Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Highly Diastereoselective Synthesis of *ortho*-Quinone Monoketals via λ^3-Iodane-Mediated Oxidative Dearomatization of Phenols**

Laurent Pouységu, Stefan Chassaing, Delphine Dejugnac, Anne-Marie Lamidey, Karinne Miqueu, Jean-Marc Sotiropoulos, and Stéphane Quideau*

[*] Dr. L. Pouységu, Dr. S. Chassaing, Dr. D. Dejugnac, A.-M. Lamidey, Prof. S. Quideau

Université de Bordeaux

Institut des Sciences Moléculaires (CNRS-UMR 5255)

and Institut Européen de Chimie et Biologie

2 rue Robert Escarpit, 33607 Pessac Cedex (France)

Fax: (+33) 540-00-22-15

E-mail: s.quideau@iecb.u-bordeaux.fr

Dr. J.-M. Sotiropoulos, Dr. K. Miqueu

IPREM (CNRS-UMR 5254)

Université de Pau et des Pays de l'Adour

avenue de l'Université, 64013 Pau Cedex (France)

SUPPORTING INFORMATION

Supporting Information

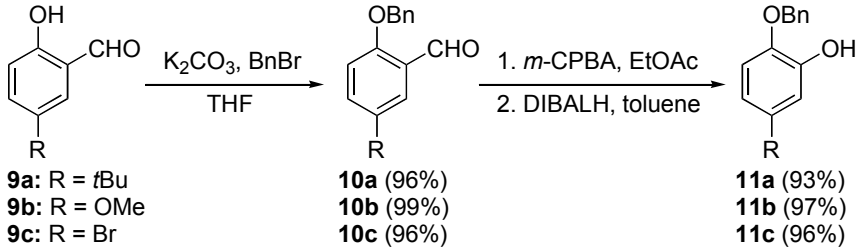
CONTENTS

Experimental Section

General. All moisture and oxygen sensitive reactions were carried out in flame-dried glassware under N_2. Tetrahydrofuran (THF) was purified immediately before use either by distillation from sodium/benzophenone under N_2, or by filtration through alumina under N_2. Methanol (MeOH), toluene (PhMe) and dimethylformamide (DMF) were distilled under N_2 prior to use from Mg/I_2, $CaCl_2$, and P_2O_5, respectively. Synthesis grade 2,2,2-trifluoroethanol (TFE; Aldrich), ethyl acetate (EtOAc), and (diacetoxyiodo)benzene (DIB; SIMAFEX) were used as received. Evaporations were conducted under reduced pressure at temperatures less than 30 °C unless otherwise noted. Column chromatography was carried out under positive pressure using 40-63 μm silica gel (Merck) and the indicated solvents. Melting points were measured in open capillary tubes and are uncorrected. NMR spectra of samples in the indicated solvent were run at 250, 300 or 400 MHz and calibrated using residual solvent as an internal standard. Carbon multiplicities were determined by either DEPT135 or *J*-Mod experiments. Stereochemical assignments were achieved by NOESY experiments. Electron impact (EIMS, 50-70 eV), chemical ionization (CIMS), elecrospray (ESIMS), and liquid secondary ion mass spectrometry (LSIMS) low and/or high resolution (HRMS) mass spectrometric analyses were obtained from either the mass spectrometry laboratory at the Centre d'Etude Structurale et d'Analyse des Molécules Organiques (CESAMO), Université Bordeaux 1, or the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université Rennes 1, France. Elemental analyses were carried out at the Service Central d'Analyses du CNRS, Vernaison. The X-ray crystallographic analyses were performed at the Institut Européen de Chimie et Biologie (IECB); X-ray diffraction data were collected at 100 K on a crystal in a cryoloop under oil, using Cu Kα radiation on a Bruker AXS rotating anode diffractometer.

Preparation of the phenols 11a-c (Scheme S1). Phenols **11a-c** were prepared in excellent yields from commercially available salicyladehydes **9a-c** substituted in position 5. The first step consisted in a benzylation of the phenol function under standard conditions to give the 2-benzyloxybenzaldehydes **10a-c** in nearly quantitative yields (Scheme S1). A Baeyer-Villiger oxidation of these aldehydes, using *meta*-chloroperbenzoic acid (*m*-CPBA) in ethyl acetate, furnished the corresponding formates, which were further reduced upon treatment with diisobutylaluminum hydride (DIBALH) in toluene to afford the phenols **11a-c** in very good overall yields (Scheme S1).

Scheme S1. Preparation of phenols **11a-c**.

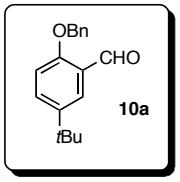


General procedure for 2-benzyloxyphenols 11a-c preparation. To a stirred solution of commercially available 5-substituted salicyladehyde **9a-c** (5.0 g, ca. 30 mmol) in dry DMF (50 mL, ca. 0.6 M) were added K_2CO_3 (1.20 equiv) and benzyl bromide (1.05 equiv), and the mixture was heated at 40 °C under a nitrogen atmosphere for 5 hours. The solution was diluted with water (20 mL), treated with ice-cold 3% aq. HCl until pH 7, and extracted with EtOAc (3 × 30 mL); the combined organic layers were washed with brine (3 × 20 mL) and dried over Na_2SO_4. Evaporation of the solvent furnished a brown solid, which was purified by column chromatography, eluting with hexanes/Et_2O (9:1), to give the corresponding 2-benzyloxybenzaldehyde **10a-c**.

A stirred ice-cold solution of this aldehyde **10a-c** (8.0 g, ca. 30 mmol) in EtOAc (70 mL, ca. 0.4 M) was slowly treated with *m*-CPBA (1.10 equiv). After 30 min, the mixture was allowed to warm to room temperature, and was stirred under a nitrogen atmosphere overnight. It was then diluted with

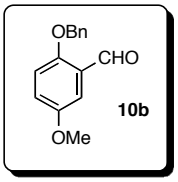
EtOAc (30 mL), washed with ice-cold 3% aq. NaOH until aqueous phase clear, further washed with brine (3 × 20 mL), dried over Na_2SO_4, filtered and evaporated to furnish the corresponding phenyl formate (quantitative yield), which was used without further purification. To a stirred ice-cold solution of this material (8.0 g, ca. 30 mmol) in dry THF (70 mL, ca. 0.4 M) was added dropwise DIBALH (1.5 M in toluene, 1.5 equiv) *via* syringe. After stirring for 1 h at 0 °C, the mixture was diluted with water (50 mL), neutralized with a few drops of concentrated HCl, extracted with EtOAc (4 × 25 mL), washed with brine (3 × 25 mL), dried over Na_2SO_4, filtered and evaporated. The resulting solid residue was purified by column chromatography to afford phenol **11a-c**.

2-Benzyloxy-5-*tert*-butylbenzaldehyde (10a).[1]



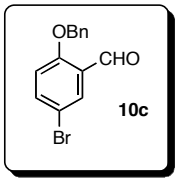
White amorphous powder (96%): mp 75-76 °C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, 9H), 5.19 (s, 2H), 7.01 (d, J = 8.7 Hz, 1H), 7.26-7.47 (m, 5H), 7.58 (dd, J = 2.6, 8.7 Hz, 1H), 7.90 (d, J = 2.6 Hz, 1H), 10.58 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 189.9, 159.1, 143.8, 136.3, 133.0, 128.6, 128.1, 127.2, 124.8, 124.4, 112.7, 70.4, 34.2, 31.2; EIMS *m/z* (%) 268 (5) [M^+], 253 (4), 240 (2), 239 (7), 177 (6), 161 (6), 91 (100).

2-Benzyloxy-5-methoxybenzaldehyde (10b).[1]



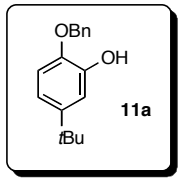
Pale yellow solid (99%): mp 48-49 °C (lit.[2] mp 48-49 °C); IR (KBr) 1684 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.79 (s, 3H), 5.14 (s, 2H), 7.00 (d, J = 9.1 Hz, 1H), 7.12 (dd, J = 3.3, 9.1 Hz, 1H), 7.34-7.44 (m, 6H), 10.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 189.4, 155.7, 153.7, 136.2, 128.6, 128.1, 127.3, 125.4, 123.4, 114.9, 110.1, 71.1, 55.7; EIMS *m/z* (%) 242 (9) [M^+], 214 (3), 213 (4), 151 (6), 91 (100).

2-Benzyloxy-5-bromobenzaldehyde (10c).[1]



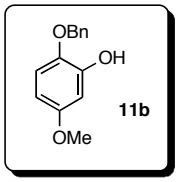
Pale yellow solid (96%): mp 70-71 °C (lit.[3] mp 67.5-69.5 °C; lit.[4] mp 74 °C); IR (KBr) 1685 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.02 (s, 2H), 6.81 (d, J = 8.7 Hz, 1H), 7.23-7.33 (m, 5H), 7.43 (dd, J = 2.6, 8.7 Hz, 1H), 7.78 (d, J = 2.6 Hz, 1H), 10.32 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 188.1, 159.9, 138.3, 135.7, 130.9, 128.9, 128.6, 127.5, 126.5, 115.3, 113.9, 70.9; LSIMS *m/z* (%) 315 (99) [MNa$^+$], 313 (100) [MNa$^+$], 293 (13) [MH$^+$], 292 (12) [M^+], 291 (19) [MH$^+$], 290 (10) [M^+], 212 (14).

2-Benzyloxy-5-*tert*-butylphenol (11a).



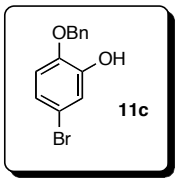
Purification by column chromatography, eluting with hexanes/Et_2O (9:1), gave **11a** as a white amorphous powder (93%): mp 49-50 °C; IR (KBr) 3512 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (s, 9H), 5.09 (s, 2H), 5.63 (s, 1H), 6.86 (s, 2H), 7.03 (s, 1H), 7.39-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 145.2, 145.1, 143.5, 136.6, 128.6, 128.3, 127.7, 116.5, 112.3, 111.6, 71.1, 34.2, 31.4; LSIMS *m/z* (%) 279 (9) [MNa$^+$], 257 (24) [MH$^+$], 256 (100) [M^+], 241 (6), 165 (4); HRMS (EIMS) calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1445; Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86; O, 12.48. Found: C, 79.98; H, 7.86.

2-Benzyloxy-5-methoxyphenol (11b).[5]



Purification by column chromatography, eluting with hexanes/Et_2O (7:3), gave **11b** as a white amorphous powder (97%): mp 43-44 °C (lit.[6] mp 43.5-45 °C, lit.[7] mp 42 °C); IR (KBr) 3496 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.76 (s, 3H), 5.06 (s, 2H), 5.75 (bs, 1H), 6.38 (dd, J = 3.1, 8.8 Hz, 1H), 6.59 (d, J = 3.1 Hz, 1H), 6.85 (d, J = 8.8 Hz, 1H), 7.26-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 154.8, 146.7, 140.0, 136.5, 128.6, 128.3, 127.8, 113.3, 104.3, 101.7, 71.9, 55.5; LSIMS *m/z* (%) 253 (6) [MNa$^+$], 231 (37) [MH$^+$], 230 (100) [M^+], 139 (49).

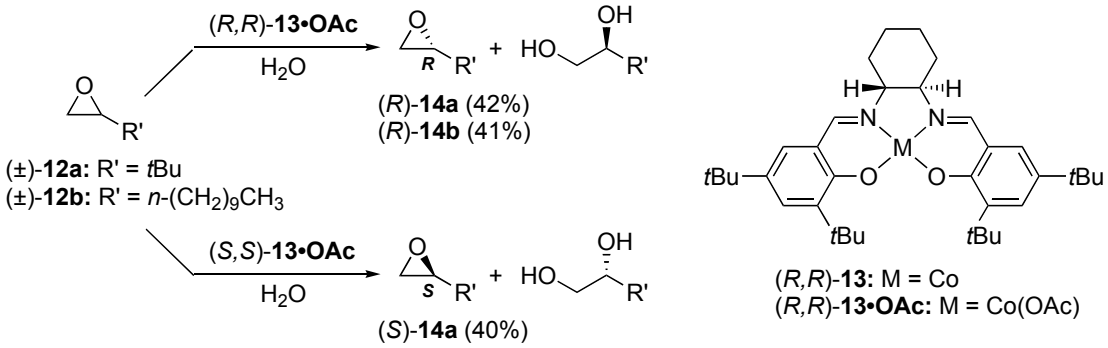
2-Benzyloxy-5-bromophenol (11c).[8]



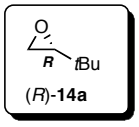
Purification by column chromatography, eluting with hexanes/acetone (4:1), gave **11c** as a pale yellow oil (96%): IR (NaCl) 3508 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 5.08 (s, 2H), 5.86 (bs, 1H), 6.79 (d, J = 8.5 Hz, 1H), 6.98 (dd, J = 2.4, 8.5 Hz, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.26-7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 146.6, 144.9, 135.7, 128.7, 128.4, 127.7, 127.2, 122.7, 117.9, 113.5, 113.3, 71.1; EIMS *m/z* (%) 280 (33) [M^+], 278 (36) [M^+], 199 (27), 189 (5), 187 (5), 91 (100).

Preparation of the enantioenriched terminal epoxides (Scheme S2). Enantioenriched terminal epoxides were either commercially available [(*R*)- and (*S*)-**14c**: R' = Et; Aldrich) or prepared by a Hydrolytic Kinetic Resolution (HKR) reaction according to Jacobsen's procedure,[9] using both commercially available enantiomers of the (salen)Co^{II} complex **13**, i.e., (*R,R*)-(–)- and (*S,S*)-(+)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexadiaminocobalt(II) (Scheme S2). Compounds (*R*)- and (*S*)-**14a** (R' = *t*Bu) as well as (*R*)-**14b** [R' = *n*-$(CH_2)_9CH_3$] were thus obtained with the concomitant diol by-product from commercially available (±)-3,3-dimethyl-1,2-epoxybutane (**12a**) and (±)-1,2-epoxydodecane (**12b**), respectively (Scheme S2).

Scheme S2. Preparation of the enantioenriched terminal epoxides.

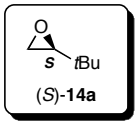


(*R*)-(–)-3,3-Dimethyl-1,2-epoxybutane [(*R*)-14a].[9,10]



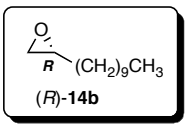
To a stirred solution of (*R,R*)-(–)-(salen)Co^{II} catalyst (483 mg, 800 μmol, 0.02 equiv) in dry PhMe (3 mL) was added dropwise AcOH (500 μL). After stirring at room temperature for 15 min, over which time the color changed from orange-red to dark brown, the solvent was completely removed in vacuo to give a crude brown sirup. To this material was then added at room temperature the commercially available (±)-3,3-dimethyl-1,2-epoxybutane [(±)-**12a**, 4.00 g, 4.87 mL, 40 mmol, 1.00 equiv], and (±)-1,2-hexanediol (1.2 mL) as a co-solvent; the solution was then cooled to 0 °C, and H_2O (400 μL, 22 mmol, 0.55 equiv) was added dropwise over 5 min. The mixture was allowed to warm to room temperature and was stirred 48 h, after which time the enantioenriched epoxide (*R*)-**14a** was isolated from the reaction mixture by vacuum transfer at 0.2-0.3 mmHg into a cooled (–78 °C) receiving flask, and was obtained as a colorless liquid (1.68 g, 42%): $[\alpha]^{20}_D$ –14.6 (*c* 2.16, PhH); IR (NaCl) 3047, 2958, 1479, 1362, 914, 845 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.90 (s, 9H), 2.52-2.64 (m, 2H), 2.69-2.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 60.1, 44.1, 30.5, 25.5; EIMS *m/z* (%) 100 (1) [M^+], 85 (15), 70 (92), 55 (100), 43 (10); HRMS (EIMS) calcd for $C_6H_{12}O$ 100.0885, found 100.0888.

(*S*)-(+)-3,3-Dimethyl-1,2-epoxybutane [(*S*)-14a].[10]



The same procedure as that described above for (*R*)-**14a**, using the (*S,S*)-(–)-(salen)Co^{II} catalyst, furnished (*S*)-**14a** as a colorless liquid (1.60 g, 40%): $[\alpha]^{20}_D$ +12.8 (*c* 1.92, PhH). All other spectroscopic data were identical to those reported for (*R*)-**14a**.

(*R*)-(+)-1,2-Epoxydodecane [(*R*)-14b)].[9,11]

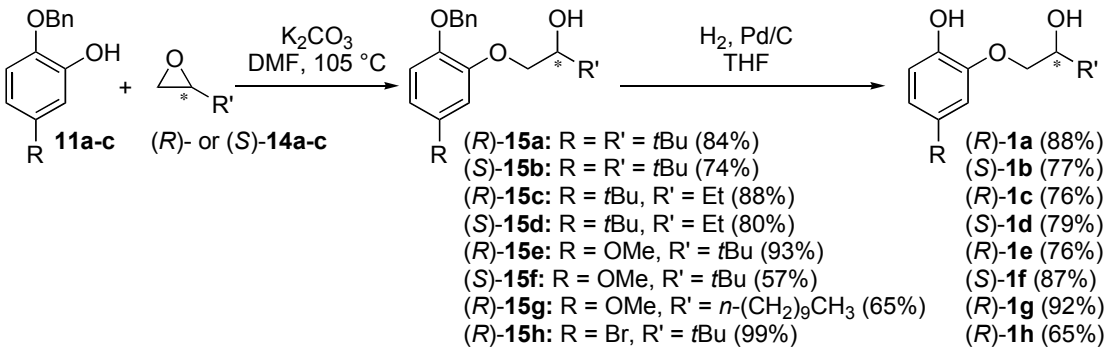


To a stirred solution of (*R,R*)-(–)-(salen)Co^{II} catalyst (75.5 mg, 125 μmol, 0.005 equiv) in dry CH_2Cl_2 (2 mL) was added dropwise AcOH (75 μL). After stirring at room temperature for 15 min, over which time the color changed from orange-red to dark brown, the solvent was completely removed in vacuo to give a crude brown sirup. To this material was then

added at room temperature commercially available (±)-1,2-epoxydodecane [(±)-**12b**, 4.60 g, 3.20 mL, 25 mmol, 1.00 equiv], and *i*PrOH (1 mL) as a co-solvent ; the solution was then cooled to 0 °C, and H_2O (450 μL, 25 mmol, 1.00 equiv) was added dropwise over 5 min. The mixture was allowed to warm to room temperature and was stirred 24 h, after which time it was diluted with hexanes (50 mL) and filtered to remove the 1,2-diol by-product as a precipitate. Evaporation of the solvent, followed by vacuum distillation ($Eb_{0.2\text{-}0.3}$ = 91-92 °C), afforded the enantioenriched epoxide (*R*)-**14b** as a colorless liquid (1.89 g, 41%): $[\alpha]^{20}_D$ +9.7 (*c* 2.21, $CHCl_3$) [lit.[11] +6.9 (*c* 1.04, $CHCl_3$)]; IR (NaCl) 3039, 2925, 1463, 1377, 915, 835 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.87 (bt, *J* = 6.6 Hz, 3H), 1.25-1.51 (m, 18H), 2.73 (dd, *J* = 2.7, 5.2 Hz, 1H), 2.73 (dd, *J* = 3.9, 4.9 Hz, 1H), 2.85-2.93 (m, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 52.4, 47.1, 32.5, 31.9, 29.6, 29.5, 29.4, 29.3, 25.9, 22.6, 14.1; LSIMS *m/z* (%) 207 (5) [*M*Na^+], 185 (100) [*M*H^+], 169 (3), 155 (24).

Preparation of the chiral phenolic alcohols 1a-h (Scheme S3). A Williamson-type reaction between the 2-benzyloxyphenols **11a-c** and the terminal epoxides (*R*)- and (*S*)-**14a-c** was achieved in dry DMF, heating at 105 °C, in the presence of potassium carbonate, to give the secondary alcohol **15a-h** in very good to excellent yields (Scheme S3). It is noteworthy that no primary alcohol was obtained, probably because of both the basic conditions, and the steric demand of the benzyloxy group *ortho* to the phenolate. Subsequent debenzylation of **15a-h** in standard conditions furnished the corresponding chiral phenolic alcohol **1a-h** in very good yields (Scheme S3).

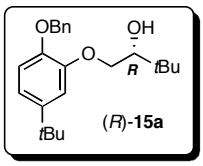
Scheme S3. Preparation of the chiral phenolic alcohols **1a-h**.



General procedure for chiral phenolic alcohols 1a-h preparation. To a stirred solution of phenol **11a-c** (1.05 g, ca. 4.0 mmol, 1.00 equiv) in dry DMF (15 mL, ca. 0.3 M) was added K_2CO_3 (2.00 equiv) and, after 10 min, terminal epoxide (*R*)- or (*S*)-**14a-c** (2.00 equiv). The mixture was then heated at 105 °C until TLC monitoring [hexanes/Et_2O (3:1)] indicated complete consumption of the starting material (ca. 24 h). The reaction mixture was poured over water (10 mL), treated dropwise with 1 M aq. HCl until pH acidic, and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (3 × 5 mL), dried over Na_2SO_4, filtered and evaporated. Purification of the resulting oily residue by column chromatography furnished the chiral alcohol **15a-h** in good to excellent yield.

Debenzylation of this material (ca. 1.50 g) in 30 mL of dry THF was carried out under H_2 (balloon) overnight at room temperature in the presence of 10 wt % Pd/C as a catalyst (ca. 150 mg), except for the brominated compound **15h**, which was cleanly debenzylated using Adam's catalyst (PtO_2).[12] The reaction mixture was filtered through Celite, and the solid was washed with EtOAc (3 × 10 mL). Evaporation of the combined filtrates and washings afforded a brown oil, which was purified by column chromatography, eluting with hexanes/Et_2O (3:1), to give the chiral phenolic alcohol **1a-h**.

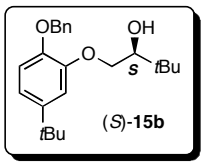
(*R*)-(–)-1-[2-(Benzyloxy)-5-*tert*-butylphenoxy]-3,3-dimethylbutan-2-ol [(*R*)-15a].



Colorless oil (84%): $[\alpha]^{20}_D$ –30.8 (*c* 0.88, $CHCl_3$); IR (NaCl) 3507 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.01 (s, 9H), 1.33 (s, 9H), 2.94 (bs, 1H), 3.69 (dd, *J* = 2.4, 9.2 Hz, 1H), 3.93 (bt, *J* = 9.4 Hz, 1H), 4.27 (dd, *J* = 2.4, 9.6 Hz, 1H), 5.12 (s, 2H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.98 (dd, *J* = 2.3, 8.7 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 7.31-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 148.1, 147.2, 144.7, 137.1, 128.5, 127.8, 127.3, 118.9, 114.4, 113.7, 76.9, 72.5, 70.9, 34.2, 33.3, 31.4, 26.0; LSIMS *m/z* (%) 379 (45) [*M*Na^+], 357 (28) [*M*H^+],

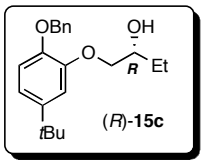
356 (100) [M^+], 341 (3), 283 (12); Anal. Calcd for $C_{23}H_{32}O_3$: C, 77.49; H, 9.05; O, 13.46. Found: C, 77.82; H, 8.87.

(*S*)-(+)-1-[2-(Benzyloxy)-5-*tert*-butylphenoxy]-3,3-dimethylbutan-2-ol [(*S*)-15b].



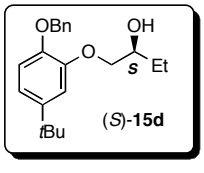
White amorphous solid (74%): mp 59-60 °C; $[\alpha]^{20}_D$ +28.3 (*c* 0.45, $CHCl_3$); IR (NaCl) 3509 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.99 (s, 9H), 1.32 (s, 9H), 2.78 (bs, 1H), 3.68 (dd, *J* = 2.4, 9.2 Hz, 1H), 3.91 (bt, *J* = 9.3 Hz, 1H), 4.26 (dd, *J* = 2.4, 9.5 Hz, 1H), 5.11 (s, 2H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.97 (dd, *J* = 2.1, 8.5 Hz, 1H), 7.03 (d, *J* = 2.1 Hz, 1H), 7.32-7.47 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 148.1, 147.2, 144.7, 137.1, 128.5, 127.8, 127.3, 118.9, 114.4, 113.6, 76.9, 72.5, 70.9, 33.3, 31.4, 26.0; LSIMS *m/z* (%) 379 (29) [*M*Na^+], 357 (27) [*M*H^+], 356 (100) [M^+], 341 (5), 299 (2); HRMS (EIMS) calcd for $C_{23}H_{32}O_3$ 356.2351, found 356.2351.

(*R*)-(–)-1-[2-(Benzyloxy)-5-*tert*-butylphenoxy]butan-2-ol [(*R*)-15c].



Colorless oil (88%): $[\alpha]^{20}_D$ –31.5 (*c* 0.44, $CHCl_3$); IR (NaCl) 3484 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.04 (t, *J* = 7.5 Hz, 3H), 1.34 (s, 9H), 1.56-1.67 (m, 2H), 3.22 (bs, 1H), 3.87-3.97 (m, 2H), 4.07-4.16 (m, 1H), 5.12 (s, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.98 (dd, *J* = 2.1, 8.2 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 7.33-7.49 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 148.2, 146.9, 144.8, 137.1, 128.4, 127.7, 127.2, 118.6, 113.9, 74.8, 71.2, 71.1, 34.2, 31.4, 25.7, 9.9; LSIMS *m/z* (%) 351 (54) [*M*Na^+], 329 (25) [*M*H^+], 328 (100) [*M*H^+], 313 (4), 255 (8), 237 (2); HRMS (EIMS) calcd for $C_{21}H_{28}O_3$ 328.2038, found 328.2026.

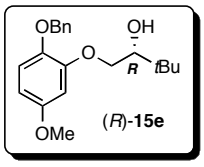
(*S*)-(+)-1-[2-(Benzyloxy)-5-*tert*-butylphenoxy]butan-2-ol [(*S*)-15d].



Colorless oil (80%): $[\alpha]^{20}_D$ +29.1 (*c* 0.65, $CHCl_3$); IR (NaCl) 3489 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.01 (t, *J* = 7.5 Hz, 3H), 1.31 (s, 9H), 1.52-1.64 (m, 2H),

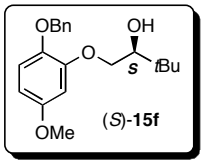
2.82 (s, 1H), 3.83-3.95 (m, 2H), 4.05-4.14 (m, 1H), 5.10 (s, 2H), 6.88 (d, J = 8.2 Hz, 1H), 6.93-7.02 (m, 2H), 7.32-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 148.2, 147.1, 144.9, 137.1, 128.5, 127.8, 127.3, 118.8, 114.2, 113.9, 74.9, 71.3, 71.2, 34.3, 31.4, 25.7, 9.9; LSIMS *m/z* (%) 351 (45) [MNa$^+$], 329 (27) [MH$^+$], 328 (100) [M^+], 313 (3), 255 (8), 237 (2); HRMS (EIMS) calcd for $C_{21}H_{28}O_3$ 328.2038, found 328.2026.

(*R*)-(–)-1-[2-(Benzyloxy)-5-methoxyphenoxy]-3,3-dimethylbutan-2-ol [(*R*)-15e].



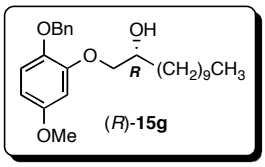
Colorless oil (93%): $[\alpha]^{20}_D$ –31.4 (*c* 0.79, $CHCl_3$); IR (NaCl) 3501 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.99 (s, 9H), 2.79 (bs, 1H), 3.68 (dd, J = 2.4, 9.2 Hz, 1H), 3.76 (s, 3H), 3.88 (bt, J = 9.4 Hz, 1H), 4.18 (dd, J = 2.3, 9.5 Hz, 1H), 5.05 (s, 2H), 6.42 (d, J = 2.8, 8.8 Hz, 1H), 6.57 (d, J = 3.0 Hz, 1H), 6.86 (d, J = 8.7 Hz, 1H), 7.31-7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 154.7, 149.9, 143.2, 137.3, 128.4, 127.8, 127.4, 116.0, 104.8, 103.4, 76.8, 72.2, 71.6, 55.6, 33.4, 25.9; ; LSIMS *m/z* (%) 353 (28) [MNa$^+$], 331 (36) [MH$^+$], 330 (100) [M^+], 313 (4), 239 (6), 229 (2); Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93; O, 19.37. Found: C, 72.79; H, 7.88.

(*S*)-(+)-1-[2-(Benzyloxy)-5-methoxyphenoxy]-3,3-dimethylbutan-2-ol [(*S*)-15f].



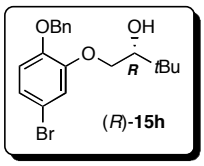
Colorless oil (57%): $[\alpha]^{20}_D$ +36.3 (*c* 1.12, $CHCl_3$); IR (NaCl) 3498 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.99 (s, 9H), 2.79 (bs, 1H), 3.68 (dd, J = 2.4, 9.2 Hz, 1H), 3.76 (s, 3H), 3.88 (bt, J = 9.3 Hz, 1H), 4.18 (dd, J = 2.4, 9.2 Hz, 1H), 5.05 (s, 2H), 6.42 (dd, J = 2.9, 8.7 Hz, 1H), 6.57 (d, J = 2.7 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 7.31-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 154.7, 149.8, 143.1, 137.2, 128.4, 127.8, 127.4, 115.8, 104.6, 103.2, 76.7, 72.1, 71.5, 55.5, 33.4, 25.9; LSIMS *m/z* (%) 353 (25) [MNa$^+$], 331 (38) [MH$^+$], 330 (100) [M^+], 313 (4), 239 (6); HRMS (LSIMS) calcd for $C_{20}H_{26}O_4$ 330.1831, found 330.1833.

(*R*)-(–)-1-[2-(Benzyloxy)-5-methoxyphenoxy]dodecan-2-ol [(*R*)-15g].



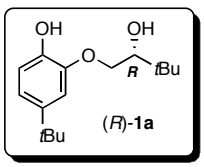
White amorphous powder (65%): mp 41 °C; $[\alpha]^{20}_{D}$ –14.6 (*c* 0.72, $CHCl_3$); IR (KBr) 3400 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.88 (bt, *J* = 6.6 Hz, 3H), 1.26-1.51 (m, 18H), 2.37 (bs, 1H), 3.76 (s, 3H), 3.81-3.85 (m, 1H), 3.92-4.04 (m, 2H), 5.04 (s, 2H), 6.42 (dd, *J* = 2.7, 8.8 Hz, 1H), 6.55 (d, *J* = 2.7 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 7.30-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 154.9, 149.9, 143.1, 137.3, 128.5, 127.9, 127.4, 116.4, 104.9, 103.3, 74.5, 72.4, 69.8, 55.6, 32.8, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 25.5, 22.7, 14.1; LSIMS *m/z* (%) 437 (52) [*M*Na^+], 415 (49) [*M*H^+], 414 (100) [M^+], 397 (5), 213 (9); Anal. Calcd for $C_{26}H_{38}O_4$: C, 75.32; H, 9.24; O, 15.44. Found: C, 75.72; H, 9.29.

(*R*)-(–)-1-[2-(Benzyloxy)-5-bromophenoxy]-3,3-dimethylbutan-2-ol [(*R*)-15h].



Pale yellow oil (99%): $[\alpha]^{20}_{D}$ –51.8 (*c* 1.53, $CHCl_3$); IR (KBr) 3505 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.98 (s, 9H), 2.32 (bs, 1H), 3.67 (dd, *J* = 2.1, 8.9 Hz, 1H), 3.85 (bt, *J* = 9.3 Hz, 1H), 4.16 (dd, *J* = 2.2, 9.3 Hz, 1H), 5.08 (s, 2H), 6.79 (d, *J* = 8.5 Hz, 1H), 7.00-7.05 (m, 2H), 7.31-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 149.6, 148.2, 136.5, 128.6, 128.1, 127.3, 124.4, 118.3, 115.5, 113.2, 76.8, 71.7, 71.2, 33.4, 26.0; EIMS *m/z* (%) 380 (17) [M^+], 378 (17) [M^+], 279 (0.5), 277 (0.6), 198 (13), 91 (100); Anal. Calcd for $C_{19}H_{23}BrO_3$: C, 60.17; H, 6.11; Br, 21.07; O, 12.65. Found: C, 60.41; H, 6.17; Br, 20.97.

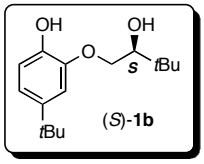
(*R*)-(–)-2-(2-Hydroxy-3,3-dimethylbutoxy)-4-*tert*-butylphenol [(*R*)-1a].



White amorphous solid (88%): mp 97-98 °C; $[\alpha]^{20}_{D}$ –34.4 (*c* 0.78, $CHCl_3$); IR (KBr) 3378, 3277 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.99 (s, 9H), 1.29 (s, 9H), 3.71 (dd, *J* = 2.1, 9.2 Hz, 1H), 3.88 (bt, *J* = 9.6 Hz, 1H), 4.22 (dd, *J* = 1.9, 9.9 Hz, 1H), 6.85-6.95 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 145.5, 144.4, 143.2, 119.3, 115.1, 112.0, 77.9, 71.5, 34.2, 33.7, 31.5, 25.9; LSIMS *m/z* (%) 289 (57) [*M*Na^+], 267 (20) [*M*H^+], 266 (100)

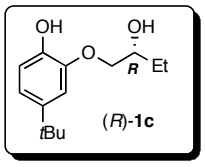
[M^+], 251 (11), 249 (5), 165 (11); Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84; O, 18.02. Found: C, 72.29; H, 9.89.

(*S*)-(+)-2-(2-Hydroxy-3,3-dimethylbutoxy)-4-*tert*-butylphenol [(*S*)-1b].



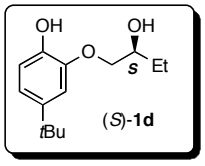
Colorless syrup (77%): $[\alpha]^{20}_D$ +25.6 (*c* 0.86, $CHCl_3$); IR (KBr) 3400 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.99 (s, 9H), 1.29 (s, 9H), 3.71 (dd, *J* = 1.9, 9.0 Hz, 1H), 3.88 (d, *J* = 9.6 Hz, 1H), 4.23 (bd, *J* = 9.0 Hz, 1H), 6.85-6.94 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 145.5, 144.5, 143.3, 119.4, 115.1, 112.3, 112.2, 77.9, 71.7, 34.2, 33.7, 31.5, 25.9; LSIMS *m/z* (%) 289 (48) [*M*Na^+], 267 (22) [*M*H^+], 266 (100) [M^+], 251 (7), 249 (5); Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84; O, 18.02. Found: C, 72.24; H, 9.67.

(*R*)-(–)-2-(2-Hydroxybutoxy)-4-*tert*-butylphenol [(*R*)-1c].



White amorphous powder (76%): mp 77-78 °C; $[\alpha]^{20}_D$ –30.7 (*c* 0.72, $CHCl_3$); IR (KBr) 3356, 3260 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.00 (t, *J* = 7.5 Hz, 3H), 1.28 (s, 9H), 1.53-1.68 (m, 2H), 3.84-4.07 (m, 3H), 5.09 (bs, 2H), 6.83-6.92 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 145.5, 143.9, 143.2, 118.8, 114.9, 110.8, 73.0, 71.9, 34.3, 31.5, 26.0, 9.9; LSIMS *m/z* (%) 261 (20) [*M*Na^+], 239 (19) [*M*H^+], 238 (100) [M^+], 223 (13), 221 (6); HRMS (EIMS) calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1558; Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30; O, 20.14. Found: C, 70.18; H, 9.18.

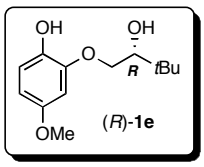
(*S*)-(+)-2-(2-Hydroxybutoxy)-4-*tert*-butylphenol [(*S*)-1d].



White amorphous powder (79%): mp 76-77 °C; $[\alpha]^{20}_D$ +34.4 (*c* 0.61, $CHCl_3$); IR (KBr) 3512, 3277 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.99 (t, *J* = 7.5 Hz, 3H), 1.28 (s, 9H), 1.56-1.68 (m, 2H), 3.82-4.06 (m, 3H), 6.85-6.87 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 145.5, 143.8, 143.2, 118.7, 114.9, 110.6, 72.7, 71.9, 34.3, 31.5, 25.9, 9.9; LSIMS *m/z* (%) 261 (93) [*M*Na^+], 239 (19) [*M*H^+], 238 (100) [M^+], 223 (17), 221 (7), 181 (3), 165

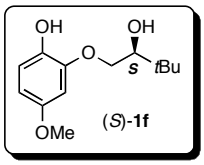
(17); HRMS (EIMS) calcd for $C_{14}H_{22}O_3$ 238,1569, found 238, 1581; Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30; O, 20.14. Found: C, 70.51; H, 9.23.

(*R*)-(–)-2-(2-Hydroxy-3,3-dimethylbutoxy)-4-methoxyphenol [(*R*)-1e].



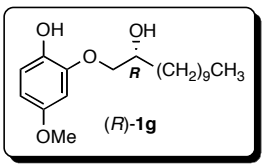
White amorphous powder (76%): mp 98-99 °C; $[\alpha]^{20}_D$ –44.1 (*c* 0.99, $CHCl_3$); IR (KBr) 3519, 3348 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.97 (s, 9H), 3.46 (bs, 1H), 3.68 (dd, *J* = 1.7, 9.3 Hz, 1H), 3.73 (s, 3H), 3.82 (bt, *J* = 9.6 Hz, 1H), 4.12 (dd, *J* = 1.9, 9.6 Hz, 1H), 6.36-6.43 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 7.08 (bs, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 153.2, 146.6, 140.3, 115.3, 105.3, 101.5, 77.7, 70.7, 55.7, 33.7, 25.9; LSIMS *m/z* (%) 263 (34) [*M*Na^+], 241 (27) [*M*H^+], 240 (100) [M^+], 223 (7); Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39; O, 26.63. Found: C, 64.87; H, 8.39.

(*S*)-(+)-2-(2-Hydroxy-3,3-dimethylbutoxy)-4-methoxyphenol [(*S*)-1f].



White amorphous powder (87%): mp 75-76 °C; $[\alpha]^{20}_D$ +47.6 (*c* 0.30, $CHCl_3$); IR (KBr) 3519, 3442 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (s, 9H), 3.68 (bd, *J* = 8.3 Hz, 1H), 3.73 (s, 3H), 3.83 (bt, *J* = 9.4 Hz, 1H), 4.13 (d, *J* = 9.8 Hz, 1H), 6.39 (dd, *J* = 3.0, 8.7 Hz, 1H), 6.44 (bd, *J* = 1.9 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 153.3, 146.6, 140.4, 115.4, 105.5, 101.7, 77.7, 70.8, 55.7, 33.7, 25.9; LSIMS *m/z* (%) 263 (23) [*M*Na^+], 241 (28) [*M*H^+], 240 (100) [M^+], 223 (9); Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39; O, 26.63. Found: C, 64.67; H, 8.47.

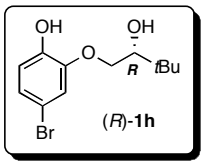
(*R*)-(–)-2-(2-Hydroxydodecyloxy)-4-methoxyphenol [(*R*)-1g].



White sirup (92%): mp 40 °C; $[\alpha]^{20}_D$ –13.5 (*c* 0.74, $CHCl_3$); IR (NaCl) 3428 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (bt, *J* = 6.8 Hz, 3H), 1.25-1.56 (m, 18H), 3.72 (s, 3H), 3.74-3.80 (m, 1H), 3.93-4.01 (m, 2H), 6.35-6.39 (m, 2H), 6.82 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 153.3, 146.5, 140.2, 115.3, 105.2, 100.9,

72.9, 70.5, 55.7, 33.0, 31.9, 29.7, 29.6, 29.5, 29.3, 25.5, 22.6, 14.1; LSIMS *m/z* (%) 347 (33) [*M*Na$^+$], 325 (36) [*M*H$^+$], 324 (100) [*M*$^+$], 307 (6); Anal. Calcd for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94; O, 19.72. Found: C, 70.51; H, 9.98.

(*R*)-(+)-2-(2-Hydroxy-3,3-dimethylbutoxy)-4-bromophenol [(*R*)-1h].

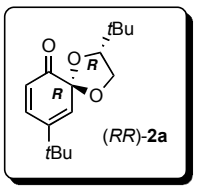


White solid (65%): mp 123-126 °C; $[\alpha]^{20}_D$ +37.7 (*c* 1.53, $CHCl_3$); IR (KBr) 3425 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.00 (s, 9H), 2.44 (bs, 1H), 3.70-3.73 (m, 1H), 3.86 (bt, *J* = 9.6 Hz, 1H), 4.19 (dd, *J* = 1.9, 10.0 Hz, 1H), 6.72 (bs, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 7.01-7.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 146.8, 146.2, 125.5, 117.8, 116.8, 111.2, 77.9, 72.0, 33.8, 25.9; LSIMS *m/z* (%) 313 (13) [*M*Na$^+$], 311 (10) [*M*Na$^+$], 291 (34) [*M*H$^+$], 290 (100) [*M*H$^+$], 289 (33) [*M*H$^+$], 288 (98) [*M*$^+$], 275 (24), 273 (32), 210 (21); HRMS (LSIMS) calcd for $C_{12}H_{17}{}^{79}BrO_3$ 288.0361, found 288.0358.

General procedure for chiral *ortho*-quinone monoketals preparation. A stirred solution of phenol **1a-h** (ca. 110 mg, 1.00 equiv) in CF_3CH_2OH (10 mL, ca. 0.04 M), a polar and poorly nucleophilic solvent,[13] was cooled at –35 °C, and was treated dropwise, over 5 min, with a solution of DIB (1.02 equiv) in CF_3CH_2OH (1 mL). The reaction mixture immediately became pale yellow, and then slowly changed to yellow-pink. After 20 min, TLC monitoring [hexanes/Et_2O (7:3)] indicated complete consumption of the starting material. Powdered $NaHCO_3$ was added in one portion to the reaction mixture, which was kept under stirring at –35 °C for 15 min. After CF_3CH_2OH removal in vacuo, the residue was taken up with CCl_4 (3 × 5 mL), filtered, and evaporated. Further drying under high vacuum allowed complete removal of the iodobenzene by-product, and afforded a diastereomeric mixture of the corresponding chiral *ortho*-quinone monoketals **2a-h:3a-h** (d.r., i.e. diastereomeric ratios, were determined by ^{1}H NMR analysis; see Table 1) as a yellow oils. Although further purification revealed not necessary before engaging

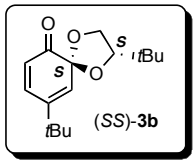
these products in subsequent reactions, they could be separated by silica gel column chromatography for identification and characterization purposes.

(+)-2*R*,9-di-*tert*-Butyl-1,4-dioxaspiro[4.(5*R*)]deca-7,9-dien-6-one [(*RR*)-2a)].



Bright yellow oil (d.r. ≥ 95:5, quantitative crude yield; 72% after SiO_2 column chromatography): $[\alpha]^{20}_D$ +28.8 (*c* 0.32, $CHCl_3$); IR (NaCl) 1684, 1650, 1253, 1110, 1038, 1018, 990 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.93 (s, 9H), 1.14 (s, 9H), 3.86 (bt, *J* = 6.8 Hz, 1H), 4.25 (bt, *J* = 7.5 Hz, 1H), 4.39 (bt, *J* = 6.6 Hz, 1H), 5.79 (d, *J* = 2.3 Hz, 1H), 5.94 (d, *J* = 10.5 Hz, 1H), 6.98 (dd, *J* = 2.3, 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 198.7, 146.9, 140.8, 127.3, 124.6, 97.9, 85.2, 66.1, 34.3, 33.1, 28.1, 25.3; LSIMS *m/z* (%) 287 (4) [*M*Na^+], 265 (31) [*M*H^+], 264 (100) [M^+], 249 (5), 207 (2); HRMS (LSIMS) calcd for $C_{16}H_{24}O_3$ 264.1725, found 264.1722.

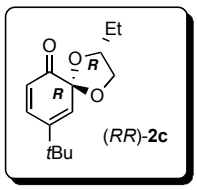
(–)-2*S*,9-di-*tert*-Butyl-1,4-dioxaspiro[4.(5*S*)]deca-7,9-dien-6-one [(*SS*)-3b)].



Bright yellow oil (d.r. ≥ 95:5, quantitative crude yield; 64% after SiO_2 column chromatography): $[\alpha]^{20}_D$ –24.4 (*c* 1.08, $CHCl_3$); IR (NaCl) 1685, 1649, 1256, 1109, 1036, 1015, 987 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.92 (s, 9H), 1.13 (s, 9H), 3.85 (bt, *J* = 7.5 Hz, 1H), 4.24 (bt, *J* = 7.5 Hz, 1H), 4.38 (bt, *J* = 7.5 Hz, 1H), 5.79 (d, *J* = 2.4 Hz, 1H), 5.94 (d, *J* = 10.4 Hz, 1H), 6.98 (dd, *J* = 2.3, 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 198.7, 146.9, 140.8, 127.2, 124.5, 97.9, 85.1, 66.0, 34.3, 33.0, 28.1, 25.3; LSIMS *m/z* (%) 287 (5) [*M*Na^+], 265 (30) [*M*H^+], 264 (100) [M^+], 249 (6), 207 (3); HRMS (LSIMS) calcd for $C_{16}H_{24}O_3$ 264.1725, found 264.1722.

(+)-9-*tert*-Butyl-2*R*-ethyl-1,4-dioxaspiro[4.(5*R*)]deca-7,9-dien-6-one [(*RR*)-2c)].

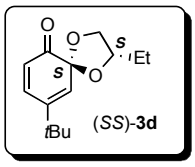
Bright yellow oil (d.r. 60:40, quantitative crude yield), which was identified as a 3:2 mixture of (*RR*)-**2c** and (*RS*)-**3c**. SiO_2 purification, eluting with hexanes/Et_2O (4:1), allowed separation of some pure (*RR*)-**2c** as a bright yellow oil (23%) and a (*RR*)-**2c**:(*RS*)-**3c** mixture (27%).



Compound (*RR*)-**2c**: $[\alpha]^{20}_D$ +36.2 (*c* 0.74, $CHCl_3$); IR (NaCl) 1685, 1648, 1253, 1109, 1039, 1023, 990 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.97 (t, *J* = 7.5 Hz, 3H), 1.14 (s, 9H), 1.55-1.81 (m, 2H), 3.70 (dd, *J* = 6.4, 7.0 Hz, 1H), 4.37 (bt, *J* = 7.0 Hz, 1H), 4.58 (bt, *J* = 6.4 Hz, 1H), 5.82 (d, *J* = 2.4 Hz, 1H), 5.96 (d, *J* = 10.4 Hz, 1H), 6.99 (dd, *J* = 2.4, 10.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 198.6, 146.9, 140.9, 127.8, 124.5, 97.7, 78.6, 69.9, 34.3, 28.1, 26.7, 9.8; LSIMS *m/z* (%) 259 (10) [*M*Na^+], 237 (47) [*M*H^+], 236 (100) [M^+], 221 (16), 207 (6); HRMS (LSIMS) calcd for $C_{14}H_{20}O_3$ 236.1412, found 236.1406.

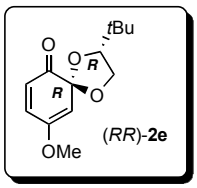
(–)-9-*tert*-Butyl-2*S*-ethyl-1,4-dioxaspiro[4.(5*S*)]deca-7,9-dien-6-one [(*SS*)-3d)].

Bright yellow oil (d.r. 40:60, quantitative crude yield), which was identified as a 2:3 mixture of (*SR*)-**2d** and (*SS*)-**3d**. SiO_2 purification, eluting with hexanes/Et_2O (4:1), allowed separation of some pure (*SS*)-**3d** as a bright yellow oil (8%) and a (*SR*)-**2d**:(*SS*)-**3d** mixture (41%).



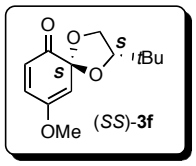
Compound (*SS*)-**3d**: $[\alpha]^{20}_D$ –29.8 (*c* 0.31, $CHCl_3$); IR (NaCl) 1685, 1649, 1256, 1109, 1041, 1021, 990 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, *J* = 7.5 Hz, 3H), 1.15 (s, 9H), 1.54-1.77 (m, 2H), 3.70 (bt, *J* = 6.6 Hz, 1H), 4.37 (bt, *J* = 7.0 Hz, 1H), 4.58 (bt, *J* = 6.4 Hz, 1H), 5.82 (d, *J* = 1.9 Hz, 1H), 5.96 (d, *J* = 10.9 Hz, 1H), 7.00 (dd, *J* = 2.4, 10.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 198.6, 146.9, 140.8, 127.8, 124.5, 97.7, 78.6, 69.9, 34.3, 28.1, 26.7, 9.7; LSIMS *m/z* (%) 259 (10) [*M*Na^+], 237 (39) [*M*H^+], 236 (100) [M^+], 221 (20), 207 (6); HRMS (LSIMS) calcd for $C_{14}H_{20}O_3$ 236.1412, found 236.1411.

(+)-9-Methoxy-2*R*-*tert*-butyl-1,4-dioxaspiro[4.(5*R*)]deca-7,9-dien-6-one [(*RR*)-2e)].



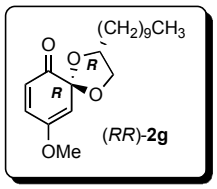
Yellow oil (d.r. ≥ 95:5, quantitative crude yield; 54% after SiO_2 column chromatography): $[\alpha]^{20}_D$ +31.3 (*c* 0.38, $CHCl_3$); IR (NaCl) 1689, 1651, 1255, 1077, 1019 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.96 (s, 9H), 3.65 (s, 3H), 3.85-4.13 (m, 3H), 5.06 (d, *J* = 2.8 Hz, 1H), 5.96 (d, *J* = 10.4 Hz, 1H), 6.69 (dd, *J* = 3.0, 10.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 200.0, 154.6, 140.9, 125.8, 103.1, 101.3, 85.6, 68.2, 55.6, 32.5, 26.5; LSIMS *m/z* (%) 261 (15) [*M*Na^+], 239 (37) [*M*H^+], 238 (100) [M^+], 223 (10), 207 (20); HRMS (LSIMS) calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1203.

(–)-9-Methoxy-2*S*-*tert*-butyl-1,4-dioxaspiro[4.(5*S*)]deca-7,9-dien-6-one [(*SS*)-3f)].



Yellow oil (d.r. ≥ 95:5, quantitative crude yield; 47% after SiO_2 column chromatography): $[\alpha]^{20}_D$ –27.6 (*c* 0.26, $CHCl_3$); IR (NaCl) 1692, 1649, 1258, 1078, 1016 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (s, 9H), 3.67 (s, 3H), 3.86 (bt, *J* = 7.2 Hz, 1H), 4.25 (bt, *J* = 7.3 Hz, 1H), 4.34 (bt, *J* = 7.3 Hz, 1H), 4.97 (d, *J* = 3.0 Hz, 1H), 5.94 (d, *J* = 10.2 Hz, 1H), 6.66 (dd, *J* = 3.0, 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 197.7, 155.1, 140.5, 125.5, 100.9, 99.9, 84.7, 66.1, 55.3, 33.0, 25.3, 25.2; LSIMS *m/z* (%) 261 (18) [*M*Na^+], 239 (41) [*M*H^+], 238 (100) [M^+], 223 (16), 207 (19); HRMS (LSIMS) calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1208.

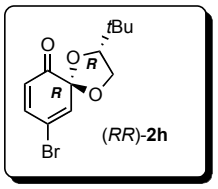
(+)-2*R*-Dodecyl-9-methoxy-1,4-dioxaspiro[4.(5*R*)]deca-7,9-dien-6-one [(*RR*)-2g)].



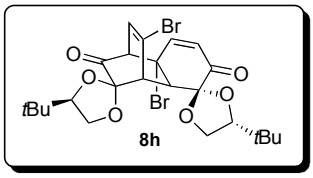
Yellow oil (d.r. 60:40, quantitative crude yield; 48% after SiO_2 purification): $[\alpha]^{20}_D$ +34.1 (*c* 0.22, $CHCl_3$); IR (NaCl) 1691, 1654, 1258, 1187, 1073, 1021 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.21-1.69 (m, 18H), 3.67 (s, 3H), 4.18-4.22 (m, 1H), 4.35 (t, *J* = 7.0 Hz, 1H), 4.53-4.62 (m, 1H), 4.99-5.04 (m, 1H), 5.93-5.98 (m, 1H), 6.65-6.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 197.5, 155.0, 154.6, 140.5, 125.4, 125.3, 102.1, 101.5, 99.6, 99.0, 78.3, 70.5, 70.3, 55.3, 55.2, 33.9, 32.7, 31.9, 29.6, 29.5, 29.4, 29.3, 26.0, 25.6, 22.6, 14.1; LSIMS *m/z* (%) 345 (11) [*M*Na^+], 323 (45) [*M*H^+], 322 (100) [M^+], 307 (11), 293 (10), 291 (8), 237 (22); HRMS (LSIMS) calcd for $C_{19}H_{30}O_4$ 322.2144, found 322.2147.

(+)-9-Bromo-2*R*-*tert*-Butyl-1,4-dioxaspiro[4.(5*R*)]deca-7,9-dien-6-one [(*RR*)-2h] and (–)-7*R*,11-dibromo-3*R*,10*R*-bis(2'-*tert*-butyl-1',4'-dioxaspirocyclopentane)-tricyclo[6.2.2.0^{2,7}]dodecane-5,11-diene-4,9-dione (8h).

Yellow oil (d.r. ≥ 95:5, quantitative crude yield), which was clearly identified as the *ortho*-quinone monoketal (*RR*)-**2h** by ^{1}H NMR analysis. This compound started to transform into its cyclodimer **8h** during ^{13}C NMR data acquisition. Proton NMR monitoring of the resulting orange oily mixture in a $CDCl_3$ solution (ca. 0.3 M) indicated that quasi complete [4+2] cyclodimerization of **2h** into **8h** was achieved after 15 days at room temperature. Subsequent purification by column chromatography, eluting with cyclohexane/acetone (5:1), gave pure cyclodimer **8h** as a pale orange oil (27 mg, 54%)



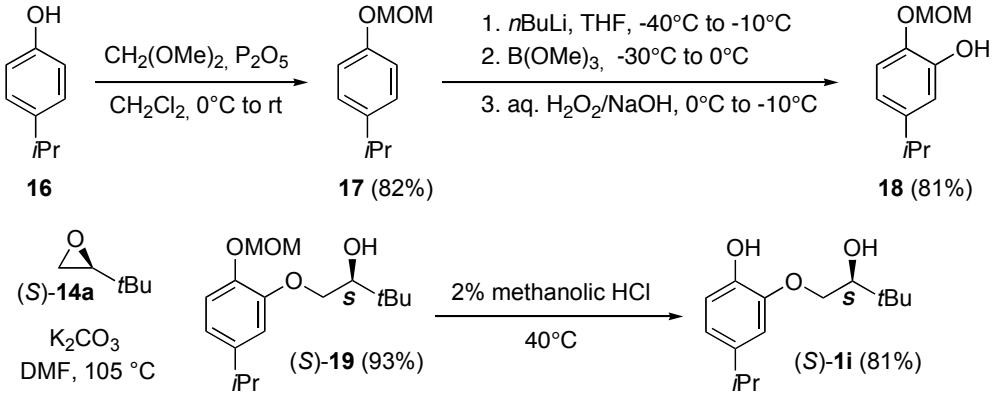
Compound (*RR*)-**2h**: IR (NaCl) 1687, 1647, 1253, 1110, 1038, 1018, 990 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (s, 9H), 3.91 (bt, J = 6.8 Hz, 1H), 4.31 (bt, J = 7.3 Hz, 1H), 4.39 (bt, J = 6.7 Hz, 1H), 5.95 (d, J = 10.2 Hz, 1H), 6.44 (d, J = 2.3 Hz, 1H), 6.89 (dd, J = 2.3, 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 196.9, 143.9, 136.9, 126.1, 120.8, 98.9, 85.7, 67.5, 33.4, 25.7; CIMS *m/z* (%) 306 (41) [MNH$_4^+$], 304 (18) [MNH$_4^+$], 289 (54) [MH$^+$], 288 (40) [M^+], 287 (21) [MH$^+$], 286 (14) [M^+], 273 (15), 271 (11), 241 (16), 239 (16), 207 (18), 189 (22), 187 (100).



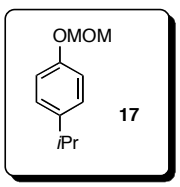
Compound **8h**: $[\alpha]^{20}_D$ –161.7 (*c* 0.35, $CHCl_3$); IR (NaCl) 1748, 1708, 1194, 1107, 1008 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.92 (s, 9H), 0.95 (s, 9H), 3.45-3.49 (m, 2H), 3.66-3.98 (m, 4H), 4.29 (dd, J = 7.3, 14.2 Hz, 2H), 4.39 (bt, J = 6.7 Hz, 1H), 6.04 (d, J = 10.2 Hz, 1H), 6.19 (dd, J = 2.4, 6.8 Hz, 1H), 6.49 (d, J = 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 200.6, 189.6, 146.5, 127.9, 127.3, 125.1, 102.4, 100.5, 85.9, 85.5, 67.7, 66.2, 63.2, 55.8, 53.9, 53.8, 33.4, 32.8, 25.3, 25.2; CIMS *m/z* (%) 594 (39) [MNH$_4^+$], 592 (77) [MNH$_4^+$], 590 (39) [MNH$_4^+$], 577 (24) [MH$^+$], 575 (46) [MH$^+$], 573 (24) [MH$^+$], 467 (100); HRMS (ESI) calcd for $C_{24}H_{30}O_6{}^{79}Br_2Na$ 595.0307, found 595.0308.

Preparation of the chiral phenolic alcohol 1i (Scheme S4). First, 4-*iso*-propylphenol (**16**) was protected by methoxymehtyl (MOM) group, using dimethoxymethane [$CH_2(OMe)_2$] in the presence of an excess of phosphorus pentoxide (P_2O_5) in CH_2Cl_2,[14] to give **17** in a good yield of 82% (Scheme S4). Introduction of the phenolic function at the *ortho*-position to the MOM ether was then achieved by using a three-step sequence: *ortho*-lithiation of **17** with *n*-butyllithium, carried out in THF from –40 °C to –10 °C over 3.5 hours,[15] was followed by transformation, upon treatment with trimethyl borate [$B(OMe_3)$] in THF from –30 °C to 0 °C over 1.5 hour,[15] into the corresponding boronic ester, which was further oxidized at 0 °C with a 1:1 mixture of aq. 35% H_2O_2/10% NaOH to afford the desired phenol **18** in a good overall yield of 81% (Scheme S4). A Williamson-type reaction between **18** and the terminal epoxide (*S*)-**14a** was then achieved in dry DMF, heating at 105 °C, in the presence of potassium carbonate, to give the secondary alcohol (*S*)-**19a** in a very good 93% yield (Scheme S4). The last step consisted in the MOM cleavage of (*S*)-**19a** upon treatment with 2% methanolic HCl, heating at 40 °C, to furnish the corresponding phenolic alcohol (*S*)-**1i** in a good yield of 81% (Scheme S4).

Scheme S4. Preparation of the chiral phenolic alcohols **1i**.



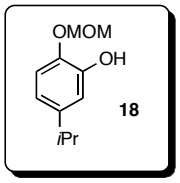
1-Methoxymethoxy-4-*iso*-propylbenzene (17).



To a stirred ice-cold solution of 4-*iso*-propylphenol (**16**, 3.94 g, 30 mmol) in dry CH_2Cl_2 (120 mL) and $CH_2(OMe)_2$ (40 mL, 450 mmol, 15.0 equiv) was added P_2O_5

(20 g, ca. 150 mmol, 5.0 equiv) in two portions.[14] The mixture was stirred at room temperature for 30 min. The liquid phase was then discarded, and the solid residue was washed with CH_2Cl_2 (2 × 50 mL); the combined CH_2Cl_2 layers were washed with saturated aq. $NaHCO_3$ (70 mL), 1 M aq. NaOH (70 mL), water (3 × 70 mL), brine (70 mL), dried over Na_2SO_4, filtered and evaporated. The resulting liquid residue was purified by column chromatography, eluting with cyclohexane/EtOAc (10:1), to give **17** as a colorless liquid (4.45 g, 82%): IR (neat) 2963, 1614, 1507, 1458, 1244, 1200, 1156, 1082, 1011, 921, 831 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (d, J = 6.9 Hz, 6H), 2.88 (sept, J = 6.9 Hz, 1H), 3.49 (s, 3H), 5.16 (s, 2H), 6.98 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 155.3, 142.2, 127.2, 116.1, 94.5, 55.7, 33.2, 24.1; CIMS *m/z* (%) 198 (100) [$M$$NH_4^+$], 180 (6) [$M^+$]; Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; O, 17.75. Found: C, 72.76; H, 9.00.

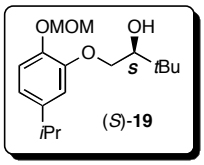
2-Methoxymethoxy-5-*iso*-propylphenol (18).



To a stirred solution of **17** (922 mg, 5.1 mmol, 1.0 equiv) in THF (15 mL) was added dropwise *n*BuLi (1.6 M in hexanes, 4 mL, 6.4 mmol, 1.25 equiv) at –40 °C.[15] The solution was slowly warmed to –10 °C over 2 h, and then stirred for 90 min. The resulting orange solution was cooled to –30 °C, and $B(OMe)_3$ (1.8 mL, 15.4 mmol, 3.0 equiv) was added in one portion.[15] The mixture was stirred at –30 °C for 30 min, and stirred at 0 °C for an additional 1 h. Then, 10 mL of a 1:1 mixture of aq. 35% H_2O_2/10% NaOH was added, and the reaction mixture was vigorously stirred at 0 °C for 30 min. The mixture was quenched at 0 °C with 10 mL of saturated $NaHSO_3$ and stirred at 0 °C for 10 min. The resulting mixture was extracted with EtOAc (3 × 30 mL), and the combined organic layers were washed with water (3 × 30 mL), brine (30 mL), dried over Na_2SO_4, filtered and evaporated. The resulting yellow residue was purified by column chromatography, eluting with cyclohexane/EtOAc (8:1), to afford **18** as a pale yellow oil (938 mg, 81%): IR (neat) 3419, 2964, 1595, 1509, 1458, 1273, 1158, 1088, 1003 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (d, J = 6.9 Hz, 6H), 2.83 (sept, J = 6.9 Hz, 1H), 3.52 (s,

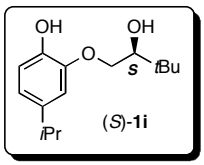
3H), 5.17 (s, 2H), 5.96 (bs, 1H), 6.68 (dd, J = 2.1, 8.4 Hz, 1H), 6.84 (d, J = 1.8 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 146.2, 144.4, 142.5, 118.0, 115.7, 113.5, 96.3, 56.3, 33.6, 24.0; CIMS *m/z* (%) 214 (100) [MNH$_4^+$], 196 (10) [M^+]; HRMS (ESI) calcd for $C_{11}H_{16}O_3Na$ 219.0997, found 219.0989; Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22; O, 24.46. Found: C, 67.01; H, 8.25.

(*S*)-(+)-1-[2-(Methoxymethoxy)-5-*iso*-propylphenoxy]-3,3-dimethylbutan-2-ol [(*S*)-19].



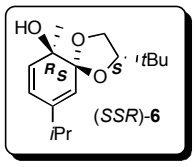
To a stirred solution of phenol **18** (830 mg, 4.23 mmol, 1.00 equiv) in dry DMF (10 mL) was added K_2CO_3 (1.17 g, 8.46 mmol, 2.00 equiv) and, after 10 min, terminal epoxide (*S*)-**14a** (1.0 mL, 8.46 mmol, 2.00 equiv). The mixture was then heated at 105 °C until TLC monitoring [cyclohexane/EtOAc (6:1)] indicated complete consumption of the starting material (ca. 24 h). The reaction mixture was diluted with EtOAc (100 mL), and the resulting organic phase was washed with water (5 × 50 mL), brine (50 mL), dried over Na_2SO_4, filtered and evaporated. Purification of the resulting orange oily residue by column chromatography, eluting with cyclohexane/EtOAc (6:1), furnished the alcohol (*S*)-**19** as a colorless oil (1.16 g, 93%): $[\alpha]^{20}_D$ +17.8 (*c* 0.91, $CHCl_3$); IR (neat) 3507, 2959, 2874, 1513, 1464, 1427, 1261, 1158, 1132, 1084, 1002, 925 cm^{-1}; ^{1}H NMR (acetone-d_6, 300 MHz) 1.00 (s, 9H), 1.21 (d, J = 6.9 Hz, 6H), 2.85 (sept, J = 6.9 Hz, 1H), 3.46 (s, 3H), 3.63 (ddd, , J = 2.7, 3.9, 8.4 Hz, 1H), 3.86 (d, J = 3.9 Hz, 1H), 3.90 (dd, J = 8.4, 9.6 Hz, 1H), 4.27 (dd, J = 2.7, 9.6 Hz, 1H), 5.12 (d, J = 6.6 Hz, 1H), 5.15 (d, J = 6.6 Hz, 1H), 6.77 (dd, J = 1.8, 8.1 Hz, 1H), 6.96 (d, J = 1.8 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H); ^{13}C NMR (acetone-d_6, 75.5 MHz) δ 150.8, 146.0, 144.6, 119.5, 119.2, 114.3, 96.9, 77.6, 72.4, 56.2, 34.5, 26.5, 24.5; ESIMS *m/z* (%) 615 (50) [M_2Na$^+$], 319 (100) [MNa$^+$], 235 (55); HRMS (ESI) calcd for $C_{17}H_{28}O_4Na$ 319.1885, found 319.1878; Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52; O, 21.59. Found: C, 68.48; H, 9.36.

(*S*)-(+)-2-(2-Hydroxy-3,3-dimethylbutoxy)-4-*iso*-propylphenol [(*S*)-1i].



A stirred solution of (*S*)-**19** (1.0 g, 3.34 mmol) in 15 mL of 2% methanolic HCl was heated at 40 °C for 30 min, after which time the reaction mixture was diluted with EtOAc (150 mL). The organic phase was washed with water (3 × 60 mL), brine (60 mL), dried over Na_2SO_4, filtered and evaporated. The resulting yellow oily residue was purified by column chromatography, eluting with cyclohexane/EtOAc (6:1 to 2:1), to give the phenolic alcohol (*S*)-**1i** as a pale yellow oil (681 mg, 81%): $[\alpha]^{20}_{D}$ +55.3 (*c* 0.72, $CHCl_3$); IR (neat) 3409, 2962, 2867, 1608, 1515, 1469, 1435, 1266, 1186, 1041, 1023, 927 cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz) 1.00 (s, 9H), 1.19 (d, *J* = 6.9 Hz, 6H), 2.82 (sept, *J* = 6.9 Hz, 1H), 3.65 (dd, , *J* = 2.1, 9.3 Hz, 1H), 3.83 (t, *J* = 9.3 Hz, 1H), 4.28 (dd, *J* = 2.1, 9.6 Hz, 1H), 6.69 (dd, *J* = 1.5 Hz, 8.1 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (acetone-d_6, 75.5 MHz) δ 147.4, 145.9, 141.0, 119.8, 115.7, 112.8, 77.7, 72.1, 34.4, 34.2, 26.5, 24.6; ESIMS *m/z* (%) 316 (100) [*M*(CH_3CN)Na^+], 275 (55) [*M*Na^+]; HRMS (ESI) calcd for $C_{15}H_{24}O_3Na$ 275.1623, found 275.1614; Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59; O, 19.02. Found: C, 71.12; H, 9.62.

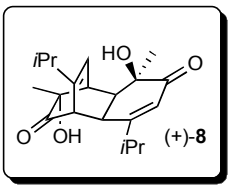
(–)-2*S*-*tert*-butyl-(6*R*)-methyl-9-*iso*-propyl-1,4-dioxaspiro[4.(5*S*)]deca-7,9-dien-6-ol [(*SSR*)-6].



A stirred solution of phenol (*S*)-**1i** (259 mg, 1.03 mmol, 1.00 equiv) in CF_3CH_2OH (10 mL) was cooled at –35 °C, and was treated dropwise, over 5 min, with a solution of DIB (338 mg, 1.05 mmol, 1.02 equiv) in CF_3CH_2OH (2 mL). The reaction mixture immediately became pale yellow, and then slowly changed to pronounced yellow. After 20 min, TLC monitoring [cyclohexane/EtOAc (2:1)] indicated complete consumption of the starting material. Powdered $NaHCO_3$ (173 mg, 2.06 mmol, 2.00 equiv) was added in one portion to the reaction mixture, which was kept under stirring at –35 °C for 30 min. Further freezing of the reaction mixture in liquid nitrogen, followed by CF_3CH_2OH sublimation in vacuo, furnished a yellow solid residue, which was diluted with –40 °C-cold THF (15 mL). The supernatant was then transferred at –40 °C in a flame-dried round-bottomed flask. The resulting solution was cooled to –

78 °C and treated dropwise with MeMgBr (3.0 M in THF, 2 mL, 6.00 equiv). After stirring at –78 °C for 1 h, the reaction mixture was allowed to warm to 0 °C, and was stirred for additional 30 min. It was then hydrolyzed at 0 °C with saturated NH_4Cl (10 mL) and water (10 mL), and extracted with EtOAc (3 × 15 mL). The combined EtOAc extracts were washed with water (3 × 10 mL), brine (10 mL), dried over Na_2SO_4, filtered and evaporated. The resulting oily residue was purified by column chromatography, eluting with cyclohexane/acetone (9:1), to give (*SSR*)-**6** as a colorless oil (148 mg, 0.55 mmol, 54%): $[\alpha]^{20}_D$ –15.2 (*c* 0.80, $CHCl_3$); IR (neat) 3473, 2962, 2935, 2883, 1469, 1400, 1361, 1292, 1213, 1151, 1099, 1033, 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (s, 9H), 1.02 (d, *J* = 6.6 Hz, 3H), 1.03 (d, *J* = 6.6 Hz, 3H), 1.31 (s, 3H), 2.28 (sept, *J* = 6.6 Hz, 1H), 2.59 (bs, 1H,), 3.81 (m, 2H), 4.11 (dd, *J* = 10.2, 11.4 Hz, 1H), 5.32 (bs, 1H), 5.72 (dd, *J* = 1.5, 9.9 Hz, 1H), 5.80 (d, *J* = 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 143.5, 138.3, 123.5, 120.5, 110.3, 85.5, 74.9, 66.1, 32.8, 32.6, 25.6, 21.1, 20.8, 20.7; ESIMS *m/z* (%) 539 (50), 330 (100) [$M(CH_3CN)Na^+$], 289 (80) [MNa^+], 194 (72), 185 (50); HRMS (ESI) calcd for $C_{16}H_{26}O_3Na$ 289.1780, found 289.1770.

(3*R*,10*R*)-(+)-6,12-di-*iso*-propyl-3,10-dihydroxy-3,10-dimethyltricyclo[6.2.2.0^{2,7}]dodecane-5,11-diene-4,9-dione (8).



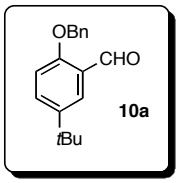
To a stirred solution of (*SSR*)-**6** (120 mg, 0.45 mmol, 1.0 equiv) in wet acetone (10 mL) was added *p*-TsOH•H_2O (44 mg, 0.23 mmol, 0.5 equiv). After stirring 6 h at room temperature, TLC monitoring [cyclohexane/EtOAc (2:1)] indicated complete consumption of the starting material. The reaction mixture was diluted with EtOAc (50 mL), and then concentrated under reduced pressure. The organic phase was washed with saturated $NaHCO_3$ (20 mL), water (3 × 20 mL), brine (20 mL), dried over Na_2SO_4, filtered and evaporated. The resulting oily residue was purified by column chromatography, eluting with cyclohexane/EtOAc (4:1 to 2:1), to give (+)-biscarvacrol (**8**) as a white solid (42 mg, 56%; er 93:7, chiral normal phase using a Chiralpak AS-H column): mp 145-146 °C (lit.[16] mp 149-150 °C);

$[\alpha]^{20}_{D}$ +35.5 (*c* 0.61, $CHCl_3$) [lit.[16] +55.1 (*c* 0.55, $CHCl_3$)]; IR (neat) 3452, 2968, 2926, 2872, 1733, 1679, 1465, 1383, 1363, 1153, 1093, 957, 911, 857 cm^{-1}; 0.85 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 3H), 1.23 (s, 3H), 1.25 (s, 3H), 1.84 (sept, *J* = 6.6 Hz, 1H), 2.44-2.55 (m, 2H), 3.12 (dd, *J* = 2.1, 8.7 Hz, 1H), 3.16 (bs, 1H), 3.23 (dd, *J* = 1.5, 8.7 Hz, 1H), 3.26 (dd, *J* = 2.4, 6.9 Hz, 1H), 4.06 (bs, 1H), 5.85 (d, *J* = 6.6 Hz, 1H), 5.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 212.3, 201.9, 166.5, 145.7, 126.1, 120.0, 73.5, 72.9, 55.9, 44.7, 42.1, 40.9, 33.3, 32.9, 32.3, 25.9, 23.0, 20.8, 20.1, 19.3; ESIMS *m/z* (%) 355 (100) [$M$$Na^+$], 333 (6) [$M$$H^+$]; HRMS (ESI) calcd for $C_{20}H_{28}O_4Na$ 355.1885, found 355.1897.

Crystallization from $CHCl_3$ by slow evaporation furnished (+)-**8** as fine white needles, the X-ray analysis of which unambiguously confirmed the structure and absolute configuration of this natural bis(monoterpene) (CCDC 671171).

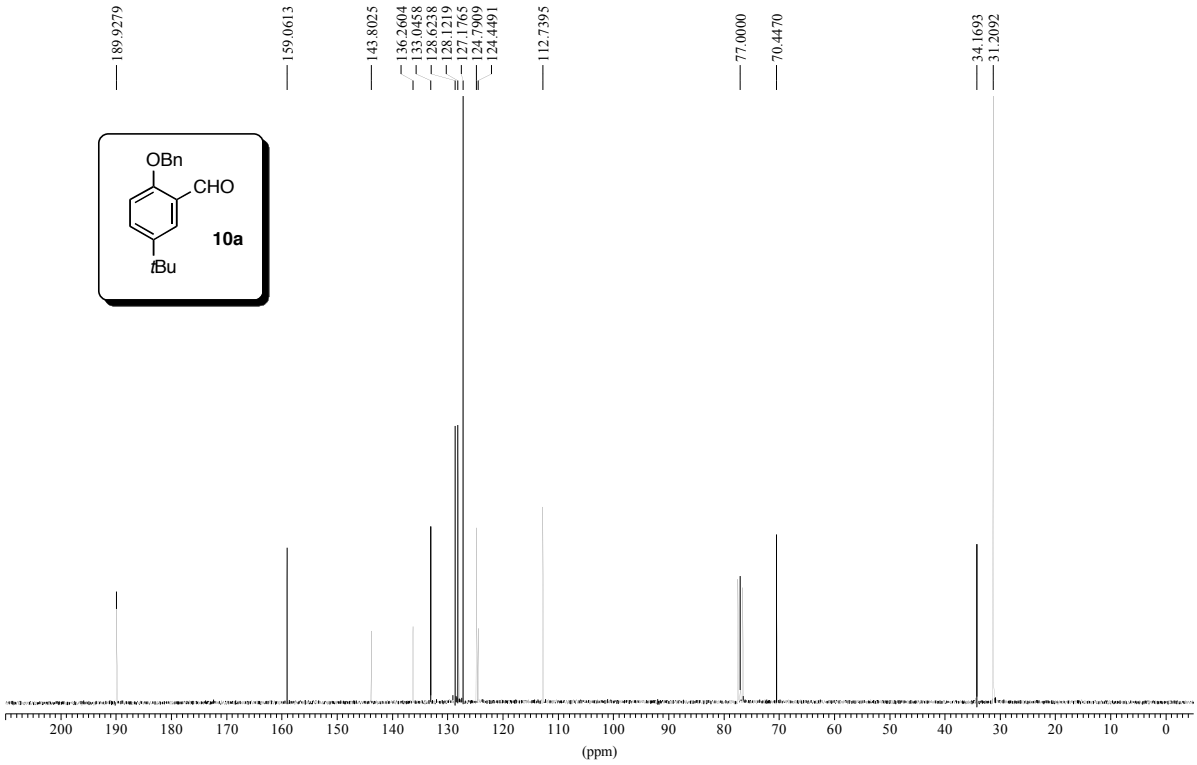
NMR Spectra

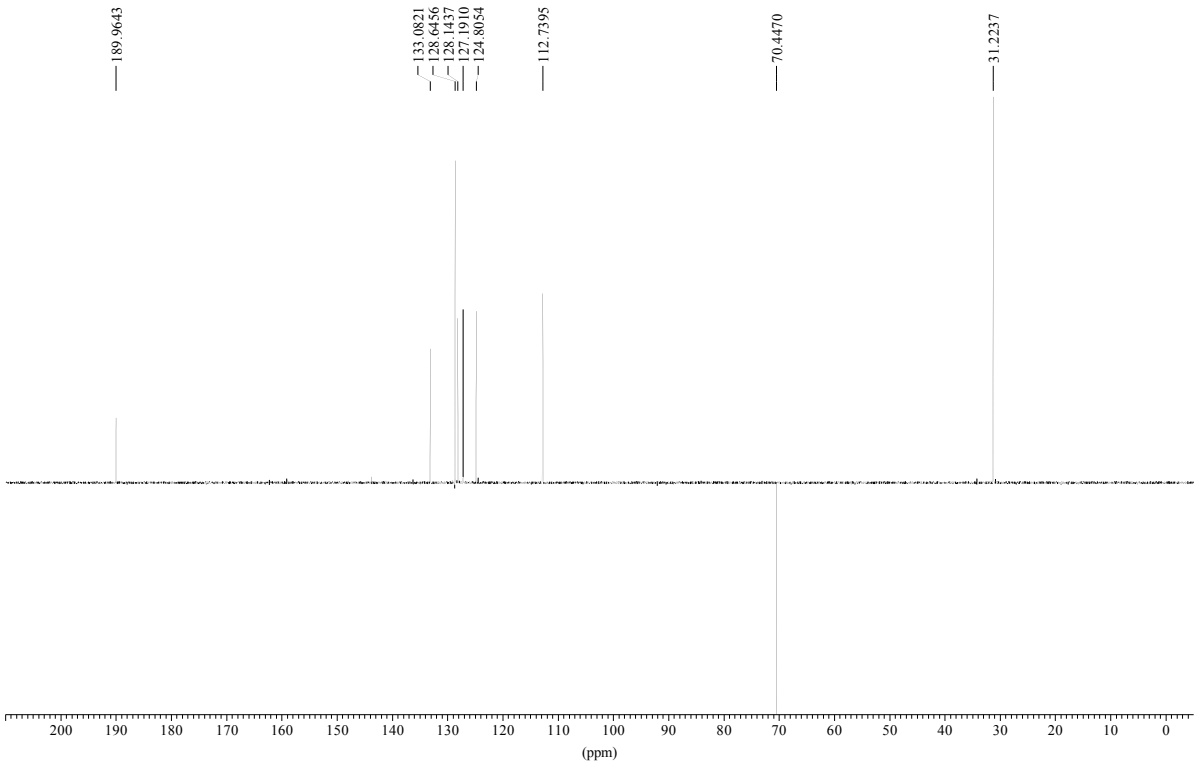
AM-B154-2 / 21110515.1/1 cd-cl3 DPX 300



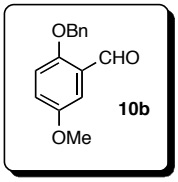
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	7313	3177.21	10.5861	210599	16.9
2	9444	2374.33	7.9110	100071	8.0
3	9451	2371.69	7.9022	106409	8.6
4	9689	2282.02	7.6034	52494	4.2
5	9696	2279.39	7.5947	50243	4.0
6	9712	2273.36	7.5746	57620	4.6
7	9719	2270.72	7.5658	55381	4.5
8	9793	2242.84	7.4729	27488	2.2
9	9798	2240.96	7.4666	43339	3.5
10	9819	2233.04	7.4403	164274	13.2
11	9840	2225.13	7.4139	129565	10.4
12	9860	2217.60	7.3888	61928	5.0
13	9865	2215.71	7.3825	44855	3.6
14	9870	2213.83	7.3762	54418	4.4
15	9877	2211.19	7.3674	27631	2.2
16	9888	2207.05	7.3536	43191	3.5
17	9961	2179.54	7.2620	15974	1.3
18	10152	2107.58	7.0222	100403	8.1
19	10175	2098.92	6.9934	93334	7.5
20	11614	1556.76	5.1870	306868	24.7
21	14688	398.60	1.3281	1244328	100.0

AM-B154-2 / 21110515.2/1 cd-cl3 DPX 300



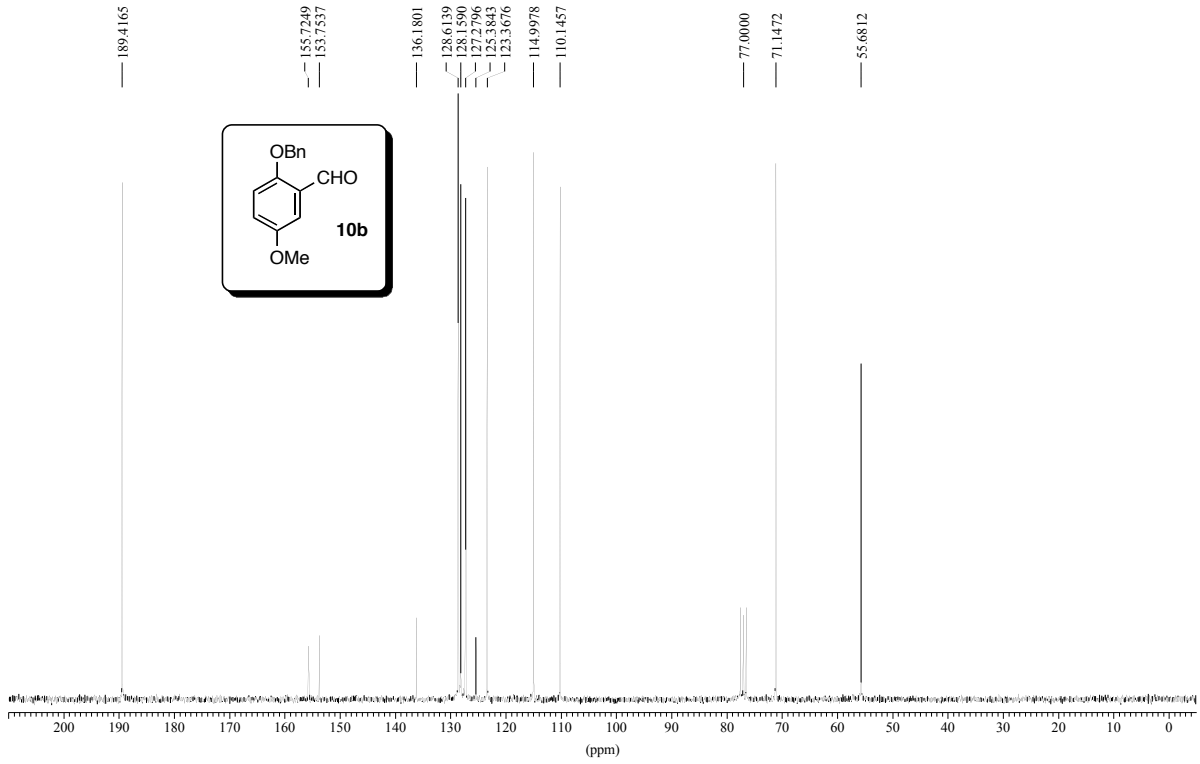


AM-B126 / MA030F.102 cd-cl3 AC 250

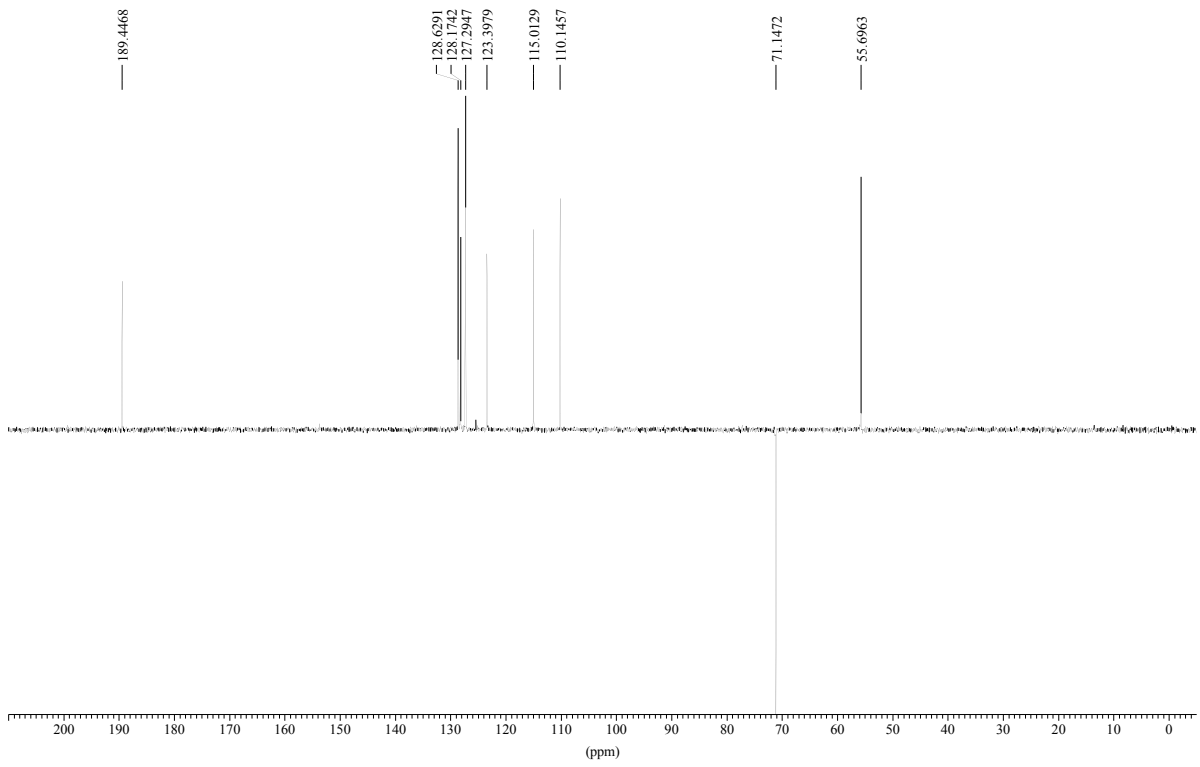


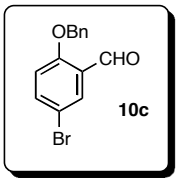
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	4313	2630.67	10.5171	12738	36.8
2	6831	1862.24	7.4450	1242	3.6
3	6845	1857.97	7.4279	4216	12.2
4	6850	1856.44	7.4218	6586	19.0
5	6852	1855.83	7.4194	6207	17.9
6	6857	1854.31	7.4133	6347	18.3
7	6863	1852.48	7.4060	3595	10.4
8	6867	1851.25	7.4011	6334	18.3
9	6869	1850.64	7.3986	6314	18.2
10	6877	1848.20	7.3889	1426	4.1
11	6888	1844.85	7.3755	2455	7.1
12	6894	1843.02	7.3681	2950	8.5
13	6907	1839.05	7.3523	4932	14.2
14	6917	1836.00	7.3401	6046	17.5
15	6981	1816.46	7.2620	1296	3.7
16	7080	1786.25	7.1412	2294	6.6
17	7091	1782.90	7.1278	2003	5.8
18	7110	1777.10	7.1046	4212	12.2
19	7121	1773.74	7.0912	3406	9.8
20	7180	1755.73	7.0192	5694	16.4
21	7210	1746.58	6.9826	2992	8.6
22	8716	1286.98	5.1452	14844	42.9
23	9823	949.16	3.7946	34613	100.0

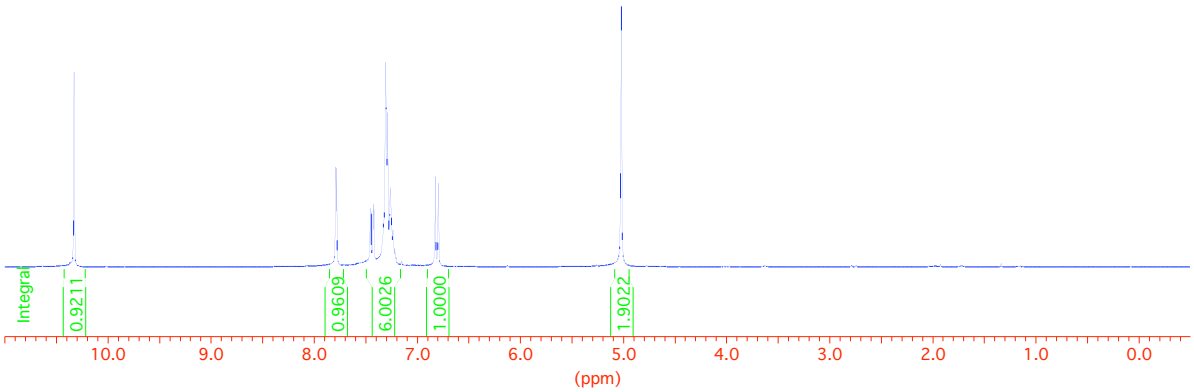
AM-B126 / MA031F.102 cd-cl3 AC 250



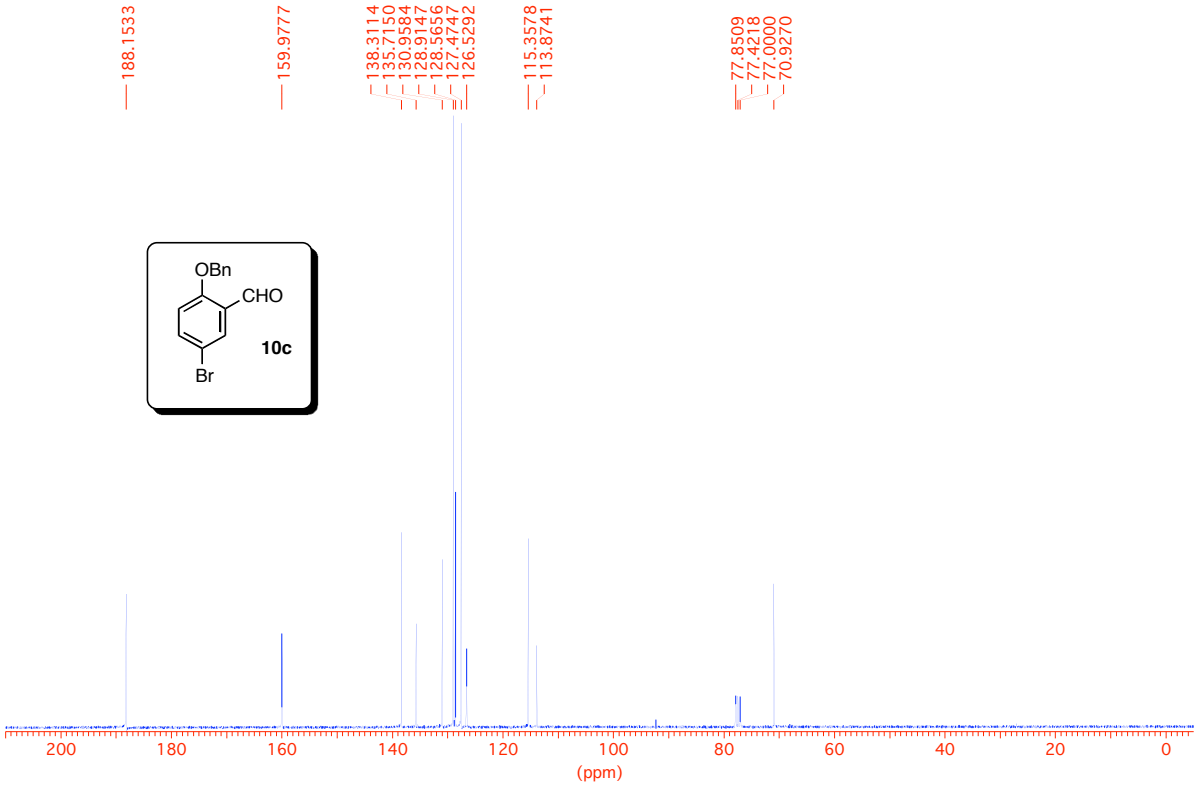
AM-B126 / MA032F.102 cd-cl3 AC 250

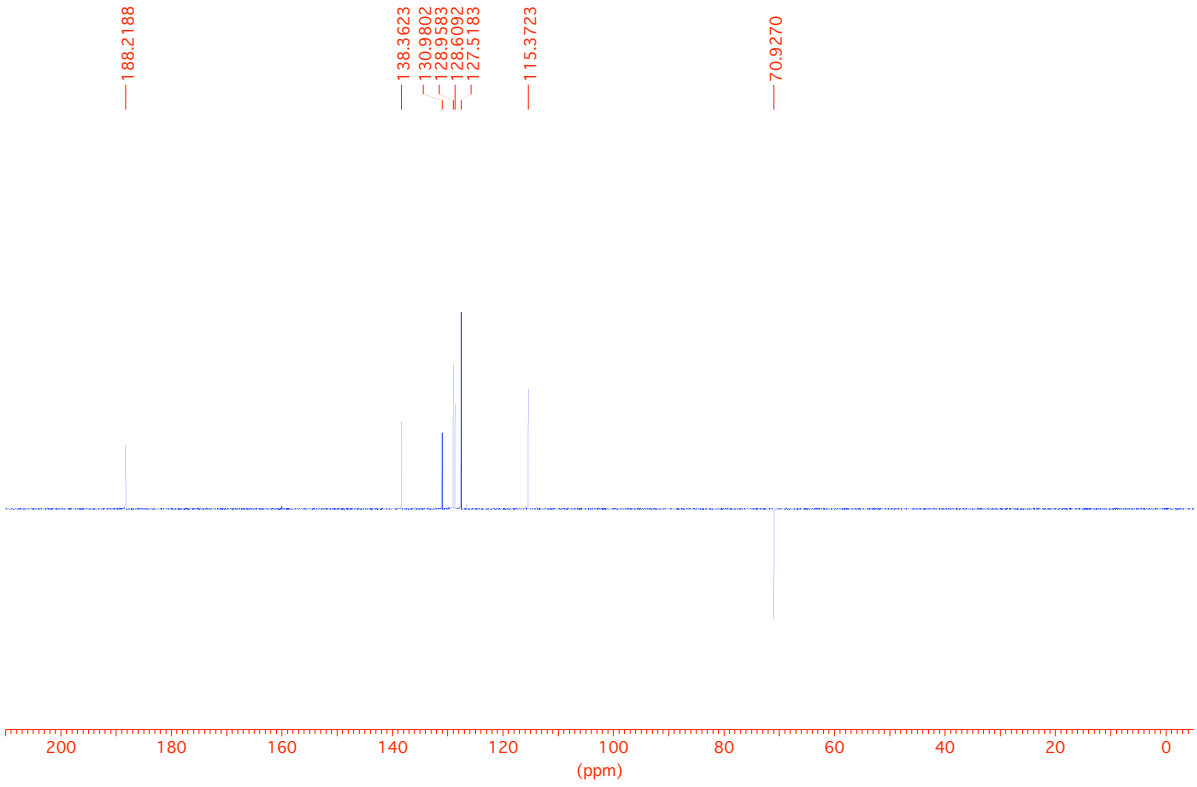




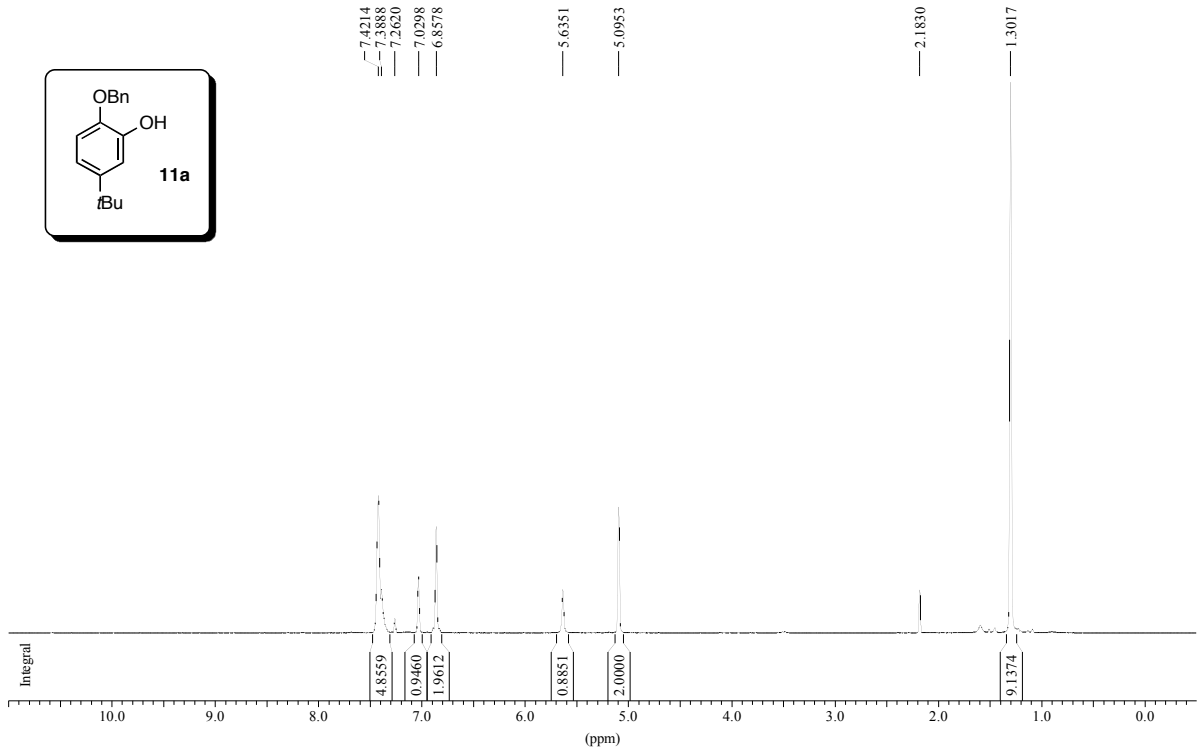


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	7432	3099.37	10.3268	142179	74.7
2	9453	2337.94	7.7898	72937	38.3
3	9460	2335.30	7.7810	72322	38.0
4	9720	2237.34	7.4546	42725	22.5
5	9727	2234.71	7.4458	38705	20.3
6	9743	2228.68	7.4257	45803	24.1
7	9750	2226.04	7.4169	41593	21.9
8	9823	2198.54	7.3253	34688	18.2
9	9839	2192.51	7.3052	149485	78.6
10	9844	2190.63	7.2989	116265	61.1
11	9853	2187.23	7.2876	112780	59.3
12	9875	2178.95	7.2600	57579	30.3
13	9881	2176.69	7.2525	42619	22.4
14	9887	2174.43	7.2449	27439	14.4
15	9896	2171.03	7.2336	27000	14.2
16	10223	2047.83	6.8232	65920	34.6
17	10246	2039.17	6.7943	61038	32.1
18	11661	1506.05	5.0180	190252	100.0


188.1533
159.9777
138.3114
135.7150
130.9584
128.9147
128.5656
127.4747
126.5292
115.3578
113.8741
77.8509
77.4218
77.0000
70.9270
OBn
CHO
Br
10c
200
180
160
140
120
100
80
60
40
20
0
(ppm)

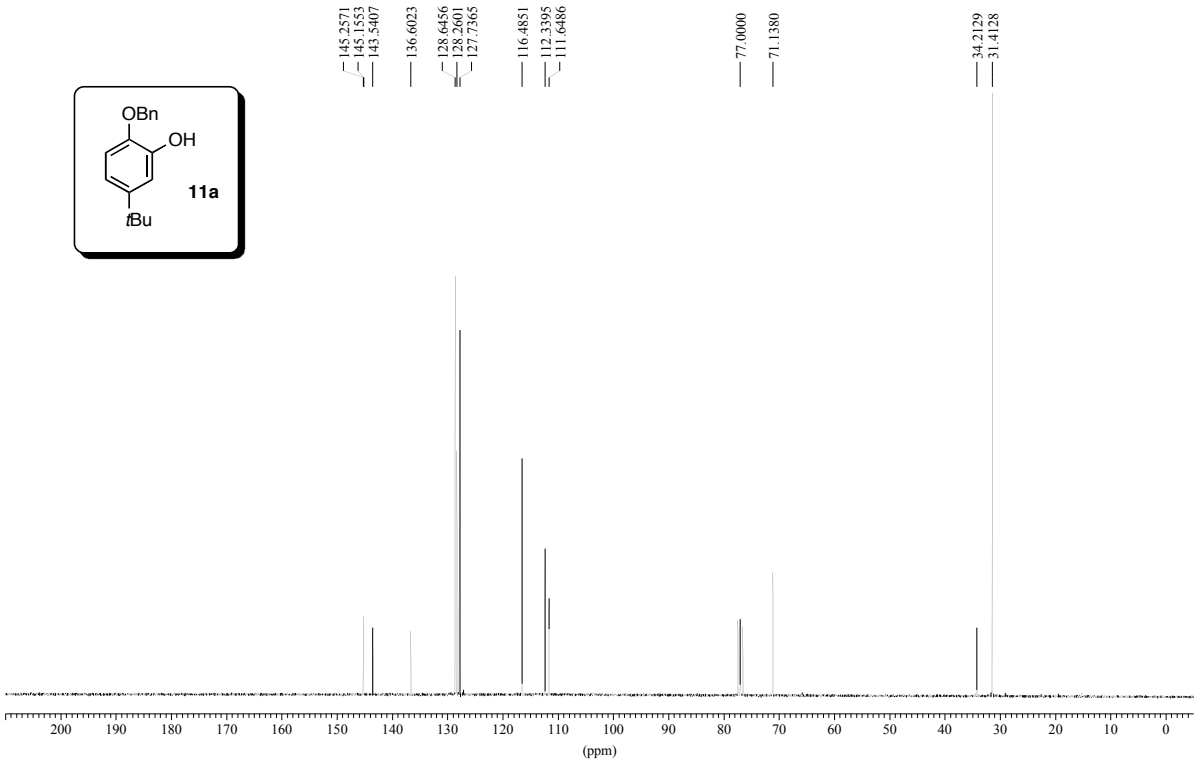

188.2188
138.3623
130.9802
128.9583
128.6092
127.5183
115.3723
70.9270
200
180
160
140
120
100
80
60
40
20
0
(ppm)

AM-B155 / 21110516.1/1 cd-cl3 DPX 300

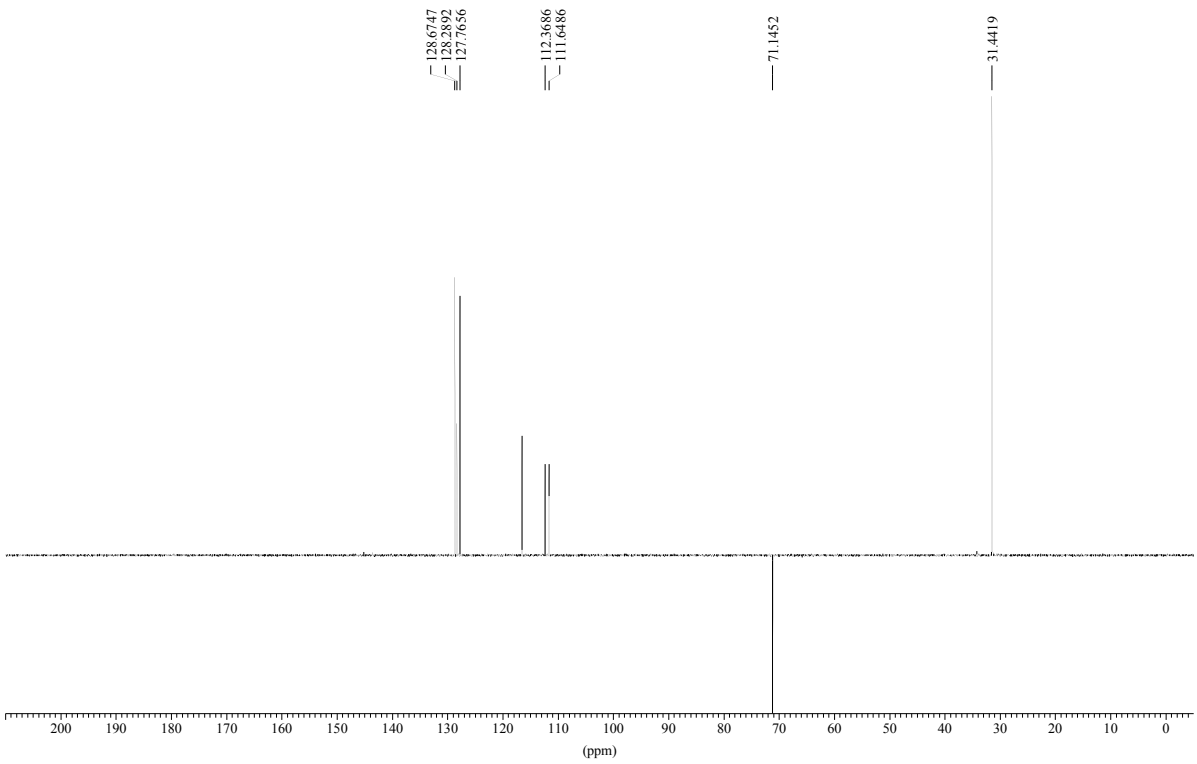


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9831	2227.39	7.4214	-62708	-473.0
2	9857	2217.60	7.3888	13258	100.0
3	9958	2179.54	7.2620	-1337	-10.1
4	10143	2109.84	7.0298	-13798	-104.1
5	10280	2058.23	6.8578	-18275	-137.8
6	11254	1691.26	5.6351	-18699	-141.0
7	11684	1529.26	5.0953	-58361	-440.2
8	14004	655.17	2.1830	-26767	-201.9
9	14706	390.69	1.3017	-286853	-2163.7

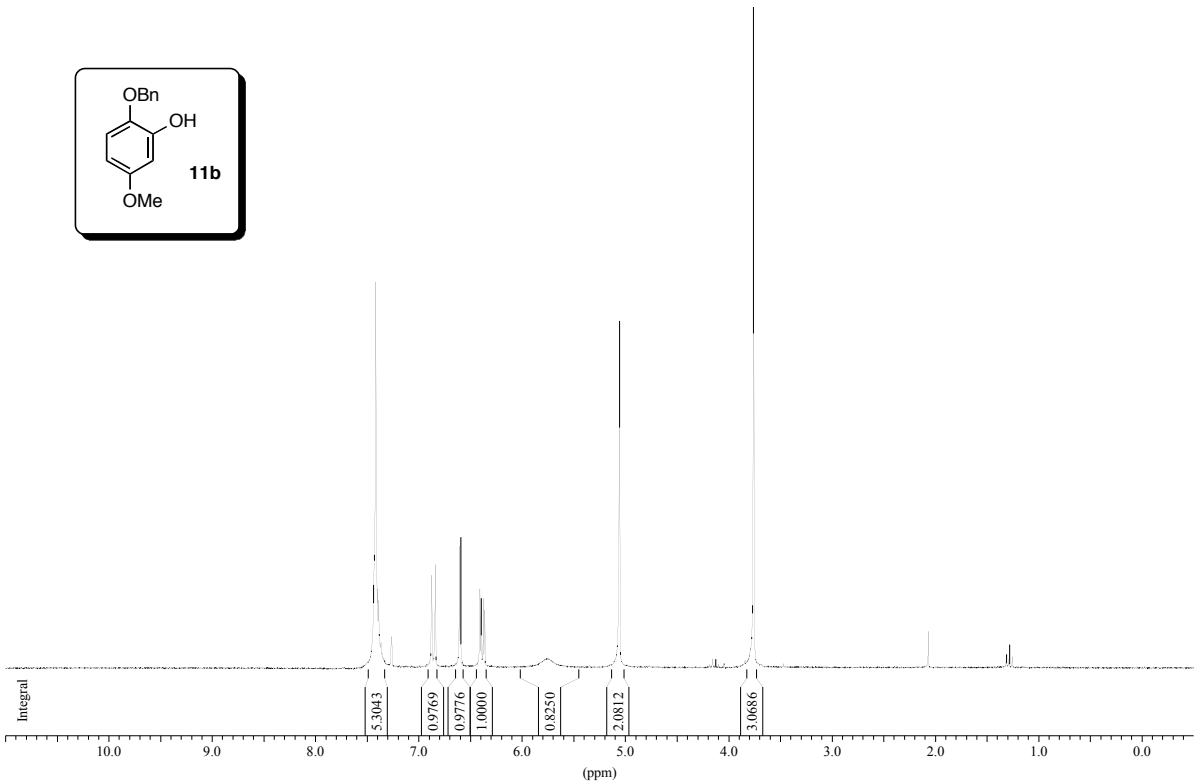
AM-B138-1 / 0407058 cd-cl3 DPX 300



AM-B138-1 /0407058 cd-cl3 DPX 300

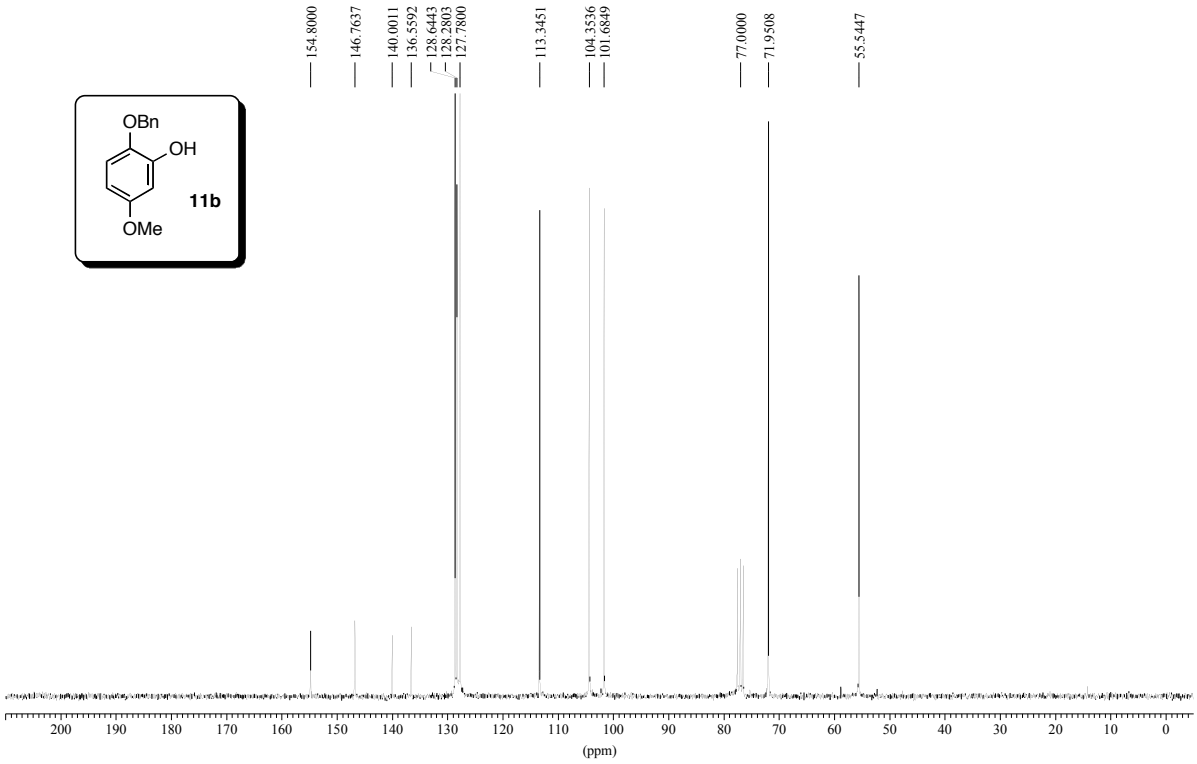


AM-B127 / DC070F.101 cd-cl3 AC 250

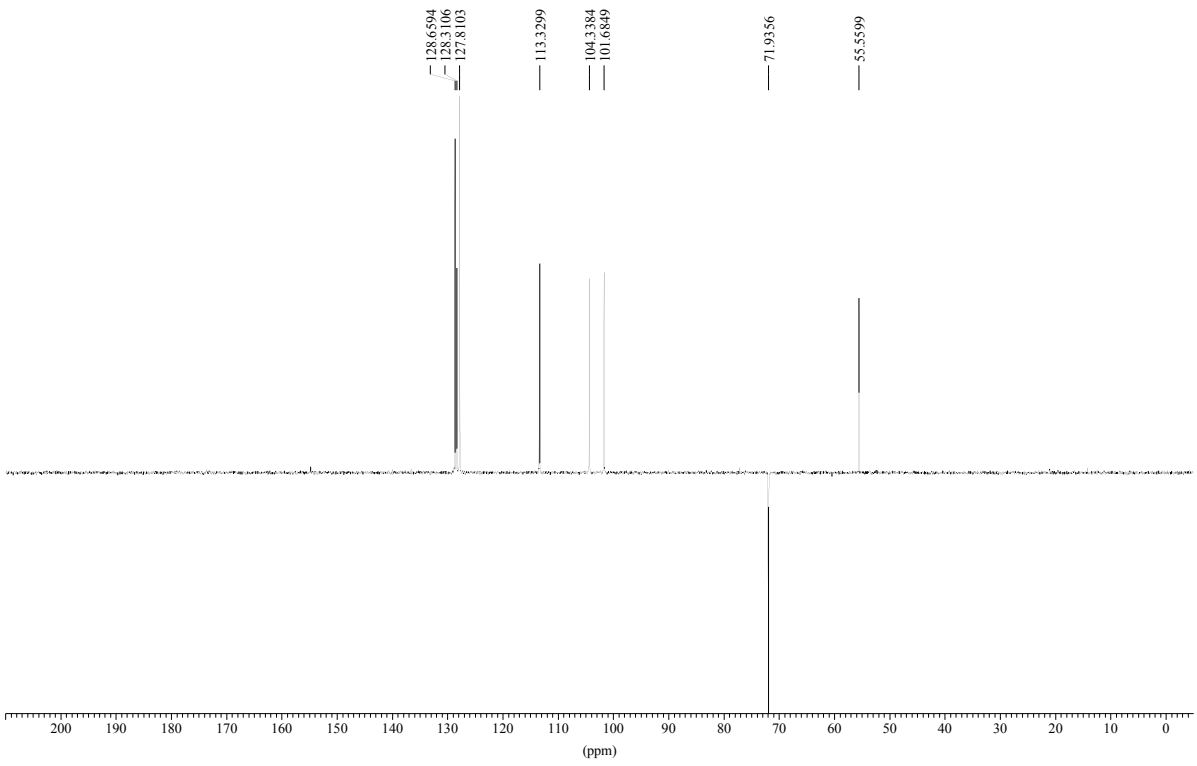


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6856	1854.61	7.4145	10714	58.2
2	6981	1816.46	7.2620	844	4.6
3	7300	1719.11	6.8728	2551	13.9
4	7329	1710.26	6.8374	2849	15.5
5	7520	1651.98	6.6044	3361	18.3
6	7530	1648.92	6.5922	3613	19.6
7	7682	1602.54	6.4067	2169	11.8
8	7692	1599.48	6.3945	1920	10.4
9	7711	1593.69	6.3714	1902	10.3
10	7721	1590.63	6.3592	1584	8.6
11	8221	1438.05	5.7491	239	1.3
12	8788	1265.01	5.0574	9635	52.4
13	9853	940.00	3.7580	18394	100.0

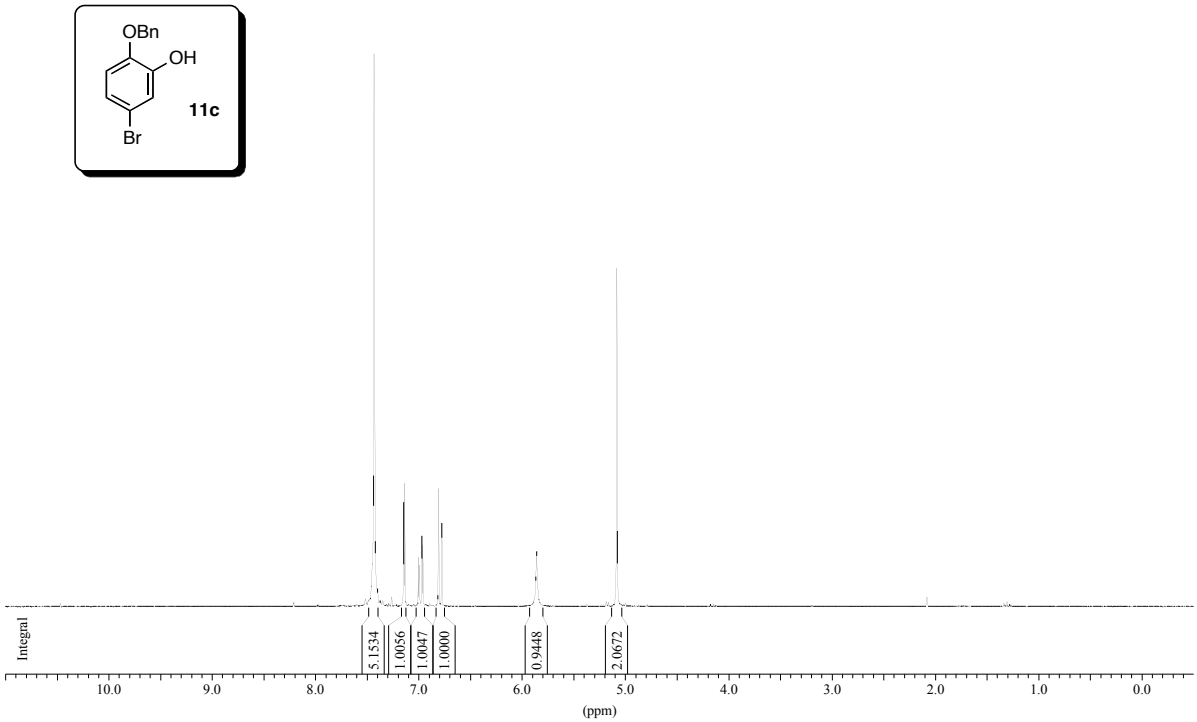
AM-B127 / DC071F.101 cd-cl3 AC 250



AM-B127 / DC072F.101 cd-cl3 AC 250

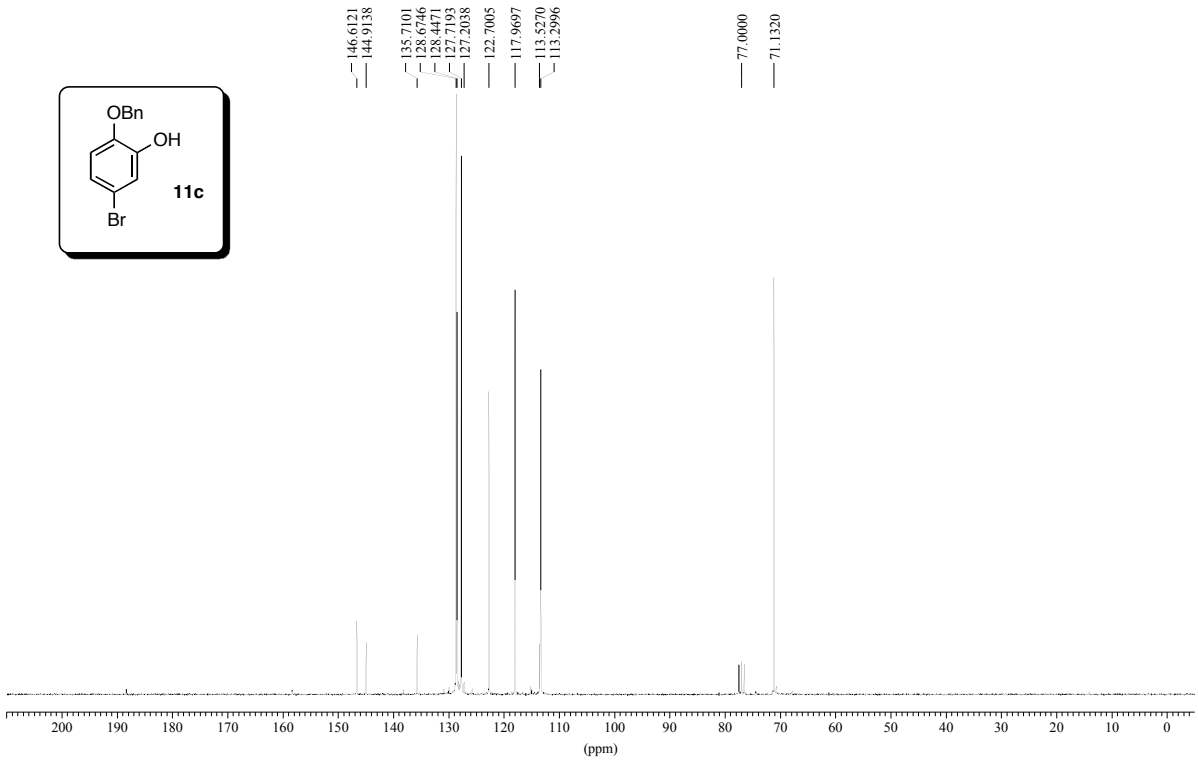


AM-B156/ DC010F.102 cd-cl3 AC 250

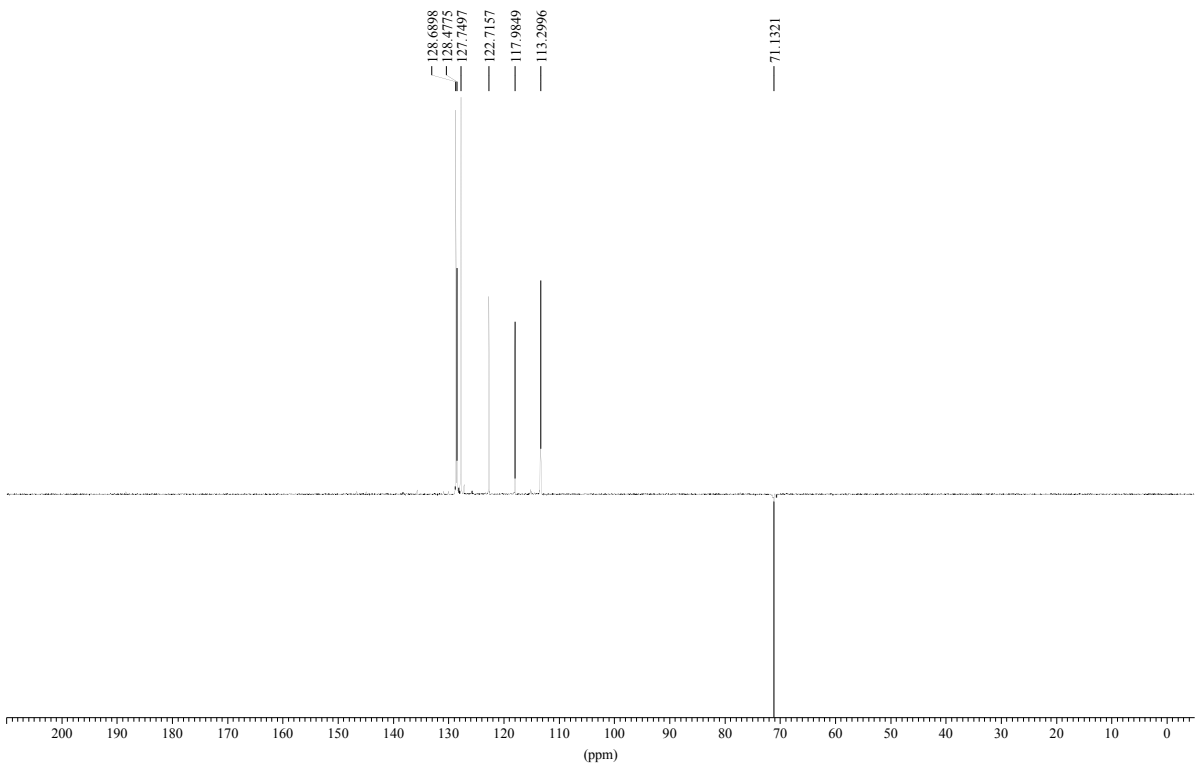


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6841	1858.88	7.4316	25194	100.0
2	6980	1816.46	7.2620	413	1.6
3	7076	1787.17	7.1449	4744	18.8
4	7084	1784.73	7.1351	5600	22.2
5	7192	1751.77	7.0033	2225	8.8
6	7200	1749.33	6.9936	1861	7.4
7	7220	1743.22	6.9692	3198	12.7
8	7228	1740.78	6.9594	2772	11.0
9	7352	1702.94	6.8081	5357	21.3
10	7380	1694.39	6.7740	3784	15.0
11	8130	1465.51	5.8589	2492	9.9
12	8767	1271.12	5.0818	15416	61.2

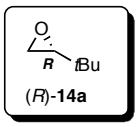
AM-B156 / DC011F.102 cd-cl3 AC 250



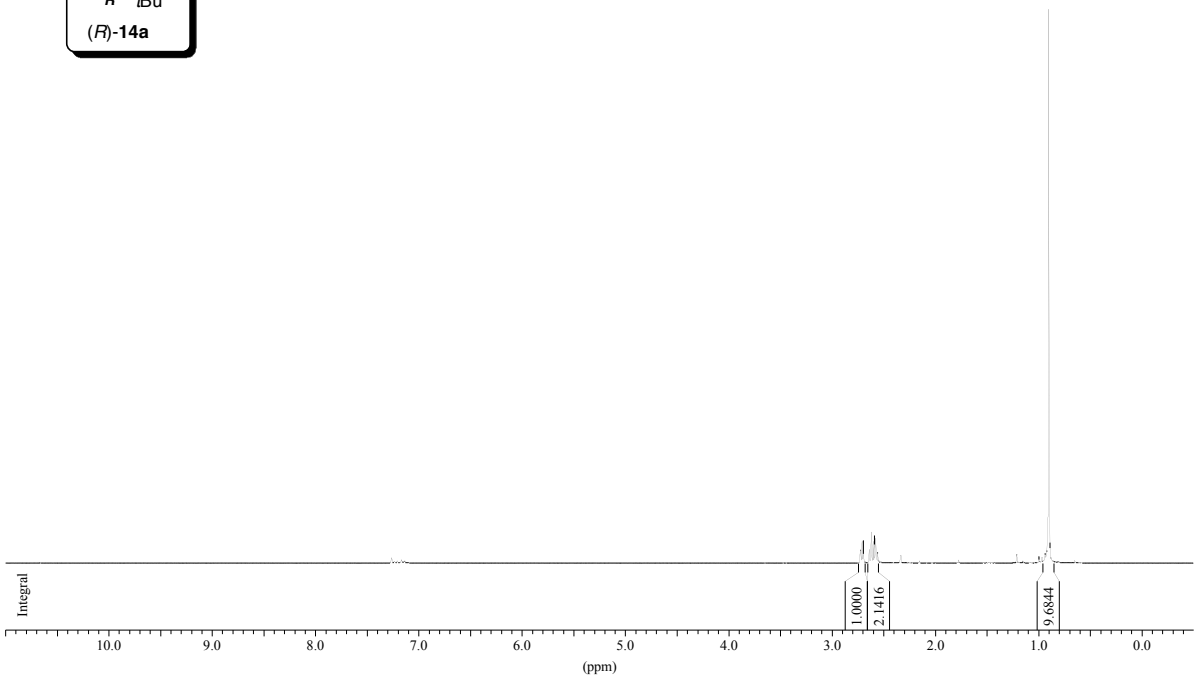
AM-B156 / DC012F.102 cd-cl3 AC 250



AM-B163 / JV200F.101 cd-cl3 AC 250

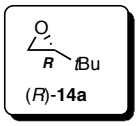


(*R*)-**14a**



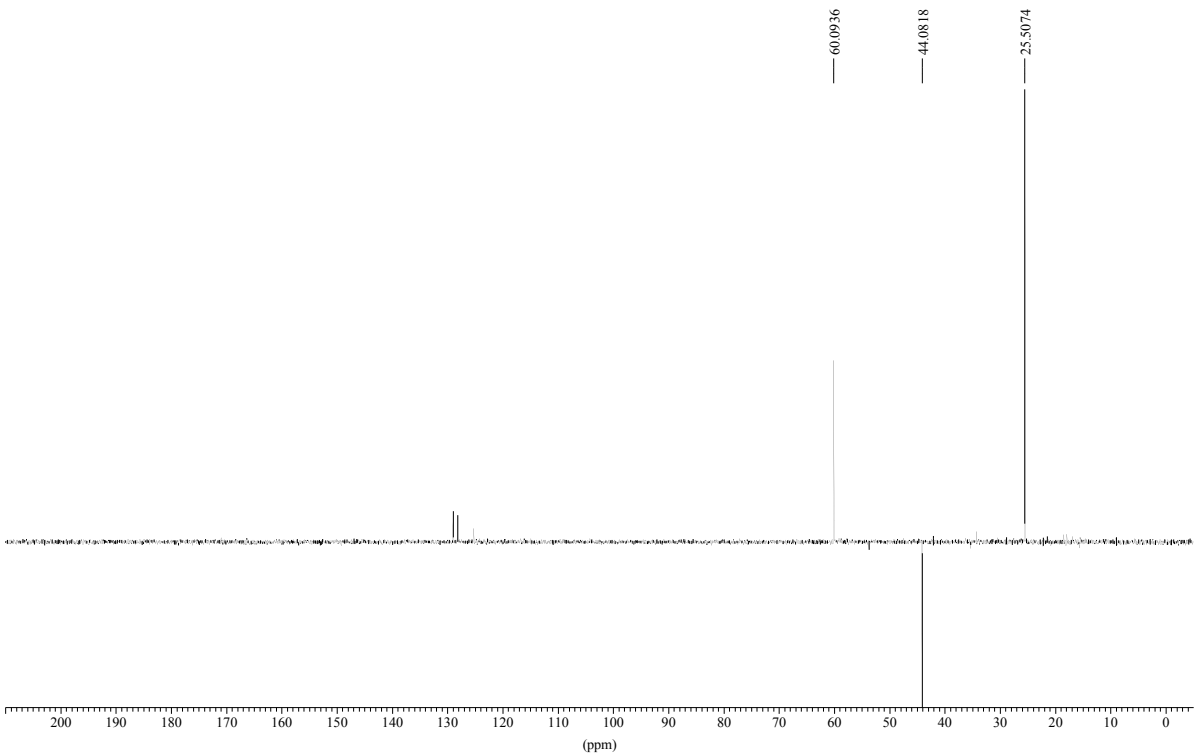
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6980	1816.46	7.2620	581	0.9
2	10699	681.52	2.7246	1455	2.3
3	10709	678.46	2.7124	1990	3.2
4	10713	677.24	2.7075	2419	3.9
5	10722	674.50	2.6966	2554	4.1
6	10770	659.85	2.6380	1511	2.4
7	10785	655.27	2.6197	3509	5.6
8	10799	651.00	2.6026	2420	3.9
9	10811	647.34	2.5880	3092	4.9
10	10820	644.59	2.5770	2780	4.4
11	10826	642.76	2.5697	1552	2.5
12	10836	639.71	2.5575	1182	1.9
13	10847	636.35	2.5440	350	0.6
14	10863	631.47	2.5245	159	0.3
15	12194	225.28	0.9006	62792	100.0

AM-B163 / JV201F.101 cd-cl3 AC 250

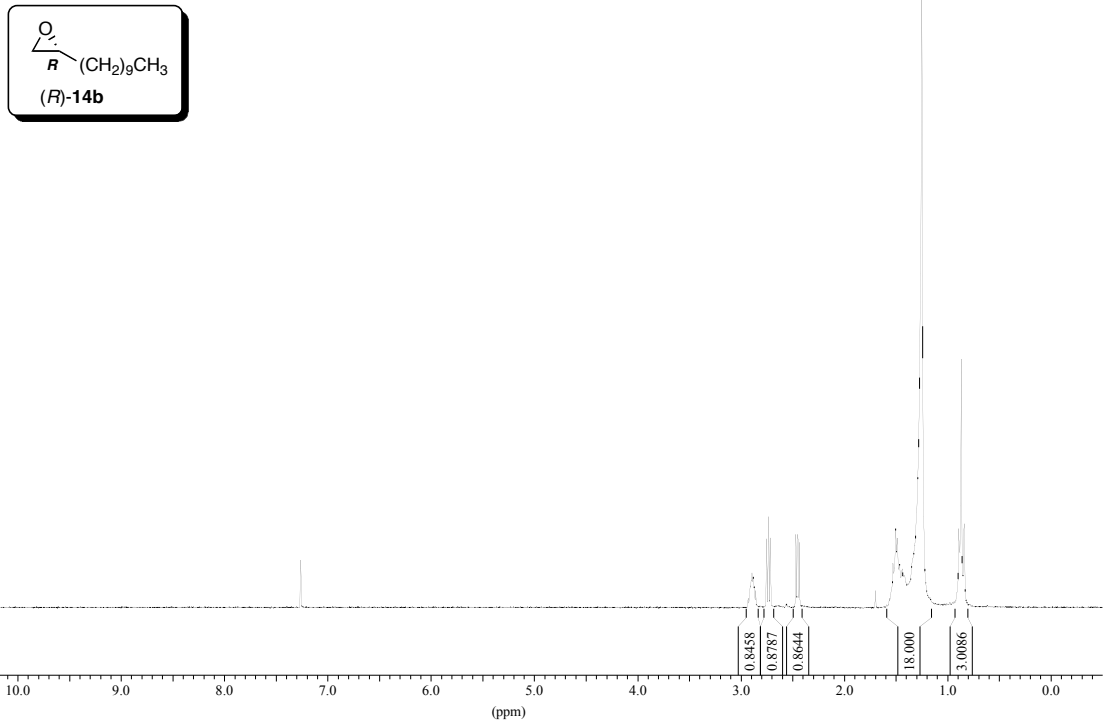


(*R*)-**14a**

AM-B163 / JV202F.101 cd-cl3 AC 250

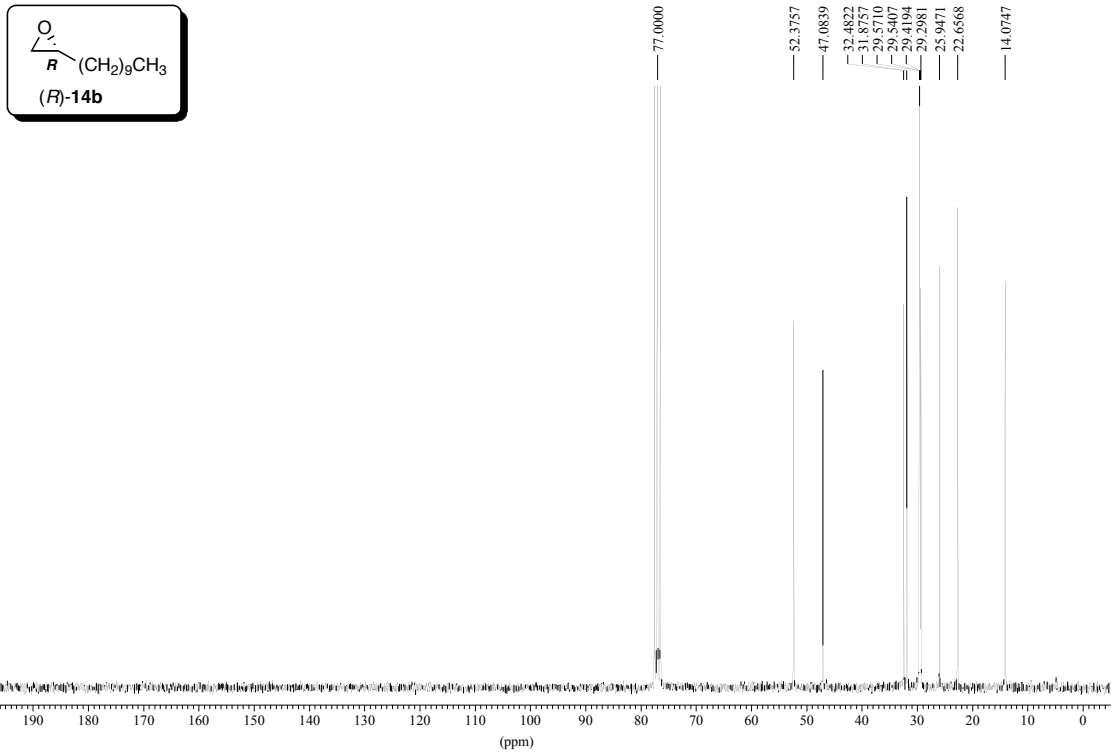


AM-B129 / MS230F.101 cd-cl3 AC 250

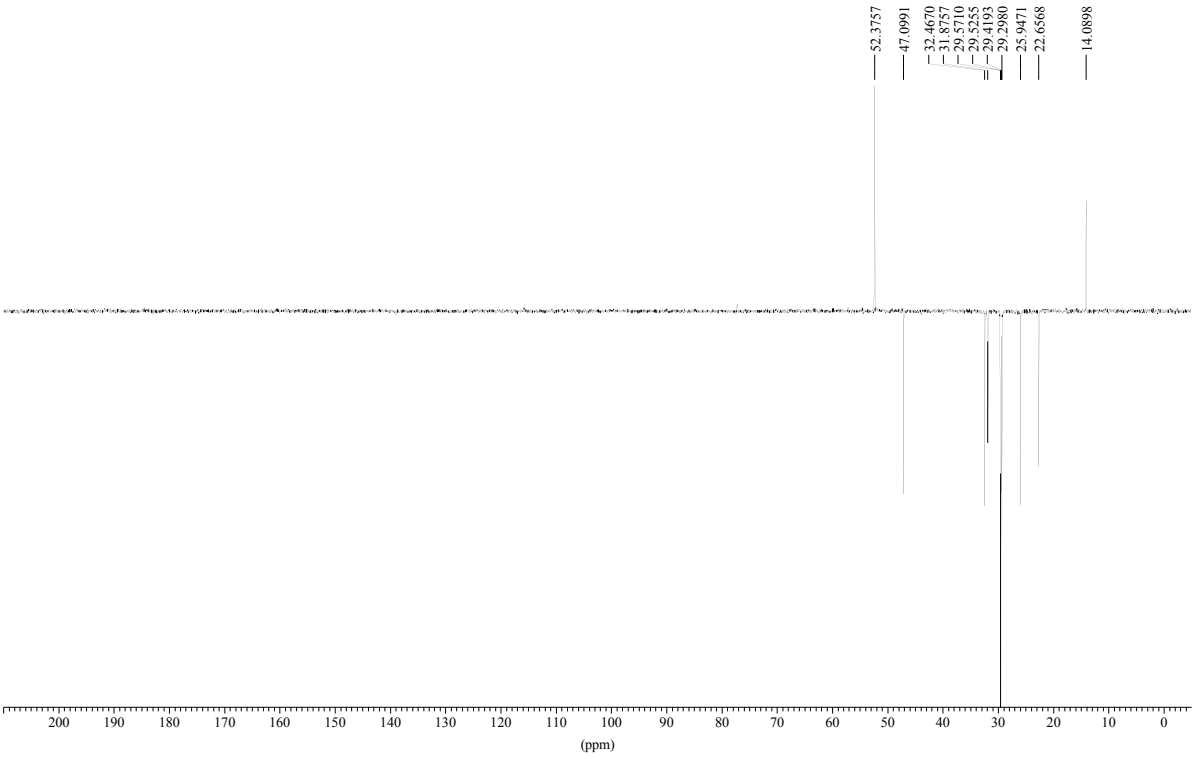


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6981	1816.46	7.2620	819	7.0
2	10533	732.48	2.9284	148	1.3
3	10550	727.29	2.9076	435	3.7
4	10560	724.24	2.8954	573	4.9
5	10563	723.33	2.8918	590	5.0
6	10568	721.80	2.8857	464	3.9
7	10572	720.58	2.8808	522	4.4
8	10581	717.83	2.8698	352	3.0
9	10590	715.09	2.8588	280	2.4
10	10678	688.23	2.7515	1197	10.2
11	10691	684.26	2.7356	1141	9.7
12	10694	683.35	2.7319	1593	13.6
13	10707	679.38	2.7161	1215	10.3
14	10911	617.12	2.4672	1277	10.9
15	10920	614.38	2.4562	1278	10.9
16	10928	611.94	2.4464	1194	10.2
17	10937	609.19	2.4355	1140	9.7
18	11682	381.83	1.5265	768	6.5
19	11701	376.04	1.5033	1382	11.8
20	11716	371.46	1.4850	1206	10.3
21	11732	366.57	1.4655	749	6.4
22	11908	312.86	1.2508	11752	100.0
23	12202	223.14	0.8921	1381	11.8
24	12222	217.04	0.8677	4396	37.4
25	12245	210.02	0.8396	1465	12.5

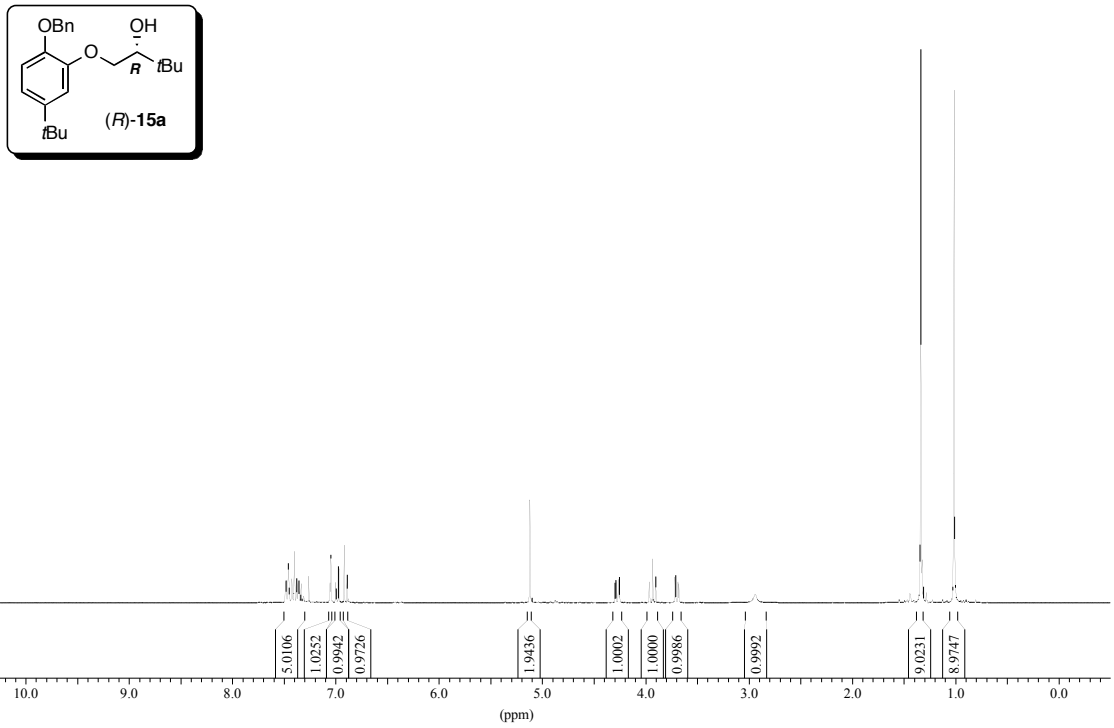
AM-B129 / MS231F.101 cd-cl3 AC 250

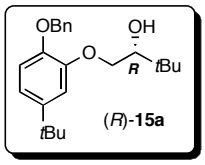


AM-B129 / MS232F.101 cd-cl3 AC 250



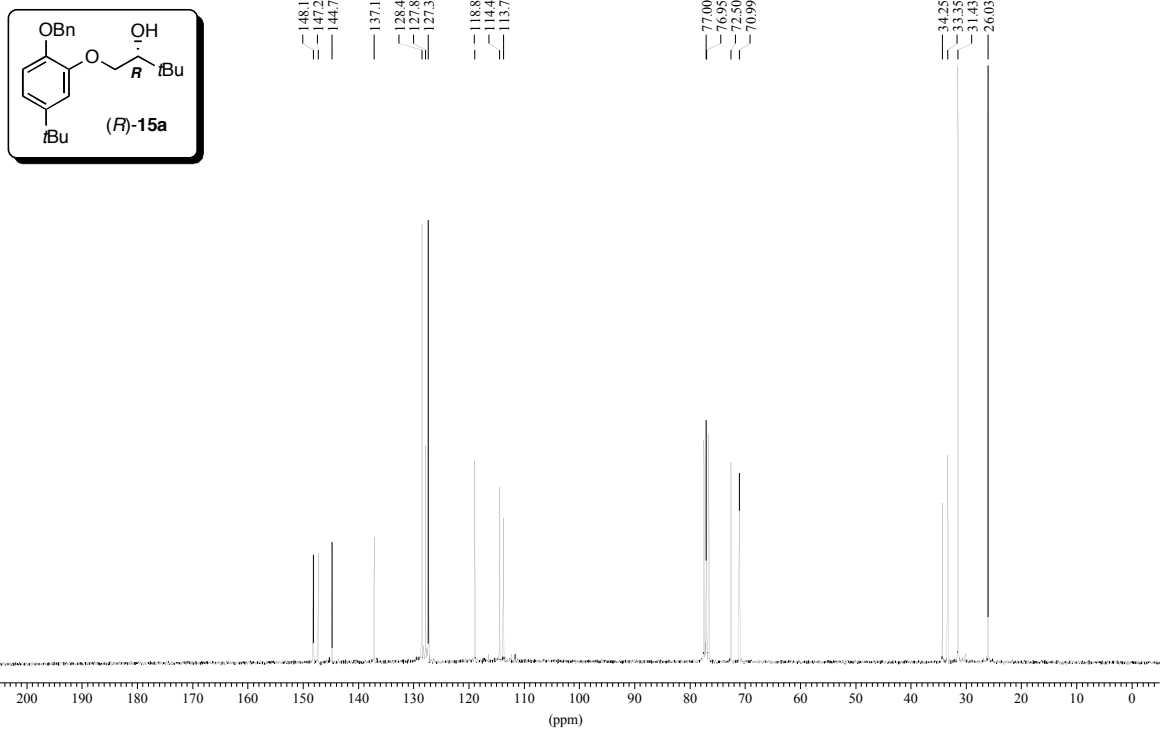
AM-B166 / 06020620.1-1 cd-cl3 DPX 300



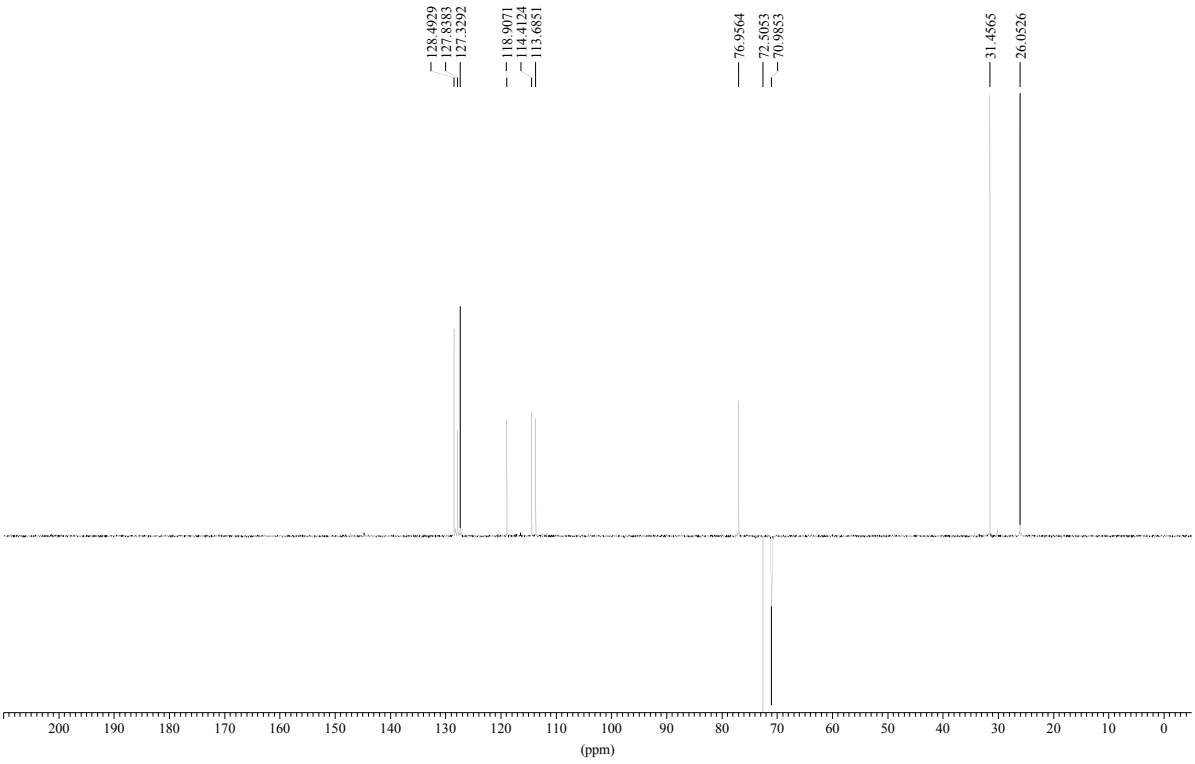


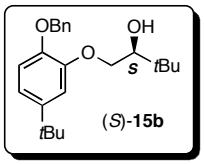
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9781	2246.98	7.4867	30218	2.9
2	9785	2245.48	7.4817	40807	4.0
3	9803	2238.70	7.4591	73251	7.1
4	9828	2229.28	7.4277	32781	3.2
5	9832	2227.77	7.4227	43879	4.3
6	9837	2225.89	7.4164	16206	1.6
7	9850	2220.99	7.4001	95196	9.2
8	9854	2219.48	7.3951	31964	3.1
9	9865	2215.34	7.3813	22920	2.2
10	9869	2213.83	7.3762	44726	4.3
11	9880	2209.68	7.3624	21807	2.1
12	9884	2208.18	7.3574	40702	4.0
13	9888	2206.67	7.3524	20040	1.9
14	9895	2204.03	7.3436	11596	1.1
15	9902	2201.40	7.3348	35147	3.4
16	9921	2194.24	7.3110	12039	1.2
17	9960	2179.54	7.2620	48849	4.7
18	10125	2117.38	7.0549	73242	7.1
19	10131	2115.12	7.0473	88683	8.6
20	10168	2101.18	7.0009	37610	3.7
21	10174	2098.92	6.9934	25778	2.5
22	10191	2092.51	6.9720	67327	6.5
23	10197	2090.25	6.9645	60765	5.9
24	10234	2076.31	6.9180	107047	10.4
25	10257	2067.65	6.8892	51763	5.0
26	11664	1537.54	5.1229	190806	18.5
27	12324	1288.88	4.2944	36487	3.5
28	12331	1286.25	4.2856	41814	4.1
29	12350	1279.09	4.2618	43063	4.2
30	12356	1276.83	4.2542	47285	4.6
31	12587	1189.79	3.9643	38739	3.8
32	12612	1180.38	3.9329	81338	7.9
33	12637	1170.96	3.9015	48306	4.7
34	12783	1115.95	3.7182	47626	4.6
35	12790	1113.31	3.7094	50369	4.9
36	12808	1106.53	3.6868	38105	3.7
37	12814	1104.27	3.6793	35365	3.4
38	13403	882.36	2.9399	15449	1.5
39	14680	401.24	1.3369	1029220	100.0
40	14936	304.78	1.0155	953348	92.6

AM-B166 / 06020620.2-1 cd-cl3 DPX 300



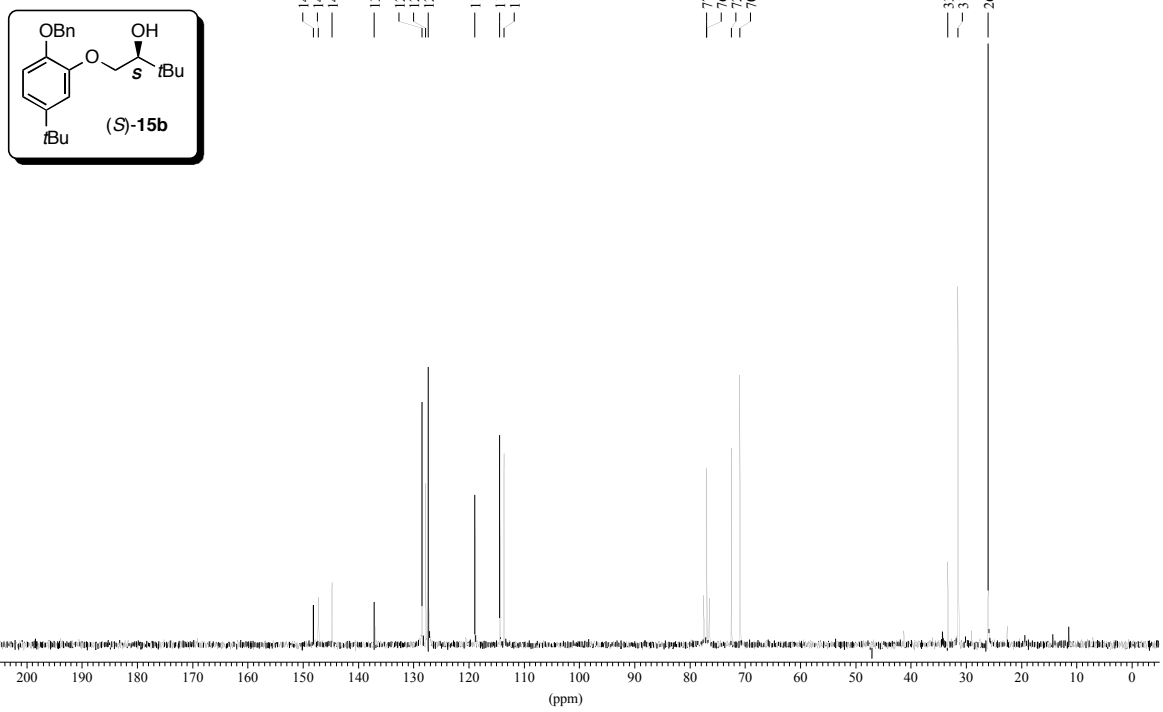
AM-B166 / 06020620.3-1 cd-cl3 DPX 300



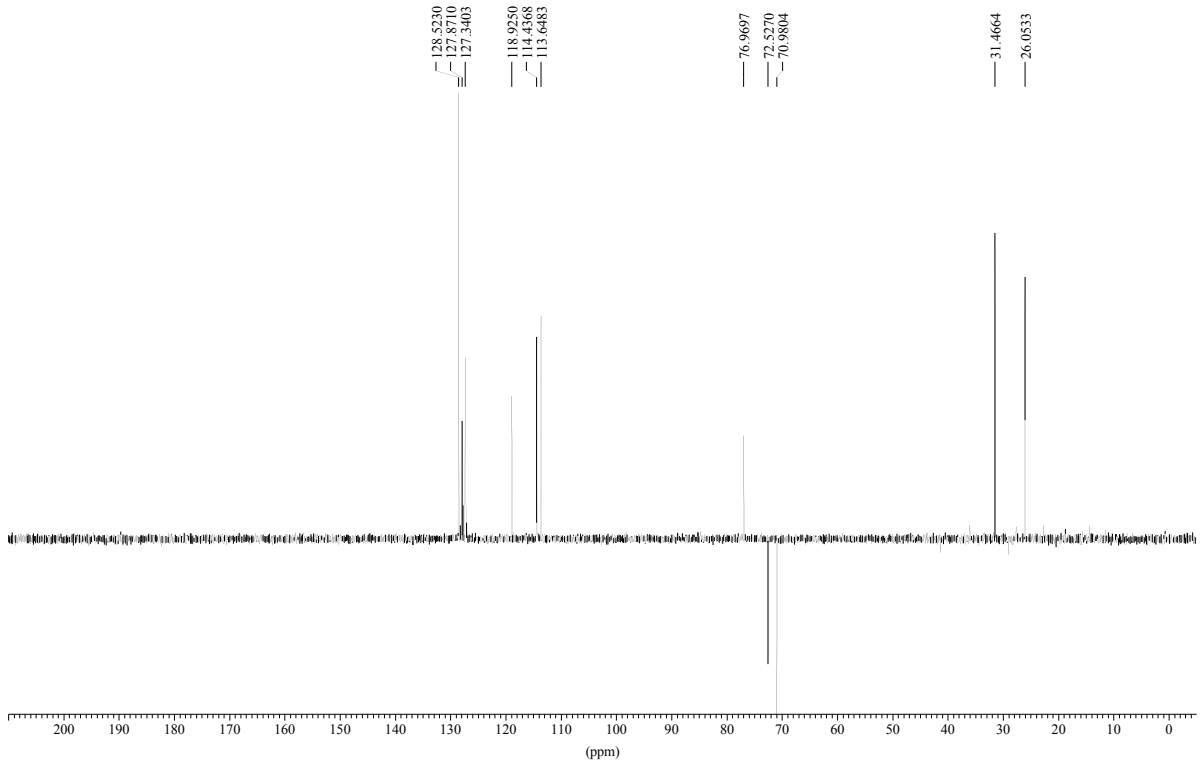


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6811	1868.34	7.4694	469	3.0
2	6836	1860.72	7.4389	1129	7.2
3	6855	1854.92	7.4157	546	3.5
4	6876	1848.51	7.3901	1183	7.6
5	6902	1840.57	7.3584	751	4.8
6	6910	1838.13	7.3486	584	3.7
7	6932	1831.42	7.3218	414	2.6
8	6981	1816.46	7.2620	408	2.6
9	7168	1759.40	7.0338	796	5.1
10	7175	1757.26	7.0253	1040	6.6
11	7205	1748.11	6.9887	372	2.4
12	7212	1745.97	6.9802	225	1.4
13	7233	1739.56	6.9545	726	4.6
14	7240	1737.42	6.9460	649	4.1
15	7275	1726.74	6.9033	1195	7.6
16	7303	1718.20	6.8691	523	3.3
17	8745	1278.13	5.1098	2775	17.7
18	9425	1070.62	4.2802	378	2.4
19	9433	1068.17	4.2704	411	2.6
20	9456	1061.15	4.2424	485	3.1
21	9464	1058.71	4.2326	504	3.2
22	9697	987.61	3.9483	404	2.6
23	9728	978.15	3.9105	800	5.1
24	9758	968.99	3.8739	459	2.9
25	9896	926.88	3.7055	502	3.2
26	9904	924.44	3.6958	514	3.3
27	9926	917.72	3.6689	383	2.4
28	9934	915.28	3.6592	365	2.3
29	10652	696.16	2.7832	173	1.1
30	11854	329.34	1.3167	15660	100.0
31	12116	249.39	0.9970	14769	94.3

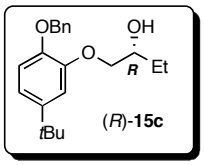
AM-B148 / SP081F.103 cd-cl3 AC 250



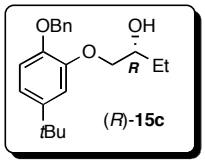
AM-B146 / SP082F.103 cd-cl3 AC 250



AM-B159 / DC150F.104 cd-cl3 AC 250



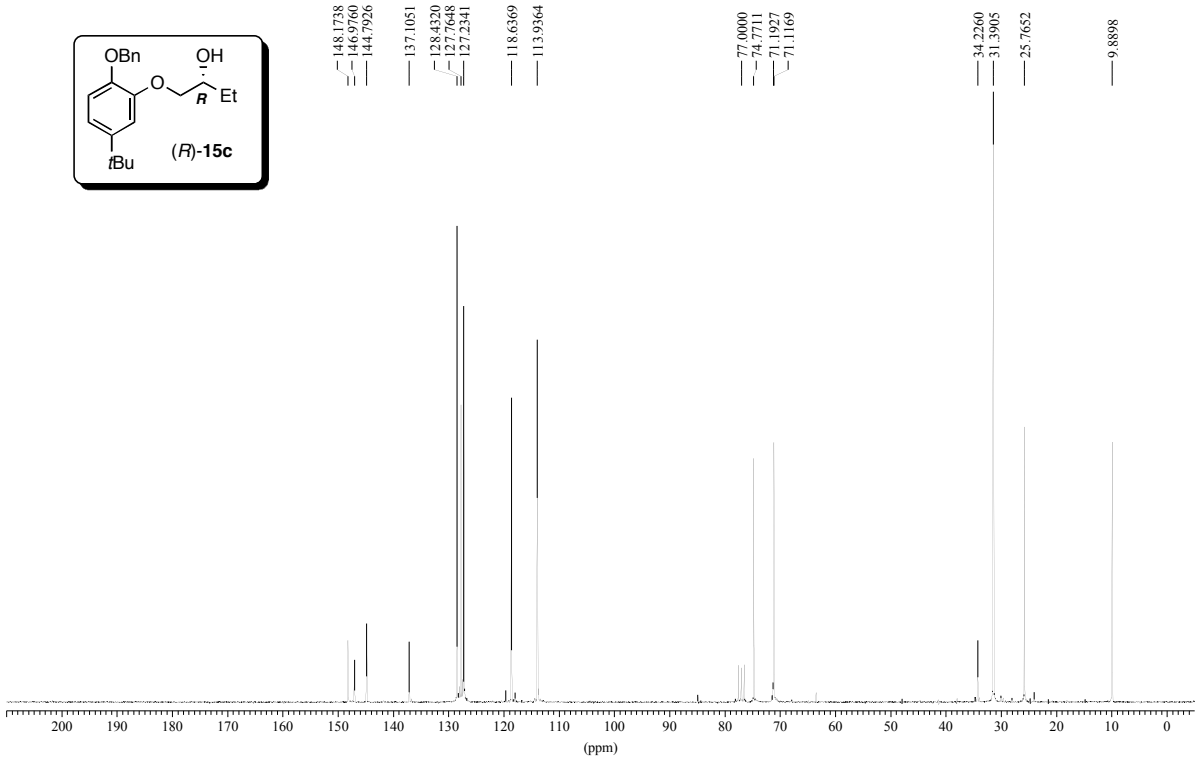
(*R*)-**15c**



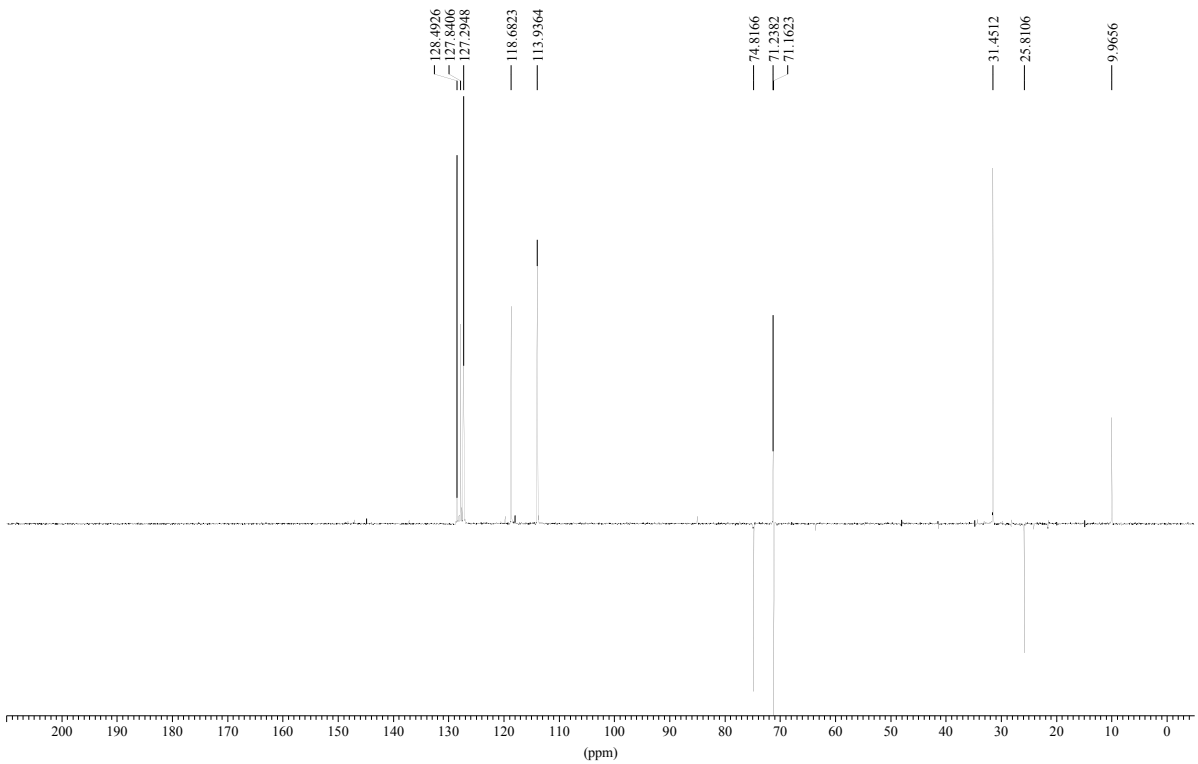
(*R*)-**15c**

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6785	1875.67	7.4987	1313	2.4
2	6791	1873.84	7.4914	1701	3.2
3	6814	1866.82	7.4633	3342	6.2
4	6833	1861.02	7.4401	1350	2.5
5	6839	1859.19	7.4328	1674	3.1
6	6846	1857.05	7.4243	786	1.5
7	6860	1852.78	7.4072	3829	7.1
8	6866	1850.95	7.3999	1240	2.3
9	6886	1844.85	7.3755	2221	4.1
10	6895	1842.10	7.3645	1825	3.4
11	6917	1835.39	7.3376	1353	2.5
12	6979	1816.46	7.2620	479	0.9
13	7149	1764.58	7.0546	2797	5.2
14	7156	1762.45	7.0461	3524	6.5
15	7192	1751.46	7.0021	1207	2.2
16	7199	1749.33	6.9936	742	1.4
17	7219	1743.22	6.9692	2650	4.9
18	7226	1741.09	6.9606	2257	4.2
19	7255	1732.24	6.9253	4356	8.1
20	7282	1724.00	6.8923	1619	3.0
21	8731	1281.80	5.1245	8820	16.4
22	9523	1040.10	4.1582	234	0.4
23	9546	1033.08	4.1301	1630	3.0
24	9554	1030.64	4.1204	570	1.1
25	9560	1028.81	4.1130	528	1.0
26	9568	1026.36	4.1033	2045	3.8
27	9591	1019.35	4.0752	534	1.0
28	9674	994.02	3.9740	219	0.4
29	9703	985.17	3.9386	1442	2.7
30	9716	981.20	3.9227	2348	4.4
31	9729	977.23	3.9068	1753	3.3
32	9734	975.71	3.9007	2083	3.9
33	9754	969.60	3.8763	345	0.6
34	10288	806.64	3.2248	1719	3.2
35	11559	418.76	1.6741	335	0.6
36	11584	411.13	1.6436	1273	2.4
37	11603	405.33	1.6205	1458	2.7
38	11608	403.81	1.6144	1582	2.9
39	11628	397.70	1.5900	1583	2.9
40	11652	390.38	1.5607	483	0.9
41	11829	336.36	1.3447	53842	100.0
42	12052	268.31	1.0727	4650	8.6
43	12076	260.98	1.0434	8619	16.0
44	12101	253.35	1.0129	3484	6.5

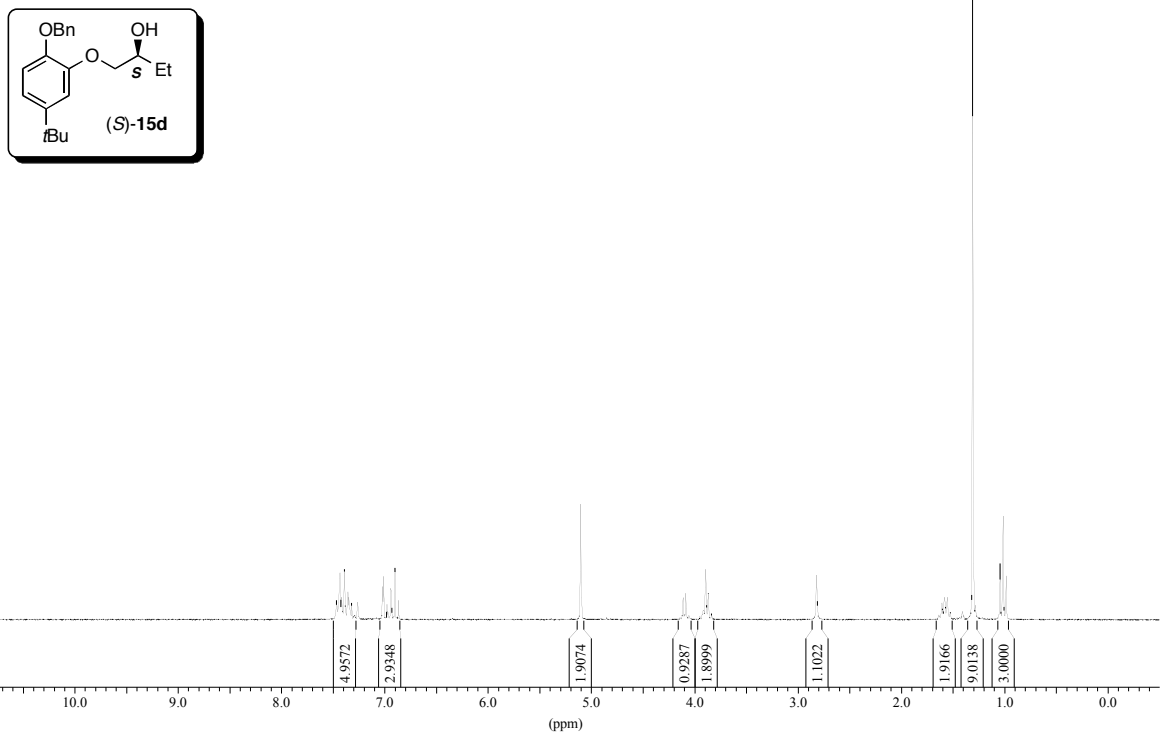
AM-B159 / DC151F.104 cd-cl3 AC 250

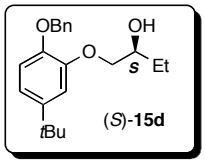


AM-B159 / DC152F.104 dc-cl3 AC 250



AM-B162 / JV120F.102 cd-cl3 AC 250

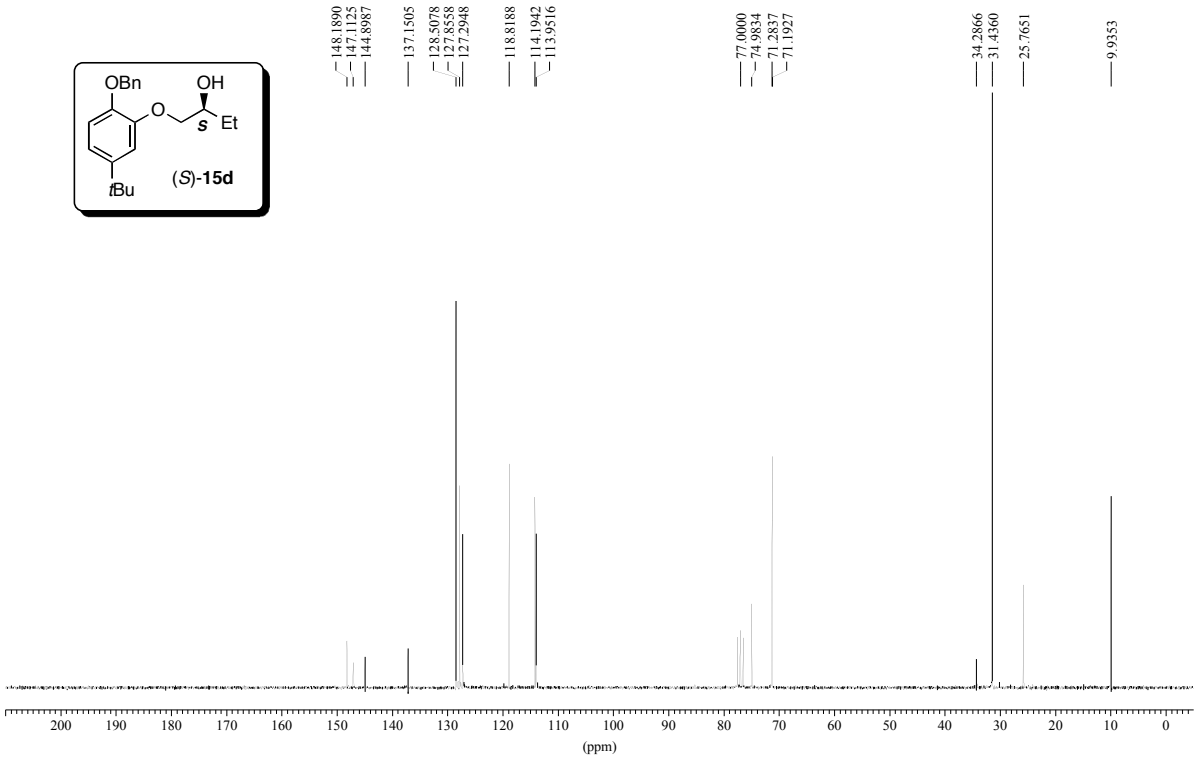




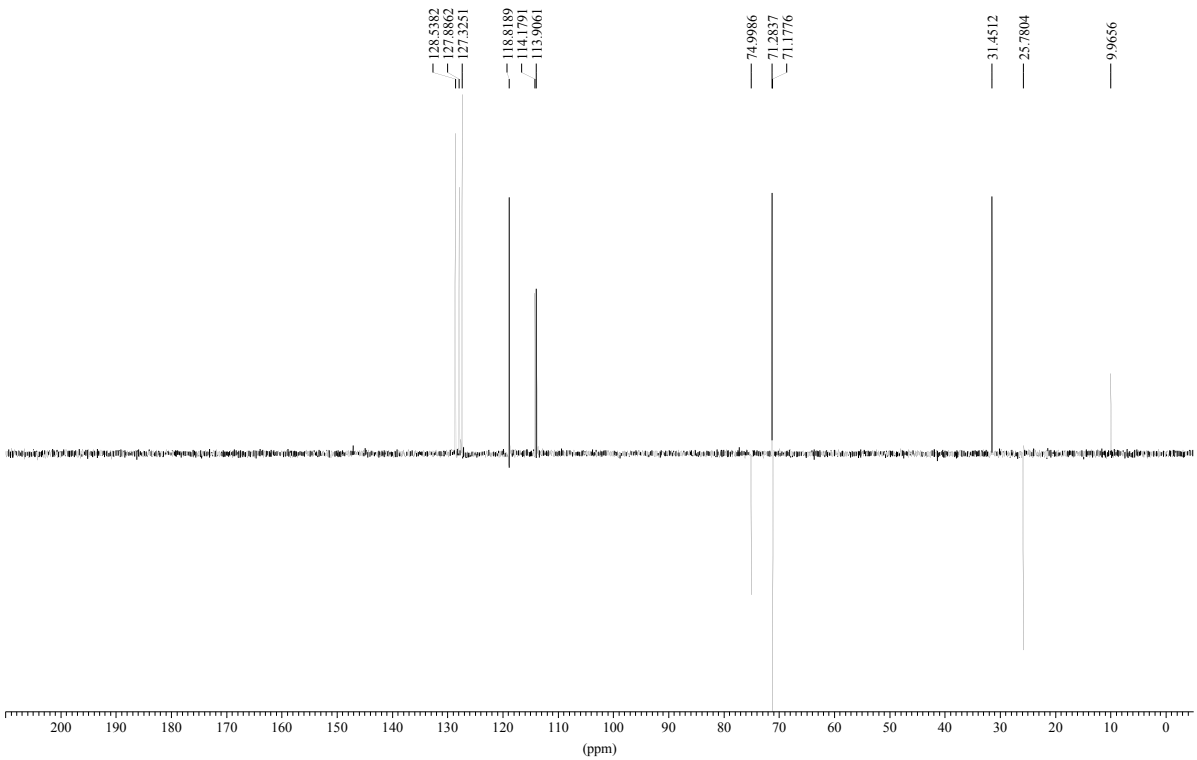
(*S*)-**15d**

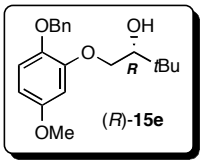
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6815	1867.43	7.4657	1052	2.9
2	6841	1859.49	7.4340	2560	7.0
3	6851	1856.44	7.4218	1075	2.9
4	6856	1854.92	7.4157	1213	3.3
5	6878	1848.20	7.3889	2766	7.5
6	6904	1840.27	7.3572	1501	4.1
7	6912	1837.83	7.3474	1216	3.3
8	6935	1830.81	7.3193	888	2.4
9	6982	1816.46	7.2620	939	2.6
10	7180	1756.04	7.0204	1804	4.9
11	7187	1753.90	7.0119	2361	6.4
12	7214	1745.66	6.9789	817	2.2
13	7221	1743.53	6.9704	427	1.2
14	7242	1737.12	6.9448	1696	4.6
15	7249	1734.98	6.9362	1539	4.2
16	7278	1726.13	6.9009	2831	7.7
17	7305	1717.89	6.8679	1046	2.8
18	8753	1276.00	5.1013	6366	17.3
19	9539	1036.13	4.1423	85	0.2
20	9564	1028.50	4.1118	1200	3.3
21	9575	1025.14	4.0984	287	0.8
22	9585	1022.09	4.0862	1440	3.9
23	9611	1014.16	4.0545	211	0.6
24	9697	987.91	3.9496	153	0.4
25	9723	979.98	3.9178	478	1.3
26	9728	978.45	3.9117	506	1.4
27	9743	973.87	3.8934	2758	7.5
28	9765	967.16	3.8666	1441	3.9
29	9791	959.23	3.8349	316	0.9
30	10624	705.01	2.8186	2433	6.6
31	11593	409.30	1.6363	240	0.7
32	11617	401.97	1.6070	889	2.4
33	11640	394.96	1.5790	1217	3.3
34	11660	388.85	1.5546	1223	3.3
35	11685	381.22	1.5241	389	1.1
36	11862	327.21	1.3081	36727	100.0
37	12079	260.98	1.0434	3074	8.4
38	12103	253.66	1.0141	5699	15.5
39	12128	246.03	0.9836	2398	6.5

AM-B162 / JV121F.102 cd-cl3 AC 250



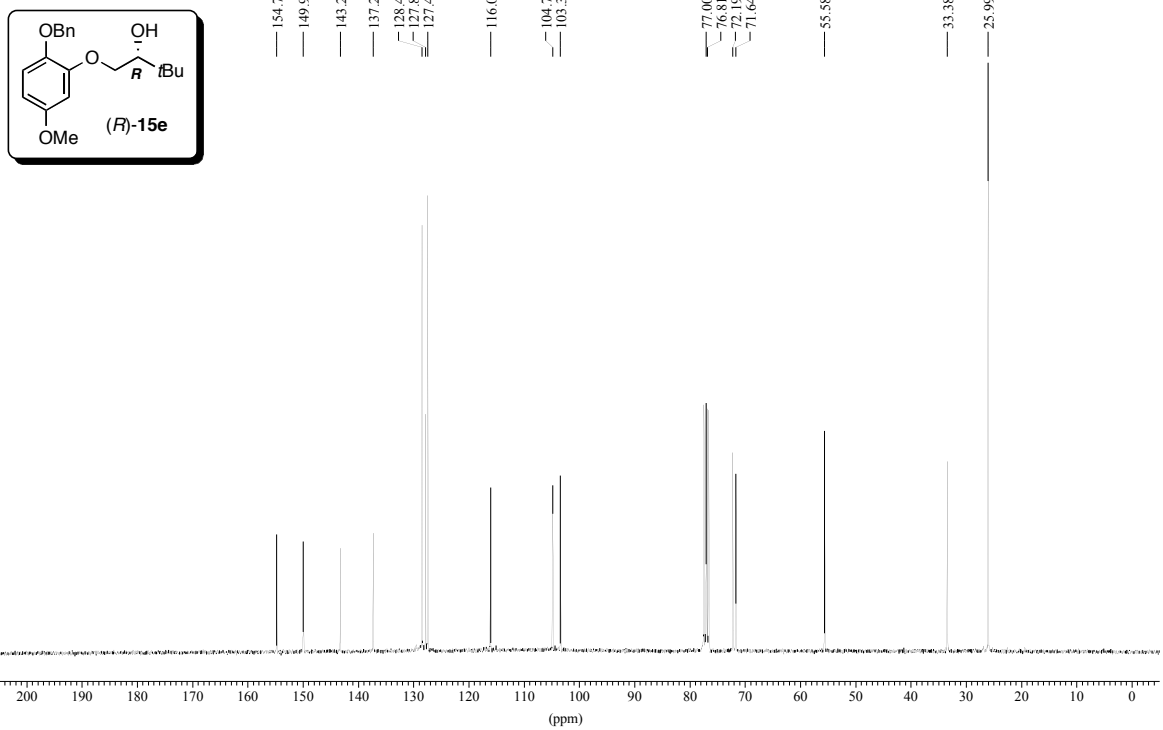
AM-B162 / JV122F.102 cd-cl3 AC 250



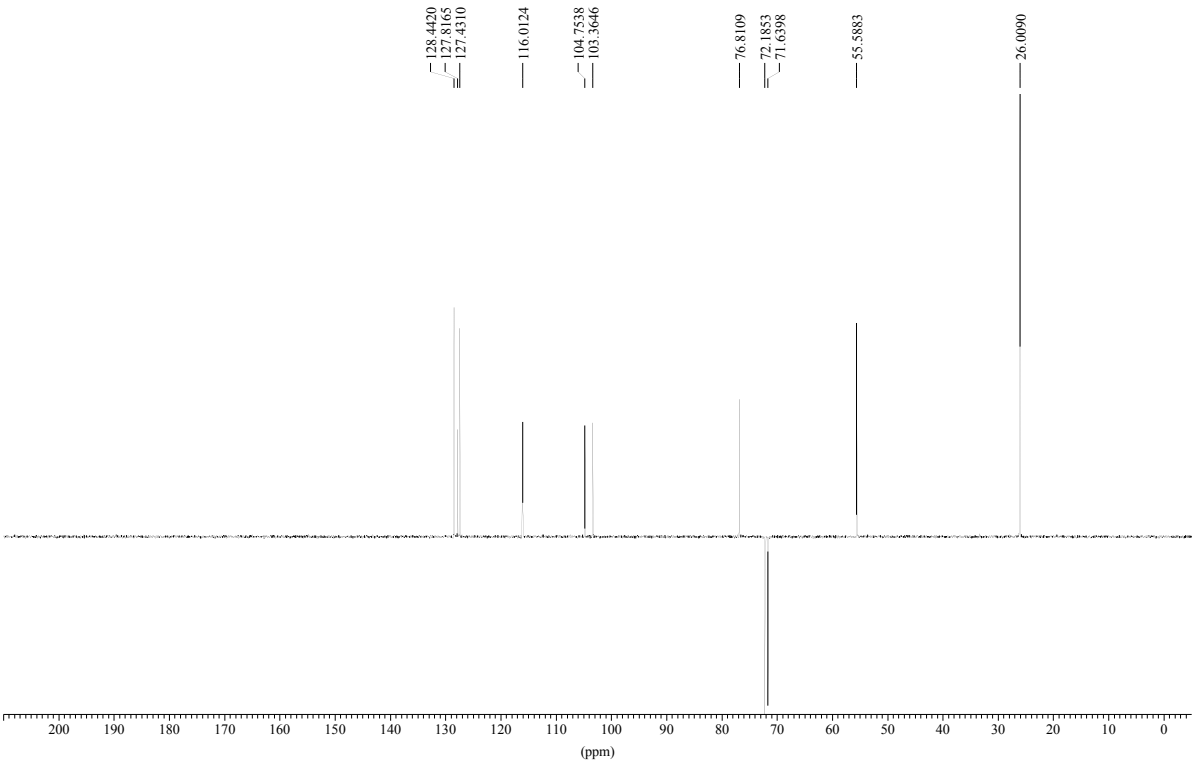


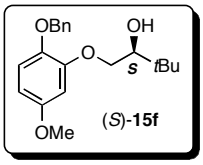
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9816	2233.80	7.4428	43165	4.0
2	9834	2227.02	7.4202	94859	8.8
3	9836	2226.26	7.4177	95638	8.9
4	9849	2221.36	7.4013	39889	3.7
5	9852	2220.23	7.3976	46004	4.3
6	9869	2213.83	7.3762	97547	9.1
7	9890	2205.92	7.3499	51598	4.8
8	9897	2203.28	7.3411	28384	2.6
9	9902	2201.40	7.3348	41979	3.9
10	9920	2194.61	7.3122	37447	3.5
11	9960	2179.54	7.2620	23891	2.2
12	10267	2063.88	6.8766	78738	7.3
13	10290	2055.21	6.8477	88326	8.2
14	10506	1973.83	6.5766	78256	7.3
15	10514	1970.82	6.5665	88244	8.2
16	10612	1933.90	6.4435	48171	4.5
17	10619	1931.26	6.4347	42056	3.9
18	10635	1925.23	6.4147	43392	4.0
19	10643	1922.22	6.4046	37335	3.5
20	11720	1516.45	5.0526	249553	23.2
21	12402	1259.50	4.1965	37059	3.5
22	12408	1257.23	4.1890	37773	3.5
23	12427	1250.08	4.1651	45389	4.2
24	12433	1247.82	4.1576	45462	4.2
25	12632	1172.84	3.9078	39290	3.7
26	12656	1163.80	3.8776	75550	7.0
27	12681	1154.38	3.8463	43081	4.0
28	12747	1129.51	3.7634	459578	42.8
29	12799	1109.92	3.6981	47014	4.4
30	12806	1107.28	3.6893	46305	4.3
31	12824	1100.50	3.6668	35195	3.3
32	12830	1098.24	3.6592	34488	3.2
33	13517	839.41	2.7968	51920	4.8
34	14956	297.25	0.9904	1073488	100.0

AM-B168 / 06020621.2-1 cd-cl3 DPX 300



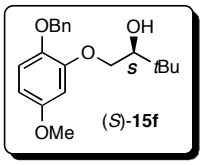
AM-B168 / 06020621.3-1 cd-cl3 DPX 300



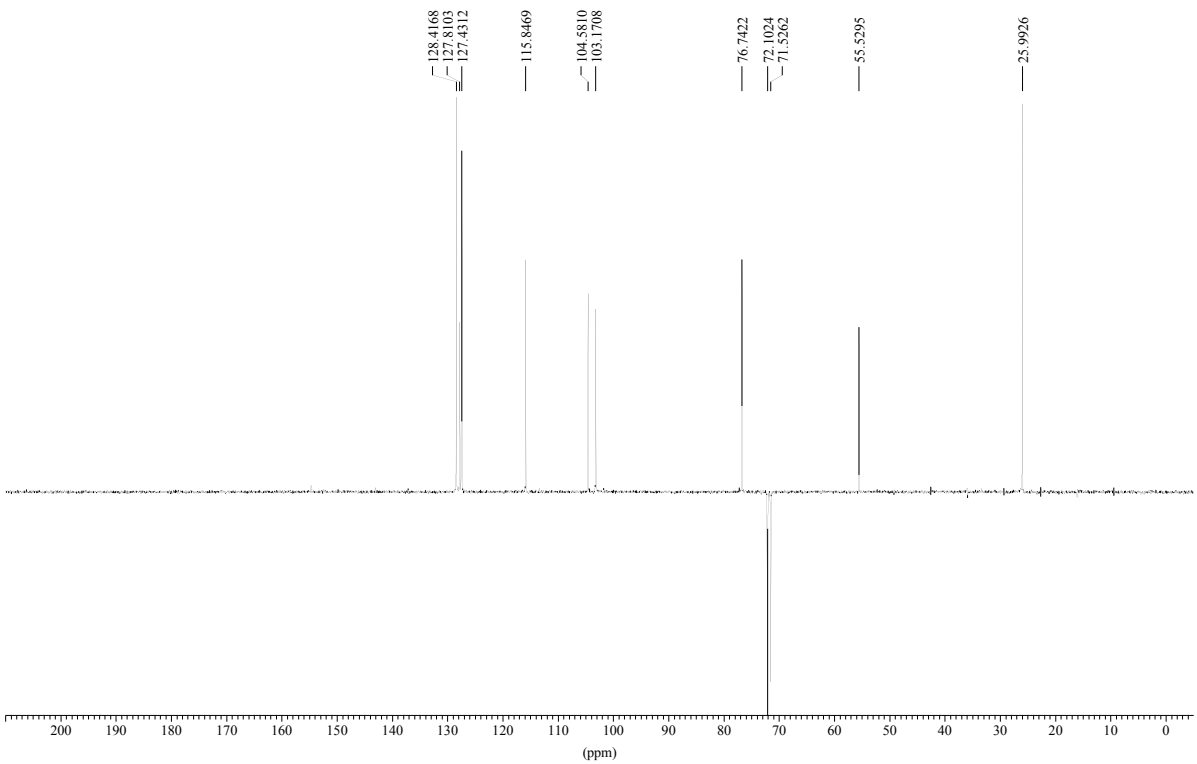


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6821	1865.29	7.4572	409	2.4
2	6827	1863.46	7.4499	538	3.2
3	6848	1857.05	7.4243	1133	6.7
4	6853	1855.53	7.4182	1244	7.4
5	6859	1853.70	7.4108	726	4.3
6	6865	1851.87	7.4035	668	4.0
7	6886	1845.46	7.3779	1312	7.8
8	6892	1843.63	7.3706	461	2.7
9	6910	1838.13	7.3486	916	5.4
10	6917	1836.00	7.3401	699	4.1
11	6938	1829.59	7.3145	401	2.4
12	6981	1816.46	7.2620	204	1.2
13	7293	1721.25	6.8813	1012	6.0
14	7322	1712.40	6.8460	1135	6.7
15	7540	1645.87	6.5800	1049	6.2
16	7549	1643.12	6.5690	1158	6.9
17	7649	1612.61	6.4470	650	3.8
18	7658	1609.86	6.4360	575	3.4
19	7677	1604.06	6.4128	558	3.3
20	7687	1601.01	6.4006	486	2.9
21	8793	1263.49	5.0513	3096	18.3
22	9490	1050.78	4.2009	457	2.7
23	9498	1048.34	4.1911	471	2.8
24	9520	1041.62	4.1643	571	3.4
25	9528	1039.18	4.1545	563	3.3
26	9722	979.98	3.9178	468	2.8
27	9753	970.52	3.8800	967	5.7
28	9783	961.36	3.8434	558	3.3
29	9848	941.53	3.7641	6899	40.8
30	9896	926.88	3.7055	616	3.6
31	9904	924.44	3.6958	602	3.6
32	9926	917.72	3.6689	442	2.6
33	9934	915.28	3.6592	395	2.3
34	10642	699.22	2.7954	158	0.9
35	12116	249.39	0.9970	16894	100.0

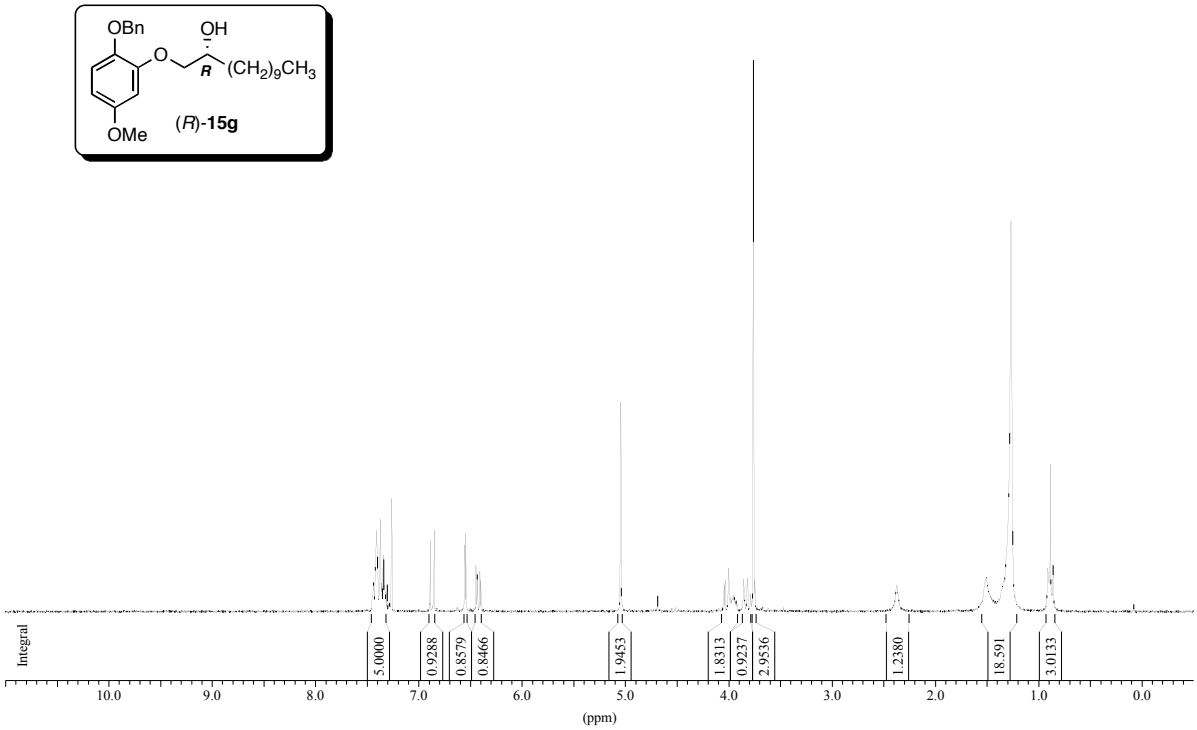
AM-B146 / SP081F.104 cd-cl3 AC 250

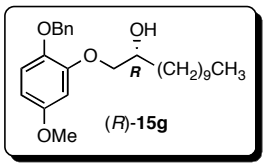


AM-B146 / SP082F.104 cd-cl3 AC 250



AM-B 114 / AR270F.101 cd-cl3 AC 250

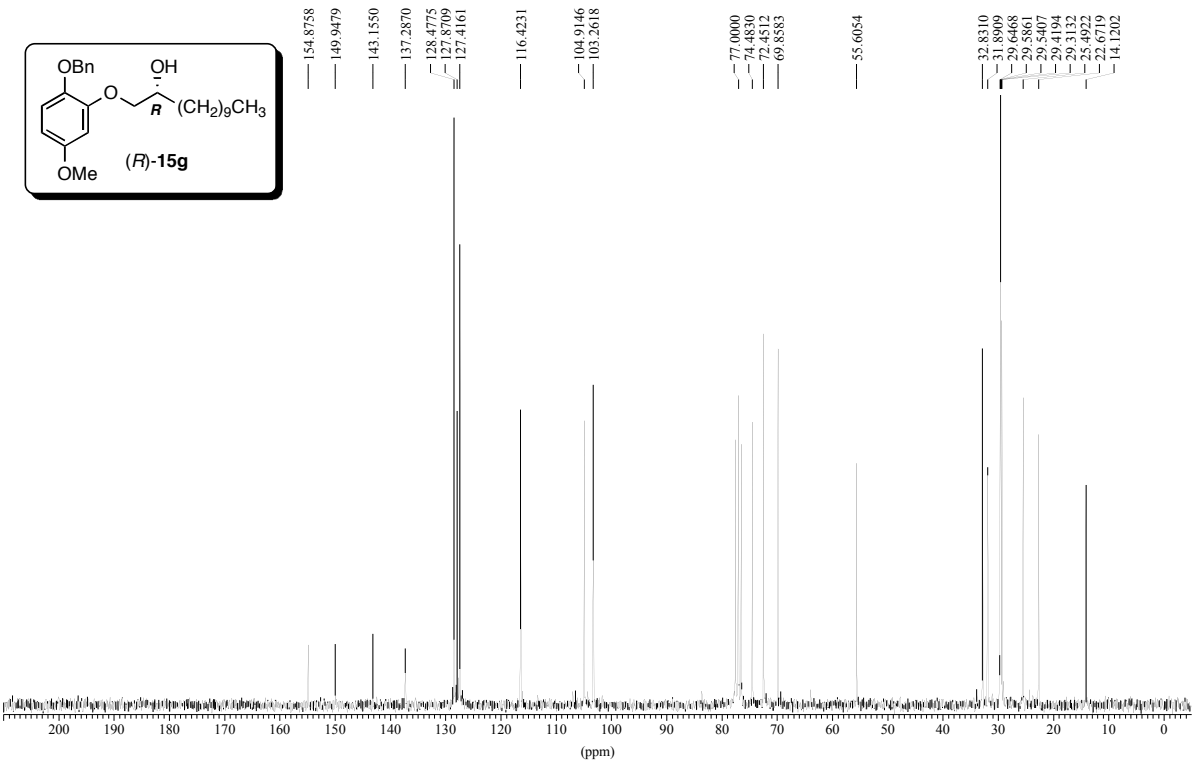




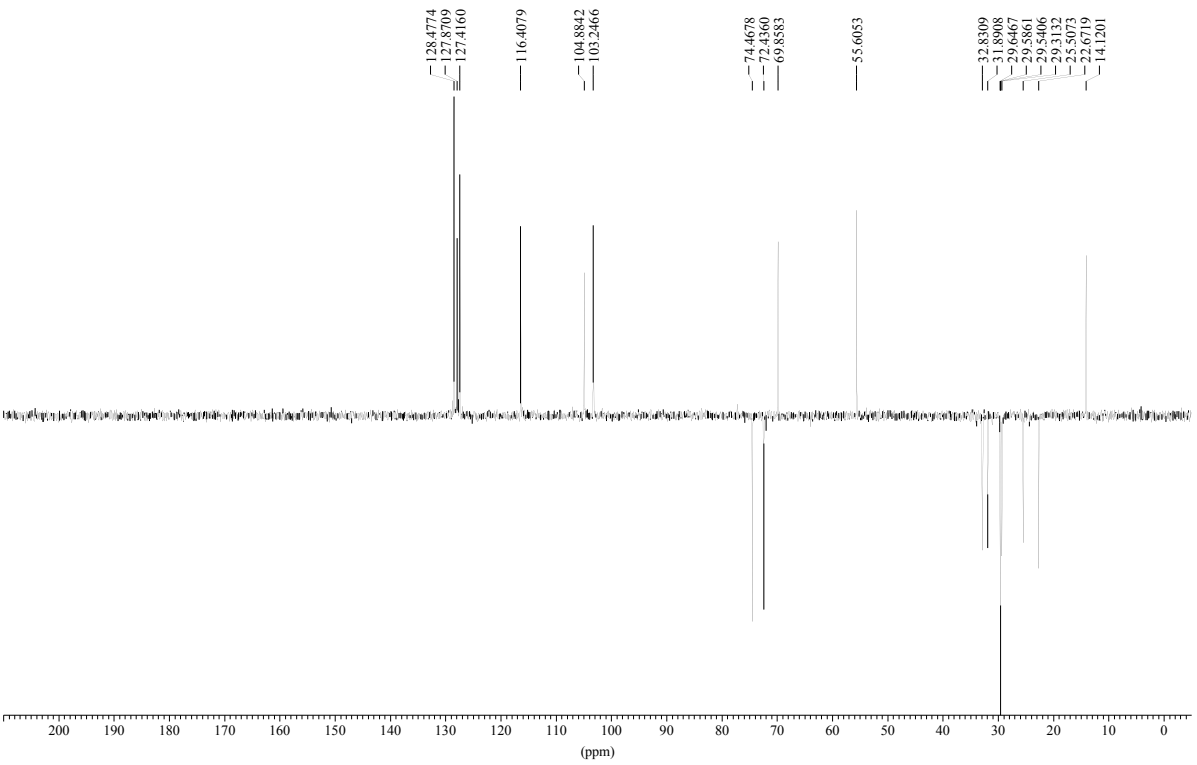
(*R*)-**15g**

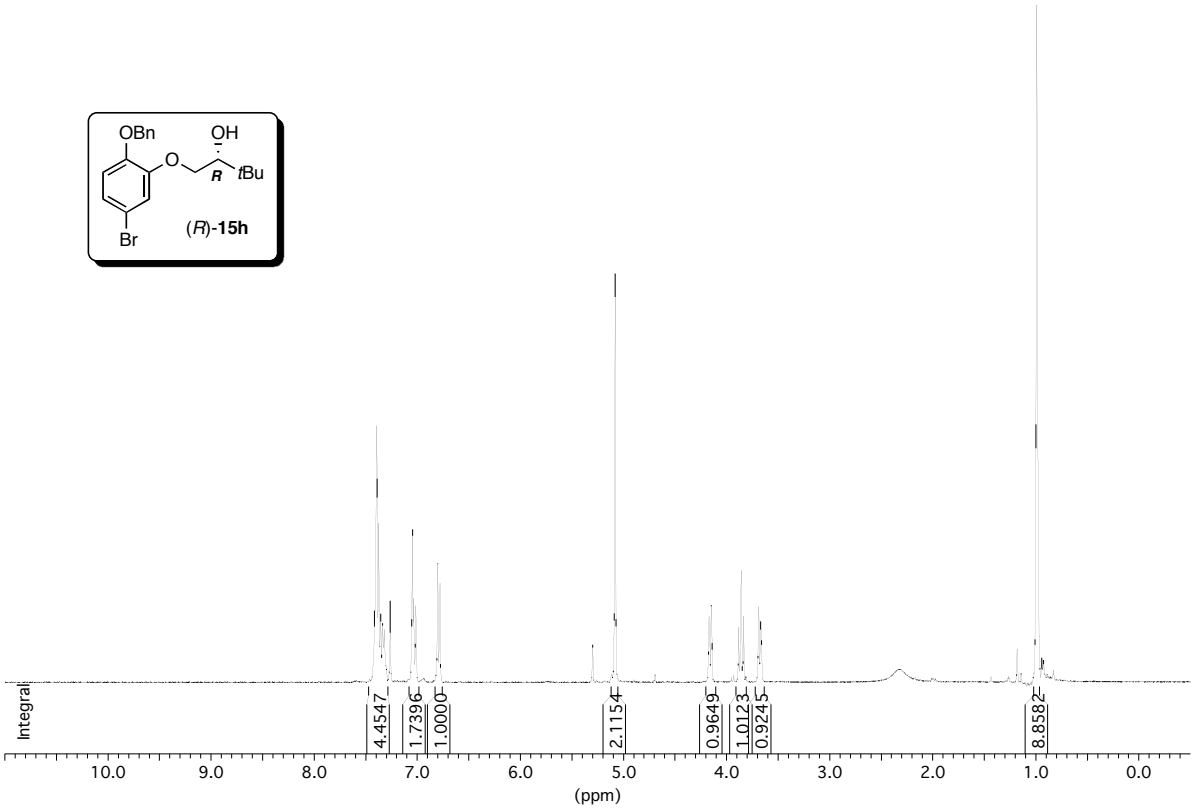
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6827	1862.55	7.4462	539	3.5
2	6833	1860.72	7.4389	784	5.1
3	6854	1854.31	7.4133	1851	12.1
4	6859	1852.78	7.4072	2220	14.5
5	6868	1850.03	7.3962	1492	9.8
6	6876	1847.59	7.3864	425	2.8
7	6889	1843.63	7.3706	2547	16.7
8	6895	1841.79	7.3633	836	5.5
9	6899	1840.57	7.3584	765	5.0
10	6907	1838.13	7.3486	847	5.5
11	6913	1836.30	7.3413	1541	10.1
12	6920	1834.17	7.3328	1224	8.0
13	6926	1832.33	7.3254	610	4.0
14	6930	1831.11	7.3206	455	3.0
15	6942	1827.45	7.3059	723	4.7
16	6978	1816.46	7.2620	3108	20.3
17	7286	1722.47	6.8862	1955	12.8
18	7315	1713.62	6.8508	2240	14.6
19	7558	1639.46	6.5544	1829	12.0
20	7567	1636.72	6.5434	2148	14.0
21	7648	1612.00	6.4446	1268	8.3
22	7658	1608.95	6.4324	1006	6.6
23	7677	1603.15	6.4092	1101	7.2
24	7686	1600.40	6.3982	836	5.5
25	8796	1261.66	5.0439	5803	37.9
26	9616	1011.41	4.0435	710	4.6
27	9625	1008.66	4.0325	869	5.7
28	9645	1002.56	4.0081	522	3.4
29	9653	1000.12	3.9984	1193	7.8
30	9664	996.76	3.9849	360	2.4
31	9672	994.32	3.9752	287	1.9
32	9687	989.74	3.9569	441	2.9
33	9697	986.69	3.9447	382	2.5
34	9711	982.42	3.9276	279	1.8
35	9772	963.80	3.8532	887	5.8
36	9797	956.17	3.8227	841	5.5
37	9801	954.95	3.8178	897	5.9
38	9826	947.32	3.7873	465	3.0
39	9849	940.31	3.7592	15294	100.0
40	10985	593.63	2.3732	709	4.6
41	11697	376.34	1.5046	925	6.0
42	11892	316.83	1.2667	10833	70.8
43	12184	227.72	0.9104	1175	7.7
44	12204	221.62	0.8860	4073	26.6
45	12227	214.60	0.8579	1263	8.3

AMB114 / FV241F.102 cd-cl3 AC 250

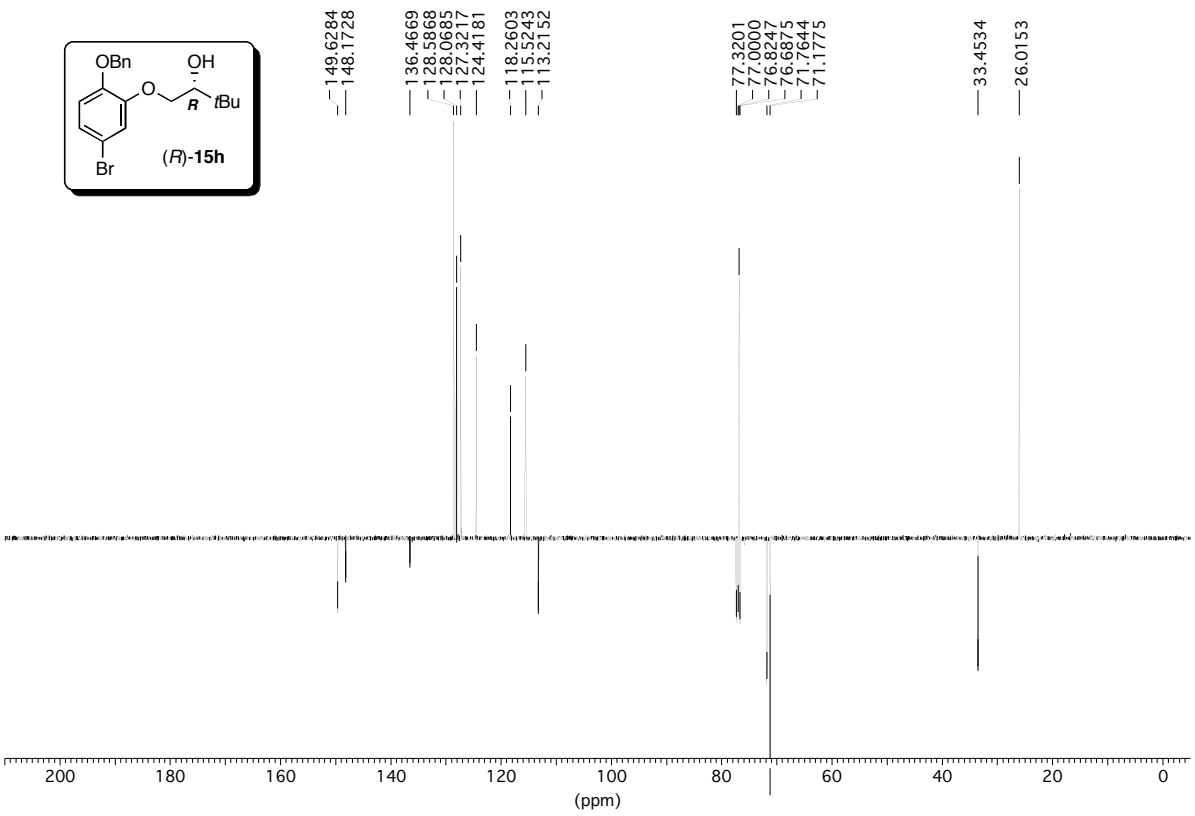


AMB114 / FV242F.102 cd-cl3 AC 250

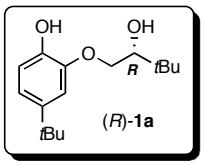




Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	11766	2965.47	7.4113	8261	3.6
2	11802	2957.80	7.3921	29711	12.8
3	11839	2949.91	7.3724	18404	7.9
4	11875	2942.24	7.3532	7893	3.4
5	11910	2934.78	7.3346	6787	2.9
6	11942	2927.96	7.3175	6078	2.6
7	12050	2904.94	7.2600	9424	4.1
8	12446	2820.55	7.0491	13851	6.0
9	12455	2818.63	7.0443	17682	7.6
10	12472	2815.01	7.0352	9677	4.2
11	12513	2806.27	7.0134	8852	3.8
12	12523	2804.14	7.0081	6957	3.0
13	12914	2720.82	6.7998	13711	5.9
14	12954	2712.29	6.7785	11450	4.9
15	16146	2032.04	5.0784	47381	20.4
16	17852	1668.47	4.1698	7563	3.3
17	17862	1666.34	4.1645	7402	3.2
18	17895	1659.31	4.1469	8898	3.8
19	17906	1656.96	4.1411	8241	3.5
20	18398	1552.11	3.8790	6356	2.7
21	18442	1542.73	3.8556	12962	5.6
22	18485	1533.57	3.8327	7644	3.3
23	18756	1475.82	3.6883	8722	3.7
24	18766	1473.69	3.6830	8332	3.6
25	18798	1466.87	3.6660	7007	3.0
26	21325	928.33	2.3201	1469	0.6
27	23829	394.70	0.9864	232613	100.0

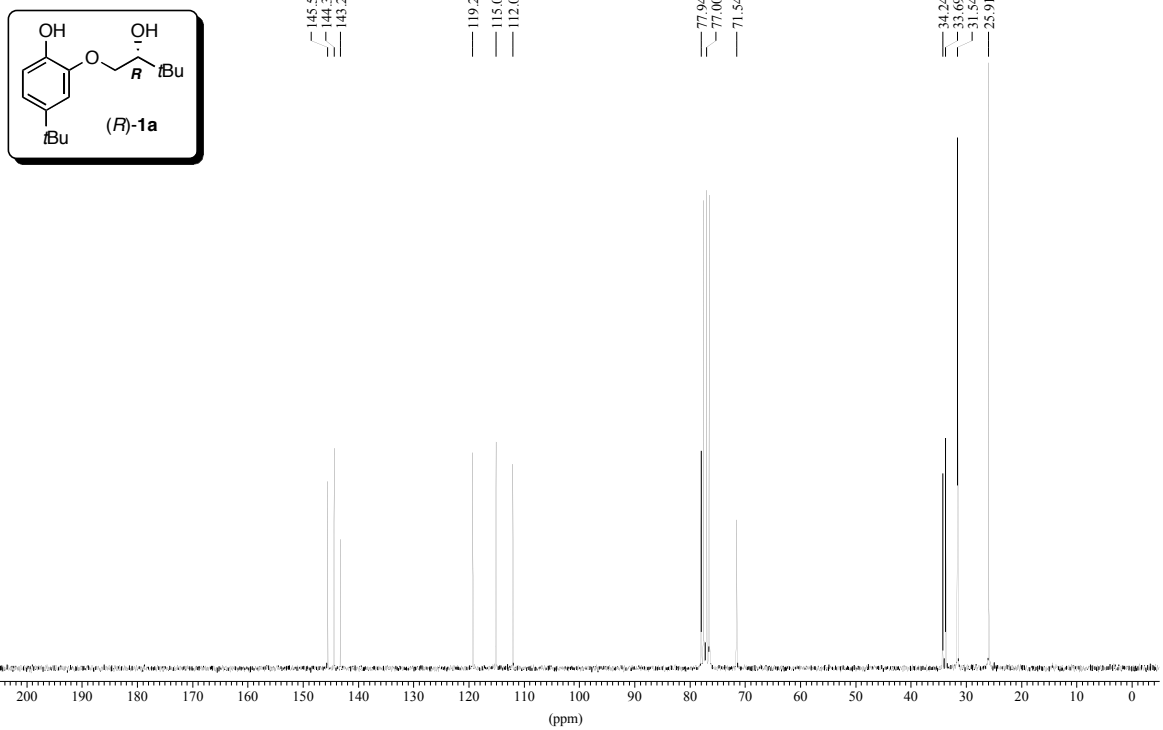

OBn
OH
O
R
tBu
Br
(R)-15h
149.6284
148.1728
136.4669
128.5868
128.0685
127.3217
124.4181
118.2603
115.5243
113.2152
77.3201
77.0000
76.8247
76.6875
71.7644
71.1775
33.4534
26.0153
200
180
160
140
120
100
80
60
40
20
0
(ppm)

AM-B170 / FV090F.103 cd-cl3 AC 250

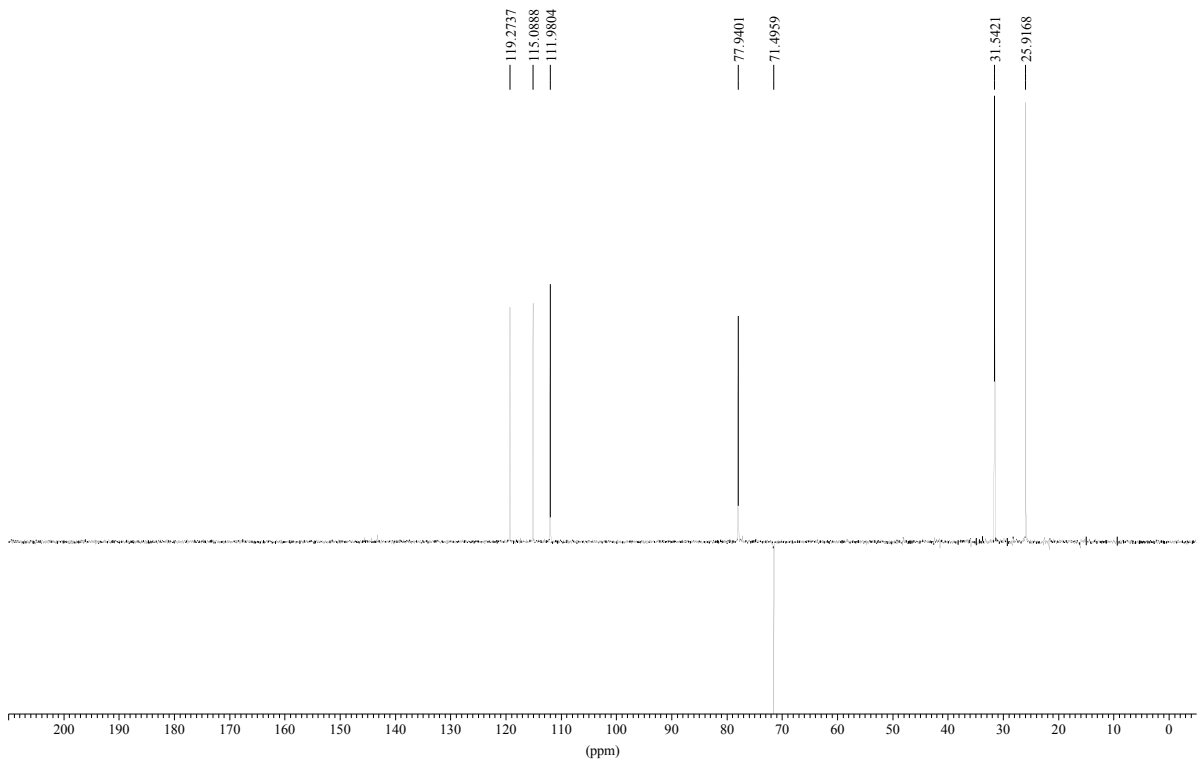


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6979	1816.46	7.2620	1109	2.1
2	7237	1737.73	6.9472	525	1.0
3	7244	1735.59	6.9387	858	1.6
4	7270	1727.66	6.9070	7626	14.6
5	7286	1722.78	6.8874	2971	5.7
6	7315	1713.93	6.8521	895	1.7
7	9451	1062.07	4.2460	1073	2.1
8	9458	1059.93	4.2375	1162	2.2
9	9484	1052.00	4.2058	1365	2.6
10	9490	1050.17	4.1984	1385	2.7
11	9720	979.98	3.9178	1049	2.0
12	9752	970.21	3.8788	2088	4.0
13	9783	960.75	3.8410	1333	2.6
14	9871	933.90	3.7336	1509	2.9
15	9878	931.76	3.7251	1537	2.9
16	9901	924.74	3.6970	1039	2.0
17	9908	922.60	3.6885	960	1.8
18	11872	323.24	1.2923	52214	100.0
19	12121	247.25	0.9885	40194	77.0

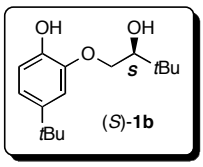
AM-B170 / FV091F.103 cd-cl3 AC 250



AM-B170 / FV092F.103 cd-cl3 AC 250

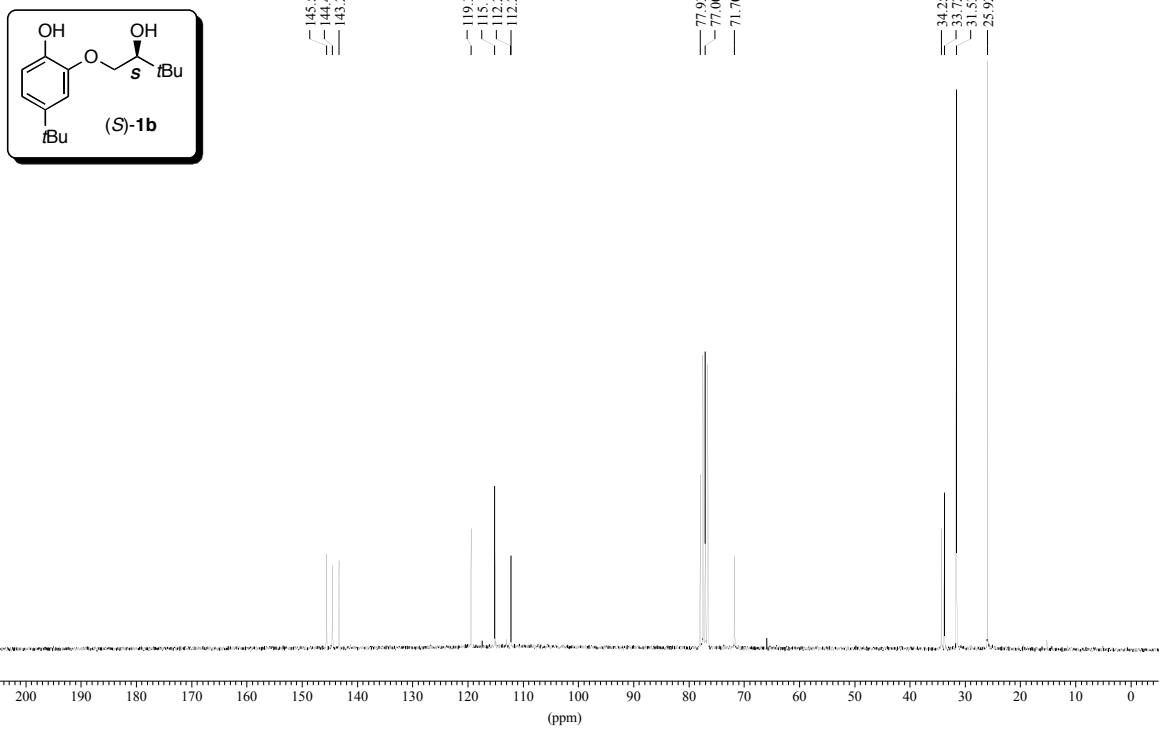


AM-B150 / 16090521.1-1 cd-cl3 DPX 300

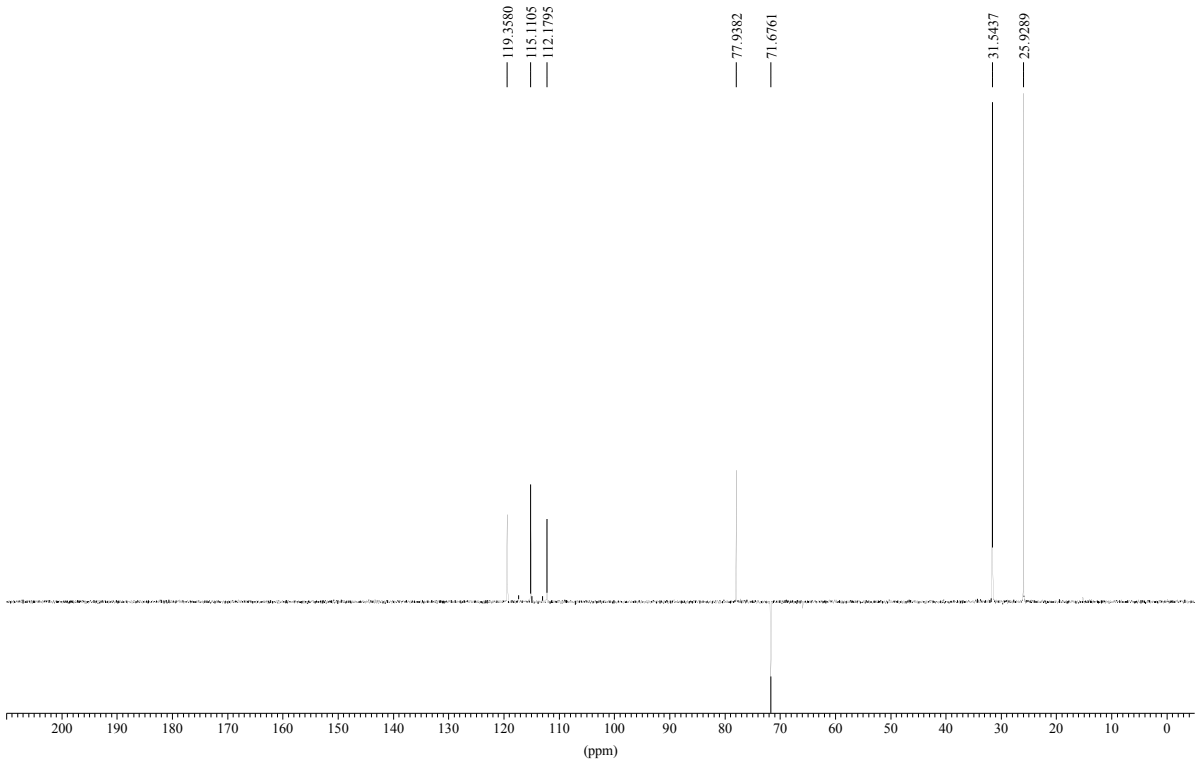


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9959	2179.54	7.2620	16623	1.8
2	10216	2082.72	6.9394	24219	2.6
3	10235	2075.56	6.9155	167337	17.7
4	10259	2066.52	6.8854	67816	7.2
5	10282	2057.85	6.8565	24832	2.6
6	12362	1274.19	4.2455	27803	2.9
7	12386	1265.15	4.2153	33512	3.6
8	12625	1175.10	3.9153	25519	2.7
9	12651	1165.31	3.8827	48397	5.1
10	12676	1155.89	3.8513	31050	3.3
11	12770	1120.47	3.7333	35471	3.8
12	12775	1118.59	3.7270	38260	4.1
13	12794	1111.43	3.7032	26031	2.8
14	12799	1109.54	3.6969	25798	2.7
15	14713	388.43	1.2942	943927	100.0
16	14953	298.00	0.9929	835644	88.5

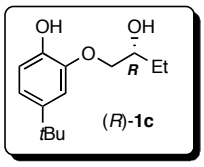
AM-B150 / 16090521.2-1 cd-cl3 DPX 300



AM-B150 / 16090521.3-1 cd-cl3 DPX 300

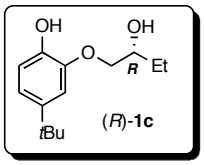


AM-B161 / JV120F.101 cd-cl3 AC 250

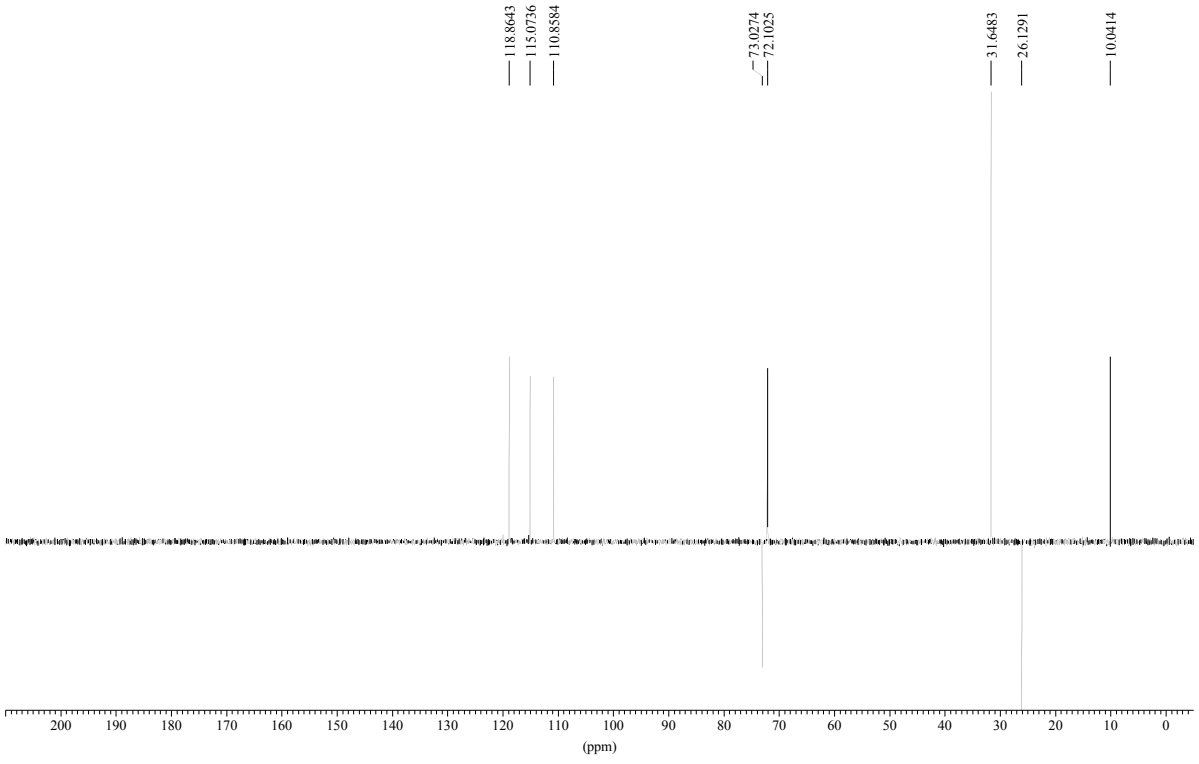


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6982	1816.46	7.2620	854	2.2
2	7262	1731.01	6.9204	289	0.8
3	7266	1729.79	6.9155	309	0.8
4	7295	1720.94	6.8801	3288	8.5
5	7302	1718.81	6.8716	6235	16.2
6	7330	1710.26	6.8374	444	1.2
7	8759	1274.17	5.0940	259	0.7
8	9596	1018.73	4.0728	613	1.6
9	9603	1016.60	4.0642	826	2.1
10	9633	1007.44	4.0276	1185	3.1
11	9651	1001.95	4.0057	262	0.7
12	9672	995.54	3.9800	610	1.6
13	9694	988.83	3.9532	729	1.9
14	9701	986.69	3.9447	666	1.7
15	9720	980.89	3.9215	432	1.1
16	9735	976.31	3.9032	1278	3.3
17	9764	967.46	3.8678	996	2.6
18	9788	960.14	3.8385	468	1.2
19	11555	420.89	1.6827	296	0.8
20	11579	413.57	1.6534	1206	3.1
21	11603	406.25	1.6241	1720	4.5
22	11625	399.53	1.5973	1293	3.4
23	11649	392.21	1.5680	411	1.1
24	11680	382.75	1.5302	149	0.4
25	11883	320.80	1.2825	38484	100.0
26	12085	259.15	1.0361	2652	6.9
27	12109	251.83	1.0068	5019	13.0
28	12134	244.20	0.9763	2204	5.7

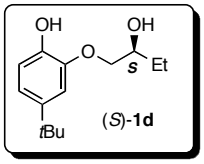
AM-B161 / JV121F.101 cd-cl3 AC 250



AM-B161 / JV122F.101 cd-cl3 AC 250



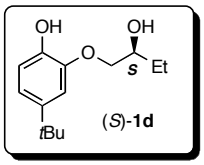
AM-B165 / JV260F.102 cd-cl3 AC 250



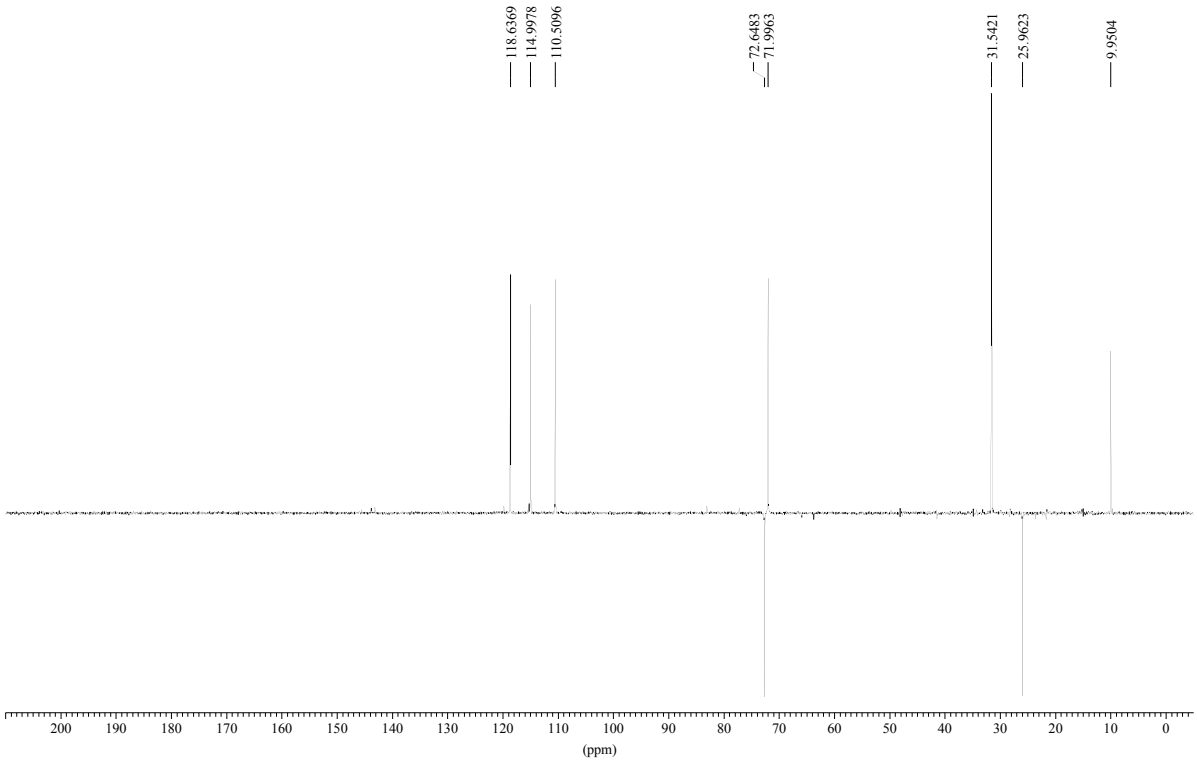
(*S*)-**1d**

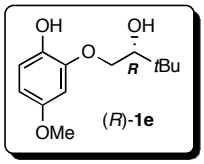
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6980	1816.46	7.2620	712	1.6
2	7298	1719.42	6.8740	6345	14.0
3	7311	1715.45	6.8582	2853	6.3
4	7314	1714.54	6.8545	2804	6.2
5	9600	1016.90	4.0655	757	1.7
6	9607	1014.77	4.0569	942	2.1
7	9630	1007.75	4.0289	1058	2.3
8	9637	1005.61	4.0203	1331	2.9
9	9652	1001.04	4.0020	363	0.8
10	9674	994.32	3.9752	722	1.6
11	9697	987.30	3.9471	895	2.0
12	9703	985.47	3.9398	794	1.8
13	9718	980.89	3.9215	484	1.1
14	9723	979.37	3.9154	485	1.1
15	9741	973.87	3.8934	1405	3.1
16	9766	966.25	3.8629	876	1.9
17	9771	964.72	3.8568	1113	2.5
18	9795	957.40	3.8275	571	1.3
19	11555	420.29	1.6802	344	0.8
20	11579	412.96	1.6510	1242	2.7
21	11601	406.25	1.6241	1749	3.9
22	11624	399.23	1.5961	1486	3.3
23	11648	391.90	1.5668	496	1.1
24	11880	321.10	1.2837	45304	100.0
25	12092	256.41	1.0251	3118	6.9
26	12116	249.08	0.9958	6105	13.5
27	12141	241.45	0.9653	2566	5.7

AM-B165/ JV261F.102 cd-cl3 AC 250



AM-B165/ JV262F.102 cd-cl3 AC 250

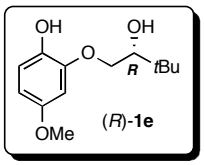




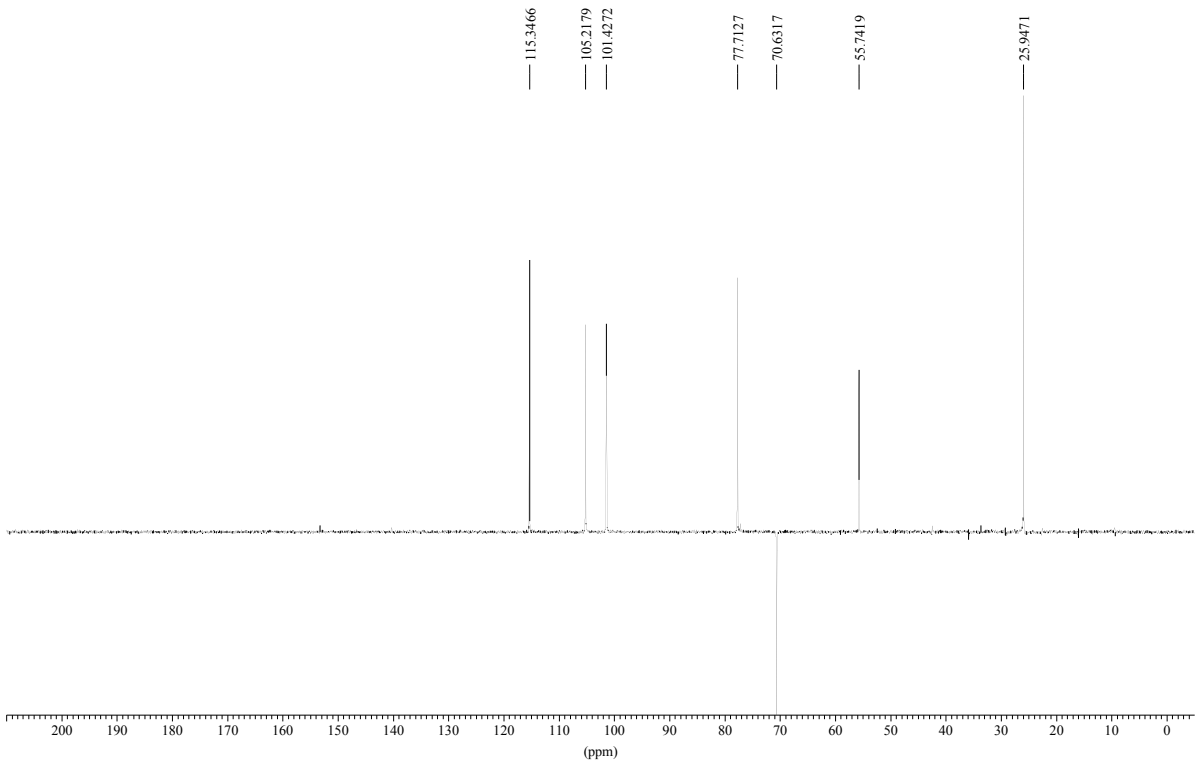
(*R*)-**1e**

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6981	1816.46	7.2620	1170	2.7
2	7126	1772.21	7.0851	915	2.1
3	7323	1712.09	6.8447	2560	6.0
4	7351	1703.55	6.8106	3029	7.1
5	7665	1607.72	6.4275	1982	4.6
6	7674	1604.98	6.4165	3611	8.5
7	7682	1602.54	6.4067	2591	6.1
8	7691	1599.79	6.3958	954	2.2
9	7710	1593.99	6.3726	1682	3.9
10	7719	1591.25	6.3616	1117	2.6
11	9539	1035.83	4.1411	1087	2.5
12	9545	1033.99	4.1338	1128	2.6
13	9570	1026.36	4.1033	1432	3.4
14	9577	1024.23	4.0947	1375	3.2
15	9769	965.63	3.8605	989	2.3
16	9800	956.17	3.8227	2133	5.0
17	9832	946.41	3.7836	1355	3.2
18	9876	932.98	3.7299	18950	44.4
19	9901	925.35	3.6994	1414	3.3
20	9906	923.83	3.6933	1358	3.2
21	9931	916.20	3.6628	846	2.0
22	9937	914.37	3.6555	790	1.9
23	10093	866.76	3.4652	557	1.3
24	12139	242.37	0.9690	42642	100.0

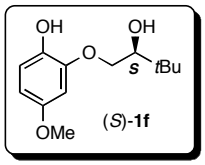
AM-B171 / MS231F.102 cd-cl3 AC 250



AM-B171 / MS232F.102 cd-cl3 AC 250

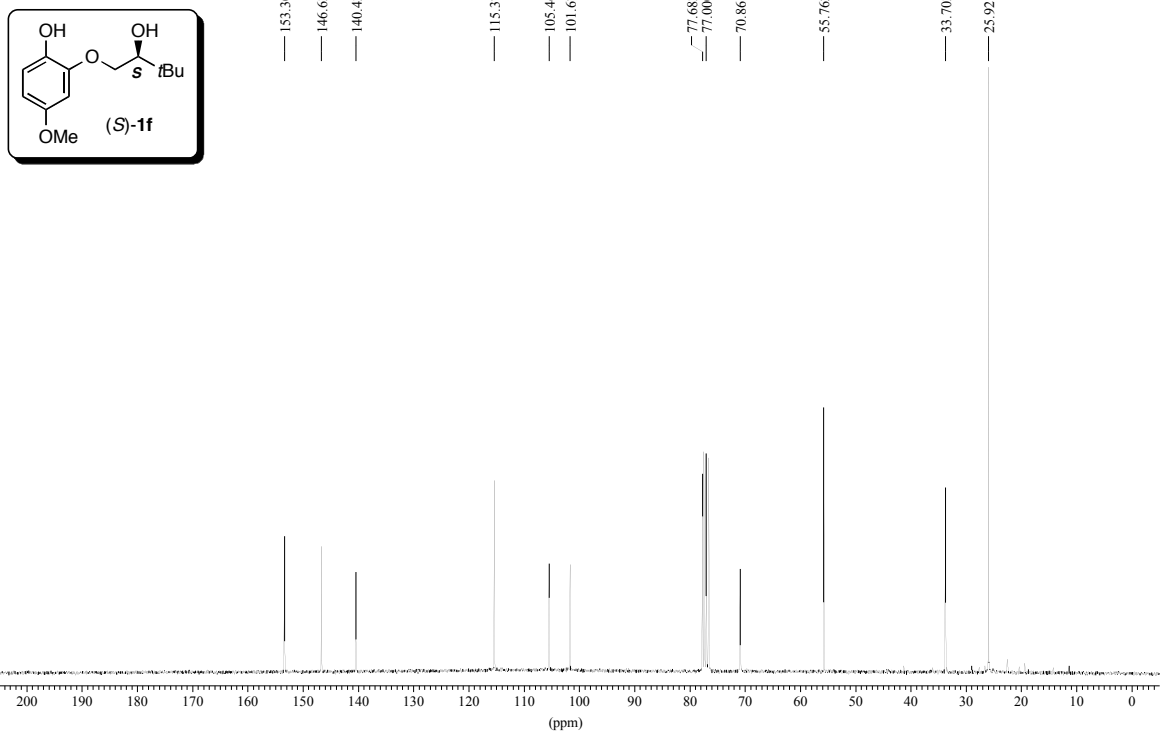


AM-B149 / 16090519.1-1 cd-cl3 DPX 300

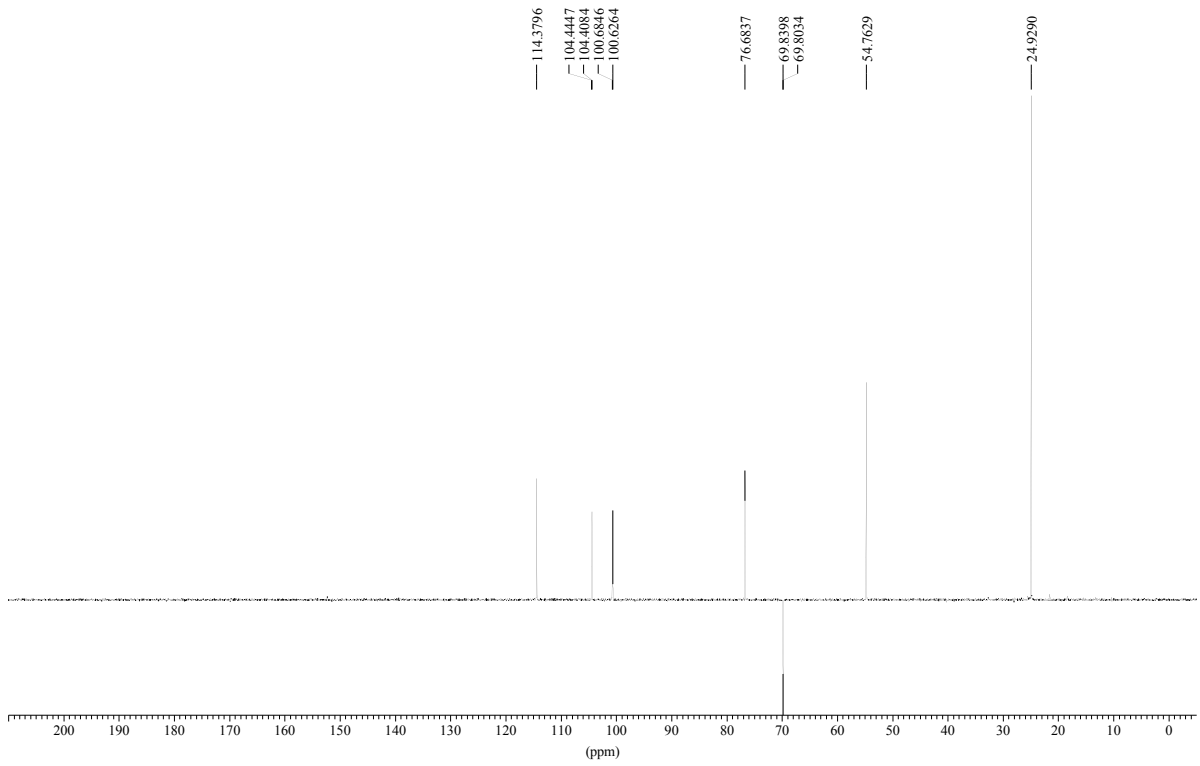


Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9959	2179.54	7.2620	17598	1.6
2	10292	2054.08	6.8440	72818	6.4
3	10314	2045.79	6.8164	84664	7.5
4	10611	1933.90	6.4435	74476	6.6
5	10616	1932.01	6.4373	74320	6.6
6	10634	1925.23	6.4147	54881	4.9
7	10642	1922.22	6.4046	39456	3.5
8	10657	1916.57	6.3858	47035	4.2
9	10665	1913.55	6.3757	39994	3.5
10	12437	1245.93	4.1513	39504	3.5
11	12463	1236.14	4.1187	49037	4.3
12	12668	1158.90	3.8613	33903	3.0
13	12693	1149.48	3.8299	69500	6.1
14	12718	1140.06	3.7986	42549	3.8
15	12770	1120.47	3.7333	496674	43.9
16	12796	1110.68	3.7006	55673	4.9
17	12818	1102.39	3.6730	37984	3.4
18	14969	291.98	0.9728	1130954	100.0

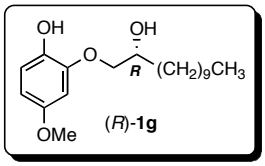
AM-B149 / 16090519.2-1 cd-cl3 DPX 300



AM-B149 / 06090519.3-1 cd-cl3 DPX 300



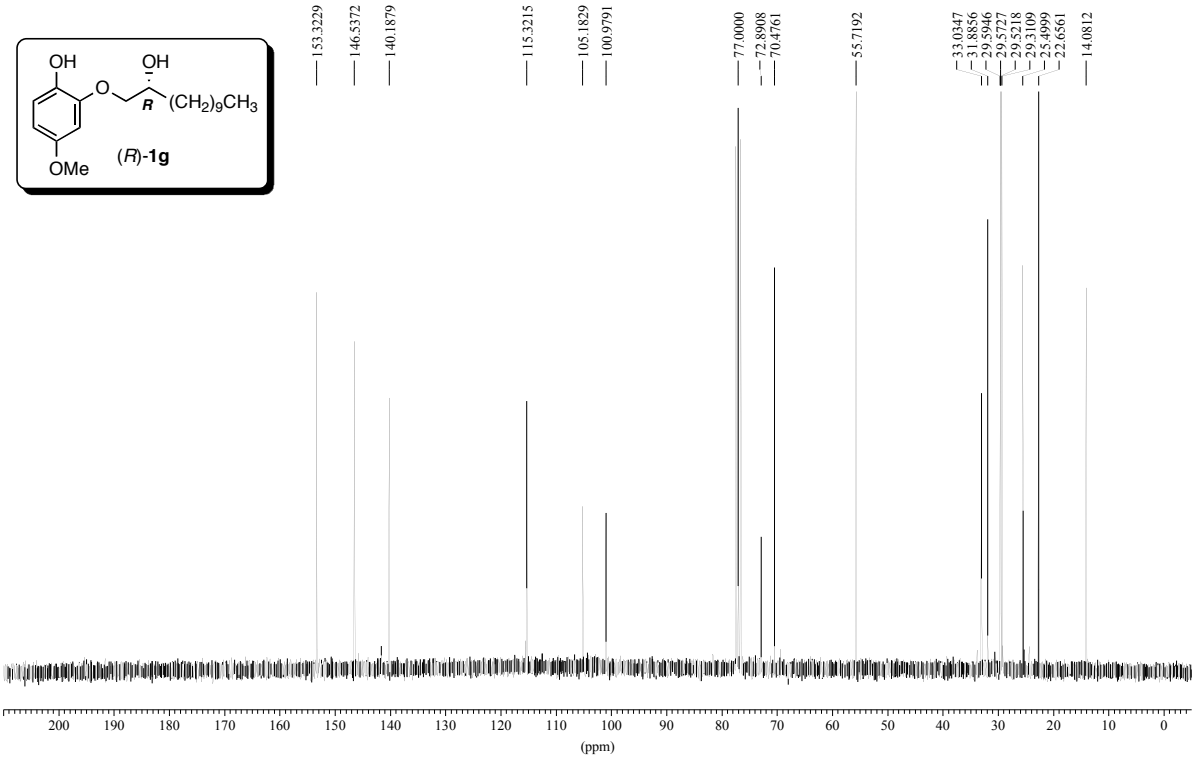
amb135 / 06060518-1 cd-cl3 DPX 300



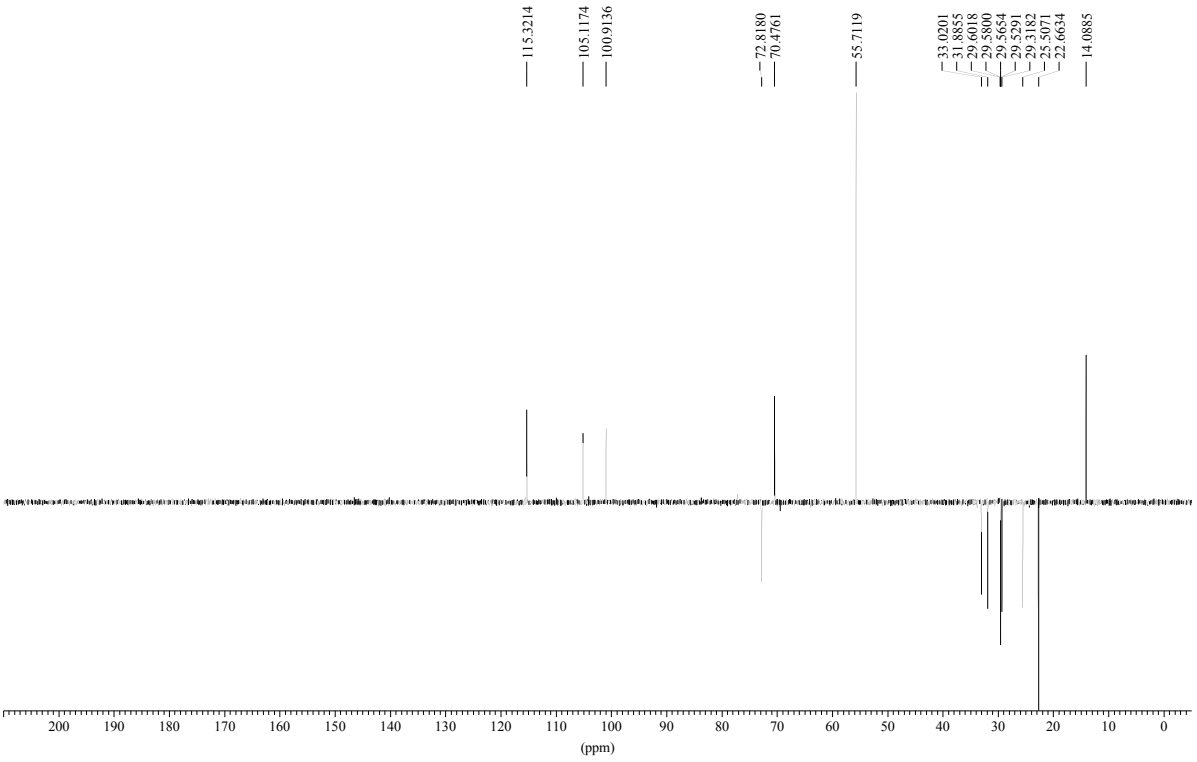
(*R*)-**1g**

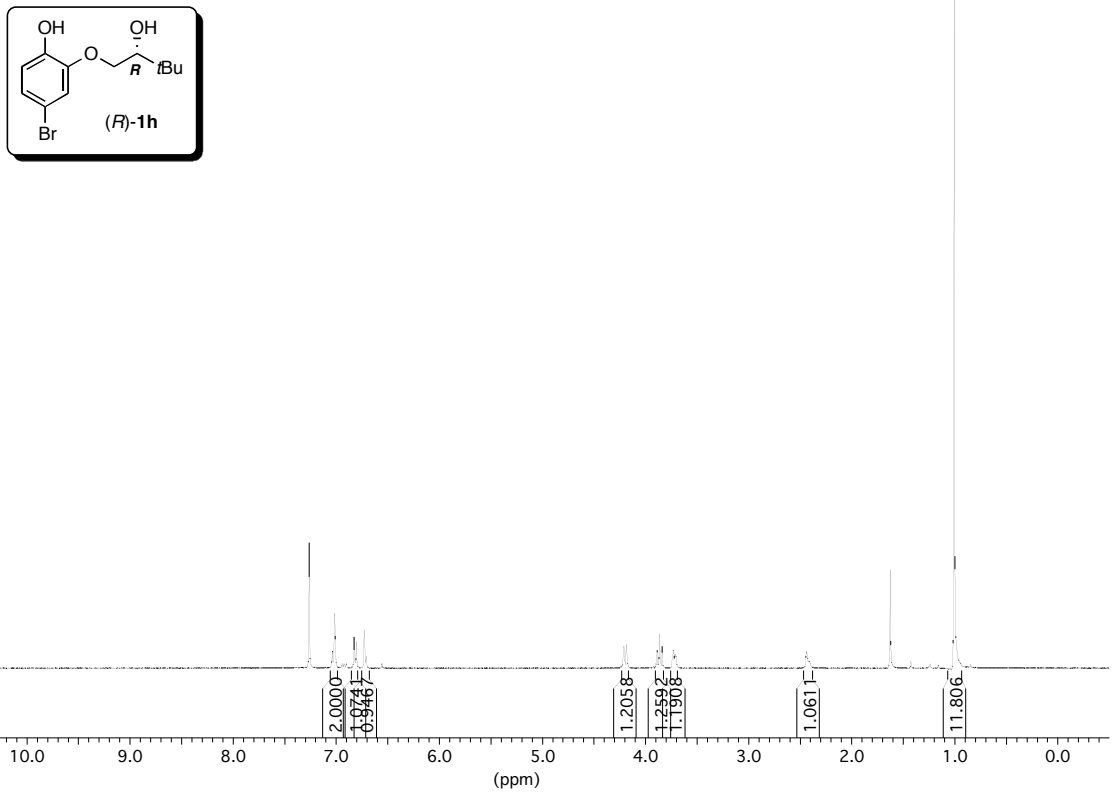
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9960	2179.54	7.2620	35511	7.6
2	10295	2053.33	6.8415	42939	9.2
3	10298	2052.20	6.8377	33819	7.2
4	10317	2045.04	6.8138	44488	9.5
5	10319	2044.29	6.8113	49079	10.5
6	10651	1919.20	6.3946	154726	33.1
7	10672	1911.29	6.3682	40284	8.6
8	10680	1908.28	6.3582	24964	5.3
9	12550	1203.73	4.0107	13639	2.9
10	12575	1194.32	3.9793	33751	7.2
11	12582	1191.68	3.9705	23218	5.0
12	12601	1184.52	3.9467	31840	6.8
13	12608	1181.88	3.9379	23353	5.0
14	12716	1141.19	3.8023	25094	5.4
15	12737	1133.28	3.7760	24754	5.3
16	12742	1131.40	3.7697	23818	5.1
17	12762	1123.86	3.7446	16504	3.5
18	12777	1118.21	3.7258	398840	85.4
19	14505	467.17	1.5566	18042	3.9
20	14530	457.75	1.5252	18080	3.9
21	14743	377.50	1.2578	467008	100.0
22	15023	272.01	0.9063	47818	10.2
23	15040	265.60	0.8850	153675	32.9
24	15058	258.82	0.8624	52651	11.3

amb135 / 06060518-2 cd-cl3 DPX 300

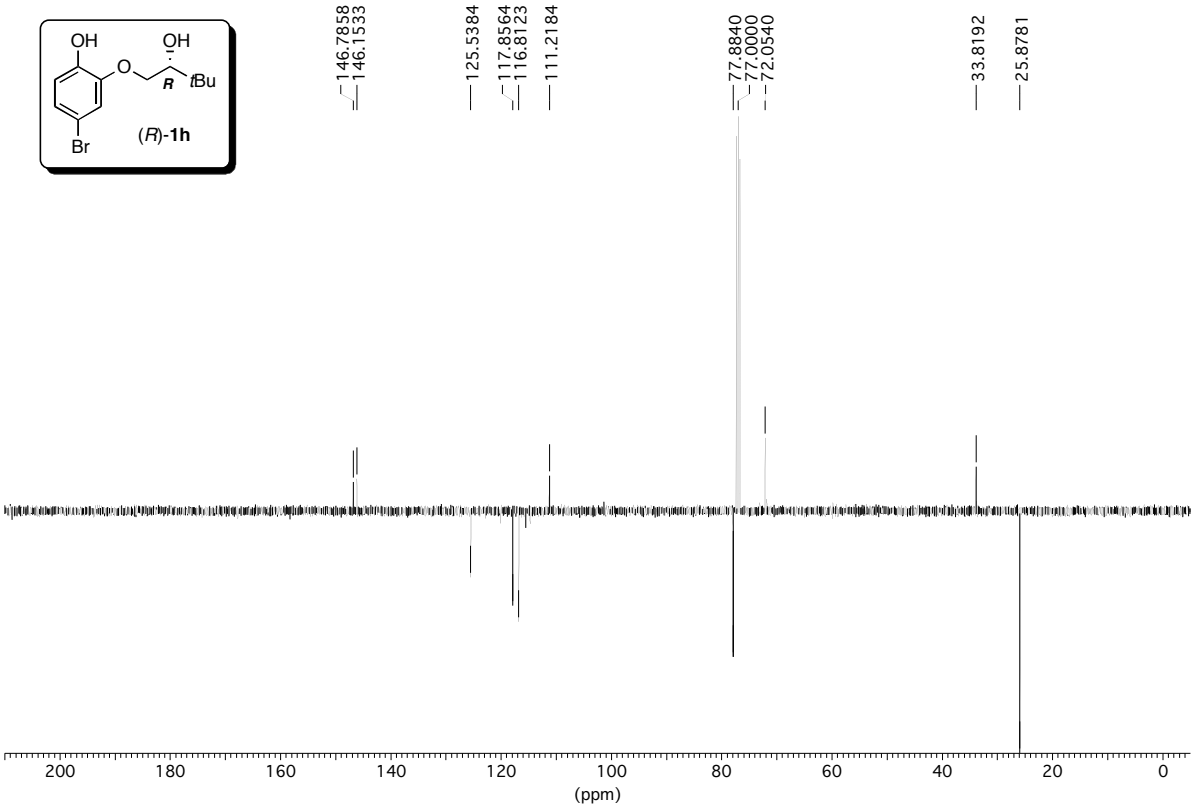


amb135 / 06060518-3 cd-cl3 DPX 300

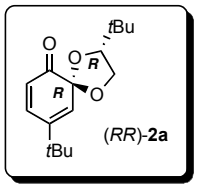




Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	12056	2904.94	7.2600	132507	18.4
2	12480	2814.58	7.0342	17777	2.5
3	12521	2805.85	7.0123	57877	8.1
4	12876	2730.19	6.8233	33160	4.6
5	12914	2722.09	6.8030	28037	3.9
6	13060	2690.98	6.7253	40406	5.6
7	17784	1684.24	4.2092	23445	3.3
8	17793	1682.32	4.2044	18415	2.6
9	17831	1674.22	4.1842	25339	3.5
10	17840	1672.31	4.1794	20611	2.9
11	18393	1554.46	3.8849	18552	2.6
12	18437	1545.08	3.8614	36418	5.1
13	18483	1535.28	3.8369	22883	3.2
14	18685	1492.23	3.7294	18850	2.6
15	18727	1483.28	3.7070	14520	2.0
16	21105	976.50	2.4405	16568	2.3
17	21119	973.51	2.4330	16954	2.4
18	23804	401.31	1.0029	718324	100.0

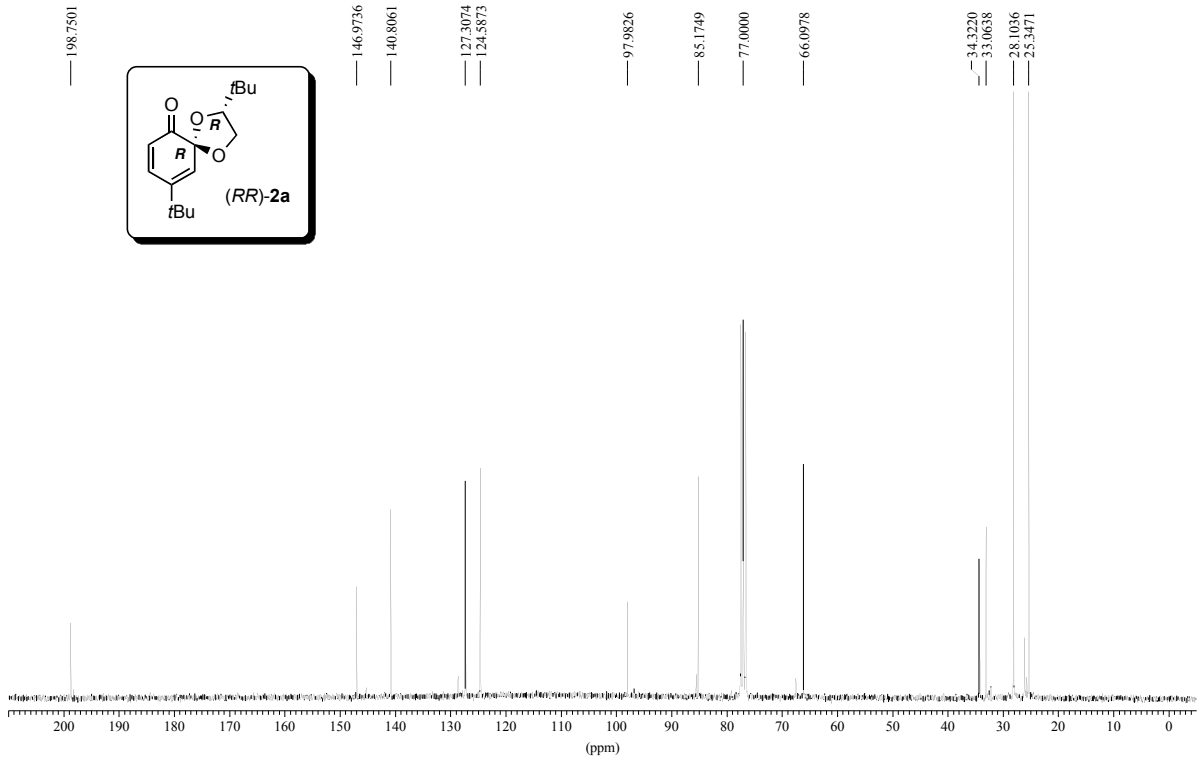

OH
OH
O
R
tBu
Br
(R)-1h
146.7858
146.1533
125.5384
117.8564
116.8123
111.2184
77.8840
77.0000
72.0540
33.8192
25.8781
200
180
160
140
120
100
80
60
40
20
0
(ppm)

AM-B172 / 13020615.1-1 cd-cl3 DPX 300

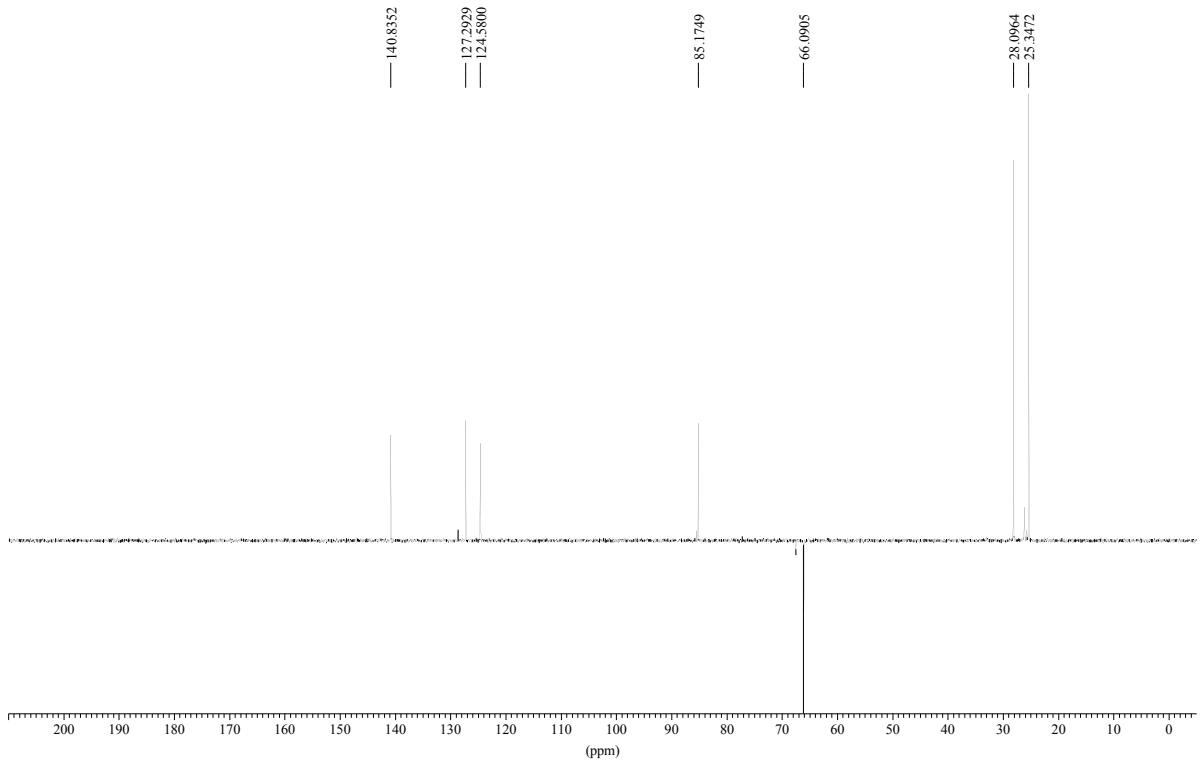


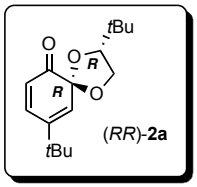
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9960	2179.54	7.2620	26286	2.6
2	10167	2101.55	7.0021	34545	3.4
3	10173	2099.29	6.9946	34632	3.5
4	10194	2091.38	6.9683	36841	3.7
5	10200	2089.12	6.9607	36395	3.6
6	10995	1789.60	5.9627	64566	6.4
7	11023	1779.05	5.9276	59713	6.0
8	11123	1741.37	5.8021	65578	6.5
9	11129	1739.11	5.7945	65225	6.5
10	12228	1325.05	4.4149	26527	2.6
11	12246	1318.27	4.3923	40839	4.1
12	12263	1311.87	4.3710	39344	3.9
13	12342	1282.10	4.2718	37883	3.8
14	12362	1274.57	4.2467	65947	6.6
15	12382	1267.03	4.2216	31064	3.1
16	12655	1164.18	3.8789	36789	3.7
17	12672	1157.77	3.8576	41568	4.1
18	12691	1150.61	3.8337	30764	3.1
19	14836	342.46	1.1410	1003426	100.0
20	15005	278.79	0.9289	943838	94.1

AM-B172 / 13020615.2-1 cd-cl3 DPX 300



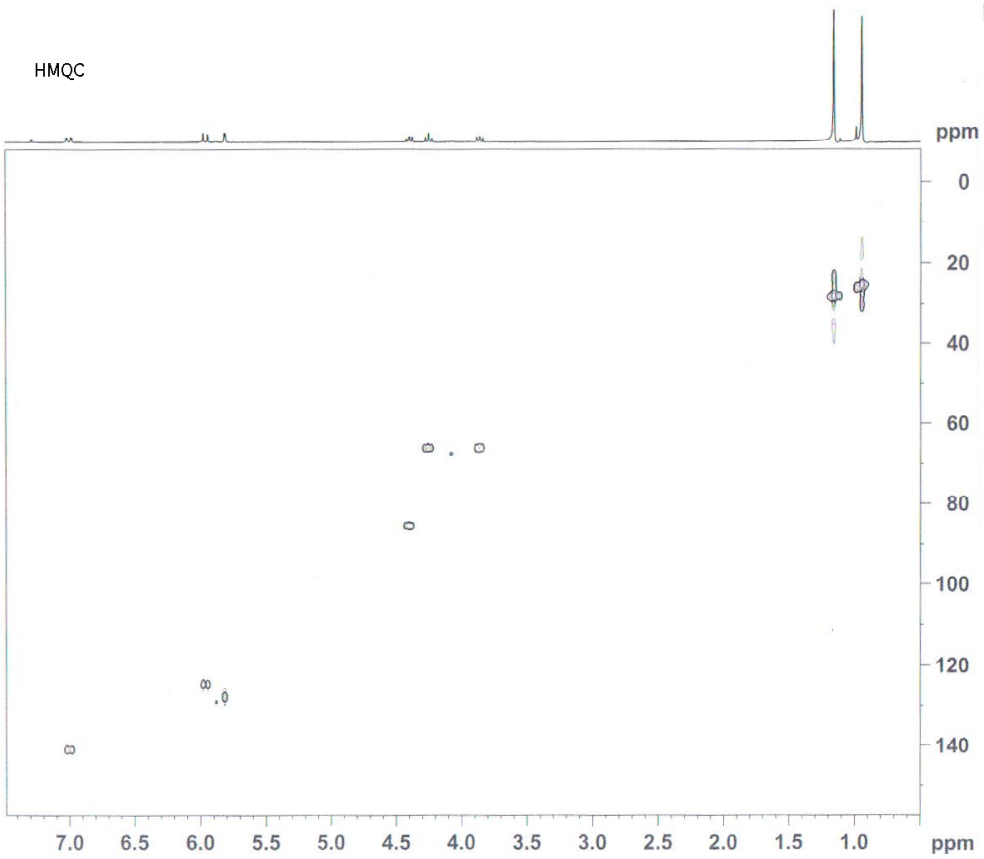
AM-B172 / 13020615.3-1 cd-cl3 DPX 300



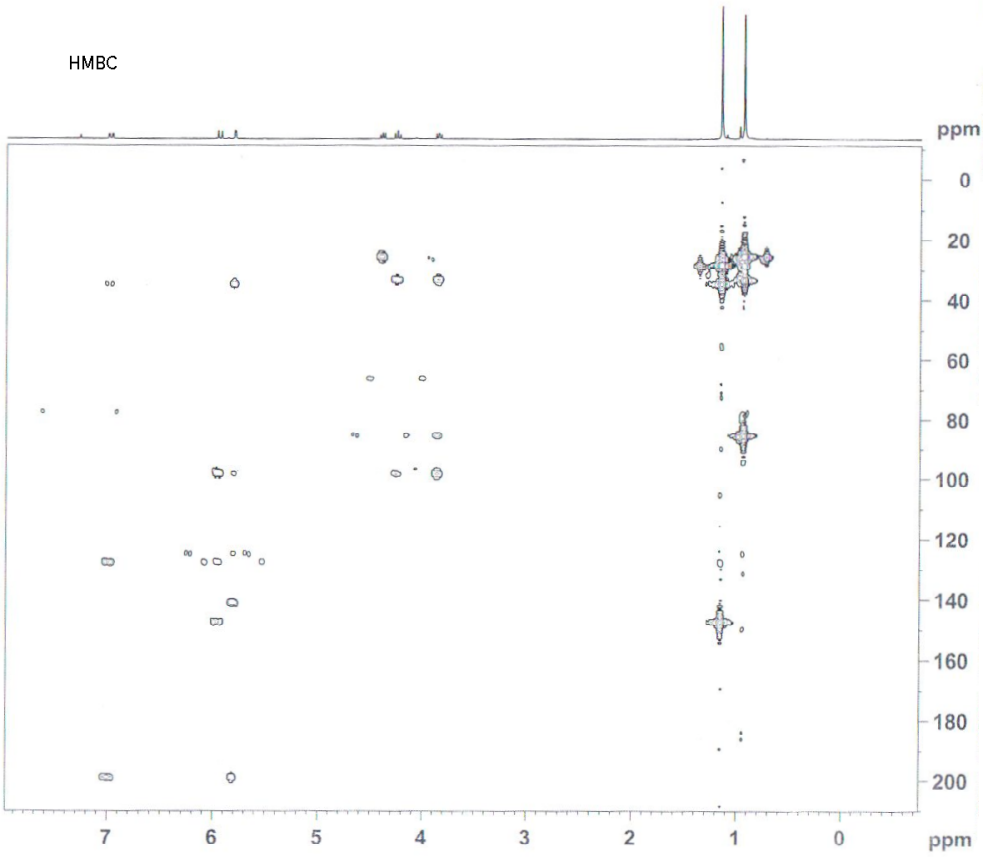


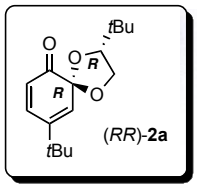
(*RR*)-**2a**

HMQC

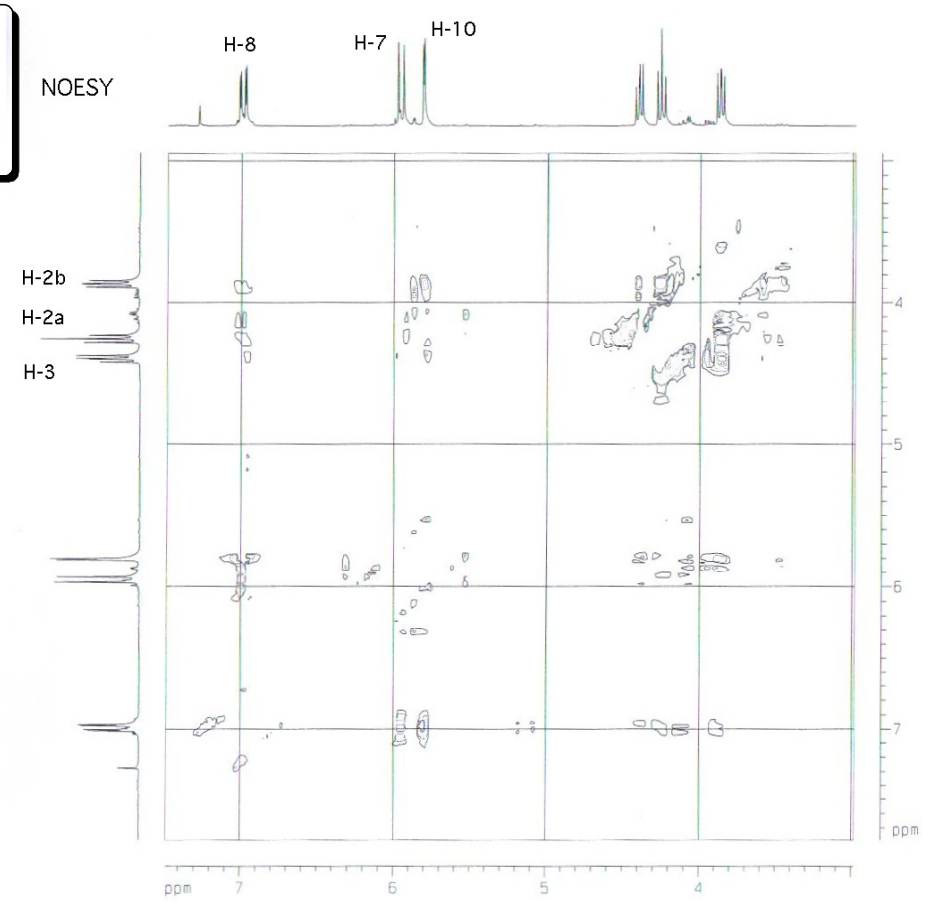


HMBC

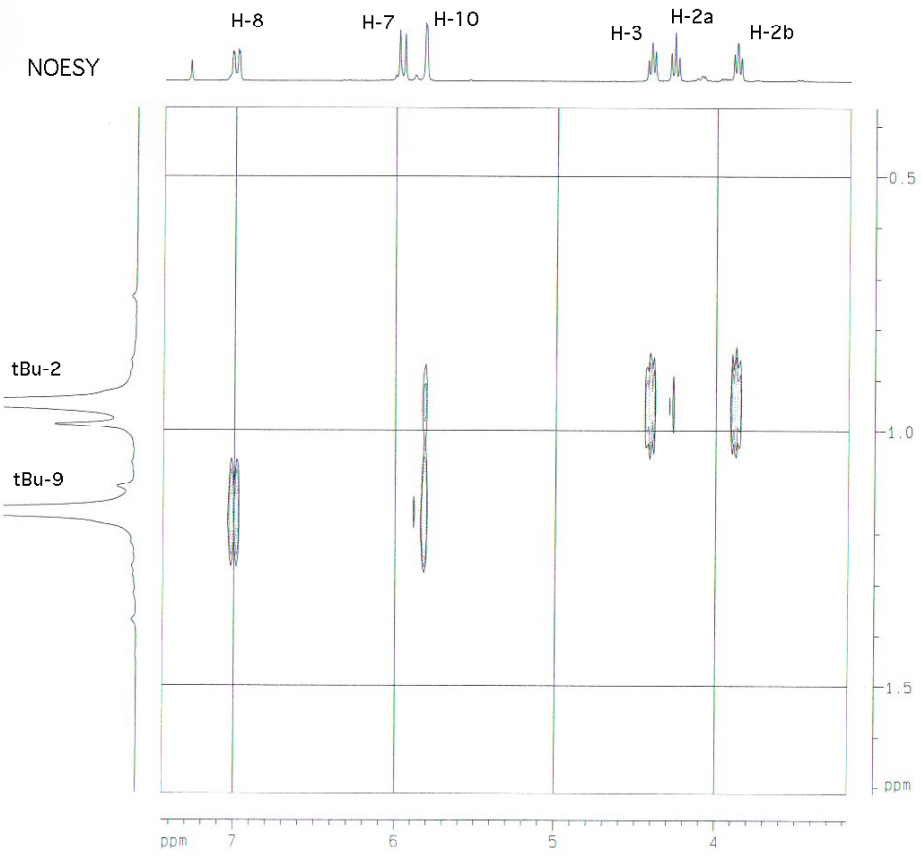



tBu
O
O
R
R
O
tBu
(RR)-2a

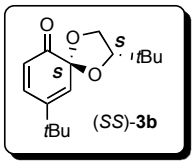
NOESY


H-8
H-7
H-10
H-2b
H-2a
H-3
4
5
6
7
ppm
ppm
7
6
5
4

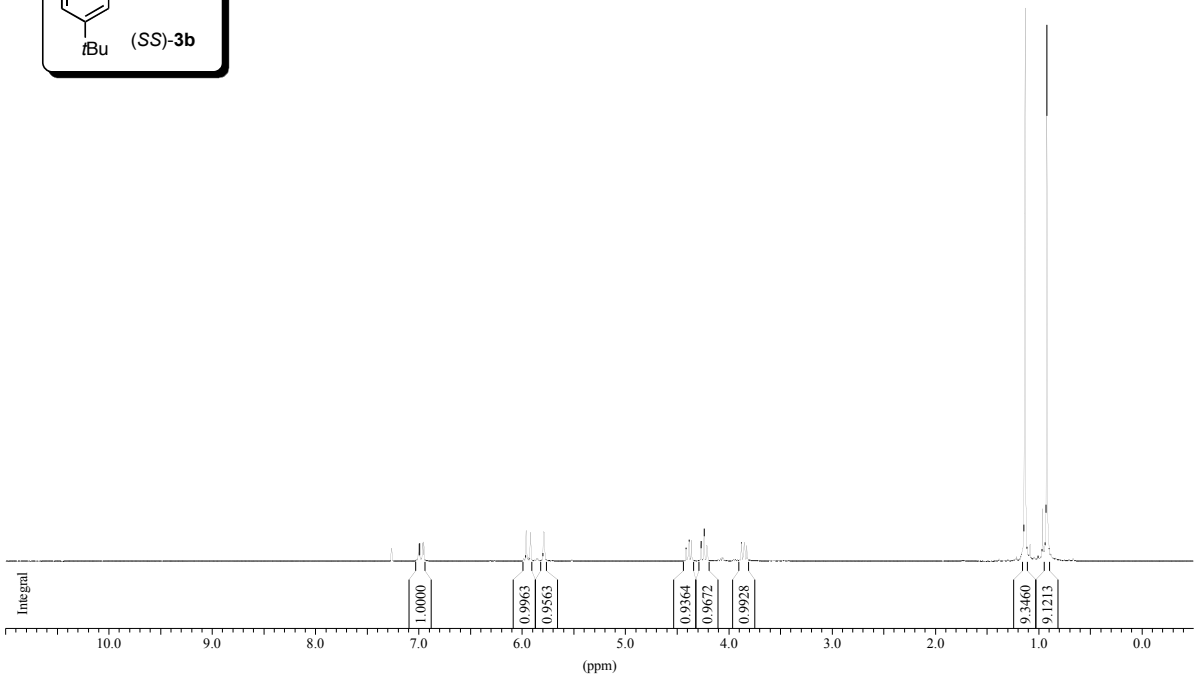
NOESY


H-8
H-7
H-10
H-3
H-2a
H-2b
tBu-2
tBu-9
0.5
1.0
1.5
ppm
ppm
7
6
5
4

AM-B175 / FV230F.101 cd-cl3 AC 250

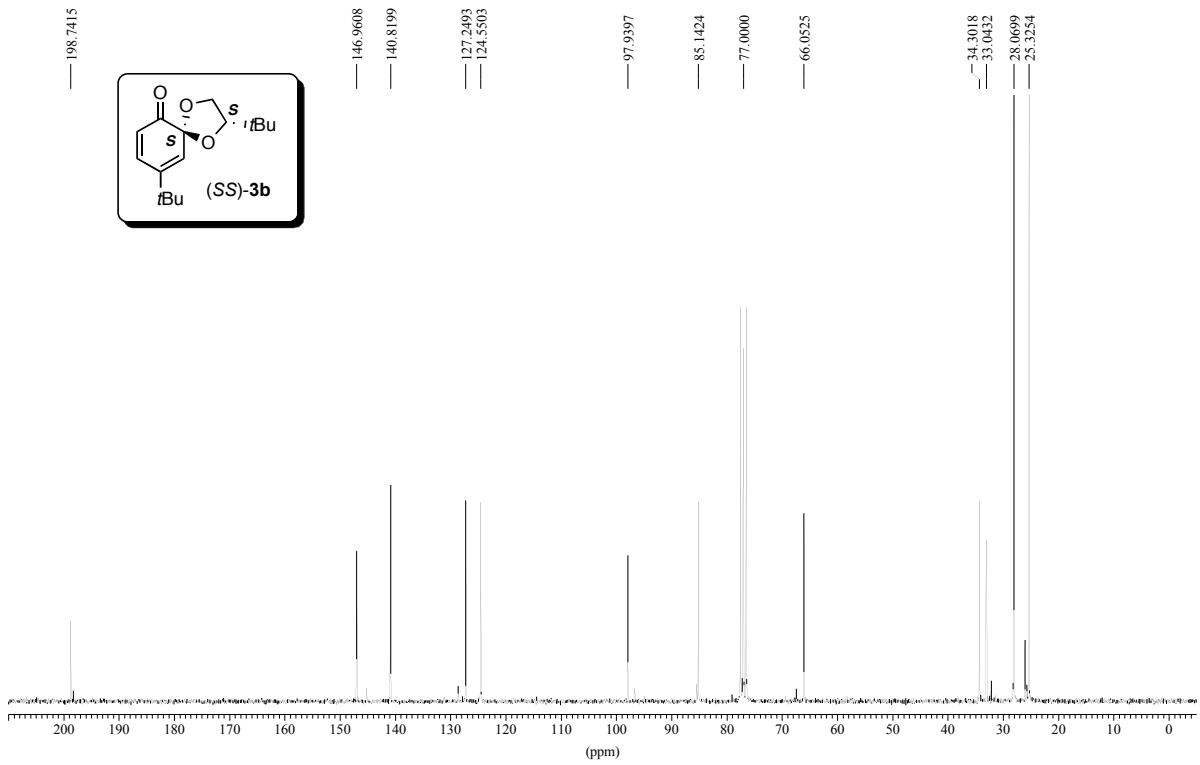


(*SS*)-**3b**

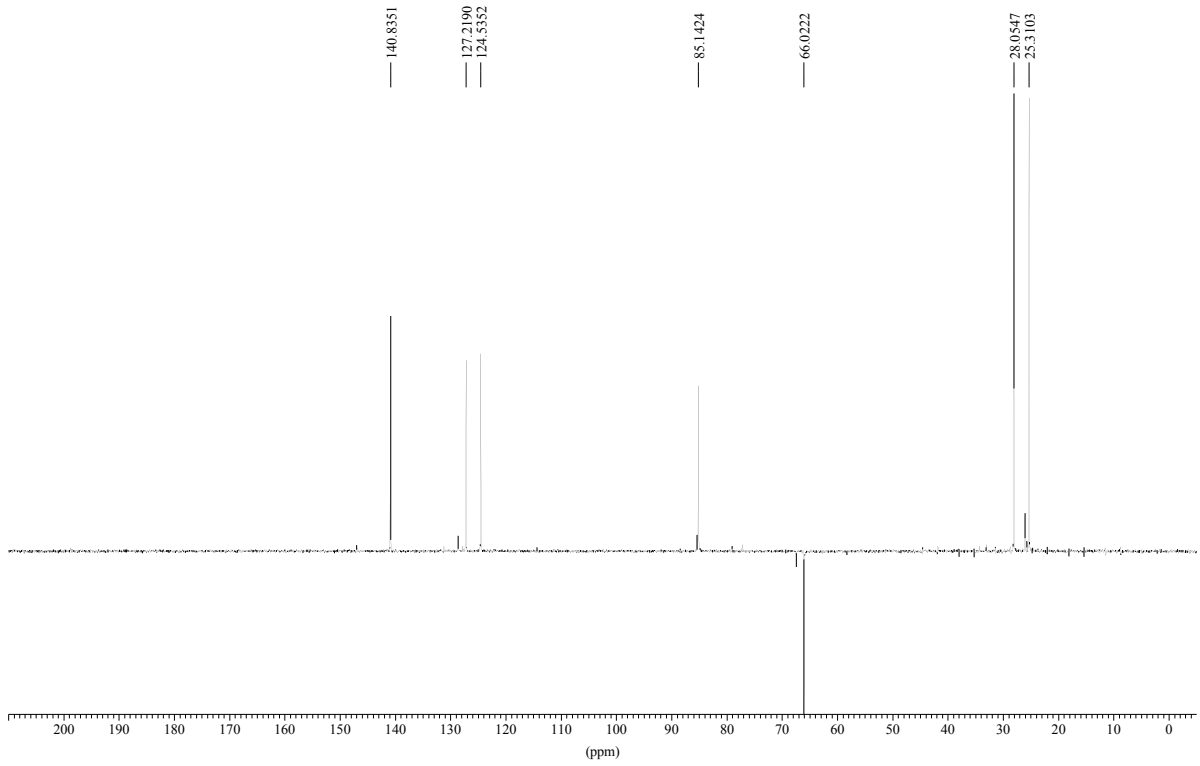


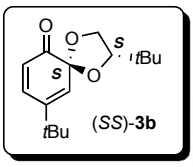
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6980	1816.46	7.2620	629	2.3
2	7193	1751.46	7.0021	841	3.1
3	7201	1749.02	6.9924	860	3.2
4	7227	1741.09	6.9606	888	3.3
5	7234	1738.95	6.9521	930	3.4
6	8048	1490.54	5.9590	1479	5.5
7	8082	1480.16	5.9175	1409	5.2
8	8184	1449.03	5.7931	1434	5.3
9	8192	1446.59	5.7833	1410	5.2
10	9315	1103.88	4.4132	633	2.3
11	9334	1098.08	4.3900	770	2.8
12	9339	1096.56	4.3839	1032	3.8
13	9359	1090.45	4.3595	1007	3.7
14	9434	1067.56	4.2680	965	3.6
15	9459	1059.93	4.2375	1578	5.8
16	9483	1052.61	4.2082	766	2.8
17	9755	969.60	3.8763	900	3.3
18	9775	963.50	3.8519	902	3.3
19	9780	961.97	3.8458	889	3.3
20	9799	956.17	3.8227	758	2.8
21	12005	282.96	1.1312	27111	100.0
22	12179	229.86	0.9189	26274	96.9

AM-B175 / FV231F.101 cd-cl3 AC 250



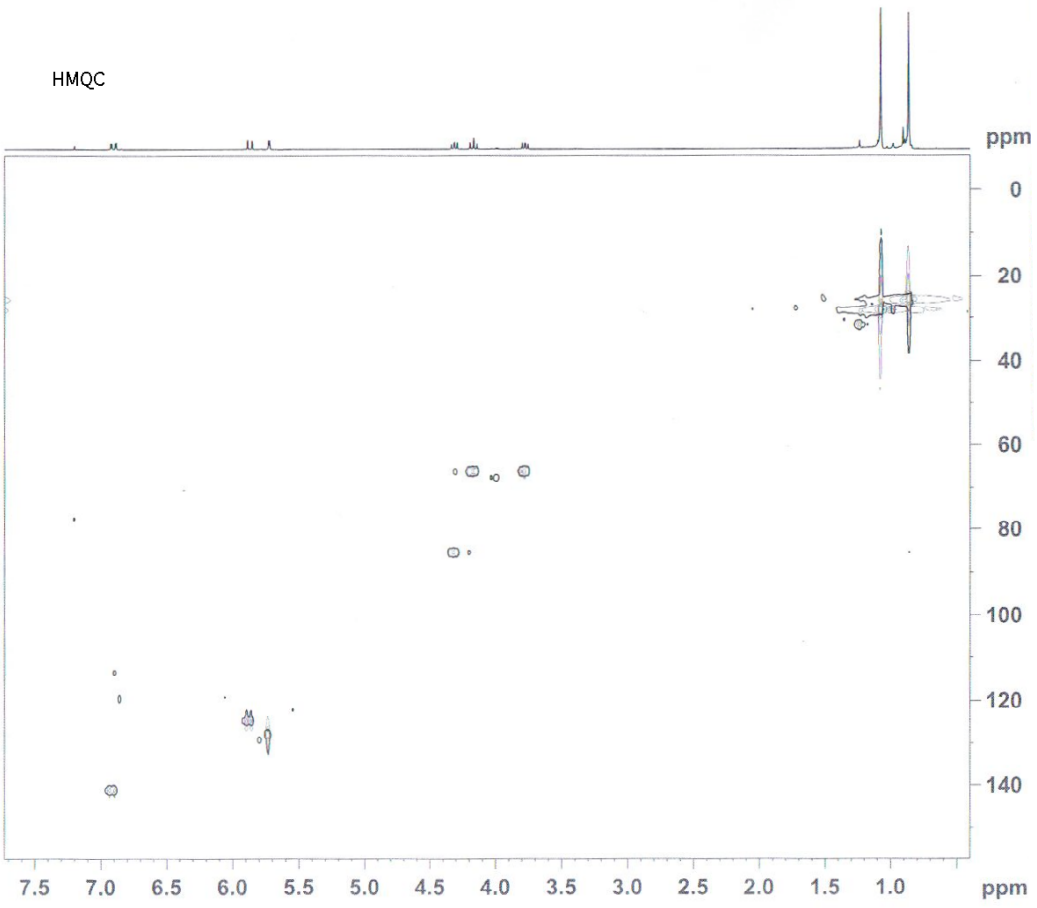
AM-B175 / FV232F.101 cd-cl3 AC 250



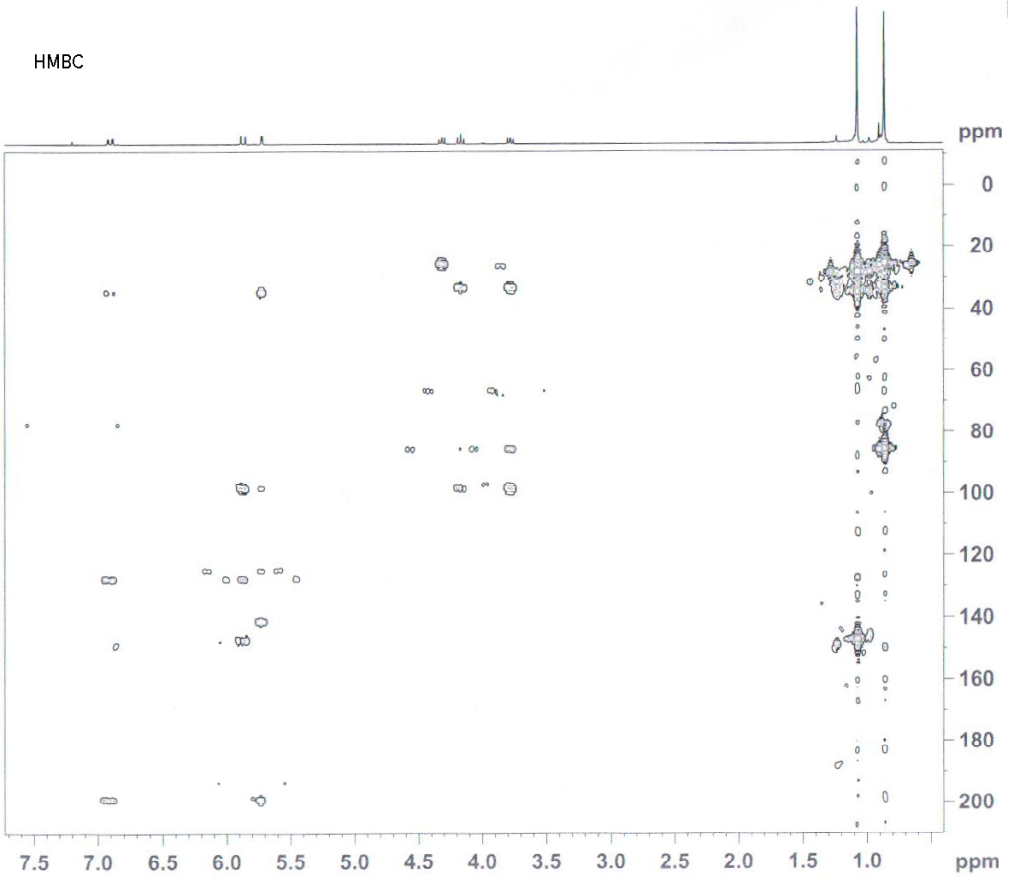


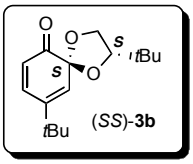
(*SS*)-**3b**

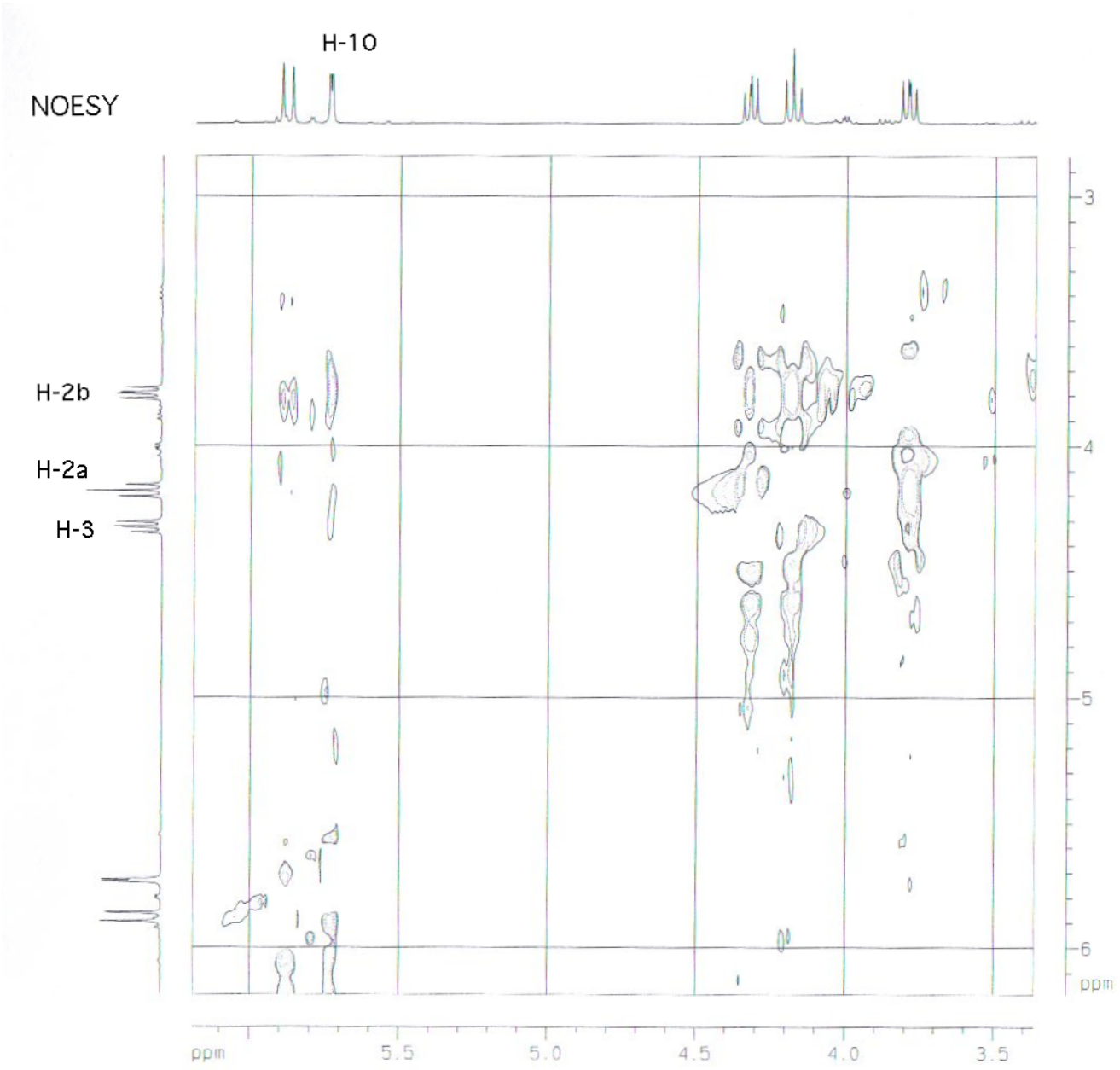
HMQC



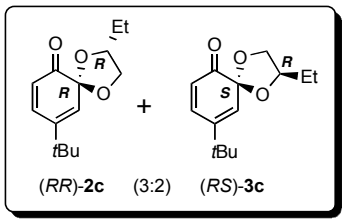
HMBC



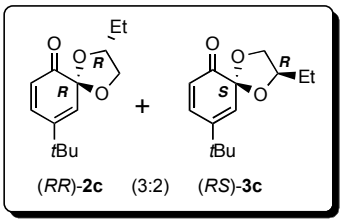

O
O
S
tBu
S
O
tBu
(SS)-3b


NOESY
H-10
H-2b
H-2a
H-3
3
4
5
6
ppm
ppm
5.5
5.0
4.5
4.0
3.5

AM-B176-1 / 27020617.1-1 cd-cl3 DPX 300



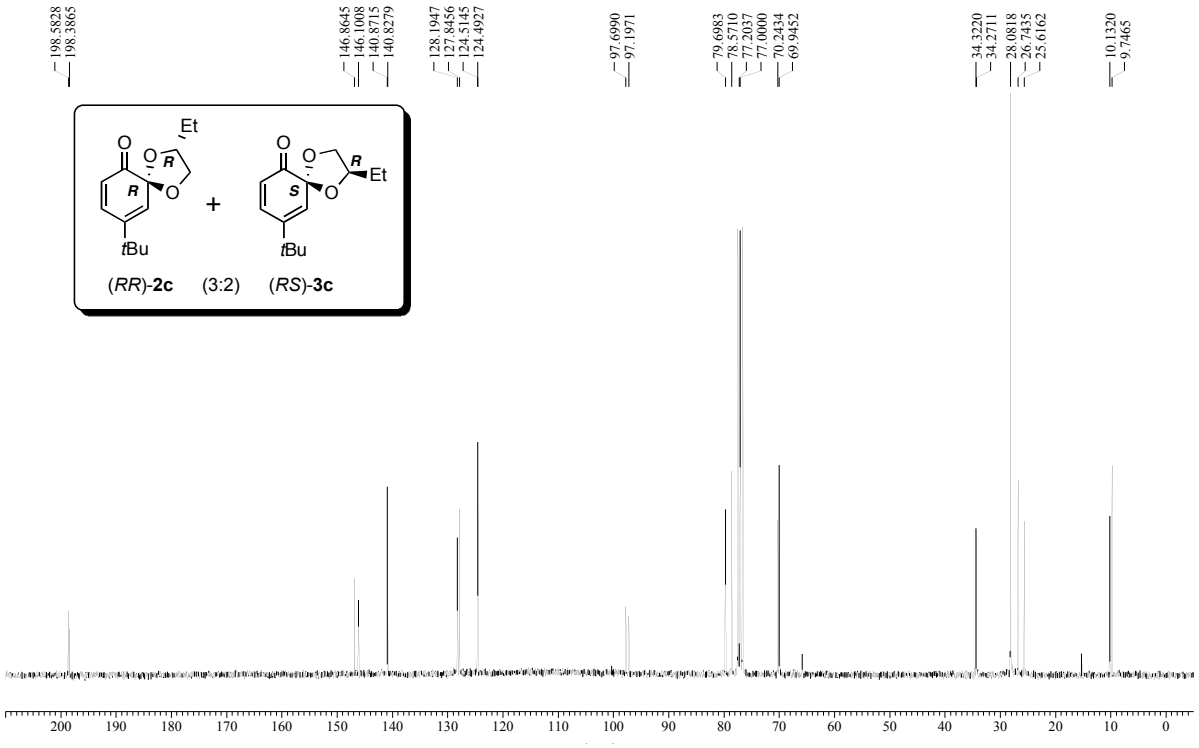
(*RR*)-**2c** (3:2) (*RS*)-**3c**



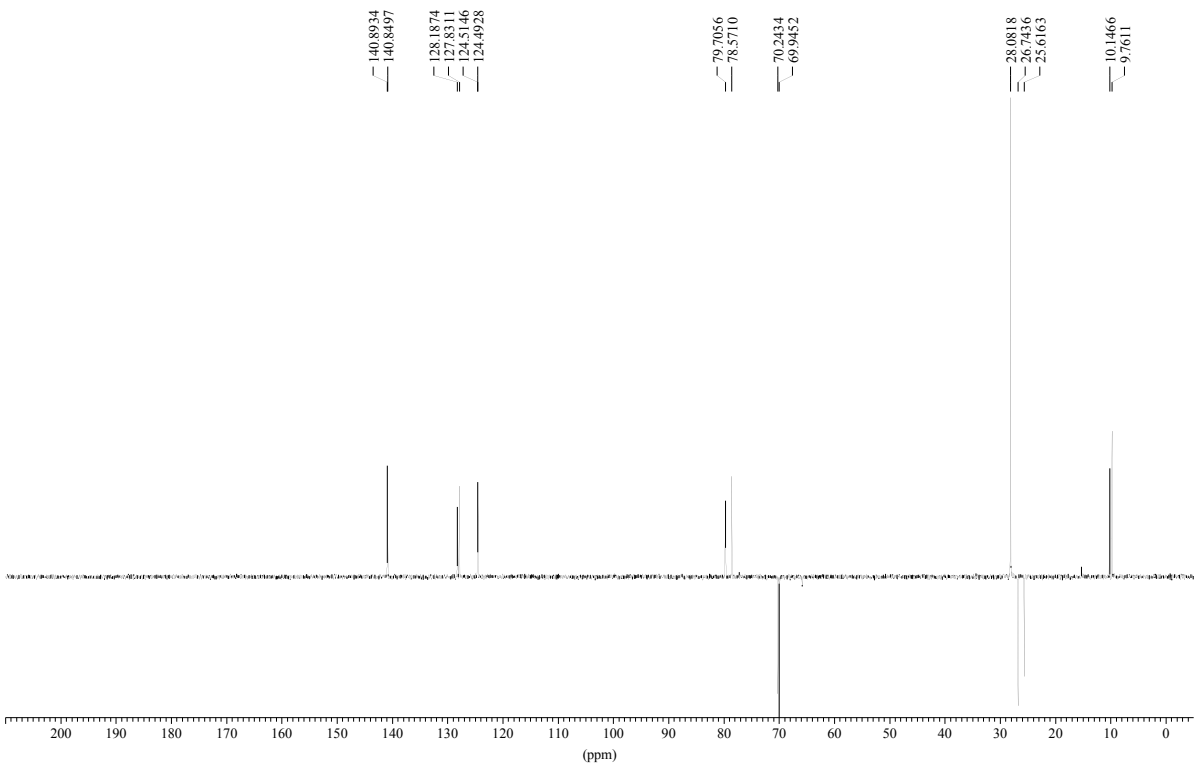
(*RR*)-**2c** (3:2) (*RS*)-**3c**

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9961	2179.54	7.2620	993963	2.5
2	10162	2103.82	7.0097	1390413	3.5
3	10168	2101.55	7.0021	1059386	2.6
4	10189	2093.64	6.9758	1489082	3.7
5	10195	2091.38	6.9683	1113162	2.8
6	10976	1797.13	5.9878	1173534	2.9
7	10992	1791.10	5.9678	1559318	3.9
8	11003	1786.96	5.9540	1170393	2.9
9	11021	1780.18	5.9314	1429193	3.6
10	11087	1755.31	5.8485	1371982	3.4
11	11119	1743.26	5.8083	1824505	4.5
12	12071	1384.58	4.6133	165177	0.4
13	12088	1378.18	4.5919	700727	1.7
14	12105	1371.77	4.5706	1116255	2.8
15	12122	1365.37	4.5492	804063	2.0
16	12139	1358.96	4.5279	225616	0.6
17	12256	1314.88	4.3810	895989	2.2
18	12272	1308.85	4.3609	1573991	3.9
19	12293	1300.94	4.3346	806875	2.0
20	12372	1271.18	4.2354	412039	1.0
21	12387	1265.52	4.2166	1060972	2.6
22	12398	1261.38	4.2028	1655352	4.1
23	12413	1255.73	4.1839	781231	1.9
24	12431	1248.95	4.1614	461719	1.1
25	12446	1243.30	4.1425	159289	0.4
26	12570	1196.58	3.9869	293655	0.7
27	12598	1186.03	3.9517	1273569	3.2
28	12614	1180.00	3.9316	247969	0.6
29	12627	1175.10	3.9153	196598	0.5
30	12792	1112.94	3.7082	875598	2.2
31	12809	1106.53	3.6868	1609235	4.0
32	12825	1100.50	3.6668	820561	2.0
33	14212	577.94	1.9256	156176	0.4
34	14232	570.40	1.9005	316165	0.8
35	14251	563.24	1.8767	426077	1.1
36	14268	556.84	1.8553	4605549	1.1
37	14288	549.30	1.8302	300353	0.7
38	14305	542.90	1.8089	100464	0.2
39	14348	526.70	1.7549	264366	0.7
40	14368	519.16	1.7298	655102	1.6
41	14387	512.00	1.7059	1027349	2.6
42	14404	505.60	1.6846	1231966	3.1
43	14424	498.06	1.6595	921965	2.3
44	14432	495.05	1.6494	726088	1.8
45	14452	487.51	1.6243	928913	2.3
46	14471	480.36	1.6005	777018	1.9
47	14488	473.95	1.5792	501274	1.2
48	14507	466.79	1.5553	249708	0.6
49	14844	339.82	1.1323	40242684	100.0
50	14963	294.99	0.9829	4334278	10.8
51	14983	287.45	0.9578	8058422	20.0
52	15003	279.95	0.9327	3891617	9.7

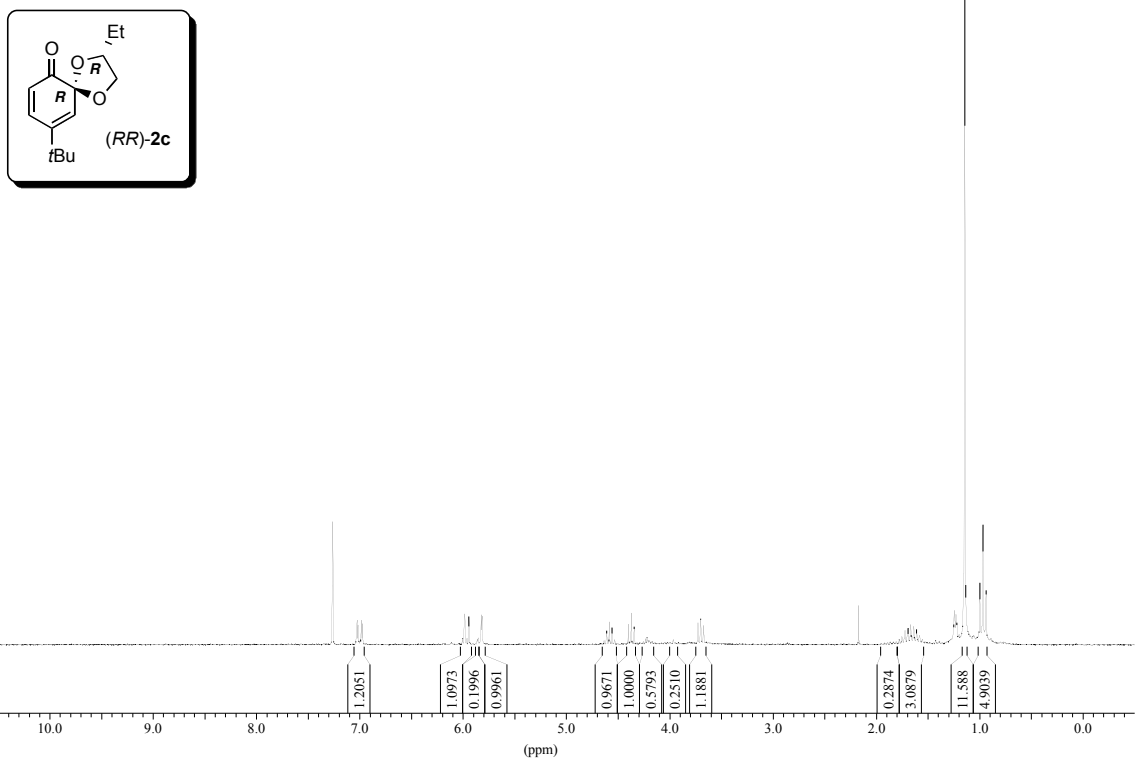
AM-B176-1 / 27020617.2-1 cd-cl3 DPX 300

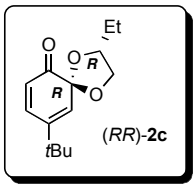


AM-B176-1 / 27020617.3-1 cd-cl3 DPX 300



AM-B176-2 / MS010F.101 cd-cl3 AC 250

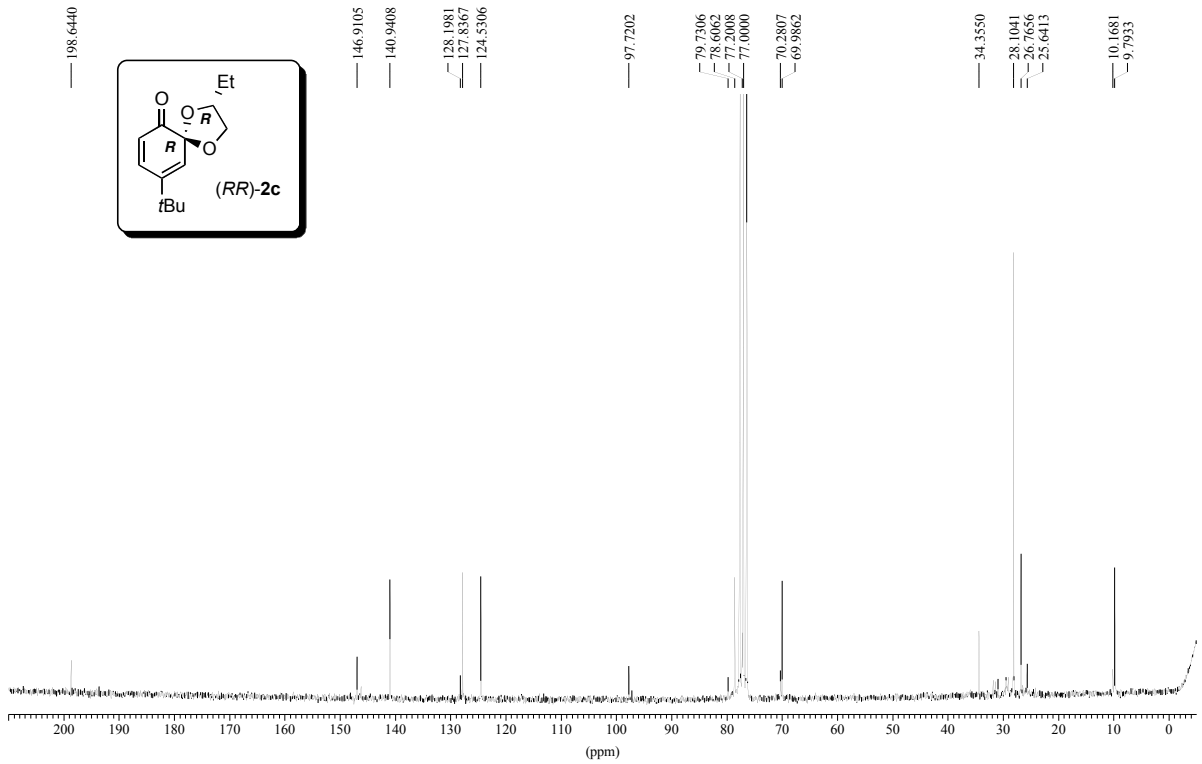




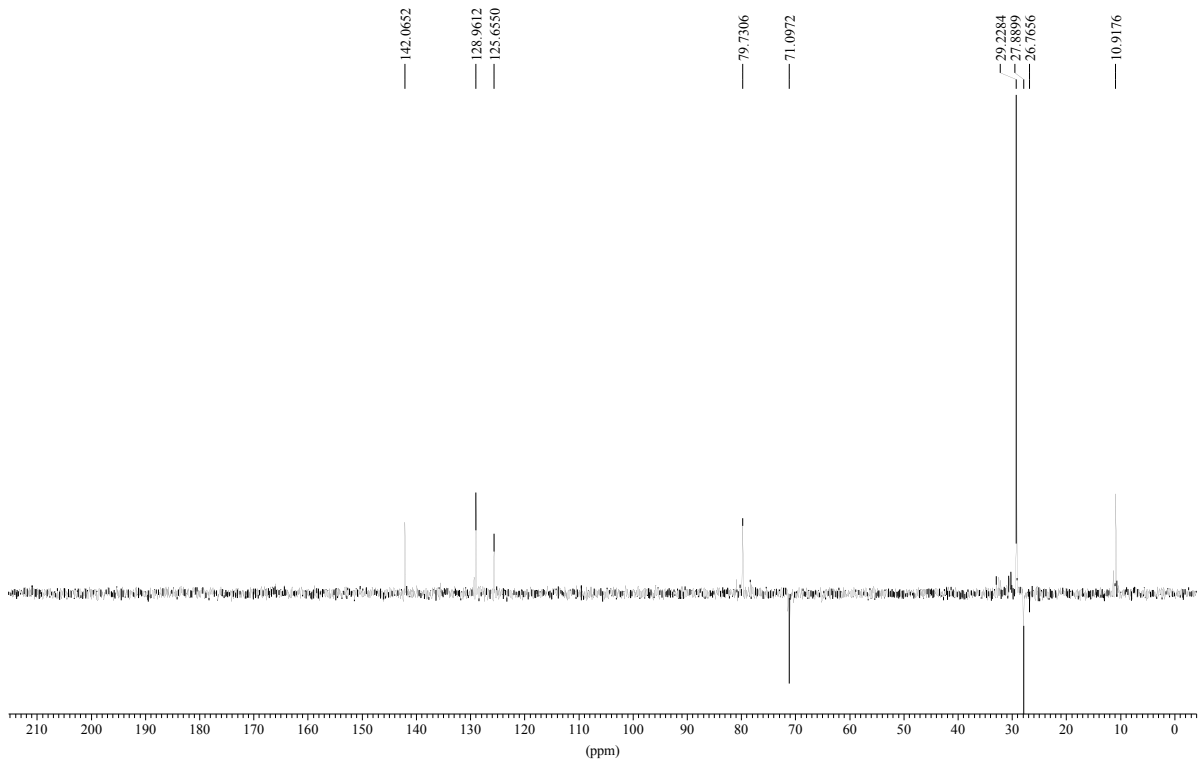
(*RR*)-**2c**

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6979	1816.46	7.2620	3696	18.5
2	7166	1759.40	7.0338	214	1.1
3	7174	1756.96	7.0241	728	3.6
4	7182	1754.51	7.0143	583	2.9
5	7200	1749.02	6.9924	139	0.7
6	7208	1746.58	6.9826	725	3.6
7	7216	1744.14	6.9728	627	3.1
8	8010	1501.83	6.0041	184	0.9
9	8027	1496.64	5.9834	920	4.6
10	8044	1491.45	5.9626	181	0.9
11	8061	1486.26	5.9419	838	4.2
12	8126	1466.43	5.8626	160	0.8
13	8133	1464.29	5.8541	189	0.9
14	8158	1456.66	5.8236	889	4.5
15	8165	1454.53	5.8150	842	4.2
16	9133	1159.12	4.6340	109	0.5
17	9154	1152.71	4.6084	412	2.1
18	9175	1146.30	4.5828	680	3.4
19	9196	1139.89	4.5571	499	2.5
20	9216	1133.79	4.5327	135	0.7
21	9325	1100.52	4.3998	604	3.0
22	9349	1093.20	4.3705	936	4.7
23	9371	1086.48	4.3436	531	2.7
24	9444	1064.21	4.2546	92	0.5
25	9462	1058.71	4.2326	167	0.8
26	9475	1054.75	4.2167	201	1.0
27	9495	1048.64	4.1923	118	0.6
28	9512	1043.45	4.1716	75	0.4
29	9685	990.66	3.9605	140	0.7
30	9877	932.07	3.7263	647	3.2
31	9898	925.66	3.7007	740	3.7
32	9900	925.05	3.6982	773	3.9
33	9921	918.64	3.6726	573	2.9
34	11335	487.12	1.9474	29	0.1
35	11358	480.10	1.9194	44	0.2
36	11382	472.78	1.8901	62	0.3
37	11405	465.76	1.8620	62	0.3
38	11426	459.35	1.8364	60	0.3
39	11450	452.02	1.8071	70	0.4
40	11475	444.39	1.7766	140	0.7
41	11495	438.29	1.7522	235	1.2
42	11519	430.97	1.7230	427	2.1
43	11544	423.34	1.6924	487	2.4
44	11565	416.93	1.6668	596	3.0
45	11589	409.60	1.6375	538	2.7
46	11612	402.59	1.6095	451	2.3
47	11635	395.57	1.5814	280	1.4
48	11657	388.85	1.5546	151	0.8
49	11994	286.01	1.1434	19958	100.0
50	12113	249.69	0.9982	1848	9.3
51	12138	242.06	0.9677	3598	18.0
52	12162	234.74	0.9385	1624	8.1

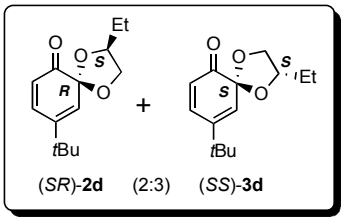
AM-B176-2 / MA02-lam cd-cl3 DPX 200



AM-B176-2 / MA02-Lam cd-cl3 DPX 200



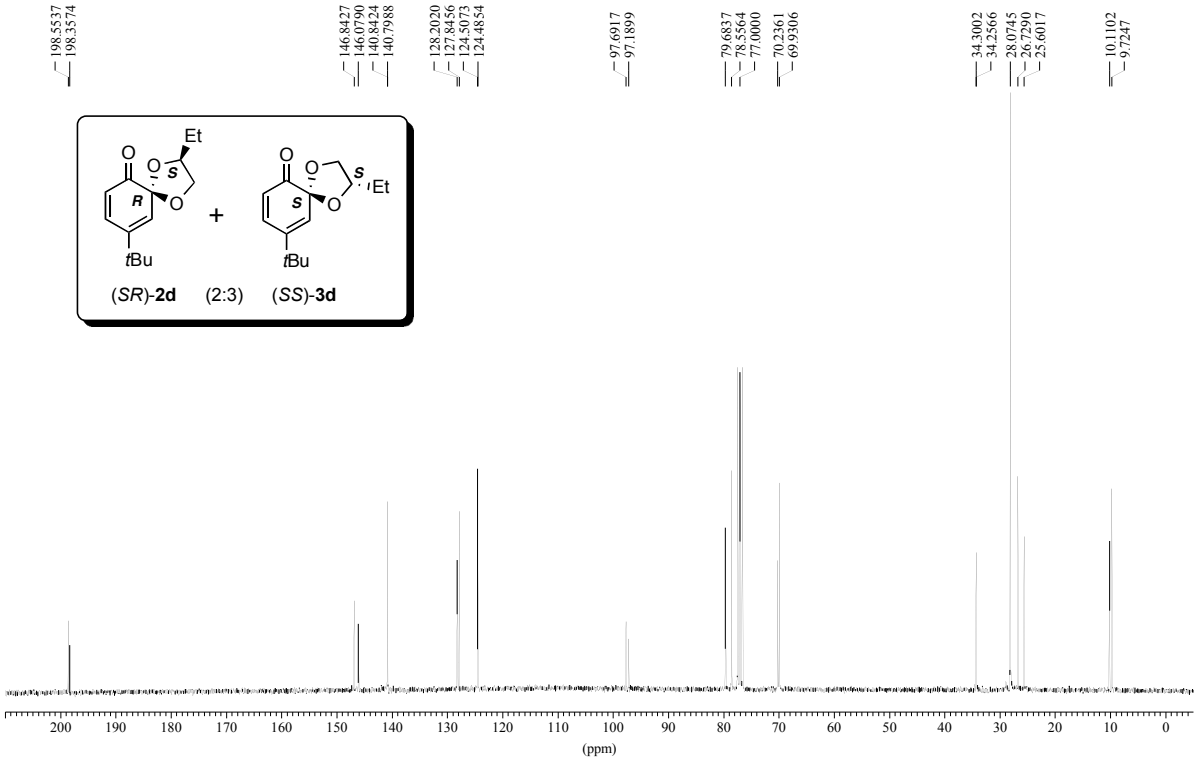
AMB178-1 / 06030631.1-1 cd-cl3 DPX 300



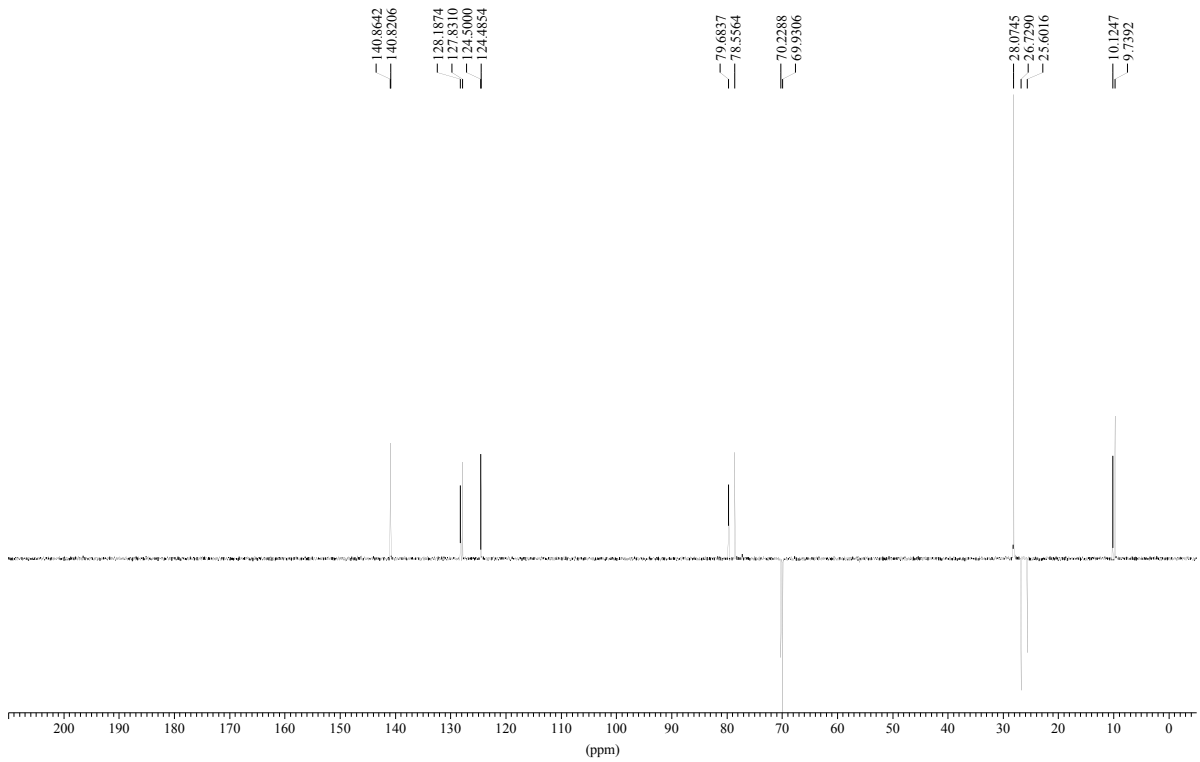
(*SR*)-**2d** (2:3) (*SS*)-**3d**

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9960	2179.54	7.2620	52803	4.3
2	10158	2104.95	7.0134	32986	2.7
3	10165	2102.31	7.0047	56933	4.6
4	10173	2099.29	6.9946	46565	3.8
5	10186	2094.40	6.9783	33728	2.7
6	10193	2091.76	6.9695	59702	4.8
7	10200	2089.12	6.9607	50481	4.1
8	10979	1795.63	5.9828	44985	3.6
9	10981	1794.87	5.9803	44071	3.6
10	10996	1789.22	5.9615	65222	5.3
11	11007	1785.08	5.9477	46003	3.7
12	11023	1779.05	5.9276	64397	5.2
13	11086	1755.31	5.8485	45535	3.7
14	11093	1752.67	5.8397	46500	3.7
15	11118	1743.26	5.8083	62989	5.1
16	11124	1740.99	5.8008	65750	5.3
17	12073	1383.45	4.6095	7992	0.6
18	12090	1377.04	4.5882	32687	2.6
19	12107	1370.64	4.5668	51611	4.2
20	12124	1364.23	4.5455	37472	3.0
21	12141	1357.83	4.5241	10418	0.8
22	12258	1313.75	4.3773	50670	4.1
23	12276	1306.97	4.3547	71373	5.8
24	12295	1299.81	4.3308	43069	3.5
25	12374	1270.04	4.2316	20123	1.6
26	12389	1264.39	4.2128	48914	3.9
27	12402	1259.50	4.1965	58041	4.7
28	12407	1257.61	4.1902	18893	1.5
29	12414	1254.97	4.1814	19818	1.6
30	12417	1253.84	4.1777	21552	1.7
31	12434	1247.44	4.1563	14526	1.2
32	12450	1241.41	4.1362	6349	0.5
33	12571	1195.82	3.9843	9242	0.7
34	12574	1194.69	3.9806	7524	0.6
35	12581	1192.06	3.9718	9380	0.8
36	12587	1189.79	3.9643	9592	0.8
37	12599	1185.27	3.9492	35687	2.9
38	12602	1184.14	3.9454	35087	2.8
39	12614	1179.62	3.9304	7459	0.6
40	12619	1177.74	3.9241	5976	0.5
41	12629	1173.97	3.9115	5872	0.5
42	12794	1111.81	3.7044	49507	4.0
43	12811	1105.40	3.6831	60215	4.9
44	12813	1104.65	3.6806	54119	4.4
45	12830	1098.24	3.6592	43095	3.5
46	14196	583.59	1.9444	1719	0.1
47	14216	576.05	1.9193	6122	0.5
48	14234	569.27	1.8967	9436	0.8
49	14253	562.11	1.8729	14808	1.2
50	14273	554.58	1.8478	13508	1.1
51	14290	548.17	1.8264	11066	0.9
52	14310	540.64	1.8013	4261	0.3
53	14333	531.97	1.7725	3472	0.3
54	14353	524.44	1.7474	11498	0.9
55	14370	518.03	1.7260	18343	1.5
56	14373	516.90	1.7223	19013	1.5
57	14389	510.87	1.7022	38251	3.1
58	14406	504.47	1.6808	31814	2.6
59	14409	503.34	1.6771	39592	3.2
60	14426	496.93	1.6557	30894	2.5
61	14429	495.80	1.6520	21139	1.7
62	14436	493.17	1.6432	23776	1.9
63	14446	489.40	1.6306	15849	1.3
64	14453	486.76	1.6218	29429	2.4
65	14473	479.22	1.5967	29470	2.4
66	14492	472.07	1.5729	17753	1.4
67	14509	465.66	1.5515	9737	0.8
68	14528	458.50	1.5277	3530	0.3
69	14845	339.07	1.1297	1240233	100.0
70	14849	337.56	1.1247	947573	76.4
71	14965	293.86	0.9791	173957	14.0
72	14985	286.32	0.9540	340094	27.4
73	15005	278.79	0.9289	157523	12.7

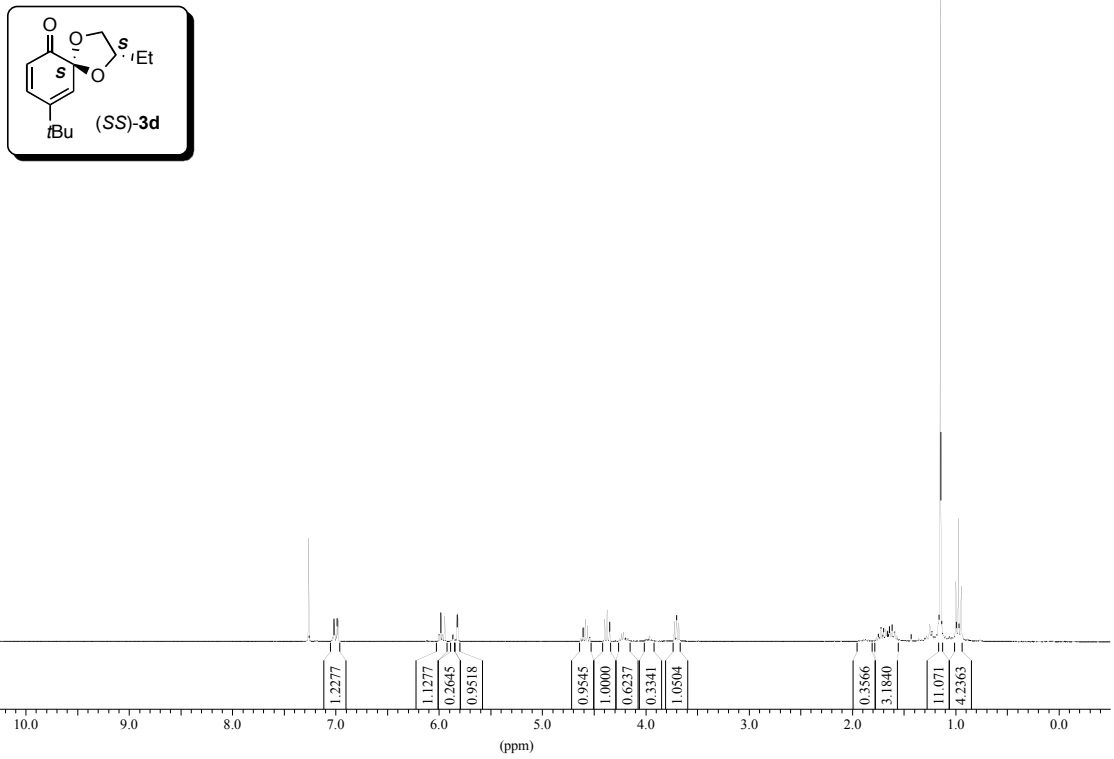
AMB178-1 / 06030631.2-1 cd-cl3 DPX 300

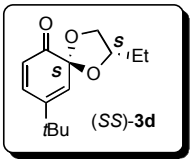


AMB178-1 / 06030631.3-1 cd-cl3 DPX 300



AM-B178-2 / 06030632.1-1 cd-cl3 DPX 300

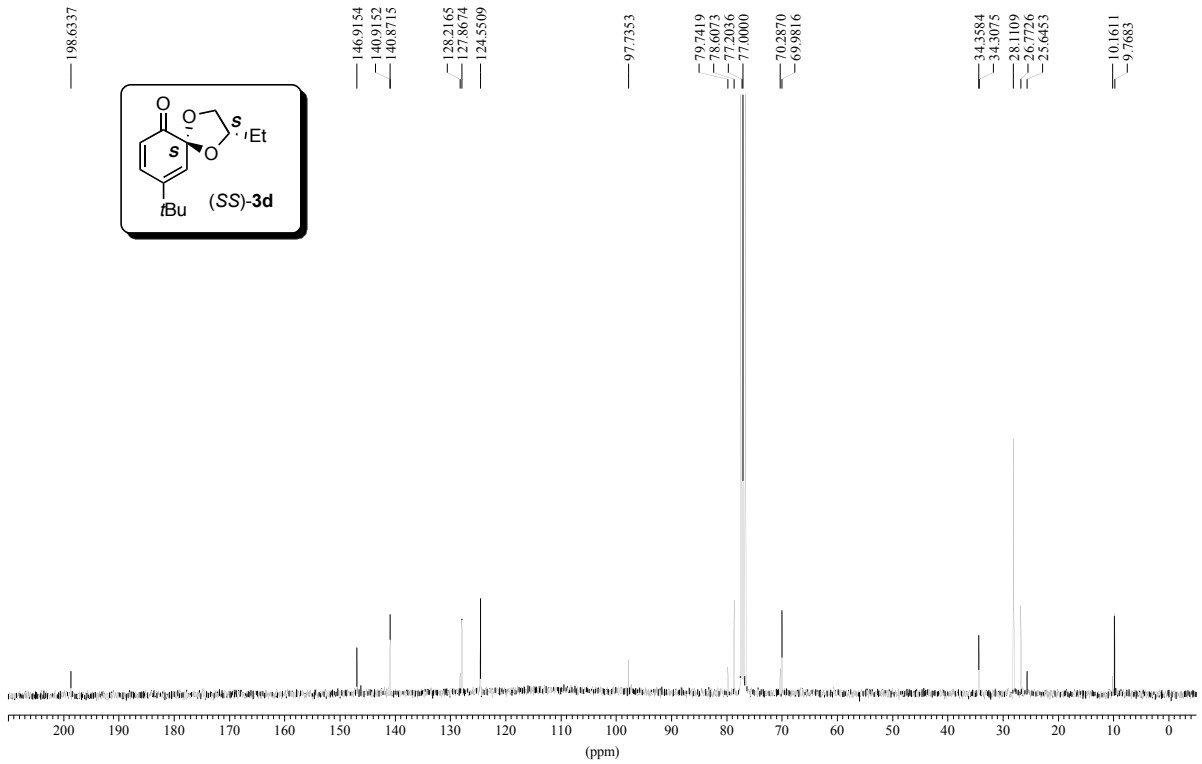




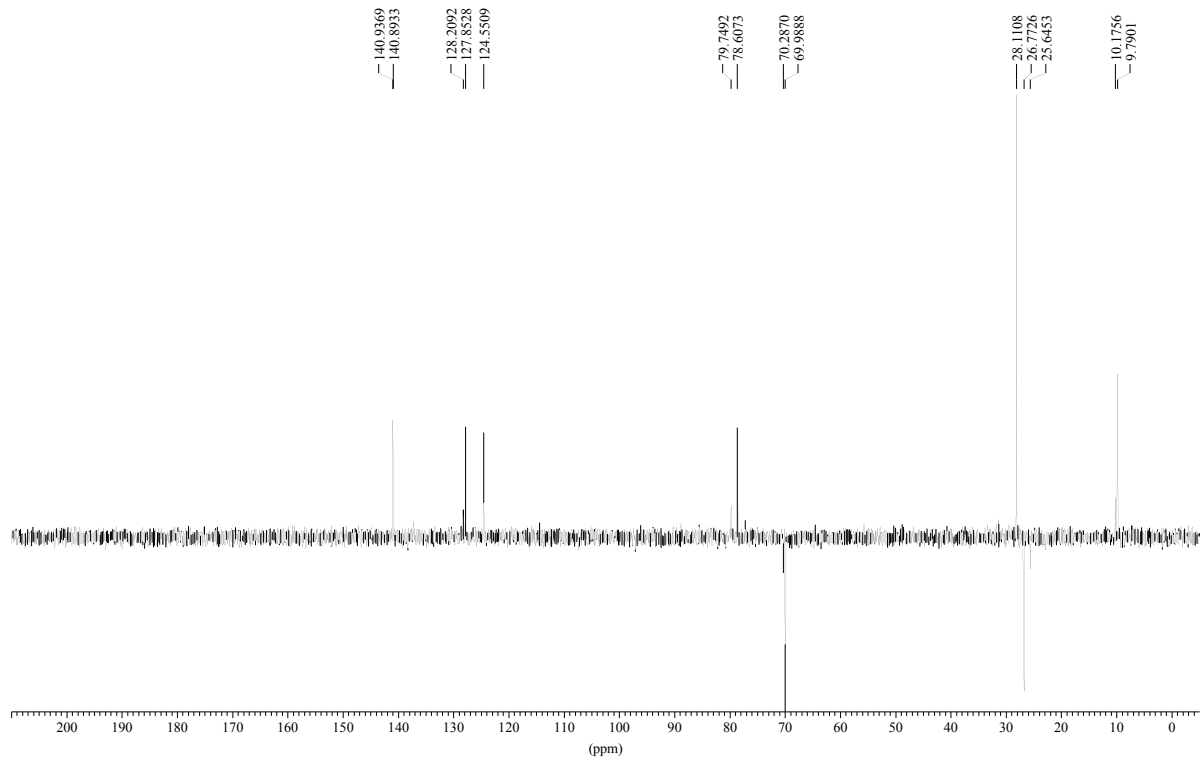
(*SS*)-**3d**

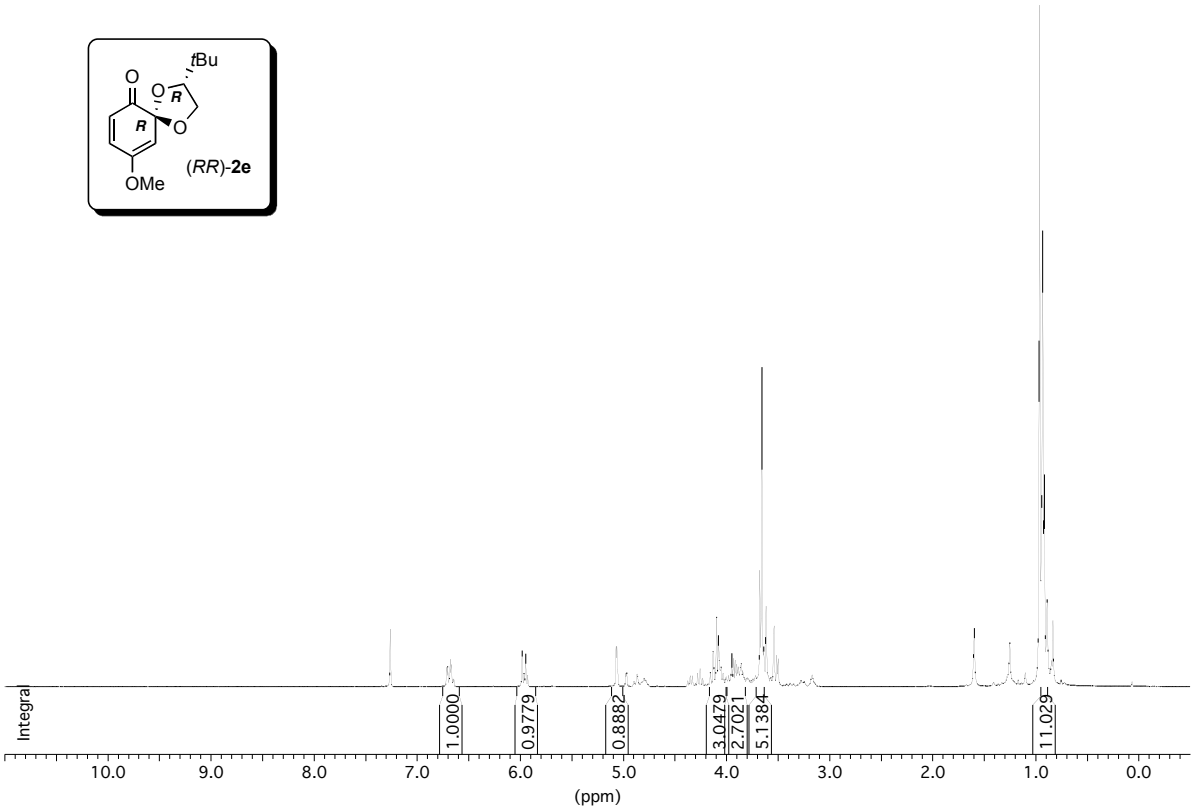
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9960	2179.54	7.2620	166412	15.6
2	10146	2109.47	7.0285	10537	1.0
3	10154	2106.45	7.0185	36406	3.4
4	10160	2104.19	7.0109	30441	2.9
5	10173	2099.29	6.9946	9830	0.9
6	10181	2096.28	6.9846	37495	3.5
7	10188	2093.64	6.9758	35028	3.3
8	10964	1801.28	6.0017	11426	1.1
9	10980	1795.25	5.9816	46483	4.4
10	10982	1794.49	5.9791	43354	4.1
11	10991	1791.10	5.9678	11697	1.1
12	11009	1784.32	5.9452	40699	3.8
13	11072	1760.59	5.8661	11023	1.0
14	11079	1757.95	5.8573	11589	1.1
15	11105	1748.15	5.8247	43592	4.1
16	11110	1746.27	5.8184	45724	4.3
17	12059	1388.72	4.6271	5661	0.5
18	12076	1382.32	4.6057	22626	2.1
19	12093	1375.91	4.5844	36089	3.4
20	12110	1369.51	4.5631	26322	2.5
21	12127	1363.10	4.5417	7332	0.7
22	12243	1319.40	4.3961	36278	3.4
23	12262	1312.24	4.3722	50957	4.8
24	12280	1305.46	4.3496	31828	3.0
25	12360	1275.32	4.2492	5286	0.5
26	12374	1270.04	4.2316	13173	1.2
27	12387	1265.15	4.2153	15460	1.5
28	12403	1259.12	4.1952	6065	0.6
29	12420	1252.71	4.1739	4559	0.4
30	12556	1201.47	4.0032	2978	0.3
31	12572	1195.45	3.9831	3023	0.3
32	12585	1190.55	3.9668	9610	0.9
33	12587	1189.79	3.9643	8630	0.8
34	12600	1184.90	3.9479	2816	0.3
35	12780	1117.08	3.7220	32039	3.0
36	12796	1111.05	3.7019	42553	4.0
37	12815	1103.89	3.6781	30478	2.9
38	14219	574.92	1.9156	2756	0.3
39	14238	567.76	1.8917	4100	0.4
40	14255	561.36	1.8704	3836	0.4
41	14275	553.82	1.8453	3298	0.3
42	14337	530.46	1.7674	7020	0.7
43	14354	524.06	1.7461	12791	1.2
44	14374	516.52	1.7210	23097	2.2
45	14391	510.12	1.6997	21579	2.0
46	14394	508.99	1.6959	21791	2.0
47	14403	505.60	1.6846	8550	0.8
48	14410	502.96	1.6758	19778	1.9
49	14422	498.44	1.6607	18141	1.7
50	14430	495.43	1.6507	11698	1.1
51	14439	492.03	1.6394	24241	2.3
52	14442	490.90	1.6356	22670	2.1
53	14459	484.50	1.6143	27382	2.6
54	14478	477.34	1.5904	16034	1.5
55	14495	470.94	1.5691	9422	0.9
56	14515	463.40	1.5440	4096	0.4
57	14831	344.34	1.1473	1065112	100.0
58	14835	342.84	1.1423	365936	34.4
59	14951	299.13	0.9967	96055	9.0
60	14971	291.60	0.9716	197713	18.6
61	14991	284.06	0.9465	89508	8.4

AM-B178-2 / 06030632.2-1 cd-cl3 DPX 300

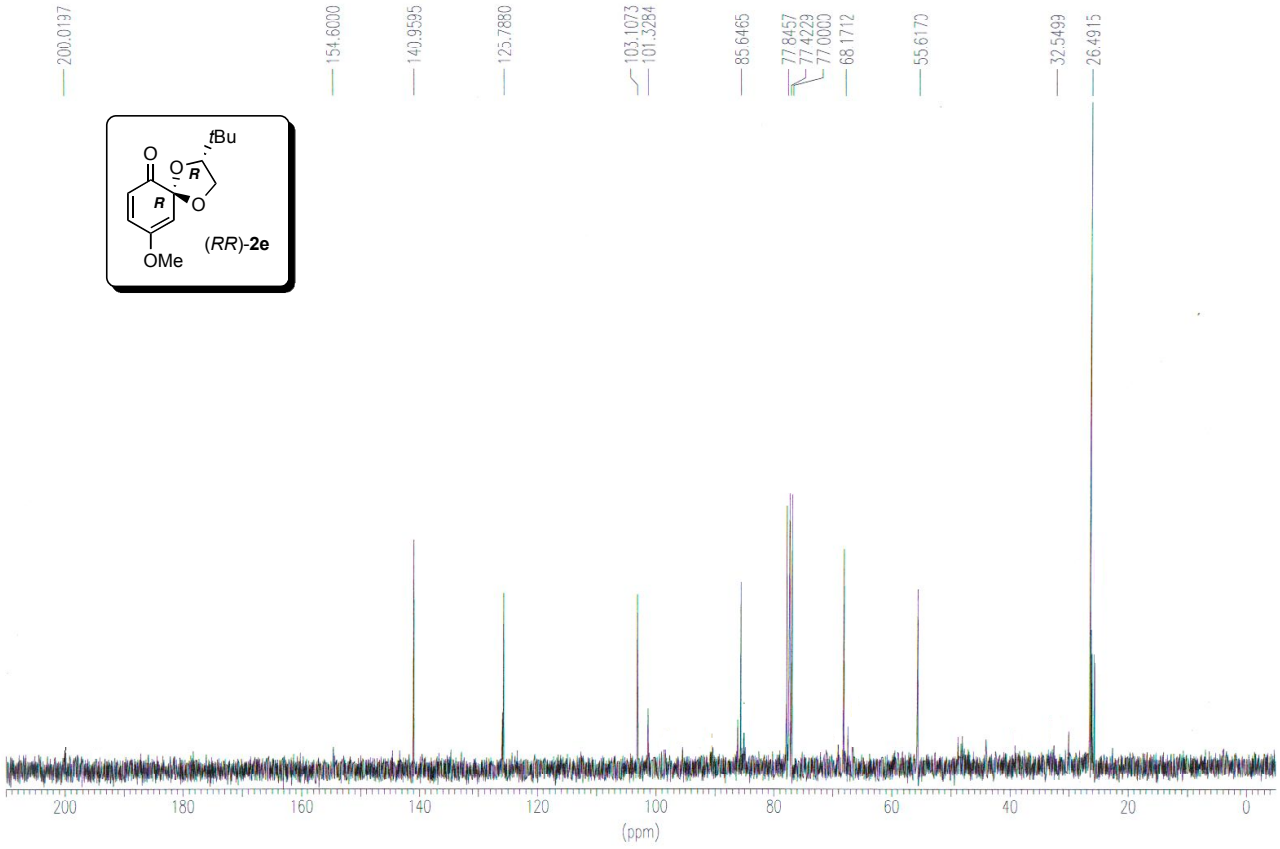


AM-B178-2 / 06030632.3-1 cd-cl3 DPX 300

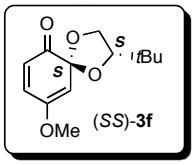




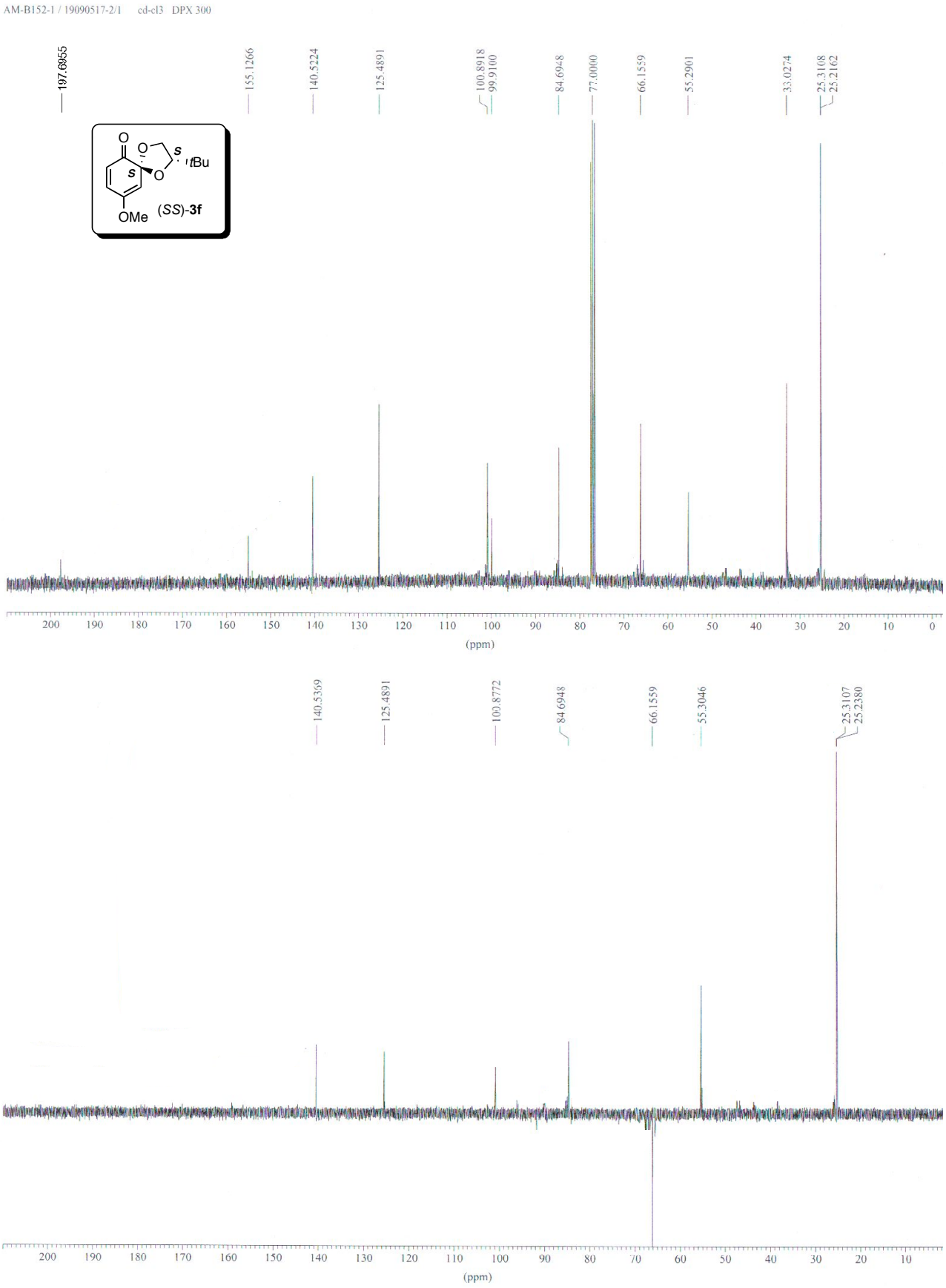
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	15500	2014.27	6.7113	9774202	2.0
2	15516	2011.25	6.7013	10320438	2.1
3	15555	2003.88	6.6767	14020304	2.9
4	15571	2000.86	6.6667	11289101	2.3
5	16661	1795.02	5.9808	18201334	3.7
6	16716	1784.63	5.9462	16674334	3.4
7	18110	1521.38	5.0691	20304086	4.1
8	18125	1518.55	5.0596	20637898	4.2
9	19603	1239.43	4.1297	18132156	3.7
10	19658	1229.05	4.0950	35529492	7.3
11	19690	1223.00	4.0749	25986632	5.3
12	19717	1217.90	4.0579	9676643	2.0
13	19730	1215.45	4.0497	10113820	2.1
14	19892	1184.86	3.9478	16945132	3.5
15	19920	1179.57	3.9302	14327842	2.9
16	19945	1174.85	3.9145	13582396	2.8
17	19973	1169.56	3.8968	11484181	2.3
18	19993	1165.78	3.8843	10102834	2.1
19	20039	1157.10	3.8553	11936590	2.4
20	20062	1152.75	3.8408	8332246	1.7
21	20356	1097.23	3.6559	162524208	33.2
22	24637	288.78	0.9622	489389344	100.0


200.0197
154.6000
140.9595
125.7880
103.1073
101.3284
85.6465
77.8457
77.4229
77.0000
68.1712
55.6170
32.5499
26.4915
tBu
O
O
R
R
O
OMe
(RR)-2e
200
180
160
140
120
100
80
60
40
20
0
(ppm)

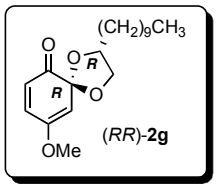
AM-B152-1 / 19090517-1/1 cd-cl3 DPX 300



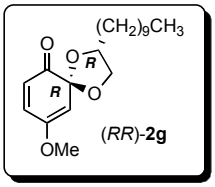
Peak Nr.	Frequency	PPM	Intensity	%Int.
1	2004.99	6.6833	84808075	1.7
2	2001.99	6.6733	89796793	1.8
3	1994.82	6.6494	79819370	1.6
4	1991.82	6.6394	84808071	1.7
5	1786.56	5.9552	99774202	2.0
6	1776.39	5.9213	94785491	1.9
7	1491.69	4.9723	89796787	1.8
8	1488.66	4.9622	89796785	1.8
9	1310.55	4.3685	64853231	1.3
10	1304.52	4.3484	84808073	1.7
11	1303.02	4.3434	84808072	1.7
12	1297.35	4.3245	84808082	1.7
13	1281.93	4.2731	89796781	1.8
14	1274.76	4.2492	104762912	2.1
15	1267.23	4.2241	84808077	1.7
16	1163.67	3.8789	79819362	1.6
17	1158.03	3.8601	84808080	1.7
18	1156.53	3.8551	84808072	1.7
19	1150.86	3.8362	69841941	1.4
20	1100.79	3.6693	1711127564	34.3
21	277.53	0.9251	4988710100	100.0


AM-B152-1 / 19090517-2/1 cd-cl3 DPX 300
197.6955
155.1266
140.5224
125.4891
100.8918
99.9100
84.6948
77.0000
66.1559
55.2901
33.0274
25.3108
25.2162
(SS)-3f
(ppm)
140.5369
125.4891
100.8772
84.6948
66.1559
55.3046
25.3107
25.2380
(ppm)

AM-B143 / 18070511.1-1 cd-cl3 DPX 300



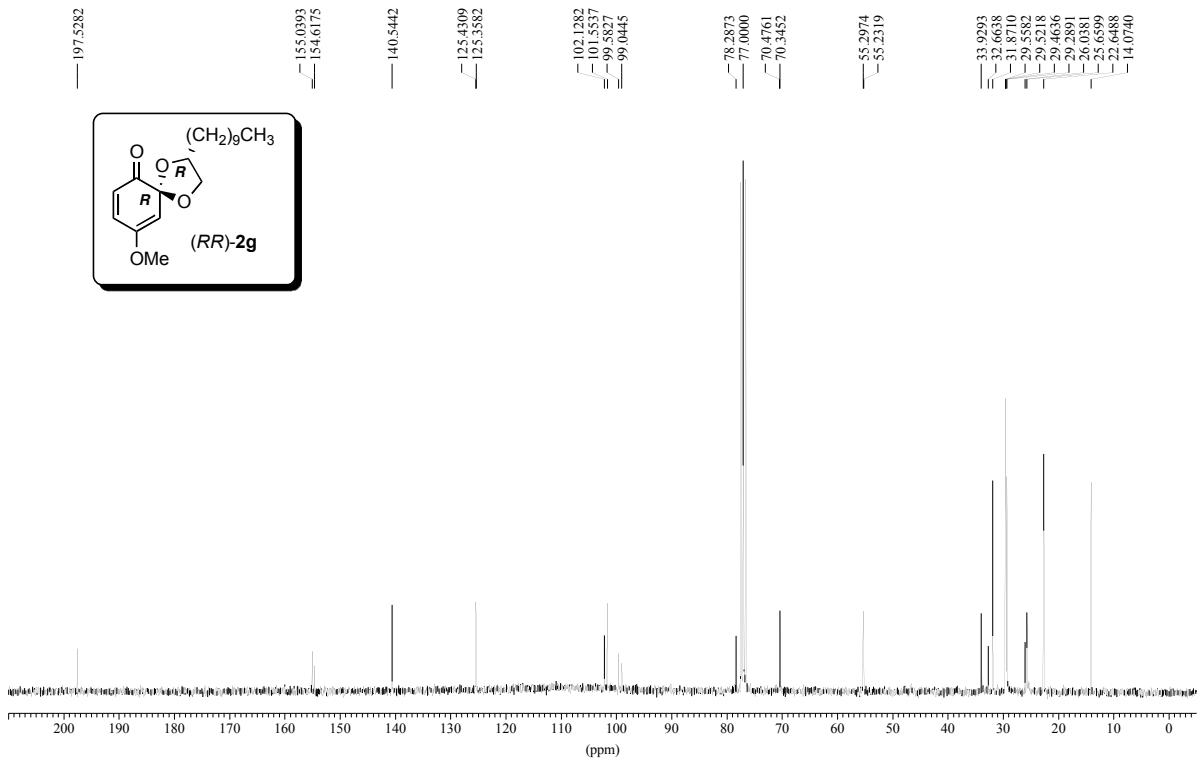
(*RR*)-**2g**



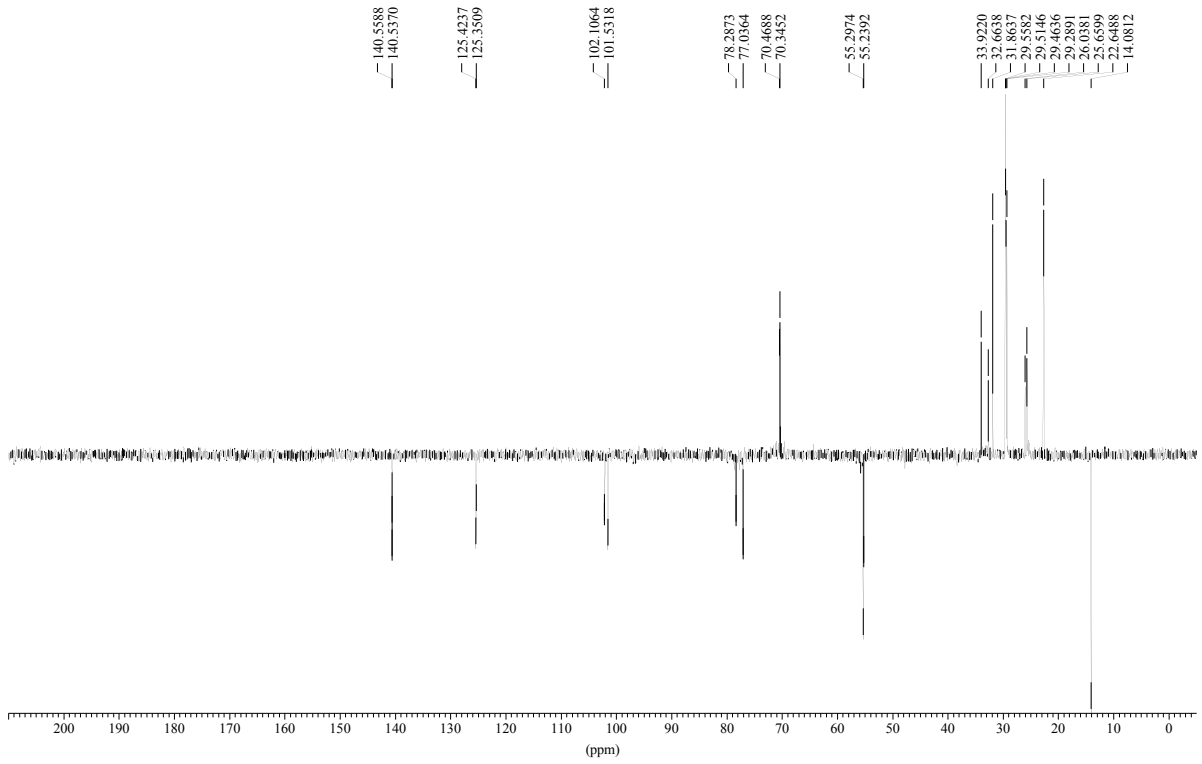
(*RR*)-**2g**

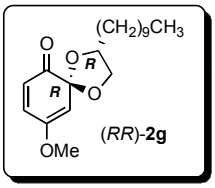
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9960	2179.54	7.2620	44095	12.3
2	10404	2012.26	6.7046	9838	2.7
3	10412	2009.25	6.6946	11022	3.1
4	10415	2008.12	6.6908	14246	4.0
5	10422	2005.48	6.6820	13551	3.8
6	10431	2002.09	6.6707	10723	3.0
7	10439	1999.08	6.6607	12513	3.5
8	10442	1997.95	6.6569	17442	4.9
9	10450	1994.93	6.6469	15710	4.4
10	10978	1796.00	5.9841	14157	3.9
11	10993	1790.35	5.9653	22840	6.4
12	11006	1785.45	5.9489	13439	3.7
13	11020	1780.18	5.9314	20000	5.6
14	11732	1511.92	5.0376	12732	3.5
15	11740	1508.91	5.0275	12367	3.4
16	11763	1500.25	4.9987	20018	5.6
17	11770	1497.61	4.9899	18634	5.2
18	12065	1386.46	4.6195	2609	0.7
19	12082	1380.06	4.5982	8918	2.5
20	12099	1373.65	4.5769	13584	3.8
21	12116	1367.25	4.5555	10546	2.9
22	12133	1360.84	4.5342	3577	1.0
23	12257	1314.13	4.3785	14973	4.2
24	12275	1307.34	4.3559	23666	6.6
25	12294	1300.19	4.3321	12429	3.5
26	12378	1268.54	4.2266	7783	2.2
27	12385	1265.90	4.2178	15536	4.3
28	12397	1261.38	4.2028	13817	3.9
29	12412	1255.73	4.1839	7336	2.0
30	12583	1191.30	3.9693	5174	1.4
31	12609	1181.51	3.9366	10184	2.8
32	12612	1180.38	3.9329	9663	2.7
33	12638	1170.58	3.9002	3917	1.1
34	12824	1100.50	3.6668	145282	40.5
35	12836	1095.98	3.6517	98629	27.5
36	14748	375.62	1.2515	358871	100.0
37	15033	268.24	0.8937	51484	14.3
38	15050	261.83	0.8724	137697	38.4
39	15069	254.68	0.8486	50881	14.2

AM-B143 / 18070511.2-1 cd-cl3 DPX 300



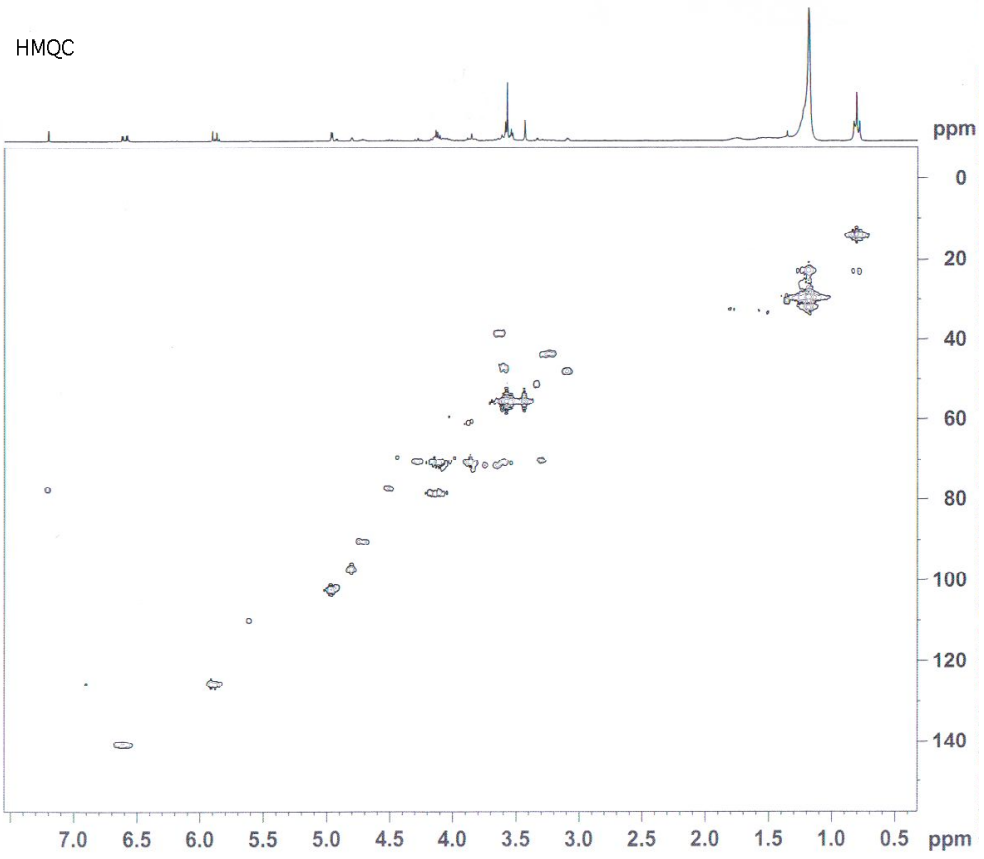
AM-B143 / 18070511.3-1 cd-cl3 DPX 300



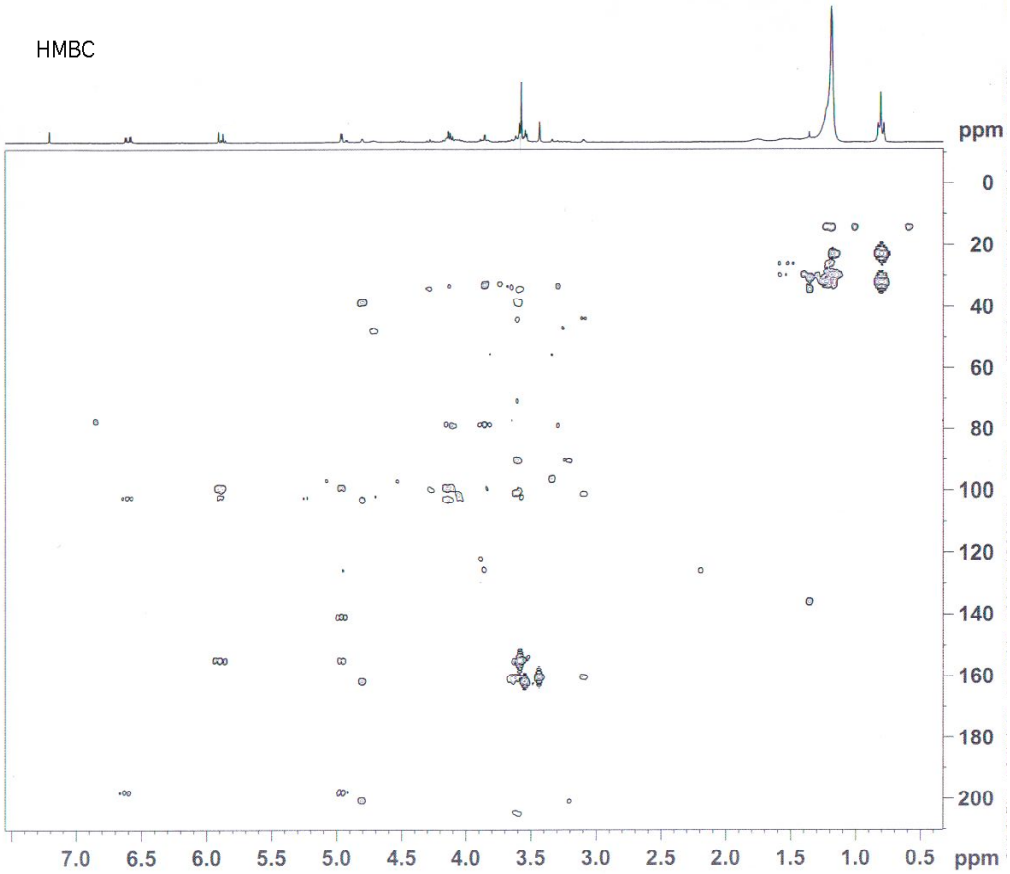


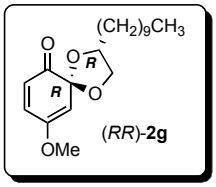
(*RR*)-**2g**

HMQC

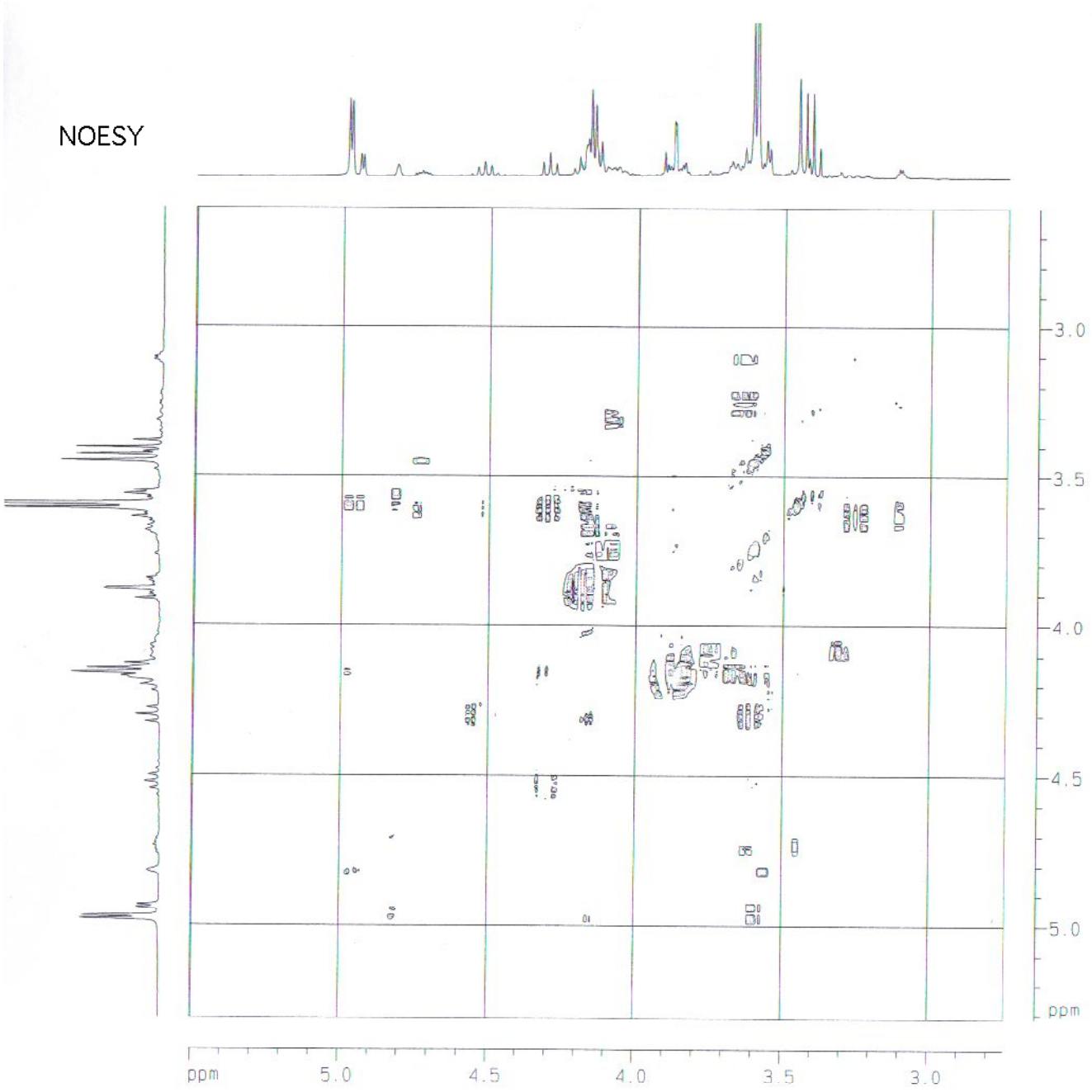


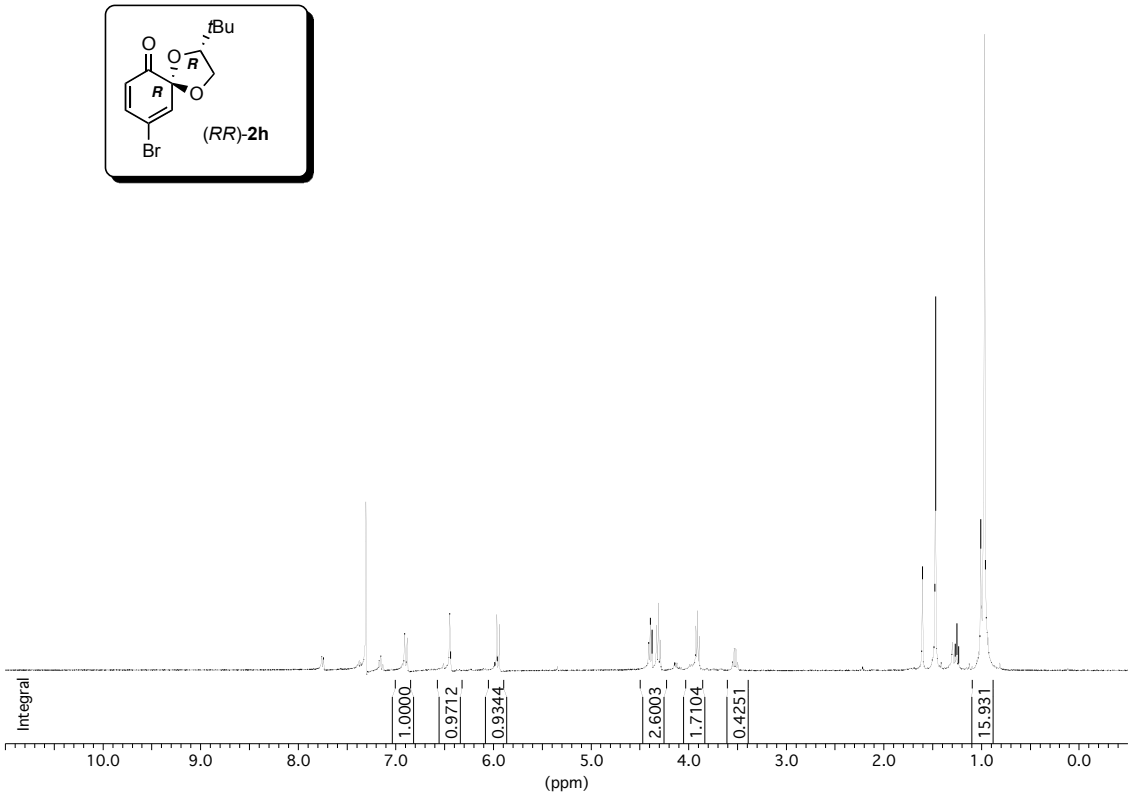
HMBC



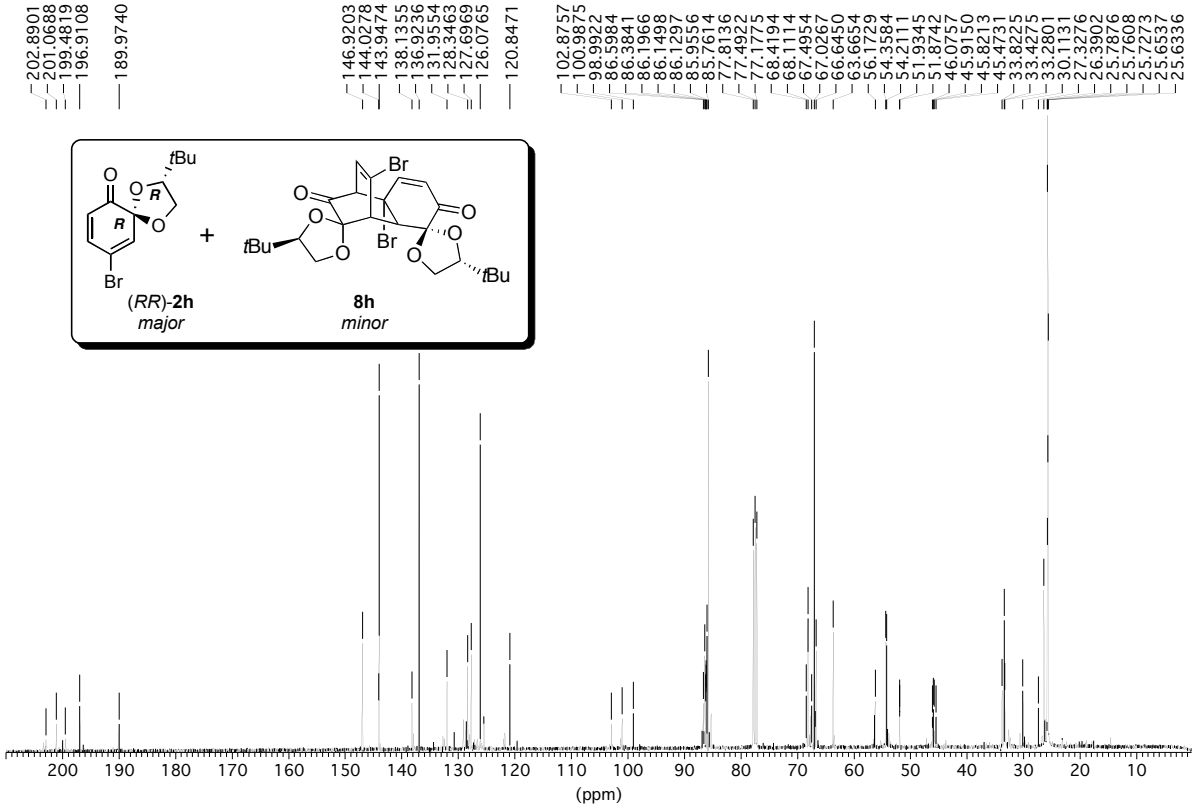


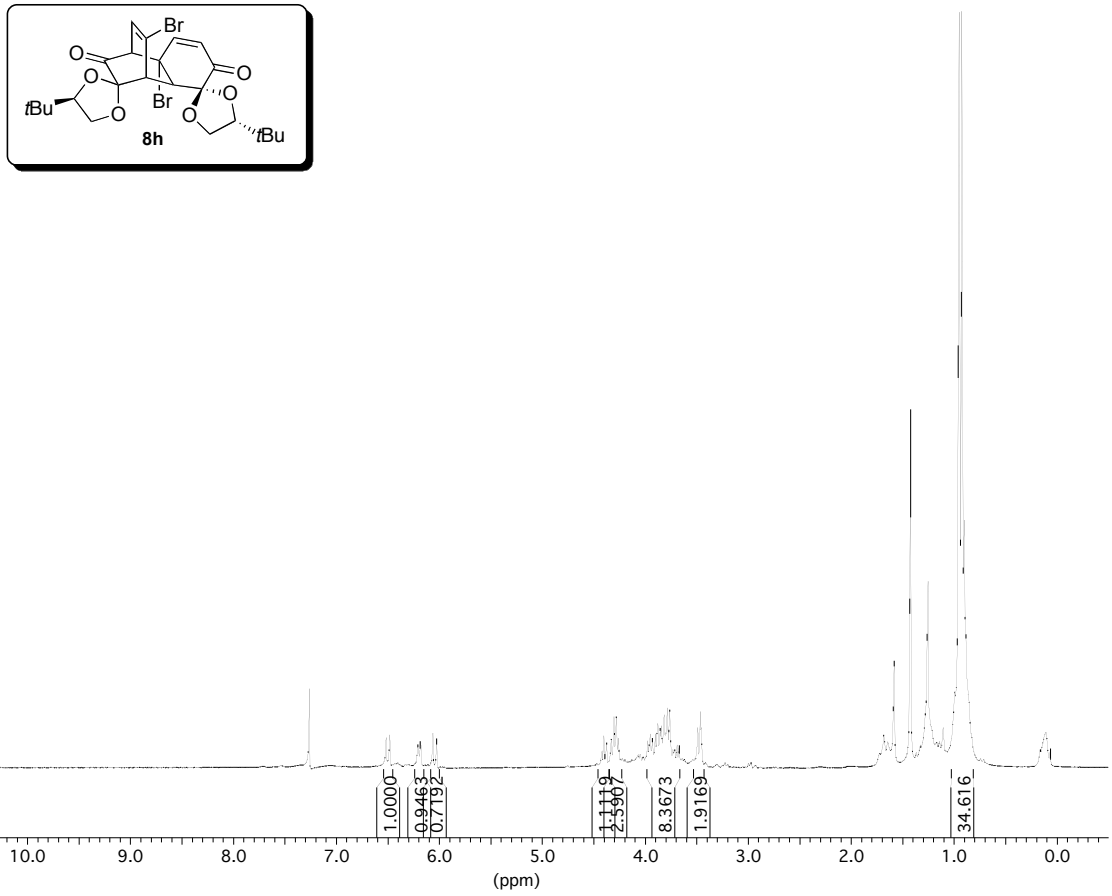
(*RR*)-**2g**

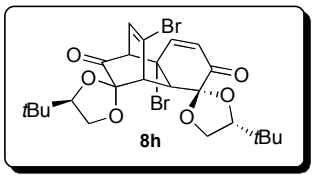




Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	12054	2923.42	7.3062	62709	11.5
2	12056	2923.00	7.3051	63740	11.7
3	12801	2764.23	6.9083	15479	2.8
4	12812	2761.88	6.9025	11257	2.1
5	12849	2754.00	6.8828	12350	2.3
6	12860	2751.65	6.8769	8194	1.5
7	13668	2579.46	6.4466	24330	4.5
8	13679	2577.11	6.4407	16456	3.0
9	14579	2385.31	5.9613	23442	4.3
10	14627	2375.09	5.9358	18309	3.3
11	17494	1764.09	4.4088	12828	2.3
12	17525	1757.49	4.3923	22583	4.1
13	17557	1750.67	4.3752	16613	3.0
14	17652	1730.42	4.3247	19235	3.5
15	17686	1723.18	4.3065	27291	5.0
16	17721	1715.72	4.2879	11593	2.1
17	18405	1569.95	3.9236	18872	3.5
18	18435	1563.56	3.9076	25010	4.6
19	18469	1556.31	3.8895	13241	2.4
20	19142	1412.89	3.5311	9206	1.7
21	19175	1405.85	3.5135	8819	1.6
22	23955	387.18	0.9676	546670	100.0

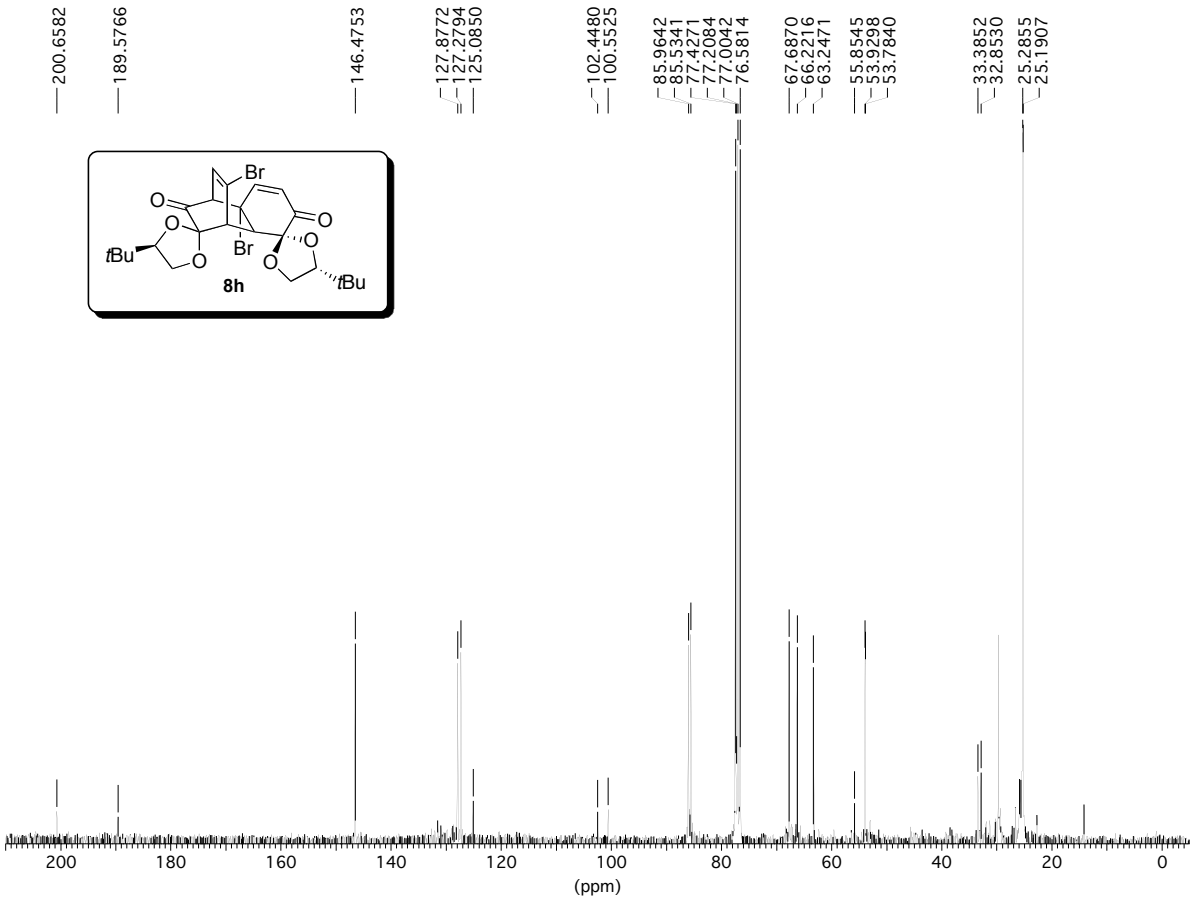

202.8901
201.0688
199.4819
196.9108
189.9740
146.9203
144.0278
143.9474
138.1355
136.9236
131.9554
128.3463
127.6969
126.0765
120.8471
102.8757
100.9875
98.9922
86.5984
86.3841
86.1966
86.1498
86.1297
85.9556
85.7614
77.8136
77.4922
77.1775
68.4194
68.1114
67.4954
67.0267
66.6450
63.6654
56.1729
54.3584
54.2111
51.9345
51.8742
46.0757
45.9150
45.8213
45.4731
33.8225
33.4275
33.2801
30.1131
27.3276
26.3902
25.7876
25.7608
25.7273
25.6537
25.6336
tBu
O
O
R
R
O
Br
+
Br
O
O
tBu
O
Br
O
O
tBu
(RR)-2h
major
8h
minor
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

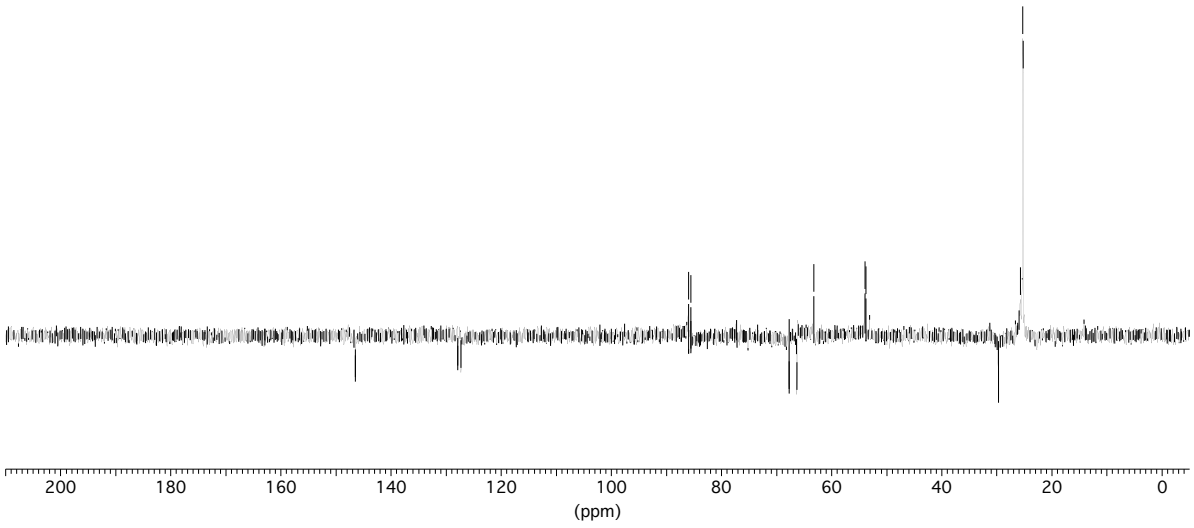

Br
O
O
O
tBu
O
Br
O
O
tBu
8h
Integral
1.0000
0.9463
0.7792
1.1119
2.5307
8.3673
1.9169
34.616
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

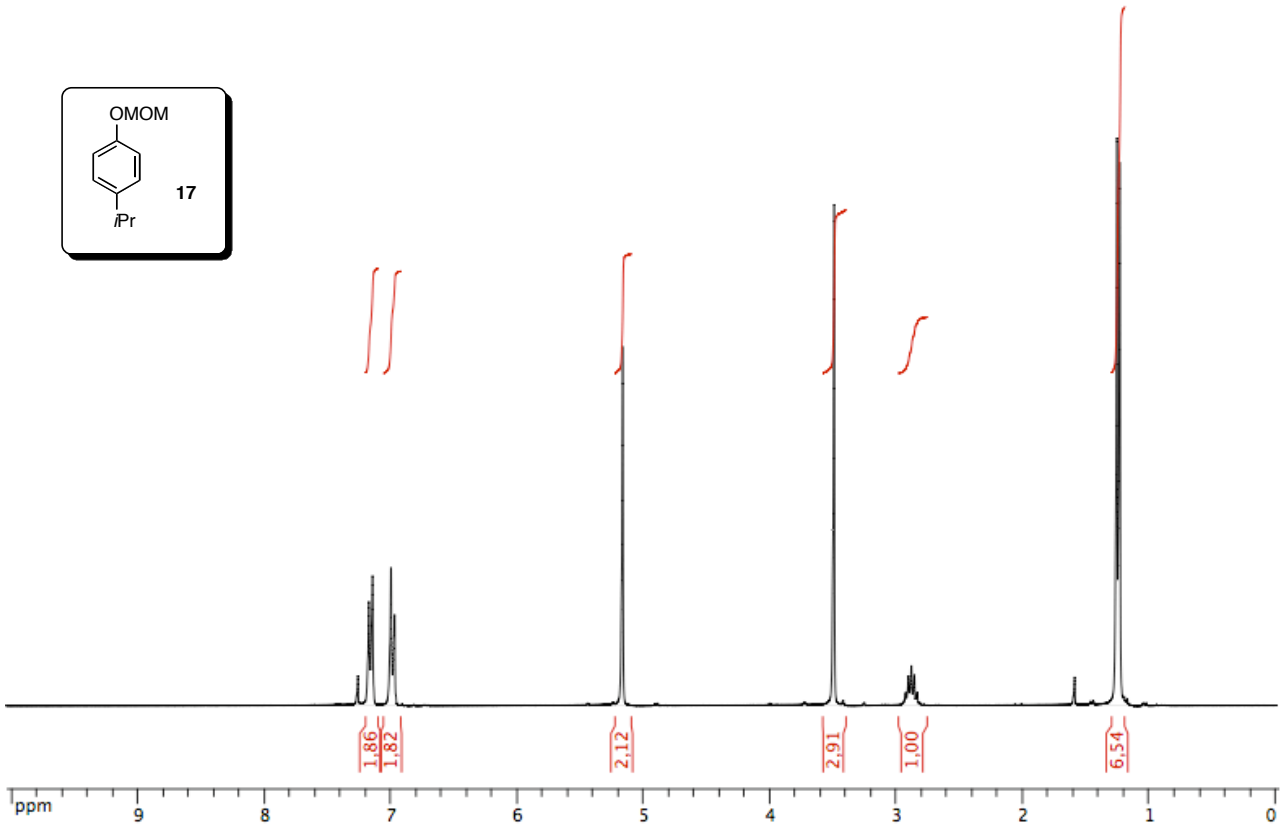


8h

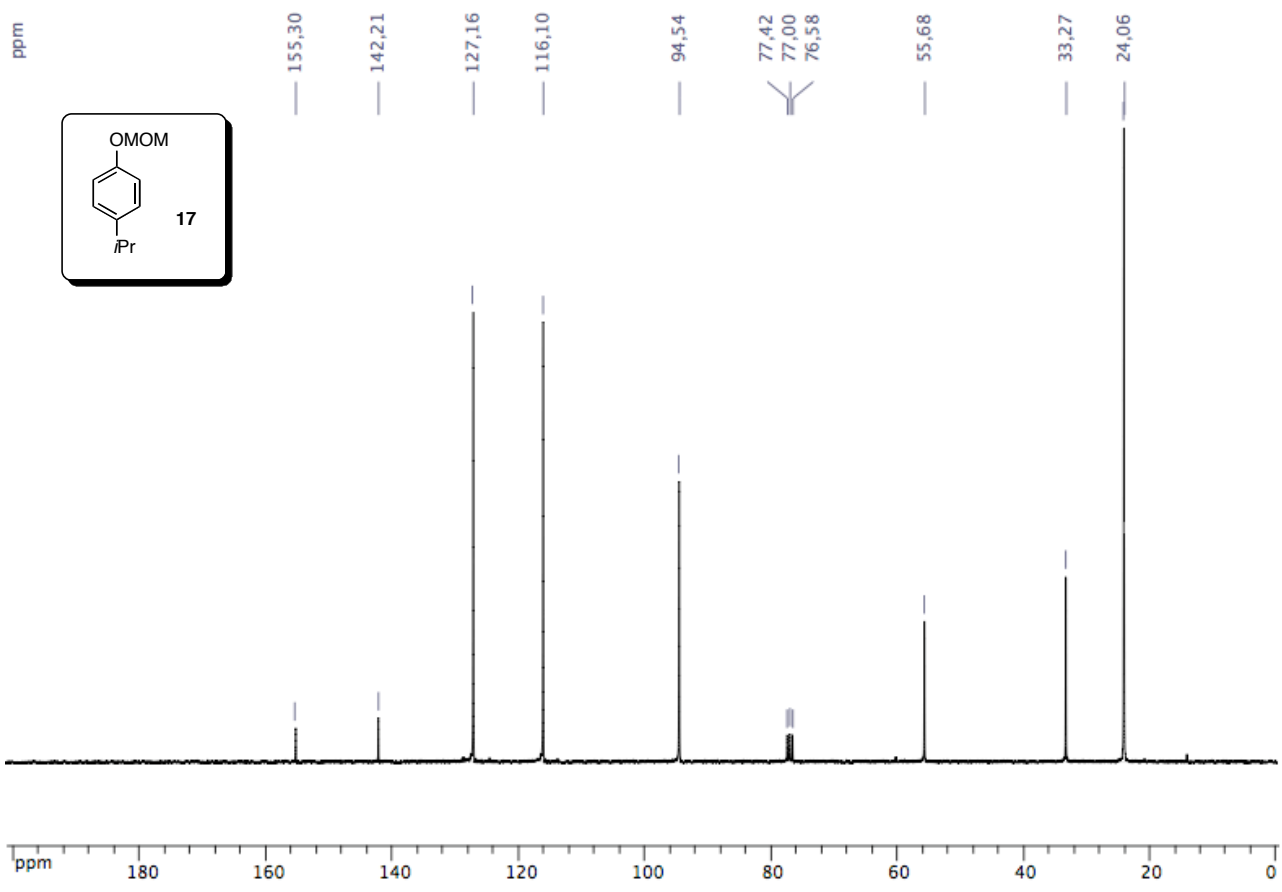
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14629	2178.94	7.2600	34706168	10.5
2	15812	1955.54	6.5156	13381328	4.1
3	15866	1945.34	6.4817	14550787	4.4
4	16302	1863.00	6.2073	10520717	3.2
5	16315	1860.55	6.1991	8808725	2.7
6	16339	1856.02	6.1840	11876054	3.6
7	16351	1853.75	6.1765	9788279	3.0
8	16538	1818.44	6.0588	15509057	4.7
9	16592	1808.24	6.0248	12977020	3.9
10	19142	1326.68	4.4204	7582041	2.3
11	19177	1320.07	4.3983	14166933	4.3
12	19213	1313.27	4.3757	11310800	3.4
13	19289	1298.92	4.3279	12911380	3.9
14	19328	1291.55	4.3033	22621730	6.9
15	19365	1284.57	4.2800	22525652	6.8
16	19403	1277.39	4.2561	13162968	4.0
17	19851	1192.79	3.9742	11968265	3.6
18	19880	1187.31	3.9560	12515632	3.8
19	19895	1184.48	3.9466	15142879	4.6
20	19923	1179.19	3.9289	13172089	4.0
21	19970	1170.32	3.8994	15060840	4.6
22	20004	1163.89	3.8780	19533276	5.9
23	20043	1156.53	3.8534	17636968	5.3
24	20063	1152.75	3.8408	18705490	5.7
25	20102	1145.39	3.8163	23331846	7.1
26	20128	1140.48	3.7999	15609039	4.7
27	20153	1135.76	3.7842	26317048	8.0
28	20188	1129.15	3.7622	25525486	7.7
29	20240	1119.33	3.7295	8278759	2.5
30	20268	1114.04	3.7119	8310358	2.5
31	20306	1106.86	3.6879	10317608	3.1
32	20336	1101.20	3.6691	9986610	3.0
33	20623	1047.00	3.4885	17769660	5.4
34	20660	1040.01	3.4652	24738732	7.5
35	20676	1036.99	3.4551	17779082	5.4
36	24657	285.19	0.9502	329392736	99.9
37	24701	276.88	0.9225	329750080	100.0

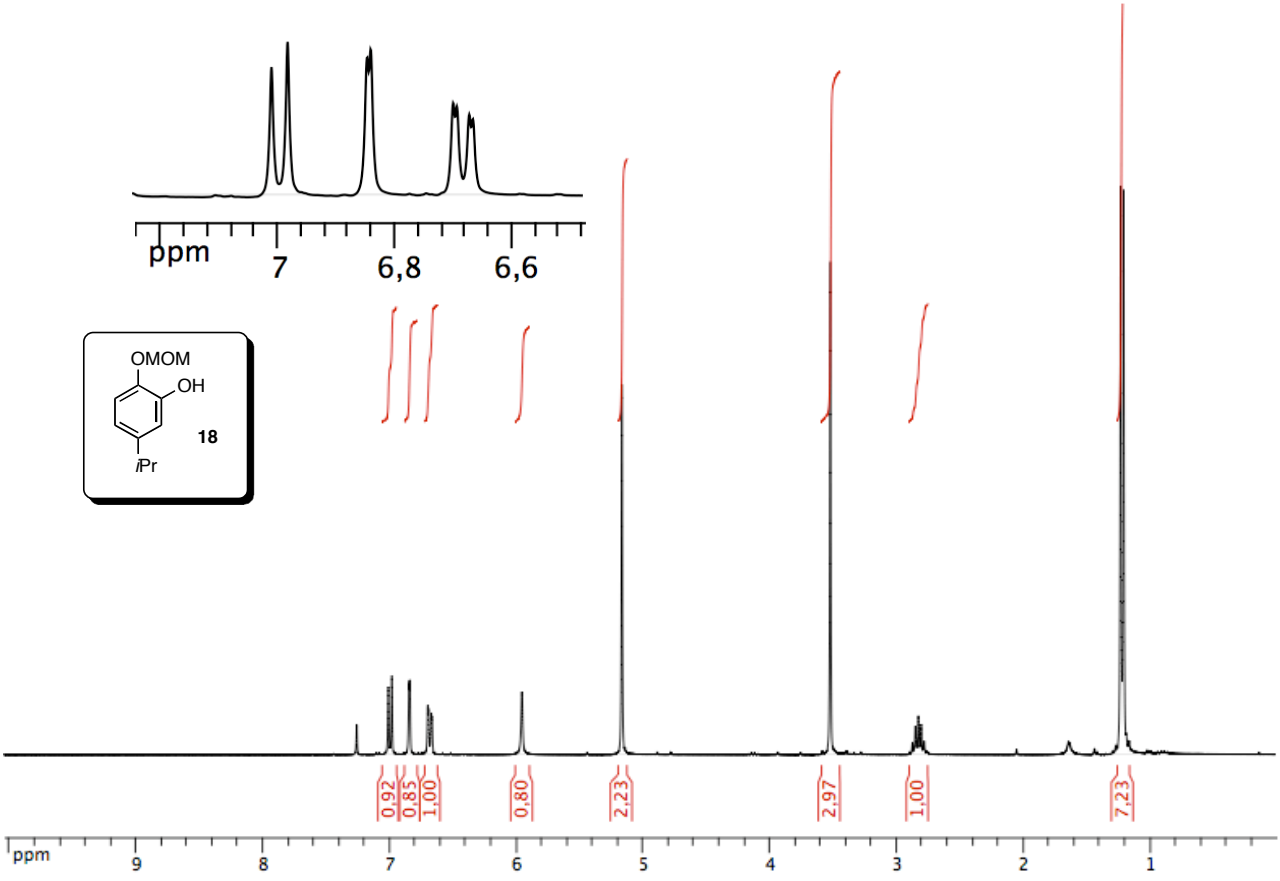

200.6582
189.5766
146.4753
127.8772
127.2794
125.0850
102.4480
100.5525
85.9642
85.5341
77.4271
77.2084
77.0042
76.5814
67.6870
66.2216
63.2471
55.8545
53.9298
53.7840
33.3852
32.8530
25.2855
25.1907
Br
O
O
O
O
O
Br
tBu
tBu
8h
200
180
160
140
120
100
80
60
40
20
0
(ppm)


200
180
160
140
120
100
80
60
40
20
0
(ppm)

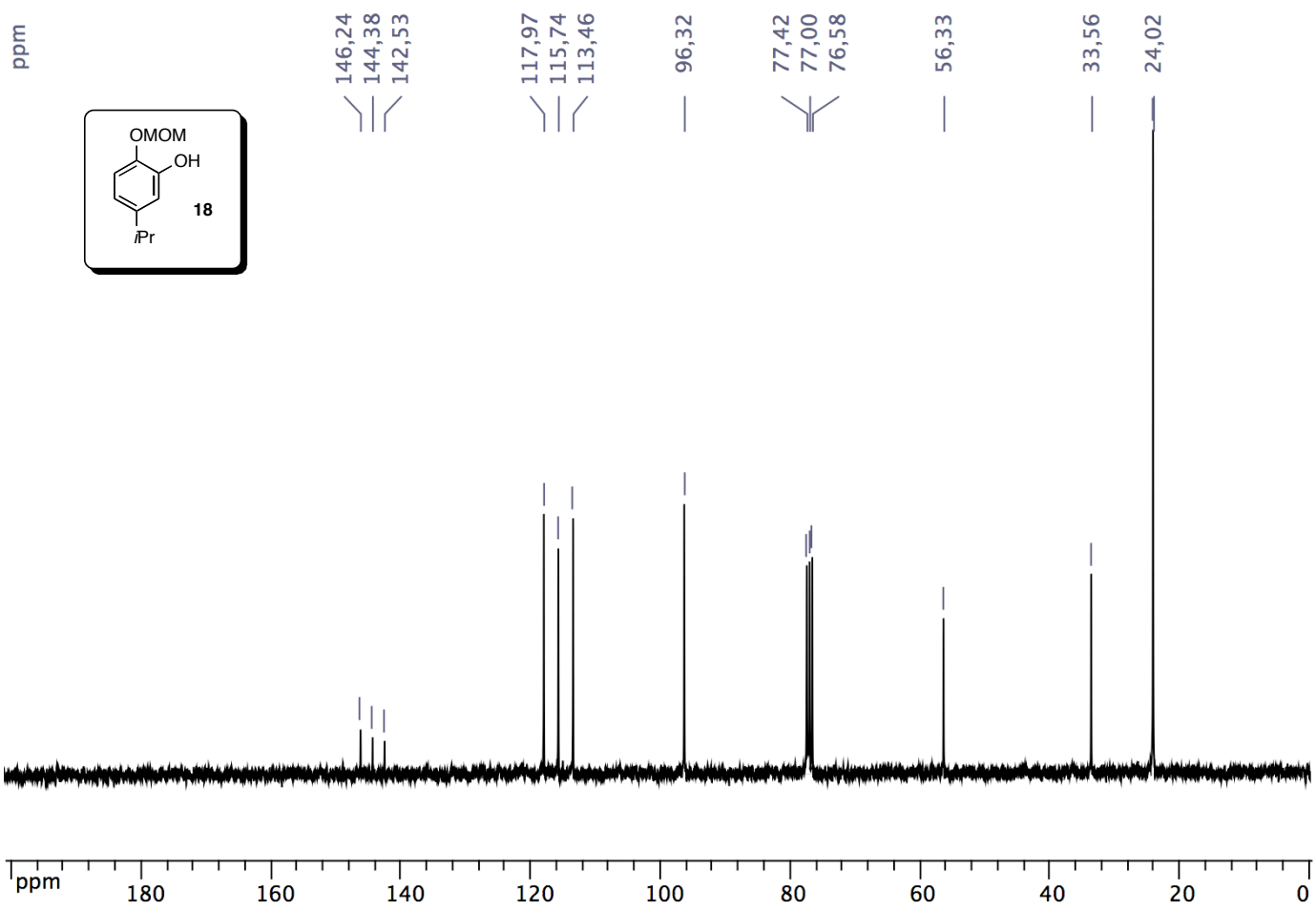


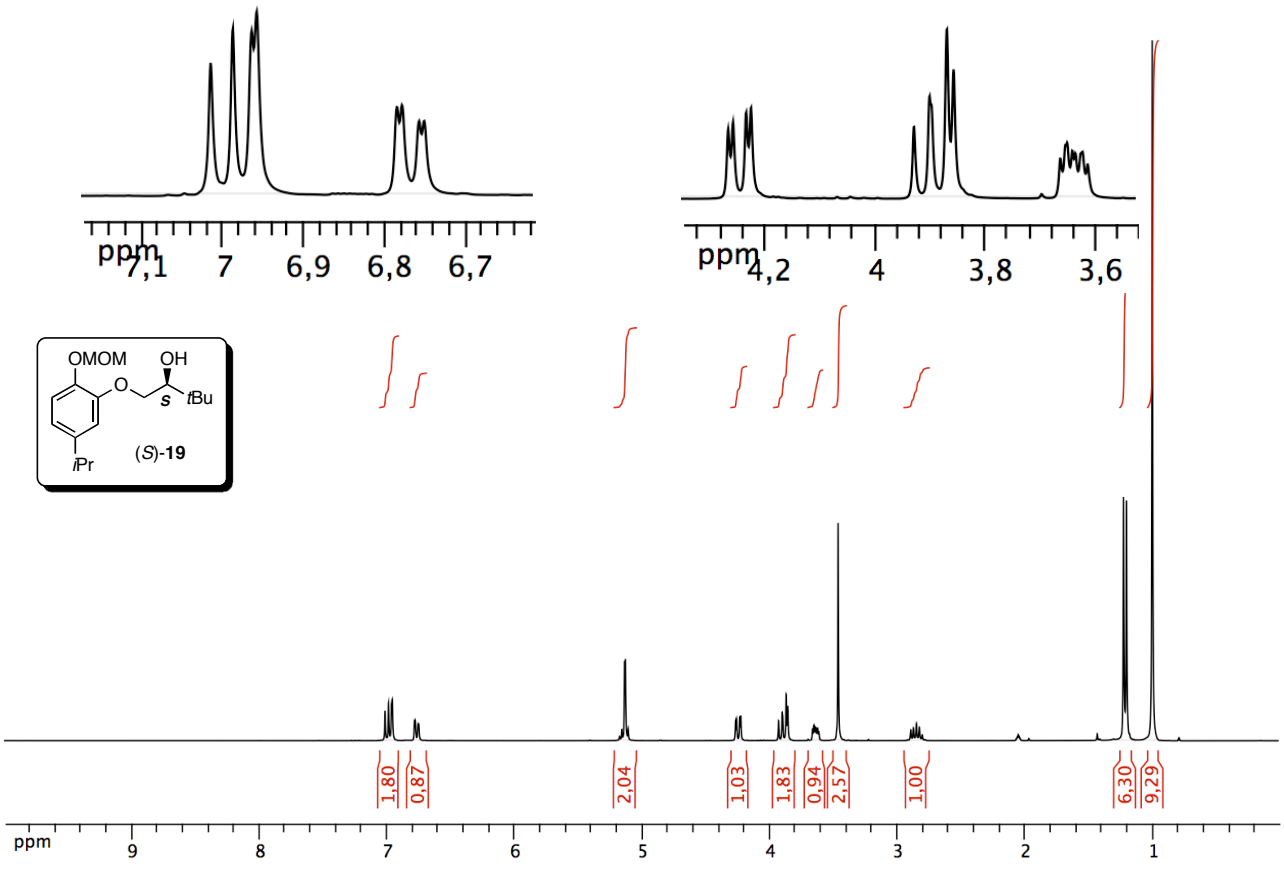
Label	Intensity	Frequency(point)	Frequency(ppm)	Frequency(Hz)
1	14721679	14632	7,26	2178,957
2	50599764	14770	7,173	2152,896
3	65410632	14815	7,145	2144,397
4	68346992	15048	6,998	2100,395
5	46856796	15093	6,97	2091,897
6	179376656	17963	5,164	1549,891
7	247921760	20622	3,491	1047,733
8	6489258	21521	2,925	877,955
9	15045376	21558	2,902	870,967
10	19997624	21594	2,879	864,169
11	15391023	21631	2,856	857,181
12	6696433,5	21667	2,833	850,382
13	280627872	24180	1,252	375,797
14	265291440	24217	1,229	368,809

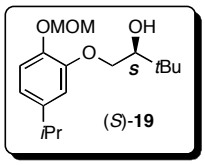

ppm
155,30
142,21
127,16
116,10
94,54
77,42
77,00
76,58
55,68
33,27
24,06
OMOM
17
iPr
ppm
180
160
140
120
100
80
60
40
20
0



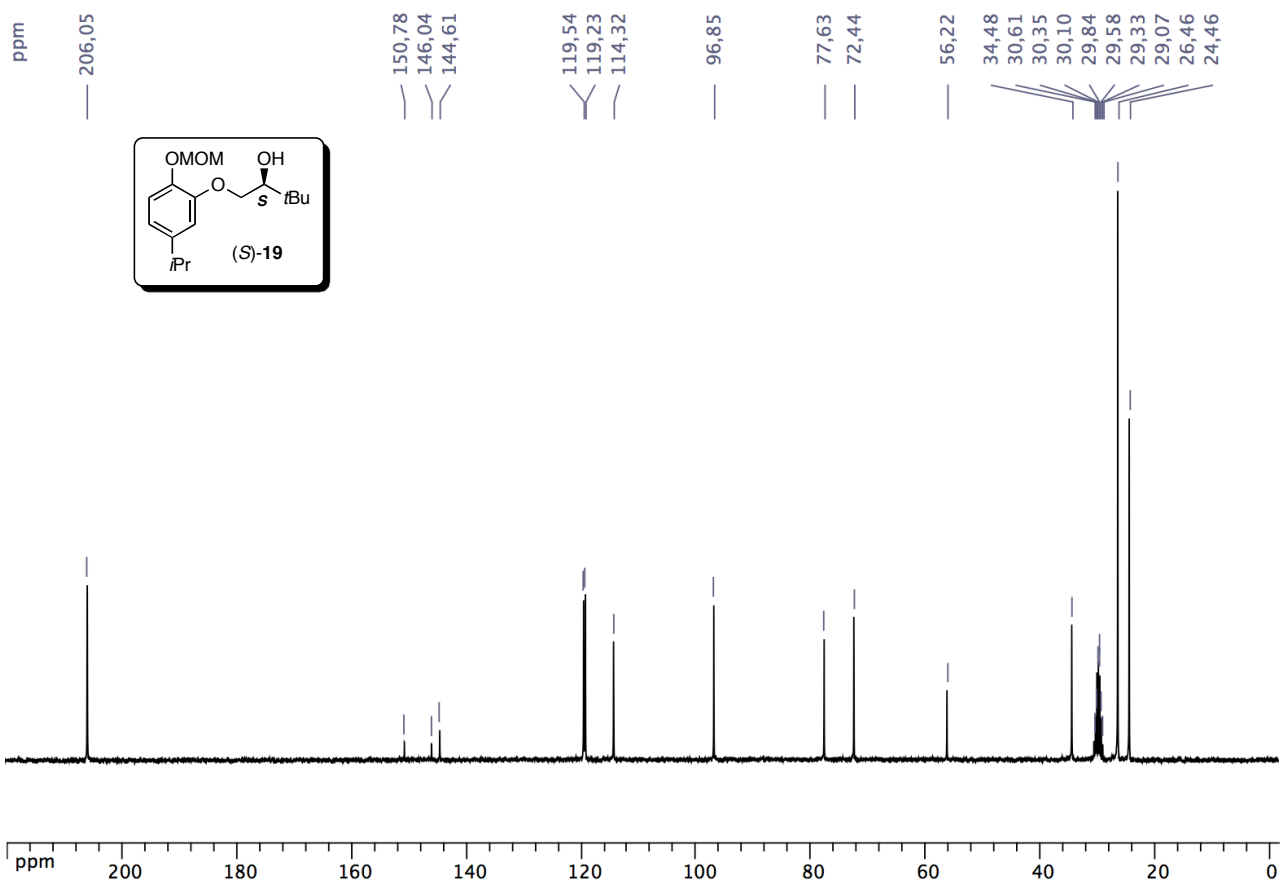
Label	Intensity	Frequency(point)	Frequency(ppm)	Frequency(Hz)
1	18249978	14630	7,26	2178,957
2	41286996	15026	7,011	2104,172
3	48318332	15070	6,983	2095,862
4	44626800	15286	6,847	2055,07
5	45562500	15296	6,841	2053,182
6	30093106	15521	6,699	2010,69
7	28026848	15531	6,693	2008,802
8	25613738	15565	6,672	2002,381
9	23330688	15575	6,665	2000,492
10	38272644	16702	5,956	1787,656
11	224881920	17957	5,167	1550,646
12	299737728	20572	3,521	1056,798
13	1414863,75	21566	2,896	869,079
14	7091899	21603	2,872	862,091
15	17432748	21639	2,85	855,293
16	23733594	21676	2,826	848,305
17	18612550	21712	2,804	841,506
18	8185277,5	21749	2,781	834,519
19	1935276,875	21785	2,758	827,72
20	345712224	24214	1,229	368,998
21	343448288	24251	1,206	362,011

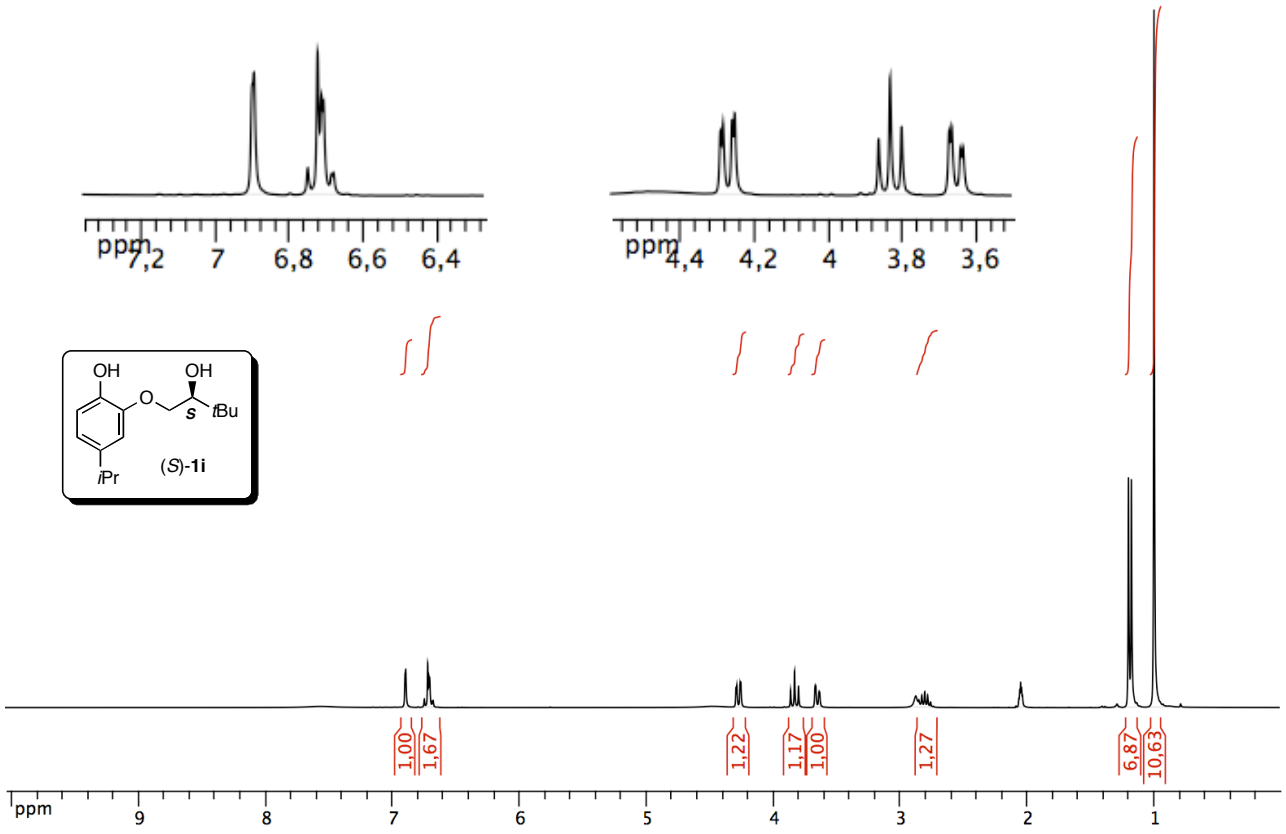

ppm
146,24
144,38
142,53
117,97
115,74
113,46
96,32
77,42
77,00
76,58
56,33
33,56
24,02
OMOM
OH
18
iPr
ppm
180
160
140
120
100
80
60
40
20
0


OMOM
OH
O
s
tBu
iPr
(S)-19
ppm
7,1
7
6,9
6,8
6,7
ppm
4,2
4
3,8
3,6
1,80
0,87
2,04
1,03
1,83
0,94
2,57
1,00
6,30
9,29
ppm
9
8
7
6
5
4
3
2
1

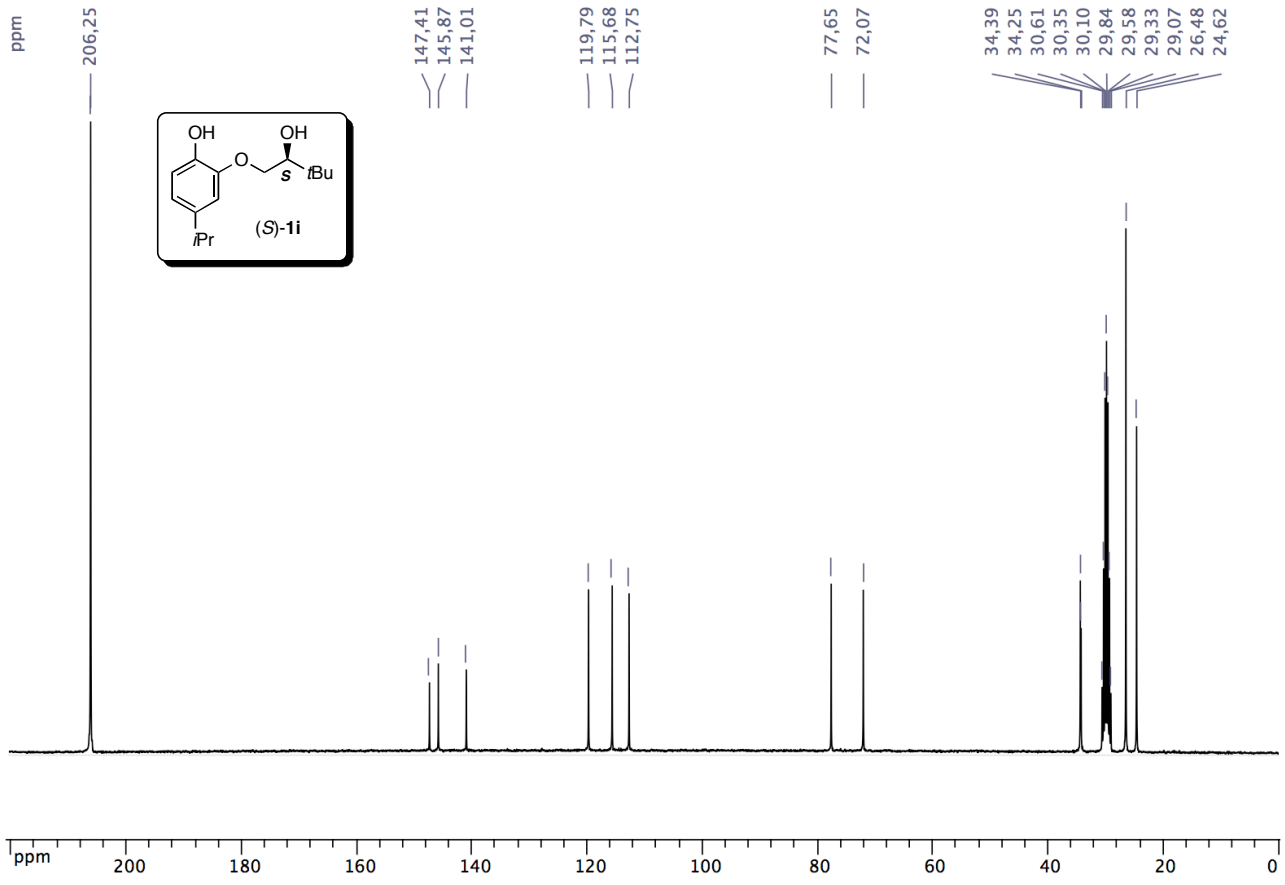


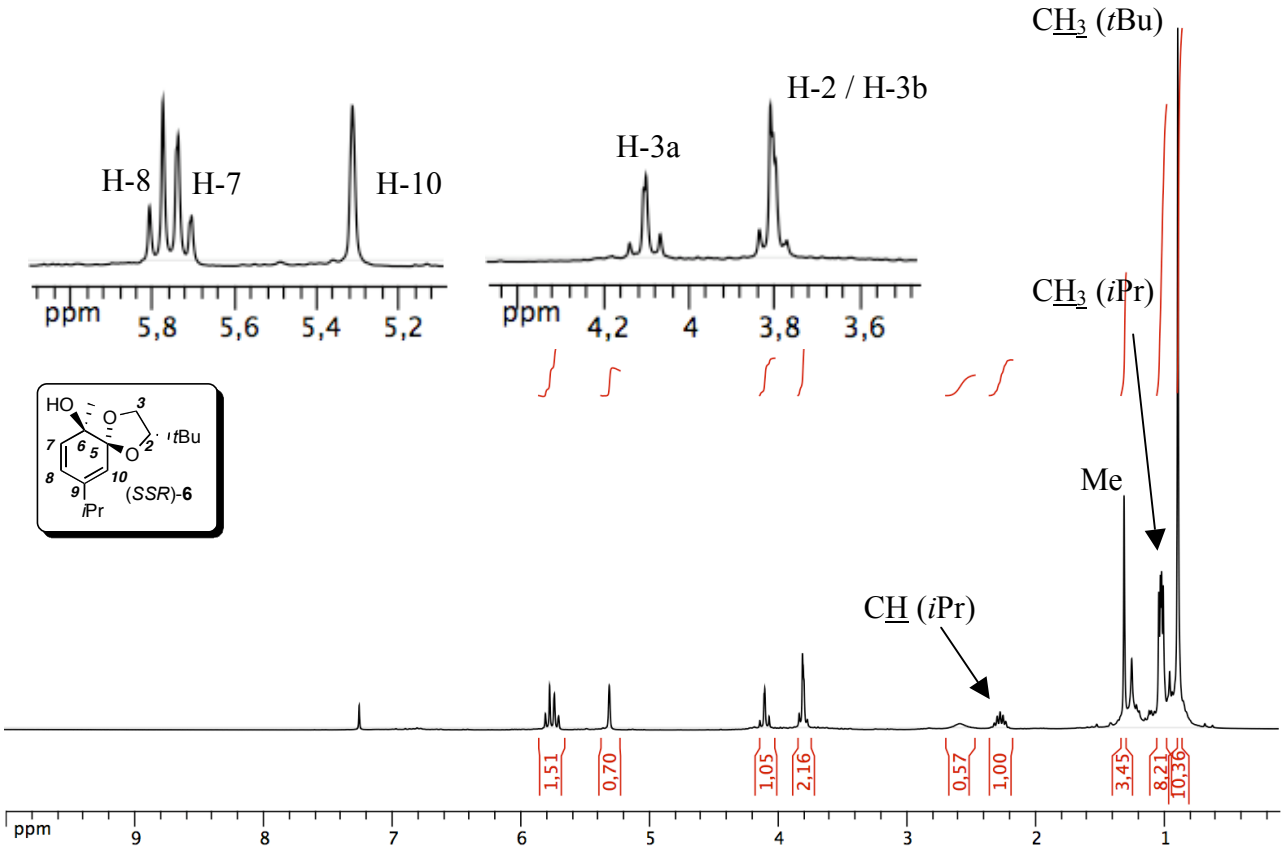
Label	Intensity	Frequency(point)	Frequency(ppm)	Frequency(Hz)
1	94809040	15029	7,015	2105,503
2	119276680	15073	6,988	2097,193
3	117826968	15110	6,964	2090,206
4	131552176	15120	6,958	2088,317
5	63124812	15396	6,784	2036,194
6	64559092	15406	6,778	2034,305
7	53150152	15440	6,757	2027,884
8	53204396	15450	6,75	2025,996
9	33666792	17980	5,158	1548,2
10	252256256	18014	5,137	1541,779
11	262132864	18024	5,131	1539,89
12	40377080	18059	5,109	1533,281
13	60439824	19397	4,267	1280,596
14	66485868	19411	4,258	1277,953
15	75028080	19449	4,234	1270,776
16	79030048	19463	4,225	1268,132
17	62215644	19934	3,929	1179,183
18	89136064	19979	3,901	1170,685
19	147478544	20029	3,869	1161,242
20	112574152	20048	3,857	1157,654
21	34541952	20356	3,663	1099,487
22	46484804	20371	3,654	1096,654
23	48599668	20376	3,651	1095,71
24	41428240	20391	3,641	1092,877
25	39225712	20400	3,636	1091,178
26	39321716	20416	3,626	1088,156
27	40577612	20421	3,622	1087,212
28	29436266	20436	3,613	1084,379
29	697145536	20675	3,463	1039,243
30	2432325	21541	2,918	875,697
31	33543500	21582	2,892	867,955
32	40156644	21614	2,872	861,911
33	55129108	21651	2,848	854,924
34	43398284	21688	2,825	847,936
35	19083108	21724	2,803	841,138
36	4155993,25	21760	2,78	834,339
37	6272141,5	22897	2,064	619,614
38	12908329	22909	2,057	617,348
39	18680584	22920	2,05	615,27
40	14162938	22932	2,042	613,004
41	8019462,5	22943	2,036	610,927
42	773893248	24232	1,224	367,496
43	772503616	24269	1,201	360,509
44	2238245888	24590	0,999	299,887


ppm
206,05
150,78
146,04
144,61
119,54
119,23
114,32
96,85
77,63
72,44
56,22
34,48
30,61
30,35
30,10
29,84
29,58
29,33
29,07
26,46
24,46
OMOM
OH
O
s
tBu
iPr
(S)-19
ppm
200
180
160
140
120
100
80
60
40
20
0

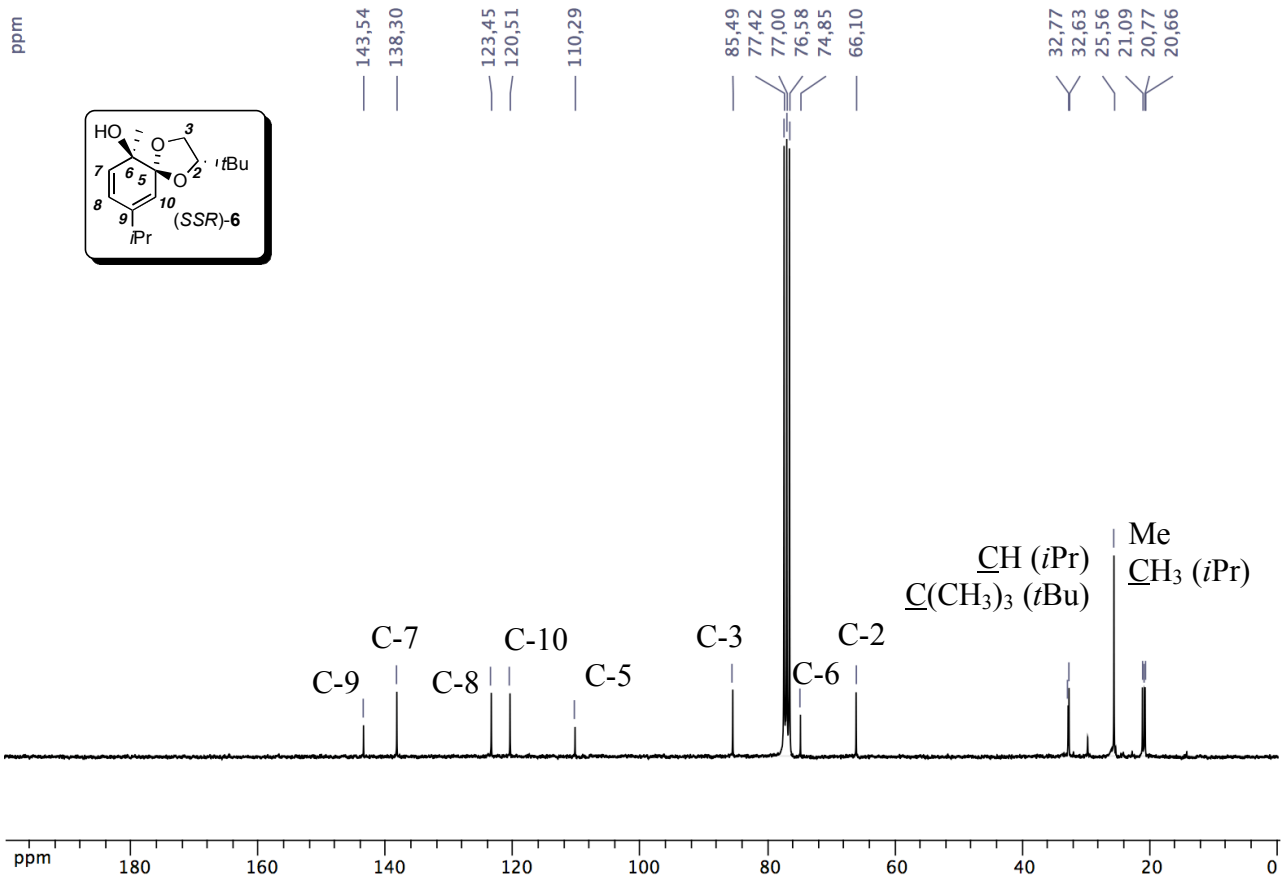


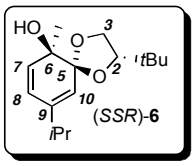
Label	Intensity	Frequency(point)	Frequency(ppm)	Frequency(Hz)
1	553796096	15210	6,902	2071,32
2	610891328	15217	6,897	2069,998
3	138383696	15450	6,75	2025,996
4	712824640	15492	6,723	2018,064
5	497303936	15509	6,713	2014,854
6	471264576	15518	6,708	2013,154
7	109477176	15553	6,686	2006,544
8	115751424	15561	6,681	2005,033
9	321596000	19354	4,294	1288,717
10	362444512	19365	4,287	1286,64
11	380918240	19404	4,262	1279,275
12	409392064	19415	4,255	1277,197
13	286127488	20038	3,863	1159,542
14	587359616	20088	3,832	1150,1
15	341215488	20138	3,801	1140,657
16	320251936	20343	3,672	1101,942
17	346957664	20354	3,665	1099,865
18	233402544	20392	3,641	1092,689
19	246312064	20403	3,634	1090,611
20	187645392	21607	2,876	863,233
21	127885440	21645	2,852	856,057
22	199247936	21682	2,829	849,069
23	255978128	21719	2,806	842,082
24	202809184	21755	2,783	835,283
25	91443928	21792	2,76	828,296
26	142326352	22897	2,064	619,614
27	286307904	22909	2,057	617,348
28	414686048	22920	2,05	615,27
29	324380672	22931	2,043	613,193
30	196770288	22943	2,036	610,927
31	3691744256	24271	1,2	360,131
32	3662365952	24307	1,177	353,332
33	11183722496	24591	0,999	299,698


ppm
206,25
147,41
145,87
141,01
119,79
115,68
112,75
77,65
72,07
34,39
34,25
30,61
30,35
30,10
29,84
29,58
29,33
29,07
26,48
24,62
OH
OH
O
S
tBu
iPr
(S)-1i
ppm
200
180
160
140
120
100
80
60
40
20
0

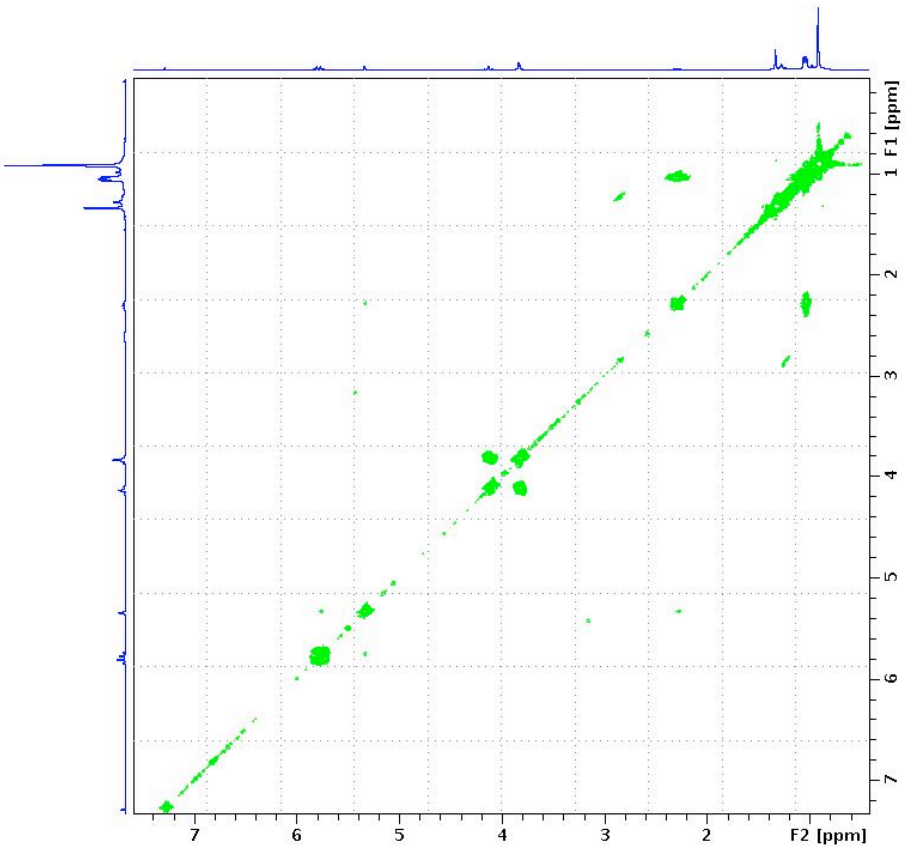


Label	Intensity	Frequency(point)	Frequency(ppm)	Frequency(Hz)
1	56651420	14629	7,26	2178,957
2	35238376	16931	5,812	1744,22
3	105076472	16983	5,779	1734,399
4	85998016	17043	5,741	1723,068
5	30775748	17095	5,708	1713,248
6	105112040	17720	5,315	1595,215
7	17887750	19582	4,143	1243,573
8	85321424	19636	4,109	1233,375
9	98615304	19643	4,105	1232,053
10	29064772	19696	4,072	1222,043
11	35266224	20068	3,838	1151,79
12	183823120	20109	3,812	1144,048
13	157322704	20117	3,807	1142,537
14	123356320	20127	3,8	1140,648
15	22608640	20169	3,774	1132,716
16	10806763	22055	2,587	776,541
17	2492804,5	22446	2,341	702,7
18	12303547	22481	2,319	696,09
19	29164236	22517	2,297	689,292
20	39860800	22552	2,275	682,682
21	31826820	22588	2,252	675,883
22	16835088	22620	2,232	669,84
23	2229330,75	22657	2,209	662,852
24	574739264	24084	1,311	393,36
25	335732448	24513	1,041	312,343
26	378655456	24532	1,029	308,754
27	390060288	24548	1,019	305,733
28	356679808	24568	1,007	301,956
29	1735204736	24748	0,893	267,962

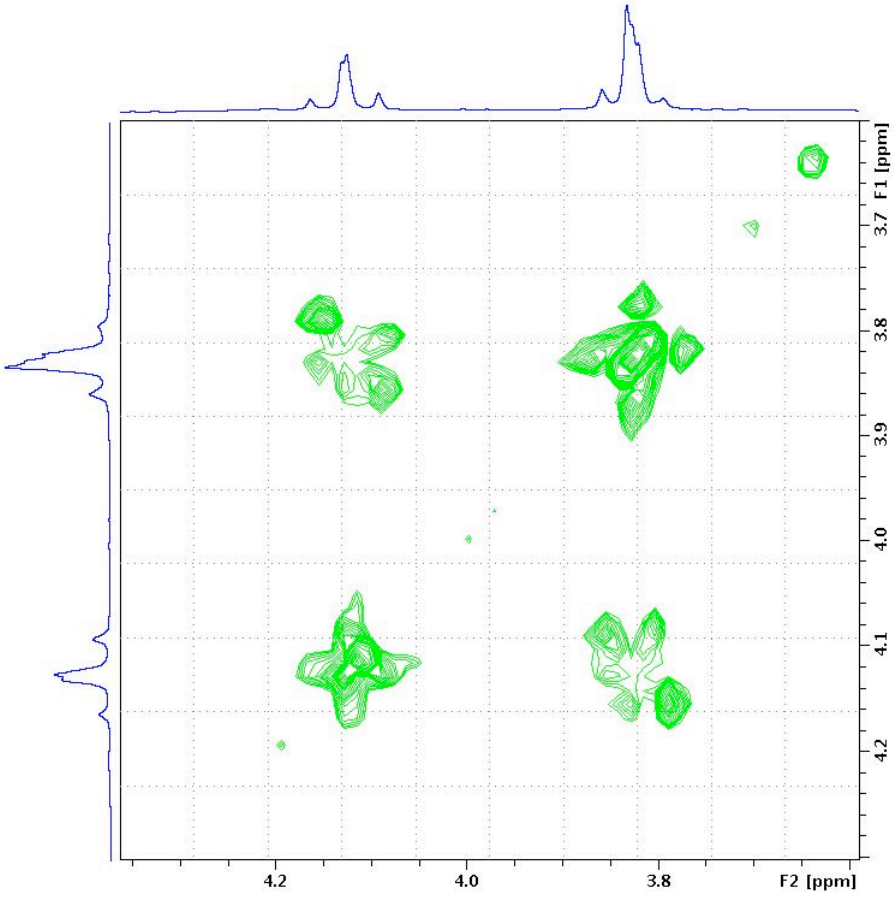

ppm
143,54
138,30
123,45
120,51
110,29
85,49
77,42
77,00
76,58
74,85
66,10
32,77
32,63
25,56
21,09
20,77
20,66
HO
O
O
3
2
7
6
5
8
9
10
tBu
iPr
(SSR)-6
C-9
C-7
C-8
C-10
C-5
C-3
C-6
C-2
CH (iPr)
C(CH3)3 (tBu)
Me
CH3 (iPr)
ppm
180
160
140
120
100
80
60
40
20
0

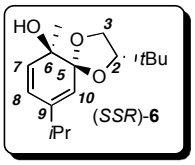


COSY

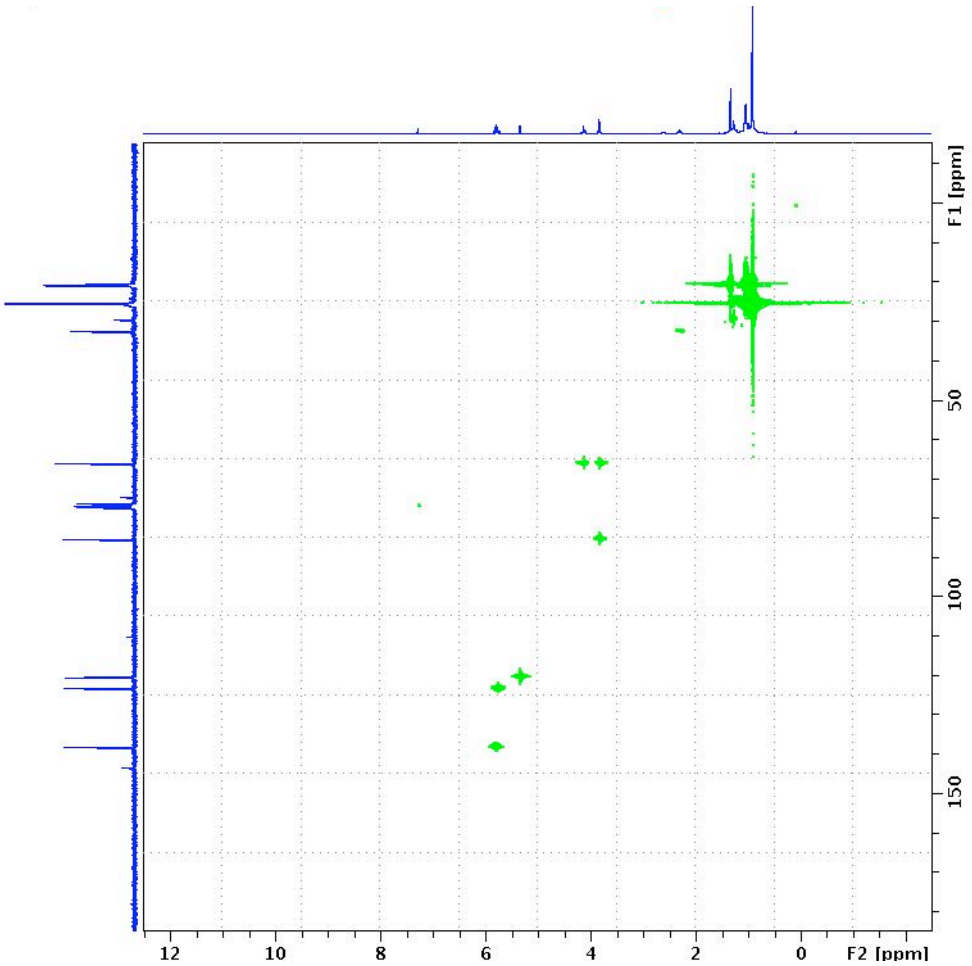


COSY
(zoom)

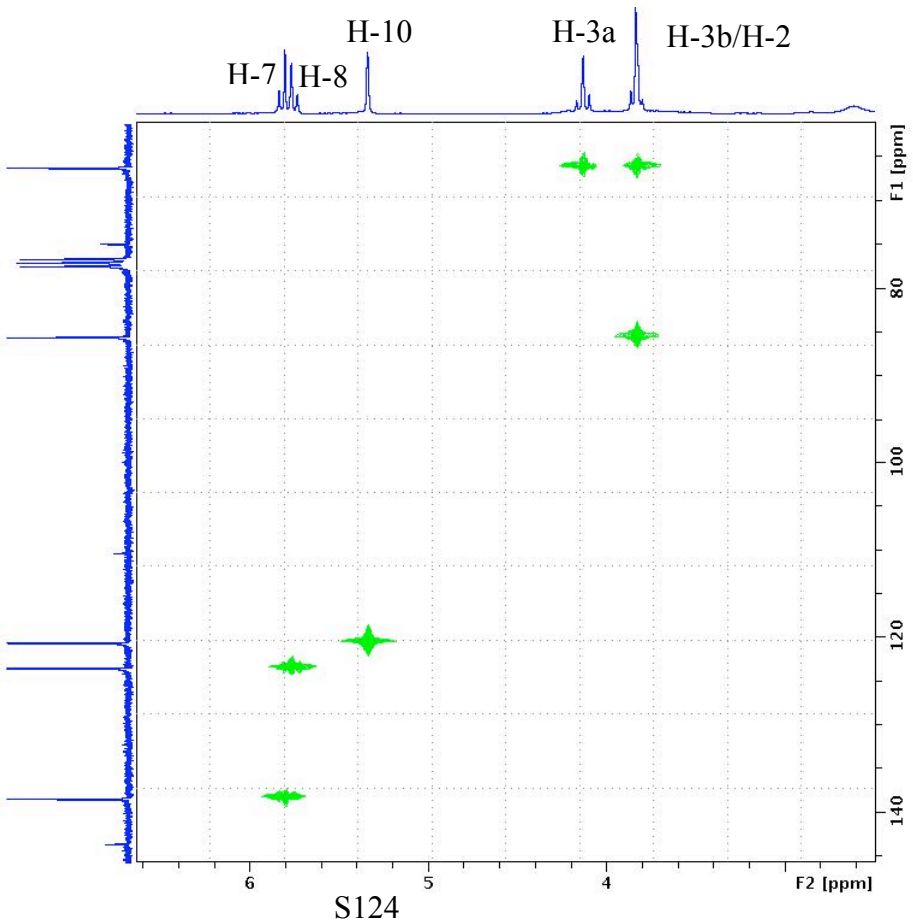


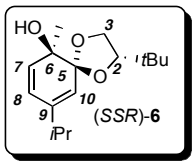


HMQC

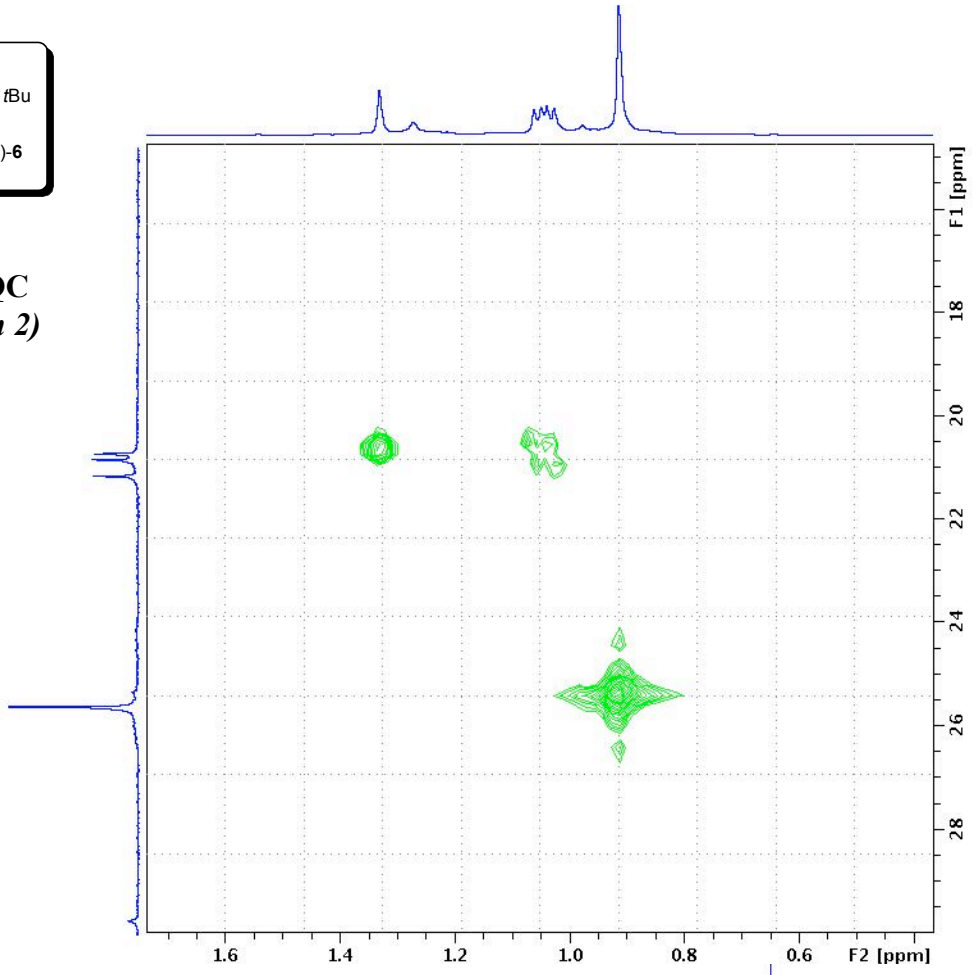


HMQC
(zoom 1)

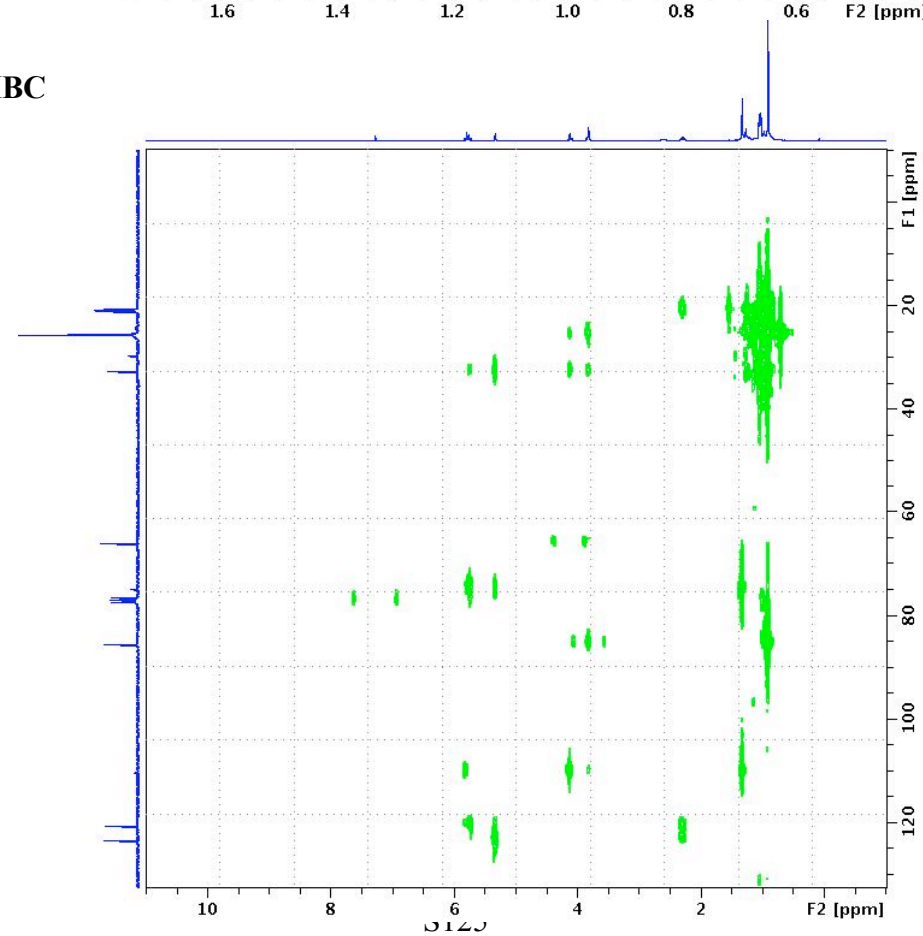


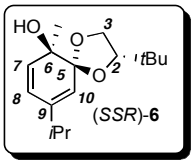


HMQC
(zoom 2)

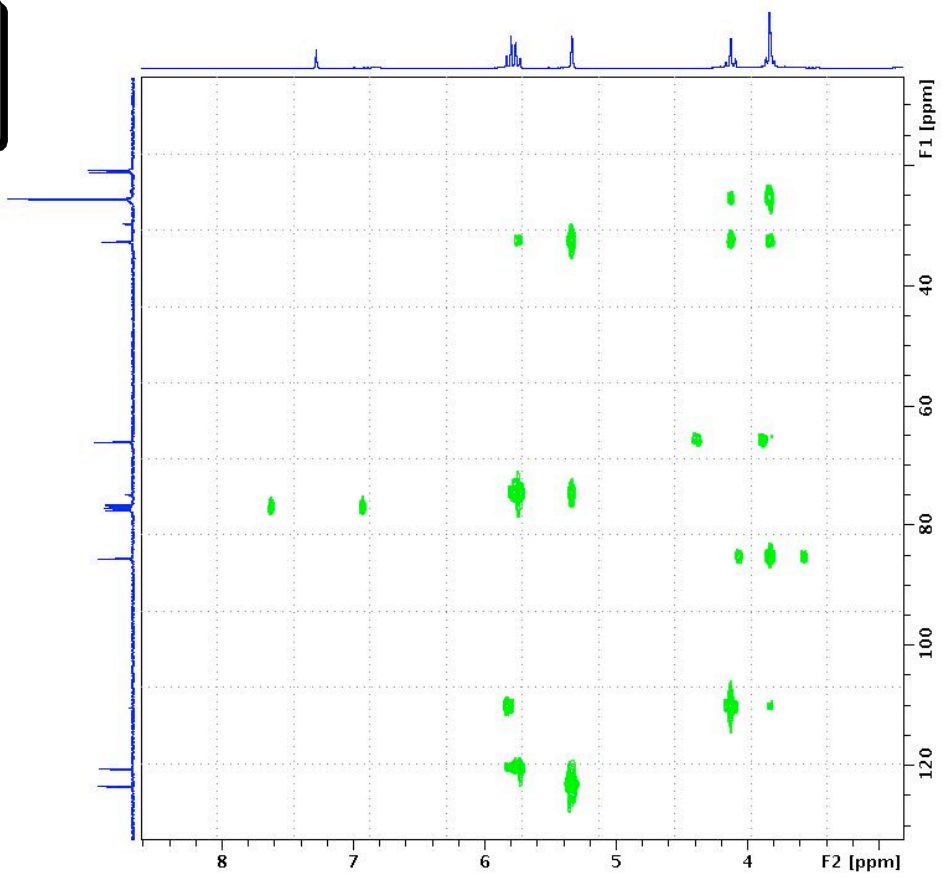


HMBC

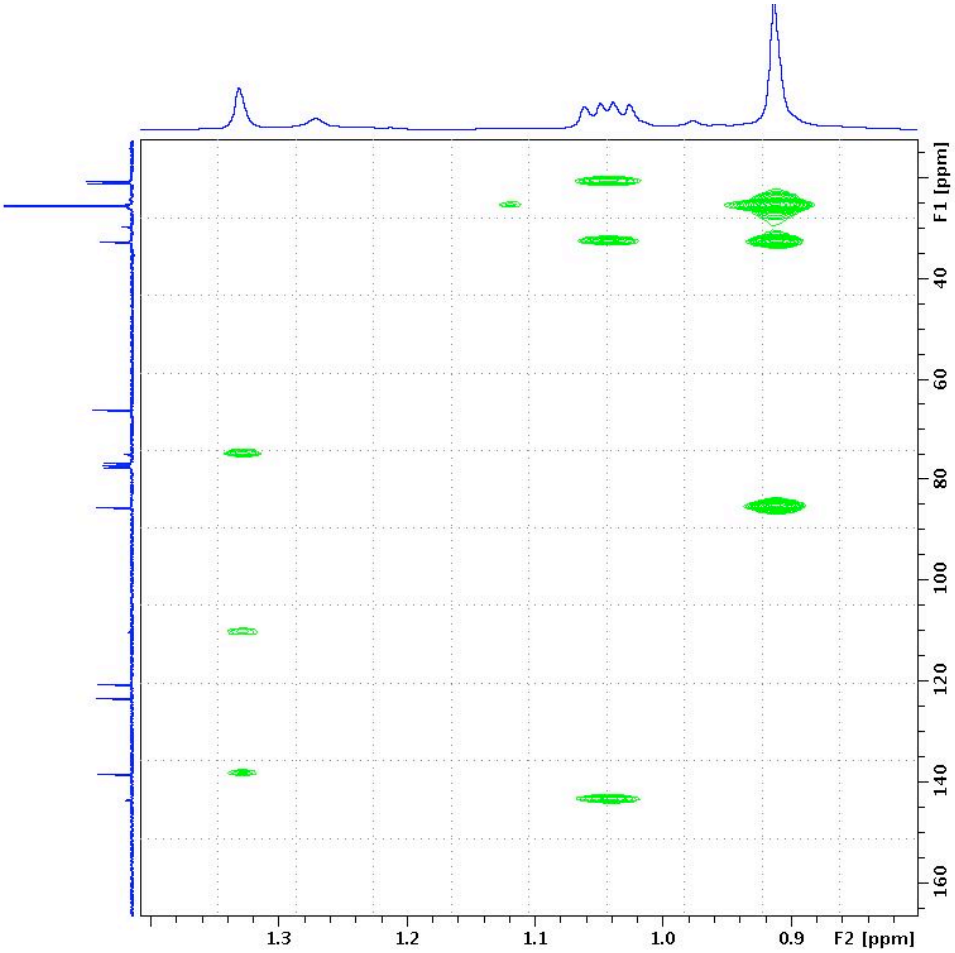


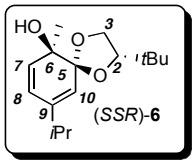


HMBC
(zoom 1)

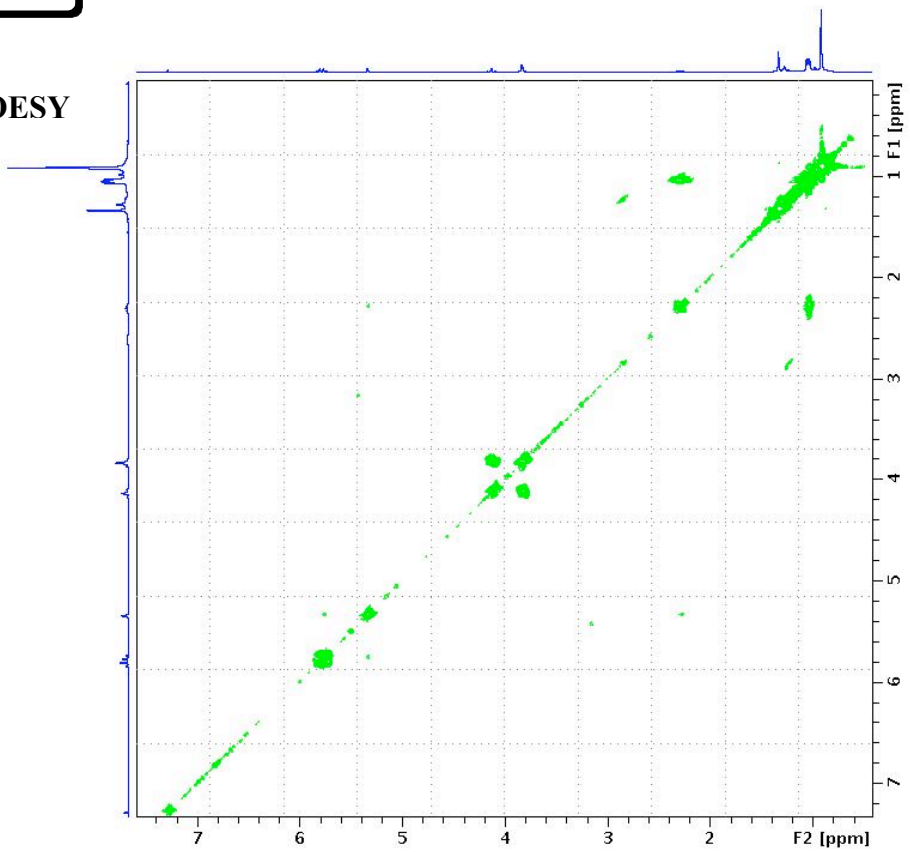


HMBC
(zoom 2)





NOESY



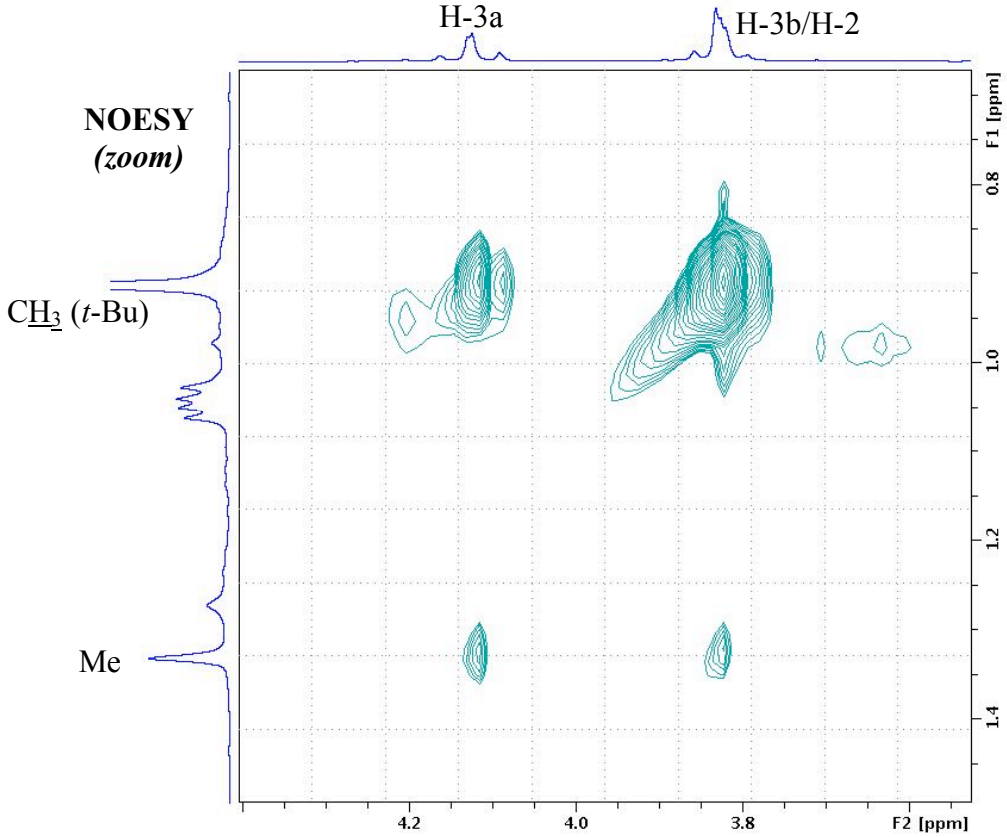
NOESY
(zoom)

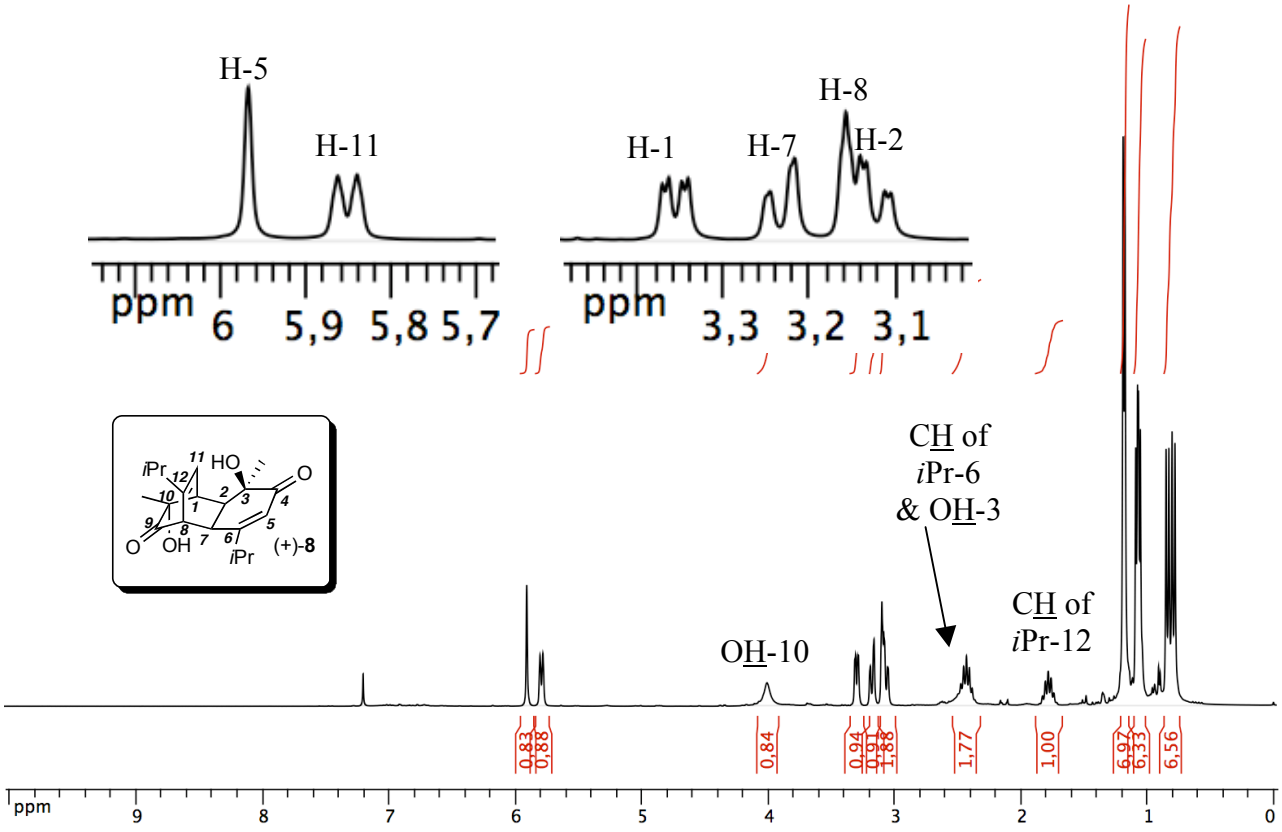
H-3a

H-3b/H-2

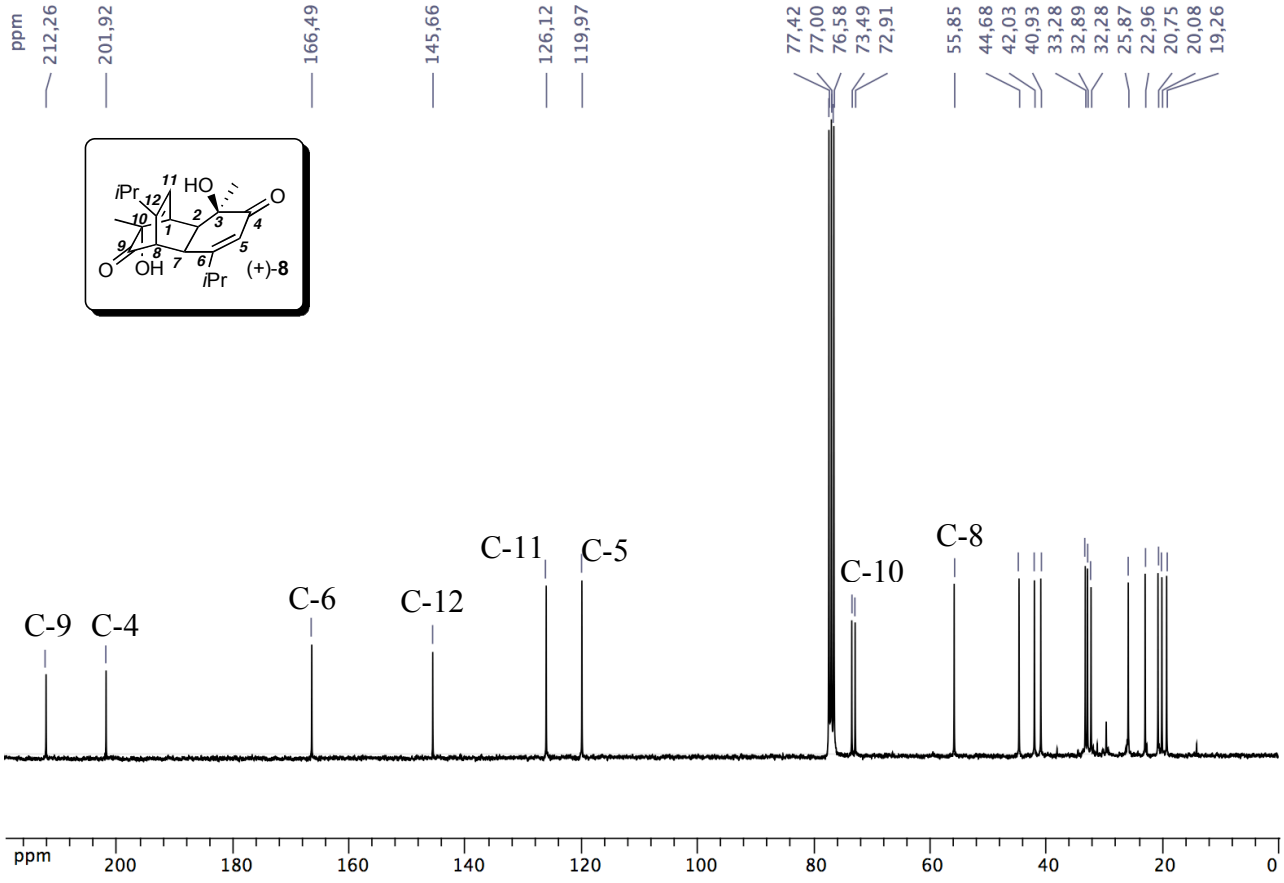
$\underline{CH_3}$ (*t*-Bu)

Me



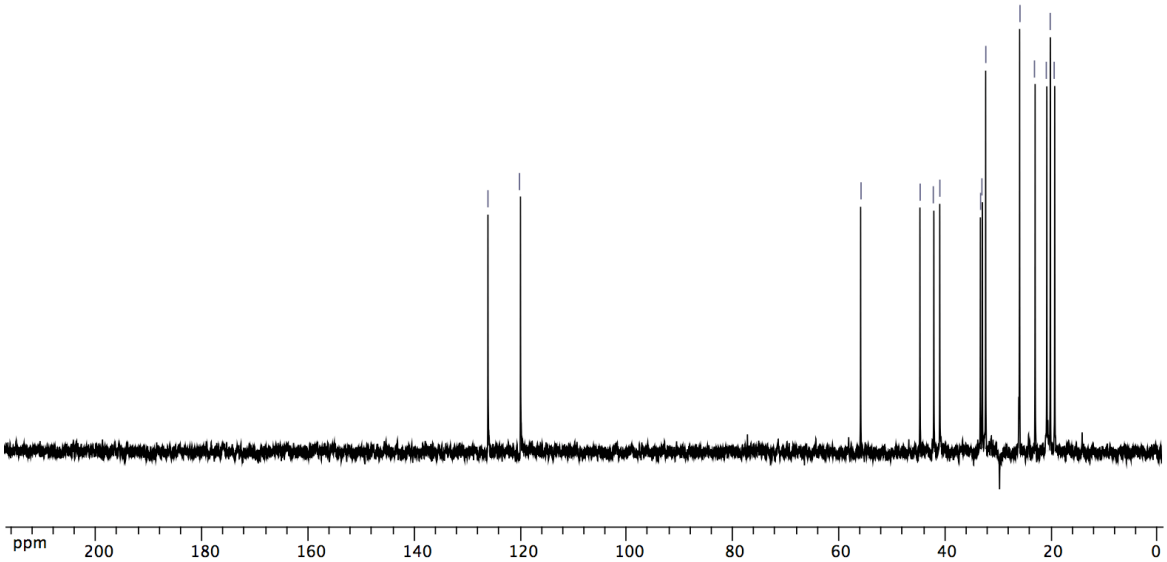


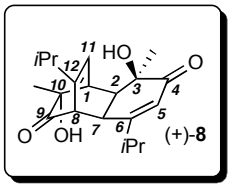
Label	Intensity	Frequency(point)	Frequency(ppm)	Frequency(Hz)
1	68777744	14630	7,26	2178,957
2	182942560	16683	5,968	1791,244
3	78500952	16851	5,862	1759,517
4	79870408	16887	5,84	1752,718
5	72974920	19710	4,064	1219,588
6	69232392	20808	3,373	1012,229
7	76603312	20820	3,365	1009,962
8	72096864	20844	3,35	1005,43
9	75843504	20856	3,342	1003,164
10	60431352	21009	3,246	974,269
11	99574080	21055	3,217	965,582
12	153834912	21151	3,157	947,452
13	102379744	21178	3,14	942,353
14	95317328	21189	3,133	940,276
15	60795512	21224	3,111	933,666
16	58561284	21235	3,104	931,589
17	22518264	22145	2,531	759,733
18	53769316	22181	2,509	752,935
19	86192336	22216	2,487	746,325
20	81524568	22252	2,464	739,526
21	40729532	22286	2,443	733,105
22	7424070,5	22111	2,553	766,154
23	15355621	23173	1,884	565,593
24	36858076	23209	1,862	558,795
25	51626376	23244	1,84	552,185
26	42873776	23279	1,818	545,575
27	21602296	23314	1,796	538,965
28	8044550,5	23348	1,774	532,544
29	4222586,5	23138	1,907	572,203
30	826316480	24185	1,248	374,475
31	840901824	24211	1,231	369,565
32	379476352	24344	1,148	344,447
33	464614336	24367	1,133	340,104
34	462642784	24379	1,126	337,838
35	412573632	24403	1,111	333,305
36	379377280	24725	0,908	272,495
37	383413600	24761	0,885	265,696
38	409566496	24801	0,86	258,142
39	395430272	24838	0,837	251,155


ppm
212,26
201,92
166,49
145,66
126,12
119,97
77,42
77,00
76,58
73,49
72,91
55,85
44,68
42,03
40,93
33,28
32,89
32,28
25,87
22,96
20,75
20,08
19,26
C-9
C-4
C-6
C-12
C-11
C-5
C-10
C-8
ppm
200
180
160
140
120
100
80
60
40
20
0

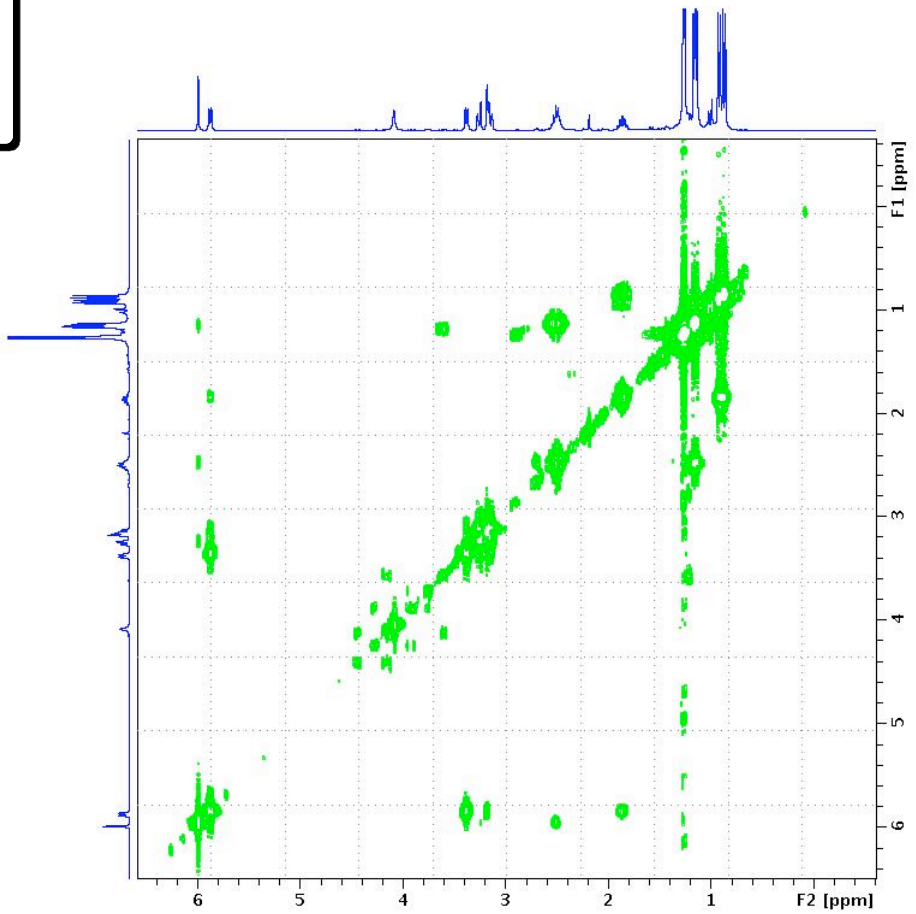

ppm
126,14
120,01
55,88
44,70
42,08
40,97
33,31
32,93
32,31
25,91
22,99
20,78
20,11
19,29

DEPT 135

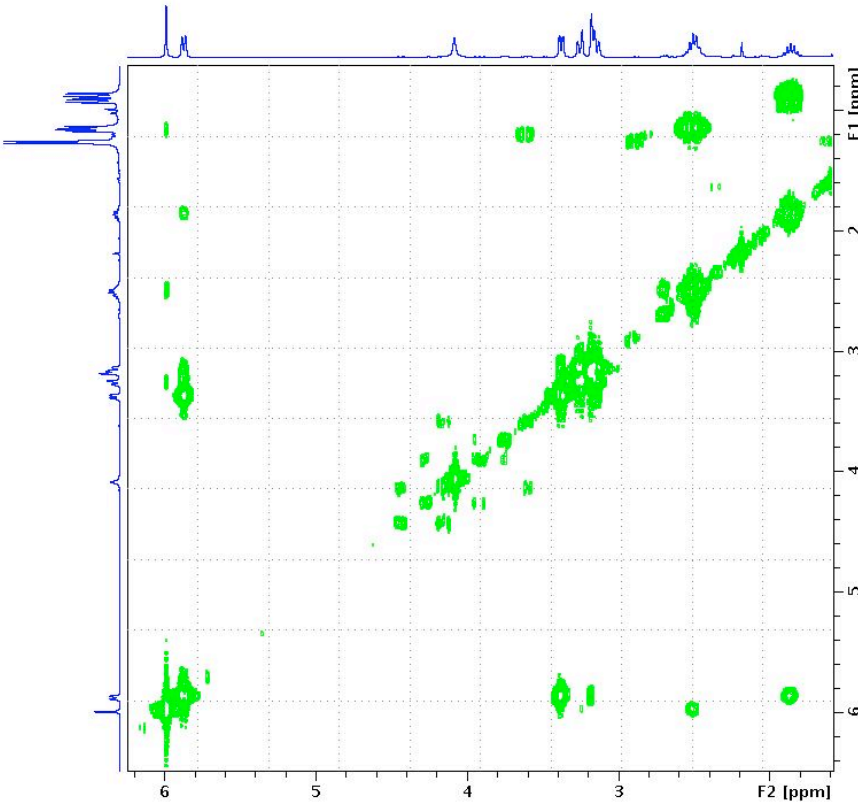

ppm
200
180
160
140
120
100
80
60
40
20
0

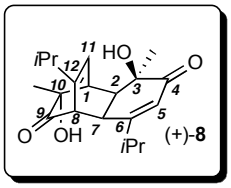


COSY

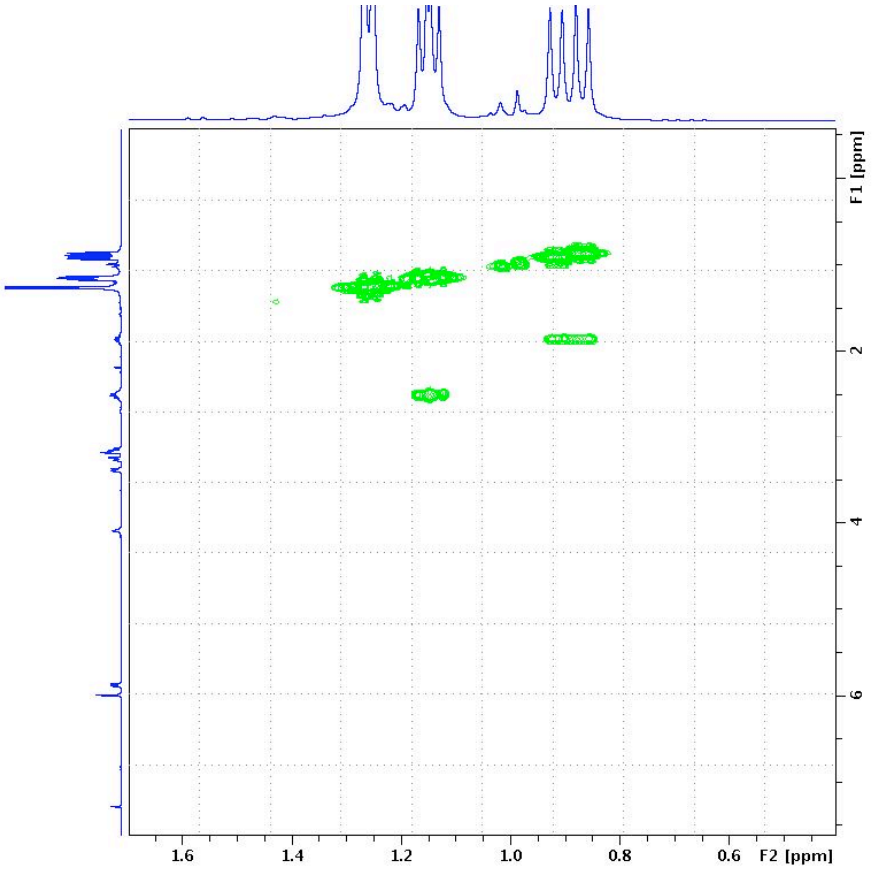


COSY
(zoom 1)

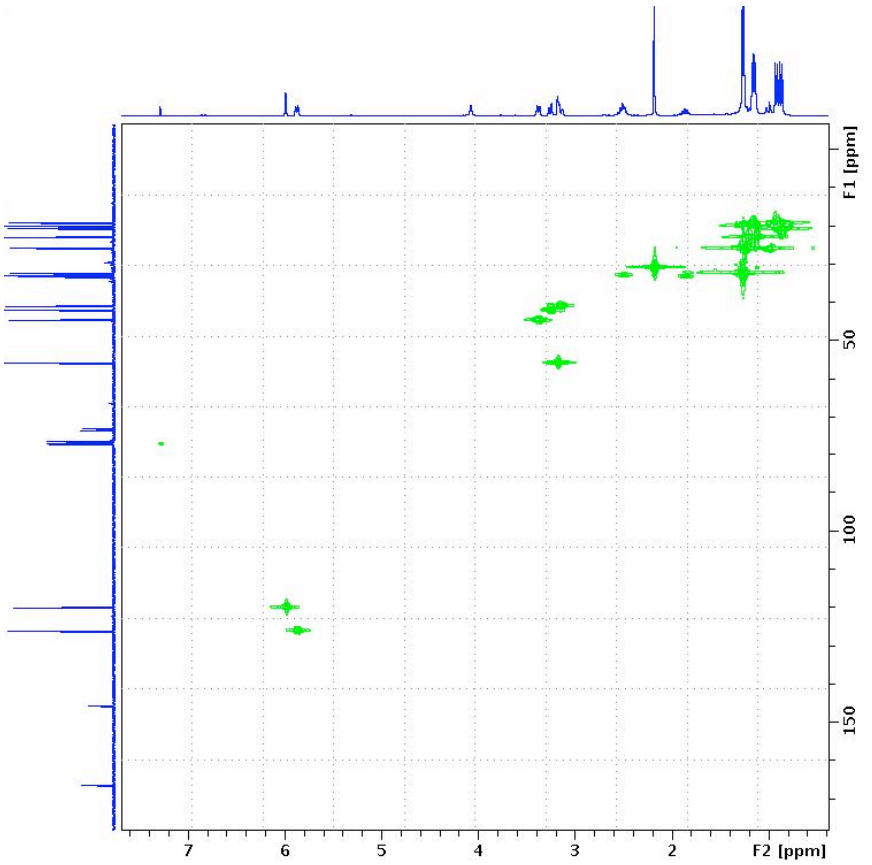


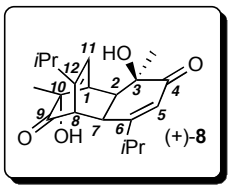


COSY
(zoom 2)

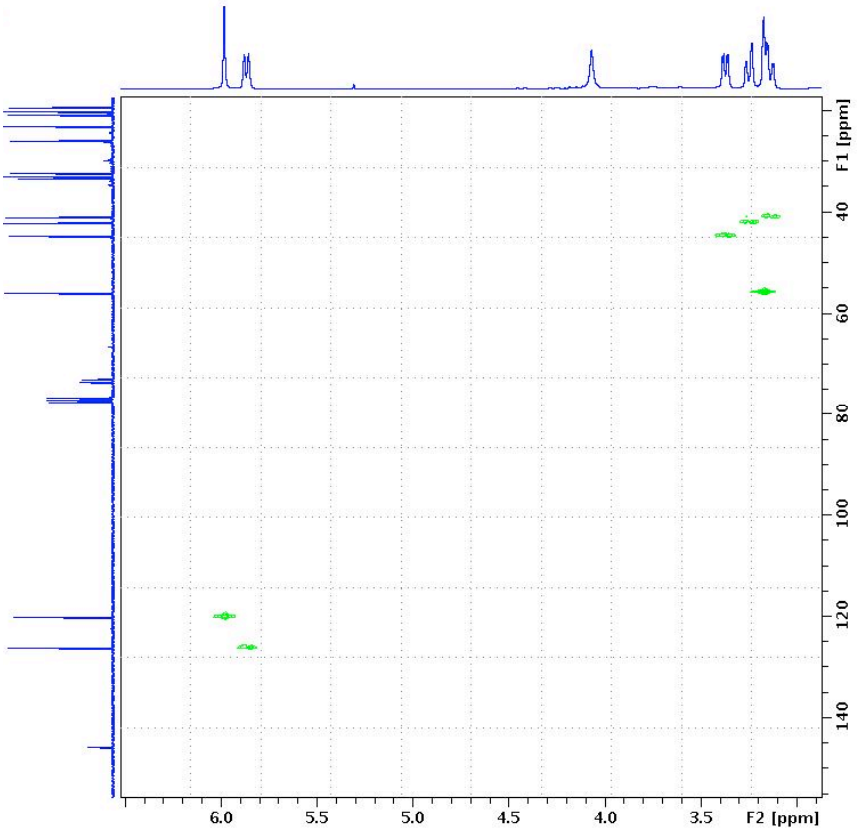


HMQC

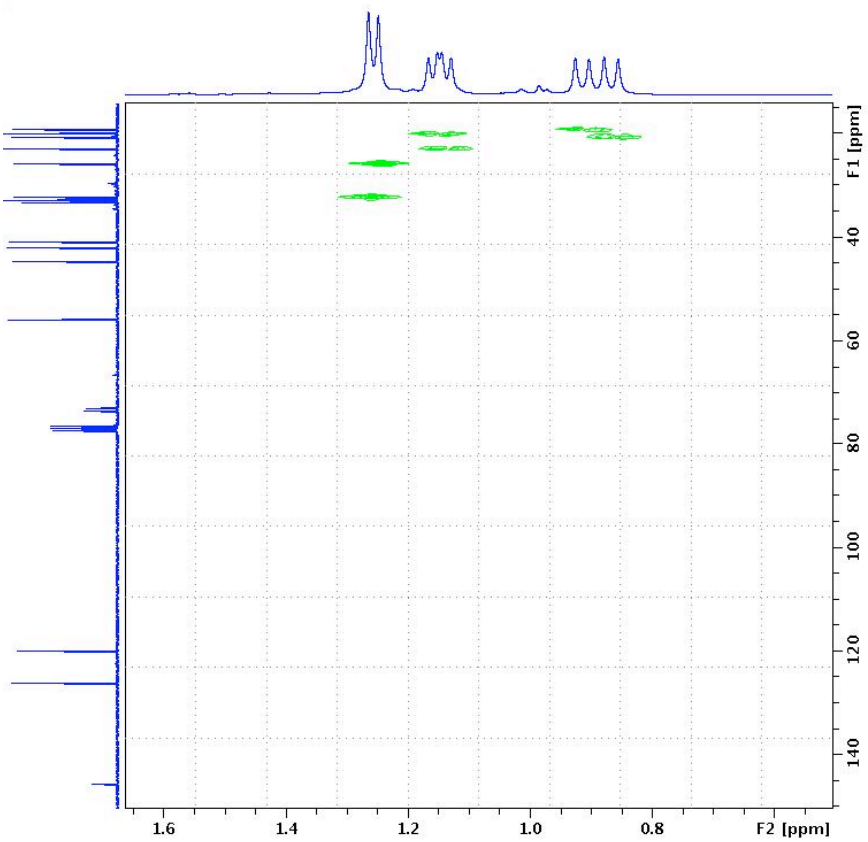


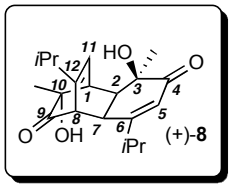


HMQC
(zoom 1)

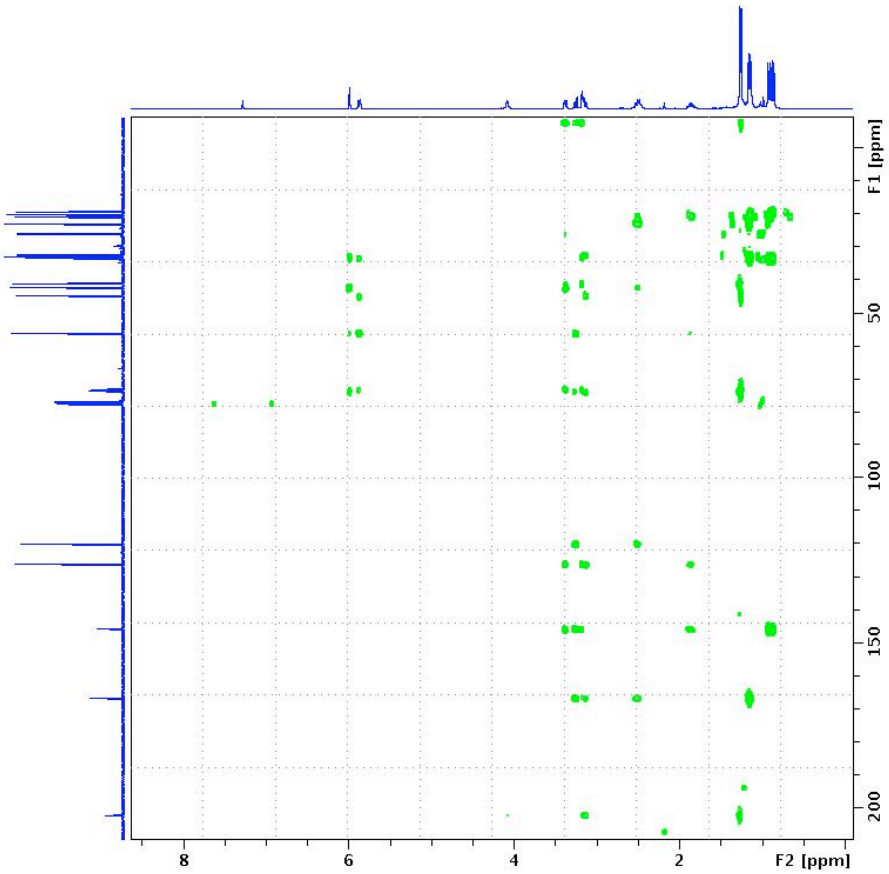


HMQC
(zoom 2)

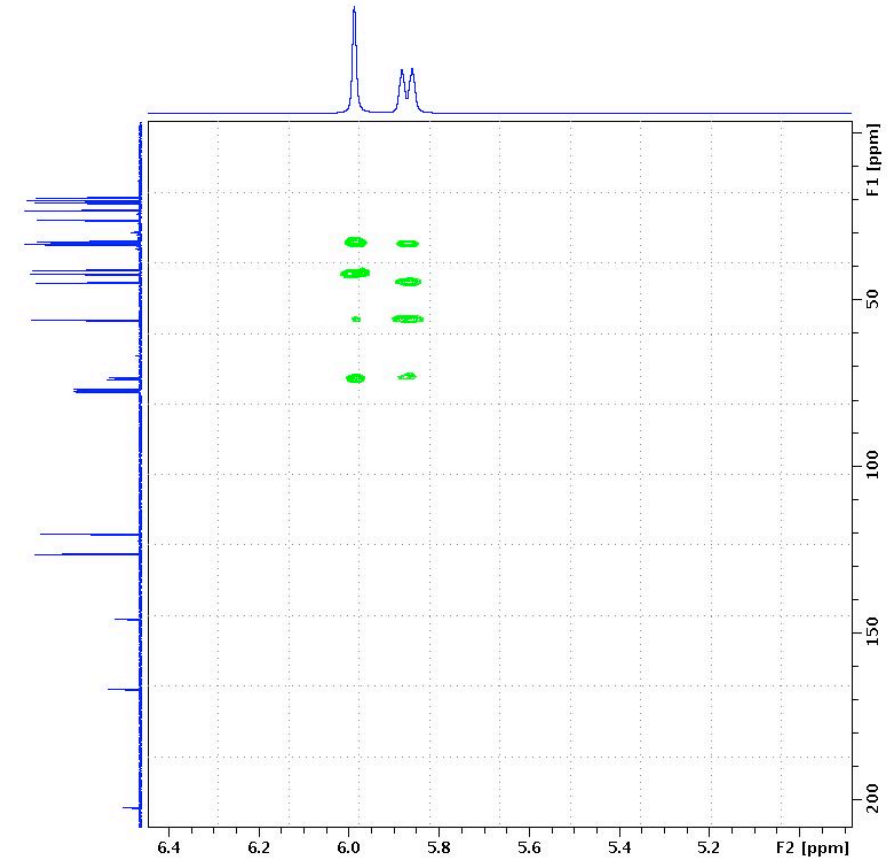


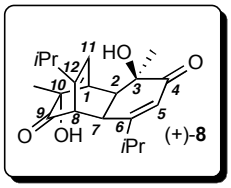


HMBC

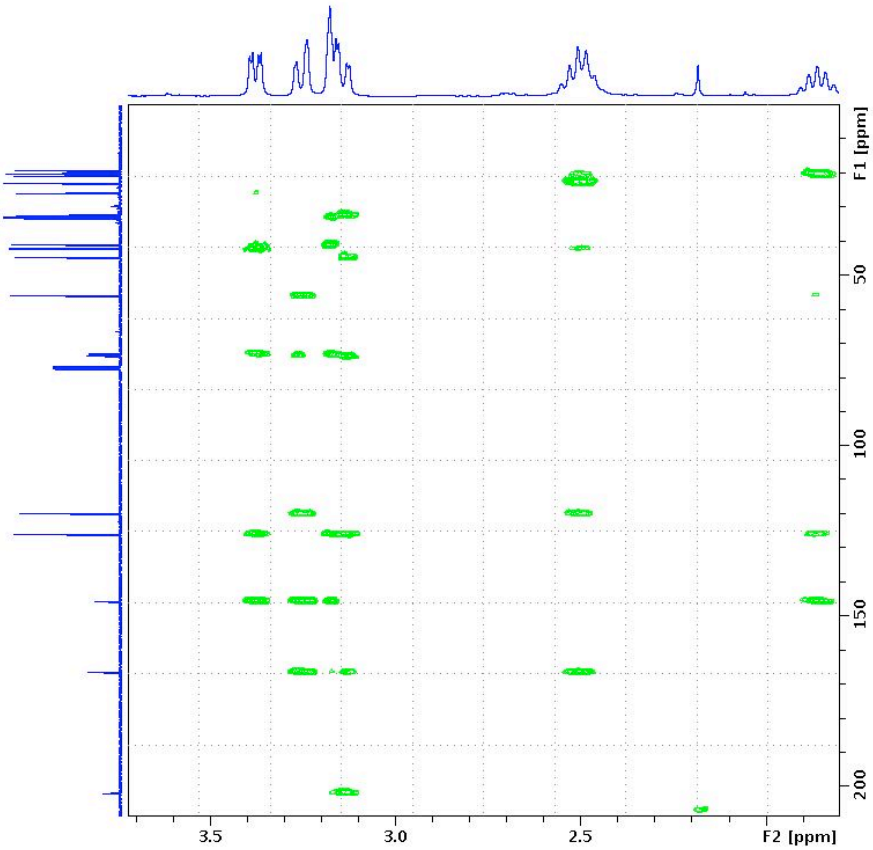


HMBC
(zoom 1)

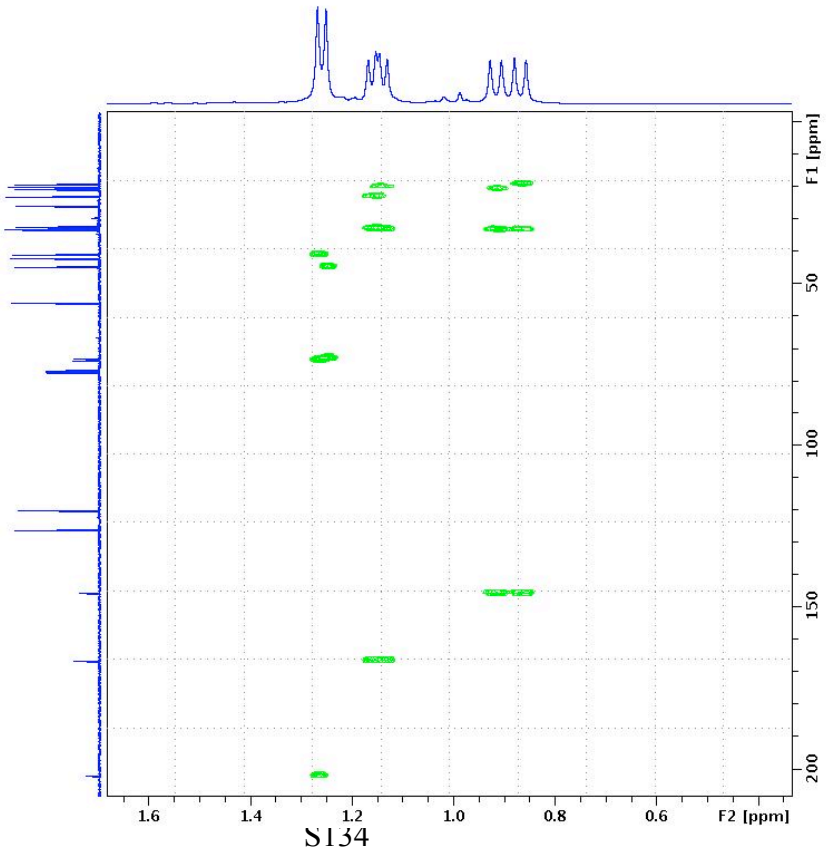


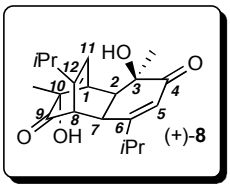


HMBC
(zoom 2)

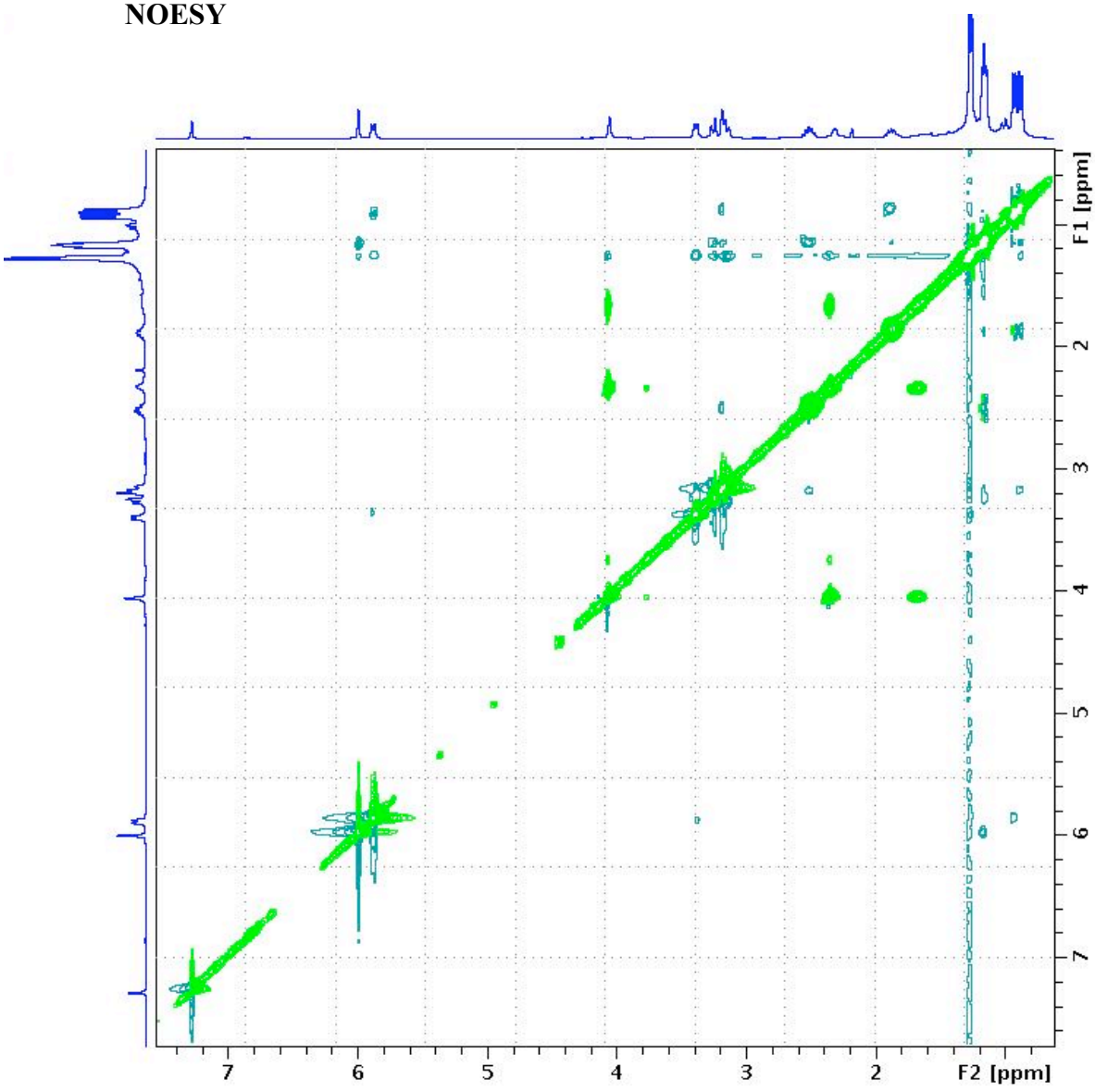


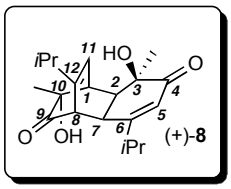
HMBC
(zoom 3)





NOESY



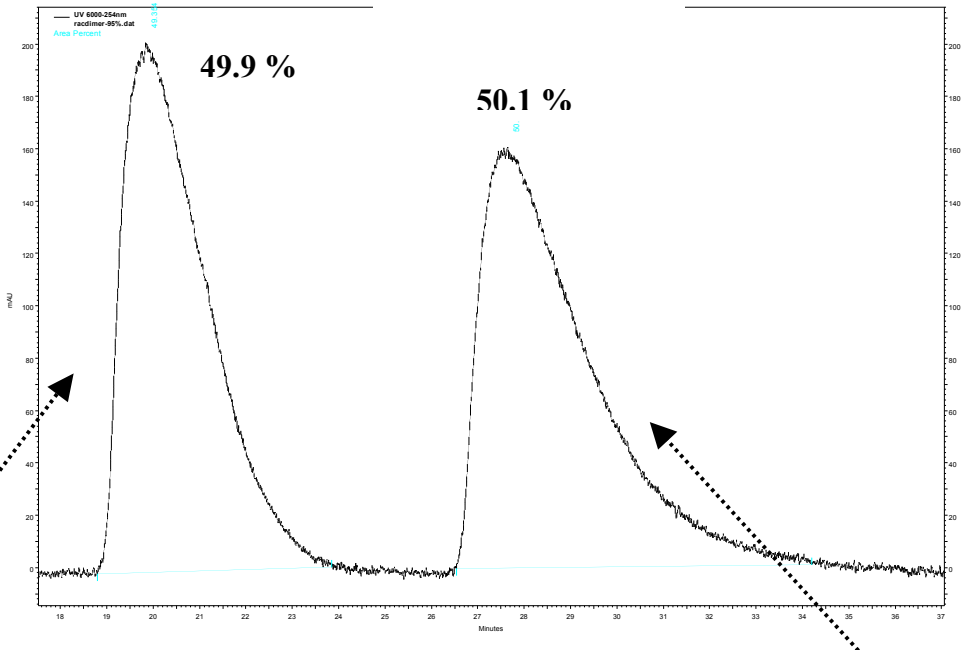


HPLC analysis: chiral normal phase using a Chiralpak AS-H column, eluting with 5% *i*-PrOH in hexane at 0.5 mL/min and a detection wavelength of 254 nm.

Chromatogram A: racemate (±)-**8** previously obtained via a hydroxylative phenol dearomatization / [4+2] cyclodimerization sequence.[17,18]

Chromatogram B: highly enantioselective synthesis of (+)-**8** reported herein.

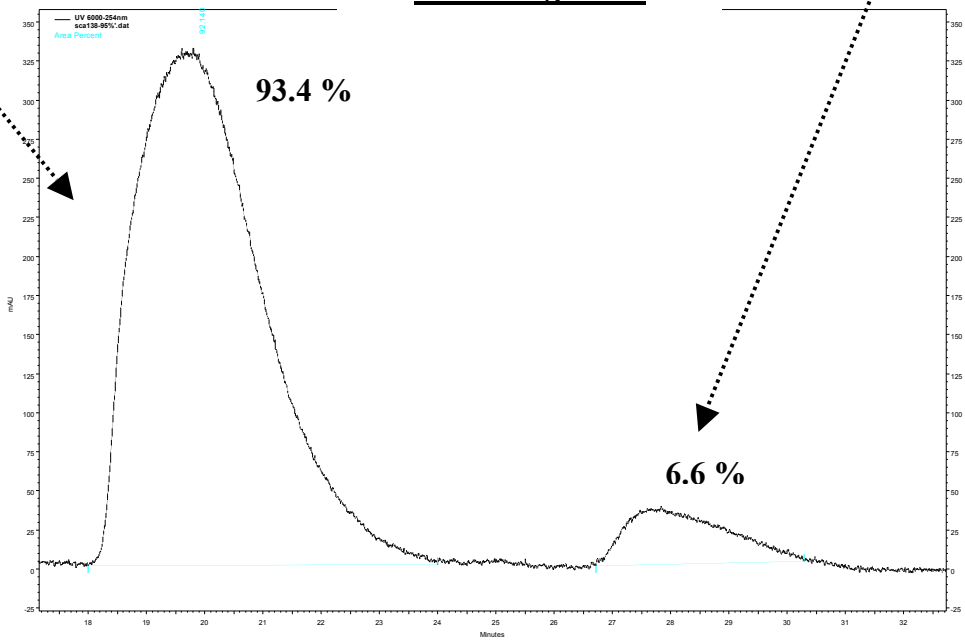
Chromatogram A



(+)-**8**: t_r = 19.5 min

(-)-**8**: t_r = 27.8 min

Chromatogram B



Theoretical Calculations

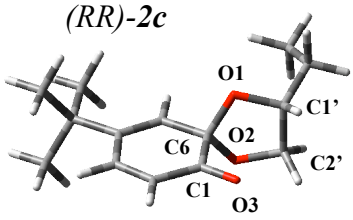
General. Calculations were performed with the Gaussian 03 program,[19,20] using the density functional method.[21] The hybrid exchange functional B3LYP[22-24] in conjunction with the 6-31G** basis set for C,H,O and the RECP (relativistic effective core potential) LanL2DZ(d,p)[25-27] basis set for I were used. B3LYP is a three parameter functional developed by Becke which combines the Becke gradient-corrected exchange functional and the Lee-Yang-Parr and Vosko-Wilk-Nusair correlation functionals with part of exact HF exchange energy. The optimized structures were confirmed as true minima on the potential energy through vibrational analysis. The frequencies were calculated with analytical second derivatives. All total energies have been zero-point energy (ZPE) and temperature corrected using unscaled density functional frequencies. The free Gibbs energies, G, were calculated for T = 298.15 K. The electronic structure of the iodine compounds was studied using Natural Bond Orbital (NBO) analysis.[28,29] The NBO-3.1 program was used to gain insight into the nature of the interaction between iodine(III) and carbon C_6 atoms. The Natural Localized Molecular Orbitals (NLMO) obtained from the NBO analysis were plotted by using the molecular graphic package Molekel.[30,31]

Geometrical parameters.

Table S1 presents the geometrical parameters calculated for the compounds **2a**/**c** and **3a**/**c**. (*RR*)-isomers were found slightly more stable than (*RS*)- ones.

Table S1. Bond lengths in angstroms (Å) and bond angles in degrees (°) for compounds **2a**/**c** and **3a**/**c**. Relative total energy (ΔE) and total Gibbs energies (ΔG) in kcal/mol between (*RR*)- and (*RS*)-isomers, respectively. Eelec and Erep are, respectively, the electronic and repulsion energies in au.

	(*RR*)-**2a**	(*RS*)-**3a**	(*RR*)-**2c**	(*RS*)-**3c**
C6O1	1.418	1.419	1.417	1.425
O1C1'	1.442	1.441	1.442	1.442
C1'C2'	1.551	1.547	1.550	1.533
C2'O2	1.433	1.426	1.432	1.427
O2C6	1.418	1.419	1.421	1.423
O1C1'C2'	103.54	103.35	103.80	101.87
O2C2'C1'	105.20	104.76	105.01	103.48
C6O1C1'	108.20	105.59	108.25	109.43
O2C601	105.97	106.34	106.01	107.16
C2'O2C6	107.26	106.64	106.92	107.39
O3C1C6O2	-58.1	54.7	-55.4	57.9
Erep	1550.837956	1552.513361	1287.038841	1276.677005
Eelec	-2401.253774	-2401.924523	-2058.201803	-2047.837442
ΔE	0	2.9	0	1.3
ΔG	0	3.4	0	1.3



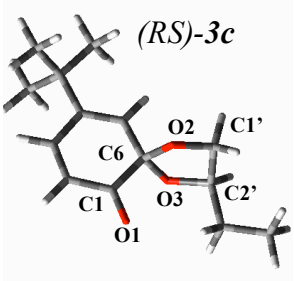
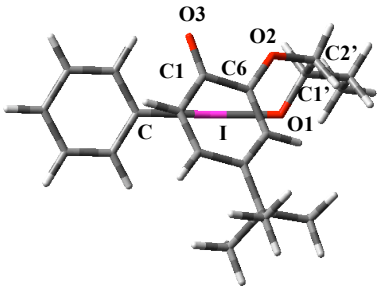


Table S2 presents the geometrical parameters calculated for the intermediates **4a**/**c** and **5a**/**c**. Pro-(*S*)- isomers were found slightly more stable than pro-(*R*)- ones.

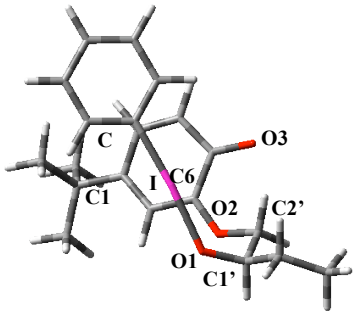
Table S2. Bond lengths in angstroms (Å) and bond angles in degrees (°) for intermediates **4a**/**c** and **5a**/**c**. Relative total energies (ΔE) and total Gibbs energies (ΔG) in kcal/mol between the pro-(*R*)-**4a**/**c** and pro-(*S*)-**5a**/**c** isomers, respectively. Eelec and Erep are, respectively, the electronic and repulsion energies in au. Relative total energies (ΔE1) and total Gibbs energies (ΔG1) in kcal/mol between the pro-(*R*)-**4a**/**c** and pro-(*S*)-**5a**/**c** isomers, respectively, and their corresponding products (*RR*)-**2a**/**c** + PhI and (*RS*)-**3a**/**c** + PhI.

	pro-(*R*)-**4a**	pro-(*S*)-**5a**	pro-(*R*)-**4c**	pro-(*S*)-**5c**
IO1	2.100	2.519	2.100	2.454
IC6	2.800	3.251	2.945	3.219
O1C1'	1.401	1.381	1.400	1.388
C1'C2'	1.537	1.525	1.534	1.523
C2'O2	1.457	1.488	1.455	1.487
IC	2.208	2.146	2.210	2.154
O2C6	1.316	1.297	1.313	1.297
CIO1	168.85	173.70	168.03	172.52
C6IC	100.24	106.28	100.89	104.92

C6IO1	66.66	70.14	67.25	69.41
O2C2'C1'O1	-59.5	-52.8	-59.3	-46.9
O2C2'C1'O1	56.6	-4.9	57.2	-9.7
Erep	2371.334309	2324.742404	2050.003089	2027.887199
Eelec	-3464.063814	-3417.478991	-3041.991560	-3041.997964
ΔE	5.2	0	4.2	0
ΔG	6.3	0	3.3	0
ΔE1	59.9	51.9	72.9	68.9
ΔG1	62.9	53.1	76.7	73.4



*pro-(R)-**4c***



*pro-(S)-**5c***

chair-like conformations with a T-shaped iodine(III) center

Four minima, pro-(*R*)-**4a**/**c** and pro-(*S*)-**5a**/**c**, were found on the potential energy surface for the iodine(III)-containing intermediates **4a**/**c** and **5a**/**c**. Pro-(*S*)-**5a**/**c** were calculated slightly more stable than pro-(*R*)-**4a**/**c**, respectively. They all adopt chair-like conformations with a T-shaped iodine(III) center (see representation on top). The energetic difference between the pro-(*R*)-**4a**/**c** and the pro-(*S*)-**5a**/**c** intermediates and their corresponding products (*RR*)-**2a**/**c** and (*RS*)-**3a**/**c**, respectively, was found very high (between 50 and 73 kcal/mol). Thus, the driving force of the reaction corresponds to the formation of the *o*-quinone monoketals (*RR*)-**2a**/**c** and (*RS*)-**3a**/**c**.

I^{III}–C_6 interaction.

In order to gain further insight into the nature of the I^{III}–C_6 interaction, NBO calculations were carried out since the second order perturbation theory is particularly adapted to the description of donor/acceptor interactions. A Natural Localized Molecular Orbital (NLMO) was found to account for the I^{III}–C_6 bonding interaction. Figures S1 and S2 exemplify the NLMO associated with the I^{III}→C_6 interaction in pro-(*S*)-**5a** and pro-(*S*)-**5c**. The NLMO presents a major contribution from the $2p_\pi$ iodine orbital [around 87 % for pro-(*S*)-**5a** and 84% for pro-(*S*)-**5c**] and delocalization tails" (3-

5%) from a $2p_{\pi}^{*}$ carbon (C_6) orbital (see Table S3). The plots of the NLMO show a more important deformation from iodine to the C_6 carbon with the ethyl group than with the *tert*-butyl one, in agreement with an I^{III}–C_6 bond length slightly shorter in pro-(*S*)-**5c** than in pro-(*S*)-**5a**. This result is also visible in the NBO delocalization energies ΔE_{ij} associated with the $I^{III}\rightarrow C_6$ interaction (see Table S3), which is slightly higher in pro-(*S*)-**5c** (ca. 14 kcal/mol) than in pro-(*S*)-**5a** (ca. 12 kcal/mol).

Figure S1. Molekel plots (cutoff: 0.05) for (a) the donor NBO, (b) the acceptor NBO, and (c) the corresponding NLMO associated with the $I^{III}\rightarrow C_6$ interaction in pro-(*S*)-**5a**.

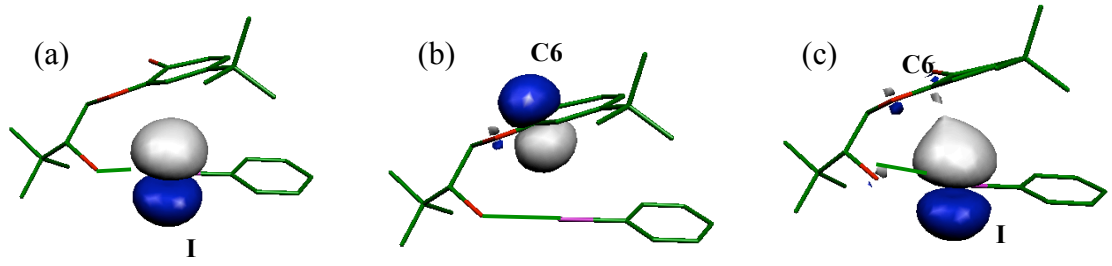


Figure S2. Molekel plots (cutoff: 0.05) for (a) the donor NBO, (b) the acceptor NBO, and (c) the corresponding NLMO associated with the $I^{III}\rightarrow C_6$ interaction in pro-(*S*)-**5c**.

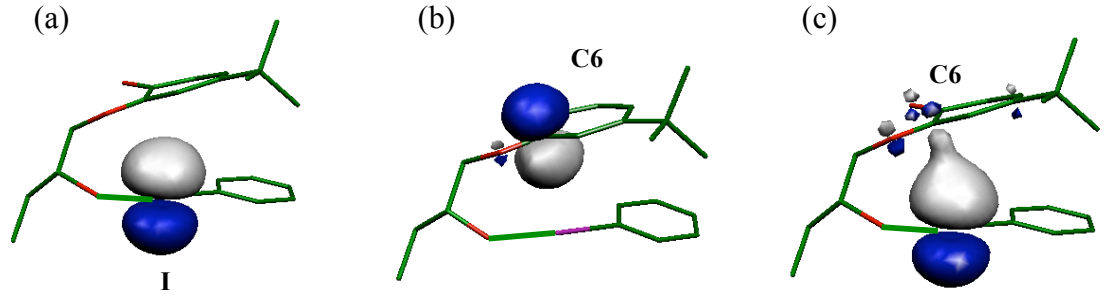


Table S3 summarizes the NBO delocalization energies ΔE_{ij} associated with the $I^{III}\rightarrow C_6$ interaction as well as the percentage of each atom in the corresponding NLMO. For the pro-(*S*) isomers, the shortest I^{III}–C_6 bond length in pro-(*S*)-**5c** corresponds to the NLMO where the iodine percentage is the smallest and the carbon percentage the highest (weak overlap).

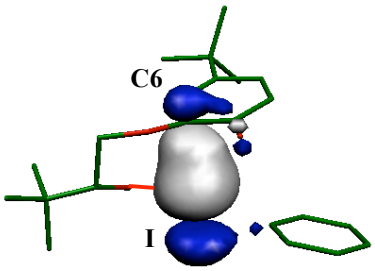
Table S3. NBO analysis of the $I^{III}\rightarrow C_6$ interaction for pro-(*R*)-**4a**/**c** and pro-(*S*)-**5a**/**c** at the B3LYP/6–31G** level of theory.

	ΔE_{ij}[a]	% I[b]	% C[b]
pro-(*R*)-4a	/	**65.7**	**24.0**
pro-(*R*)-4c	/	**65.9**	**22.6**
pro-(*S*)-5a	**11.7**	**87.4**	**3.6**
pro-(*S*)-5c	**13.6**	**84.3**	**5.4**

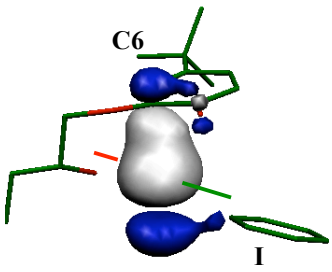
[a] NBO stabilizing energy associated with the $I\rightarrow C_6$ interaction, in kcal/mol.
[b] Percentage of the donor and acceptor NBO in the corresponding NLMO.

Figure S3 represents the NLMO associated with the $I^{III}\rightarrow C_6$ interaction in pro-(*R*)-**4a** and pro-(*R*)-**4c**. The plots of these NLMO show that the overlap between iodine and carbon is more important than in the corresponding pro-(*S*)-**5a**/**c** isomers, in agreement with a shortest I^{III}–C_6 bond length (intermediate between a donor-acceptor bond and a covalent bond).

Figure S3. Molekel plots (cutoff: 0.05) NLMO associated with the $I^{III}\rightarrow C_6$ interaction in pro-(*R*)-**4a** and pro-(*R*)-**4c**.



*pro-(R)-**4a***



*pro-(R)-**4c***

The results of Table 3 are coherent with the plots of Figure S3 since the pro-(*R*)- isomers have the more important carbon percentage, which leads to a better overlap of the iodine(III)- and carbon C_6-centered orbitals.

Z-matrix

(*RR*)-**2a**

O	-4.991449	-0.058513	4.351924
C	-5.282794	1.130349	5.067776
O	-6.284906	0.783149	6.009608
C	-6.068650	-0.585141	6.375501
C	-5.200950	-1.178881	5.235115
C	-5.855210	2.141866	4.113391
C	-5.318848	3.356104	3.899757
C	-4.098001	3.729707	4.640577
C	-3.481995	2.926665	5.532478
C	-4.002566	1.588811	5.825805
O	-3.469317	0.835431	6.630633
C	-5.904326	4.387430	2.925161
C	-4.855191	4.713880	1.834742
C	-5.799167	-2.359234	4.433255
C	-4.794898	-2.752753	3.331209
C	-6.265225	5.678124	3.700252
C	-7.177285	3.869474	2.232344
C	-7.142484	-1.980460	3.784014
C	-5.987514	-3.551452	5.391996
H	-2.585153	3.231469	6.063928
H	-3.677028	4.713493	4.451508
H	-6.752721	1.802779	3.608990
H	-6.676306	6.426925	3.013002
H	-5.395128	6.127109	4.191429
H	-7.017080	5.474091	4.470719
H	-7.562542	4.633557	1.548108
H	-7.968064	3.642552	2.955948
H	-6.980583	2.966145	1.644373
H	-5.255425	5.460044	1.138057
H	-4.596094	3.817133	1.260786
H	-3.929363	5.121351	2.255285
H	-7.054624	-1.049514	6.462560
H	-5.552049	-0.648106	7.337495
H	-4.230877	-1.488371	5.641281
H	-7.527910	-2.820474	3.194198
H	-7.021982	-1.122483	3.116008
H	-7.905830	-1.726837	4.528814
H	-6.345036	-4.429160	4.841204
H	-6.720942	-3.336567	6.178429
H	-5.043033	-3.826714	5.877675
H	-5.169977	-3.608305	2.756867
H	-3.826595	-3.036485	3.761948
H	-4.624898	-1.921948	2.639866

Sum of electronic and zero-point Energies= -849.415818 au
Sum of electronic and thermal Free Energies= -849.463991 au

(*RS*)-**3a**

O	-4.955879	-0.026550	4.255732
C	-5.455893	-1.252572	4.766064
O	-6.837938	-1.047697	5.014073
C	-7.290381	-0.101010	4.047746
C	-6.042064	0.750638	3.715730
C	-5.259593	-2.349082	3.744136
C	-4.591853	-3.492874	3.984474
C	-4.008313	-3.692129	5.321656

C	-4.090117	-2.792343	6.325238
C	-4.779842	-1.515675	6.147395
O	-4.845159	-0.669037	7.022229
C	-4.394546	-4.607225	2.946172
C	-5.033888	-5.916132	3.469248
C	-6.011399	2.194494	4.276896
C	-4.615307	2.787275	4.000648
C	-2.880612	-4.828737	2.711523
C	-5.044262	-4.260037	1.594560
C	-6.290209	2.223486	5.790930
C	-7.069379	3.025297	3.523665
H	-3.640165	-2.969561	7.297451
H	-3.476167	-4.621796	5.505787
H	-5.705158	-2.148629	2.775237
H	-2.725668	-5.628820	1.977973
H	-2.355502	-5.118804	3.627961
H	2.406486	-3.918420	2.327845
H	-4.876723	-5.076630	0.883572
H	-4.615891	-3.349745	1.160073
H	-6.127212	-4.120208	1.687703
H	-4.889323	-6.723644	2.741685
H	-6.110624	-5.789374	3.627977
H	-4.592412	-6.245096	4.416206
H	-8.104118	0.464945	4.505342
H	-7.678816	-0.608694	3.153745
H	-5.905886	0.810557	2.626321
H	-6.151359	3.240961	6.175434
H	-5.620555	1.548695	6.329705
H	7.319838	1.926884	6.023253
H	-7.052794	4.064105	3.872423
H	-8.085138	2.643921	3.685721
H	-6.880874	3.035282	2.442312
H	-4.571030	3.829600	4.337853
H	-4.379833	2.771793	2.928550
H	-3.840522	2.222060	4.525890

Sum of electronic and zero-point Energies=	-849.411162	au
Sum of electronic and thermal Free Energies=	-849.458614	au

(*RR*)-**2c**

C	0.004110	0.038638	-0.016640
C	-0.004384	0.040391	1.540008
C	1.353804	0.043111	2.185283
C	2.508627	0.017831	1.497211
C	2.452054	-0.008861	0.022342
C	1.305457	-0.004196	-0.688473
O	-0.714218	-1.102502	1.997995
C	-2.103063	-0.752383	2.013144
C	-2.125997	0.795724	2.084615
O	-0.734506	1.164537	2.000622
C	2.725105	1.395508	3.359670
H	-3.784389	1.104434	3.397735
C	3.895175	0.014560	2.156408
C	3.804443	0.042260	3.692449
O	-1.054911	0.069021	-0.630868
C	4.685027	1.263088	1.694166
C	4.658970	-1.265425	1.738313
H	-2.711541	2.488016	3.257579
C	-2.013766	0.997441	4.656213

H	1.296770	-0.019424	-1.774447
H	3.395574	-0.031990	-0.516462
H	1.319227	0.058624	3.268483
H	5.655199	-1.274732	2.196048
H	4.796393	-1.334137	0.653739
H	4.125314	-2.164376	2.066439
H	4.812254	0.040629	4.122230
H	3.275334	-0.834001	4.082993
H	3.291749	0.941326	4.051812
H	5.683307	1.265668	2.147601
H	4.172435	2.183727	1.994681
H	4.818700	1.293315	0.607392
H	-2.545897	-1.232144	2.891284
H	-2.601907	-1.114347	1.109375
H	-2.648507	1.196842	1.209724
H	-2.490563	1.475050	5.519013
H	-0.965844	1.309483	4.629656
H	-2.037362	-0.085535	4.824061

Sum of electronic and zero-point Energies= -770.844054 au
Sum of electronic and thermal Free Energies= -770.888780 au

(*RS*)-**3c**

C	-0.122330	-0.135347	0.427883
C	0.075765	-0.082501	1.976086
C	1.512994	-0.016356	2.431061
C	2.567320	0.004853	1.595419
C	2.311665	-0.054558	0.145053
C	1.080399	-0.118688	-0.405017
O	-0.640134	1.057192	2.438550
C	1.364136	0.662286	3.603598
C	-1.671061	-0.818062	3.349040
O	-0.529071	-1.227958	2.569138
C	-2.983171	-1.091794	2.611300
C	-4.218355	-0.905409	3.499516
C	4.028592	0.085485	2.061510
C	4.143131	0.138691	3.595334
O	-1.249139	-0.192231	-0.036222
C	4.681568	1.363774	1.481919
C	4.798330	-1.161118	1.562062
H	-2.942093	-2.124154	2.243679
H	-3.028641	-0.449350	1.726226
H	0.929843	-0.161000	-1.479660
H	3.172329	-0.045263	-0.518573
H	1.634746	0.017238	3.508455
H	5.846479	-1.109038	1.880141
H	4.791477	-1.245654	0.469984
H	4.363528	-2.079575	1.972048
H	5.198241	0.194120	3.885298
H	3.716923	-0.754967	4.064748
H	3.638545	1.018673	4.009646
H	5.729352	1.429112	1.798416
H	4.162662	2.262063	1.834774
H	4.668562	1.378184	0.386682
H	-2.250723	1.297866	3.670112
H	-0.756149	0.800509	4.509651
H	-1.635456	-1.398983	4.279116
H	-5.132466	-1.142024	2.944905
H	-4.315351	0.126348	3.859594
H	-4.185482	-1.561156	4.379146

Sum of electronic and zero-point Energies= -770.841997 au
Sum of electronic and thermal Free Energies= -770.886718 au

Pro-(*R*)-**4a**

C	4.986046	-2.325224	-0.241273
C	4.587186	-1.362863	-1.173213
C	3.237574	-1.026350	-1.298017
C	2.274863	-1.658076	-0.498938
C	2.682119	-2.610473	0.445391
C	4.033115	-2.945530	0.568466
I	0.126771	-1.202181	-0.733552
O	-1.850855	-0.499977	-0.656704
C	-2.725474	-0.966770	0.333319
C	-2.601009	-0.019096	1.536542
O	-1.216506	-0.043759	1.989546
C	-0.235430	0.592466	1.384950
C	1.111729	0.332357	2.031576
C	2.176299	1.258659	1.638826
C	1.924506	2.343741	0.872115
C	0.603478	2.637767	0.326480
C	-0.422585	1.770032	0.571647
O	1.273866	-0.573017	2.840027
C	0.433052	3.896699	-0.529858
C	-1.016754	4.087306	-1.011627
C	-4.179844	-1.123033	-0.213678
C	-4.134053	-2.169018	-1.343963
C	1.349286	3.782659	-1.775294
C	0.838797	5.139992	0.299160
C	-4.697615	0.210920	-0.783916
C	-5.123266	-1.625957	0.897071
H	3.162083	1.049356	2.041187
H	2.738944	3.023424	0.640857
H	-1.395245	1.920352	0.130702
H	0.734172	6.044093	-0.311656
H	1.877649	5.092817	0.641797
H	0.197614	5.250049	1.180879
H	-1.086392	5.002425	-1.609335
H	-1.713475	4.188558	-0.171734
H	-1.352489	3.255390	-1.640178
H	1.242164	4.678563	-2.397958
H	1.078541	2.911848	-2.382303
H	2.406922	3.691975	-1.506344
H	-2.891199	1.005033	1.290440
H	-3.152091	-0.351004	2.417958
H	-2.418148	-1.965619	0.700540
H	-5.127555	-2.300866	-1.789695
H	-3.804431	-3.144856	-0.964879
H	-3.438342	-1.857476	-2.127747
H	2.934902	-0.278337	-2.027513
H	1.945815	-3.093366	1.082011
H	5.326925	-0.879446	-1.807503
H	4.340091	-3.689992	1.299210
H	6.036706	-2.586912	-0.144975
H	-5.671127	0.069842	-1.268861
H	-4.833869	0.969060	-0.001876
H	-3.996682	0.604774	-1.525988
H	-6.108405	-1.867303	0.480009
H	-4.734039	-2.536510	1.370446

```
H       -5.282037   -0.877505    1.683232

Sum of electronic and zero-point Energies=          -1092.265811 au
Sum of electronic and thermal Free Energies=        -1092.326399 au
```

Pro-(*S*)-**5a**

```
C        0.126797   -1.159027    1.997042
C        0.182557   -1.710576    0.628591
C        0.875407   -2.201665   -0.189850
C        2.194162   -2.062260    0.166044
C        2.506191   -1.392494    1.419481
C        1.547305   -0.936512    2.261292
I       -0.485696    1.302434   -0.553732
O       -2.500752   -0.071531   -1.185028
C       -3.374431   -0.884198   -0.490387
C       -2.627166   -1.333896    0.760777
O       -1.379950   -1.877143    0.159089
C        3.347733   -2.559353   -0.707912
C        4.161791   -3.610741    0.088978
O       -0.742630   -0.994653    2.854715
C        1.360569    2.306626   -0.121804
C        1.582219    2.877804    1.137702
C        2.780366    3.543460    1.402631
C        3.765188    3.641416    0.416618
C        3.546337    3.071915   -0.838872
C        2.349019    2.404585   -1.109588
C       -4.759790   -0.202827   -0.201032
C       -5.384491    0.143145   -1.565235
C        4.267032   -1.365843   -1.072320
C        2.855222   -3.211262   -2.012364
H        1.787155   -0.463128    3.207869
H        3.548898   -1.257621    1.688502
H        0.574996   -2.649798   -1.128672
H        5.085394   -1.714793   -1.712567
H        4.714783   -0.899168   -0.189195
H        3.713303   -0.591833   -1.613820
H        3.715050   -3.555873   -2.596514
H        2.293866   -2.505486   -2.634335
H        2.218842   -4.081789   -1.818380
H        5.007091   -3.959842   -0.515265
H        3.542888   -4.478886    0.341357
H        4.567154   -3.202579    1.020639
H        2.374011   -0.497112    1.404860
H       -3.055099   -2.145721    1.354935
H       -3.604898   -1.801547   -1.074706
H        0.819376    2.808154    1.908204
H        2.942080    3.990271    2.380561
H        4.695729    4.162681    0.624876
H        4.305874    3.149147   -1.613000
H        2.181099    1.970476   -2.091526
H       -6.349106    0.649136   -1.433943
H       -5.557200   -0.763091   -2.159671
H       -4.718275    0.796193   -2.135924
H       -4.577292    1.088643    0.615083
H       -4.208305    0.889178    1.629132
H        3.866214    1.756536    0.119951
H       -5.533262    1.616902    0.716853
H       -5.681933   -1.181955    0.550378
H       -6.693588   -0.766382    0.636669
H       -5.762944   -2.139898    0.020600
H       -5.328224   -1.386438    1.568575
```

```
Sum of electronic and zero-point Energies=          -1092.274052 au
Sum of electronic and thermal Free Energies=        -1092.336418 au
```

Pro-(*R*)-**4c**

```
I         0.000000    0.000000    0.000000
O         0.000000    0.000000    2.100000
C         1.207207    0.000000    2.809068
C         1.084785   -0.804162    4.114762
C         0.760702   -2.278333    3.861507
C         0.732561    2.615738    1.138783
C         1.149268    3.208728   -0.189445
C         0.097154    3.939647   -0.898620
C        -1.108597    4.172768   -0.330527
C        -1.470808    3.660207    0.983739
C        -0.568370    2.891546    1.671682
O         2.296807    3.105311   -0.608454
C         2.867185    3.973858    1.528552
C        -3.925378    3.378490    0.564214
O         1.747815    2.166264    1.839404
C         1.604123    1.453322    3.100053
C         3.050785    5.509391    1.614347
C         3.100968    3.377913    2.928740
H         0.293174   -0.351312    4.727772
H         2.022225   -0.717928    4.684321
H         0.360640    4.323589   -1.878683
H        -1.844238    4.754610   -0.876992
H        -0.831737    2.442469    2.616172
H        -4.055172    5.741942    1.986649
H        -2.938480    5.999006    0.641453
H        -2.322845    5.954771    2.301709
H        -4.107480    3.638687    3.273074
H        -2.389310    3.772605    3.662878
H        -3.025170    2.285156    2.925939
H        -4.931753    3.594375    0.941586
H        -3.816352    2.291390    0.486165
H        -3.852868    3.799216   -0.444011
H         0.865417    1.954610    3.732561
H         2.592500    1.543622    3.557328
H         2.028039   -0.441691    2.211069
H         0.640013   -2.825065    4.803357
H         1.560988   -2.765331    3.290589
H        -0.165562   -2.367870    3.286923
C         0.057632    0.454881   -2.162237
C        -1.131845    0.564476   -2.895348
C         1.286701    0.625202   -2.815267
C        -1.092266    0.813266   -4.269176
H        -2.092041    0.442497   -2.398854
C         1.322502    0.881938   -4.188305
H         2.215013    0.554437   -2.255594
C         0.135073    0.975906   -4.917185
H        -2.019589    0.880324   -4.833893
H         2.280048    1.007786   -4.688209
H         0.165053    1.174486   -5.985516

Sum of electronic and zero-point Energies=          -1013.697305 au
Sum of electronic and thermal Free Energies=        -1013.757186 au
```

Pro-(*S*)-**5c**

C	0.074860	0.775049	0.223307
C	0.242283	0.957240	1.710252
C	1.539253	0.848670	2.290239
C	2.620039	0.408558	1.566858
C	2.422485	0.050633	0.170005
C	1.228117	0.184866	-0.455010
I	-0.921565	-2.018943	2.095456
O	-1.978937	-0.467318	3.676262
C	-2.758695	0.648707	3.405244
C	-2.154030	1.317016	2.178005
O	-0.704265	1.342455	2.508731
C	4.014618	0.245055	2.173438
C	5.017476	1.118164	1.376680
O	-0.917897	1.184580	-0.380916
C	0.246344	-3.249506	0.760469
C	-0.118713	-3.380348	-0.585797
C	0.637487	-4.181976	-1.442688
C	1.763952	-4.856563	-0.964429
C	2.129155	-4.729514	0.376775
C	1.374946	-3.927698	1.237907
C	-4.246795	0.316952	3.170564
C	-4.880544	-0.357074	4.389807
H	-4.318418	-0.350289	2.300312
H	-4.795957	1.237489	2.919507
C	4.437621	-1.243195	2.078820
C	4.066402	0.673230	3.651557
H	1.094710	-0.055901	-1.504525
H	3.268344	-0.335818	-0.389177
H	1.606144	1.084032	3.345102
H	5.439903	-1.369474	2.504380
H	4.467255	-1.603483	1.045645
H	3.745831	-1.883823	2.635976
H	5.085744	0.549666	4.032111
H	3.404724	0.064230	4.277020
H	3.791166	1.725953	3.781115
H	6.023201	1.000547	1.796174
H	4.748006	2.178617	1.433603
H	5.065857	0.838268	0.319356
H	-2.302803	0.713568	1.286154
H	-2.441160	2.352983	1.974282
H	-2.699835	1.366777	4.250128
H	-0.994646	-2.860245	-0.964302
H	0.343563	-4.283197	-2.484648
H	2.349980	-5.481682	-1.632961
H	3.000439	-5.257409	0.757025
H	1.660656	-3.838771	2.282735
H	-5.923919	-0.631123	4.196841
H	-4.862806	0.308882	5.261610
H	-4.323756	-1.262334	4.649530

Sum of electronic and zero-point Energies= -1013.703962 au
Sum of electronic and thermal Free Energies= -1013.762439 au

(*RR*)-**2a** + PhI

C	-0.4603977541	2.6944774145	-0.1248998536
C	-0.7926954493	2.9833187787	1.2727177078
C	0.0388770798	2.6163748322	2.2694698602
C	1.3307206292	1.9351991189	2.0561796113

C	1.7393648074	1.7087260094	0.7951855272
C	0.9625973024	2.1364239521	-0.4180039751
O	-1.2340358378	2.9095235306	-1.0489472126
C	2.1280076269	1.5167337235	3.2990019194
C	2.4756034492	2.7733914977	4.1335373268
C	3.4412041938	0.803628933	2.9298805064
C	1.2721502526	0.5480665114	4.1510961488
O	1.6960825971	3.1590823274	-1.0822067057
I	-1.1228093873	-1.3499067783	-0.296549525
C	1.3435886953	3.0697565874	-2.4674245141
C	0.979116561	1.5804174583	-2.6849525541
O	0.8871114045	1.0578215442	-1.3380577055
C	-2.3711630824	-2.8931621158	0.4512462657
C	-3.7457456602	-2.6735870766	0.5701602641
C	-4.5622086199	-3.694729582	1.0615127125
C	-4.0133088912	-4.9236445452	1.4305928616
C	-2.638950398	-5.1321256715	1.3067802243
C	-1.8108796908	-4.1196787033	0.816991963
C	1.9812819378	0.7410555412	-3.5152859881
C	3.4008872281	0.8019350384	-2.9229748911
C	1.9845043927	1.2839600722	-4.959009784
C	1.5037516896	-0.7244455669	-3.5379833401
H	-1.7514150542	3.4569707563	1.4623085969
H	-0.2587395031	2.8190561668	3.2945344606
H	2.6791027404	1.2206776683	0.5649834579
H	3.0356971951	2.485056072	5.030882353
H	1.5826786143	3.3143080476	4.4653298804
H	3.0938766613	3.4688239657	3.555001372
H	3.9750800764	0.5184524106	3.8430906143
H	4.1046688447	1.4511710416	2.3459033584
H	3.258301039	-0.1100517017	2.3534985467
H	1.8306415175	0.2391068481	5.0426465852
H	1.0144375754	-0.3508840369	3.580246894
H	0.337784067	1.0069881276	4.4920161613
H	2.2163040945	3.3997855097	-3.0349176536
H	0.4941882264	3.7205513312	-2.695035619
H	-0.0119791559	1.5038850526	-3.1455503373
H	-4.1763578782	-1.7200394566	0.2827315238
H	-5.6315981516	-3.5236534659	1.153349772
H	-4.6530452692	-5.7146886946	1.8117354636
H	-2.2026821513	-6.0862985678	1.5906942443
H	-0.7429519821	-4.2861474396	0.7208934315
H	4.0851249252	0.1868920443	-3.5191720429
H	3.411483685	0.4200118912	-1.8976501981
H	3.8031159764	1.8213376197	-2.9087326259
H	2.6350415281	0.6696943417	-5.5920864823
H	2.35298155	2.3150842332	-5.0150177486
H	0.9787205897	1.2610884751	-5.3968190939
H	2.1654167874	-1.3318947784	-4.1672612239
H	0.4876115234	-0.8063841873	-3.9429030026
H	1.499498466	-1.1559821926	-2.532974254

Sum of electronic and zero-point Energies= -1092.361275 au
Sum of electronic and thermal Free Energies= -1092.426575 au

(*RS*)-**3a** + PhI

C	2.6477260239	0.4570032755	1.808339182
C	2.3312671248	1.7858102691	2.32882609
C	1.8646474396	2.7634072287	1.522794034
C	1.6381669525	2.6019341866	0.0769856028

C	1.9156590414	1.4102066881	-0.483913952
C	2.4840197724	0.2316925307	0.2723724866
O	3.0332966888	-0.4570949305	2.5168962665
C	1.0953587853	3.8101470459	-0.700288206
C	-0.2732652284	4.2285043778	-0.1107356041
C	0.9006335541	3.4964005577	-2.1944261996
C	2.0945312969	4.9861759397	-0.5779121976
O	3.7675141016	-0.0998419944	-0.2325911001
I	-1.6424283733	-0.5474681895	0.0509444154
C	3.5521570197	-0.9945571619	-1.3227204266
C	2.2700950362	-1.7668123267	-0.9410128914
O	1.6700699617	-0.9198239527	0.0671195754
C	-3.7606178373	-0.4369734138	0.0192022298
C	-4.4674189734	-0.4157182059	1.2242171643
C	-5.8621523614	-0.3472018363	1.1984592413
C	-6.5458847981	-0.3007640321	-0.0172617097
C	-5.8295012142	-0.3229485889	-1.2147032558
C	-4.4345209125	-0.3912413982	-1.203820751
C	2.4639658475	-3.2147616834	-0.4227174509
C	3.520414513	-3.290967637	0.6949557142
C	2.8933741289	-4.0896152846	-1.6183615074
C	1.1136123462	-3.7274045703	0.1146492605
H	2.4757333617	1.9356311379	3.3944777459
H	1.63532449	3.7298001024	1.9638314864
H	1.7603776985	1.2369382833	-1.5434696694
H	-0.6681866626	5.0946799235	-0.6548753693
H	-0.2027713721	4.5097276914	0.9455820087
H	-0.9992759601	3.4123378585	-0.1925861698
H	0.5122599906	4.3819003349	-2.7095257947
H	0.1835691122	2.6823086081	-2.3474415279
H	1.8446544419	3.2203461254	-2.677885492
H	1.7160277501	5.8602663939	-1.1210790183
H	3.0688439137	4.7178882857	-1.0016661927
H	2.2539032214	5.2904853987	0.4622592667
H	4.4406855517	-1.6225351499	-1.4058593555
H	3.4247057416	-0.4428790835	-2.2645368682
H	1.5781898538	-1.8022356524	-1.7931706064
H	-3.9399165492	-0.453742433	2.1716382222
H	-6.411594076	-0.3313012476	2.1360470905
H	-7.6308948895	-0.2482087034	-0.0314447717
H	-6.3535020126	-0.2879434354	-2.1662794484
H	,-3.8816832931	-0.4099394384	-2.1373597463
H	3.5609839986	-4.3105933242	1.0964347326
H	3.2864915499	-2.6017634934	1.5096535158
H	4.5249019784	-3.0474364409	0.3285634683
H	3.0077036596	-5.1319899611	-1.3001454815
H	3.8548421348	-3.7705334824	-2.0394148112
H	2.1480529871	-4.0684660648	-2.4238805345
H	1.203965238	-4.7737149286	0.4296880505
H	0.3297071508	-3.6739655111	-0.6514051422
H	0.7850826206	-3.1380127655	0.9750067461

Sum of electronic and zero-point Energies= -1092.356793 au
Sum of electronic and thermal Free Energies= -1092.420990 au

(*RR*)-**2c** + PhI

C	0.005163	0.543306	0.096596
C	0.006979	0.524764	1.561093
C	1.154953	0.357256	2.249824

```
C        2.479637    0.193637    1.619419
C        2.562301    0.226664    0.277676
C        1.378495    0.427366   -0.625863
O       -1.020318    0.656558   -0.563165
C        3.689260   -0.009883    2.542649
C        3.834692    1.217316    3.474972
C        4.998562   -0.172617    1.750317
C        3.475046   -1.285261    3.393911
O        1.590071    1.601578   -1.394953
I        1.206529   -3.751274   -0.743743
C        0.937259    1.405245   -2.655539
C        0.805163   -0.131303   -2.808146
O        1.331835   -0.639827   -1.562464
C        1.078232   -5.817253   -0.276672
C       -0.154372   -6.369521    0.081096
C       -0.233664   -7.730916    0.382878
C        0.905686   -8.535017    0.328587
C        2.131884   -7.973096   -0.029630
C        2.225183   -6.613153   -0.333938
C        1.607525   -0.741156   -3.954887
H        2.647319   -0.396840   -3.878260
C        1.027881   -0.402631   -5.332797
H        1.623248   -1.829221   -3.817840
H       -0.954309    0.633982    2.054542
H        1.109090    0.336712    3.335150
H        3.500086    0.116828   -0.254498
H        4.689325    1.078265    4.147585
H        2.948742    1.374335    4.099832
H        4.003120    2.131808    2.895320
H        5.833871   -0.314424    2.444909
H        5.218493    0.712710    1.143398
H        4.965598   -1.044578    1.087800
H        4.330082   -1.436490    4.063466
H        3.379830   -2.170946    2.755997
H        2.577208   -1.223982    4.018432
H        1.581272    1.853032   -3.419627
H       -0.039515    1.897436   -2.665677
H       -0.249678   -0.415746   -2.885565
H       -1.043254   -5.748644    0.123527
H       -1.192992   -8.159788    0.660505
H        0.838343   -9.593551    0.563803
H        3.024485   -8.591627   -0.074981
H        3.180377   -6.180773   -0.613369
H        1.616066   -0.873508   -6.127348
H        1.025815    0.677897   -5.522168
H       -0.005067   -0.758446   -5.427837

Sum of electronic and zero-point Energies=          -1013.791677  au
Sum of electronic and thermal Free Energies=        -1013.854528  au
```

(*RS*)-**3c** + PhI

```
C        0.026511   -0.158775    0.070411
C        0.014416   -0.257560    1.528755
C        1.161272   -0.272135    2.241280
C        2.505227   -0.198440    1.643618
C        2.604777   -0.123981    0.303322
C        1.419100   -0.114458   -0.632512
O       -0.990143   -0.115640   -0.600803
C        3.710933   -0.207569    2.594891
C        3.616322    1.004088    3.553831
```

C	5.046839	-0.117012	1.835928
C	3.707194	-1.519977	3.415570
O	1.469652	-1.223313	-1.515500
I	2.359407	4.020372	-0.588261
C	2.255789	-0.819514	-2.634985
C	2.014711	0.701339	-2.749613
O	1.467155	1.048379	-1.456578
C	3.029706	6.003588	-0.237682
C	2.119853	6.973126	0.191487
C	2.564183	8.278138	0.415463
C	3.903555	8.613883	0.212865
C	4.803770	7.637562	-0.216090
C	4.372904	6.328577	-0.443483
C	1.066479	1.153610	-3.863092
C	-0.288740	0.441268	-3.909250
H	1.599648	1.027747	-4.817083
H	0.915521	2.233276	-3.738253
H	-0.960939	-0.306159	2.003381
H	1.094256	-0.339429	3.323874
H	3.570123	-0.065474	-0.188424
H	4.469689	1.005561	4.242356
H	2.705383	0.984061	4.161867
H	3.625897	1.946606	2.995299
H	5.877842	-0.127982	2.549830
H	5.120797	0.809283	1.255380
H	5.185316	-0.964120	1.154528
H	4.554457	-1.531202	4.111457
H	3.794139	-2.392990	2.758970
H	2.794184	-1.637347	4.009297
H	1.904408	-1.383887	-3.501908
H	3.318223	-1.049027	-2.472511
H	2.968458	1.232580	-2.861609
H	1.077109	6.717220	0.348096
H	1.855764	9.031950	0.748831
H	4.243870	9.630707	0.387667
H	5.848632	7.889983	-0.377068
H	5.076396	5.573253	-0.778202
H	-0.926136	0.895018	-4.676207
H	-0.798262	0.503741	-2.945122
H	-0.183493	-0.621285	-4.158790

Sum of electronic and zero-point Energies= -1013.786146 au
Sum of electronic and thermal Free Energies= -1013.849701 au

Additional References

[1] H. Chen, Y.-H. Fan, A. Natarajan, Y. Guo, J. Iyasere, F. Harbinski, L. Luus, W. Christ, H. Aktas, J. A. Halperin, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 5401-5405.

[2] M. Fujita, A. Ota, S. Ito, K. Yamamoto, Y. Kawashima, *Synthesis* **1998**, 599-604.

[3] P. M. Fresneda, P. Molina, J. A. Bleda, *Tetrahedron* **2001**, *57*, 2355-2363.

[4] U. Schmidt, R. Meyer, V. Leitenberger, H. Griesser, A. Lieberknecht, *Synthesis* **1992**, 1025-1030.

[5] M. Hirata, E. Taniguchi, *J. Fac. Agr., Kyushu Univ.* **1997**, *42*, 101-112.

[6] A. Paulsen, *Medd. Norsk Farm. Selskap* **1959**, *22*, 11-14.

[7] A. Funke, A. Paulsen, R. Gombert, *Bull. Soc. Chim. Fr.* **1960**, 1644-1646.

[8] K. Suzuki, N. Satake, A. Sugiura, T. Fujii, *Chem. Abstr.* **1994**, *120*, 134493t.

[9] S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, *124*, 1307-1315.

[10] M. Mischitz, W. Kroutil, U. Wandel, K. Faber, *Tetrahedron: Asymmetry* **1995**, *6*, 1261-1272.

[11] S. S. Prashant, M. J. Lamoreaux, J. F. Berry, R. D. Gandour, *Tetrahedron: Asymmetry* **1998**, *9*, 1843-1846.

[12] Y. Fukuyama, H. Yaso, T. Mori, H. Takahashi, H. Minami, M. Kodama, *Heterocycles* **2001**, *54*, 259-274.

[13] Y. Kita, H. Tohma, K. Kikuchi, M. Inagaki, T. Yakura, *J. Org. Chem.* **1991**, *56*, 435-438.

[14] V. Diemer, H. Chaumeil, A. Defoin, A. Fort, A. Boeglin, C. Carré, *Eur. J. Org. Chem.* **2006**, 2727-2738.

[15] H. Abe, Y. Aoyagi, M. Inoue, *Org. Lett.* **2005**, *7*, 59-61.

[16] R. M. Carman, L. K. Lambert, W. T. Robinson, J. M. A. M. Van Dongen, *Aust. J. Chem.* **1986**, *39*, 1843-1850.

[17] J. Gagnepain, R. Méreau, D. Dejugnac, J.-M. Léger, F. Castet, D. Deffieux, L. Pouységu, S. Quideau, *Tetrahedron* **2007**, *63*, 6493-6505.

[18] N. Lebrasseur, J. Gagnepain, A. Ozanne-Beaudenon, J.-M. Léger, S. Quideau, *J. Org. Chem.* **2007**, *72*, 6280-6283.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. J. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennuci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C.

Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, in *Gaussian 03, Revision D-02*, Gaussian Inc., Pittsburgh, PA, **2003**.

[20] W. J. Hehre, L. Radom, P. v. P. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, **1986**.

[21] R. G. Parr, W. Yang, *Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[22] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100.

[23] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[24] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

[25] T. H. Dunning Jr, P. J. Hay, in *Modern Theoretical Chemistry* (Ed.: H. F. Schaefer III), Plenum, New York, **1976**, pp. 1-28.

[26] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270-283.

[27] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 284-298.

[28] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899-926.

[29] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211-7218.

[30] P. F. Flükiger, PhD Dissertation, University of Geneva, **1992**.

[31] S. Portmann, H. P. Lüthi, *Chimia* **2000**, *54*, 766.