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Electrochemical Aziridination of Internal Alkenes with Primary Amines

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Aziridines are useful synthetic building blocks, widely employed for the preparation of various nitrogen-containing derivatives. As the current methods require the use of prefunctionalized amines, the development of a synthetic strategy towards aziridines, that can establishe the union of alkenes and amines, would be of great synthetic value. Herein, we report an electrochemical approach, which realizes this concept via an oxidative coupling between alkenes and primary alkyl amines. The reaction is carried out in an electrochemical flow reactor, leading to short reaction times (5 min), high yields and broad scope. At the cathode, hydrogen is generated, which can be used in a second reactor to reduce the aziridine, yielding the corresponding hydroaminated product. Mechanistic investigations and DFT calculations revealed that the alkene is first anodically oxidized and subsequently reacted with the amine coupling partner.

Electrochemical Aziridination of Internal Alkenes with Primary Amines

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ABSTRACT: Aziridines are useful synthetic building blocks, widely employed for the preparation of various nitrogen-containing derivatives. As the current methods require the use of prefunctionalized amines, the development of a synthetic strategy towards aziridines, that can establishe the union of alkenes and amines, would be of great synthetic value. Herein, we report an electrochemical approach, which realizes this concept via an oxidative coupling between alkenes and primary alkyl amines. The reaction is carried out in an electrochemical flow reactor, leading to short reaction times (5 min), high yields and broad scope. At the cathode, hydrogen is generated, which can be used in a second reactor to reduce the aziridine, yielding the corresponding hydroaminated product. Mechanistic investigations and DFT calculations revealed that the alkene is first anodically oxidized and subsequently reacted with the amine coupling partner.

Aziridines are a synthetically useful class of three-membered *N*-containing saturated heterocycles, which play an essential role in the preparation of different nitrogen-containing derivatives.[1] Despite their remarkable reactivity, imparted by the ring-strain (28 kcal mol^{-1}), aziridines are also present in many pharmacologically active natural products, such as antibiotics and anticancer agents.[2] Consequently, the development of new methods to prepare aziridine structural motifs remains a contemporary subject of interest to synthetic organic chemists. Promising results have been obtained for the synthesis of both racemic and enantiomerically-enriched aziridines,[3] which can be essentially categorized in three main categories: i) addition of a nitrogen-containing moiety to an alkene, ii) addition of substituted carbenes to a C=N bond, and iii) cyclization of 2-haloamines or 2-aminoalcohols.[1a] Amongst these different approaches,[4] the addition of a nitrogen-containing reagent to an alkene is the most popular due its efficiency and versatility.[5] However, most of these methodologies require the use of a transition metal catalyst, such as copper,[6] rhodium,[7] gold,[8] cobalt,[9] iron[10] or palladium,[11] in combination with a suitable and activated nitrene precursor, such as iminoiodinanes and organic azides (Figure 1A).[12]

In order to foster more sustainable and transition-metal free alternatives, new strategies to access aziridines have been devised using electrochemical activation (Figure 1B).[13] Yudin and coworkers developed an electrochemical aziridination, which uses *N*-amino-phthalimide as the source of electrophilic nitrogen.[2b, 14] An iodide-mediated electrocatalytic variant of this protocol was realized by Little, Zheng, and coworkers.[15] Recently, Cheng *et al.* established an electrochemical strategy, which utilizes a trifluoromethylated sulfamate as coupling partner.[16]

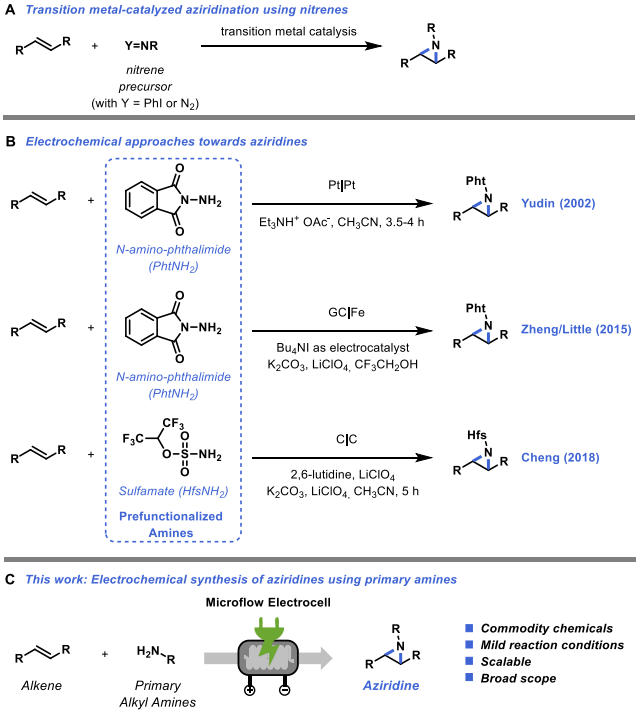


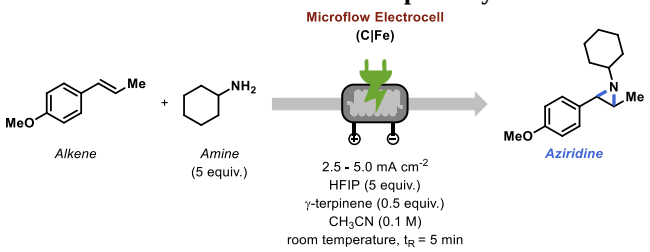
Figure 1. Development of an electrochemical synthesis of aziridines starting from alkenes and primary alkyl amines. (A) Transition metal-catalyzed aziridination of alkenes with nitrene precursors. (B) Established synthetic routes for the synthesis of aziridines using electrochemistry. (C) Electrochemical synthesis of aziridines using primary alkyl amines as aminating reagents.

Despite the synthetic value of these electrochemical and other approaches towards aziridines, the scope of the nitrogen-containing coupling partners remains restricted to a limited set of prefunctionalized amines, either $PhtNH_2$ or $HfsNH_2$ (Figure 1B). It is, however, manifest that an electrochemical coupling between olefins and amines would be of significant value given the broad availability and the low cost of these building blocks (Figure 1C). Such a strategy would also remove the requirement for substrate prefunctionalization, thereby increasing the atom efficiency of the transformation while expanding the scope of available molecular fragments. Based on recent work from our lab involving the electrochemical synthesis of sulfonamides[17] and sulfonyl fluorides,[18] we surmised that direct electrochemical activation of either olefins or amines via anodic oxidation might enable the expedient formation of a carbon-nitrogen bond, eventually leading to the targeted aziridines. Herein, we report on our efforts to develop such an approach, enabling for the first time the union of olefins and amines, as convenient and widely available starting materials, to prepare aziridines.

Our investigation into this new aziridination protocol began with the introduction of *trans*-anethole and cyclohexylamine into an electrochemical microflow reactor with a small interelectrode gap (250 μm) between the carbon anode and stainless steel cathode (Table 1).[19] After an extensive optimization of the different reaction variables (See Supporting Information), a good isolated yield (72% yield) could be obtained in only 5 minutes of residence time under galvanostatic conditions using an excess of amine (5 equiv.) in CH_3CN (Table 1, Entry 1). Addition of 5 equivalents of hexafluoroisopropanol (HFIP) proved beneficial for the targeted transformation and serves as a radical-stabilizing co-solvent and as a proton source for the cathodic half-reaction, generating hydrogen as a useful byproduct (Table 1, Entries 1 and 2).[20] Reducing the amount of amine resulted in lower yields (Table 1, Entry 3). Interestingly, the presence of a substoichiometric amount of γ-terpinene proved beneficial to prevent overoxidation of the starting material (Table 1, Entry 4). Other electrode combinations did not lead to improved results or were less effective for different substrate combinations (Table 1, Entry 5; see also Table S6). HFIP was the optimal proton source for the electrochemical aziridination, while other acids proved less effective (Table 1, Entry 6; see also Table S4). As expected, the reaction was electrochemical in nature as no conversion was observed in the absence of electricity (Table 1, Entry 7). Finally, the reaction was less effective in a batch reactor, requiring longer reaction times which resulted in an increased generation of byproducts (Table 1, Entry 8).[21]

Having established optimal reaction conditions, we next investigated the generality of this electrochemical aziridination reaction. As shown in Figure 2, a wide variety of structurally and electronically diverse primary alkyl amines and alkenes can be readily engaged in this transformation. In most cases, the targeted aziridines could be isolated as pure compounds (product A) in good isolated yields, while other compounds proved to be too fragile to be isolated via standard work-up and chromatographic procedures. We opted to isolate those compounds after subsequent ring opening with a suitable nucleophile, i.e. 4-bromothiophenol, as the corresponding 1,2-amino thioether (product B).[22] Interestingly, unprotected N–H aziridines (**1** and **28**) can be prepared by using ammonia in either water (40% w/w) or methanol (7 M). It should be noted that these N–H aziridines are extremely challenging to make and only recently a method towards these compounds using rhodium catalysis and *O*-(2,4-dinitrophenyl)hydroxylamine, as an electrophilic nitrogen reagent, was reported.[7] Furthermore, a variety of primary amines are competent coupling partners in this electrochemical aziridination protocol, including methylamine (**2**), butylamine (**3**), isopropylamine (**4**), *tert*-butylamine (**5**), cyclopropanemethylamine (**6**), cyclobutylamine (**7**), cyclopentylamine (**8**) and cyclohexylamine (**9**), furnishing the targeted products in good isolated yields. The use of a narrow-gap flow cell allows us to readily scale the reaction conditions without the need for reoptimization;[21, 23] by pumping the reagents continuously into the reactor for a prolonged amount of time, compound **9** was isolated on a 10 mmol scale. Also activated amines, such as propargylamine (**10**), benzylamine (**11-12**) and α-methylbenzylamine (**13**) are effective in this transformation. Finally, the esters of amino acids glycine (**14**) and phenylalanine (**15**) can be readily engaged in this aziridination protocol, providing opportunities for peptide modification. Notably, no racemization of the chiral center occurs under the electrochemical reaction conditions.

Table 1. Optimization of the electrochemical aziridination between alkenes and primary amines.



Entry	Variation from the standard conditions	Yield (%)[b]
1[a]	none	88 (72)[c]
2	neat HFIP	traces
3	2.5 equiv. amine	75
4	no γ-terpinene	78
5	graphite cathode	59
6	*p*-TsOH (1 equiv.)	32
7	no electricity	0
8	batch (t_R = 16 h)	14[d]

[a]Reaction Conditions: anethole (2 mmol), γ-terpinene (0.5 equiv.), cyclohexylamine (5 equiv.), HFIP (5 equiv.), CH_3CN (0.1 M), C anode/Fe cathode, 2.5-5 mA cm^{-2}. [b]Yield determined by GC-FID with biphenyl as internal standard. [c]Isolated yield. [d]Batch reaction conditions: Electrasyn, 3.1 mA cm^{-2}, 3.5 F, C anode/Fe cathode, 0.5 mmol scale.

Similarly, we investigated the variability of the alkene reaction partner that is compatible with the reaction conditions. Both electro-neutral and electron-rich internal alkenes can be effectively reacted with cyclohexylamine. For instance, (*E*)-1-methoxy-2-(prop-1-en-1-yl)benzene (**16**) and (*E*)-1,2-dimethoxy-4-(prop-1-enyl)benzene (**17**) delivered the desired functionalized product in good yield. When the substrate contained two double bonds, the

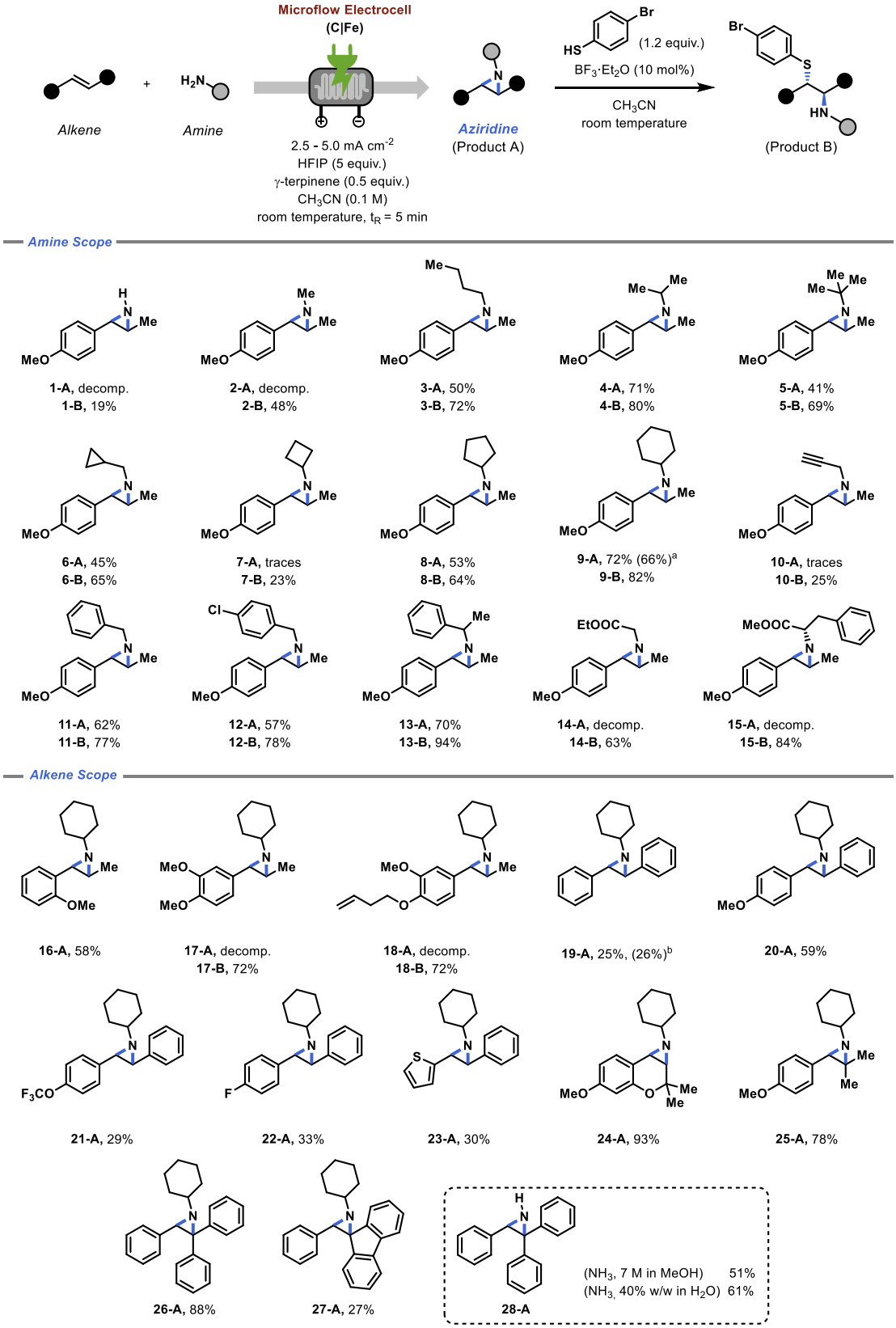


Figure 2. Substrate scope for the electrochemical aziridine synthesis. Reaction Conditions **A**: alkene (1 mmol), amine (5 equiv.), HFIP (5 equiv.), γ-terpinene (0.5 equiv.), CH_3CN (0.1 M), C anode/Fe cathode, 2.5-5 mA cm^{-2}. Decomposition refers to instability of the product, making isolation of the compound impossible. Reaction Conditions **B**: isolated yields refer to the ring-opened product. The nucleophilic quenching was carried out in the collection vial with 4-bromothiophenol (1.2 equiv.) in the presence of $BF_3.OEt_2$ (10 mol%). [a]10 mmol scale reaction. [b]*cis*-Stilbene used as a substrate.

terminal double bond remained intact providing exclusively the internal *trans*-aziridine (**18**). This site specificity may be exploited for the selective aziridination of other poly-ene compounds. Next, a variety of stilbenes (**19-22**) was subjected to the reaction conditions, highlighting the breadth of our transformation in comparison to previous electrochemical aziridination strategies. Both *cis*- and *trans*-stilbene led to the same *trans*-aziridine (**19-A**). In addition, heterocyclic moieties like thiophene (**23-A**) are compatible with the electrochemical conditions, yielding synthetically useful quantities of the targeted aziridine. The cyclic alkene of precocene I (**24-A**), a natural chromene, was found to be an adequate reaction partner and furnished the targeted product in excellent yield. Next, we moved our attention to the functionalization of trisubstituted alkenes. Even for such sterically congested double bonds, the targeted product can be obtained in good to excellent yields for both electron-rich (**25-A**) and electron-neutral (**26-A**) alkenes. Notably, a spirocyclic aziridine (**27-A)** could be accessed as well using this electrochemical aziridination strategy.

All single electron transfer events relevant for the electrochemical aziridination occur at the anode, while the other half-reaction generates hydrogen as a useful yet hazardous byproduct at the cathode. We wondered if this hydrogen could be productively used in a follow-up hydrogenation step to form the corresponding hydroaminated product (Figure 3). Indeed, by connecting a packed-bed reactor filled with Pd/C to the electrochemical flow reactor, the gas-liquid flow exiting the first reactor can be directed over the Pd/C bed without intermediate isolation. To our delight, the corresponding hydroaminated product (**9C**) could be promptly obtained in good overall yield.[24] Furthermore, we observed a single phase exiting the packed-bed reactor indicating that nearly all hydrogen gas was consumed. In contrast, when this experiment was conducted in batch, additional hydrogen to compensate for leakage to the headspace was required to obtain full conversion, albeit at a lower isolated yield. It should be further noted that this paired reaction sequence in flow not only increases the yield and the atom efficiency of the process, but also allows for facile reuse and recycling of the Pd/C bed and it reduces the risks associated with the handling of combustible hydrogen gas due its immediate consumption in a follow-up reaction.[21, 25]

To obtain insights into the underlying mechanism, we performed additional experiments and studied possible mechanistic pathways by means of density functional theory (DFT) calculations (Figure 4). Cyclic voltammetry (CV) experiments revealed two subsequent oxidations of the alkene moiety (Figure 4A). The first oxidation results in the formation of a radical cation, while the second oxidation leads to oxidative cleavage of the olefin. Small quantities of the corresponding Schiff base could be found in the reaction mixture confirming this hypothesis (Figure 4B).[26] We anticipated that this overoxidation could be countered by adding a suitable donor of hydrogens and electrons. Indeed, 0.5 equivalents 1,4-cyclohexadiene (1,4-CHD) allowed to reduce the amount of imine significantly. Also, γ-terpinene, which is a more stable, non-toxic and cheaper alternative for 1,4-CHD, enabled the suppression of the overoxidation of the alkene as shown in the CV (Figure 4A).[27] While our experimental results indicate that oxidation of the alkene is most likely the first step, CV analysis showed that a competitive activation of cyclohexylamine could occur as well (See Supporting Information). However, due to the irreversible nature of the oxidation of both reaction partners and the similar set-off potentials, it is difficult to predict the first anodic event in this aziridination protocol. Hence, we decided to obtain further insights via DFT calculations. These computational studies revealed that the anodic oxidation of anethole is indeed the first step in the electrochemical aziridination (ΔG^{o}_{298K} = +28.3 kcal mol^{-1} and +1.226 V vs SCE) (Figure 4D). An alternative pathway starting from the oxidation of the amine coupling partner, yielding the aminium radical, is energetically disfavored due to the higher required energy input (ΔG^{o}_{298K} = +38.4 kcal mol^{-1} and +1.665 V vs SCE) (see Supporting Information). However, we cannot exclude that for some substrate combinations, the reaction can be initiated via the formation of the aminium radical. Once the radical cation of anethole is formed, it readily reacts with an amine coupling partner yielding intermediate **C** (Figure 4D) via a low-barrier transition state. After deprotonation and subsequent single electron transfer, a carbocation (**E**) is formed which can undergo a rapid barrier-less intramolecular ring closure and deprotonation to yield the target aziridine (**F**).[28] The reaction is exergonic after the initial oxidation (ΔG^{o}_{298K} = –11.7 kcal mol^{-1}) but endergonic with respect to the starting materials, consistent with the required energy input in the form of electrons during the reaction.

The electrochemical approach reported herein demonstrates the possibility to convert directly olefins and primary alkyl amines into synthetically useful aziridines. We expect that the operational simplicity of this protocol and its potential to use common and broadly available starting materials will find widespread use among organic chemistry practitioners both in academia and industry.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, reaction optimization, mechanistic data, analytical data (^{1}H, ^{19}F and ^{13}C NMR, HRMS) and details of the computational study.

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Author Contributions

§ These authors contributed equally to this work.

Notes

The authors declare no competing financial interests.

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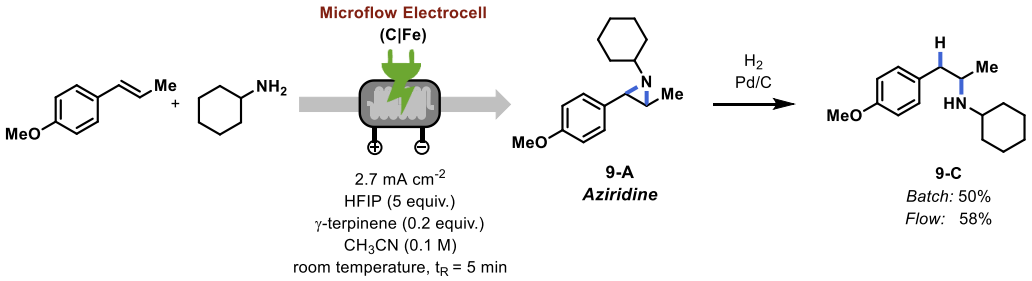

Figure 3. Two-step hydroamination protocol by combining the electrochemical aziridine synthesis and a subsequent hydrogenation. Reaction Conditions C: alkene (1 mmol), amine (5 equiv.), HFIP (5 equiv.), γ-terpinene (0.2 equiv.), CH_3CN (0.1 M), C anode/Fe cathode, 2.7 mA cm^{-2}. Batch conditions: Pd/C (5 mol%), H_2 (1 bar). Flow conditions: Pd/C (150 mg cartridge).

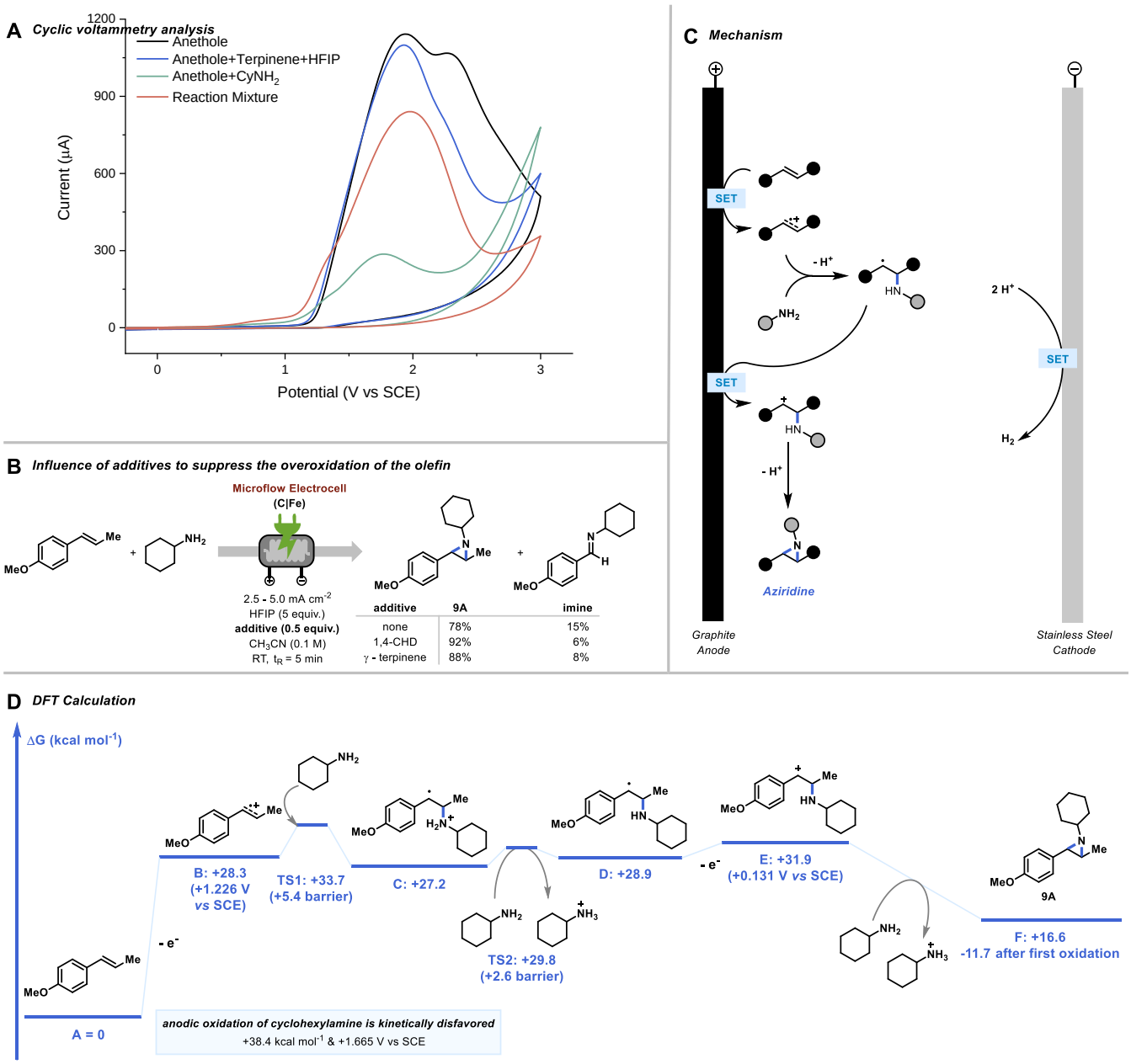

Figure 4. Mechanistic investigation. (A) Cyclic voltammetry experiments. (B) Addition of a reducing agent to suppress overoxidation of the alkene. (C) Proposed mechanism. (D) DFT Gibbs free energy profile at 298 K (in kcal mol^{-1}). Calculations were performed at the B3LYP/def2-TZVP//B3LYP/def2-TZVP(COSMO) level of theory on an m4 grid with disp3 dispersion corrections.

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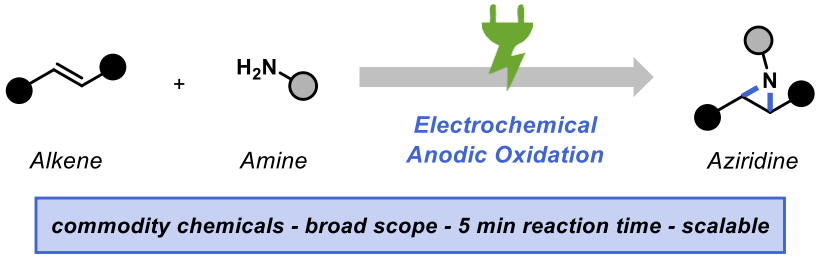
TOC graphic



Supporting Information (SI)

Electrochemical Aziridination of Internal Alkenes with Primary Amines

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Table of Contents

1. General information

All reagents and solvents were used as received without further purification. Reagents and solvents were bought from Sigma Aldrich, TCI and Fluorochem. Technical solvents were bought from VWR International and Biosolve, and are used as received. All capillary tubing and microfluidic fittings were purchased from IDEX Health & Science. Disposable syringes were from BD Discardit II® or NORM-JECT®, purchased from VWR Scientific. Syringe pumps were purchased from Chemix Inc. model Fusion 200 Touch. The crude products were purified either by crystallization or by flash column chromatography on silica gel using Biotage® Isolera Four, with Biotage® SNAP KP-Sil 25 or 50 g flash chromatography cartridges and 25 g Flash Cartridge Sferical C18 silica (C18.SMB 100-20/45). TLC analysis was performed using Silica on aluminum foils TLC plates (F254, Supelco Sigma- Aldrich™) with visualization under ultraviolet light (254 nm and 365 nm) or appropriate TLC staining (permanganate and ninhydrin). ^{1}H (400 MHz), ^{19}F (377 MHz) and ^{13}C (100 MHz) spectra were recorded on ambient temperature using a Bruker-Avance 400. ^{1}H NMR spectra are reported in parts per million (ppm) downfield relative to CD_3OD (3.31 ppm) or $CDCl_3$ (7.26 ppm) and ^{13}C NMR spectra are reported in ppm relative to CD_3OD (49.00 ppm) or $CDCl_3$ (77.16 ppm) unless stated otherwise. NMR spectra uses the following abbreviations to describe the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, hept = heptet, m = multiplet, dd = double doublet, td = triple doublet. NMR data was processed using the MestReNova 12.0.4 and 14.0.1 software packages. Known products were characterized by comparing to the corresponding ^{1}H NMR and ^{13}C NMR from literature. High resolution mass spectra were recorded by using an Agilent Technologies 6220A Accurate-Mass TOF LC/MS spectrometer equipped with a multimode ESI/APCI ionization source. The cyclic voltammetry analysis were performed with an PalmSens EmStat3+. GC analyses were performed on a GC-MS combination (Shimadzu GC-2010 Plus coupled to a Mass Spectrometer; Shimadzu GCMS-QP 2010 Ultra) with an auto sampler unit (AOC-20i, Shimadzu) and GC-FID (Shimadzu GC-2010) with an auto sampler unit (AOC-20i, Shimadzu). Chiral HPLC analysis was performed by using Chiralcel OJ-H (250 × 4.6 mm) and Chiralcel OD-H (250 × 4.6 mm) columns. The names of all products were generated using the PerkinElmer ChemBioDraw Ultra v.18.0.0 software package.

For all electrochemical continuous-flow reactions, a homemade flow cell was used, together with a Velleman LABPS3005D power supply (Figure S1). The cell consists of a working electrode and a counter electrode, with a PTFE (Polytetrafluoroethylene) gasket containing micro-channels in between. The material used for the electrodes were Stainless Steel electrode (316L) and Graphite AC-K800 premium Grade (purchased by AgieCharmilles). The active reactor volume is 700µL. This results in an undivided electrochemical cell. In the cell, direct contact between the electrode surface and the reaction mixture is established. The reaction mixture is pumped through the system via syringe pump, and is collected in a glass vial. All the technical data of the electrochemical microreactor are reported elsewhere.[1]

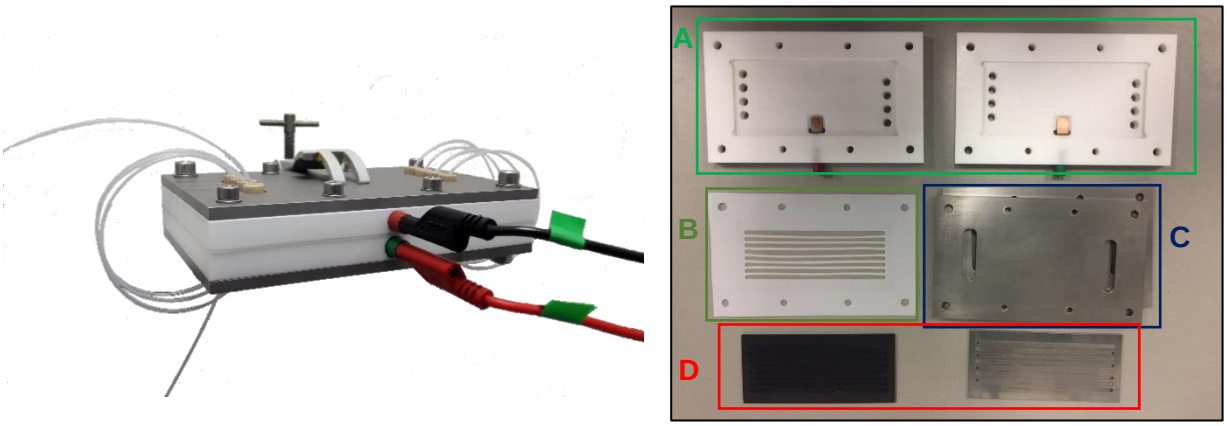

Figure S1: Left - Assembled Flow reactor. **Right** - Components of the electrochemical flow cell. **A**: PTFE electrode holders. **B**: PTFE gasket (8 channel configuration). **C**: Outer Stainless Steel plates. **D**: Electrodes (Left Graphite, Right Stainless Steel).

2. Reaction optimization

During the screening, the solution was pumped through the electrocell at a fixed flowrate of 0.15 mL/min to give a residence time of 5 minutes. The current was varied from 50 to 120 mA. After 2 residence times had elapsed and the reaction had reached steady state (10 minutes at 0.15 ml/min), the corresponding potential was noted and a sample (0.1 ml) was collected in a vial and complemented with acetonitrile (1 mL) and analyzed using GC-FID. GC yields were calculated with an internal standard (biphenyl).

2.1. Equivalents of amine

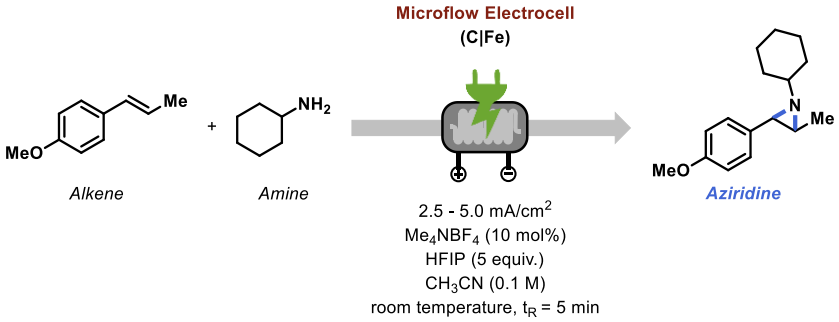

Table S1: Equivalents of amine

Entry	Amine (equiv.)	Yield (%)
1	1	25
2	2.5	53
3	5	73
4	7.5	77
5	10	78

Reaction Conditions: anethole (2 mmol), cyclohexylamine, Me_4NBF_4 (10 mol%), HFIP (5 equiv.), CH_3CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm^2. Yield determined by GC-FID with biphenyl as internal standard.

Preliminary screening of the reaction conditions revealed that the amount of amine is critical to achieve higher yields (Table S1). The excess of amine is required to quickly trap cation-radical formed upon oxidation of internal alkene and prevent it from further oxidation leading to side-product formation. The optimal yield was obtained with 5 equivalents of the amine (Table S1, Entry 3).

2.2. Residence time optimization

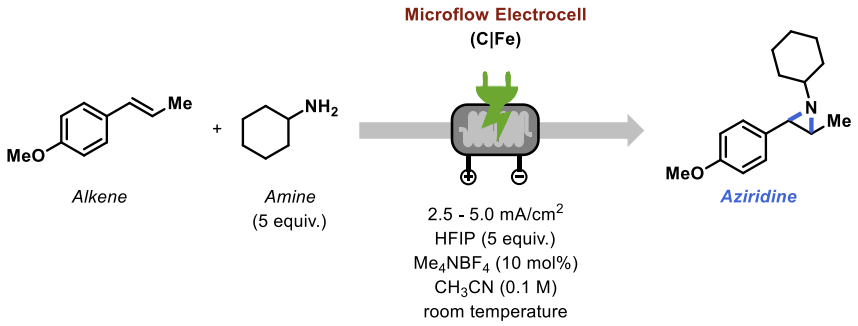

Table S2: Residence time optimization

Entry	Residence time	Yield (%)
1	2.5	66
2	5	73
3	10	66

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), Me_4NBF_4 (10 mol%), HFIP (5 equiv.), CH_3CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm^2. Yield determined by GC-FID with biphenyl as internal standard.

Next, the required residence time was investigated (Table S2). At 5 minutes residence time, full conversion was observed with good yield. Higher applied current was needed in order to reach full conversion at 2.5 minutes residence time, which resulted in an increased by-product formation. On the contrary, longer residence time (10 minutes) led to degradation of the desired product by nucleophilic opening.

2.3. Solvent screening

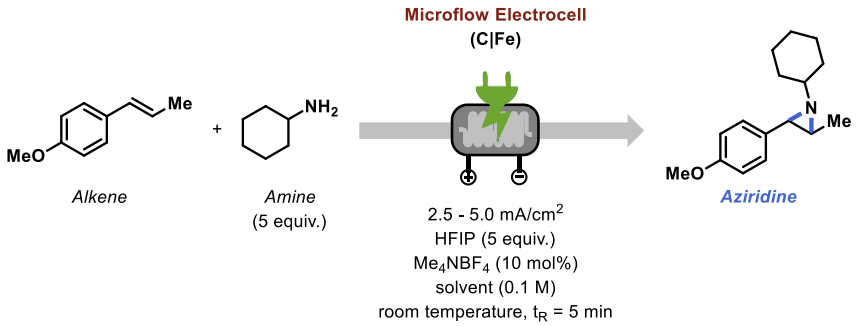

Table S3: Solvent screening

Entry	Solvent	Yield (%)
1	CH_3CN	73
2	HFIP	11
3	dry CH_3CN	77

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), Me_4NBF_4 (10 mol%), HFIP (5 equiv.), solvent (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm^2. Yield determined by GC-FID with biphenyl as internal standard.

Based on our previous results acetonitrile was chosen as the main solvent for the reaction, due to its stability under the electrochemical conditions and good solubilizing properties. Performing the reaction in pure hexafluoroisopropanol (HFIP) caused dramatic decrease of the desired product yield, while dry acetonitrile did not improve the performance considerably.

2.4. Acid screening

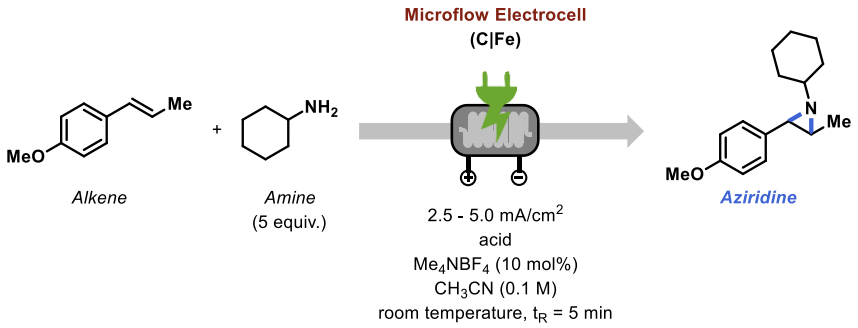

Table S4: Acid screening

Entry	Acid	Yield (%)
1	HFIP (1 equiv.)	42
2	HFIP (2.5 equiv.)	62
3	HFIP (5 equiv.)	73
4	HFIP (10 equiv.)	66
5	CF_3CH_2OH (5 equiv.)	65
6	3M HCl (0.75 equiv.)	53
7	3M H_2SO_4 (0.75 equiv.)	57
8	*p*-TsOH (1 equiv.) + H_2O (1.5 mL)	32
9	PhCOOH (1 equiv.) + H_2O (1.5 mL)	49

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), Me_4NBF_4 (10 mol%), CH_3CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm^2. Yield determined by GC-FID with biphenyl as internal standard.

An acid or protic co-solvent is required for the reduction reaction that occurs on the cathode (Table S4). A small amount of water was added to dissolve precipitated salt formed upon addition of the corresponding acid to a solution of cyclohexylamine in pure acetonitrile. However, the presence of aqueous acid solution caused considerable degradation of the alkene (Table S4, Entries 6-9). An excess of fluorinated alcohols proved to be efficient to facilitate the reaction, and 5 equivalents of HFIP was chosen as an optimal option (Table S4, Entry 3).

2.5. Electrolyte screening

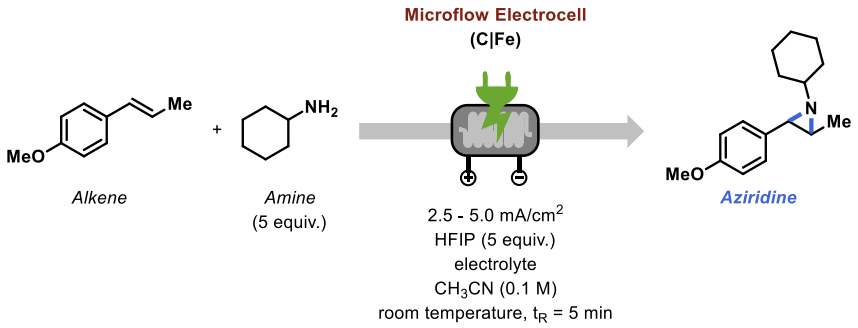

Table S5: Electrolyte screening

Entry	Electrolyte	Yield (%)
1	Me_4NBF_4 (10 mol%)	73
2	Me_4NBF_4 (50 mol%)	79
3	Me_4NBF_4 (100 mol%)	84
4	$LiClO_4$ (10 mol%)	75
5	$LiClO_4$ (50 mol%)	62
6	$LiClO_4$ (100 mol%)	59
7	no electrolyte	78

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), HFIP (5 equiv.), CH_3CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm^2. Yield determined by GC-FID with biphenyl as internal standard.

After varying the nature and the amount of supporting electrolyte, we discovered that the electrochemical reaction runs well without any additional electrolyte (Table S5, Entry 7). This is a notable advantage of using flow electrochemistry and can be attributed to the small inter-electrode gap, which keeps the Ohmic drop low. The option to alleviate the need for supporting electrolyte makes the overall transformation more sustainable and avoids more intense purification processes.

2.6. Electrode material

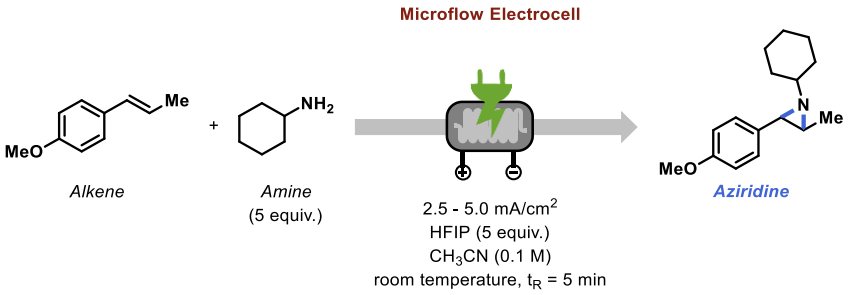

Table S6: Electrode material

Entry	Anode	Cathode	Yield (%)
1	Graphite	Stainless steel	78
2	Stainless steel	Stainless steel	48
3	Graphite	Graphite	57
4	Graphite	Copper	94
5	Graphite	Nickel	87

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), HFIP (5 equiv.), CH_3CN (0.1 M), 2.5-5 mA/cm^2. Yield determined by GC-FID with biphenyl as internal standard.

For anodic oxidations, the electrode material is chosen based on the potential required to perform the reaction and its compatibility with the reaction medium. Surprisingly, a high yield of the desired product was achieved when copper and nickel were chosen for cathode (Table S6, Entries 4-5). Although the copper electrode provided a superior result, the use of copper led to reproducibility issues during the scope exploration. This is probably due to the early passivation of the electrode surface of the electrode. For this reason, we decided to continue our research using a combination of a steel cathode and graphite anode (Table S6, Entry 1), which is also advantageous with regard to cost and safety (e.g. copper leaching vs. iron).

2.7. Additive screening

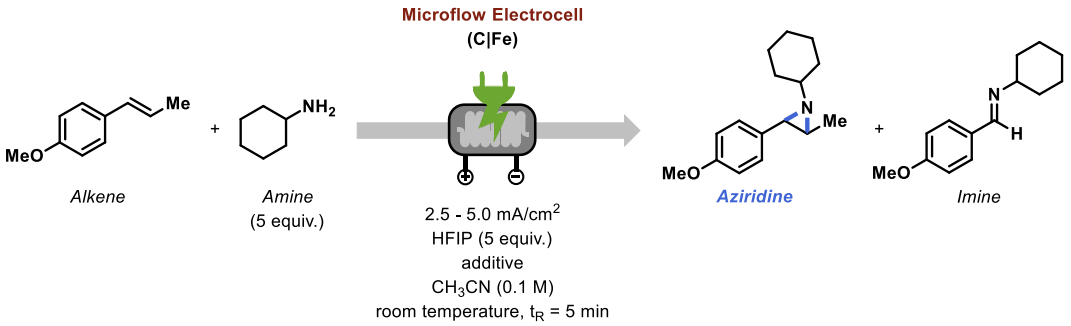

Table S7: Additive screening

Entry	Additive	Azirdine yield (%)	Imine yield (%)
1	No additive	78	15
2	Ph_3SiH (1 equiv.)	85	7
3	Hantzsch ester (1 equiv.)	88	6
4	1,4-cyclohexadiene (1 equiv.)	86	7
5	1,4-cyclohexadiene (0.5 equiv.)	92	6
6	1,4-cyclohexadiene (0.2 equiv.)	90	8
7	γ-terpinene (0.5 equiv.)	88	8

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), HFIP (5 equiv.), CH_3CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm^2. Aziridine yield determined by GC-FID with biphenyl as internal standard. Imine yield determined by ^{1}H NMR with biphenyl as internal standard.

Based on the preliminary results, we envisioned that addition of a small amount of a reducing agent can potentially suppress the overoxidation of the alkene leading to the formation of imine. To our delight, addition of one equivalent of reductant resulted in ~10% increase for the targeted aziridine (Table S7, Entries 2-3). The best results were achieved with sub-stoichiometric amounts of 1,4-cyclohexadiene (Table S7, Entry 5). Finally, comparable results were obtained, when we exchanged 1,4-cyclohexadiene for γ-terpinene, which is non-toxic, inexpensive natural compound (Table S7, Entry 7).

3. Cyclic Voltammetry analysis

All the cyclic voltammetry experiments were performed in a batch setup. The analysis was performed with a PalmSens EmStat3+ equipped with a glassy carbon working electrode (3 mm), a platinum wire counter electrode and a SCE reference electrode. All measurements were carried out at a concentration of 0.1 M in anhydrous CH_3CN with an electrolyte (Me_4NBF_4, 0.05M), using a scan rate of 100 mV/s.

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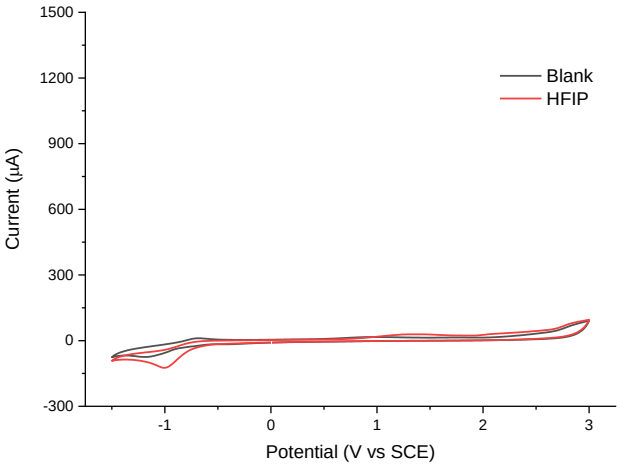
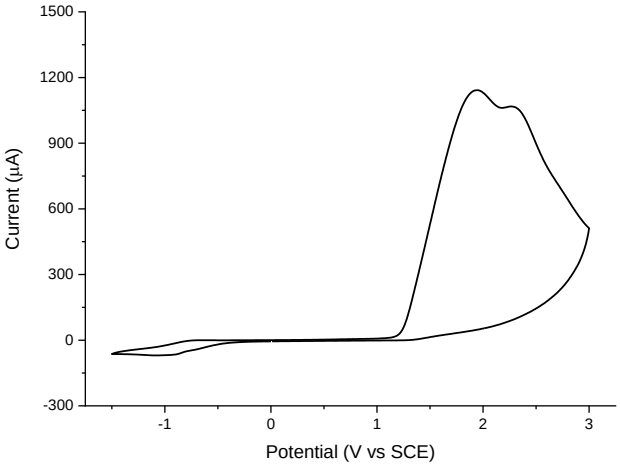
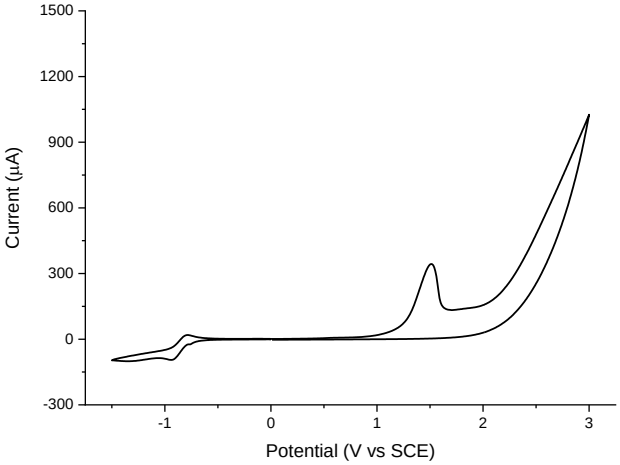


Anethole

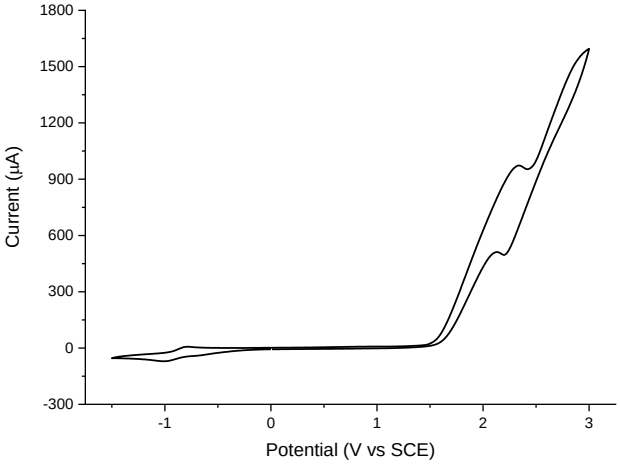


When anethole was scanned, two different oxidation events were observed. We surmise these are correlated to the first and the second oxidation of the double bond. Particularly, the second oxidation event is related to the degradation of the starting material.

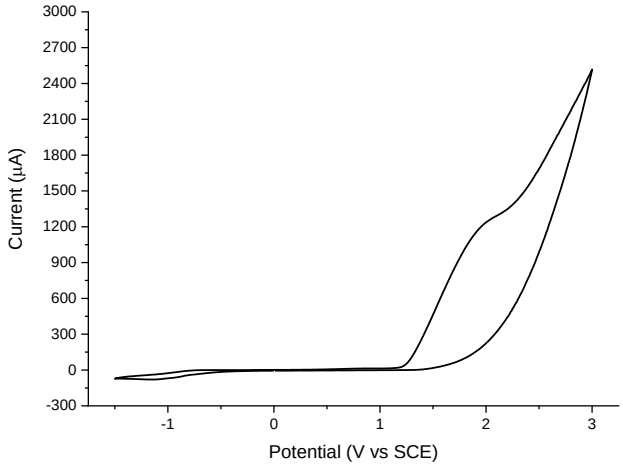
Cyclohexylamine



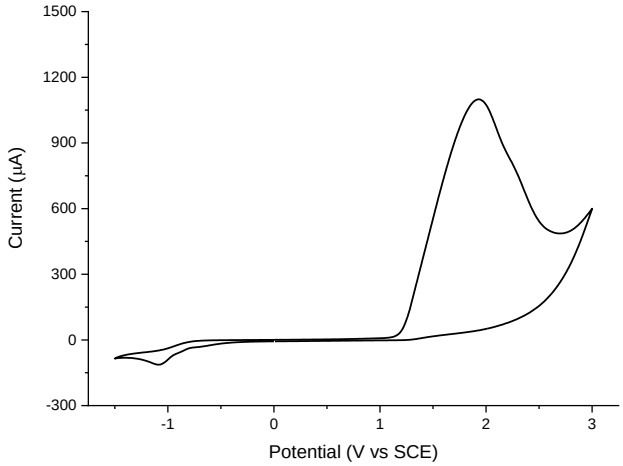
γ-Terpinene



Anethole+γ-Terpinene

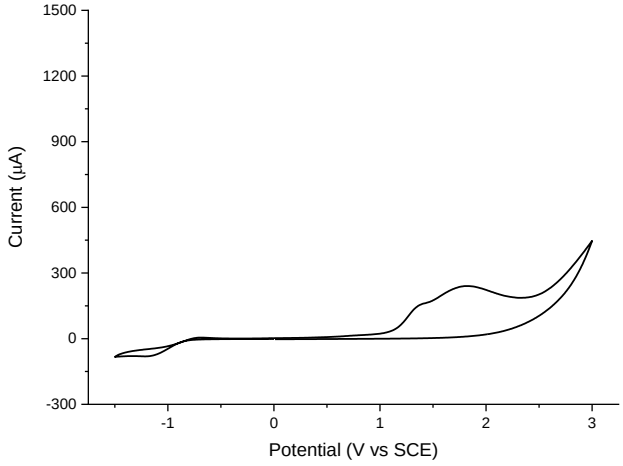


Anethole+γ-Terpinene+HFIP



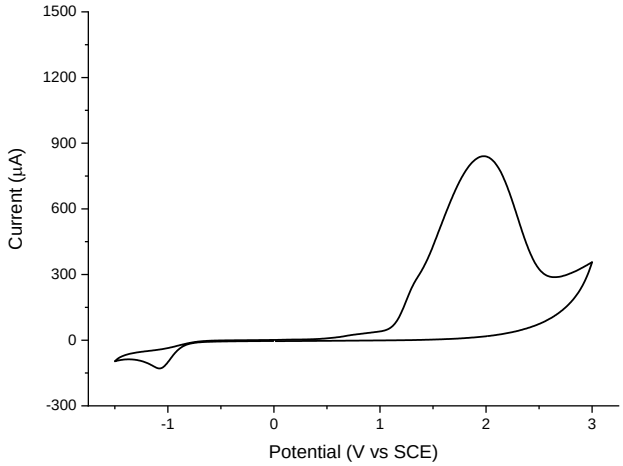
Notably, the addition of γ-terpinene showed that the second oxidation of anethole is attenuated, indicating a beneficial effect of the sacrificial reductant in the reaction (similar results can be observed without HFIP, but the interpretation of the CV is difficult because of the low conductivity).

Anethole+Cyclohexylamine



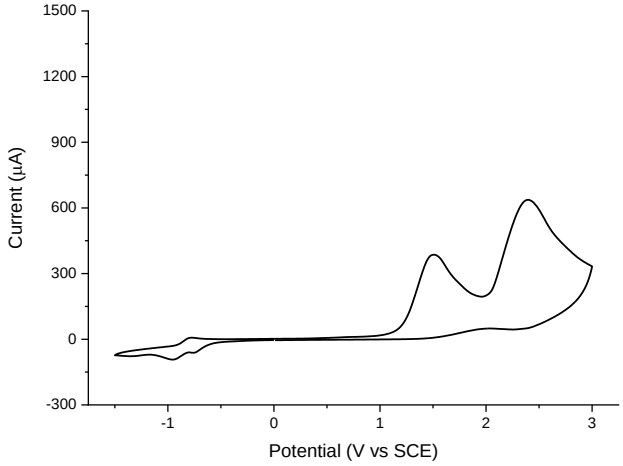
When a mixture of cyclohexylamine and anethole is analyzed, both oxidation events were observed. Moreover, an attenuation of anethole overoxidation was also observed.

Reaction mixture



When a cyclic voltammetry analysis of the reaction mixture was conducted, a major peak could be observed in the region of anethole oxidation, indicating it as the main oxidative event.

trans-1-cyclohexyl-2-(4-methoxyphenyl)-3-methylaziridine (9-A)



Finally, the cyclic voltammetry analysis of the isolated product was carried out. Here, an irreversible oxidation at high potential could be observed. This shows that a prolonged exposure of the generated product to electricity can lead to its degradation. Hence, carrying out the reaction under flow conditions, where the residence can be minimized to what is kinetically required, leads to higher isolated yields.

4. DFT Calculations

DFT studies were performed on full atomic models (no simplifications) using TURBOMOLE 7.3[2] coupled to the PQS Baker optimizer[3] via the BOpt package.[4] The geometry optimizations, location of transition states and frequency analysis was performed at the B3LYP[5]/ def2-TZVP[6] level of theory (unless noted otherwise) on an m4 grid, using Grimme's version 3 (disp3, "zero damping") dispersion corrections.[7] All minima (no imaginary frequencies) and transition states (one imaginary frequency along the reaction coordinate) were characterized by calculating the Hessian matrix. Inclusion of implicit solvation mimicking the CH_3CN solvent was achieved by usage of COSMO[8] ($\varepsilon = 36.6$) in a single point calculation at the B3LYP[9]/def2-TZVP[6] level of theory on an m4 grid, using Grimme's version 3 (disp3, "zero damping") dispersion corrections,[10] on the optimized geometries. Energy output was reported in Hartree and was converted to kcal mol^{-1} by multiplication with 627.503.

4.1. Calculation of redox potentials

The redox potentials ($E^{o,calc}{}_{½}$ in V *vs* $Fc^{+/0}$) were calculated by first benchmarking the DFT method to literature known oxidation potentials (in V *vs* $Fc^{+/0}$) [11] and deriving a correction factor (C^{DFT}) based on our method. This can be achieved via a literature method wherein the difference in (COSMO solvated) calculated Gibbs free energies at 298 K (ΔG_{298K}) of the reduced (red) and oxidized (ox) substrates is divided by the product of n_e (number of electron transferred) and F (Faraday constant, 23.061 kcal mol^{-1} V^{-1}), see formula 1.[12] A correction ($E^{o,corr}{}_{½}$) to report the calculated redox potential versus $Fc^{+/0}$ ($E^{o,Fc}{}_{½}$ = 0.400 V vs SCE in $CH_3CN/[NBu_4]PF_6$[11]) was achieved via first referencing the calculated redox potential to SHE (absolute value $E^{o,SHE}{}_{½}$ = 4.281 V) and then to SCE ($E^{o,SCE}{}_{½}$ = –0.141 V *vs* SHE in CH_3CN). The total correction factor is therefore: –4.281–0.141–0.400 = –4.822 V. To calculate the oxidation potentials versus SCE a correction ($E^{o,corr}{}_{½}$ in V *vs* SCE) of -4.281-0.141= –4.422 is applied.

A training set to determine C^{DFT} was chosen based on literature known (reversible with the exception of anethole) oxidation potentials in CH_3CN. We selected several molecules in the training set with an amine center to correctly describe the calculated oxidation potentials of the formed amines during the reactions under study. The experimentally determined redox potentials in CH_3CN were found to be underestimated 0.301 V by the calculated redox potential (without C^{DFT}). We therefore set C^{DFT} to +0.301, after which the calculated redox potential only had an average deviation from the experimentally found redox potentials of –0.003 V (
Table **S8**). We therefore concluded that the applied DFT method could be used to provide insight into the relative oxidation potentials of the systems under study.

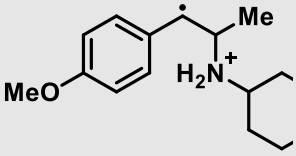
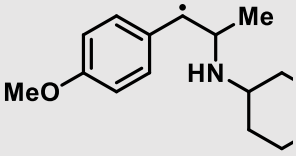
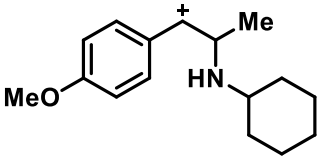
Formula 1: $$E^{o,calc}_{1/2}\left(\text{V } vs \text{ } Fc^{+/0}\right) = -\frac{(G_{298K}[red] - G_{298K}[ox])}{n_e * F} + E^{o,corr}_{1/2} + C^{DFT}$$

Table S8: Gibbs free energies, calculated redox potentials and literature reported redox potentials. Calculations were performed at the B3LYP/def2-TZVP//B3LYP/def2-TZVP(COSMO) level of theory on an m4 grid with disp3 dispersion corrections.

Compound	G_{298K} (kcal mol^{-1})	Literature redox potential[11] (V *vs* $Fc^{+/0}$)	Calculated redox potential (formula 1) (V *vs* $Fc^{+/0}$)	Deviation (V)
anethole	-290685.8326	+0.84 [12]	+0.826	–0.014
$[anethole]^{\cdot+}$	-290562.5282			
NEt_3	-183333.6673	+0.47	+0.496	+0.026
$[NEt_3]^{\cdot+}$	-183217.9808			
$N(2,4,6\text{-tribromophenyl})_3$	-15003845.09	+1.36	+1.389	+0.029
$[N(2,4,6\text{-tribromophenyl})_3]^{\cdot+}$	-15003708.8			
$N(4\text{-bromophenyl})_3$	-5314747.206	+0.67	+0.722	+0.052
$[N(4\text{-bromophenyl})_3]^{\cdot+}$	-5314626.292			
thianthrene	-789516.2677	+0.86	+0.764	–0.096
[thianthrenium]$^{\cdot+}$	-789394.394			
average deviation				–0.003 V

4.2. Calculation of the proposed mechanisms

Calculations were performed according to the general method as described above. All energies for the structures are reported in Table S9, and plausible mechanisms are reported in Scheme S1, Scheme S2 and Scheme S3. The composition of the states for the mechanisms are described in

Entry	Description	Multi-plicity	<s2>	SCF (Hartree)	ZPE correction (Hartree)	Enthalpy correction (Hartree)	Entropy correction (Hartree)	ΔGo298K (Hartree)
1	anethole	1	-	-463.39826	0.19325	0.20509	0.15612	-463.24214
2	[anethole]$^{\cdot+}$	2	0.7642	-463.20270	0.19373	0.20560	0.15706	-463.04564
3	NH2-C6H11	1	-	-291.15729	0.18712	0.19499	0.15678	-291.00051
4	[NH2-C6H11]$^{\cdot+}$	2	0.7551	-290.94233	0.18507	0.19331	0.15445	-290.78788
5	[NH3-C6H11]$^{+}$	1	-	-291.62111	0.20209	0.21014	0.17151	-291.44960
6	TS for amine attack on [anethole]$^{\cdot+}$	2	0.7634	-754.37435	0.38425	0.40328	0.33693	-754.03742
7		2	0.7740	-754.38859	0.38725	0.40600	0.34071	-754.04788
8	TS for deprotonation of radical cation (entry 7)	2	0.7764	-1045.56095	0.57259	0.59904	0.51669	-1045.04426
9		2	0.7759	-753.92068	0.37164	0.39035	0.32461	-753.59606
10a		1	-	-753.76854	0.37462	0.39307	0.32875	-753.43979
11	*cis-aziridine* adduct with [NH3-C6H11]$^{+}$	1	-	-1044.97177	0.56354	0.59010	0.50697	-1044.46479
12	*cis-aziridine*	1	-	-753.33071	0.36147	0.37957	0.31578	-753.01493
13	*trans-aziridine*	1	-	-753.32351	0.36149	0.37961	0.31497	-753.00853
14	TS for *cis- trans-isomerization*	1	-	-753.30538	0.36006	0.37785	0.31402	-752.99136
15	*p-methoxystyrene* + NH2-C6H11	1	-	-715.25491	0.35389	0.37309	0.30428	-714.95062
16	[*p-methoxystyrene*]$^{\cdot+}$ + NH2-C6H11	2	0.7611	-715.05308	0.35372	0.37295	0.30501	-714.74807
17	*p-methoxystyrene*	1	-	-424.09218	0.16540	0.17565	0.13038	-423.96180
18	[*p-methoxystyrene*]$^{\cdot+}$	2	0.7705	-423.88941	0.16591	0.17618	0.13150	-423.75791
19	*trans-β-methylstyrene* + NH2-C6H11	1	-	-640.04323	0.34897	0.36734	0.30099	-639.74225
20	[*trans-β-methylstyrene*]$^{\cdot+}$ + NH2-C6H11	2	0.7598	-639.83599	0.34846	0.36672	0.30096	-639.53503
21	*trans-β-methylstyrene*	1	-	-348.88087	0.16071	0.17006	0.12591	-348.75496
22	[*trans-β-methylstyrene*]$^{\cdot+}$	2	0.7655	-348.66905	0.16057	0.16995	0.12720	-348.54186
23	styrene + NH2-C6H11	1	-	-600.73619	0.32112	0.33790	0.27527	-600.46092
24	[styrene]$^{\cdot+}$ + NH2-C6H11	2	0.7612	-600.52673	0.32120	0.33769	0.27601	-600.25073
25	styrene	1	-	-309.57450	0.13287	0.14062	0.10108	-309.47342
26	[styrene]$^{\cdot+}$	2	0.7709	-309.35265	0.13277	0.14056	0.10176	-309.25089
27	*cis-stilbene*	1	-	-540.57466	0.21451	0.22646	0.17681	-540.39785

28	[*cis-stilbene*]$^{\cdot+}$	2	0.7640	-540.36943	0.21513	0.22708	0.17788	-540.19155
29	[*trans-stilbene*]	1	-	-540.58162	0.21394	0.22626	0.17444	-540.40719
30	[*trans-stilbene*]$^{\cdot+}$	2	0.7664	-540.37967	0.21490	0.22710	0.17695	-540.20272
31	NEt3	1	-	-292.33498	0.20504	0.21530	0.17117	-292.16381
32	[NEt3]$^{\cdot+}$	2	0.7548	-292.14823	0.20498	0.21565	0.16877	-291.97945
33	N(2,4,6-tribromophenyl)$_3$	1	-	-23910.51473	0.18519	0.21464	0.11894	-23910.39579
34	[N(2,4,6-tribromophenyl)$_3$]$^{\cdot+}$	2	0.7620	-23910.29649	0.18472	0.21417	0.11790	-23910.17859
35	N(4-bromophenyl)$_3$	1	-	-8469.87008	0.24735	0.26760	0.19391	-8469.67617
36	[N(4-bromophenyl)$_3$]$^{\cdot+}$	2	0.7667	-8469.67927	0.24812	0.26808	0.19579	-8469.48348
37	thianthrene	1	-	-1258.31289	0.16191	0.17355	0.12565	-1258.18724
38	[thianthrenium]$^{\cdot+}$	2	0.7565	-1258.11858	0.16240	0.17417	0.12556	-1257.99302

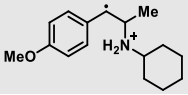
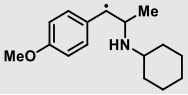
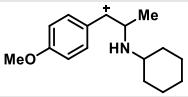
[a] The CSS spin state was found to be the most stable. The OSS spin state converged to a CSS solution and the triplet spin sate was found at ΔGo298K = +24.5 kcal mol-1 relative to the CSS state.

Table S10. Calculation of the relative energy for electron transfer was achieved via multiplication of the calculated oxidation potential with the Faraday constant (23.061 kcal mol^{-1} V^{-1}). We referenced intermediates with the same amount of electrons to each other and added the required energy for electron transfer to these relative energies to reference every intermediate to state **A** (set at 0 kcal mol^{-1}). The oxidation potentials were calculated using the data in Table S9 and formula 1 (see above). Pathway 1 (Scheme S2) was deemed less plausible than Pathway 2 (Scheme S3) due to the higher energy requirement for the first oxidation. Calculated oxidation potentials for various alkenes and alkene adducts with cyclohexylamine are included in Table S11.

Amine oxidation cannot be fully excluded, because it is used in 5-fold excess and the measured offset potentials for oxidation of anethole and cyclohexylamine are similar (See Section 3). However, the anodic currents for the amine are much lower than those for anethole at the same concentration, suggesting that alkene oxidation at the anode is kinetically favored. This is also observed in mixtures with a 5-fold excess of the amine (see Section 3), where again the current seems to be dominated by anethole oxidation. Since the measured offset potentials in CV are not the equilibrium potentials, which are impossible to determine for these irreversible oxidation processes, we rely on the DFT computed redox potential for these compounds which are in favor of alkene oxidation. Furthermore, the actual coulometric reactions might actually not be (thermodynamically) voltage controlled but rather (kinetically) current controlled. The estimated applied cell potential under the synthetic couloumetric conditions is about 3 to 4 V, which might be high enough to oxidize both the alkene and the amine. As such, the reaction could well be dominated by electrode kinetics favoring alkene oxidation over amine oxidation.

Table S9: Calculated <s^2>, SCF corrections, ZPE corrections, enthalpy corrections and ΔG^o_{298K} (in Hartree) and relative energies (in kcal mol^{-1}) at the B3LYP/def2-SVP//B3LYP/def2-TZVP(COSMO) level of theory on an m4 grid with Grimme's version 3 zero-damping dispersion corrections. *cis*-aziridine and *trans*-aziridine describe the relative orientation of the methyl and cyclohexyl groups on the aziridine. NH_2-C_6H_{11} = cyclohexylamine.

Entry	Description	Multi-plicity	<s^2>	SCF (Hartree)	ZPE correction (Hartree)	Enthalpy correction (Hartree)	Entropy correction (Hartree)	ΔG^o_{298K} (Hartree)
1	anethole	1	-	-463.39826	0.19325	0.20509	0.15612	-463.24214
2	[anethole]$^{\cdot+}$	2	0.7642	-463.20270	0.19373	0.20560	0.15706	-463.04564
3	NH_2-C_6H_{11}	1	-	-291.15729	0.18712	0.19499	0.15678	-291.00051
4	[NH_2-C_6H_{11}]$^{\cdot+}$	2	0.7551	-290.94233	0.18507	0.19331	0.15445	-290.78788
5	[NH_3-C_6H_{11}]$^+$	1	-	-291.62111	0.20209	0.21014	0.17151	-291.44960
6	TS for amine attack on	2	0.7634	-754.37435	0.38425	0.40328	0.33693	-754.03742

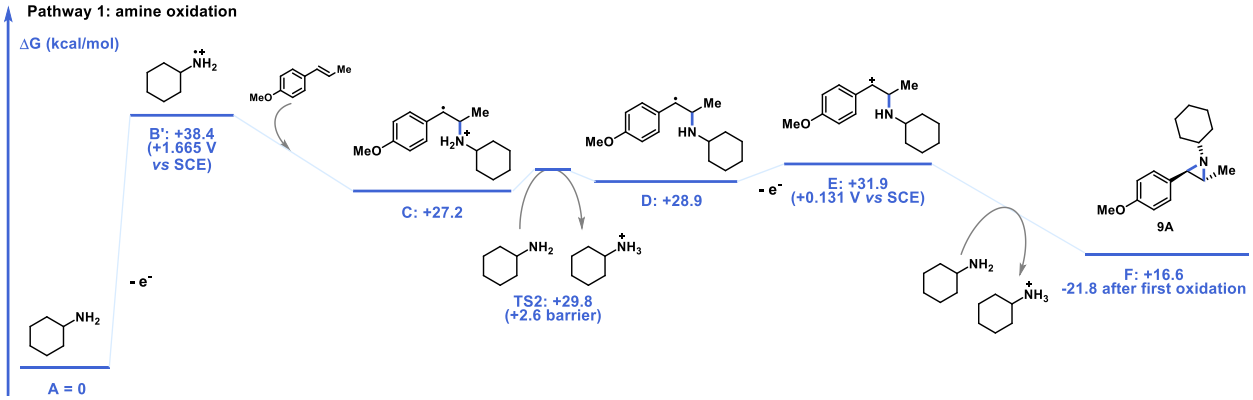
	[anethole]$^{\cdot+}$							
7		2	0.7740	-754.38859	0.38725	0.40600	0.34071	-754.04788
8	TS for deprotonation of radical cation (entry 7)	2	0.7764	-1045.56095	0.57259	0.59904	0.51669	-1045.04426
9		2	0.7759	-753.92068	0.37164	0.39035	0.32461	-753.59606
10[a]		1	-	-753.76854	0.37462	0.39307	0.32875	-753.43979
11	*cis*-aziridine adduct with $[NH_3\text{-}C_6H_{11}]^+$	1	-	-1044.97177	0.56354	0.59010	0.50697	-1044.46479
12	*cis*-aziridine	1	-	-753.33071	0.36147	0.37957	0.31578	-753.01493
13	*trans*-aziridine	1	-	-753.32351	0.36149	0.37961	0.31497	-753.00853
14	TS for *cis*- *trans*-isomerization	1	-	-753.30538	0.36006	0.37785	0.31402	-752.99136
15	*p*-methoxystyrene + $NH_2\text{-}C_6H_{11}$	1	-	-715.25491	0.35389	0.37309	0.30428	-714.95062
16	[*p*-methoxystyrene]$^{\cdot+}$ + $NH_2\text{-}C_6H_{11}$	2	0.7611	-715.05308	0.35372	0.37295	0.30501	-714.74807
17	*p*-methoxystyrene	1	-	-424.09218	0.16540	0.17565	0.13038	-423.96180
18	[*p*-methoxystyrene]$^{\cdot+}$	2	0.7705	-423.88941	0.16591	0.17618	0.13150	-423.75791
19	*trans*-β-methylstyrene + $NH_2\text{-}C_6H_{11}$	1	-	-640.04323	0.34897	0.36734	0.30099	-639.74225
20	[*trans*-β-methylstyrene]$^{\cdot+}$ + $NH_2\text{-}C_6H_{11}$	2	0.7598	-639.83599	0.34846	0.36672	0.30096	-639.53503
21	*trans*-β-methylstyrene	1	-	-348.88087	0.16071	0.17006	0.12591	-348.75496
22	[*trans*-β-methylstyrene]$^{\cdot+}$	2	0.7655	-348.66905	0.16057	0.16995	0.12720	-348.54186
23	styrene + $NH_2\text{-}C_6H_{11}$	1	-	-600.73619	0.32112	0.33790	0.27527	-600.46092
24	[styrene]$^{\cdot+}$ + $NH_2\text{-}C_6H_{11}$	2	0.7612	-600.52673	0.32120	0.33769	0.27601	-600.25073
25	styrene	1	-	-309.57450	0.13287	0.14062	0.10108	-309.47342
26	[styrene]$^{\cdot+}$	2	0.7709	-309.35265	0.13277	0.14056	0.10176	-309.25089
27	*cis*-stilbene	1	-	-540.57466	0.21451	0.22646	0.17681	-540.39785
28	[*cis*-stilbene]$^{\cdot+}$	2	0.7640	-540.36943	0.21513	0.22708	0.17788	-540.19155
29	[*trans*-stilbene]	1	-	-540.58162	0.21394	0.22626	0.17444	-540.40719
30	[*trans*-stilbene]$^{\cdot+}$	2	0.7664	-540.37967	0.21490	0.22710	0.17695	-540.20272
31	NEt_3	1	-	-292.33498	0.20504	0.21530	0.17117	-292.16381
32	$[NEt_3]^{\cdot+}$	2	0.7548	-292.14823	0.20498	0.21565	0.16877	-291.97945
33	N(2,4,6-tribromophenyl)$_3$	1	-	-23910.51473	0.18519	0.21464	0.11894	-23910.39579
34	[N(2,4,6-tribromophenyl)$_3$]$^{\cdot+}$	2	0.7620	-23910.29649	0.18472	0.21417	0.11790	-23910.17859
35	N(4-bromophenyl)$_3$	1	-	-8469.87008	0.24735	0.26760	0.19391	-8469.67617
36	[N(4-bromophenyl)$_3$]$^{\cdot+}$	2	0.7667	-8469.67927	0.24812	0.26808	0.19579	-8469.48348
37	thianthrene	1	-	-1258.31289	0.16191	0.17355	0.12565	-1258.18724
38	[thianthrenium]$^{\cdot+}$	2	0.7565	-1258.11858	0.16240	0.17417	0.12556	-1257.99302

[a] The CSS spin state was found to be the most stable. The OSS spin state converged to a CSS solution and the triplet spin sate was found at ΔG^{o}_{298K} = +24.5 kcal mol^{-1} relative to the CSS state.

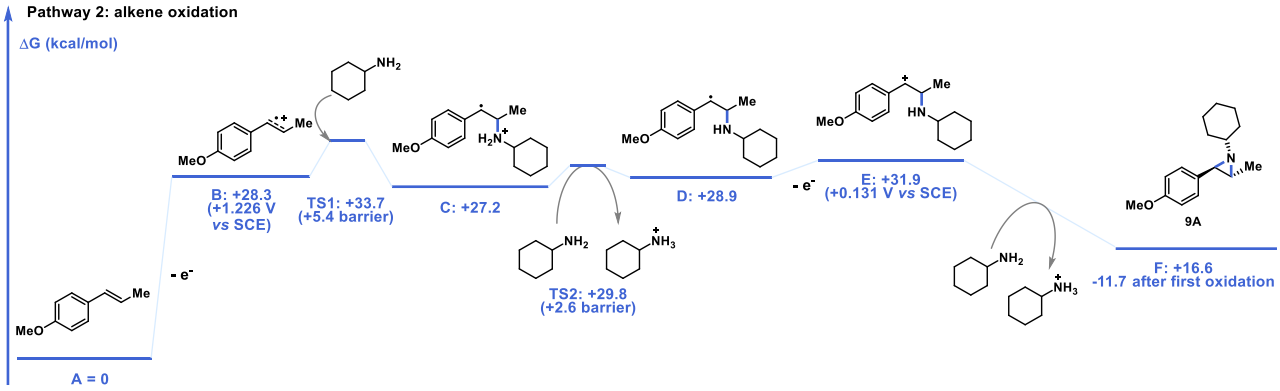
Table S10: Composition of the states in the calculation of the mechanisms.

State in Scheme S1, Scheme S2 and Scheme S3	Composition from entries in Table S9
A	1 + 3 + 3 + 3
B	2 + 3 + 3 + 3

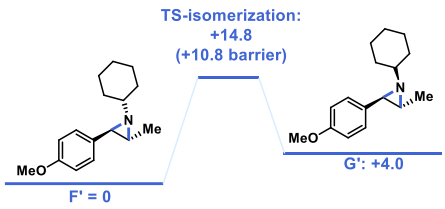
B’	1 + 3 + 3 + 4
TS1	6 + 3 + 3
C	7 + 3 + 3
TS2	8 + 3
D	9 + 3 + 5
E	10 + 3 + 5
F	11 + 5
F’	12 + 3 + 3
TS isomerization	14 + 3 + 3
G’	13 + 3 + 3



Scheme S1. Calculated pathway for initial amine oxidation. Calculations were performed at the B3LYP/def2-TZVP//B3LYP/def2-TZVP(COSMO) level of theory on an m4 grid with disp3 dispersion corrections.



Scheme S2. Calculated pathway for initial anethole oxidation. Calculations were performed at the B3LYP/def2-TZVP//B3LYP/def2-TZVP(COSMO) level of theory on an m4 grid with disp3 dispersion corrections.



Scheme S3. Calculated pathway for *cis*- *trans*-isomerization (methyl and cyclohexyl) of the aziridine. Calculations were performed at the B3LYP/def2-TZVP//B3LYP/def2-TZVP(COSMO) level of theory on an m4 grid with disp3 dispersion corrections.

Table S11: Calculated oxidation potentials for different alkenes. See formula 1 and Table S9 for the energies of the neutral and cationic compounds.

Alkene	Oxidation potential (V *vs* SCE)
anethole	+1.226
p-methoxystyrene + NH_2-C_6H_{11}	+1.391
p-methoxystyrene	+1.427
trans-β-methylstyrene + NH_2-C_6H_{11}	+1.518
trans-β-methylstyrene	+1.678
styrene + NH_2-C_6H_{11}	+1.599
styrene	+1.934
cis-stilbene	+1.493
trans-stilbene	+1.443

4.3. XYZ coordinates for all DFT calculated structures

Anethole

23 atoms

H	-0.0935821	-0.1914165	-0.0365558
C	-0.0624357	-0.1249760	1.0452710
C	0.0158993	0.0771353	3.7983730
C	-0.0431707	-1.3011339	1.7972383
C	-0.0379174	1.1359164	1.6354885
C	0.0032647	1.2425360	3.0233053
C	-0.0078636	-1.1637158	3.1959560
H	-0.0520194	2.0144658	1.0068783
H	-0.0056388	-2.0445233	3.8251795
H	0.0407714	0.1756180	4.8760823
O	0.0291201	2.4157157	3.7144054
C	0.0201566	3.6319551	2.9849607
H	0.8960204	3.7151617	2.3328380
H	0.0481056	4.4274064	3.7267739
H	-0.8884849	3.7318799	2.3820189
H	-0.1820114	-2.5322746	0.0291596
C	-0.0605334	-2.5955768	1.1088851
C	0.0628701	-3.8113869	1.6469640
H	0.1991940	-3.9135882	2.7202302
C	0.0342074	-5.0910474	0.8722273
H	0.9630663	-5.6555537	1.0060963
H	-0.1028809	-4.9123690	-0.1960387
H	-0.7771378	-5.7422280	1.2142626

[Anethole]$^{\cdot+}$

23 atoms

H	-0.1018690	-0.1883159	-0.0787309
C	-0.0587964	-0.1091382	1.0004463
C	0.0511071	0.0418551	3.7888386
C	-0.0157890	-1.3084706	1.7726530
C	-0.0449544	1.1277902	1.5818128
C	0.0108555	1.2237982	2.9952781
C	0.0389063	-1.1815349	3.1953481
H	-0.0767413	2.0167229	0.9696414
H	0.0695882	-2.0646921	3.8174982
H	0.0912563	0.1552993	4.8638434
O	0.0289842	2.3508744	3.6665248
C	-0.0026320	3.6333514	2.9978250
H	0.8711791	3.7421904	2.3547914
H	0.0250981	4.3678273	3.7958984
H	-0.9244988	3.7344357	2.4244239
H	-0.0841361	-2.5049182	0.0052829
C	-0.0290696	-2.5539453	1.0887303
C	0.0249425	-3.7976274	1.6583881
H	0.0856137	-3.8890243	2.7382519
C	0.0105768	-5.0628694	0.8981065
H	0.9149982	-5.6420365	1.1204955
H	-0.0622850	-4.9121740	-0.1779177
H	-0.8233345	-5.6913981	1.2325700

NH_2-C_6H_{11}

20 atoms

H	0.0989232	-0.0370860	-0.0476768
C	0.0107023	0.0299620	1.0402589
C	0.1329650	1.5800581	3.0318038
C	-1.5674853	-0.3054182	3.0111531
C	-1.2578724	1.1187485	3.4781789
C	-1.3829692	-0.4214645	1.4893195
C	0.3101912	1.4546380	1.5155805
H	0.8917269	0.9677438	3.5333732
H	-2.0151998	1.7949223	3.0589501
H	-2.1446201	0.2008056	1.0017964
H	-0.3724210	2.1514649	1.0143798
H	0.7613267	-0.6528248	1.4560971
H	0.3059538	2.6113454	3.3513065
H	-1.3575257	1.1698105	4.5647354
H	-1.5720556	-1.4532967	1.1755695
H	1.3235370	1.7467074	1.2262951
H	-0.8442344	-0.9780693	3.4902788
N	-2.8926542	-0.7035219	3.4951220
H	-3.6050553	-0.1006920	3.0938135
H	-3.1112328	-1.6488332	3.1976646

[NH_2-C_6H_{11}]$^{\cdot+}$

20 atoms

H	0.0969147	-0.0203379	-0.0404544
C	0.0267140	0.0412629	1.0547813
C	0.1265349	1.5764642	3.0369306
C	-1.5719205	-0.3044291	3.0372547
C	-1.2743371	1.1406899	3.4568137
C	-1.3840976	-0.4116143	1.3834838
C	0.3326936	1.4599601	1.5245995
H	0.8703696	0.9716234	3.5649608
H	-2.0282537	1.8040902	3.0191876
H	-2.1453323	0.2351325	0.9463871
H	-0.3191967	2.1687821	1.0044170
H	0.7537168	-0.6683333	1.4583786
H	0.2817027	2.6084396	3.3582443
H	-1.3822679	1.1929930	4.5434966
H	-1.5783385	-1.4481666	1.1146256

H	1.3583112	1.7240415	1.2649889
H	-0.8548172	-1.0293587	3.4280626
N	-2.8626225	-0.7266712	3.3148982
H	-3.6458823	-0.0837911	3.2541425
H	-3.0878912	-1.7057771	3.4528011

$[NH_3\text{-}C_6H_{11}]^+$

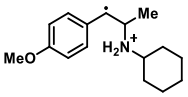
21 atoms

H	-0.0377229	0.2536526	-0.0377665
N	-0.0277503	-0.0396175	0.9425102
H	-0.4034490	-0.9898228	0.9975547
H	-0.6619844	0.5763857	1.4585301
C	1.3872941	0.0394691	1.5378443
C	3.3002853	1.5741412	2.0305630
C	2.7419267	-0.3216129	3.6095907
C	3.2902133	1.1022438	3.4866590
C	1.3439946	-0.4390636	2.9830881
C	1.9047412	1.4649184	1.3972670
H	4.0061998	0.9714424	1.4500417
H	3.4185516	-1.0240748	3.1122387
H	2.6777495	1.7830696	4.0874796
H	0.6409329	0.1851974	3.5480341
H	1.2193327	2.1491180	1.9123217
H	1.9798794	-0.6446950	0.9260243
H	3.6412438	2.6076544	1.9597120
H	2.6882241	-0.6280446	4.6548765
H	4.2997538	1.1472792	3.8977135
H	0.9867195	-1.4718919	3.0372541
H	1.9388644	1.7612513	0.3444632

TS for amine attack on [anethole]$^{\cdot+}$

43 atoms

H	0.1332447	0.4125863	0.4811384
C	-0.0986313	0.2461260	1.5262323
C	-0.6881119	-0.1948005	4.2081350
C	-0.3117645	-1.0828400	1.9743186
C	-0.1856396	1.3272345	2.3720215
C	-0.4856343	1.1201716	3.7310534
C	-0.6017345	-1.2610824	3.3576971
H	-0.0210581	2.3226228	1.9873376
H	-0.7478991	-2.2552754	3.7581140
H	-0.9018004	-0.3271904	5.2603154
O	-0.5951867	2.0841991	4.6412462
C	-0.3894529	3.4559067	4.2712037
H	0.6242068	3.6057428	3.8943231
H	-0.5301983	4.0258743	5.1845660
H	-1.1217352	3.7682729	3.5238488
H	0.0357570	-1.8688709	0.0217906
C	-0.2317808	-2.1414480	1.0381560
C	-0.5160820	-3.4912930	1.2702396
H	-0.6192342	-3.8101398	2.3004113
C	-0.0442804	-4.5439879	0.3167460
H	1.0147633	-4.7421005	0.5097460
H	-0.1342950	-4.2207267	-0.7213831
H	-0.5738521	-5.4878384	0.4476897
H	-2.7219059	-3.9508417	0.0127152
N	-2.6024328	-3.7328570	0.9981853
H	-2.7996095	-4.5726967	1.5360710
C	-3.4385000	-2.5898539	1.4207736
C	-4.3508609	-0.3432143	0.7528323
C	-5.6581375	-1.8250225	2.3337623
C	-5.7428793	-0.7608982	1.2358840
C	-4.8321304	-3.0345853	1.8800766
C	-3.5305518	-1.5555850	0.3011229
H	-3.8170752	0.1647509	1.5642369
H	-5.1967961	-1.3912756	3.2280981
H	-6.3140591	-1.1582389	0.3896396
H	-5.3372908	-3.5391703	1.0489765
H	-4.0124670	-2.0202239	-0.5684119
H	-2.9267534	-2.1342255	2.2741861
H	-4.4280692	0.3737843	-0.0668041
H	-6.6569479	-2.1536344	2.6271847
H	-6.2915981	0.1101187	1.5999642
H	-4.7434467	-3.7618369	2.6935977
H	-2.5310891	-1.2476368	-0.0120383



43 atoms

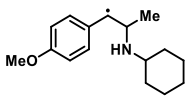
H	-1.4777608	-0.7011039	0.6252835
C	-0.7431319	-0.4384485	1.3770445
C	1.1484782	0.2458662	3.2953832
C	0.1572356	-1.4404988	1.8292950
C	-0.7162624	0.8491884	1.8658230
C	0.2274576	1.2087371	2.8426195
C	1.1166011	-1.0359962	2.8052059
H	-1.4239339	1.5734698	1.4898518
H	1.8804235	-1.7268816	3.1453225
H	1.8871988	0.5500452	4.0252952
O	0.3384382	2.4250609	3.3948362
C	-0.5407092	3.4746826	2.9801927
H	-0.4126002	3.6946426	1.9175181
H	-0.2575943	4.3426908	3.5687062
H	-1.5825816	3.2166594	3.1857790
H	-0.6769668	-2.9600428	0.5619156

C	0.0551681	-2.7519145	1.3312971
C	0.7334241	-5.1625272	1.0086254
H	1.2630192	-6.0019006	1.4631902
H	1.1900691	-4.9692954	0.0380957
H	-0.3040662	-5.4500131	0.8364430
C	-0.8134344	-5.0179827	3.6578380
C	-2.0644718	-6.0909700	5.5668108
C	-3.3226290	-5.0897933	3.6253254
C	-3.3410246	-5.3708212	5.1285276
C	-2.0782521	-4.2933125	3.2093987
C	-0.8150002	-5.2996152	5.1624471
H	-2.0259327	-7.0846993	5.1082611
H	-3.3440188	-6.0370537	3.0753947
H	-3.4326822	-4.4259979	5.6755953
H	-2.1039738	-3.2988976	3.6692181
H	-0.8005425	-4.3460143	5.7043124
H	-0.7059881	-5.9573069	3.1134606
H	-2.0565962	-6.2456031	6.6469320
H	-4.2140845	-4.5371374	3.3240517
H	-4.2163190	-5.9685515	5.3885723
H	-2.0722931	-4.1419169	2.1304585
H	0.0885185	-5.8491733	5.4467366
C	0.8365200	-3.9003621	1.8454937
H	1.8906363	-3.6301569	1.9632266
N	0.4373740	-4.2148048	3.3397858
H	1.2269737	-4.6976216	3.7739585
H	0.3603140	-3.3096283	3.8114712

TS for deprotonation of radical cation

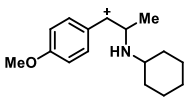
63 atoms

H	-0.8373428	-0.9885749	0.2509922
C	-0.2088642	-0.5168538	0.9971236
C	1.4027433	0.7059025	2.8969368
C	0.5160167	-1.3445505	1.8966256
C	-0.1527817	0.8604618	1.0479347
C	0.6477278	1.4942634	2.0105878
C	1.3476142	-0.6670556	2.8374730
H	-0.7266076	1.4397661	0.3391918
H	1.9767896	-1.2343901	3.5124964
H	2.0463478	1.2103617	3.6063472
O	0.7716693	2.8259390	2.1596989
C	0.0882716	3.6983854	1.2588268
H	0.4117769	3.5302826	0.2284285
H	0.3567748	4.7059720	1.5642362
H	-0.9953308	3.5710407	1.3326062
H	-0.2640225	-3.1425701	1.0545787
C	0.3655984	-2.7411027	1.8393929
C	1.4338457	-5.0025418	2.0165086
H	1.8973761	-5.7241496	2.6923967
H	2.1598387	-4.7537882	1.2422113
H	0.5830886	-5.4809283	1.5298655
C	-0.8250594	-5.0904145	3.9663008
C	-2.3574397	-6.4620565	5.4437787
C	-3.0476588	-5.8891276	3.0864017
C	-3.5320160	-6.1485038	4.5142014
C	-1.9991037	-4.7712937	3.0415889
C	-1.3045144	-5.3505903	5.3992478
H	-1.8956325	-7.4079177	5.1411597
H	-2.6139822	-6.8080995	2.6770802
H	-4.0621705	-5.2628652	4.8845600
H	-2.4604384	-3.8309127	3.3546200
H	-1.7369656	-4.4300471	5.8084107
H	-0.3460760	-6.0061441	3.6061906
H	-2.7025341	-6.5994452	6.4705045
H	-3.8859641	-5.6274764	2.4373608
H	-4.2519168	-6.9690655	4.5266552
H	-1.6527923	-4.6269189	2.0181459
H	-0.4531318	-5.6129897	6.0363666
C	1.0267613	-3.7253544	2.7490107
H	1.9367991	-3.2743316	3.1508657
N	0.2001268	-4.0018365	4.0039676
H	0.8719038	-4.2875568	4.7157525
H	-0.3340672	-2.8217283	4.5025651
H	-0.1908708	-0.9979501	4.6000131
N	-0.7099404	-1.7585660	5.0439736
H	-0.4010580	-1.7994467	6.0144892
C	-2.1784428	-1.4637470	4.9929368
C	-4.0812832	-0.1548920	5.9958172
C	-4.0637101	-0.6838583	3.5234255
C	-4.4924037	0.3185522	4.5987015
C	-2.5626151	-0.9772078	3.5985920
C	-2.5791922	-0.4521506	6.0657296
H	-4.6385608	-1.0629430	6.2517904
H	-4.6213442	-1.6186447	3.6521222
H	-4.0265072	1.2890224	4.3939917
H	-1.9978201	-0.0645114	3.3761274
H	-2.0117286	0.4728635	5.9092799
H	-2.6844642	-2.4120459	5.1962737
H	-4.3428938	0.5918847	6.7477172
H	-4.3120659	-0.3096512	2.5281430
H	-5.5720413	0.4759539	4.5586519
H	-2.2694342	-1.7102566	2.8459936
H	-2.3122809	-0.8305991	7.0580365



42 atoms

H	-1.2067004	-0.7087796	0.3729372
C	-0.6428249	-0.4822611	1.2708059
C	0.7949450	0.1123821	3.5645695
C	0.0974596	-1.5206138	1.8897947
C	-0.6708371	0.8071899	1.7715423
C	0.0525621	1.1175095	2.9279200
C	0.8173673	-1.1693960	3.0674003
H	-1.2528407	1.5608026	1.2603650
H	1.3640538	-1.9372897	3.5944529
H	1.3425937	0.3718824	4.4619159
O	0.0968343	2.3477478	3.5101618
C	-0.6457951	3.4045405	2.9247337
H	-0.3069297	3.6172376	1.9053334
H	-0.4705526	4.2773157	3.5504619
H	-1.7176553	3.1807152	2.9087029
H	-0.4745632	-2.9664286	0.4287534
C	0.0969498	-2.8165262	1.3387620
C	0.7186516	-5.2002201	0.9190015
H	1.2670045	-6.0634460	1.3024152
H	1.1217421	-4.9478708	-0.0642281
H	-0.3251196	-5.4930641	0.7855918
N	0.5194401	-4.3111232	3.2857928
H	1.2894040	-4.8436535	3.6750819
C	-0.7313852	-5.0043057	3.6045987
C	-1.9913814	-6.0645664	5.5454567
C	-3.2573061	-4.8393601	3.7430615
C	-3.2189577	-5.2063546	5.2285239
C	-1.9649032	-4.1475979	3.2984639
C	-0.7025520	-5.3740698	5.0931265
H	-2.0860868	-7.0307606	5.0355682
H	-3.4033253	-5.7520078	3.1522415
H	-3.1790623	-4.2869714	5.8248108
H	-1.8527975	-3.1859503	3.8095528
H	-0.5516366	-4.4539115	5.6680432
H	-0.8348537	-5.9455102	3.0360744
H	-1.9416225	-6.2812800	6.6162556
H	-4.1134217	-4.1929286	3.5312403
H	-4.1347861	-5.7298283	5.5176628
H	-2.0122183	-3.9241219	2.2309744
H	0.1600750	-6.0192107	5.2946110
C	0.8454136	-4.0043075	1.8746933
H	1.9096184	-3.7296070	1.9117723



42 atoms

H	-0.6386753	-0.6422441	0.0959411
C	-0.3754297	-0.4749452	1.1334978
C	0.3305033	-0.0922090	3.8143030
C	0.1233432	-1.5785134	1.9040284
C	-0.5242767	0.7700306	1.6691832
C	-0.1682091	0.9802220	3.0259233
C	0.4654570	-1.3332948	3.2794324
H	-0.9026261	1.5815930	1.0662361
H	0.8203011	-2.1679928	3.8663933
H	0.5884709	0.1161221	4.8439006
O	-0.2648912	2.1328417	3.6433546
C	-0.7611230	3.3119782	2.9705126
H	-0.1140182	3.5679467	2.1309767
H	-0.7297927	4.0974025	3.7185280
H	-1.7869456	3.1524006	2.6369275
H	0.0098813	-2.7925884	0.2122573
C	0.2692016	-2.7903517	1.2685557
C	0.4244162	-5.2475826	0.8118471
H	0.8969363	-6.1711221	1.1452917
H	0.7577771	-5.0465554	-0.2076480
H	-0.6540750	-5.4036236	0.7942131
N	0.6294240	-4.3314888	3.1848646
H	1.4026052	-4.8889034	3.5276957
C	-0.6357275	-4.9657653	3.6049659
C	-1.8518913	-5.8988567	5.6178910
C	-3.1453604	-4.7519955	3.7747375
C	-3.0791394	-5.0506655	5.2753933
C	-1.8510775	-4.0938929	3.2846366
C	-0.5631971	-5.2462642	5.1089932
H	-1.9586663	-6.8913416	5.1665531
H	-3.3076449	-5.6853748	3.2245240
H	-3.0325667	-4.1058247	5.8293414
H	-1.7260008	-3.1186861	3.7673662
H	-0.3919854	-4.2990715	5.6324215
H	-0.7774863	-5.9316826	3.0974721
H	-1.7840066	-6.0545953	6.6966741
H	-3.9971373	-4.1063150	3.5494195
H	-3.9915404	-5.5569162	5.5980357
H	-1.9212772	-3.9035181	2.2070334
H	0.2963954	-5.8889360	5.3246691
C	0.8191451	-4.0927055	1.7548207
H	1.9049099	-3.9427145	1.6178357

***cis*-aziridine adduct with $[NH_3\text{-}C_6H_{11}]^+$**
(*cis* methyl and cyclohexyl)
62 atoms

H	-0.3424427	-1.7232395	3.8093917
C	0.6501336	-1.8632750	3.3966371
C	3.1922374	-2.1856432	2.3463288
C	0.8456464	-2.7932203	2.3776394
C	1.6998235	-1.1087207	3.9075009
C	2.9886911	-1.2796423	3.3930247
C	2.1331059	-2.9234189	1.8466435
H	1.5062273	-0.3964793	4.6959467
H	2.3149104	-3.6006799	1.0214694
H	4.1877826	-2.2833651	1.9338509
O	4.0870581	-0.6306064	3.8347813
C	3.9477111	0.3566989	4.8546188
H	3.2845849	1.1646451	4.5343300
H	4.9459701	0.7519485	5.0221236
H	3.5705983	-0.0831433	5.7829173
H	-1.2160738	-3.0705403	1.7150160
C	-0.3003375	-3.6228002	1.9095101
C	-1.0962580	-5.2669196	0.0308569
H	-1.1830643	-6.3502478	-0.0646510
H	-0.6924390	-4.8820820	-0.9072243
H	-2.0933150	-4.8473354	0.1531931
N	-0.5422396	-4.9288474	2.5820981
H	0.5876298	-5.3806345	3.4950878
C	-1.9177650	-5.2871401	2.9807280
C	-3.4598375	-7.2085169	3.5306278
C	-3.6893491	-5.0041755	4.7515962
C	-3.8456028	-6.5250216	4.8456686
C	-2.2749163	-4.6172927	4.3079364
C	-2.0493375	-6.8080883	3.0843450
H	-4.1748414	-6.9264889	2.7499995
H	-4.4145880	-4.6068542	4.0330136
H	-3.2062925	-6.9045490	5.6516706
H	-1.5582959	-4.9371147	5.0720731
H	-1.3202392	-7.1767006	3.8176592
H	-2.6267404	-4.9302507	2.2256561
H	-3.5222722	-8.2941719	3.6295761
H	-3.9162198	-4.5357110	5.7116677
H	-4.8714628	-6.7823787	5.1166305
H	-2.1810443	-3.5316819	4.2156434
H	-1.8002472	-7.2730618	2.1277808
C	-0.1607218	-4.8867744	1.1494479
H	0.8510918	-5.2531664	1.0010100
H	2.1533044	-6.1445162	3.4019071
N	1.4912570	-5.7778752	4.0855260
H	1.1818516	-6.5709283	4.6480042
C	2.1725534	-4.7549431	4.9590774
C	1.9285308	-3.3202081	7.0050303
C	4.1910892	-4.2383374	6.3545042
C	3.2808903	-3.8247122	7.5140328
C	3.5107145	-5.2850997	5.4646809
C	1.2431817	-4.3475106	6.0963149
H	2.0744956	-2.3960305	6.4372235
H	4.4364414	-3.3600416	5.7473272
H	3.1251497	-4.6827778	8.1773731
H	3.3467299	-6.2052225	6.0391861
H	0.9764350	-5.2361143	6.6831165
H	2.3478356	-3.8966593	4.3123613
H	1.2678583	-3.0763092	7.8391295
H	5.1366219	-4.6345987	6.7286937
H	3.7660632	-3.0524579	8.1144281
H	4.1563938	-5.5412956	4.6184217
H	0.3193436	-3.9336737	5.6888397

***cis*-aziridine** (*cis* methyl and cyclohexyl)
41 atoms

H	-0.9416354	-0.8007537	0.4895835
C	-0.4999014	-0.4161237	1.4025841
C	0.6131291	0.5896305	3.7262275
C	-0.1030755	-1.3029061	2.3968976
C	-0.3469945	0.9618282	1.5469568
C	0.2162760	1.4699981	2.7155735
C	0.4535865	-0.7743445	3.5666871
H	-0.6714850	1.6167338	0.7514816
H	0.7429529	-1.4524372	4.3595455
H	1.0397639	1.0022104	4.6316276
O	0.4159321	2.7957703	2.9690043
C	0.0187944	3.7387173	1.9885393
H	0.5582871	3.5922813	1.0464743
H	0.2664184	4.7175660	2.3944287
H	-1.0585523	3.6900199	1.7963978
H	-0.9490687	-3.0421045	1.4091153
C	-0.2490390	-2.7688186	2.1994163
C	1.0561048	-4.9189109	1.4490460
H	1.5312938	-5.7620582	1.9566339
H	1.7070509	-4.6190904	0.6244602
H	0.1173926	-5.2674809	1.0189180
C	-1.2453317	-4.6859375	3.4704306
C	-1.8381024	-6.8711065	4.5996145
C	-3.6199632	-5.1152997	4.2333546
C	-3.1301509	-6.2496562	5.1392182
C	-2.5303618	-4.0607640	4.0198693
C	-0.7548887	-5.8093439	4.3867836
H	-2.0494064	-7.3695560	3.6459557

H	-3.9173464	-5.5330310	3.2638282
H	-2.9438269	-5.8516303	6.1434678
H	-2.2928657	-3.5685420	4.9687149
H	-0.4714007	-5.3657008	5.3471720
H	-1.4870015	-5.1269265	2.4890388
H	-1.4741981	-7.6453628	5.2804165
H	-4.5135894	-4.6486970	4.6568150
H	-3.9049592	-7.0144244	5.2435897
H	-2.8774388	-3.2788160	3.3387274
H	0.1487264	-6.2602935	3.9687277
C	0.8652945	-3.7525547	2.3889506
H	1.7969378	-3.3452005	2.7760166
N	-0.2203577	-3.6528837	3.3587092

***trans*-aziridine** (*trans* methyl and cyclohexyl)

41 atoms

H	0.8591859	-0.2958911	0.1733816
C	0.5236902	-0.0943160	1.1844753
C	-0.3090663	0.4366192	3.7668851
C	-0.0804632	-1.1145537	1.9155440
C	0.7079105	1.1803715	1.7130734
C	0.2852132	1.4517729	3.0141142
C	-0.4847820	-0.8235287	3.2218573
H	1.1781070	1.9420184	1.1080876
H	-0.9422410	-1.5979918	3.8246469
H	-0.6214414	0.6585118	4.7791196
O	0.4111846	2.6577140	3.6348700
C	1.0117098	3.7277317	2.9235882
H	2.0453319	3.4957466	2.6464843
H	1.0045104	4.5794524	3.6005864
H	0.4442943	3.9791467	2.0214784
C	-0.2520860	-2.4591031	1.2886372
C	-1.3645754	-3.3802622	1.6357583
H	0.6876938	-2.9125983	0.9780458
H	-2.0791504	-2.9900842	2.3551337
C	-1.1957634	-4.8773548	1.6827808
H	-0.4593915	-5.2009372	0.9457752
H	-2.1407256	-5.3794077	1.4589664
H	-0.8647030	-5.2011611	2.6733522
N	-1.3348608	-2.7460262	0.3261505
C	-2.2921488	-1.7063118	-0.0904354
C	-3.9297089	-1.1390874	-1.9500176
C	-4.2729190	-0.1972411	0.3641890
C	-4.9601088	-0.6783007	-0.9158155
C	-3.3405148	-1.2677368	0.9416651
C	-2.9857195	-2.1951513	-1.3687982
H	-3.3414528	-0.2737442	-2.2793073
H	-3.6892713	0.7047530	0.1451338
H	-5.6255512	-1.5154944	-0.6730515
H	-3.9344107	-2.1402903	1.2379588
H	-3.5478289	-3.1059240	-1.1304248
H	-1.6971674	-0.8221749	-0.3504003
H	-4.4296678	-1.5310180	-2.8401629
H	-5.0168121	0.0893561	1.1130278
H	-5.5907917	0.1134683	-1.3301130
H	-2.8560770	-0.8858211	1.8414867
H	-2.2234307	-2.4811503	-2.0967273

TS for *cis*- *trans*-isomerization

41 atoms

H	-1.8541930	-0.0980471	1.1451495
C	-0.9098306	-0.0201374	1.6707867
C	1.5172464	0.1797062	2.9890785
C	-0.2263521	-1.1857032	2.0015423
C	-0.4065481	1.2370644	1.9938857
C	0.8150771	1.3409162	2.6593642
C	0.9993557	-1.0613266	2.6608912
H	-0.9678819	2.1184316	1.7186905
H	1.5579149	-1.9544842	2.9194109
H	2.4678373	0.2764641	3.4977109
O	1.4050793	2.5169222	3.0207667
C	0.7501358	3.7309476	2.6957242
H	0.6263464	3.8439641	1.6132468
H	1.3913930	4.5274487	3.0679837
H	-0.2303754	3.8023077	3.1786853
C	-0.7801477	-2.5360310	1.6800081
C	-2.1882982	-2.9624065	2.1437843
H	-0.0272452	-3.3308296	1.7112426
H	-2.7371399	-2.1932488	2.6985716
C	-2.4609694	-4.3758175	2.6112816
H	-1.8169806	-5.0850505	2.0870818
H	-3.4996240	-4.6561424	2.4155649
H	-2.2871412	-4.4702912	3.6862969
N	-1.8678574	-2.6886596	0.8087788
C	-2.3100348	-2.6511675	-0.5552004
C	-1.5313815	-2.3976743	-2.9473928
C	-3.5148885	-3.8749201	-2.4156003
C	-2.3160110	-3.6528902	-3.3435257
C	-3.0770897	-3.9223450	-0.9490390
C	-1.1059420	-2.4405791	-1.4773141
H	-2.1570517	-1.5136669	-3.1169725
H	-4.2338763	-3.0587301	-2.5541689
H	-1.6522438	-4.5237054	-3.2853147
H	-2.4220474	-4.7845075	-0.7813826
H	-0.4020374	-3.2651861	-1.3182861
H	-2.9950415	-1.7975763	-0.7066358

H	-0.6511126	-2.2818999	-3.5853123
H	-4.0380134	-4.7973276	-2.6817802
H	-2.6475038	-3.5803783	-4.3830844
H	-3.9411167	-4.0467943	-0.2904706
H	-0.5864091	-1.5216487	-1.1950473

NEt_3

22 atoms

N	-0.2175044	-0.1193690	0.8011964
C	0.0148429	-0.1706482	-0.6382118
H	1.0923214	-0.2625041	-0.7951836
H	-0.4452719	-1.0677110	-1.0943482
C	-0.4775951	1.0769526	-1.3647533
H	-0.0020911	1.9687067	-0.9521091
H	-1.5587706	1.2001535	-1.2784011
H	-0.2384892	1.0134611	-2.4288563
C	-1.6411474	-0.1419489	1.1654921
H	-1.8376103	-0.9859897	1.8362574
H	-2.2479118	-0.3331537	0.2732282
C	-2.1069510	1.1517866	1.8282263
H	-1.5403472	1.3415855	2.7412241
H	-3.1690302	1.0985567	2.0847587
H	-1.9551096	2.0018475	1.1611707
C	0.5877357	-1.0832428	1.5434685
H	1.5956983	-1.0647253	1.1219502
H	0.2126285	-2.1159801	1.4118698
C	0.6773650	-0.7619968	3.0319921
H	1.3281091	-1.4810302	3.5350164
H	-0.2984841	-0.8061322	3.5190799
H	1.0836130	0.2403820	3.1799325

$[NEt_3]^{\cdot+}$

22 atoms

N	-0.4098154	-0.4849661	0.7271522
C	0.1350862	-0.0338817	-0.5479338
H	1.1920780	0.1889423	-0.3764276
H	0.1253979	-0.9330145	-1.1870920
C	-0.5630888	1.1193902	-1.2465714
H	-0.4535593	2.0500044	-0.6921791
H	-1.6208034	0.9302443	-1.4268846
H	-0.0875261	1.2542101	-2.2180837
C	-1.7892732	-0.2493777	1.1247403
H	-2.0590329	-1.0307452	1.8339972
H	-2.4136050	-0.3548249	0.2350813
C	-2.0193286	1.1363680	1.7608388
H	-1.3875634	1.2793933	2.6349074
H	-3.0621082	1.1803642	2.0758745
H	-1.8415226	1.9439381	1.0562602
C	0.4346775	-1.3251414	1.5664533
H	1.3367594	-1.5637123	1.0058005
H	-0.1150848	-2.2526494	1.7543895
C	0.7887580	-0.6509464	2.9020841
H	1.4656696	-1.3138734	3.4408289
H	-0.0933034	-0.4921500	3.5202160
H	1.2931888	0.3014283	2.7395480

$N(2,4,6\text{-tribromophenyl})_3$

34 atoms

N	-0.4658908	-0.8106066	0.6888973
C	-0.3995008	-0.7414437	-0.7289295
C	-0.2672942	-0.6038439	-3.5444500
C	-0.5976493	0.4645509	-1.4309067
C	-0.1310435	-1.8743083	-1.5231839
C	-0.0395392	-1.8098892	-2.9056229
C	-0.5592500	0.5353878	-2.8154647
H	0.1732033	-2.7026807	-3.4733751
H	-0.7219495	1.4801744	-3.3110205
C	0.5701361	-1.4536916	1.4187255
C	2.6271468	-2.7271439	2.8717336
C	1.9324385	-1.1694565	1.1960240
C	0.3013451	-2.4163597	2.4123455
C	1.3052890	-3.0277974	3.1482607
C	2.9497958	-1.8088565	1.8884770
H	3.9797760	-1.5621534	1.6813892
C	-1.5683307	-0.2362897	1.3775635
C	-3.7575311	0.9002211	2.7481533
C	-2.9025108	-0.4908649	1.0016060
C	-1.3976732	0.6232505	2.4812896
C	-2.4687208	1.1655577	3.1756076
C	-3.9829075	0.0835629	1.6543433
H	-2.2904429	1.8149563	4.0188522
H	-4.9879416	-0.1364571	1.3285708
Br	-5.2350437	1.6662061	3.6742543
Br	-0.1778408	-0.5108113	-5.4450027
Br	-1.4620972	-3.0403575	2.7862465
Br	2.5130612	0.1846194	-0.0154741
Br	0.0468857	-3.6248451	-0.7860458
Br	-0.8504782	2.1359201	-0.5467221
Br	-3.3610921	-1.7180060	-0.3850786
Br	0.3205751	1.1979461	3.0782405
H	1.0519467	-3.7557866	3.9035081
Br	4.0151287	-3.5847036	3.8541880

$[N(2,4,6\text{-tribromophenyl})_3]^{\cdot+}$

34 atoms

N	-0.4652508	-0.8104716	0.6887374

C	-0.3994067	-0.7416623	-0.7164108
C	-0.2703265	-0.6052945	-3.5202880
C	-0.6489506	0.4717637	-1.4126328
C	-0.0806374	-1.8828371	-1.5008834
C	-0.0093809	-1.8118306	-2.8776779
C	-0.5939244	0.5346482	-2.7905467
H	0.2171229	-2.6968155	-3.4531220
H	-0.7706214	1.4722088	-3.2959398
C	0.5610798	-1.4485554	1.4119704
C	2.6091987	-2.7154085	2.8599917
C	1.9314162	-1.1858092	1.1437757
C	0.2724901	-2.3821474	2.4436001
C	1.2797513	-2.9964539	3.1601311
C	2.9362220	-1.8154329	1.8503908
H	3.9699551	-1.5855918	1.6403448
C	-1.5579314	-0.2414722	1.3714296
C	-3.7379850	0.8904040	2.7359259
C	-2.8958313	-0.4683666	0.9501111
C	-1.3713361	0.5839919	2.5128714
C	-2.4439897	1.1318043	3.1872832
C	-3.9650761	0.0956103	1.6164428
H	-2.2759135	1.7697857	4.0418901
H	-4.9735380	-0.1058824	1.2877404
Br	-5.1978171	1.6475325	3.6503556
Br	-0.1842627	-0.5140005	-5.3979953
Br	-1.4850924	-2.9888107	2.8346717
Br	2.5142103	0.1447613	-0.0807060
Br	0.1237466	-3.6238688	-0.7676446
Br	-0.9259934	2.1345524	-0.5359144
Br	-3.3555731	-1.6696246	-0.4484415
Br	0.3395280	1.1358916	3.1282463
H	1.0355126	-3.7153884	3.9275897
Br	3.9806047	-3.5612298	3.8317032

N(4-bromophenyl)$_3$

34 atoms

N	-0.4688612	-0.8142708	0.6884914
C	-0.4015130	-0.7430787	-0.7231062
C	-0.2689534	-0.6028644	-3.5038564
C	-0.7585997	0.4299462	-1.3943811
C	0.0232015	-1.8445477	-1.4716850
C	0.0987363	-1.7750820	-2.8553726
C	-0.7021574	0.5000581	-2.7789396
H	0.4271273	-2.6336756	-3.4248162
H	-0.9793582	1.4130018	-3.2879611
C	0.5629967	-1.4539345	1.4152996
C	2.5948107	-2.7108977	2.8506850
C	1.9027771	-1.2686214	1.0626123
C	0.2606003	-2.2818847	2.5002131
C	1.2700794	-2.9019933	3.2221975
C	2.9159871	-1.8998308	1.7696762
H	3.9492968	-1.7479982	1.4895031
C	-1.5658484	-0.2412092	1.3744344
C	-3.7265828	0.8865223	2.7263682
C	-2.8660687	-0.3831847	0.8814925
C	-1.3688383	0.4768258	2.5574401
C	-2.4432436	1.0321302	3.2373047
C	-3.9427761	0.1842496	1.5475706
H	-2.2793964	1.5870093	4.1508535
H	-4.9447705	0.0668855	1.1584008
H	1.0248716	-3.5414401	4.0590454
H	-3.0338617	-0.9400523	-0.0307370
H	-0.3674112	0.5985435	2.9483249
H	-0.7723490	-2.4380712	2.7816564
H	0.2984978	-2.7604679	-0.9658452
H	2.1519095	-0.6274676	0.2274935
H	-1.0853206	1.2918755	-0.8277562
Br	3.9877621	-3.5710116	3.8359992
Br	-5.2078638	1.6591062	3.6536804
Br	-0.1778801	-0.5065694	-5.4102863

[N(4-bromophenyl)$_3$]$^{\cdot+}$

34 atoms

N	-0.4676603	-0.8128373	0.6885752
C	-0.4013417	-0.7425510	-0.7155188
C	-0.2707020	-0.6035851	-3.4849556
C	-0.8076612	0.4246477	-1.3821377
C	0.0712718	-1.8392446	-1.4542471
C	0.1315982	-1.7713855	-2.8317846
C	-0.7380103	0.4950211	-2.7590694
H	0.4740896	-2.6221859	-3.4041263
H	-1.0294474	1.4003063	-3.2731216
C	0.5579506	-1.4503422	1.4113592
C	2.5806836	-2.7028492	2.8413104
C	1.8973389	-1.2959225	1.0190792
C	0.2449041	-2.2416147	2.5283119
C	1.2507576	-2.8682190	3.2362468
C	2.9032978	-1.9151082	1.7334381
H	3.9369237	-1.7794663	1.4471728
C	-1.5593942	-0.2437387	1.3708574
C	-3.7120124	0.8780663	2.7169958
C	-2.8553771	-0.3535349	0.8418057
C	-1.3556029	0.4355664	2.5827318
C	-2.4258224	0.9974589	3.2494858
C	-3.9263287	0.2004062	1.5140869
H	-2.2688033	1.5401003	4.1712013

H	-4.9279479	0.0982405	1.1203313
H	1.0107161	-3.4952971	4.0835169
H	-3.0185020	-0.8988793	-0.0777296
H	-0.3551594	0.5446620	2.9786122
H	-0.7877252	-2.3844170	2.8160154
H	0.3595546	-2.7488904	-0.9453324
H	2.1433475	-0.6660012	0.1751698
H	-1.1466029	1.2803021	-0.8142189
Br	3.9545142	-3.5510544	3.8140950
Br	-5.1739569	1.6394313	3.6315385
Br	-0.1818904	-0.5090846	-5.3656955

Thianthrene

22 atoms

H	-0.4548977	0.9319773	0.6624368
C	-0.3823165	0.4908991	1.6486905
C	-0.1302185	-0.6628246	4.1650035
C	-0.5276107	-0.8888355	1.7929445
C	-0.1548338	1.2918798	2.7601573
C	-0.0287002	0.7145560	4.0193510
C	-0.4006803	-1.4697019	3.0598251
H	-0.0609714	2.3635267	2.6386884
H	0.1641637	1.3327676	4.8868708
H	-0.0065219	-1.1203146	5.1386419
S	-0.9294195	-1.8626000	0.3654543
S	-0.6342682	-3.2110860	3.3058598
C	0.0693245	-3.3057653	0.6245507
C	0.1966795	-3.8865641	1.8913907
C	0.7003940	-3.8946670	-0.4711245
H	0.6205397	-3.4267065	-1.4443612
C	0.9538519	-5.0478284	2.0452389
H	1.0713399	-5.4779630	3.0320136
C	1.5444163	-5.6508981	0.9424586
H	2.1154674	-6.5615811	1.0709771
C	1.4174810	-5.0738804	-0.3167702
H	1.8887808	-5.5313903	-1.1772976

[Thianthrenium]$^{\cdot+}$

22 atoms

H	-0.4786756	1.0691677	0.7203059
C	-0.3807145	0.6175347	1.6999732
C	-0.1272890	-0.5411680	4.2269846
C	-0.0694260	-0.7498225	1.8029033
C	-0.5570829	1.3786540	2.8334723
C	-0.4297796	0.7962334	4.1036799
C	0.0590168	-1.3365521	3.0825222
H	-0.7936408	2.4301998	2.7411389
H	-0.5682153	1.3982023	4.9918149
H	-0.0287167	-0.9886435	5.2084969
S	0.1205438	-1.5646686	0.2856594
S	0.4343493	-2.9964488	3.4082028
C	0.5392695	-3.2140329	0.6117578
C	0.6680260	-3.8006864	1.8913754
C	0.7598941	-4.0010423	-0.5323969
H	0.6625156	-3.5531993	-1.5138582
C	1.0142120	-5.1596009	1.9946003
H	1.1140611	-5.6108464	2.9742532
C	1.2277844	-5.9116969	0.8614228
H	1.4961905	-6.9555864	0.9540224
C	1.0999501	-5.3293377	-0.4087569
H	1.2697271	-5.9236594	-1.2965741

***p*-methoxystyrene + NH_2-C_6H_{11}**

40 atoms

H	-0.0522740	-0.9696611	-1.1705654
C	-0.3290591	-0.8968927	-0.1151651
C	-1.7979909	0.3108364	1.5532881
C	-1.3332747	-2.1625714	1.8334876
C	-2.3485526	-1.0357137	2.0322808
C	-0.8906526	-2.2368689	0.3703419
C	-1.3392371	0.2358128	0.0935688
H	-0.9507324	0.6068515	2.1839346
H	-3.2562439	-1.2822535	1.4767994
H	-1.7534439	-2.5222947	-0.2385754
H	-2.2122562	0.0584077	-0.5425665
H	0.5920456	-0.6658505	0.4336970
H	-2.5619451	1.0838485	1.6709508
H	-2.6310376	-0.9748137	3.0892410
H	-0.1422117	-3.0282521	0.2507033
H	-0.9074317	1.1913922	-0.2177944
H	-0.4432946	-1.9181848	2.4387742
N	-1.9255041	-3.4474482	2.2373501
H	-2.2612783	-3.3968446	3.1937446
H	-1.2256755	-4.1821599	2.2098694
C	-7.4034507	1.0250397	1.9651654
H	-7.5350603	0.2196941	2.6773841
C	-6.7151967	0.8798504	0.8315955
H	-6.6270534	1.7449477	0.1791237
C	-6.0359243	-0.3223571	0.3386160
C	-4.6493611	-2.5660951	-0.6628516
C	-5.2801570	-0.2496302	-0.8405145
C	-6.0900766	-1.5608097	0.9865349
C	-5.4109160	-2.6697246	0.5042602
C	-4.5999796	-1.3457728	-1.3381291
H	-5.2181554	0.6939886	-1.3709222
H	-6.6682568	-1.6681041	1.8955753

H	-5.4579316	-3.5991615	1.0517971
H	-4.0086057	-1.2774273	-2.2420017
H	-7.8624418	1.9714939	2.2188392
O	-3.9220702	-3.5772618	-1.2018910
C	-3.8367091	-4.8077201	-0.4869859
H	-3.4159977	-4.6465180	0.5095088
H	-3.1708547	-5.4403254	-1.0706939
H	-4.8167510	-5.2904459	-0.4147753

[*p*-methoxystyrene]$^{\cdot+}$ + NH_2-C_6H_{11}

40 atoms

H	0.4967325	-0.9913474	-0.5882935
C	0.0391313	-0.6190984	0.3307853
C	-0.9591353	1.4104309	1.4661652
C	-1.9316680	-0.8801911	1.8859959
C	-2.2345342	0.6142110	1.7595294
C	-1.2372829	-1.4120193	0.6307701
C	-0.2500427	0.8808490	0.2163663
H	-0.2837129	1.3401867	2.3258055
H	-2.9509327	0.7541787	0.9420997
H	-1.9321755	-1.3284614	-0.2111915
H	-0.8818638	1.0615893	-0.6615805
H	0.7672240	-0.7890542	1.1315566
H	-1.2029854	2.4684855	1.3494766
H	-2.7147285	0.9795461	2.6730489
H	-1.0076596	-2.4759553	0.7515469
H	0.6782910	1.4311226	0.0492526
H	-1.2368261	-1.0083166	2.7334482
N	-3.1574412	-1.6310866	2.1537140
H	-3.6599516	-1.3060533	2.9716878
H	-3.0164658	-2.6332386	2.2040506
C	-6.8009966	-0.1093853	2.4538208
H	-7.2593368	-0.9911524	2.8828431
C	-5.9604120	-0.1558282	1.4043520
H	-5.5664801	0.7799524	1.0222410
C	-5.5426580	-1.3400926	0.6948588
C	-4.9429575	-3.5726524	-0.9090184
C	-4.8379138	-1.1984134	-0.5354011
C	-5.9087024	-2.6570180	1.0954973
C	-5.6213764	-3.7485612	0.3224115
C	-4.5532112	-2.2758456	-1.3213292
H	-4.5483878	-0.2066085	-0.8578032
H	-6.4340978	-2.8041006	2.0292620
H	-5.9185048	-4.7339903	0.6494517
H	-4.0325980	-2.1745562	-2.2640015
H	-7.0685985	0.8373013	2.9036068
O	-4.6268175	-4.5526809	-1.7344739
C	-4.9901138	-5.9180334	-1.4471458
H	-4.5091167	-6.2544644	-0.5274149
H	-4.6225325	-6.4940248	-2.2903854
H	-6.0741608	-6.0146233	-1.3726056

***p*-methoxystyrene**

20 atoms

C	-7.4428262	1.0177996	1.9415247
H	-7.5643768	0.2185142	2.6625688
C	-6.7350550	0.8762914	0.8196818
H	-6.6609378	1.7345646	0.1564591
C	-6.0195737	-0.3151913	0.3512962
C	-4.6009541	-2.5479604	-0.6289098
C	-5.2716534	-0.2458840	-0.8336575
C	-6.0360855	-1.5400454	1.0247042
C	-5.3414159	-2.6450595	0.5520606
C	-4.5730296	-1.3354775	-1.3196440
H	-5.2385124	0.6881098	-1.3832306
H	-6.6051697	-1.6446967	1.9397126
H	-5.3850572	-3.5716417	1.1060975
H	-3.9976071	-1.2723718	-2.2340986
H	-7.9285746	1.9555952	2.1767448
O	-3.8857243	-3.5660742	-1.1795364
C	-3.8717984	-4.8231346	-0.5215956
H	-3.4437105	-4.7453525	0.4831405
H	-3.2449845	-5.4721016	-1.1294875
H	-4.8769531	-5.2518836	-0.4538307

[*p*-methoxystyrene]$^{\cdot+}$

20 atoms

C	-7.4446192	0.9816008	1.9250397
H	-7.5939657	0.1648510	2.6187993
C	-6.6985328	0.8687458	0.7937426
H	-6.6049972	1.7453656	0.1611638
C	-6.0120738	-0.2995646	0.3472492
C	-4.6199444	-2.5437774	-0.6072137
C	-5.2597696	-0.2348082	-0.8632431
C	-6.0380911	-1.5408903	1.0560252
C	-5.3656289	-2.6363963	0.6005545
C	-4.5817667	-1.3179637	-1.3320058
H	-5.2311083	0.6975505	-1.4128651
H	-6.6018332	-1.6222548	1.9747614
H	-5.4005891	-3.5637621	1.1527657
H	-4.0054189	-1.2852466	-2.2468595
H	-7.9240629	1.9191928	2.1731671
O	-3.9366516	-3.5270273	-1.1341636
C	-3.8722763	-4.8363687	-0.5162959
H	-3.4293881	-4.7583726	0.4767414
H	-3.2338954	-5.4225360	-1.1687879

H	-4.8693866	-5.2743380	-0.4685754

***trans*-β-methylstyrene + NH_2-C_6H_{11}**

39 atoms

H	-1.1970909	-0.5991603	-1.0636875
C	-1.1521384	-0.5722549	0.0284080
C	-1.8715082	0.7131834	2.0865652
C	-1.7962569	-1.8210637	2.1345494
C	-2.4997892	-0.5642552	2.6509463
C	-1.7921083	-1.8387346	0.6046405
C	-1.8446499	0.6886478	0.5549262
H	-0.8476408	0.8170196	2.4656835
H	-3.5509524	-0.6192024	2.3562554
H	-2.8245685	-1.9256018	0.2568027
H	-2.8728178	0.7107890	0.1822643
H	-0.0894108	-0.5416808	0.2982038
H	-2.4265145	1.5866883	2.4399018
H	-2.4741284	-0.5490609	3.7463802
H	-1.2606709	-2.7280649	0.2476249
H	-1.3472598	1.5837985	0.1702311
H	-0.7447007	-1.7764420	2.4697059
N	-2.4846476	-3.0137087	2.6436692
H	-2.4345577	-3.0498758	3.6564030
H	-2.0422538	-3.8569782	2.2937315
C	-5.9001394	1.0015019	1.9674402
H	-5.9764493	0.1629347	2.6535503
C	-5.6857858	0.7756426	0.6696475
H	-5.5976009	1.6393296	0.0139320
C	-5.5119783	-0.5204865	0.0039402
C	-5.0853562	-2.9479912	-1.3536527
C	-5.1252451	-0.5408971	-1.3428016
C	-5.6840340	-1.7509967	0.6529216
C	-5.4721721	-2.9462509	-0.0159765
C	-4.9115645	-1.7376010	-2.0146970
H	-4.9814310	0.3987447	-1.8643850
H	-5.9725850	-1.7792569	1.6950335
H	-5.5931327	-3.8818018	0.5150409
H	-4.6070998	-1.7241163	-3.0542438
H	-4.9159823	-3.8836676	-1.8718536
C	-6.0309285	2.3572696	2.5841568
H	-5.9373423	3.1501261	1.8398465
H	-5.2624555	2.5141782	3.3484740
H	-6.9970515	2.4722964	3.0864216

[*trans*-β-methylstyrene]$^{\cdot+}$ + NH_2-C_6H_{11}

39 atoms

H	0.2312392	-0.4320723	-0.9899412
C	-0.1264518	-0.4988673	0.0392653
C	-0.8268822	0.8302659	2.0752010
C	-2.0117990	-1.3210751	1.4936856
C	-2.1602799	0.0771304	2.1112752
C	-1.4603135	-1.2523173	0.0709819
C	-0.2614261	0.8973879	0.6538178
H	-0.1091963	0.3248685	2.7303385
H	-2.9153328	0.6251350	1.5381830
H	-2.1903105	-0.7348752	-0.5606296
H	-0.9249630	1.5058839	0.0282588
H	0.6256034	-1.0707849	0.5932168
H	-0.9644885	1.8345708	2.4811575
H	-2.5311400	-0.0035604	3.1376546
H	-1.3421346	-2.2616701	-0.3355773
H	0.7075845	1.4001445	0.6589852
H	-1.2858497	-1.8790679	2.1122625
N	-3.2758294	-2.0285338	1.5354613
H	-3.6846049	-2.1660616	2.4497818
H	-3.3870691	-2.8277583	0.9249907
C	-6.7200693	0.6482979	2.1526502
H	-7.2693932	-0.1323207	2.6701368
C	-5.9440847	0.3281095	1.0909548
H	-5.4248428	1.1360473	0.5838707
C	-5.7572564	-0.9831549	0.5295855
C	-5.5193248	-3.4499786	-0.8004410
C	-5.0335753	-1.1024081	-0.6904480
C	-6.3231591	-2.1656851	1.0786858
C	-6.2048974	-3.3697133	0.4234417
C	-4.9319872	-2.3136451	-1.3501790
H	-4.5959103	-0.2113616	-1.1225729
H	-6.8693466	-2.1205957	2.0109594
H	-6.6542980	-4.2597962	0.8445469
H	-4.4000385	-2.3754082	-2.2903072
H	-5.4525622	-4.3991544	-1.3170175
C	-6.9024186	2.0229461	2.6756721
H	-6.3309911	2.7638116	2.1174404
H	-6.6119138	2.0688360	3.7311233
H	-7.9622868	2.2994307	2.6495285

***Trans*-β-methylstyrene**

19 atoms

C	-5.9099872	1.0035223	1.9690807
H	-6.0524380	0.1653832	2.6456522
C	-5.6189400	0.7761256	0.6863612
H	-5.4802981	1.6397871	0.0392467
C	-5.4546289	-0.5208154	0.0182785
C	-5.1117771	-2.9502895	-1.3640659
C	-5.1209099	-0.5426753	-1.3420680
C	-5.6143970	-1.7528469	0.6699777

C	-5.4451504	-2.9482859	-0.0111306
C	-4.9506498	-1.7398482	-2.0266720
H	-4.9928790	0.3967183	-1.8681645
H	-5.8753026	-1.7789781	1.7201910
H	-5.5744055	-3.8866144	0.5147563
H	-4.6920712	-1.7257454	-3.0785387
H	-4.9805433	-3.8861294	-1.8927701
C	-6.0613266	2.3607357	2.5790130
H	-5.9058287	3.1532580	1.8447371
H	-5.3467197	2.5072860	3.3956525
H	-7.0587470	2.4884123	3.0124629

[*Trans*-β-methylstyrene]$^{\cdot+}$

19 atoms

C	-5.9140234	0.9950976	1.9622468
H	-6.0585669	0.1509142	2.6286285
C	-5.6104880	0.7664133	0.6355685
H	-5.4688535	1.6383653	0.0039416
C	-5.4575882	-0.4965459	0.0118247
C	-5.1150758	-2.9225628	-1.3338193
C	-5.1163239	-0.5235063	-1.3752661
C	-5.6244785	-1.7408412	0.6976334
C	-5.4553322	-2.9262560	0.0306548
C	-4.9467881	-1.7158165	-2.0325310
H	-4.9902421	0.4144694	-1.9014535
H	-5.8867604	-1.7537834	1.7459816
H	-5.5822716	-3.8671018	0.5491375
H	-4.6858226	-1.7317524	-3.0821687
H	-4.9817244	-3.8637677	-1.8526548
C	-6.0552148	2.3306809	2.5592623
H	-5.9105200	3.1412277	1.8474221
H	-5.3436567	2.4398569	3.3888033
H	-7.0432689	2.4239088	3.0287885

Styrene + NH_2-C_6H_{11}

36 atoms

H	-1.0760656	-0.6690642	-1.1154481
C	-1.0401384	-0.6461585	-0.0228062
C	-1.7672334	0.6332035	2.0355991
C	-1.7011230	-1.9010632	2.0747820
C	-2.4027288	-0.6438716	2.5924162
C	-1.6868633	-1.9130852	0.5447039
C	-1.7335734	0.6139476	0.5041461
H	-0.7443524	0.7310569	2.4191009
H	-3.4531192	-0.6928627	2.2937929
H	-2.7173095	-1.9957402	0.1899098
H	-2.7600139	0.6390886	0.1256726
H	0.0204759	-0.6190319	0.2556843
H	-2.3207951	1.5067276	2.3900728
H	-2.3819816	-0.6325847	3.6878237
H	-1.1553800	-2.8024515	0.1879951
H	-1.2330658	1.5097274	0.1248822
H	-0.6516226	-1.8613317	2.4164095
N	-2.3964649	-3.0937633	2.5746614
H	-2.3616899	-3.1279481	3.5880991
H	-1.9475966	-3.9371073	2.2333816
C	-5.8478169	1.0339392	1.9652840
H	-5.9207091	0.2390264	2.6969822
C	-5.6309456	0.8037055	0.6700458
H	-5.5576685	1.6612033	0.0062650
C	-5.4520146	-0.4961291	0.0108927
C	-5.0401697	-2.9305525	-1.3310326
C	-5.1012360	-0.5245978	-1.3448035
C	-5.5928271	-1.7196224	0.6791406
C	-5.3881073	-2.9198099	0.0174474
C	-4.8952150	-1.7263867	-2.0100916
H	-4.9819722	0.4111946	-1.8791016
H	-5.8509444	-1.7375825	1.7294707
H	-5.4817831	-3.8507306	0.5615129
H	-4.6199092	-1.7219037	-3.0576638
H	-5.9556594	2.0436399	2.3389295
H	-4.8763801	-3.8700818	-1.8441564

[Styrene]$^{\cdot+}$ + NH_2-C_6H_{11}

36 atoms

H	0.4991124	-0.8827417	-0.8899359
C	0.0533305	-0.7261805	0.0939173
C	-0.7391991	1.0151208	1.7521727
C	-1.9937335	-1.1529141	1.4953305
C	-2.1141397	0.3404709	1.8085837
C	-1.3205070	-1.4033766	0.1445219
C	-0.0515836	0.7695896	0.4059129
H	-0.1123697	0.6237356	2.5606027
H	-2.7794237	0.7991926	1.0688876
H	-1.9616454	-0.9939327	-0.6431732
H	-0.6206089	1.2666832	-0.3881169
H	0.7202509	-1.2061773	0.8180146
H	-0.8514760	2.0849893	1.9365721
H	-2.5743103	0.4841890	2.7910546
H	-1.2291675	-2.4783282	-0.0385384
H	0.9416121	1.2221579	0.4058076
H	-1.3584066	-1.6096358	2.2762081
N	-3.2887317	-1.8067495	1.5707399
H	-3.8533765	-1.6032999	2.3868269
H	-3.3349662	-2.7773976	1.2842271
C	-7.1061525	0.0927394	2.4606311

H	-7.7564913	-0.7178986	2.7634530
C	-6.1990459	-0.0259066	1.4784454
H	-5.5908747	0.8402489	1.2361550
C	-5.9424268	-1.2103205	0.6803136
C	-5.3959819	-3.3907895	-1.0257378
C	-4.9116408	-1.1533494	-0.3055876
C	-6.6492380	-2.4183597	0.8159649
C	-6.3778107	-3.4850338	-0.0156713
C	-4.6717137	-2.2291512	-1.1714028
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H	-7.4284665	-2.5126863	1.5595616
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H	-3.9203702	-2.1384859	-1.9442551
H	-7.2279281	1.0288882	2.9887584
H	-5.2263931	-4.2306341	-1.6870550

Styrene

16 atoms

C	-7.0929558	0.0952929	2.4728989
H	-7.7505171	-0.7112864	2.7730385
C	-6.2074591	-0.0251931	1.4835535
H	-5.5859721	0.8353298	1.2497801
C	-5.9548788	-1.2046453	0.6450711
C	-5.3921598	-3.4061847	-1.0115642
C	-4.9634371	-1.1345801	-0.3411380
C	-6.6609202	-2.4083671	0.7812515
C	-6.3830691	-3.4931089	-0.0355473
C	-4.6831538	-2.2208737	-1.1611794
H	-4.4054541	-0.2130856	-0.4636780
H	-7.4356994	-2.4982165	1.5318451
H	-6.9412595	-4.4133445	0.0872946
H	-3.9106765	-2.1405229	-1.9162263
H	-7.1874532	1.0224326	3.0227522
H	-5.1779342	-4.2556465	-1.6481522

[Styrene]$^{\cdot+}$

16 atoms

C	-7.1046329	0.0650573	2.4574859
H	-7.7636318	-0.7445823	2.7416602
C	-6.1776070	-0.0439022	1.4523780
H	-5.5622890	0.8248759	1.2420378
C	-5.9442989	-1.1924063	0.6510934
C	-5.4063385	-3.3830329	-0.9930159
C	-4.9337245	-1.1174895	-0.3584173
C	-6.6742876	-2.4158330	0.8051829
C	-6.4049198	-3.4857955	-0.0052672
C	-4.6723190	-2.1942348	-1.1645585
H	-4.3792546	-0.1949397	-0.4764681
H	-7.4416500	-2.4984185	1.5617373
H	-6.9544891	-4.4106884	0.1073281
H	-3.9088379	-2.1380678	-1.9288501
H	-7.2048190	0.9909397	3.0091489
H	-5.1999003	-4.2334820	-1.6314752

***cis*-stilbene**

26 atoms

H	-1.4168764	0.1458810	0.7597120
C	-0.8579605	0.1091308	1.6851113
C	0.5454472	0.0110746	4.0816786
C	-0.0787302	-1.0191833	1.9724820
C	-0.9253869	1.1713006	2.5747615
C	-0.2179845	1.1316996	3.7737315
C	0.6043211	-1.0564693	3.1943929
H	-1.5380916	2.0320653	2.3353482
H	-0.2713010	1.9628029	4.4660384
H	1.1953682	-1.9305969	3.4435311
H	1.0910892	-0.0349576	5.0164915
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H	0.0280364	-3.1387699	1.5836739
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C	0.0782269	-1.1276084	-1.2464586
C	0.2188353	0.8970584	-3.1885569
C	0.8565654	0.0179900	-1.0348630
C	-0.6030991	-1.2475756	-2.4640357
C	-0.5435146	-0.2423183	-3.4212864
C	0.9245276	1.0178689	-1.9939657
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H	-1.1932577	-2.1369224	-2.6545644
H	-1.0877042	-0.3517980	-4.3516869
H	1.5364109	1.8932191	-1.8122483
H	0.2727012	1.6796137	-3.9352440

[*cis*-stilbene]$^{\cdot+}$

26 atoms

H	-1.2373722	0.3230150	0.7658192
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C	-0.8079430	1.2234510	2.6502822
C	-0.1903059	1.0690884	3.8966424
C	0.5578291	-1.1310157	3.2894475
H	-1.3680521	2.1234775	2.4337886
H	-0.2602398	1.8612396	4.6313638
H	1.0715376	-2.0531115	3.5320163
H	0.9525505	-0.2259169	5.1848337

C	0.0895182	-2.0632661	1.0847474
H	0.2968688	-3.0256067	1.5455974
C	-0.0904967	-2.1095074	-0.2904537
H	-0.2976319	-3.1006352	-0.6856314
C	0.0103350	-1.0853923	-1.2745694
C	0.1910754	0.8262706	-3.3070004
C	0.7217986	0.1279669	-1.0681548
C	-0.5572395	-1.3280814	-2.5534439
C	-0.4896422	-0.3731394	-3.5437015
C	0.8073729	1.0645628	-2.0732982
H	1.2351206	0.2935193	-0.1319416
H	-1.0705130	-2.2645741	-2.7338595
H	-0.9500277	-0.5531249	-4.5060292
H	1.3670256	1.9773232	-1.9174298
H	0.2616188	1.5670281	-4.0934369

[*trans*-stilbene]

26 atoms

H	-0.0187314	0.1459411	-0.0061718
C	-0.0101515	0.0915729	1.0747301
C	0.0097221	0.0085768	3.8520029
C	-0.0012170	-1.1580883	1.7153626
C	-0.0086317	1.2683518	1.8062490
C	0.0014795	1.2355148	3.1995739
C	0.0081774	-1.1703110	3.1178297
H	-0.0155197	2.2199458	1.2885610
H	0.0026141	2.1576060	3.7671992
H	0.0149791	-2.1227390	3.6358351
H	0.0174828	-0.0320061	4.9344112
C	-0.0012341	-2.4343077	1.0015386
H	-0.0004100	-3.3057600	1.6490266
C	-0.0008021	-2.6197182	-0.3275614
H	0.0005623	-1.7482638	-0.9750397
C	-0.0006618	-3.8959257	-1.0414068
C	0.0013409	-6.2894943	-2.5256953
C	0.0086324	-3.8836652	-2.4438708
C	-0.0095195	-5.1456125	-0.4008069
C	-0.0083637	-6.3223710	-1.1323637
C	0.0097161	-5.0625347	-3.1780862
H	0.0151820	-2.9312205	-2.9618578
H	-0.0180484	-5.2000136	0.6800995
H	-0.0155025	-7.2739833	-0.6147012
H	0.0169765	-5.0219207	-4.2605040
H	0.0019283	-7.2115736	-3.0933536

[*trans*-stilbene]$^{\cdot+}$

26 atoms

H	0.0000000	0.1218122	-0.0377706
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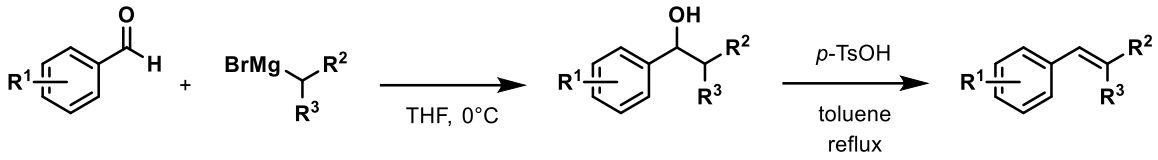
C	0.0000000	-1.1874664	1.7037764
C	0.0000000	1.2393435	1.7683317
C	0.0000000	1.1960536	3.1692381
C	0.0000000	-1.2030929	3.1248761
H	0.0000000	2.1942850	1.2599338
H	0.0000000	2.1202027	3.7333419
H	0.0000000	-2.1556313	3.6404173
H	0.0000000	-0.0513382	4.9256793
C	0.0000000	-2.4332433	1.0219324
H	0.0000000	-3.3111123	1.6576973
C	0.0000000	-2.6201065	-0.3491021
H	0.0000000	-1.7423331	-0.9850295
C	0.0000000	-3.8661454	-1.0304871
C	0.0000000	-6.2505170	-2.4944896
C	0.0000000	-3.8513397	-2.4515838
C	0.0000000	-5.1248549	-0.3680944
C	0.0000000	-6.2929783	-1.0935839
C	0.0000000	-5.0260956	-3.1701184
H	0.0000000	-2.8991289	-2.9677178
H	0.0000000	-5.1743702	0.7117812
H	0.0000000	-7.2475908	-0.5845899
H	0.0000000	-5.0042065	-4.2516564
H	0.0000000	-7.1750057	-3.0580244

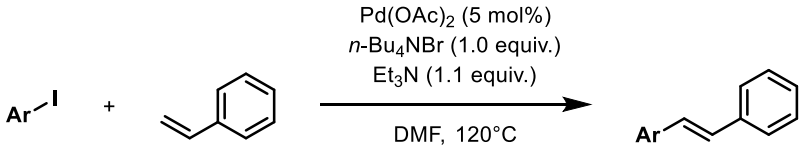
5. Synthesis of the starting materials

5.1. General procedure S1



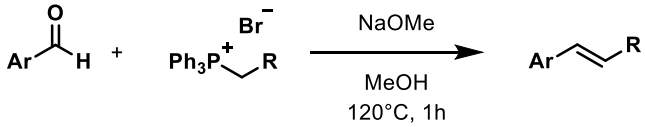
Alkylmagnesium bromide (1 equiv., 20 mmol) was added dropwise to a stirred solution of corresponding benzaldehyde (1.1 equiv., 22.0 mmol) in dry THF (40 mL) at 0°C under Ar. The solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched by addition of sat. aq. NH_4Cl and the aqueous phase was extracted three times with MTBE (methyl tert-butyl ether). The combined organic phases were washed with aq. $NaHSO_3$ (0.1 kg/L, 2x 50 mL), water (50 mL), and brine (50 mL), dried over $MgSO_4$, and filtered. The solvents were removed by evaporation to give a crude product, which was used in the next step without further purification. The crude benzyl alcohol and *p*-toluenesulfonic acid monohydrate (1 mol%) were dissolved in toluene (40 mL) and heated to reflux. After the completion of the reaction, the solvents were removed by evaporation and the residue was purified by flash column chromatography on silica gel.

5.2. General procedure S2

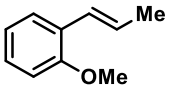


Aryl iodide (1.0 equiv., 10.0 mmol), styrene (2 equiv., 20.0 mmol, 2.3 mL), triethylamine (1.1 equiv., 11.0 mmol, 1.5 mL), $Pd(OAc)_2$ (5 mol%, 0.50 mmol, 112 mg), and *n*-Bu_4NBr (1.0 equiv., 10.0 mmol, 3.22 g) were dissolved in DMF (40 mL) and the solution was stirred at 120°C for 24 h. After cooling to room temperature, aqueous 1M HCl was added and the solution was extracted three times with ethyl acetate. The combined organic phases were washed with water and brine, dried over $MgSO_4$ and filtered. The solvents were evaporated and the residue was purified by crystallization from *n*-hexane.

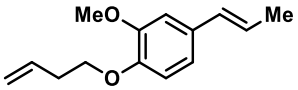
5.3. General procedure S3



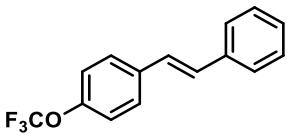
NaOMe (1.1 equiv., 5M in MeOH, 22.0 mmol, 4.4 mL) was added dropwise to a stirred solution of alkyltriphenylphosphonium bromide (1.1 equiv., 22.0 mmol) in MeOH (36 mL) under Ar. The mixture was stirred at room temperature for 5 minutes, then corresponding benzaldehyde (1 equiv., 20 mmol) was added dropwise and the mixture was heated to 40°C. After the completion of the reaction, the mixture was cooled to room temperature, quenched with sat. aq. NH_4Cl and extracted with MTBE (3x 40 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and filtered. The solvents were removed by evaporation, and to the resulting viscous oil, *n*-hexane was added. The white precipitate (Ph_3PO) was filtered off and washed five times with *n*-hexane. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel or by crystallization.



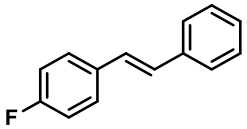
(*E*)-1-methoxy-2-(prop-1-en-1-yl)benzene:[13] The titled compound was synthesized according to the general procedure **S1** from *o*-anisaldehyde (1.1 equiv., 22.0 mmol, 3.00 g) and ehtylmagnesium bromide (1.0 equiv., 3M solution in Et_2O, 20.0 mmol, 6.7 mL). The crude product was purified by flash column chromatography on silica gel (cyclohexane) to give yellow oil in 42% total yield (1.24 g, 8.37 mmol, *E*/*Z* = 25:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.20 (ddd, *J* = 8.9, 7.5, 1.7 Hz, 1H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.87 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.75 (dq, *J* = 15.9, 1.8 Hz, 1H), 6.25 (dq, *J* = 15.8, 6.6 Hz, 1H), 3.86 (s, 3H), 1.93 (dd, *J* = 6.6, 1.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 127.9, 127.2, 126.7, 126.6, 125.8, 120.8, 110.8, 55.5, 19.1.



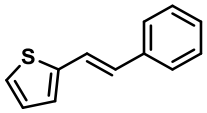
(*E*)-1-(but-3-en-1-yloxy)-2-methoxy-4-(prop-1-en-1-yl)benzene: NaH (1.1 equiv., 60% in mineral oil, 22.0 mmol, 880 mg) was added in portions to a stirred solution of isoeugenol (1.0 equiv., 20.0 mmol, 3.28 g) DMF (10 mL) under Ar. After 5 minutes, 4-bromobut-1-ene (1.6 eq., 32.0 mmol, 3.2 mL) was added and the reaction mixture was stirred at 100°C overnight. After cooling to room temperature, the reaction mixture was diluted with Et_2O and washed three times with aq. 1M HCl, three times with aq. NaOH (1M), once with water, and once with brine. The organic phase was dried over $MgSO_4$ and filtered. The crude product was purified by flash column chromatography on silica gel (2% of EtOAc in cyclohexane) to give colorless oil in 23% yield (1.02 g, 4.67 mmol). ^{1}H NMR (399 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.87 – 6.78 (m, 2H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.10 (dq, *J* = 15.8, 6.6 Hz, 1H), 5.91 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.06 (t, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 2.59 (q, *J* = 6.9 Hz, 2H), 1.86 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 147.6, 134.4, 131.6, 130.7, 124.0, 118.8, 117.2, 113.6, 109.3, 68.5, 56.1, 33.8, 18.5.



(*E*)-1-styryl-4-(trifluoromethoxy)benzene: The titled compound was synthesized according to the general procedure **S3** from 4-(trifluoromethoxy)benzaldehyde (1.1 equiv., 20.0 mmol, 4.4 mL) and benzyltriphenylphosphonium bromide (1.1 equiv., 22.0 mmol, 9.53 g). The crude product was purified by crystallization from MeOH to give white crystals in 34% yield (1.81 mg, 6.85 mmol, *E*/*Z* > 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 4H), 7.43 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 7.24 – 7.18 (m, 2H), 7.09 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.63 (q, *J* = 1.8 Hz), 137.1, 136.3, 129.9, 128.9, 128.1, 127.8, 127.2, 126.7, 121.3, 120.65 (q, *J* = 257.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8.

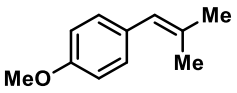


(*E*)-1-fluoro-4-styrylbenzene:[14] The titled compound was synthesized according to the general procedure **S2** from *p*-fluoroiodobenzene (1.0 equiv., 10.0 mmol, 1.4 mL) and styrene (2 equiv., 20.0 mmol, 2.3 mL). The crude product was purified by crystallization from *n*-hexane to give colorless crystals in 79% yield (1.56 g, 7.87 mmol, *E*/*Z* > 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 4H), 7.40 – 7.33 (m, 2H), 7.31 – 7.22 (m, 1H), 7.12 – 6.98 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.26 (ddd, *J* = 14.0, 8.7, 5.4 Hz).

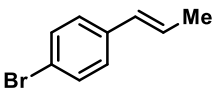


(*E*)-2-styrylthiophene:[15] The titled compound was synthesized according to the general procedure **S2** from 2-iodothiophene (1.0 equiv., 10.0 mmol, 1.2 mL) and styrene (2 equiv., 20.0 mmol, 2.3 mL). The crude product was purified by crystallization from *n*-hexane to give yellow crystals in 43% yield (805 mg, 4.32 mmol, *E*/*Z* > 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 2H), 7.39 – 7.31 (m, 2H), 7.29 – 7.15 (m, 3H), 7.08 (d, *J* =

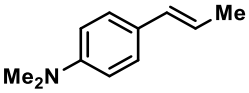
3.5 Hz, 1H), 7.01 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.94 (d, *J* = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 137.1, 128.8, 128.5, 127.7, 126.4, 126.2, 124.5, 121.9.



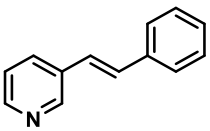
1-methoxy-4-(2-methylprop-1-en-1-yl)benzene:[16] The titled compound was synthesized according to the general **S1** procedure from *p*-anisaldehyde (1.1 equiv., 22.0 mmol, 2.60 g) and isopropylmagnesium bromide (1.0 equiv., 2M solution in THF, 20.0 mmol, 10 mL). The crude product was purified by flash column chromatography on silica gel (cyclohexane) to give colorless oil in 63% total yield (2.05 g, 12.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.21 (s, 1H), 3.81 (s, 3H), 1.89 (d, *J* = 1.5 Hz, 3H), 1.85 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 134.1, 131.5, 129.9, 124.6, 113.6, 55.4, 27.0, 19.5.



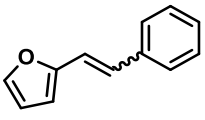
(*E*)-1-bromo-4-(prop-1-en-1-yl)benzene:[17] The titled compound was synthesized according to the general procedure **S1** from *p*-bromobenzaldehyde (1.0 equiv., 20.0 mmol, 3.70 g) and ethylmagnesium bromide (2.1 equiv., 3M solution in THF, 42.0 mmol, 14 mL). The crude product was purified by flash column chromatography on silica gel (cyclohexane) to give colorless oil in 69% total yield (3.07 g, 88% purity, 13.7 mmol, *E*/*Z* = 19:1). ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.23 (dq, *J* = 15.7, 6.3 Hz, 1H), 1.87 (dd, *J* = 6.4, 1.4 Hz, 3H).



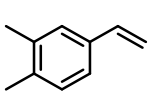
(*E*)-*N*,*N*-dimethyl-4-(prop-1-en-1-yl)aniline:[13] The titled compound was synthesized according to the general procedure **S1** from *p*-(dimethylamino)benzaldehyde (1.0 equiv., 20.0 mmol, 2.98 g) and ethylmagnesium bromide (1.1 equiv., 3M solution in Et_2O, 22.0 mmol, 7.3 mL). The crude product was purified by flash column chromatography on silica gel (0 → 100% of EtOAc in cyclohexane) to give yellow solid in 24% total yield (778 mg, 4.82 mmol, *E*/*Z* = 11:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.32 (dd, *J* = 15.7, 1.8 Hz, 1H), 6.03 (dq, *J* = 15.7, 6.6 Hz, 1H), 2.94 (s, 6H), 1.85 (dd, *J* = 6.6, 1.7 Hz, 3H).



(*E*)-3-styrylpyridine:[18] The titled compound was synthesized according to the general procedure **S2** from 3-iodopyridine (1.0 equiv., 10.0 mmol, 1.2 mL) and styrene (2 equiv., 20.0 mmol, 2.3 mL). The crude product was purified by crystallization from *n*-hexane to give orange solid in 47% yield (858 mg, 4.73 mmol, *E*/*Z* > 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.3 Hz, 1H), 8.49 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.85 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.43 – 7.35 (m, 2H), 7.34 – 7.27 (m, 2H), 7.17 (d, *J* = 16.4 Hz, 1H), 7.07 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 136.7, 133.3, 133.0, 131.1, 128.9, 128.4, 126.8, 124.9, 123.8.

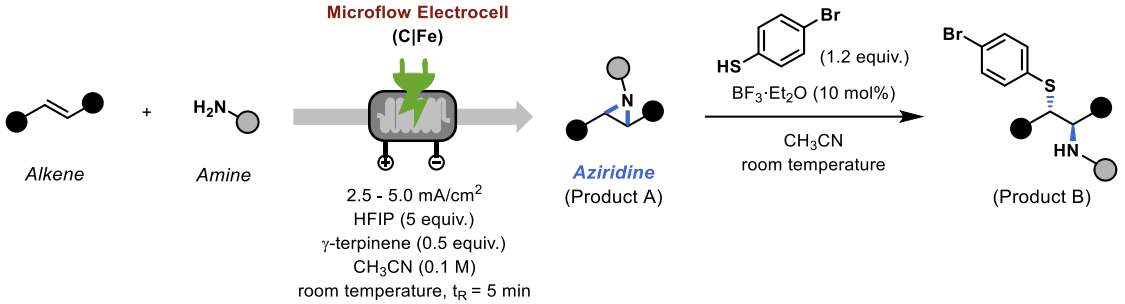


2-styrylfuran:[19] The titled compound was synthesized according to the general procedure **S3** from furfural (1.0 equiv., 20.0 mmol, 1.1 mL) and benzyltriphenylphosphonium bromide (1.1 equiv., 22.0 mmol, 9.53 g). The crude product was purified by flash column chromatography on silica gel (cyclohexane) to give yellow oil in 98% yield (3.34 g, 19.6 mmol, *E*/*Z* = 1.16:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 4H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.38 – 7.22 (m, 7H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.91 (d, *J* = 16.2 Hz, 1H), 6.49 (d, *J* = 12.6 Hz, 1H), 6.43 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.41 – 6.35 (m, 2H), 6.32 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.25 (d, *J* = 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 152.3, 142.3, 141.7, 137.5, 137.2, 128.8, 128.8, 128.3, 128.1, 127.7, 127.5, 127.3, 126.5, 118.2, 116.7, 111.8, 111.3, 110.1, 108.7.



1,2-dimethyl-4-vinylbenzene:[20] The titled compound was synthesized according to the general procedure **S3** from 3,4-dimethylbenzaldehyde (1.0 equiv., 20.0 mmol, 2.6 mL) and methyltriphenylphosphonium bromide (1.1 equiv., 22.0 mmol, 7.86 g). The crude product was purified by flash column chromatography on silica gel (cyclohexane) to give yellow oil in 69% yield (1.82 g, 13.8 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 1.8 Hz, 1H), 7.17 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (dd, *J* = 17.6, 1.1 Hz, 1H), 5.18 (dd, *J* = 10.8, 1.1 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 136.7, 136.5, 135.4, 129.9, 127.6, 123.8, 112.7, 19.9, 19.7.

6. Electrochemical aziridination in flow



6.1. General procedure A

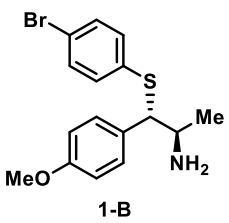
Alkene (1.0 equiv., 2.0 mmol), together with amine (5.0 equiv., 10.0 mmol), hexafluoroisopropanol (HFIP, 5.0 equiv., 10.0 mmol, 1.05 mL) and γ-terpinene (0.5 equiv., 1.0 mmol, 0.16 mL) were dissolved in acetonitrile using a 20 mL volumetric flask (0.1M). The mixture was swirled until homogeneous and placed in a 20 ml disposable syringe. The solution was pumped through the electrochemical setup with a fixed flowrate of 0.15 mL/min to give a residence time of 5 minutes in the active part of the reactor, equipped with a graphite anode, steel cathode divided by a 0.25 mm thick Teflon gasket. The first fraction was discarded after which a constant current (selected on the basis of the voltammograms recorded) was applied. The reaction mixture was collected in a vial cooled at 0°C for 67 minutes, which corresponds to 1.0 mmol scale. The crude mixture was concentrated under vacuum at room temperature, to prevent decomposition of the product and directly purified by flash column chromatography on silica gel.

Since proton donating solvents significantly increase *N*-inversion barriers, two sharp sets of signals were observed in NMR for the majority of aziridines, when the spectra were recorded in CD_3OD.[21] On the contrary, spectra recorded in $CDCl_3$ featured broad and overlapping signals in ^1H NMR and low intensity peaks in ^{13}C NMR, because of the quick inversion of the *N*-atom centered chiral center. Both diastereoisomers have *trans*-configuration of substituents at C-atoms of aziridine core leading to same *anti*-product after ring opening by nucleophiles. We have also observed that aziridines are partially opened by CD_3OD overtime giving rise to additional signals, which can be clearly seen in some ^{13}C NMR spectra, as measuring of carbon spectrum takes considerably longer time than ^1H NMR.

6.2. General procedure B

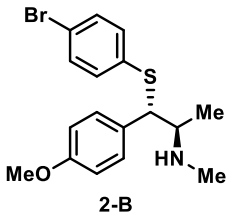
Alkene (1.0 equiv., 2.0 mmol), together with amine (5.0 equiv., 10.0 mmol), hexafluoroisopropanol (HFIP, 5.0 equiv., 10.0 mmol, 1.05 mL) and γ-terpinene (0.5 equiv., 1.0 mmol, 0.16 mL) were dissolved in acetonitrile using a 20 mL volumetric flask (0.1M). The mixture was swirled until homogeneous and placed in a 20 ml disposable syringe. The solution was pumped through the electrochemical setup with a fixed flowrate of 0.15 mL/min to give a residence time of 5 minutes in the active part of the reactor, equipped with a graphite anode, steel cathode divided by a 0.25 mm thick Teflon gasket. The first fraction was discarded after which a constant current (selected on the basis of the voltammograms recorded) was applied. The reaction mixture was collected in a vial containing a stirred solution of 4-bromothiophenol (1.2 mmol, 227 mg) and $BF_3{\cdot}Et_2O$ (0.1 mmol, 12.7 µL) in acetonitrile (5 mL) for 67 minutes, which corresponds to 1.0 mmol scale. The crude mixture was concentrated under vacuum and dissolved in methanol (5 mL). Subsequently, $NaBH_4$ (0.26 mmol, 10 mg) was added and the solution was stirred for 1 hour at room temperature. The crude mixture was concentrated under vacuum and

purified by flash column chromatography on silica gel and analysed by TLC, GC-MS, ^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR.



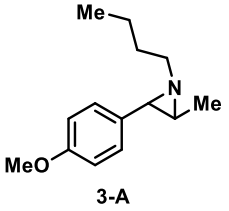
1-B

***anti*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-amine (1-B):** Following the general procedure **B** (7M NH_3 solution in MeOH was used), obtained at 50 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 10% of MeOH in DCM) to give amorphous yellow solid (66 mg, 19%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.15 (d, *J* = 6.9 Hz, 1H), 3.76 (s, 3H), 3.24 (p, *J* = 6.6 Hz, 1H), 1.23 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.6, 135.6, 134.8, 132.8, 132.2, 130.9, 121.9, 114.9, 61.8, 55.7, 52.2, 20.5. HRMS (ESI) *m/z* $[M-NH_3+H]^+$ calcd for $C_{16}H_{16}BrOS$ 335.0100, found 335.0096.



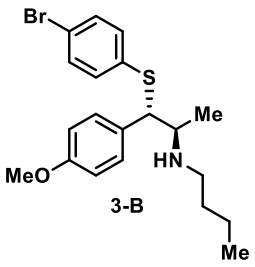
2-B

***anti*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)-*N*-methylpropan-2-amine (2-B):** Following the general procedure **B** (9.8M $MeNH_3$ solution in MeOH was used), obtained at 95 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 10% of MeOH in DCM) to give viscous yellow oil (176 mg, 48%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.32 (d, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 2.94 (p, *J* = 6.5 Hz, 1H), 2.33 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.5, 135.8, 134.4, 132.8, 132.5, 130.8, 121.8, 114.9, 60.5, 59.5, 55.7, 33.6, 16.8. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{20}NOS$ 366.0522, found 366.0513.



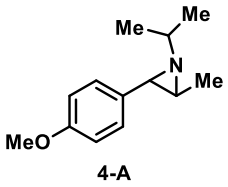
3-A

***trans*-1-butyl-2-(4-methoxyphenyl)-3-methylaziridine (3-A):** Following the general procedure **A**, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 50% of EtOAc in cyclohexane) to give viscous brown oil (109 mg, 50%) as a mixture of two diastereoisomers (d.r. 1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.24 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.87 (d, *J* = 3.9 Hz, 1H), 2.77 (dt, *J* = 11.9, 7.2 Hz, 1H), 2.46 (dt, *J* = 11.9, 7.5 Hz, 1H), 2.31 – 2.09 (m, 4H), 1.96 (ddd, *J* = 12.1, 9.0, 6.2 Hz, 1H), 1.67 – 1.54 (m, 2H), 1.40 (d, *J* = 5.8 Hz, 3H), 1.32 (d, *J* = 5.6 Hz, 3H), 1.49 – 1.13 (m, 6H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 161.0, 160.4, 132.9, 132.4, 128.7, 126.5, 114.8, 114.6, 55.7, 55.7, 52.5, 52.4, 49.8, 48.2, 41.7, 40.0, 33.4, 32.8, 21.6, 21.5, 18.1, 14.4, 14.3, 11.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{21}NO$ 220.1696, found 220.1687.



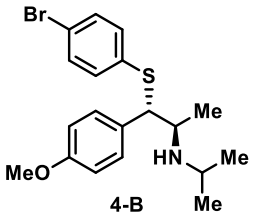
3-B

***anti*-*N*-(1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)butan-1-amine (3-B):** Following the general procedure **B**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (295 mg, 72%) as a single diastereoisomer. ^{1}H NMR (399 MHz, CD_3OD) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.29 (d, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 3.04 (p, *J* = 6.5 Hz, 1H), 2.69 – 2.57 (m, 1H), 2.54 – 2.42 (m, 1H), 1.44 – 1.29 (m, 2H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.27 – 1.16 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 160.6, 135.8, 134.5, 132.8, 132.6, 130.8, 121.8, 115.0, 59.8, 58.8, 55.7, 47.4, 32.6, 21.3, 17.5, 14.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{26}BrNOS$ 408.0991, found 408.0974.



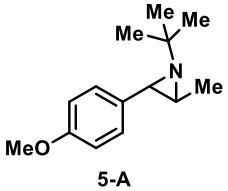
4-A

***trans*-1-isopropyl-2-(4-methoxyphenyl)-3-methylaziridine (4-A):** Following the general procedure **A**, obtained at 60 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of EtOAc in cyclohexane) to give viscous yellow oil (146 mg, 71%) as a mixture of two diastereoisomers (d.r. 1:1).^{1}H NMR (400 MHz, CD_3OD) δ 7.26 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.91 (d, *J* = 4.0 Hz, 1H), 2.52 (hept, *J* = 6.2 Hz, 1H), 2.39 – 2.27 (m, 3H), 1.96 (hept, *J* = 6.3 Hz, 1H), 1.45 (d, *J* = 5.7 Hz, 3H), 1.31 (d, *J* = 5.6 Hz, 3H), 1.18 (d, *J* = 6.4 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H), 0.71 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 161.0, 160.4, 133.0, 132.5, 128.9, 126.2, 114.8, 114.5, 55.7, 55.7, 53.0, 51.4, 48.9, 48.4, 41.8, 38.2, 23.1, 22.8, 22.6, 21.7, 18.4, 11.3. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{13}H_{20}NO$ 206.1545, found 206.1535.



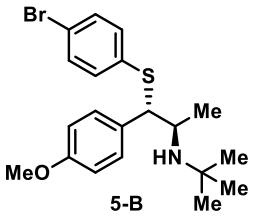
4-B

***anti*-1-((4-bromophenyl)thio)-*N*-isopropyl-1-(4-methoxyphenyl)propan-2-amine (4-B):** Following the general procedure **B**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 40% of EtOAc in cyclohexane) to give viscous yellow oil (317 mg, 80%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.34 – 7.27 (m, 4H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.33 (d, *J* = 6.1 Hz, 1H), 3.76 (s, 3H), 3.17 (p, *J* = 6.4 Hz, 1H), 2.93 (hept, *J* = 6.3 Hz, 1H), 1.16 (d, *J* = 6.5 Hz, 3H), 1.03 (d, *J* = 6.3 Hz, 3H), 0.97 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.5, 136.1, 134.0, 132.8, 132.8, 130.8, 121.6, 114.9, 59.8, 56.0, 55.7, 46.5, 23.0, 22.6, 17.7. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{19}H_{25}BrNOS$ 394.0840, found 394.0827.



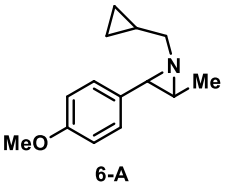
5-A

***trans*-1-(*tert*-butyl)-2-(4-methoxyphenyl)-3-methylaziridine (5-A):** Following the general procedure **A**, obtained at 85 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of EtOAc in cyclohexane) to give viscous brown oil (91 mg, 41%). The titled compound decomposed to quickly in CD_3OD to obtain good quality NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.68 (broad s, 1H), 2.21 (broad s, 1H), 1.44 (d, *J* = 5.9 Hz, 3H), 1.12 (s, 9H). ^{13}C NMR selected peaks (101 MHz, $CDCl_3$) δ 158.7, 129.2, 128.7, 113.7, 55.4, 42.1, 29.7, 16.0. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{14}H_{22}NO$ 220.1696, found 220.1695.



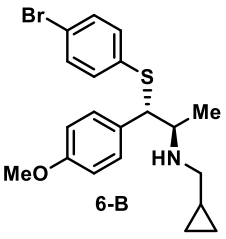
5-B

***anti*-1-((4-bromophenyl)thio)-*N*-(tert-butyl)-1-(4-methoxyphenyl)propan-2-amine (5-B):** Following the general procedure **B**, obtained at 85 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 40% of EtOAc in cyclohexane) to give viscous yellow oil (281 mg, 69%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.23 (d, *J* = 5.8 Hz, 1H), 3.75 (s, 3H), 3.21 (p, *J* = 6.4 Hz, 1H), 1.20 (d, *J* = 6.4 Hz, 3H), 1.05 (s, 9H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.5, 136.6, 133.5, 133.0, 132.7, 131.1, 121.1, 114.7, 62.1, 55.7, 53.8, 52.4, 30.0, 21.3. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{26}BrNOS$ 408.0991, found 408.0974.



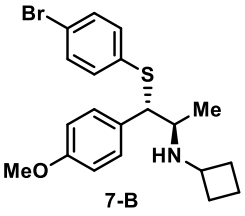
6-A

***trans*-1-(cyclopropylmethyl)-2-(4-methoxyphenyl)-3-methylaziridine (6-A):** Following the general procedure **A**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of EtOAc in cyclohexane) to give viscous brown oil (98 mg, 45%) as a mixture of two diastereoisomers (d.r. 1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.22 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.88 (d, *J* = 4.0 Hz, 1H), 2.82 (dd, *J* = 12.5, 5.9 Hz, 1H), 2.34 (d, *J* = 3.6 Hz, 1H), 2.27 (ddt, *J* = 9.2, 5.5, 3.1 Hz, 2H), 2.19 (dd, *J* = 12.5, 7.5 Hz, 1H), 2.13 (dd, *J* = 12.7, 6.4 Hz, 1H), 1.76 (dd, *J* = 12.7, 7.3 Hz, 1H), 1.39 (d, *J* = 6.0 Hz, 3H), 1.34 (d, *J* = 5.6 Hz, 3H), 1.12 – 0.98 (m, 1H), 0.89 – 0.79 (m, 1H), 0.57 – 0.49 (m, 2H), 0.48 – 0.41 (m, 1H), 0.40 – 0.32 (m, 1H), 0.31 – 0.24 (m, 1H), 0.24 – 0.16 (m, 1H), 0.06 (dq, *J* = 9.4, 4.9 Hz, 1H), -0.15 (dq, *J* = 9.6, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 161.0, 160.4, 132.8, 132.4, 128.9, 126.5, 114.8, 114.6, 57.4, 57.4, 55.7, 55.7, 49.7, 48.0, 41.0, 39.9, 18.1, 11.8, 11.4, 11.3, 4.2, 3.9, 3.8, 3.7. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{14}H_{20}NO$ 218.1539, found 218.1530.



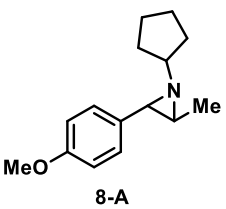
6-B

***anti*-1-((4-bromophenyl)thio)-*N*-(cyclopropylmethyl)-1-(4-methoxyphenyl)propan-2-amine (6-b):** Following the general procedure **B**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of EtOAc in cyclohexane) to give viscous yellow oil (264 mg, 65%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.26 (d, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 3.10 (p, *J* = 6.5 Hz, 1H), 2.56 (dd, *J* = 12.0, 6.6 Hz, 1H), 2.25 (dd, *J* = 12.0, 7.4 Hz, 1H), 1.23 (d, *J* = 6.4 Hz, 3H), 0.89 – 0.77 (m, 1H), 0.45 – 0.34 (m, 2H), 0.06 – -0.09 (m, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.6, 135.7, 134.6, 132.8, 132.5, 130.8, 121.9, 114.9, 59.8, 58.3, 55.7, 52.7, 17.6, 11.5, 3.9, 3.7. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{25}BrNOS$ 406.0835, found 406.0818.



7-B

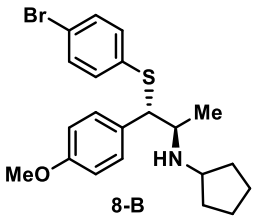
***anti*-*N*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)cyclobutanamine (7-B):** Following the general procedure **B**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (94 mg, 23%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.23 (d, *J* = 6.7 Hz, 1H), 3.76 (s, 3H), 3.39 – 3.32 (m, 1H), 3.03 (p, *J* = 6.4 Hz, 1H), 2.23 – 2.06 (m, 2H), 1.73 – 1.49 (m, 4H), 1.17 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.6, 135.9, 134.2, 132.8, 132.5, 130.9, 121.6, 114.9, 59.9, 56.8, 55.7, 52.7, 32.0, 31.9, 17.6, 15.5. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{25}BrNOS$ 406.0835, found 406.0834.



8-A

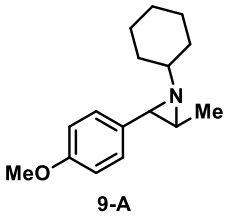
***trans*-1-cyclopentyl-2-(4-methoxyphenyl)-3-methylaziridine (8-A):** Following the general procedure **A**, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to give viscous brown oil (122 mg, 53%) as a mixture of two diastereoisomers (d.r. 1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.25 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.90 (d, *J* = 4.0 Hz, 1H), 2.82 (p, *J* = 6.5 Hz, 1H), 2.39 (d, *J* = 3.7 Hz, 1H), 2.31 (dqd, *J* = 11.9, 5.8, 3.9 Hz, 2H), 2.20 (p, *J* = 6.9 Hz, 1H), 1.96 – 1.14 (m, 16H), 1.43 (d, *J* = 6.0 Hz, 3H), 1.31 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.9, 160.3, 132.9, 132.5, 129.4, 129.0, 126.9, 115.1, 114.7, 114.5, 63.8, 62.8, 55.7, 55.7, 41.5, 39.1, 34.4, 33.9, 33.5, 32.7, 25.8, 25.6, 25.4, 25.4, 18.1, 11.8. HRMS (ESI)

m/*z* $[M+H]^+$ calcd for $C_{15}H_{22}NO$ 232.1701, found 232.1685.



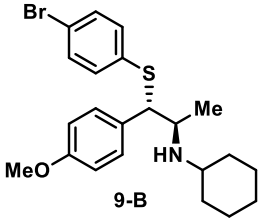
8-B

***anti-N*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)cyclopentanamine (8-B):** Following the general procedure **B**, obtained at 110 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 40% of EtOAc in cyclohexane) to give viscous yellow oil (272 mg, 64%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.28 (d, *J* = 6.8 Hz, 1H), 3.76 (s, 3H), 3.19 (p, *J* = 6.8 Hz, 1H), 3.12 (p, *J* = 6.2 Hz, 1H), 1.87 (pd, *J* = 7.2, 4.5 Hz, 1H), 1.78 (dq, *J* = 12.0, 5.8 Hz, 1H), 1.66 – 1.45 (m, 4H), 1.34 – 1.12 (m, 2H), 1.22 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.6, 135.9, 134.3, 132.8, 132.6, 130.8, 121.7, 114.9, 59.8, 57.8, 57.2, 55.7, 34.0, 33.0, 24.6, 24.5, 17.6. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{21}H_{27}BrNOS$ 420.0991, found 420.0976.



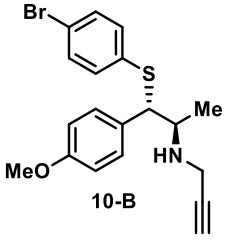
9-A

***trans*-1-cyclohexyl-2-(4-methoxyphenyl)-3-methylaziridine (9-A):** Following the general procedure **A**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to give viscous brown oil (177 mg, 72%) as a mixture of two diastereoisomers (d.r. 1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.26 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 2.90 (d, *J* = 4.0 Hz, 1H), 2.33 (td, *J* = 5.5, 5.0, 3.6 Hz, 3H), 2.15 (td, *J* = 10.1, 4.0 Hz, 1H), 1.44 (d, *J* = 5.4 Hz, 3H), 2.00 – 0.95 (m, 20H), 1.30 (d, *J* = 5.6 Hz, 3H), 0.79 – 0.60 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.9, 160.3, 133.0, 132.4, 129.0, 126.4, 114.7, 114.4, 61.2, 59.5, 55.7, 55.7, 48.5, 47.8, 41.3, 37.7, 34.3, 34.3, 33.9, 33.1, 27.1, 27.0, 26.3, 26.2, 25.8, 25.6, 18.5, 11.4. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{16}H_{24}NO$ 246.1858, found 246.1845.



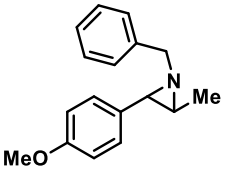
9-B

***anti-N*-(1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)cyclohexanamine (9-B):** Following the general procedure **B**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 40% of EtOAc in cyclohexane) to give viscous yellow oil (356 mg, 82%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.28 (d, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 3.25 (p, *J* = 6.5 Hz, 1H), 2.55 (tt, *J* = 10.3, 3.5 Hz, 1H), 1.89 – 1.73 (m, 2H), 1.72 – 1.51 (m, 3H), 1.19 (d, *J* = 6.4 Hz, 3H), 1.33 – 0.90 (m, 5H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.6, 135.9, 134.2, 132.8, 132.6, 130.8, 121.7, 114.9, 59.9, 55.7, 55.3, 54.6, 34.4, 33.5, 27.0, 26.0, 25.9, 17.9. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{29}BrNOS$ 434.1148, found 434.1139.



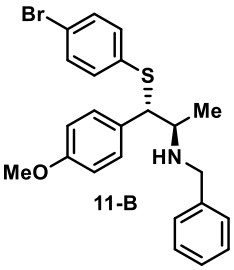
10-B

***anti-N*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)prop-2-yn-1-amine (10-B):** Following the general procedure **B**, obtained at 50 mA for 33.3 minutes (0.5 mmol scale). Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give amorphous yellow solid (49 mg, 25%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.31 (d, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 3.49 – 3.36 (m, 2H), 3.36 – 3.32 (m, 1H), 2.61 (t, *J* = 2.4 Hz, 1H), 1.19 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.6, 135.6, 134.6, 132.8, 132.1, 131.0, 121.9, 114.9, 81.4, 73.8, 59.5, 56.7, 55.7, 36.0, 16.9. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{19}H_{21}BrNOS$ 390.0527, found 390.0516.



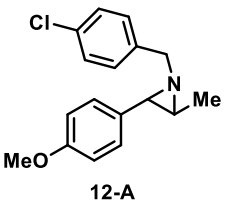
11-A

***trans*-1-benzyl-2-(4-methoxyphenyl)-3-methylaziridine (11-A):** Following the general procedure **A**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (157 mg, 62%) as a mixture of two diastereoisomers (d.r. 1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.41 – 7.33 (m, 2H), 7.32 – 7.19 (m, 8H), 7.17 – 7.13 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.96 (d, *J* = 14.0 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.70 (d, *J* = 14.0 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.12 (d, *J* = 13.8 Hz, 1H), 2.99 (d, *J* = 4.0 Hz, 1H), 2.51 (d, *J* = 3.2 Hz, 1H), 2.44 (p, *J* = 5.3 Hz, 1H), 2.41 – 2.34 (m, 1H), 1.49 (d, *J* = 6.0 Hz, 3H), 1.32 (d, *J* = 5.5 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 161.1, 160.4, 140.7, 140.4, 132.7, 132.6, 129.4, 129.3, 129.2, 129.1, 128.7, 128.0, 127.9, 126.3, 114.7, 114.7, 56.3, 56.2, 55.7, 55.7, 49.8, 48.7, 42.3, 40.2, 18.0, 11.6. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{20}NO$ 254.1545, found 254.1535.



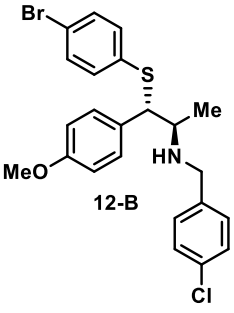
11-B

***anti*-*N*-benzyl-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-amine (11-B):** Following the general procedure **B**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (341 mg, 77%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 – 7.20 (m, 5H), 7.19 – 7.14 (m, 4H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.28 (d, *J* = 7.0 Hz, 1H), 3.79 (d, *J* = 13.1 Hz, 1H), 3.75 (s, 3H), 3.64 (d, *J* = 13.1 Hz, 1H), 3.04 (p, *J* = 6.4 Hz, 1H), 1.24 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.5, 140.4, 135.8, 134.5, 132.8, 132.5, 130.9, 129.5, 129.4, 128.3, 121.8, 114.9, 59.8, 57.3, 55.7, 51.6, 17.6. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{25}BrNOS$ 442.0840, found 442.0817.



12-A

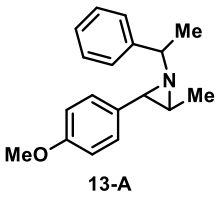
***trans*-1-(4-chlorobenzyl)-2-(4-methoxyphenyl)-3-methylaziridine (12-A):** Following the general procedure **A**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (163 mg, 57%) as a mixture of two diastereoisomers (d.r. 1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.22 (m, 6H), 7.12 (d, *J* = 6.2 Hz, 2H), 7.10 (d, *J* = 6.3 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.94 (d, *J* = 14.2 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.69 (d, *J* = 14.2 Hz, 1H), 3.28 (d, *J* = 14.0 Hz, 1H), 3.17 (d, *J* = 14.0 Hz, 1H), 3.00 (d, *J* = 3.7 Hz, 1H), 2.49 (d, *J* = 3.1 Hz, 1H), 2.44 (p, *J* = 5.2 Hz, 1H), 2.40 – 2.31 (m, 1H), 1.47 (d, *J* = 6.0 Hz, 3H), 1.32 (d, *J* = 5.5 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 161.1, 160.4, 139.7, 139.2, 133.7, 133.7, 132.6, 132.6, 130.8, 130.6, 129.4, 129.3, 128.6, 126.1, 114.8, 114.7, 55.7, 55.7, 55.5, 55.5, 49.7, 48.8, 42.5, 40.2, 18.0, 11.5. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{19}ClNO$ 288.1155, found 288.1140.



12-B

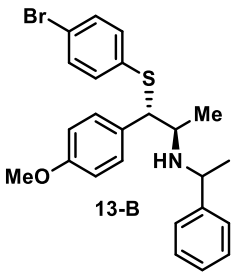
***anti*-1-((4-bromophenyl)thio)-*N*-(4-chlorobenzyl)-1-(4-methoxyphenyl)propan-2-amine (12-B):** Following the general procedure **B**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (370 mg, 78%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.28 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 4.29 (d, *J* = 6.6 Hz, 1H), 3.78 (d, *J* = 13.6 Hz, 1H), 3.75 (s, 3H), 3.63 (d, *J* = 13.4 Hz, 1H), 3.01 (p, *J* = 6.4 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.5, 139.6, 135.9, 134.3, 133.9, 132.8, 132.4, 131.0, 130.9, 129.5, 121.7, 114.8, 59.8, 57.3, 55.7, 50.9, 17.6.

HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{24}ClBrNOS$ 476.0451, found 476.0425.



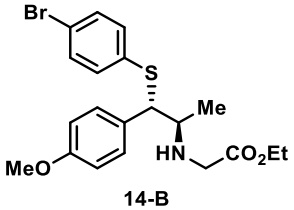
13-A

***trans*-2-(4-methoxyphenyl)-3-methyl-1-(1-phenylethyl)aziridine (13-A):** Following the general procedure **A**, obtained at 60 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give two viscous yellow oils (in total 186 mg, 70%) as separated *trans*-isomers derived from the α-chiral center of amine (d.r. 1:1), both as mixtures of two diastereoisomers (d.r. ap. 1:1). **First *trans*-isomer:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.48 – 7.43 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.12 – 7.05 (m, 3H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.90 – 6.83 (m, 4H), 6.68 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.73 (s, 3H), 3.55 (q, *J* = 6.5 Hz, 1H), 2.96 – 2.87 (m, 2H), 2.53 – 2.44 (m, 2H), 2.40 – 2.32 (m, 1H), 1.45 (d, *J* = 6.5 Hz, 3H), 1.42 (d, *J* = 5.6 Hz, 3H), 1.40 (d, *J* = 6.7 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.8, 160.4, 146.7, 145.3, 133.2, 132.6, 129.3, 129.1, 128.8, 127.7, 127.7, 127.7, 127.5, 126.3, 114.8, 114.0, 62.4, 61.4, 55.7, 55.7, 49.3, 49.0, 42.4, 39.4, 25.0, 24.0, 18.3, 12.0. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{22}NO$ 268.1701, found 268.1686. **Second *trans*-isomer:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.40 – 7.18 (m, 12H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 3.71 (s, 3H), 3.51 (q, *J* = 6.5 Hz, 1H), 3.10 (d, *J* = 4.1 Hz, 1H), 2.88 (q, *J* = 6.5 Hz, 1H), 2.48 (qd, *J* = 6.0, 3.8 Hz, 1H), 2.33 (d, *J* = 3.7 Hz, 1H), 2.27 (qd, *J* = 5.5, 4.1 Hz, 1H), 1.57 (d, *J* = 6.0 Hz, 3H), 1.46 (d, *J* = 6.6 Hz, 3H), 1.16 (d, *J* = 5.5 Hz, 3H), 1.03 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 161.2, 160.2, 145.9, 145.9, 132.7, 132.7, 129.5, 129.3, 128.9, 128.3, 128.2, 128.1, 128.0, 125.8, 114.7, 114.6, 61.6, 60.3, 55.7, 55.6, 49.9, 48.3, 42.5, 38.4, 23.8, 22.8, 17.9, 11.3. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{22}NO$ 268.1701, found 268.1686.



13-B

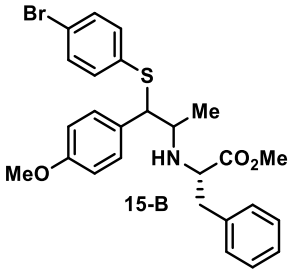
***anti*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)-*N*-(1-phenylethyl)propan-2-amine (13-B):** Following the general procedure **B**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of EtOAc in cyclohexane) to give two viscous yellow oils (in total 431 mg, 94%) as separated *trans*-isomers derived from the α-chiral center of amine (d.r. 1:1). **First *anti*-isomer:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.37 – 7.21 (m, 7H), 7.17 – 7.11 (m, 4H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.47 (d, *J* = 5.0 Hz, 1H), 3.87 (q, *J* = 6.5 Hz, 1H), 3.73 (s, 3H), 2.89 (qd, *J* = 6.6, 4.9 Hz, 1H), 1.26 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.3, 146.2, 136.7, 133.3, 133.1, 132.9, 130.6, 129.6, 128.3, 127.9, 121.2, 114.7, 58.5, 56.8, 56.5, 55.7, 24.5, 17.8. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{27}BrNOS$ 456.0997, found 456.0977. **Second *anti*-isomer:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 – 7.20 (m, 5H), 7.11 – 7.03 (m, 4H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.10 (d, *J* = 7.4 Hz, 1H), 3.86 (q, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 2.75 (dq, *J* = 7.3, 6.3 Hz, 1H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.20 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.6, 145.3, 135.8, 134.4, 132.7, 132.4, 131.0, 129.6, 128.3, 127.7, 121.6, 114.8, 60.3, 56.2, 55.7, 55.4, 24.3, 17.5. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{27}BrNOS$ 456.0997, found 456.0983.



14-B

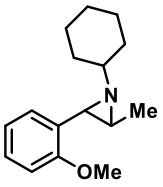
Ethyl (*anti*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)glycinate (14-B): Following the general procedure **B**, obtained at 60 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (275 mg, 63%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.26 (d, *J* = 6.9 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.40 (d, *J* = 17.2 Hz, 1H), 3.31 (d, *J* = 17.2 Hz, 1H), 3.10 (p, *J* = 6.4 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.20 (d, *J* = 6.4 Hz, 3H). ^{13}C

NMR (101 MHz, CD_3OD) δ 173.1, 160.6, 135.7, 134.6, 132.8, 132.3, 131.0, 121.8, 114.8, 62.0, 60.1, 58.0, 55.7, 48.9, 17.7, 14.5. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{25}BrNO_3S$ 438.0739, found 438.0726.



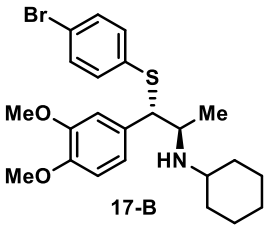
15-B

Methyl (*anti*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)-*L*-phenylalaninate (15-B): Following the general procedure **B**, obtained at 50 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give two viscous yellow oils (in total 435 mg, 84%) as separated *trans*-isomers derived from the α-chiral center of amine (d.r. 1:1). **First *anti*-isomer:** chiral HPLC analysis *ee* > 99% [Chiralcel OJ-H column, hexane/iPrOH 90:10, flow rate 1 mL/min, 25°C, λ = 265 nm; t_R (major) = 43.1 min and t_R (minor) = 22.3 min]. ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.15 (m, 5H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.12 (d, *J* = 7.1 Hz, 1H), 3.77 (s, 3H), 3.65 (t, *J* = 6.8 Hz, 1H), 3.54 (s, 3H), 2.98 (p, *J* = 6.3 Hz, 1H), 2.86 (dd, *J* = 13.3, 6.4 Hz, 1H), 2.79 (dd, *J* = 13.4, 7.2 Hz, 1H), 1.10 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 175.6, 160.5, 138.2, 135.6, 134.9, 132.8, 131.9, 131.2, 130.2, 129.4, 127.7, 121.9, 114.7, 61.1, 60.7, 55.8, 55.7, 52.0, 40.7, 17.8. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{29}BrNO_3S$ 514.1052, found 514.1042. **Second *anti*-isomer:** chiral HPLC analysis *ee* > 99% [Chiralcel OD-H column, hexane/iPrOH 98:2, flow rate 1 mL/min, 25°C, λ = 265 nm; t_R (major) = 21.2 min and t_R (minor) = 15.5 min]. ^{1}H NMR (400 MHz, CD_3OD) δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.14 (m, 5H), 7.11 – 6.99 (m, 4H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.19 (d, *J* = 5.8 Hz, 1H), 3.76 (s, 3H), 3.62 (s, 3H), 3.55 (dd, *J* = 7.3, 6.5 Hz, 1H), 2.98 (p, *J* = 6.4 Hz, 1H), 2.85 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.75 (dd, *J* = 13.4, 7.4 Hz, 1H), 1.09 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 176.5, 160.4, 138.4, 136.4, 133.8, 132.7, 132.5, 131.1, 130.3, 129.5, 127.8, 121.3, 114.7, 62.9, 60.0, 58.2, 55.7, 52.3, 40.4, 19.1. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{29}BrNO_3S$ 514.1052, found 514.1040.



16-A

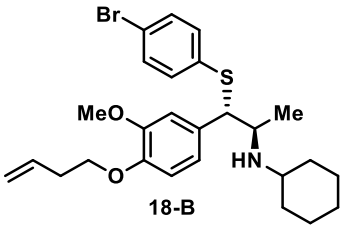
***trans*-1-cyclohexyl-2-(2-methoxyphenyl)-3-methylaziridine (16-A):** Following the general procedure **A**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to give viscous brown oil (142 mg, 58%) as a mixture of two diastereoisomers (d.r. 1.2:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.20 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.12 (ddd, *J* = 9.7, 7.5, 1.8 Hz, 2H), 6.99 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.96 – 6.86 (m, 2H), 6.86 (td, *J* = 7.5, 1.0 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.11 (d, *J* = 4.4 Hz, 1H), 2.57 (d, *J* = 3.7 Hz, 1H), 2.34 (dt, *J* = 10.5, 5.5 Hz, 1H), 2.28 (qd, *J* = 6.0, 3.9 Hz, 1H), 2.16 (tt, *J* = 10.4, 3.9 Hz, 1H), 2.07 – 1.95 (m, 1H), 1.93 – 1.61 (m, 6H), 1.46 (d, *J* = 6.0 Hz, 3H), 1.54 – 1.17 (m, 10H), 1.31 (d, *J* = 5.6 Hz, 3H), 1.18 – 1.02 (m, 3H), 0.65 (qt, *J* = 13.1, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 161.3, 159.8, 131.3, 130.5, 129.2, 128.9, 128.1, 123.0, 121.4, 120.7, 111.4, 111.2, 61.1, 60.3, 55.8, 55.7, 44.6, 43.5, 40.7, 36.9, 34.4, 34.1, 34.0, 33.0, 27.1, 27.0, 26.3, 26.2, 25.9, 25.7, 18.4, 11.6.



17-B

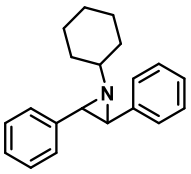
***anti*-1-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)cyclohexanamine (17-B):** Following the general procedure **B**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to viscous white off oil (334 mg, 72%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.96 (s, 1H), 6.86 (d, *J* = 1.1 Hz, 2H), 4.23 (d, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.26 (p, *J* = 6.4 Hz, 1H), 2.54 (tt, *J* = 10.3, 3.8 Hz, 1H), 1.89 – 1.74 (m, 2H), 1.71 – 1.50 (m, 3H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.33 – 0.85 (m, 6H). ^{13}C NMR

(100 MHz, CD_3OD) δ 150.5, 150.1, 135.8, 134.5, 133.4, 132.8, 122.6, 121.9, 113.4, 112.7, 60.4, 56.5, 56.5, 55.1, 54.6, 34.6, 33.5, 27.0, 26.0, 25.9, 18.2. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{31}BrNO_2S$ 464.1259, found 464.1244.



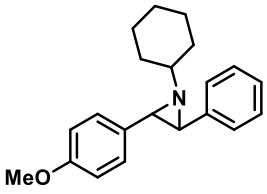
18-B

***anti-N*-1-((4-bromophenyl)thio)-1-(4-(but-3-en-1-yloxy)-3-methoxyphenyl)propan-2-yl)cyclohexanamine (18-B):** Following the general procedure **B**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to viscous brown oil (364 mg, 72%) as a single diastereoisomer. ^{1}H NMR (399 MHz, CD_3OD) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.95 (s, 1H), 6.84 (s, 2H), 5.91 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.14 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.06 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.21 (d, *J* = 7.0 Hz, 1H), 3.99 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 3H), 3.23 (p, *J* = 6.5 Hz, 1H), 2.57 – 2.44 (m, 3H), 1.88 – 1.73 (m, 2H), 1.69 – 1.49 (m, 3H), 1.21 (d, *J* = 6.4 Hz, 3H), 1.35 – 0.81 (m, 5H). ^{13}C NMR (100 MHz, CD_3OD) δ 150.9, 149.3, 135.9, 135.9, 134.5, 133.8, 132.8, 122.6, 121.8, 117.3, 114.6, 113.8, 69.7, 60.5, 56.7, 55.0, 54.4, 34.8, 34.7, 33.6, 27.0, 26.0, 25.9, 18.4.



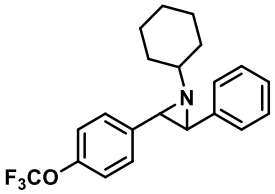
19-A

***trans*-1-cyclohexyl-2,3-diphenylaziridine (19-A):**[22] Following the general procedure **A**, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of DCM in cyclohexane) to give viscous colorless oil (70 mg, 25%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.68 – 7.12 (m, 10H), 3.46 (d, *J* = 11.8 Hz, 2H), 2.02 – 1.84 (m, 2H), 1.81 – 1.69 (m, 1H), 1.57 – 1.04 (m, 7H), 0.80 – 0.67 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 140.7, 134.4, 131.4, 129.4, 129.2 (2C), 128.3, 128.1, 60.2, 50.1, 44.9, 34.1, 33.0, 27.0, 26.1, 25.5. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{24}N$ 278.1909, found 278.1915.



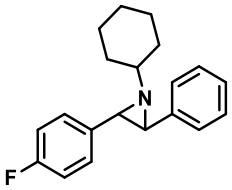
20-A

***trans*-1-cyclohexyl-2-(4-methoxyphenyl)-3-phenylaziridine (20-A):**[23] Following the general procedure **A**, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of DCM in cyclohexane) to give viscous pale yellow oil (181 mg, 59%) as a mixture of two diastereoisomers (d.r. 1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.55 – 7.23 (m, 14H), 6.99 – 6.87 (m, 4H), 3.82 (s, 3H), 3.78 (s, 3H), 3.54 – 3.47 (m, 2H), 3.46 – 3.39 (m, 2H), 2.04 – 1.82 (m, 4H), 1.82 – 1.69 (m, 2H), 1.62 – 1.03 (m, 14H), 0.85 – 0.66 (m, 2H). ^{13}C NMR selected peaks (100 MHz, CD_3OD) δ 161.1, 160.7, 132.5, 131.4, 129.5, 129.3, 129.2, 128.3, 128.1, 125.9, 114.9, 114.6, 60.2, 55.7, 45.1, 44.5, 34.1, 32.9, 27.0, 26.2, 25.6. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{21}H_{26}NO$ 308.2014, found 308.2019.



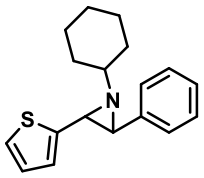
21-A

***trans*-1-cyclohexyl-2-phenyl-3-(4-(trifluoromethoxy)phenyl)aziridine (21-A):** Following the general procedure **A**, obtained at 105 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (10 → 90% of DCM in cyclohexane) to give viscous yellow oil (103 mg, 29%) as a single diastereoisomer. ^{1}H NMR (400 MHz, CD_3OD) δ 7.69 – 7.12 (m, 9H), 3.48 (d, *J* = 3.9 Hz, 1H), 3.45 (d, *J* = 3.9 Hz, 1H), 2.01 – 1.85 (m, 2H), 1.79 – 1.68 (m, 1H), 1.61 – 1.04 (m, 7H), 0.83 – 0.66 (m, 1H). ^{13}C NMR selected peaks (101 MHz, CD_3OD) δ 149.6, 140.3, 133.0, 131.3, 129.6, 129.2, 128.0, 122.0, 121.6, 60.1, 50.7, 45.2, 43.9, 34.0, 33.0, 26.9, 26.0, 25.4. ^{19}F NMR (376 MHz, CD_3OD) δ -59.5.



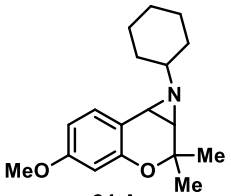
22-A

***trans*-1-cyclohexyl-2-(4-fluorophenyl)-3-phenylaziridine (22-A):** Following the general procedure **A**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 100% of DCM in cyclohexane) to give viscous colorless oil (97 mg, 33%) as a mixture of two diastereoisomers (d.r. 1.1:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.62 – 7.23 (m, 14H), 7.17 – 7.00 (m, 4H), 3.53 – 3.39 (m, 4H), 1.99 – 1.81 (m, 4H), 1.80 – 1.70 (m, 2H), 1.61 – 1.01 (m, 14H), 0.84 – 0.68 (m, 2H). ^{13}C NMR selected peaks (100 MHz, CD_3OD) δ 164.8, 162.3, 140.5, 136.7, 134.2, 133.3, 133.2, 133.1, 131.3, 130.4, 129.9, 129.8, 129.4, 129.2, 128.4, 128.0, 116.2, 116.0, 60.1, 50.3, 45.1, 44.1, 34.0, 33.0, 26.9, 26.1, 25.5. ^{19}F NMR (376 MHz, CD_3OD) δ -116.13, -117.55.



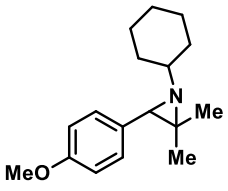
23-A

***trans*-1-cyclohexyl-2-phenyl-3-(thiophen-2-yl)aziridine (23-A):** Following the general procedure **A**, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 100% of dichloromethane in cyclohexane) to give viscous yellow oil (85 mg, 30%) as a mixture of two diastereoisomers (d.r. 2.8:1). ^{1}H NMR (400 MHz, CD_3OD) δ 7.53 – 6.94 (m, 16H), 3.67 (s, 1H), 3.59 (d, *J* = 3.7 Hz, 1H), 3.22 (d, *J* = 3.8 Hz, 1H), 2.27 – 0.57 (m, 22H). ^{13}C NMR *major isomer* (100 MHz, CD_3OD) δ 140.3, 137.6, 130.0, 129.5, 128.5, 128.1, 127.9, 127.0, 60.9, 48.1, 44.6, 34.0, 33.3, 27.0, 26.1, 25.5.



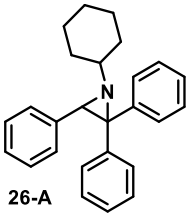
24-A

1-cyclohexyl-5-methoxy-2,2-dimethyl-1,1a,2,7b-tetrahydrochromeno[3,4-b]azirine (24-A): Following the general procedure **A**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (8% of EtOAc in cyclohexane) to viscous transparent oil (267 mg, 93%) as a single diastereoisomer. ^{1}H NMR (399 MHz, CD_3OD) δ 7.22 (d, *J* = 8.3 Hz, 1H), 6.48 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.31 (d, *J* = 2.6 Hz, 1H), 3.72 (s, 3H), 2.67 (d, *J* = 7.1 Hz, 1H), 2.25 (d, *J* = 7.1 Hz, 1H), 1.96 – 1.84 (m, 2H), 1.83 – 1.70 (m, 2H), 1.70 – 1.58 (m, 1H), 1.50 (s, 3H), 1.53 – 1.11 (m, 6H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 161.8, 154.4, 130.1, 116.4, 108.0, 104.7, 73.3, 69.0, 55.7, 51.5, 38.5, 33.4, 33.1, 27.0, 26.7, 26.2, 26.1, 24.2. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{26}NO_2$ 288.1964, found 288.1957.



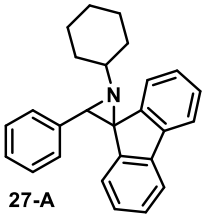
25-A

1-cyclohexyl-3-(4-methoxyphenyl)-2,2-dimethylaziridine (25-A): Following the general procedure **A**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil as a single diastereoisomer (202 mg, 78%). ^{1}H NMR (399 MHz, CD_3OD) δ 7.19 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 2.48 (s, 1H), 2.09 (tt, *J* = 10.8, 3.6 Hz, 1H), 1.91 – 1.73 (m, 4H), 1.71 – 1.62 (m, 1H), 1.43 (s, 3H), 1.55 – 1.18 (m, 5H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.0, 131.7, 129.8, 114.4, 62.7, 55.7, 52.4, 44.1, 34.5, 34.2, 27.1, 26.3, 25.8, 23.1, 18.3.



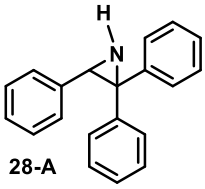
26-A

1-cyclohexyl-2,2,3-triphenylaziridine (26-A): Following the general procedure **A**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (0 → 10% of DCM in cyclohexane) to give viscous yellow oil as a single diastereoisomer (311 mg, 88%). ^{1}H NMR (400 MHz, CD_3OD) δ 7.53 – 7.40 (m, 2H), 7.36 – 7.24 (m, 3H), 7.22 – 7.14 (m, 4H), 7.09 – 7.01 (m, 4H), 7.01 – 6.92 (m, 2H), 3.75 (s, 1H), 1.87 – 1.67 (m, 5H), 1.66 – 1.55 (m, 1H), 1.56 – 1.41 (m, 2H), 1.38 – 1.24 (m, 1H), 1.23 – 1.09 (m, 1H), 1.06 – 0.92 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 142.8, 140.1, 139.4, 132.4, 130.6, 128.9, 128.7, 128.5, 128.4, 128.3, 127.2, 127.1, 61.0, 60.6, 49.7, 34.0, 33.6, 27.3, 25.6, 25.1. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{28}N$ 354.2222, found 354.2227.



27-A

1-cyclohexyl-3-phenylspiro[aziridine-2,9'-fluorene] (27-A): Following the general procedure **A**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of dichloromethane in cyclohexane) to give viscous transparent oil as a single diastereoisomer (95 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.34 – 7.26 (m, 3H), 7.25 – 7.21 (m, 2H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 3.97 (s, 1H), 2.94 (tt, *J* = 8.8, 4.3 Hz, 1H), 2.20 – 2.06 (m, 1H), 2.00 – 1.89 (m, 1H), 1.87 – 1.73 (m, 1H), 1.74 – 1.18 (m, 4H), 1.17 – 0.99 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.7, 141.3, 139.9, 137.6, 128.5, 128.2, 127.5, 127.3, 127.2, 126.9, 126.4, 123.8, 123.1, 120.3, 119.3, 60.1, 55.8, 53.8, 33.5, 32.3, 26.2, 24.9, 24.2. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{26}N$ 352.2065, found 352.2048.



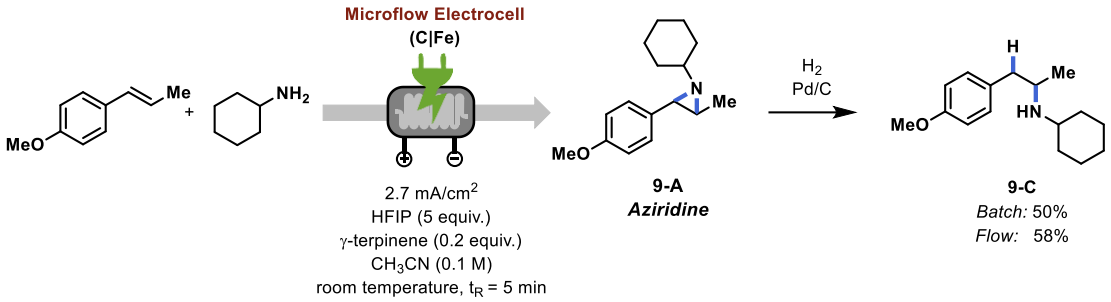
28-A

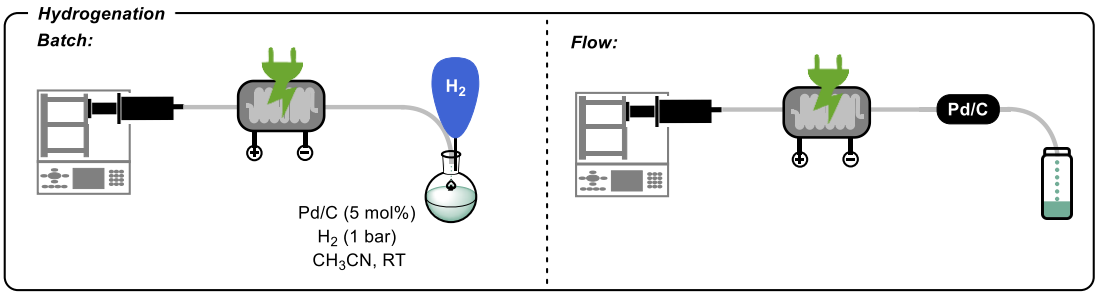
Triphenylaziridine (28-A):[24] Following the general procedure **A**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 10% of ethyl acetate in cyclohexane) to give viscous transparent oil (40% w/w NH_3 solution in water 166 mg, 61%; 7M NH_3 solution in MeOH 138 mg, 51%). ^{1}H NMR (400 MHz, CD_3OD) δ 7.46 – 7.39 (m, 2H), 7.37 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.22 – 7.17 (m, 2H), 7.15 – 6.99 (m, 8H), 3.96 (s, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 145.4, 139.9, 138.4, 130.7, 129.6, 128.7, 128.6, 128.4, 128.3, 127.7, 127.7, 53.7, 47.3. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{18}N$ 272.1439, found 272.1443.

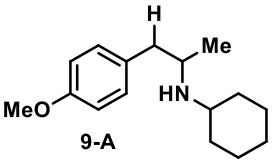
6.3. Procedure for scale-up experiment

trans-Anethole (1.0 equiv., 12.0 mmol, 1.78 g), together with cyclohexylamine (5.0 equiv., 60.0 mmol, 6.90 mL), hexafluoroisopropanol (HFIP, 5.0 equiv., 60.0 mmol, 6.30 mL) and γ-terpinene (0.5 equiv., 6.0 mmol, 0.96 mL) were dissolved in acetonitrile using a 120 mL volumetric flask (0.1M). The mixture was swirled until homogeneous and placed in two 60 ml disposable syringes. The solution was pumped through the electrochemical setup with a fixed flowrate of 0.15 mL/min to give a residence time of 5 minutes in the active part of the reactor, equipped with a graphite anode, steel cathode divided by a 0.25 mm thick Teflon gasket. The first fraction was discarded after which a constant current of 80 mA was applied. The reaction mixture was collected in a flask cooled at 0°C for 667 minutes, which corresponds to 10.0 mmol scale. The crude mixture was concentrated under vacuum at room temperature, to prevent decomposition of the product. The resulting crude mixture was directly purified by flash column chromatography on silica gel (2 → 40% of EtOAc in cyclohexane; and then 30 → 100% of DCM in cyclohexane) to give ***trans*-1-cyclohexyl-2-(4-methoxyphenyl)-3-methylaziridine (9-A)** as a viscous brown oil in 66% yield (1.63 g, 6.64 mmol, d.r. 1:1).

7. Procedure for formal electrochemical hydroamination in flow

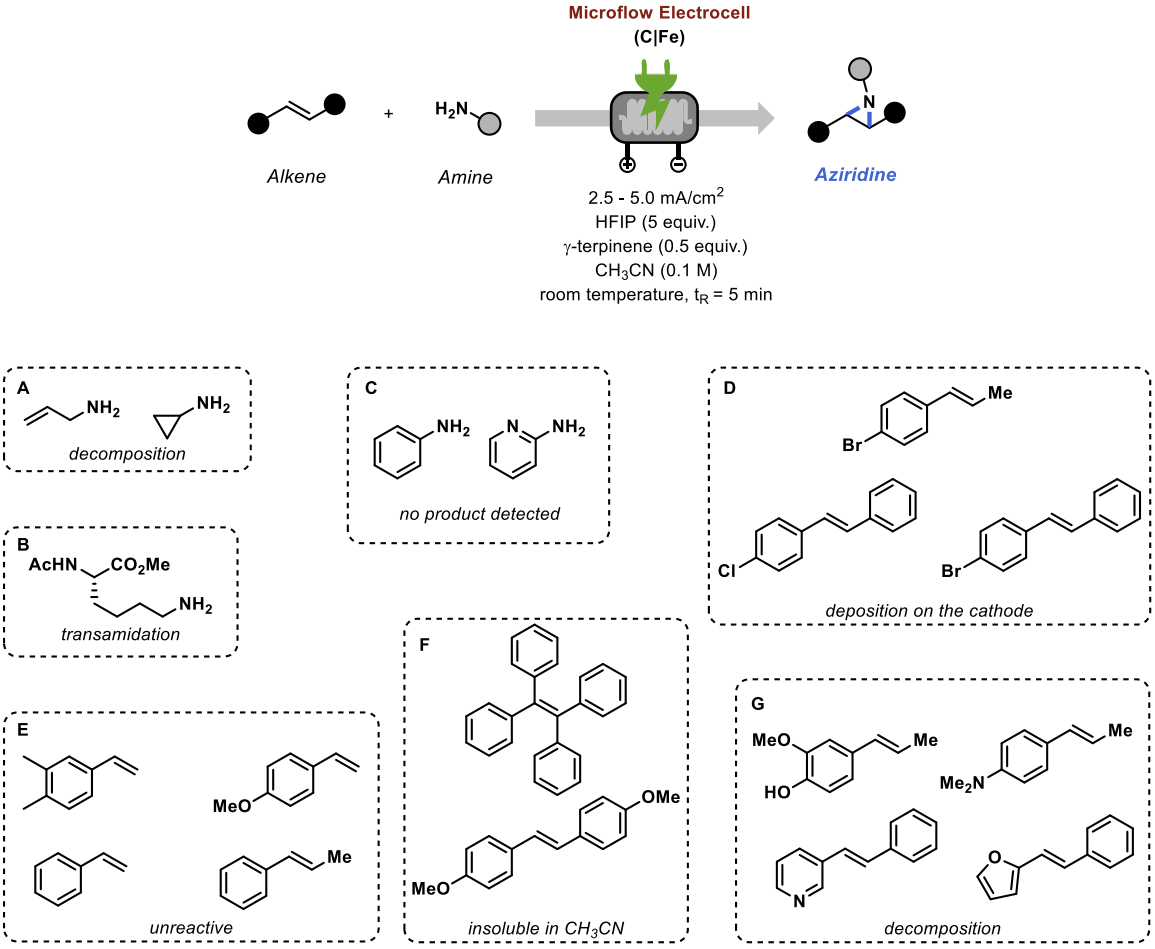






***N*-(1-(4-methoxyphenyl)propan-2-yl)cyclohexanamine (9-A):** *trans*-Anethole (1.0 equiv., 2.0 mmol, 296 mg), together with cyclohexylamine (5.0 equiv., 10.0 mmol, 1.15 mL), hexafluoroisopropanol (HFIP, 5.0 equiv., 10.0 mmol, 1.05 mL) and γ-terpinene (0.2 equiv., 1.0 mmol, 64 µL) were dissolved in acetonitrile using a 20 mL volumetric flask (0.1M). The mixture was swirled until homogeneous and placed in a 20 ml disposable syringe. The solution was pumped through the electrochemical setup with a fixed flowrate of 0.15 mL/min to give a residence time of 5 minutes in the active part of the reactor, equipped with a graphite anode, steel cathode divided by a 0.25 mm thick Teflon gasket. The first fraction was discarded after which a constant current of 70 mA was applied. The reaction mixture was collected for 67 minutes (1.0 mmol scale) in a flask containing a stirred suspension of Pd/C (10 wt%, 50 µmol, 53 mg) in acetonitrile (5 mL) with an hydrogen balloon in case of batch quenching. Otherwise, a self-made packed bed reactor filled with Pd/C (150 mg) and glass beads, was connected to the outlet of electrochemical reactor. The crude mixture was concentrated under vacuum and purified by flash column chromatography on silica gel (normal phase: 2 → 40% of MeOH in DCM; and then reversed phase: 10 → 100% of CH_3CN in water) to give the desired compound as a viscous transparent oil in 50% yield (0.497 mmol, 123 mg) for reduction under the batch conditions and 58% yield (0.582 mmol, 144 mg) for reduction in flow. ^{1}H NMR (400 MHz, CD_3OD) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.04 (h, *J* = 6.5 Hz, 1H), 2.68 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.62 – 2.53 (m, 1H), 2.50 (dd, *J* = 13.4, 7.3 Hz, 1H), 1.94 – 1.81 (m, 2H), 1.76 – 1.56 (m, 3H), 1.36 – 1.03 (m, 4H), 1.01 (d, *J* = 6.3 Hz, 3H), 0.98 – 0.87 (m, 1H). ^{13}C NMR (101 MHz, CD_3OD) δ 159.8, 132.3, 131.2, 114.9, 55.6, 54.3, 52.0, 43.2, 34.6, 33.6, 27.1, 26.2, 26.1, 19.9. HRMS (ESI) *m*/*z* $[M+H]^+$ calcd for $C_{16}H_{26}BrNOS$ 248.2014, found 248.2019.

8. Unsuccessful substrates



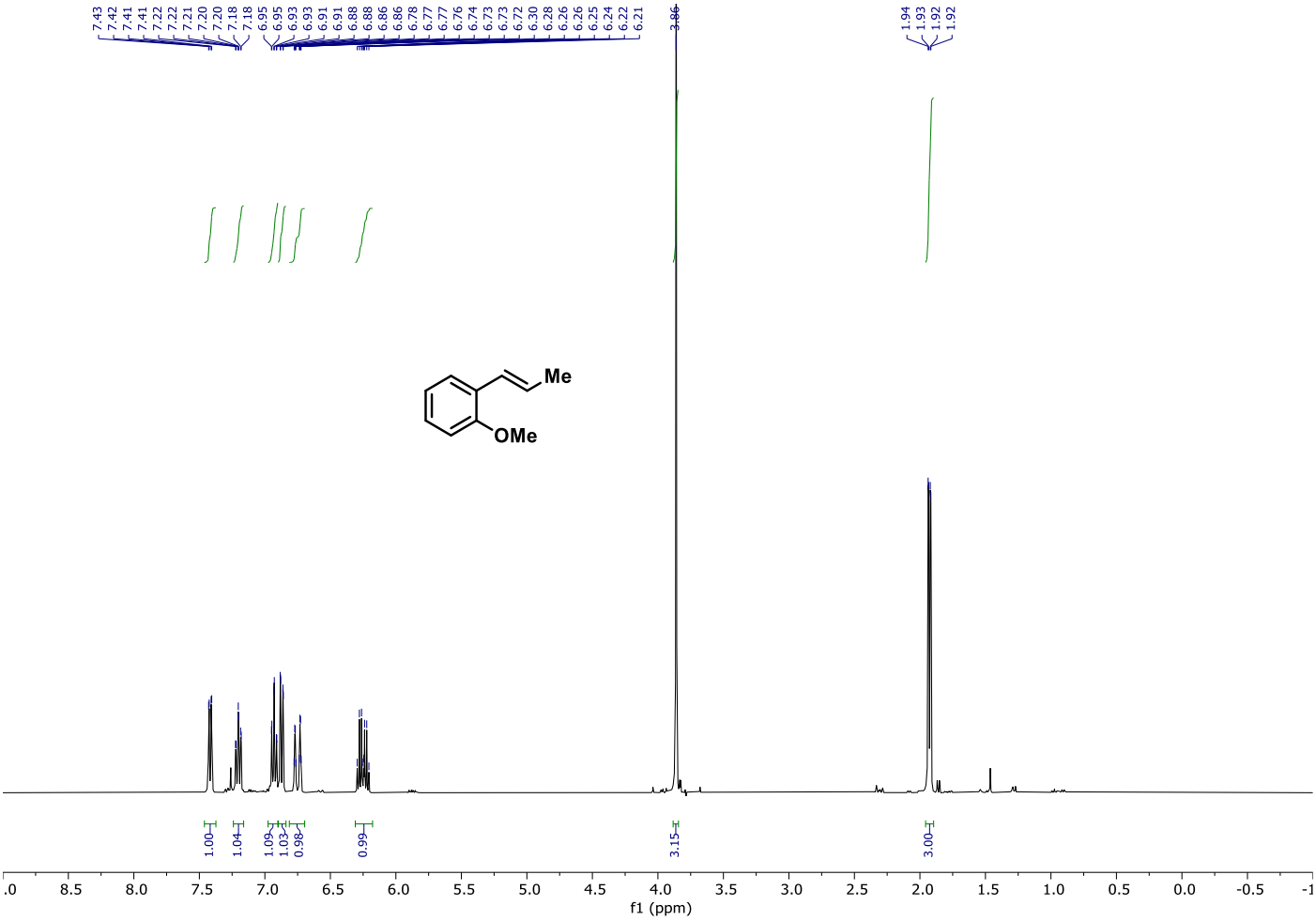
Reactions with allylamine and cyclopropylamine showed no formation of the desired aziridines, due to the decomposition of these highly reactive amines under the electrochemical conditions (**A**). Although protected lysine derivative with a terminal free amino-group can be used to trap a radical cation, the carboalkoxy group is prone to undergo transamidation leading to the formation of inseparable mixture of transamidated products (**B**). Aromatic amines are known to polymerize electrochemically, both in acidic or neutral conditions and thus are the most important limitation for this transformation (**C**). Bromo- and chloroaryl substituted alkenes were partially reduced and deposed on the cathode, causing drop of current and shutting down the reaction completely, while fluorosubstituted stilbene reacted efficiently (**D**). This issue can be potentially solved by transferring the reaction to a divided-cell microflow reactor. No desired product formation was observed, when styrene and its derivatives were used, since they require much higher currents to be electrochemically oxidized comparing to anethole- and stilbene-type alkenes, which is not compatible with our transformation (**E**). From our experience, tetraphenylethelene and dimethoxystilbene should undergo electrochemical aziridation effortlessly, however, due to the very poor solubility in acetonitrile, they cannot be used in the described continues-flow transformation (**F**). Finally, alkenes bearing unprotected phenol or aniline fragment decomposed under the electrochemical conditions as well as N- and O-atom containing heterocyclic substrates (**G**).

9. Cleaning procedure

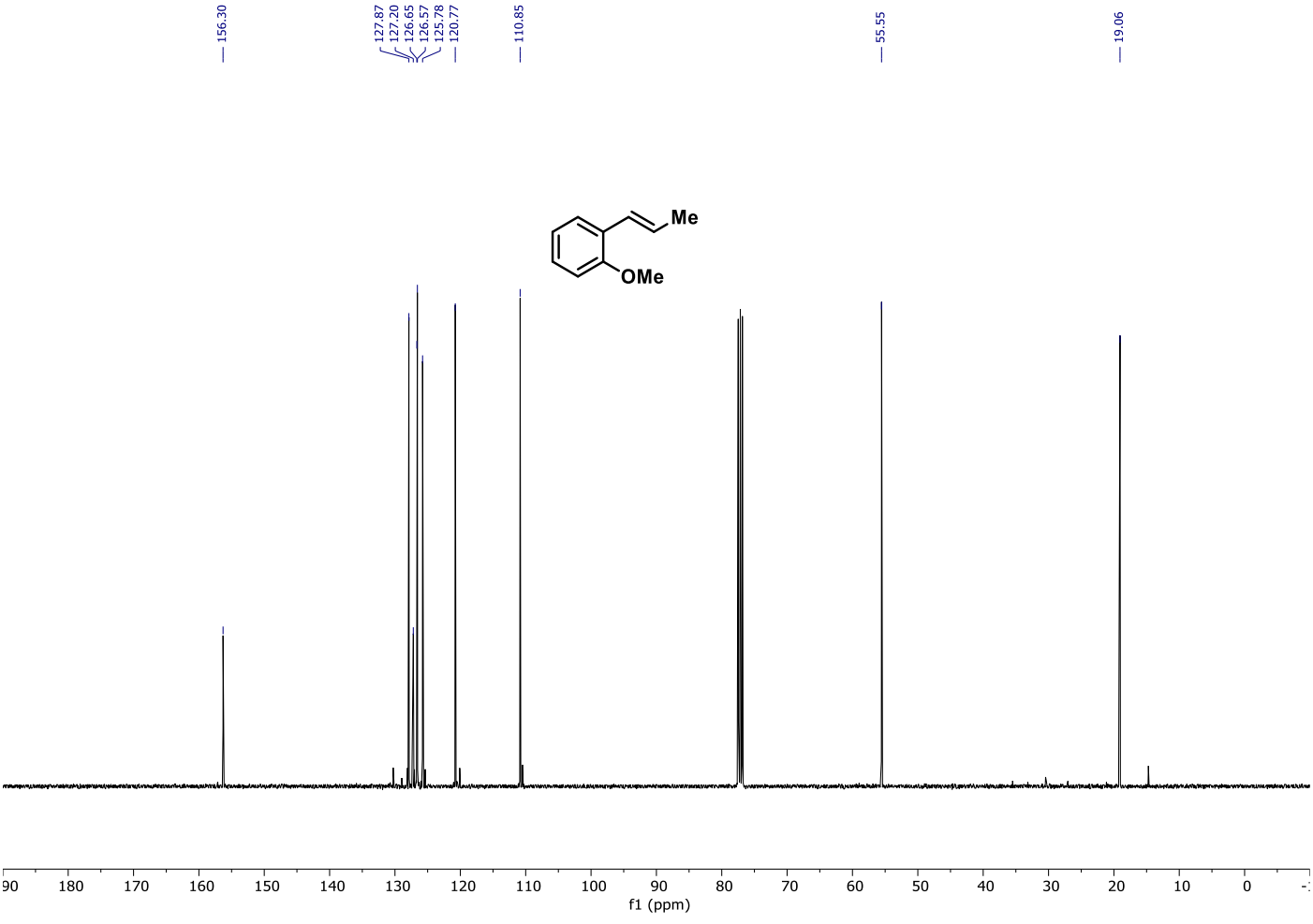
After collecting the product for specified time, the collecting vial was changed, the power supply turned off and the reactor was washed with CH_3CN (15 mL) and disassembled. First, the gasket was cleaned with acetone on both the sides. The stainless steel electrode was first washed with HCl 1M and scrubbed with a sponge twice, then rinsed with acetone. Next, the gasket, the loops and the stainless steel electrode were submerged in a beaker full of acetone and sonicated for 15 minutes .The graphite electrode was wiped with paper and washed with CH_3CN 5 times. The electrode holders were washed with acetone and dried with paper. The copper contacts were first washed with HCl 1M, then scrubbed with a sponge in case of carbon deposit (anode) could be observed. Finally, they were rinsed with acetone and reassembled. After these process, all the components were dried with paper and the reactor was reassembled.

10. NMR Spectra

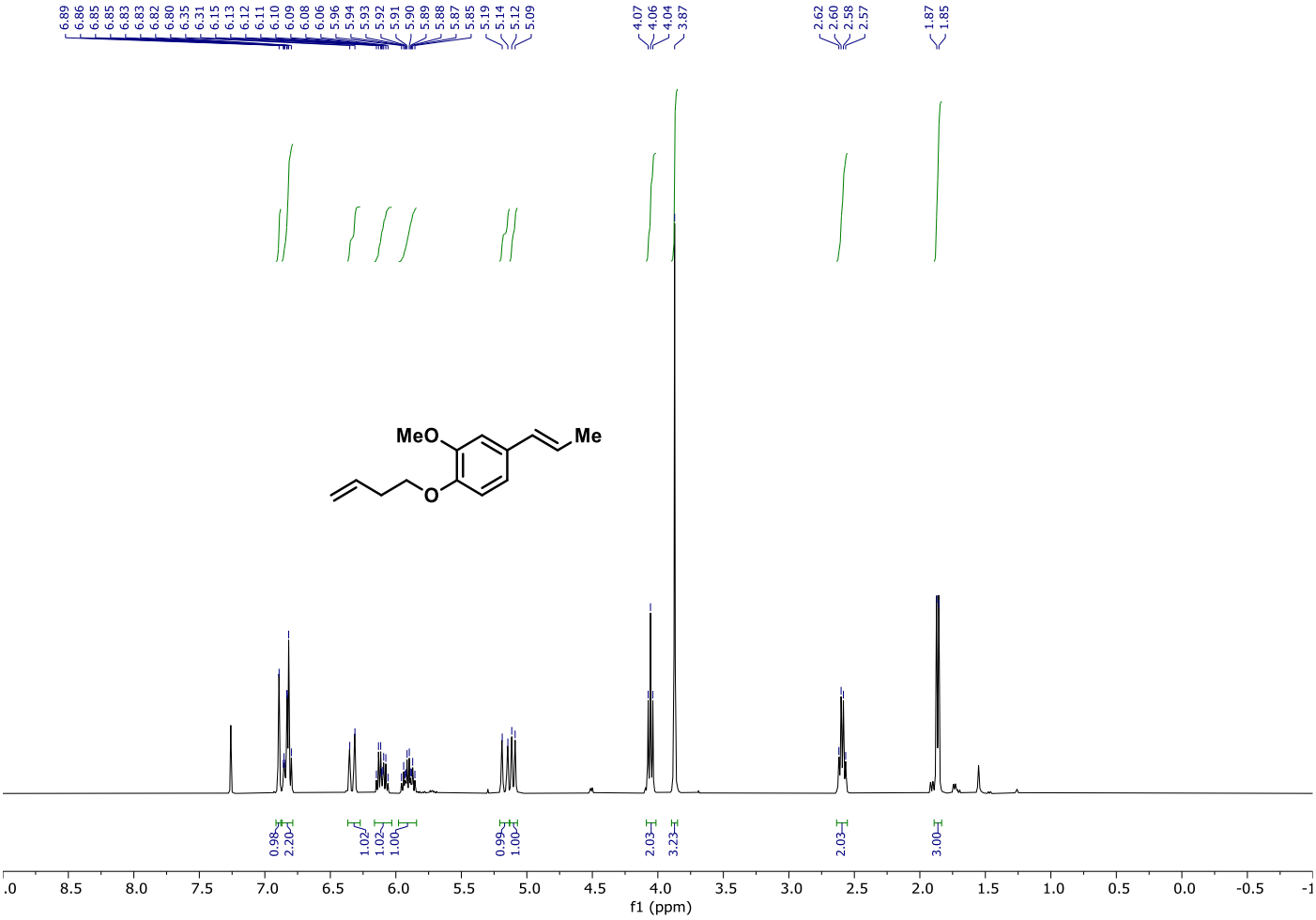
^{1}H NMR (400 MHz, $CDCl_3$)



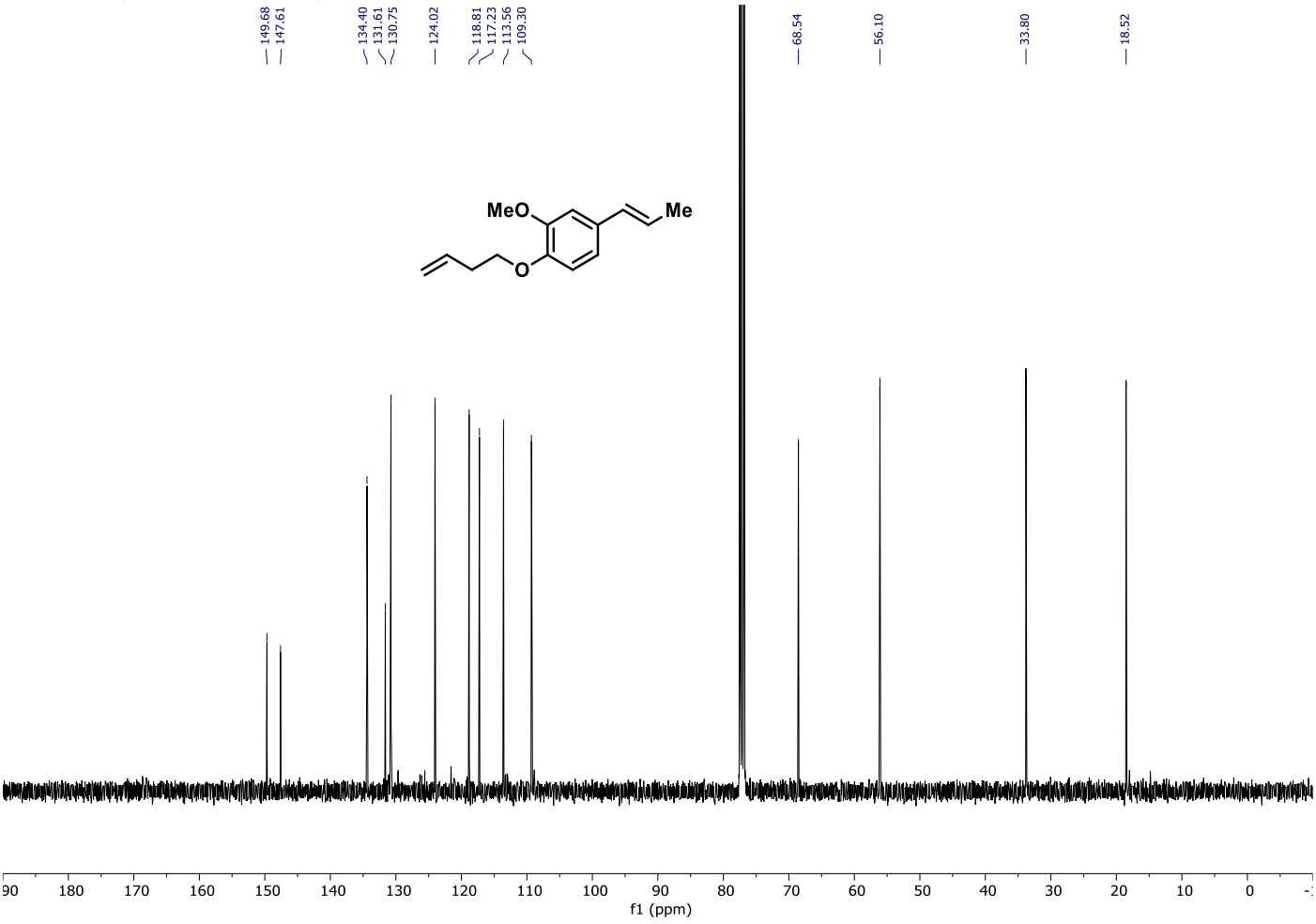
^{13}C NMR (101 MHz, $CDCl_3$)



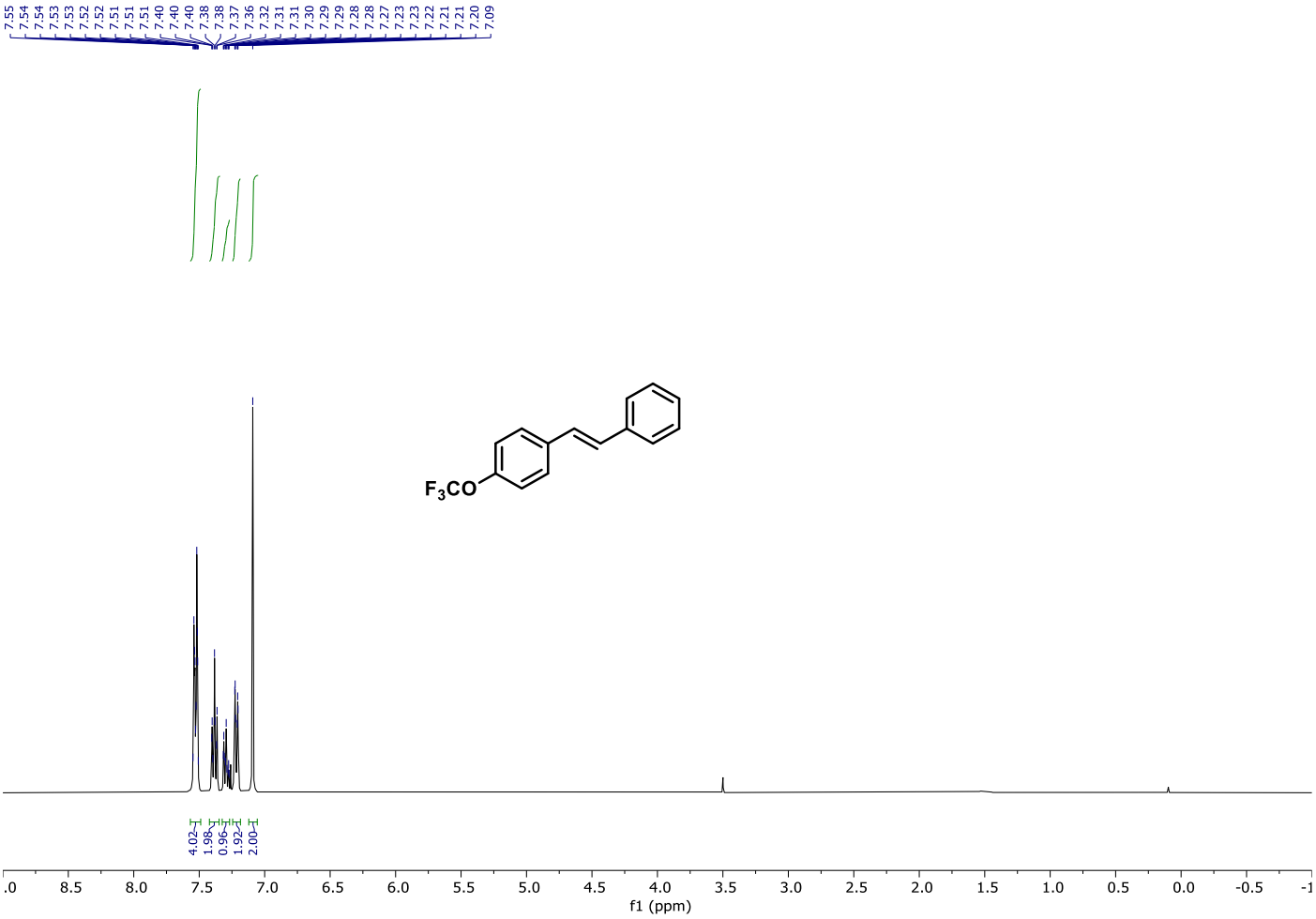
^{1}H NMR (400 MHz, $CDCl_3$)



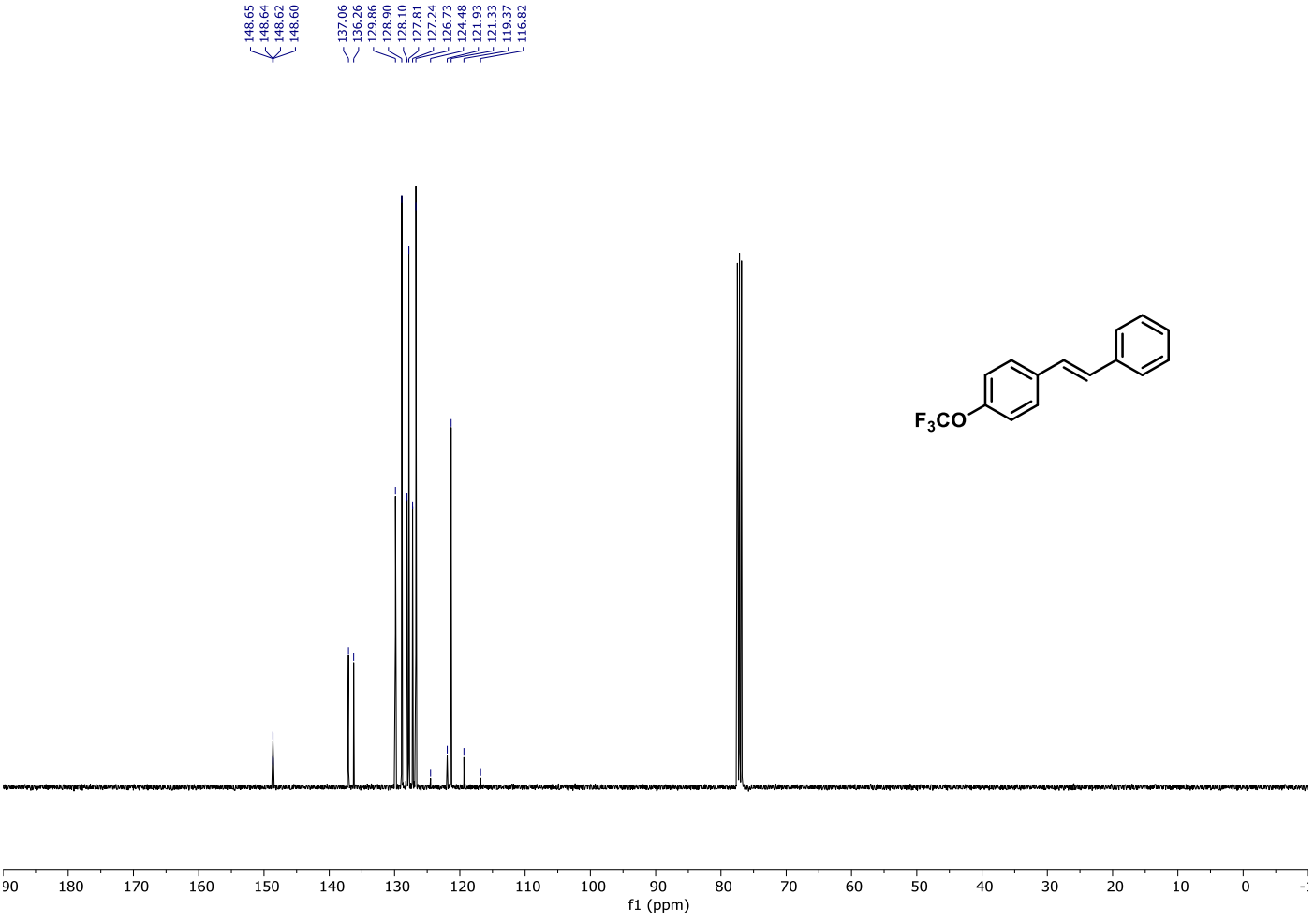
^{13}C NMR (101 MHz, $CDCl_3$)



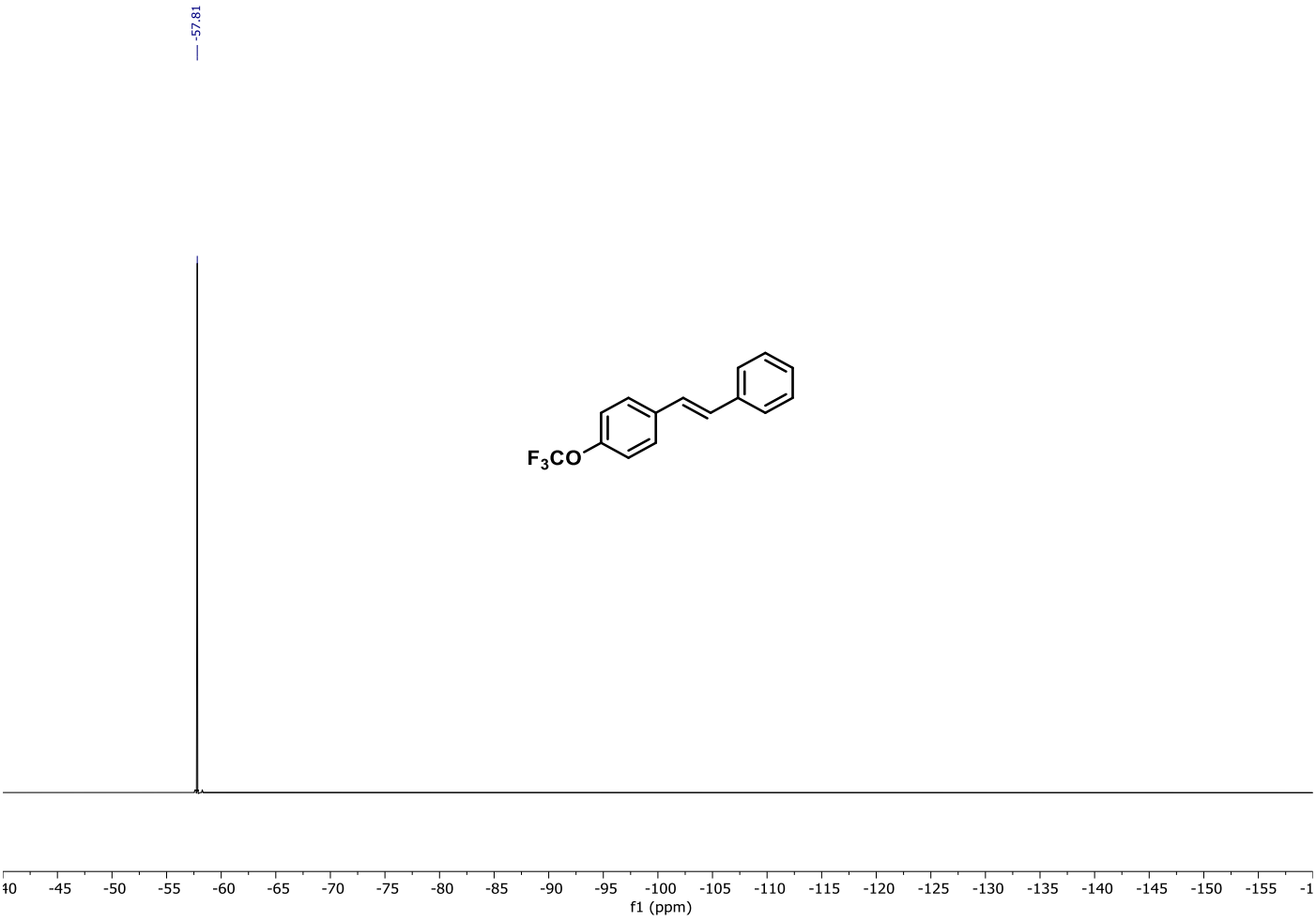
^{1}H NMR (400 MHz, $CDCl_3$)



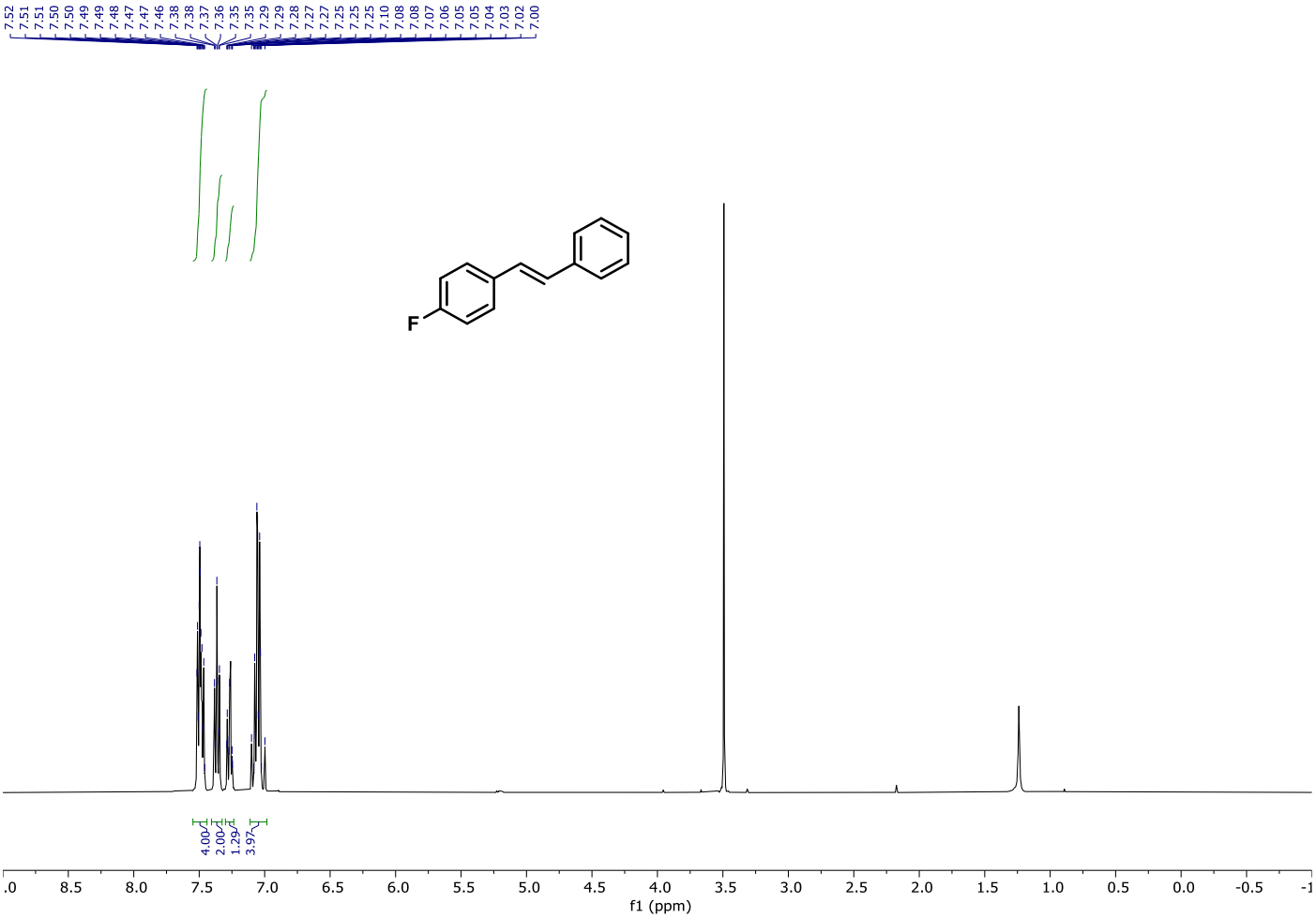
^{13}C NMR (101 MHz, $CDCl_3$)



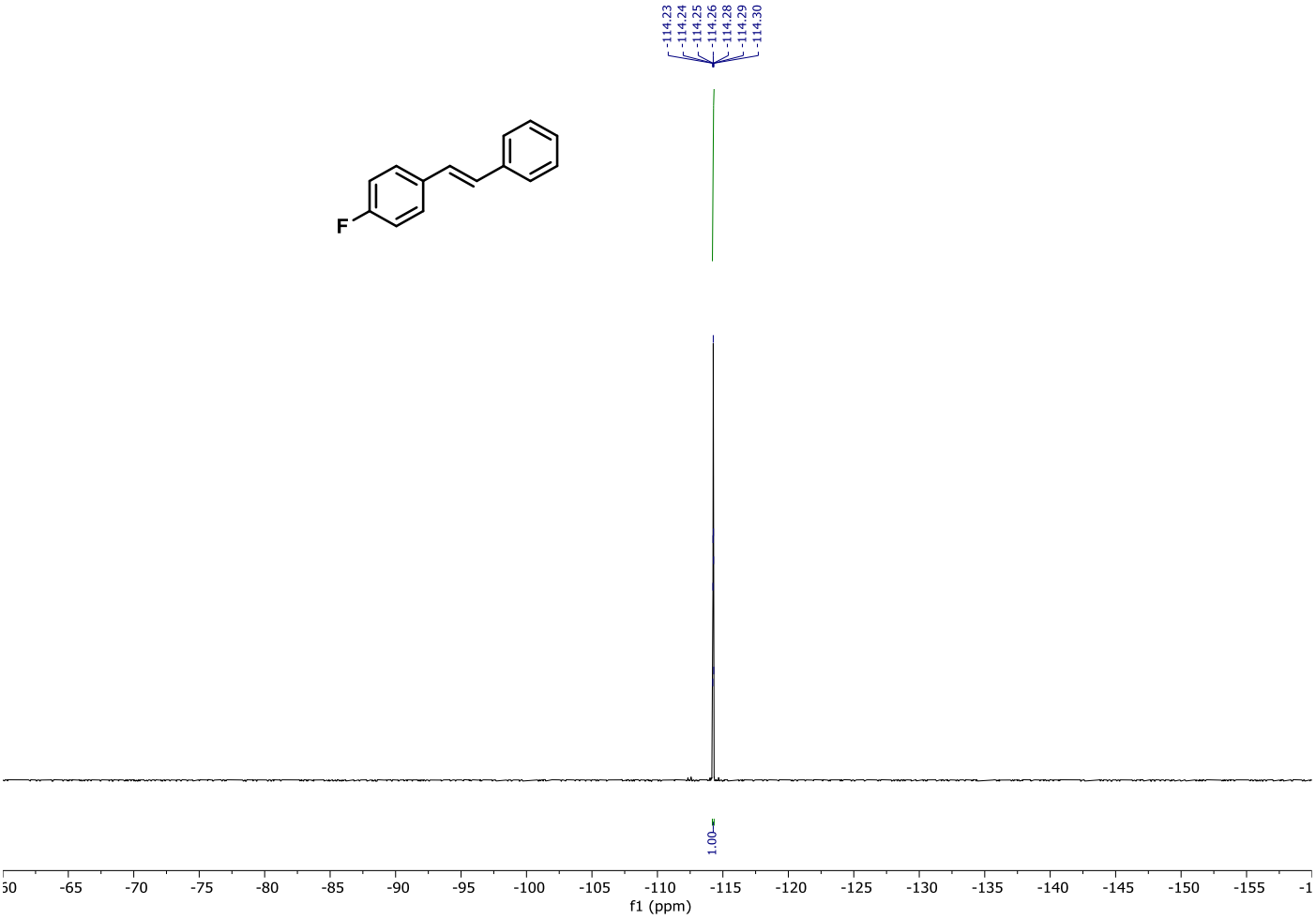
^{19}F NMR (376 MHz, CD_3OD)



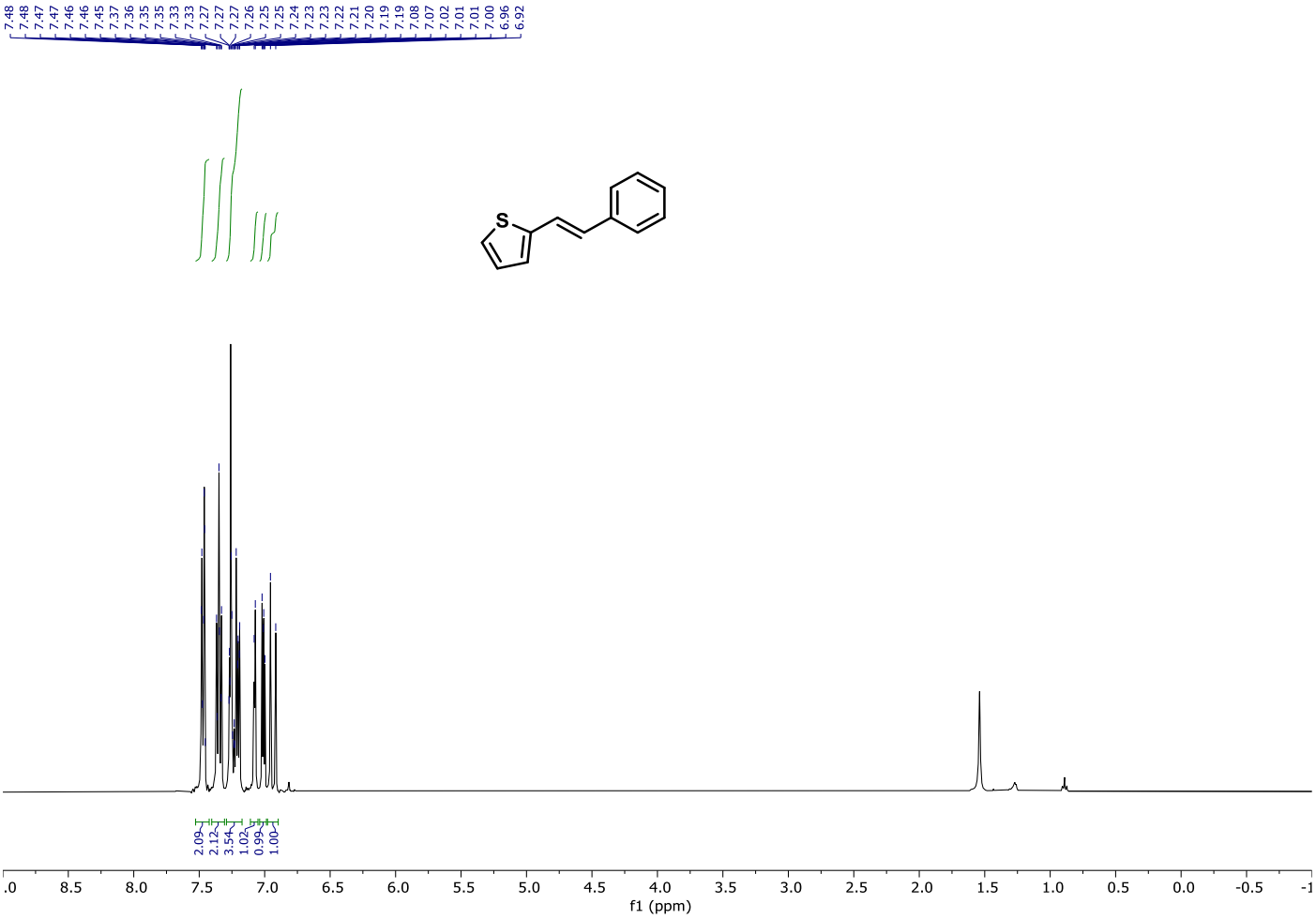
^{1}H NMR (400 MHz, $CDCl_3$)



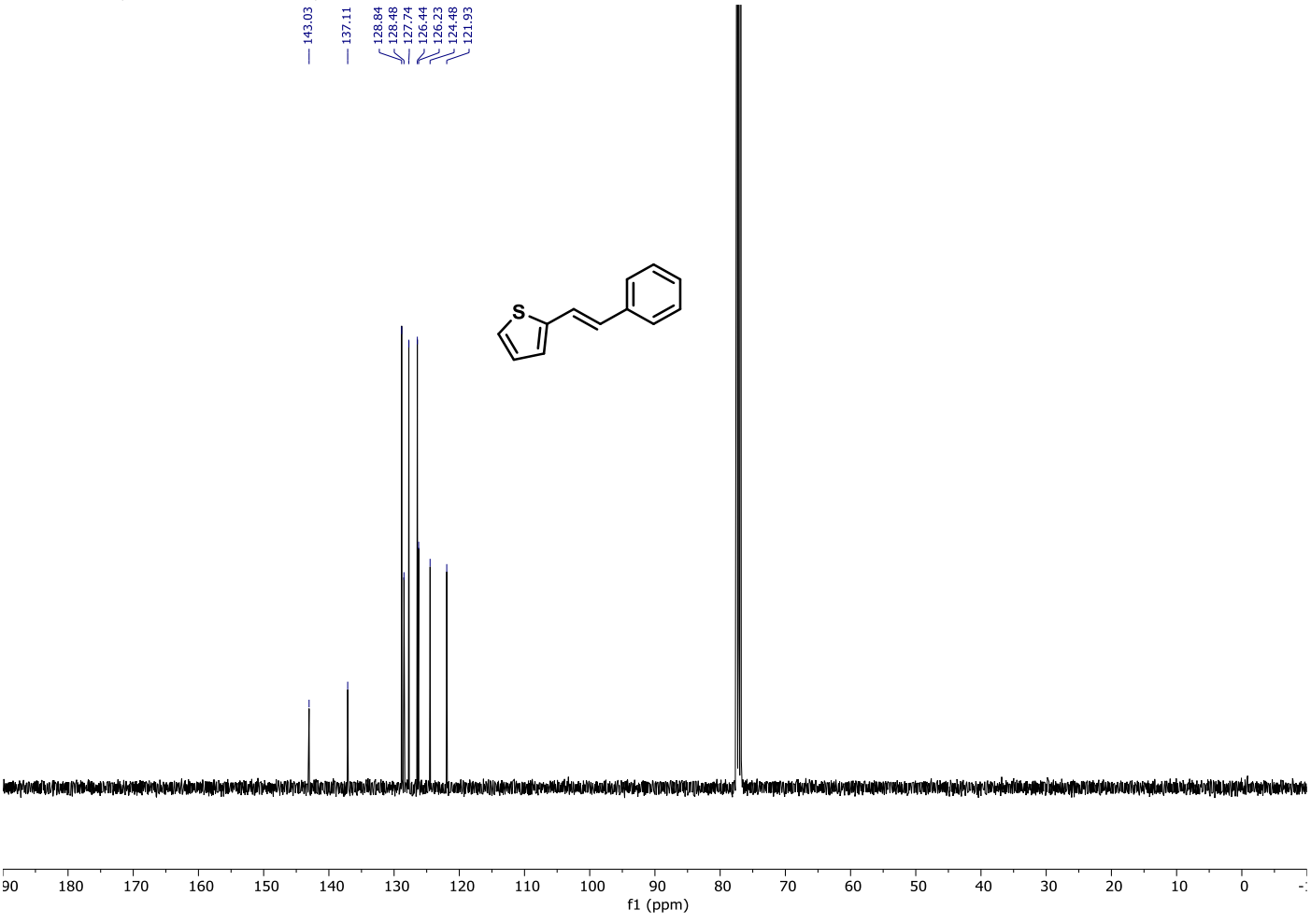
^{19}F NMR (376 MHz, CD_3OD)



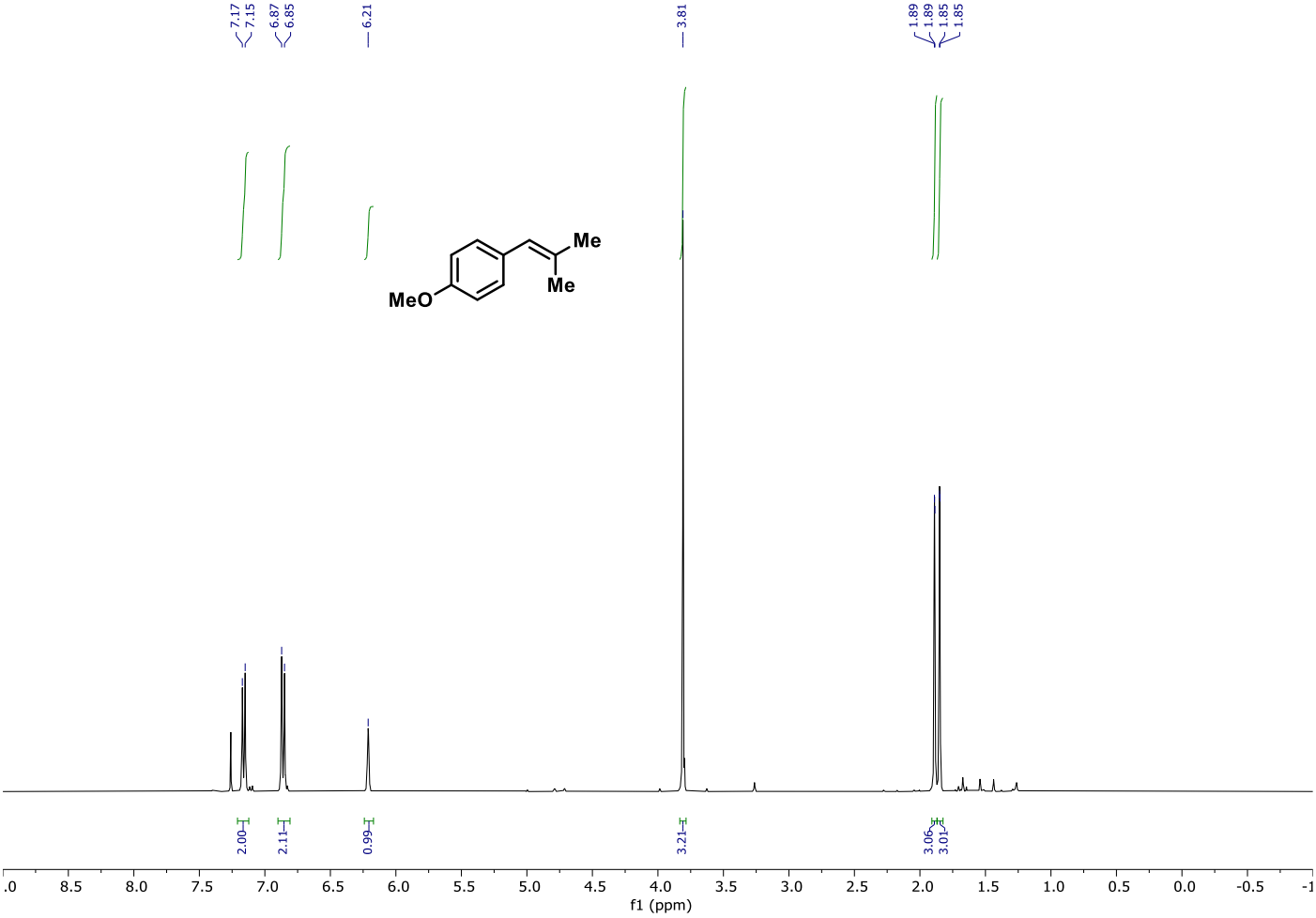
^{1}H NMR (400 MHz, $CDCl_3$)



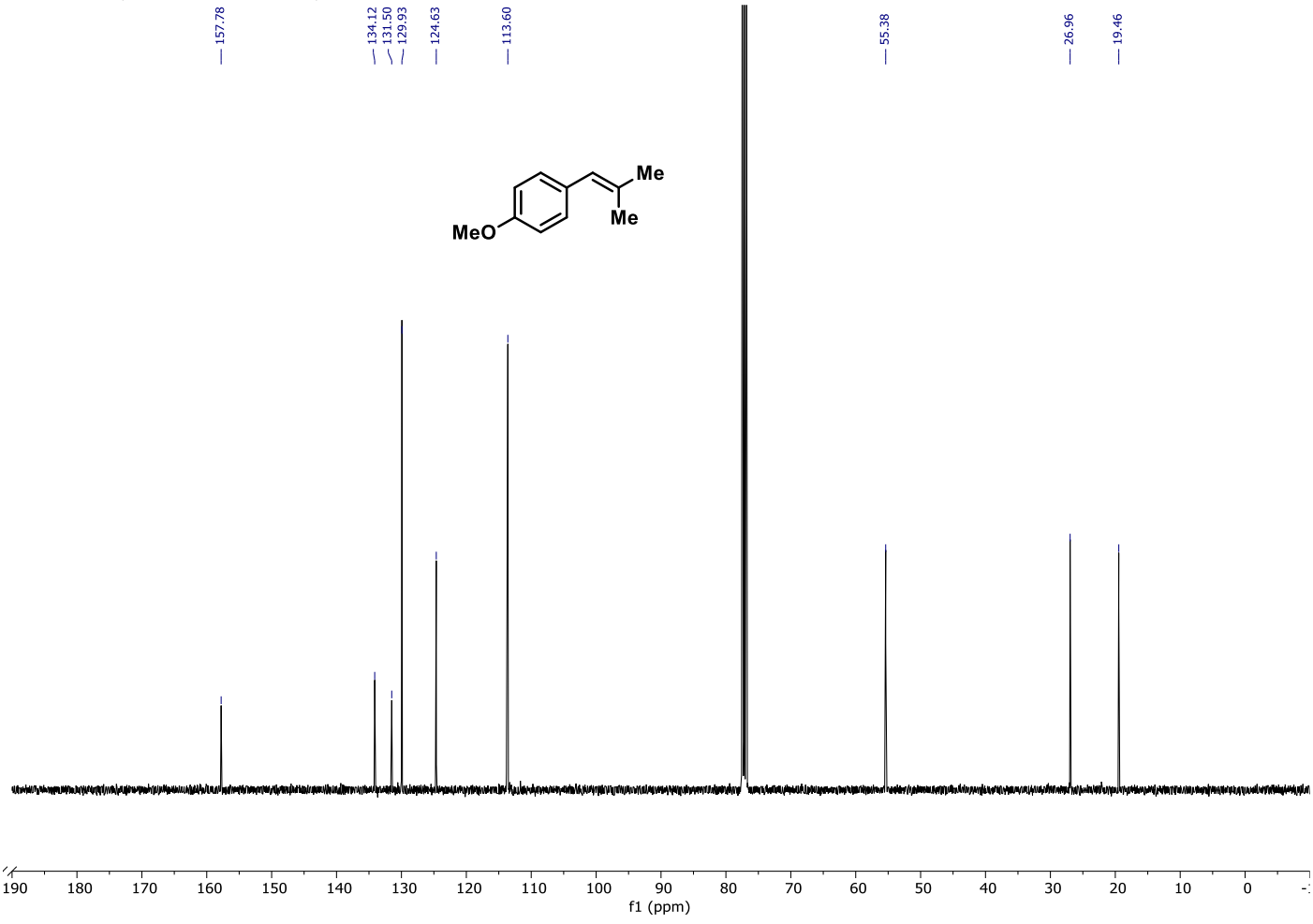
^{13}C NMR (101 MHz, $CDCl_3$)



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



^{13}C NMR (101 MHz, $CDCl_3$)



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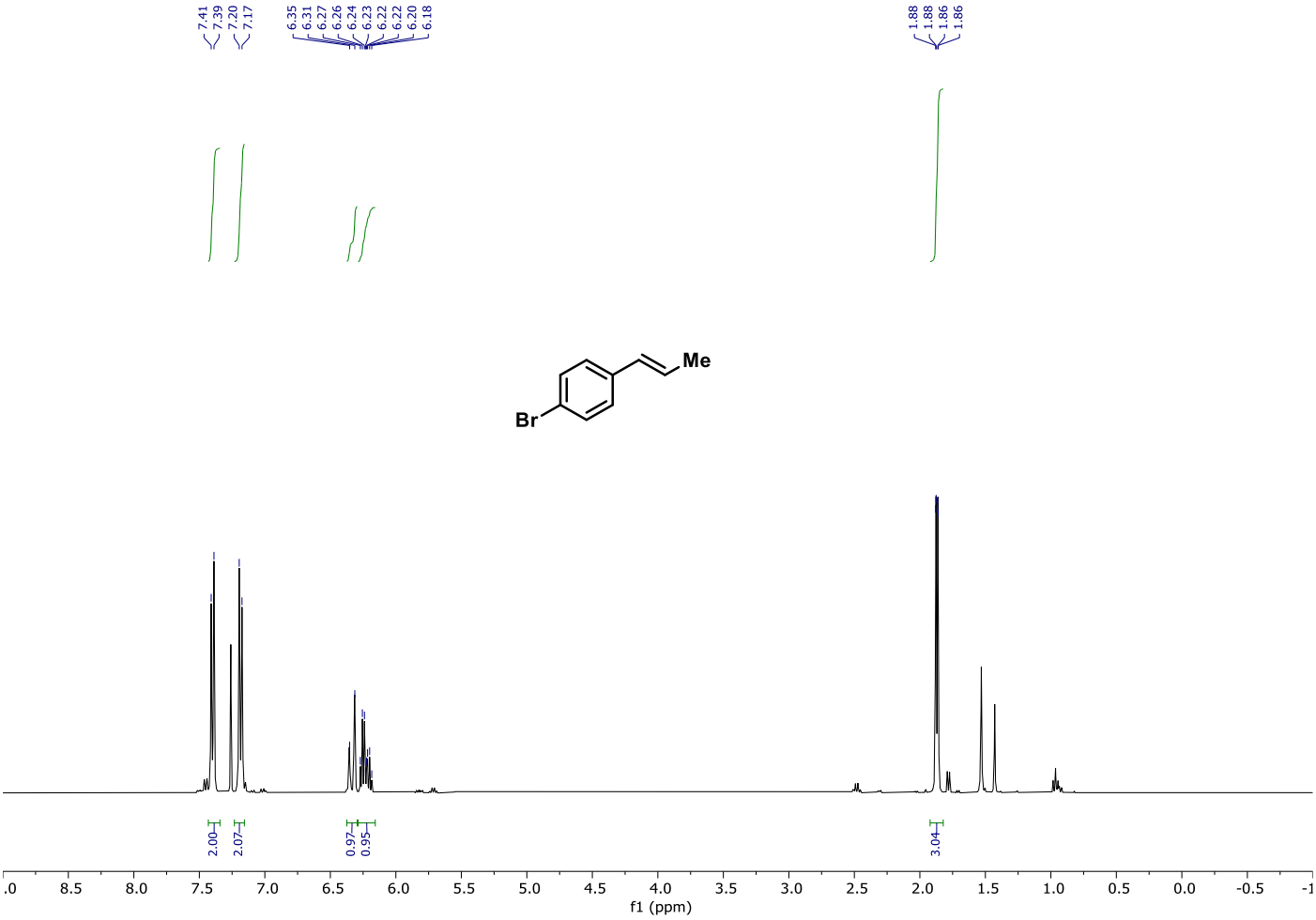

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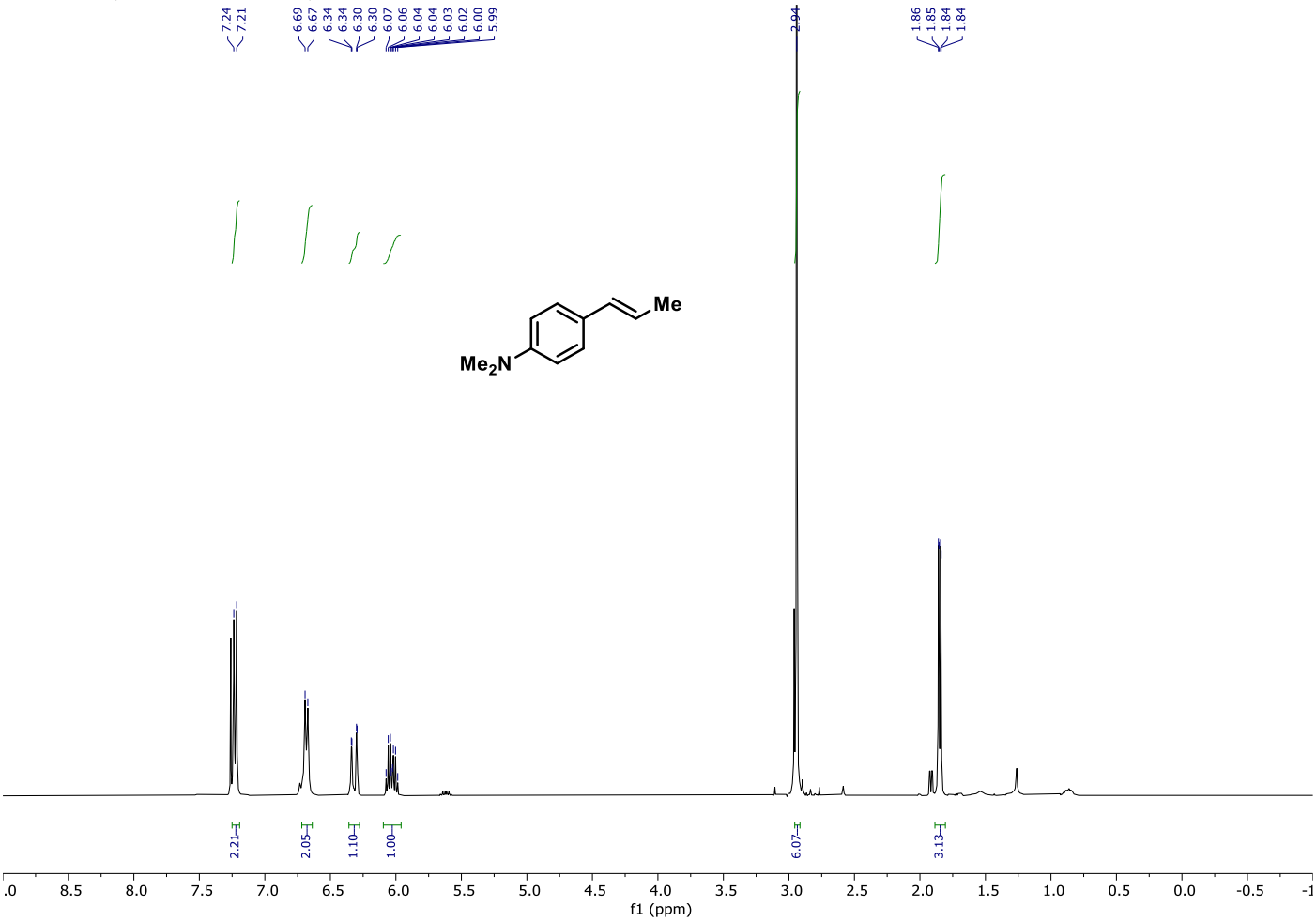

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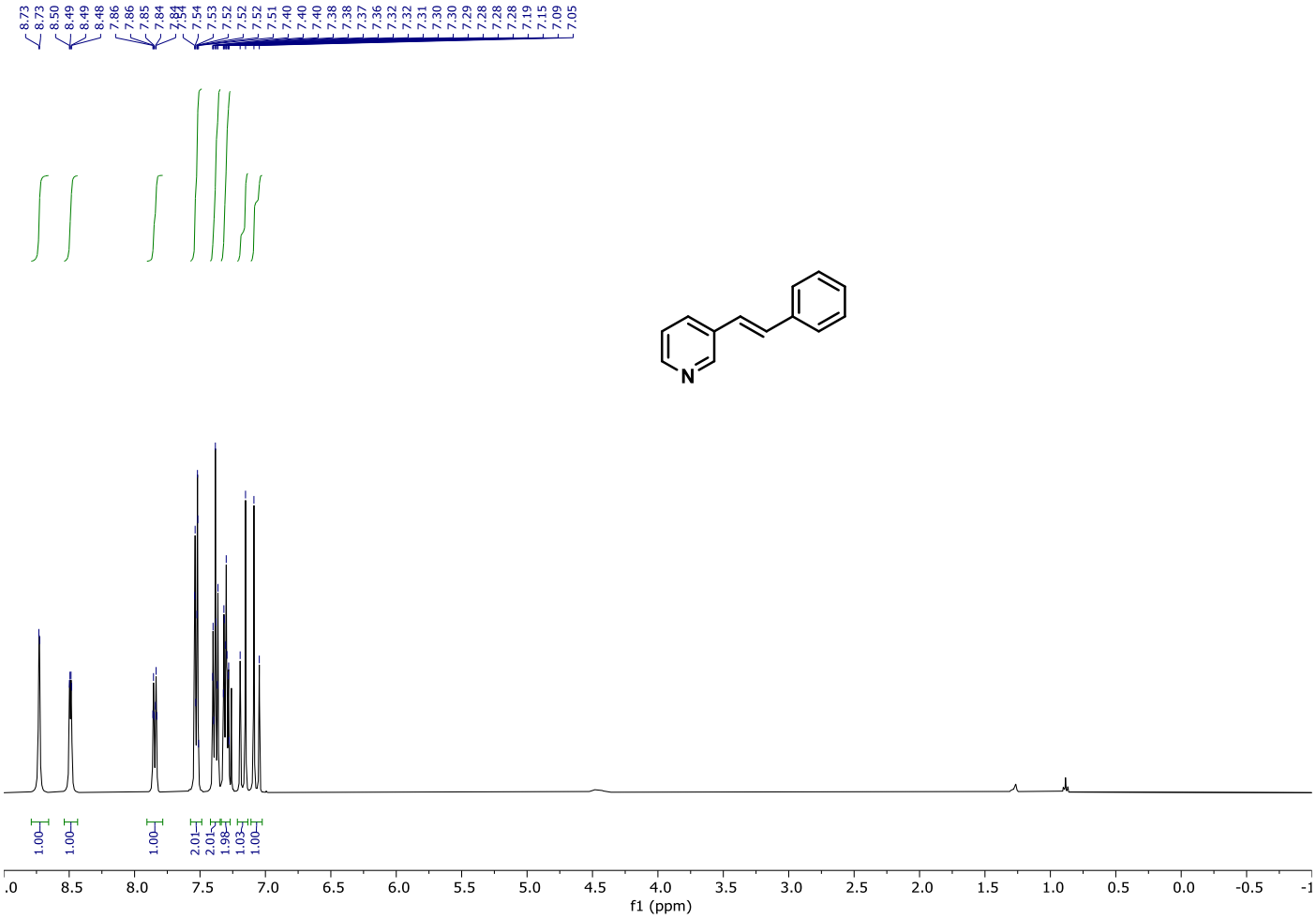
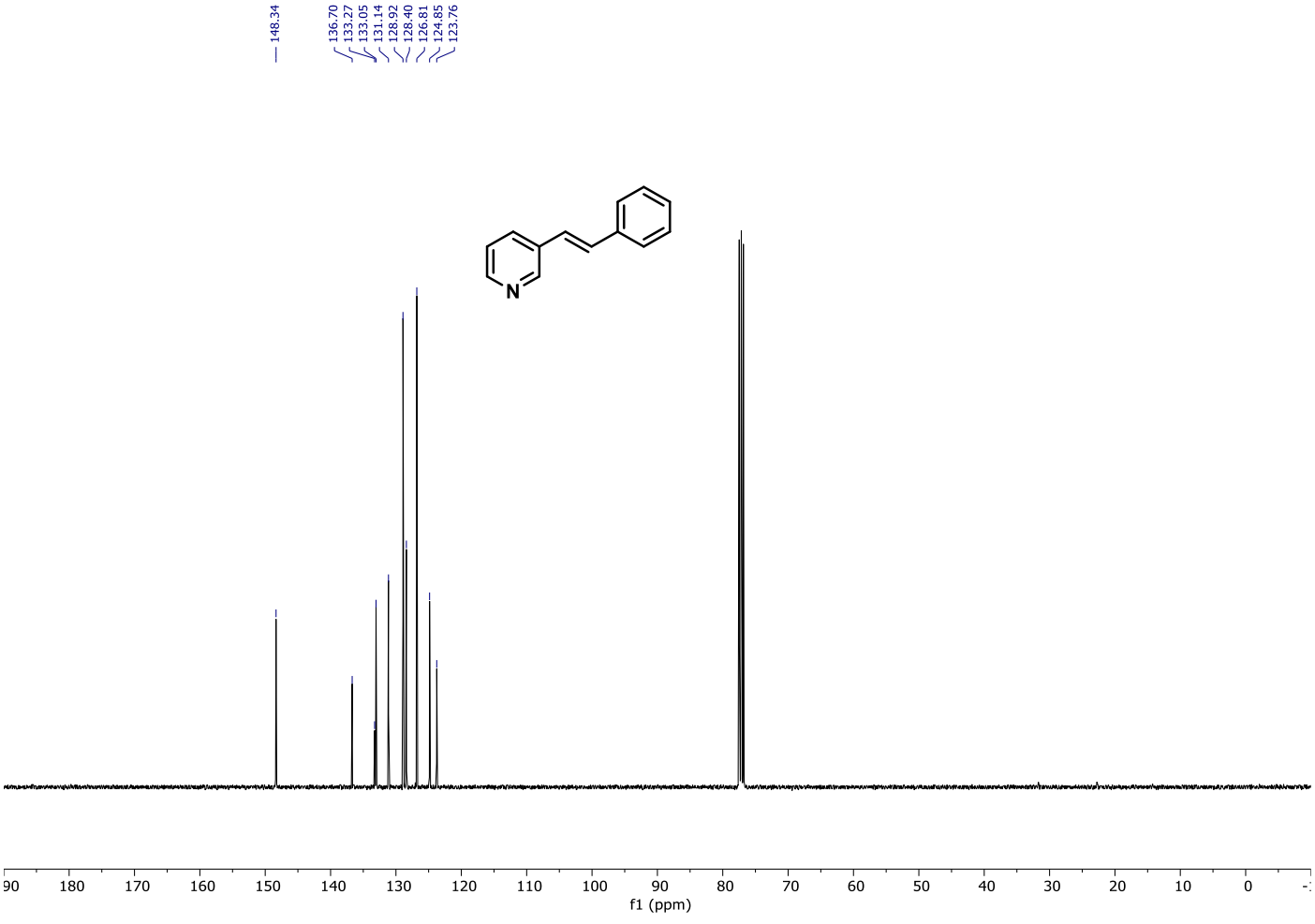
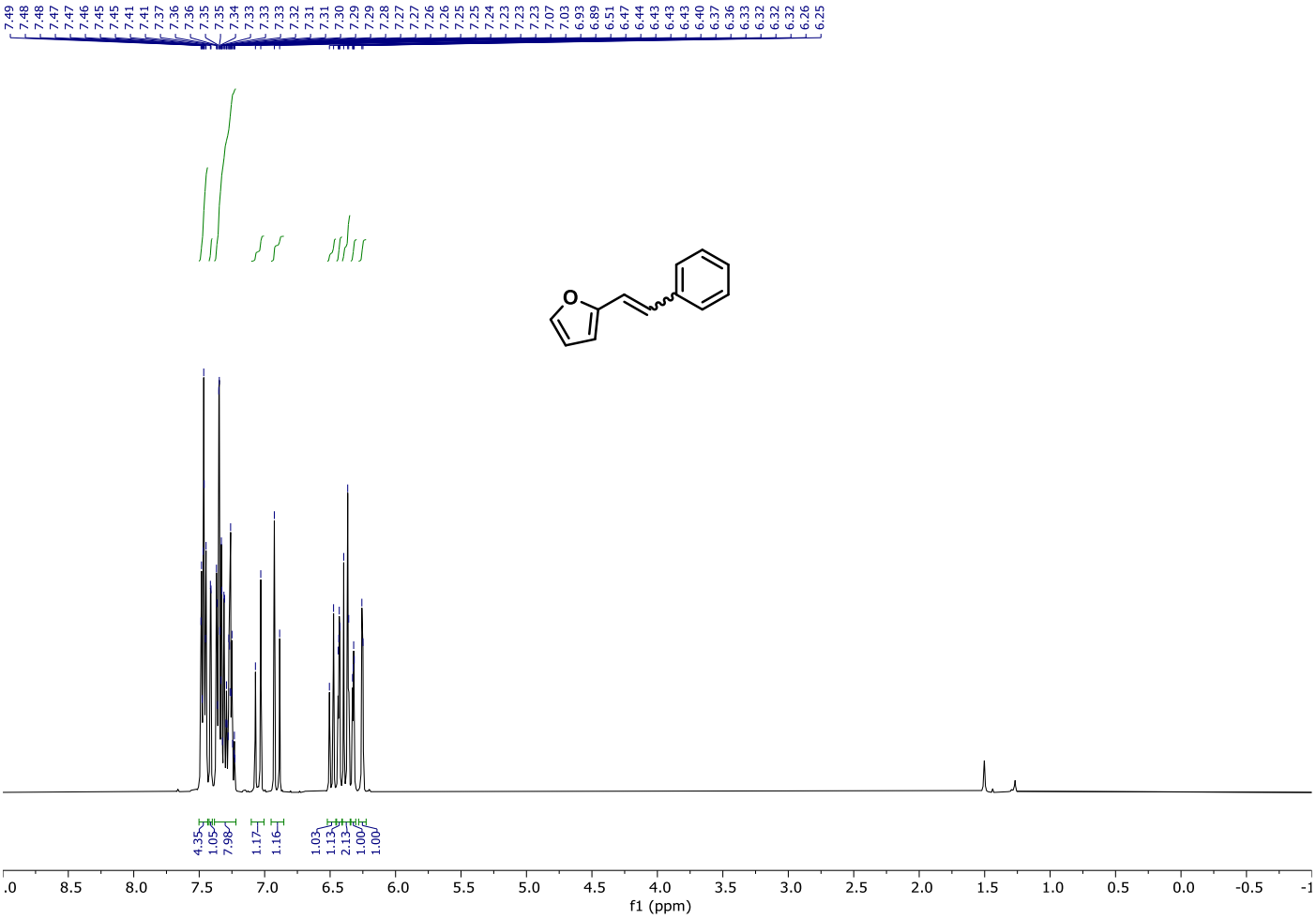


^{13}C NMR (101 MHz, $CDCl_3$)



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



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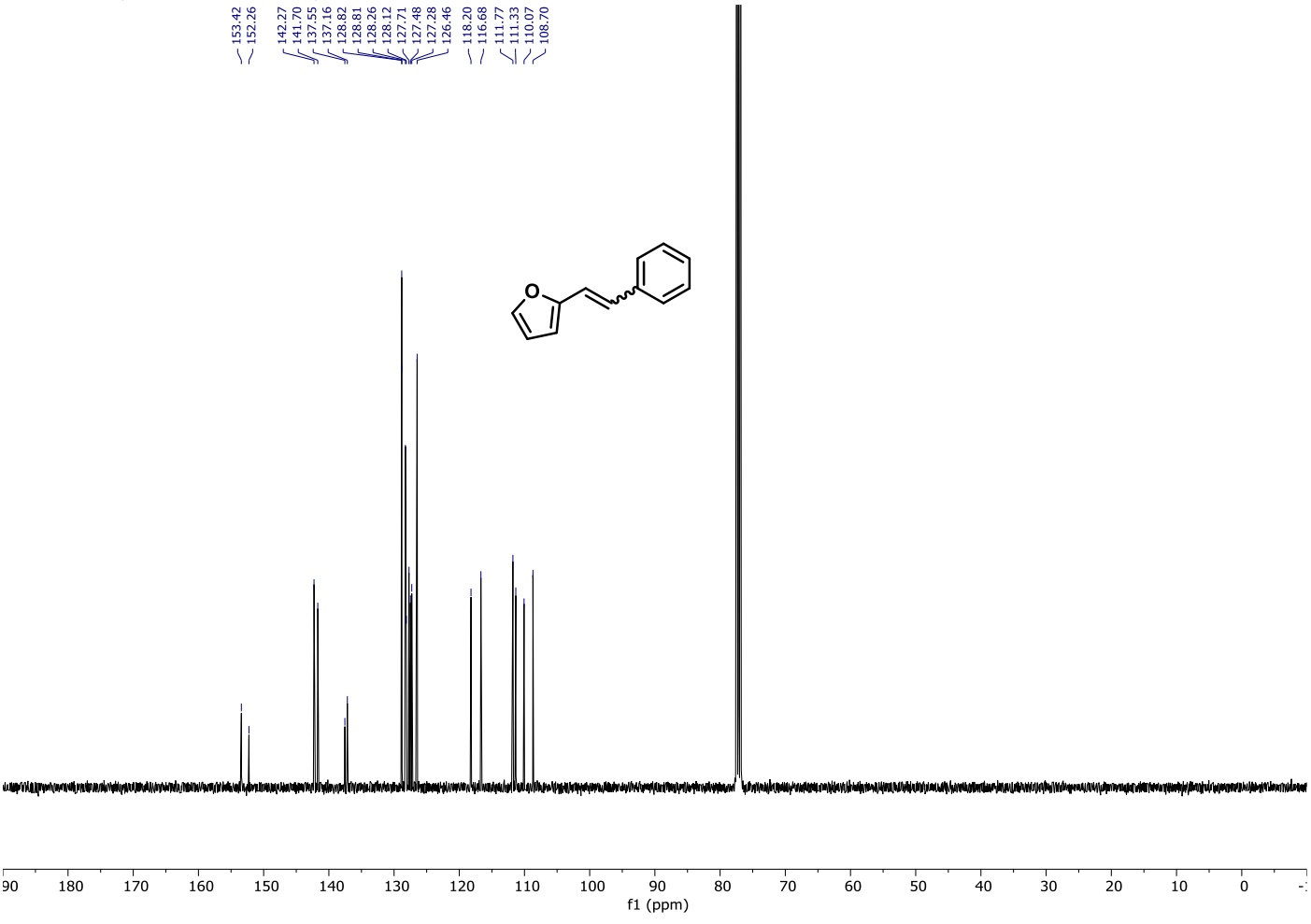

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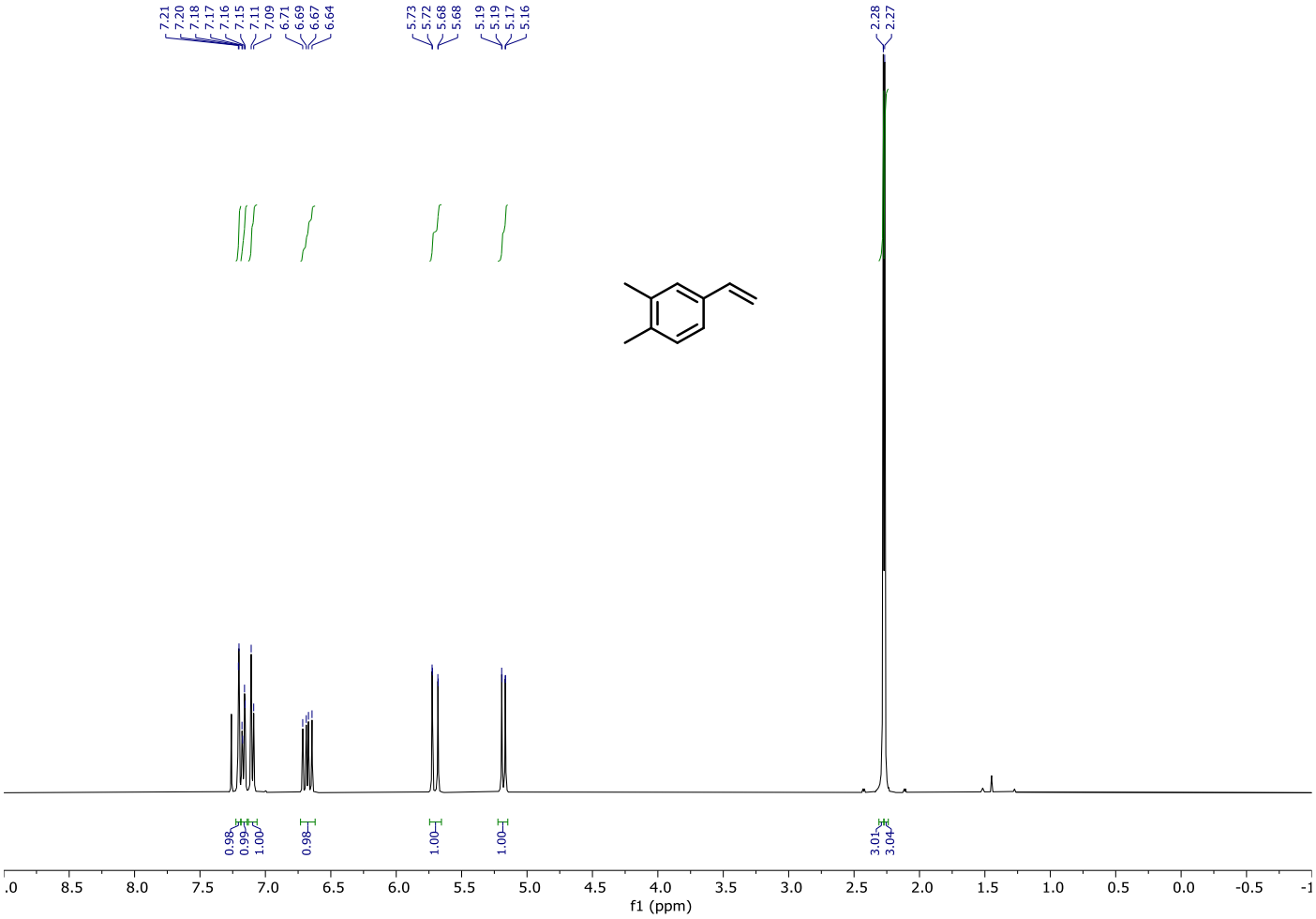

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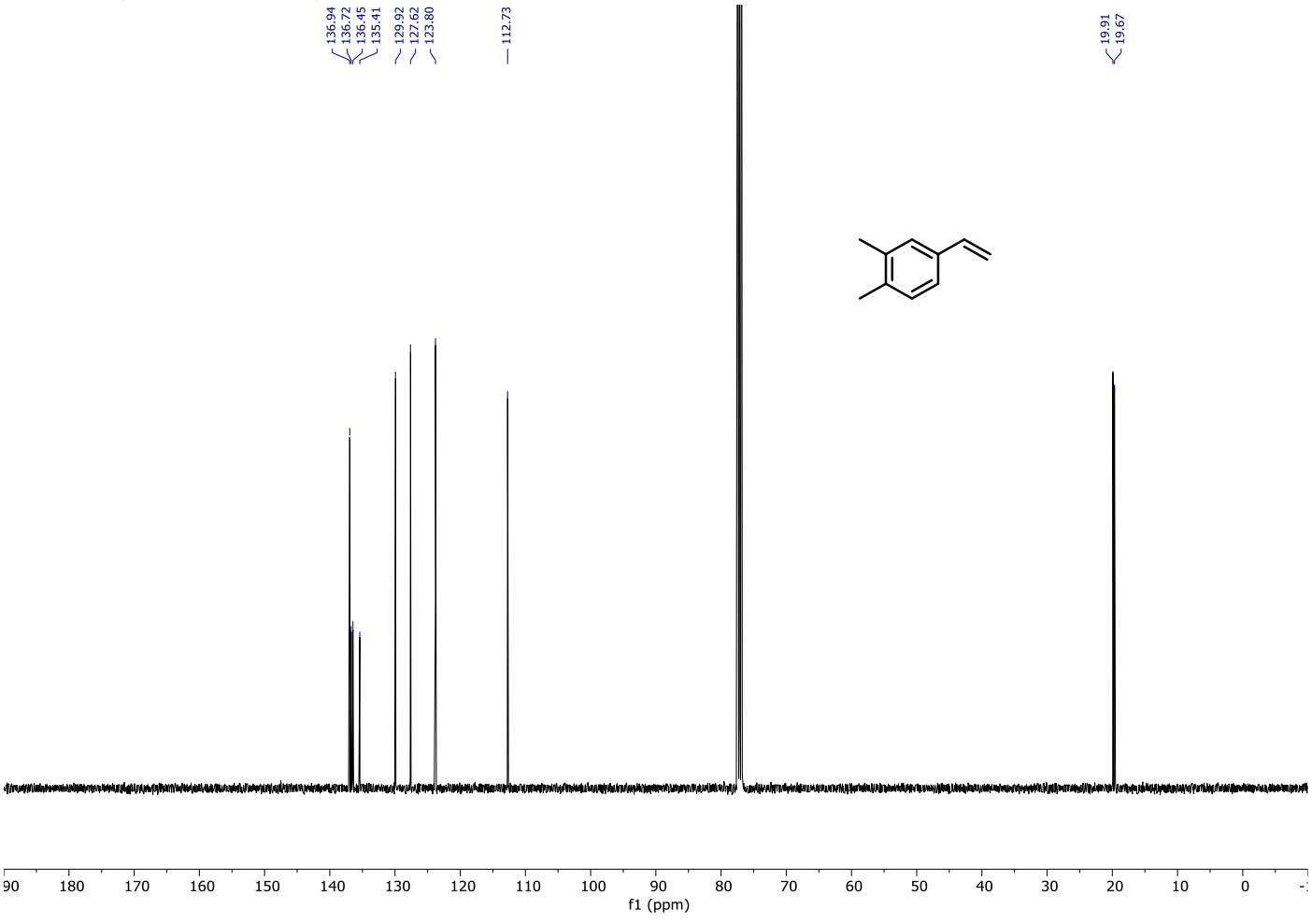
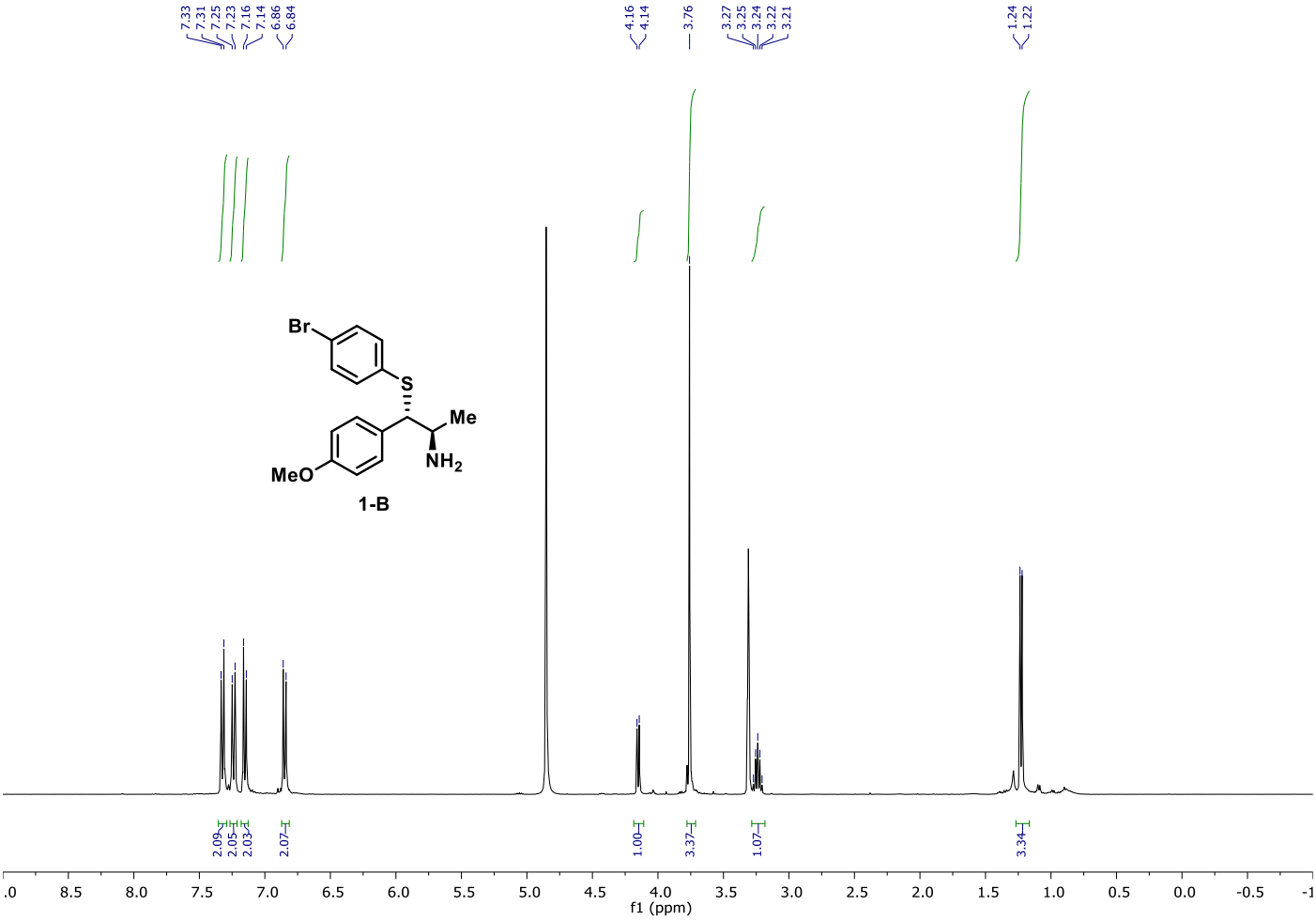
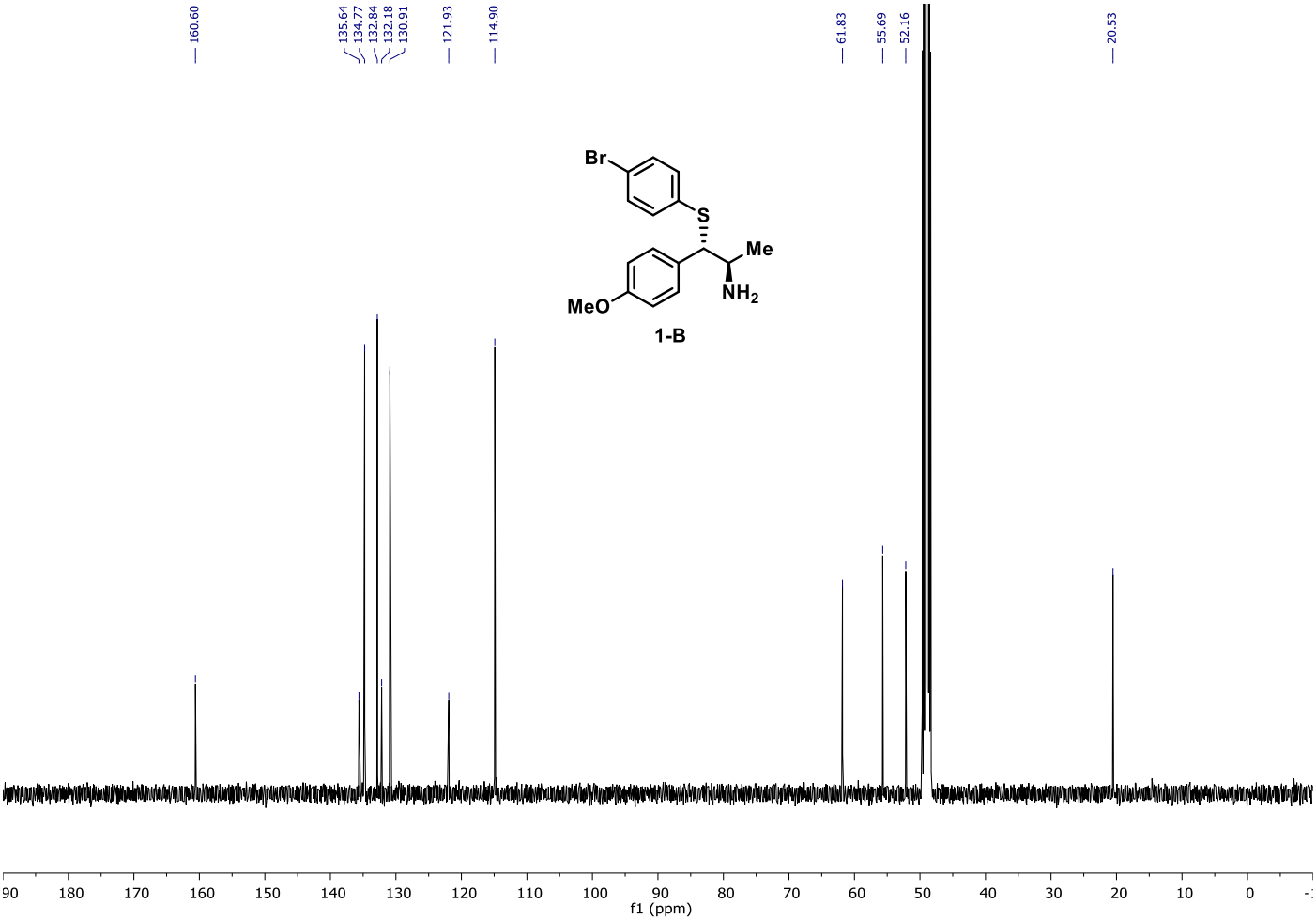


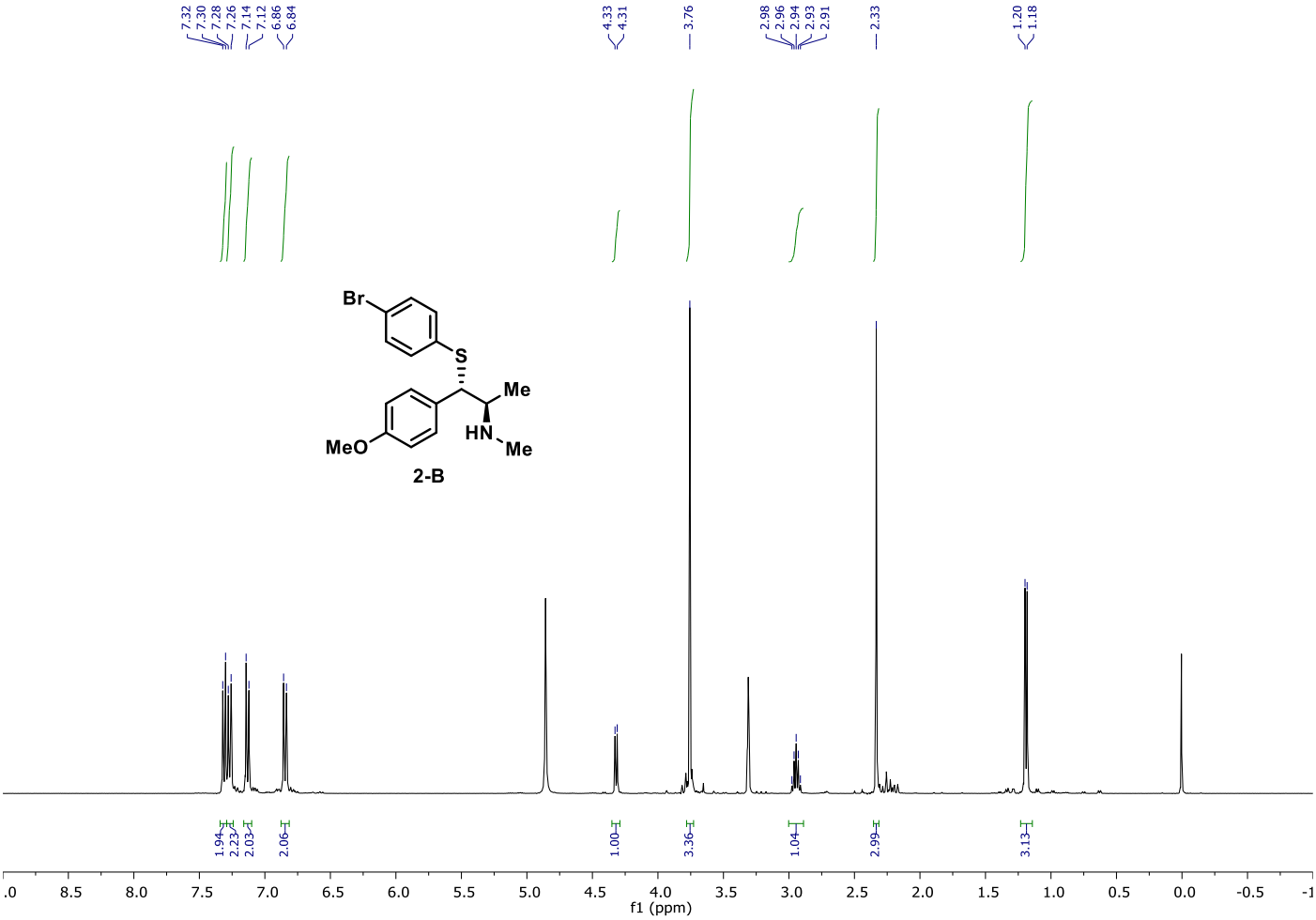
^{1}H NMR (400 MHz, CD_3OD)



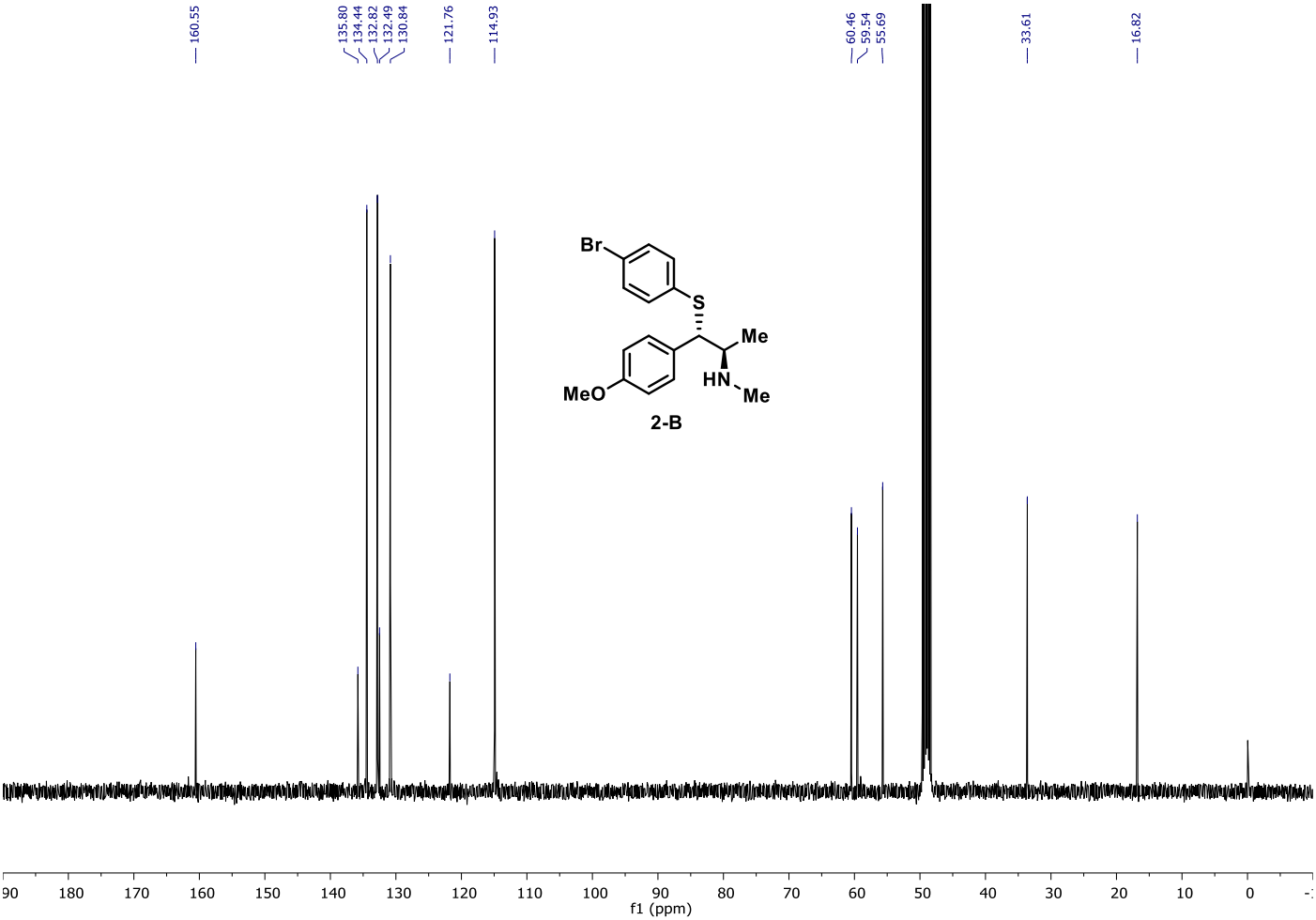
^{13}C NMR (101 MHz, CD_3OD)



^{1}H NMR (400 MHz, CD_3OD)



^{13}C NMR (101 MHz, CD_3OD)



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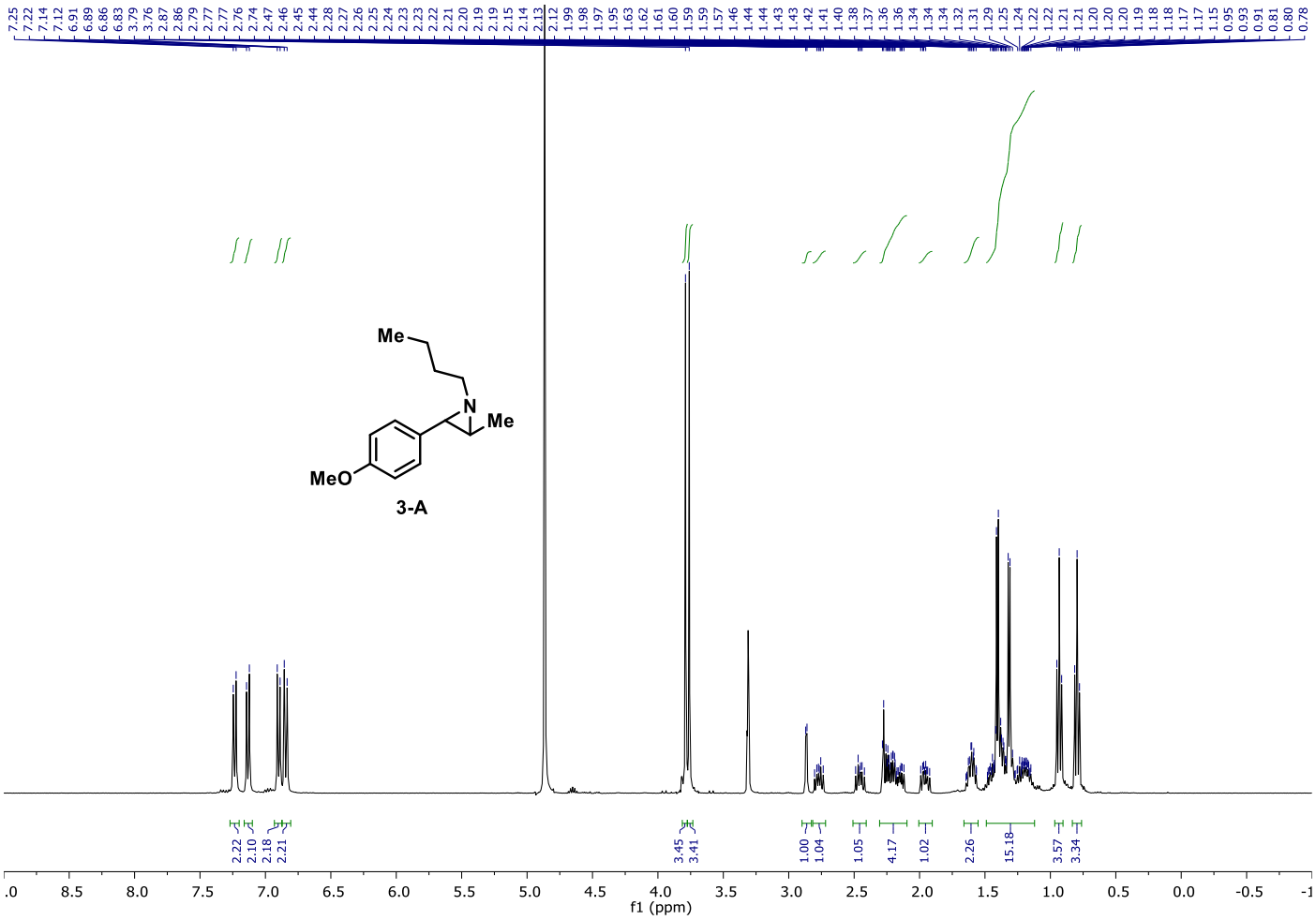
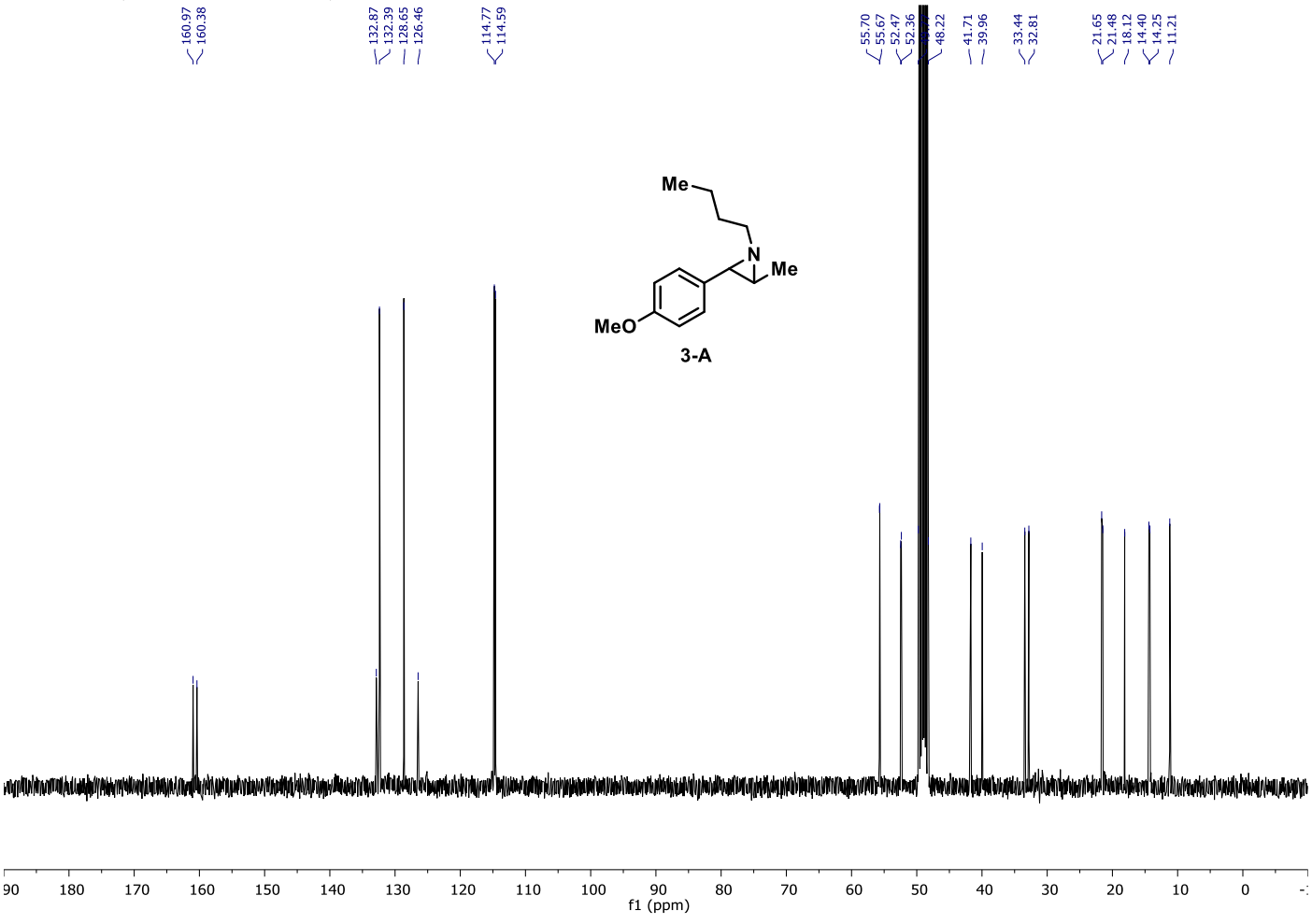


^{13}C NMR (101 MHz, CD_3OD)



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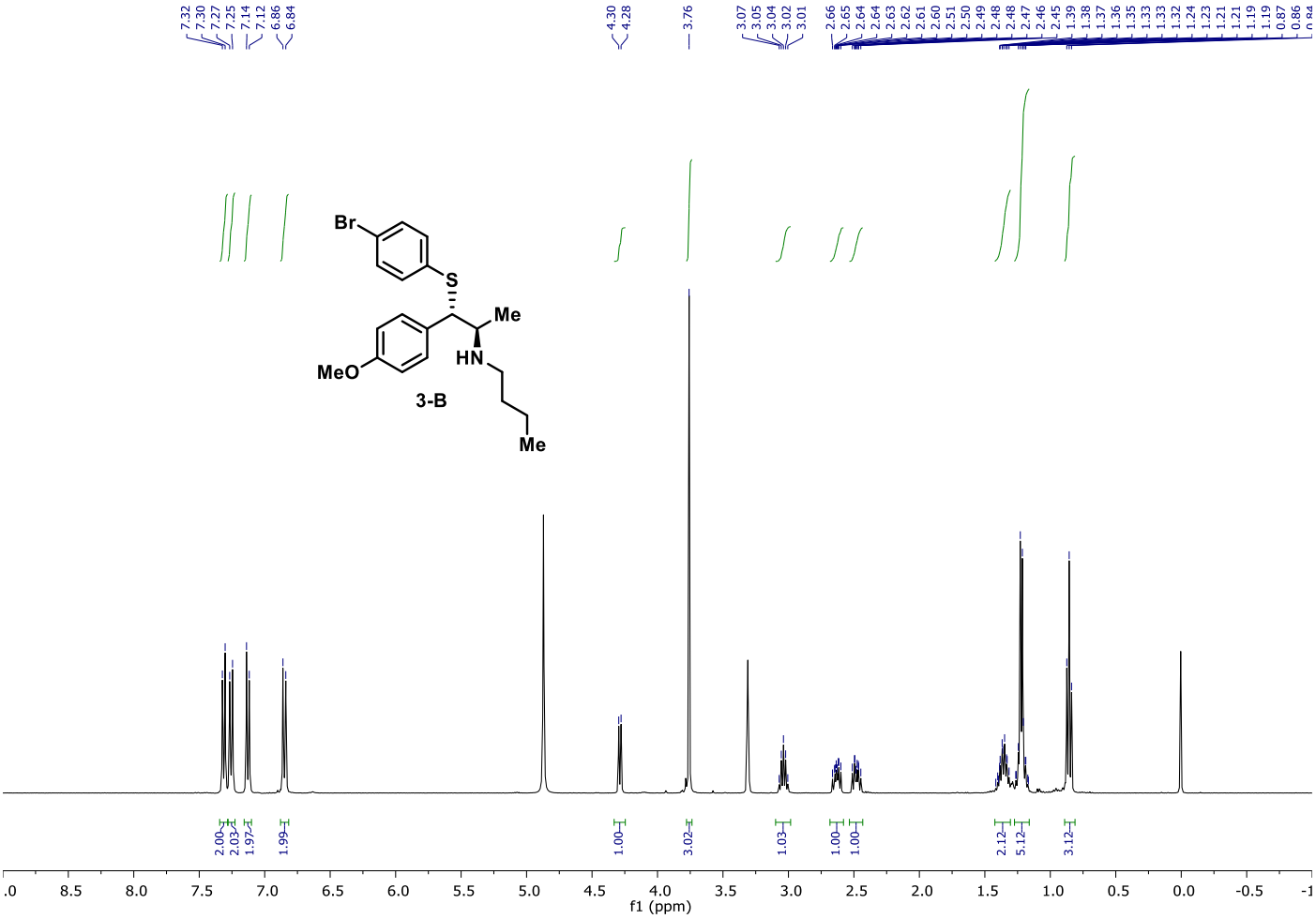
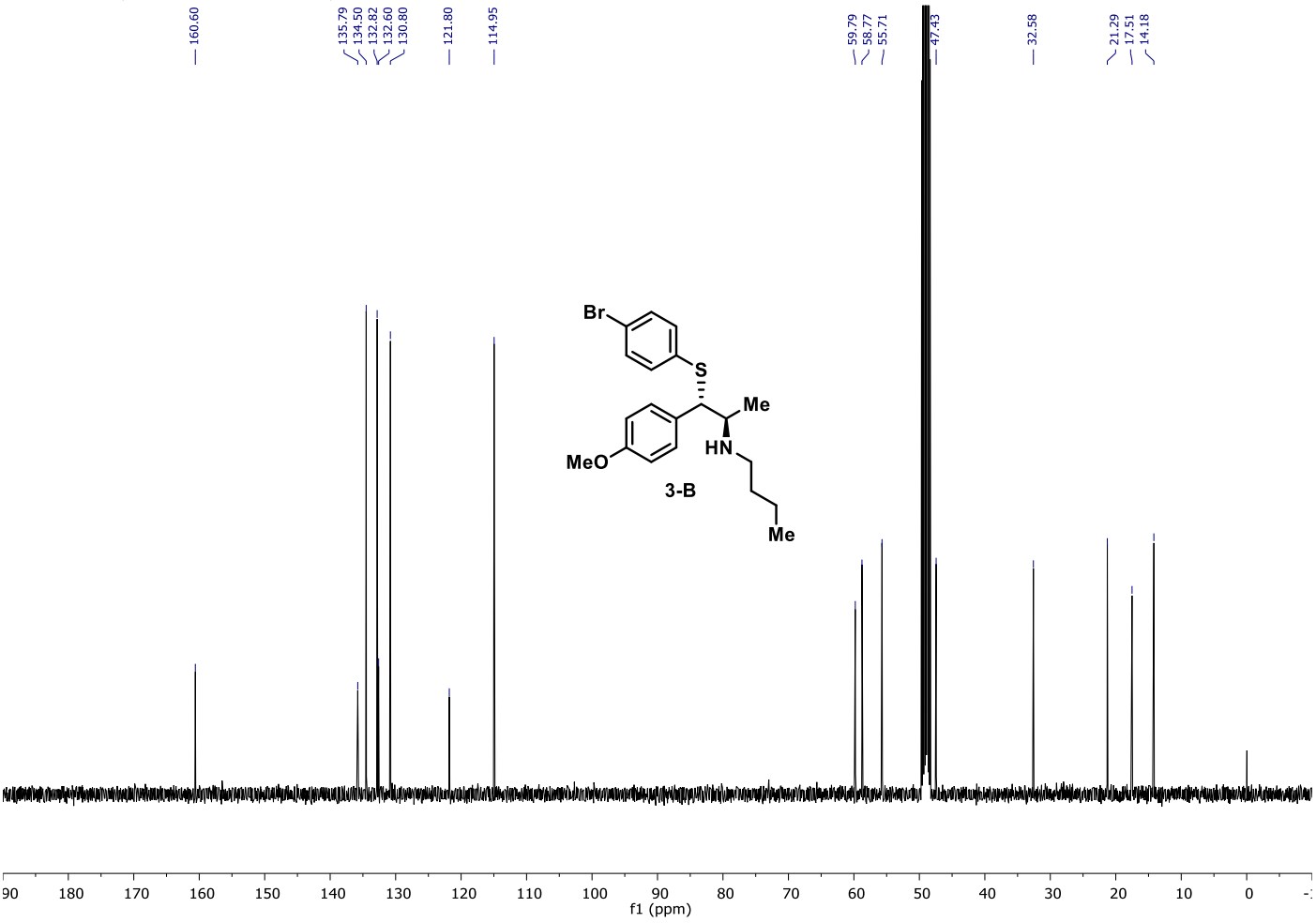


^{13}C NMR (101 MHz, CD_3OD)



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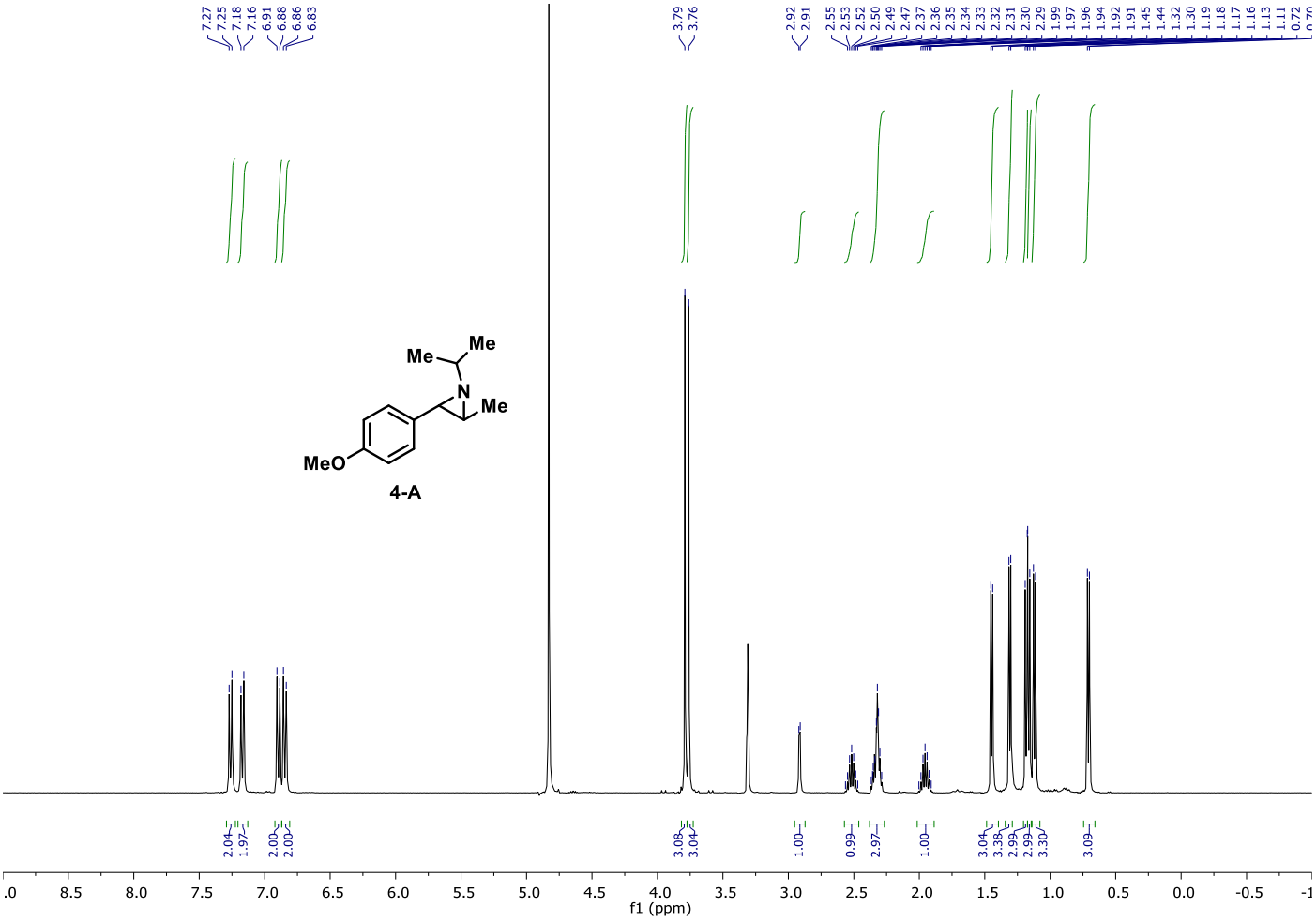
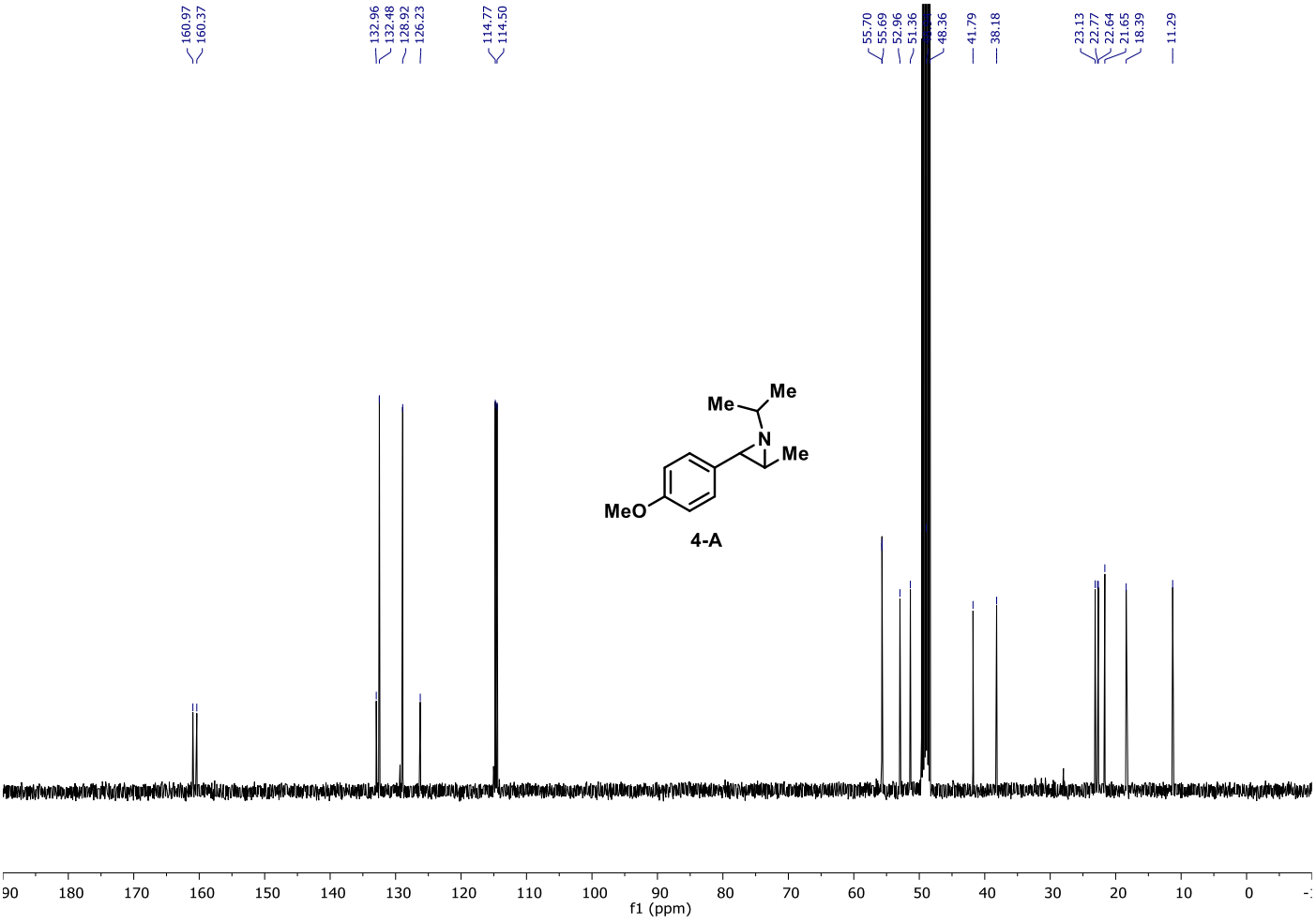
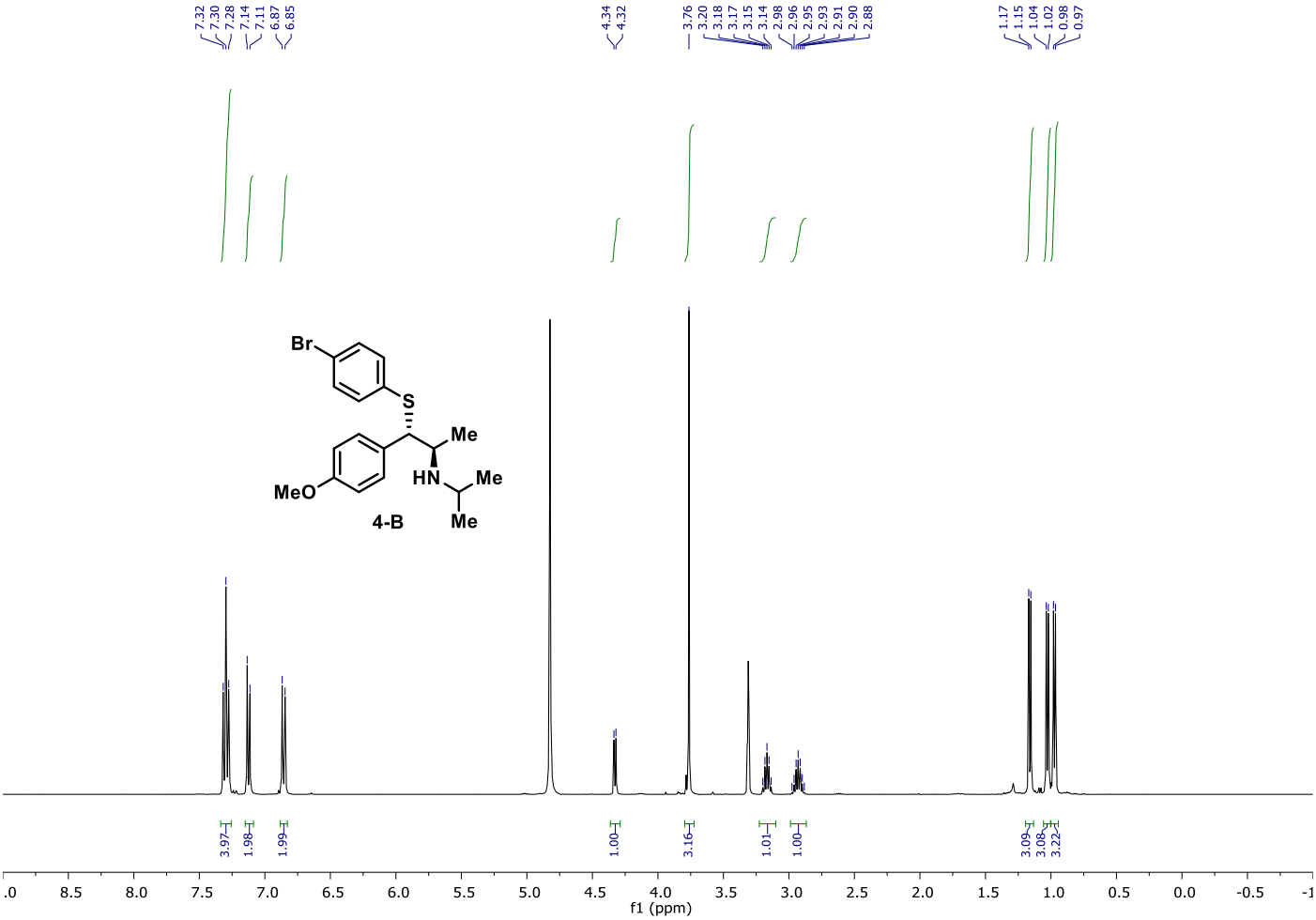


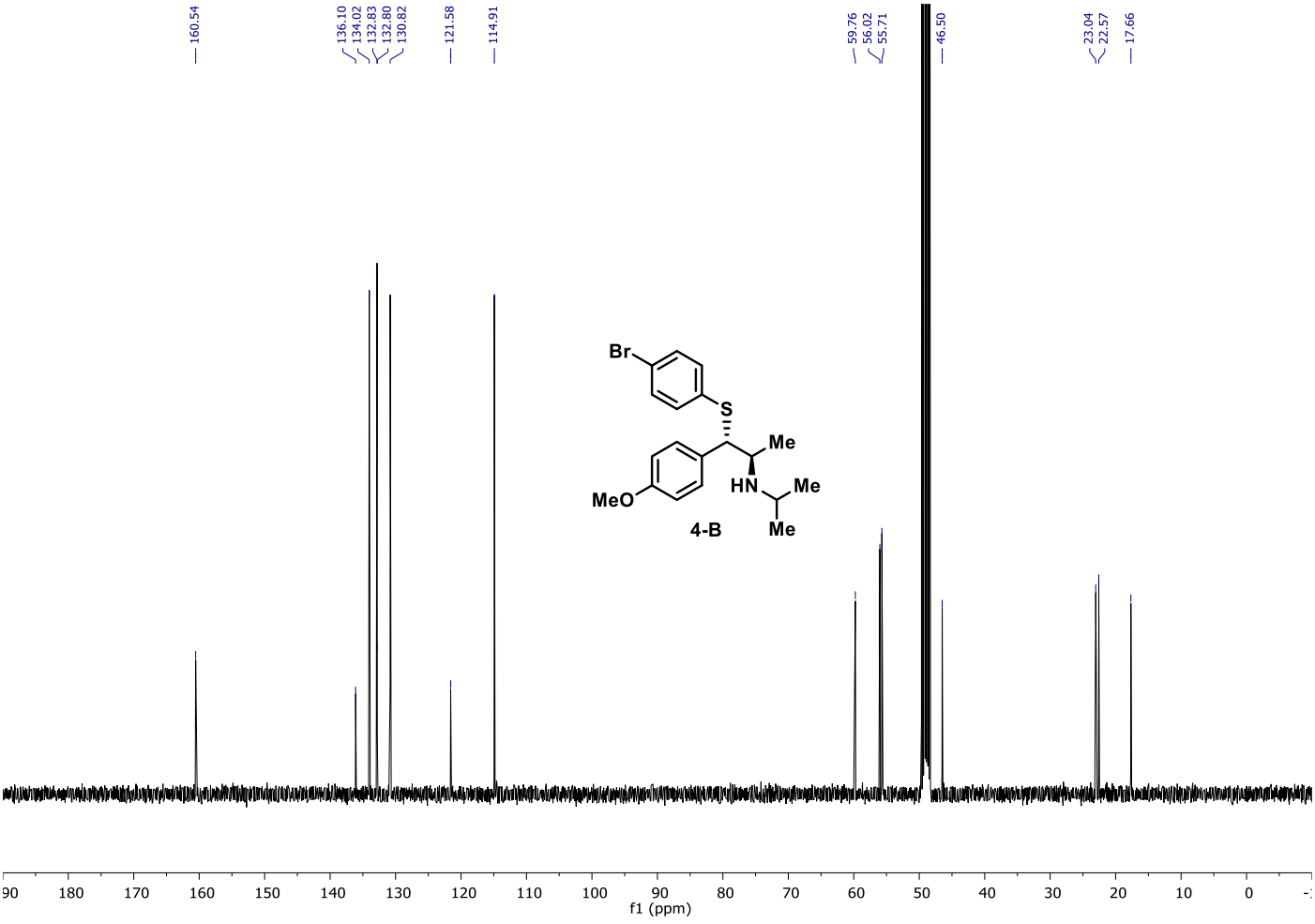
^{13}C NMR (101 MHz, CD_3OD)



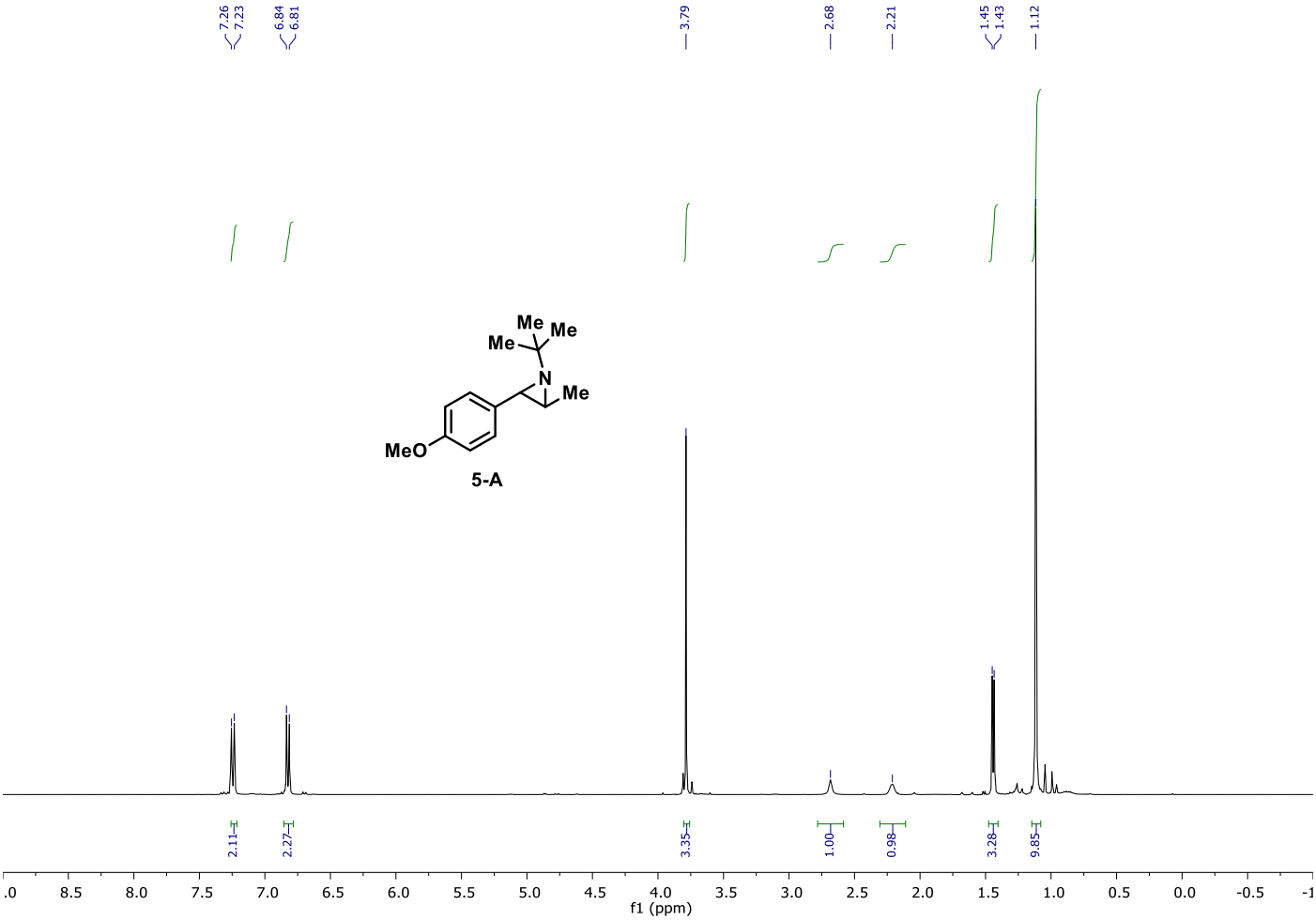
^{1}H NMR (400 MHz, CD_3OD)



^{13}C NMR (101 MHz, CD_3OD)



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



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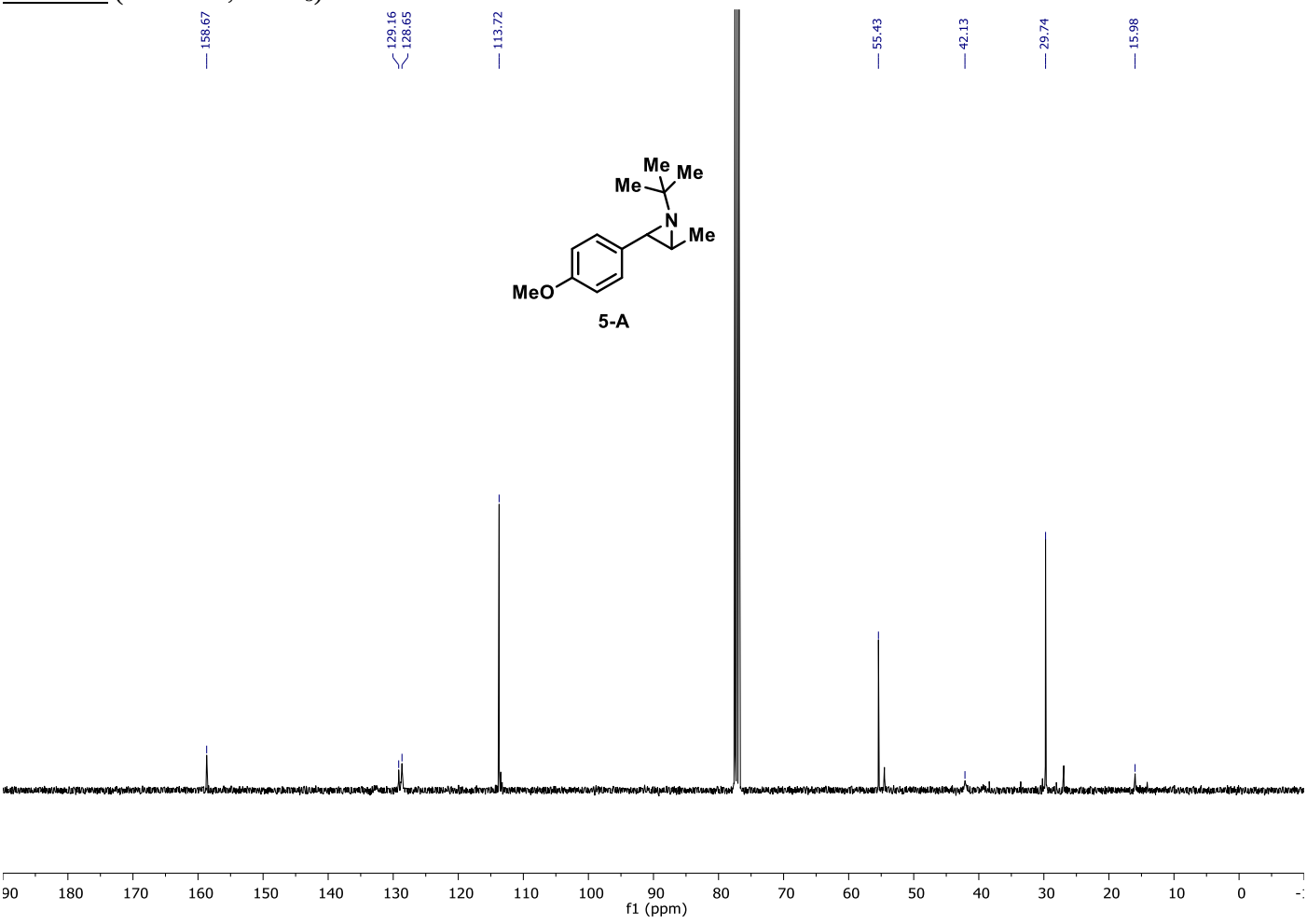
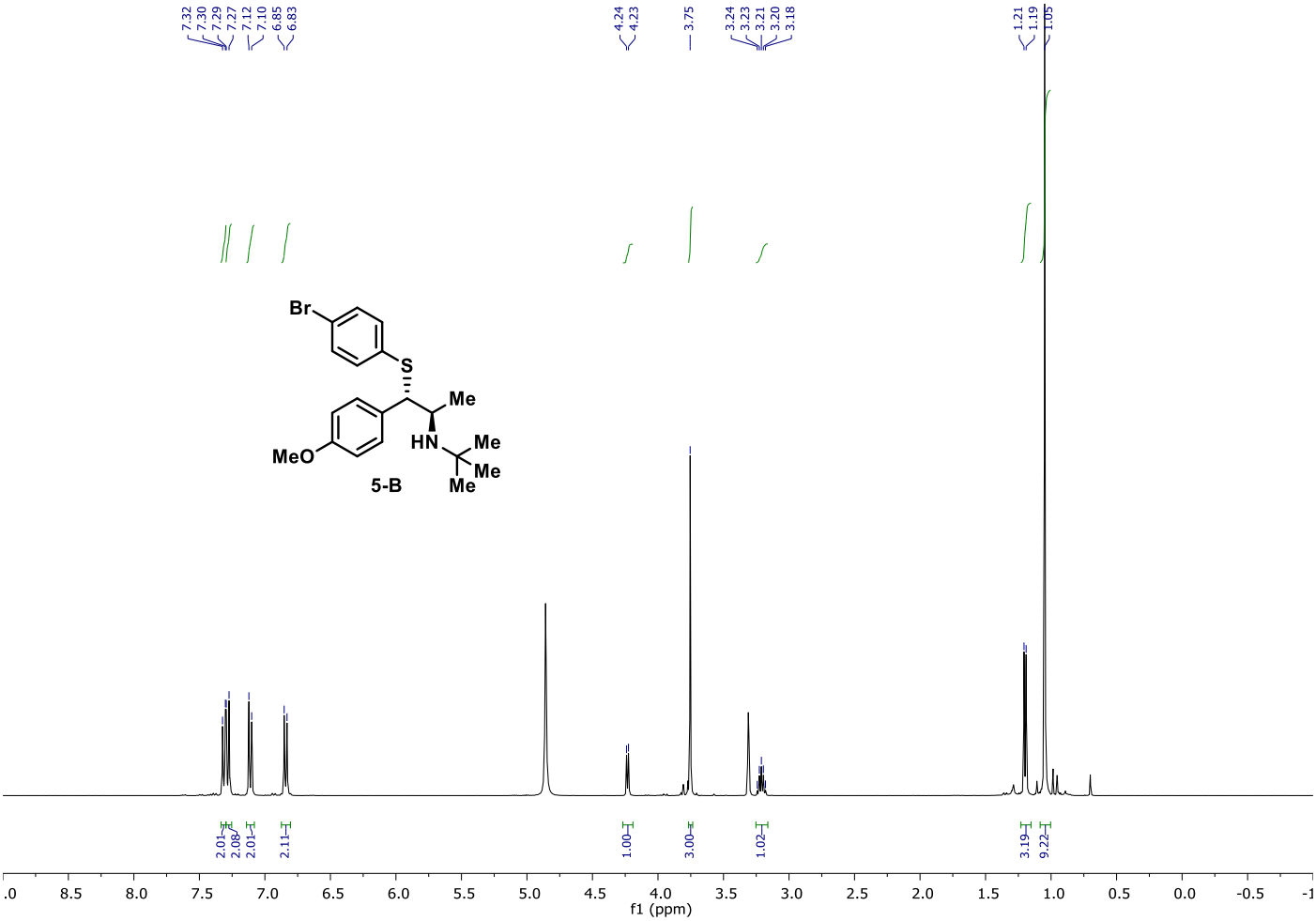
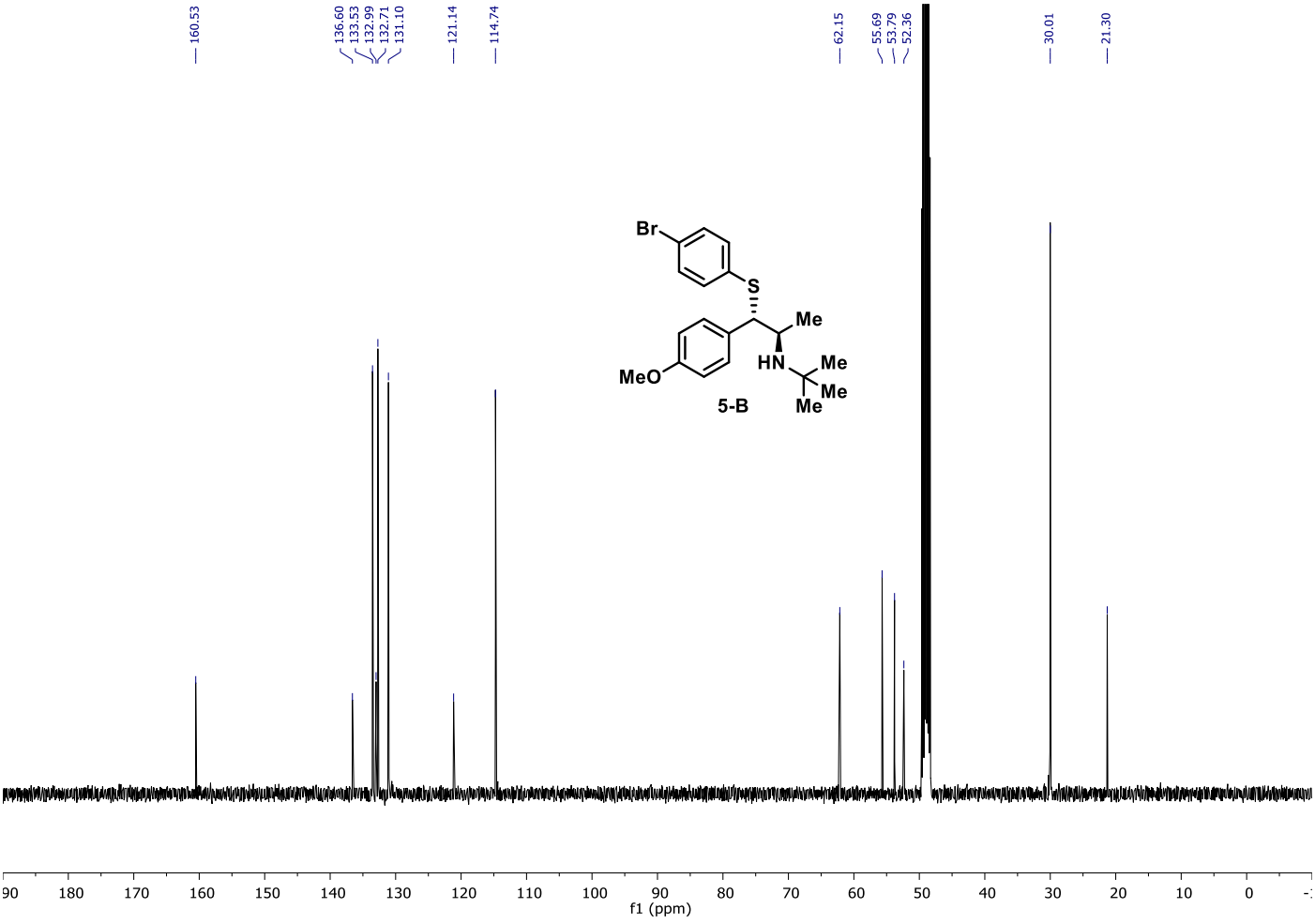


^{1}H NMR (400 MHz, CD_3OD)



^{13}C NMR (101 MHz, CD_3OD)



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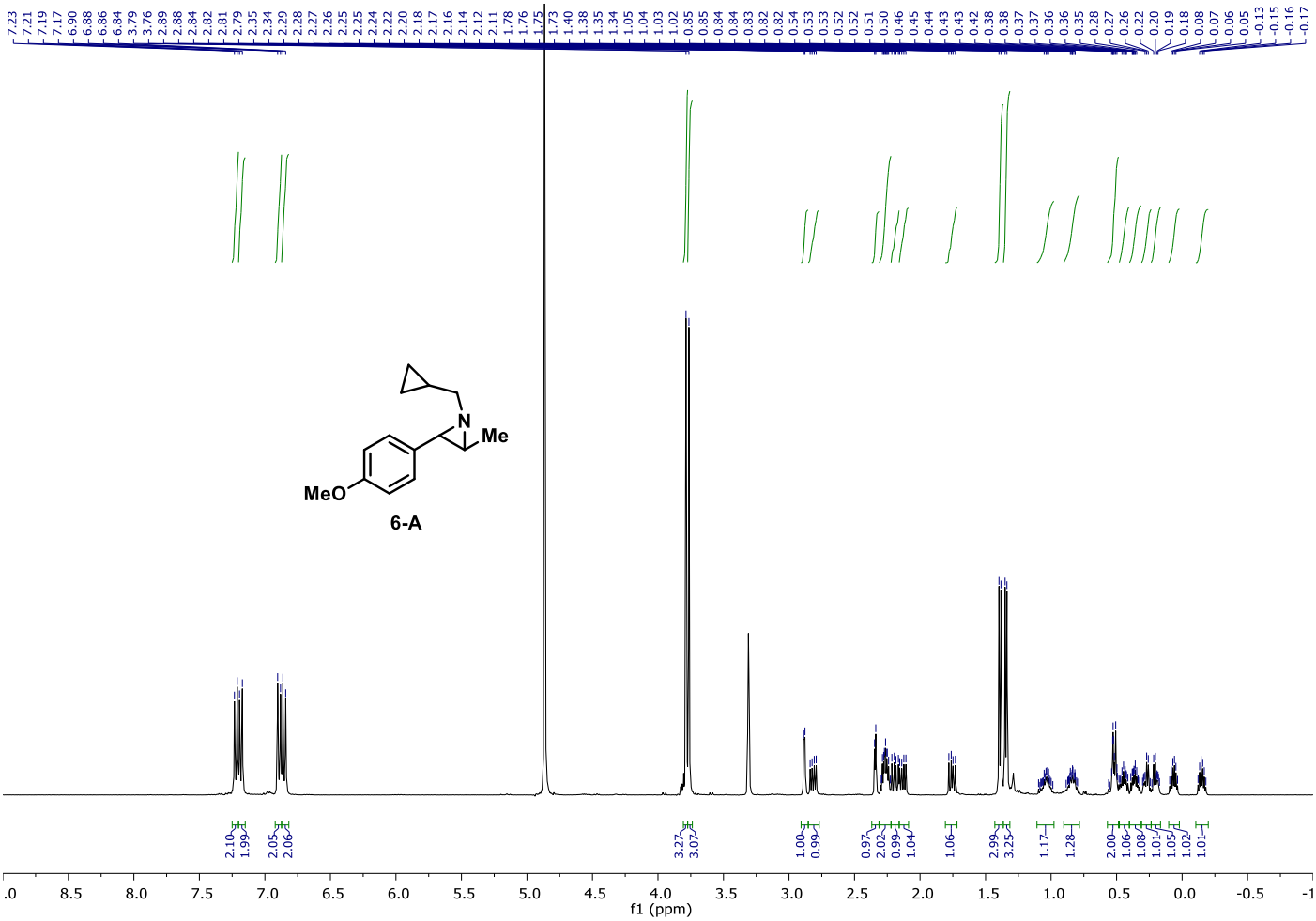

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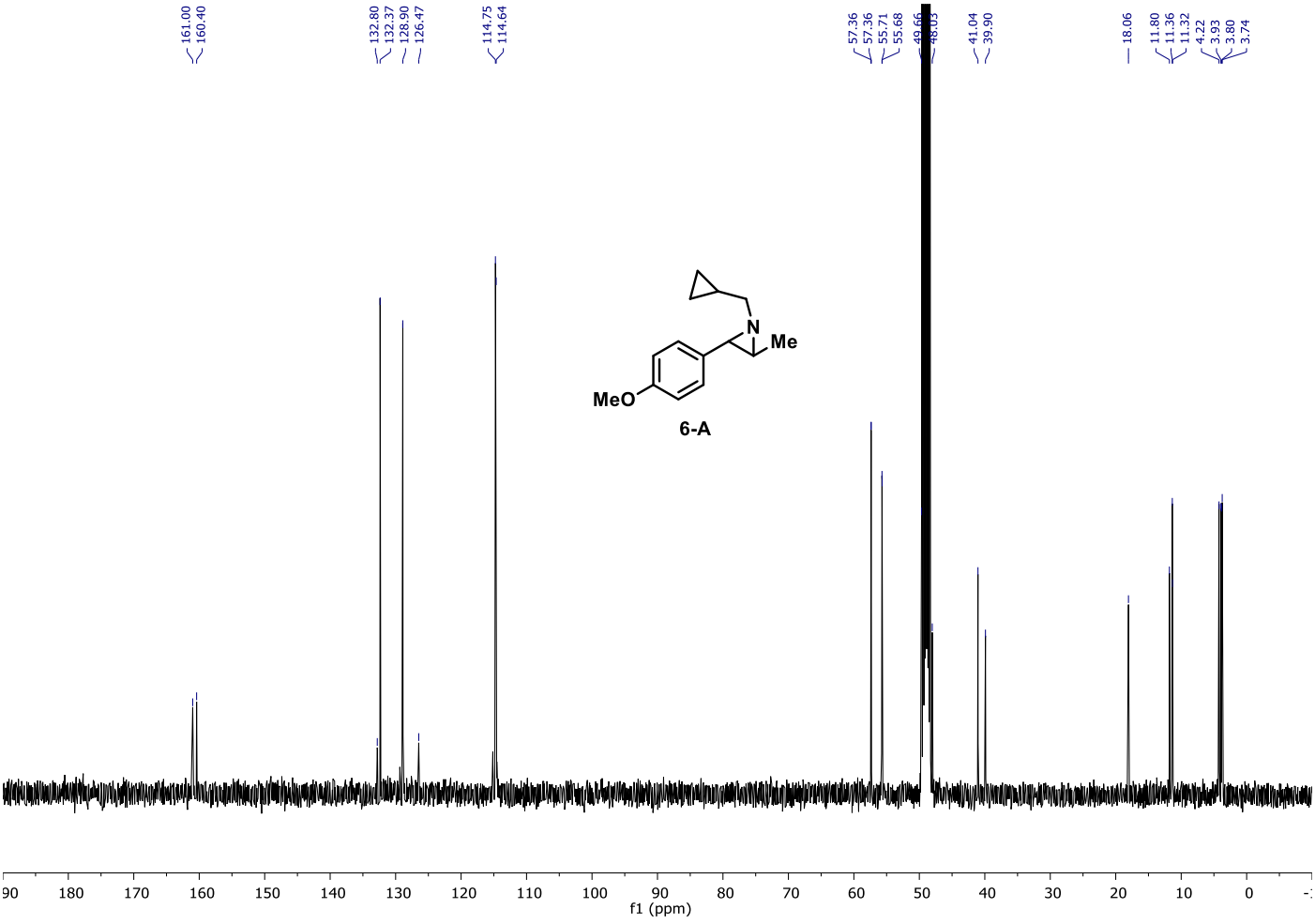

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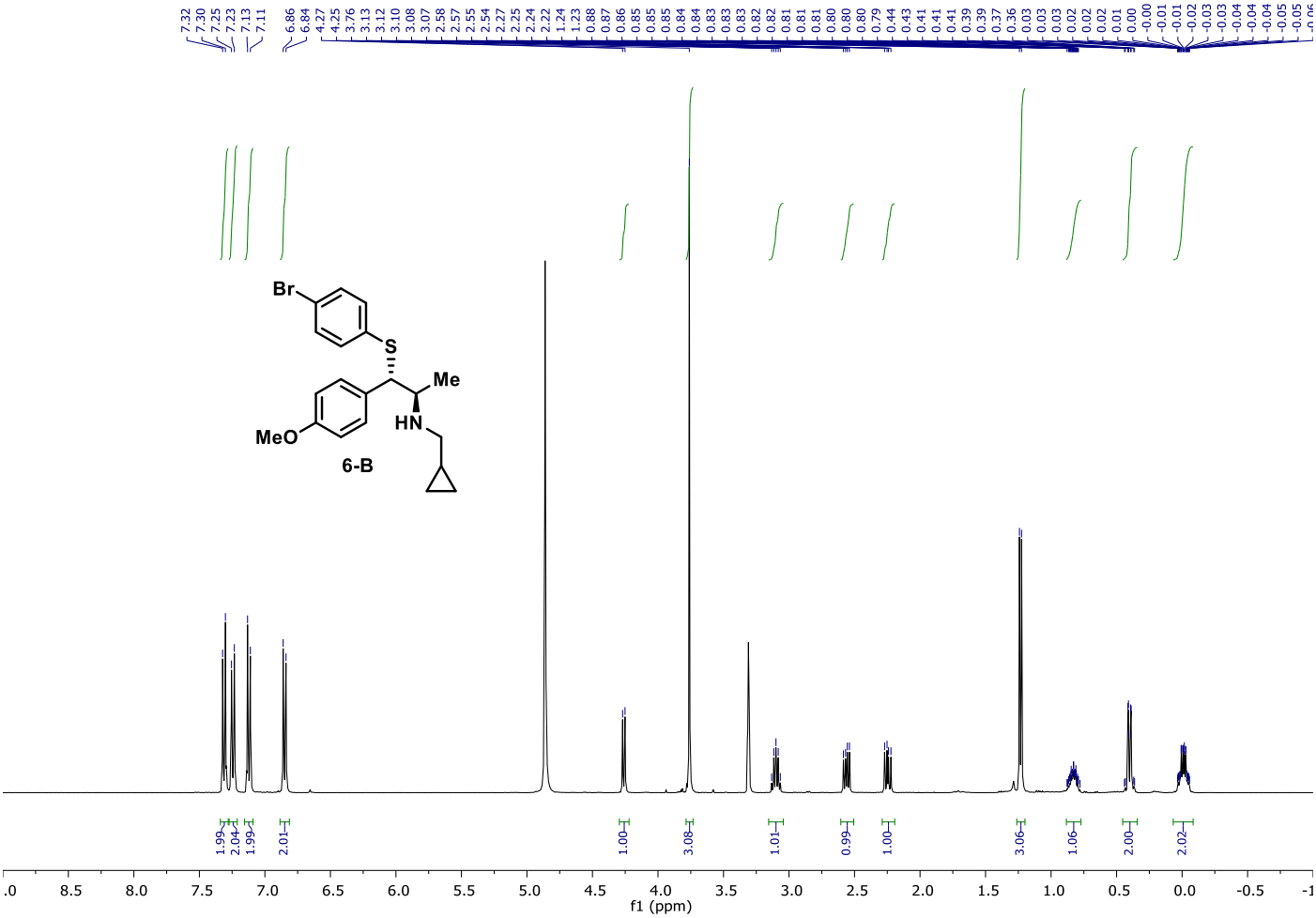

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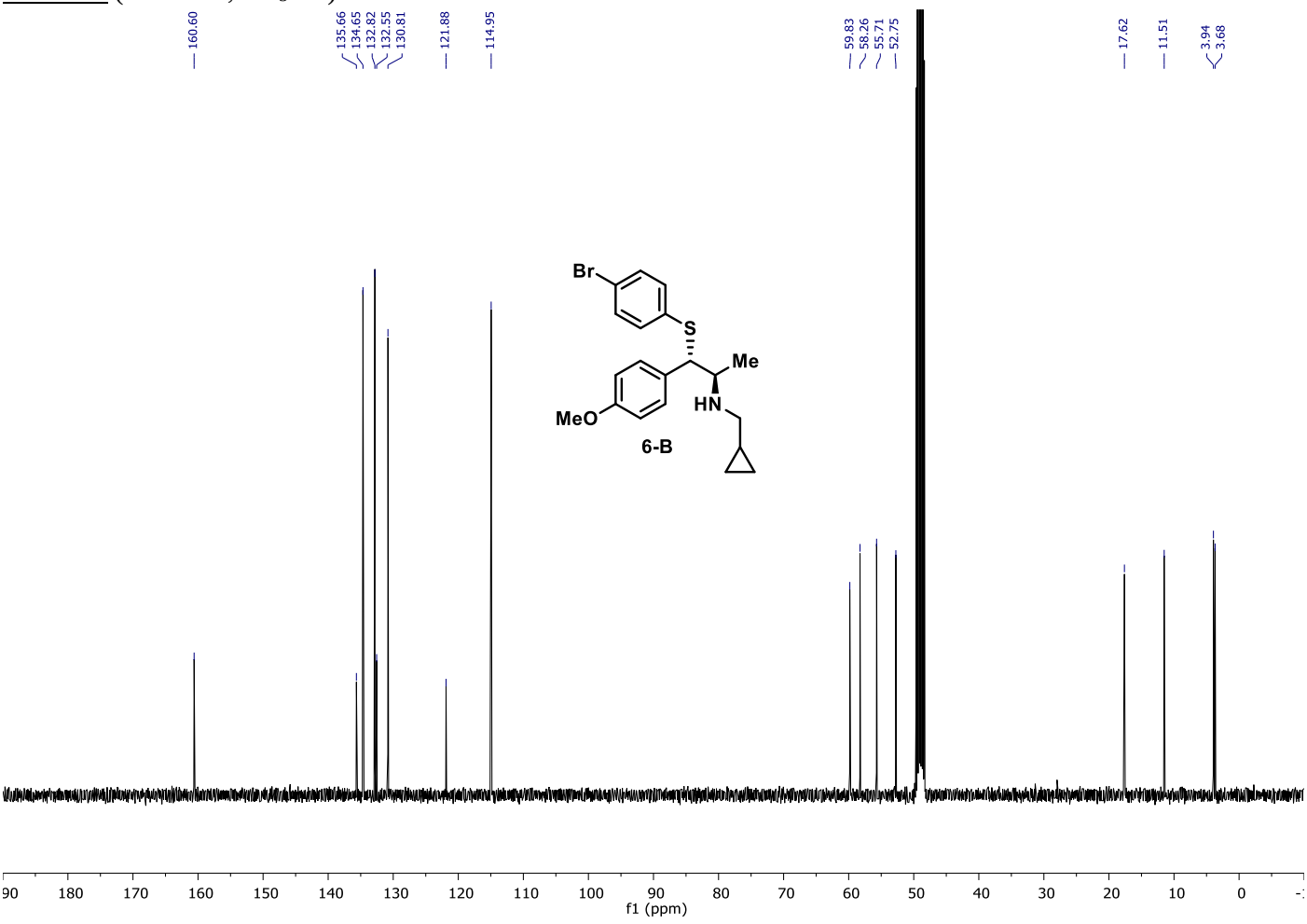

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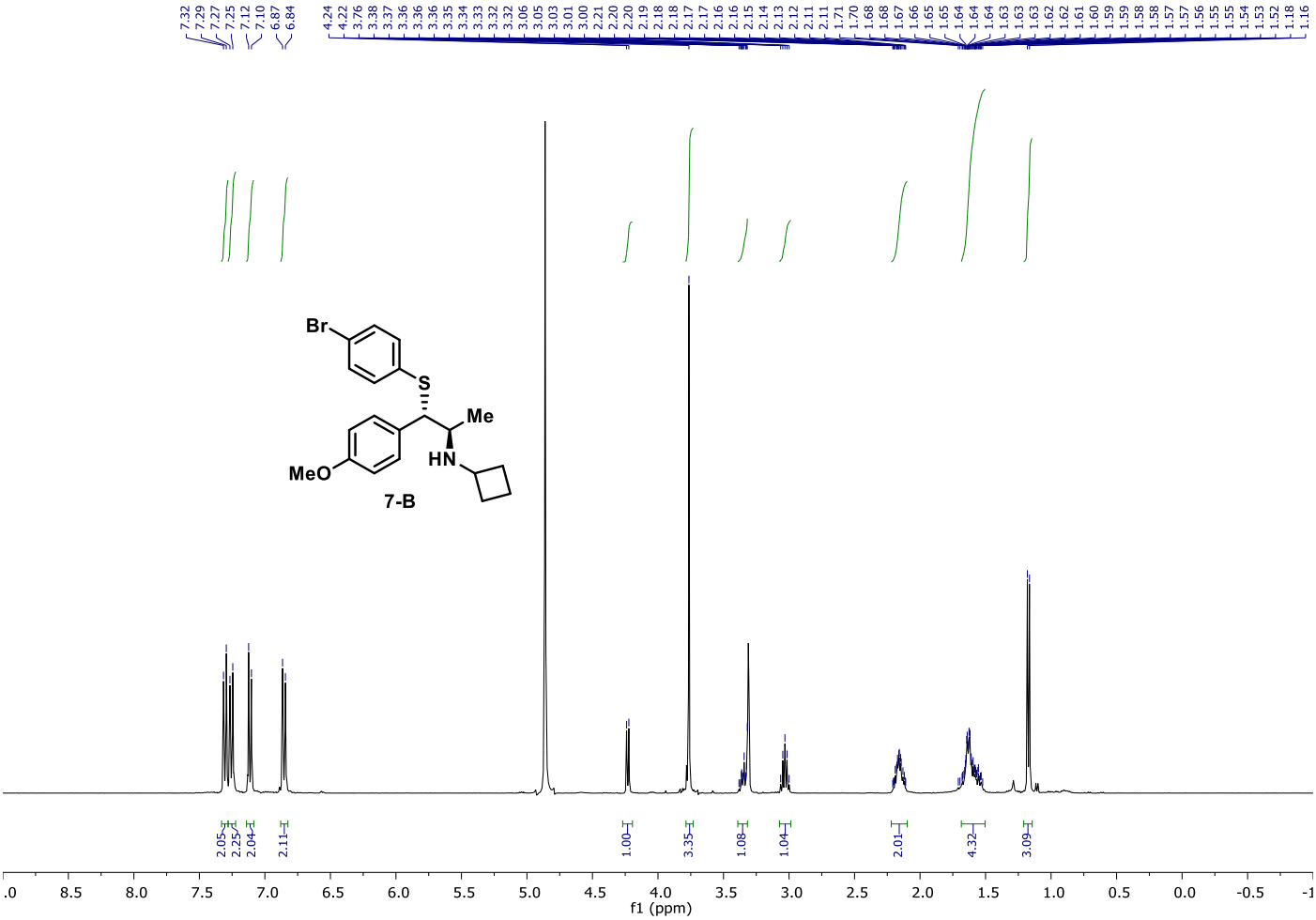

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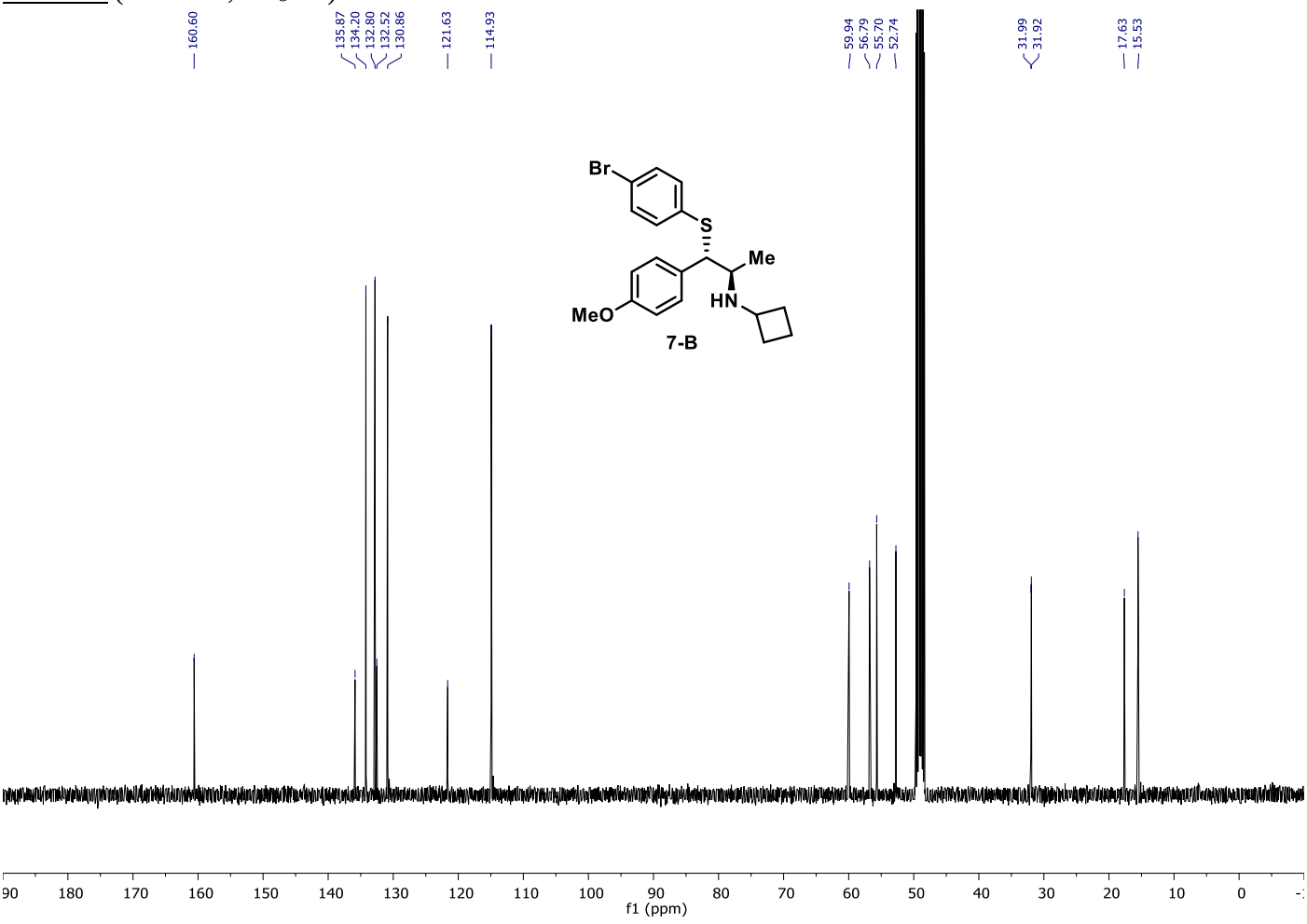

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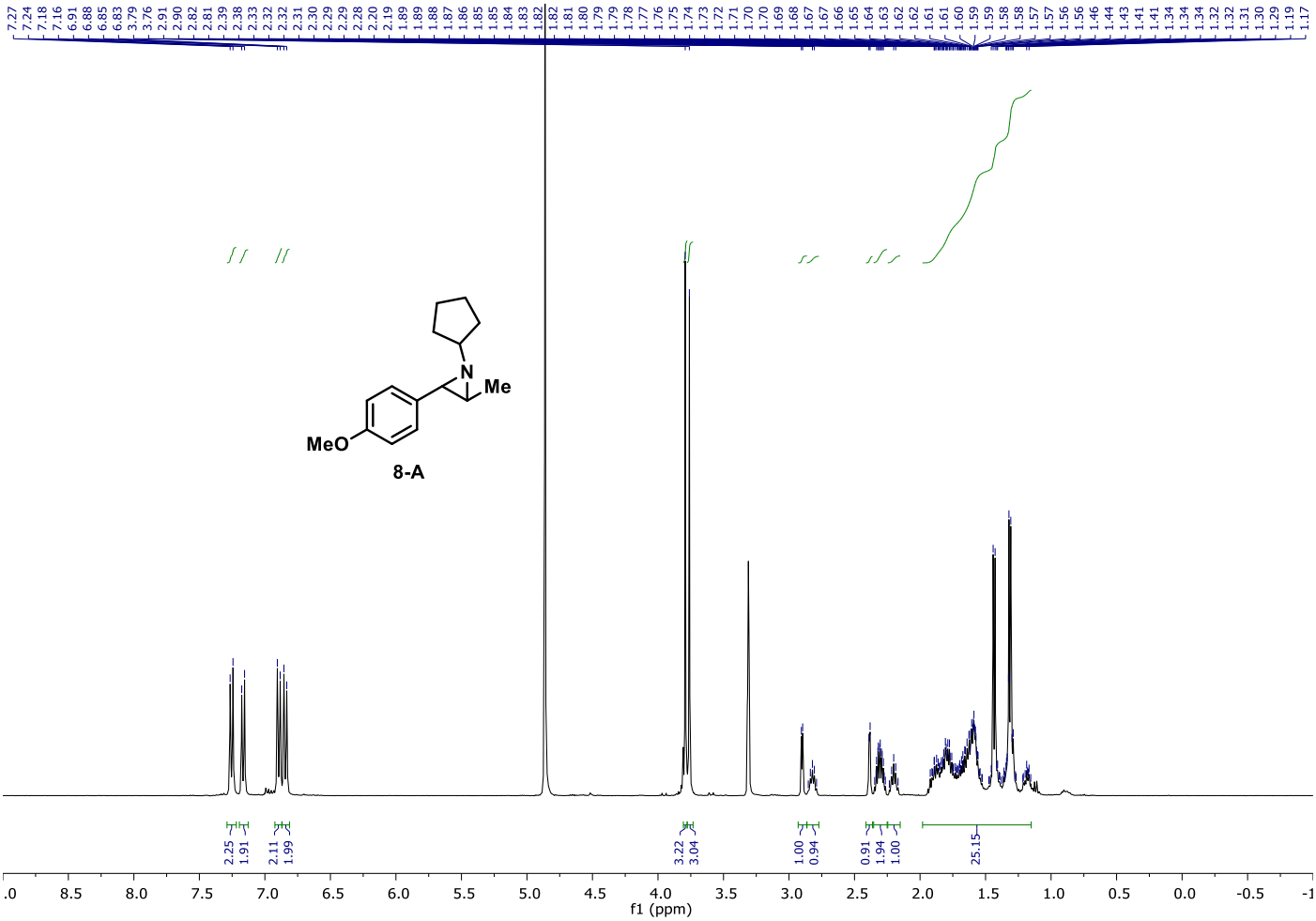

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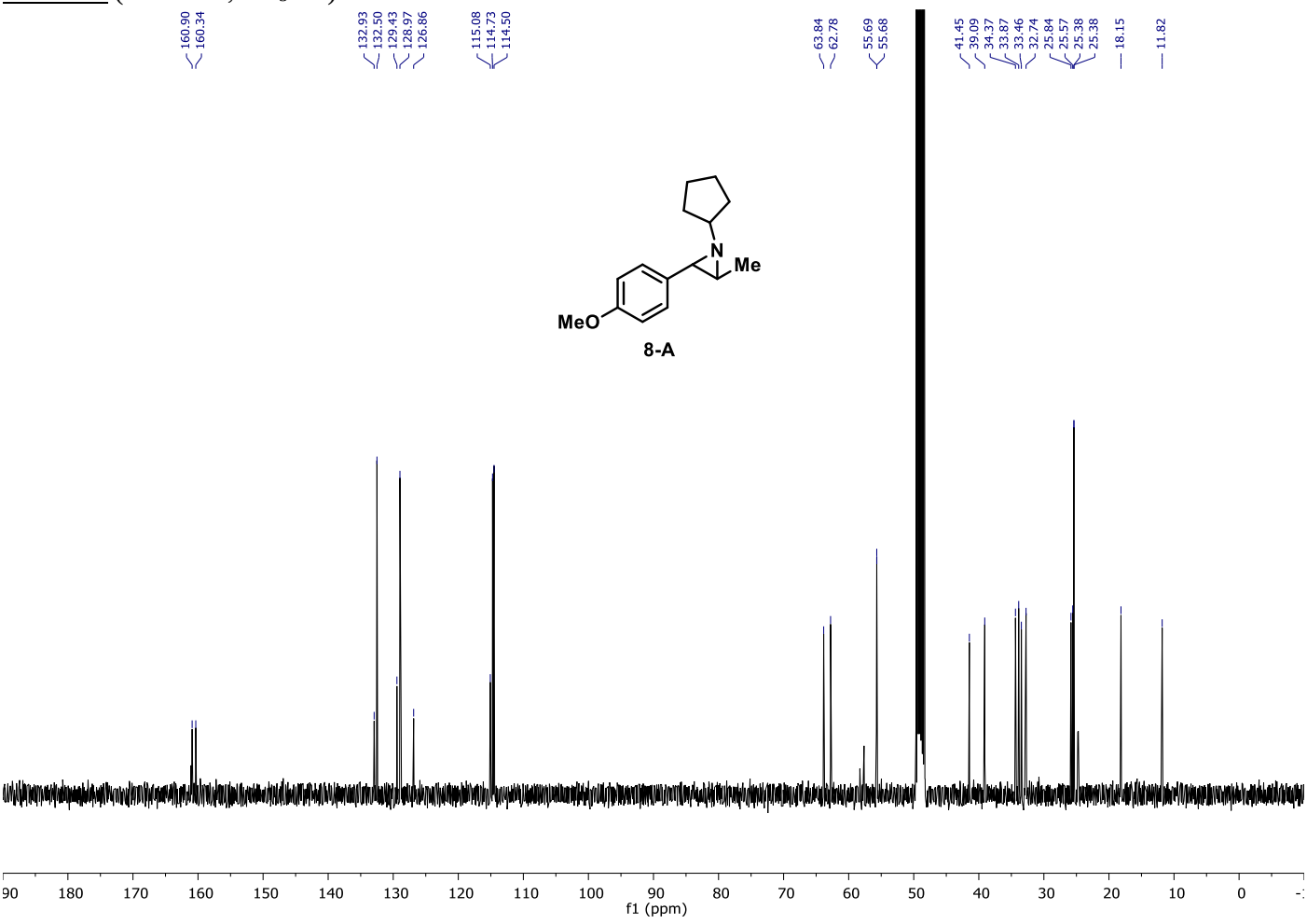

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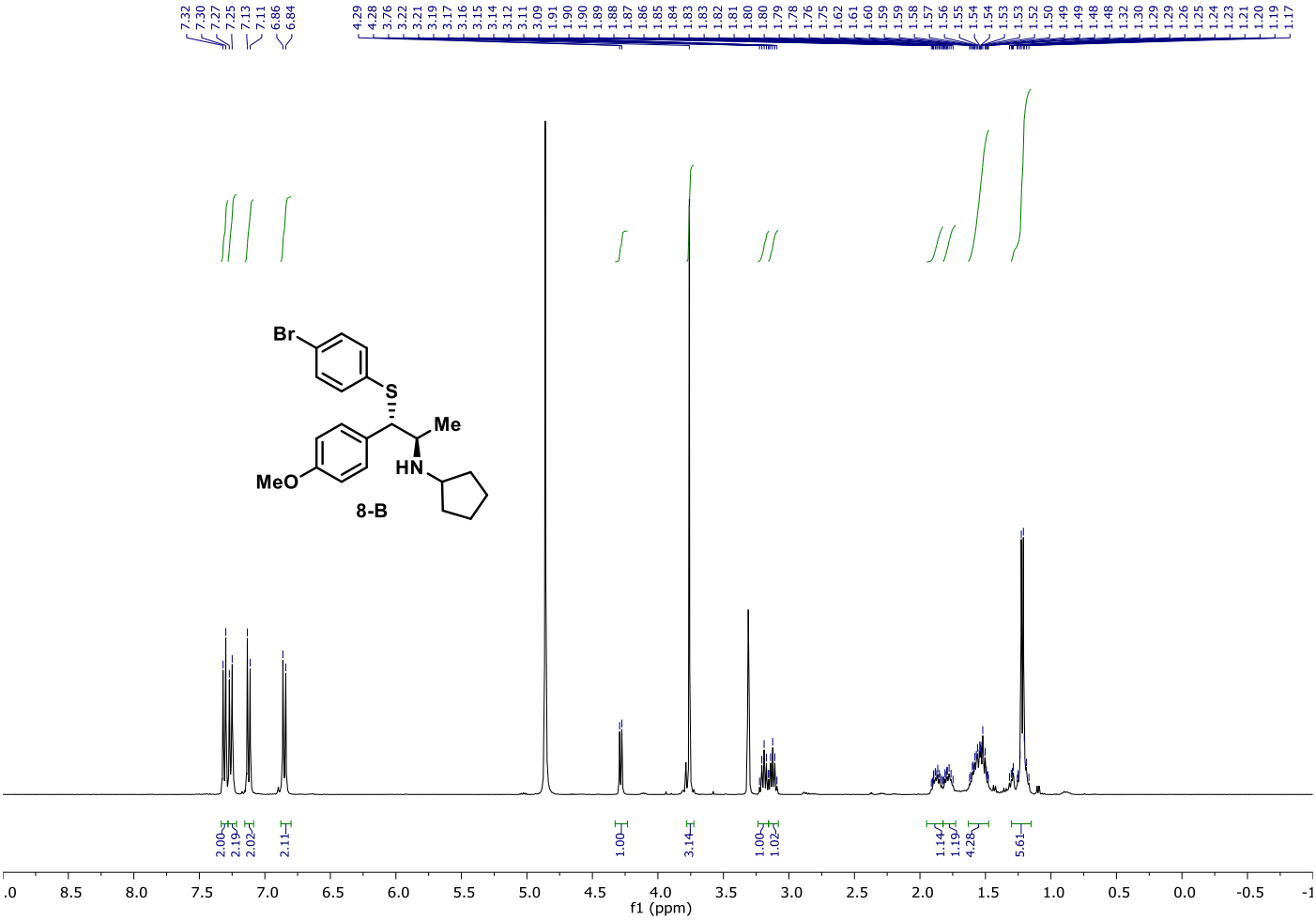

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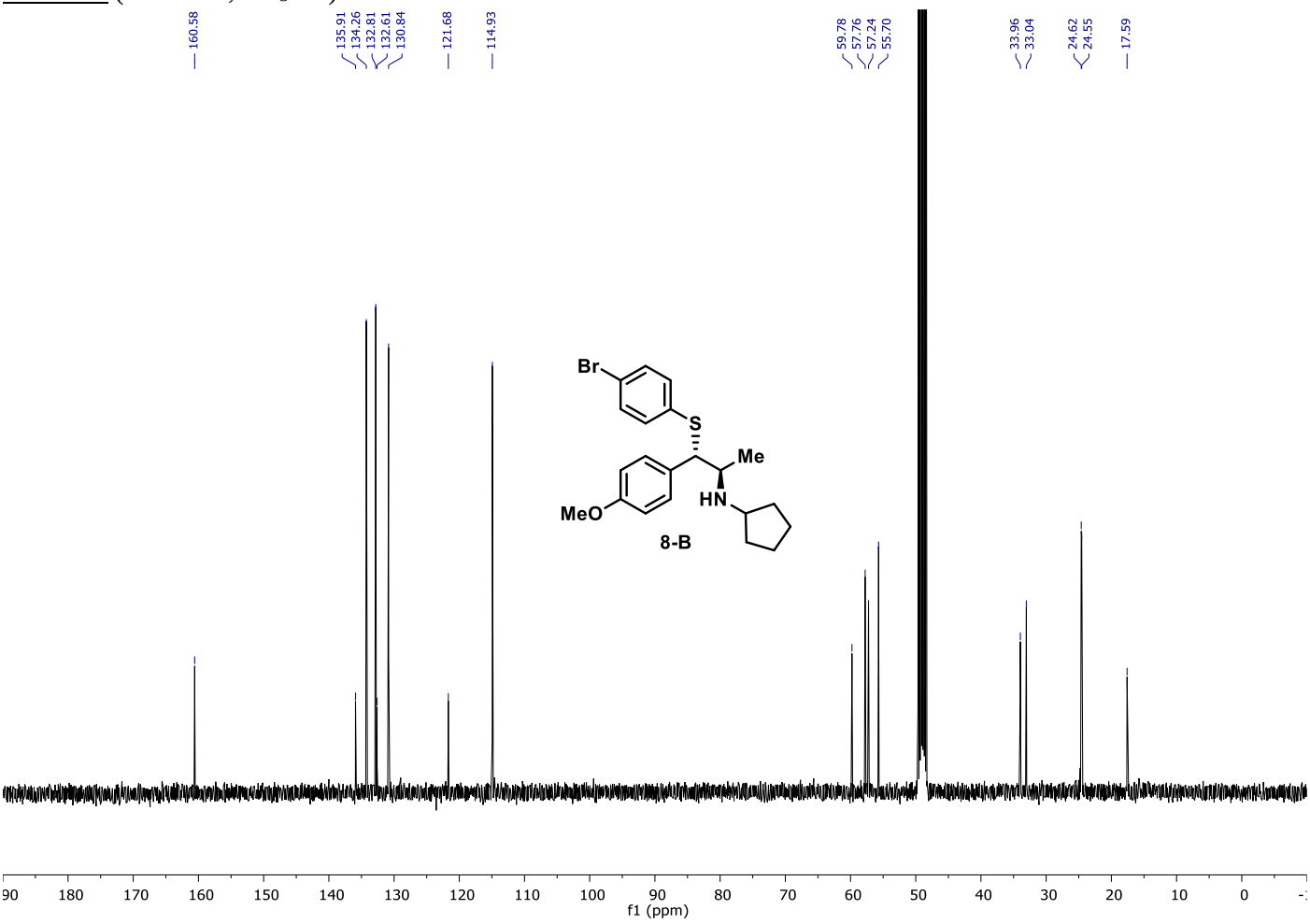
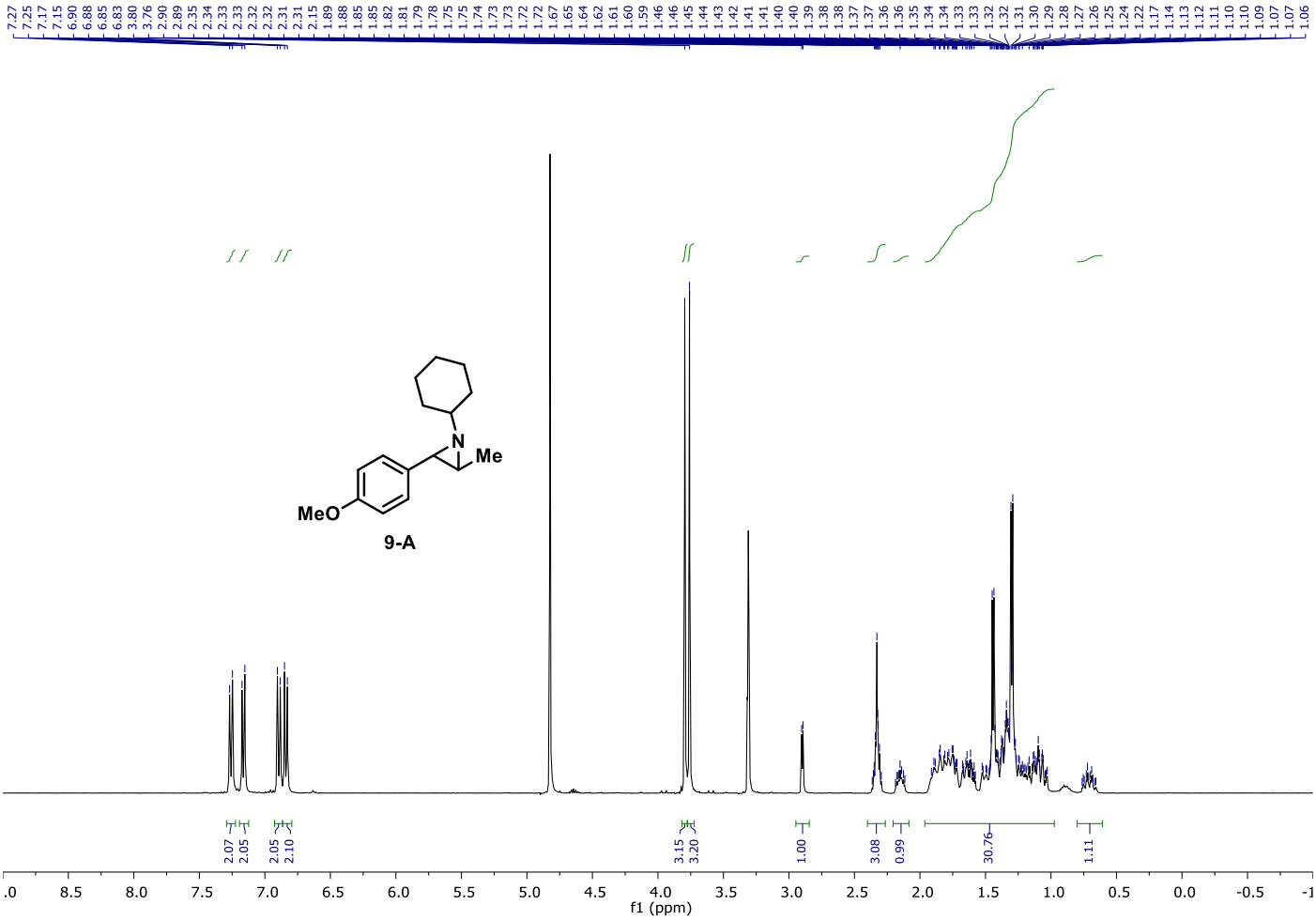


^{1}H NMR (400 MHz, CD_3OD)



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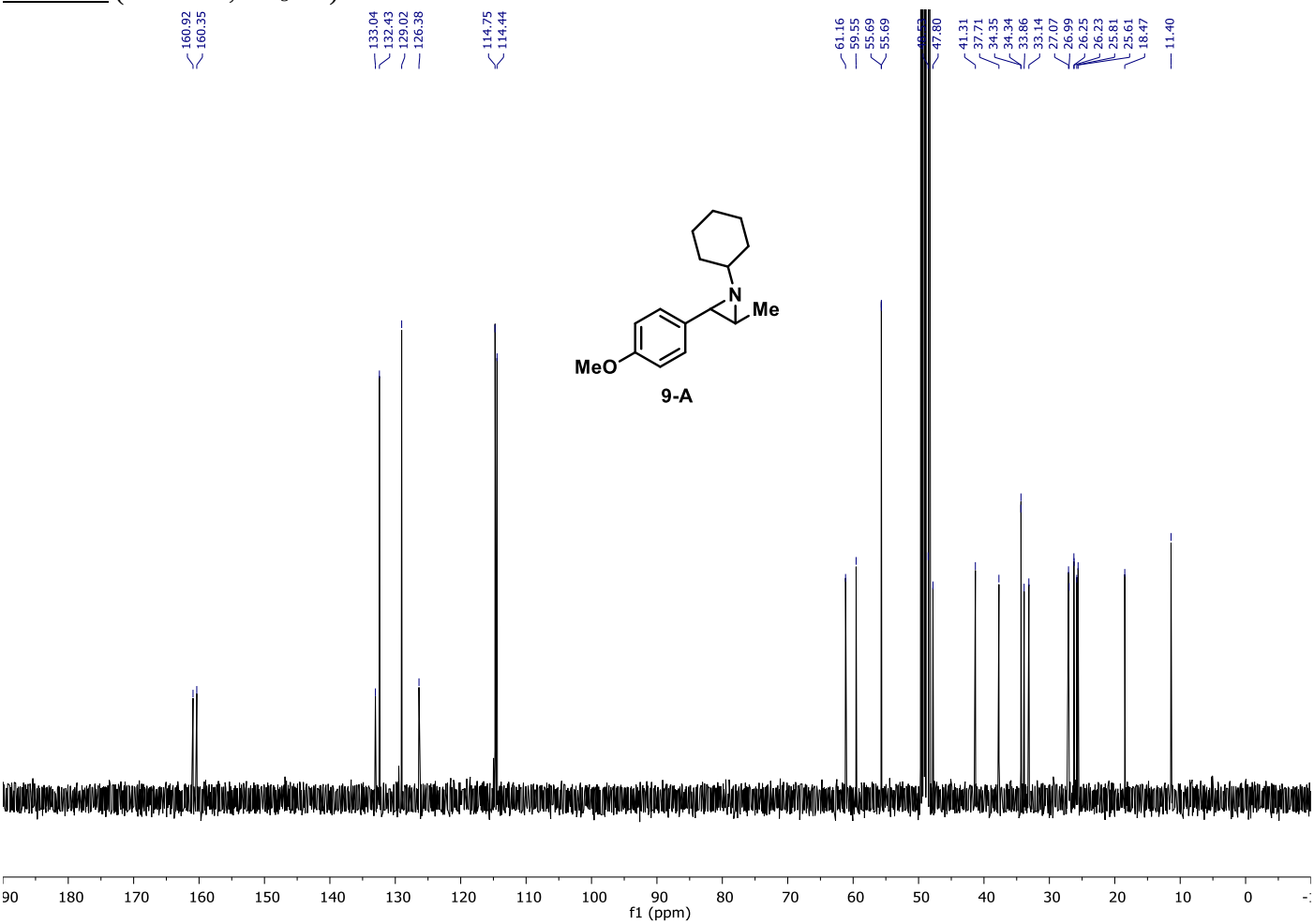

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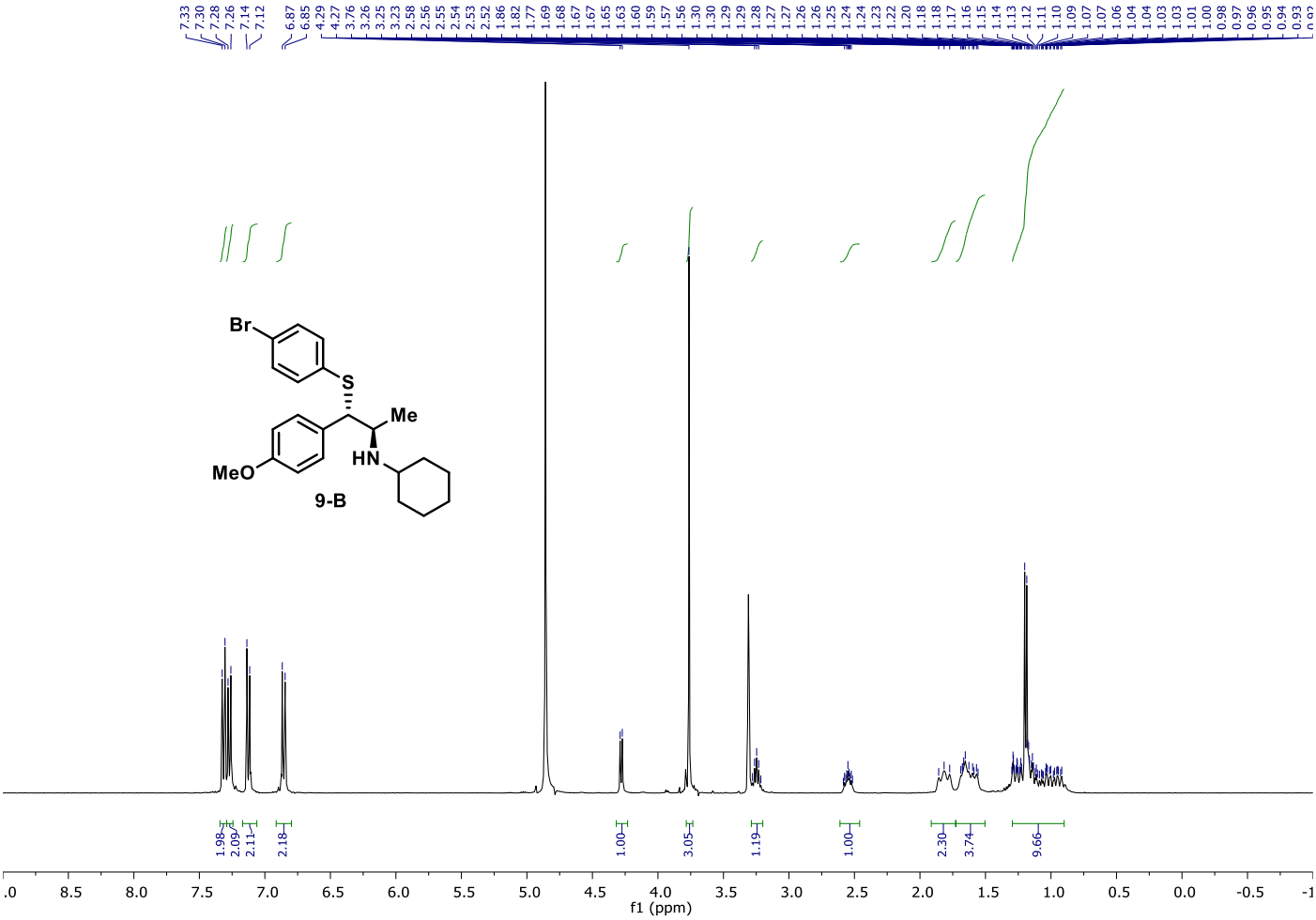

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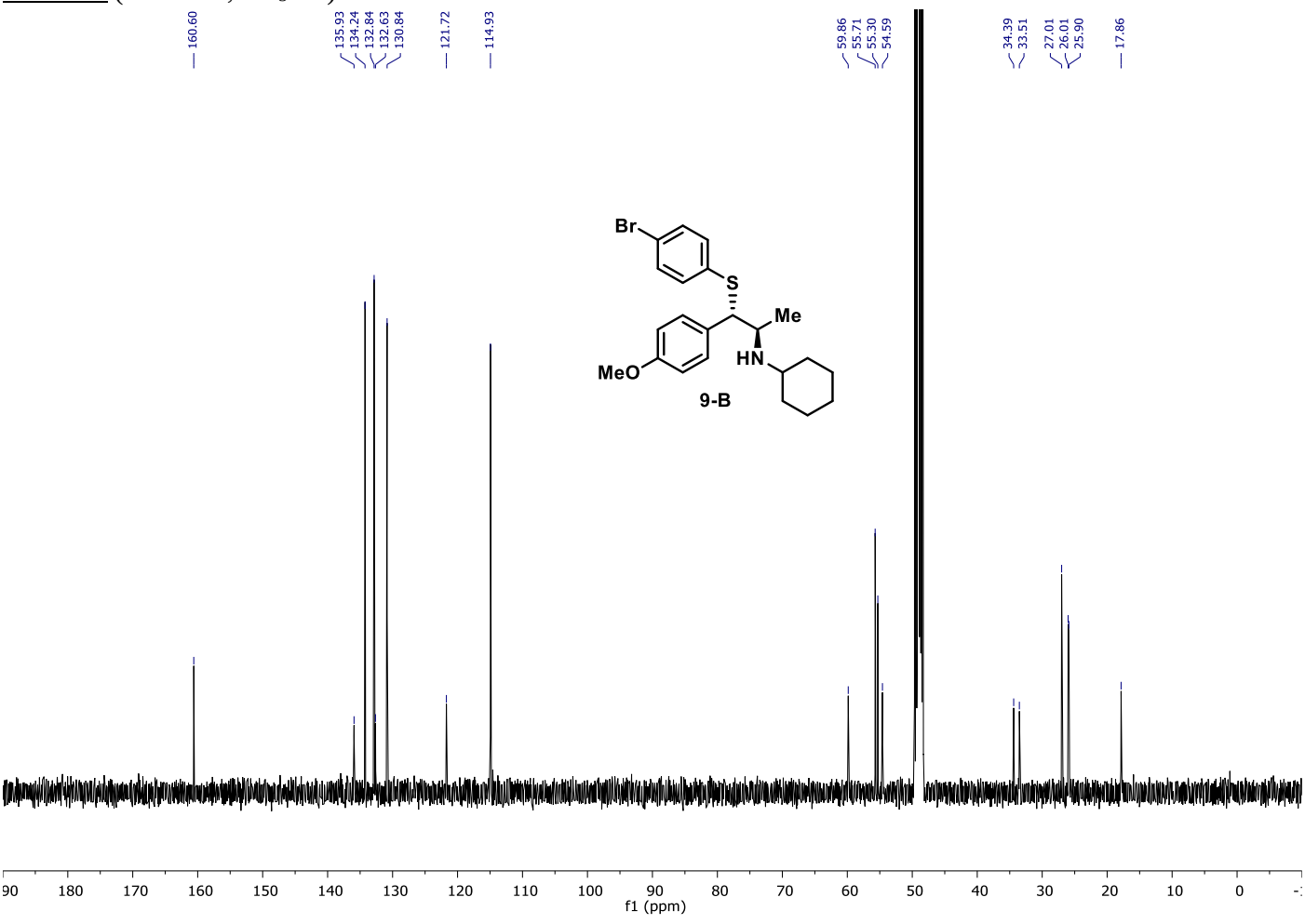

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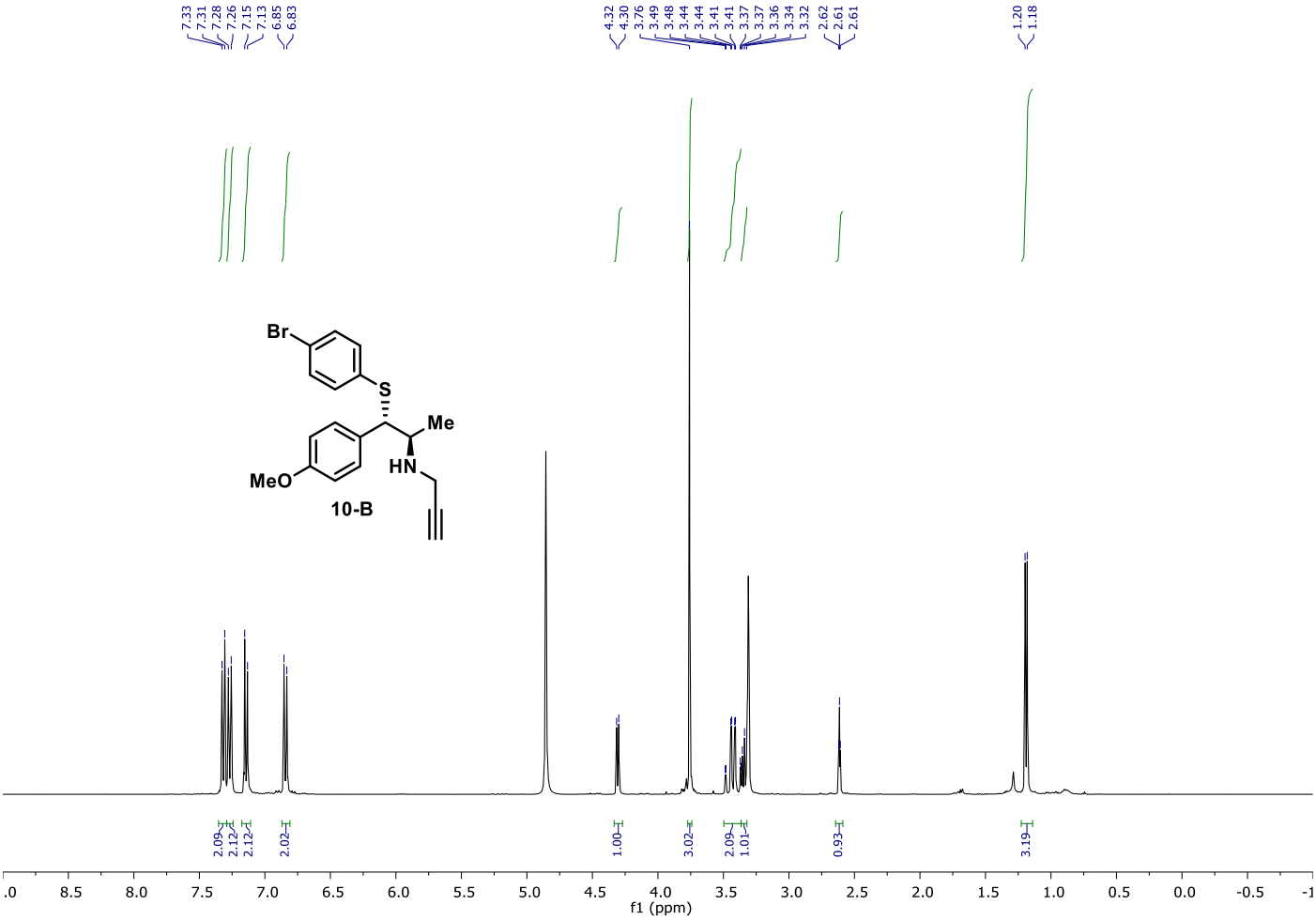

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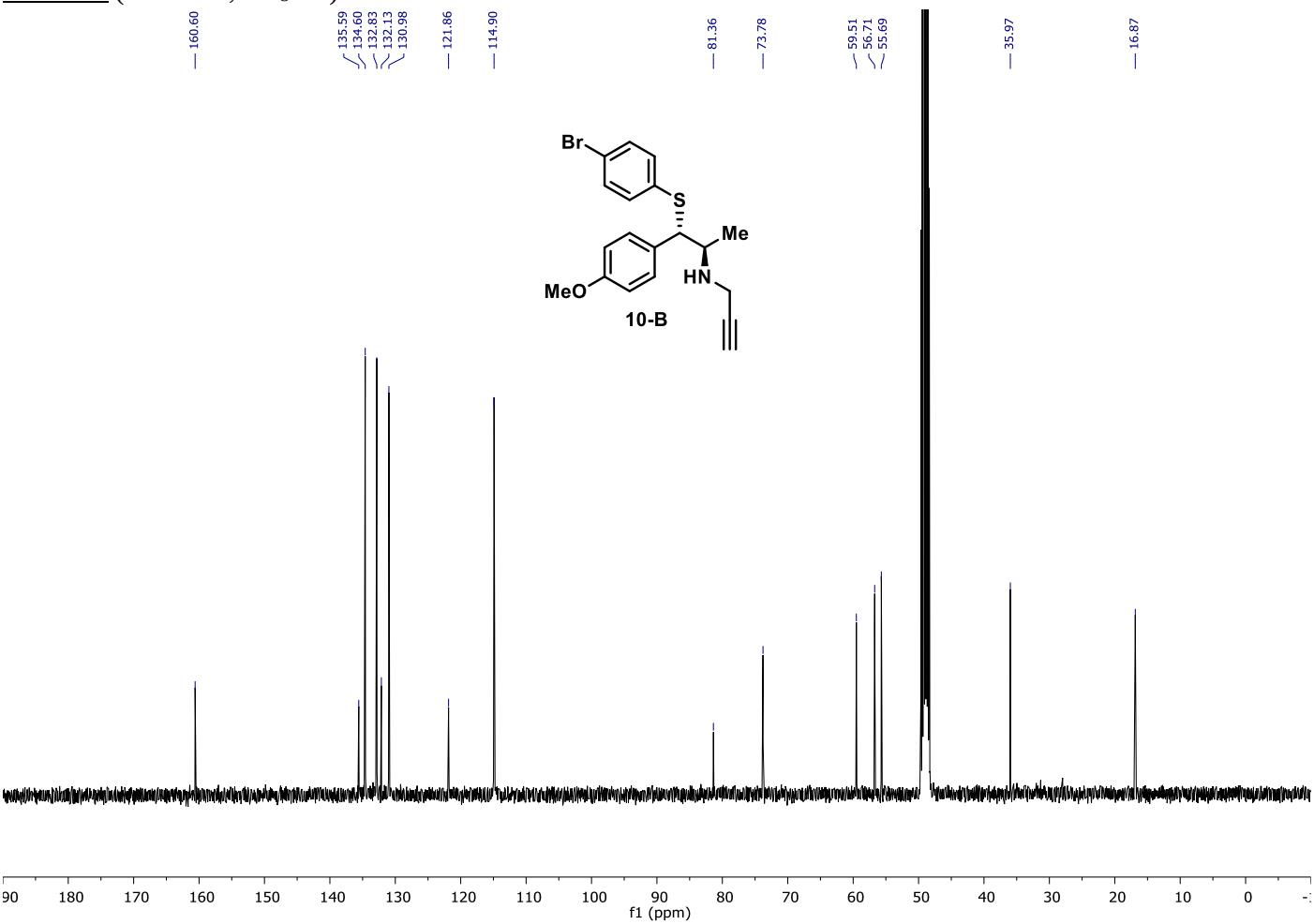

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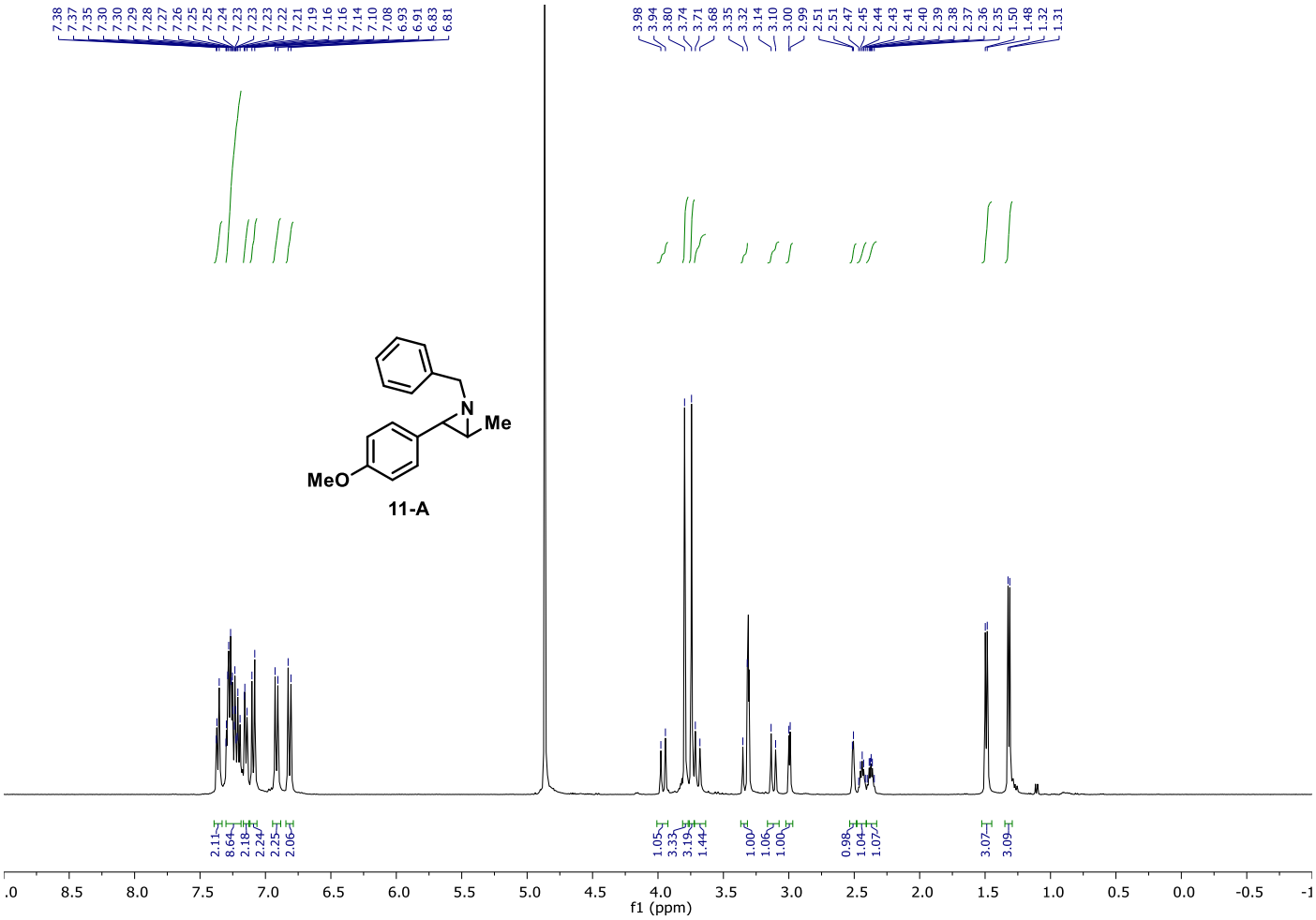

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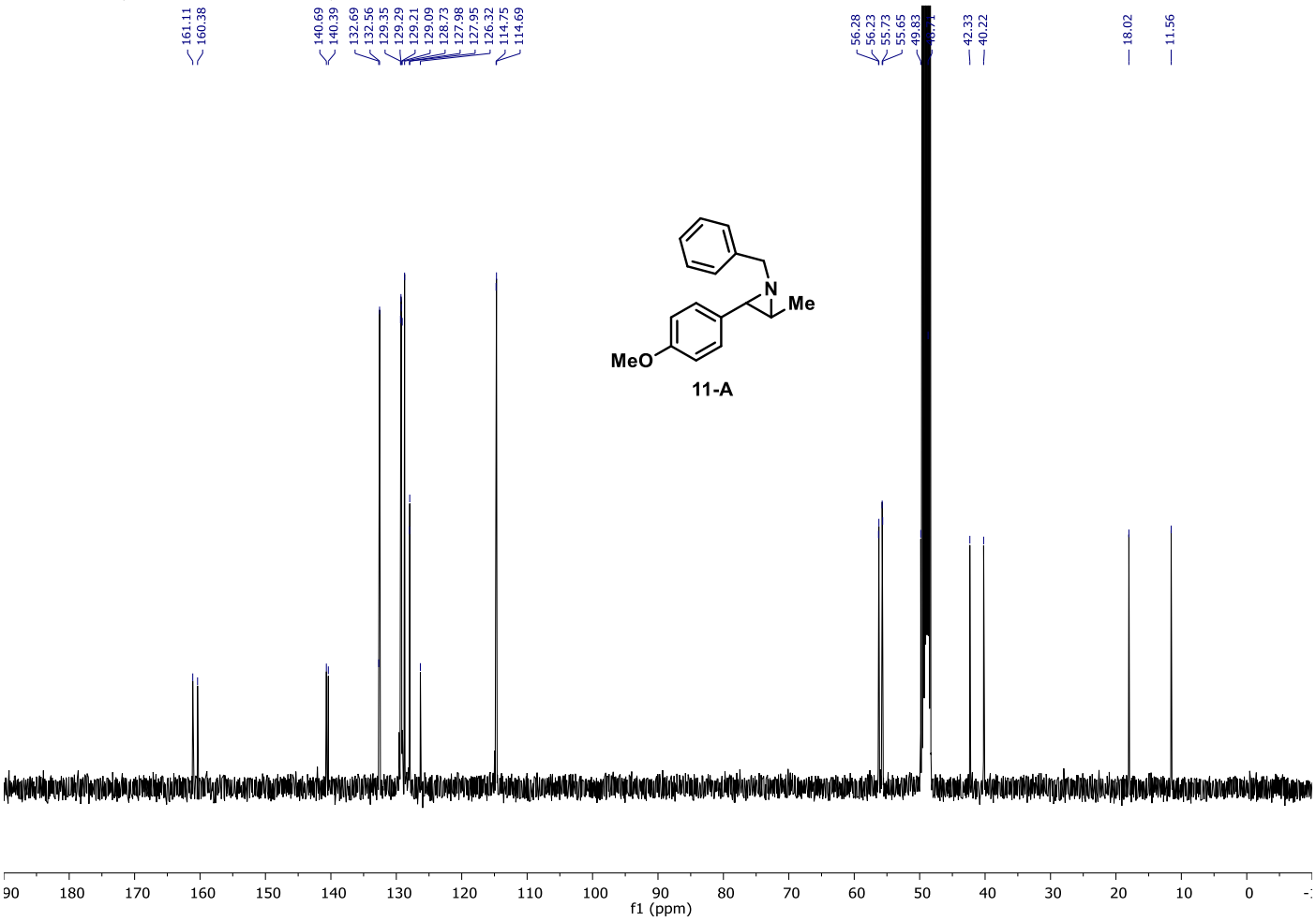

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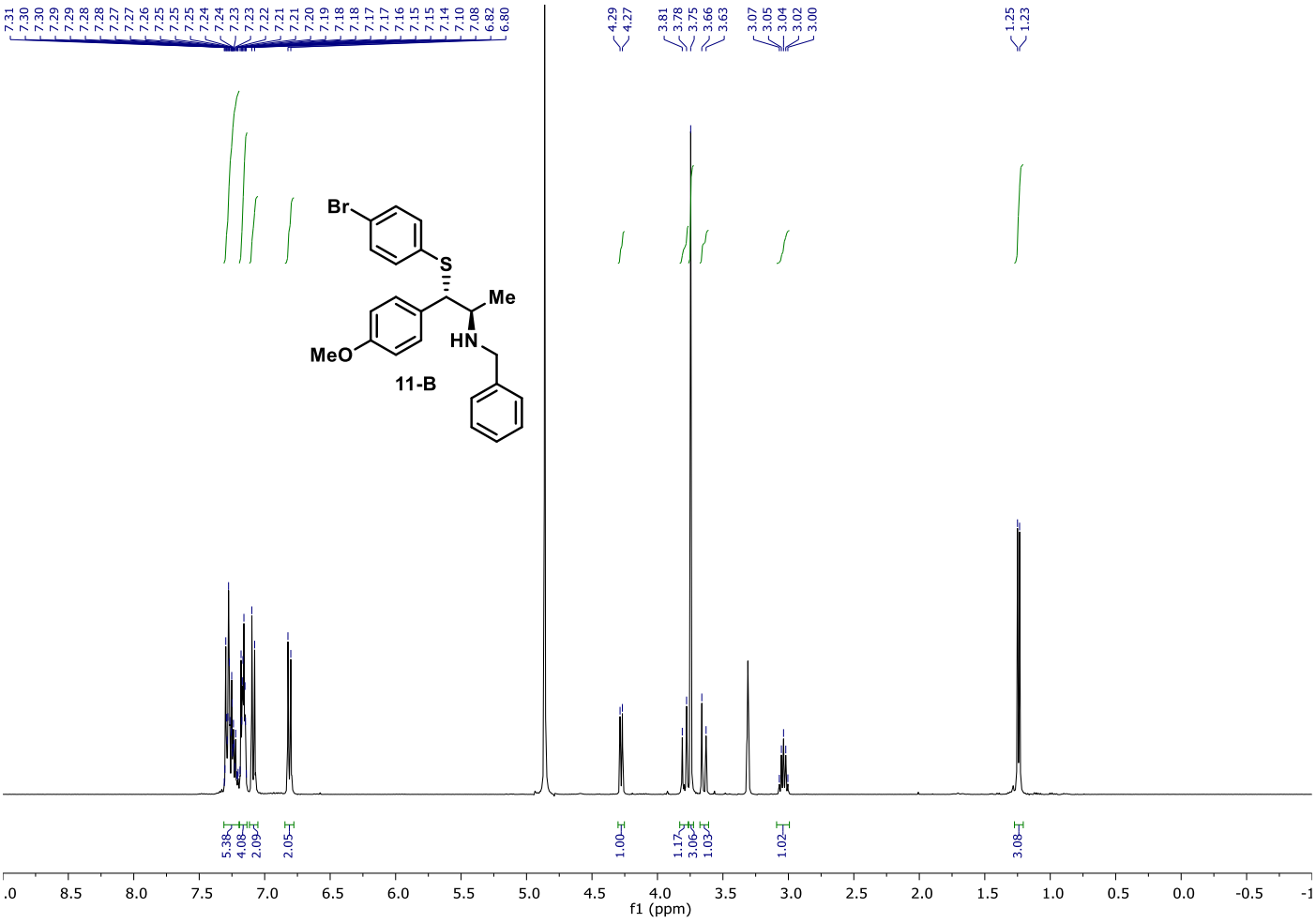

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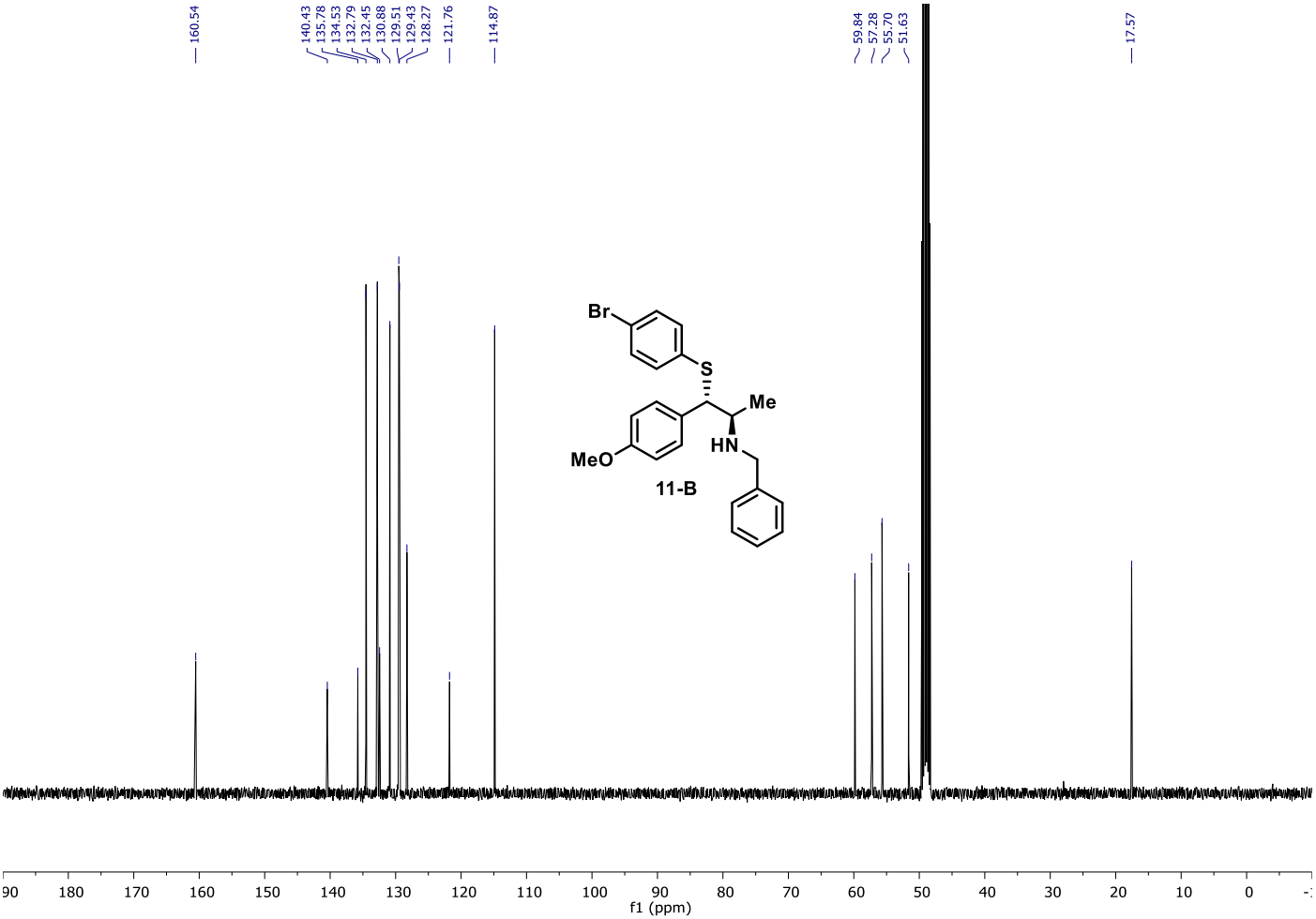

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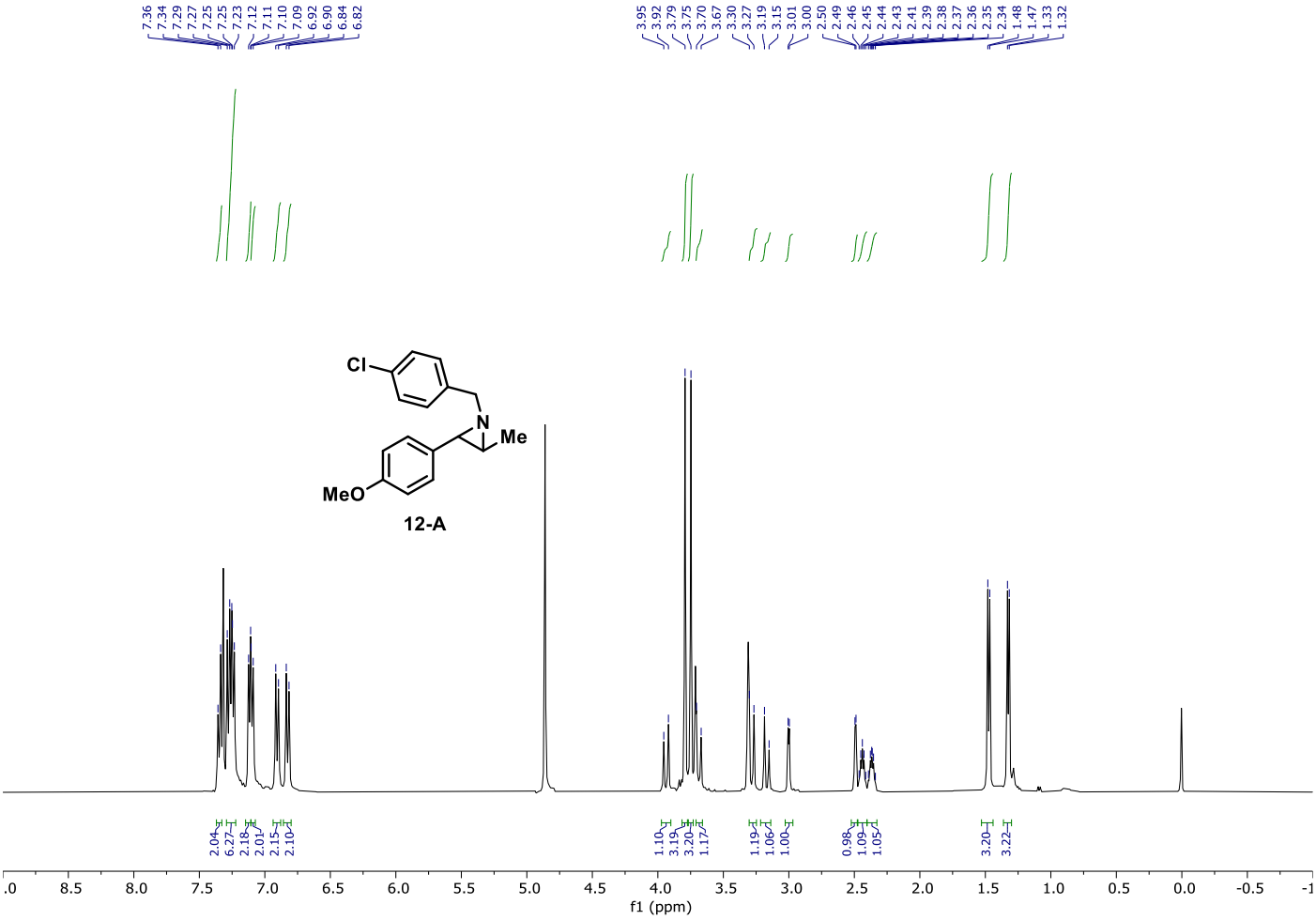

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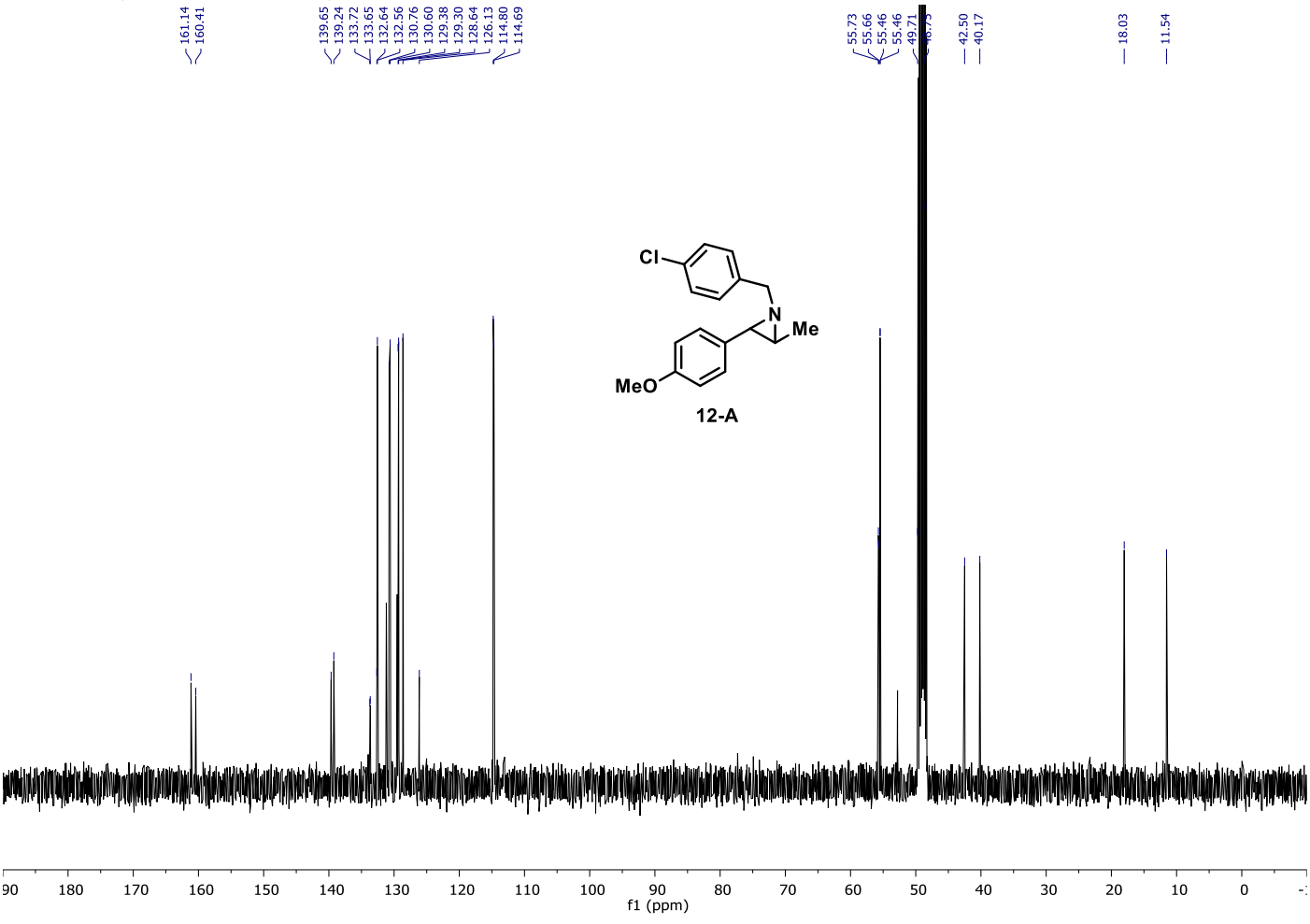

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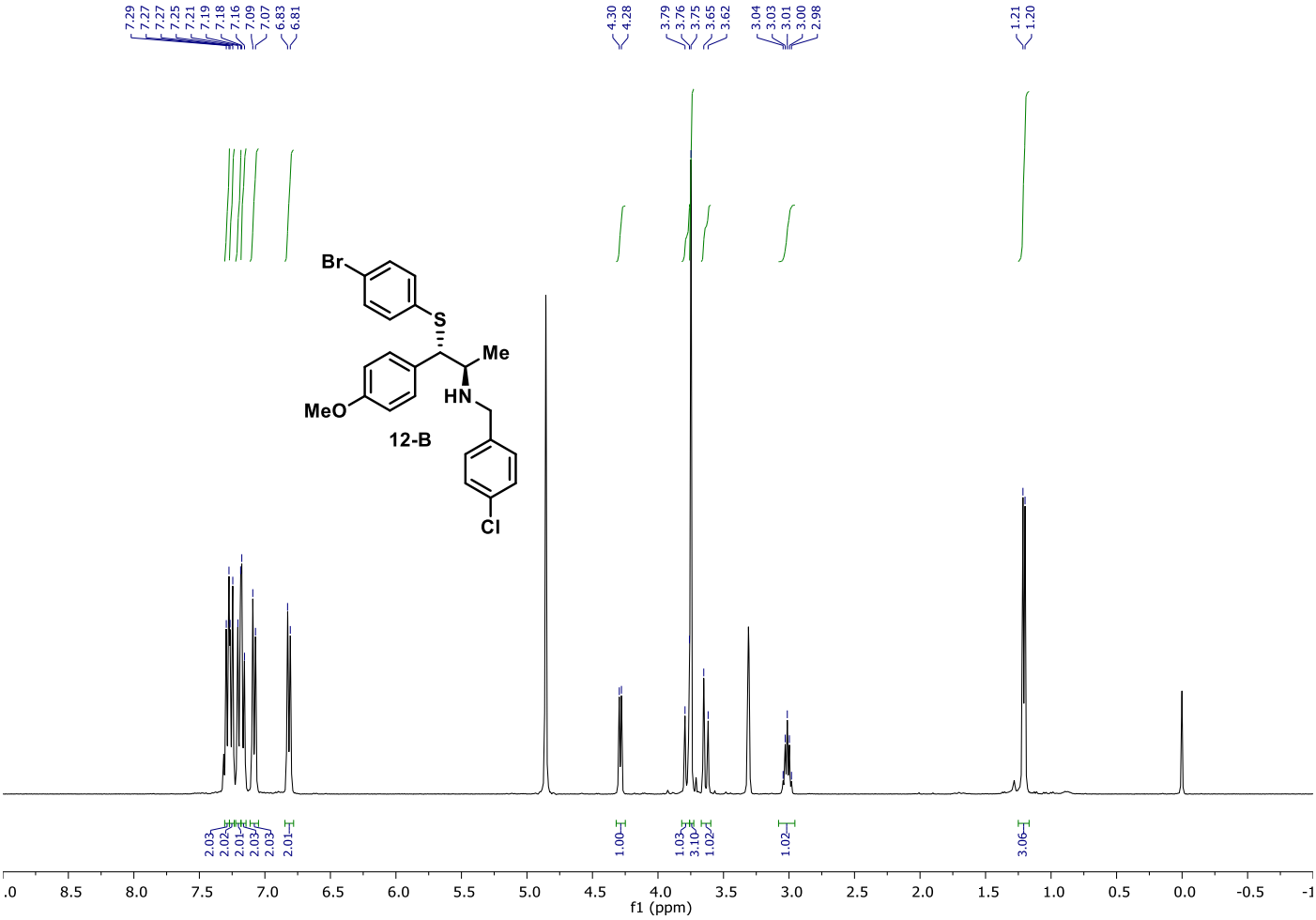

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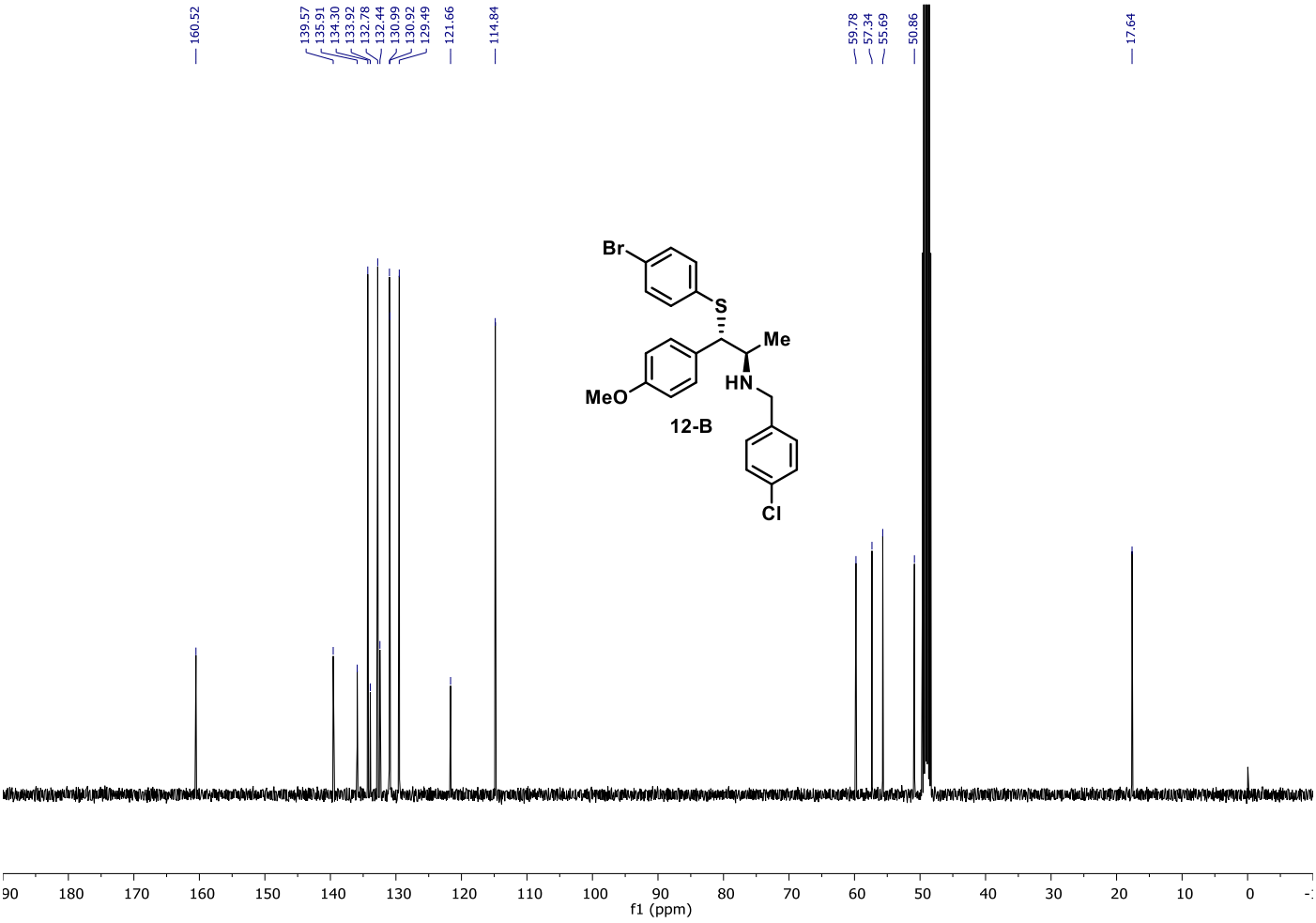

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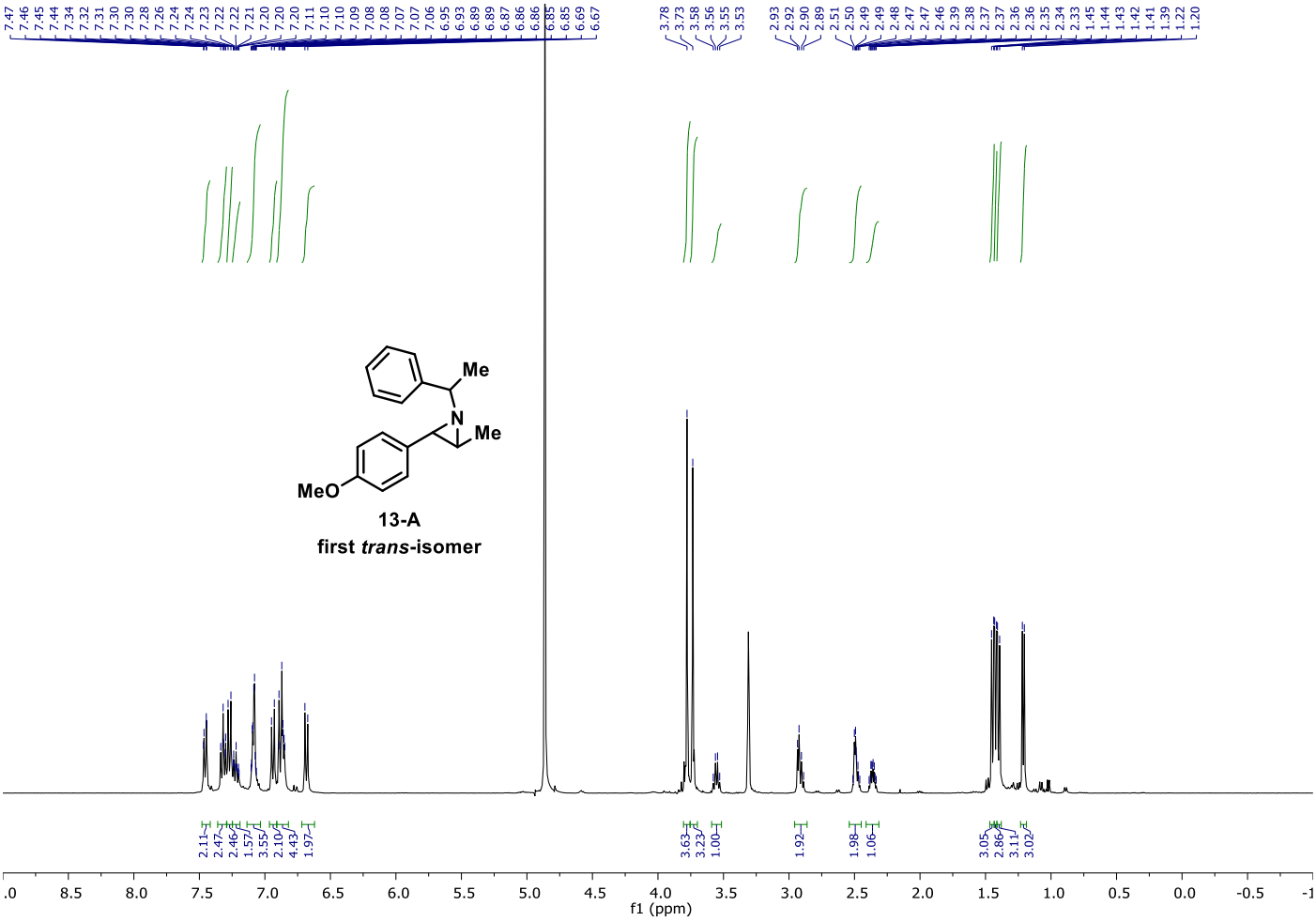

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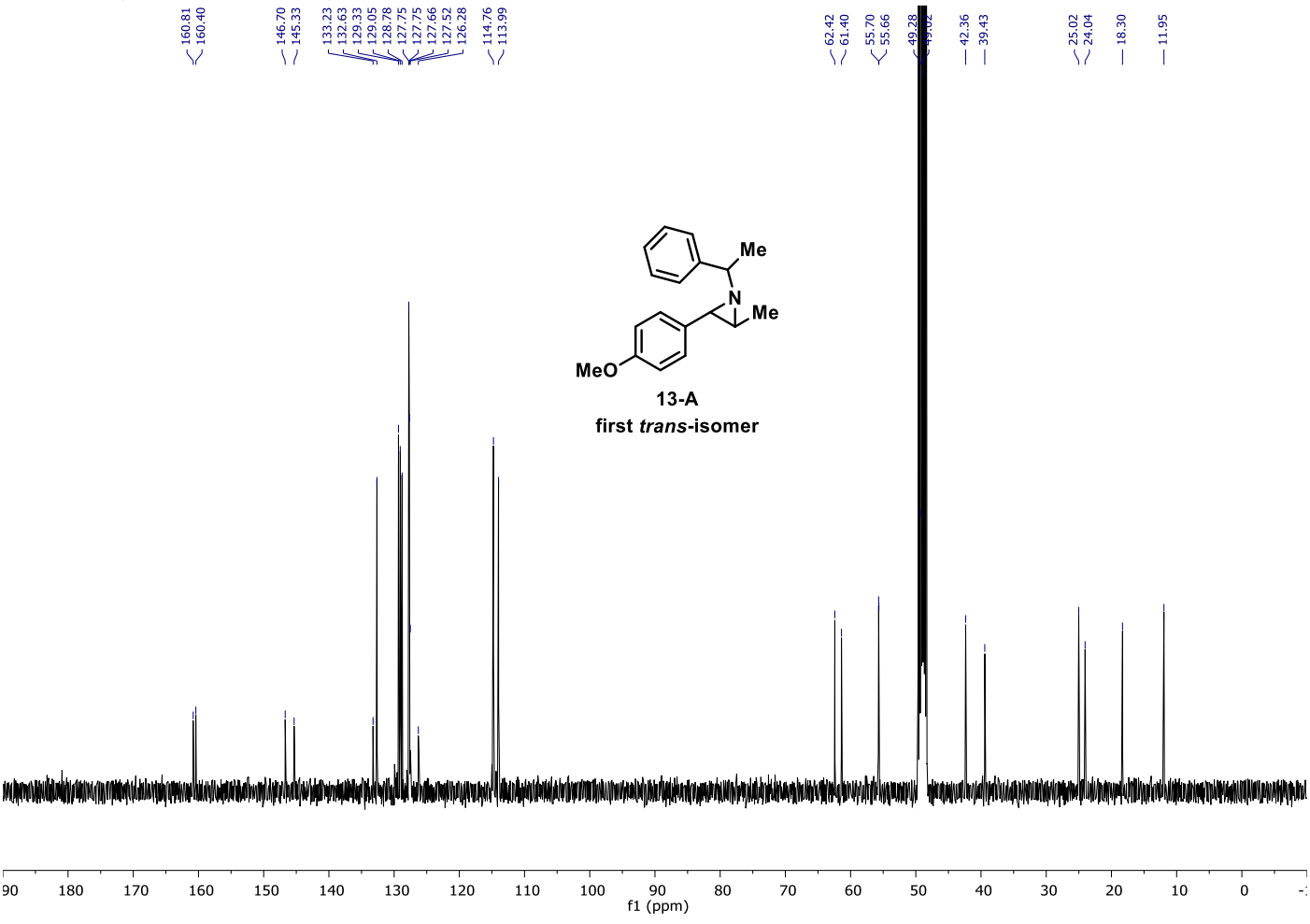

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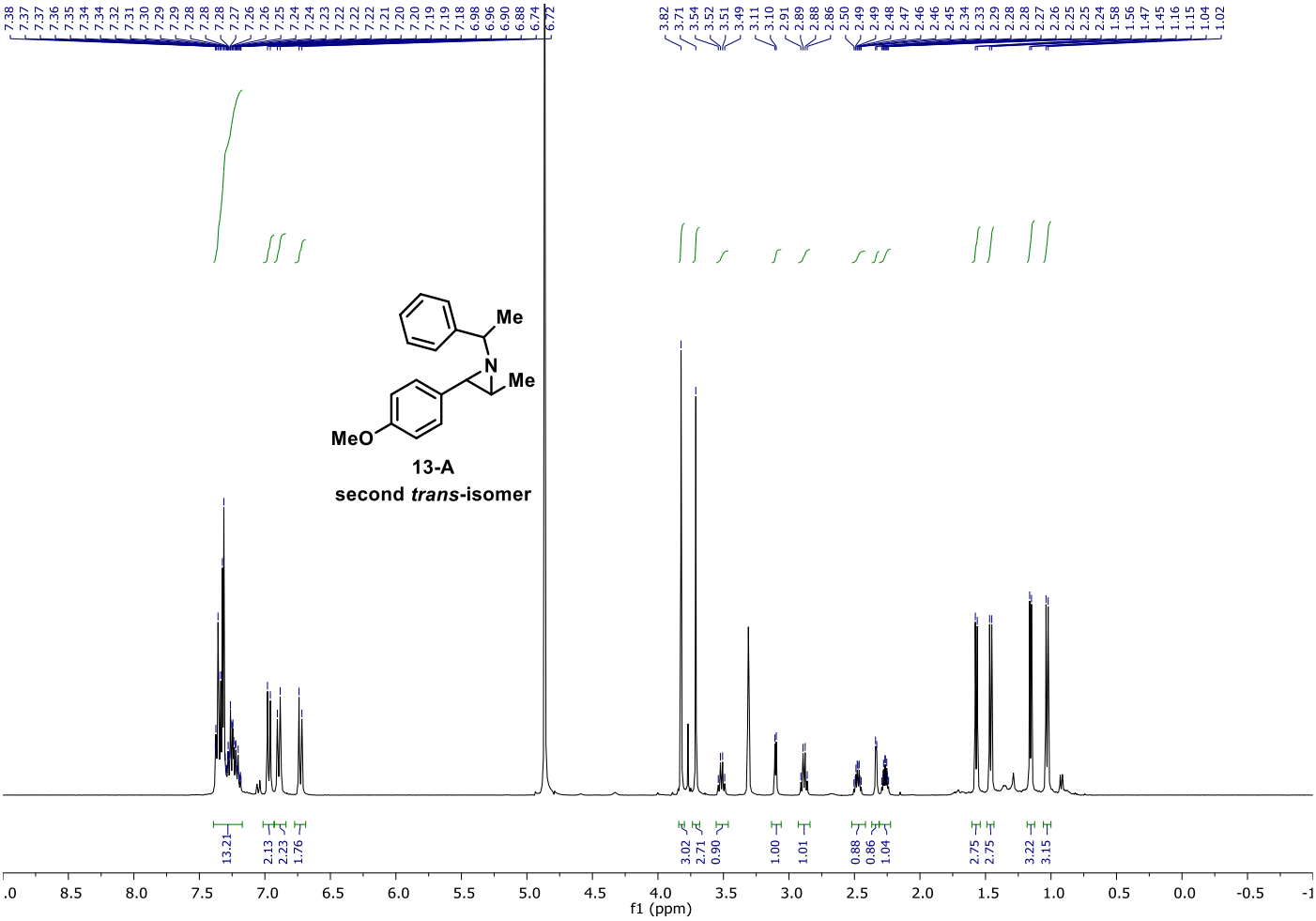

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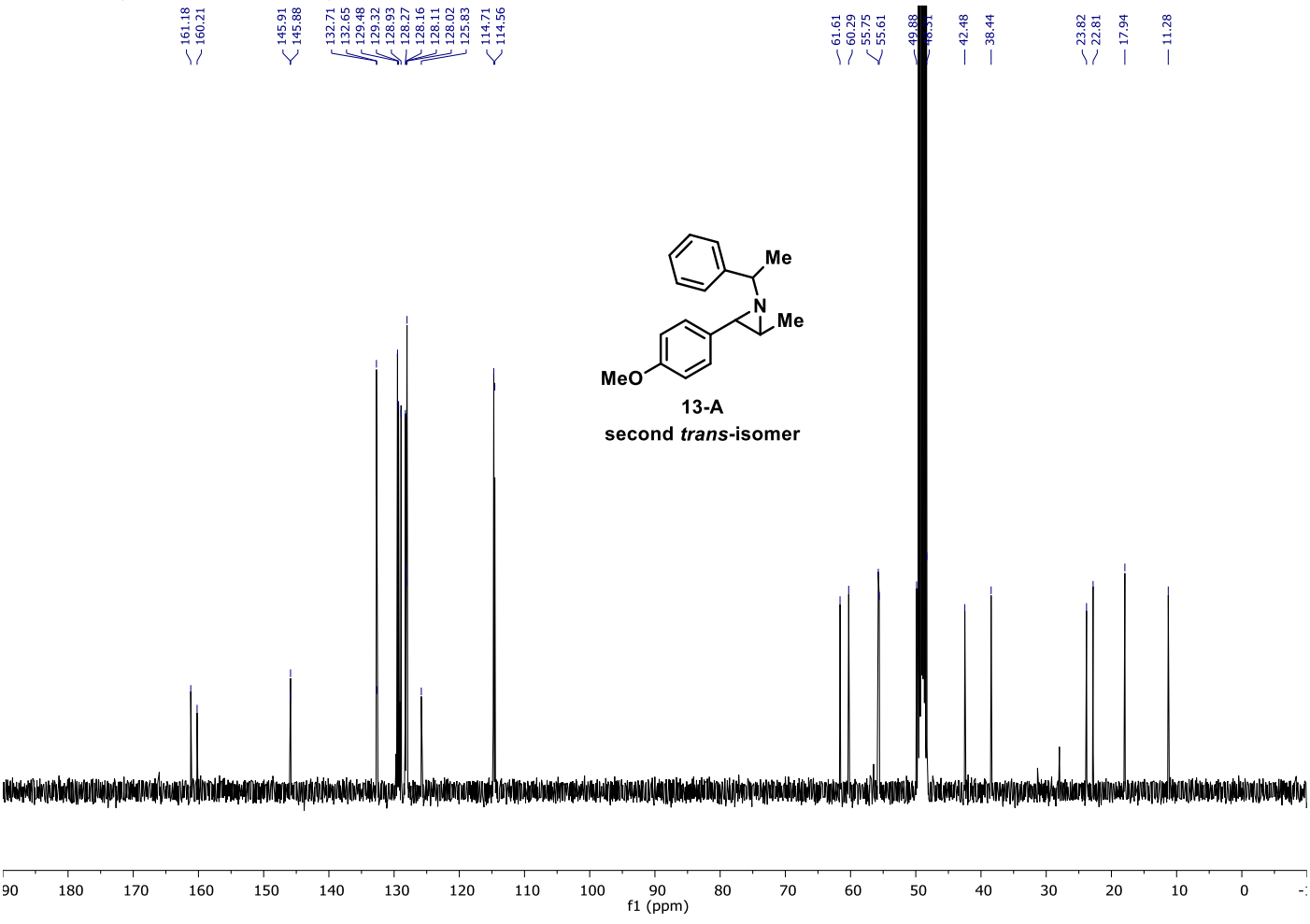
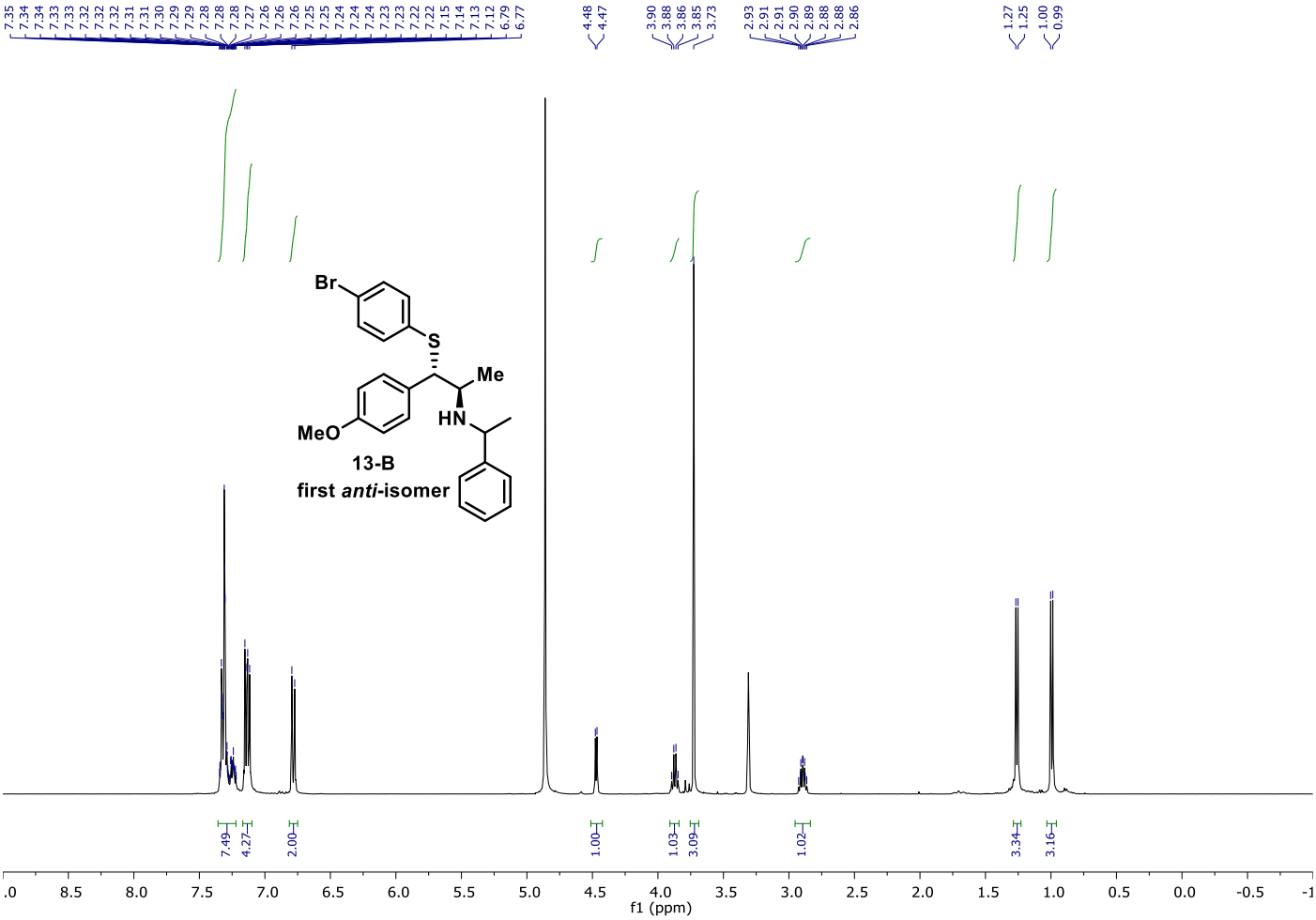


^{1}H NMR (400 MHz, CD_3OD)



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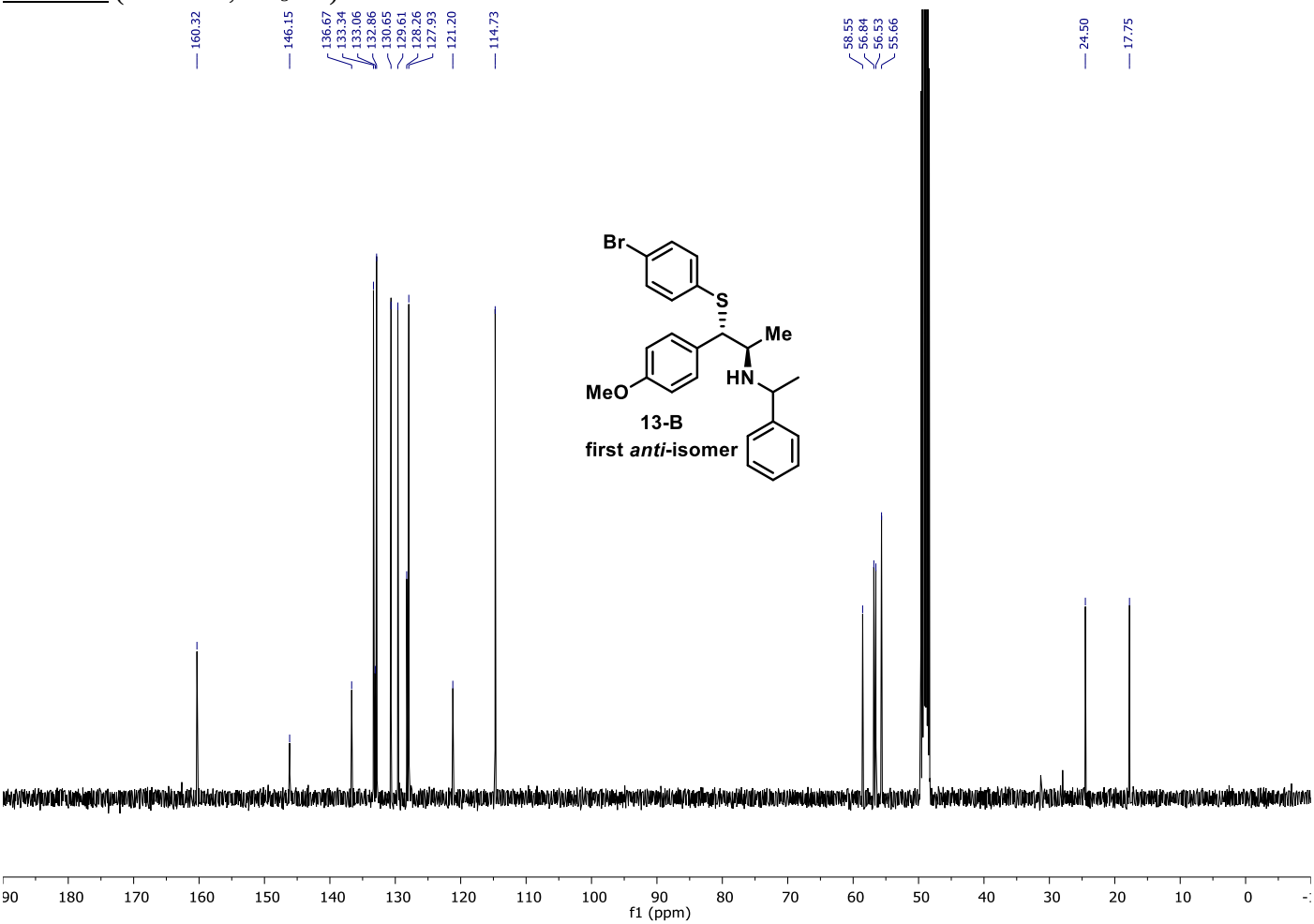

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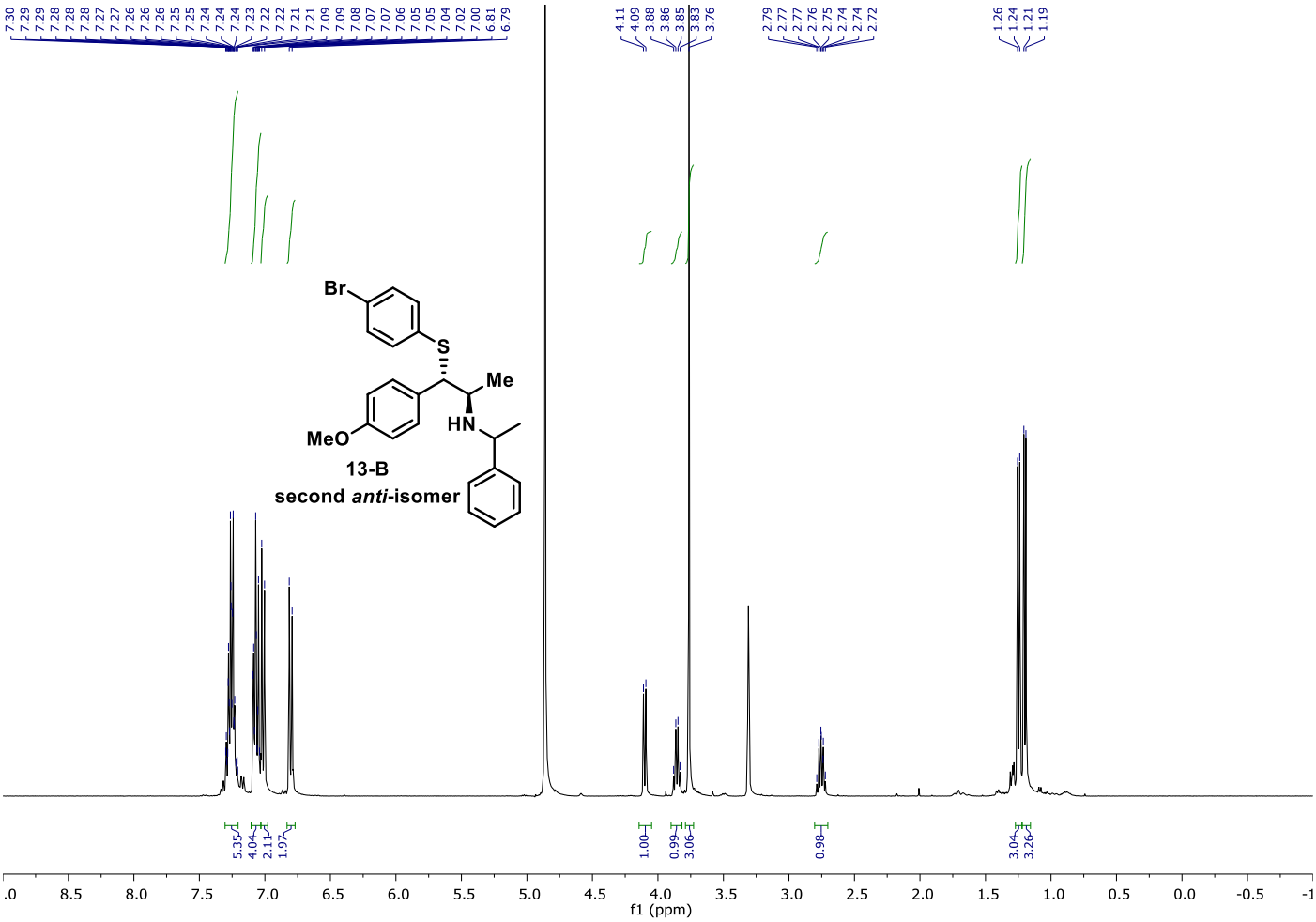

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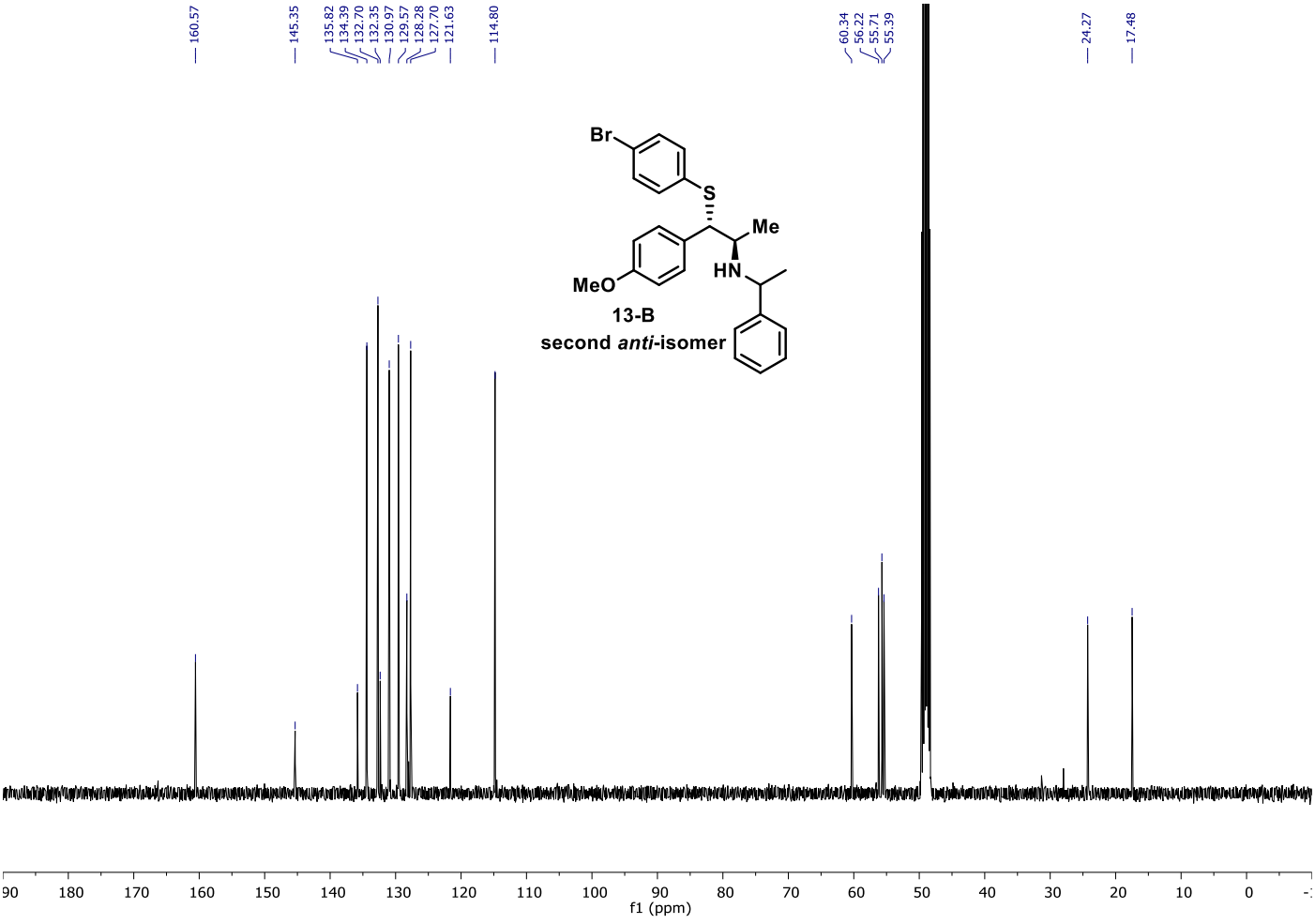

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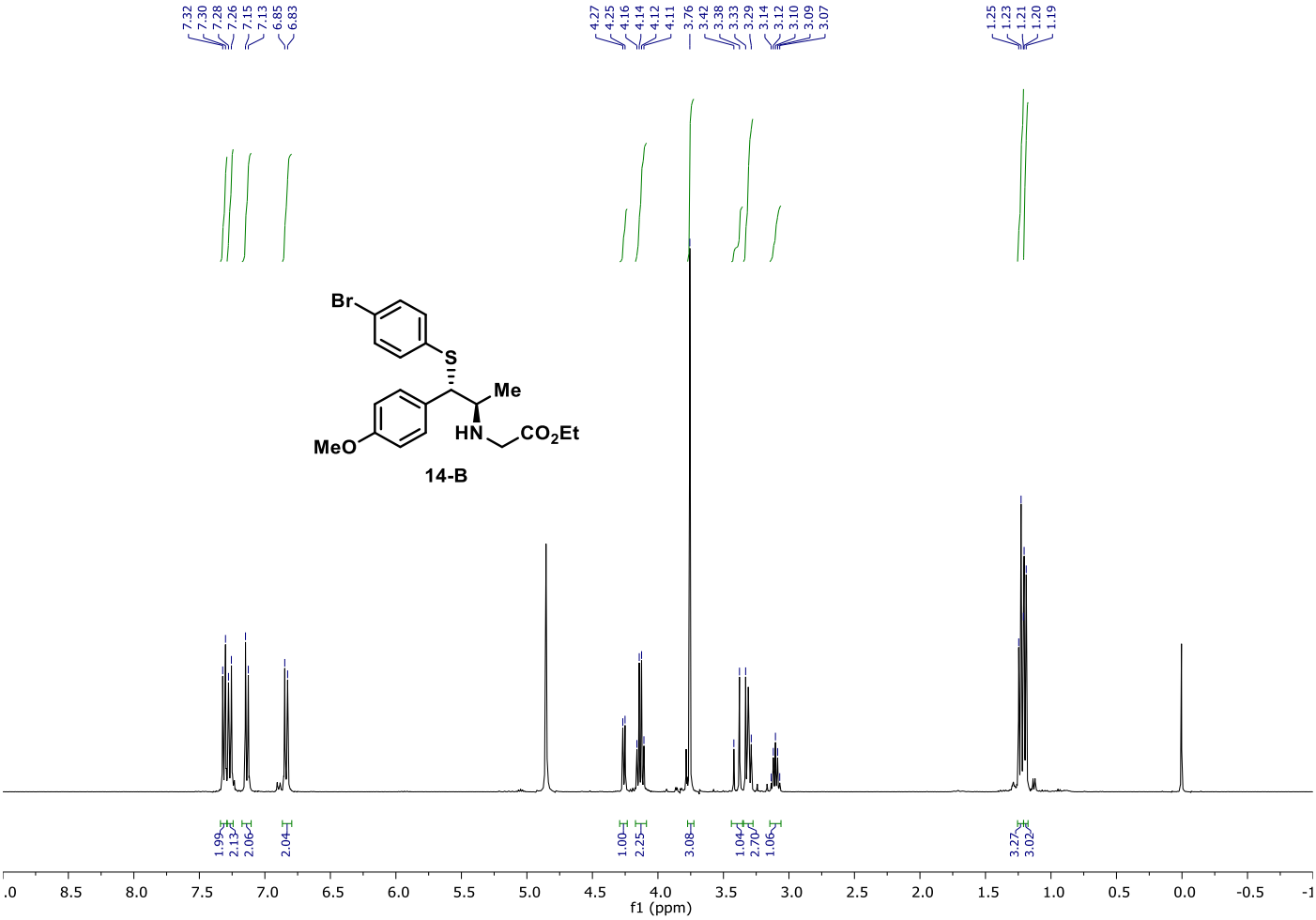

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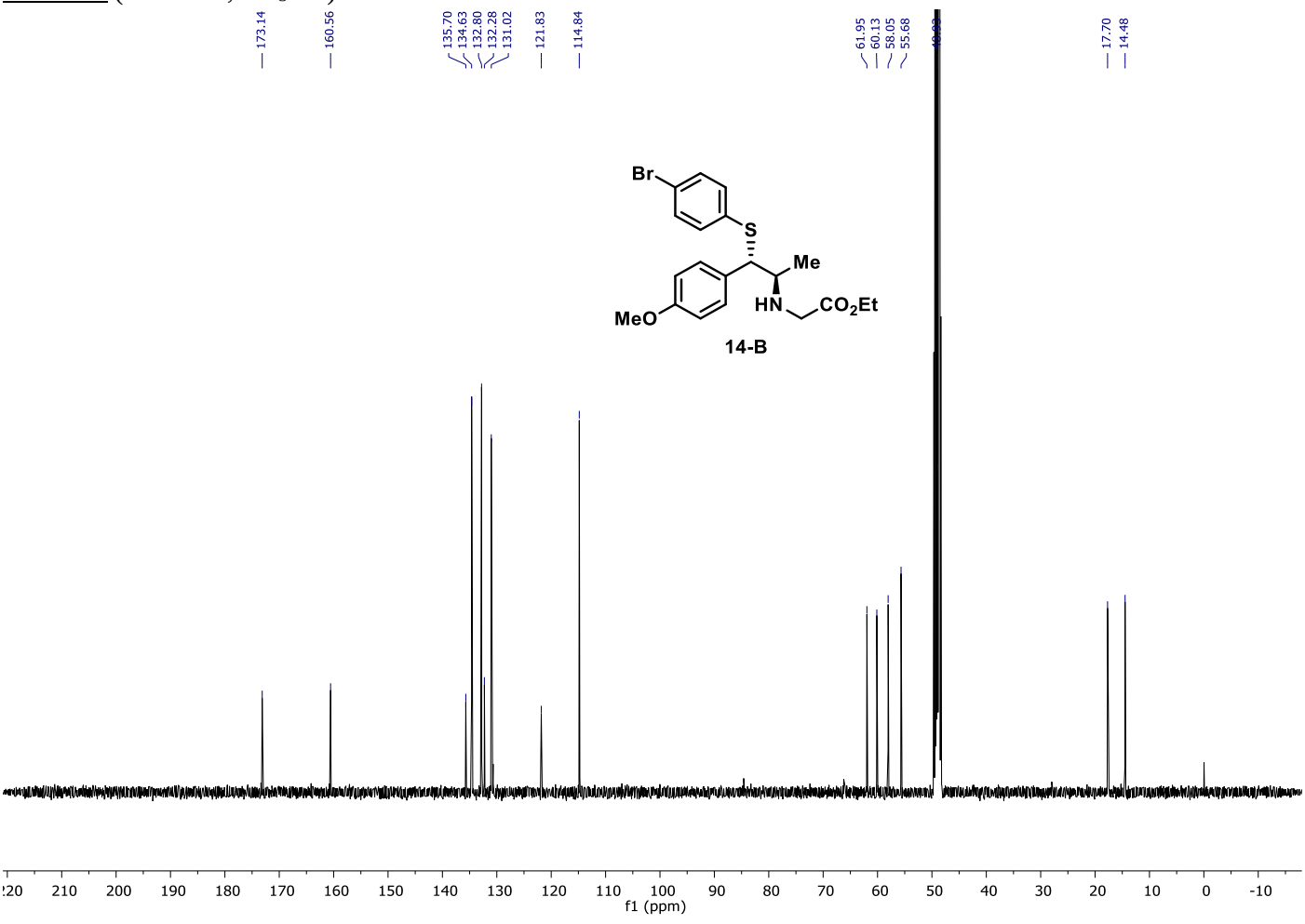

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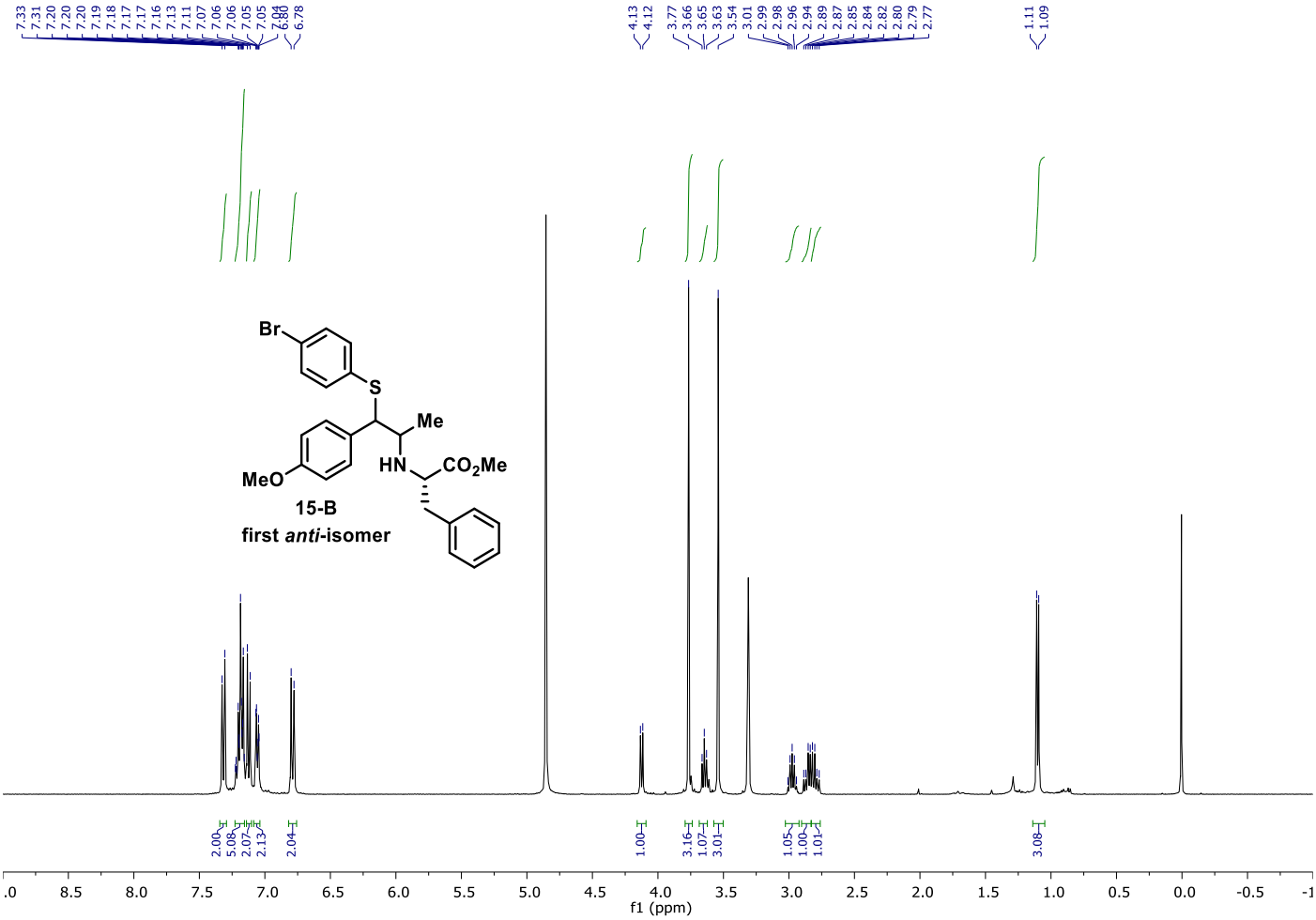

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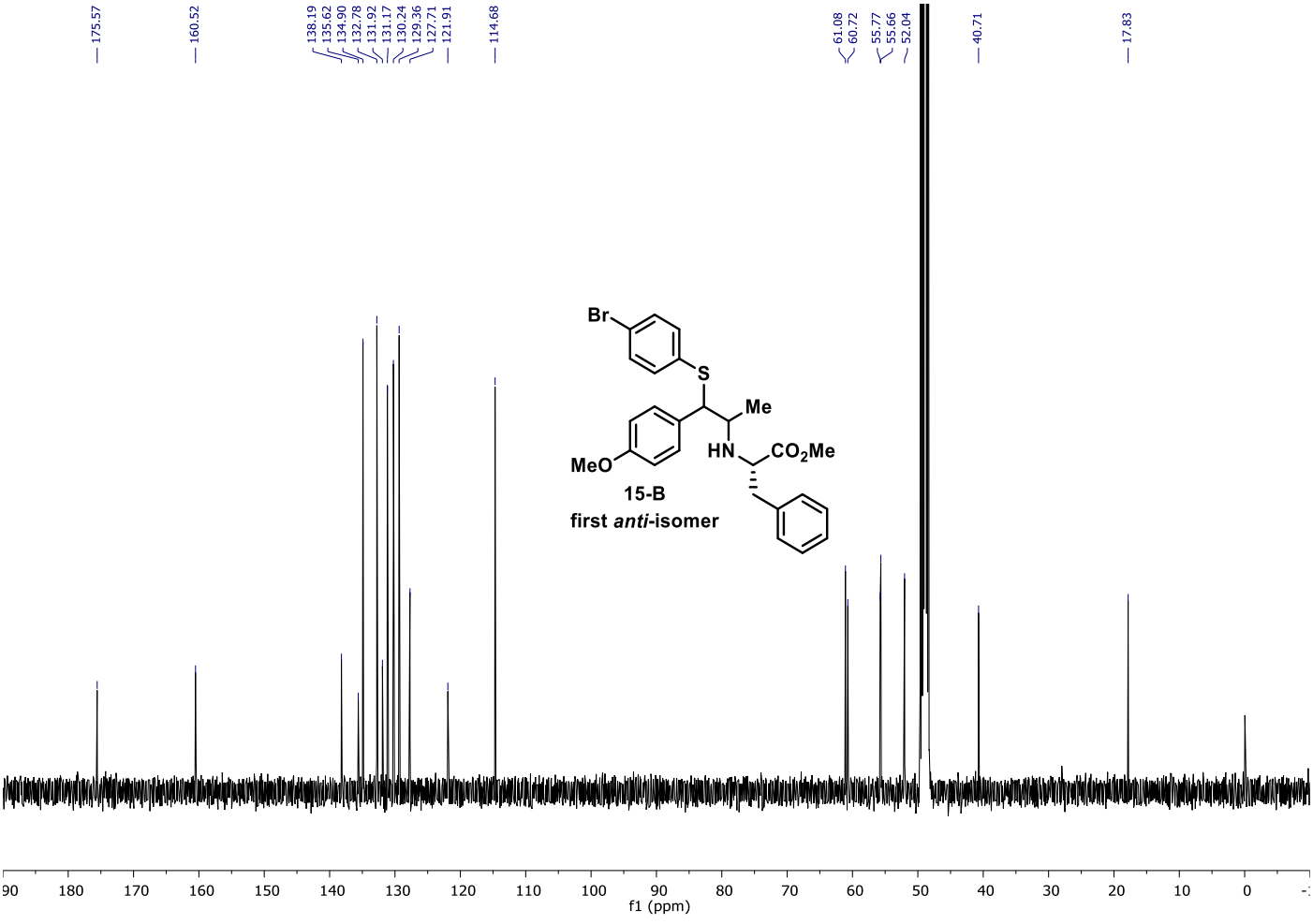

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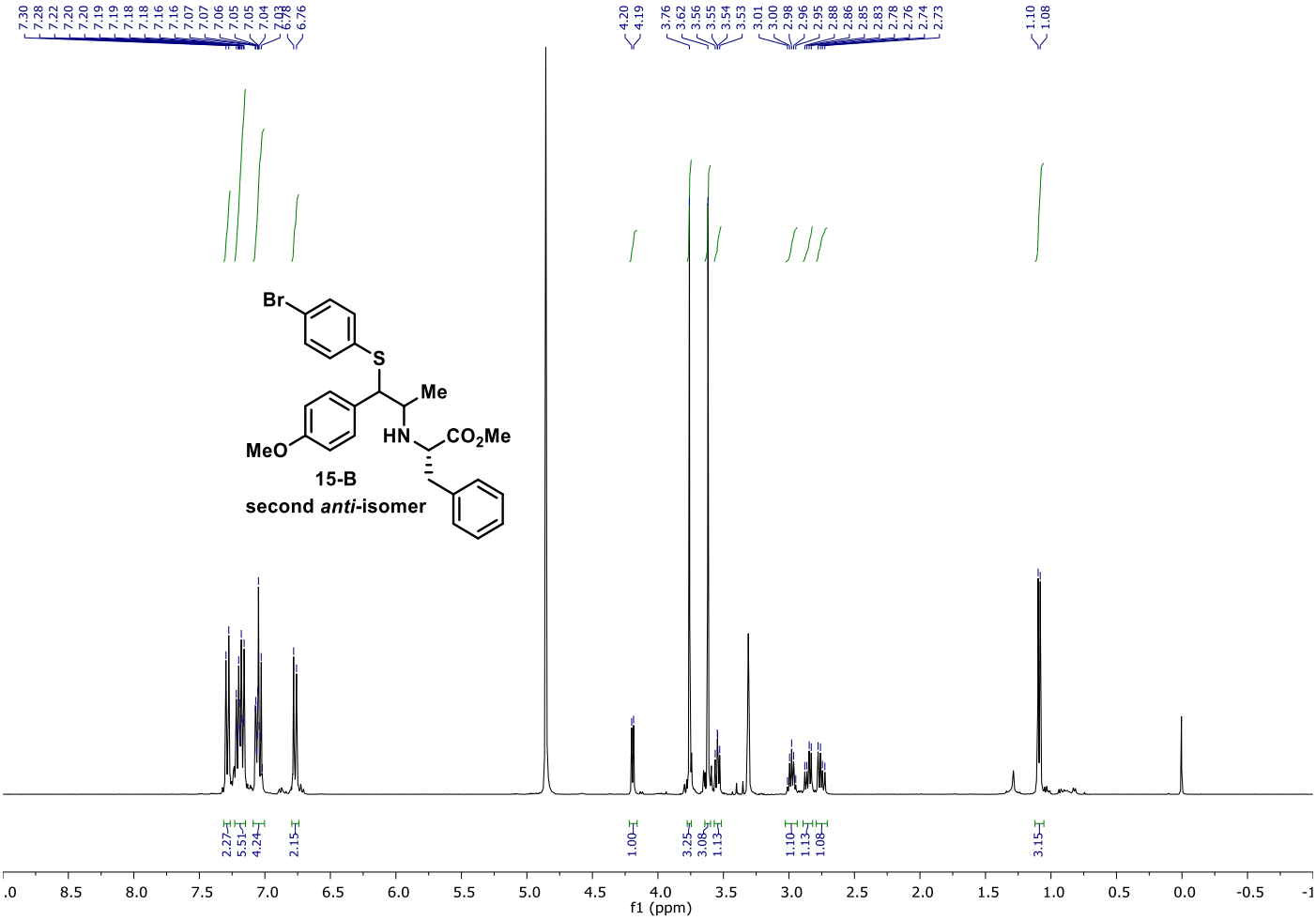

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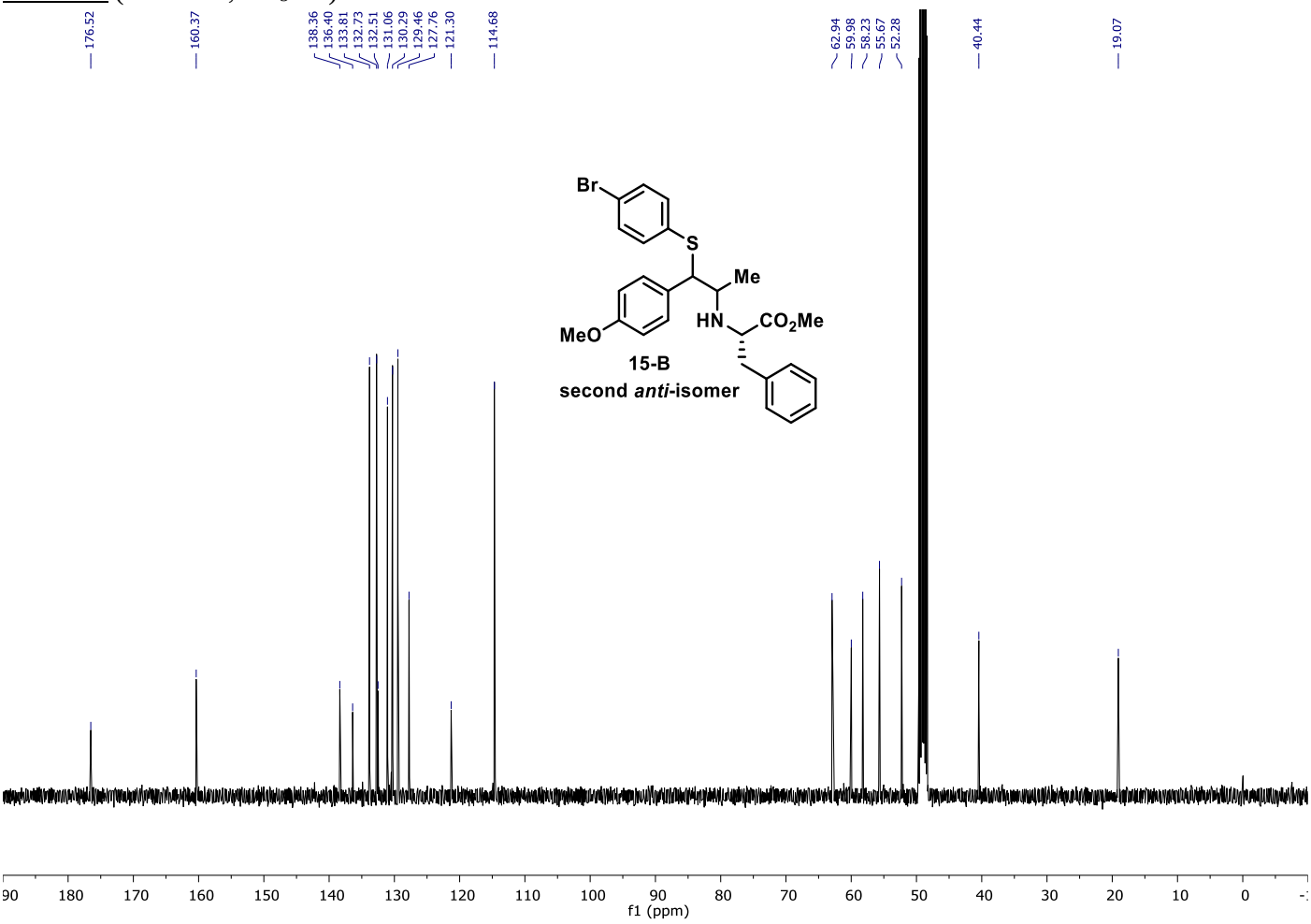
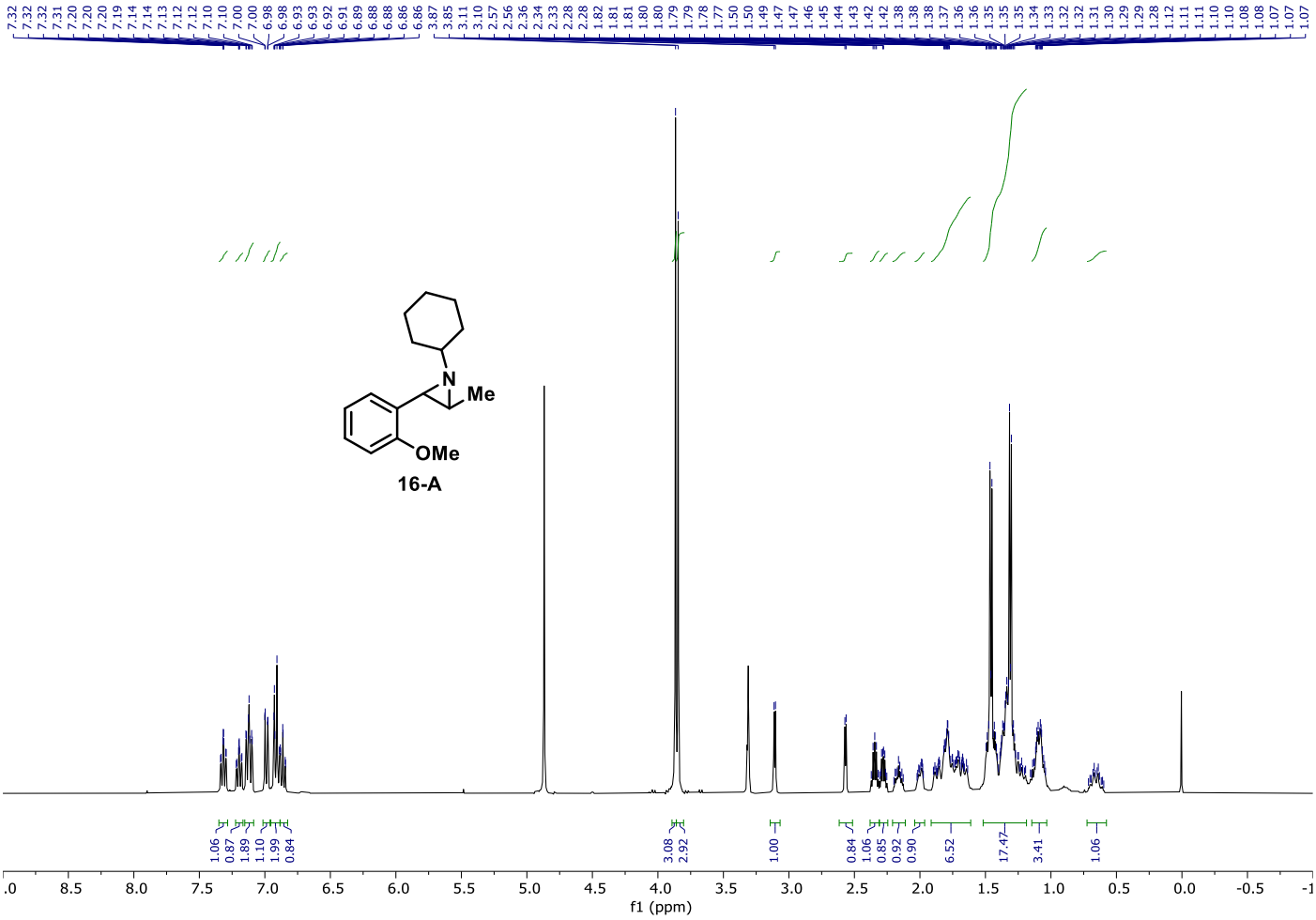
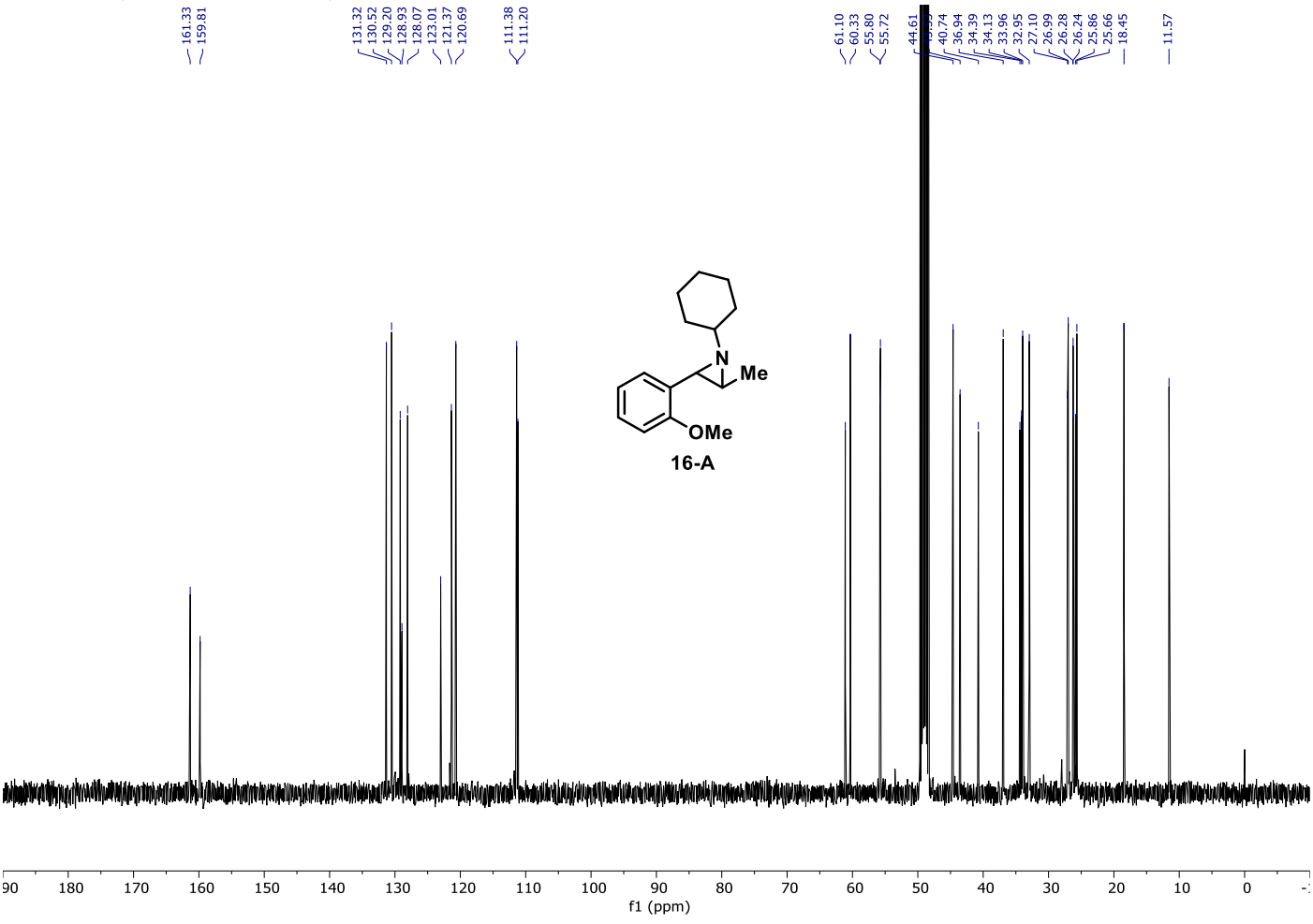


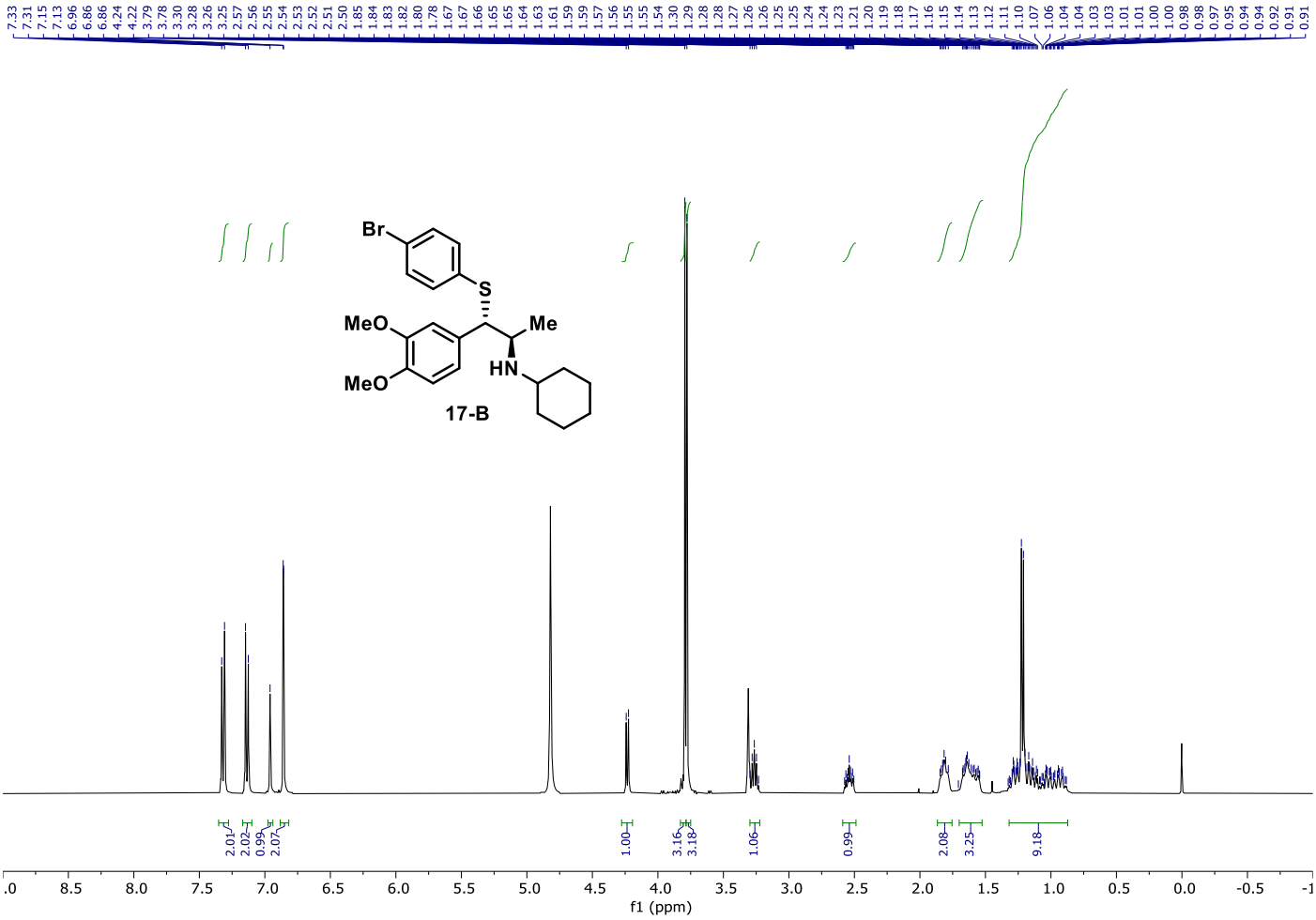
^{1}H NMR (400 MHz, CD_3OD)



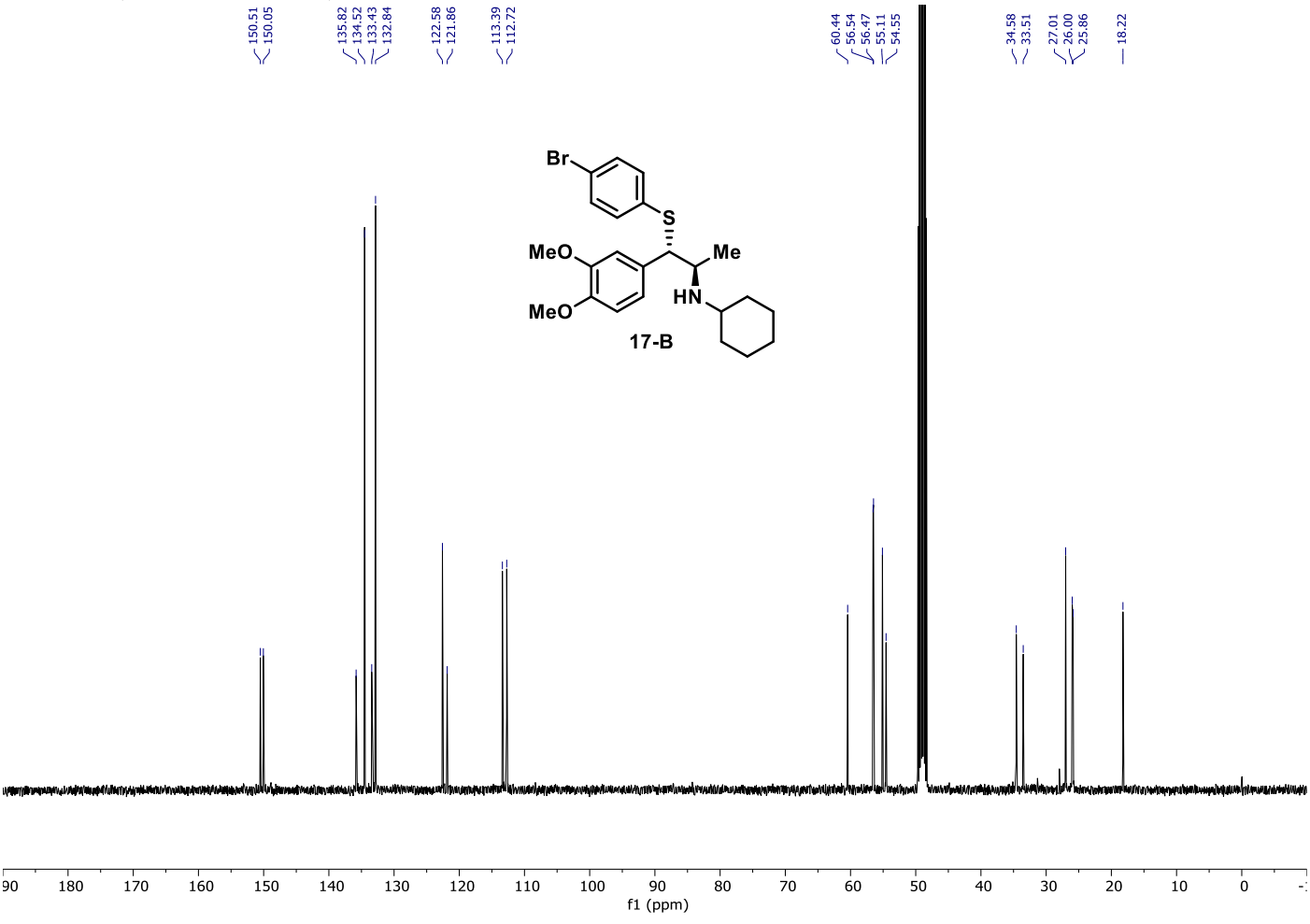
^{13}C NMR (101 MHz, CD_3OD)



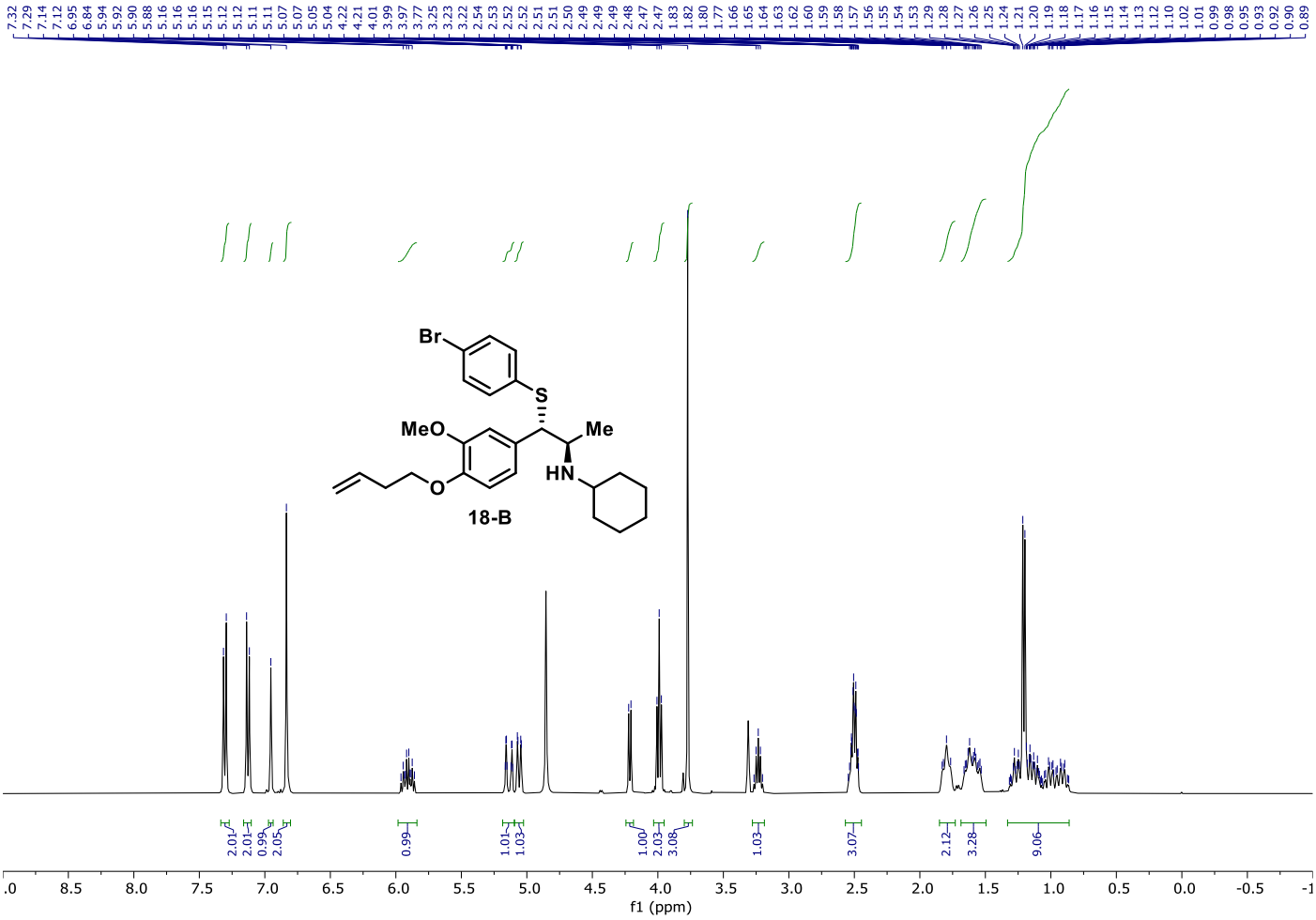
^{1}H NMR (400 MHz, CD_3OD)



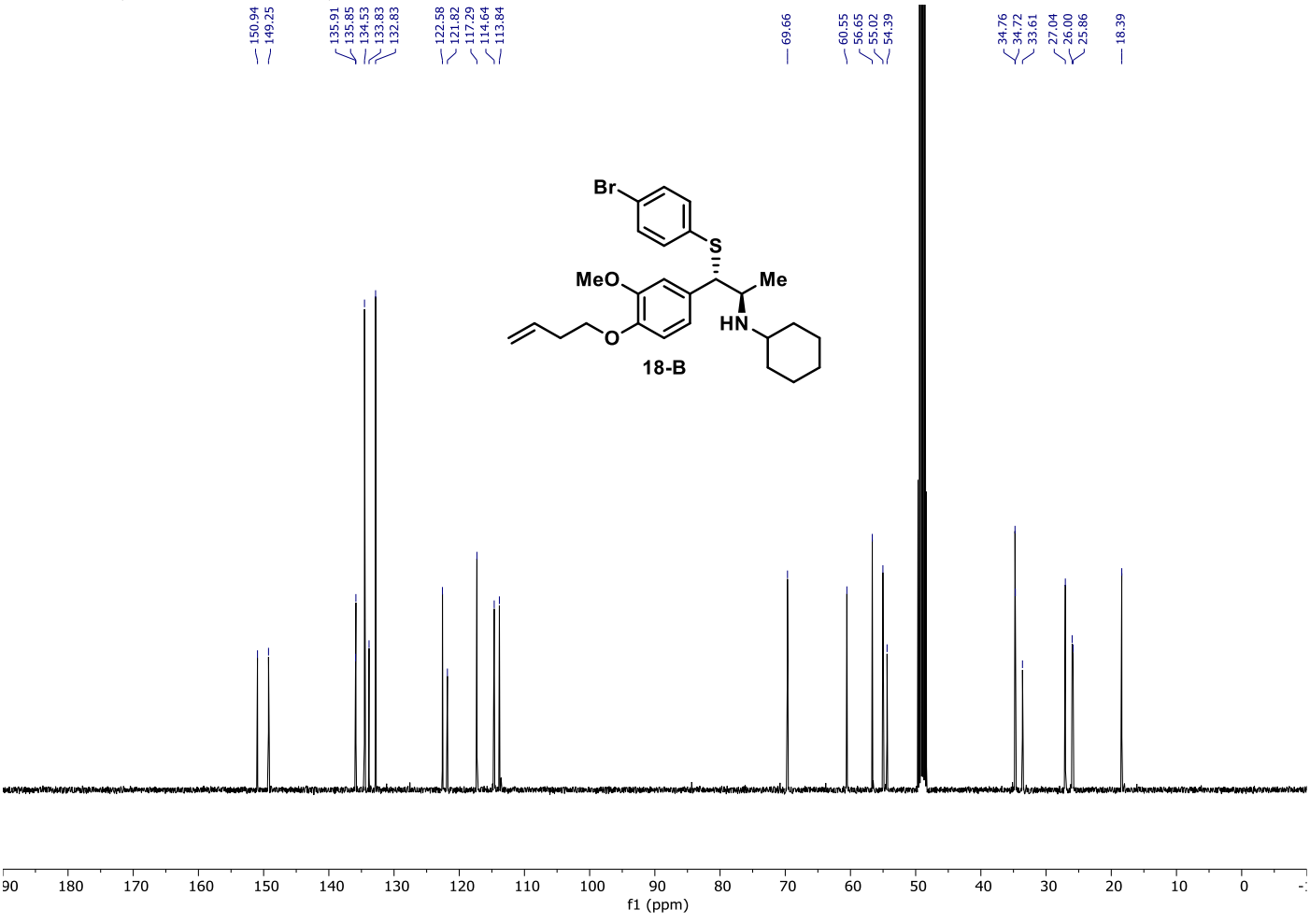
^{13}C NMR (101 MHz, CD_3OD)



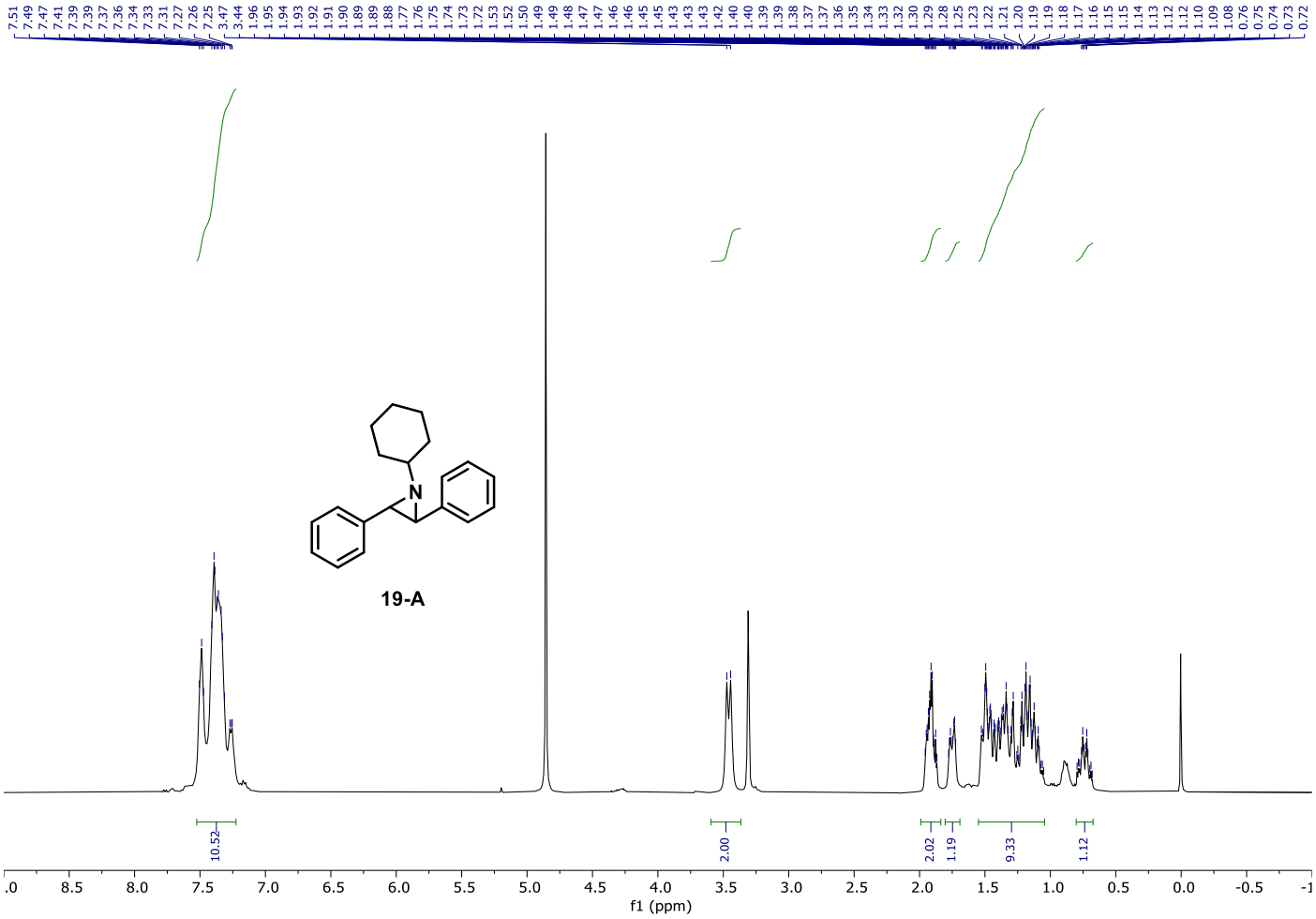
^{1}H NMR (400 MHz, CD_3OD)



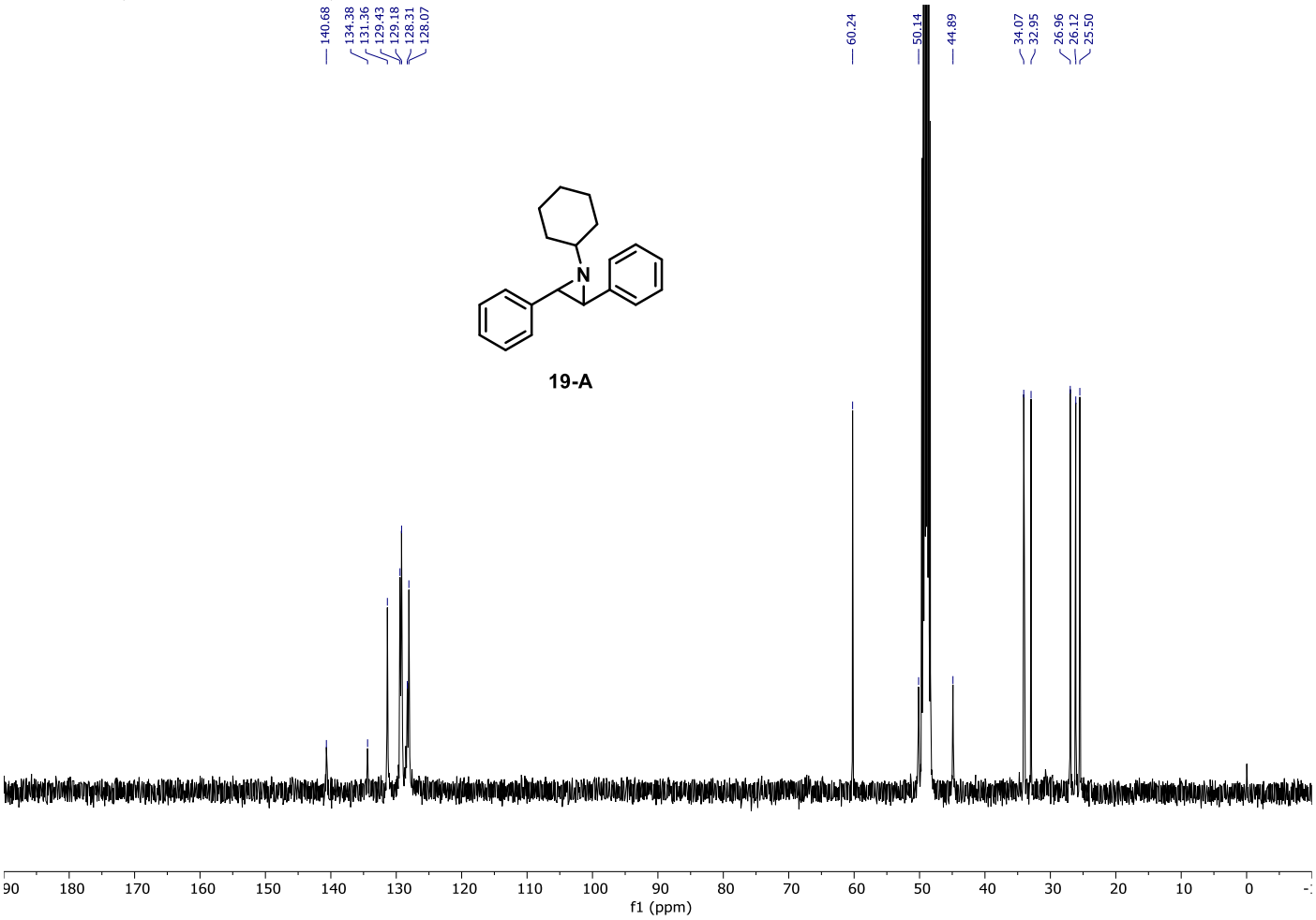
^{13}C NMR (101 MHz, CD_3OD)



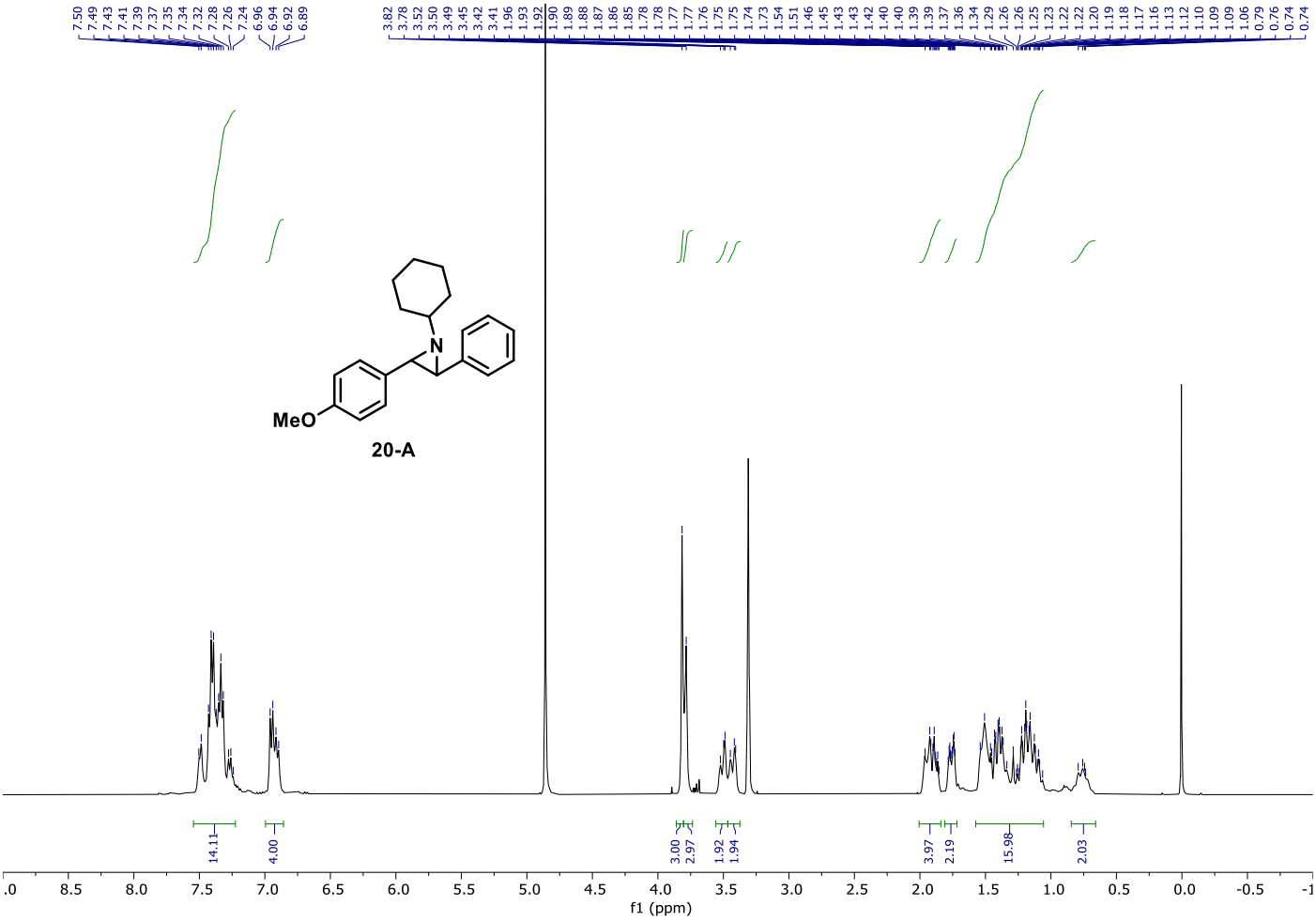
^{1}H NMR (400 MHz, CD_3OD)



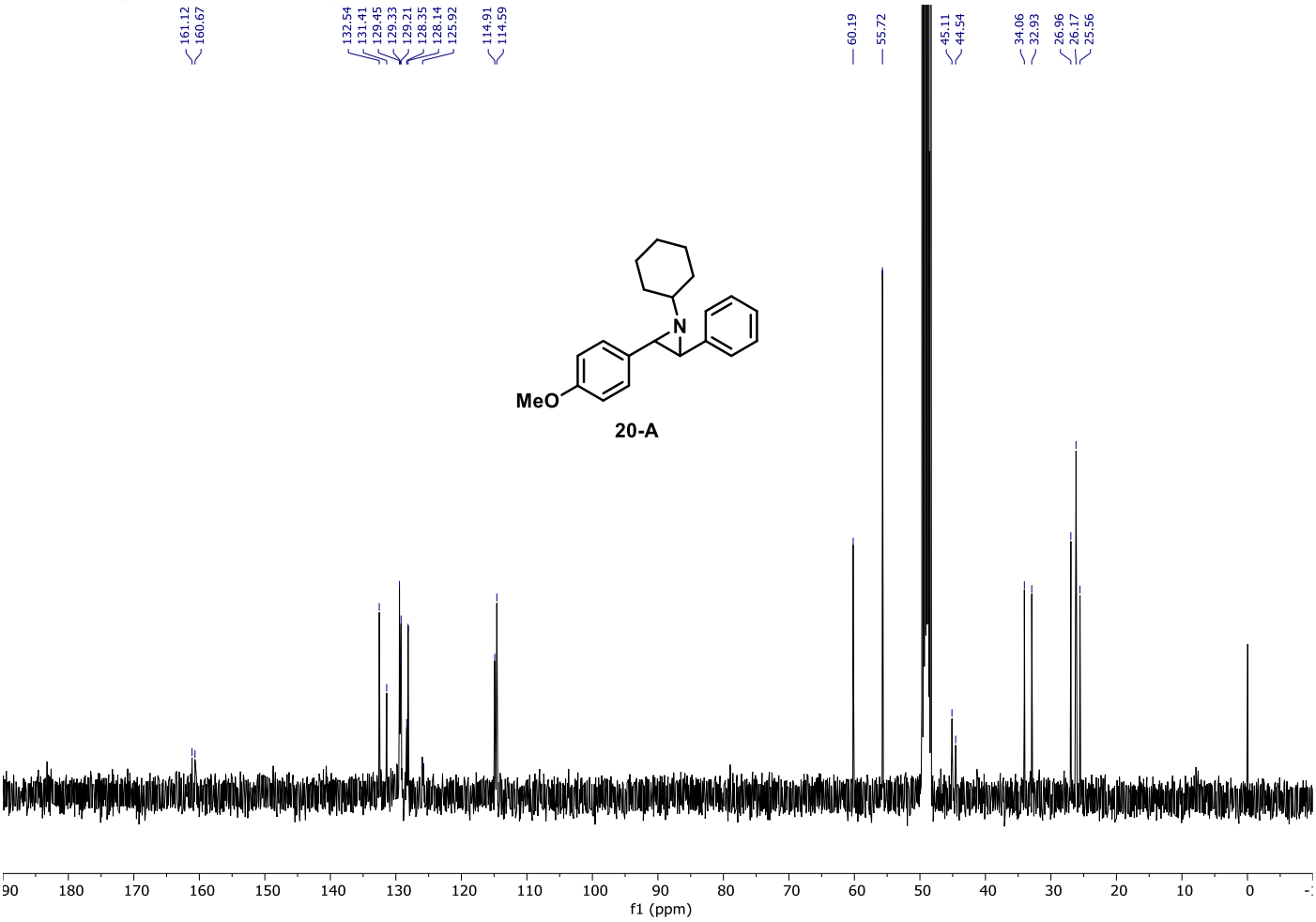
^{13}C NMR (101 MHz, CD_3OD)



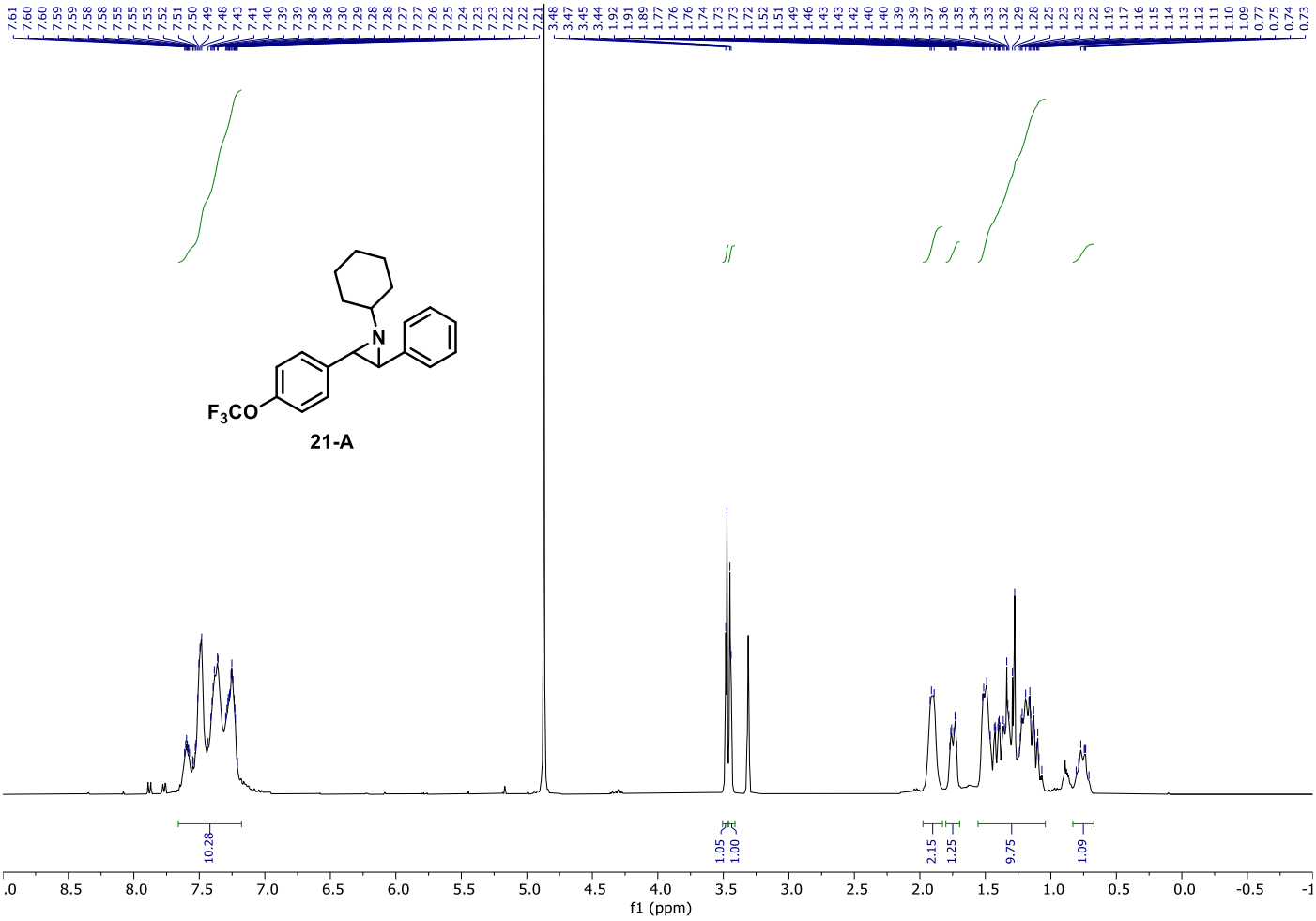
^{1}H NMR (400 MHz, CD_3OD)



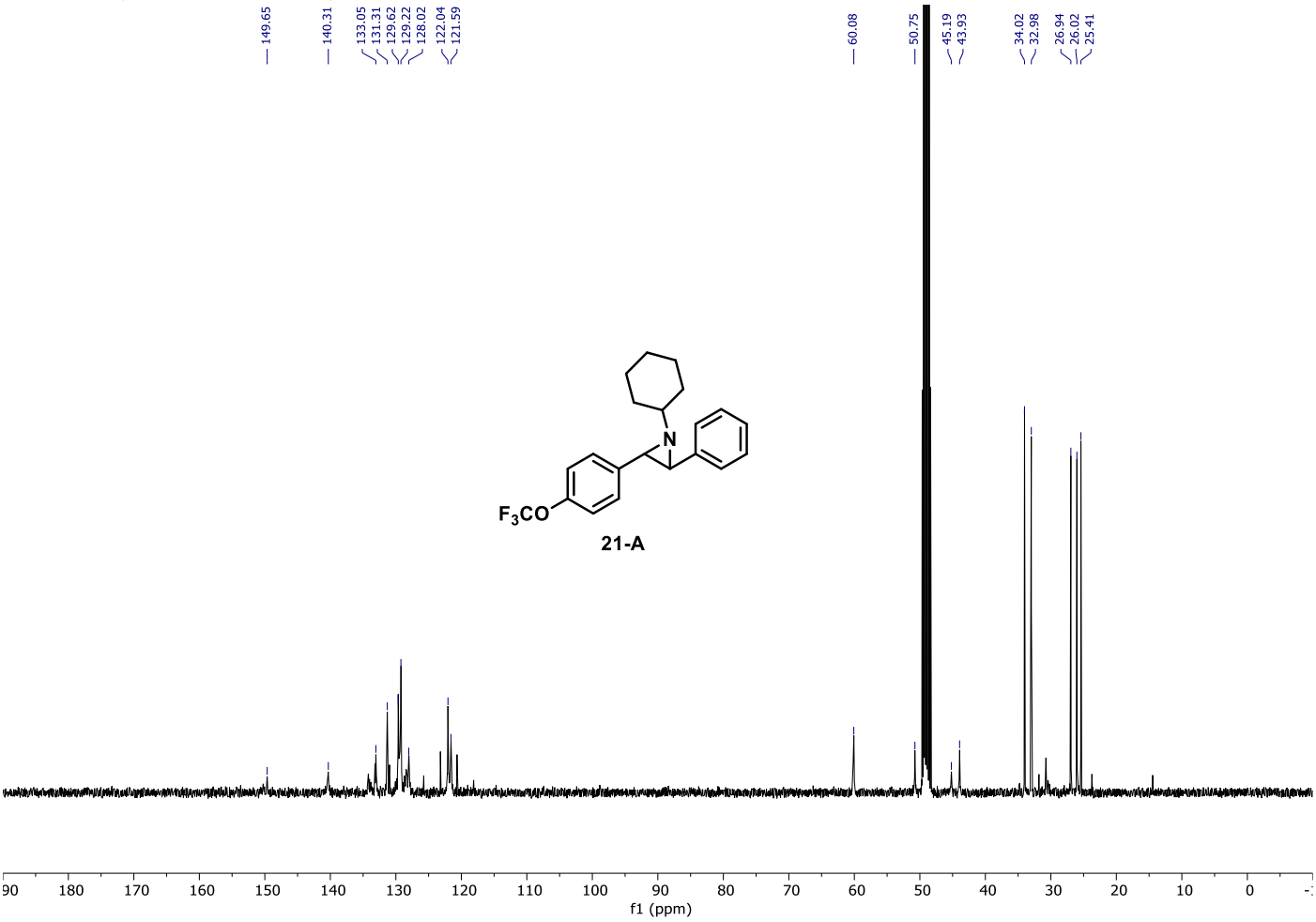
^{13}C NMR (101 MHz, CD_3OD)



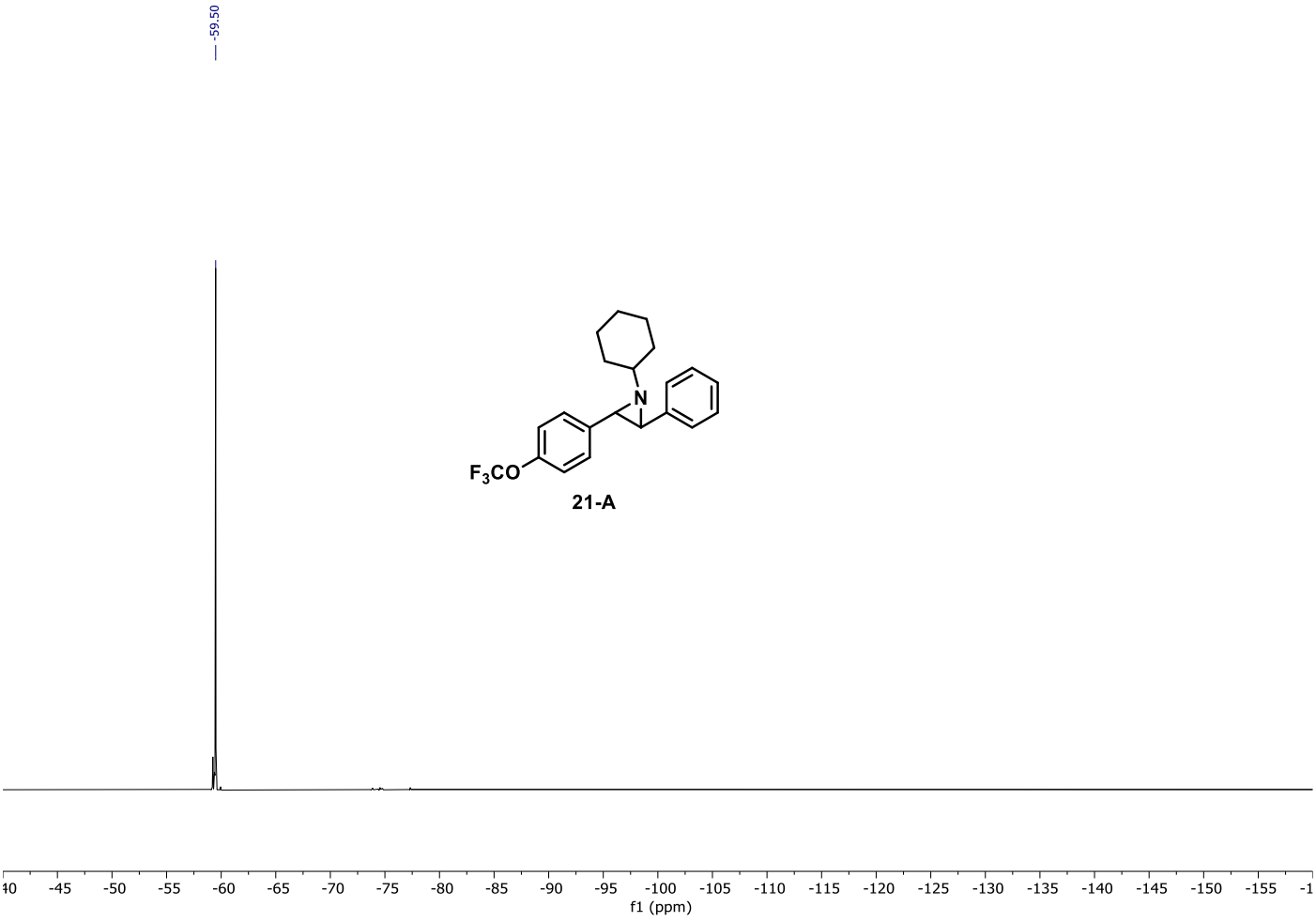
^{1}H NMR (400 MHz, CD_3OD)



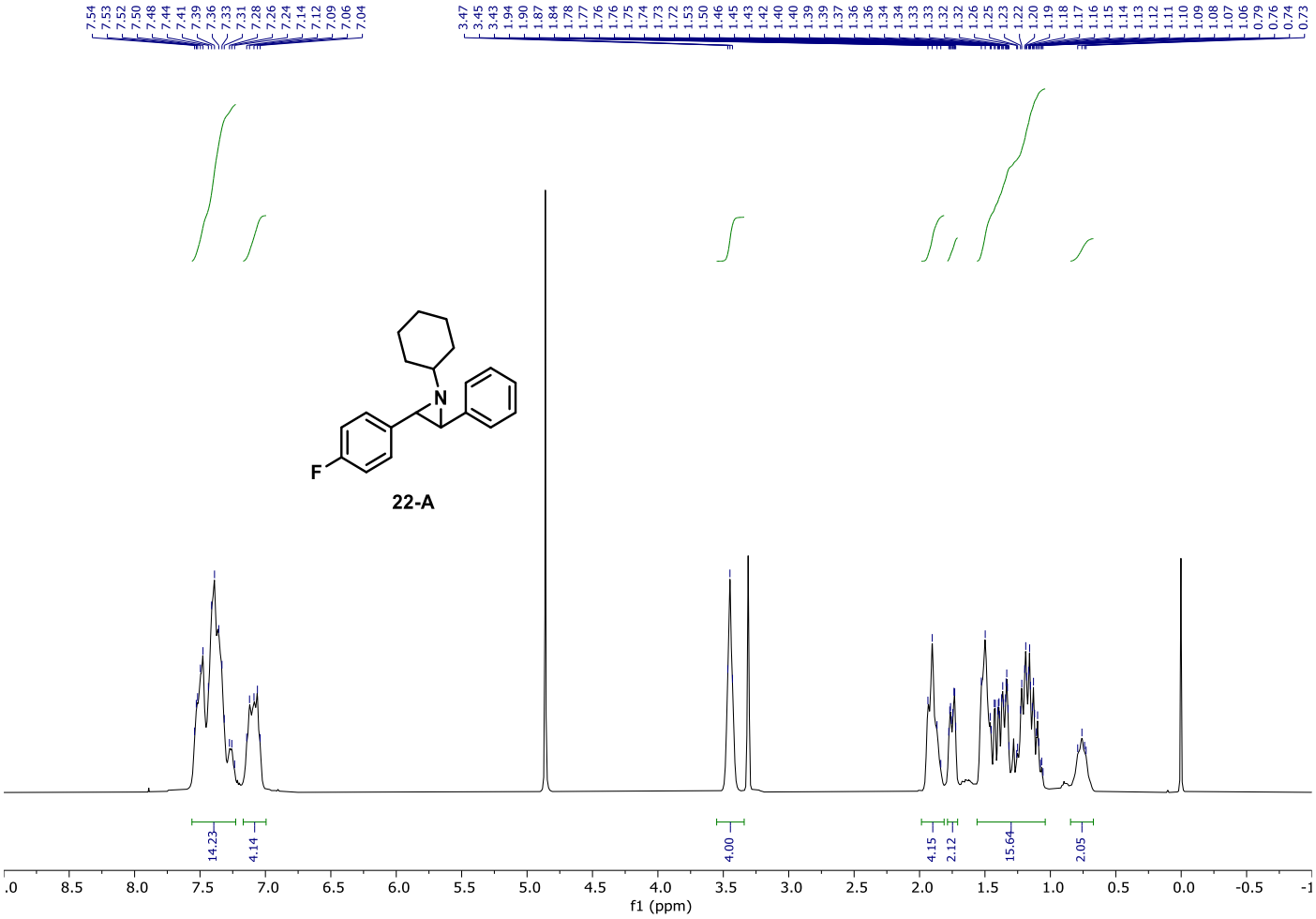
^{13}C NMR (101 MHz, CD_3OD)



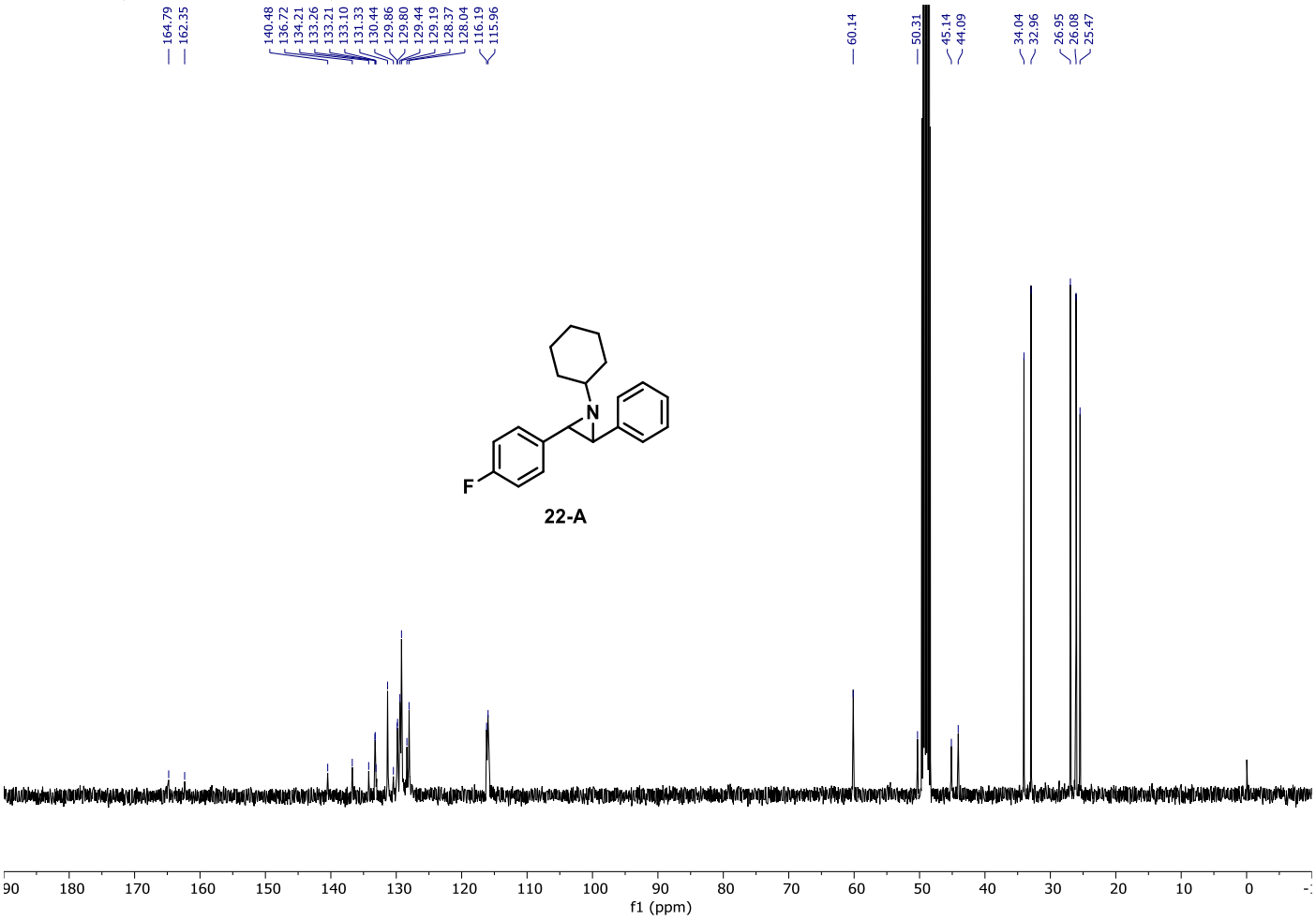
^{19}F NMR (376 MHz, CD_3OD)



^{1}H NMR (400 MHz, CD_3OD)

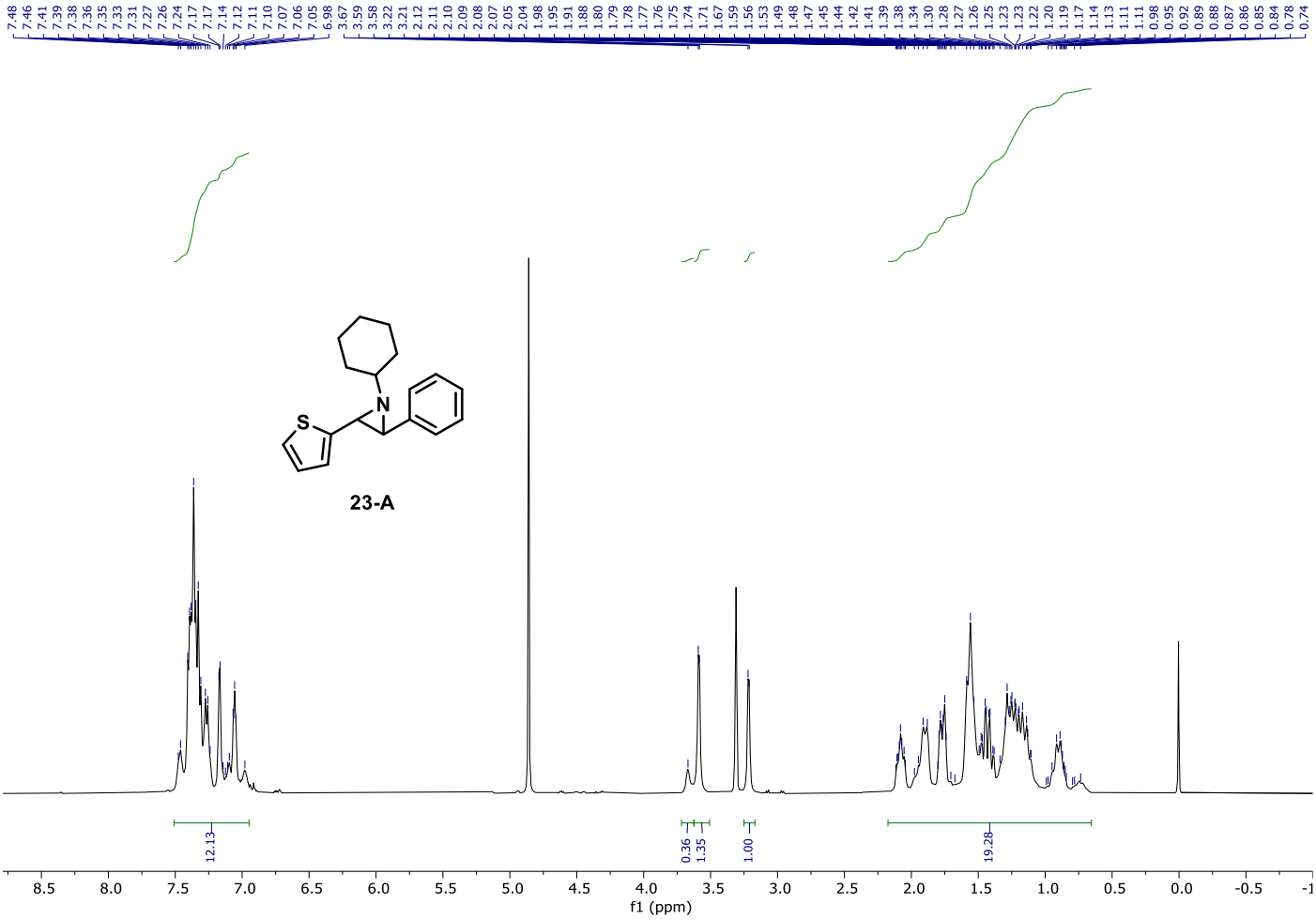


^{13}C NMR (101 MHz, CD_3OD)

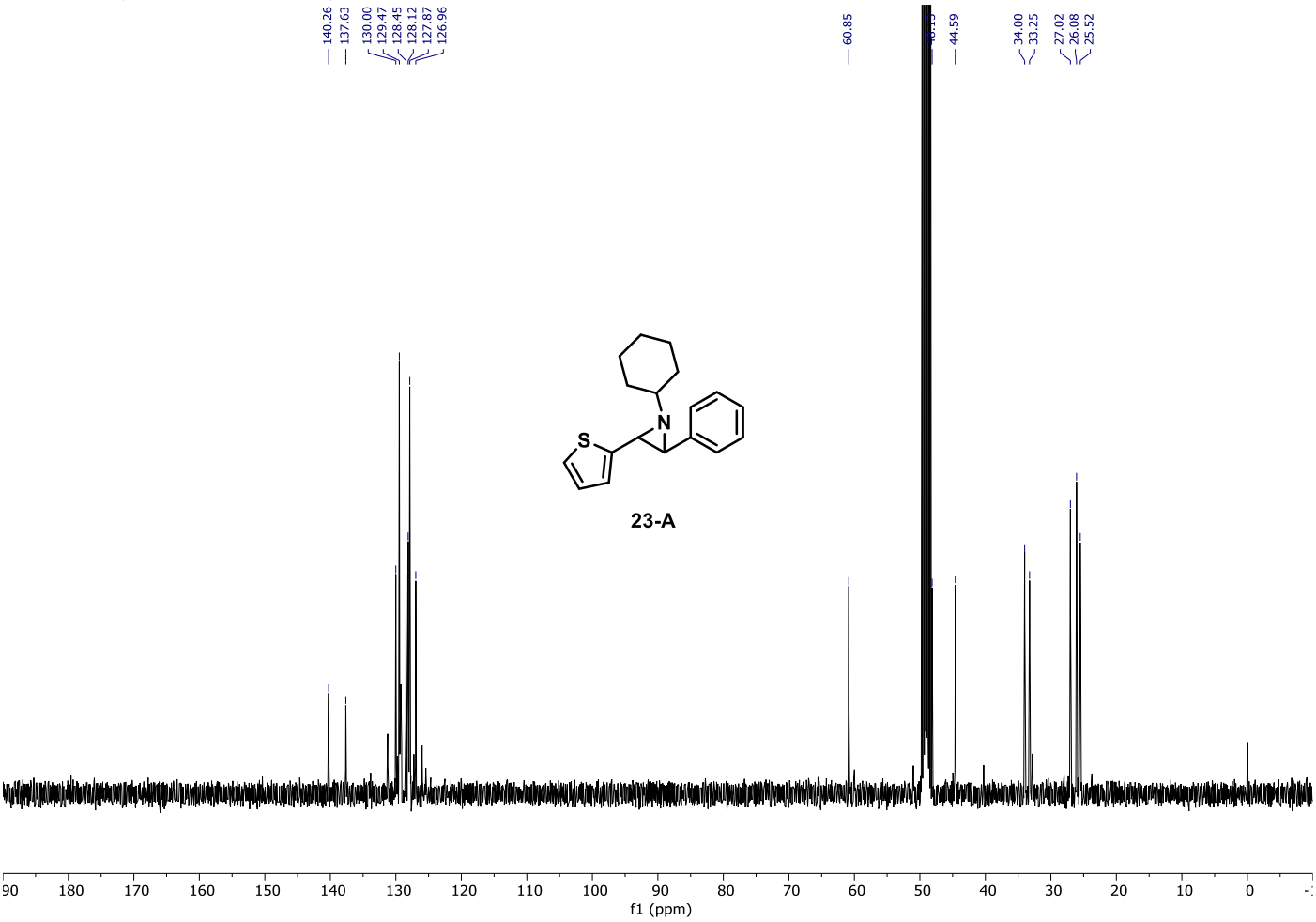


^{19}F NMR (376 MHz, CD_3OD)

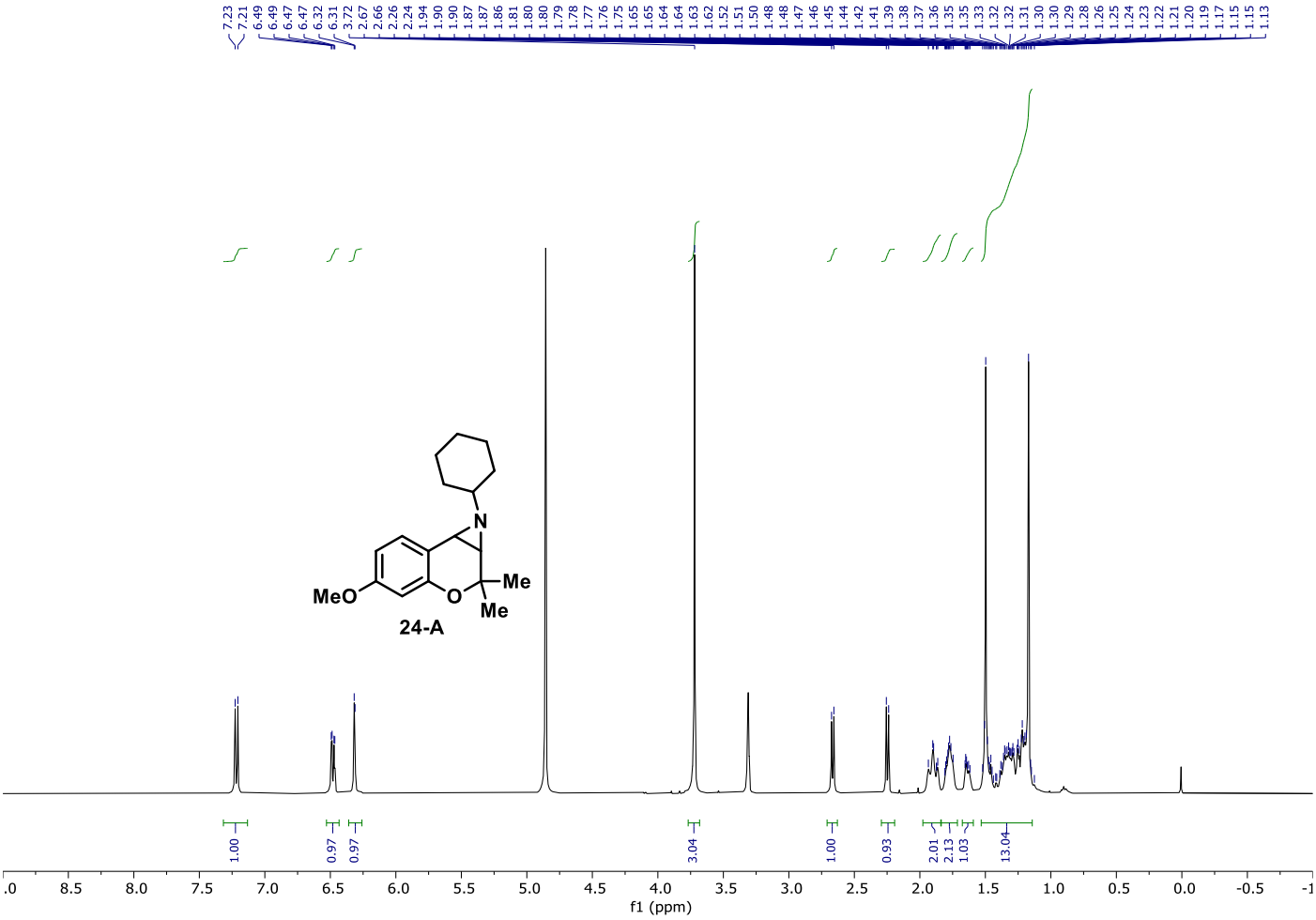
^{1}H NMR (400 MHz, CD_3OD)



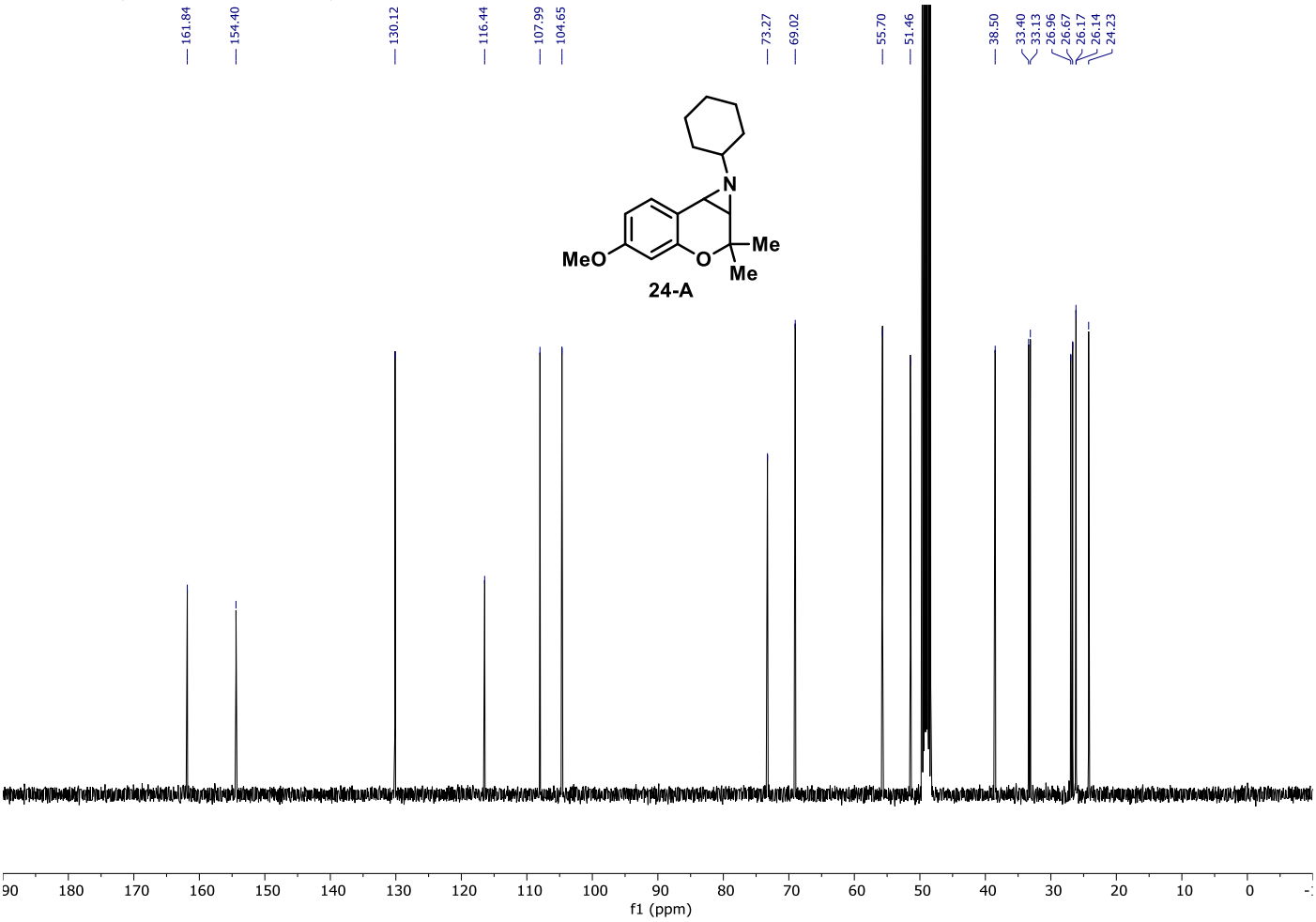
^{13}C NMR (101 MHz, CD_3OD)



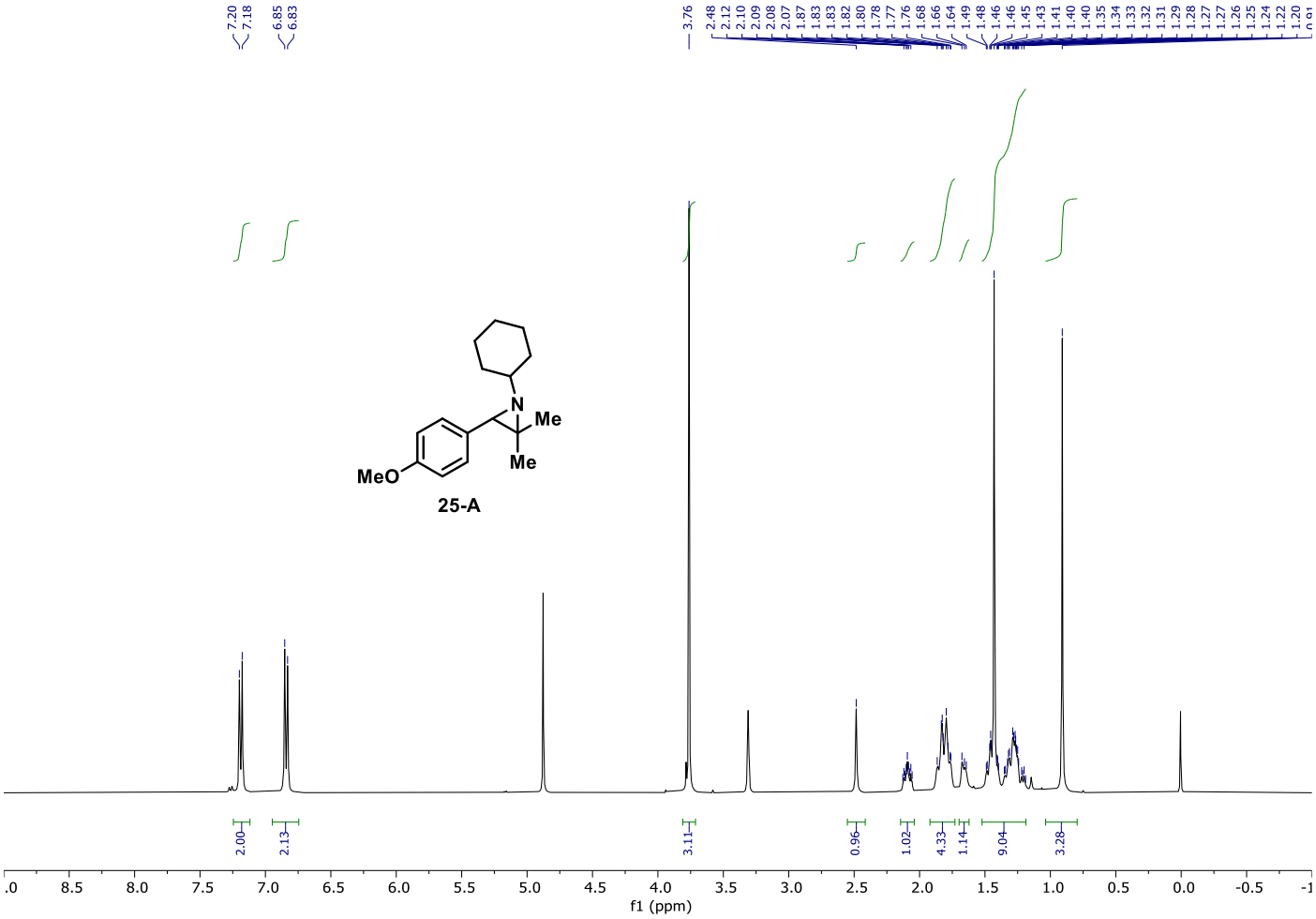
^{1}H NMR (400 MHz, CD_3OD)



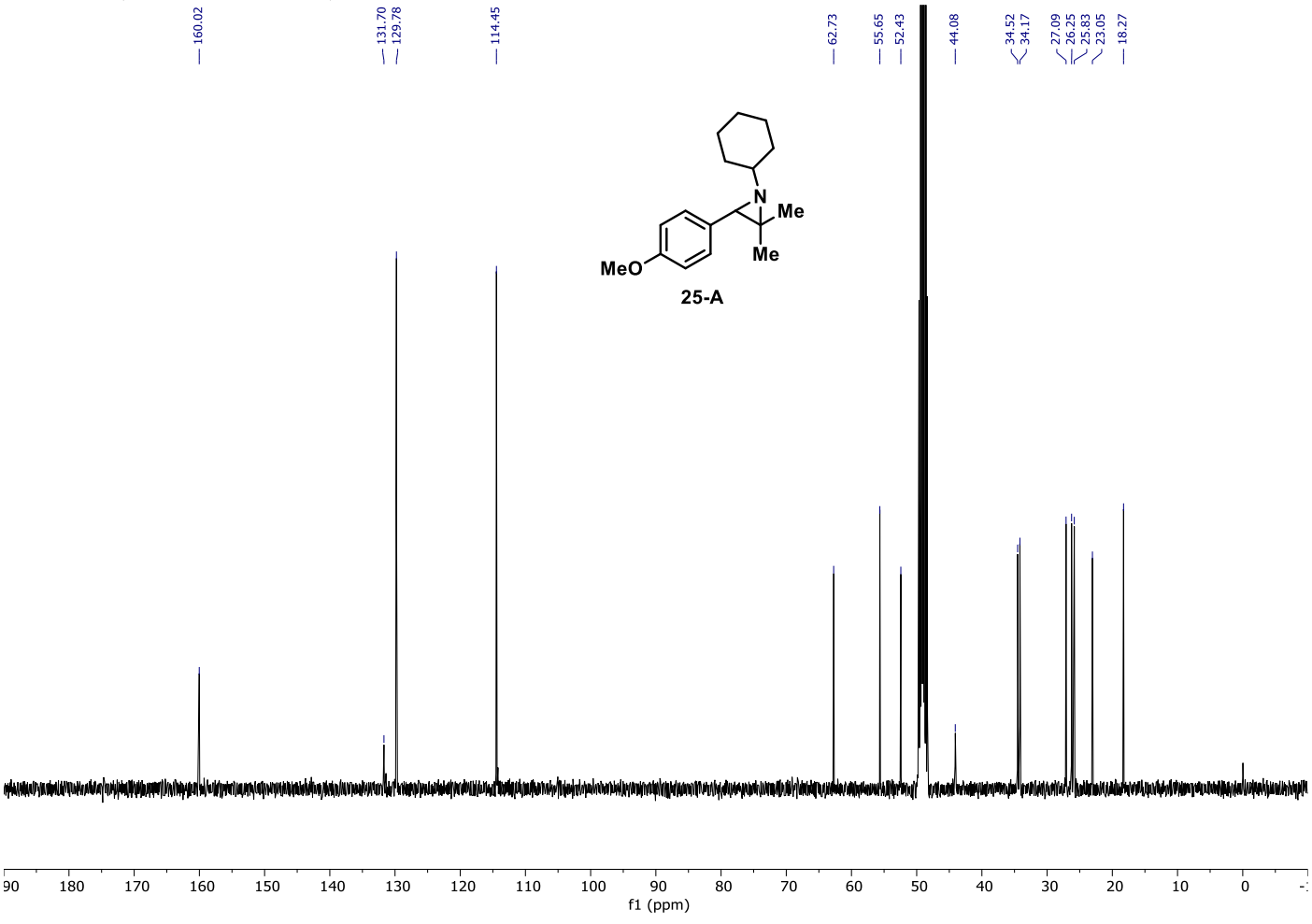
^{13}C NMR (101 MHz, CD_3OD)



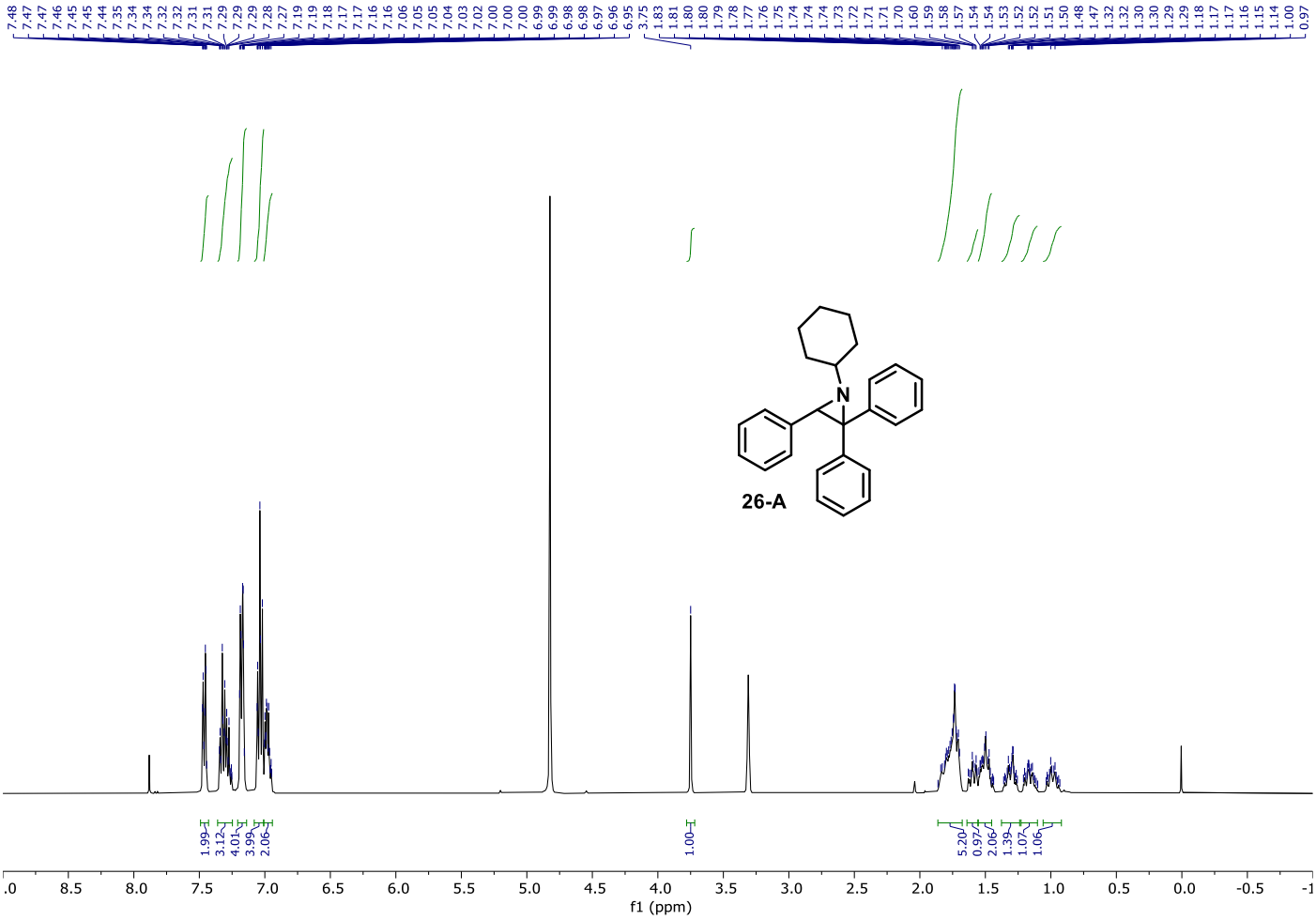
^{1}H NMR (400 MHz, CD_3OD)



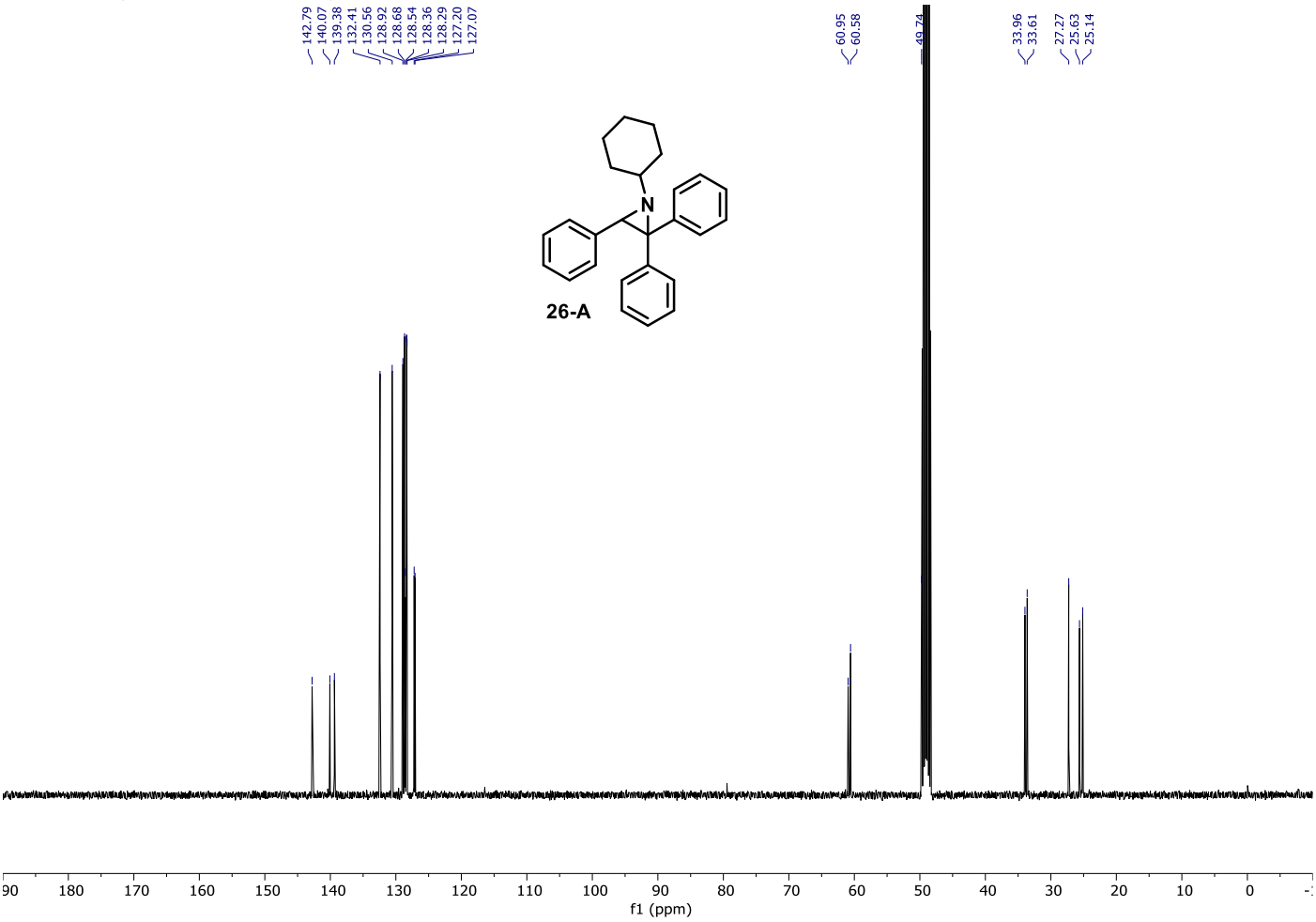
^{13}C NMR (101 MHz, CD_3OD)



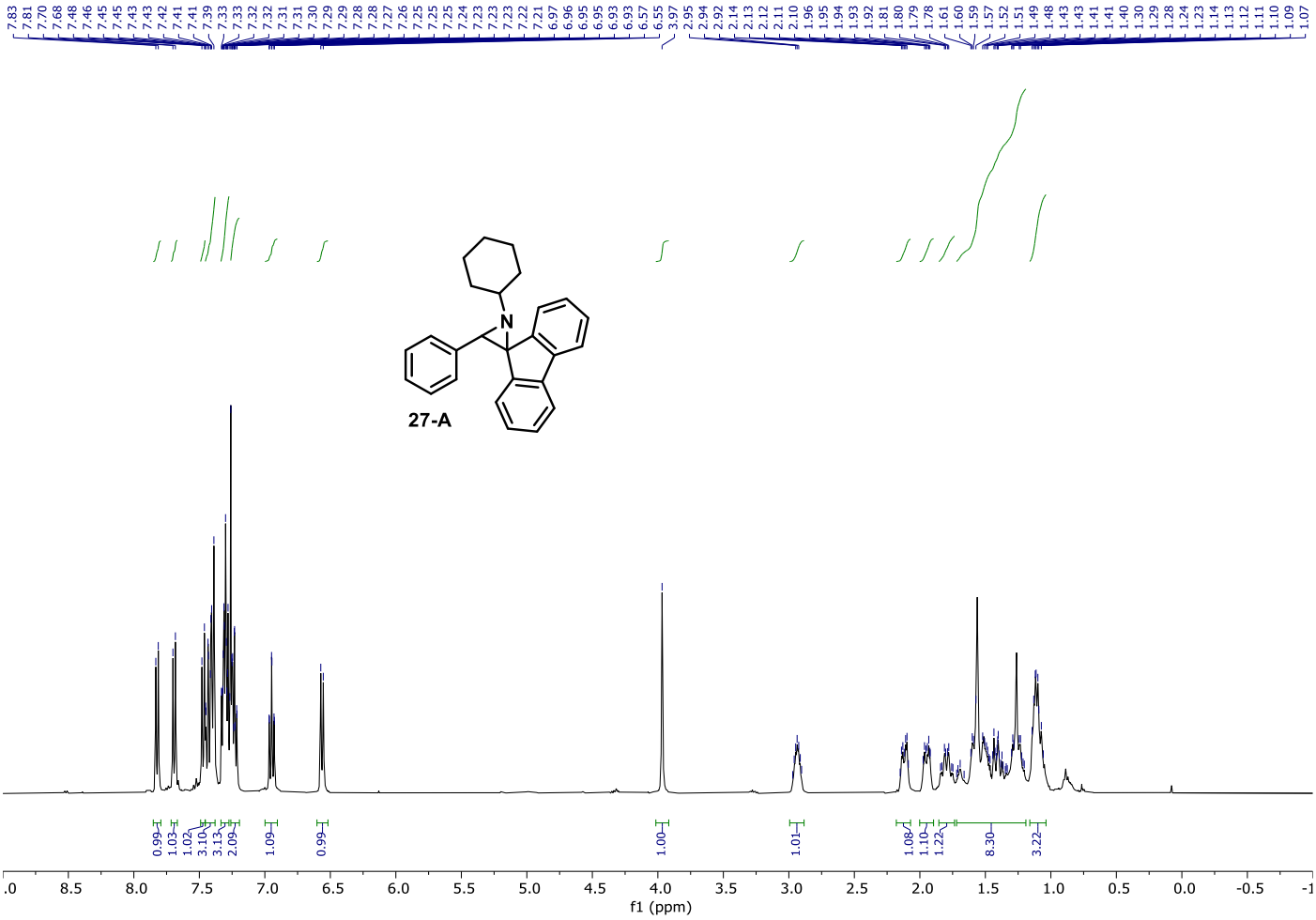
^{1}H NMR (400 MHz, CD_3OD)



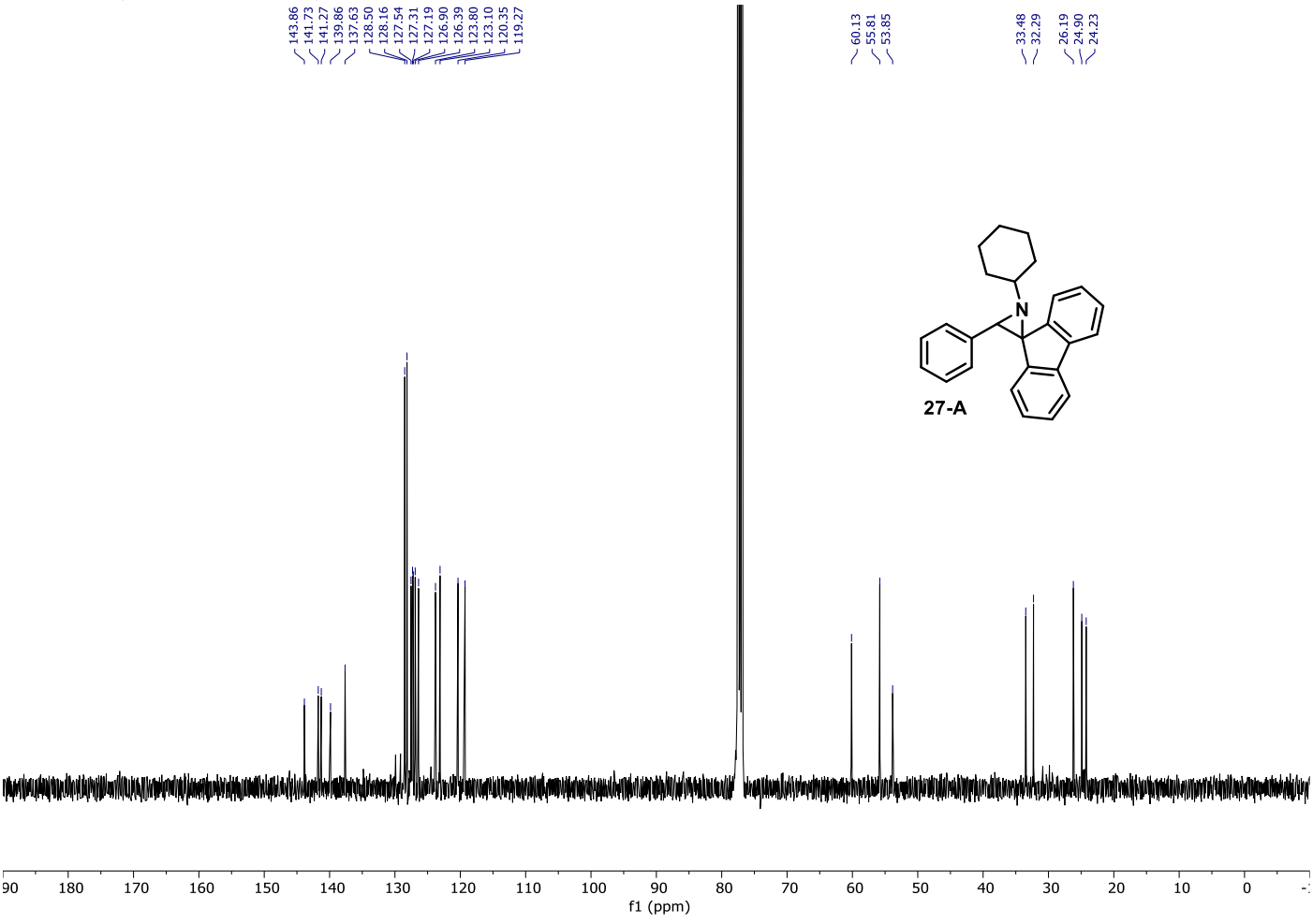
^{13}C NMR (101 MHz, CD_3OD)



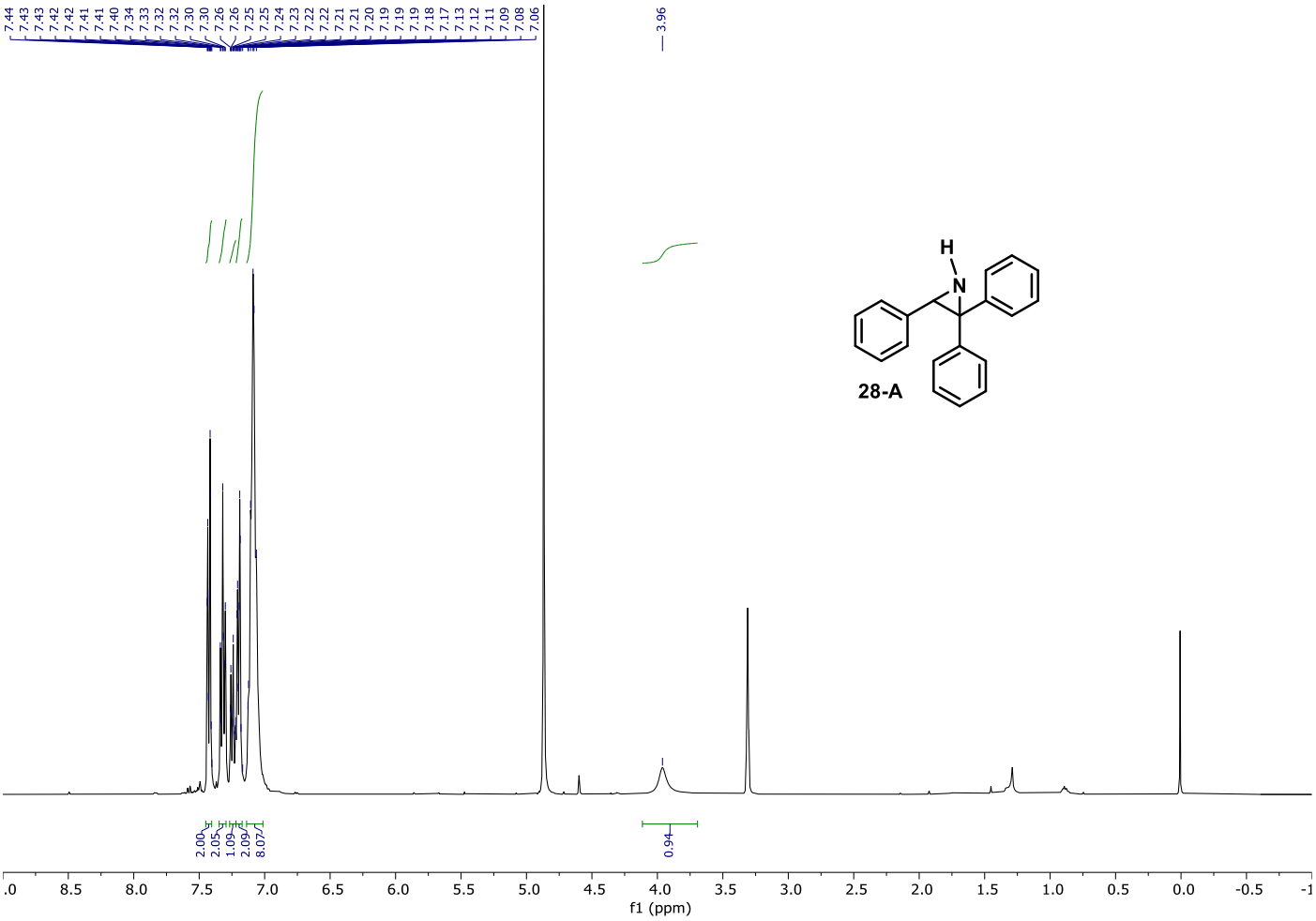
^{1}H NMR (400 MHz, CD_3Cl)



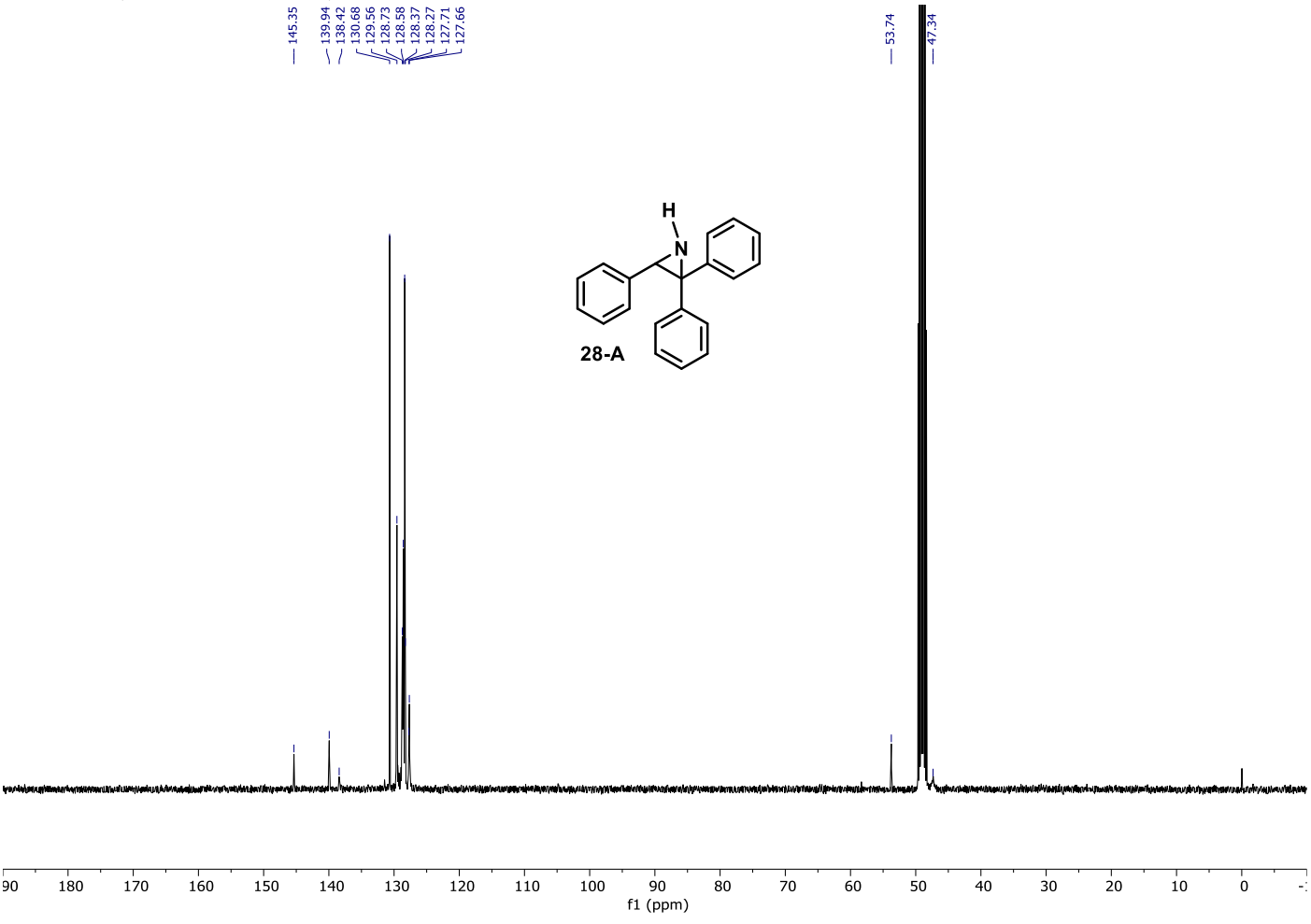
^{13}C NMR (101 MHz, CD_3Cl)



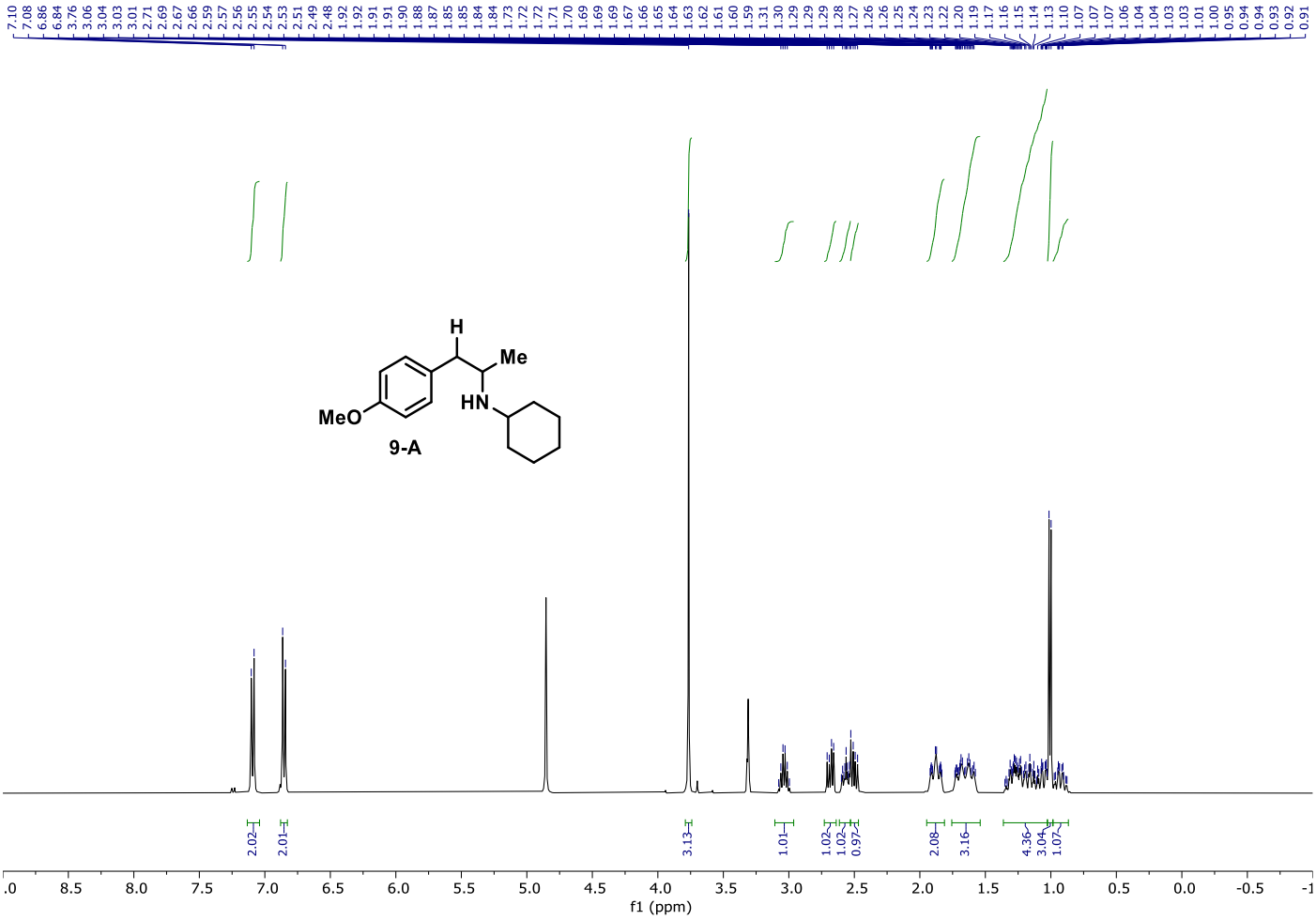
^{1}H NMR (400 MHz, CD_3OD)



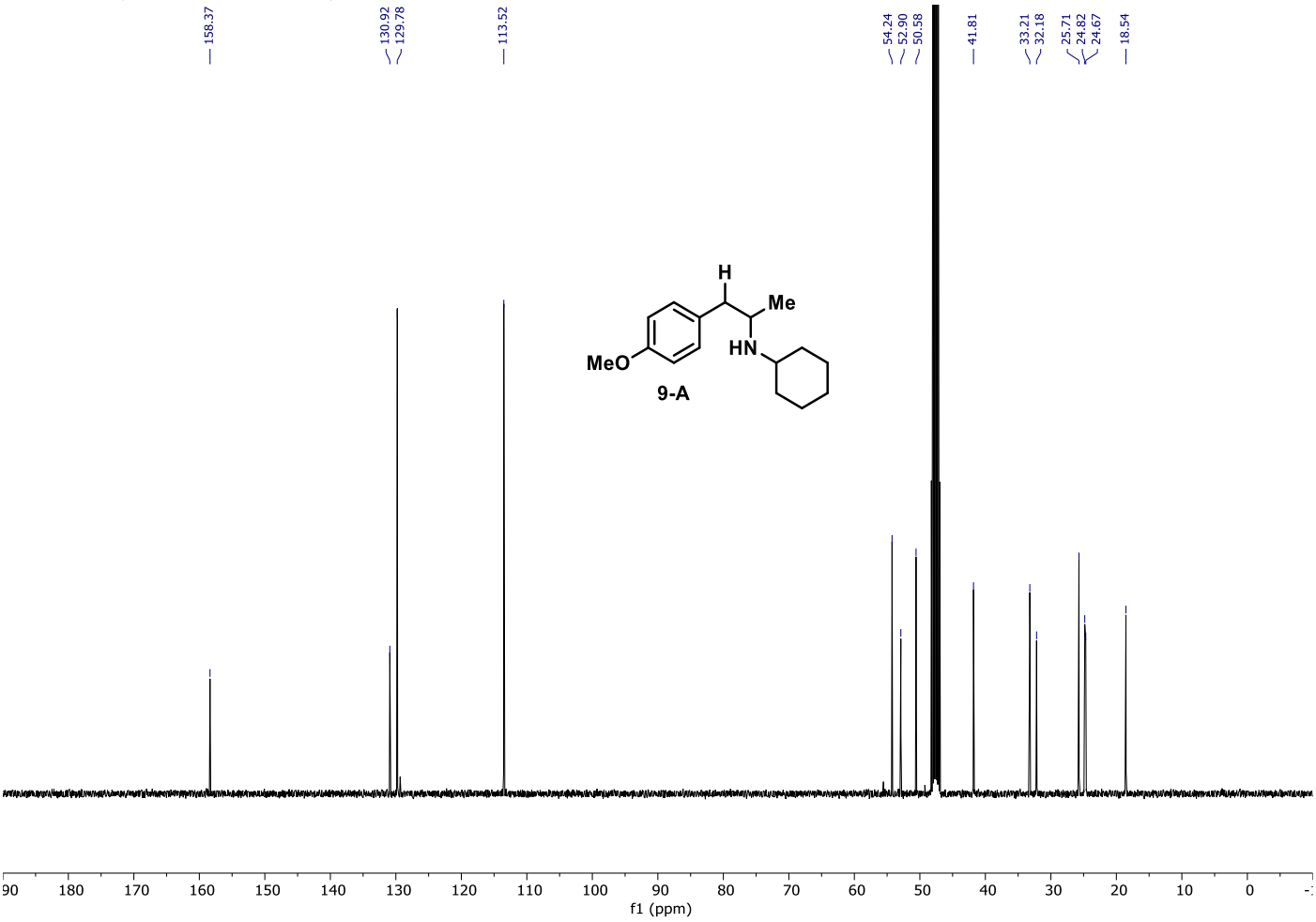
^{13}C NMR (101 MHz, CD_3OD)



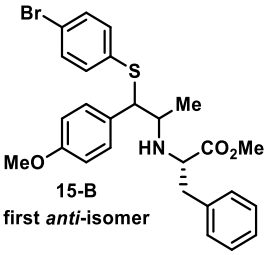
^{1}H NMR (400 MHz, CD_3OD)



^{13}C NMR (101 MHz, CD_3OD)

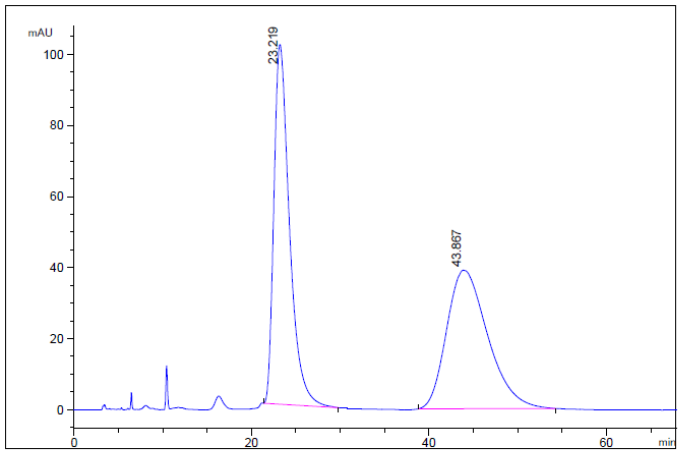


11. Chiral HPLC



15-B
first *anti*-isomer

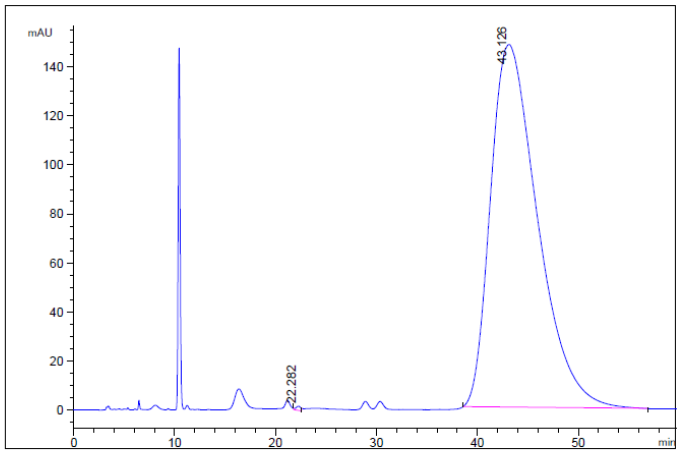
Chiral HPLC of racemic **first *anti*-isomer 15-B**



Signal 1: VWD1 A, Wavelength=265 nm

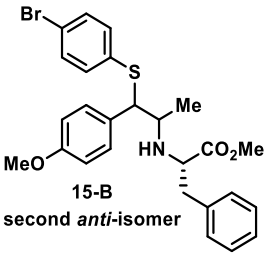
Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	23.219	BB	1.813	12349.408	49.568	
2	43.867	BB	3.794	12564.585	50.432	

Chiral HPLC of **first *anti*-isomer 15-B**



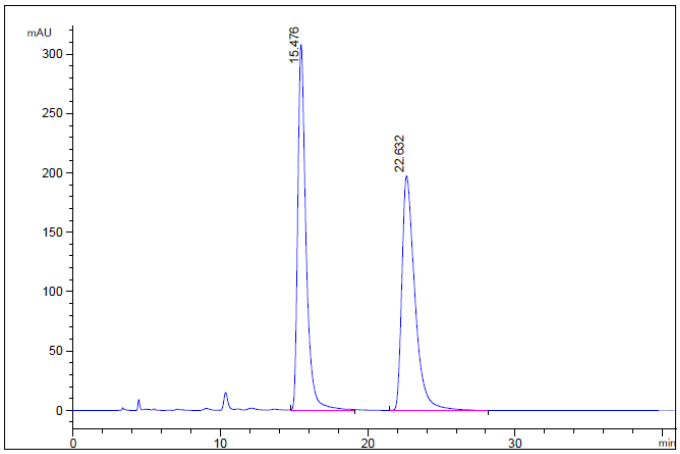
Signal 1: VWD1 A, Wavelength=265 nm

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	22.282	MM	0.548	57.286	0.120	
2	43.126	BB	3.941	47866.309	99.880	



15-B
second *anti*-isomer

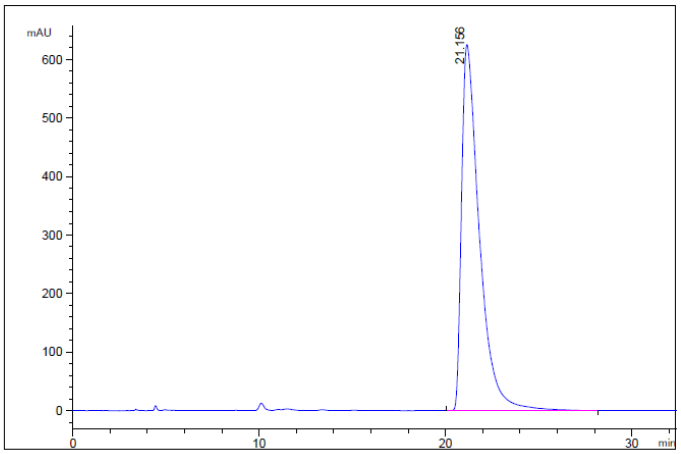
Chiral HPLC of racemic **second *anti*-isomer 15-B**



Signal 1: VWD1 A, Wavelength=265 nm

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	15.476	MM	0.653	12077.081	50.050	
2	22.632	BB	0.900	12052.797	49.950	

Chiral HPLC of **second *anti*-isomer 15-B**



Signal 1: VWD1 A, Wavelength=265 nm

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	21.156	BB	0.998	41554.102	100.000	

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