Development of Enantioselective Synthetic Routes to (–)-Kinamycin F and (–)-Lomaiviticin Aglycon

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Supporting Information

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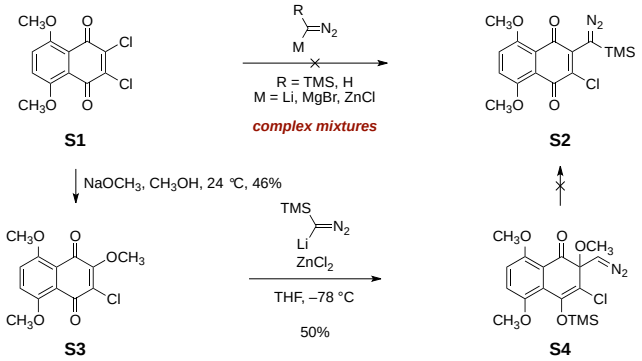
Additional Experimental Information.

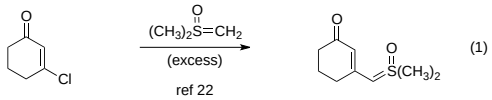
1. Initial efforts focusing on appending the one-carbon synthon and dinitrogen substituents to the napthoquinone 16:

We were initially confronted with the option of appending the one-carbon synthon and dinitrogen substituents to the naphthoquinone **16**, followed by bond formation to the enone **17**, or homologation of the enone **17** followed by addition to the quinone **16**. The former pathway was initially pursued, as we expected it would lead to a higher level of convergence when more functionalized enone partners were employed.



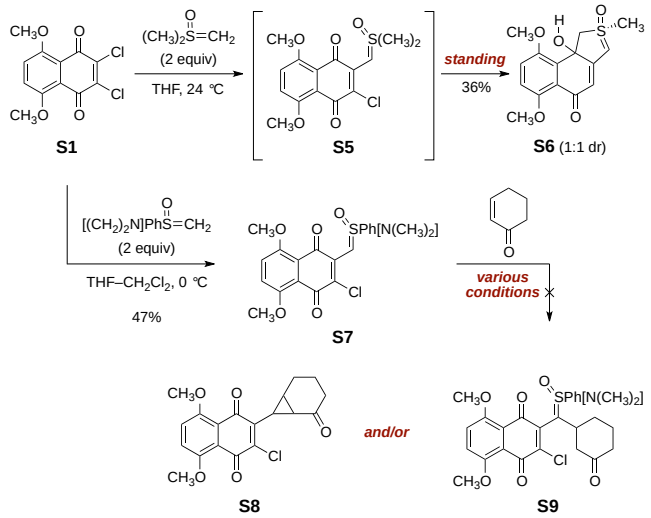
Scheme S1. Initial Approaches to the Diazonaphthoquinone **S2**.

Our studies began with the symmetrical reagent 2,3-dichloro-5,8-dimethoxynaphthoquinone (**S1**, Scheme S1), which is available in two steps from 2,3-dichloromaleic anhydride.[1] Initial attempts to couple this reagent with diazomethane, or its functional equivalent, to form the addition–elimination product **S2**, were unsuccessful. For example, treatment of **S1** with lithio(trimethylsilyl)diazomethane led to intractable mixtures of products. Reasoning that electron-transfer to the electrophilic naphthoquinone may occur, we investigated the transmetalation of this reagent to metals (e.g. Mg, Zn) which form more covalent bonds to carbon. These experiments also resulted in complex mixtures of products. In order to lower the oxidation potential of the naphthoquinone, we prepared 2-chloro-3,5,8-trimethoxynaphthoquinone (**S3**) by treatment of 2,3-dichloro-5,8-dimethoxynaphthoquinone (**S1**) with sodium methoxide (46%).[1] We were surprised to observe that exposure of **S3** to a reagent formed from lithio trimethylsilyldiazomethane and zinc chloride formed the stable addition product **S4** (50%). However, all attempts to cleave the enoxysilane and eliminate methoxide (e.g. *tetra*-butylammonium fluoride) led to unidentifiable decomposition products.



The failure of these experiments led us to consider introduction of the one-carbon synthon without the dinitrogen substituent. Tamura[2,3] reported that the reaction of 3-chloro-cyclohex-2-ene-1-one with an excess of dimethylsulfoxonium methylide[4,5] formed an extended ylide (eq 1). We targeted the analogous ylide **S5**, derived from the naphthoquinone **S1** (Scheme S2). In the event, addition of an excess of dimethylsulfoxonium methylide to **S1** formed a mixture of diastereomeric tricyclic sulfonium salts (**S6**, 36%, 1:1 dr). We reasoned that the tricycles **S6** formed via small concentrations of a methylidene ylide, itself derived from the expected addition–elimination product **S5**. To circumvent this, we investigated the application of dimethylaminophenylsulfoxonium methylide[6] in the addition step. This reagent underwent smooth 1,4-addition–elimination to 2,3-dichloro-5,8-dimethoxynaphthoquinone (**S1**), forming the isolable ylide **S7** (47%). Although **S7** exhibited limited stability in solution (complete decomposition after

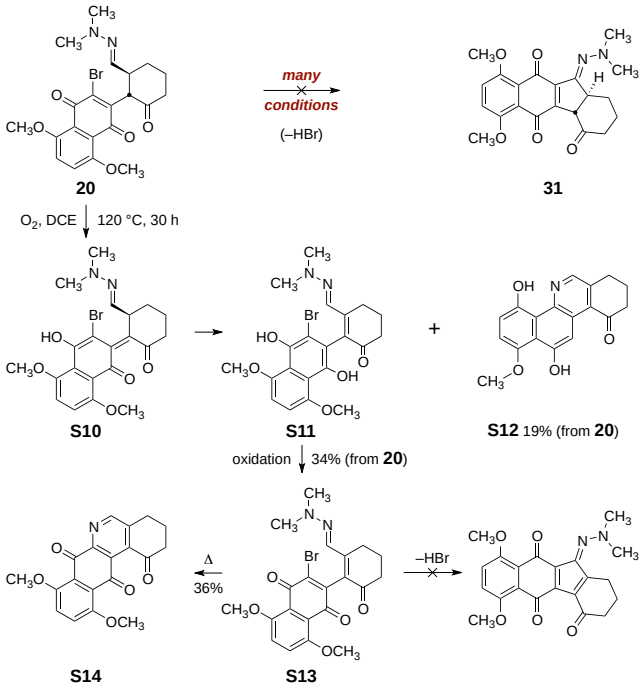
standing for 3 h at 24 °C in methanol), we made several attempts to synthesize the cyclopropanation or 1,4-addition products **S8** and **S9**, respectively, by reaction with cyclohex-2-ene-1-one. However, under ambient conditions the ylide **S7** was unreactive toward cyclohex-2-ene-1-one; attempts to accelerate the reaction (addition of dirhodium tetraacetate or Lewis acids, or heat) led to decomposition, without generation of detectable coupling products.



Scheme S2. Attempted Formation of the Cyclopropanation and 1,4-Addition Products **S8** and **S9**.

2. Conditions examined in the attempted conversion of the α-quinonylated product 20 to the cyclization product 31:

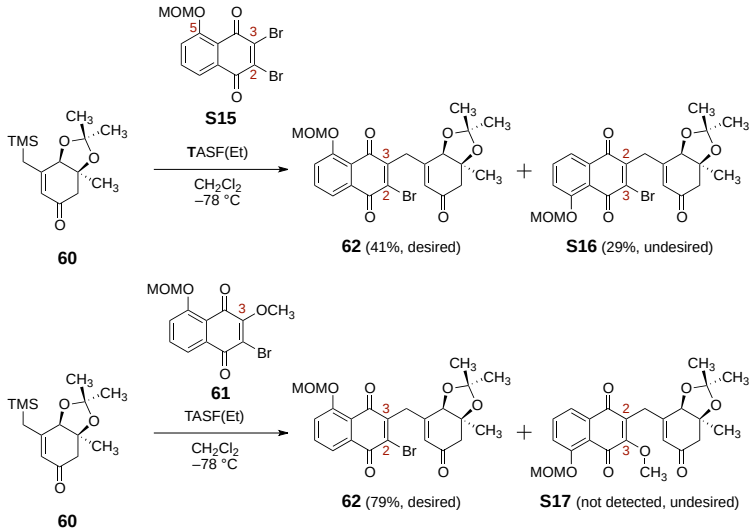
In the course of these studies, we found that thermolysis of **20** (1,2-dichloroethane, 120°C, sealed tube) produced the pyridine derivative **S12** (19%) and the unsaturated ketone **S13** (34%, Scheme S3). The latter may form by sequential enolization steps (**20**→**S10**→**S11**), followed by oxidation. The product **S13** was deemed useful, as in its generation an oxidation required for construction of the diazofluorene was accomplished. Moreover the planar topology of **S13** (compared to **20**) was expected to facilitate cyclization. Unfortunately, we were unable to advance **S13** to the cyclization product; efforts to promote cyclization under free radical or transition metal-mediated pathways, or in the presence of Lewis acids, resulted in recovery of starting material. Under forcing thermal conditions **S13** transformed, unexpectedly, to the pyridine **S14** (36%).



Scheme S3. Attempted Elaboration of the Hydrazone **20**.

3. Development of a regioselective naphthoquinone coupling in the synthesis of (–)-kinamycin F (9):

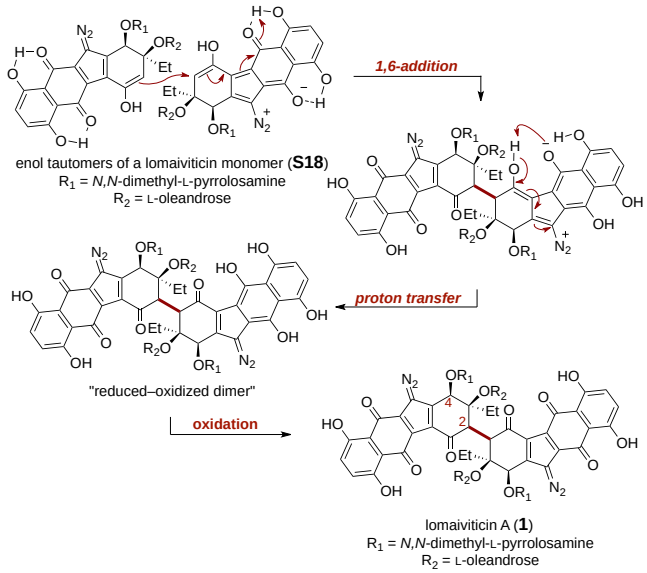
A significant obstacle toward the synthesis of (–)-kinamycin F (**9**) involved the regiocontrolled coupling of the β-trimethylsilylmethyl-α,β-unsaturated ketone **60** with an oxidized juglone derivative. Although the C-5 juglone hydroxyl substituent was anticipated to bias nucleophilic addition to the C-3 position, early experiments revealed that TASF-mediated coupling of the enone **60** and *O*-(methoxymethyl)-2,3-dibromojuglone (**S15**)[7,8] formed mixtures of C-3 (**62**) and C-2 (**S16**) substitution products (41%, 29%, respectively, Scheme S4). To increase the bias of the system toward C-3 addition, *O*-(methoxymethyl)-2-bromo-3-methoxyjuglone (**61**) was prepared by heating a methanolic solution of *O*-(methoxymethyl)-2,3-dibromo-juglone (**S15**) and sodium carbonate (96%). Fluoride-mediated coupling with this substrate now proceeded with complete regioselectivity, forming the C-3 substituted product **62** in 79% yield. Owing to the absence of long range C–H couplings, the connectivity of **62** could not be determined by multidimensional NMR analysis; it was ultimately secured by X-ray diffraction.[9]



Scheme S4. TASF(Et) Coupling of the Kinamycin Enone **60** and the Juglone Derivatives **S15** and **61**.

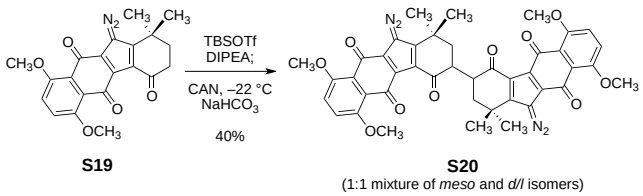
4. A potential mechanism for the biosynthetic oxidative coupling of monomeric diazofluorenes:

When we began our studies in 2008, we hypothesized that, given the existence of the kinamycins, nature may synthesize lomaiviticins A (**1**) and B (**2**) by oxidative coupling of monomeric diazofluorenes. A working mechanism for the putative biosynthetic dimerization is shown in Scheme S5. In this mechanism, the enol tautomers of a putative lomaiviticin monomer (**S18**) may dimerize by a 1,6-addition reaction, to form a reduced–oxidized dimer that may be reoxidized to generate lomaiviticin A (**1**). This pathway was provocative from a synthetic standpoint, as it suggested that the naphthoquinone might behave as the oxidant in the dimerization process; the internal redox process observed in the conversion of **20** to **S13** (Scheme S3) provided some tangential support for this reactivity. Two assumptions implicit to this hypothesis are that enols such as **S18** exist in concentrations sufficient to promote dimerization and that these enols are ambiphilic. Support for the second criteria is found in seminal studies by Koch and co-workers, who showed that 11-deoxyanthracyclines undergo dimerization via ambiphilic enol intermediates.[10,11] Spectroscopic data of lomaiviticin A (**1**)[12] and an X-ray of a kinamycin derivative[13] suggest that the C-2 and C-4 substituents occupy pseudoaxial positions. Although this is not necessarily the preferred conformation in the dimerization transition state, these data provide some encouragement that the dimerization may occur to give the natural stereochemistry.



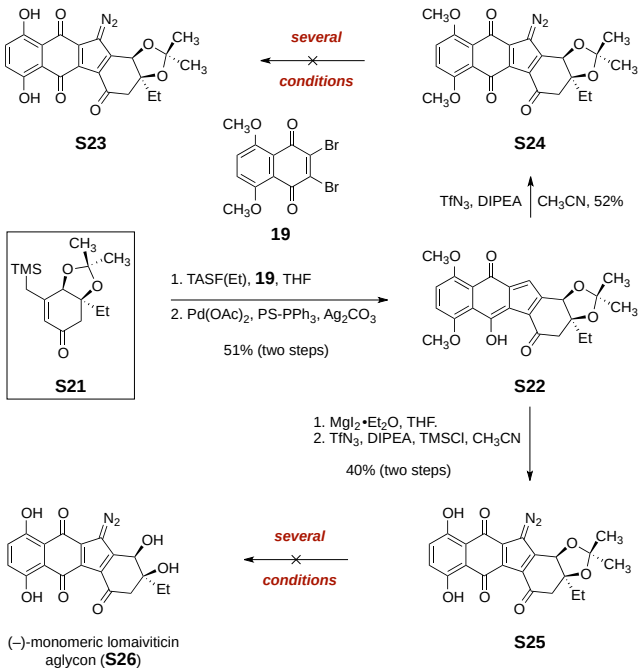
Scheme S5. Postulated Dimerization in Lomaiviticin A (**1**) Biosynthesis.

5. Initial model studies aimed at evaluating the oxidative dimerization of diazofluorenes:



Scheme S6. Oxidative Dimerization of the Diazofluorene **S19**.

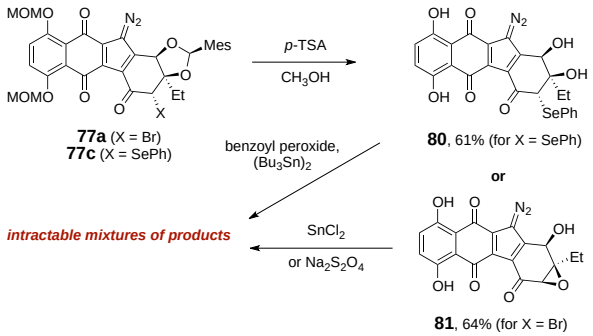
In an early model study, we generated the enoxysilane of the diazofluorene **S19** (TBSOTf, DIPEA) and treated the unpurified enoxysilane with ceric ammonium nitrate (CAN, Scheme S6). Under these conditions, the dimeric diazofluorene **S20** was formed in 40% yield as a 1:1 mixture of *meso* and *d*/*l* isomers. This result motivated us to study this transformation in more detail using a fully-functionalized substrate. Toward this end, we prepared the diazofluorene (Scheme S7). The cyclized product **S22** was obtained in two steps from the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S21** and 5,8-dimethoxy-2,3-dibromonaphthoquinone (**19**, 51% overall). Diazo transfer to the cyclized product **S22** formed the diazofluorene **S24** (52%). In anticipation of deprotection of the oxidative coupling product, we attempted to cleave the methyl ether functions of **S24** (**S24→S23**). However, under all conditions examined (e.g., magnesium iodide, chlorotrimethylsilane–sodium iodide, boron tribromide) extensive hydrodediazotization and decomposition was observed (UPLC/MS analysis). To circumvent this, we first cleaved these ethers (magnesium iodide) and then implemented the diazo transfer (trifluoromethanesulfonyl azide, DIPEA, chlorotrimethylsilane)[14] and in this way the diazofluorene **S25** was obtained in 40% yield (two steps). Further exploratory studies revealed that removal of the acetonide of **S25** was also problematic; in the presence of a variety of acids (e.g., iodotrimethylsilane, trimethylsilyl trifluoromethane-sulfonate, trifluoroacetic acid), only starting material **S25** or unidentified decomposition products were observed. These results prompted us to reconsider our protecting group scheme before proceeding further.



Scheme S7. Attempted Synthesis of the Diazofluorene **S23**, and the (–)-Monomeric Lomaiviticin Aglycon (**S26**).

6. Reactivity of the diazofluorene toward reducing agents:

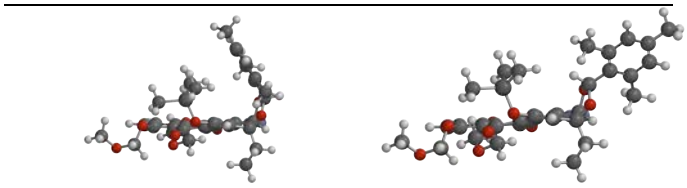
Although we were cognizant of the reactivity of the diazofluorene toward reducing agents,[15-17] we examined the possibility of conducting a reductive coupling reaction using the α-phenylselenyl and α, β-epoxy ketones **80** and **81** (respectively) as precursors to an α-keto radical.[18-21] The α-phenylselenyl ketone **80** was prepared by deprotection of the α-phenylselenyl diazofluorene **77c** (61%). The α, β-epoxyketone **81** was obtained by mild thermolysis (50 °C) of the deprotected α-bromoketone derivative (64%). A variety of radical initiators (benzoyl peroxide, hexabutyldistannane) and reducing agents (tin(II) chloride, sodium thiosulfate) were added to the selenyl ketone **80** and the epoxide **81** in an attempt to form an α-keto radical. Unfortunately, under these conditions extensive decomposition of the substrate was observed (including hydrodediazotization; UPLC/MS analysis).



Scheme S8. Attempted Reductive Dimerization Reactions.

7. Computational studies of enoxysilanes S27 and S28.

Inspection of molecular models, and later, computational studies, clearly revealed the origins of the steric bias in the dimerization of the *endo*-mesityl diazofluorene **71** (Figure S1). In the energy-minimized structure of the enoxysilane **S27** (derived from **71**), the mesityl substituent protrudes into the cavity of the 6-5 system. Approach from the bottom face to afford the undesired *anti*, *anti*-stereochemistry is kinetically favored. In considering ways to invert this bias, we recognized that epimerization of the mesityl substituent, to the *exo* orientation, might promote bond formation to the desired (concave) face of the enoxysilane. The minimized structure of the *exo*-enoxysilane **S28** shows that the concave face of this diastereomer is significantly less hindered than that of the *endo*-isomer **S27**.



endo-enoxysilane **S27** *exo*-enoxysilane **S28**

Figure S1. Energy Minimized Structures of the Enoxysilanes **S27** and **S28**.

8. Proposed model between the manganese anion and the radical cation during dimerization:

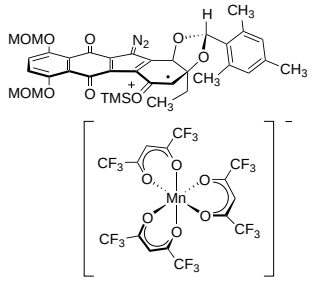
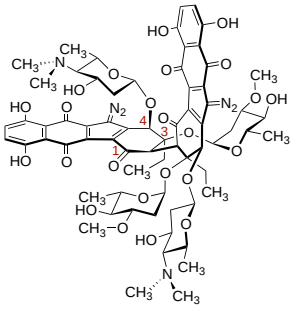


Figure S2. Proposed Association Between the Radical Cation and Manganese Anion Intermediates in the Oxidative Coupling of **87**.

9. Preparation of semisynthetic lomaiviticin B (2):

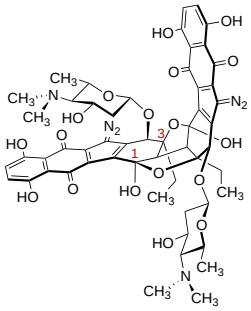
To probe for potential effects of charge on chemical shifts, semisynthetic lomaiviticin B (**2**) was obtained by partial hydrolysis of lomaiviticin A[22] (**1**, trifluoroacetic acid, aqueous methanol, 45 °C, 82%, Scheme S9). The H-2 and C-2 resonances (as well as all other resonances) of the bis(trifluoroacetate) salt of lomaiviticin B (**2**) obtained in this way were in complete agreement with literature values. The free base of **2** was obtained by a simple basic wash. Although the free base was considerably less stable than the protonated form (complete decomposition after standing for 12 h at 23 °C in *N*,*N*-dimethylformamide-d_7), this species exhibited sufficient stability in methanol-d_4 to allow for collection of 1H, COSY, and HSQC spectra. The chemical shifts of H-2 and C-2 in the free base form were in better agreement with (–)-lomaiviticin aglycon (**6**, free base of **2**: δ H-2 = 3.64, δ C-2 = 71.3, methanol-d_4). Thus, the initial chemical shift discrepancies observed between (–)-lomaiviticin aglycon (**6**) and natural lomaiviticin B (**2**) are attributed to the charged state of **2** when it was obtained from the producing organism.[1]



(–)-lomaiviticin A (**1**)

TFA, H_2O–CH_3OH, 45 °C

82%



(–)-lomaiviticin B (**2**)

species	δ H-2	δ C-2
(–)-**2**•2 HOTFA	2.61 (lit.[1] 2.64)	43.5 (lit.[1] 44.0)
(–)-**2** (free base)	3.64	71.3
(–)-**6**	3.41	62.1

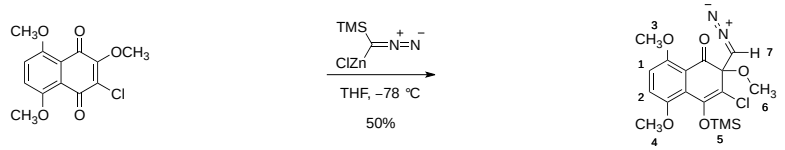
Scheme S9. Semisynthesis of (–)-lomaiviticin B (**2**). Spectroscopic data for **2** were obtained in methanol-d_4. Spectroscopic data for **6** were obtained in 33% *N*,*N*-dimethylformamide-d_7–methanol-d_4.

General Experimental Procedures. All reactions were performed in single-neck, flame-dried, round-bottomed flasks fitted with rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula, or were handled in a nitrogen-filled drybox (working oxygen level <1 ppm). Organic solutions were concentrated by rotary evaporation at 30–33 °C. Normal and reverse phase flash-column chromatography was performed as described by Still and co-workers.[23] Normal phase purifications employ silica gel (60 Å, 40–63 μm particle size) purchased from Sorbent Technologies (Atlanta, GA). Reverse phase purifications employ C_{18}-labeled silica gel (125 Å, 55–105 μm particle size) purchased from Waters Corporation (Milford, MA). Analytical thin-layered chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm). Preparative TLC (PTLC) was performed using glass plates precoated with silica gel (1.0 mm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or submersion in aqueous ceric ammonium molybdate solution (CAM), acidic *p*-anisaldehyde solution (PAA), or aqueous potassium permanganate solution ($KMnO_4$), followed by brief heating on a hot plate (120 °C, 10–15 s).

Materials. Commercial solvents and reagents were used as received with the following exceptions. Benzene, dichloromethane, and toluene were purified according to the method of Pangborn and co-workers.[24] Acetonitrile, *N*,*N*-di-*iso*-propylethylamine, and triethylamine were distilled from calcium hydride under an atmosphere of nitrogen immediately before use. Tetrahydrofuran was distilled from sodium/benzophenone under an atmosphere of nitrogen immediately before use. Methanol was distilled from magnesium methoxide under an atmosphere of nitrogen immediately before use. Chloromethyl methyl ether, hexamethylphosphoramide, and trimethylsilylchloride were distilled from calcium hydride and stored under nitrogen. Trimethylsilyl triflate and ditertbutylmethyl triflate were distilled and stored under nitrogen. 4-Å Molecular sieves were activated by heating overnight in vacuo (200 °C, 200 mTorr), stored in a gravity oven (120 °C), and were flame-dried in vacuo (100 mTorr) immediately before use. Cerium trichloride was dried by heating in vacuo (100 °C, 100 mTorr) for 30 min immediately before use. Tris(diethylamino)sulfonium difluorotrimethylsilicate [TASF(Et)] was prepared by a modification[25] of the procedure of Middleton,[26] and was stored in a nitrogen-filled drybox at −20 °C. Polymer-bound triphenylphosphine (styrene-divinylbenzene copolymer, 20% cross-linked, 3.00 mmol triphenylphosphine/gram resin) was obtained from Strem Chemicals (Newburyport, MA) and was stored in a nitrogen-filled drybox. Magnesium iodide was prepared according to the procedure of Yamaguchi and co-workers.[27] *N*,*N*-(Dimethylamino)methylphenylsulfoxonium tetrafluoroborate was prepared according to the procedure of Johnson and co-workers.[28] Manganese tris(hexafluoroacetylacetonate) was prepared according to the procedure of Mayer and co-workers[29] and was sublimed in vacuo (60–70 °C, 200 mTorr) immediately before use. Solutions of trifluoromethanesulfonyl azide in hexanes were prepared according to the procedure of Charette and co-workers.[30] The concentration of trifluoromethanesulfonyl azide was determined by ^{19}F NMR analysis using α,α,α-trifluoroacetophenone as an internal standard (TfN_3 $\delta = -76.34$; $PhCOCF_3$ $\delta = -72.11$), as described by Wong and co-workers.[31] Nonaflyl azide was prepared according to the procedure of Chiara and co-workers.[32] 2,3-Dibromo-5,6-dimethoxynaphthoquinone (**19**) was prepared according to the procedure of Huot and Brassard.[1] Mesitylaldehyde dimethyl acetal was prepared according to the procedure of Myers and co-workers.[33] Solutions of *n*-butyllithium in hexanes were standardized (in triplicate) using diphenylacetic acid as indicator.[34] (−)-Lomaiviticin aglycon (**6**) was prepared by deprotection of the *syn*,*syn*-dimer **91**, as previously described.[35] (−)-Lomaiviticin A (**1**) was prepared according to the method of Herzon and co-workers.[36] Diazofluorene **103** was prepared according to the procedure of Herzon and co-workers.[37] All other known compounds contain references to their preparation within the experimentals in which they are employed.

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 300, 400, 500, or 800 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent [$(CD_3)_2NCHO$, δ 8.03; $CHCl_3$, δ 7.26; C_6HD_5, δ 7.15; CHD_2OD, 3.31]. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet and/or multiple resonances, br = broad, app = apparent), integration, coupling constant in Hertz, and assignment. Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 75, 100, 125, or 200 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent [$(CD_3)_2N\mathbf{C}DO$, δ 163.2; C_6D_6, δ 128.0; $CDCl_3$, δ 77.0; CD_3OD, δ 49.0]. Distortionless enhancement by polarization transfer spectra [DEPT (135)] were recorded at 100 or 125 MHz at 24 °C, unless otherwise noted. ^{13}C NMR and DEPT (135) data are combined and represented as follows: chemical shift, carbon type [obtained from DEPT (135) experiments]. Carbon-decoupled fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 100 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane. Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were obtained using a Thermo Electron Corporation Nicolet 6700 FTIR spectrometer referenced to a polystyrene standard. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). Analytical ultra high-performance liquid chromatography/mass spectrometry (UPLC/MS) was performed on a Waters UPLC/MS instrument equipped with a reverse-phase C_{18} column (1.7 μm particle size, 2.1 × 50 mm), dual atmospheric pressure chemical ionization (API)/electrospray (ESI) mass spectrometry detector, and photodiode array detector. Samples were eluted with a linear gradient of 20% acetonitrile–water containing 0.1% formic acid→100% acetonitrile containing 0.1% formic acid over 3 min, followed by 100% acetonitrile containing 0.1% formic acid for 1 min, at a flow rate of 800 μL/min. Analytical UPLC/MS data are represented as follows: retention time (t_R) in minutes. High-resolution mass spectrometry (HRMS) were obtained at the W. M. Keck Foundation Biotechnology Resource Laboratory at Yale University or using a Waters UPLC/HRMS instrument equipped with a dual API/ESI high-resolution mass spectrometry detector and photodiode array detector. Unless otherwise noted, samples were eluted over a reverse-phase C_{18} column (1.7 μm particle size, 2.1 × 50 mm) with a linear gradient of 5% acetonitrile–water containing 0.1% formic acid→95% acetonitrile–water containing 0.1% formic acid over 1.6 min, followed by 100% acetonitrile containing 0.1% formic acid for 1 min, at a flow rate of 600 μL/min.

Synthetic Procedures.[38]

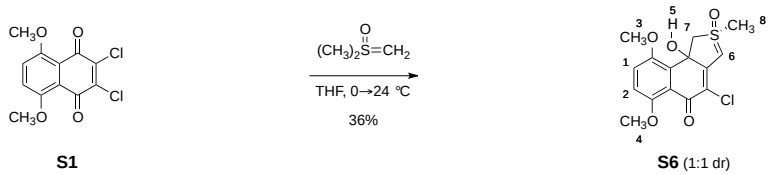


2-Chloro-3,5,8-trimethoxynaphthoquinone (**S3**) was prepared according to the procedure of Huot and Brassard.[1]

*Addition of Trimethylsilyl Diazomethane to 2-Chloro-3,5,8-trimethoxynaphthoquinone (**S3**):*

A solution of *n*-butyllithium in hexanes (2.05 M, 80.0 μL, 138 μmol, 1.30 equiv) was added dropwise via syringe to a stirred solution of trimethylsilyldiazomethane in hexanes (2.00 M, 80.0 μL, 160 μmol, 1.50 equiv) in tetrahydrofuran (500 μL) at −78 °C. The resulting mixture was stirred for 1 h at −78 °C. A solution of zinc dichloride in ether (1.00 M, 138 μL, 138 μmol, 1.30 equiv) was then added dropwise via syringe to the stirred solution at −78 °C. The resulting mixture was stirred for 30 min at −78 °C. A solution of 2-chloro-3,5,8-trimethoxynaphthoquinone [**S3**, 30.0 mg, 106 μmol, 1 equiv; dried by azeotropic distillation with benzene (2 × 500 μL)] in tetrahydrofuran (500 μL) was added via cannula to the stirred solution at −78 °C. The vessel containing 2-chloro-3,5,8-trimethoxynaphthoquinone (**S3**) was rinsed with tetrahydrofuran (500 μL) and the rinse was added to the reaction vessel via cannula. The reaction mixture was stirred for 15 min at −78 °C. The stirred solution was warmed over 10 min to 0 °C, and the warmed solution was stirred for 1 h at 0 °C. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (10 mL) and the diluted solution was poured into a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 50% ethyl acetate–hexanes) to afford the addition product **S4** as a yellow solid (21.0 mg, 50%).

R_f = 0.44 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (d, 1H, J = 9.0 Hz, H_1/H_2), 7.07 (d, 1H, J = 9.5 Hz, H_1/H_2), 5.31 (s, 1H, H_7), 3.90 (s, 3H, H_3/H_4), 3.88 (s, 3H, H_3/H_4), 3.01 (s, 3H, H_6), −0.09 (s, 9H, H_5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8 (C), 154.0 (C), 151.6 (C), 146.9 (C), 128.0 (C), 120.9 (C), 118.2 (C), 117.0 (CH), 115.4 (CH), 95.8 (C), 56.9 (CH_3), 56.2 (CH_3), 51.0 (CH_3), 49.2 (CH), 0.3 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2956 (w), 2087 (s), 1649 (m), 1564 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{17}H_{22}Cl^{35/37}N_2O_5Si$, 397.0987/399.0957; found, 397.0989/399.0970.

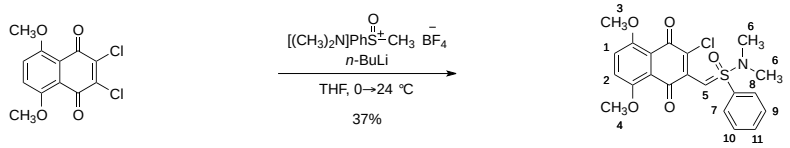


2,3-Dichloro-5,8-dimethoxynaphthoquinone (**S1**) was prepared according to the procedure of Huot and Brassard.[1]

*Synthesis of the Tricyclic Sulfonium Ylides **S6**:*

A solution of *n*-butyllithium in hexanes (2.20 M, 319 μL, 702 μmol, 2.00 equiv) was added to a stirred solution of trimethylsulfoxonium chloride (90.0 mg, 702 μmol, 2.00 equiv) in tetrahydrofuran (5.0 mL) at 24 °C. The resulting mixture was stirred for 20 min at 24 °C. The stirred solution was cooled to −78 °C. A solution of 2,3-dichloro-5,8-dimethoxynaphthoquinone [**S1**, 100 mg, 351 μmol, 1 equiv; dried by azeotropic distillation with benzene (1.0 mL)] in tetrahydrofuran (1.0 mL) was then added via cannula to the cold solution. The vessel containing 2,3-dichloro-5,8-dimethoxynaphthoquinone (**S1**) was rinsed with tetrahydrofuran (1.0 mL) and the rinse was added to the reaction vessel via cannula. The reaction mixture was stirred for 15 min at −78 °C. The stirred solution was warmed over 10 min to 24 °C, and the warmed solution was stirred for 30 min at 24 °C. The product mixture was filtered over a celite pad (1 × 2 cm). The celite pad was washed with methanol (3 × 5 mL). The filtrates were combined, and the combined filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% methanol–ethyl acetate) to afford the tricyclic sulfonium ylides **S6** as a yellow solid (43.8 mg, 36%, 1:1 mixture of diastereomers).

R_f = 0.55 (20% methanol–ethyl acetate; UV, CAM). ^{1}H NMR (500 MHz, DMF-d_7, 1:1 mixture of diastereomers): δ 7.24–7.15 (m, 4H, H_1/H_2/H_{1*}/H_{2*}), 6.86 (s, 1H, H_5), 6.77 (s, 1H, H_{5*}), 5.34 (d, 1H, J = 14.0 Hz, H_7), 5.14 (s, 1H, H_6), 4.94 (s, 1H, H_{6*}), 4.62 (d, 1H, J = 14.0 Hz, H_{7*}), 4.53 (d, 1H, J = 14.0 Hz, H_{7*}), 4.02 (d, 1H, J = 14.0 Hz, H_7), 3.90 (s, 6H, H_{3*}/H_{4*}), 3.89 (s, 3H, H_{8*}), 3.86 (s, 3H, H_8), 3.81 (s, 6H, H_3/H_4). ^{13}C NMR (125 MHz, DMF-d_7, 1:1 mixture of diastereomers): δ 173.6 (C), 173.5 (C*), 161.6 (C), 160.6 (C*), 154.3 (C), 154.3 (C*), 152.2 (C), 152.0 (C*), 130.4 (C), 130.3 (C*), 124.5 (C), 124.0 (C*), 117.3 (CH/CH*), 116.8 (CH), 116.6 (CH*), 104.4 (C), 104.3 (C*), 75.1 (C), 74.9 (CH_2), 74.5 (CH_2*), 72.7 (C*), 65.9 (CH), 65.7 (CH*), 58.0 (CH_3/CH_3*), 57.2 (CH_3), 57.1 (CH_3*), 46.4 (CH_3), 44.3 (CH_3*). IR (ATR-FTIR), cm^{-1}: 3262 (b), 2927 (w), 1530 (s), 1259 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{15}H_{16}Cl^{35/37}O_5S$, 343.0301; found, 343.0394.

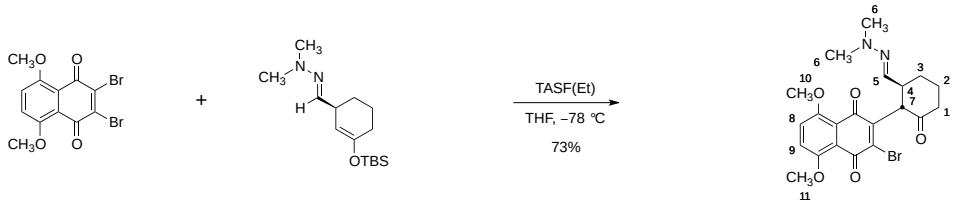


S1 **S7**

*Addition of N,N-(Dimethylamino)-methylphenylsulfoxonium Tetrafluoroborate to 2,3-Dichloro-5,8-dimethoxynaphthoquinone (**S1**):*

A solution of *n*-butyllithium in hexanes (2.20 M, 319 μL, 702 μmol, 2.00 equiv) was added to a stirred solution of *N,N*-(dimethylamino)-methylphenylsulfoxonium tetrafluoroborate (200 mg, 737 μmol, 2.10 equiv) in tetrahydrofuran (2.0 mL) at 24 °C. The resulting mixture was stirred for 30 min at 24 °C, and then cooled over 5 min to 0 °C. A solution of 2,3-dichloro-5,8-dimethoxynaphthoquinone [**S1**, 100 mg, 351 μmol, 1 equiv; dried by azeotropic distillation with toluene (1.0 mL)] in dichloromethane (1.0 mL) was added dropwise via cannula to the stirred solution at 0 °C. The vessel containing 2,3-dichloro-5,8-dimethoxynaphthoquinone (**S1**) was rinsed with dichloromethane (2 × 1.0 mL) and the rinse was added to the reaction vessel via cannula. The reaction mixture was stirred for 30 min at 0 °C. The product mixture was concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 50% ethyl acetate–dichloromethane, grading to 75% ethyl acetate–dichloromethane, one step) to afford the ylide **S7** as a yellow solid (58.1 mg, 37%).

R_f = 0.17 (70% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, 1H, J = 9.0 Hz, H_7/H_8), 7.71 (t, 1H, J = 9.0 Hz, H_{11}), 7.66 (d, 1H, J = 10.0 Hz, H_7/H_8), 7.64–7.62 (m, 1H, H_9/H_{10}), 7.57 (dd, 1H, J = 6.0, 2.0 Hz, H_9/H_{10}), 7.38 (d, 1H, J = 12.0 Hz, H_1/H_2), 7.25 (d, 1H, J = 12.0 Hz, H_1/H_2), 3.92 (br s, 1H, H_5), 3.85 (s, 3H, H_3/H_4), 3.71 (s, 3H, H_3/H_4), 2.83 (s, 4H, H_6), 2.67 (s, 2H, H_6). ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.6 (C), 176.4 (C), 155.3 (C), 154.5 (C), 139.3 (C), 134.9 (CH), 132.6 (2 × CH), 131.6 (C), 130.8 (CH), 130.4 (CH), 128.8 (CH), 127.1 (CH), 123.6 (C), 123.2 (C), 120.3 (C), 57.5 (CH_3), 57.2 (CH_3), 39.4 (CH), 38.6 (CH_3), 37.5 (CH_3). IR (ATR-FTIR), cm^{-1}: 2918 (w), 1665 (m), 1509 (s), 1054 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{21}Cl^{35/37}NO_5S$, 434.0829/436.0799; found, 434.0830/436.0801.



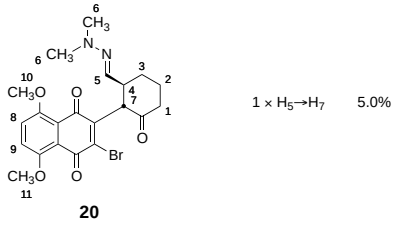
19 **18** **20**

The hydrazone **18** was prepared according to the procedure of Vazquez and co-workers.[39] 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) was prepared according to the procedure of Huot and Brassard.[1]

*Coupling of the Hydrazone **18** and 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**):*

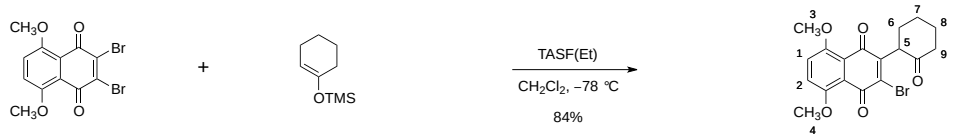
A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 2.04 g, 5.46 mmol, 1.00 equiv) and the hydrazone **18** (1.34 g, 5.46 mmol, 1 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (5.0 mL). The dried mixture was dissolved in tetrahydrofuran (60 mL) and the resulting solution was cooled to −78 °C. A solution of TASF(Et) (2.06 g, 5.73 mmol, 1.05 equiv) in tetrahydrofuran (20 mL) was added dropwise via cannula to the cold, stirred solution. The resulting black mixture was stirred for 10 min at −78 °C. The cold product mixture was diluted with saturated aqueous sodium bicarbonate solution (200 mL), and the diluted solution was warmed over 45 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted sequentially with ethyl acetate (100 mL) and dichloromethane (2 × 150 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 30% acetone–hexanes) to afford the α-quinonylated ketone **20** as a red solid (1.84 g, 73%).

The stereochemistry of the hydrazone substituent was determined by NOE analysis.



20

R_f = 0.19 (100% ethyl acetate; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$, major diastereomer): δ 7.25–7.24 (m, 2H, H_8/H_9), 6.22 (d, 1H, J = 6.0 Hz, H_5), 4.00–3.91 (m, 1H, H_7), 3.87 (app s, 6H, H_{10}/H_{11}), 3.40–3.34 (m, 1H, H_4), 2.60 (d, 1H, J = 14.5 Hz, H_1), 2.33 (dt, 1H, J = 13.0, 6.0 Hz, H_1), 2.08–1.99 (m, 3H, H_2/H_3), 1.69 (dq, 1H, J = 12.5, 3.0 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$, major diastereomer): δ 205.4 (C), 176.2 (2 × C), 153.8 (2 × C), 148.6 (2 × C), 136.4 (CH), 120.6 (CH), 120.2 (CH), 119.9 (C), 119.5 (C), 56.7 (CH_3), 56.6 (CH_3), 45.2 (CH), 42.4 (2 × CH_3), 40.2 (CH), 29.9 (CH_2), 23.0 (CH_2), 22.9 (CH_2). IR (ATR-FTIR), cm^{-1}: 2943 (w), 1706 (m), 1633 (s), 1266 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{24}Br^{79/81}N_2O_5$, 463.0869/465.0848; found, 463.0876/465.0848.



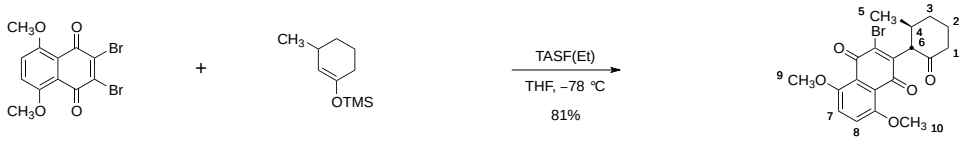
19 **S29** **21**

1-Cyclohexenyloxytrimethylsilane (**S29**) was prepared according to the procedure reported by Wilesa and co-workers.[40]

*Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and 1-Cyclohexenyloxytrimethylsilane (**S29**):*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 226 mg, 598 μmol, 3.40 equiv) and 1-cyclohexenyloxytrimethylsilane (**S29**, 30.0 mg, 176 μmol, 1 equiv) was prepared in a 100-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 10 mL). The dried mixture was dissolved in dichloromethane (22 mL) and the resulting solution was cooled to –78 °C. A solution of TASF(Et) (73.0 mg, 265 μmol, 1.50 equiv) in dichloromethane (1.0 mL) was added dropwise via cannula to the cold, stirred solution. The resulting mixture was stirred for 1 h at –78 °C. The dark red product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The diluted solution was warmed over 30 min to 24 °C. The warmed, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL) and the organic layers were combined. The combined organic layers were dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate-dichloromethane initially, grading to 10% ethyl acetate-dichloromethane, one step) to afford the α-quinonylated ketone **21** as a red solid (58.0 mg, 84%).

R_f = 0.44 (20% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.29 (app s, H_1/H_2), 3.95 (s, 3H, H_3/H_4), 3.94 (s, 3H, H_3/H_4), 3.85–3.83 (m, 1H, H_5), 2.68–2.63 (m, 1H, H_9), 2.35–1.65 (m, 7H, H_6/H_7/H_8/H_9). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.0 (C), 180.3 (C), 176.6 (C), 154.1 (2 × C), 150.3 (C), 139.4 (C), 120.8 (2 × C), 120.7 (CH), 120.2 (CH), 57.1 (CH_3), 57.0 (CH_3), 54.5 (CH), 40.9 (CH_2), 30.2 (CH_2), 24.5 (2 × CH_2). IR (ATR-FTIR), cm^{-1}: 2939 (w), 1664 (s), 1267 (s), 1210 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{18}H_{18}Br^{79/81}O_5$, 393.0338/395.0317; found, 393.0320/395.0302.



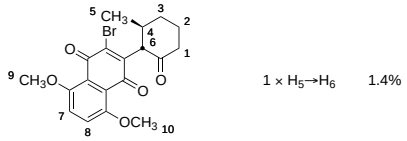
19 **S30** **22**

3-Methyl-1-trimethylsilyloxycyclohexene (**S30**) was prepared according to the procedure of Denmark and Dappen.[41]

*Coupling of 3-Methyl-1-trimethylsilyloxycyclohexene (**S30**) and 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**):*

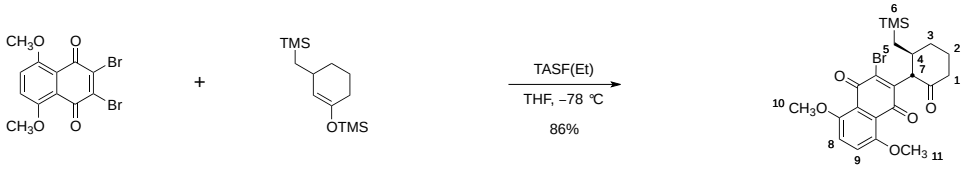
A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 200 mg, 532 μmol, 1.00 equiv) and 3-methyl-1-trimethylsilyloxycyclohexene (**S30**, 103 mg, 559 μmol, 1 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (2 × 1.0 mL). The dried mixture was dissolved in tetrahydrofuran (8.0 mL) and the resulting solution was cooled to −78 °C. A solution of TASF(Et) (210 mg, 586 μmol, 1.05 equiv) in tetrahydrofuran (1.0 mL) was added dropwise via cannula to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The product mixture was then warmed over 20 min to 24 °C. The warmed solution was stirred for 10 min at 24 °C. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (200 mL), and the resulting biphasic mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 50% ethyl acetate–hexanes) to afford the α-quinonylated ketone **22** as a red solid (175 mg, 81%, 5:1 mixture of diastereomers).

The stereochemistry of the α-quinonylated substituent was determined by NOE analysis.



22

R_f = 0.11 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (app s, 2H, H_7/H_8), 3.89–3.86 (m, 4H, H_9/H_{10}/H_6), 3.84 (s, 3H, H_9/H_{10}), 2.50–2.43 (m, 4H, H_1/H_2), 2.08–2.00 (m, 3H, H_3/H_4), 1.79 (app s, 3H, H_5). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.7 (C), 180.5 (C), 176.6 (C), 160.4 (C), 154.2 (C), 154.0 (C), 143.3 (C), 143.2 (C), 130.4 (C), 121.0 (CH), 120.8 (CH), 120.5 (CH), 120.4 (CH), 56.9 (CH_3), 56.8 (CH_3), 37.2 (CH_2), 32.1 (CH_2), 22.5 (CH_3), 21.9 (CH_2). IR (ATR-FTIR), cm^{-1}: 1664 (s), 1477 (m), 1264 (s), 1220 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{19}H_{20}Br^{79/81}O_5$, 407.0494/409.0474; found, 407.0490/409.0475.

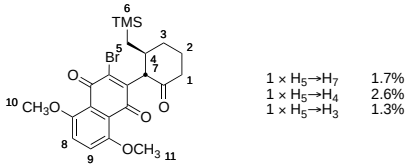


19 **S31** **23**

Trimethylsilyl-1-trimethylsilyloxycyclohexene (**S31**) was prepared according to the procedure of Hatanaka and Kuwajima.[42]

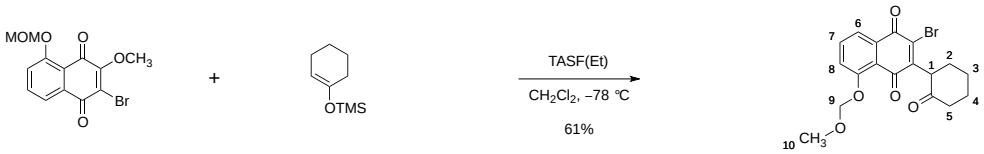
*Coupling of Trimethylsilyl-1-trimethylsilyloxycyclohexene (**S31**) and 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**):*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 200 mg, 532 μmol, 2.00 equiv) and trimethylsilyl-1-trimethylsilyloxycyclohexene (**S31**, 100 mg, 279 μmol, 1 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (2 × 1.0 mL). The dried mixture was dissolved in tetrahydrofuran (4.4 mL) and the resulting solution was cooled to −78 °C. A solution of TASF(Et) (100 mg, 279 μmol, 1.05 equiv) in tetrahydrofuran (250 μL) was added dropwise via cannula to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The mixture was then warmed over 20 min to 0 °C. The warmed solution was stirred for 10 min at 0 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 10 mL), and the resulting biphasic mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 50% ethyl acetate–hexanes) to afford the α-quinonylated ketone **23** as a red solid (110 mg, 86%, 9:1 mixture of diastereomers). The stereochemistry of the α-quinonylated substituent was determined by NOE analysis.



23

R_f = 0.30 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 1H, J = 9.6 Hz, H_8/H_9), 7.35 (d, 1H, J = 9.6 Hz, H_8/H_9), 4.00 (s, 3H, H_{10}/H_{11}), 3.98 (s, 3H, H_{10}/H_{11}), 3.85 (d, 1H, J = 9.6 Hz, H_7), 2.79–2.75 (m, 1H, H_4), 2.63 (td, 1H, J = 15.6, 2.0 Hz, H_1), 2.39 (dt, 1H, J = 15.6, 6.4 Hz, H_1), 2.19–2.14 (m, 1H, H_3), 2.14–2.10 (m, 1H, H_2), 2.01 (td, 1H, J = 13.5, 4.5 Hz, H_2), 1.50 (dq, 1H, J = 12.4, 2.8 Hz, H_3), 0.70–0.62 (m, 2H, H_5), 0.00 (s, 9H, H_6). ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.3 (C), 180.1 (C), 176.2 (C), 153.7 (C), 153.6 (C), 148.5 (C), 141.3 (C), 120.5 (CH), 120.1 (CH), 119.9 (C), 119.5 (C), 65.6 (CH), 56.6 (CH_3), 56.5 (CH_3), 40.2 (CH_2), 38.5 (CH), 33.2 (CH_2), 23.4 (CH_2), 22.7 (CH_2), 1.0 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2946 (m), 1706 (m), 1667 (s), 1478 (m), 1267 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{22}H_{28}Br^{79/81}O_5Si$, 479.0889/481.0869; found, 479.0888/481.0862.

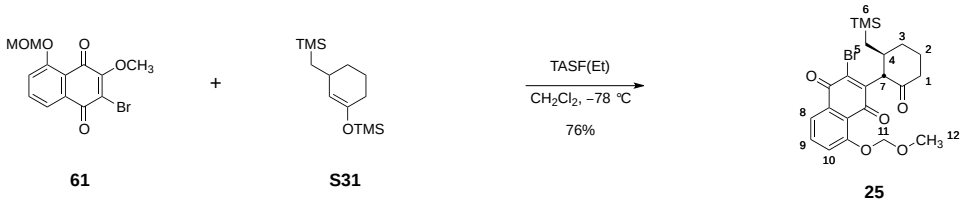


1-Cyclohexenyloxytrimethylsilane (**S29**) was prepared according to the procedure of Liu and co-workers.[43] 2-Bromo-3-methoxy-5-methoxymethyloxynaphthoquinone (**61**) was prepared according to the procedure of Herzon and co-workers.[9]

*Coupling of 2-Bromo-3-methoxy-5-methoxymethyloxynaphthoquinone (**61**) and 1-Cyclohexenyloxytrimethylsilane (**S29**):*

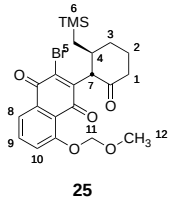
A neat mixture of 2-bromo-3-methoxy-5-methoxymethyloxynaphthoquinone (**61**, 111 mg, 340 μmol, 3.40 equiv) and 1-cyclohexenyloxytrimethylsilane (**S29,** 17.0 mg, 100 μmol, 1 equiv) was prepared in a 25-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 2.0 mL). The dried mixture was dissolved in dichloromethane (12 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to –78 °C. A solution of TASF(Et) (42.0 mg, 150 μmol, 1.50 equiv) in dichloromethane (250 μL) was added dropwise to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 10 mL). The diluted solution was warmed over 45 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 4% ethyl acetate–dichloromethane initially, grading to 10% ethyl acetate–dichloromethane, one step) to afford the α-quinonylated product **24** as a yellow oil (24.0 mg, 61%).

R_f = 0.50 (50% ethyl acetate-hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, 1H, J = 7.6, 1.2 Hz, $H_{8/6}$), 7.62 (t, 1H, J = 8.0 Hz, H_7), 7.54 (dd, 1H, J = 8.4, 1.2 Hz, $H_{6/8}$), 5.36 (d, 1H, J = 7.1 Hz, H_9), 5.32 (d, 1H, J = 7.1 Hz, H_9), 4.00–3.83 (m, 1H, H_1), 3.53–3.48 (m, 1H, H_5), 3.51 (s, 3H, H_{10}), 2.73–2.57 (m, 1H, H_5), 2.42–2.25 (m, 1H, H_4), 2.27–2.13 (m, 2H, H_2/H_4), 2.13–1.90 (m, 2H, H_2/H_3), 1.72 (ddt, 1H, J = 13.4, 8.1, 4.3 Hz, H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.8 (C), 179.5 (C), 177.6 (C), 157.6 (C), 152.5 (C), 137.8 (C), 134.6 (CH), 132.9 (C), 122.6 (CH), 121.6 (CH), 120.5 (C), 95.1 (CH_2), 56.6 (CH_3), 55.7 (CH), 40.8 (CH_2), 30.2 (CH_2), 24.5 (CH_2), 24.4 (CH_2). IR (ATR-FTIR), cm^{-1}: 2942 (w), 1706 (m), 1669 (s), 1584 (m), 1466 (m), 1448 (m), 1256 (s), 1129 (m), 978 (m). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{18}H_{18}Br^{79/81}O_5$, 393.0327/395.0314; found, 393.0327/395.0310.



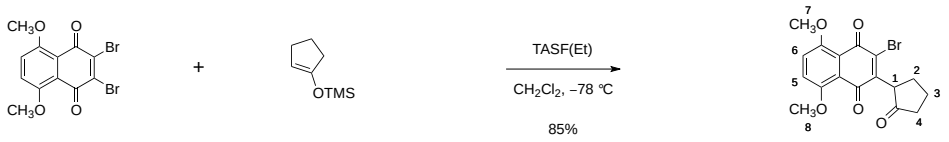
*Coupling of Trimethylsilyl-1-trimethylsilyloxy-cyclohexene (**S31**) and* O*-(Methoxymethyl)-3-bromo-2-methoxyjuglone (**61**):*

A neat mixture of *O*-(methoxymethyl)-3-bromo-2-methoxyjuglone (**61**, 422 mg, 1.42 mmol, 4.00 equiv) and trimethylsilyl-1-trimethylsilyloxy-cyclohexene (**S31**, 91.0 mg, 355 μmol, 1 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (2 × 2.5 mL). The dried mixture was dissolved in dichloromethane (35 mL) and the resulting solution was cooled to −78 °C. A solution of TASF(Et) (140 mg, 390 μmol, 1.10 equiv) in dichloromethane (1.4 mL) was added dropwise via cannula to the cold, stirred solution. The resulting dark red mixture was stirred for 10 min at −78 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The resulting biphasic mixture was warmed over 20 min to 24 °C. The warmed mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 3% ethyl acetate–hexanes initially, grading to 10% ethyl acetate–hexanes, one step) to afford the α-quinonylated ketone **25** as an orange solid (121 mg, 76%, 9:1 mixture of diastereomers). The stereochemistry of the α-quinonylated substituent was determined by NOE analysis.



1 × H_5→H_7	2.3%
1 × H_5→H_4	2.4%
1 × H_5→H_3	1.6%
1 × H_5→H_6	2.1%

R_f = 0.74 (10% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 1H, J = 7.5 Hz, H_8), 7.57 (t, 1H, J = 7.5 Hz, H_9), 7.48 (d, 1H, J = 7.5 Hz, H_{10}), 5.28 (app s, 2H, H_{11}), 3.84–3.76 (m, 1H, H_7), 3.44 (s, 3H, H_{12}), 2.68–2.63 (m, 1H, H_4), 2.53 (d, 1H, J = 16.0 Hz, H_1), 2.28 (dt, 1H, J = 8.5, 6.5 Hz, H_1), 2.06 (app d, 1H, J = 13.0 Hz, H_3), 2.01–1.99 (m, 1H, H_2), 1.99–1.89 (m, 1H, H_2), 1.40 (dq, 1H, J = 12.5, 3.0 Hz, H_3), 0.59–0.54 (m, 2H, H_5), −0.11 (s, 9H, H_6). ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.3 (C), 179.5 (C), 177.3 (C), 157.4 (C), 151.2 (C), 134.7 (C), 134.4 (CH), 132.7 (C), 122.4 (CH), 121.3 (CH), 120.2 (C), 94.8 (CH_2), 66.1 (C), 56.3 (CH_3), 40.3 (CH_2), 38.9 (CH), 33.3 (CH_2), 23.4 (CH_2), 23.2 (CH_2), −0.9 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2948 (m), 1672 (s), 1255 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{22}H_{28}Br^{79/81}O_5Si$, 479.0889/481.0869; found, 479.0886/481.0864.

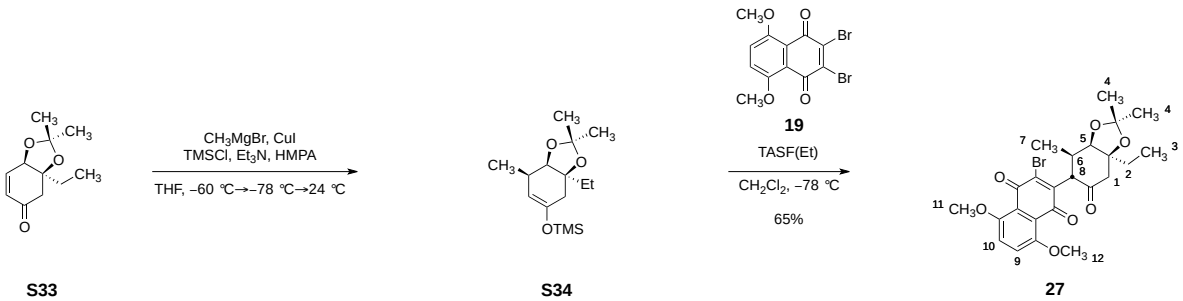


1-Trimethylsilyloxycyclopentene (**S32**) was prepared according to the procedure of Stoltz and co-workers.[44]

*Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and 1-Trimethylsilyloxycyclopentene (**S32**):*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 251 mg, 680 μmol, 3.40 equiv) and the 1-trimethylsilyloxycyclopentene (**S32**, 31.0 mg, 200 μmol, 1 equiv) was prepared in a 50-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 3.0 mL). The dried mixture was dissolved in dichloromethane (25 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to –78 °C. A solution of TASF(Et) (83.0 mg, 300 μmol, 1.50 equiv) in dichloromethane (500 μL) was added dropwise to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The diluted solution was warmed over 45 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 30% ethyl acetate–dichloromethane, one step) to afford the α-quinonylated product **26** as a red powder (54.0 mg, 85%).

R_f = 0.50 (40% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (app s, 2H, H_5/H_6), 3.95 (s, 3H, H_7/H_8), 3.93 (s, 3H, H_7/H_8), 3.69 (s, 1H, H_1), 2.78 (dd, 1H, J = 18.9, 10.3 Hz, H_4), 2.45–2.31 (m, 2H, H_2/H_4), 2.30–2.11 (m, 2H, H_2/H_3), 2.01–1.88 (m, 1H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 215.8 (C), 176.3 (2 × C), 154.3 (C), 154.3 (C), 120.6 (2 × C), 120.6 (2 × CH), 120.1 (C), 120.1 (C), 57.0 (CH), 56.9 (2 × CH_3), 38.0 (CH), 29.3 (CH_2), 22.0 (CH_2). IR (ATR-FTIR), cm^{-1}: 2941 (w), 2841 (w), 1733 (s), 1651 (s), 1611 (m), 1585 (m), 1562 (m), 1476 (m), 1262 (s), 1216 (s), 1140 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{17}H_{16}Br^{79/81}O_5$, 379.0176/381.0161; found, 379.0170/381.0151.

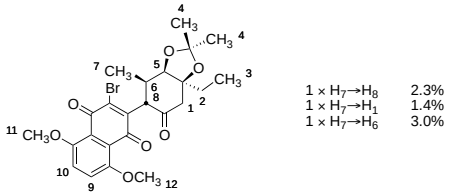


The acetonide **S33** was prepared according to the procedure of Herzon and co-workers.[45]

*Synthesis of the α-Quinonylated Ketone **27**:*

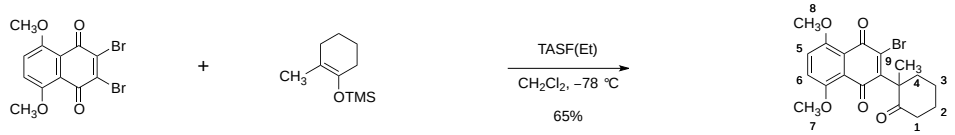
Cuprous iodide (6.0 mg, 31.6 μmol, 0.10 equiv) was added to a stirred solution of methylmagnesium bromide in ether (3.00 M, 116 μL, 348 μmol, 1.10 equiv) at 24 °C. The resulting solution was cooled to −30 °C, to afford a cloudy suspension. A solution of the acetonide **S33** [62.0 mg, 316 mmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in tetrahydrofuran (200 μL) was then added dropwise via cannula. The flask containing the acetonide **S33** was rinsed with tetrahydrofuran (2 × 100 μL) and the rinses were added to the reaction vessel via cannula. The reaction mixture was cooled to −50 °C and then was stirred at this temperature for 30 min. The mixture was then was cooled to −60 °C. Hexamethylphosphoramide (60.5 μL, 348 μmol, 1.10 equiv), triethylamine (87.0 μL, 633 μmol, 2.00 equiv), and trimethylsilyl chloride (79.0 μL, 633 μmol, 2.00 equiv) were added in sequence to the cooled solution. The resulting mixture was further cooled to −78 °C, and was stirred at this temperature for 1 h. The product mixture was warmed over 10 min to 24 °C, and the warmed solution was stirred for 10 min at 24 °C. The product mixture was diluted with ether (40 mL). The diluted solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (20 mL). The layers that formed were separated, and the aqueous layer was extracted with ether (20 mL). The organic layers were combined and the combined organic layers were washed sequentially with saturated aqueous sodium bicarbonate solution (20 mL) and saturated aqueous sodium chloride solution (20 mL). The washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was dissolved in ether (20 mL) and the resulting solution was eluted over a pad of silica gel (2 × 5 cm). The pad of silica gel was washed with ether (3 × 10 mL), and the filtrates were combined. The combined filtrates were concentrated.

The residue obtained in the previous step was mixed with 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 356 mg, 948 μmol, 3.00 equiv) in a 50-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (2 × 3.0 mL). The dried mixture was dissolved in dichloromethane (30 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to −78 °C. A solution of TASF(Et) (125 mg, 348 μmol, 1.10 equiv) in dichloromethane (1.0 mL) was added dropwise via cannula to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 25 mL). The diluted mixture was allowed to warm over 15 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 15 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 40% ethyl acetate–dichloromethane, one step) to afford the α-quinonylated ketone **27** as a red solid (104 mg, 65%). The stereochemistry of the α-quinonylated substituent was determined by NOE analysis.



27

R_f = 0.22 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.30 (m, 2H, H_9/H_{10}), 3.94 (s, 3H, H_{11}/H_{12}), 3.93 (s, 3H, H_{11}/H_{12}), 3.82 (d, 1H, J = 15.0 Hz, H_1), 3.79 (d, 1H, J = 9.0 Hz, H_5), 3.43 (d, 1H, J = 12.0 Hz, H_8), 3.32 (d, 1H, J = 15.0 Hz, H_1), 2.88–2.83 (m, 1H, H_6), 1.72–1.67 (m, 1H, H_2), 1.57–1.54 (m, 1H, H_2), 1.49 (s, 3H, H_4), 1.43 (s, 3H, H_4), 1.08 (d, 3H, J = 6.5 Hz, H_7), 1.01 (t, 3H, J = 7.5 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.5 (C), 179.8 (C), 176.0 (C), 154.4 (C), 154.3 (C), 148.4 (C), 143.3 (C), 120.8 (CH), 120.6 (CH), 119.9 (C), 119.6 (C), 109.8 (C), 86.6 (CH), 81.5 (C), 56.9 (2 × CH_3), 56.6 (CH), 48.0 (CH_2), 37.7 (CH), 34.4 (CH_2), 29.0 (CH_3), 27.5 (CH_3), 16.6 (CH_3), 7.9 (CH_3). IR (ATR-FTIR), cm^{-1}: 2971 (w), 1716 (m), 1667 (s), 1478 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{24}H_{28}Br^{79/81}O_7$, 507.1018/509.0998; found, 507.1015/509.0992.



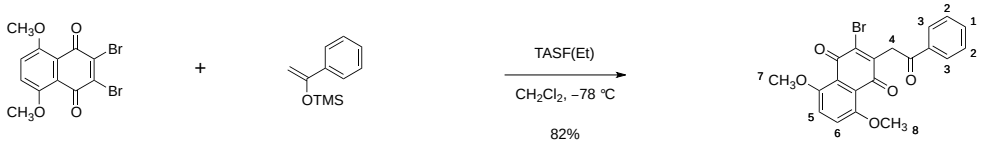
19 **S35** **28**

2-Methyl-1-trimethylsilyloxycyclohexene (**S35**) was prepared according to the procedure of Stoltz and co-workers.[46]

*Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and 2-Methyl-1-trimethylsilyloxycyclohexene (**S35**):*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 251 mg, 680 μmol, 3.40 equiv) and 2-methyl-1-trimethylsilyloxycyclohexene **(S35**, 33.0 mg, 200 μmol, 1 equiv) was prepared in a 50-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 3.0 mL). The dried mixture was dissolved in dichloromethane (25 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to –78 °C. A solution of TASF(Et) (83.0 mg, 300 μmol, 1.50 equiv) in dichloromethane (500 μL) was added dropwise to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The diluted solution was warmed over 45 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 20% ethyl acetate–dichloromethane, one step) to afford the α-quinonylated product **28** as a red oil (47.0 mg, 65%).

R_f = 0.40 (70% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, 1H, J = 9.5 Hz, H_5), 7.22 (d, 1H, J = 9.4 Hz, H_6), 3.93 (s, 3H, H_7/H_8), 3.90 (s, 3H, H_7/H_8), 2.93–2.85 (m, 1H, H_1), 2.51 (td, 1H, J = 8.8, 4.6 Hz, H_1), 2.44 (dt, 1H, J = 14.0, 5.8 Hz, H_2), 2.07–1.95 (m, 1H, H_4), 1.92–1.74 (m, 1H, H_4), 1.73–1.60 (m, 2H, H_2/H_3), 1.56 (s, 3H, H_9), 1.52–1.36 (m, 1H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.5 (C), 183.3 (C), 176.4 (C), 155.8 (C), 153.4 (C), 152.4 (C), 136.7 (C), 122.7 (C), 120.3 (CH), 119.6 (C), 119.0 (CH), 57.1 (CH_3), 56.8 (CH_3), 42.4 (C), 39.6 (CH_2), 29.6 (CH_2), 28.6 (CH_2), 22.2 (CH_2), 21.8 (CH_3). IR (ATR-FTIR), cm^{-1}: 2935 (m), 2840 (m), 1708 (m), 1665 (s), 1597 (m), 1564 (m), 1479 (s), 1258 (s), 1207 (m), 1109 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{19}H_{20}Br^{79/81}O_5$, 407.0489/409.0471; found, 407.0484/409.0465.



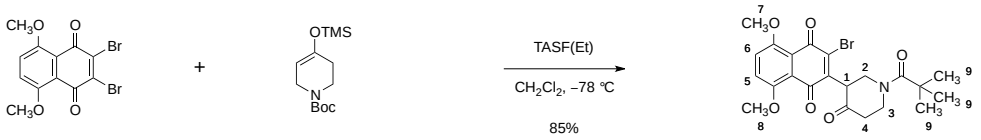
19 **S36** **29**

α-Trimethylsilyloxystyrene (**S36**) was prepared according to the procedure of Drewes and co-workers.[47]

*Coupling of α-Trimethylsilyloxystyrene (**S36**) and 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**):*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 340 mg, 910 μmol, 3.50 equiv) and α-trimethylsilyloxystyrene (**S36**, 50.0 mg, 250 μmol, 1 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (4.0 mL). The dried mixture was dissolved in dichloromethane (26 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to −78 °C. A solution of TASF(Et) (103 mg, 286 μmol, 1.10 equiv) in dichloromethane (500 μL) was added dropwise via cannula to the cold, stirred solution. The resulting dark red mixture was stirred for 15 min at −78 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The mixture was allowed to warm over 20 min to 24 °C. The warmed, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting initially with 5% ethyl acetate–hexanes, grading to 10% ethyl acetate–hexanes, one step) to afford the α-quinonylated ketone **29** as an orange solid (88.5 mg, 82%).

R_f = 0.50 (10% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, 2H, J = 7.0 Hz, H_3), 7.56 (t, 1H, J = 7.5 Hz, H_1), 7.45 (t, 2H, J = 8.0 Hz, H_2), 7.27 (app s, 2H, H_5/H_6), 4.51 (s, 2H, H_4), 3.90 (s, 3H, H_7/H_8), 3.86 (s, 3H, H_7/H_8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9 (C), 180.4 (C), 176.2 (C), 154.1 (C), 153.9 (C), 145.5 (C), 140.3 (C), 136.2 (C), 133.4 (CH), 128.5 (2 × CH), 128.1 (2 × CH), 120.5 (CH), 120.4 (CH), 119.9 (C), 119.8 (C), 56.7 (CH_3), 56.6 (CH_3), 41.6 (CH_2). IR (ATR-FTIR), cm^{-1}: 1653 (s), 1562 (m), 1265 (s), 1204 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{20}H_{16}Br^{79/81}O_5$, 415.0181/417.0161; found, 415.0185/417.0166.



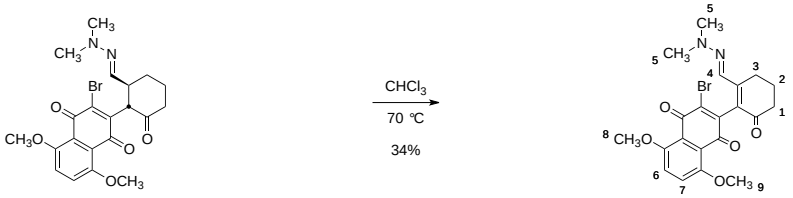
19 **S37** **30**

The enoxysilane **S37** was prepared according to the procedure of ARRAY BIOPHARMA INC.[48]

*Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the Enoxysilane **S37**:*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 125 mg, 340 μmol, 3.40 equiv) and the enoxysilane **S37** (27.0 mg, 100 μmol, 1 equiv) was prepared in a 25-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 2.0 mL). The dried mixture was dissolved in dichloromethane (12 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to –78 °C. A solution of TASF(Et) (42.0 mg, 150 μmol, 1.50 equiv) in dichloromethane (250 μL) was added dropwise via cannula to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 10 mL). The diluted solution was warmed over 45 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 30% ethyl acetate–dichloromethane, one step) to afford the α-quinonylated product **30** as a red oil (42.0 mg, 85%).

R_f = 0.30 (70% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (app s, 2H, H_5/H_6), 4.34 (br s, 2H, H_2), 3.96 (s, 3H, H_7/H_8), 3.94 (s, 3H, H_7/H_8), 3.92–3.86 (m, 1H, H_1), 3.45 (br, 2H, H_3), 2.70 (d, 1H, J = 16.9 Hz, H_4), 2.57 (br, 1H, H_4), 1.51 (s, 9H, H_9). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.0 (C), 180.1 (C), 176.1 (C), 154.3 (C), 154.2 (C), 154.1 (2 × C), 147.1 (C), 120.7 (CH), 120.5 (CH), 120.11 (C), 119.9 (C), 80.7 (C), 56.9 (CH_3), 56.9 (CH_3), 55.0 (CH), 41.8 (CH_2), 39.6 (2 × CH_2), 28.3 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2975 (w), 1696 (s), 1666 (s), 1478 (m), 1409 (m), 1268 (s), 1220 (s), 1161 (s), 1061 (m), 993 (m). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{22}H_{25}{}^{79/81}BrNO_7$, 494.0814/496.0792; found, 494.0807/496.0789.

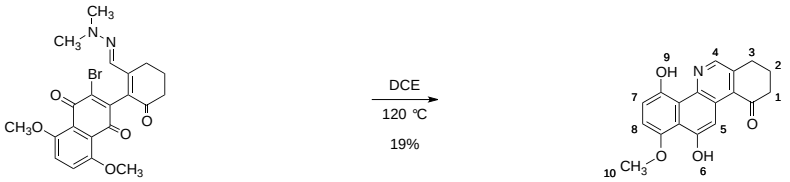


20 **S11**

*Oxidation of the α-Quinonylated Ketone **20**:*

A 500-mL round-bottomed flask that had been fused to a Teflon valve was charged with the α-quinonylated ketone **20** (1.02 g, 2.20 mmol, 1 equiv) and chloroform (250 mL). The resulting solution was sparged with air for 1 h at 24 °C. The flask was sealed and the reaction mixture was heated to 70 °C. The reaction mixture was stirred and heated for 72 h at 70 °C. The product mixture was cooled over 15 min to 24 °C, and the cooled solution was concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 70% ethyl acetate–hexanes) to afford the oxidized product **S11** as a red solid (348 mg, 34%, 1.5:1 mixture of diastereomers).

R_f = 0.19 (100% ethyl acetate; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$, * denotes the second diastereomer): δ 7.28–7.26 (m, 2H, $H_6/H_7/H_{6*}/H_{7*}$), 6.49 (s, 1H, H_4), 6.46 (s, 1H, H_{4*}), 3.88 (s, 3H, H_{8*}/H_{9*}), 3.87 (s, 3H, H_8/H_9), 3.83 (s, 6H, $H_8/H_9/H_{8*}/H_{9*}$), 2.94 (s, 12H, H_5/H_{5*}), 2.88–2.75 (m, 4H, H_1/H_{1*}), 2.54–2.45 (m, 3H, H_3/H_{3*}), 2.11–2.00 (m, 4H, H_2/H_{2*}). ^{13}C NMR (125 MHz, $CDCl_3$, * denotes the second diastereomer): δ 196.2 (C*), 196.0 (C), 180.6 (C*), 180.1 (C), 176.7 (C), 176.6 (C*), 154.6 (C*), 154.2 (C), 153.4 (C*), 153.9 (C), 153.8 (C), 153.7 (C*), 147.5 (C, C*), 143.6 (C), 142.9 (C), 139.0 (C, C*), 128.2 (C, C*), 126.1 (CH*), 125.7 (CH), 121.0 (CH*), 120.8 (CH), 120.7 (C*), 120.6 (C*), 120.0 (CH), 119.9 (C*), 56.6 (2 × CH_3, 2 × CH_3*), 42.2 (2 × CH_3, 2 × CH_3*), 38.0 (CH_2, CH_2*), 24.8 (CH_2*) 24.7 (CH_2), 21.8 (CH_2, CH_2*). IR (ATR-FTIR), cm^{-1}: 1706 (m), 1655 (s), 1264 (s), 1216 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{22}Br^{79/81}N_2O_5$, 461.0712/463.0692; found, 461.0721/463.0690.

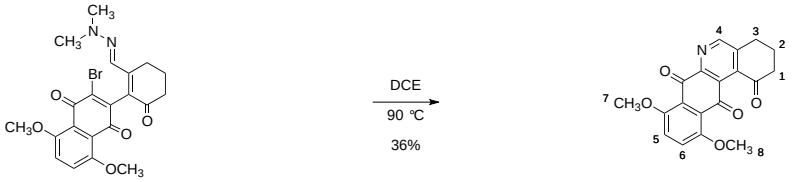


S11 **S12**

*Thermoylsis of the Oxidized Product **S11**:*

A 1-dram vial was charged with the α,β unsaturated enone **S11** (10.0 mg, 21.6 μmol, 1 equiv) and dichloroethane (3.0 mL). The flask was sealed with a Teflon-lined cap. The mixture was stirred and heated for 30 h at 120 °C. The product mixture was cooled over 20 min to 24 °C. The cooled solution was concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 40% acetone–hexanes) to afford the pyridine **S12** as a yellow solid (1.3 mg, 19%).

R_f = 0.69 (60% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 15.04 (s, 1H, H_9), 10.15 (s, 1H, H_6), 8.57 (app s, 2H, H_5/H_4), 7.20 (d, 1H, J = 8.5 Hz, H_7/H_8), 7.17 (d, 1H, J = 8.5 Hz, H_7/H_8), 4.10 (s, 3H, H_{10}), 3.16 (t, 2H, J = 6.0 Hz, H_1), 2.85 (t, 2H, J = 6.5 Hz, H_3), 2.27 (quin, 2H, J = 6.0 Hz, H_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7 (C), 157.2 (C), 154.2 (C), 147.6 (C), 143.8 (C), 141.8 (CH), 137.7 (C), 130.3 (C), 126.2 (C), 117.2 (C), 116.4 (C), 114.5 (CH), 111.7 (CH), 104.2 (CH), 57.4 (CH_3), 41.1 (CH_2), 28.0 (CH_2), 22.8 (CH_2). IR (ATR-FTIR), cm^{-1}: 3323 (br), 2943 (br), 1680 (s), 1422 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{18}H_{17}NO_4$, 310.1079; found, 310.1070.

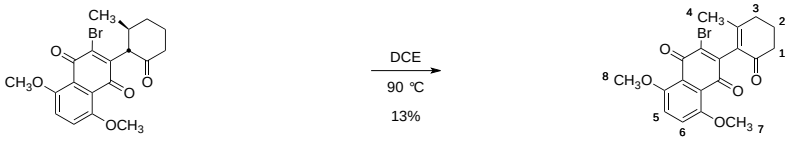


S11 **S14**

*Thermolysis of the Oxidized Product **S11** to Provide the Pyridine **S14**:*

A 50-mL round-bottomed flask that had been fused to a Teflon-coated valve was charged with the α,β-unsaturated product **S11** (100 mg, 207 μmol, 1 equiv) and dichloroethane (25 mL). The resulting solution was sparged with air for 1 h at 24 °C. The flask was sealed and the reaction mixture was heated to 90 °C. The reaction mixture was stirred and heated for 72 h at 90 °C. The product mixture was cooled over 10 min to 24 °C, and the cooled solution was concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 50% acetone–hexanes) to afford the pyridine **S14** as a red solid (24.0 mg, 36%).

R_f = 0.06 (100% ethyl acetate; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (s, 1H, H_4), 7.30 (d, 1H, J = 9.0 Hz, H_5/H_6), 7.26 (d, 1H, J = 9.5 Hz, H_5/H_6), 3.97 (s, 3H, H_7/H_8), 3.95 (s, 3H, H_7/H_8), 2.99 (t, 2H, J = 6.0 Hz, H_1), 2.88 (t, 2H, J = 6.5 Hz, H_3), 2.27 (quin, 2H, J = 6.5 Hz, H_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.9 (C), 183.7 (C), 180.8 (C), 154.4 (CH), 153.9 (C), 152.5 (C), 148.5 (C), 142.6 (C), 140.1 (C), 131.8 (C), 124.6 (C), 122.2 (C), 120.6 (CH), 119.3 (CH), 57.3 (CH_3), 57.0 (CH_3), 39.0 (CH_2), 26.7 (CH_2), 22.9 (CH_2). IR (ATR-FTIR), cm^{-1}: 1681 (s), 1480 (m), 1269 (s), 1242 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{19}H_{16}NO_5$, 338.1029; found, 338.1023.

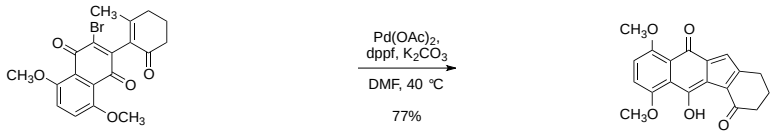


34 **35**

*Oxidation of the α-Quinonylated Ketone **34***:

A 20-mL scintillation vial fitted with a 24/40 female ground glass adaptor was charged with the α-quinonylated ketone **34** (60.0 mg, 147 μmol, 1 equiv) and 1,2-dichloroethane (17 mL). The top of the ground glass adaptor was fitted with a septum. The solution was sparged with air using a 20-gauged stainless steel needle, and was vented with a 20-gauge stainless steel needle. The mixture was sparged continuously while heating and stirring for 24 h at 90 °C. The product mixture was cooled over 15 min to 24 °C, and the cooled solution was concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 30% acetone–hexanes) to afford the α,β-unsaturated ketone **35** as a red solid (8.0 mg, 13%).

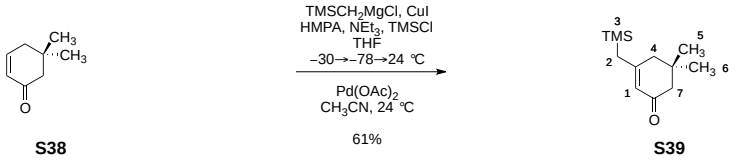
R_f = 0.09 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (app s, 2H, H_5/H_6), 3.96 (s, 3H, H_7/H_8), 3.92 (s, 3H, H_7/H_8), 2.53–2.48 (m, 4H, H_1/H_3), 2.14–2.05 (m, 2H, H_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.5 (C), 180.1 (C), 176.8 (C), 159.9 (C), 154.3 (C), 154.2 (C), 147.2 (C), 139.3 (C), 132.5 (C), 128.3 (C), 120.7 (CH), 120.5 (C), 120.3 (CH), 57.0 (CH_3), 56.9 (CH_3), 37.3 (CH_2), 32.1 (CH_2), 22.4 (CH_2), 21.9 (CH_3). IR (ATR-FTIR), cm^{-1}: 1665 (s), 1478 (m), 1263 (s), 1217 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{19}H_{18}Br^{79/81}O_5$, 405.0338/407.0317; found, 405.0327/407.0310.



35 **37**

*Cyclization of the Unsaturated Ketone **35**:*

Palladium acetate (33.3 mg, 49.4 μmol, 0.40 equiv) was added to a solution of 1,1′-bis(diphenylphosphino)ferrocene (55.0 mg, 98.8 μmol, 0.80 equiv) in *N*,*N*-dimethylformamide (390 μL) at 24 °C. The resulting mixture was placed in an oil bath that had been preheated to 40 °C. The solution was stirred and heated for 1 h at 40 °C. The resulting mixture was then cooled over 10 min to 24 °C. A separate flask was charged with the unsaturated ketone **35** (50.0 mg, 123 μmol, 1 equiv). The ketone **35** was dried by azeotropic distillation with benzene (500 μL). The palladium–ligand solution was added via cannula to the flask containing the unsaturated ketone **35** at 24 °C. Potassium carbonate (34.0 mg, 246 μmol, 2.00 equiv) was then added. The reaction flask was placed in an oil bath that had been preheated to 50 °C. The solution was stirred and heated for 1 h at 50 °C. The product mixture was cooled over 10 min to 24 °C. The cooled solution was sequentially diluted with 1 N aqueous sulfuric acid solution (10 mL) and dichloromethane (15 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (2 × 15 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 30% acetone–hexanes) to afford the hydroxyfulvene **37** as a purple solid (31.0 mg, 77%). ^{1}H NMR spectroscopic data for the hydroxyfulvene **37** obtained in this way was in agreement with those previously reported.[9]



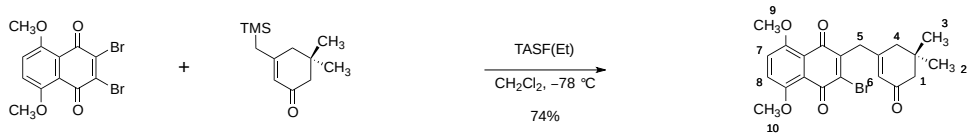
S38 **S39**

*Synthesis of the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S38**:*

Cuprous iodide (272 mg, 1.43 mmol, 0.10 equiv) was added to a stirred solution of trimethylsilylmethylmagnesium chloride in ether (1.00 M, 15.7 mL, 15.7 mmol, 1.10 equiv) at 24 °C. The resulting solution was cooled to −30 °C, to afford a cloudy suspension. To this mixture was added a solution of the cyclohexenone **S38** (1.80 g, 14.3 mmol, 1 equiv) in tetrahydrofuran (4.5 mL) dropwise via cannula. The flask containing the cyclohexenone **S38** was rinsed with tetrahydrofuran (2 × 2.5 mL) and the rinses were added to the reaction vessel via cannula. The reaction mixture was cooled to −50 °C and stirred at this temperature for 30 min. The reaction mixture was then cooled to −60 °C and hexamethylphosphoramide (2.70 mL, 15.7 mmol, 1.10 equiv), triethylamine (3.96 mL, 28.6 mmol, 2.00 equiv), and trimethylsilyl chloride (3.63 mL, 28.6 mmol, 2.00 equiv) were added in sequence. Upon completion of the addition, the solution was cooled to −78 °C and the reaction mixture was stirred at this temperature for 1 h. The product mixture was warmed over 15 min to 24 °C, and the warmed solution was stirred for 10 min at 24 °C. Ether (50 mL) and saturated aqueous sodium bicarbonate solution (50 mL) were added in sequence and the resulting biphasic mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with ether (50 mL). Each organic layer was separately washed with saturated aqueous sodium bicarbonate solution (30 mL), and saturated aqueous sodium chloride solution (20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was eluted over a pad of silica (2 cm × 4 cm). The silica pad was washed with ether (3 × 15 mL), and the filtrates were combined. The combined filtrates were concentrated.

The residue obtained was dissolved in ether (20 mL) and eluted over a pad of silica gel (4 × 5 cm). The filtrates were combined, and the filtrate was concentrated. The residue obtained was dissolved in acetonitrile (57 mL). Palladium acetate (3.80 g, 16.8 mmol, 1.20 equiv) was added, and the resulting black mixture was stirred for 12 h at 24 °C. The product mixture was filtered through a pad of celite (5 × 6 cm). The celite pad was washed with ether (2 × 40 mL) and the filtrates were combined. The combined filtrates were concentrated to dryness, and the residue obtained was purified by flash-column chromatography (eluting with 20% ether−pentane) to afford the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S39** as a clear, colorless oil (1.78 g, 61%).

R_f = 0.38 (30% ether−hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.73 (s, 1H, H_1), 2.14 (s, 2H, H_7), 2.12 (s, 2H, H_4), 1.75 (s, 2H, H_2), 0.99 (s, 6H, H_5/H_6), 0.04 (s, 9H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7 (C), 165.4 (C), 122.9 (CH), 50.3 (CH_2), 46.1 (CH_2), 33.5 (C), 30.9 (CH_2), 28.3 (2 × CH_3), 1.2 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2955 (m), 1657 (s), 1609 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{12}H_{23}OSi$, 211.1413; found, 211.1413.

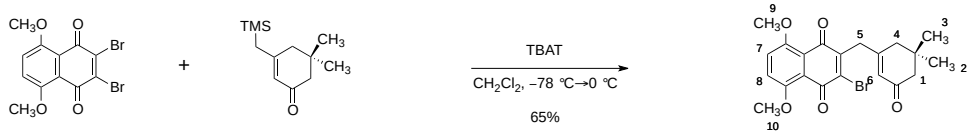


19 **S39** **40**

*Fluoride-mediated Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the β-Trimethylsilylmethyl-α,β-unsaturated Ketone **S39**:*

A neat mixture of the β-trimethylsilylmethyl-α,β-unsaturated ketone **S39** (286 mg, 1.36 mmol, 1 equiv) and 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 1.79 g, 4.76 mmol, 3.50 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (2 × 15 mL). The dried mixture was dissolved in dichloromethane (140 mL) at −78 °C. A solution of TASF(Et) (513 mg, 1.43 mmol, 1.05 equiv) in dichloromethane (10.0 mL) was added dropwise via cannula to the stirred solution the stirred solution at −78 °C. The reaction mixture was stirred for 5 min at −78 °C. The dark red product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 100 mL). The diluted solution was warmed over 30 min to 24 °C. The warmed, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL) and the organic layers were combined. The combined organic layers were dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 40% ethyl acetate–dichloromethane, one step) to afford the δ-ketoquinone **40** as a red solid (434 mg, 74%).

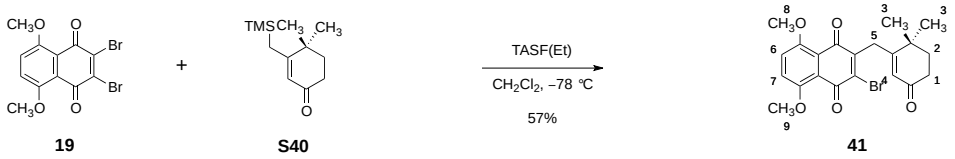
R_f = 0.60 (10% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (app s, 2H, H_7/H_8), 5.73 (s, 1H, H_6), 3.98 (s, 3H, H_9/H_{10}), 3.96 (s, 3H, H_9/H_{10}), 3.67 (s, 2H, H_5), 2.31 (s, 2H, H_1), 2.21 (s, 2H, H_4), 1.04 (s, 6H, H_2/H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 (C), 180.6 (C), 176.4 (C), 158.3 (C), 154.3 (C), 154.1 (C), 146.4 (C), 140.7 (C), 125.1 (CH), 120.6 (2 × CH), 120.2 (C), 120.0 (C), 57.0 (CH_3), 56.8 (CH_3), 50.9 (CH_2), 44.4 (CH_2), 38.6 (CH_2), 33.7 (C), 28.3 (2 × CH_3). IR (ATR-FTIR), cm^{-1}: 2956 (m), 1657 (s), 1267 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{22}Br^{79/81}O_5$, 433.0651/435.0630; found, 433.0655/435.0623.



19 **S39** **40**

*Fluoride-mediated Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the β-Trimethylsilylmethyl-α,β-unsaturated Ketone **S39**:*

A neat mixture of the β-trimethylsilylmethyl-α,β-unsaturated ketone **S39** (90.0 mg, 426 μmol, 1 equiv) and 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 483 mg, 1.28 mmol, 3.00 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (2 × 3.0 mL). The dried mixture was dissolved in dichloromethane (20 mL) at −78 °C. Tetrabutylammonium triphenyldifluorosilicate (254 mg, 471 μmol, 1.10 equiv) was added to the stirred solution the stirred solution at −78 °C. The reaction mixture was stirred for 30 min at 0 °C. The dark red product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 40 mL). The diluted solution was warmed over 15 min to 24 °C. The warmed, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (2 × 20 mL) and the organic layers were combined. The combined organic layers were dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate-dichloromethane initially, grading to 40% ethyl acetate−dichloromethane, one step) to afford the δ-ketoquinone **40** as a red solid (121 mg, 65%). ^{1}H NMR spectroscopic data for the δ-ketoquinone **40** obtained in this way was in agreement with those previously reported (vide supra).



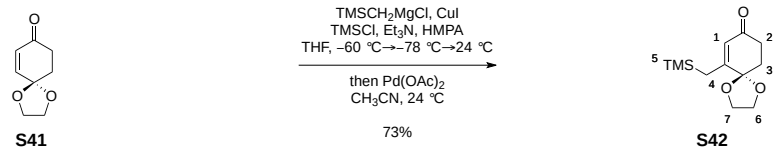
19 **S40** **41**

The β-trimethylsilylmethyl-α,β-unsaturated ketone **S40** was prepared according to the procedure of Herzon and co-workers.[37]

*Fluoride-mediated Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the β-Trimethylsilylmethyl-α,β-unsaturated Ketone **S40**:*

A neat mixture of the β-trimethylsilylmethyl-α,β-unsaturated ketone **S40** (90.0 mg, 426 μmol, 1 equiv) and 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 400 mg, 1.06 mmol, 2.50 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (10 mL). The dried mixture was dissolved in dichloromethane (20 mL) at −78 °C. A solution of TASF(Et) (168 mg, 468 μmol, 1.10 equiv) in dichloromethane (1.0 mL) was added dropwise via cannula to the stirred solution at −78 °C. The resulting dark red mixture was stirred for 10 min at −78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 30 mL). The resulting biphasic mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–hexanes) to afford the δ-ketoquinone **41** as a red solid (105 mg, 57%).

R_f = 0.20 (20% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (app s, 2H, H_6/H_7), 5.33 (s, 1H, H_4), 3.92 (s, 3H, H_8/H_9), 3.89 (s, 3H, H_8/H_9), 3.67 (s, 2H, H_5), 2.38 (t, 2H, J = 7.0 Hz, H_1), 1.87 (t, 2H, J = 7.0 Hz, H_2), 1.30 (s, 6H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.7 (C), 180.1 (C), 176.0 (C), 166.8 (C), 154.1 (C), 154.0 (C), 146.8 (C), 140.8 (C), 123.6 (CH), 120.6 (CH), 120.5 (CH), 120.0 (C), 119.8 (C), 56.9 (CH_3), 56.7 (CH_3), 37.5 (CH_2), 35.8 (C), 34.1 (CH_2), 34.0 (CH_2), 26.3 (2 × CH_3). IR (ATR-FTIR), cm^{-1}: 2966 (w), 1659 (s), 1268 (s), 1213 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{22}Br^{79/81}O_5$, 433.0651/435.0630; found, 433.0656/435.0625.



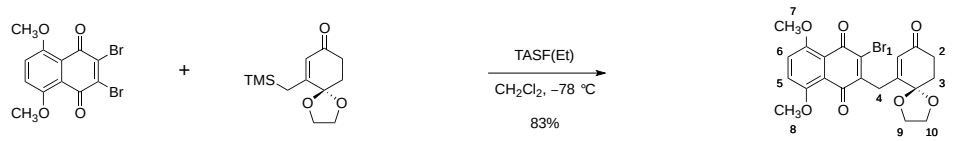
S41 **S42**

*Synthesis of the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S42**:*

Cuprous iodide (27.0 mg, 140 μmol, 0.10 equiv) was added to a stirred solution of trimethylsilylmethylmagnesium chloride in ether (1.00 M, 1.54 mL, 1.54 mmol, 1.10 equiv) at 24 °C. The resulting solution was cooled to −30 °C, to afford a cloudy suspension. A solution of the cyclohexenone **S41** [216 mg, 1.40 mmol, 1 equiv; dried by azeotropic distillation with benzene (2.0 mL)] in tetrahydrofuran (1.0 mL) was then added dropwise via cannula. The reaction mixture was cooled to −50 °C and then was stirred at this temperature for 30 min. The mixture was then was cooled to −60 °C and hexamethylphosphoramide (268 μL, 1.54 mmol, 1.10 equiv), triethylamine (390 μL, 2.80 mmol, 2.00 equiv), and trimethylsilyl chloride (266 μL, 2.80 mmol, 2.00 equiv) were added in sequence to the cooled solution. The resulting mixture was further cooled to −78 °C, and was stirred at this temperature for 1 h. The product mixture was warmed over 10 min to 24 °C, and the warmed solution was stirred for 10 min at 24 °C. The warmed product mixture was diluted with ether (20 mL) and the diluted solution was filtered through a pad of celite (5 × 5 cm). The filtrate was then transferred to a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (20 mL). The layers that formed were separated, and the aqueous layer was extracted with ether (20 mL). The organic layers was washed separately with saturated aqueous sodium bicarbonate solution (2 × 15 mL), 3% aqueous ammonium hydroxide solution (15 mL), distilled water (15 mL), and saturated aqueous sodium chloride solution (15 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained was dissolved in acetonitrile (5.0 mL). Palladium acetate (345 mg, 1.54 mmol, 1.20 equiv) was added, and the resulting black mixture was stirred for 4 h at 24 °C. The product mixture was diluted with dichloromethane (20 mL) and the diluted solution was filtered through a pad of celite (5 × 5 cm). The celite pad was washed with dichloromethane (3 × 25 mL) and the filtrates were combined. The combined filtrates were washed with saturated aqueous sodium bicarbonate solution (15 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% ether−hexanes) to afford the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S42** as a clear, colorless oil (246 mg, 73%).

R_f = 0.40 (30% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (s, 1H, H_1), 4.05 (s, 4H, H_6/H_7), 2.54 (t, 2H, J = 6.5 Hz, H_2), 2.06 (d, 2H, J = 6.5 Hz, H_3), 1.75 (s, 2H, H_4), 0.06 (s, 9H, H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9 (C), 163.1 (C), 127.1 (CH), 105.8 (C), 65.3 (2 × CH_2), 34.9 (CH_2), 32.1 (CH_2), 22.6 (CH_2), –0.8 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2952 (m), 2891 (m), 1664 (s), 1612 (m), 1349 (w), 1277 (w), 1234 (m), 1134 (s), 1111 (s). HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{12}H_{20}O_3SiNa$, 263.1074; found, 263.1071.

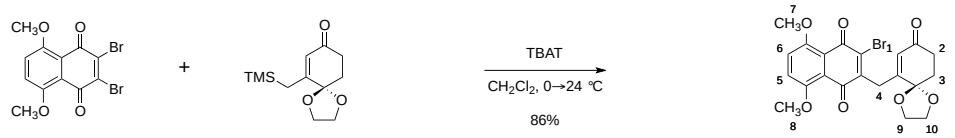


19 **S42** **42**

*Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S42**:*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 251 mg, 680 μmol, 3.40 equiv) and the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S42** (48.0 mg, 200 μmol, 1 equiv) was prepared in a 50-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 3.0 mL). The dried mixture was dissolved in dichloromethane (25 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to –78 °C. A solution of TASF(Et) (83.0 mg, 300 μmol, 1.50 equiv) in dichloromethane (500 μL) was added dropwise to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The diluted solution was warmed over 45 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 40% ethyl acetate–dichloromethane, one step) to afford the δ-ketoquinone **42** as a red solid (77.0 mg, 83%).

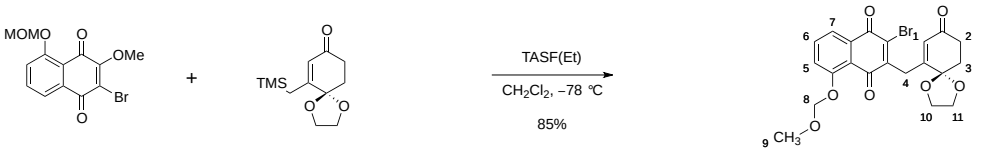
R_f = 0.40 (40% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (app s, 2H, H_5/H_6), 5.69 (t, 1H, J = 1.8 Hz, H_1), 4.16–4.14 (m, 2H, H_9/H_{10}), 4.11–4.05 (m, 2H, H_{10}/H_9), 3.97 (s, 3H, H_7/H_8), 3.94 (s, 3H, H_7/H_8), 3.79 (d, 2H, J = 1.9 Hz, H_4), 2.57 (t, 2H, J = 6.8 Hz, H_2), 2.14 (d, 2H, J = 6.8 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.0 (C), 180.4 (C), 176.4 (C), 156.6 (2 × C), 154.2 (C), 154.0 (C), 147.0 (C), 140.2 (2 × C), 128.8 (CH), 120.5 (CH), 120.4 (CH), 105.6 (C), 65.7 (2 × CH_2), 57.0 (CH_3), 56.8 (CH_3), 35.0 (CH_2), 32.4 (CH_2), 31.9 (CH_2). IR (ATR-FTIR), cm^{-1}: 2939 (m), 2894 (m), 2840 (w), 1657 (s), 1618 (m), 1563 (m), 1476 (m), 1433 (m), 1265 (s), 1209 (s), 1118 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{21}H_{20}{}^{79/81}BrO_7$, 463.0387/465.0370; found, 463.0381/465.0361.



19 **S42** **42**

*Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S42**:*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 125 mg, 340 μmol, 3.40 equiv) and the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S42** (24.0 mg, 100 μmol, 1 equiv) was prepared in a 50-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 2.0 mL). The dried mixture was dissolved in dichloromethane (12 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to 0 °C. Tetrabutylammonium triphenydifluorosilicate (81.0 mg, 150 μmol, 1.50 equiv) was added in one portion to the cold, stirred solution. The resulting black mixture was stirred for 30 min at 0 °C. The reaction vessel was removed from the cooling bath and was allowed to warm up over 30 min to 24 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 15 mL). The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 40% ethyl acetate–dichloromethane, one step) to afford the δ-ketoquinone **42** as a red solid (40.0 mg, 86%).

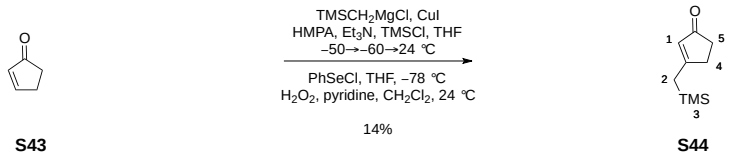


61 **S42** **43**

*Coupling of 2-Bromo-3-methoxy-5-methoxymethyloxynaphthoquinone (**61**) and the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S42**:*

A neat mixture of 2-bromo-3-methoxy-5-(methoxymethoxy)naphthoquinone (**61**, 222 mg, 680 μmol, 3.40 equiv) and the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S42** (48.0 mg, 200 μmol, 1 equiv) was prepared in a 50-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 3.0 mL). The dried mixture was dissolved in dichloromethane (25 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to –78 °C. A solution of TASF(Et) (83.0 mg, 300 μmol, 1.50 equiv) in dichloromethane (500 μL) was added dropwise to the cold, stirred solution. The resulting black mixture was stirred for 30 min at −78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The diluted solution was warmed over 45 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–dichloromethane initially, grading to 20% ethyl acetate–dichloromethane, one step) to afford the δ-ketoquinone **43** as a yellow amorphous solid (79.0 mg, 85%).

R_f = 0.20 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, 1H, J = 7.6, 1.2 Hz, H_7), 7.65 (t, 1H, J = 8.1 Hz, H_6), 7.55 (dd, 1H, J = 8.6, 1.2 Hz, H_5), 5.66 (d, 1H, J = 1.6 Hz, H_1), 5.33 (s, 2H, H_8), 4.18–4.05 (m, 4H, H_{10}/H_{11}), 3.84 (d, 2H, J = 1.8 Hz, H_4), 3.51 (s, 3H, H_9), 2.57 (t, 2H, J = 6.5 Hz, H_2), 2.15 (t, 2H, J = 6.5 Hz, H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9 (C), 179.6 (C), 177.4 (C), 157.6 (C), 156.5 (C), 149.2 (C), 138.6 (C), 134.9 (CH), 133.0 (C), 128.6 (CH), 122.3 (CH), 121.6 (CH), 119.9 (C), 105.6 (C), 95.0 (CH_2), 65.7 (2 × CH_2), 56.7 (CH_3), 35.0 (CH_2), 32.3 (CH_2), 32.2 (CH_2). IR (ATR-FTIR), cm^{-1}: 1667 (s), 1607 (w), 1585 (s), 1466 (m), 1255 (s), 1139 (m), 1016 (m), 941 (m). HRMS-ESI(m/z): $[M+H]^+$ calculated for $C_{21}H_{20}Br^{79/81}O_7$, 463.0387/465.0370; found, 463.0383/465.0362.



S43 **S44**

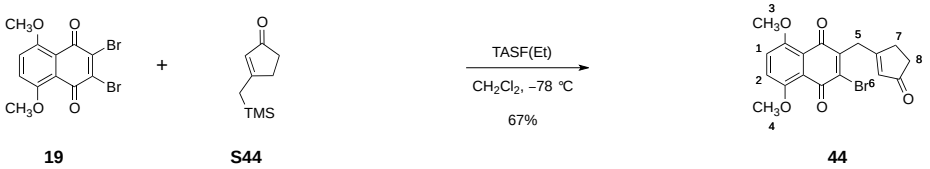
*Synthesis of 3-Trimethylsilylmethyl-cyclopent-2-ene-1-one (**S44**):*

Cuprous iodide (116 mg, 609 μmol, 0.10 equiv) was added to a stirred solution of trimethysilylmethylmagnesium chloride in ether (1.00 M, 6.70 mL, 6.70 mmol, 1.10 equiv) at 24 °C. The solution was cooled to –50 °C, to afford a cloudy suspension. A solution of 2-cyclopenten-1-one (**S43**, 500 mg, 6.09 mmol, 1 equiv) in tetrahydrofuran (3.0 mL) was then added dropwise via cannula. The flask containing 2-cyclopenten-1-one (**S43**) was rinsed with tetrahydrofuran (2 × 500 μL) and the rinses were added to the reaction vessel via cannula. The reaction mixture was stirred at –50 °C for 30 min. The mixture was then cooled to –60 °C and hexamethylphosphoramide (1.16 mL, 6.70 mmol, 1.10 equiv), triethylamine (2.53 mL, 18.3 mmol, 3.00 equiv), and trimethylsilylchloride (1.55 mL, 12.2 mmol, 2.00 equiv) were added in sequence to the cooled solution. The resulting mixture was stirred for 1 h at –60 °C. The mixture was then warmed over 10 min to 24 °C, and the warmed solution was stirred for 10 min at 24 °C. The product mixture was diluted with 50% ether–pentane (50 mL) and the diluted solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (50 mL). The layers that formed were separated, and the aqueous layer was extracted with 50% ether–pentane (2 × 20 mL). The organic layer was washed sequentially with 3% aqueous ammonium hydroxide solution (50 mL), water (3 × 50 mL), and saturated aqueous sodium chloride solution (50 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained from the preceding step was dissolved in tetrahydrofuran (53 mL). The resulting mixture was cooled to –78 °C. A solution of phenylselenyl chloride (1.38 g, 7.20 mmol, 1.18 equiv) in tetrahydrofuran (7.0 mL) was added dropwise via cannula over 5 min to the cooled mixture. The resulting mixture was stirred for 10 min at –78 °C and then was warmed over 15 min to 24 °C. The warmed solution was stirred for 20 min at 24 °C. The product mixture was diluted with saturated aqueous ammonium chloride solution (70 mL) and the diluted mixture was transferred to a separatory funnel. The layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 100 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the preceding step was dissolved in dichloromethane (9.6 mL) at 24 °C. Pyridine (480 μL, 5.97 mmol, 0.98 equiv) and 30% aqueous hydrogen peroxide solution (733 μL, 5.97 mmol, 0.98 equiv) were added in sequence. The reaction mixture was stirred for 15 min at 24 °C. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (10 mL). The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic layers were combined, and the combined layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 50% ether–hexane) to afford 3-trimethylsilylmethyl-cyclopent-2-en-1-one (**S44**) as a clear, colorless oil (58.0 mg, 14%).

R_f = 0.54 (50% ethyl acetate–hexanes; UV, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (s, 1H, H_1), 2.53–2.51 (m, 2H, H_5), 2.36–2.31 (m, 2H, H_4), 2.02 (s, 2H, H_2), 0.06 (s, 9H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.8 (C), 184.1 (C), 129.0 (CH), 37.0 (CH_2), 35.1 (CH_2), 28.2 (CH_2), 0.00 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2954 (w), 1696 (s), 1594 (s), 1248 (m), 1185 (m). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_9H_{17}BrO_7$,169.1049; found, 169.1033.

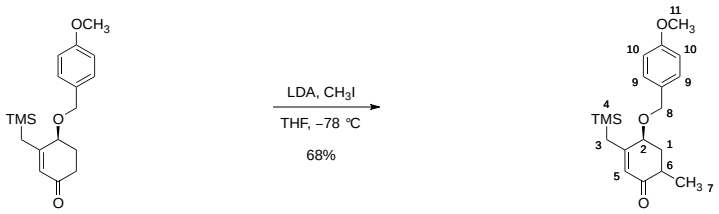


19 **S44** **44**

*Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and 3-Trimethylsilylmethyl-cyclopent-2-ene-1-one (**S44**):*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 122 mg, 324 μmol, 3.40 equiv) and 3-trimethylsilylmethyl-cyclopent-2-ene-1-one (**S44**, 16.0 mg, 95.2 μmol, 1 equiv) was prepared in a 100-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 10 mL). The dried mixture was dissolved in dichloromethane (13 mL) and was cooled to –78 °C. A solution of TASF(Et) (39.0 mg, 143 μmol, 1.50 equiv) in dichloromethane (1.0 mL) was added dropwise via cannula to the cold, stirred solution. The resulting mixture was stirred for 1 h at –78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 20% ethyl acetate–dichloromethane, one step) to afford the δ-ketoquinone **44** as an orange solid (25.0 mg, 67%).

R_f = 0.20 (20% ethyl acetate–dichloromethane; UV, PAA). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (app s, 2H, H_1/H_2), 5.91–5.89 (m, 1H, H_6), 3.97 (s, 3H, H_3), 3.96 (s, 3H, H_4), 3.88 (s, 2H, H_5), 2.71–2.69 (m, 2H, H_7), 2.42–2.40 (m, 2H, H_8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.1 (C), 180.5 (C), 176.4 (C), 176.2 (C), 154.3 (C), 154.1 (C), 146.4 (C), 140.2 (C), 130.8 (CH), 120.6 (2 × CH), 120.0 (C), 119.9 (C), 57.0 (CH_3), 56.8 (CH_3), 35.4 (CH_2), 35.2 (CH_2), 31.9 (CH_2). IR (ATR-FTIR), cm^{-1}: 1653 (m), 1476 (m), 1211 (s), 1186 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{18}H_{16}Br^{79/81}O_5$, 391.0181/393.0161; found, 391.0150/393.0151.



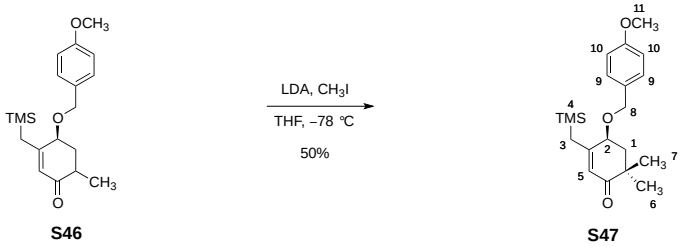
S45 **S46**

The β-trimethylsilylmethyl α,β-unsaturated ketone **S45** was prepared according to the procedure of Herzon and co-workers.[37]

*Methylation of the β-Trimethylsilylmethyl α,β-unsaturated Ketone **S45**:*

In a nitrogen-filled dry box, a 10-mL round-bottom flask that had been fused to a Teflon valve was charged with solid lithium diisopropylamide (69.9 mg, 1.11 mmol, 2.40 equiv), and tetrahydrofuran (3.1 mL). The vessel was sealed, and the sealed vessel was removed from the dry box. The solution was then cooled to −78 °C under a positive pressure of argon. A solution of the β-trimethylsilylmethyl α,β-unsaturated ketone **S45** (147 mg, 462 μmol, 1 equiv) in tetrahydrofuran (3.1 mL) was added dropwise via syringe over 5 min to the cooled solution. The reaction mixture was stirred for 30 min at –78 °C. Iodomethane (69.1 μL, 1.11 mmol, 2.40 equiv) was added and the reaction mixture was stirred for 30 min at –78 °C. The mixture was then warmed over 30 min to 24 °C. The product solution was diluted with saturated aqueous sodium bicarbonate solution (20 mL). The diluted solution was transferred to a separatory funnel, and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–hexanes initially, grading to 25% ethyl acetate–hexanes, four steps) to afford the α'-methyl-α,β-unsaturated ketone **S46** as a colorless oil (105 mg, 68%, 1:1 mixture of diastereomers).

R_f = 0.46 (25% ethyl acetate–hexanes; UV, PAA). ^{1}H NMR (400 MHz, $CDCl_3$, *denotes the second diastereomer): δ 7.28 (d, 4H, J = 8.4 Hz, H_9/H_{9*}), 6.90 (d, 4H, J = 8.8 Hz, H_{10}/H_{10*}), 5.72 (s, 1H, H_5), 5.70 (s, 1H, H_{5*}), 4.69 (d, 1H, J = 11.2 Hz, H_8), 4.65 (d, 1H, J = 9.6 Hz, H_{8*}), 4.43 (app d, 2H, J = 11.6 Hz, H_8/H_{8*}), 4.16 (dd, 1H, J = 6.0, 3.6 Hz, H_2), 3.85 (app t, 1H, J = 3.6 Hz, H_{2*}), 3.77 (s, 6H, H_{11}/H_{11*}), 2.73–2.67 (m, 1H, H_{6*}), 2.47–2.42 (m, 1H, H_1), 2.34–2.20 (m, 3H, H_{1*}/H_6), 1.80–1.64 (m, 6H, H_1/H_{1*}/H_3/H_{3*}), 1.18 (d, 3H, J = 6.8 Hz, H_7), 1.14 (d, 3H, J = 7.2 Hz, H_{7*}), 0.03 (s, 9H, H_4), –0.03 (s, 9H, H_{4*}). ^{13}C NMR (125 MHz, $CDCl_3$, *denotes the second diastereomer): δ 201.1 (C), 200.1 (C*), 167.3 (C), 161.8 (C*), 159.6 (C), 159.4 (C*), 130.0 (C), 130.0 (C*), 129.9 (CH), 129.5 (CH*), 125.0 (CH), 124.2 (CH*), 113.9 (CH), 113.9 (CH*), 76.0 (CH), 73.0 (CH*), 71.5 (CH_2), 70.6 (CH_2*), 55.4 (CH_3), 55.3 (CH_3*), 40.0 (CH), 36.9 (CH_2), 35.9 (CH*), 34.3 (CH_2*), 26.8 (CH_2), 25.0 (CH_2*), 15.4 (CH_3), 15.2 (CH_3*), –0.9 (CH_3), –1.3 (CH_3*). IR (ATR-FTIR), cm^{-1}: 2955 (w), 1663 (m), 1513 (m), 1245 (s), 839 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{19}H_{29}O_3Si$, 333.1886; found, 333.1883.

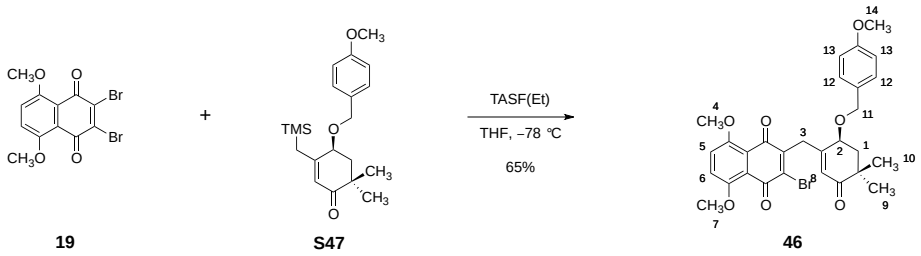


S46 **S47**

*Methylation of the α'-Methyl-α,β-unsaturated Ketone **S46**:*

In a nitrogen-filled dry box, a 10-mL round-bottom flask that had been fused to a Teflon valve was charged with solid lithium diisopropylamide (4.60 mg, 72.0 μmol, 2.40 equiv), and tetrahydrofuran (115 μL). The vessel was sealed, and the sealed vessel was removed from the dry box. The solution was then cooled to –78 °C under a positive pressure of argon. A solution of the α'-methyl-α,β-unsaturated ketone **S46** (10.0 mg, 30.0 μmol, 1 equiv) in tetrahydrofuran (487 μL) was added dropwise via syringe over 5 min to the cooled solution at –78 °C. The reaction mixture was stirred for 30 min at –78 °C. Iodomethane (5.6 μL, 90.0 μmol, 3.00 equiv) was added and the reaction mixture was stirred for 30 min at –78 °C. The mixture was then warmed to 24 °C over 30 min. The product solution was diluted with saturated aqueous sodium bicarbonate solution (10 mL). The diluted solution was transferred to a separatory funnel, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting initially with 10% ethyl acetate–hexanes, grading to 25% ethyl acetate–hexanes, four steps) to afford the α',α'-dimethyl-α,β-unsaturated ketone **S47** as a colorless oil (5.2 mg, 50%).

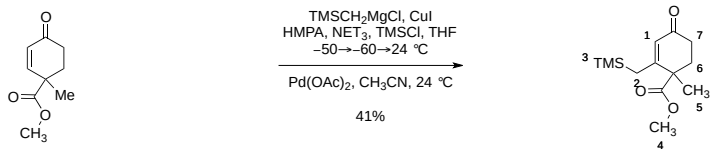
R_f = 0.53 (25% ethyl acetate–hexanes; UV, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, 2H, J = 8.7 Hz, H_9), 6.90 (d, 2H, J = 8.6 Hz, H_{10}), 5.64 (s, 1H, H_5), 4.64 (d, 1H, J = 11.1 Hz, H_8), 4.42 (d, 1H, J = 11.0 Hz, H_8), 4.14 (dd, 1H, J = 9.2, 4.7 Hz, H_2), 3.81 (s, 3H, H_{11}), 2.17–2.11 (m, 2H, H_1, H_3), 1.88 (dd, 1H, J = 13.0, 9.5 Hz, H_1), 1.71 (d, 1H, J = 11.7 Hz, H_3), 1.17 (s, 3H, H_6/H_7), 1.10 (s, 3H, H_6/H_7), 0.02 (s, 9H, H_4). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.9 (C), 165.0 (C), 159.5 (C), 130.2 (C), 129.7 (CH), 123.4 (CH), 114.0 (CH), 73.8 (CH), 70.8 (CH_2), 55.5 (CH_3), 41.8 (CH_2), 41.5 (C), 26.1 (CH_3), 25.2 (CH_2), 25.0 (CH_3), –0.8 (CH_3). IR (ATR-FTIR), cm^{-1}: 2957 (w), 1661 (m), 1514 (m), 1248 (s), 849 (s). HRMS-ESI (*m/z*): [M + H]$^+$ calculated for $C_{20}H_{31}O_3Si$, 347.2042; found, 347.2040.



*Fluoride-mediated Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the β-Trimethylsilylmethyl-α,β-unsaturated Enone **S47**:*

A mixture of 2,3-dibromo-5,6-dimethoxynaphthoquinone (**19**, 128 mg, 340 μmol, 3.01 equiv) and the β-trimethylsilylmethyl-α,β-unsaturated ketone (**S47**, 39.2 mg, 113 μmol, 1 equiv) was dried by azeotropic distillation from 33% benzene–dichloromethane (2 × 1.5 mL). The resulting red residue was heated under vacuum for 1 h at 40 °C. The residue was dissolved in tetrahydrofuran (10 mL) and the solution that formed was cooled to −78 °C. A solution of TASF(Et) (34.3 mg, 125 μmol, 1.10 equiv) in tetrahydrofuran (1.0 mL) was added over 1 min to the cold solution. The reaction mixture was stirred for 5 min at −78 °C. The dark red product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 30 mL). The diluted solution was warmed over 30 min to 24 °C. The warmed, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL), and the organic layers were combined. The combined organic layers were dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 60% ethyl acetate–10% dichloromethane–hexanes initially, grading to 30% ethyl acetate–30% dichloromethane–hexanes, two steps) to afford the δ-ketoquinone **46** as an orange foam (41.6 mg, 65%).

R_f = 0.34 (75% ethyl acetate–hexanes; UV, PAA). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (s, 2H, H_5/H_6), 7.25 (d, 2H, J = 8.5 Hz, H_{12}), 6.85 (d, 2H, J = 8.5 Hz, H_{13}), 5.56 (br s, 1H, H_8), 4.68 (d, 1H, J = 11.2 Hz, H_{11}), 4.48 (d, 1H, J = 11.2 Hz, H_{11}), 4.41 (dd, 1H, J = 7.7, 5.0 Hz, H_2), 3.99 (d, 1H, J = 18.5 Hz, H_3), 3.96 (s, 3H, H_4/H_7), 3.91 (s, 3H, H_4/H_7), 3.80 (s, 3H, H_{14}), 3.62 (d, 1H, J = 16.7 Hz, H_3), 2.16 (dd, 1H, J = 13.2, 5.0 Hz, H_1), 1.96 (dd, 1H, J = 13.1, 9.1 Hz, H_1), 1.14 (s, 3H, H_9/H_{10}), 1.08 (s, 3H, H_9/H_{10}). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3 (C), 180.7 (C), 176.6 (C), 159.4 (C), 158.9 (C), 154.3 (C), 154.1 (C), 147.8 (C), 140.2 (C), 130.0 (C), 129.4 (CH), 125.1 (CH), 120.6 (CH), 120.6 (CH), 120.4 (C), 120.3 (C), 114.0 (CH), 74.0 (CH), 71.2 (CH_2), 57.1 (CH_3), 56.9 (CH_3), 55.4 (CH_3), 41.9 (CH_2), 41.7 (C), 34.9 (CH_2), 25.8 (CH_3), 24.8 (CH_3). IR (ATR-FTIR), cm^{-1}: 2967 (w), 1661 (m), 1266 (s), 1213 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{29}H_{30}{}^{79/81}BrO_7$, 569.1177/571.1154; found, 569.1175/571.1148.



S48 **S49**

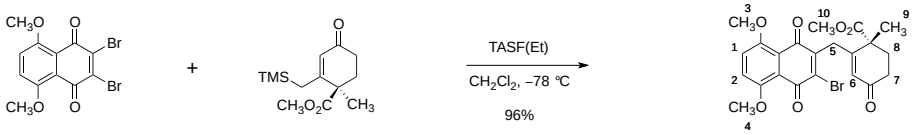
The β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S48** was prepared according to the procedure reported by Danishefsky and co-workers.[49]

*Synthesis of the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S49**:*

Cuprous iodide (16.4 mg, 85.7 μmol, 0.10 equiv) was added to a stirred solution of trimethysilylmethylmagnesium chloride in ether (1.00 M, 943 μL, 943 μmol, 1.10 equiv) at 24 °C. The solution was cooled to –50 °C, to afford a cloudy suspension. A solution of the cyclohexenone **S48** [144 mg, 857 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in tetrahydrofuran (400 μL) was then added dropwise via cannula. The flask containing the cyclohexenone **S48** was rinsed with tetrahydrofuran (2 × 200 μL) and the rinses were added to the reaction vessel via cannula. The reaction mixture was stirred for 30 min at –50 °C. The mixture was then cooled to –60 °C and hexamethylphosphoramide (164 μL, 943 μmol, 1.10 equiv), triethylamine (356 μL, 2.57 μmol, 3.00 equiv), and trimethylsilylchloride (215 μL, 1.71 μmol, 2.00 equiv) were added in sequence to the cooled solution. The resulting mixture was stirred for 1 h at –60 °C. The mixture was then warmed over 10 min to 24 °C, and the warmed solution was stirred for 10 min at 24 °C. The product mixture was diluted with 50% ether–pentane (10 mL) and the diluted solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (10 mL). The layers that formed were separated, and the aqueous layer was extracted with 50% ether–pentane (2 × 10 mL). The organic layers were combined, and the combined organic layers were washed sequentially with 3% aqueous ammonium hydroxide solution (10 mL), water (3 × 10 mL), and saturated aqueous sodium chloride solution (10 mL).

The residue obtained in the preceding step was dissolved in acetonitrile (3.5 mL). Palladium acetate (170 mg, 760 μmol, 0.89 equiv) was added, and the resulting black mixture was stirred for 4 h at 24 °C. The product mixture was diluted with ether (10 mL) and the diluted solution was filtered through a pad of celite (5 × 5 cm). The celite pad was washed with ether (3 × 10 mL) and the filtrates were combined. The combined filtrates were concentrated to dryness, and the residue obtained was purified by flash-column chromatography (eluting with 20% ethyl acetate–hexanes) to afford the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S49** as a clear, colorless oil (89.0 mg, 41%).

R_f = 0.44 (30% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (s, 1H, H_1), 3.69 (s, 3H, H_4), 2.49–2.33 (m, 3H, H_6/H_7), 1.97–1.81 (m, 2H, H_7/H_2), 1.67 (d, 1H, J = 13.5 Hz, H_2), 1.40 (s, 3H, H_5), 0.06 (s, 9H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.1 (C), 175.2 (C), 165.9 (C), 127.1 (CH), 53.0 (CH_3), 44.8 (C), 35.0 (CH_2), 34.4 (CH_2), 25.9 (CH_2), 23.1 (CH_3), 0.01 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2951 (w), 1728 (s), 1662 (s), 1601 (m), 1247 (m). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{13}H_{23}O_3Si$, 255.1417; found, 255.1411.

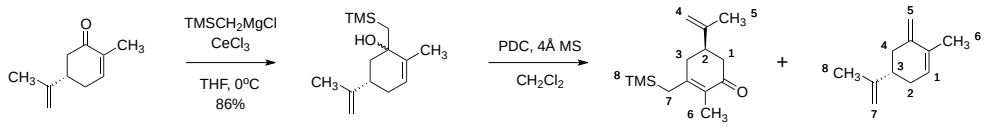


19 **S49** **47**

*Fluoride-mediated Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S49**:*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 200 mg, 534 μmol, 3.40 equiv) and the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S49** (40.0 mg, 157 μmol, 1 equiv) was prepared in a 100-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (2 × 1.0 mL). The dried mixture was dissolved in dichloromethane (20 mL) and was cooled to –78 °C. A solution of TASF(Et) (100 mg, 361 μmol, 2.30 equiv) in dichloromethane (1.0 mL) was added dropwise via cannula to the cold, stirred solution. The reaction mixture was stirred for 5 min at −78 °C. The dark red product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The diluted solution was warmed over 30 min to 24 °C. The warmed, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL) and the organic layers were combined. The combined organic layers were dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 20% ethyl acetate–dichloromethane, one step) to afford the δ-ketoquinone **47** as a red solid (72.2 mg, 96%).

R_f = 0.29 (20% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (app s, 2H, H_1/H_2), 5.53 (t, 1H, J = 1.5 Hz, H_6), 3.96 (s, 3H, H_3/H_4), 3.93 (s, 3H, H_3/H_4), 3.80 (s, 3H, H_{10}), 3.76 (app d, 2H, J = 2.0 Hz, H_5), 2.53–2.37 (m, 3H, H_7/H_8), 2.05–1.98 (m, 1H, H_8), 1.63 (s, 3H, H_9). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.8 (C), 180.1 (C), 176.2 (C), 174.2 (C), 159.4 (C), 154.3 (C), 154.1 (C), 146.3 (C), 141.3 (C), 125.9 (CH), 120.7 (CH), 120.6 (CH), 120.2 (C), 120.0 (C), 57.0 (CH_3), 56.8 (CH_3), 52.7 (CH_3), 47.4 (C), 34.9 (CH_2), 34.3 (CH_2), 34.1 (CH_2), 22.8 (CH_3). IR (ATR-FTIR), cm^{-1}: 2940 (w), 1656 (m), 1265 (s), 1210 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{22}H_{22}Br^{79/81}O_7$, 477.0549/479.0528; found, 477.0546/479.0521.



S50 **S51** **S52**, 5% **S53**, 52%

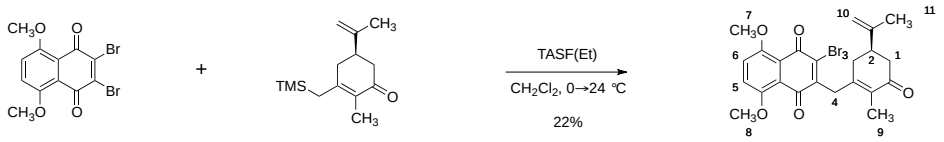
*Synthesis of the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S52**:*

Anhydrous cerium chloride (740 mg, 3.00 mmol, 1.50 equiv) was suspended in tetrahydrofuran (10 mL) and well stirred under argon for 2.5 h. The flask was then immersed in an ice bath. A solution of trimethylsilylmethylmagnesium chloride in ether (1.00 M, 3.00 mL, 3.00 mmol, 1.50 equiv) was added. The resulting mixture was stirred for 1.5 h at 0 °C. D-Carvone (**S50**, 310 μL, 2.00 mmol, 1 equiv) was added dropwise via syringe. The reaction mixture was stirred for 1 h at 0 °C. The reaction mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The aqueous layer was extracted with ether (3 × 20 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the preceding step was charged with dichloromethane (5.0 mL), activated 4 Å molecular sieves (260 mg), and pyridium dichromate (442 mg, 1.17 mmol, 0.59 equiv) at 24 °C. The resulting black mixture was stirred for 1 h at 24 °C. The product mixture was diluted with dichloromethane (20 mL) and the diluted solution was filtered through a pad of celite (5 × 5 cm). The celite pad was washed with dichloromethane (3 × 25 mL) and the filtrates were combined. The combined filtrates were washed with saturated aqueous sodium bicarbonate solution (15 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with hexanes initially, grading to 10% ether−hexanes, one step) to afford separately the 1-methyl-6-methylene-4-(prop-1-en-2-yl)cyclohex-1-ene (**S53**, clear liquid, 37.0 mg, 52%) and the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S52** (clear, colorless oil, 6.0 mg, 5%).

*1-Methyl-6-methylene-4-(prop-1-en-2-yl)cyclohex-1-ene (**S53**):* R_f = 0.90 (10% ethyl acetate–hexanes; UV, $KMnO_4$). ^{1}H NMR (400 MHz, C_6D_6): δ 5.53 (s, 1H, H_1), 4.96 (s, 1H, H_5), 4.81 (s, 1H, H_5), 4.76 (s, 1H, H_7), 4.75 (s, 1H, H_7), 2.54–2.38 (m, 1H, H_3), 2.35–2.19 (m, 2H, H_2), 2.15–1.86 (m, 2H, H_4), 1.79 (s, 3H, H_6), 1.57 (s, 3H, H_8). ^{13}C NMR (125 MHz, C_6D_6): δ 149.0 (C), 144.9 (C), 132.7 (C), 128.3 (CH), 109.4 (CH_2), 108.6 (CH_2), 42.4 (CH), 37.7 (CH_2), 32.1 (CH_2), 20.6 (CH_3), 19.5 (CH_3). IR (ATR-FTIR), cm^{-1}: 2968 (w), 2939 (w), 2280 (m), 2150 (w), 2060 (w), 2000 (w), 1644 (w), 1440 (m), 1330 (m). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{11}H_{17}$, 149.1330; found, 149.1331.

*β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S52**:* R_f = 0.30 (10% ethyl acetate–hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.79 (s, 1H, H_4), 4.74 (s, 1H, H_4), 2.61–2.54 (m, 2H, H_1), 2.32 – 2.22 (m, 3H, H_2/H_3), 1.94 (dd, 1H, J = 12.0, 4.0 Hz, H_7), 1.82 (dd, 1H, J = 12.1, 3.6 Hz, H_7), 1.74 (s, 3H, H_6), 1.72 (s, 3H, H_5), 0.09 (s, 9H, H_8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.5 (C), 158.8 (C), 146.9 (C), 127.9 (C), 110.2 (CH_2), 42.6 (CH_2), 41.5 (CH), 38.7 (CH_2), 28.6 (CH_2), 20.5 (CH_3), 11.5 (CH_3), –0.5 (2 × CH_3). IR (ATR-FTIR), cm^{-1}: 2953 (w), 1657 (s), 1615 (m), 1379 (w), 1315 (m), 1249 (m), 1153 (w), 1118 (w), 1082 (w). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{14}H_{25}OSi$, 237.1675; found, 237.1671.

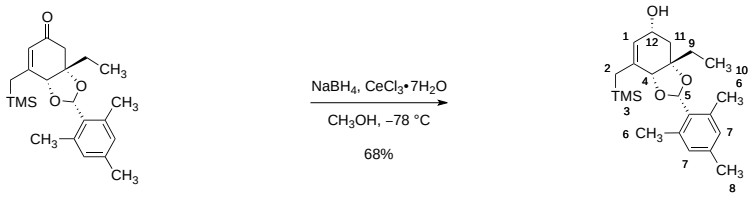


19 **S52** **48**

*Coupling of 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**) and the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S52**:*

A neat mixture of 2,3-dibromo-5,8-dimethoxynaphthoquinone (**19**, 27.0 mg, 71.9 μmol, 3.40 equiv) and the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S52** (5.0 mg, 21.1 μmol, 1 equiv) was prepared in a 10-mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 1.0 mL). The dried mixture was dissolved in dichloromethane (2.0 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to 0 °C. A solution of TASF(Et) (8.7 mg, 31.6 μmol, 1.50 equiv) in dichloromethane (200 μL) was added dropwise to the cold, stirred solution. The resulting black mixture was stirred for 2.5 h at 0 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 15% ethyl acetate–dichloromethane, one step) to afford the δ-ketoquinone **48** as a red oil (2.1 mg, 22%).

R_f = 0.35 (70% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (app s, 2H, H_5/H_6), 4.73 (s, 1H, H_{10}), 4.67 (s, 1H, H_{10}), 3.98 (s, 3H, H_7/H_8), 3.97 (s, 3H, H_7/H_8), 3.88 (d, 1H, J = 15.1 Hz, H_4), 3.81 (d, 1H, J = 15.1 Hz, H_4), 2.64–2.50 (m, 2H, H_1), 2.36–2.24 (m, 2H, H_3), 2.23–2.13 (m, 1H, H_2), 1.94 (d, 3H, J = 1.7 Hz, H_9), 1.66 (s, 3H, H_{11}). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8 (C), 181.1 (C), 176.4 (C), 154.2 (C), 154.0 (C), 152.0 (C), 147.7 (C), 146.5 (C), 140.3 (C), 132.4 (C), 120.5 (CH), 120.4 (CH), 120.2 (C), 120.0 (C), 110.6 (CH_2), 57.0 (CH_3), 56.9 (CH_3), 42.5 (CH_2), 41.3 (CH), 36.6 (CH_2), 34.5 (CH_2), 20.5 (CH_3), 11.3 (CH_3). IR (ATR-FTIR), cm^{-1}: 1660 (s), 1477 (m), 1268 (s), 1215 (s), 1058 (m). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{23}H_{24}Br^{79/81}O_5$, 459.0807/461.0787; found, 459.0803/461.0782.

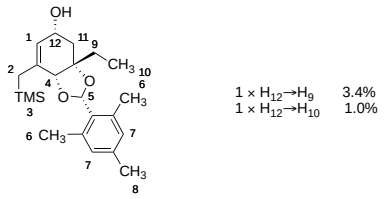


S54 **S55** (7:1 dr)

The β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S54** was prepared according to the procedure of Herzon and co-workers (vide infra).

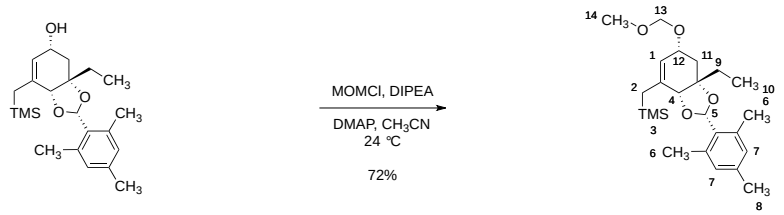
*Reduction of the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S54**:*

Cerium trichloride heptahydrate (49.8 mg, 134 μmol, 1.00 equiv) was added to a stirred solution of the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S54** (50.0 mg, 134 μmol, 1 equiv) in methanol (1.3 mL) at 24 °C. The mixture was cooled to −78 °C and sodium borohydride (5.1 mg, 134 μmol, 1.00 equiv) was added to the cooled solution. The resulting mixture was stirred for 30 min at −78 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL), and the mixture was allowed to warm over 10 min to 24 °C. The warmed solution was transferred to a separatory funnel and the aqueous layer was extracted with dichloromethane (5 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–hexanes) to afford the alcohol **S55** as a clear, colorless oil (34.0 mg, 68%; 7:1 mixture of diastereomers). The stereochemistry of the alcohol was determined by NOE analysis.



S55 (7:1 dr)

R_f = 0.30 (20% ethyl acetate–hexanes, UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$; major diastereomer): δ 6.80 (s, 2H, H_7), 6.22 (s, 1H, H_5), , 5.54 (s, 1H, H_1), 4.48–4.40 (m, 1H, H_{12}), 3.91 (s, 1H, H_4), 2.45 (s, 6H, H_6), 2.25–2.21 (m, 4H, H_8/H_2), 1.87–1.74 (m, 4H, H_2/H_{11}/H_9), 1.66–1.50 (m, 1H, H_{11}), 1.09 (t, 3H, J = 7.6 Hz, H_{10}), 0.05 (s, 9H, H_3). ^{13}C NMR (100 MHz, $CDCl_3$; major diastereomer): δ 139.9 (C), 139. 0 (C), 136.0 (C), 131.3 (2 × C), 129.1 (2 × CH), 128.7 (C), 102.0 (CH), 82.1 (CH), 81.3 (C), 67.5 (CH), 40.1 (CH_2), 30.7 (CH_2), 25.0 (CH_2), 22.0 (CH_3), 21.7 (2 × CH_3), 9.08 (CH_3), 0.00 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 3404 (b), 2953 (m), 1029 (s), 1106 (s). HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{22}H_{34}NaO_3Si$, 397.2175; found, 397.2157.



S55 (7:1 dr) **S56** (7:1 dr)

*Synthesis of the Methoxymethyl Ether **S56**:*

Chloromethyl methyl ether (24.0 µL, 320 µmol, 4.00 equiv) was added to a solution of the allylic alcohol **S55** (30.0 mg, 80.1 µmol, 1 equiv) and 4-(dimethylamino)pyridine (3.0 mg, 24.5 µmol, 0.30 equiv) in acetonitrile (400 µL) at 24 °C. *N*,*N*-Diisopropylethylamine (101 µL, 641 µmol, 8.00 equiv) was then added. The reaction mixture was stirred for 48 h at 24 °C. The product mixture was diluted with dichloromethane (10 mL) and the diluted mixture was transferred to a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (10 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ether–hexanes) to afford the methoxymethyl ether **S56** as a clear, colorless oil (24.0 mg, 72%, 7:1 mixtures of diastereomers).

R_f = 0.26 (10% ethyl acetate–hexanes, UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$, major diastereomer): δ 6.80 (s, 2H, H_7), 6.21 (s, 1H, H_5), 5.63 (s, 1H, H_1), 4.73 (app s, 2H, H_{13}), 4.11–4.07 (m, 1H, H_{12}), 3.87 (s, 1H, H_4), 3.40 (s, 3H, H_{14}), 2.45 (s, 6H, H_6), 2.31 (dd, 1H, J = 8.4, 4.4 Hz, H_2), 2.23 (s, 3H, H_8), 1.85–1.56 (m, 5H, H_2/H_9/H_{11}), 1.09 (t, 3H, J = 7.2 Hz, H_{10}), 0.05 (s, 9H, H_3). ^{13}C NMR (100 MHz, $CDCl_3$, major diastereomer): δ 139.8 (C), 139.1 (C), 135.6 (C), 131.2 (2 × CH), 128.6 (2 × C), 127.7 (CH), 102.2 (CH), 96.5 (CH_2), 82.4 (CH), 80.8 (C), 73.2 (CH), 56.5 (CH_3), 37.5 (CH_2), 30.7 (CH_2), 24.9 (CH_2), 22.0 (CH_3), 21.7 (2 × CH_3), 9.2 (CH_3), 0.00 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2952 (m), 1450 (m), 1274 (m), 1039 (s), 1027 (s). HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{24}H_{38}NaO_4Si$, 441.2437; found, 441.2418.

39 R = H
50 R = CH_3

37 R = H
51 R = CH_3

Optimization of the Palladium-mediated Cyclization Reaction.

*An Illustrative Procedure for the Cyclization of the δ-Ketoquinone **50** (Entry 8, Table 3):*

A dry mixture of palladium acetate (23.8 mg, 106 μmol, 0.25 equiv), polymer-bound triphenylphosphine (44.4 mg, 133 μmol, 0.31 equiv), and silver carbonate (235 mg, 852 μmol, 2.00 equiv) were added to a stirred solution of the δ-ketoquinone **50** [185 mg, 426 μmol, 1 equiv; dried by azeotropic distillation with benzene (1.0 mL)] in toluene (21 mL) at 24 °C. The reaction vessel was placed in an oil bath that had been preheated to 80 °C. The reaction mixture was stirred and heated for 2 h at 80 °C. The product mixture was cooled over 10 min to 24 °C. The cooled solution was filtered over a celite pad (1 × 2 cm). The filter cake was washed with ethyl acetate (4 × 10 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% acetone–hexanes) to afford the hydroxyfulvene **51** as a purple solid (129 mg, 86%).

Entry 1. Prepared analogously as above (heated to 50 °C for 2 h), using the δ-ketoquinone **39** (20.0 mg, 49.5 mmol, 1 equiv), palladium acetate (11.1 mg, 49.5 mmol, 1.00 equiv), 1,1′-bis(diphenylphosphino)ferrocene (41.1 mg, 74.2 mmol, 1.50 equiv), and potassium carbonate (13.7 mg, 99.0 mmol, 2.00 equiv) in *N*,*N*-dimethylformamide (500 μL). Column chromatography (eluting with 20% acetone–hexanes) afforded the hydroxyfulvene **37** as a purple solid (0.5 mg, <5%).

Entry 2. Prepared analogously as above (heated to 50 °C for 2 h), using the δ-ketoquinone **39** (45.8 mg, 113 μmol, 1 equiv), palladium acetate (20.3 mg, 90.5 μmol, 0.80 equiv), triphenylphosphine (23.7 mg, 90.5 μmol, 0.80 equiv), and cesium carbonate (73.7 mg, 226 μmol, 2.00 equiv) in tetrahydrofuran (1.1 mL). Column chromatography (eluting with 30% acetone–hexanes) afforded the hydroxyfulvene **37** as a purple solid (11.5 mg, 31%).

Entry 3. Prepared analogously as above (heated to 50 °C for 4 h), using the δ-ketoquinone **39** (21.0 mg, 64.8 μmol, 1 equiv), palladium acetate (14.5 mg, 64.8 μmol, 1.00 equiv), triphenylphosphine (17.0 mg, 64.8 μmol, 1.00 equiv), and triethylamine (30.0 μL, 324 μmol, 5.00 equiv) in tetrahydrofuran (430 μL). Column chromatography (eluting with 20% acetone–hexanes) afforded the hydroxyfulvene **37** as a purple solid (0.6 mg, <5%).

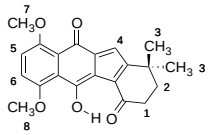
Entry 4. Prepared analogously as above (heated to 50 °C for 2.5 h), using the δ-ketoquinone **39** (15.0 mg, 30.5 μmol, 1 equiv), palladium acetate (6.8 mg, 46.3 μmol, 1.52 equiv), triphenylphosphine (8.0 mg, 46.3 μmol, 1.52 equiv), and silver phosphate (25.6 mg, 92.6 μmol, 2.00 equiv) in tetrahydrofuran (300 mL). A complex mixture of products was obtained.

Entry 5. Prepared analogously as above (heated to 80 °C for 1.5 h), using the δ-ketoquinone **39** (40.3 mg, 99.5 μmol, 1 equiv), palladium acetate (16.7 mg, 74.6 μmol, 0.75 equiv), polymer-supported triphenylphosphine (99.5 mg, 299 μmol, 3.00 equiv), and silver carbonate (54.7 mg, 199 μmol, 2.00 equiv) in toluene (660 μL). Column chromatography (eluting with 20% acetone–hexanes) afforded the hydroxyfulvene **37** as a purple solid (7.0 mg, 22%).

Entry 6. Prepared analogously as above (heated to 80 °C for 1.5 h), using the δ-ketoquinone **39** (40.6 mg, 100 μmol, 1 equiv), palladium acetate (22.5 mg, 100 μmol, 1.00 equiv), polymer-supported triphenylphosphine (66.8 mg, 200 μmol, 2.00 equiv), and silver carbonate (55.2 mg, 200 μmol, 2.00 equiv) in toluene (1.0 mL). Column chromatography (eluting with 20% acetone–hexanes) afforded the hydroxyfulvene **37** as a purple solid (13.0 mg, 40%).

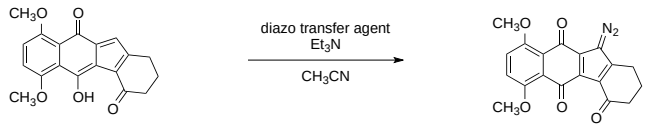
Entry 7. Prepared analogously as above (heated to 80 °C for 2 h), using the δ-ketoquinone **50** (465 mg, 1.32 mmol, 1 equiv), palladium acetate (572 mg, 1.32 mmol, 1.00 equiv), polymer-supported triphenylphosphine (658 mg, 1.97 mmol, 1.50 equiv), and silver carbonate (724 mg, 2.63 mmol, 2.00 equiv) in toluene (66 mL). Column chromatography (eluting with 20% acetone–hexanes) afforded the hydroxyfulvene **51** as a purple solid (367 mg, 79%).

^{1}H NMR spectroscopic data for the hydroxyfulvene **51** obtained in this way were in agreement with those previously reported.[9]



51

Hydroxyfulvene **51**: R_f = 0.40 (10% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14–7.24 (m, 2H, H_5/H_6), 6.81 (s, 1H, H_4), 4.00 (s, 3H, H_7/H_8), 3.98 (s, 3H, H_7/H_8), 2.82 (t, 2H, J = 7.2 Hz, H_1), 2.01 (t, 2H, J = 7.2 Hz, H_2), 1.38 (s, 6H, H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4 (C), 181.3 (C), 174.4 (C), 160.2 (C), 155.5 (C), 155.3 (C), 137.4 (C), 122.7 (C), 121.9 (C), 121.6 (CH), 121.3 (C), 121.2 (C), 120.5 (CH), 117.3 (CH), 57.1 (CH_3), 56.8 (CH_3), 38.2 (CH_2), 32.1 (CH_2), 31.2 (CH_2), 28.1 (2 × CH_3). IR (ATR-FTIR), cm^{-1}: 2927 (m), 1593 (s), 1405 (s), 1259 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{21}O_5$, 353.1389; found, 353.1385.



37 **53**

*Evaluation of Conditions for Diazotransfer to the Hydroxyfulvene **37**.*

*An Illustrative Procedure for Diazotransfer to the Hydroxyfulvene **37** (Entry 6, Table 4):*

Triethylamine (21.4 μL, 154 μmol, 5.00 equiv) and nonaflyl azide (25.0 mg, 77.2 μmol, 2.50 equiv) were added in sequence to a stirred solution of the hydroxyfulvene **37** [10.0 mg, 30.9 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in acetonitrile (620 μL) at 0 °C. The resulting mixture was stirred for 20 min at 0 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 10 mL). The resulting biphasic mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 30% acetone–hexanes) to afford diazofluorene **53** as a yellow solid (9.2 mg, 85%).

Entry 1. Prepared analogously to **37** above (stirred for 4 h at 24 °C), using the hydroxyfulvene **37** (11.0 mg, 34.0 μmol, 1 equiv), triethylamine (70.5 μL, 510 μmol, 15.0 equiv), and mesyl azide (27.0 μL, 255 μmol, 7.50 equiv) in acetonitrile (680 μL). Column chromatography (eluting with 30% acetone–hexanes) afforded the diazofluorene **53** as a yellow solid (0.5 mg, 4%).

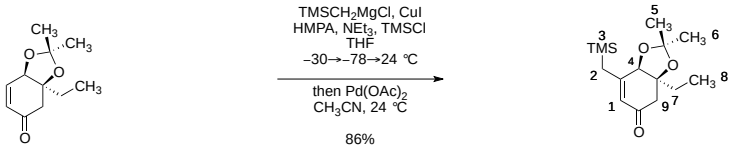
Entry 2. Prepared analogously to **37** above (stirred for 1.5 h at 24 °C), using the hydroxyfulvene **37** (15.0 mg, 46.3 μmol, 1 equiv), triethylamine (64.0 μL, 462 μmol, 10.0 equiv), and *para*-nitrobenzosulfonyl azide (52.8 mg, 232 μmol, 5.00 equiv) in acetonitrile (930 μL). Column chromatography (eluting with 30% acetone–hexanes) afforded the diazofluorene **53** as a yellow solid (3.2 mg, 20%).

Entry 3. Prepared analogously to **37** above (stirred for 4 h at 24 °C), using the hydroxyfulvene **37** (11.0 mg, 34.0 μmol, 1 equiv), triethylamine (70.5 μL, 510 μmol, 15.0 equiv), and tosyl azide (51.0 mg, 255 μmol, 7.50 equiv) in acetonitrile (680 μL). Column chromatography (eluting with 30% acetone–hexanes) afforded the diazofluorene **53** as a yellow solid (2.1 mg, 18%).

Entry 4. Prepared analogously to **37** above (stirred for 20 min at 0 °C), using the hydroxyfulvene **37** (10.0 mg, 30.9 μmol, 1 equiv), triethylamine (21.4 μL, 154 μmol, 5.00 equiv), and imidazole-1-sulfonyl azide hydrochloride (13.4 mg, 77.2 μmol, 2.50 equiv) in acetonitrile (620 μL). Column chromatography (eluting with 30% acetone–hexanes) afforded the diazofluorene **53** as a yellow solid (8.0 mg, 74%).

Entry 5. Prepared analogously to **37** above (stirred for 20 min at 24 °C), using the hydroxyfulvene **37** (8.0 mg, 25.0 μmol, 1 equiv), *N*,*N*-diisopropylethylamine (22.0 μL, 125 μmol, 5.00 equiv), and trifluoromethanesulfonyl azide in hexanes (280 mM, 110 μL, 30.8 μmol, 1.23 equiv) in acetonitrile (1.25 mL). Column chromatography (eluting with 75% ethyl acetate–hexanes) afforded the diazofluorene **53** as a yellow solid (7.0 mg, 81%).

^{1}H NMR spectroscopic data for the diazofluorene **53** obtained in this way were in agreement with those previously reported.[9]



S33 **S21**

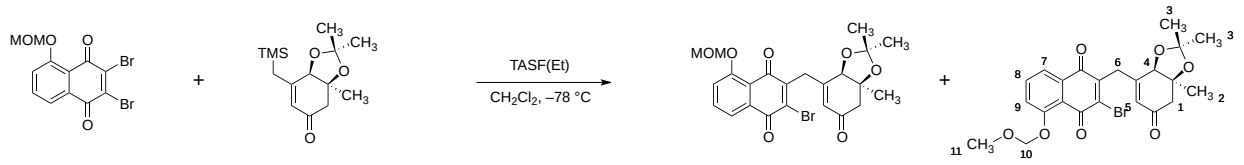
The α,β-unsaturated ketone **S33** was prepared according to the procedure of Herzon and co-workers.[35]

*Synthesis of the β-Trimethylsilylmethyl-α,β-unsaturated Ketone **S21**:*

Cuprous iodide (146 mg, 765 μmol, 0.10 equiv) was added to a stirred solution of trimethylsilylmethylmagnesium chloride in ether (1.00 M, 8.42 mL, 8.42 mmol, 1.10 equiv) at 24 °C. The resulting solution was cooled to −30 °C, to afford a cloudy suspension. To this mixture was added a solution of the α,β-unsaturated ketone **S33** [1.50 g, 7.65 mmol, 1 equiv; dried by azeotropic distillation with benzene (8.0 mL)] in tetrahydrofuran (3.0 mL) dropwise via cannula. The flask containing the α,β-unsaturated ketone **S33** was rinsed with tetrahydrofuran (2 × 1.0 mL) and the rinses were added to the reaction vessel via cannula. The reaction mixture was cooled to −50 °C and stirred at this temperature for 30 min. The mixture was then was cooled to −60 °C and hexamethylphosphoramide (1.46 mL, 8.42 mmol, 1.10 equiv), triethylamine (3.18 mL, 22.9 mmol, 3.00 equiv), and trimethylsilyl chloride (1.94 mL, 15.3 mmol, 2.00 equiv) were added in sequence to the cooled solution. The resulting mixture was further cooled to −78 °C, and the reaction mixture was stirred at this temperature for 0.5 h. The product mixture was then warmed over 10 min to 0 °C, and the warmed solution was stirred for 20 min at 0 °C. The product mixture was diluted with pentane (50 mL) and saturated aqueous sodium bicarbonate solution (100 mL). The resulting pale yellow biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with pentane (3 × 150 mL). Each organic layer was washed with saturated aqueous sodium bicarbonate solution (2 × 30 mL), and saturated aqueous sodium chloride solution (15 mL). The organic layers were combined and the combined layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was eluted over a silica pad (3 × 5 cm). The silica pad was washed with ether (3 × 50 mL), and the filtrates were combined. The combined filtrate was concentrated.

The residue obtained in the previous step was dissolved in acetonitrile (75 mL) at 24 °C. Palladium acetate (2.00 g, 8.91 mmol, 1.19 equiv) was added, and the resulting black mixture was stirred for 13 h at 24 °C. The product mixture was diluted with ether (60 mL) and the diluted solution was filtered through a pad of celite (3 × 4 cm). The celite pad was washed with ether (3 × 30 mL) and the filtrates were combined. The combined filtrates were concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 20% ether–hexanes) to afford the the β-trimethylsilylmethyl-α,β-unsaturated ketone **S21** as a clear, colorless oil (1.81 g, 86%).

R_f = 0.58 (50% ether–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.81 (s, 1H, H_1), 4.16 (s, 1H, H_4), 2.75 (d, 1H, J = 16.5 Hz, H_9), 2.45 (d, 1H, J = 16.5 Hz, H_9), 2.09 (d, 1H, J = 12.0 Hz, H_2), 1.85 (dd, 1H, J = 12.5, 1.0 Hz, H_2), 1.76–1.68 (m, 1H, H_7), 1.66–1.58 (m, 1H, H_7), 1.42 (s, 3H, H_5/H_6), 1.37 (s, 3H, H_5/H_6), 0.95 (t, 3H, J = 7.0 Hz, H_8), 0.09 (s, 9H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.4 (C), 159.4 (C), 125.4 (CH), 109.5 (C), 82.7 (C), 78.2 (CH), 44.3 (CH_2), 31.3 (CH_2), 28.1 (CH_3), 28.0 (CH_3), 27.0 (CH_2), 7.9 (CH_3), 1.1 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2983 (w), 1667 (s), 1621 (m), 1380 (m). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{15}H_{27}O_3Si$, 283.1723; found, 283.1724.



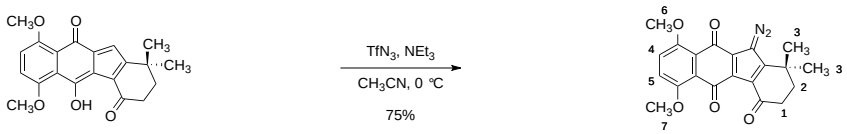
S15 **60** **62** (41%, desired) **S16** (29%, undesired)

*Fluoride-mediated Coupling of the β-Trimethylsilylmethyl-α,β-unsaturated Ketone **60** and O-(Methoxymethyl)-2,3-dibromojuglone (**S15**):*

A neat mixture of the β-trimethylsilylmethyl-α,β-unsaturated ketone **60** (50.0 mg, 177 μmol, 1 equiv) and *O*-(methoxymethyl)-2,3-dibromojuglone (**S15**, 200 mg, 531 μmol, 3.00 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3.0 mL). The dried mixture was dissolved in dichloromethane (18 mL) at −78 °C. A solution of TASF(Et) (70.0 mg, 195 μmol, 1.10 equiv) in dichloromethane (1.0 mL) was added dropwise via cannula to the stirred solution at −78 °C. The resulting dark green mixture was stirred for 10 min at −78 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 20 mL). The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2.5% ethyl acetate–hexanes initially, grading to 5% ethyl acetate–hexanes, one step) to afford separately the δ-ketoquinone **62** (desired isomer, yellow solid, 35.7 mg, 41%), and the δ-ketoquinone **S16** (undesired isomer, yellow solid, 16.7 mg, 29%).

^{1}H NMR spectroscopic data for the δ-ketoquinone **62** obtained in this way was in agreement with those previously reported. The connectivity of the coupling products **62** and **S16** were deduced by X-ray analysis of **62** and by conversion of **62** to (−)-kinamycin F (**6**).[9]

δ-Ketoquinone **S16**: R_f = 0.54 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, 1H, J = 7.5 Hz, H_7/H_9), 7.66 (t, 1H, J = 8.0 Hz, H_8), 7.53 (d, 1H, J = 8.5 Hz, H_7/H_9), 5.79 (s, 1H, H_5), 5.37 (s, 2H, H_{10}), 4.47 (s, 1H, H_4), 4.06 (dd, 1H, J = 16.5, 2.0 Hz, H_6), 3.67 (d, 1H, J = 16.0 Hz, H_6), 3.54 (s, 3H, H_{11}), 2.83 (d, 1H, J = 16.0 Hz, H_1), 2.49 (d, 1H, J = 16.5 Hz, H_1), 1.43 (s, 6H, H_3), 1.36 (s, 3H, H_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.3 (C), 181.2 (C), 175.4 (C), 157.7 (C), 153.5 (C), 145.1 (C), 143.6 (C), 135.2 (CH), 133.3 (C), 127.0 (CH), 122.2 (CH), 121.1 (CH), 119.7 (C), 110.2 (C), 95.0 (CH_2), 80.4 (C), 79.3 (CH), 56.7 (CH_3), 47.0 (CH_2), 35.8 (CH_2), 28.4 (CH_3), 28.3 (CH_3), 26.2 (CH_3). IR (ATR-FTIR), cm^{-1}: 2984 (w), 1674 (s), 1585 (m), 1239 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{23}H_{24}Br^{79/81}O_7$, 491.0705/493.0685; found, 491.0704/493.0690.

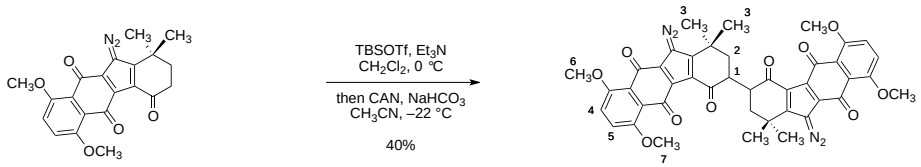


51 **S19**

*Diazotransfer to the Hydroxyfulvene **51**:*

A solution of trifluoromethanesulfonyl azide in hexanes (250 mM, 156 μL, 390 μmol, 2.50 equiv) was added dropwise via syringe to a stirred solution of triethylamine (108 μL, 780 μmol, 5.00 equiv) and the hydroxyfulvene **51** [55.0 mg, 156 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in acetonitrile (3.1 mL) at 24 °C. The resulting mixture was stirred for 5 min at 0 °C. The product mixture was diluted sequentially with dichloromethane (5 mL) and 0.1 M aqueous sodium phosphate buffer solution (pH 7, 15 mL). The resulting biphasic solution was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted sequentially with dichloromethane (3 × 5 mL) and ethyl acetate (2 × 5 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated and the residue obtained was purified by preparative thin layer chromatography (pre-developed with 10% methanol–ethyl acetate, eluting with 5% methanol–dichloromethane) to afford the diazofluorene **S19** as a yellow solid (44.1 mg, 75%).

R_f = 0.36 (5% methanol–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, 1H, J = 7.5 Hz, H_4/H_5), 7.18 (d, 1H, J = 7.5 Hz, H_4/H_5), 3.93 (s, 3H, H_6/H_7), 3.88 (s, 3H, H_6/H_7), 2.59 (t, 2H, J = 6.5 Hz, H_1), 2.00 (t, 2H, J = 6.5 Hz, H_2), 1.44 (s, 6H, H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0 (C), 179.5 (C), 178.7 (C), 158.0 (C), 154.1 (C), 153.9 (C), 132.5 (C), 131.3 (C), 125.0 (C), 123.8 (C), 121.9 (CH), 120.8 (C), 118.5 (CH), 73.8 (C), 57.2 (CH_3), 56.6 (CH_3), 38.8 (CH_2), 35.9 (CH_2), 33.8 (C), 27.5 (2 × CH_3). IR (ATR-FTIR), cm^{-1}: 2930 (m), 2129 (s), 1677 (s), 1273 (m). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{21}H_{19}N_2O_5$, 379.1294; found, 379.1295.



S19 **S20**

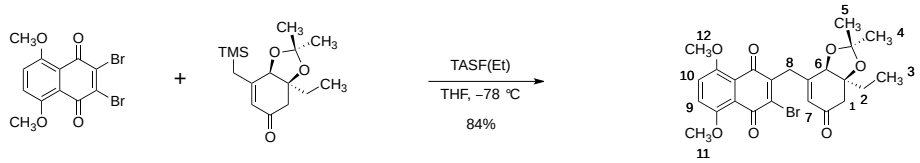
*Oxidative Dimerization of the Diazofluorene **S19**:*

Triethylamine (32.0 μL, 231 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (26.6 μL, 116 μmol, 2.50 equiv) were added in sequence to a stirred solution of the diazofluorene **S19** [17.5 mg, 46.3 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (1.0 mL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (5 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the preceding step [dried by azeotropic distillation with benzene (2 × 500 μL)] was dissolved in acetonitrile (100 μL). The resulting solution was cooled to –22 °C. Sodium bicarbonate (77.8 mg, 926 μmol, 20.0 equiv) and a solution of ceric ammonium nitrate (50.7 mg, 92.6 μmol, 2.00 equiv) in acetonitrile (230 μL) were added in sequence to the vigorously stirred solution at –22 °C. The reaction mixture was stirred for 30 min at –22 °C. The product mixture was diluted sequentially with dichloromethane (2 mL) and distilled water (4 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 2 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 1% methanol–dichloromethane) to afford the dimeric diazofluorene **S20** as an orange solid (6.9 mg, 40%, 1:1 mixture of diastereomers).

Note: ^{1}H and ^{13}C NMR data are normalized to the monomeric structure. UPLC/MS analysis of the unpurified dimeric diazofluorene suggested a 1:1 mixture of meso and d/l isomers were produced.

R_f = 0.44 (5% methanol–dichloromethane; UV, CAM). t_R = 0.69/1.04. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, 1H, J = 9.2 Hz, H_4/H_5), 7.20 (d, 1H, J = 9.2 Hz, H_4/H_5), 3.96 (s, 3H, H_6/H_7), 3.90 (s, 3H, H_6/H_7), 3.85–3.82 (m, 1H, H_1), 2.08–1.88 (m, 2H, H_2), 1.61 (s, 3H, H_3), 1.44 (s, 3H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.0 (C), 179.8 (C), 178.6 (C), 157.8 (C), 154.2 (C), 154.1 (C), 132.8 (C), 131.4 (C), 125.3 (C), 124.1 (C), 121.9 (CH), 121.0 (C), 118.4 (CH), 73.6 (C), 57.2 (CH_3), 56.7 (CH_3), 34.3 (CH), 29.7 (C), 28.8 (CH_2), 26.9 (2 × CH_3). IR (ATR-FTIR), cm^{-1}: 2924 (m), 2121 (s), 1680 (s), 1638 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{42}H_{35}N_4O_{10}$, 755.2353; found, 755.2355.

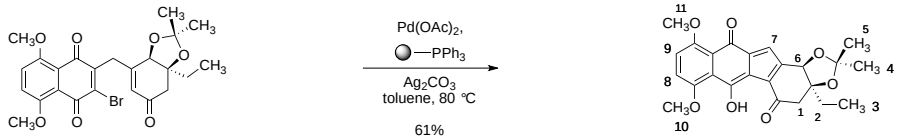


19 **S21** **S57**

*Fluoride-mediated Coupling of the β-Trimethylsilyl-α,β-unsaturated Ketone **S21** and the 2,3-Dibromo-5,8-dimethoxynaphthoquinone (**19**):*

A neat mixture of the β-trimethylsilylmethyl-α,β-unsaturated ketone **S21** (1.10 g, 3.92 mmol, 1 equiv) and 2,3-dibromo-5,6-dimethoxyquinone (**19**, 4.40 g, 11.7 mmol, 3.00 equiv) was prepared in a round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (25.0 mL). The dried mixture was dissolved in tetrahydrofuran (390 mL) at −78 °C. A solution of TASF(Et) (1.47 g, 4.09 mmol, 1.05 equiv) in tetrahydrofuran (55 mL) was added dropwise via cannula to a stirred solution the stirred solution at −78 °C. The resulting black mixture was stirred for 15 min at −78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 300 mL). The diluted solution was warmed over 10 min to 24 °C. The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (2 × 200 mL). The organic layers were combined and the combined layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 15% ethyl acetate–dichloromethane initially, grading to 35% acetone–hexanes, one step) to afford the δ-ketoquinone **S57** as a red solid (1.66 g, 84%).

R_f = 0.50 (70% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (app s, 2H, H_9/H_{10}), 5.74 (s, 1H, H_7), 4.49 (s, 1H, H_6), 3.99 (dd, 1H, J = 16.0, 1.5 Hz, H_8), 3.95 (s, 3H, H_{11}/H_{12}), 3.93 (s, 3H, H_{11}/H_{12}), 3.65 (d, 1H, J = 16.5 Hz, H_8), 2.81 (d, 1H, J = 16.5 Hz, H_1), 2.42 (d, 1H, J = 16.5 Hz, H_1), 1.85−1.77 (m, 1H, H_2), 1.67−1.58 (m, 1H, H_2), 1.39 (s, 3H, H_4/H_5), 1.35 (s, 3H, H_4/H_5), 0.94 (t, 3H, J = 7.5 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5 (C), 180.4 (C), 176.3 (C), 154.5 (C), 154.2 (C), 154.0 (C), 146.5 (C), 140.5 (C), 126.6 (CH), 120.5 (CH), 120.4 (CH), 120.0 (C), 119.9 (C), 110.0 (C), 83.0 (C), 78.4 (CH), 56.9 (CH_3), 56.7 (CH_3), 44.0 (CH_2), 35.8 (CH_2), 31.6 (CH_2), 28.4 (CH_3), 28.3 (CH_3), 7.7 (CH_3). IR (ATR-FTIR), cm^{-1}: 2979 (w), 1657 (s), 1562 (m), 1476 (m). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{24}H_{25}Br^{79/81}O_7$, 507.0839/505.0862; found, 507.0836/505.0858.

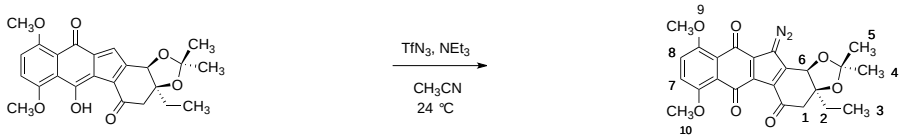


S57 **S22**

*Cyclization of the δ-Ketoquinone **S57**:*

A mixture of palladium acetate (733 mg, 3.27 mmol, 1.00 equiv), polymer-bound triphenylphosphine (2.73 g, 8.18 mmol, 2.20 equiv), and silver carbonate (2.70 g, 9.82 mmol, 2.00 equiv) was added to a stirred solution of the coupled product **S57** [1.65 g, 3.27 mmol, 1 equiv; dried by azeotropic distillation with benzene (12 mL)] in toluene (22 mL) at 24 °C. The resulting dark brown mixture was placed in an oil bath that had been preheated to 80 °C. The reaction mixture was stirred and heated for 60 min at 80 °C. The product solution was cooled over 10 min to 24 °C and the cooled solution was filtered over a pad of celite (5 cm × 5 cm). The celite pad was washed with ethyl acetate (4 × 20 mL), and the filtrates were combined. The combined filtrates were concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 35% acetone–hexanes initially, grading to 3% methanol–dichloromethane, one step) to afford the hydroxyfulvene **S22** as a dark purple solid (850 mg, 61%).

R_f = 0.43 (5% methanol–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, 1H, J = 9.5 Hz, H_8/H_9) 7.25 (d, 1H, J = 9.5 Hz, H_8/H_9), 7.02 (s, 1H, H_7), 4.94 (s, 1H, H_6), 3.99 (s, 3H, H_{10}/H_{11}), 3.96 (s, 3H, H_{10}/H_{11}), 3.17 (d, 1H, J = 18.0 Hz, H_1), 2.82 (d, 1H, J = 18.0 Hz, H_1), 1.83−1.70 (m, 2H, H_2), 1.48 (s, 3H, H_4/H_5), 1.35 (s, 3H, H_4/H_5), 0.95 (t, 3H, J = 7.5 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.8 (C), 181.0 (C), 176.3 (C), 156.6 (C), 156.5 (C), 142.9 (C), 137.7 (C), 122.8 (C), 122.4 (CH), 122.3 (C), 121.9 (C), 121.9 (CH), 121.0 (C), 120.5 (CH), 109.7 (C), 85.2 (C), 73.8 (CH), 57.2 (CH_3), 57.0 (CH_3), 42.7 (CH_2), 30.8 (CH_2), 28.0 (CH_3), 27.6 (CH_3), 8.2 (CH_3). IR (ATR-FTIR), cm^{-1}: 2969 (m), 1646 (s), 1592 (m), 1560 (s), 1406 (m), 1261 (m), 1041 (s), 730 (m). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{24}H_{24}O_7$, 425.1594; found, 425.1596.

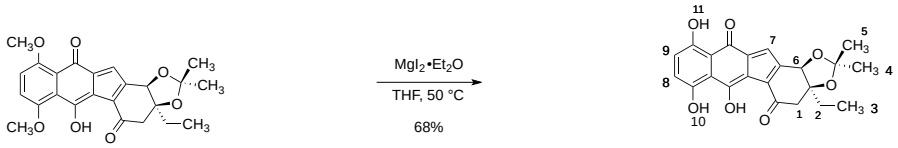


S22 **S24**

*Diazotransfer to the Hydroxyfulvene **S22**:*

Triethylamine (78.0 μL, 566 μmol, 10.0 equiv) was added to a stirred solution of the cyclized product **S22** [24.0 mg, 56.6 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in acetonitrile (2.8 mL) at 24 °C. After stirring for 5 min at 24 °C, a solution of trifluoromethanesulfonyl azide in hexanes (570 mM, 500 μL, 283 μmol, 5.00 equiv) was added. The resulting brown mixture was stirred for 40 min at 24 °C. The product mixture was diluted sequentially with dichloromethane (15 mL) and saturated sodium bicarbonate solution (15 mL). The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 40% acetone–hexanes) to provide the diazofluorene **S24** as an orange solid (13.0 mg, 52%).

R_f = 0.34 (50% acetone–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, 1H, J = 9.0 Hz, H_7/H_8), 7.17 (d, 1H, J = 9.0 Hz, H_7/H_8), 5.05 (s, 1H, H_6), 3.91 (s, 3H, H_9/H_{10}), 3.84 (s, 3H, H_9/H_{10}), 2.98 (d, 1H, J = 16.0 Hz, H_1), 2.66 (d, 1H, J = 16.0 Hz, H_1), 1.84–1.80 (m, 1H, H_2), 1.70–1.66 (m, 1H, H_2), 1.39 (s, 3H, H_5/H_4), 1.02 (s, 3H, H_5/H_4), 0.95 (t, 3H, J = 7.5 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.5 (C), 179.6 (C), 178.3 (C), 154.5 (C), 154.4 (C), 146.7 (C), 133.7 (C), 129.6 (C), 124.8 (C), 124.4 (C), 122.2 (CH), 120.8 (C), 118.8 (CH), 111.0 (C), 85.9 (C), 75.8 (C), 73.0 (CH), 57.2 (CH_3), 56.7 (CH_3), 46.3 (CH_2), 31.3 (CH_2), 28.5 (CH_3), 28.2 (CH_3), 7.9 (CH_3). IR (ATR-FTIR), cm^{-1}: 2979 (w), 2139 (s), 1683 (s), 1440 (m). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{24}H_{23}N_2O_7$, 451.1511; found, 451.1506.

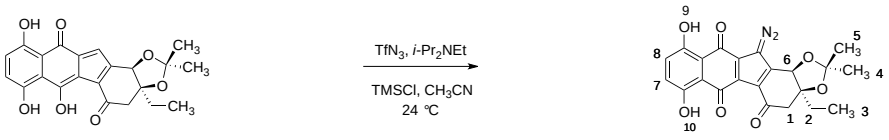


S22 **S58**

*Demethylation of the Hydroxyfulvene **S22**:*

A freshly prepared solution of magnesium iodide in ether (0.10 M, 7.10 mL, 710 μmol, 5.00 equiv) was added dropwise via syringe to a stirred solution of the hydroxyfulvene **S22** [60.0 mg, 142 μmol, 1 equiv; dried by azeotropic distillation with benzene (5.0 mL)] in tetrahydrofuran (2.3 mL) at 24 °C. The reaction mixture was heated for 2 h at 50 °C. The product solution was cooled over 10 min to 24 °C. The cooled solution was diluted sequentially with dichloromethane (25 mL) and 1 N aqueous sulfuric acid solution (25 mL). The diluted solution was transferred to a separatory funnel that had been charged with dichloromethane (25 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% acetic acid–dichloromethane) to furnish the deprotected hydroxyfulvene **S58** as an orange solid (38.6 mg, 68%).

R_f = 0.31 (5% methanol–dichloromethane; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.37 (s, 1H, H_{10}/H_{11}), 11.62 (s, 1H, H_{10}/H_{11}), 7.21 (d, 1H, J = 9.6 Hz, H_8/H_9) 7.15 (d, 1H, J = 9.5 Hz, H_8/H_9), 7.07 (s, 1H, H_7), 4.99 (s, 1H, H_6), 3.28 (d, 1H, J = 18.4 Hz, H_1), 2.91 (d, 1H, J = 18.8 Hz, H_1), 1.85–1.76 (m, 2H, H_2), 1.50 (s, 3H, H_4/H_5), 1.35 (s, 3H, H_4/H_5), 0.98 (t, 3H, J = 7.2 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.2 (C), 184.9 (C), 179.9 (C), 159.4 (C), 158.0 (C), 142.8 (C), 139.5 (C), 130.5 (CH), 128.9 (CH), 125.5 (C), 120.7 (CH), 119.0 (C), 113.0 (C), 112.3 (C), 109.9 (C), 85.2 (C), 73.7 (CH), 40.9 (CH_2), 30.9 (CH_2), 28.0 (CH_3), 27.7 (CH_3), 8.2 (CH_3). IR (ATR-FTIR), cm^{-1}: 2980 (m), 1635 (s), 1582 (m), 1451 (m), 1398 (s), 1169 (m), 1067 (m), 832 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{22}H_{20}O_7$, 397.1281; found, 397.1278.

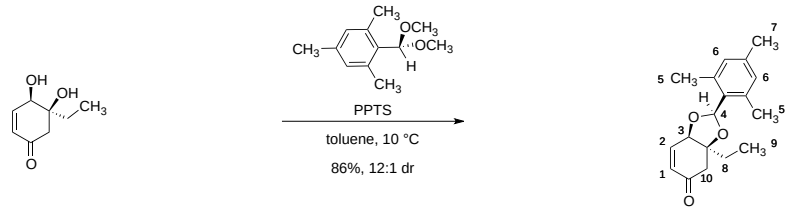


S58 **S25**

*Diazotransfer to the Deprotected Hydroxyfulvene **S58**:*

N,*N*-Diisopropylethylamine (42.0 μL, 242 μmol, 6.00 equiv) and trimethylsilyl chloride (15.0 μL, 120 μmol, 3.00 equiv) were added in sequence to a stirred solution of the deprotected hydroxyfulvene **S58** [16.0 mg, 40.0 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in acetonitrile (2.0 mL) at 24 °C. After stirring for 5 min at 24 °C, a solution of trifluoromethanesulfonyl azide in hexanes (370 μM, 189 μL, 70.4 μmol, 1.75 equiv) was added. The resulting brown mixture was stirred for 20 min at 24 °C. The product mixture was diluted sequentially with dichloromethane (15 mL) and 1 N aqueous sulfuric acid solution (15 mL). The resulting biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the organic layers were combined. The combined organic layers were dried over sodium sulfate. The dried solution was filtered, and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 1% methanol–dichloromethane) to provide the diazofluorene **S25** as an orange solid (10.3 mg, 59%).

R_f = 0.40 (40% acetone–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.21 (s, 1H, H_9/H_{10}), 12.4 (s, 1H, H_9/H_{10}), 7.24 (d, 1H, J = 9.5 Hz, H_7/H_8), 7.17 (d, 1H, J = 9.5 Hz, H_7/H_8), 5.16 (s, 1H, H_6), 3.12 (d, 1H, J = 16.0 Hz, H_1), 2.77 (d, 1H, J = 16.0 Hz, H_1), 1.98−1.90 (m, 1H, H_2), 1.82−1.74 (m, 1H, H_2), 1.49 (s, 3H, H_4/H_5), 1.11 (s, 3H, H_4/H_5), 1.05 (t, 3H, J = 7.5 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.5 (C), 181.9 (C), 181.7 (C), 158.5 (C), 158.2 (C), 147.7 (C), 132.6 (C), 130.5 (CH), 128.5 (CH), 128.0 (C), 125.5 (C), 112.9 (CH), 112.0 (C), 111.3 (C), 77.2 (C, determined indirectly by HMBC), 72.9 (CH), 46.3 (CH_2), 31.3 (CH_2), 28.5 (CH_3), 28.3 (CH_3), 7.9 (CH_3). IR (ATR-FTIR), cm^{-1}: 2978 (m), 2150 (m), 1689 (s), 1636 (m), 1445 (m), 1337 (s), 1146 (s), 1039 (s), 843 (s). HRMS-ESI (*m*/*z*): $[M + H]^+$ calculated for $C_{22}H_{18}N_2O_7$, 423.1186; found, 423.1173.

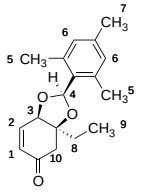


68 **69**

The enone **68** was prepared according to the procedure of Herzon and co-workers.[35]

Synthesis of endo-*Mesityl Acetal **68**:*

Mesitylaldehyde dimethylacetal (5.01 g, 25.7 mmol, 2.00 equiv) and pyridinium *para*-toluenesulfonate (323 mg, 1.29 mmol, 0.10 equiv) were added in sequence to a stirred solution of the enone **68** (2.00 g, 12.8 mmol, 1 equiv) in toluene (128 mL) at 24 °C. The resulting mixture was cooled to 10 °C, and the cooled solution was stirred for 2 h at 10 °C. Mesitylaldehyde dimethylacetal (2.55 g, 12.8 mmol, 1 equiv) was added and the mixture was stirred for 10 h at 10 °C. The product mixture was diluted with triethylamine (3.64 mL, 26.3 mmol, 2.06 equiv), and the diluted solution was warmed to 24 °C. The product mixture was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (200 mL). The layers that formed were separated, and the aqueous layer was extracted with ethyl acetate (3 × 100 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 25% ether–hexanes) to afford the *endo*-mesityl acetal **69** as a clear, colorless oil (2.80 g, 85%, 12:1 mixture of diastereomers). The stereochemistry of the mesityl acetal was determined by NOE analysis.



69

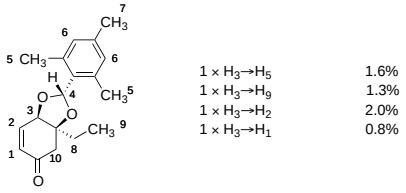
1 × $H_4 \rightarrow H_3$	1.9%
1 × $H_4 \rightarrow H_9$	1.0%
1 × $H_4 \rightarrow H_8$	2.5%
1 × $H_4 \rightarrow H_8$	1.6%

R_f = 0.76 (60% ether–hexanes; UV, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (dd, 1H, J = 7.0, 4.0 Hz, H_2), 6.81 (s, 2H, H_6), 6.28 (s, 1H, H_4), 6.20 (dd, 1H, J = 5.6, 1.2 Hz, H_1) , 4.46 (dd, 1H, J = 4.0, 1.2 Hz, H_3), 3.00 (d, 1H, J = 16.5 H, H_{10}), 2.70 (d, 1H, J = 16.5 Hz, H_{10}), 2.38 (s, 6H, H_5), 2.24 (s, 3H, H_7), 2.05–1.95 (m, 1H, H_8), 1.81–1.72 (m, 1H, H_8), 1.00 (t, 3H, J = 7.6 Hz, H_9). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.7 (C), 142.9 (CH), 139.1 (C), 137.9 (2 × C), 130.4 (CH), 130.3 (2 × CH), 126.9 (C), 100.2 (CH), 80.1 (C), 75.2 (CH), 45.0 (CH_2), 31.1 (CH_2), 20.9 (CH_3), 20.5 (2 × CH_3), 7.3 (CH_3). IR (ATR-FTIR), cm^{-1}: 2970 (w), 1687 (s), 1062 (s), 1029 (s). HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{18}H_{22}O_3Na$, 309.1462; found 309.1461.

69 **69** **S59**

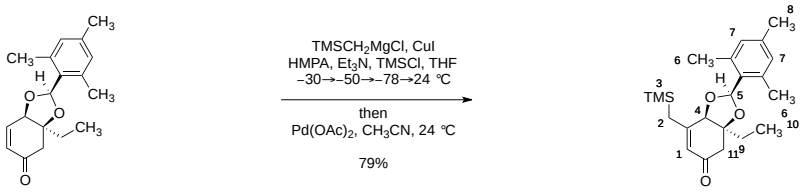
Epimerization of the endo-*Mesityl* ***69****:*

Pyridinium *para*-toluenesulfonate (1.5 mg, 8.00 μmol, 0.10 equiv) was added to a stirred solution of the *endo*-mesityl **69** (22.9 mg, 80.0 μmol, 1 equiv) in acetonitrile (500 μL) at 24 °C. The resulting mixture was stirred for 2 h at 50 °C, The product solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (5 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 2 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by preparatory thin layer chromatography (eluting with 30% ethyl acetate–hexanes) to afford the acetal **69** (clear oil, 11.4 mg, 50%), and the *exo*-mesityl **S59** (clear oil, 9.1 mg, 40%). The stereochemistry of the mesityl substituent was determined by NOE analysis.



S59

exo-Mesityl **S59**: R_f = 0.83 (40% ethyl acetate–hexanes; UV, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (dd, 1H, J = 14.5, 4.5 Hz, H_2), 6.82 (s, 2H, H_6), 6.30 (s, 1H, H_4), 6.28 (d, 1H, J = 10.0 Hz, H_1), 4.53 (d, 1H, J = 4.0 Hz, H_3), 2.93 (d, 1H, J = 16.5 Hz, H_{10}), 2.72 (d, 1H, J = 16.5 Hz, H_{10}), 2.42 (s, 6H, H_5), 2.25 (s, 3H, H_7), 1.97–1.92 (m, 1H, H_8), 1.87–1.82 (m, 1H, H_8), 0.99 (t, 3H, J = 7.5 Hz, H_9). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4 (C), 142.6 (CH), 139.0 (C), 137.9 (2 × C), 131.6 (CH), 130.2 (2 × CH), 127.4 (C), 100.2 (CH), 82.3 (C), 74.9 (CH), 43.6 (CH_2), 32.9 (CH_2), 20.9 (CH_3), 20.3 (2 × CH_3), 8.2 (CH_3). IR (ATR-FTIR), cm^{-1}: 1687 (s), 1612 (m), 1448 (m), 1060 (s). HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{18}H_{22}O_3Na$, 309.1462; found 309.1461.



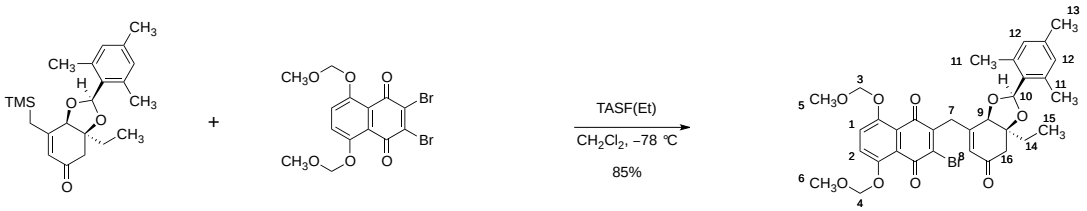
69 **S60**

*Synthesis of the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S60**:*

Cuprous iodide (138 mg, 702 μmol, 0.10 equiv) was added to a stirred solution of trimethylsilylmethylmagnesium chloride in ether (1.00 M, 7.70 mL, 7.70 mmol, 1.10 equiv) at 24 °C. The resulting solution was cooled to −30 °C, to afford a cloudy suspension. A solution of the *endo*-mesityl acetal **69** [2.00 g, 7.02 mmol, 1 equiv; dried by azeotropic distillation with benzene (5.0 mL)] in tetrahydrofuran (1.0 mL) was then added dropwise via cannula. The flask containing the *endo*-mesityl acetal **69** was rinsed with tetrahydrofuran (2 × 2.0 mL) and the rinses were added to the reaction vessel via cannula. The reaction mixture was cooled to −50 °C and then was stirred at this temperature for 30 min. The mixture was then was cooled to −60 °C. Hexamethylphosphoramide (1.34 mL, 7.72 mmol, 1.10 equiv), triethylamine (1.94 mL, 14.0 mmol, 2.00 equiv), and trimethylsilyl chloride (1.78 mL, 14.0 mmol, 2.00 equiv) were added in sequence to the cooled solution at −60 °C. The resulting mixture was further cooled to −78 °C, and was stirred for 1 h at −78 °C. The mixture was then warmed over 10 min to 24 °C, and the warmed solution was stirred for 20 min at 24 °C. The product mixture was diluted with ether (100 mL) and the diluted solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (100 mL). The layers that formed were separated, and the aqueous layer was extracted with ether (100 mL). The organic layers were combined, and the combined organic layers were washed with saturated aqueous sodium bicarbonate solution (2 × 70 mL) and saturated aqueous sodium chloride solution (60 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was dissolved in ether (20 mL) and the resulting solution was eluted over a pad of silica gel (2 × 5 cm). The pad of silica gel was washed with ether (3 × 10 mL), and the filtrates were combined. The combined filtrates were concentrated.

The residue obtained in the preceding step was dissolved in acetonitrile (70 mL) at 24 °C. Palladium acetate (1.88 g, 8.40 mmol, 1.20 equiv) was added, and the resulting black mixture was stirred for 12 h at 24 °C. The product mixture was diluted with ether (50 mL) and the diluted solution was filtered through a pad of celite (5 × 5 cm). The celite pad was washed with ether (3 × 50 mL) and the filtrates were combined. The combined filtrates were concentrated, and the residue obtained was purified by flash-column chromatography (eluting with 15% ether–hexanes) to afford the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S60** as a clear, colorless oil (2.06 g, 79%).

R_f = 0.33 (20% ether–hexanes; UV, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 2H, H_7), 6.25 (s, 1H, H_5), 5.90 (s, 1H, H_1), 4.26 (s, 1H, H_4), 2.91 (d, 1H, J = 16.8 Hz, H_2), 2.64 (d, 1H, J = 16.8 Hz, H_2), 2.37 (s, 6H, H_6), 2.24 (s, 3H, H_8), 2.12 (d, 1H, J = 12.8 Hz, H_{11}), 1.99–1.90 (m, 2H, H_{11}/H_9), 1.79–1.70 (m, 1H, H_9), 1.00 (t, 3H, J = 7.6 Hz, H_{10}), 0.10 (s, 9H, H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1 (C), 159.7 (C), 140.2 (C), 139.1 (2 × C), 131.3 (2 × CH), 128.0 (C), 126.5 (CH), 100.9 (CH), 81.7 (C), 80.4 (CH), 45.8 (CH_2), 32.6 (CH_2), 28.3 (CH_2), 22.0 (CH_3), 21.4 (2 × CH_3), 8.5 (CH_3), 0.0 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2955 (m), 1669 (s), 1249 (m), 1063 (m). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{22}H_{33}O_3Si$, 373.2194; found 373.2197.

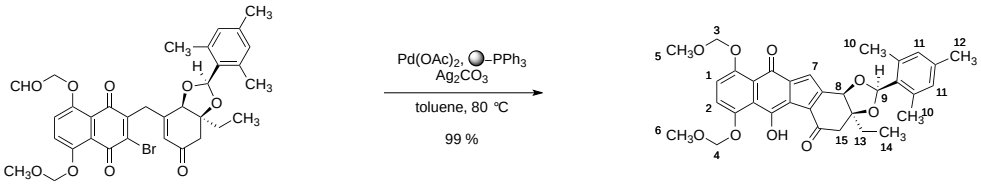


S60 + **70** → **S61**

*Coupling of 2,3-Dibromo-5,8-(dimethoxymethyloxy)naphthoquinone (**70**) and the β-(Trimethylsilylmethyl)-α,β-unsaturated Ketone **S60**:*

A neat mixture of 2,3-dibromo-5,8-(dimethoxymethyloxy)naphthoquinone (**70**, 6.14 g, 14.1 mmol, 3.50 equiv) and the β-(trimethylsilylmethyl)-α,β-unsaturated ketone **S60** (1.50 g, 4.03 mmol, 1 equiv) was prepared in a 1-L round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 20 mL). The dried mixture was dissolved in dichloromethane (780 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to –78 °C. A solution of TASF(Et) (1.59 g, 4.43 mmol, 1.10 equiv) in dichloromethane (9.0 mL) was added dropwise via cannula to the cold, stirred solution. The resulting black mixture was stirred for 15 min at –78 °C. The dark red product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 200 mL). The diluted solution was warmed over 30 min to 24 °C. The warmed, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 150 mL) and the organic layers were combined. The combined organic layers were dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated. The residue obtained was diluted with dichloromethane (100 mL) and the diluted solution was filtered to partially remove unreacted 2,3-dibromo-5,8-(dimethoxymethyloxy)naphthoquinone (**70**). The filtrate was concentrated, and the residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate-dichloromethane initially, grading to 40% ethyl acetate-dichloromethane, one step) to afford the δ-ketoquinone **S61** as a red solid (2.23 g, 85%).

R_f = 0.55 (20% ethyl acetate–hexanes; UV, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (app d, 2H, J = 2.0 Hz, H_1/H_2), 6.75 (s, 2H, H_{12}), 6.24 (s, 1H, H_{10}), 5.90 (s, 1H, H_8), 5.27 (app s, 2H, H_3/H_4), 5.22 (app s, 2H, H_3/H_4), 4.48 (s, 1H, H_9), 4.02 (dd, 1H, J = 15.6, 1.6 Hz, H_7), 3.71 (d, 1H, J = 16.0 Hz, H_7), 3.55 (s, 3H, H_5/H_6), 3.51 (s, 3H, H_5/H_6), 2.95 (d, 1H, J = 16.8 Hz, H_{16}), 2.65 (d, 1H, J = 16.0 Hz, H_{16}), 2.31 (s, 6H, H_{11}), 2.22 (s, 3H, H_{13}), 2.04–1.95 (m, 1H, H_{14}), 1.81–1.72 (m, 1H, H_{14}), 0.99 (t, 3H, J = 7.6 Hz, H_{15}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3 (C), 180.3 (C), 176.2 (C), 152.8 (C), 152.5 (C), 152.4 (C), 146.6 (C), 140.2 (C), 139.0 (C), 137.9 (2 × C), 130.1 (2 × CH), 127.1 (CH), 126.9 (C), 124.9 (CH), 124.7 (CH), 121.3 (C), 121.1 (C), 100.2 (CH), 95.8 (CH_2), 95.7 (CH_2), 81.2 (C), 78.7 (CH), 56.7 (CH_3), 56.6 (CH_3), 44.8 (CH_2), 36.2 (CH_2), 31.2 (CH_2), 20.9 (CH_3), 20.6 (2 × CH_3), 7.3 (CH_3). IR (ATR-FTIR), cm^{-1}: 2968 (w), 1670 (s), 1255 (m), 1150 (s). HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{33}H_{35}Br^{79/81}O_9Na$, 677.1357/679.1337; found 677.1359/679.1356.

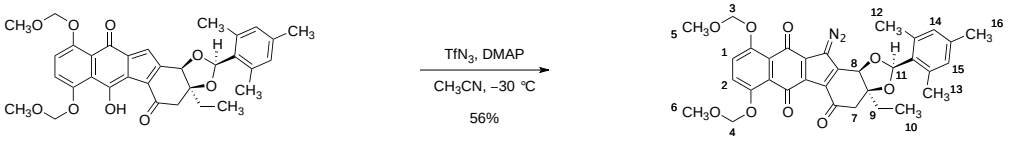


S61 **S62**

*Cyclization of the δ-Ketoquinone **S61**:*

A mixture of palladium acetate (513 mg, 2.29 mmol, 1.00 equiv), polymer-supported triphenylphosphine (1.91 g, 5.72 mmol, 2.50 equiv), and silver carbonate (1.26 g, 4.58 mmol, 2.00 equiv) were added to a stirred solution of the γ-quinonylated ketone **S61** [1.50 g, 2.29 mmol, 1 equiv; dried by azeotropic distillation with benzene (5.0 mL)] in toluene (110 mL) at 24 °C. The reaction vessel was placed in an oil bath that had been preheated to 80 °C. The reaction mixture was stirred and heated for 2 h at 80 °C. The product solution was cooled over 10 min to 24 °C and the cooled solution was filtered over a celite pad (6 × 8 cm). The celite pad was washed with ethyl acetate (4 × 50 mL). The filtrates were combined and the combined filtrates were concentrated. The residue obtained was purified by flash-column chromatography (eluting with 25% acetone–hexanes initially, grading to 3% methanol–dichloromethane, one step) to afford the hydroxyfulvene **S62** as a dark purple solid (1.30 g, 99%).

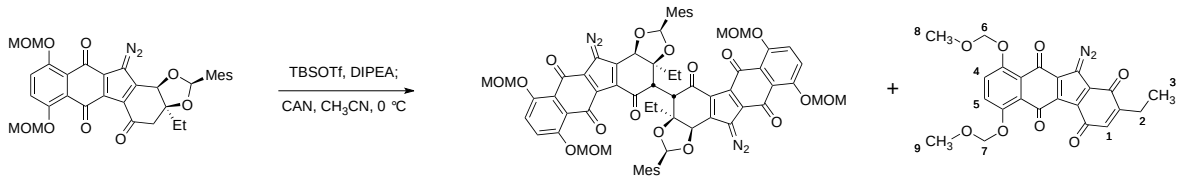
R_f = 0.70 (2% methanol–dichloromethane; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, 1H, J = 9.6 Hz, H_1/H_2), 7.42 (d, 1H, J =9.6 Hz, H_1/H_2), 7.07 (s, 1H, H_7), 6.77 (s, 2H, H_{11}), 6.35 (s, 1H, H_9), 5.32 (s, 2H, H_3/H_4), 5.27 (s, 2H, H_4/H_3), 5.01 (s, 1H, H_8), 3.59 (s, 3H, H_5/H_6), 3.56 (s, 3H, H_5/H_6), 3.34 (d, 1H, J = 18.8 Hz, H_{15}), 3.01 (d, 1H, J =18.8 Hz, H_{15}), 2.31 (s, 6H, H_{10}), 2.21 (s, 3H, H_{12}), 2.11–2.02 (m, 1H, H_{13}), 1.92–1.83 (m, 1H, H_{13}), 1.02 (t, J = 7.2 Hz, H_{14}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.1 (C), 180.7 (C), 175.4 (C), 154.4 (C), 154.3 (C), 144.0 (C), 139.0 (C), 137.9 (C), 137.8 (2 × C), 130.2 (2 × CH), 127.4 (CH), 127.0 (C), 125.1 (CH), 124.4 (C), 122.4 (1 × C, 1 × CH), 122.3 (C), 121.3 (C), 100.5 (CH), 96.4 (CH_2), 96.3 (CH_2), 83.2 (C), 75.5 (CH), 56.7 (CH_3), 56.7 (CH_3), 43.2 (CH_2), 31.8 (CH_2), 20.9 (CH_3), 20.3 (2 × CH_3), 7.8 (CH_3). IR (ATR-FTIR), cm^{-1}: 2924 (m), 1597 (s), 1413 (m), 1153 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{33}H_{35}O_9$, 575.2281; found 575.2295.



S62 **71**

*Diazotransfer to the Hydroxyfulvene **S62**:*

4-Dimethylaminopyridine (213 mg, 1.74 mmol, 5.00 equiv) was added to a stirred solution of the hydroxyfulvene **S62** [200 mg, 348 μmol, 1 equiv; dried by azeotropic distillation with benzene (2.0 mL)] in acetonitrile at 24 °C. The resulting mixture was stirred for 2 min at 24 °C, and then was cooled over 5 min to –30 °C. A solution of trifluoromethanesulfonyl azide in hexanes (242 mM, 3.60 mL, 870 μmol, 2.50 equiv) was added dropwise over 2 min via syringe to the cooled solution at –30 °C. The resulting mixture was stirred for 2 h at –30 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 50 mL). The diluted solution was poured into a separatory funnel that had been charged with 50% ethyl acetate–hexanes (400 mL), and the layers that formed were separated. The organic layer was washed with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 3 × 150 mL). The washed organic layer was dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated. The residue obtained was dried by azeotropic distillation with benzene (5.0 mL). The dried residue was then purified by flash-column chromatography (eluting with 60% ethyl acetate–hexanes) to afford the *endo*-mesityl diazofluorene **71** as a yellow solid (117 mg, 56%). ^{1}H NMR spectroscopic data for the *endo*-mesityl diazofluorene **71** obtained in this way was in agreement with those previously reported.[35]



71 **73** (42%) **74** (8%)

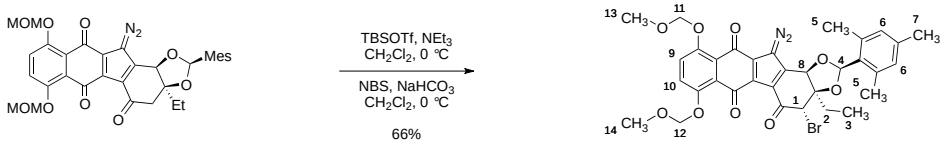
Dimerization of endo-*Mesityl Diazofluorene **71**:*

Triethylamine (14.0 μL, 100 μmol, 3.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (15.3 μL, 66.5 μmol, 2.00 equiv) were added in sequence to a stirred solution of the *endo*-mesityl diazofluorene **71** [20.0 mg, 33.3 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (650 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the previous step [dried by azeotropic distillation with benzene (500 μL)] was dissolved in acetonitrile (670 μL). Sodium bicarbonate (56.0 mg, 667 μmol, 20.0 equiv) was added, and the resulting suspension was cooled to 0 °C. A solution of ceric ammonium nitrate in acetonitrile (0.40 M, 167 μL, 66.7 μmol, 2.00 equiv) was added rapidly via syringe to the vigorously stirred solution at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and then was sequentially diluted with water (4 mL) and ethyl acetate (5 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 1% methanol–dichloromethane) to afford separately (10*S*, 10'*S*)-dimeric diazofluorene **73** (orange solid, 8.4 mg, 42%), the monomeric *endo*-mesityl diazofluorene **71** (yellow solid, 4.3 mg, 22%), and the monomeric dehydration–oxidation product **74** (yellow solid, 1.2 mg, 8%).

^{1}H NMR spectroscopic data for the (10*S*, 10'*S*)-dimeric diazofluorene **73** obtained in this way were identical to those previously reported.[35]

The monomeric dehydration–oxidation product **74**: R_f = 0.39 (60% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, 1H, J = 9.6 Hz, H_4/H_5), 7.46 (d, 1H, J = 9.6 Hz, H_4/H_5), 6.60 (t, 1H, J = 1.6 Hz, H_1), 5.32 (s, 2H, H_6/H_7), 5.28 (s, 2H, H_6/H_7), 3.56 (s, 3H, H_8/H_9), 3.55 (s, 3H, H_8/H_9), 2.5 (dq, 2H, J = 7.2, 1.6 Hz, H_2), 1.74 (t, 3H, J = 7.2 Hz, H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.2 (C), 180.0 (C), 179.5 (C), 177.6 (C), 153.3 (C), 153.2 (C), 149.6 (C), 135.8 (CH), 135.3 (C), 133.9 (C), 129.7 (C), 127.4 (CH), 127.1 (CH), 125.7 (C), 123.5 (C), 122.0 (C), 96.5 (CH_2), 95.6 (CH_2), 77.2 (C), 56.7 (CH_3), 56.6 (CH_3), 21.6 (CH_2), 11.9 (CH_3). IR (ATR-FTIR), cm^{-1}: 2934 (w), 2170 (m), 1649 (s), 1456 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{23}H_{19}N_2O_8$, 451.1136; found, 451.1135.

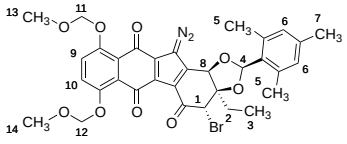


71 **77a**

*Synthesis of the α-Bromodiazofluorene **77a**:*

Triethylamine (197 μL, 143 μmol, 3.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (218 μL, 95.0 μmol, 2.00 equiv) were added in sequence to a stirred solution of the *endo*-mesityl diazofluorene **71** [28.5 mg, 47.5 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (950 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

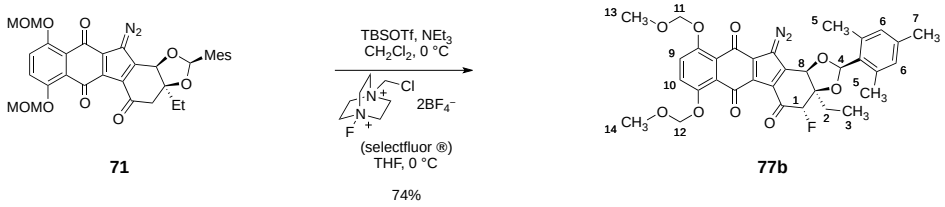
The residue obtained in the preceding step was dried by azeotropic distillation from benzene (500 μL). The dried residue was dissolved in tetrahydrofuran (3.5 mL) and the resulting solution was cooled to 0 °C. Sodium bicarbonate (21.1 mg, 252 μmol, 5.30 equiv) and *n*-bromosuccinimide (9.3 mg, 52.3 μmol, 1.10 equiv) was added in sequence to the stirred solution at 0 °C. The reaction mixture was stirred for 10 min at 0 °C. The product mixture was diluted sequentially with dichloromethane (5 mL) and 0.1 M aqueous sodium phosphate buffer solution (5 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted dichloromethane (2 × 4 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 50% ethyl acetate–hexanes) to afford the α-bromodiazofluorene **77a** as an orange solid (21.2 mg, 66%). The stereochemistry of the bromine substituent was determined by NOE analysis.



77a

2 × $H_1 \rightarrow H_5$	2.3%
1 × $H_1 \rightarrow H_7$	0.8%

R_f = 0.29 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, 1H, J = 9.5 Hz, H_9/H_{10}), 7.46 (d, 1H, J = 9.5 Hz, H_9/H_{10}), 6.76 (s, 2H, H_6), 6.43 (s, 1H, H_4), 5.31 (app s, 2H, H_{11}/H_{12}), 5.27 (app q, 2H, J = 7.0 Hz, H_{11}/H_{12}), 5.15 (s, 1H, H_8), 4.92 (s, 1H, H_1), 3.57 (s, 3H, H_{13}/H_{14}), 3.56 (s, 3H, H_{13}/H_{14}), 2.37–2.34 (m, 2H, H_2), 2.22 (s, 6H, H_5), 2.21(s, 3H, H_7), 1.07 (t, 3H, J = 7.5 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.8 (C), 179.1 (C), 177.6 (C), 153.2 (2 × C), 143.1 (C), 139.6 (C), 138.0 (C), 134.1 (C), 130.3 (2 × CH), 129.8 (C), 128.3 (C), 127.3 (CH), 126.2 (C), 125.5 (C), 123.6 (CH), 122.1 (C), 102.7 (CH), 96.7 (CH_2), 95.6 (CH_2), 86.9 (C), 76.2 (C), 72.7 (CH), 56.6 (CH_3), 56.5 (CH_3), 54.1 (CH), 29.7 (C), 26.6 (CH_2), 20.8 (CH_3), 20.3 (2 × CH_3), 6.5 (CH_3). IR (ATR-FTIR), cm $^{-1}$: 2927 (w), 2144 (s), 1709 (m), 1449 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{33}H_{32}Br^{79/81}N_2O_9$, 679.1291/681.1271; found, 679.1299/681.1273.



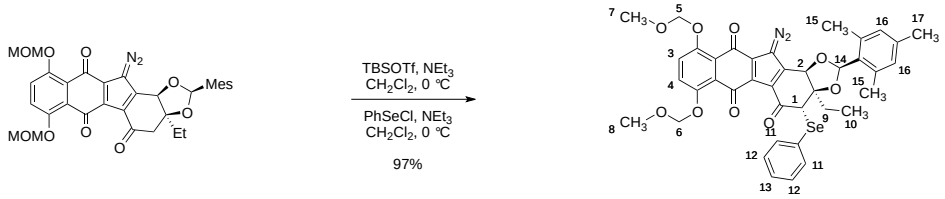
71 **77b**

*Synthesis of the α-Fluorodiazofluorene **77b**:*

Triethylamine (208 μL, 150 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (172 μL, 75.0 μmol, 2.50 equiv) were added in sequence to a stirred solution of the diazofluorene **71** [18.0 mg, 30.0 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (600 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the preceding step was dried by azeotropic distillation from benzene (500 μL). The dried residue was dissolved in tetrahydrofuran (300 μL) and the resulting solution was cooled to 0 °C. Selectfluor® (21.3 mg, 60.0 μmol, 2.00 equiv) was added to the cooled, stirred solution at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. The product mixture was then was diluted sequentially with ether (7 mL) and water (5 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ether (2 × 7 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 50% ethyl acetate–hexanes) to afford the α-fluorodiazofluorene **77b** as an orange solid (13.8 mg, 74%). The relative stereochemistry of the α-fluorodiazofluorene **77b** was assigned by analogy to that of the α-bromodiazofluorene **77a**.

R_f = 0.18 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, 1H, J = 9.5 Hz, H_9/H_{10}), 7.46 (d, 1H, J = 9.5 Hz, H_9/H_{10}), 6.84 (s, 2H, H_6), 6.44 (s, 1H, H_4), 5.51 (d, 1H, J = 48.5 Hz, H_1), 5.32 (d, 2H, J = 1.5 Hz, H_{11}/H_{12}), 5.28 (s, 1H, H_8), 5.27 (app s, 2H, H_{11}/H_{12}), 3.57 (s, 3H, H_{13}/H_{14}), 3.55 (s, 3H, H_{13}/H_{14}), 2.39 (s, 6H, H_5), 2.26 (s, 3H, H_7), 2.13–2.09 (m, 2H, H_2), 1.02 (t, 3H, J = 7.5 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 184.4 (d, C, J = 18.0 Hz), 179.1 (C), 177.6 (C), 140.1 (C), 139.7 (C), 138.0 (C), 153.2 (C), 139.9 (C), 138.0 (C), 134.6 (C), 130.4 (2 × CH), 129.3 (C), 127.4 (CH), 125.9 (C), 125.3 (C), 123.7 (CH), 122.8 (C), 121.9 (C), 103.3 (CH), 96.6 (CH_2), 95.7 (CH_2), 94.5 (CH, J = 195.1 Hz), 85.1 (C, J = 19.0 Hz), 76.7 (C, determined indirectly by HMBC), 74.0 (d, CH, J = 19.5 Hz), 56.7 (CH_3), 56.6 (CH_3), 25.5 (d, CH_2, J = 19.0 Hz), 20.9 (CH_3), 20.4 (2 × CH_3), 7.4 (CH_3). ^{19}F NMR (375 MHz, $CDCl_3$): δ –80.69. IR (ATR-FTIR), cm^{-1}: 2969 (w), 2148 (s), 1714 (s), 1652 (s), 1450 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{33}H_{32}FN_2O_9$, 619.2092; found, 619.2100.



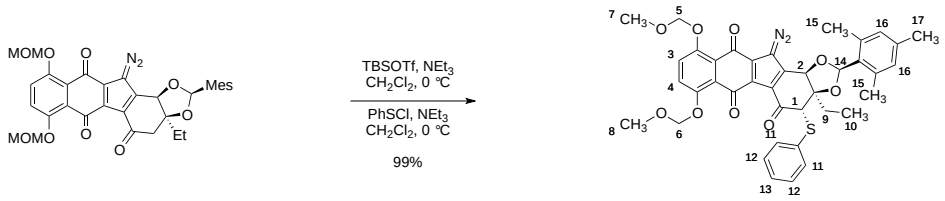
71 **77c**

*Synthesis of the α-Phenylselenyldiazofluorene **77c**:*

Triethylamine (23.1 μL, 167 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (19.0 μL, 83.3 μmol, 2.50 equiv) were added in sequence to a stirred solution of the *endo*-mesityl diazofluorene **71** [20.0 mg, 33.3 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (670 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the preceding step was dried by azeotropic distillation from benzene (500 μL). The dried residue was dissolved in dichloromethane (670 μL) and the resulting solution was cooled to 0 °C. Triethylamine (18.4 μL, 133 μmol, 4.00 equiv) and phenylselenium chloride (19.0 mg, 99.9 μmol, 3.00 equiv) were added in sequence to the cooled, stirred solution at 0 °C. The reaction mixture was stirred for 20 min at 0 °C. The yellow product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 10 mL), and the diluted solution was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 30% ethyl acetate–hexanes) to afford the α-phenylselenyldiazofluorene **77c** as a yellow solid (24.5 mg, 97%). The relative stereochemistry of the α-selenyldiazofluorene **77c** was assigned by analogy to that of the α-bromodiazofluorene **77a**.

R_f = 0.58 (60% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, 2H, J = 9.0 Hz, H_{11}), 7.53 (d, 1H, J = 9.5 Hz, H_3/H_4), 7.45 (d, 1H, J = 9.5 Hz, H_3/H_4), 7.31 (t, 1H, J = 7.0 Hz, H_{13}), 7.26–7.23 (m, 2H, H_{12}), 6.70 (s, 2H, H_{16}), 6.36 (s, 1H, H_{14}), 5.33–5.30 (m, 2H, H_5/H_6), 5.29 (app s, 2H, H_5/H_6), 4.92 (s, 1H, H_2), 4.23 (s, 1H, H_1), 3.58 (s, 3H, H_7/H_8), 3.56 (s, 3H, H_7/H_8), 2.61–2.56 (m, 1H, H_9), 2.39–2.35 (m, 1H, H_9), 2.18 (s, 3H, H_{17}), 2.12 (s, 6H, H_{15}), 0.96 (t, 3H, J = 7.0 Hz, H_{10}). ^{13}C NMR (125 MHz, $CDCl_3$): δ 184.7 (C), 179.1 (C), 177.7 (C), 153.1 (C), 153.0 (C), 144.5 (C), 139.2 (C), 138.0 (C), 136.1 (CH), 133.8 (C), 130.2 (2 × CH), 129.9 (C), 129.1 (2 × CH), 129.0 (2 × CH), 127.7 (C), 127.0 (CH), 126.7 (C), 125.7 (C), 124.3 (C), 123.4 (CH), 122.2 (C), 101.6 (CH), 96.7 (CH_2), 95.8 (CH_2), 88.4 (C), 77.4 (C, determined indirectly by HMBC), 75.5 (C), 72.0 (CH), 56.6 (CH_3), 56.5 (CH_3), 54.1 (CH), 25.8 (CH_2), 20.8 (CH_3), 20.3 (2 × CH_3), 6.5 (CH_3). IR (ATR-FTIR), cm $^{-1}$: 2969 (w), 2137 (s), 1684 (s), 1439 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{39}H_{36}N_2O_9Se$, 757.1664; found, 757.1645.



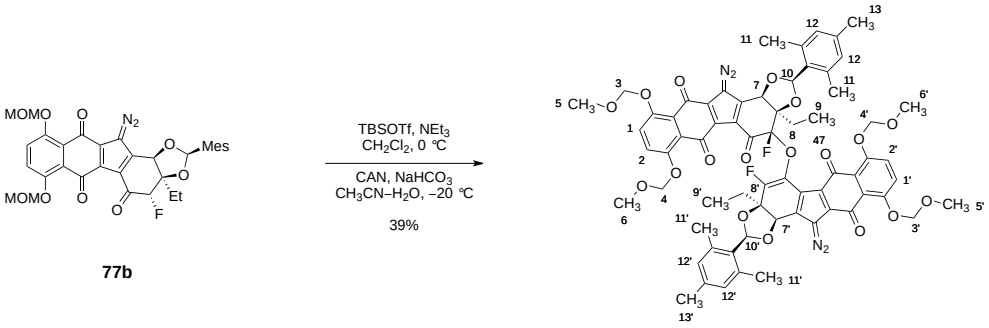
71 **77d**

*Synthesis of the α-Phenylsulfenyldiazofluorene **77d**:*

Triethylamine (12.0 μL, 83.5 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (10.0 μL, 41.8 μmol, 2.50 equiv) were added in sequence to a stirred solution of the diazofluorene **71** [10.0 mg, 16.7 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (330 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the preceding step was dried by azeotropic distillation from benzene (500 μL). The dried residue was dissolved in dichloromethane (330 μL) and the resulting solution was cooled to 0 °C. Triethylamine (9.2 μL, 66.8 μmol, 4.00 equiv) and phenylsulfenyl chloride (7.2 mg, 50.0 μmol, 3.00 equiv) were added in sequence to the cooled, stirred solution at 0 °C. The reaction mixture was stirred for 20 min at 0 °C. The yellow product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 10 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted dichloromethane (2 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 30% ethyl acetate–hexanes) to afford the α-phenylsulfenyldiazofluorene **77d** as an orange solid (11.8 mg, 99%). The relative stereochemistry of the α-sulfenyldiazofluorene **77d** was assigned by analogy to that of the α-bromodiazofluorene **77a**.

R_f = 0.56 (60% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.54 (m, 2H, H_{11}), 7.52 (d, 1H, J = 9.6 Hz, H_3/H_4), 7.44 (d, 1H, J = 9.6 Hz, H_3/H_4), 7.31–7.28 (m, 3H, H_{12}/H_{13}), 6.72 (s, 2H, H_{16}), 6.40 (s, 1H, H_{14}), 5.31 (app s, 2H, H_5/H_6), 5.28 (app s, 2H, H_5/H_6), 5.07 (s, 1H, H_2), 4.23 (s, 1H, H_1), 3.57 (s, 3H, H_7/H_8), 3.55 (s, 3H, H_7/H_8), 2.50–2.45 (m, 1H, H_9), 2.33–2.29 (m, 1H, H_9), 2.19 (s, 3H, H_{17}), 2.14 (s, 6H, H_{15}), 0.99 (t, 3H, J = 7.2 Hz, H_{10}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.59 (C), 179.13 (C), 177.7 (C), 153.1 (C), 153.0 (C), 143.9 (C), 139.2 (C), 138.0 (C), 133.9 (C), 133.4 (2 × CH), 132.9 (C), 130.2 (2 × CH), 130.0 (C), 129.2 (2 × CH), 128.5 (CH), 127.0 (CH), 126.5 (C), 125.6 (C), 124.0 (C), 123.5 (CH), 122.2 (C), 101.7 (CH), 96.6 (CH_2), 95.7 (CH_2), 87.9 (C), 77.2 (C), 75.8 (C), 72.4 (CH), 59.8 (CH), 56.6 (CH_3), 56.5 (CH_3), 25.2 (CH_2), 20.8 (CH_3), 20.3 (2 × CH_3), 6.6 (CH_3). IR (ATR-FTIR), cm^{-1}: 2970 (w), 2137 (s), 1690 (m), 1645 (m). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{39}H_{36}N_2O_9S$, 709.2214; found, 709.2187.



77b **79**

*Dimerization of the α-Fluorodiazofluorene **77b**:*

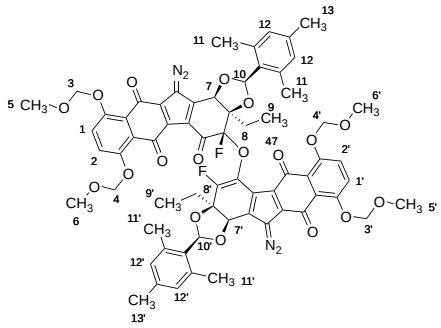
Triethylamine (34.8 μL, 252 μmol, 12.0 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (28.6 μL, 168 μmol, 8.00 equiv) were added in sequence to a stirred solution of the α-fluorodiazofluorene **77b** [13.0 mg, 21.0 μmol, 1 equiv; dried by azeotropic distillation with benzene (700 μL)] in dichloromethane (210 μL) at 0 °C. The resulting mixture was stirred for 1 h at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 8 mL) and dichloromethane (5 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the preceding step was dried by azeotropic distillation from benzene (500 μL). A solution of acetonitrile–water (95:5 v/v, 300 μL) and sodium bicarbonate (27.0 mg, 321 μmol, 15.3 equiv) were added. The resulting mixture was cooled over 5 min to –20 °C. A solution of ceric ammonium nitrate in acetonitrile (0.40 M, 120 μL, 48.0 μmol, 2.29 equiv) was then added rapidly via syringe to the vigorously stirred solution at –20 °C. The reaction mixture was stirred for 30 min at –20 °C. The product mixture was diluted sequentially with deionized water (5 mL) and ethyl acetate (5 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (1 × 5 mL) and dichloromethane (3 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by reverse-phase flash-column chromatography (eluting with 20% acetonitrile–water initially, grading to 100% acetonitrile, four steps) to afford the fluorinated dimer **79** as a red solid (5.0 mg, 39%).

Note: The dimeric product was partially characterized by ^{1}H, ^{13}C, ^{19}F NMR and HMBC, HMQC experiments. Due to C–F couplings, not all carbon resonances could be unequivocally identified.

R_f = 0.18 (50% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, 1H, J = 9.5 Hz, H_1/H_2), 7.39 (d, 1H, J = 9.5 Hz, H_1/H_2), 7.35 (app s, 2H, H_{1*}/H_{2*}), 6.72 (s, 2H, H_{12}), 6.70 (s, 2H, H_{12*}), 6.51 (s, 1H, H_{10}), 6.33 (s, 1H, H_{10*}), 5.35–5.33 (m, 2H, $H_3/H_4/H_7$), 5.30 (s, 1H, H_{7*}), 5.27 (d, 1H, J = 7.0 Hz, H_3/H_4), 5.22 (d, 1H, J = 7.0 Hz, H_3/H_4), 5.17–5.14 (m, 4H, $H_3/H_4/H_{3*}/H_{4*}$), 5.02 (d, 1H, J = 7.0 Hz, H_{3*}/H_{4*}), 3.70 (s, 3H, H_5/H_6), 3.60 (s, 3H, H_5/H_6), 3.52 (s, 3H, H_{5*}/H_{6*}), 3.46 (s, 3H, H_{5*}/H_{6*}), 3.17–3.15 (m, 1H, H_8), 3.05–3.00 (m, 1H, H_8), 2.46–2.39 (m, 1H, H_{8*}), 2.34–2.28 (m, 1H, H_{8*}), 2.19 (s, 3H, H_{13}), 2.17 (s, 3H, H_{13*}), 2.15 (s, 6H, H_{11}), 2.18 (s, 6H, H_{11*}), 1.41 (t, 3H, J = 8.5 Hz, H_9), 1.36 (t, 3H, J = 8.5 Hz, H_{9*}). ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.1 (C, J = 30.6 Hz), 177.8 (C), 177.4 (C), 176.7 (C), 175.9 (C), 154.3 (C), 153.5 (C), 152.8 (C), 150.9 (C), 149.9 (C), 144.8 (C), 133.2 (C), 133.0 (C), 131.3 (CH), 131.1 (CH), 132.2 (C, J = 239.6, 20.9 Hz), 130.3 (C), 130.2 (2 × CH), 130.1 (2 × CH), 128.5 (2 × C), 128.4 (2 × C), 128.0 (C), 126.9 (C), 127.5 (C), 126.8 (C), 126.5 (C), 126.4 (C), 126.3 (C), 126.1 (C),

125.1 (C), 124.2 (CH), 123.6 (CH), 122.2 (C, J = 102.4, 32.5 Hz), 119.3 (C), 114.1 (C), 109.9 (C), 101.8 (CH), 99.5 (CH_2), 98.3 (CH), 97.5 (CH_2), 96.0 (CH_2), 95.7 (CH_2), 87.6 (C), 84.4 (C), 80.1 (C, determined indirectly by HMBC), 77.6 (C, determined indirectly by HMBC), 73.9 (CH), 73.5 (CH), 57.1 (CH_3), 56.7 (CH_3), 56.5 (CH_3), 56.3 (CH_3), 29.7 (CH_2), 27.8 (CH_2), 20.9 (CH_3), 20.8 (CH_3), 20.2 (2 × CH_3), 19.8 (2 × CH_3), 8.1 (CH_3), 7.9 (CH_3). ^{19}F NMR (375 MHz, $CDCl_3$): δ –125.15 (F, J = 53.3 Hz), 131.55 (F, J = 53.3 Hz). IR (ATR-FTIR), cm^{-1}: 2926 (m), 2129 (s), 1719 (m), 1649 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{66}H_{60}F_2N_4O_{18}$, 1257.3763; found, 1257.3780.

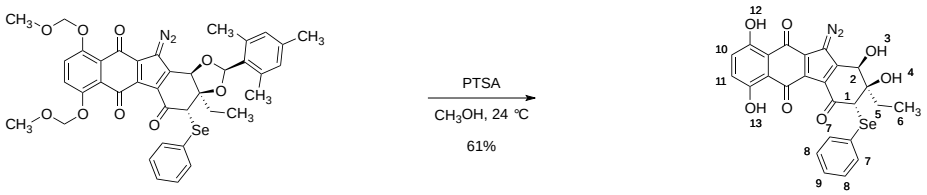


79

Table S1. Selected NMR Data and C–H couplings of the fluorinated dimer **79** ($CDCl_3$):

Position	δH	Multiplicity, Integration, *J*-Value	δC	HMBC $_{(H–C)}$
1	7.43	d, 1H, J = 9.5 Hz	128.4	C_2, C_{14}, C_{16}
2	7.39	d, 1H, J = 9.5 Hz	124.2	C_1, C_{15}, C_{17}
3	5.35–5.33 5.27	m, 1H d, 1H, J = 7.0 Hz	99.5	C_5, C_{14}
4	5.22 5.17–5.14	d, 1H, J = 7.0 Hz m, 1H	97.5	C_6, C_{15}
5	3.70	s, 3H	57.1	C_3
6	3.60	s, 3H	56.7	C_4
7	5.35–5.33	m, 1H	73.9	C_8, C_{22}, C_{23}, C_{24}, C_{26}
8	3.17–3.15 3.05–3.00	m, 1H m, 1H	29.7	C_9, C_{25}
9	1.41	t, 3H, J = 8.5 Hz	8.1	C_8, C_{25}
10	6.51	s, 1H	101.8	C_{28}, C_{29}, C_7, C_{25}
11	2.15	s, 6H	20.2	C_{12}, C_{28}, C_{29}
12	6.72	s, 2H	130.2	C_{11}/C_{13}, C_{12}, C_{29}/C_{30}
13	2.19	s, 3H	20.9	C_{30}, C_{12}
14	–	–	154.3	
15	–	–	153.5	
16	–	–		
17	–	–		
18	–	–	177.8	
19	–	–	177.4	
20	–	–		
21	–	–		

22	–	–		
23	–	–	80.0	
24	–	–		
25	–	–	87.6	
26	–	–		
27	–	–	180.1	
28	–	–		
29	–	–		
30	–	–		
1'	7.35	app s, 2H	130.3	$C_{2'}$, $C_{14'}$, $C_{16'}$, $C_{18'}$
2'	7.35	app s, 2H	123.6	$C_{1'}$, $C_{15'}$, $C_{17'}$, $C_{19'}$
3'	5.17–5.14	m, 2H	96.0	$C_{5'}$, $C_{14'}$
4'	5.17–5.14 5.02	m, 1H d, 1H, J = 7.0 Hz	95.7	$C_{6'}$, $C_{15'}$
5'	3.52	s, 3H	56.5	C_3
6'	3.46	s, 3H	56.3	C_4
7'	5.30	s, 1H	73.5	$C_{8'}$, $C_{22'}$, $C_{23'}$, $C_{24'}$, $C_{26'}$
8'	2.46–2.39 2.34–2.28	m, 1H m, 1H	27.8	$C_{9'}$, $C_{25'}$
9'	1.36	t, 3H, J = 8.5 Hz	7.9	$C_{8'}$, $C_{25'}$
10'	6.33	s, 1H	98.3	$C_{28'}$, $C_{29'}$, $C_{7'}$, $C_{25'}$
11'	2.18	s, 6H	20.2	$C_{12'}$, $C_{28'}$, $C_{29'}$
12'	6.70	s, 2H	130.1	$C_{11'}/C_{13'}$, $C_{12'}$, $C_{29'}/C_{30'}$
13'	2.17	s, 3H	20.9	$C_{30'}$, $C_{12'}$
14'	–	–	152.8	
15'	–	–	150.9	
16'	–	–		
17'	–	–		
18'	–	–	176.7	
19'	–	–	175.9	
20'	–	–		
21'	–	–		
22'	–	–		
23'	–	–	77.6	
24'	–	–		
25'	–	–	84.4	
26'	–	–		
27'	–	–		
28'	–	–		
29'	–	–		
30'	–	–		

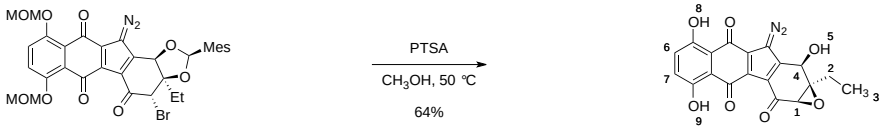


77c **80**

*Deprotection of the α-Phenylselenyl Diazofluorene **77c**:*

para-Toluenesulfonic acid (1.5 mg, 8.11 μmol, 0.25 equiv) was added to a stirred solution of the α-phenylselenyldiazofluorene **77c** [24.5 mg, 32.4 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in methanol (1.6 mL) at 24 °C. The resulting mixture was stirred for 1 h at 24 °C. The product mixture was diluted sequentially with ethyl acetate (5 mL) and 0.1 M aqueous sodium phosphate buffer solution (pH 7, 10 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (2 × 7 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 100% dichloromethane initially, grading to 5% methanol–dichloromethane, one step) to afford the α-phenylselenyldiazofluorene **80** as a purple solid (10.6 mg, 61%).

R_f = 0.58 (70% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, DMF-d_7): δ 13.36 (s, 1H, H_{12}/H_{13}), 12.54 (s, 1H, H_{12}/H_{13}), 7.70–7.67 (m, 2H, H_7), 7.40–7.37 (m, 3H, H_8/H_9), 7.36 (d, 1H, J = 9.0 Hz, H_{10}/H_{11}), 7.32 (d, 1H, J = 9.0 Hz, H_{10}/H_{11}), 6.53 (d, 1H, J = 8.5 Hz, H_3), 5.37 (s, 1H, H_4), 5.19 (d, 1H, J = 8.0 Hz, H_2), 3.92 (s, 1H, H_1), 2.23–2.17 (m, 1H, H_5), 2.12–2.07 (m, 1H, H_5), 0.96 (t, 3H, J = 7.5 Hz, H_6). ^{13}C NMR (125 MHz, DMF-d_7): δ 186.9 (C), 183.7 (C), 183.4 (C), 159.1 (C), 158.5 (C), 152.6 (C), 135.2 (2 × CH), 132.3 (C), 131.0 (CH), 130.5 (2 × CH), 129.6 (2 × C), 129.4 (CH), 129.2 (CH), 124.1 (C), 114.4 (C), 113.6 (C), 81.3 (C), 80.8 (C), 72.4 (CH), 57.0 (CH), 28.9 (CH_2), 7.1 (CH_3). IR (ATR-FTIR), cm^{-1}: 2918 (m), 2169 (m), 1633 (s), 1446 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{25}H_{19}N_2O_7Se$, 539.0357; found, 539.0355.

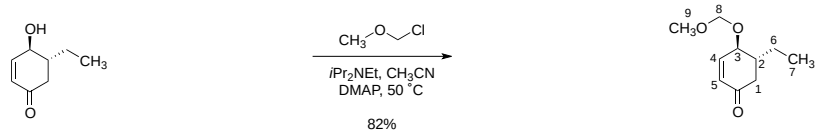


77a **81**

*Deprotection of the α-Bromodiazofluorene **77a**:*

A solution of *para*-toluenesulfonic acid in methanol (10.0 mM, 63.0 μL, 3.30 μmol, 0.20 equiv) was added to a stirred solution of the α-bromodiazofluorene **77a** [11.2 mg, 16.5 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in methanol (1.7 mL) at 24 °C. The resulting mixture was placed in an oil bath that had been preheated to 50 °C, and was stirred for 2 h at 50 °C. The product mixture was cooled over 10 min to 24 °C, and the cooled solution was diluted sequentially with ethyl acetate (5 mL) and 0.1 M aqueous sodium phosphate buffer solution (pH 7, 10 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (2 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by reverse-phase flash-column chromatography (eluting with 100% water initially, grading to 40% acetonitrile–water, two steps) to afford the epoxide **81** as a pink solid (4.0 mg, 64%).

R_f = 0.44 (5% methanol–dichloromethane; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.13 (s, 1H, H_8/H_9), 12.45 (s, 1H, H_8/H_9), 7.26–7.25 (m, 1H, H_6/H_7), 7.19 (d, 1H, J = 9.0 Hz, H_6/H_7), 5.25 (d, 1H, J = 9.2 Hz, H_4), 3.63 (s, 1H, H_1), 2.62 (d, 1H, J = 9.2 Hz, H_5), 2.32–2.27 (m, 1H, H_2), 1.92–1.88 (m, 1H, H_2), 1.08 (t, 1H, J = 7.5 Hz, H_3). ^{13}C NMR (125 MHz, DMF-d_7): δ 188.1 (C), 183.9 (C), 183.4 (C), 159.1 (C), 158.6 (C), 150.9 (C), 132.3 (C), 131.1 (C), 129.5 (CH), 128.6 (CH), 121.3 (C), 114.3 (C), 113.6 (C), 81.2 (C), 67.0 (CH), 65.3 (C), 61.0 (CH), 24.8 (CH_2), 9.2 (CH_3). IR (ATR-FTIR), cm^{-1}: 2925 (m), 2115 (s), 1634 (s), 1445 (m). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{19}H_{13}N_2O_7$, 381.0723; found, 381.0720.



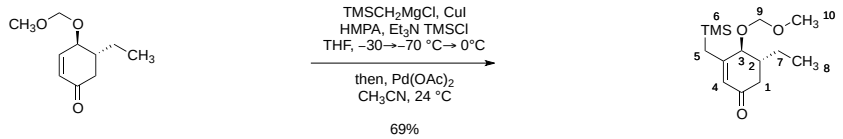
82 **S63**

The enone **82** was prepared according to the procedure of Bräse and co-workers.[50]

*Synthesis of the Methoxymethyl Ether **S63**:*

4-(Dimethylamino)pyridine (133 mg, 1.09 mmol, 0.30 equiv), *N*,*N*-diisopropylethylamine (2.52 mL, 14.5 mmol, 4.05 equiv), and chloromethyl methyl ether (540 µL, 7.24 mmol, 2.03 equiv) were added in sequence to a stirred solution of the enone **82** (500 mg, 3.57 mmol, 1 equiv) in acetonitrile (7.2 mL) at 24 °C. Upon completion of the addition, the reaction vessel was placed in an oil bath that had been preheated to 50 °C. The reaction mixture was stirred and heated for 16 h at 50 °C. The product mixture was cooled over 15 min to 24 °C. The cooled solution was diluted with saturated aqueous sodium bicarbonate solution (30 mL), and the diluted solution was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% ethyl acetate–hexanes) to afford the methoxymethyl ether **S63** as a clear, colorless oil (540 mg, 82%).

R_f = 0.65 (30% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (dd, 1H, J = 10.4, 2.4 Hz, H_4), 5.96 (ddd, 1H, J = 10.4, 2.0, 1.2 Hz, H_5), 4.80 (d, 1H, J = 6.8 Hz, H_8), 4.72 (d, 1H, J = 7.2 Hz, H_8), 4.11 (m, 1H, H_3), 3.43 (s, 3H, H_9), 2.63 (d, 1H, J = 13.2 Hz, H_1), 2.12–2.03 (m, 2H, H_1/H_2), 1.81–1.73 (m, 1H, H_6), 1.37–1.29 (m, 1H, H_6), 0.92 (t, 3H, J = 7.6 Hz, H_7). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2 (C), 150.9 (CH), 129.5 (CH), 96.8 (CH_2), 76.5 (CH), 56.1 (CH_3), 43.4 (CH), 40.8 (CH_2), 24.4 (CH_2), 10.4 (CH_3). IR (ATR-FTIR), cm^{-1}: 2962 (w), 2881 (w), 1684 (s), 1147 (m), 1033 (s). HRMS-ESI (m/z): $[M + Na]^+$ calculated for $C_{10}H_{16}O_3Na$, 207.0997; found, 207.1002.



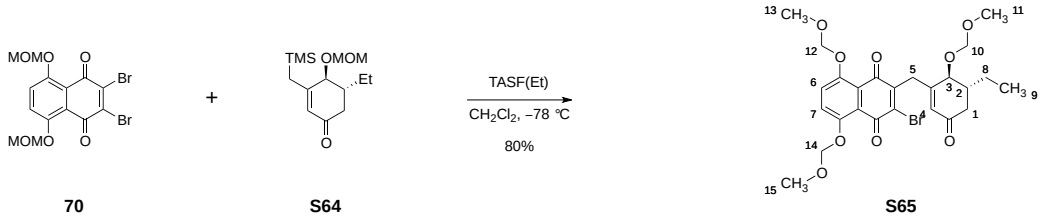
S63 **S64**

*Synthesis of the β-Trimethylsilylmethyl-α,β-unsaturated Ketone **S64**:*

Cuprous iodide (56.4 mg, 296 μmol, 0.10 equiv) was added to a stirred solution of trimethylsilylmethylmagnesium chloride in ether (1.00 M, 8.90 mL, 8.90 mmol, 3.00 equiv) at 24 °C. The resulting solution was cooled to −30 °C, to afford a cloudy suspension. A solution of the methoxymethyl ether **S63** [540 mg, 2.97 mmol, 1 equiv; dried by azeotropic distillation with benzene (2.0 mL)] in tetrahydrofuran (5.0 mL) was then added dropwise via cannula. The flask containing the methoxymethyl ether **S63** was rinsed with tetrahydrofuran (2 × 1.2 mL) and the rinses were added to the reaction vessel via cannula. The reaction mixture was cooled to −50 °C and then was stirred at this temperature for 30 min. The mixture was then cooled to −60 °C. Hexamethylphosphoramide (1.55 mL, 8.91 mmol, 3.00 equiv), triethylamine (1.24 mL, 8.90 mmol, 3.00 equiv), and trimethylsilyl chloride (740 μL, 5.83 mmol, 1.96 equiv) were added in sequence to the cooled solution. The resulting mixture was further cooled to −78 °C, and was stirred at this temperature for 1 h. The mixture was warmed over 10 min to 24 °C, and the warmed solution was stirred for 10 min at 24 °C. The product mixture was diluted with ether (50 mL). The diluted solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (40 mL). The layers that formed were separated, and the aqueous layer was extracted with ether (2 × 50 mL). The organic layers were combined and the combined organic layers were washed sequentially with saturated aqueous sodium bicarbonate solution (3 × 50 mL) and saturated aqueous sodium chloride solution (50 mL). The washed solution was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the previous step was dissolved in acetonitrile (14 mL) at 24 °C. Palladium acetate (774 mg, 3.45 mmol, 1.20 equiv) was added, and the resulting black mixture was stirred for 12 h at 24 °C. The product mixture was diluted with ether (50 mL). The diluted solution was filtered through a pad of celite (3 × 3 cm). The celite pad was washed with ether (3 × 25 mL) and the filtrates were combined. The combined filtrates were concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 20% ether–hexanes) to afford the β-trimethylsilylmethyl-α, β-unsaturated ketone **S64** as a clear, colorless oil (556 mg, 69%).

R_f = 0.32 (20% ether–hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.73 (s, 1H, H_4), 4.78 (d, 1H, J = 7.0 Hz, H_9), 4.70 (d, 1H, J = 7.0 Hz, H_9), 3.84 (d, 1H, J = 4.0 Hz, H_3), 3.44 (s, 3H, H_{10}), 2.70 (dd, 1H, J = 16.5, 4.5 Hz, H_1), 2.20 (dd, 1H, J = 16.5, 5.0 Hz, H_1), 2.16–2.10 (m, 1H, H_2), 1.90 (d, 1H, J = 12.0 Hz, H_5), 1.84 (d, 1H, J = 12.0 Hz, H_5), 1.48–1.42 (m, 1H, H_7), 1.26–1.21 (m, 1H, H_7), 0.93 (t, 3H, J = 7.5 Hz, H_8), 0.07 (s, 9H, H_6). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.2 (C), 161.6 (C), 125.7 (CH), 97.0 (CH_2), 78.6 (CH), 56.4 (CH_3), 40.9 (CH), 37.7 (CH_2), 27.3 (CH_2), 24.8 (CH_2), 12.0 (CH_3), -0.2 (3 × CH_3). IR (ATR-FTIR), cm^{-1}: 2958 (w), 1662 (s), 1149 (m), 1024 (s), 839 (s). HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{14}H_{27}O_3Si$, 271.1729; found 271.1733.

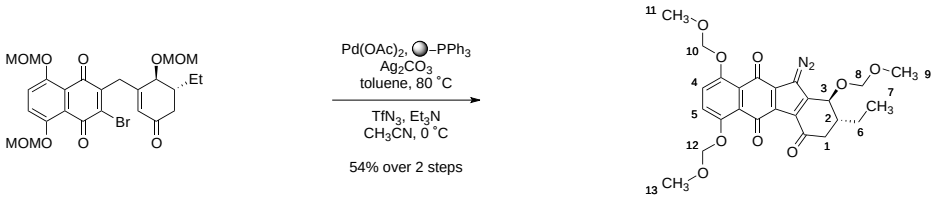


70 **S64** **S65**

*Fluoride-mediated Coupling of the β-Trimethylsilylmethyl-α,β-unsaturated Ketone **S64** and 2,3-Dibromo-5,8-(dimethoxymethyloxy)naphthoquinone (**70**):*

A mixture of 2,3-dibromo-5,8-(dimethoxymethyloxy)naphthoquinone (**70**, 2.43 g, 5.57 mmol, 4.01 equiv) and the β-trimethylsilylmethyl-α,β-unsaturated ketone **S64** (376 mg, 1.39 mmol, 1 equiv) was prepared in a 500 mL round-bottomed flask. The mixture was dried by azeotropic distillation with benzene (3 × 8.0 mL). The dried mixture was dissolved in dichloromethane (278 mL) and was stirred at 24 °C until homogenous (ca. 10 min). The resulting red, homogenous mixture was cooled to –78 °C. A solution of TASF(Et) (518 mg, 1.53 mmol, 1.10 equiv) in dichloromethane (5.0 mL) was added dropwise via cannula to the cold, stirred solution. After 15 min, a second portion of TASF(Et) (235 mg, 690 μmol, 0.50 equiv) in dichloromethane (3.0 mL) was added dropwise via cannula. The resulting black mixture was stirred for 15 min at –78 °C. The cold product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 200 mL). The diluted solution was warmed over 30 min to 24 °C. The warmed biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was diluted with dichloromethane (30 mL) and the diluted solution was filtered over filter paper to partially remove unreacted 2,3-dibromo-5,8-(dimethoxymethyloxy)naphthoquinone (**70**). The filtrate was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–dichloromethane initially, grading to 30% ethyl acetate–dichloromethane, one step) to afford the δ-ketoquinone **S65** as an orange solid (615 mg, 80%).

R_f = 0.52 (20% acetone–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.47 (m, 2H, H_6/H_7), 5.61 (s, 1H, H_4), 5.28 (app s, 2H, H_{12}/H_{14}), 5.24 (app s, 2H, H_{12}/H_{14}), 4.81 (d, 1H, J = 6.8 Hz, H_{10}), 4.78 (d, 1H, J = 6.8 Hz, H_{10}), 4.12 (d, 1H, J = 4.4 Hz, H_3), 3.97 (dd, 1H, J = 16.4, 1.6 Hz, H_5), 3.64 (d, 1H, J = 16.0 Hz, H_5), 3.54 (s, 3H, H_{11}/H_{13}/H_{15}), 3.49 (s, 3H, H_{11}/H_{13}/H_{15}), 3.47 (s, 3H, H_{11}/H_{13}/H_{15}), 2.74 (dd, 1H, J = 18.4, 6.4 Hz, H_1), 2.24–2.15 (m, 2H, H_1/H_2), 1.56–1.50 (m, 1H, H_8), 1.31–1.24 (m, 1H, H_8), 0.93 (t, 3H, J = 7.6 Hz, H_9). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6 (C), 180.3 (C), 176.3 (C), 156.5 (C), 152.8 (C), 152.7 (C), 147.1 (2 × C), 140.9 (2 × C), 126.7 (CH), 125.2 (CH), 125.0 (CH), 97.4 (CH_2), 96.0 (CH_2), 95.9 (CH_2), 78.5 (CH), 56.9 (CH_3), 56.8 (CH_3), 56.6 (CH_3), 41.3 (CH), 38.5 (CH_2), 36.4 (CH_2), 24.5 (CH_2), 11.7 (CH_3). IR (ATR-FTIR), cm^{-1}: 2960 (w), 1668 (s), 1150 (s), 997 (s). HRMS-ESI (m/z): $[M + Na]^+$ calculated for $C_{25}H_{29}Br^{79/81}O_9Na$, 575.0893/577.0873; found, 575.0899/577.0896.



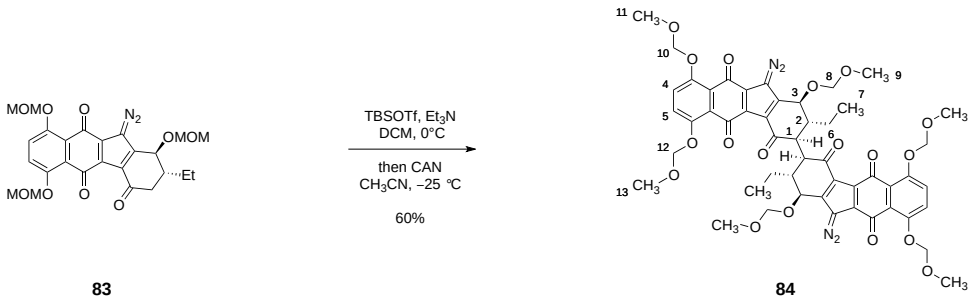
S65 **83**

*Synthesis of the Protected 2-Deoxydiazofluorene **83**:*

A mixture of palladium acetate (203 mg, 906 μmol, 1.00 equiv), polymer-supported triphenylphosphine (755 mg, 2.27 mmol, 2.50 equiv), and silver carbonate (499 mg, 1.81 mmol, 2.00 equiv) were added to a stirred solution of the δ-ketoquinone **S65** [500 mg, 906 μmol, 1 equiv; dried by azeotropic distillation with benzene (3.0 mL)] in toluene (45 mL) at 24 °C. The resulting mixture was placed in an oil bath that had been preheated to 80 °C. The reaction mixture was stirred and heated for 2 h at 80 °C. The product solution was cooled over 10 min to 24 °C and the cooled solution was filtered over a celite pad (4 × 5 cm). The celite pad was washed with ethyl acetate (4 × 30 mL) and dichloromethane (2 × 30 mL). The filtrates were combined and the combined filtrates were concentrated.

The residue obtained in the preceding step was dried by azeotropic distillation with benzene (3.0 mL). The dried residue was dissolved in acetonitrile (18 mL), and the resulting solution was cooled to 0 °C. *N*,*N*-diisopropylethylamine (369 μL, 2.12 mmol, 5.00 equiv), and a solution of trifluoromethanesulfonyl azide in hexanes (246 mM, 4.31 mL, 1.06 mmol, 2.50 equiv) were added in sequence, and the resulting mixture was stirred for 0.5 h at 0 °C. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (30 mL). The diluted solution was poured into a separatory funnel that had been charged with ethyl acetate (200 mL). The layers that formed were separated, and the organic layer was washed sequentially with 1 N aqueous sulfuric acid solution (2 × 75 mL), saturated aqueous sodium bicarbonate solution (3 × 100 mL), and saturated aqueous sodium chloride solution (1 × 100 mL). The washed organic layer was dried over sodium sulfate and the dried solution was filtered. The residue obtained was purified by flash-column chromatography (eluting with 80% ethyl acetate–hexanes) to afford the protected 2-deoxydiazofluorene **83** as a dark yellow oil (98.0 mg, 54% over 2 steps).

R_f = 0.65 (80% ethyl acetate–hexanes; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, 1H, J = 9.2 Hz, H_4/H_5), 7.40 (d, 1H, J = 9.6 Hz, H_4/H_5), 5.30 (app s, 2H, H_{10}/H_{12}), 5.23 (app s, 2H, H_{10}/H_{12}), 4.78 (app s, 2H, H_8), 4.66 (d, 1H, J = 6.4 Hz, H_3), 3.54 (s, 3H, H_{11}/H_{13}), 3.53 (s, 3H, H_{11}/H_{13}), 3.40 (s, 3H, H_9), 2.90 (dd, 1H, J = 16.0, 4.0 Hz, H_1), 2.40–2.30 (m, 2H, H_1/H_2), 1.67–1.57 (m, 1H, H_6), 1.38–1.29 (m, 1H, H_6), 0.96 (t, 3H, J = 7.2 Hz, H_7). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7 (C), 179.4 (C), 178.4 (C), 153.1 (C), 152.9 (C), 147.9 (C), 132.9 (C), 130.2 (C), 127.3 (CH), 124.8 (C), 123.8 (C), 123.4 (CH), 122.1 (C), 96.9 (CH_2), 96.9 (CH_2), 95.8 (CH_2), 77.3 (C), 74.2 (CH), 56.6 (CH_3), 56.6 (CH_3), 56.0 (CH_3), 44.1 (CH), 41.2 (CH_2), 24.2 (CH_2), 11.2 (CH)$_3$. IR (ATR-FTIR), cm^{-1}: 2931 (m), 2147 (s), 1681 (s), 1441 (s), 1151 (s). HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{25}H_{27}N_2O_9$, 499.1717; found, 499.1720.



83 **84**

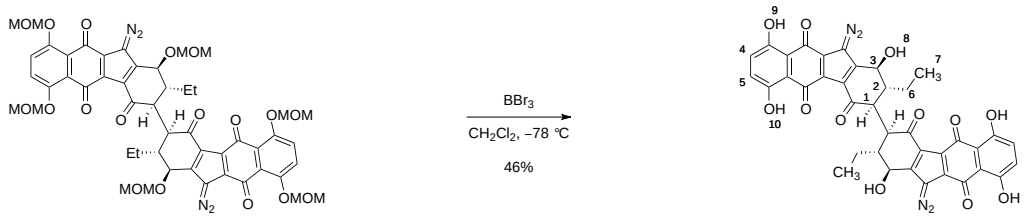
*Dimerization of the Protected 2-Deoxydiazofluorene **83**:*

Triethylamine (69.7 μL, 500 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (57.5 μL, 250 μmol, 2.50 equiv) were added in sequence to a stirred solution of the diazofluorene **83** [50.0 mg, 100 μmol, 1 equiv; dried by azeotropic distillation with benzene (2 × 5.0 mL)] in dichloromethane (5.0 mL) at 0 °C. The resulting mixture was stirred for 20 min at 0 °C. The red product mixture was diluted with methanol (300 μL) and the diluted solution was transferred to a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (30 mL) and dichloromethane (50 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the preceding step was dried by azeotropic distillation with benzene (2 × 3.0 mL). The dried residue was dissolved in acetonitrile (2.0 mL). Sodium bicarbonate (168 mg, 2.00 mmol, 20.0 equiv) was added, and the resulting mixture was cooled to –25 °C. A solution of cerium ammonium nitrate in acetonitrile (0.40 M, 500 μL, 200 μmol, 2.00 equiv) was then added, and the reaction mixture was stirred for 15 min at –25 °C. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (5 mL). The diluted solution was transferred to a separatory funnel that had been charged with dichloromethane (100 mL) and saturated aqueous sodium bicarbonate solution (30 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined, and the combined layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 3% methanol–dichloromethane initially, grading to 7% methanol–dichloromethane, one step) to afford the 2,2′-dideoxydimeric diazofluorene **84** as a dark yellow oil (30.0 mg, 60% over 2 steps).

*Note: ^{1}H and ^{13}C NMR data are normalized to the monomeric structure. The relative stereochemistry of the dimeric 2-deoxydiazofluorene **84** was elucidated by an observed w-coupling between $H_1/H_{1'}$–$H_3/H_{3'}$ by COSY.*

R_f = 0.42 (5% methanol–dichloromethane; UV, CAM). ^{1}H NMR [500 MHz, 30% $CDCl_3$–MeOD (v/v)]: δ 7.57 (m, 2H, H_4/H_5), 5.44 (d, 1H, J = 7.0 Hz, H_{10}/H_{12}), 5.39 (d, 1H, J = 7.0 Hz, H_{10}/H_{12}), 5.30 (d, 1H, J = 7.5 Hz, H_{10}/H_{12}), 5.29 (d, 1H, J = 7.0 Hz, H_{10}/H_{12}), 5.10 (d, 1H, J = 7.0 Hz, H_8), 4.98 (d, 1H, J = 2.0 Hz, H_3), 4.91 (d, 1H, J = 7.0 Hz, H_8), 3.63 (s, 3H, H_{11}/H_{13}), 3.58 (s, 3H, H_{11}/H_{13}), 3.54 (s, 3H, H_9), 3.40 (s, 1H, H_1), 2.97 (t, 1H, J = 6.5 Hz, H_2), 1.59–1.52 (m, 1H, H_6), 1.41–1.32 (m, 1H, H_6), 1.10 (t, 3H, J = 7.5 Hz, H_7). ^{13}C NMR [125 MHz, 30% $CDCl_3$–MeOD (v/v)]: δ 196.3 (C), 180.2 (C), 179.9 (C), 154.0 (C), 153.5 (C), 145.2 (C), 134.7 (C), 130.6 (C), 127.9 (CH), 126.4 (C), 124.6 (C), 124.1 (CH), 122.5 (C), 97.5 (CH_2), 97.2 (CH_2), 96.3 (CH_2), 81.7 (C), 72.4 (CH), 57.0 (2 × CH_3), 56.4 (CH_3), 54.9 (CH), 44.2 (CH), 25.8 (CH_2), 12.3 $(CH)_3$. IR (ATR-FTIR), cm^{-1}: 2927 (m), 2161 (s), 1677 (s), 1448 (s). HRMS-ESI (m/z): $[M + Na]^+$ calculated for $C_{50}H_{50}N_4O_{19}Na$, 1017.3018; found, 1017.3023.



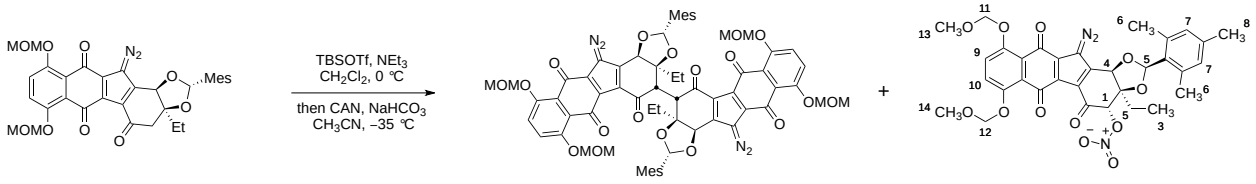
84 **85**

*Deprotection of the 2,2′-Dideoxydimeric Diazofluorene **84**:*

A solution of boron tribromide in dichloromethane (1.00 M, 60.3 µL, 60.3 µmol, 10.0 equiv) was added to a stirred solution of the 2,2′-dideoxydimeric diazofluorene **84** (6.0 mg, 6.03 µmol, 1 equiv) in dichloromethane (600 µL) at −78 °C. The resulting mixture was stirred for 1.5 h at −78 °C. The product mixture was diluted with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 12 mL, added via syringe pump at a rate of 1 mL/min). Upon completion of addition, the cooling bath was removed and the biphasic mixture was allowed to warm to 21 °C over 30 min. The reaction vessel was then placed in a water bath at 21 °C and was stirred for 15 min, until the aqueous phase melted completely. The resulting biphasic solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (4 × 8 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was triturated with dichloromethane (3 × 1 mL) to afford the 2,2′-dideoxydiazofluorene **85** as a purple solid (2.0 mg, 46%).

Note: ^{1}H and ^{13}C NMR data are normalized to the monomeric structure. Line broadening was observed in tetrahydrofuran-d_8, acetonitrile-d_4, N,N-dimethylformamide-d_7, dimethylsulfoxide-d_6, and methanol-d_4. The compound was sparingly soluble in chloroform-d and 30% methanol-d_4–chloroform-d. Complete carbon-13 NMR data could not be obtained in any of these solvents.

^{1}H NMR (500 MHz, $CDCl_3$): δ 12.87 (s, 1H, H_9/H_{10}), 12.29 (s, 1H, H_9/H_{10}), 7.01 (d, 1H, J = 9.5 Hz, H_4/H_5), 6.94 (d, 1H, J = 9.5 Hz, H_4/H_5), 5.50 (d, 1H, J = 11.5 Hz, H_8), 4.78 (d, 1H, J = 11.5 Hz, H_3), 3.07 (s, 1H, H_1), 2.54 (t, 1H, J = 7.0 Hz, H_2), 1.49–1.44 (m, 2H, H_6), 1.07 (t, 3H, J = 7.5 Hz, H_7). ^{13}C NMR (125 MHz, $CDCl_3$, determined indirectly by HMQC): 130.5 (CH), 128.5 (CH), 65.8 (CH), 58.2 (CH), 51.8 (CH), 27.1 (CH_2), 11.9 (CH_3). IR (ATR-FTIR), cm^{-1}: 3450 (m), 2923 (m), 2153 (m), 1635 (s), 1442 (s). HRMS-ESI (*m/z*): $[M + Na]^+$ calculated for $C_{38}H_{26}N_4O_{12}Na$, 753.1445; found, 753.1447.



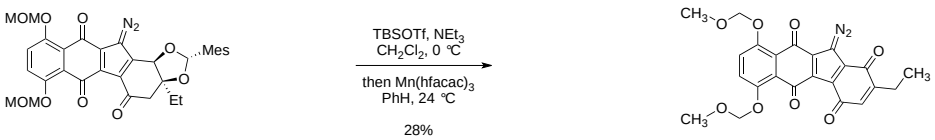
Dimerization of the exo-*Mesityl Diazofluorene **87** (Entry 1, Table 5):*

Triethylamine (11.5 μL, 83.0 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (9.50 μL, 41.7 μmol, 2.50 equiv) were added in sequence to a stirred solution of the *exo*-mesityl diazofluorene **87** [10.0 mg, 16.7 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (330 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the previous step was dried by azeotropic distillation with benzene (500 μL). The dried residue was dissolved in acetonitrile (330 μL) at 24 °C. Sodium bicarbonate (28.0 mg, 334 μmol, 20.0 equiv) was added, and the resulting mixture was cooled to −35 °C. A solution of ceric ammonium nitrate in acetonitrile (0.40 M, 84.0 μL, 33.4 μmol, 2.00 equiv) was added rapidly via syringe to the vigorously stirred solution at −35 °C. The reaction mixture was stirred for 30 min at −35 °C. The product mixture was diluted sequentially with water (4 mL) and ethyl acetate (5 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by preparatory thin layer chromatography (pre-developed with 30% methanol–ethyl acetate, eluting with 60% ethyl acetate–hexanes) to afford separately the (10*S*, 10'*S*)-dimeric diastereomer **90** (orange solid, 1.5 mg, 24%), the α-nitrated diazofluorene **93** (yellow solid, 1.5 mg, 14%), and the recovered diazofluorene **87** (yellow solid, 0.4 mg, 3%).

^{1}H NMR spectroscopic data for the (10*S*, 10'*S*)-dimeric diazofluorene **90** obtained in this way was identical to those previously reported.[35]

α-Nitrated diazofluorene **93**: R_f = 0.89 (40% ethyl acetate–dichloromethane; UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, 1H, J = 9.2 Hz, H_9/H_{10}), 7.47 (d, 1H, J = 9.2 Hz, H_9/H_{10}), 6.87 (s, 2H, H_7), 6.61 (s, 1H, H_5), 6.12 (s, 1H, H_4), 5.33 (s, 2H, H_{11}/H_{12}), 5.29–5.26 (m, 3H, H_1/H_{11}/H_{12}), 3.56 (s, 3H, H_{13}/H_{14}), 3.55 (s, 3H, H_{13}/H_{14}), 2.44 (s, 6H, H_6), 2.29–2.23 (m, 1H, H_2), 2.28 (s, 3H, H_8), 2.20–1.99 (m, 1H, H_2), 0.94 (t, 3H, J = 7.6 Hz, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 181.9 (C), 179.1 (C), 177.5 (C), 153.3 (C), 153.2 (C), 142.0 (C), 139.9 (C), 138.1 (2 × C), 134.5 (C), 130.4 (2 × CH), 129.2 (C), 127.3 (CH), 126.2 (C), 125.1 (C), 123.7 (CH), 122.7 (C), 121.8 (C), 101.9 (CH), 96.5 (CH_2), 95.7 (CH_2), 86.4 (C), 80.6 (CH), 77.2 (C), 73.8 (CH), 56.6 (2 × CH_3), 31.9 (CH_2), 29.6 (2 × CH_3), 20.3 (CH_3), 8.6 (CH_3). IR (ATR-FTIR), cm^{-1}: 2924 (s), 2141 (m), 1716 (s), 1653 (s). HRMS-ESI (m/z): $[M + H]^+$ calculated for $C_{33}H_{32}N_3O_{12}$, 662.1981; found, 662.1949.



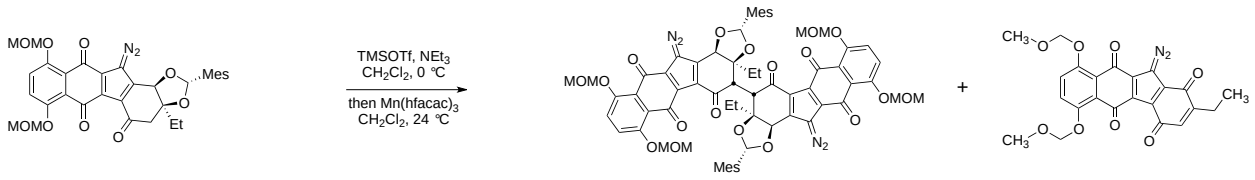
87 **74**

*Dimerization of the exo-Mesityl Diazofluorene **87** (Entry 2, Table 5):*

Triethylamine (11.5 μL, 83.0 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (9.5 μL, 41.7 μmol, 2.50 equiv) were added in sequence to a stirred solution of the *exo*-mesityl diazofluorene **87** [10.0 mg, 16.7 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (330 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the previous step was dried by azeotropic distillation with benzene (2 × 500 μL). The dried residue was dissolved in benzene (500 μL) at 24 °C. A solution of manganese tris(hexafluoroacetylacetonate) (**94**) in benzene (80.0 mM, 250 μL, 20.0 μmol, 1.20 equiv) was added rapidly via syringe to the vigorously stirred solution at 24 °C. The reaction mixture was stirred for 20 min at 24 °C. The product solution was transferred to a separatory funnel that had been charged with 50% ethyl acetate–hexanes (20 mL) and 1 N aqueous sodium hydroxide solution (10 mL). The separatory funnel was sealed and the sealed funnel was vigorously shaken. The layers that formed were separated and the organic layer was washed sequentially with 1 N aqueous sodium hydroxide solution (2 × 10 mL), saturated aqueous sodium bicarbonate solution (10 mL), distilled water (10 mL), and saturated aqueous sodium chloride solution (10 mL). The organic layer was dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated and the residue obtained was purified by preparatory thin layer chromatography (pre-developed with 30% methanol–ethyl acetate, eluting with 60% ethyl acetate–hexanes) to afford separately the *exo*-mesityl diazofluorene **87** (yellow solid, 0.5 mg, 5%) and the dehydrated monomer **74** (yellow solid, 2.1 mg. 28%).

^{1}H NMR spectroscopic data for the dehydrated monomer **74** obtained in this way was identical to those previously reported (vide supra).



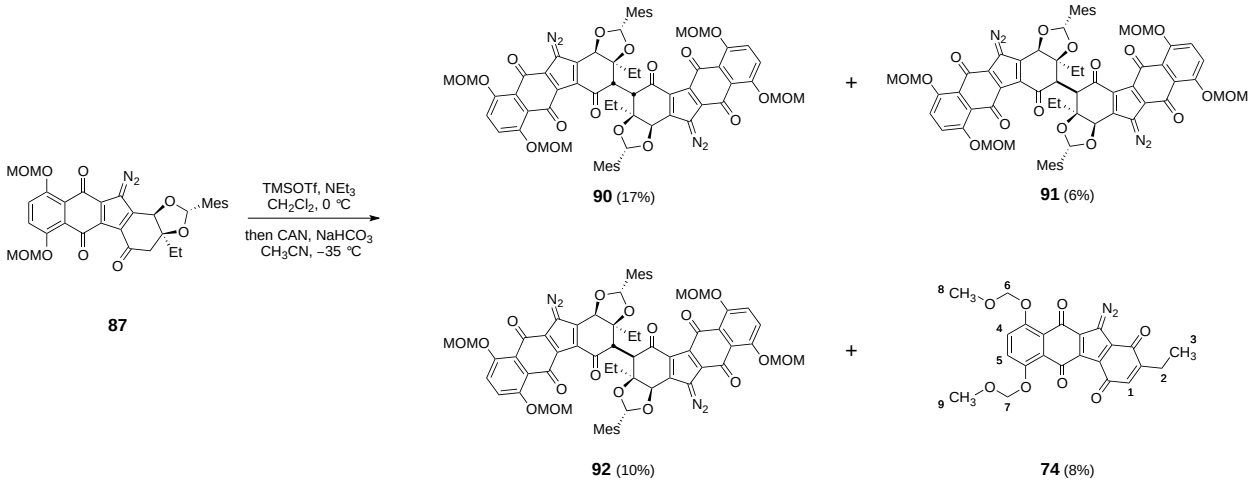
87 **90** (26%) **74** (15%)

Dimerization of the exo-*Mesityl Diazofluorene **87** (Entry 3, Table 5):*

Triethylamine (23.0 μL, 167 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (19.0 μL, 83.4 μmol, 2.50 equiv) were added in sequence to a stirred solution of the *exo*-mesityl diazofluorene **87** [20.0 mg, 33.3 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (670 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the previous step was dried by azeotropic distillation with benzene (2 × 500 μL). The dried residue was dissolved in dichloromethane (500 μL) at 24 °C. A solution of manganese tris(hexafluoroacetylacetonate) (**94**) in dichloromethane (80.0 mM, 500 μL, 40.0 μmol, 1.20 equiv) was added rapidly via syringe to the vigorously stirred solution at 24 °C. The reaction mixture was stirred for 2 min at 24 °C. The product solution was transferred to a separatory funnel that had been charged with 50% ethyl acetate–hexanes (10 mL) and 1 N aqueous sodium hydroxide solution (10 mL). The separatory funnel was sealed and the sealed funnel was vigorously shaken. The layers that formed were separated and the organic layer was washed sequentially with 1 N aqueous sodium hydroxide solution (2 × 10 mL), saturated aqueous sodium bicarbonate solution (10 mL), distilled water (10 mL) and saturated aqueous sodium chloride solution (10 mL). The organic layer was dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated and the residue obtained was purified by preparatory thin layer chromatography (pre-developed with 30% methanol–ethyl acetate, eluting with 60% ethyl acetate–hexanes) to afford separately the (10*S*, 10′*S*)-dimeric diazofluorene **90** (orange solid, 3.3 mg, 26%), the recovered diazofluorene **87** (yellow solid, 0.4 mg, <5%), and the aromatized product **74** (yellow solid, 2.2 mg, 15%).

^{1}H NMR spectroscopic data for the (10*S*, 10'*S*)-dimeric diazofluorene **90** and the dehydrated monomer **74** obtained in this way was identical to those previously reported.[35]

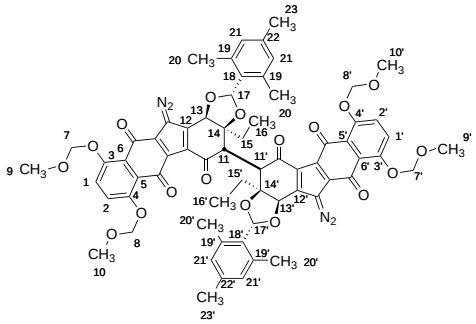


Dimerization of the exo-*Mesityl Diazofluorene* ***87*** *(Entry 4, Table 5):*

Triethylamine (23.0 μL, 167 μmol, 5.00 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (19.0 μL, 83.4 μmol, 2.50 equiv) were added in sequence to a stirred solution of the *exo*-mesityl diazofluorene **87** [20.0 mg, 33.3 μmol, 1 equiv; dried by azeotropic distillation with benzene (500 μL)] in dichloromethane (670 μL) at 0 °C. The resulting mixture was stirred for 10 min at 0 °C. The red product mixture was transferred to a separatory funnel that had been charged with 0.1 M aqueous sodium phosphate buffer solution (pH 7, 5 mL) and dichloromethane (3 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (2 × 3 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

The residue obtained in the previous step was dried by azeotropic distillation with benzene (500 μL). The dried residue was dissolved in acetonitrile (670 μL) at 24 °C. Sodium bicarbonate (56.0 mg, 666 μmol, 20 equiv) was added, and the resulting mixture was cooled to −35 °C. A solution of ceric ammonium nitrate in acetonitrile (0.40 M, 167 μL, 66.6 μmol, 2.00 equiv) was added rapidly via syringe to the vigorously stirred solution at −35 °C. The reaction mixture was stirred for 30 min at −35 °C and then was diluted sequentially with deionized water (10 mL) and ethyl acetate (15 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by preparatory thin layer chromatogaphy (pre-developed with 30% methanol–ethyl acetate, eluting with 60% ethyl acetate–hexanes) to afford separately the (10*S*, 10'*S*)-dimeric diastereomer **90** (orange solid, 2.1 mg, 17%), the (10*S*, 10'*R*)-dimeric diastereomer **92** (yellow solid, 1.3 mg, 10%), the (10*R*, 10'*R*)-dimeric diastereomer dimer **91** (yellow solid, 0.7 mg, 6%), the recovered diazofluorene **87** (yellow solid, 1.5 mg, 8%), and the aromatized product **74** (yellow solid, 1.2 mg, 8%).

Selected NMR data for the C_1-symmetric dimer **92**.



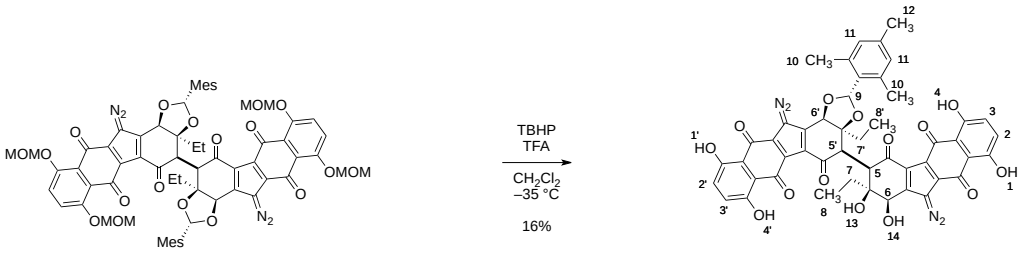
92

Table S2. NMR Data and C–H couplings ($CDCl_3$):

Position	δH	Multiplicity, Integration, *J*-Value	δC	HMBC $_{(H–C)}$
1	7.51	d, 2H, J = 9.5 Hz	126.3	C_3/C_4, C_5/C_6
2	7.51	d, 2H, J = 9.5 Hz	126.3	C_3/C_4, C_5/C_6
3	–	–	152.6	
4	–	–	152.6	
5	–	–	124.7	
6	–	–	124.7	
7	5.36	dd, 2H, J = 7.0, 2.5 Hz	96.0	C_9, C_3
8	5.24	app t, 2H, J = 7.0 Hz	96.1	C_{10}, C_4
9	3.61	s, 3H	56.3	C_7
10	3.59	s, 3H	56.3	C_8
11	3.72	d, 1H, J = 4.5 Hz	55.6	–
12	–	–	128.7	
13	5.57	s, 1H	72.7	C_{12}, C_{17}
14	–	–	88.2	
15	2.99–2.94	m, 1H	20.6	–
15	2.86–2.81	m, 1H	20.6	–
16	1.17	t, 3H, J = 7.5 Hz	6.4	C_{14}, C_{15}
17	6.35	s, 1H	101.3	C_{18}
18	–	–	137.6	
19	–	–	127.2	
20	2.29	s, 6H	20.2	C_{18}, C_{19}, C_{21}
21	6.75	s, 2H	130.0	C_{19}, C_{20}/C_{23}
22	–	–	138.4	
23	2.21	s, 3H	20.6	C_{22}, C_{21}
1'	7.32	app d, 2H, J = 9.5 Hz	124.3	$C_{3'}/C_{4'}$, $C_{5'}/C_{6'}$
2'	7.32	app d, 2H, J = 9.5 Hz	124.3	$C_{3'}/C_{4'}$, $C_{5'}/C_{6'}$
3'	–	–	153.6	
4'	–	–	153.6	
5'	–	–	121.1	
6'	–	–	121.1	
7'	5.07–5.01	m, 2H	96.2	$C_{9'}$, $C_{3'}$
8'	5.07–5.01	m, 2H	96.2	$C_{10'}$, $C_{4'}$

9'	3.48	s, 3H	56.3	C_{7}
10'	3.47	s, 3H	56.3	C_{8}
11'	3.67	d, 1H, J = 4.5 Hz	54.3	–
12'	–	–	125.3	
13'	5.30	s, 1H	70.8	$C_{12'}$, $C_{17'}$
14'	–	–	86.0	
15'	2.45–2.40	m, 1H	20.2	–
15'	2.28–2.25	m, 1H	20.2	–
16'	1.10	t, 3H, J = 7.5 Hz	7.2	$C_{14'}$, $C_{15'}$
17'	5.69	s, 1H	99.4	$C_{18'}$
18'	–	–	137.4	
19’	–	–	126.8	
20’	2.05	s, 6H	20.2	$C_{18'}$, $C_{19'}$, $C_{21'}$
21’	6.66	s, 2H	130.0	$C_{19'}$, $C_{20'}$/$C_{23'}$
22’	–	–	138.7	
23’	2.15	s, 3H	20.5	$C_{22'}$, $C_{21'}$

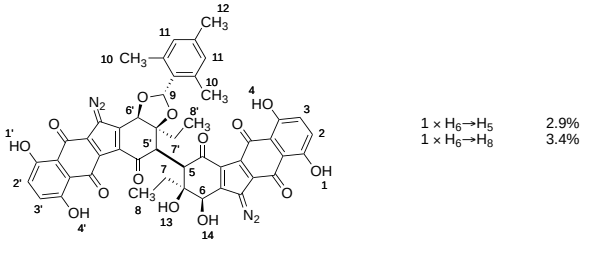
R_f = 0.73 (5% methanol–dichloromethane; UV, CAM). t_R= 2.98. IR (ATR-FTIR), cm^{-1}: 2925 (w), 2141 (s), 1686 (s), 1443 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{66}H_{63}N_4O_{18}$, 1199.4137; found, 1199.4142.



91 **95**

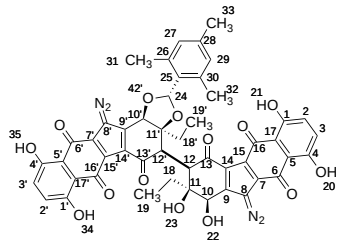
*Deprotection of the (14R,14'R)-Dimeric Diazofluorene **91**:*

A 50-mL round-bottomed flask was charged with a solution of the (14*R*, 14'*R*)-dimeric diazofluorene **91** (5.0 mg, 4.2 μmol, 1 equiv) in 20% dichloromethane–benzene (v/v, 2.0 mL). The solution was concentrated to dryness at 24 °C. The residue obtained was dissolved in dichloromethane (800 μL) and solution of anhydrous *tert*-butylhydroperoxide in decane (5.50 M, 100 μL, 550 μmol, 132 equiv) was added. The resulting orange, homogeneous mixture was cooled to –35 °C. Trifluoroacetic acid (100 μL, 1.32 mmol, 317 equiv) was then added dropwise over 1 min via syringe to the cold mixture. The reaction mixture was stirred for 3 h at –35 °C. The purple product mixture was cooled to –78 °C. Dichloromethane (10 mL) and 0.1 M aqueous sodium phosphate buffer solution (pH 7, 15 mL) were then added in sequence via syringe pump at a rate of 1 mL/min. Upon completion of the addition, the cooling bath was removed and the biphasic mixture was allowed to warm over 1 h to 24 °C. The resulting biphasic solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (2 × 5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by preparative thin layer chromatography (pre-developed with 30% methanol–ethyl acetate, eluting with 5% methanol–dichloromethane) to afford the monomesityl lomaiviticin aglycon **95** as a purple solid (0.6 mg, 16%). The configuration of the C-5 and C-5′ stereocenters was determined by NOE analysis (see structure below).



95

R_f = 0.47 (5% methanol–dichloromethane; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.14 (s, 1H, H_1/H_4), 13.00 (s, 1H, H_1/H_4), 12.43 (s, 1H, $H_{1'}$/$H_{4'}$), 12.42 (s, 1H, $H_{1'}$/$H_{4'}$), 7.17 (d, 1H, J = 9.5 Hz, H_2/H_3), 7.15 (d, 1H, J = 9.5 Hz, H_2/H_3), 7.10 (d, 1H, J = 9.5 Hz, $H_{2'}$/$H_{3'}$), 7.08 (d, 1H, J = 9.5 Hz, $H_{2'}$/$H_{3'}$), 6.79 (s, 2H, H_{11}), 6.56 (s, 1H, H_9), 6.31 (s, 1H, H_{13}), 5.43 (s, 1H, $H_{6'}$), 5.04 (d, 1H, J = 11.0 Hz, H_6), 3.99 (d, 1H, J = 11.5 Hz, H_{14}), 3.72 (s, 1H, H_5), 3.39 (s, 1H, $H_{5'}$), 2.49 (s, 6H, H_{10}), 2.21 (s, 3H, H_{12}), 1.11 (t, 3H, J = 7.5 Hz, H_8), 1.10 (t, 3H, J = 7.5 Hz, $H_{8'}$). ^{13}C NMR (125 MHz, $CDCl_3$): 193.5 (C), 188.3 (C), 159.1 (C), 158.7 (C), 150.4 (C), 158.3 (C), 147.4 (C), 139.1 (C), 131.7 (CH), 130.7 (CH), 130.4 (CH), 128.7 (2 × CH), 126.5 (C), 126.1 (C), 124.8 (C), 113.0 (C), 112.6 (2 × C), 103.4 (CH), 85.2 (C), 78.7 (C), 78.4 (C), 77.4 (C), 72.6 (CH), 70.0 (CH), 58.7 (CH), 49.0 (CH), 34.4 (CH_2), 30.0 (CH_2), 10.7 (CH_3), 8.4 (CH_3). IR (ATR-FTIR), cm^{-1}: 3448 (b), 2929 (m), 2148 (s), 2105 (m), 1595 (s), 1446 (s). HRMS-ESI (*m/z*): $[M + H]^+$ calculated for $C_{48}H_{37}N_4O_{14}$, 893.2306; found, 893.2310.

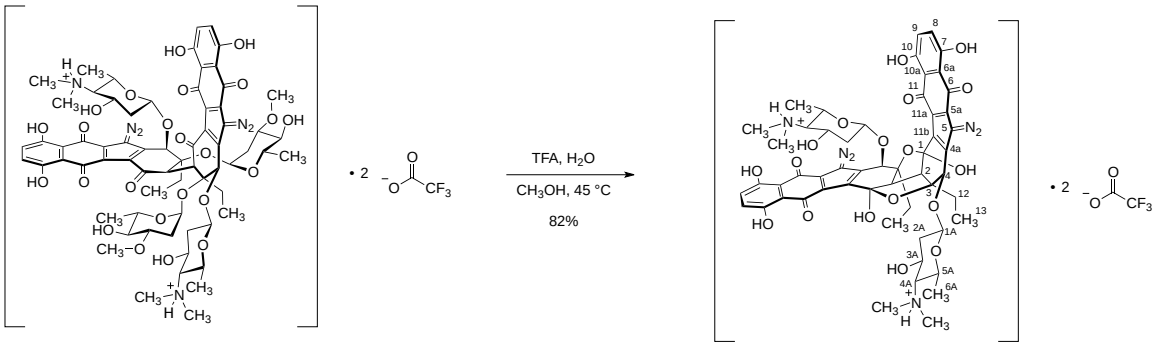


95

Table S3. NMR Data and C–H couplings (10% CD_3OD–$CDCl_3$):

Position	δH	Multiplicity, Integration, J-Value	δC	HMBC $_{(H–C)}$
1	–	–	159.1	
2	7.17	d, 1H, J = 9.5 Hz	130.4	
3	7.15	d, 1H, J = 9.5 Hz	131.7	
4	–	–	158.7	
5	–	–	113.0	
6	–	–		
7	–	–		
8	–	–	78.4	
9	–	–	150.4	
10	5.04	d, 1H, J = 11.0 Hz	70.0	C_8, C_9, C_{14}
11	–	–	78.7	
12	3.72	s, 1H	58.7	C_{13}, $C_{13'}$, C_{11}, $C_{11'}$, $C_{12'}$, C_{10}
13	–	–	188.3	
14	–	–	124.8	
15	–	–		
16	–	–		
17	–	–	112.6	
18	–	–	30.0	
19	1.11	t, 3H, J = 7.5 Hz	8.4	
20	13.14	s, 1H		C_5, C_3, C_4
21	13.00	s, 1H		C_2, C_1, C_{17}
22	3.99	d, OH, J = 11.5 Hz		
23	6.31	s, OH		
24	6.56	s, 1H	103.4	
25	–	–	126.1	
26, 30	–	–	139.1	
27, 29	6.79	s, 2H	130.7	
28	–	–		
31, 32	2.49	s, 6H		
33	2.21	s, 3H		
1'	–	–	158.3	
2'	7.10	d, 1H, J = 9.5 Hz	128.7	
3'	7.08	d, 1H, J = 9.5 Hz		

4'	–	–		
5'	–	–	112.6	
6'	–	–		
7'	–	–		
8'	–	–	77.4	
9'	–	–	147.4	
10'	5.43	s, 1H	72.6	$C_{8'}$, $C_{9'}$, $C_{14'}$, $C_{24'}$, $C_{18'}$
11'	–	–	85.2	
12'	3.39	s, 1H	49.0	C_{13}, $C_{13'}$, C_{11}, $C_{11'}$, C_{12}, $C_{18'}$
13'	–	–	193.5	
14'	–	–	126.5	
15'	–	–		
16'	–	–		
17'	–	–		
18'	–	–	34.4	
19'	1.10	t, 3H, J = 7.5 Hz	10.7	
34	12.43	s, 1H		$C_{5'}$, $C_{3'}$, $C_{4'}$
35	12.42	s, 1H		$C_{2'}$, $C_{1'}$, $C_{17'}$



(–)-lomaiviticin A (**1**) (–)-lomaiviticin B (**2**)

*Synthesis of (–)-Lomaiviticin B (**2**):*

Methanol (200 μL, 33% v/v) was added via syringe to a stirred solution of trifluoroacetic acid (200 μL, 33% v/v) and (–)-lomaiviticin C (**3**, 3.1 mg, 2.27 μmol, 1 equiv) in water (200 μL, 33% v/v) at 24 °C. The resulting mixture was placed in a preheated hot plate at 45 °C. The warmed solution was stirred and heated for 2 h at 45 °C. The product mixture was concentrated to dryness. The residue obtained was purified by reverse phase flash-column chromatography (eluting with 20% acetonitrile–water containing 0.1% trifluoroacetic acid initially, grading to 40% acetonitrile–water containing 0.1% trifluoroacetic acid, five steps) to afford (–)-lomaiviticin B (**2**) as a pink solid (2.0 mg, 82%).

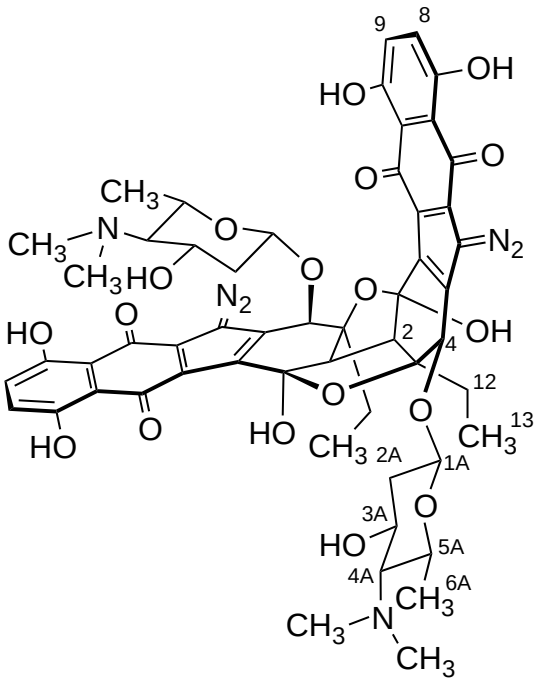
t_R = 1.36. $[\alpha]_D^{20}$ = −87.5° (*c* 0.2, CH_3OH); lit.[12] $[\alpha]_D^{20}$ = –71.4° (*c* 0.07, CH_3OH). HRMS-ESI (*m/z*): $[M + 2H]^{2+}$ calculated for $C_{54}H_{56}N_6O_{18}$, 539.1898; found, 539.1900. ^1H and HMQC NMR spectroscopic data for semisynthetic (–)-lomaiviticin B (**2**) were identical to those previously reported.[12]

*Neutralization of (–)-Lomaiviticin B (**2**):*

The purified (–)-lomaiviticin B (**2**) obtained in the preceding step was sequentially dissolved with saturated sodium bicarbonate solution (1 mL) and dichloromethane (0.5 mL). The diluted solution was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with dichloromethane (2 × 0.5 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to afford the free base lomaiviticin B (**2**) as a pink solid (1.9 mg, 99%).

t_R = 1.36. Due to the limited stability of the free base lomaiviticin B (**2**), only ^1H, COSY, and HSQC NMR spectroscopic data were obtained.

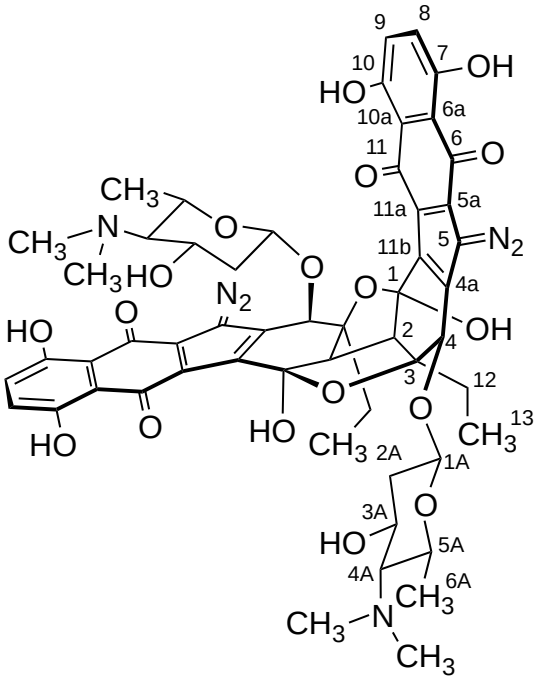
Selected NMR data for (–)-lomaiviticin B (**2**):



(–)-lomaiviticin B (**2**)

Table S4. Comparison of ^{1}H NMR Data for (–)-Lomaiviticin B (**2**).

position	δ H Lit.[12] (methanol-d_4, 500 MHz) (int., mult., J-value)	δ H Free base (methanol-d_4, 800 MHz) (int., mult., J-value)	δ H TFA Salt (methanol-d_4, 500 MHz) (int., mult., J-value)
2	2.64 (1H, br s)	3.64 (1H, br s)	2.61 (1H, br s)
4	4.99 (1H, br s)	5.49 (1H, s)	4.96 (1H, br s)
8	7.23 (1H, br s)	7.24 (1H, d, J = 8.8 Hz)	7.20 (1H, app s)
9	7.22 (1H, br s)	7.22 (1H, d, J = 8.8 Hz)	7.20 (1H, app s)
12	1.82 (1H, m); 1.70 (1H, m)	1.82–1.79 (1H, m); 1.73–1.69 (1H, m)	1.82–1.78 (1H, m); 1.69–1.60 (1H, m)
13	0.93 (3H, t, J = 7.0 Hz)	0.94 (3H, t, J = 7.2 Hz)	0.90 (3H, t, J = 7.2 Hz)
1A	5.42 (1H, dd, J = 9.5, 1.6 Hz)	5.26 (1H, dd, J = 10.4, 2.4 Hz)	5.40 (1H, dd, J = 9.5, 1.5 zHz)
2A	2.27 (1H, ddd, J = 11.5, 5.0, 1.6 Hz); 1.55 (1H, ddd, J = 11.5, 9.5, 9.5 Hz)	2.13–2.10 (1H, m); 1.37–1.34 (1H, m)	2.24 (1H, ddd, J = 11.0, 5.0, 2.0 Hz); 1.51 (1H, app q, J = 11.6 Hz)
3A	4.17 (1H, ddd, J = 9.5, 9.5, 9.5 Hz)	3.91 (1H, td, J = 11.9, 4.9 Hz)	4.14 (1H, td, J = 10.5, 5.0 Hz)
4A	2.84 (1H, dd, J = 9.5, 9.5 Hz)	1.92–1.88 (1H, m)	2.82 (1H, t, J = 10.0 Hz)
4A $N(CH_3)_2$	2.97 (6H, br s)	2.44 (6H, s)	2.94 (6H, br s)
5A	3.94 (1H, m)	3.57–3.51 (1H, m)	3.92 (1H, qd, J = 9.5, 6.5 Hz)
6A	1.36 (3H, d, J = 6.5 Hz)	1.13 (3H, d, J = 5.6 Hz)	1.33 (3H, d, J = 6.0 Hz)

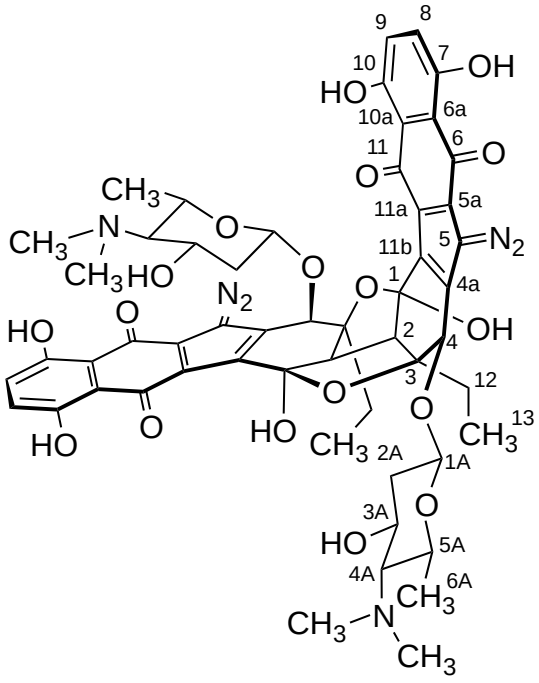


(–)-lomaiviticin B (**2**)

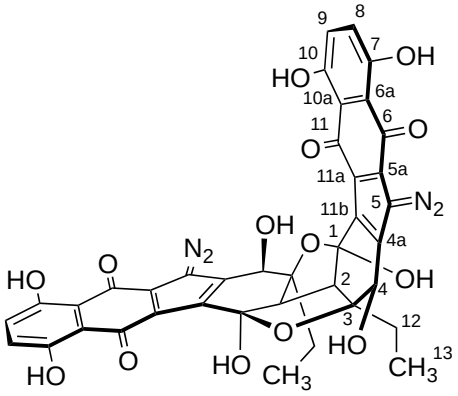
Table S5. Comparison of NMR Data and C–H couplings for (–)-lomaiviticin B (**2**).

position	δ H Lit.[12] (methanol-d_4, 500 MHz)	δ C Lit.[12] (methanol-d_4, 500 MHz)	δ H TFA salt (methanol-d_4, 500 MHz)	δ C HMQC (methanol-d_4, 500 MHz)	δ H Free base (methanol-d_4, 800 MHz)	δ C HSQC (methanol-d_4, 800 MHz)
1	–	96.5	–	–	–	–
2	2.69	44.0	2.61	43.5	3.64	71.3
3	–	78.0	–	–	–	–
4	4.99	78.1	4.96	77.6	5.49	76.4
4a	–	141.7	–	–	–	–
5	–	76.1	–	–	–	–
5a	–	133.4	–	–	–	–
6	–	186.2	–	–	–	–
6a	–	114.3	–	–	–	–
7	–	159.3	–	–	–	–
8	7.23	130.1	7.20	129.7	7.24	130.3
9	7.22	130.4	7.20	129.7	7.22	130.7
10	–	159.2	–	–	–	–
10a	–	114.5	–	–	–	–
11	–	183.6	–	–	–	–
11a	–	130.3	–	–	–	–
11b	–	125.1	–	–	–	–
12	1.82/1.70	25.5	1.82–1.78/ 1.69–1.60	25.0	1.82–1.79/ 1.73–1.69	25.5

13	0.93	7.5	0.90	7.0	0.94	7.7
1A	5.42	103.5	5.40	102.9	5.26	103.7
2A	2.27/1.55	41.7	2.24/1.51	41.2	2.13–2.10/ 1.37–1.34	41.7
3A	4.17	65.8	4.14	65.2	3.91	67.6
4A	2.84	73.8	2.82	73.1	1.92–1.88	72.9
4A-$N(CH_3)_2$	2.97	42.7	2.94	42.1	2.44	42.1
5A	3.94	68.3	3.92	67.8	3.57–3.51	71.5
6A	1.36	19.5	1.33	19.0	1.13	20.0



(–)-lomaiviticin B (**2**)



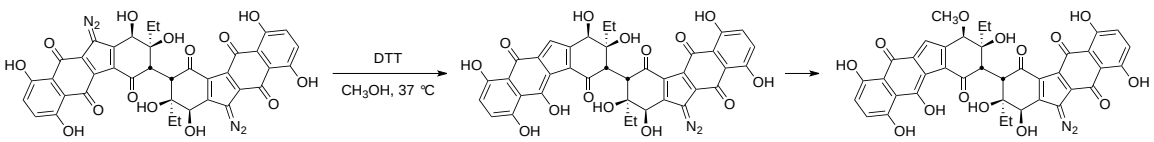
(–)-lomaiviticin aglycon (**6**)

Table S6. Comparison of NMR Data and C–H couplings for free base (–)-lomaiviticin B (**2**) and lomaiviticin aglycon (**6**).

position	δ H Free base (methanol-d_4, 800 MHz)	δ C HSQC (methanol-d_4, 800 MHz)	δ H Lit.[35] (DMF-d_7, 500 MHz)	δ C Lit.[35] (DMF-d_7, 500 MHz)
1	–	–	–	102.7
2	3.64	71.3	3.30	61.9
3	–	–	–	90.1
4	5.49	76.4	4.69	70.3
4a	–	–	–	142.0
5	–	–	–	78.9
5a	–	–	–	130.9
6	–	–	–	184.3
6a	–	–	–	114.2
7	–	–	–	159.1
8	7.24	130.3	7.25	129.6
9	7.22	130.7	7.18	127.9
10	–	–	–	158.6
10a	–	–	–	113.4
11	–	–	–	181.9
11a	–	–	–	130.7
11b	–	–	–	131.4
12	1.82–1.79/ 1.73–1.69	25.5	2.04–1.97/ 1.93–1.89	31.4

13	0.94	7.7	1.03	10.1
1A	5.26	103.7	–	–
2A	2.13–2.10/ 1.37–1.34	41.7	–	–
3A	3.91	67.6	–	–
4A	1.92–1.88	72.9	–	–
4A-$N(CH_3)_2$	2.44	42.1	–	–
5A	3.57–3.51	71.5	–	–
6A	1.13	20.0	–	–

Hydrodediazotization Studies.



75 **99** **101**

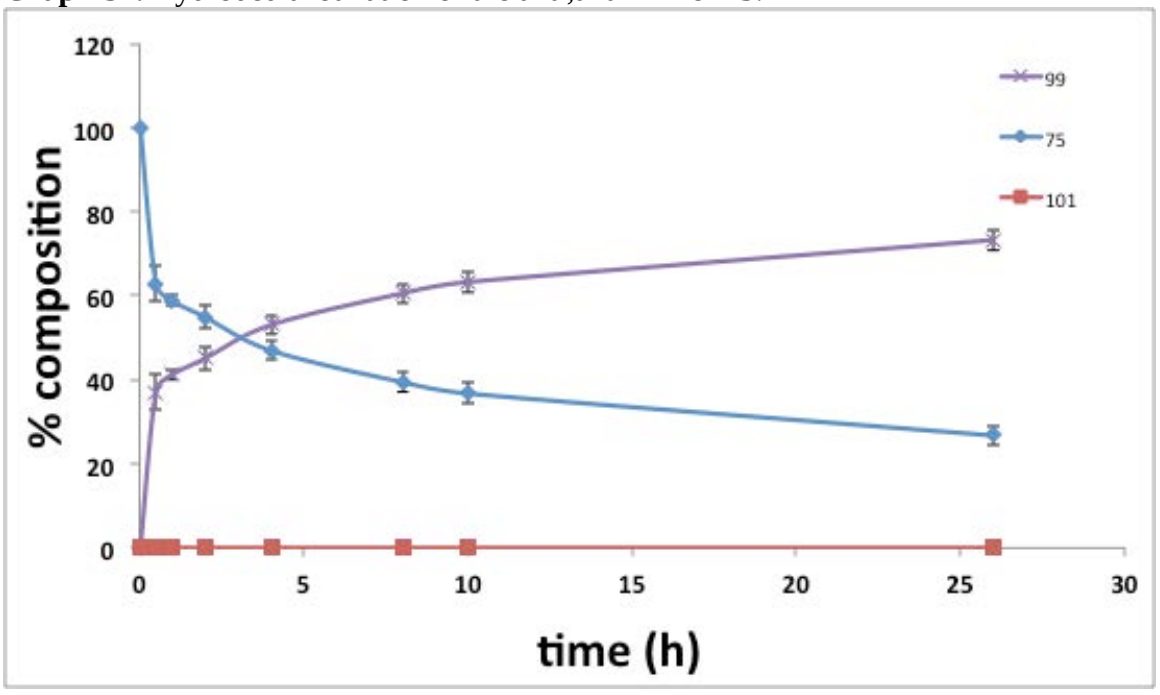
Determination of the Relative Extinction Coefficients of the anti,anti-*Dimer* ***75*** *and the Hydroxyfulvene* ***99****:*

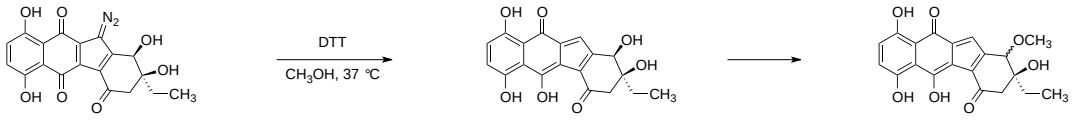
Solutions of the diazofluorene **75** and the hydroxyfulvene **99** in methanol were prepared separately. A stock solution of **75**:**99** was prepared in a 1:2 ratio. The mixture was analyzed by LC/MS, with UV detection at 254 nm. The relative extinction coefficient (254 nm) of **75** and **99** was determined to be 1.72:1, respectively.

Reduction–Solvolysis of the anti,anti-*Dimer* ***75****:*

Methanol was sparged with nitrogen for 1 h before use. Methanol (500 μL) was added to an LC/MS vial that had been charged with the diazofluorene **75** (0.15 mg, 200 nmol, 1 equiv). *N*,*N*-dimethylbenzylamine in methanol (10.0 mM, 10.0 μL, 200 nmol, 1.00 equiv) was added as an internal standard. A freshly prepared solution of dithiothreitol in methanol (DTT, 10.0 mM, 10.0 μL, 200 nmol, 1.00 equiv) was added. The resulting solution was warmed to 37 °C. The reduction–solvolysis reaction was monitored by LC/MS (for conditions, please see the *Instrumentation* section above).

Graph S1. Hydrodediazotization of the anti,anti-Dimer **75**.





72 100 102

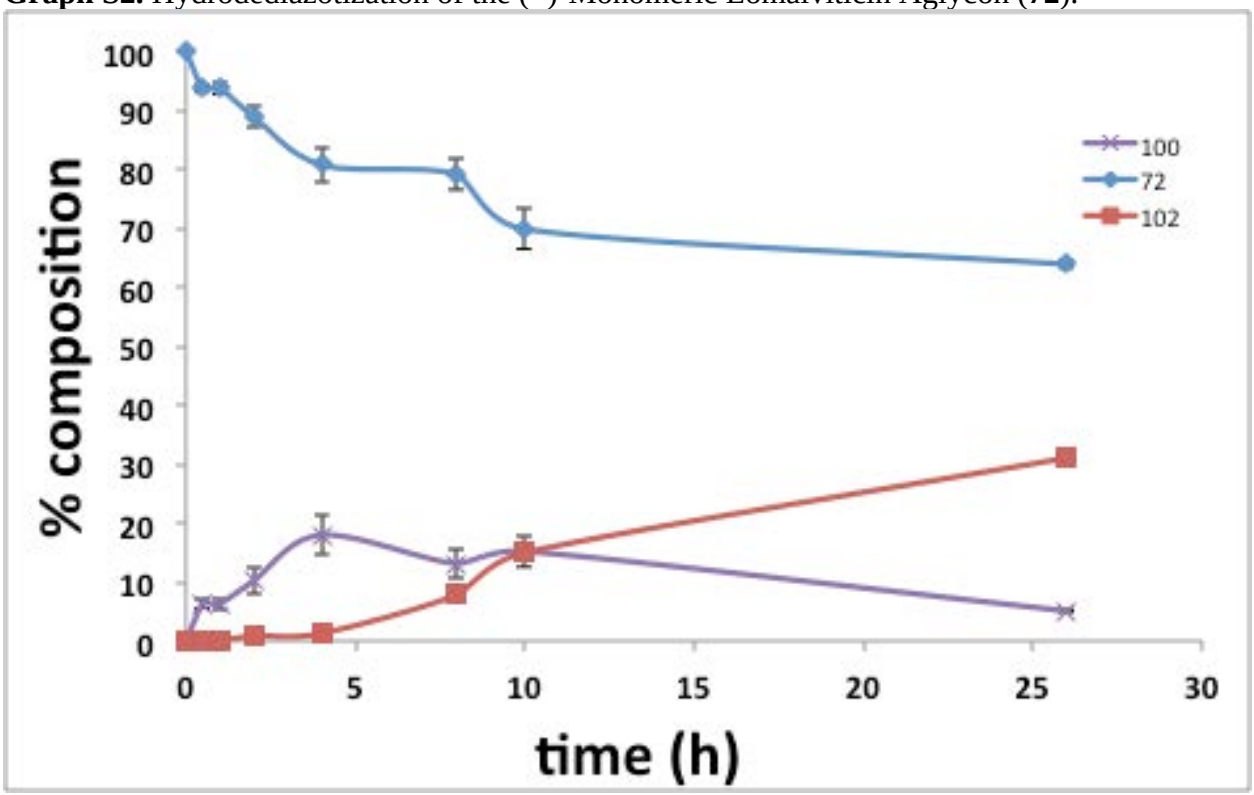
*Determination of the Relative Extinction Coefficients of the Monomeric Lomaiviticin Aglycon **72** and the Hydroxyfulvene **100**:*

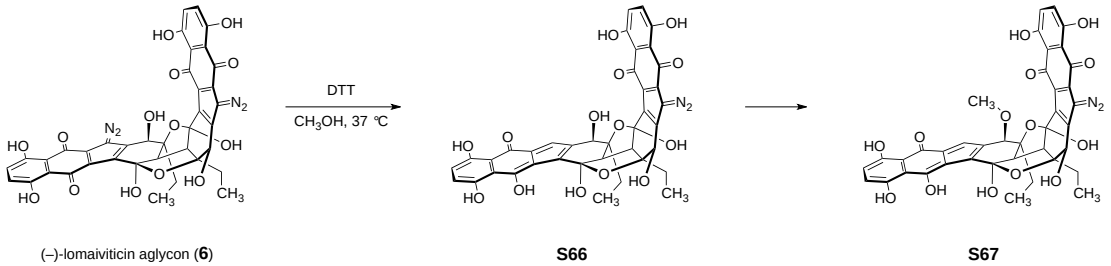
Solutions of the diazofluorene **72** and the hydroxyfulvene **100** in methanol were prepared separately. A stock solution of **72**:**100** was prepared in a 1:2 ratio. The mixture was analyzed by LC/MS, with UV detection at 254 nm. The relative extinction coefficient (254 nm) of **72** and **100** was determined to be 1.25:1, respectively.

*Reduction–Solvolysis of the Monomeric Lomaiviticin Aglycon **72**:*

Methanol was sparged with nitrogen for 1 h before use. Methanol (500 μL) was added to an LC/MS vial that had been charged with the monomeric lomaiviticin aglycon **72** (0.08 mg, 200 nmol, 1 equiv). *N*,*N*-dimethylbenzylamine in methanol (10.0 mM, 10.0 μL, 200 nmol, 1.00 equiv) was added as an internal standard. A freshly prepared solution of dithiothreitol in methanol (DTT, 10.0 mM, 10.0 μL, 200 nmol, 1.00 equiv) was added. The resulting solution was warmed to 37 °C. The reduction–solvolysis reaction was monitored by LC/MS (for conditions, please see the *Instrumentation* section above).

Graph S2. Hydrodediazotization of the (–)-Monomeric Lomaiviticin Aglycon (**72**).



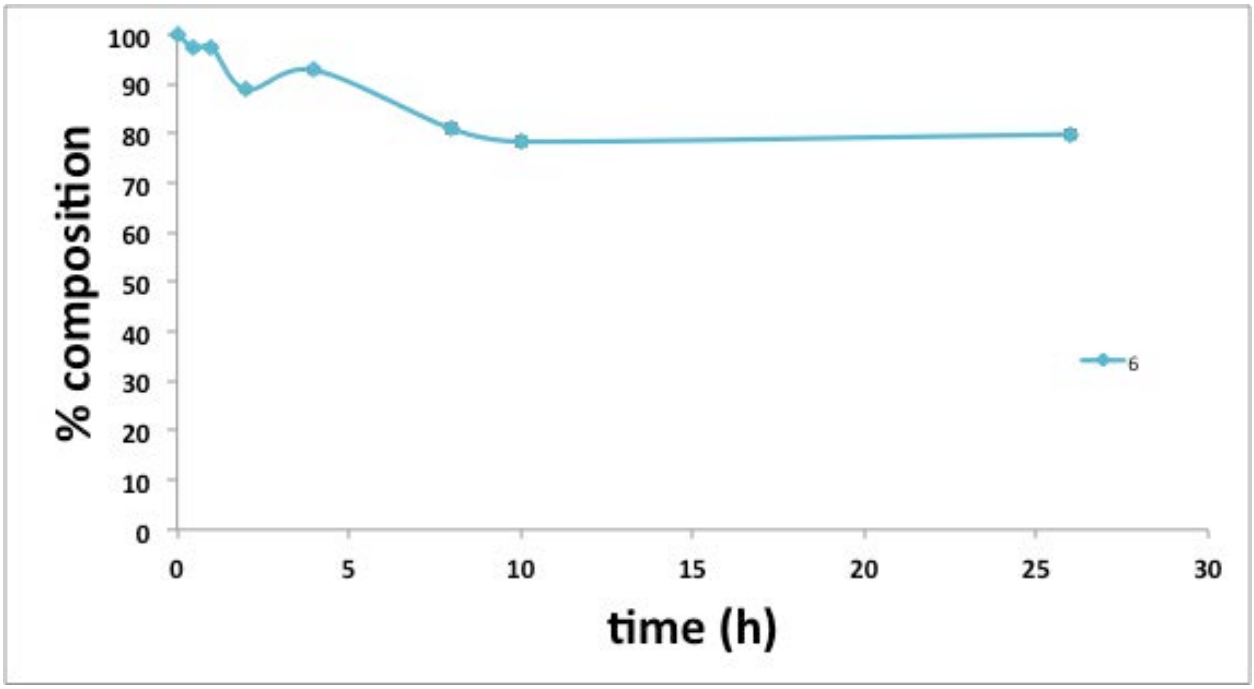


(–)-lomaiviticin aglycon (**6**) **S66** **S67**

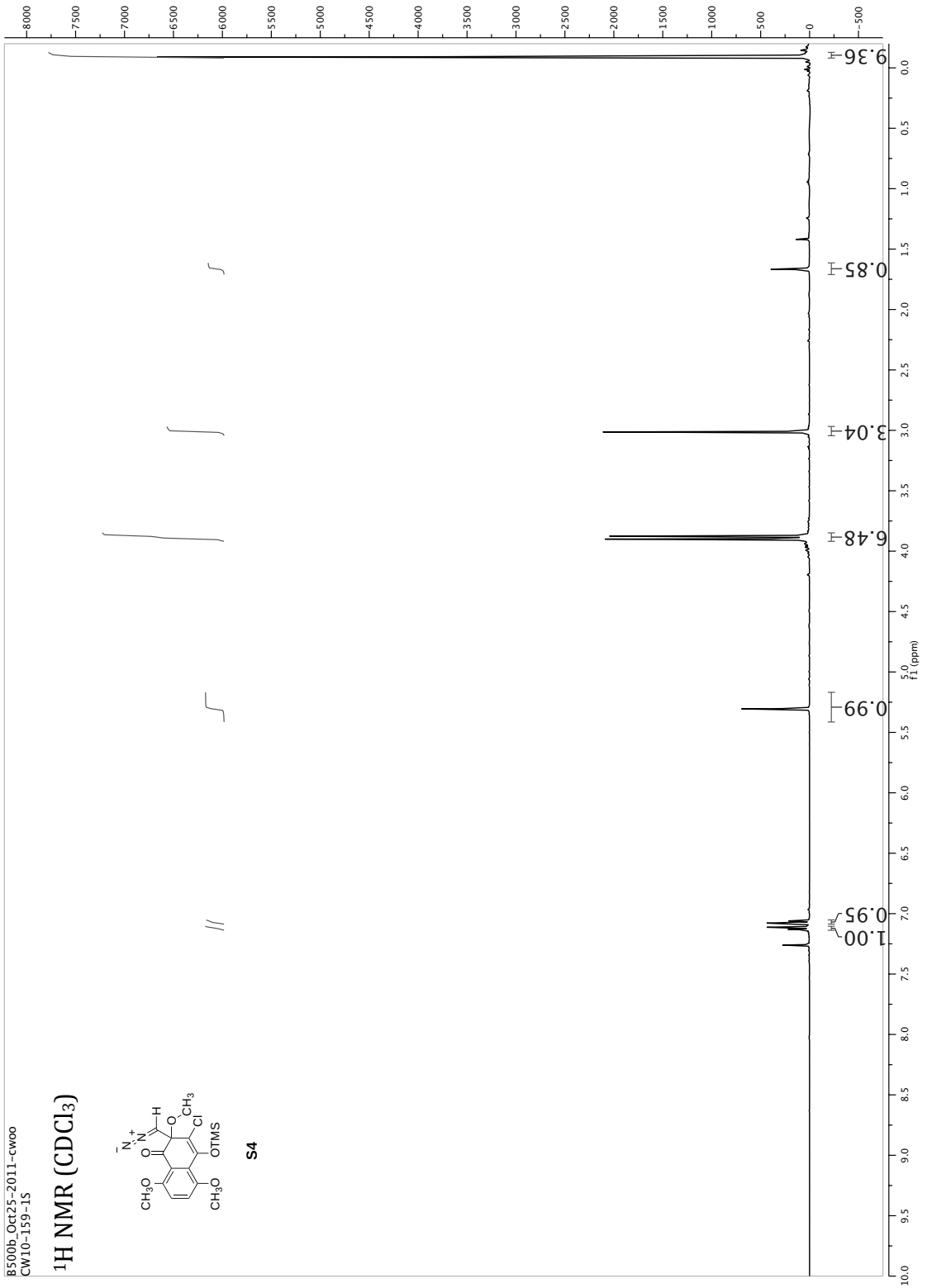
*Reduction–Solvolysis of the (–)-Lomaiviticin Aglycon (**6**):*

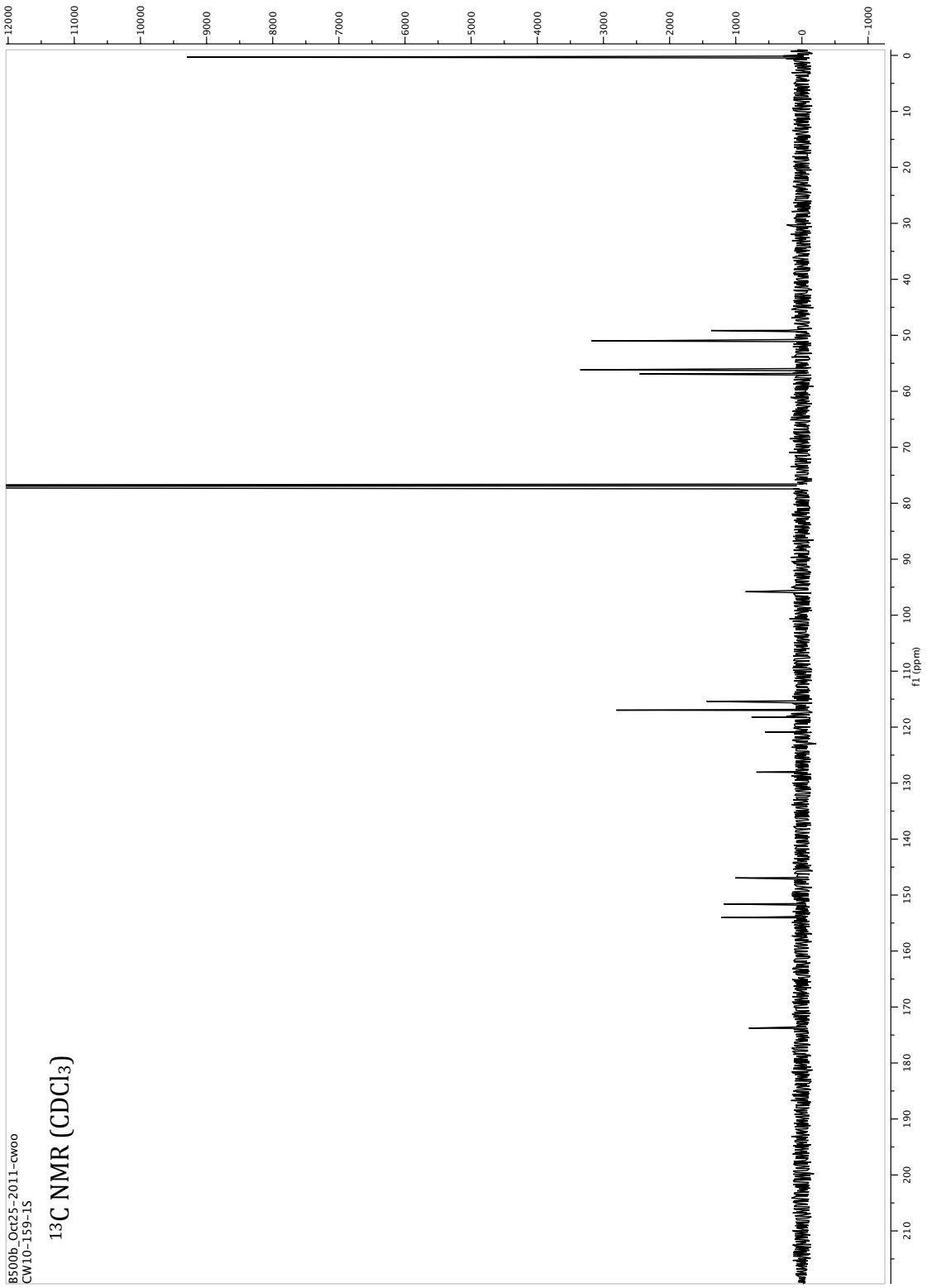
Methanol was sparged with nitrogen for 1 h before use. Methanol (500 μL) was added to an LC/MS vial that had been charged with the (–)-lomaiviticin aglycon (**6**, 0.15 mg, 200 nmol, 1 equiv). *N*,*N*-dimethylbenzylamine in methanol (10.0 mM, 10.0 μL, 200 nmol, 1.00 equiv) was added as an internal standard. A freshly prepared solution of dithiothreitol in methanol (DTT, 10.0 mM, 10.0 μL, 200 nmol, 1.00 equiv) was added. The resulting solution was warmed to 37 °C. The reduction–solvolysis reaction was monitored by LC/MS (for conditions, please see the *Instrumentation* section above). Hydrodediazotization was not observed, and the percent composition of the (–)-lomaiviticin aglycon (**6**) was calibrated against the internal standard.

Graph 3. Percent composition of the (–)-lomaiviticin aglycon (**6**).

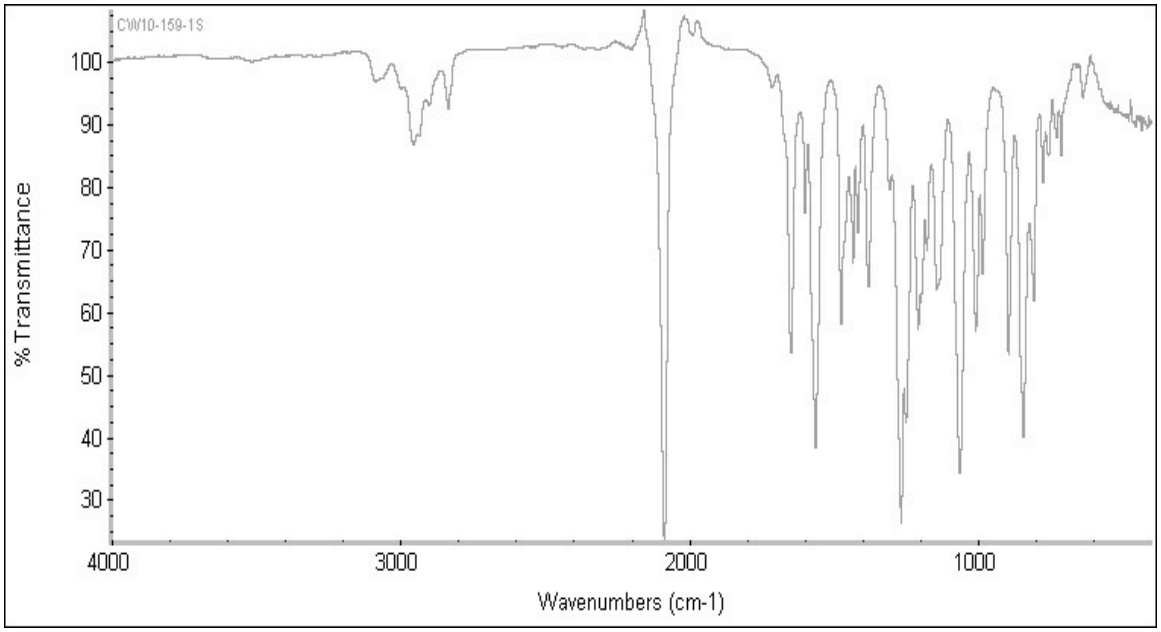


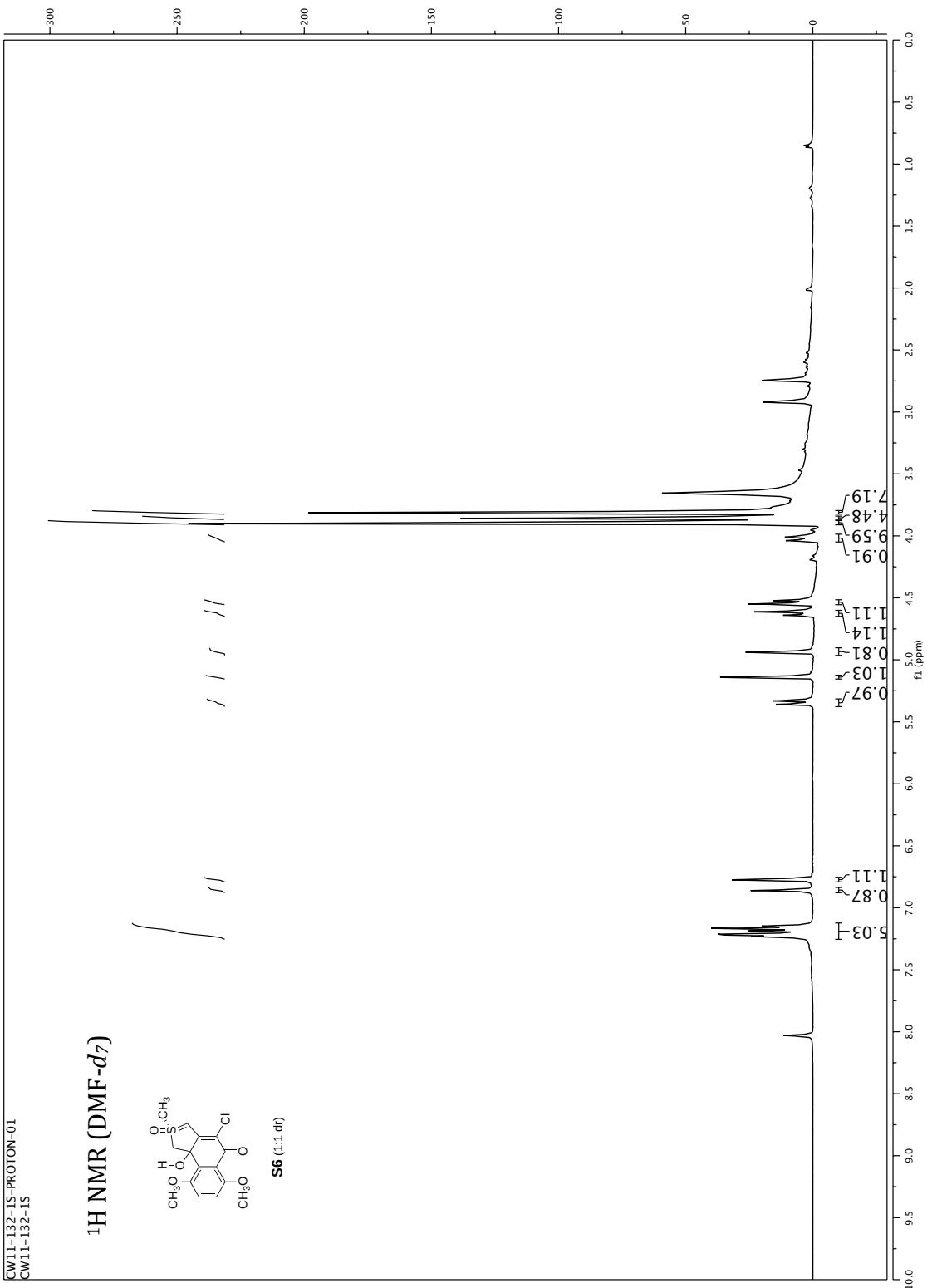
Catalog of Nuclear Magnetic Resonance Spectra.

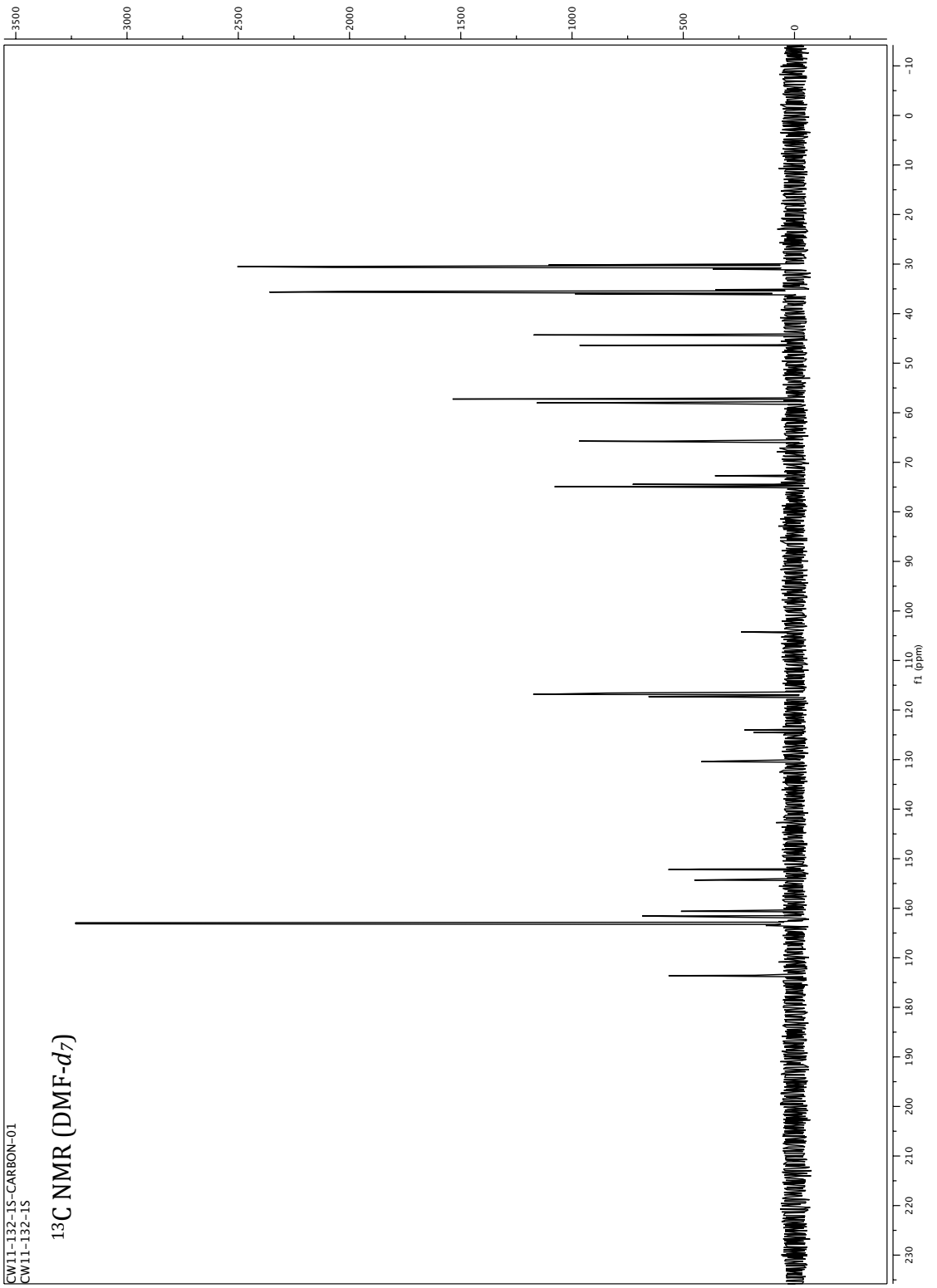



B500b_Oct25-2011-cwoo
CW10-159-1S
13C NMR (CDCl3)
f1 (ppm)

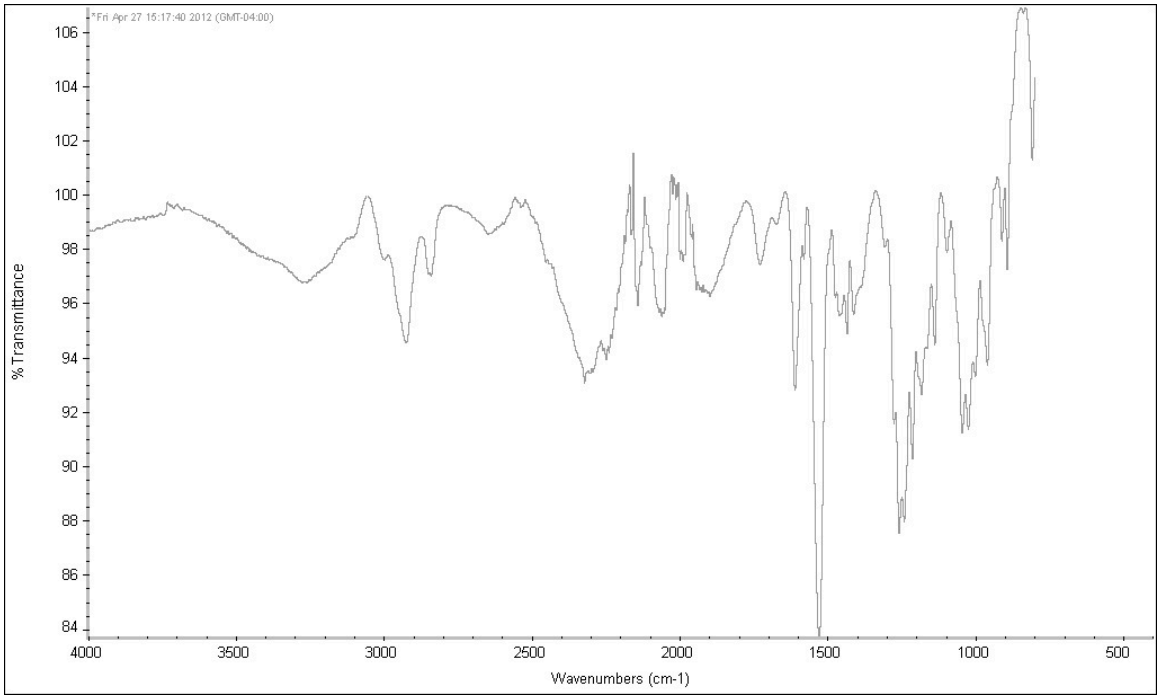
IR

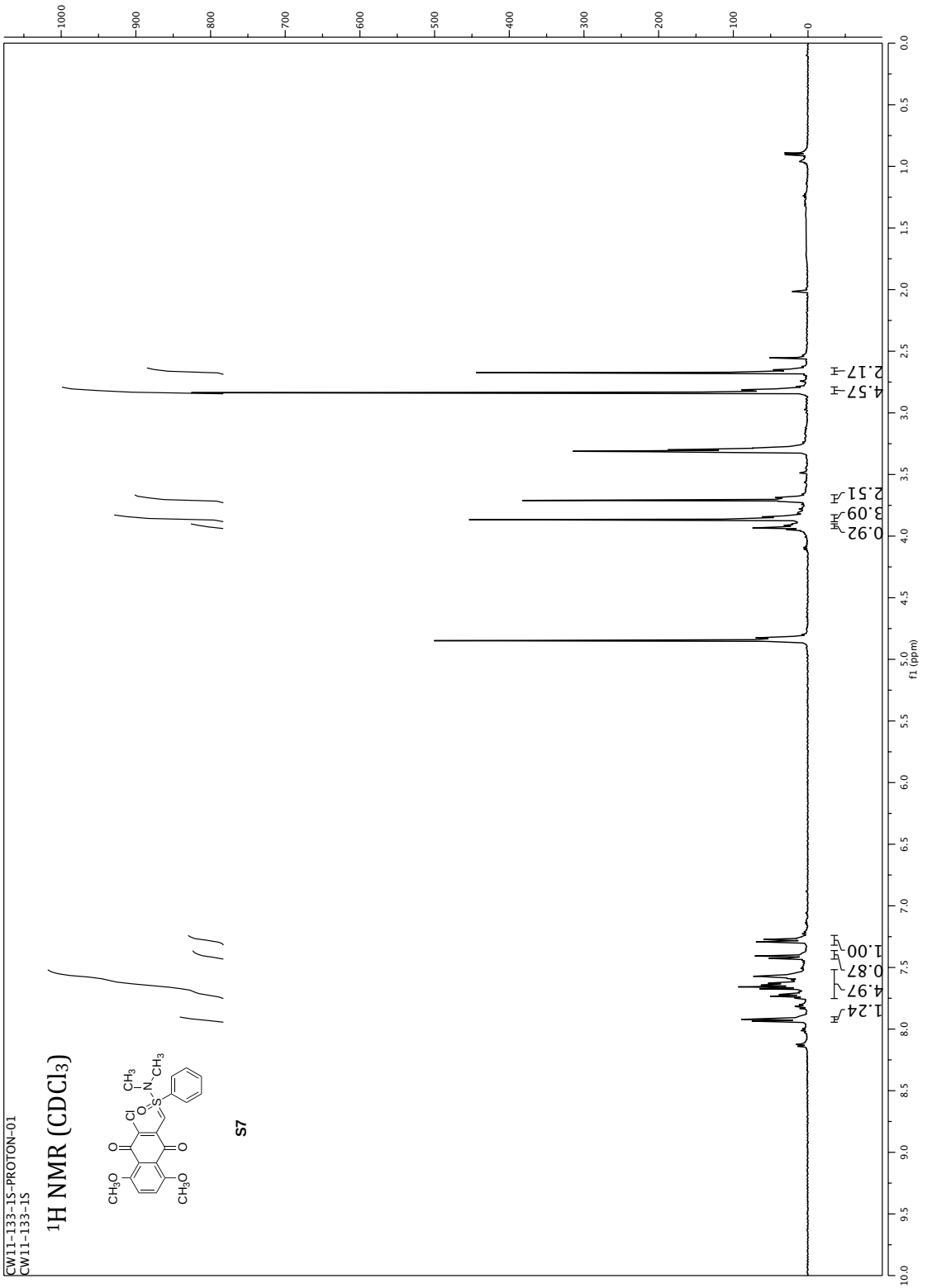

CW10-159-1S
100
90
80
70
60
50
40
30
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

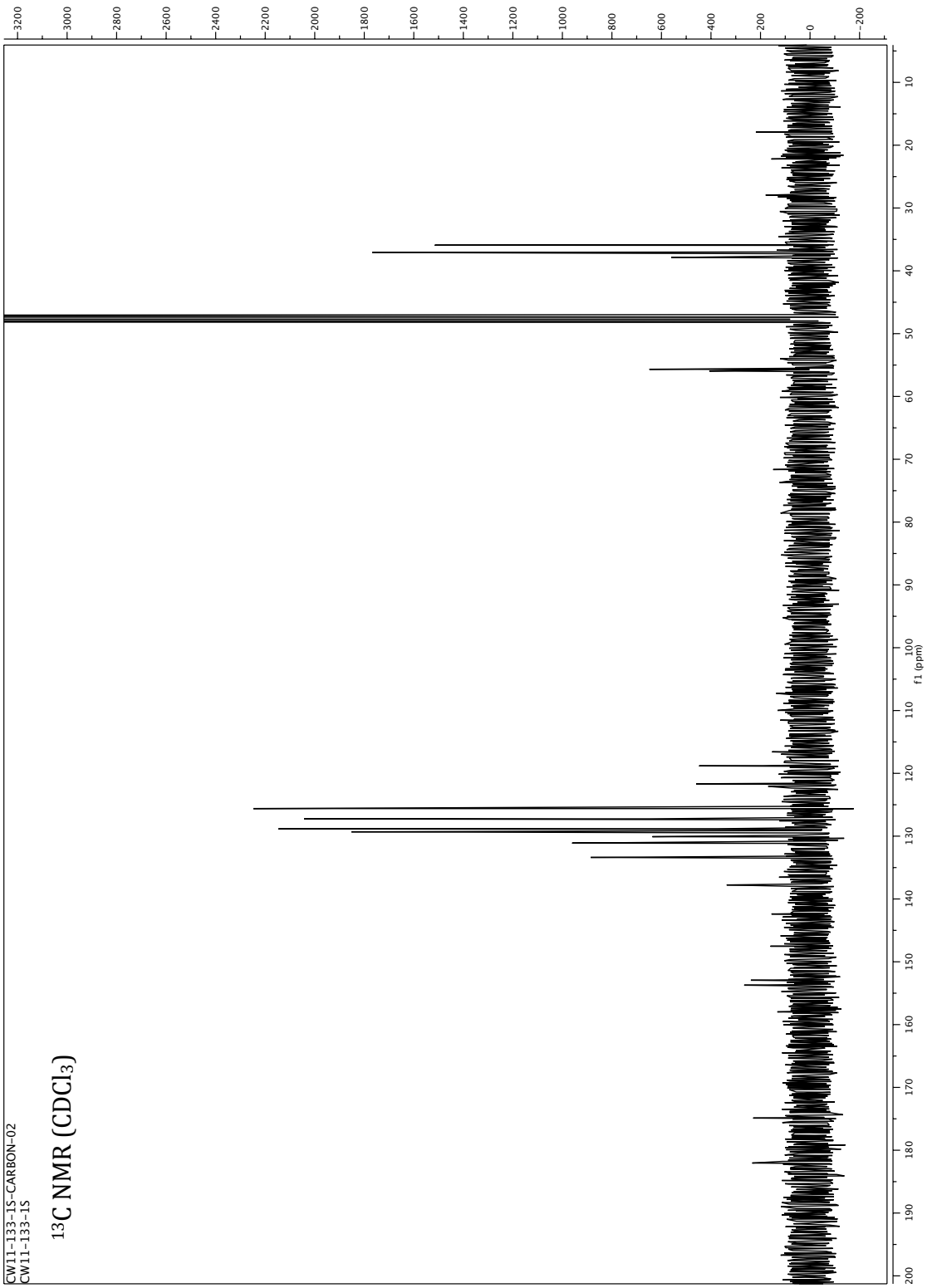

CW11-132-1S-PROTON-01
CW11-132-1S
^{1}H NMR (DMF-d_7)
S6 (1:1 dr)
5.03
0.87
1.11
0.97
1.03
0.81
1.14
1.11
0.91
9.59
4.48
7.19
f1 (ppm)


CW11-132-1S-CARBON-01
CW11-132-1S
^{13}C NMR (DMF-d_7)
f1 (ppm)

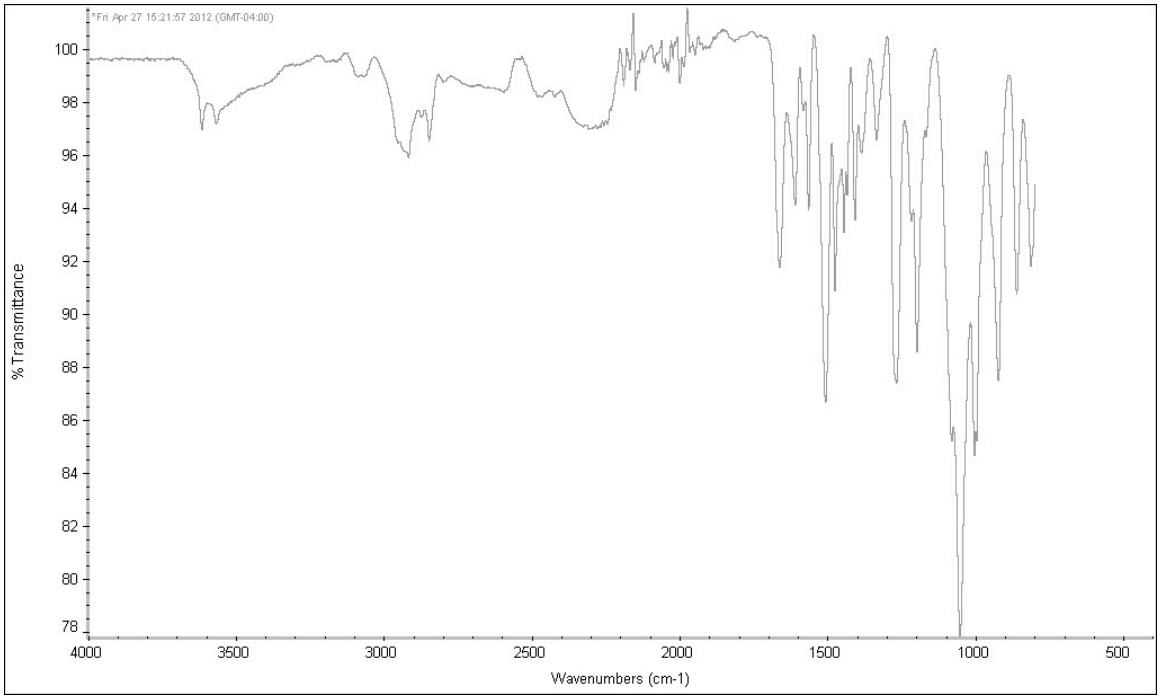
IR

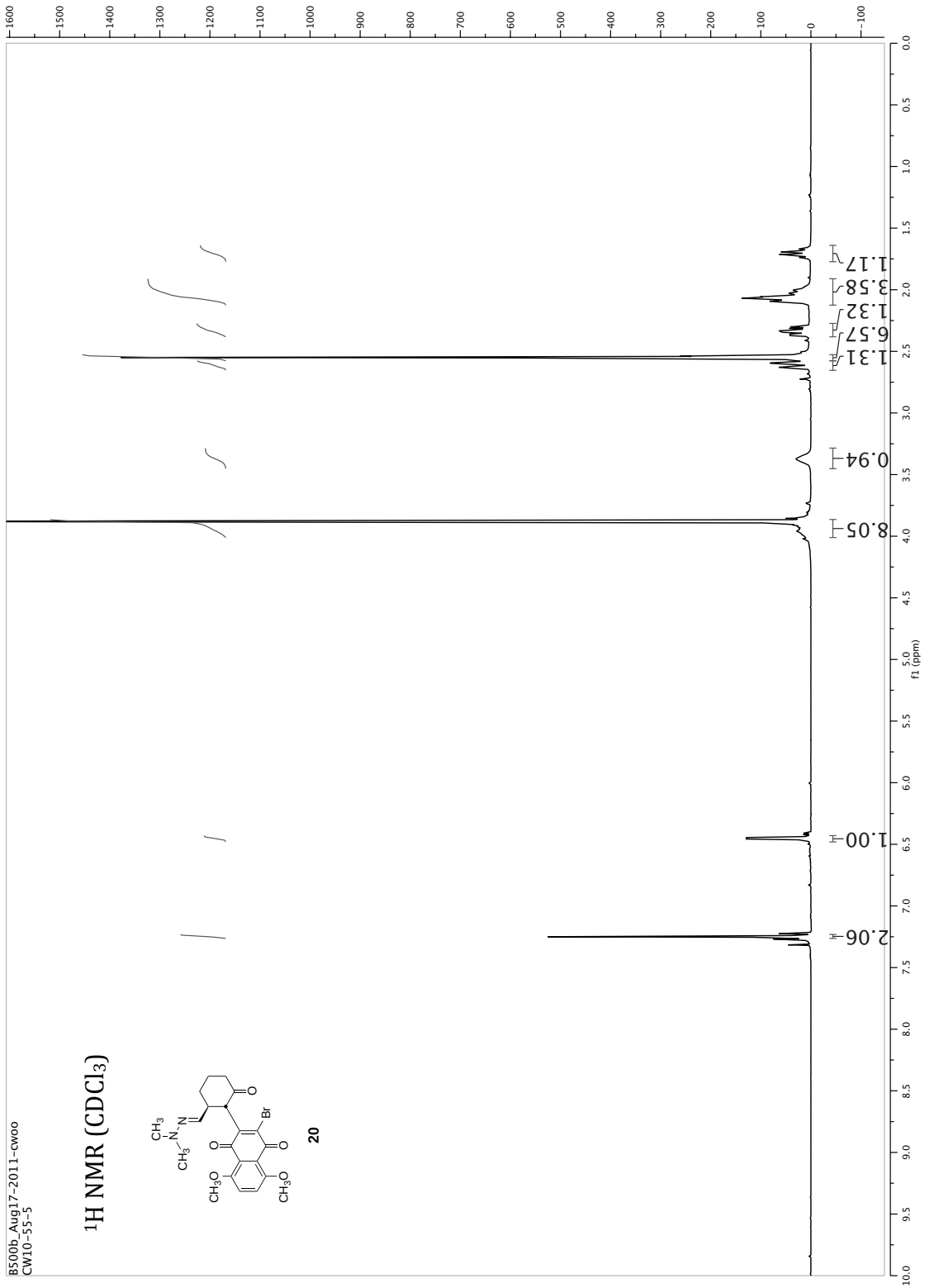

Fri Apr 27 15:17:40 2012 (GMT-04:00)
% Transmittance
106
104
102
100
98
96
94
92
90
88
86
84
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

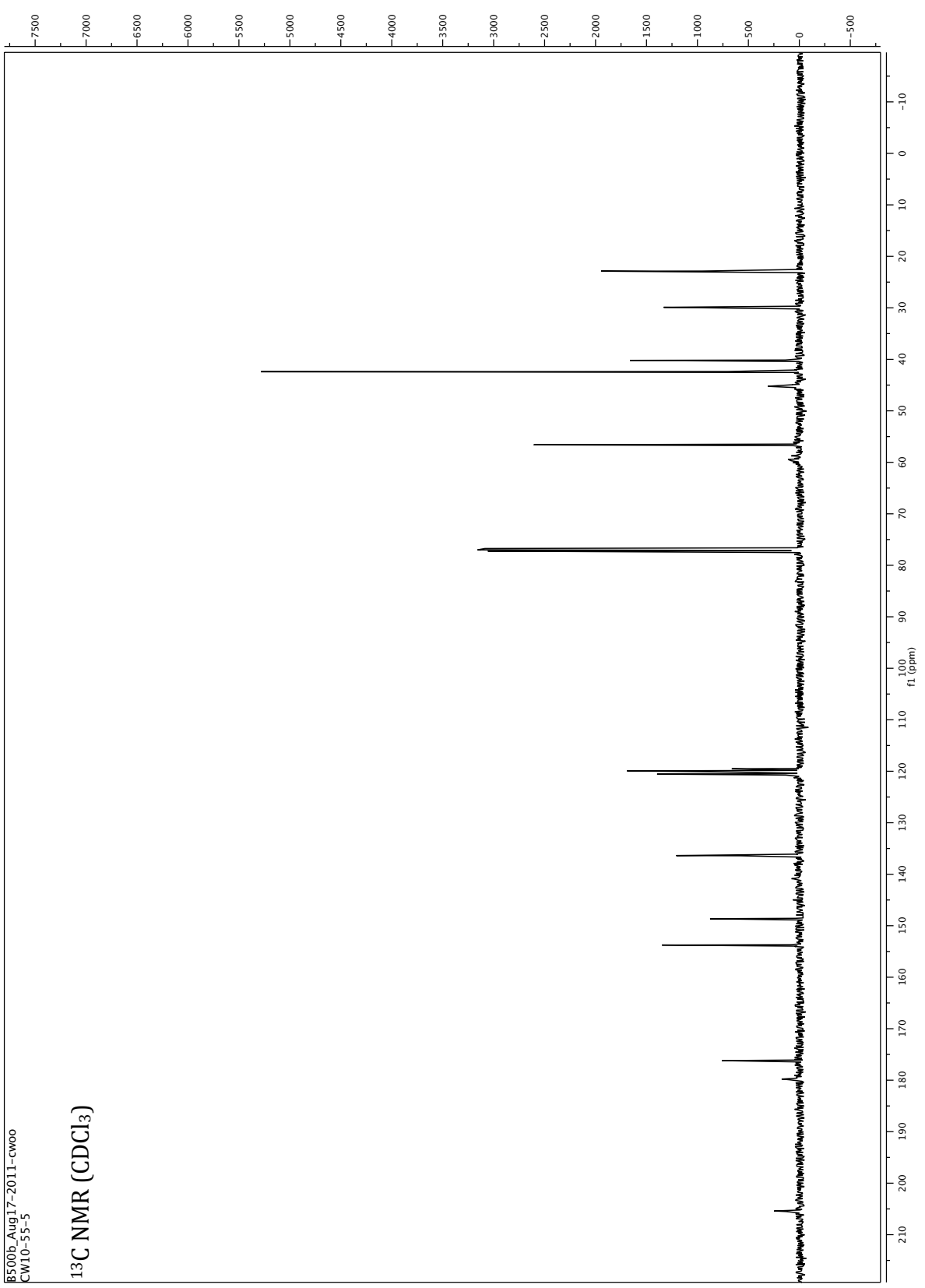

CW11-133-1S-PROTON-01
CW11-133-1S
^{1}H NMR ($CDCl_3$)
S7
2.17
4.57
2.51
3.09
0.92
1.24
4.97
0.87
1.00
f1 (ppm)


CW11-133-1S-CARBON-02
CW11-133-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

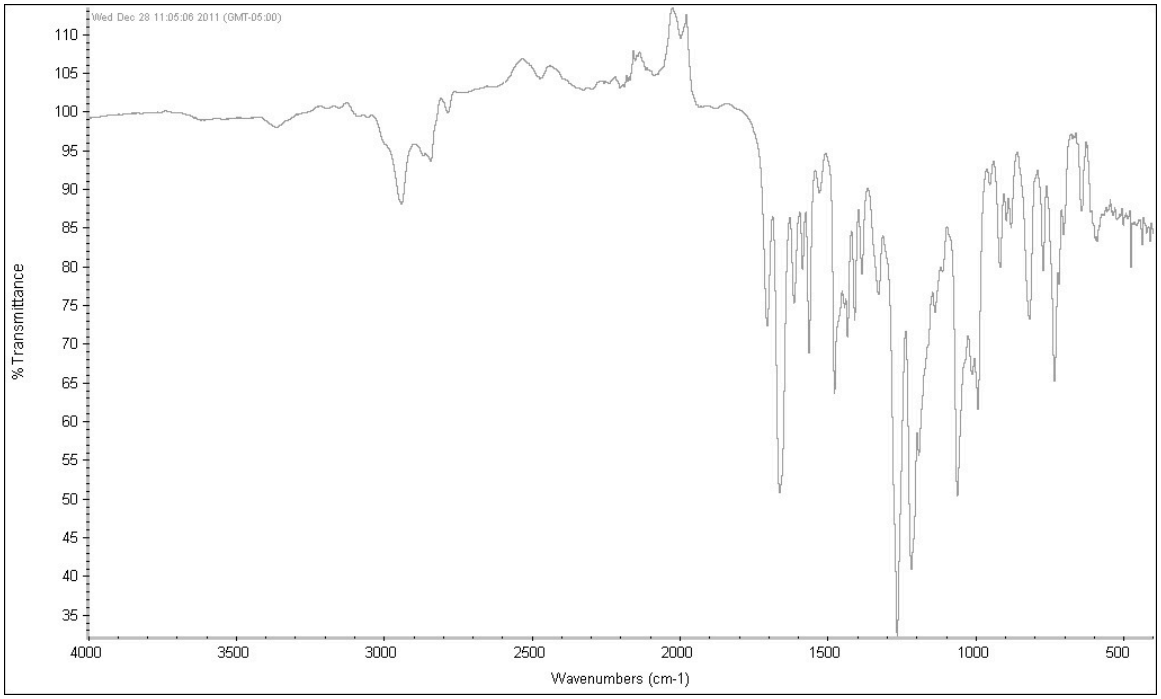
IR

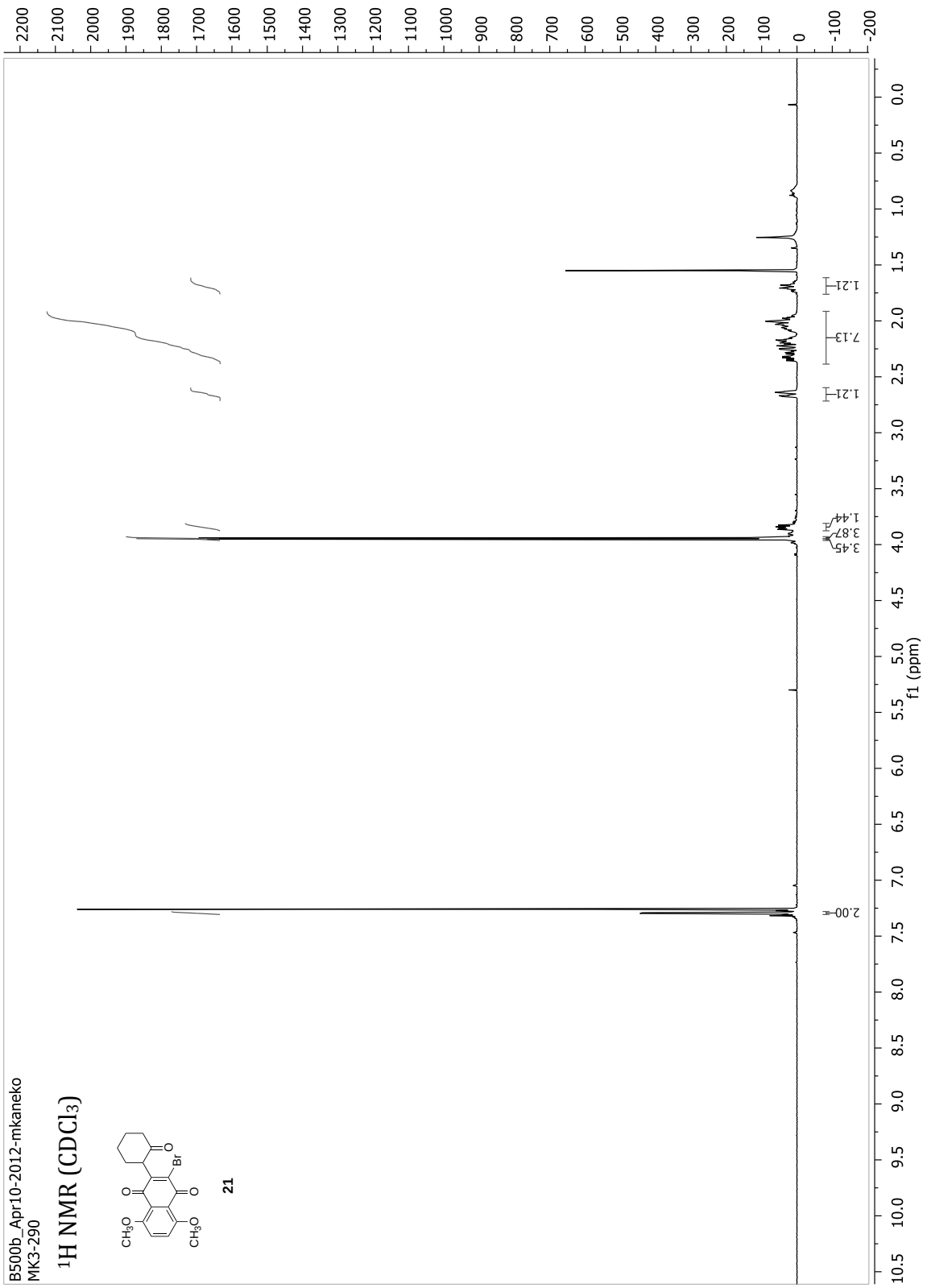

Fri Apr 27 15:21:57 2012 (GMT-04:00)
% Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

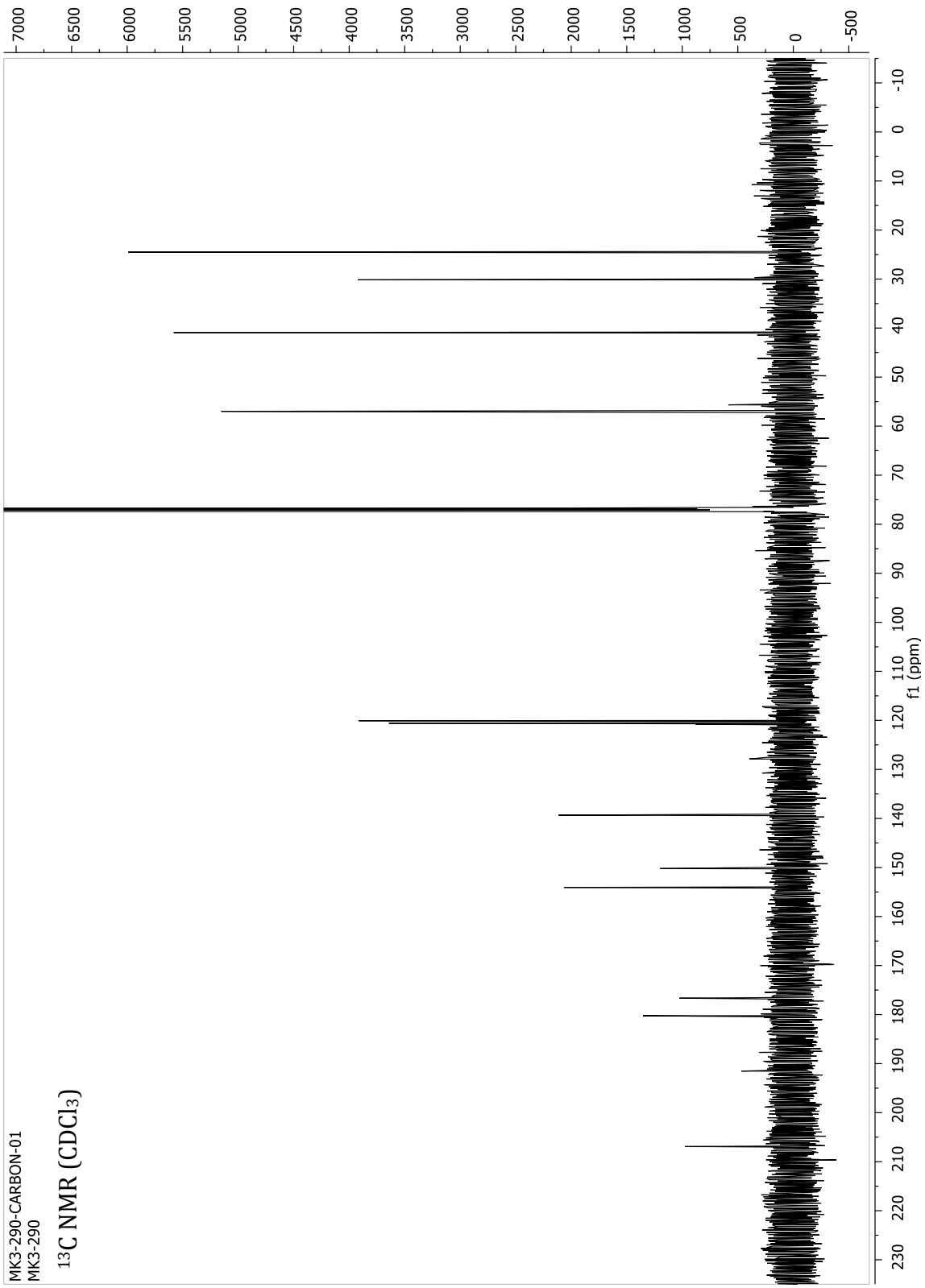

^{1}H NMR ($CDCl_3$)
B500b_Aug17-2011-cwoo
CW10-55-5
20
2.06
1.00
8.05
0.94
1.31
6.57
1.32
3.58
1.17
f1 (ppm)


B500b_Aug17-2011-cwoo
CW10-55-5
^{13}C NMR ($CDCl_3$)
f1 (ppm)

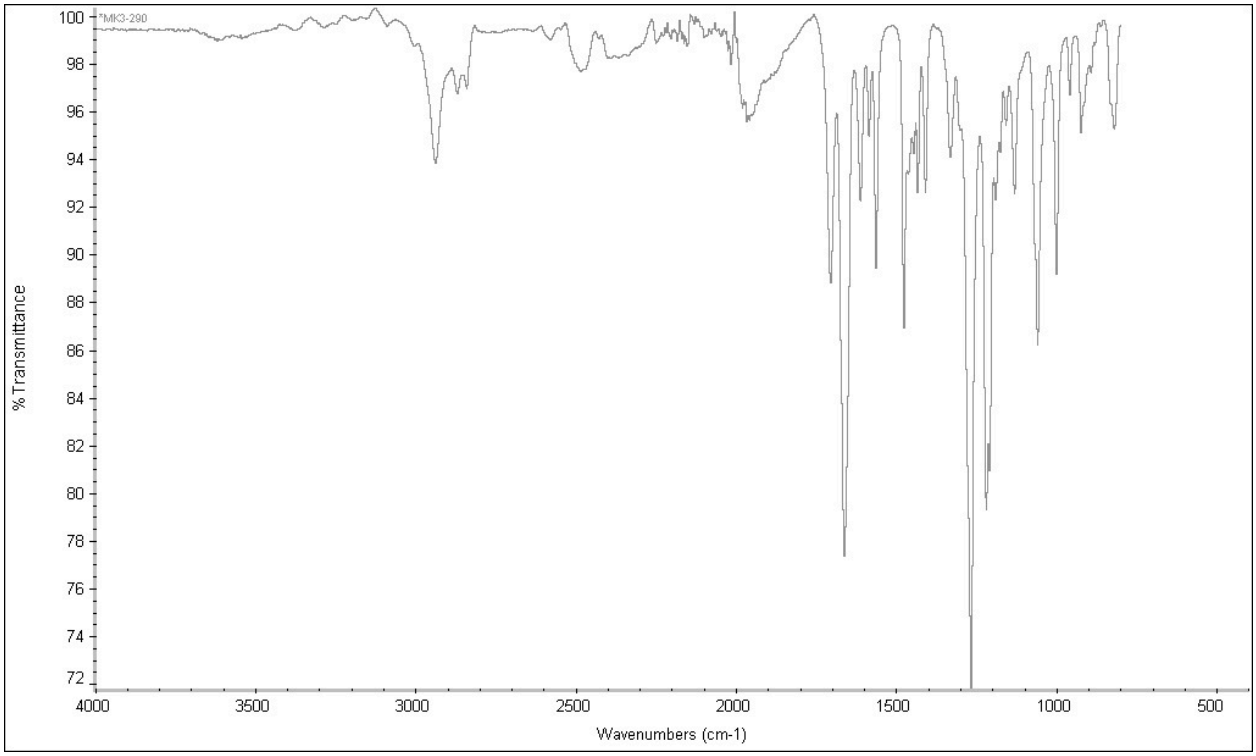
IR

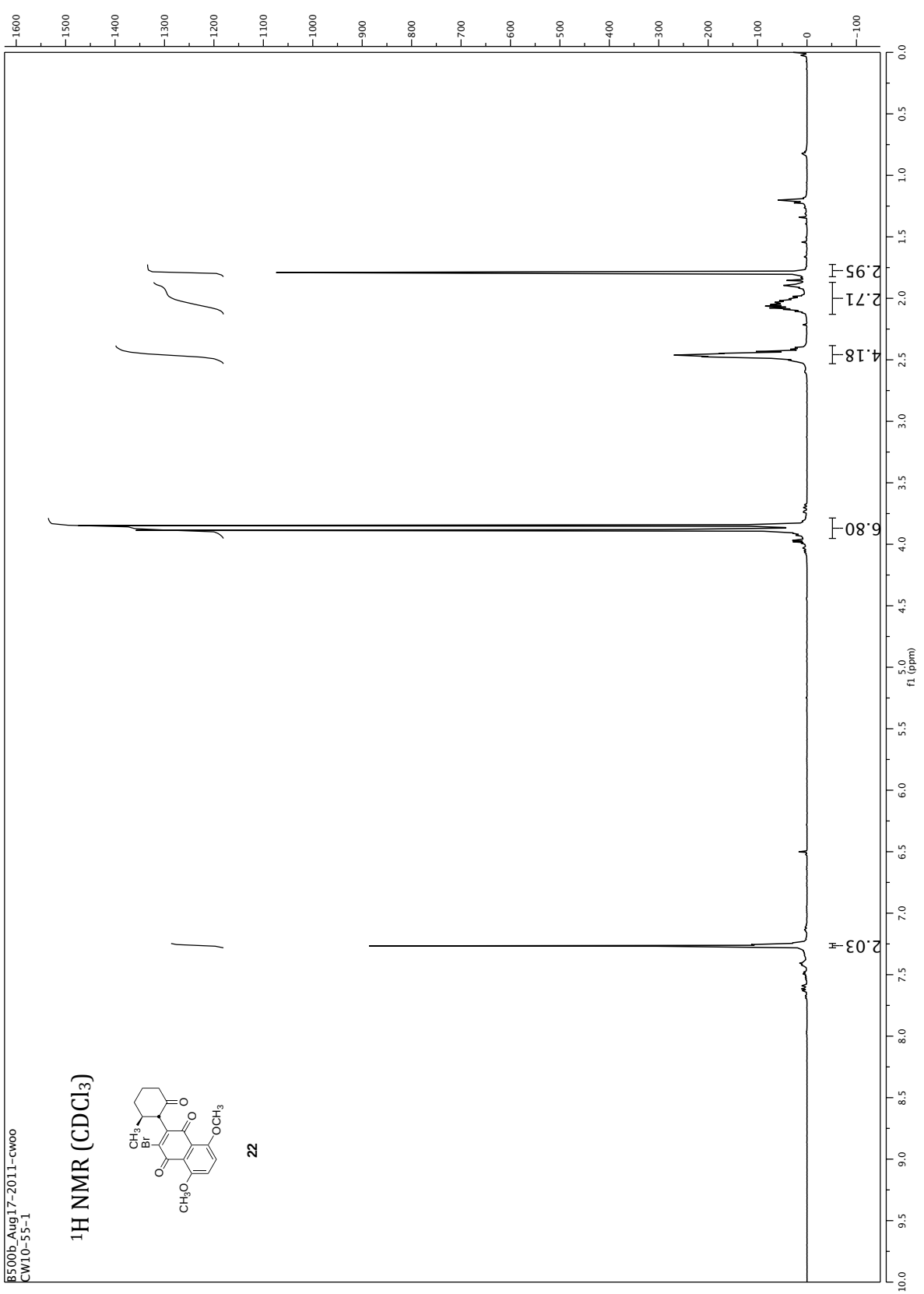

Wed Dec 28 11:05:06 2011 (GMT-05:00)
% Transmittance
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

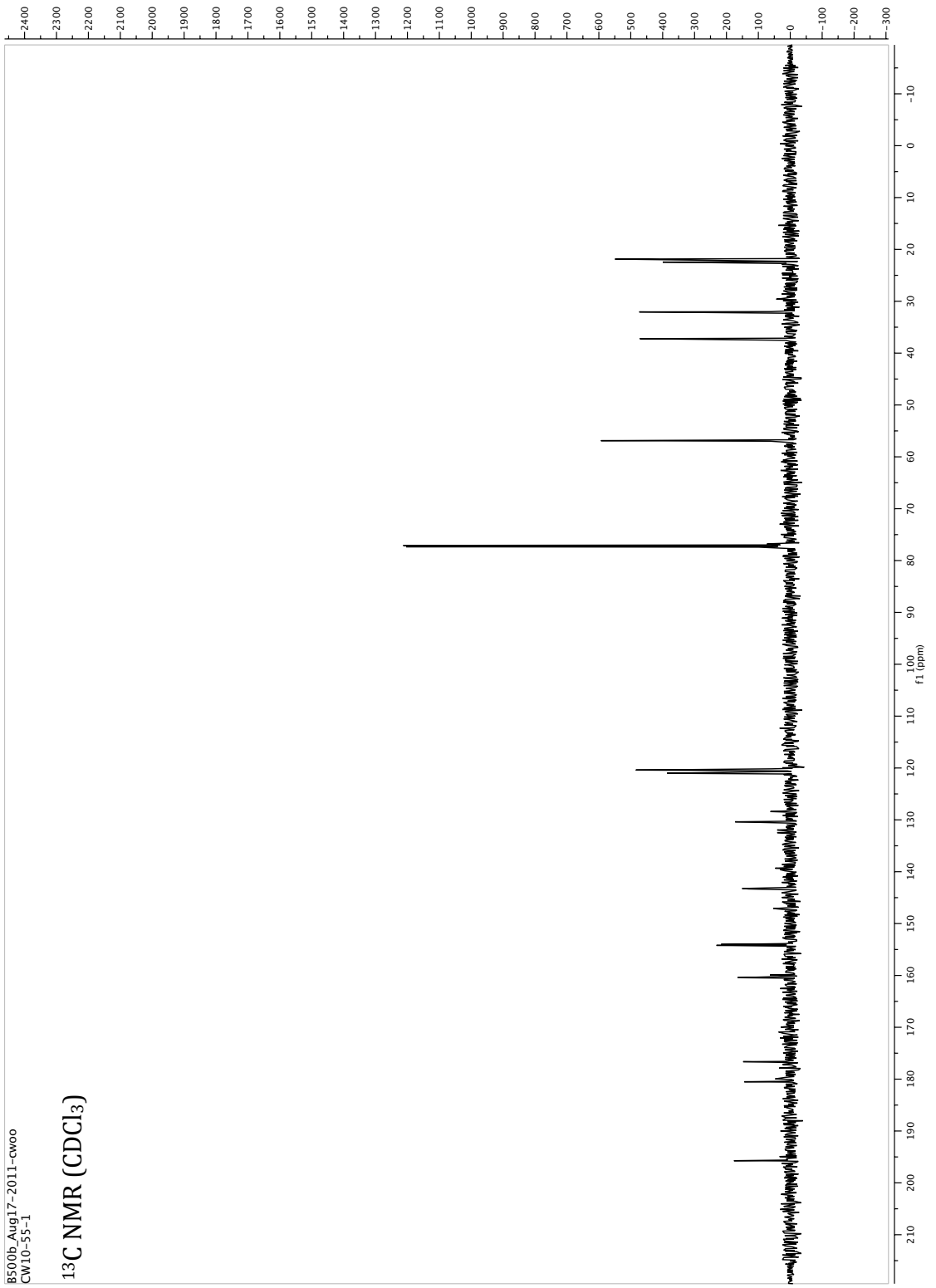

B500b_Apr10-2012-mkaneko
MK3-290
^{1}H NMR ($CDCl_3$)
21
2.00
1.21
7.13
1.21
3.45
3.87
1.44
f1 (ppm)


MK3-290-CARBON-01
MK3-290
^{13}C NMR ($CDCl_3$)
f1 (ppm)

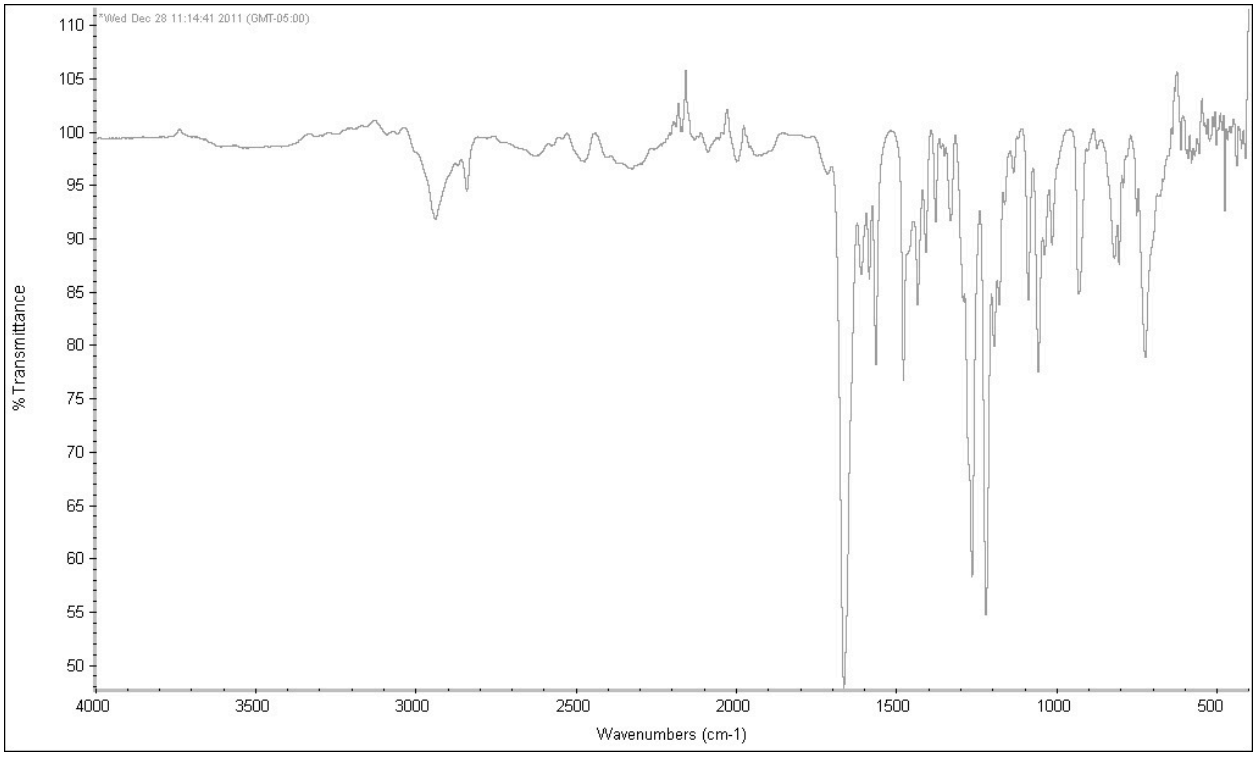
IR


MK3-29D
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


B500b_Aug17-2011-cwoo
CW10-55-1
^{1}H NMR ($CDCl_3$)
22
2.03
6.80
4.18
2.71
2.95
f1 (ppm)


B500b_Aug17-2011-cwoo
CW10-55-1
13C NMR (CDCl3)
f1 (ppm)

IR


Wed Dec 28 11:14:41 2011 (GMT-05:00)
% Transmittance
110
105
100
95
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85
80
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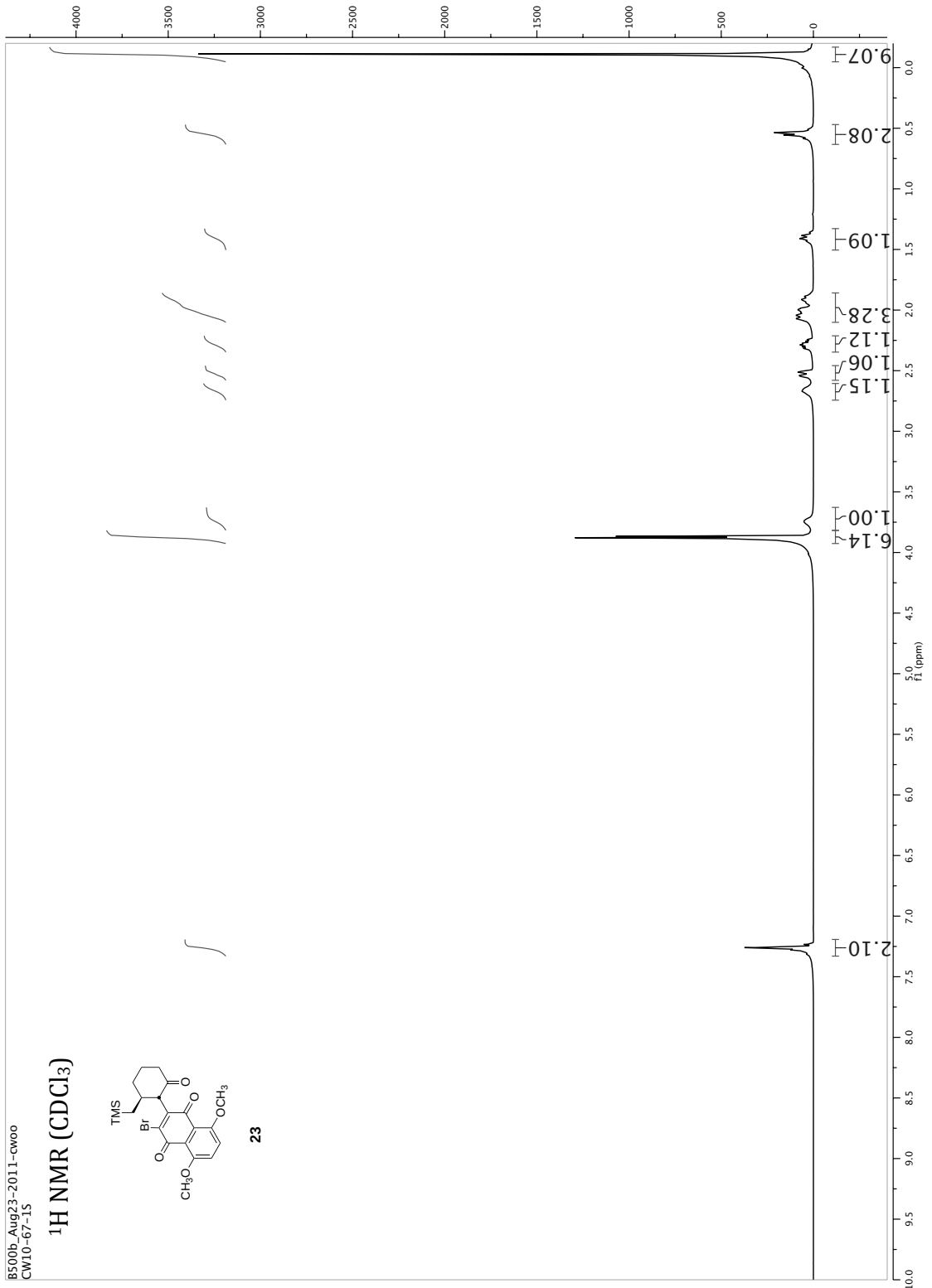
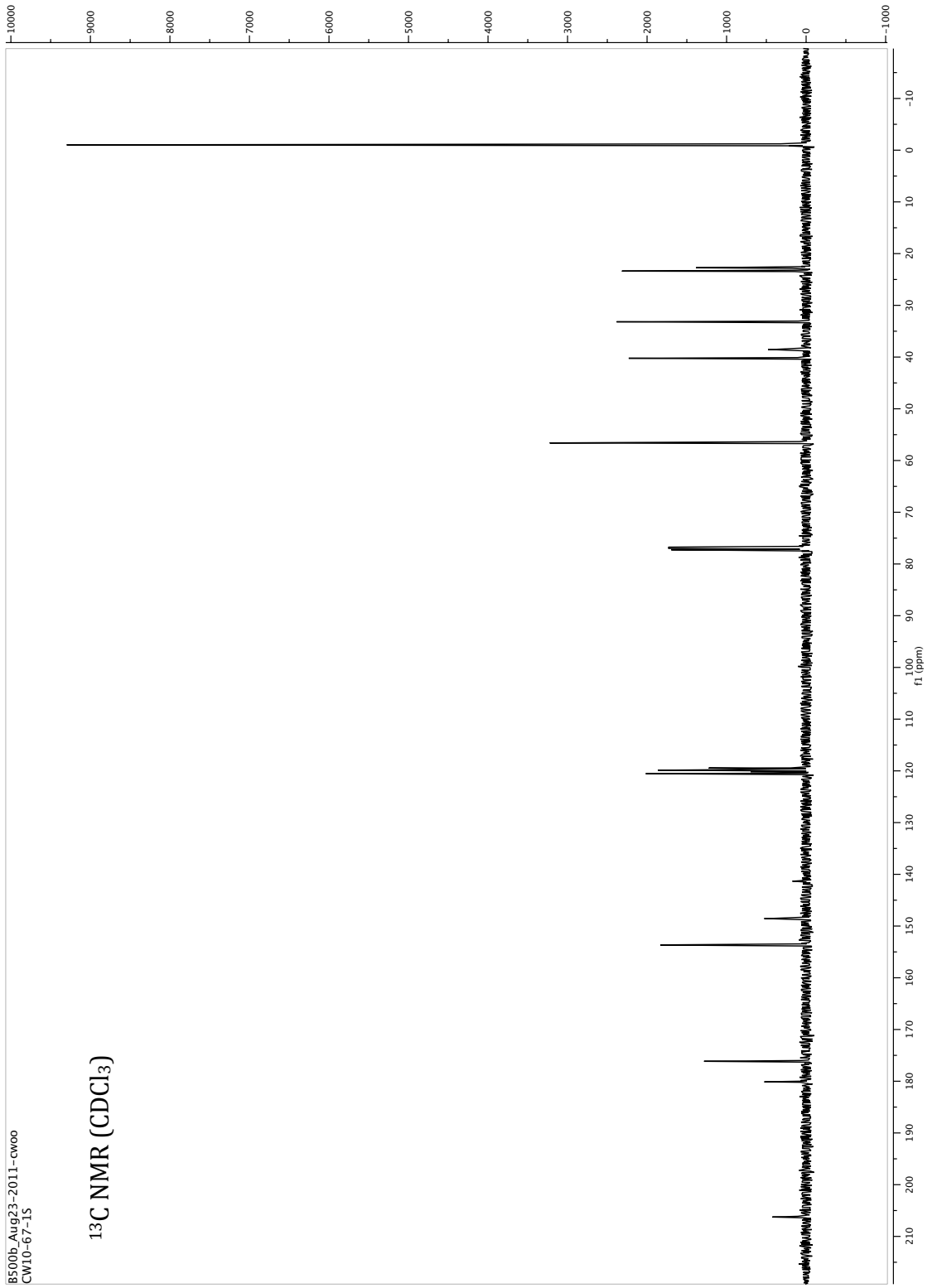
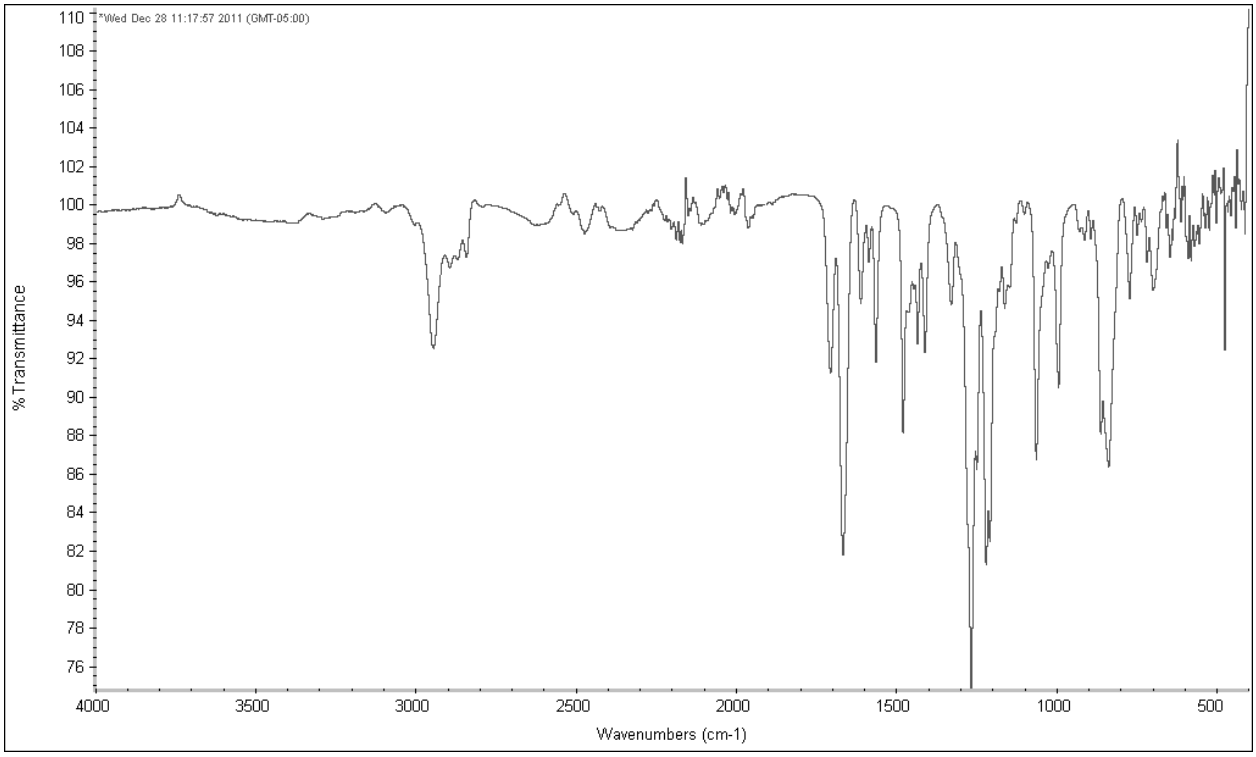
70
65
60
55
50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


B500b_Aug23-2011-cwoo
CW10-67-1S
^{1}H NMR ($CDCl_3$)
TMS
Br
O
O
O
OCH_3
CH_3O
23
9.07
2.08
1.09
3.28
1.12
1.06
1.15
1.00
6.14
2.10
f1 (ppm)


B500b_Aug23-2011-cwoo
CW10-67-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

IR


Wed Dec 28 11:17:57 2011 (GMT-05:00)
% Transmittance
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108
106
104
102
100
98
96
94
92
90
88
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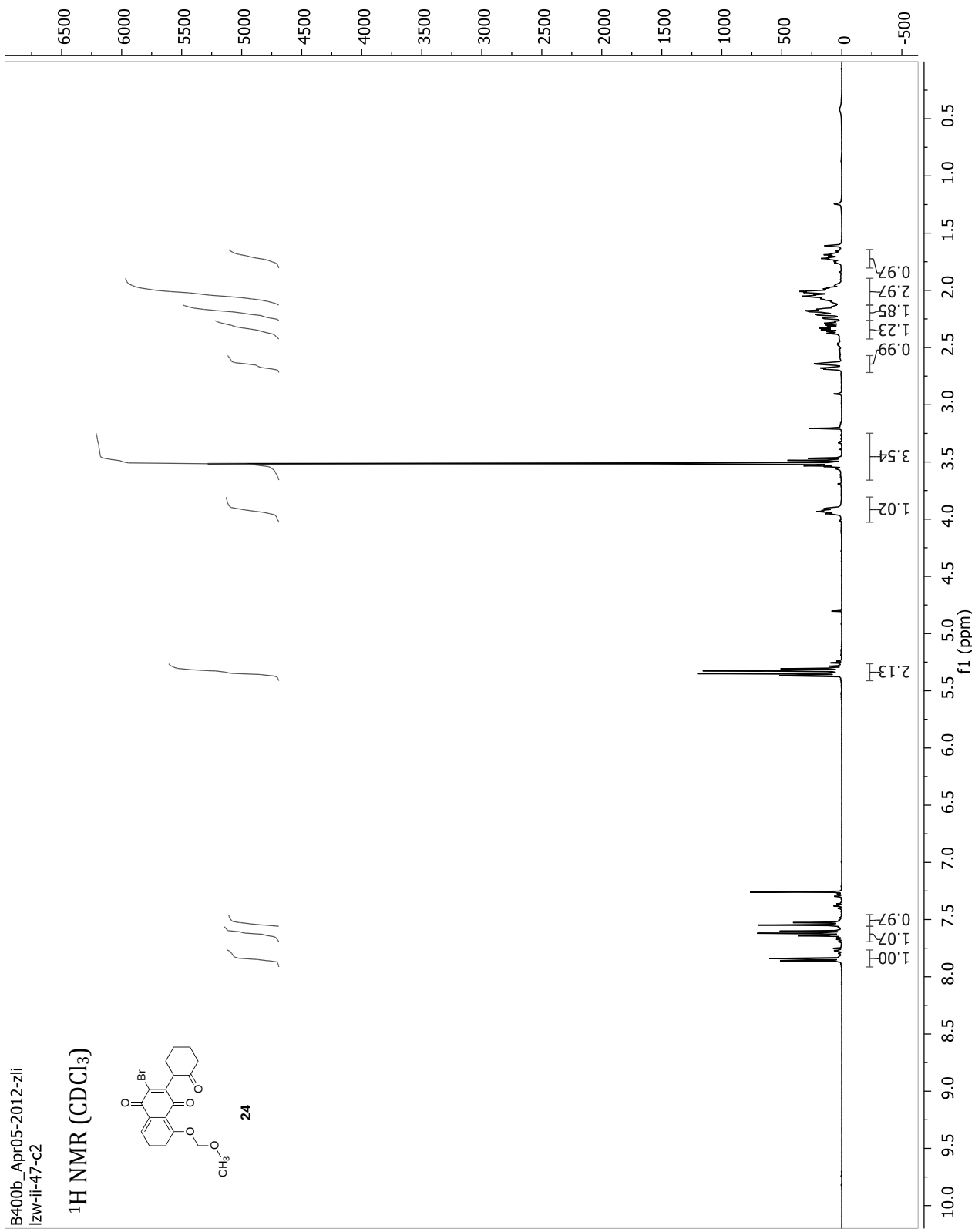
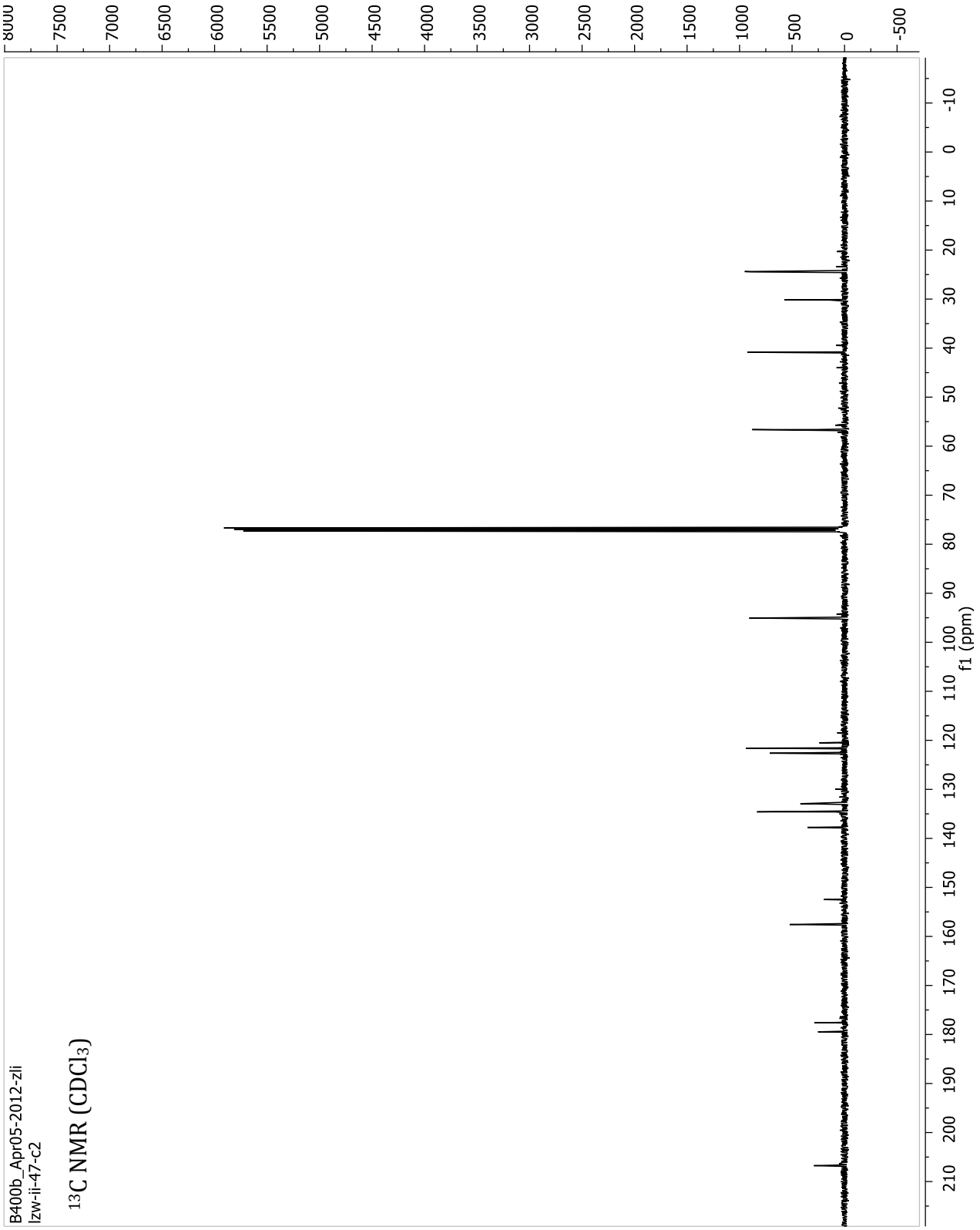
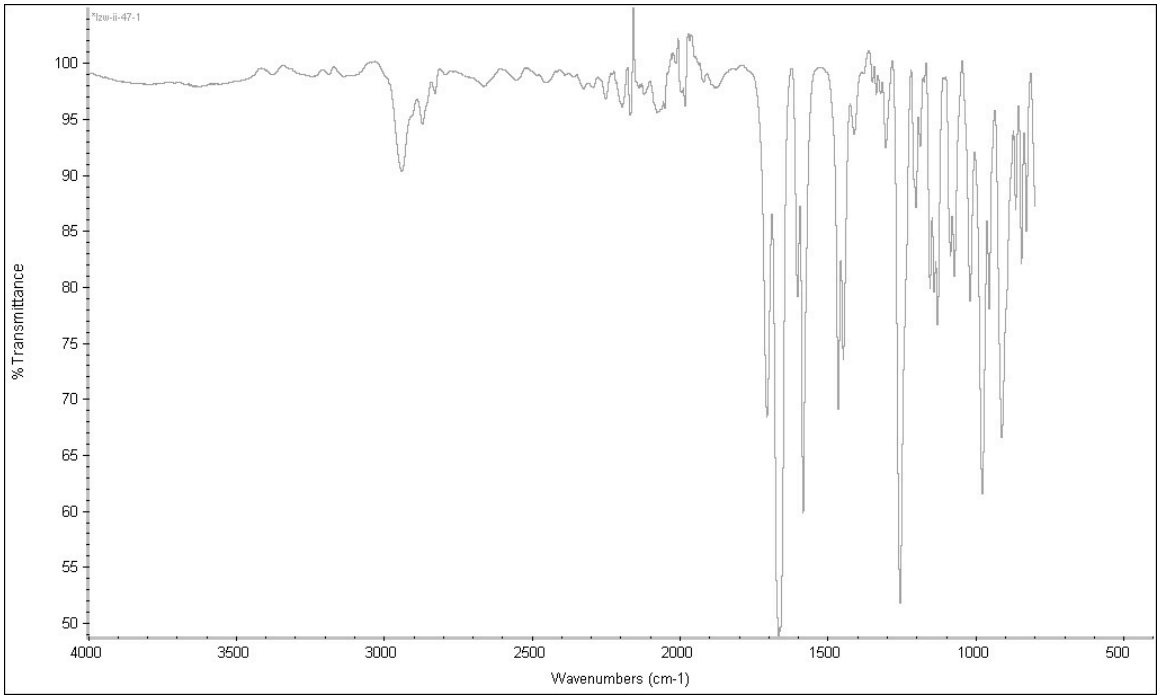
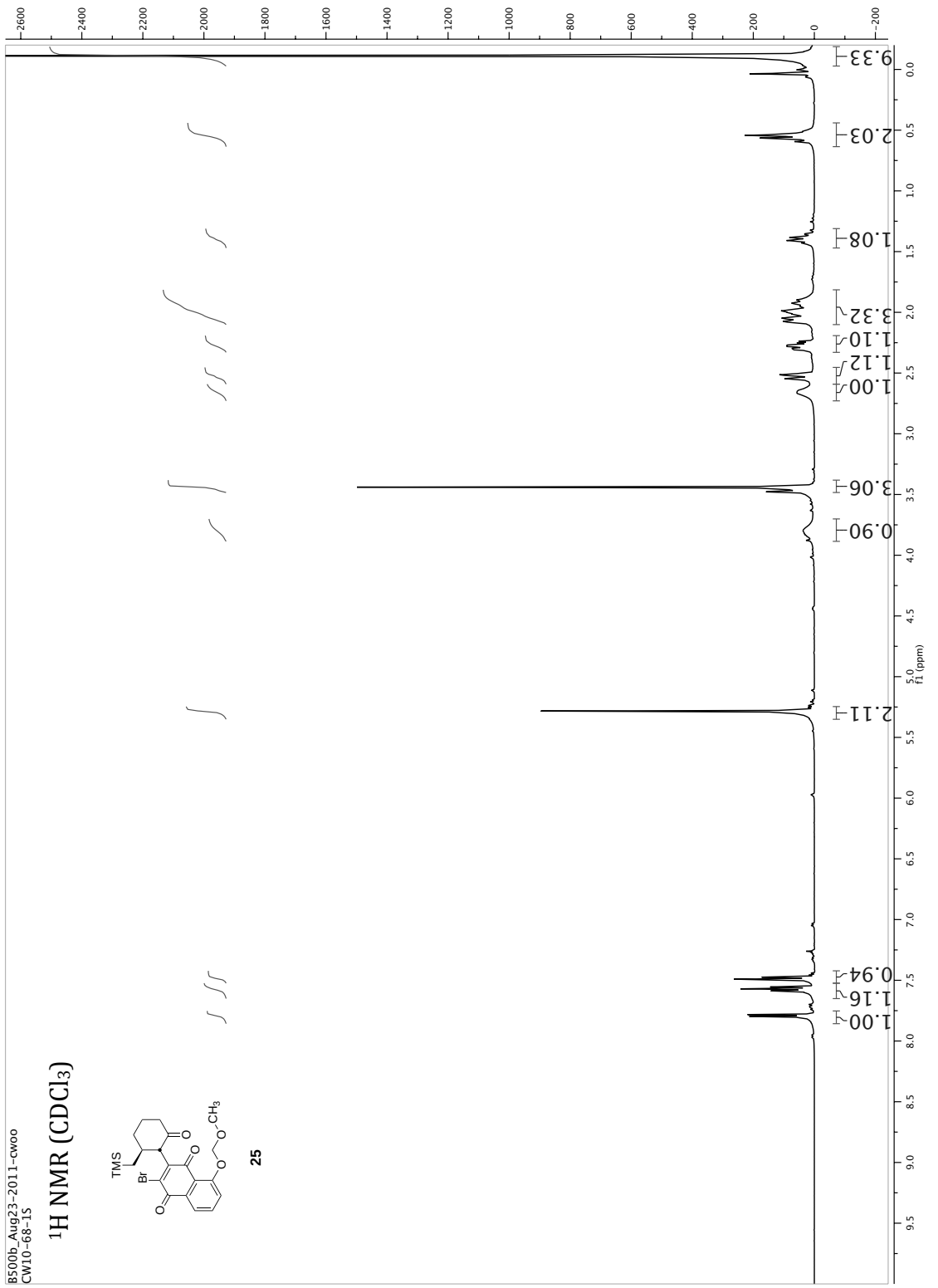
84
82
80
78
76
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

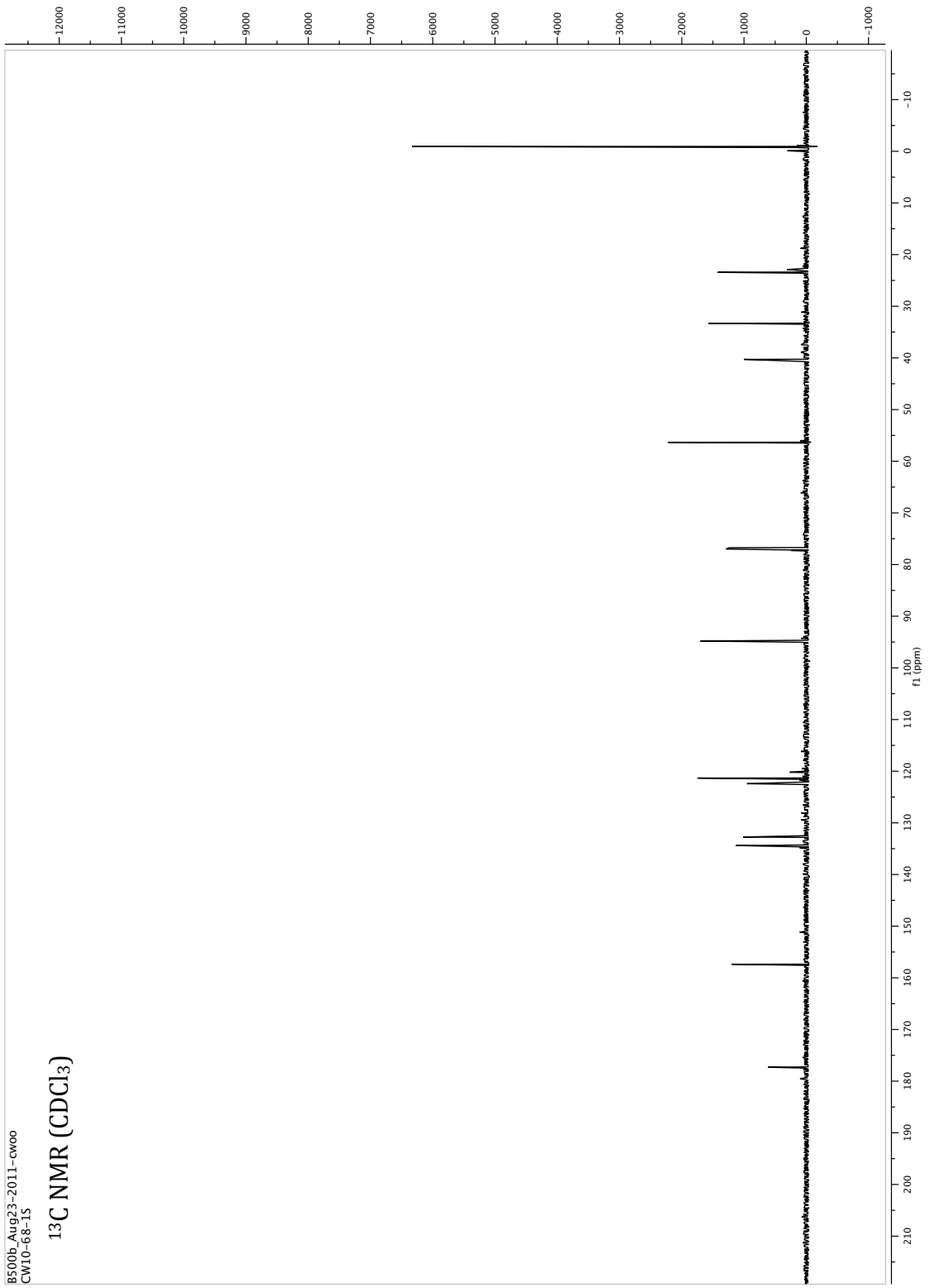

B400b_Apr05-2012-zli
lzw-ii-47-c2
^{1}H NMR ($CDCl_3$)
24
Br
O
O
O
O
CH_3
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0.97
2.97
1.85
1.23
0.99
3.54
1.02
2.13
0.97
1.07
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


B400b_Apr05-2012-zli
lzw-ii-47-c2
^{13}C NMR ($CDCl_3$)
f1 (ppm)

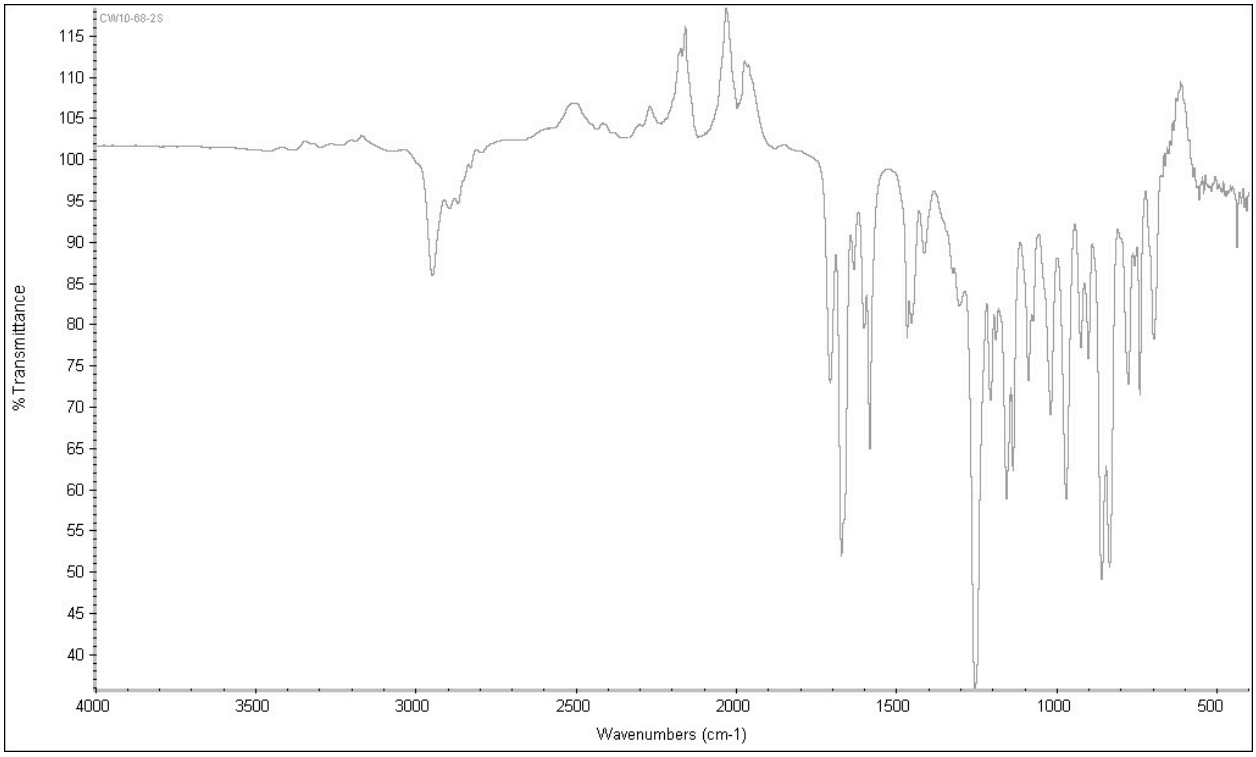
IR

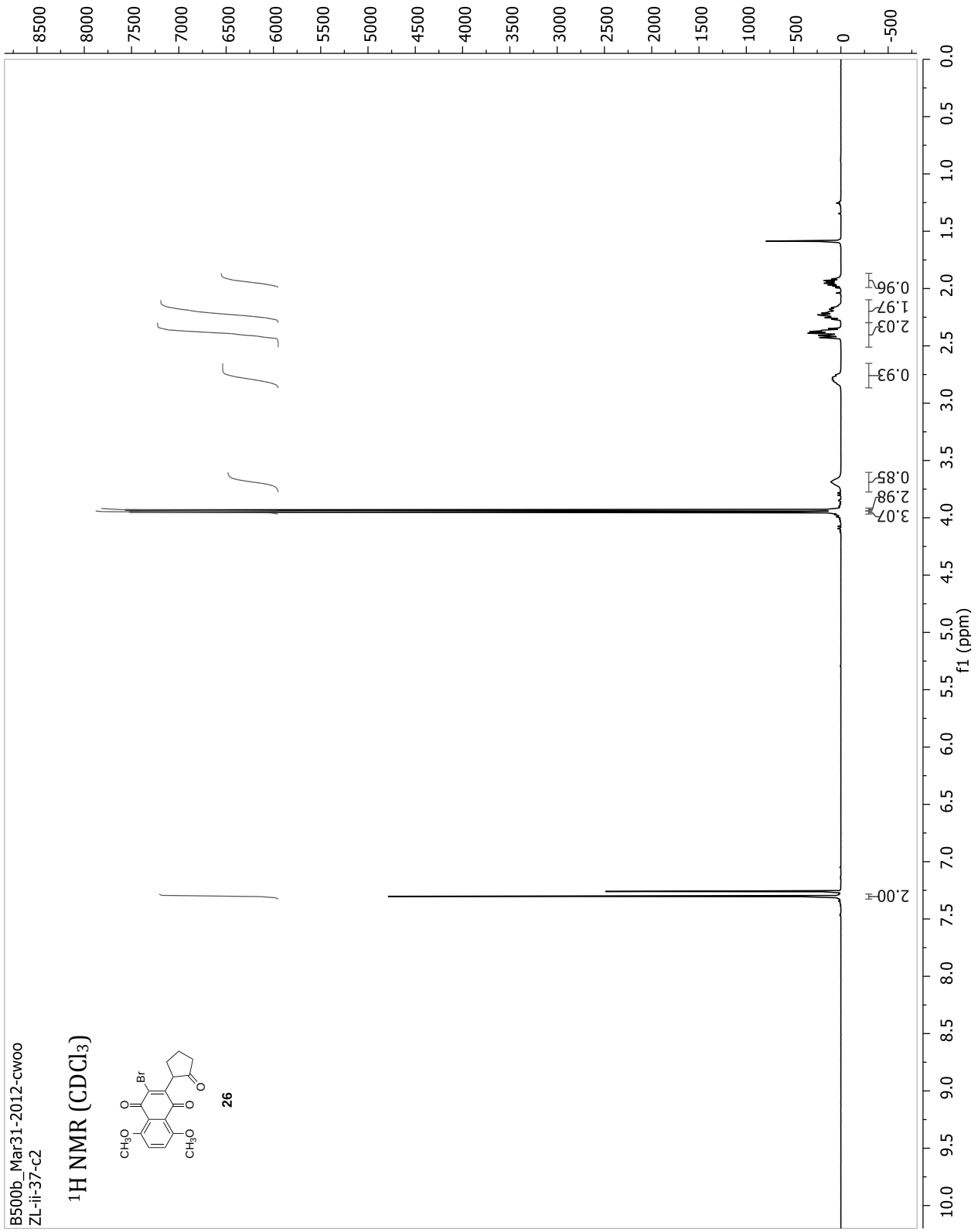

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

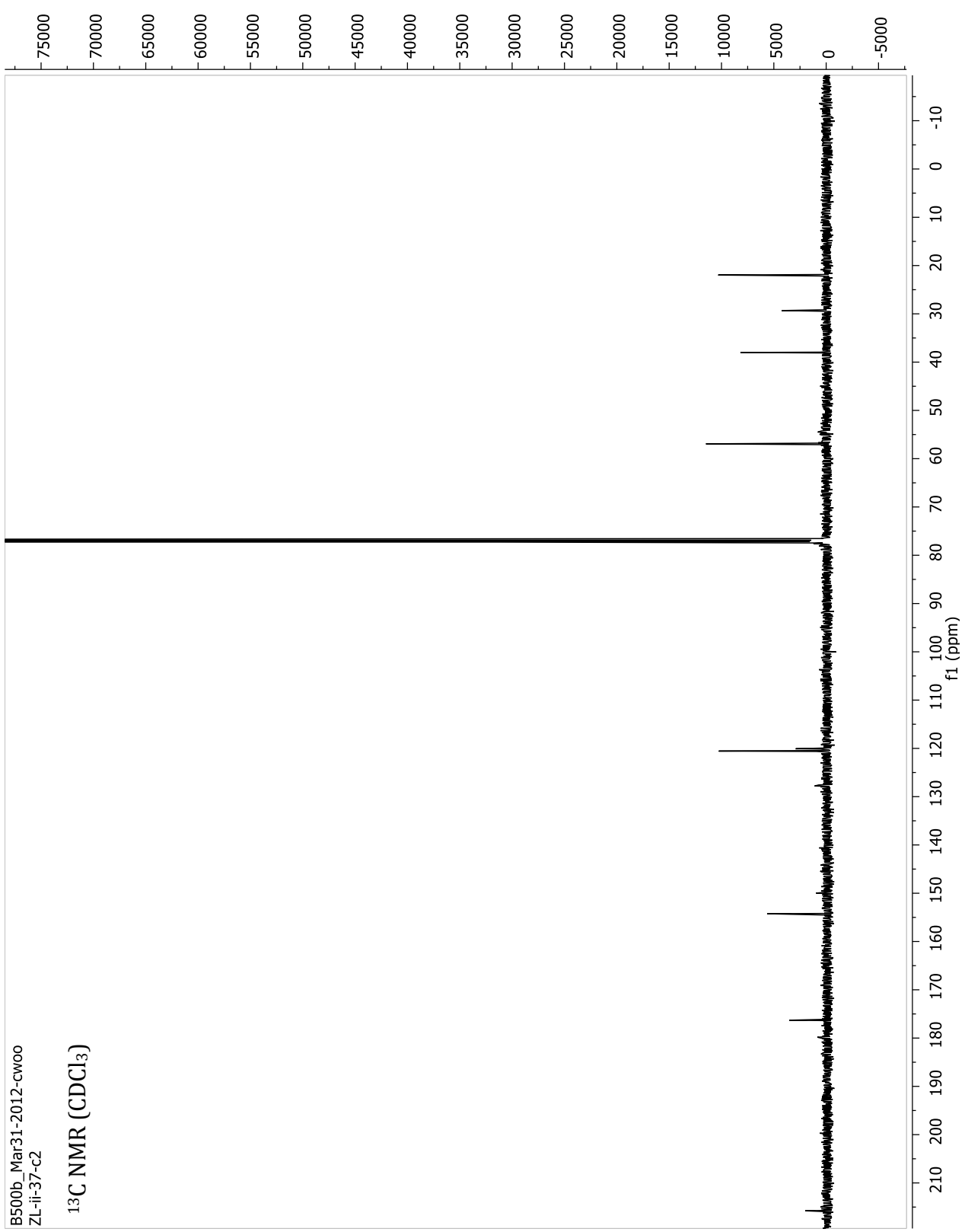

B500b_Aug23-2011-cwoo
CW10-68-1S
^{1}H NMR ($CDCl_3$)
TMS
Br
CH_3
25
9.33
2.03
1.08
3.32
1.10
1.12
1.00
3.06
0.90
2.11
0.94
1.16
1.00
f1 (ppm)


B500b_Aug23-2011-cwoo
CW10-68-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

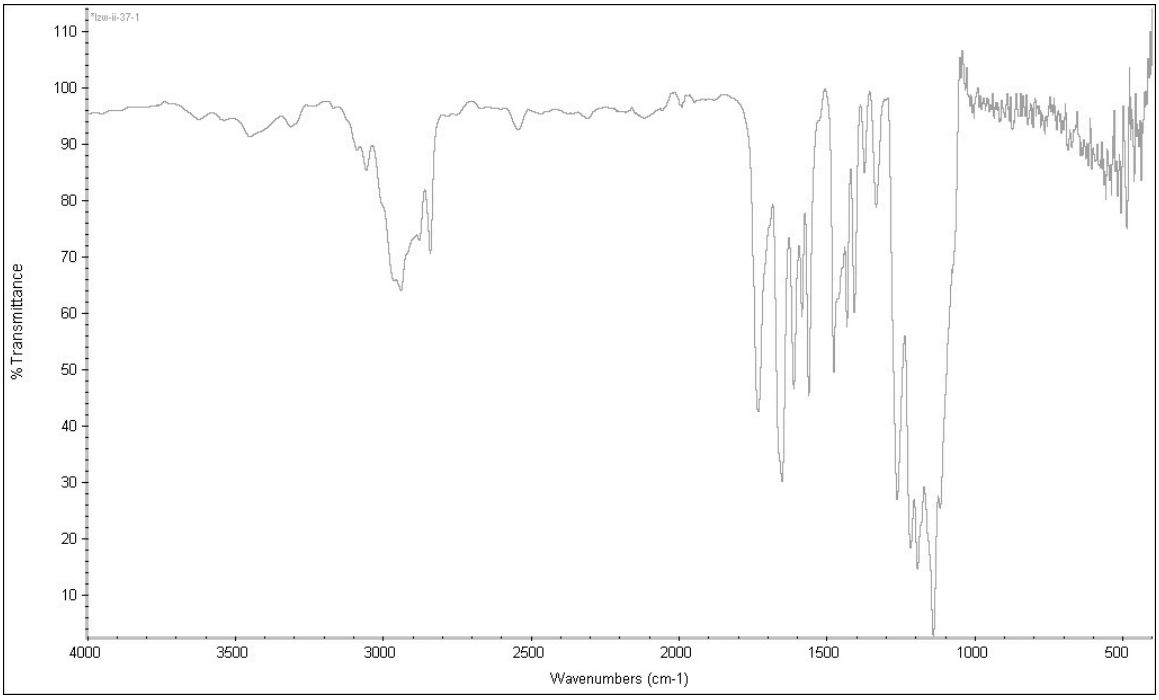
IR

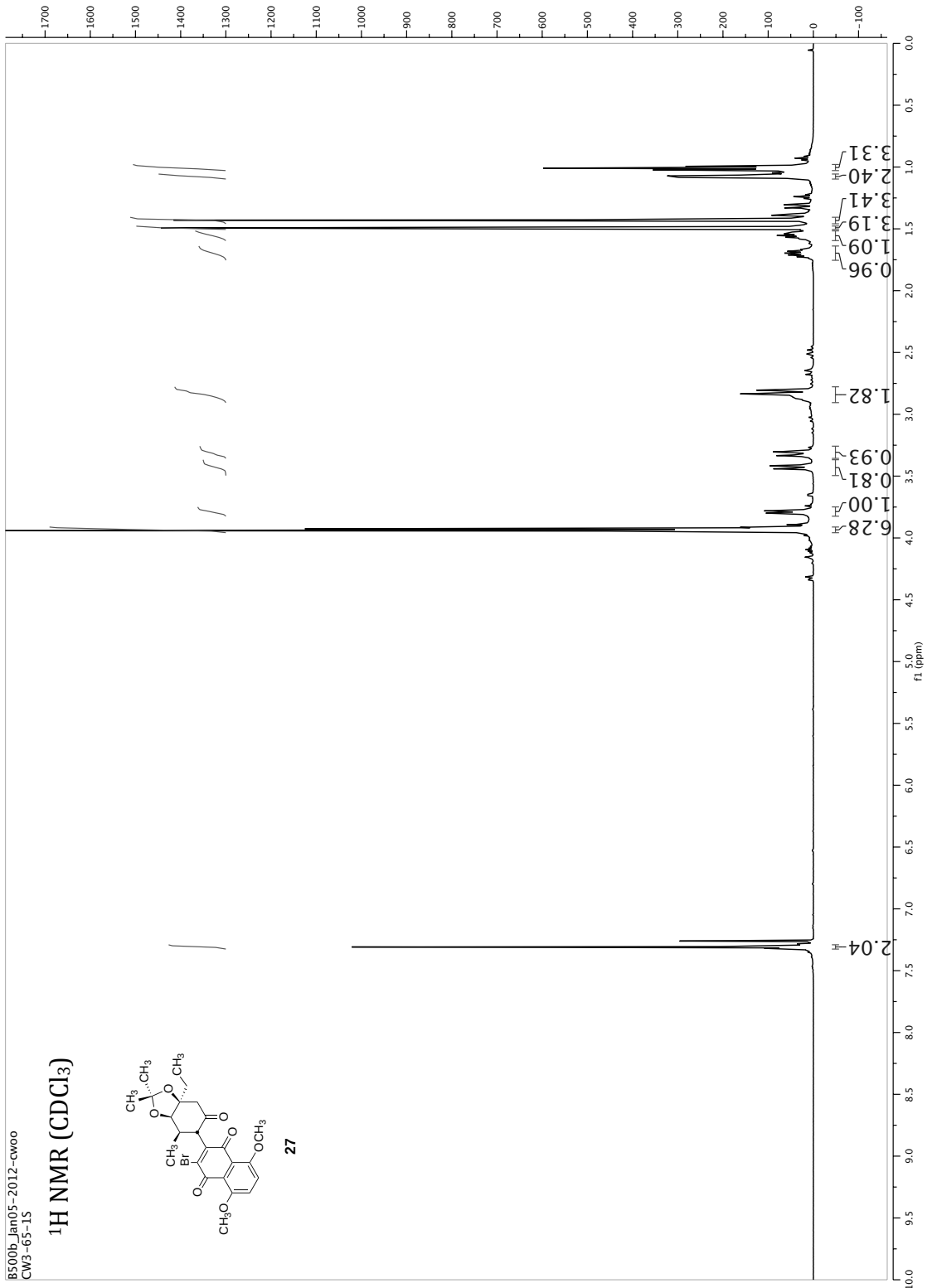

CW10-68-2S
% Transmittance
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

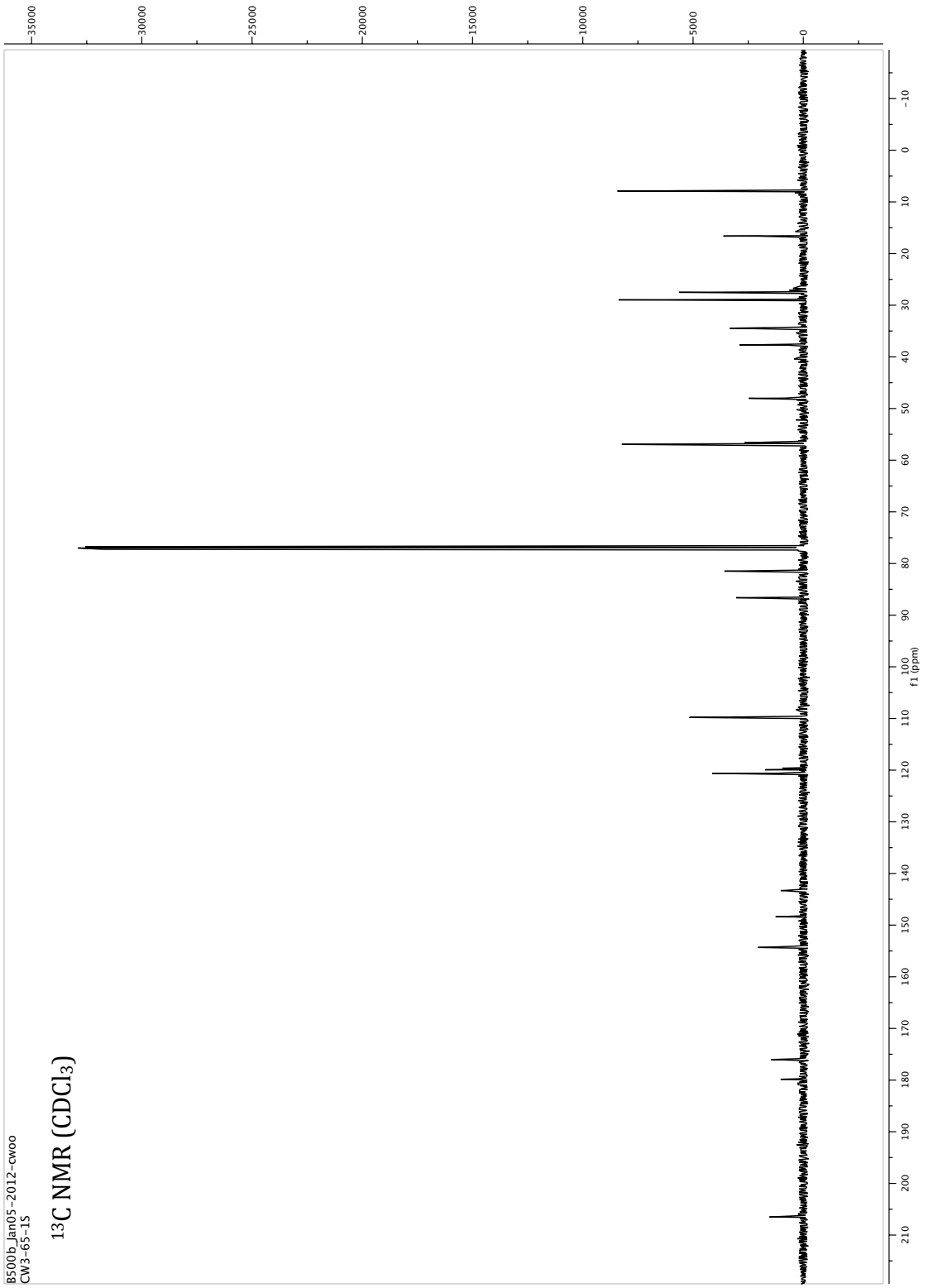

B500b_Mar31-2012-cwoo
ZL-ii-37-c2
^{1}H NMR ($CDCl_3$)
26
2.00
3.07
2.98
0.85
0.93
2.03
1.97
0.96
f1 (ppm)


B500b_Mar31-2012-cwoo
ZL-ii-37-c2
^{13}C NMR ($CDCl_3$)
f1 (ppm)

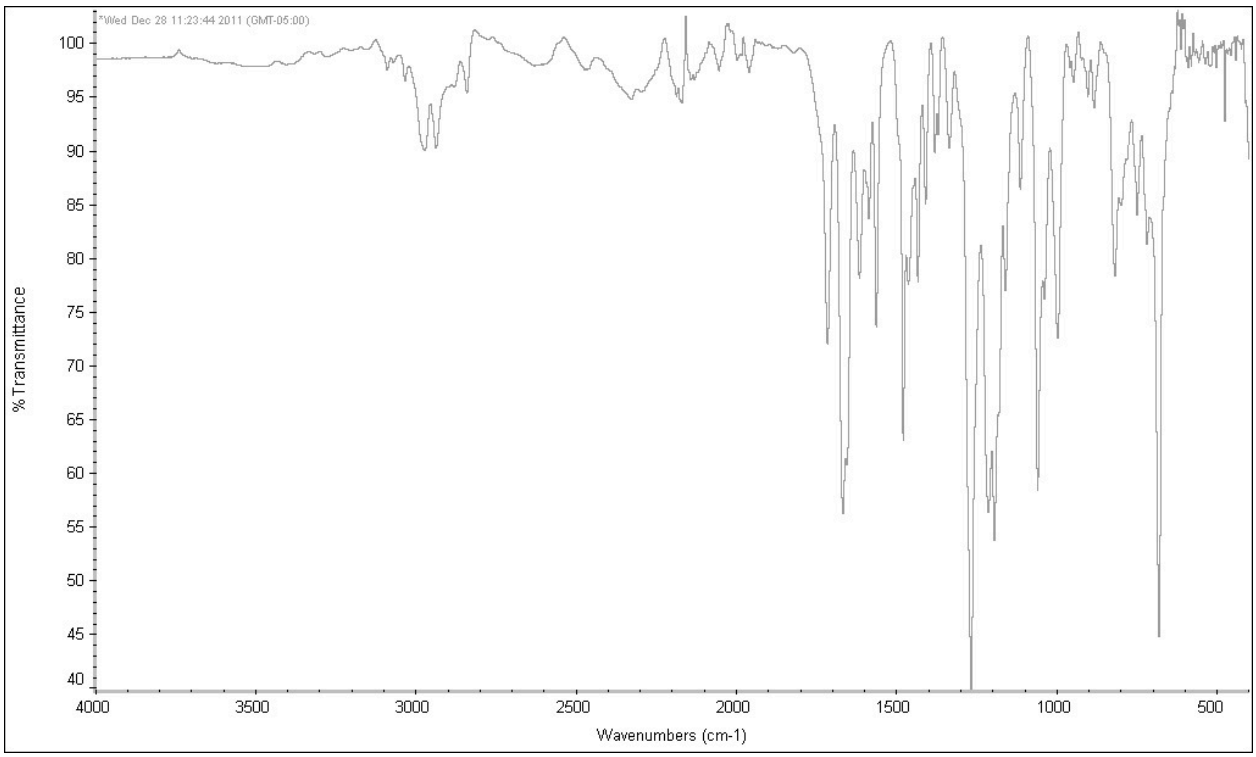
IR

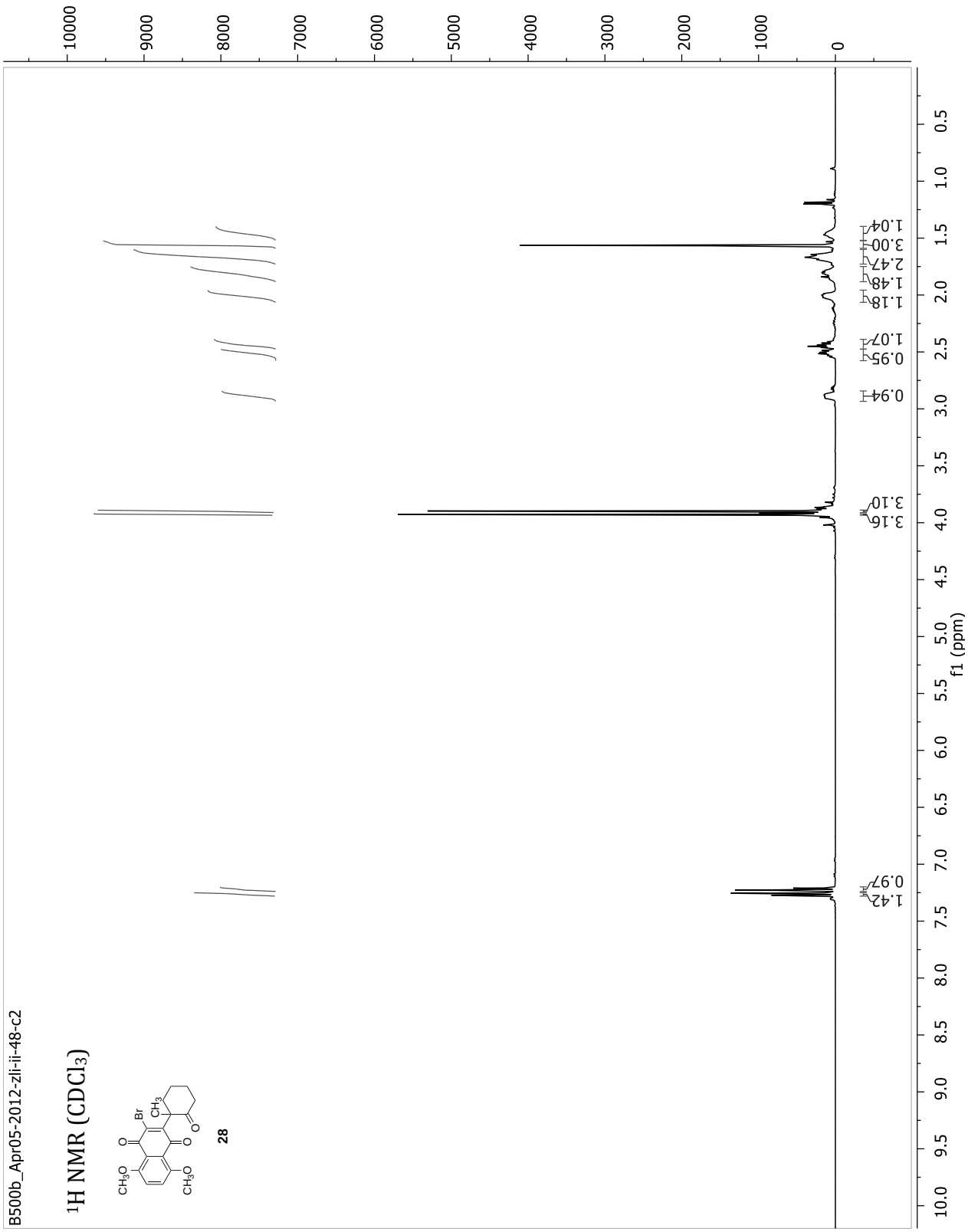

%Transmittance
110
100
90
80
70
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

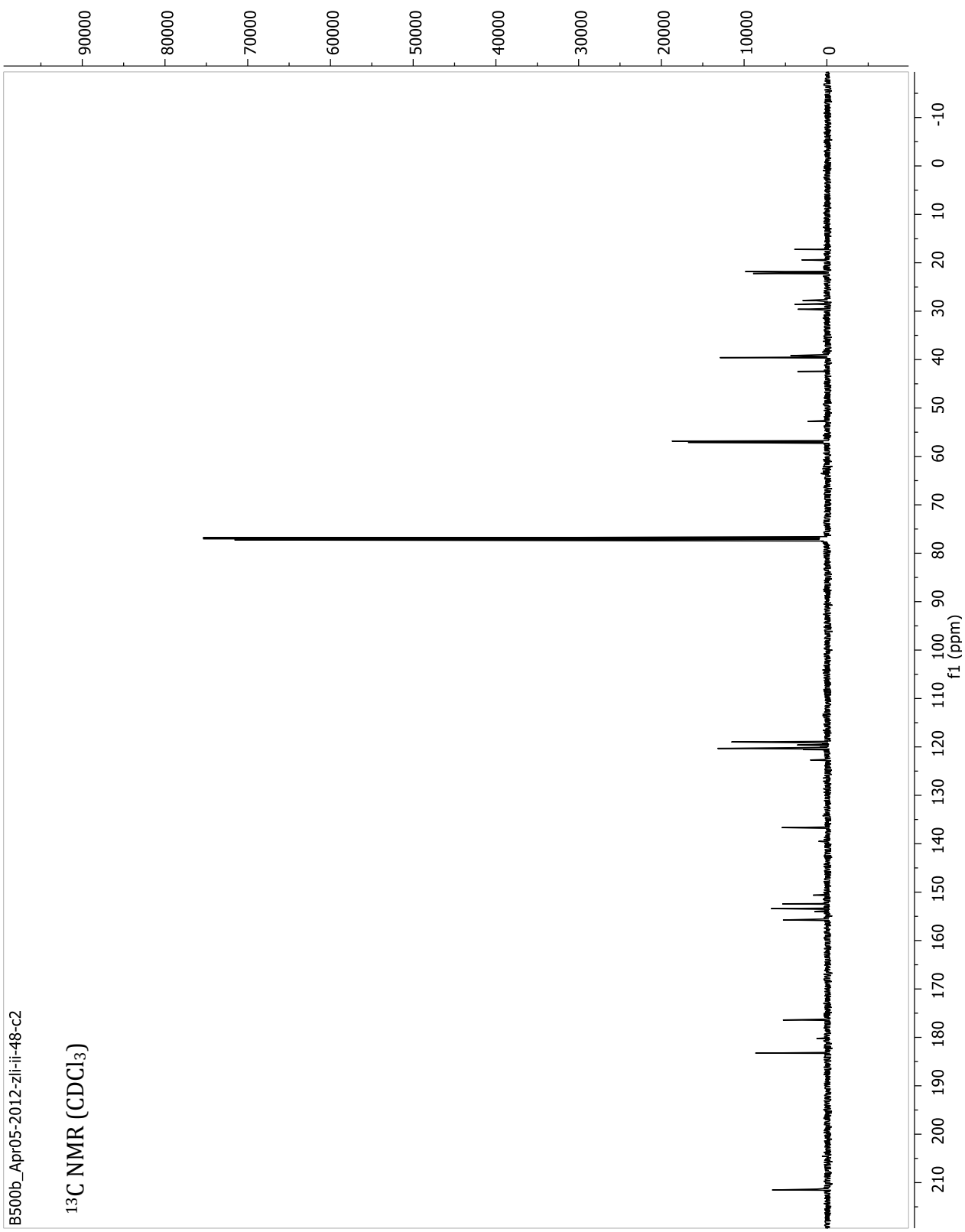

B500b_Jan05-2012-cwoo
CW3-65-1S
^{1}H NMR ($CDCl_3$)
27
2.04
6.28
1.00
0.81
0.93
1.82
0.96
1.09
3.19
3.41
2.40
3.31
f1 (ppm)


B500b_Jan05-2012-cwoo
CW3-65-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

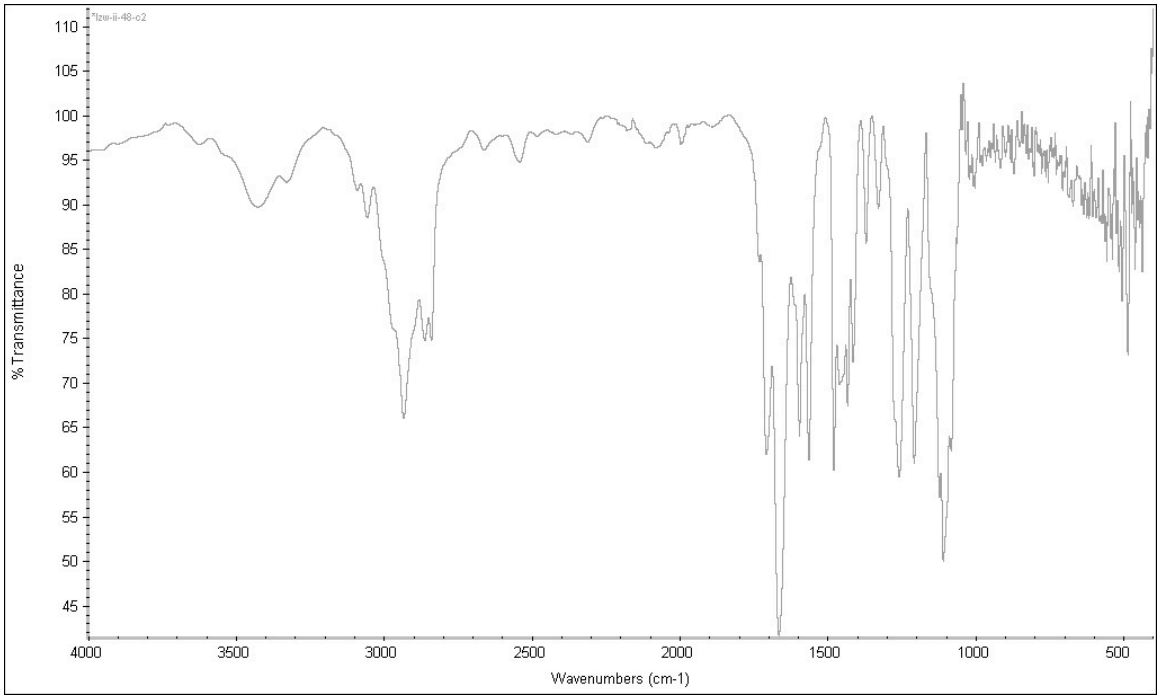
IR

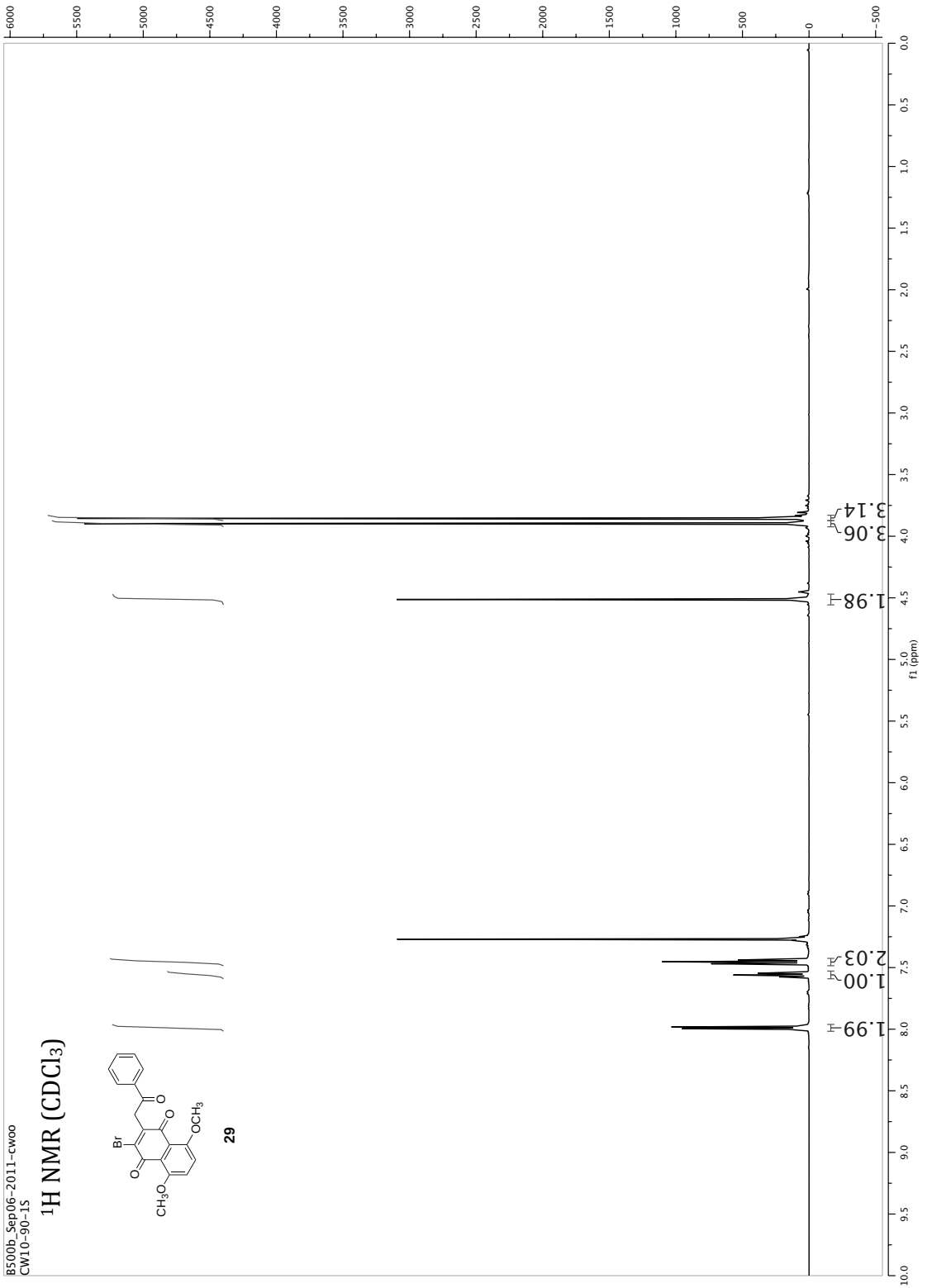

Wed Dec 28 11:23:44 2011 (GMT-05:00)
% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

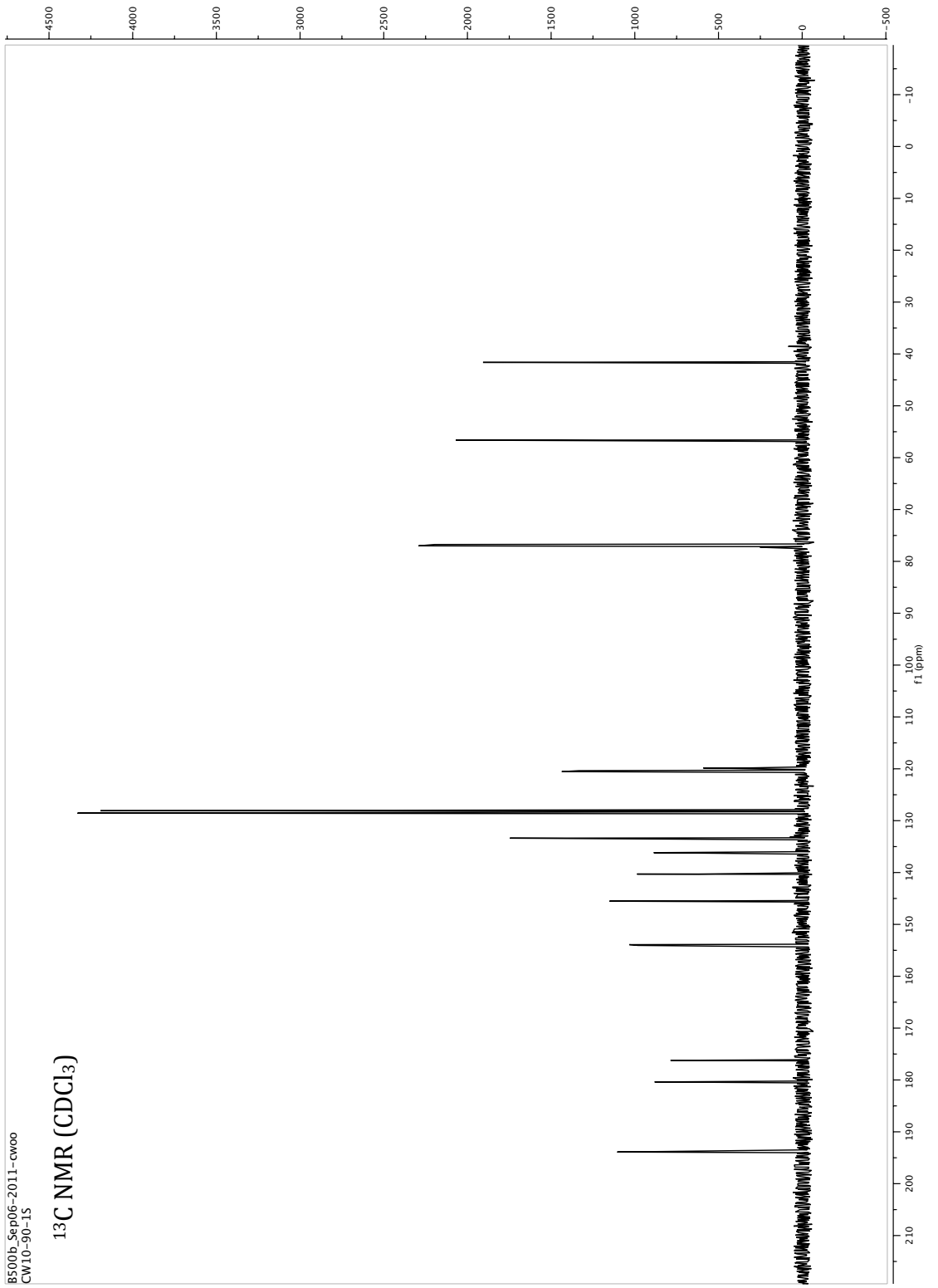

B500b_Apr05-2012-zli-ii-48-c2
^{1}H NMR ($CDCl_3$)
28
f1 (ppm)
1.42
0.97
3.16
3.10
0.94
0.95
1.07
1.18
1.48
2.47
3.00
1.04


B500b_Apr05-2012-zli-ii-48-c2
^{13}C NMR ($CDCl_3$)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

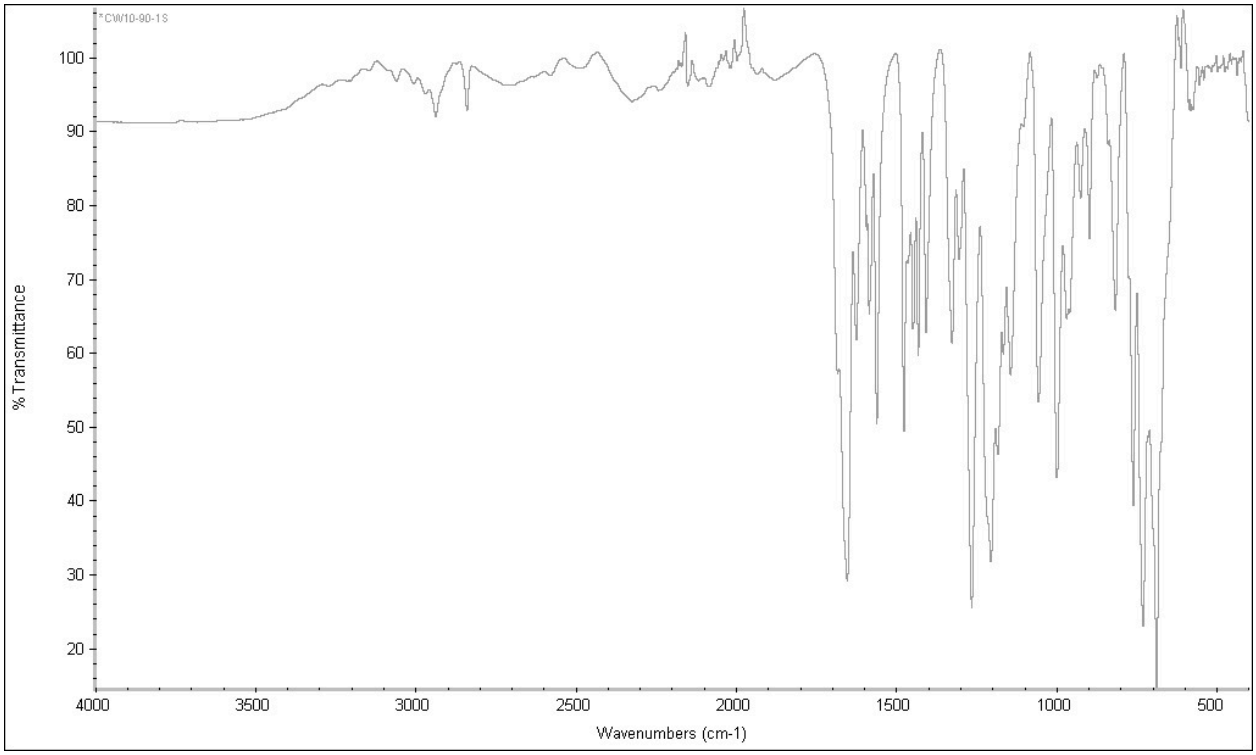
IR

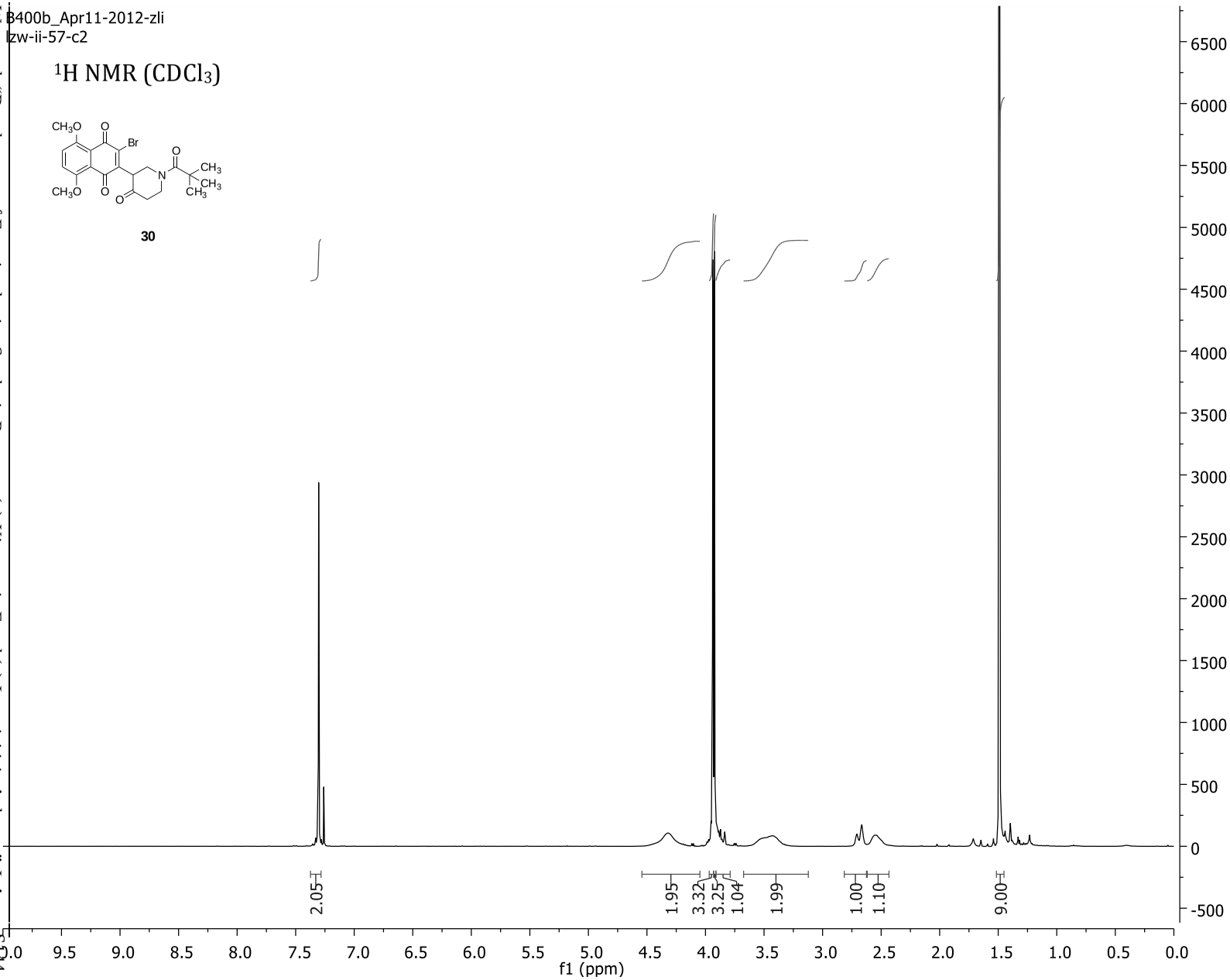

% Transmittance
110
105
100
95
90
85
80
75
70
65
60
55
50
45
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

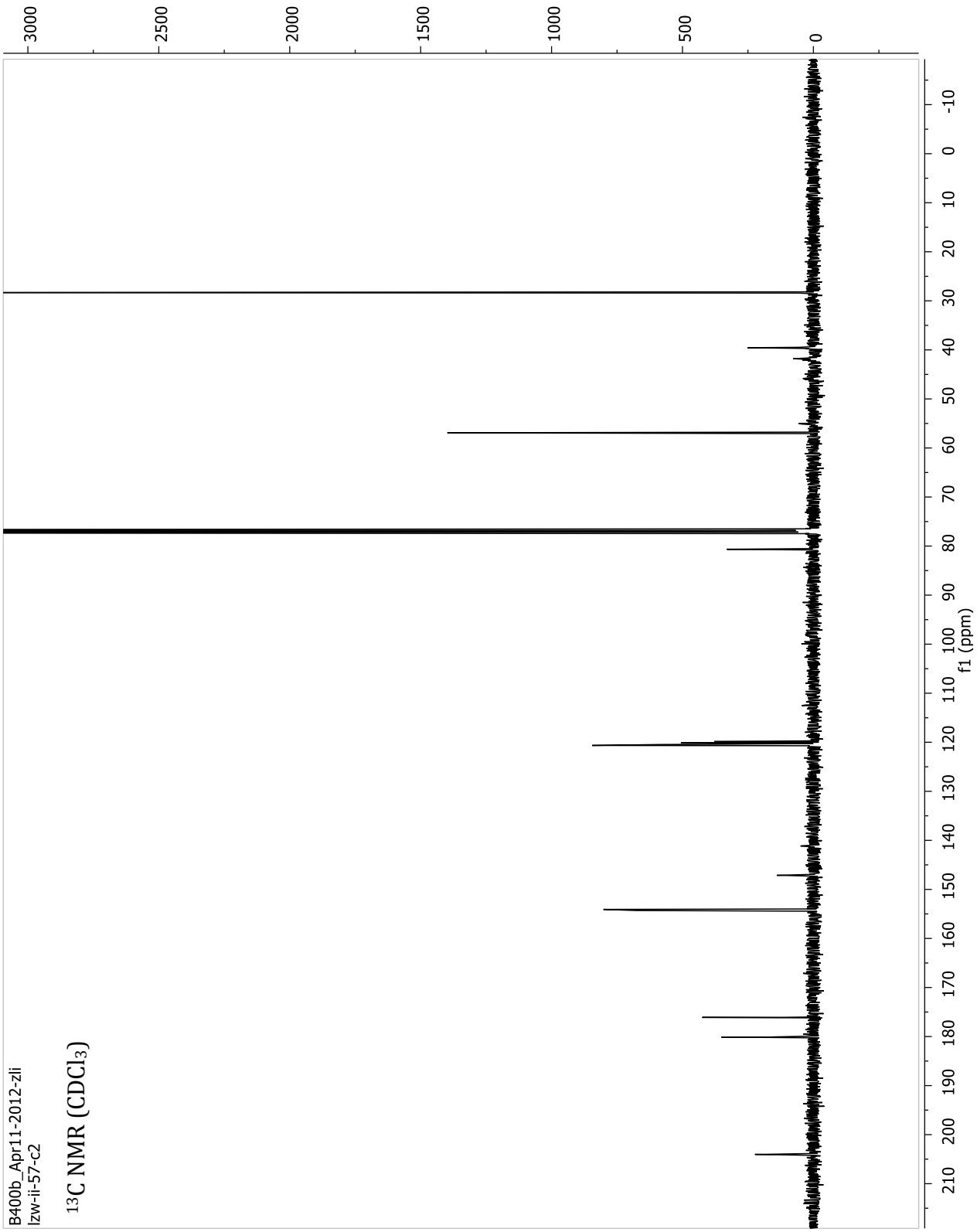

B500b_Sep06-2011-cwoo
CW10-90-1S
^{1}H NMR ($CDCl_3$)
29
3.14
3.06
1.98
2.03
1.00
1.99
f1 (ppm)


^{13}C NMR ($CDCl_3$)
B500b_Sep06-2011-cwoo
CW10-90-1S
f1 (ppm)

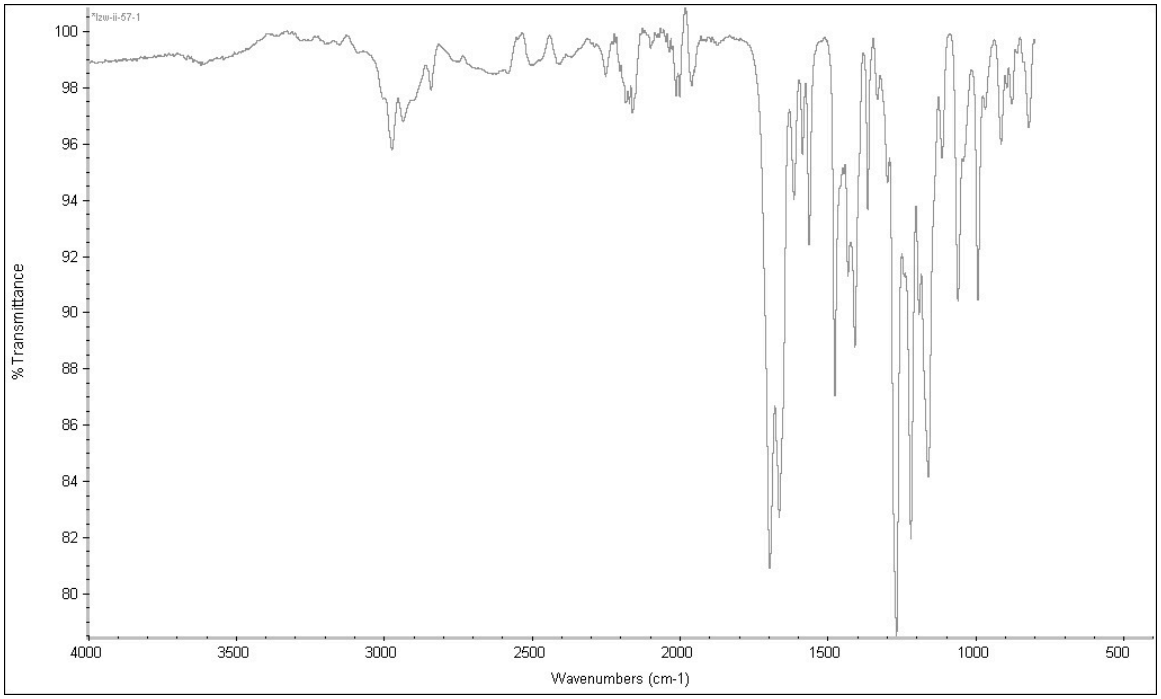
IR

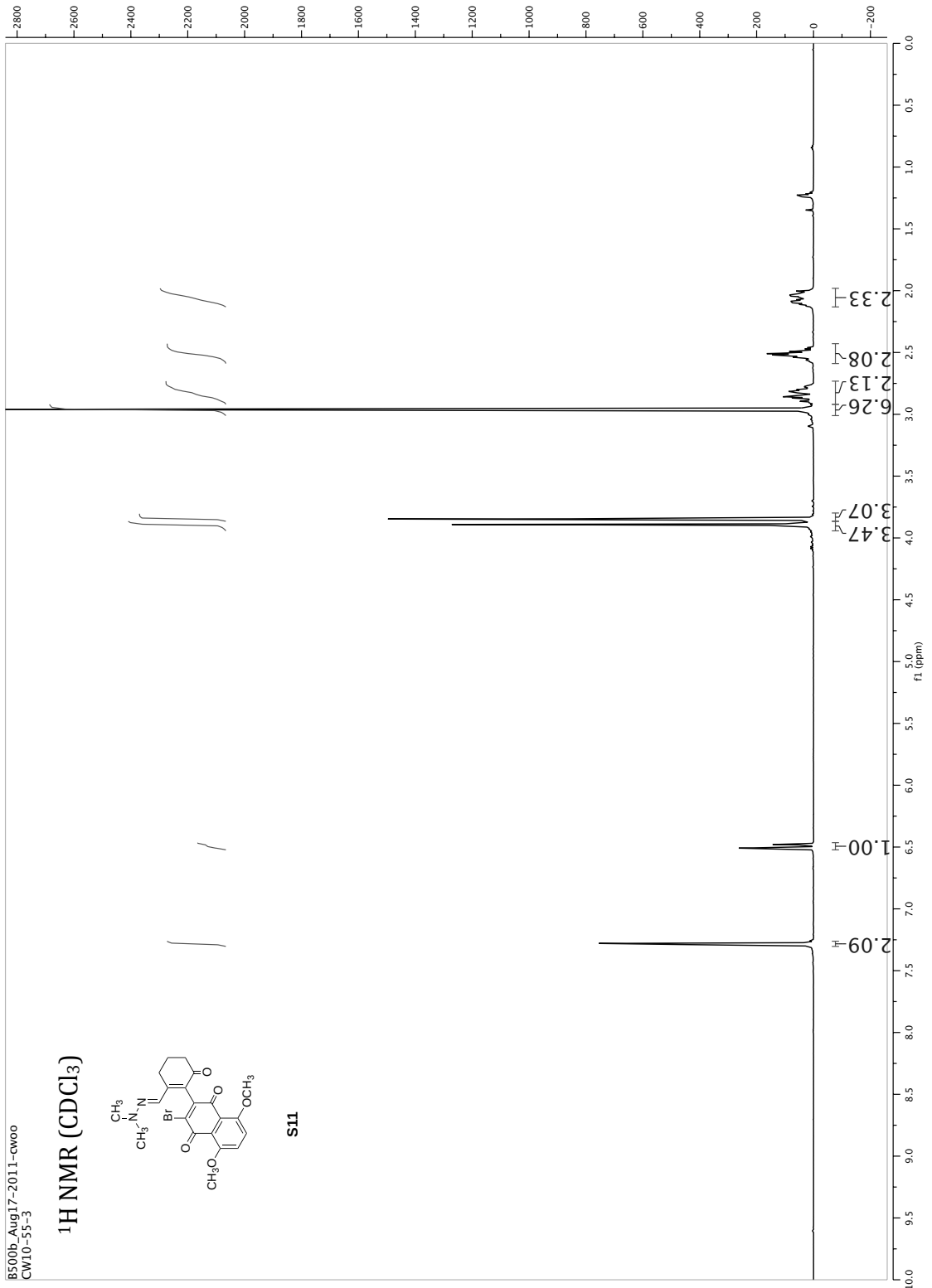

*CW10-90-1S
100
90
80
70
60
50
40
30
20
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

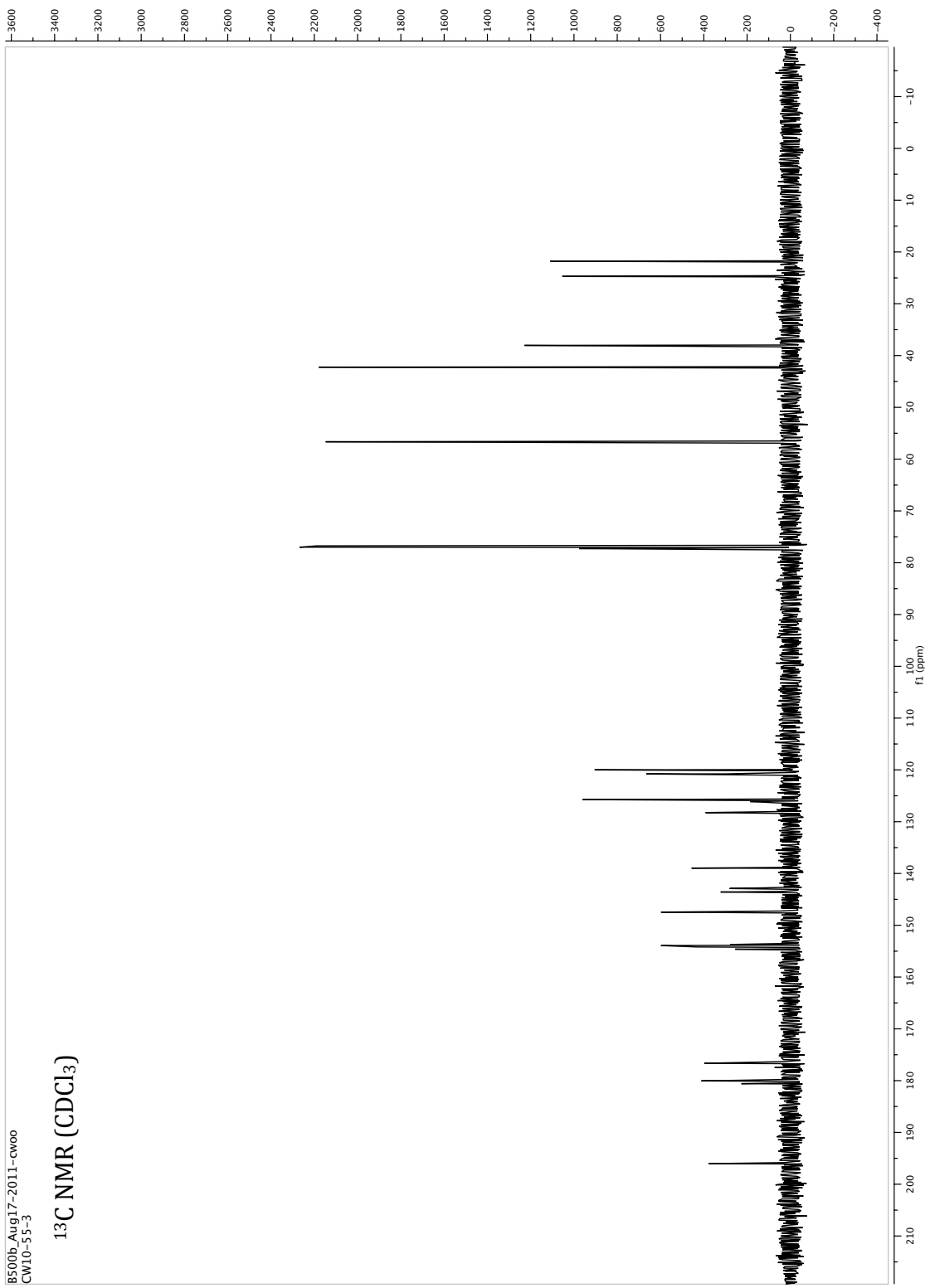

B400b_Apr11-2012-zli
lzw-ii-57-c2
^{1}H NMR ($CDCl_3$)
30
f1 (ppm)
2.05
1.95
3.32
3.25
1.04
1.99
1.00
1.10
9.00


B400b_Apr11-2012-zli
lzw-ii-57-c2
13C NMR (CDCl3)
3000
2500
2000
1500
1000
500
0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

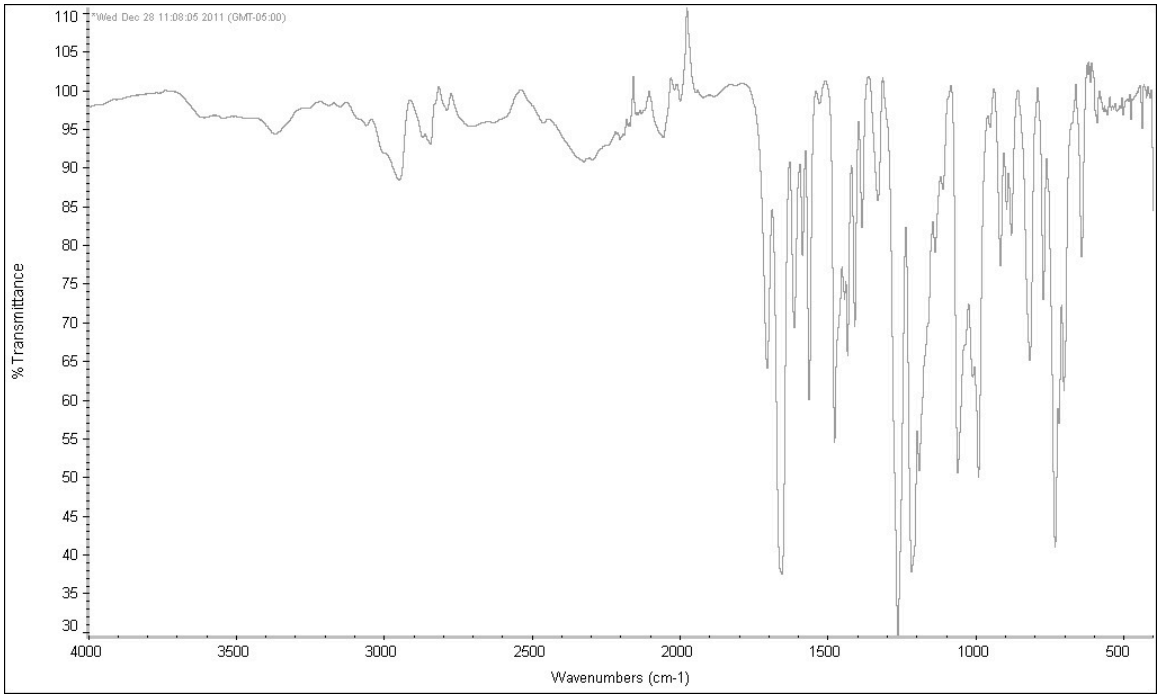
IR

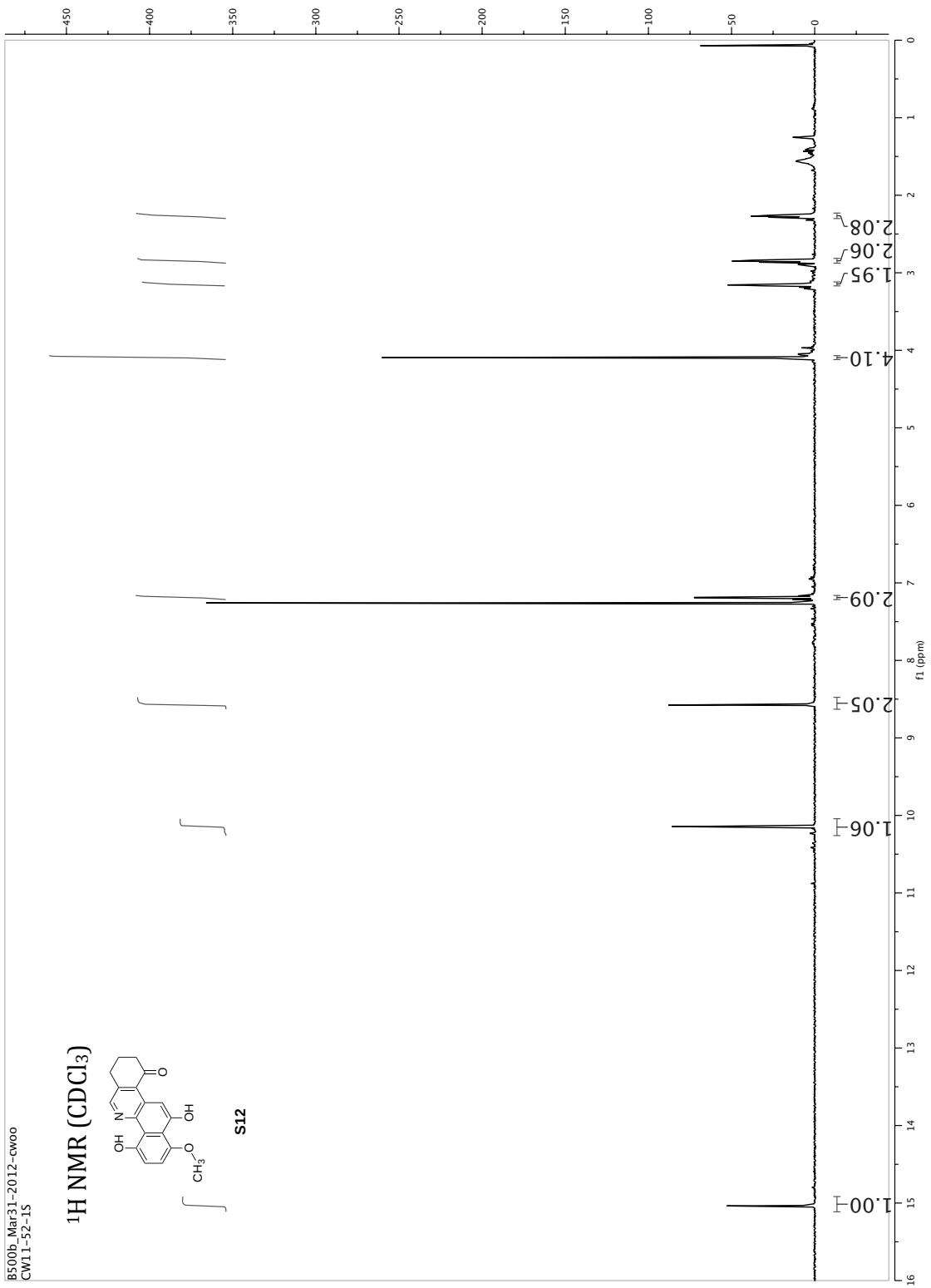

*lzw-ii-57-1
100
98
96
94
92
90
88
86
84
82
80
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

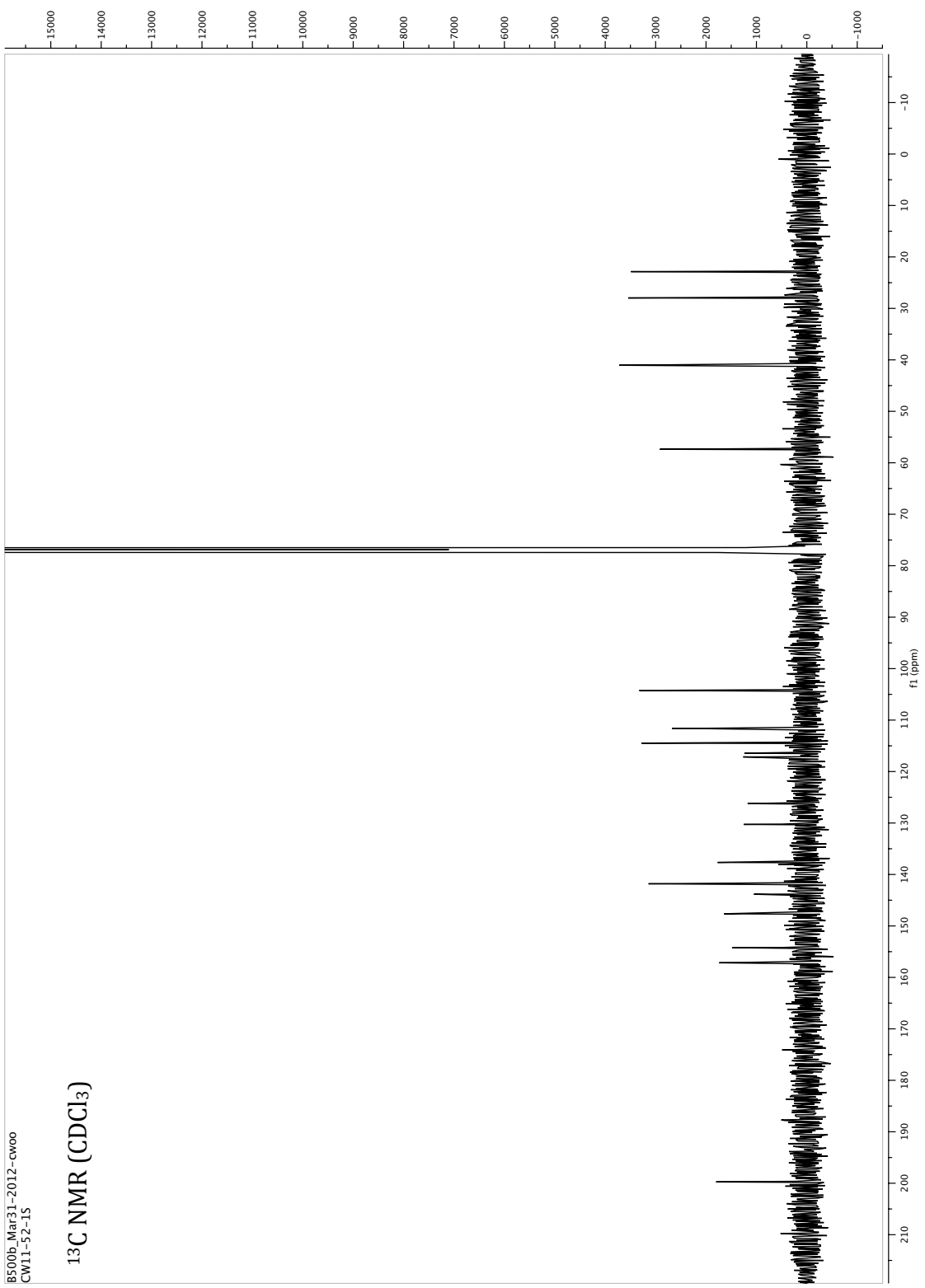

B500b_Aug17-2011-cwoo
CW10-55-3
^{1}H NMR ($CDCl_3$)
S11
2.33
2.08
2.13
6.26
3.07
3.47
1.00
2.09
f1 (ppm)


B500b_Aug17-2011-cwoo
CW10-55-3
^{13}C NMR ($CDCl_3$)
f1 (ppm)

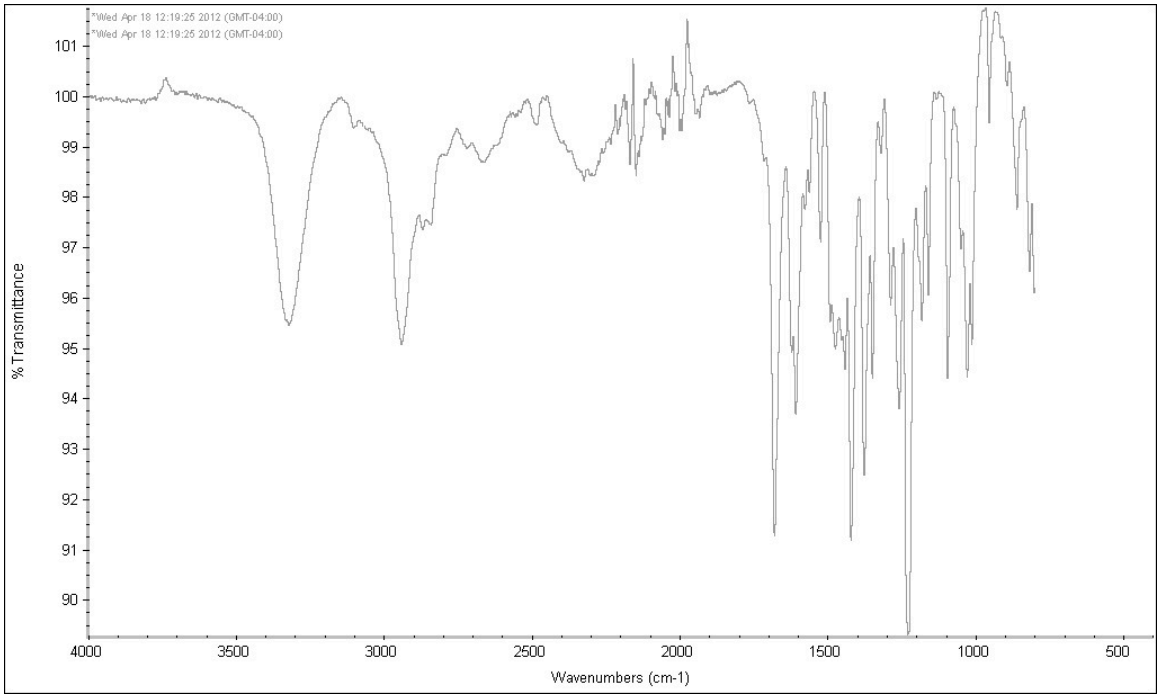
IR

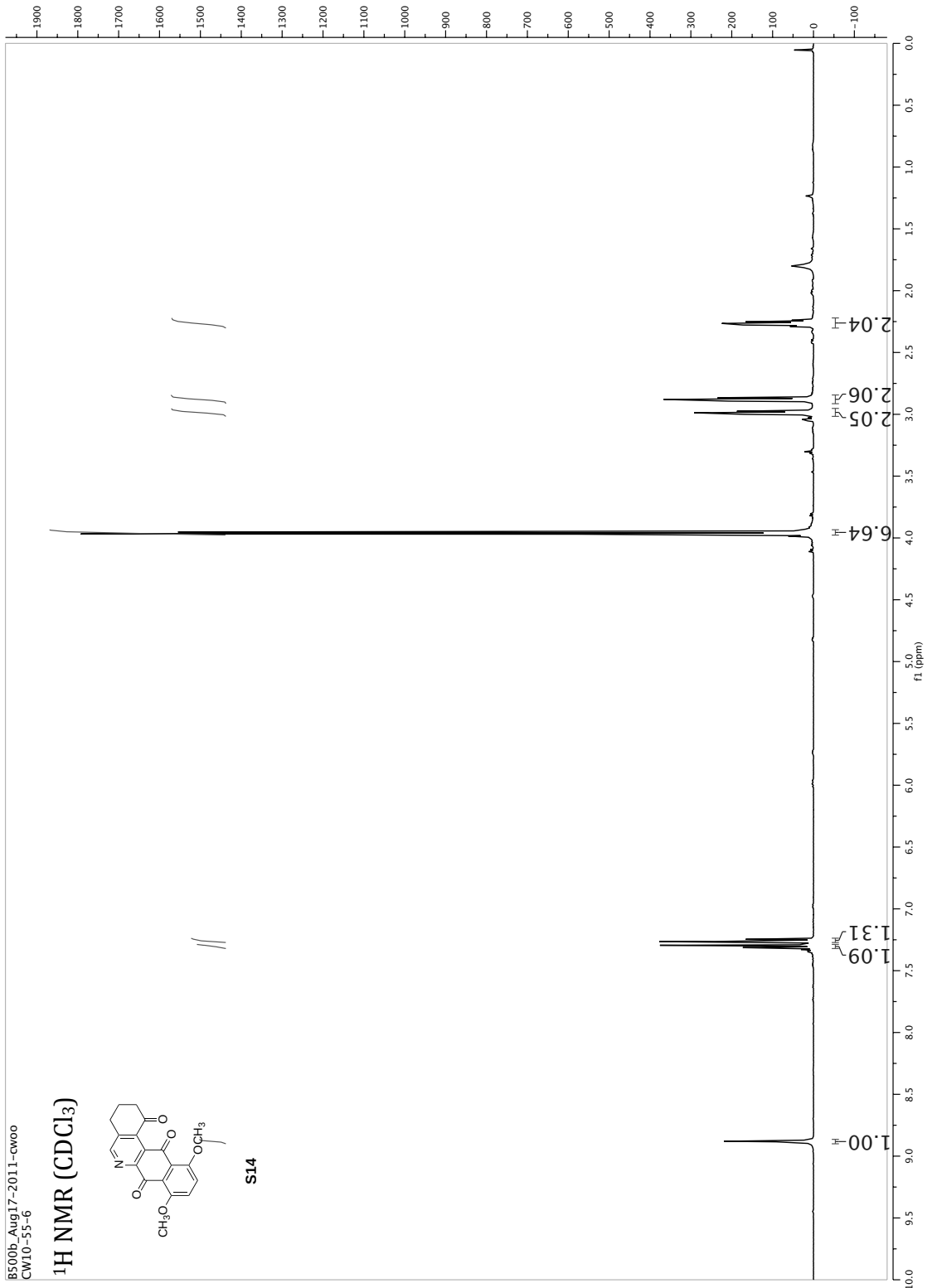

Wed Dec 28 11:08:05 2011 (GMT-05:00)
% Transmittance
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

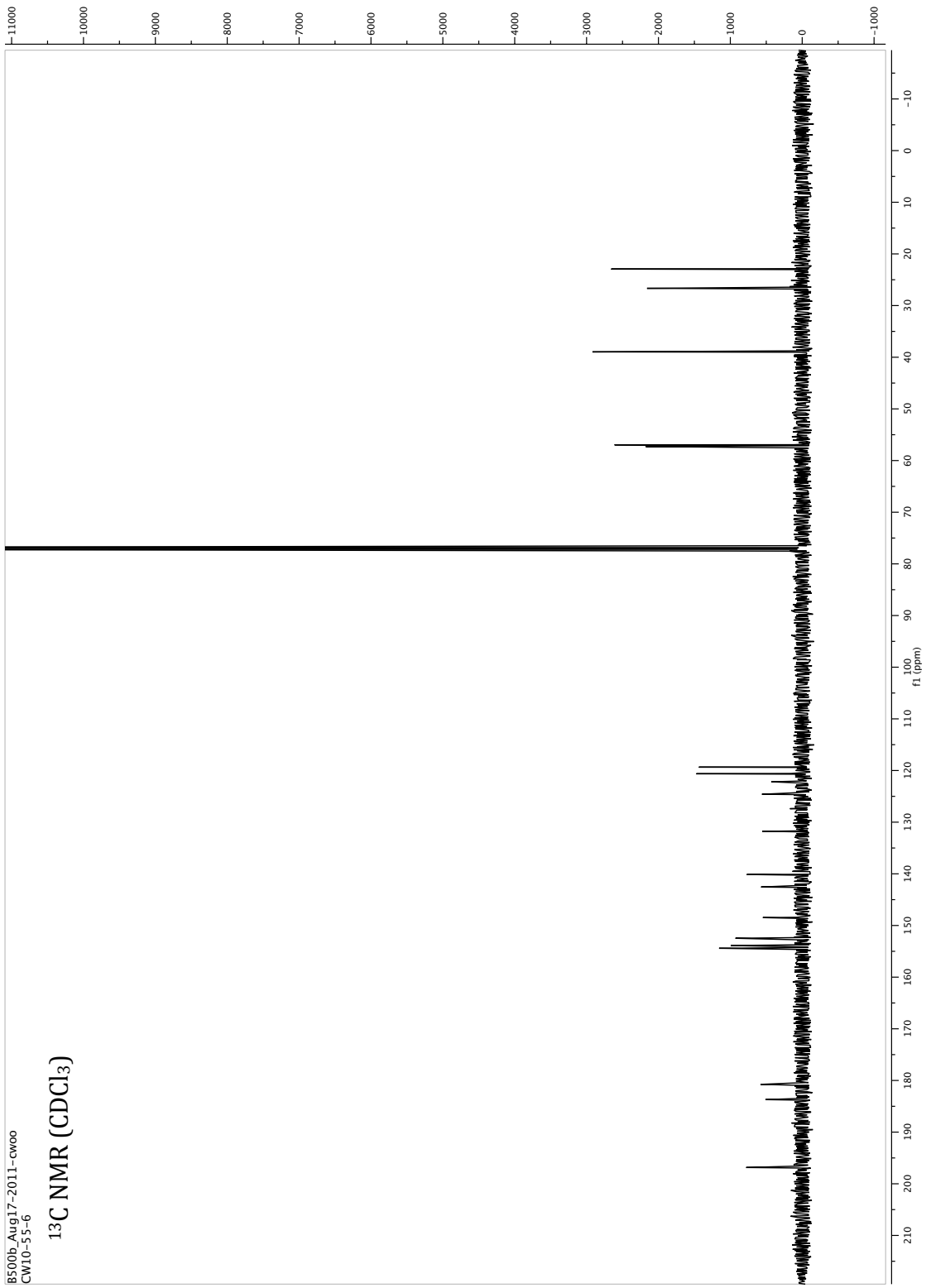

B500b_Mar31-2012-cwoo
CW11-52-1S
^{1}H NMR ($CDCl_3$)
S12
1.00
1.06
2.05
2.09
4.10
1.95
2.06
2.08
f1 (ppm)


B500b_Mar31-2012-cwoo
CW11-52-1S
13C NMR (CDCl3)
f1 (ppm)

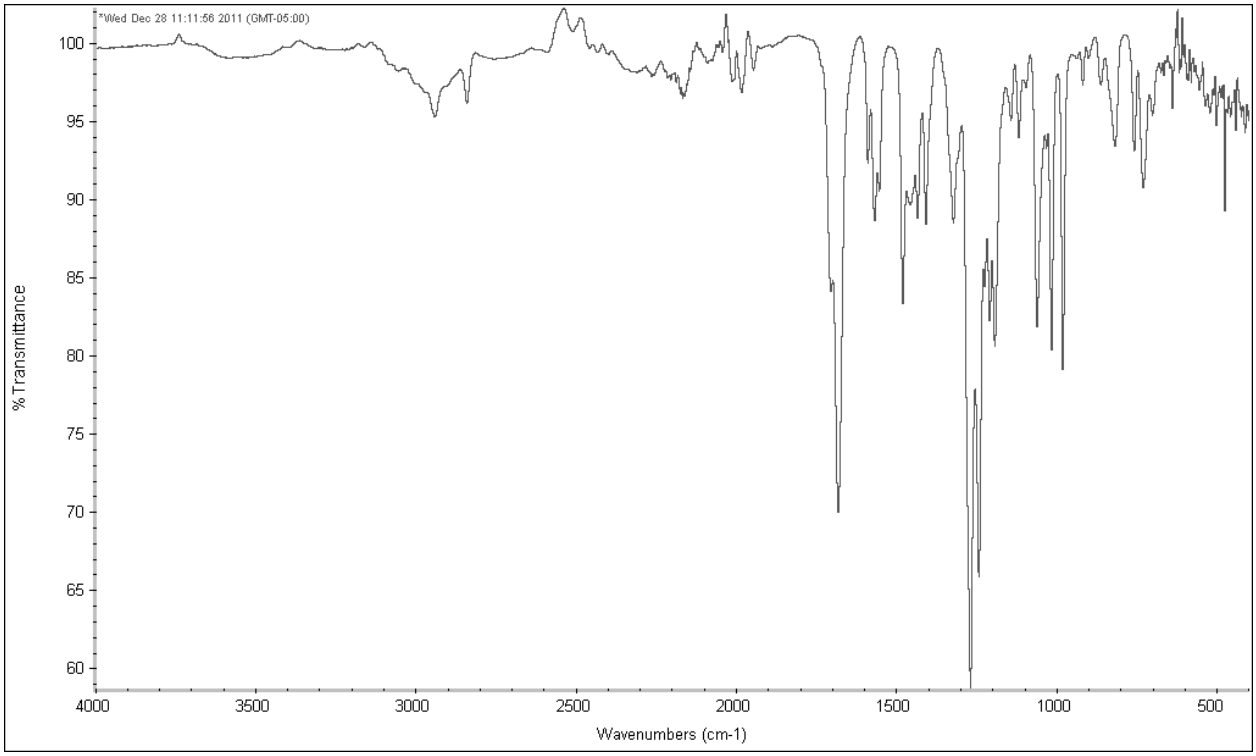
IR

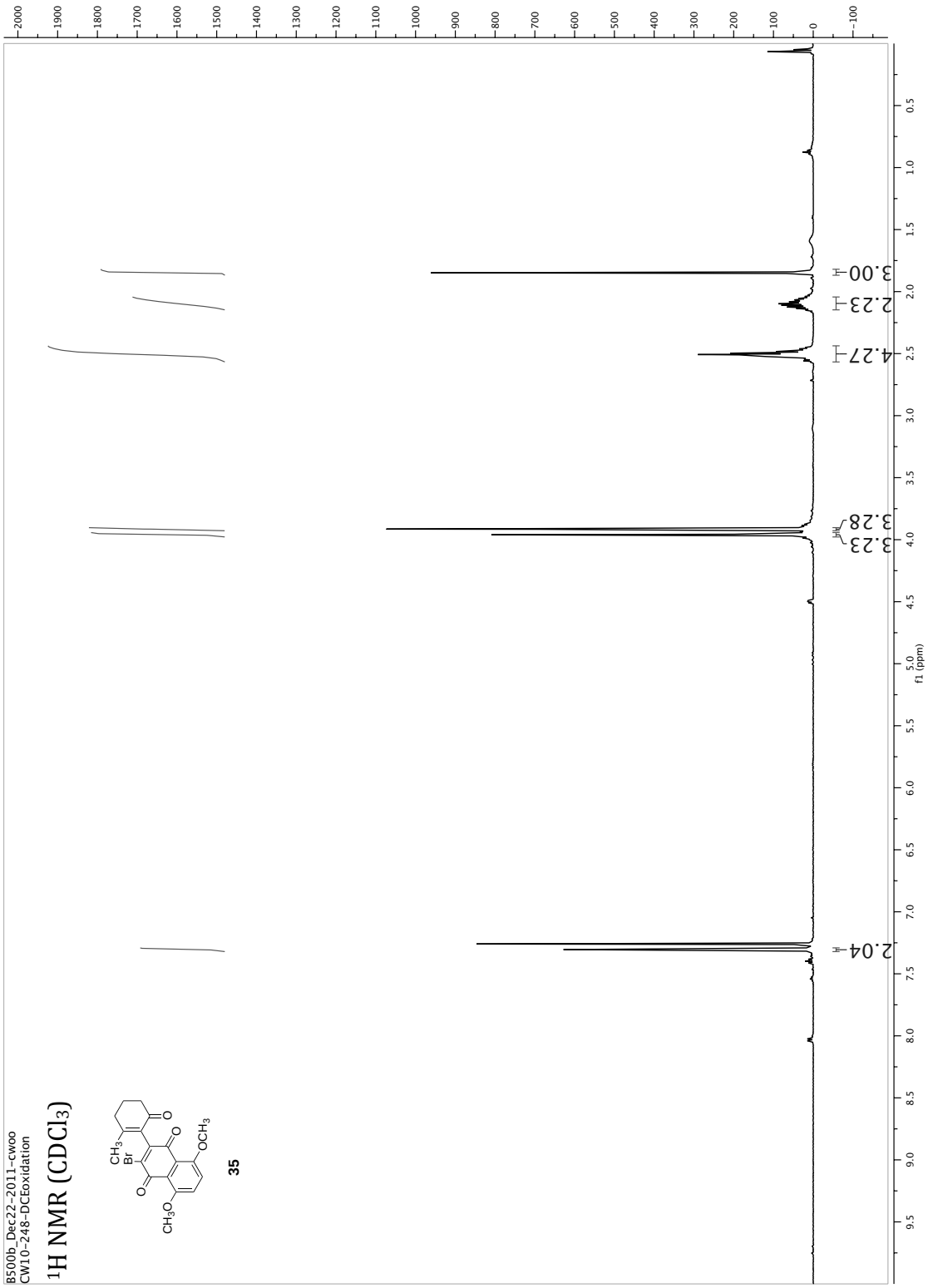

*Wed Apr 18 12:19:25 2012 (GMT-04:00)
*Wed Apr 18 12:19:25 2012 (GMT-04:00)
% Transmittance
101
100
99
98
97
96
95
94
93
92
91
90
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

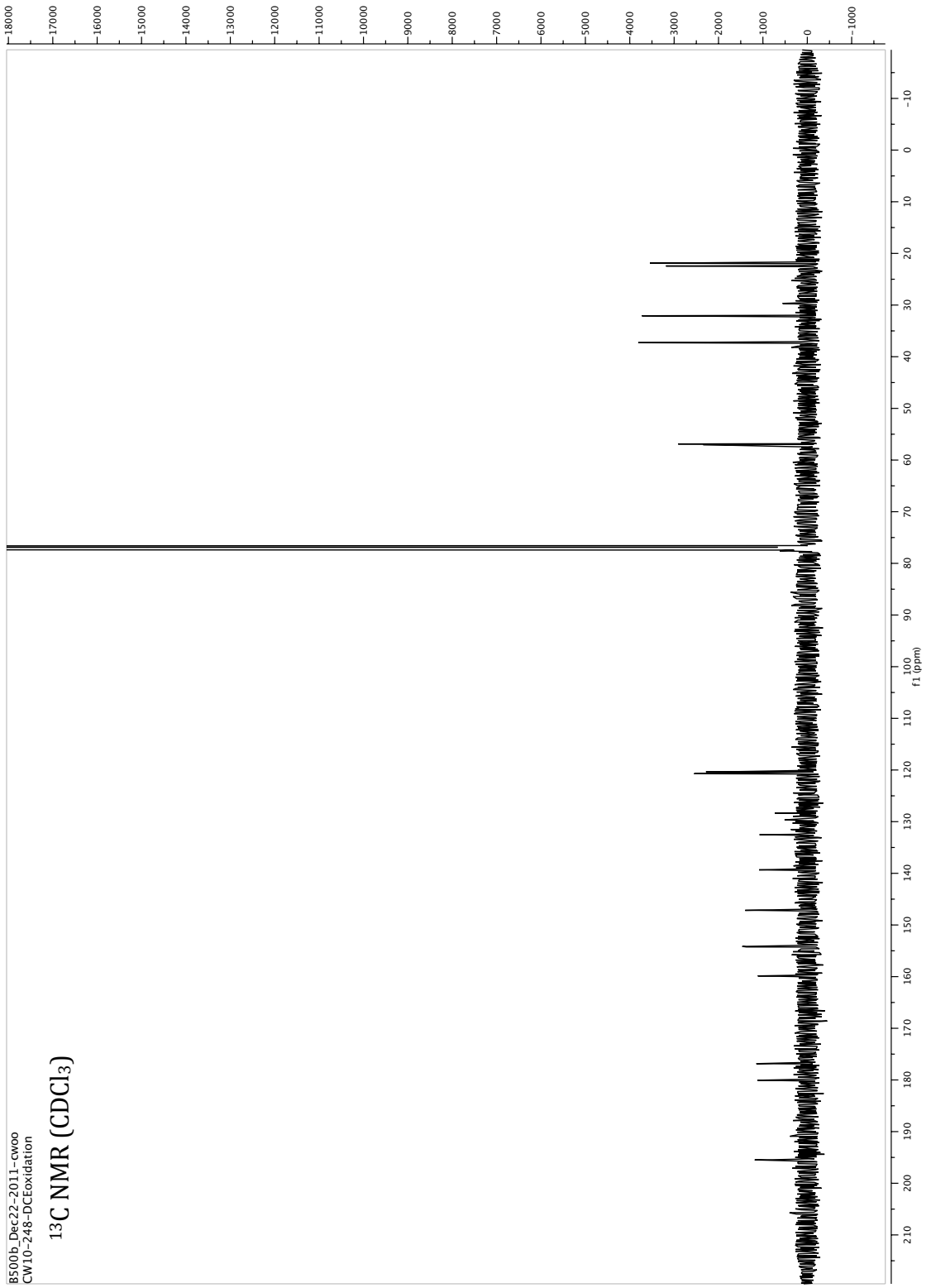

B500b_Aug17-2011-cwoo
CW10-55-6
1H NMR (CDCl3)
S14
1.00
1.09
1.31
2.04
2.05
2.06
6.64
f1 (ppm)


B500b_Aug17-2011-cwoo
CW10-55-6
^{13}C NMR ($CDCl_3$)
f1 (ppm)

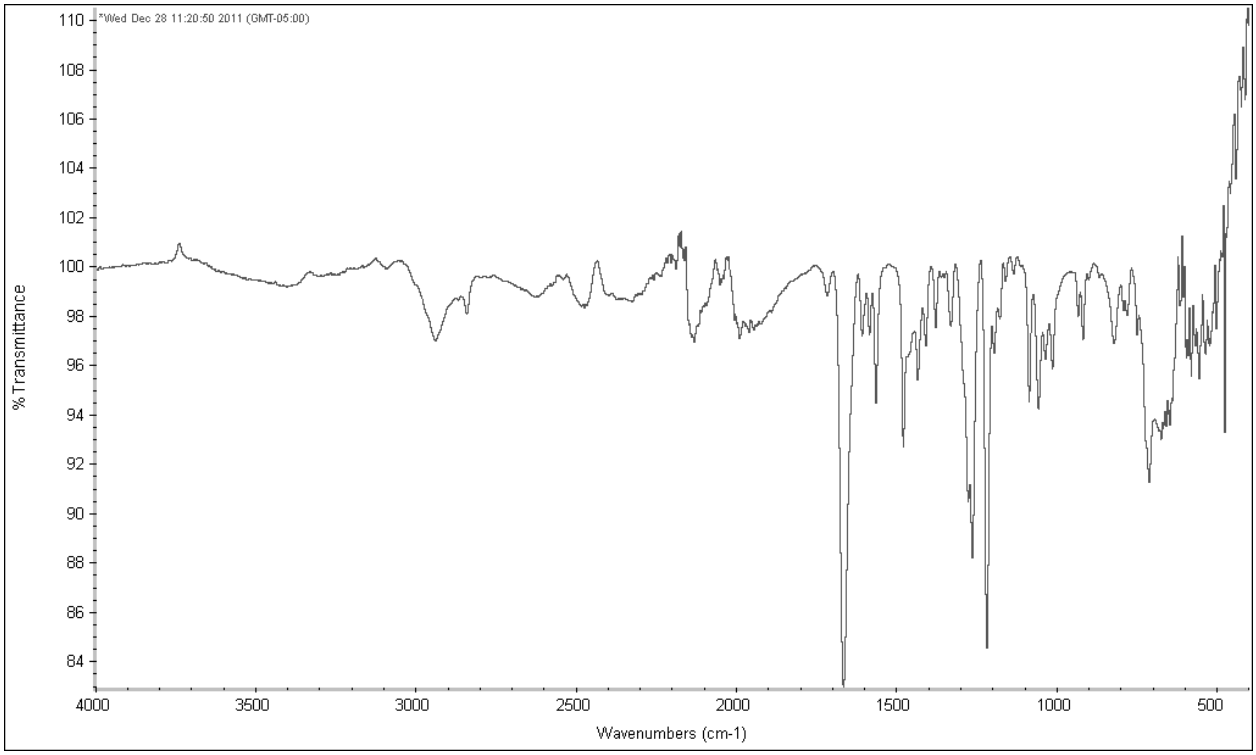
IR

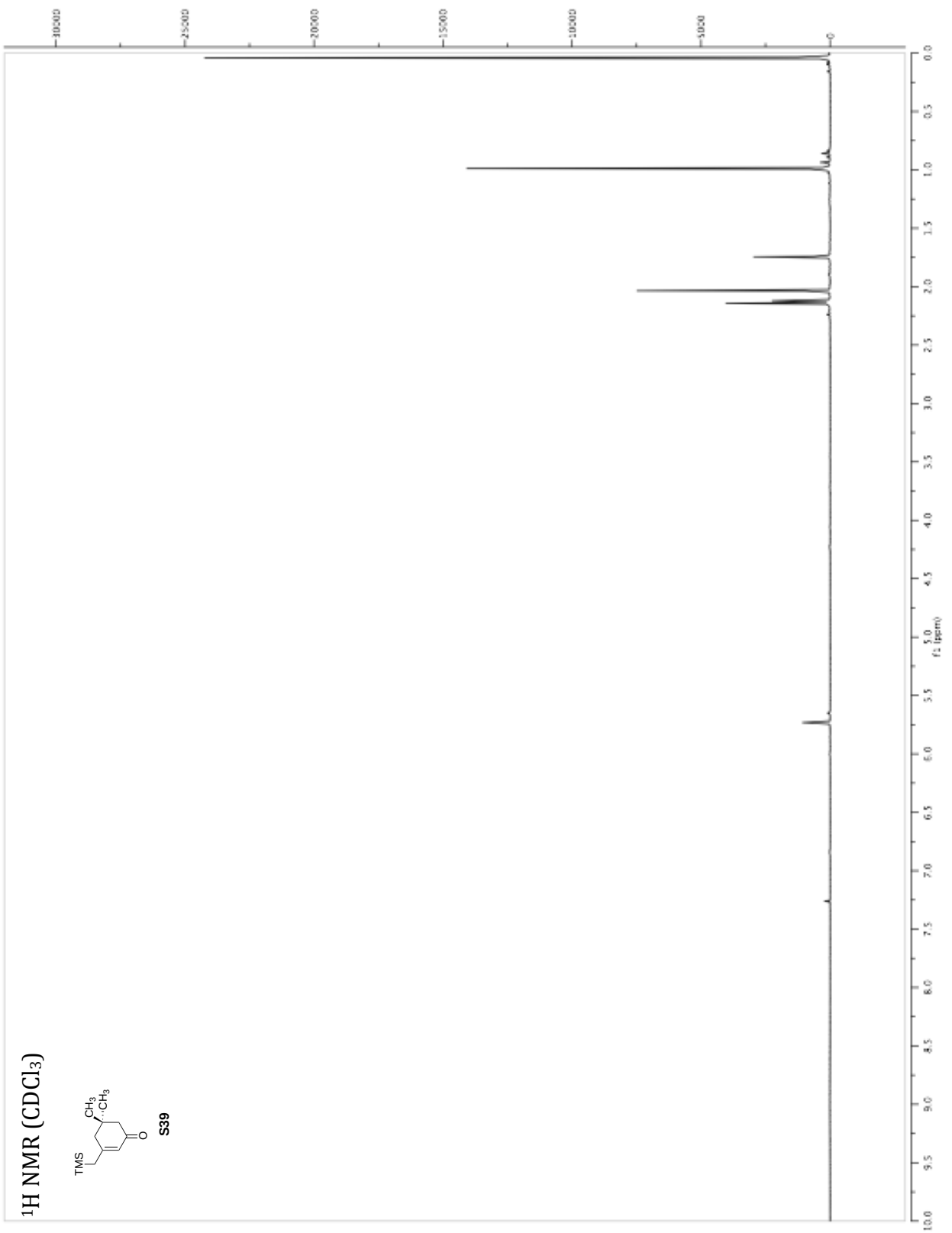

Wed Dec 28 11:11:56 2011 (GMT-05:00)
100
95
90
85
80
75
70
65
60
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

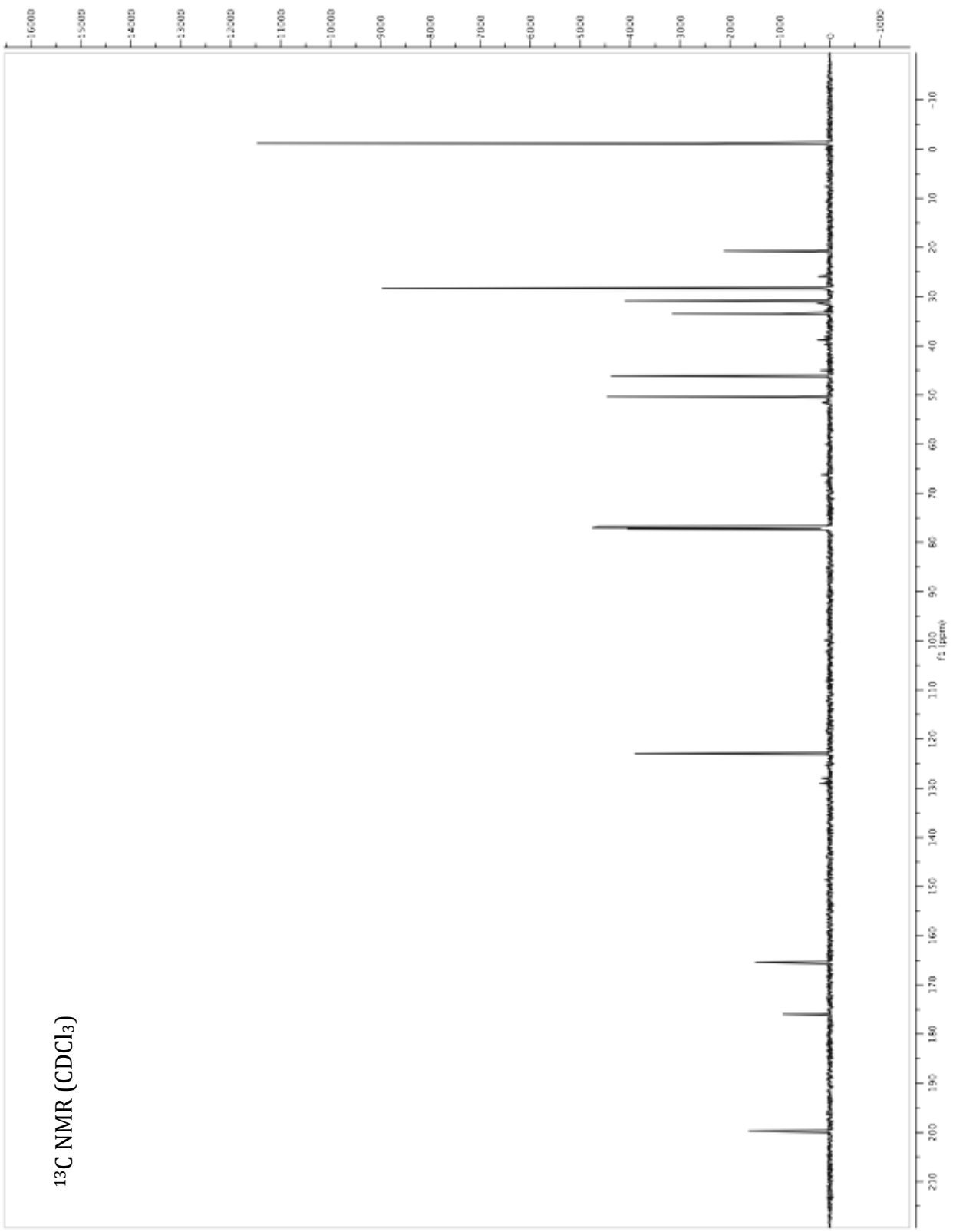

B500b_Dec22-2011-cwoo
CW10-248-DCEoxidation
1H NMR (CDCl3)
35
3.00
2.23
4.27
3.28
3.23
2.04
f1 (ppm)


B500b_Dec22-2011-cwoo
CW10-248-DCEoxidation
^{13}C NMR ($CDCl_3$)
f1 (ppm)

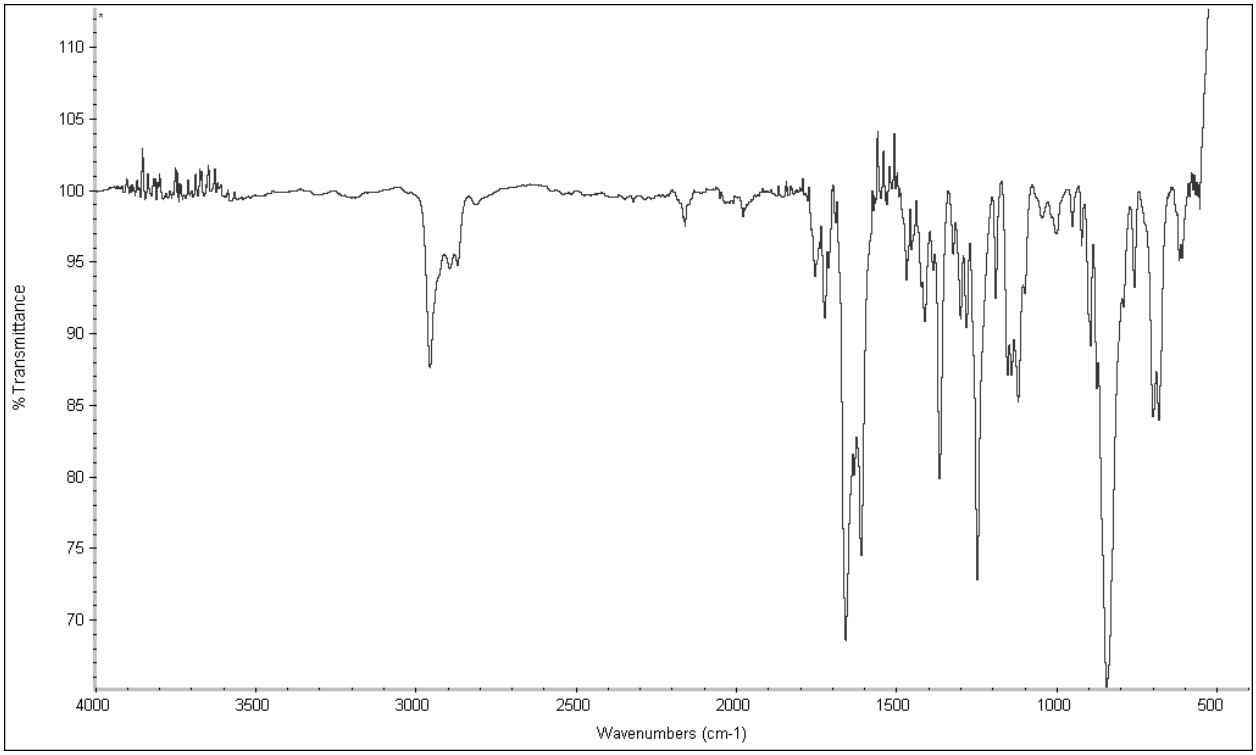
IR

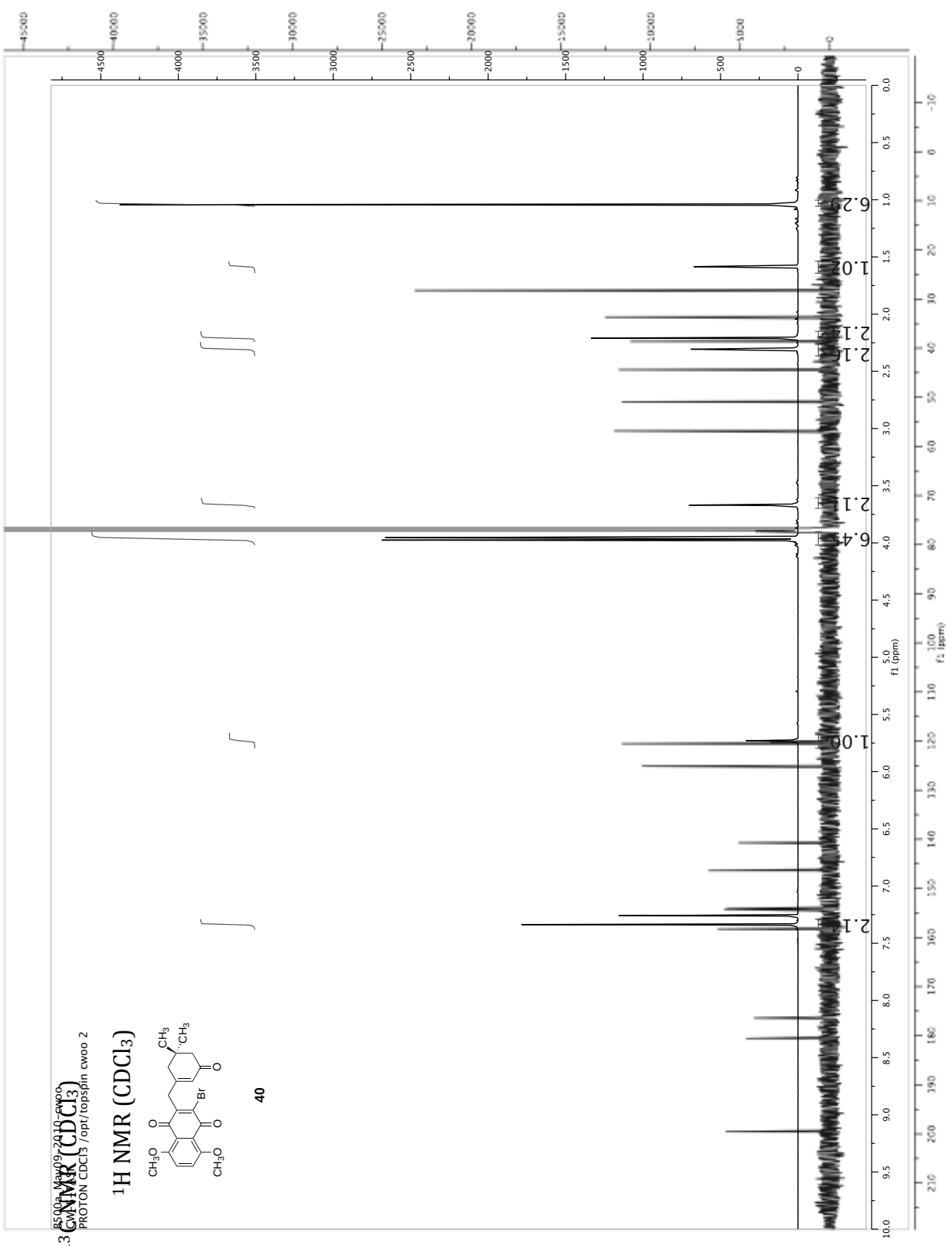

Wed Dec 28 11:20:50 2011 (GMT-05:00)
% Transmittance
110
108
106
104
102
100
98
96
94
92
90
88
86
84
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


1H NMR (CDCl3)
TMS
CH3
CH3
O
S39
f2 (ppm)

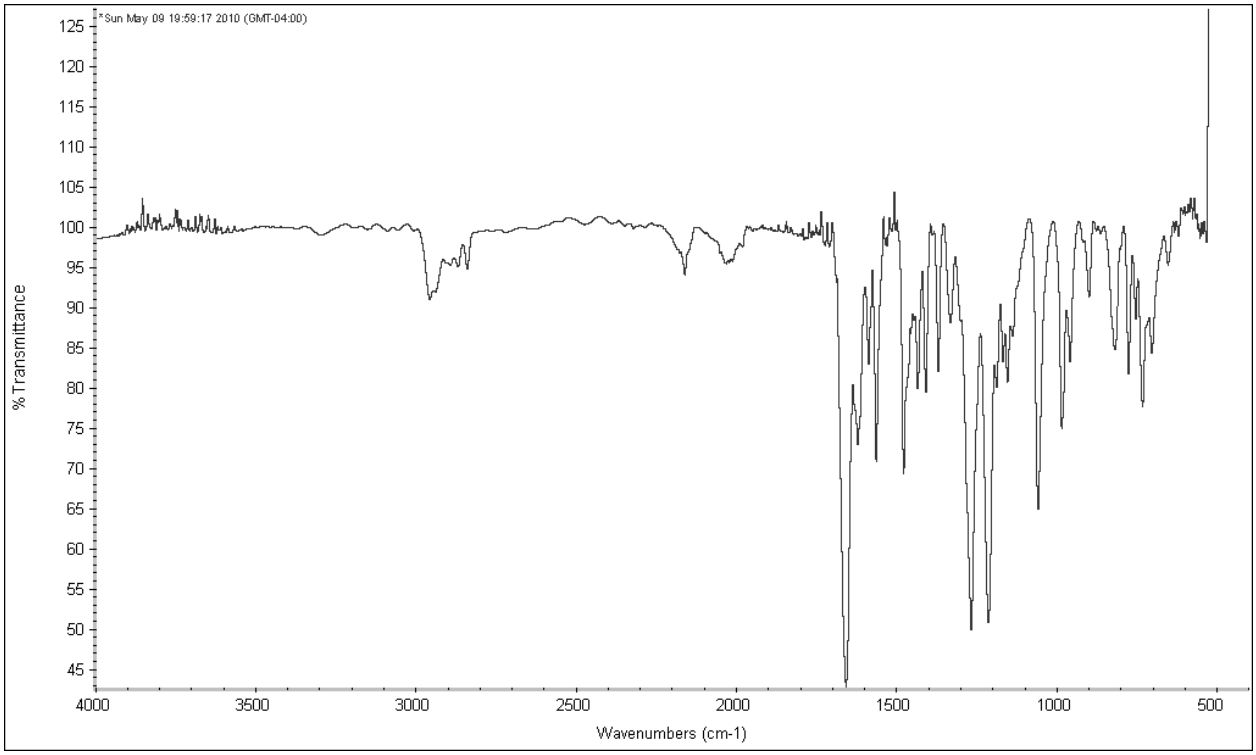

^{13}C NMR ($CDCl_3$)

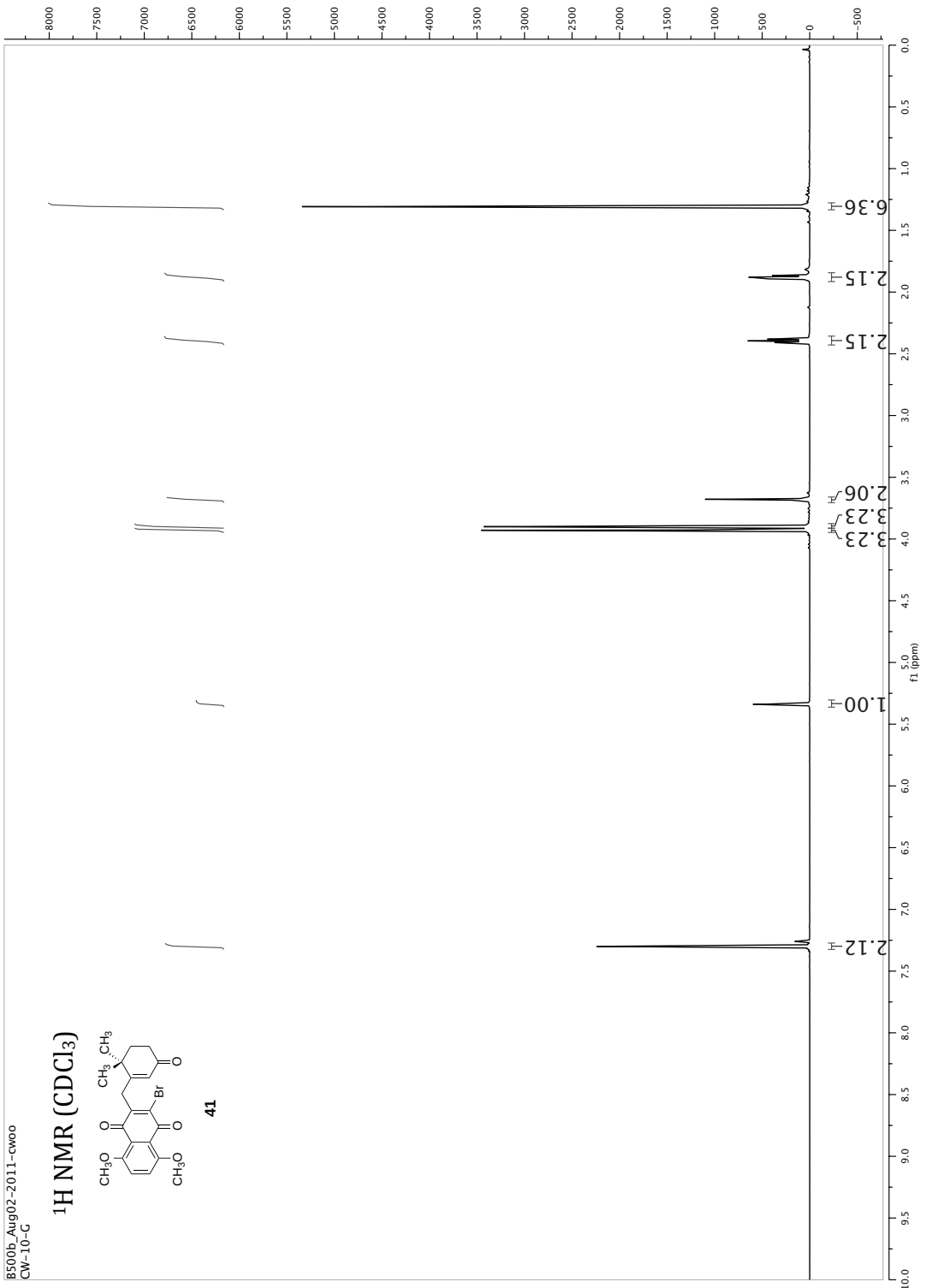
IR

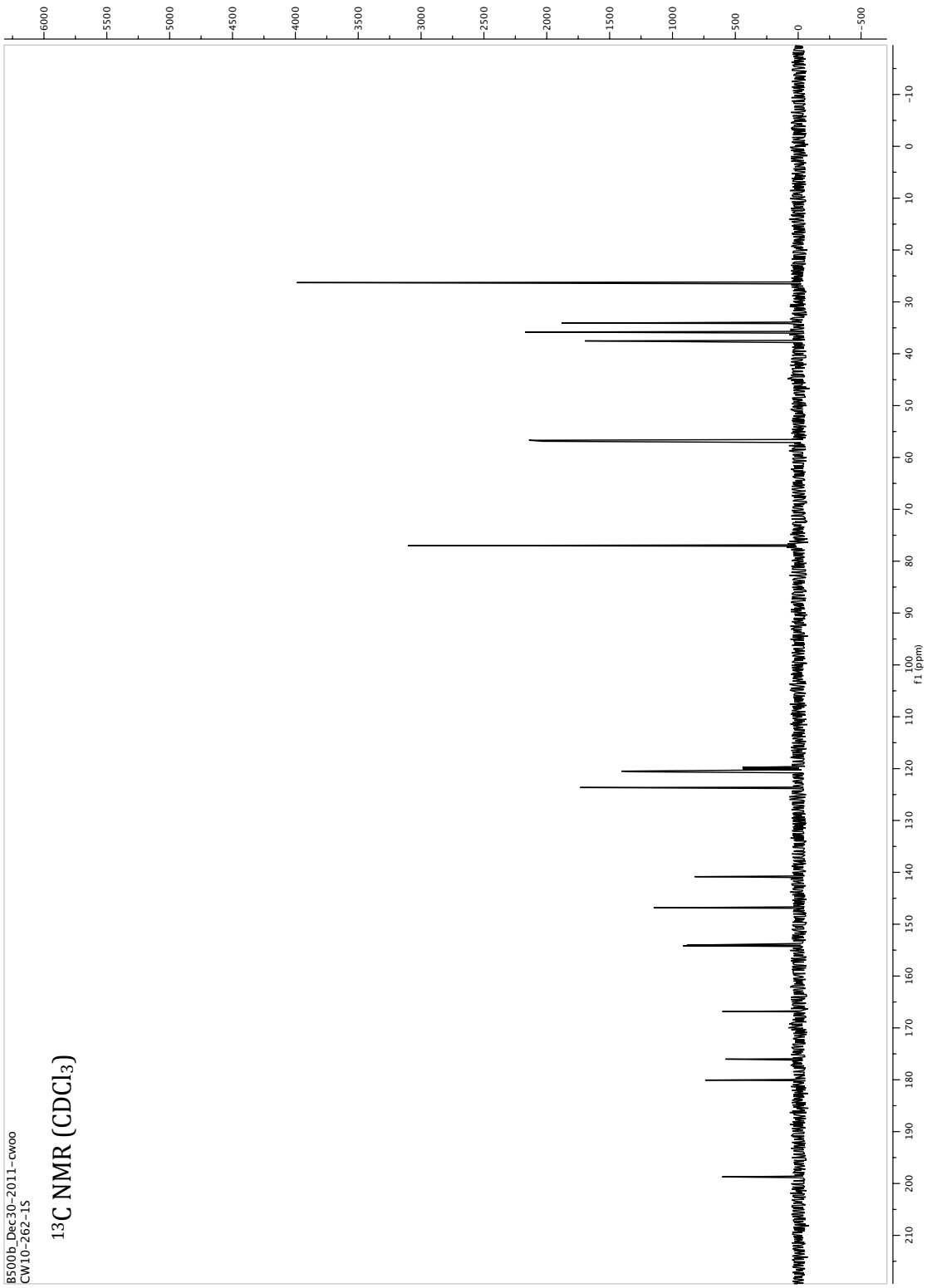

% Transmittance
110
105
100
95
90
85
80
75
70
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


13 CNMR (CDCl3)
PROTON CDCl3 /opt/topspin cwoo 2
1H NMR (CDCl3)
40
6.29
1.02
2.12
2.16
2.11
6.45
1.00
2.14
f1 (ppm)

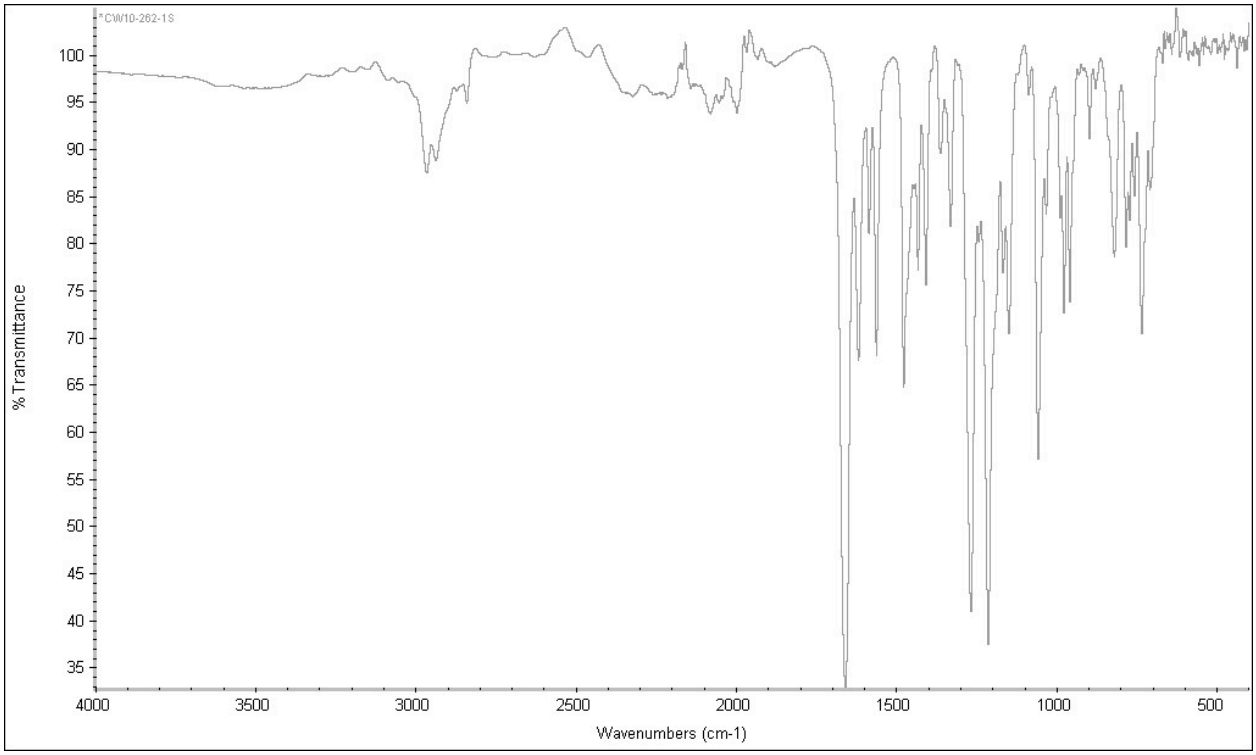
IR

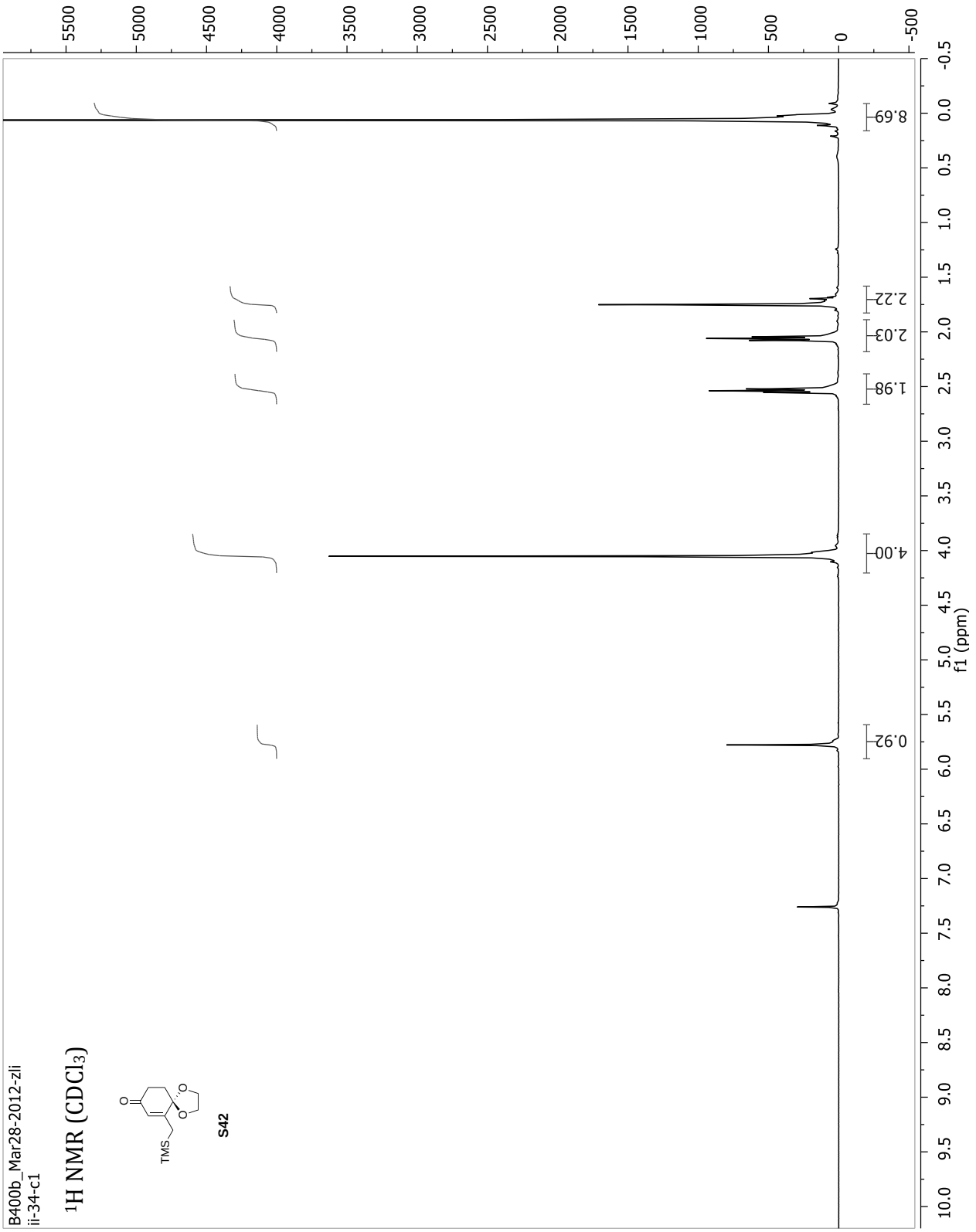

Sun May 09 19:59:17 2010 (GMT-04:00)
% Transmittance
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

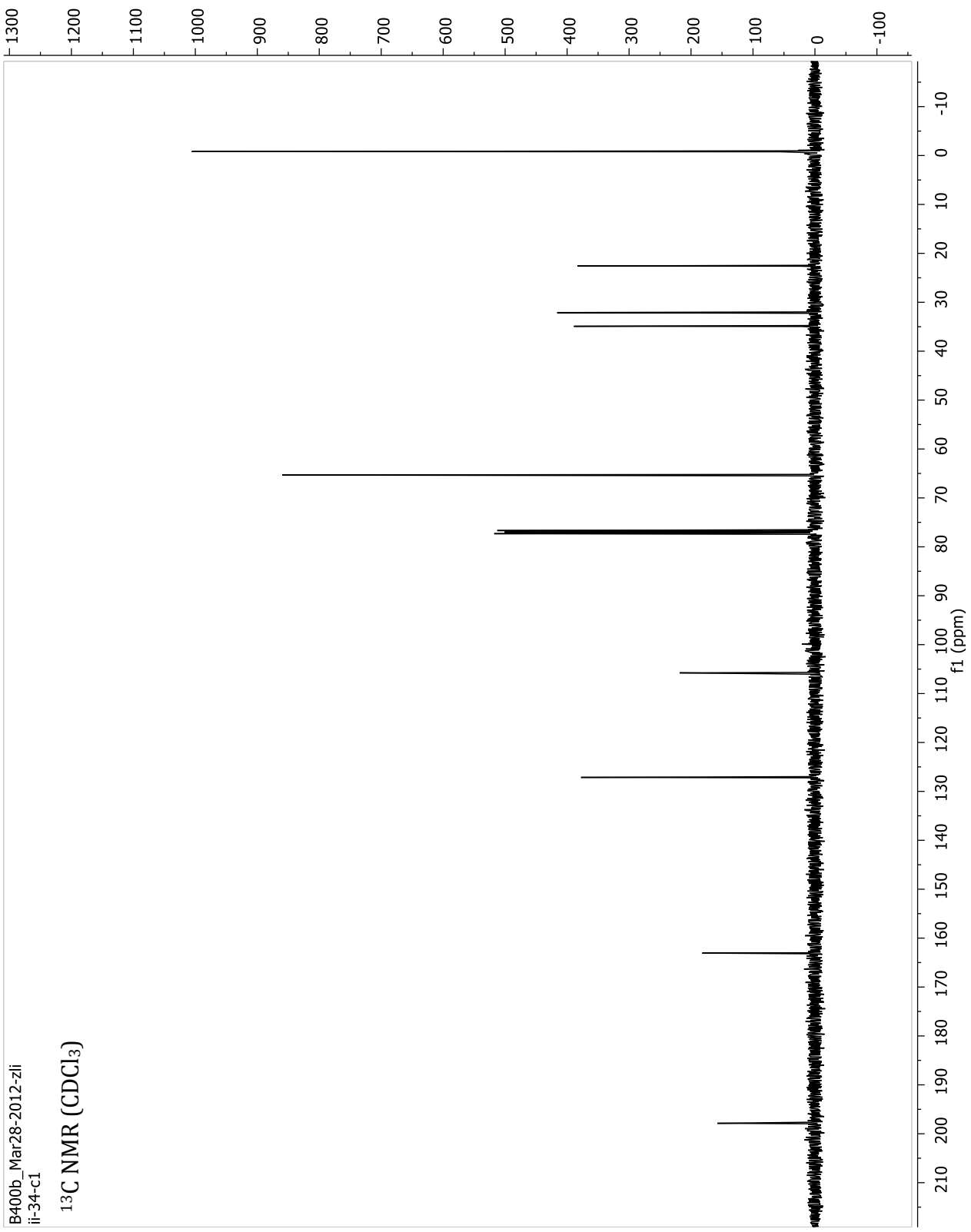

B500b_Aug02-2011-cwoo
CW-10-G
^{1}H NMR ($CDCl_3$)
41
6.36
2.15
2.15
2.06
3.23
3.23
1.00
2.12
f1 (ppm)


B500b_Dec30-2011-cwoo
CW10-262-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

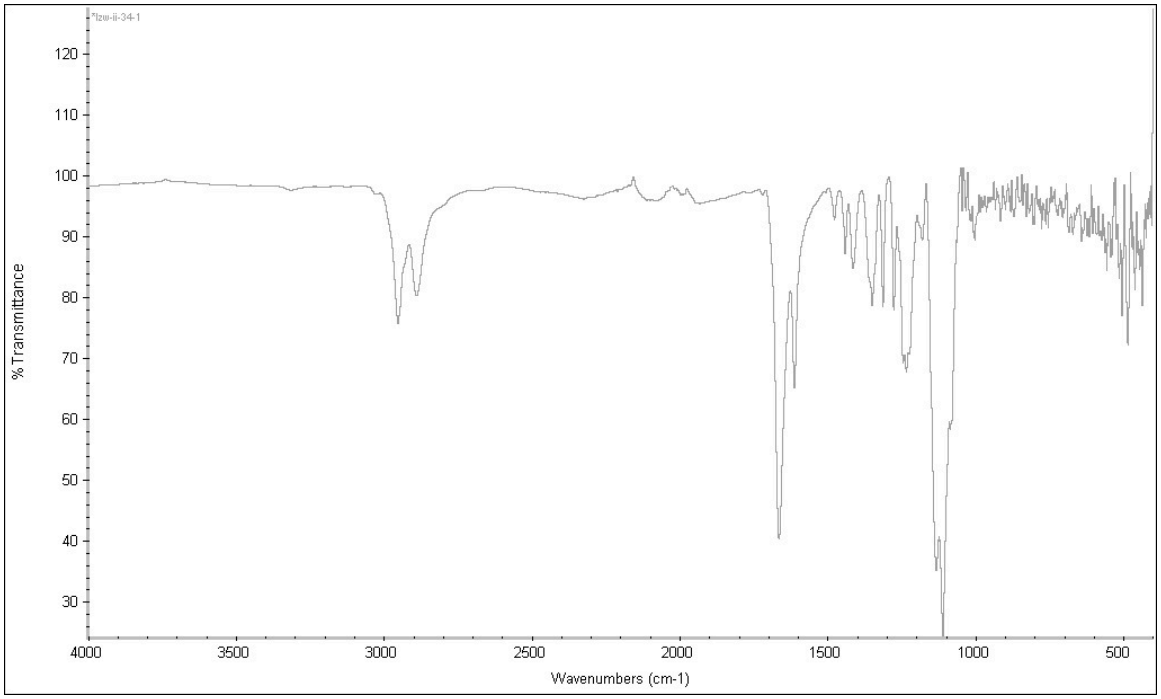
IR

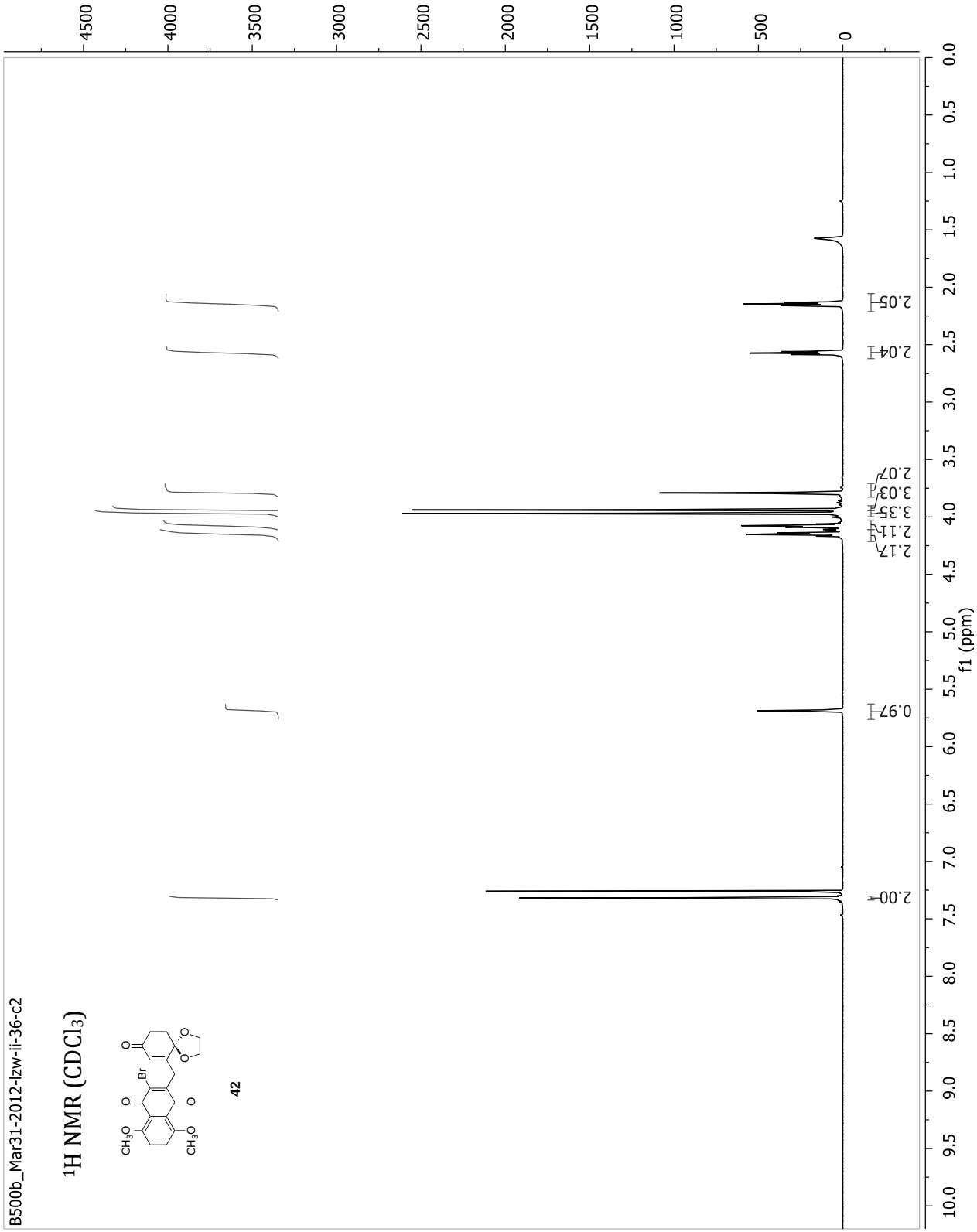

CW10-262-1S
% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

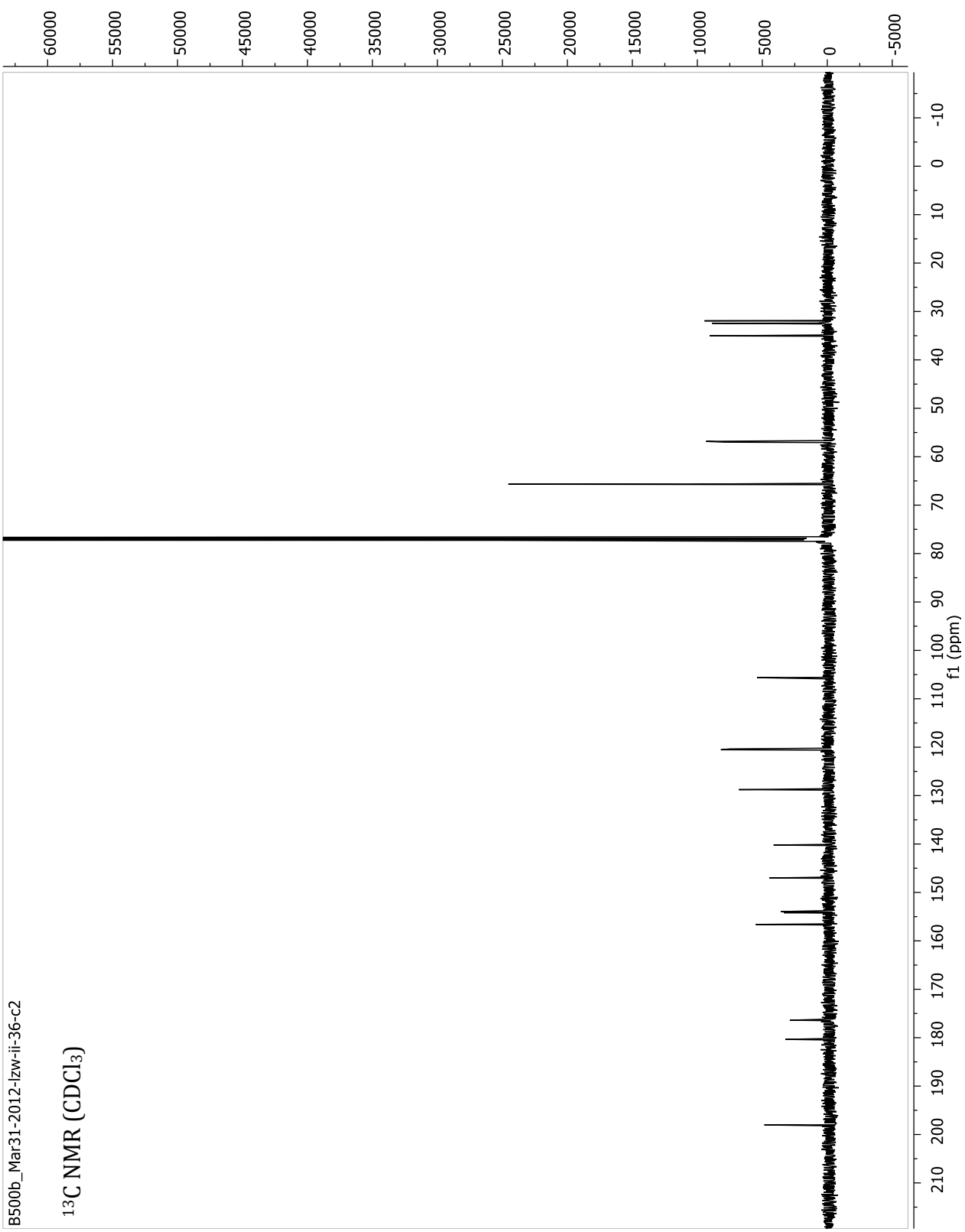

B400b_Mar28-2012-zli
ii-34-c1
^{1}H NMR ($CDCl_3$)
TMS
S42
8.69
2.22
2.03
1.98
4.00
0.92
f1 (ppm)


B400b_Mar28-2012-zli
ii-34-c1
13C NMR (CDCl3)
f1 (ppm)

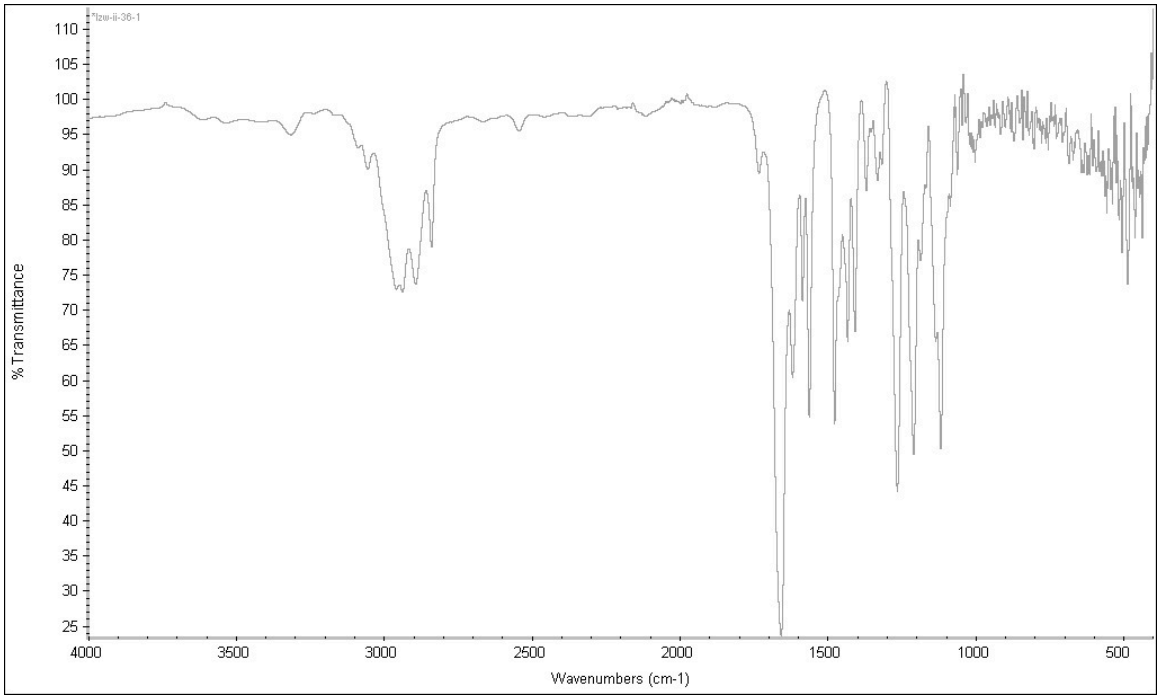
IR

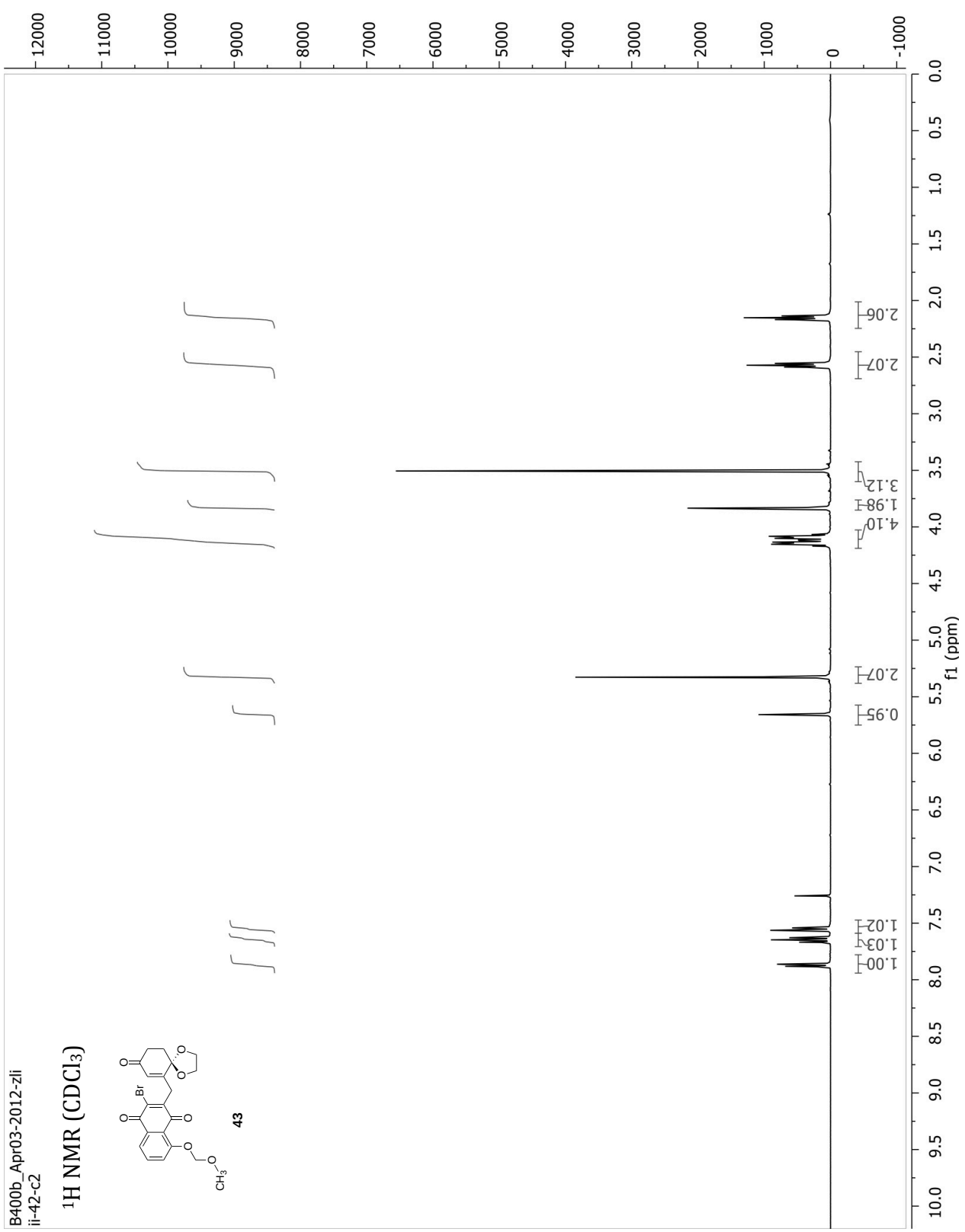

*lzw-ii-34-1
120
110
100
90
80
70
60
50
40
30
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

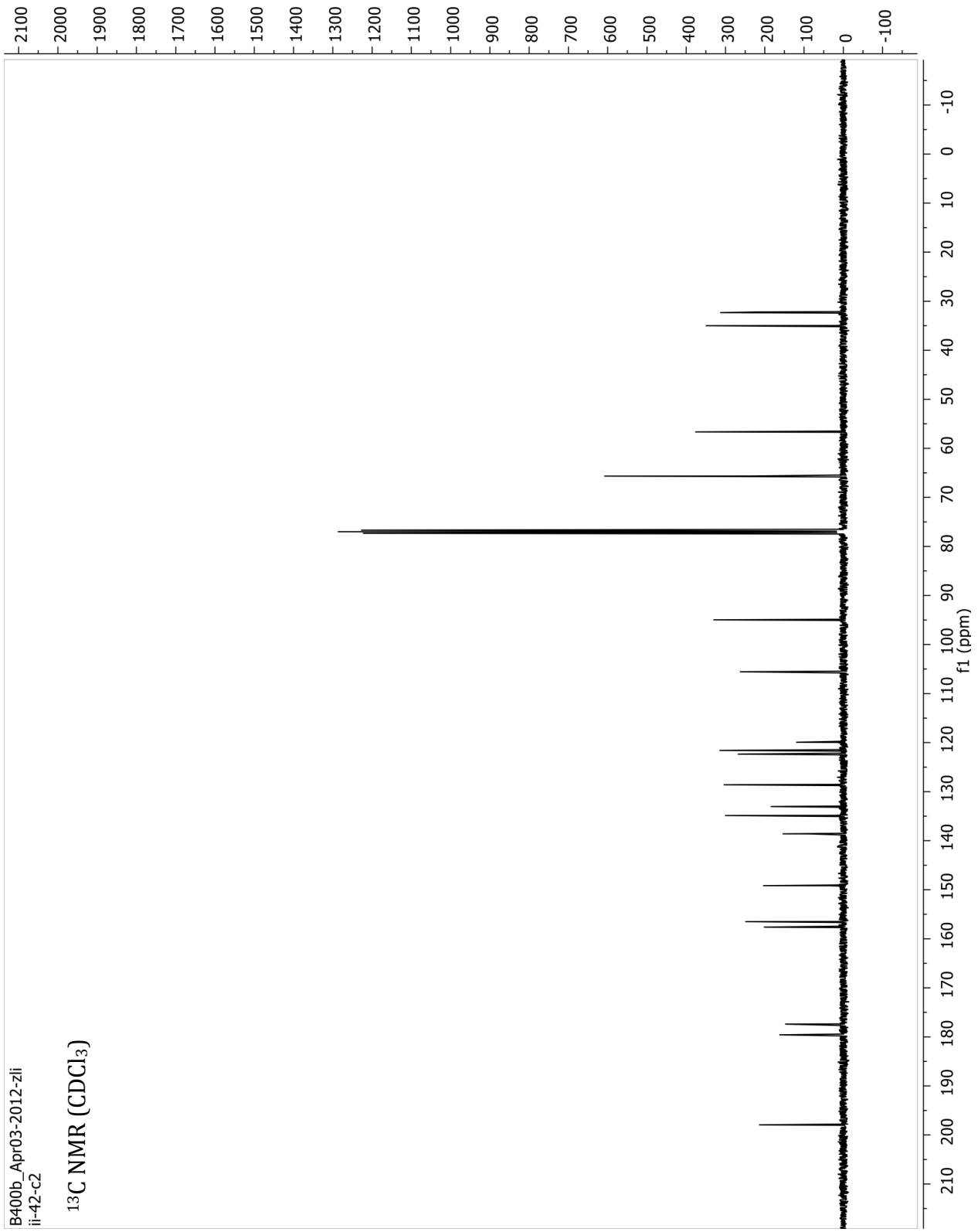

B500b_Mar31-2012-lzw-ii-36-c2
^{1}H NMR ($CDCl_3$)
42
f1 (ppm)
2.00
0.97
2.05
2.04
2.07
3.03
3.35
2.11
2.17


B500b_Mar31-2012-lzw-ii-36-c2
^{13}C NMR ($CDCl_3$)
f1 (ppm)

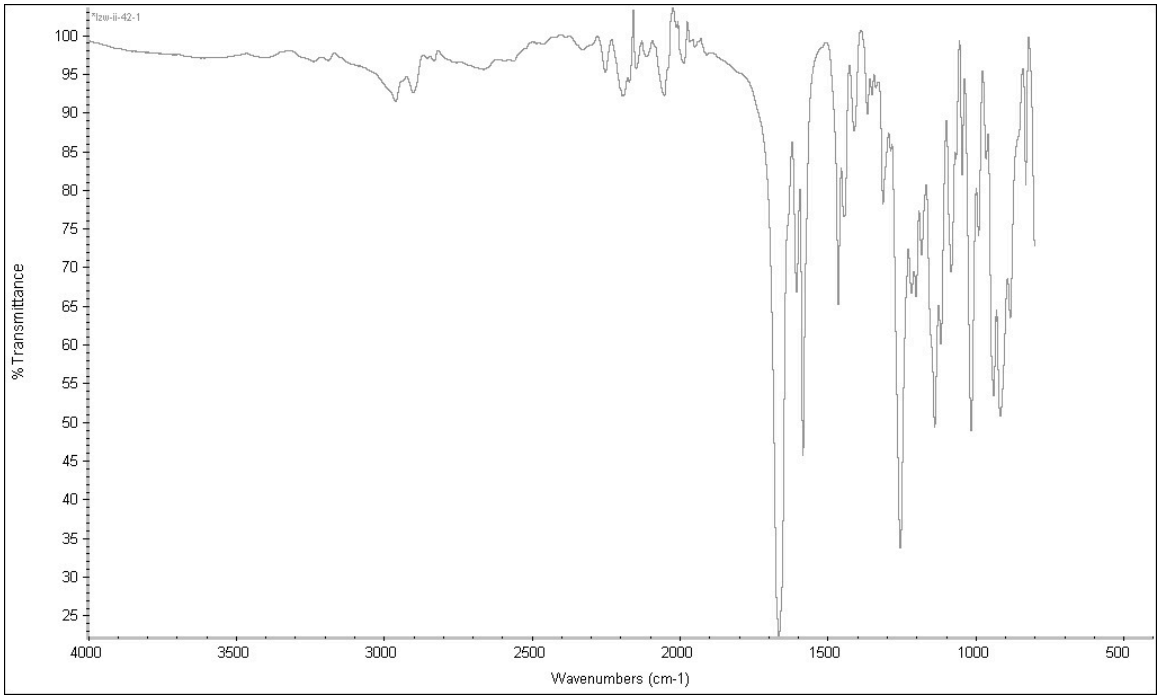
IR

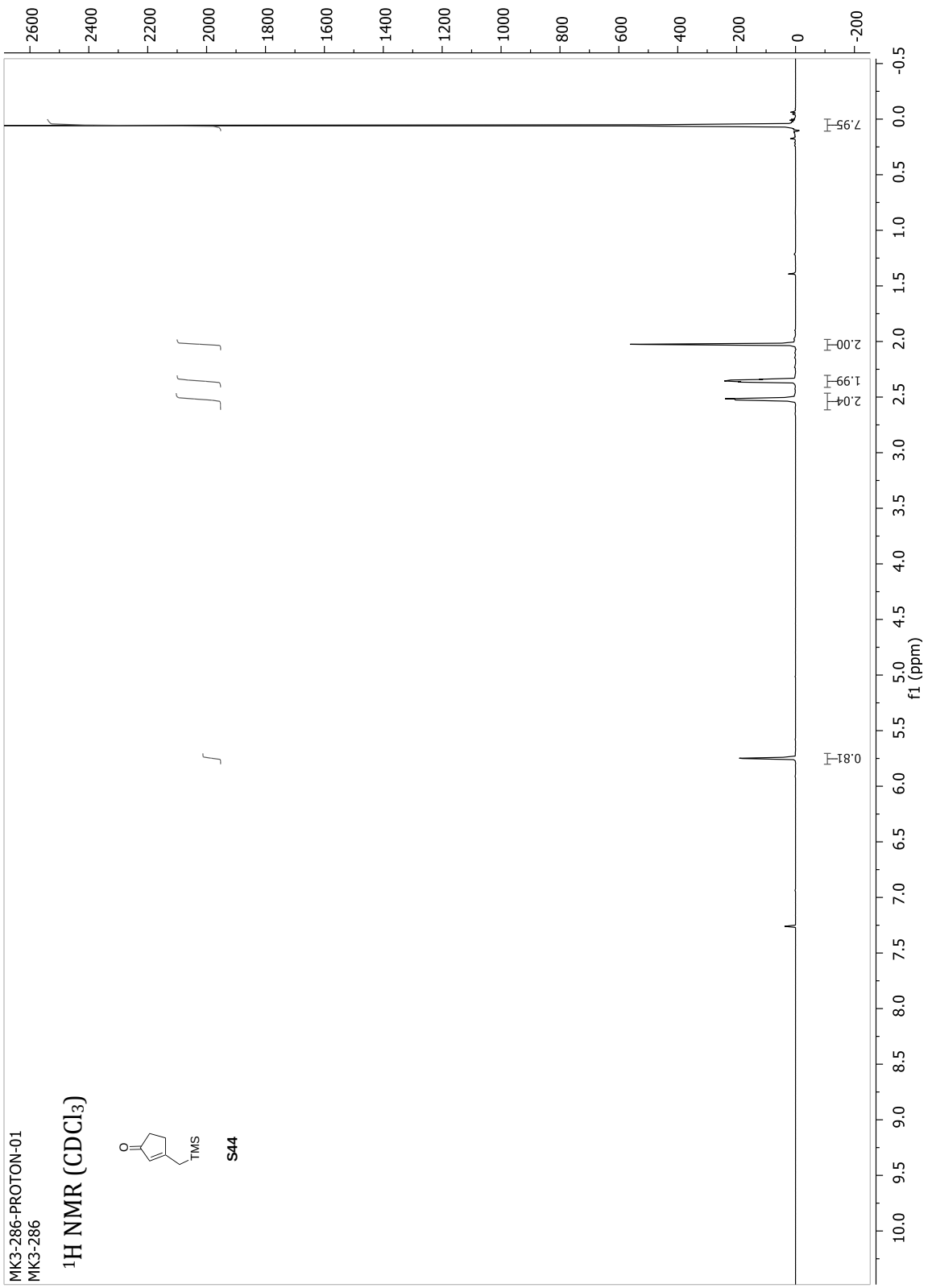

% Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500

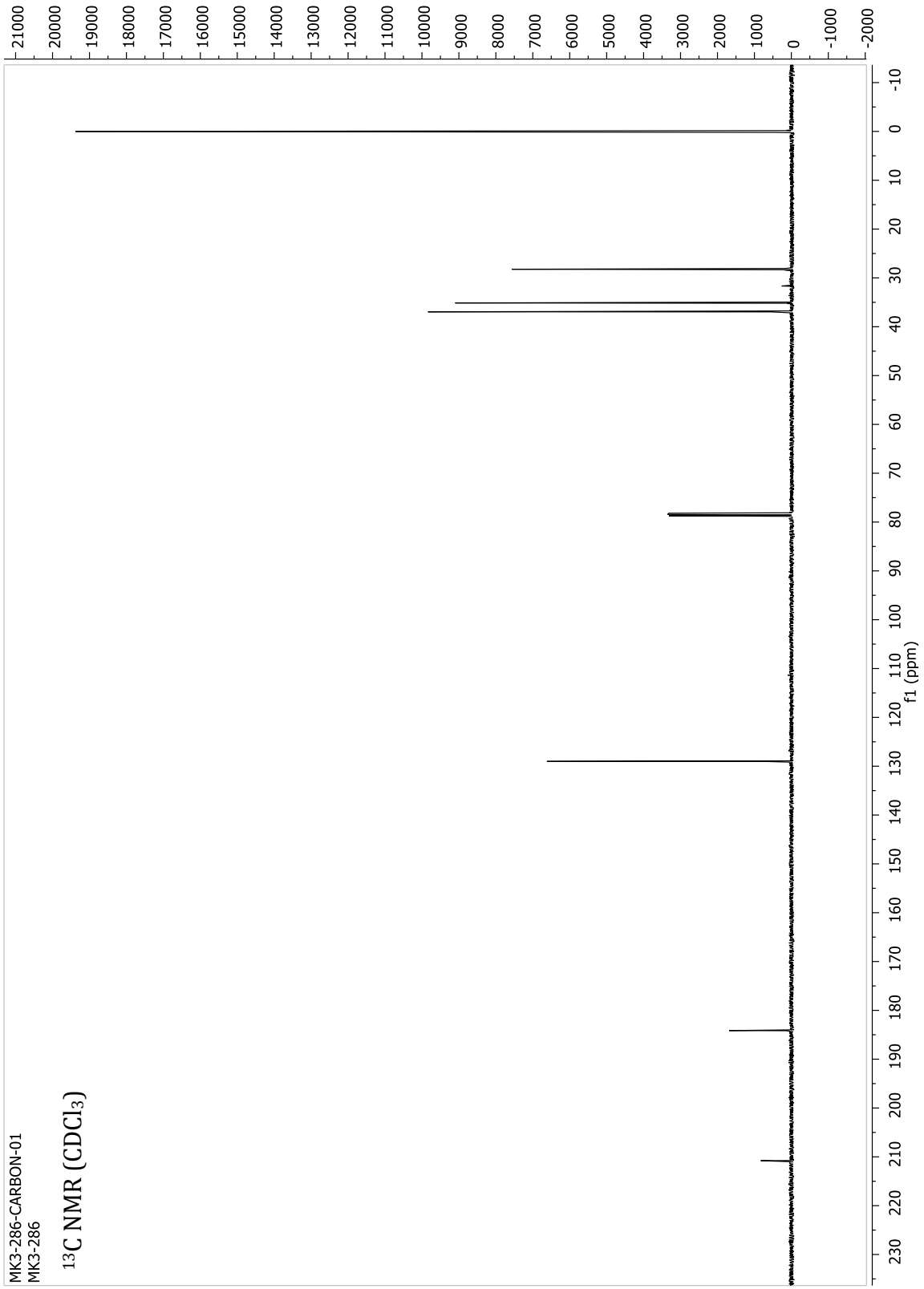

B400b_Apr03-2012-zli
ii-42-c2
^{1}H NMR ($CDCl_3$)
43
2.06
2.07
3.12
1.98
4.10
2.07
0.95
1.00
1.03
1.02
f1 (ppm)


B400b_Apr03-2012-zli
ii-42-c2
^{13}C NMR ($CDCl_3$)
f1 (ppm)

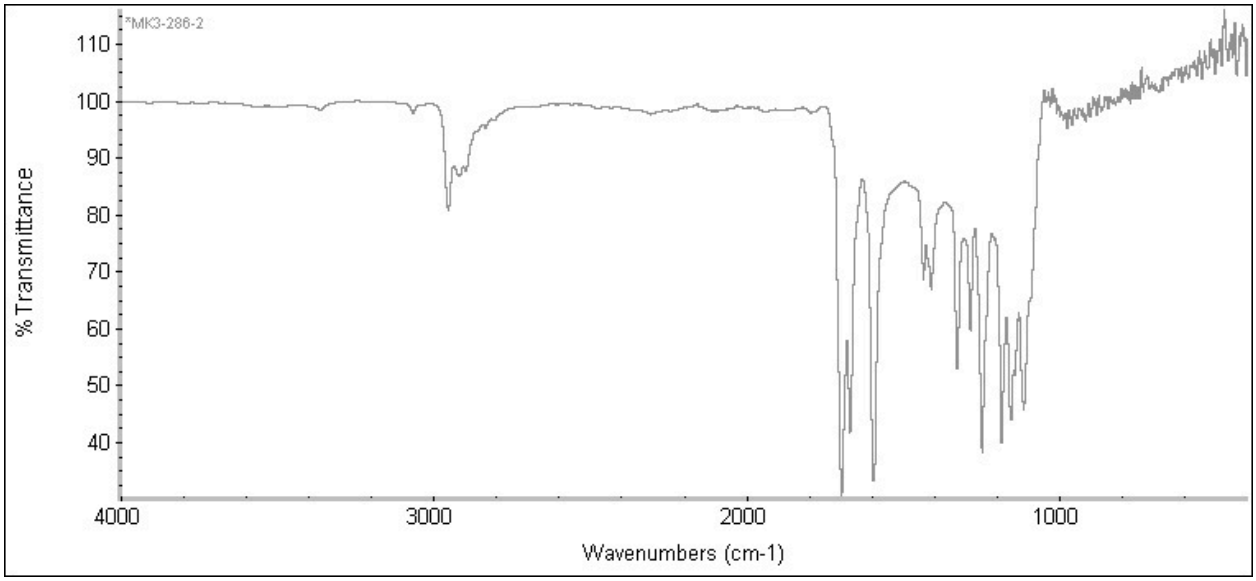
IR

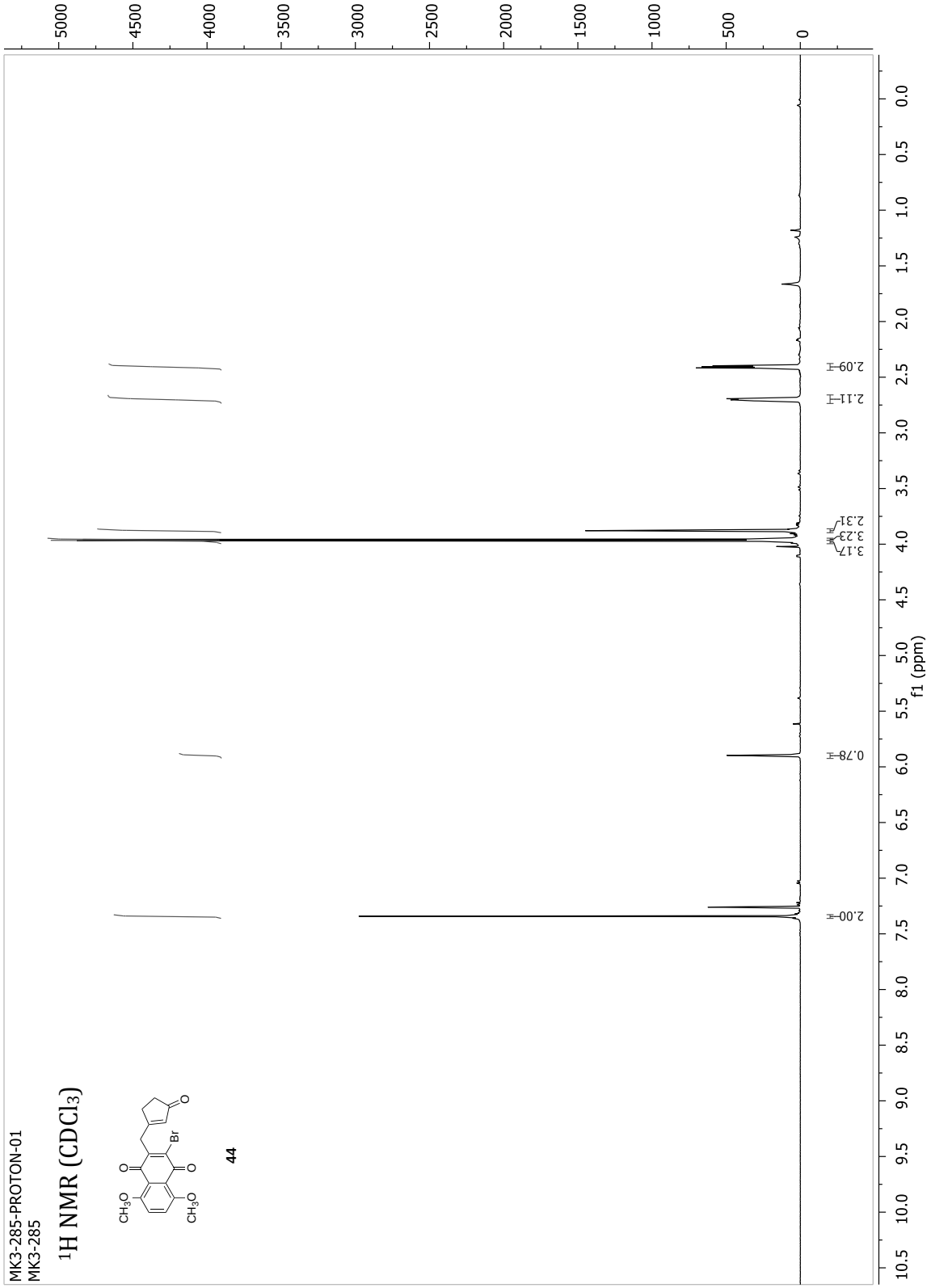

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

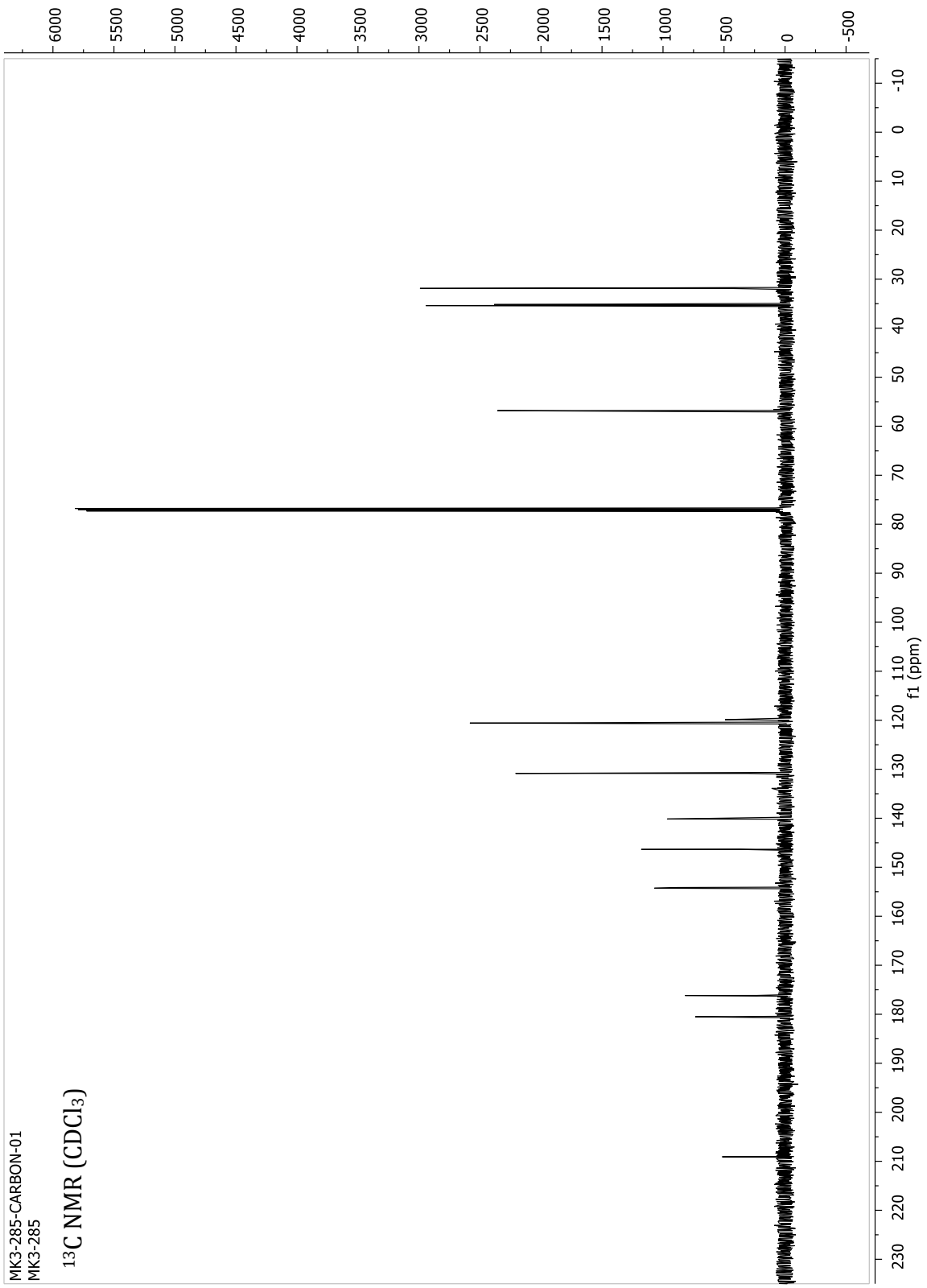

MK3-286-PROTON-01
MK3-286
1H NMR (CDCl3)
TMS
S44
7.95
2.00
1.99
2.04
0.81
f1 (ppm)


MK3-286-CARBON-01
MK3-286
13C NMR (CDCl3)
f1 (ppm)

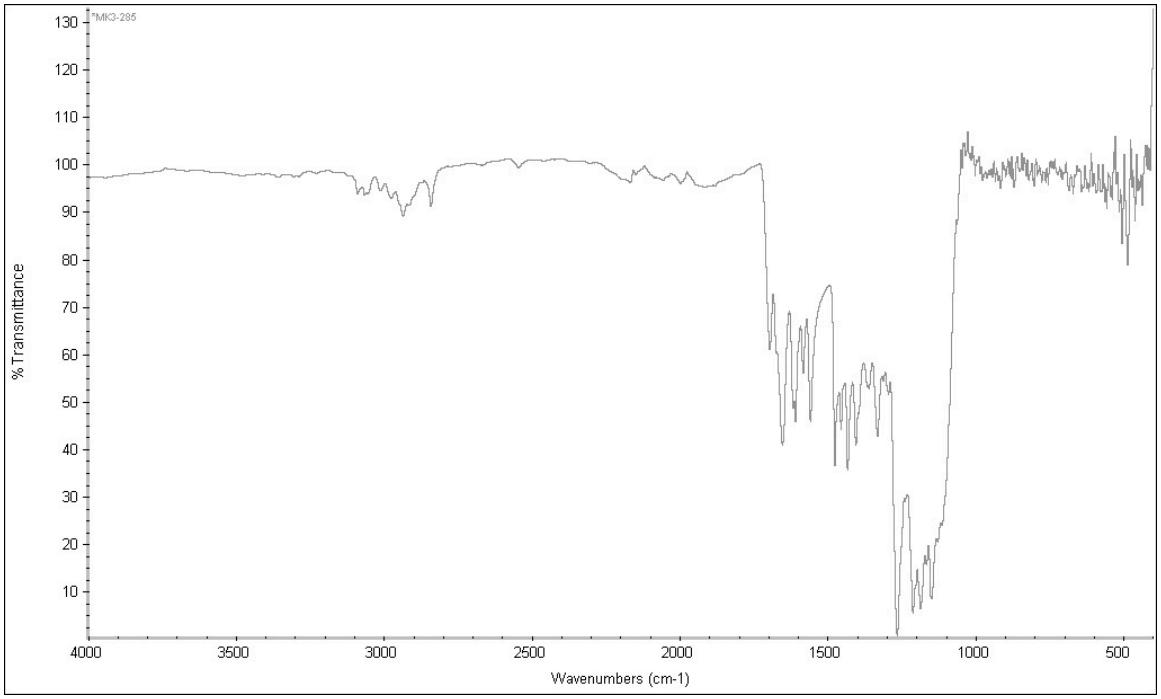
IR

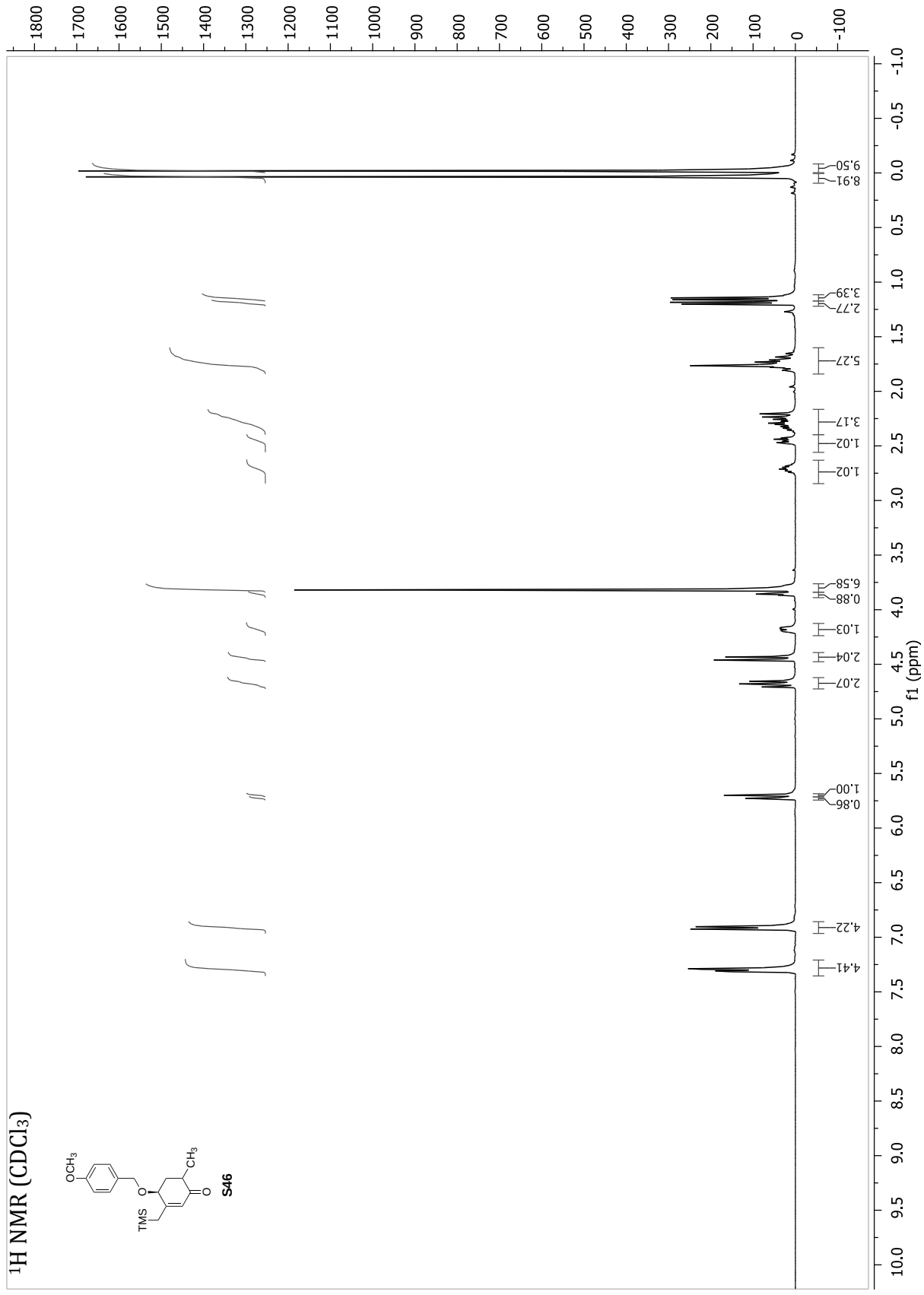

*MK3-286-2
110
100
90
80
70
60
50
40
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

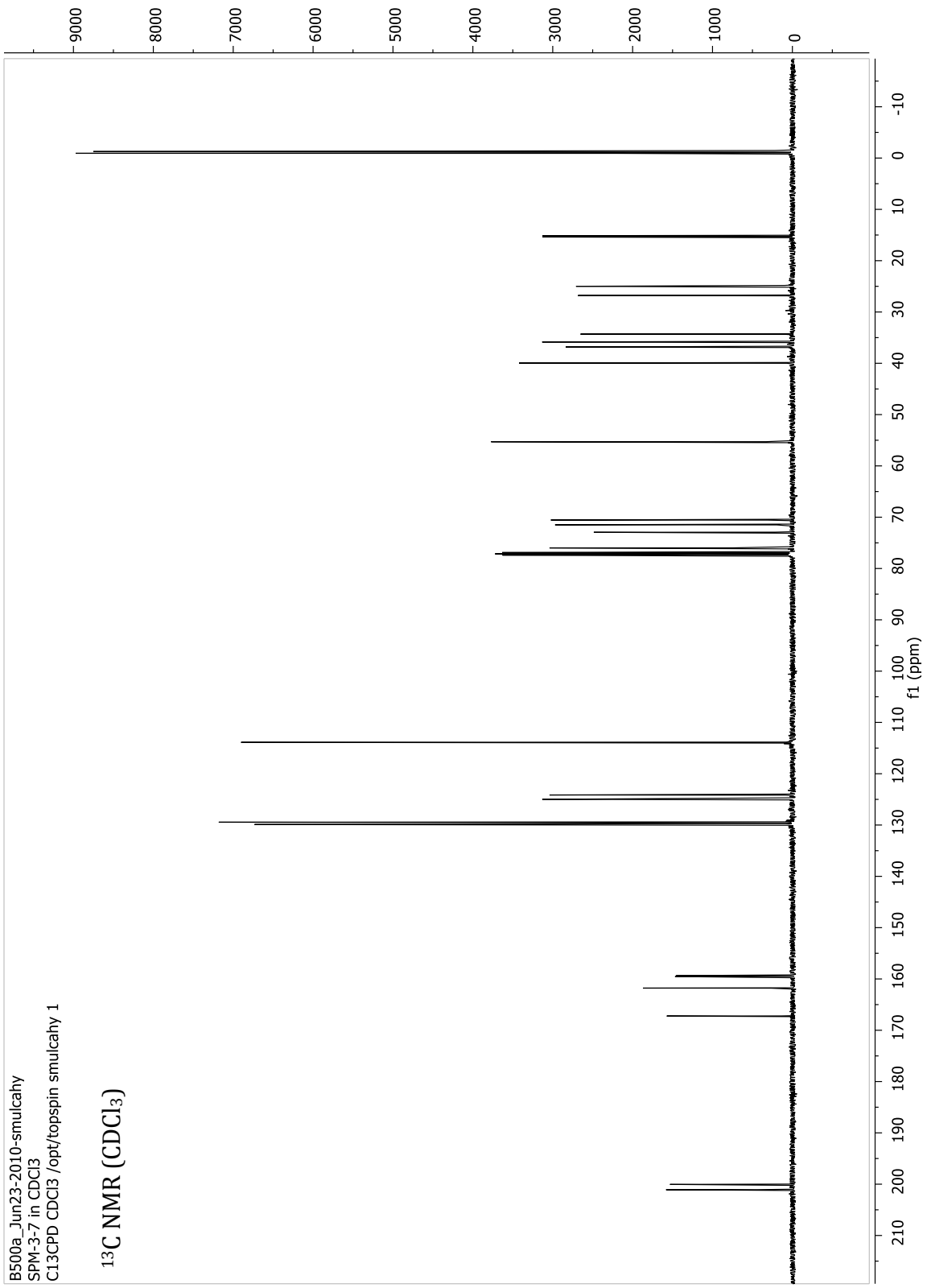

MK3-285-PROTON-01
MK3-285
^{1}H NMR ($CDCl_3$)
44
2.00
0.78
3.17
3.23
2.31
2.11
2.09
f1 (ppm)


MK3-285-CARBON-01
MK3-285
^{13}C NMR ($CDCl_3$)
f1 (ppm)

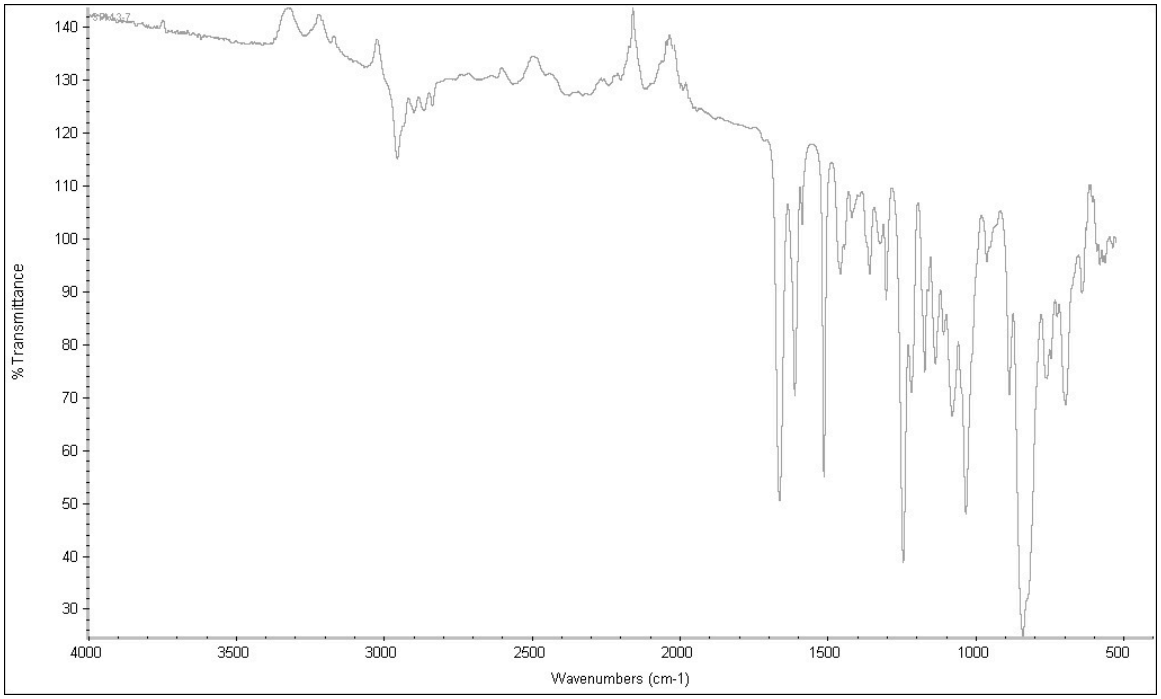
IR

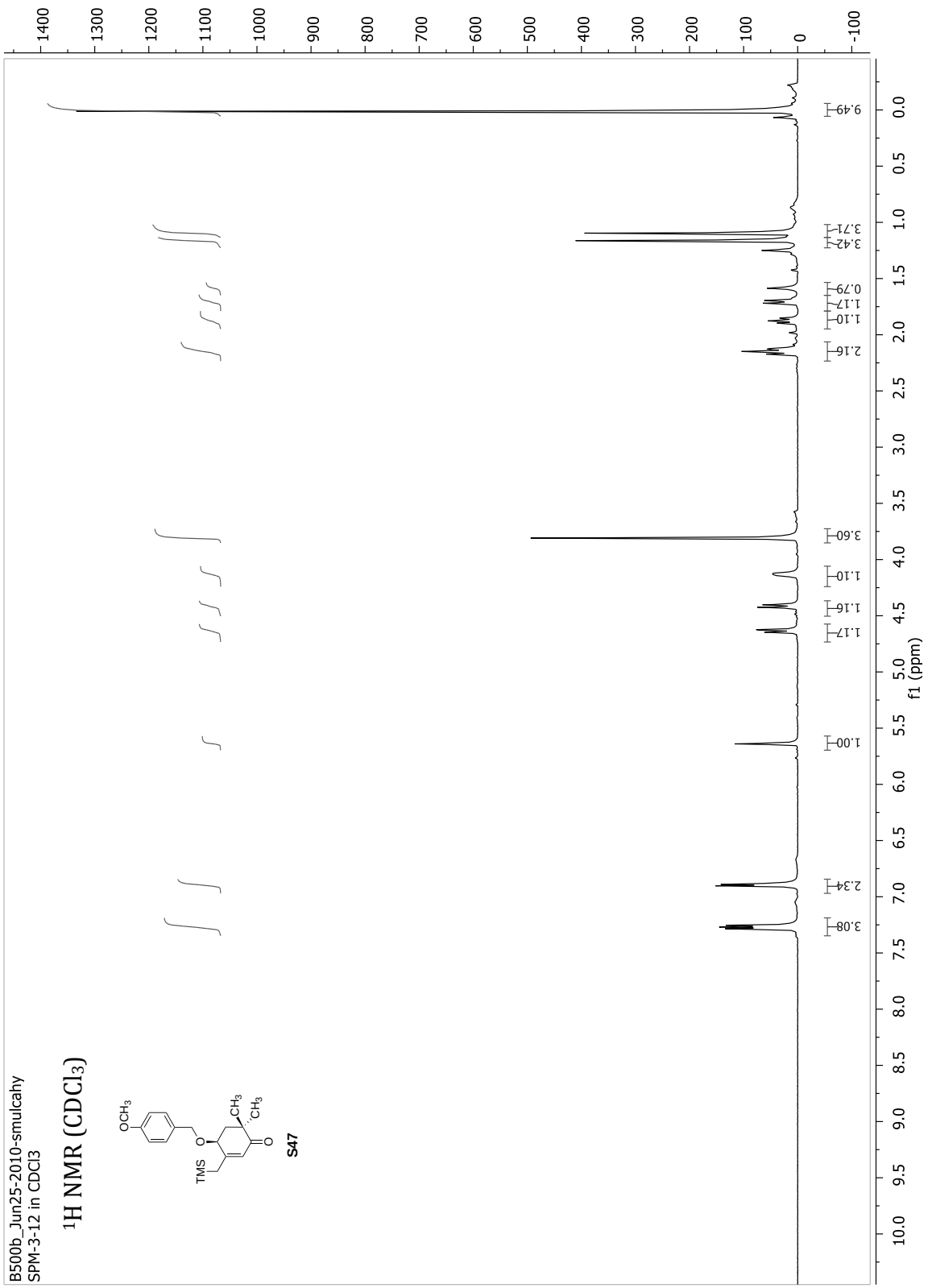

MK3-285
% Transmittance
Wavenumbers (cm-1)
130
120
110
100
90
80
70
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500

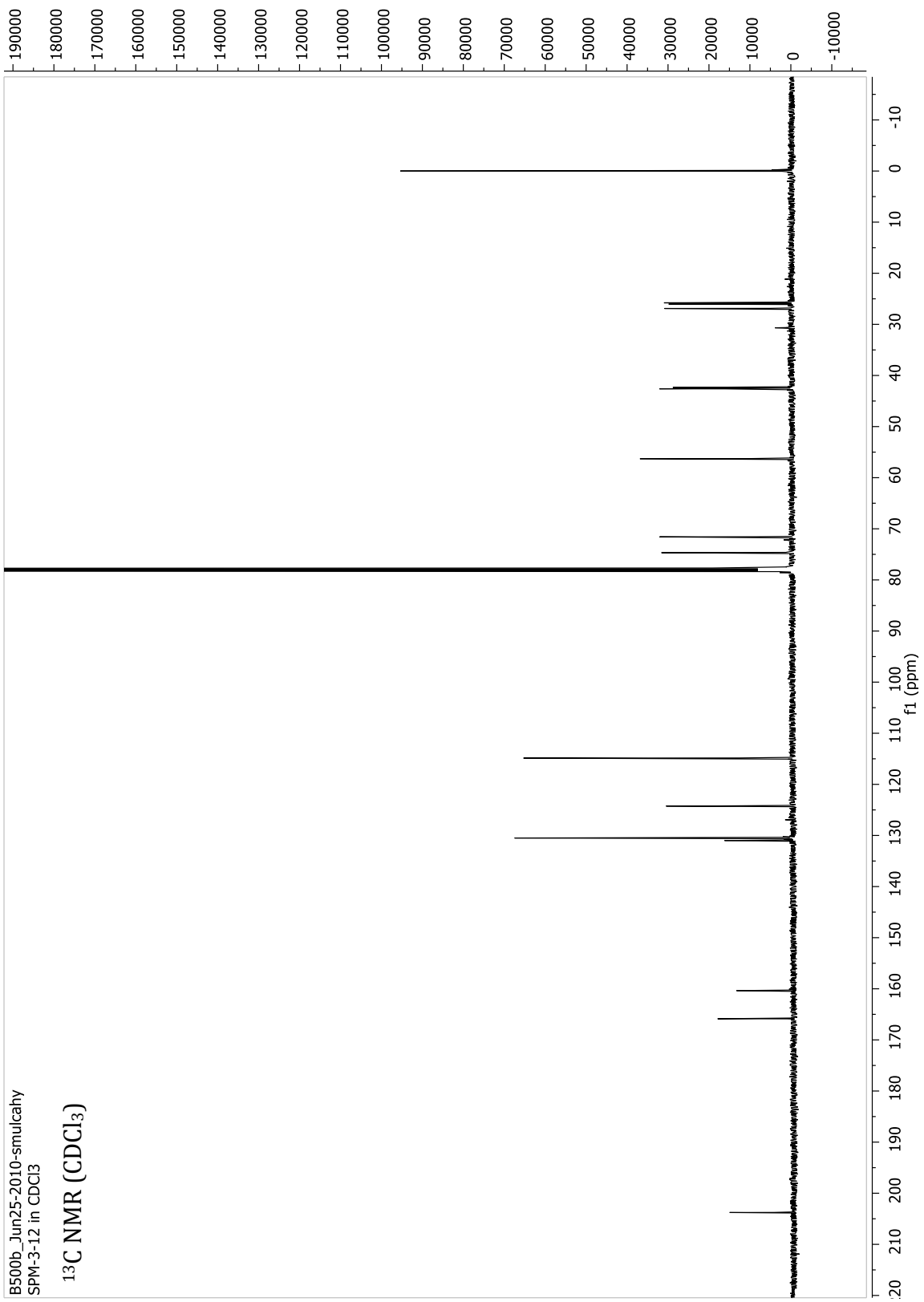

^{1}H NMR ($CDCl_3$)
S46
TMS
OCH_3
CH_3
O
f1 (ppm)
9.50
8.91
3.39
2.77
5.27
3.17
1.02
1.02
6.58
0.88
1.03
2.04
2.07
1.00
0.86
4.22
4.41


B500a_Jun23-2010-smulcahy
SPM-3-7 in CDCl3
C13CPD CDCl3 /opt/topspin smulcahy 1
^{13}C NMR ($CDCl_3$)
f1 (ppm)

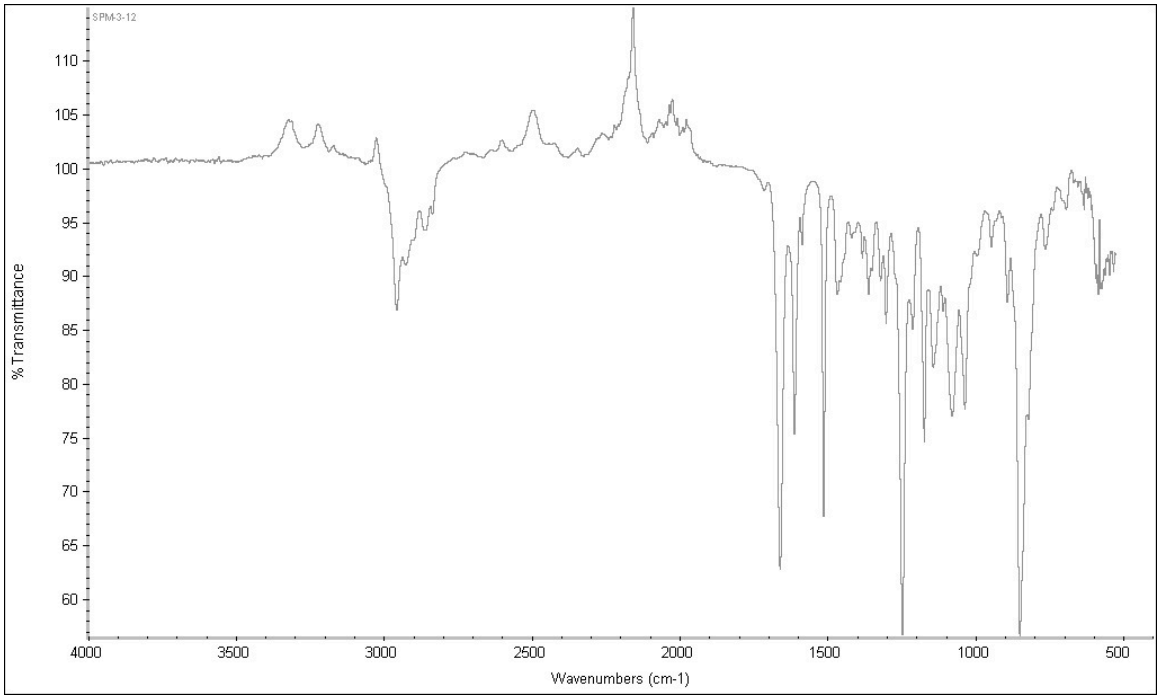
IR

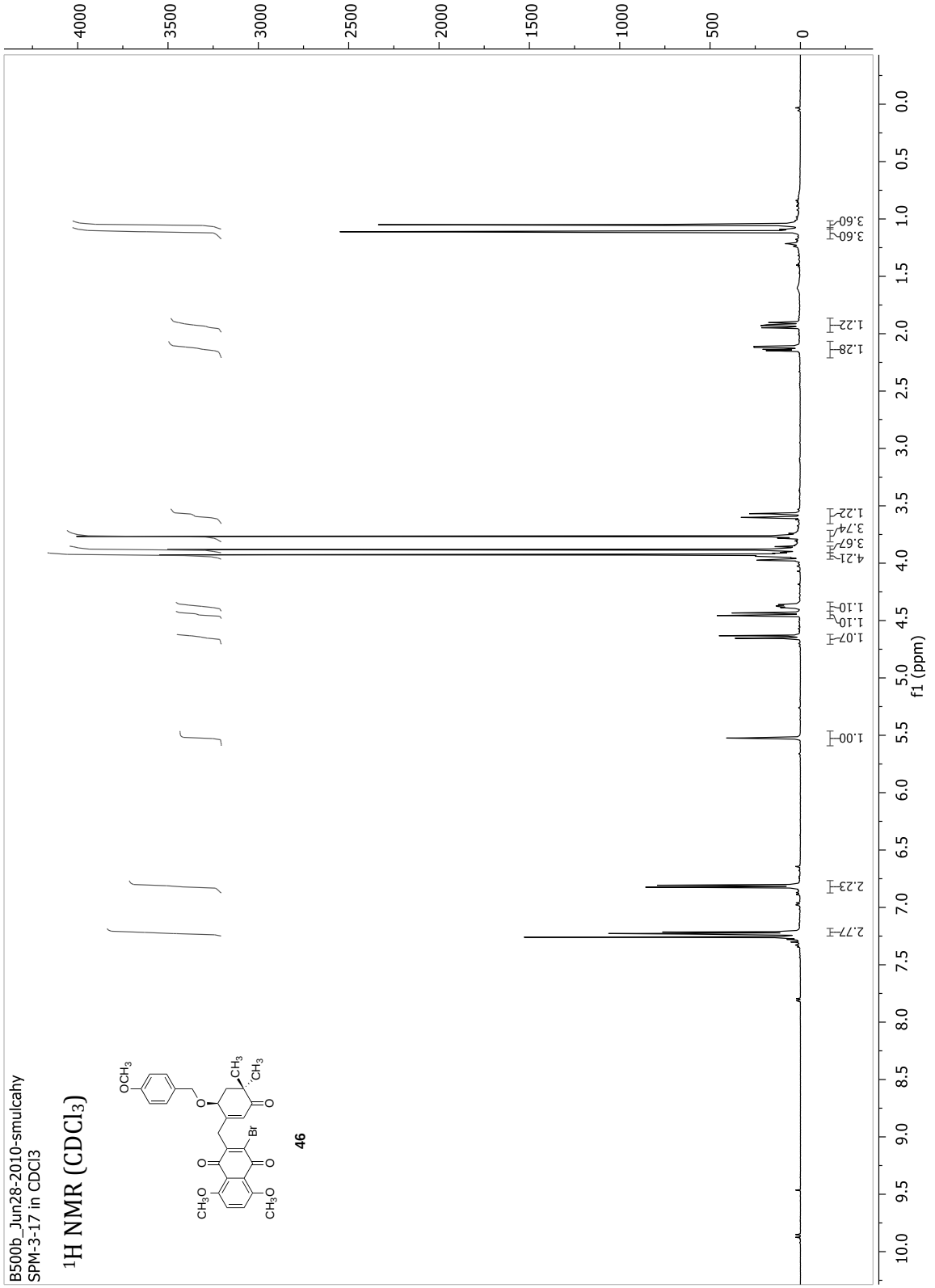

% Transmittance
140
130
120
110
100
90
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

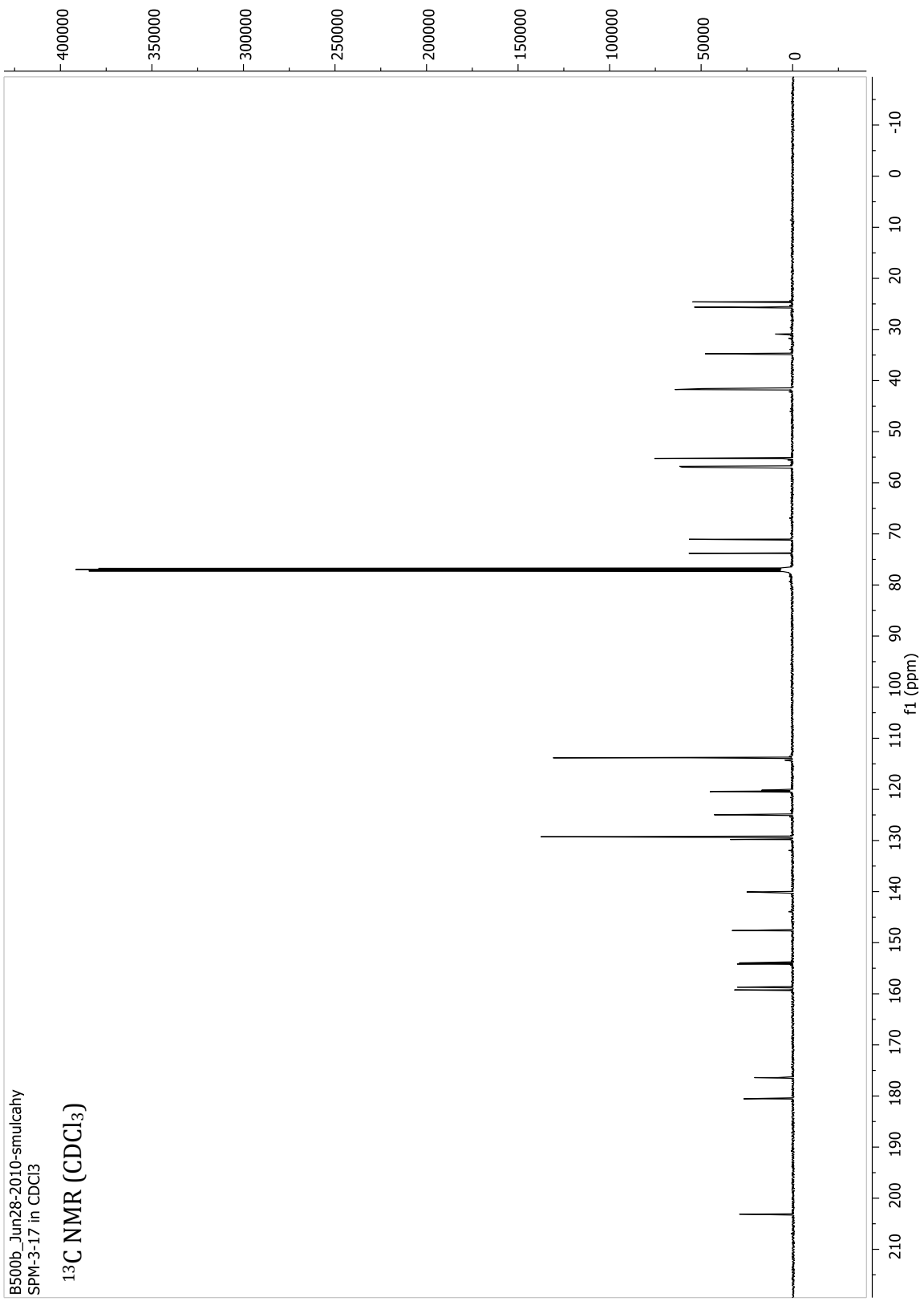

B500b_Jun25-2010-smulcahy
SPM-3-12 in CDCl3
^{1}H NMR ($CDCl_3$)
S47
9.49
3.71
3.42
0.79
1.17
1.10
2.16
3.60
1.10
1.16
1.17
1.00
2.34
3.08
f1 (ppm)


B500b_Jun25-2010-smulcahy
SPM-3-12 in CDCl3
13C NMR (CDCl3)
f1 (ppm)

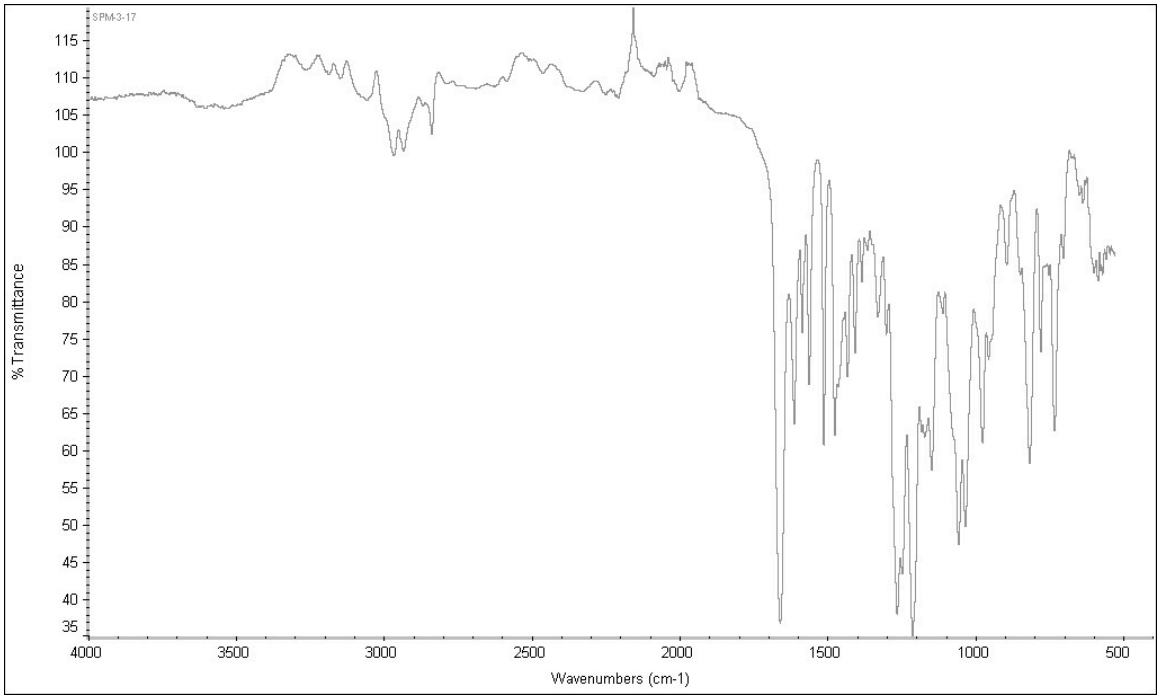
IR

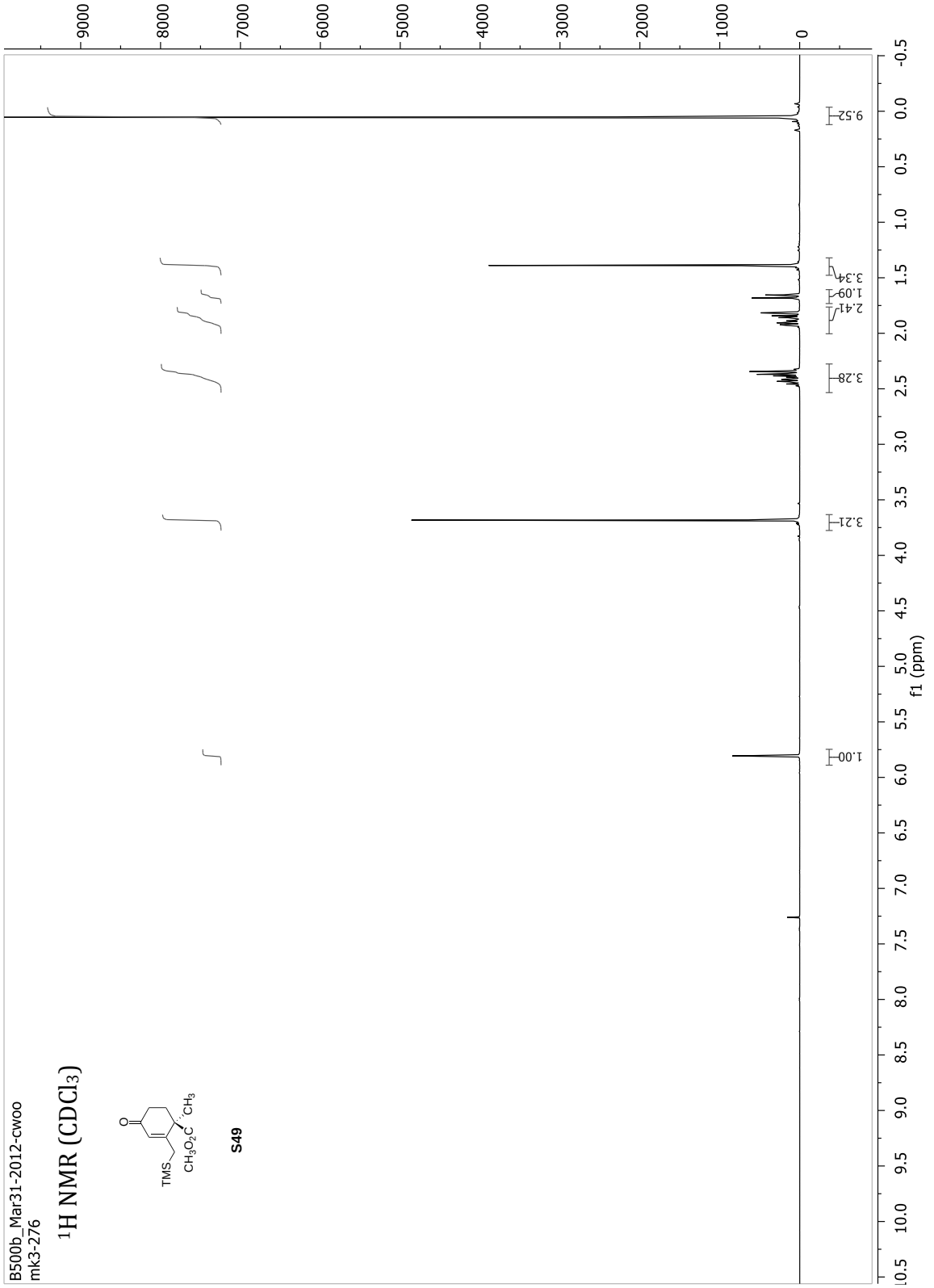

SPM-3-12
% Transmittance
110
105
100
95
90
85
80
75
70
65
60
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

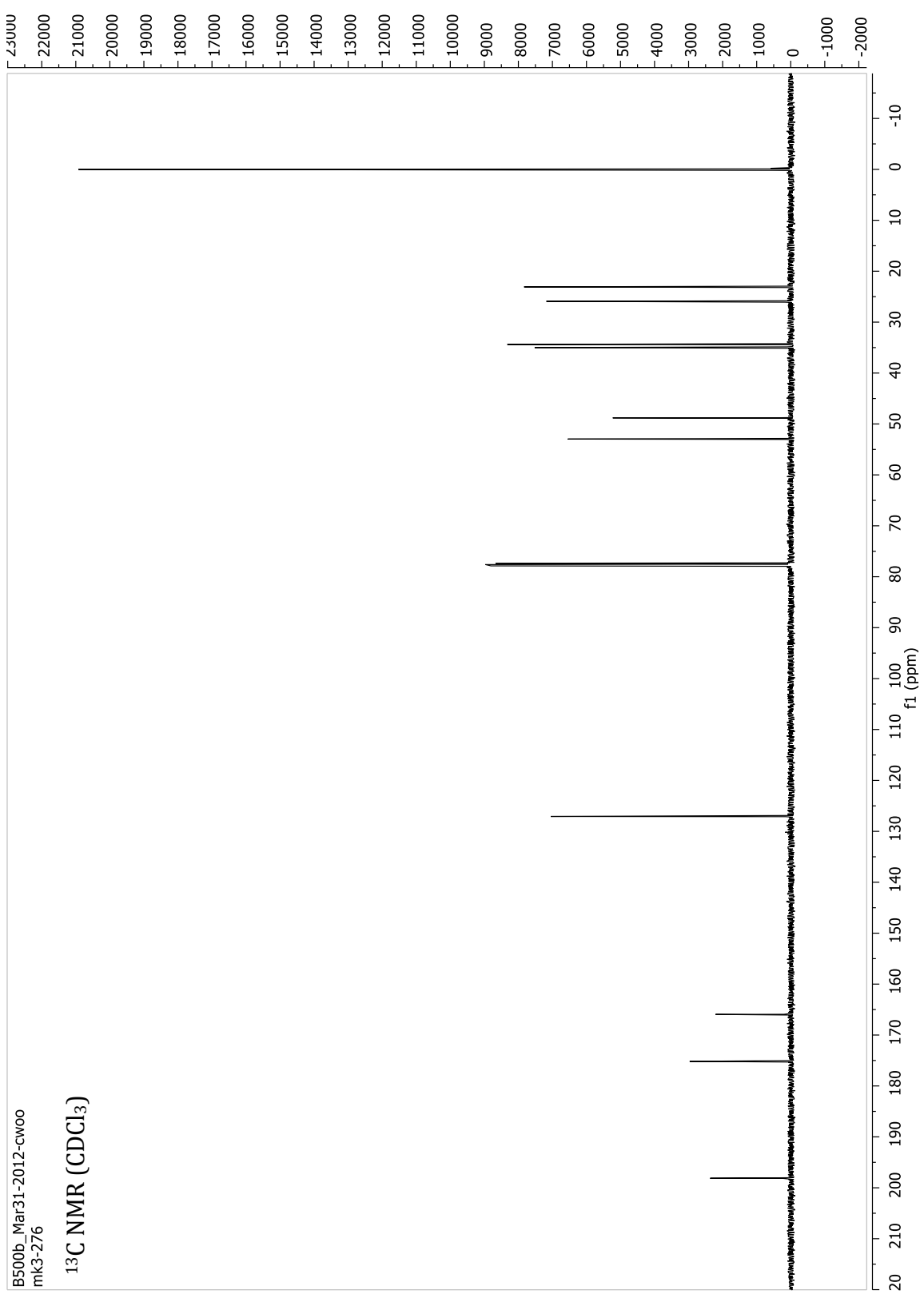

B500b_Jun28-2010-smulcahy
SPM-3-17 in CDCl3
1H NMR (CDCl3)
46
2.77
2.23
1.00
1.07
1.10
1.10
4.21
3.67
3.74
1.22
1.28
1.22
3.60
3.60
f1 (ppm)


B500b_Jun28-2010-smulcahy
SPM-3-17 in CDCl3
13C NMR (CDCl3)
400000
350000
300000
250000
200000
150000
100000
50000
0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

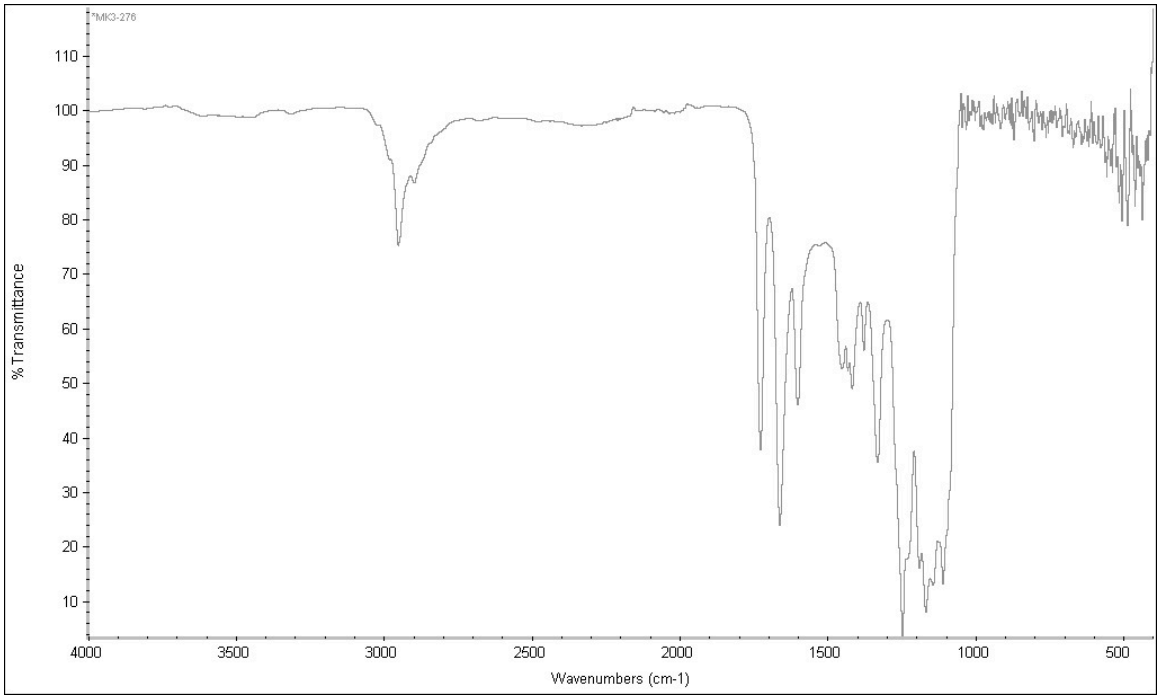
IR

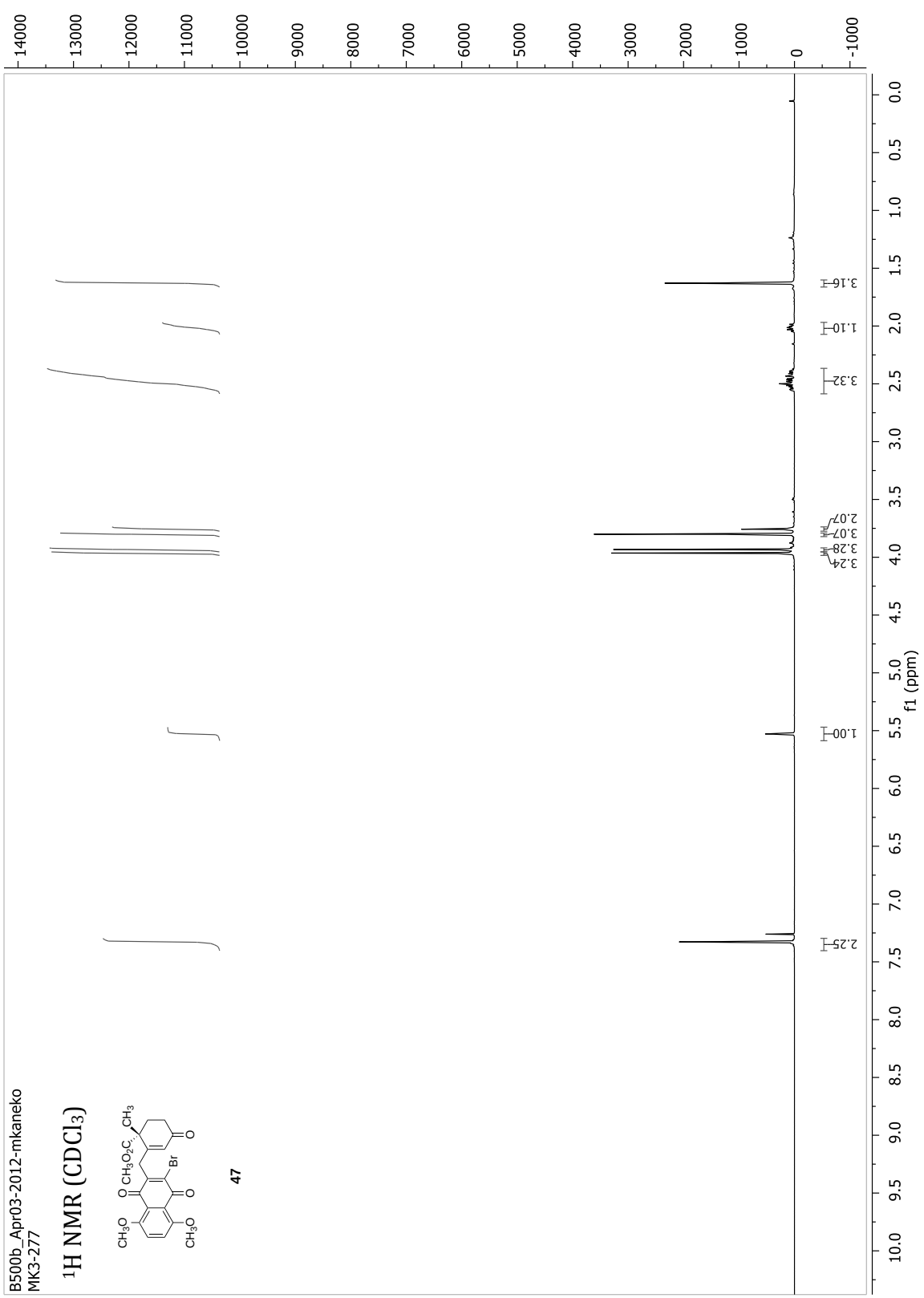

SPM-3-17
% Transmittance
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

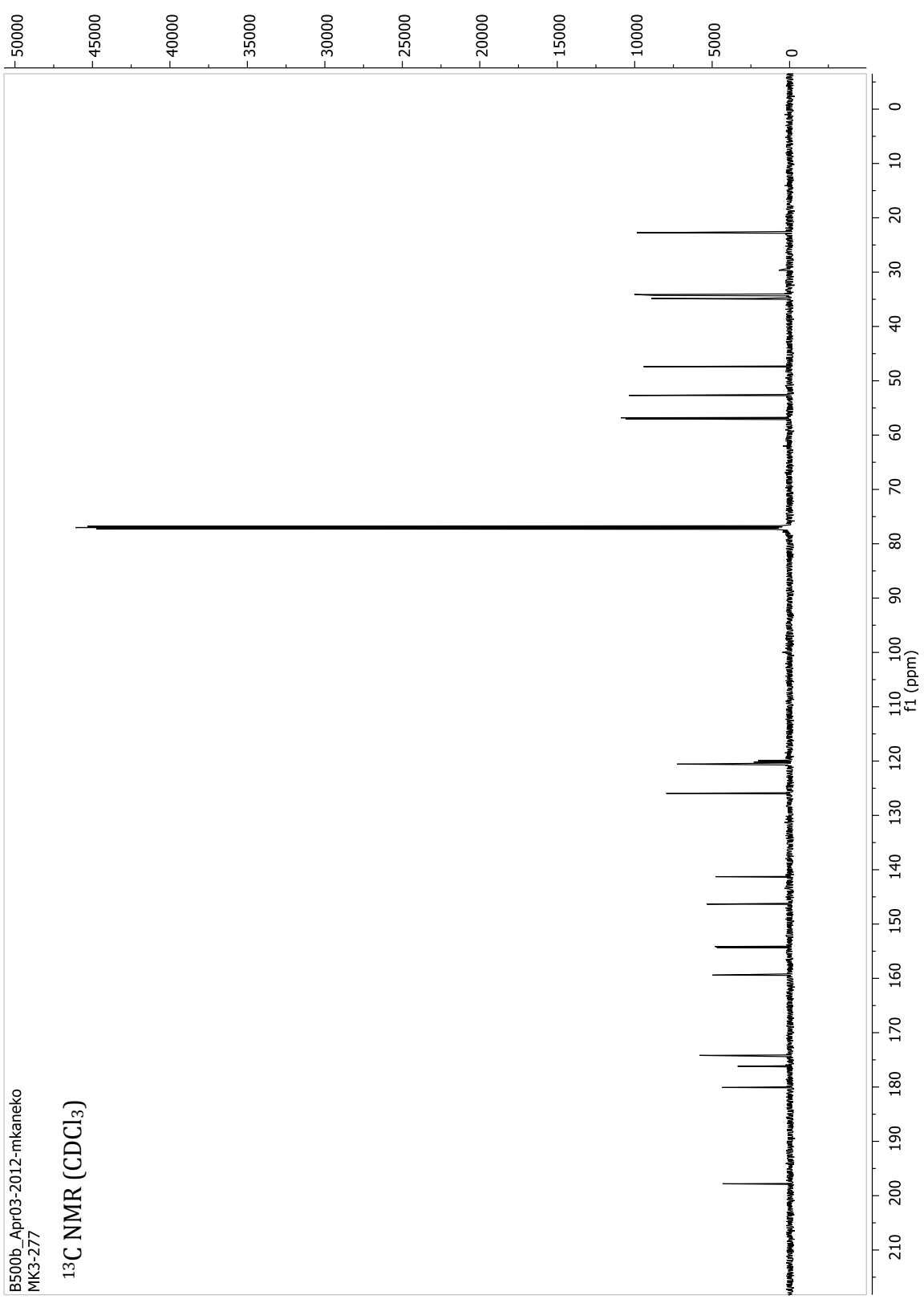

B500b_Mar31-2012-cwoo
mk3-276
^{1}H NMR ($CDCl_3$)
S49
TMS
CH_3O_2C
CH_3
O
9.52
3.34
1.09
2.41
3.28
3.21
1.00
f1 (ppm)


B500b_Mar31-2012-cwoo
mk3-276
^{13}C NMR ($CDCl_3$)
f1 (ppm)

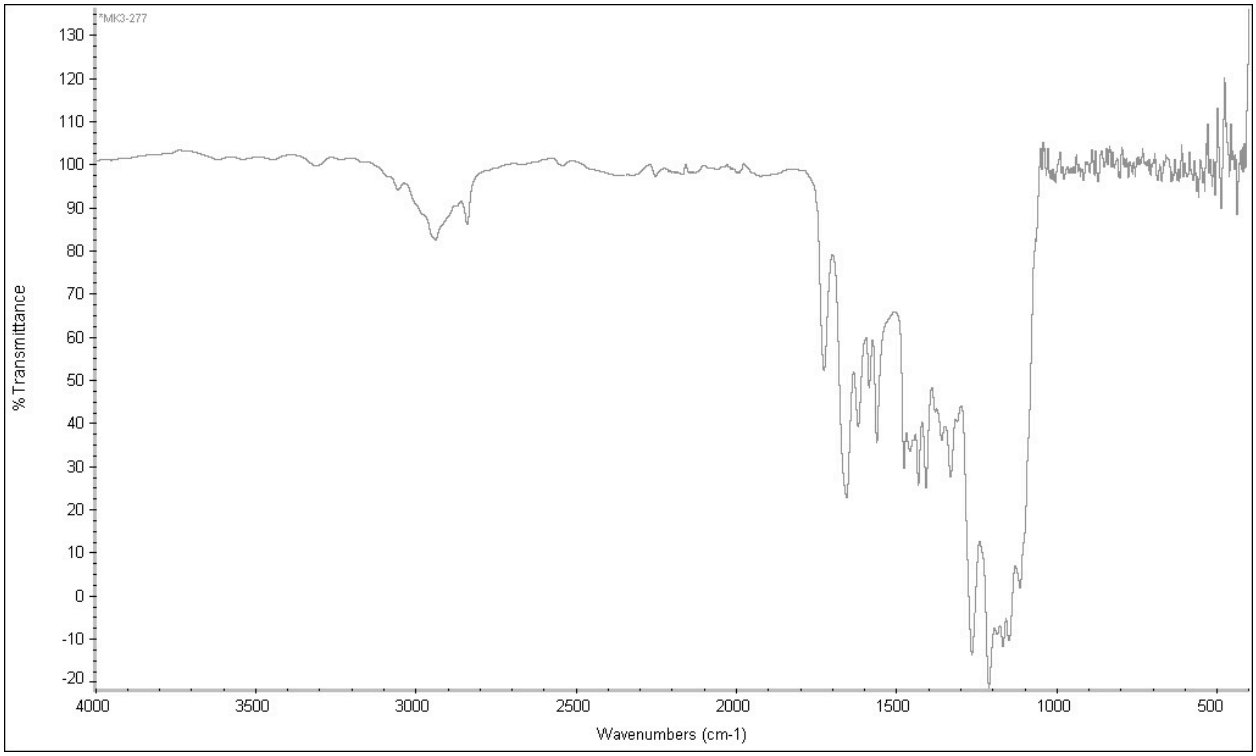
IR

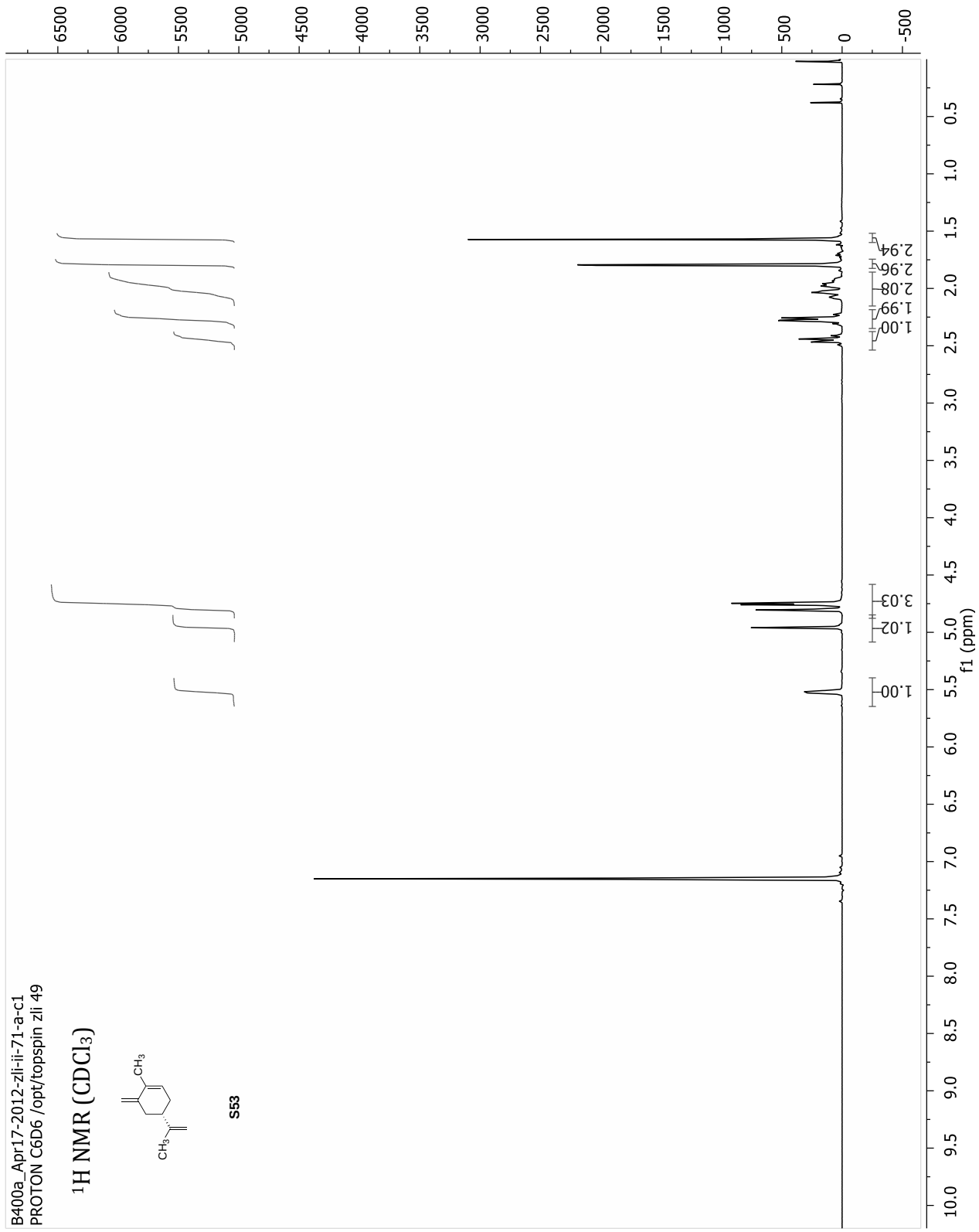

*MK3-276
% Transmittance
110
100
90
80
70
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

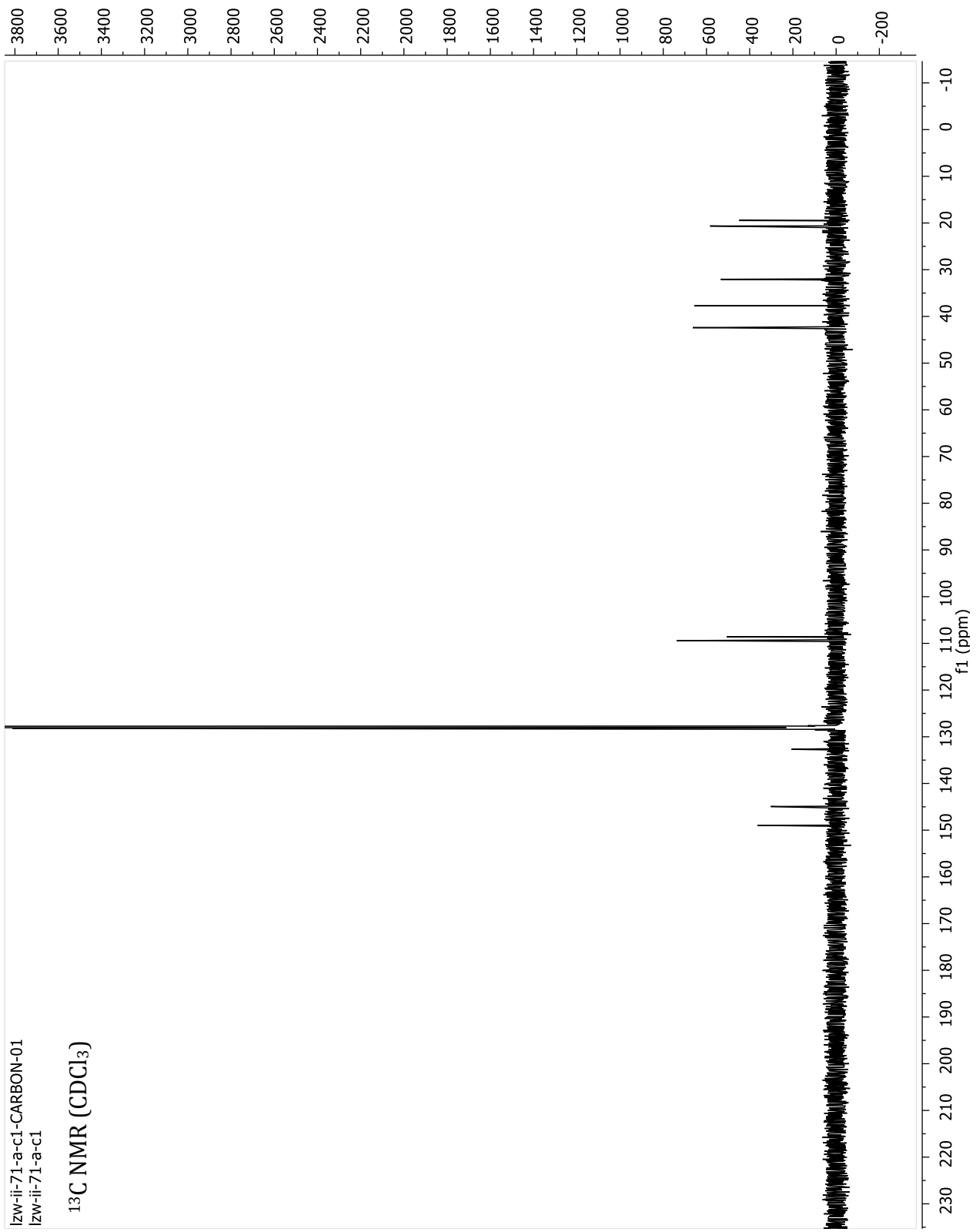

B500b_Apr03-2012-mkaneko
MK3-277
1H NMR (CDCl3)
47
2.25
1.00
3.24
3.28
3.07
2.07
3.32
1.10
3.16
f1 (ppm)


B500b_Apr03-2012-mkaneko
MK3-277
13C NMR (CDCl3)
f1 (ppm)

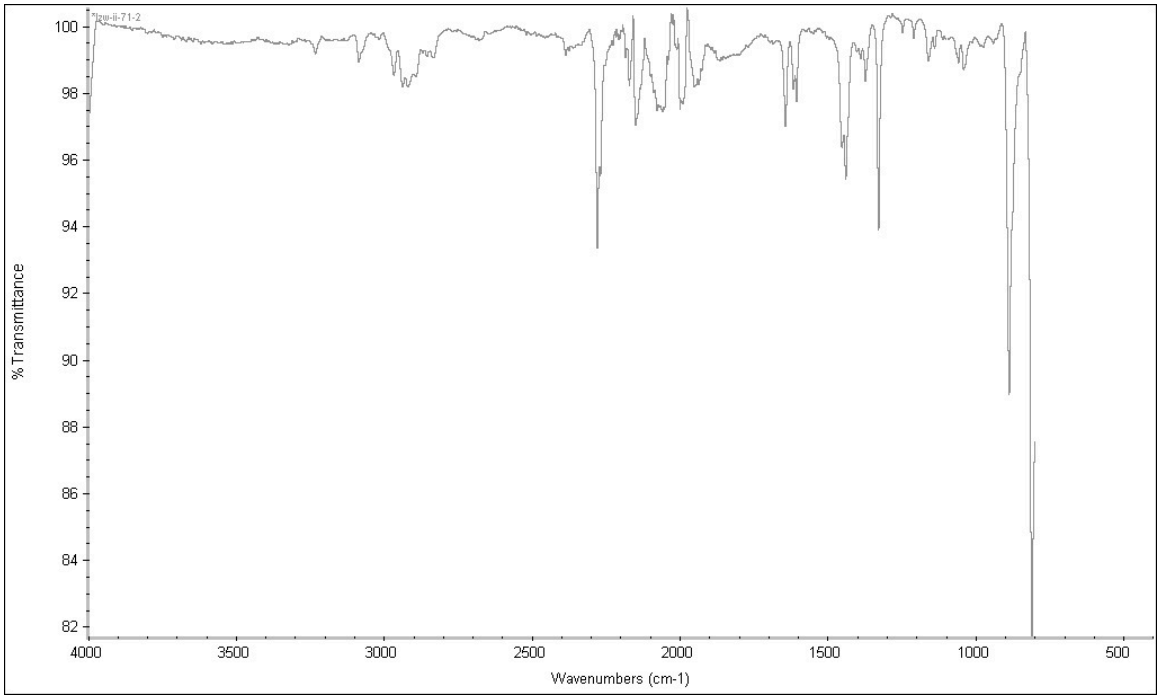
IR

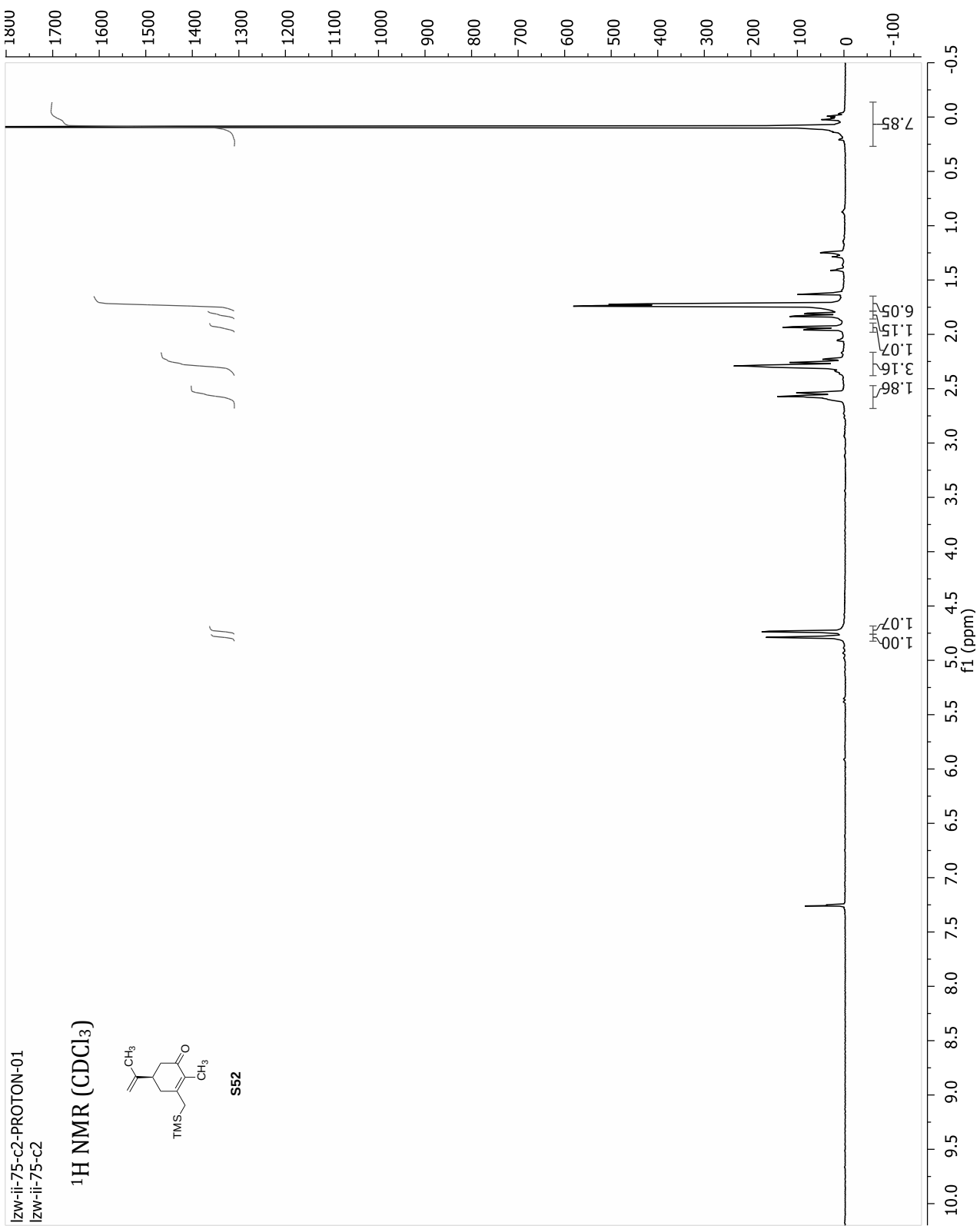

MK3-277
% Transmittance
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

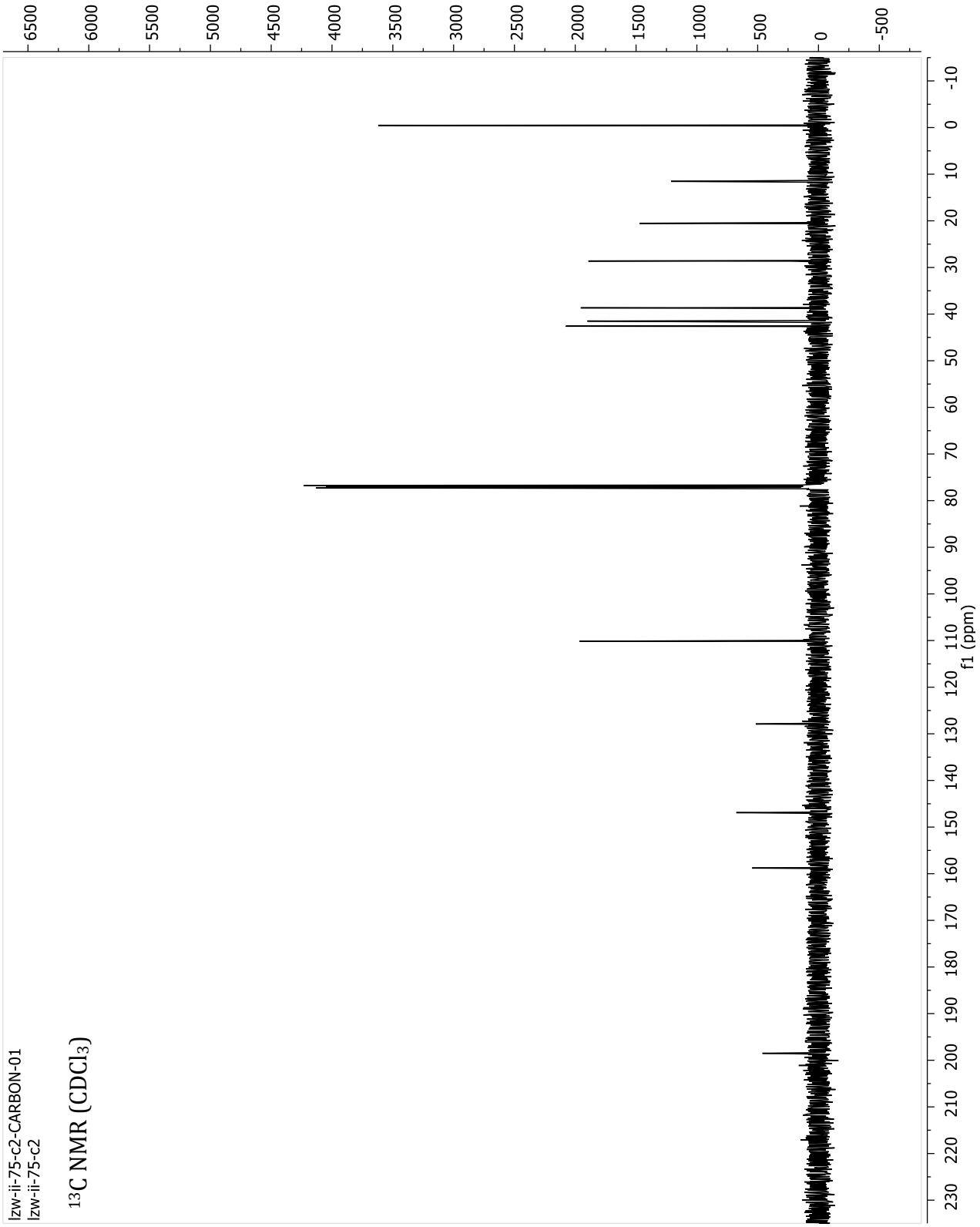

B400a_Apr17-2012-zli-ii-71-a-c1
PROTON C6D6 /opt/topspin zli 49
^{1}H NMR ($CDCl_3$)
S53
CH3
CH3
1.00
1.02
3.03
1.00
1.99
2.08
2.96
2.94
f1 (ppm)


lzw-ii-71-a-c1-CARBON-01
lzw-ii-71-a-c1
^{13}C NMR ($CDCl_3$)
f1 (ppm)

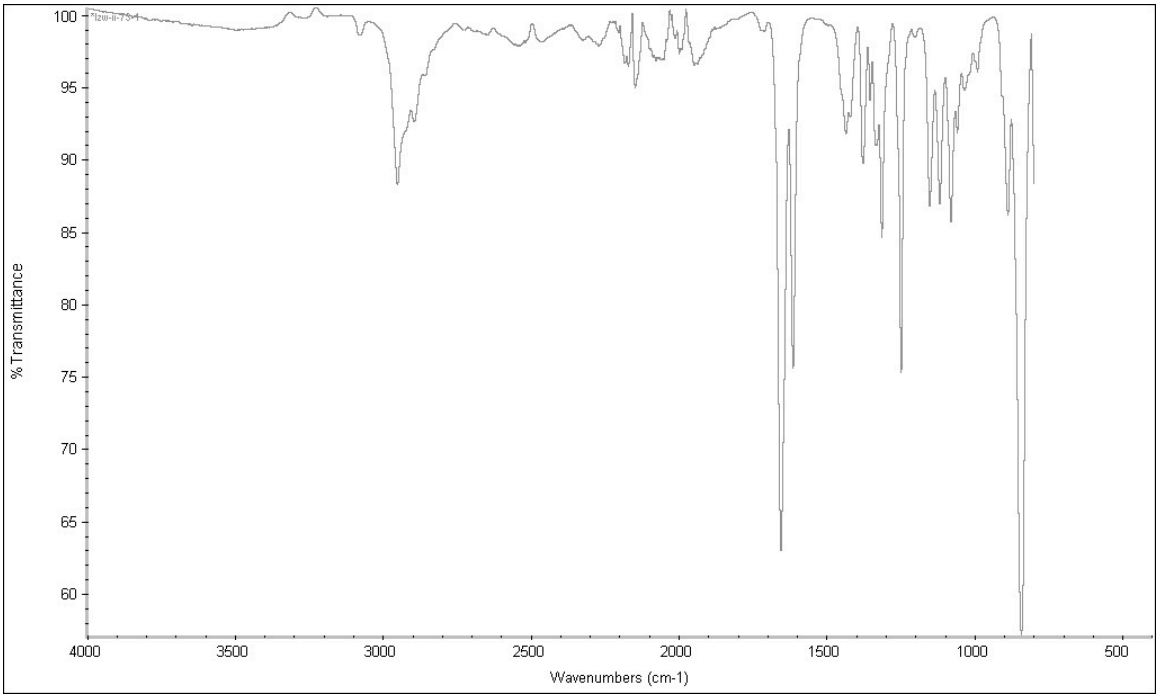
IR

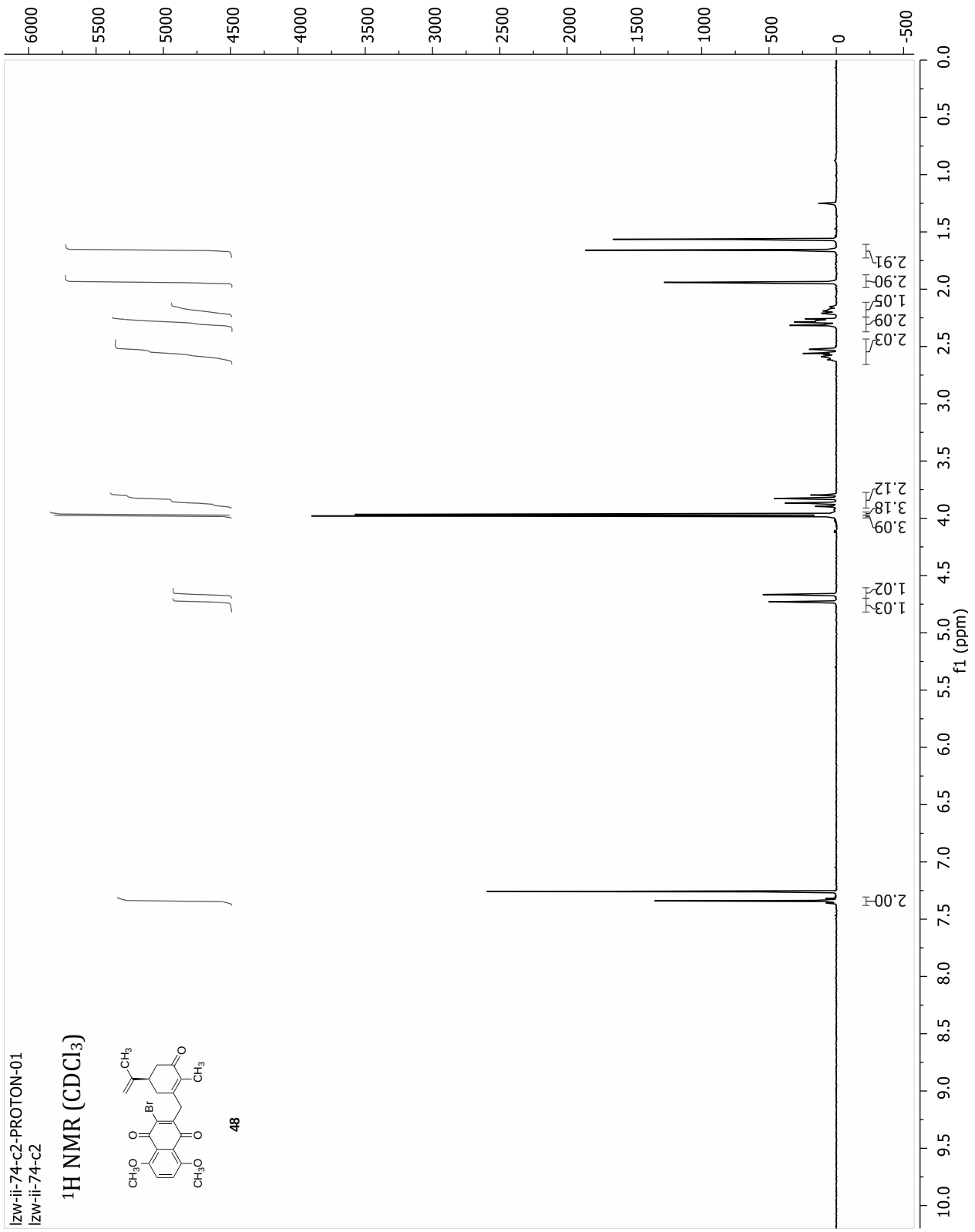

100
98
96
94
92
90
88
86
84
82
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

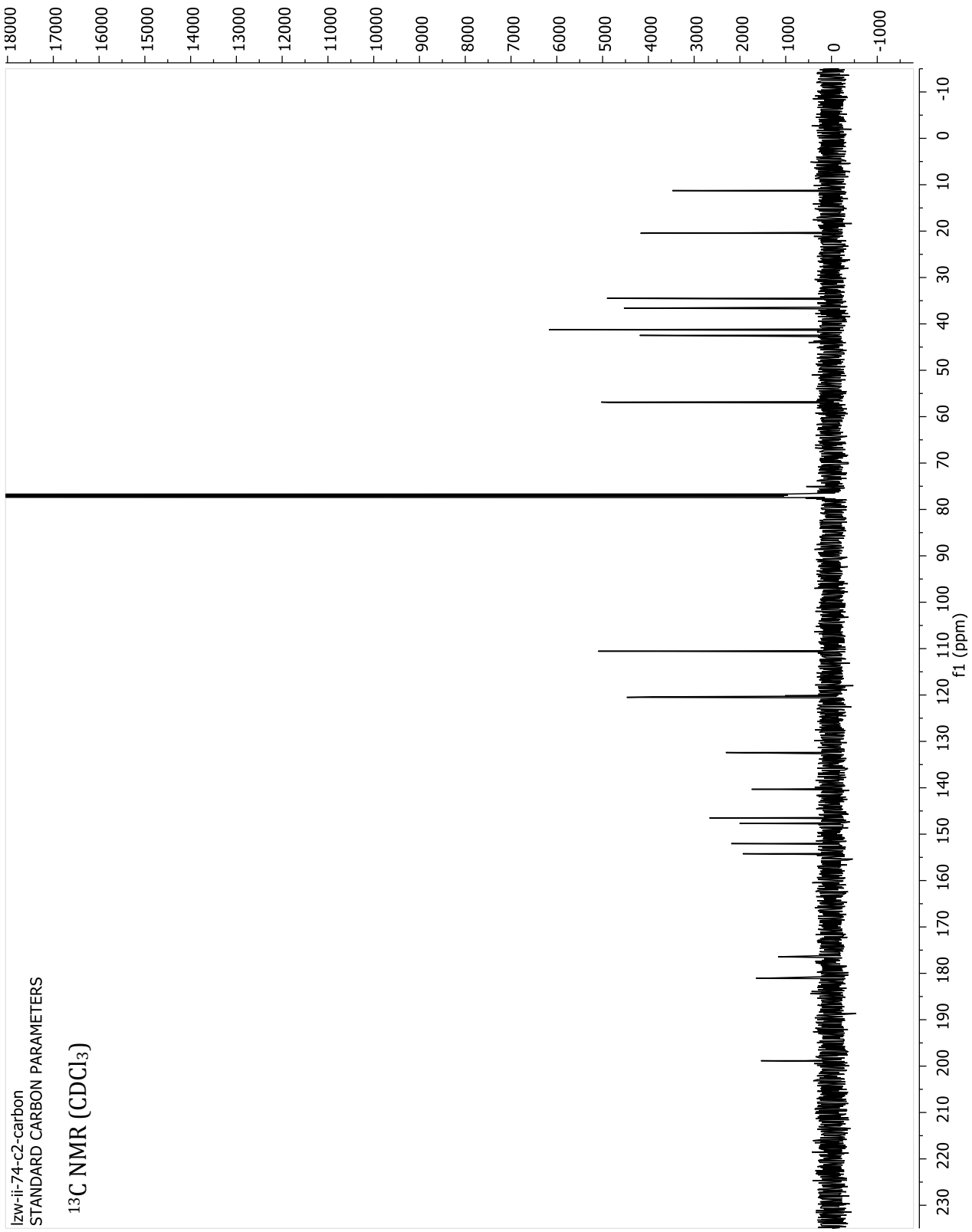

lzw-ii-75-c2-PROTON-01
lzw-ii-75-c2
^{1}H NMR ($CDCl_3$)
S52
TMS
CH_3
CH_3
O
7.85
6.05
1.15
1.07
3.16
1.86
1.00
1.07
f1 (ppm)


lzw-ii-75-c2-CARBON-01
lzw-ii-75-c2
13C NMR (CDCl3)
f1 (ppm)

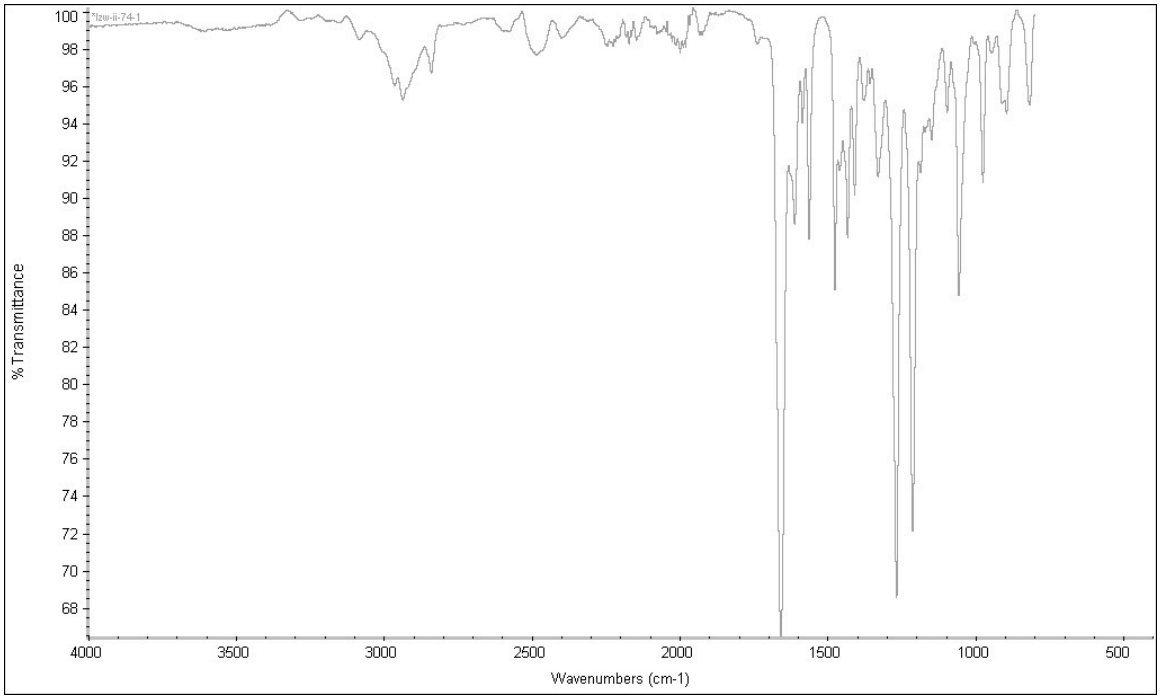
IR

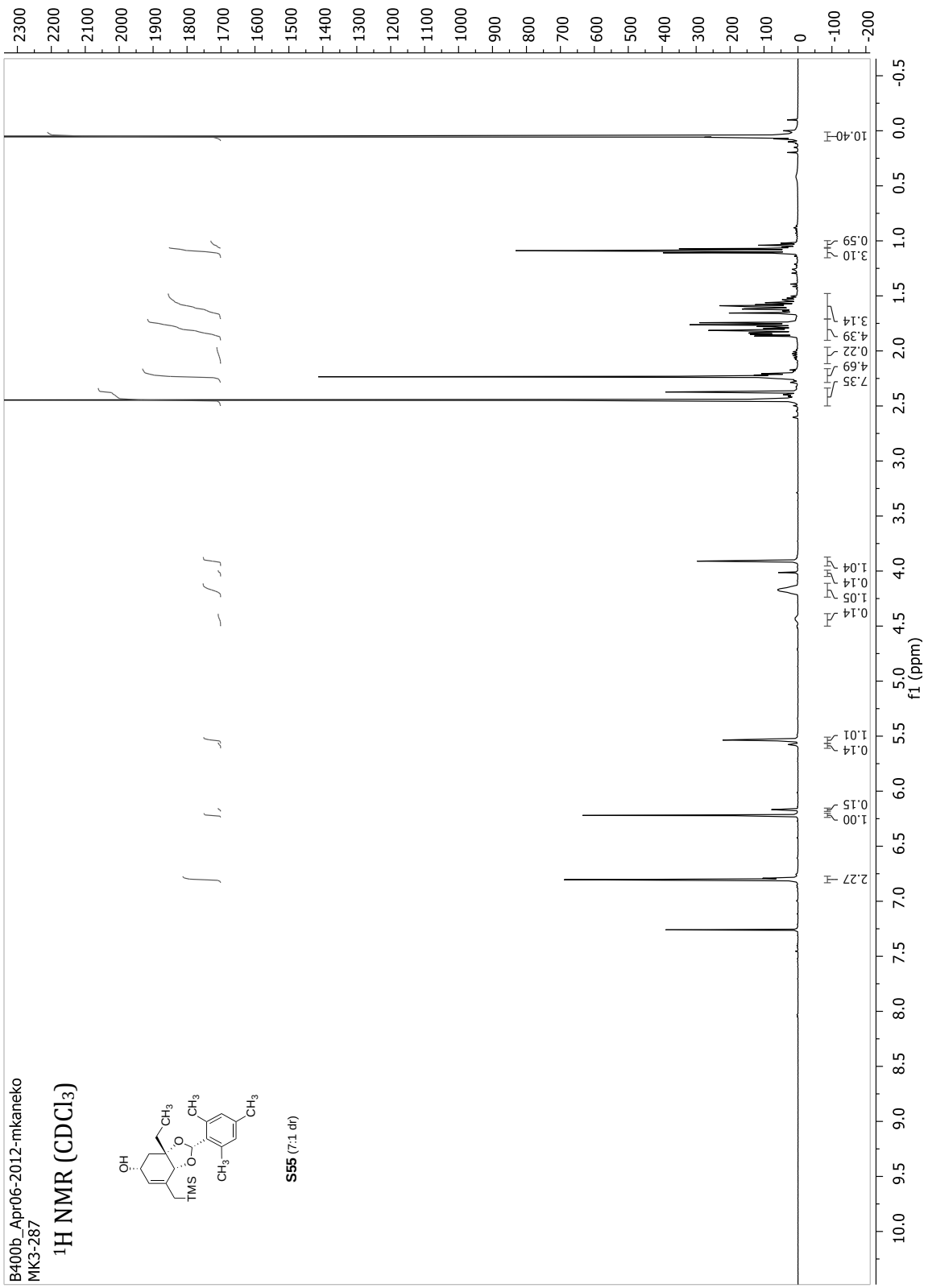

100
95
90
85
80
75
70
65
60
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

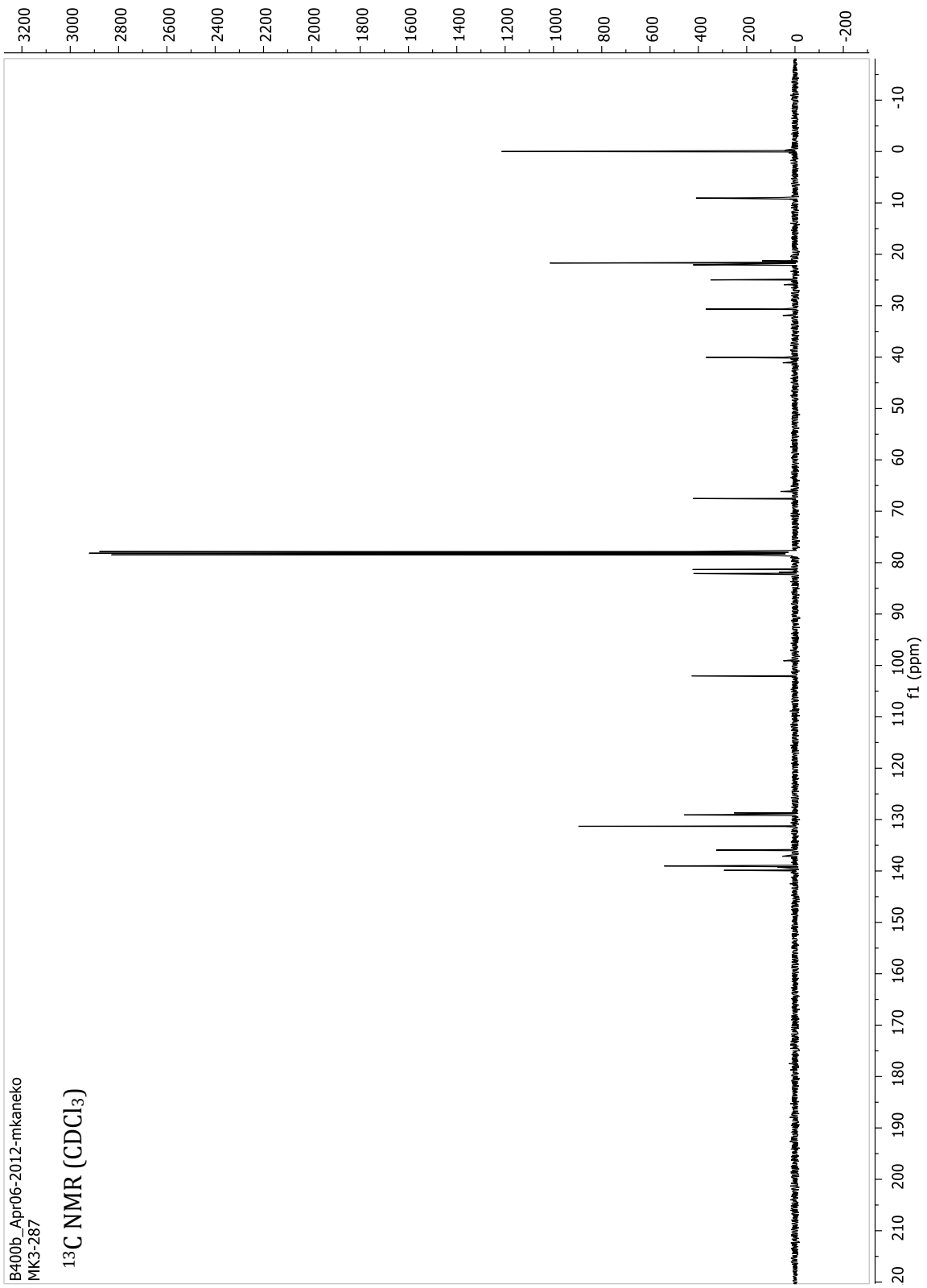

lzw-ii-74-c2-PROTON-01
lzw-ii-74-c2
1H NMR (CDCl3)
48
2.00
1.03
1.02
3.09
3.18
2.12
2.03
2.09
1.05
2.90
2.91
f1 (ppm)


lzw-ii-74-c2-carbon
STANDARD CARBON PARAMETERS
13C NMR (CDCl3)
f1 (ppm)

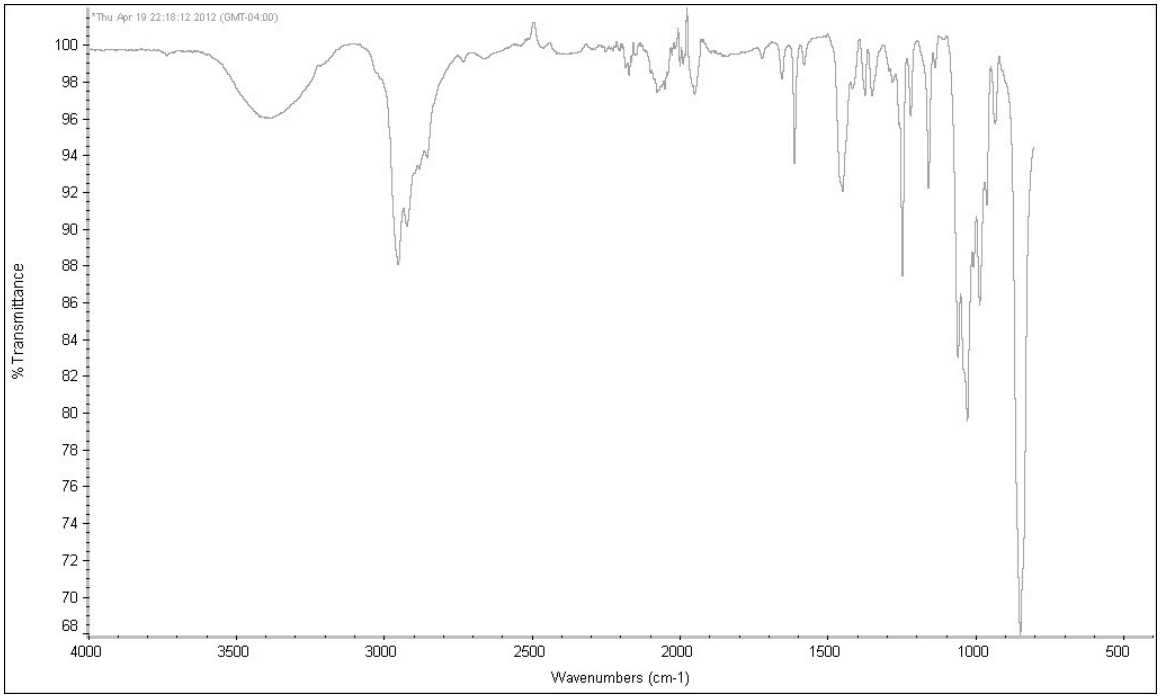
IR

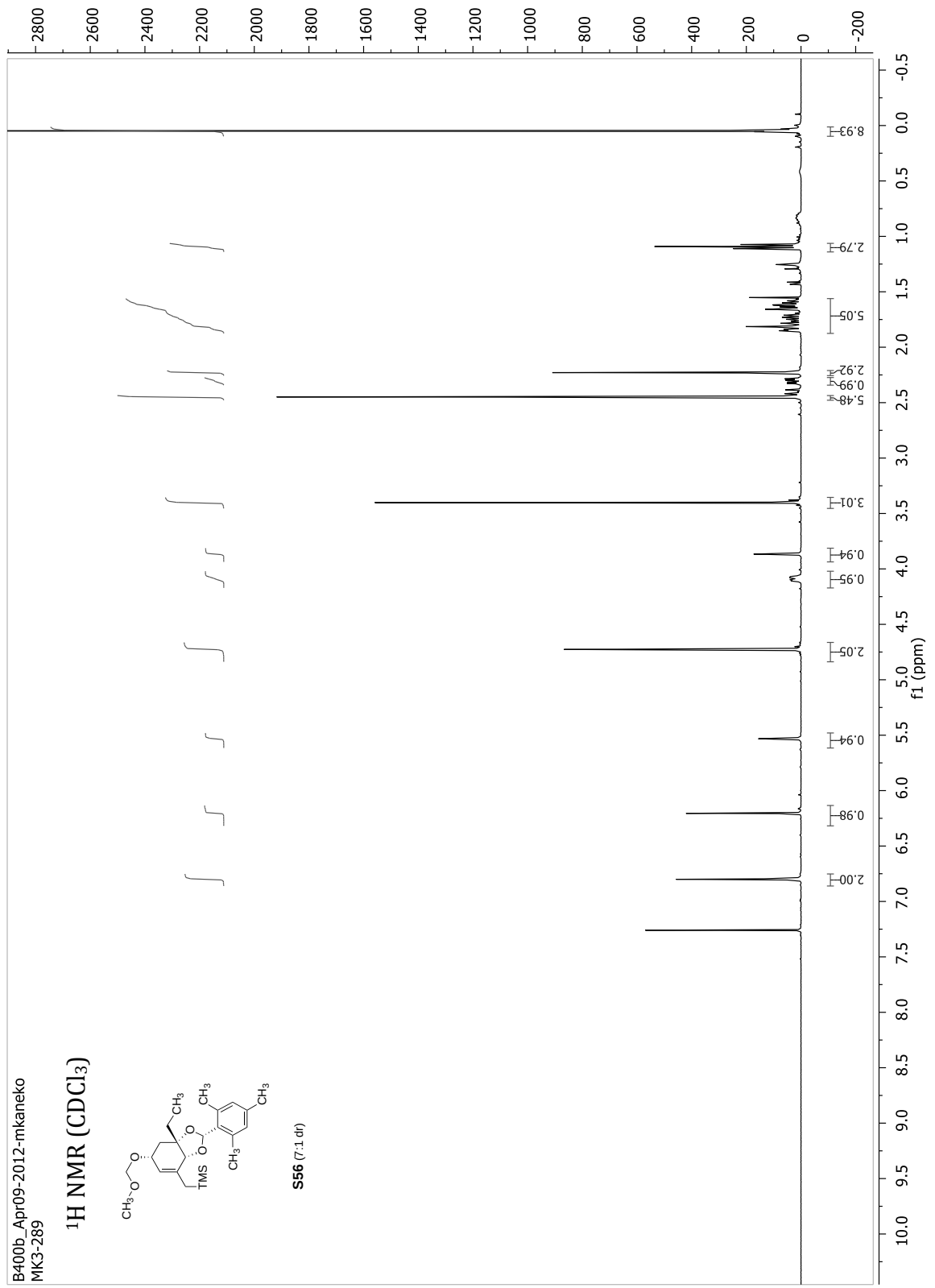

100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

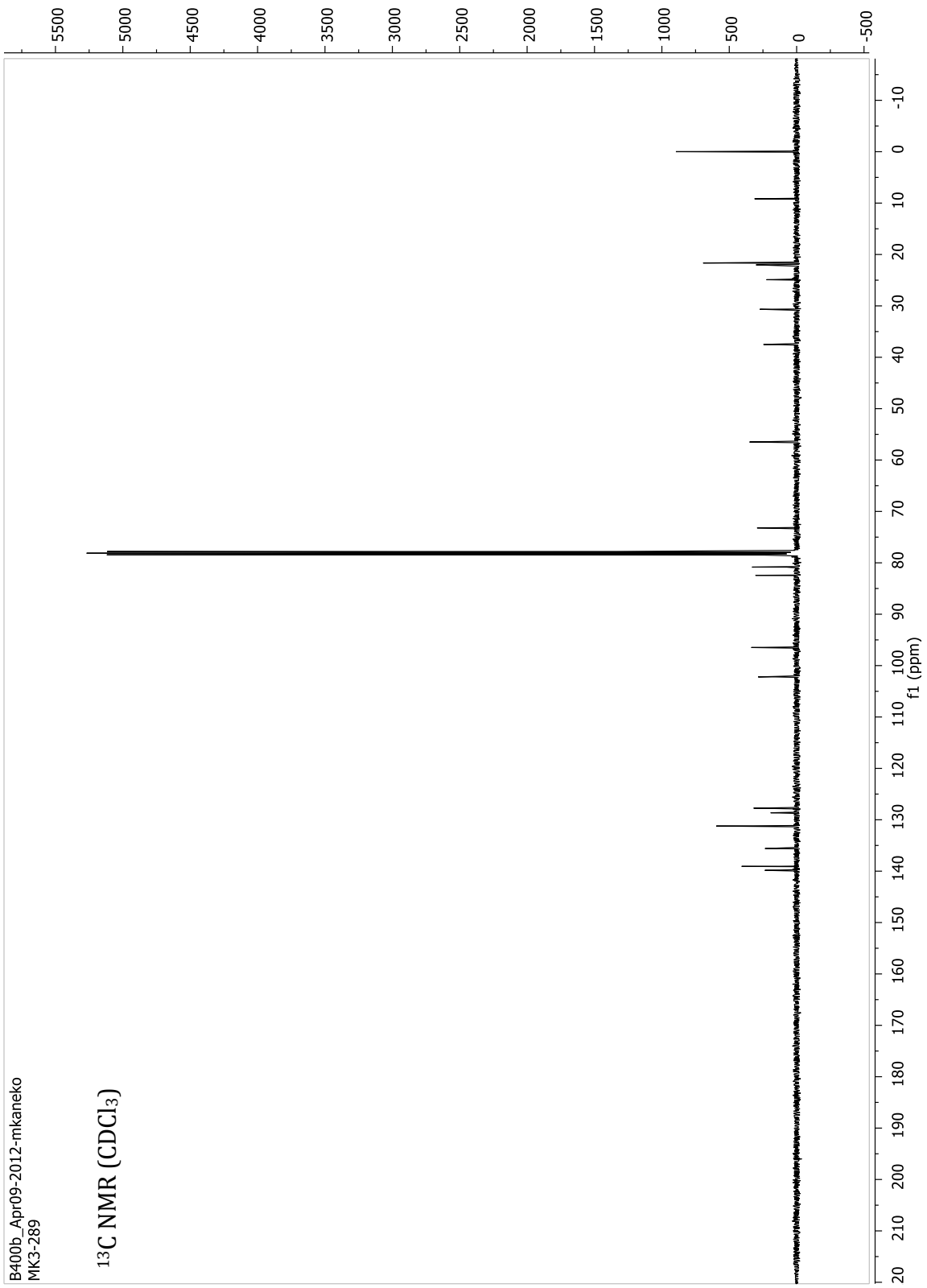

B400b_Apr06-2012-mkaneko
MK3-287
1H NMR (CDCl3)
S55 (7:1 dr)
f1 (ppm)


B400b_Apr06-2012-mkaneko
MK3-287
^{13}C NMR ($CDCl_3$)
f1 (ppm)

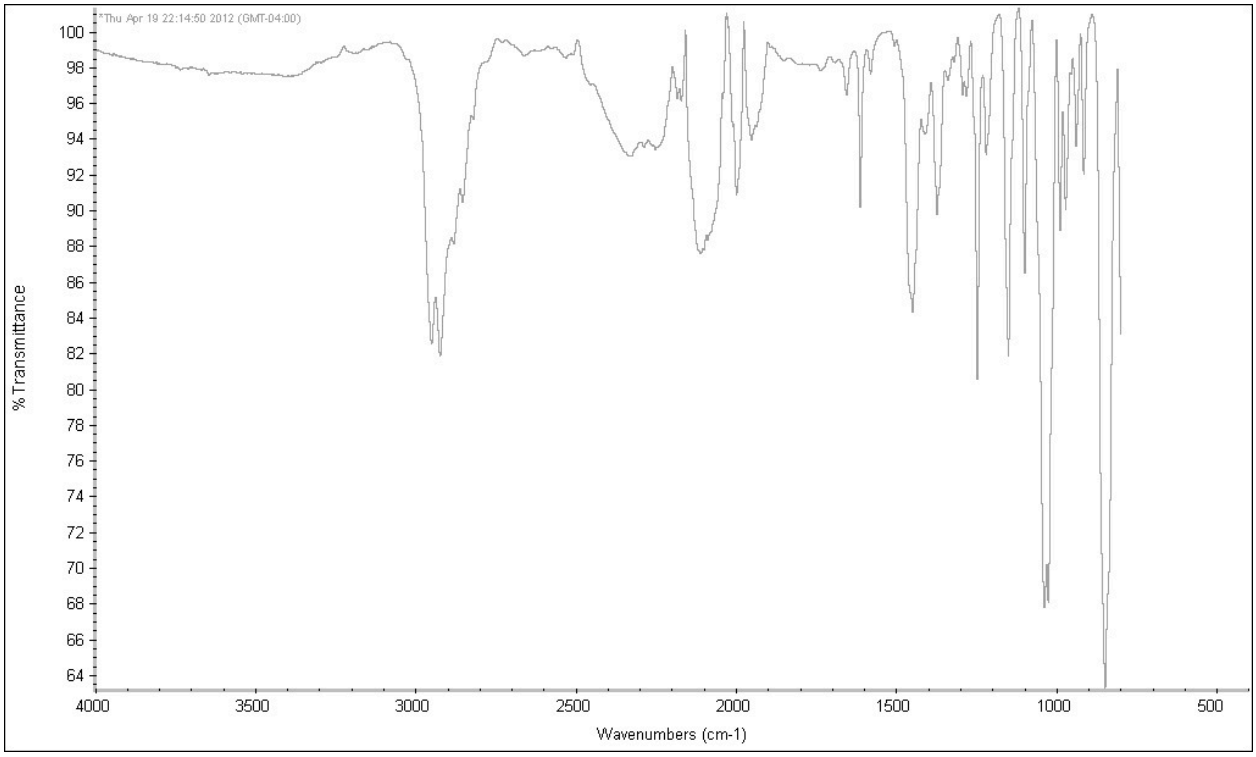
IR

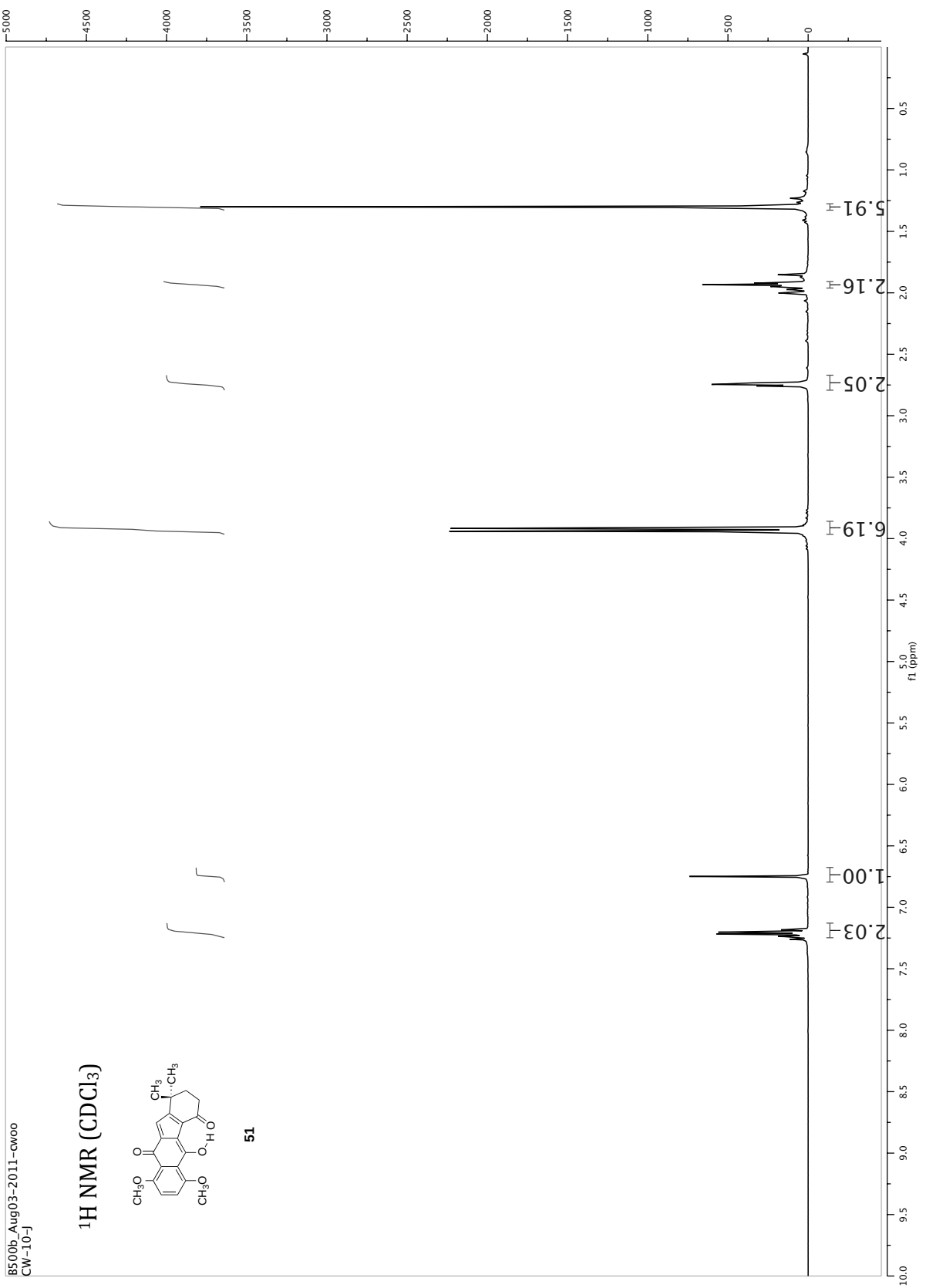

Thu Apr 19 22:18:12 2012 (GMT-04:00)
% Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

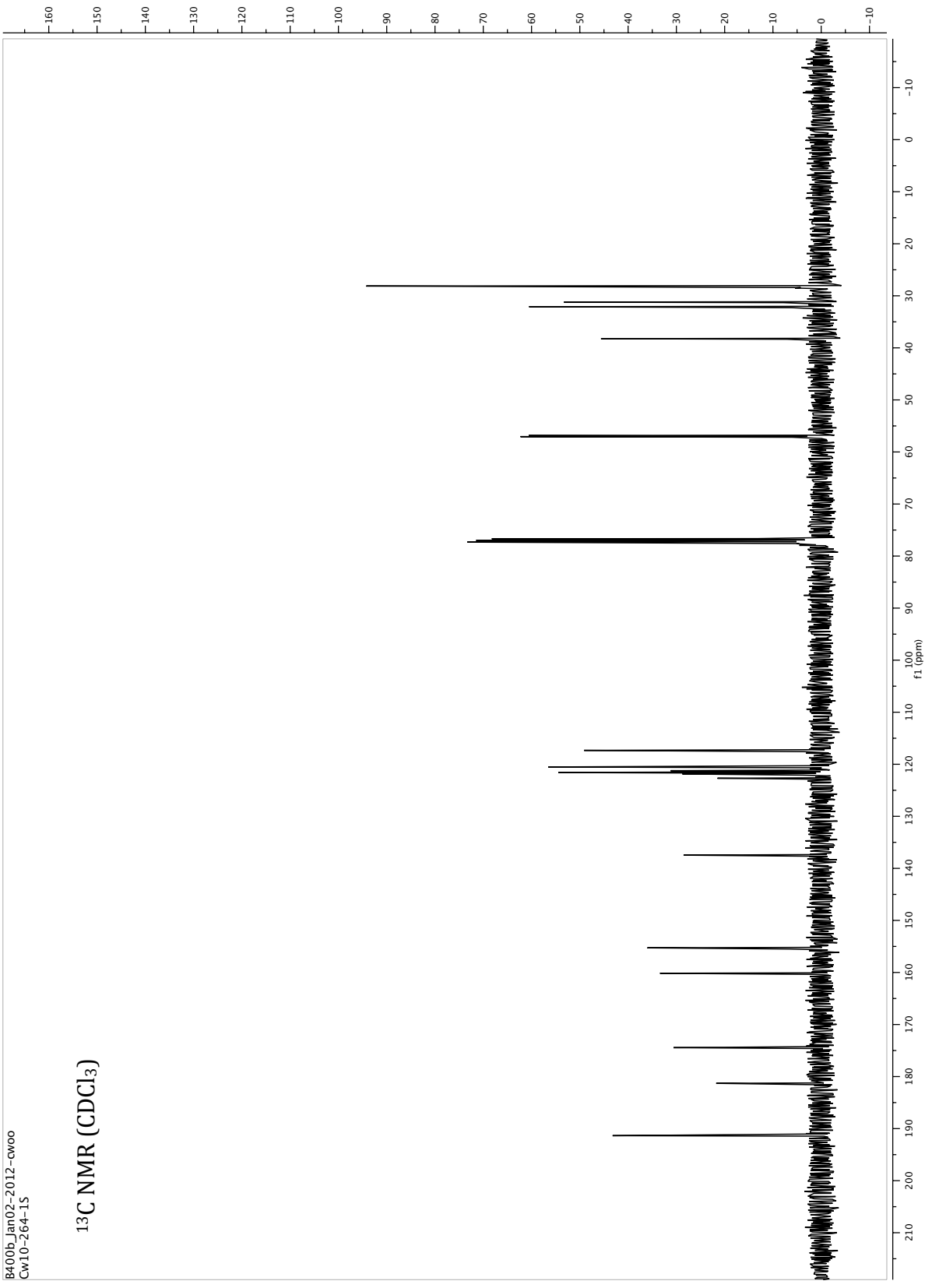

B400b_Apr09-2012-mkaneko
MK3-289
^{1}H NMR ($CDCl_3$)
S56 (7:1 dr)
8.93
2.79
5.05
2.92
0.99
5.48
3.01
0.94
0.95
2.05
0.94
0.98
2.00
f1 (ppm)


B400b_Apr09-2012-mkaneko
MK3-289
^{13}C NMR ($CDCl_3$)
f1 (ppm)

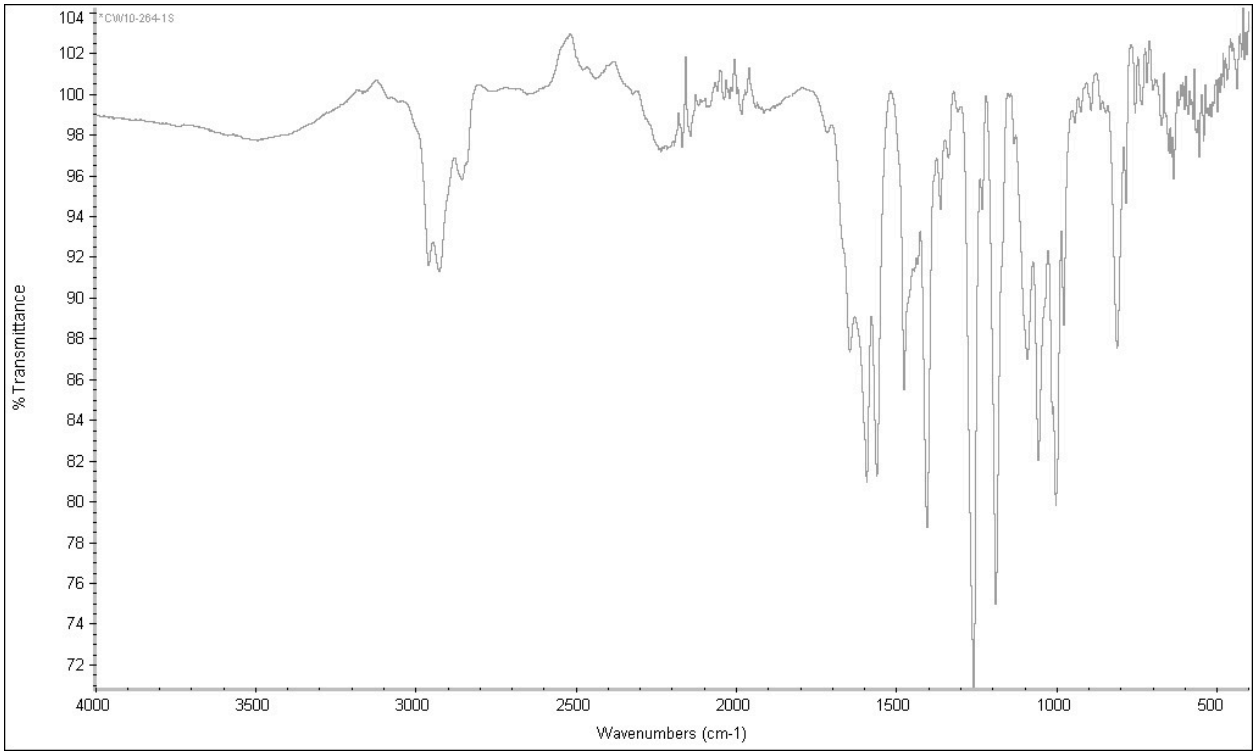
IR

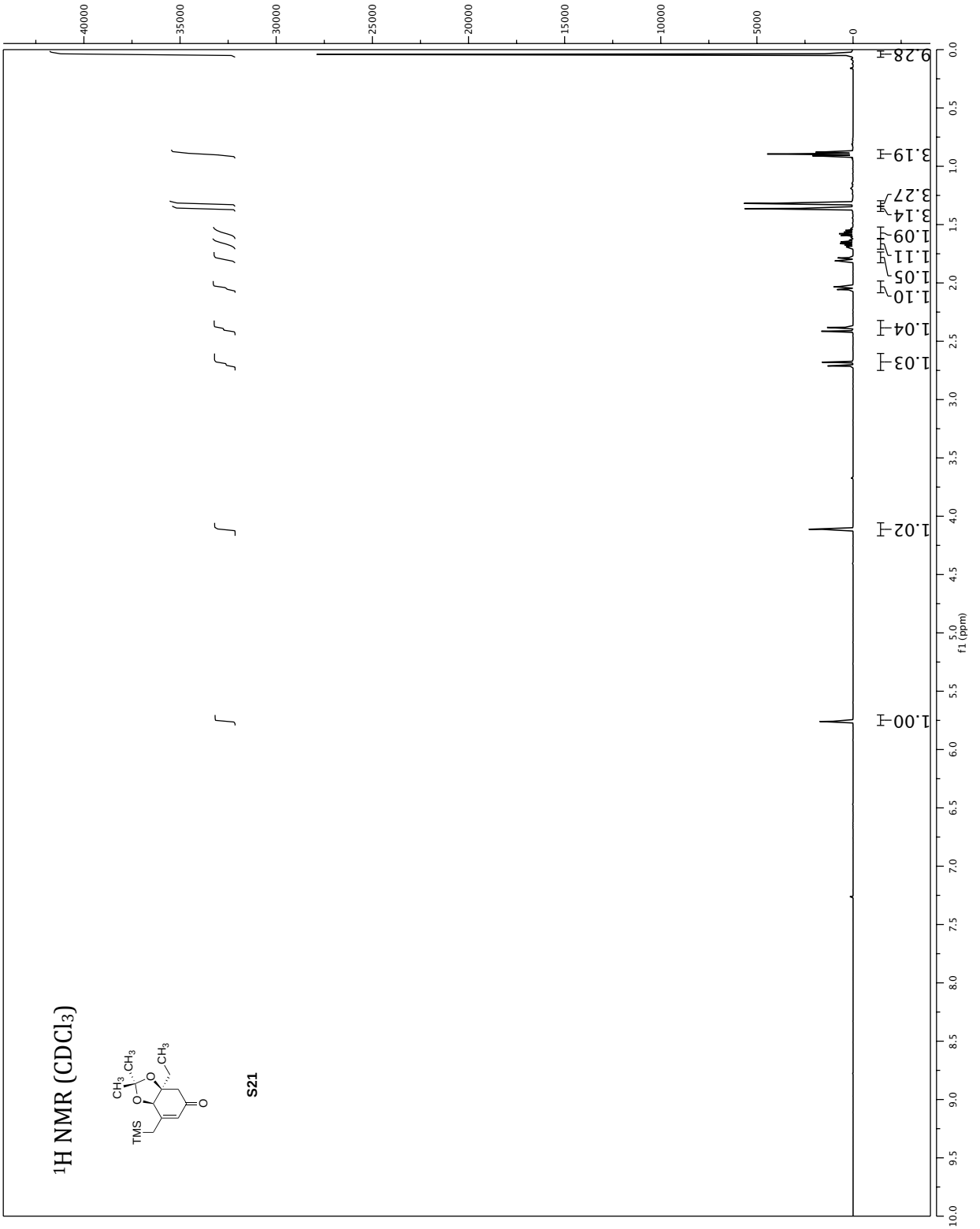

Thu Apr 19 22:14:50 2012 (GMT-04:00)
% Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


B500b_Aug03-2011-cwoo
CW-10-J
^{1}H NMR ($CDCl_3$)
51
5.91
2.16
2.05
6.19
1.00
2.03
f1 (ppm)

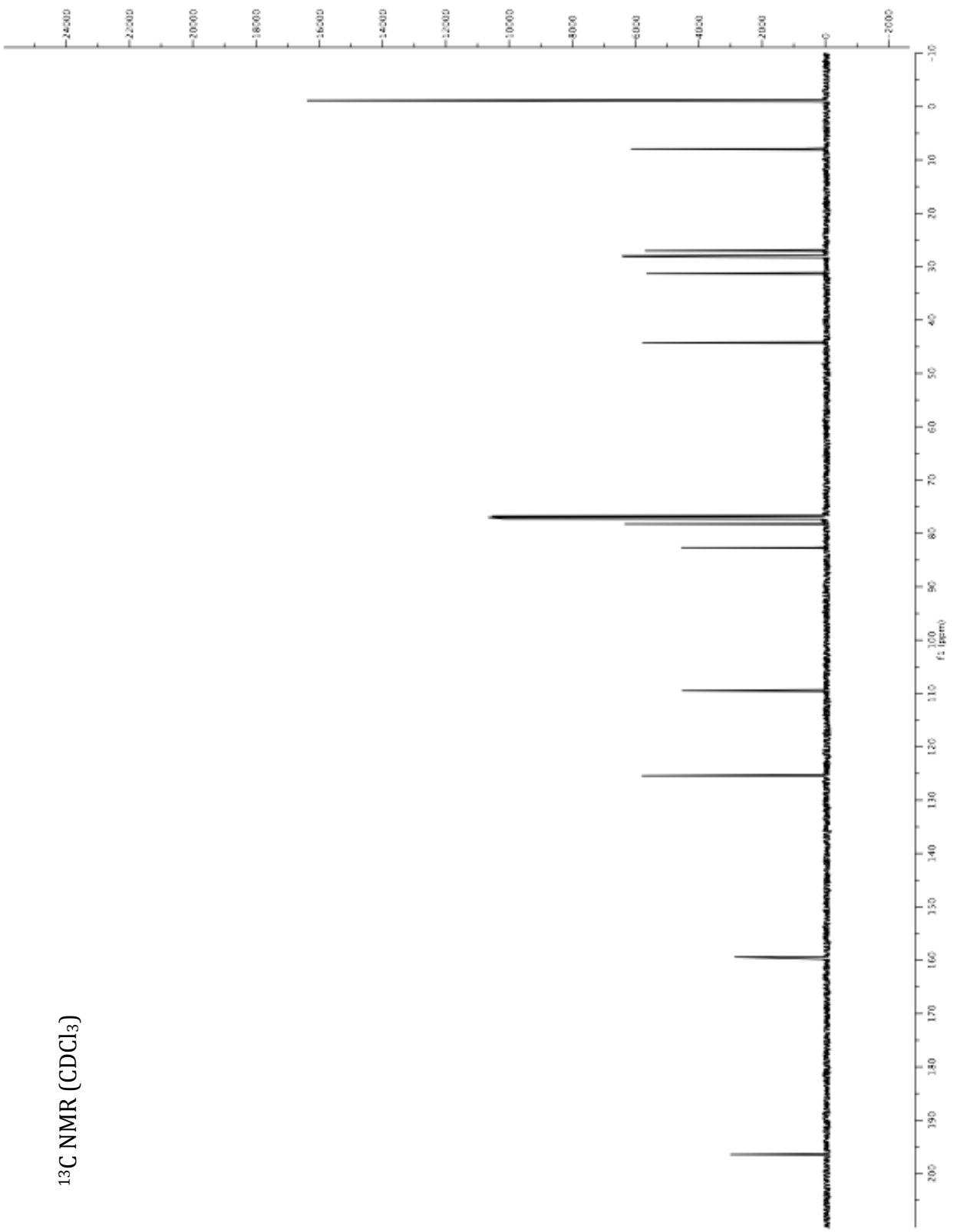

^{13}C NMR ($CDCl_3$)
B400b_Jan02-2012-cwoo
Cw10-264-1S
f1 (ppm)

IR

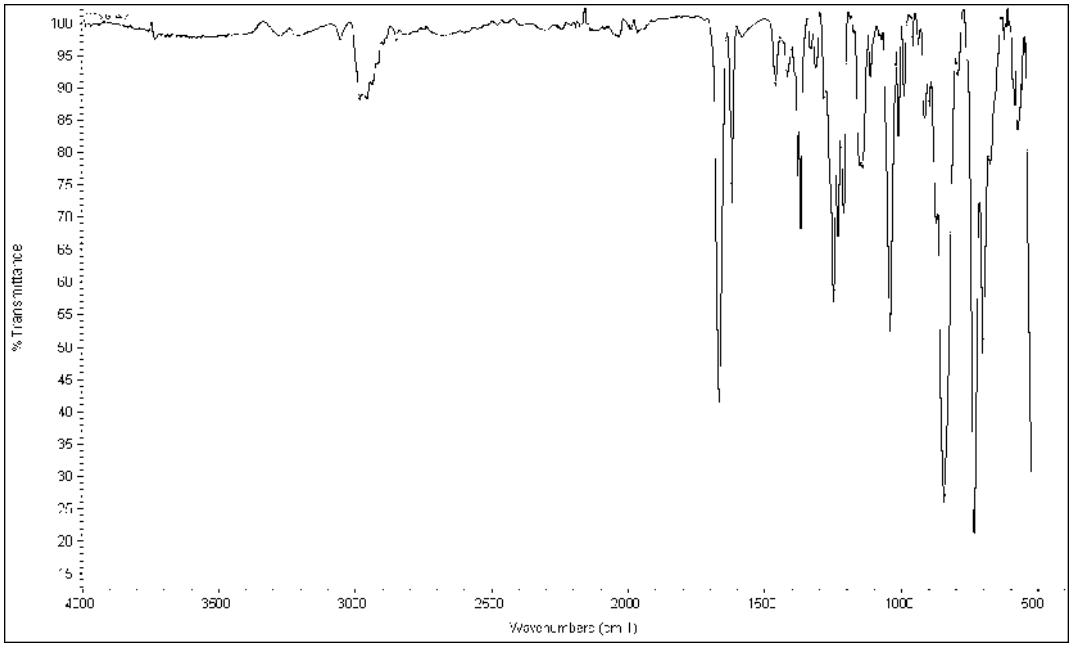

CW10-264-1S
% Transmittance
Wavenumbers (cm-1)
104
102
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
4000
3500
3000
2500
2000
1500
1000
500

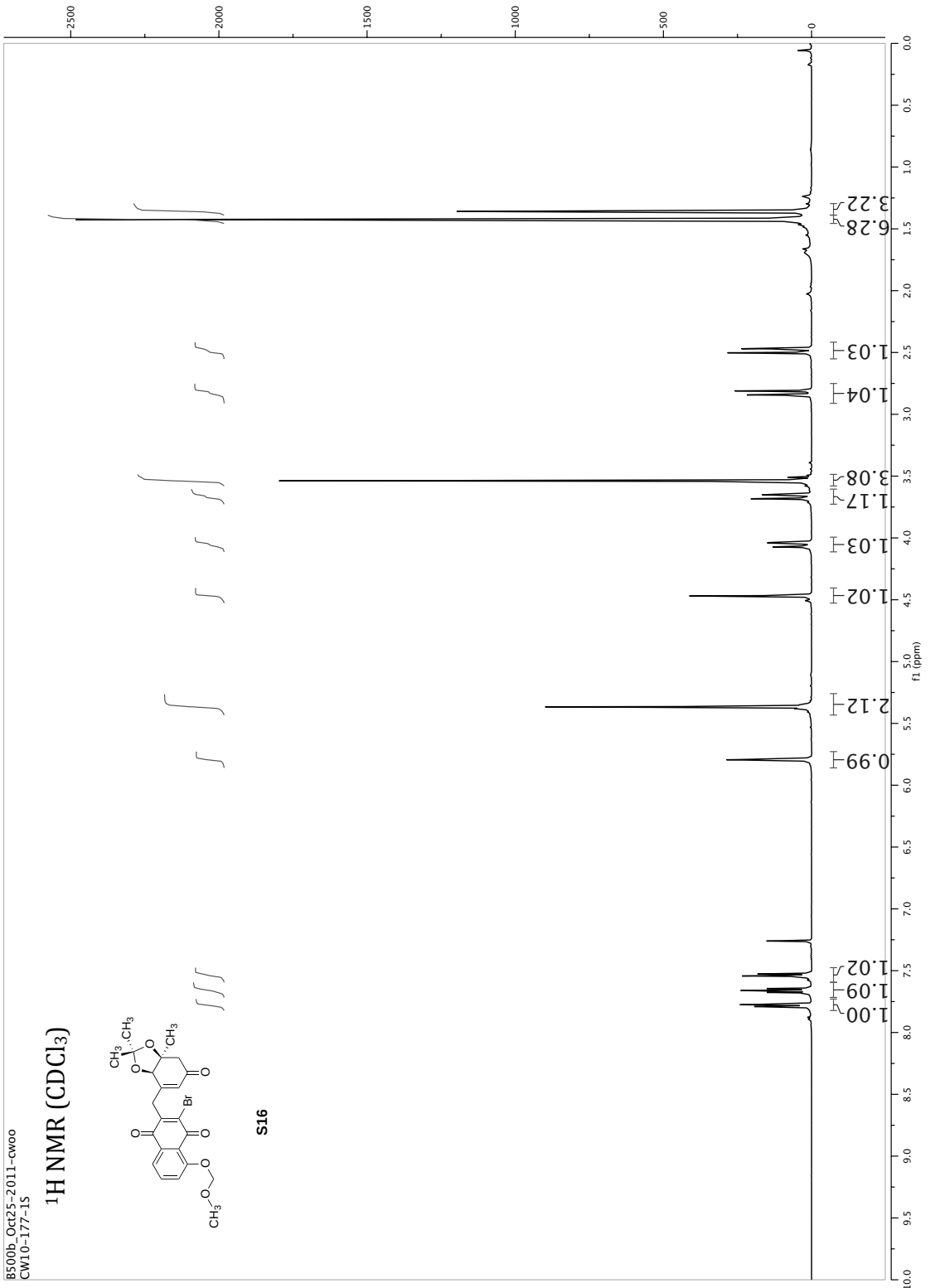

^{1}H NMR ($CDCl_3$)
S21
TMS
9.28
3.19
3.27
3.14
1.09
1.11
1.05
1.10
1.04
1.03
1.02
1.00
f1 (ppm)

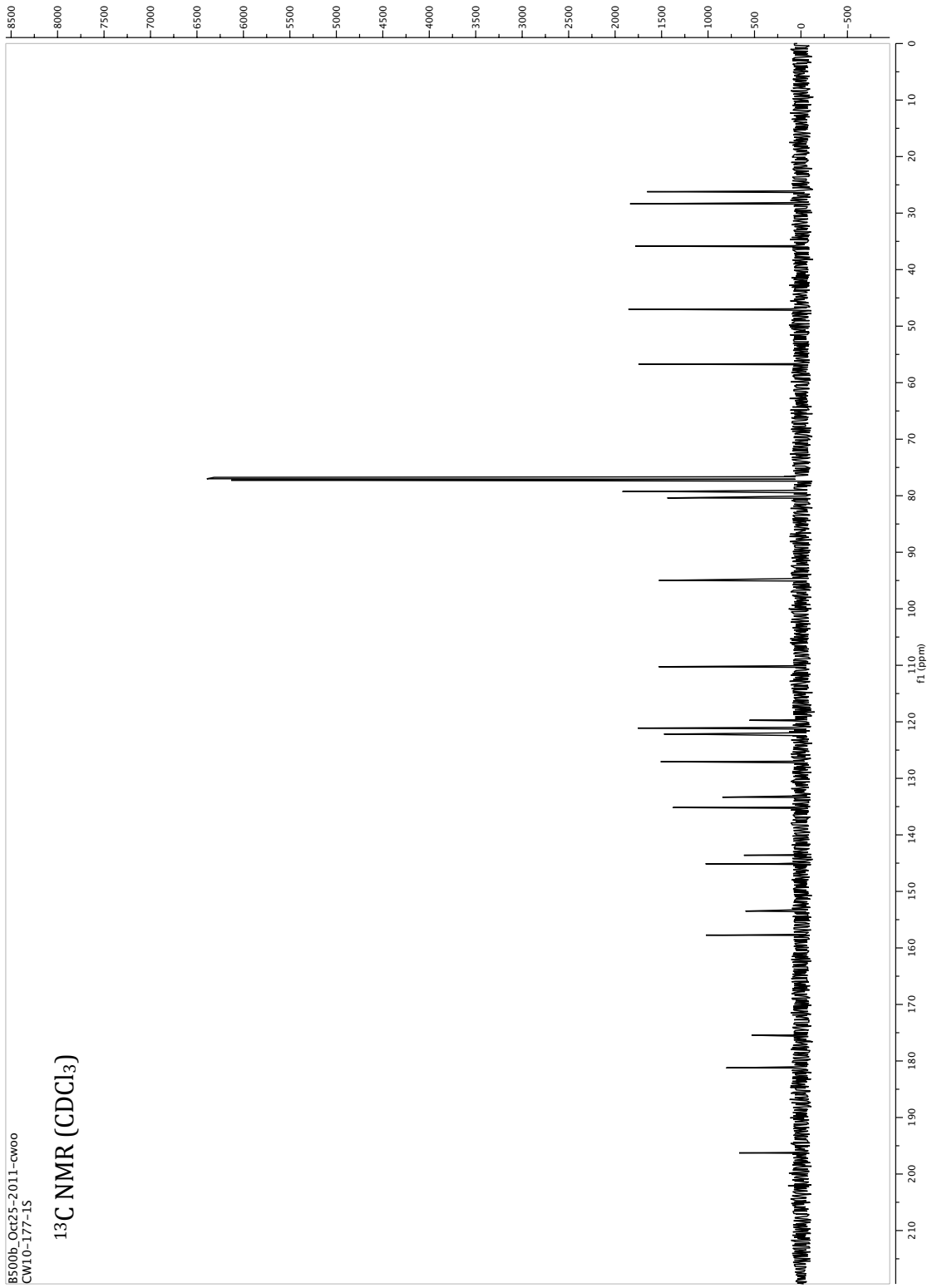
^{13}C NMR ($CDCl_3$)



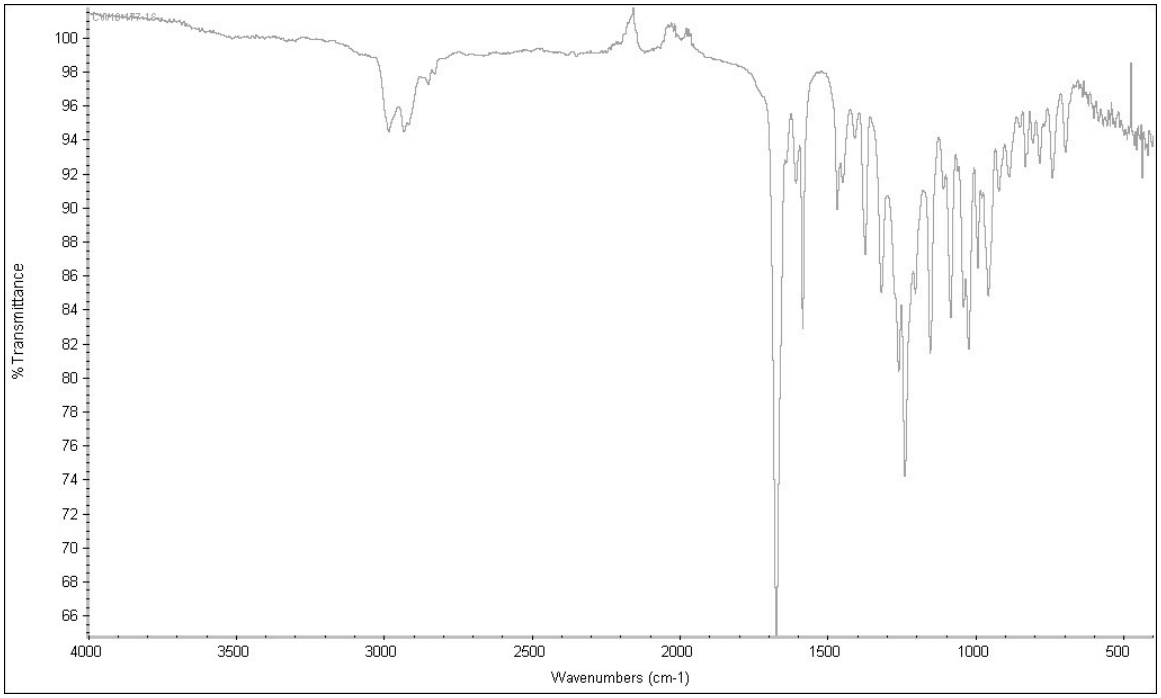
IR

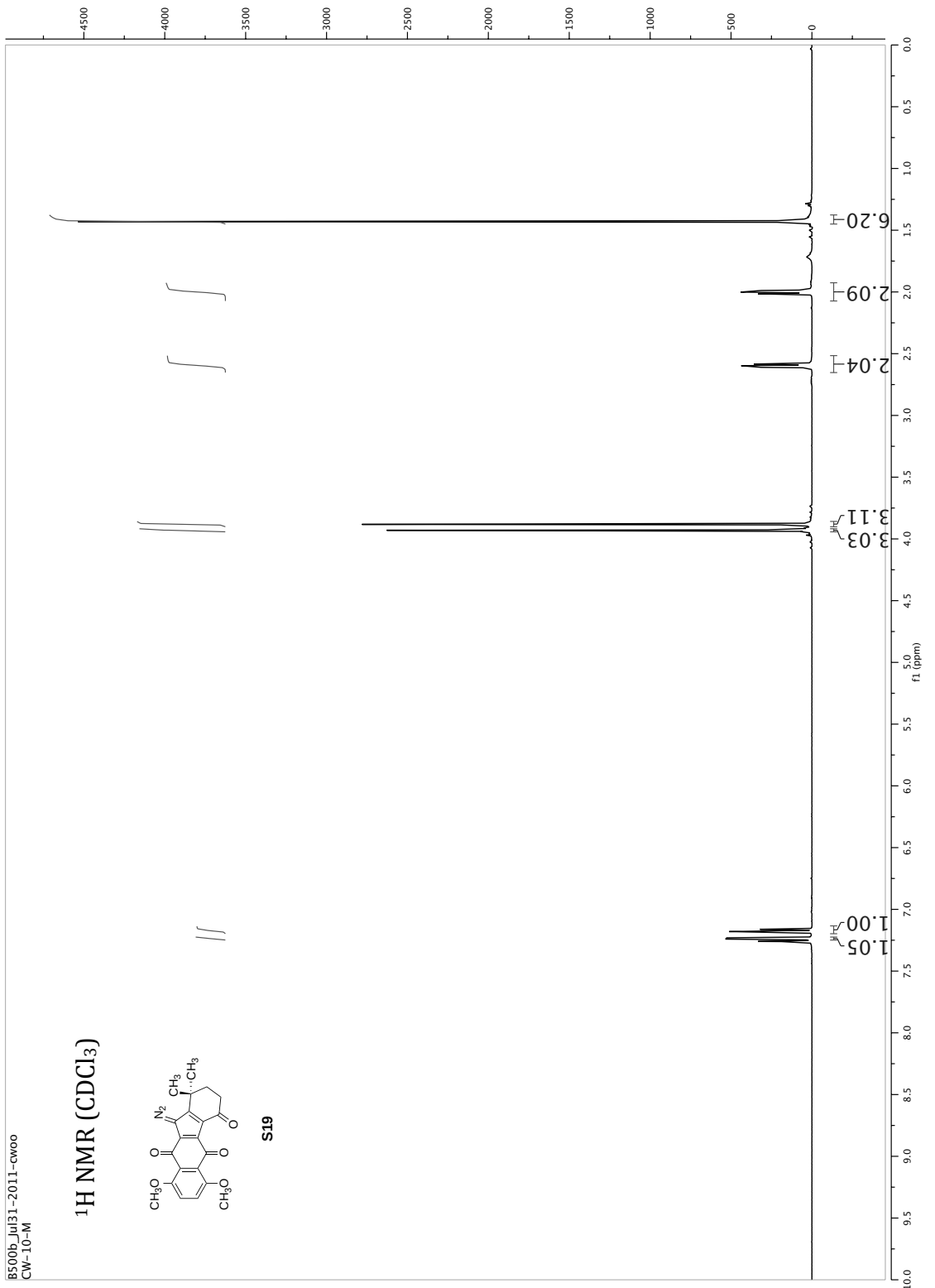

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

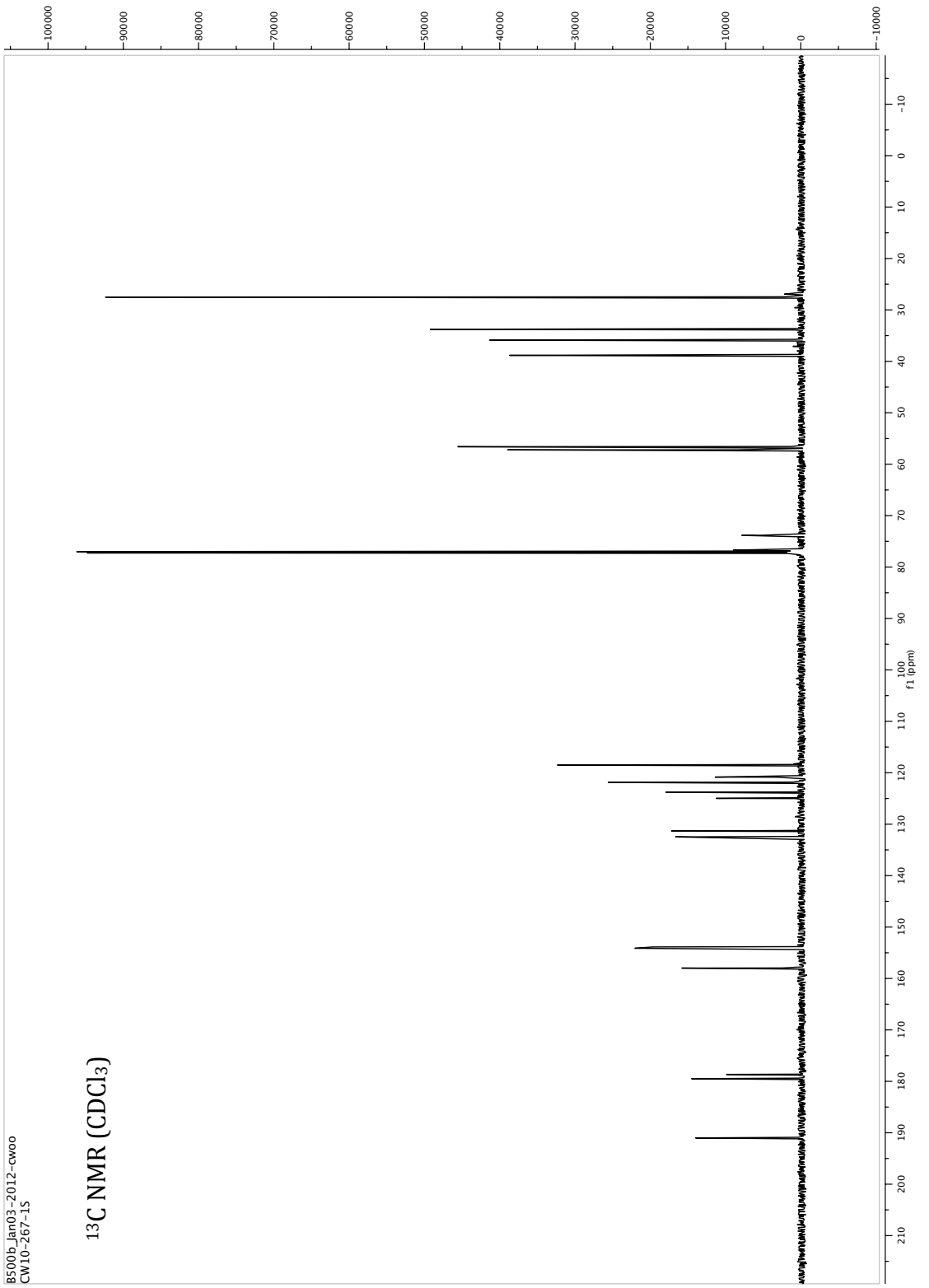

B500b_Oct25-2011-cwoo
CW10-177-1S
^{1}H NMR ($CDCl_3$)
S16
6.28
3.22
1.03
1.04
3.08
1.17
1.03
1.02
2.12
0.99
1.02
1.09
1.00
f1 (ppm)


B500b_Oct25-2011-cwoo
CW10-177-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

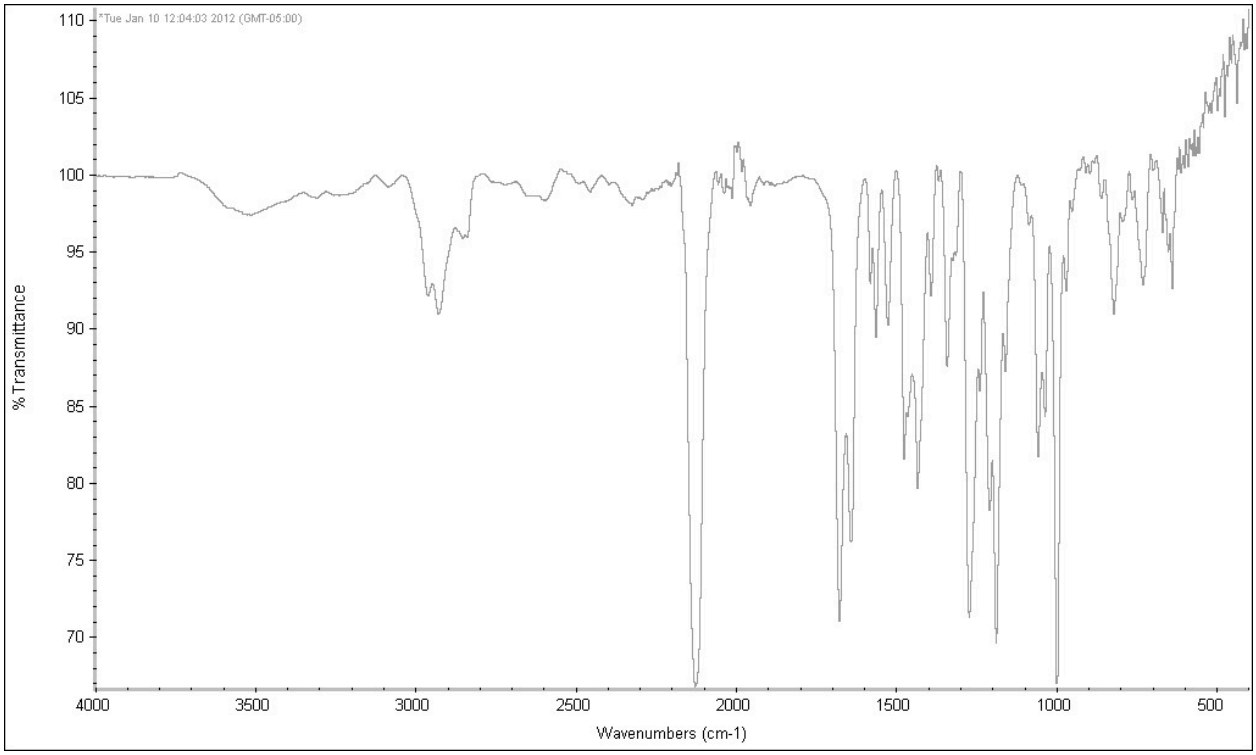
IR

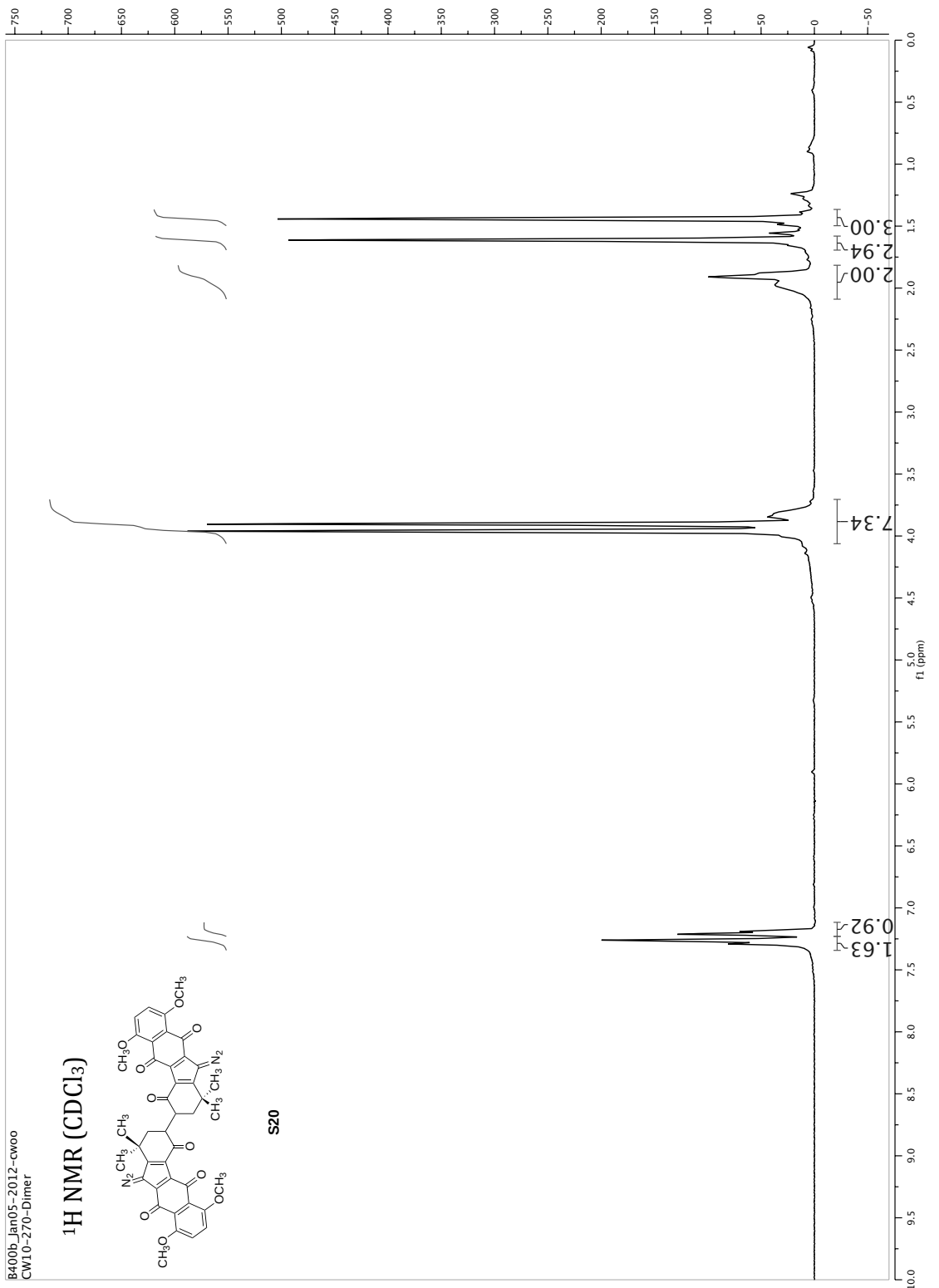

% Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

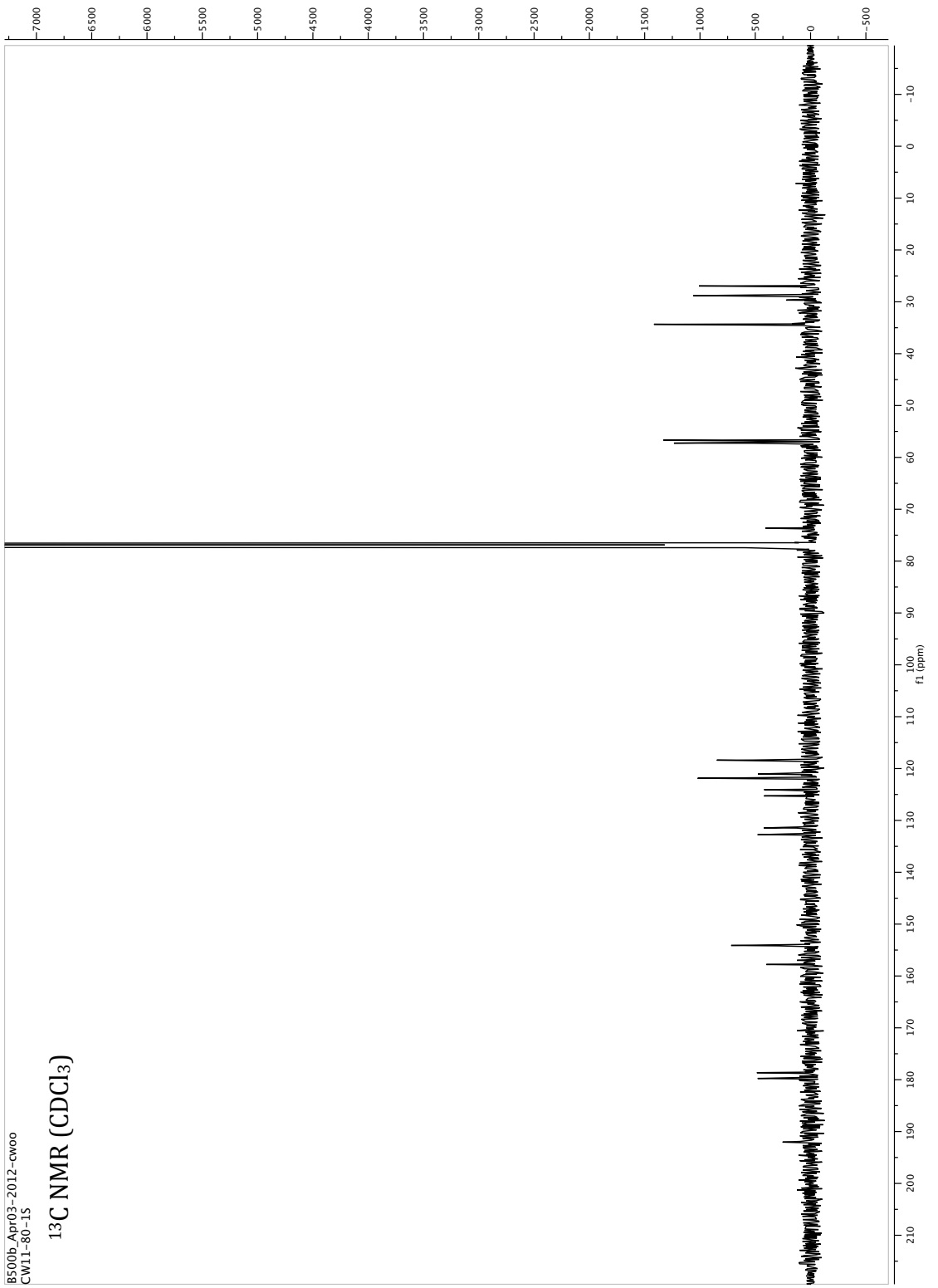

^{1}H NMR ($CDCl_3$)
S19
6.20
2.09
2.04
3.11
3.03
1.05
1.00
f1 (ppm)
B500b_Jul31-2011-cwoo
CW-10-M


B500b_Jan03-2012-cwoo
CW10-267-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

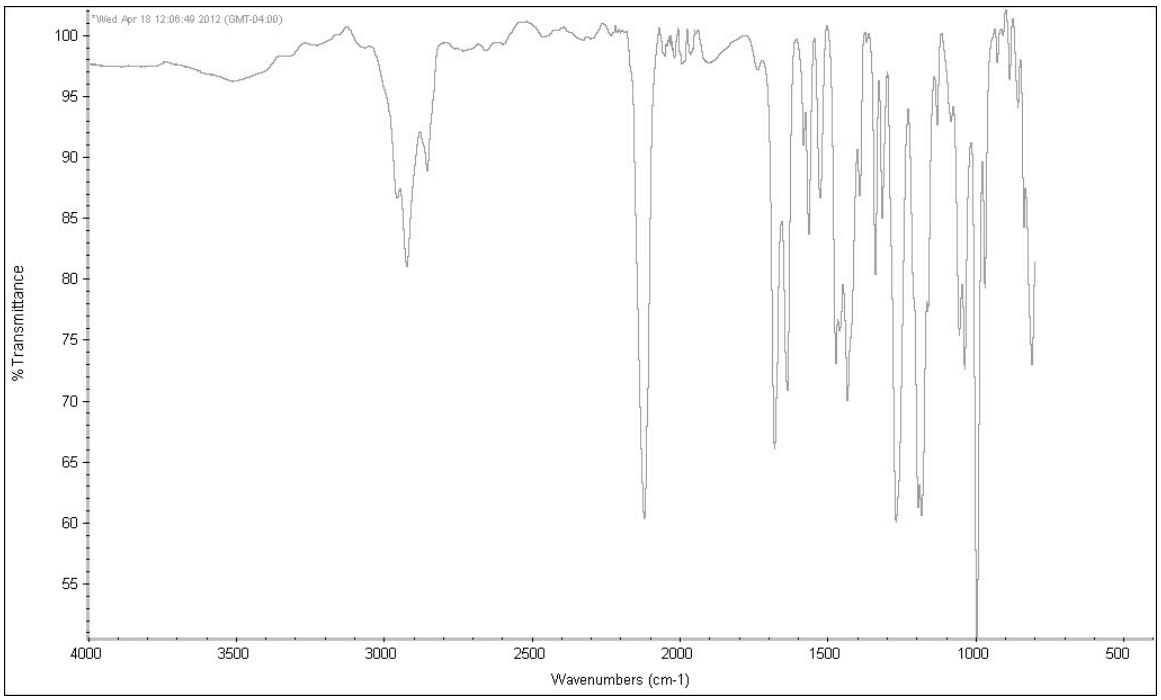
IR

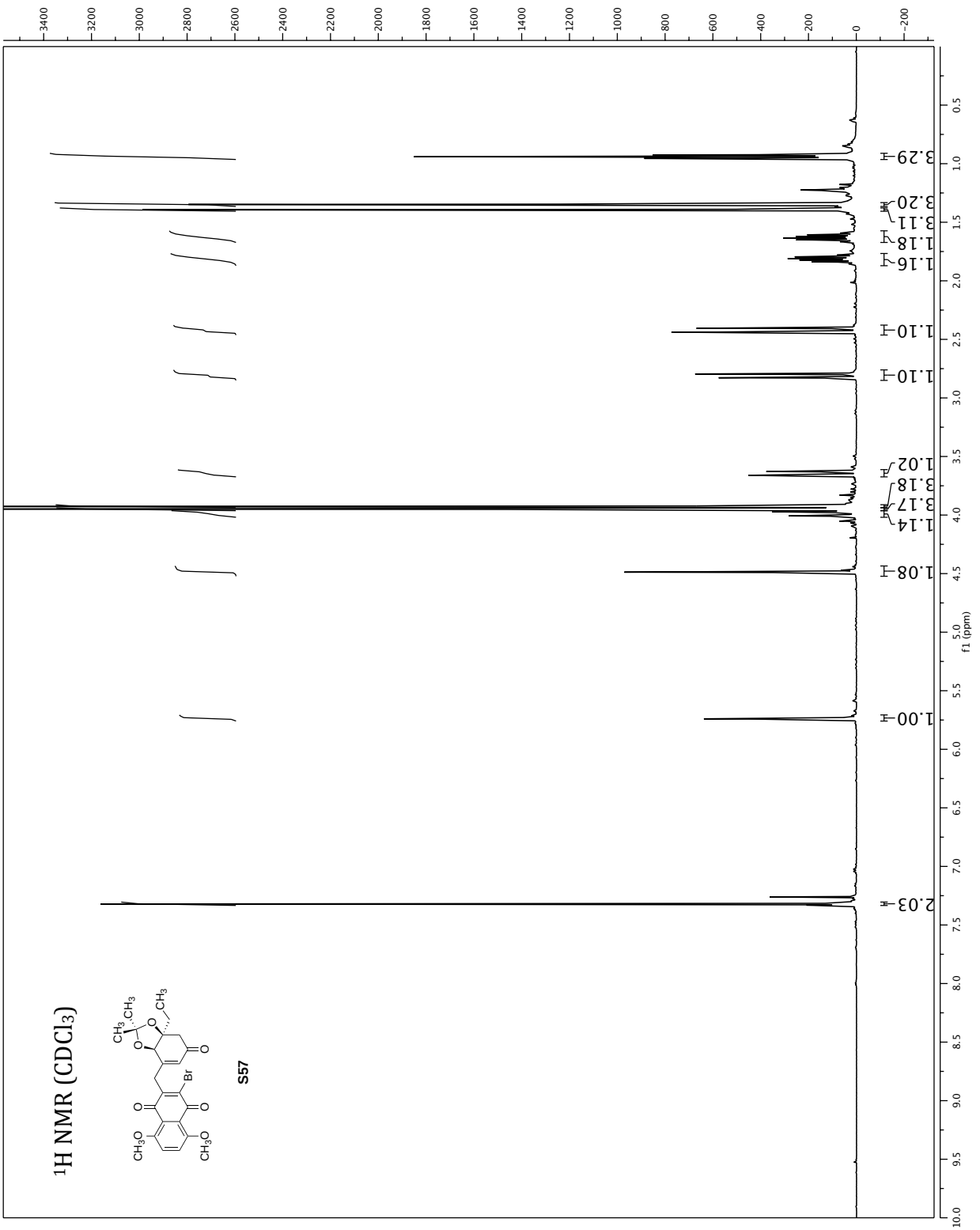

Tue Jan 10 12:04:03 2012 (GMT-05:00)
% Transmittance
110
105
100
95
90
85
80
75
70
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


B400b_Jan05-2012-cwoo
CW10-270-Dimer
1H NMR (CDCl3)
S20
1.63
0.92
7.34
2.00
2.94
3.00
f1 (ppm)

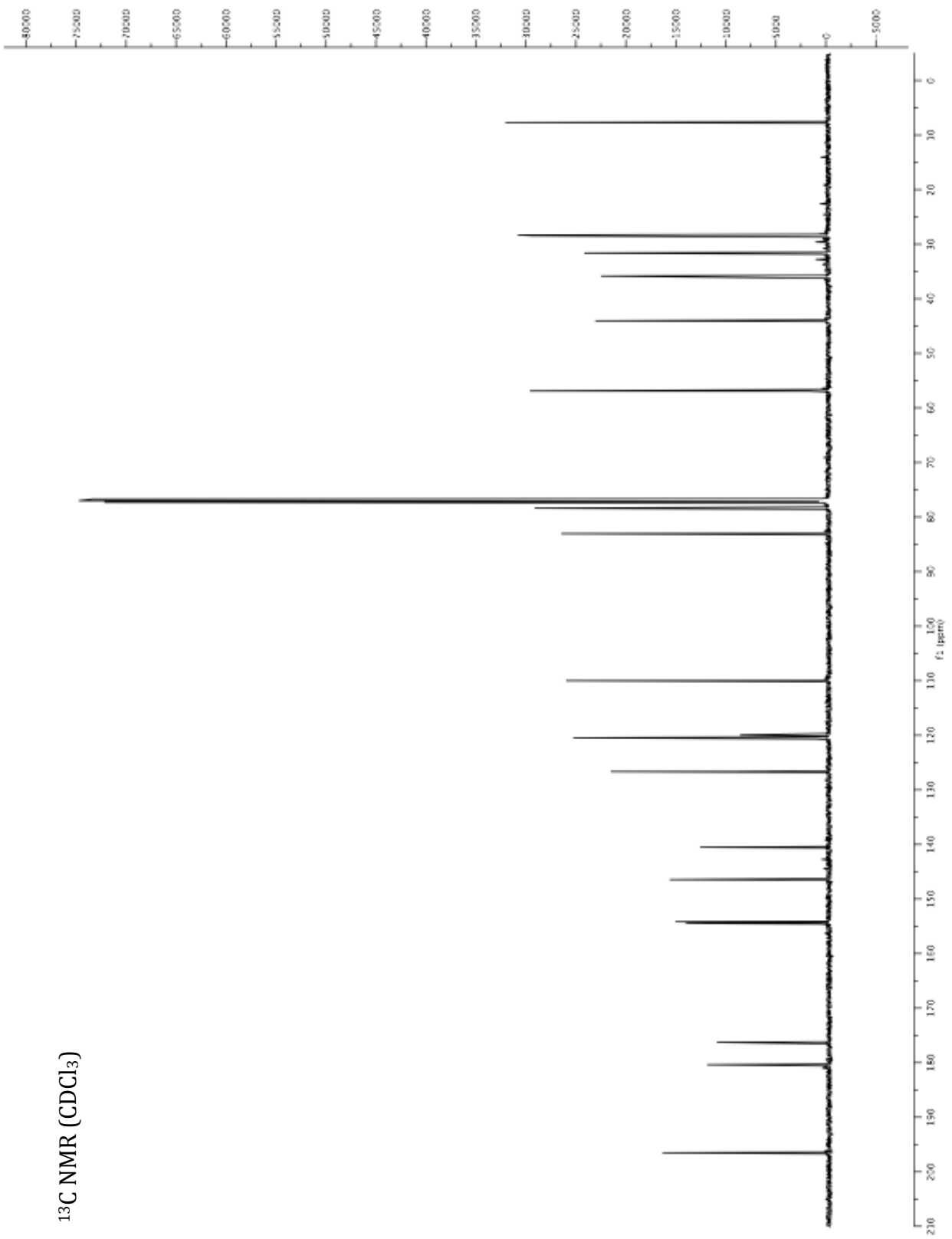

B500b_Apr03-2012-cwoo
CW11-80-1S
13C NMR (CDCl3)
f1 (ppm)

IR

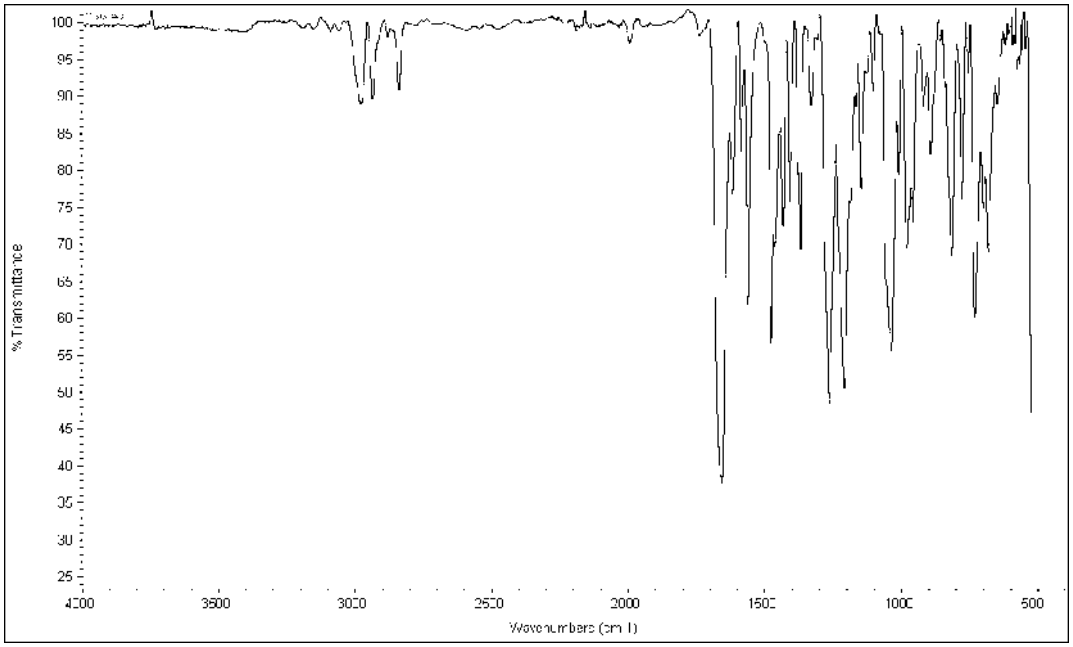

Wed Apr 18 12:06:49 2012 (GMT-04:00)
% Transmittance
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

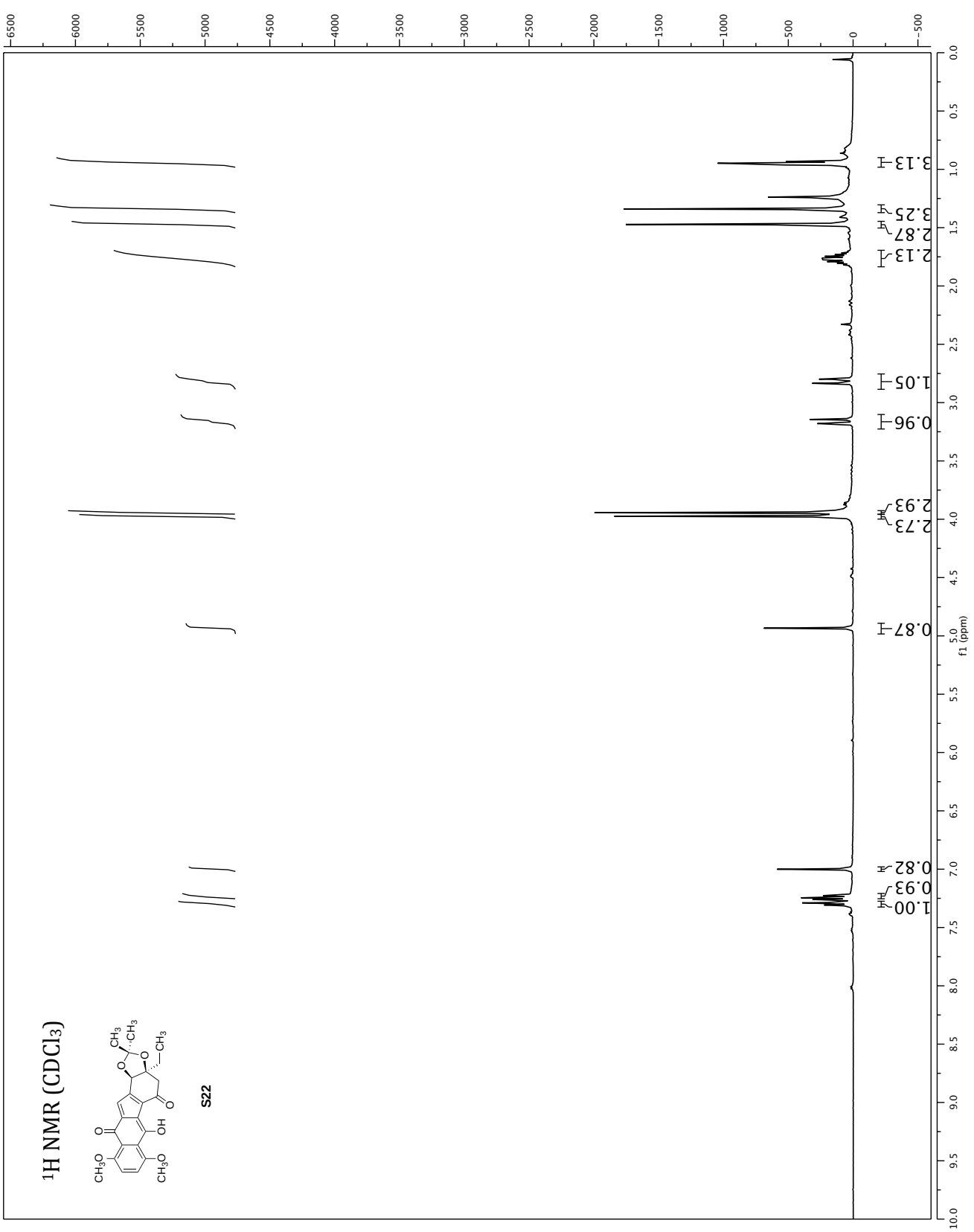

^{1}H NMR ($CDCl_3$)
S57
Br
CH_3O
CH_3O
2.03
1.00
1.08
1.14
3.17
3.18
1.02
1.10
1.10
1.16
1.18
3.11
3.20
3.29
f1 (ppm)

^{13}C NMR ($CDCl_3$)

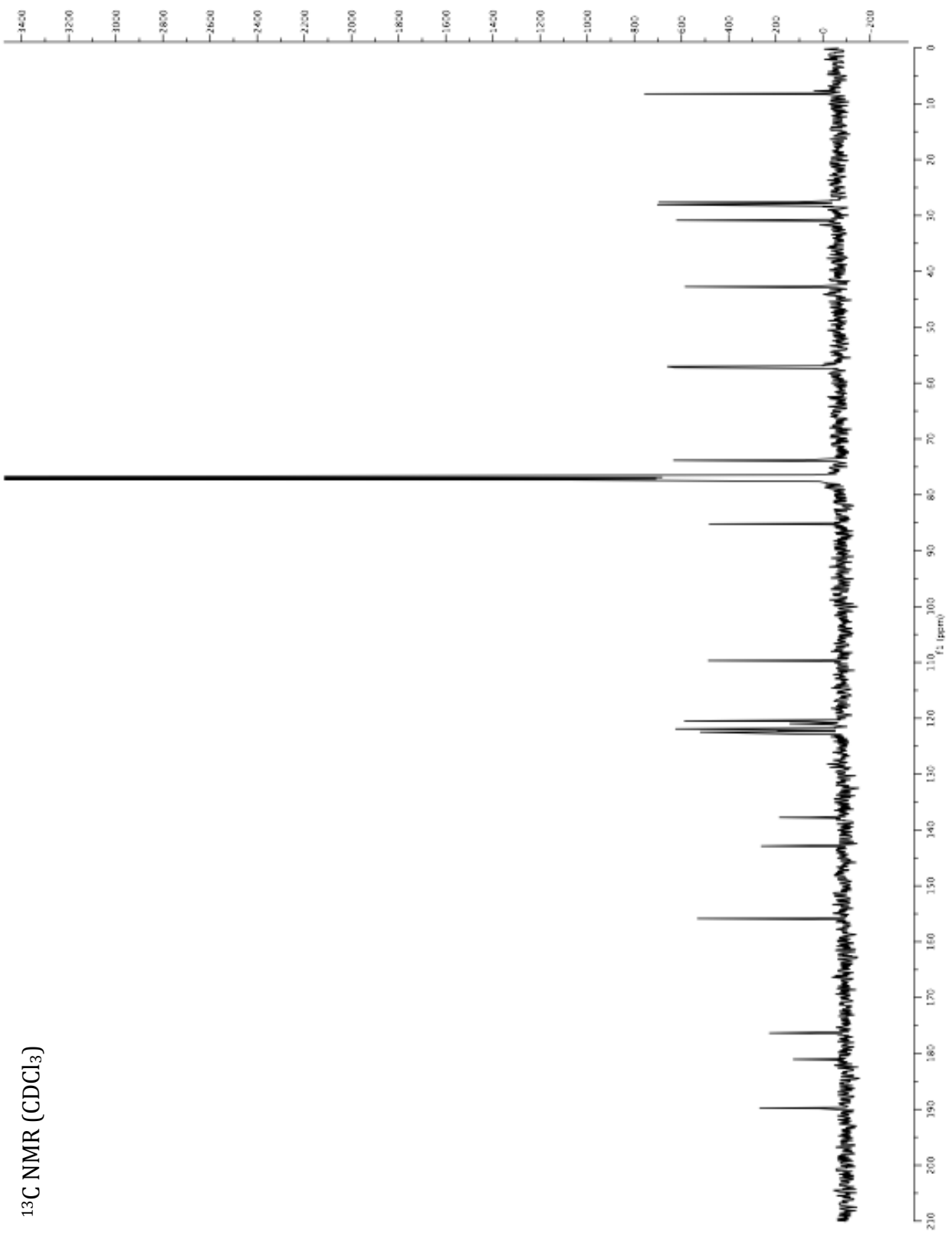


IR

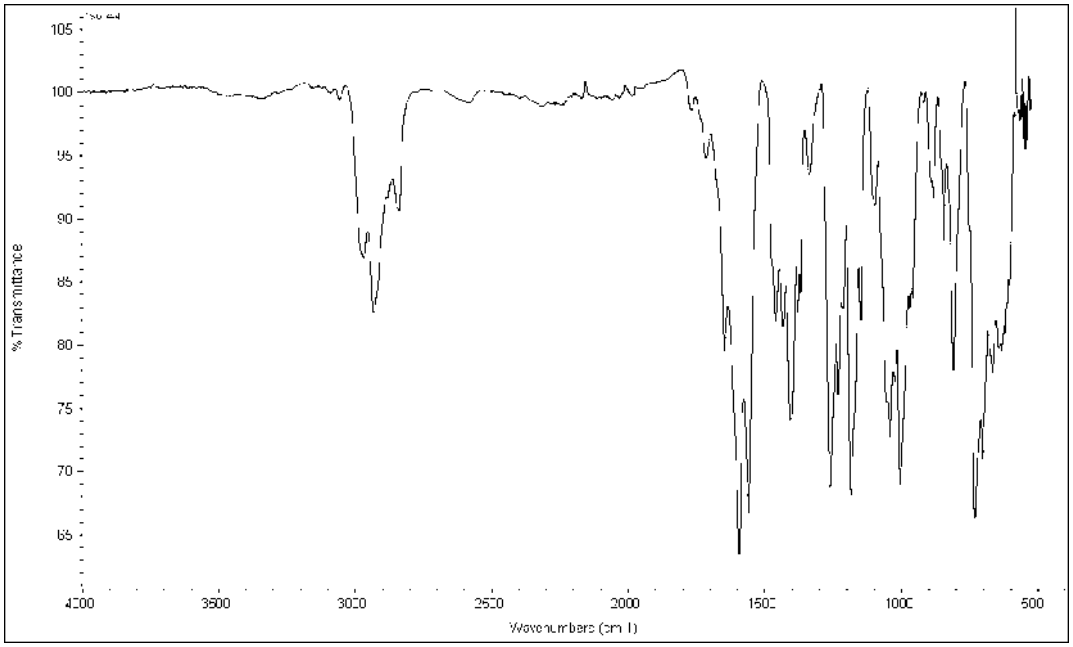

% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

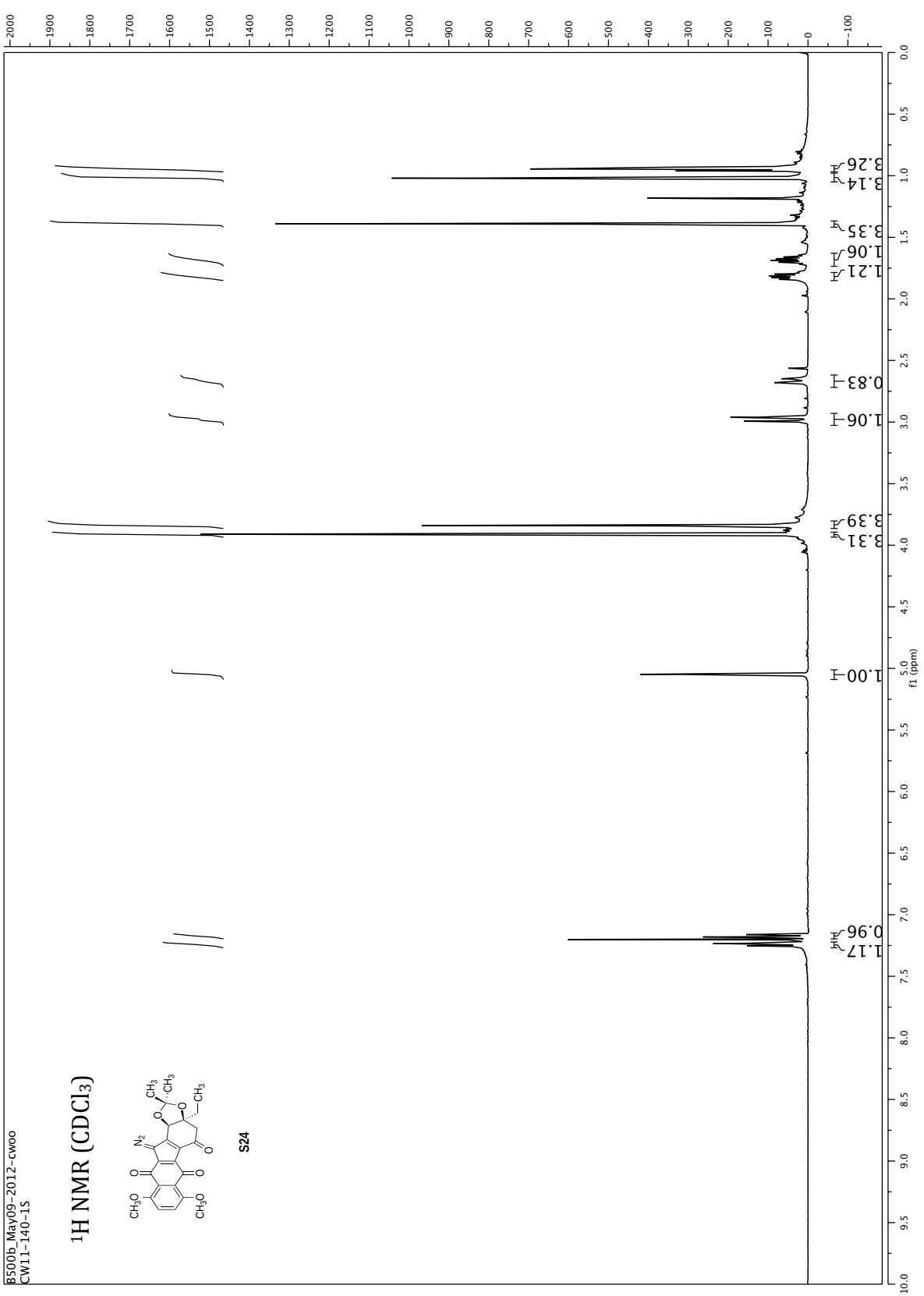

^{1}H NMR ($CDCl_3$)
S22
3.13
3.25
2.87
2.13
1.05
0.96
2.93
2.73
0.87
0.82
0.93
1.00
f1 (ppm)

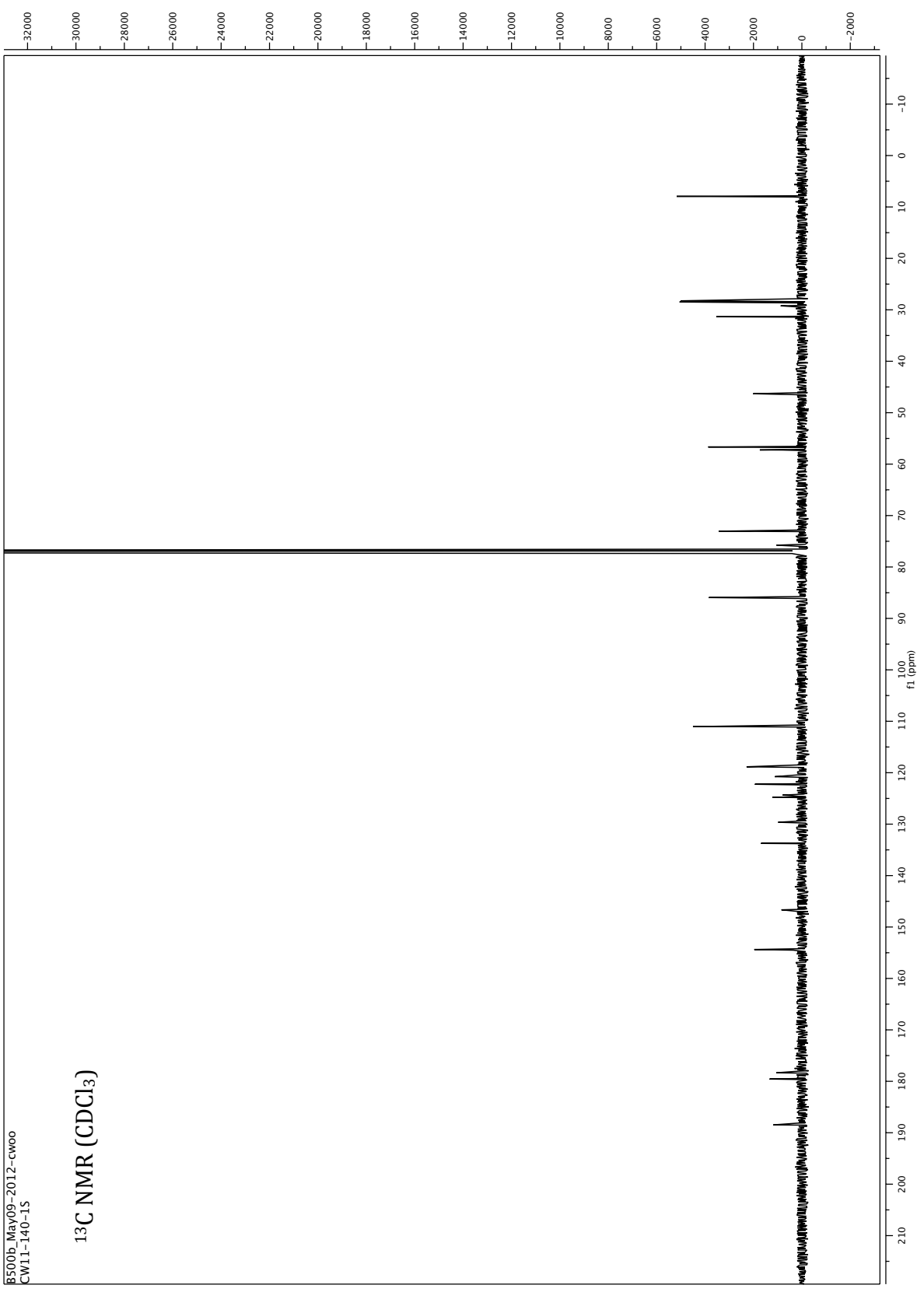
^{13}C NMR ($CDCl_3$)



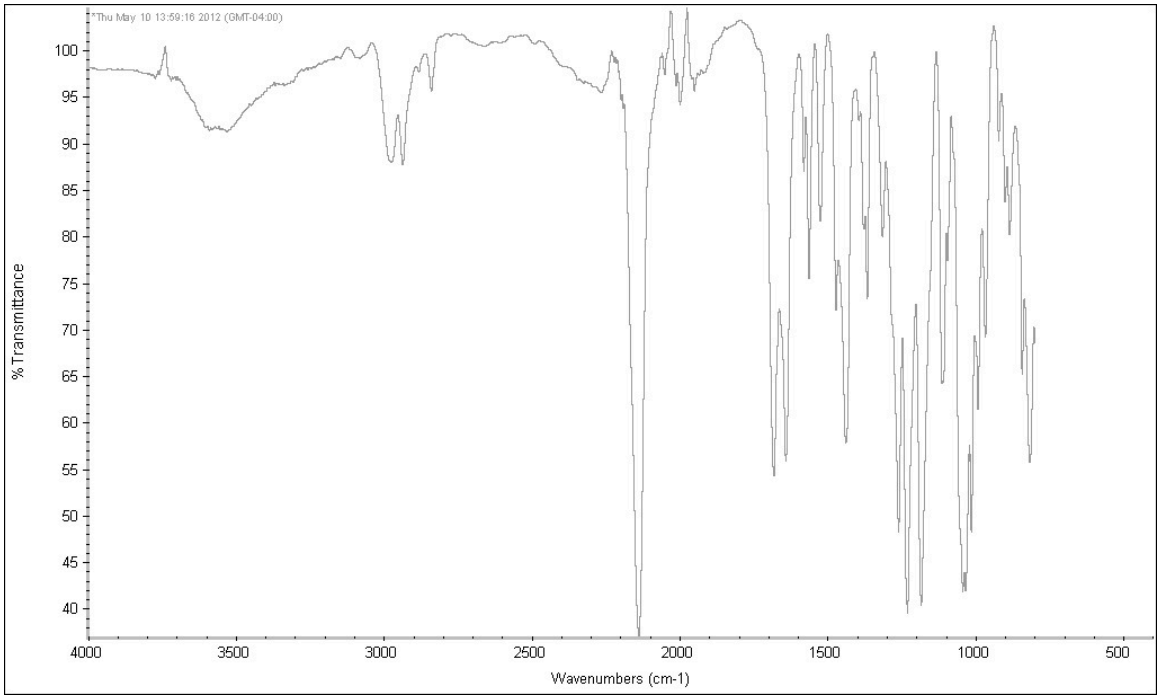
IR

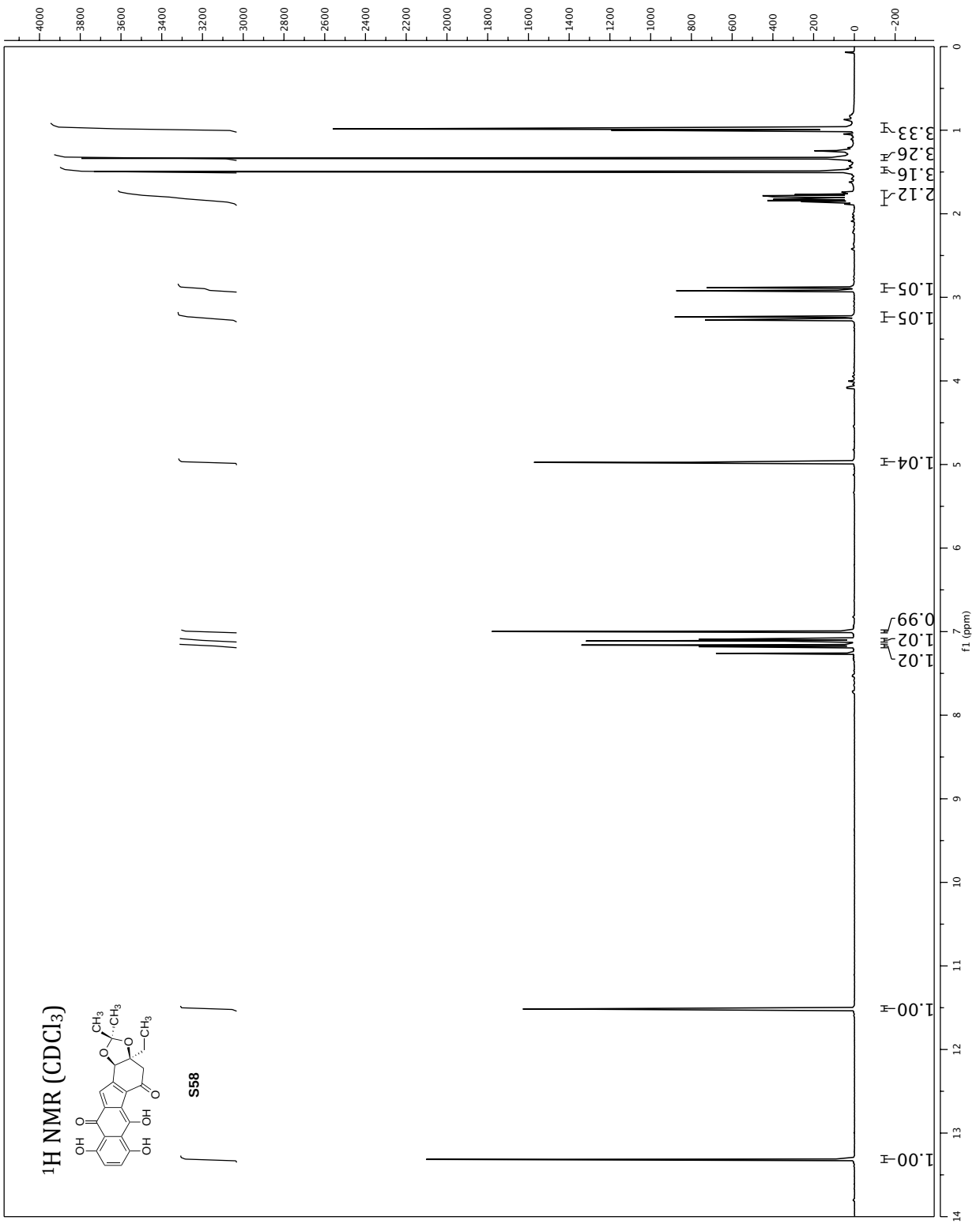

% Transmittance
105
100
95
90
85
80
75
70
65
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


B500b_May09-2012-cwoo
CW11-140-1S
^{1}H NMR ($CDCl_3$)
S24
3.26
3.14
3.35
1.21
1.06
0.83
1.06
3.31
3.39
1.00
1.17
0.96
f1 (ppm)

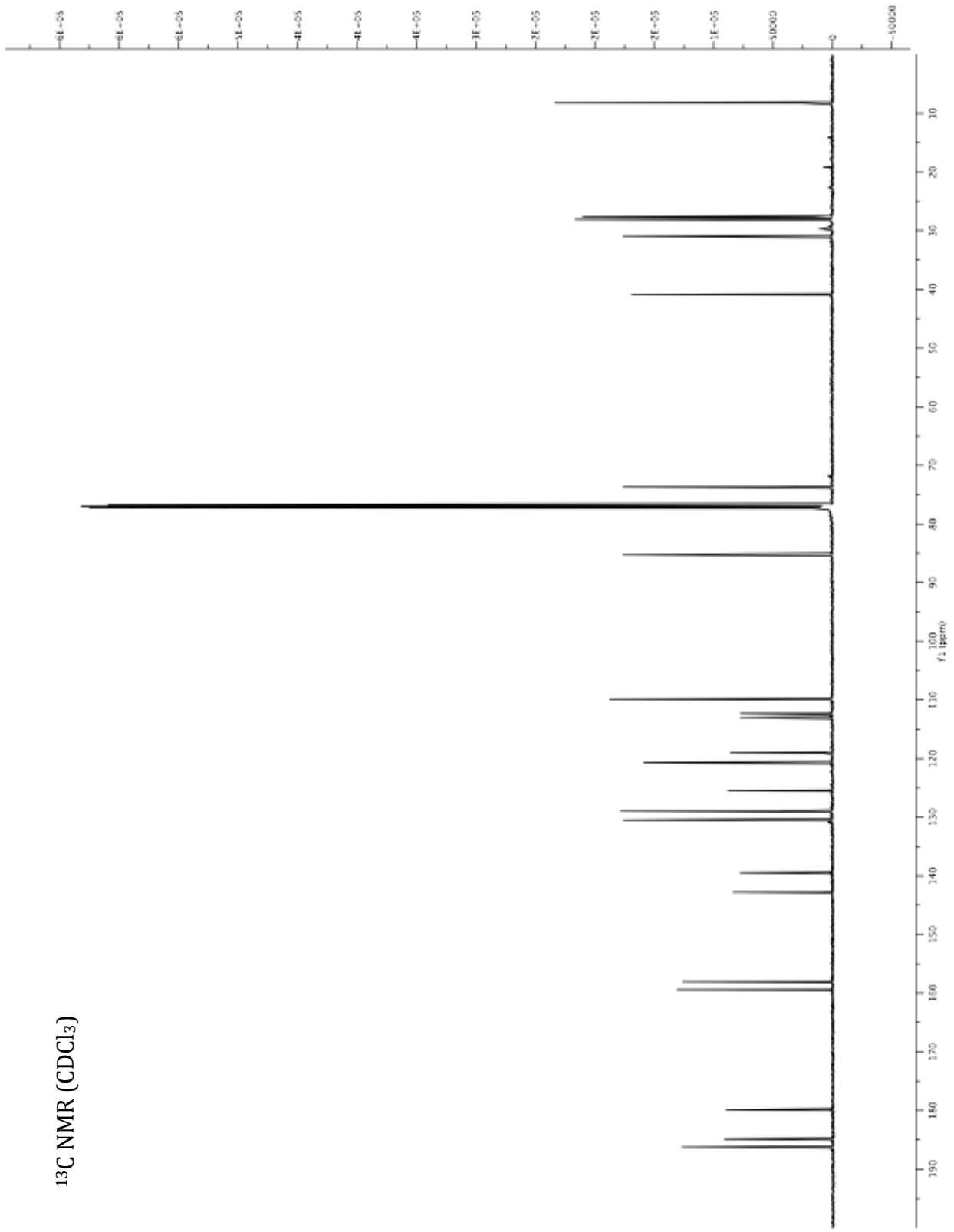

B500b_May09-2012-cwoo
CW11-140-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

IR

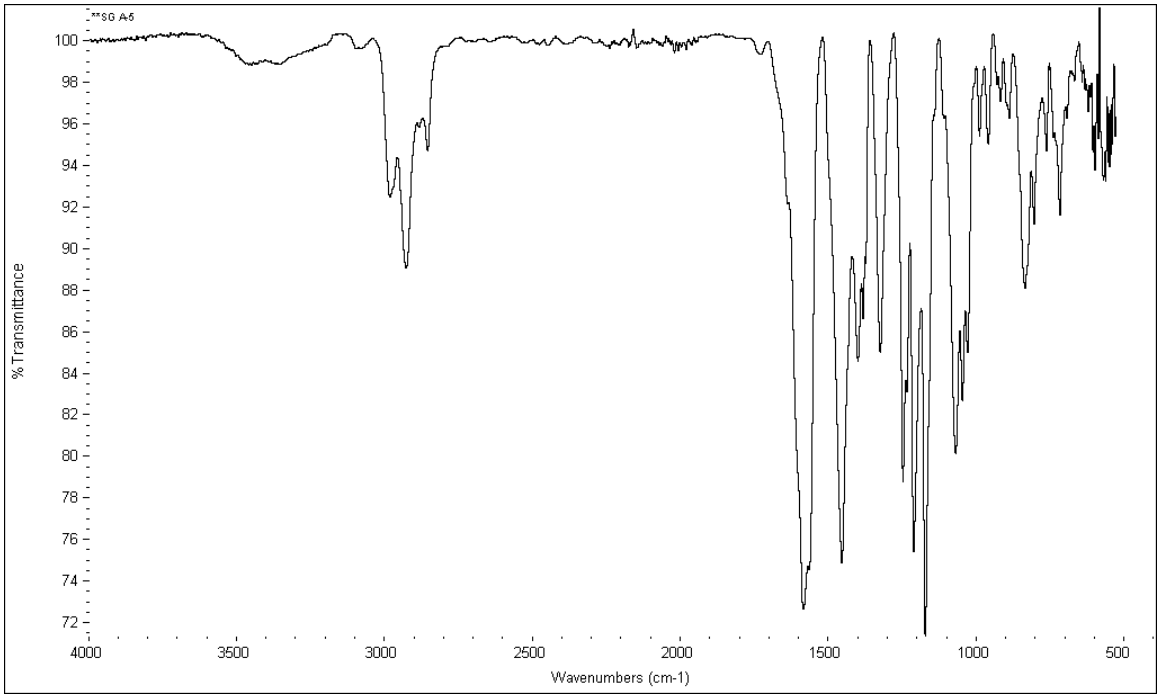

Thu May 10 13:59:16 2012 (GMT-04:00)
% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

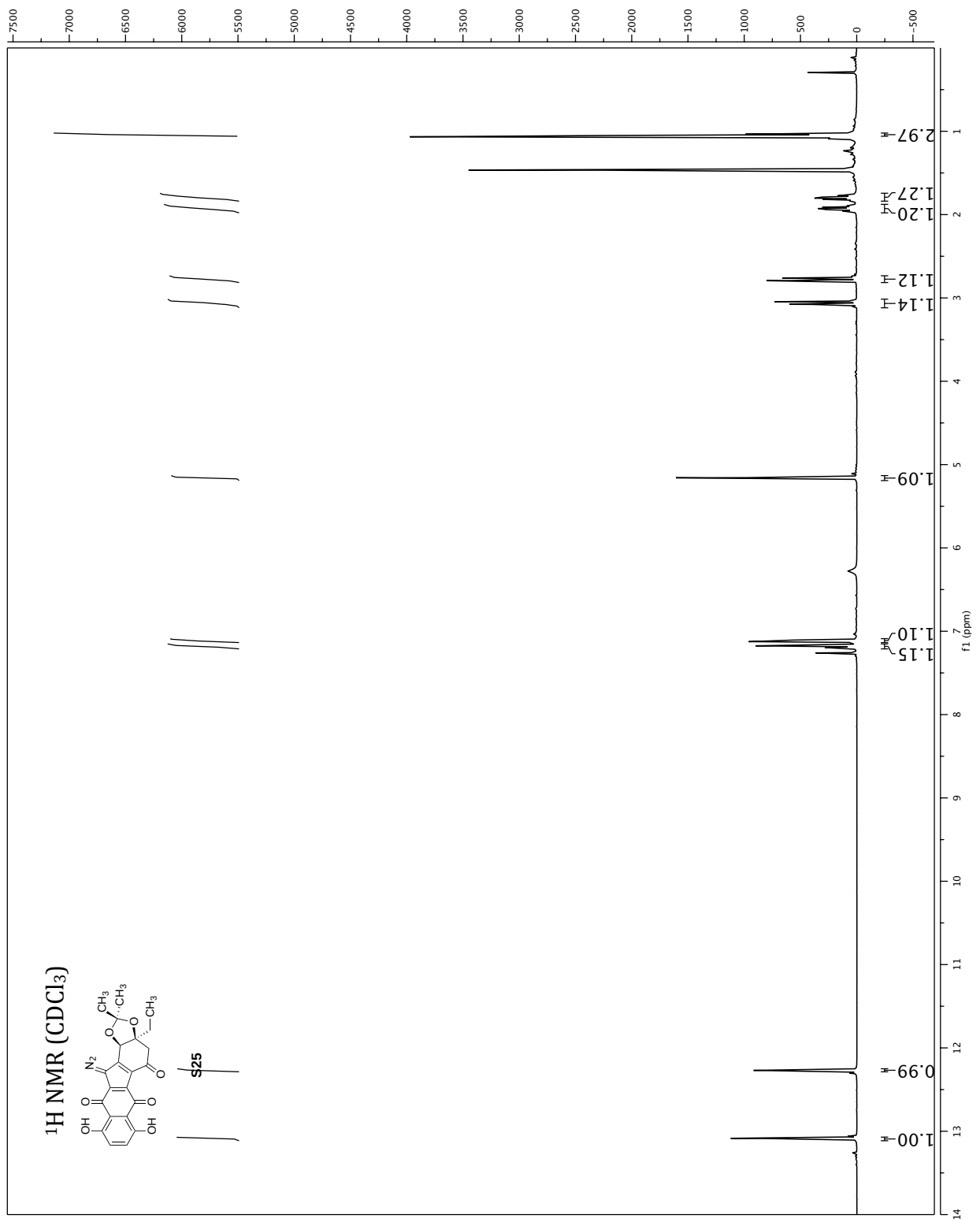

^{1}H NMR ($CDCl_3$)
S58
3.33
3.26
3.16
2.12
1.05
1.05
1.04
0.99
1.02
1.02
1.00
1.00
f1 (ppm)

^{13}C NMR ($CDCl_3$)

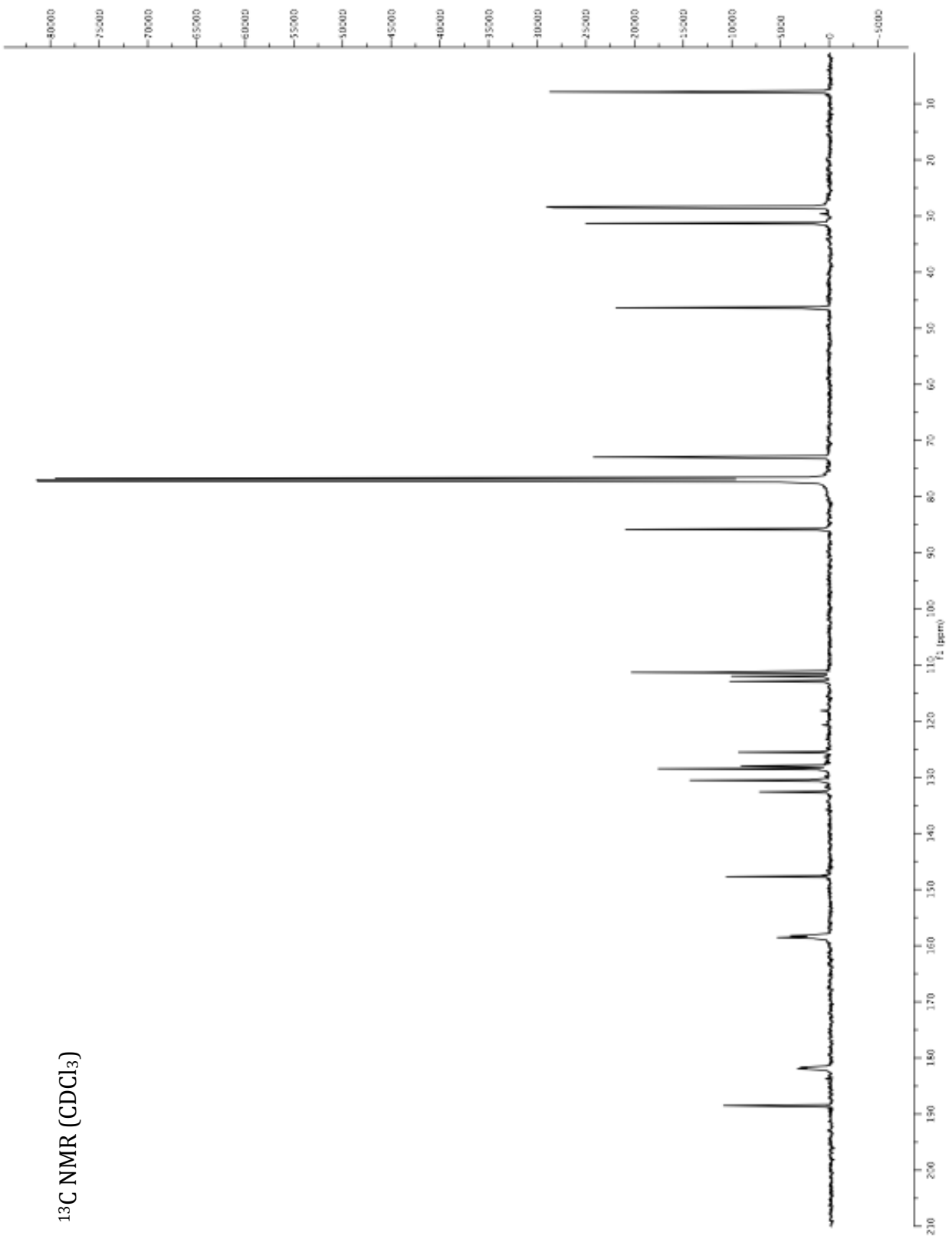


IR

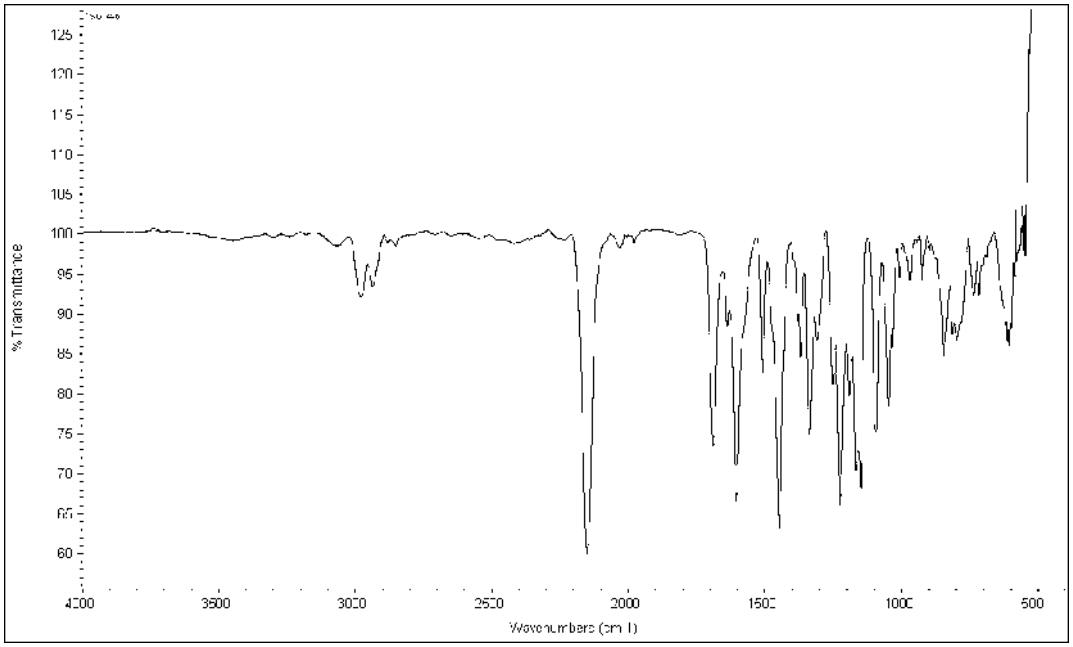

**SG A-5
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

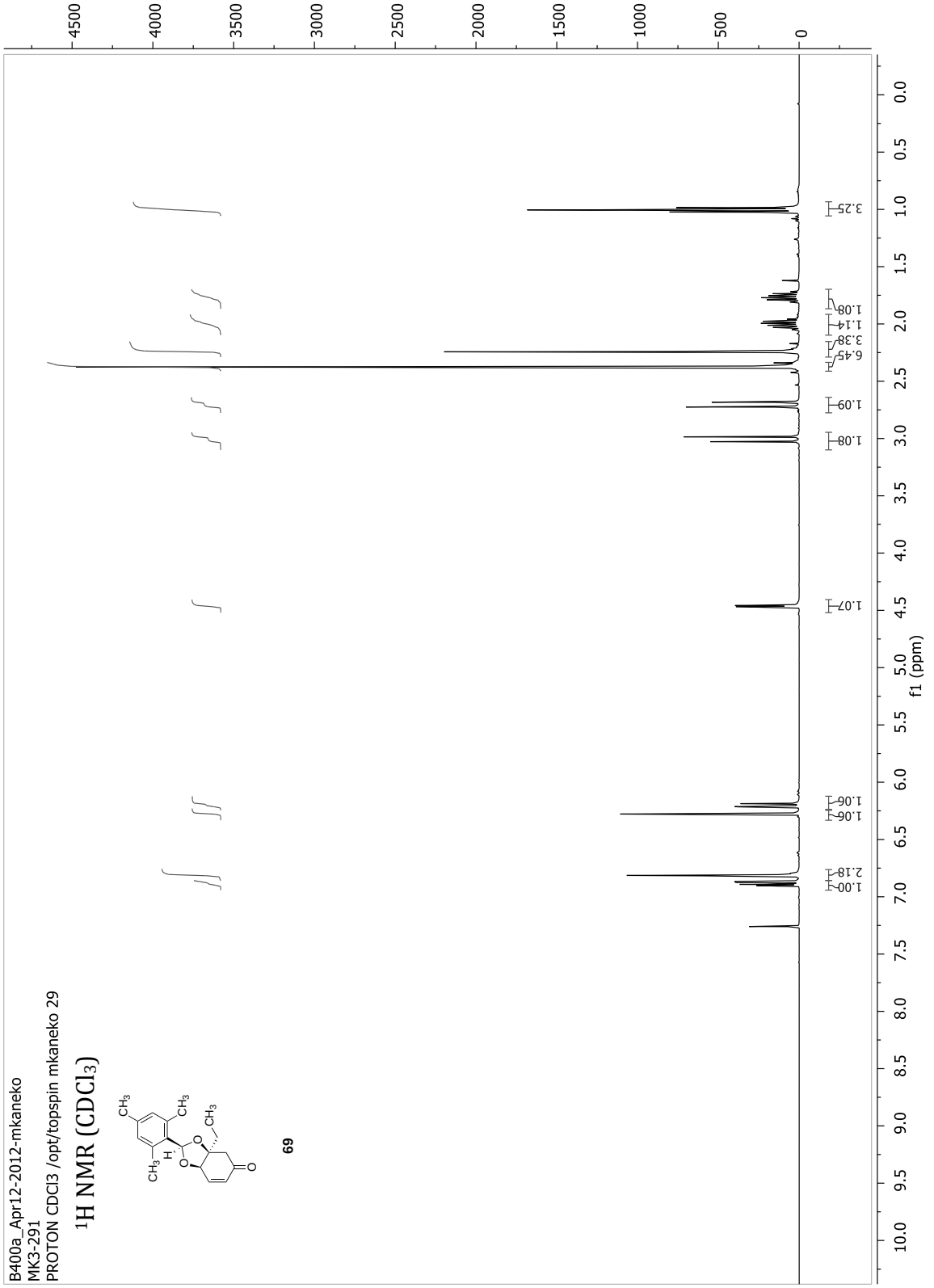

1H NMR (CDCl3)
S25
2.97
1.27
1.20
1.12
1.14
1.09
1.10
1.15
0.99
1.00
f1 (ppm)

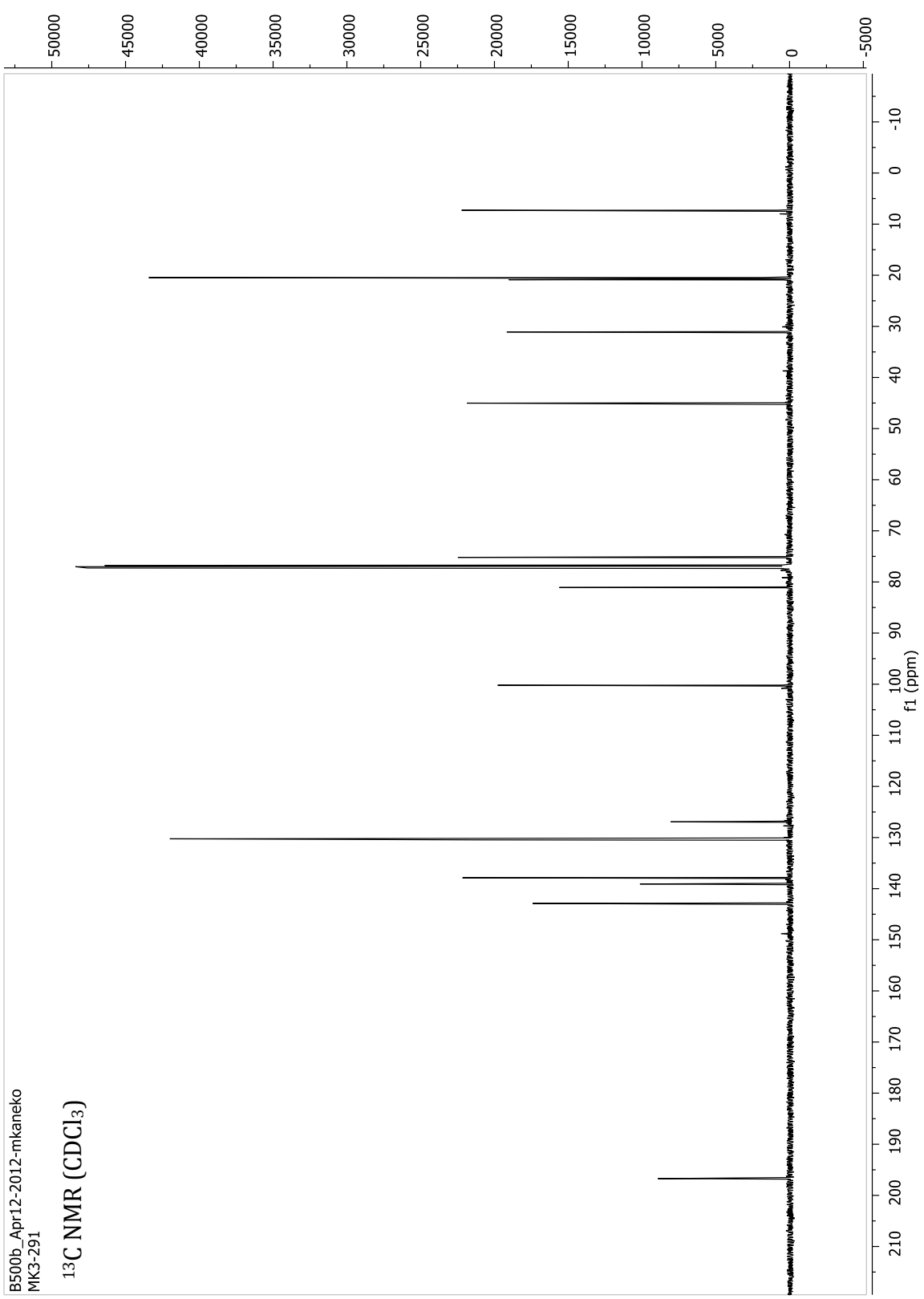
^{13}C NMR ($CDCl_3$)



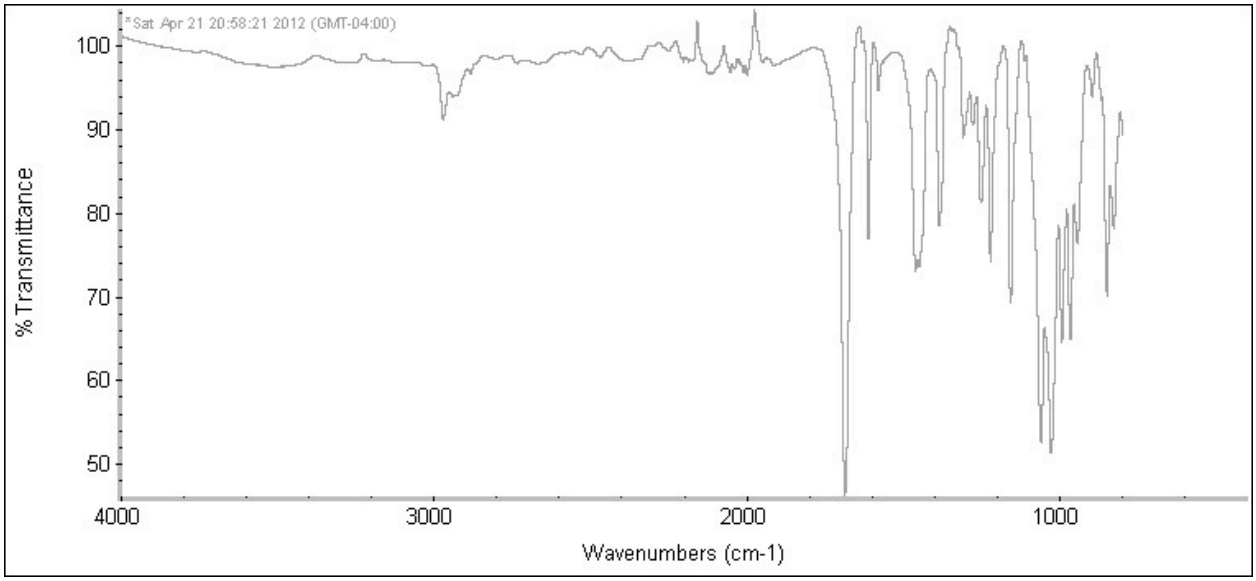
IR

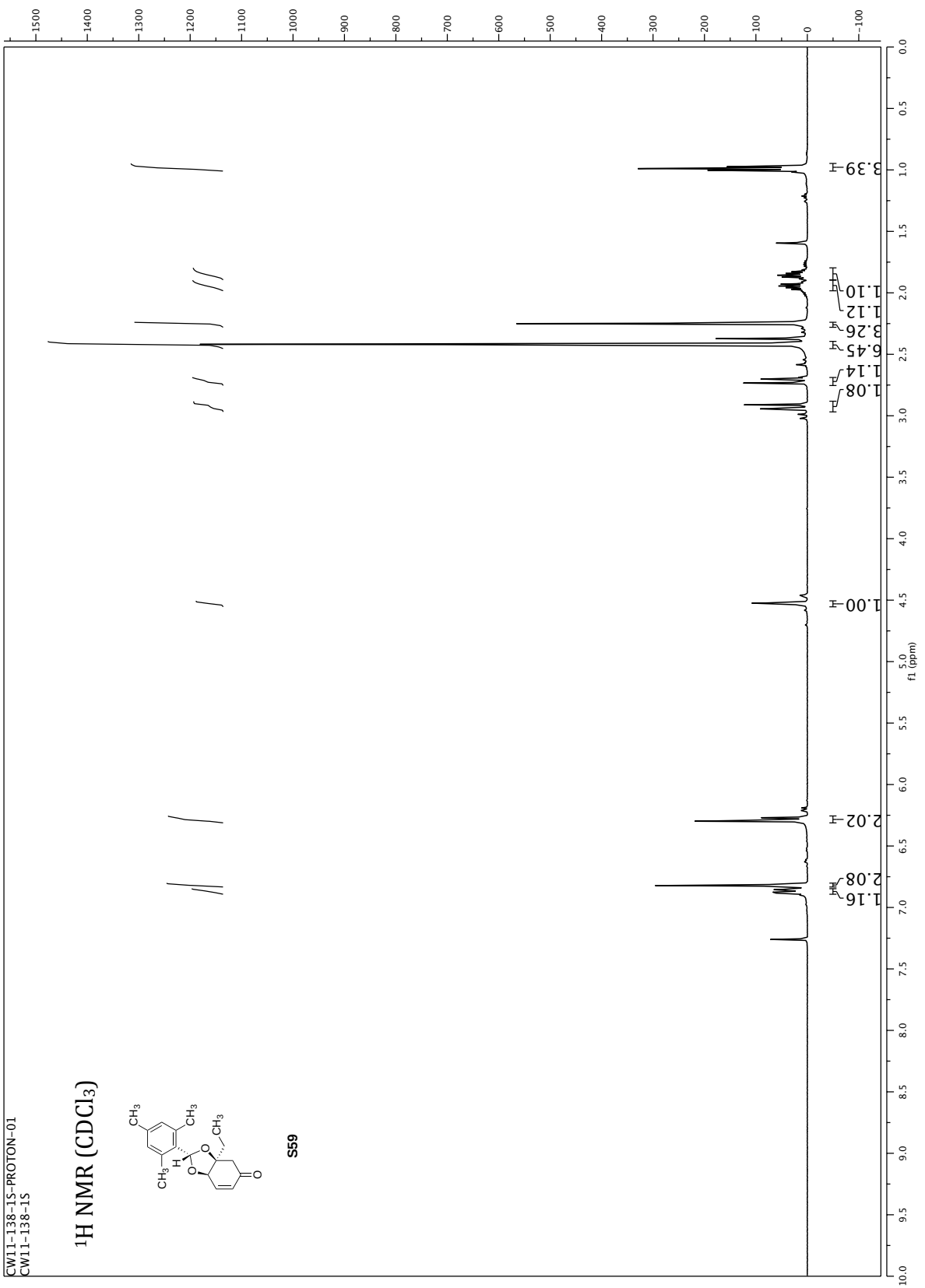

% Transmittance
125
120
115
110
105
100
95
90
85
80
75
70
65
60
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

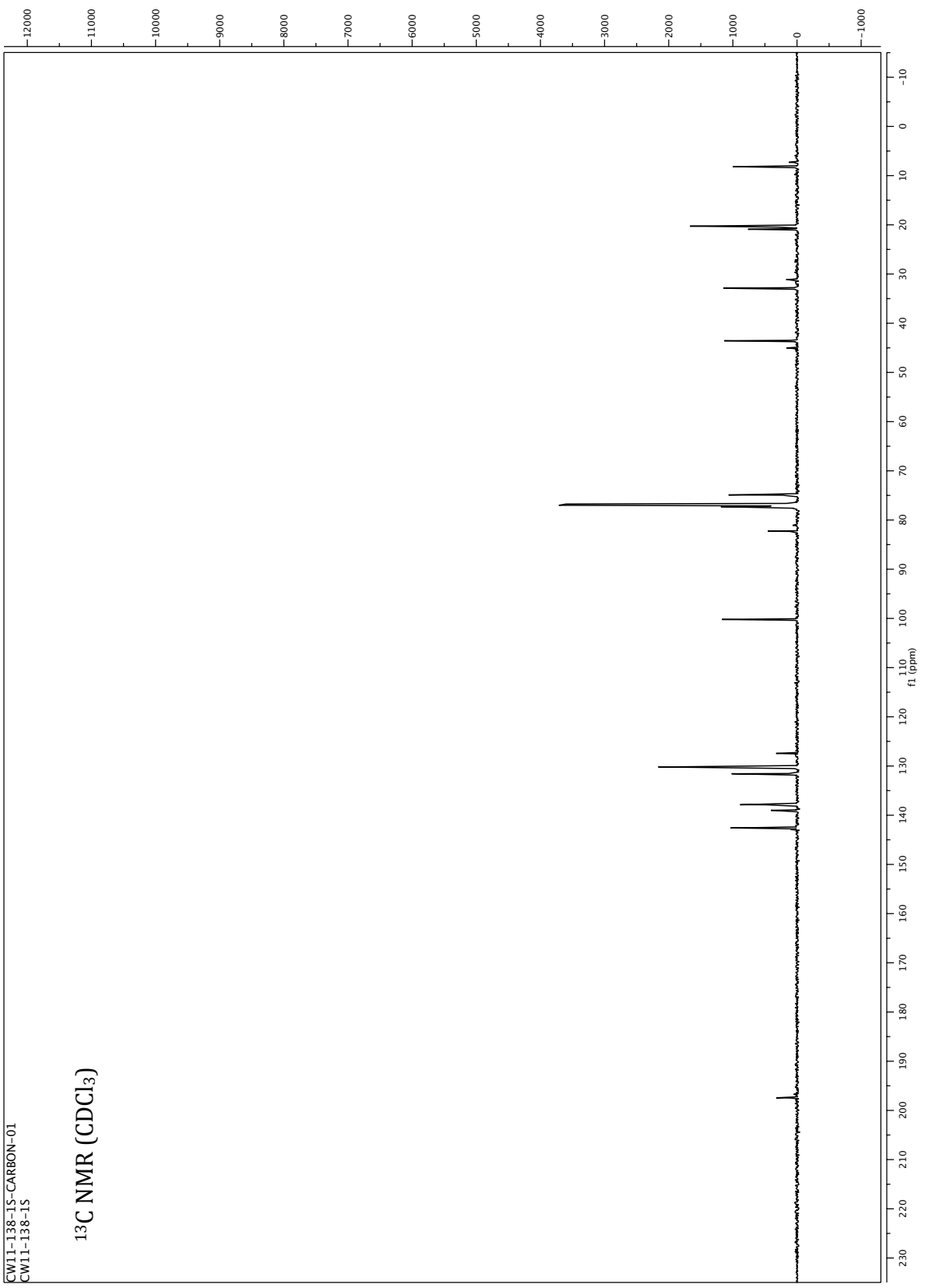

B400a_Apr12-2012-mkaneko
MK3-291
PROTON CDCl3 /opt/topspin mkaneko 29
^{1}H NMR ($CDCl_3$)
69
f1 (ppm)
3.25
1.08
1.14
3.38
6.45
1.09
1.08
1.07
1.06
1.06
2.18
1.00


B500b_Apr12-2012-mkaneko
MK3-291
13C NMR (CDCl3)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

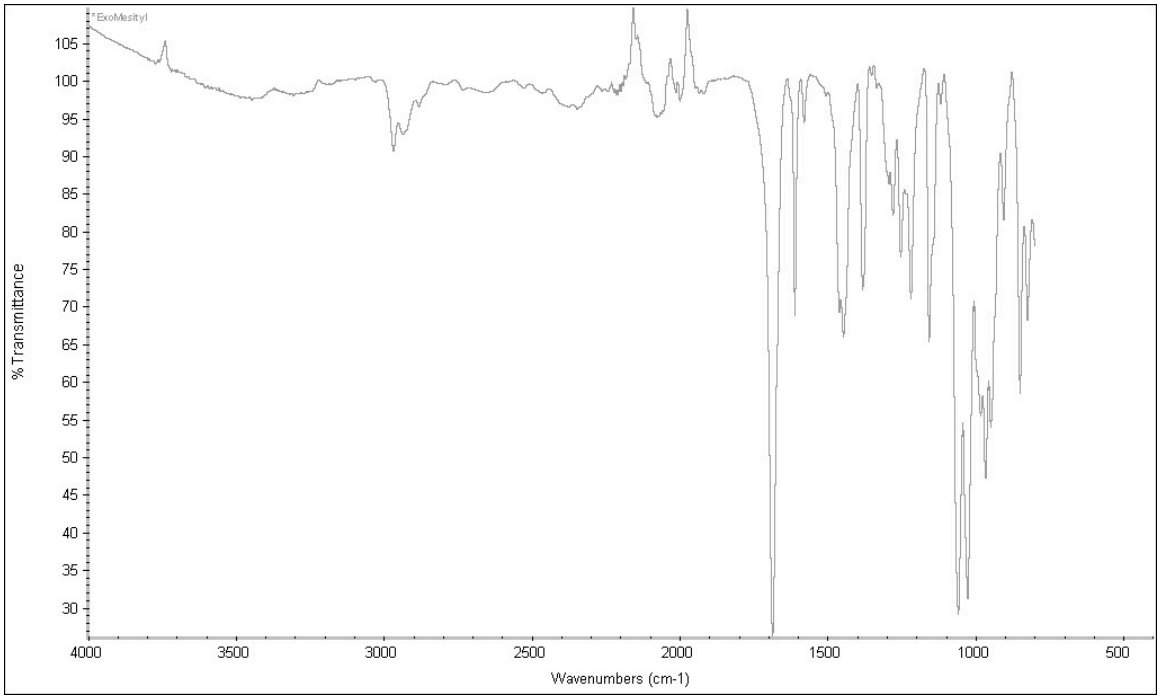
IR

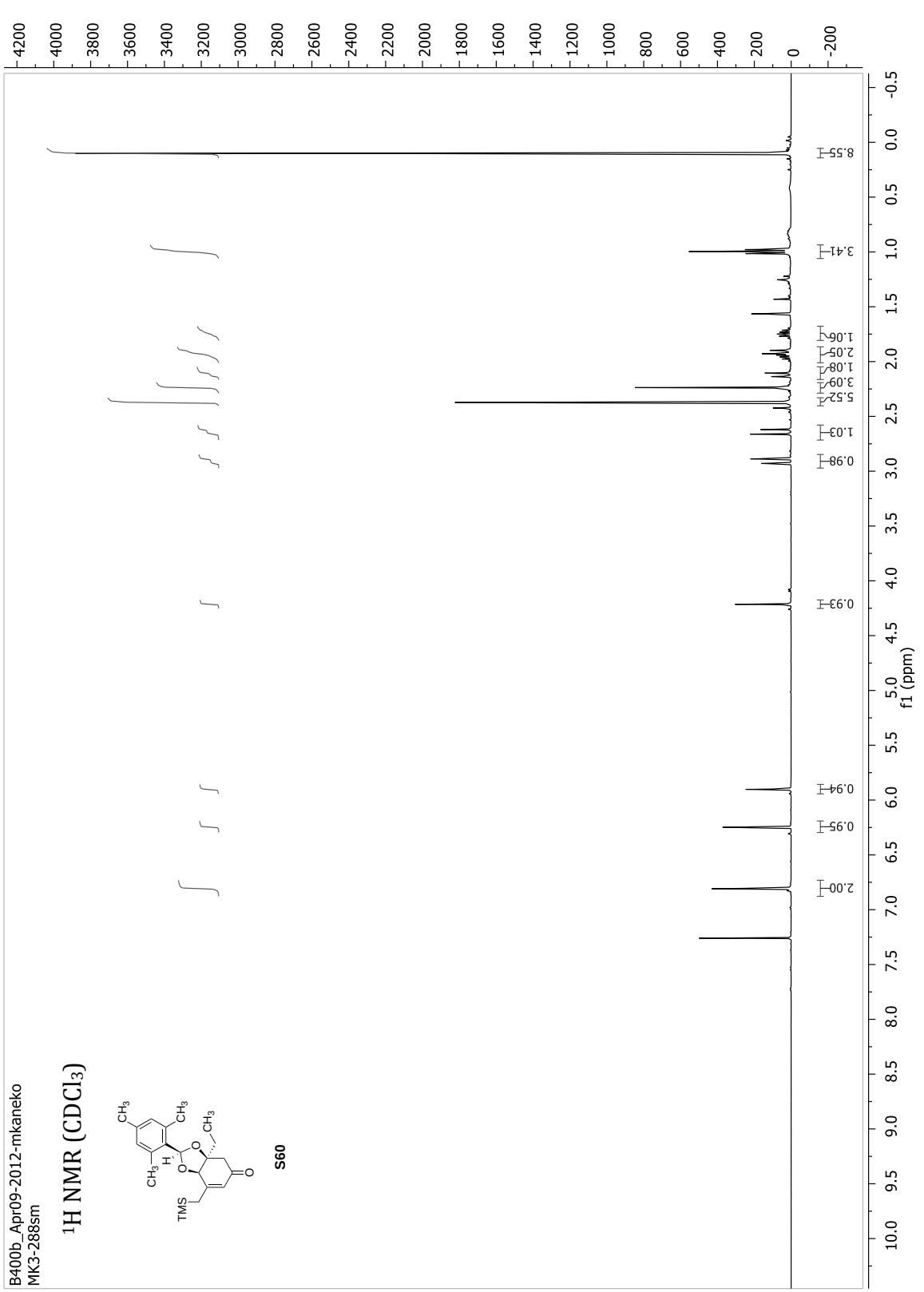

Sat Apr 21 20:58:21 2012 (GMT-04:00)
% Transmittance
100
90
80
70
60
50
4000
3000
2000
1000
Wavenumbers (cm-1)

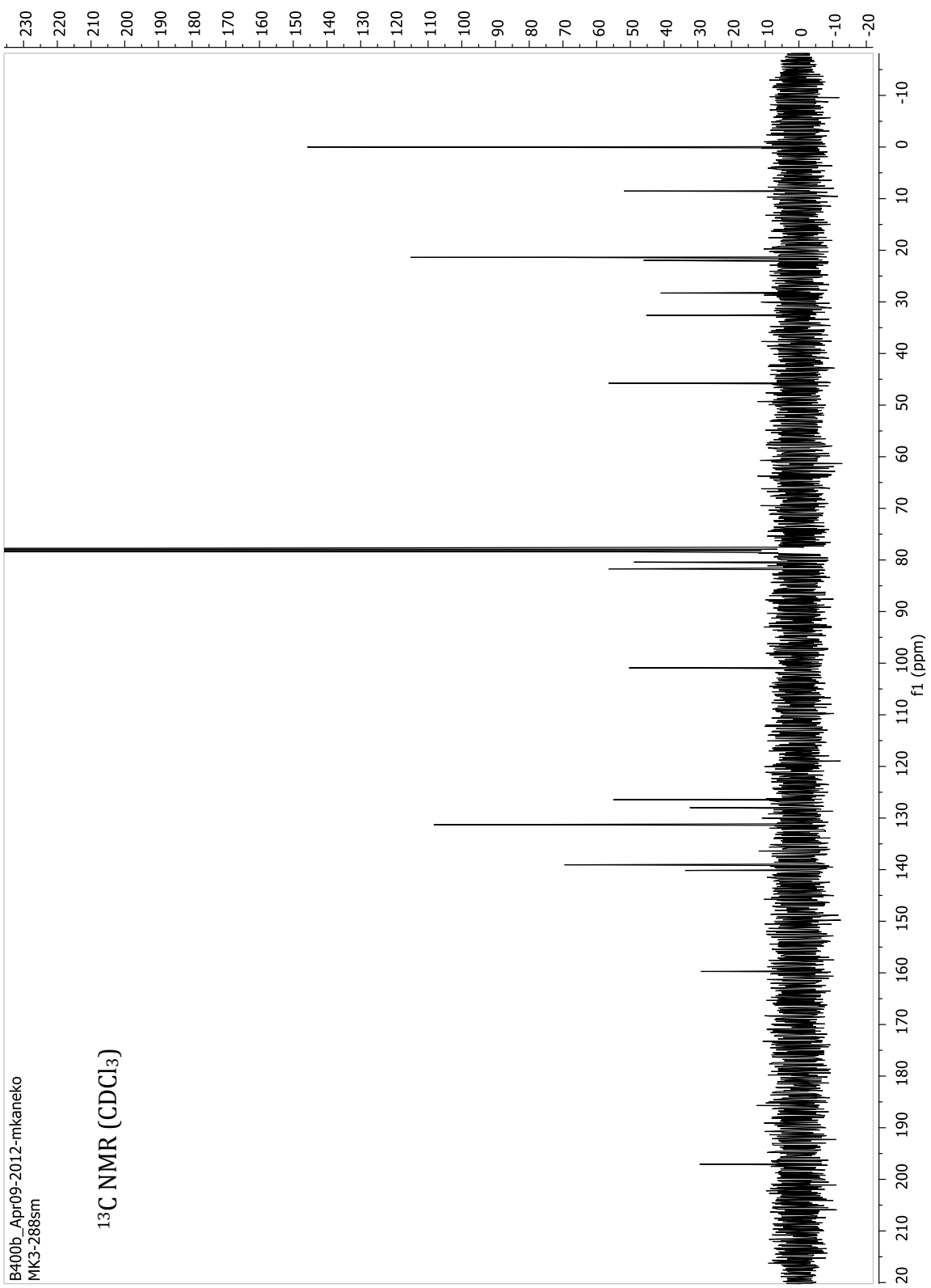

CW11-138-1S-PROTON-01
CW11-138-1S
1H NMR (CDCl3)
S59
3.39
1.10
1.12
3.26
6.45
1.14
1.08
1.00
2.02
2.08
1.16
f1 (ppm)


CW11-138-1S-CARBON-01
CW11-138-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

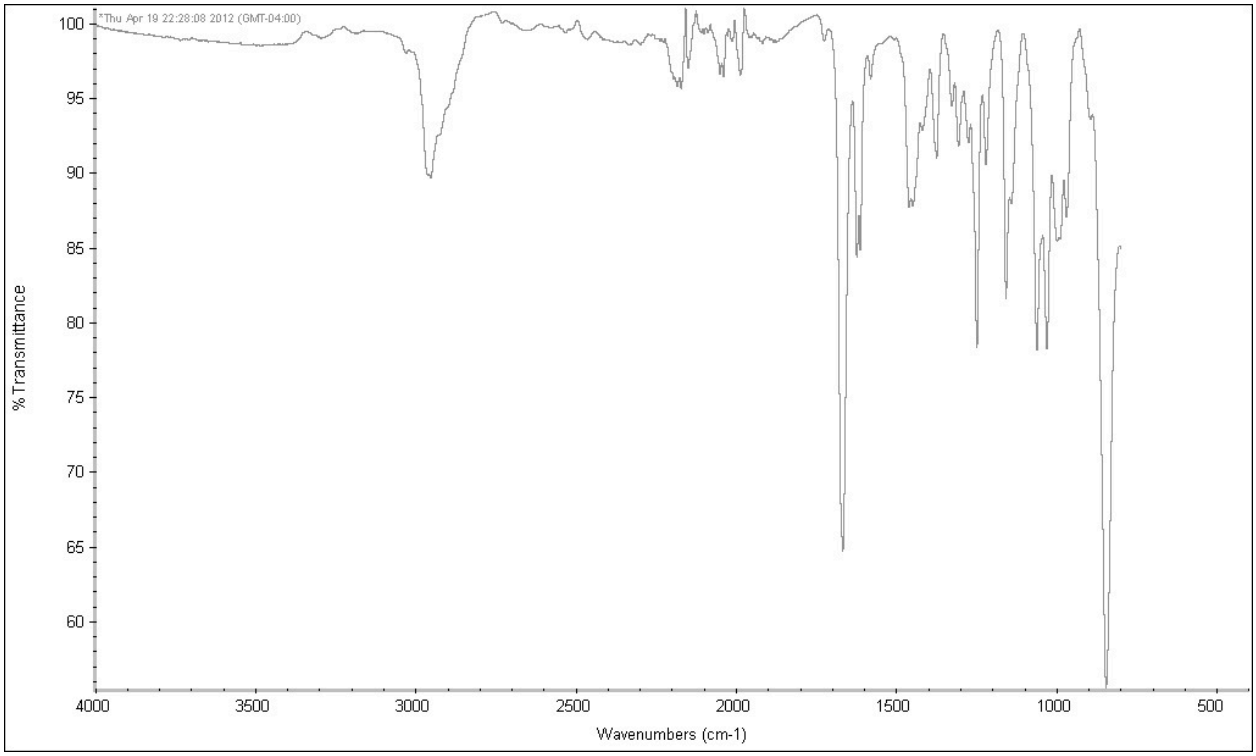
IR

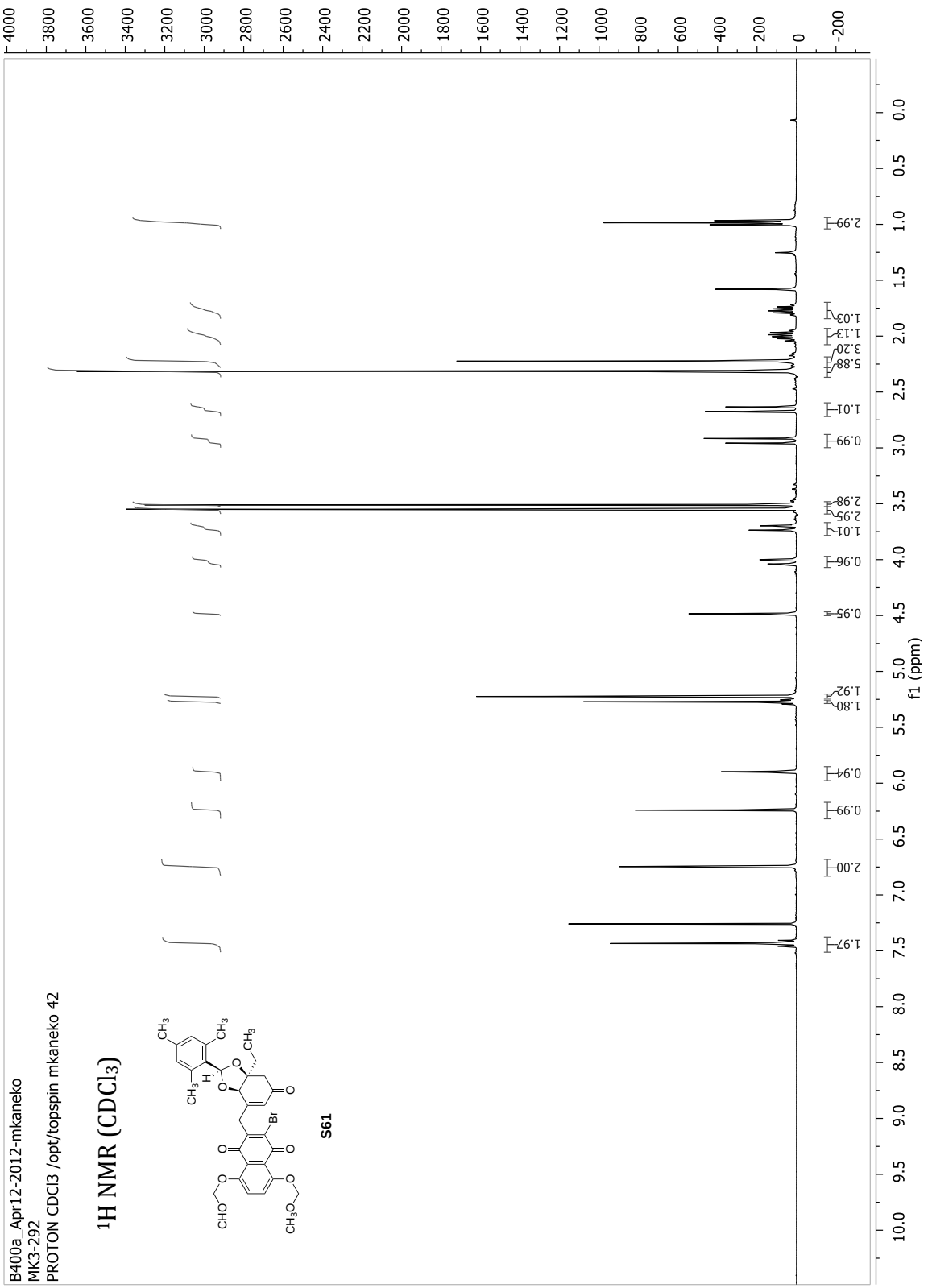

*ExoMesityl
% Transmittance
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

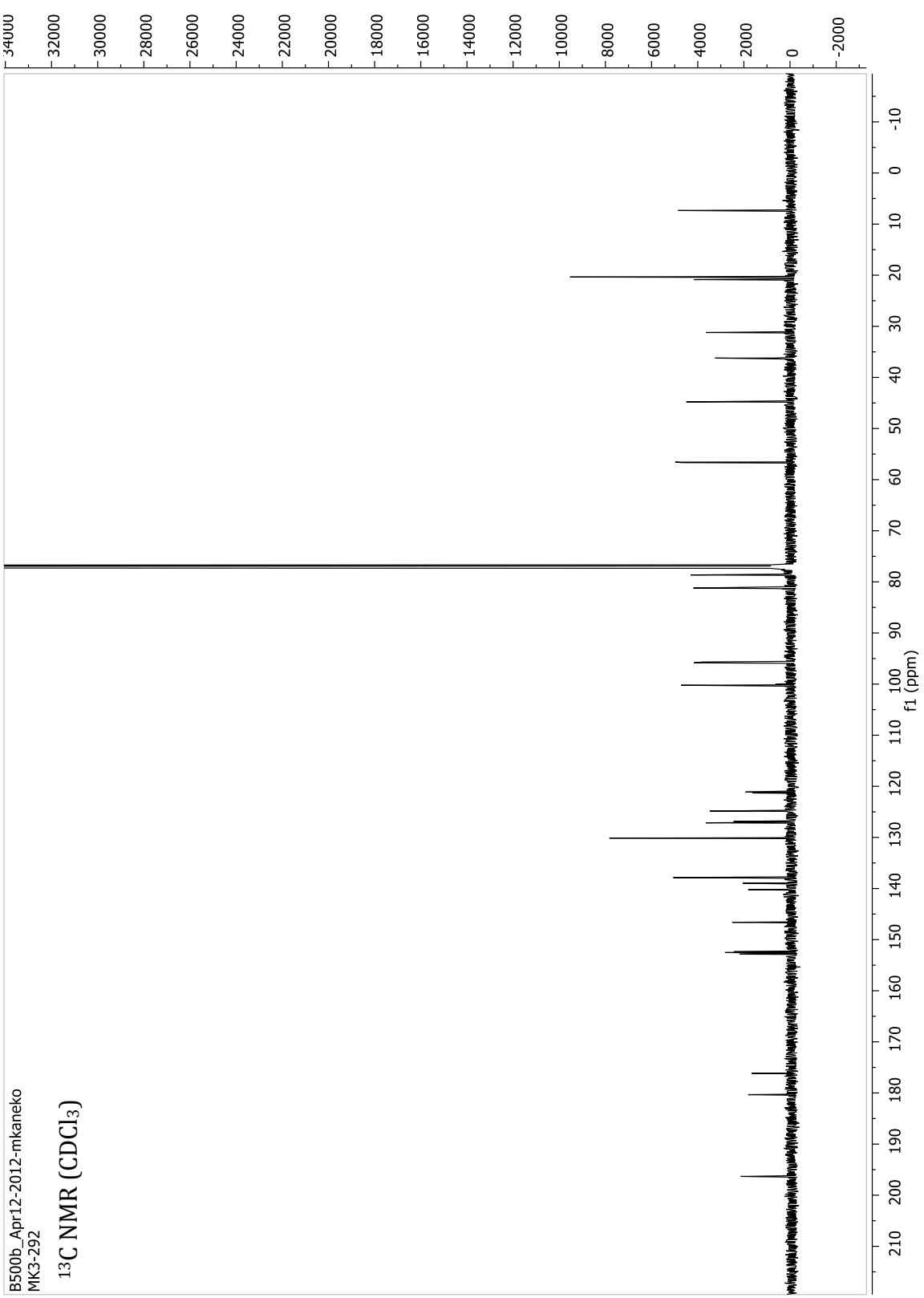

B400b_Apr09-2012-mkaneko
MK3-288sm
^{1}H NMR ($CDCl_3$)
S60
8.55
3.41
1.06
2.05
1.08
3.09
5.52
1.03
0.98
0.93
0.94
0.95
2.00
f1 (ppm)


B400b_Apr09-2012-mkaneko
MK3-288sm
^{13}C NMR ($CDCl_3$)
f1 (ppm)

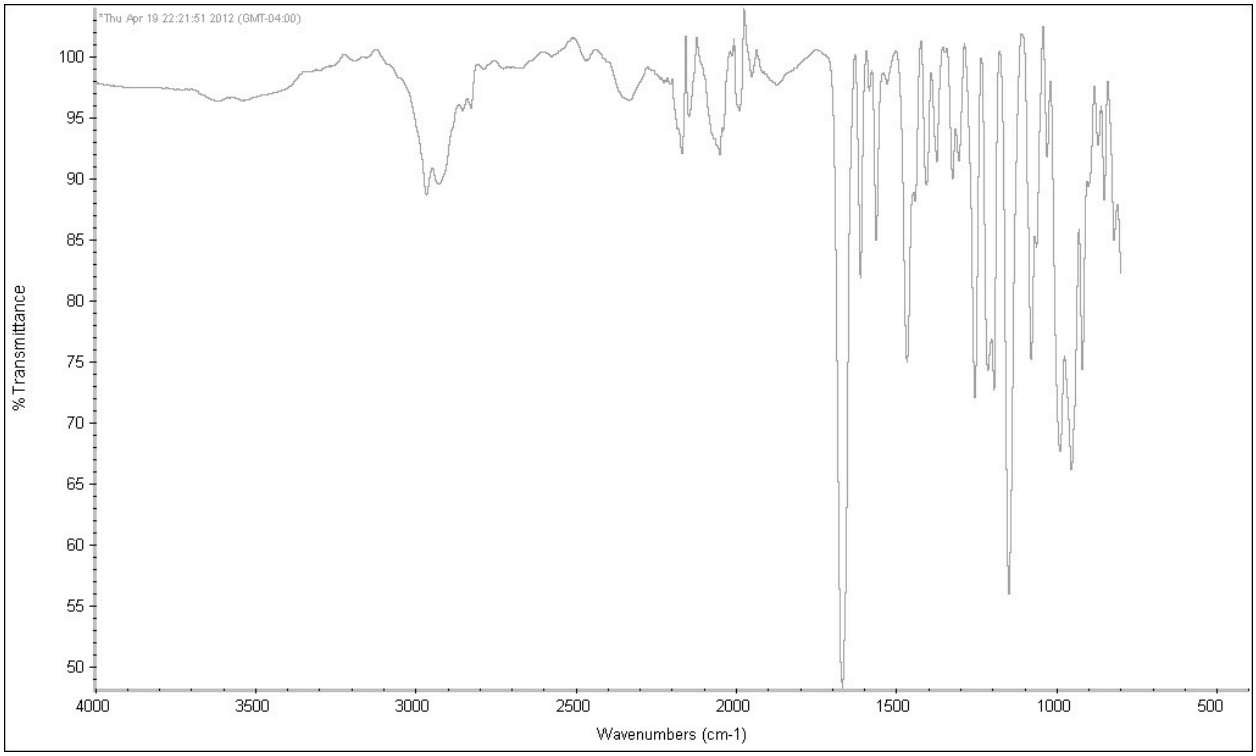
IR

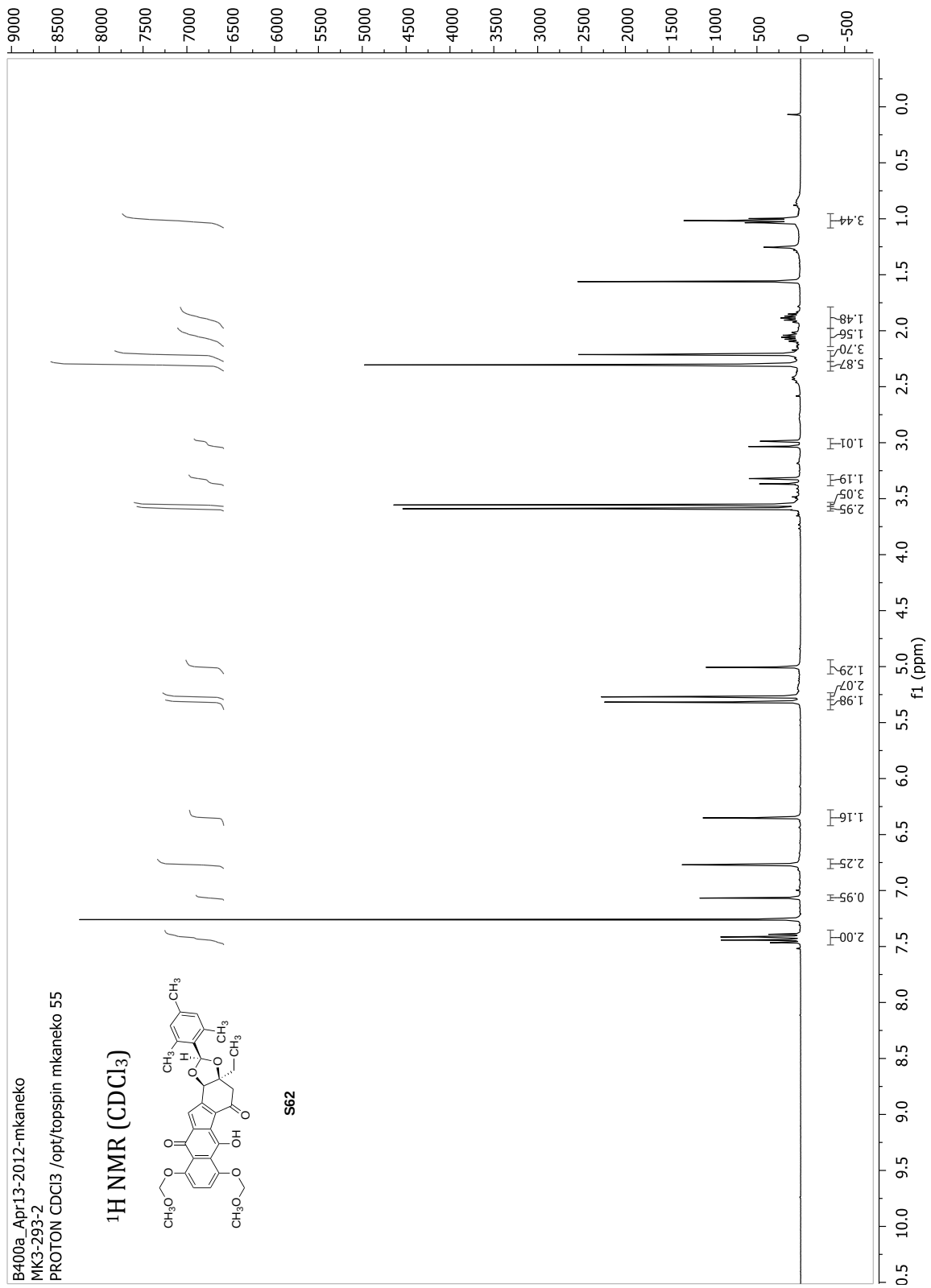

Thu Apr 19 22:28:08 2012 (GMT-04:00)
% Transmittance
100
95
90
85
80
75
70
65
60
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

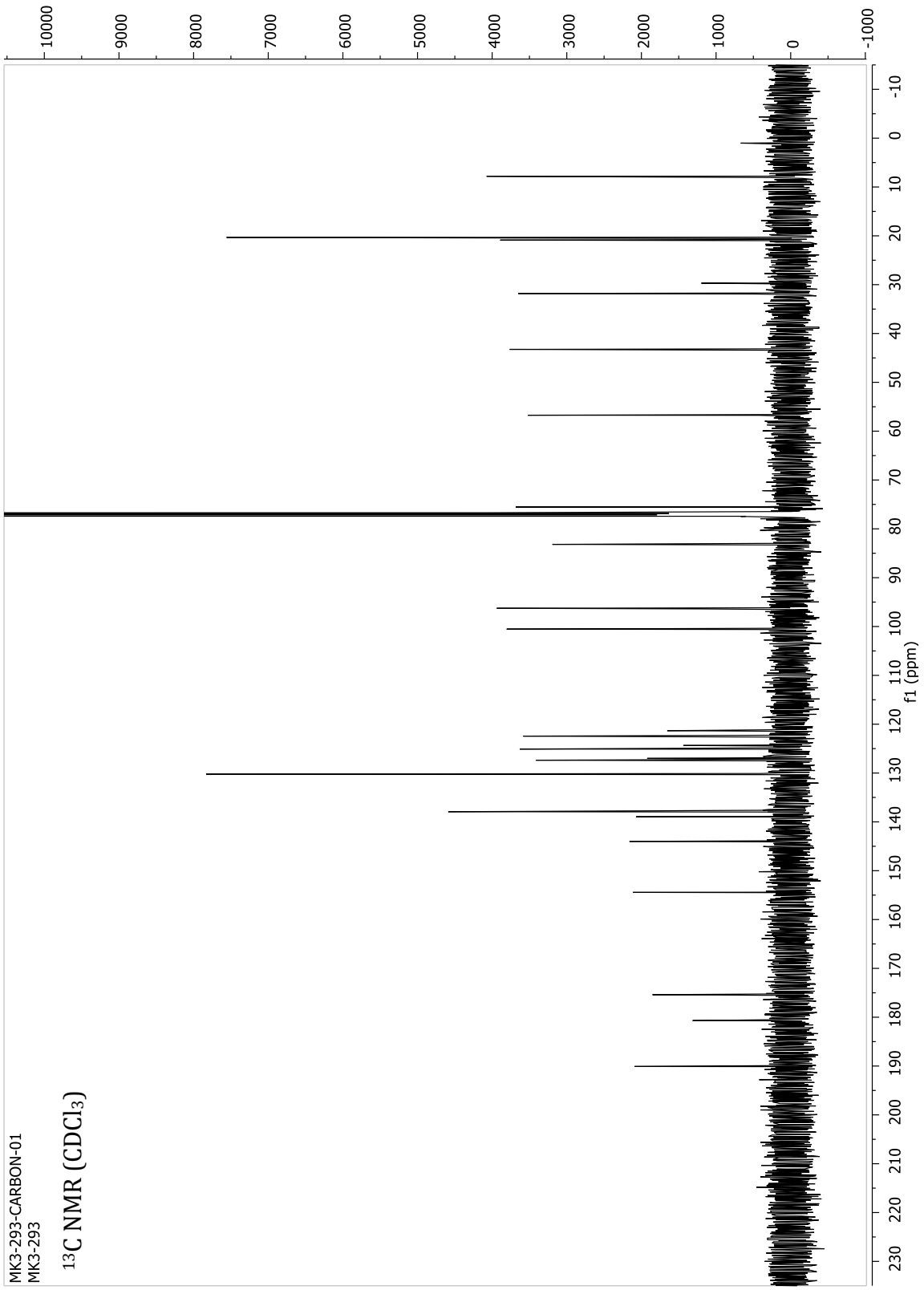

B400a_Apr12-2012-mkaneko
MK3-292
PROTON CDCl3 /opt/topspin mkaneko 42
^{1}H NMR ($CDCl_3$)
S61
f1 (ppm)


B500b_Apr12-2012-mkaneko
MK3-292
^{13}C NMR ($CDCl_3$)
f1 (ppm)

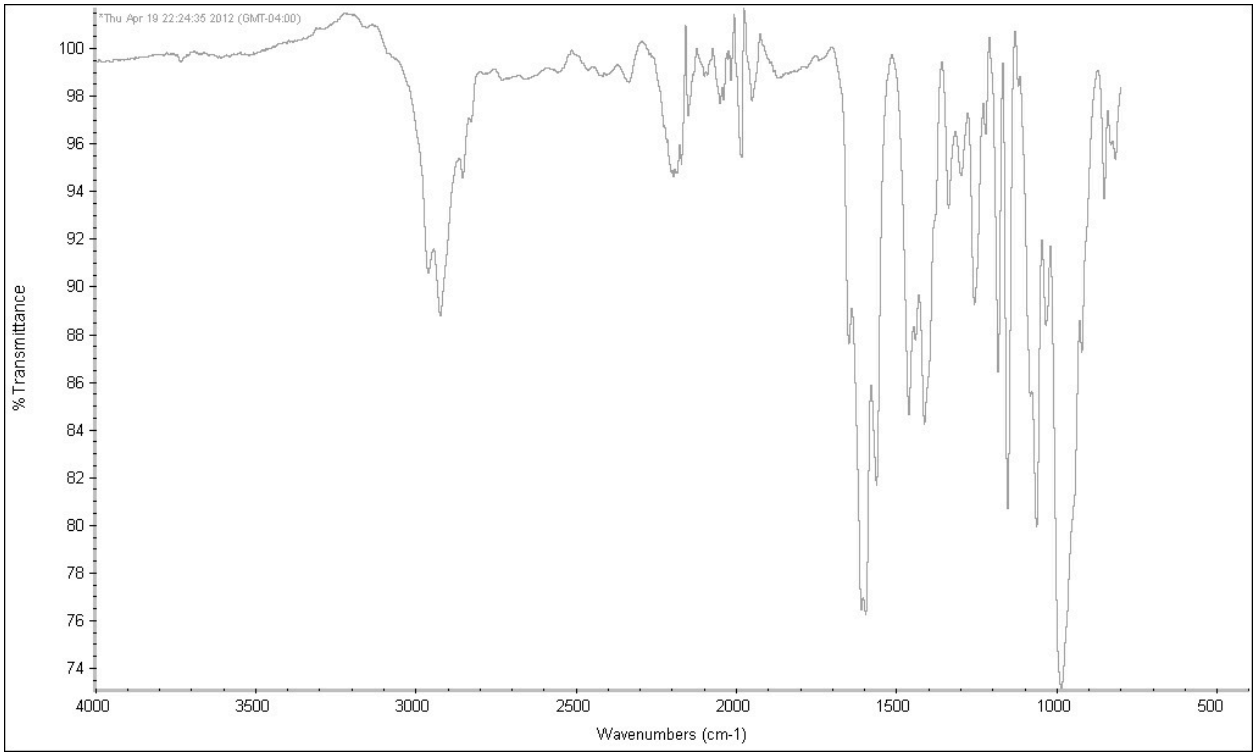
IR

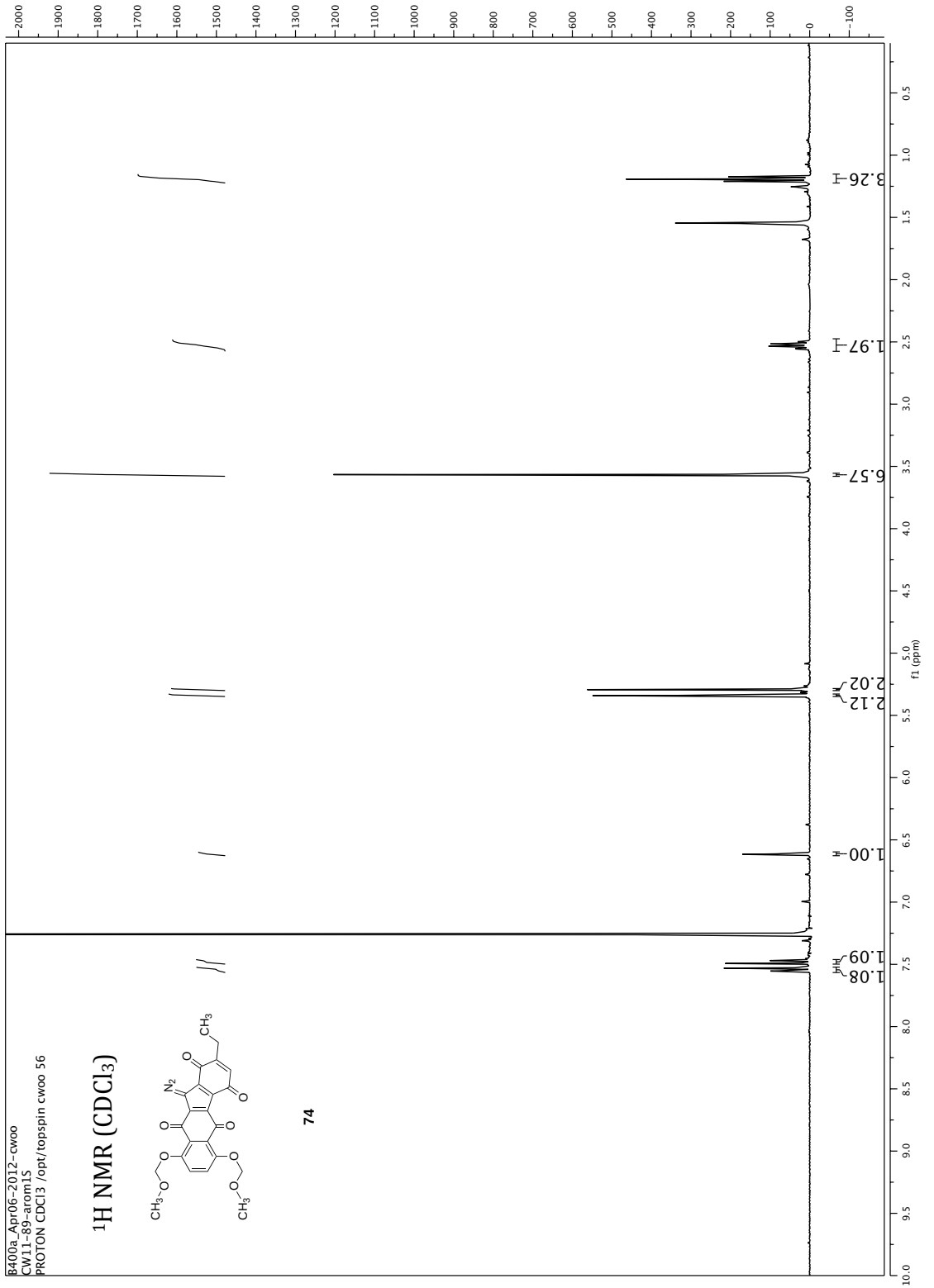

Thu Apr 19 22:21:51 2012 (GMT-04:00)
% Transmittance
100
95
90
85
80
75
70
65
60
55
50
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

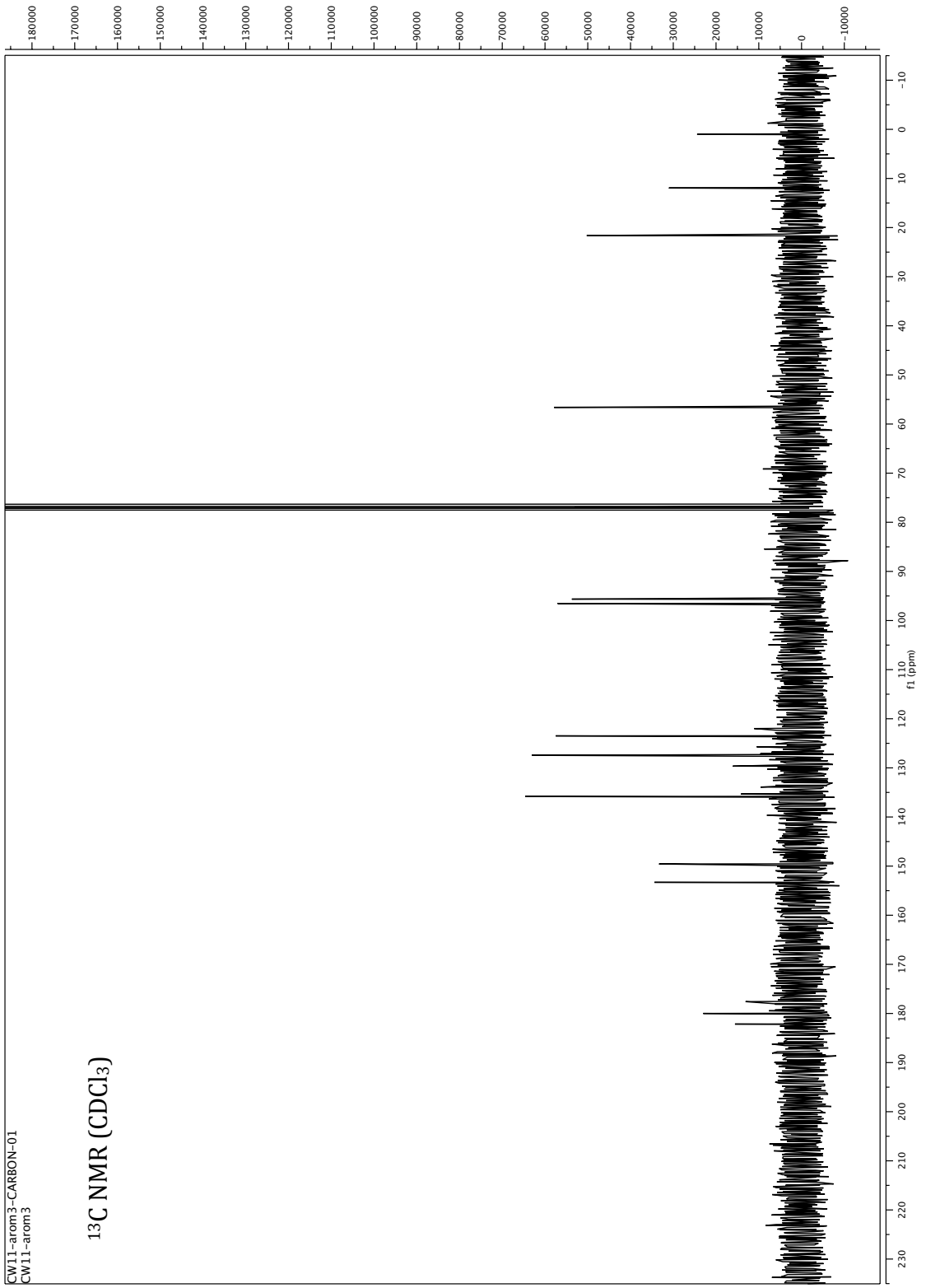

B400a_Apr13-2012-mkaneko
MK3-293-2
PROTON CDCl3 /opt/topspin mkaneko 55
^{1}H NMR ($CDCl_3$)
S62
f1 (ppm)
2.00
0.95
2.25
1.16
1.98
2.07
1.29
2.95
3.05
1.19
1.01
5.87
3.70
1.56
1.48
3.44


MK3-293-CARBON-01
MK3-293
^{13}C NMR ($CDCl_3$)
f1 (ppm)

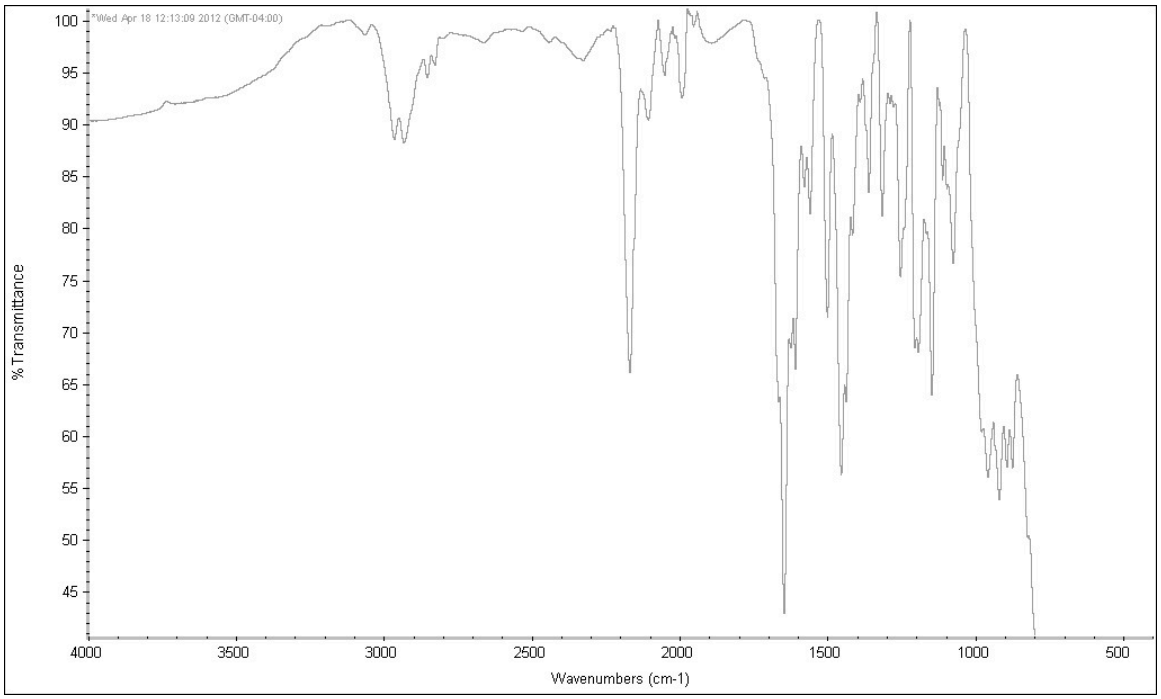
IR

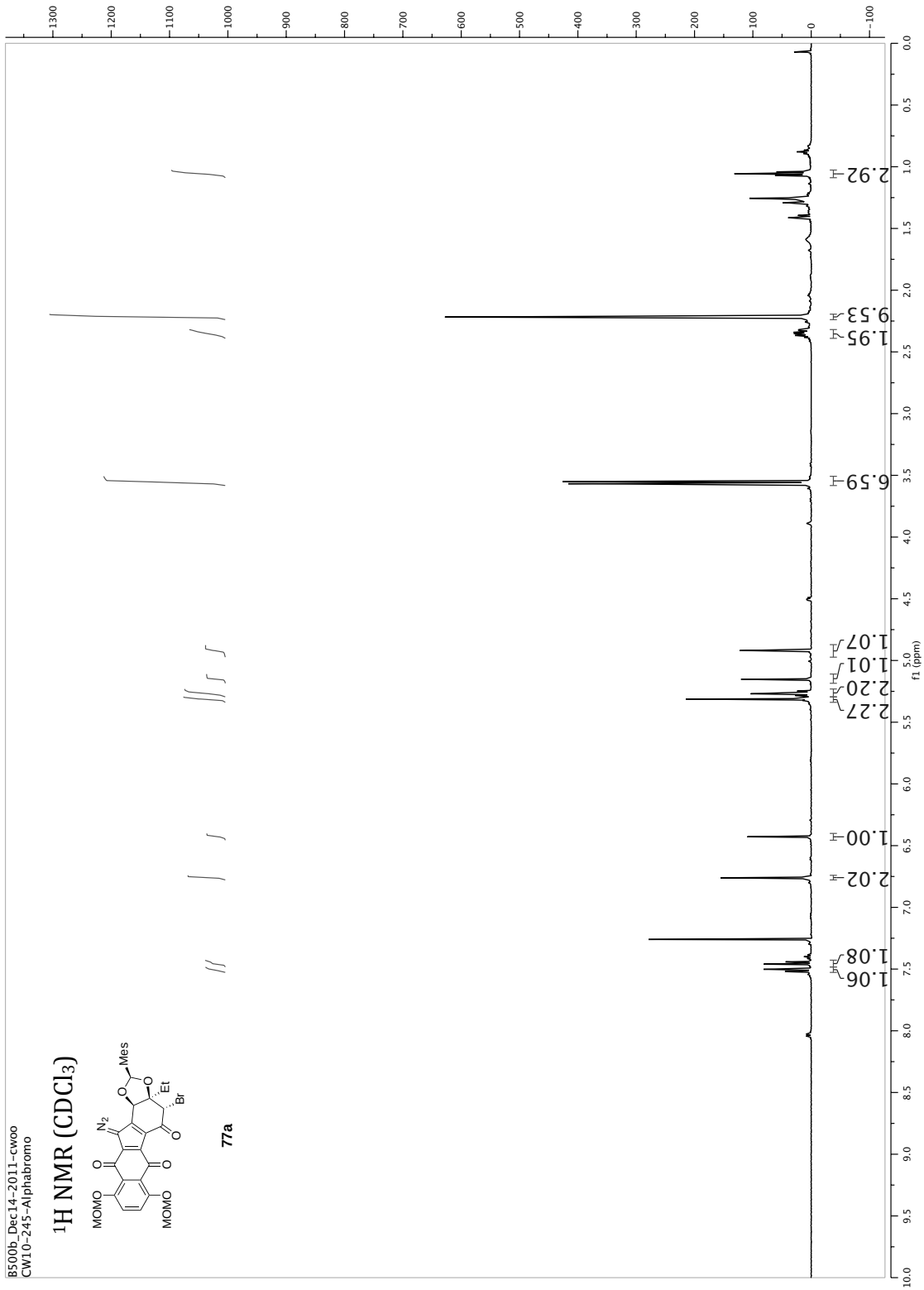

Thu Apr 19 22:24:35 2012 (GMT-04:00)
% Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

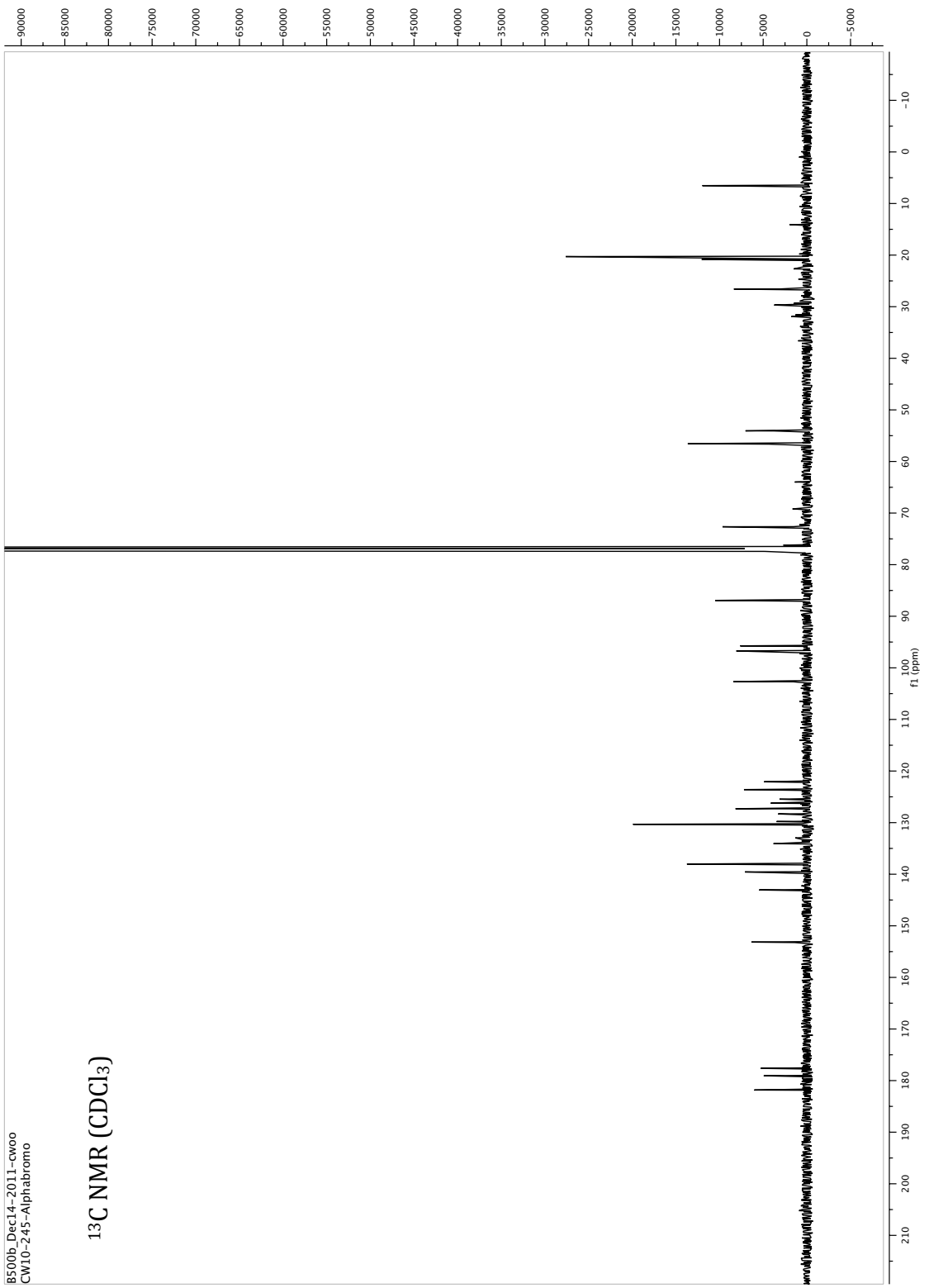

B400a_Apr06-2012-cwoo
CW11-89-arom1S
PROTON CDCl3 /opt/topspin cwoo 56
^{1}H NMR ($CDCl_3$)
74
8.26
1.97
6.57
2.02
2.12
1.00
1.09
1.08
f1 (ppm)


^{13}C NMR ($CDCl_3$)
CW11-arom3-CARBON-01
CW11-arom3
f1 (ppm)

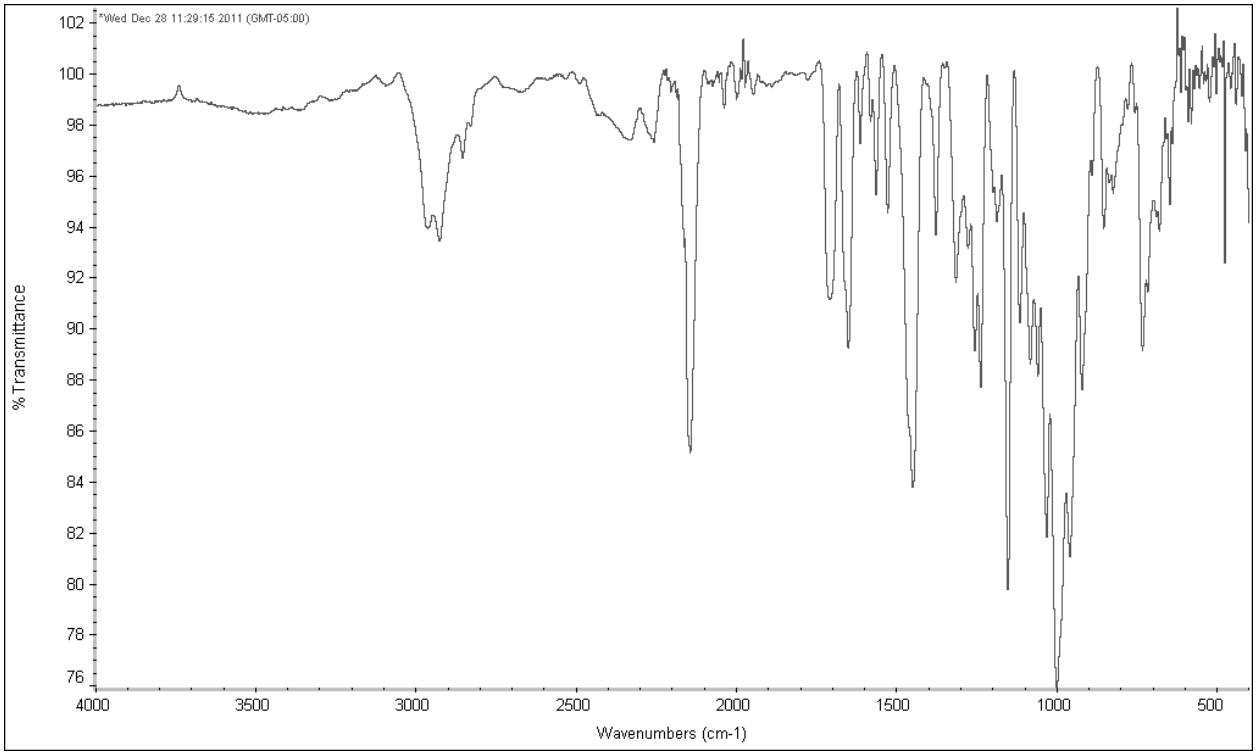
IR

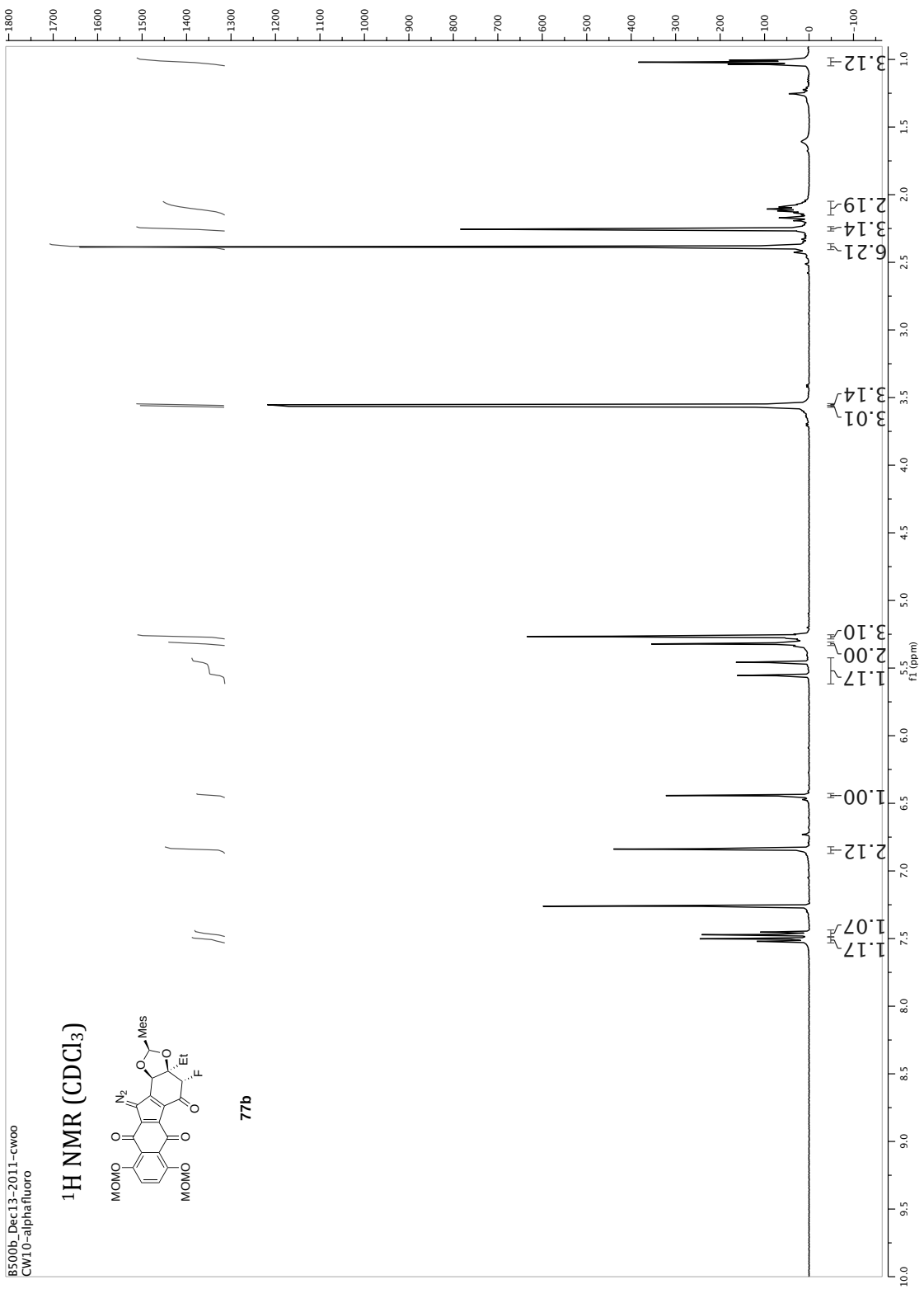

Wed Apr 18 12:13:09 2012 (GMT-04:00)
% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

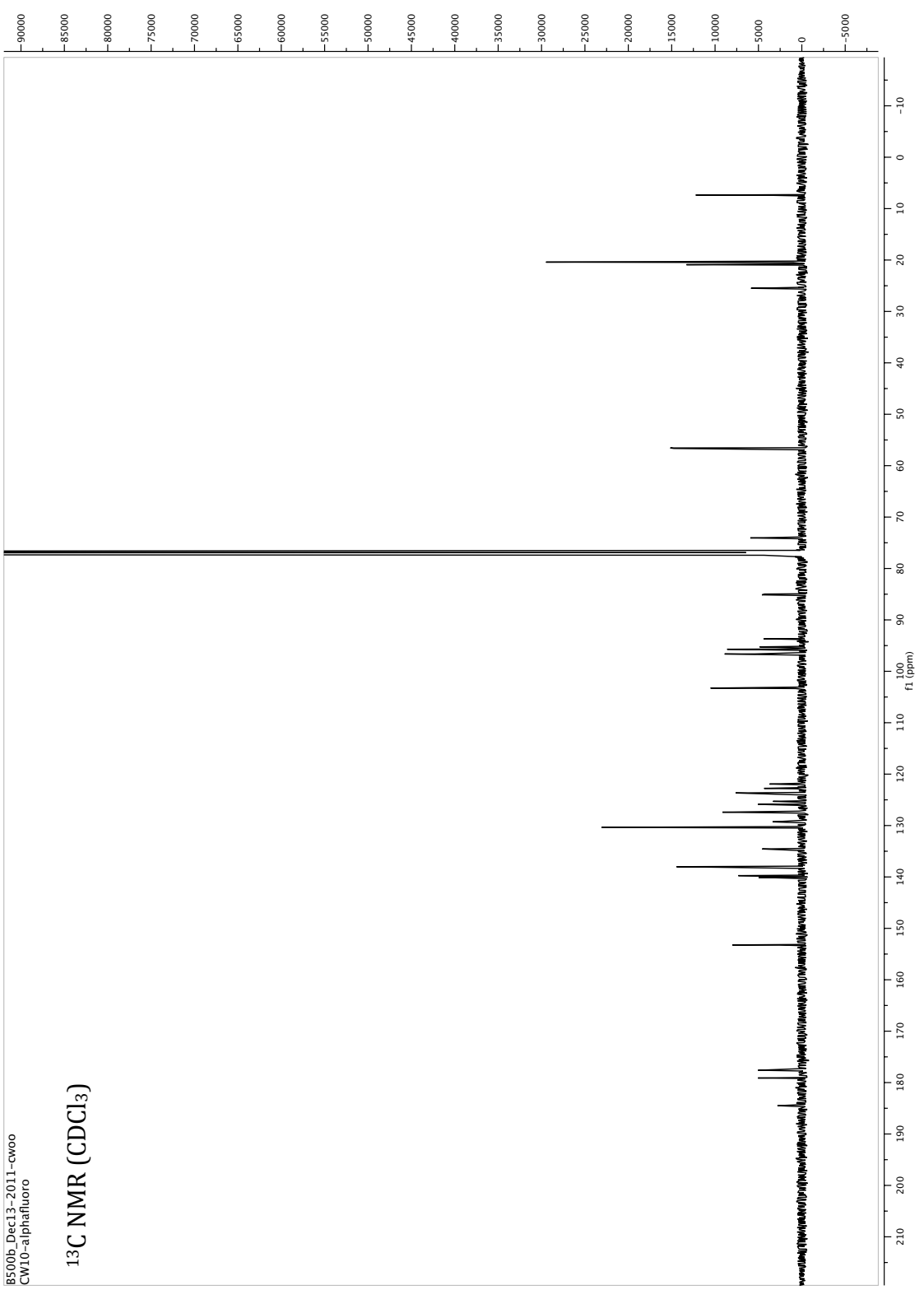

B500b_Dec14-2011-cwoo
CW10-245-Alphabromo
^{1}H NMR ($CDCl_3$)
77a
MOMO
MOMO
Mes
Et
Br
N_2
2.92
9.53
1.95
6.59
1.07
1.01
2.20
2.27
1.00
2.02
1.08
1.06
f1 (ppm)

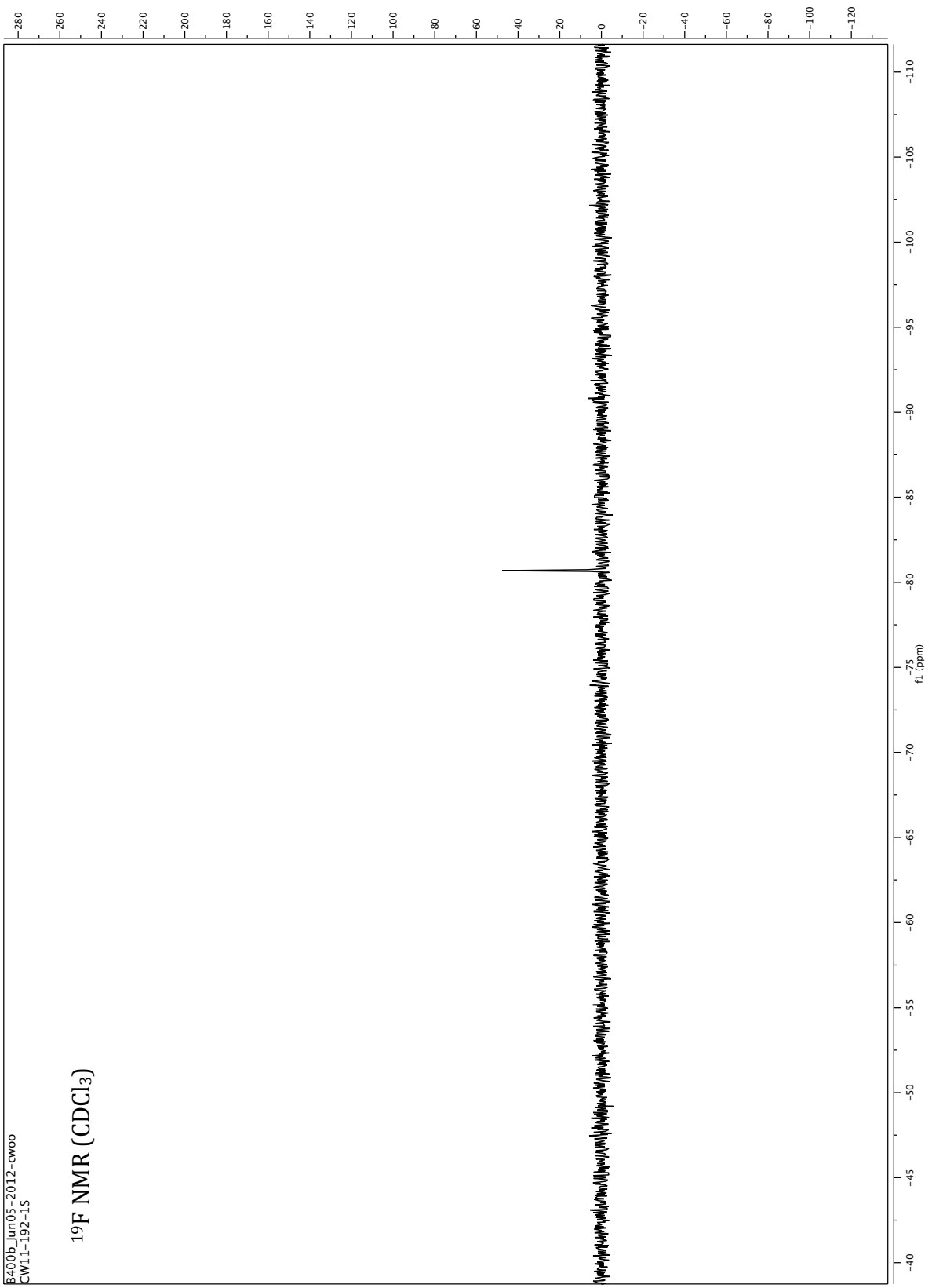

B500b_Dec14-2011-cwoo
CW10-245-Alphabromo
^{13}C NMR ($CDCl_3$)
f1 (ppm)

IR

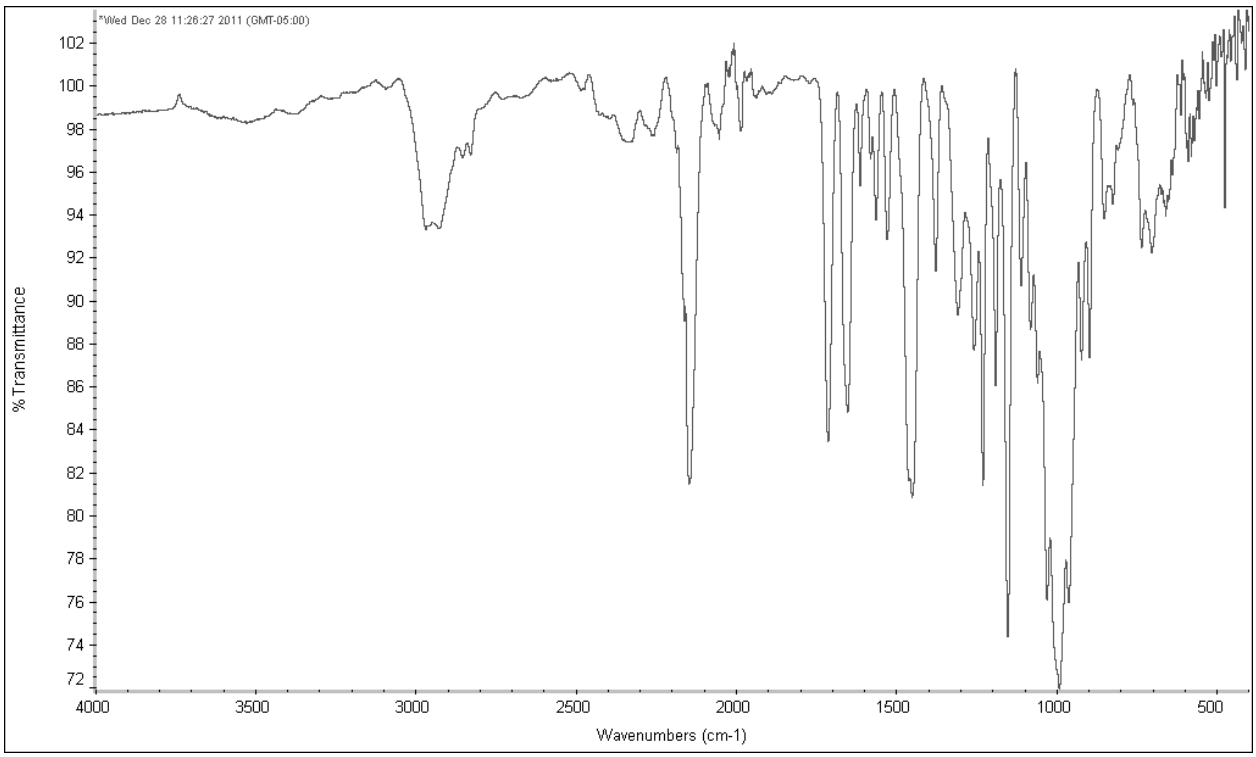

Wed Dec 28 11:29:15 2011 (GMT-05:00)
% Transmittance
102
100
98
96
94
92
90
88
86
84
82
80
78
76
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

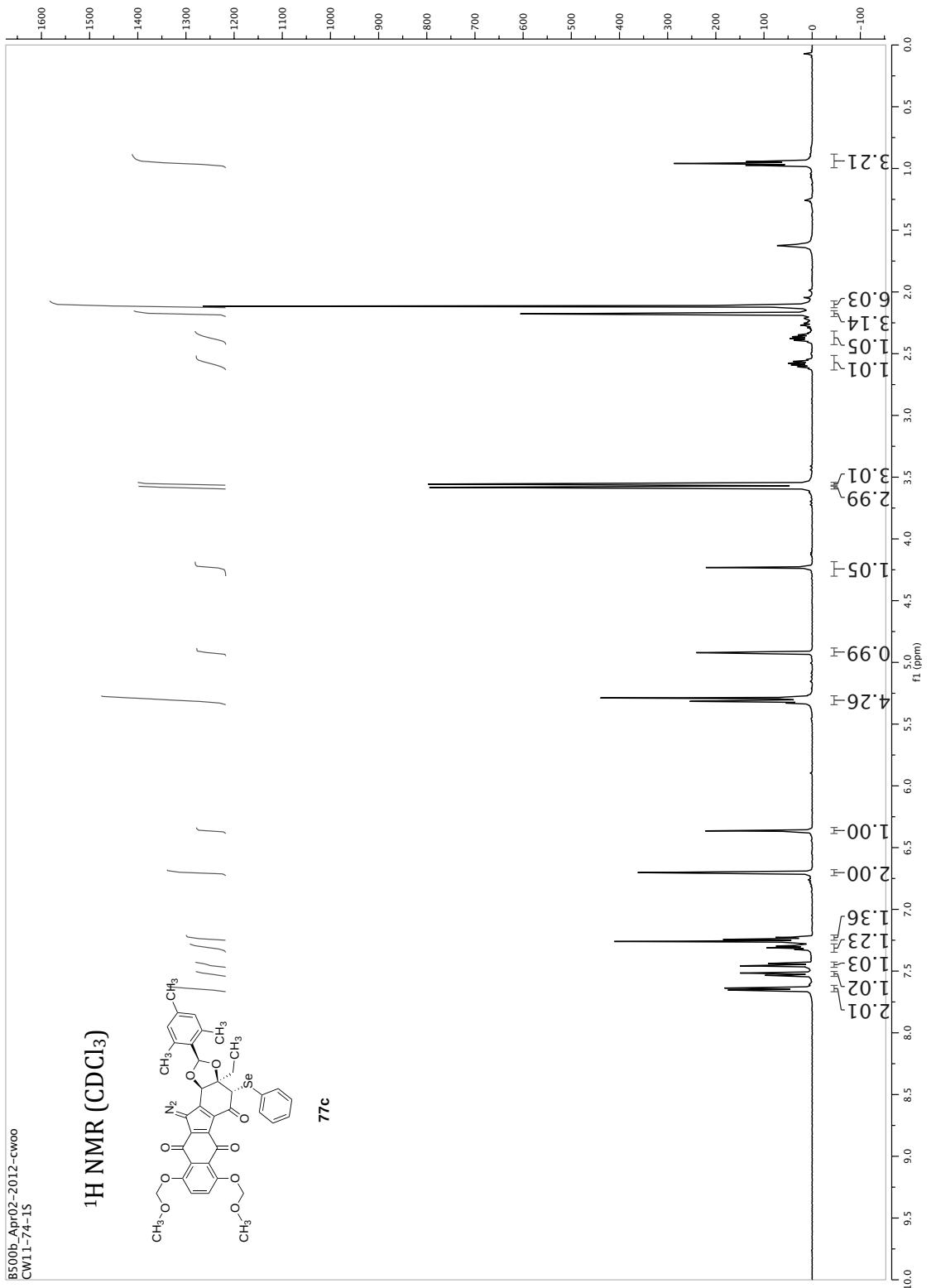

B500b_Dec13-2011-cwoo
CW10-alphafluoro
^{1}H NMR ($CDCl_3$)
77b
MOMO
MOMO
Mes
Et
F
N_2
3.12
2.19
3.14
6.21
3.01
3.14
3.10
2.00
1.17
1.00
2.12
1.07
1.17
f1 (ppm)

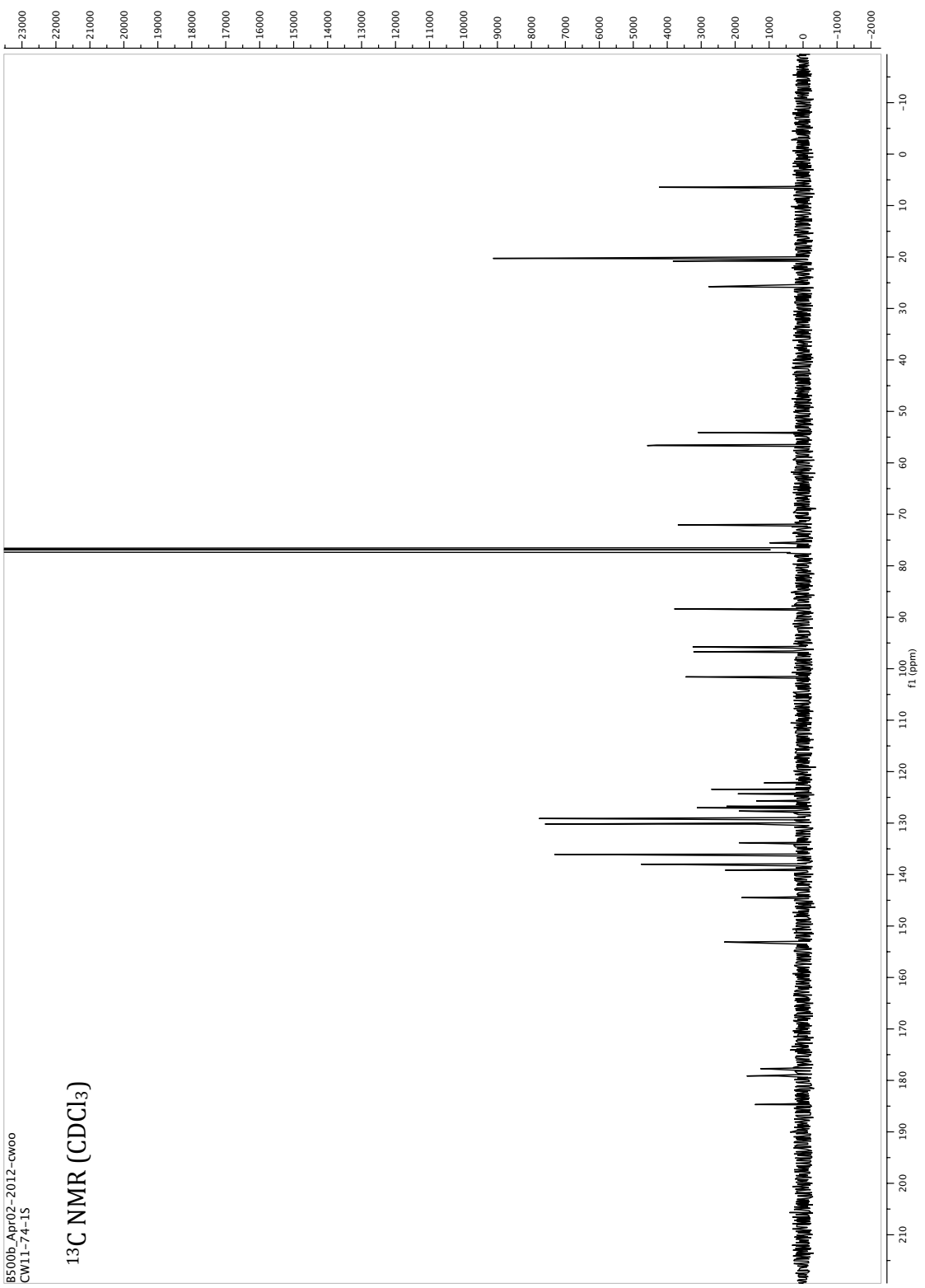

B500b_Dec13-2011-cwoo
CW10-alphafluoro
^{13}C NMR ($CDCl_3$)
f1 (ppm)


B400b_Jun05-2012-cwoo
CW11-192-1S
^{19}F NMR ($CDCl_3$)
f1 (ppm)

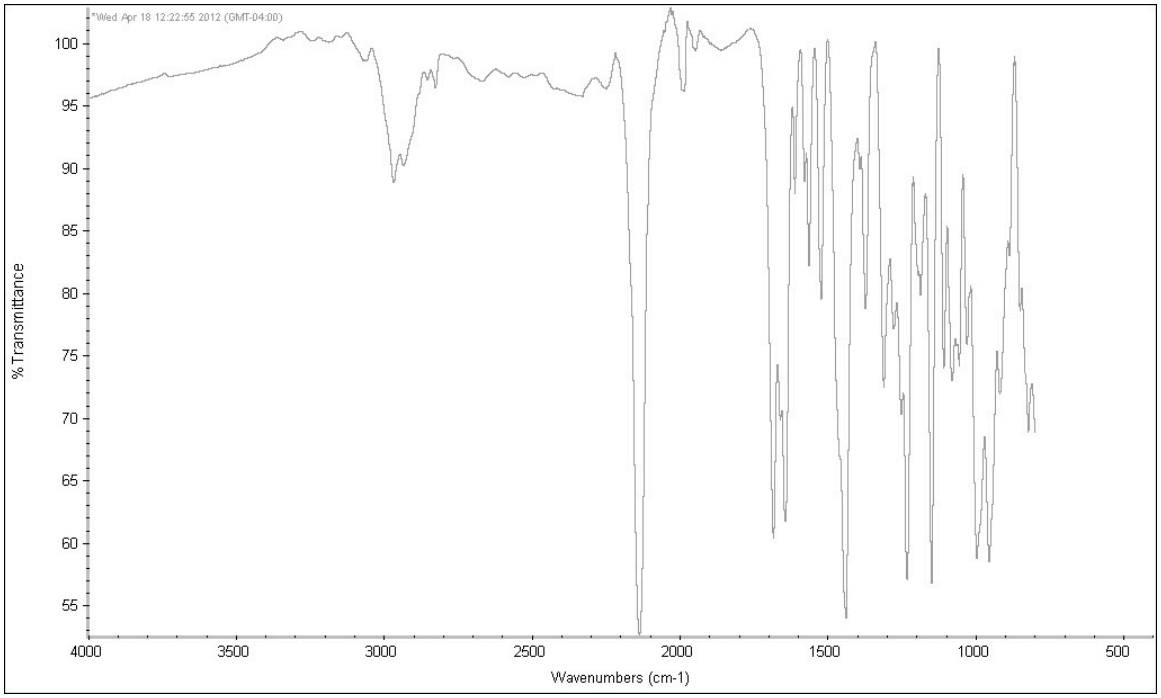
IR

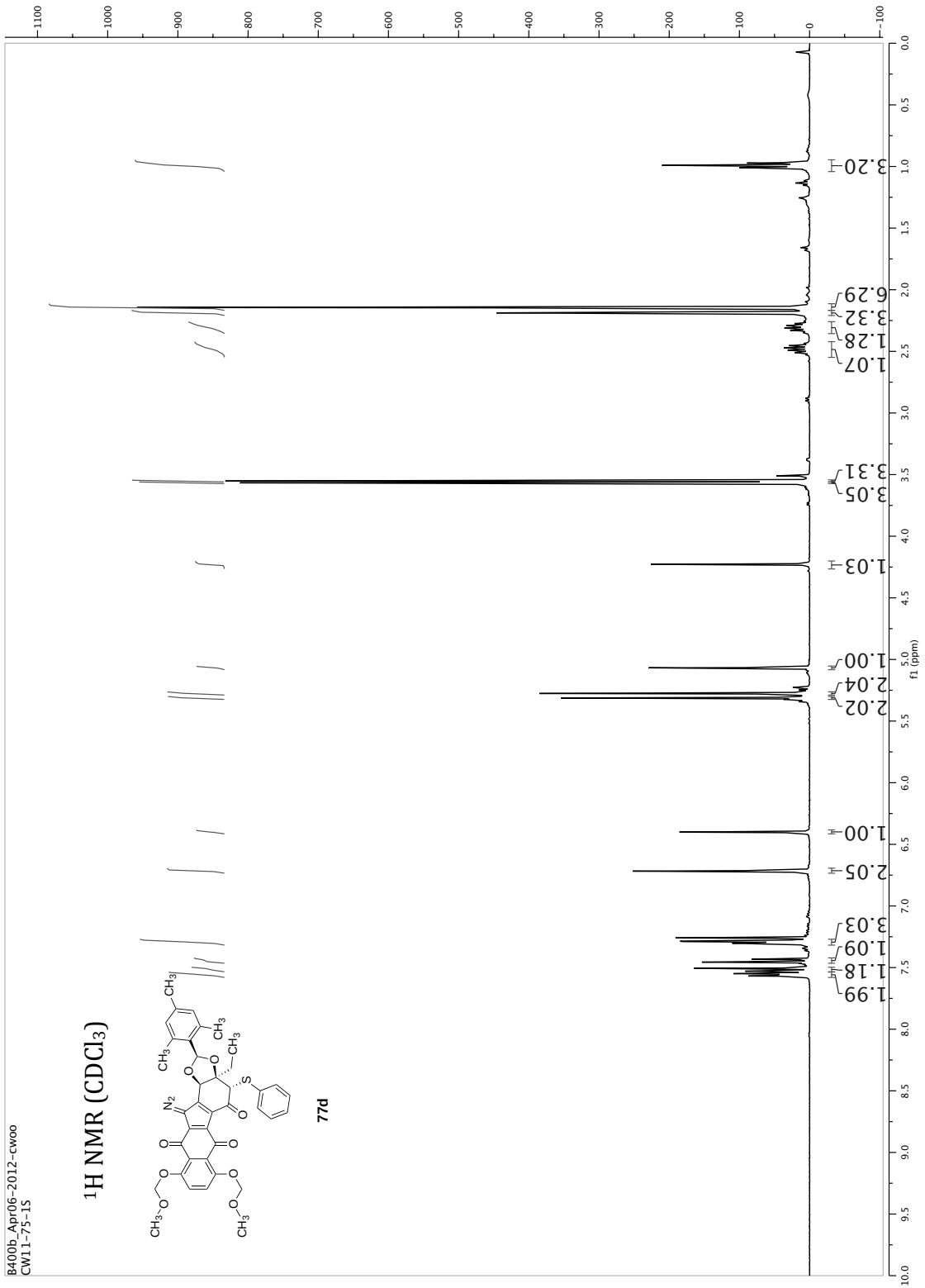

Wed Dec 28 11:26:27 2011 (GMT-05:00)
% Transmittance
102
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

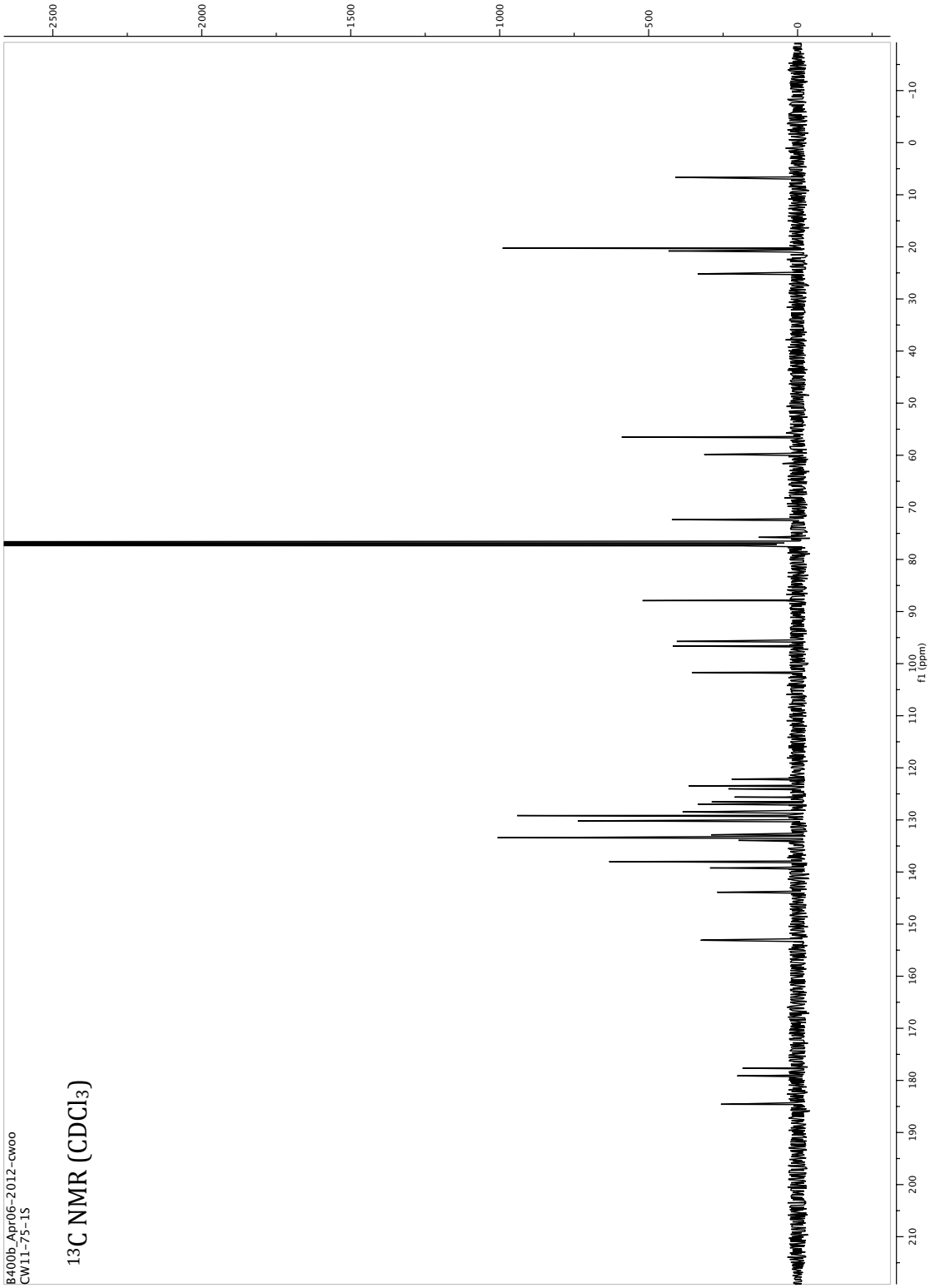

B500b_Apr02-2012-cwoo
CW11-74-1S
^{1}H NMR ($CDCl_3$)
77c
3.21
6.03
3.14
1.05
1.01
3.01
2.99
1.05
0.99
4.26
1.00
2.00
1.36
1.23
1.03
1.02
2.01
f1 (ppm)


B500b_Apr02-2012-cwoo
CW11-74-1S
13C NMR (CDCl3)
f1 (ppm)

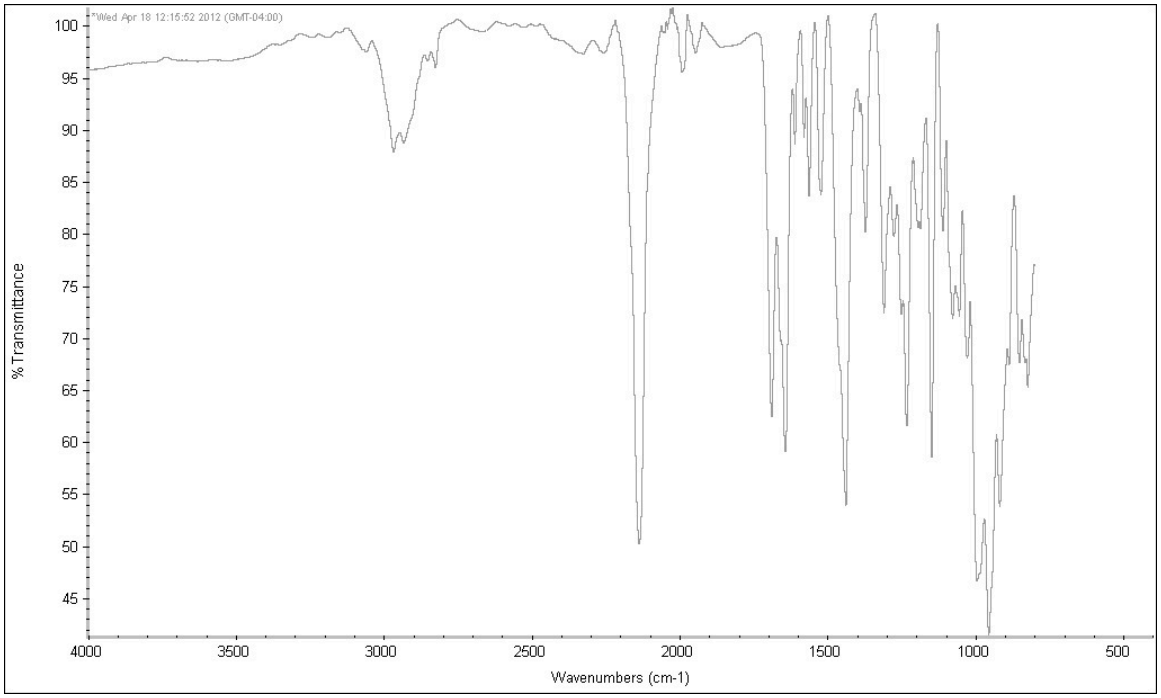
IR

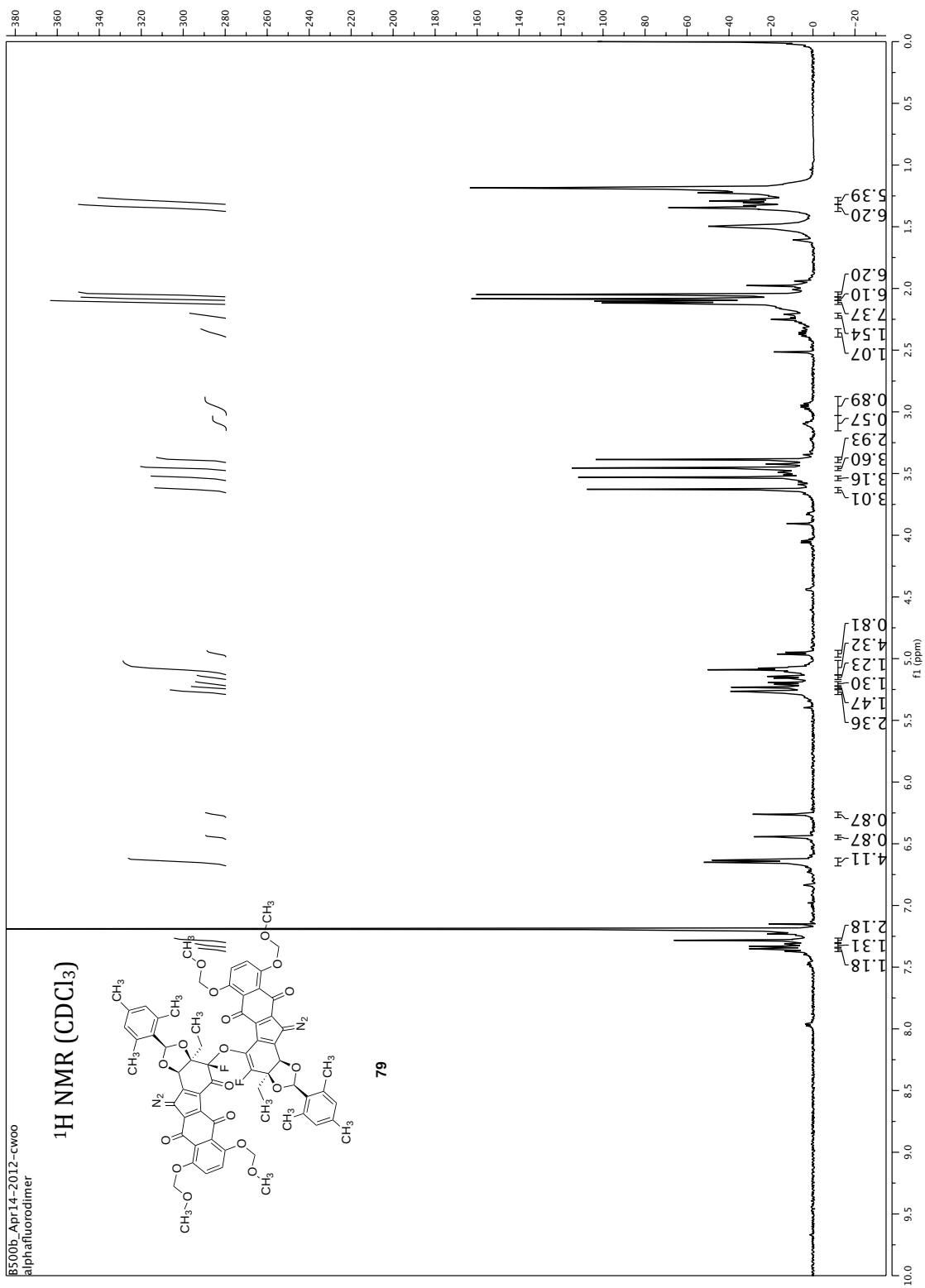

Wed Apr 18 12:22:55 2012 (GMT-04:00)
% Transmittance
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

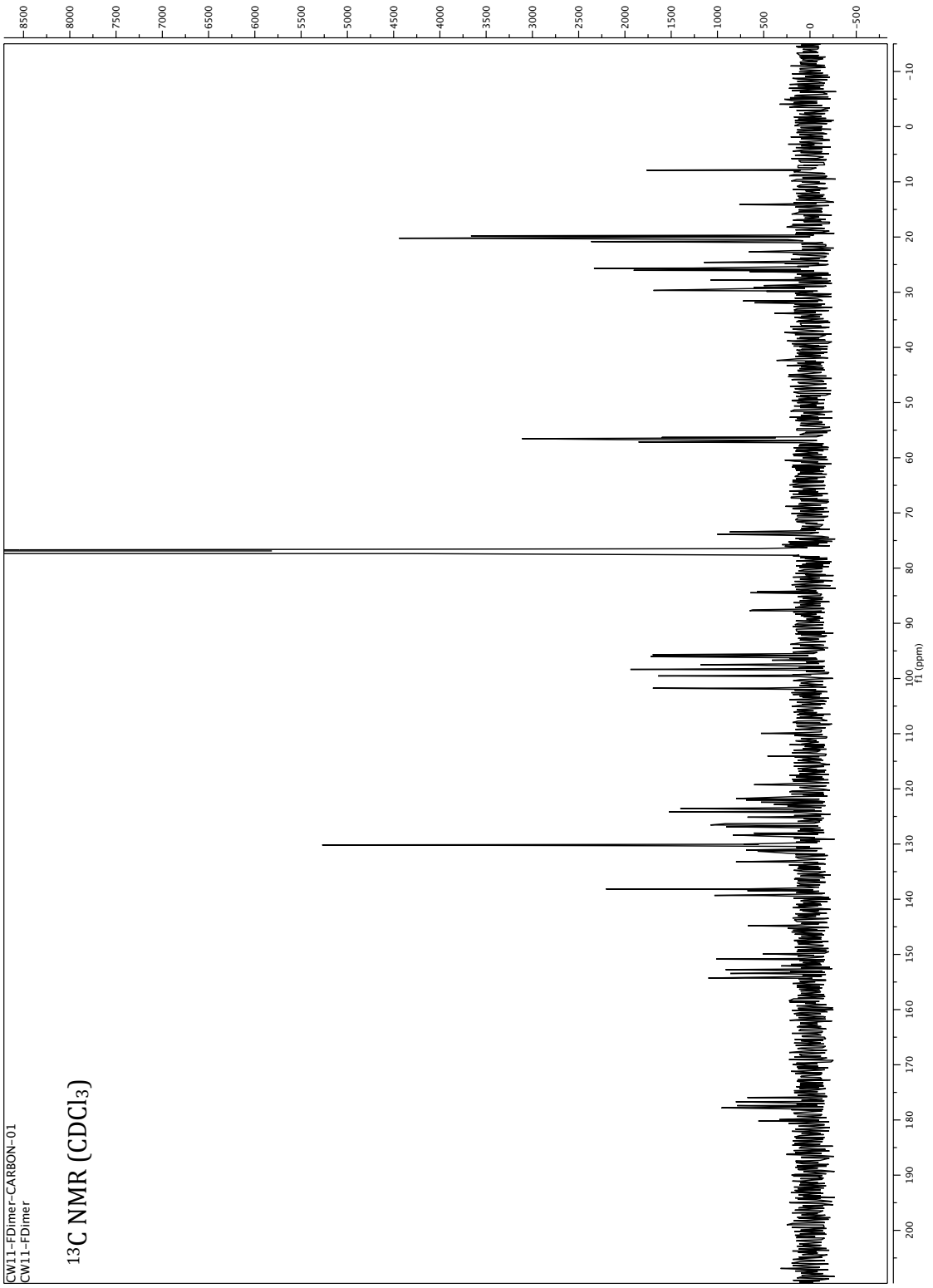

B400b_Apr06-2012-cwoo
CW11-75-1S
^{1}H NMR ($CDCl_3$)
77d
3.20
6.29
3.32
1.28
1.07
3.05
3.31
1.03
1.00
2.04
2.02
1.00
2.05
3.03
1.09
1.18
1.99
f1 (ppm)

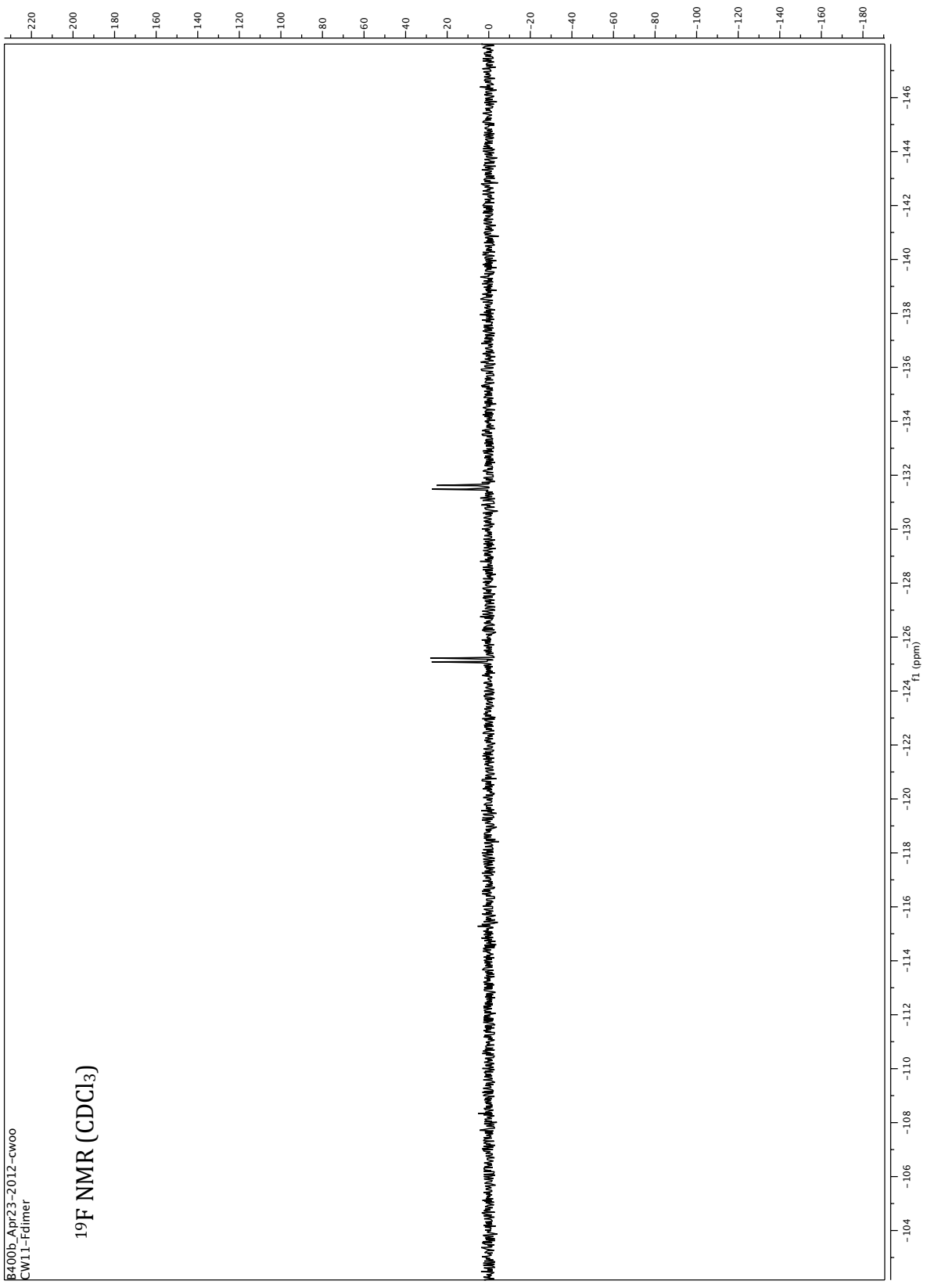

B400b_Apr06-2012-cwoo
CW11-75-1S
13C NMR (CDCl3)
2500
2000
1500
1000
500
0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

IR

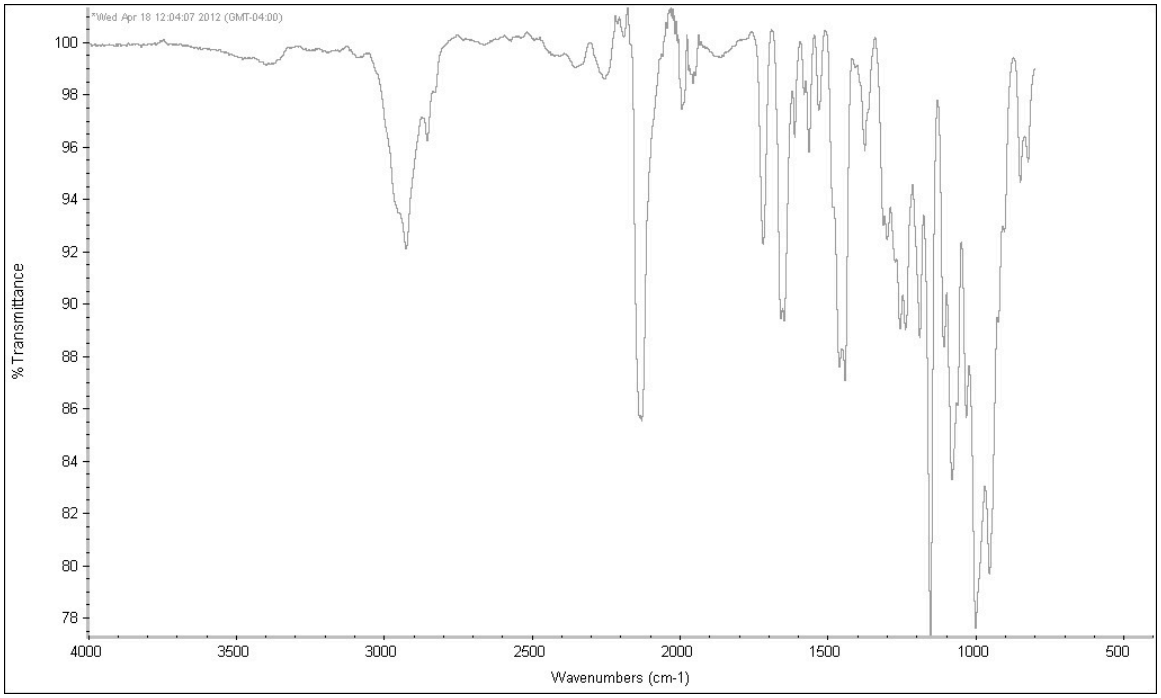

Wed Apr 18 12:15:52 2012 (GMT-04:00)
% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

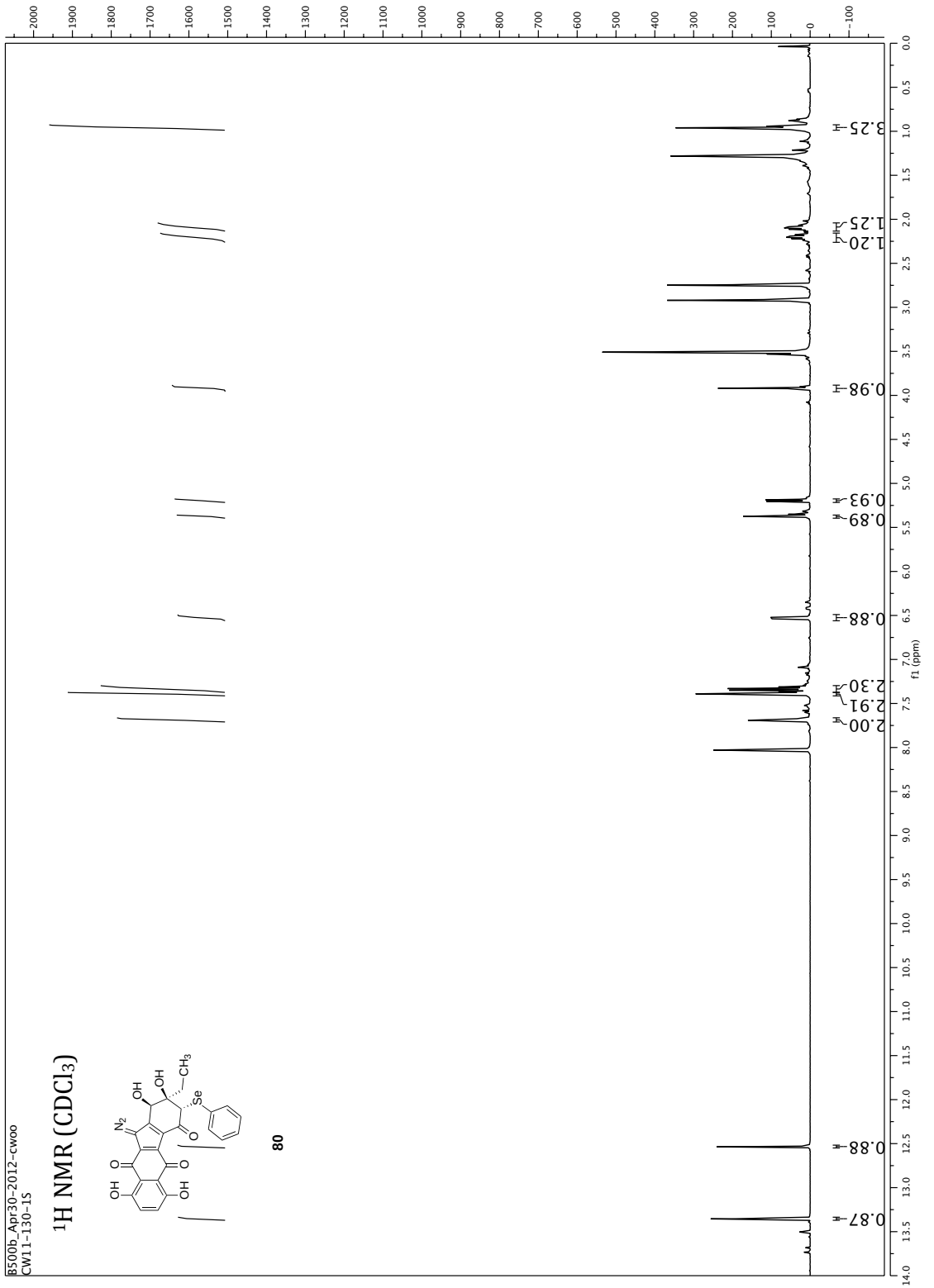

B500b_Apr14-2012-cwoo
alphafluorodimer
^{1}H NMR ($CDCl_3$)
79
1.18
1.31
2.18
4.11
0.87
0.87
2.36
1.47
1.30
1.23
4.32
0.81
3.01
3.16
3.60
2.93
0.57
0.89
1.07
1.54
7.37
6.10
6.20
6.20
5.39
f1 (ppm)

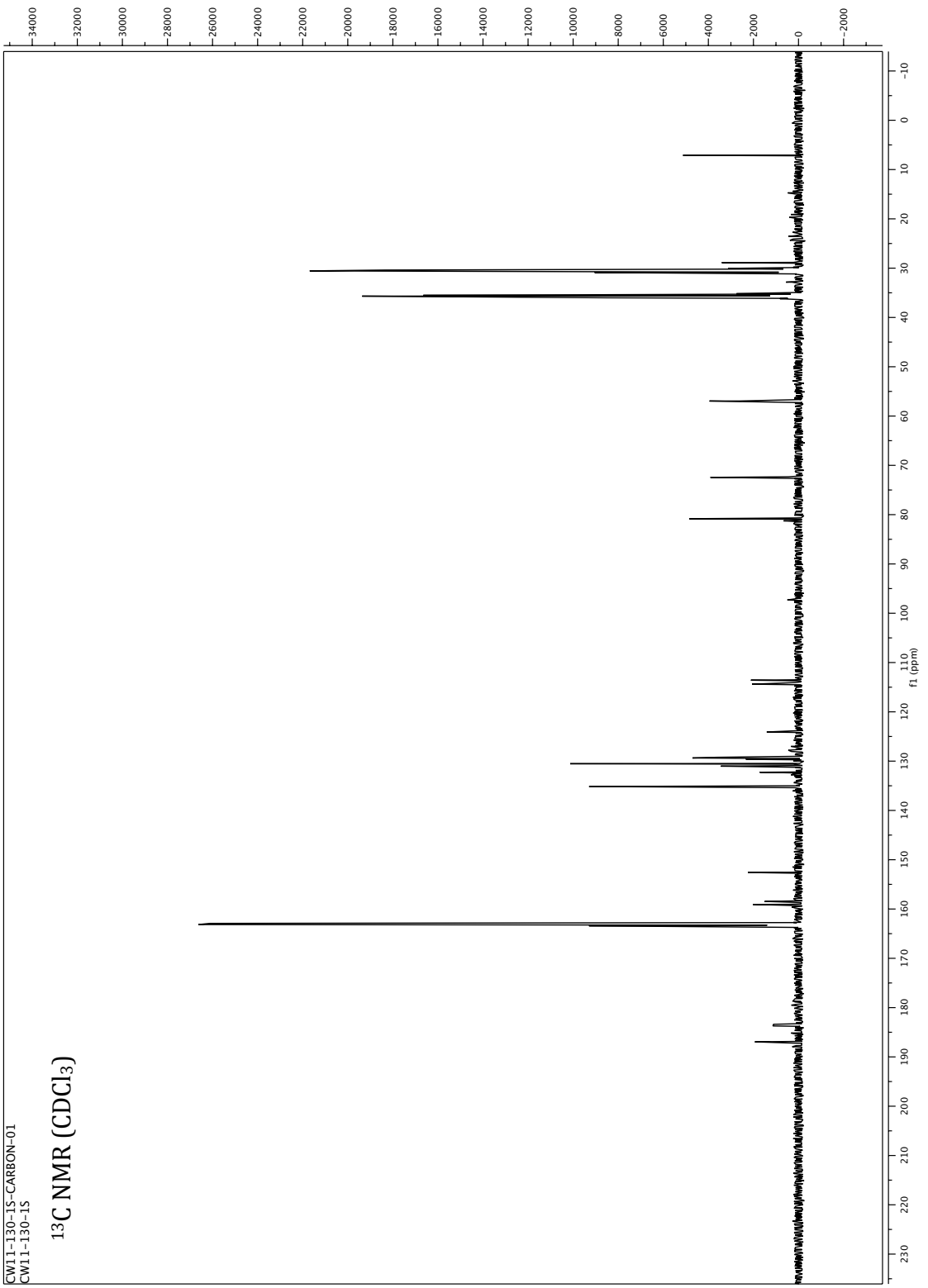

CW11-FDimer-CARBON-01
CW11-FDimer
^{13}C NMR ($CDCl_3$)
f1 (ppm)


B400b_Apr23-2012-cwoo
CW11-Fdimer
^{19}F NMR ($CDCl_3$)
f1 (ppm)

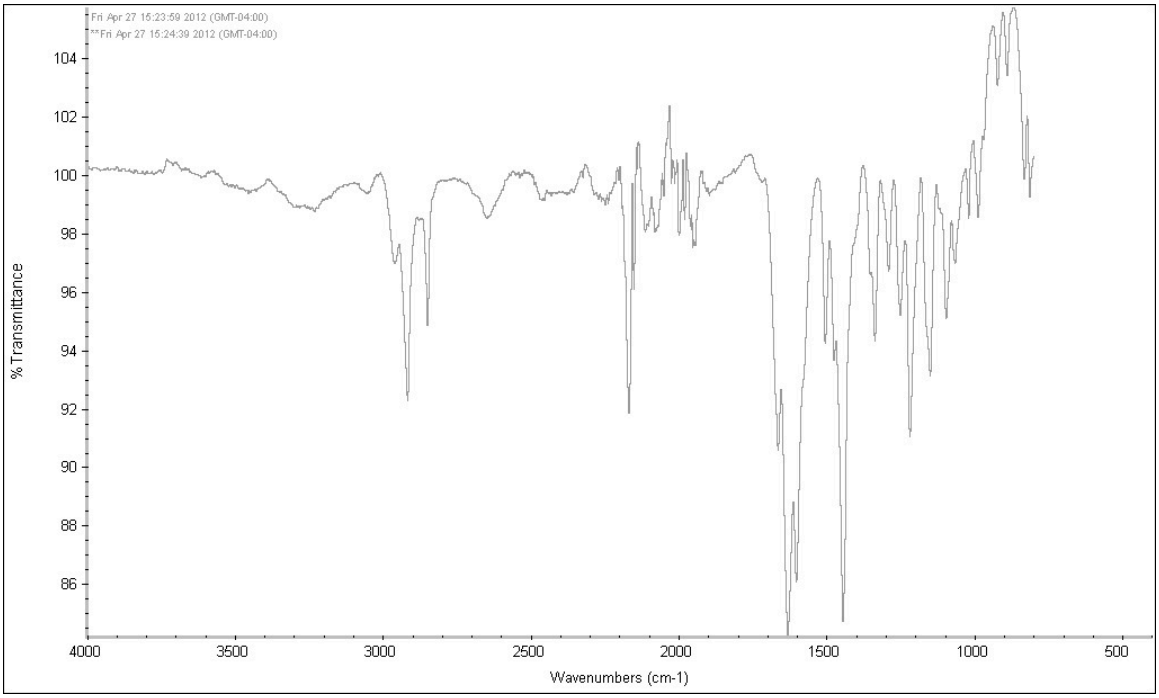
IR


Wed Apr 18 12:04:07 2012 (GMT-04:00)
% Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

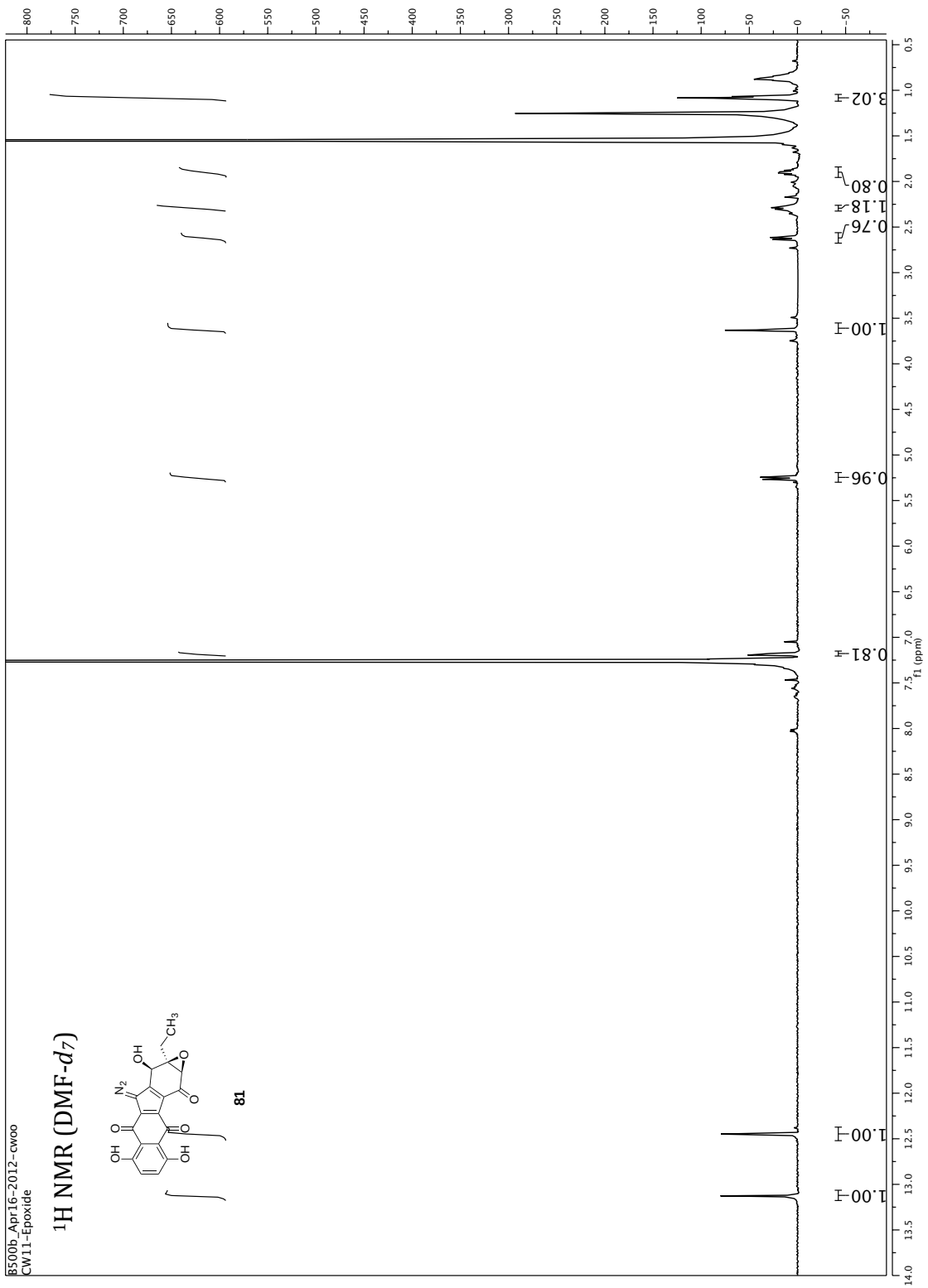

B500b_Apr30-2012-cwoo
CW11-130-1S
^{1}H NMR ($CDCl_3$)
80
3.25
1.20
1.25
0.98
0.89
0.93
0.88
2.30
2.91
2.00
0.88
0.87
f1 (ppm)

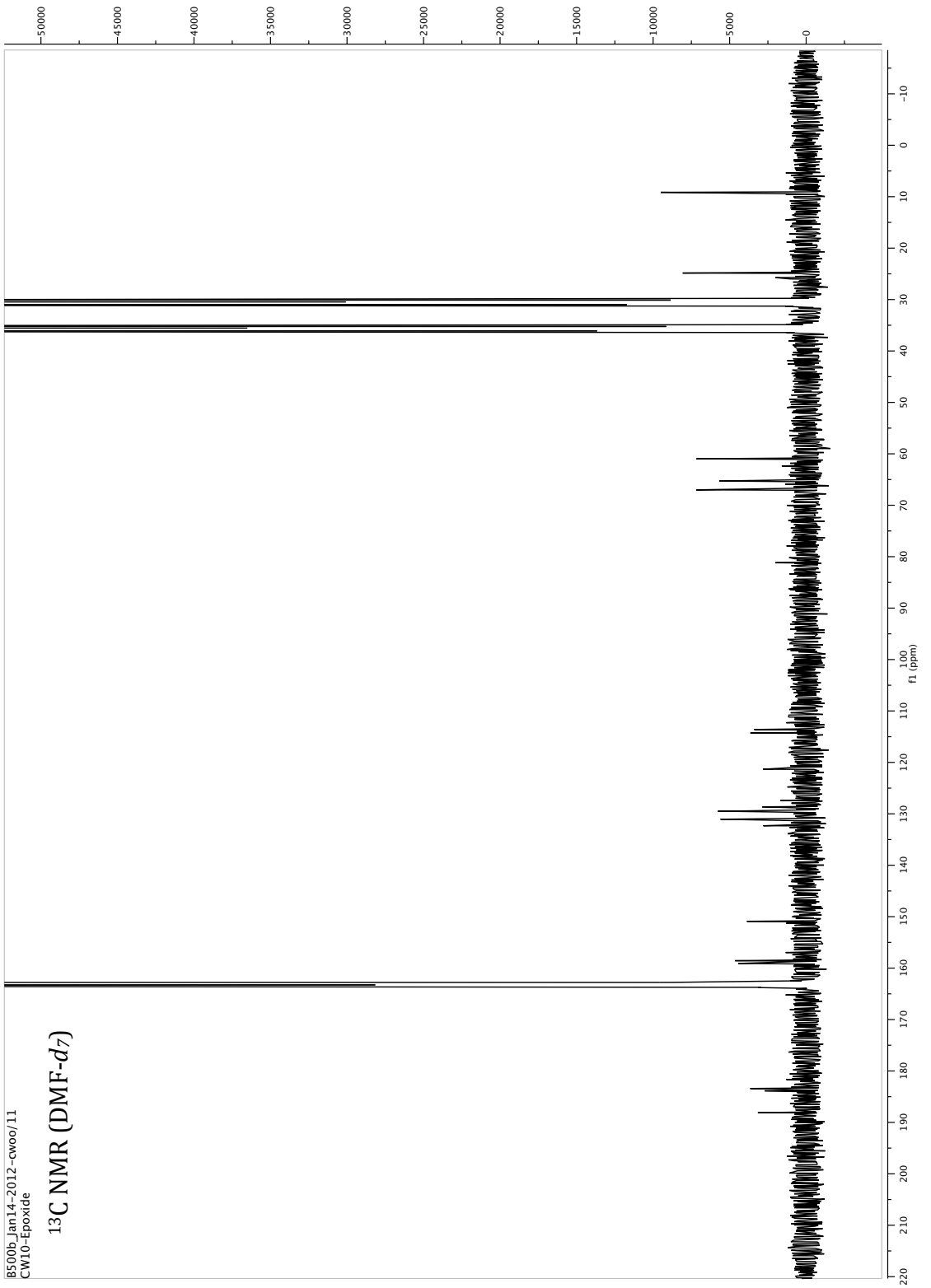

CW11-130-1S-CARBON-01
CW11-130-1S
^{13}C NMR ($CDCl_3$)
f1 (ppm)

IR

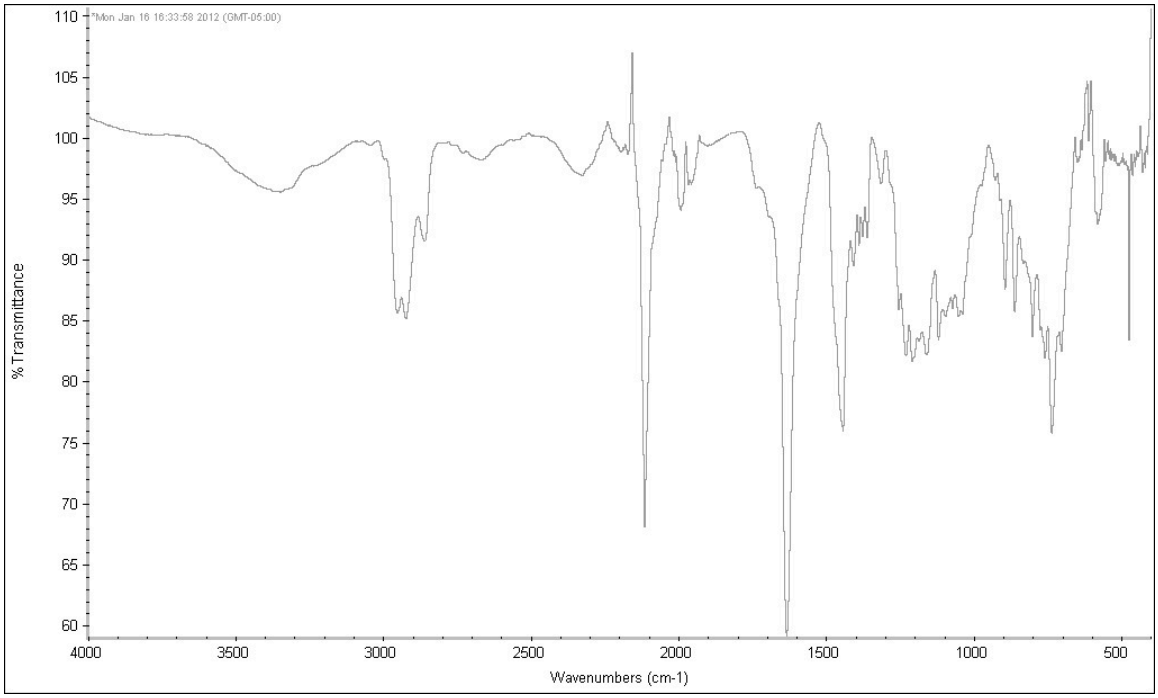

Fri Apr 27 15:23:59 2012 (GMT-04:00)
** Fri Apr 27 15:24:39 2012 (GMT-04:00)
% Transmittance
104
102
100
98
96
94
92
90
88
86
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

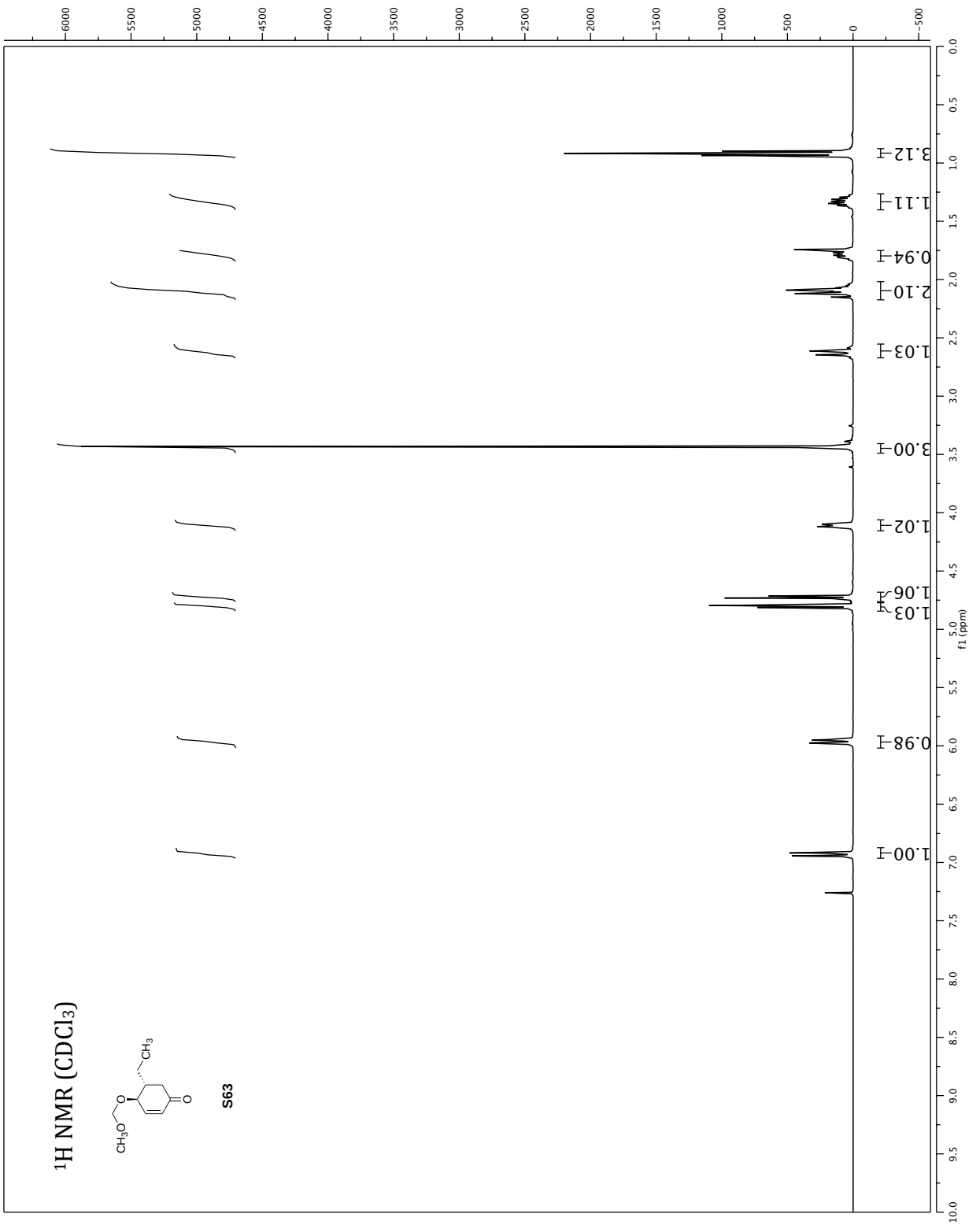
1


^{1}H NMR (DMF-d_7)
B500b_Apr16-2012-cwoo
CW11-Epoxide
81
3.02
0.80
1.18
0.76
1.00
0.96
0.81
1.00
1.00
f1 (ppm)

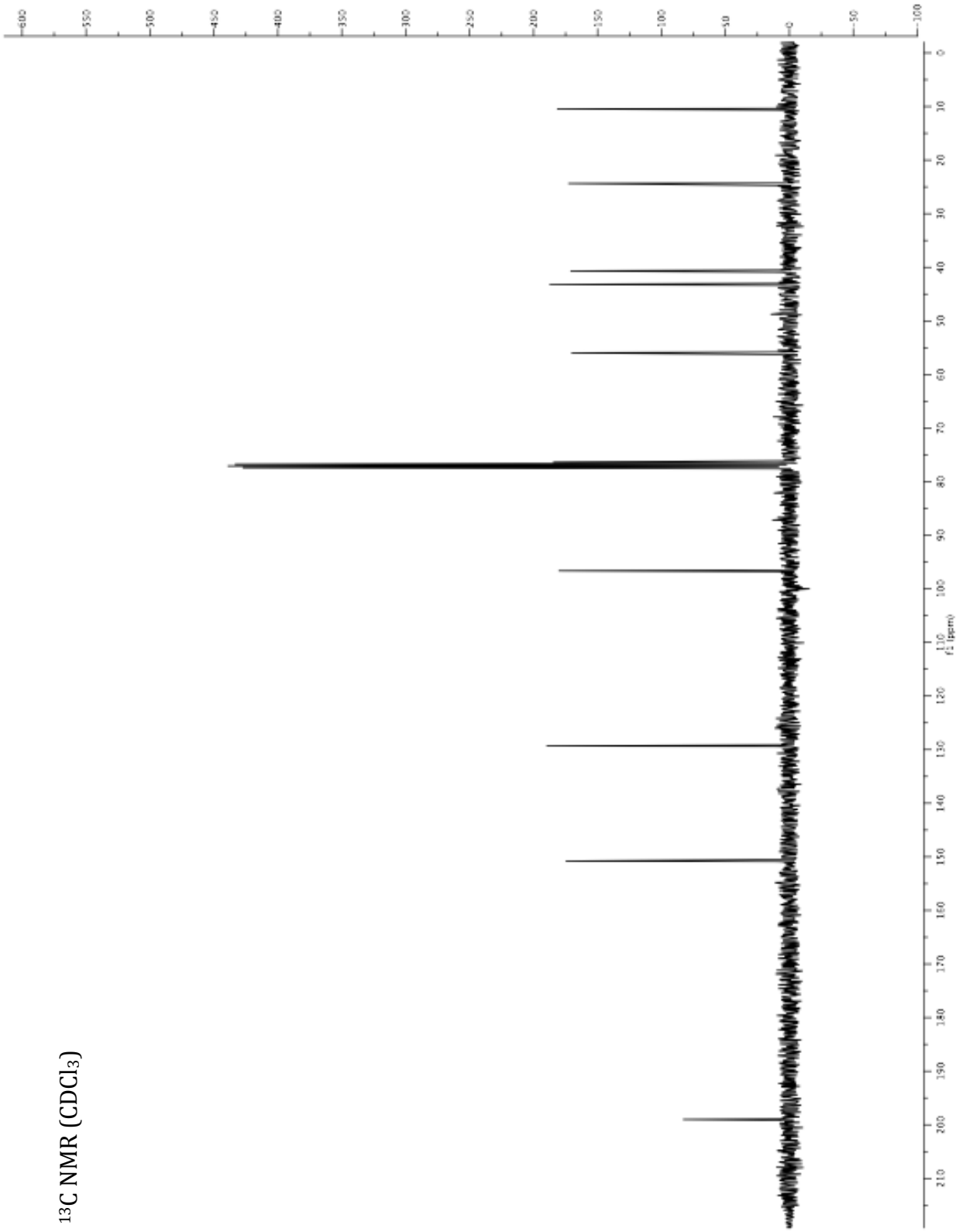

B500b_Jan14-2012-cwoo/11
CW10-Epoxide
13C NMR (DMF-d7)
f1 (ppm)

IR

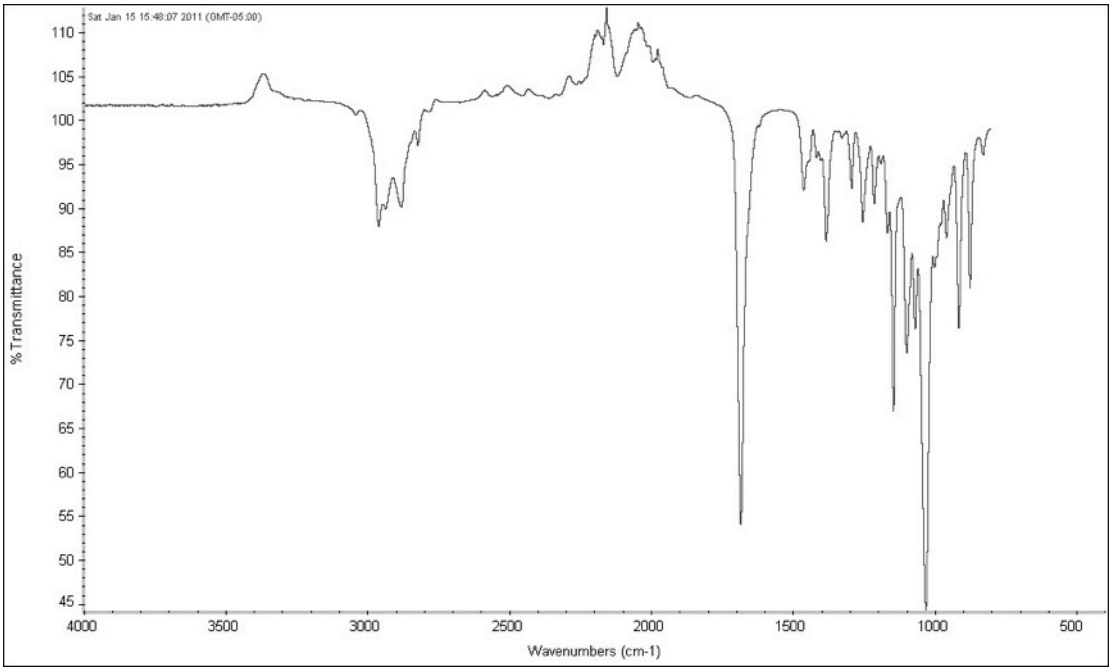

"Mon Jan 16 16:33:58 2012 (GMT-05:00)
% Transmittance
110
105
100
95
90
85
80
75
70
65
60
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

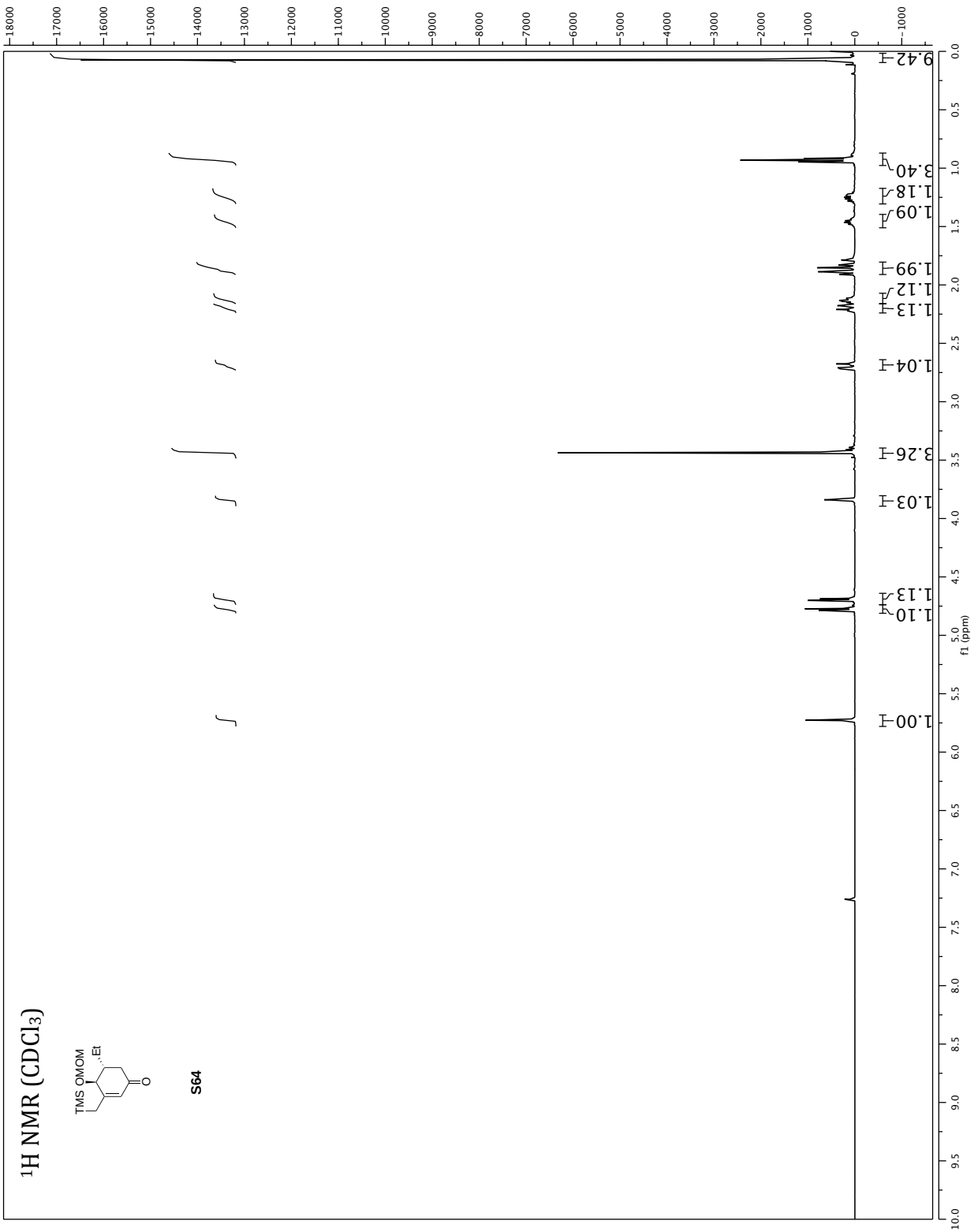

^{1}H NMR ($CDCl_3$)
S63
3.12
1.11
0.94
2.10
1.03
3.00
1.02
1.06
1.03
0.98
1.00
f1 (ppm)

^{13}C NMR ($CDCl_3$)

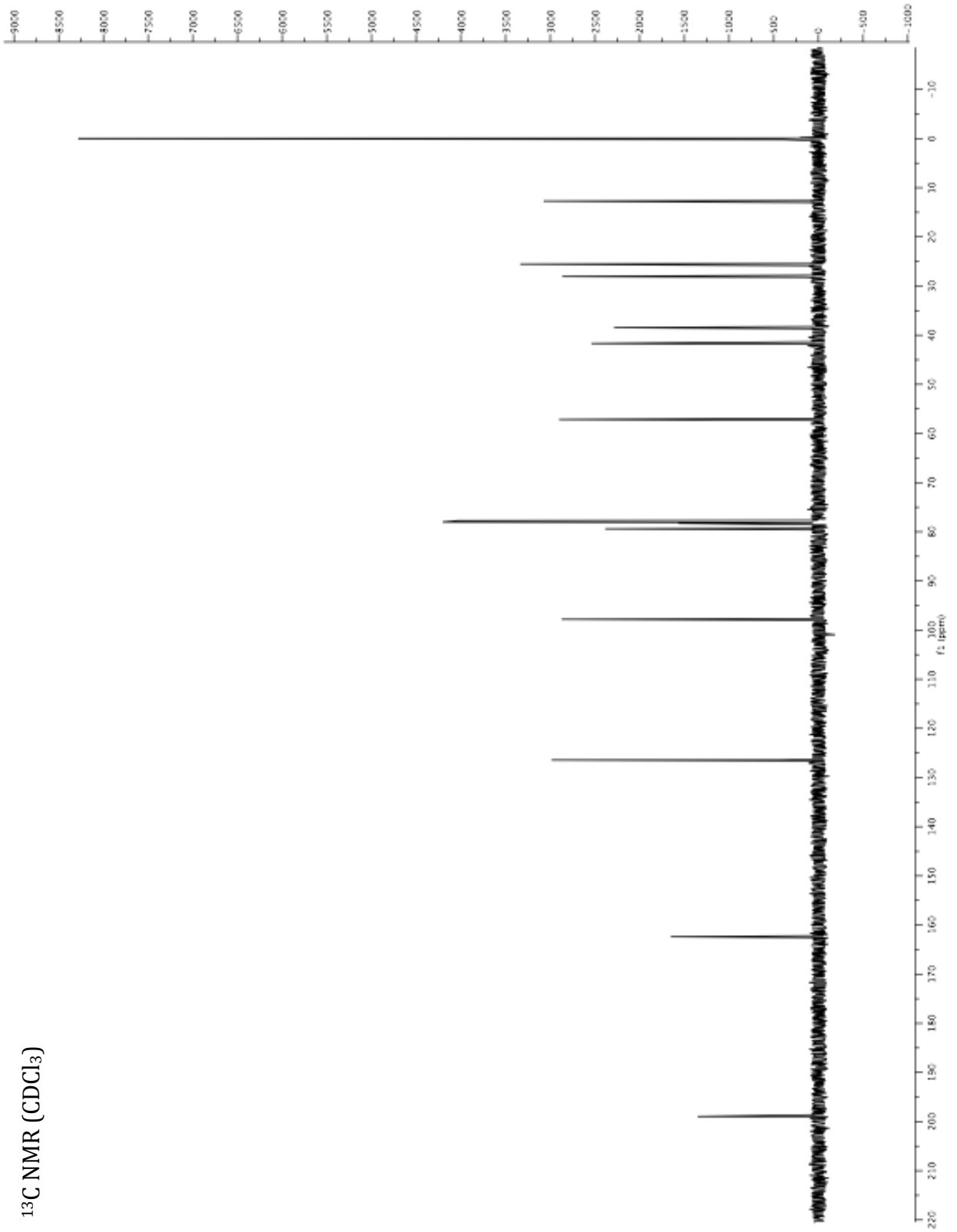


IR

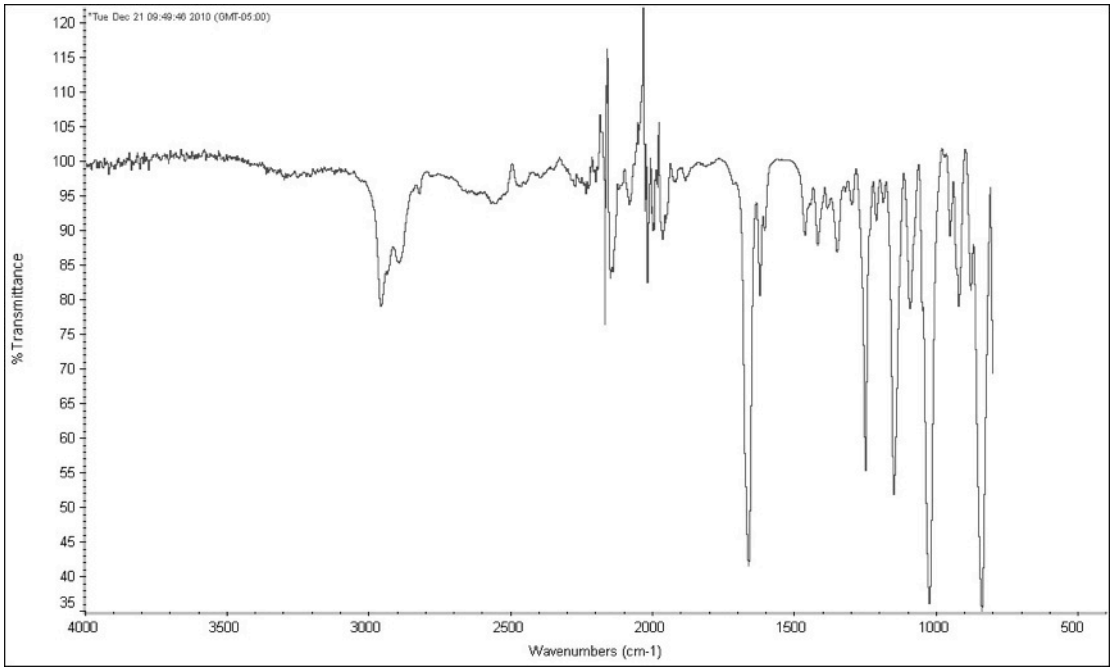

Sat Jan 15 15:48:07 2011 (GMT-05:00)
% Transmittance
110
105
100
95
90
85
80
75
70
65
60
55
50
45
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

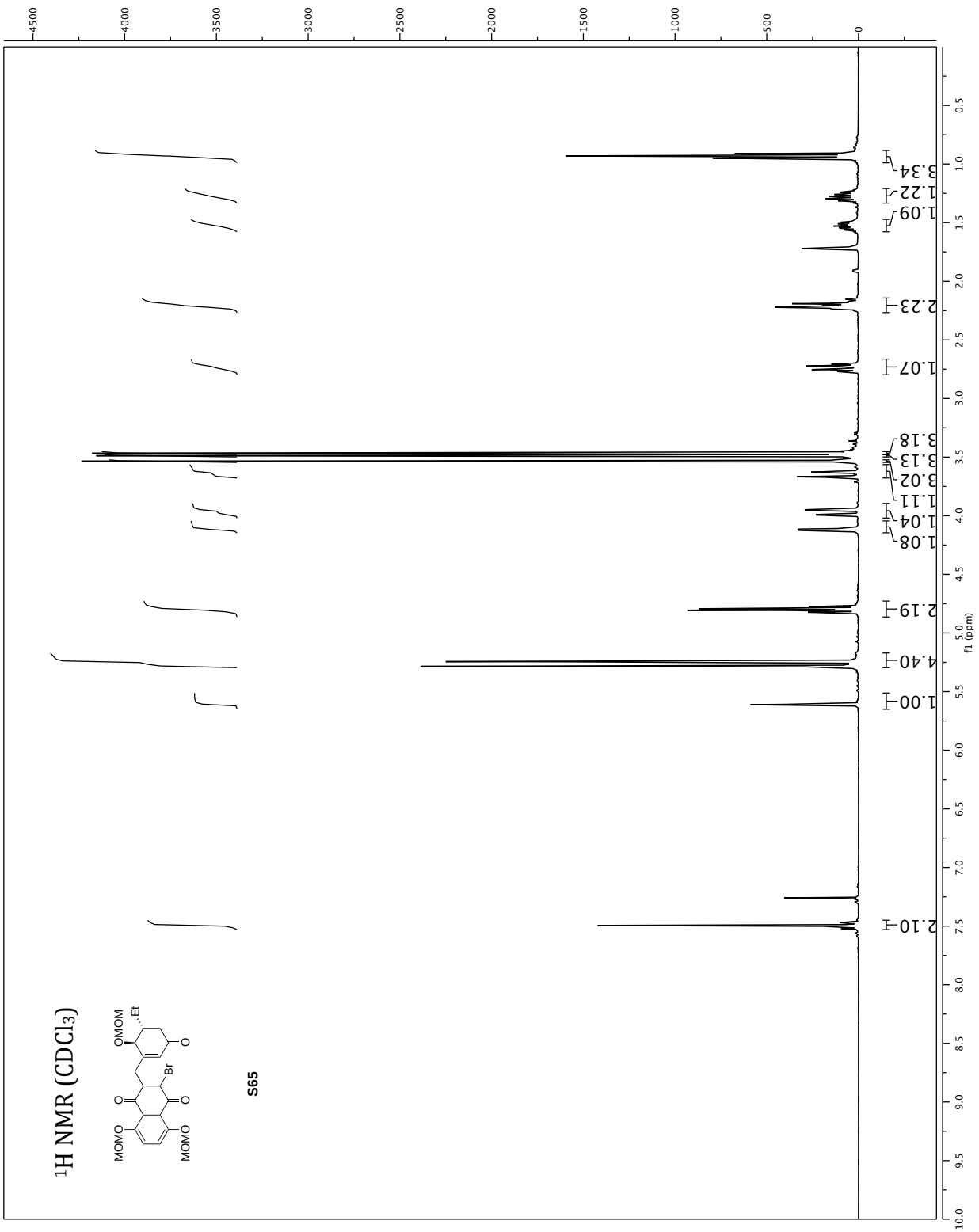

^{1}H NMR ($CDCl_3$)
TMS OMOM
Et
O
S64
9.42
3.40
1.18
1.09
1.99
1.12
1.13
1.04
3.26
1.03
1.10
1.13
1.00
f1 (ppm)

^{13}C NMR ($CDCl_3$)

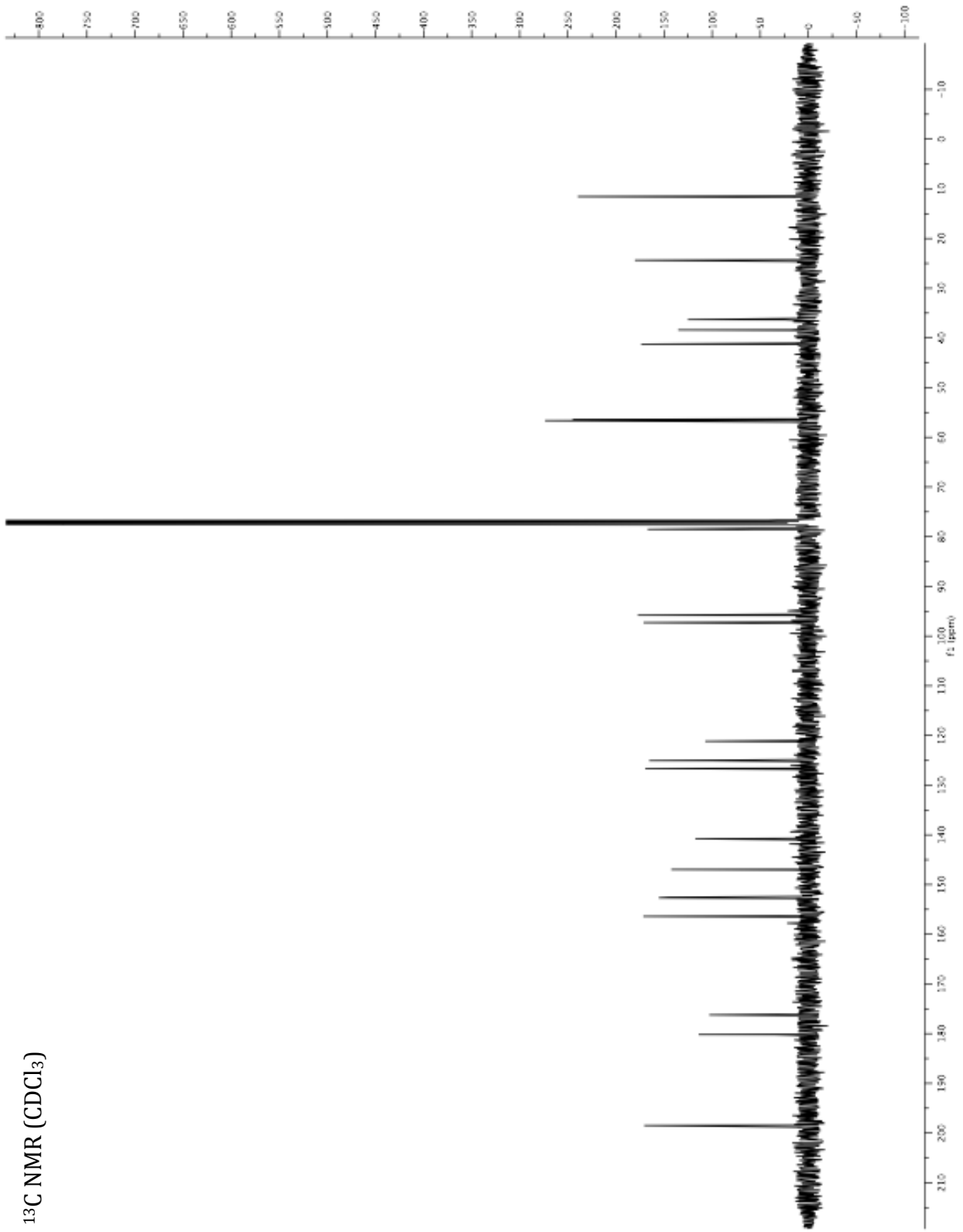


IR

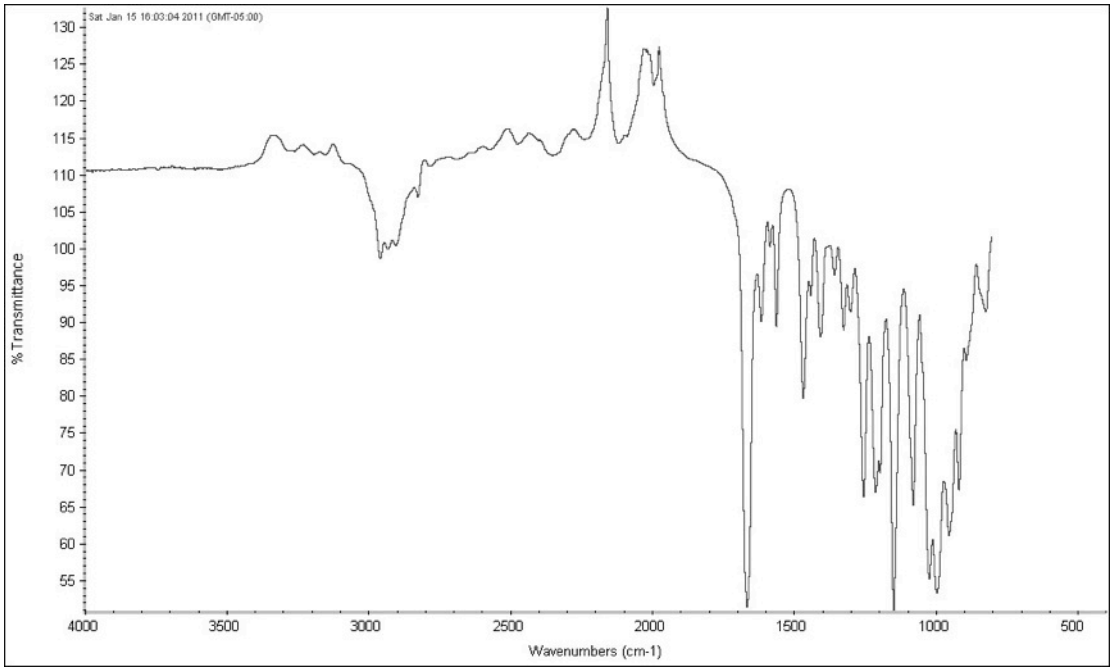

Tue Dec 21 09:49:46 2010 (GMT-05:00)
% Transmittance
Wavenumbers (cm-1)
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
500

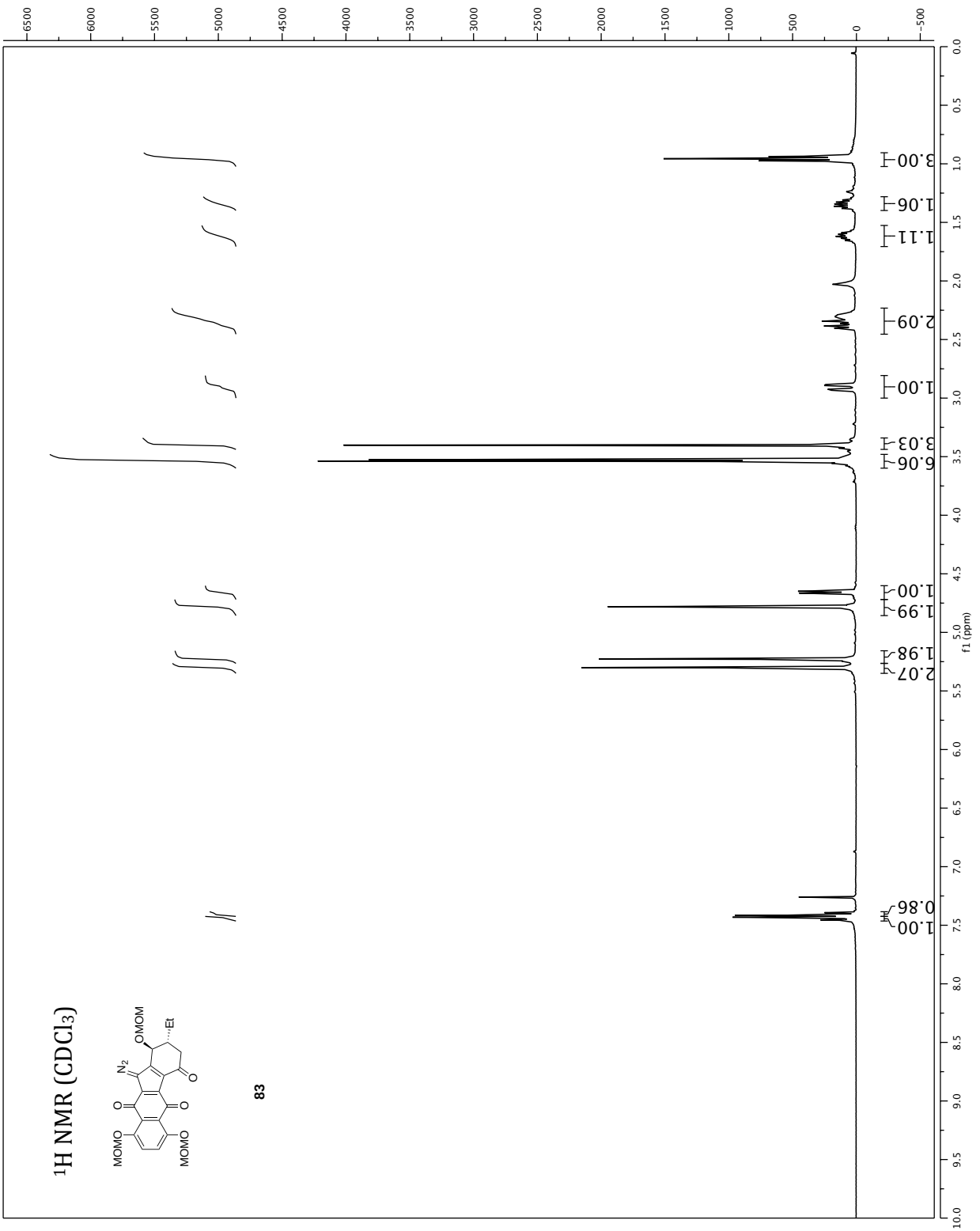

^{1}H NMR ($CDCl_3$)
S65
MOMO
MOMO
OMOM
Et
Br
O
O
O
O
2.10
1.00
4.40
2.19
1.08
1.04
1.11
3.02
3.13
3.18
1.07
2.23
1.09
1.22
3.34
f1 (ppm)

^{13}C NMR ($CDCl_3$)

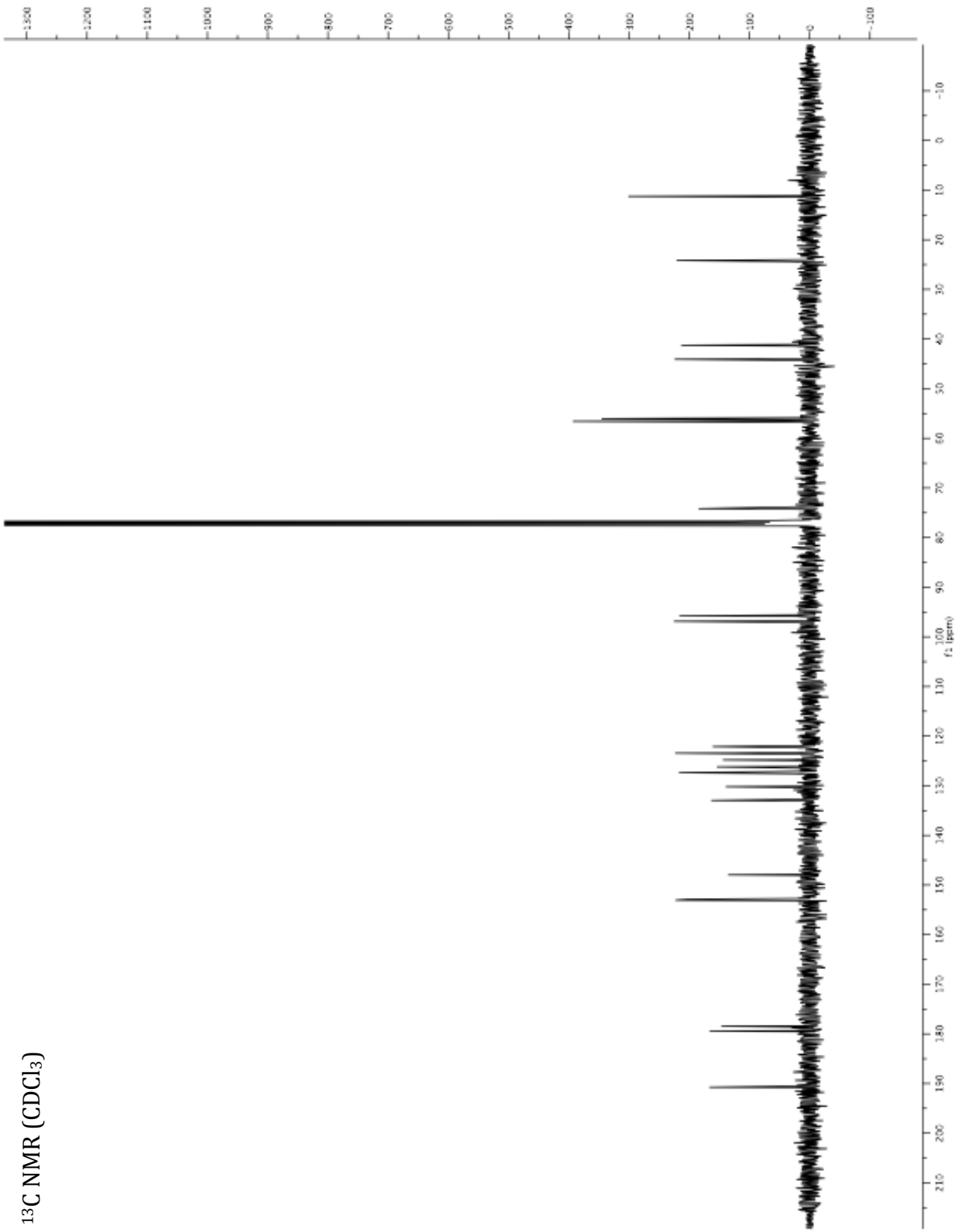


IR

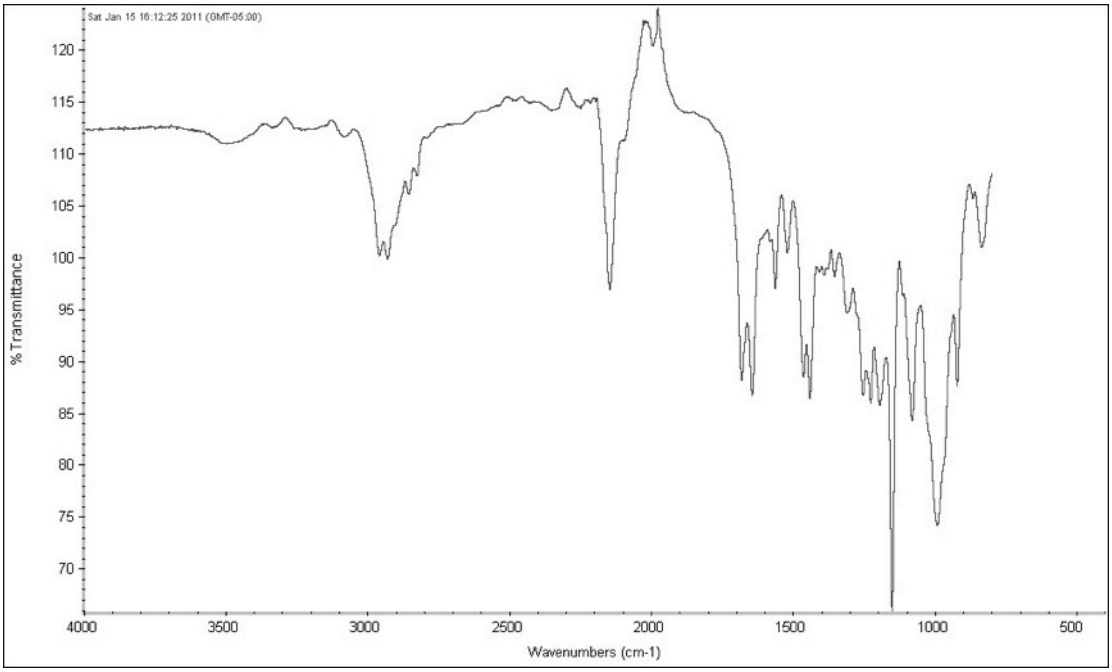

Sat Jan 15 16:03:04 2011 (GMT-05:00)
% Transmittance
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

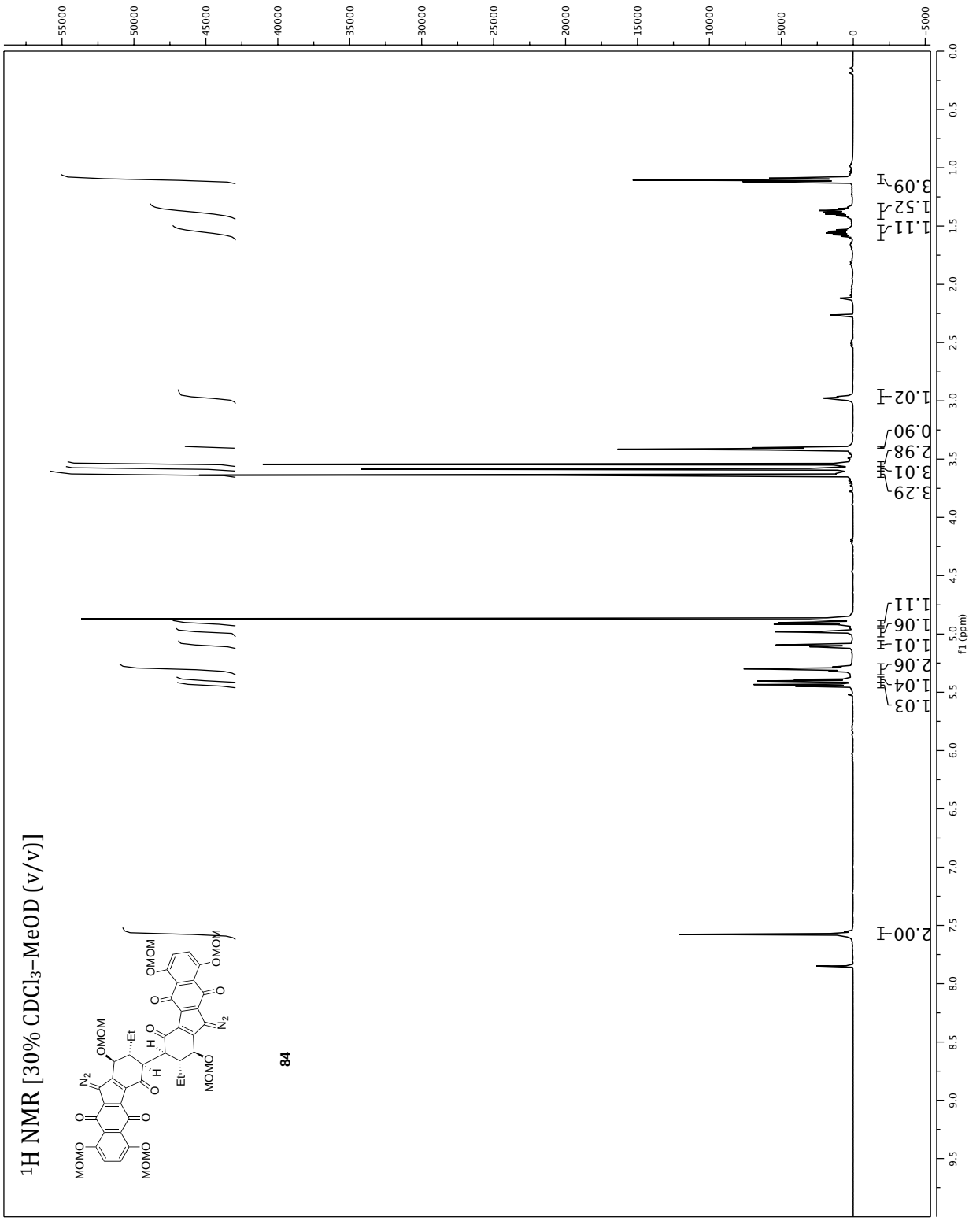

^{1}H NMR ($CDCl_3$)
83
MOMO
MOMO
OMOM
Et
N_2
O
O
O
3.00
1.06
1.11
2.09
1.00
3.03
6.06
1.00
1.99
1.98
2.07
0.86
1.00
f1 (ppm)

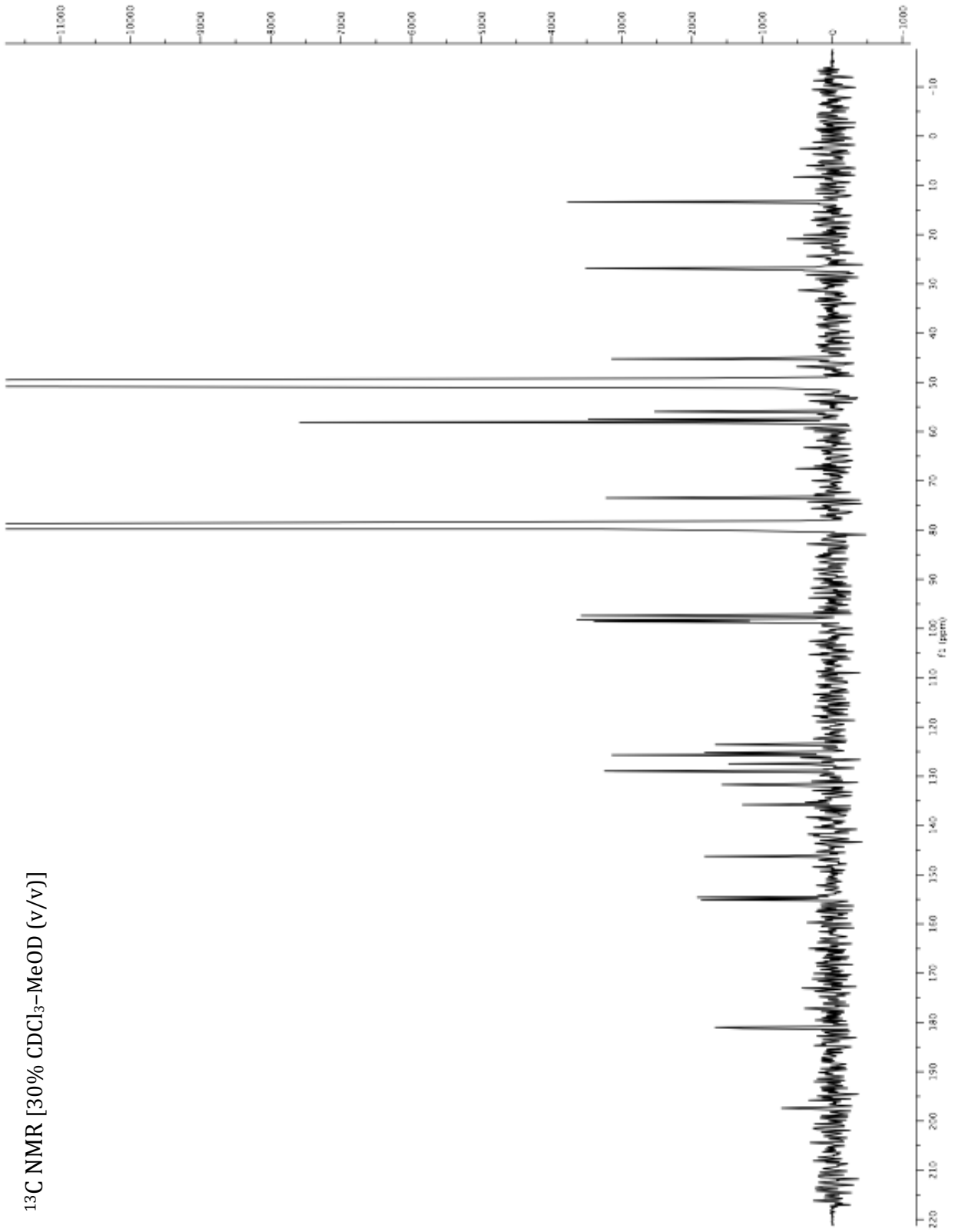
^{13}C NMR ($CDCl_3$)



IR

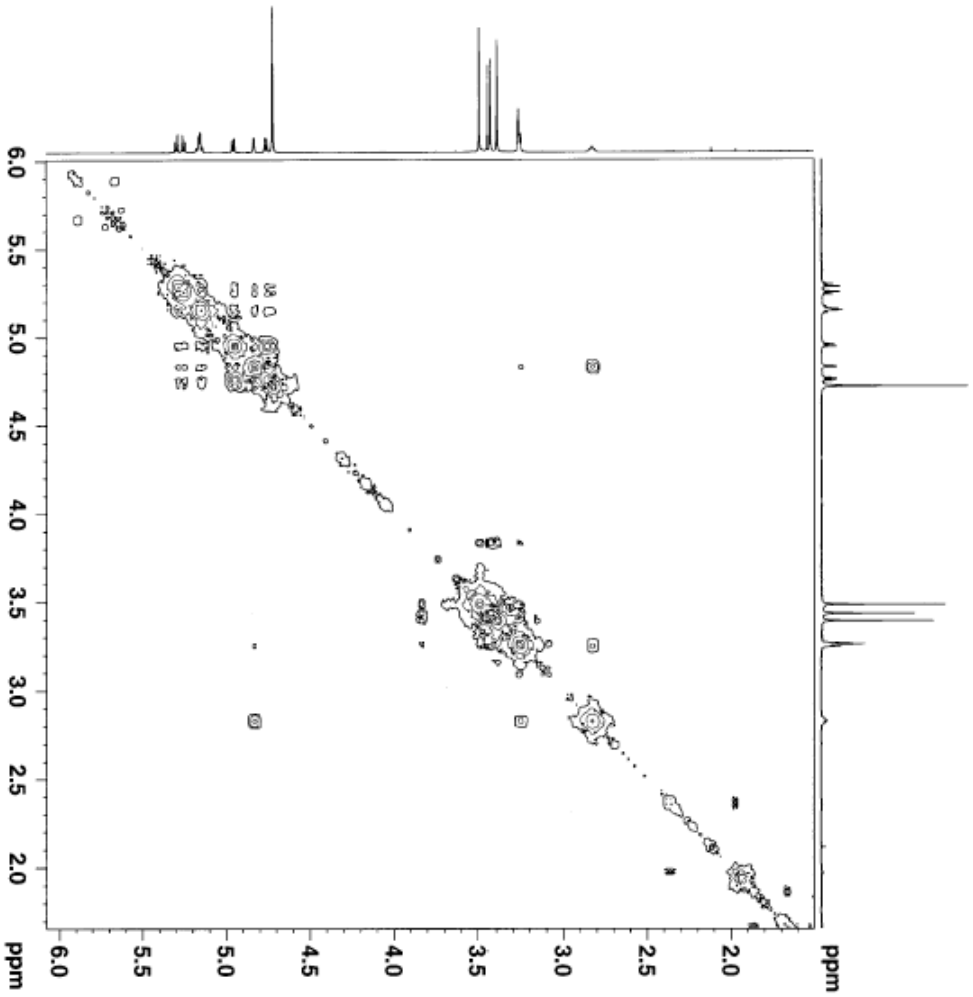

Sat Jan 15 16:12:25 2011 (GMT-05:00)
% Transmittance
120
115
110
105
100
95
90
85
80
75
70
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


^{1}H NMR [30% $CDCl_3$–MeOD (v/v)]
84
MOMO
MOMO
OMOM
Et
H
O
N_2
O
O
H
Et
MOMO
OMOM
OMOM
O
O
N_2
2.00
1.03
1.04
2.06
1.01
1.06
1.11
3.29
3.01
2.98
0.90
1.02
1.11
1.52
3.09
f1 (ppm)

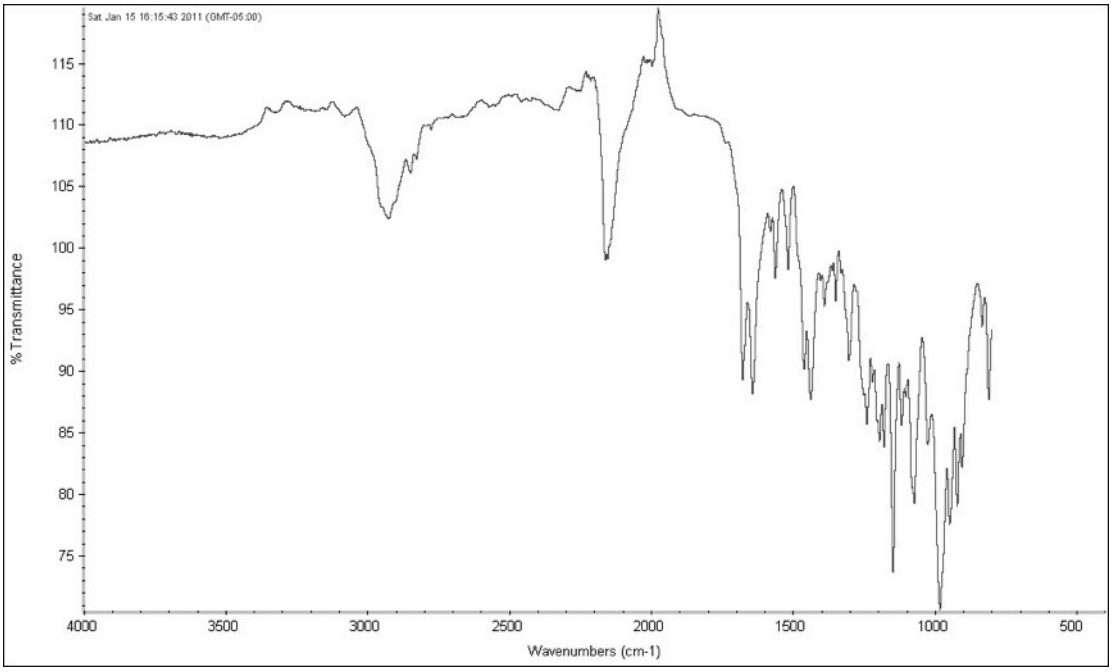


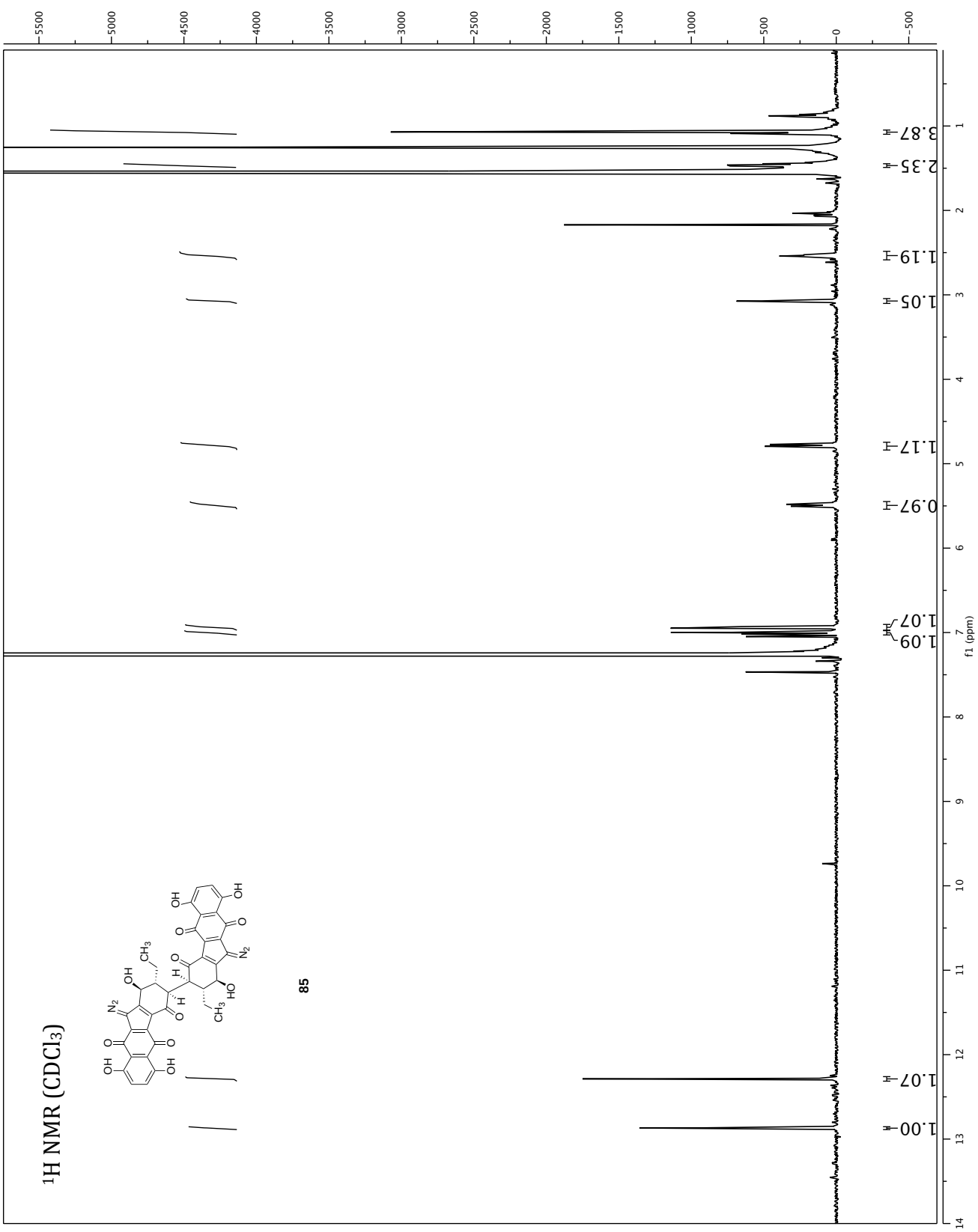
^{13}C NMR [30% $CDCl_3$–MeOD (v/v)]

COSY [30% $CDCl_3$–MeOD (v/v)]

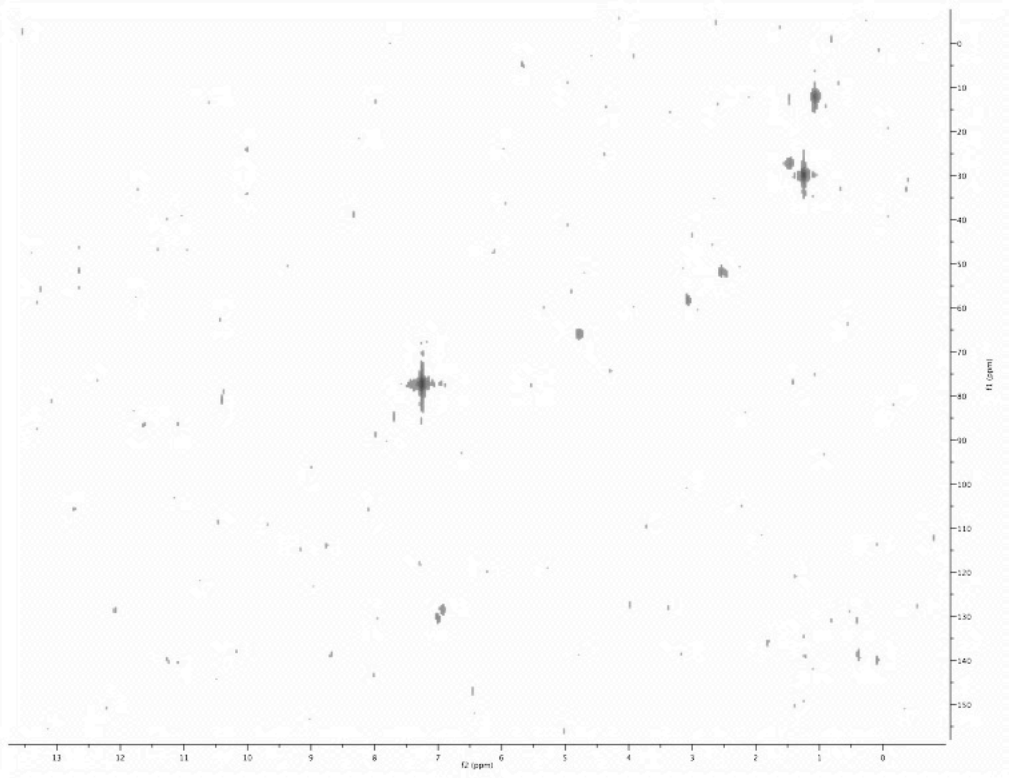


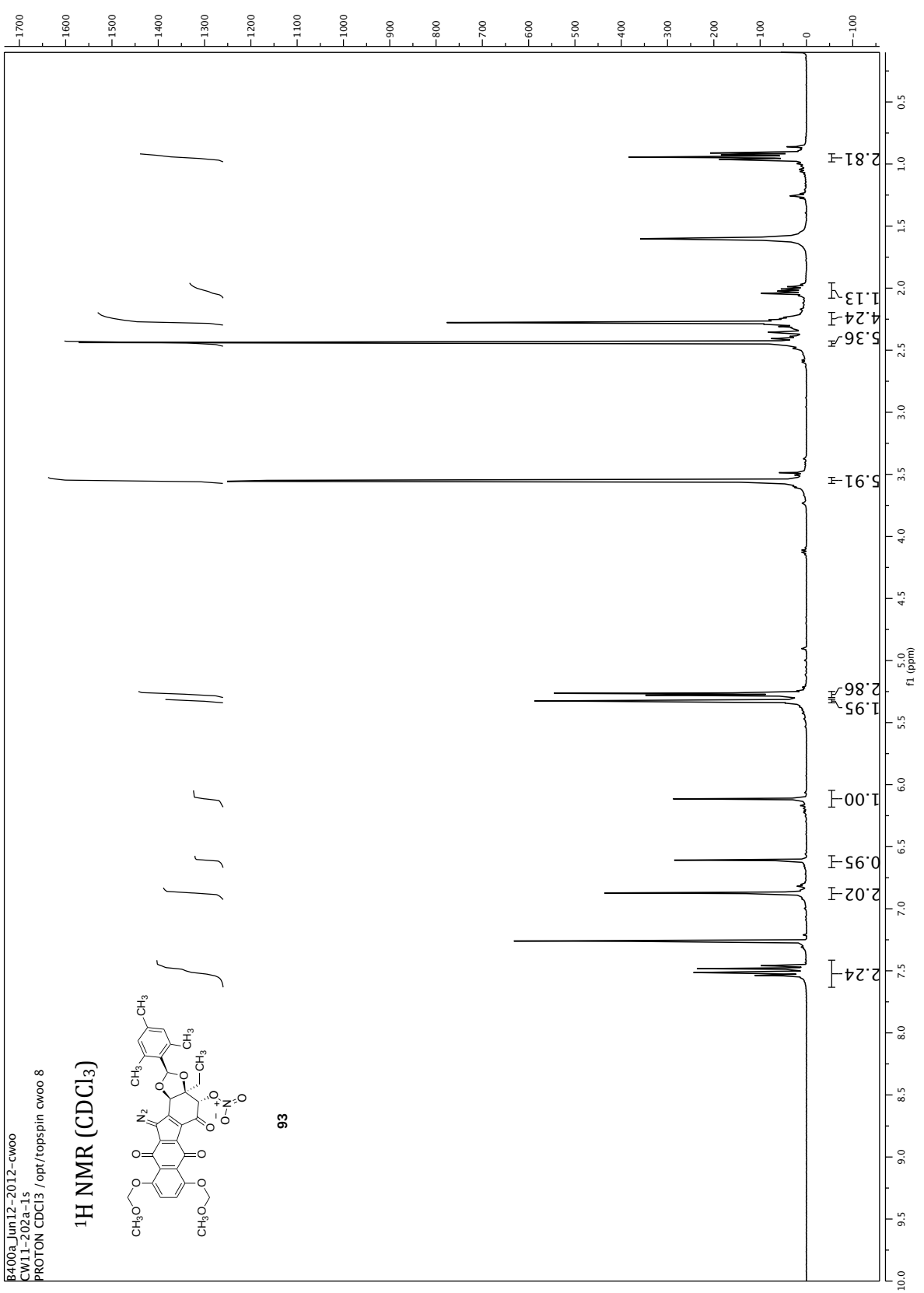
IR

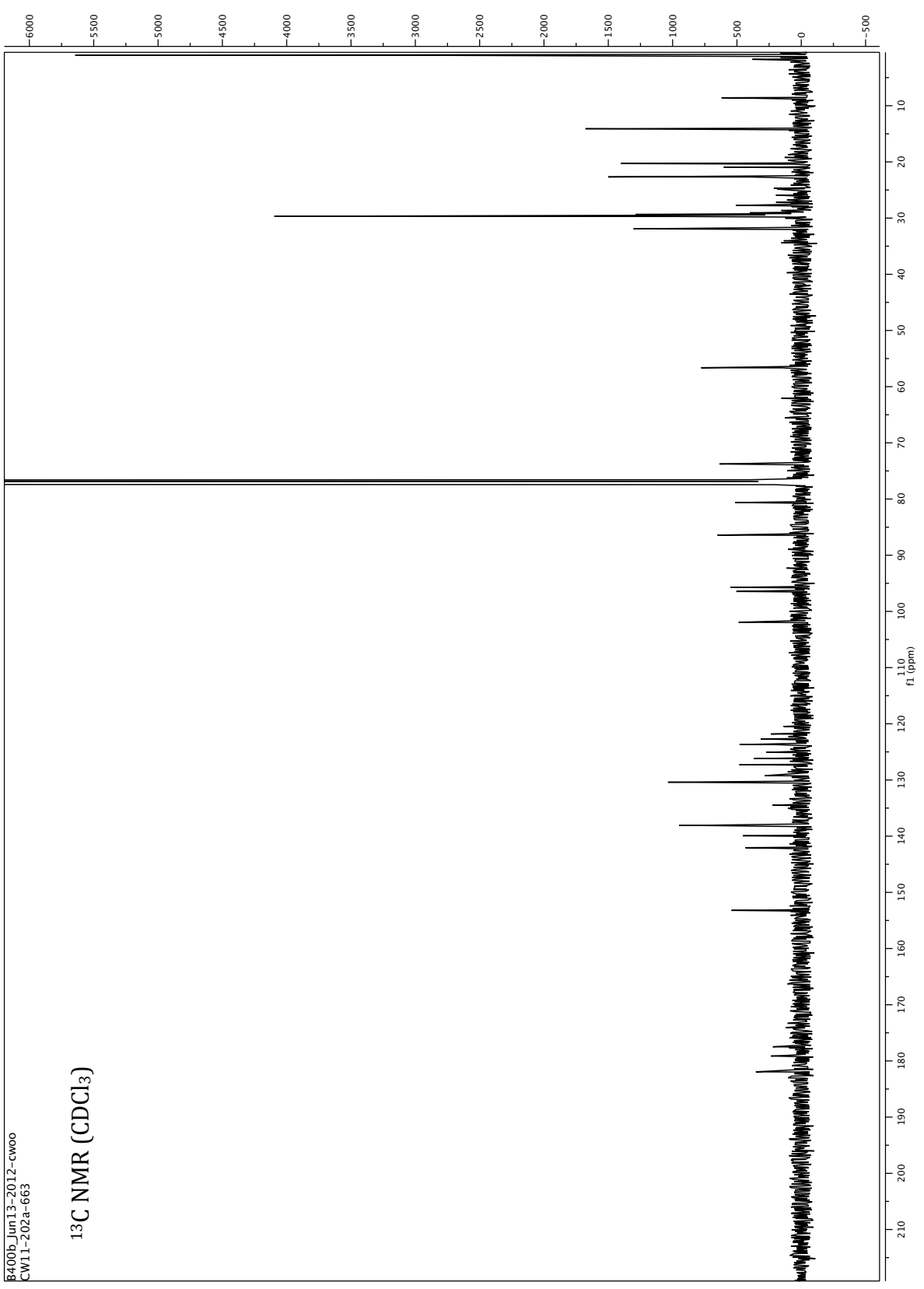

Sat Jan 15 10:15:43 2011 (GMT-05:00)
% Transmittance
115
110
105
100
95
90
85
80
75
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


^{1}H NMR ($CDCl_3$)
85
3.87
2.35
1.19
1.05
1.17
0.97
1.07
1.09
1.07
1.00
f1 (ppm)

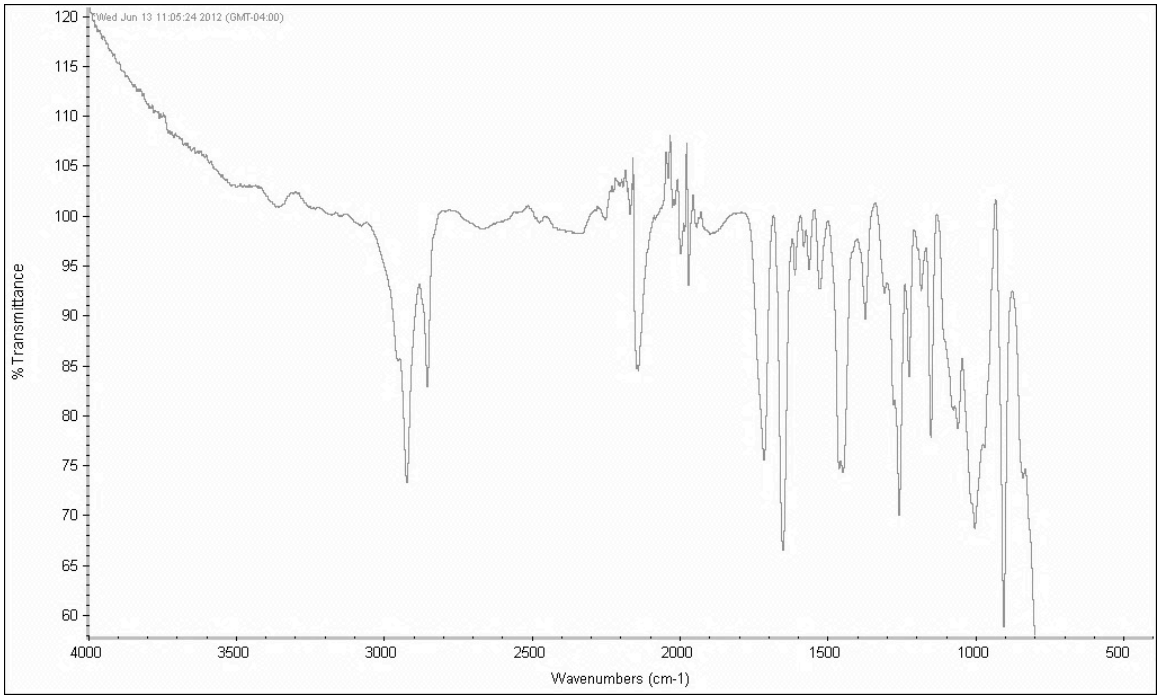
HMQC($CDCl_3$)

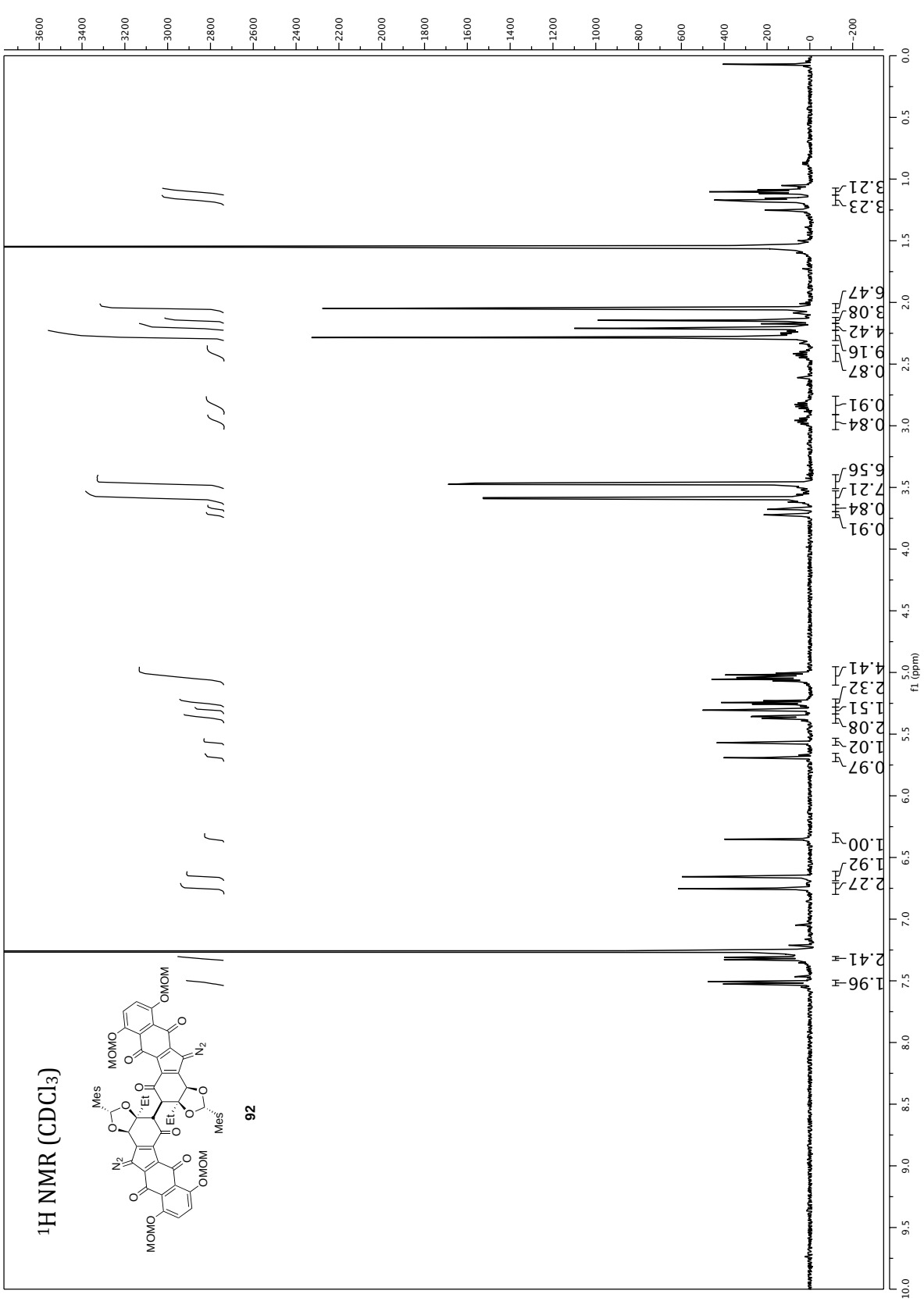



B400a_Jun12-2012-cwoo
CW11-202a-1s
PROTON CDCl3 /opt/topspin cwoo 8
^{1}H NMR ($CDCl_3$)
93
2.81
1.13
4.24
5.36
5.91
2.86
1.95
1.00
0.95
2.02
2.24
f1 (ppm)

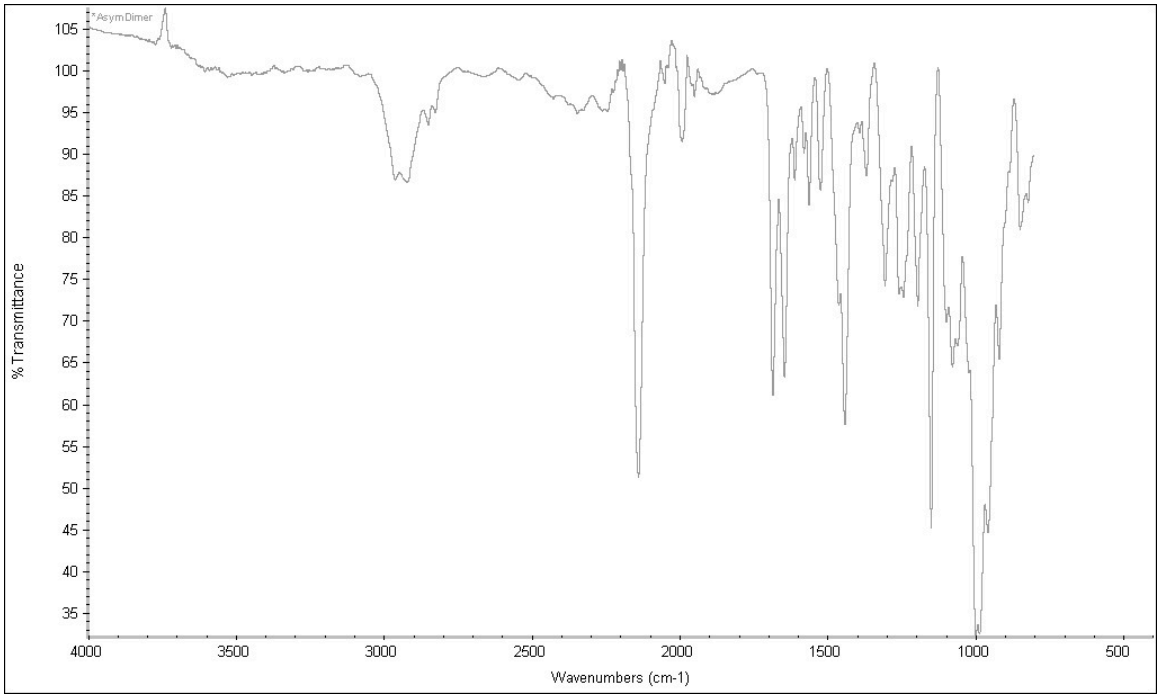

^{13}C NMR ($CDCl_3$)
B400b_Jun13-2012-cwoo
CW11-202a-663
f1 (ppm)

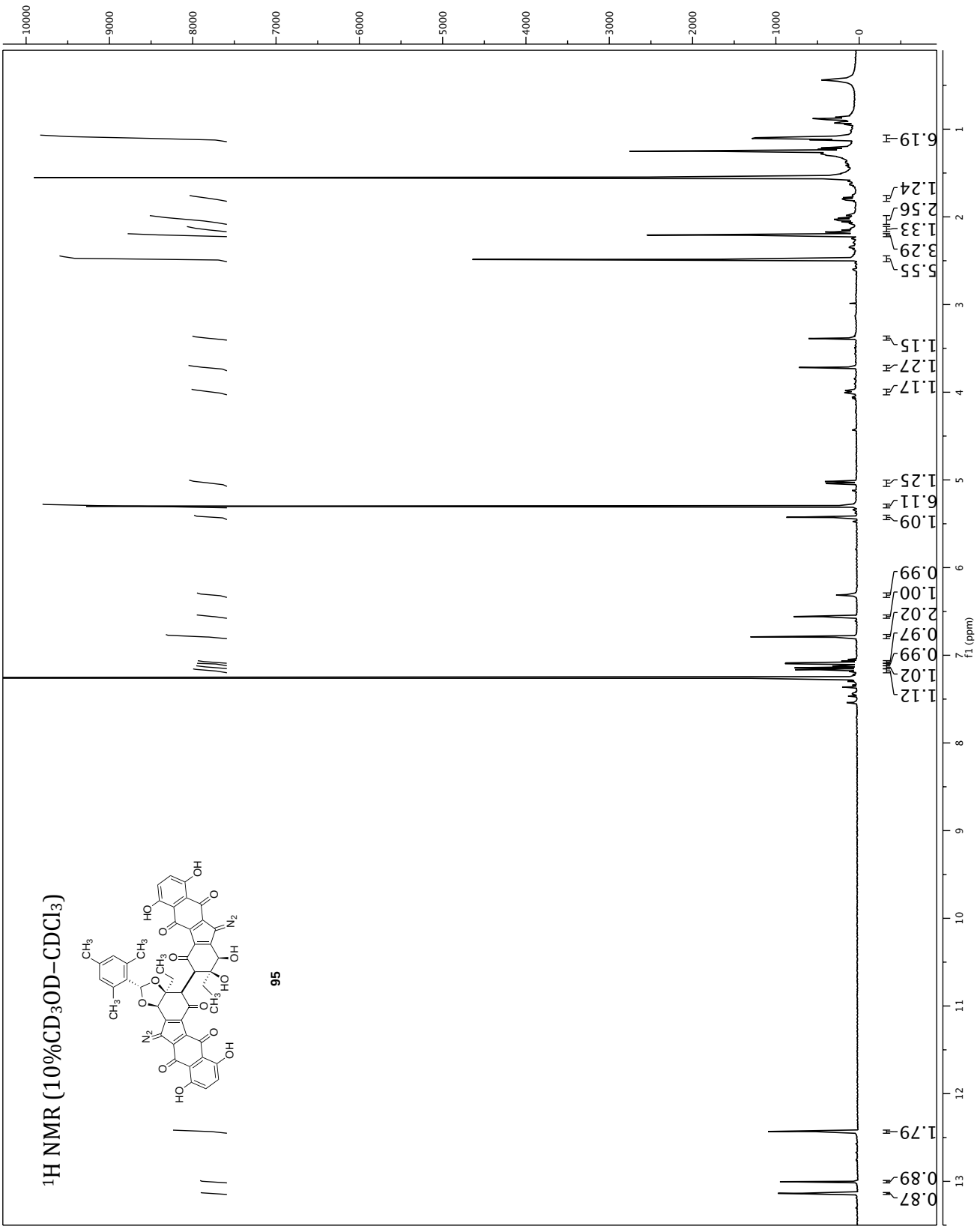
IR


Wed Jun 13 11:05:24 2012 (GMT-04:00)
% Transmittance
120
115
110
105
100
95
90
85
80
75
70
65
60
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

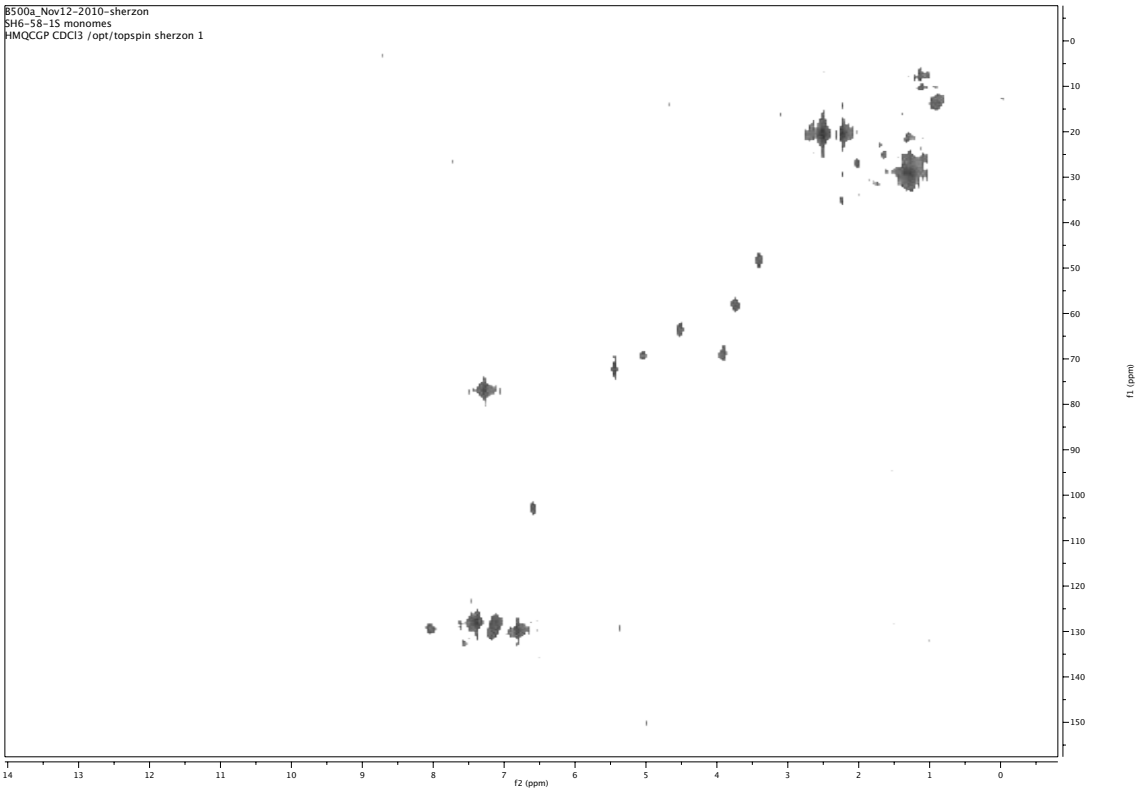

^{1}H NMR ($CDCl_3$)
92
MOMO
OMOM
Mes
Et
Et
Mes
MOMO
OMOM
N_2
N_2
3.21
3.23
5.47
3.08
4.42
9.16
0.87
0.91
0.84
6.56
7.21
0.84
0.91
4.41
2.32
1.51
2.08
1.02
0.97
1.00
1.92
2.27
2.41
1.96
f1 (ppm)

IR

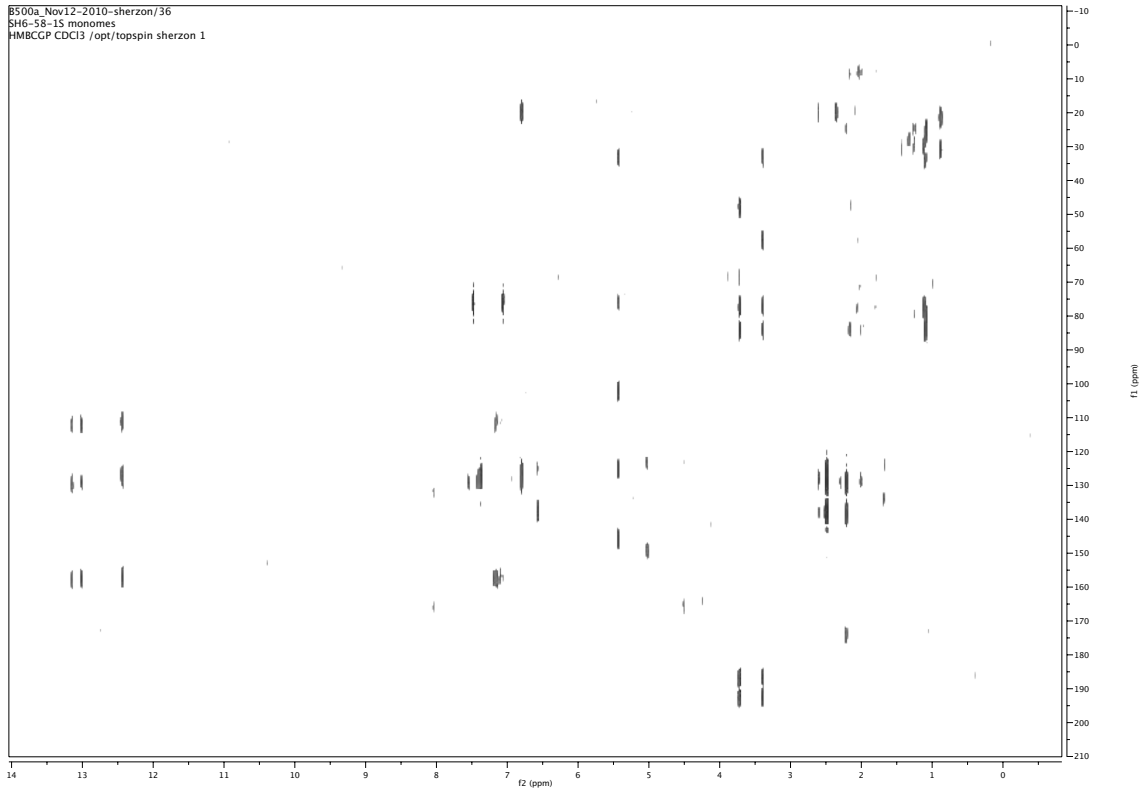

*AsymDimer
% Transmittance
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


^{1}H NMR (10%CD_3OD–$CDCl_3$)
95
6.19
1.24
2.56
1.33
3.29
5.55
1.15
1.27
1.17
1.25
6.11
1.09
0.99
1.00
2.02
0.97
0.99
1.02
1.12
1.79
0.89
0.87
f1 (ppm)

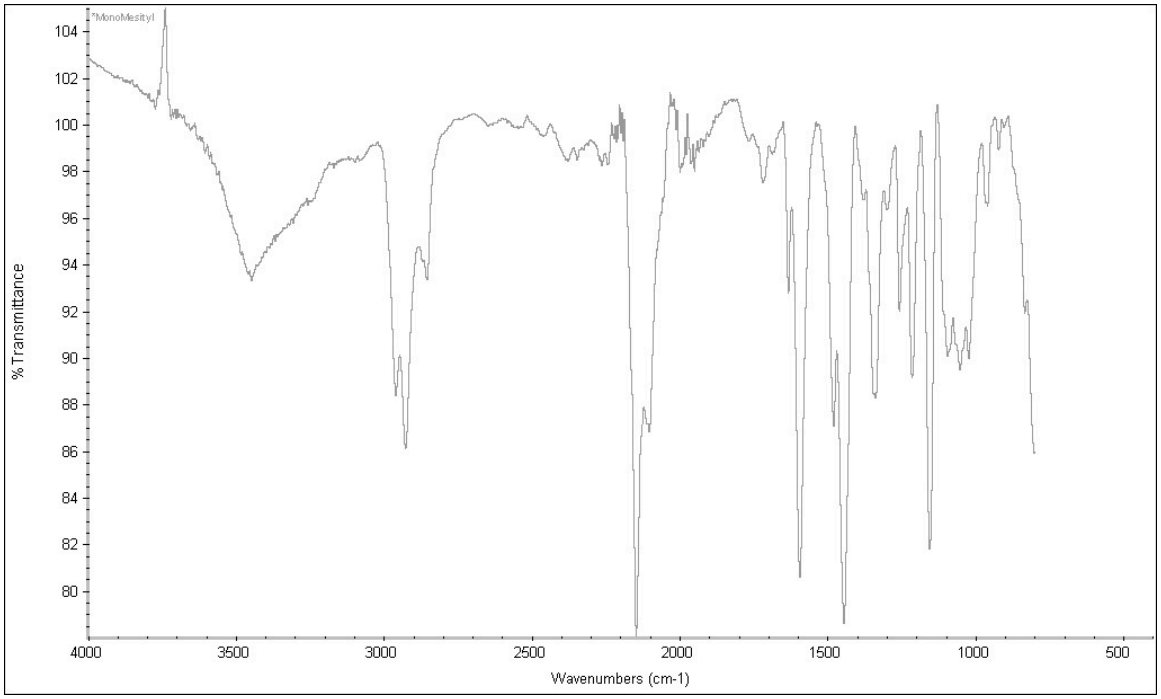
HMQC (10%CD_3OD–$CDCl_3$)

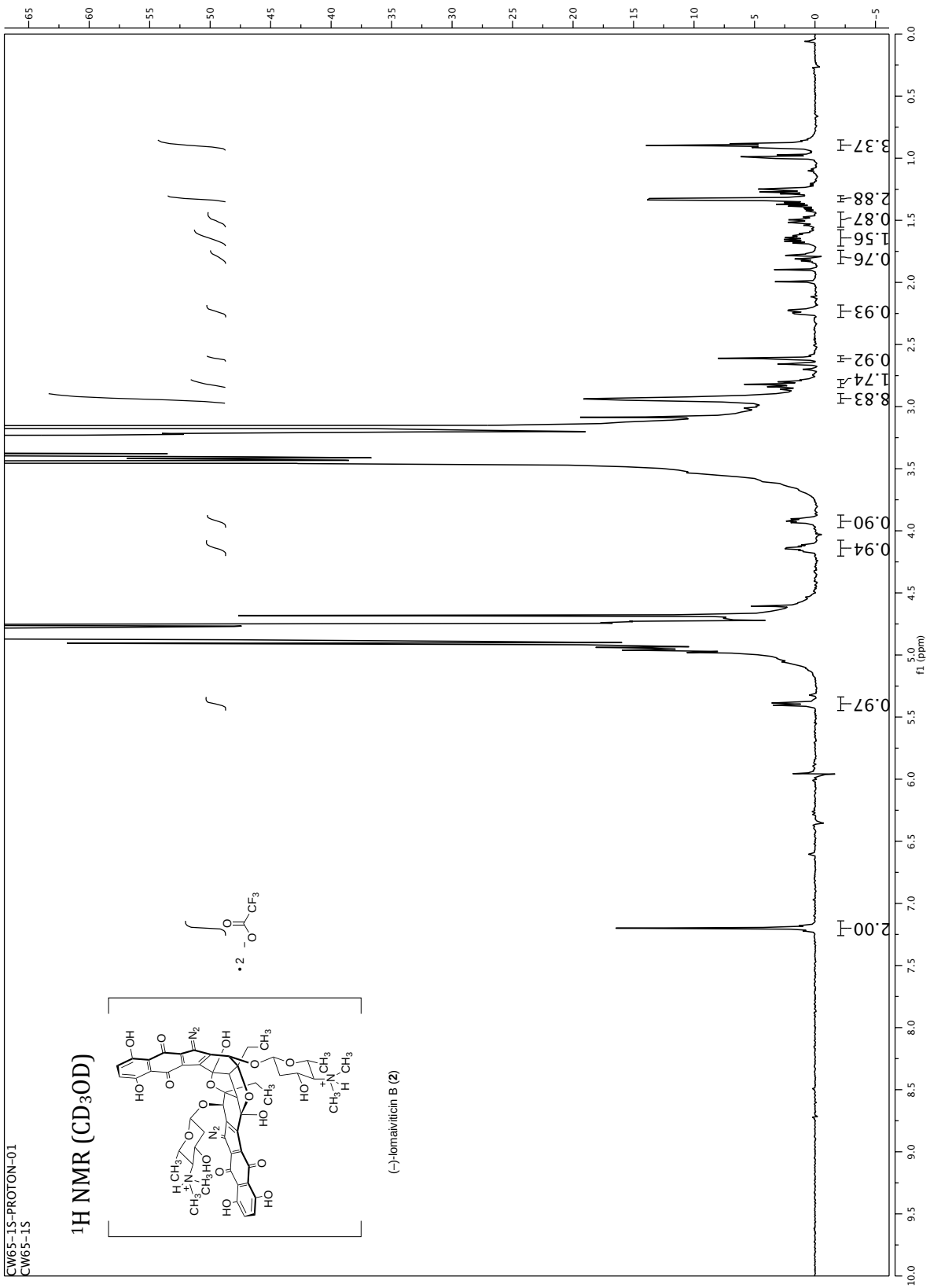


HMBC (10%CD_3OD–$CDCl_3$)

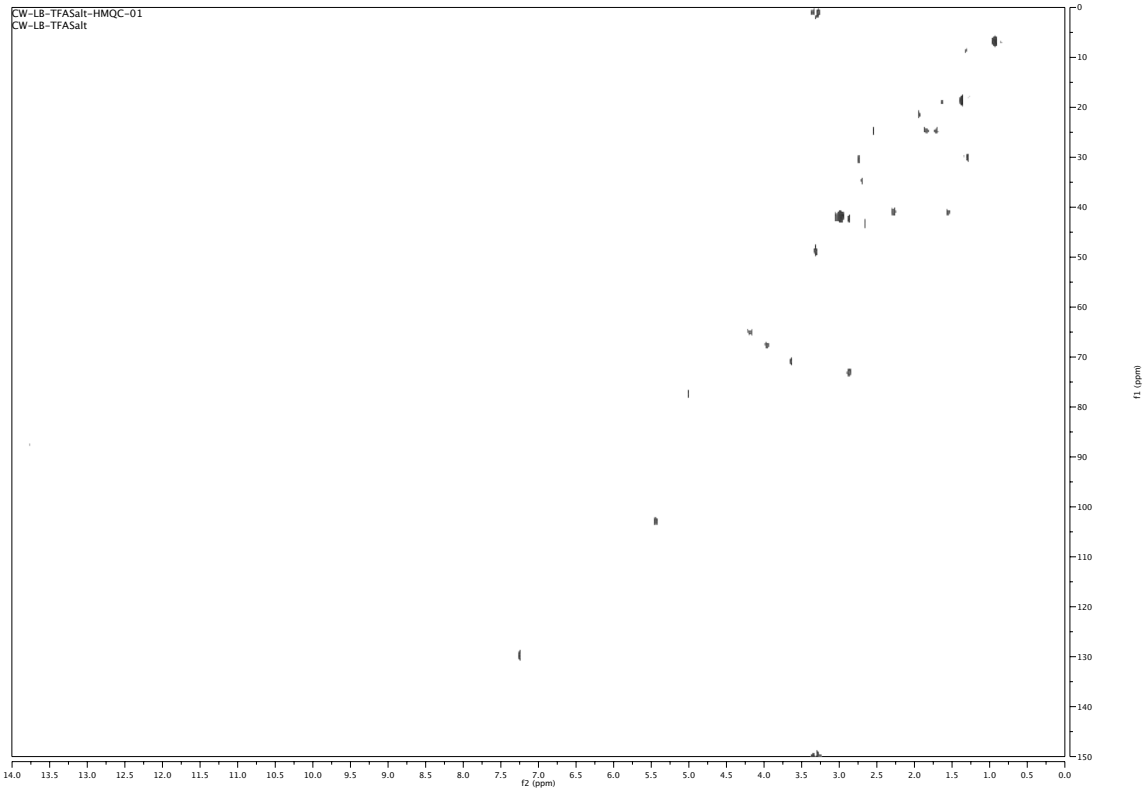


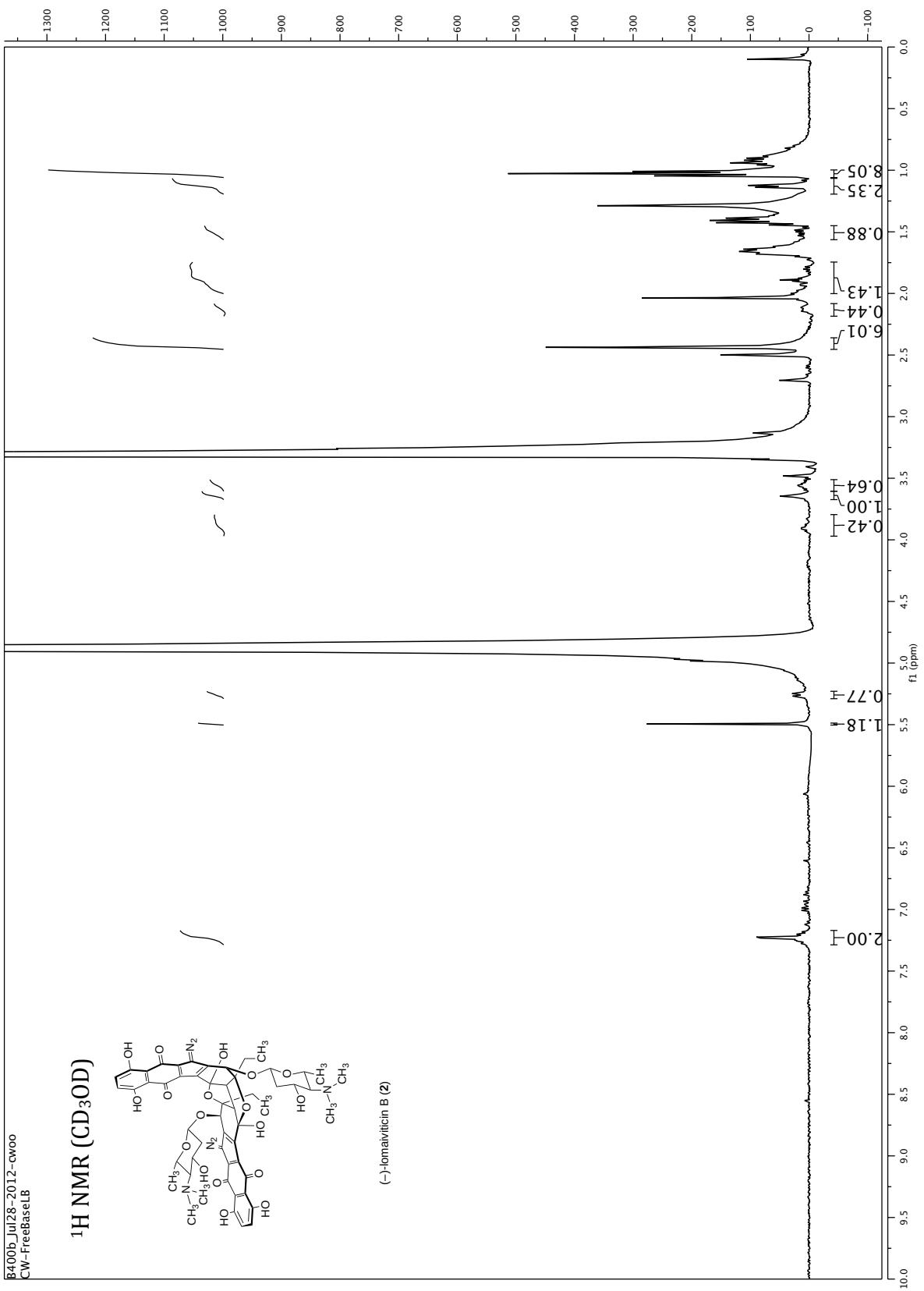
IR


*MonoMesityl
% Transmittance
Wavenumbers (cm-1)
104
102
100
98
96
94
92
90
88
86
84
82
80
4000
3500
3000
2500
2000
1500
1000
500

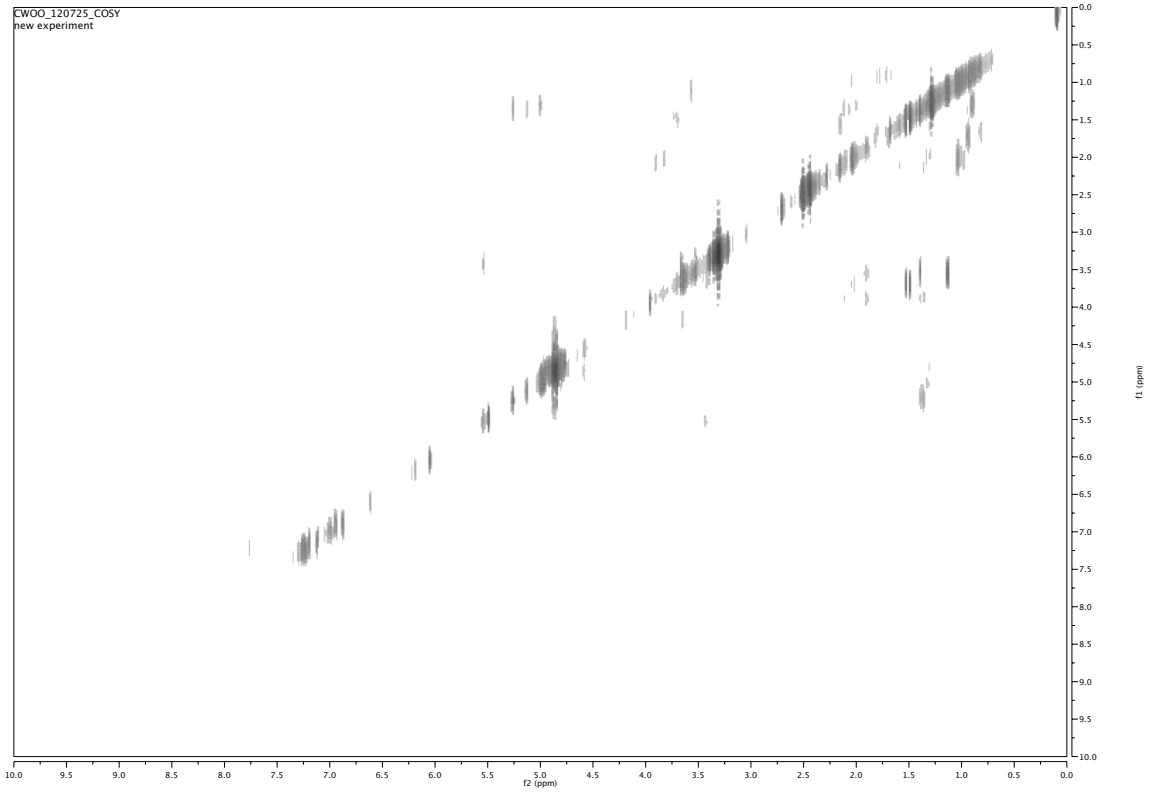

CW65-1S-PROTON-01
CW65-1S
^{1}H NMR (CD_3OD)
(–)-lomaiviticin B (2)
2.00
0.97
0.90
0.94
8.83
1.74
0.92
0.93
0.76
1.56
0.87
2.88
3.37
f1 (ppm)

HMQC (CD_3OD)

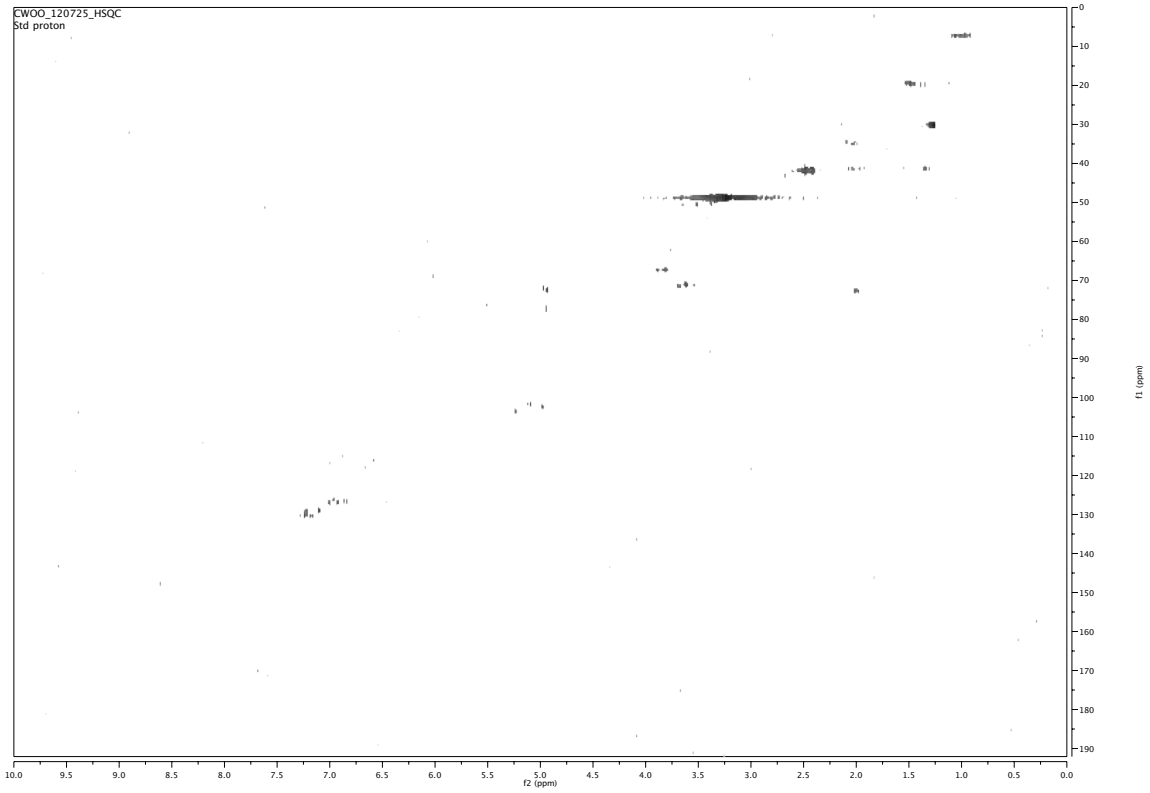



^{1}H NMR (CD_3OD)
B400b_Jul28-2012-cwoo
CW-FreeBaseLB
(–)-lomaiviticin B (2)
f1 (ppm)
2.00
1.18
0.77
1.00
0.42
0.64
6.01
0.44
1.43
0.88
2.35
8.05

COSY (CD_3OD)



HSQC (CD_3OD)



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