – 4.61 (m, 3H), 4.56 – 4.51 (m, 2H), 4.49 – 4.44 (m, 2H), 4.41 – 4.39 (m, 3H), 4.08 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.78 (dd, *J* = 5.4, 2.8 Hz, 1H), 3.68 (d, *J* = 5.0 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 203.5, 138.4, 138.1, 137.8, 137.5, 128.5 (3), 128.3, 128.0 (2), 127.9 (2), 127.8, 101.0, 75.4 (2), 74.2, 73.8, 73.7, 73.3, 73.2, 72.9, 72.5, 57.8; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 203.5, 138.4, 138.1, 137.8, 137.5, 128.5 (3), 128.3, 128.0 (2), 127.9 (2), 127.8, 101.0, 75.4 (2), 74.2, 73.8, 73.7, 73.3, 73.2, 72.9, 72.5, 57.8; HRMS (ESI) *m/z* calcd for $C_{36}H_{38}O_7Na$ $[M + Na]^+$ 605.2515, found 605.2514.



18

2-(Benzyloxy)-1-((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-one (18).

According to the general protocol A, tributyl((2*R*,3*S*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl 2-(benzyloxy)ethanethioate **14** (25.8 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **18** (88.0 mg, 50%) as a colorless oil: $[a]_D^{20}$ = +4.66 (c = 1.60, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 20H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.85 – 4.80 (m, 3H), 4.70 – 4.53 (m, 5H), 4.31 – 4.22 (m, 3H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.72 (t, *J* = 9.4 Hz, 1H), 3.54 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 203.6, 138.6, 138.0, 137.9, 137.2, 128.6 (2), 128.5 (2), 128.3, 128.2 (2), 128.1, 128.0 (2), 127.9, 127.8, 98.9, 81.8, 79.5, 78.7, 76.0, 75.3, 74.0, 73.7, 73.4, 71.0, 55.8; HRMS (ESI) *m/z* calcd for $C_{36}H_{38}O_7Na$ $[M + Na]^+$ 605.2515, found 605.2507.

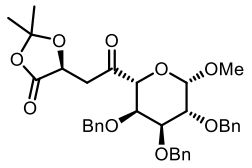


19

((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (19).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl (*R*)-2,2-dimethyl-1,3-dioxolane-4-carbothioate **15** (23.8 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **19** (38.0 mg, 68%) as a white solid: $[a]_D^{20}$ = +72.8 (c = 0.21, $CHCl_3$); ^{1}H NMR (500 MHz,

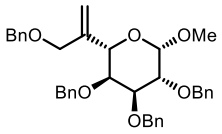
$CDCl_3$) δ 7.35 – 7.25 (m, 15H), 4.83 (t, *J* = 6.5 Hz, 1H), 4.80 (s, 1H), 4.75 (d, *J* = 12.4 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 4.60 (d, *J* = 7.8 Hz, 1H, H-5), 4.58 – 4.49 (m, 4H), 4.20 (t, *J* = 7.9 Hz, 1H), 4.15 – 4.12 (m, 2H), 3.77 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.69 (d, *J* = 5.7 Hz, 1H), 3.52 (s, 3H), 1.43 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 203.9, 138.5, 138.3, 138.1, 128.5, 128.3, 127.9 (2), 127.8 (2), 110.9, 101.3, 78.5, 75.6, 74.5, 74.1, 73.9, 73.4, 73.3, 72.8, 65.8, 57.9, 26.1, 25.6; HRMS (ESI) *m/z* calcd for $C_{33}H_{38}O_8Na$ $[M + Na]^+$ 585.2464, found 585.2456.



20

(*S*)-2,2-dimethyl-5-(2-oxo-2-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethyl)-1,3-dioxolan-4-one (20).

According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl (*S*)-2-(2,2-dimethyl-5-oxo-1,3-dioxolan-4-yl)ethanethioate **16** (26.6 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 4:1) **20** (51.5 mg, 87%) as a colorless oil: $[a]_D^{20}$ = +73.9 (c = 0.21, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 15H), 4.81 (dd, *J* = 6.6, 3.7 Hz, 1H), 4.77 (d, *J* = 1.8 Hz, 1H), 4.74 (d, *J* = 12.4 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 4.57 – 4.52 (m, 3H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.32 (d, *J* = 7.8 Hz, 1H, H-5), 4.06 (dd, *J* = 7.8, 2.7 Hz, 1H), 3.76 (dd, *J* = 5.6, 2.7 Hz, 1H), 3.69 (dd, *J* = 5.7, 1.8 Hz, 1H), 3.53 (s, 3H), 3.27 (dd, *J* = 18.2, 3.6 Hz, 1H), 3.14 (dd, *J* = 18.3, 6.7 Hz, 1H), 1.60 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 202.8, 172.9, 138.4, 138.2, 137.9, 128.5 (2), 128.4, 127.9 (2), 127.8, 111.1, 100.9, 78.0, 75.5, 74.5, 73.8, 73.5, 73.3, 72.7, 69.8, 58.0, 40.5, 26.9, 25.9; HRMS (ESI) *m/z* calcd for $C_{34}H_{38}O_9Na$ $[M + Na]^+$ 613.2414, found 613.2411.

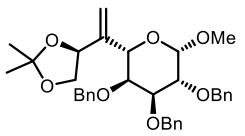


21

(2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-2-(3-(benzyloxy)prop-1-en-2-yl)-6-methoxytetrahydro-2*H*-pyran (21).

Under N_2, 2-(benzyloxy)-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-one **17** (39.6 mg, 0.068 mmol) was dissolved in THF (3.40 ml), then $TMSCH_2MgCl$ (0.105 ml, 0.136 mmol, 1.3 M in THF) was added at 0 ºC. The solution was warmed up to room temperature, stirred overnight, quenched with H_2O, and extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), concentrated, and directly to use next step without further purification. The crude material was dissolved with THF (3.40 mL), KHMDS was added (0.136 ml, 0.136 mmol, 1.0 M in THF) at 0 ºC. The solution was warmed up to room temperature and stirred overnight, quenched with H_2O, and extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 8:1) to yield **21** (32.1 mg, 81%) as a pale yellow oil:

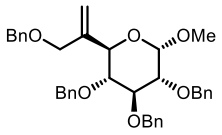
$[a]_D^{20}$ = +43.2 (c = 1.63, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 20H), 5.44 (s, 2H), 4.82 (d, *J* = 12.6 Hz, 1H), 4.76 (s, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.48 – 4.45 (m, 2H), 4.40 – 4.37 (m, 2H), 4.31 (d, *J* = 11.7 Hz, 1H), 4.22 – 4.16 (m, 2H), 3.79 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.73 (t, *J* = 3.4 Hz, 1H), 3.60 (d, *J* = 3.5 Hz, 1H), 3.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.5, 138.8 (2), 138.4, 138.3, 128.4 (4), 128.0 (2), 127.9, 127.8, 127.7 (2), 127.5, 115.0, 100.6, 76.1, 75.7, 74.2, 74.0, 73.7, 73.1, 72.4, 71.9, 70.6, 57.3; HRMS (ESI) *m/z* calcd for $C_{37}H_{40}O_6Na$ $[M + Na]^+$ 603.2723, found 603.2719.



22

(2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-2-(1-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-6-methoxytetrahydro-2*H*-pyran (22).

Under N_2, ((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone **19** (44.6 mg, 0.079 mmol) was dissolved in THF (4.00 ml), then $TMSCH_2MgCl$ (0.122 ml, 0.159 mmol, 1.3 M in THF) was added at 0 ºC. The solution was warmed up to room temperature, stirred overnight, quenched with H_2O, and extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), concentrated, and directly to use next step without further purification. The crude material was dissolved with THF (4.00 mL), KHMDS was added (0.159 ml, 0.159 mmol, 1.0 M in THF) at 0 ºC. The solution was warmed up to room temperature and stirred overnight, quenched with H_2O, and extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 5:1) to yield **22** (28.5 mg, 64%) as a white solid: $[a]_D^{20}$ = +65.5 (c = 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 15H), 5.56 (s, 1H), 5.42 (s, 1H), 4.84 (d, *J* = 12.6 Hz, 1H), 4.74 – 4.71 (m, 2H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.48 – 4.43 (m, 2H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.30 (d, *J* = 11.5 Hz, 1H), 4.23 (d, *J* = 9.3 Hz, 1H, H-5), 4.15 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.76 – 3.72 (m, 2H), 3.69 (t, *J* = 8.0 Hz, 1H), 3.61 (d, *J* = 3.2 Hz, 1H), 3.51 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 144.5, 138.8, 138.2, 138.0, 128.5 (2), 128.4, 128.0 (2), 127.9 (2), 127.8 (2), 113.8, 109.0, 100.7, 77.2, 76.7, 75.6, 73.9, 73.1, 72.7, 71.7, 70.1, 57.4, 26.5, 26.2; HRMS (ESI) *m/z* calcd for $C_{34}H_{40}O_7Na$ $[M + Na]^+$ 583.2672, found 583.2670.

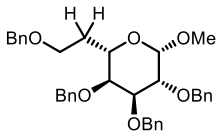


23

(2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-2-(3-(benzyloxy)prop-1-en-2-yl)-6-methoxytetrahydro-2*H*-pyran (23).

Under N_2, 2-(benzyloxy)-1-((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-one **18** (27.1 mg, 0.047 mmol) was dissolved in THF (2.30 ml), then $TMSCH_2MgCl$ (0.072 ml, 0.093 mmol, 1.3 M in THF) was added at 0 ºC. The solution was warmed up to room temperature, stirred overnight, quenched with H_2O, and extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), concentrated, and directly to use next step without further purification. The crude material was dissolved with THF (2.30 mL), KHMDS

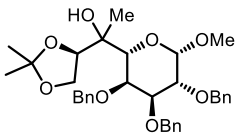
was added (0.093 ml, 0.093 mmol, 1.0 M in THF) at 0 ºC. The solution was warmed up to room temperature and stirred overnight, quenched with H_2O, and extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 4:1) to yield **23** (17.5 mg, 65%) as a pale yellow oil: $[a]_D^{20}$ = -5.04 (c = 0.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 20H), 5.43 (s, 1H), 5.38 (s, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.84 – 4.80 (m, 2H), 4.76 (d, *J* = 10.7 Hz, 1H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.61 – 4.57 (m, 2H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.17 (d, *J* = 9.9 Hz, 1H, H-5), 4.09 (d, *J* = 13.1 Hz, 1H), 4.04 (d, *J* = 13.1 Hz, 1H), 3.99 (t, *J* = 9.2 Hz, 1H), 3.56 – 3.49 (m, 2H), 3.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.2, 138.9, 138.4 (2), 128.6, 128.5 (2), 128.4, 128.2, 128.1, 128.0 (2), 127.7 (3), 116.3, 98.3, 82.2, 81.5, 80.0, 76.0, 74.9, 73.5, 72.5, 71.5, 70.6, 55.3; HRMS (ESI) *m/z* calcd for $C_{37}H_{40}O_6Na$ [M + Na]$^+$ 603.2723, found 603.2715.



24

(2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-2-(2-(benzyloxy)ethyl)-6-methoxytetrahydro-2*H*-pyran (24).

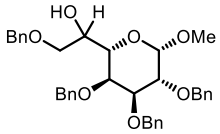
A solution of 2-(benzyloxy)-1-((2*S*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-ol **26** (45.2 mg, 0.077 mmol) in 1:1 THF:CS_2 (3.80 mL) was treated with a 60% dispersion of NaH in mineral oil (9.30 mg, 0.232 mmol) at 0 °C. The ice bath was removed after a brief period and the reaction mixture was stirred for 1 h at rt, then treated with CH_3I (0.048 mL, 0.773 mmol) and stirred overnight. The reaction mixture was quenched with saturated NH_4Cl solution (1.00 mL), extracted with CH_2Cl_2 (3 × 10.0 mL), washed with brine (4.00 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on SiO_2 (Hexanes:EtOAc, 4:1) to yield the xanthate (51.5 mg, 99%) as a yellow oil. This was redissolved in degassed toluene (3.00 mL) and treated with Bu_3SnH (0.110 mL, 0.409 mmol) and AIBN (6.30 mg, 0.038 mmol), then heated to 140 ºC and stirred for another 1 h. The reaction mixture was allowed to cool to rt, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on SiO_2 (Hexanes:EtOAc, 4:1) to yield **24** (29.6 mg, 68%) as a colorless oil: $[a]_D^{20}$ = +21.3 (c = 1.54, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 20H), 4.82 (d, *J* = 12.7 Hz, 1H), 4.68 (s, 1H), 4.56 – 4.46 (m, 5H), 4.42 – 4.36 (m, 2H), 4.00 – 3.96 (m, 1H), 3.72 – 3.66 (m, 3H), 3.62 (d, *J* = 3.9 Hz, 1H), 3.56 (dd, *J* = 9.4, 2.5 Hz, 1H), 3.46 (s, 3H), 2.32 – 2.25 (m, 1H), 1.86 – 1.79 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.8, 138.7, 138.3, 138.1, 128.4 (3), 128.1, 128.0 (2), 127.8 (2), 127.5, 100.3, 77.0, 75.5, 73.9, 73.6, 73.0, 72.9, 71.9, 70.1, 66.9, 57.0, 32.3; HRMS (ESI) *m/z* calcd for $C_{36}H_{40}O_6Na$ [M + Na]$^+$ 591.2723, found 591.2713.



25

1-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-ol (25).

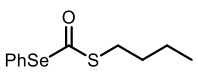
Under N_2, ((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone **19** (28.9 mg, 0.051 mmol) was dissolved in anhydrous THF (2.60 mL), then MeMgBr was added (0.051 ml, 0.154 mmol, 3.0 M in diethyl ether) at 0 ºC. The solution was warmed up to room temperature, stirred overnight, quenched with H_2O, and extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 2:1) to yield **25** (29.1 mg, 98%, d.r. = 2.3:1) as a colorless oil. Characterization data for the major configurational product: $[\alpha]_D^{20}$ = +32.6 (c = 1.31, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 13H), 7.23 – 7.21 (m, 2H), 4.83 – 4.78 (m, 2H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.4 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 11.4 Hz, 1H), 4.38 – 4.35 (m, 2H), 4.05 (dd, *J* = 8.5, 6.6 Hz, 1H), 3.98 – 3.94 (m, 2H), 3.87 (d, *J* = 8.6 Hz, 1H, H-5), 3.82 (dd, *J* = 4.9, 2.9 Hz, 1H), 3.68 (dd, *J* = 4.9, 1.5 Hz, 1H), 3.54 (s, 3H), 3.19 (s, 1H), 1.43 (s, 3H), 1.31 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.7, 138.2, 137.7, 128.6, 128.5 (2), 128.0 (2), 127.9, 109.0, 100.9, 78.4, 76.1, 75.7, 74.4, 74.2, 74.0, 73.2, 71.2, 65.1, 57.6, 26.5, 25.1, 19.4; HRMS (ESI) *m/z* calcd for $C_{34}H_{42}O_8Na$ $[M + Na]^+$ 601.2777, found 601.2772.



26

2-(Benzyloxy)-1-((2*S*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-ol (26).

Under N_2, 2-(benzyloxy)-1-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)ethan-1-one **17** (41.2 mg, 0.071 mmol) was dissolved in EtOH (3.50 ml), then $NaBH_4$ (53.5 mg, 1.41 mmol) was added at 0 ºC. The solution was allowed to warm to room temperature and stirred overnight. After removal of the solvent under reduced pressure, the residue was dissolved in ethyl acetate (16.0 mL) and successively washed with saturated aqueous NH_4Cl (4.00 mL) and 1 N HCl (4.00 mL). The aqueous layers were back-extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 2:1) to yield **26** (40.1 mg, 97%, d.r. = 4.7:1) as a colorless oil. Characterization data for the major configurational product: $[\alpha]_D^{20}$ = +22.4 (c = 0.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 20H), 4.81 (d, *J* = 12.6 Hz, 1H), 4.71 (d, *J* = 1.6 Hz, 1H), 4.55 – 4.46 (m, 5H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.32 (d, *J* = 11.5 Hz, 1H), 4.11 – 4.08 (m, 1H), 3.98 (dd, *J* = 8.7, 5.7 Hz, 1H, H-5), 3.91 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.78 (dd, *J* = 4.4, 2.8 Hz, 1H), 3.67 – 3.64 (m, 3H), 3.45 (s, 3H) , 3.25 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.6, 138.5, 138.2, 137.5, 128.6, 128.5 (2), 128.4, 128.2, 128.1 (2), 127.9, 127.6, 100.7, 75.8, 75.4, 74.1, 73.5, 73.3, 72.9, 72.7, 72.5, 71.3, 70.9, 57.3; HRMS (ESI) *m/z* calcd for $C_{36}H_{40}O_7Na$ $[M + Na]^+$ 607.2672, found 607.2667.

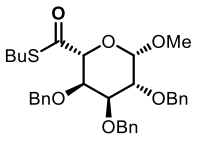


28

***Se*-Phenyl-*S*-butyl selenothiolate (28).**

Under N_2, Ph_2Se_2 (312 mg, 1.00 mmol) and $NaBH_4$ (75.7 mg, 2.00 mmol) were dissolved in anh. EtOAc (10.0 mL) and stirred at 40 °C for 1 h. The mixture was cooled to rt before the dropwise

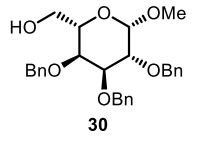
addition of *S*-butyl chlorothioformate (0.325 mL, 2.10 mmol). After 2 h, TLC indicated completion; the mixture was concentrated and purified by chromatography on SiO_2 (Hexanes) to afford **28** (458 mg, 84%) as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.9 Hz, 2H), 7.45 – 7.38 (m, 3H), 2.95 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.56 (m, 2H), 1.40 – 1.33 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 186.6, 136.7, 129.6 (2), 126.1, 31.7, 31.4, 21.9, 13.6; HRMS (ESI) *m/z* calcd for $C_{11}H_{15}OSSe$ $[M + H]^+$ 275.0009, found 275.0017.



29

***S*-Butyl (2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbothioate (29).**

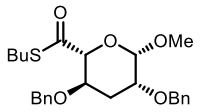
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *Se*-phenyl-*S*-butyl selenothiolate **28** (27.3 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **29** (52.9 mg, 96%) as a white solid: $[a]_D^{20}$ = +52.8 (c = 0.53, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 15H), 4.80 – 4.77 (m, 2H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.58 – 4.52 (m, 3H), 4.46 – 4.42 (m, 2H), 4.14 (dd, *J* = 7.9, 2.8 Hz, 1H), 3.79 (dd, *J* = 5.4, 2.8 Hz, 1H), 3.69 (dd, *J* = 5.6, 1.8 Hz, 1H), 3.53 (s, 3H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.62 – 1.56 (m, 2H), 1.46 – 1.38 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.6, 138.6, 138.3, 138.0, 128.4, 128.2, 127.9 (2), 127.8 (3), 101.1, 78.7, 75.4, 75.0, 74.8, 73.8, 73.3, 72.8, 57.8, 31.5, 28.3, 22.1, 13.7; HRMS (ESI) *m/z* calcd for $C_{32}H_{38}O_6SNa$ $[M + Na]^+$ 573.2287, found 573.2281.



30

((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanol (30).

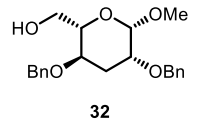
Under N_2, *S*-butyl (2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbothioate **29** (30.8 mg, 0.056 mmol) was dissolved in EtOH (2.80 ml), then $NaBH_4$ (42.3 mg, 1.12 mmol) was added at 0 ºC. The solution was allowed to warm to room temperature and stirred overnight. After removal of the solvent under reduced pressure, the residue was dissolved in ethyl acetate (16.0 mL) and successively washed with saturated aqueous NH_4Cl (4.00 mL) and 1 N HCl (4.00 mL). The aqueous layers were back-extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 2:1) to yield **30** (20.7 mg, 80%) as a colorless oil: $[a]_D^{20}$ = +25.8 (c = 1.09, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 15H), 4.79 – 4.77 (m, 2H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.49 – 4.46 (m, 2H), 4.42 (s, 2H), 3.94 – 3.89 (m, 2H), 3.83 – 3.73 (m, 3H), 3.61 (d, *J* = 4.0 Hz, 1H), 3.53 (s, 3H), 2.17 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.5, 138.2, 138.0, 128.5 (2), 128.2, 128.0 (2), 127.9 (2), 100.5, 75.5, 73.9, 73.7, 73.5, 73.1, 73.0, 71.9, 63.0, 57.4; HRMS (ESI) *m/z* calcd for $C_{28}H_{32}O_6Na$ $[M + Na]^+$ 487.2097, found 487.2093.



31b

***S*-Butyl (2*R*,3*R*,5*R*,6*S*)-3,5-bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbothioate (31b).**

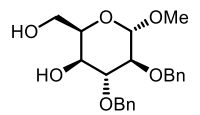
According to the general protocol A, ((2*S*,3*R*,5*R*,6*S*)-3,5-bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)tributylstannane **9h** (123 mg, 0.200 mmol), *Se*-phenyl-*S*-butyl selenothiolate **28** (27.3 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **31b** (39.7 mg, 89%) as a colorless oil: $[a]_D^{20}$ = +32.8 (c = 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H), 4.70 (d, *J* = 12.5 Hz, 1H), 4.61 – 4.58 (m, 2H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.16 – 4.10 (m, 2H), 3.80 – 3.77 (m, 1H), 3.53 (s, 3H), 2.97 – 2.87 (m, 2H), 2.24 – 2.19 (m, 1H), 1.81 – 1.76 (m, 1H), 1.62 – 1.56 (m, 2H), 1.45 – 1.38 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.9, 138.7, 138.0, 128.5, 128.4, 127.9, 127.8, 127.7, 102.0, 81.3, 72.4, 72.1 (2), 71.8, 57.9, 31.5, 30.2, 28.3, 22.1, 13.7; HRMS (ESI) *m/z* calcd for $C_{25}H_{32}O_5SNa$ $[M + Na]^+$ 467.1868, found 467.1860.



32

((2*S*,3*R*,5*R*,6*S*)-3,5-Bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanol (32).

Under N_2, *S*-butyl (2*R*,3*R*,5*R*,6*S*)-3,5-bis(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbothioate **31b** (30.6 mg, 0.069 mmol) was dissolved in EtOH (3.40 ml), then $NaBH_4$ (52.1 mg, 1.38 mmol) was added at 0 ºC. The solution was allowed to warm to room temperature and stirred overnight. After removal of the solvent under reduced pressure, the residue was dissolved in ethyl acetate (16.0 mL) and successively washed with saturated aqueous NH_4Cl (4.00 mL) and 1 N HCl (4.00 mL). The aqueous layers were back-extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:1) to yield **32** (22.4 mg, 91%) as a colorless oil: $[a]_D^{20}$ = +21.9 (c = 0.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 10H), 4.76 (d, *J* = 12.6 Hz, 1H), 4.59 (d, *J* = 12.6 Hz, 1H), 4.52 – 4.44 (m, 3H), 3.90 (dd, *J* = 11.7, 3.1 Hz, 1H), 3.81 – 3.72 (m, 3H), 3.54 – 3.51 (m, 4H), 2.35 – 2.29 (m, 2H), 1.57 – 1.52 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.8, 138.1, 128.6, 128.4, 128.0 (2), 127.9, 127.7, 102.7, 78.4, 73.6, 72.6, 71.5, 71.0, 63.3, 57.2, 32.3; HRMS (ESI) *m/z* calcd for $C_{21}H_{26}O_5Na$ $[M + Na]^+$ 381.1678, found 381.1675.

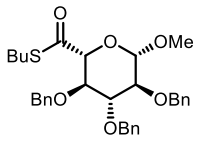


33

(2*R*,3*S*,4*R*,5*S*,6*S*)-4,5-Bis(benzyloxy)-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-3-ol (33).

Under N_2, a mixture of (4a*R*,6*S*,7*S*,8*S*,8a*R*)-6-methoxy-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxine-7,8-diol[8] (9.25 g, 32.8 mmol) and TBAI (2.42 g, 6.55 mmol) was dissolved in DMF

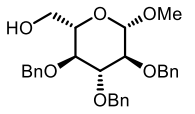
(200 mL). To the stirred solution, NaH (60% in oil, 3.93 g, 98.3 mmol) was added in an ice bath, followed shortly by the addition of benzyl bromide (9.70 mL, 81.7 mmol). The ice bath was then removed, and the reaction mixture was stirred at rt overnight. The reaction mixture was diluted with ethyl acetate, washed with water (3 × 50 mL) and brine, dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and used directly in the next step without further purification. The crude material and *p*-TsOH (2.86 g, 16.6 mmol) were added to MeOH (120 mL) and DCM (180 mL). After stirring at rt overnight, the reaction mixture was quenched with Et_3N (0.910 mL) and concentrated under reduced pressure. The crude product was purified by was purified by chromatographic purification on SiO_2 (CH_2Cl_2: EtOAc, 1:1) to afford **33** (8.34 g, 68%) as a white solid: $[a]_D^{20}$ = +36.0 (c = 1.31, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 10H), 4.84 (s, 1H), 4.63 (d, *J* = 12.3 Hz, 1H), 4.57 – 4.52 (m, 3H), 4.20 – 3.72 (m, 5H), 3.58 (s, 1H), 3.45 (s, 3H), 3.32 (s, 1H), 2.45 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 137.8, 136.9, 128.7, 128.6, 128.3, 128.1, 128.0, 127.8, 99.9, 73.7, 72.7, 71.9, 68.3, 67.2, 63.7, 55.6; HRMS (ESI) *m/z* calcd for $C_{21}H_{26}O_6Na$ $[M + Na]^+$ 397.1627, found 397.1620.



34

***S*-Butyl (2*R*,3*R*,4*R*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbothioate (34).**

According to the general protocol A, tributyl((2*S*,3*R*,4*S*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane **9k** (145 mg, 0.200 mmol), *Se*-phenyl-*S*-butyl selenothiolate **28** (27.3 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) **34** (50.4 mg, 91%) as a pale yellow oil: $[a]_D^{20}$ = +11.6 (c = 0.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 15H), 4.90 – 4.86 (m, 2H), 4.78 (d, *J* = 11.0 Hz, 1H), 4.73 – 4.69 (m, 2H), 4.60 (d, *J* = 10.4 Hz, 1H), 4.38 (d, *J* = 7.7 Hz, 1H), 3.95 (d, *J* = 9.5 Hz, 1H, H-5), 3.79 (t, *J* = 9.2 Hz, 1H), 3.66 (t, *J* = 8.9 Hz, 1H), 3.58 (s, 3H), 3.50 – 3.46 (m, 1H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.44 – 1.36 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 196.5, 138.5, 138.4, 137.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8 (2), 104.9, 84.0, 81.7, 79.8, 79.7, 75.9, 75.3, 74.9, 57.4, 31.3, 28.4, 22.1, 13.7; HRMS (ESI) *m/z* calcd for $C_{32}H_{38}O_6SNa$ $[M + Na]^+$ 573.2287, found 573.2281.

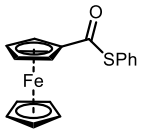


35

((2*S*,3*S*,4*R*,5*S*,6*S*)-3,4,5-Tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanol (35).

Under N_2, *S*-butyl (2*R*,3*R*,4*R*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-carbothioate **34** (38.4 mg, 0.070 mmol) was dissolved in EtOH (3.50 ml), then $NaBH_4$ (52.8 mg, 1.39 mmol) was added at 0 ºC. The solution was allowed to warm to room temperature and stirred overnight. After removal of the solvent under reduced pressure, the residue was dissolved in ethyl acetate (16.0 mL) and successively washed with saturated aqueous NH_4Cl (4.00 mL) and 1 N HCl

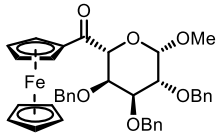
(4.00 mL). The aqueous layers were back-extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), concentrated and directly purified by column chromatography on SiO_2 (Hexanes:EtOAc, 2:1) to yield **35** (23.5 mg, 73%) as a white solid: $[a]_D^{20}$ = -6.15 (c = 0.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 15H), 4.96 – 4.91 (m, 2H), 4.88 (d, *J* = 10.9 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.66 (d, *J* = 10.9 Hz, 1H), 4.37 (d, *J* = 7.8 Hz, 1H), 3.89 (dd, *J* = 11.9, 2.6 Hz, 1H), 3.74 (dd, *J* = 11.9, 4.5 Hz, 1H), 3.69 (t, *J* = 9.1 Hz, 1H), 3.61 – 3.57 (m, 4H), 3.43 – 3.37 (m, 2H), 1.86 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.6, 138.5, 138.1, 128.6, 128.5 (2), 128.2, 128.1, 128.0, 127.8 (2), 104.9, 84.6, 82.5, 77.7, 75.8, 75.2, 75.1, 75.0, 62.1, 57.4; HRMS (ESI) *m/z* calcd for $C_{28}H_{32}O_6Na$ $[M + Na]^+$ 487.2097, found 487.2093.



36

***S*-Phenyl ferrocenecarbothioate (36).**

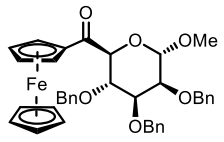
According to the general protocol B, ferrocenecarboxylic acid (460 mg, 2.00 mmol), Ph_2S_2 (480 mg, 2.20 mmol), and P(*n*-Bu)$_3$ (0.544 mL, 2.20 mmol) were dissolved in anh. CH_2Cl_2 (20.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 20:1) afforded **36** (593 mg, 92%) as a orange-red solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 5H), 4.93 (s, 2H), 4.53 (s, 2H), 4.29 (s, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 191.8, 135.1, 129.3, 129.2, 128.0, 78.9, 72.1, 70.8, 69.3; HRMS (ESI) *m/z* calcd for $C_{17}H_{14}OSFeNa$ $[M + Na]^+$ 345.0012, found 345.0011.



39

Ferrocenyl ((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (39).

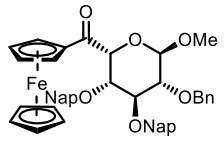
According to the general protocol A, tributyl((2*S*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane[1] (145 mg, 0.200 mmol), *S*-phenyl ferrocenecarbothioate **36** (32.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) **39** (55.0 mg, 85%) as a orange-red oil: $[a]_D^{20}$ = +74.0 (c = 1.87, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 15H), 4.92 – 4.91 (m, 2H), 4.77 – 4.69 (m, 7H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 20.3 Hz, 2H), 4.41 – 4.39 (m, 1H), 4.13 (s, 5H), 4.03 (dd, *J* = 7.3, 3.1 Hz, 1H), 3.86 (dd, *J* = 7.1, 2.5 Hz, 1H), 3.24 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 200.4, 138.8 (2), 138.4, 128.5 (2), 128.4 (2), 127.9 (2), 127.7 (2), 101.5, 77.3, 76.1, 76.0, 75.5, 73.7 (2), 73.5, 73.3, 72.7, 72.4, 70.4, 70.0, 69.7, 57.9; HRMS (ESI) *m/z* calcd for $C_{38}H_{38}O_6FeNa$ $[M + Na]^+$ 669.1916, found 669.1908.



40

Ferrocenyl ((2*S*,3*S*,4*S*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanone (40).

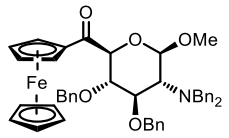
According to the general protocol A, tributyl((2*R*,3*S*,4*R*,5*S*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)stannane **9f** (145 mg, 0.200 mmol), *S*-phenyl ferrocenecarbothioate **36** (32.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 6:1) **40** (33.9 mg, 52%) as a orange-red solid: $[\alpha]_D^{20}$ = -20.7 (c = 0.81, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 10H), 7.24 – 7.15 (m, 5H), 4.96 (s, 1H), 4.91 (s, 1H), 4.84 – 4.74 (m, 4H), 4.69 (d, *J* = 11.8 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.59 (d, *J* = 10.5 Hz, 1H), 4.55 – 4.49 (m, 3H), 4.39 (t, *J* = 9.4 Hz, 1H), 4.22 (s, 5H), 3.99 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.84 – 3.83 (m, 1H), 3.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 199.7, 138.6, 138.4, 128.5, 128.4, 128.2, 128.0, 127.8, 127.7 (2), 127.6, 100.5, 79.7, 77.8, 75.9, 75.2, 74.6, 73.5, 73.0, 72.9, 72.7, 72.4, 70.5, 69.9 (2), 55.9; HRMS (ESI) *m/z* calcd for $C_{38}H_{38}O_6FeNa$ $[M + Na]^+$ 669.1916, found 669.1913.



41

((2*S*,3*S*,4*S*,5*R*,6*R*)-5-(Benzyloxy)-6-methoxy-3,4-bis(naphthalen-2-ylmethoxy)tetrahydro-2*H*-pyran-2-yl)(ferrocenyl)methanone (41).

According to the general protocol A, ((2*R*,3*S*,4*R*,5*R*,6*R*)-5-(benzyloxy)-6-methoxy-3,4-bis(naphthalen-2-ylmethoxy)tetrahydro-2*H*-pyran-2-yl)tributylstannane[1] (165 mg, 0.200 mmol), *S*-phenyl ferrocenecarbothioate **36** (32.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **41** (39.6 mg, 53%) as a orange-red solid: $[\alpha]_D^{20}$ = -54.6 (c = 1.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.83 (m, 1H), 7.79 – 7.72 (m, 4H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.62 (m, 1H), 7.54 (s, 1H), 7.50 – 7.39 (m, 7H), 7.35 – 7.29 (m, 3H), 7.26 – 7.25 (m, 1H), 5.15 (d, *J* = 11.3 Hz, 1H), 5.04 (d, *J* = 11.3 Hz, 1H), 4.99 (d, *J* = 11.1 Hz, 1H), 4.96 – 4.93 (m, 2H), 4.87 – 4.84 (m, 2H), 4.79 (d, *J* = 11.1 Hz, 1H), 4.61 (s, 1H), 4.57 (s, 1H), 4.55 (d, *J* = 7.6 Hz, 1H), 4.35 (d, *J* = 9.6 Hz, 1H, H-5), 4.25 (d, *J* = 1.2 Hz, 5H), 4.13 (t, *J* = 9.3 Hz, 1H), 3.89 (t, *J* = 9.1 Hz, 1H), 3.64 – 3.58 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.4, 138.6, 136.2, 135.6, 133.4, 133.3, 133.1, 133.0, 128.5, 128.2, 128.1, 128.0 (2), 127.8 (2), 127.7, 127.1, 126.5 (2), 126.1, 126.0, 125.9 (3), 105.6, 84.5, 82.1, 78.9, 77.7, 76.0, 75.8, 75.3, 74.9, 73.3, 73.1, 70.3, 70.0, 69.7, 57.4; HRMS (ESI) *m/z* calcd for $C_{46}H_{42}O_6FeNa$ $[M + Na]^+$ 769.2229, found 769.2234.

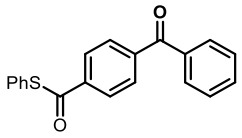


42

((2*S*,3*S*,4*R*,5*R*,6*R*)-3,4-Bis(benzyloxy)-5-(dibenzylamino)-6-methoxytetrahydro-2*H*-pyran-2-yl)(ferrocenyl)methanone (42).

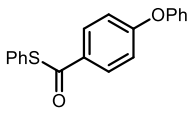
According to the general protocol A, (2*R*,3*R*,4*R*,5*S*,6*R*)-*N*,*N*-dibenzyl-4,5-bis(benzyloxy)-2-methoxy-6-(tributylstannyl)tetrahydro-2*H*-pyran-3-amine **9j** (163 mg, 0.200 mmol), *S*-phenyl ferrocenecarbothioate **36** (32.2 mg, 0.100 mmol), $Pd_2(dba)_3$ (2.30 mg, 0.0025 mmol), ligand **L6** (8.00 mg, 0.010 mmol), CuCl (9.90 mg, 0.100 mmol) in 1,4-dioxane (2.00 mL) heated under Ar at 90 ºC for 72 h afforded after chromatographic purification on SiO_2 (Hexanes:EtOAc, 8:1) **42** (47.7 mg, 65%) as a orange-red oil: $[a]_D^{20}$ = -27.5 (c = 2.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 9H), 7.30 – 7.21 (m, 9H), 7.14 – 7.12 (m, 2H), 5.05 (d, *J* = 11.2 Hz, 1H), 4.96 – 4.87 (m, 3H), 4.71 (d, *J* = 10.3 Hz, 1H), 4.66 – 4.64 (m, 2H), 4.59 – 4.58 (m, 2H), 4.31 (d, *J* = 9.4 Hz, 1H, H-5), 4.24 (s, 5H), 4.12 – 4.05 (m, 3H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.88 (d, *J* = 13.8 Hz, 2H), 3.53 (s, 3H), 3.08 (dd, *J* = 9.4, 7.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.8, 139.7, 139.1, 138.1, 129.1, 128.5, 128.4, 128.3, 127.7, 127.4 (2), 127.0, 103.9, 80.9, 79.3, 77.7, 76.2, 75.0, 74.3, 73.2, 72.9, 70.1, 70.0, 69.9, 63.7, 56.5, 55.1; HRMS (ESI) *m/z* calcd for $C_{45}H_{46}NO_5Fe$ $[M + H]^+$ 736.2725, found 736.2718.

6. Detailed Experimental Procedures for Compounds S1-S11



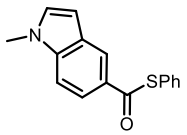
S1

***S*-Phenyl 4-benzoylbenzothioate (S1).**
According to the general protocol B, 4-benzoylbenzoic acid (452 mg, 2.00 mmol), Ph_2S_2 (480 mg, 2.20 mmol), and P(*n*-Bu)$_3$ (0.544 mL, 2.20 mmol) were dissolved in anh. CH_2Cl_2 (20.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO2 (Hexanes:EtOAc, 10:1) afforded **S1** (578 mg, 91%) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.83 – 7.81 (m, 2H), 7.65 – 7.62 (m, 1H), 7.56 – 7.47 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.9, 189.9, 142.0, 139.4, 137.0, 135.1, 133.2, 130.3 (2), 129.9, 129.5, 128.7, 127.5, 127.0; HRMS (ESI) *m/z* calcd for $C_{20}H_{15}O_2S$ $[M + H]^+$ 319.0793, found 319.0791.



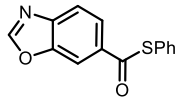
S2

***S*-Phenyl 4-phenoxybenzothioate (S2).**
According to the general protocol B, 4-phenoxybenzoic acid (428 mg, 2.00 mmol), Ph_2S_2 (480 mg, 2.20 mmol), and P(*n*-Bu)$_3$ (0.544 mL, 2.20 mmol) were dissolved in anh. CH_2Cl_2 (20.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 20:1) afforded **S2** (607 mg, 99%) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.40 (m, 7H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 188.8, 162.7, 155.4, 135.3, 131.1, 130.2, 129.8, 129.6, 129.4, 127.5, 124.9, 120.4, 117.5; HRMS (ESI) *m/z* calcd for $C_{19}H_{14}O_2SNa$ $[M + Na]^+$ 329.0612, found 329.0611.



S3

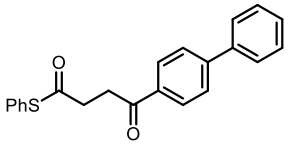
***S*-Phenyl 1-methyl-1*H*-indole-5-carbothioate (S3).**
According to the general protocol B, 1-methyl-1*H*-indole-5-carboxylic acid (210 mg, 1.20 mmol), Ph_2S_2 (288 mg, 1.32 mmol), and P(*n*-Bu)$_3$ (0.326 mL, 1.32 mmol) were dissolved in anh. CH_2Cl_2 (18.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) afforded **S3** (303 mg, 95%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 1.6 Hz, 1H), 7.92 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.49 – 7.44 (m, 3H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.14 (d, *J* = 3.2 Hz, 1H), 6.64 (dd, *J* = 3.1, 0.9 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 190.1, 139.6, 135.4, 130.8, 129.3, 129.2, 128.6, 128.4, 128.1, 122.3, 121.2, 109.3, 103.2, 33.2; HRMS (ESI) *m/z* calcd for $C_{16}H_{13}NOSNa$ $[M + Na]^+$ 290.0616, found 290.0617.



S4

***S*-Phenyl benzo[*d*]oxazole-6-carbothioate (S4).**

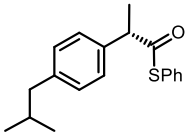
According to the general protocol B, benzo[*d*]oxazole-6-carboxylic acid (326 mg, 2.00 mmol), Ph_2S_2 (480 mg, 2.20 mmol), and P(*n*-Bu)$_3$ (0.544 mL, 2.20 mmol) were dissolved in anh. CH_2Cl_2 (20.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) afforded **S4** (375 mg, 73%) as a pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 13.2 Hz, 2H), 8.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.47 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 189.5, 155.4, 150.0, 144.4, 135.2, 134.5, 129.9, 129.5, 127.1, 124.5, 120.9, 110.8; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}NO_2S$ $[M + H]^+$ 256.0432, found 256.0430.



S5

***S*-Phenyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanethioate (S5).**

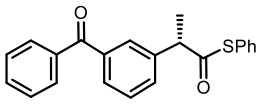
According to the general protocol B, Fenbufen (509 mg, 2.00 mmol), Ph_2S_2 (480 mg, 2.20 mmol), and P(*n*-Bu)$_3$ (0.544 mL, 2.20 mmol) were dissolved in anh. CH_2Cl_2 (20.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) afforded **S5** (684 mg, 99%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.49 – 7.39 (m, 8H), 3.41 (t, *J* = 6.6 Hz, 2H), 3.17 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.2, 197.0, 146.1, 139.9, 135.2, 134.7, 129.6, 129.3, 129.1, 128.8, 128.4, 127.7, 127.4 (2), 37.6, 33.7; HRMS (ESI) *m/z* calcd for $C_{22}H_{18}O_2SNa$ $[M + Na]^+$ 369.0925, found 369.0921.



S6

***S*-Phenyl (*S*)-2-(4-isobutylphenyl)propanethioate (S6).**

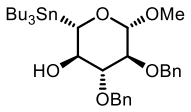
According to the general protocol B, (*S*)-(+)-Ibuprofen (413 mg, 2.00 mmol), Ph_2S_2 (480 mg, 2.20 mmol), and P(*n*-Bu)$_3$ (0.544 mL, 2.20 mmol) were dissolved in anh. CH_2Cl_2 (20.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) afforded **S6** (590 mg, 99%) as a white solid: $[\alpha]_D^{20}$ = +194.4 (c = 0.61, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 5H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.01 – 3.97 (m, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.92 – 1.84 (m, 1H), 1.58 (d, *J* = 7.1 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 199.4, 141.2, 136.8, 134.6, 129.6, 129.3, 129.2, 128.2, 127.9, 53.9, 45.2, 30.3, 22.5, 18.8; HRMS (ESI) *m/z* calcd for $C_{19}H_{22}OSNa$ $[M + Na]^+$ 321.1289, found 321.1296.



S7

***S*-Phenyl (*S*)-2-(3-benzoylphenyl)propanethioate (S7).**

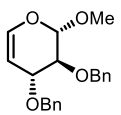
According to the general protocol B, (*S*)-(+)-Ketoprofen (509 mg, 2.00 mmol), Ph_2S_2 (480 mg, 2.20 mmol), and P(*n*-Bu)$_3$ (0.544 mL, 2.20 mmol) were dissolved in anh. CH_2Cl_2 (20.0 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 10:1) afforded **S7** (675 mg, 97%) as a white solid: $[\alpha]_D^{20}$ = +170.6 (c = 0.76, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 3H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.51 – 7.47 (m, 3H), 7.40 – 7.35 (m, 5H), 4.11 – 4.07 (m, 1H), 1.62 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.7, 196.5, 140.0, 138.2, 137.6, 134.5, 132.7, 132.0, 130.2, 129.8, 129.5 (2), 129.3, 128.9, 128.4, 127.7, 53.9, 18.8; HRMS (ESI) *m/z* calcd for $C_{22}H_{18}O_2SNa$ [M + Na]$^+$ 369.0925, found 369.0922.



S8

(2*S*,3*R*,4*R*,5*S*,6*S*)-4,5-Bis(benzyloxy)-6-methoxy-2-(tributylstannyl)tetrahydro-2*H*-pyran-3-ol (S8).

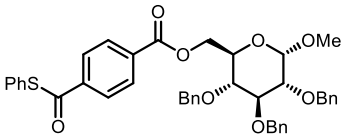
According to the general protocol C, to a solution of (2*S*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-methoxy-3,4-dihydro-2*H*-pyran **S9** (3.43 g, 10.5 mmol) in a cooled (0 °C), vigorously stirring biphasic solution of CH_2Cl_2 (87.0 mL), saturated aq. $NaHCO_3$ (146 mL), and acetone (18.0 mL), a solution of Oxone® (25.8 g, 42.0 mmol) in H_2O (102 mL) was added dropwise over 15 min. The reaction mixture was stirred at 0 °C for 0.5 h then at rt for 2 h, the organic phase was separated, and extracted with CH_2Cl_2 (2 × 30.0 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to afford the epoxide as a white solid. The crude epoxide was dissolved in anh. and degassed THF (26.0 mL), cooled to -15 °C, and a solution of $MeMgSnBu_3$ (5.19 g, 15.8 mmol) in THF was added. The reaction was stirred at -15 °C for 1.5 h, then warmed to -10 °C and stirred for 1 h, quenched with H_2O (30.0 mL), filtered twice through Celite®, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 30.0 mL), and the combined organic layers were dried (Na_2SO_4), concentrated, and purified by column chromatography on SiO_2 (Hexanes:EtOAc, 1:0 then 15:1) to afford **S8** (1.15 g, 17%) as a colorless oil: $[\alpha]_D^{20}$ = -6.92 (c = 0.77, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 10H), 4.99 – 4.94 (m, 2H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 11.2 Hz, 1H), 4.15 (d, *J* = 7.4 Hz, 1H), 3.72 – 3.68 (m, 1H), 3.55 (s, 3H), 3.42 – 3.31 (m, 3H), 2.15 (s, 1H), 1.57 – 1.47 (m, 6H), 1.35 – 1.28 (m, 6H), 0.97 – 0.88 (m, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 138.7, 128.7, 128.5, 128.3, 128.2, 128.0, 127.8, 108.1, 86.4, 82.6, 75.5, 74.7, 73.4, 69.9, 57.0, 29.2, 27.6, 13.9, 9.0; HRMS (ESI) *m/z* calcd for $C_{32}H_{50}O_5SnNa$ [M + Na]$^+$ 657.2578, found 657.2582.



S9

(2*S*,3*S*,4*R*)-3,4-Bis(benzyloxy)-2-methoxy-3,4-dihydro-2*H*-pyran (S9).

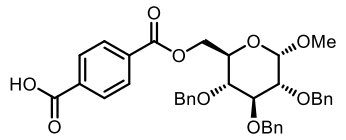
At room temperature, (2*R*,3*S*,4*R*,5*S*,6*S*)-4,5-bis(benzyloxy)-2-(hydroxymethyl)-6-methoxytetrahydro-2*H*-pyran-3-ol **33** (5.29 g, 14.1 mmol) was dissolved in CH_2Cl_2 (85.0 mL) and H_2O (28.0 mL), then treated with TEMPO (0.331 g, 2.12 mmol) and BAIB (9.10 g, 28.3 mmol). After vigorous stirring overnight, the reaction mixture was quenched with saturated $Na_2S_2O_3$ solution, extracted with CH_2Cl_2 (3 × 30.0 mL), washed once with brine, dried over Na_2SO_4, concentrated under reduced pressure, and used for next step without further purification. A solution of the crude carboxylic acid (~5.49 g, 14.1 mmol) in degassed DMF (141 mL) was treated with DMF dineopentyl acetal (16.3 g, 19.7 mL, 70.6 mmol) in a high-pressure reaction vessel. The reaction mixture was heated at 200 °C for 6 h and then cooled to room temperature. It was diluted with ethyl acetate and washed with water (3 × 50 mL), followed by a single wash with brine. The organic layer was dried over anhydrous Na_2SO_4 and purified by silica gel chromatography (hexanes/EtOAc = 10:1) to afford **S9** (2.97 g, 22%) as a yellow solid: $[a]_D^{20}$ = -5.98 (c = 1.23, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 10H), 6.35 (dd, *J* = 6.2, 1.4 Hz, 1H), 4.94 (dd, *J* = 6.2, 3.2 Hz, 1H), 4.83 – 4.79 (m, 2H), 4.70 (d, *J* = 11.7 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.09 – 4.07 (m, 1H), 3.75 – 3.73 (m, 1H), 3.57 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.1, 138.5, 138.2, 128.5 (2), 128.1, 127.9, 127.7, 101.7, 101.6, 77.4, 73.6, 73.3, 71.0, 57.1; HRMS (ESI) *m/z* calcd for $C_{20}H_{22}O_4Na$ [M + Na]$^+$ 349.1416, found 349.1419.



S10

((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methyl 4-((phenylthio)carbonyl)benzoate (S10)

According to the general protocol B, 4-((((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methoxy)carbonyl)benzoic acid **S11** (221 mg, 0.361 mmol), Ph_2S_2 (86.6 mg, 0.397 mmol), and P(*n*-Bu)$_3$ (98.1 μL, 0.398 mmol) were dissolved in anh. CH_2Cl_2 (3.60 mL). The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 5:1) afforded **S10** (249 mg, 98%) as a white solid: $[a]_D^{20}$ = +45.7 (c = 0.83, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 4H), 7.54 – 7.47 (m, 5H), 7.39 – 7.27 (m, 14H), 7.24 – 7.21 (m, 1H), 5.03 (d, *J* = 10.7 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.64 – 4.62 (m, 2H), 4.56 (dd, *J* = 11.9, 1.9 Hz, 1H), 4.48 (dd, *J* = 11.9, 4.8 Hz, 1H), 4.07 (t, *J* = 9.2 Hz, 1H), 3.98 – 3.95 (m, 1H), 3.60 – 3.56 (m, 2H), 3.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 189.8, 165.3, 140.2, 138.6, 138.2, 137.9, 135.1, 134.3, 130.1, 129.9, 129.5, 128.7, 128.6, 128.2 (3), 128.1 (2), 127.9, 127.5, 126.9, 98.2, 82.2, 80.2, 77.5, 76.1, 75.2, 73.6, 68.7, 64.1, 55.4; HRMS (ESI) *m/z* calcd for $C_{42}H_{40}O_8SNa$ [M + Na]$^+$ 727.2342, found 727.2350.



S11

4-((((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-Tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methoxy)carbonyl)benzoic acid (S11)

Under N_2, ((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methanol (465 mg, 1.00 mmol) was dissolved in DCM (5.00 ml).Terephthalic acid (249 mg, 1.50 mmol), EDCI (345 mg, 1.80 mmol), DMAP (36.7 mg, 0.300 mmol), and DIPEA (233 mg, 1.80 mmol) were then added. The reaction mixture stirred under N_2 at rt overnight, the volatiles were removed *in vacuo*, and chromatographic purification on SiO_2 (Hexanes:EtOAc, 1:1) afforded **S11** (405 mg, 66%) as a white solid: $[\alpha]_D^{20}$ = +53.1 (c = 0.71, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.25 (m, 9H), 7.23 – 7.21 (m, 5H), 7.19 – 7.15 (m, 1H), 4.99 (d, *J* = 10.7 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 10.7 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.59 – 4.57 (m, 2H), 4.51 (dd, *J* = 11.9, 2.2 Hz, 1H), 4.43 (dd, *J* = 11.9, 4.6 Hz, 1H), 4.03 (t, *J* = 9.2 Hz, 1H), 3.93 – 3.90 (m, 1H), 3.58 – 3.54 (m, 2H), 3.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.5, 165.4, 138.5, 138.1, 137.8, 134.5, 133.3, 130.3, 129.8, 128.7, 128.6 (2), 128.3, 128.2 (3), 128.1, 128.0, 98.2, 82.3, 80.1, 77.4, 76.2, 75.2, 73.6, 68.8, 64.1, 55.4; HRMS (ESI) *m/z* calcd for $C_{36}H_{36}O_9Na$ $[M + Na]^+$ 635.2257, found 635.2257.

7. References

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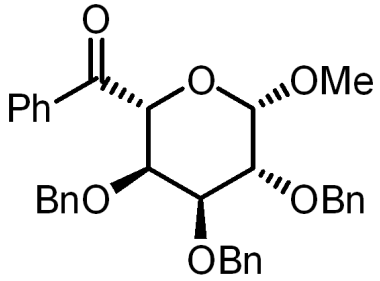
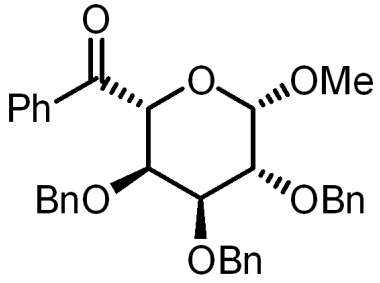
8. Copies of 1D and 2D NMR Spectra

12a (^{1}H NMR, 500MHz, $CDCl_3$)

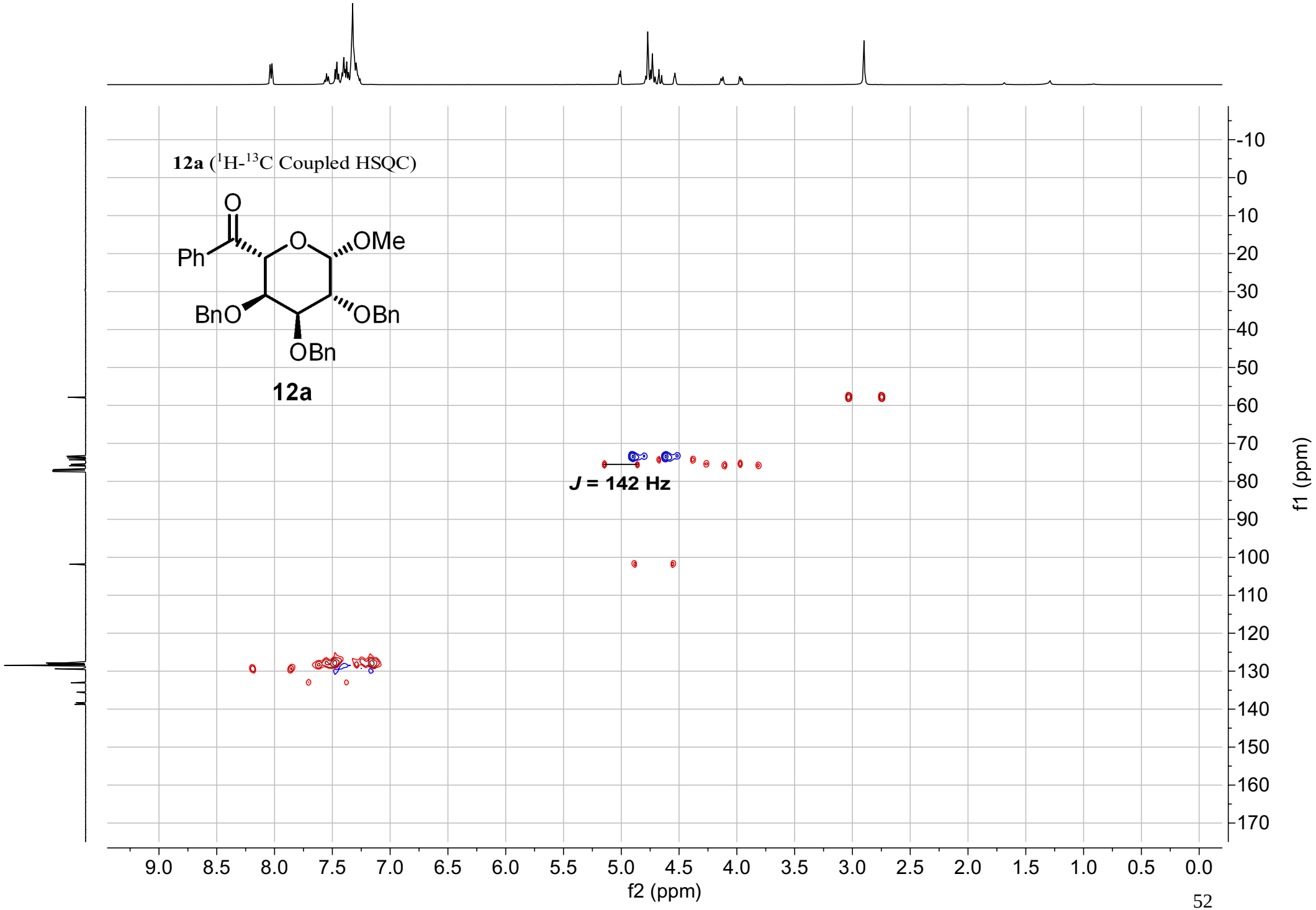


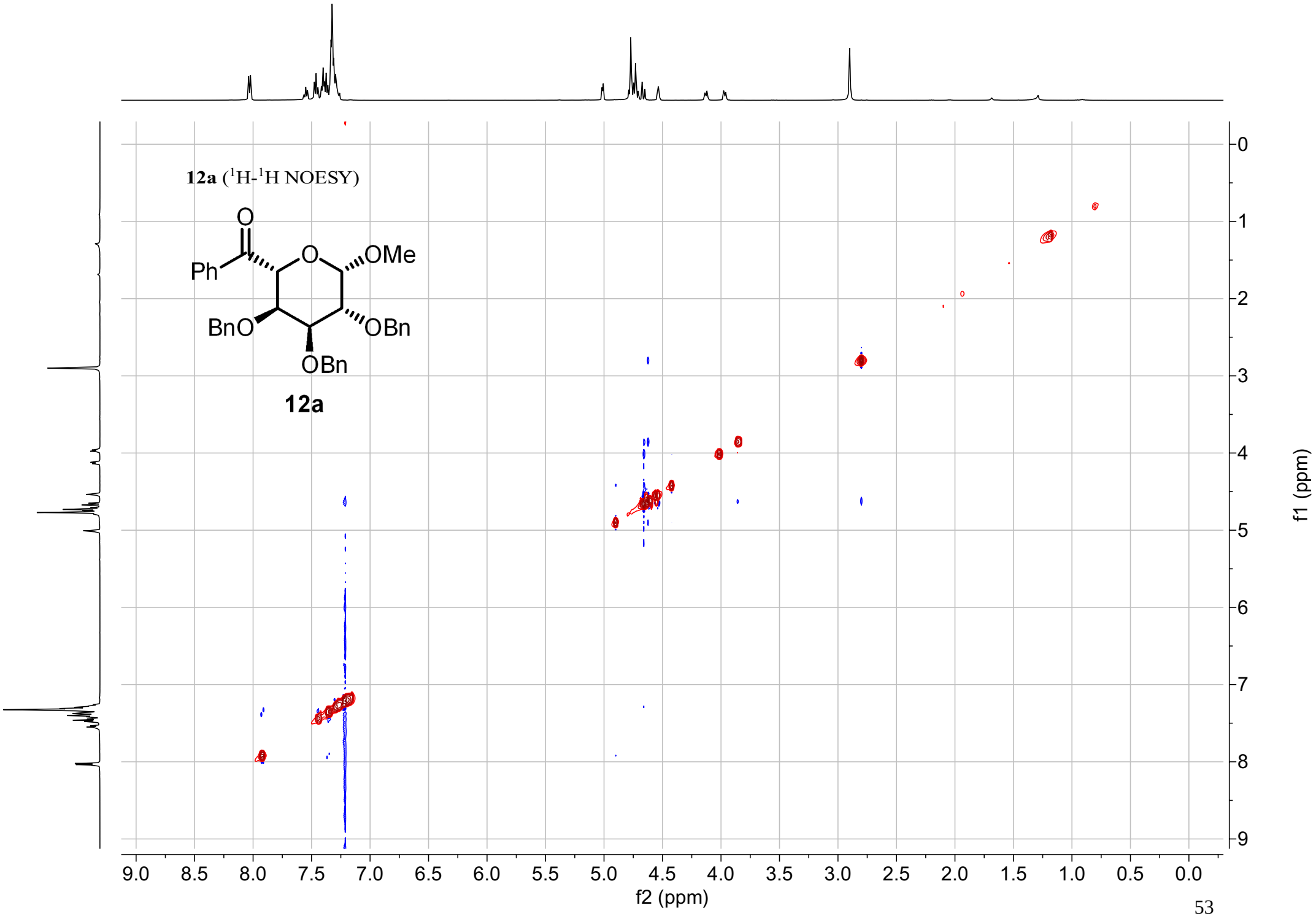
12a

12a (^{13}C NMR, 126MHz, $CDCl_3$)

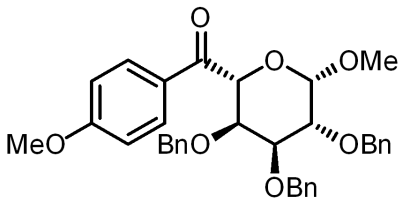


12a


12a (1H-13C Coupled HSQC)
O
Ph
O
OMe
BnO
OBn
OBn
12a
J = 142 Hz
f2 (ppm)
f1 (ppm)

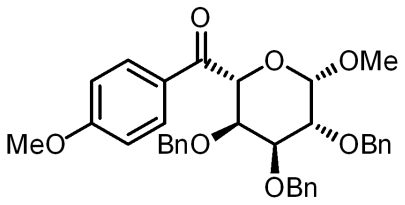

12a (^{1}H-^{1}H NOESY)
O
Ph
O
OMe
BnO
OBn
OBn
12a
f2 (ppm)
f1 (ppm)

12b (^{1}H NMR, 500MHz, $CDCl_3$)

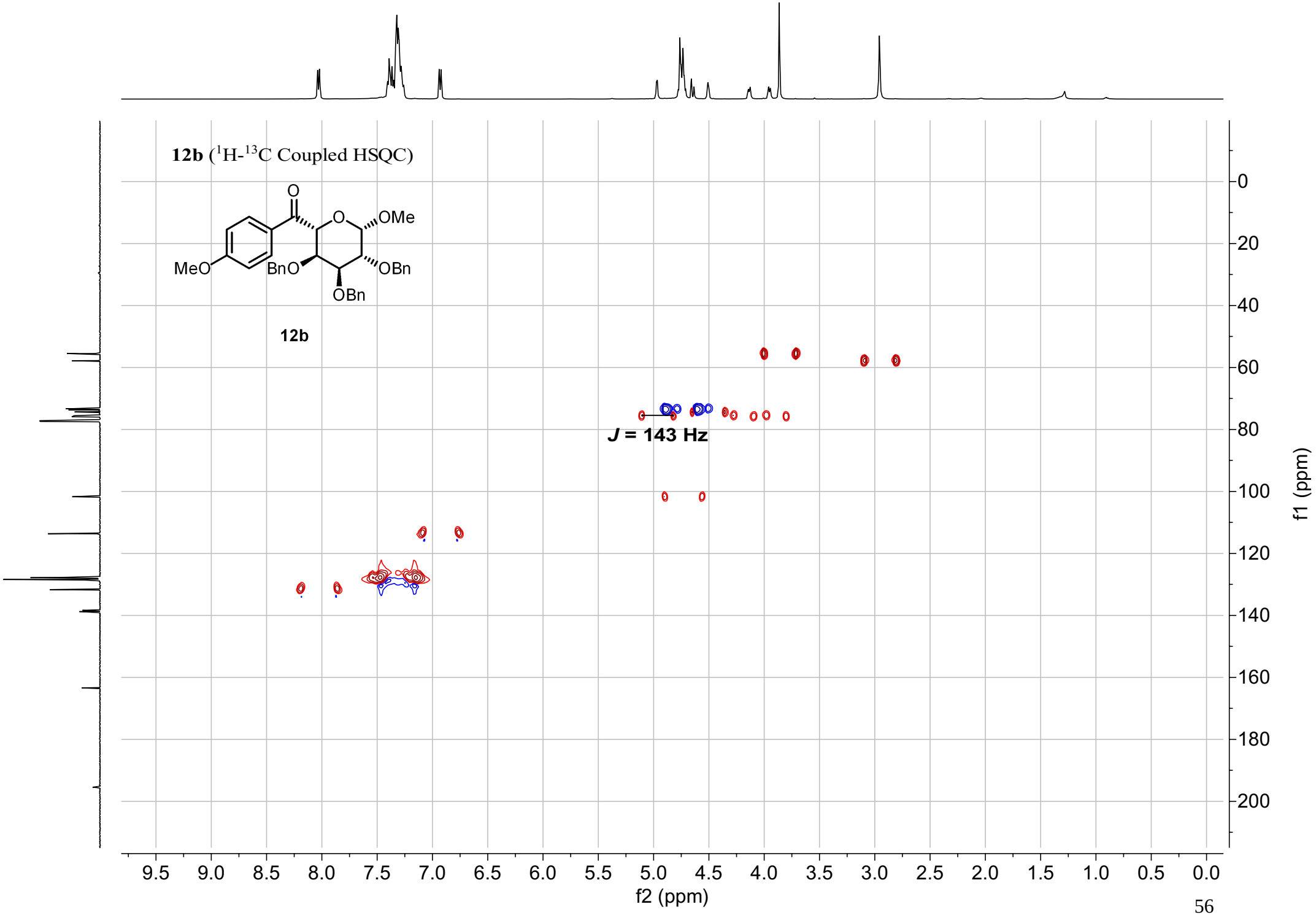


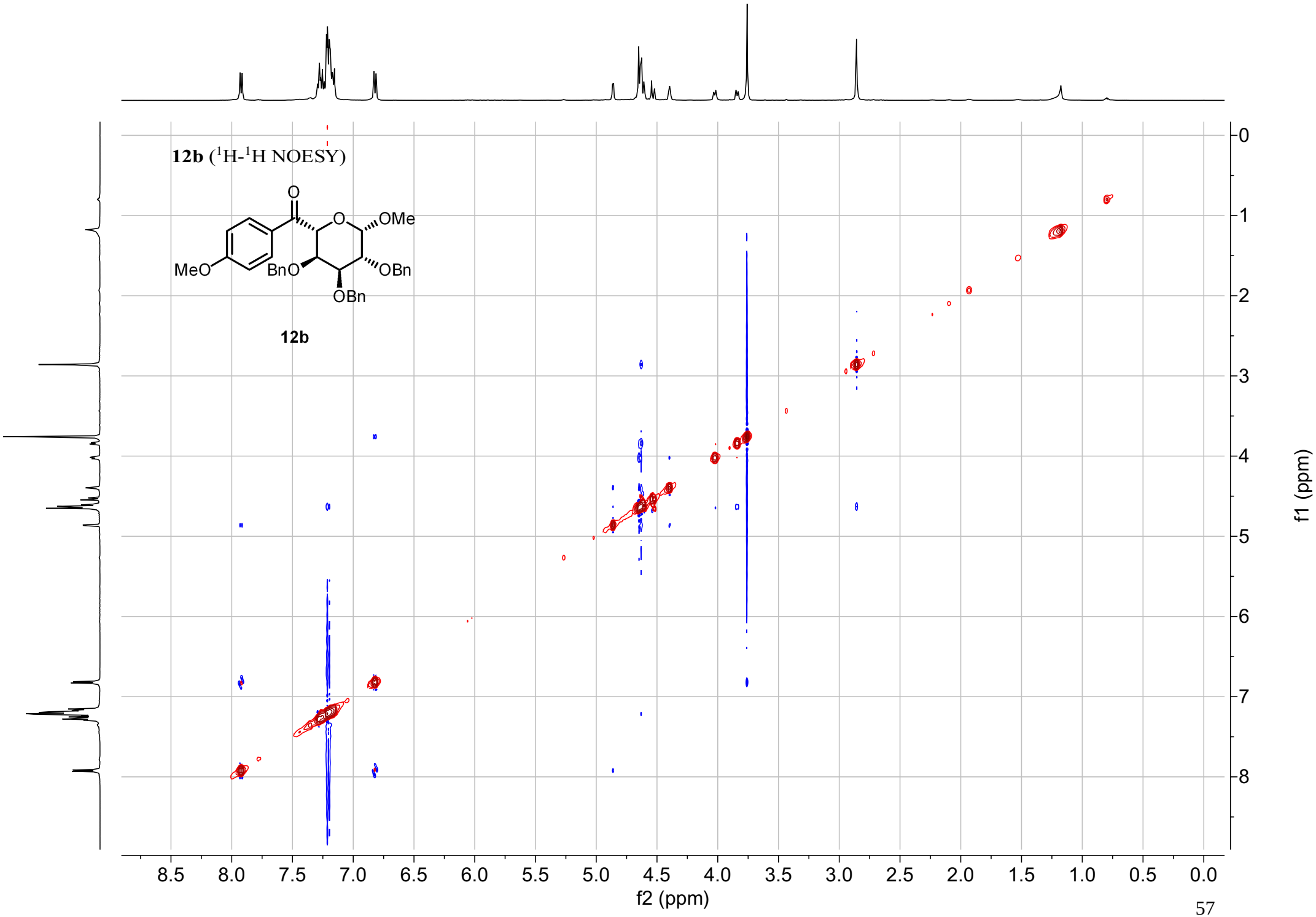
12b

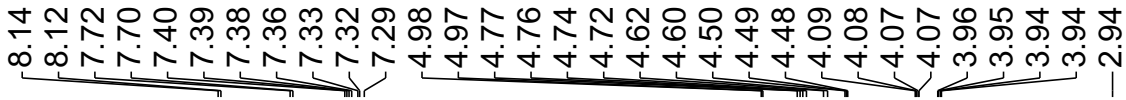
12b (^{13}C NMR, 126MHz, $CDCl_3$)



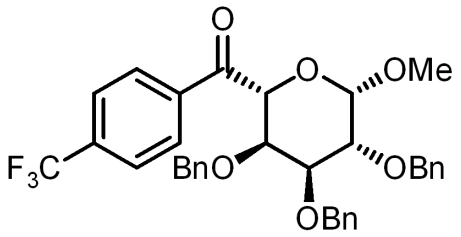
12b


12b (1H-13C Coupled HSQC)
O
O
OMe
MeO
BnO
OBn
OBn
12b
J = 143 Hz
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

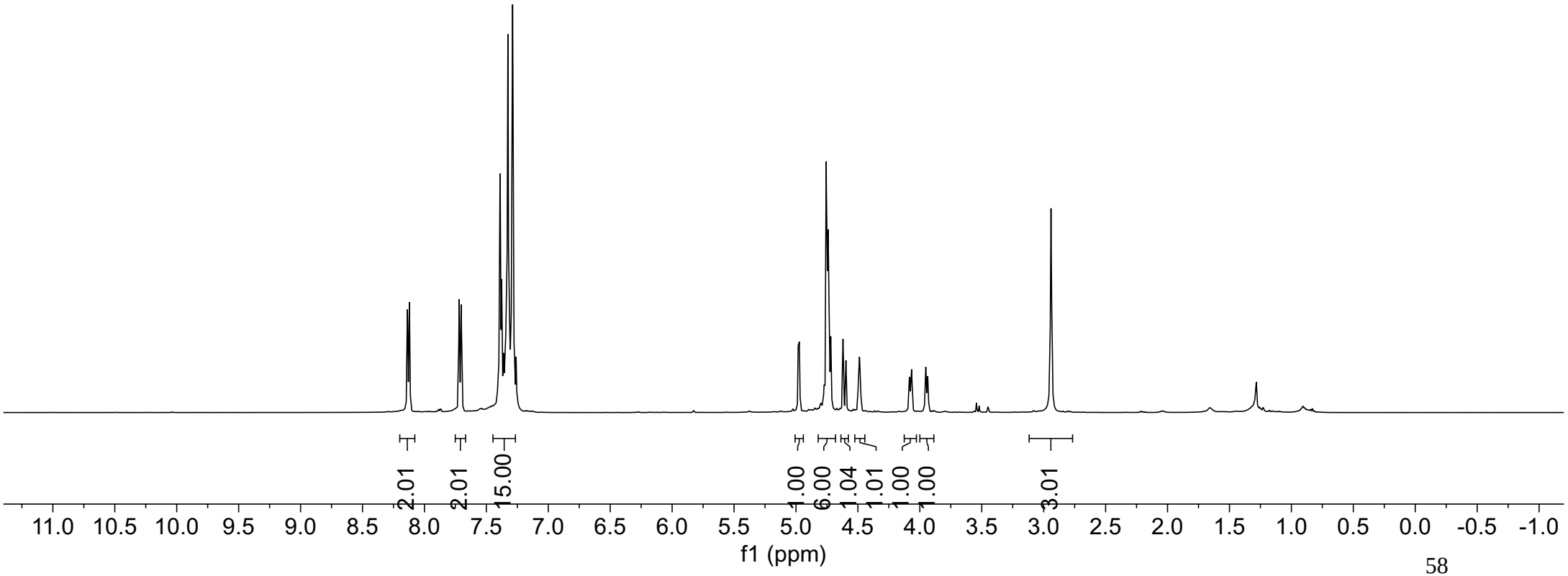

12b (1H-1H NOESY)
O
O
OMe
MeO
BnO
OBn
OBn
12b
f2 (ppm)
f1 (ppm)



12c (^{1}H NMR, 500MHz, $CDCl_3$)

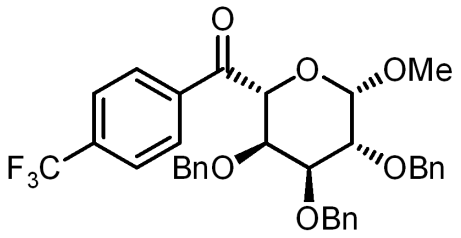


12c

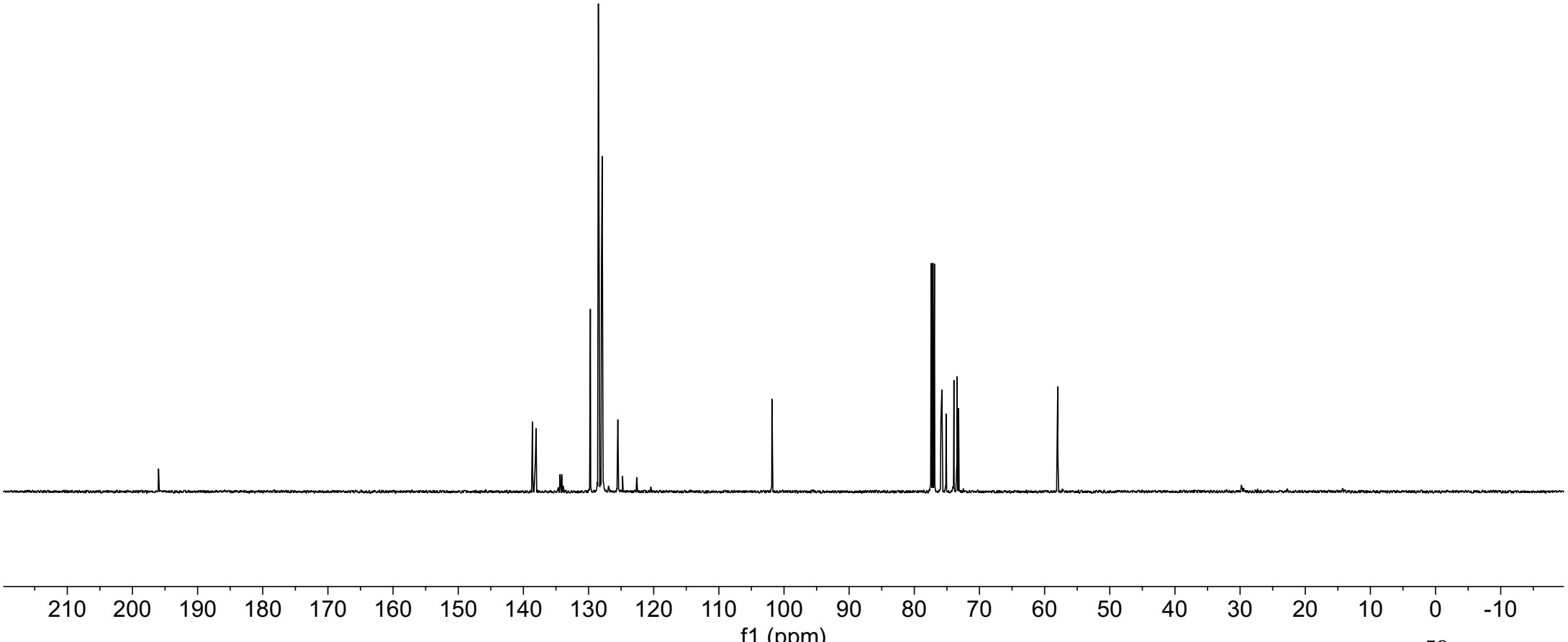


196.00
138.62
138.59
138.16
138.05
134.64
134.38
134.12
133.86
129.72
128.51
128.49
128.17
128.01
127.91
127.86
127.80
126.95
125.56
125.53
125.51
125.48
124.78
122.61
120.44
101.85
77.16
75.92
75.77
75.12
74.05
73.92
73.45
73.21
57.99

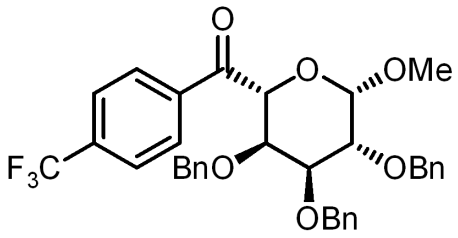
12c (^{13}C NMR, 126MHz, $CDCl_3$)



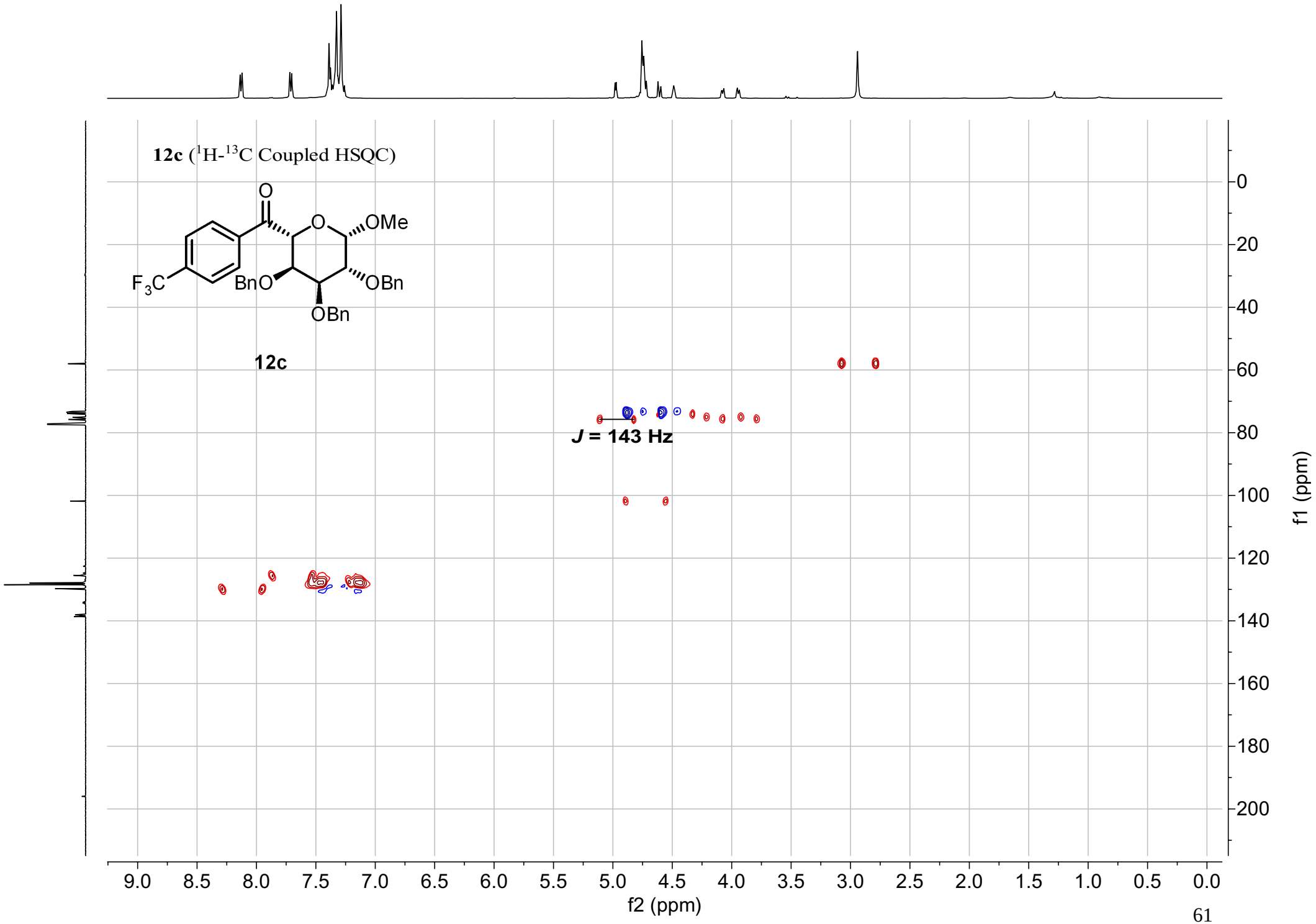
12c

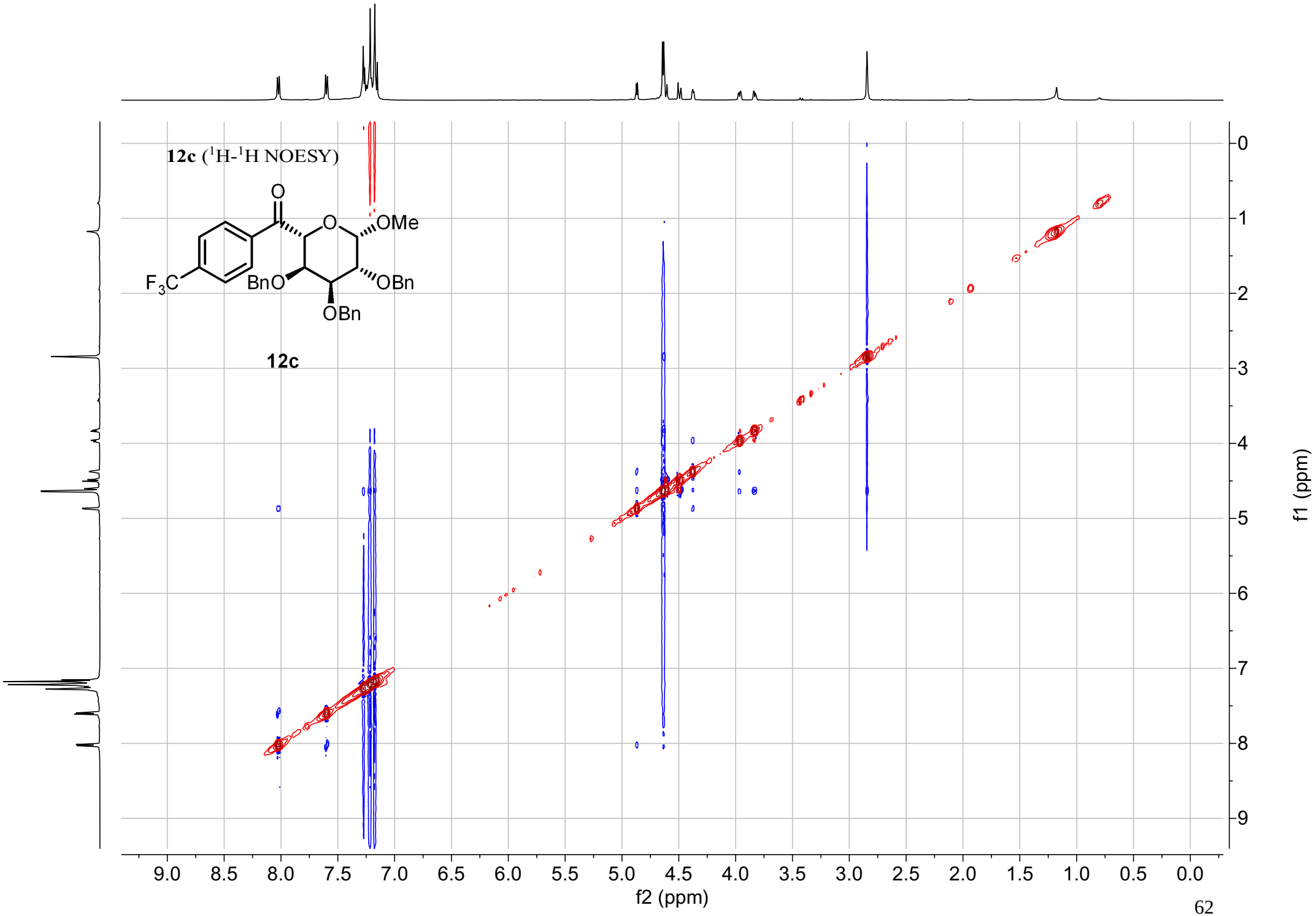


12c (^{19}F NMR, 471MHz, $CDCl_3$)

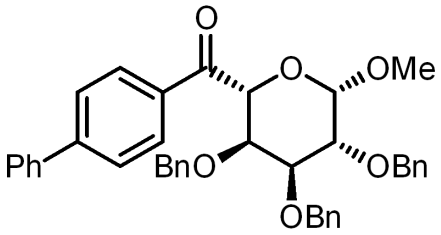


12c


12c (1H-13C Coupled HSQC)
O
O
OMe
F3C
BnO
OBn
OBn
12c
J = 143 Hz
0
20
40
60
80
100
120
140
160
180
200
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
f2 (ppm)

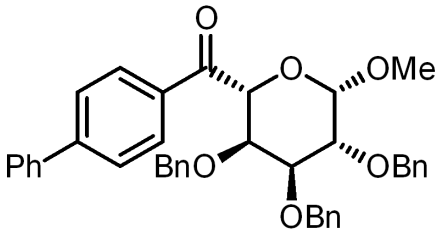

12c (1H-1H NOESY)
O
O
OMe
F3C
BnO
OBn
OBn
12c
f2 (ppm)
f1 (ppm)

12d (^{1}H NMR, 500MHz, $CDCl_3$)

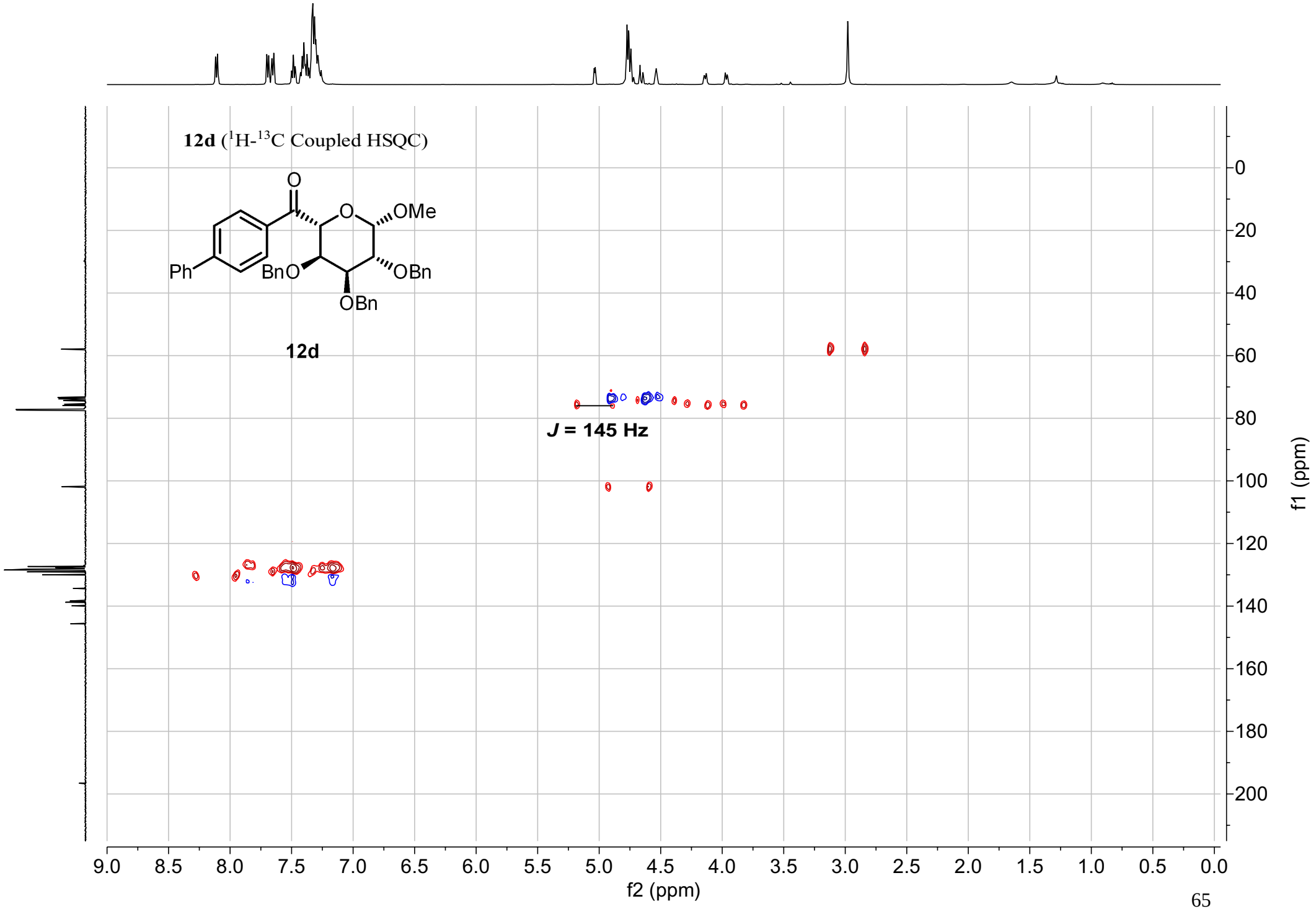


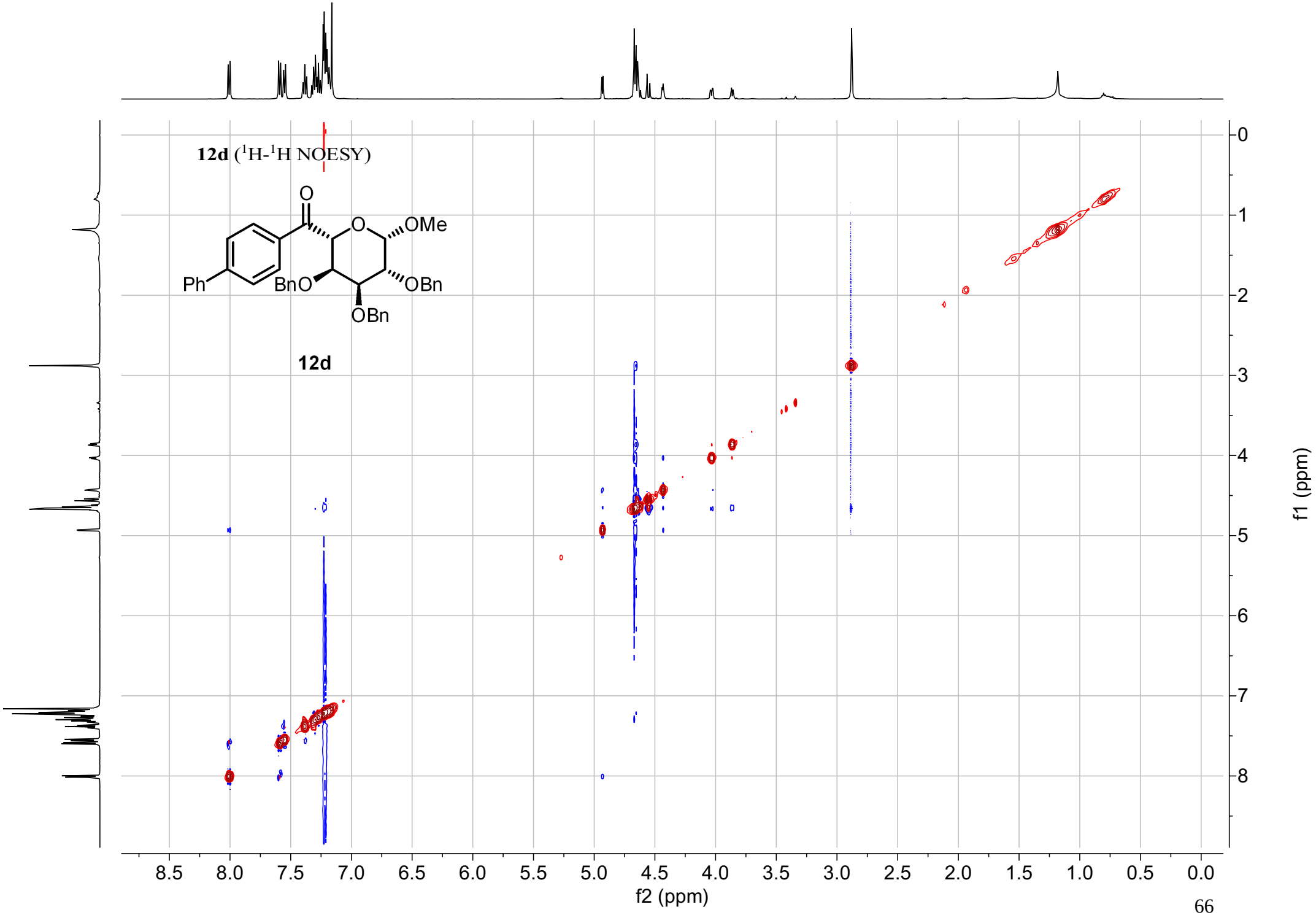
12d

12d (^{13}C NMR, 126MHz, $CDCl_3$)

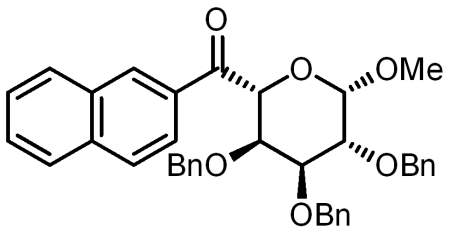


12d

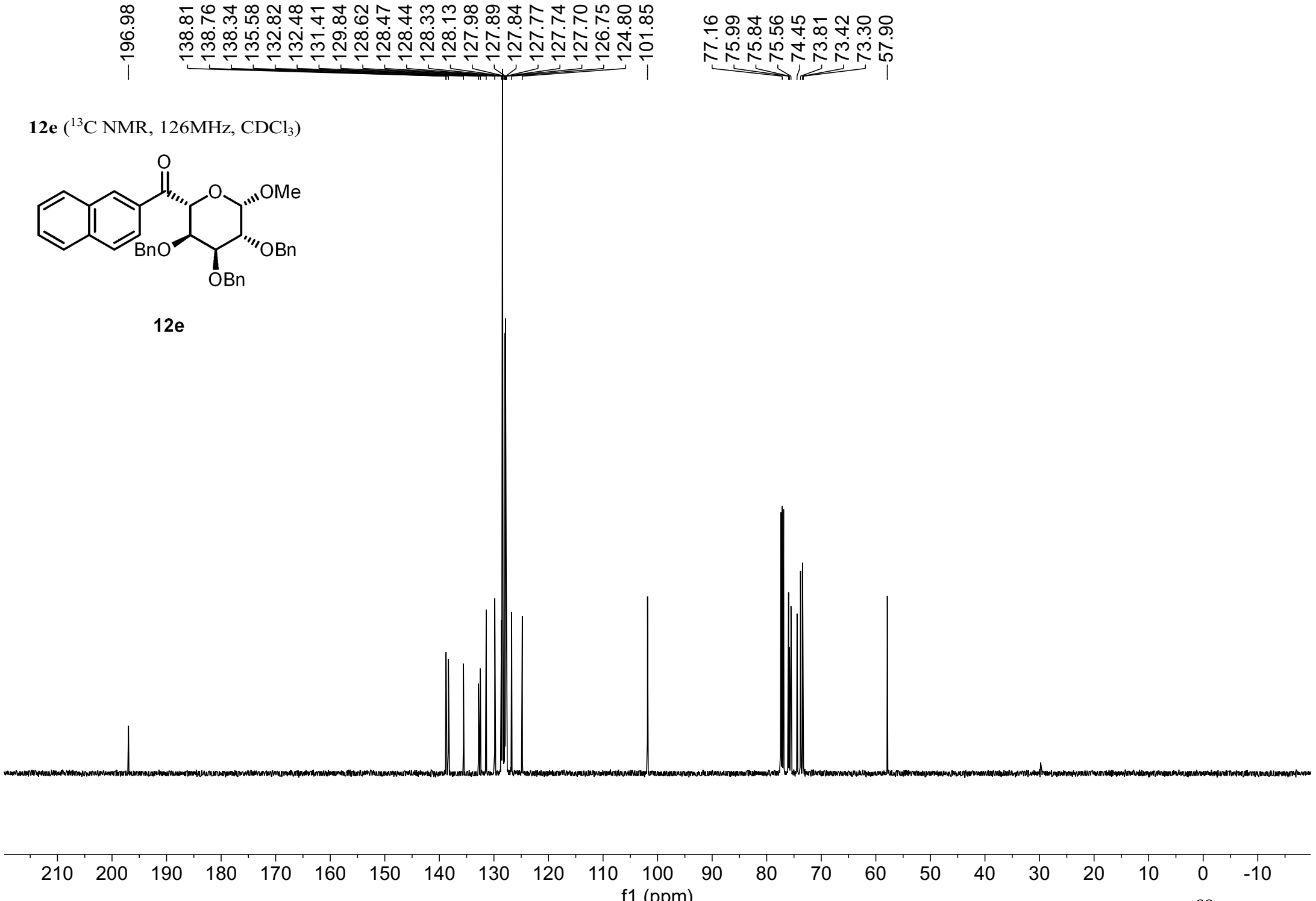

12d (1H-13C Coupled HSQC)
O
O
OMe
Ph
BnO
OBn
OBn
12d
J = 145 Hz
f1 (ppm)
f2 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
140
160
180
200

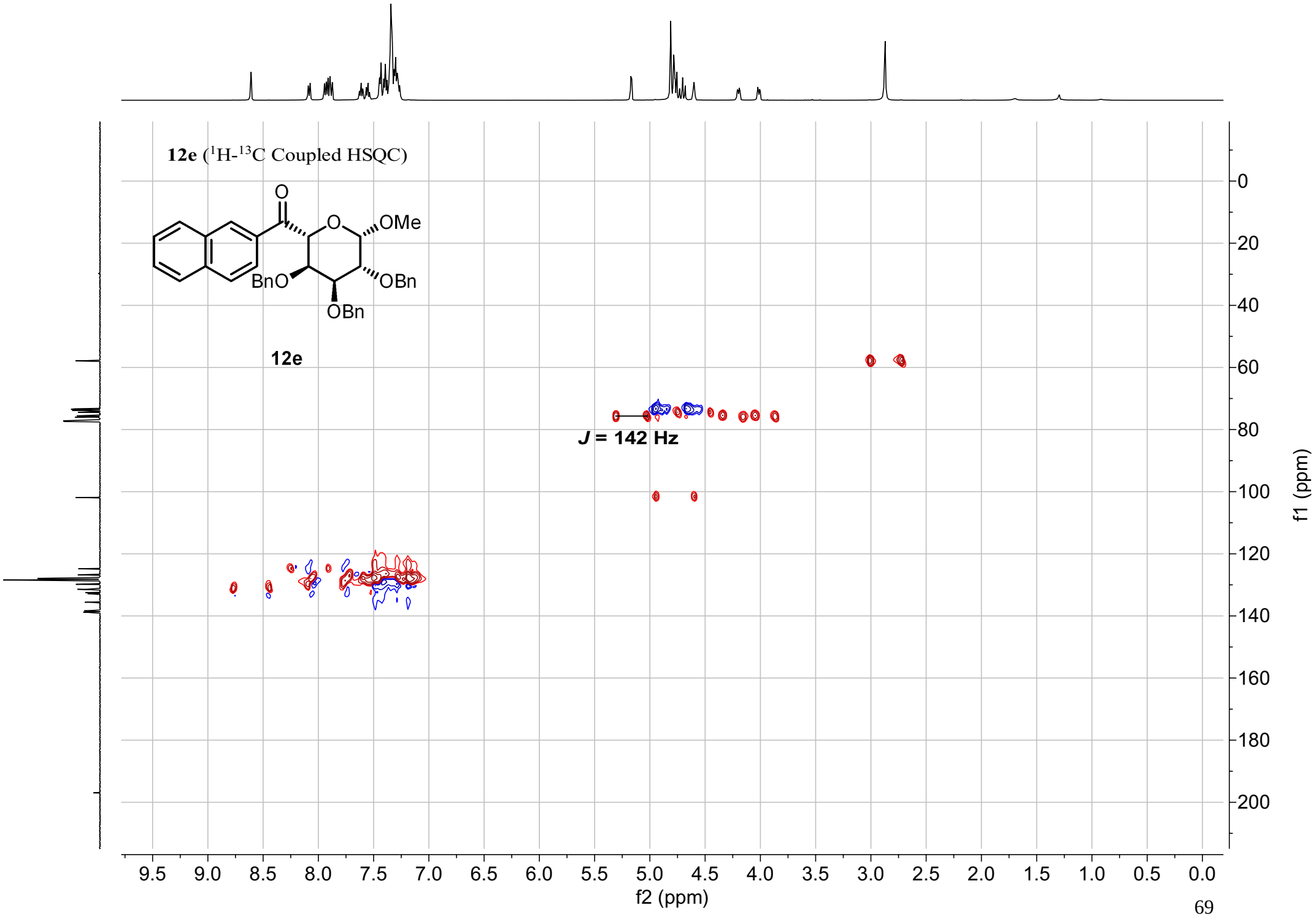

12d (1H-1H NOESY)
O
O
OMe
Ph
BnO
OBn
OBn
12d
f2 (ppm)
f1 (ppm)

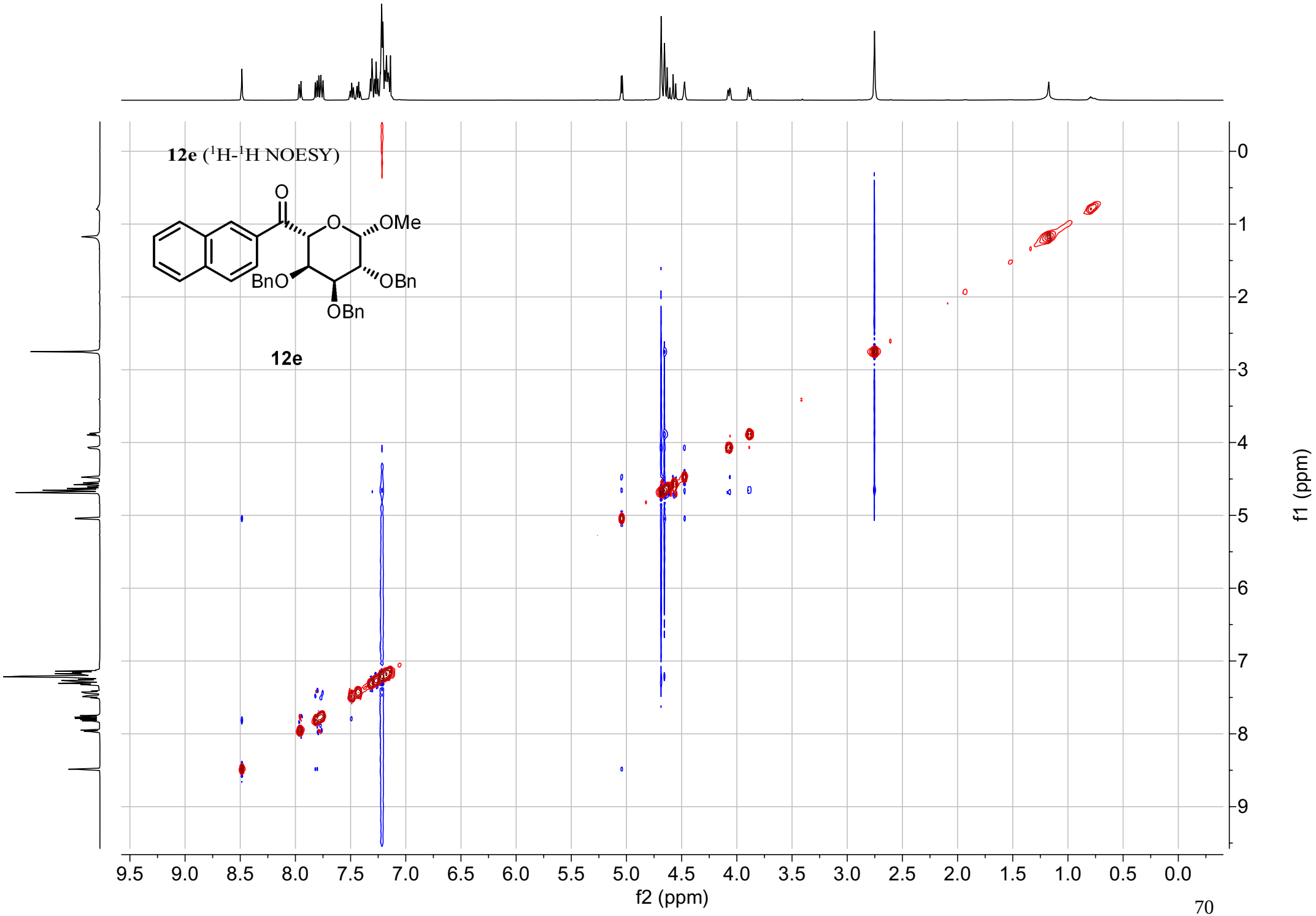
12e (^{1}H NMR, 500MHz, $CDCl_3$)



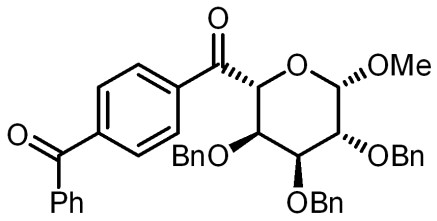
12e


196.98
138.81
138.76
138.34
135.58
132.82
132.48
131.41
129.84
128.62
128.47
128.44
128.33
128.13
127.98
127.89
127.84
127.77
127.74
127.70
126.75
124.80
101.85
77.16
75.99
75.84
75.56
74.45
73.81
73.42
73.30
57.90
12e (13C NMR, 126MHz, CDCl3)
O
O
OMe
BnO
OBn
OBn
12e
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)


12e (1H-13C Coupled HSQC)
O
O
OMe
BnO
OBn
OBn
12e
J = 142 Hz
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

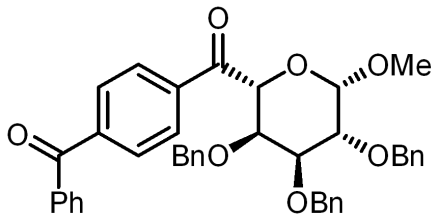

12e (1H-1H NOESY)
O
O
OMe
BnO
OBn
OBn
12e
f2 (ppm)
f1 (ppm)

12f (^{1}H NMR, 500MHz, $CDCl_3$)

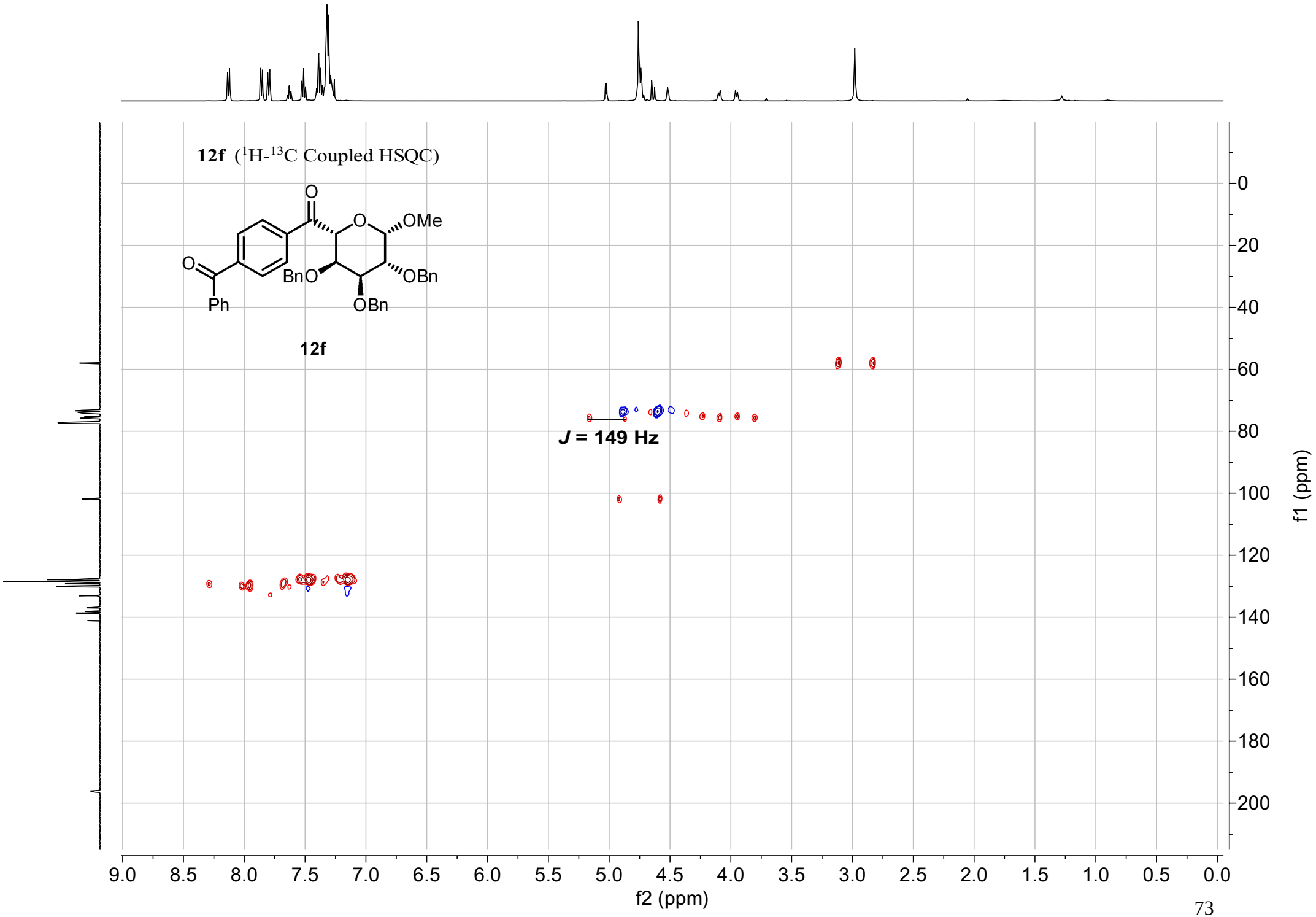


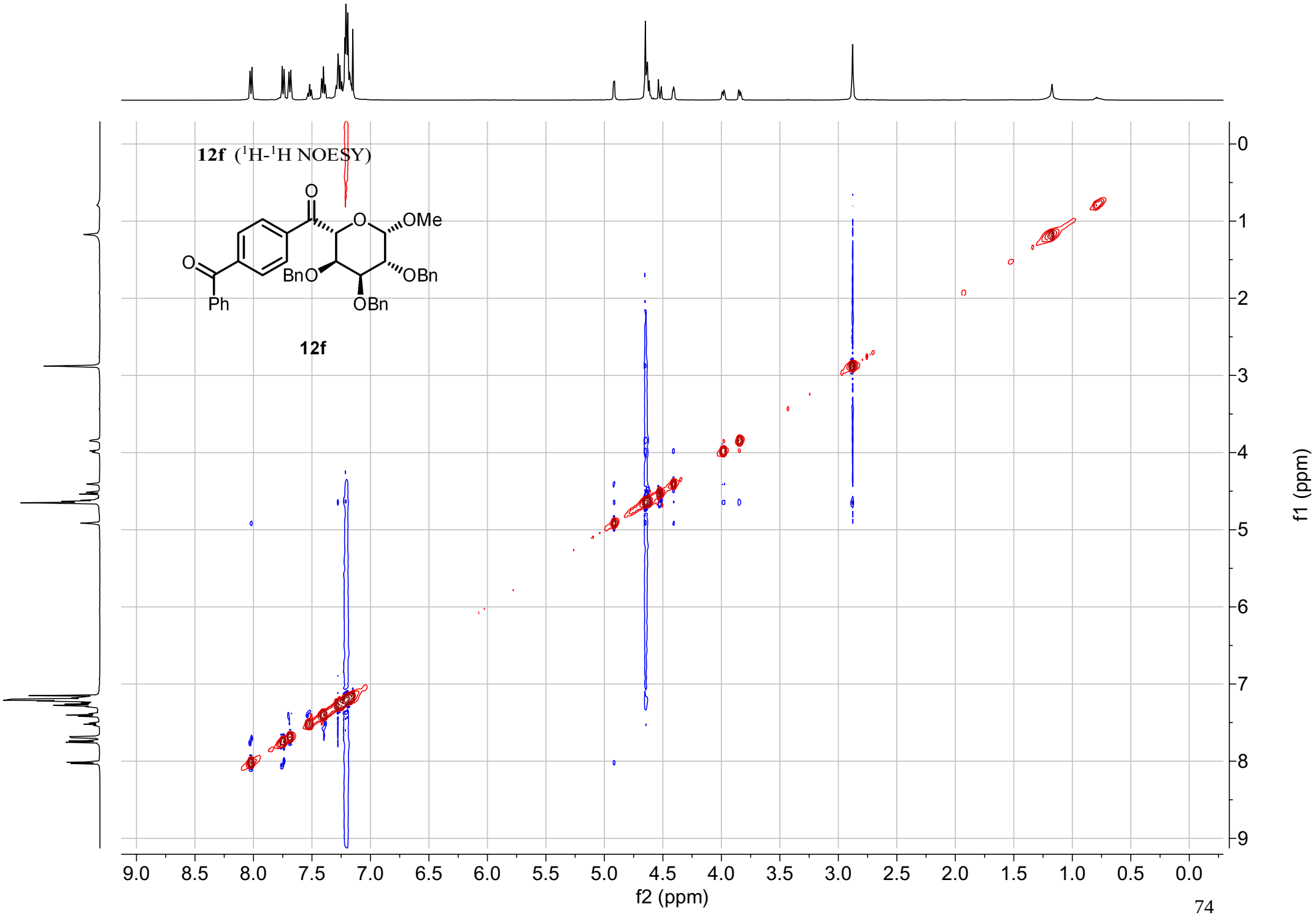
12f

12f (^{13}C NMR, 126MHz, $CDCl_3$)

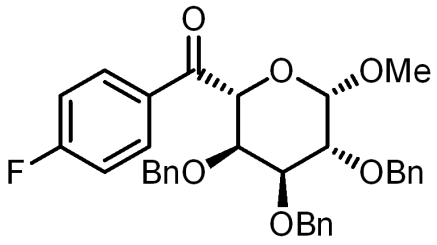


12f

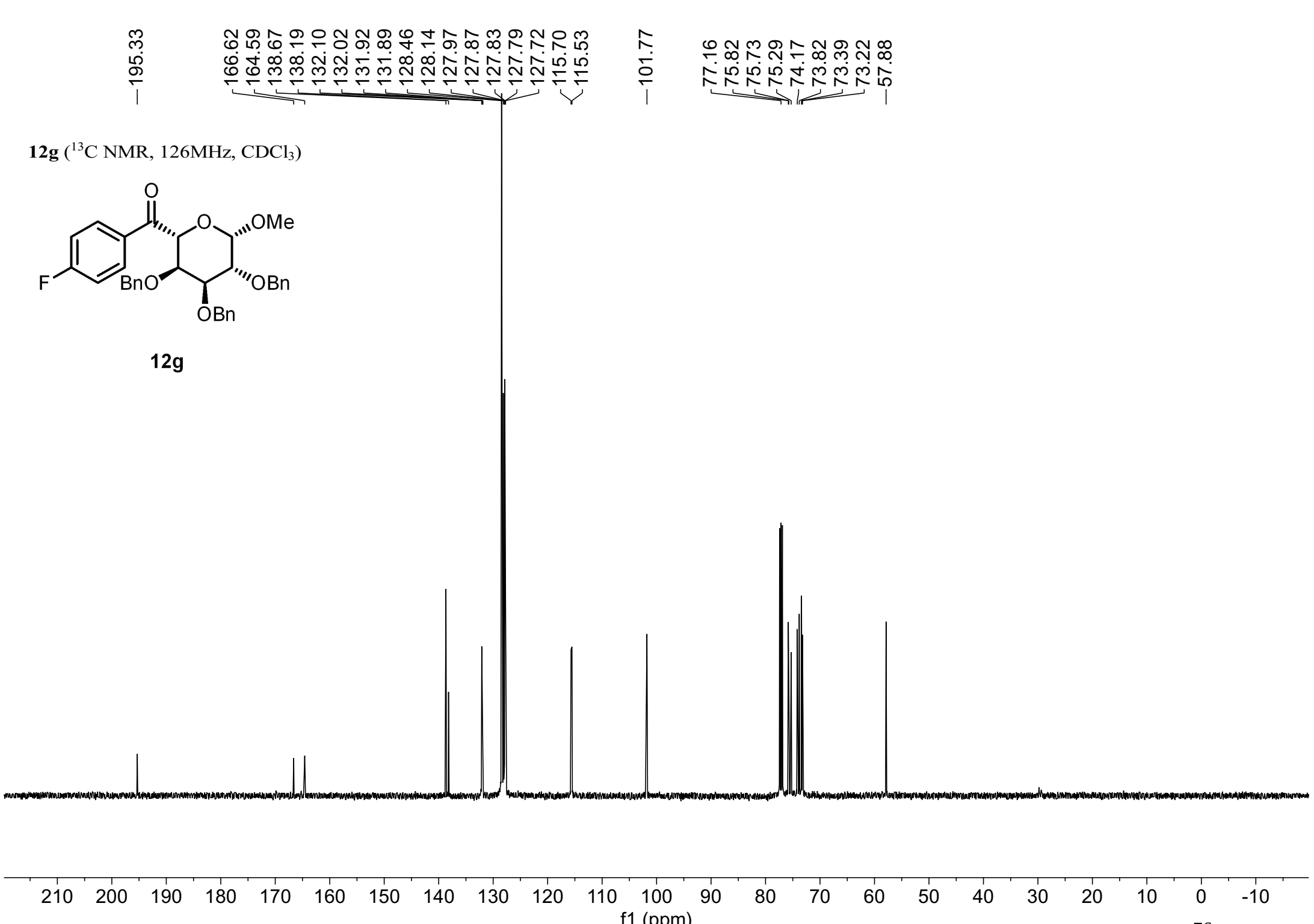

12f (1H-13C Coupled HSQC)
O
O
OMe
O
BnO
OBn
OBn
Ph
12f
J = 149 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


12f (1H-1H NOESY)
O
O
OMe
O
BnO
OBn
Ph
OBn
12f
f2 (ppm)
f1 (ppm)

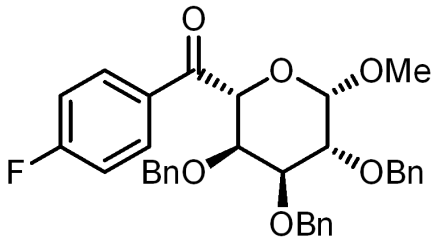
12g (^{1}H NMR, 500MHz, $CDCl_3$)



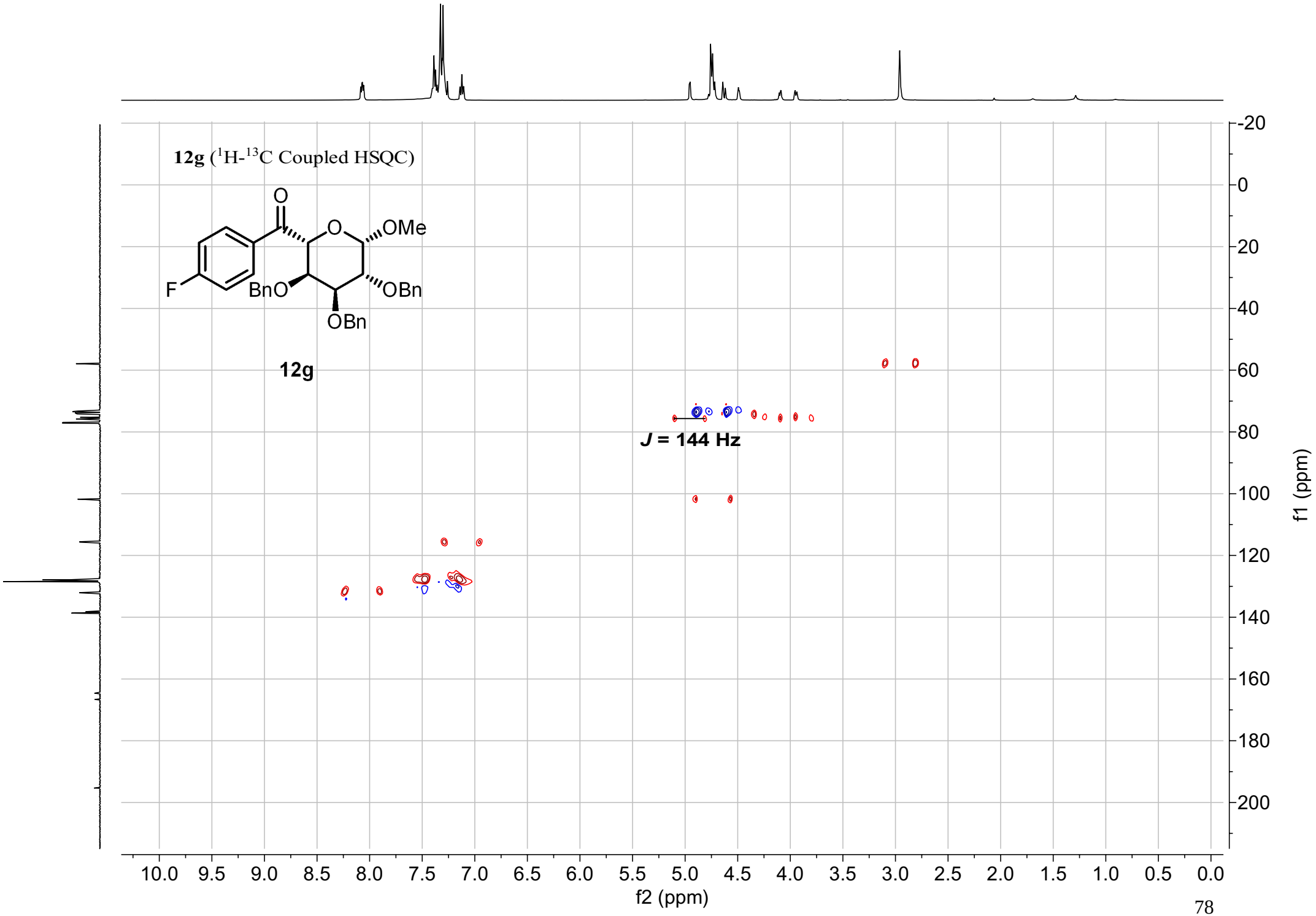
12g

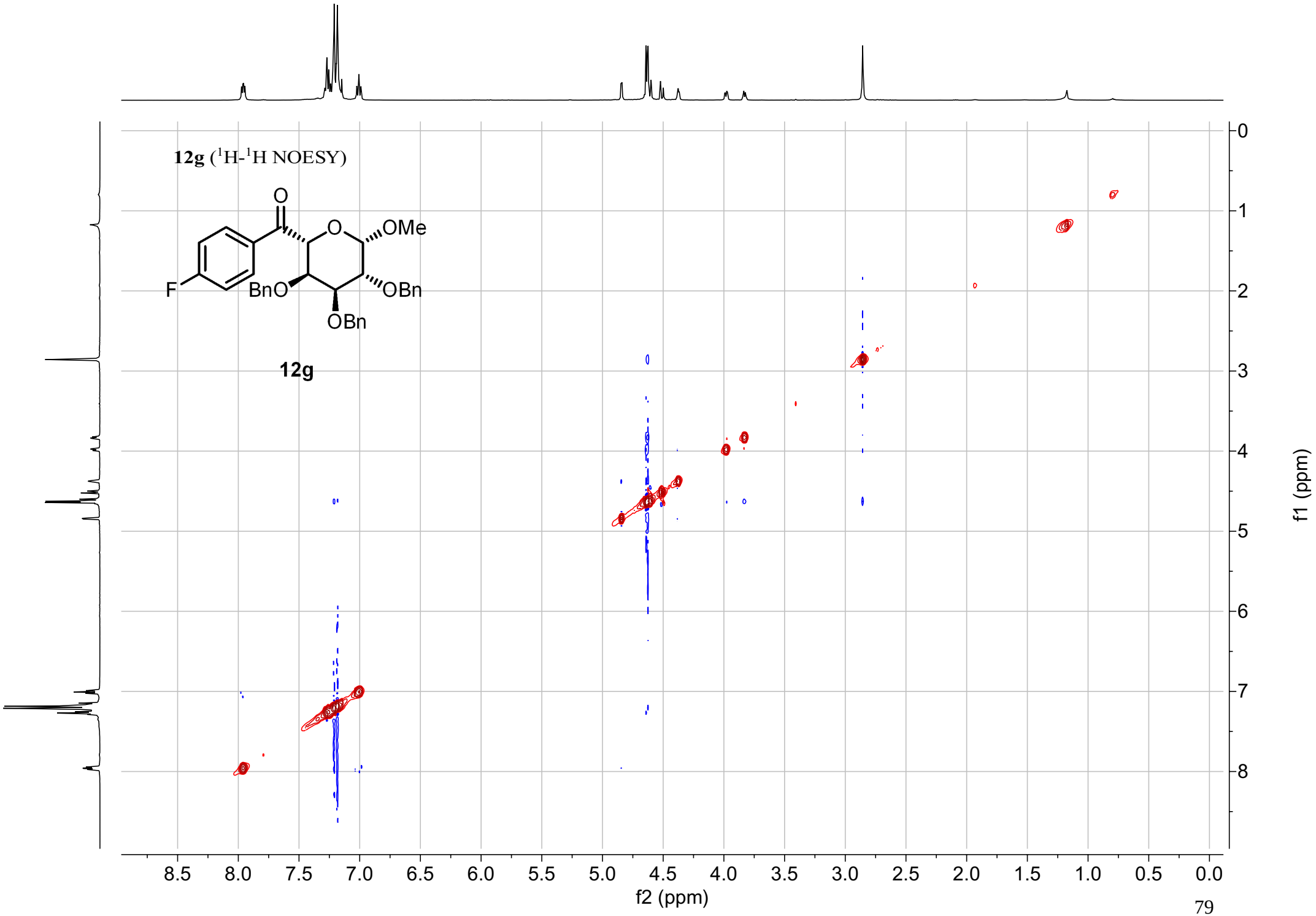

195.33
166.62
164.59
138.67
138.19
132.10
132.02
131.92
131.89
128.46
128.14
127.97
127.87
127.83
127.79
127.72
115.70
115.53
101.77
77.16
75.82
75.73
75.29
74.17
73.82
73.39
73.22
57.88
12g (13C NMR, 126MHz, CDCl3)
O
O
OMe
F
BnO
OBn
OBn
12g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

12g (^{19}F NMR, 471MHz, $CDCl_3$)

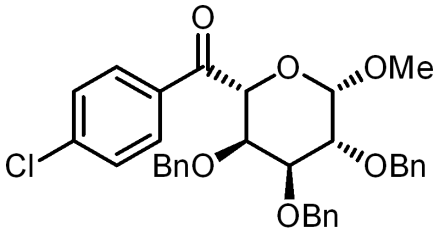


12g


12g (^{1}H-^{13}C Coupled HSQC)
O
O
OMe
F
BnO
OBn
OBn
12g
J = 144 Hz
-20
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

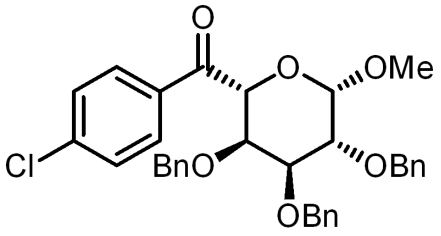

12g (1H-1H NOESY)
O
O
OMe
F
BnO
OBn
OBn
12g
f2 (ppm)
f1 (ppm)

12h (^{1}H NMR, 500MHz, $CDCl_3$)

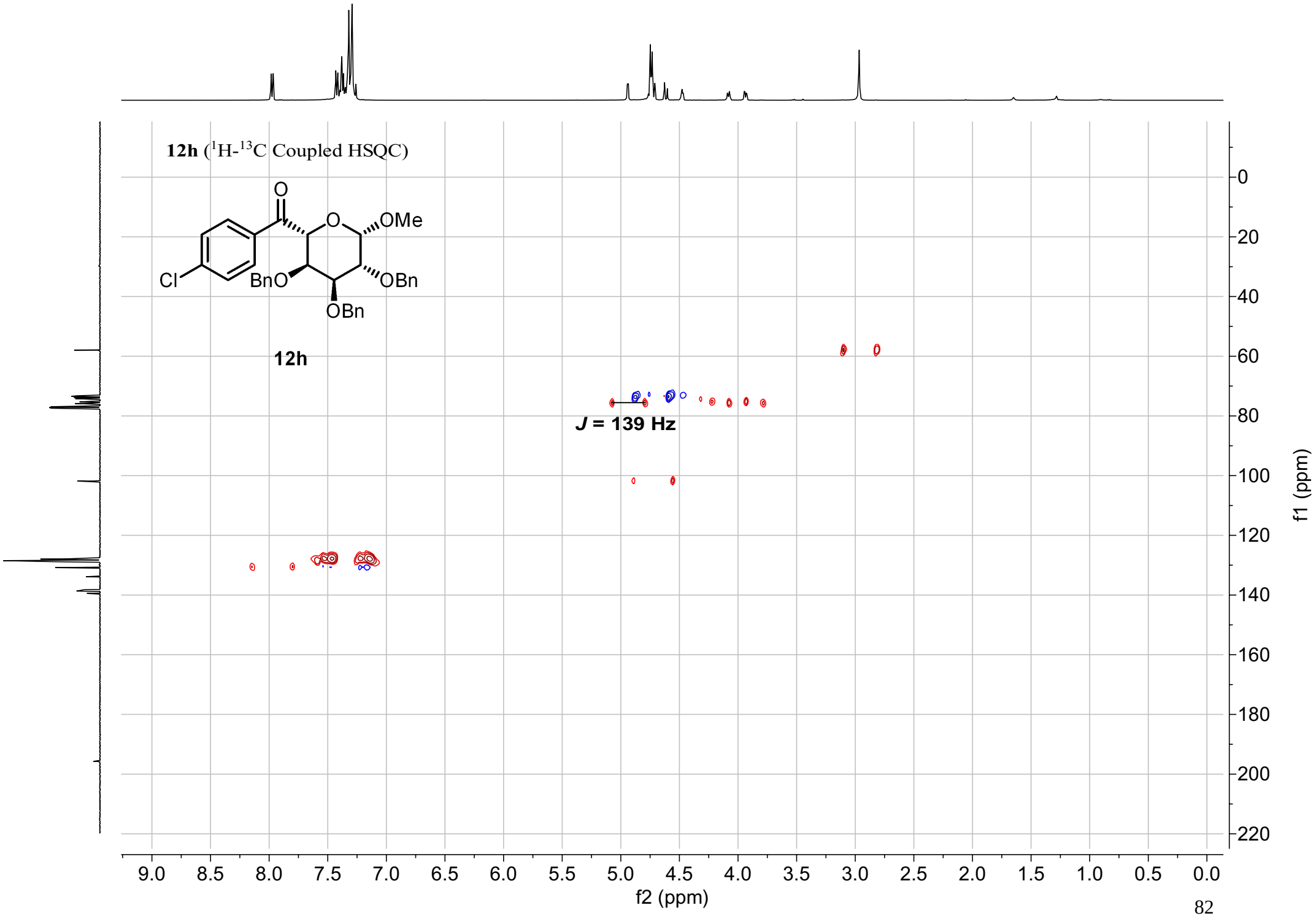


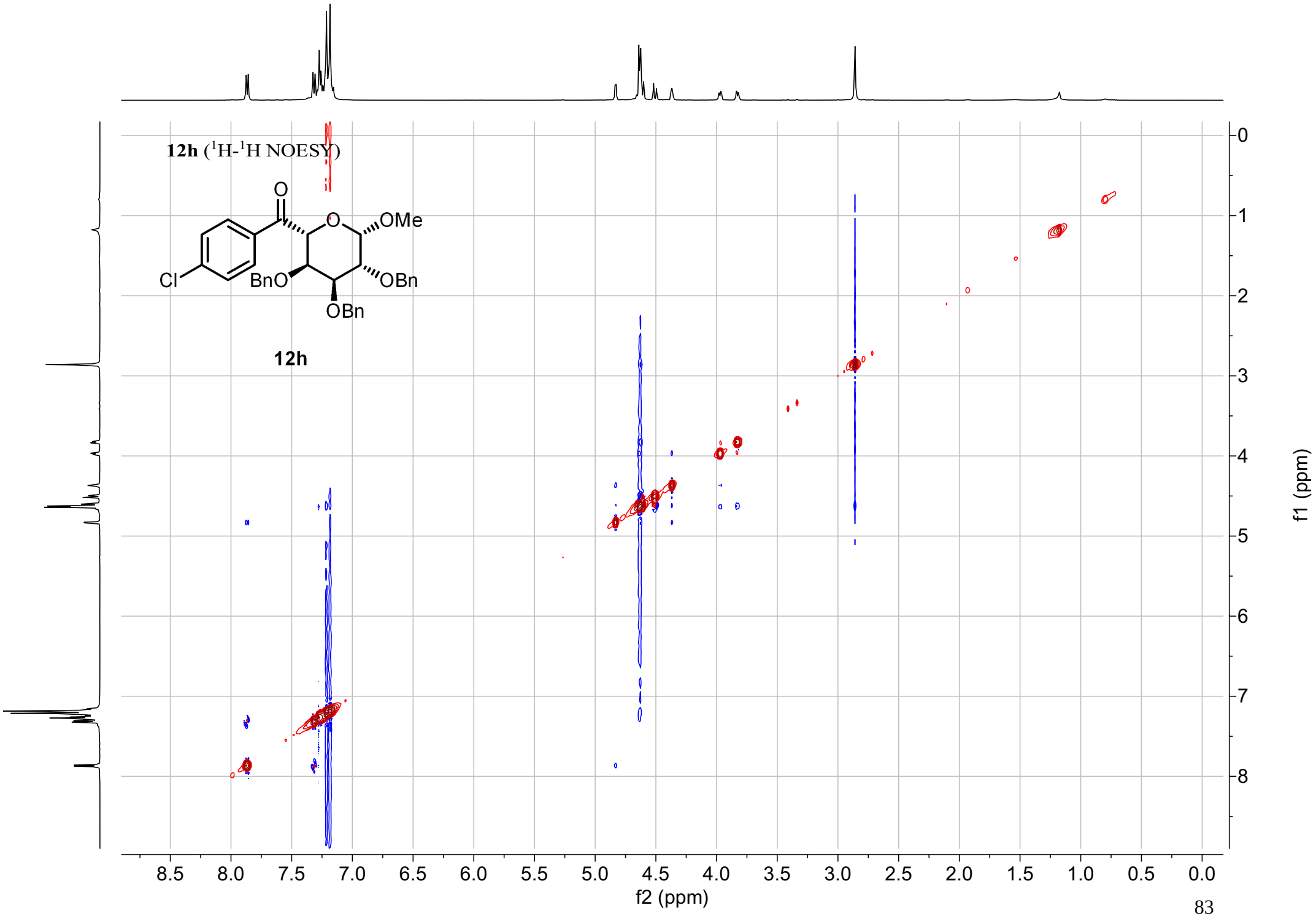
12h

12h (^{13}C NMR, 126MHz, $CDCl_3$)



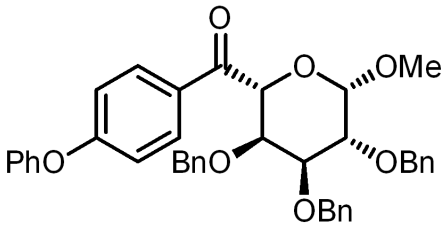
12h


12h (1H-13C Coupled HSQC)
O
O
OMe
Cl
BnO
OBn
OBn
12h
J = 139 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
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

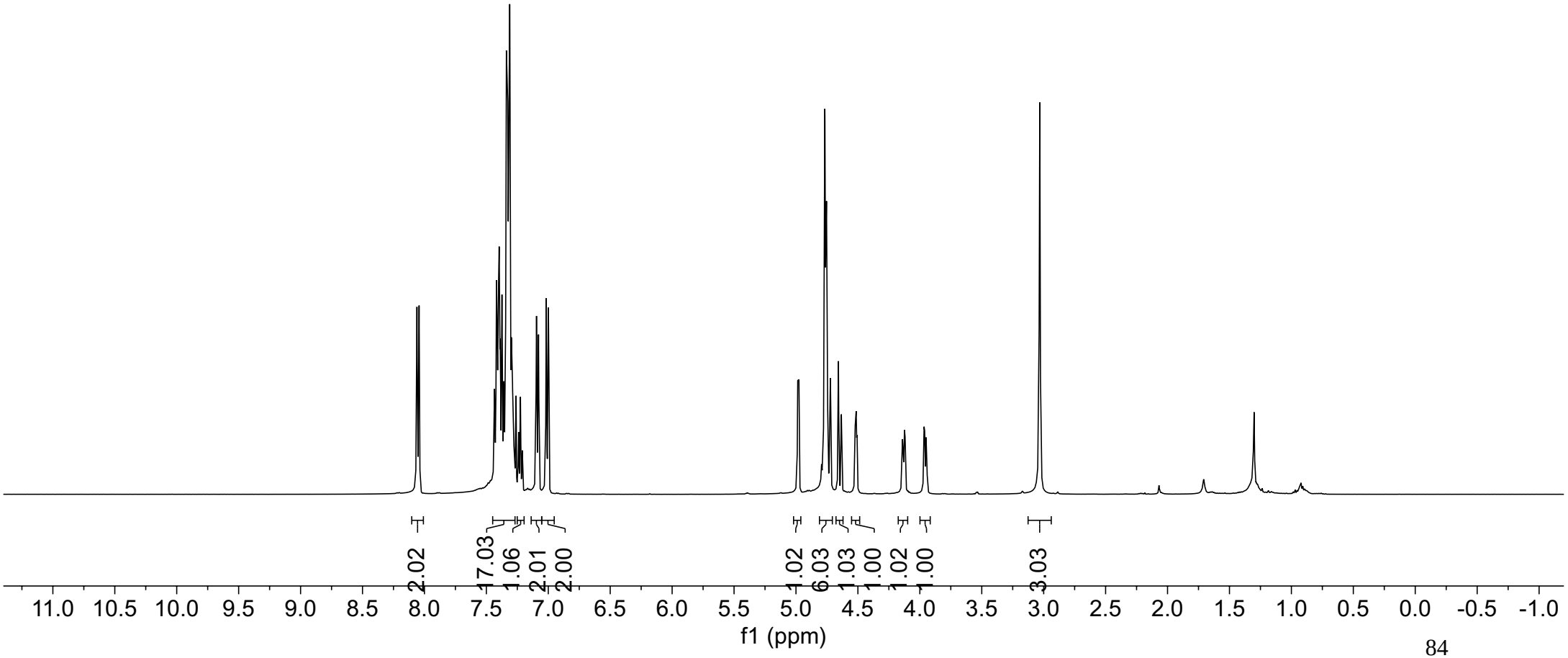

12h (1H-1H NOESY)
O
O
OMe
Cl
BnO
OBn
OBn
12h
f2 (ppm)
f1 (ppm)

8.06 8.04 7.43 7.42 7.41 7.40 7.40 7.39 7.37 7.36 7.34 7.33 7.33 7.32 7.31 7.30 7.29 7.28 7.24 7.22 7.21 7.10 7.08 7.02 7.00 4.99 4.98 4.79 4.77 4.75 4.72 4.66 4.63 4.52 4.52 4.51 4.51 4.14 4.13 4.12 4.12 3.97 3.96 3.95 3.94 3.03

12i (^{1}H NMR, 500MHz, $CDCl_3$)

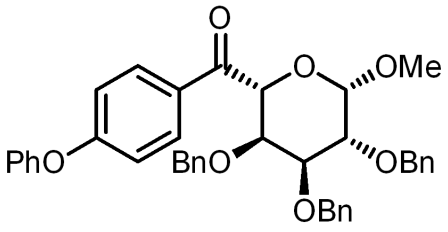


12i

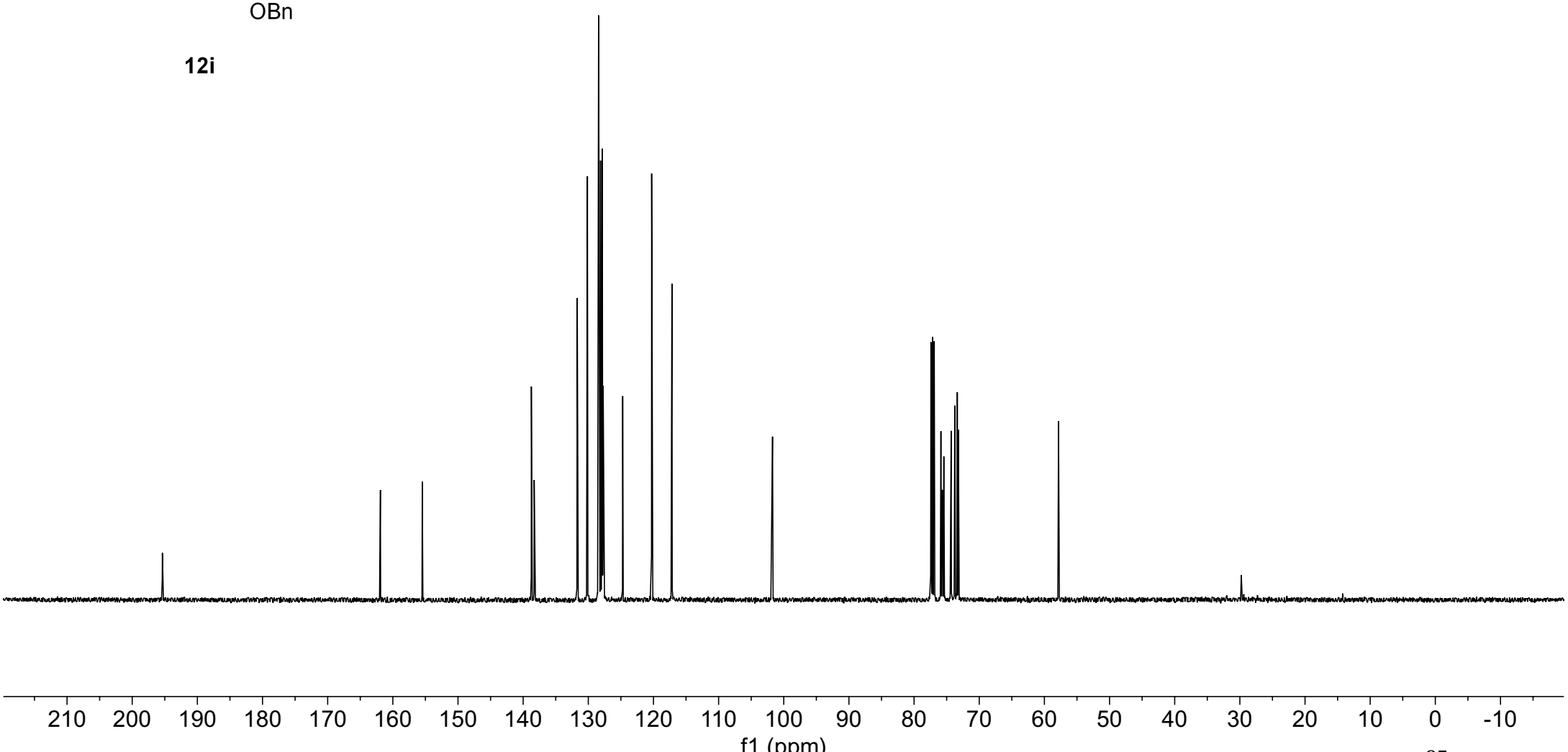


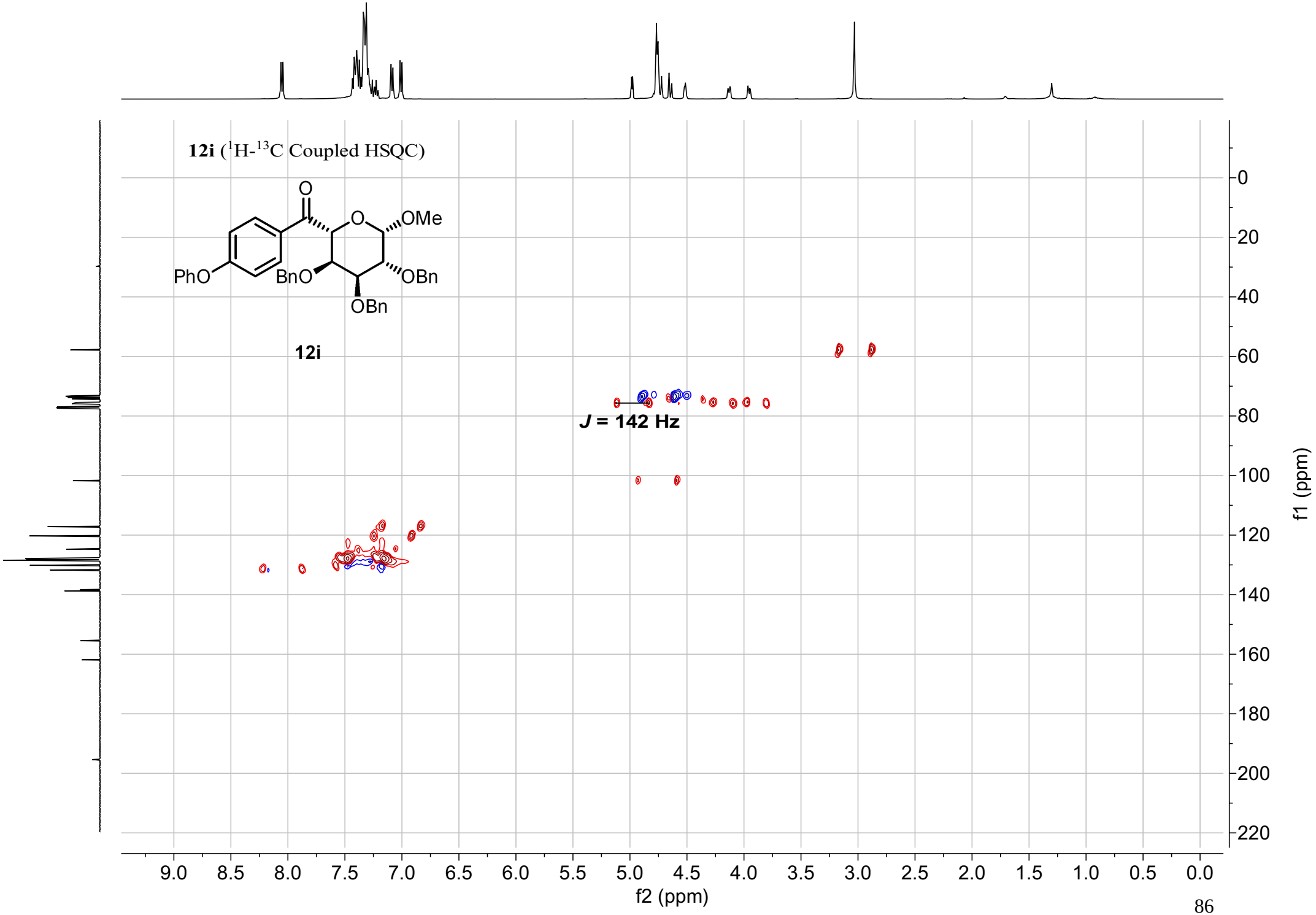
195.37
161.91
155.48
138.74
138.31
131.70
130.21
130.14
128.44
128.42
128.41
128.12
127.94
127.84
127.76
127.72
127.67
124.72
120.28
117.16
101.72
77.16
75.88
75.67
75.43
74.31
73.75
73.36
73.20
57.83

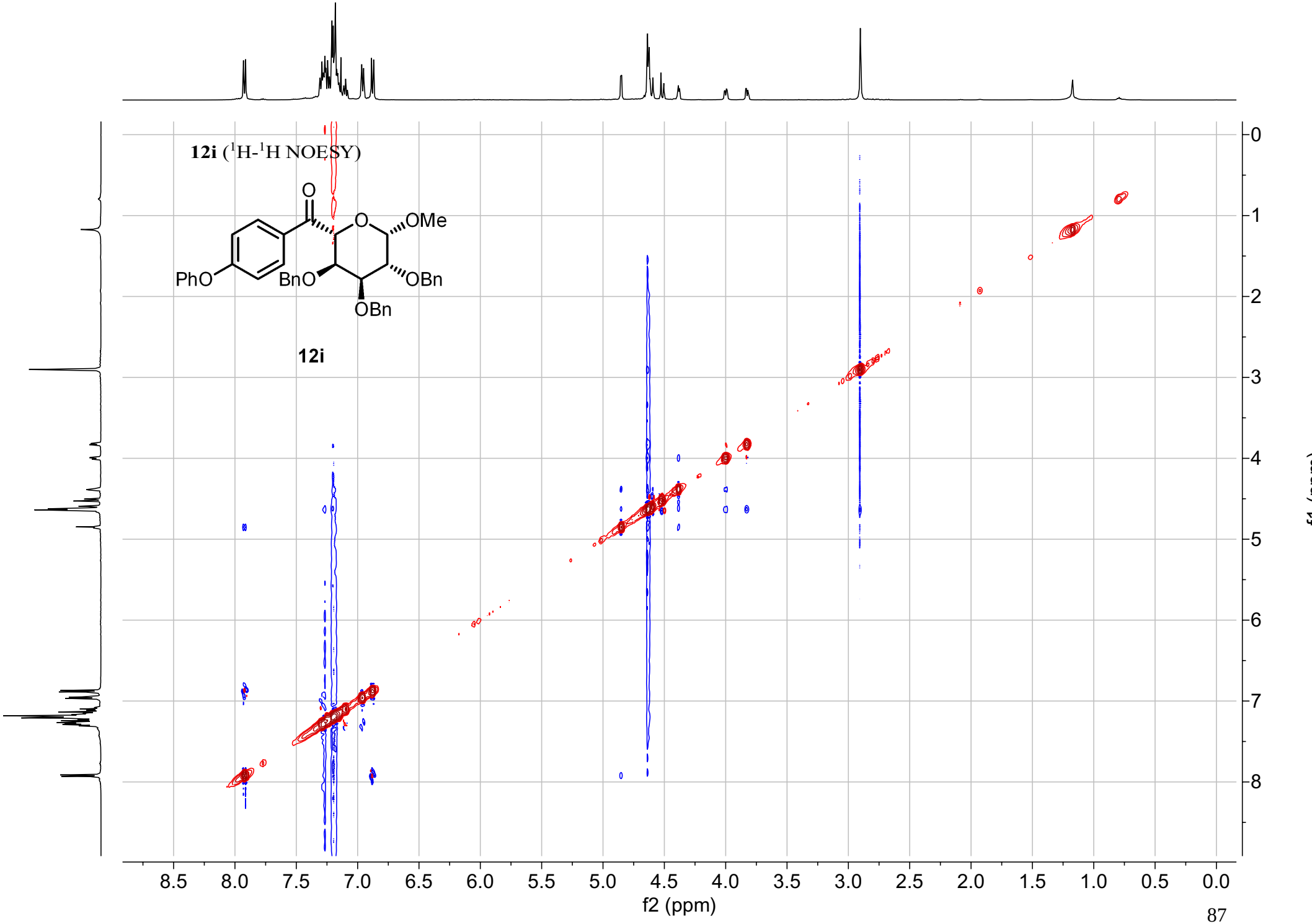
12i (^{13}C NMR, 126MHz, $CDCl_3$)



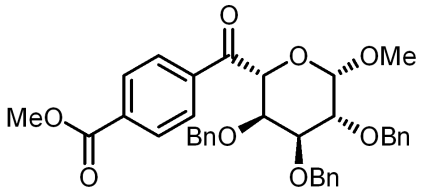
12i




12i (1H-13C Coupled HSQC)
O
O
OMe
PhO
BnO
OBn
OBn
12i
J = 142 Hz
f1 (ppm)
f2 (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
0
20
40
60
80
100
120
140
160
180
200
220

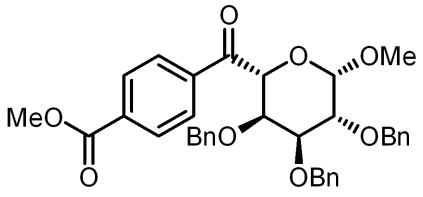

12i (1H-1H NOESY)
O
O
OMe
PhO
BnO
OBn
OBn
12i
f2 (ppm)
f1 (ppm)

12j (^{1}H NMR, 500MHz, $CDCl_3$)

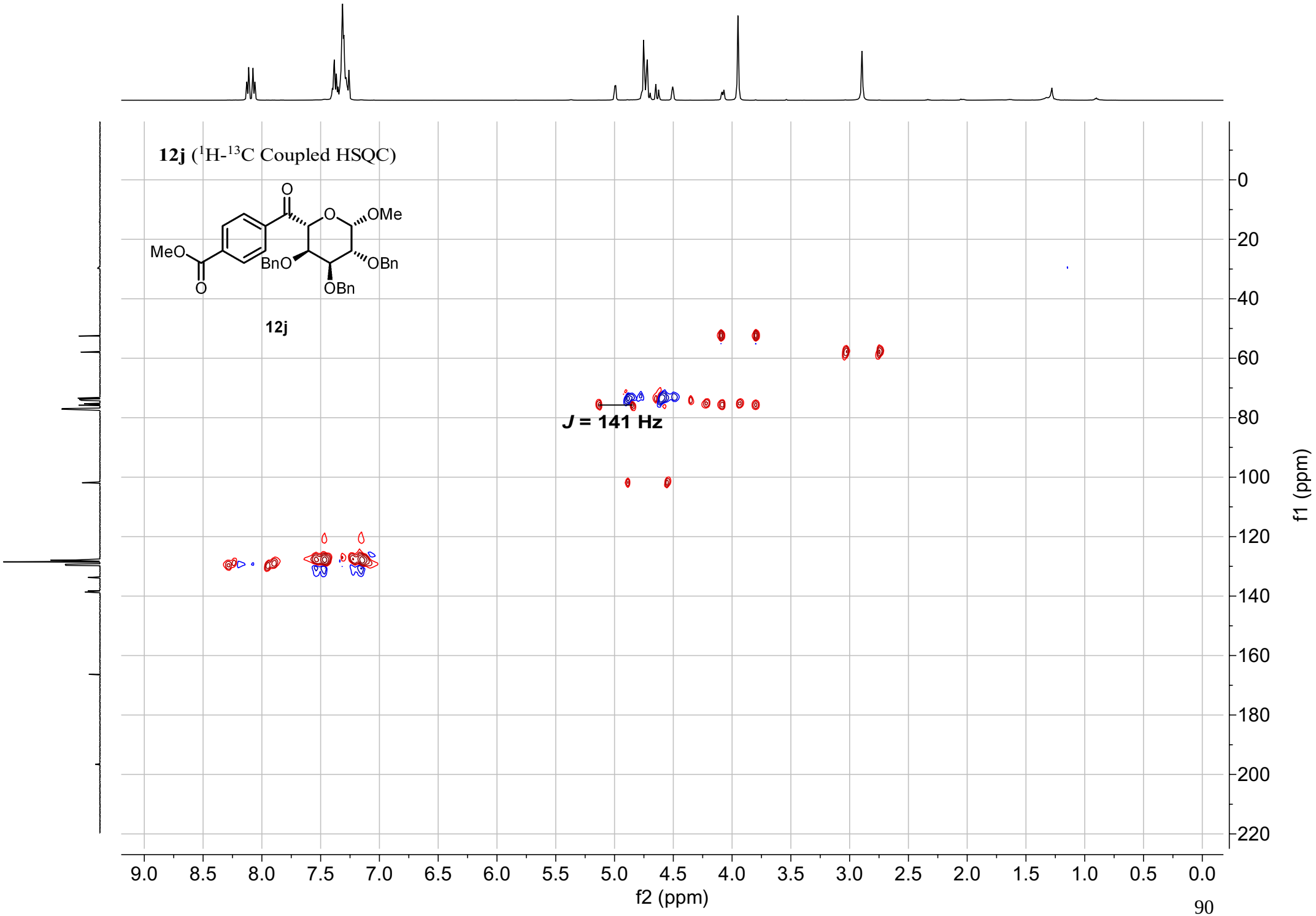


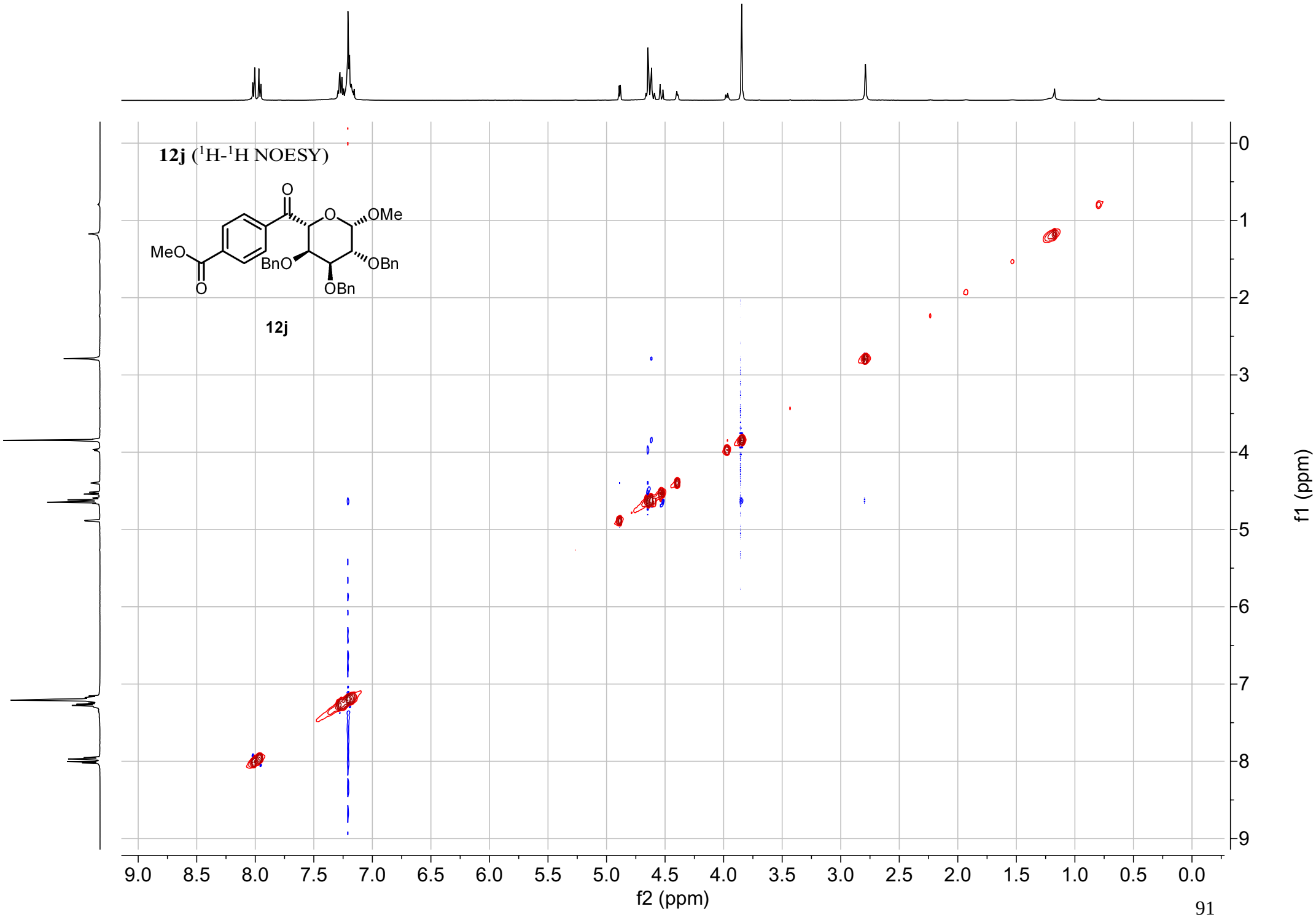
12j

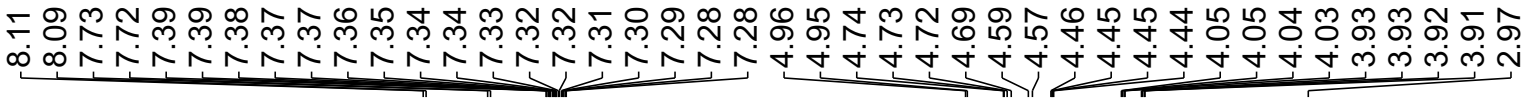
12j (^{13}C NMR, 126MHz, $CDCl_3$)



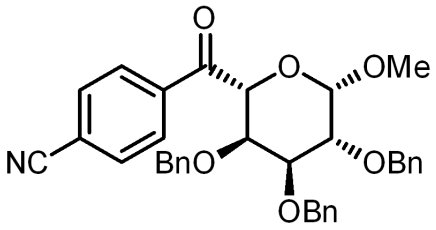
12j


12j (^{1}H-^{13}C Coupled HSQC)
O
O
OMe
MeO
BnO
OBn
O
OBn
12j
J = 141 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
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

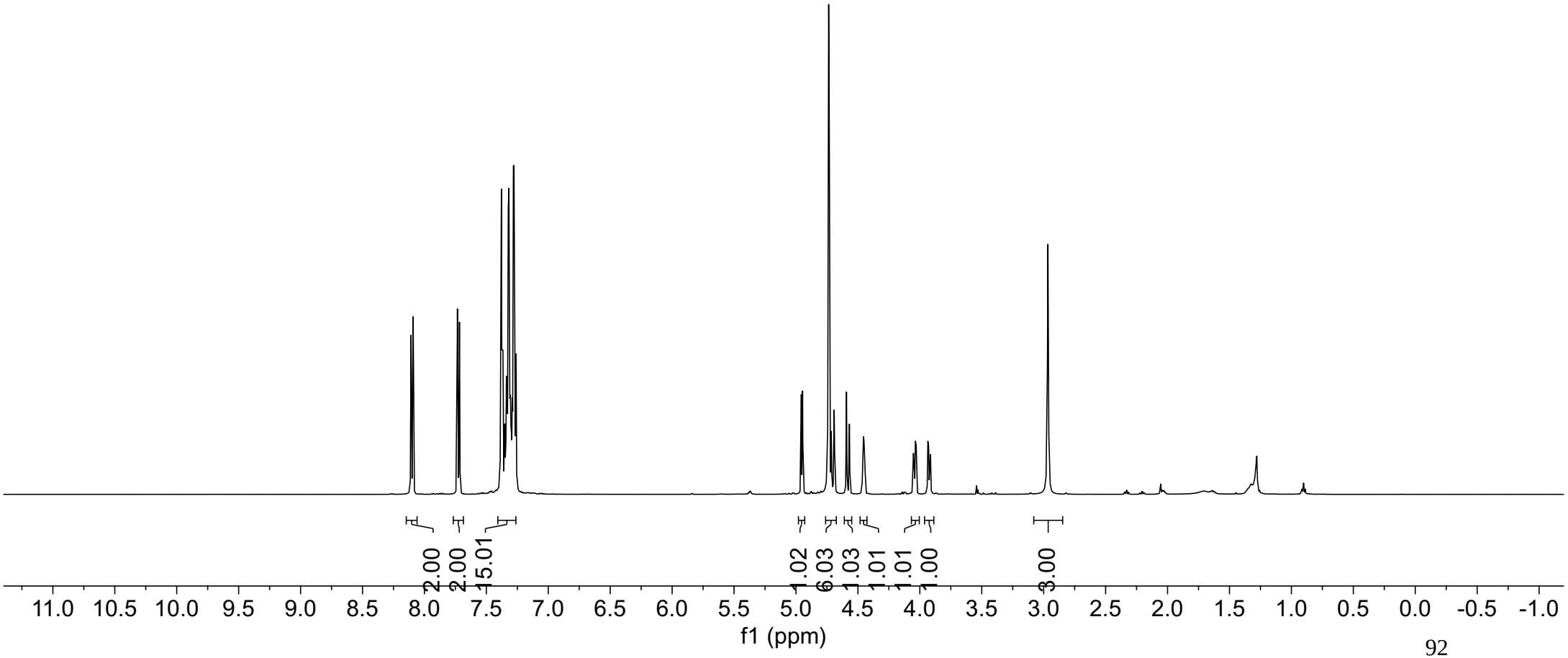

12j (^{1}H-^{1}H NOESY)
O
O
OMe
MeO
BnO
OBn
O
OBn
12j
f2 (ppm)
f1 (ppm)



12k (^{1}H NMR, 500MHz, $CDCl_3$)

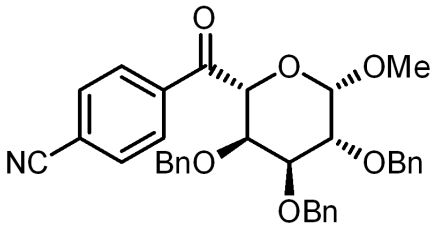


12k

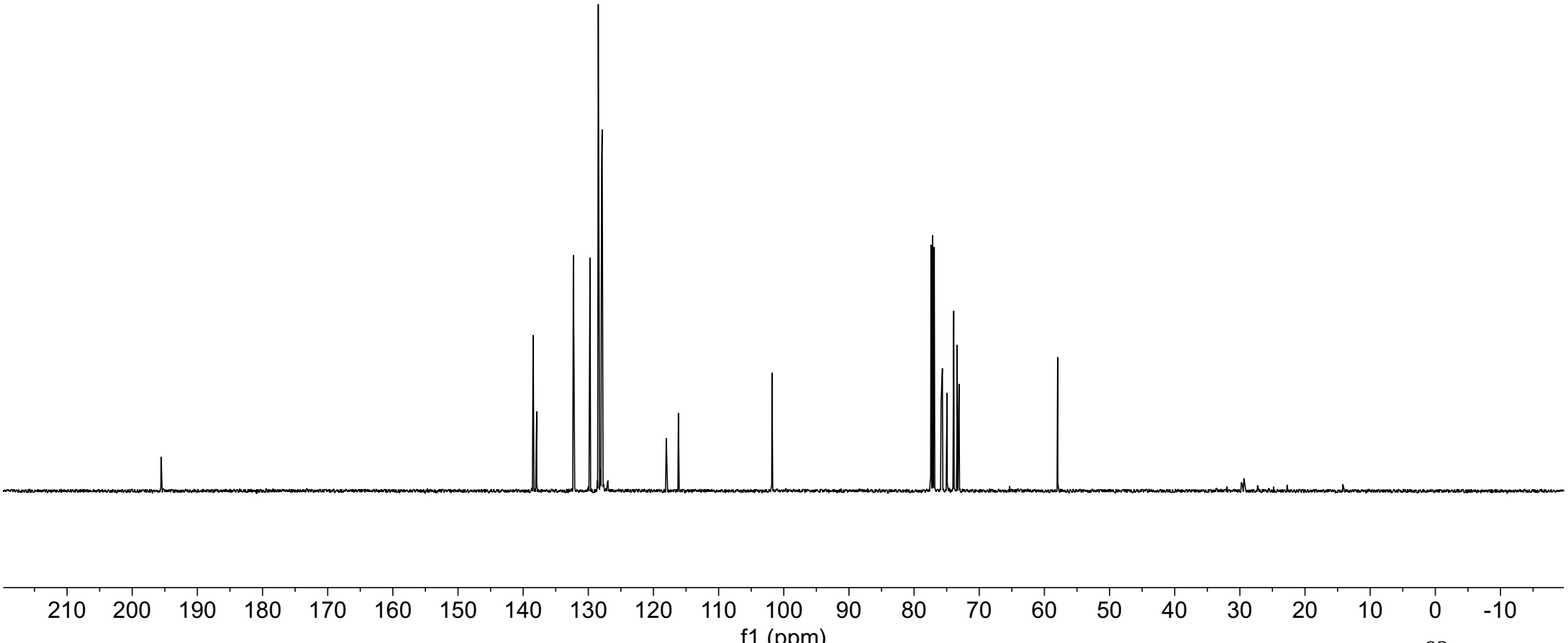


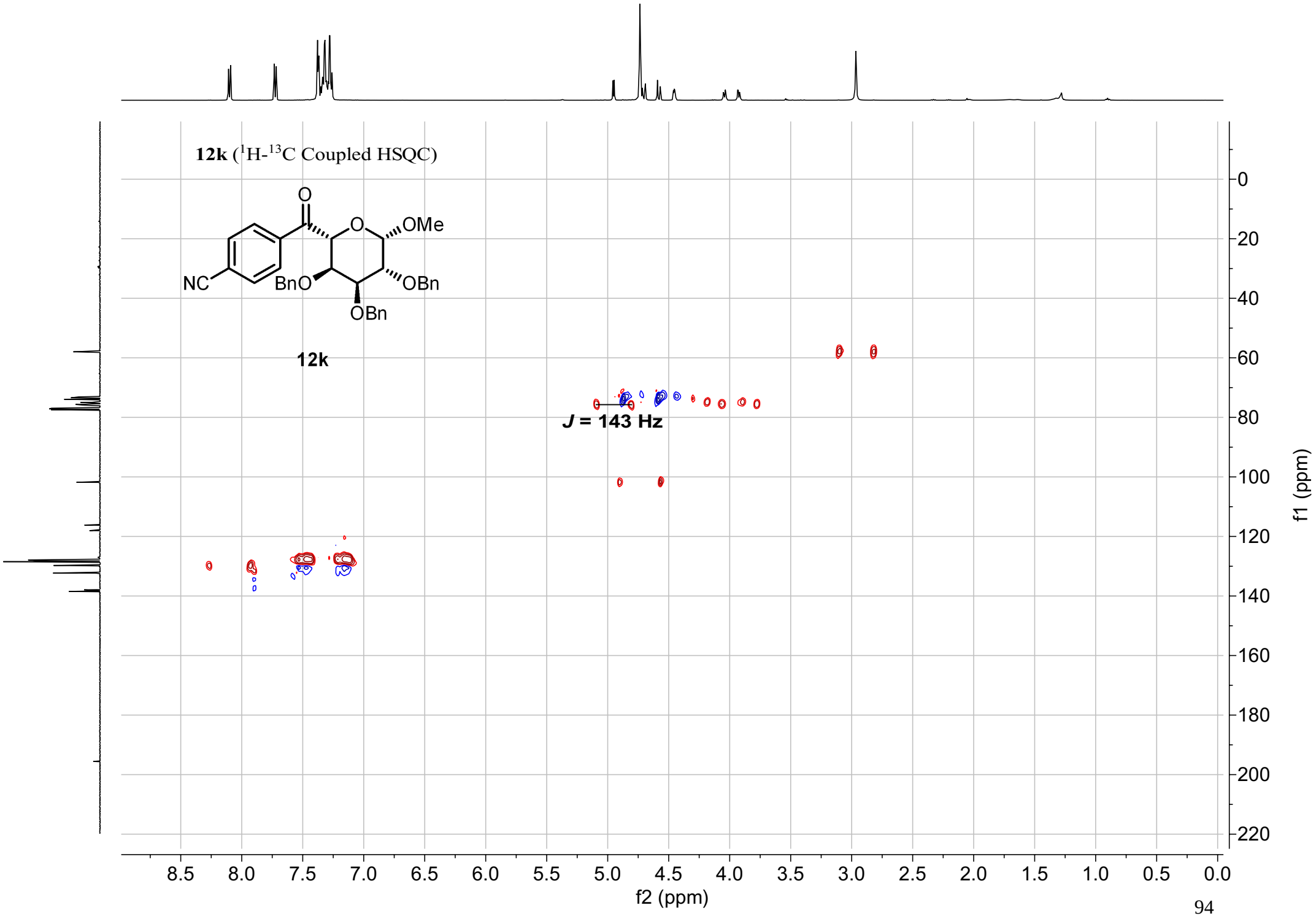
195.56
138.51
138.47
137.93
132.30
129.74
128.48
128.47
128.13
127.96
127.91
127.88
127.86
127.80
118.04
116.18
101.81
77.16
75.86
75.66
74.94
73.93
73.91
73.42
73.11
57.97

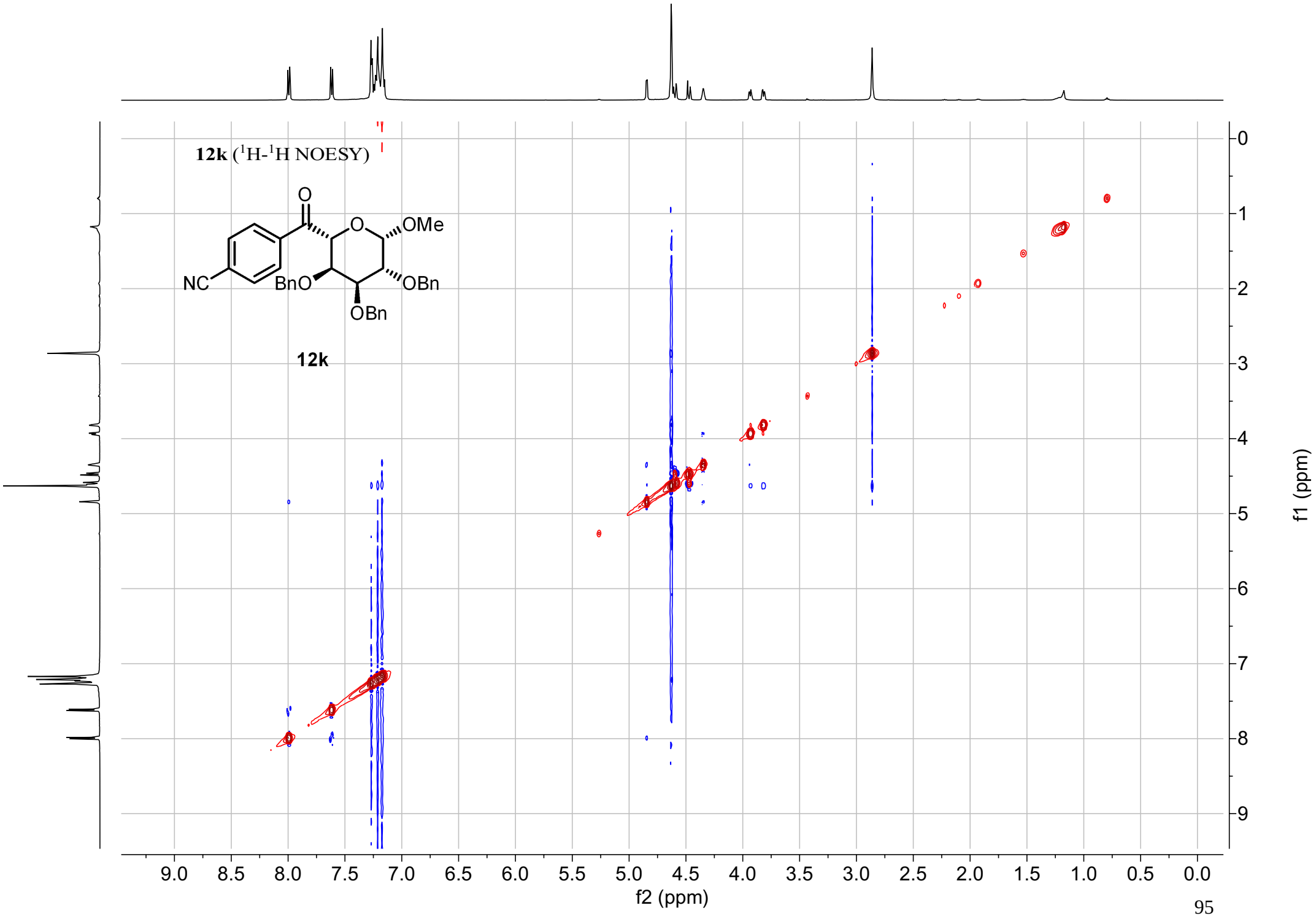
12k (^{13}C NMR, 126MHz, $CDCl_3$)



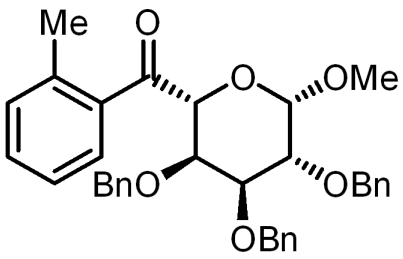
12k




12k (1H-13C Coupled HSQC)
O
O
OMe
NC
BnO
OBn
OBn
12k
J = 143 Hz
0
20
40
60
80
100
120
140
160
180
200
220
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
f2 (ppm)

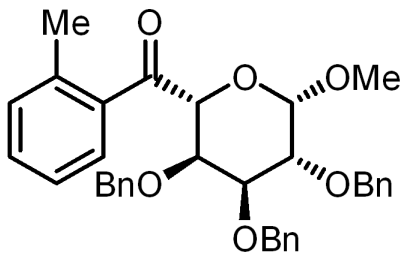

12k (1H-1H NOESY)
O
O
OMe
NC
BnO
OBn
OBn
12k
f2 (ppm)
f1 (ppm)

12l (^{1}H NMR, 500MHz, $CDCl_3$)

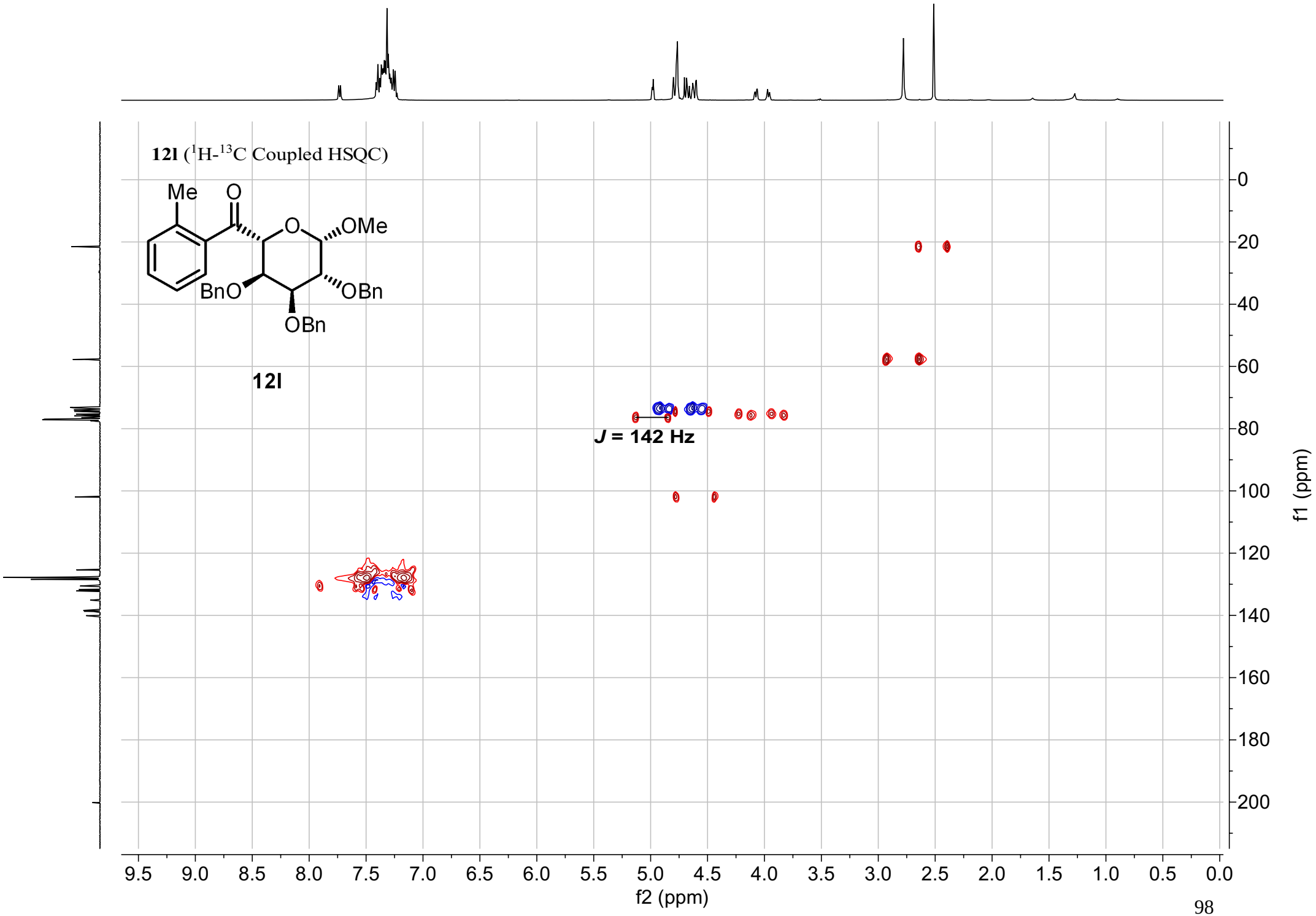


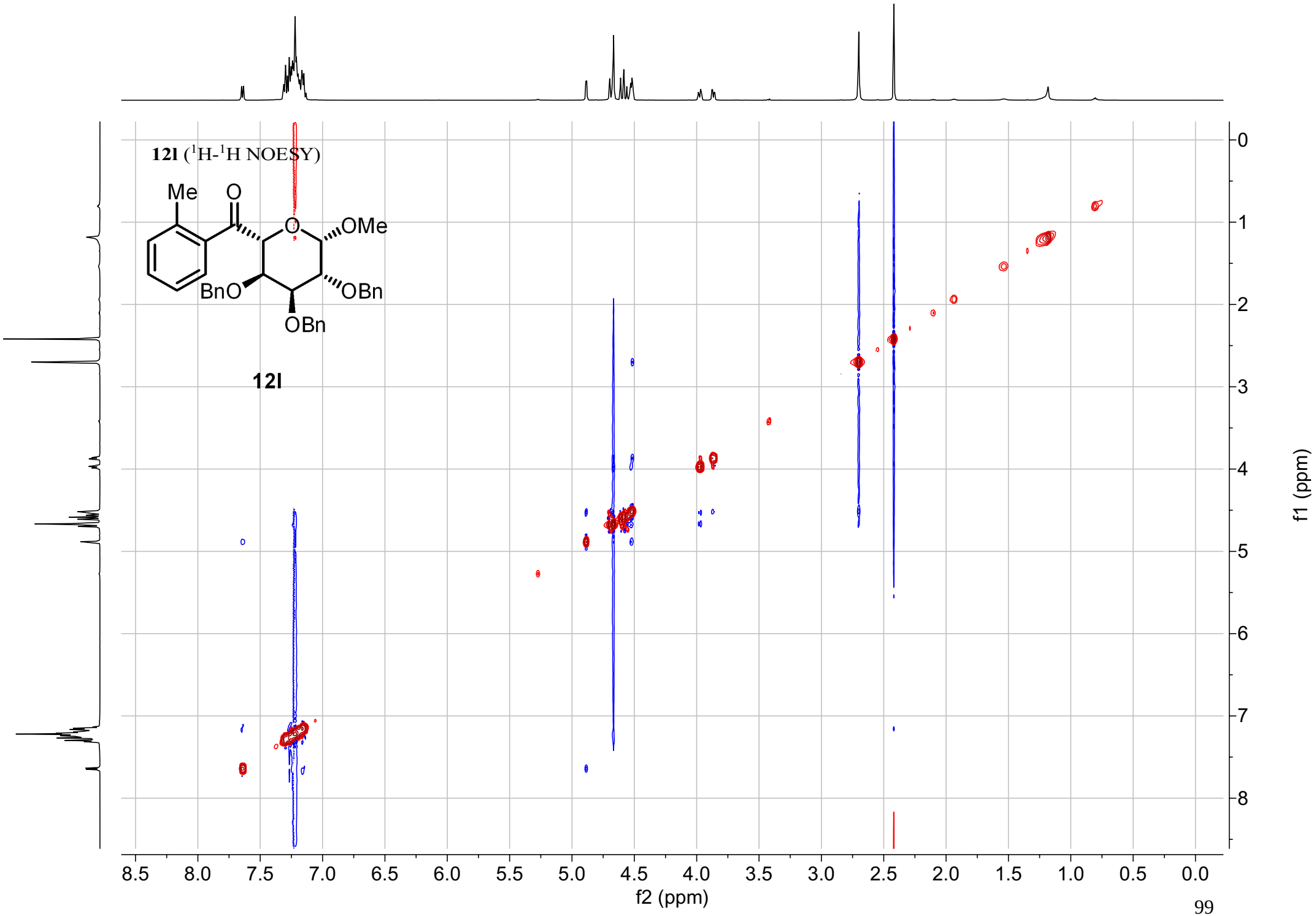
12l

12l (^{13}C NMR, 126MHz, $CDCl_3$)

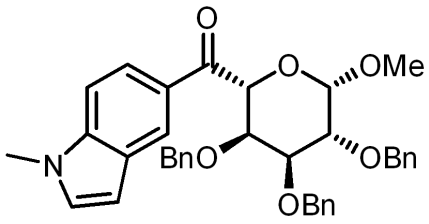


12l

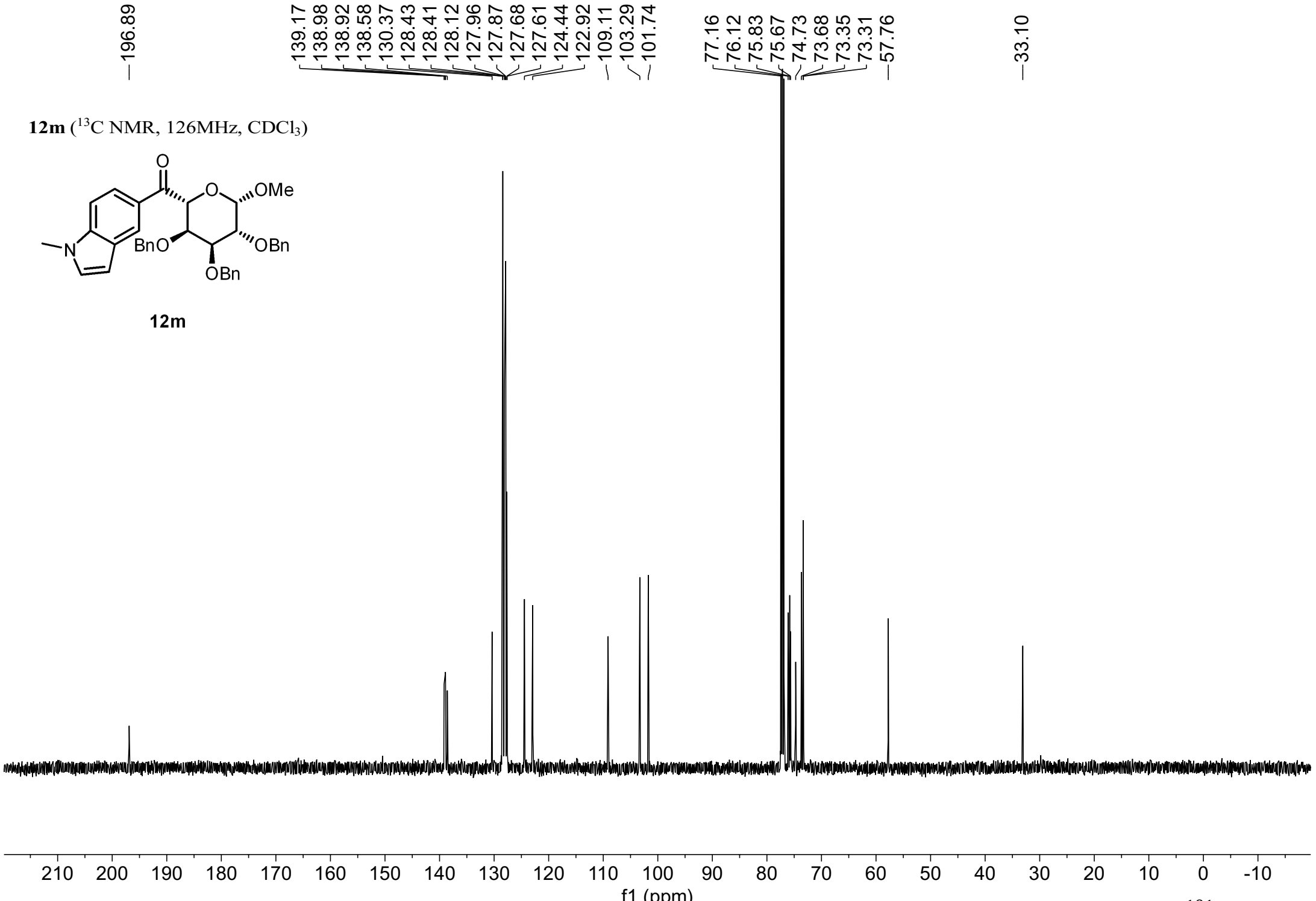

12l (^{1}H-^{13}C Coupled HSQC)
Me
O
O
OMe
BnO
OBn
OBn
12l
J = 142 Hz
f1 (ppm)
f2 (ppm)

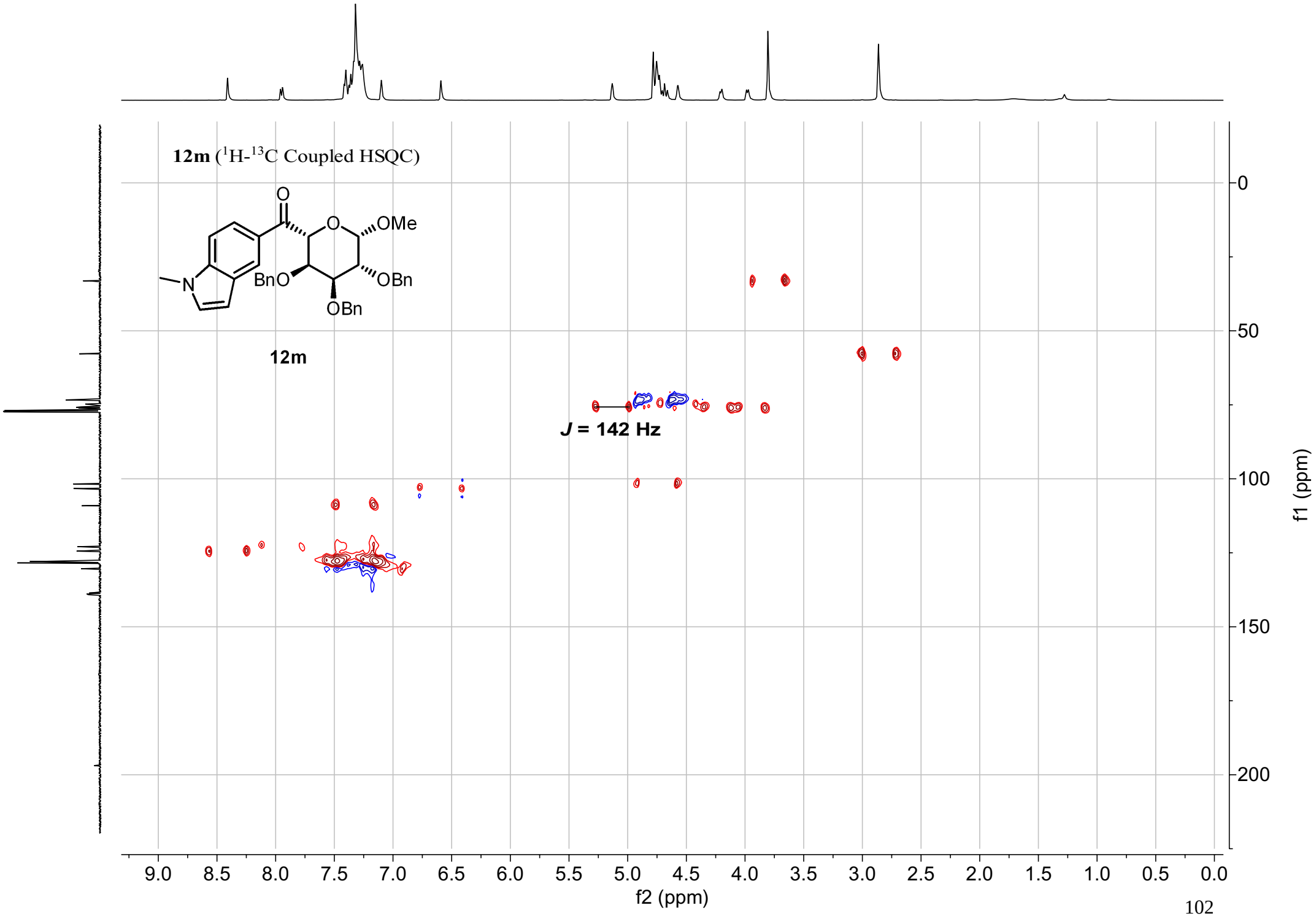

12l (1H-1H NOESY)
Me
O
O
OMe
BnO
OBn
OBn
12l
f2 (ppm)
f1 (ppm)

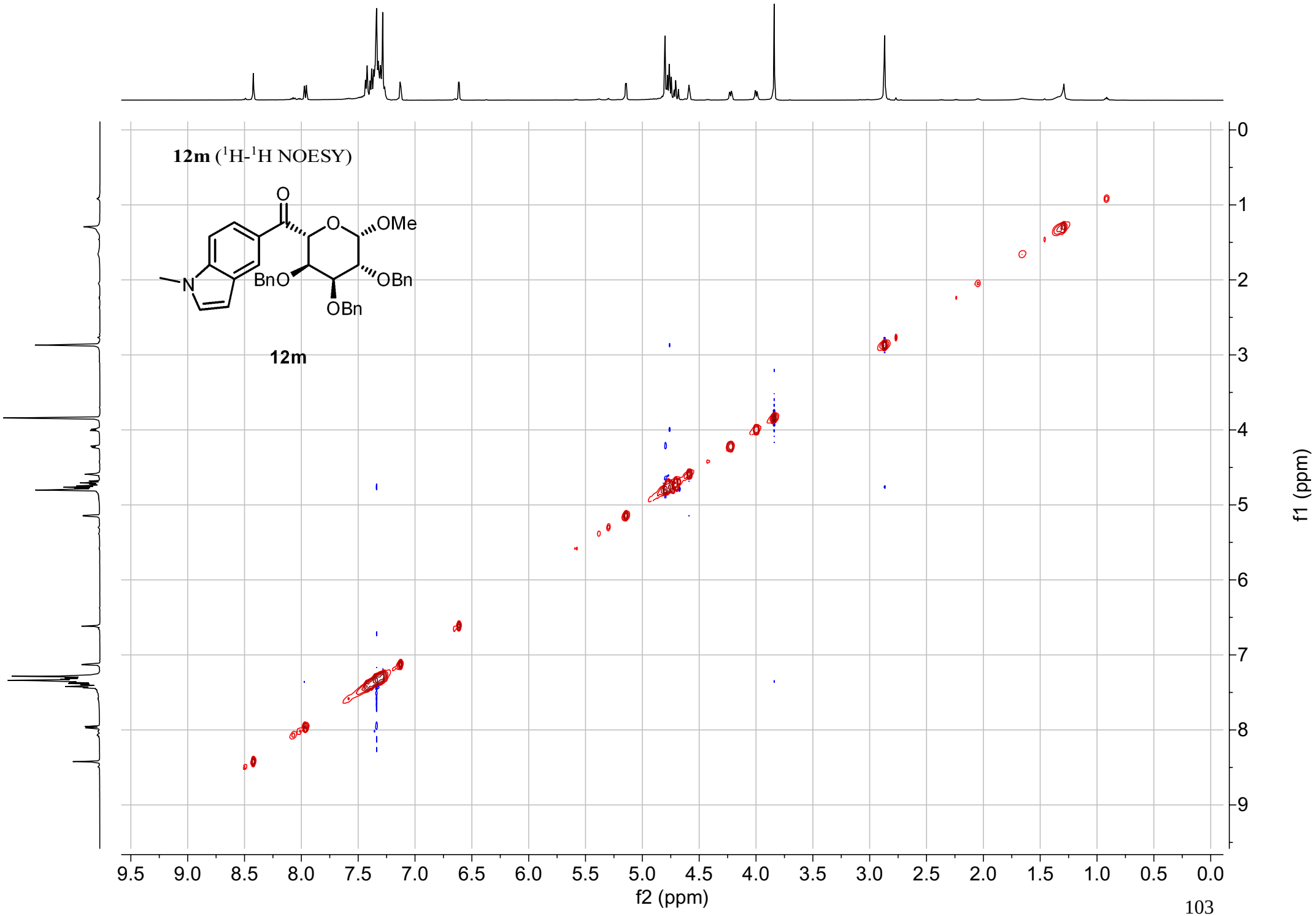
12m (^{1}H NMR, 500MHz, $CDCl_3$)



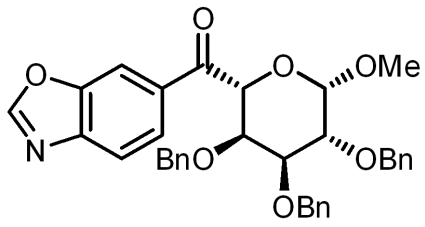
12m


196.89
139.17
138.98
138.92
138.58
130.37
128.43
128.41
128.12
127.96
127.87
127.68
127.61
124.44
122.92
109.11
103.29
101.74
77.16
76.12
75.83
75.67
74.73
73.68
73.35
73.31
57.76
33.10
12m (13C NMR, 126MHz, CDCl3)
O
O
OMe
N
BnO
OBn
OBn
12m
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)


12m (1H-13C Coupled HSQC)
O
O
OMe
N
BnO
OBn
OBn
12m
J = 142 Hz
0
50
100
150
200
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
f2 (ppm)

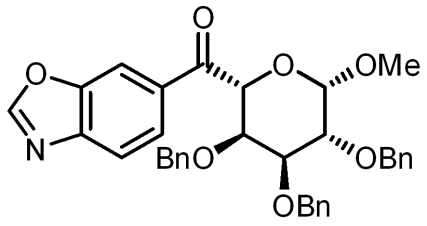

12m (1H-1H NOESY)
O
O
OMe
BnO
OBn
OBn
N
12m
f2 (ppm)
f1 (ppm)

12n (^{1}H NMR, 500MHz, $CDCl_3$)

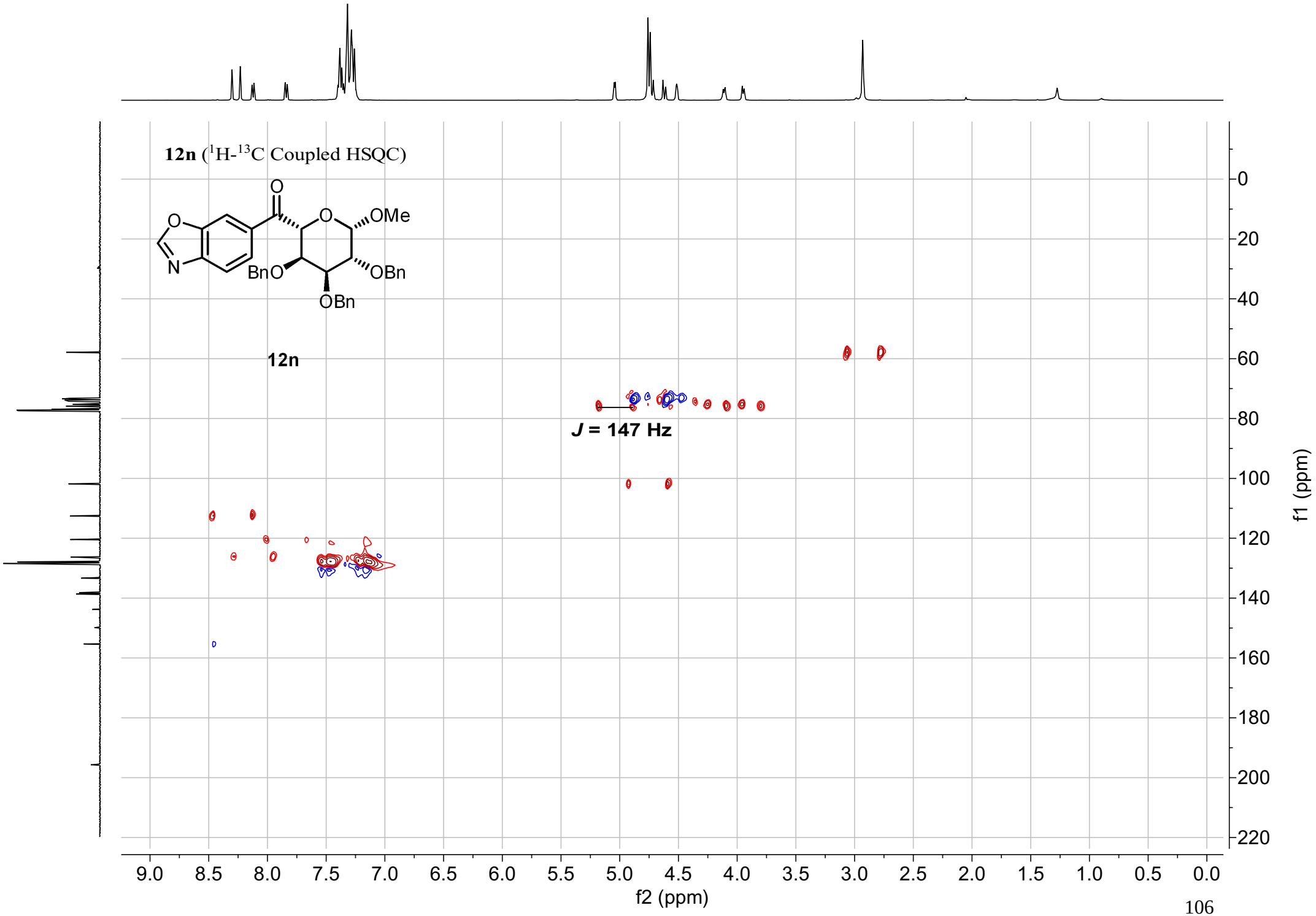


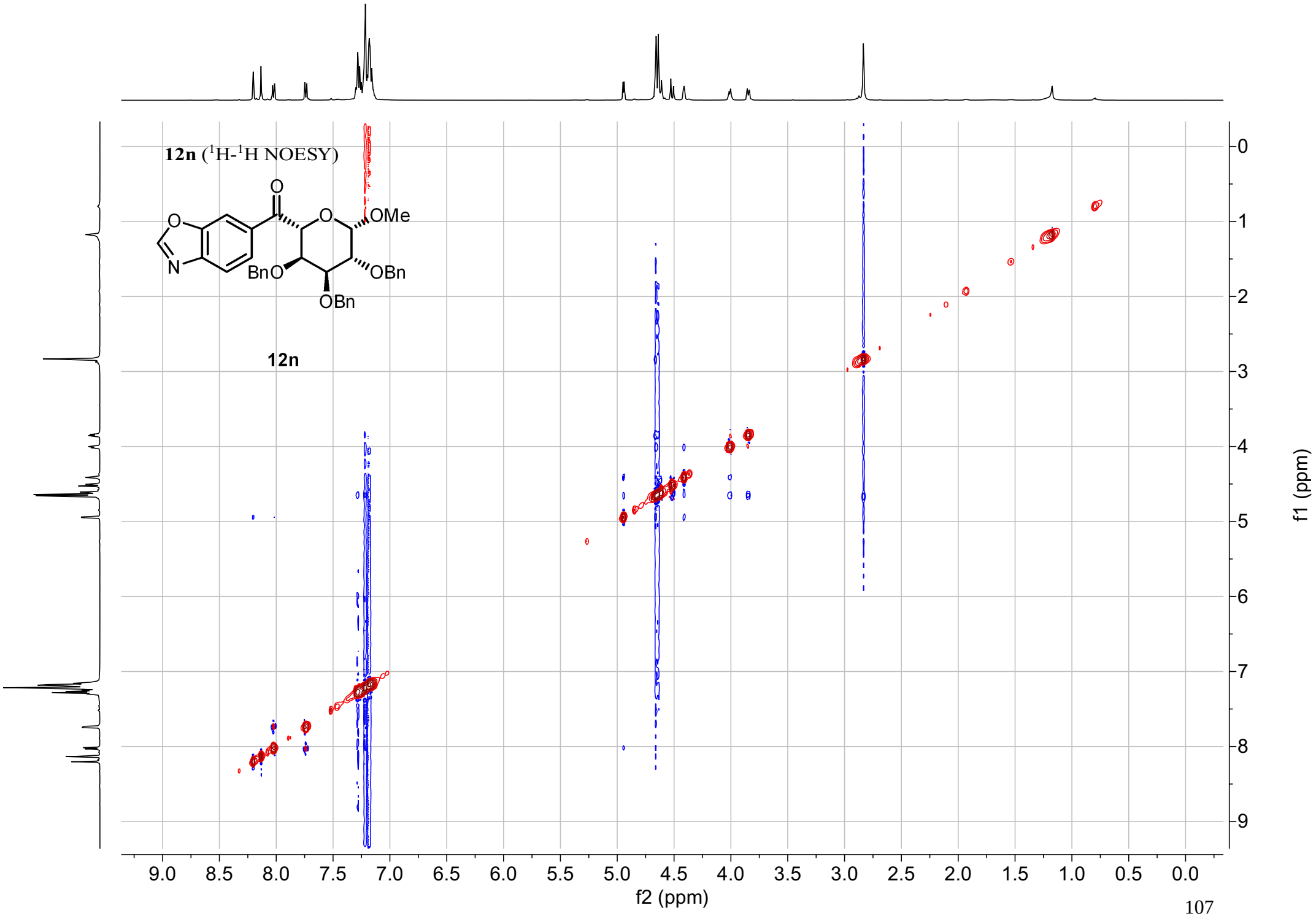
12n

12n (^{13}C NMR, 126MHz, $CDCl_3$)

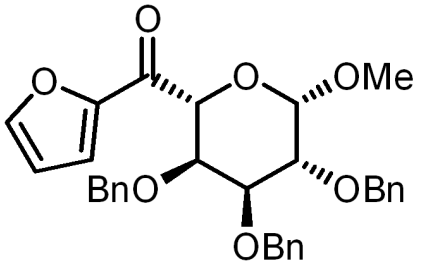


12n


12n (^{1}H-^{13}C Coupled HSQC)
12n
J = 147 Hz
f2 (ppm)
f1 (ppm)

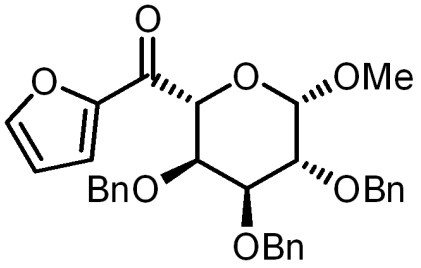

12n (1H-1H NOESY)
O
O
N
O
OMe
BnO
OBn
OBn
12n
f2 (ppm)
f1 (ppm)

12o (^{1}H NMR, 500MHz, $CDCl_3$)

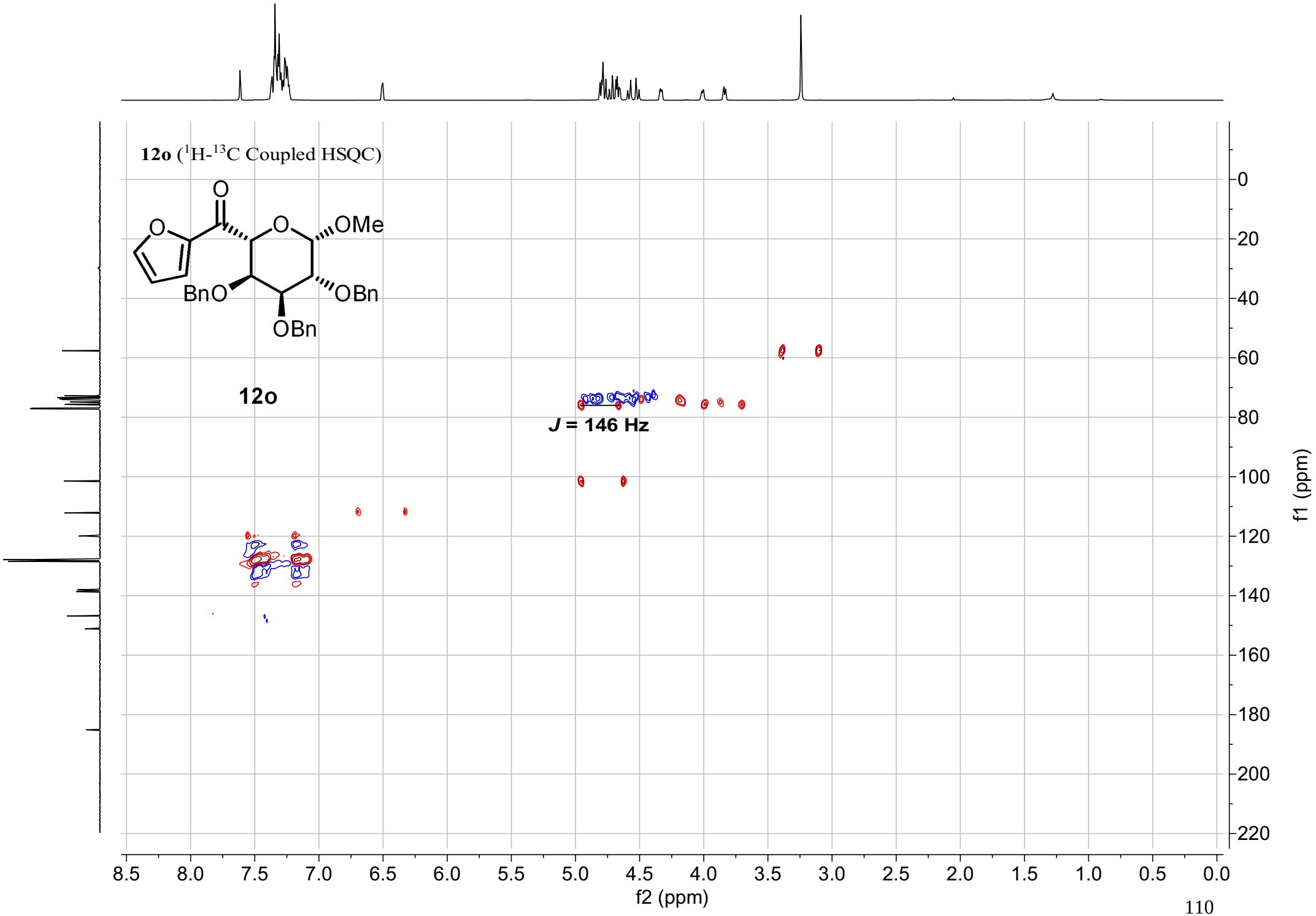


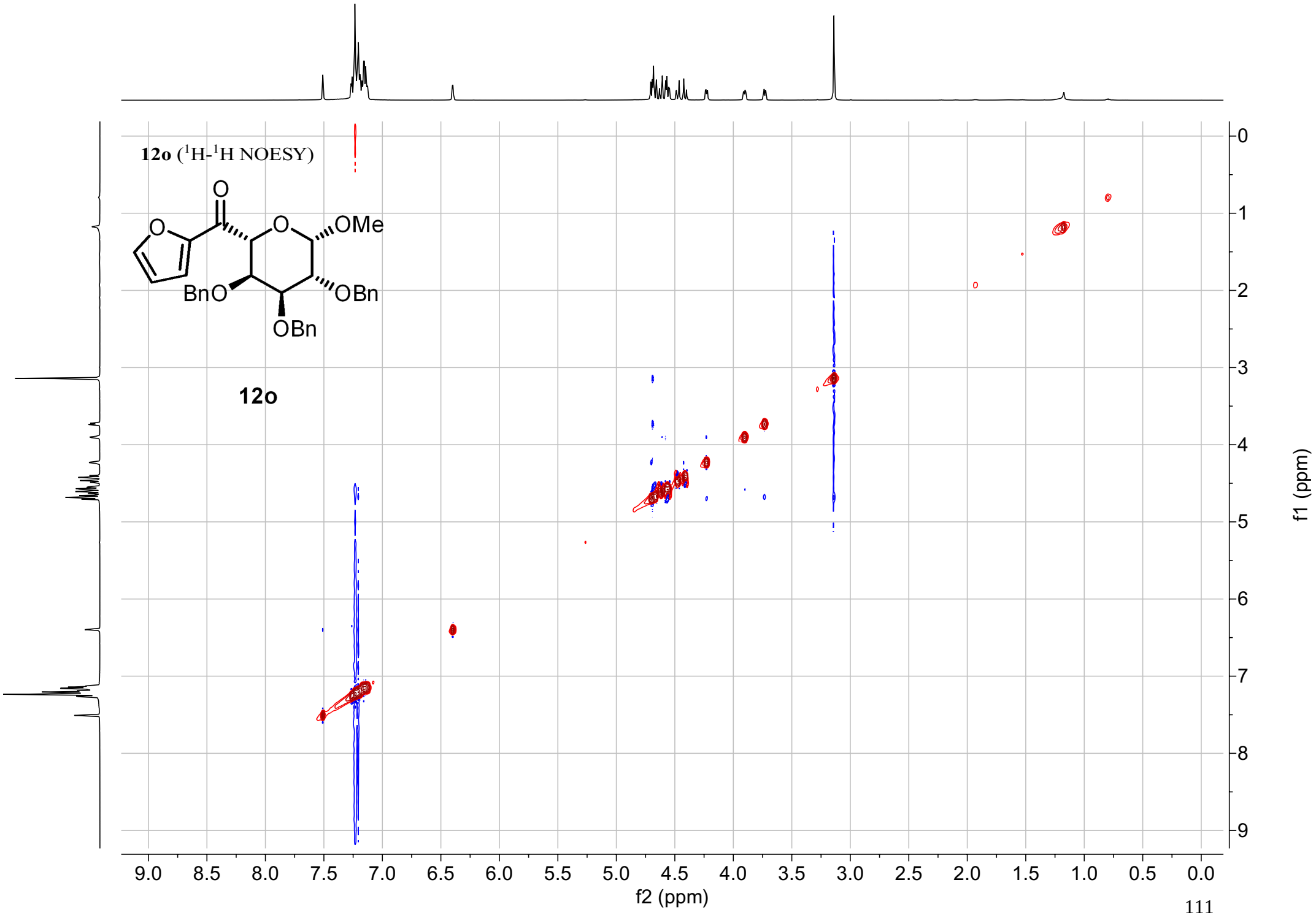
12o

12o (^{13}C NMR, 126MHz, $CDCl_3$)

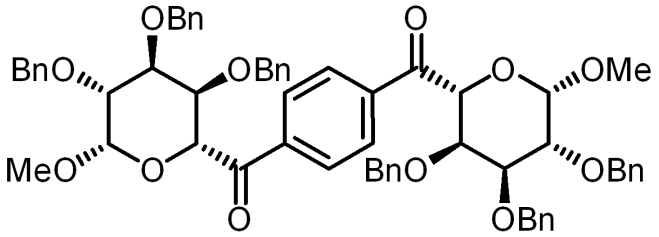


12o


12o (1H-13C Coupled HSQC)
O
O
OMe
BnO
OBn
OBn
12o
J = 146 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
0
20
40
60
80
100
120
140
160
180
200
220

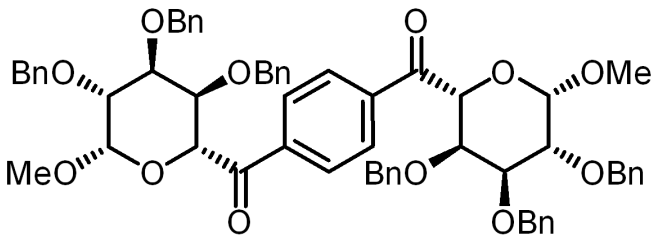

12o (1H-1H NOESY)
O
O
O
OMe
BnO
OBn
OBn
12o
f2 (ppm)
f1 (ppm)

12p (^{1}H NMR, 500MHz, $CDCl_3$)

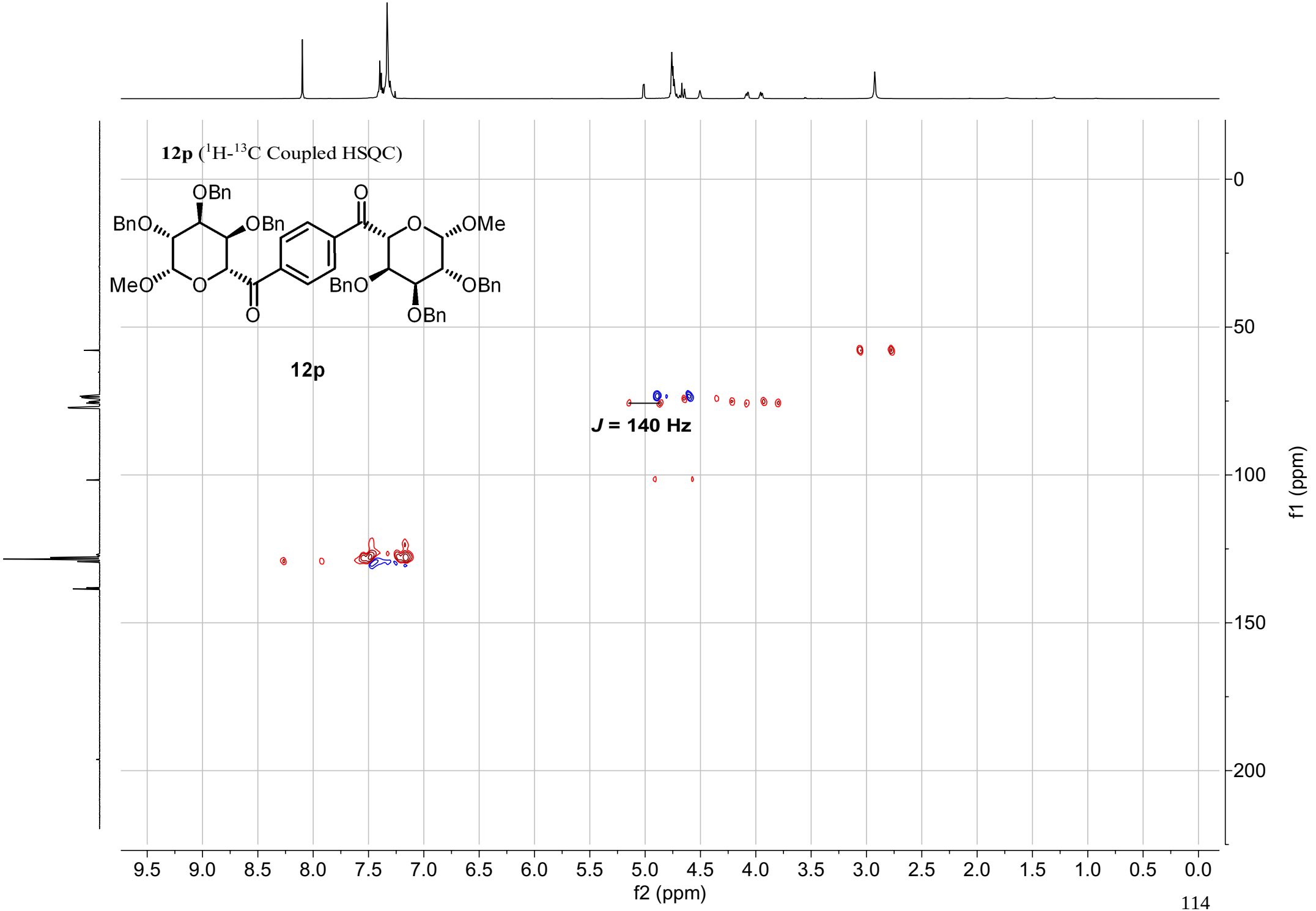


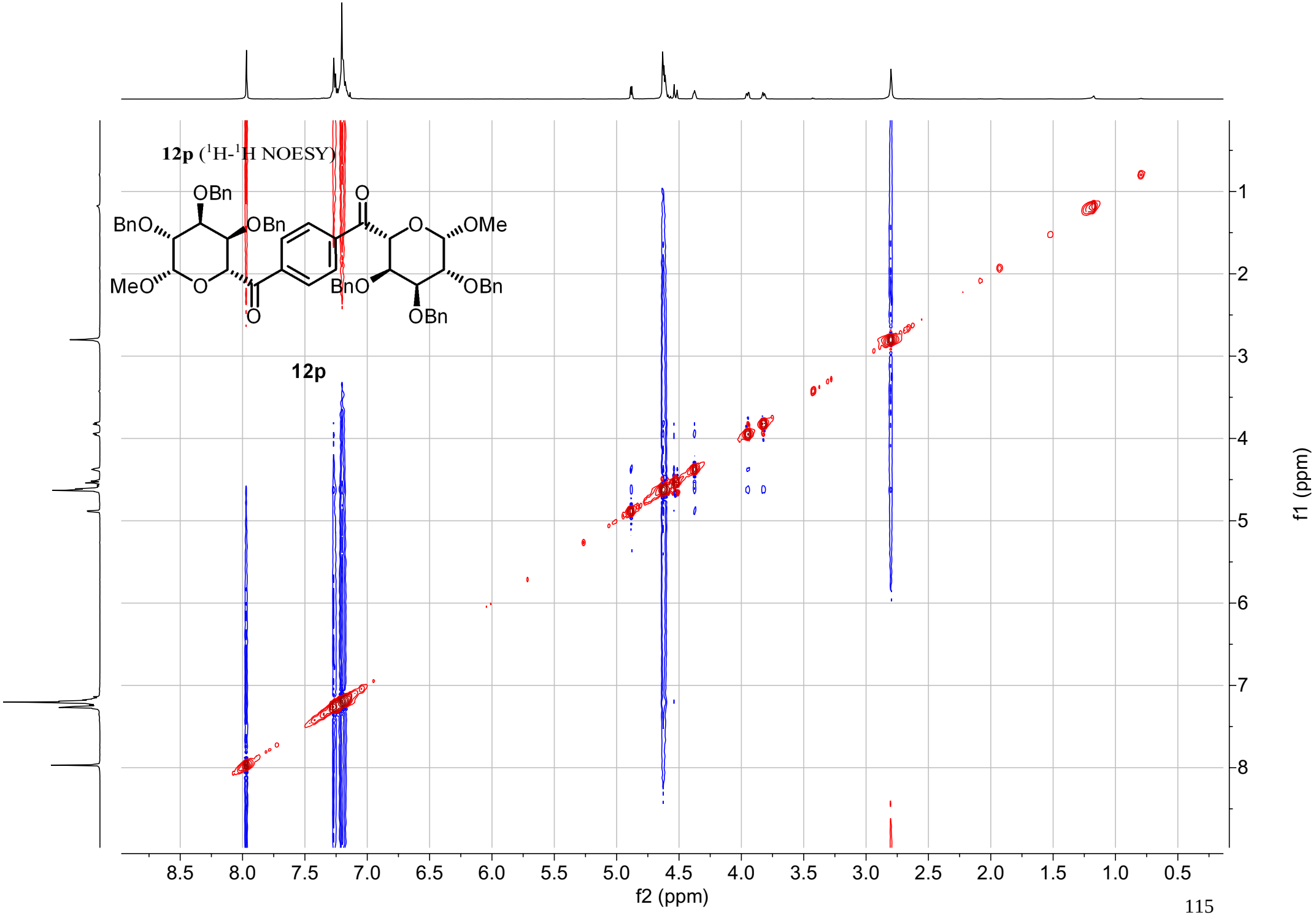
12p

12p (^{13}C NMR, 126MHz, $CDCl_3$)

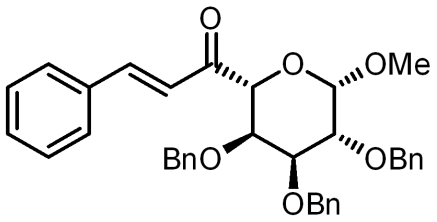


12p

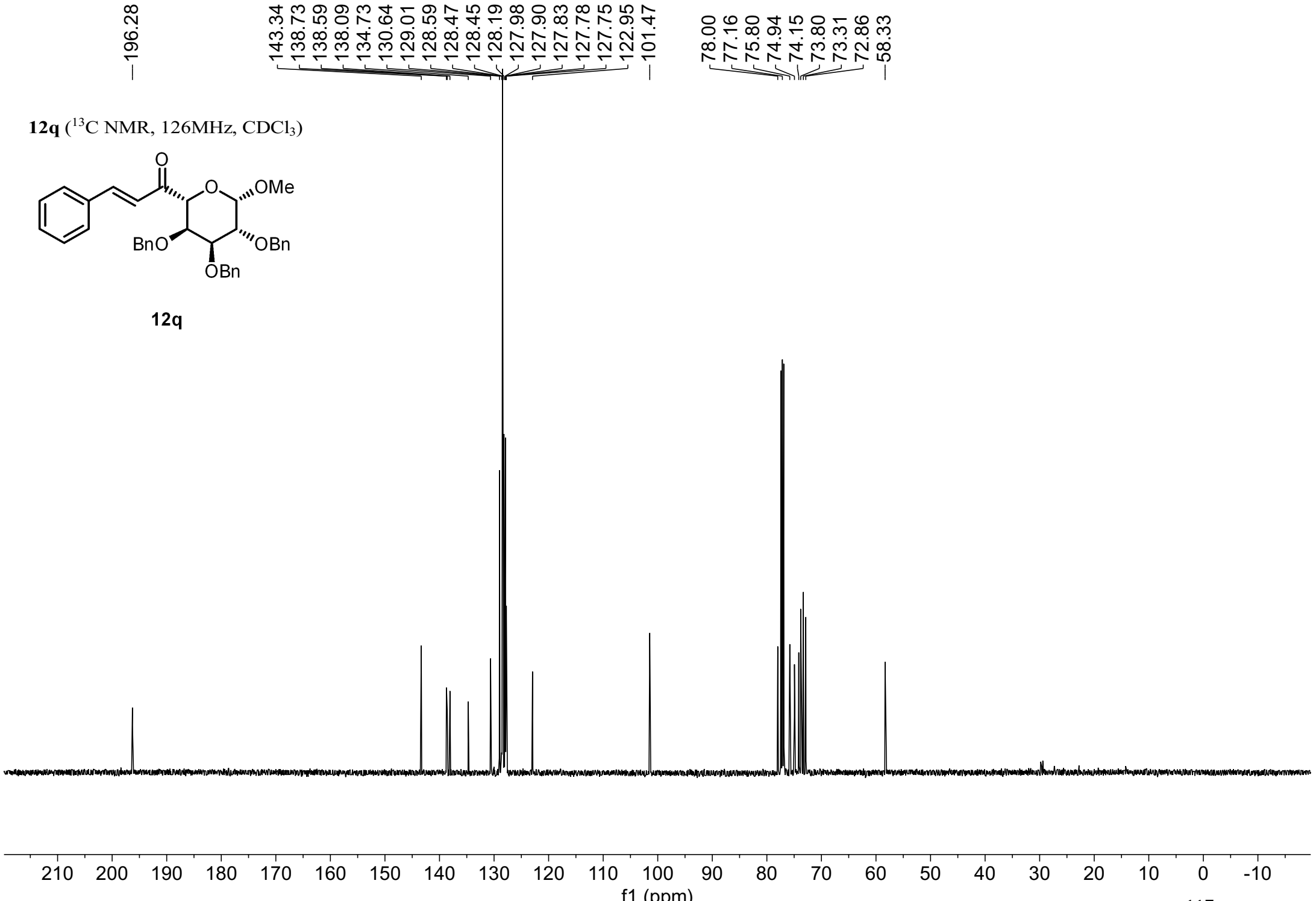

12p (1H-13C Coupled HSQC)
OBn
BnO
OBn
MeO
O
O
O
O
O
OMe
BnO
OBn
OBn
12p
J = 140 Hz
0
50
100
150
200
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

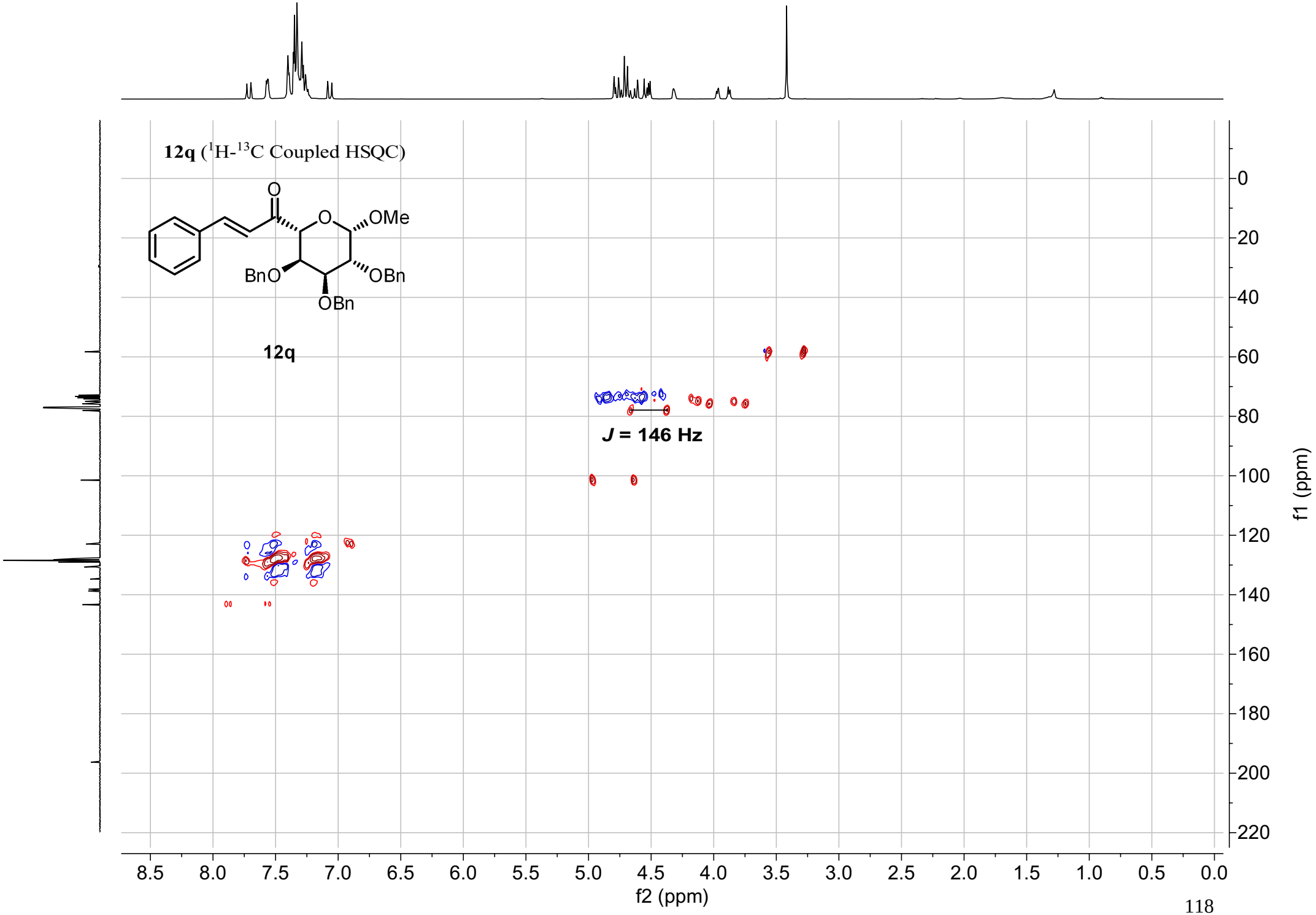

12p (^{1}H-^{1}H NOESY)
OBn
BnO
OBn
MeO
O
O
O
O
OMe
BnO
OBn
OBn
12p
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

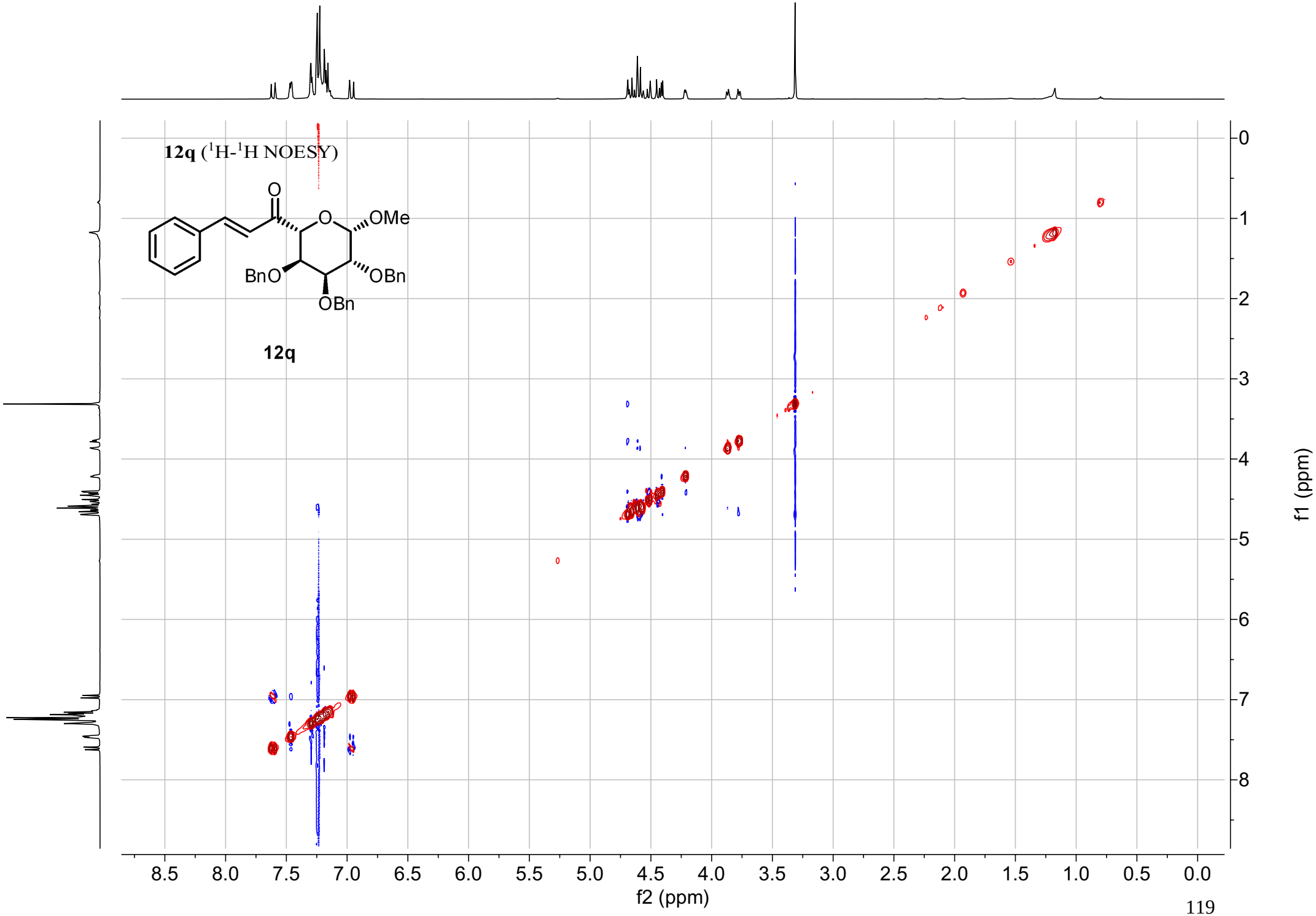
12q (^{1}H NMR, 500MHz, $CDCl_3$)



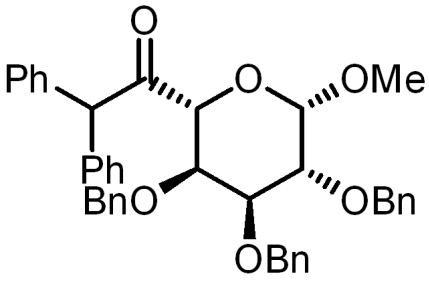
12q


196.28
143.34
138.73
138.59
138.09
134.73
130.64
129.01
128.59
128.47
128.45
128.19
127.98
127.90
127.83
127.78
127.75
122.95
101.47
78.00
77.16
75.80
74.94
74.15
73.80
73.31
72.86
58.33
12q (13C NMR, 126MHz, CDCl3)
O
O
OMe
BnO
OBn
OBn
12q
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)


12q (^{1}H-^{13}C Coupled HSQC)
O
O
OMe
BnO
OBn
OBn
12q
J = 146 Hz
f2 (ppm)
f1 (ppm)

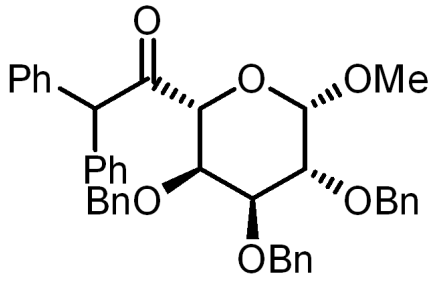

12q (1H-1H NOESY)
O
O
OMe
BnO
OBn
OBn
12q
f2 (ppm)
f1 (ppm)

12r (^{1}H NMR, 500MHz, $CDCl_3$)

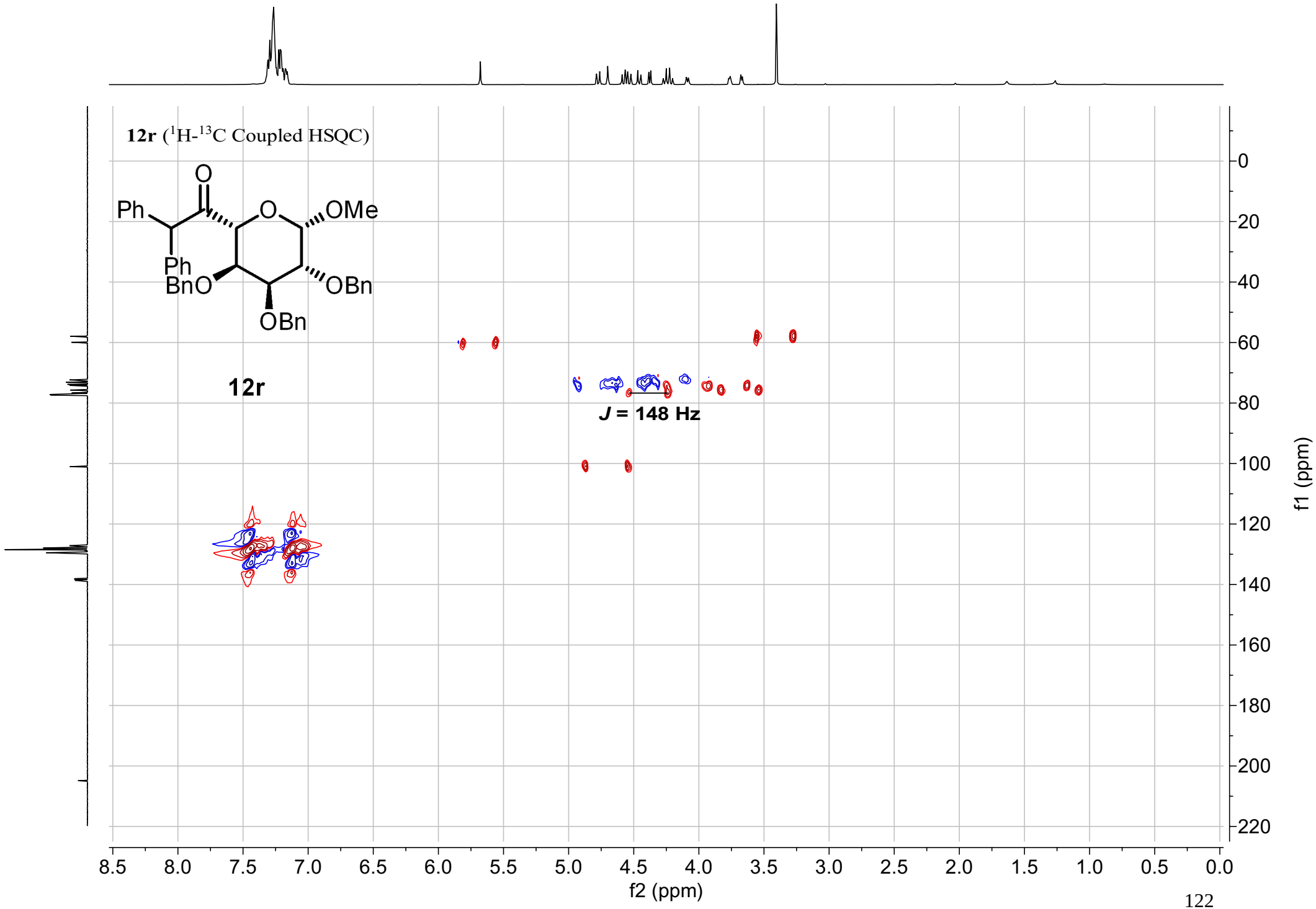


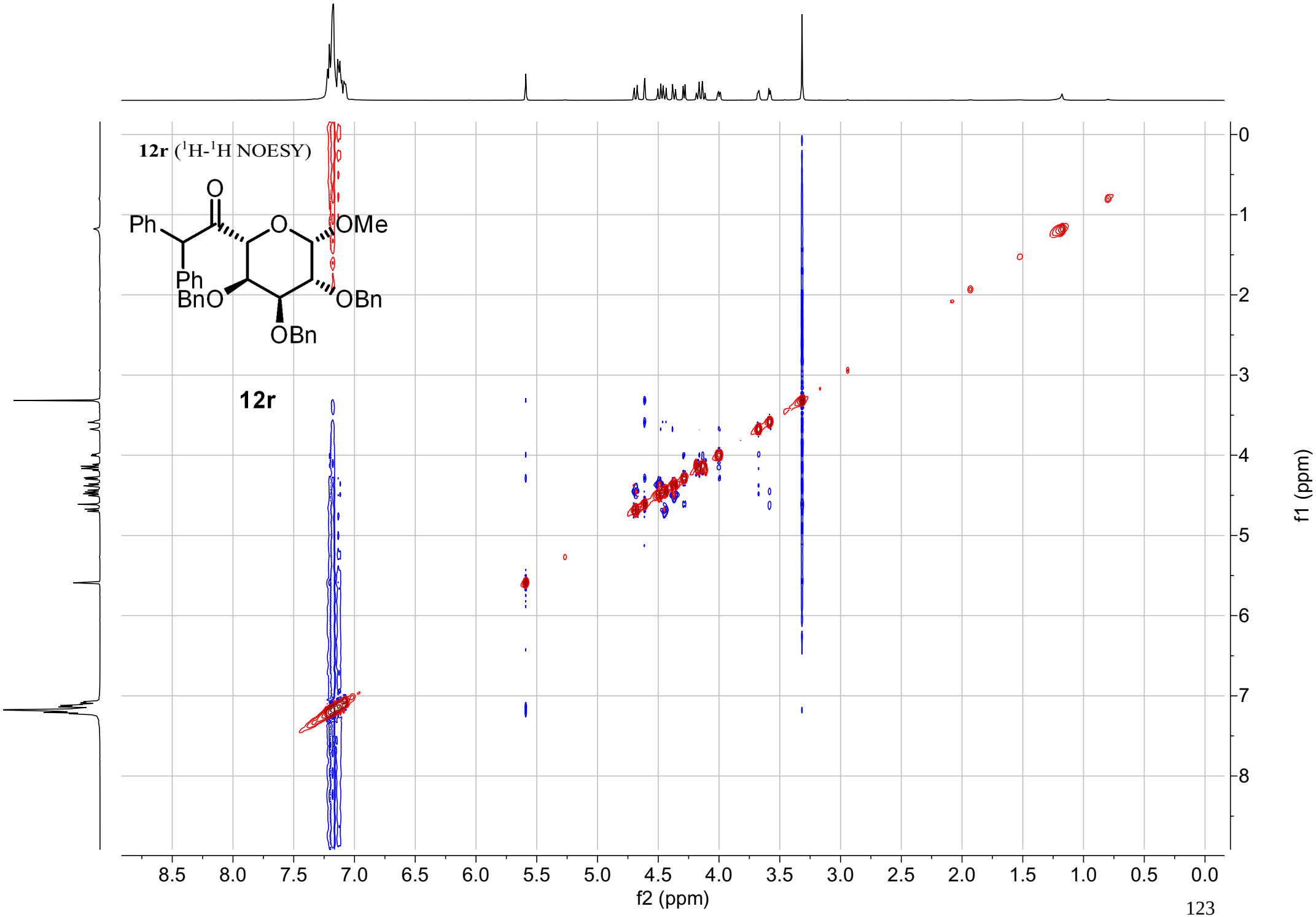
12r

12r (^{13}C NMR, 126MHz, $CDCl_3$)

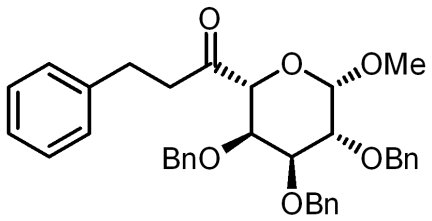


12r


12r (1H-13C Coupled HSQC)
O
Ph
O
OMe
Ph
BnO
OBn
OBn
12r
J = 148 Hz
f1 (ppm)
f2 (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
20
40
60
80
100
120
140
160
180
200
220

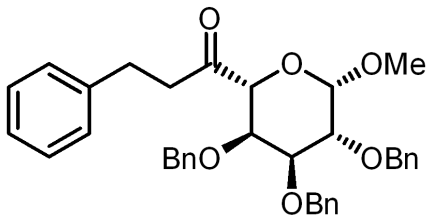

12r (1H-1H NOESY)
O
Ph
O
OMe
Ph
BnO
OBn
OBn
12r
f2 (ppm)
f1 (ppm)

12s (^{1}H NMR, 500MHz, $CDCl_3$)

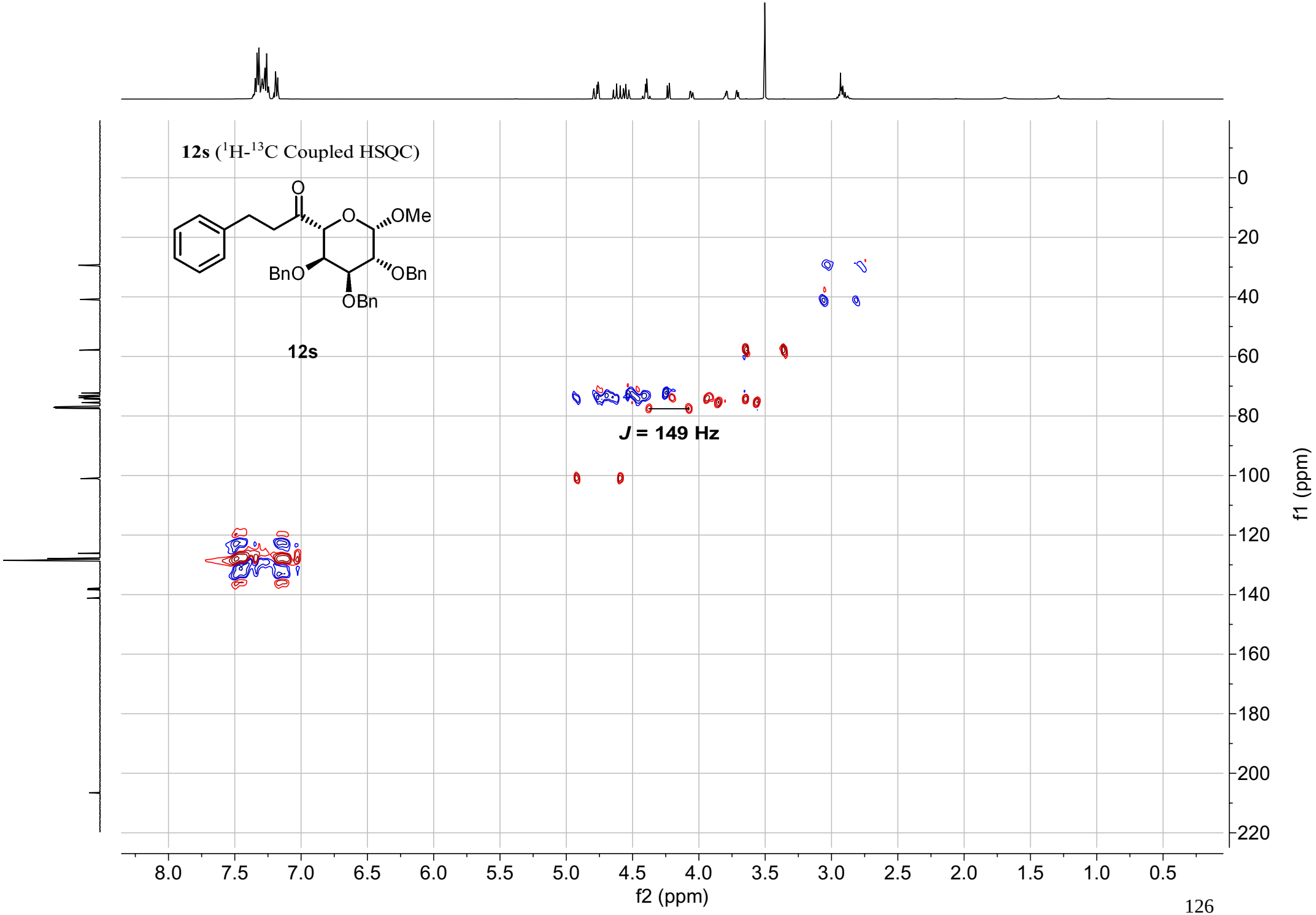


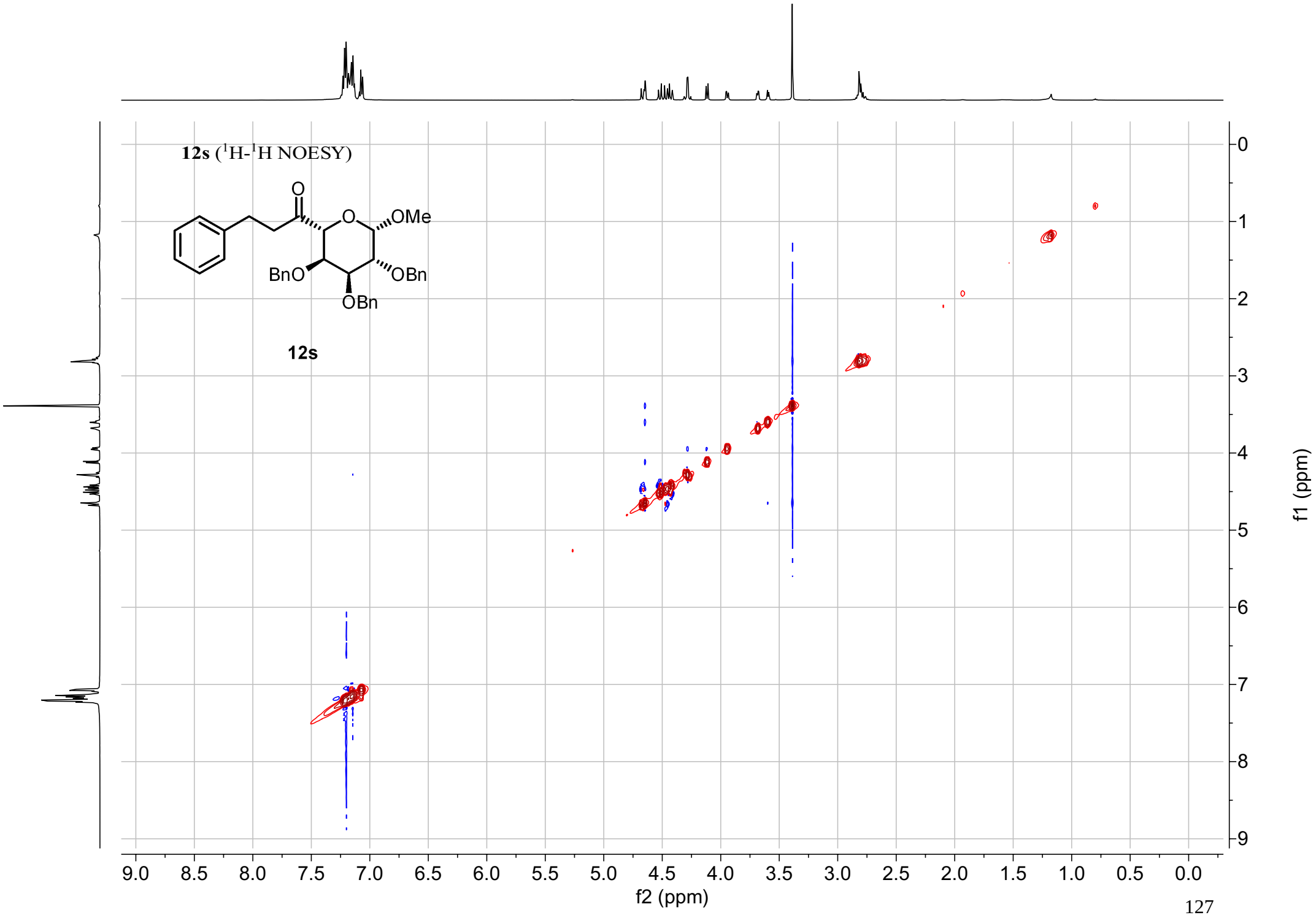
12s

12s (^{13}C NMR, 126MHz, $CDCl_3$)

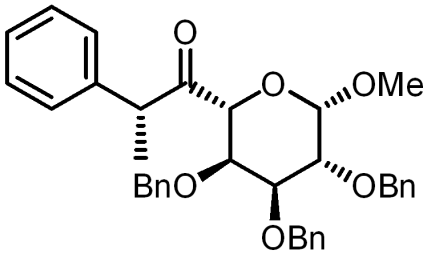


12s


12s (1H-13C Coupled HSQC)
O
O
OMe
BnO
OBn
OBn
12s
J = 149 Hz
0
20
40
60
80
100
120
140
160
180
200
220
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
f2 (ppm)

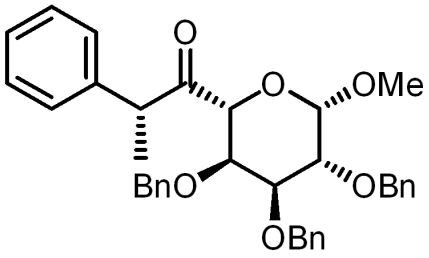

12s (1H-1H NOESY)
O
O
OMe
BnO
OBn
OBn
12s
f2 (ppm)
f1 (ppm)

12t (^{1}H NMR, 500MHz, $CDCl_3$)

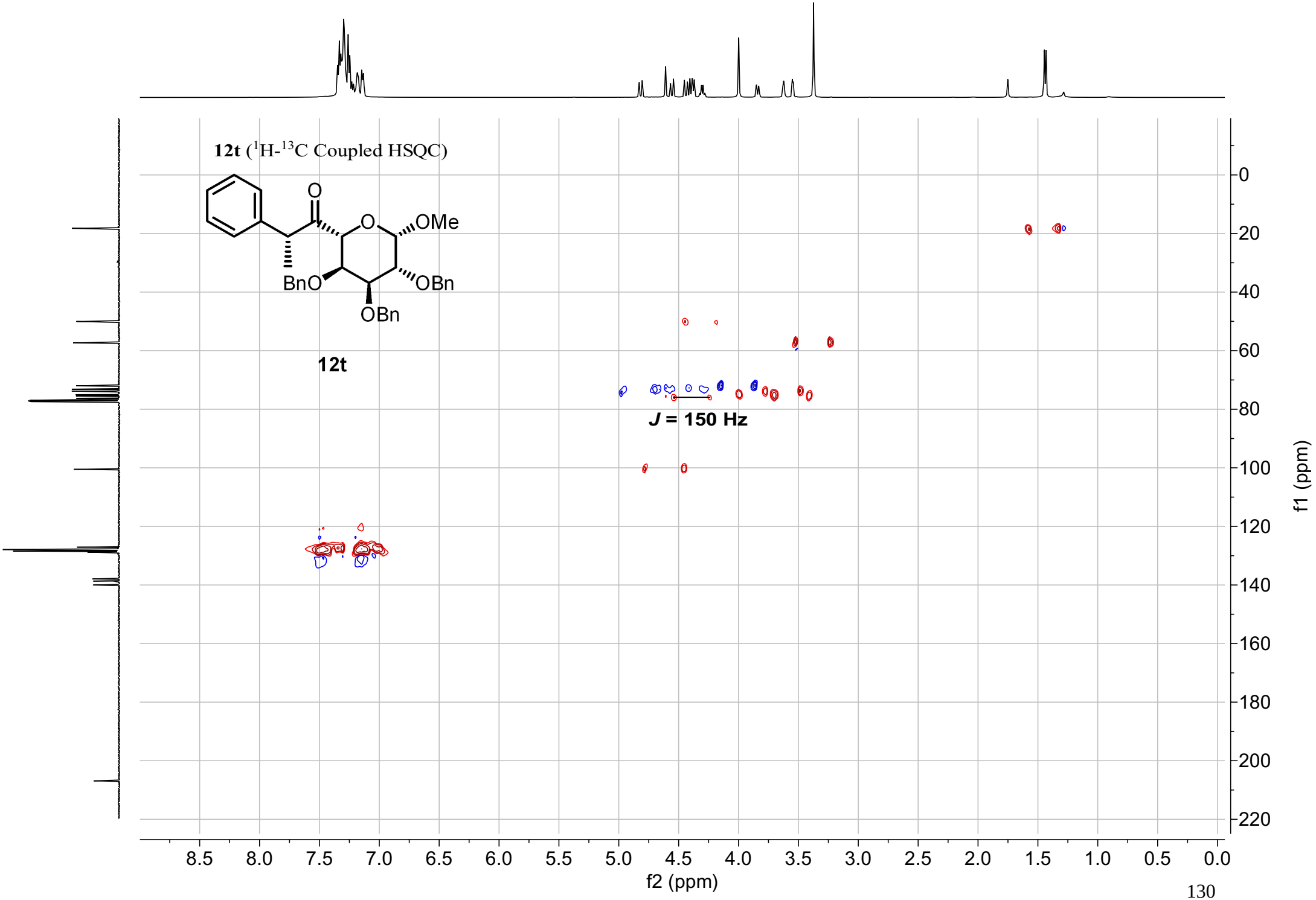


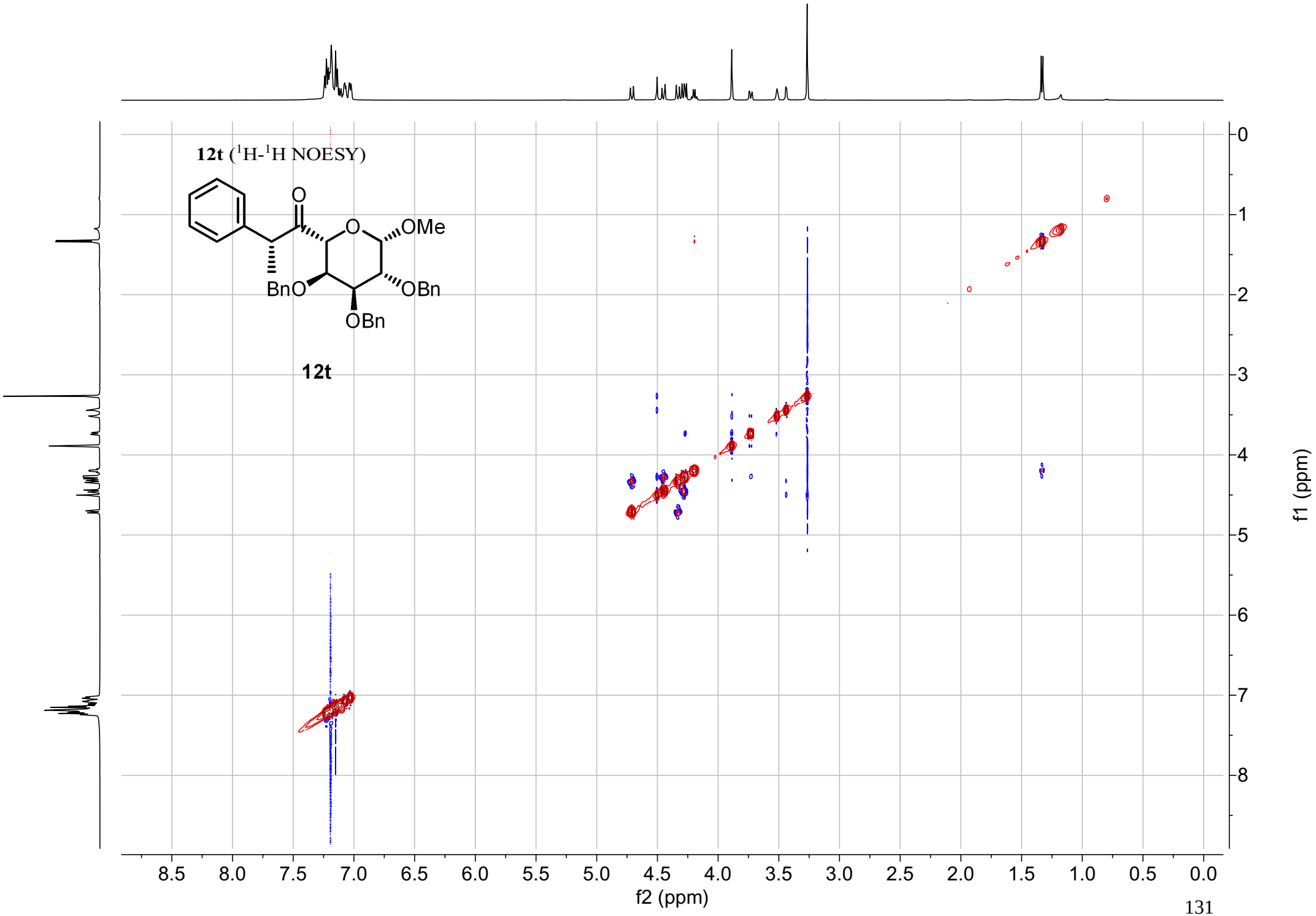
12t

12t (^{13}C NMR, 126MHz, $CDCl_3$)

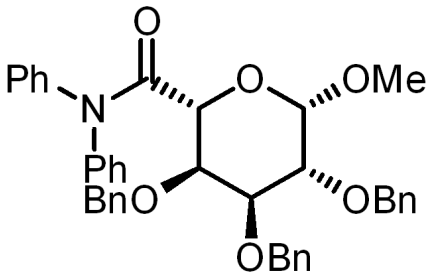


12t


12t (1H-13C Coupled HSQC)
O
O
OMe
BnO
OBn
OBn
12t
J = 150 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
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

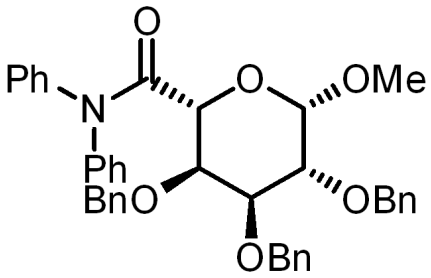

12t (1H-1H NOESY)
O
O
OMe
BnO
OBn
OBn
12t
f2 (ppm)
f1 (ppm)

12u (^{1}H NMR, 500MHz, $CDCl_3$)

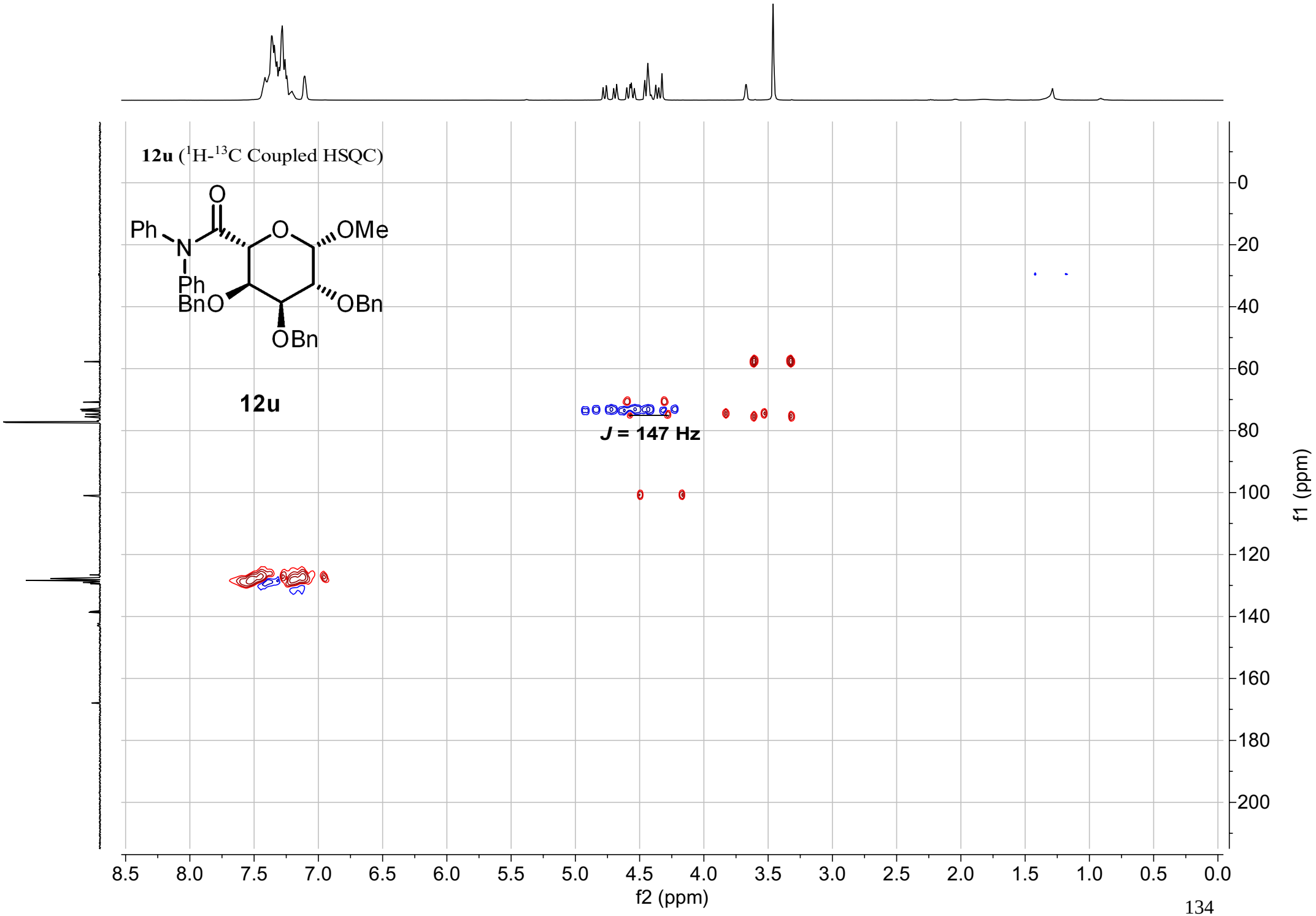


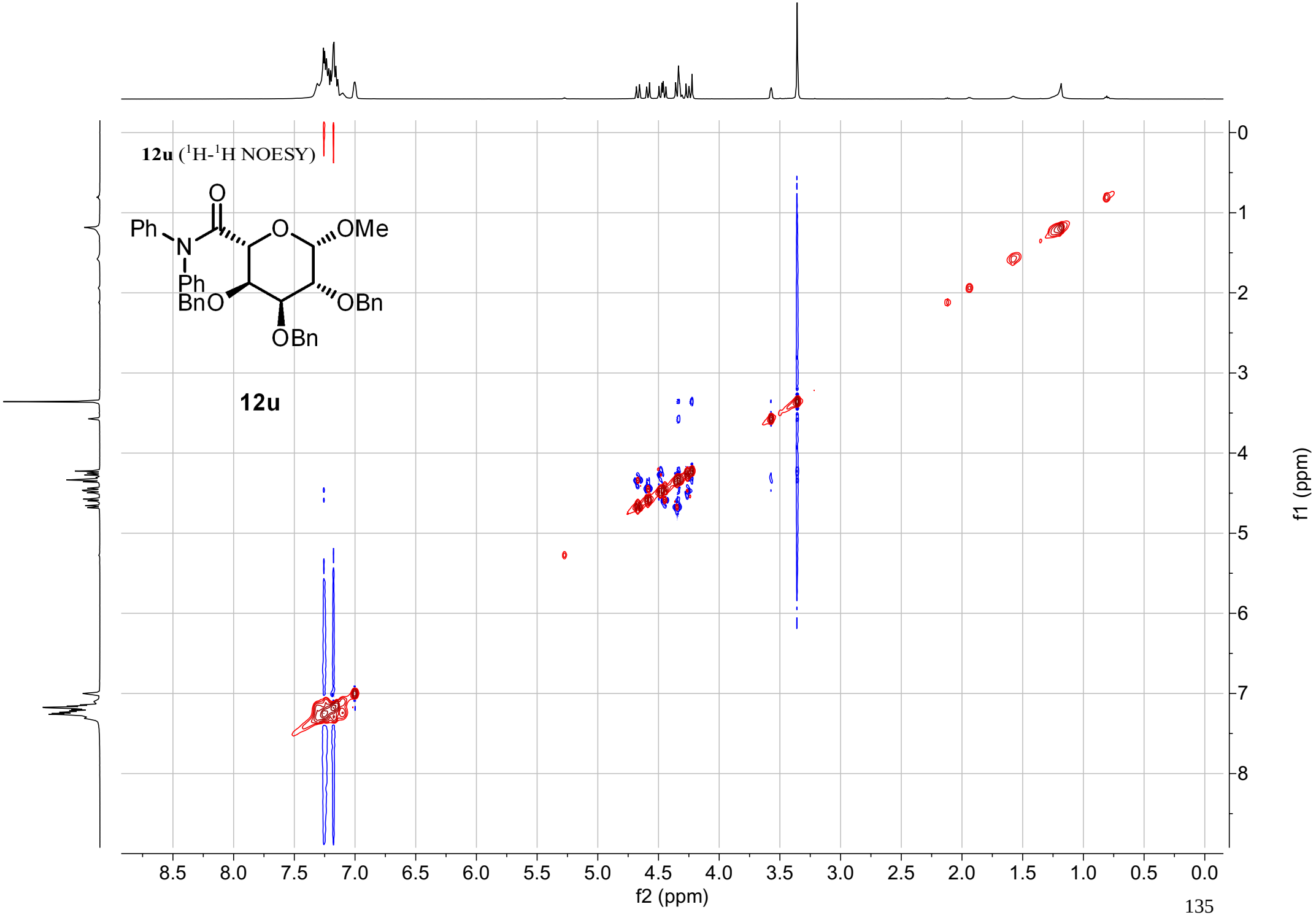
12u

12u (^{13}C NMR, 126MHz, $CDCl_3$)

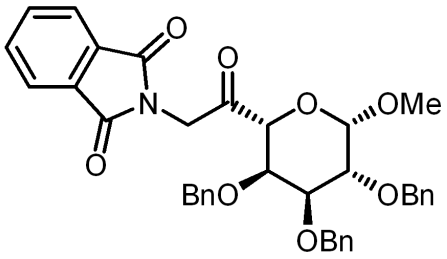


12u


12u (1H-13C Coupled HSQC)
Ph
N
Ph
O
O
OMe
BnO
OBn
OBn
12u
J = 147 Hz
f1 (ppm)
f2 (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
20
40
60
80
100
120
140
160
180
200

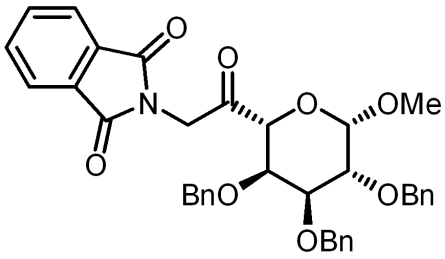

12u (1H-1H NOESY)
Ph
N
Ph
BnO
O
OMe
OBn
OBn
12u
f2 (ppm)
f1 (ppm)

12v (^{1}H NMR, 500MHz, $CDCl_3$)

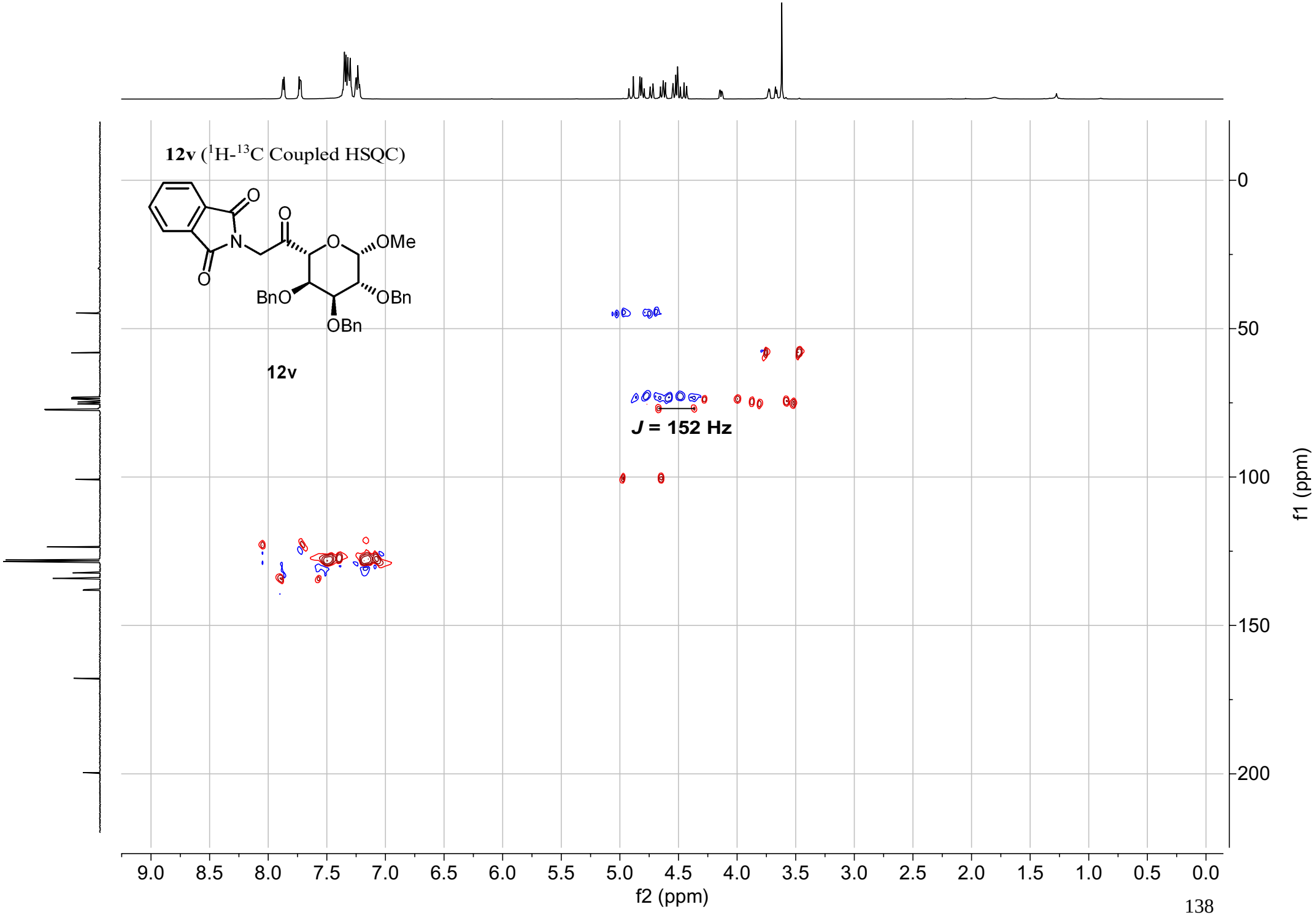


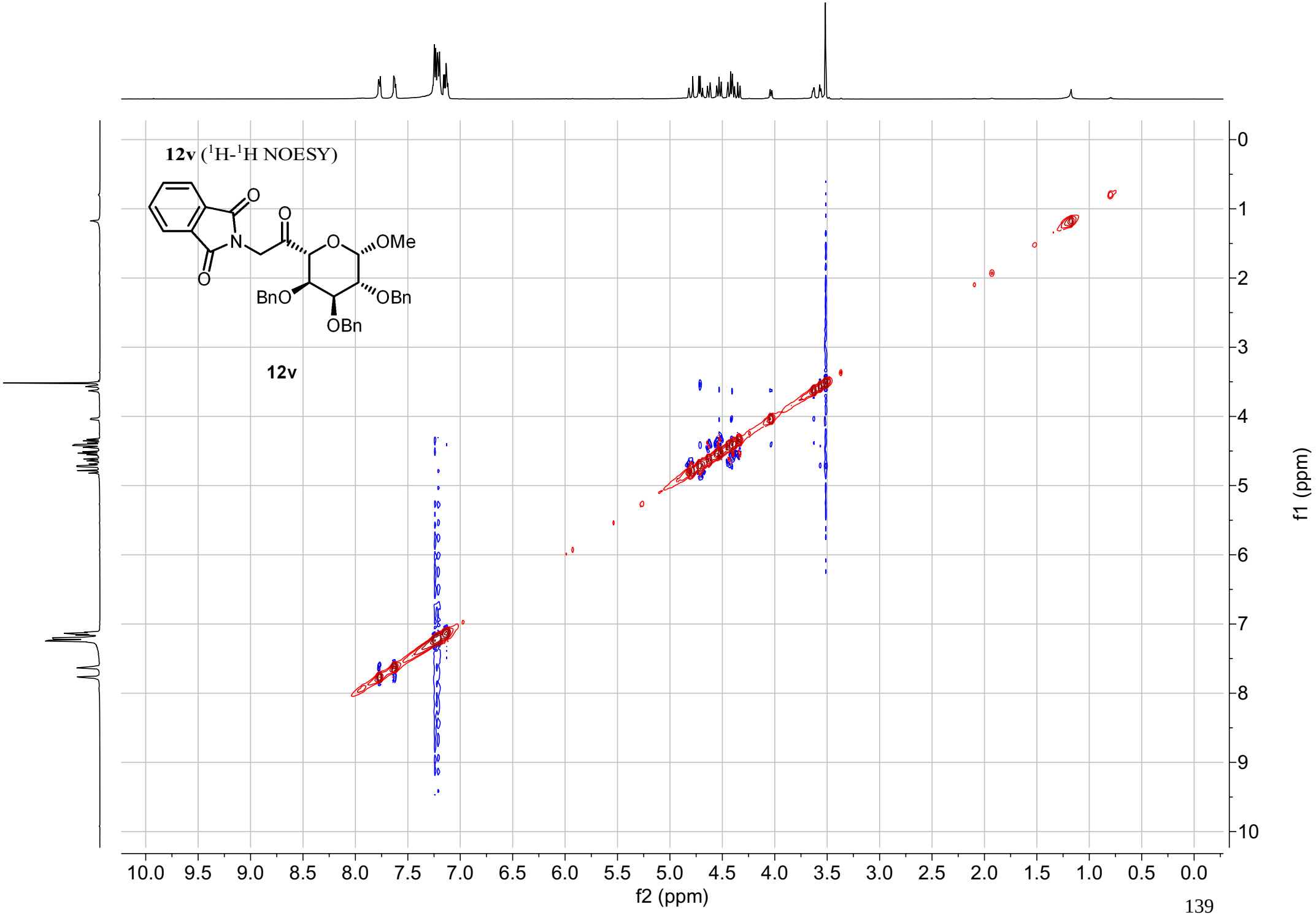
12v

12v (^{13}C NMR, 126MHz, $CDCl_3$)

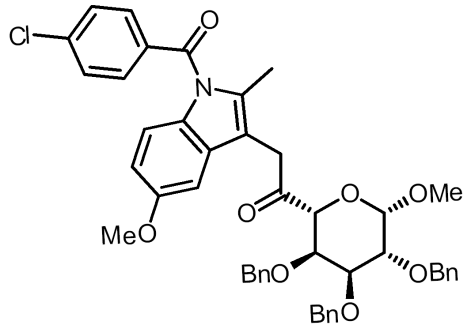


12v


12v (1H-13C Coupled HSQC)
O
O
N
O
O
OMe
BnO
OBn
OBn
12v
J = 152 Hz
0
50
100
150
200
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
f2 (ppm)

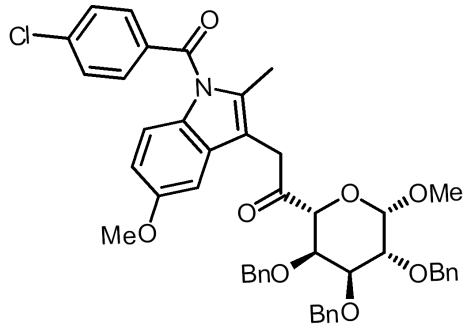

12v (1H-1H NOESY)
O
O
N
O
OMe
O
BnO
OBn
OBn
12v
f2 (ppm)
f1 (ppm)

12w (^{1}H NMR, 500MHz, $CDCl_3$)

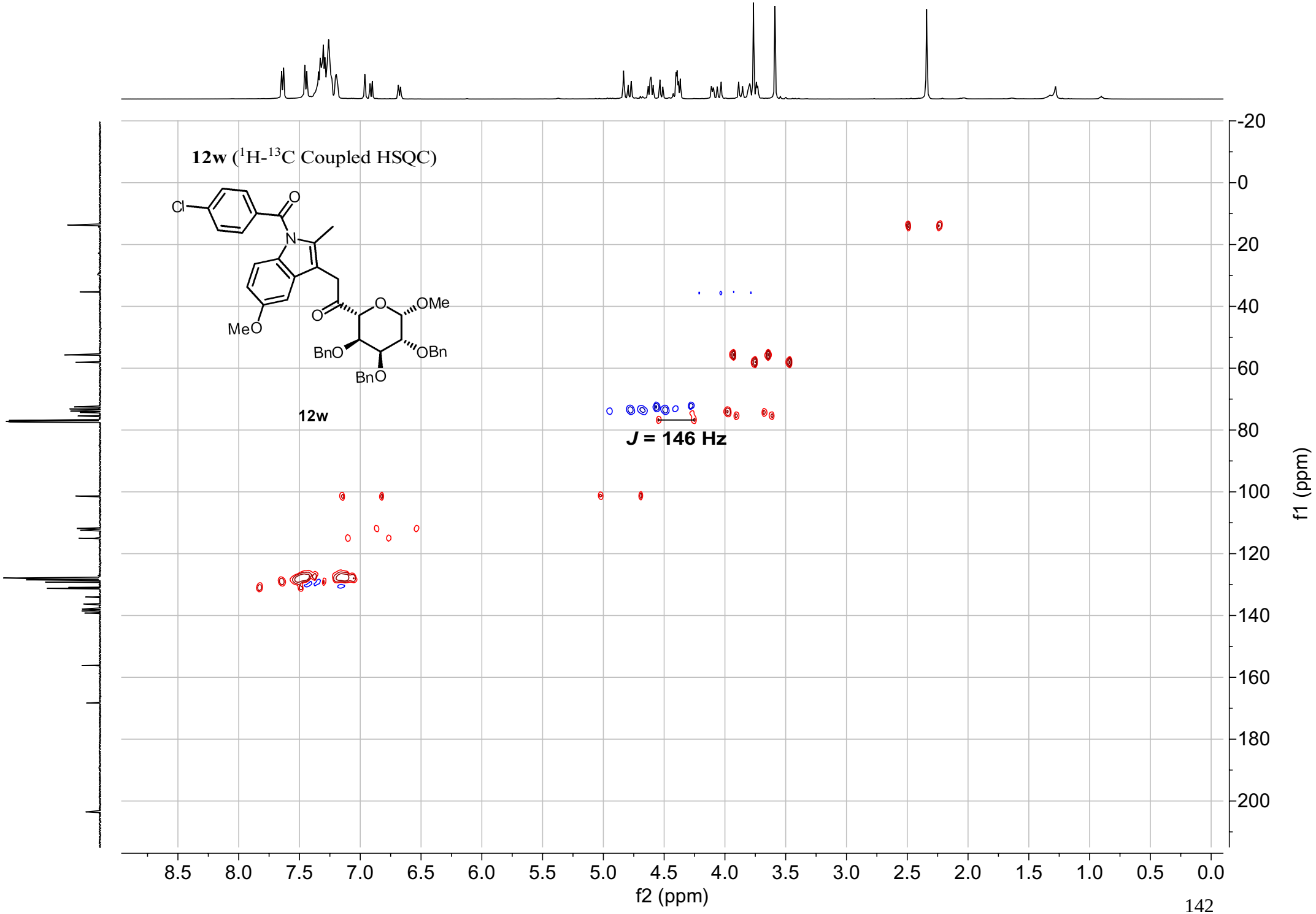


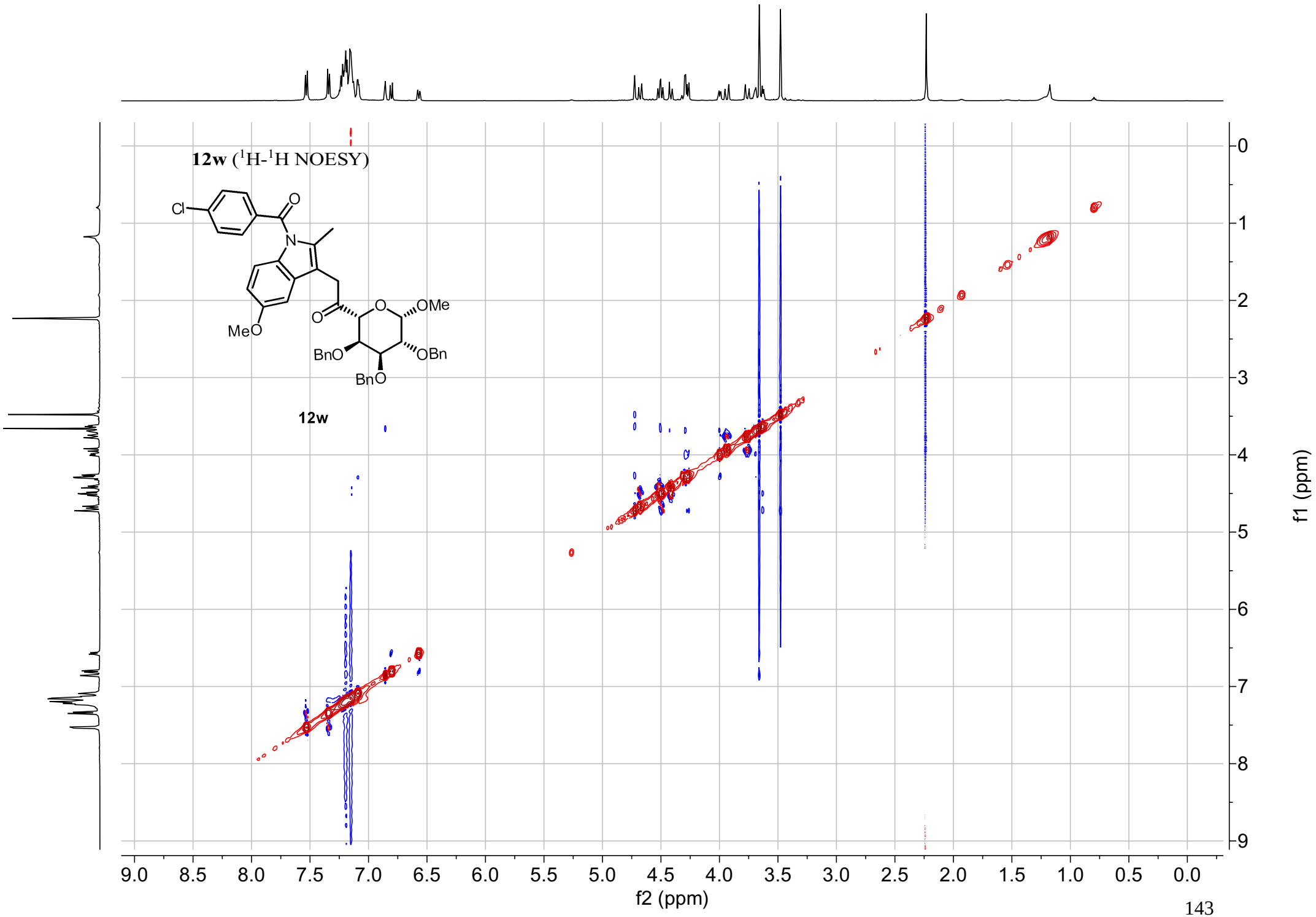
12w

12w (^{13}C NMR, 126MHz, $CDCl_3$)

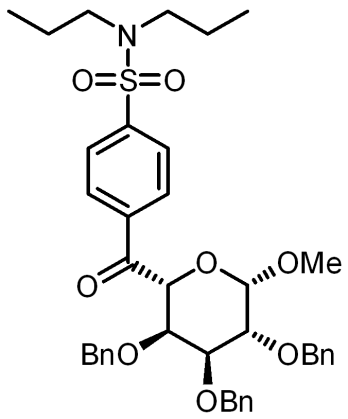


12w


12w (1H-13C Coupled HSQC)
Cl
O
N
MeO
O
O
OMe
BnO
OBn
BnO
12w
J = 146 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
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)

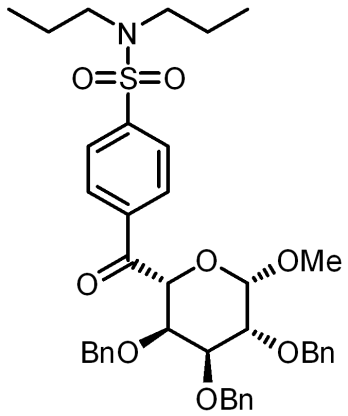

12w (1H-1H NOESY)
Cl
O
N
MeO
O
O
OMe
BnO
OBn
BnO
12w
f2 (ppm)
f1 (ppm)

12x (^{1}H NMR, 500MHz, $CDCl_3$)

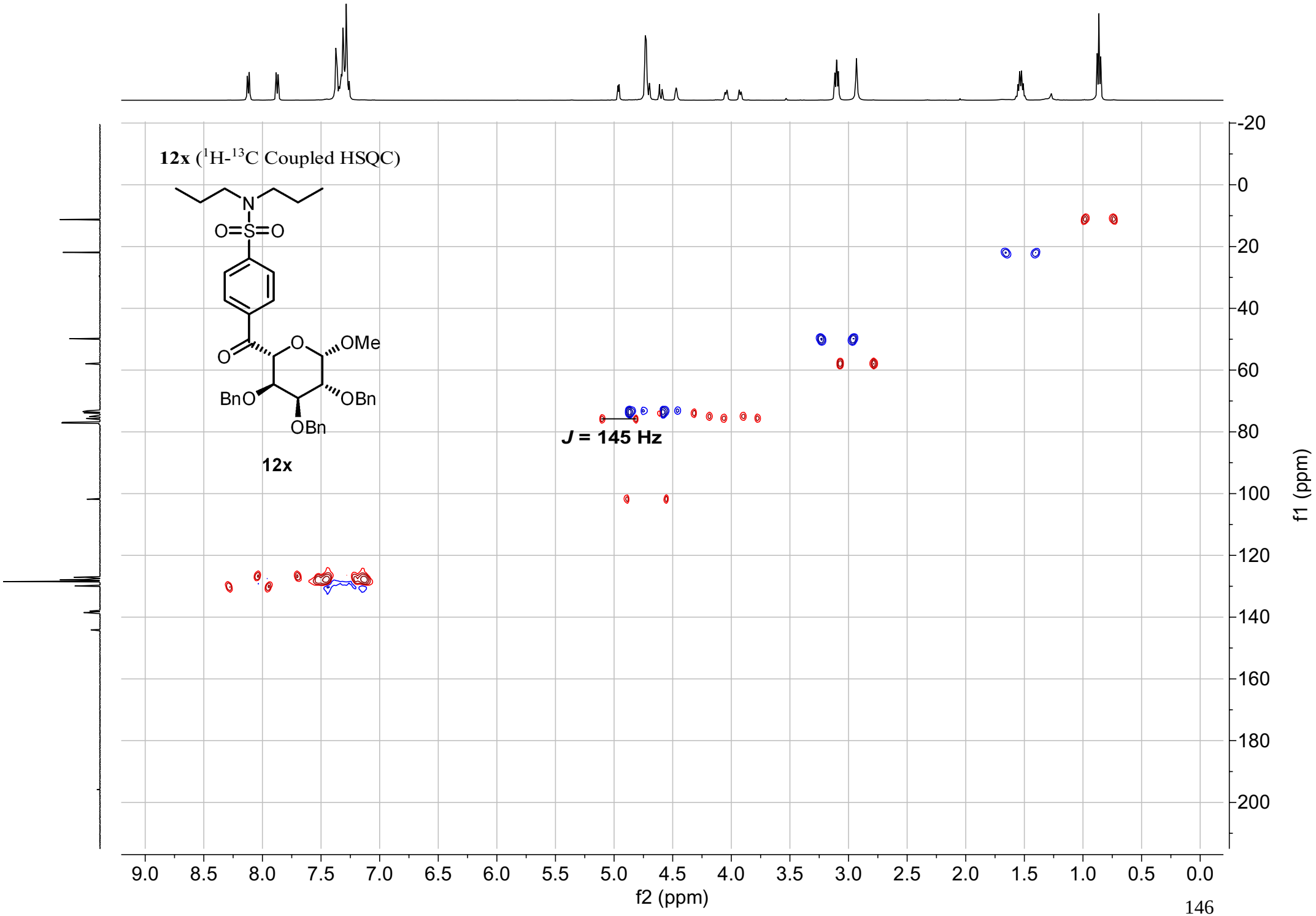


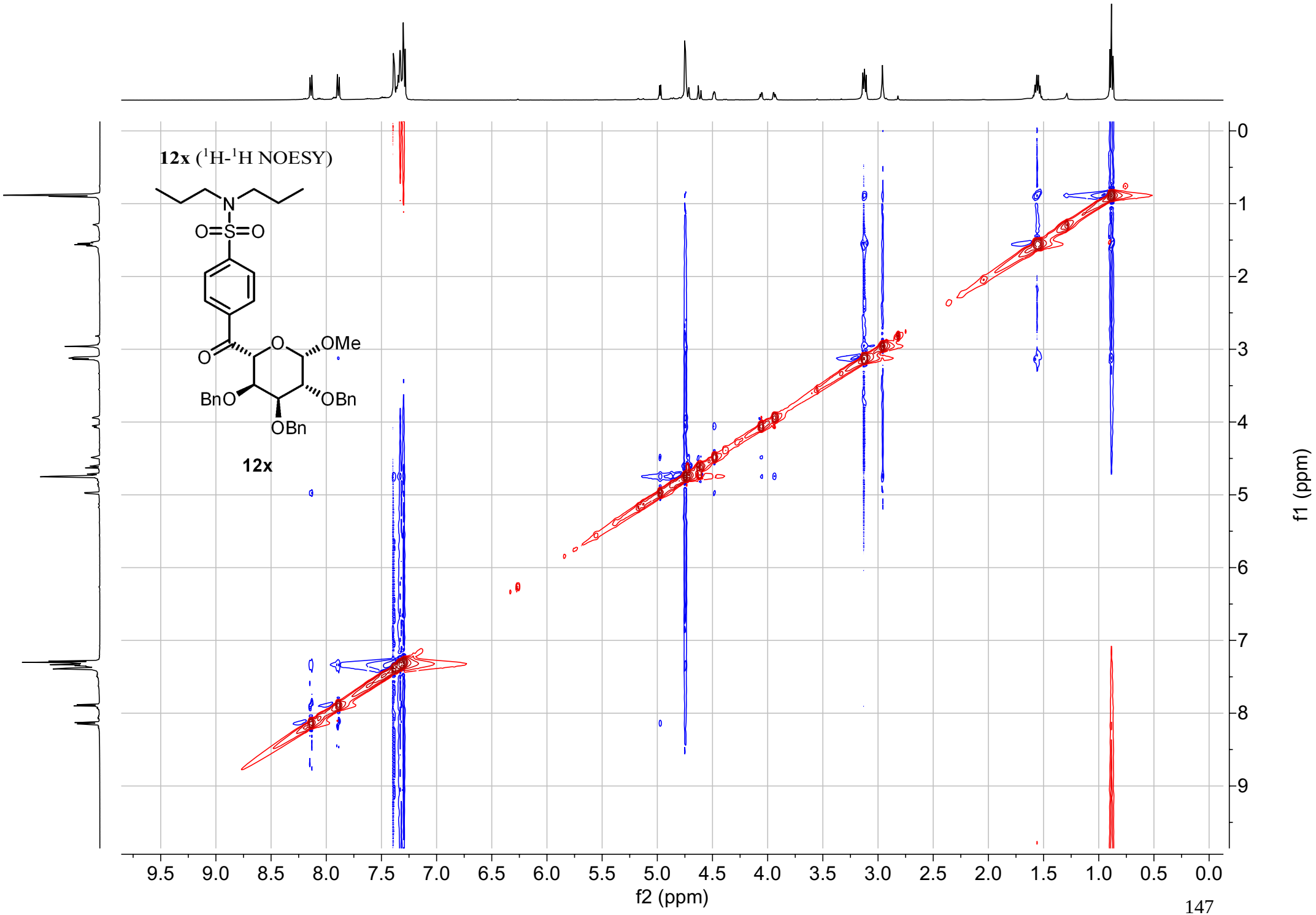
12x

12x (^{13}C NMR, 126MHz, $CDCl_3$)

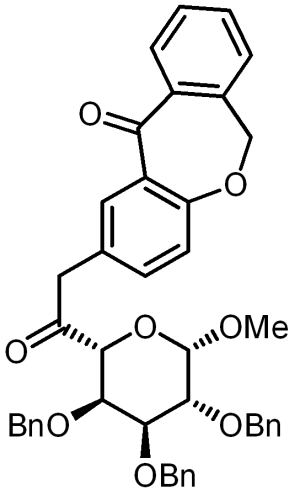


12x

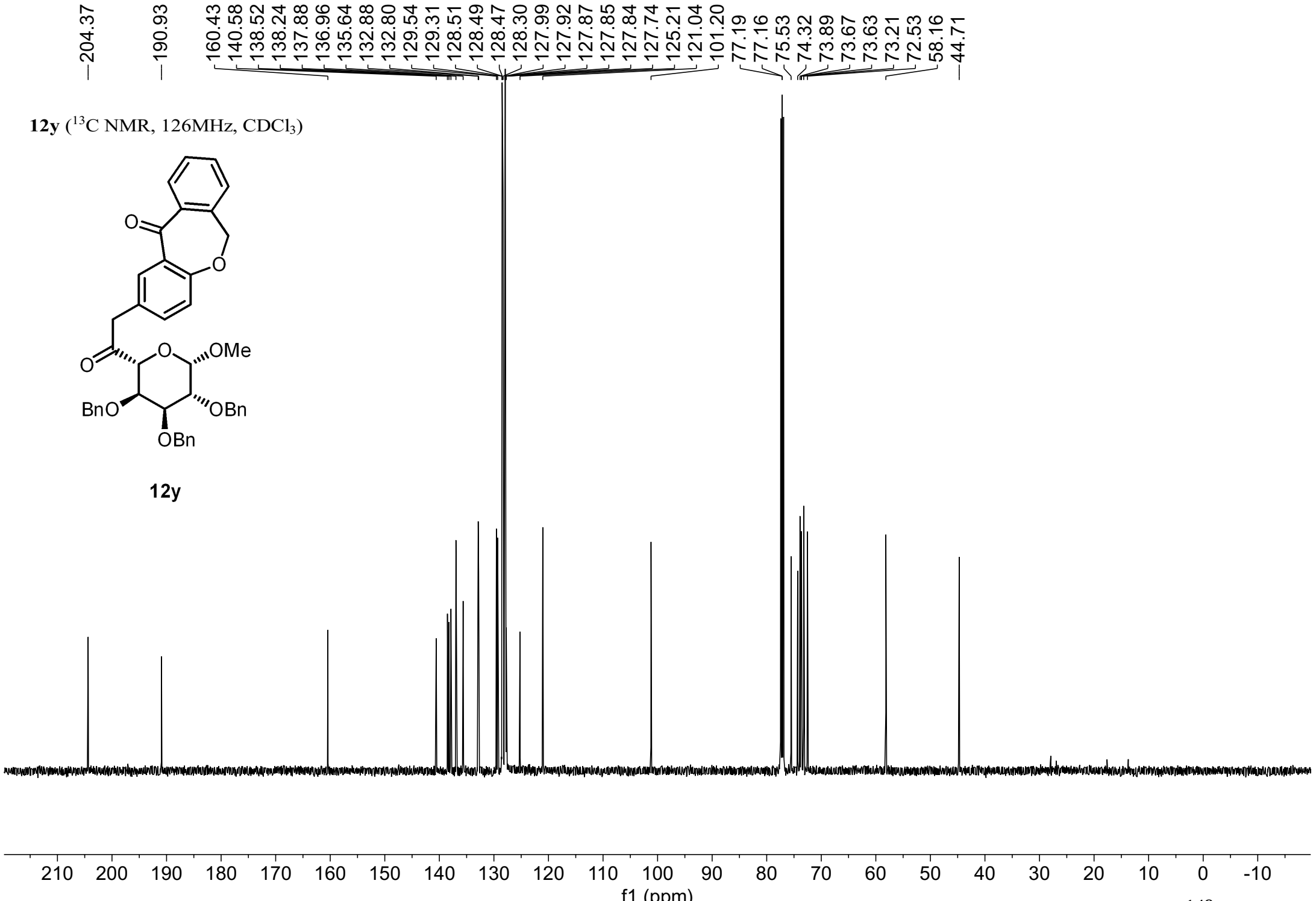

12x (1H-13C Coupled HSQC)
N
O=S=O
O
OMe
BnO
OBn
OBn
12x
J = 145 Hz
f2 (ppm)
f1 (ppm)

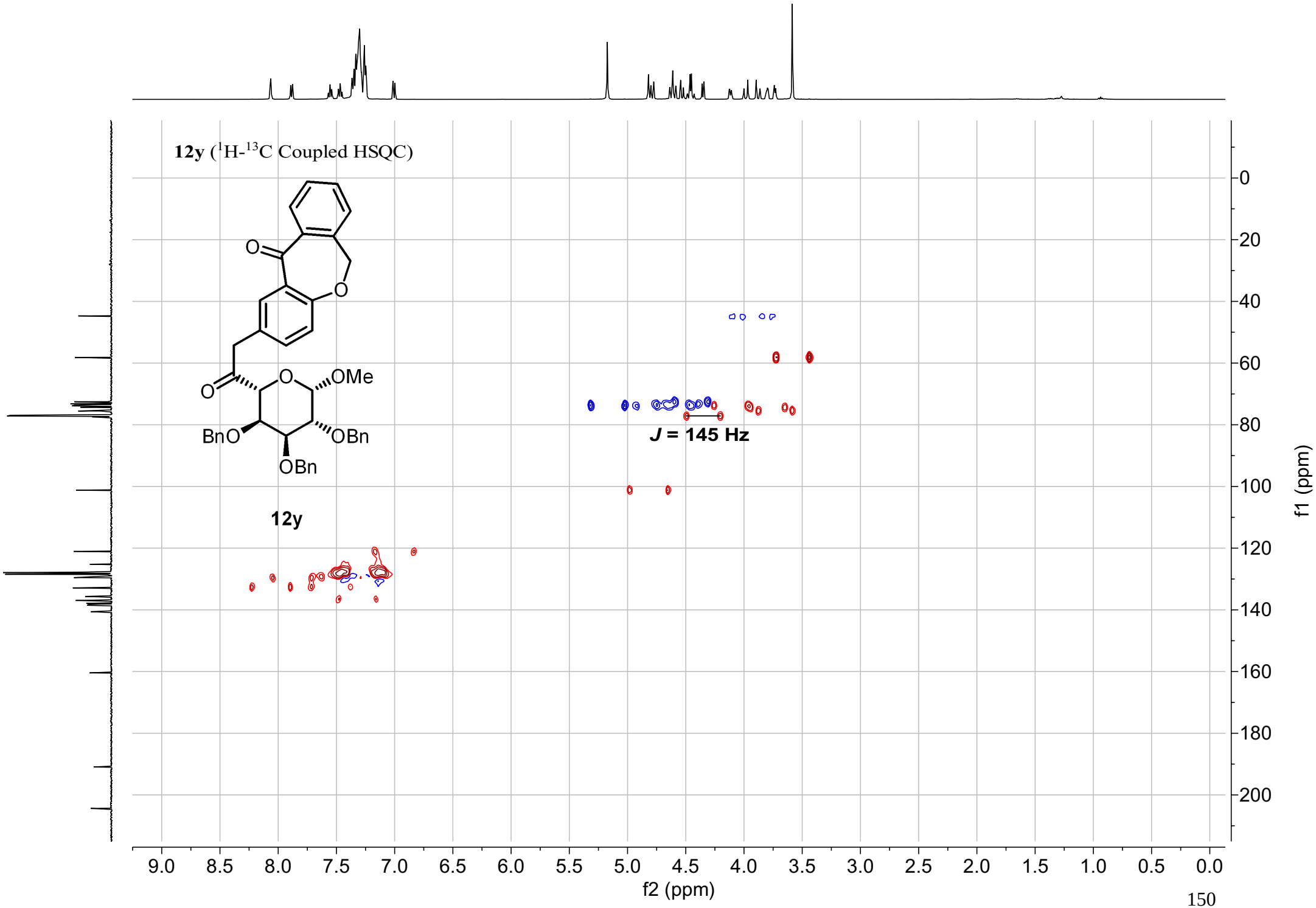

12x (1H-1H NOESY)
N
O=S=O
O
OMe
BnO
OBn
OBn
12x
f2 (ppm)
f1 (ppm)

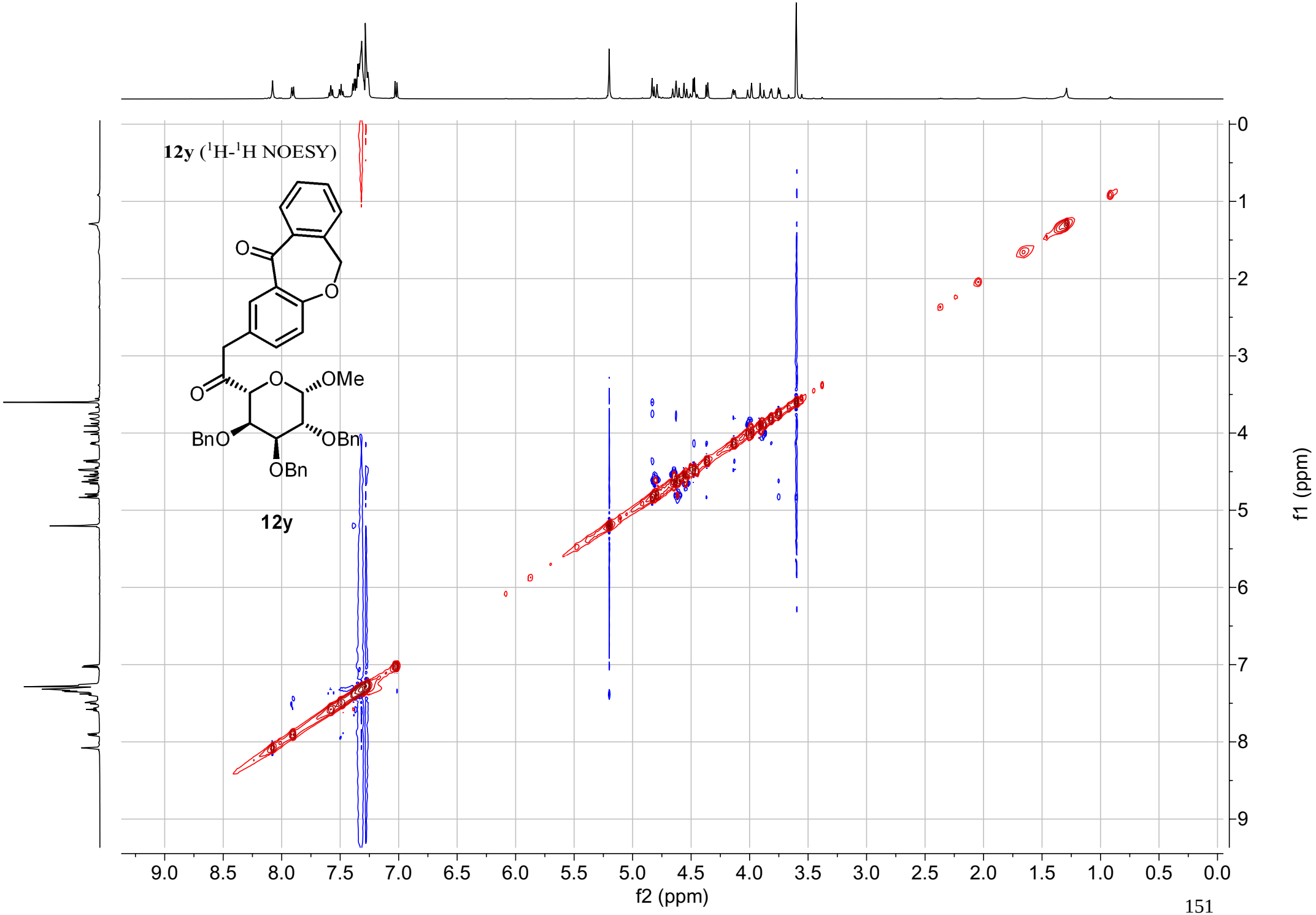
12y (^{1}H NMR, 500MHz, $CDCl_3$)



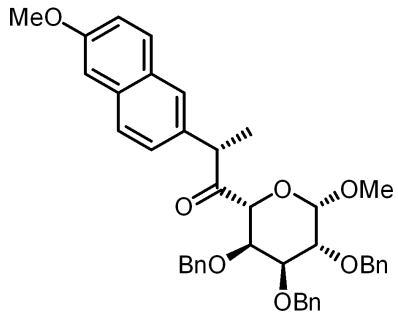
12y


204.37
190.93
160.43
140.58
138.52
138.24
137.88
136.96
135.64
132.88
132.80
129.54
129.31
128.51
128.49
128.47
128.30
127.99
127.92
127.87
127.85
127.84
127.74
125.21
121.04
101.20
77.19
77.16
75.53
74.32
73.89
73.67
73.63
73.21
72.53
58.16
44.71
12y (13C NMR, 126MHz, CDCl3)
O
O
O
OMe
O
BnO
OBn
OBn
12y
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)

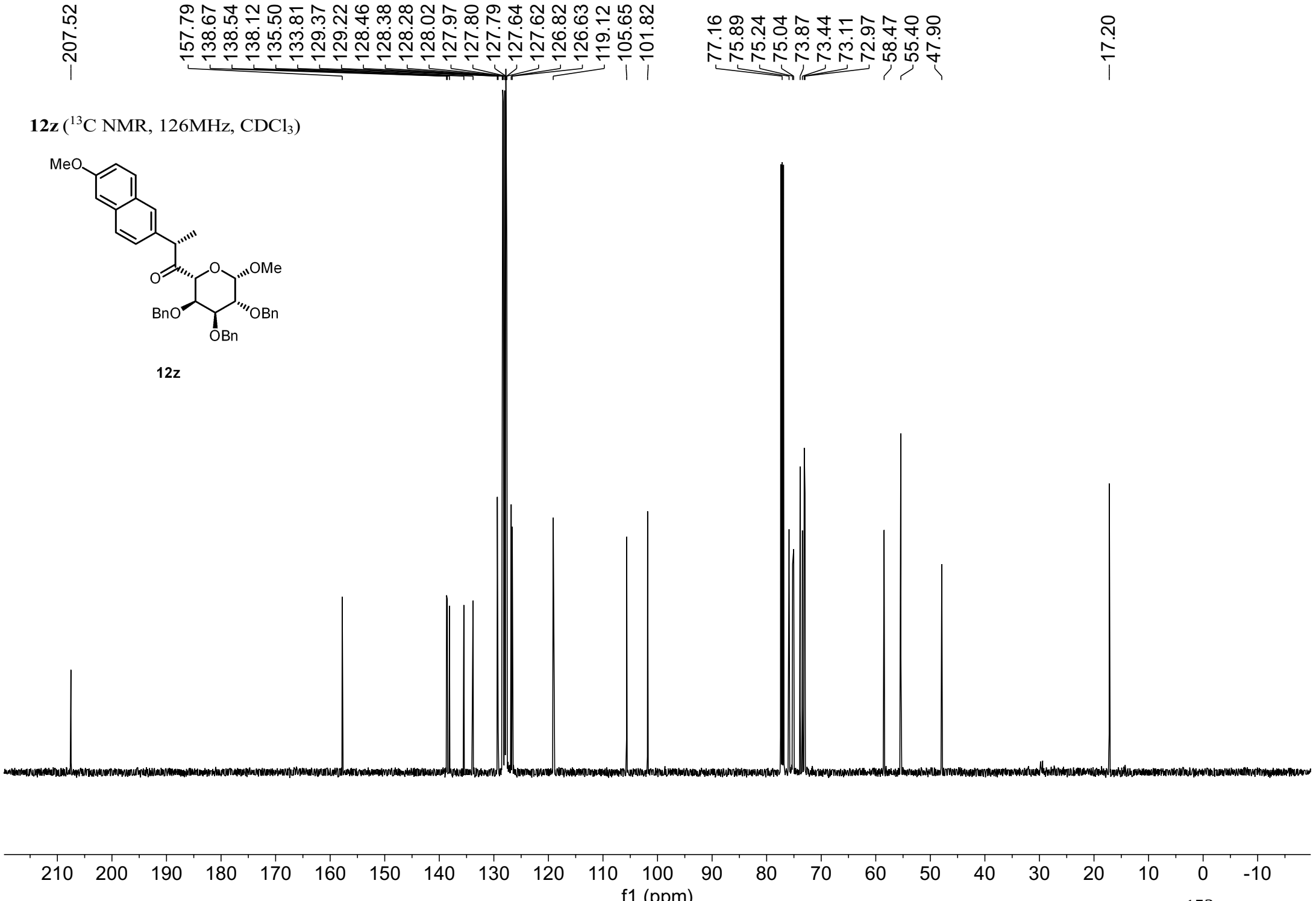

12y (1H-13C Coupled HSQC)
O
O
O
OMe
BnO
OBn
OBn
12y
J = 145 Hz
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

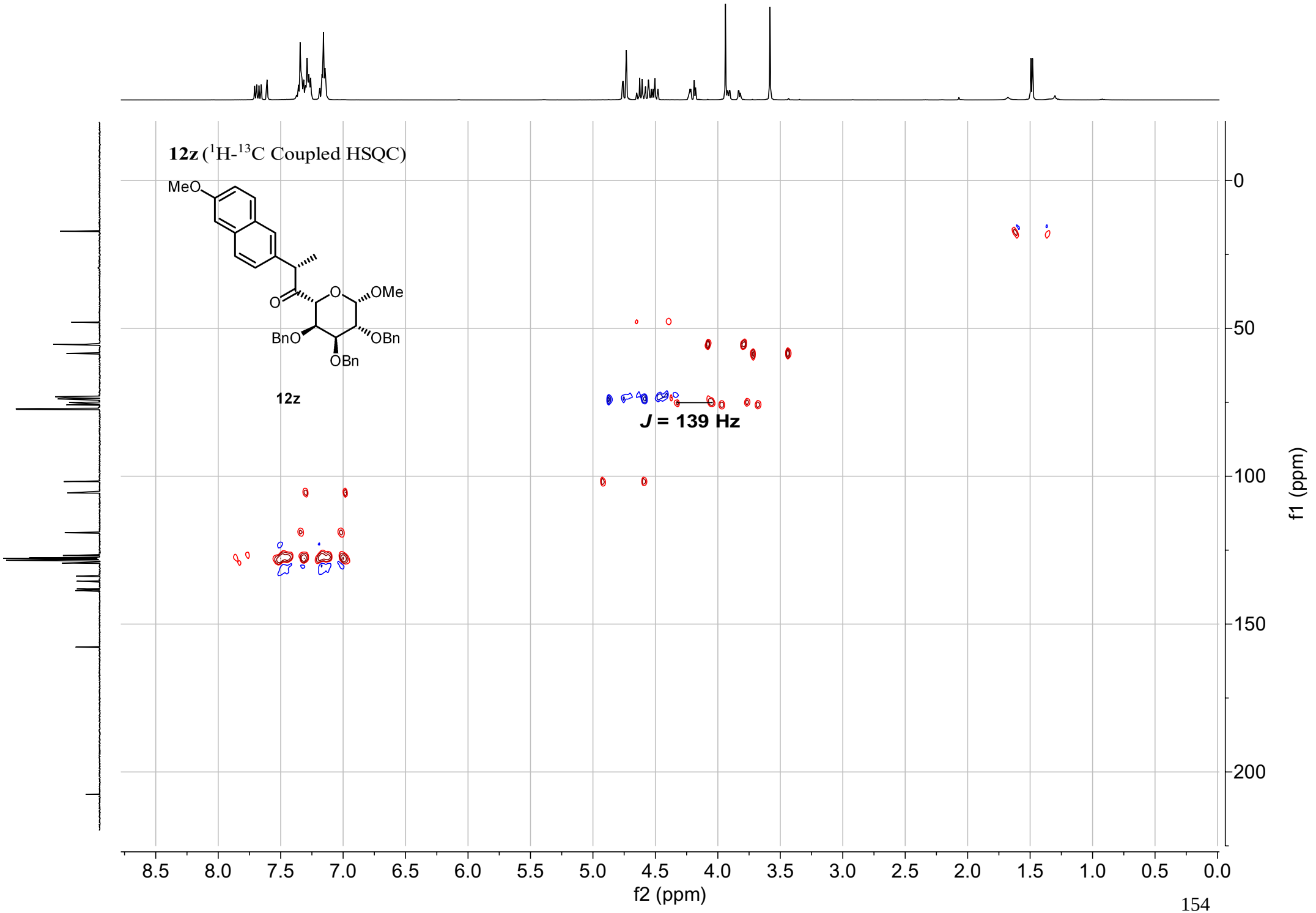

12y (^{1}H-^{1}H NOESY)
O
O
O
OMe
BnO
OBn
OBn
12y
f2 (ppm)
f1 (ppm)

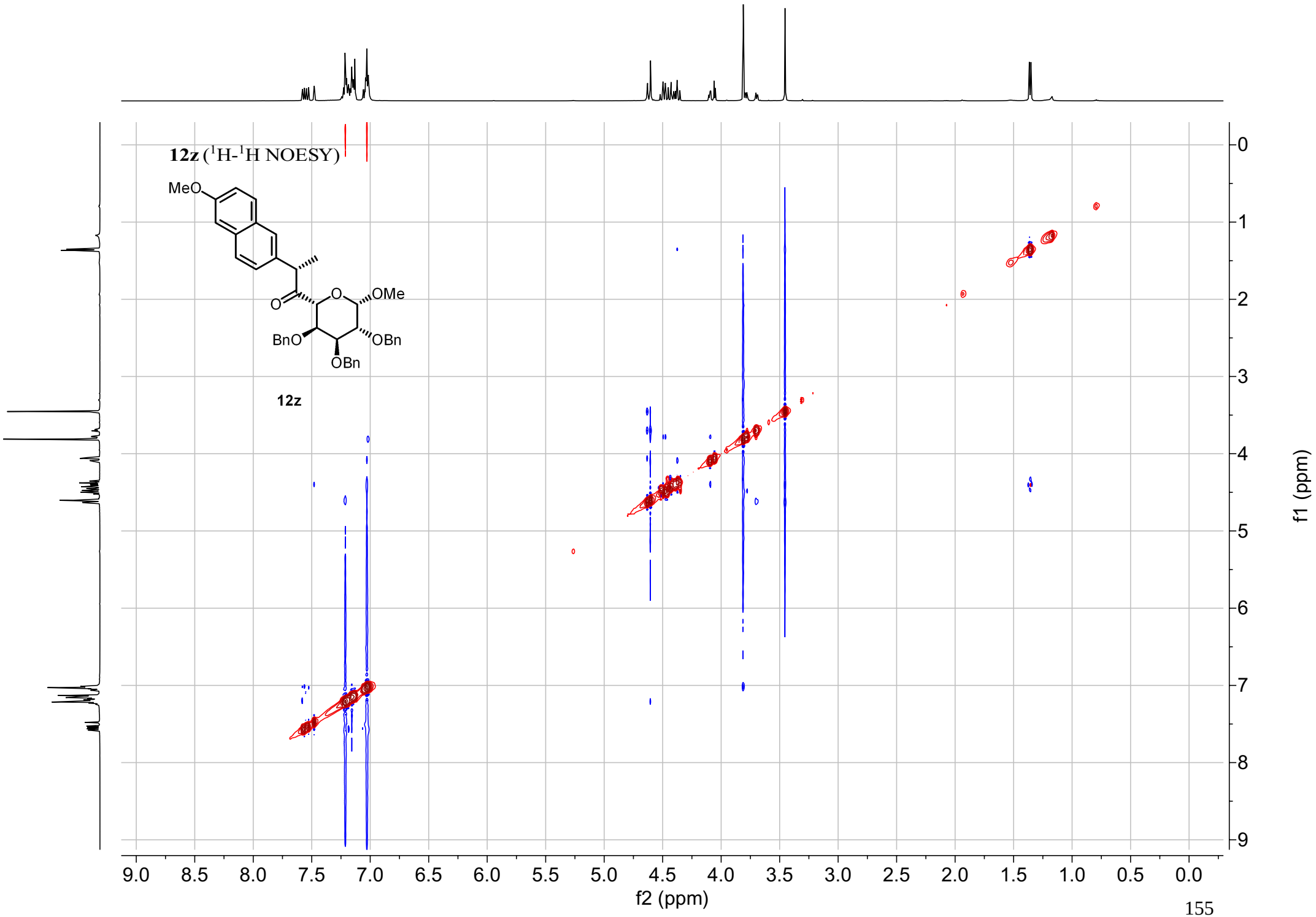
12z (^{1}H NMR, 500MHz, $CDCl_3$)



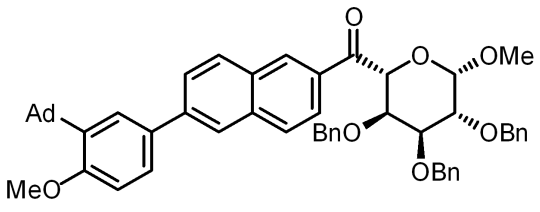
12z


207.52
157.79
138.67
138.54
138.12
135.50
133.81
129.37
129.22
128.46
128.38
128.28
128.02
127.97
127.80
127.79
127.64
127.62
126.82
126.63
119.12
105.65
101.82
77.16
75.89
75.24
75.04
73.87
73.44
73.11
72.97
58.47
55.40
47.90
17.20
12z (13C NMR, 126MHz, CDCl3)
MeO
O
O
OMe
BnO
OBn
OBn
12z
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)


12z (1H-13C Coupled HSQC)
MeO
O
OMe
BnO
OBn
OBn
12z
J = 139 Hz
0
50
100
150
200
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
f2 (ppm)

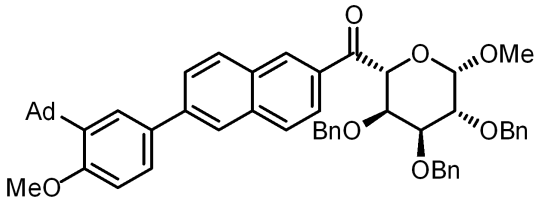

12z (1H-1H NOESY)
MeO
O
O
OMe
BnO
OBn
OBn
12z
f2 (ppm)
f1 (ppm)

12aa (^{1}H NMR, 500MHz, $CDCl_3$)



12aa

12aa (^{13}C NMR, 126MHz, $CDCl_3$)

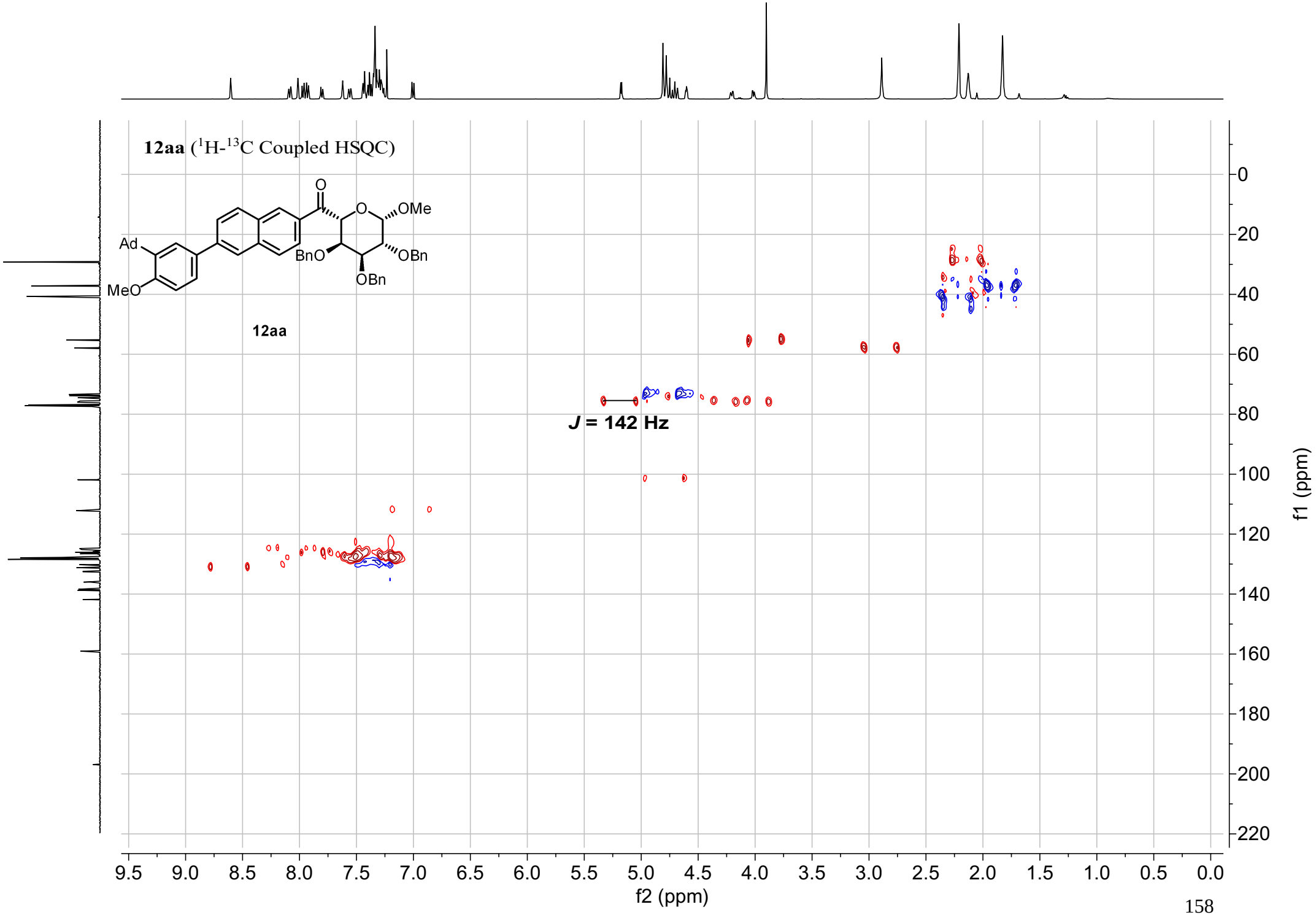


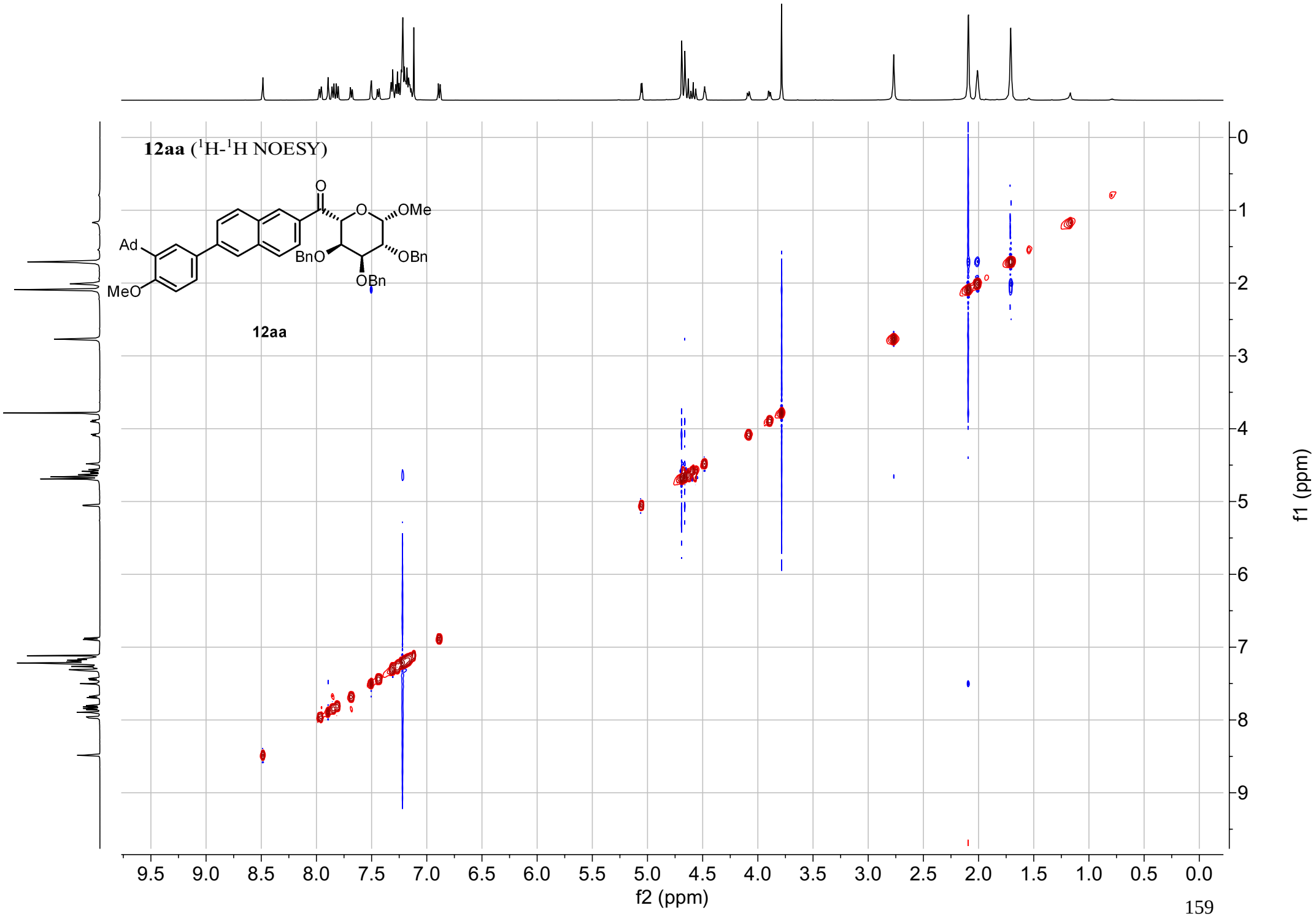
12aa

196.87
159.04
141.81
139.08
138.82
138.77
138.37
136.02
132.58
132.40
131.20
131.19
130.20
128.45
128.43
128.42
128.38
128.11
127.97
127.88
127.75
127.72
127.67
126.56
126.07
125.81
125.15
124.79
112.19
101.84
77.36
77.16
76.00
75.80
75.59
74.49
73.78
73.40
73.29
57.90
55.23
40.69
37.29
37.21
29.19

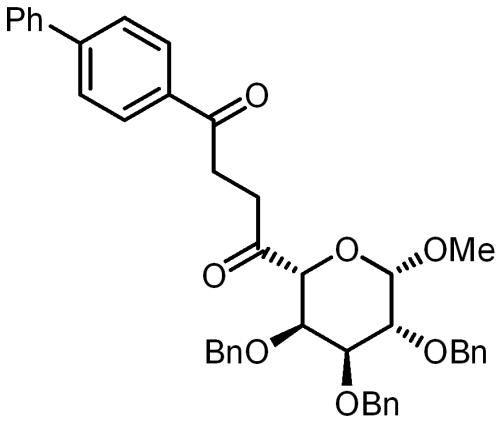
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

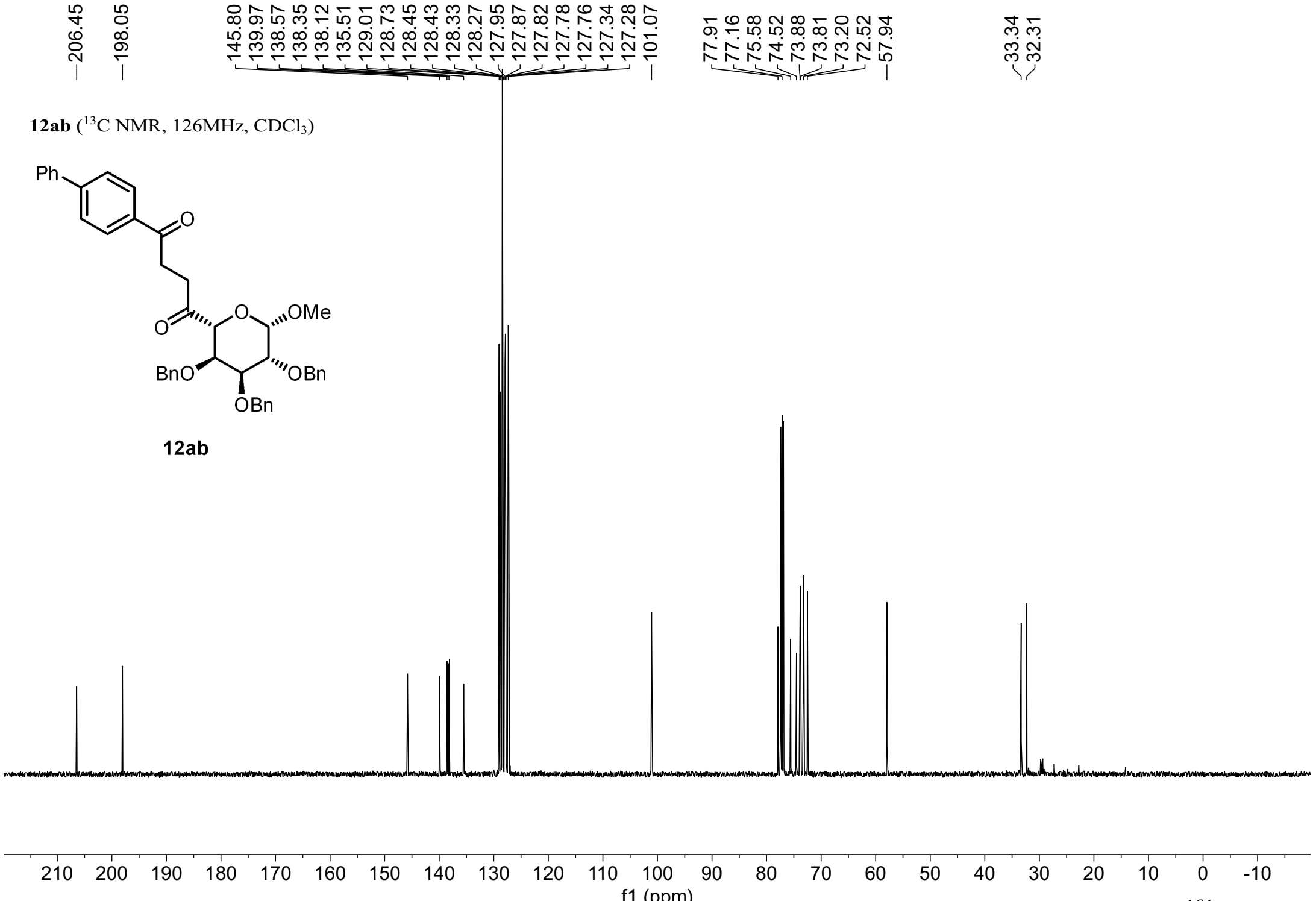

12aa (1H-13C Coupled HSQC)
O
O
OMe
Ad
BnO
OBn
MeO
OBn
12aa
J = 142 Hz
f1 (ppm)
f2 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 20 40 60 80 100 120 140 160 180 200 220

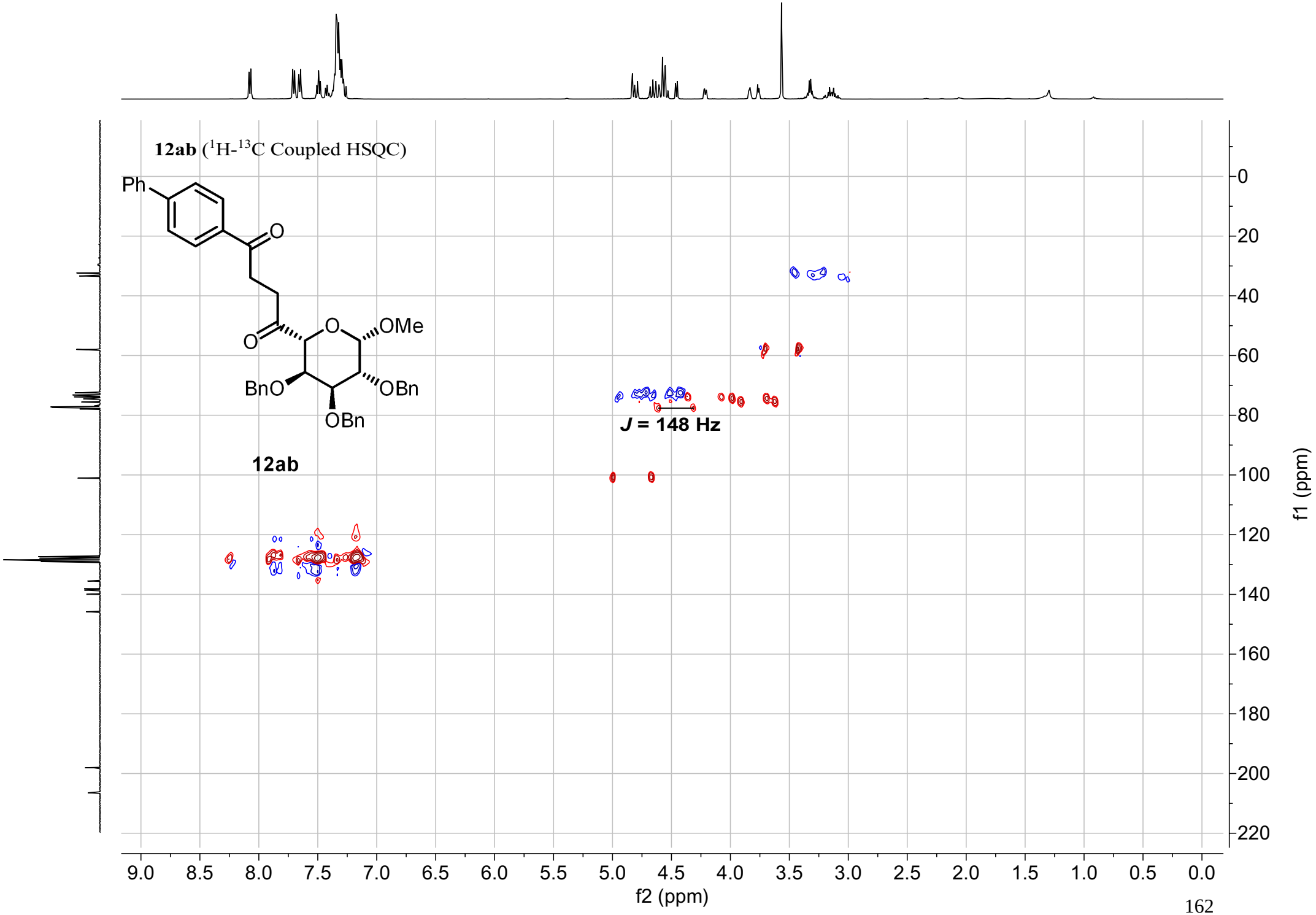

12aa (^{1}H-^{1}H NOESY)
O
O
OMe
Ad
BnO
OBn
MeO
OBn
12aa
f2 (ppm)
f1 (ppm)

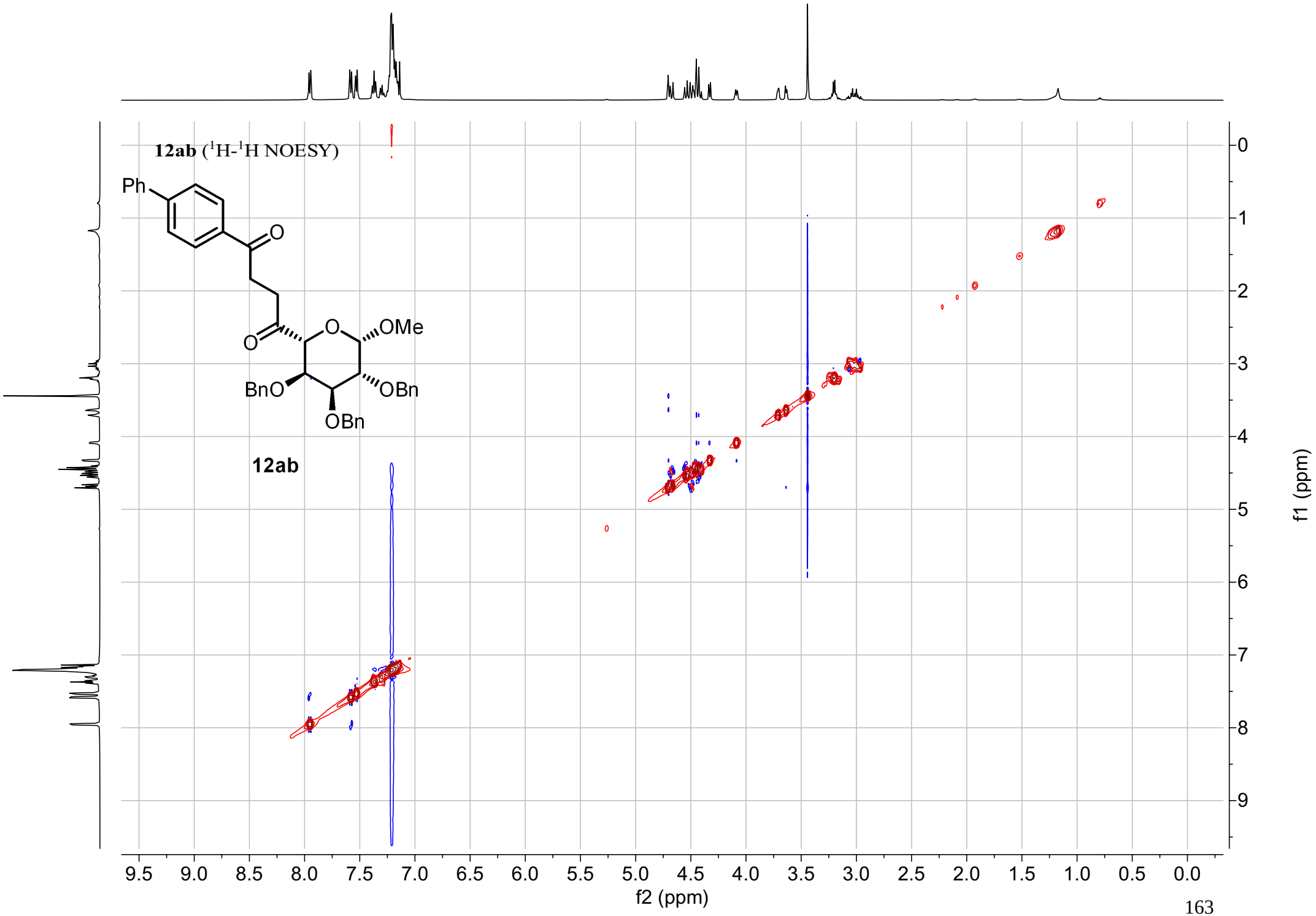
12ab (^{1}H NMR, 500MHz, $CDCl_3$)



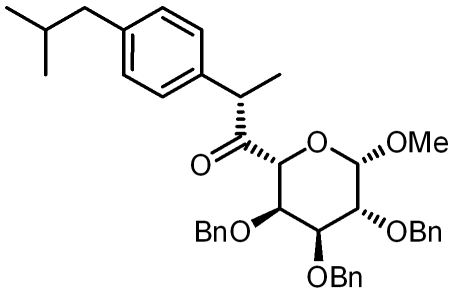
12ab


206.45
198.05
145.80
139.97
138.57
138.35
138.12
135.51
129.01
128.73
128.45
128.43
128.33
128.27
127.95
127.87
127.82
127.78
127.76
127.34
127.28
101.07
77.91
77.16
75.58
74.52
73.88
73.81
73.20
72.52
57.94
33.34
32.31
12ab (^{13}C NMR, 126MHz, $CDCl_3$)
Ph
O
O
O
OMe
BnO
OBn
OBn
12ab
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)


12ab (1H-13C Coupled HSQC)
Ph
O
O
O
OMe
BnO
OBn
OBn
12ab
J = 148 Hz
f2 (ppm)
f1 (ppm)


12ab (1H-1H NOESY)
Ph
O
O
O
OMe
BnO
OBn
OBn
12ab
f2 (ppm)
f1 (ppm)

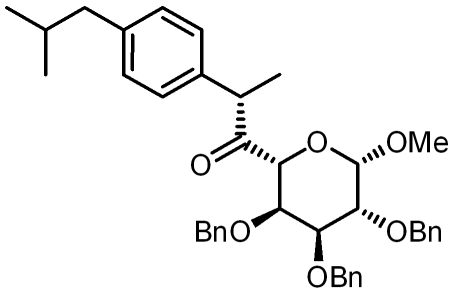
12ac (^{1}H NMR, 500MHz, $CDCl_3$)



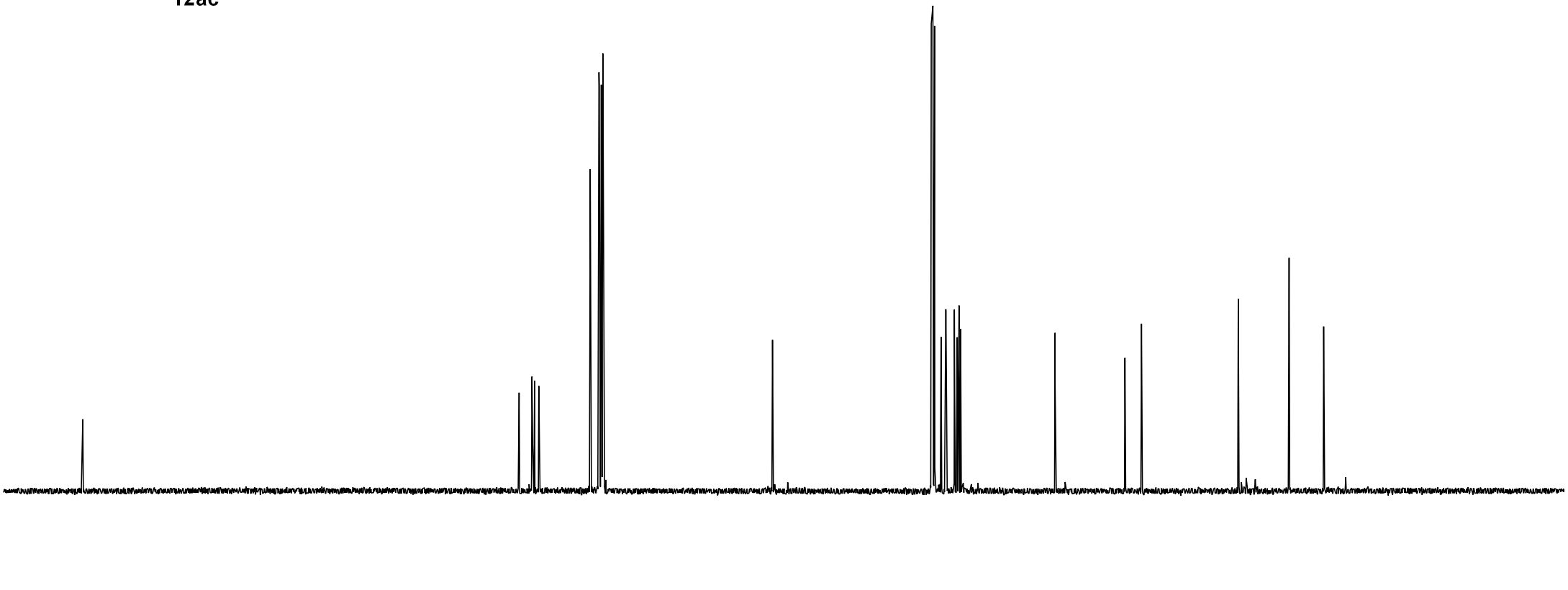
12ac

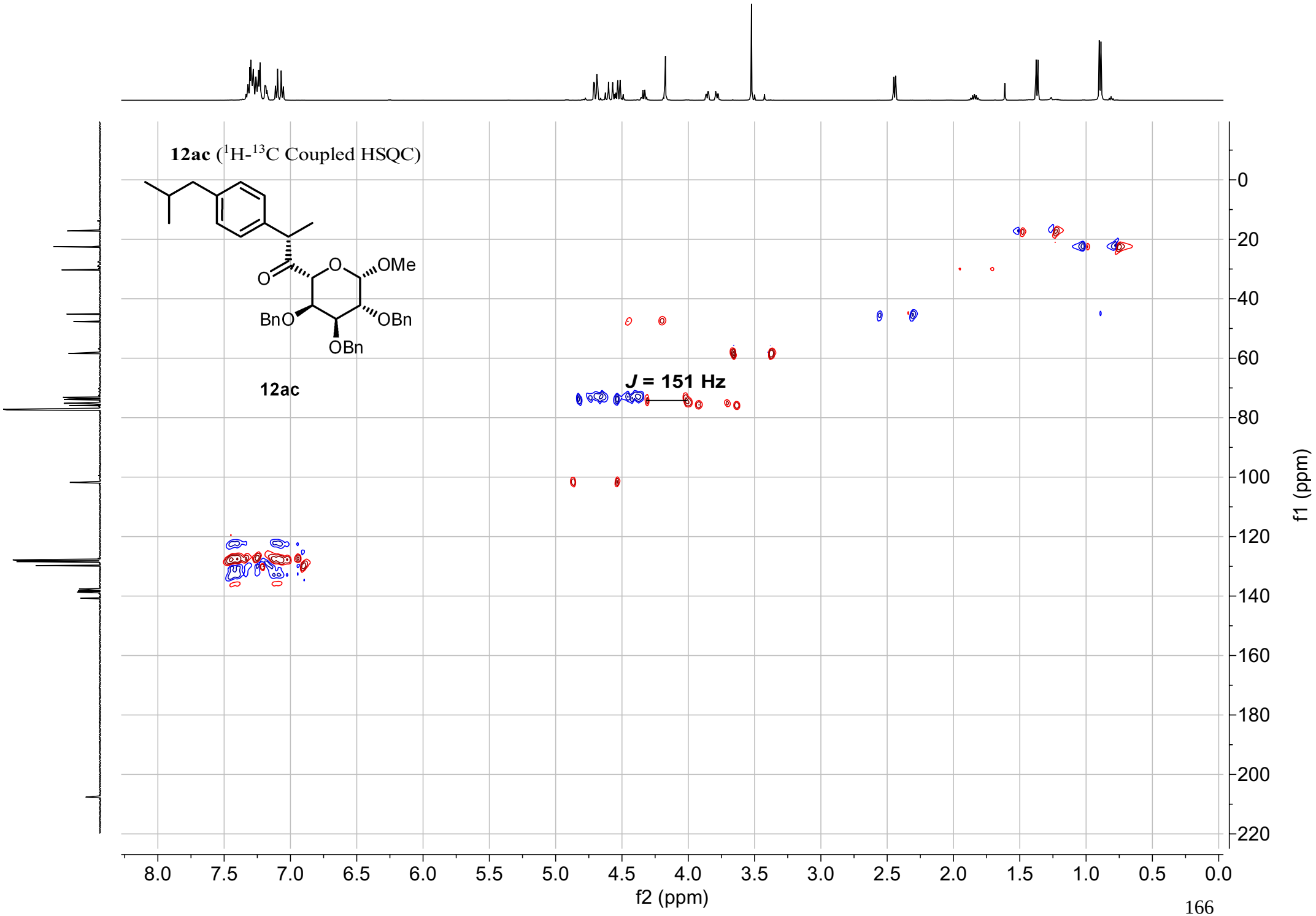
207.63
140.67
138.70
138.60
138.29
137.65
129.75
128.47
128.41
128.36
128.06
127.99
127.87
127.81
127.79
127.68
127.67
101.78
77.16
75.91
75.17
75.16
73.87
73.42
73.15
72.90
58.42
47.68
45.15
30.29
22.51
22.49
17.19

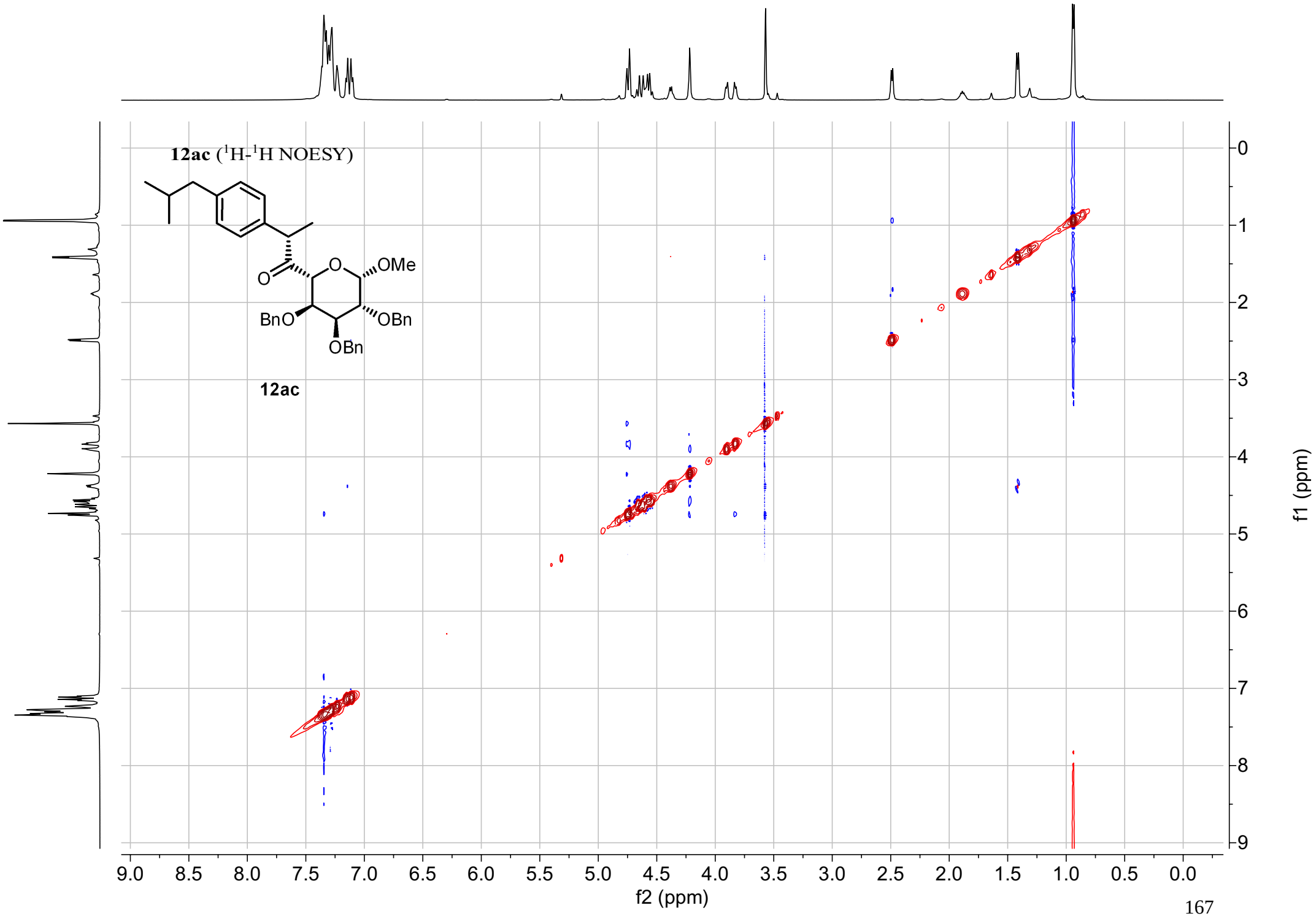
12ac (^{13}C NMR, 126MHz, $CDCl_3$)



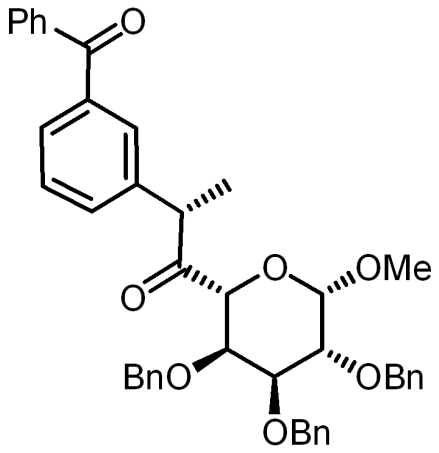
12ac



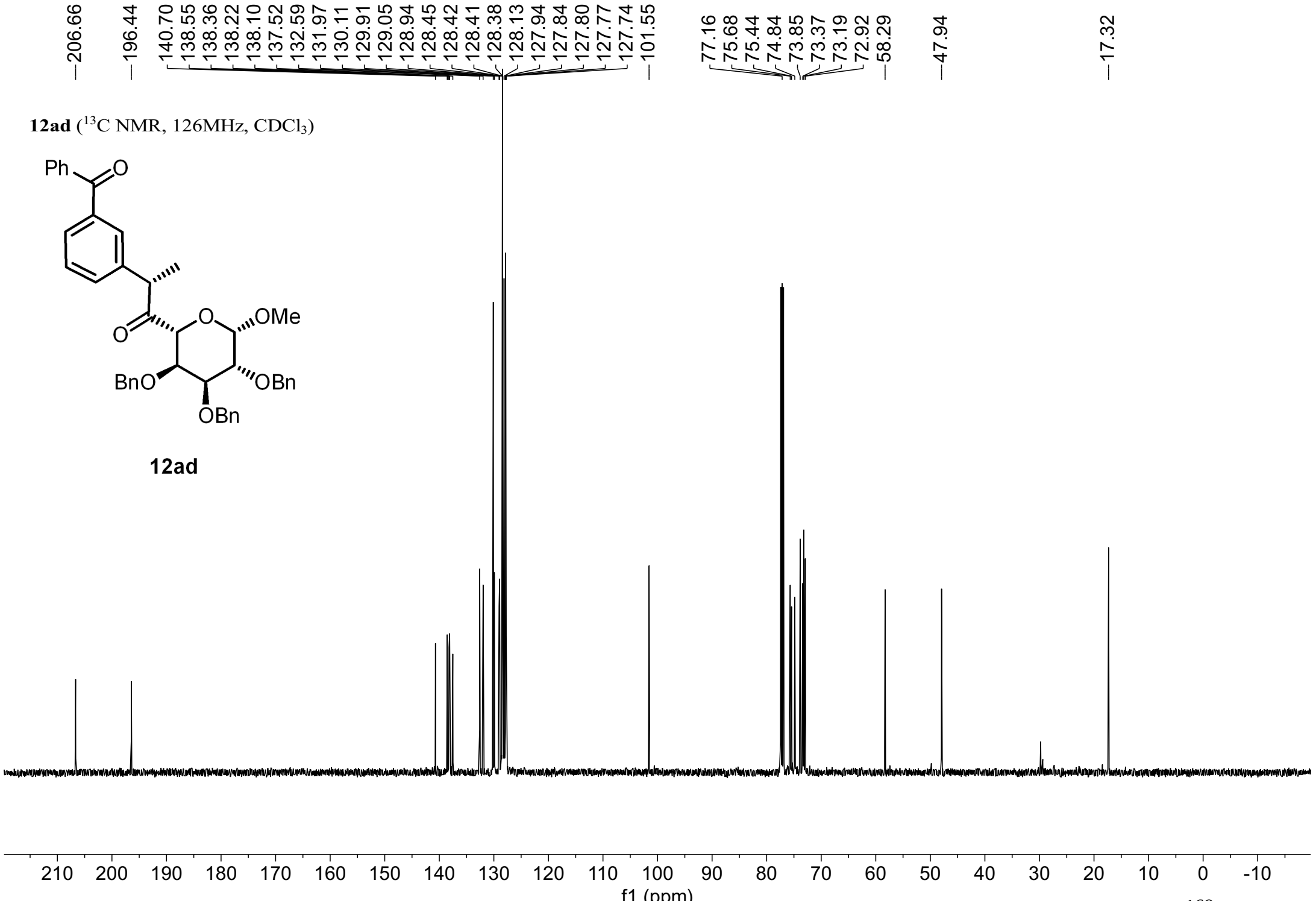

12ac (^{1}H-^{13}C Coupled HSQC)
OMe
BnO
OBn
OBn
O
O
12ac
J = 151 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

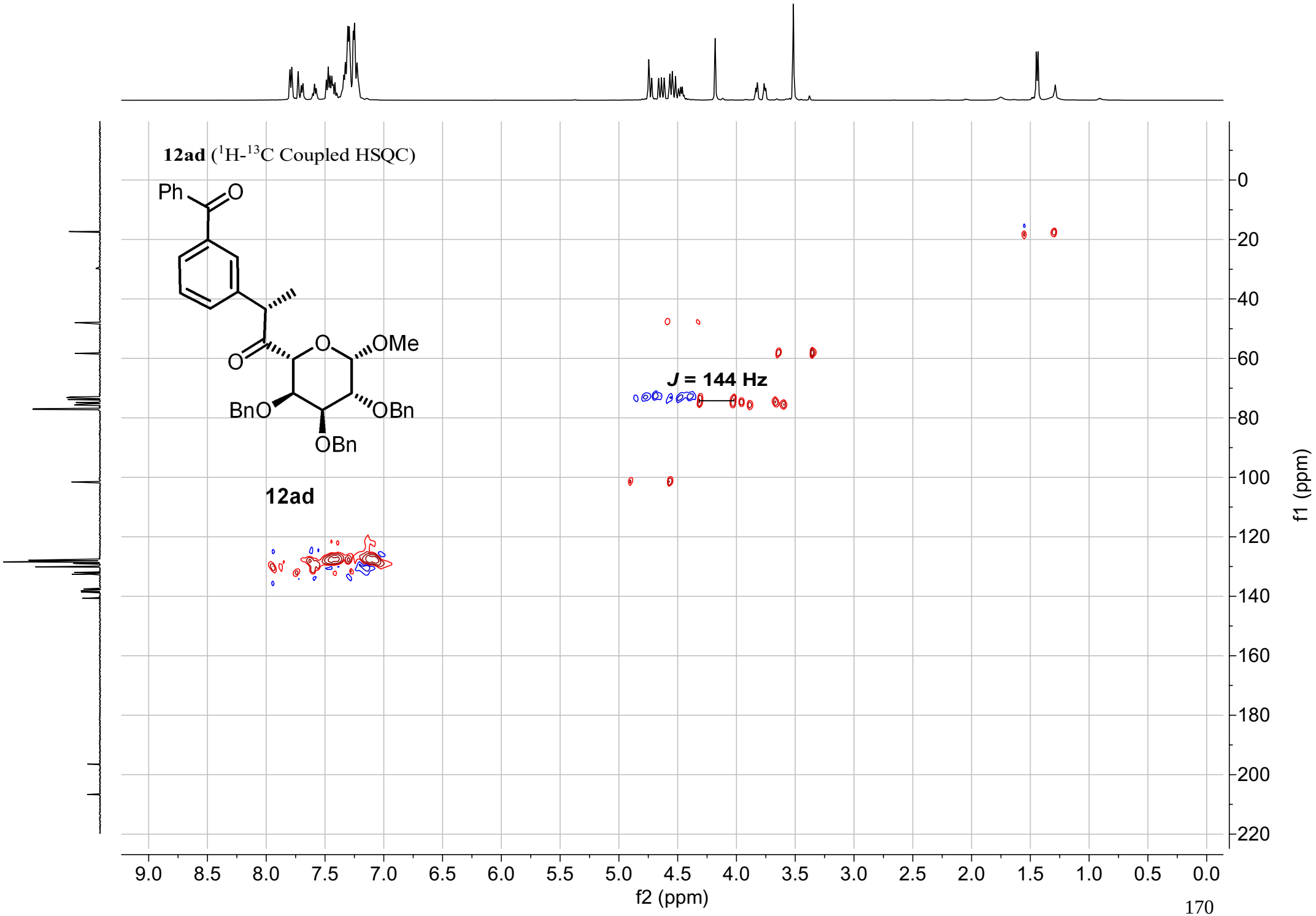

12ac (^{1}H-^{1}H NOESY)
O
OMe
BnO
OBn
OBn
12ac
f2 (ppm)
f1 (ppm)

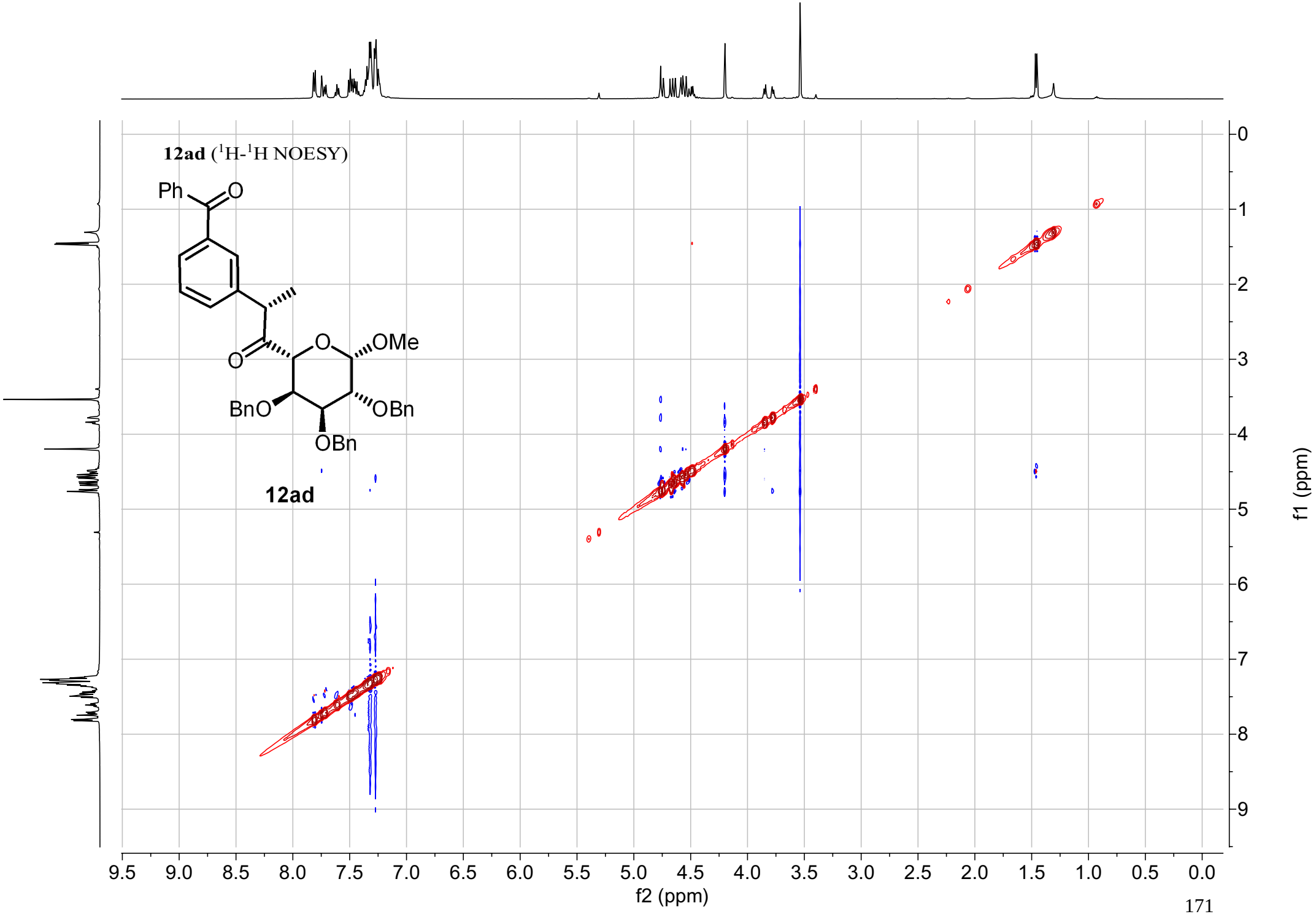
12ad (^{1}H NMR, 500MHz, $CDCl_3$)



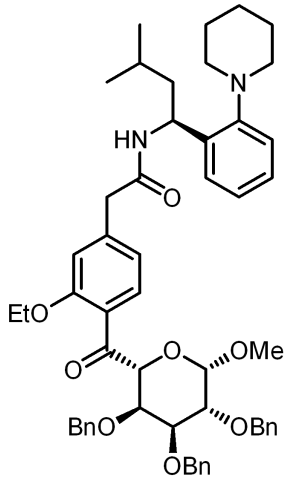
12ad


206.66
196.44
140.70
138.55
138.36
138.22
138.10
137.52
132.59
131.97
130.11
129.91
129.05
128.94
128.45
128.42
128.41
128.38
128.13
127.94
127.84
127.80
127.77
127.74
101.55
77.16
75.68
75.44
74.84
73.85
73.37
73.19
72.92
58.29
47.94
17.32
12ad (^{13}C NMR, 126MHz, $CDCl_3$)
Ph
O
O
O
OMe
BnO
OBn
OBn
12ad
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)


12ad (1H-13C Coupled HSQC)
Ph
O
O
O
OMe
BnO
OBn
OBn
12ad
J = 144 Hz
f2 (ppm)
f1 (ppm)


12ad (1H-1H NOESY)
Ph
O
O
O
OMe
BnO
OBn
OBn
12ad
f2 (ppm)
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8
9

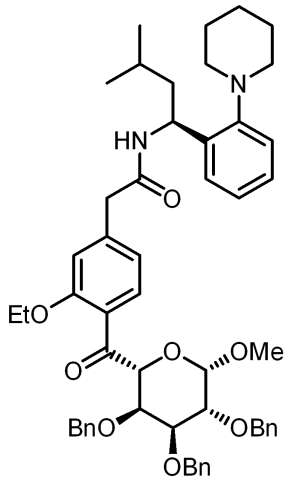
12ae (^{1}H NMR, 500MHz, $CDCl_3$)



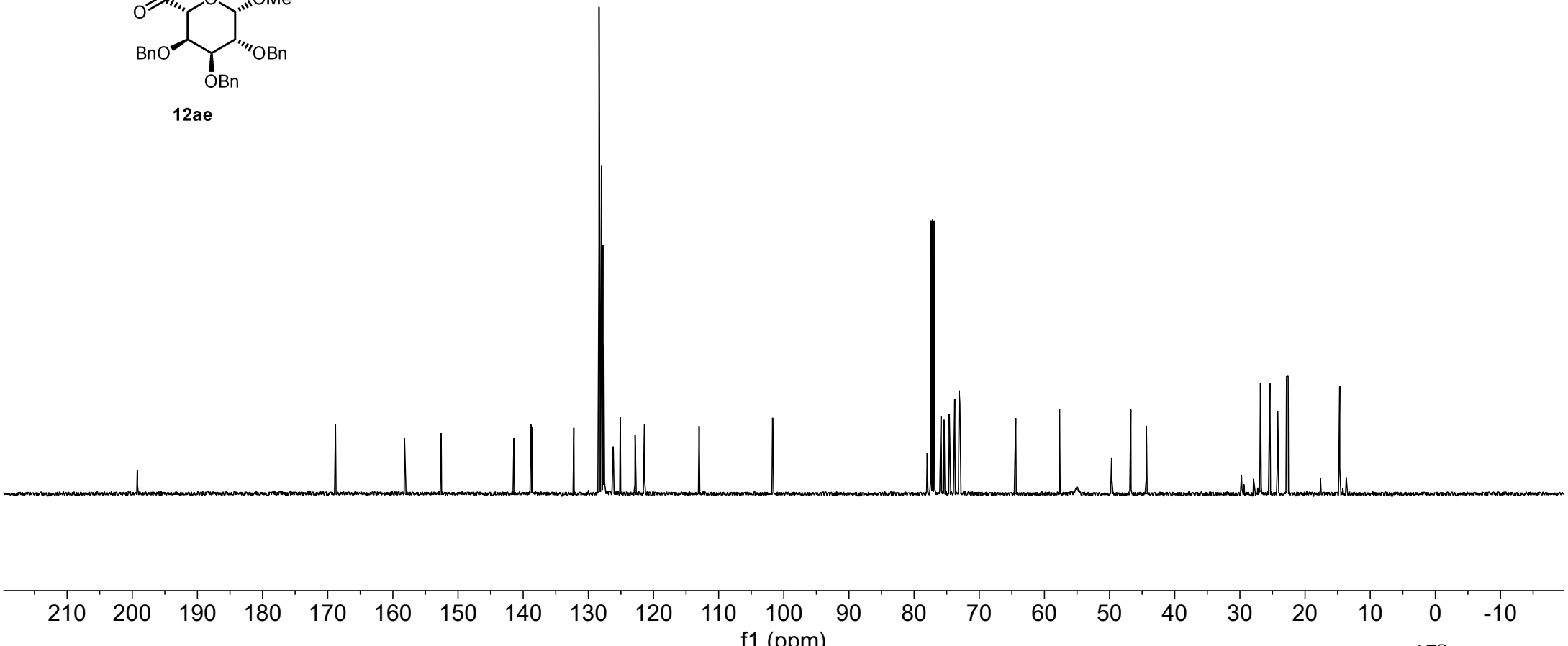
12ae

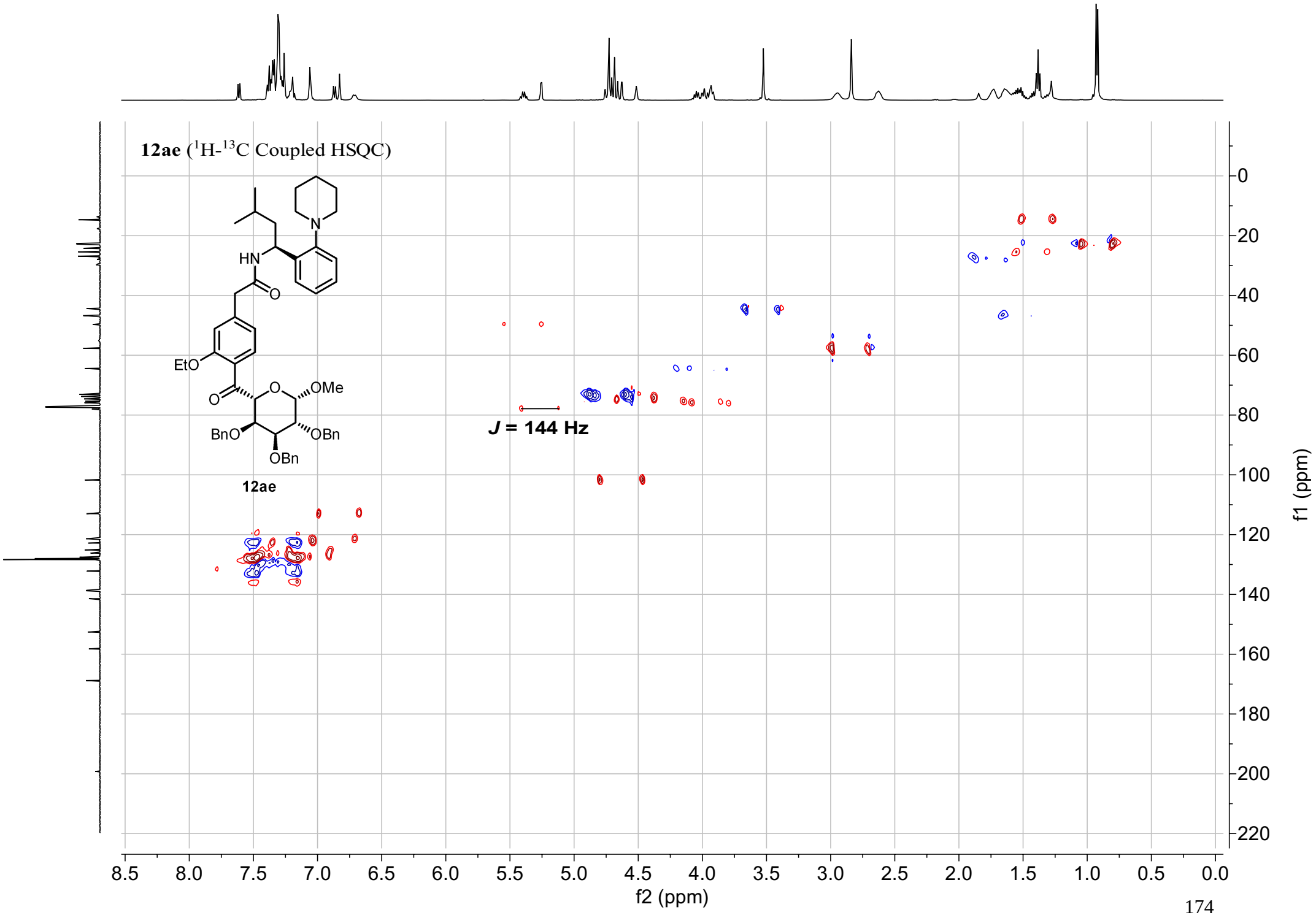
199.23
168.81
158.22
152.58
141.43
138.89
138.80
138.72
138.59
132.22
128.36
127.99
127.97
127.78
127.66
127.62
127.54
126.17
125.10
122.83
121.38
113.00
101.72
77.99
77.16
75.87
75.41
74.60
73.77
73.09
72.98
64.40
57.68
49.69
46.74
44.35
26.84
25.40
24.21
22.84
22.59
14.68

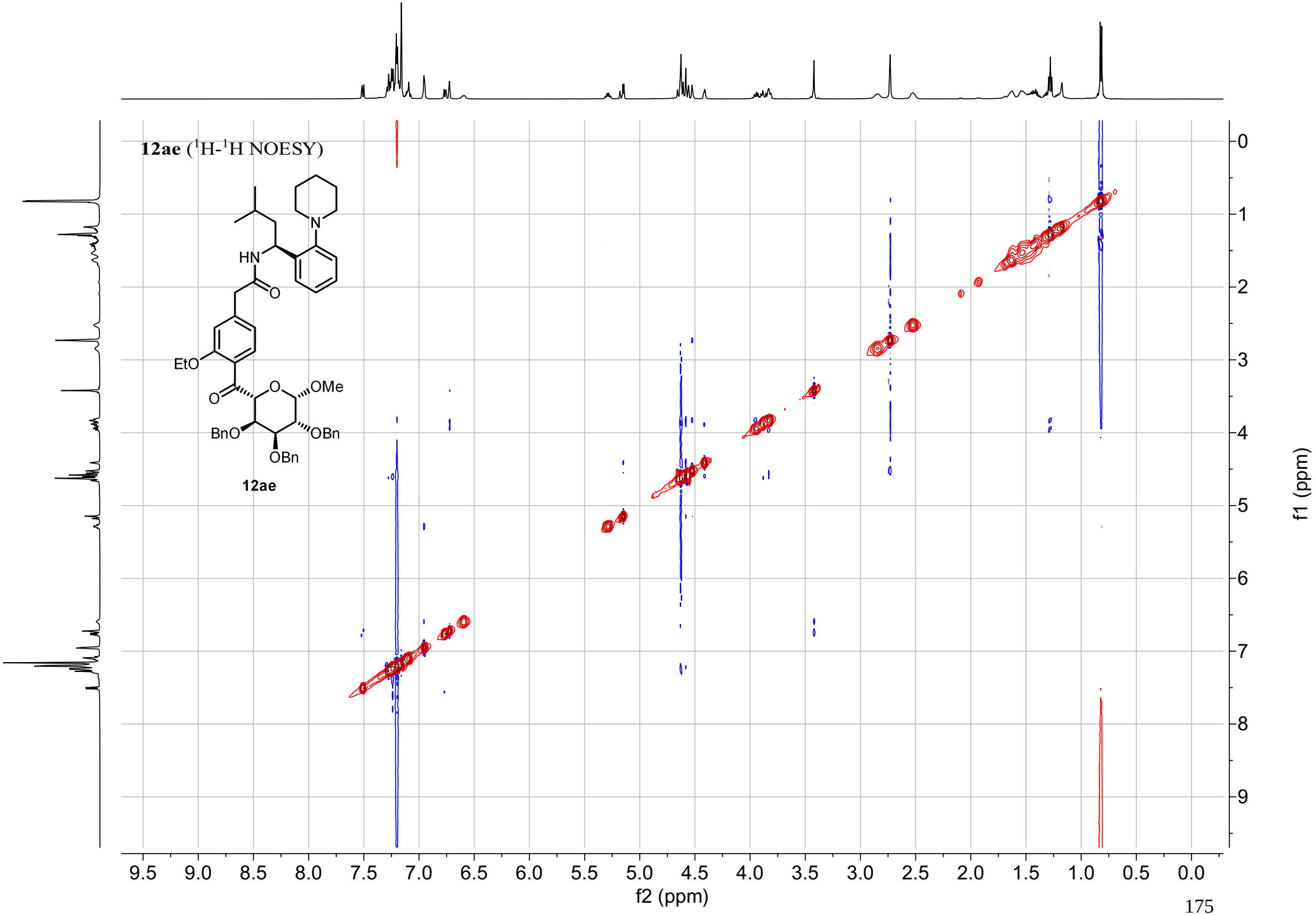
12ae (^{13}C NMR, 126MHz, $CDCl_3$)



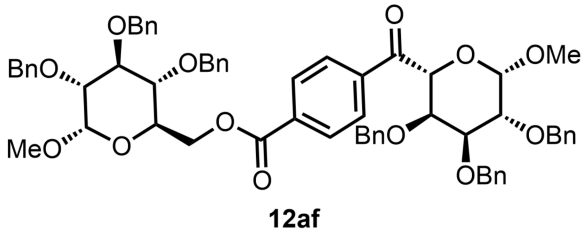
12ae




12ae (^{1}H-^{13}C Coupled HSQC)
HN
N
O
EtO
O
O
OMe
BnO
OBn
OBn
12ae
J = 144 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
0
20
40
60
80
100
120
140
160
180
200
220

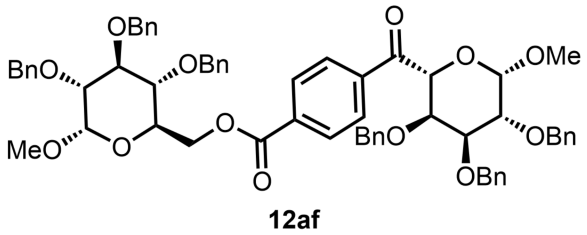

12ae (^{1}H-^{1}H NOESY)
HN
N
O
EtO
O
O
OMe
BnO
OBn
OBn
12ae
f2 (ppm)
f1 (ppm)

12af (^{1}H NMR, 500MHz, $CDCl_3$)

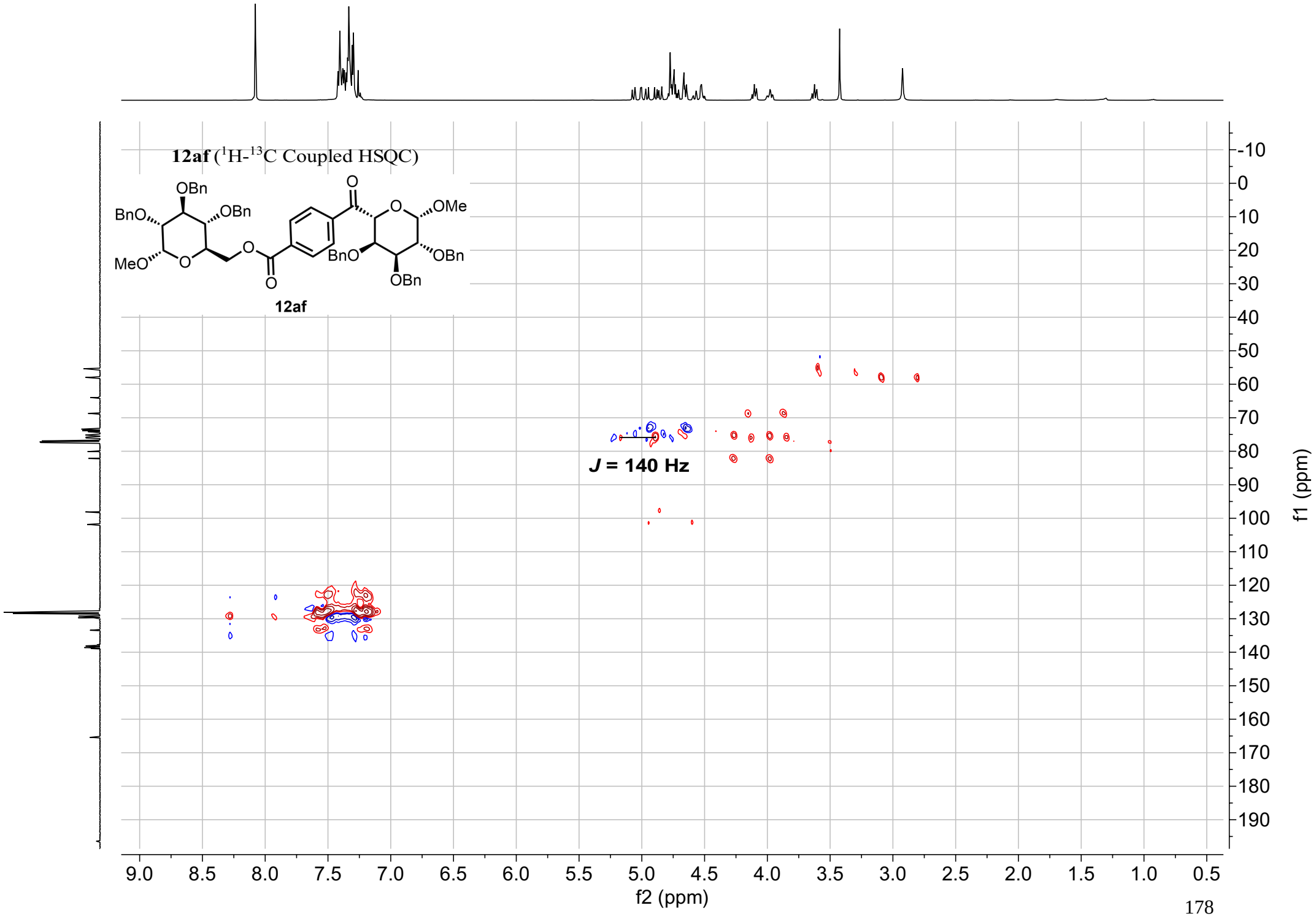


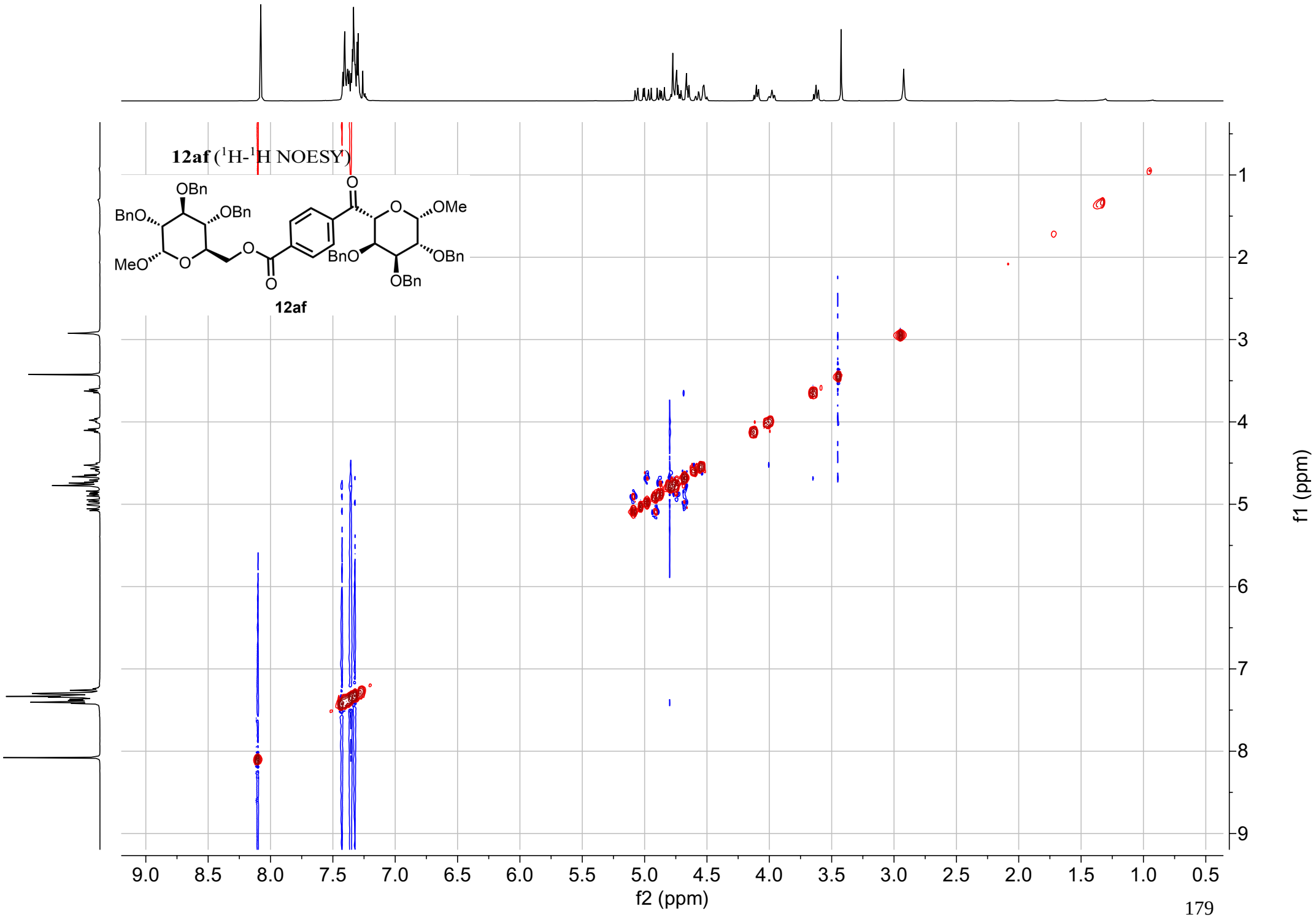
12af

12af (^{13}C NMR, 126MHz, $CDCl_3$)

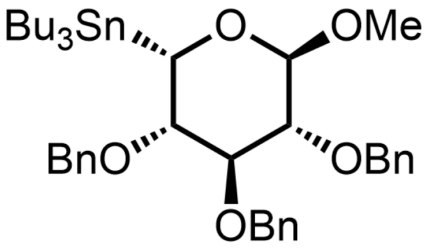


12af


12af (^{1}H-^{13}C Coupled HSQC)
12af
J = 140 Hz
f2 (ppm)
f1 (ppm)

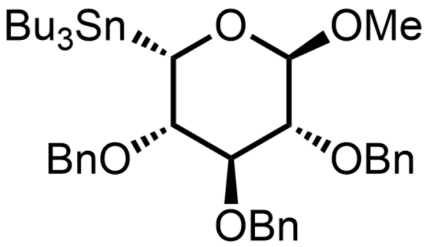

12af (1H-1H NOESY)
OBn
BnO
OBn
MeO
O
O
O
O
O
OMe
BnO
OBn
OBn
12af
f2 (ppm)
f1 (ppm)

9e' (^{1}H NMR, 500MHz, $CDCl_3$)

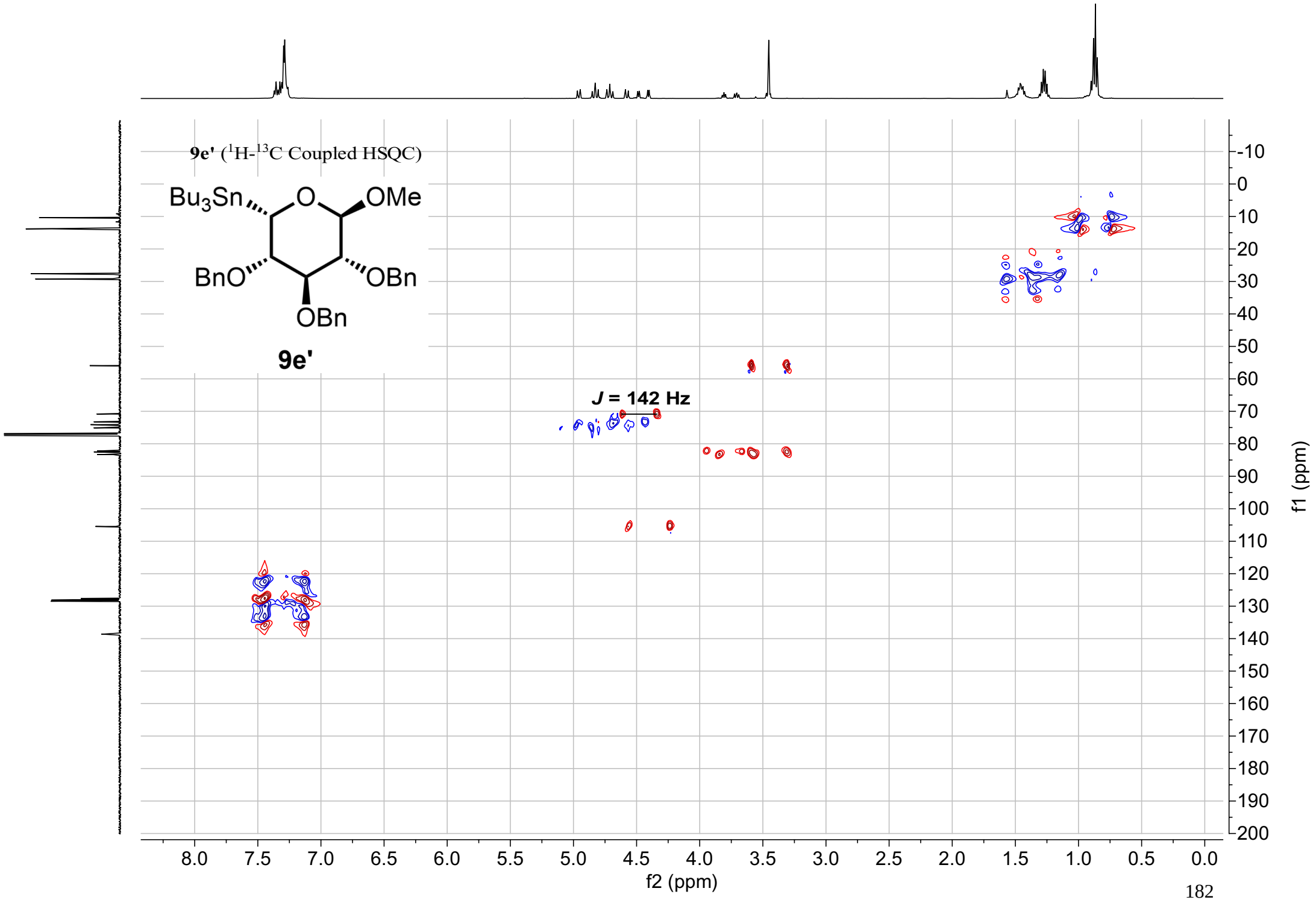


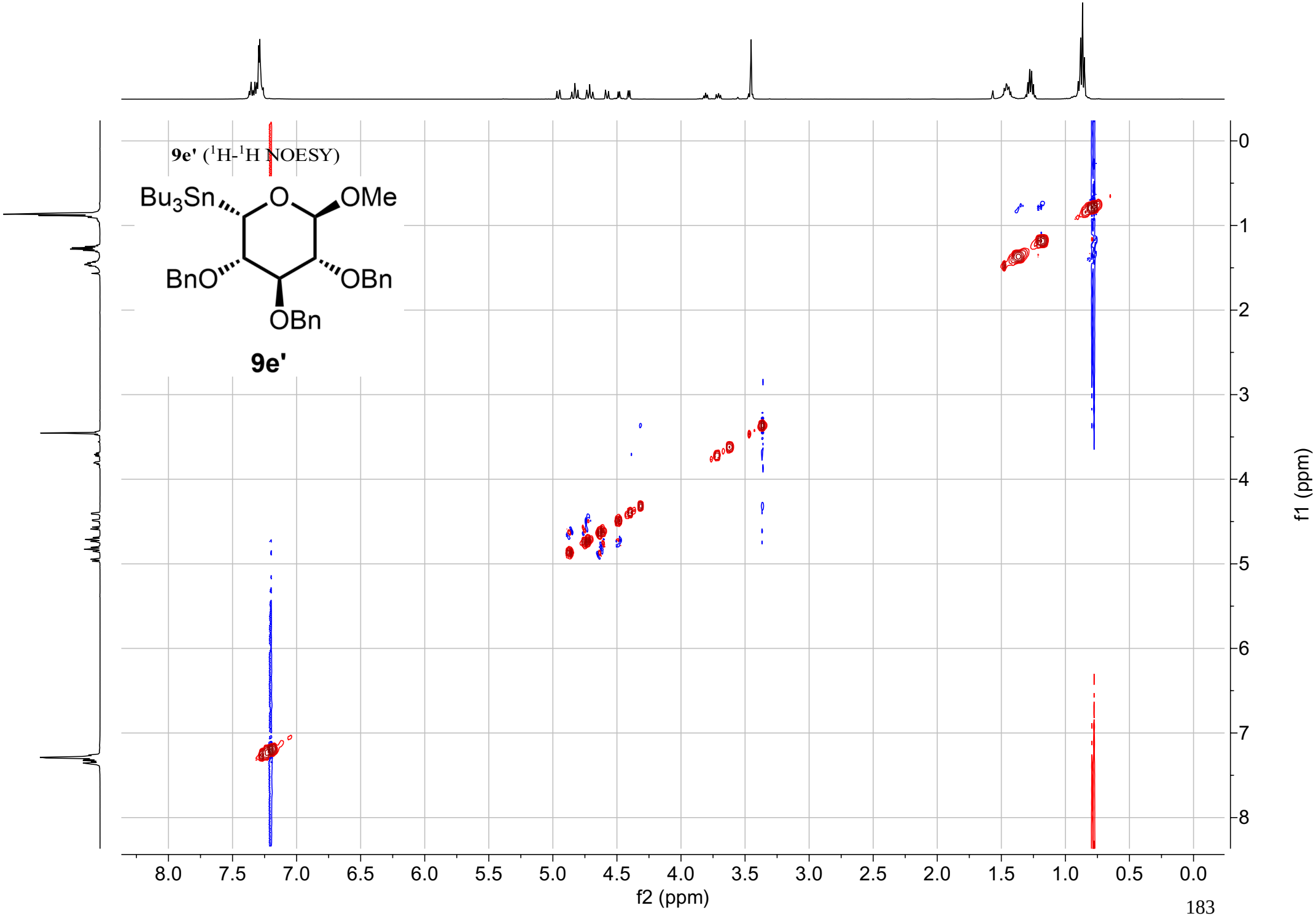
9e'

9e' (^{13}C NMR, 126MHz, $CDCl_3$)

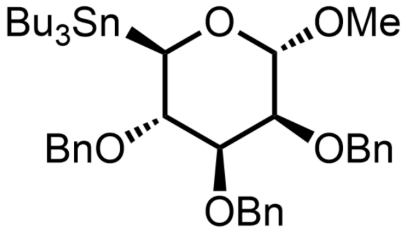


9e'


9e' (^{1}H-^{13}C Coupled HSQC)
Bu3Sn
O
OMe
BnO
OBn
OBn
9e'
J = 142 Hz
f2 (ppm)
f1 (ppm)

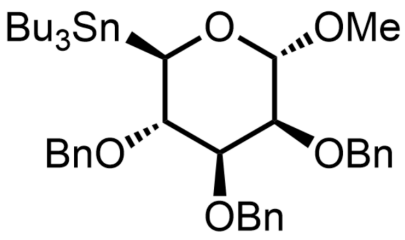

9e' (1H-1H NOESY)
Bu3Sn
O
OMe
BnO
OBn
OBn
9e'
f2 (ppm)
f1 (ppm)

9f (^{1}H NMR, 500MHz, $CDCl_3$)

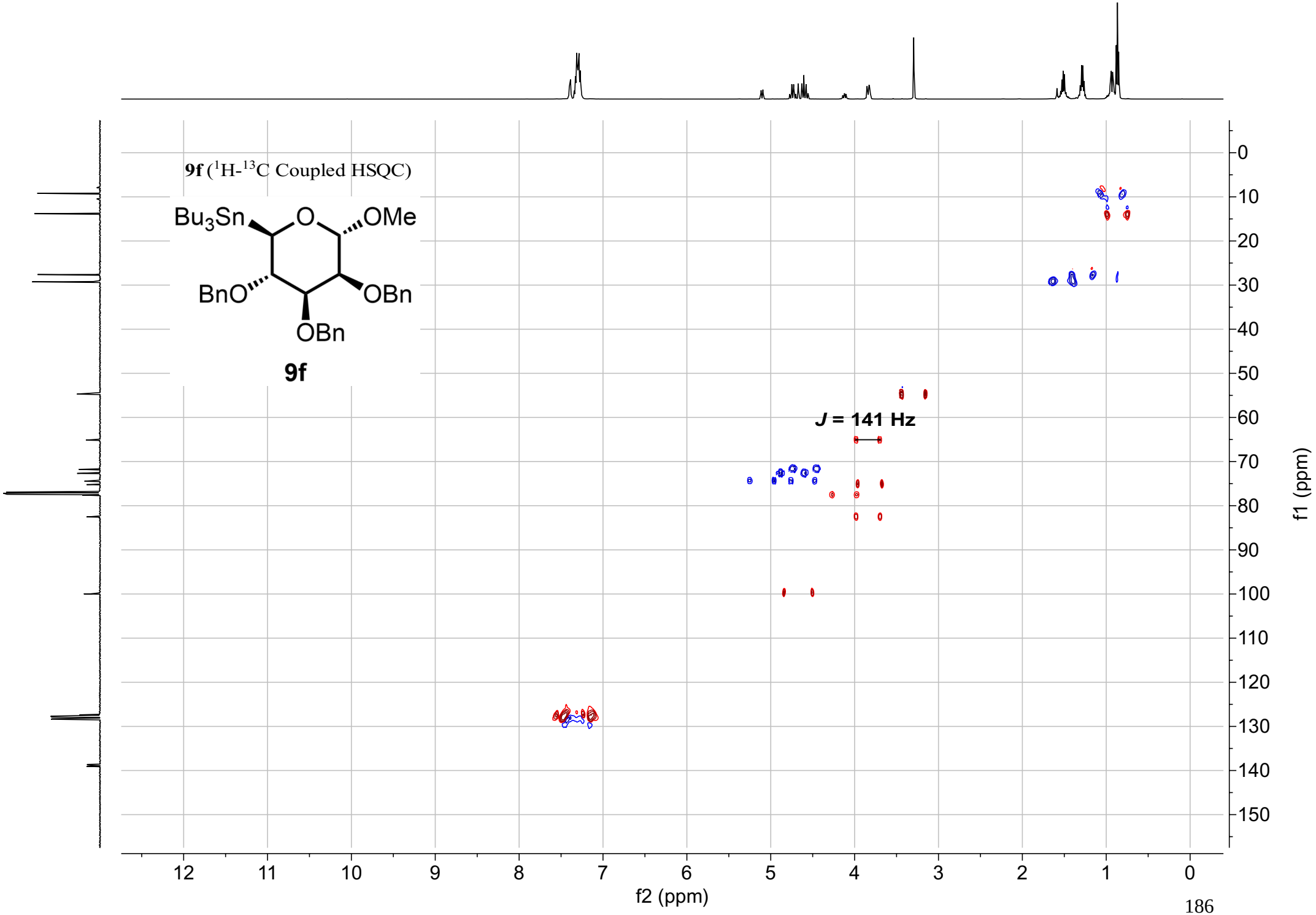


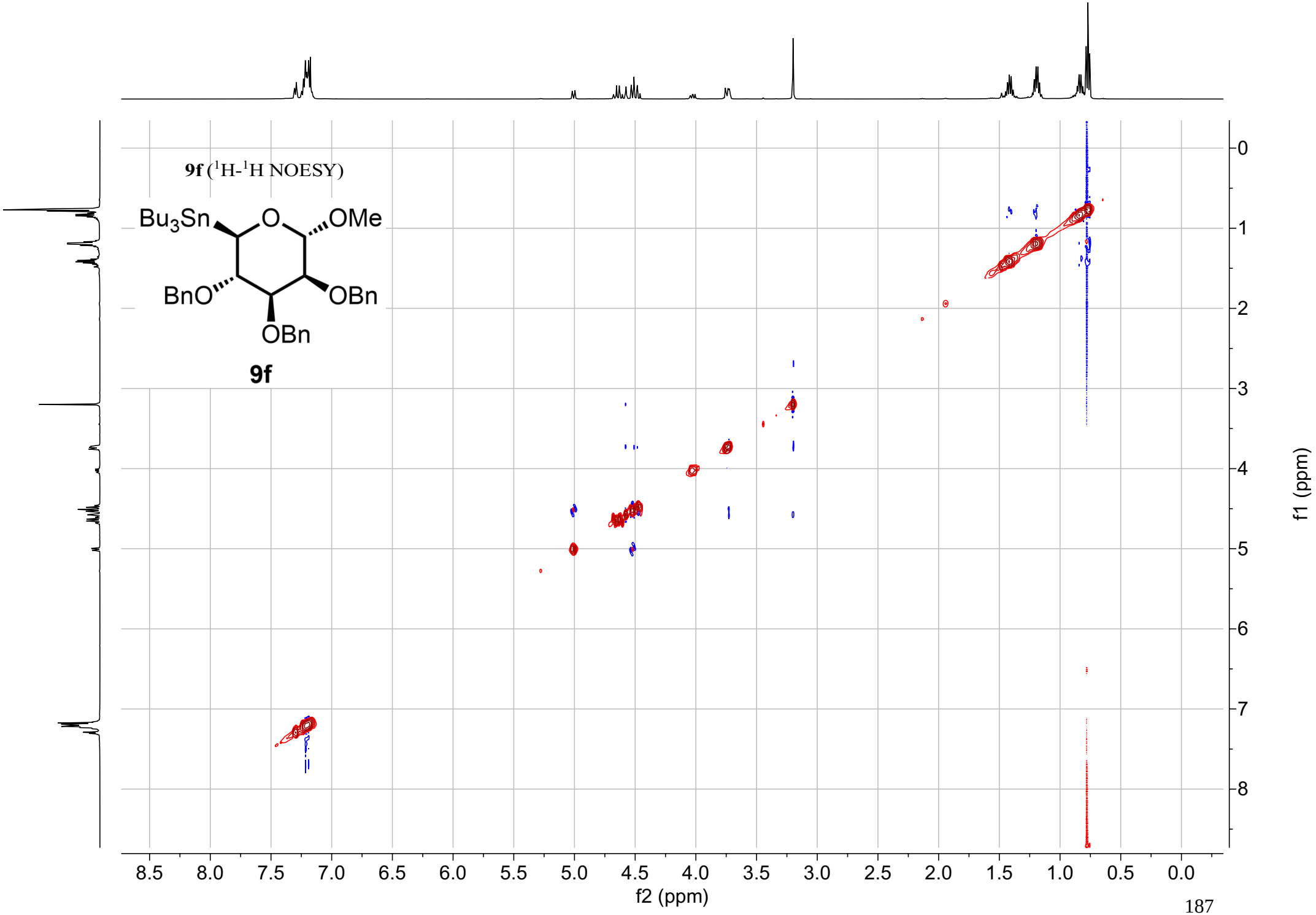
9f

9f (^{13}C NMR, 126MHz, $CDCl_3$)

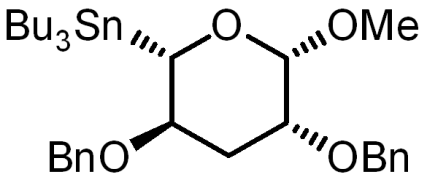


9f


9f (1H-13C Coupled HSQC)
Bu3Sn
O
OMe
BnO
OBn
OBn
9f
J = 141 Hz
f2 (ppm)
f1 (ppm)

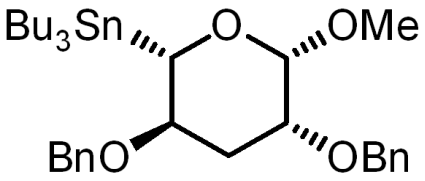

9f (1H-1H NOESY)
Bu3Sn
O
OMe
BnO
OBn
OBn
9f
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

9h (^{1}H NMR, 500MHz, $CDCl_3$)

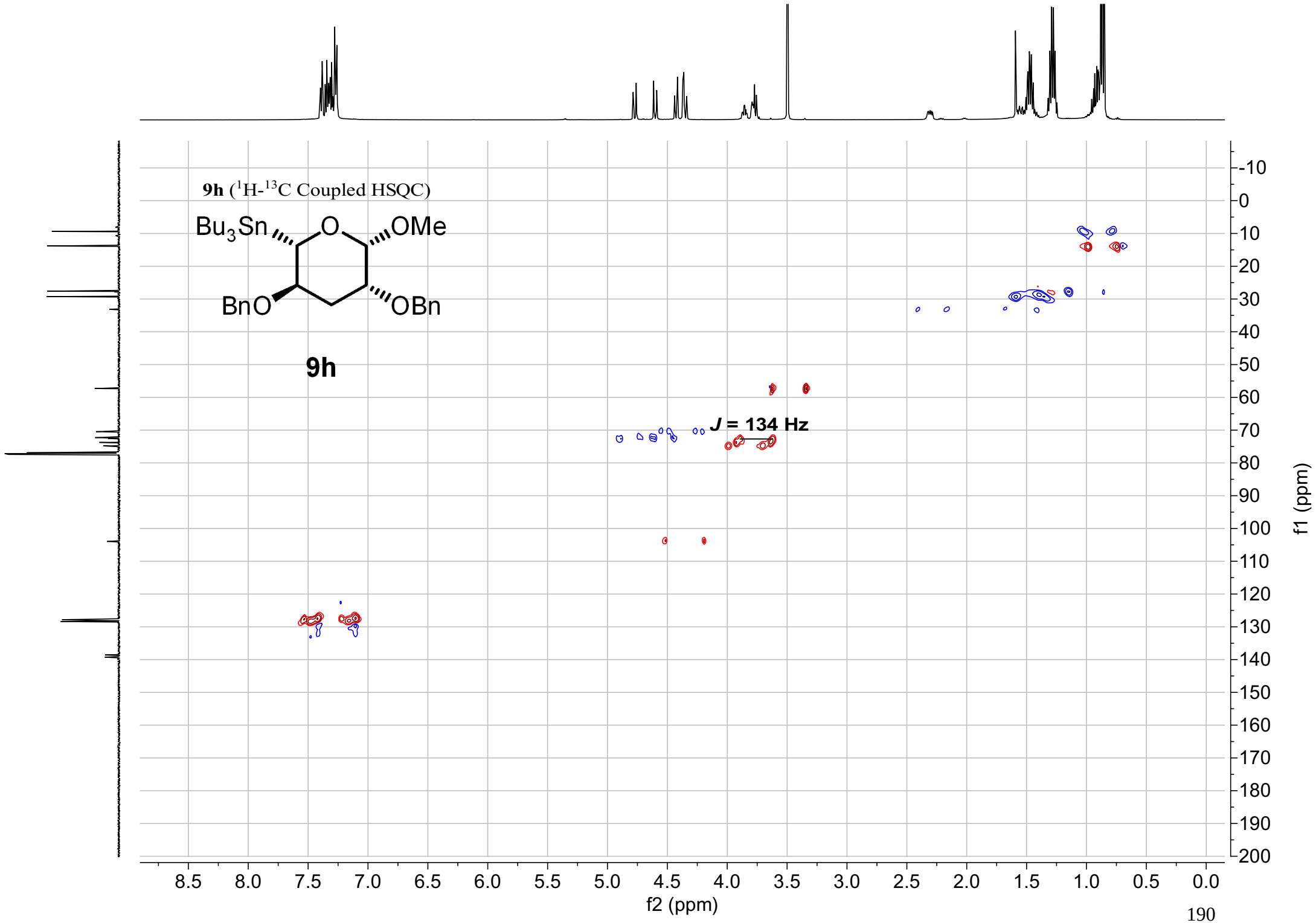


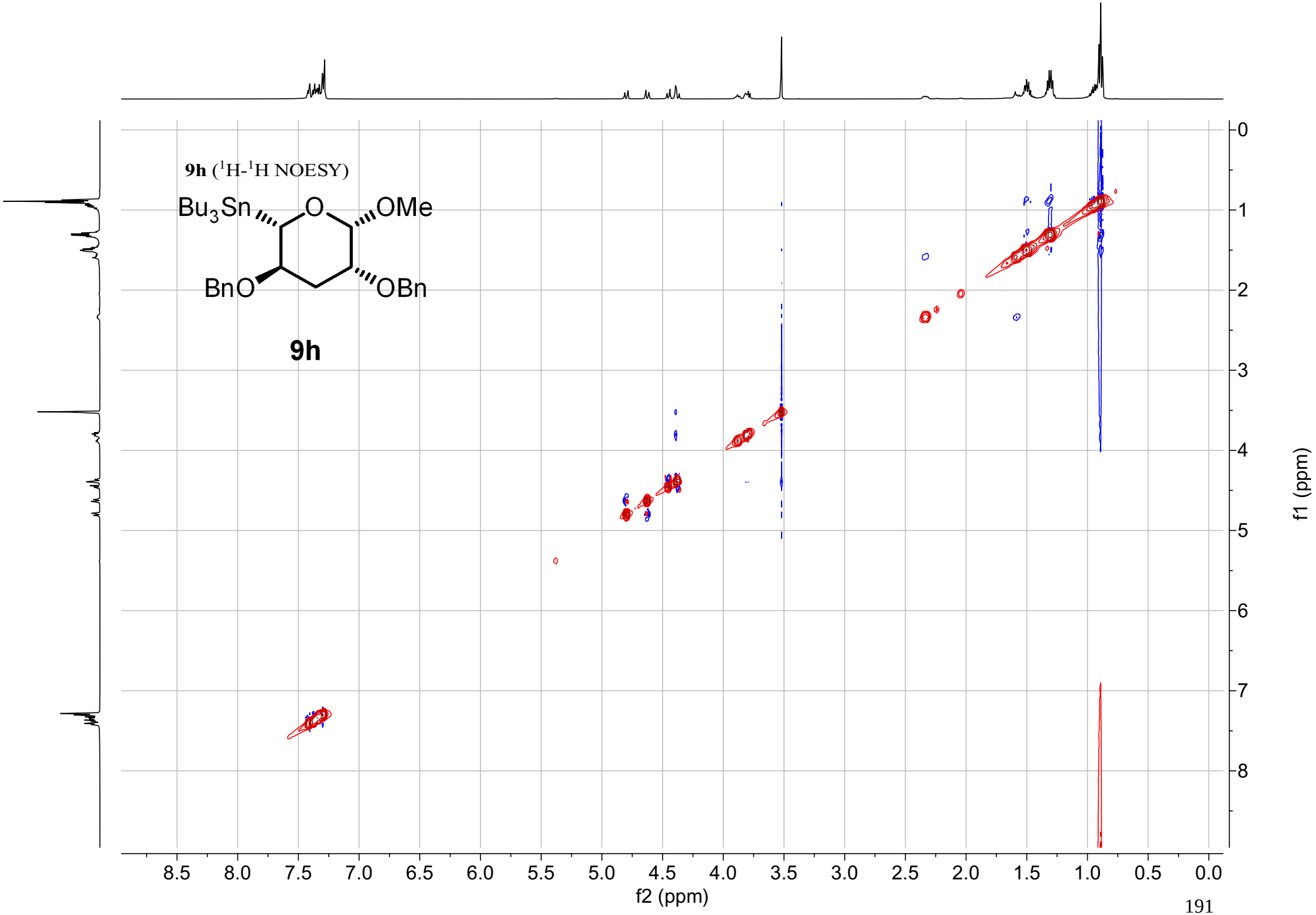
9h

9h (^{13}C NMR, 126MHz, $CDCl_3$)

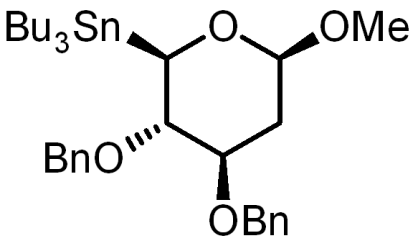


9h

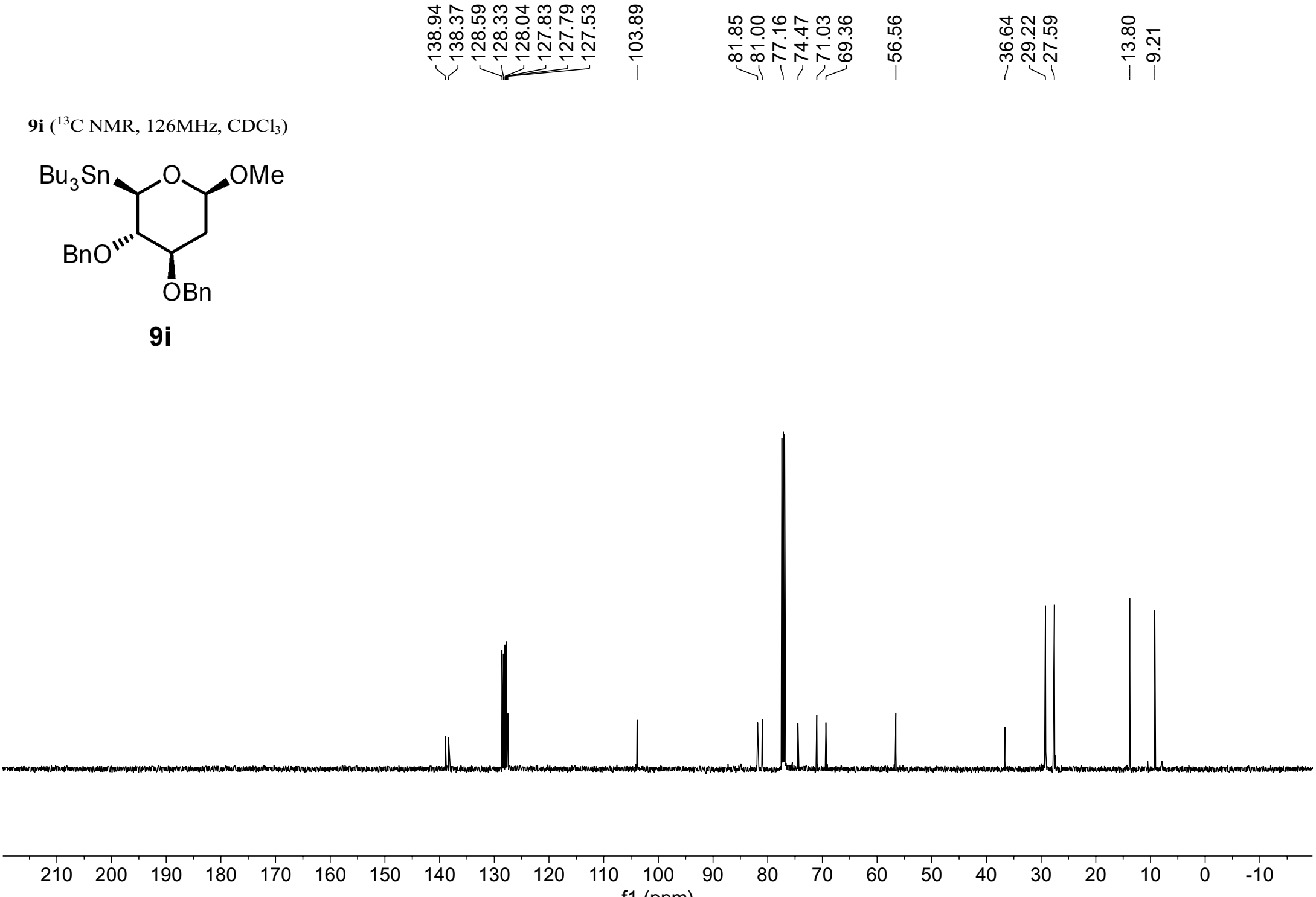

9h (1H-13C Coupled HSQC)
Bu3Sn
O
OMe
BnO
OBn
9h
J = 134 Hz
f2 (ppm)
f1 (ppm)


9h (1H-1H NOESY)
Bu3Sn
O
OMe
BnO
OBn
9h
f2 (ppm)
f1 (ppm)

9i (^{1}H NMR, 500MHz, $CDCl_3$)

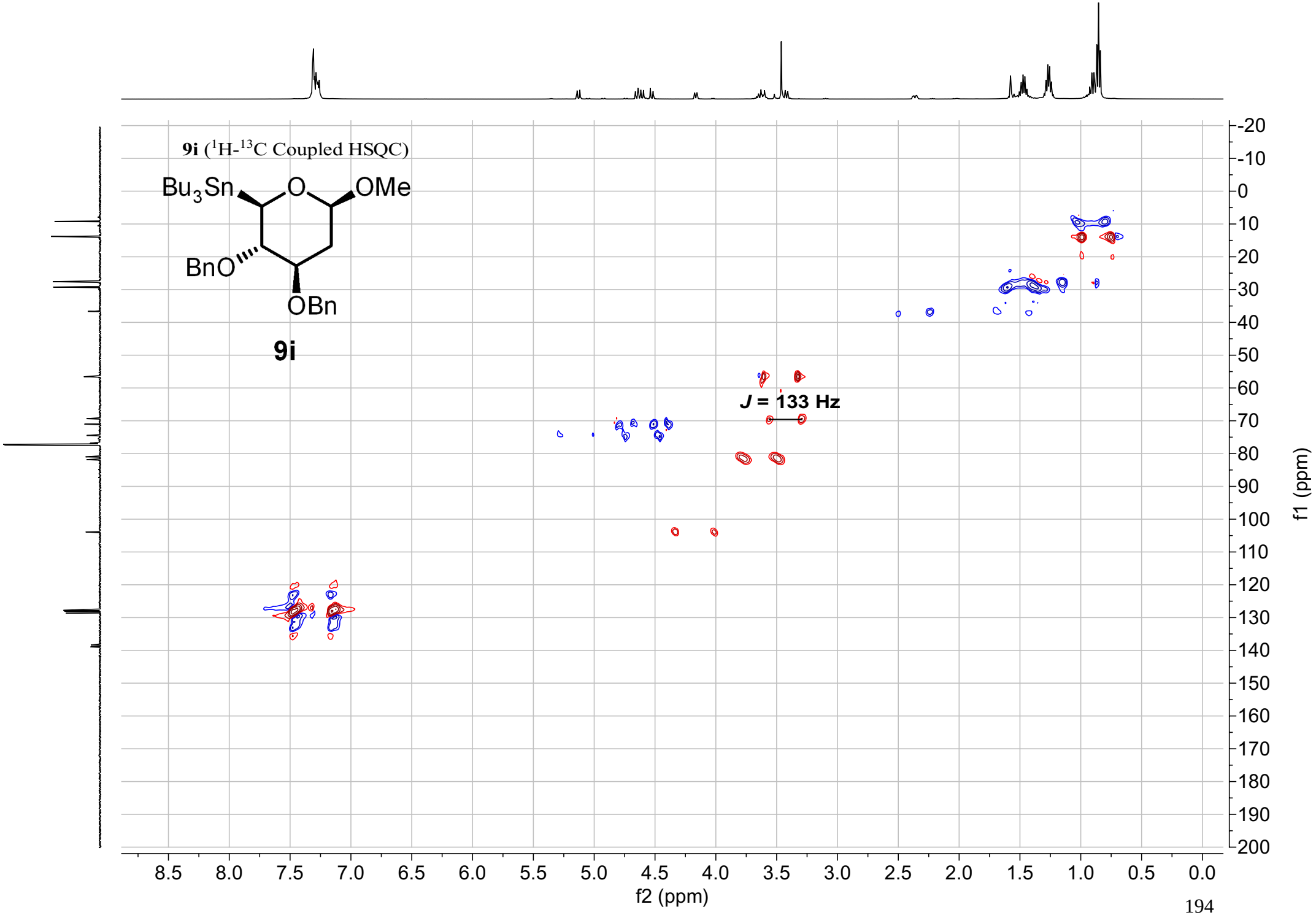


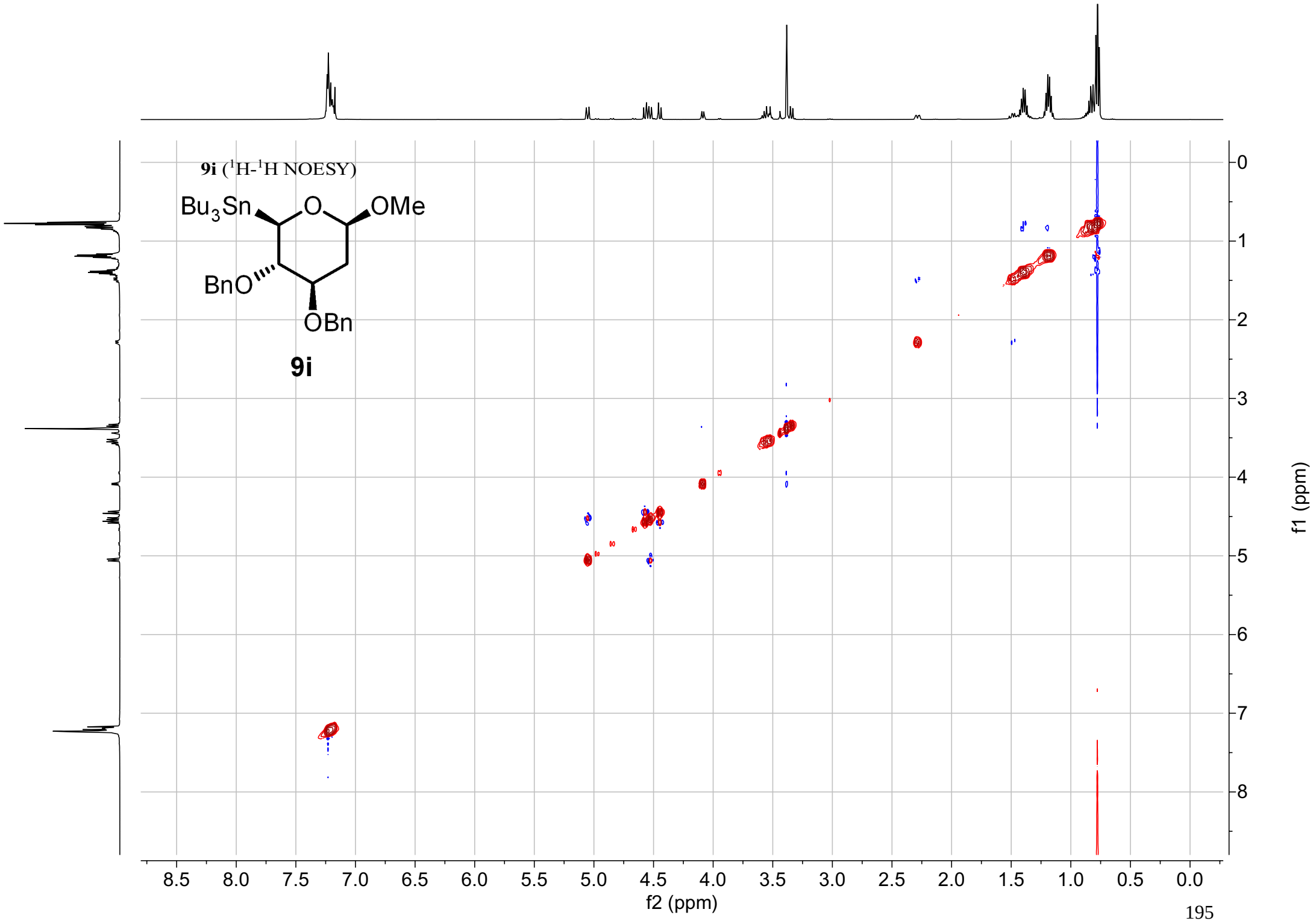
9i



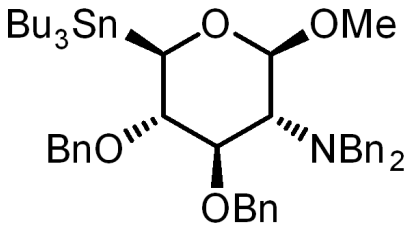
9i (^{13}C NMR, 126MHz, $CDCl_3$)

9i

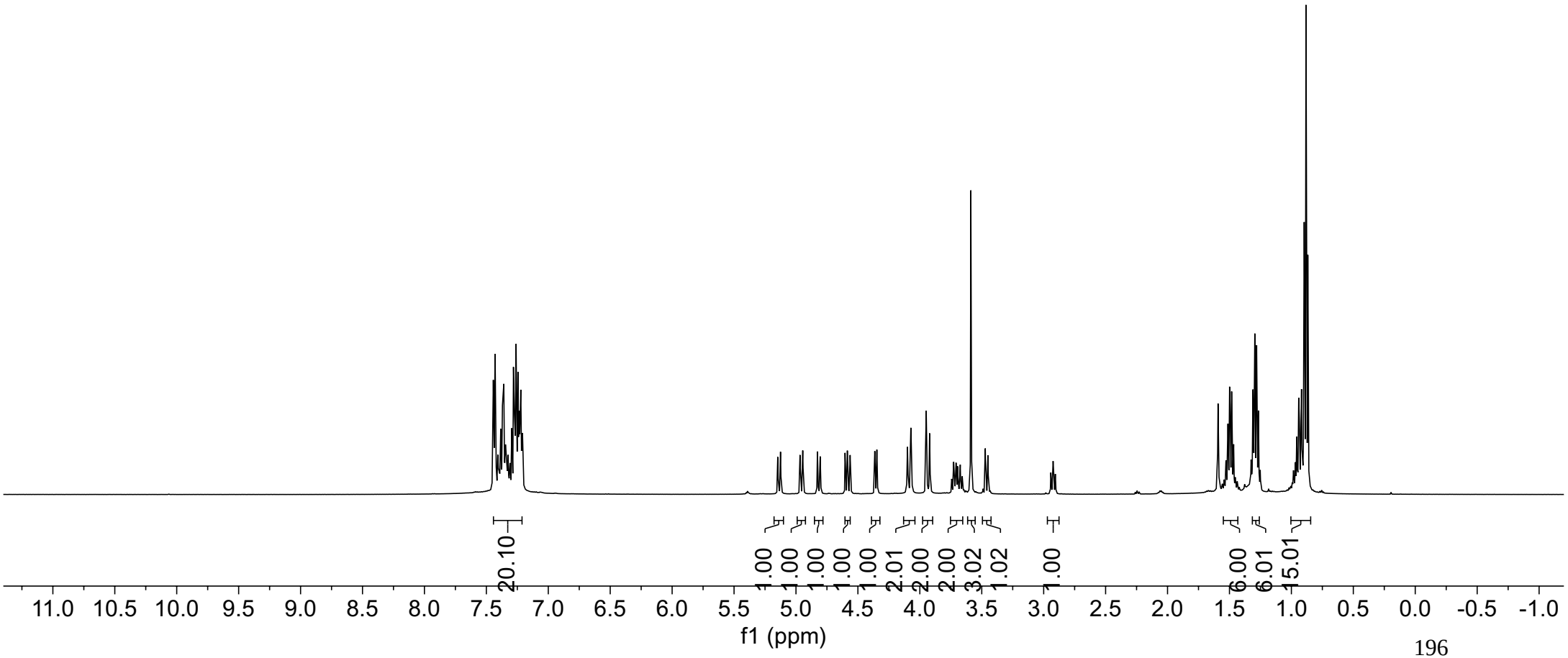

9i (1H-13C Coupled HSQC)
Bu3Sn
O
OMe
BnO
OBn
9i
J = 133 Hz
f2 (ppm)
f1 (ppm)

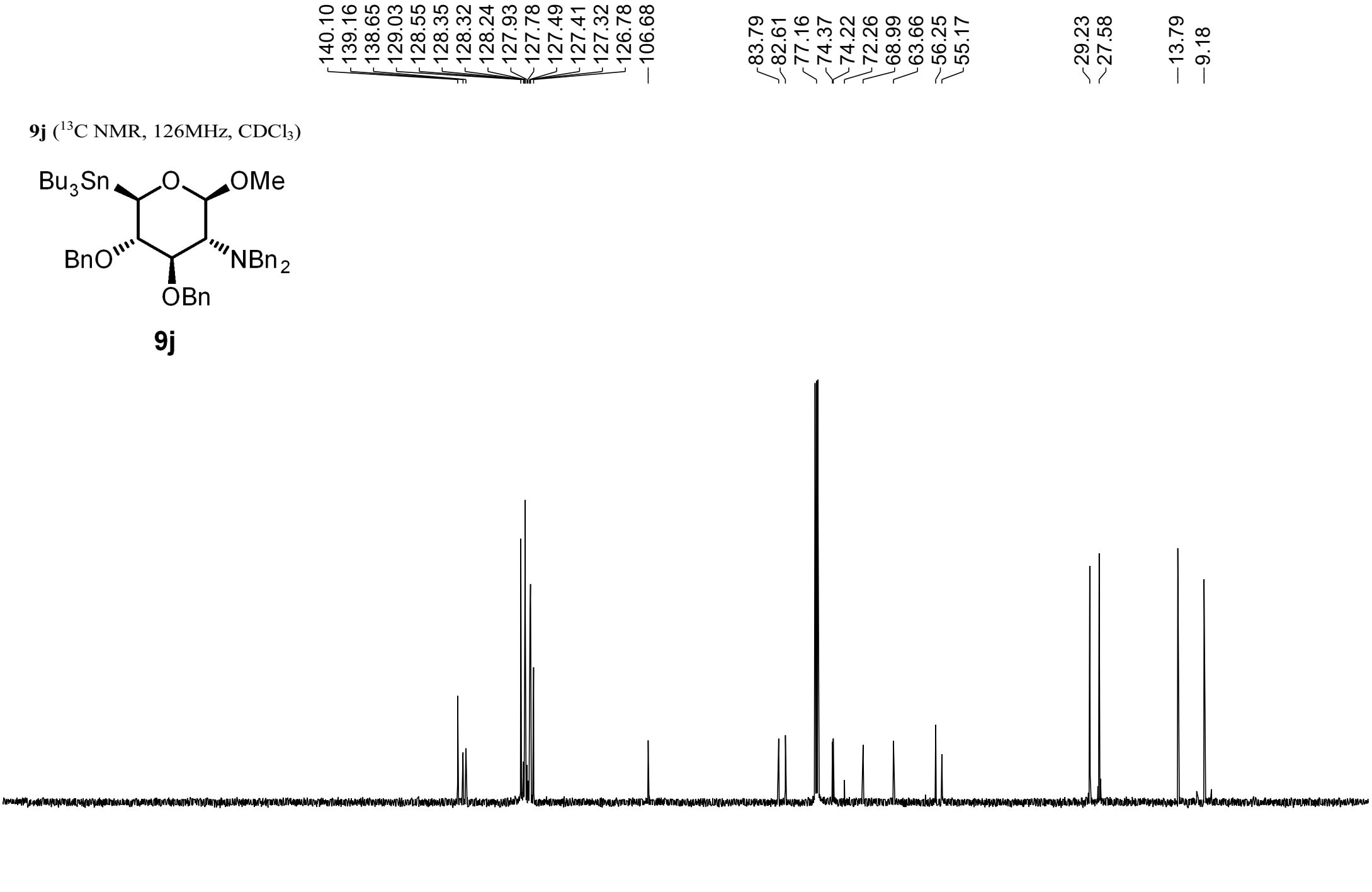

9i (1H-1H NOESY)
Bu3Sn
O
OMe
BnO
OBn
9i
f2 (ppm)
f1 (ppm)

9j (^{1}H NMR, 500MHz, $CDCl_3$)



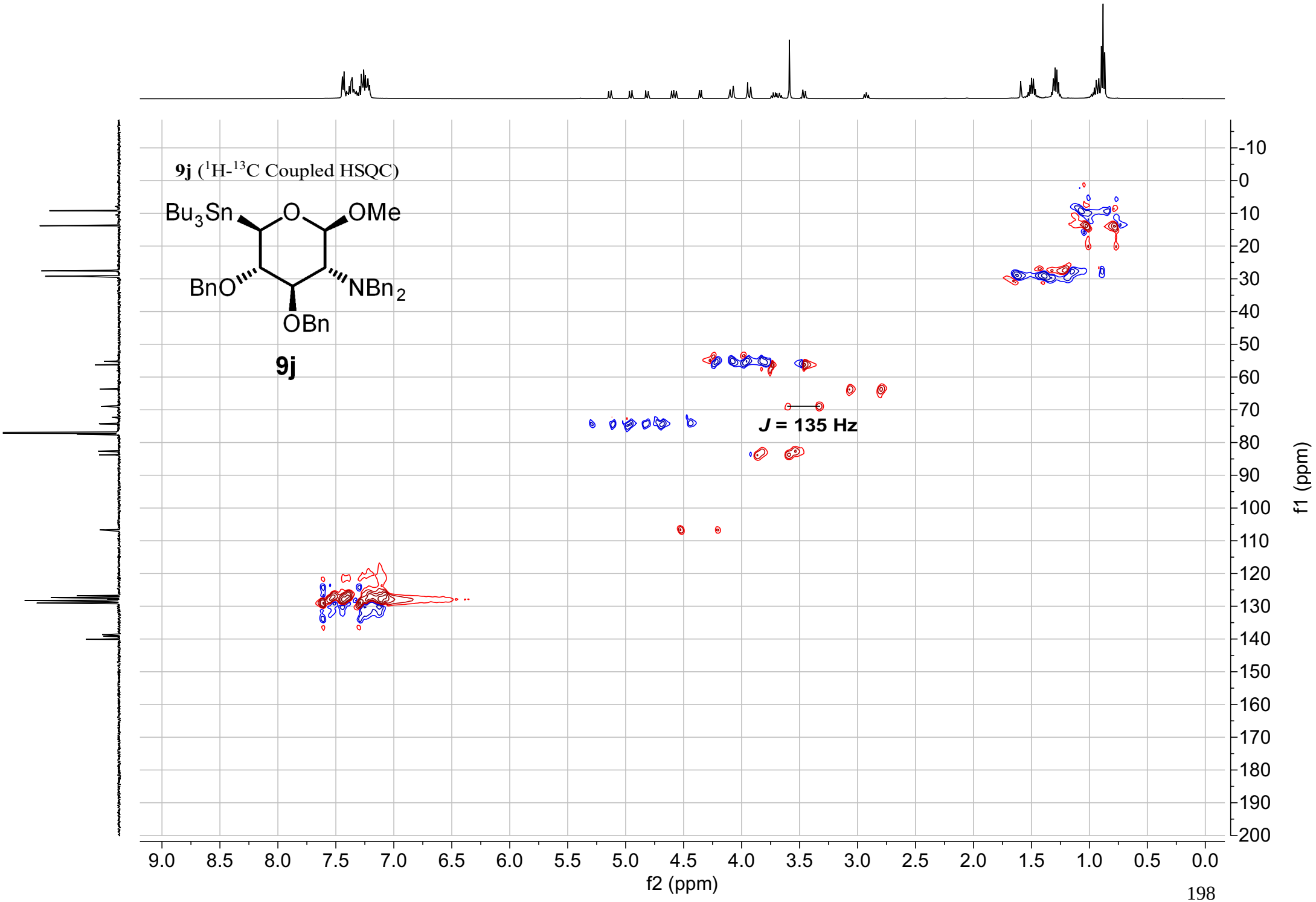
9j

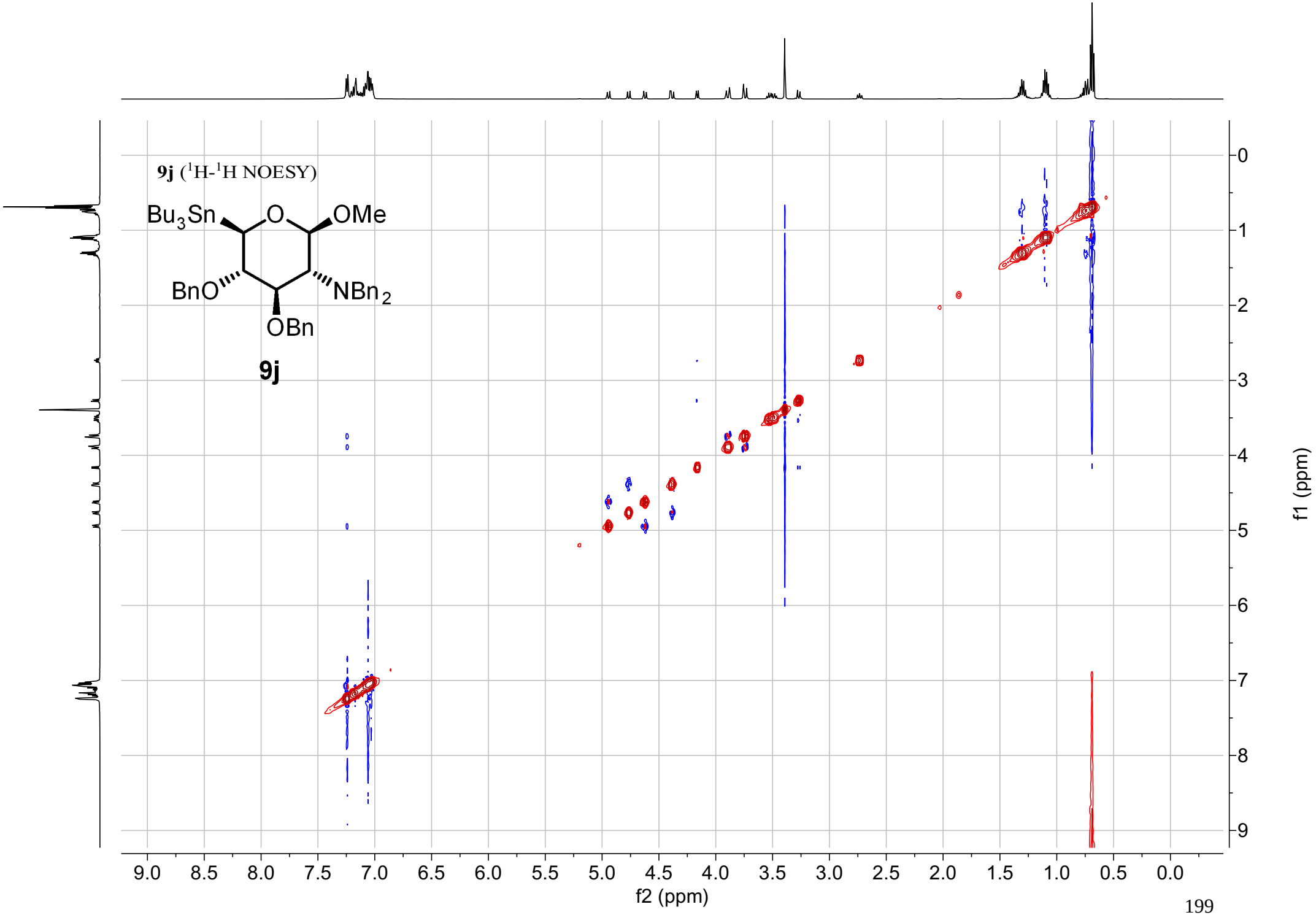




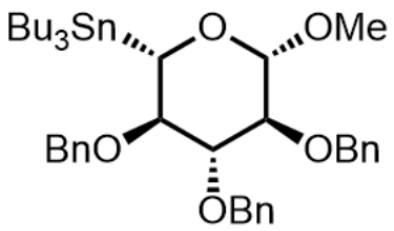
9j (^{13}C NMR, 126MHz, $CDCl_3$)

9j


9j (1H-13C Coupled HSQC)
Bu3Sn
O
OMe
BnO
NBn2
OBn
9j
J = 135 Hz
f2 (ppm)
f1 (ppm)

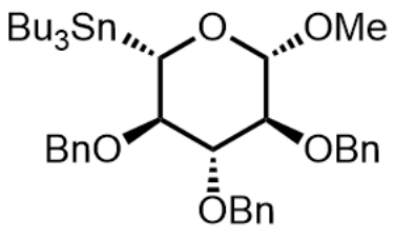

9j (1H-1H NOESY)
Bu3Sn
O
OMe
BnO
NBn2
OBn
9j
f2 (ppm)
f1 (ppm)

9l (^{1}H NMR, 500MHz, $CDCl_3$)

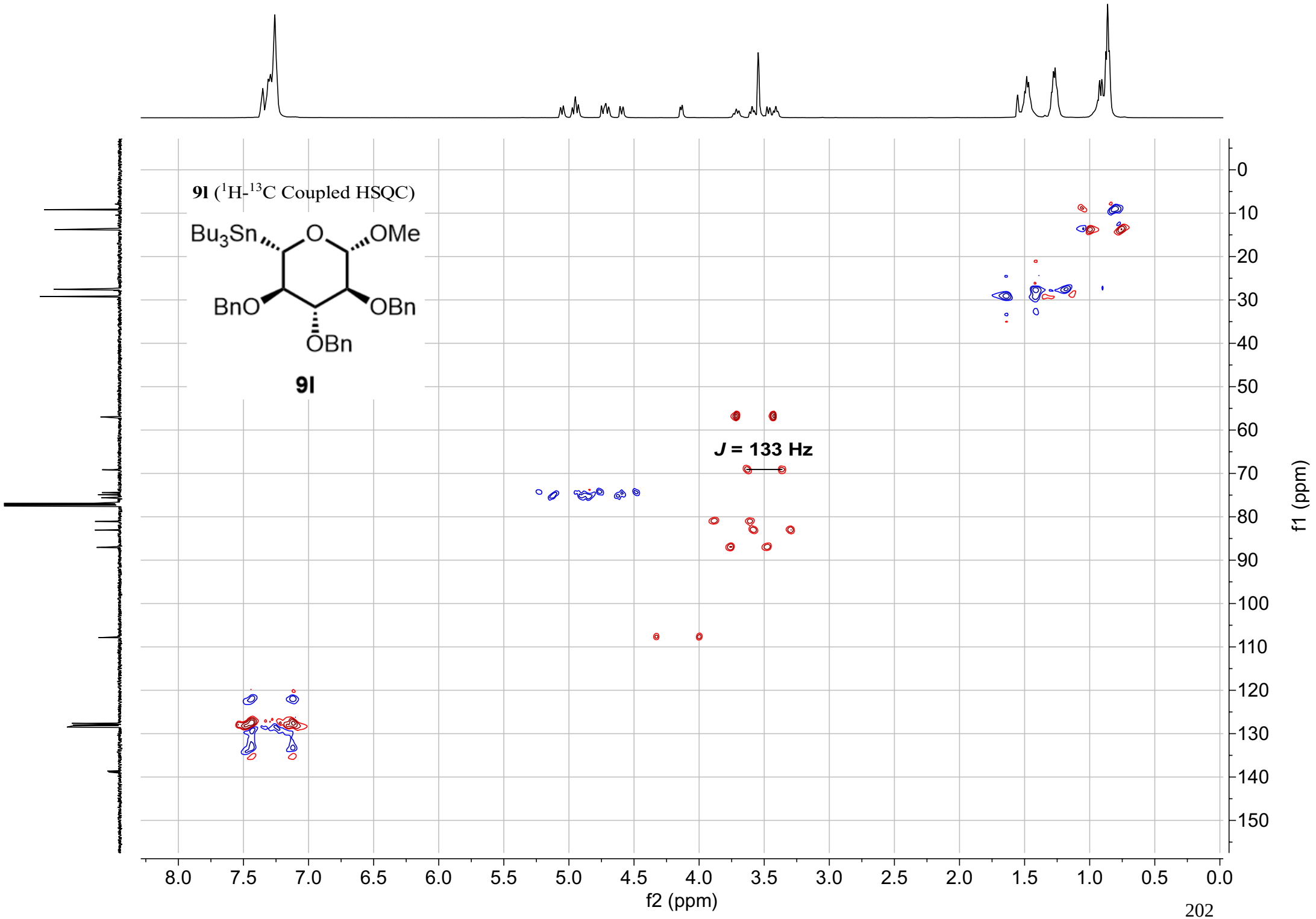


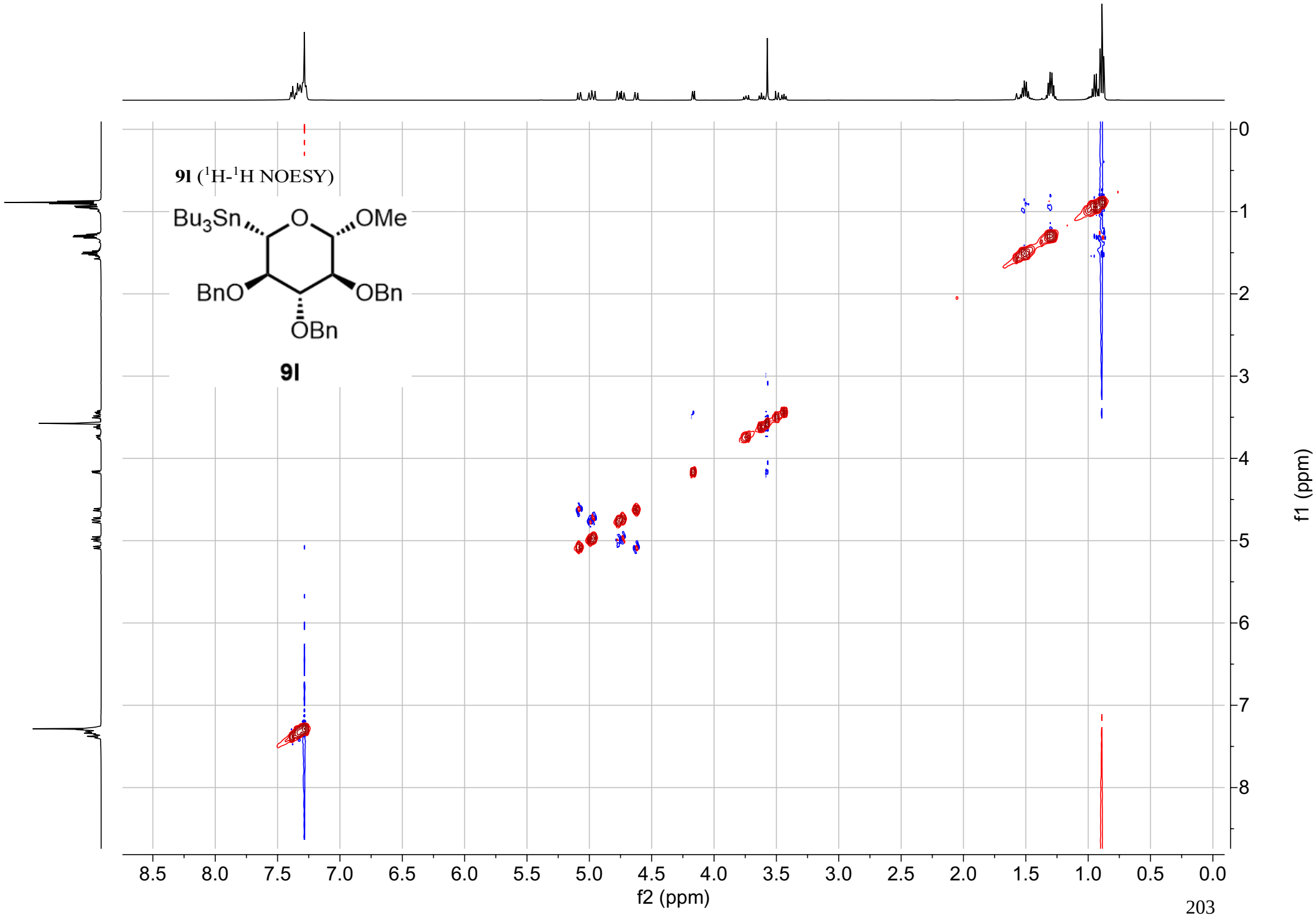
9l

9l (^{13}C NMR, 126MHz, $CDCl_3$)

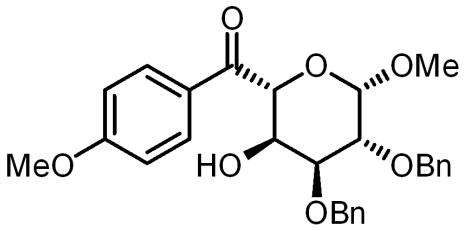


9l


9l (1H-13C Coupled HSQC)
Bu3Sn
O
OMe
BnO
OBn
OBn
9l
J = 133 Hz
f2 (ppm)
f1 (ppm)

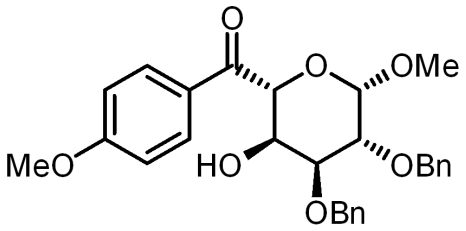

9l (1H-1H NOESY)
Bu3Sn
O
OMe
BnO
OBn
OBn
9l
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

13a (^{1}H NMR, 500MHz, $CDCl_3$)

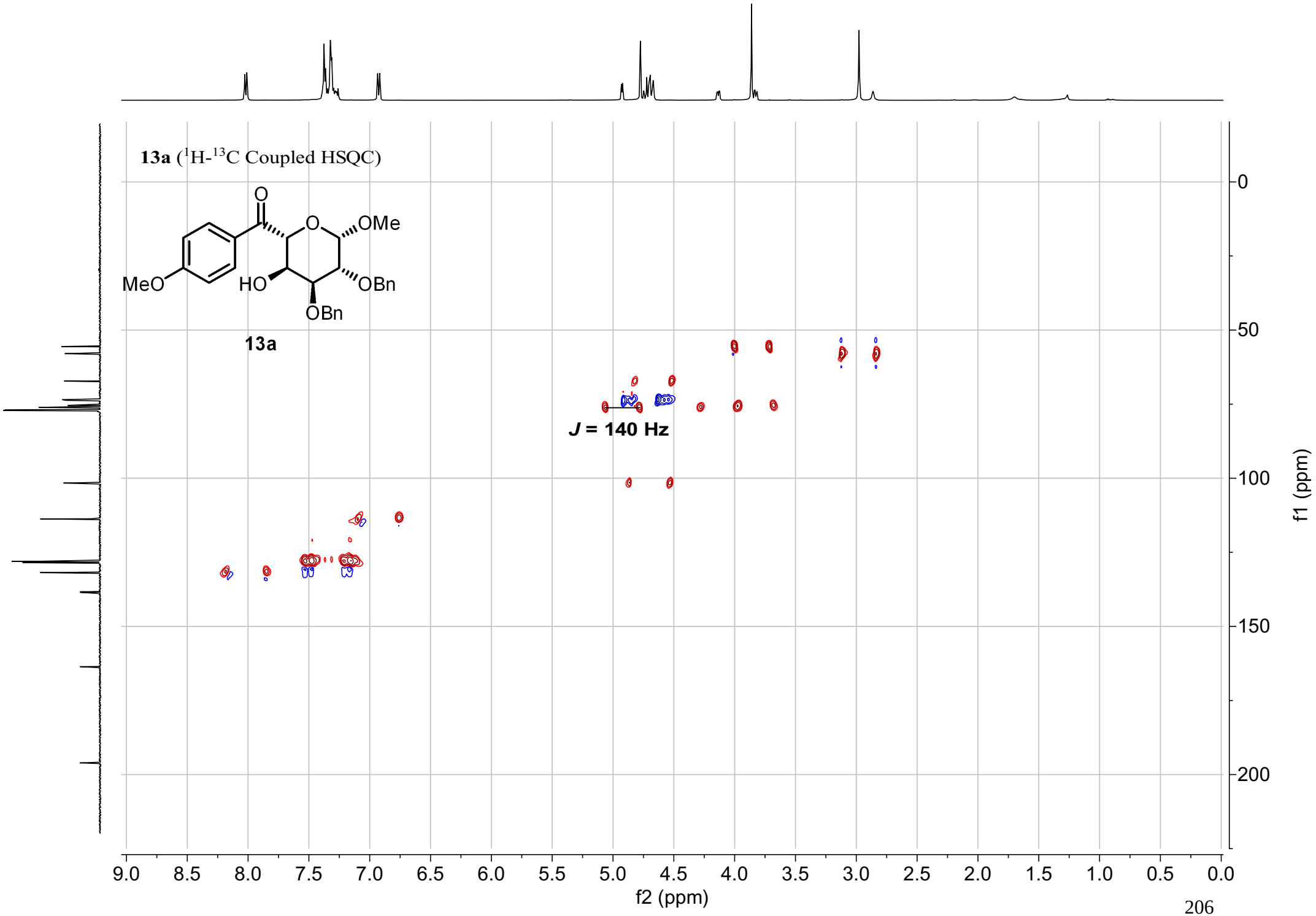


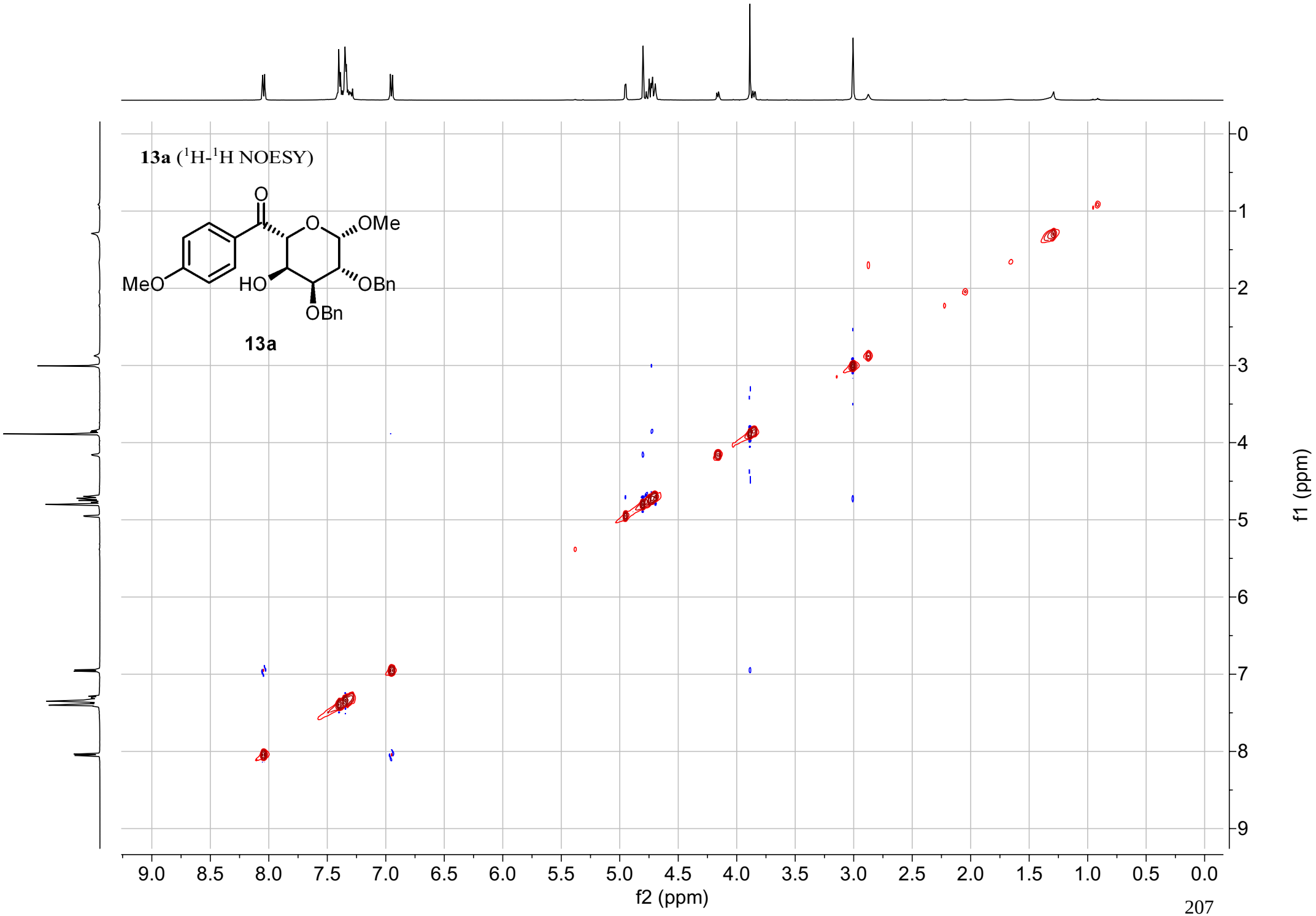
13a

13a (^{13}C NMR, 126MHz, $CDCl_3$)

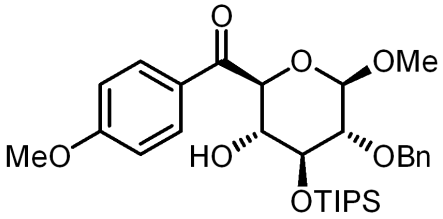


13a


13a (1H-13C Coupled HSQC)
O
O
OMe
MeO
HO
OBn
OBn
13a
J = 140 Hz
0
50
100
150
200
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
f2 (ppm)

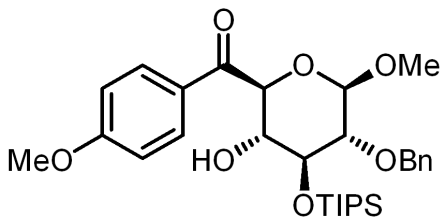

13a (^{1}H-^{1}H NOESY)
O
O
OMe
MeO
HO
OBn
OBn
13a
f2 (ppm)
f1 (ppm)

13b (^{1}H NMR, 500MHz, $CDCl_3$)

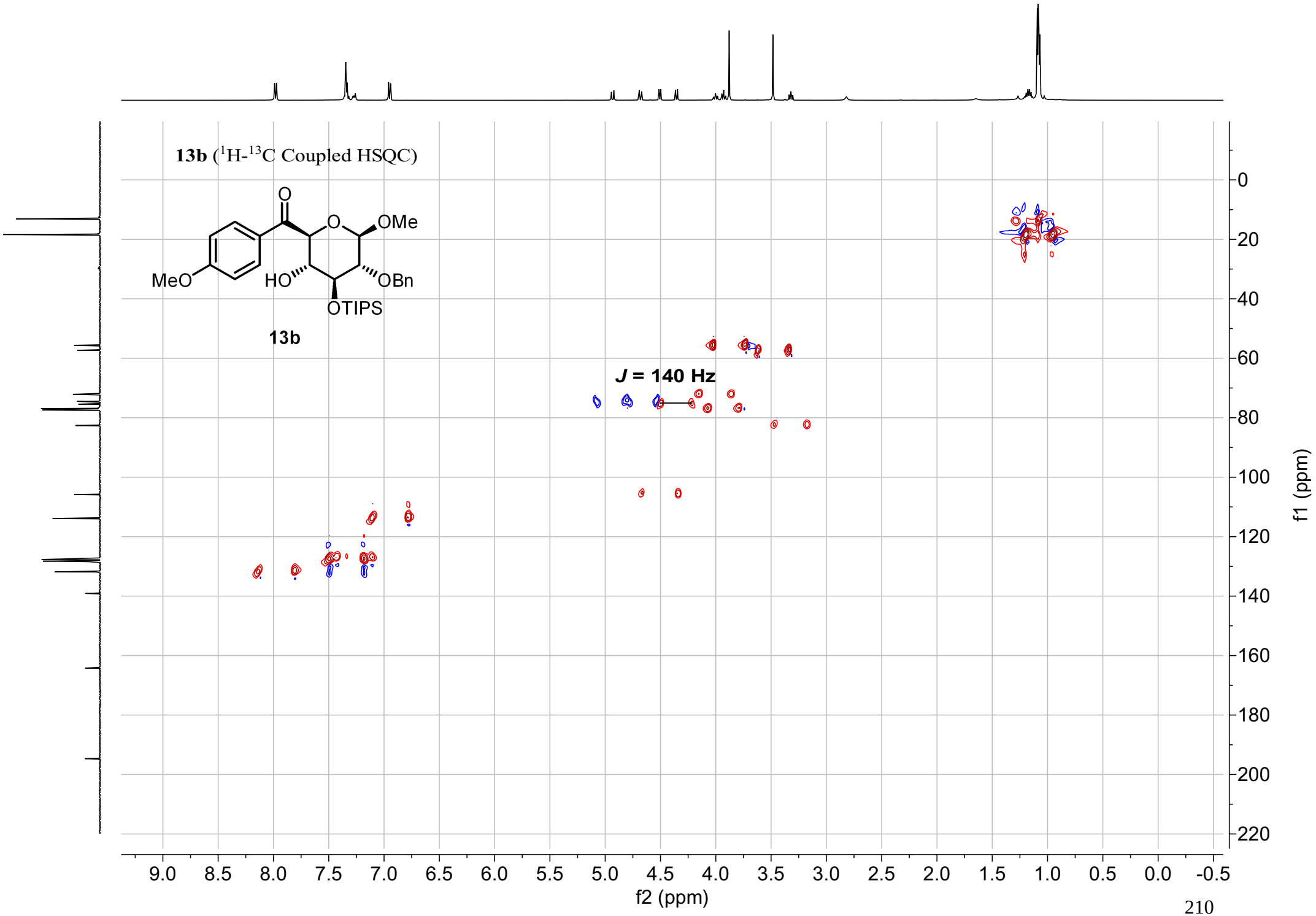


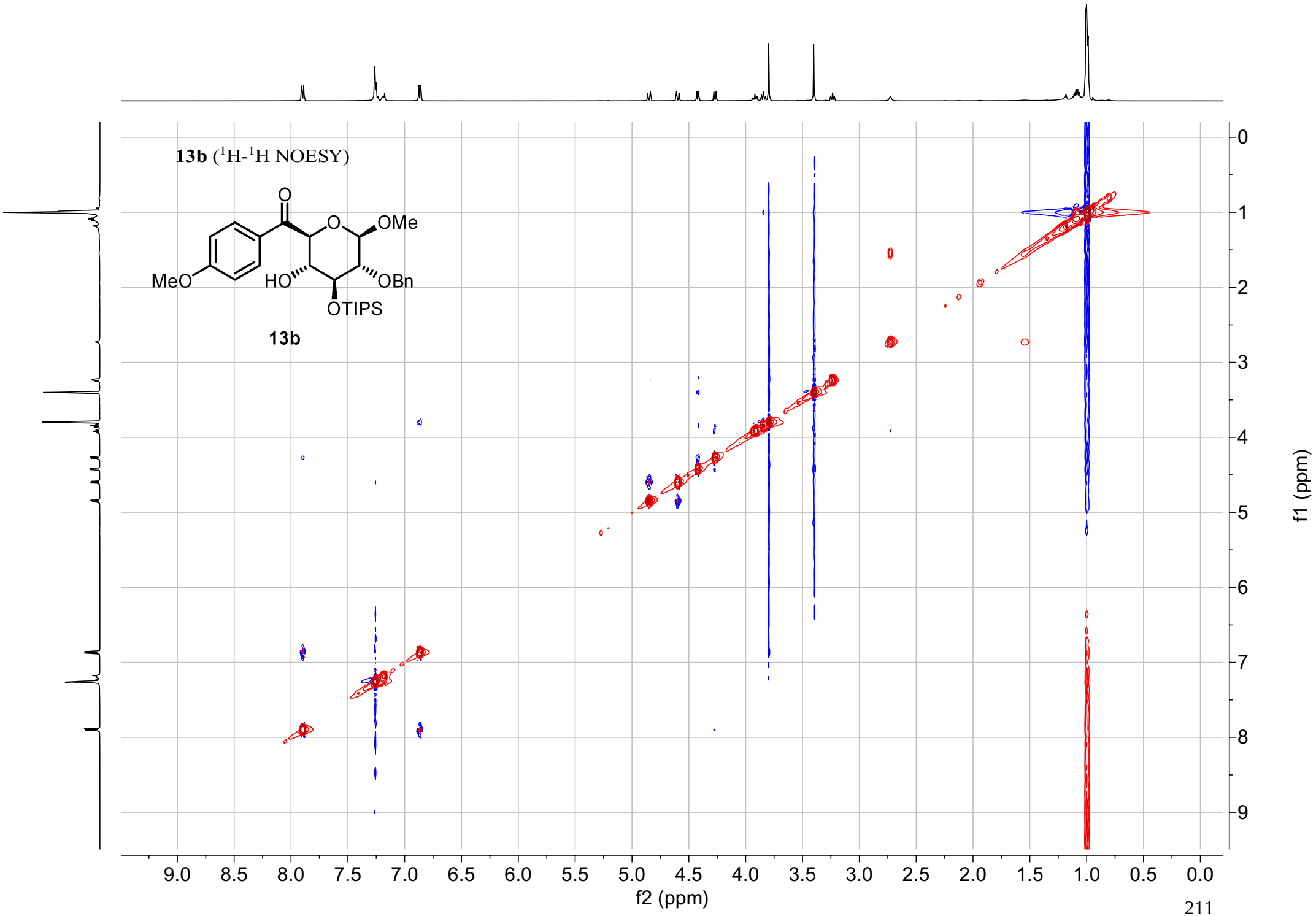
13b

13b (^{13}C NMR, 126MHz, $CDCl_3$)

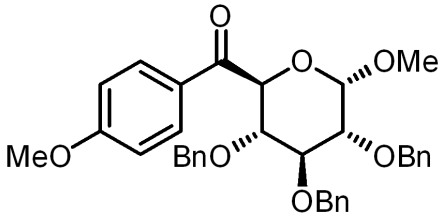


13b

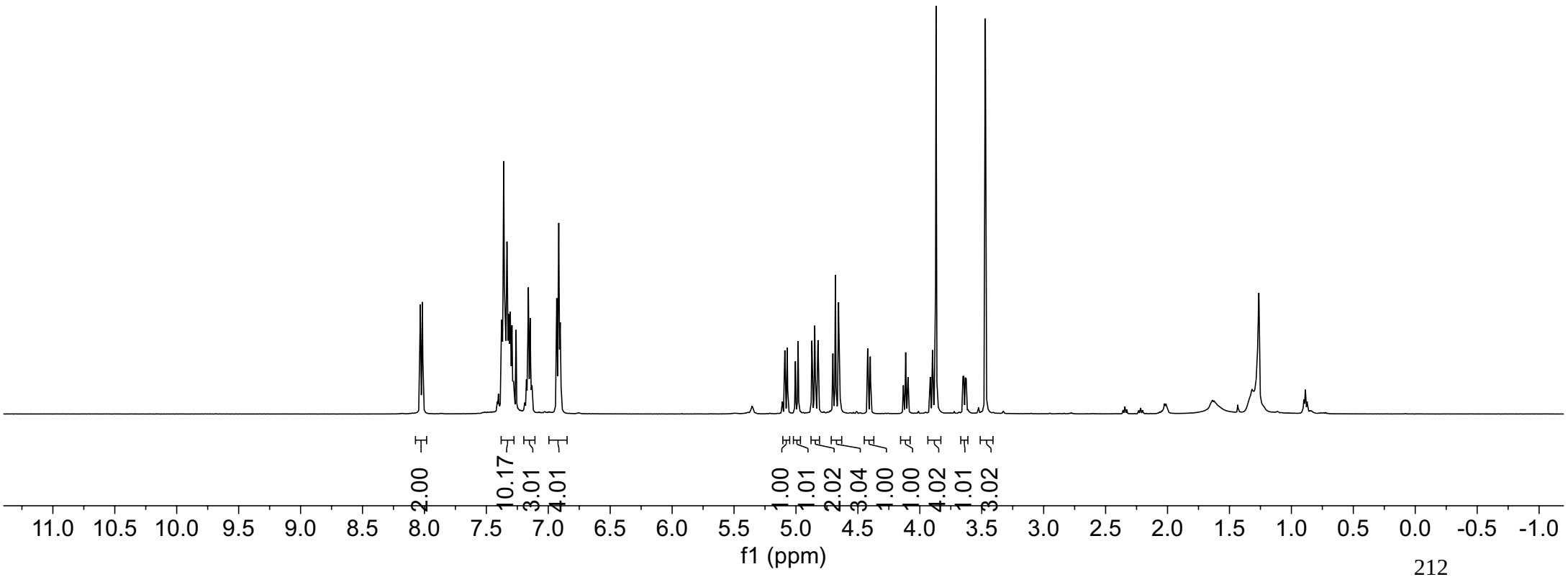

13b (1H-13C Coupled HSQC)
O
O
OMe
MeO
HO
OBn
OTIPS
13b
J = 140 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


13b (1H-1H NOESY)
O
O
OMe
MeO
HO
OBn
OTIPS
13b
f2 (ppm)
f1 (ppm)

13c (^{1}H NMR, 500MHz, $CDCl_3$)

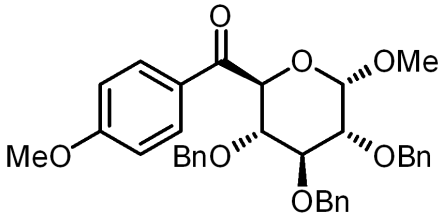


13c

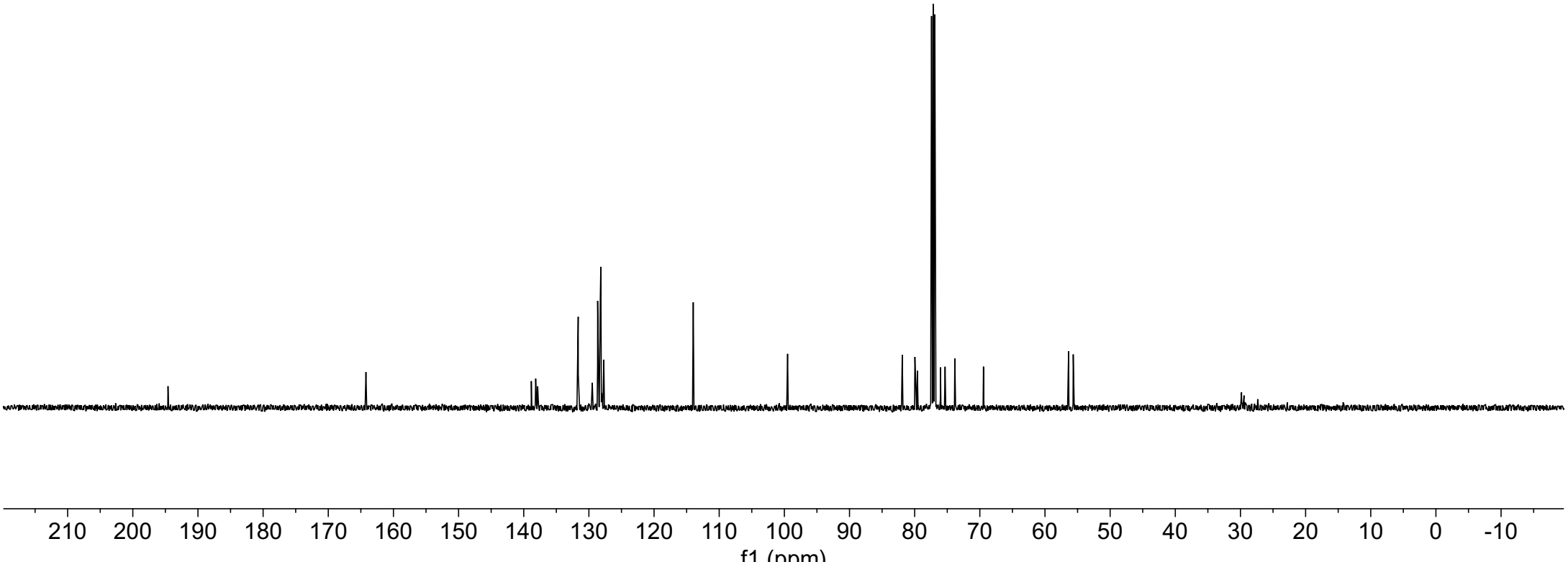


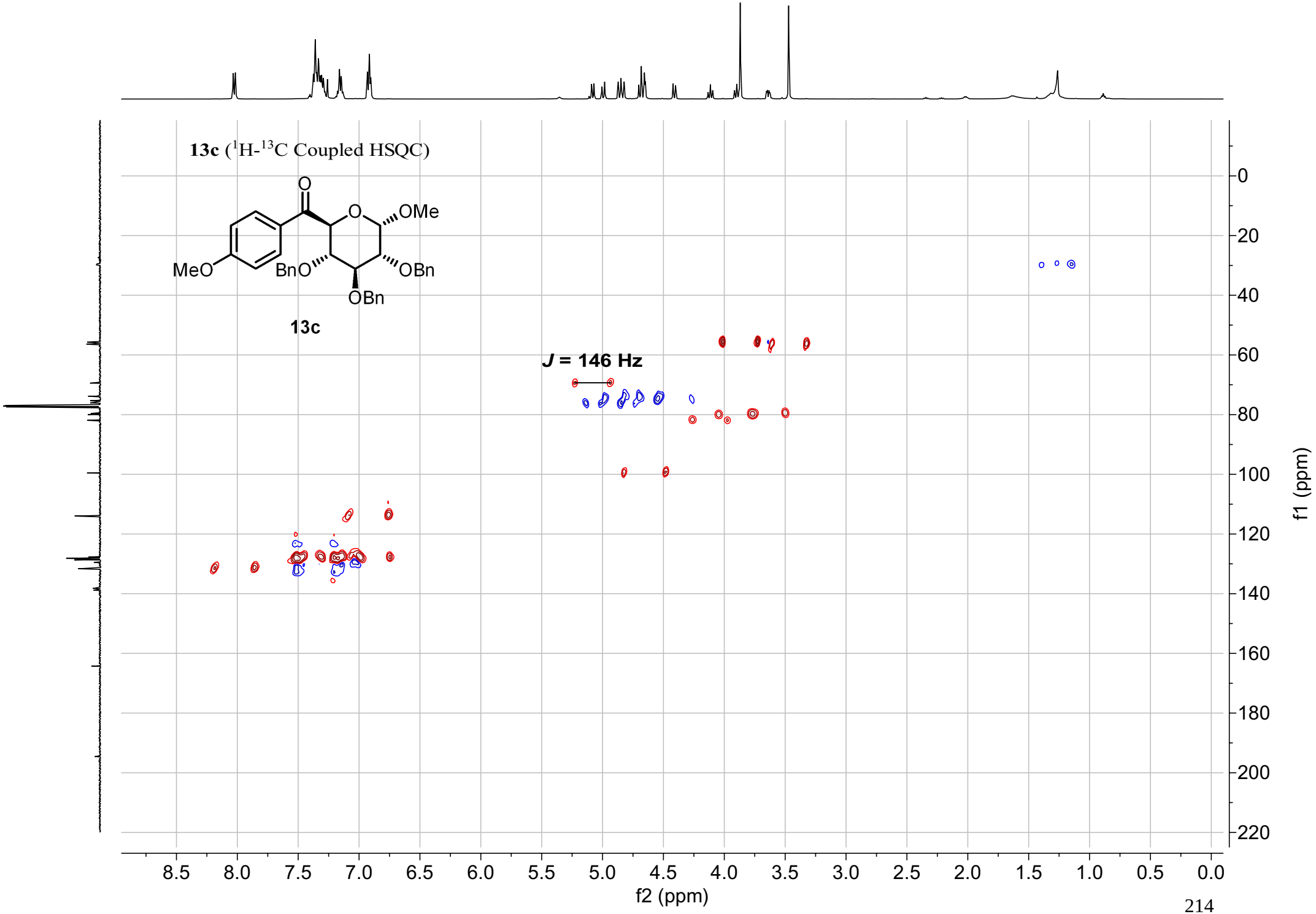
194.60
164.22
138.83
138.17
137.86
131.64
129.48
128.66
128.54
128.35
128.25
128.17
128.05
127.77
127.71
113.98
99.50
81.90
79.96
79.59
77.16
76.04
75.33
73.83
69.44
56.38
55.66

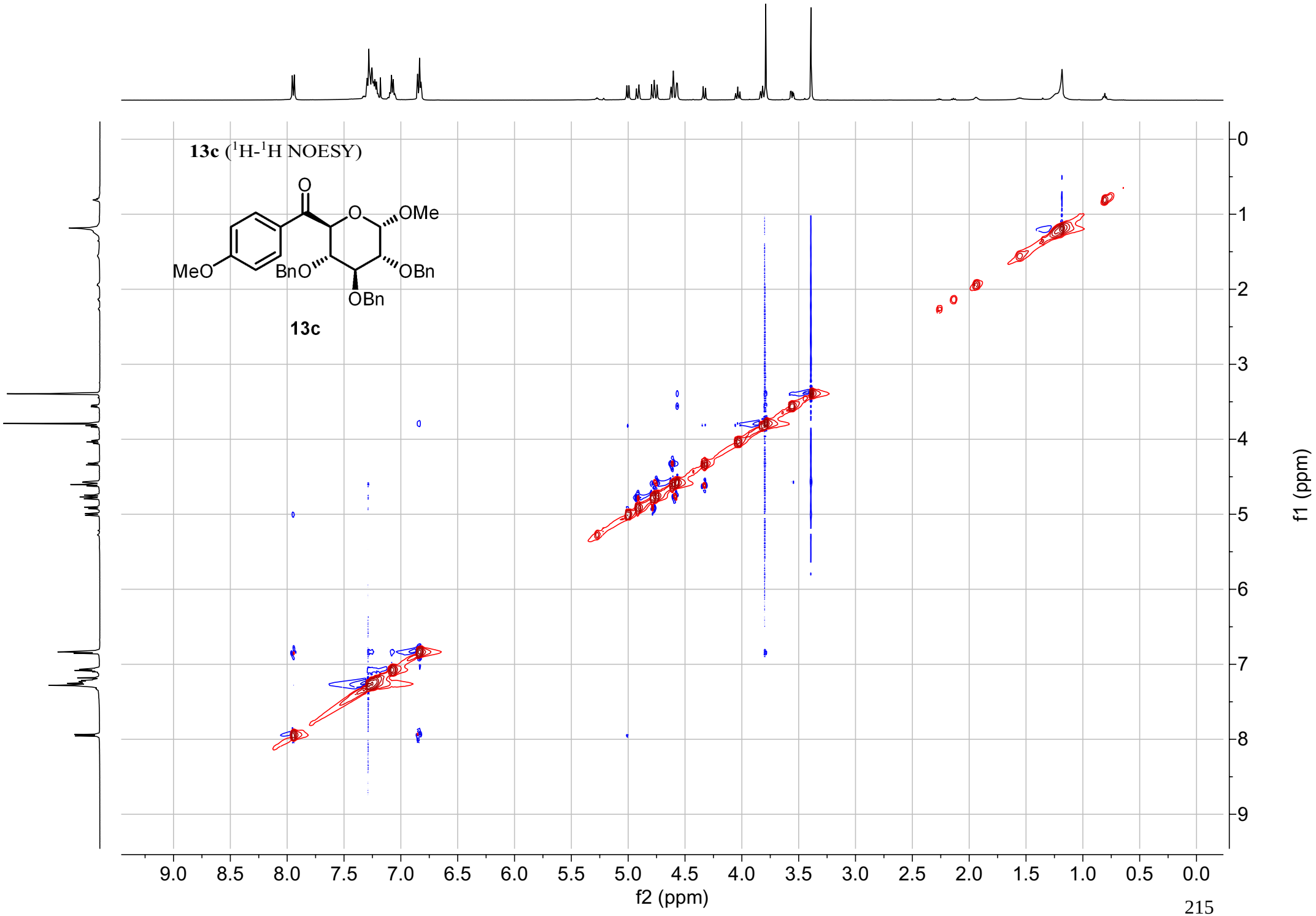
13c (^{13}C NMR, 126MHz, $CDCl_3$)



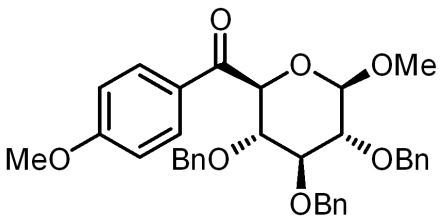
13c




13c (^{1}H-^{13}C Coupled HSQC)
O
O
OMe
MeO
BnO
OBn
OBn
13c
J = 146 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
0
20
40
60
80
100
120
140
160
180
200
220

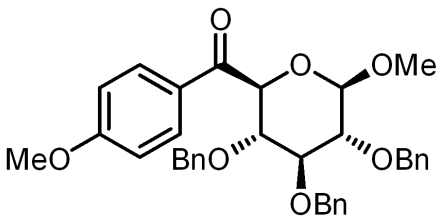

13c (1H-1H NOESY)
O
O
OMe
MeO
BnO
OBn
OBn
13c
f2 (ppm)
f1 (ppm)

13d (^{1}H NMR, 500MHz, $CDCl_3$)

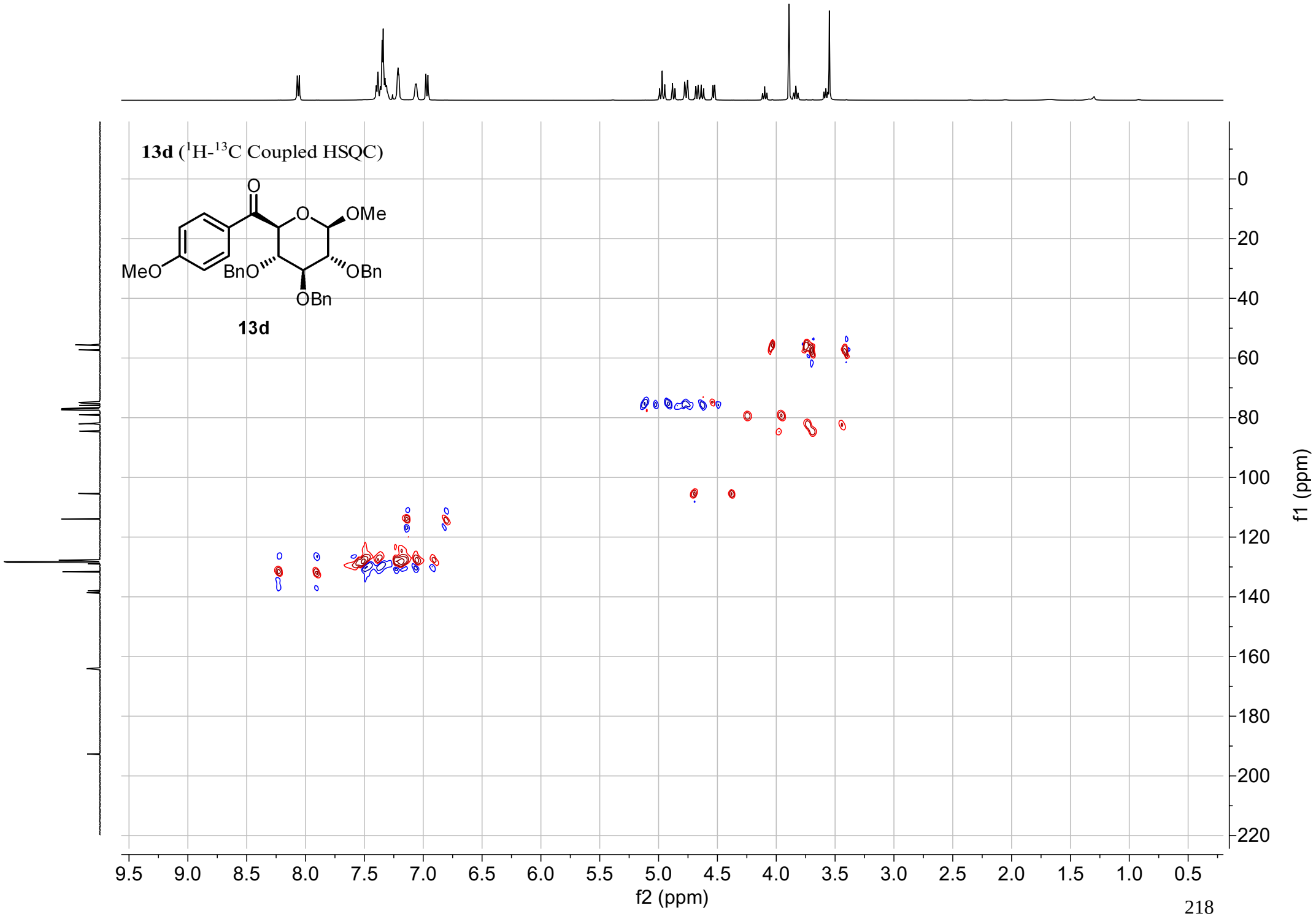


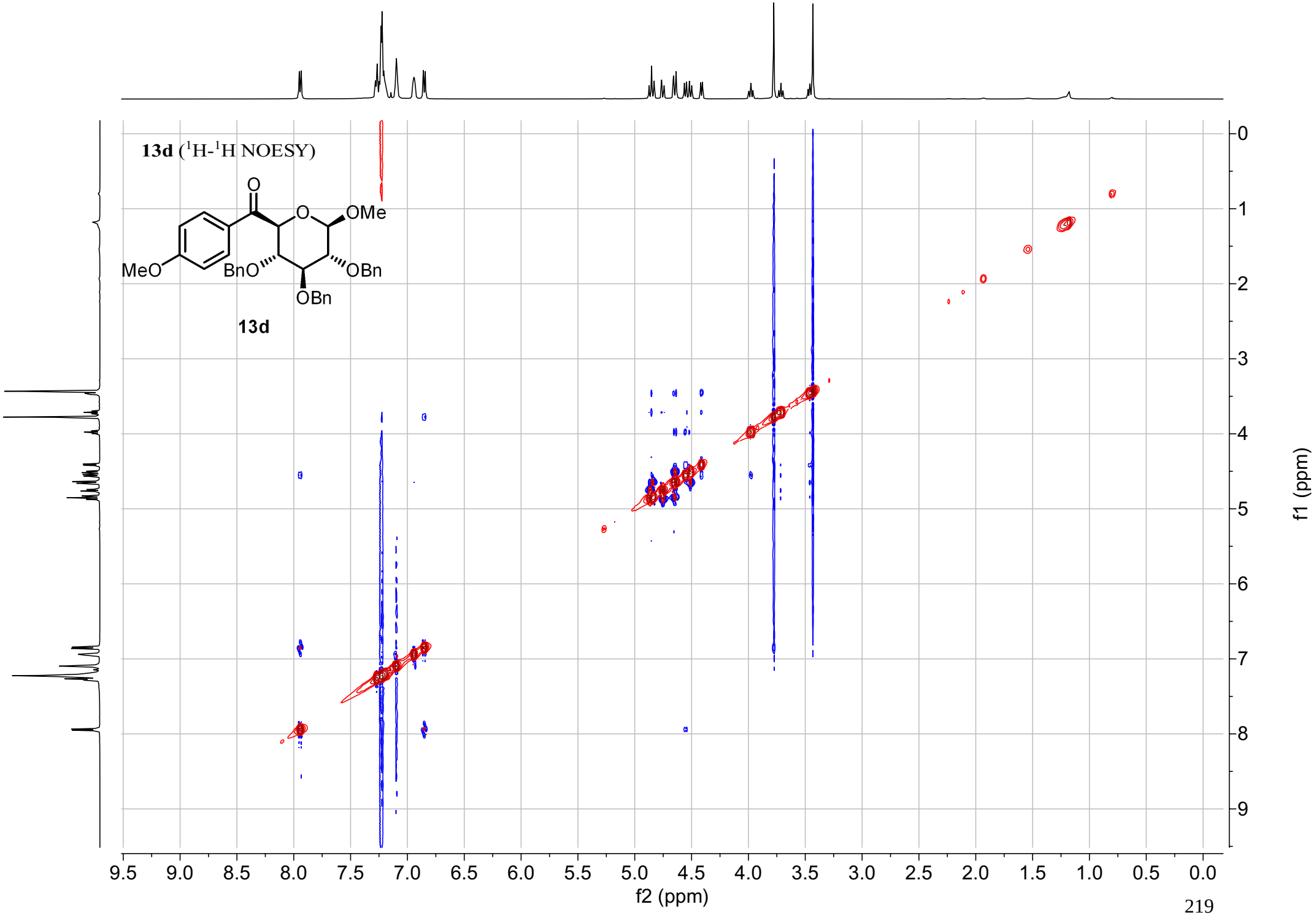
13d

13d (^{13}C NMR, 126MHz, $CDCl_3$)

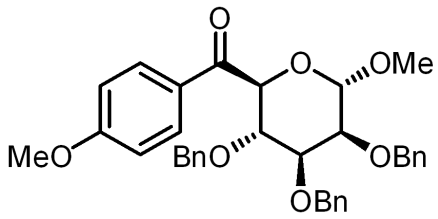


13d


13d (1H-13C Coupled HSQC)
O
O
OMe
MeO
BnO
OBn
OBn
13d
f2 (ppm)
f1 (ppm)

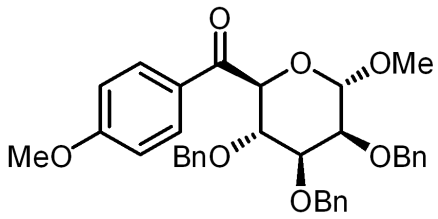

13d (1H-1H NOESY)
O
O
OMe
MeO
BnO
OBn
OBn
13d
f2 (ppm)
f1 (ppm)

13e (^{1}H NMR, 500MHz, $CDCl_3$)



13e

13e (^{13}C NMR, 126MHz, $CDCl_3$)

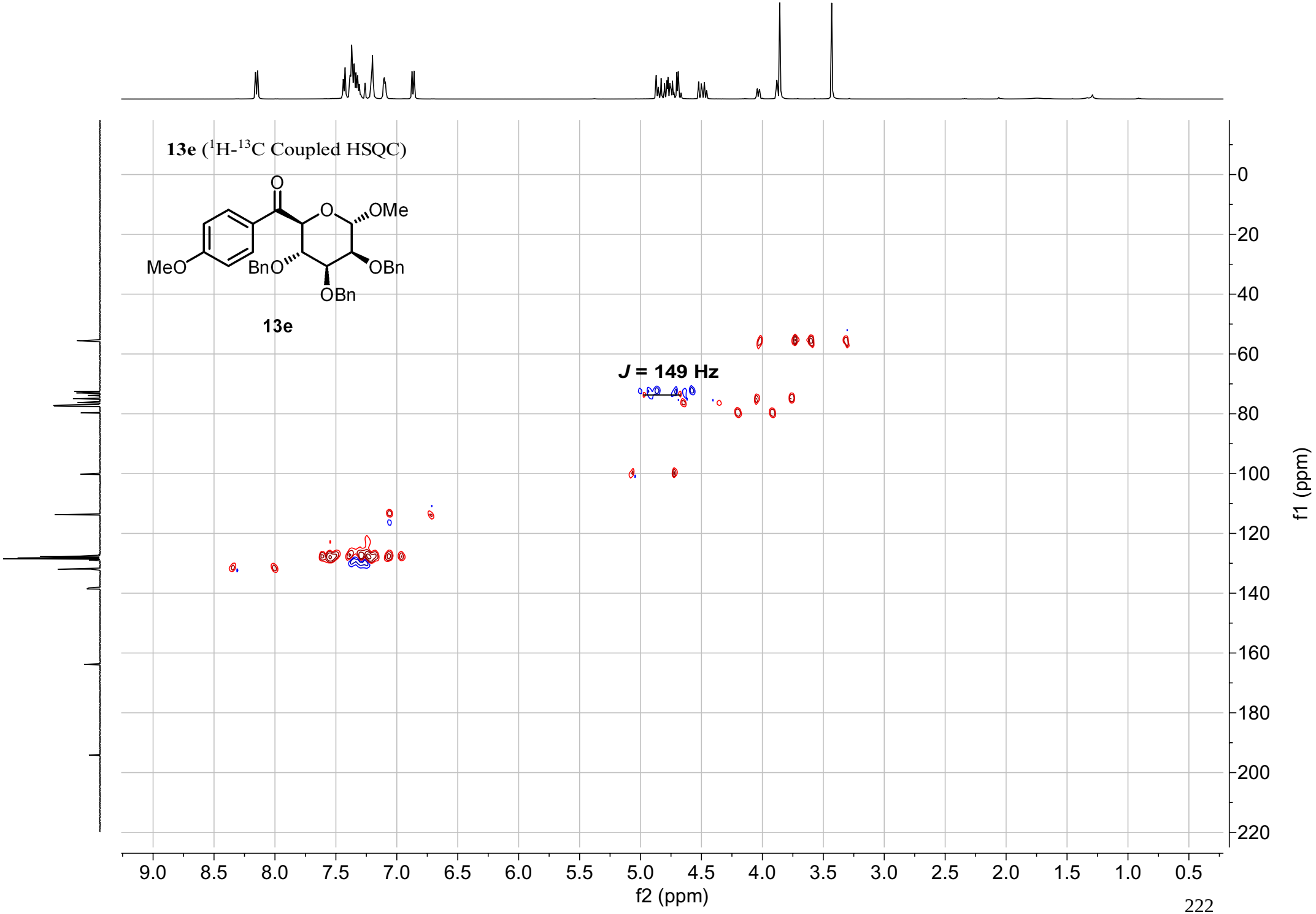


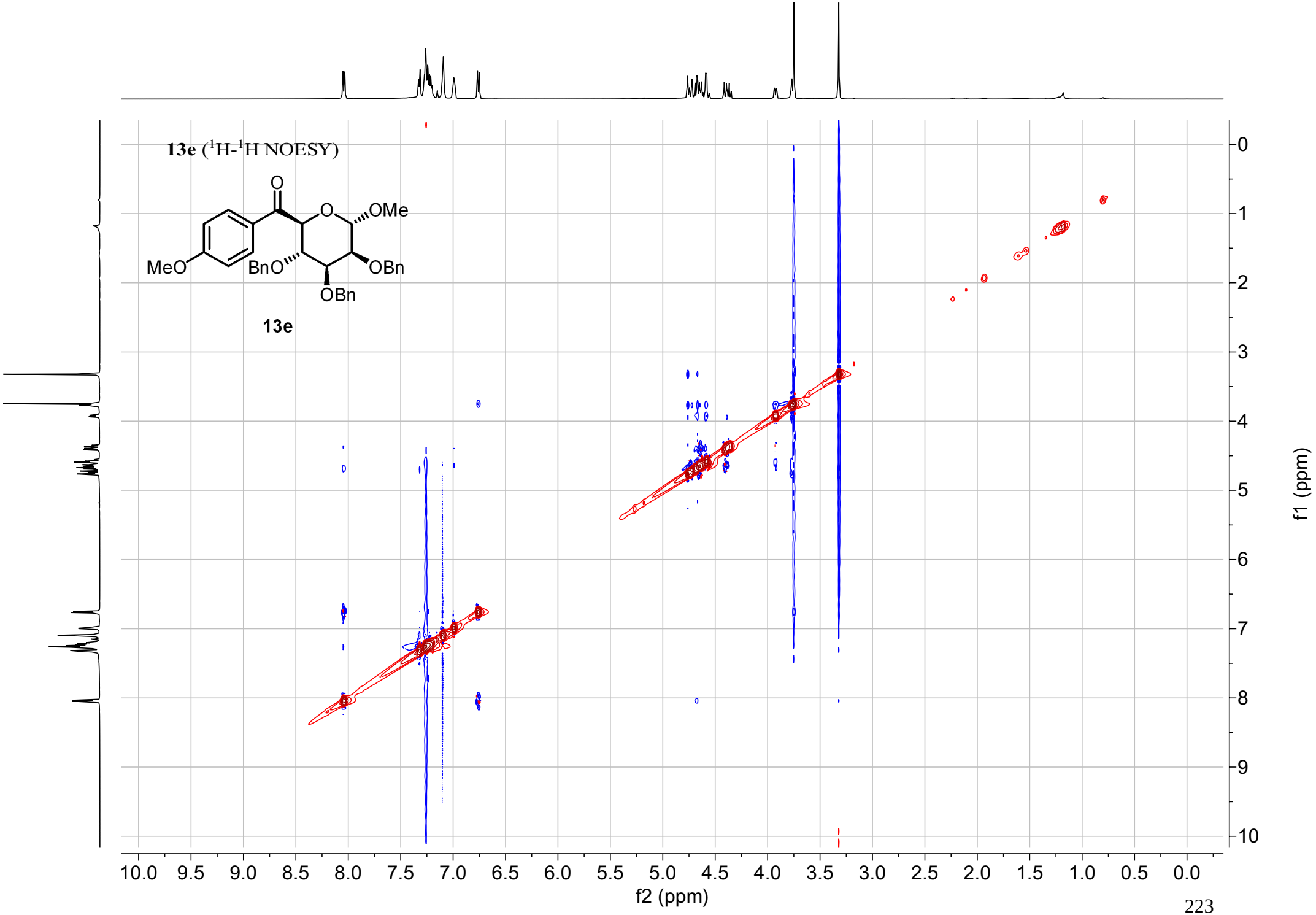
13e

194.09
163.79
138.58
138.38
138.22
131.96
128.85
128.47
128.22
127.99
127.77
127.70
127.58
113.75
100.16
79.70
77.16
76.24
74.95
73.87
73.02
72.54
55.77
55.54

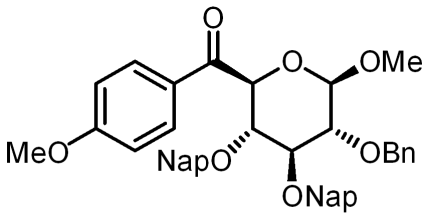
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)


13e (1H-13C Coupled HSQC)
O
O
OMe
MeO
BnO
OBn
OBn
13e
J = 149 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
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

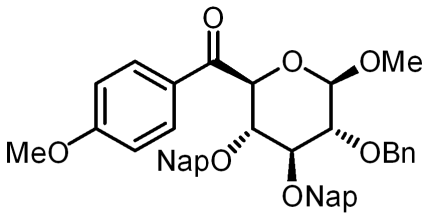

13e (1H-1H NOESY)
O
O
OMe
MeO
BnO
OBn
OBn
13e
f2 (ppm)
f1 (ppm)

13f (^{1}H NMR, 500MHz, $CDCl_3$)

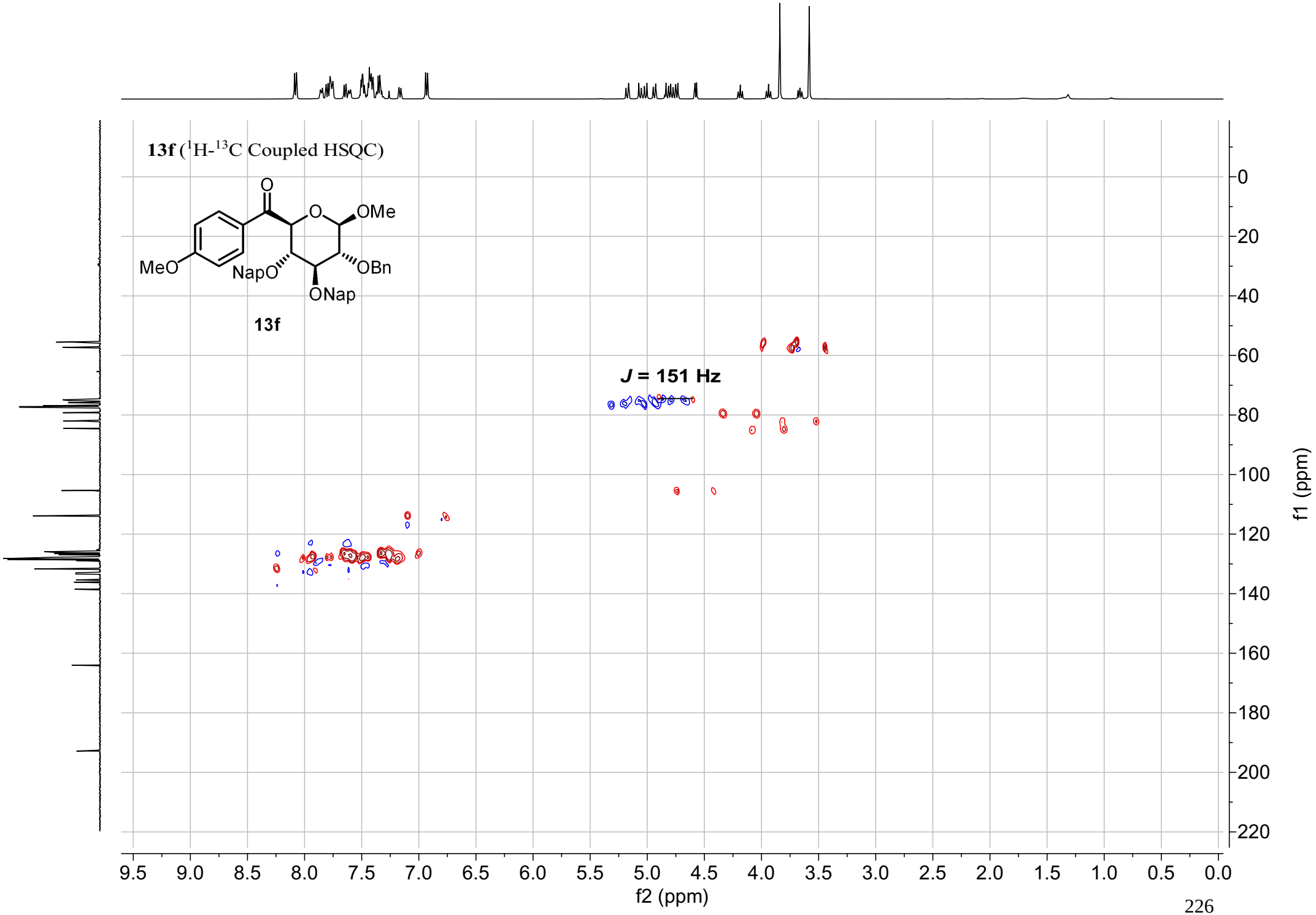


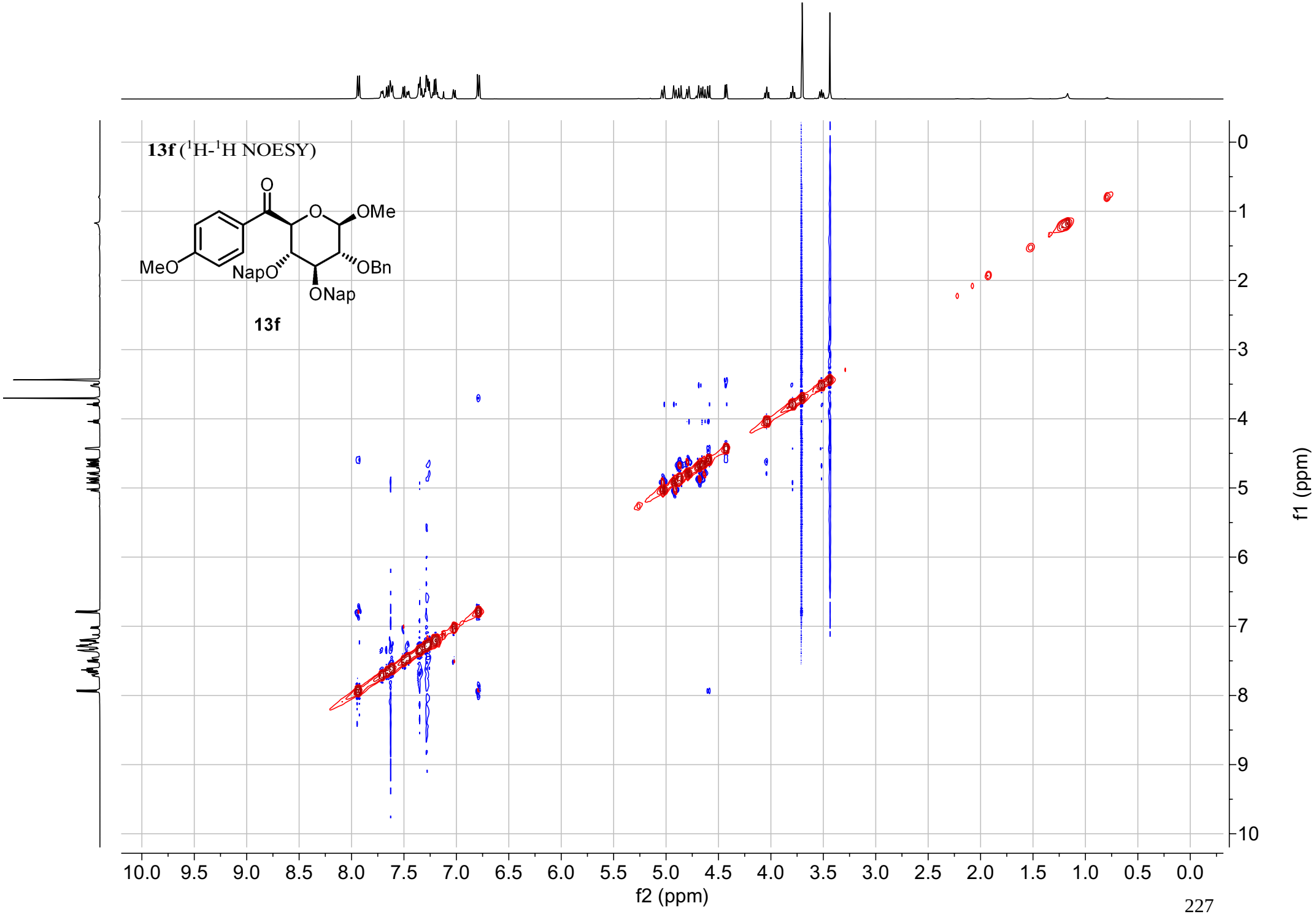
13f

13f (^{13}C NMR, 126MHz, $CDCl_3$)

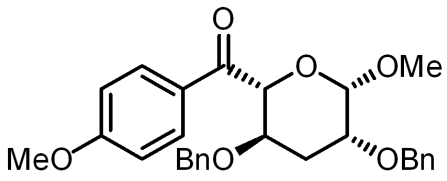


13f


13f (1H-13C Coupled HSQC)
O
O
OMe
MeO
NapO
OBn
ONap
13f
J = 151 Hz
f1 (ppm)
f2 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 20 40 60 80 100 120 140 160 180 200 220

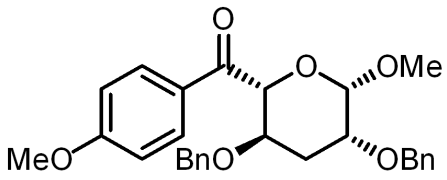

13f (1H-1H NOESY)
O
O
OMe
MeO
NapO
OBn
ONap
13f
f2 (ppm)
f1 (ppm)

13g (^{1}H NMR, 500MHz, $CDCl_3$)

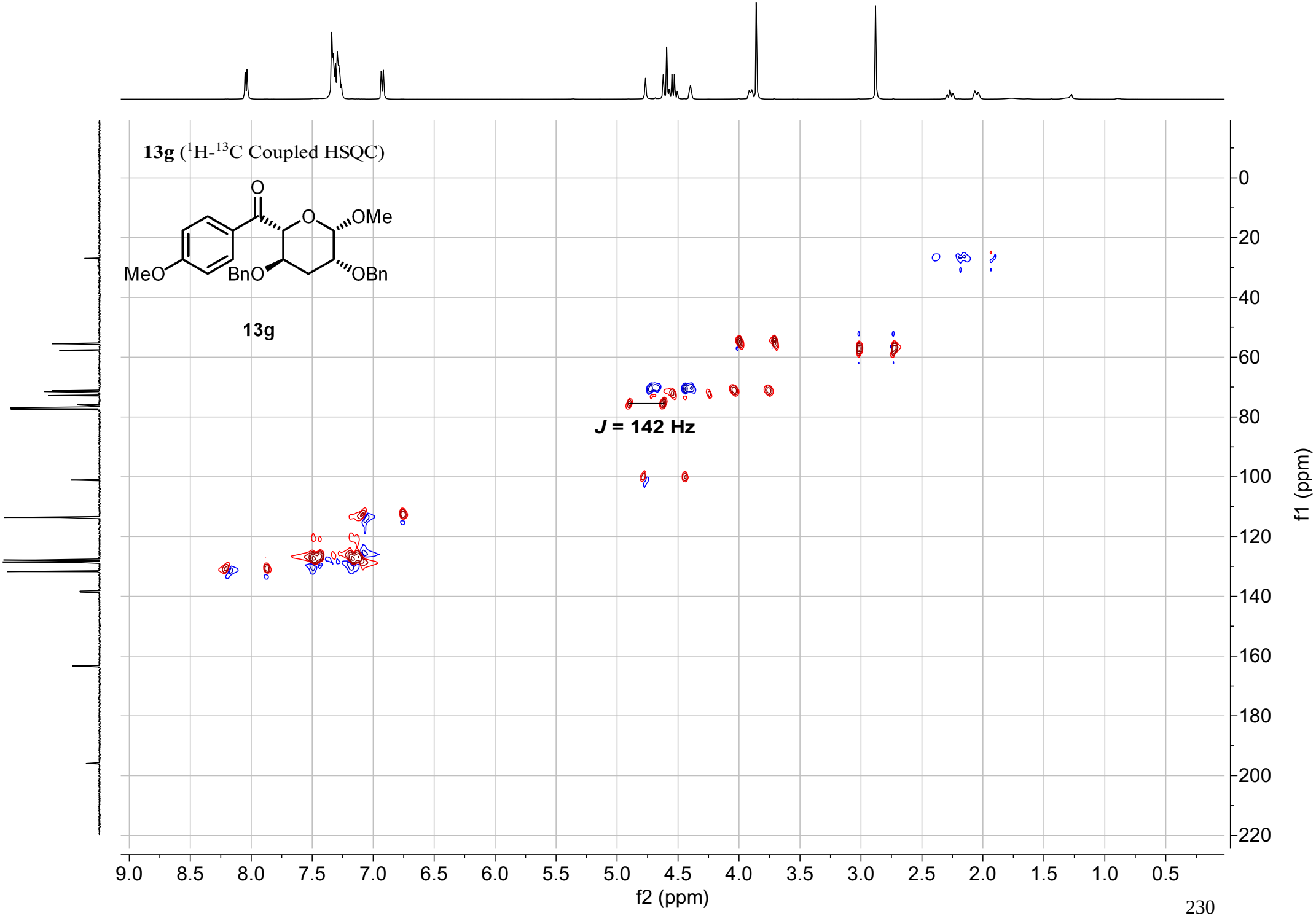


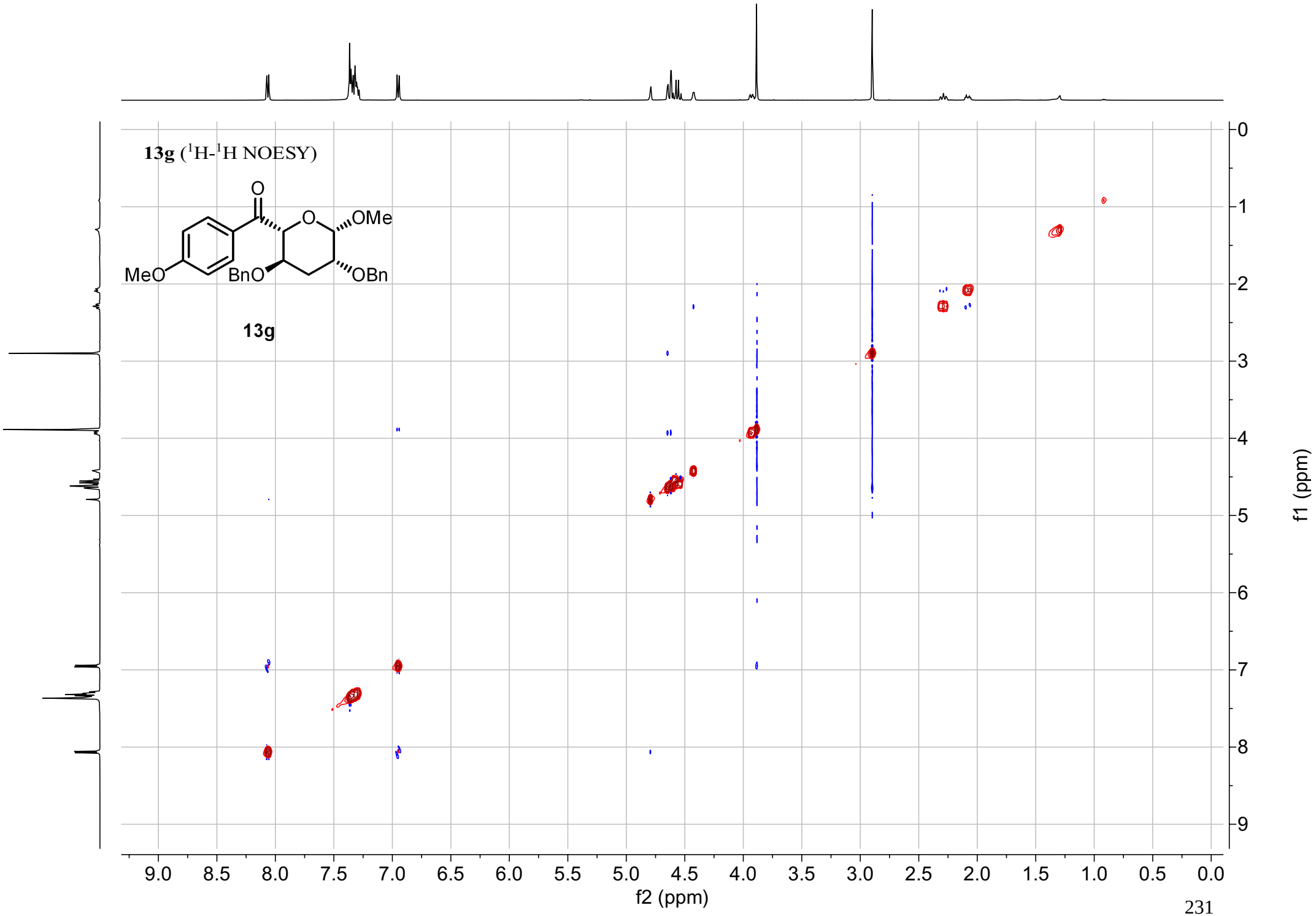
13g

13g (^{13}C NMR, 126MHz, $CDCl_3$)

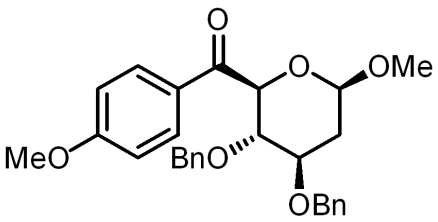


13g


13g (1H-13C Coupled HSQC)
O
O
OMe
MeO
BnO
OBn
13g
J = 142 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
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


13g (1H-1H NOESY)
O
O
OMe
MeO
BnO
OBn
13g
f2 (ppm)
f1 (ppm)

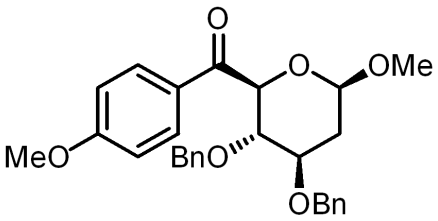
13h (^{1}H NMR, 500MHz, $CDCl_3$)



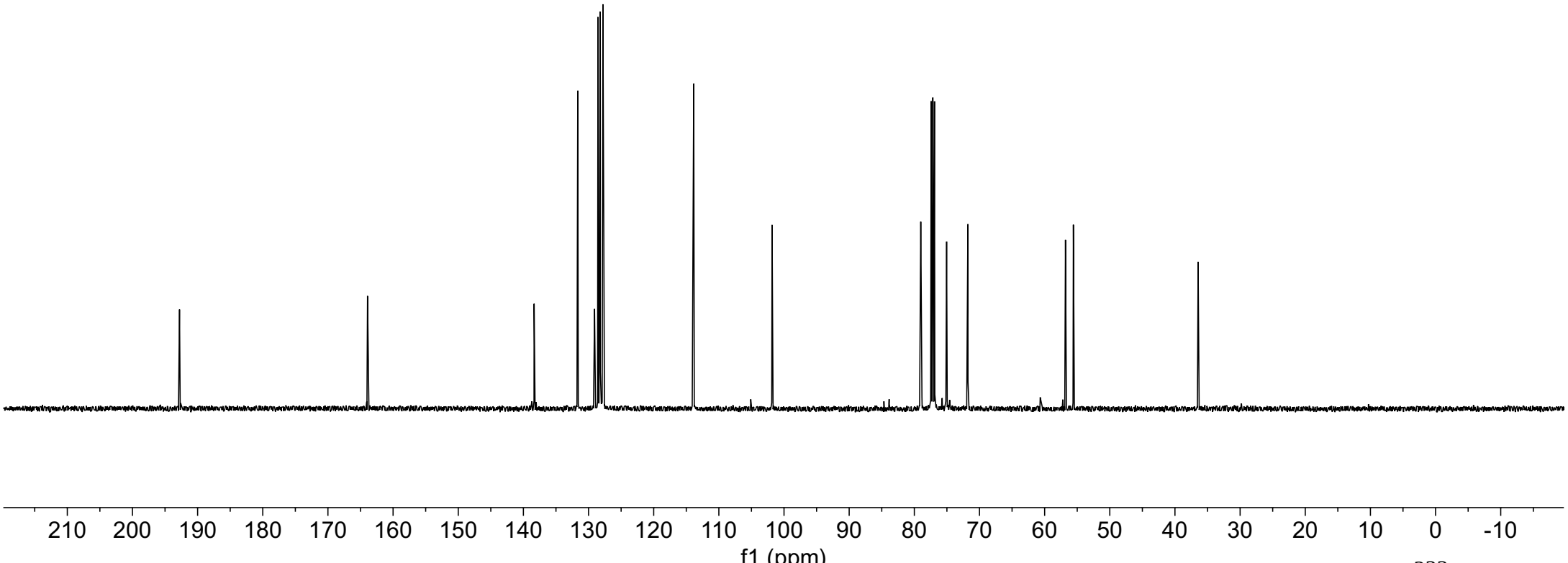
13h

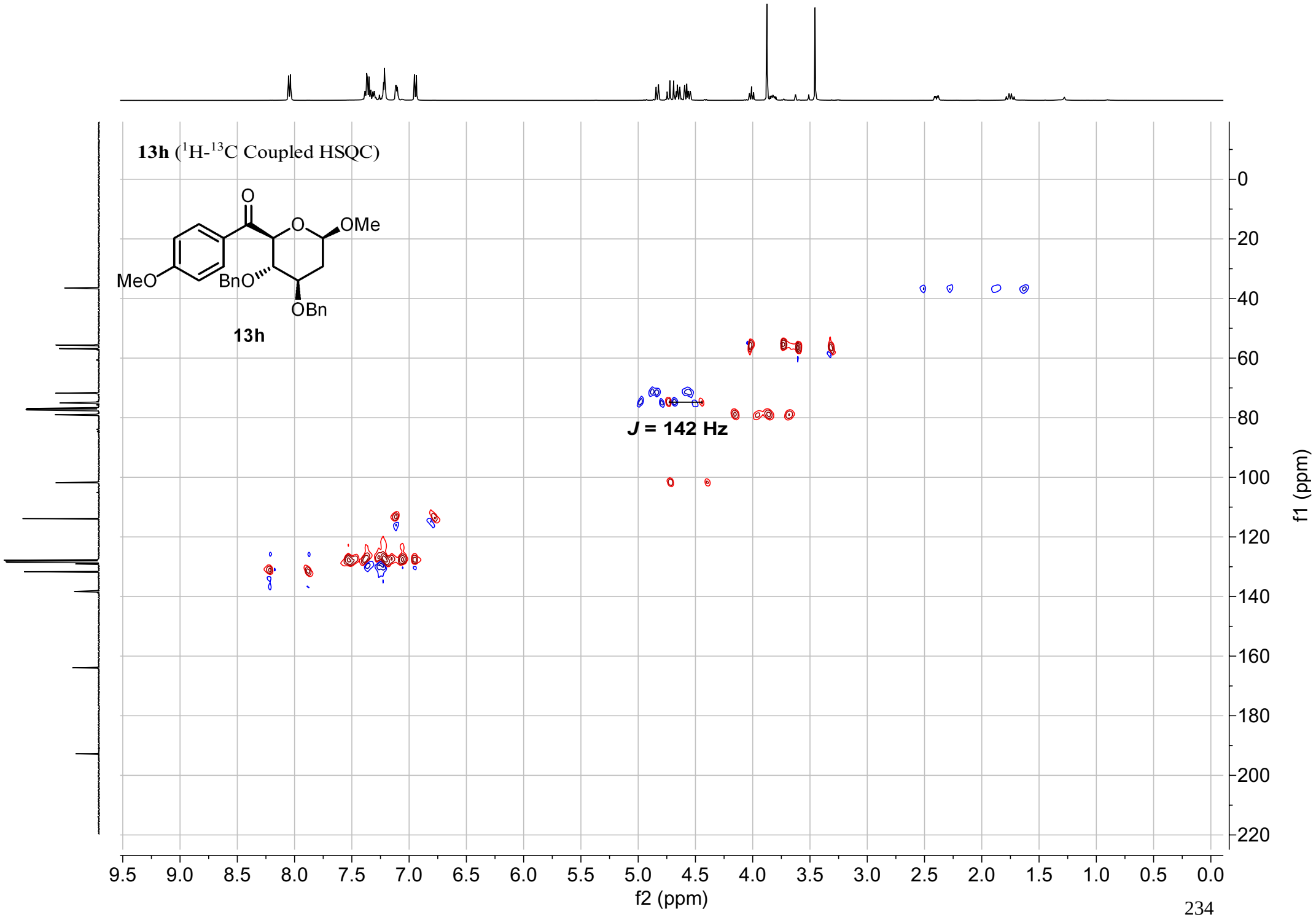
192.78
163.92
138.35
138.28
131.66
129.08
128.56
128.27
128.22
127.83
127.80
127.66
113.85
101.83
79.08
79.01
77.16
75.11
75.04
71.78
56.80
55.59
36.45

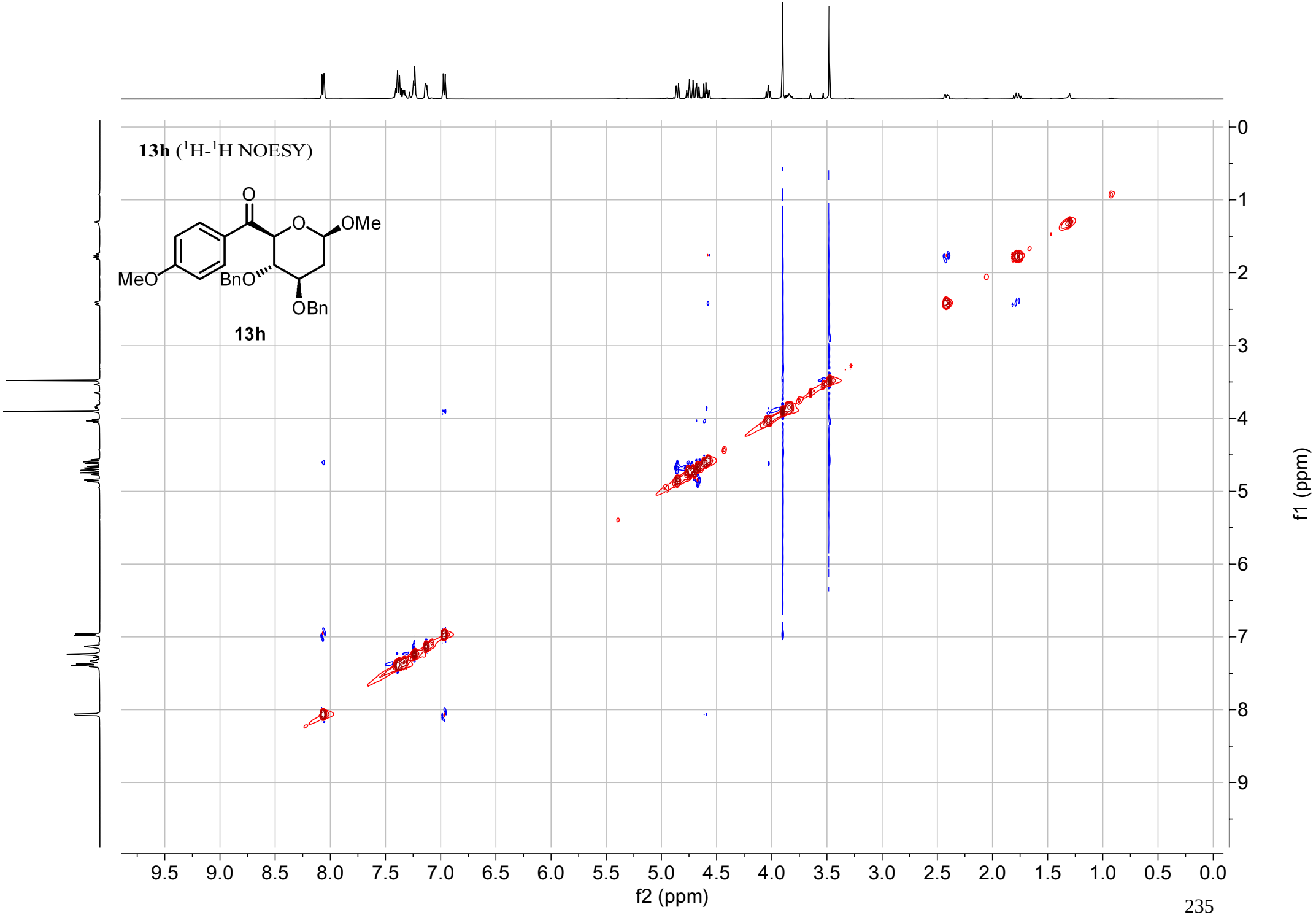
13h (^{13}C NMR, 126MHz, $CDCl_3$)



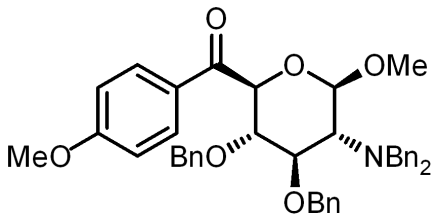
13h




13h (1H-13C Coupled HSQC)
O
O
OMe
MeO
BnO
OBn
13h
J = 142 Hz
f1 (ppm)
f2 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

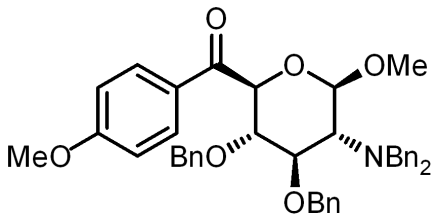

13h (1H-1H NOESY)
O
O
OMe
MeO
BnO
OBn
13h
f2 (ppm)
f1 (ppm)

13i (^{1}H NMR, 500MHz, $CDCl_3$)

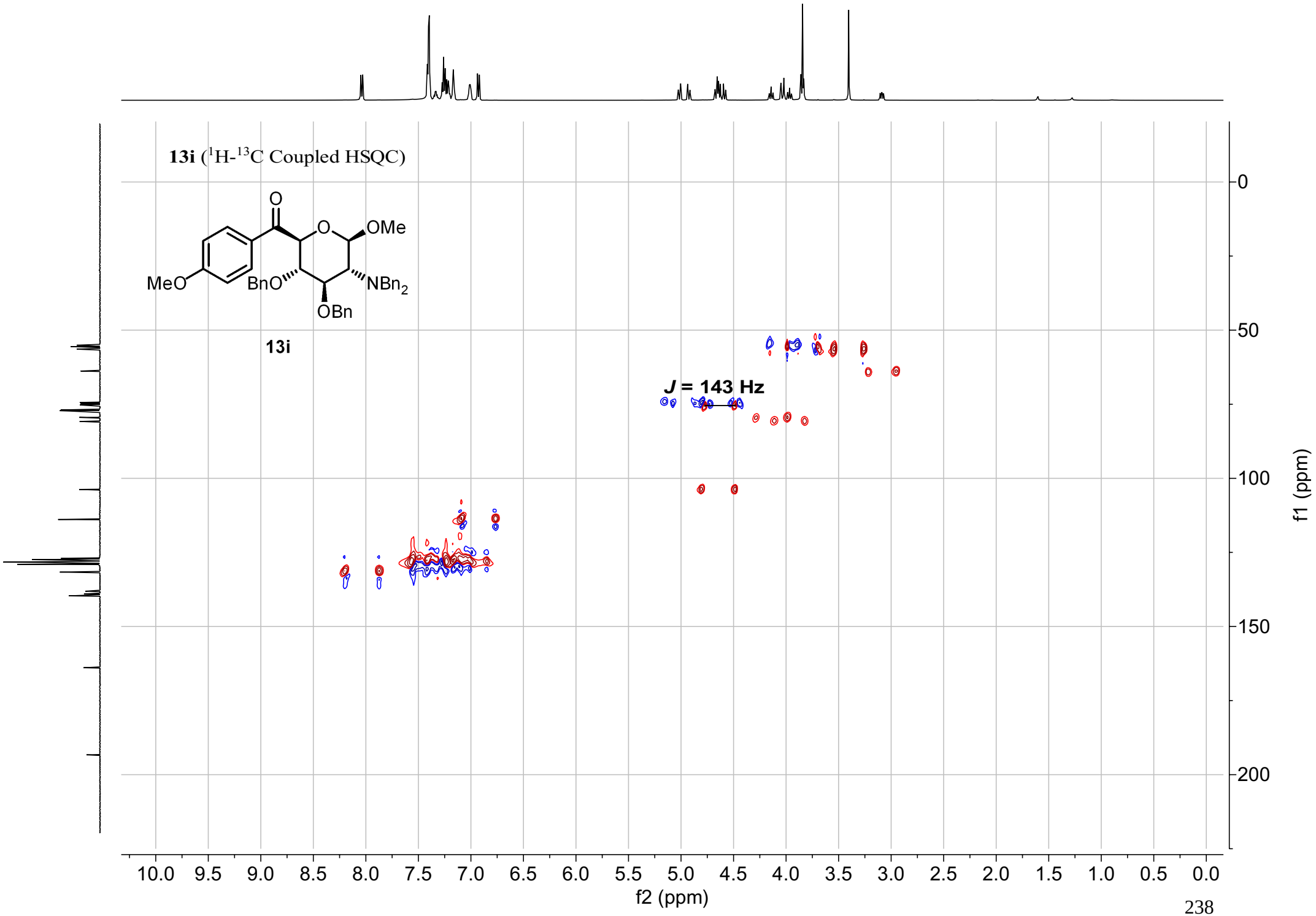


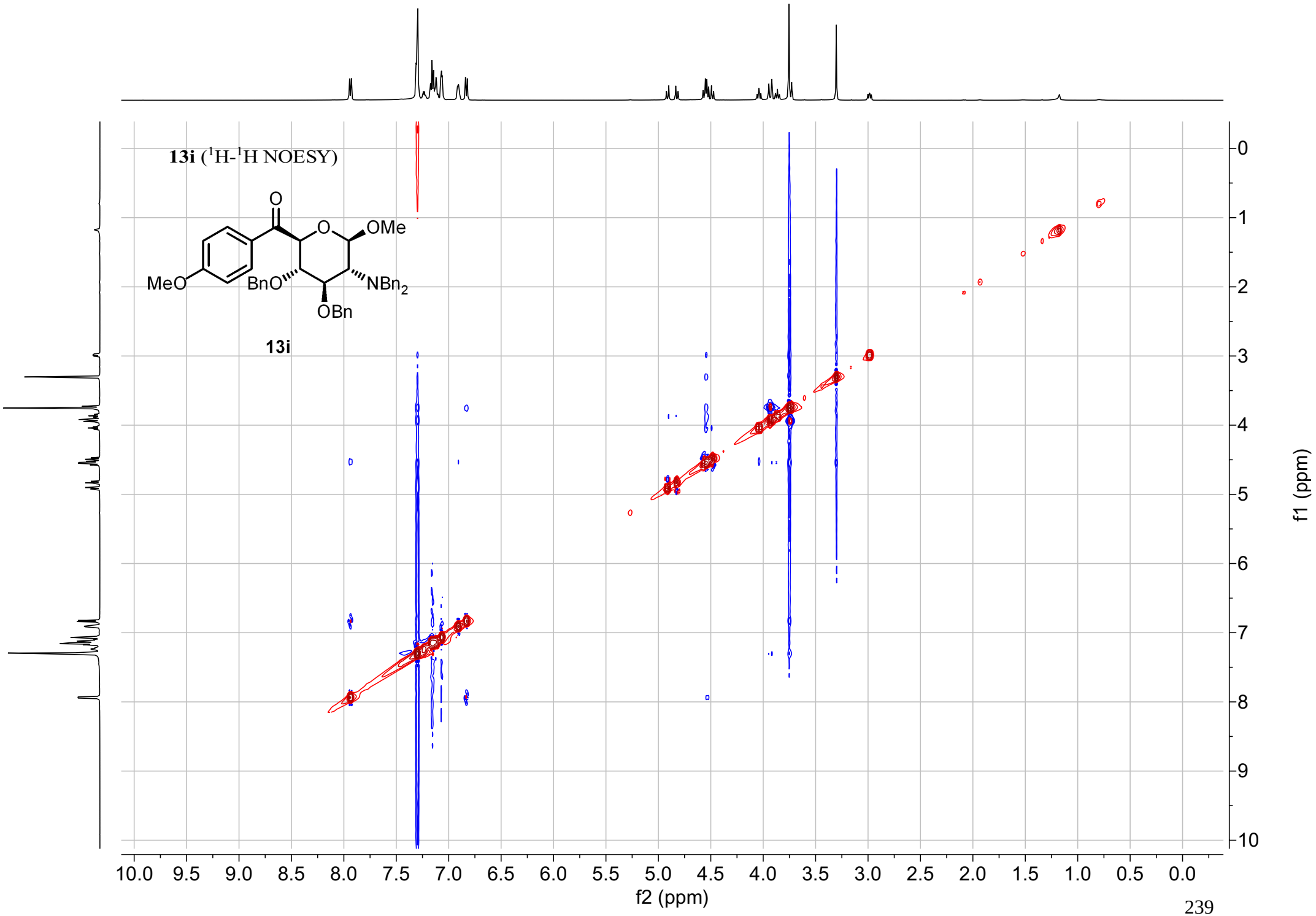
13i

13i (^{13}C NMR, 126MHz, $CDCl_3$)

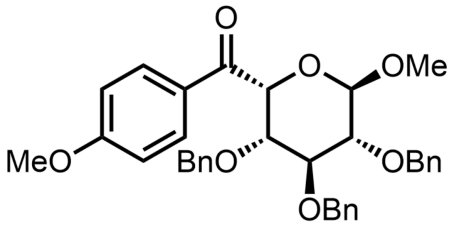


13i


13i (1H-13C Coupled HSQC)
O
O
OMe
MeO
BnO
NBn2
OBn
13i
J = 143 Hz
0
50
100
150
200
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)


13i (1H-1H NOESY)
O
O
OMe
MeO
BnO
NBn2
OBn
13i
f2 (ppm)
f1 (ppm)

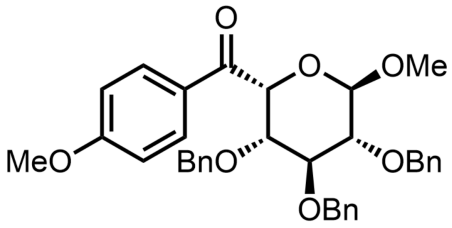
13j (^{1}H NMR, 500MHz, $CDCl_3$)



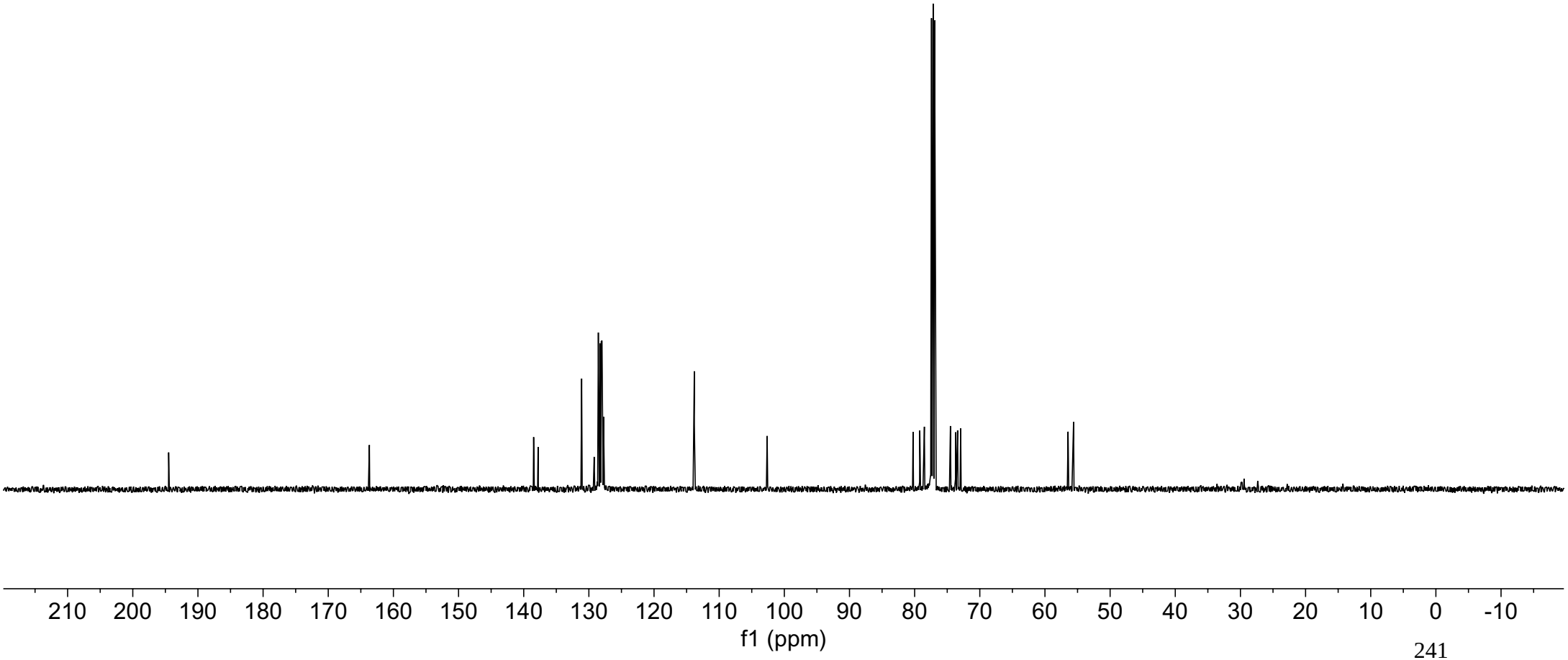
13j

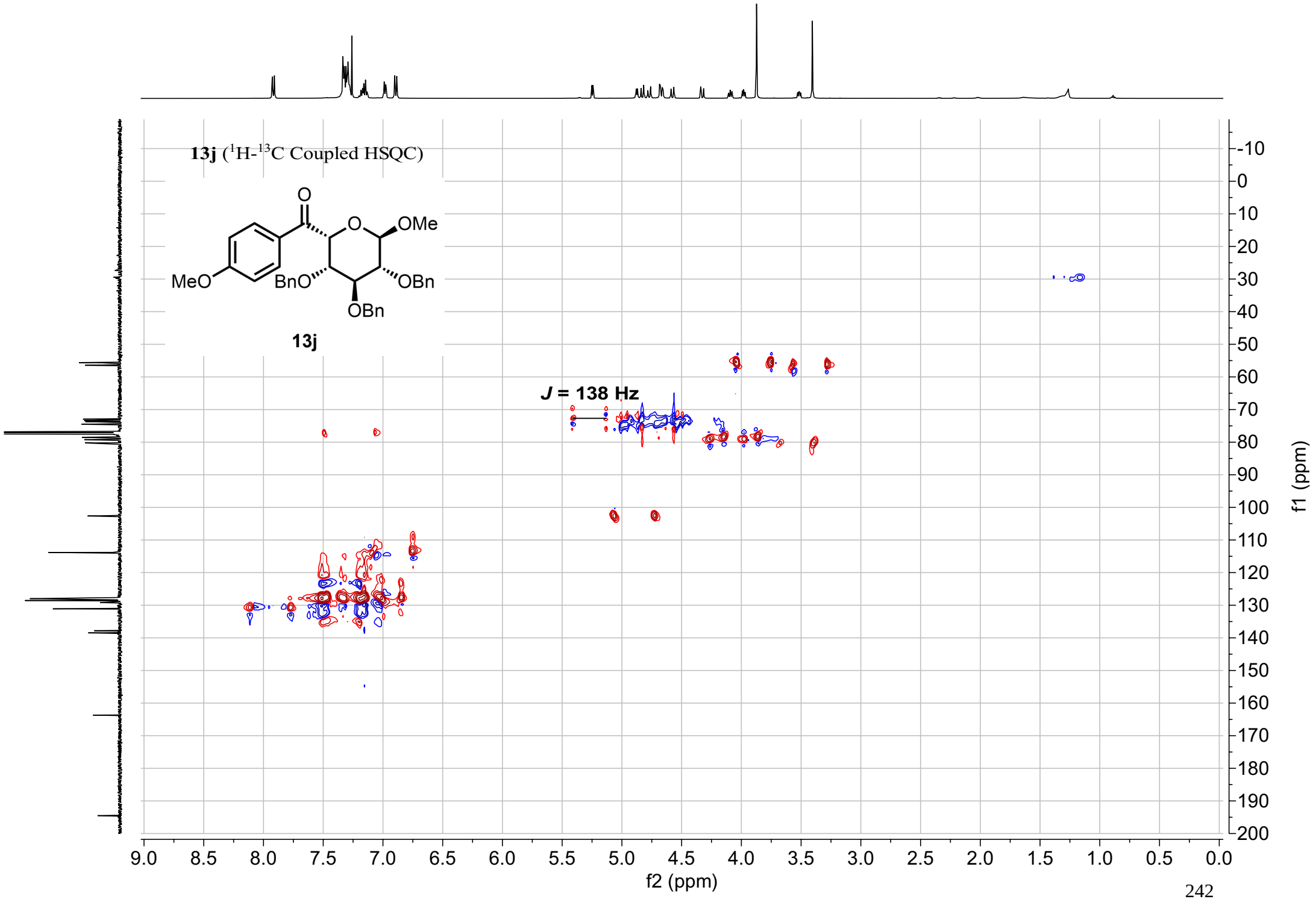
194.49
163.69
138.47
138.47
137.80
131.11
129.19
128.55
128.47
128.26
128.11
127.99
127.97
127.86
127.75
127.66
113.82
102.64
80.25
79.21
78.51
77.16
74.51
73.71
73.41
72.94
56.45
55.61

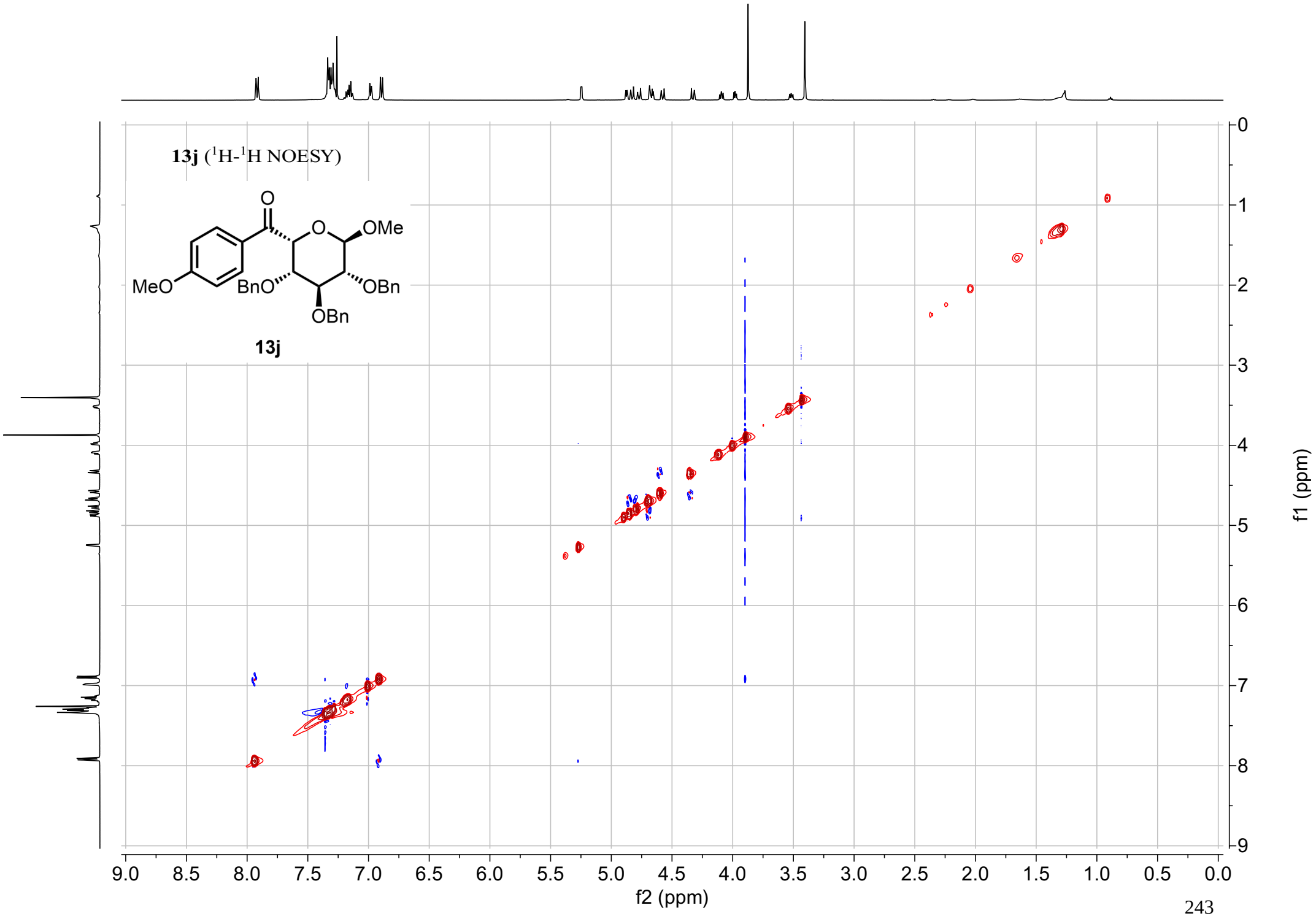
13j (^{13}C NMR, 126MHz, $CDCl_3$)



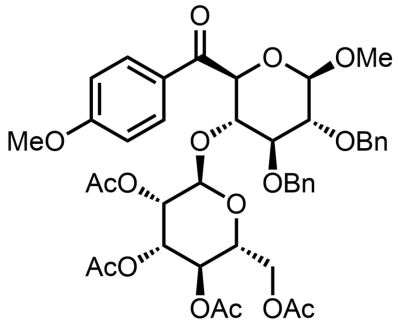
13j




13j (1H-13C Coupled HSQC)
O
O
OMe
MeO
BnO
OBn
OBn
13j
J = 138 Hz
f2 (ppm)
f1 (ppm)


13j (1H-1H NOESY)
O
O
OMe
MeO
BnO
OBn
OBn
13j
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
0
1
2
3
4
5
6
7
8
9

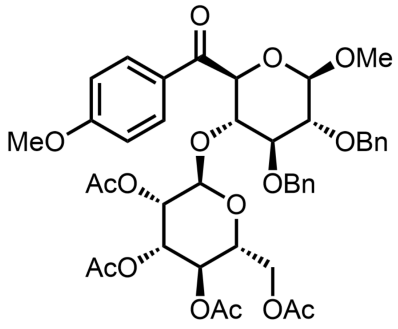
13k (^{1}H NMR, 500MHz, $CDCl_3$)



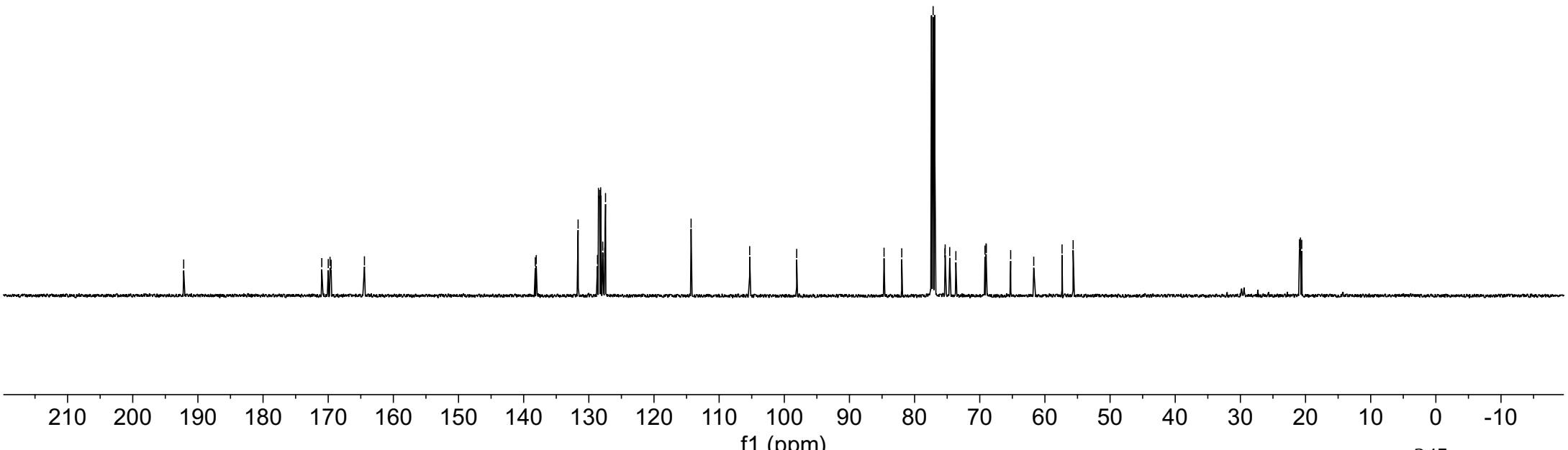
13k

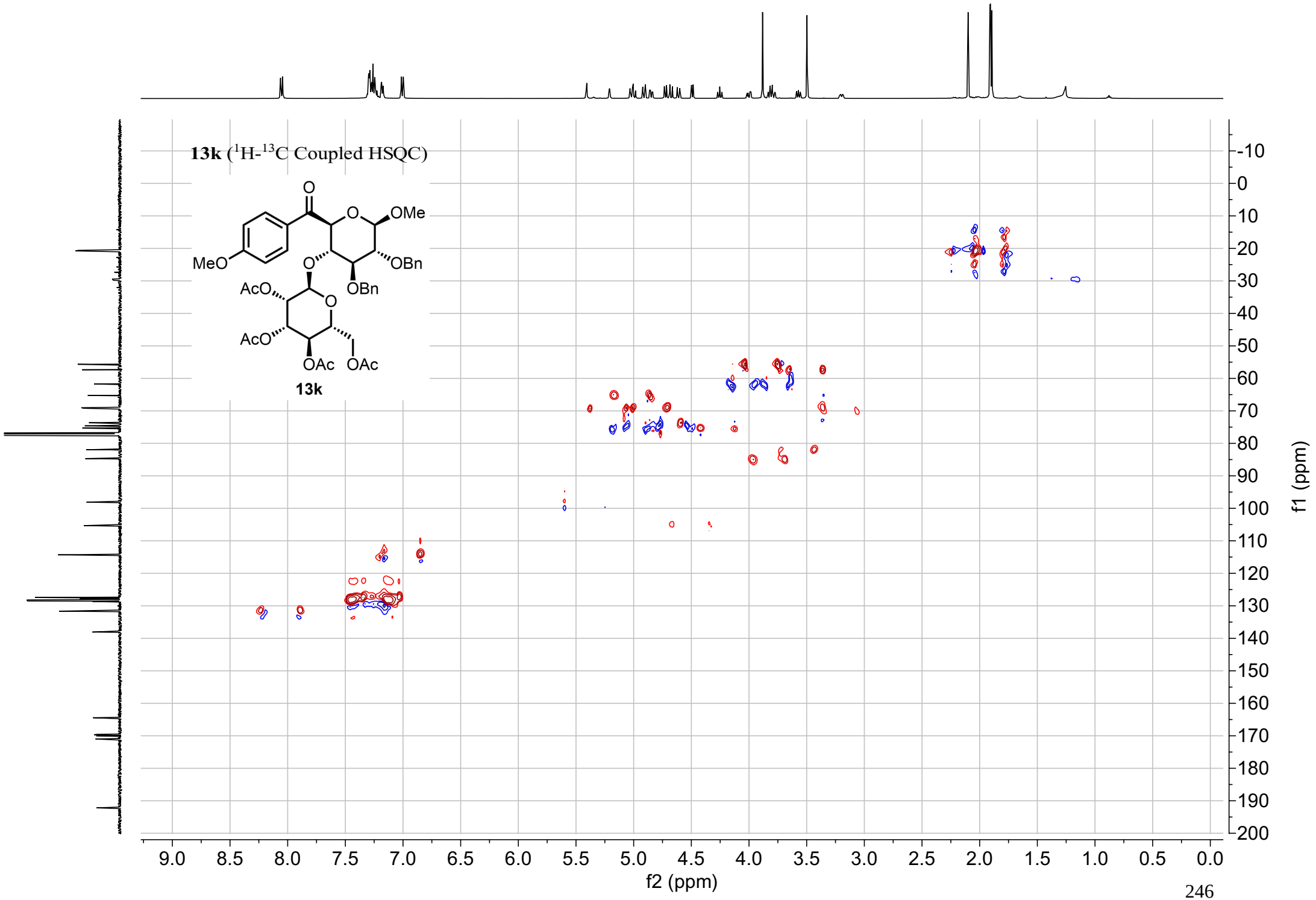
192.18
170.99
169.99
169.72
169.55
164.44
138.22
138.07
131.65
128.67
128.52
128.33
128.18
127.86
127.54
127.44
114.31
105.31
98.10
84.69
81.97
77.16
75.34
75.31
74.61
73.67
69.20
69.03
69.01
65.26
61.71
57.37
55.67
20.93
20.77
20.74
20.59

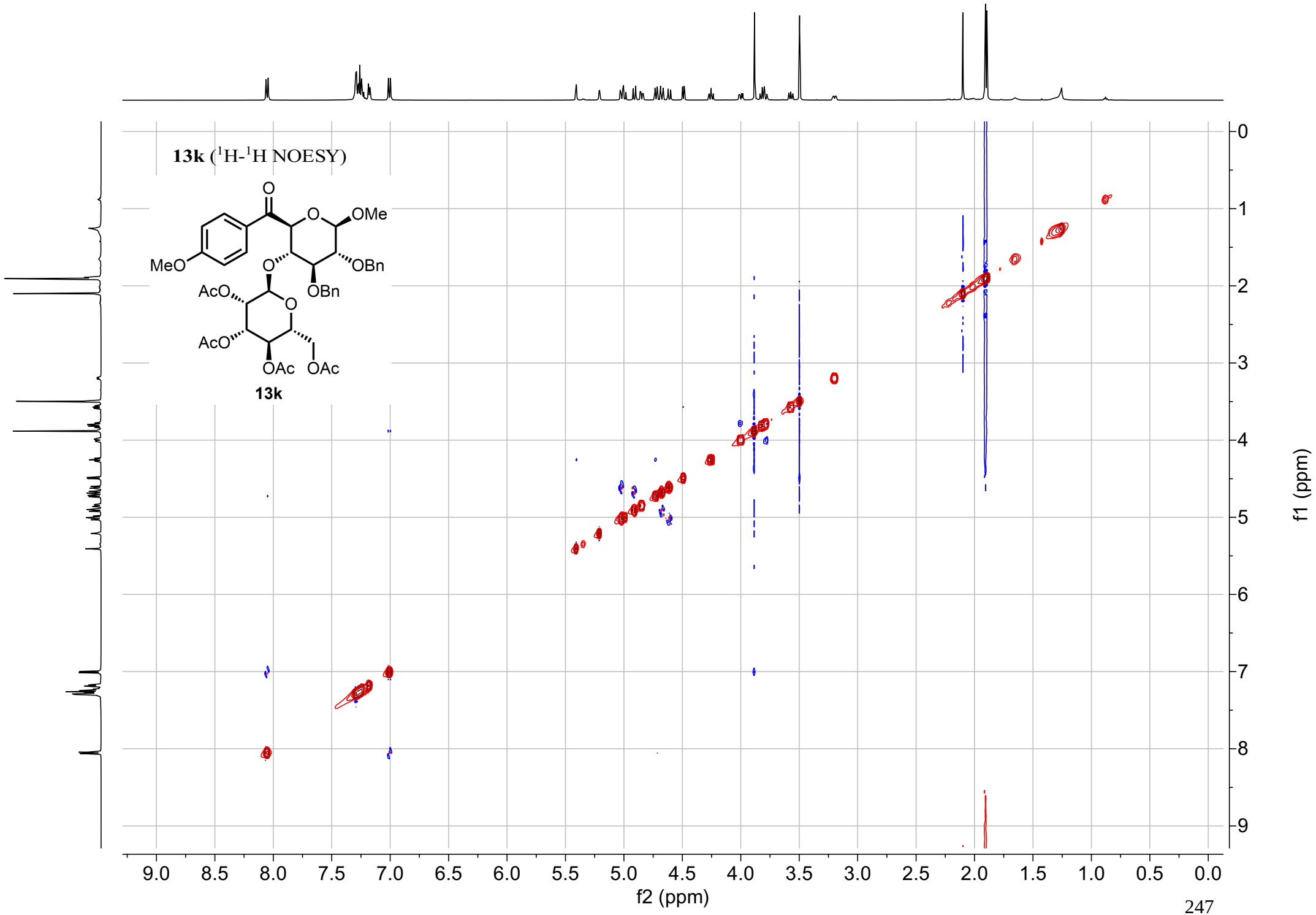
13k (^{13}C NMR, 126MHz, $CDCl_3$)



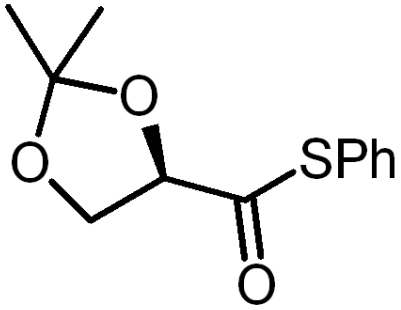
13k




13k (1H-13C Coupled HSQC)
MeO
OMe
OBn
OBn
AcO
AcO
OAc
OAc
13k
f2 (ppm)
f1 (ppm)

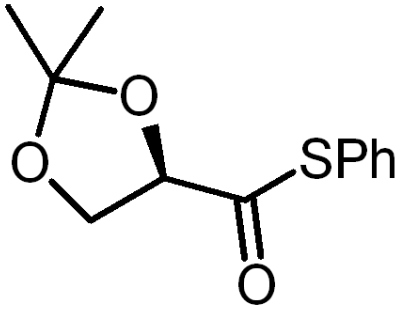

13k (1H-1H NOESY)
O
O
OMe
MeO
O
OBn
OBn
AcO
O
AcO
OAc
OAc
13k
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8
9

15 (^{1}H NMR, 500MHz, $CDCl_3$)



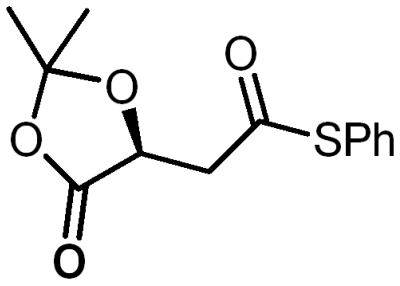
15

15 (^{13}C NMR, 126MHz, $CDCl_3$)



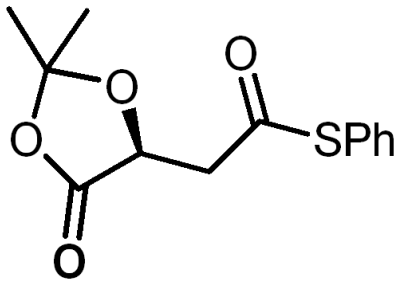
15

16 (^{1}H NMR, 500MHz, $CDCl_3$)



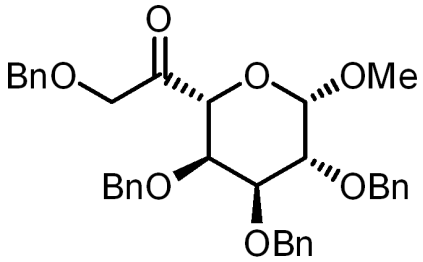
16

16 (^{13}C NMR, 126MHz, $CDCl_3$)



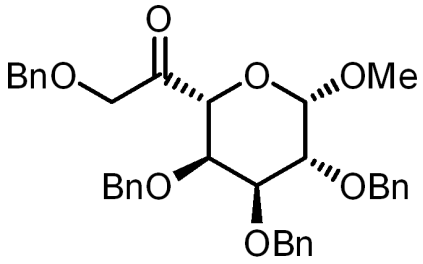
16

17 (^{1}H NMR, 500MHz, $CDCl_3$)

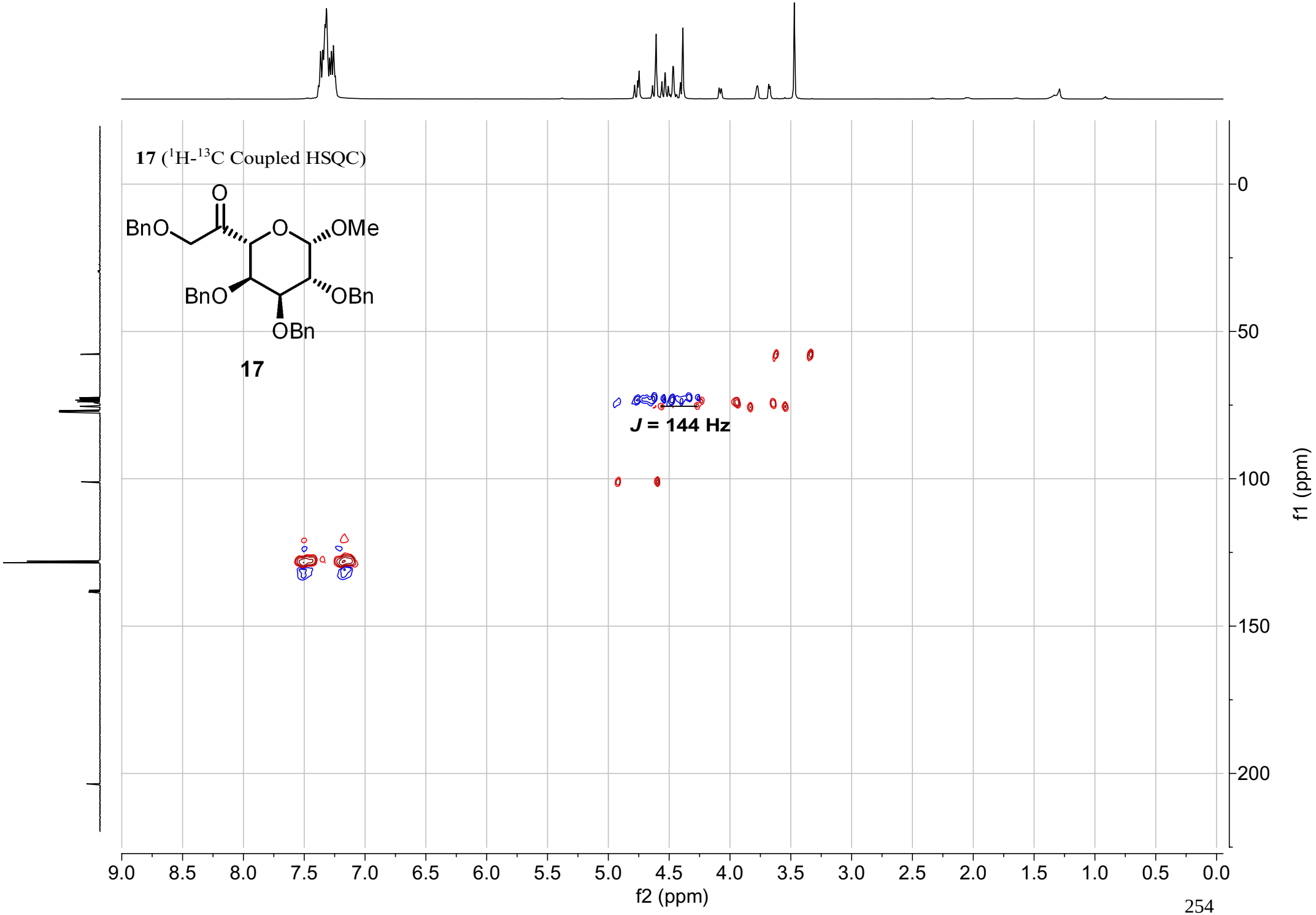


17

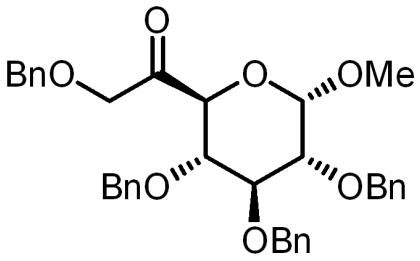
17 (^{13}C NMR, 126MHz, $CDCl_3$)



17

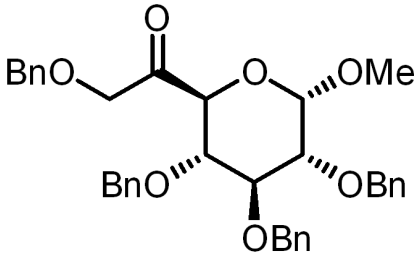

17 (1H-13C Coupled HSQC)
BnO
O
OMe
BnO
OBn
OBn
17
J = 144 Hz
0
50
100
150
200
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

18 (^{1}H NMR, 500MHz, $CDCl_3$)

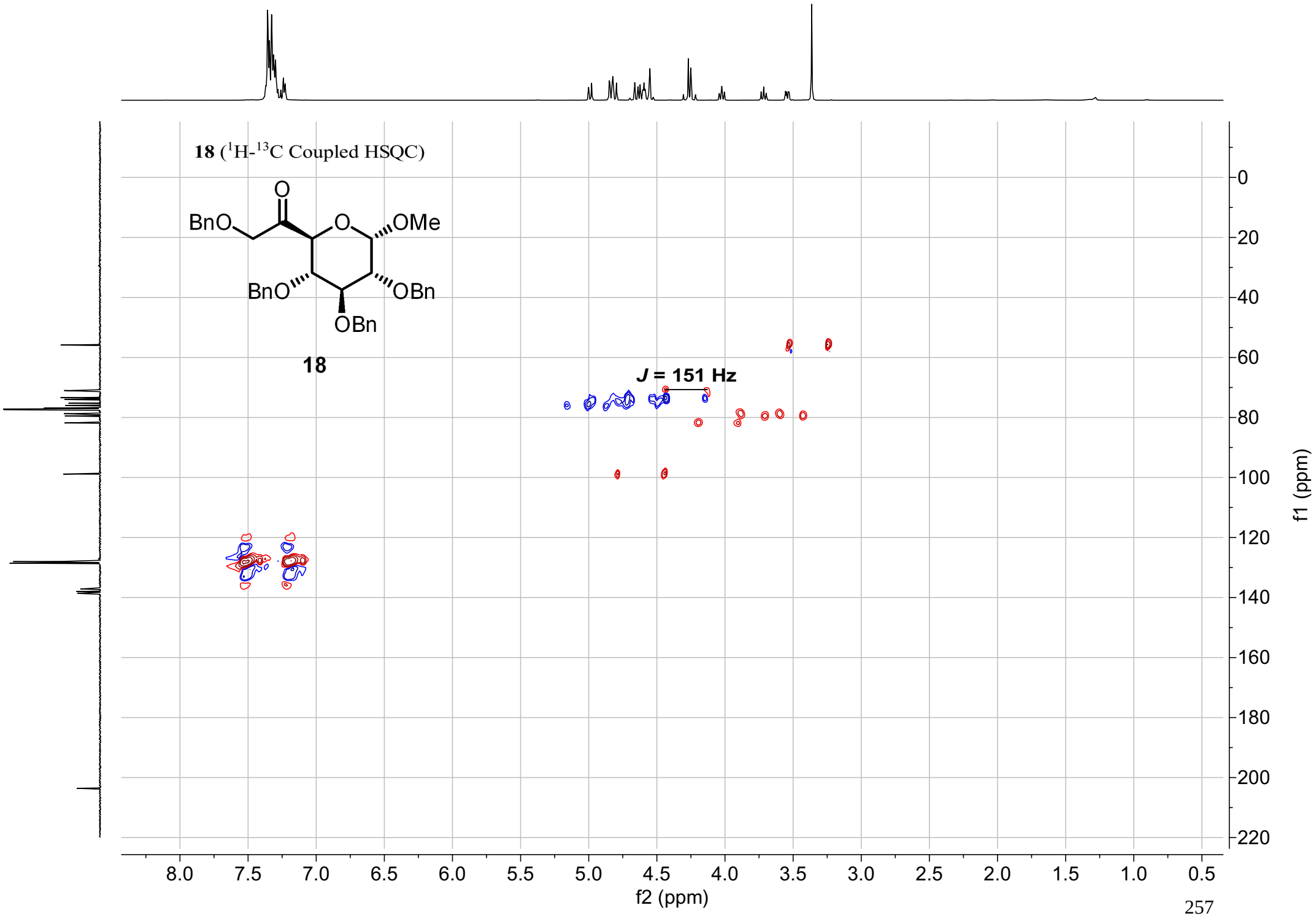


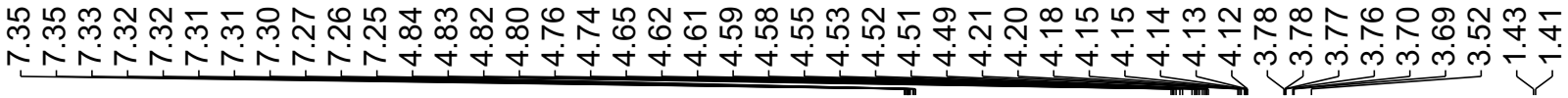
18

18 (^{13}C NMR, 126MHz, $CDCl_3$)

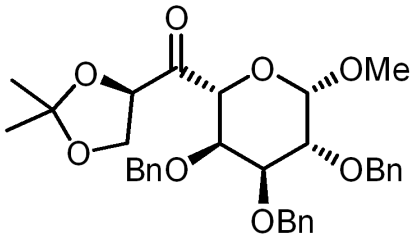


18

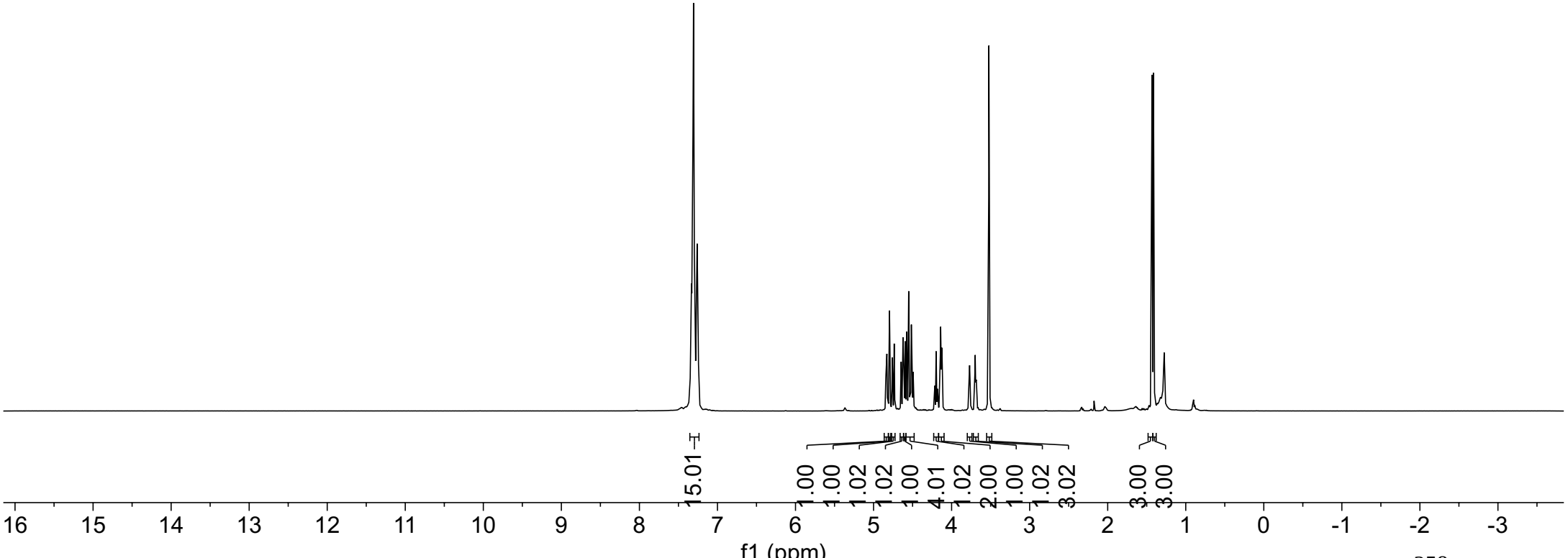

18 (1H-13C Coupled HSQC)
BnO
O
OMe
BnO
OBn
OBn
18
J = 151 Hz
f2 (ppm)
f1 (ppm)



19 (^{1}H NMR, 500MHz, $CDCl_3$)

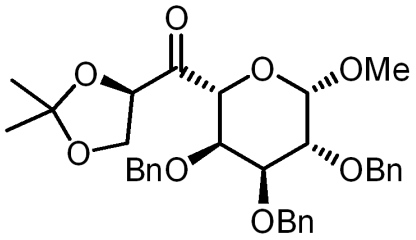


19

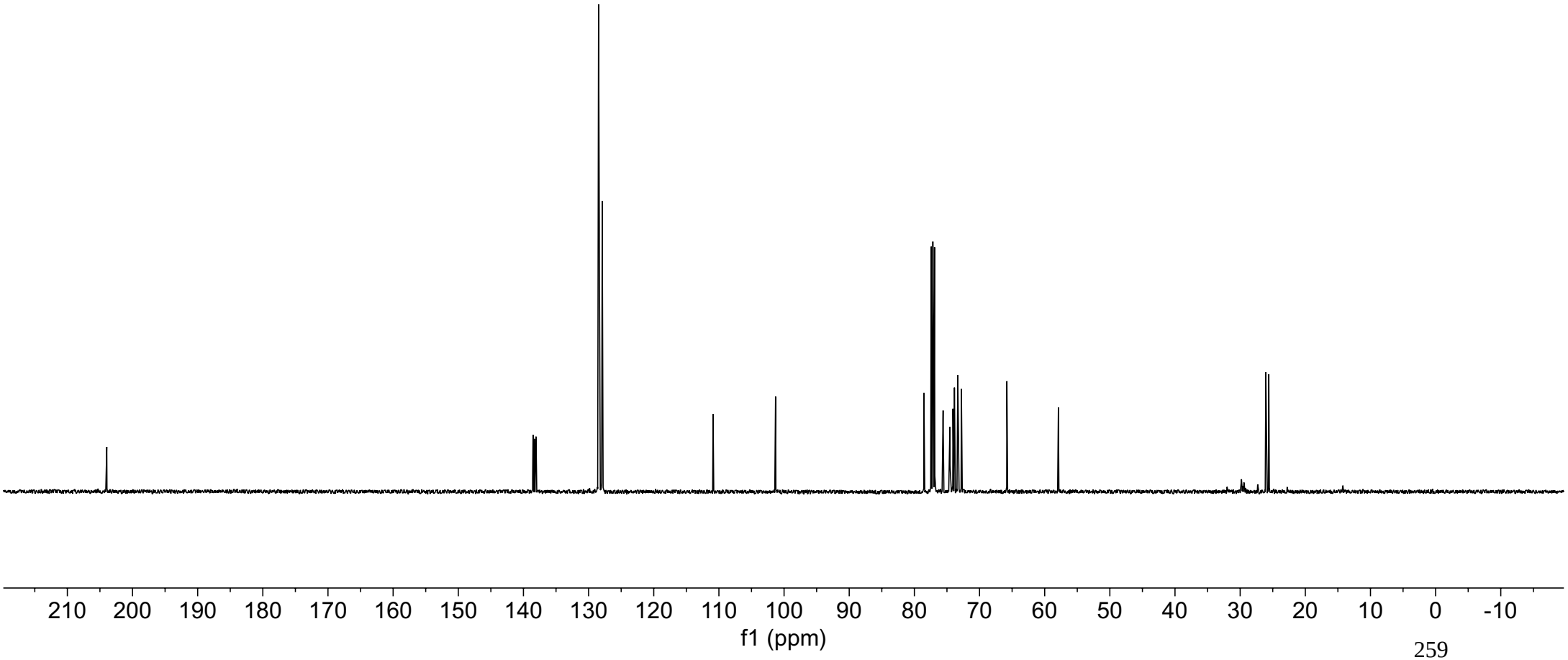


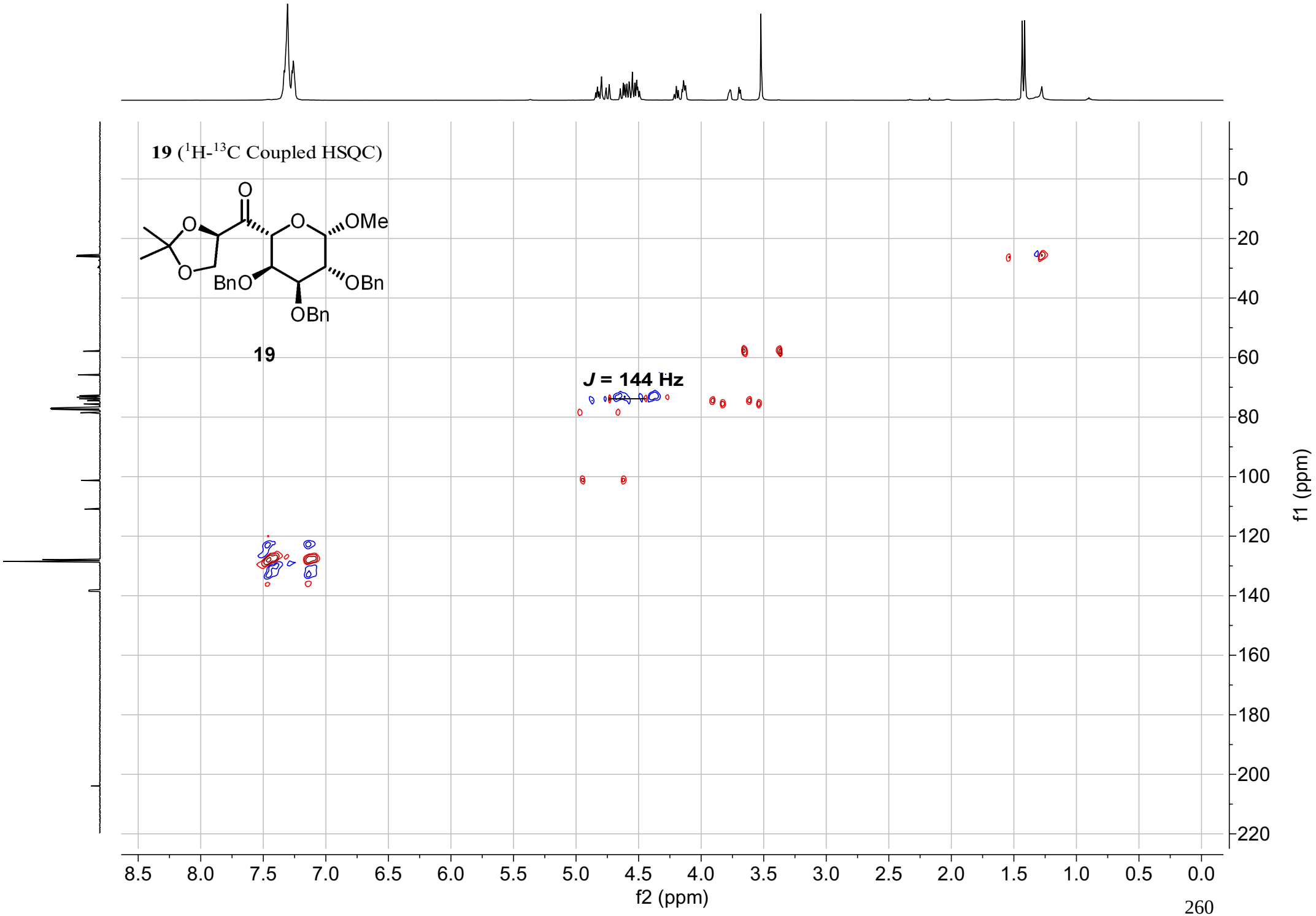
203.95
138.53
138.31
138.07
128.47
128.32
127.92
127.91
127.84
127.81
110.89
101.31
78.53
77.16
75.59
74.55
74.08
73.85
73.37
73.34
72.79
65.80
57.90
26.06
25.60

19 (^{13}C NMR, 126MHz, $CDCl_3$)

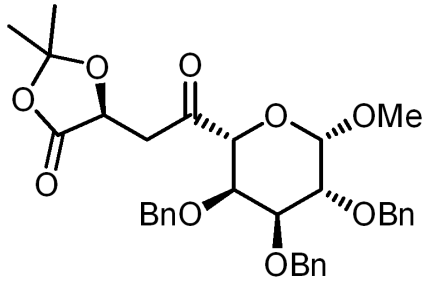


19



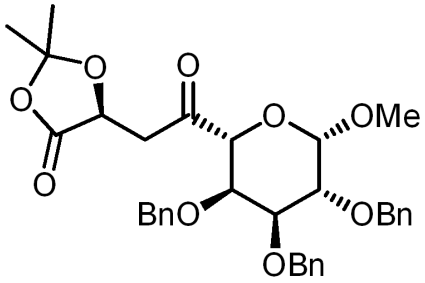

19 (1H-13C Coupled HSQC)
O
O
O
O
OMe
BnO
OBn
OBn
19
J = 144 Hz
0
20
40
60
80
100
120
140
160
180
200
220
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

20 (^{1}H NMR, 500MHz, $CDCl_3$)

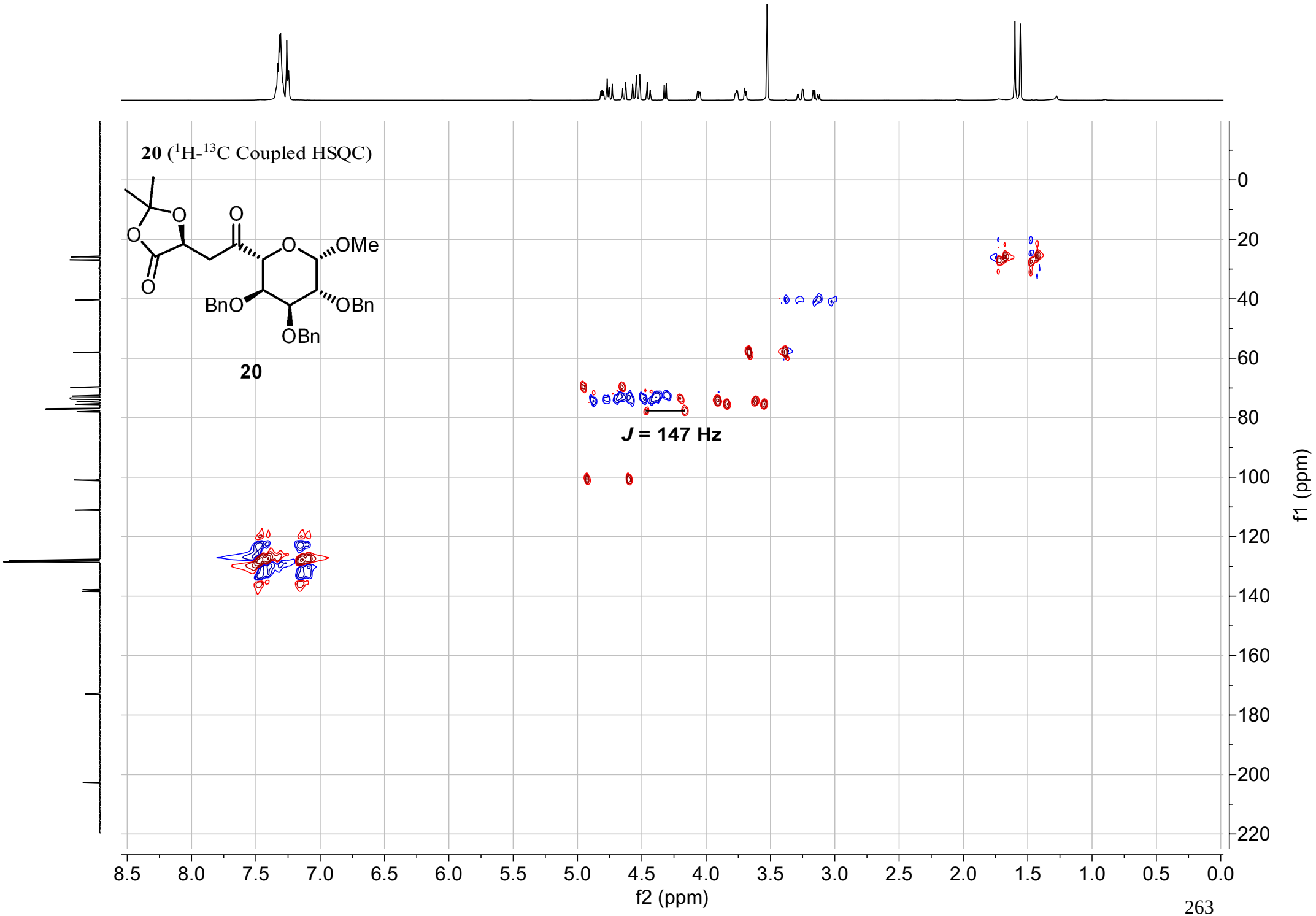


20

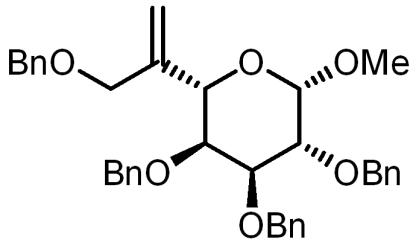
20 (^{13}C NMR, 126MHz, $CDCl_3$)



20

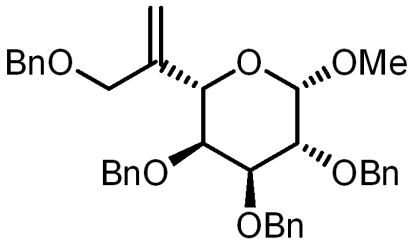

20 (1H-13C Coupled HSQC)
O
O
O
O
O
OMe
BnO
OBn
OBn
20
J = 147 Hz
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
140
160
180
200
220

21 (^{1}H NMR, 500MHz, $CDCl_3$)



21

21 (^{13}C NMR, 126MHz, $CDCl_3$)

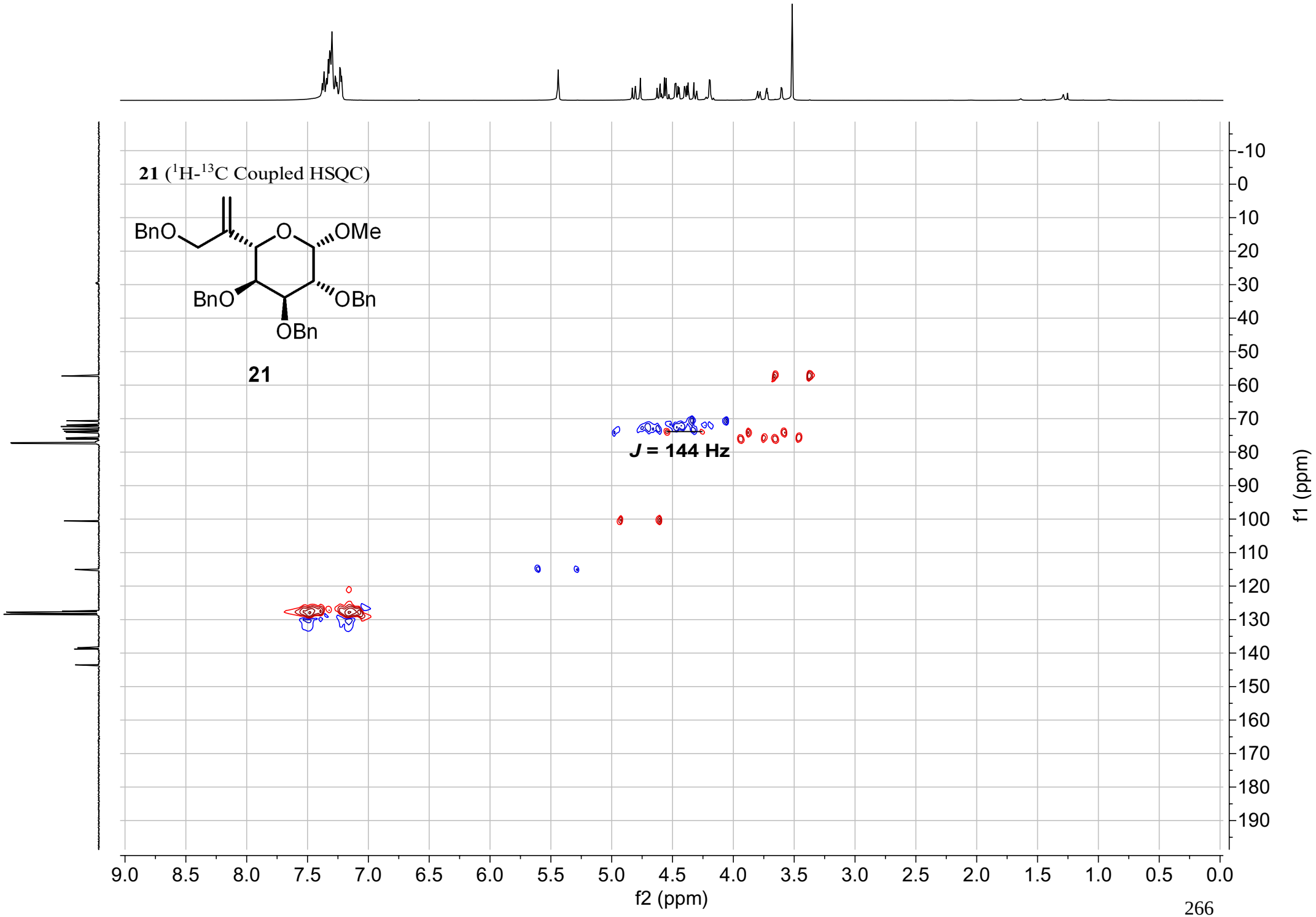


21

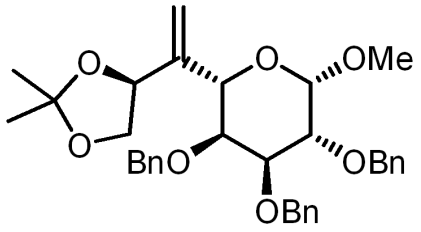
143.51
138.78
138.77
138.39
138.33
128.45
128.44
128.39
128.37
127.98
127.96
127.91
127.81
127.74
127.67
127.50
115.04
100.56
77.16
76.10
75.72
74.20
74.03
73.72
73.13
72.36
71.87
70.64
57.30

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)

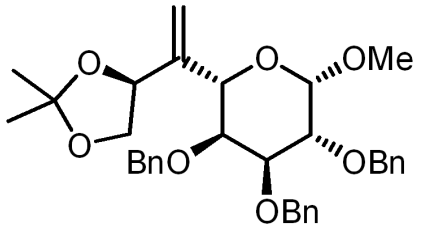

21 (1H-13C Coupled HSQC)
BnO
O
OMe
BnO
OBn
OBn
21
J = 144 Hz
f2 (ppm)
f1 (ppm)

22 (^{1}H NMR, 500MHz, $CDCl_3$)



22

22 (^{13}C NMR, 126MHz, $CDCl_3$)

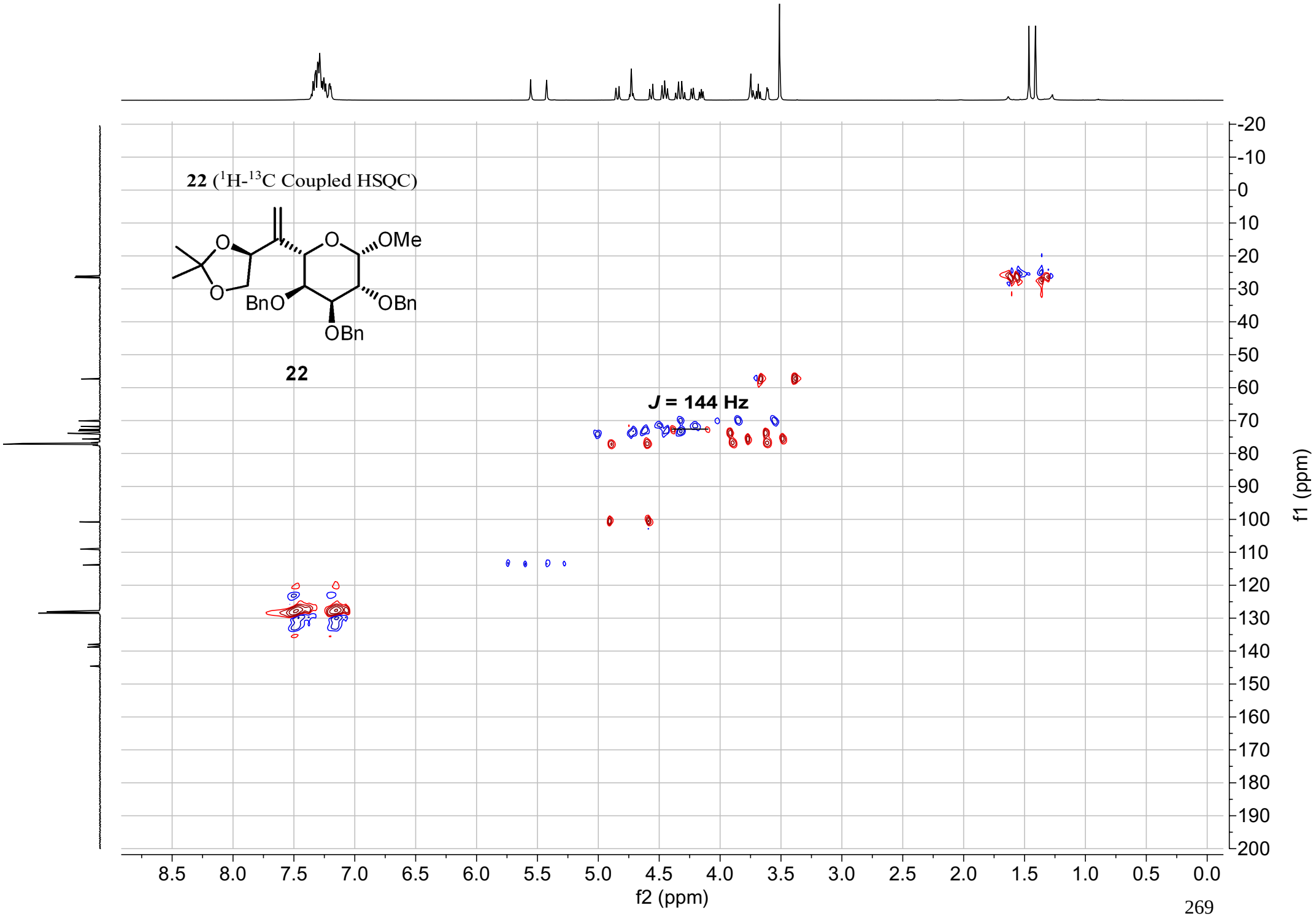


22

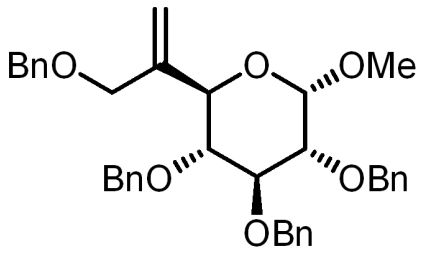
144.54
138.79
138.24
138.00
128.50
128.49
128.43
128.03
128.01
127.95
127.91
127.83
127.81
113.84
109.01
100.74
77.16
76.75
75.58
73.87
73.13
72.72
71.74
70.10
57.36
26.55
26.16

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)

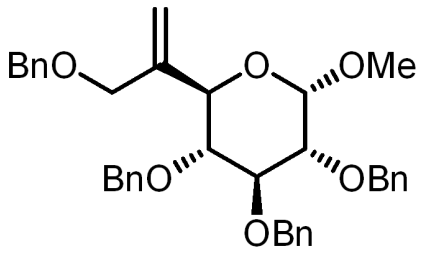

22 (1H-13C Coupled HSQC)
O
O
O
OMe
BnO
OBn
OBn
22
J = 144 Hz
f2 (ppm)
f1 (ppm)

23 (^{1}H NMR, 500MHz, $CDCl_3$)

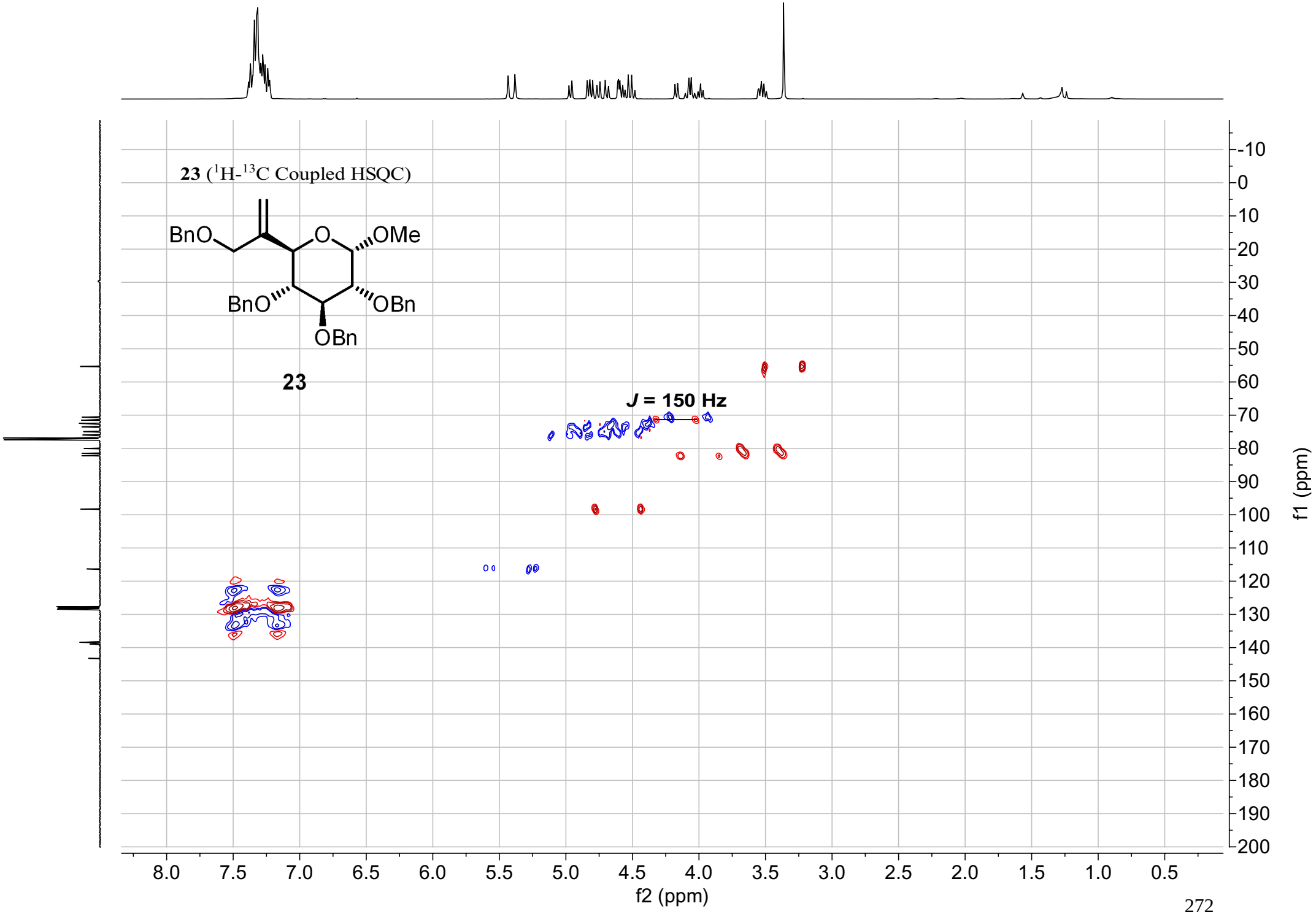


23

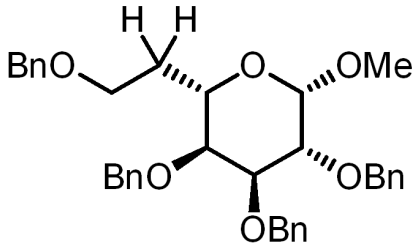
23 (^{13}C NMR, 126MHz, $CDCl_3$)



23

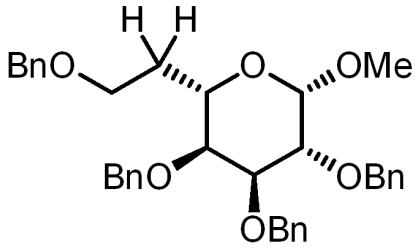

23 (1H-13C Coupled HSQC)
BnO
O
OMe
BnO
OBn
OBn
23
J = 150 Hz
f2 (ppm)
f1 (ppm)

24 (^{1}H NMR, 500MHz, $CDCl_3$)

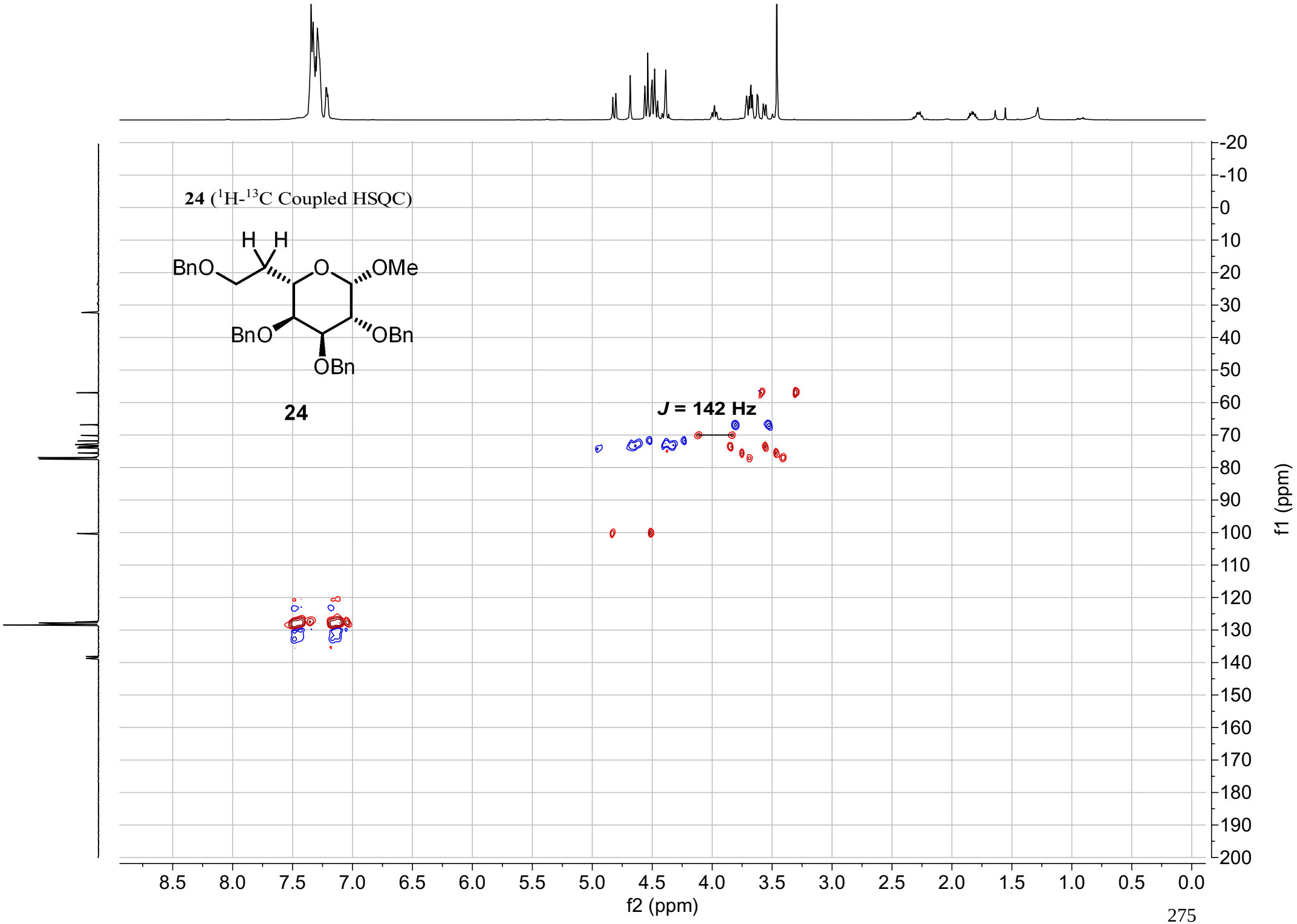


24

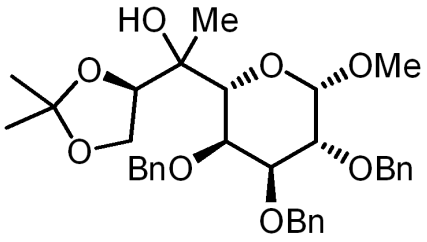
24 (^{13}C NMR, 126MHz, $CDCl_3$)



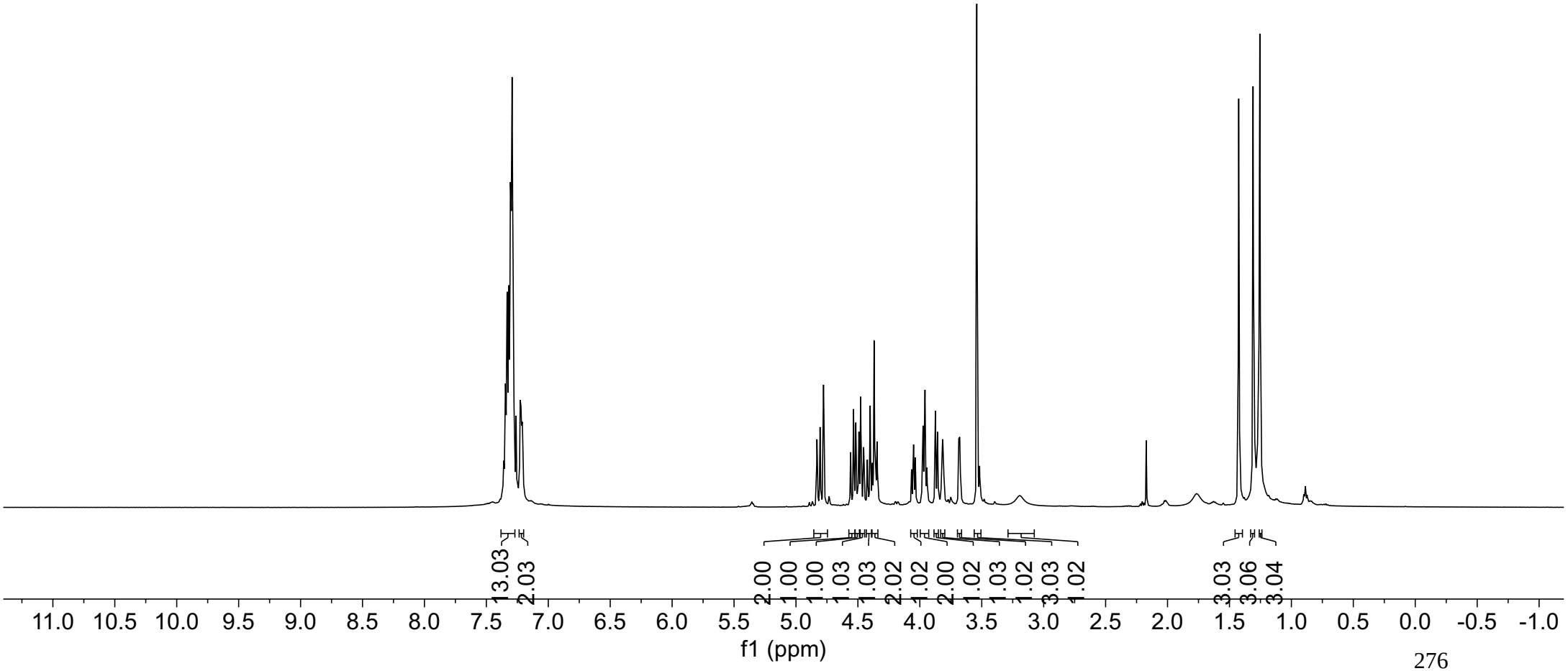
24


24 (1H-13C Coupled HSQC)
H H
BnO
O
OMe
BnO
OBn
OBn
24
J = 142 Hz
f2 (ppm)
f1 (ppm)

25 (^{1}H NMR, 500MHz, $CDCl_3$)

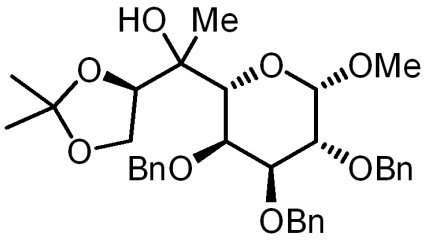


25

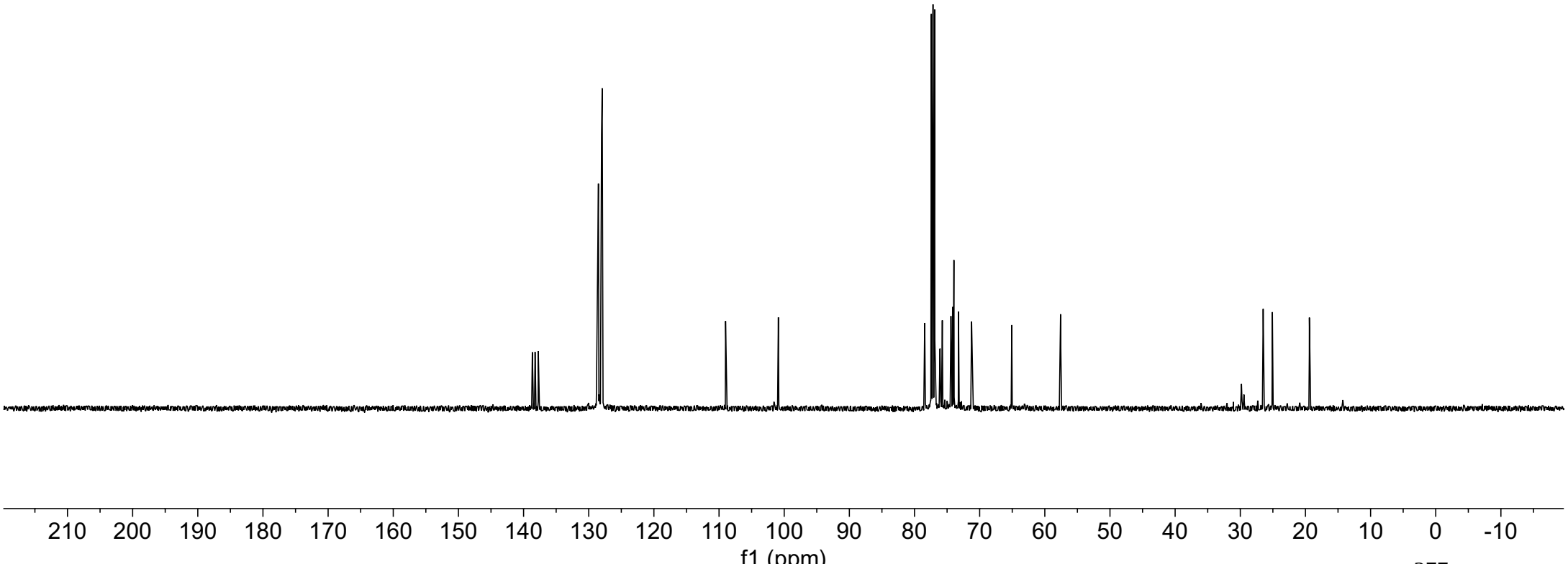


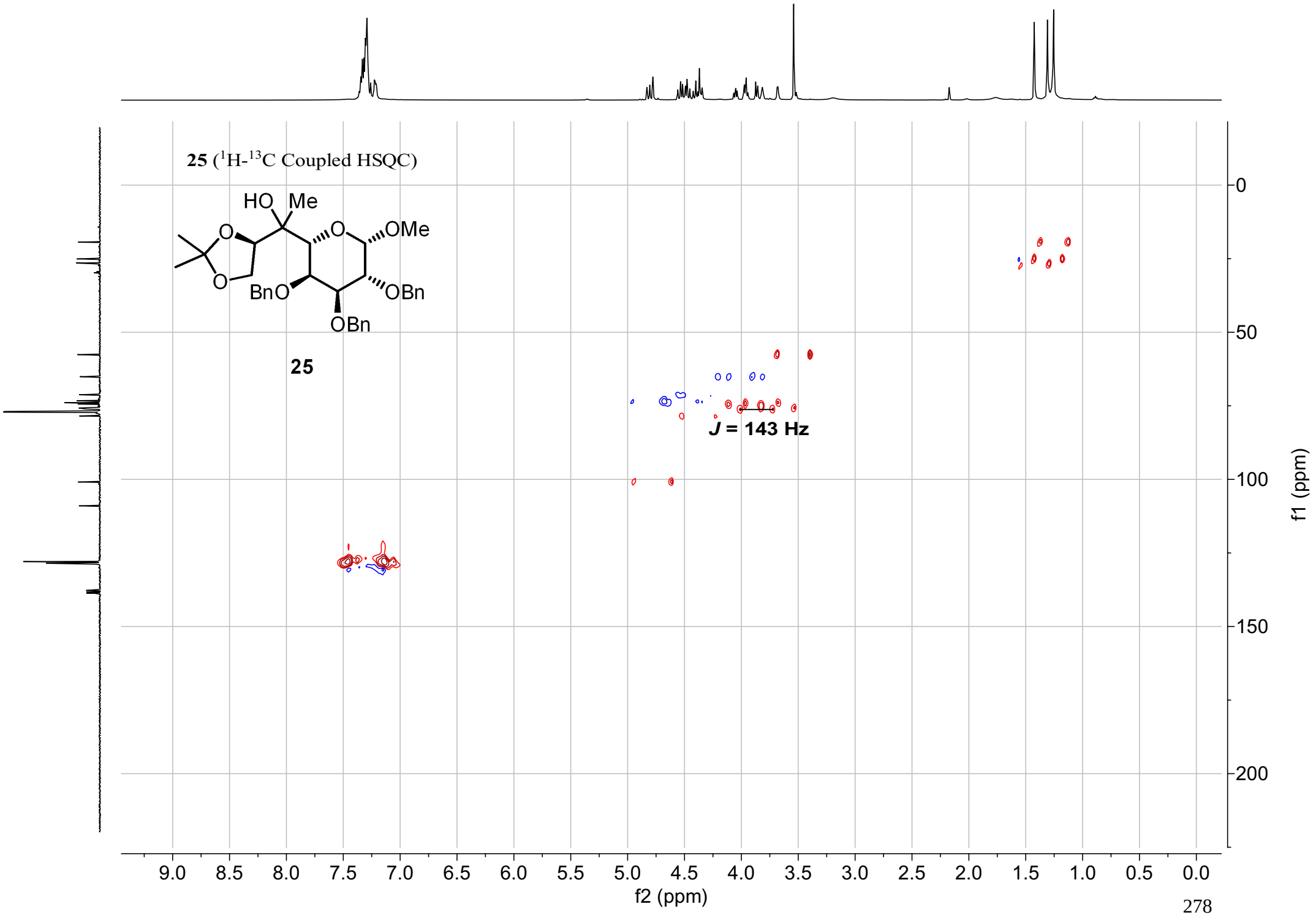
138.66
138.23
137.74
128.58
128.55
128.51
128.05
128.03
127.94
109.00
100.89
78.43
77.16
76.08
75.73
74.41
74.15
73.95
73.25
71.24
65.07
57.58
26.49
25.08
19.40

25 (^{13}C NMR, 126MHz, $CDCl_3$)

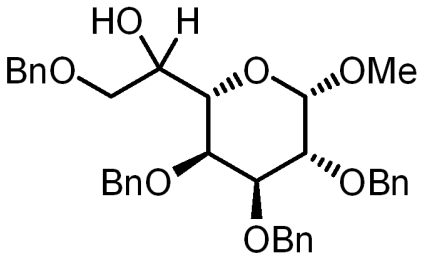


25



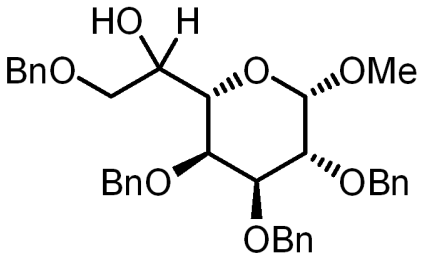

25 (1H-13C Coupled HSQC)
HO
Me
O
O
OMe
O
O
BnO
OBn
OBn
25
J = 143 Hz
0
50
100
150
200
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

26 (^{1}H NMR, 500MHz, $CDCl_3$)

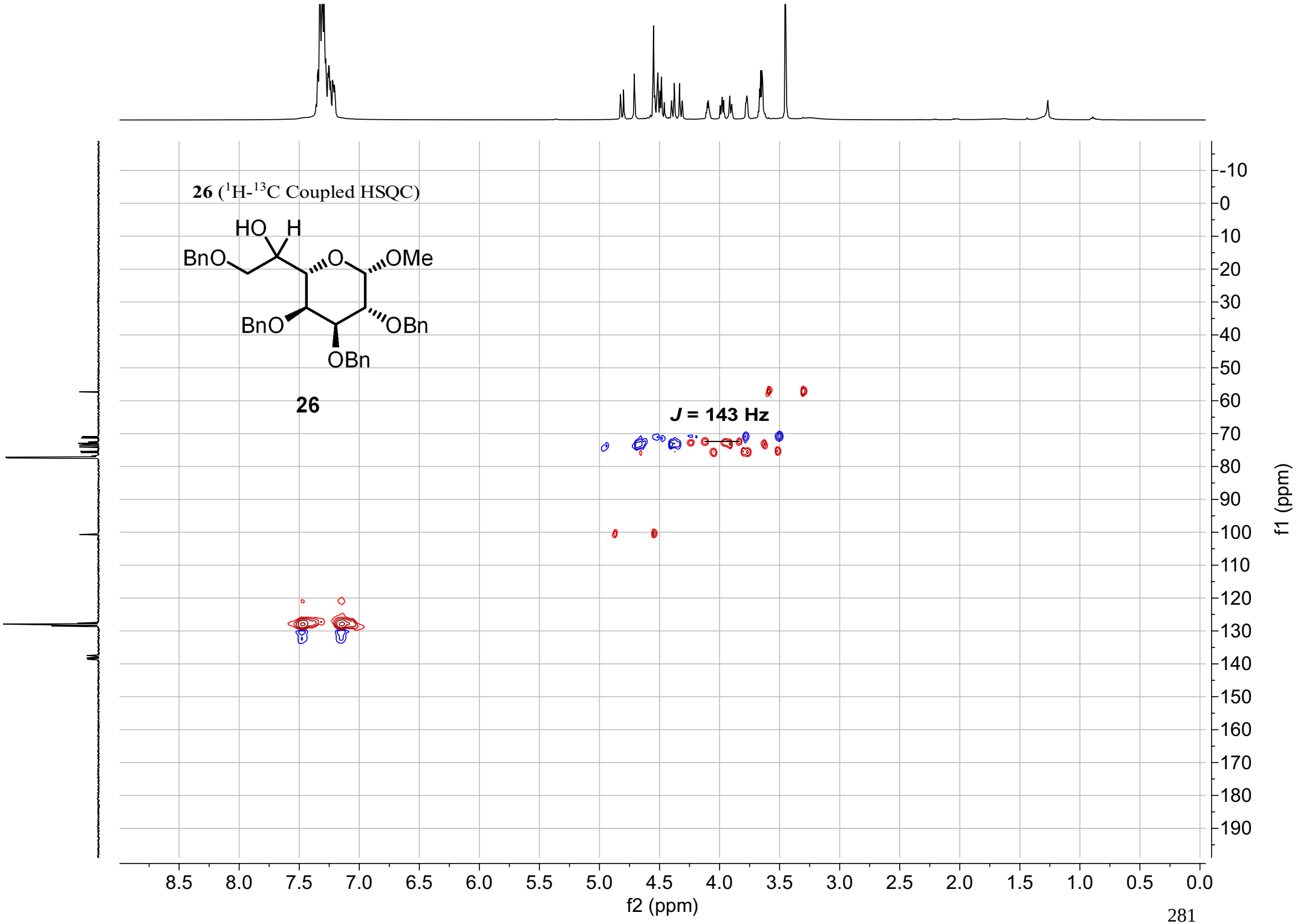


26

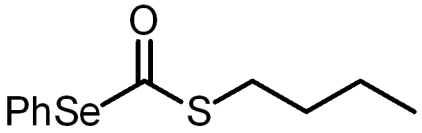
26 (^{13}C NMR, 126MHz, $CDCl_3$)



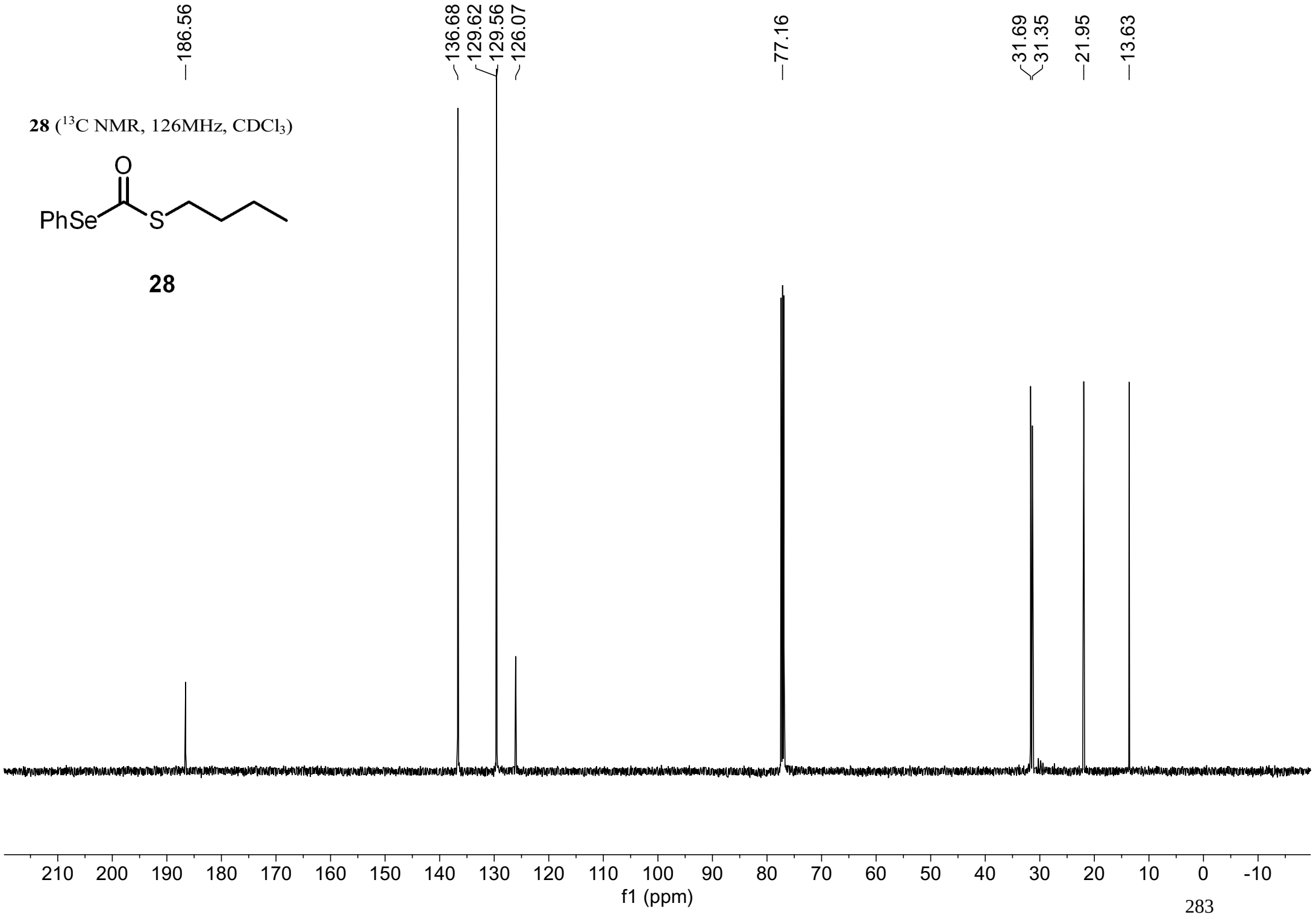
26


26 (1H-13C Coupled HSQC)
HO
H
BnO
O
OMe
BnO
OBn
OBn
26
J = 143 Hz
f2 (ppm)
f1 (ppm)

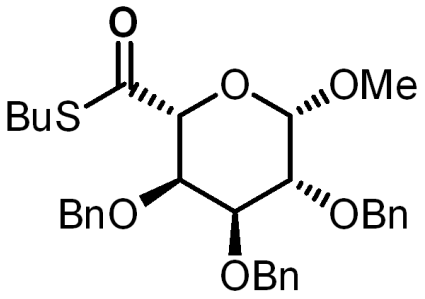
28 (^{1}H NMR, 500MHz, $CDCl_3$)



28

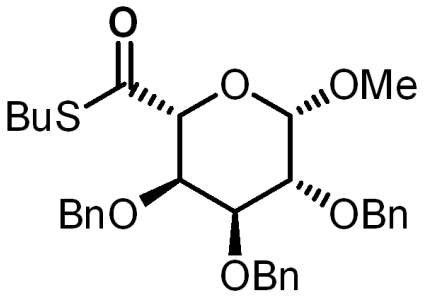

186.56
136.68
129.62
129.56
126.07
77.16
31.69
31.35
21.95
13.63
28 (13C NMR, 126MHz, CDCl3)
O
PhSe
S
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

29 (^{1}H NMR, 500MHz, $CDCl_3$)

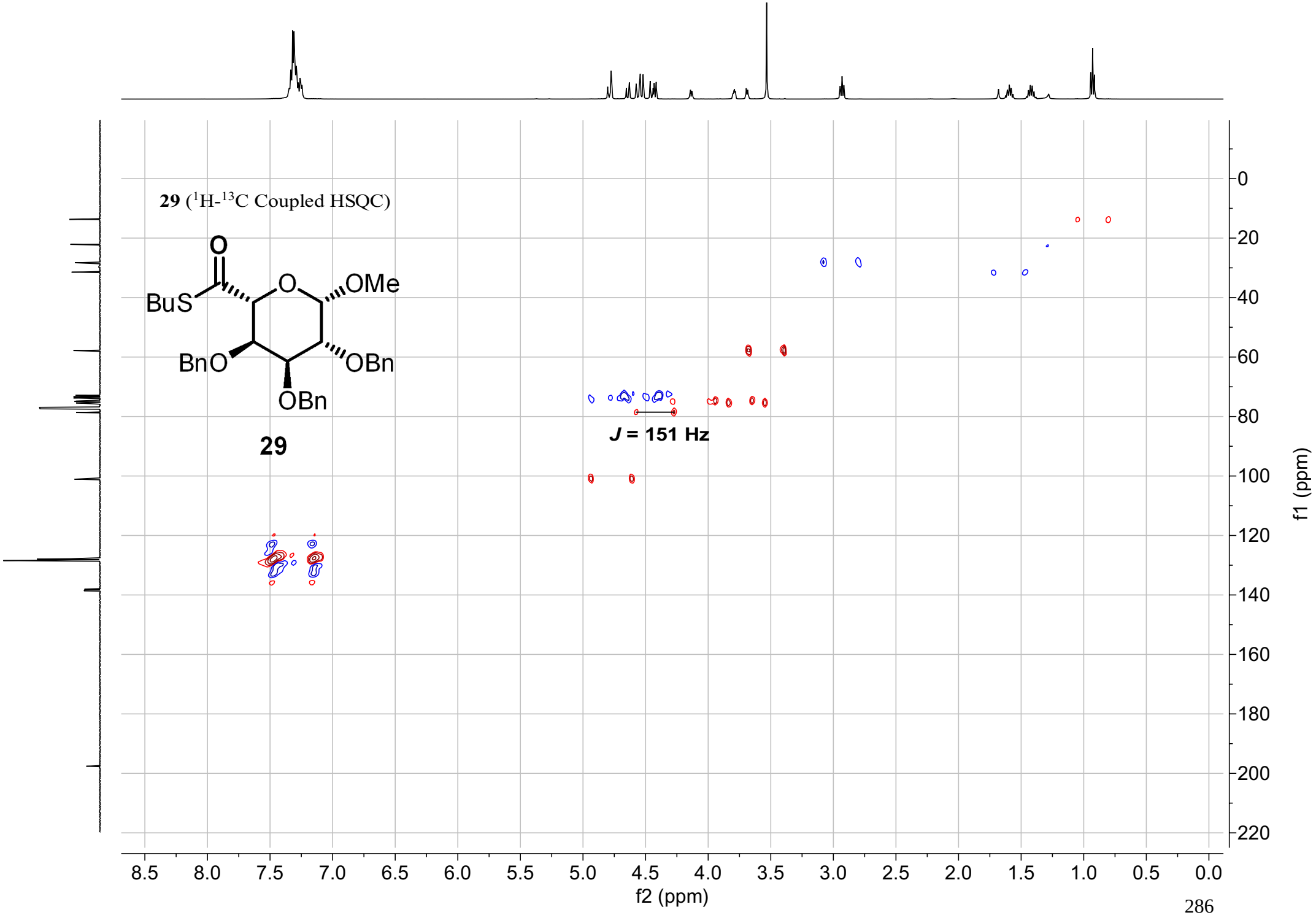


29

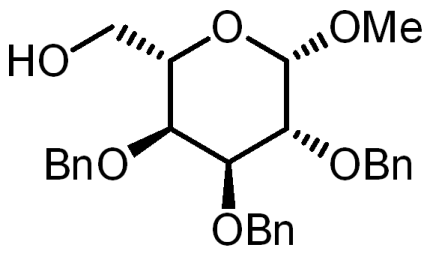
29 (^{13}C NMR, 126MHz, $CDCl_3$)



29

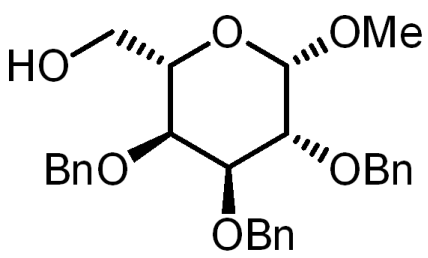

29 (1H-13C Coupled HSQC)
BuS
O
OMe
BnO
OBn
OBn
29
J = 151 Hz
f2 (ppm)
f1 (ppm)

30 (^{1}H NMR, 500MHz, $CDCl_3$)

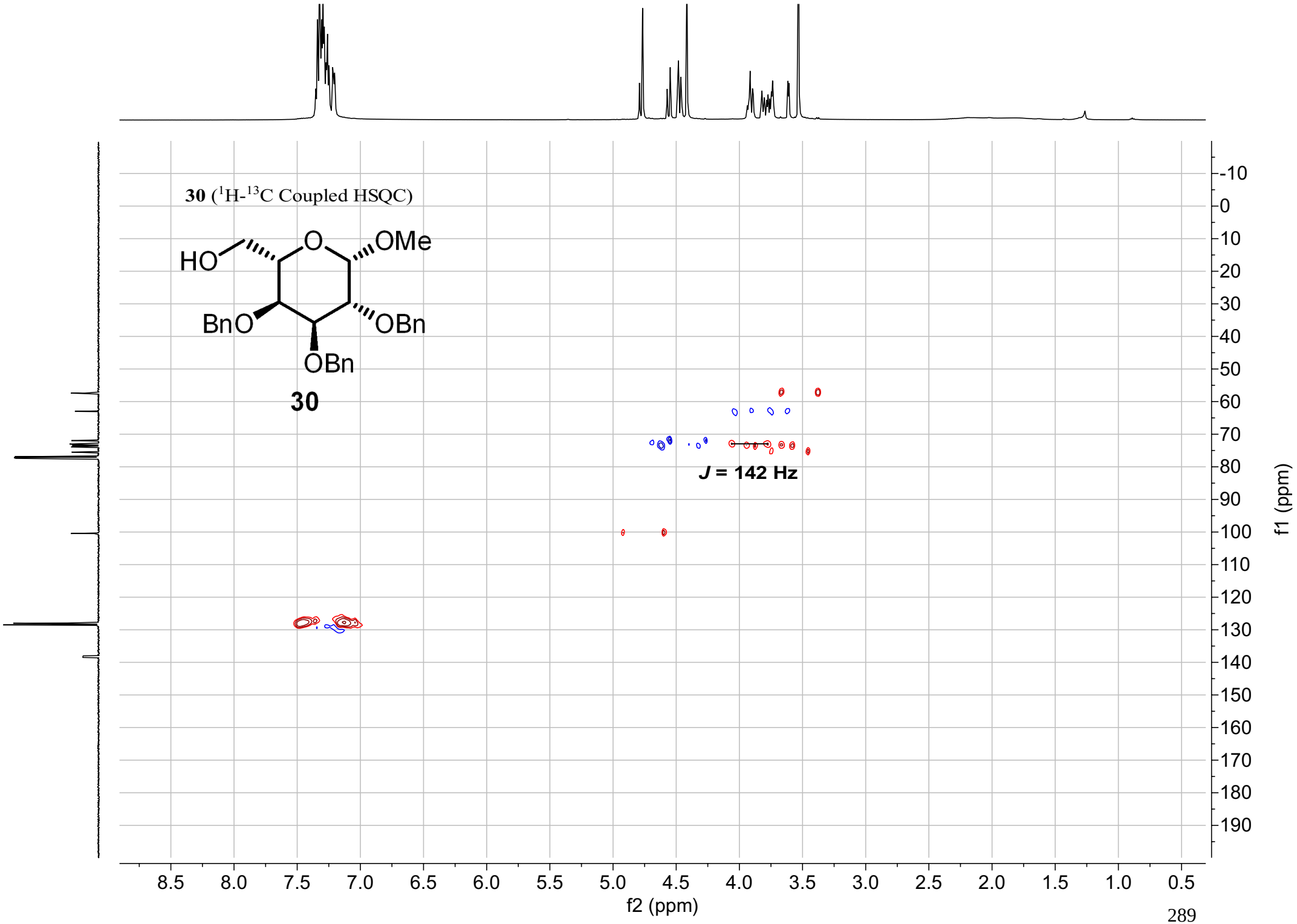


30

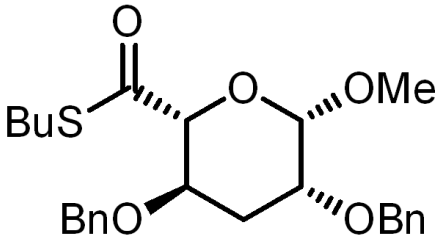
30 (^{13}C NMR, 126MHz, $CDCl_3$)



30

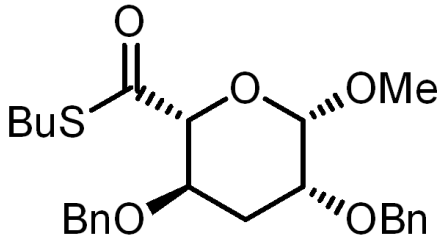

30 (1H-13C Coupled HSQC)
HO
O
OMe
BnO
OBn
OBn
30
J = 142 Hz
f2 (ppm)
f1 (ppm)

31b (^{1}H NMR, 500MHz, $CDCl_3$)

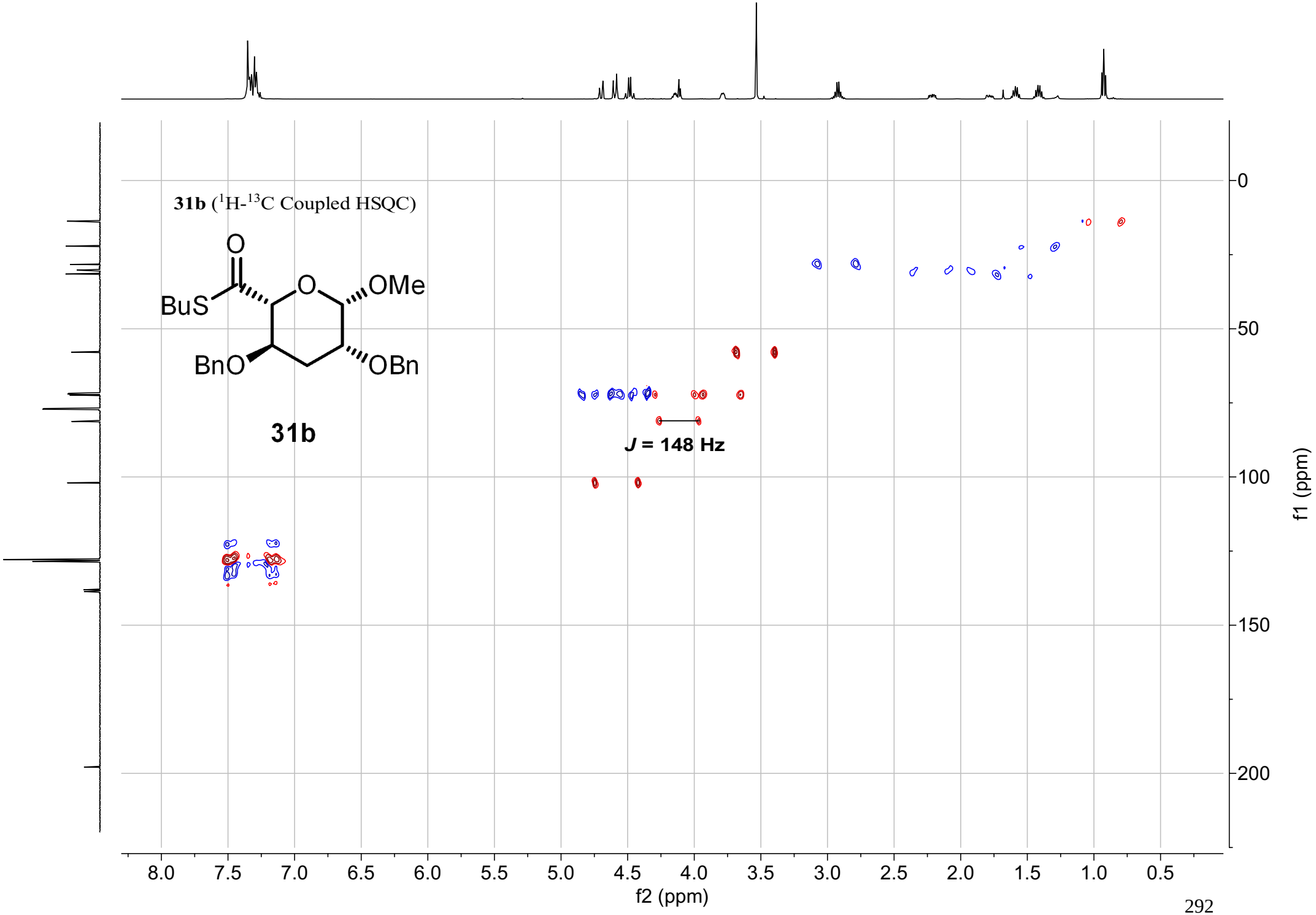


31b

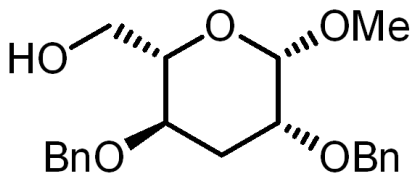
31b (^{13}C NMR, 126MHz, $CDCl_3$)



31b

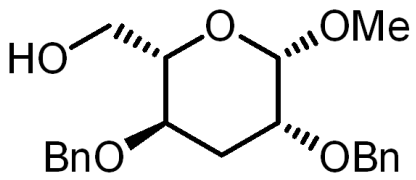

31b (1H-13C Coupled HSQC)
O
BuS
O
OMe
BnO
OBn
31b
J = 148 Hz
0
50
100
150
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

32 (^{1}H NMR, 500MHz, $CDCl_3$)

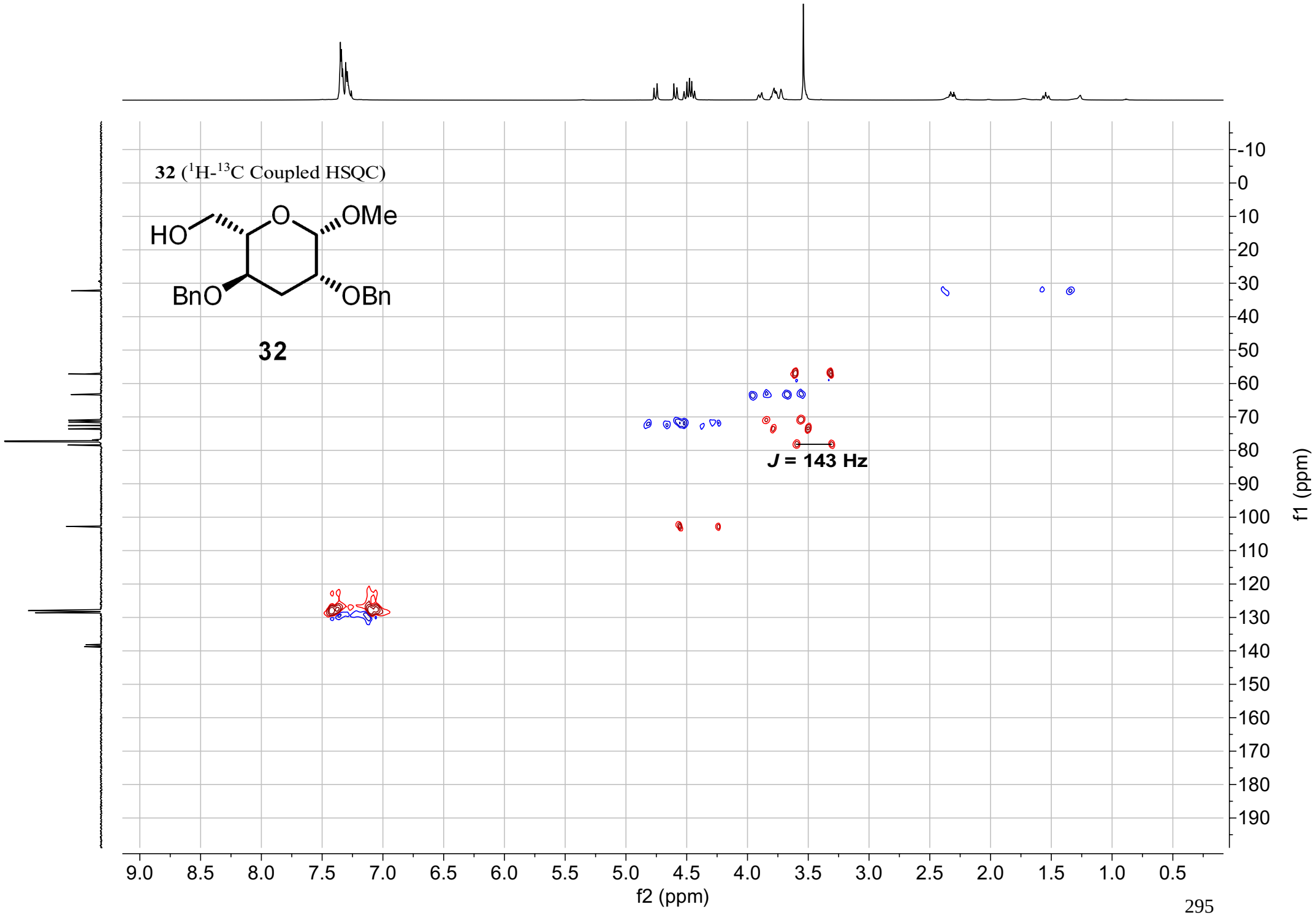


32

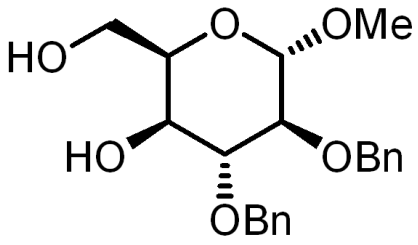
32 (^{13}C NMR, 126MHz, $CDCl_3$)



32

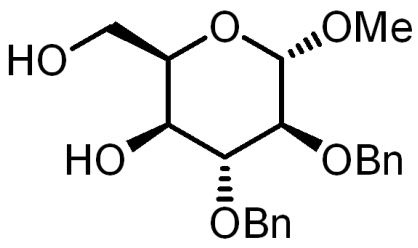

32 (1H-13C Coupled HSQC)
HO
O
OMe
BnO
OBn
32
J = 143 Hz
f2 (ppm)
f1 (ppm)

33 (^{1}H NMR, 500MHz, $CDCl_3$)



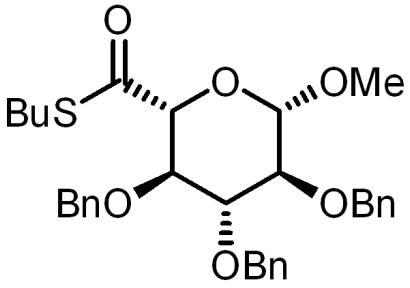
33

33 (^{13}C NMR, 126MHz, $CDCl_3$)

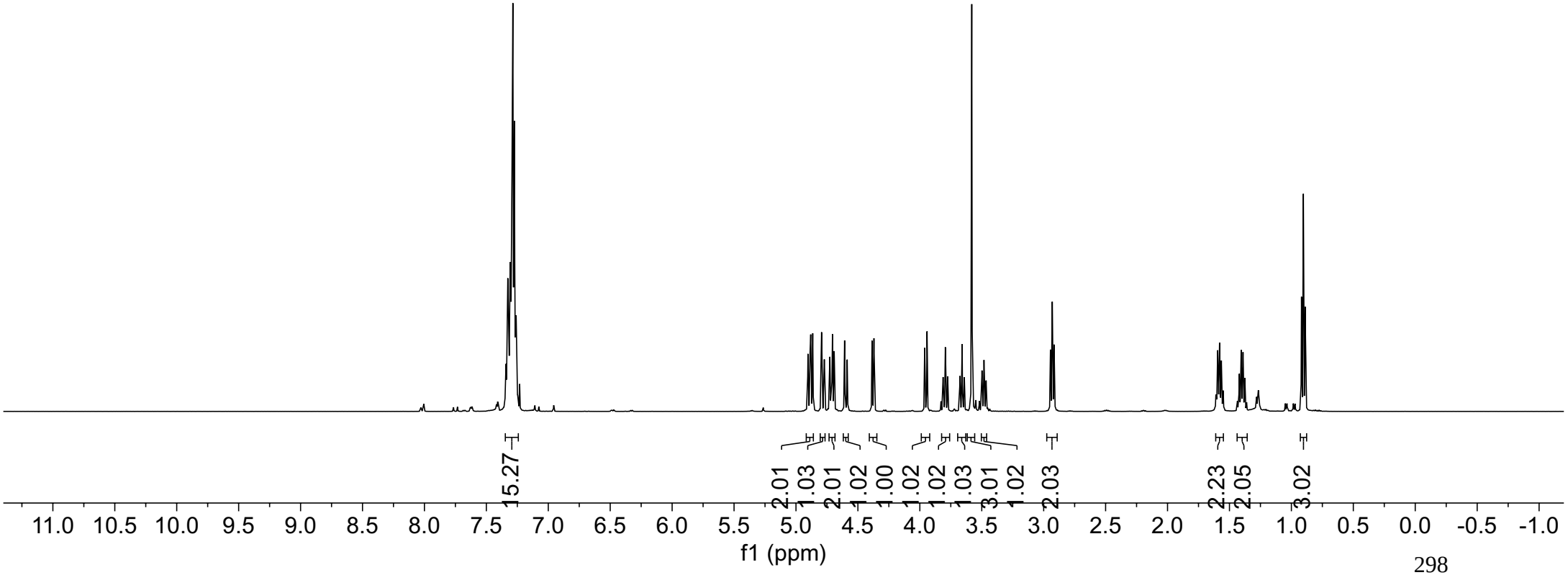


33

34 (^{1}H NMR, 500MHz, $CDCl_3$)

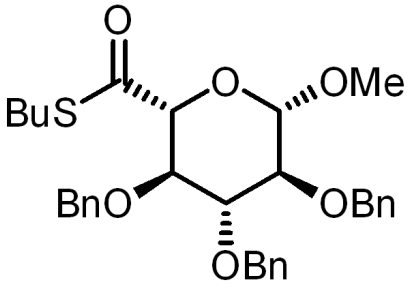


34

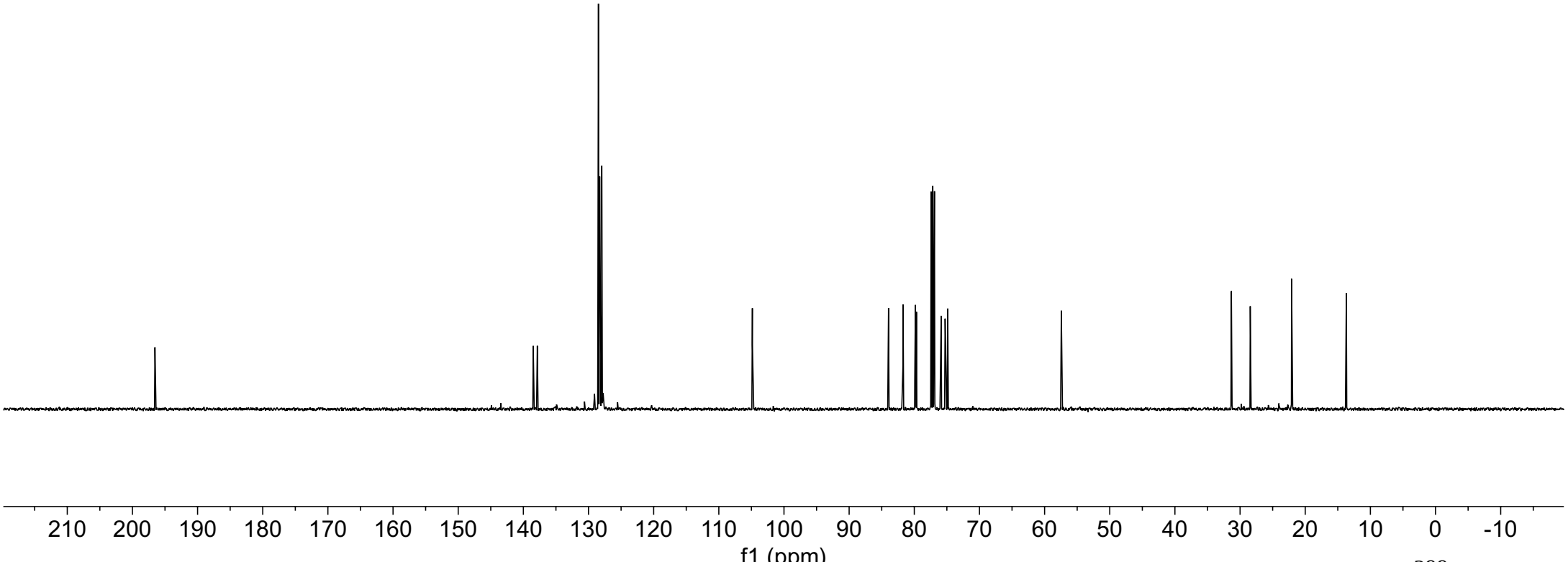


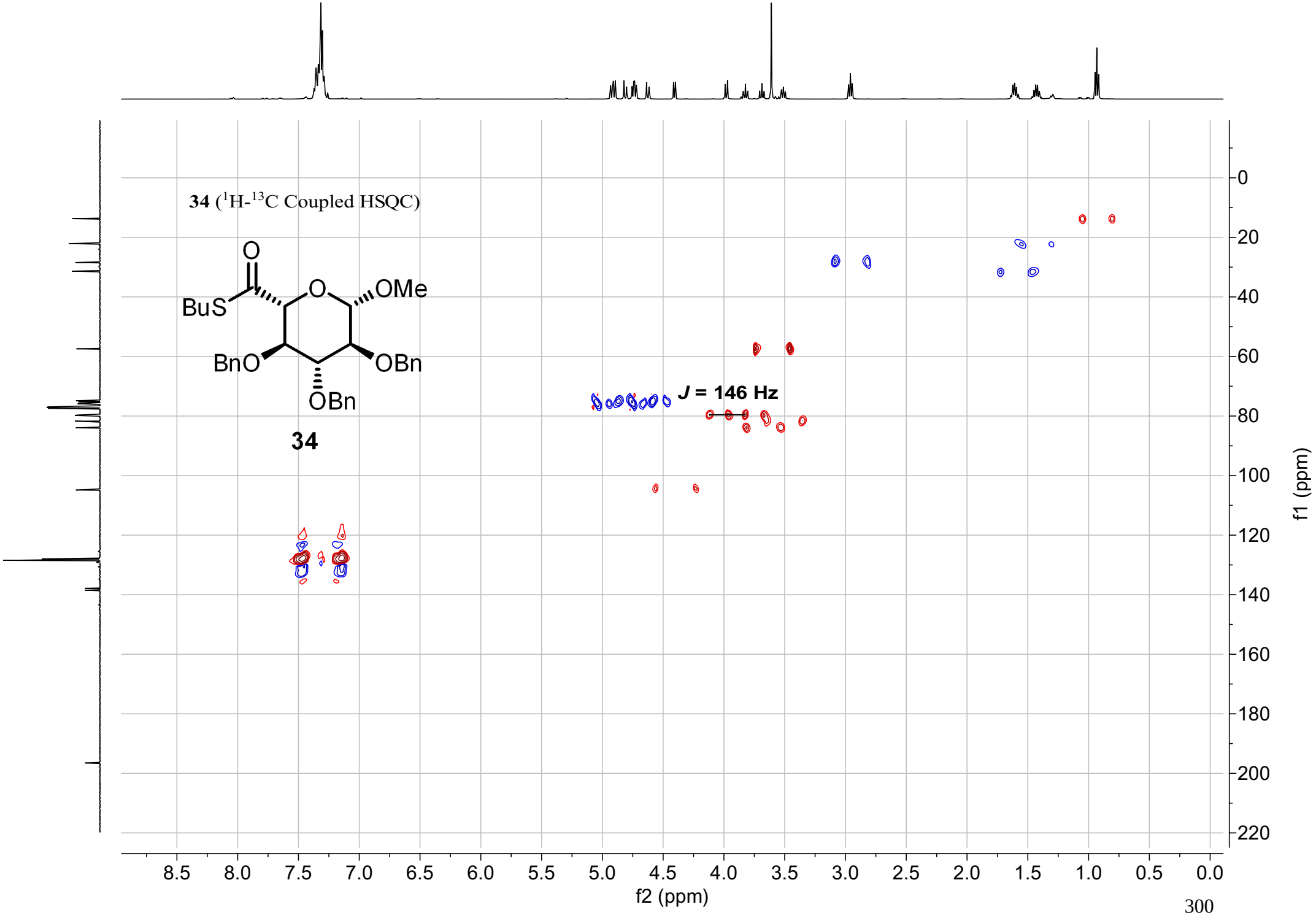
196.54
138.48
138.40
137.86
128.48
128.45
128.29
128.19
127.96
127.92
127.82
127.77
104.85
83.95
81.72
79.83
79.66
77.16
75.87
75.27
74.87
57.43
31.33
28.44
22.10
13.68

34 (^{13}C NMR, 126MHz, $CDCl_3$)

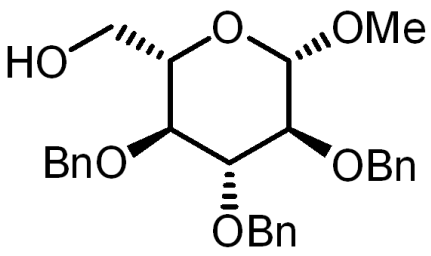


34



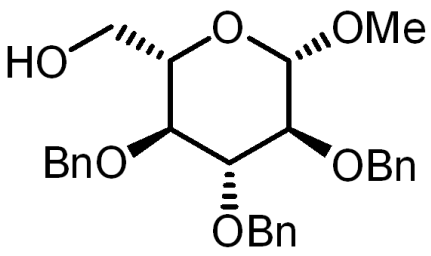

34 (1H-13C Coupled HSQC)
BuS
O
OMe
BnO
OBn
OBn
34
J = 146 Hz
f2 (ppm)
f1 (ppm)

35 (^{1}H NMR, 500MHz, $CDCl_3$)

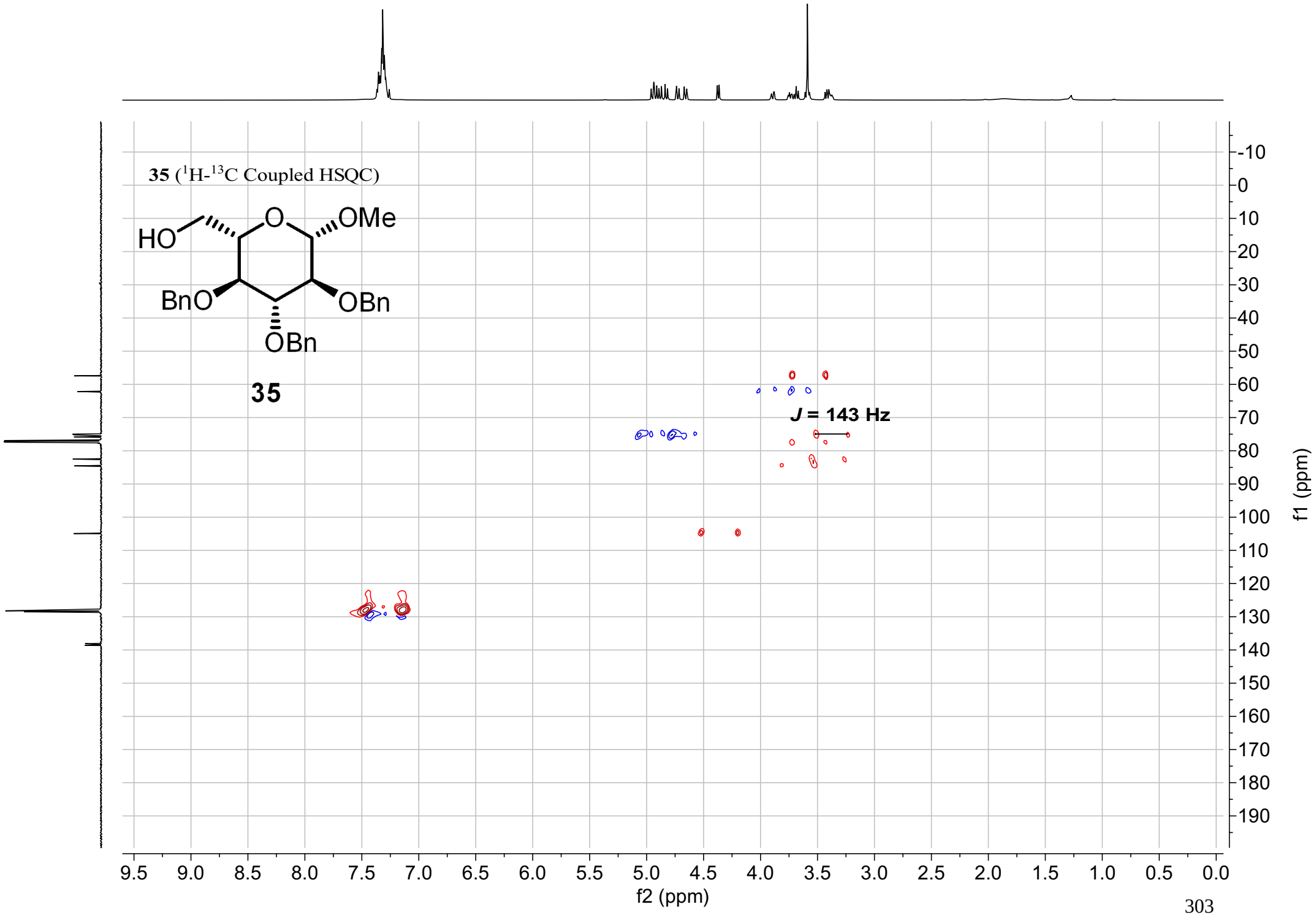


35

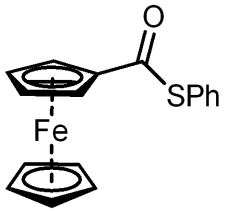
35 (^{13}C NMR, 126MHz, $CDCl_3$)



35

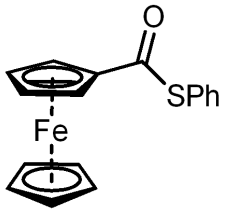

35 (1H-13C Coupled HSQC)
HO
O
OMe
BnO
OBn
OBn
35
J = 143 Hz
f2 (ppm)
f1 (ppm)

36 (^{1}H NMR, 500MHz, $CDCl_3$)



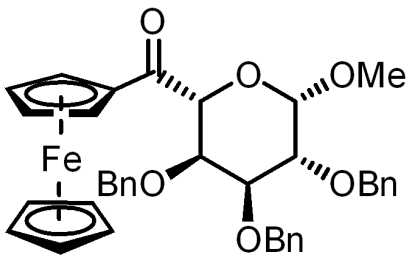
36

36 (^{13}C NMR, 126MHz, $CDCl_3$)



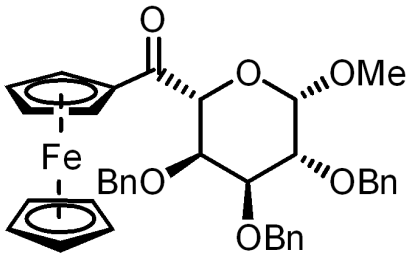
36

39 (^{1}H NMR, 500MHz, $CDCl_3$)

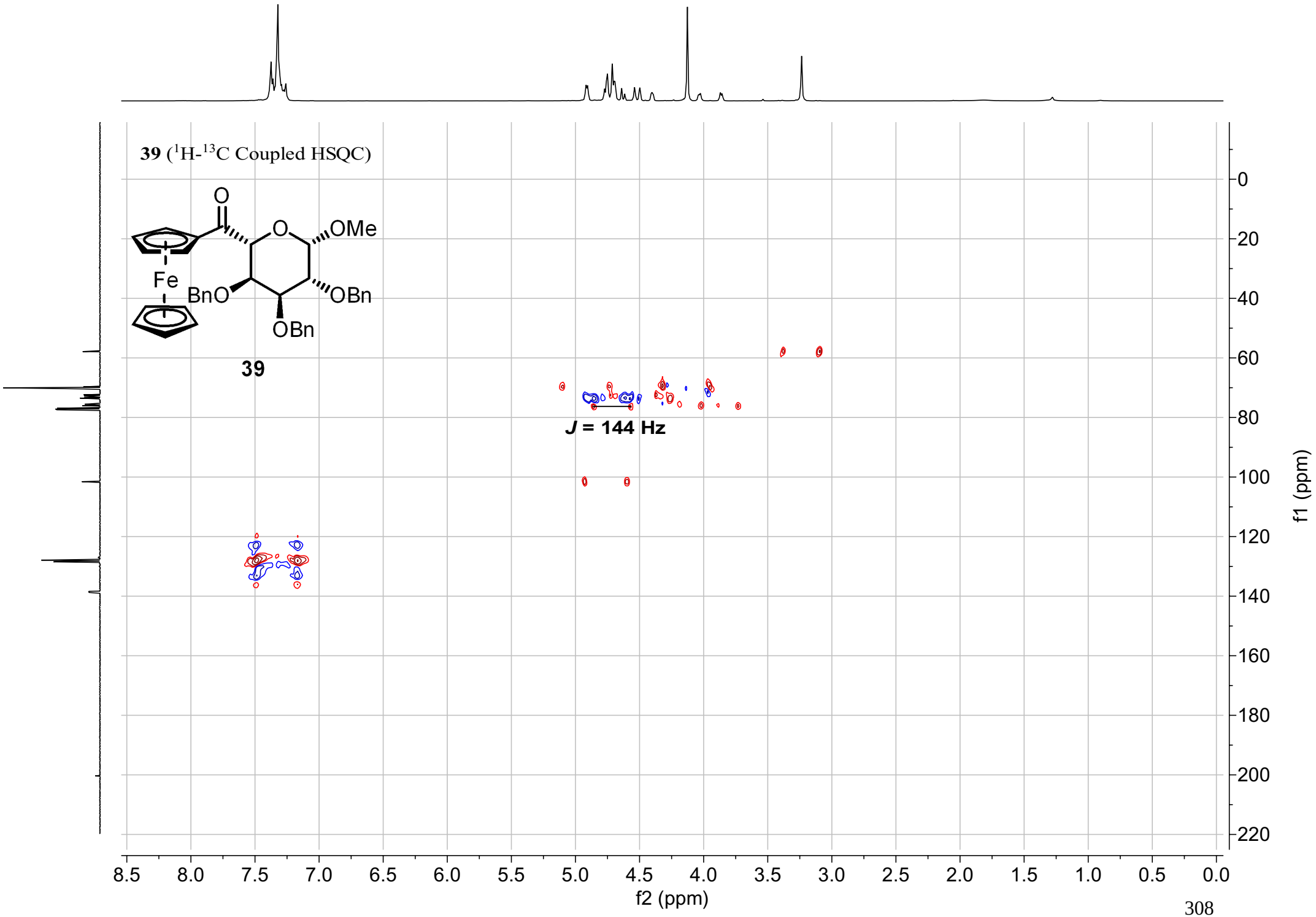


39

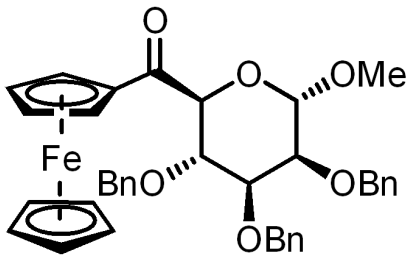
39 (^{13}C NMR, 126MHz, $CDCl_3$)



39

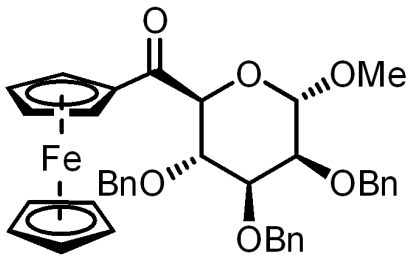

39 (1H-13C Coupled HSQC)
O
O
OMe
Fe
BnO
OBn
OBn
39
J = 144 Hz
f1 (ppm)
f2 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
140
160
180
200
220

40 (^{1}H NMR, 500MHz, $CDCl_3$)

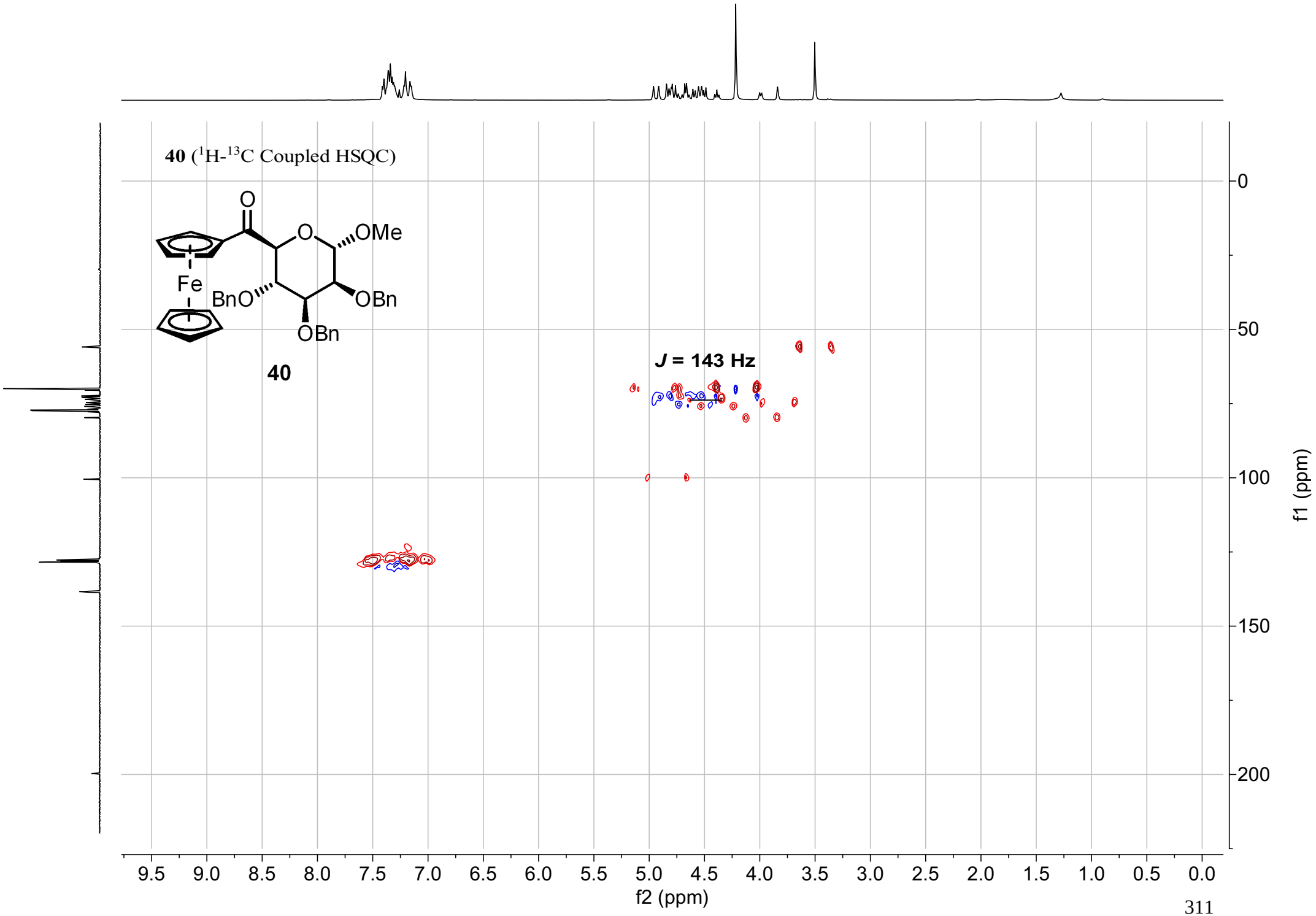


40

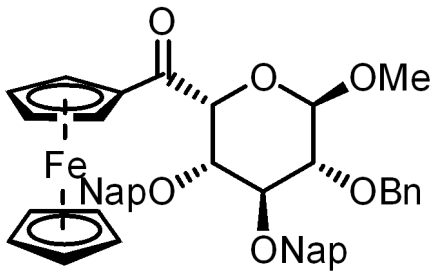
40 (^{13}C NMR, 126MHz, $CDCl_3$)



40


40 (1H-13C Coupled HSQC)
O
O
OMe
Fe
BnO
OBn
OBn
40
J = 143 Hz
0
50
100
150
200
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

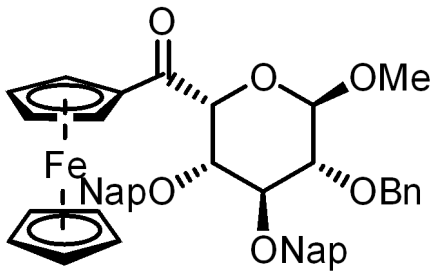
41 (^{1}H NMR, 500MHz, $CDCl_3$)



41

198.38
138.58
136.20
135.56
133.43
133.27
133.06
133.03
128.51
128.19
128.07
128.03
127.99
127.80
127.79
127.68
127.12
126.52
126.47
126.12
126.04
125.95
125.91
125.86
105.61
84.49
82.06
78.93
77.71
77.16
75.97
75.82
75.33
74.89
73.34
73.08
70.30
70.01
69.74
57.43

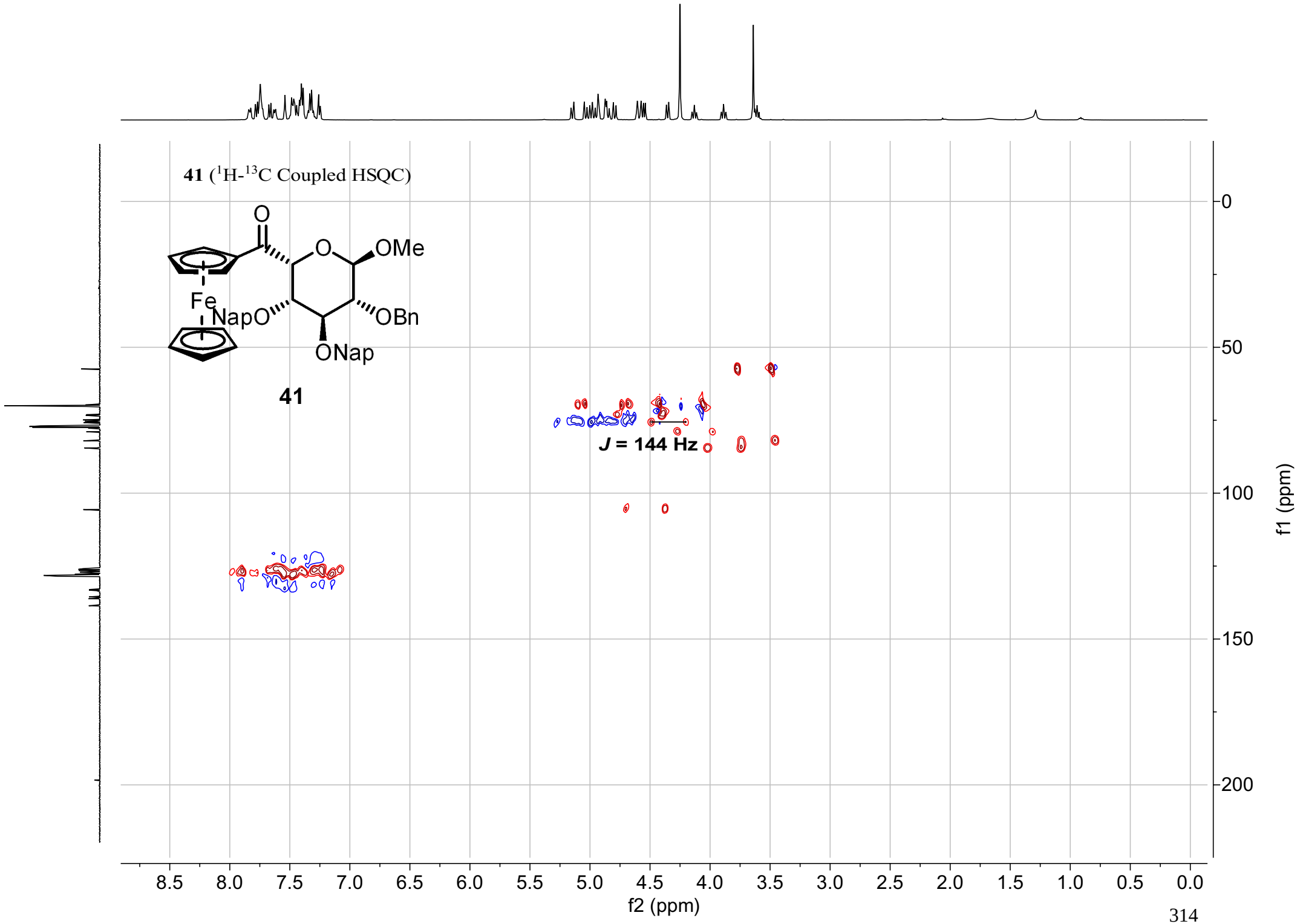
41 (^{13}C NMR, 126MHz, $CDCl_3$)



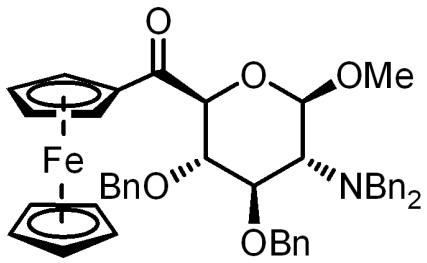
41

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)

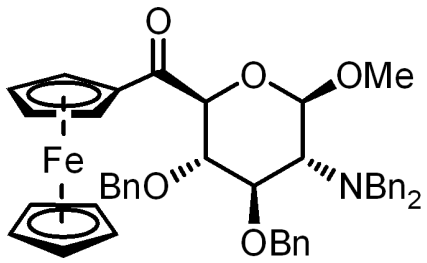

41 (1H-13C Coupled HSQC)
O
O
OMe
Fe
NapO
OBn
ONap
41
J = 144 Hz
0
50
100
150
200
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

42 (^{1}H NMR, 500MHz, $CDCl_3$)

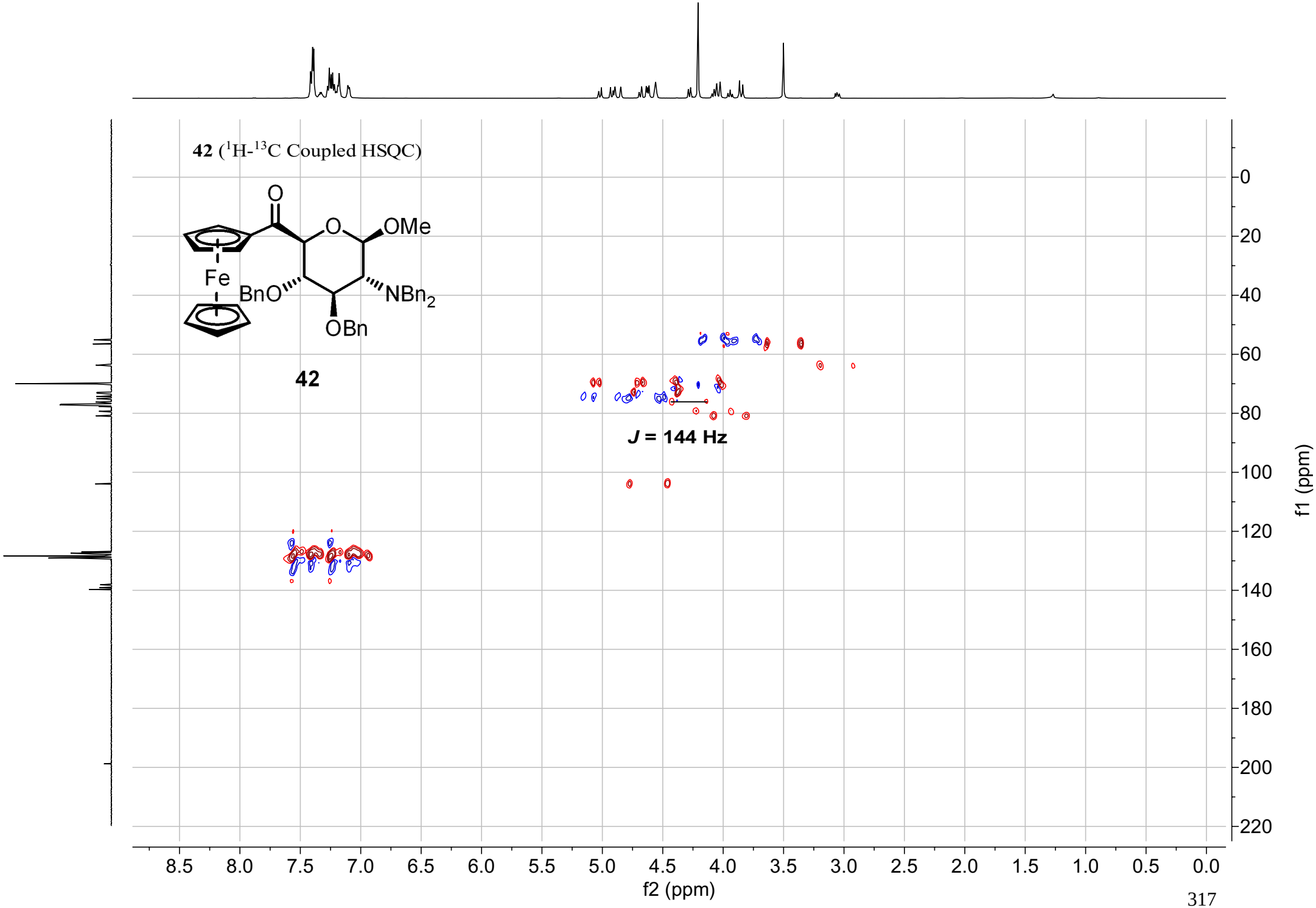


42

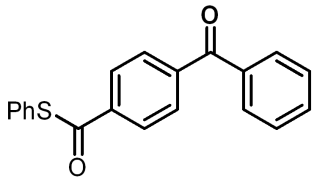
42 (^{13}C NMR, 126MHz, $CDCl_3$)



42

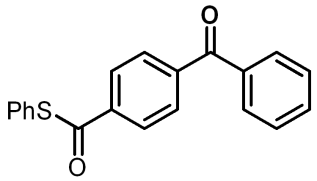

42 (1H-13C Coupled HSQC)
O
O
OMe
Fe
BnO
NBn2
OBn
42
J = 144 Hz
f1 (ppm)
f2 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
140
160
180
200
220

S1 (^{1}H NMR, 500MHz, $CDCl_3$)



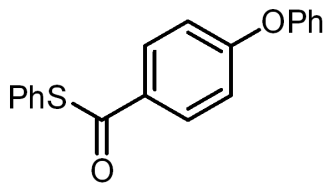
S1

S1 (^{13}C NMR, 126MHz, $CDCl_3$)

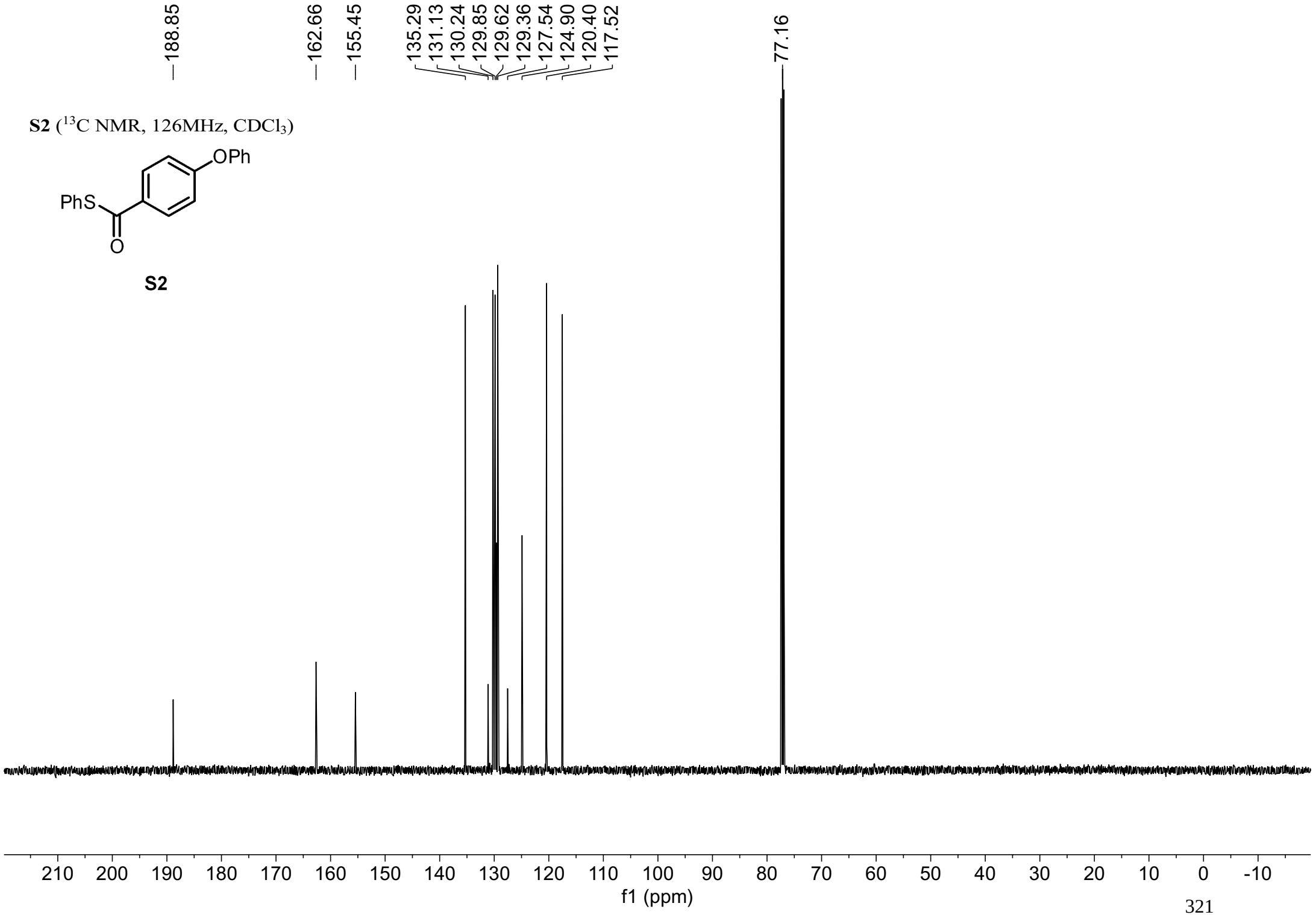


S1

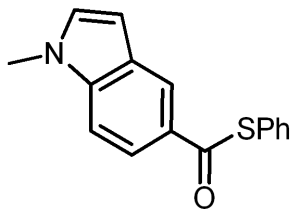
S2 (^{1}H NMR, 500MHz, $CDCl_3$)



S2

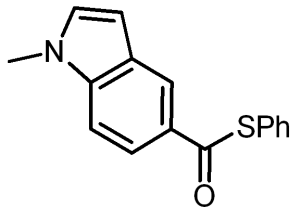

188.85
162.66
155.45
135.29
131.13
130.24
129.85
129.62
129.36
127.54
124.90
120.40
117.52
77.16
S2 (13C NMR, 126MHz, CDCl3)
OPh
PhS
O
S2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S3 (^{1}H NMR, 400MHz, $CDCl_3$)



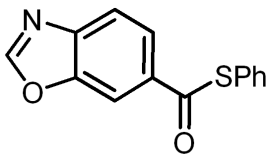
S3

S3 (^{13}C NMR, 126MHz, $CDCl_3$)



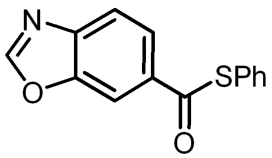
S3

S4 (^{1}H NMR, 400MHz, $CDCl_3$)



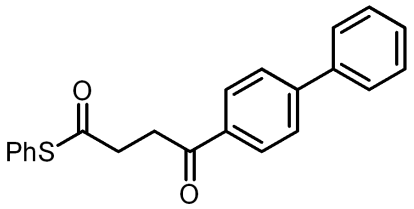
S4

S4 (^{13}C NMR, 126MHz, $CDCl_3$)



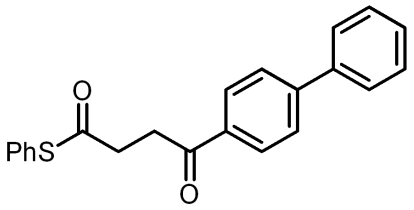
S4

S5 (^{1}H NMR, 400MHz, $CDCl_3$)



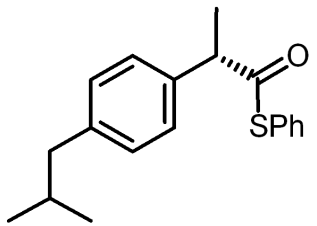
S5

S5 (^{13}C NMR, 126MHz, $CDCl_3$)



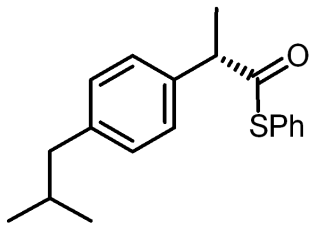
S5

S6 (^{1}H NMR, 500MHz, $CDCl_3$)



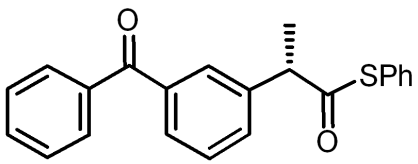
S6

S6 (^{13}C NMR, 126MHz, $CDCl_3$)

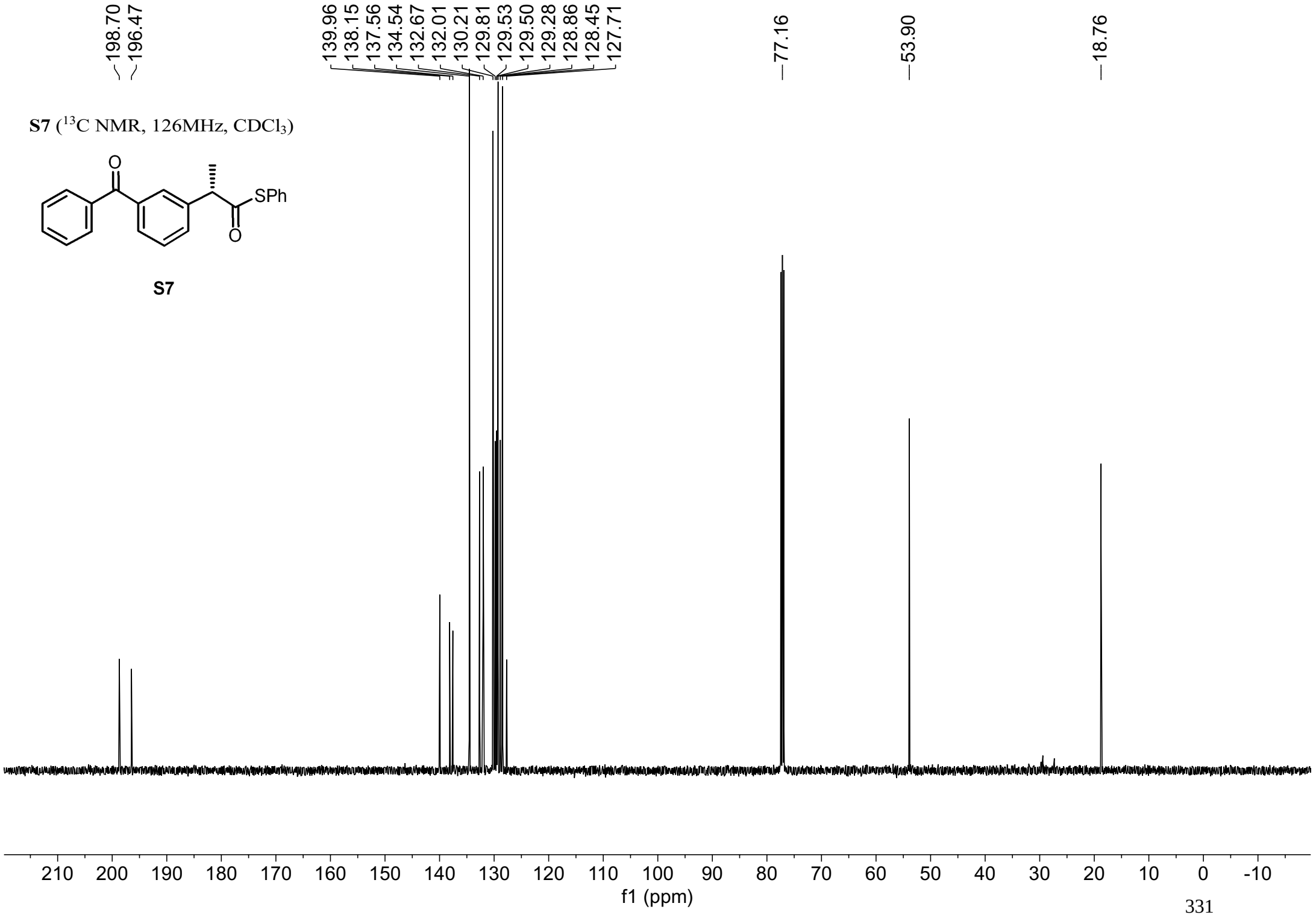


S6

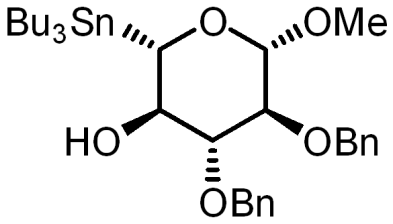
S7 (^{1}H NMR, 500MHz, $CDCl_3$)



S7

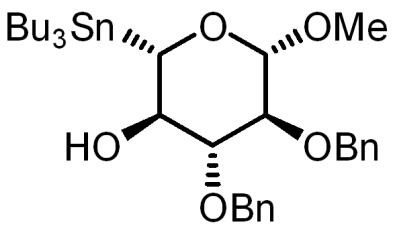

198.70
196.47
139.96
138.15
137.56
134.54
132.67
132.01
130.21
129.81
129.53
129.50
129.28
128.86
128.45
127.71
77.16
53.90
18.76
S7 (13C NMR, 126MHz, CDCl3)
O
SPh
O
S7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

S8 (^{1}H NMR, 500MHz, $CDCl_3$)

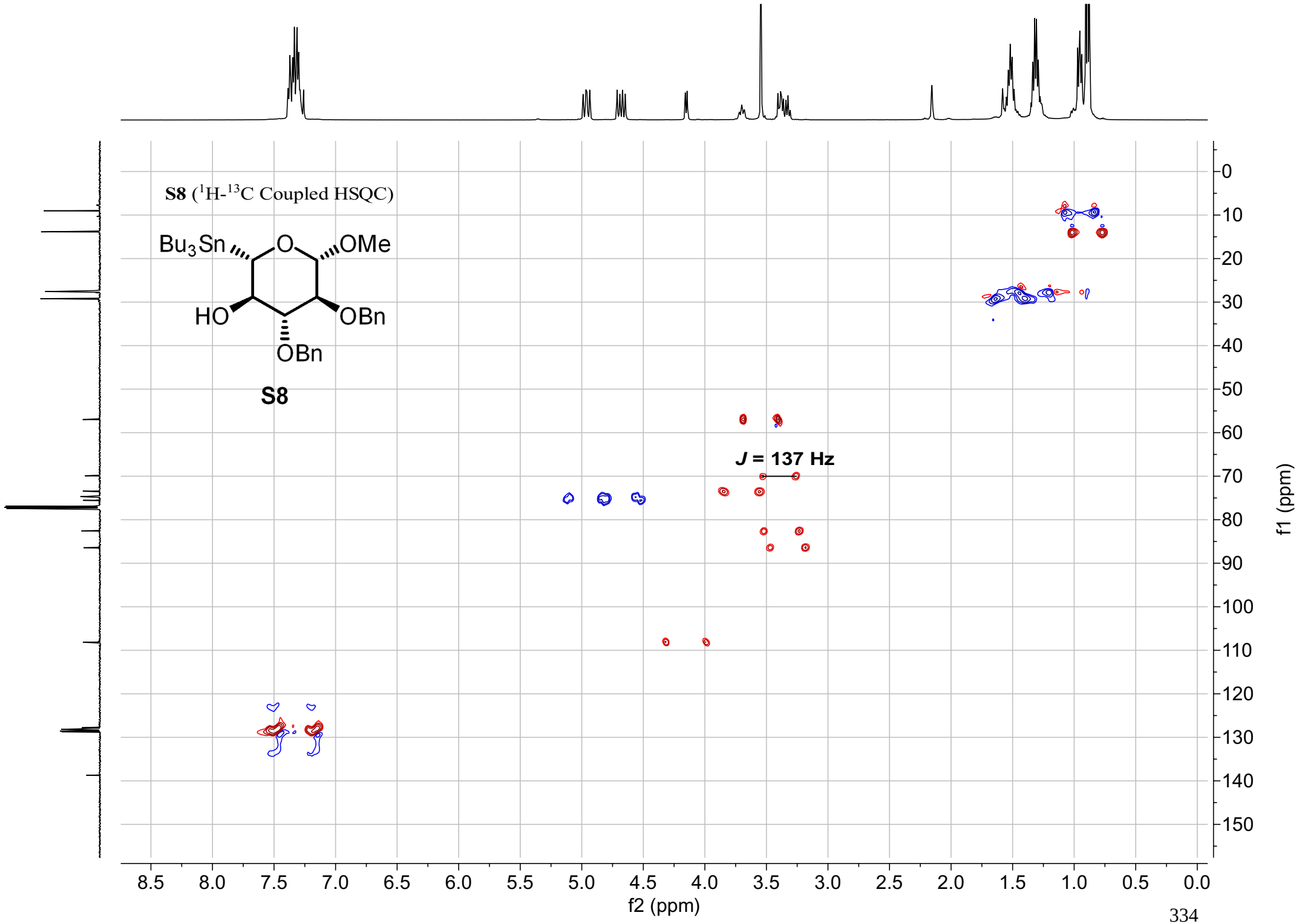


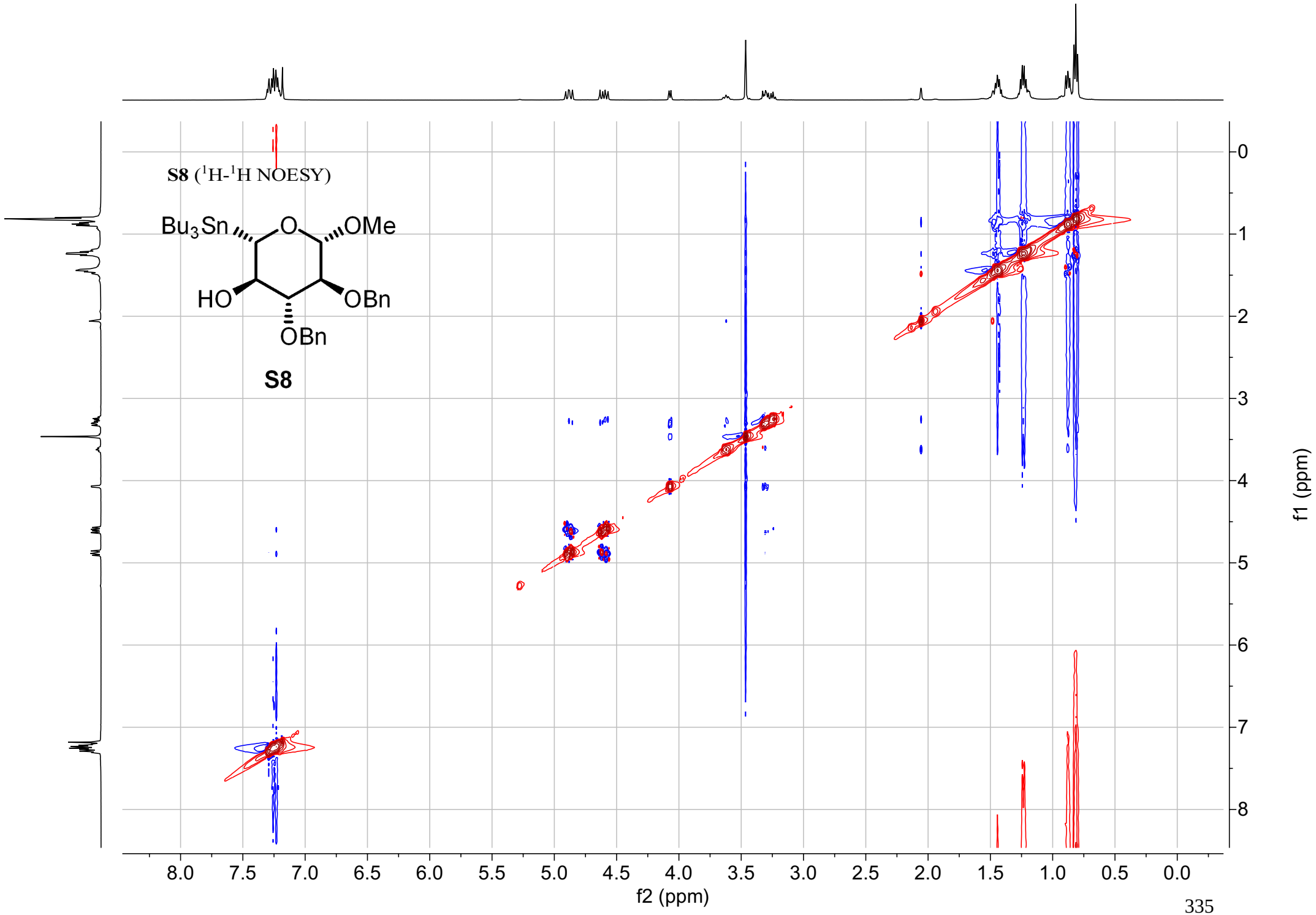
S8

S8 (^{13}C NMR, 126MHz, $CDCl_3$)

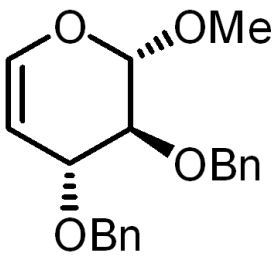


S8


S8 (1H-13C Coupled HSQC)
Bu3Sn
O
OMe
HO
OBn
OBn
S8
J = 137 Hz
f2 (ppm)
f1 (ppm)

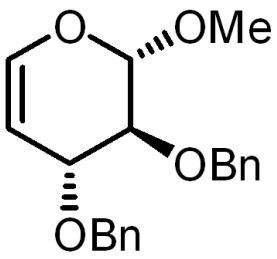

S8 (1H-1H NOESY)
Bu3Sn
O
OMe
HO
OBn
OBn
S8
f2 (ppm)
f1 (ppm)

S9 (^{1}H NMR, 500MHz, $CDCl_3$)



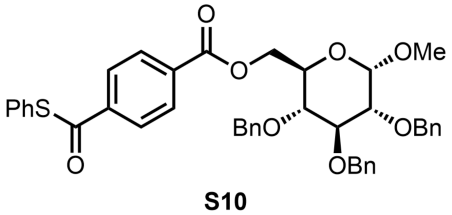
S9

S9 (^{13}C NMR, 126MHz, $CDCl_3$)



S9

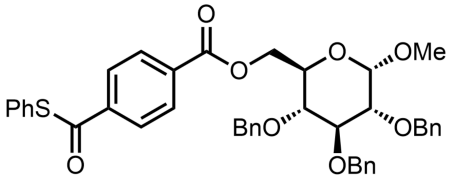
S10 (^{1}H NMR, 500MHz, $CDCl_3$)



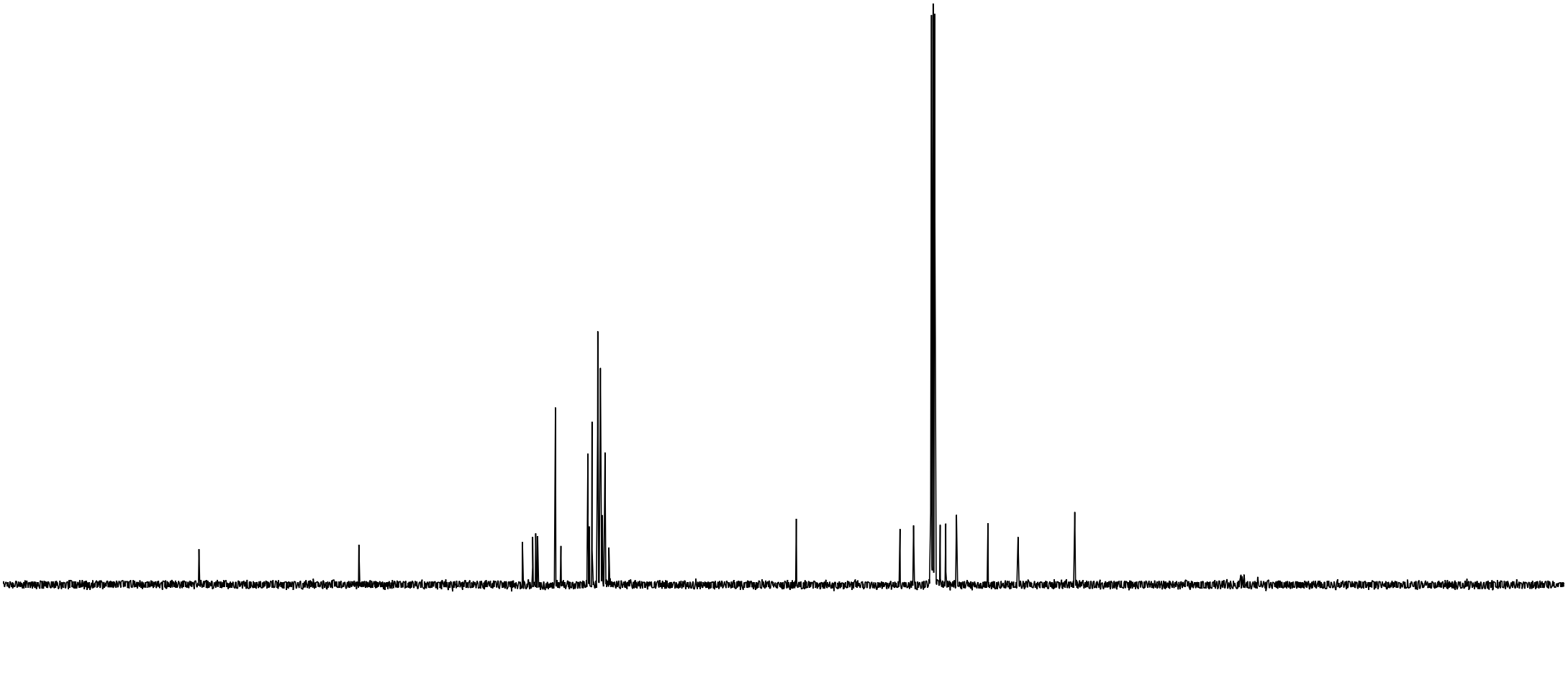
S10

189.84
165.30
140.19
138.62
138.16
137.86
135.13
134.28
130.15
129.93
129.52
128.66
128.63
128.24
128.22
128.21
128.14
128.09
127.92
127.52
126.92
98.17
82.25
80.16
77.54
77.16
76.08
75.22
73.58
68.75
64.13
55.42

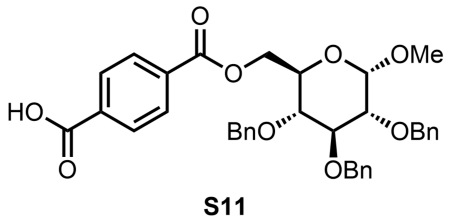
S10 (^{13}C NMR, 126MHz, $CDCl_3$)



S10

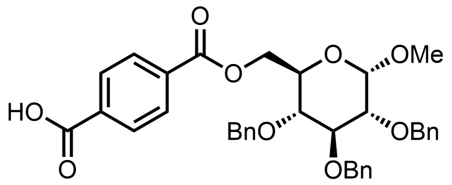


S11 (^{1}H NMR, 500MHz, $CDCl_3$)



S11

S11 (^{13}C NMR, 126MHz, $CDCl_3$)



S11