

## SUPPORTING INFORMATION

### STEREOSPECIFIC NICKEL-CATALYZED CROSS-COUPPLING REACTIONS OF BENZYLIC ETHERS WITH ISOTOPICALLY LABELED GRIGNARD REAGENTS

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## I. GENERAL PROCEDURES

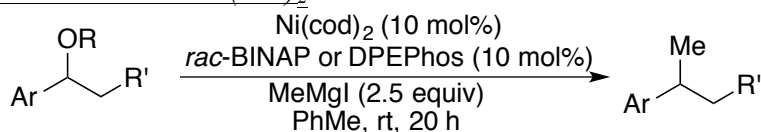
All reactions were carried out under a N<sub>2</sub> atmosphere, unless otherwise noted. All glassware was either oven dried or flame-dried before use. Toluene (PhMe), diethyl ether (Et<sub>2</sub>O), benzene (C<sub>6</sub>H<sub>6</sub>), methanol (MeOH), and tetrahydrofuran (THF) were degassed with argon and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 12 hours) to remove H<sub>2</sub>O. Other solvents were purchased “anhydrous” commercially. <sup>1</sup>H NMR were recorded on Bruker DRX-400 (400 MHz <sup>1</sup>H, 100 MHz <sup>13</sup>C), or CRYO-500 (500 MHz <sup>1</sup>H, 125.7 MHz <sup>13</sup>C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal trimethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), triplet of doublets (td), quartet (q), quintet (quint), sextet (sext), septet (sept), multiplet (m), apparent doublet (ad)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the solvent resonance as the internal standard (CDCl<sub>3</sub>, δ 77.16 ppm). NMR data were collected at 25 °C. Infrared spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm<sup>-1</sup>). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60Å F254 precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with potassium permanganate (KMnO<sub>4</sub>) solution. Flash chromatography was performed using Silica Gel 60 (170-400 mesh) from Fisher Scientific or silver impregnated silica gel.<sup>1</sup> Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. Optical rotations were measured with a Rudolph Research Analytical Autopol III Automatic Polarimeter. SFC determinations of enantiopurity were performed on a Berger Analytical instrument using a Daicel™ Chiralpak® column (AD-H; 100 bar, 215 nm, 50 °C). High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center.

Bis(1,5-cyclooctadiene)nickel was purchased from Strem, stored in a glove box freezer (-20 °C) under an atmosphere of N<sub>2</sub> and used as received. All ligands were purchased from Strem or Sigma Aldrich and were stored under N<sub>2</sub> atmosphere and used as received. Isotopically-labeled alkyl and aryl halides were purchased from Cambridge Isotope Laboratories, stored in a freezer (-20 °C) and used as received. All Grignard reagents were titrated with iodine prior to use.<sup>2</sup> All other chemicals were purchased commercially and used as received, unless otherwise noted.

## II. SYNTHESIS AND CHARACTERIZATION

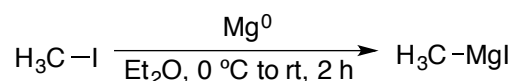
### A. General Procedures for Cross-Coupling Reactions

#### METHOD A: KUMADA-TYPE CROSS-COUPLING OF BENZYLIC ETHERS WITH METHYL GRIGNARD REAGENT USING Ni(cod)<sub>2</sub>



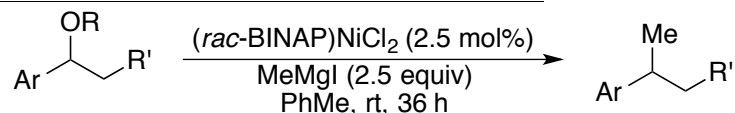
In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with substrate (1.0 equiv), Ni(cod)<sub>2</sub> (0.10 equiv), *rac*-BINAP or DPEPhos (0.10 equiv), and toluene. MeMgI (2.5 equiv) was then added dropwise. After 20 h the reaction was removed from the glovebox, quenched with methanol, filtered through a plug of silica gel (neat Et<sub>2</sub>O), and concentrated in vacuo. Phenyltrimethylsilane (PhTMS) was added as internal standard and a <sup>1</sup>H NMR yield was obtained before purification by flash column chromatography.

### 1) PREPARATION OF METHYL GRIGNARD REAGENT



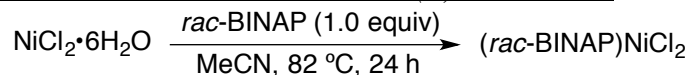
Under a N<sub>2</sub> atmosphere, a 3-necked flask equipped with a stir bar, reflux condenser, and Schlenk filtration apparatus was charged with magnesium turnings (1.1 g, 45 mmol, 1.5 equiv). The flask and magnesium turnings were then flame-dried under vacuum and the flask was backfilled with N<sub>2</sub>. Anhydrous Et<sub>2</sub>O (7 mL) and a crystal of iodine (ca. 2 mg) were added to the flask. Freshly distilled iodomethane (1.9 mL, 31 mmol, 1.0 equiv) was slowly added at 0 °C over 30 min to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature then filtered through the fritted Schlenk filter into the Schlenk bomb under N<sub>2</sub> atmosphere. The magnesium turnings were washed with Et<sub>2</sub>O (2 x 1.0 mL) then the Schlenk bomb was sealed, removed, and placed under an argon atmosphere. The resulting methyl Grignard reagent was typically between 2.4 and 3.0 M as titrated by Knochel's method<sup>2</sup> and could be stored (sealed under argon atmosphere or in a glovebox) for up to 4 weeks.

### METHOD B: KUMADA-TYPE CROSS-COUPLING OF BENZYLIC ETHERS WITH METHYL GRIGNARD REAGENT USING AN AIR STABLE CATALYST



On the benchtop, a flame-dried 500 mL round bottom flask equipped with a stir bar was charged with substrate (1.0 equiv) and (*rac*-BINAP)NiCl<sub>2</sub> (0.025 equiv), then evacuated and backfilled with N<sub>2</sub> three times. PhMe was added, followed by methyl Grignard reagent (2.5 equiv). After stirring for 36 h the reaction was quenched with methanol, filtered through a plug of silica gel (neat Et<sub>2</sub>O), and concentrated in vacuo. Phenyltrimethylsilane (PhTMS) was added as internal standard and a <sup>1</sup>H NMR yield was obtained before purification by flash column chromatography.

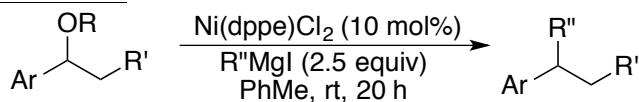
### 1) PREPARATION OF AIR STABLE NICKEL(II) COMPLEX



The title compound was prepared according to a procedure by Jamison.<sup>3</sup> To a 100 mL round bottom flask equipped with a stir bar was added NiCl<sub>2</sub>•6H<sub>2</sub>O (0.480 g, 2.00 mmol, 1.00 equiv). The contents were then flame-dried under vacuum until the green color had almost completely given way to orange. After cooling to room temperature, *rac*-BINAP (1.24 g, 2.00 mmol, 1.00 equiv) was quickly added, at which point the flask was equipped with reflux condenser and placed under N<sub>2</sub> atmosphere. Anhydrous MeCN (40 mL) was added, and the mixture was stirred at reflux for 24 h. Upon cooling to room temperature, the mixture was filtered, yielding a fine brown powder. This powder was washed with cold EtOH (2 x 10 mL) and dried under vacuum

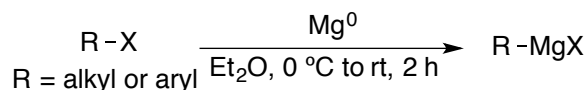
overnight (1.41 g, 1.89 mmol, 95%). The resulting brown powder was insoluble in most organic solvents and was stored on the benchtop for periods exceeding 5 weeks with no apparent loss of reactivity. **m.p.** 358–360 °C; **HRMS** (TOF MS ES+) *m/z* calcd for C<sub>44</sub>H<sub>32</sub>ClNiP<sub>2</sub> (M – Cl)<sup>+</sup> 715.1021, found 715.1029.

METHOD C: KUMADA-TYPE CROSS-COUPLING OF BENZYLIC ETHERS WITH ARYL AND ALKYL GRIGNARD REAGENTS



On the benchtop, a flame-dried 7 mL vial equipped with a stir bar was charged with substrate (1.0 equiv) and Ni(dppe)Cl<sub>2</sub> (0.10 equiv), flushed with N<sub>2</sub>, and capped with a Teflon-lined septum. PhMe was added, followed by the alkyl or aryl Grignard reagent (2.5 equiv). After stirring for 20 h the reaction was quenched with methanol, filtered through a plug of silica gel (neat Et<sub>2</sub>O), and concentrated in vacuo. Phenyltrimethylsilane (PhTMS) was added as internal standard and a <sup>1</sup>H NMR yield was obtained before purification by flash column chromatography.

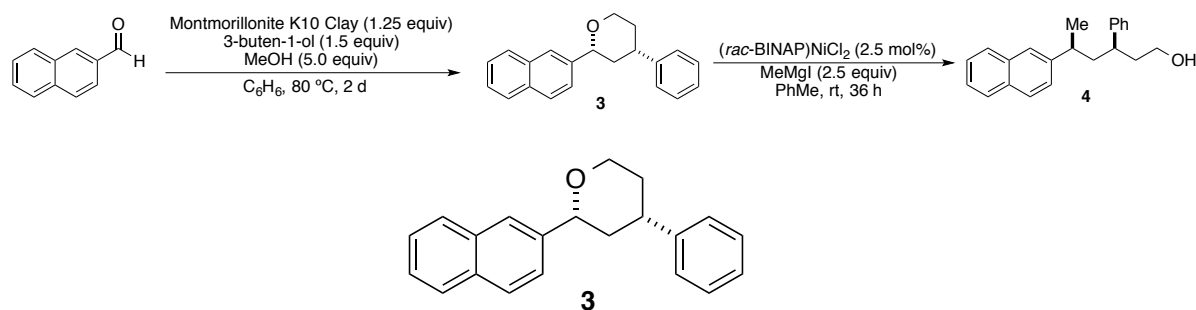
1) PREPARATION OF ALKYL OR ARYL GRIGNARD REAGENT



A 2-necked flask equipped with a stir bar and reflux condenser was charged with magnesium turnings (3.0 equiv). The reaction apparatus was flame-dried under vacuum and cooled under N<sub>2</sub>. Anhydrous Et<sub>2</sub>O and a crystal of iodine (ca. 2 mg) were added to the flask. The organohalide (1.0 equiv) was added slowly over 30 min at 0 °C to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature. The resulting Grignard reagent was typically between 1.5 and 2.5 M as titrated by Knochel's method.<sup>2</sup>

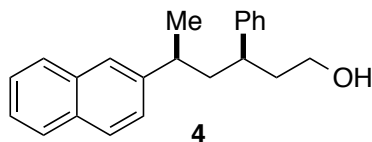
**B. Large Scale Cross-Coupling Reaction**

**Scheme SI 1. Synthesis of Cross-coupling Product 4**



**cis-(±)-2-(2-naphthyl)-4-phenyl-tetrahydropyran (3).** The title compound was prepared according to a modified procedure reported by Dintzer.<sup>4</sup> Montmorillonite K10 clay was activated by heating at 200 °C for 2 h immediately prior to use. 2-Naphthaldehyde (9.00 g, 30.0 mmol, 1.00 equiv) and Montmorillonite K10 clay (12.0 g, 1.25 equiv by mass) were added to flame dried baffled round bottom flask equipped with stir bar. The flask was evacuated and backfilled

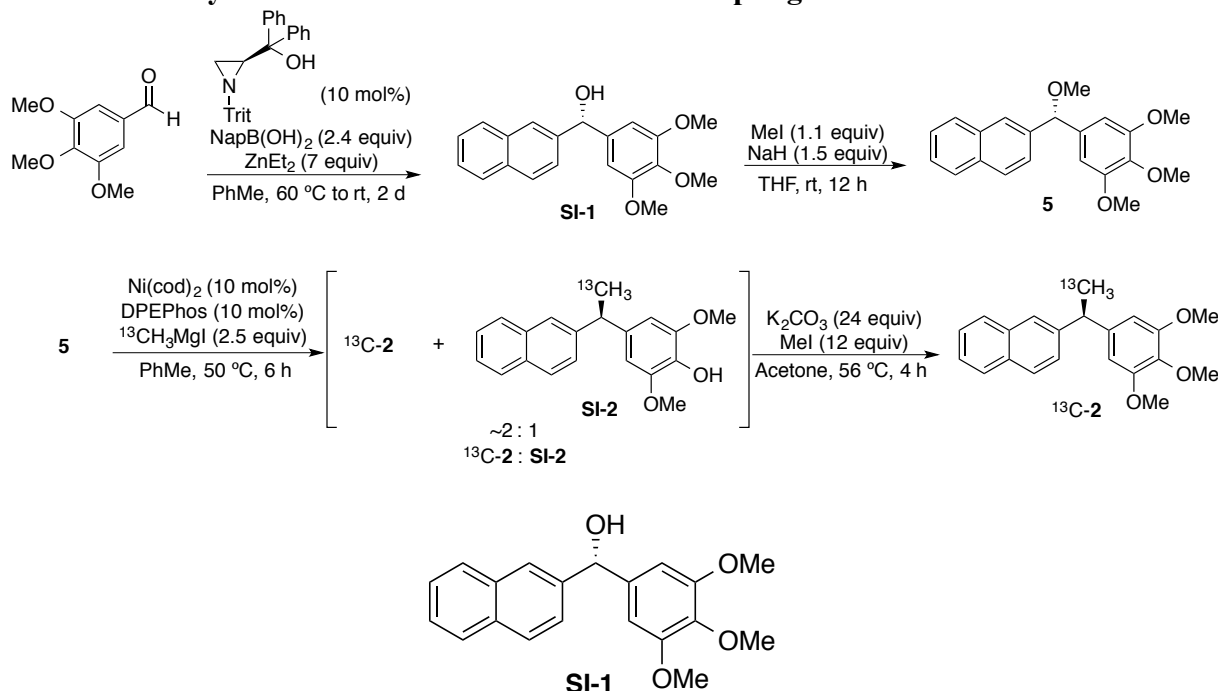
with N<sub>2</sub> at which point anhydrous benzene (500 mL), anhydrous MeOH (12 mL, 150 mmol, 5.0 equiv), and 3-buten-1-ol (7.5 mL, 45 mmol, 1.5 equiv) were added. The reaction was set to stir at reflux for 2 days. The reaction mixture was then cooled to room temperature and passed through a silica plug (neat Et<sub>2</sub>O) and concentrated in vacuo. The compound was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a yellow oil (4.42 g, 15.3 mmol, dr >20:1, 50% yield). The dr was determined based on integration of the benzylic methines in the <sup>1</sup>H NMR spectrum. Analytical data is consistent with literature values.<sup>5</sup> **TLC R<sub>f</sub>** = 0.6 (5% EtOAc/hexanes); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.84 (s, 1H), 7.81–7.74 (m, 3H) 7.48 (d, J = 9.0, 1H), 7.43–7.36 (m, 2H), 7.30–7.25 (m, 2H), 7.23–7.15 (m, 3H), 4.59 (d, J = 11.0, 1H), 4.30 (dd, J = 11.5, 4.5, 1H), 3.75 (td, J = 11.8, 2.5, 1H), 2.97–2.89 (m, 1H), 2.10 (ad, J = 13.2, 1H), 1.96–1.79 (m, 3H); **<sup>13</sup>C NMR** (125.7 MHz, CDCl<sub>3</sub>) δ 145.5, 140.3, 133.5, 133.0, 128.68, 128.67, 128.14, 128.11, 127.7, 126.89, 126.88, 126.5, 126.1, 125.8, 124.4, 124.3, 80.0, 68.9, 42.3, 41.6, 33.5.



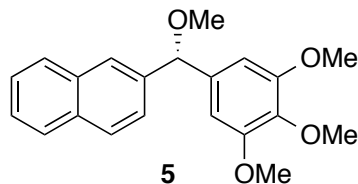
***syn*-(±)-5-(2-naphthyl)-3-phenylhexan-1-ol (4)**. The title compound was prepared according to Method B. The following amounts of reagents were used: substrate **3** (5.00 g, 17.3 mmol, 1.00 equiv), (*rac*-BINAP)NiCl<sub>2</sub> (0.323 g, 0.433 mmol, 0.025 equiv), and MeMgI (14.4 mL, 43.3 mmol, 3.00 M in Et<sub>2</sub>O, 2.50 equiv), and PhMe (200 mL). <sup>1</sup>H NMR of the crude reaction mixture showed a calculated 73% crude yield of the desired product with a smaller amount of styrene byproduct (2.6 mmol, 15%). An oxidative workup was employed for facile removal of the styrene byproduct.<sup>6</sup> The crude reaction mixture was added to a 50 mL round-bottom flask, which was then charged with *N*-methylmorpholine *N*-oxide (NMO, 323 mg, 2.83 mmol, 1.10 equiv), osmium tetroxide (161 μL, 0.0259 mmol, 4% solution in H<sub>2</sub>O, 1 mol% relative to styrene), 6 mL acetone, and 2 mL water. The reaction was allowed to stir open to air for 24 h, at which point saturated NaHCO<sub>3</sub> (15 mL) was added, and the mixture was filtered over celite. The mixture was extracted with EtOAc (3 x 10 mL), and the combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The product was purified by flash column chromatography (20% EtOAc/hexanes) to afford the title compound as a yellow oil (3.67 g, 12.1 mmol, dr >20:1, 70%). The dr was determined based on integration of the benzylic methines in the <sup>1</sup>H NMR spectrum. Analytical data is consistent with literature values.<sup>7</sup> **TLC R<sub>f</sub>** = 0.3 (20% EtOAc/hexanes); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.82–7.75 (m, 3H), 7.47–7.40 (m, 3H), 7.33–7.21 (m, 4H), 7.06 (d, J = 7.2, 2H), 3.38–3.27 (m, 2H), 2.59 (m, 1H), 2.42 (m, 1H), 2.09–2.03 (m, 1H), 2.00–1.95 (m, 1H), 1.85–1.79 (m, 1H), 1.79–1.72 (m, 1H), 1.22 (d, J = 7.0, 3H), 1.10 (br s, 1H); **<sup>13</sup>C NMR** (125.7 MHz, CDCl<sub>3</sub>) δ 144.7, 144.3, 133.7, 132.4, 128.60, 128.59, 128.2, 128.00, 127.99, 127.7, 127.6, 126.4, 126.0, 125.9, 125.8, 125.3, 61.1, 45.2, 40.40, 40.38, 37.7, 23.8.

## C. Synthesis of Cross-Coupling Product <sup>13</sup>C-2

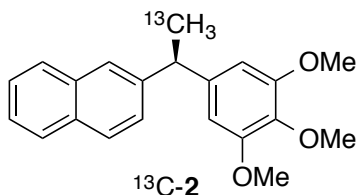
### Scheme SI 2. Synthesis of Enantioenriched Cross-coupling Product <sup>13</sup>C-2



**(S)-(3,4,5-trimethoxyphenyl)(naphthalen-6-yl)methanol (SI-1).** The title compound was prepared according to procedure by Taylor *et al.*<sup>8</sup> To a solution of naphthylboronic acid (1.2 g, 7.2 mmol, 2.4 equiv) in toluene (30 mL) was added diethylzinc (22 mL, 22 mmol, 1.0 M in toluene, 7.0 equiv). After stirring for 2 days, the reaction was cooled to room temperature and a solution of (S)-(1-methylpyrrolidin-2-yl)diphenylmethanol (0.080 g, 0.30 mmol, 0.10 equiv) in toluene (5 mL) was added. After stirring for 10 minutes, a solution of 3,4,5-trimethoxybenzaldehyde (0.59 g, 3.0 mmol, 1.0 equiv) in toluene (5 mL) was added. The reaction was allowed to stir at 4 °C for 2 days, at which point 1N hydrochloric acid (5 mL) was added and the product was extracted with EtOAc (3 x 10 mL). The combined organics were washed with brine (10 mL), dried over MgSO<sub>4</sub>, and concentrated in vacuo. The product was purified by flash column chromatography (20–50% EtOAc/hexanes) to afford the desired product as a white solid (0.490 g, 1.50 mmol, 50%). Subsequent recrystallization from EtOAc/hexanes provided enantioenriched product. Analytical data is consistent with literature values.<sup>9</sup> **m.p.** 147–150 °C; **TLC** R<sub>f</sub> = 0.7 (50% EtOAc/hexanes); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.89–1.79 (m, 4H), 7.50–7.43 (m, 3H), 7.25 (s, 2H), 6.65 (s, 2H), 5.95 (ad, J = 3.6, 1H), 3.83 (ad, J = 4.0, 9H), 2.30 (d, J = 3.5, 1H); **<sup>13</sup>C NMR** (125.7 MHz, CDCl<sub>3</sub>) δ 153.5, 141.0, 139.4, 137.5, 133.4, 133.1, 128.5, 128.3, 127.9, 126.4, 126.2, 125.2, 124.9, 103.8 (2C), 76.6, 61.0, 56.3 (3C); **[α]<sub>D</sub><sup>25</sup>** –12.2 (c 2.05, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 30% MeOH, 2.5 mL/min, 215 nm) indicated 90% ee: t<sub>R</sub> (minor) = 3.19 minutes, t<sub>R</sub> (major) = 3.42 minutes.



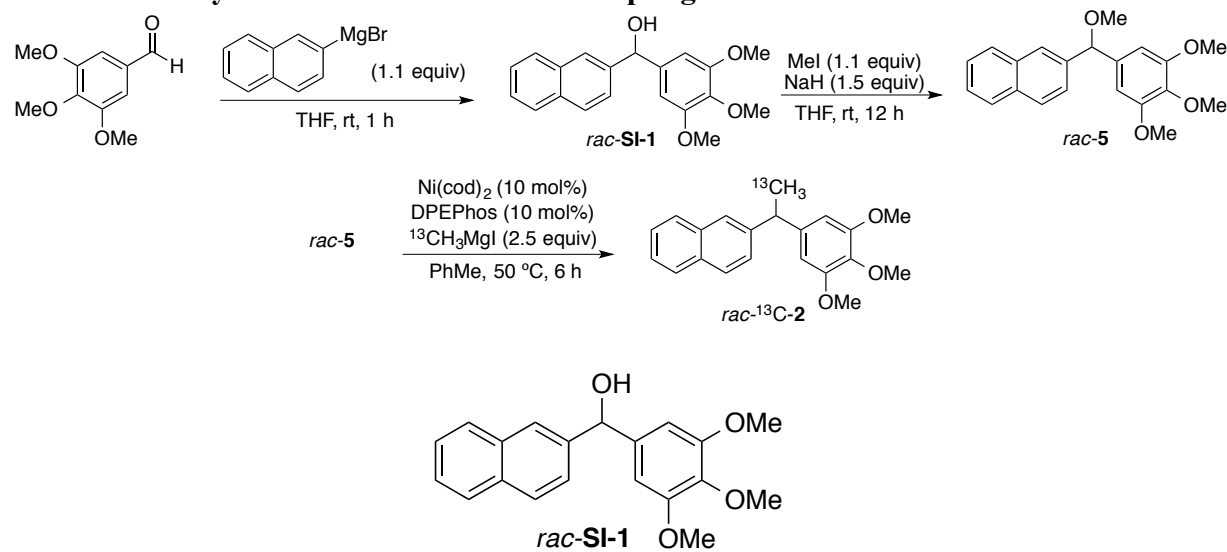
**(S)-2-(methoxy(3,4,5-trimethoxyphenyl)methyl)naphthalene (5).** To a suspension of NaH (0.036 g, 1.5 mmol, 1.5 equiv) in THF (4 mL) was added a solution of **SI-1** (0.325 g, 1.00 mmol, 1.00 equiv) in THF (3 mL). The solution was stirred for 1 h at which point iodomethane (0.068 mL, 1.1 mmol, 1.1 equiv) was added. The solution was allowed to stir overnight. Excess NaH was quenched with saturated aqueous ammonium chloride (5 mL) and the product was extracted with EtOAc (3 x 10 mL). The combined organics were washed with brine (10 mL), dried over MgSO<sub>4</sub> and concentrated in vacuo. The crude product was purified by flash column chromatography (20% Et<sub>2</sub>O/hexanes) to afford **5** as a white solid (0.229 g, 0.671 mmol, 67%). Analytical data is consistent with literature values.<sup>8</sup> **m.p.** 103–105 °C; **TLC** *R<sub>f</sub>* = 0.3 (20% Et<sub>2</sub>O/hexanes); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.86–7.79 (m, 4H), 7.51–7.42 (m, 3H), 6.63 (s, 2H), 5.33 (s, 1H), 3.83 (s, 9H), 3.44 (s, 3H); **<sup>13</sup>C NMR** (125.7, CDCl<sub>3</sub>) δ 153.4, 139.3, 137.7, 137.4, 133.3, 133.1, 128.5, 128.2, 127.8, 126.3, 126.1, 125.9, 125.0, 104.1 (2C), 85.6, 61.0, 57.3 (3C), 56.3; **[α]<sub>D</sub><sup>23</sup>** +26.7 (*c* 10.35, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 20% MeOH, 2.5 mL/min, 215 nm) indicated 89% ee: *t<sub>R</sub>* (major) = 3.36 minutes, *t<sub>R</sub>* (minor) = 3.63 minutes.



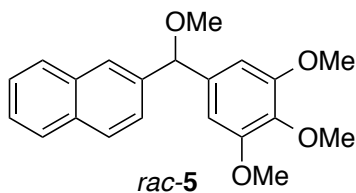
**(R)-2-(1-(3,4,5-trimethoxyphenyl)ethyl-2-<sup>13</sup>C)naphthalene (<sup>13</sup>C-2).** The title compound was prepared according to Method A. The reaction was run at 50 °C for 6 hours. The following amounts of reagents were used: Ni(cod)<sub>2</sub> (2.7 mg, 0.010 mmol, 0.10 equiv), DPEPhos (5.6 mg, 0.010 mmol, 0.10 equiv), substrate **5** (34 mg, 0.10 mmol, 1.0 equiv), <sup>13</sup>CH<sub>3</sub>MgI (110 μL, 0.25 mmol, 2.3 M in Et<sub>2</sub>O, 2.5 equiv), and PhMe (1.2 mL). Analysis by <sup>1</sup>H NMR showed the unpurified products were formed as a mixture of desired product <sup>13</sup>C-2 and phenol **SI-2** (~2:1 ratio). The products were separated by flash column chromatography (20% Et<sub>2</sub>O/hexanes) and phenol **SI-2** was subjected to methylation according our previously reported procedure.<sup>8</sup> **SI-2** (7.8 mg, 0.025 mmol, 1.0 equiv) was dissolved in acetone (3 mL) and K<sub>2</sub>CO<sub>3</sub> (0.083 g, 0.60 mmol, 24 equiv) was added, followed by iodomethane (0.019 mL, 0.30 mmol, 12 equiv). The mixture was heated to reflux and stirred for 4 hours. The reaction was then cooled to room temperature, filtered, washed with acetone and concentrated in vacuo. The product was purified by flash column chromatography (20% Et<sub>2</sub>O/hexanes) to afford the title compound <sup>13</sup>C-2 as a clear oil (19.3 mg, 0.601 mmol, 60% over two steps). **TLC** *R<sub>f</sub>* = 0.4 (20% Et<sub>2</sub>O/hexanes); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.80 (t, *J* = 6.5, 2H), 7.75 (d, *J* = 8.6, 1H), 7.68 (s, 1H), 7.49–7.41 (m, 2H), 7.32 (d, *J* = 8.6, 1H), 6.47 (s, 2H), 4.24 (q, *J* = 7.2, 1H), 3.83 (s, 3H), 3.80 (s, 6H), 1.72 (dd, *J* = 127.1, 7.2, 3H); **<sup>13</sup>C NMR** (125.7, CDCl<sub>3</sub>) δ 153.2, 143.7, 142.1, 136.4, 133.6, 132.3, 128.1, 127.9, 127.7, 126.8, 126.1, 125.6, 125.4, 105.0 (2C), 61.0, 56.2 (3C), 45.2, 22.0; **IR** (neat) 2955, 2928, 2359, 1588, 1506 cm<sup>-1</sup>; **HRMS** (TOF MS ES+) *m/z* calcd for C<sub>20</sub><sup>13</sup>CH<sub>22</sub>O<sub>3</sub>Na (M + Na)<sup>+</sup> 346.1501, found 346.1496. **[α]<sub>D</sub><sup>25</sup>** +14.1 (*c* 3.90, CHCl<sub>3</sub>); **SFC** analysis (AD-H, 20%

MeOH, 2.5 mL/min, 215 nm) indicated 89% ee:  $t_R$  (minor) = 4.23 minutes,  $t_R$  (major) = 4.58 minutes.

### Scheme SI 3. Synthesis of Racemic Cross-coupling Product $^{13}\text{C-2}$

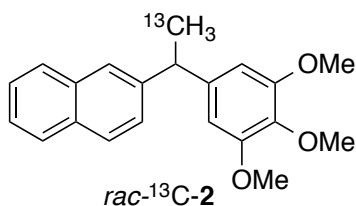


**(3,4,5-trimethoxyphenyl)(naphthalen-6-yl)methanol (*rac*-SI-1).** To a stirred solution of 2-naphthylmagnesium bromide (7.5 mL, 9.0 mmol, 1.2 M in THF, 1.1 equiv) in a flame-dried round bottom flask was added a solution of 3,4,5-trimethoxybenzaldehyde (1.60 g, 8.15 mmol, 1.0 equiv) in THF (5 mL). The reaction was allowed to stir for 1 h at which point saturated ammonium chloride was added (10 mL) and the reaction was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. The product was purified by flash column chromatography (20–50% EtOAc/hexanes) to afford the desired product as a white solid (2.37 g, 7.35 mmol, 90%). Analytical data is consistent with SI-1 (*vide supra*).



**2-(methoxy(3,4,5-trimethoxyphenyl)methyl)naphthalene (*rac*-5).** To a suspension of NaH (220 mg, 9.2 mmol, 1.5 equiv) in THF (30 mL) was added a solution of *rac*-SI-1 (2.0 g, 6.2 mmol, 1.0 equiv) in THF (10 mL). The solution was stirred for 1 h at which point iodomethane (420  $\mu\text{L}$ , 6.7 mmol, 1.1 equiv) was added. The solution was allowed to stir overnight. Excess NaH was quenched with saturated ammonium chloride (15 mL) and the product was extracted with EtOAc (3 x 20 mL). The combined organics were washed with brine (20 mL), dried over  $\text{MgSO}_4$  and concentrated in vacuo. The product was purified by flash column chromatography (20% Et<sub>2</sub>O/hexanes) to afford **5** as a white solid (1.49 g, 4.40 mmol, 71%). Analytical data is consistent with **5** (*vide supra*).

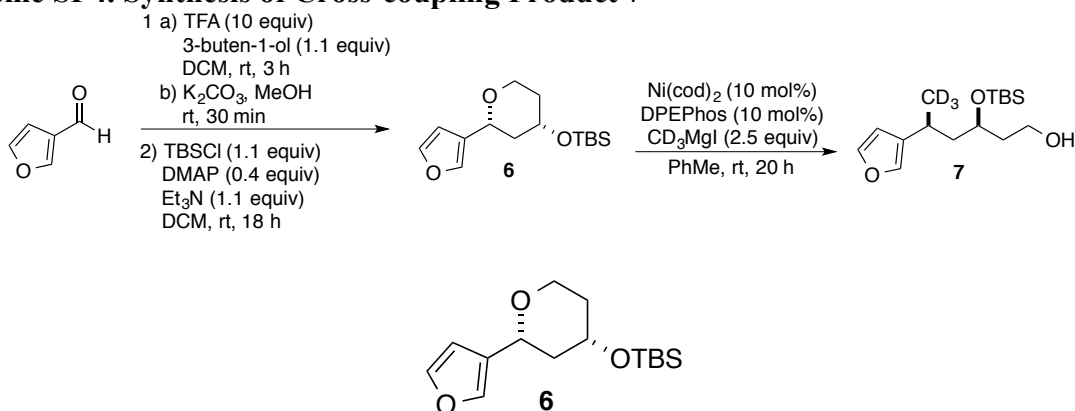




**2-(1-(3,4,5-trimethoxyphenyl)ethyl)-2-<sup>13</sup>C)naphthalene (*rac*-<sup>13</sup>C-2).** The title compound was prepared according to Method A. The reaction was run at 50 °C for 6 hours. The following amounts of reagents were used: Ni(cod)<sub>2</sub> (5.6 mg, 0.020 mmol, 0.10 equiv), DPEPhos (11 mg, 0.020 mmol, 0.10 equiv), substrate *rac*-5 (68 mg, 0.20 mmol, 1.0 equiv), <sup>13</sup>CH<sub>3</sub>MgI (220 μL, 0.50 mmol, 2.3 M in Et<sub>2</sub>O, 2.5 equiv), and PhMe (2.4 mL). The title compound was separated from phenol *rac*-SI-2 by flash column chromatography (20% Et<sub>2</sub>O/hexanes) to give a clear oil (29.7 mg, 0.0920 mmol, 46%). Analytical data is consistent with <sup>13</sup>C-2 (*vide supra*).

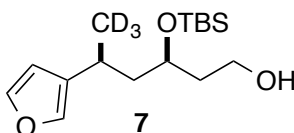
#### D. Synthesis of Cross-Coupling Product 7

##### Scheme SI 4. Synthesis of Cross-coupling Product 7



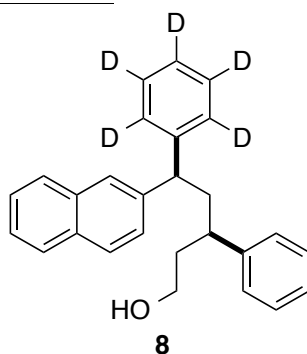
***cis*-(±)-((2-(3-furan-2-yl)tetrahydro-2H-pyran-4-yl)oxy)(*tert*-butyl)dimethylsilane (6).** The title compound was prepared according to a modified procedure by Sabitha.<sup>10</sup> To a stirring solution of 3-furancarboxaldehyde (0.86 mL, 10. mmol, 1.0 equiv) in anhydrous DCM (20 mL) under N<sub>2</sub> was added 3-buten-1-ol (1.0 mL, 11 mmol, 11 equiv). Trifluoroacetic acid (TFA, 5.6 mL, 74 mmol, 7.4 equiv) was added slowly via syringe and the reaction mixture was allowed to stir at room temperature for 3 h. Saturated sodium bicarbonate was slowly added and the pH was adjusted to >7 by addition of Et<sub>3</sub>N. The aqueous layer was extracted with DCM (3 x 15 mL), the combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was then redissolved in MeOH (20 mL) and K<sub>2</sub>CO<sub>3</sub> (4.8 g, 35 mmol, 3.5 equiv) was added, and the reaction was stirred for 30 min at room temperature. The MeOH was removed under reduced pressure, H<sub>2</sub>O was added to the residue, and the mixture was extracted with DCM (3 x 15 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. Unreacted aldehyde was removed by flash column chromatography (50% Et<sub>2</sub>O/hexanes) and the resulting product (R<sub>f</sub> = 0.2) was carried forward directly into the next step, with approximate yields calculated from <sup>1</sup>H NMR analysis.

The product from the previous step was dissolved in dry DCM (15 mL) in a flame-dried round bottom flask equipped with stir bar. 4-Dimethylaminopyridine (DMAP, 0.091 g, 0.88 mmol, 0.40 equiv relative to calculated yield in previous step) and Et<sub>3</sub>N (0.38 mL, 3.3 mmol, 1.5 equiv relative to calculated yield in previous step) were added under a flow of N<sub>2</sub>. The reaction was stirred at room temperature for 10 min, at which point *tert*-butyldimethylsilyl chloride (TBSCl, 330 mg, 2.4 mmol, 1.1 equiv relative to calculated yield in previous step) was added. The reaction was allowed to stir for 18 h at room temperature, at which point saturated aqueous ammonium chloride (10 mL) was added and the aqueous layer extracted with DCM (3 x 15 mL). The combined organics were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The product was purified by flash column chromatography (5% Et<sub>2</sub>O/hexanes) to afford the title compound as a clear oil (0.391 g, 1.38 mmol, dr >20:1, 14% over two steps). The dr was determined based on integration of the benzylic methines in the <sup>1</sup>H NMR spectrum. Analytical data was consistent with literature values.<sup>7</sup> **TLC** R<sub>f</sub> = 0.7 (5% Et<sub>2</sub>O/hexanes); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.40 (s, 1H), 7.37 (s, 1H), 6.42 (s, 1H), 4.29 (dd, J = 11.6, 1.7, 1H), 4.06 (ddd, J = 12.1, 4.9, 1.7, 1H), 3.85 (sept, J = 4.9, 1H), 3.53 (td J = 12.5, 2.0, 1H), 2.07–2.00 (m, 1H), 1.84–1.77 (m, 1H), 1.69–1.58 (m, 2H), 0.90 (s, 9H), 0.08 (s, 6H); **<sup>13</sup>C NMR** (125.7, CDCl<sub>3</sub>) δ 143.3, 139.3, 126.9, 109.0, 71.3, 68.8, 66.5, 42.5, 36.2, 26.0 (3C), 18.3, –4.37, –4.41.



***syn*-(±)-3-((*tert*-butyldimethylsilyl)oxy)-5-(furan-3-yl)hexan-6,6,6-*d*<sub>3</sub>-1-ol (7).** The title compound was prepared according to Method A. The following amounts of reagents were used: Ni(cod)<sub>2</sub> (5.5 mg, 0.020 mmol, 0.10 equiv), DPEPhos (11 mg, 0.020 mmol, 0.10 equiv), substrate **6** (56 mg, 0.20 mmol, 1.0 equiv), CD<sub>3</sub>MgI (280 μL, 0.50 mmol, 1.8 M in Et<sub>2</sub>O, 2.5 equiv), and PhMe (2.4 mL). The product was purified by flash column chromatography (20% Et<sub>2</sub>O/pentane) to afford the title compound as a clear oil (50.4 mg, 0.167 mmol, dr >20:1, 84%). The dr was determined based on integration of the benzylic methines in the <sup>1</sup>H NMR spectrum. **TLC** R<sub>f</sub> = 0.5 (20% Et<sub>2</sub>O/pentane); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.35 (s, 1H), 7.20 (s, 1H), 6.27 (s, 1H), 3.95 (quint, J = 5.4, 1H), 3.88–3.80 (m, 1H), 3.75–3.67 (m, 1H), 2.73 (sext, J = 7.1, 1H), 2.42 (br s, 1H), 1.91–1.82 (m, 1H), 1.82–1.66 (m, 2H), 1.65–1.56 (m, 1H), 0.90 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H); **<sup>13</sup>C NMR** (125.7, CDCl<sub>3</sub>) δ 143.0, 138.0, 130.8, 109.5, 70.2, 60.1, 44.5, 38.2, 27.1, 26.0 (3C), 22.3, 18.1, –4.31, –4.32; **IR** (neat) 3491, 2929, 2856, 2359, 1471 cm<sup>-1</sup>; **HRMS** (TOF MS ES+) *m/z* calcd for C<sub>16</sub>H<sub>27</sub>D<sub>3</sub>O<sub>3</sub>SiNa (M + Na)<sup>+</sup> 324.2050, found 324.2057.

## E. Synthesis of Cross-Coupling Product 8

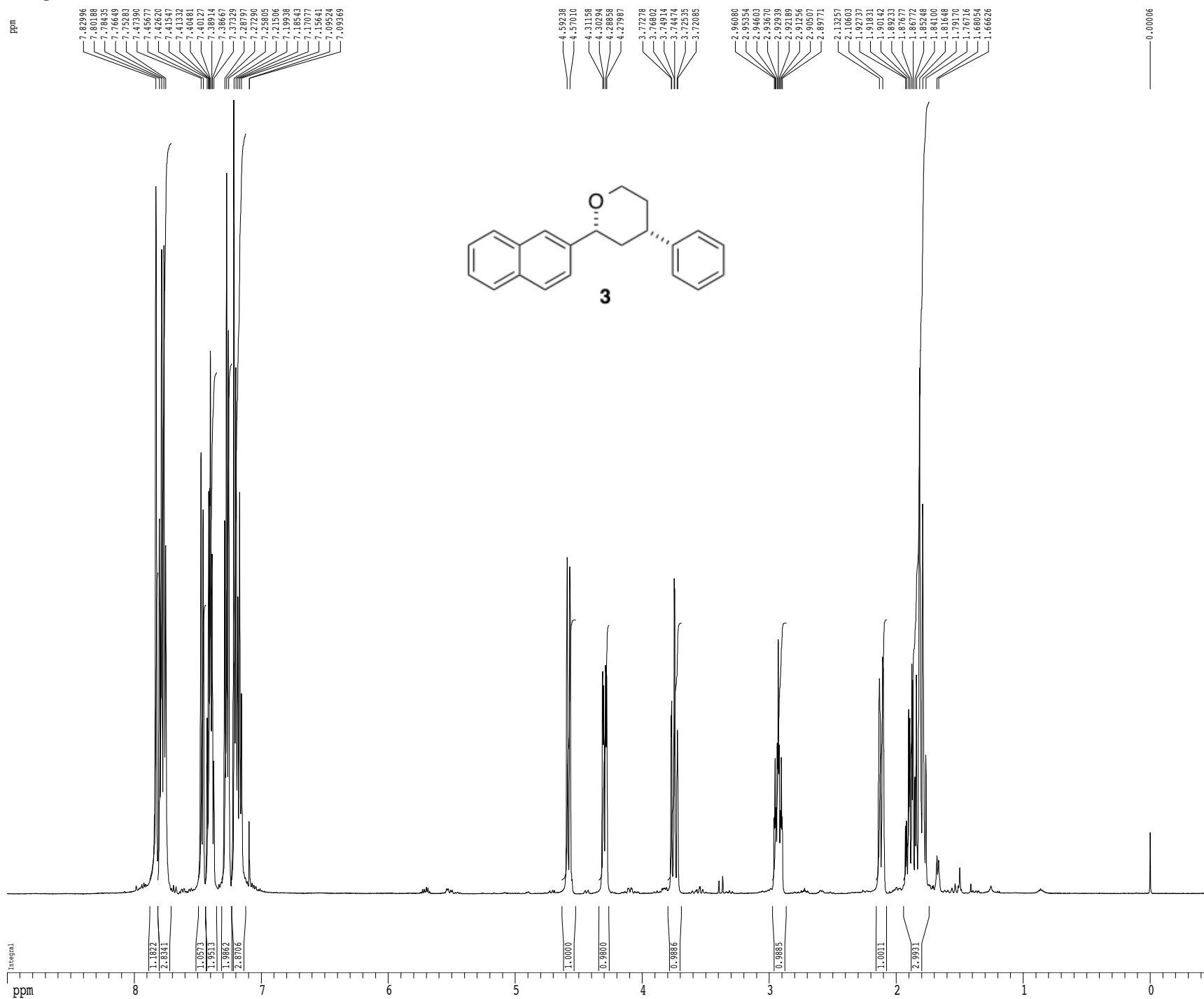


***syn*-(±)-5-(naphthalen-2-yl)-3-phenyl-5-(phenyl-*d*<sub>5</sub>)pentan-1-ol (8).** The title compound was prepared according to Method C. The following amounts of reagents were used: Ni(dppe)Cl<sub>2</sub> (11 mg, 0.020 mmol, 0.10 equiv), substrate **3** (58 mg, 0.20 mmol, 1.0 equiv), C<sub>6</sub>D<sub>5</sub>MgBr (190 μL, 0.50 mmol, 2.6 M in Et<sub>2</sub>O, 2.5 equiv). The product was purified by flash column chromatography over silver-impregnated silica gel (0–20% EtOAc/hexanes) to afford a colorless oil (65.4 mg) containing a mixture of the title compound (74% calculated yield, dr >20:1) and β-H elimination (17% calculated yield). The dr was determined based on integration of the benzylic methines in the <sup>1</sup>H NMR spectrum. A small amount of analytically pure material was obtained for characterization. **TLC** R<sub>f</sub> = 0.3 (20% EtOAc/hexanes); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.81–7.60 (m, 3H), 7.60 (s, 1H), 7.49–7.42 (m, 2H); 7.34–7.22 (m, 4H), 7.09 (d, J = 7.1, 2H), 3.85 (dd, J = 10.5, 4.7, 1H), 3.47–3.33 (m, 2H), 2.63–2.55 (m, 2H), 2.43–2.36 (m, 1H), 2.02–1.94 (m, 1H), 1.90–1.81 (m, 1H) 1.00 (br s, 1H); **<sup>13</sup>C NMR** (125.7, CDCl<sub>3</sub>) δ 145.3, 144.2, 141.3, 133.6, 132.4, 128.7 (2C), 128.5 (2C), 128.3, 127.9 (2C), 127.8, 127.69 (2C), 127.67, 126.8, 126.7, 126.6, 126.1, 126.0, 125.5, 61.2, 48.5, 42.5, 40.2, 40.1; **IR** (neat) 3365, 3024, 2928, 2359, 2341, 1599 cm<sup>-1</sup>; **HRMS** (TOF MS ES<sup>+</sup>) *m/z* calcd for C<sub>27</sub>H<sub>21</sub>D<sub>5</sub>ONa (M + Na)<sup>+</sup> 394.2195, found 394.2204.

### **III. REFERENCES**

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<sup>1</sup>H spectrum



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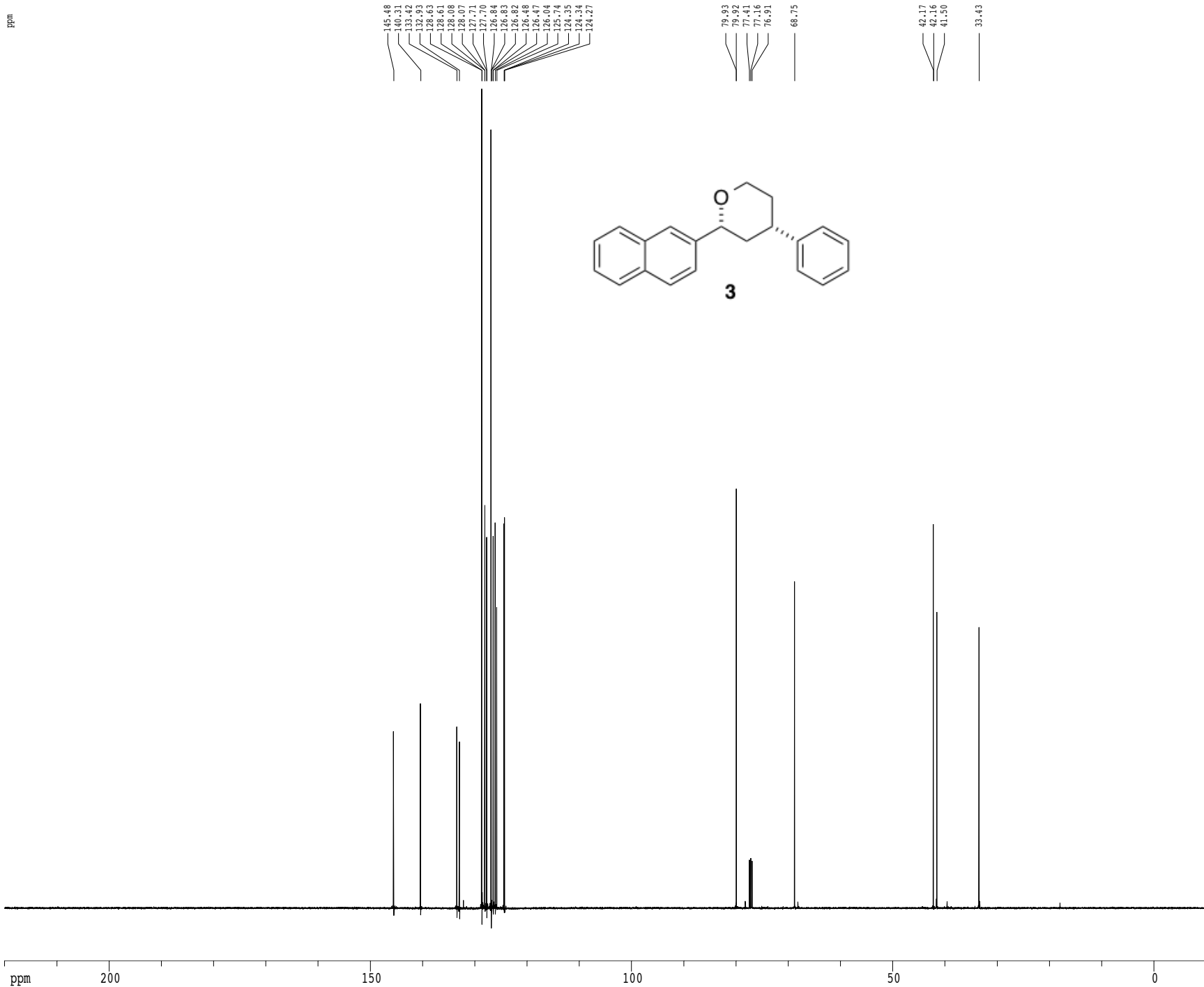
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Z-restored spin-echo 13C spectrum with 1H decoupling



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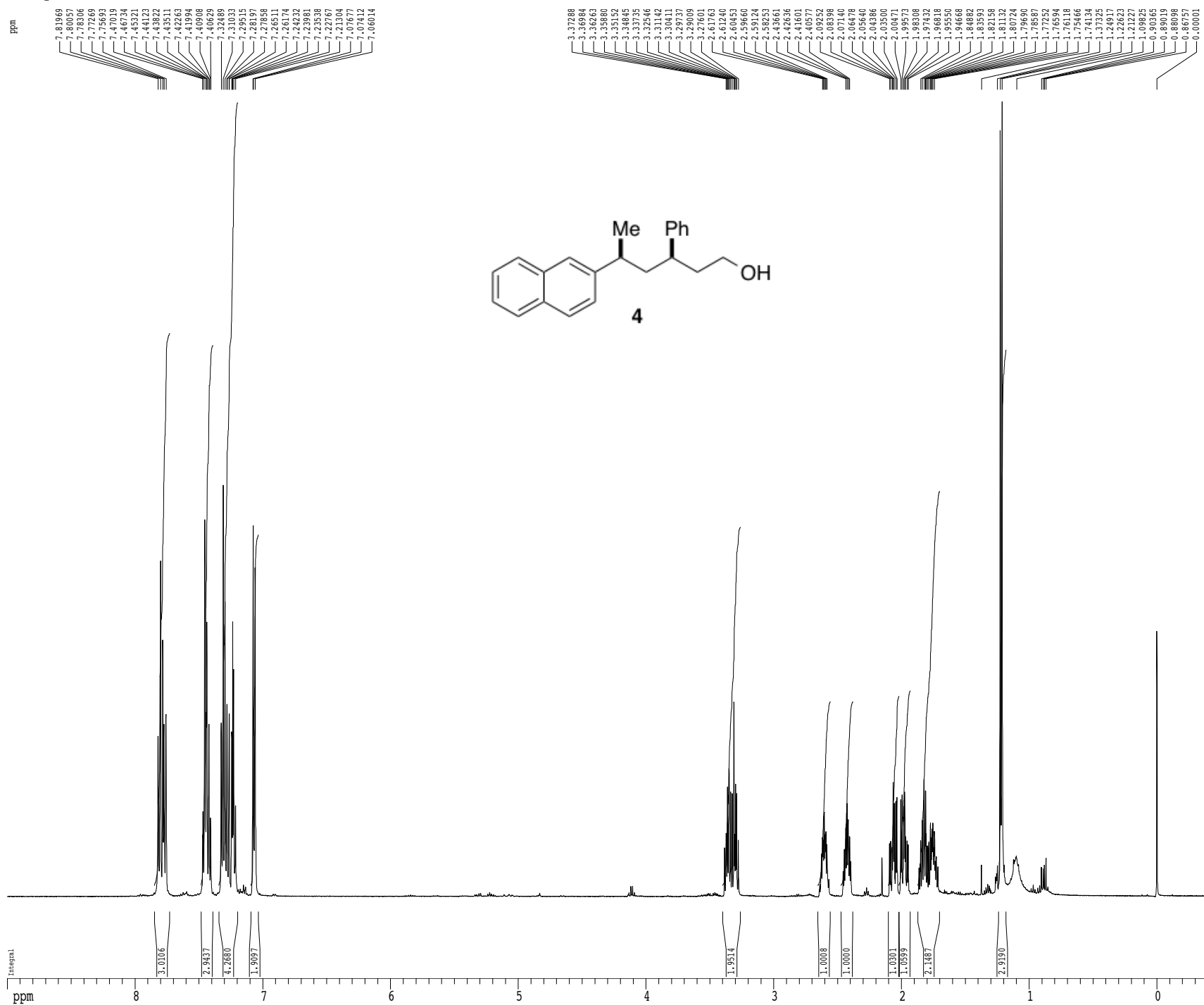
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<sup>1</sup>H spectrum



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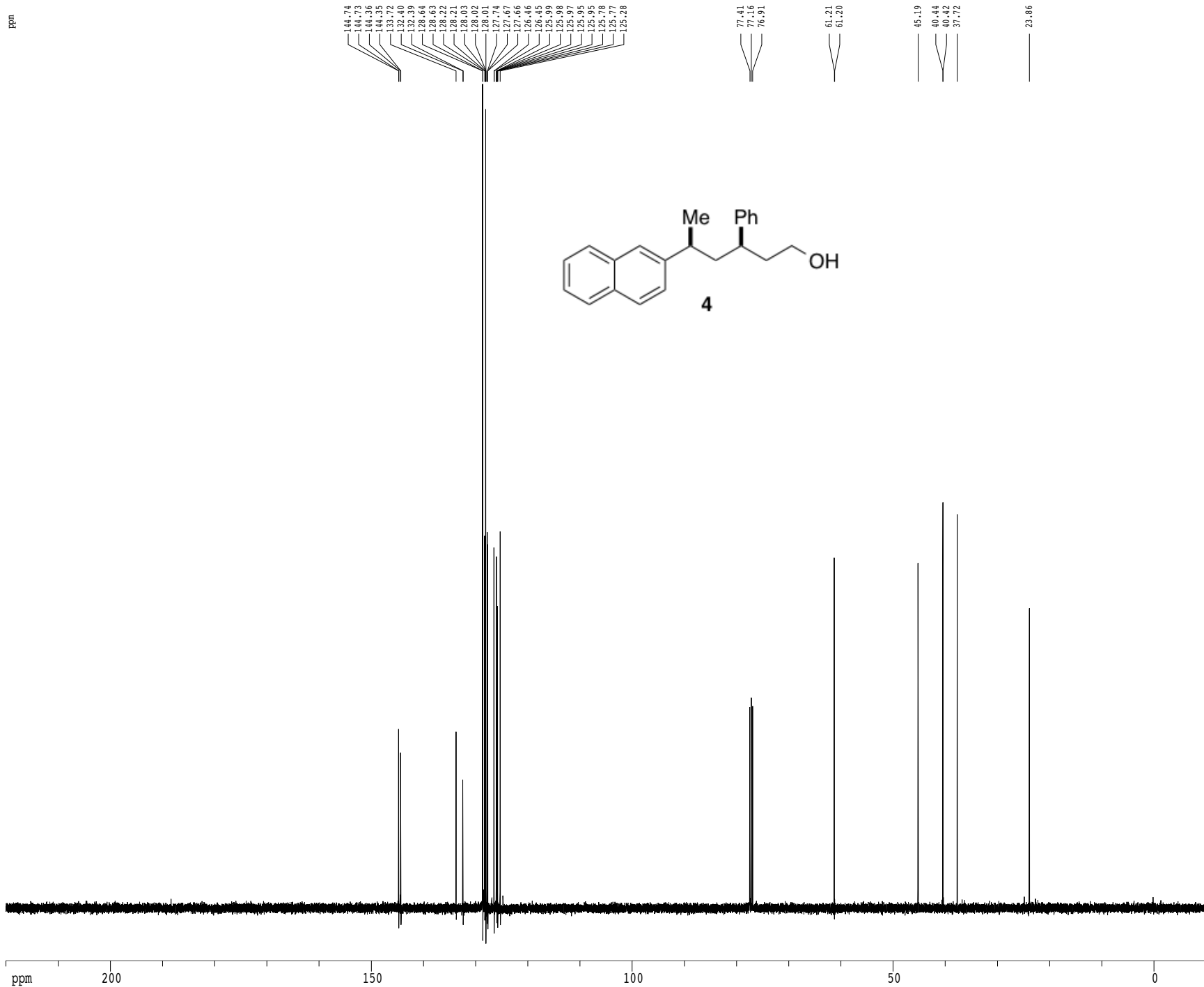
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Z-restored spin-echo 13C spectrum with 1H decoupling



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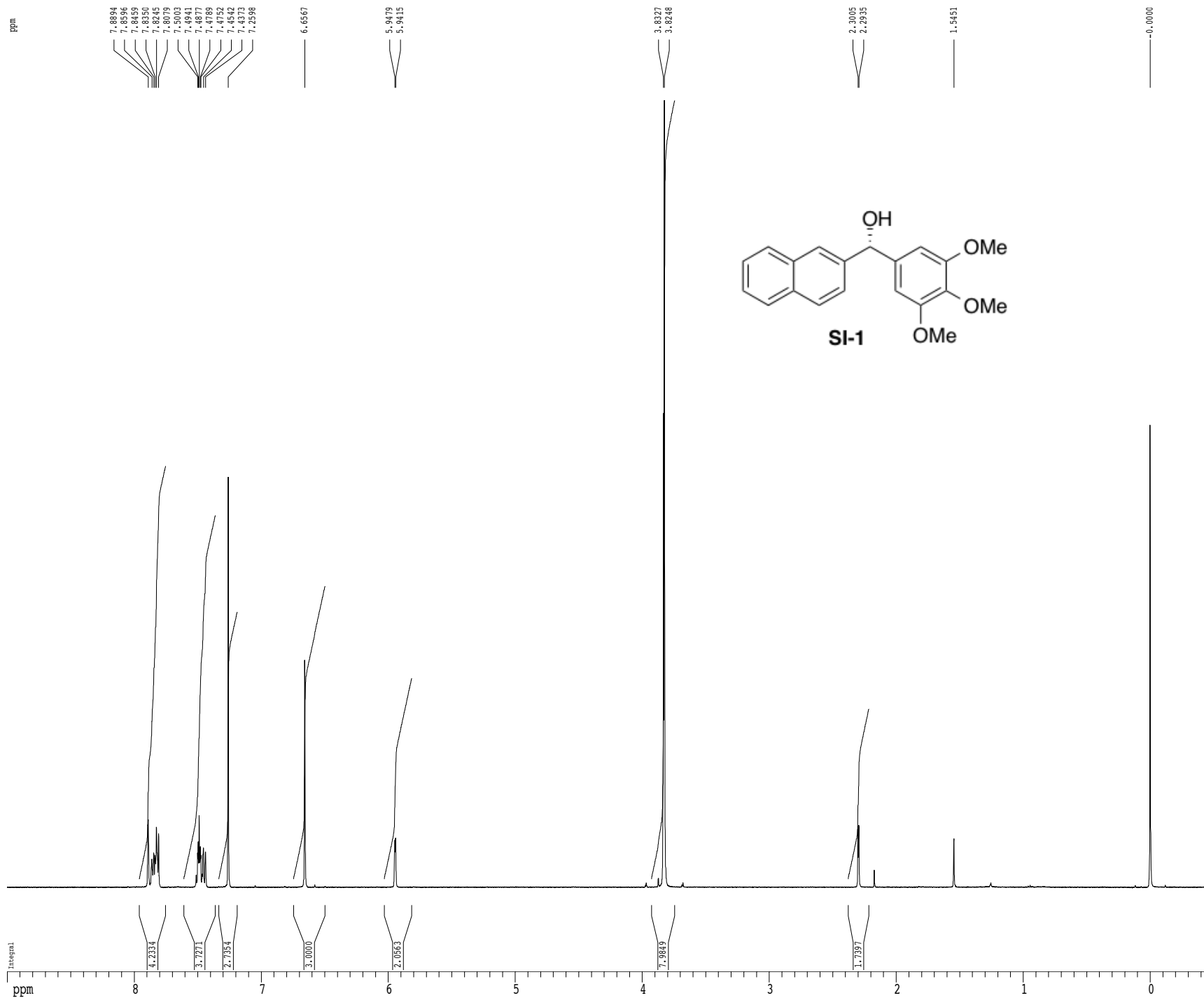
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<sup>1</sup>H spectrum



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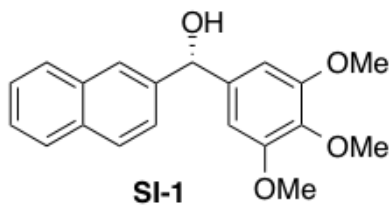
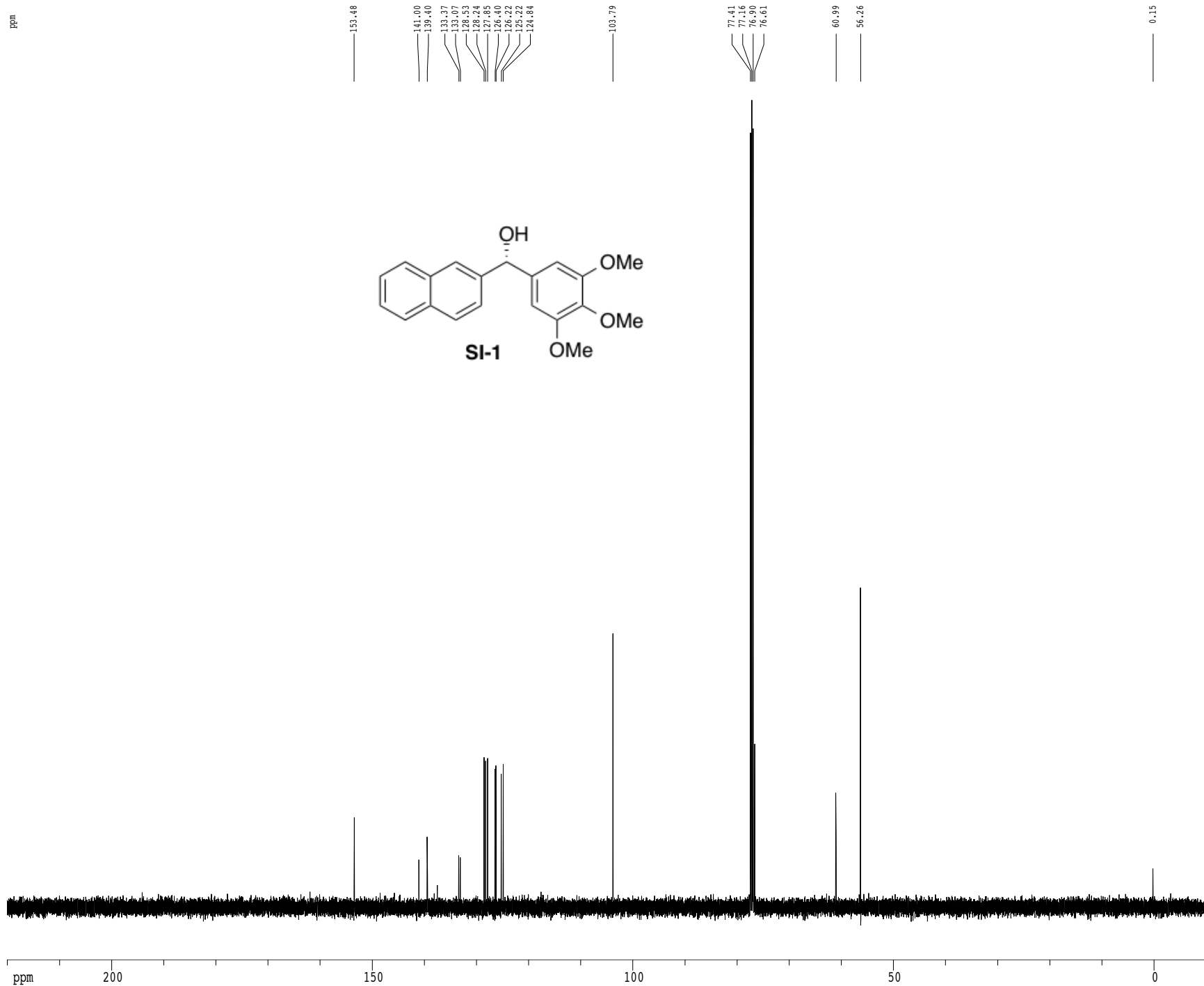
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Z-restored spin-echo 13C spectrum with 1H decoupling



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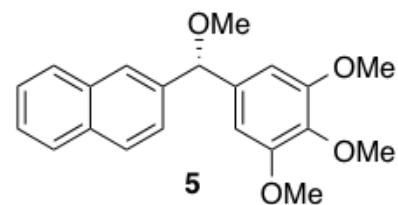
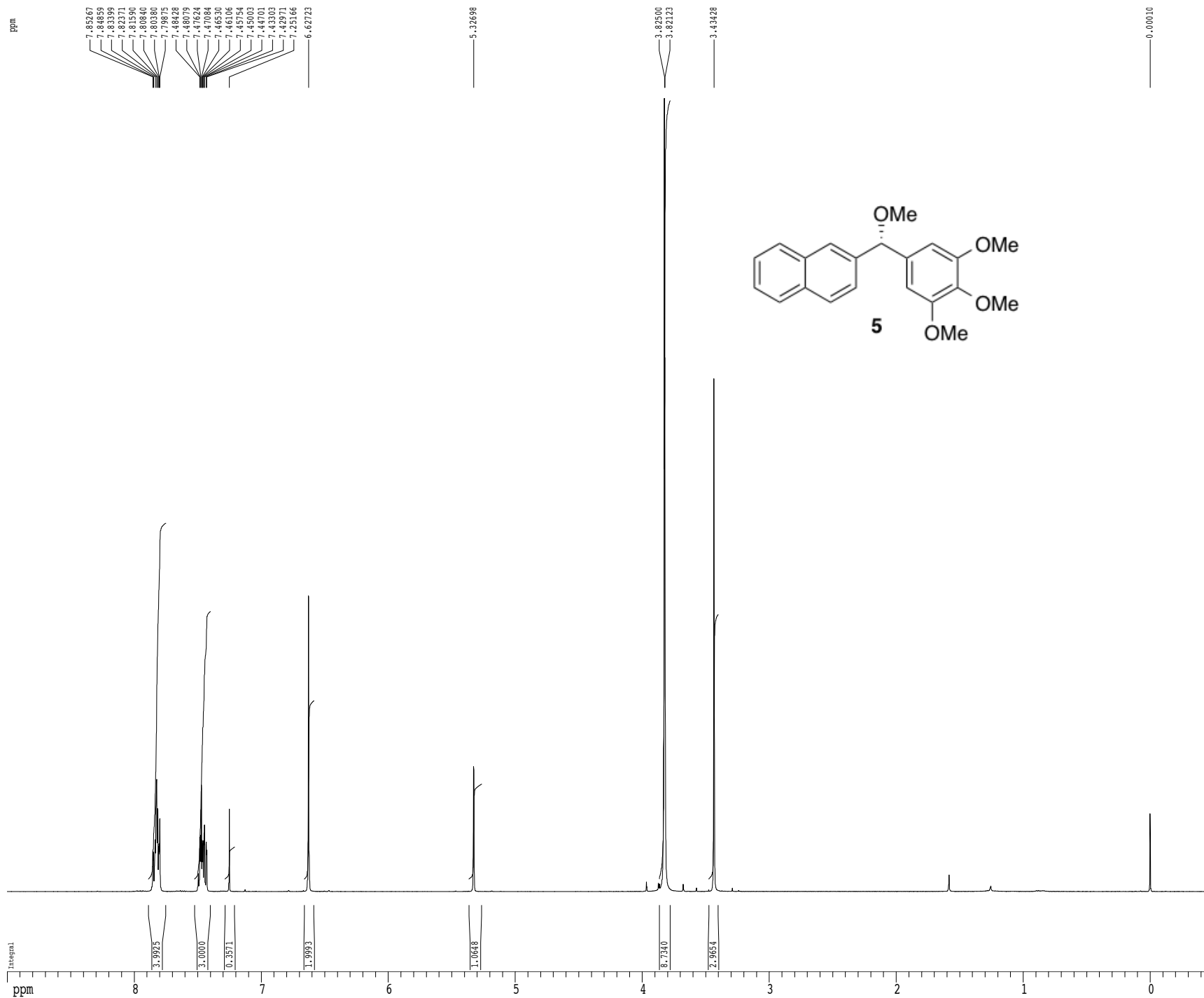
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PL12         24.50 dB
SFO2         500.2225011 MHz

===== GRADIENT CHANNEL =====
GPNAM1       SINE.100
GPNAM2       SINE.100
GPX1         0.00 %
GPX2         0.00 %
GPY1         0.00 %
GPY2         0.00 %
GPZ1         30.00 %
GPZ2         50.00 %
p15          500.00 usec
p16          1000.00 usec

F2 - Processing parameters
SI           65536
SF           125.7804076 MHz
WDW          no
SSB          0
LB           0.00 Hz
GB           0
PC           2.00

ID NMR plot parameters
CX           22.80 cm
CY           15.65 cm
F1P          220.000 ppm
F1           27671.69 Hz
F2P          -10.000 ppm
F2           -1257.80 Hz
PPMCM        10.08772 ppm/cm
HZCM         1268.83752 Hz/cm
    
```

<sup>1</sup>H spectrum



Current Data Parameters  
 USER dawsen  
 NAME DDD-2-158-pure-protonCRYO  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20150206  
 Time 17.52  
 INSTRUM cryo500  
 PROBD 5 mm CPTCI 1H-  
 PULPROG zg30  
 TD 81728  
 SOLVENT CDCl3  
 NS 8  
 DS 2  
 SWH 8012.820 Hz  
 FIDRES 0.098043 Hz  
 AQ 5.0998774 sec  
 RG 5  
 DW 62.400 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.10000000 sec  
 MCREST 0.00000000 sec  
 MCHX 0.01500000 sec

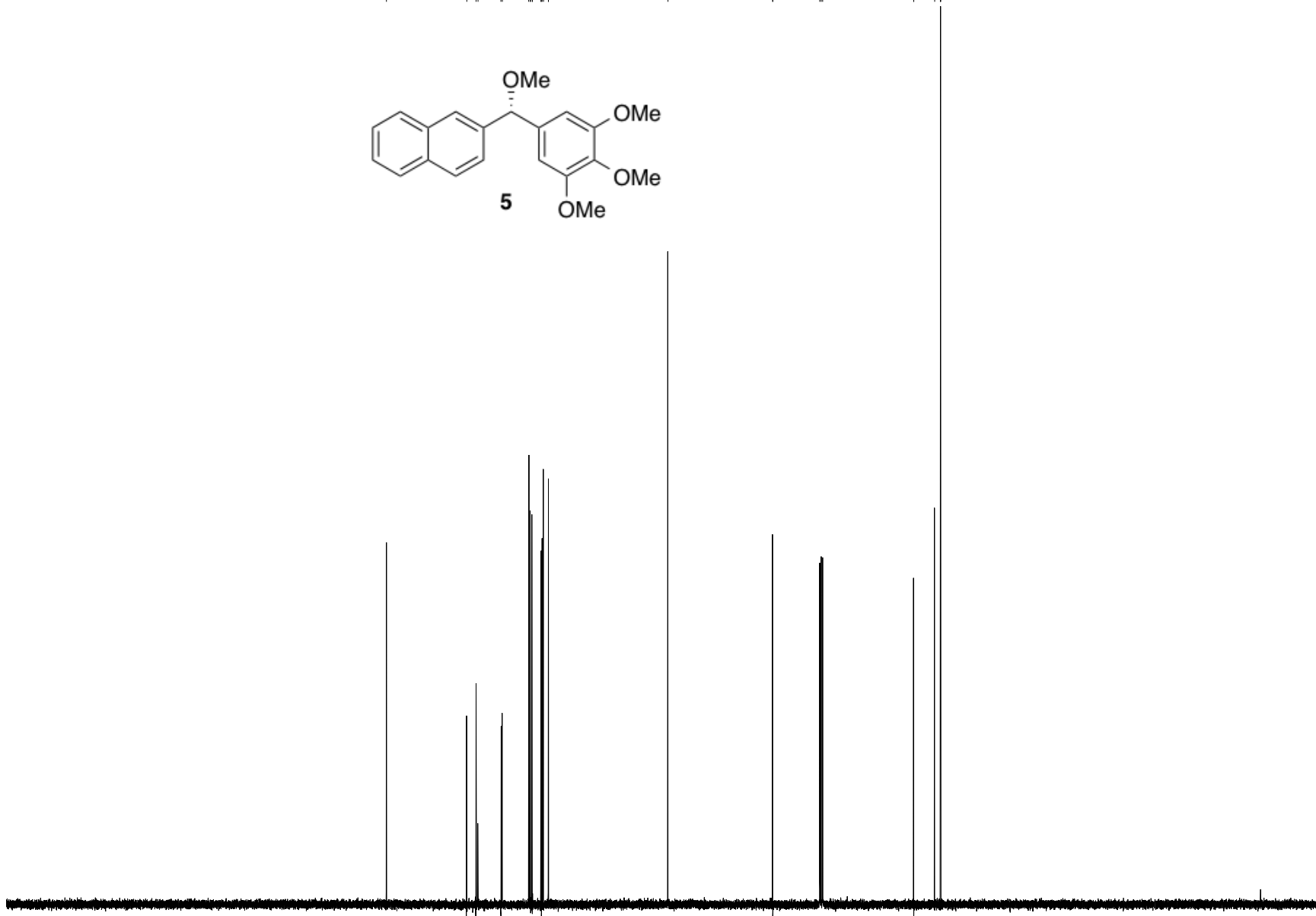
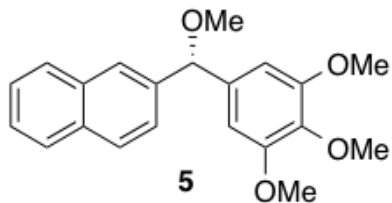
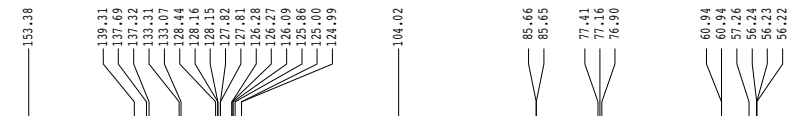
===== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.50 usec  
 PL1 1.60 dB  
 SFO1 500.2235015 MHz

F2 - Processing parameters  
 SI 65536  
 SF 500.2200352 MHz  
 WDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 4.00

1D NMR plot parameters  
 CX 22.80 cm  
 CY 15.00 cm  
 F1 9.000 ppm  
 F1 4501.88 Hz  
 F2P -0.500 ppm  
 F2 -250.11 Hz  
 FFCM 0.41667 ppm/cm  
 HECM 208.42302 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling

ppm



Current Data Parameters  
 USER dawson  
 NAME DDD-2-158-pure-carbonCryo  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20150206  
 Time 17.58  
 INSTRUM cryo500  
 PROBD 5 mm CPAC1 1H-  
 PULPROG SpinEcho30pp.prd  
 TD 65536  
 SOLVENT CDCl3  
 NS 272  
 DS 16  
 SWH 30303.031 Hz  
 FIDRES 0.462388 Hz  
 AQ 1.0813940 sec  
 RG 4896  
 DW 16.500 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.25000000 sec  
 d11 0.03000000 sec  
 D16 0.00020000 sec  
 d17 0.00019600 sec  
 MCREST 0.00000000 sec  
 WWER 0.01500000 sec  
 P2 33.10 usec

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 16.55 usec  
 P11 500.00 usec  
 P12 2000.00 usec  
 PL0 120.00 dB  
 PL1 -1.00 dB  
 SFO1 125.7942548 MHz  
 SF1 2.70 dB  
 SF2 2.70 dB  
 SFO2 125.7942548 MHz  
 SF2 2.70 dB  
 SFO2 500.2225011 MHz  
 SFO2 24.50 dB  
 SFO2 500.2225011 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 100.00 usec  
 PL2 1.60 dB  
 PL12 24.50 dB  
 SFO2 500.2225011 MHz

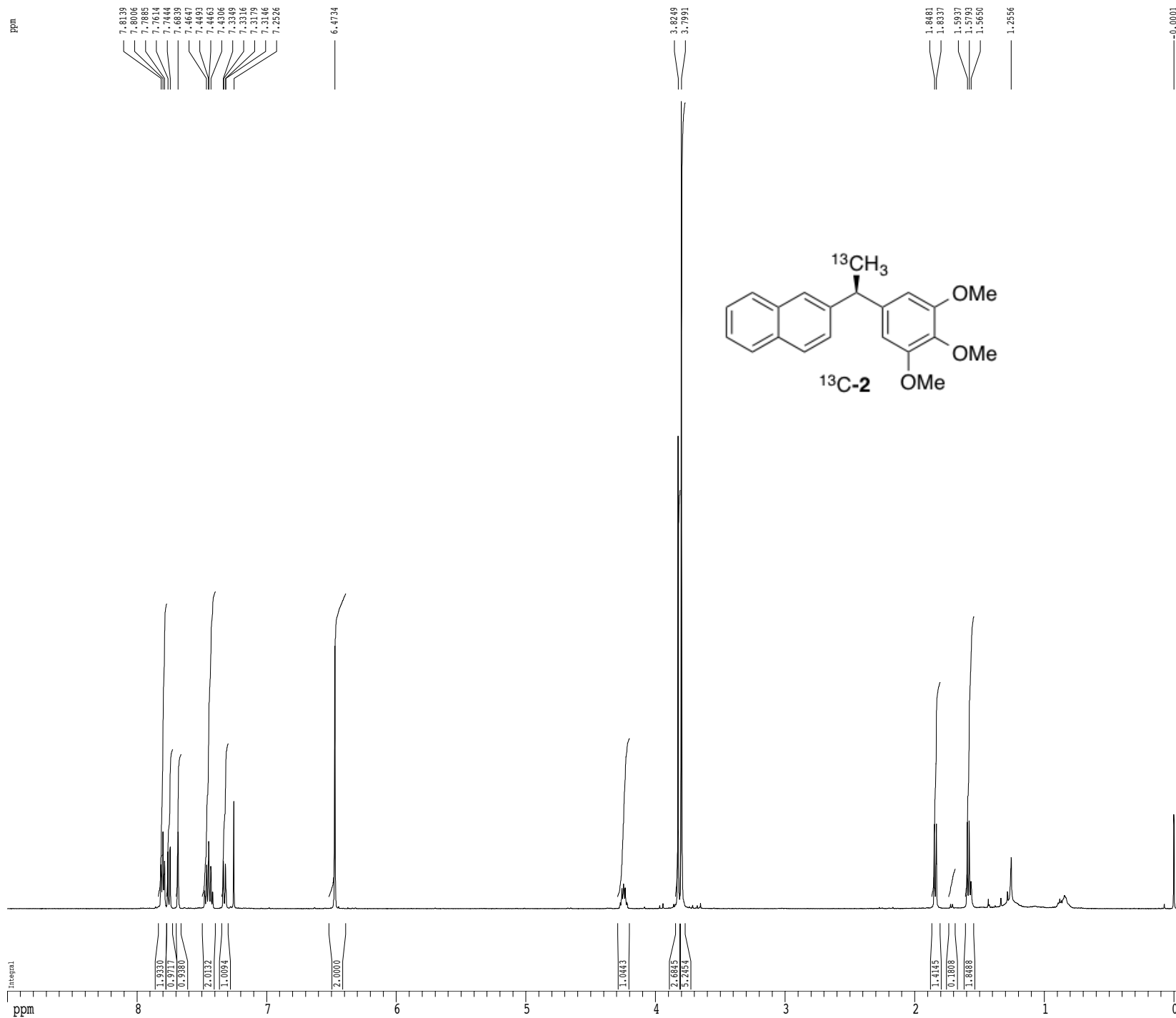
===== GRADIENT CHANNEL =====  
 GPRAM1 SINE.100  
 GPRAM2 SINE.100  
 GPC1 0.00 %  
 GPC2 0.00 %  
 GPT1 0.00 %  
 GPT2 0.00 %  
 GPC1 30.00 %  
 GPC2 50.00 %  
 p15 500.00 usec  
 p16 1000.00 usec

F2 - Processing parameters  
 SI 65536  
 SF 125.7804117 MHz  
 WDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 2.00

1D NMR plot parameters  
 CX 22.80 cm  
 CY 15.65 cm  
 FIP 220.000 ppm  
 FI 21671.68 Hz  
 FZP -10.000 ppm  
 FZ -1257.80 Hz  
 FPCX 10.08712 ppm/cm  
 HFCH 1268.83752 Hz/cm

ppm 200 150 100 50 0

<sup>1</sup>H spectrum



Current Data Parameters  
 USER dawson  
 NAME DDD-2-206-protonCRYO  
 EXPNO 1  
 PROCNO 1

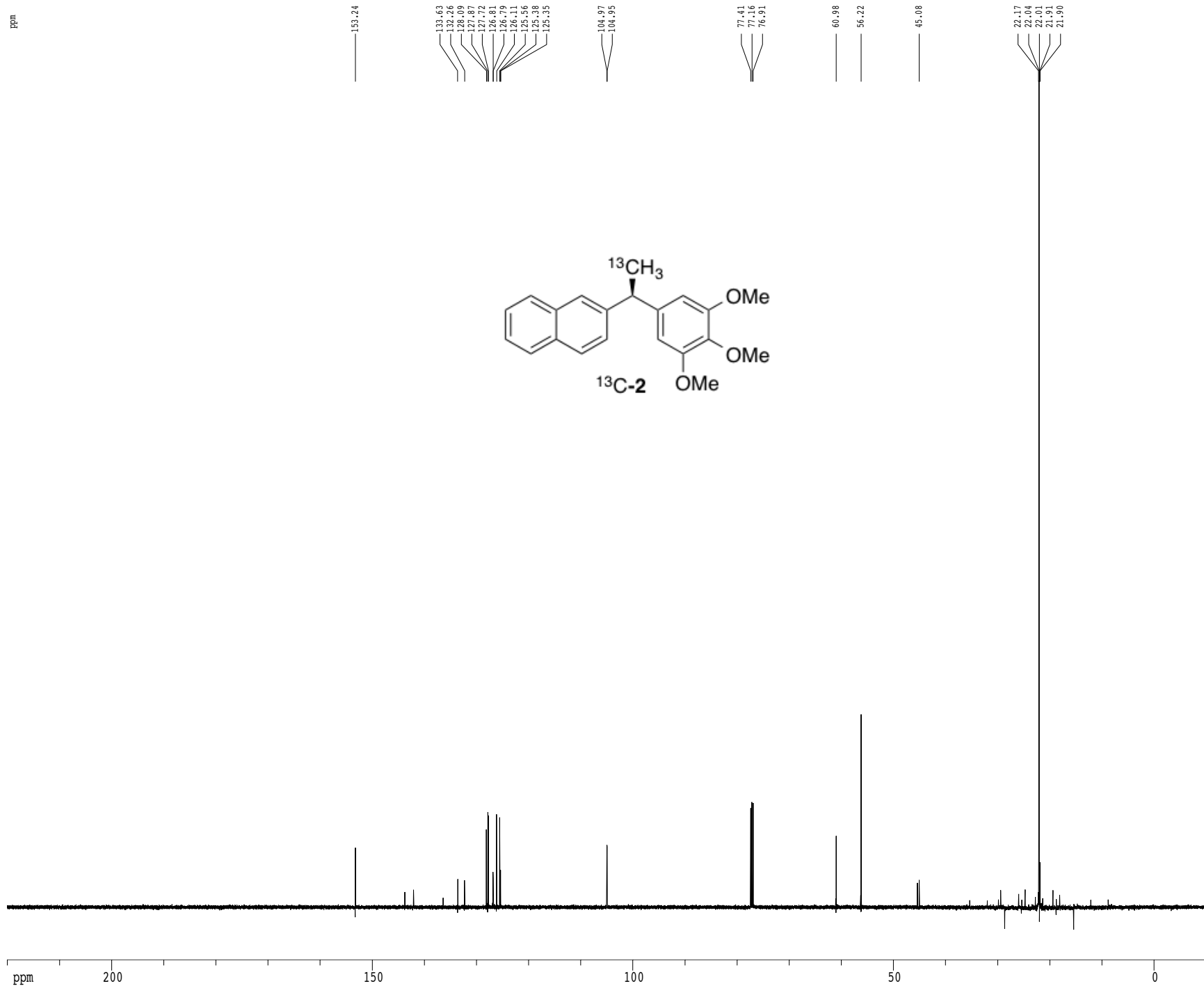
F2 - Acquisition Parameters  
 Date\_ 20150410  
 Time\_ 12.15  
 INSTRUM cryo500  
 PROBHD 5 mm CPTCI 1H-  
 PULPROG zg30  
 TD 61728  
 SOLVENT CDCl3  
 NS 8  
 DS 2  
 SWH 8012.820 Hz  
 FIDRES 0.098043 Hz  
 AQ 5.0998774 sec  
 RG 4  
 DW 62.400 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.10000000 sec  
 MCREST 0.00000000 sec  
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.50 usec  
 PL1 1.60 dB  
 SFO1 500.2235015 MHz

F2 - Processing parameters  
 SI 65536  
 SF 500.2200343 MHz  
 WDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 4.00

1D NMR plot parameters  
 CX 22.80 cm  
 CY 15.00 cm  
 FIP 9.000 ppm  
 F1 4501.98 Hz  
 F2P -0.500 ppm  
 F2 -250.11 Hz  
 PPMCM 0.41667 ppm/cm  
 HZCM 208.42502 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



```

Current Data Parameters
USER      dawson
NAME      DDD-2-206-carbonCryo
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20150410
Time      12.22
INSTRUM   cryo500
PROBHD    5 mm CPAC1 1H-
PULPROG   spinEchops30cp.prd
TD         65536
SOLVENT   CDCl3
NS         303
DS         16
SWH        30303.031 Hz
FIDRES     0.462398 Hz
AQ          1.0813940 sec
RG          5160.6
DW          16.500 usec
DE           6.00 usec
TE          298.0 K
d1          0.25000000 sec
d11         0.03000000 sec
d16         0.00020000 sec
d17         0.00019600 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec
PZ          33.10 usec

===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
P11        500.00 usec
P12        2000.00 usec
PL0        120.00 dB
PL1         -1.00 dB
SFO1       125.7942548 MHz
SP1         2.70 dB
SP2         2.70 dB
SPNAM1     Crp60,0.5,20.1
SPNAM2     Crp60ccomp,4
SPOFF1     0.00 Hz
SPOFF2     0.00 Hz

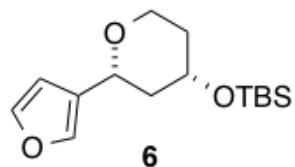
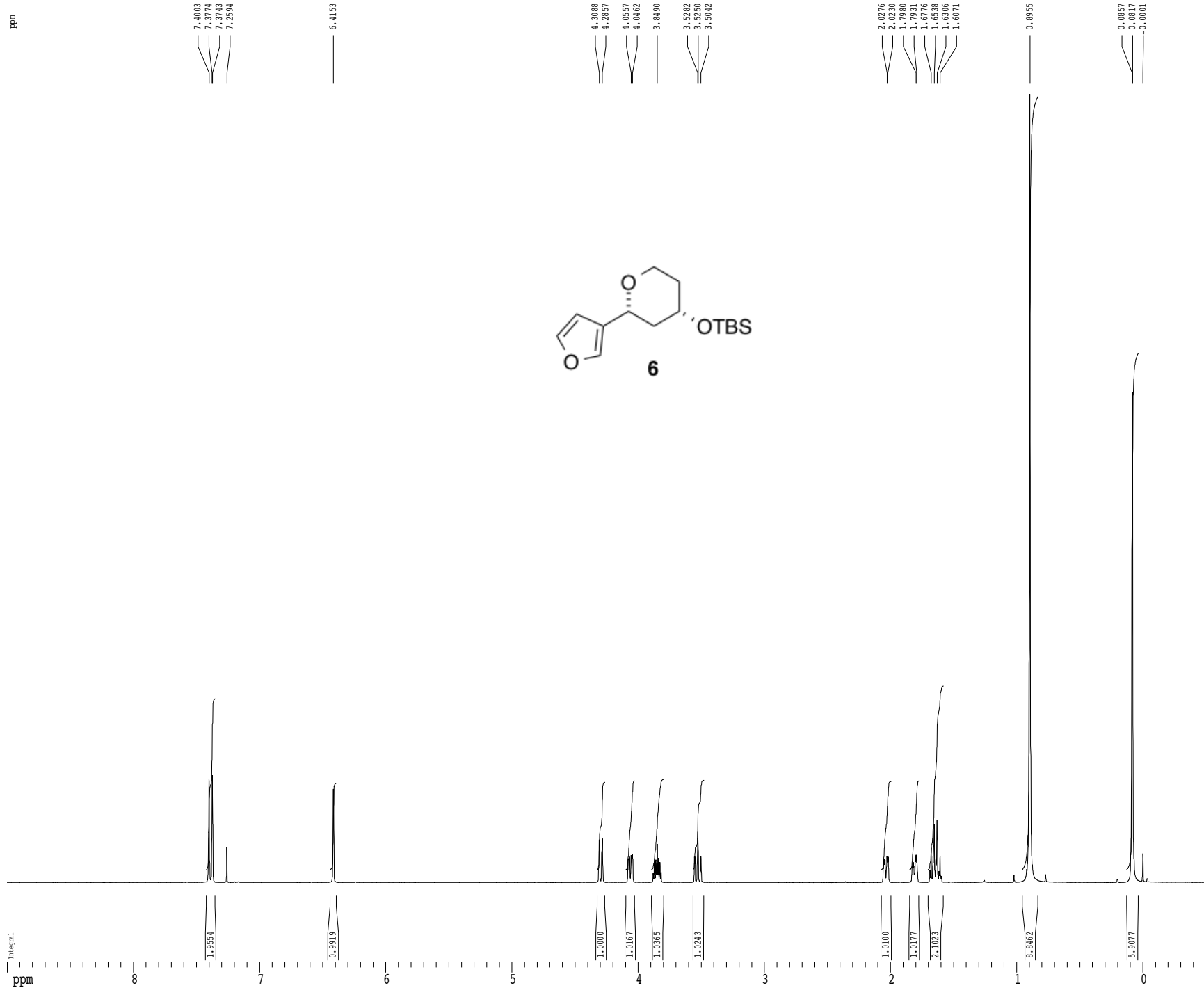
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      100.00 usec
PL2         1.60 dB
PL12        24.50 dB
SFO2       500.2225011 MHz

===== GRADIENT CHANNEL =====
GPNAM1     SINE.100
GPNAM2     SINE.100
GPY1       0.00 %
GPX2       0.00 %
GPY2       0.00 %
GPZ1       30.00 %
GPZ2       50.00 %
p15        500.00 usec
p16        1000.00 usec

F2 - Processing parameters
SI         65536
SF         125.7804094 MHz
NUC1       no
SSB         0
LB          0.00 Hz
GB          0
PC          2.00

ID NMR plot parameters
CX         22.80 cm
CY         120.00 cm
F1P        220.000 ppm
F1          27671.69 Hz
F2P        -10.000 ppm
F2          -1257.80 Hz
PPMCM      10.08772 ppm/cm
HZCM       1268.83752 Hz/cm
    
```

<sup>1</sup>H spectrum



Current Data Parameters  
 USER dawson  
 NAME DDD-2-149-protonCRYO  
 EXPNO 1  
 PROCNO 1

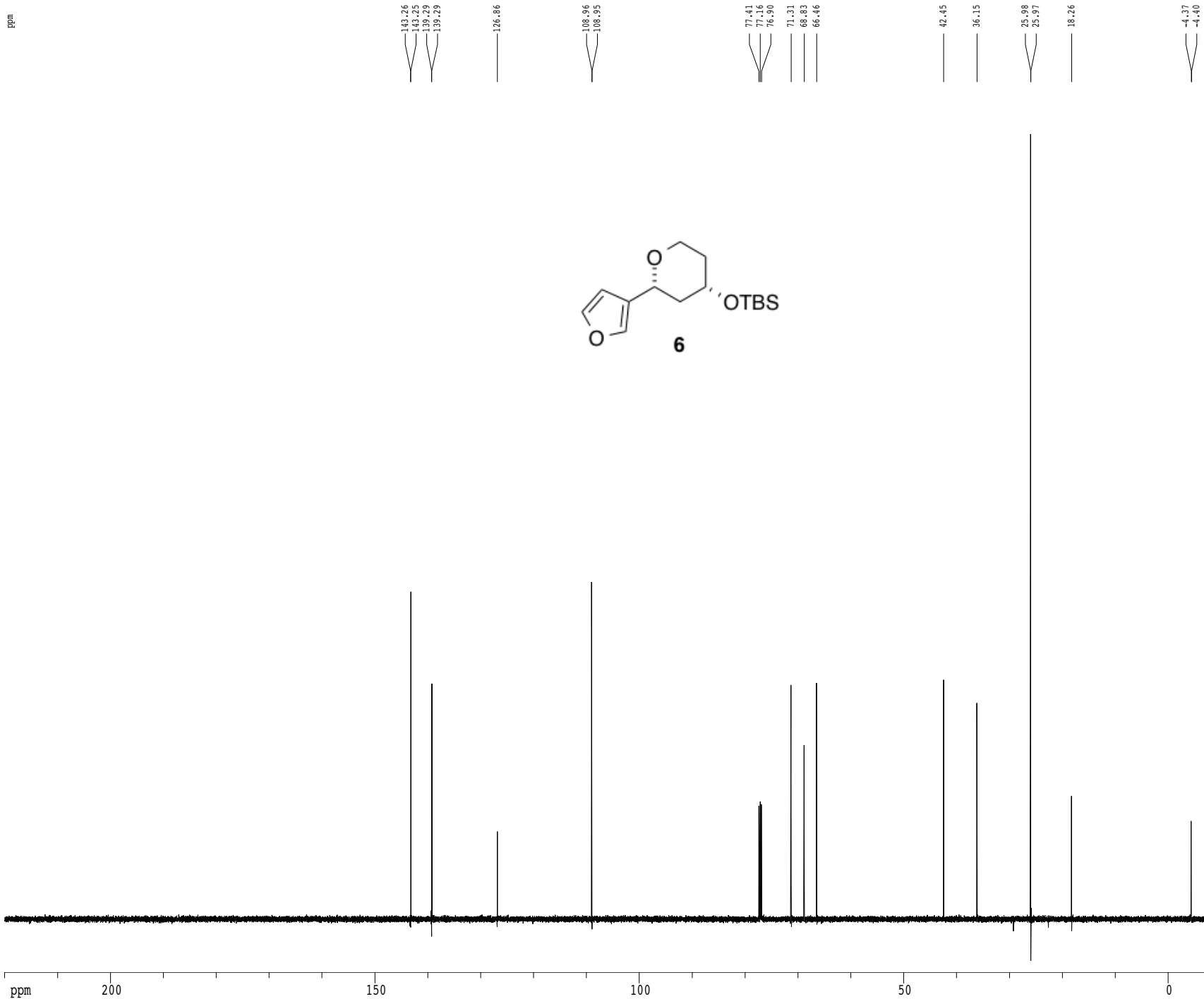
F2 - Acquisition Parameters  
 Date\_ 20150217  
 Time\_ 14.06  
 INSTRUM cryo500  
 PROBHD 5 mm CPTCI 1H-  
 PULPROG zg30  
 TD 61728  
 SOLVENT CDCl3  
 NS 8  
 DS 2  
 SWH 8012.820 Hz  
 FIDRES 0.098043 Hz  
 AQ 5.0998774 sec  
 RG 3.6  
 DW 62.400 usec  
 DE 6.00 usec  
 TE 298.0 K  
 D1 0.10000000 sec  
 MCREST 0.00000000 sec  
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.50 usec  
 PL1 1.60 dB  
 SFO1 500.2235015 MHz

F2 - Processing parameters  
 SI 65536  
 SF 500.2200307 MHz  
 WDW no  
 SSB 0  
 LB 0.00 Hz  
 GB 0  
 PC 4.00

1D NMR plot parameters  
 CX 22.80 cm  
 CT 15.00 cm  
 FIP 9.000 ppm  
 F1 4501.98 Hz  
 F2P -0.500 ppm  
 F2 -250.11 Hz  
 PPMCM 0.41667 ppm/cm  
 HZCM 208.42502 Hz/cm

Z-restored spin-echo 13C spectrum with 1H decoupling



```

Current Data Parameters
USER          dawson
NAME          DDD-2-149-carbonCryo
EXPNO         1
PROCNO        1

F2 - Acquisition Parameters
Date_         20150217
Time          14.10
INSTRUM       cryo500
PROBHD        5 mm CPACI 1H-
PULPROG       spinEchops30sp.prd
TD            65536
SOLVENT       CDCl3
NS            131
DS            16
SWH           30303.031 Hz
FIDRES        0.462398 Hz
AQ            1.0813940 sec
RG            5792.6
DW            16.500 usec
DE            6.00 usec
TE            298.0 K
D1            0.25000000 sec
d11           0.43000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
PZ            33.10 usec

===== CHANNEL f1 =====
NUC1           13C
P1            16.55 usec
P11           500.00 usec
P12           2000.00 usec
PL0           120.00 dB
PL1           -1.00 dB
SFO1          125.7942548 MHz
SP1           2.70 dB
SP2           2.70 dB
SPNAM1        Crp60,0.5,20.1
SPNAM2        Crp60ccomp,4
SPOFF1         0.00 Hz
SPOFF2         0.00 Hz

===== CHANNEL f2 =====
CPDPRG2        waltz16
NUC2            1H
PCPD2          100.00 usec
PL2            1.60 dB
PL12           24.50 dB
SFO2          500.2225011 MHz

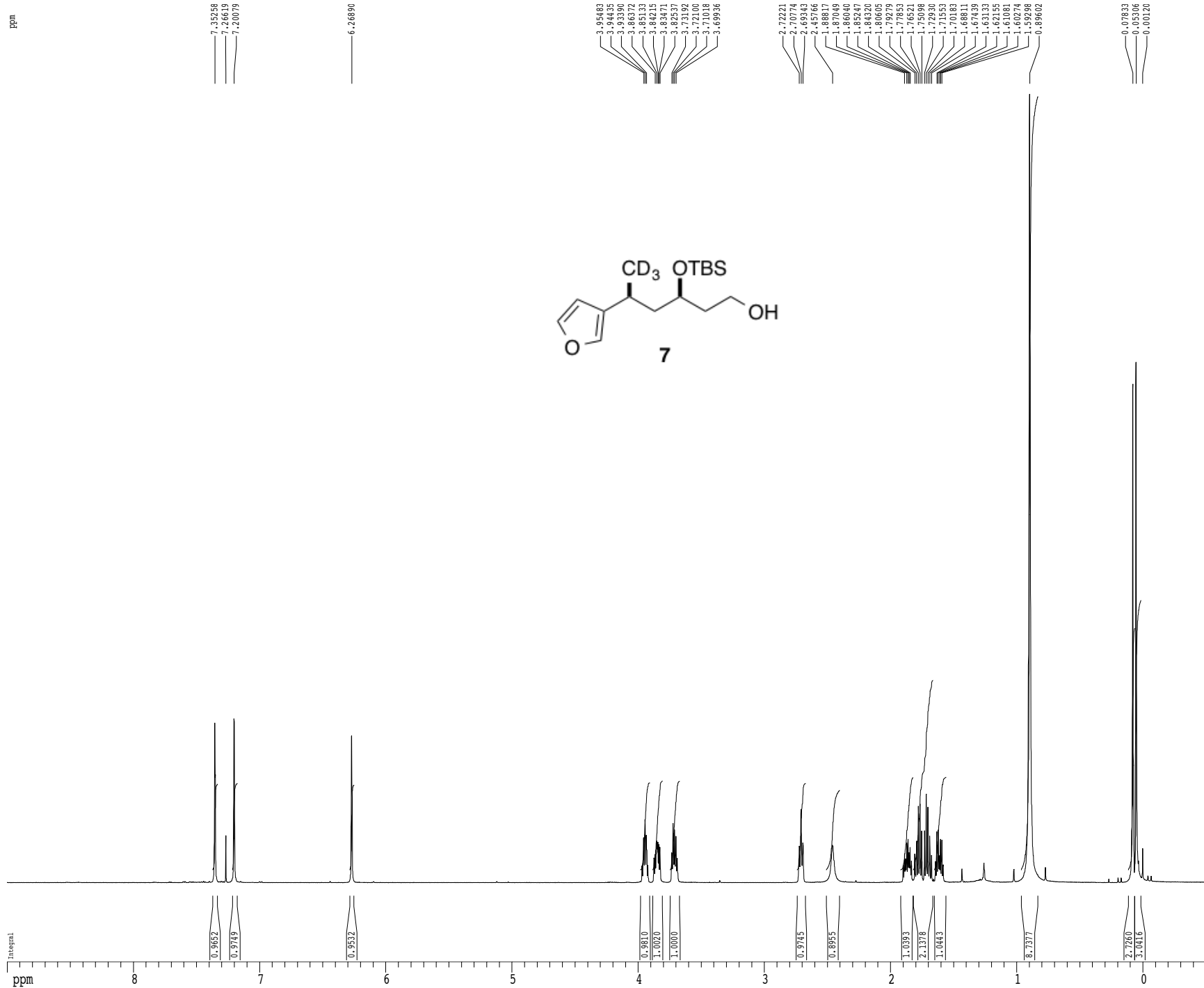
===== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1           0.00 %
GPX2           0.00 %
GPY1           0.00 %
GPY2           0.00 %
GPZ1           30.00 %
GPZ2           50.00 %
p15            500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI            65536
SF            125.7804090 MHz
NUW           no
SSB           0
LB            0.00 Hz
GB            0
PC            2.00

ID NMR plot parameters
CX            22.80 cm
CY            15.65 cm
F1P           220.000 ppm
F1            27671.69 Hz
F2P           -10.000 ppm
F2            -1257.80 Hz
PPMCM         10.08772 ppm/cm
HZCM          1268.83752 Hz/cm
    
```



<sup>1</sup>H spectrum



```

Current Data Parameters
USER          dawson
NAME         DDD-2-196-Iso-protonCRYO
EXPNO        1
PROCNO       1

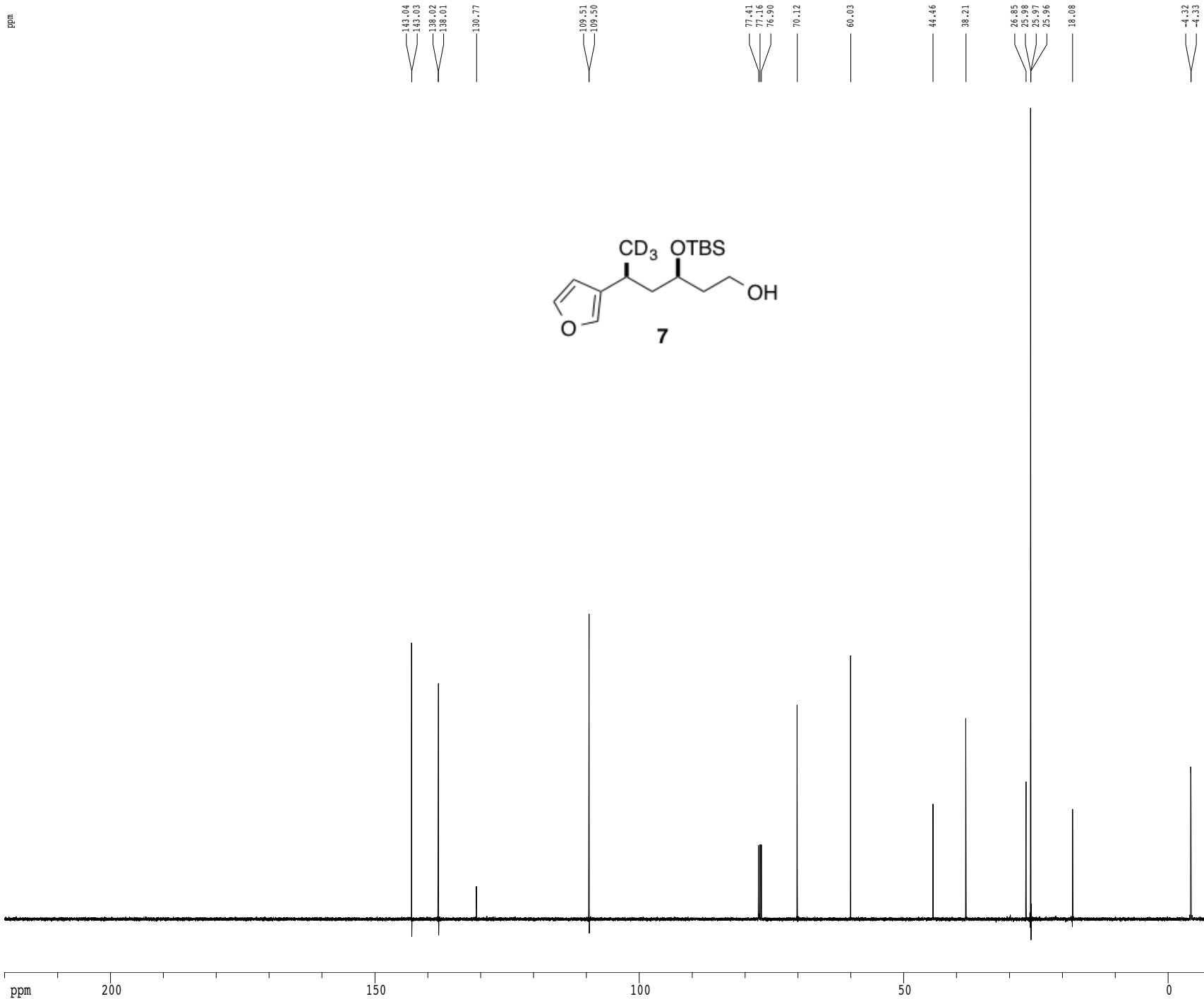
F2 - Acquisition Parameters
Date_        20150316
Time         10.06
INSTRUM      cryo500
PROBHD       5 mm CPCCI 1H-
PULPROG      zg30
TD           81728
SOLVENT      CDCl3
NS           8
DS           2
SWH          8012.820 Hz
FIDRES       0.098043 Hz
AQ           5.0998774 sec
RG           2.5
DW           62.400 usec
DE           6.00 usec
TE           298.0 K
D1           0.1000000 sec
MCREST       0.0000000 sec
MCWRX        0.0150000 sec

***** CHANNEL f1 *****
NUC1         1H
P1           7.50 usec
PL1         1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI           65536
SF           500.2200277 MHz
WDW          no
SSB          0
LB           0.00 Hz
GB           0
PC           4.00

ID NMR plot parameters
CX           22.80 cm
CY           15.00 cm
FIP          9.000 ppm
F1           4501.98 Hz
F2P          -0.500 ppm
F2           -250.11 Hz
FPMCM        0.41867 ppm/cm
HZCM         208.42502 Hz/cm
    
```

Z-restored spin-echo 13C spectrum with 1H decoupling



```

Current Data Parameters
NAME      dawson
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20150316
Time     10.11
INSTRUM  cryo500
PROBHD   5 mm CP131 H-
PULPROG  SpinEchopp3Dgpr
TD        65536
SOLVENT  CDCl3
NS        165
DS        16
SWH       30303.031 Hz
FIDRES    0.462388 Hz
AQ        1.0813940 sec
RG        5160.6
DW        16.500 usec
DE        6.00 usec
TE        298.0 K
D1        0.25000000 sec
d11       0.03000000 sec
d16       0.00020000 sec
d17       0.00019600 sec
MCREST    0.00000000 sec
MCWRX     0.01500000 sec
PZ        33.10 usec

===== CHANNEL f1 =====
NUC1      13C
P1        16.55 usec
PI1       500.00 usec
PI2       2000.00 usec
PL0       120.00 dB
PL1       -1.00 dB
SFO1      125.7942548 MHz
SF1       2.70 dB
SF2       2.70 dB
SFOFF1    Crp60,0.5,20.1
SFOFF2    Crp60comp,4
SFOFF3    0.00 Hz
SFOFF4    0.00 Hz

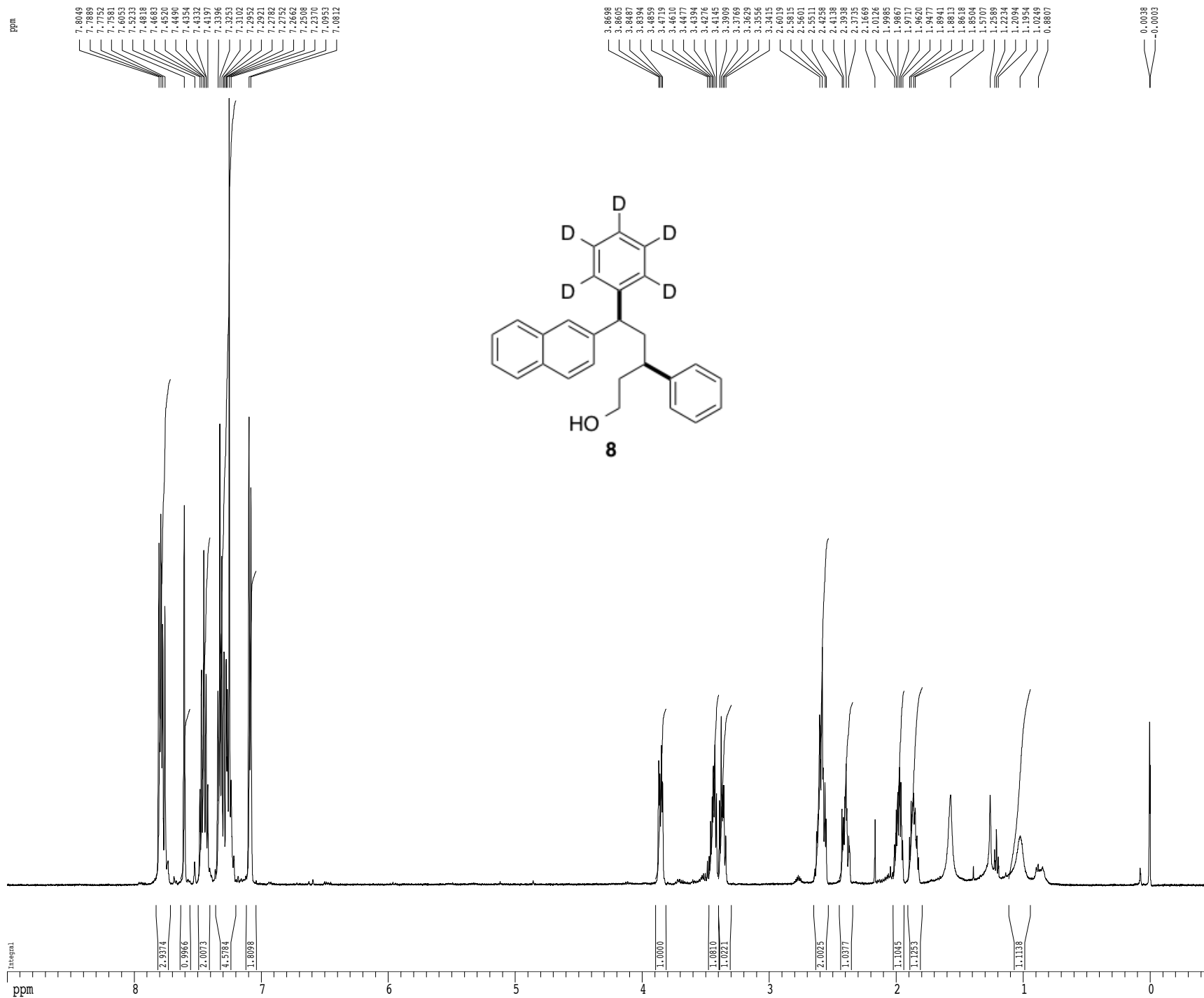
===== CHANNEL f2 =====
CPDPRG2   wait16
NUC2      1H
PCPD2    100.00 usec
PL2       1.60 dB
PL12      24.50 dB
SFO2      500.2225011 MHz

===== GRADIENT CHANNEL =====
GPNAM1    SINE.100
GPNAM2    SINE.100
GPY1      0.00 %
GPY2      0.00 %
GPY3      0.00 %
GPY4      0.00 %
GPY5      0.00 %
GPY6      0.00 %
GPY7      30.00 %
GPY8      50.00 %
p15       500.00 usec
p16       1000.00 usec

F2 - Processing parameters
SI        65536
SF        125.7804103 MHz
WDW       no
SSB       0
LB        0.00 Hz
GB        0
PC        2.00

1D NMR plot parameters
CX        22.80 cm
CY        15.65 cm
F1P       220.000 ppm
F1        27671.69 Hz
F2P       -10.000 ppm
F2        -1257.80 Hz
PPMCM     10.08772 ppm/cm
HZCM      1268.83752 Hz/cm
    
```

<sup>1</sup>H spectrum



```

Current Data Parameters
USER      dawson
NAME      DDD-2-211-iso-protonCRYO
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20150409
Time      18.20
INSTRUM   cryo500
PROBHD    5 mm CPXI 1H-
PULPROG   zg30
TD         81728
SOLVENT   CDCl3
NS         8
DS         2
SWH        8012.820 Hz
FIDRES     0.098043 Hz
AQ         5.0998774 sec
RG         4.5
DW         62.400 usec
DE         6.00 usec
TE         298.0 K
D1         0.10000000 sec
MCREST     0.00000000 sec
MCWRX      0.01500000 sec

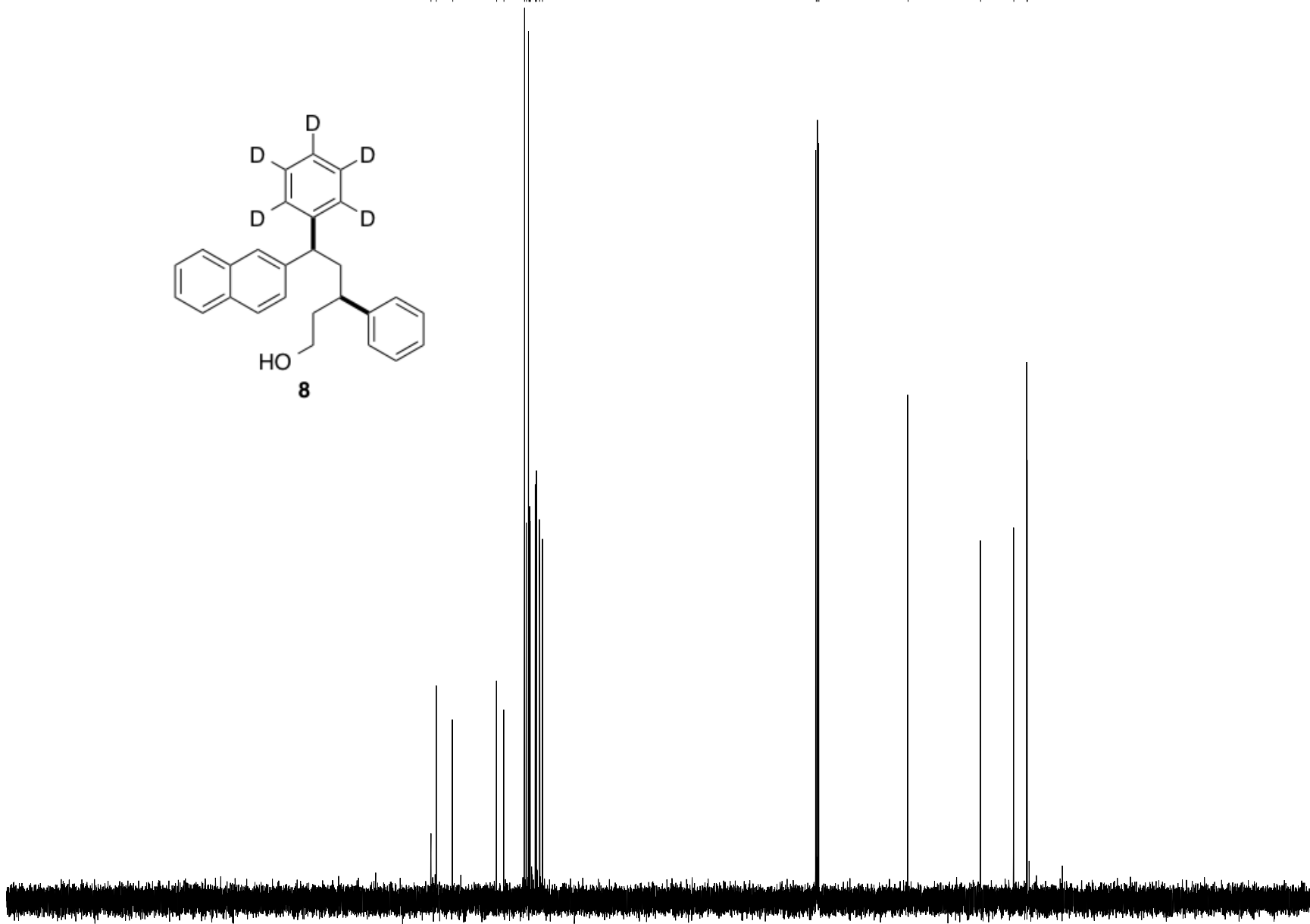
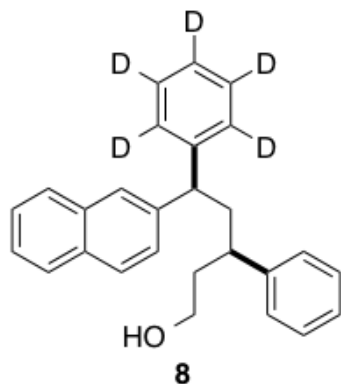
***** CHANNEL f1 *****
NUC1       1H
P1         7.50 usec
PL1        1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI         65536
SF         500.2200355 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         4.00

ID NMR plot parameters
CX         22.80 cm
CY         15.00 cm
FIP        9.000 ppm
F1         4501.98 Hz
F2P        -0.500 ppm
F2         -250.11 Hz
FPCMH      0.41867 ppm/cm
HZCM       208.42502 Hz/cm
    
```

Z-restored spin-echo 13C spectrum with 1H decoupling

ppm



```

Current Data Parameters
USER          dawson
NAME          DDD-2-211-180-carbonCryo
EXPNO        1
PROCNO       1

F2 - Acquisition Parameters
Date_        20150409
Time         18.24
INSTRUM      cryo500
PROBHD       5 mm CP131 H-
PULPROG      SpinEchopp3Dg.prd
TD           65536
SOLVENT      CDCl3
NS           214
DS           16
SWH          30303.031 Hz
FIDRES       0.462388 Hz
AQ           1.0813940 sec
RG           5160.6
DW           16.500 usec
DE           6.40 usec
TE           298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
d16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRX        0.01500000 sec
PZ           33.10 usec

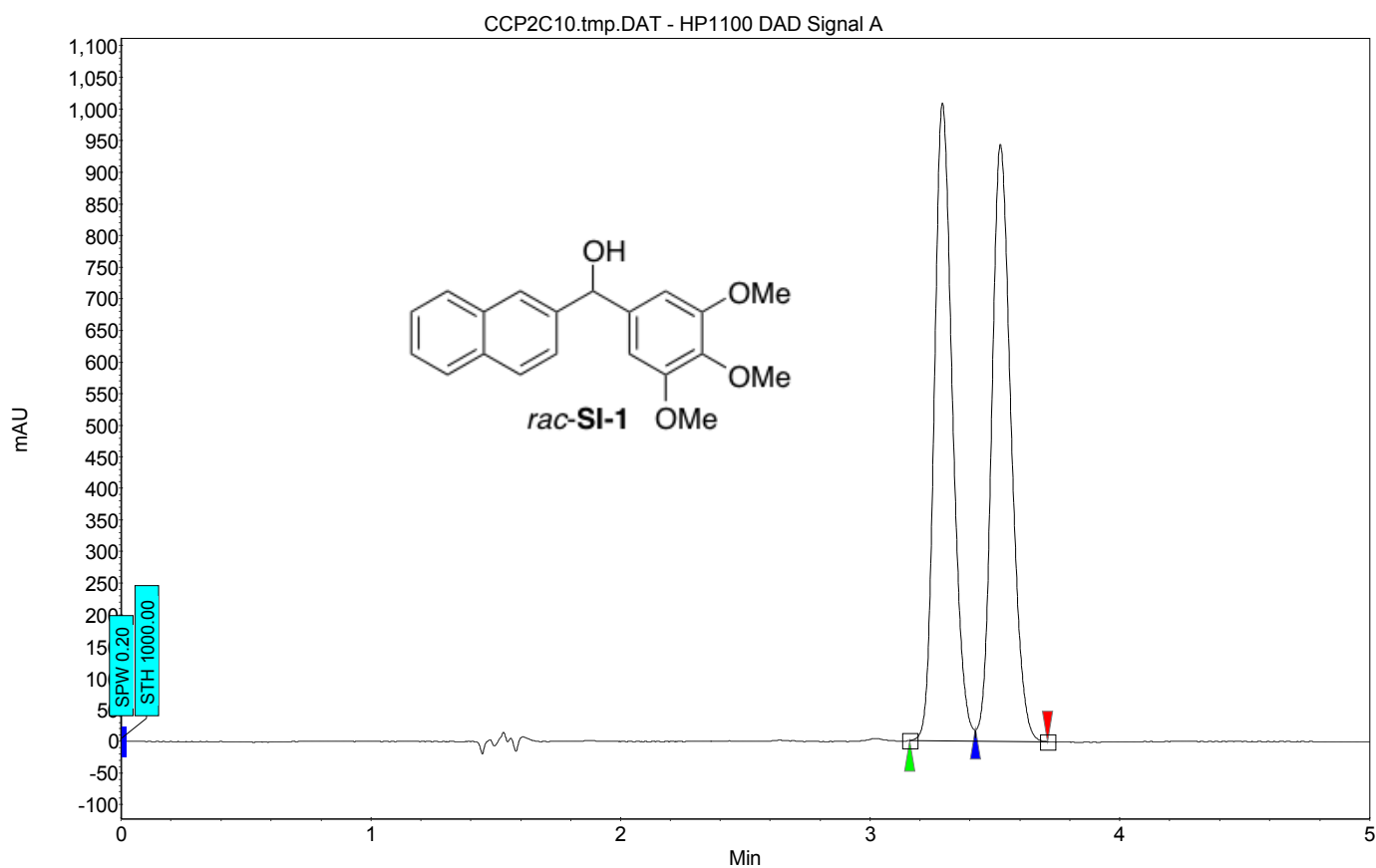
===== CHANNEL f1 =====
NUC1         13C
P1           16.55 usec
P11          500.00 usec
P12          2000.00 usec
PL0          120.00 dB
PL1          -1.00 dB
SFO1         125.7942548 MHz
SFO2         2.70 dB
SFO3         2.70 dB
SFO4         2.70 dB
SFO5         2.70 dB
SFO6         2.70 dB
SFO7         2.70 dB
SFO8         2.70 dB
SFO9         2.70 dB
SFO10        2.70 dB
SFO11        2.70 dB
SFO12        2.70 dB
SFO13        2.70 dB
SFO14        2.70 dB
SFO15        2.70 dB
SFO16        2.70 dB
SFO17        2.70 dB
SFO18        2.70 dB
SFO19        2.70 dB
SFO20        2.70 dB
SFO21        2.70 dB
SFO22        2.70 dB
SFO23        2.70 dB
SFO24        2.70 dB
SFO25        2.70 dB
SFO26        2.70 dB
SFO27        2.70 dB
SFO28        2.70 dB
SFO29        2.70 dB
SFO30        2.70 dB
SFO31        2.70 dB
SFO32        2.70 dB
SFO33        2.70 dB
SFO34        2.70 dB
SFO35        2.70 dB
SFO36        2.70 dB
SFO37        2.70 dB
SFO38        2.70 dB
SFO39        2.70 dB
SFO40        2.70 dB
SFO41        2.70 dB
SFO42        2.70 dB
SFO43        2.70 dB
SFO44        2.70 dB
SFO45        2.70 dB
SFO46        2.70 dB
SFO47        2.70 dB
SFO48        2.70 dB
SFO49        2.70 dB
SFO50        2.70 dB
SFO51        2.70 dB
SFO52        2.70 dB
SFO53        2.70 dB
SFO54        2.70 dB
SFO55        2.70 dB
SFO56        2.70 dB
SFO57        2.70 dB
SFO58        2.70 dB
SFO59        2.70 dB
SFO60        2.70 dB
SFO61        2.70 dB
SFO62        2.70 dB
SFO63        2.70 dB
SFO64        2.70 dB
SFO65        2.70 dB
SFO66        2.70 dB
SFO67        2.70 dB
SFO68        2.70 dB
SFO69        2.70 dB
SFO70        2.70 dB
SFO71        2.70 dB
SFO72        2.70 dB
SFO73        2.70 dB
SFO74        2.70 dB
SFO75        2.70 dB
SFO76        2.70 dB
SFO77        2.70 dB
SFO78        2.70 dB
SFO79        2.70 dB
SFO80        2.70 dB
SFO81        2.70 dB
SFO82        2.70 dB
SFO83        2.70 dB
SFO84        2.70 dB
SFO85        2.70 dB
SFO86        2.70 dB
SFO87        2.70 dB
SFO88        2.70 dB
SFO89        2.70 dB
SFO90        2.70 dB
SFO91        2.70 dB
SFO92        2.70 dB
SFO93        2.70 dB
SFO94        2.70 dB
SFO95        2.70 dB
SFO96        2.70 dB
SFO97        2.70 dB
SFO98        2.70 dB
SFO99        2.70 dB
SFO100       2.70 dB

===== CHANNEL f2 =====
CPDPRG2      wait16
NUC2         1H
PCPD2        100.00 usec
PL2          1.60 dB
PL12         24.50 dB
SFO2         500.2225011 MHz

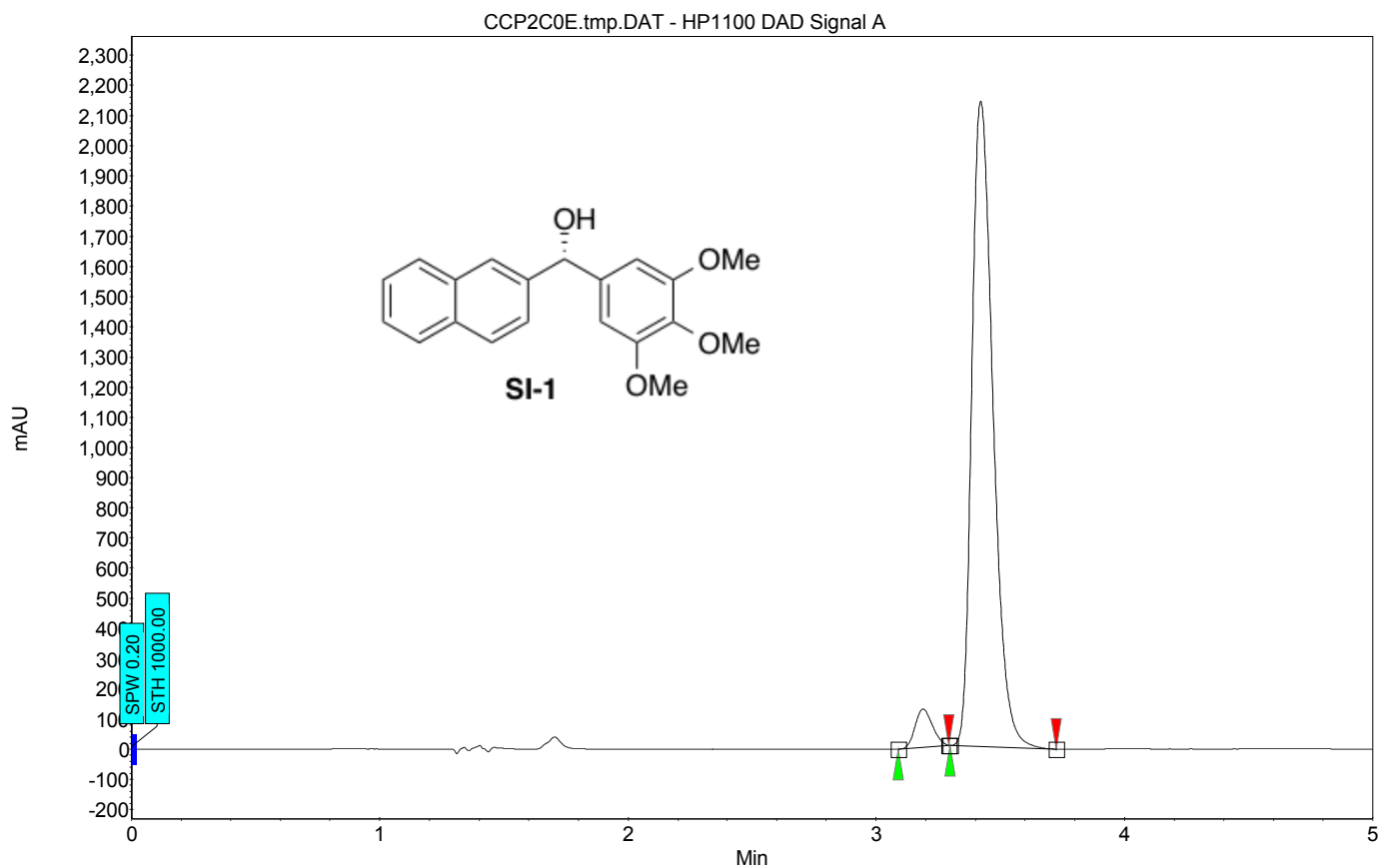
===== GRADIENT CHANNEL =====
GPRAM1       SINE.100
GPRAM2       SINE.100
GPY1         0.00 %
GPX2         0.00 %
GPY1         0.00 %
GPY2         0.00 %
GPY1         30.00 %
GPY2         50.00 %
p15          500.00 usec
p16          1000.00 usec

F2 - Processing parameters
SI           65536
SF           125.7804099 MHz
WDW          no
SSB          0
LB           0.00 Hz
GB           0
PC           2.00

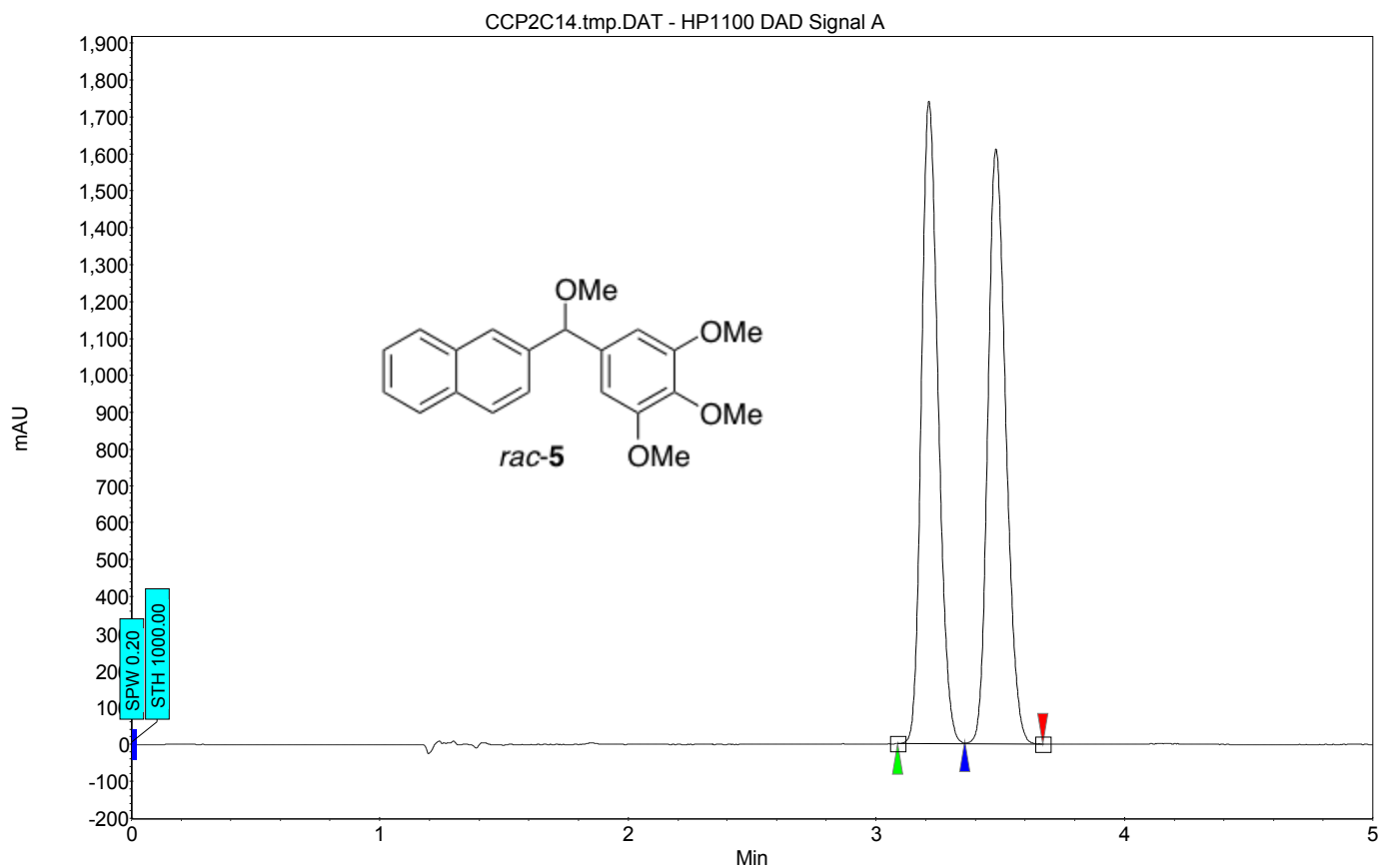
1D NMR plot parameters
CX           22.80 cm
CY           15.65 cm
F1P          220.000 ppm
F1           27671.69 Hz
F2P          -10.000 ppm
F2           -1257.80 Hz
PPMCM        10.08772 ppm/cm
HZCM         1268.83752 Hz/cm
    
```



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	3.16	3.29	3.42	0.00	50.04	1008.8	84.8	50.044
2	UNKNOWN	3.42	3.52	3.71	0.00	49.96	944.5	84.7	49.956
Total						100.00	1953.3	169.5	100.000

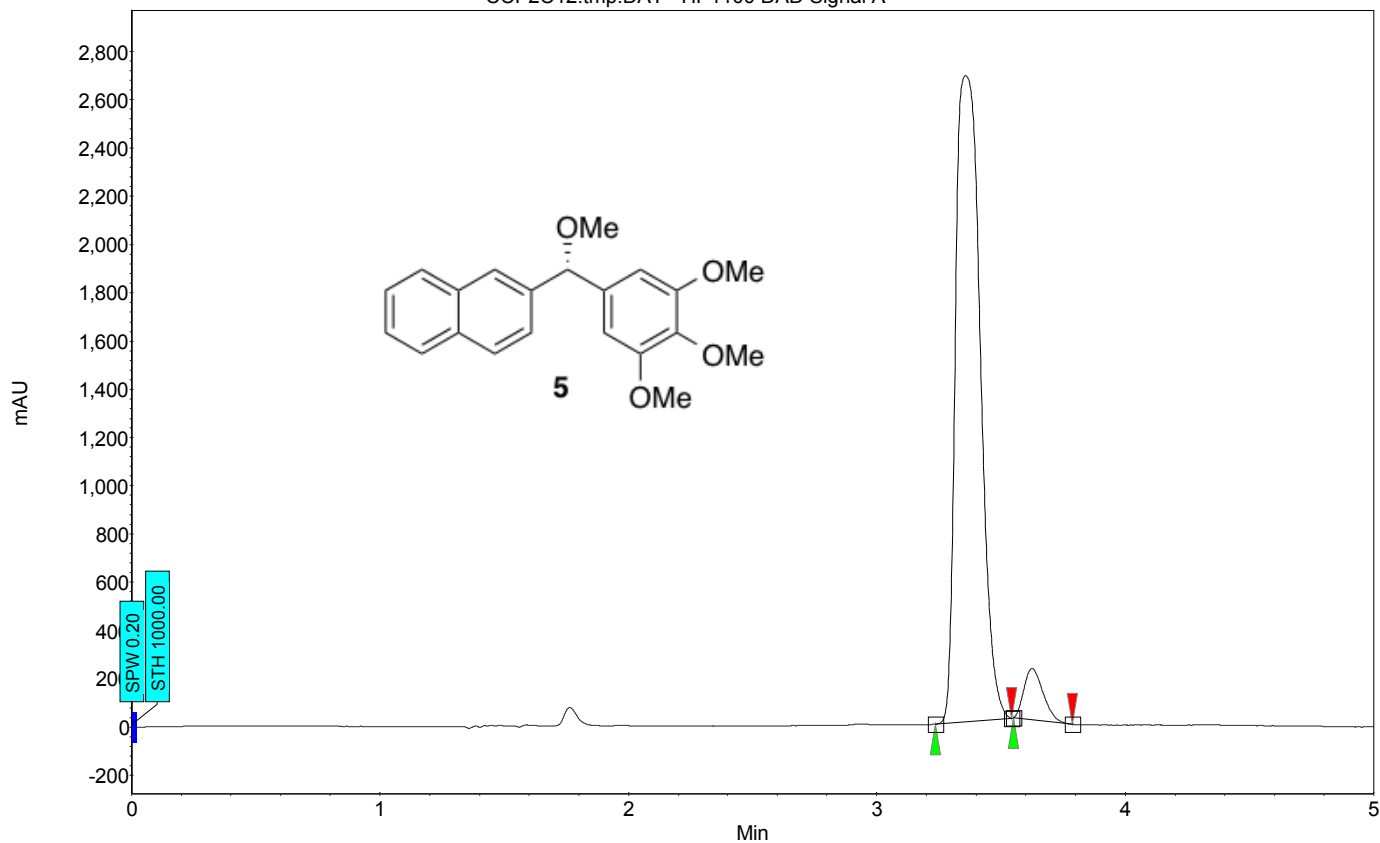


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	3.09	3.19	3.29	0.00	4.56	126.4	10.1	4.562
2	UNKNOWN	3.30	3.42	3.73	0.00	95.44	2138.6	211.9	95.438
Total						100.00	2264.9	222.1	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	3.09	3.21	3.36	0.00	50.02	1741.7	136.1	50.018
2	UNKNOWN	3.36	3.48	3.67	0.00	49.98	1613.0	136.0	49.982
Total						100.00	3354.8	272.1	100.000

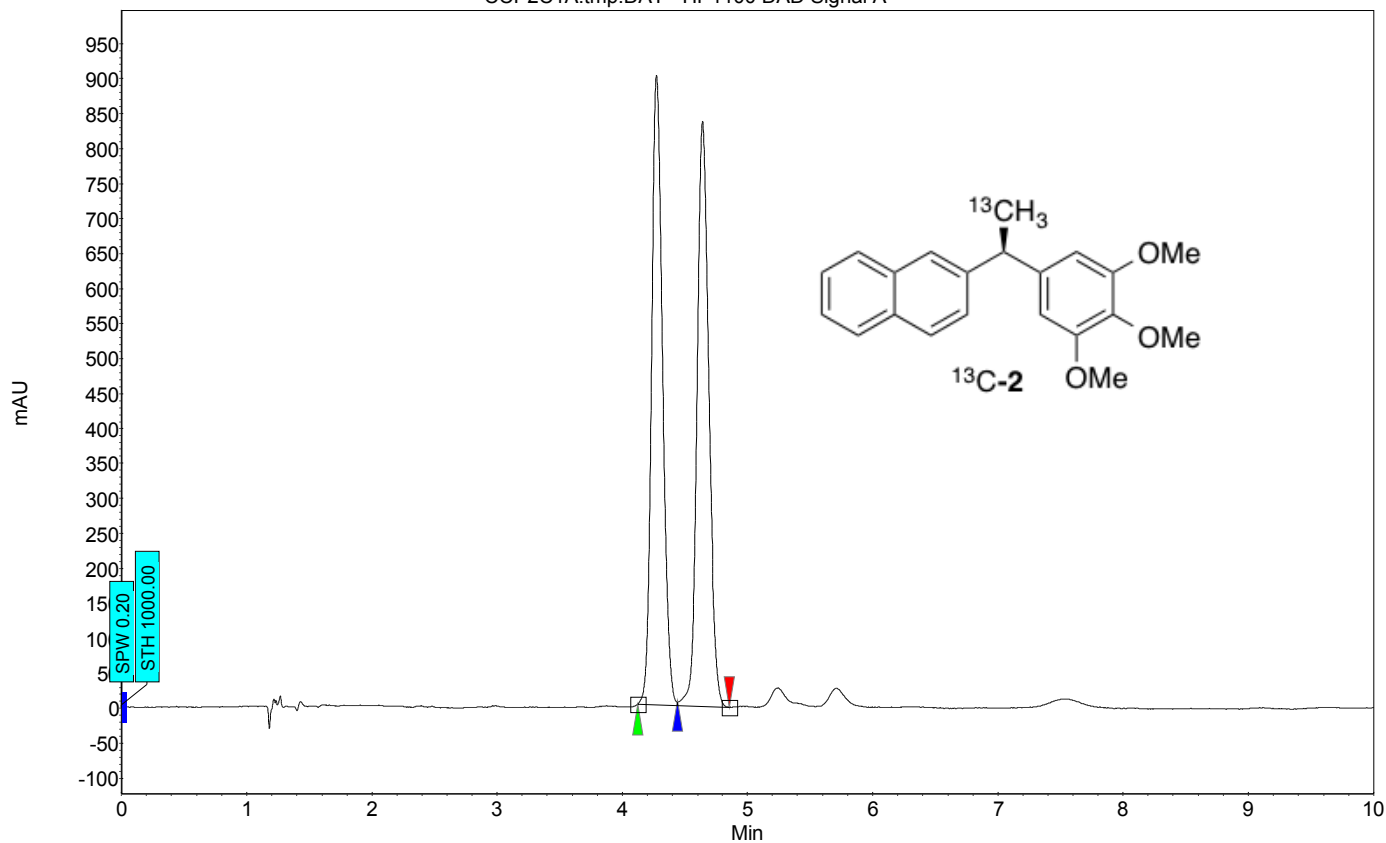
CCP2C12.tmp.DAT - HP1100 DAD Signal A



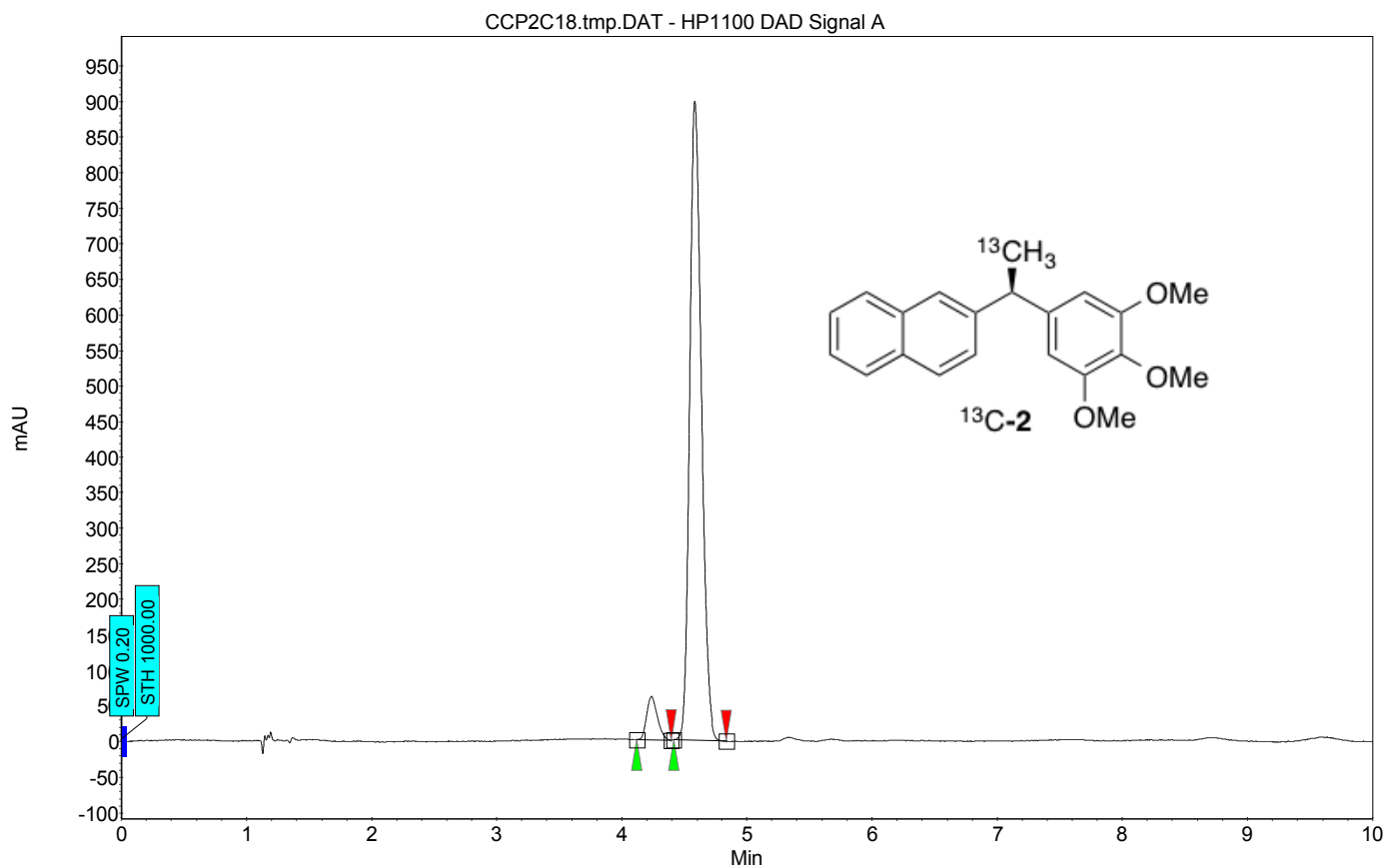
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	3.24	3.36	3.54	0.00	94.16	2680.2	307.8	94.158
2	UNKNOWN	3.55	3.63	3.79	0.00	5.84	213.4	19.1	5.842
Total						100.00	2893.6	326.9	100.000



CCP2C1A.tmp.DAT - HP1100 DAD Signal A



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μV]	[μV.Min]	[%]
1	UNKNOWN	4.12	4.27	4.44	0.00	49.75	899.8	91.7	49.753
2	UNKNOWN	4.44	4.64	4.86	0.00	50.25	836.2	92.6	50.247
Total						100.00	1736.0	184.3	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[ $\mu$ V]	[ $\mu$ V.Min]	[%]
1	UNKNOWN	4.11	4.23	4.39	0.00	5.77	61.3	6.0	5.773
2	UNKNOWN	4.41	4.58	4.84	0.00	94.23	898.8	98.1	94.227
Total						100.00	960.1	104.1	100.000