SYNTHESIS OF AN INDOLOCARBAZOLE BASED SMALL MOLECULE: TOWARDS DONOR-ACCEPTOR TYPE LADDER POLYMERS

An Undergraduate Research Scholars Thesis

by

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Submitted to the Undergraduate Research Scholars program
Texas A&M University
in partial fulfillment of the requirements for the designation as an

UNDERGRADUATE RESEARCH SCHOLAR

Approved by
Research Advisor: Dr. Lei Fang

May 2016

Major: Chemistry

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ABSTRACT

Synthesis of an Indolocarbazole Based Small Molecule: Towards Donor-Acceptor Type Ladder Polymers

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The use of donor-acceptor (D-A) type ladder polymers as *p*-type semiconducting materials in optoelectronic devices has received significant attention recently due to the possibilities of increasing the efficiency of organic solar cell devices, while simultaneously decreasing the cost required for device fabrication. As such, the synthesis of an acceptor-donor-acceptor (A-D-A) type small molecule comprised of indolo[3,2-*b*]carbazole donor units and benzo[*c*][1, 2, 5]thiadiazole acceptor units is reported. The structure-property relationships of two types of solubilizing alkyl chains were investigated. The resulting A-D-A small molecule provides a general strategy for the synthesis of indolo[3,2-*b*]carbazole and benzo[*c*][1, 2, 5]thiadiazole based D-A ladder polymers, which possess significant potential as an electron donor material for organic photovoltaic devices. The synthesis reported here is a facile and versatile method utilizing Suzuki coupling reactions, followed by highly efficient ring closing metathesis reactions to construct a defect-free small molecule, and in the future, D-A type ladder polymers.

ACKNOWLEDGMENTS

I would like to thank Dr. Lei Fang for his guidance, instruction, and support of this research. I would also like to thank Jongbok Lee for being an excellent mentor, and for his extensive work in the development of this project as well. Finally, thank you to every member of the Fang research group for always being willing to help me whenever necessary.

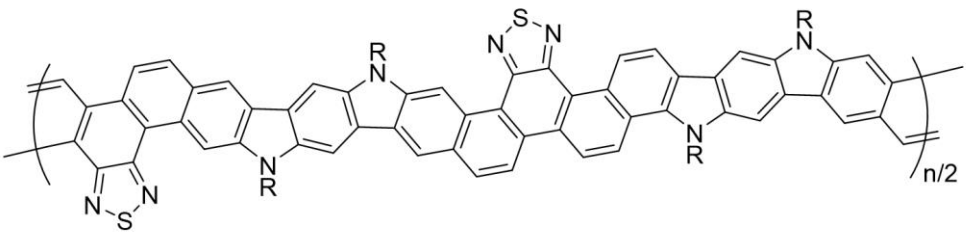
CHAPTER I

INTRODUCTION

Polymeric materials consisting of fully conjugated, coplanar backbones are a class of macromolecules that has received large amounts of attention in the last few decades on account of their complex syntheses, complex rigid structures, and their potential applications as *p*-type semiconducting materials for organic electronic devices, such as organic field-effect transistors (OFET's) and organic photovoltaic (OPV) solar cell devices.[1] Electron donating, conjugated polymers can be utilized as an active material in polymer OPV devices.[2,3] Solar cells comprised of organic polymers or small molecules are fabricated using relatively low-cost solution processing methods than their inorganic silicon-based counterparts.[4-6] Research efforts directed towards the synthesis of electron donating materials for OPV device applications have expanded tremendously in the past few decades. Recent OPV's fabricated from electron donor-acceptor (D-A) alternating copolymers with [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as the electron acceptor material have reached power conversion efficiencies of up to 10.6%.[7]

When fabricating electron donor materials for organic electronic devices, there are many qualities the polymer must possess in order to develop an efficient OPV device. One class of semiconducting polymers that are particularly intriguing for OPV applications are ladder type polymers, which consist of a fully conjugated, planar backbones comprised of fused aromatic rings throughout the polymer backbone.[6] Because of this rigid aromatic backbone, strain in the material from freely rotating σ-bonds present in the backbone is eliminated, allowing for increased effective conjugation lengths and better charge transport mobilities. The structural characteristics of ladder

polymers are what gives rise to various properties that make them promising candidates for OFET and OPV applications. Some of the ideal properties of ladder polymers for OPV applications include their high thermal, mechanical, and chemical stability.[6] However, the rigid, highly conjugated backbones of ladder polymers gives rise to strong intermolecular π-π stacking forces, which causes issues in terms of solubility in common organic solvents.[8] Additional synthetic challenges arise from the occasional presence of defects formed in the ladder polymer backbone after ring closure, such as unclosed rings or cross-linking.[8,9] Figure 1 depicts the proposed indolo[3,2-*b*]carbazole based D-A ladder polymer, and compares some of the advantages and disadvantages associated with these types of polymers.



Advantages of D-A Ladder Polymers:[6,9]
- ✓ Low optical band gap
- ✓ Thermal stability
- ✓ High hole mobility
- ✓ No torsional strain

Disadvantages of D-A Ladder Polymers:[6,9]
- o Poor solubility in common organic solvents
- o Structural defects may occur after ring-closure

Figure 1. Structural overview of the proposed indolo[3,2-*b*]carbazole based D-A ladder polymer, along with an overview of the various properties of ladder polymers

Donor-acceptor approach

Although ladder-type polymers fascinated many in the 1990's and early 2000's, many had given up on their utility in organic electronic devices due to the various solubility issues and the often

defective structures resulting from unclosed rings.[8,9] Recently, it was realized that by connecting electron-rich donor units to electron-deficient acceptor units to synthesize ladder polymers with very strong π-conjugation throughout the backbone made functionalizing these rigid ladder polymers exhibit increased solubility, and transition-metal catalyzed cross-coupling efficiently combined the electron donor and electron acceptor units with minimal structural defects.[3] These types of polymers, called Donor-Acceptor (D-A) ladder polymers, became extremely popular due to their overall low optical band gap for broad absorption of solar energy, which could easily be modified based on the electronic properties of the donor and acceptor units.[10]

The D-A approach caused the field of semiconducting polymers to again become extremely popular because the issue of poor solubility could be overcome by the instillation of long alkyl chains on the electron-donor unit, which breaks up some of the strong intermolecular packing, and allows for efficient solution processing methods to be employed.[2] However, the length of the alkyl chain has a large impact on the packing structure of the resulting ladder polymer or small molecule, and an alkyl chain that is too long will decrease the effective conjugation length of the material, therefore significantly decreasing its efficiency in terms of device performance. Although the D-A approach has offered solutions to many difficult synthetic issues, there are still many problems to be addressed in order for organic electronic devices to be the new standard energy source.

Proposed small molecule

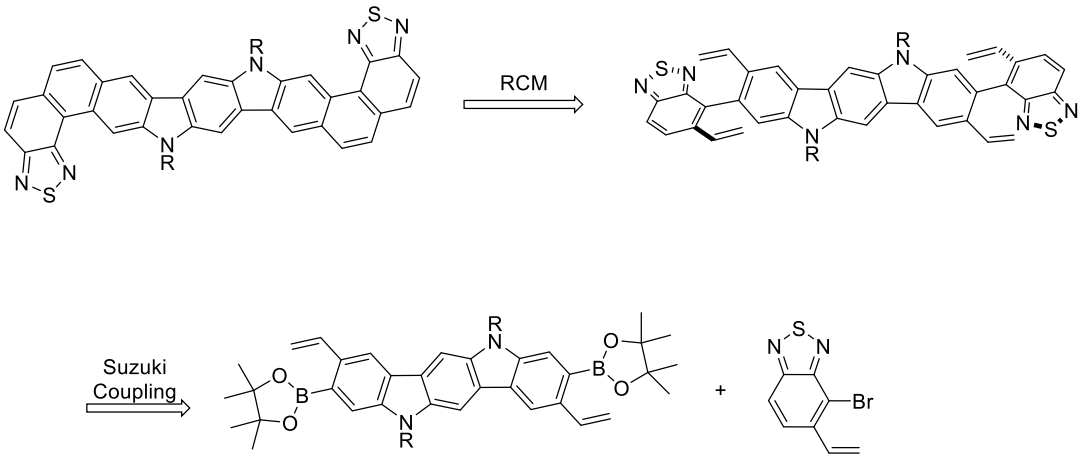
There have been many different donor and acceptor units explored since the D-A ladder polymer received its popularity, and the majority of research today is directed towards designing the electron donor unit for D-A ladder polymers. Donor units, such as thiophene-, fluorene- or

carbazole-based molecules, have received much attention due to their highly conjugated π-systems, coplanar structure, high hole mobilities, high thermal stability, and easy to functionalize structural-moieties.[9] However, the power conversion efficiencies of these devices have yet to be fully optimized. One donor unit that has emerged as a competitive candidate for use in D-A ladder polymers is indolo[3,2-*b*]carbazole. Indolocarbazole is similar to the structure of carbazole, and is essentially an extension of the carbazole structure. Indolocarbazole possesses two nitrogen atoms in its structure that can easily be functionalized with various alkyl substituents to increase its solubility. Some other ideal properties of carbazole is its low HOMO energy level, which is important for obtaining an ideal band gap, easy to functionalize groups at the 2,8- and 3,9-positions for the synthesis of a variety of ladder polymers, and an even higher hole mobility than carbazole.[11]

The electron acceptor units employed in D-A ladder polymer syntheses have been widely explored, and the acceptor units with the most desirable qualities have been well reported. The donor unit chosen for the indolocarbazole-based small molecule is benzothiadiazole. Benzothiadiazole is an ideal acceptor candidate due to its easily to functionalize 4,5- and 6,7- positions, planar morphology that compliments the coplanar backbone of indolocarbazole, and an ideal LUMO energy.[3] As such, the goal of this project is to synthesize an acceptor-donor-acceptor (A-D-A) small molecule for preliminary studies related to the synthesis of a D-A ladder polymer using indolocarbazole as the donor unit and benzothiadiazole as the acceptor unit. To determine the effects of the solubilizing alkyl chains length and branching position, an α-branched octyl chain and a β-branched ethyl hexyl chain will each be added to indolocarbazole, and X-ray diffraction

of the small molecule will show which alkyl chain gives the best solubility, intermolecular packing structure, and maintains the desired effective conjugation length.

To synthesize the A-D-A small molecule with benzothiadiazole as the acceptor unit and indolocarbazole as the donor unit, palladium-catalyzed Suzuki cross-coupling of the functionalized indolocarbazole and benzothiadiazole units is performed, to give the small molecule before ring closure, as shown in the small molecule retrosynthetic analysis in Scheme 1.



Scheme 1. Retrosynthetic analysis for the indolo[3,2-*b*]carbazole based small molecule which is synthesized by Suzuki cross-coupling, followed by ring closing olefin-metathesis

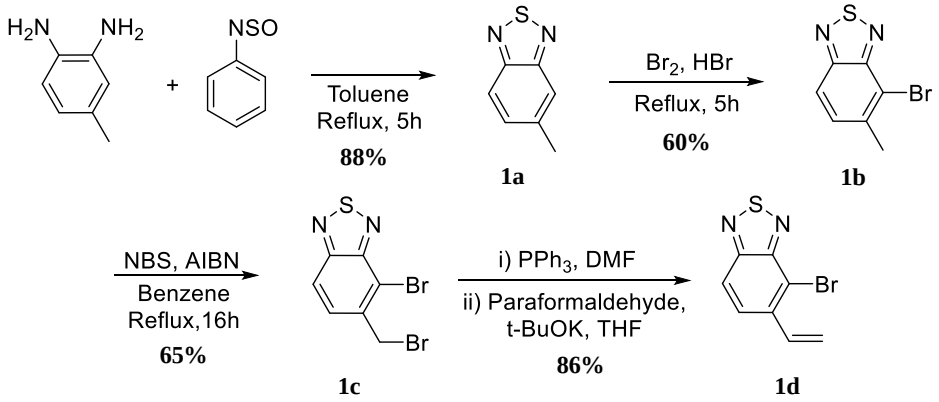
After the Suzuki coupling reaction is completed, the terminal vinyl groups undergo ruthenium-catalyzed ring closing, to give the desired A-D-A small molecule. In Scheme 1, the R groups on the nitrogen atoms of indolocarbazole represents either of the two types of solubilizing alkyl chains used in this synthesis.

CHAPTER II

ACCEPTOR UNIT SYNTHESIS

Synthesis of benzothiadiazole based acceptor unit

Scheme 2 shows the synthetic steps utilized to synthesize 5-methylbenzo[c][1,2,5]thiadiazole, and the subsequent steps implemented to functionalize the acceptor unit. First, the synthesis of 5-methylbenzo[c][1,2,5]thiadiazole, **1a**, was performed with an 88% yield, followed by aromatic bromination at the 4-position, to give **1b** with a 60% yield. Radical bromination of **1b** using the radical initiator, AIBN, to generate the bromine radical from *N*-bromosuccinimide, gave the dibrominated compound **1c** with a 65% yield after refluxing for 16 h in benzene. A Wittig reaction using **1c** and triphenylphosphine was used to give the desired acceptor unit, **1d**, in 86% yield.



Scheme 2. Synthetic scheme for the functionalization of the acceptor unit, **1d**

The bromination of the aromatic ring allows for the donor and acceptor units to be easily coupled via palladium catalyzed Suzuki coupling, and the terminal vinyl group at the 4-position of **1d** is installed, in order to perform ring-closing olefin metathesis between the donor and acceptor units

to give an indolo[3,2-*b*]carbazole-based A-D-A small molecule. The ^{1}H NMR spectra of **1c** and **1d** in $CDCl_3$ are shown in Figures 2 and 3, respectively.

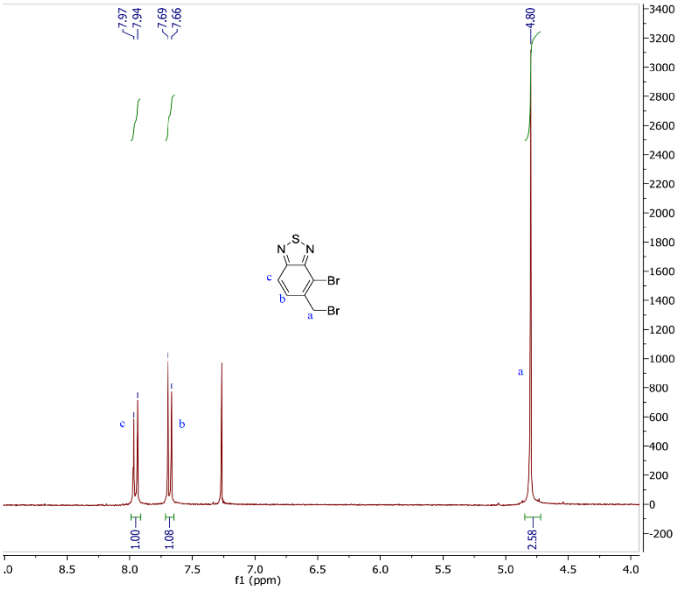


Figure 2. ^{1}H NMR spectrum of **1c** in $CDCl_3$

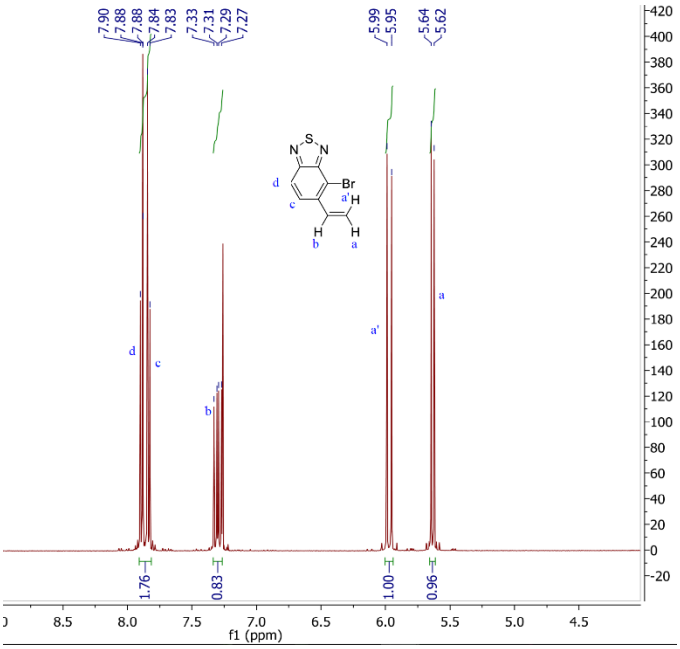


Figure 3. ^{1}H NMR spectrum of **1d** in $CDCl_3$

In Figure 2, the methylene protons (a), are shown as a singlet at 4.80 ppm; however, after the Wittig reaction of **1c** to give **1d**. The proton (b) appears as a doublet of doublets, from 7.33-7.27 ppm. The terminal vinyl protons, (a) and (a'), in Figure 3 appear as two doublets, one from 5.99-5.95 ppm, and the other from 5.64-5.62 ppm. The comparison of the spectra shown in Figures 2 and 3 confirms the desired compound, **1d**, was synthesized successfully.

Experimental procedures for acceptor unit synthesis

The experimental procedures reported below indicate the methods utilized for the synthesis of compounds **1a** through **1d**. Spectroscopic data for these compounds were obtained using a Varian Inova 300 MHz NMR Spectrometer. ^{1}H chemical shifts are reported as δ values in units of ppm relative to the solvent used, either $CDCl_3$ (7.26 ppm) or DMSO (2.50 ppm). Coupling constants (*J*) are reported in units of Hertz (Hz), where multiplicities are assigned as the following: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), bs (broad singlet), or m (multiplet). ^{1}H NMR spectra of compounds **1a** through **1d** are located in Appendix A, and correspond to Figures A1-A4.

Synthesis of 5-methylbenzo[c][1,2,5]thiadiazole

To a 100-mL, flame-dried, round bottom flask equipped with a stir bar and reflux condenser, 3,4-diaminotoluene (2.46 g, 19.5 mmol, 1.0 equiv) was dissolved in toluene (30 mL). *N*-thionylaniline (9.2 mL, 80 mmol, 4.0 equiv) was added to the reaction flask. Reaction mixture refluxed at 130°C for 5 h. Reaction quenched with 1M HCl and extracted with ethyl acetate. Organic layer dried over magnesium sulfate and concentrated *in vacuo*. The white solid product was isolated via auto

column (10:1 Hex:EtOAc) to give **1a**: (1.87 g, 64%); R_f = 0.50 (10:1 Hex:EtOAc); ^{1}H NMR ($CDCl_3$-*d*$_1$, 300 MHz, δ, ppm): δ 7.92-7.89 (d, 1 H, *J* = 9 Hz), 7.78 (s, 1 H), 7.46-7.43 (d, 1 H, *J* = 9 Hz), 2.56 (s, 3 H).

Synthesis of 4-bromo-5-methylbenzo[c][1,2,5]thiadiazole

To a 100-mL, flame-dried, three neck flask, 5-methylbenzo[*c*][1,2,5]thiadiazole (1.50 g, 10 mmol, 1.0 equiv) was dissolved in HBr (21 mL) under N_2. Br_2 (0.51 mL, 10 mmol, 1.0 equiv) in HBr (14 mL) was added dropwise to the reaction flask via addition funnel. Reaction mixture refluxed for 5 h. Reaction mixture allowed to cool to room temperature, and precipitate was filtered and washed with water and ethanol. Solid recrystallized in ethanol to give white crystalline solid, **1b**: (0.53 g, 23%); ^{1}H NMR ($CDCl_3$-*d*$_1$, 300 MHz, δ, ppm): δ 7.85-7.83 (d, 1 H, *J* = 6 Hz), 7.51-7.49 (d, 1 H, *J* = 6 Hz), 2.62 (s, 3 H).

Synthesis of 4-bromo-5-(bromomethyl)benzo[c][1,2,5]thiadiazole

To a 50-mL, flame-dried, roundbottom flask, 4-bromo-5-methylbenzo[*c*][1,2,5]thiadiazole (0.39 g, 1.7 mmol, 1.0 equiv), NBS (0.34 g, 1.9 mmol, 1.1 equiv) and AIBN (spatula tip), dissolved in benzene (15 mL). Reaction mixture refluxed at 85°C for 16 h. The reaction mixture was concentrated *in vacuo* and recrystallized in $CHCl_3$:EtOH to give a white solid, **1c**: (0.22 g, 42%); ^{1}H NMR ($CDCl_3$-*d*$_1$, 300 MHz, δ, ppm): δ 7.97-7.94 (d, 1 H, *J* = 9 Hz), 7.69-7.66 (d, 1 H, *J* = 9 Hz), 4.80 (s, 2 H).

Synthesis of 4-bromo-5-vinylbenzo[c][1,2,5]thiadiazole

To a 25-mL, flame-dried, roundbottom flask, 4-bromo-5-(bromomethyl)benzo[*c*][1,2,5]thiadiazole (0.55 g, 1.5 mmol, 1.0 equiv) and triphenyl phosphine (0.98 g, 3.7 mmol, 2.5 equiv) dissolved in DMF (9 mL) and stirred at 60°C for 15 min, and stirred at 70°C for 16 h. DMF removed *in vacuo*, and reaction mixture dissolved in THF (6 mL). Paraformaldehyde (1.02 g) added to suspension and stirred at room temperature, *t*-BuOK (0.52 g, 4.6 mmol, 3.0 equiv) added slowly to reaction flask. After approximately 15 min, reaction mixture concentrated *in vacuo*, and the product was isolated via autocolumn (3:1 Hex:DCM), to give white crystalline solid, 4-bromo-5-vinylbenzo[*c*][1,2,5]thiadiazole, **1d**: (0.31 g, 86%). R_f=0.38 (3:1 Hex:DCM). ^{1}H NMR ($CDCl_3$-d_1, 300 MHz, δ, ppm): δ 7.90-7.88 (d, 1 H, *J* = 6 Hz), 7.84-7.83 (d, 1 H, *J* = 3 Hz), 7.33-7.27 (dd, 1 H, *J* = 6, 12 Hz), 5.99-5.95 (d, 1 H, *J* = 12 Hz), 5.64-5.62 (d, 1 H, *J* = 6 Hz).

CHAPTER III

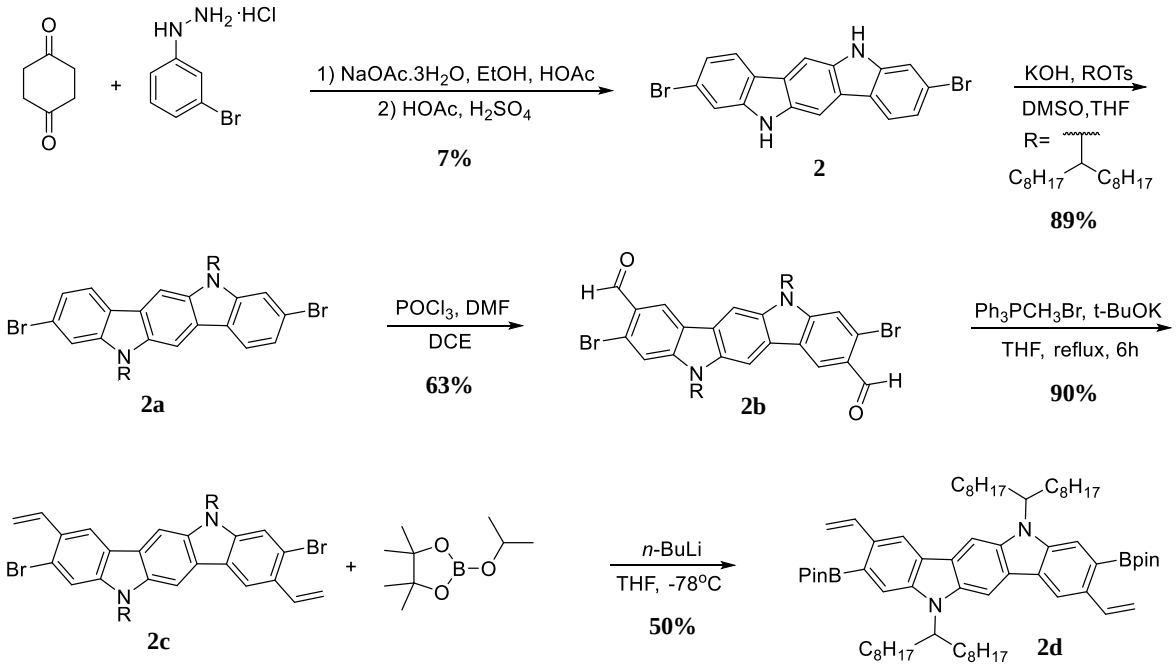
DONOR UNIT SYNTHESIS

Synthesis of indolocarbazole based donor units

The indolo[3,2-*b*]carbazole based donor units were synthesized and functionalized in order to undergo Suzuki coupling with **1d**. Two solubilizing alkyl chains were implemented, each with two different branching points. The first alkyl chain used was an α-branched alkyl chain, and the second alkyl chain used was a β-branched alkyl chain. The α-branched alkyl chain improved the solubility of the donor unit significantly, whereas the donor unit with the β-branched alkyl chain was not easily dissolved in common organic solvents.

Synthesis of donor unit with α-branched alkyl chain

To synthesize 3,9-dibromo-5,11-dihydroindolo[3,2-b]carbazole, **2**, a double Fischer indole reaction between 1,4-cyclohexanone and 3-bromophenylhydrazine hydrochloride was performed to give the desired product with a 7% yield.[12] Low yields are consistently obtained using this reaction due to the formation of various regioisomeric indoles. The synthetic scheme used for the functionalization of 3,9-dibromo-5,11-dihydroindolo[3,2-b]carbazole is shown in Scheme 3.

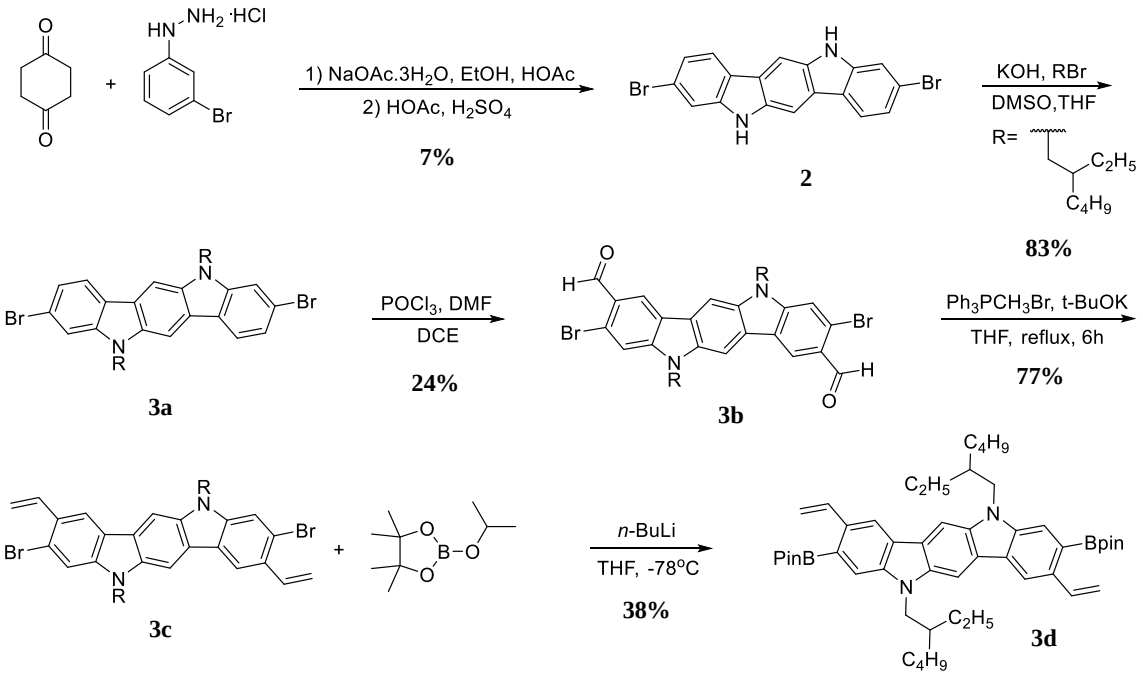


Scheme 3. Synthetic scheme for the synthesis of donor unit with α-branched alkyl chain, **2d**

After synthesizing **2**, the nitrogen atoms in the five-membered rings are alkylated with the α-branched alkyl chain using the tosylate of this alkyl chain in the presence of potassium hydroxide, dimethyl sulfoxide, and tetrahydrofuran. The alkylation reaction gave the desired product with an 89% yield. The next step in the functionalization of the donor unit is the formation of the dialdehyde via Vilsmeier-Haack formylation at the 4,8-positions. A Wittig reaction is performed give **2c**, adding two terminal vinyl groups at the 4,8-positions, with 90% yield. The final step in the donor unit synthesis is the borylation of **2c** using the cyclic boronic ester shown in Scheme 3, which gave the desired product, **2d**, with a 50% yield.

Synthesis of donor unit with β-branched alkyl chain

The synthesis of the indolocarbazole donor unit with the β-branched ethyl-hexyl alkyl chain, was synthesized using the same reactions implemented for the synthesis of the donor unit with the α-branched alkyl chain; however, the β-branched alkyl chain was purchased as 1-bromo-3-ethylhexane, so the alkylation of **2** was performed via S_N2 reaction with the nucleophilic nitrogen atoms present in indolocarbazole displacing the bromine of the alkyl chain, to give the alkylated donor unit with an 83% yield. Scheme 4 depicts the synthetic route utilized to functionalize the donor unit.



Scheme 4. Synthetic scheme for the functionalization of donor unit with β-branched alkyl chain, **3d**

Solubility issues began to arise when synthesizing **3b**, which demonstrates that the β-branched alkyl chain chosen here was not long enough to sufficiently disrupt the strong intermolecular

interactions of indolo[3,2-*b*]carbazole. This solubility issue is a large contributing factor for the low yields of **3b**, as well as the final product, **3d**.

Experimental procedures for donor unit syntheses

The experimental procedures reported below indicate the methods utilized for the synthesis of compounds **2**, **2a** through **2d**, and **3a** through **3d**. Spectroscopic data for these compounds were obtained using either a Varian Inova 300 MHz or Varian 500 MHz NMR Spectrometer. ^{1}H chemical shifts are reported as δ values in units of ppm relative to the solvent used, either $CDCl_3$ (7.26 ppm) or DMSO (2.50 ppm). Coupling constants (*J*) are reported in units of Hertz (Hz), where multiplicities are assigned as the following: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), bs (broad singlet), or m (multiplet). ^{1}H NMR spectra of compounds **2**, **2a** through **2d**, and **3a** through **3d** are located in Appendix A, and correspond to Figures A5-A13.

Synthesis of 3,9-dibromo-5,11-dihydroindolo[3,2-b]carbazole[12]

To a 1000-mL, flame-dried, three neck flask, 3-bromophenylhydrazine hydrochloride (26.0 g, 114 mmol, 1.0 equiv) was suspended in ethanol (200 mL). Sodium acetate trihydrate (46.54 g, 342 mmol, 3.0 equiv) was dissolved in distilled water (100 mL) and added to the reaction flask. Reaction mixture stirred at room temperature for 15 min, and 1,4-cyclohexanedione (6.42 g, 57 mmol, 3.0 equiv) dissolved in ethanol (200 mL) was added to reaction flask via addition funnel. Glacial acetic acid (50 mL) added to the reaction flask and stirred at 50°C for 1 h. Reaction flask warmed to room temperature and stirred at 0°C for 1 h. The precipitate was isolated via vacuum filtration and washed with water. This solid was added di a solution of glacial acetic acid (75 mL)

and sulfuric acid (15 mL) and stirred at 10°C for 15 min, then reaction flask stirred at room temperature for 15 min, and warmed to 60°C and stirred for 15 min. Then, the reaction mixture was cooled to room temperature and stirred for 24 h. The precipitate was isolated via vacuum filtration and washed with water and methanol. The solid was recrystallized twice in DMF (44 mL, 40 mL) and the resulting product was isolated via vacuum filtration to give a light green crystalline solid, **2**: (1.62 g, 7%). ^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm): δ 11.25 (s, 2 H), 8.19-8.17 (d, 4 H, J = 6 Hz), 7.63 (s, 2 H), 7.29-7.25 (dd, 4 H, J = 3, 9 Hz).

Synthesis of 3,9-dibromo-5,11-di(heptadecan-9-yl)-5,11-dihydroindolo[3,2-b]carbazole

To a 100-mL, flame-dried, round bottom flask, 3,9-dibromo-5,11-dihydroindolo[3,2-*b*]carbazole (1.67 g, 4.0 mmol, 1.0 equiv) and potassium hydroxide (2.24 g, 40 mmol, 10 equiv) were dissolved in DMSO (32 mL). Heptadecan-9-yl 4-methylbenzenesulfonate (4.93 g, 12 mmol, 3.0 equiv) dissolved in DMSO (20 mL) and THF (20 mL) and added via addition funnel over 1 h. The reaction mixture was stirred at room temperature for 24 h. Reaction mixture poured into water, and extract with DCM, wash with water (3x) to remove DMSO. The organic layer was dried over magnesium sulfate, concentrated *in vacuo*, and purified via autocolumn to give a light yellow solid, **2a**: (2.89 g, 89%). R_f=0.70 (Hexanes). ^{1}H NMR ($CDCl_3$-d_1, 300 MHz, δ, ppm): δ 8.14-7.09 (m, 2 H), 7.72 (s, 2 H), 7.56 (s, 2 H), 7.33-7.28 (m, 2 H), 4.67 (s, 1 H), 4.51 (s, 1 H), 1.59-1.14 (m, 56 H), 0.82-0.80 (t, 12 H, J = 3 Hz).

Synthesis of 3,9-dibromo-5,11-di(heptadecan-9-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde

To 250-mL, flame-dried, sealed tube, DMF (2.1 mL, 27.5 mmol, 25 equiv) dissolved in 1,2-dichloroethane (7 mL) and cooled to 0°C. $POCl_3$ (2.56 mL, 27.5 mmol, 25 equiv) added dropwise to the reaction mixture. The reaction flask was warmed to room temperature, 3,9-dibromo-5,11-di(heptadecan-9-yl)-5,11-dihydroindolo[3,2-*b*]carbazole (1.0 g, 1.1 mmol, 1.0 equiv) was added to the reaction flask, and the reaction mixture was tirred at 90°C for 48 h. The reaction was quenched with water, and 1M KOH was added to the solution until a neutral pH was achieved. Organic layer was extracted with DCM, dried over magnesium sulfate, and purified via autocolumn to give a bright yellow solid, **2b**: (0.65 g, 63%). R_f=0.65 (1:1, Hex:DCM). ^{1}H NMR ($CDCl_3$-d_1, 500 MHz, δ, ppm): δ 10.46 (s, 2 H), 8.83-8.80 (d, 2 H, *J* = 9 Hz), 8.27-8.24 (dd, 2 H, *J* = 6, 9 Hz), 7.77 (s, 1H), 7.61 (s, 1 H), 4.70 (s, 2 H), 4.56 (s, 2 H), 2.64-1.14 (m, 56 H), 0.82-0.80 (t, 12 H, *J* = 3 Hz).

Synthesis of 3,9-dibromo-5,11-di(heptadecan-9-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole

To 25-mL, flame-dried, roundbottom flask, Ph_3PCH_3Br (0.95 g, 2.66 mmol, 4.2 equiv) was dissolved in THF (10 mL) and *t*-BuOK (0.28 g, 2.52 mmol, 4.0 equiv) was added in portions to the reaction flask. The reaction mixture was stirred at room temperature and 3,9-dibromo-5,11-di(heptadecan-9-yl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (0.60 g, 0.62 mmol, 1.0 equiv) was added to the reaction flask. The reaction mixture was refluxed for 5 h and then cooled to room temperature. Reaction mixture poured into distilled water and the organic layer was extracted with DCM. The organic layer was dried over magnesium sulfate, concentrated *in*

vacuo, and purified by autocolumn (Hexanes) to give a yellow solid, **2c**: (0.19 g, 32%). R_f=0.58 (Hexanes). ^{1}H NMR ($CDCl_3$-d_1, 500 MHz, δ, ppm): δ 8.37-8.34 (d, 1 H, J = 9 Hz), 8.13-8.10 (d, 1 H, J = 9 Hz), 8.00-7.97 (d, 1 H, J = 9 Hz), 7.75 (s, 1 H), 7.59 (s, 1 H), 7.28-7.23 (m, 2 H), 5.85-5.79 (m, 2 H), 4.65-4.48 (m, 2 H).

Synthesis of 5,11-di(heptadecan-9-yl)-3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole

To a 25-mL, flame-dried, roundbottom flask, 3,9-dibromo-5,11-di(heptadecan-9-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-*b*]carbazole (0.15 g, 0.16 mmol, 1.0 equiv) was dissolved in THF (4 mL) at -78°C. *n*-BuLi (0.22 mL, 2.1 equiv) was added dropwise to the reaction flask and the reaction mixture was stirred at -78°C for 1 h. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.077 mL, 0.38 mmol, 2.4 equiv) was added to the reaction flask and then stirred at room temperature for 24 h. The reaction mixture was poured in water, and the organic layer was extracted with DCM, dried over magnesium sulfate, and concentrated *in vacuo*. The product was purified via autocolumn (4:1, Hex:DCM) to give a yellow solid, **2d:** (66 mg, 39%). R_f=0.35 (4:1, Hex:DCM). ^{1}H NMR ($CDCl_3$-d_1, 500 MHz, δ, ppm): δ 8.46 (s, 2 H), 8.18 (s, 2 H), 7.84-7.74 (m, 2 H), 7.70 (s, 2 H), 5.87-5.81 (d, 2 H), 4.70 (s, 2 H), 1.42 (d, 24 H), 0.81-0.76 (t, 12 H).

3,9-dibromo-5,11-bis(2-ethylhexyl)-5,11-dihydroindolo[3,2-b]carbazole

To a 100-mL, flame-dried, round bottom flask, 3,9-dibromo-5,11-dihydroindolo[3,2-*b*]carbazole (1.67 g, 4.0 mmol, 1.0 equiv) and potassium hydroxide (2.24 g, 40 mmol, 10 equiv) were dissolved in DMSO (32 mL). 2-Ethylhexyl bromide (2.13 mL, 12 mmol, 3.0 equiv) dissolved in DMSO (20

mL) and THF (20 mL) and added via addition funnel over 1 h. The reaction mixture was stirred at room temperature for 24 h. Reaction mixture poured into water, and extract with DCM, wash with water (3x) to remove DMSO. The organic layer was dried over magnesium sulfate, concentrated *in vacuo*, and purified via autocolumn to give a light yellow solid, **3a**: (2.12 g, 83%). ^{1}H NMR ($CDCl_3$-d_1, 500 MHz, δ, ppm): δ 8.01-8.00 (d, 2 H, J = 3 Hz), 7.88 (s, 2 H), 7.50 (s, 2 H), 7.33-7.32 (d, 2 H, J = 3 Hz), 4.20-4.11 (m, 4 H), 2.15-2.13 (m, 2 H), 1.43-1.28 (m, 18 H), 0.96-0.88 (dt, 12 H).

Synthesis of 3,9-dibromo-5,11-bis(2-ethylhexyl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde

To 250-mL, flame-dried, sealed tube, DMF (3.04 mL, 39.3 mmol, 25 equiv) dissolved in 1,2-dichloroethane (7 mL) and cooled to 0°C. $POCl_3$ (3.67 mL, 39.3 mmol, 25 equiv) added dropwise to the reaction mixture. The reaction flask was warmed to room temperature, 3,9-dibromo-5,11-bis(2-ethylhexyl)-5,11-dihydroindolo[3,2-*b*]carbazole (1.0 g, 1.57 mmol, 1.0 equiv) was added to the reaction flask, and the reaction mixture was tirred at 90°C for 48 h. The reaction was quenched with water, and 1M KOH was added to the solution until a neutral pH was achieved. Organic layer was extracted with DCM, dried over magnesium sulfate, and purified via autocolumn to give a bright yellow solid, **3b**: (0.27 g, 24%). R_f=0.65 (1:1, Hex:DCM). ^{1}H NMR (DMSO-d_6, 500 MHz, δ, ppm): δ 10.80 (s, 2 H), 9.12 (s, 2 H), 8.37 (s, 2 H), 7.59 (s, 2 H) 4.58-4.56 (d, 4 H, J = 6 Hz), 1.82-1.58 (m, 18 H), 1.32-1.20 (dt, 12 H).

Synthesis of 3,9-dibromo-5,11-bis(2-ethylhexyl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole

To 25-mL, flame-dried, roundbottom flask, Ph_3PCH_3Br (0.95 g, 2.66 mmol, 4.2 equiv) was dissolved in THF (10 mL) and *t*-BuOK (0.28 g, 2.52 mmol, 4.0 equiv) was added in portions to the reaction flask. The reaction mixture was stirred at room temperature and 3,9-dibromo-5,11-bis(2-ethylhexyl)-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehyde (0.45 g, 0.62 mmol, 1.0 equiv) was added to the reaction flask. The reaction mixture was refluxed for 5 h and then cooled to room temperature. Reaction mixture poured into distilled water and the organic layer was extracted with DCM. The organic layer was dried over magnesium sulfate, concentrated *in vacuo*, and purified by autocolumn (Hexanes) to give a yellow solid, **3c**: (0.34 g, 77%). ^{1}H NMR (DMSO-d_6, 500 MHz, δ, ppm): δ 8.68 (s, 2 H), 8.25 (s, 2 H), 7.90 (s, 2 H), 7.63-7.58 (t, 2 H), 6.18-6.14 (d, 2 H), 5.70-5.68 (d, 2 H), 4.54-4.50 (m, 4 H), 1.77-1.63 (m, 18 H), 1.31-1.23 (dt, 12 H).

Synthesis of 5,11-bis(2-ethylhexyl)-3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole

To a 25-mL, flame-dried, roundbottom flask, 3,9-dibromo-5,11-bis(2-ethylhexyl)-2,8-divinyl-5,11-dihydroindolo[3,2-*b*]carbazole (0.12 g, 0.16 mmol, 1.0 equiv) was dissolved in THF (4 mL) at -78°C. *n*-BuLi (0.22 mL, 2.1 equiv) was added dropwise to the reaction flask and the reaction mixture was stirred at -78°C for 1 h. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.077 mL, 0.38 mmol, 2.4 equiv) was added to the reaction flask and then stirred at room temperature for 24 h. The reaction mixture was poured in water, and the organic layer was extracted with DCM, dried over magnesium sulfate, and concentrated *in vacuo*. The product was purified via autocolumn (4:1, Hex:DCM) to give a yellow solid, **3d:** (50 mg, 38%). ^{1}H NMR (DMSO-d_6, 500 MHz, δ, ppm): δ 8.75 (s, 2 H), 8.29 (s, 2 H), 8.05-8.00 (dd, 2 H, J = 6 Hz, 9 Hz),

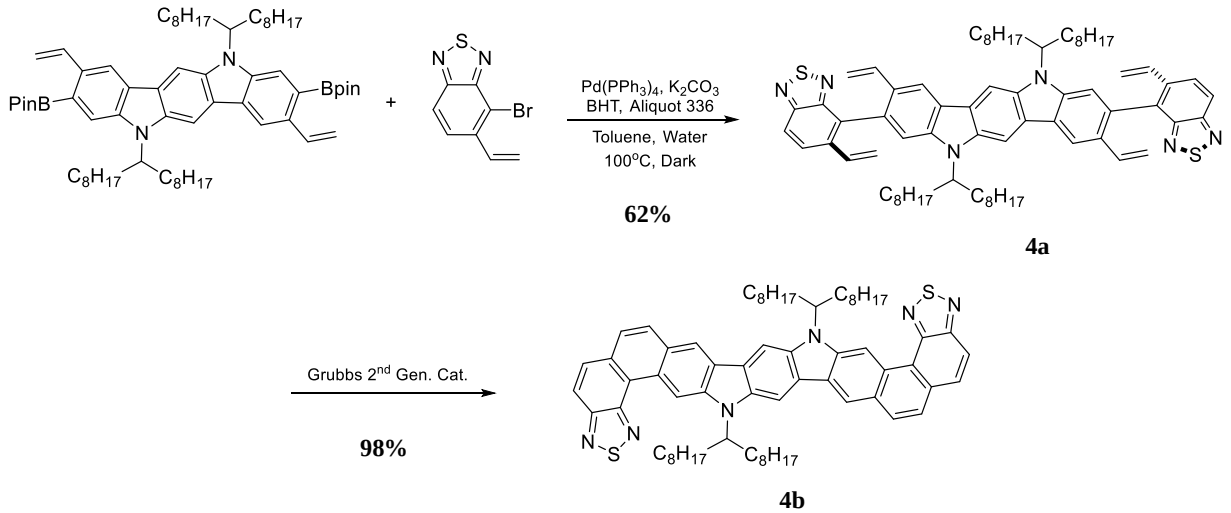
7.55 (s, 2 H), 6.14-6.11 (d, 2 H, *J* = 9 Hz), 5.55-5.52 (d, 2 H, *J* = 9 Hz), 4.64-4.53 (m, 4 H), 1.73-1.71 (m, 18 H), 1.26-1.19 (dt, 12 H).

CHAPTER IV

SMALL MOLECULE SYNTHESIS

Synthesis of small molecule with α-branched alkyl chain

Once the donor and acceptor units were successfully functionalized, Suzuki coupling at the 4-position of the acceptor unit and the 3,9-positions of the donor unit was performed in the presence of the palladium catalyst, $Pd(PPh_3)_4$. Due to the oxygen sensitivity of the palladium catalyst, the Suzuki coupling reaction was performed under inert atmosphere, to give the desired product with a 62% yield. After purification of the Suzuki coupling product via preparative gel permeation chromatography, the final step in the small molecule synthesis was the ring-closing olefin metathesis between the pendant vinyl groups of the donor and acceptor units. Scheme 5 shows the synthetic scheme utilized in the small molecule synthesis.

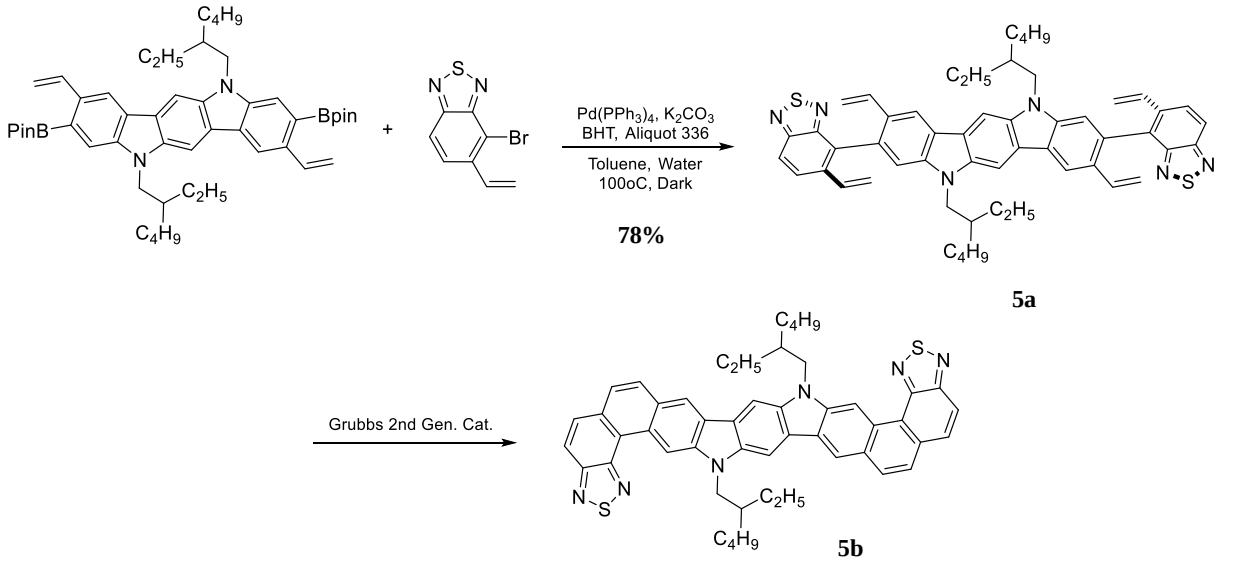


Scheme 5. Synthetic scheme utilized for the synthesis of the small molecule with α-branched alkyl chain, **4b**

The small molecule, **4b**, was obtained with a 98% yield, and characterized via ^{1}H NMR. The solubility of this small molecule was improved with the α-branched alkyl chain; however, the extensive length of the alkyl chain causes the small molecules packing structure to deviate from the desired π-π stacking. The α-branched alkyl chains installed onto the nitrogen atoms of the indolocarbazole backbone sufficiently disrupted the strong intermolecular interactions exhibited by this compound without a solubilizing chain, consequently, the packing structure of this small molecule is not suitable for OFET applications, but the corresponding D-A ladder polymer could still be a promising candidate in OPV devices.

Synthesis of small molecule with β-branched alkyl chain

Due to the fact that the small molecule containing the α-branched alkyl chain exhibiting an undesirable crystal packing structure, a β-branched ethylhexane alkyl chain was selected for use as a solubilizing chain. The β-branching point of this alkyl chain was proposed to be capable of increasing the solubility of the small molecule, but without disrupting the packing structure as in the small molecule containing the α-branched alkyl chain. The Suzuki coupling of the donor and acceptor units was performed in the same manner used previously for the synthesis of the small molecule with the α-branched alkyl chain. Ring-closing olefin metathesis was performed using the 2nd generation Grubbs catalyst. Scheme 6 shows the synthetic steps implemented to synthesize the target small molecule with the β-branched alkyl chain.



Scheme 6. Synthetic scheme utilized for the synthesis of the small molecule with β-branched alkyl chain, **5b**, was not isolated due to poor solubility and the yield could not be determined

The solubility issues that were observed in the synthesis of **3d** became even more significant for this small molecule synthesis, and this made the purification of the small molecule, **5b**, very difficult. Due to this solubility issue, the desired product was unable to be isolated via size exclusion (SEC) chromatography. However, the crude ^{1}H NMR spectrum of **5b** showed that the desired product was synthesized successfully. Although the synthesis of **5b** was completed successfully, it was found that the length of this β-branched ethylhexyl-alkyl chain was not sufficient for solubilizing the small molecule.

Experimental procedures for small molecule syntheses

The experimental procedures reported below indicate the methods utilized for the synthesis of compounds **4a**, **4b**, **5a**, and **5b**. Spectroscopic data for these compounds Spectroscopic data for these compounds were obtained using either a Varian Inova 300 MHz or Varian 500 MHz NMR Spectrometer. ^{1}H chemical shifts are reported as δ values in units of ppm relative to the solvent used, either $CDCl_3$ (7.26 ppm) or DMSO (2.50 ppm). Coupling constants (*J*) are reported in units

of Hertz (Hz), where multiplicities are assigned as the following: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), bs (broad singlet), or m (multiplet). ^{1}H NMR spectra of compounds **4a**, **4b**, **5a**, and **5b** are located in Appendix A, and correspond to Figures A14-A17.

Synthesis of 4,4'-(5,11-di(heptadecan-9-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole-3,9-diyl)bis(5-vinylbenzo[c][1,2,5]thiadiazole)

To a flame-dried Schlenk flask, 5,11-di(heptadecan-9-yl)-3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-*b*]carbazole (50 mg, 0.048 mmol, 1.0 equiv), 4-bromo-5-vinylbenzo[*c*][1,2,5]thiadiazole (29 mg, 0.12 mmol, 2.4 equiv), potassium carbonate (40 mg, 0.29 mmol, 6.0 equiv), aliquat 336 (1 drop), and BHT (several crystals) were added to the reaction flask. $Pd(PPh_3)_4$ (6 mg, 0.005 mmol, 0.1 equiv) was added to the reaction flask in a glove box. Degassed toluene (3 mL) and distilled water (0.6 mL) were added to the reaction flask which was then degassed by freezing in liquid N_2, removing gas under vacuum, and thawing (3x). The reaction flask was then stirred at 100°C for 24 h under N_2. The reaction was quenched with distilled water, and the organic layer was extracted with DCM, dried over magnesium sulfate and concentrated *in vacuo*. The resulting solid was purified once by autocolumn (2:1, Hex:DCM) and further purified by preparative gel phase chromatography to give **4a**: (36 mg, 62%), ^{1}H NMR ($CDCl_3$-d_1, 500 MHz, δ, ppm): δ 8.62-8.60 (d, 2 H, J = 6 Hz), 8.28-8-25 (d, 2 H, J = 9 Hz), 8.15-8.12 (d, 2 H, J = 9 Hz), 8.05 (m, 4 H), 6.42-6.36 (q, 2 H), 5.94-5.91 (d, 2 H, J = 9 Hz), 5.81-5.79 (d, 2 H, J = 9 Hz), 5.33-5.31 (d, 2 H, J = 6 Hz), 4.99-4.97 (d, 2 H, J = 6 Hz), 2.51 (m, 2 H).

Synthesis of 10,21-di(heptadecan-9-yl)-10,21-dihydro-[1,2,5]thiadiazolo[3',4':7,8]naphtho[1,2-b][1,2,5]thiadiazolo[4'',3'':7',8']naphtho[2',1':5,6]indolo[2,3-h]carbazole

4,4'-(5,11-di(heptadecan-9-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole-3,9-diyl)bis(5-vinylbenzo[c][1,2,5]thiadiazole) (31 mg, 0.028 mmol, 1.0 equiv) and 2nd generation Grubbs (4 mg, 0.005 mmol, 0.20 equiv) catalyst were dissolved in degassed toluene (2 mL) under N_2. In a separate flask, the remaining 2nd generation Grubbs catalyst (10 mg, 0.012 mmol, 0.40 equiv) was dissolved in degassed toluene (2 mL). The reaction flask was stirred and refluxed for 4 h, and the Grubb's catalyst solution was added to the reaction flask via syringe-pump, **4b**: (29 mg, 98%); ($CDCl_3$-*d*$_1$, 500 MHz, δ, ppm): δ 10.92 (s, 1 H), 10.74 (s, 1 H), 8.90 (m, 4 H), 8.38-8.36 (d, 4 H, *J* = 6 Hz), 7.83 (m, 4 H).

Synthesis of 4,4'-bis(2-ethylhexyl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole-3,9-diyl)bis(5-vinylbenzo[c][1,2,5]thiadiazole)

To a flame-dried Schlenk flask, 5,11-di(heptadecan-9-yl)-3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-*b*]carbazole (50 mg, 0.048 mmol, 1.0 equiv), 4-bromo-5-vinylbenzo[*c*][1,2,5]thiadiazole (29 mg, 0.12 mmol, 2.4 equiv), potassium carbonate (40 mg, 0.29 mmol, 6.0 equiv), aliquat 336 (1 drop), and BHT (several crystals) were added to the reaction flask. $Pd(PPh_3)_4$ (6 mg, 0.005 mmol, 0.1 equiv) was added to the reaction flask in a glove box. Degassed toluene (3 mL) and distilled water (0.6 mL) were added to the reaction flask which was then degassed by freezing in liquid N_2, removing gas under vacuum, and thawing (3x). The reaction flask was then stirred at 100°C for 24 h under N_2. The reaction was quenched with distilled water, and the organic layer was extracted with DCM, dried over magnesium sulfate and concentrated *in vacuo*. The resulting solid was purified once by

autocolumn (2:1, Hex:DCM) and further purified by preparative gel phase chromatography to give 4,4'-(5,11-di(heptadecan-9-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole-3,9-diyl)bis(5-vinylbenzo[c][1,2,5]thiadiazole), **5a**: (36 mg, 78%), ^{1}H NMR (DMSO-d_6, 500 MHz, δ, ppm): δ 8.91 (s, 2 H), 8.36 (s, 6 H), 7.60-7.57 (m, 4 H), 7.54-7.53 (d, 2 H, *J* = 3 Hz), 7.05-7.01 (m, 2 H), 6.73-6.68 (m, 2 H), 6.26-6.22 (d, 2 H), 6.12-6.09 (d, 2 H, *J* = 9 Hz), 5.63-5.62 (d, 2 H, *J* = 3 Hz), 5.31-5.29 (d, 2 H, *J* = 3 Hz).

Synthesis of 10,21-bis(2-ethylhexyl)-10,21-[1,2,5]thiadiazolo[3',4':7,8]naphtho[1,2-b][1,2,5]thiadiazolo[4'',3'':7',8']naphtho[2',1':5,6]indolo[2,3-h]carbazole

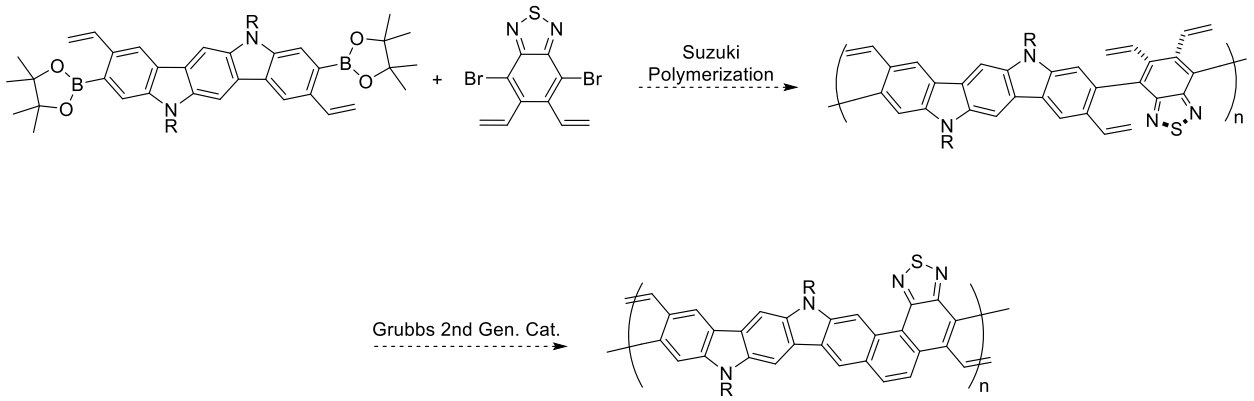
4,4'-(5,11-di(heptadecan-9-yl)-2,8-divinyl-5,11-dihydroindolo[3,2-b]carbazole-3,9-diyl)bis(5-vinylbenzo[c][1,2,5]thiadiazole) (31 mg, 0.028 mmol, 1.0 equiv) and 2nd generation Grubbs (4 mg, 0.005 mmol, 0.20 equiv) catalyst were dissolved in degassed toluene (2 mL) under N_2. In a separate flask, the remaining 2nd generation Grubbs catalyst (10 mg, 0.012 mmol, 0.40 equiv) was dissolved in degassed toluene (2 mL). The reaction flask was stirred and refluxed for 4 h, and the Grubb's catalyst solution was added to the reaction flask via syringe-pump, **5b**.

CHAPTER VI

CONCLUSION

The A-D-A small molecule containing the α-branched alkyl chain was synthesized successfully with a 98% yield. The small molecule was characterized via ^{1}H NMR; however, it was discovered that the length of the solubilizing chain was too long for the π-π stacking interactions to remain intact, making this molecule insufficient for applications in OFET devices. The small molecule with the α-branched alkyl chain could still be utilized in OPV devices, but further studies would be necessary, and the corresponding polymer would need to be synthesized.

The poor solubility of the small molecule with the β-branched alkyl chain made the isolation of this compound unachievable, therefore, the final yield of this product could not be obtained. The crude ^{1}H NMR spectrum of this small molecule did confirmed it was synthesized successfully, but isolation was not feasible. Future studies of different β-branched alkyl chains that are either longer, or with bulkier side groups, could provide the necessary disruption of intermolecular interactions in the small molecule and provide sufficient solubility for solution processing in the future. The proposed polymerization scheme is shown in Scheme 7, where the R groups represent a solubilizing alkyl chain to be tested in the future.



Scheme 7. Proposed polymerization of the difunctionalized acceptor unit, with the functionalized donor unit, where R represents a solubilizing alkyl chain to be used in the future

Once the proper solubilizing chain is discovered, polymerization of the donor and acceptor units to give an indolo[3,2-*b*]carbazole-based D-A ladder polymer, represented in Scheme 7, that can eventually undergo solution processing techniques for OPV device applications will be synthesized.[3] Any solubility issues present in the small molecule are likely to be much more pronounced after polymerization, so achieving good solubility is extremely important. In general, ladder polymers possess a variety of desirable qualities for OPV or OFET applications, but more research must be dedicated towards the solubilizing chains for indolo[3,2-*b*]carbazole based polymers is needed to make these materials a more desirable candidate for OPV and OFET device applications.

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APPENDIX A

SPECTROSCOPIC DATA

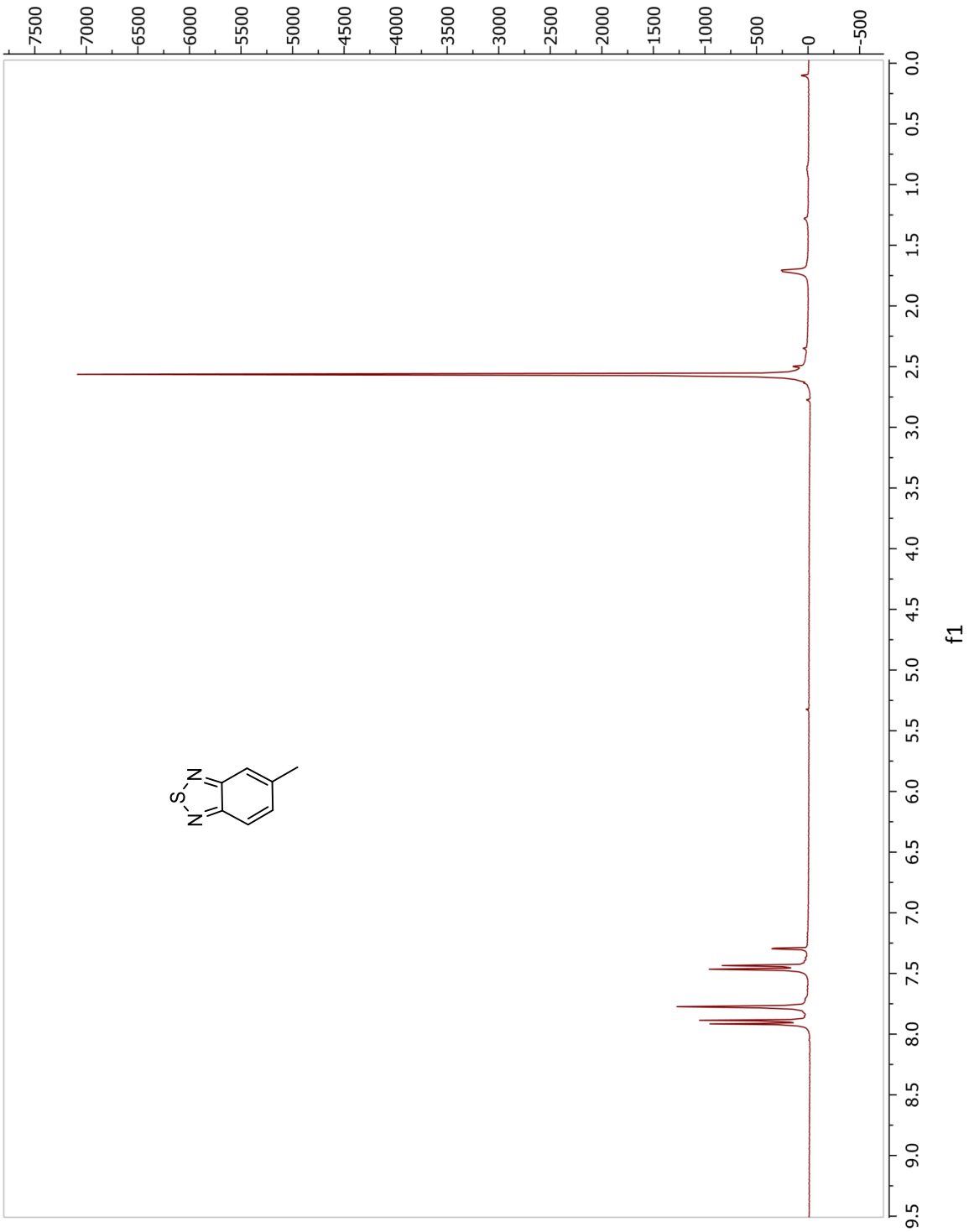

Figure A1. ^{1}H NMR spectrum of **1a** in $CDCl_3$ using 300 MHz NMR spectrometer

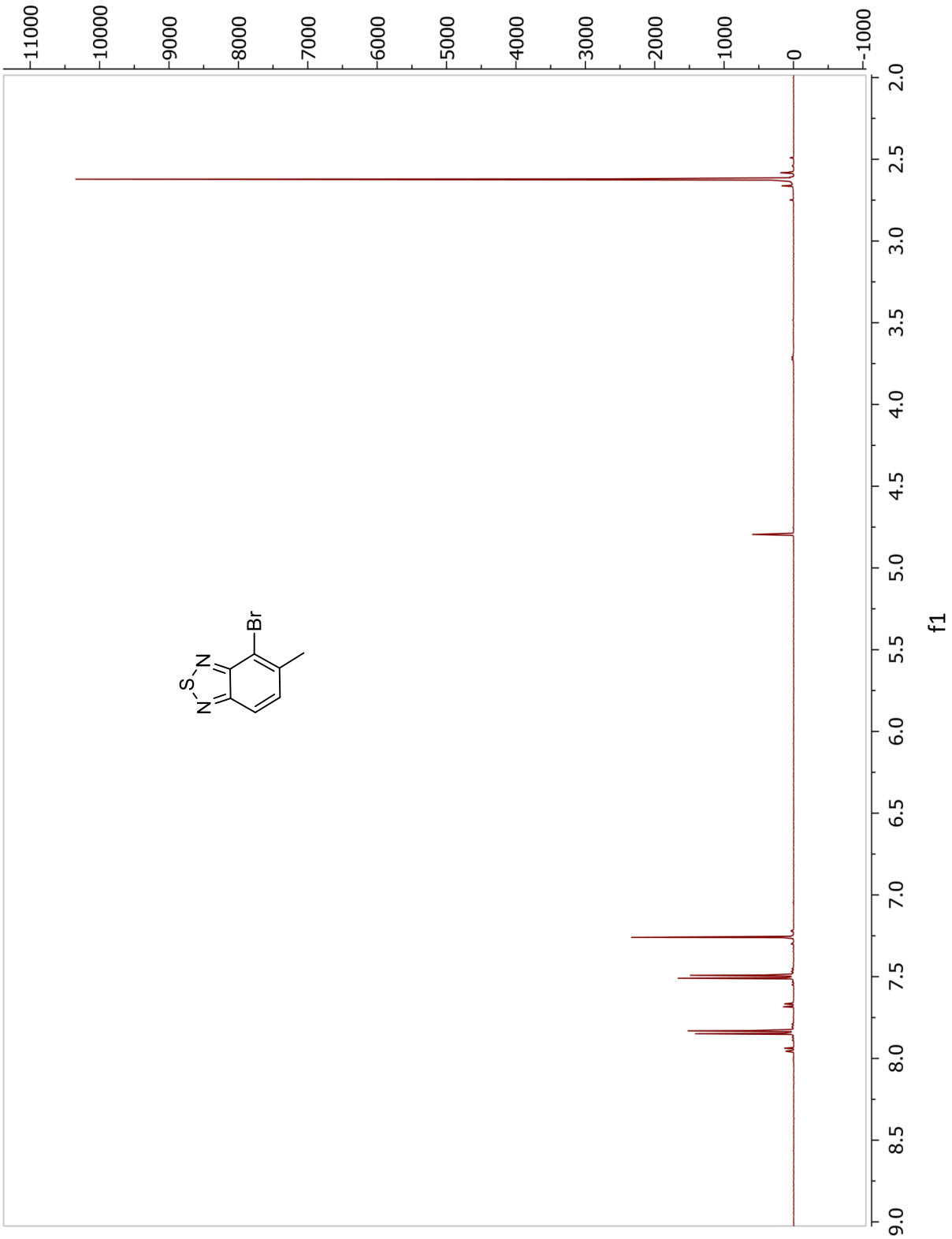

Figure A2. ^{1}H NMR spectrum of **1b** in $CDCl_3$ using 300 MHz NMR spectrometer

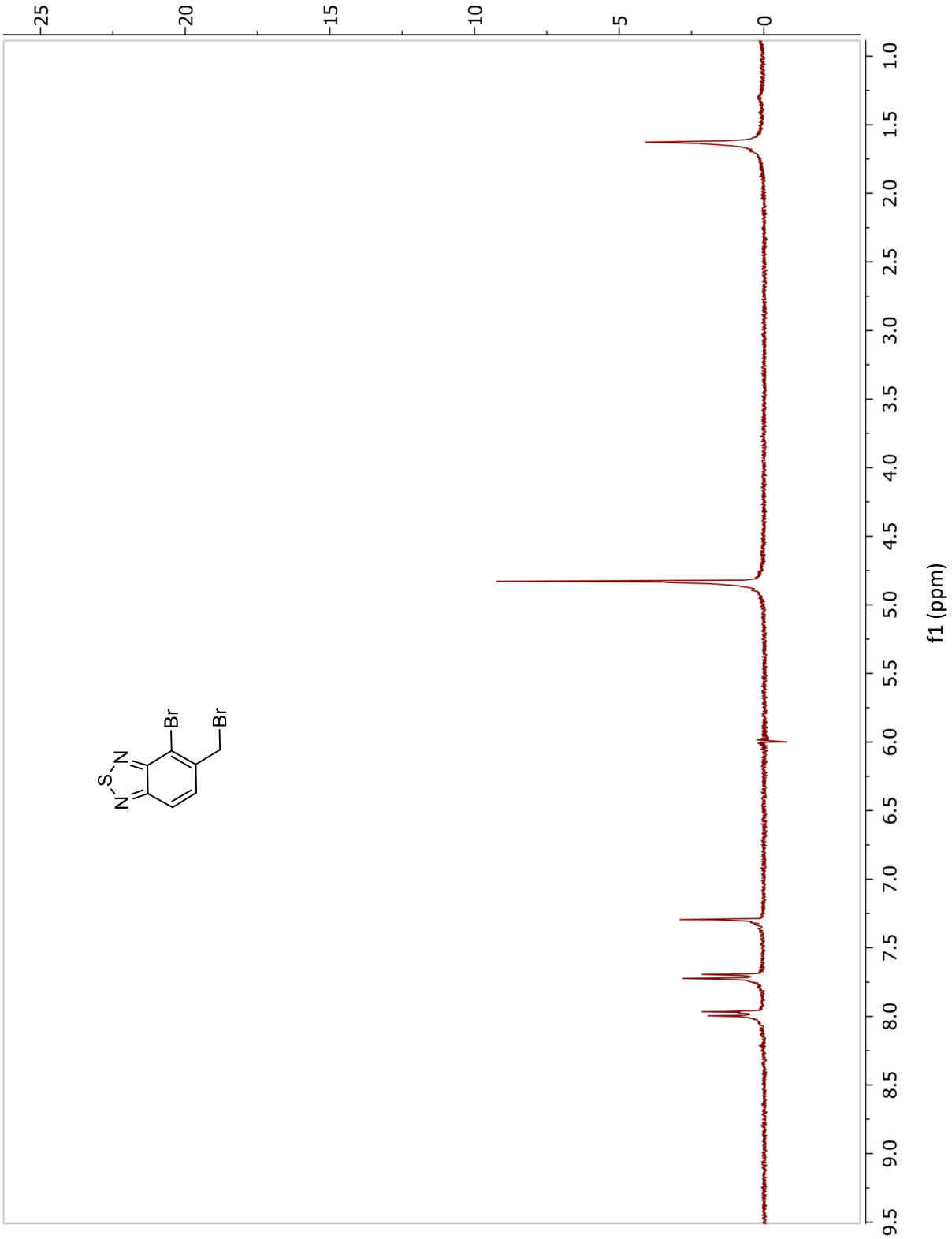

Figure A3. ^{1}H NMR spectrum of **1c** in $CDCl_3$ using 300 MHz NMR spectrometer

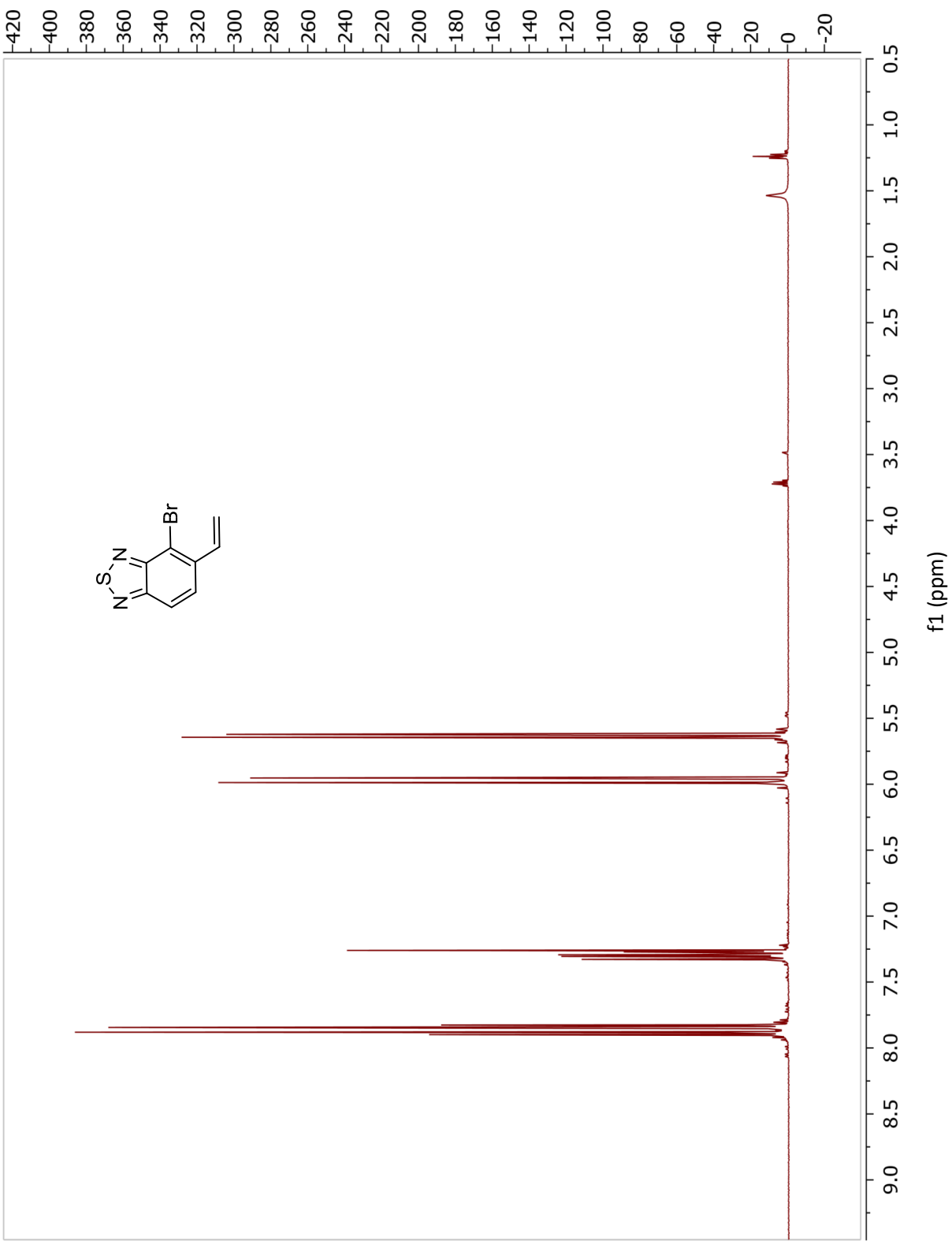

Figure A4. ^{1}H NMR spectrum of **1d** in $CDCl_3$ using 300 MHz NMR spectrometer

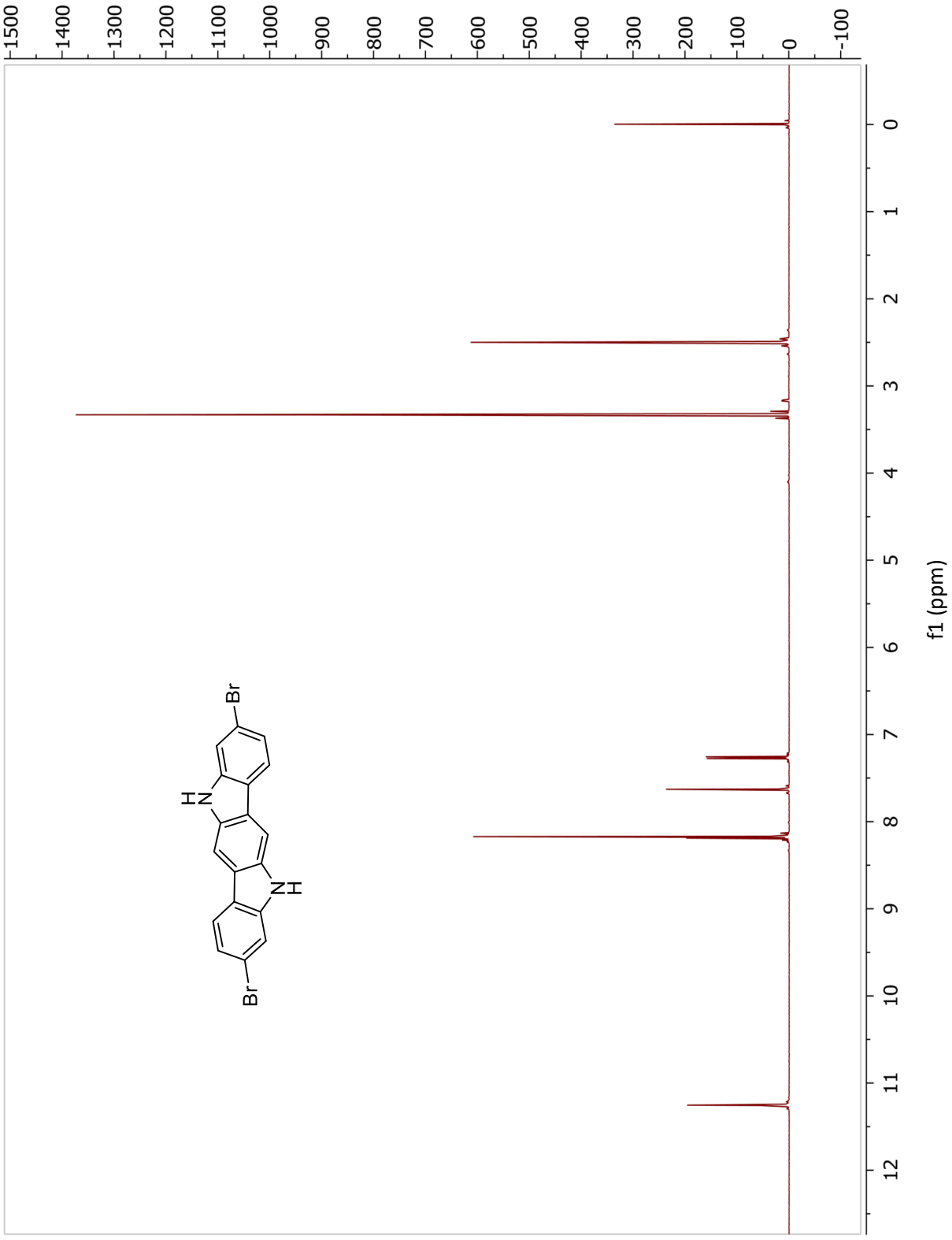

Figure A5. ^{1}H NMR spectrum of **2** in DMSO using 500 MHz NMR spectrometer

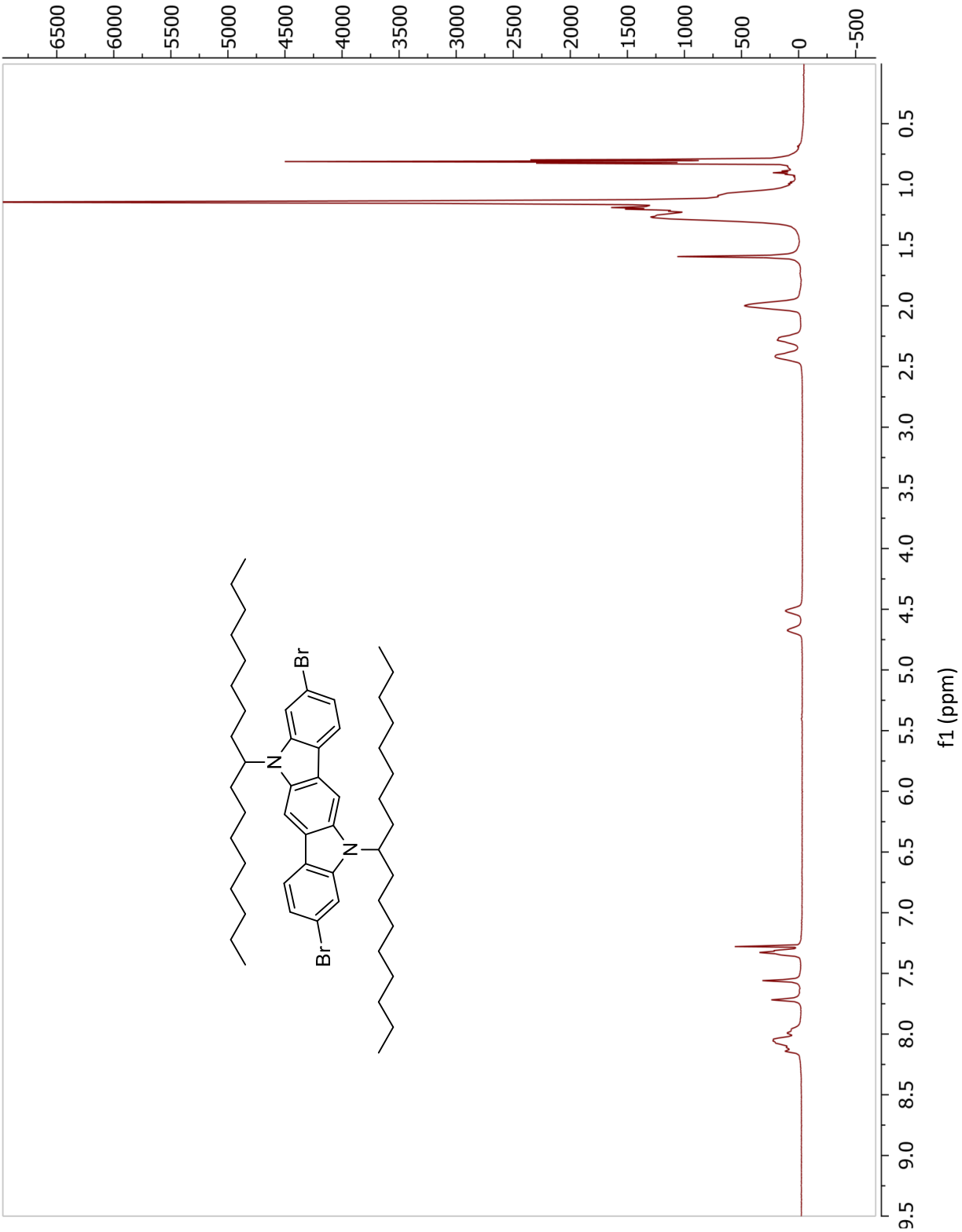

Figure A6. ^{1}H NMR spectrum of **2a** in $CDCl_3$ using 300 MHz NMR spectrometer

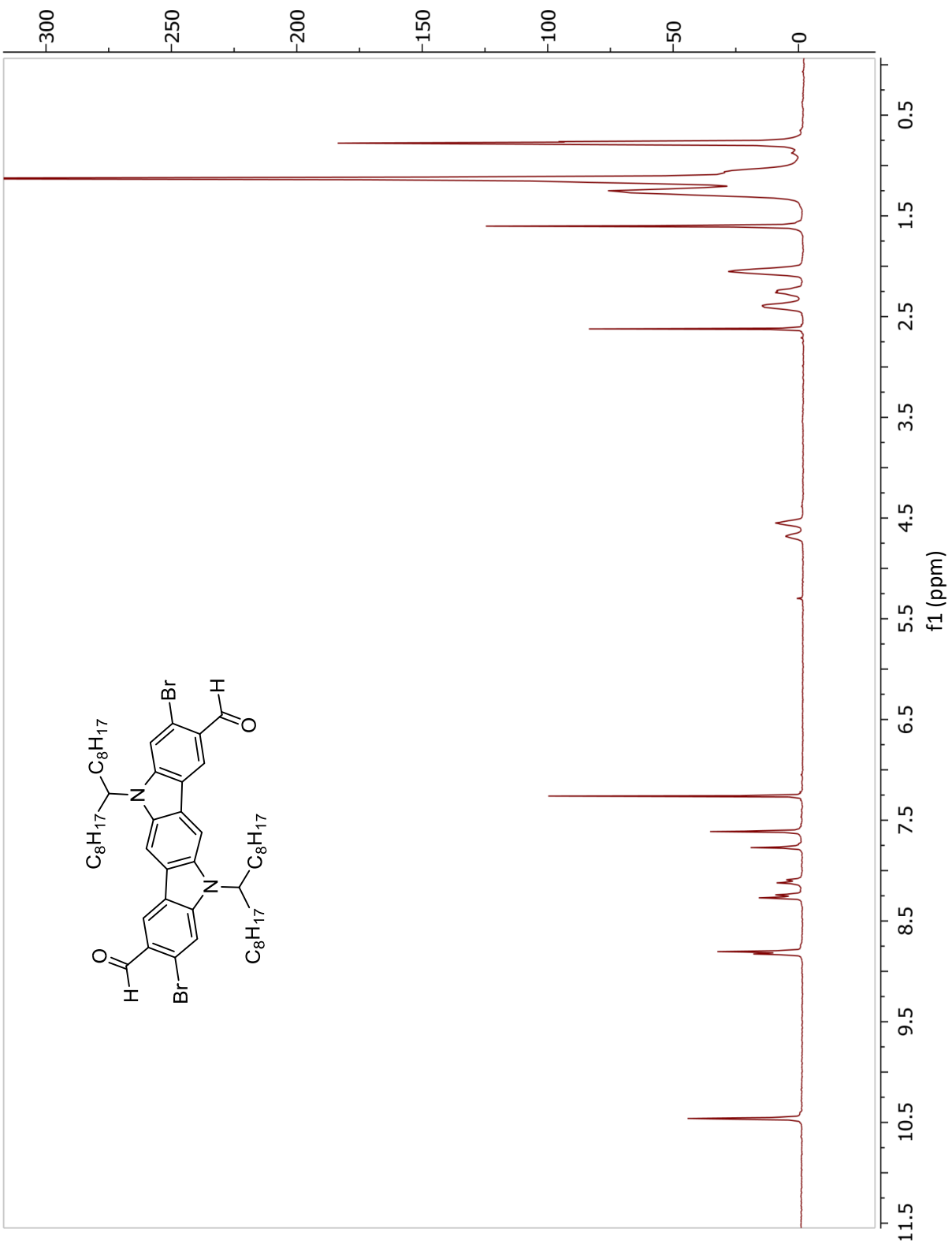

Figure A7. ^{1}H NMR spectrum of **2b** in $CDCl_3$ using 500 MHz NMR spectrometer

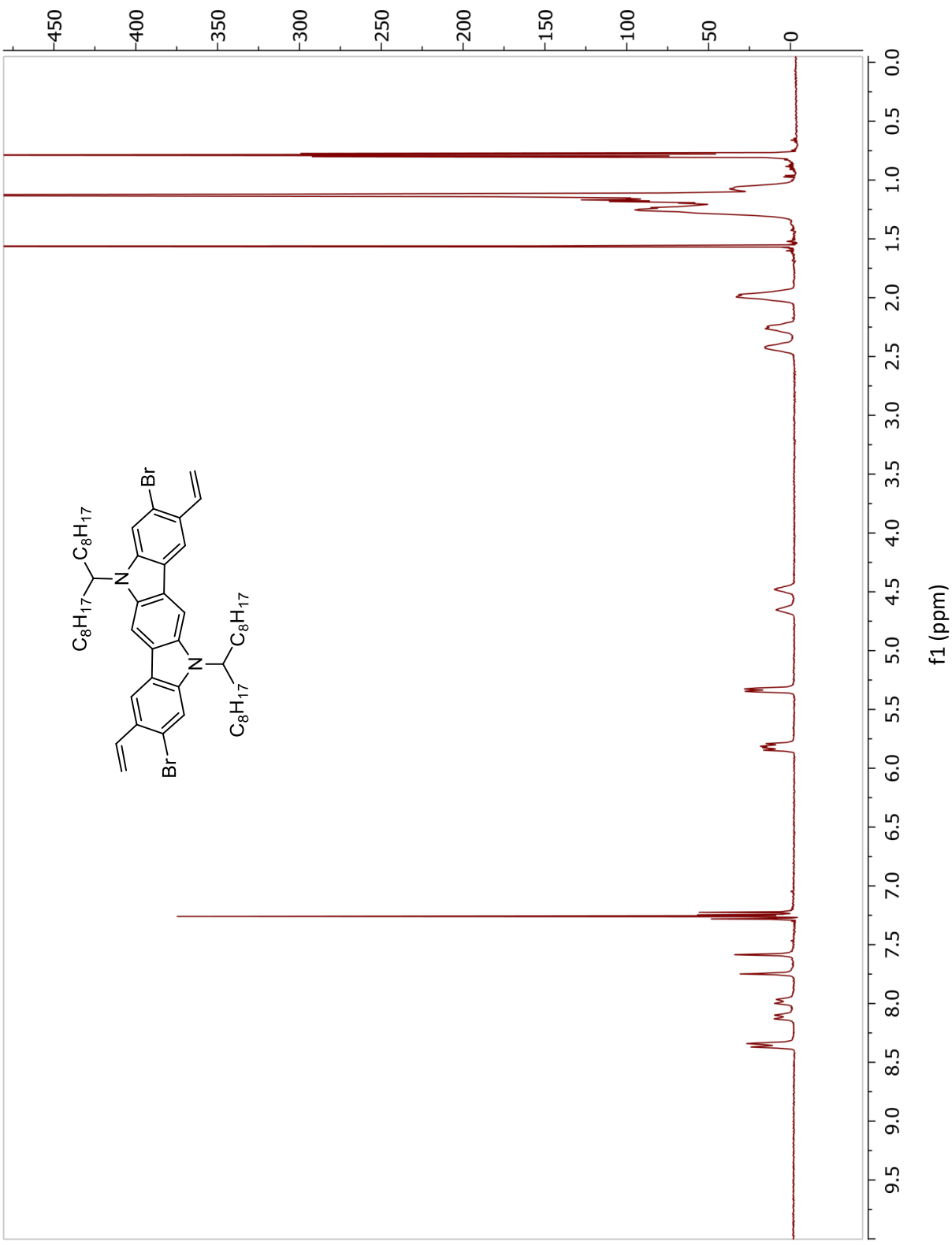

Figure A8. ^{1}H NMR spectrum of **2c** in $CDCl_3$ using 500 MHz NMR spectrometer

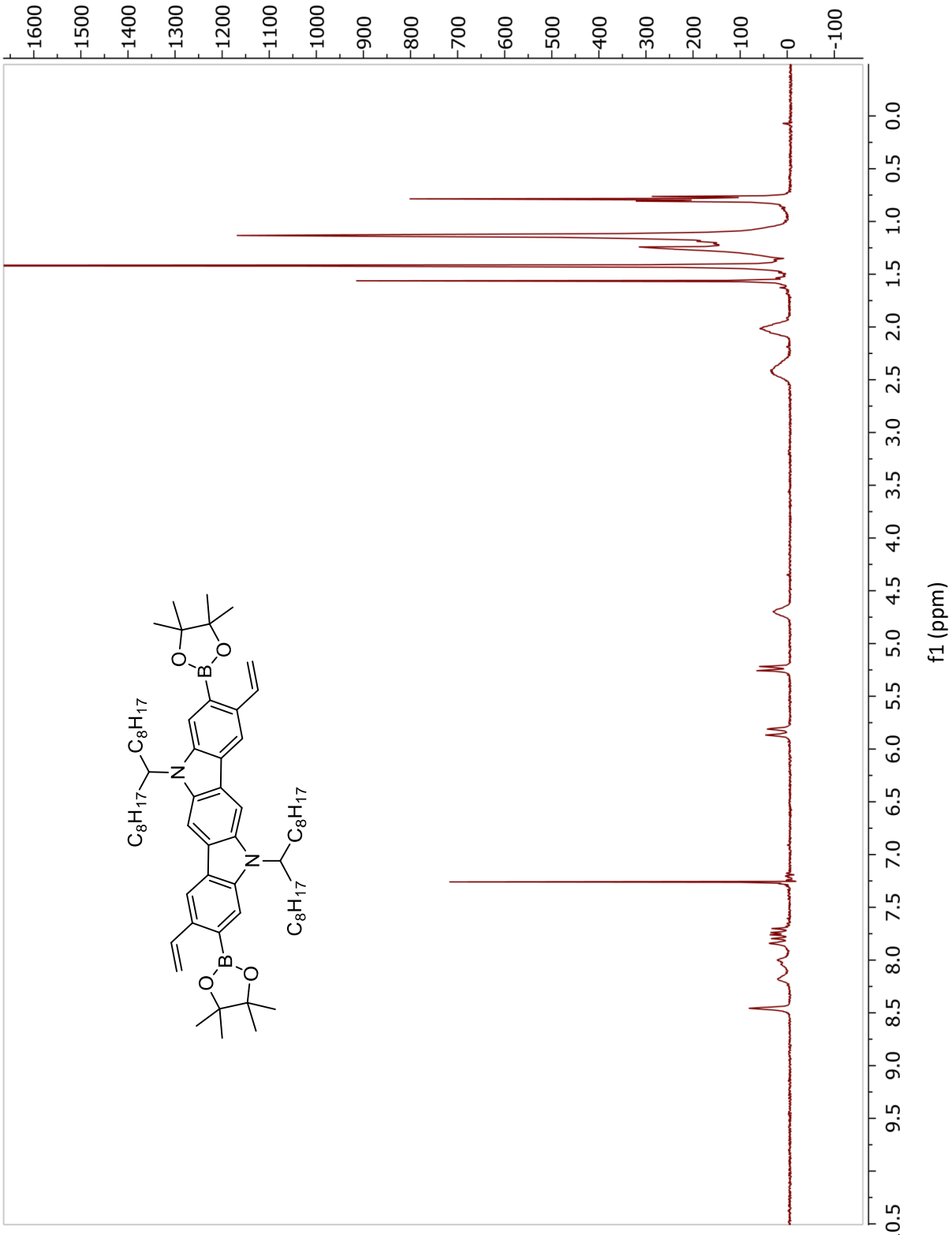

Figure A9. ^{1}H NMR spectrum of **2d** in $CDCl_3$ using 500 MHz NMR spectrometer

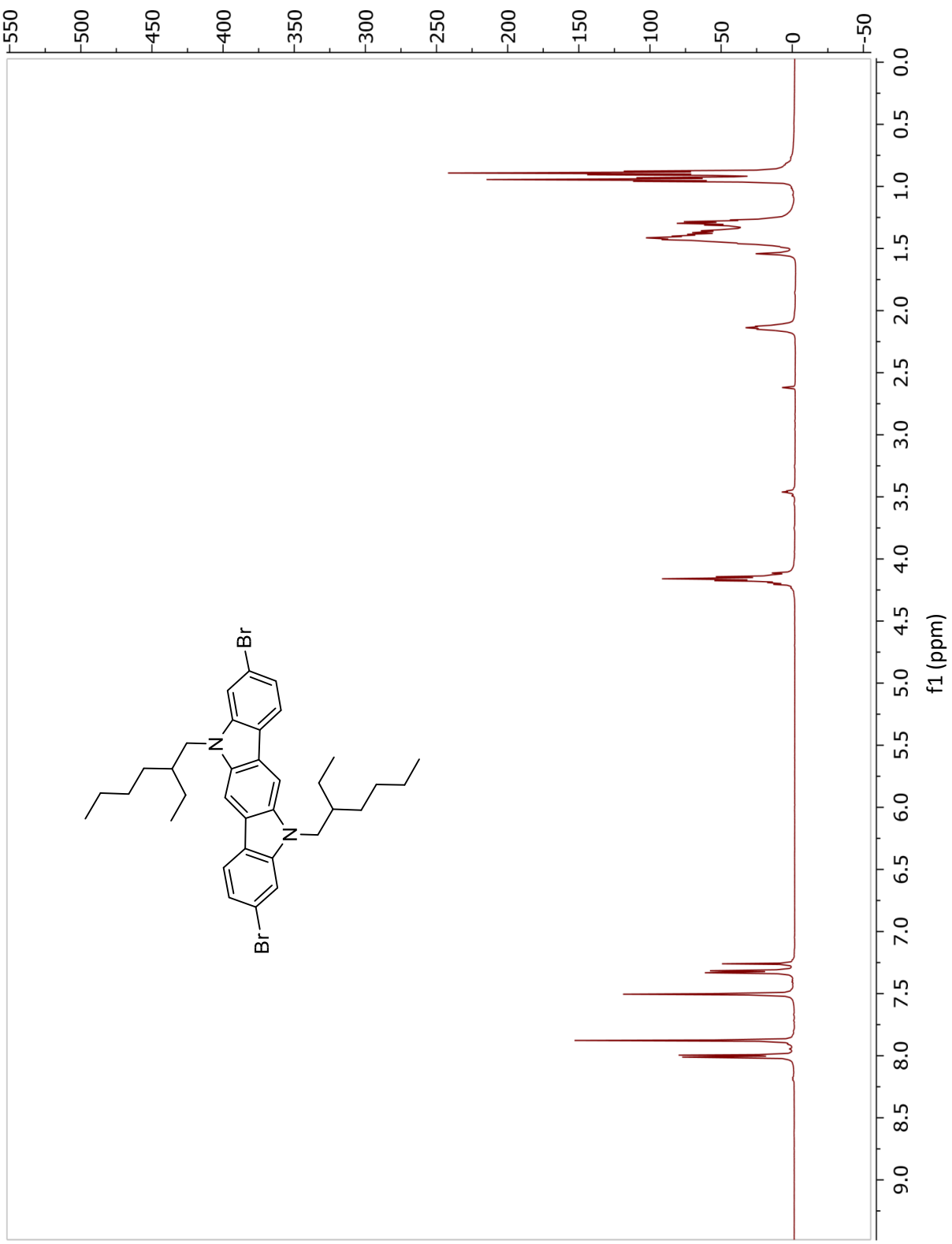

Figure A10. ^{1}H NMR spectrum of **3a** in $CDCl_3$ using 500 MHz NMR spectrometer

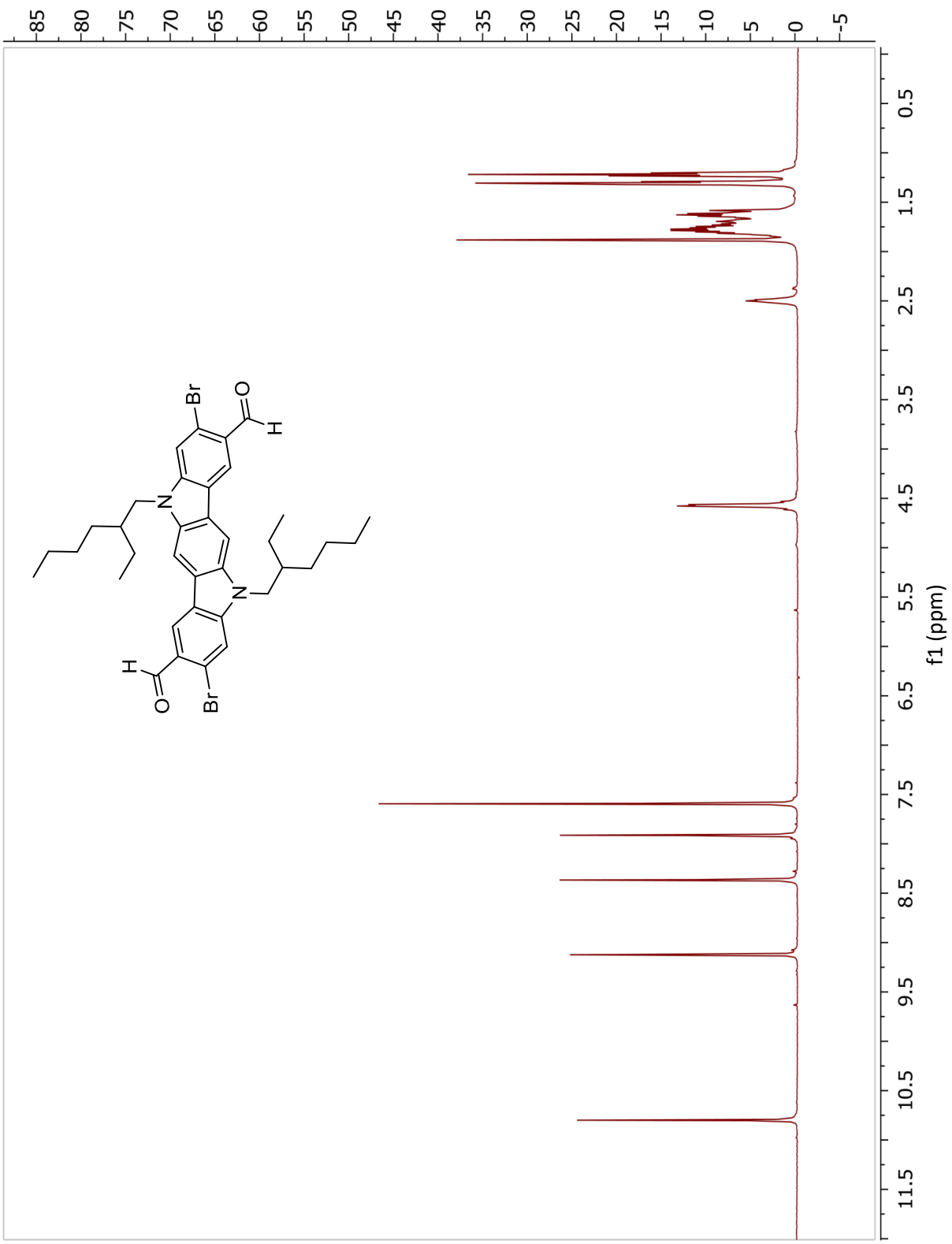

Figure A11. [1]H NMR spectrum of **3b** in DMSO using 500 MHz NMR spectrometer

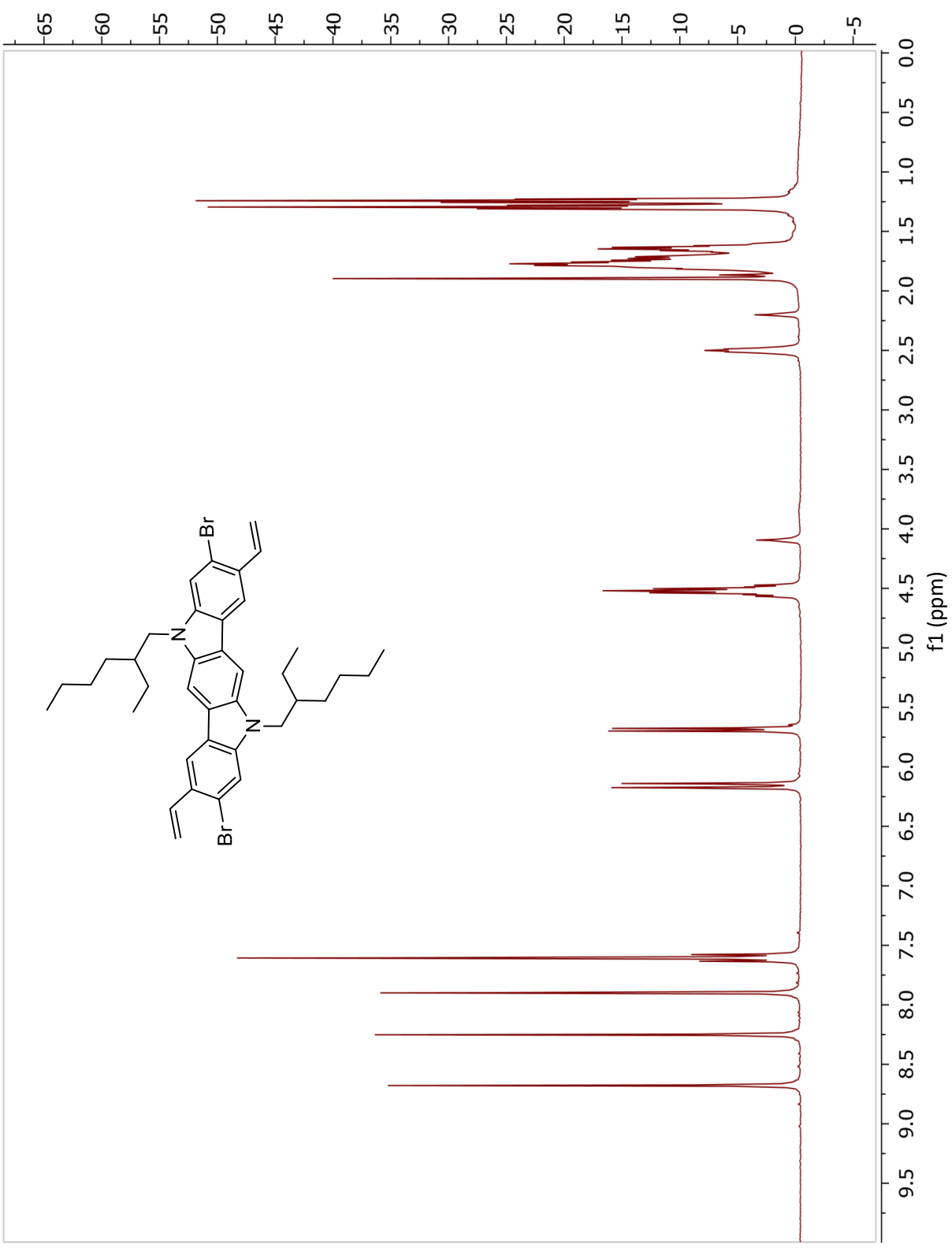

Figure A12. [1]H NMR spectrum of **3c** in DMSO using 500 MHz NMR spectrometer

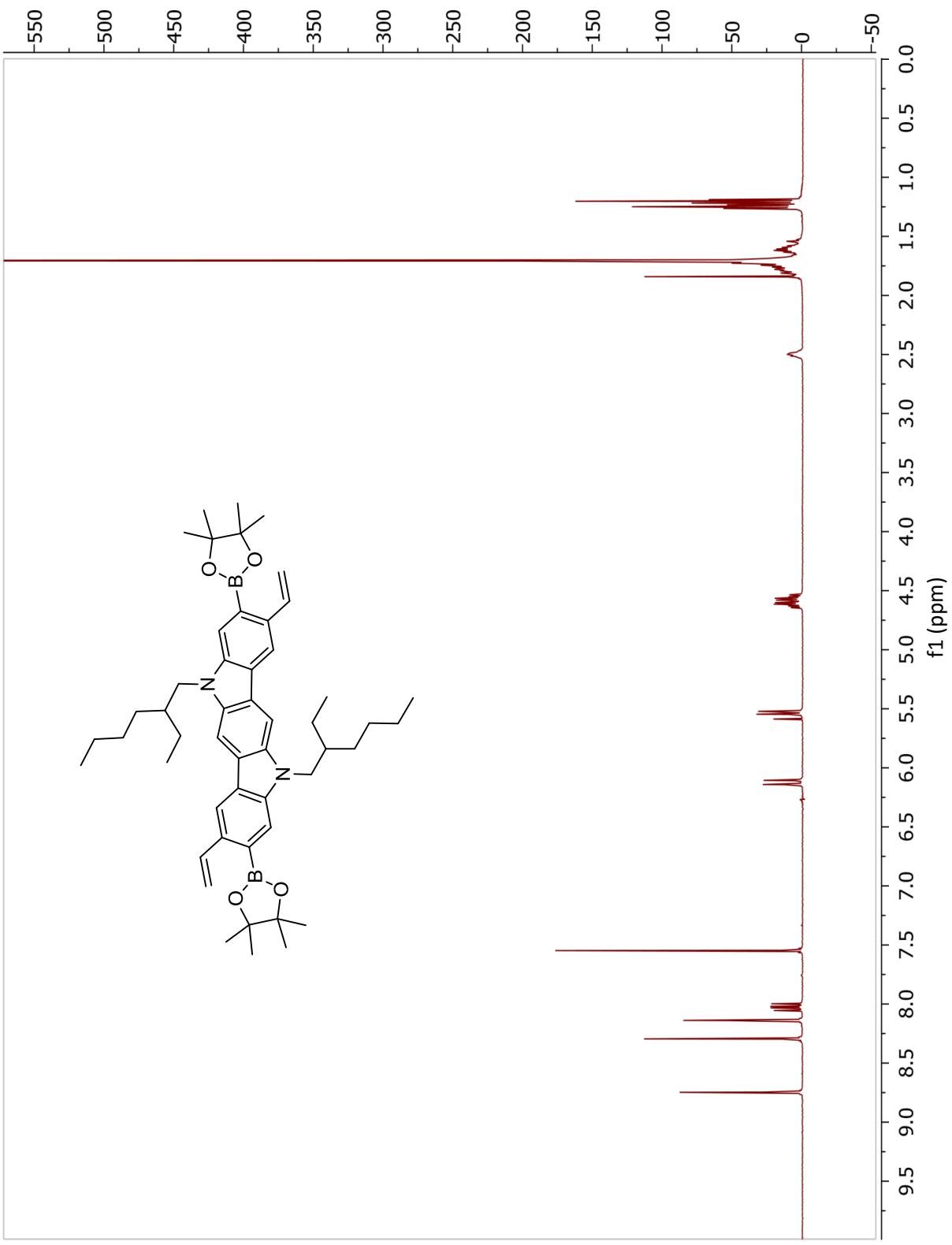

Figure A13. ^{1}H NMR spectrum of **3d** in DMSO using 500 MHz NMR spectrometer

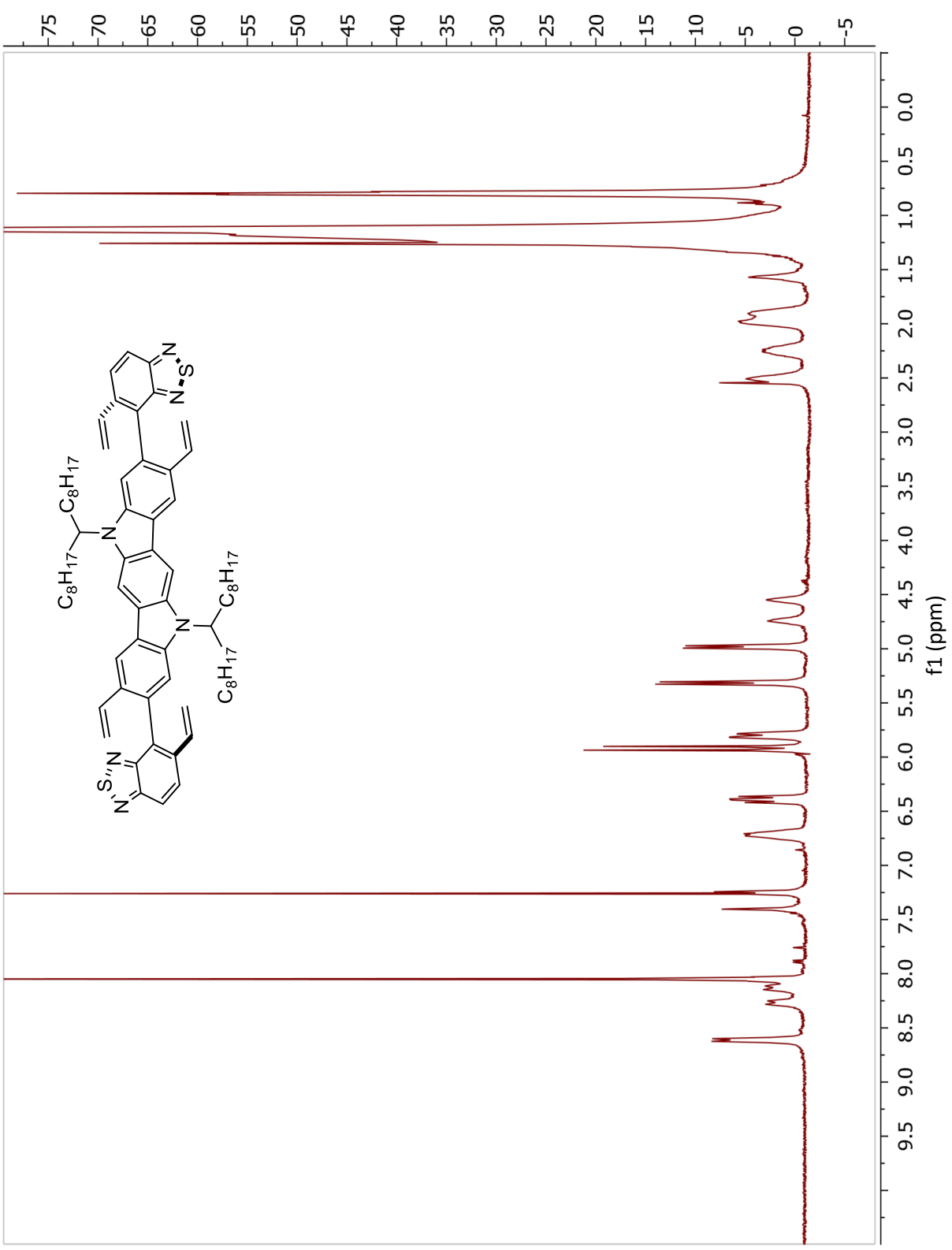

Figure A14. ^{1}H NMR spectrum of **4a** in $CDCl_3$ using 500 MHz NMR spectrometer

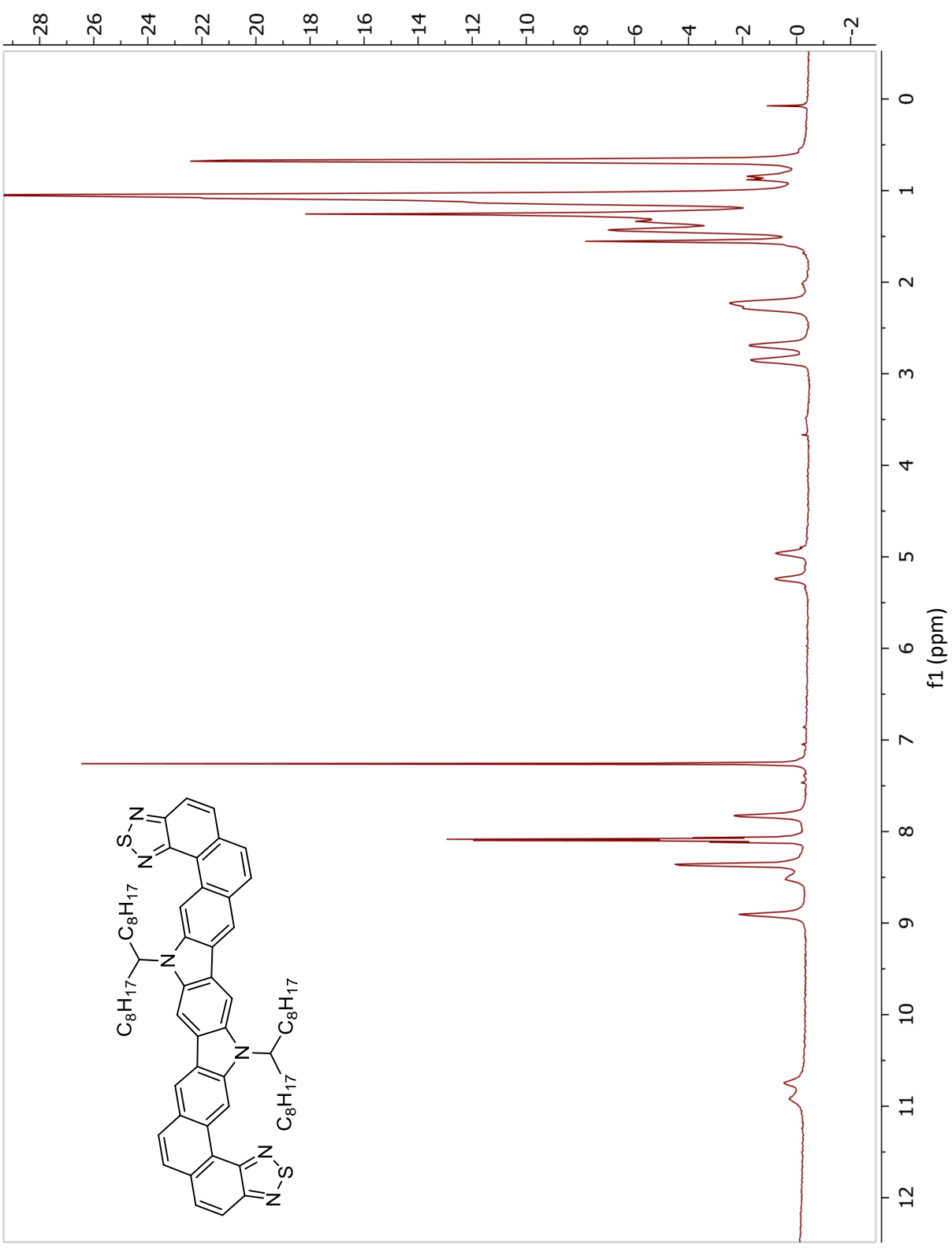

Figure A15. ^{1}H NMR spectrum of **4b** in $CDCl_3$ using 500 MHz NMR spectrometer

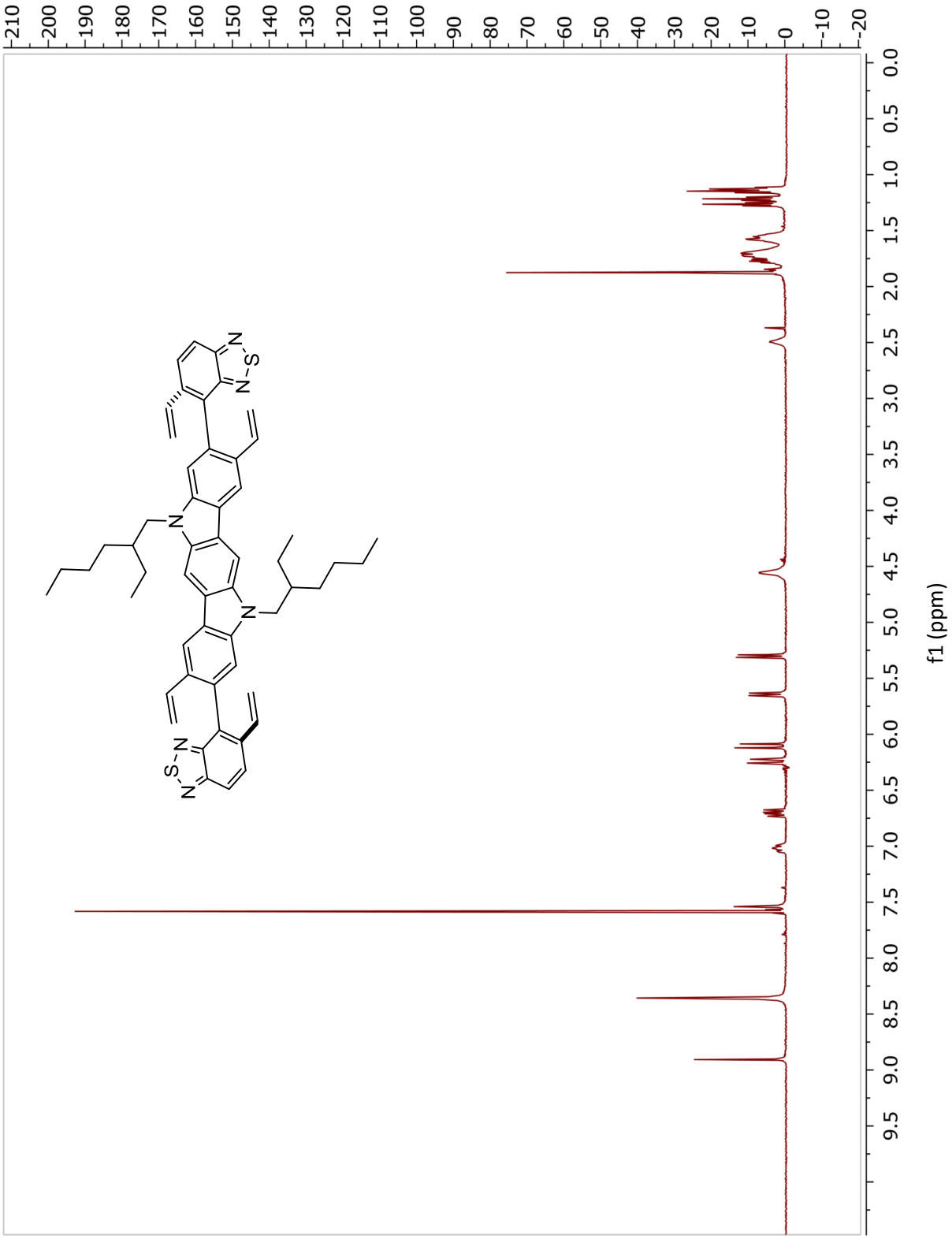

Figure A16. ^{1}H NMR spectrum of **5a** in DMSO using 500 MHz NMR spectrometer

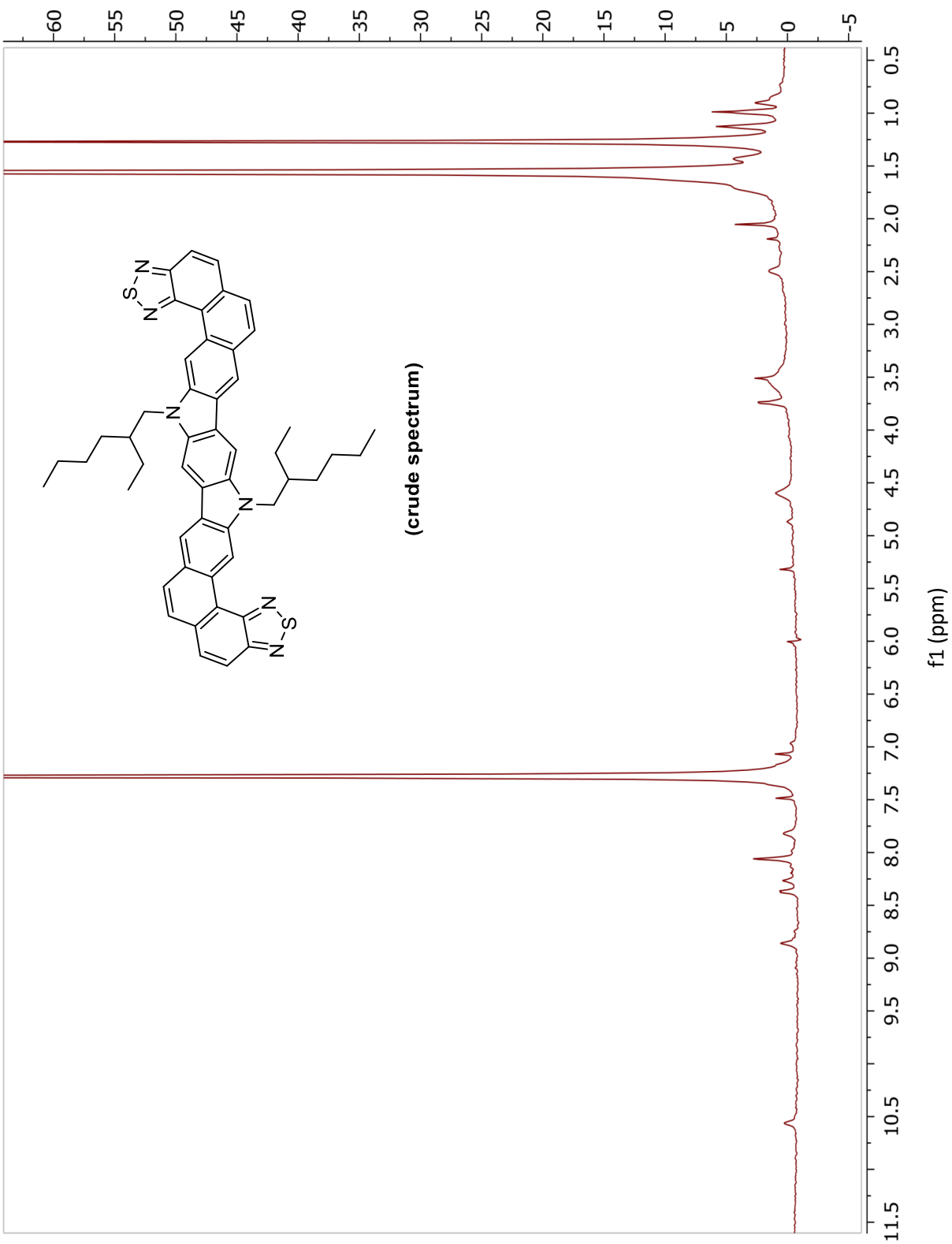

Figure A17. Crude ^{1}H NMR spectrum of **5b** in DMSO using 500 MHz NMR spectrometer