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Supplemental Information

Electrochemical Aziridination of Internal Alkenes with Primary Amines

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I. Supplemental Experimental Procedures

1. General information

Reagents and dry solvents were bought from Sigma Aldrich, TCI and Fluorochem and are used as received. 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 Spherical 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). ¹H (400 MHz), ¹⁹F (377 MHz) and ¹³C (100 MHz) spectra were recorded on ambient temperature using a Bruker-Avance 400. ¹H NMR spectra are reported in parts per million (ppm) downfield relative to CD₃OD (3.31 ppm) or CDCl₃ (7.26 ppm) and ¹³C NMR spectra are reported in ppm relative to CD₃OD (49.00 ppm) or CDCl₃ (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 ¹H NMR and ¹³C 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

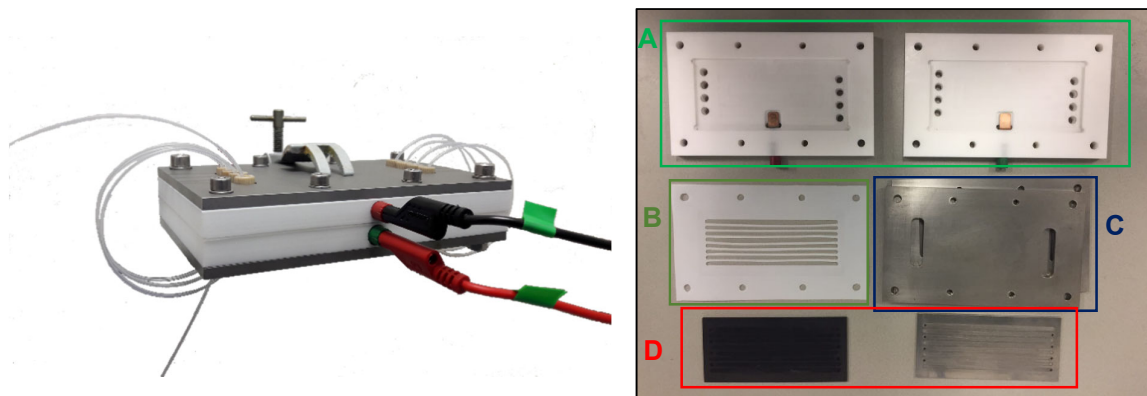


Figure S1: **Left** - Assembled Flow reactor. **Right** - Components of the electrochemical flow cell. **A:** PTFE electrode holders. **B:** PTFE gasket (8 channel configuration). **C:** Outer Stainless Steel plates. **D:** Electrodes (Left Graphite, Right Stainless Steel).

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 (12 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

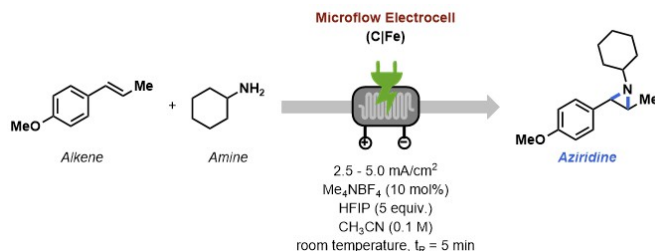


Table S1: Equivalents of amine

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, Me₄NBF₄ (10 mol%), HFIP (5 equiv.), CH₃CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm². 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

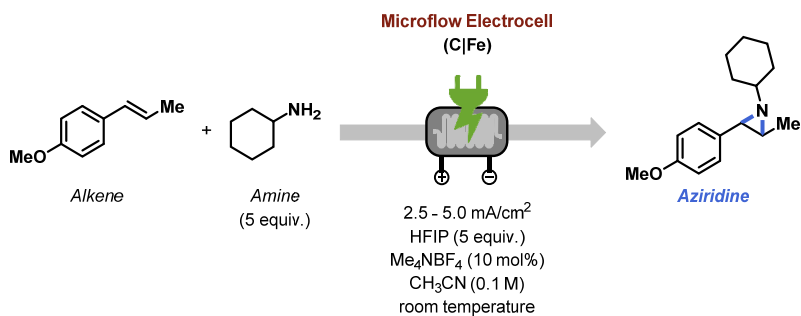


Table S2: Residence time optimization

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

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), Me₄NBF₄ (10 mol%), HFIP (5 equiv.), CH₃CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm². 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

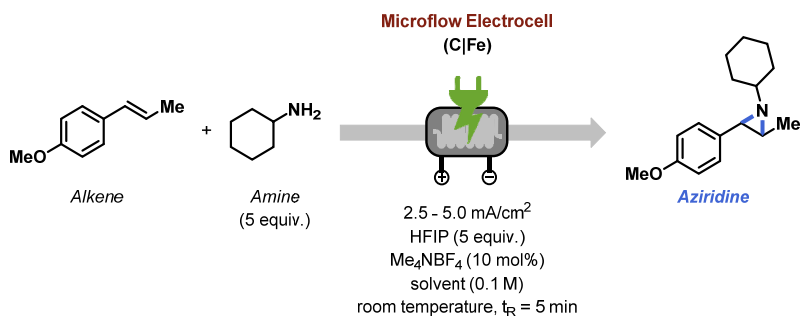


Table S3: Solvent screening

Entry	Solvent	Yield (%)
1	CH ₃ CN	73
2	HFIP	11
3 ^[a]	anhydrous CH ₃ CN	77

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), Me₄NBF₄ (10 mol%), HFIP (5 equiv.), solvent (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm². Yield determined by GC-FID with biphenyl as internal standard. ^[a] Anhydrous acetonitrile was purchased from Sigma-Aldrich and used as received.

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

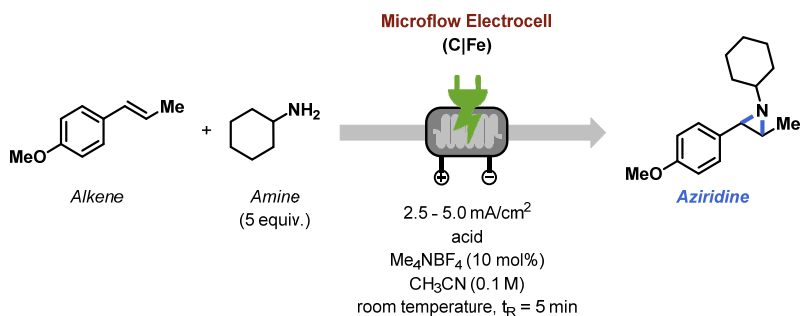


Table S4: Acid screening

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 ₃ CH ₂ OH (5 equiv.)	65
6	3M HCl (0.75 equiv.)	53
7	3M H ₂ SO ₄ (0.75 equiv.)	57
8	<i>p</i> -TsOH (1 equiv.) + H ₂ O (1.5 mL)	32
9	PhCOOH (1 equiv.) + H ₂ O (1.5 mL)	49

Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), Me₄NBF₄ (10 mol%), CH₃CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm². 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

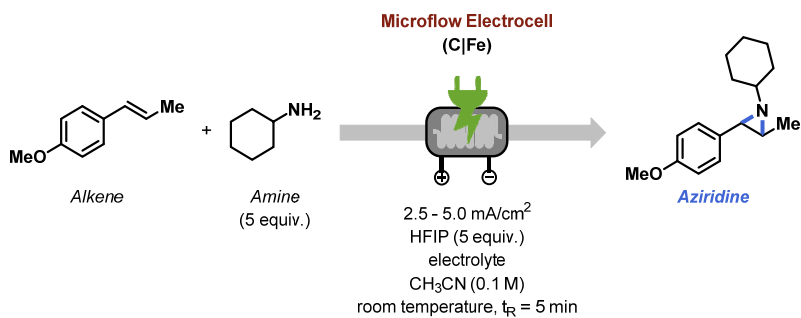


Table S5: Electrolyte screening

Entry	Electrolyte	Yield (%)
1	Me ₄ NBF ₄ (10 mol%)	73
2	Me ₄ NBF ₄ (50 mol%)	79
3	Me ₄ NBF 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.), CH₃CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm². 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

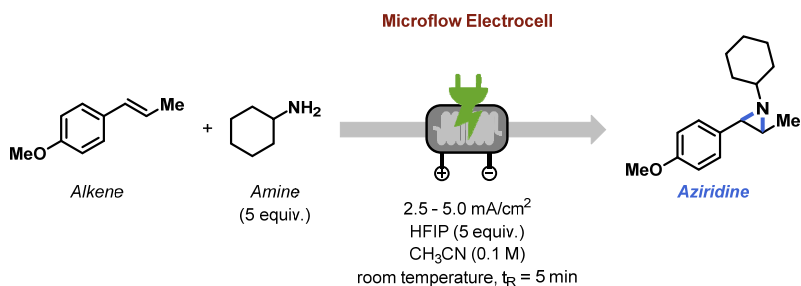


Table S6: Electrode material

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.), CH₃CN (0.1 M), 2.5-5 mA/cm². 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. Moreover, when reductive additives were introduced, the nickel electrode did not demonstrate any increased performance compared to stainless steel. For this reason, we decided to continue our research using a combination of a steel cathode and graphite anode (Table S6, Entry 1). The use of this electrode combination is also advantageous from the vantage point of cost and safety (e.g. copper or nickel leaching vs. iron).

2.7. Additive screening

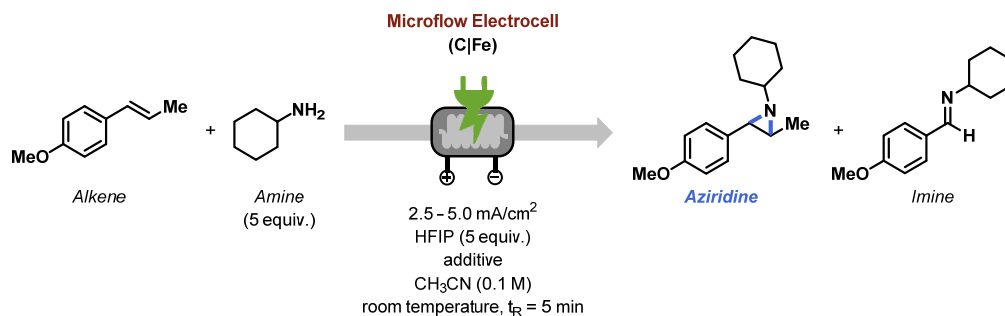


Table S7: Additive screening

Entry	Additive	Aziridine yield (%)	Imine yield (%)
1	No additive	78	15
2	Ph ₃ SiH (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

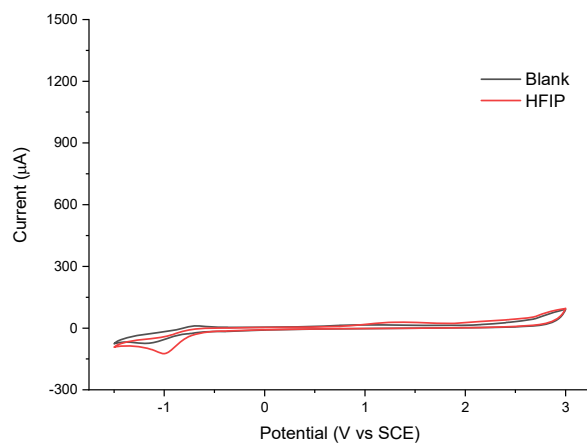
Reaction Conditions: anethole (2 mmol), cyclohexylamine (5 equiv.), HFIP (5 equiv.), CH₃CN (0.1 M), C anode/Fe cathode, 2.5-5 mA/cm². Aziridine yield determined by GC-FID with biphenyl as internal standard. Imine yield determined by ¹H NMR with biphenyl as internal standard.

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 a 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).

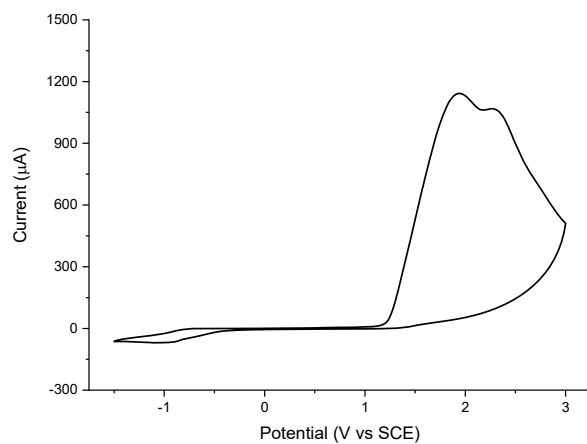
3. Cyclic Voltammetry analysis

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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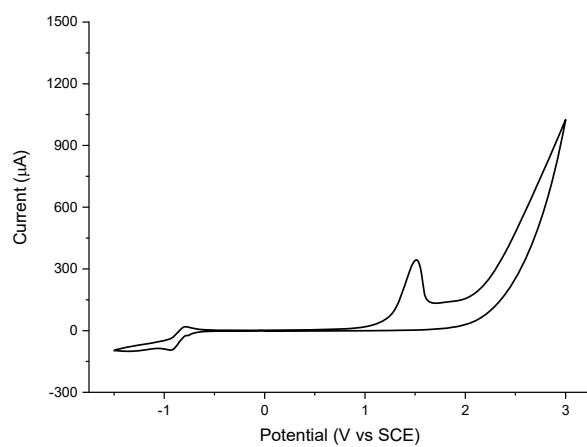


Anethole

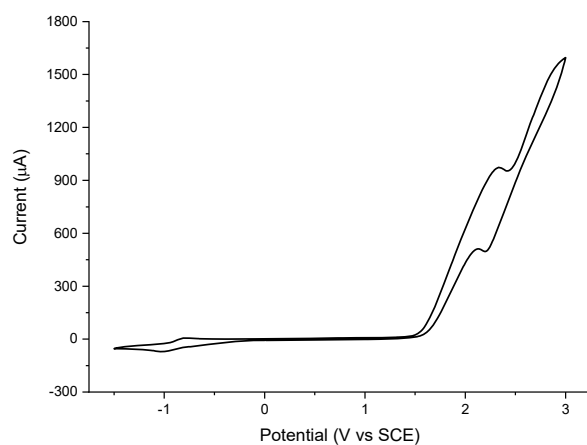


When anethole was scanned, two different oxidation events were observed. We surmise these are correlated to the first and the second oxidation of the double bond. Particularly, the second oxidation event is related to the degradation of the starting material.

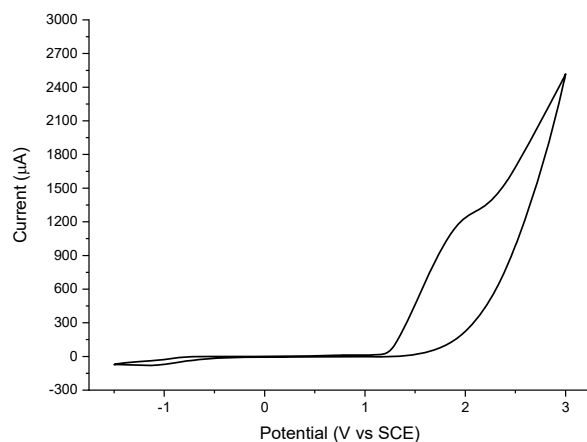
Cyclohexylamine



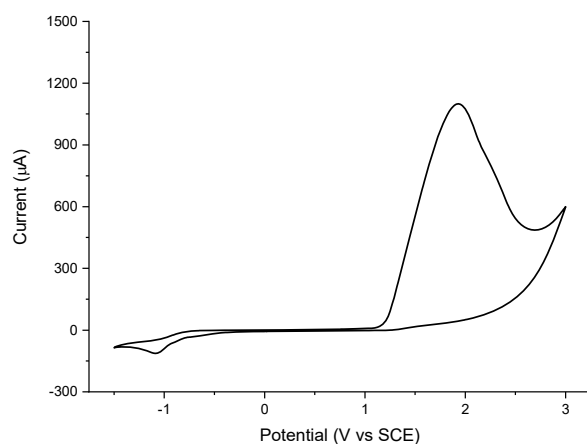
γ-Terpinene



Anethole+ γ -Terpinene

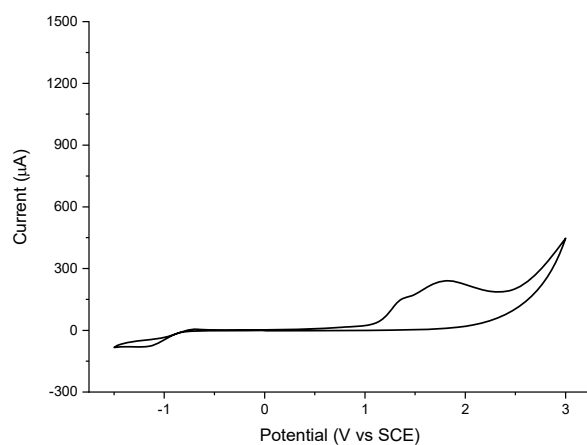


Anethole+ γ -Terpinene+HFIP



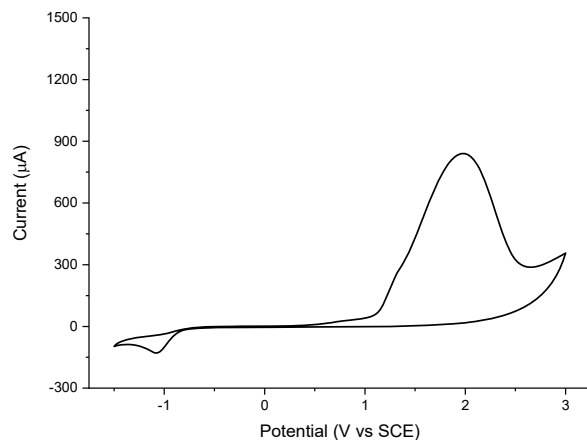
Notably, the addition of γ -terpinene showed that the second oxidation of anethole is attenuated, indicating a beneficial effect of the sacrificial reductant in the reaction (similar results can be observed without HFIP, but the interpretation of the CV is difficult because of the low conductivity).

Anethole+Cyclohexylamine



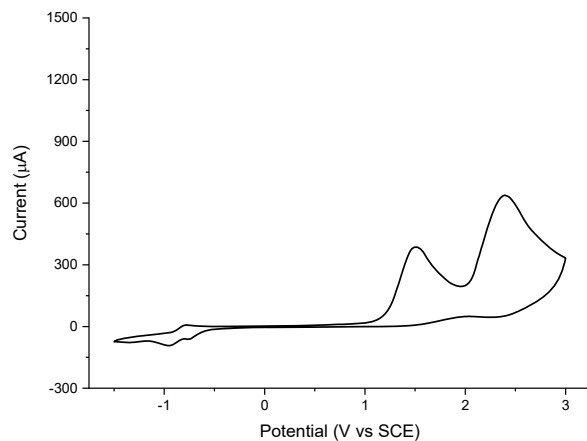
When a mixture of cyclohexylamine and anethole is analyzed, both oxidation events were observed. Moreover, an attenuation of anethole overoxidation was also observed.

Reaction mixture



When a cyclic voltammety 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 voltammety 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 7.3² coupled to the PQS Baker optimizer^{3,4} via the BOpt package.⁵ The geometry optimizations, location of transition states and frequency analysis was performed at the B3LYP^{6,7}/def2-TZVP^{8,9} level of theory (unless noted otherwise) on an m4 grid, using Grimme's version 3 (disp3, "zero damping") dispersion corrections.¹⁰ 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 CH₃CN solvent was achieved by usage of COSMO¹¹ ($\epsilon = 36.6$) in a single point calculation at the B3LYP¹²⁻¹⁴/def2-TZVP^{8,9} 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 ($E^{o,calc}_{1/2}$ in V vs $Fc^{+/0}$) were calculated by first benchmarking the DFT method to literature known oxidation potentials (in V vs $Fc^{+/0}$)¹⁵ 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 1.¹⁶ A correction ($E^{o,corr}_{1/2}$) to report the calculated redox potential versus $Fc^{+/0}$ ($E^{o,FC}_{1/2} = 0.400$ V vs SCE in CH₃CN/[NBu₄]PF₆**Error! Bookmark not defined.**) was achieved via first referencing the calculated redox potential to SHE (absolute value $E^{o,SHE}_{1/2} = 4.281$ V) and then to SCE ($E^{o,SCE}_{1/2} = -0.141$ V vs SHE in CH₃CN). The total correction factor is therefore: $-4.281 - 0.141 - 0.400 = -4.822$ V. To calculate the oxidation potentials versus SCE a correction ($E^{o,corr}_{1/2}$ 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 CH₃CN. 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 CH₃CN 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.

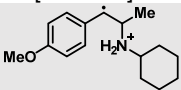
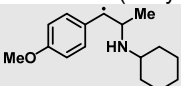
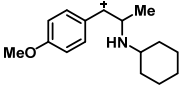
$$\text{Formula 1: } E_{1/2}^{o,calc}(\text{V vs } Fc^{+/0}) = - \frac{(G_{298K}[red] - G_{298K}[ox])}{n_e * F} + E_{1/2}^{o,corr} + C^{DFT}$$

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 Error! Bookmark not defined. (V vs $Fc^{+/0}$)	Calculated redox potential (formula 1) (V vs $Fc^{+/0}$)	Deviation (V)
anethole	-290685.8326	+0.84 Error! Bookmark not defined.	+0.826	-0.014
[anethole] ⁺	-290562.5282			
NEt ₃	-183333.6673	+0.47	+0.496	+0.026
[NEt ₃] ⁺	-183217.9808			
N(2,4,6-tribromophenyl) ₃	-15003845.09	+1.36	+1.389	+0.029
[N(2,4,6-tribromophenyl) ₃] ⁺	-15003708.8			
N(4-bromophenyl) ₃	-5314747.206	+0.67	+0.722	+0.052
[N(4-bromophenyl) ₃] ⁺	-5314626.292			
thianthrene	-789516.2677	+0.86	+0.764	-0.096
[thianthrenium] ⁺	-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	Multiplicity	<s2>	SCF (Hartree)	ZPE correction (Hartree)	Enthalpy correction (Hartree)	Entropy correction (Hartree)	ΔG_{0298K} (Hartree)
1	anethole	1	-	-463.39826	0.19325	0.20509	0.15612	-463.24214
2	[anethole] ⁺	2	0.764 2	-463.20270	0.19373	0.20560	0.15706	-463.04564
3	NH ₂ -C ₆ H ₁₁	1	-	-291.15729	0.18712	0.19499	0.15678	-291.00051
4	[NH ₂ -C ₆ H ₁₁] ⁺	2	0.755 1	-290.94233	0.18507	0.19331	0.15445	-290.78788
5	[NH ₃ -C ₆ H ₁₁] ⁺	1	-	-291.62111	0.20209	0.21014	0.17151	-291.44960
6	TS for amine attack on [anethole] ⁺	2	0.763 4	-754.37435	0.38425	0.40328	0.33693	-754.03742
7		2	0.774 0	-754.38859	0.38725	0.40600	0.34071	-754.04788
8	TS for deprotonation of radical cation (entry 7)	2	0.776 4	-1045.56095	0.57259	0.59904	0.51669	-1045.04426
9		2	0.775 9	-753.92068	0.37164	0.39035	0.32461	-753.59606
10a		1	-	-753.76854	0.37462	0.39307	0.32875	-753.43979
11	<i>cis</i> -aziridine adduct with [NH ₃ -C ₆ H ₁₁] ⁺	1	-	-1044.97177	0.56354	0.59010	0.50697	-1044.46479
12	<i>cis</i> -aziridine	1	-	-753.33071	0.36147	0.37957	0.31578	-753.01493
13	<i>trans</i> -aziridine	1	-	-753.32351	0.36149	0.37961	0.31497	-753.00853
14	TS for <i>cis</i> - <i>trans</i> -isomerization	1	-	-753.30538	0.36006	0.37785	0.31402	-752.99136
15	<i>p</i> -methoxystyrene + NH ₂ -C ₆ H ₁₁	1	-	-715.25491	0.35389	0.37309	0.30428	-714.95062
16	[<i>p</i> -methoxystyrene] ⁺ + NH ₂ -C ₆ H ₁₁	2	0.761 1	-715.05308	0.35372	0.37295	0.30501	-714.74807
17	<i>p</i> -methoxystyrene	1	-	-424.09218	0.16540	0.17565	0.13038	-423.96180
18	[<i>p</i> -methoxystyrene] ⁺	2	0.770 5	-423.88941	0.16591	0.17618	0.13150	-423.75791
19	<i>trans</i> - β -methylstyrene + NH ₂ -C ₆ H ₁₁	1	-	-640.04323	0.34897	0.36734	0.30099	-639.74225
20	[<i>trans</i> - β -methylstyrene] ⁺ + NH ₂ -C ₆ H ₁₁	2	0.759 8	-639.83599	0.34846	0.36672	0.30096	-639.53503
21	<i>trans</i> - β -methylstyrene	1	-	-348.88087	0.16071	0.17006	0.12591	-348.75496
22	[<i>trans</i> - β -methylstyrene] ⁺	2	0.765 5	-348.66905	0.16057	0.16995	0.12720	-348.54186
23	styrene + NH ₂ -C ₆ H ₁₁	1	-	-600.73619	0.32112	0.33790	0.27527	-600.46092
24	[styrene] ⁺ + NH ₂ -C ₆ H ₁₁	2	0.761 2	-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] ⁺	2	0.770 9	-309.35265	0.13277	0.14056	0.10176	-309.25089
27	<i>cis</i> -stilbene	1	-	-540.57466	0.21451	0.22646	0.17681	-540.39785
28	[<i>cis</i> -stilbene] ⁺	2	0.764 0	-540.36943	0.21513	0.22708	0.17788	-540.19155
29	[<i>trans</i> -stilbene]	1	-	-540.58162	0.21394	0.22626	0.17444	-540.40719
30	[<i>trans</i> -stilbene] ⁺	2	0.766	-540.37967	0.21490	0.22710	0.17695	-540.20272

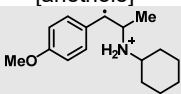
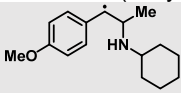
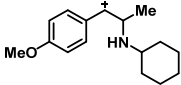
31	NEt3	1	-	-292.33498	0.20504	0.21530	0.17117	-292.16381
32	[NEt3] ⁺	2	0.754 8	-292.14823	0.20498	0.21565	0.16877	-291.97945
33	N(2,4,6-tribromophenyl) ₃	1	-	-23910.51473	0.18519	0.21464	0.11894	-23910.3957 9
34	[N(2,4,6-tribromophenyl) ₃] ⁺	2	0.762 0	-23910.29649	0.18472	0.21417	0.11790	-23910.1785 9
35	N(4-bromophenyl) ₃	1	-	-8469.87008	0.24735	0.26760	0.19391	-8469.67617
36	[N(4-bromophenyl) ₃] ⁺	2	0.766 7	-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] ⁺	2	0.756 5	-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 state was found at $\Delta G_{0298K} = +24.5$ 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 coulometric 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 $\langle s^2 \rangle$, SCF corrections, ZPE corrections, enthalpy corrections and ΔG°_{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. NH₂-C₆H₁₁ = cyclohexylamine.

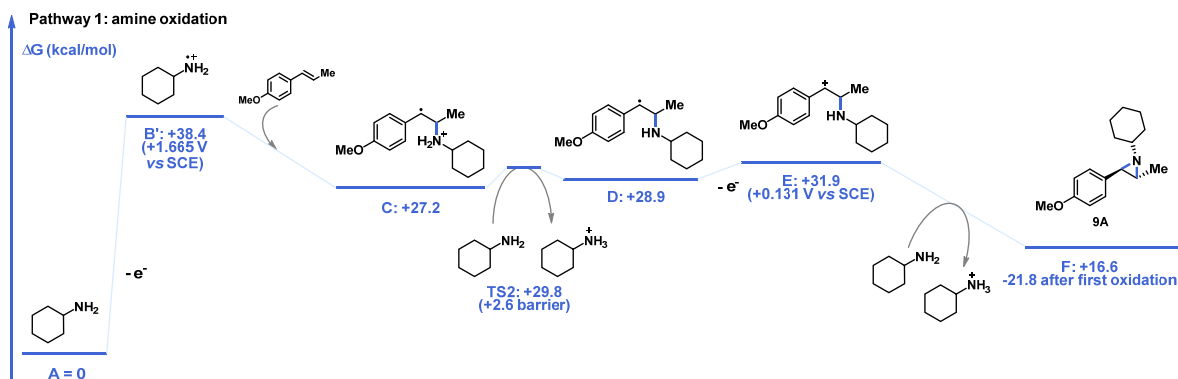
Entry	Description	Multiplicity	$\langle s^2 \rangle$	SCF (Hartree)	ZPE correction (Hartree)	Enthalpy correction (Hartree)	Entropy correction (Hartree)	ΔG°_{298K} (Hartree)
1	anethole	1	-	-463.39826	0.19325	0.20509	0.15612	-463.24214
2	[anethole] ⁺	2	0.764 2	-463.20270	0.19373	0.20560	0.15706	-463.04564
3	NH ₂ -C ₆ H ₁₁	1	-	-291.15729	0.18712	0.19499	0.15678	-291.00051
4	[NH ₂ -C ₆ H ₁₁] ⁺	2	0.755 1	-290.94233	0.18507	0.19331	0.15445	-290.78788
5	[NH ₃ -C ₆ H ₁₁] ⁺	1	-	-291.62111	0.20209	0.21014	0.17151	-291.44960
6	TS for amine attack on [anethole] ⁺	2	0.763 4	-754.37435	0.38425	0.40328	0.33693	-754.03742
7		2	0.774 0	-754.38859	0.38725	0.40600	0.34071	-754.04788
8	TS for deprotonation of radical cation (entry 7)	2	0.776 4	-1045.56095	0.57259	0.59904	0.51669	-1045.04426
9		2	0.775 9	-753.92068	0.37164	0.39035	0.32461	-753.59606
10 ^a		1	-	-753.76854	0.37462	0.39307	0.32875	-753.43979
11	<i>cis</i> -aziridine adduct with [NH ₃ -C ₆ H ₁₁] ⁺	1	-	-1044.97177	0.56354	0.59010	0.50697	-1044.46479
12	<i>cis</i> -aziridine	1	-	-753.33071	0.36147	0.37957	0.31578	-753.01493
13	<i>trans</i> -aziridine	1	-	-753.32351	0.36149	0.37961	0.31497	-753.00853

14	TS for <i>cis-trans</i> -isomerization	1	-	-753.30538	0.36006	0.37785	0.31402	-752.99136
15	<i>p</i> -methoxystyrene + NH ₂ -C ₆ H ₁₁	1	-	-715.25491	0.35389	0.37309	0.30428	-714.95062
16	[<i>p</i> -methoxystyrene] ⁺ + NH ₂ -C ₆ H ₁₁	2	0.761 1	-715.05308	0.35372	0.37295	0.30501	-714.74807
17	<i>p</i> -methoxystyrene	1	-	-424.09218	0.16540	0.17565	0.13038	-423.96180
18	[<i>p</i> -methoxystyrene] ⁺	2	0.770 5	-423.88941	0.16591	0.17618	0.13150	-423.75791
19	<i>trans</i> -β-methylstyrene + NH ₂ -C ₆ H ₁₁	1	-	-640.04323	0.34897	0.36734	0.30099	-639.74225
20	[<i>trans</i> -β-methylstyrene] ⁺ + NH ₂ -C ₆ H ₁₁	2	0.759 8	-639.83599	0.34846	0.36672	0.30096	-639.53503
21	<i>trans</i> -β-methylstyrene	1	-	-348.88087	0.16071	0.17006	0.12591	-348.75496
22	[<i>trans</i> -β-methylstyrene] ⁺	2	0.765 5	-348.66905	0.16057	0.16995	0.12720	-348.54186
23	styrene + NH ₂ -C ₆ H ₁₁	1	-	-600.73619	0.32112	0.33790	0.27527	-600.46092
24	[styrene] ⁺ + NH ₂ -C ₆ H ₁₁	2	0.761 2	-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] ⁺	2	0.770 9	-309.35265	0.13277	0.14056	0.10176	-309.25089
27	<i>cis</i> -stilbene	1	-	-540.57466	0.21451	0.22646	0.17681	-540.39785
28	[<i>cis</i> -stilbene] ⁺	2	0.764 0	-540.36943	0.21513	0.22708	0.17788	-540.19155
29	[<i>trans</i> -stilbene]	1	-	-540.58162	0.21394	0.22626	0.17444	-540.40719
30	[<i>trans</i> -stilbene] ⁺	2	0.766 4	-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] ⁺	2	0.754 8	-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	- 23910.3957 9
34	[N(2,4,6-tribromophenyl) ₃] ⁺	2	0.762 0	- 23910.29649	0.18472	0.21417	0.11790	- 23910.1785 9
35	N(4-bromophenyl) ₃	1	-	-8469.87008	0.24735	0.26760	0.19391	-8469.67617
36	[N(4-bromophenyl) ₃] ⁺	2	0.766 7	-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] ⁺	2	0.756 5	-1258.11858	0.16240	0.17417	0.12556	-1257.99302

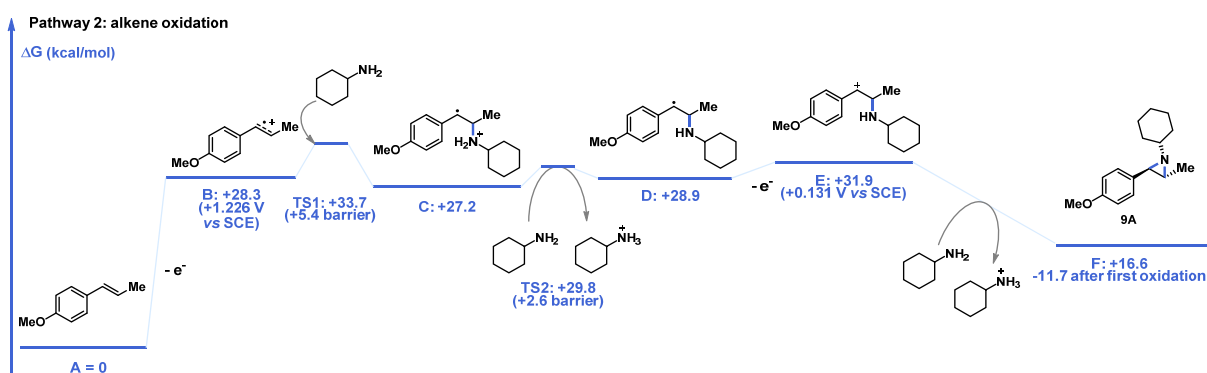
^a The CSS spin state was found to be the most stable. The OSS spin state converged to a CSS solution and the triplet spin state was found at $\Delta G^{\circ}_{298K} = +24.5 \text{ kcal mol}^{-1}$ relative to the CSS state.

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

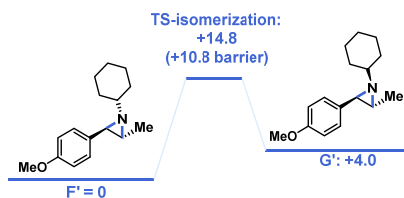
State in Scheme S1, Scheme S2 and Scheme S3	Composition from entries in Table S9
A	1 + 3 + 3 + 3
B	2 + 3 + 3 + 3
B'	1 + 3 + 3 + 4
TS1	6 + 3 + 3
C	7 + 3 + 3
TS2	8 + 3
D	9 + 3 + 5
E	10 + 3 + 5
F	11 + 5
F'	12 + 3 + 3
TS isomerization	14 + 3 + 3
G'	13 + 3 + 3



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.



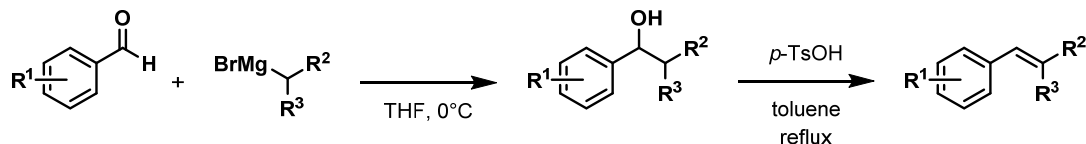
Scheme S3. Calculated pathway for *cis-trans*-isomerization (methyl and cyclohexyl) of the aziridine. Calculations were performed at the B3LYP/def2-TZVP//B3LYP/def2-TZVP(COSMO) level of theory on an m4 grid with disp3 dispersion corrections.

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
<i>p</i> -methoxystyrene + NH ₂ -C ₆ H ₁₁	+1.391
<i>p</i> -methoxystyrene	+1.427
<i>trans</i> -β-methylstyrene + NH ₂ -C ₆ H ₁₁	+1.518
<i>trans</i> -β-methylstyrene	+1.678
styrene + NH ₂ -C ₆ H ₁₁	+1.599
styrene	+1.934
<i>cis</i> -stilbene	+1.493
<i>trans</i> -stilbene	+1.443

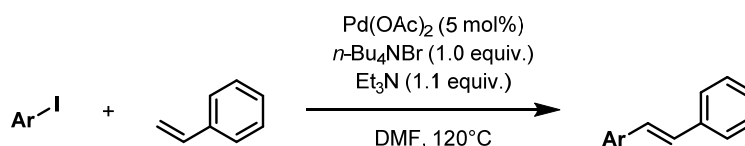
5. Synthesis of the starting materials

5.1. General procedure S1



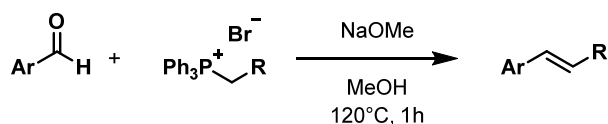
Alkylmagnesium bromide (1 equiv., 20 mmol) was added dropwise to a stirred solution of corresponding benzaldehyde (1.1 equiv., 22.0 mmol) in dry THF (40 mL) at 0°C under Ar. The solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched by addition of sat. 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

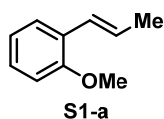


Aryl iodide (1.0 equiv., 10.0 mmol), styrene (2 equiv., 20.0 mmol, 2.3 mL), triethylamine (1.1 equiv., 11.0 mmol, 1.5 mL), Pd(OAc)_2 (5 mol%, 0.50 mmol, 112 mg), and *n*- Bu_4NBr (1.0 equiv., 10.0 mmol, 3.22 g) were dissolved in DMF (40 mL) and the solution was stirred at 120°C for 24 h. After cooling 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.

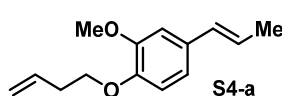
5.3. General procedure S3



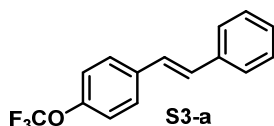
NaOMe (1.1 equiv., 5M in MeOH, 22.0 mmol, 4.4 mL) was added dropwise to a stirred solution of alkyltriphenylphosphonium bromide (1.1 equiv., 22.0 mmol) in MeOH (36 mL) under Ar. The mixture was stirred at room temperature for 5 minutes, then corresponding benzaldehyde (1 equiv., 20 mmol) was added dropwise 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.



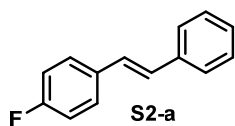
(E)-1-methoxy-2-(prop-1-en-1-yl)benzene S1-a:¹⁷ The titled compound was synthesized according to the general procedure **S1** from *o*-anisaldehyde (1.1 equiv., 22.0 mmol, 3.00 g) and ethylmagnesium bromide (1.0 equiv., 3M solution in Et₂O, 20.0 mmol, 6.7 mL). The crude product was purified by flash column chromatography on silica gel (cyclohexane) to give yellow oil in 42% total yield (1.24 g, 8.37 mmol, *E/Z* = 25:1). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 156.3, 127.9, 127.2, 126.7, 126.6, 125.8, 120.8, 110.8, 55.5, 19.1.



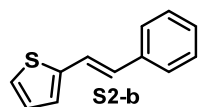
(E)-1-(but-3-en-1-yloxy)-2-methoxy-4-(prop-1-en-1-yl)benzene S4-a: NaH (1.1 equiv., 60% in mineral oil, 22.0 mmol, 880 mg) was added in portions to a stirred solution of isoeugenol (1.0 equiv., 20.0 mmol, 3.28 g) DMF (10 mL) under Ar. After 5 minutes, 4-bromobut-1-ene (1.6 eq., 32.0 mmol, 3.2 mL) was added and the reaction mixture was stirred at 100°C overnight. After cooling to room temperature, the reaction mixture was diluted with Et₂O 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 MgSO₄ 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). ¹H NMR (399 MHz, CDCl₃) 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). ¹³C NMR (100 MHz, CDCl₃) 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.



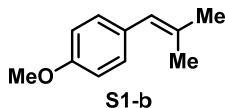
(E)-1-styryl-4-(trifluoromethoxy)benzene S3-a: The titled compound was synthesized according to the general procedure **S3** from 4-(trifluoromethoxy)benzaldehyde (1.1 equiv., 20.0 mmol, 4.4 mL) and benzyltriphenylphosphonium bromide (1.1 equiv., 22.0 mmol, 9.53 g). The crude product was purified by crystallization from MeOH to give white crystals in 34% yield (1.81 mg, 6.85 mmol, *E/Z* > 30:1). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.8.



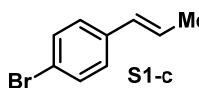
(E)-1-fluoro-4-styrylbenzene S2-a:¹⁸ The titled compound was synthesized according to the general procedure **S2** from *p*-fluoriodobenzene (1.0 equiv., 10.0 mmol, 1.4 mL) and styrene (2 equiv., 20.0 mmol, 2.3 mL). The crude product was purified by crystallization from *n*-hexane to give colorless crystals in 79% yield (1.56 g, 7.87 mmol, *E/Z* > 30:1). ¹H NMR (400 MHz, CDCl₃) 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). ¹⁹F NMR (376 MHz, CDCl₃) δ -114.26 (ddd, *J* = 14.0, 8.7, 5.4 Hz).



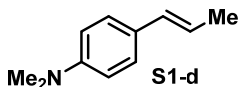
(E)-2-styrylthiophene S2-b:¹⁹ The titled compound was synthesized according to the general procedure **S2** from 2-iodothiophene (1.0 equiv., 10.0 mmol, 1.2 mL) and styrene (2 equiv., 20.0 mmol, 2.3 mL). The crude product was purified by crystallization from *n*-hexane to give yellow crystals in 43% yield (805 mg, 4.32 mmol, *E/Z* > 30:1). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 143.0, 137.1, 128.8, 128.5, 127.7, 126.4, 126.2, 124.5, 121.9.



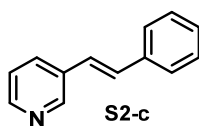
1-methoxy-4-(2-methylprop-1-en-1-yl)benzene S1-b:²⁰ The titled compound was synthesized according to the general **S1** procedure from *p*-anisaldehyde (1.1 equiv., 22.0 mmol, 2.60 g) and isopropylmagnesium bromide (1.0 equiv., 2M solution in THF, 20.0 mmol, 10 mL). The crude product was purified by flash column chromatography on silica gel (cyclohexane) to give colorless oil in 63% total yield (2.05 g, 12.6 mmol). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 157.8, 134.1, 131.5, 129.9, 124.6, 113.6, 55.4, 27.0, 19.5.



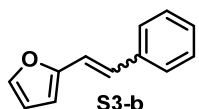
(E)-1-bromo-4-(prop-1-en-1-yl)benzene S1-c:²¹ The titled compound was synthesized according to the general procedure **S1** from *p*-bromobenzaldehyde (1.0 equiv., 20.0 mmol, 3.70 g) and ethylmagnesium bromide (2.1 equiv., 3M solution in THF, 42.0 mmol, 14 mL). The crude product was purified by flash 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). ¹H NMR (399 MHz, CDCl₃) 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).



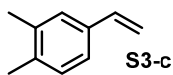
(E)-N,N-dimethyl-4-(prop-1-en-1-yl)aniline S1-d:¹⁷ The titled compound was synthesized according to the general procedure **S1** from *p*-(dimethylamino)benzaldehyde (1.0 equiv., 20.0 mmol, 2.98 g) and ethylmagnesium bromide (1.1 equiv., 3M solution in Et₂O, 22.0 mmol, 7.3 mL). The crude product was 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). ¹H NMR (400 MHz, CDCl₃) 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 S2-c:²² 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). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) δ 148.3, 136.7, 133.3, 133.0, 131.1, 128.9, 128.4, 126.8, 124.9, 123.8.

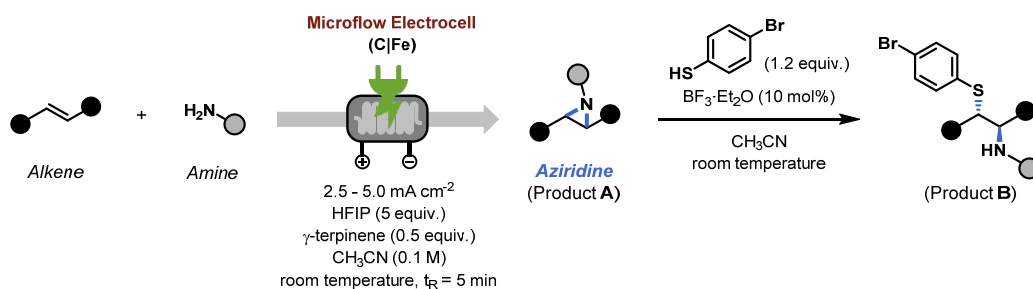


2-styrylfuran S3-b:^{23,24} The titled compound was synthesized according to the general procedure **S3** from furfural (1.0 equiv., 20.0 mmol, 1.1 mL) and benzyltriphenylphosphonium bromide (1.1 equiv., 22.0 mmol, 9.53 g). The crude product was purified by flash column chromatography on silica gel (cyclohexane) to give yellow oil in 98% yield (3.34 g, 19.6 mmol, *E/Z* = 1.16:1). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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 S3-c:²⁵ 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). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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. Voltammograms

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 taken up into 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. Next, the current was increased from 50 mA to 120 mA with increments of 10 mA. For each data point and after steady state reaction conditions were reached (12 minutes at 0.15 ml/min), the corresponding potential was noted and a sample (0.1 ml) was collected in a vial. The sample was diluted with CH₃CN and analyzed using GC-FID or GC-MS.

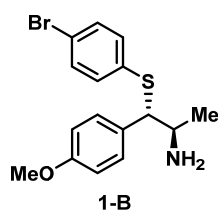
6.2. General procedure A

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 CD₃OD.^{26,27} On the contrary, spectra recorded in CDCl₃ featured broad and overlapping signals in ¹H NMR and low intensity peaks in ¹³C 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 CD₃OD overtime giving rise to additional signals, which can be clearly seen in some ¹³C NMR spectra, as measuring of carbon spectrum takes considerably longer time than ¹H NMR.

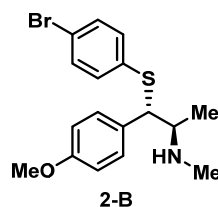
6.3. General procedure B

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 $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (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, $^1\text{H-NMR}$, $^{19}\text{F-NMR}$ and $^{13}\text{C-NMR}$.



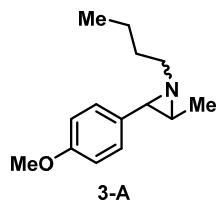
***anti*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-amine (1-B):**

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 \rightarrow 10% of MeOH in DCM) to give amorphous yellow solid (66 mg, 19%) as a single diastereoisomer. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M-NH}_3+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{BrOS}$ 335.0100, found 335.0096.



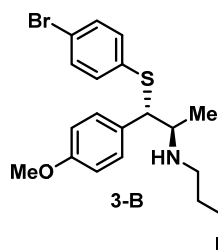
***anti*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)-*N*-methylpropan-2-amine (2-B):**

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 \rightarrow 10% of MeOH in DCM) to give viscous yellow oil (176 mg, 48%) as a single diastereoisomer. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{NOS}$ 366.0522, found 366.0513.

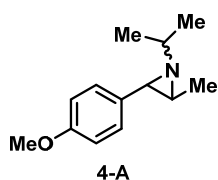


***trans*-1-butyl-2-(4-methoxyphenyl)-3-methylaziridine (3-A):**

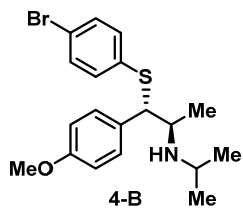
Following the general procedure A, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 \rightarrow 50% of EtOAc in cyclohexane) to give viscous brown oil (109 mg, 50%) as a mixture of two diastereoisomers (d.r. 1:1). $^1\text{H NMR}$ (400 MHz, CD_3OD) δ 7.24 (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{21}\text{NO}$ 220.1696, found 220.1687.



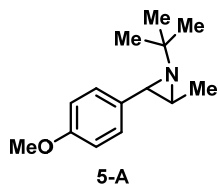
anti-N-(1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)butan-1-amine (3-B): Following the general procedure **B**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (295 mg, 72%) as a single diastereoisomer. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{BrNOS}$ 408.0991, found 408.0974.



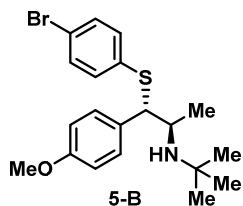
trans-1-isopropyl-2-(4-methoxyphenyl)-3-methylaziridine (4-A): Following the general procedure **A**, obtained at 60 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of EtOAc in cyclohexane) to give viscous yellow oil (146 mg, 71%) as a mixture of two diastereoisomers (d.r. 1:1). $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{20}\text{NO}$ 206.1545, found 206.1535.



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. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{25}\text{BrNOS}$ 394.0840, found 394.0827.

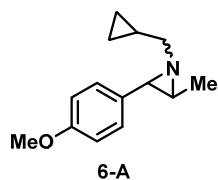


trans-1-(tert-butyl)-2-(4-methoxyphenyl)-3-methylaziridine (5-A): Following the general procedure **A**, obtained at 85 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of EtOAc in cyclohexane) to give viscous brown oil (91 mg, 41%) as a single diastereoisomer. The titled compound decomposed to quickly in CD_3OD to obtain good quality NMR spectra. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ 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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{22}\text{NO}$ 220.1696, found 220.1695.



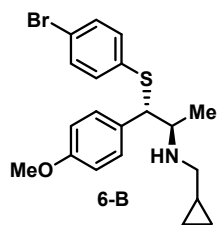
anti-1-((4-bromophenyl)thio)-N-(tert-butyl)-1-(4-methoxyphenyl)propan-2-amine (5-B): Following the general procedure **B**, obtained at 85 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 40% of EtOAc in cyclohexane) to give viscous yellow oil (281 mg, 69%) as a single diastereoisomer. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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.



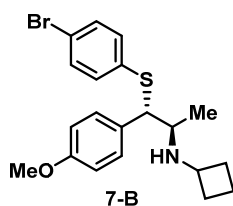
trans-1-(cyclopropylmethyl)-2-(4-methoxyphenyl)-3-methylaziridine (6-A):

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). **¹H 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). **¹³C 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.



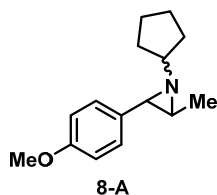
anti-1-((4-bromophenyl)thio)-N-(cyclopropylmethyl)-1-(4-methoxyphenyl)propan-2-amine (6-b):

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. **¹H 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). **¹³C 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.



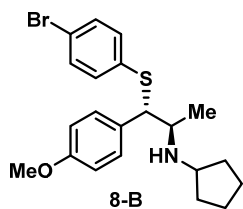
anti-N-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)cyclobutanamine (7-B):

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. **¹H 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). **¹³C 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.

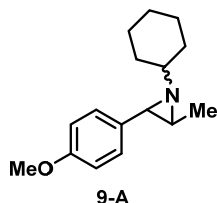


trans-1-cyclopentyl-2-(4-methoxyphenyl)-3-methylaziridine (8-A):

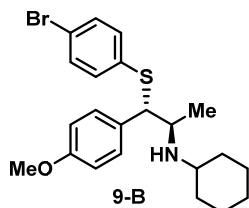
Following the general procedure **A**, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to give viscous brown oil (122 mg, 53%) as a mixture of two diastereoisomers (d.r. 1.1:1). **¹H NMR** (400 MHz, CD_3OD) δ 7.25 (d, J = 8.7 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 (dq, 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). **¹³C 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.



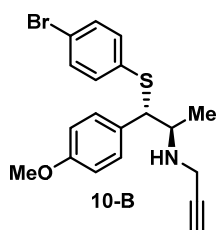
anti-N-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)cyclopentanamine (8-B): Following the general procedure **B**, obtained at 110 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 40% of EtOAc in cyclohexane) to give viscous yellow oil (272 mg, 64%) as a single diastereoisomer. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{BrNOS}$ 420.0991, found 420.0976.



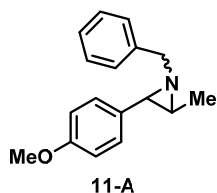
trans-1-cyclohexyl-2-(4-methoxyphenyl)-3-methylaziridine (9-A): Following the general procedure **A**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to give viscous brown oil (177 mg, 72%) as a mixture of two diastereoisomers (d.r. 1:1). $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{24}\text{NO}$ 246.1858, found 246.1845.



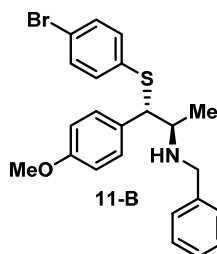
anti-N-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)cyclohexanamine (9-B): Following the general procedure **B**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 40% of EtOAc in cyclohexane) to give viscous yellow oil (356 mg, 82%) as a single diastereoisomer. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{29}\text{BrNOS}$ 434.1148, found 434.1139.



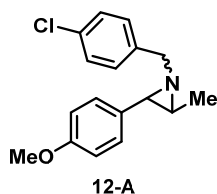
anti-N-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)prop-2-yn-1-amine (10-B): Following the general procedure **B**, obtained at 50 mA for 33.3 minutes (0.5 mmol scale). Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give amorphous yellow solid (49 mg, 25%) as a single diastereoisomer. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{BrNOS}$ 390.0527, found 390.0516.



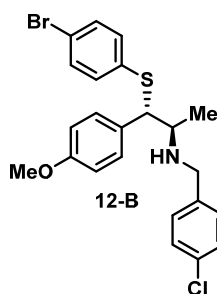
trans-1-benzyl-2-(4-methoxyphenyl)-3-methylaziridine (11-A): Following the general procedure **A**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (157 mg, 62%) as a mixture of two diastereoisomers (d.r. 1:1). ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR (101 MHz, CD₃OD) 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 C₁₇H₂₀NO 254.1545, found 254.1535.



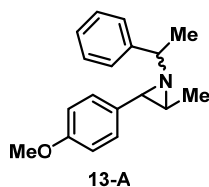
anti-N-benzyl-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-amine (11-B): Following the general procedure **B**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (341 mg, 77%) as a single diastereoisomer. ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR (101 MHz, CD₃OD) 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 C₂₃H₂₅BrNOS 442.0840, found 442.0817.



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). ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR (101 MHz, CD₃OD) 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 C₁₇H₁₉ClNO 288.1155, found 288.1140.

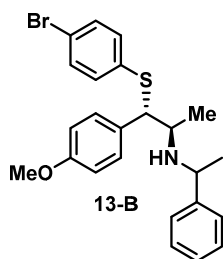


anti-1-((4-bromophenyl)thio)-N-(4-chlorobenzyl)-1-(4-methoxyphenyl)propan-2-amine (12-B): Following the general procedure **B**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (370 mg, 78%) as a single diastereoisomer. ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR (101 MHz, CD₃OD) 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 C₂₃H₂₄ClBrNOS 476.0451, found 476.0425.



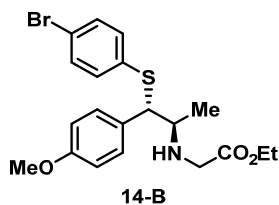
trans-2-(4-methoxyphenyl)-3-methyl-1-(1-phenylethyl)aziridine (13-A):

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. 1.1:1). **First *trans*-isomer:** $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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, 127.5, 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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{NO}$ 268.1701, found 268.1686. **Second *trans*-isomer:** $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{NO}$ 268.1701, found 268.1686.



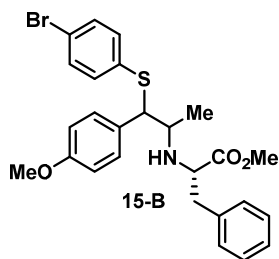
anti-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)-N-(1-phenylethyl)propan-2-amine (13-B):

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:** $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{BrNOS}$ 456.0997, found 456.0977. **Second *anti*-isomer:** $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{BrNOS}$ 456.0997, found 456.0983.

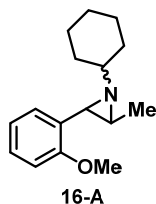


Ethyl (anti-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)glycinate (14-B):

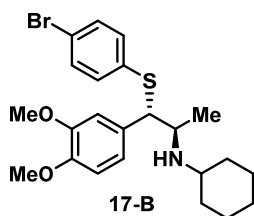
Following the general procedure **B**, obtained at 60 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give viscous yellow oil (275 mg, 63%) as a single diastereoisomer. $^1\text{H NMR}$ (400 MHz, CD_3OD) δ 7.31 (d, J = 8.6 Hz, 2H), 7.27 (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{BrNO}_3\text{S}$ 438.0739, found 438.0726.



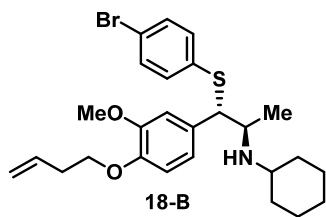
Methyl (*anti*-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)-L-phenylalaninate (15-B): Following the general procedure **B**, obtained at 50 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to give two viscous yellow oils (in total 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]. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{29}\text{BrNO}_3\text{S}$ 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]. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{29}\text{BrNO}_3\text{S}$ 514.1052, found 514.1040.



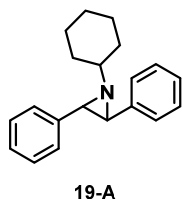
***trans*-1-cyclohexyl-2-(2-methoxyphenyl)-3-methylaziridine (16-A):** Following the general procedure **A**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to give viscous brown oil (142 mg, 58%) as a mixture of two diastereoisomers (d.r. 1.2:1). $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{24}\text{NO}$ 246.1858, found 246.1868.



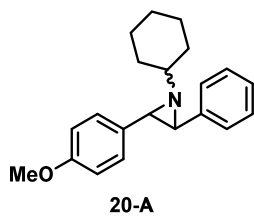
***anti*-1-1-((4-bromophenyl)thio)-1-(4-methoxyphenyl)propan-2-yl)cyclohexanamine (17-B):** Following the general procedure **B**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 30% of EtOAc in cyclohexane) to viscous white off oil (334 mg, 72%) as a single diastereoisomer. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{31}\text{BrNO}_2\text{S}$ 464.1259, found 464.1244.



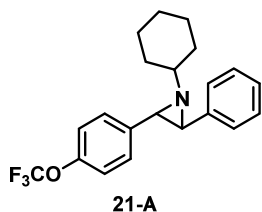
***anti*-N-1-((4-bromophenyl)thio)-1-(4-(but-3-en-1-yloxy)-3-methoxyphenyl)propan-2-yl)cyclohexanamine (18-B)**: Following the general procedure **B**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 30% of EtOAc in cyclohexane) to viscous brown oil (364 mg, 72%) as a single diastereoisomer. ¹H NMR (399 MHz, CD₃OD) 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). ¹³C NMR (100 MHz, CD₃OD) 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. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₆H₃₅BrNO₂S 504.1572, found 504.1582.



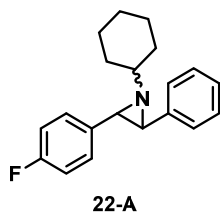
***trans*-1-cyclohexyl-2,3-diphenylaziridine (19-A)**:²⁸ Following the general procedure **A**, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (5 → 50% of DCM in cyclohexane) to give viscous colorless oil (70 mg, 25%) as a single diastereoisomer. ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR (101 MHz, CD₃OD) 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 C₂₀H₂₄N 278.1909, found 278.1915.



***trans*-1-cyclohexyl-2-(4-methoxyphenyl)-3-phenylaziridine (20-A)**:²⁹ 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). ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR selected peaks (100 MHz, CD₃OD) 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 C₂₁H₂₆NO 308.2014, found 308.2019.

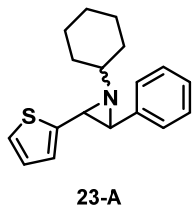


***trans*-1-cyclohexyl-2-phenyl-3-(4-(trifluoromethoxy)phenyl)aziridine (21-A)**: Following the general procedure **A**, obtained at 105 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (10 → 90% of DCM in cyclohexane) to give viscous yellow oil (103 mg, 29%) as a single diastereoisomer. ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR selected peaks (101 MHz, CD₃OD) 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. ¹⁹F NMR (376 MHz, CD₃OD) δ -59.5. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₁H₂₂F₃NO 362.1732, found 362.1740.

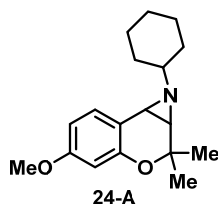


***trans*-1-cyclohexyl-2-(4-fluorophenyl)-3-phenylaziridine (22-A)**: Following the general procedure **A**, obtained at 80 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 100% of DCM in cyclohexane) to give viscous colorless oil (97 mg, 33%) as a mixture of two diastereoisomers (d.r. 1.1:1). ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR selected peaks (100 MHz, CD₃OD) 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,

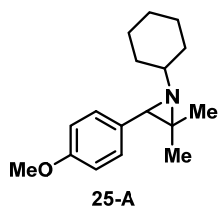
60.1, 50.3, 45.1, 44.1, 34.0, 33.0, 26.9, 26.1, 25.5. ¹⁹F NMR (376 MHz, CD₃OD) δ -116.13, -117.55. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₂₀H₂₂FN 296.1815, found 296.1821.



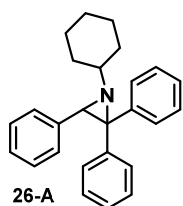
trans-1-cyclohexyl-2-phenyl-3-(thiophen-2-yl)aziridine (23-A): Following the general procedure **A**, obtained at 120 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 100% of dichloromethane in cyclohexane) to give viscous yellow oil (85 mg, 30%) as a mixture of two diastereoisomers (d.r. 2.8:1). ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR major isomer (100 MHz, CD₃OD) 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. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₈H₂₂NS 284.1473, found 284.1479.



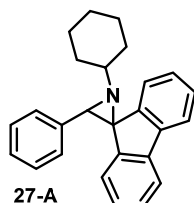
1-cyclohexyl-5-methoxy-2,2-dimethyl-1,1a,2,7b-tetrahydrochromeno[3,4-b]azirine (24-A): Following the general procedure **A**, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (8% of EtOAc in cyclohexane) to viscous transparent oil (267 mg, 93%) as a single diastereoisomer. ¹H NMR (399 MHz, CD₃OD) 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). ¹³C NMR (101 MHz, CD₃OD) 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 C₁₈H₂₆NO₂ 288.1964, found 288.1957.



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%). ¹H NMR (399 MHz, CD₃OD) 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). ¹³C NMR (101 MHz, CD₃OD) 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. HRMS (ESI) *m/z* [M+H]⁺ calcd for C₁₇H₂₆NO 260.2014, found 260.2019.

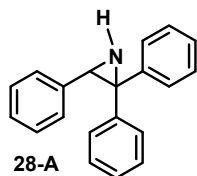


1-cyclohexyl-2,2,3-triphenylaziridine (26-A): Following the general procedure **A**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (0 → 10% of DCM in cyclohexane) to give viscous yellow oil as a single diastereoisomer (311 mg, 88%). ¹H NMR (400 MHz, CD₃OD) 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). ¹³C NMR (101 MHz, CD₃OD) 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 C₂₆H₂₈N 354.2222, found 354.2227.



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%). ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (101 MHz, CDCl₃) 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.

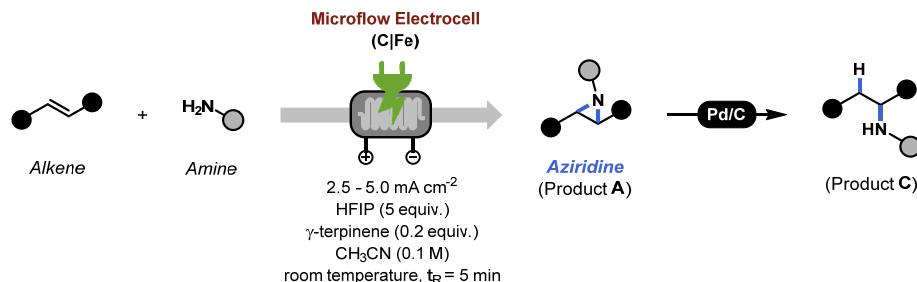


Triphenylaziridine (28-A):³⁰ Following the general procedure **A**, obtained at 90 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (2 → 10% of ethyl acetate in cyclohexane) to give viscous transparent oil (40% w/w NH_3 solution in water 166 mg, 61%; 7M NH_3 solution in MeOH 138 mg, 51%). 1H 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.

6.4. 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).

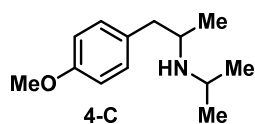
7. General procedure for formal electrochemical hydroamination in flow



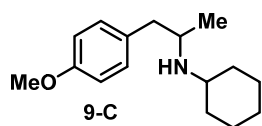
Alkene (1.0 equiv., 2.0 mmol), together with amine (5.0 equiv., 10.0 mmol), hexafluoroisopropanol (HFIP, 5.0 equiv., 10.0 mmol, 1.05 mL) and γ -terpinene (0.2 equiv., 0.4 mmol, 64 μ L) were dissolved in acetonitrile using a 20 mL volumetric flask (0.1M). The mixture was swirled until homogeneous and 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. A self-made packed bed reactor (1 mL), filled with a mixture of Pd/C (200 mg) and glass beads (500 mg), was connected to the outlet of the electrochemical reactor.

The packed bed reactor was constructed using a 1 ml in-line medical grade Poly propylene cartridge (Male luer end, Female luer snap cap; Screening Devices, part no.: ER.001.16.INLINE), which was capped with Hydrophobic PE frits (thickness 1,5mm, diameter tube 9.1mm). Pd/C (220 mg, average particle size of 15 μ m; approximately 90% <60 μ m and 10% <5 μ m) was premixed with glass beads (500 mg, 960-980 μ m) and loaded into the cartridge to form the packed bed. The addition of glass beads has two reasons: (i) additional mixing opportunity and (ii) to dissipate and minimize the exothermic temperature increase. The packed bed was about 10-11mm long.

The first fraction was discarded (about 20 min total time) after which a constant current (selected on the basis of the voltammograms recorded) was applied. The reaction mixture was collected in a vial for 67 minutes, which corresponds to 1.0 mmol scale. The crude mixture was concentrated under vacuum and purified by flash column chromatography on silica gel and analysed by TLC, GC-MS, ¹H-NMR, and ¹³C-NMR.

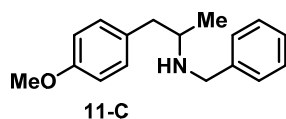


N-isopropyl-1-(4-methoxyphenyl)propan-2-amine (4-C): Following the general procedure, obtained at 60 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (normal phase: 1 \rightarrow 9% of NH₃/MeOH in DCM; and then reversed phase: 10 \rightarrow 50% of CH₃CN in water) to give the desired compound as a viscous yellow oil in 42% yield (420 μ mol, 87 mg). ¹H NMR (400 MHz, CD₃OD) δ 7.09 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.76 (s, 3H), 3.02 – 2.87 (m, 2H), 2.72 (dd, J = 13.4, 6.0 Hz, 1H), 2.46 (dd, J = 13.3, 7.7 Hz, 1H), 1.06 (d, J = 6.3 Hz, 3H), 0.99 (d, J = 6.3 Hz, 3H), 0.99 (d, J = 6.3 Hz, 3H). ¹³C NMR (101 MHz, CD₃OD) δ 159.7, 132.4, 131.2, 114.9, 55.6, 52.6, 46.3, 43.1, 23.2, 22.4, 19.8. HRMS (ESI) m/z [M+H]⁺ calcd for C₁₃H₂₂NO 208.1701, found 208.1708.

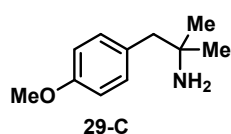


N-(1-(4-methoxyphenyl)propan-2-yl)cyclohexanamine (9-C): Following the general procedure, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (normal phase: 2 \rightarrow 40% of MeOH in DCM; and then reversed phase: 10 \rightarrow 100% of CH₃CN in water) to give the desired compound as a viscous transparent oil in 58% yield (0.582 mmol, 144 mg). ¹H NMR (400 MHz, CD₃OD) 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

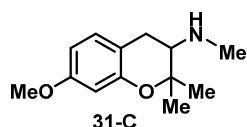
(dd, $J = 13.4, 6.5$ Hz, 1H), 2.62 – 2.53 (m, 1H), 2.50 (dd, $J = 13.4, 7.3$ Hz, 1H), 1.94 – 1.81 (m, 2H), 1.76 – 1.56 (m, 3H), 1.36 – 1.03 (m, 4H), 1.01 (d, $J = 6.3$ Hz, 3H), 0.98 – 0.87 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CD_3OD) δ 159.8, 132.3, 131.2, 114.9, 55.6, 54.3, 52.0, 43.2, 34.6, 33.6, 27.1, 26.2, 26.1, 19.9. **HRMS** (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{26}\text{NO}$ 248.2014, found 248.2019.



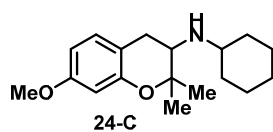
N-benzyl-1-(4-methoxyphenyl)propan-2-amine (11-C): Following the general procedure, obtained at 70 mA for 66.6 minutes. Purified by flash column chromatography on silica gel (normal phase: $\text{DCM}:\text{EtOAc}:\text{MeNH}_2/\text{MeOH}$ 400:40:1 \rightarrow 100:20:1; and then reversed phase: 10 \rightarrow 50% of CH_3CN in water) to give the desired compound as a viscous yellow oil in 51% yield (509 mmol, 130 mg). $^1\text{H NMR}$ (400 MHz, CD_3OD) δ 7.34 – 7.16 (m, 5H), 7.04 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.81 (d, $J = 13.1$ Hz, 1H), 3.75 (s, 3H), 3.67 (d, $J = 13.1$ Hz, 1H), 2.85 (h, $J = 6.5$ Hz, 1H), 2.72 (dd, $J = 13.4, 6.8$ Hz, 1H), 2.52 (dd, $J = 13.4, 7.1$ Hz, 1H), 1.06 (d, $J = 6.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CD_3OD) δ 159.7, 140.6, 132.2, 131.2, 129.5, 129.4, 128.2, 114.9, 55.6, 54.9, 51.8, 43.0, 19.5. **HRMS** (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{22}\text{NO}$ 256.1701, found 256.1717.



1-(4-methoxyphenyl)-2-methylpropan-2-amine (29-C):³¹ Following the general procedure, obtained at 50 mA for 66.6 minutes. The concentrated crude product was dissolved in 10 mL of 1M HCl and 30 mL of DCM was added. The HCl salt of the product was extracted 5 times with 10 mL of 1M HCl and the neutralized with 32% NH_3 in water. The free amine was extracted with DCM (3 x 20 mL), dried over K_2CO_3 and concentrated. Purified by flash column chromatography on silica gel (reversed phase only: 10 \rightarrow 50% of CH_3CN in water) to give the desired compound as a viscous yellow oil in 28% yield (279 mmol, 50 mg). $^1\text{H NMR}$ (400 MHz, CD_3OD) δ 7.10 (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 8.6$ Hz, 2H), 3.77 (s, 3H), 2.60 (s, 2H), 1.07 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CD_3OD) δ 159.8, 132.4, 131.4, 114.5, 55.6, 50.9, 50.4, 29.6.

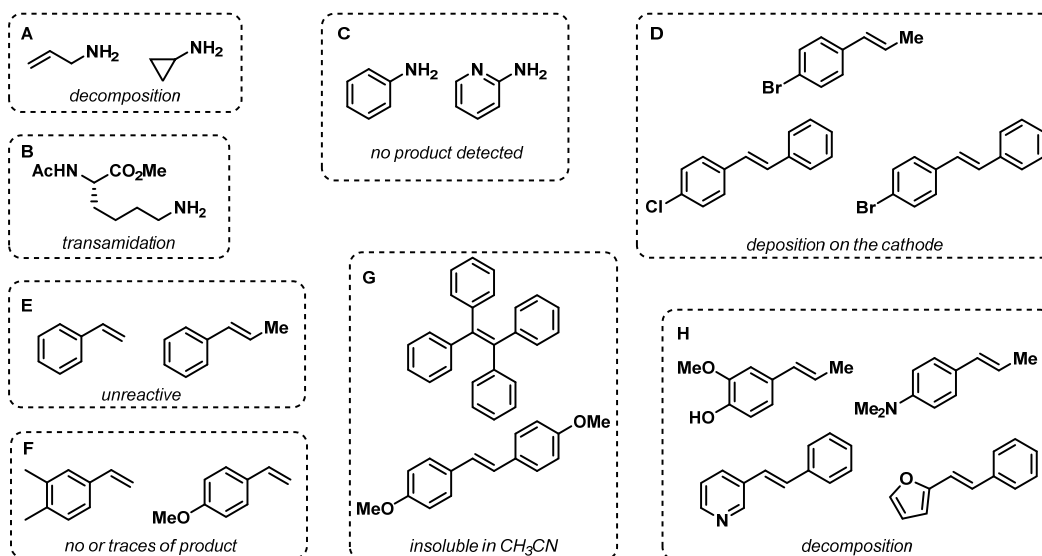
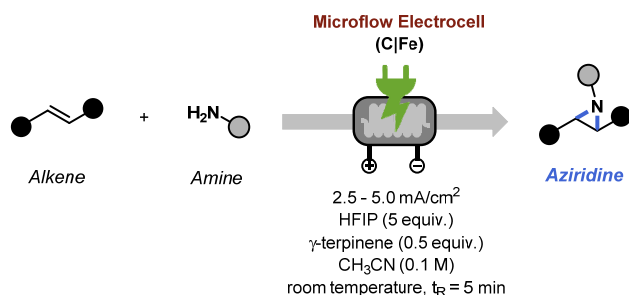


7-methoxy-N,2,2-trimethylchroman-3-amine (31-C): Following the general procedure, obtained at 80 mA for 66.6 minutes (0.88 M, which corresponds to 0.88 mmol). To achieve full hydrogenation, 10% Pd/C (100 mg) was added to the crude mixture and left stirring overnight under hydrogen atmosphere. The crude product was filtered over Celite, concentrated and purified by flash column chromatography on silica gel (normal phase only: $\text{DCM}:\text{NH}_3/\text{MeOH}$ 100:1 \rightarrow 40:1) to give the desired compound as a viscous brown oil in 60% yield (524 mmol, 116 mg). $^1\text{H NMR}$ (400 MHz, MeOD) δ 6.95 (d, $J = 8.4$ Hz, 1H), 6.43 (dd, $J = 8.4, 2.6$ Hz, 1H), 6.29 (d, $J = 2.6$ Hz, 1H), 3.71 (s, 3H), 2.96 (dd, $J = 15.9, 5.1$ Hz, 1H), 2.63 (dd, $J = 8.6, 5.1$ Hz, 1H), 2.53 (dd, $J = 15.9, 8.6$ Hz, 1H), 2.44 (s, 3H), 1.37 (s, 3H), 1.21 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, MeOD) δ 160.8, 155.1, 131.2, 113.4, 108.1, 102.8, 78.1, 61.6, 55.6, 34.9, 28.1, 27.0, 21.2. **HRMS** (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_2$ 222.1494, found 222.1484.



N-cyclohexyl-7-methoxy-2,2-dimethylchroman-3-amine (24-C): Following the general procedure, obtained at 70 mA for 66.6 minutes (0.88 M, which corresponds to 0.88 mmol). To achieve full hydrogenation, 10% Pd/C (100 mg) was added to the crude mixture and left stirring overnight under hydrogen atmosphere. The crude product was filtered over Celite, concentrated and purified by flash column chromatography on silica gel (normal phase: hexane: $\text{DCM}:\text{NH}_3/\text{MeOH}$ 100:20:1 \rightarrow 6:2:0.2; and then reversed phase: 10 \rightarrow 80% of CH_3CN in water) to give the desired compound as a viscous brown oil in 54% yield (477 mmol, 138 mg). $^1\text{H NMR}$ (400 MHz, CD_3OD) δ 6.92 (d, $J = 8.4$ Hz, 1H), 6.42 (dd, $J = 8.4, 2.6$ Hz, 1H), 6.28 (d, $J = 2.6$ Hz, 1H), 3.71 (s, 3H), 2.91 (dd, $J = 16.0, 5.2$ Hz, 1H), 2.78 (dd, $J = 8.2, 5.3$ Hz, 1H), 2.61 – 2.45 (m, 2H), 1.97 – 1.88 (m, 1H), 1.87 – 1.78 (m, 1H), 1.80 – 1.69 (m, 2H), 1.67 – 1.56 (m, 1H), 1.35 (s, 3H), 1.21 (s, 3H), 1.38 – 0.99 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CD_3OD) δ 160.7, 155.2, 131.2, 113.8, 108.0, 102.7, 78.7, 56.8, 56.4, 55.6, 35.4, 34.3, 30.2, 27.2, 26.9, 26.3, 26.1, 21.4. **HRMS** (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_2$ 290.2120, found 290.2135.

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 deposited 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. Alkenes with higher oxidation potentials (e.g. styrene or *trans*-β-methylstyrene,) did not afford the desired aziridines, likely due to excessive amine oxidation at the electrode prior to alkene oxidation (**E**). 3,4-Dimethyl- and 4-methoxystyrene and, as a terminal alkene substrate, has an accessible oxidation potential, but lacks steric protection of the β-substituent, therefore making it prone to degradative side-reactions after anodic oxidation (**F**). From our experience, tetraphenylethylene and dimethoxystilbene should undergo electrochemical aziridation effortlessly, however, due to the very poor solubility in acetonitrile, they cannot be used in the described continuous-flow transformation (**G**). Finally, alkenes bearing unprotected phenol or aniline fragment decomposed under the electrochemical conditions as well as N- and O-atom containing heterocyclic substrates (**H**).

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.

II. Supplemental Data

1. 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]⁺

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

NH₂-C₆H₁₁

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

[NH₂-C₆H₁₁]⁺

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

[NH₃-C₆H₁₁]⁺

21 atoms

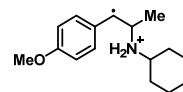
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N -0.0277503 -0.0396175 0.9425102
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H -0.6619844 0.5763857 1.4585301
C 1.3872941 0.0394691 1.5378443
C 3.3002853 1.5741412 2.0305630
C 2.7419267 -0.3216129 3.6095907
C 3.2902133 1.1022438 3.4866590
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]⁺

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
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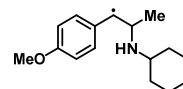
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H	-0.8005425	-4.3460143	5.7043124
H	-0.7059881	-5.9573069	3.1134606
H	-2.0565962	-6.2456031	6.6469320
H	-4.2140845	-4.5371374	3.3240517
H	-4.2163190	-5.9685515	5.3885723
H	-2.0722931	-4.1419169	2.1304585
H	0.0885185	-5.8491733	5.4467366
C	0.8365200	-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

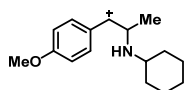
H	-0.4531318	-5.6129897	6.0363666
C	1.0267613	-3.7253544	2.7490107
H	1.9367991	-3.2743316	3.1508657
N	0.2001268	-4.0018365	4.0039676
H	0.8719038	-4.2875568	4.7157525
H	-0.3340672	-2.8217283	4.5025651
H	-0.1908708	-0.9979501	4.6000131
N	-0.7099404	-1.7585660	5.0439736
H	-0.4010580	-1.7994467	6.0144892
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 [NH₃-C₆H₁₁]⁺
(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

NEt₃

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

[NEt₃]⁺

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-tribromophenyl)₃

34 atoms

N	-0.4658908	-0.8106066	0.6888973
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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-tribromophenyl)₃]⁺

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]⁺

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]⁺

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 + NH₂-C₆H₁₁

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]⁺ + NH₂-C₆H₁₁

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]⁺

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 + NH₂-C₆H₁₁**

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]⁺ + NH₂-C₆H₁₁

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]⁺

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 + NH₂-C₆H₁₁

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]⁺ + NH₂-C₆H₁₁

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
H	-4.3903607	-0.2175696	-0.4560005
H	-7.4284665	-2.5126863	1.5595616
H	-6.9397654	-4.4040862	0.0928115
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]⁺

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
C	-0.0068099	-2.1809304	1.0715460
H	0.0280364	-3.1387699	1.5836739
C	0.0053730	-2.2260437	-0.2693700
H	-0.0303531	-3.2161201	-0.7159511
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
H	1.4141672	0.1175890	-0.1132679
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]⁺

26 atoms

H	-1.2373722	0.3230150	0.7658192
C	-0.7231347	0.2211512	1.7106050
C	0.4910133	-0.1114351	4.2130663
C	-0.0110658	-0.9752871	1.9977406
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	0.0000000	0.0716374	1.0420918
C	0.0081774	-1.1703110	3.1178297	C	0.0000000	-0.0287774	3.8441504
H	-0.0155197	2.2199458	1.2885610	C	0.0000000	-1.1874664	1.7037764
H	0.0026141	2.1576060	3.7671992	C	0.0000000	1.2393435	1.7683317
H	0.0149791	-2.1227390	3.6358351	C	0.0000000	1.1960536	3.1692381
H	0.0174828	-0.0320061	4.9344112	C	0.0000000	-1.2030929	3.1248761
C	-0.0012341	-2.4343077	1.0015386	H	0.0000000	2.1942850	1.2599338
H	-0.0004100	-3.3057600	1.6490266	H	0.0000000	2.1202027	3.7333419
C	-0.0008021	-2.6197182	-0.3275614	H	0.0000000	-2.1556313	3.6404173
H	0.0005623	-1.7482638	-0.9750397	H	0.0000000	-0.0513382	4.9256793
C	-0.0006618	-3.8959257	-1.0414068	C	0.0000000	-2.4332433	1.0219324
C	0.0013409	-6.2894943	-2.5256953	H	0.0000000	-3.3111123	1.6576973
C	0.0086324	-3.8836652	-2.4438708	C	0.0000000	-2.6201065	-0.3491021
C	-0.0095195	-5.1456125	-0.4008069	H	0.0000000	-1.7423331	-0.9850295
C	-0.0083637	-6.3223710	-1.1323637	C	0.0000000	-3.8661454	-1.0304871
C	0.0097161	-5.0625347	-3.1780862	C	0.0000000	-6.2505170	-2.4944896
H	0.0151820	-2.9312205	-2.9618578	C	0.0000000	-3.8513397	-2.4515838
H	-0.0180484	-5.2000136	0.6800995	C	0.0000000	-5.1248549	-0.3680944
H	-0.0155025	-7.2739833	-0.6147012	C	0.0000000	-6.2929783	-1.0935839
H	0.0169765	-5.0219207	-4.2605040	C	0.0000000	-5.0260956	-3.1701184
H	0.0019283	-7.2115736	-3.0933536	H	0.0000000	-2.8991289	-2.9677178
[trans-stilbene]⁺				H	0.0000000	-5.1743702	0.7117812
26 atoms				H	0.0000000	-7.2475908	-0.5845899
H	0.0000000	0.1218122	-0.0377706	H	0.0000000	-5.0042065	-4.2516564
				H	0.0000000	-7.1750057	-3.0580244

2. NMR Spectra

Figure S2. ^1H NMR (400 MHz, CDCl_3) of S1-a

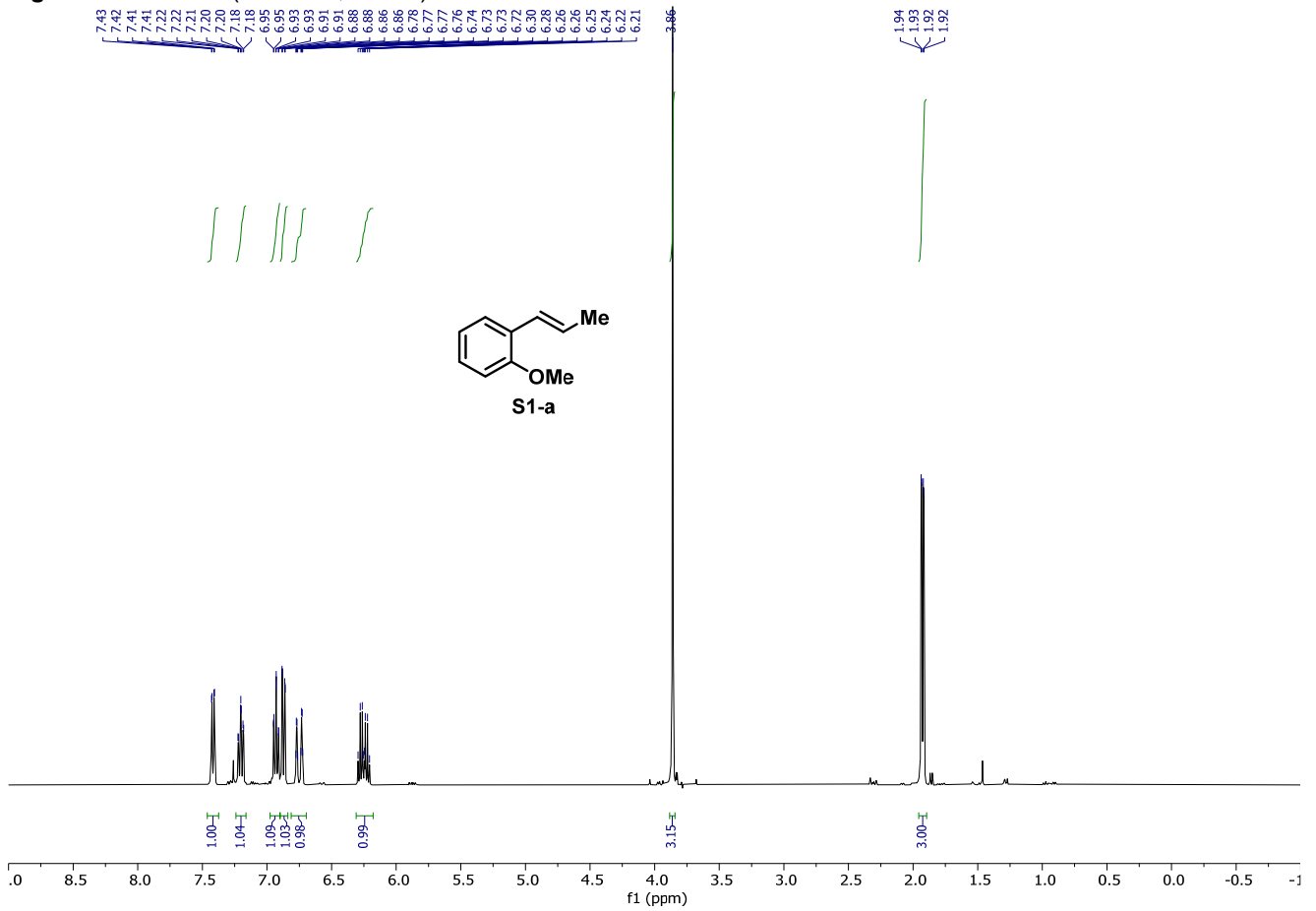


Figure S3. ^{13}C NMR (101 MHz, CDCl_3) of S1-a

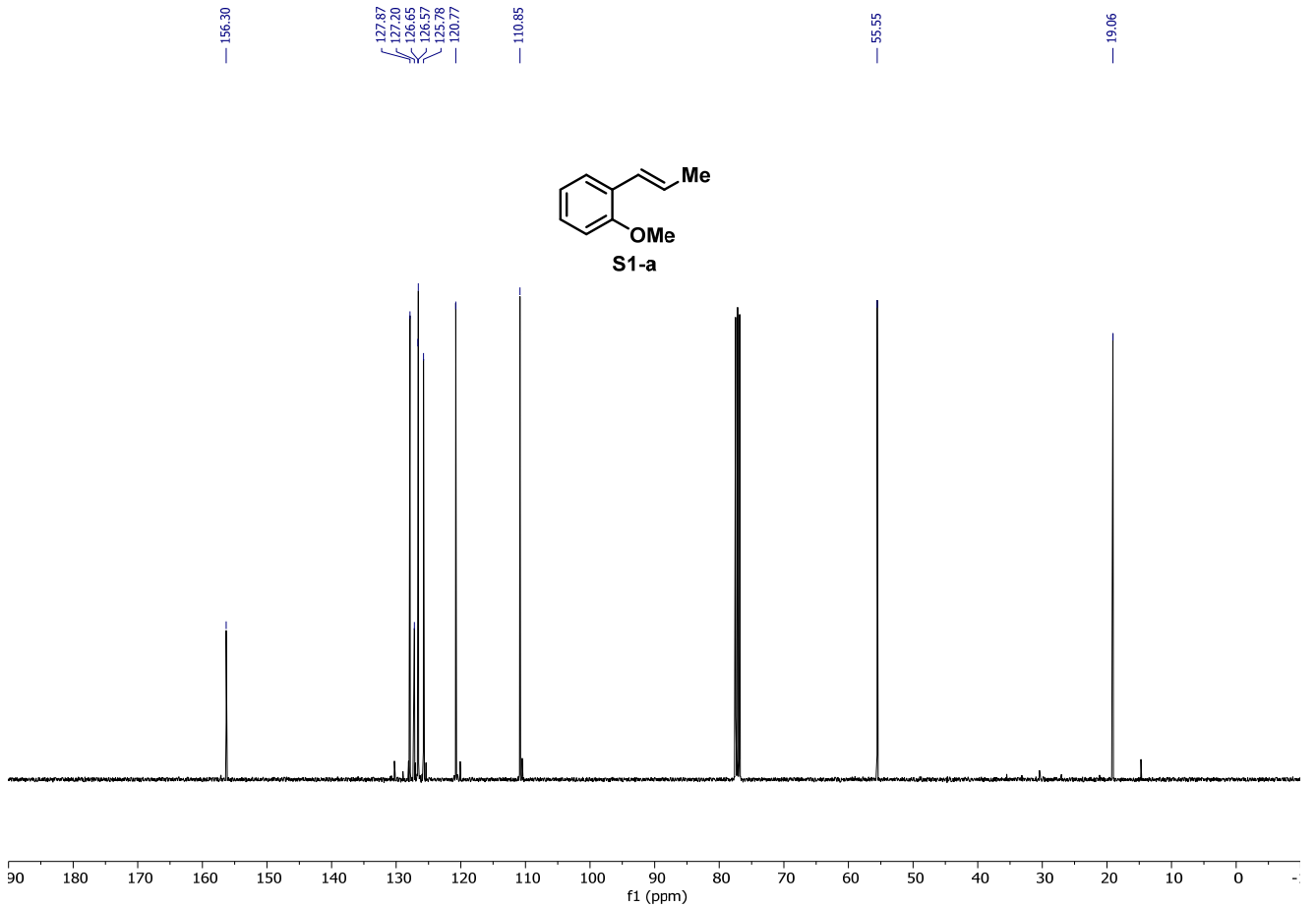


Figure S4. ^1H NMR (400 MHz, CDCl_3) of S4-a

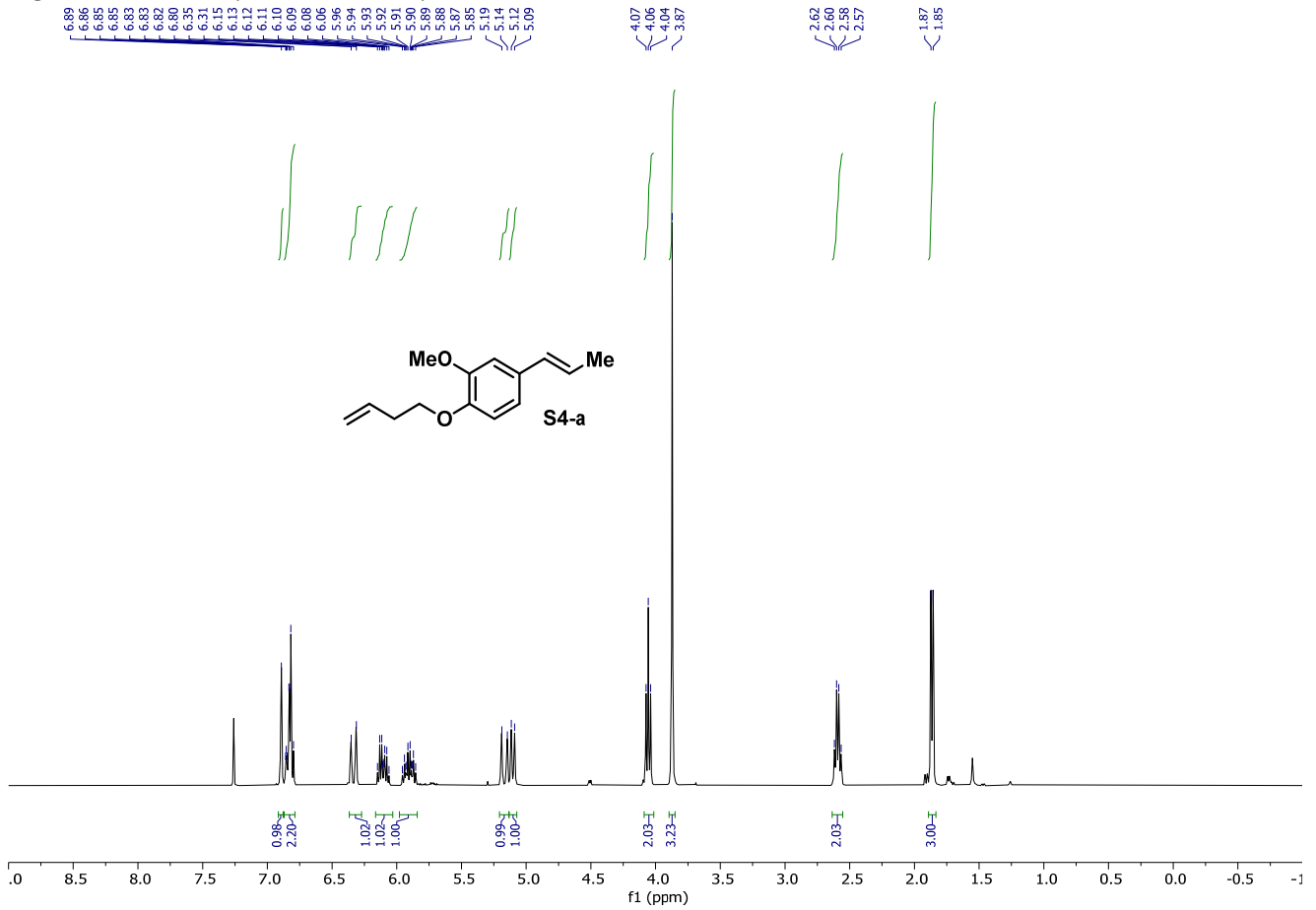


Figure S5. ^{13}C NMR (101 MHz, CDCl_3) of S4-a

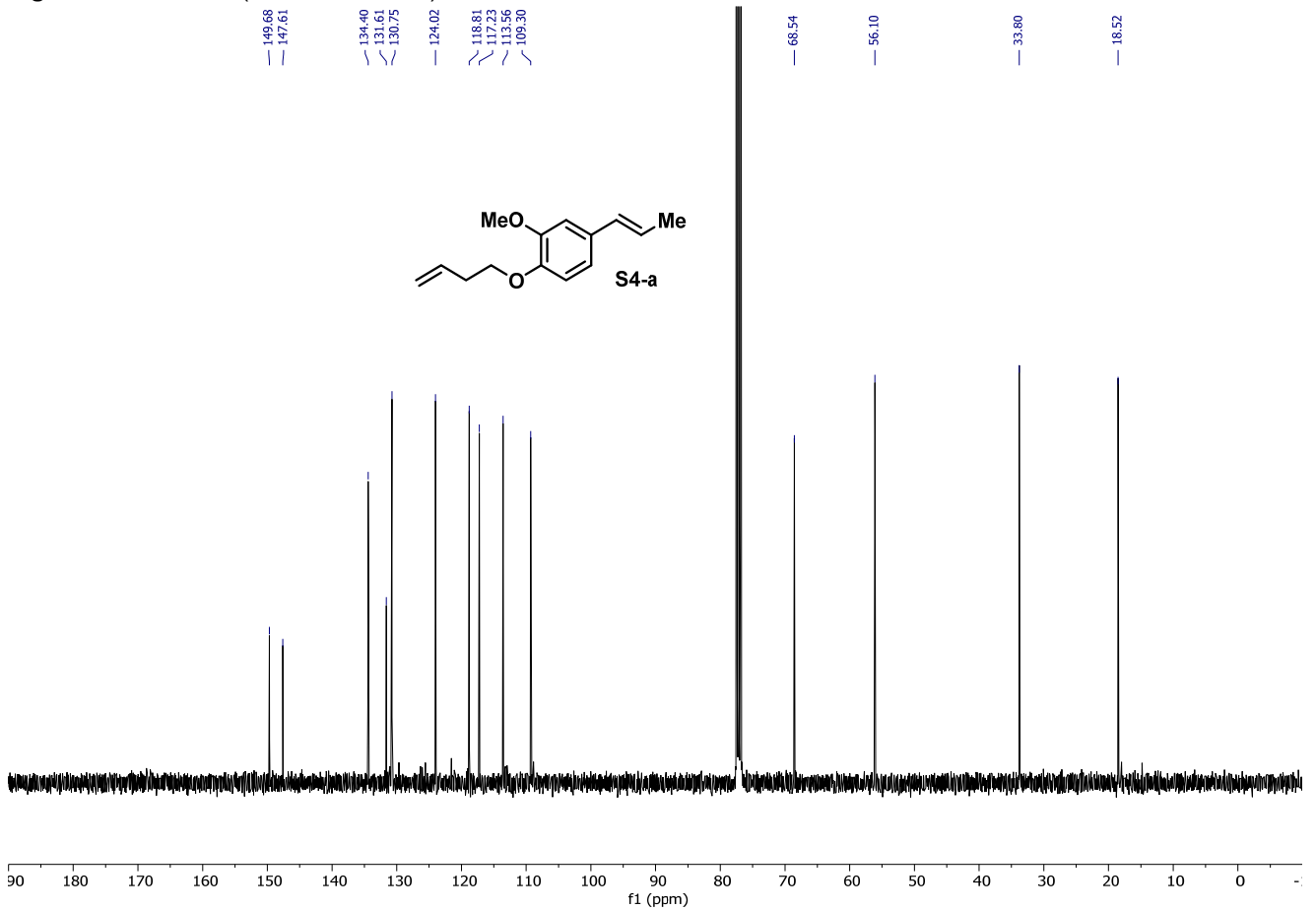


Figure S6. ¹H NMR (400 MHz, CDCl₃) of S3-a

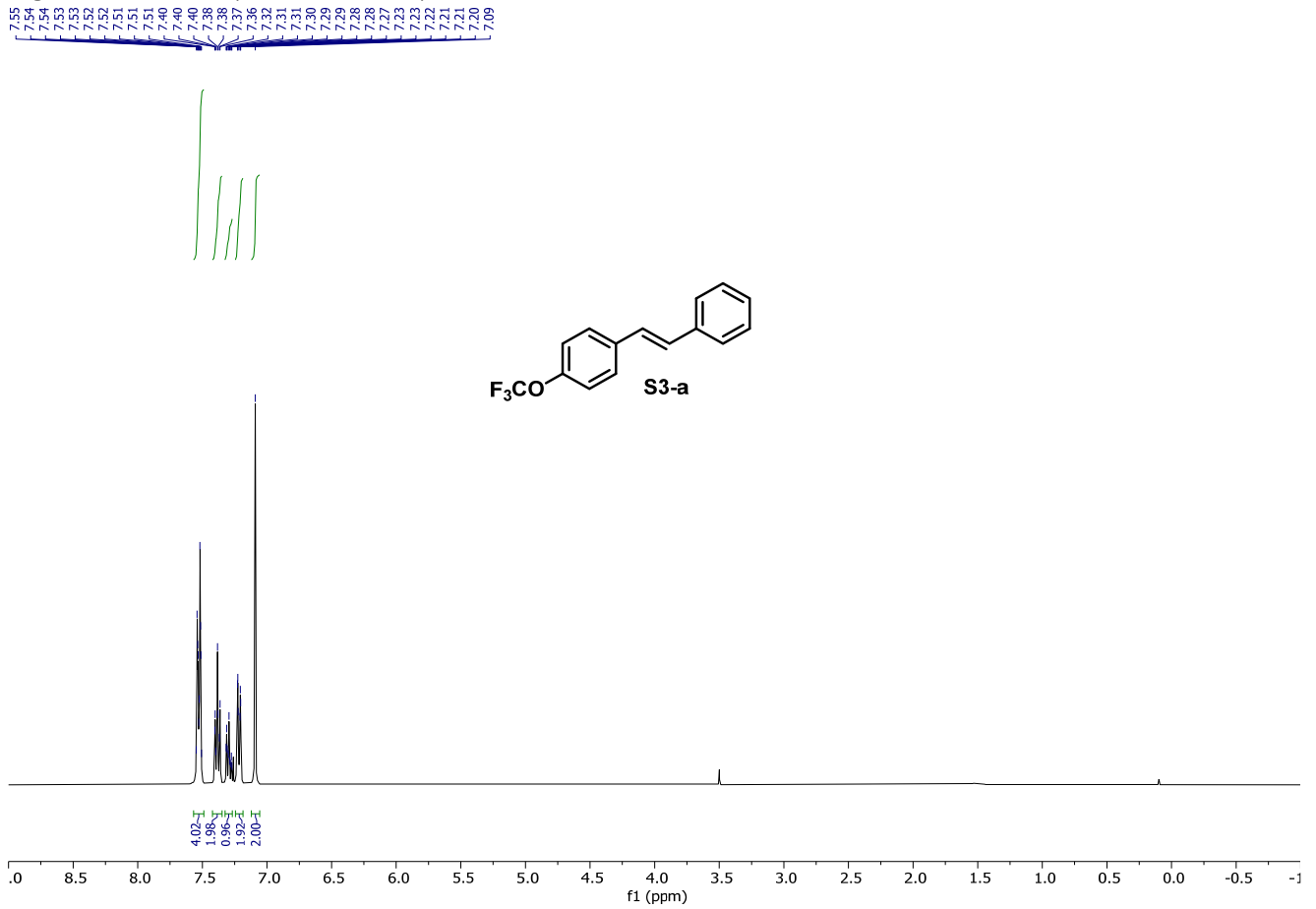


Figure S7. ¹³C NMR (101 MHz, CDCl₃) of S3-a

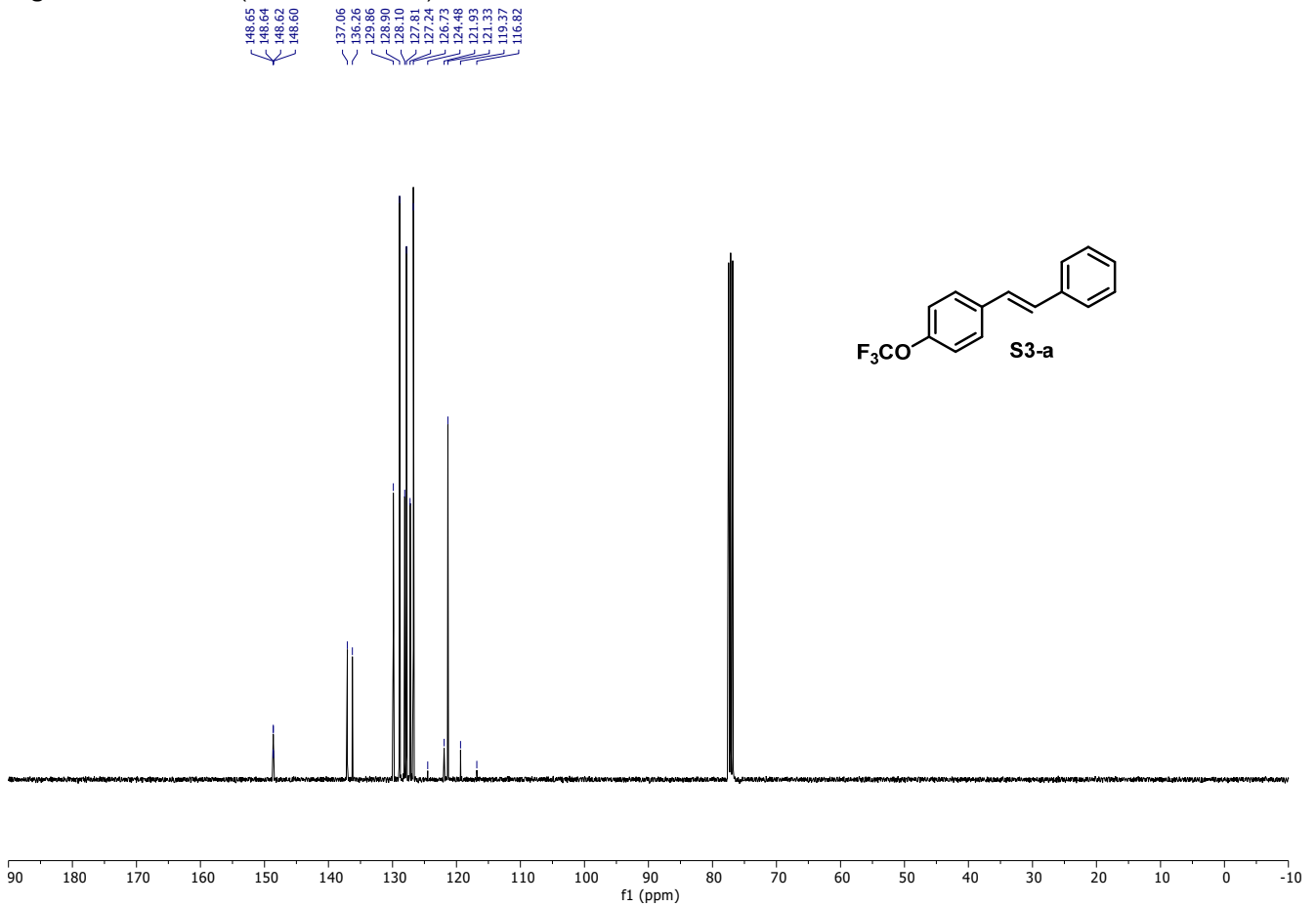


Figure S8. ^{19}F NMR (376 MHz, CD_3OD) of S3-a

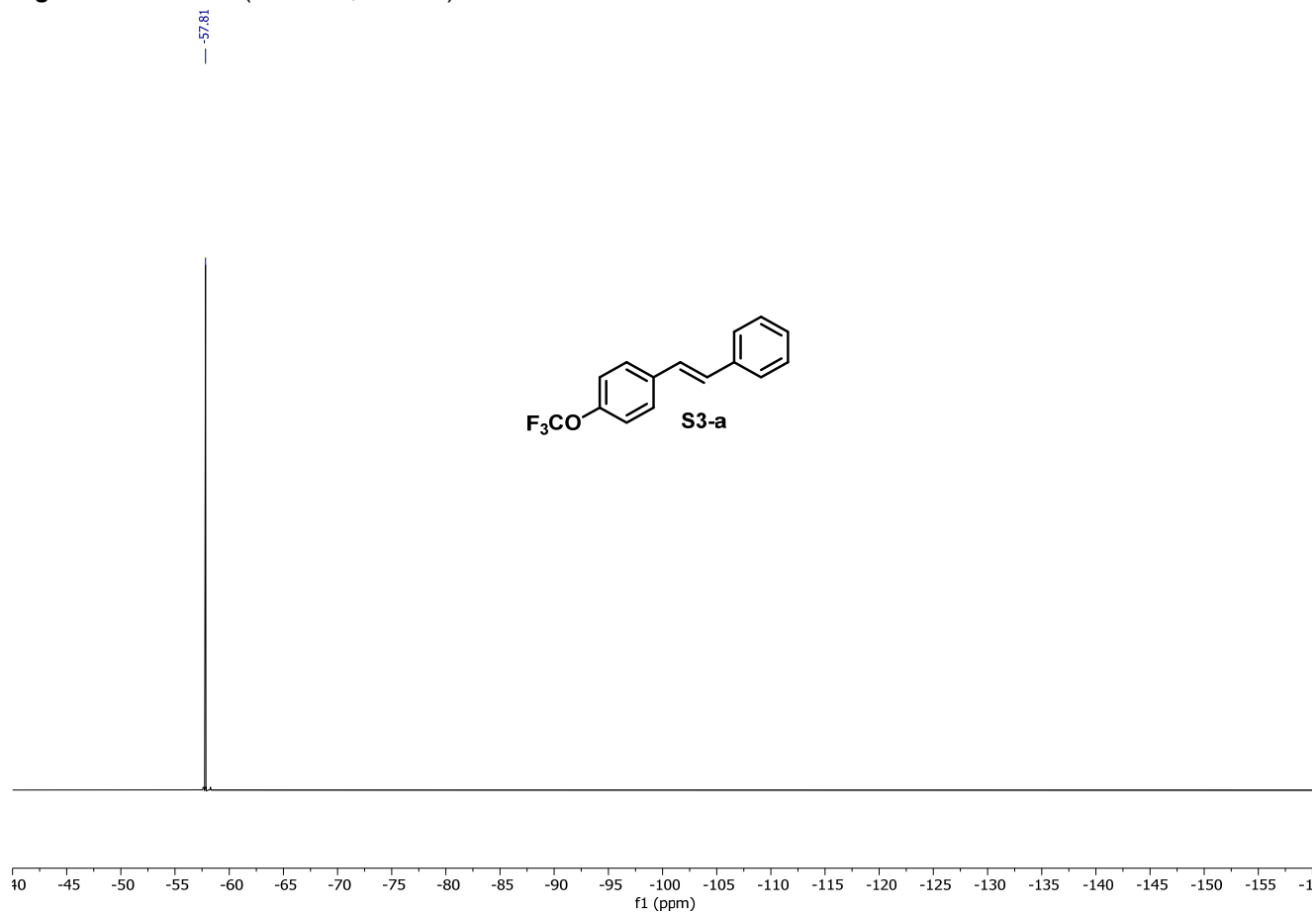


Figure S9. ^1H NMR (400 MHz, CDCl_3) of S2-a

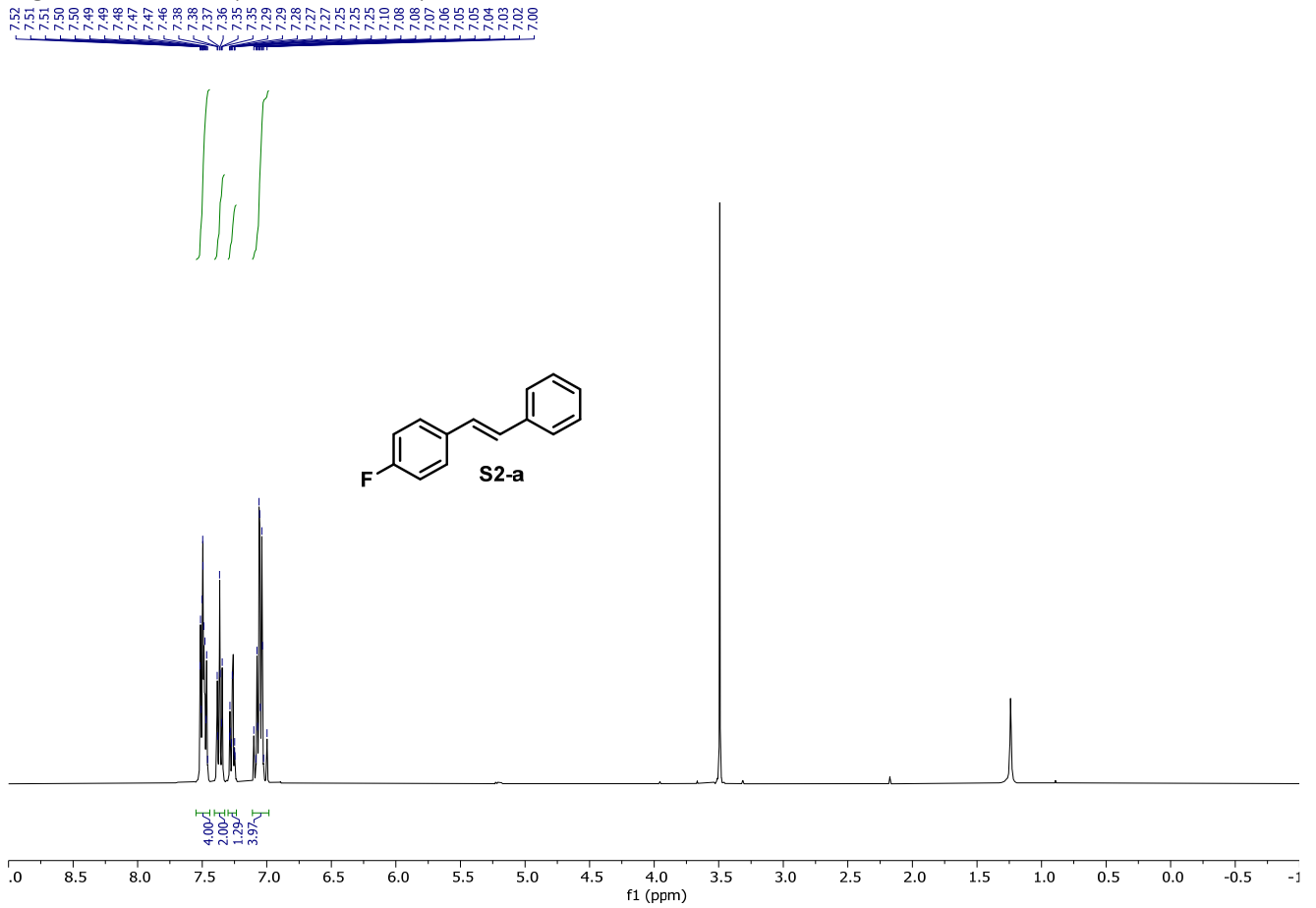


Figure S10. ^{19}F NMR (376 MHz, CD_3OD) of S2-a

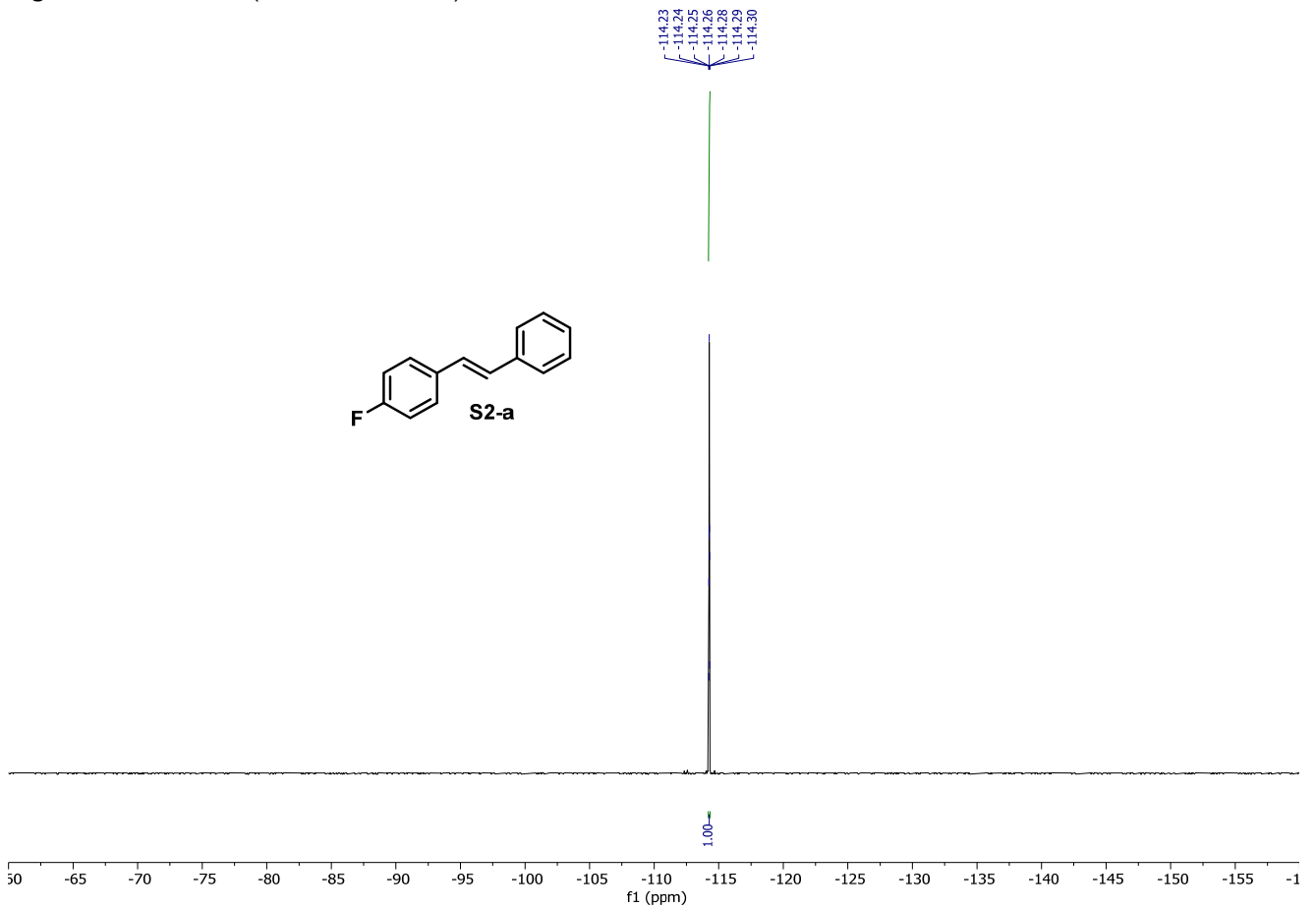


Figure S11. ¹H NMR (400 MHz, CDCl₃) of S2-b

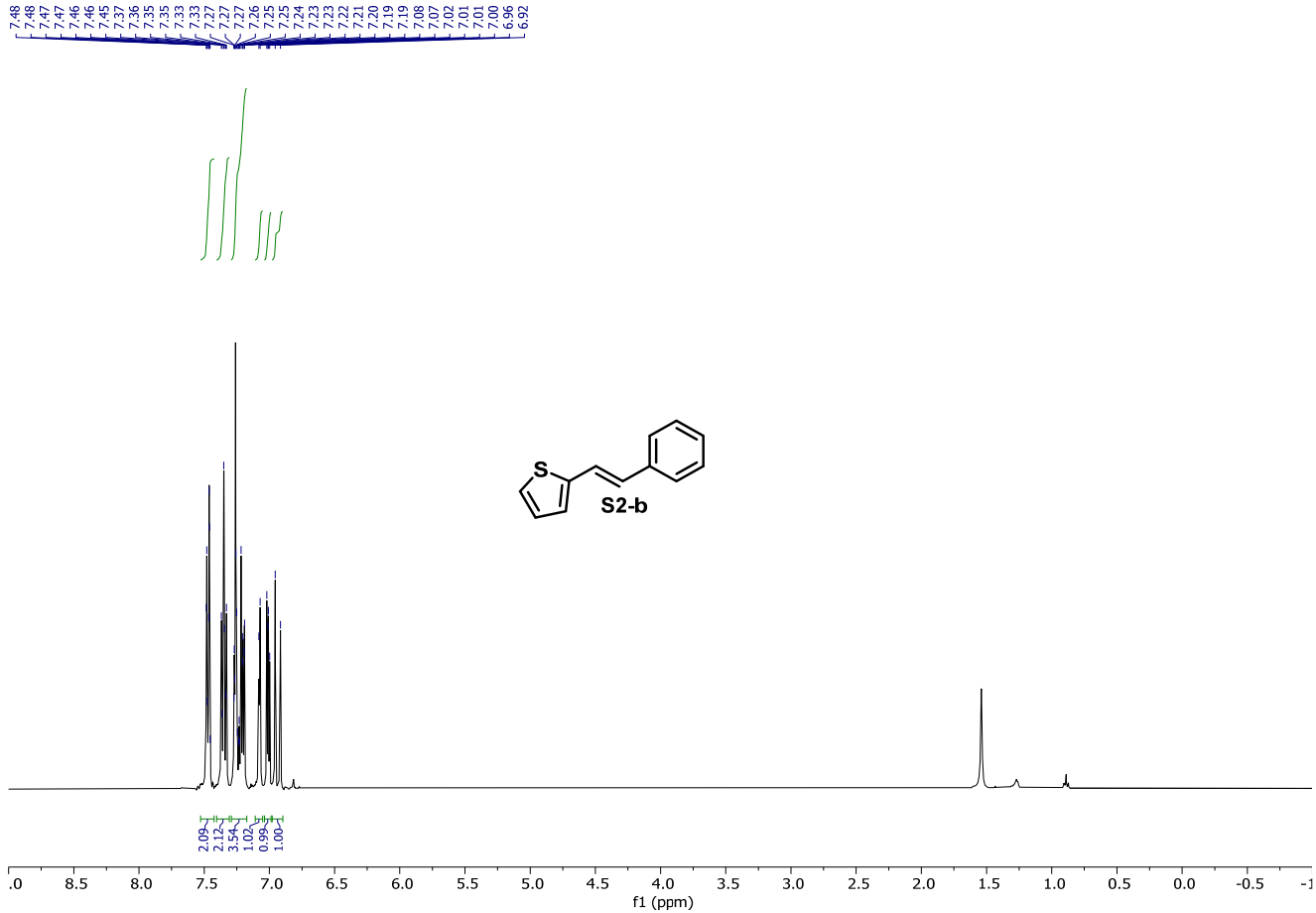


Figure S12. ¹³C NMR (101 MHz, CDCl₃) of S2-b

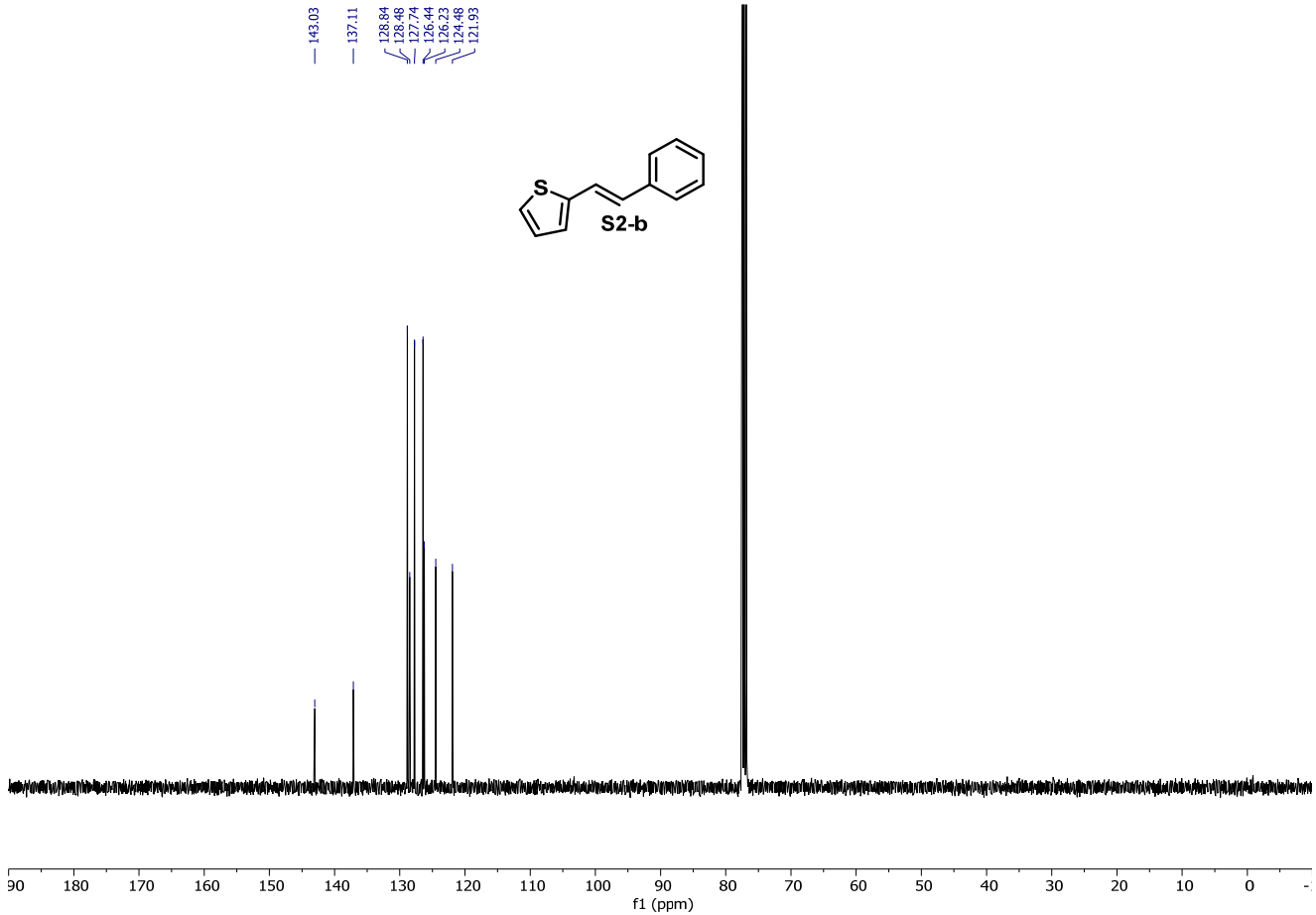


Figure S13. ¹H NMR (400 MHz, CDCl₃) of S1-b

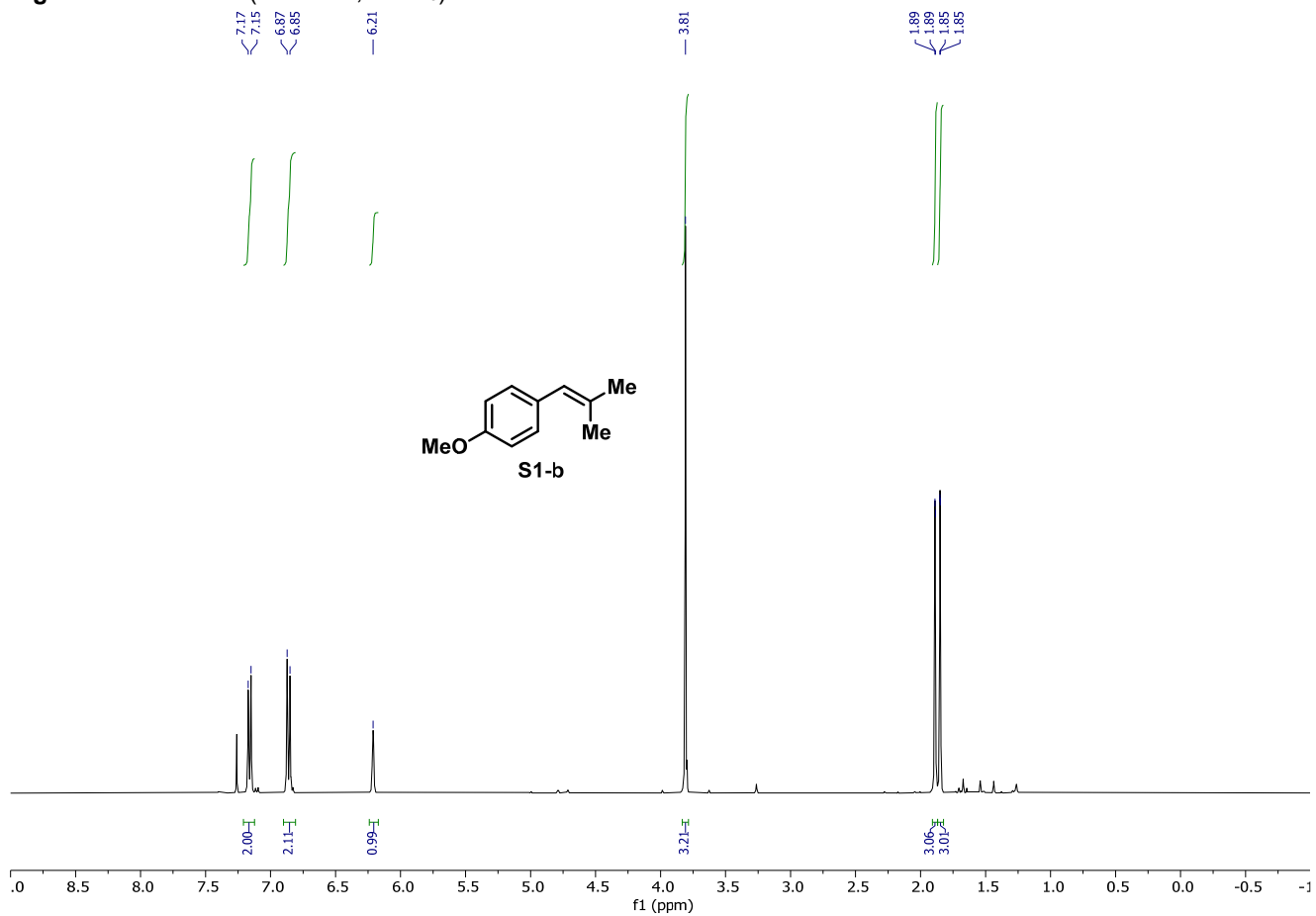


Figure S14. ¹³C NMR (101 MHz, CDCl₃) of S1-b

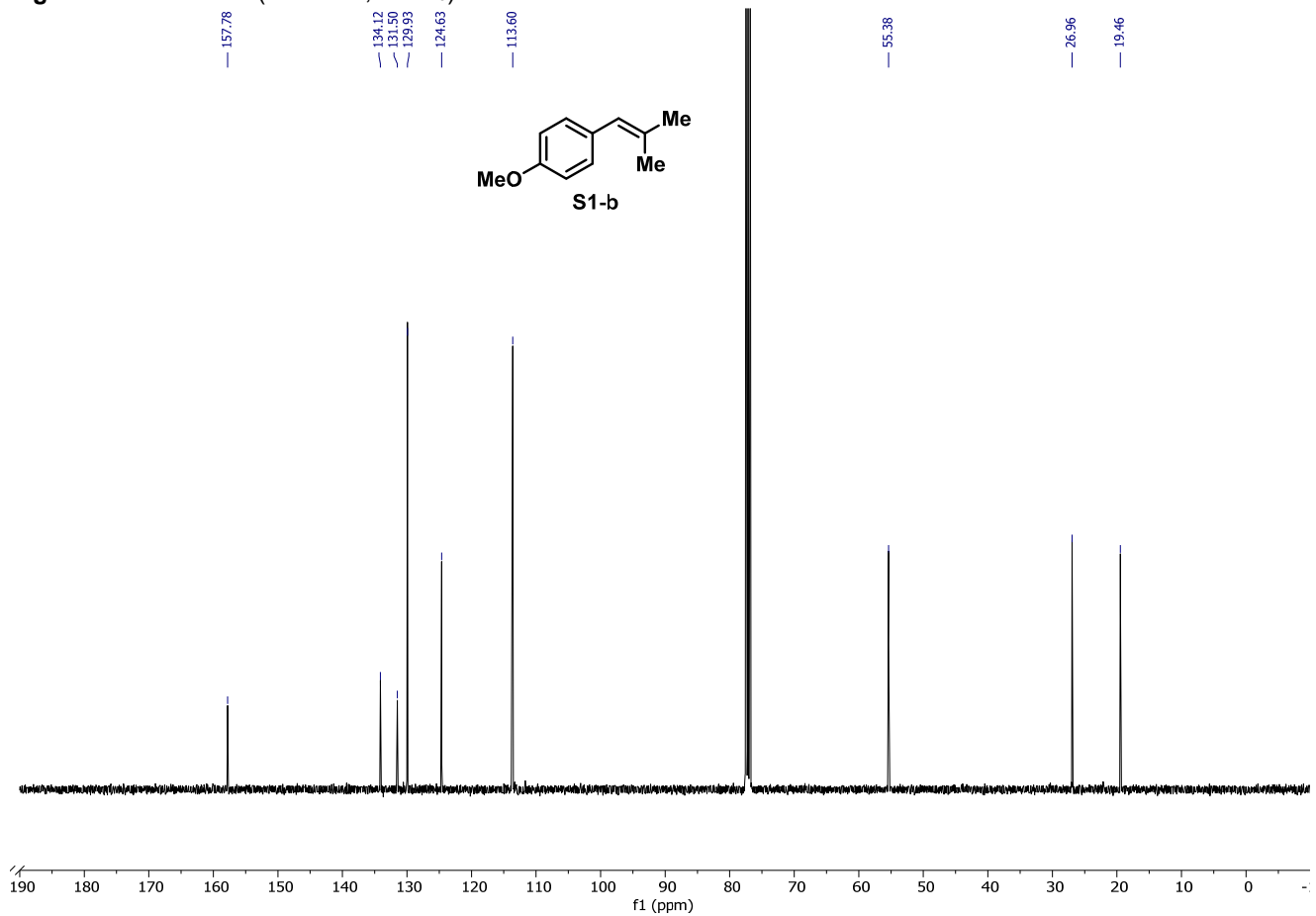


Figure S15. ^1H NMR (400 MHz, CDCl_3) of S1-c

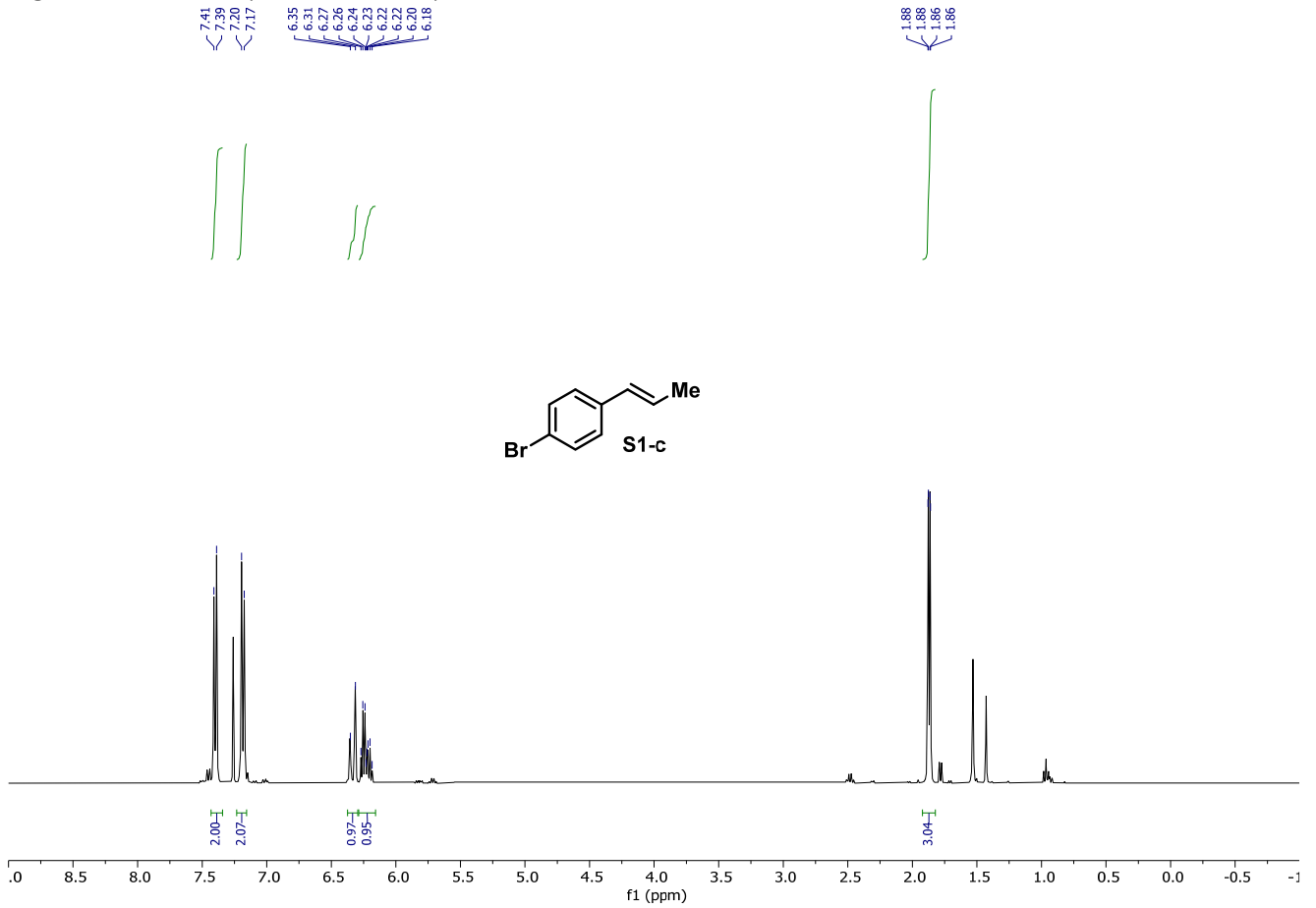


Figure S16. ^1H NMR (400 MHz, CDCl_3) of S1-d

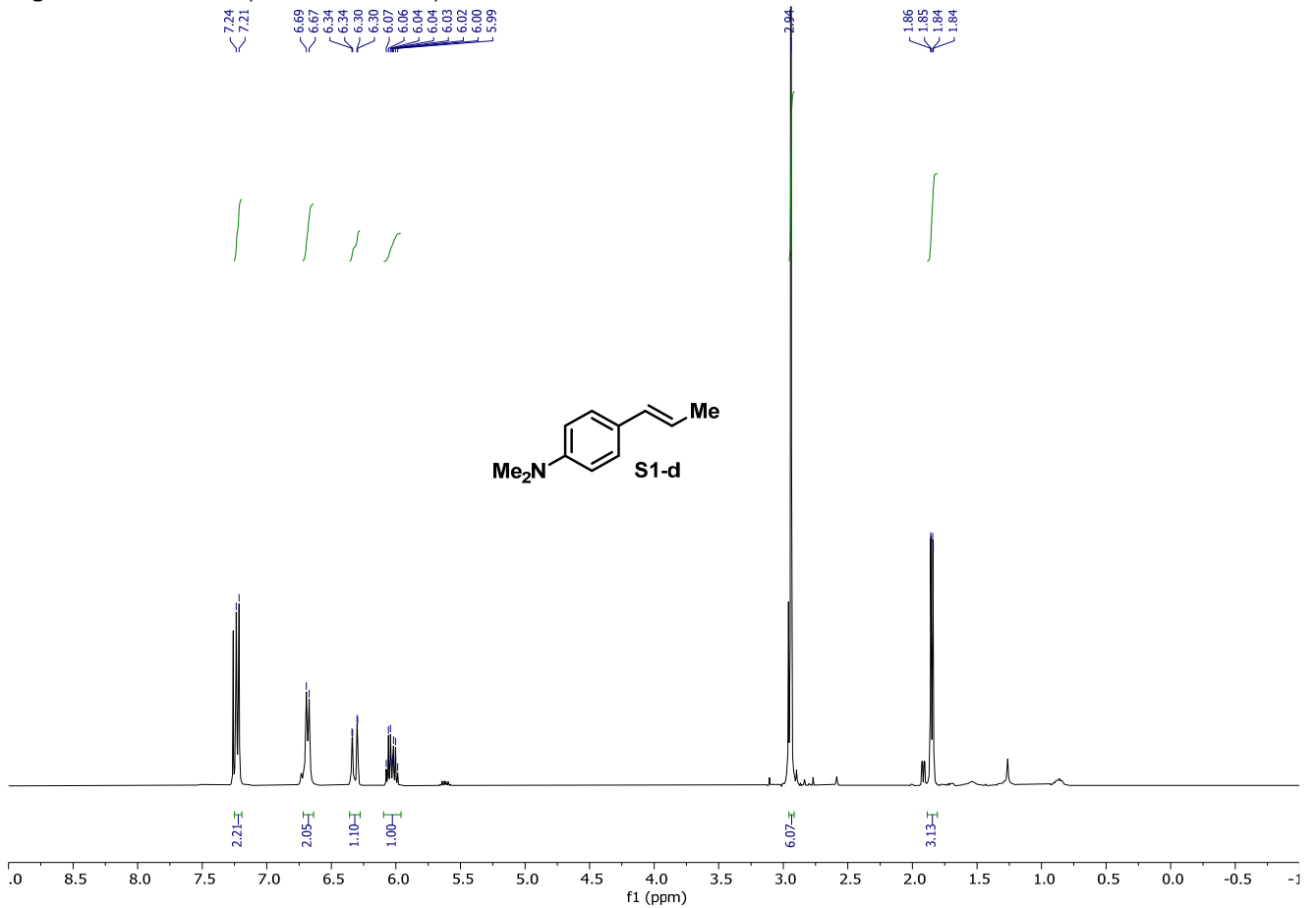


Figure S17. ¹H NMR (400 MHz, CDCl₃) of S2-c

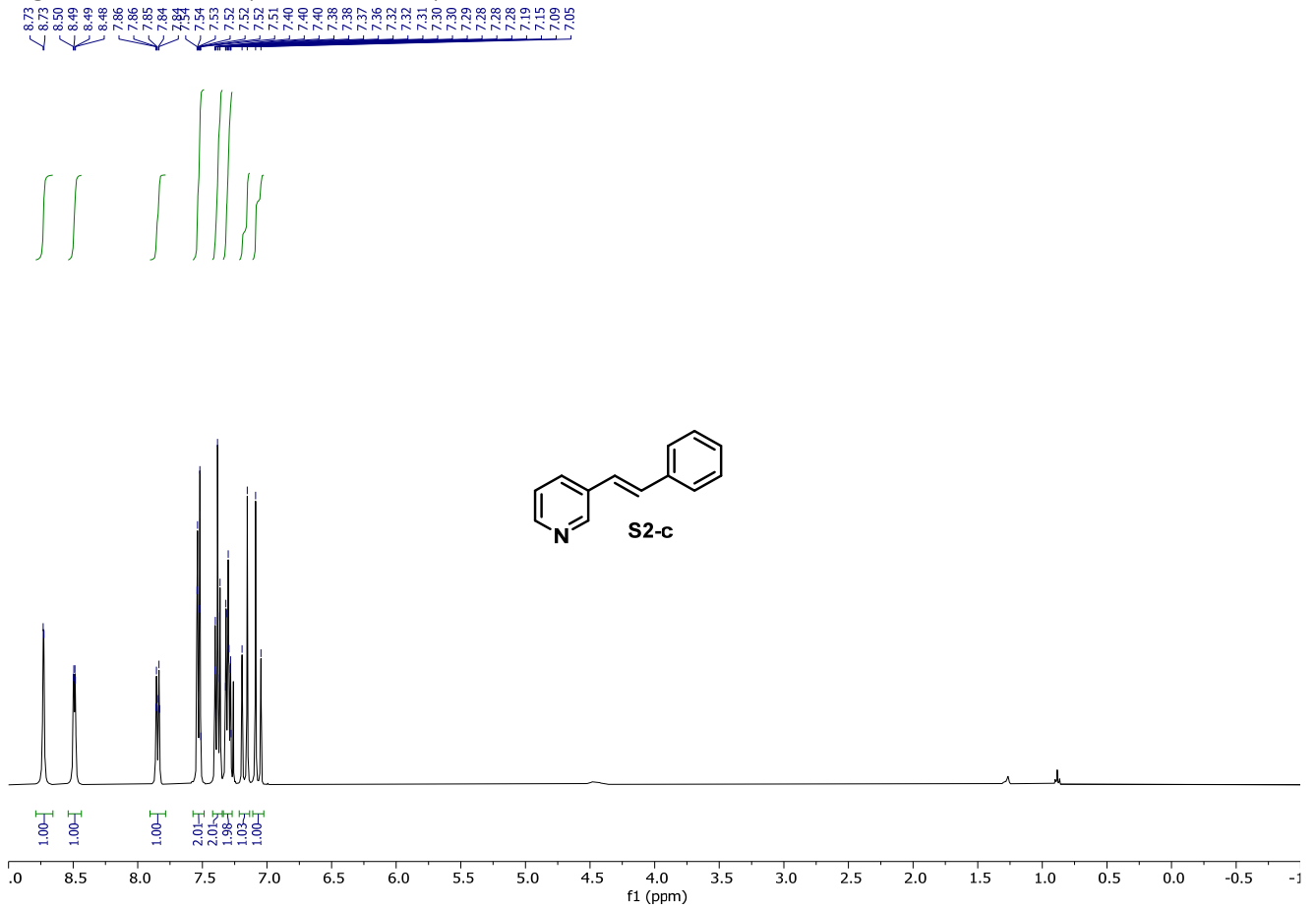


Figure S18. ¹³C NMR (101 MHz, CDCl₃) of S2-c

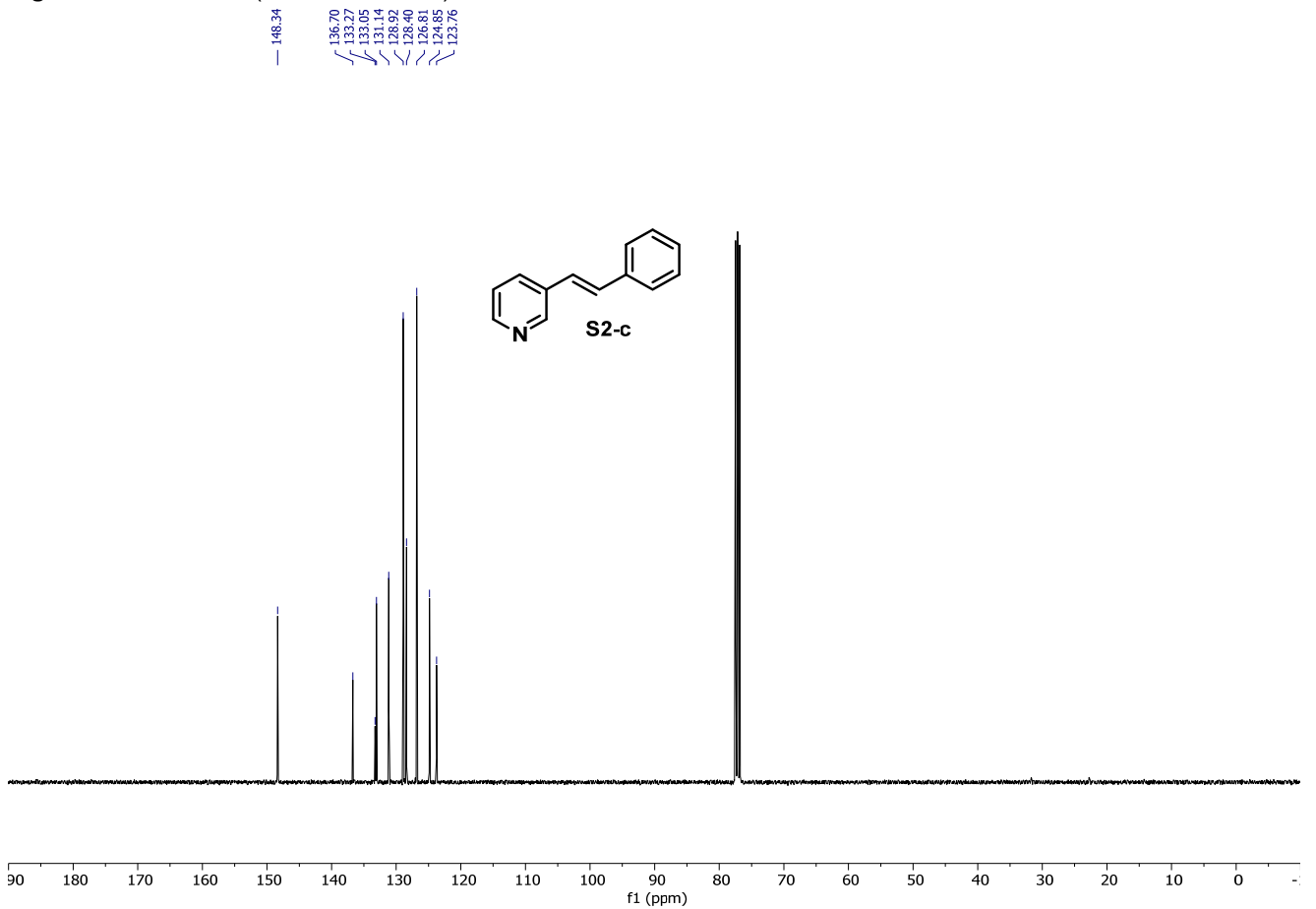


Figure S19. ¹H NMR (400 MHz, CDCl₃) of S3-b

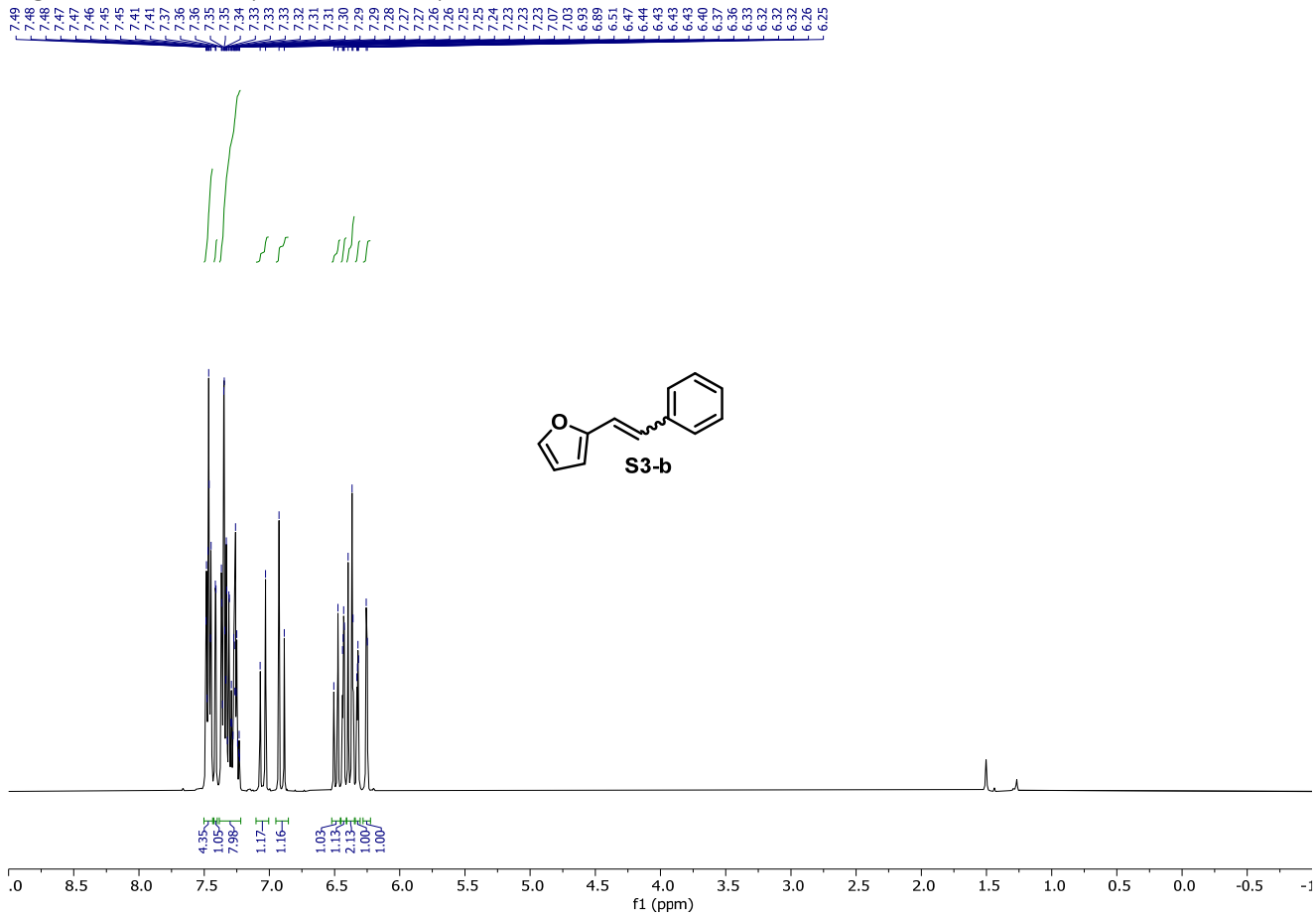


Figure S20. ¹³C NMR (101 MHz, CDCl₃) of S3-b

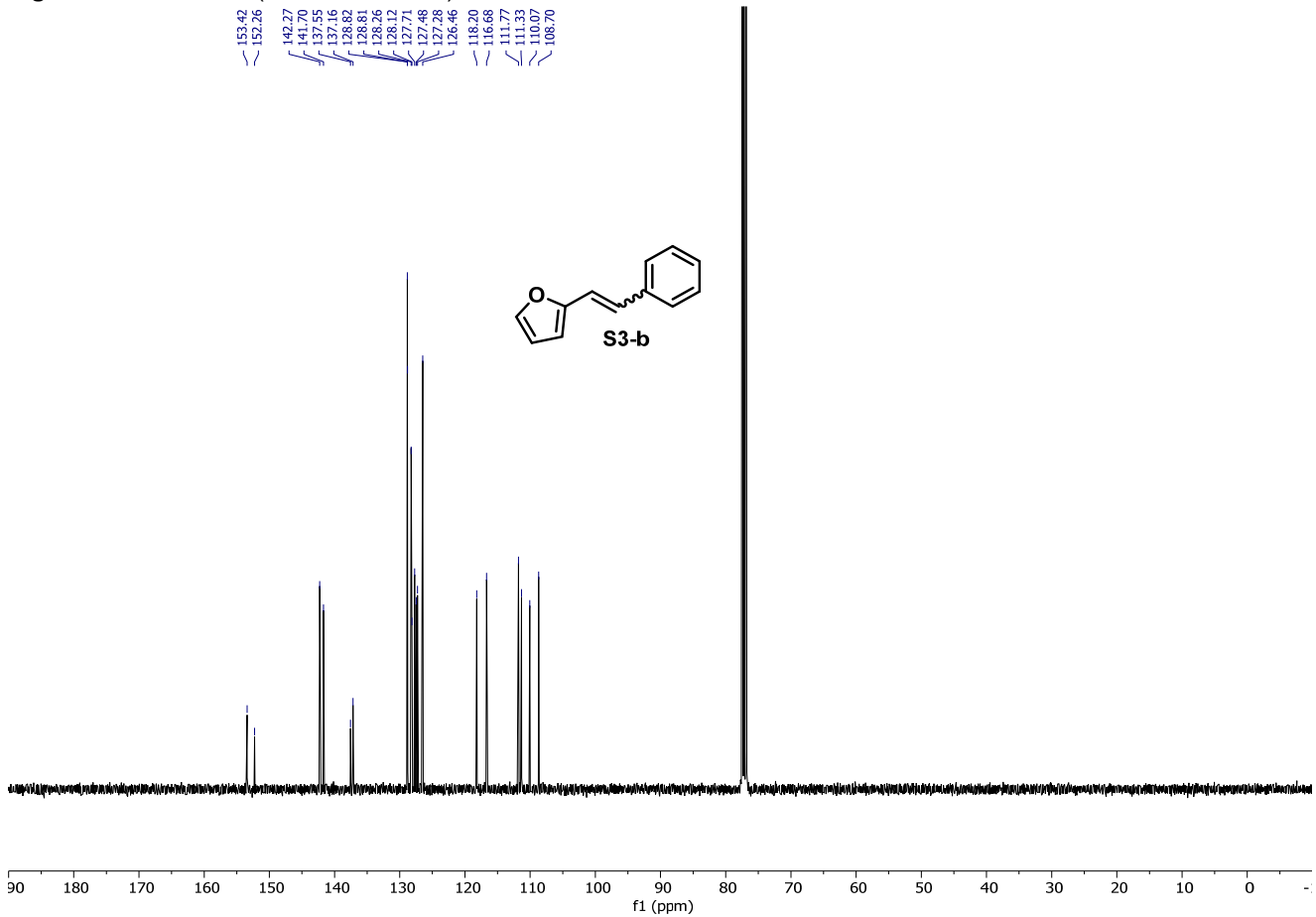


Figure S21. ^1H NMR (400 MHz, CDCl_3) of S3-c

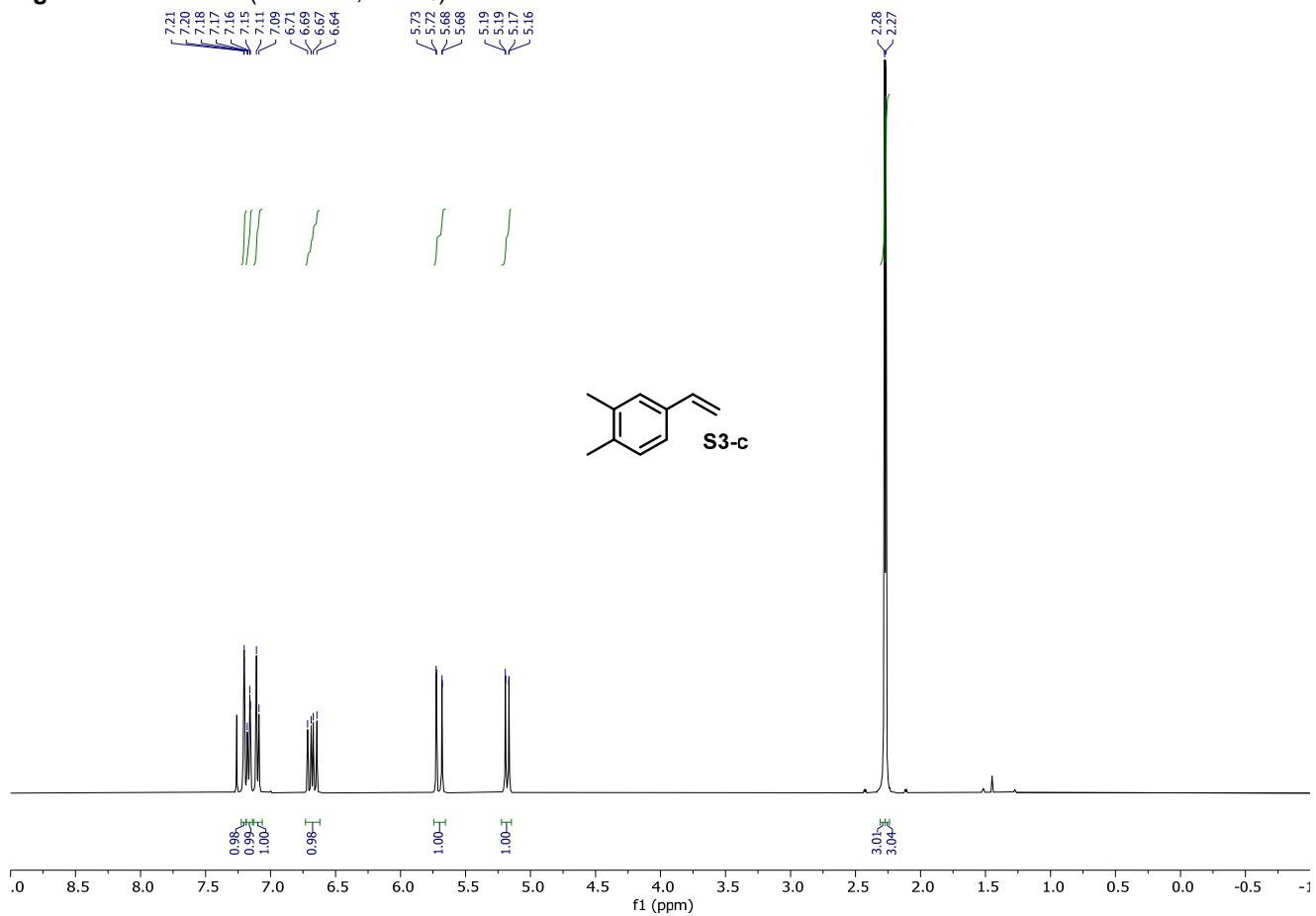


Figure S22. ^{13}C NMR (101 MHz, CDCl_3) of S3-c

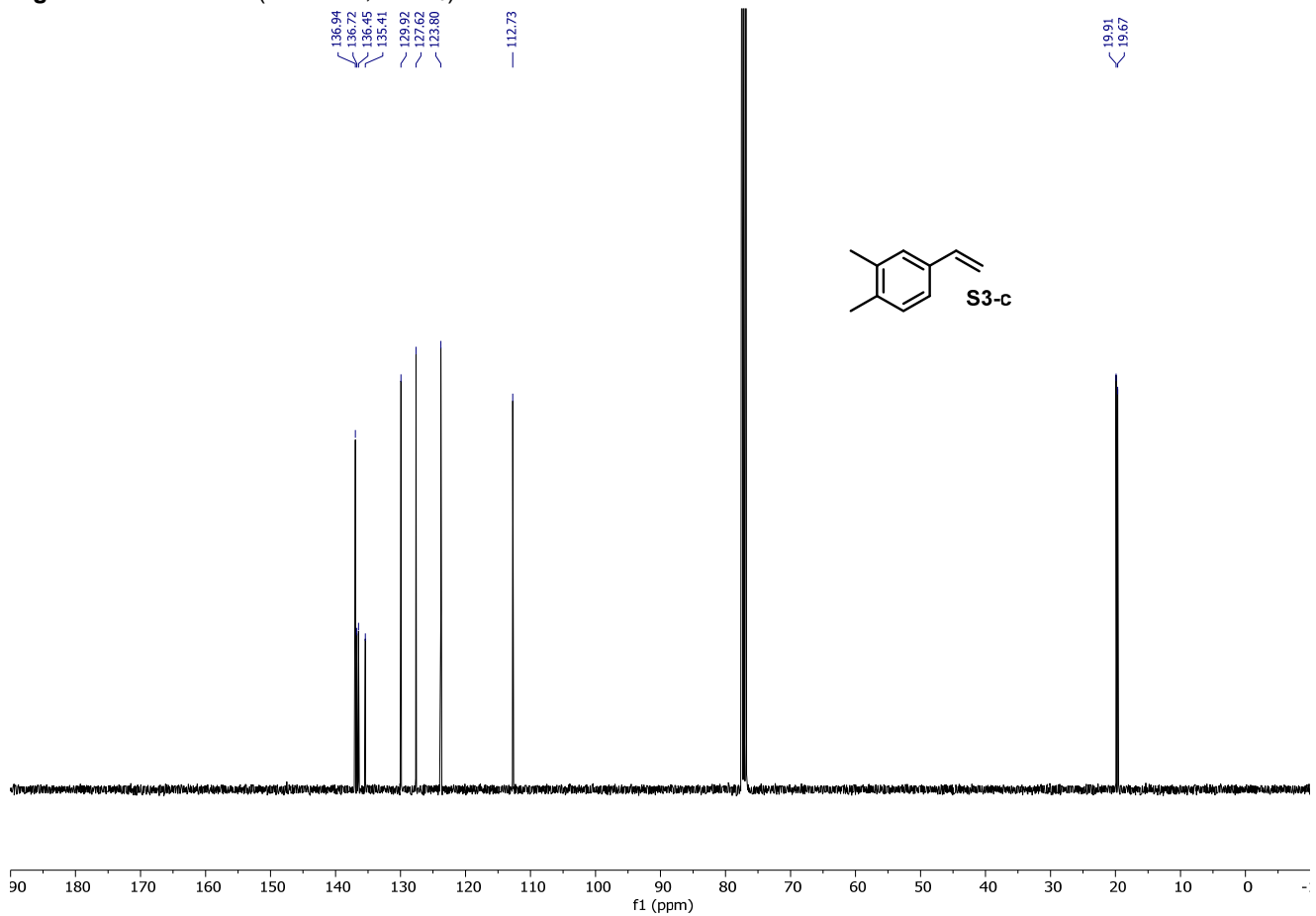


Figure S23. ^1H NMR (400 MHz, CD_3OD) of 1-B

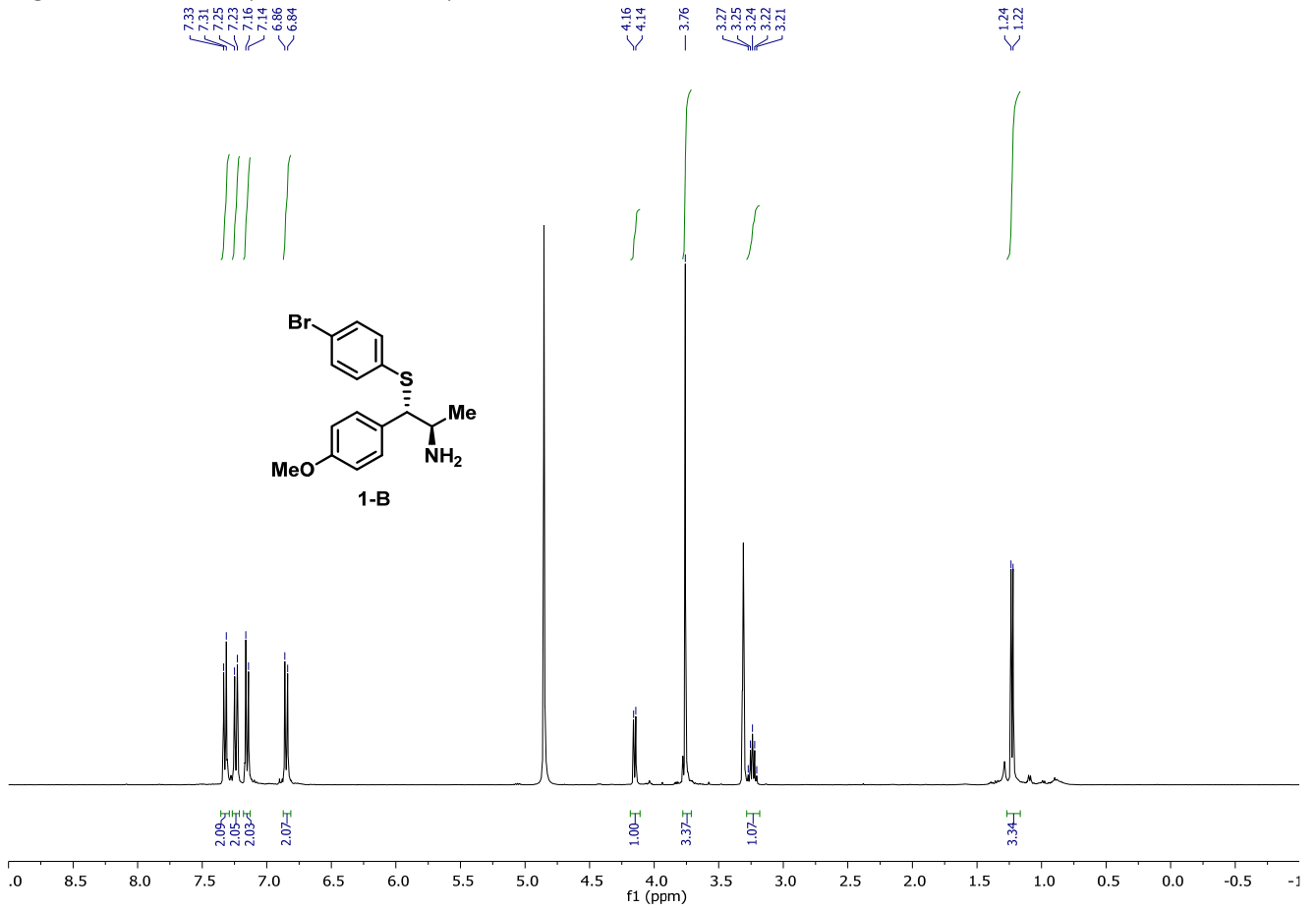


Figure S24. ^{13}C NMR (101 MHz, CD_3OD) of 1-B

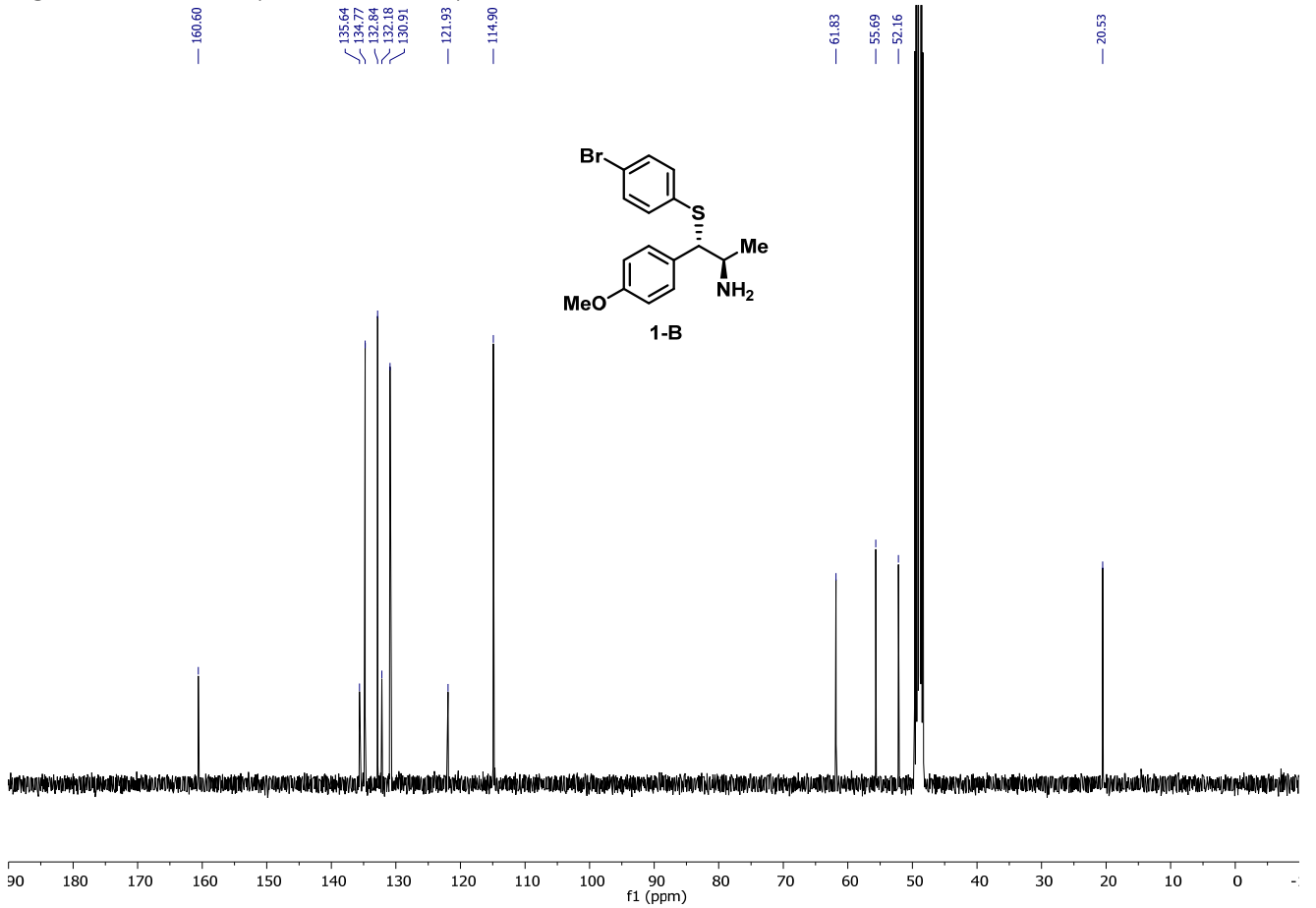


Figure S25. ¹H NMR (400 MHz, CD₃OD) of 2-B

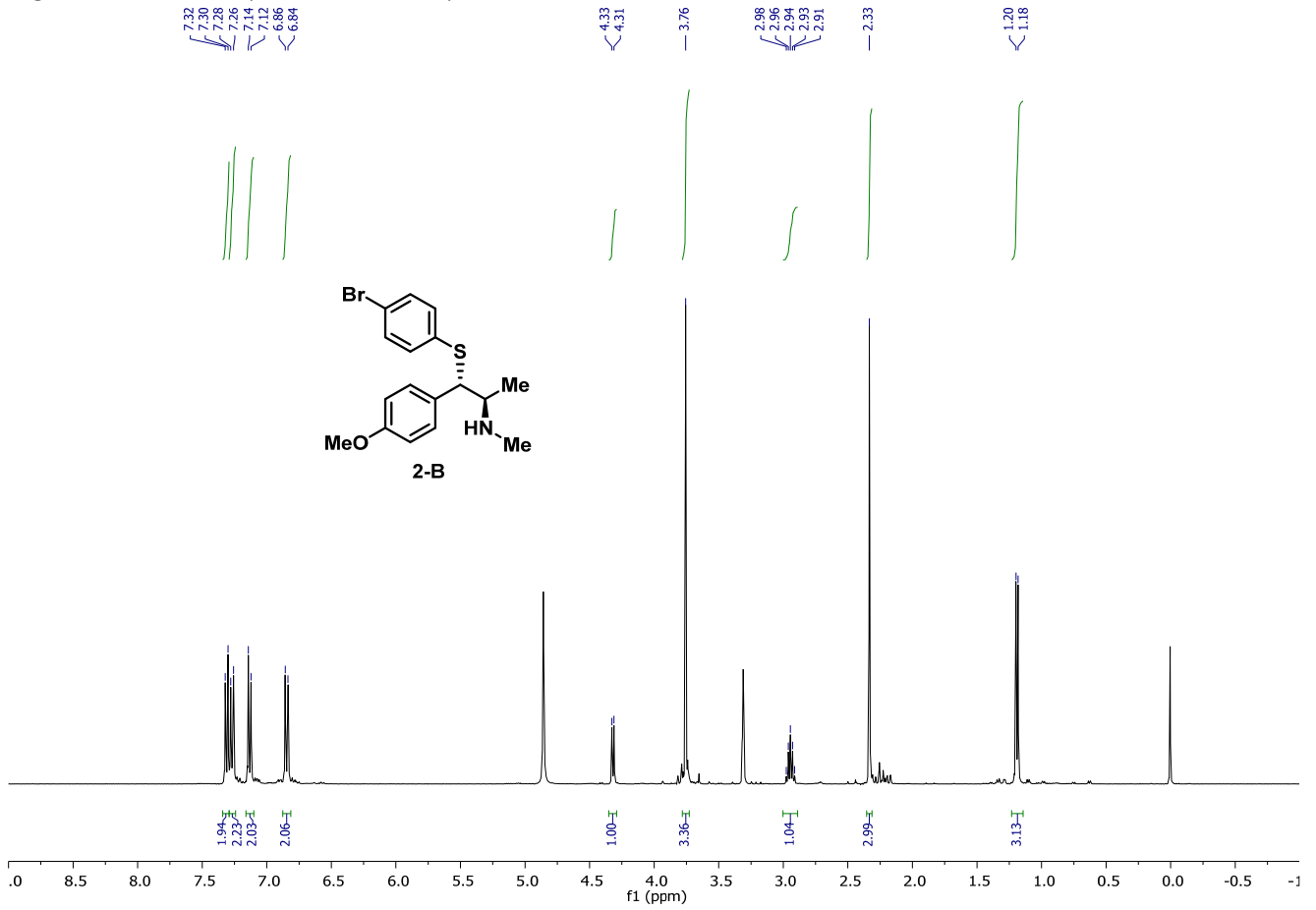


Figure S26. ¹³C NMR (101 MHz, CD₃OD) of 2-B

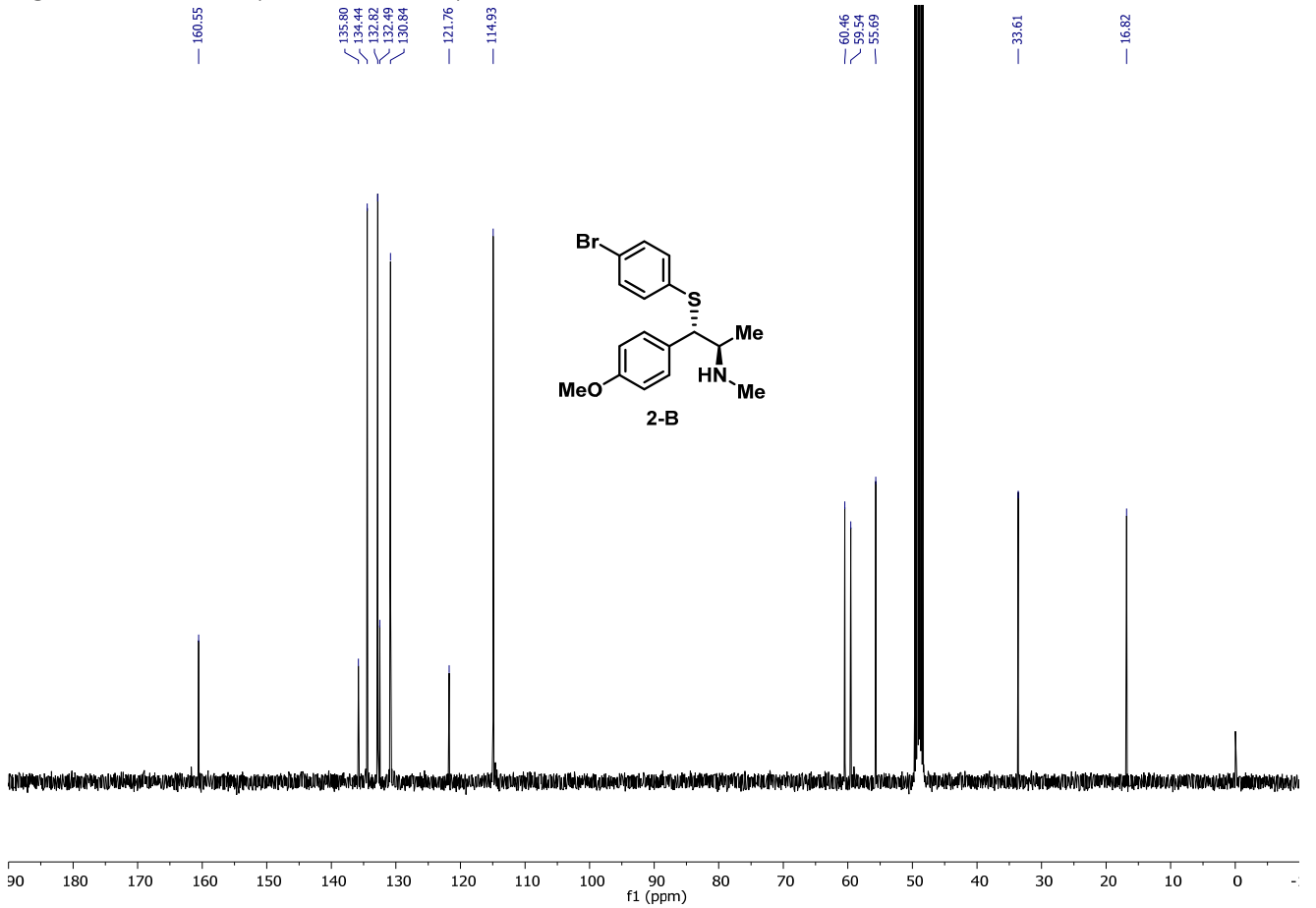


Figure S27. ¹H NMR (400 MHz, CD₃OD) of 3-A

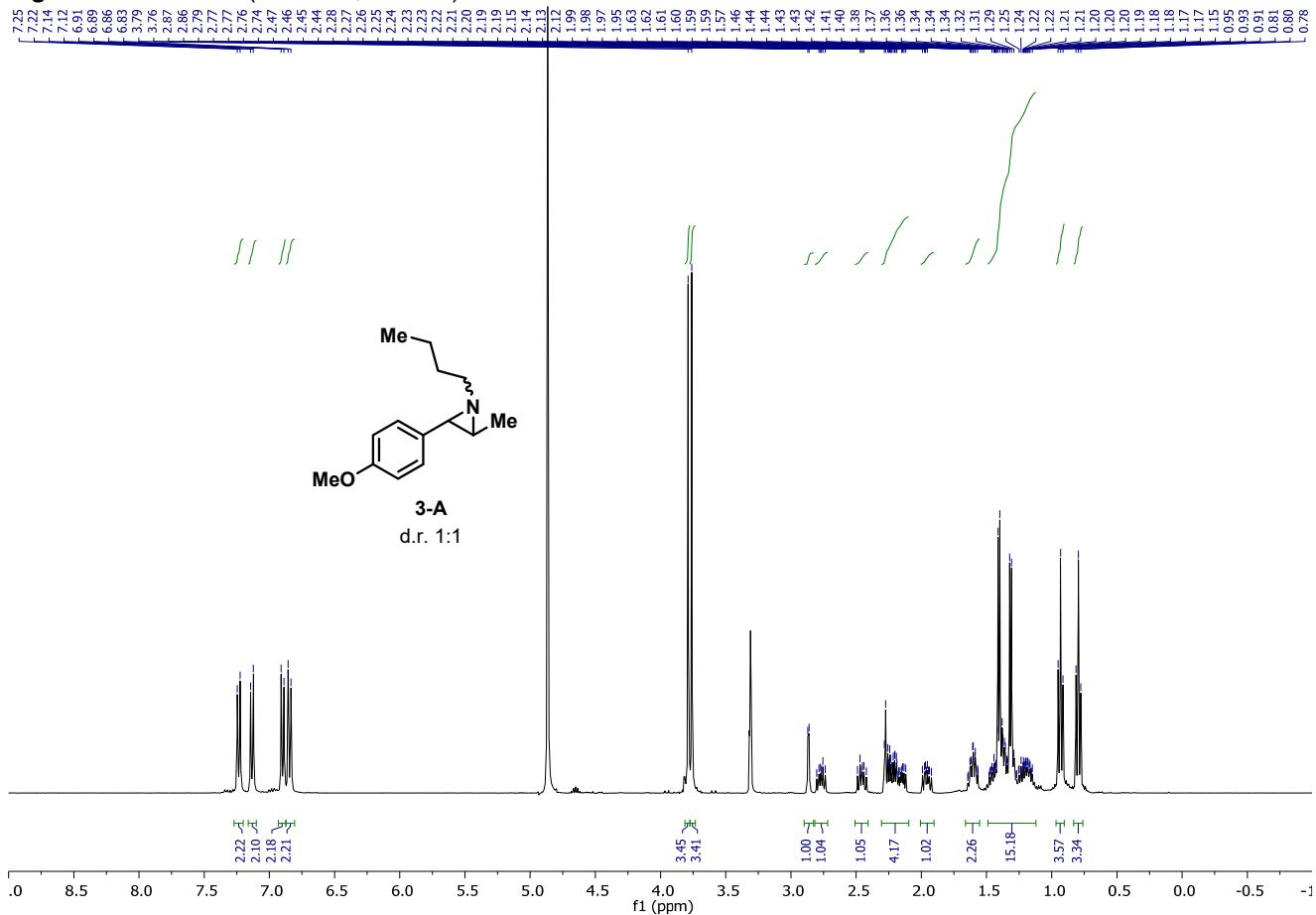


Figure S28. ¹³C NMR (101 MHz, CD₃OD) of 3-A

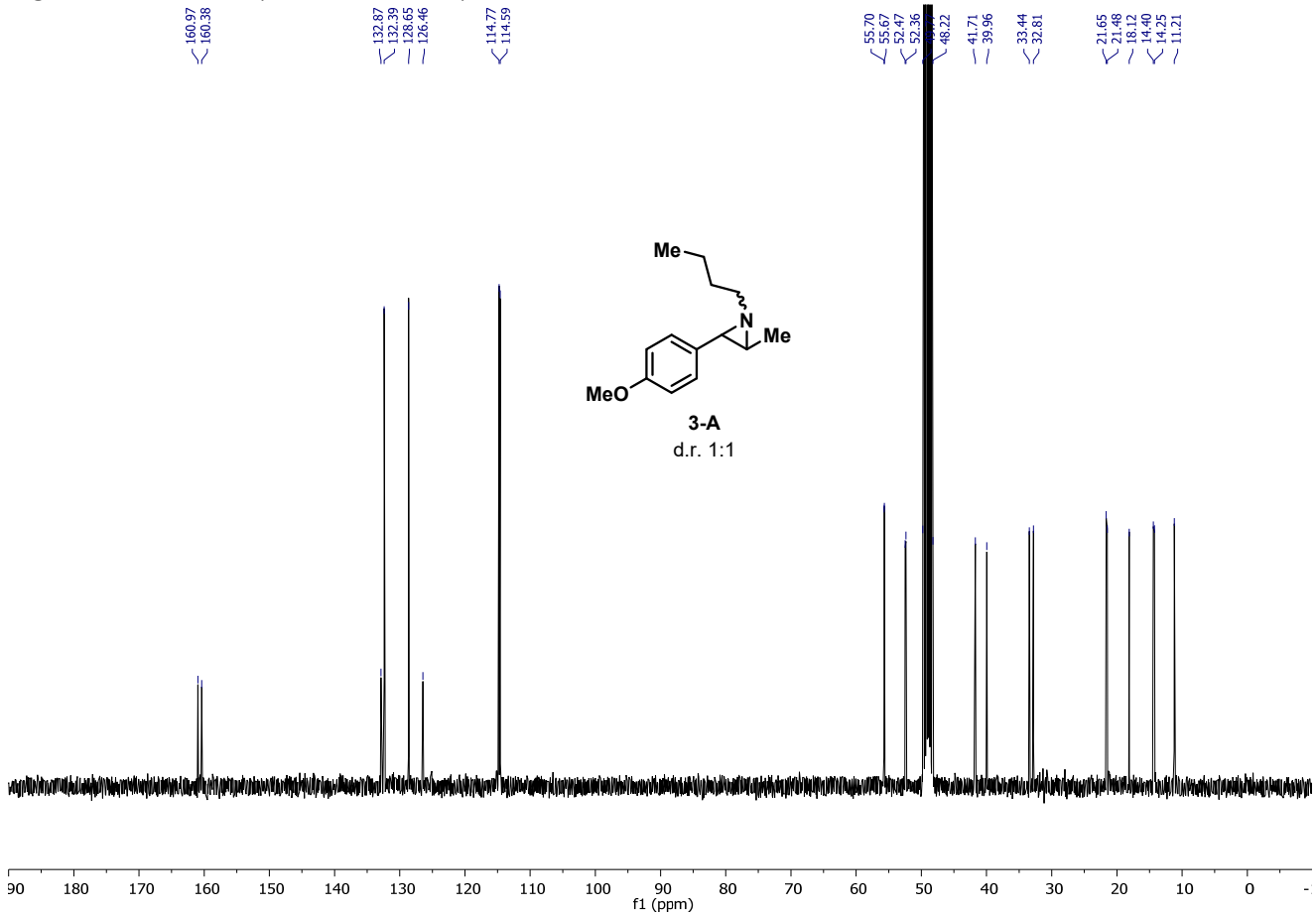


Figure S29. ¹H NMR (400 MHz, CD₃OD) of 3-B

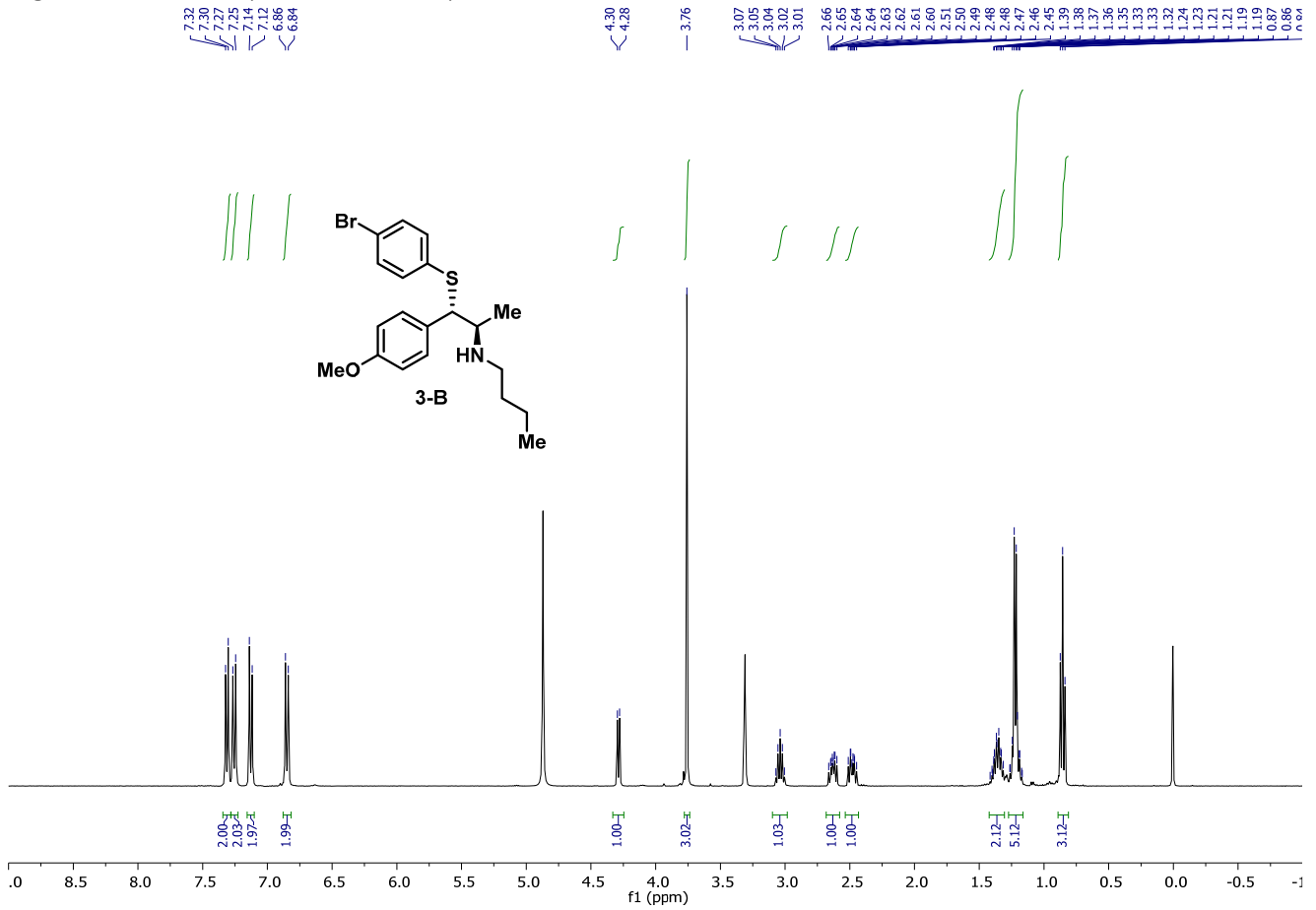


Figure S30. ¹³C NMR (101 MHz, CD₃OD) of 3-B

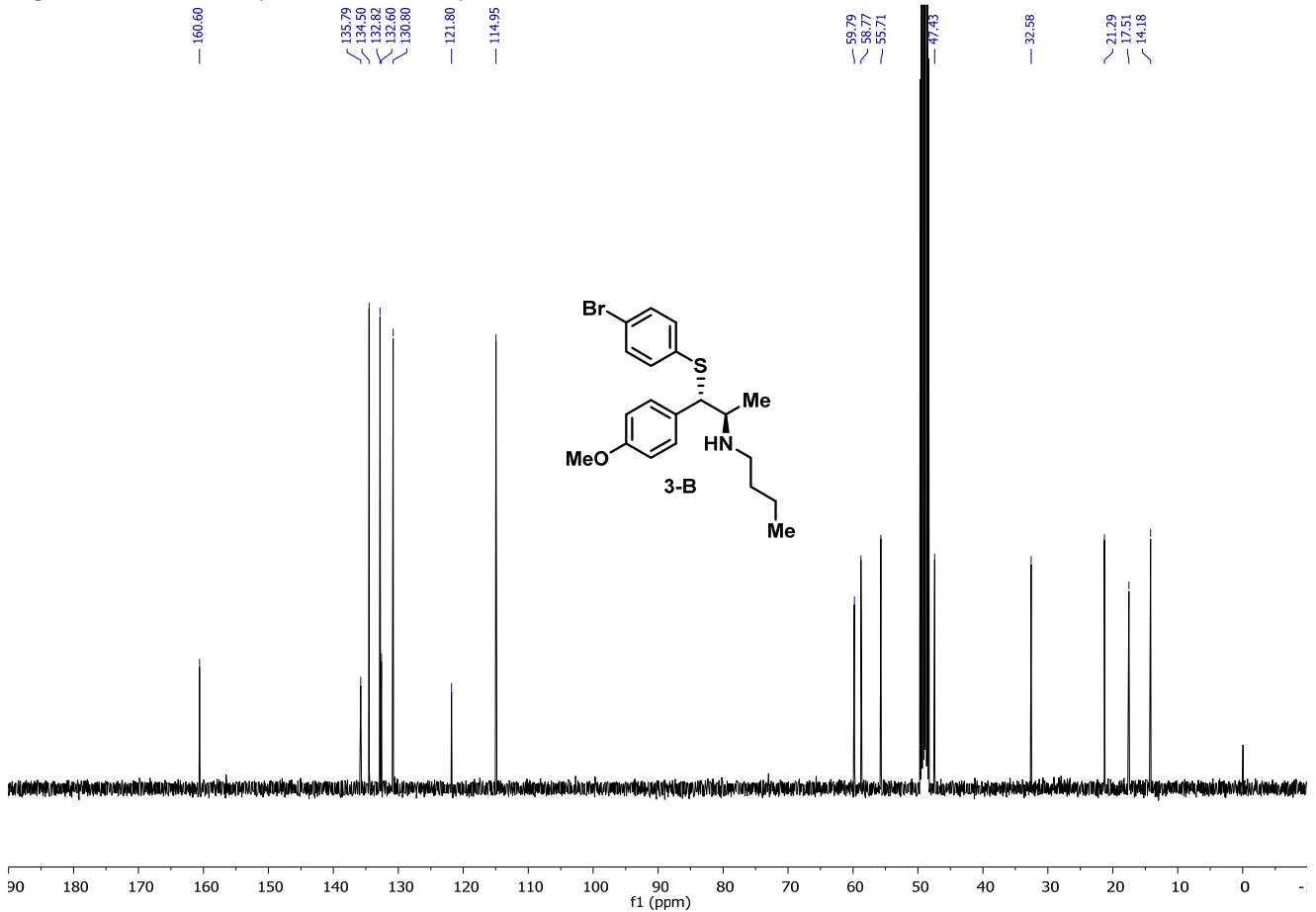


Figure S31. ¹H NMR (400 MHz, CD₃OD) of 4-A

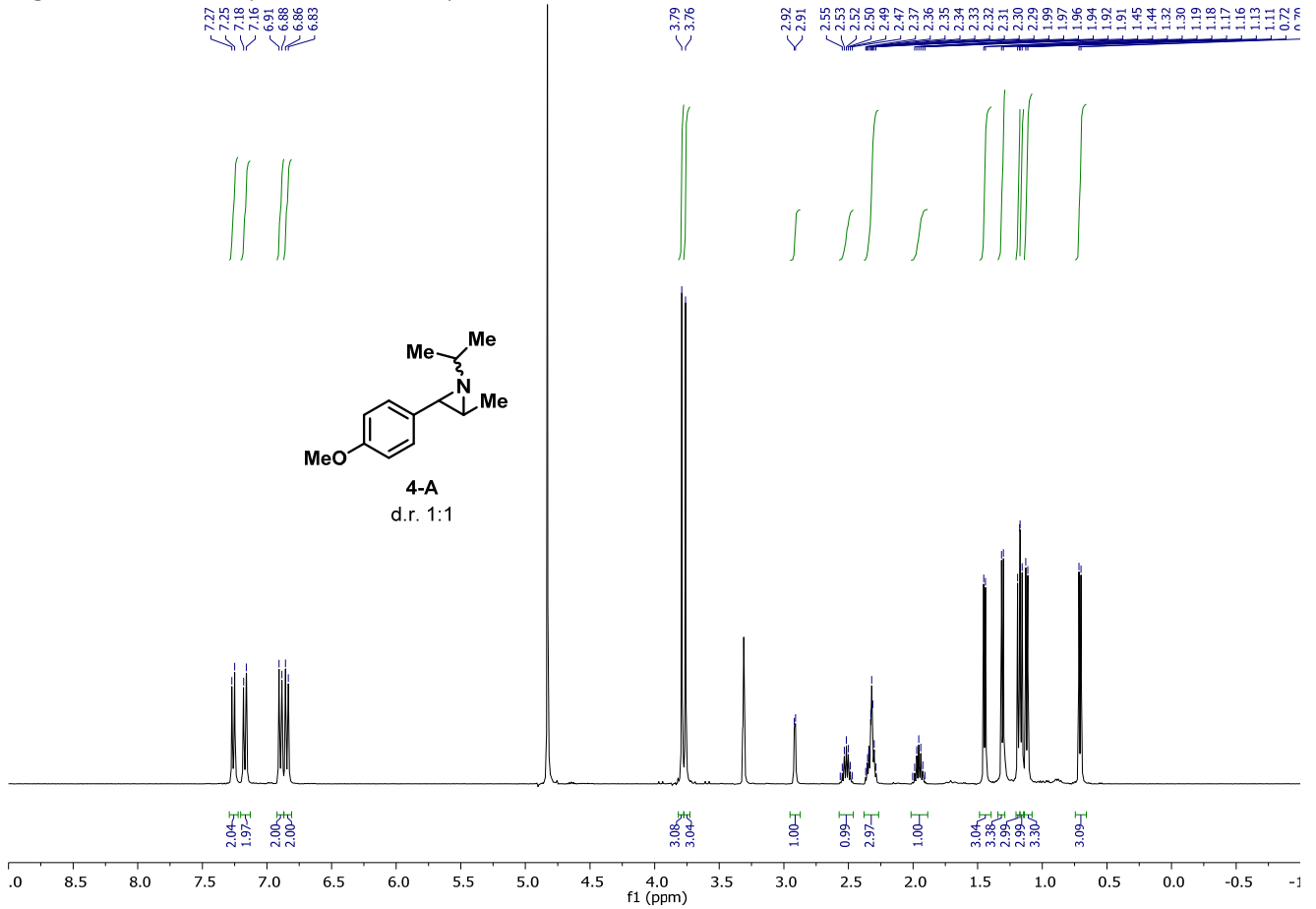


Figure S32. ¹³C NMR (101 MHz, CD₃OD) of 4-A

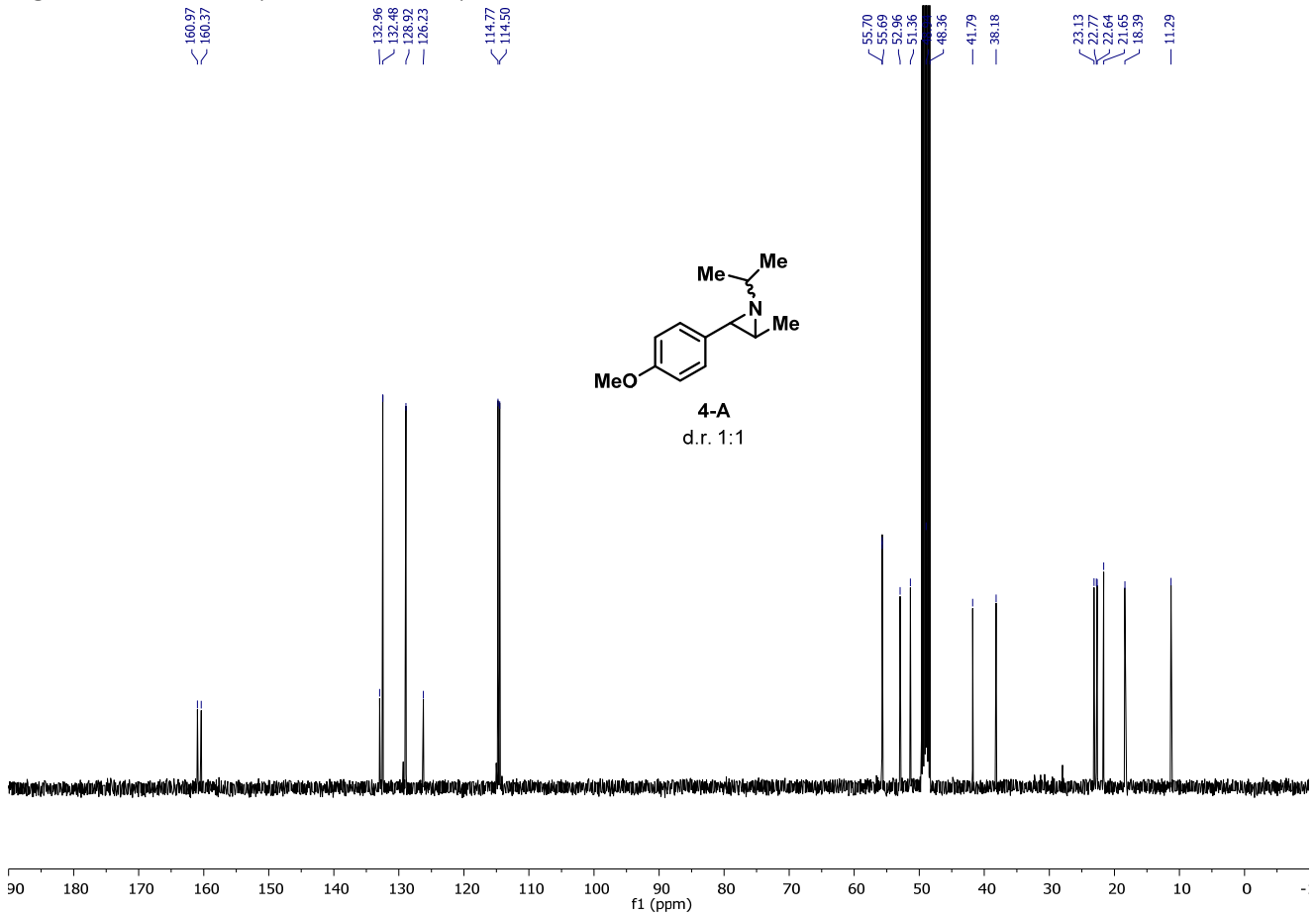


Figure S33. ¹H NMR (400 MHz, CD₃OD) of 4-B

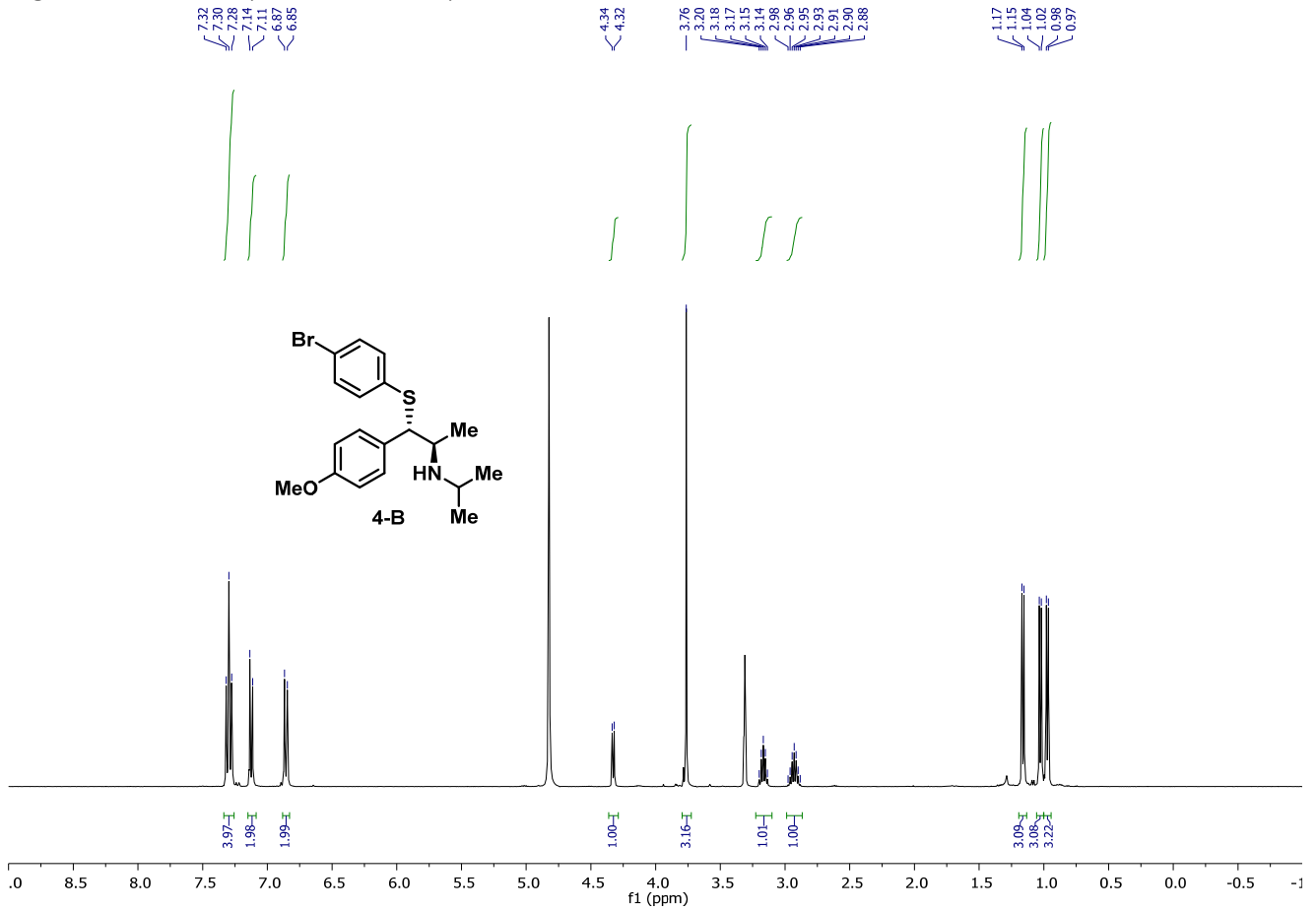


Figure S34. ¹³C NMR (101 MHz, CD₃OD) of 4-B

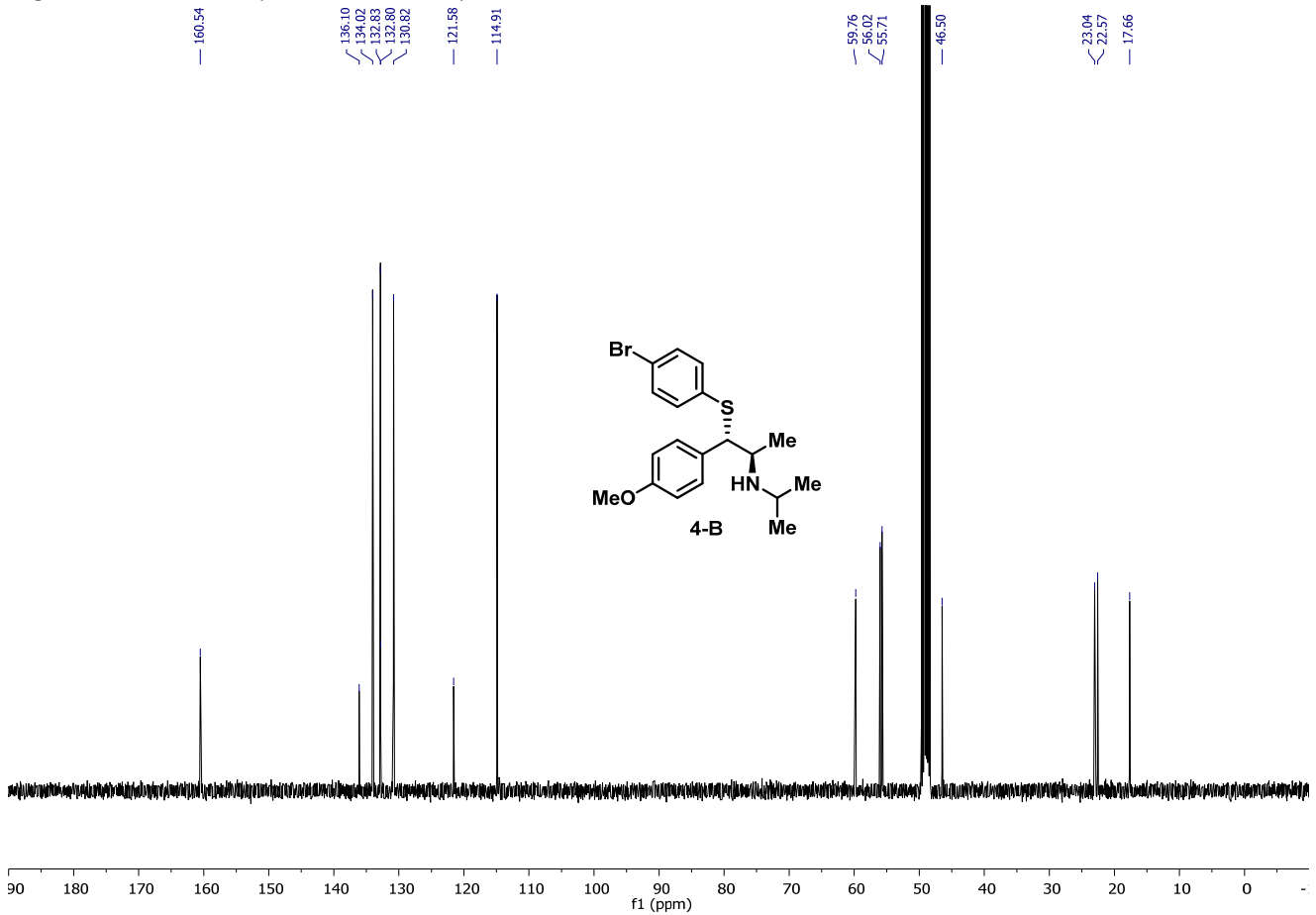


Figure S35. ^1H NMR (400 MHz, CDCl_3) of **5-A**

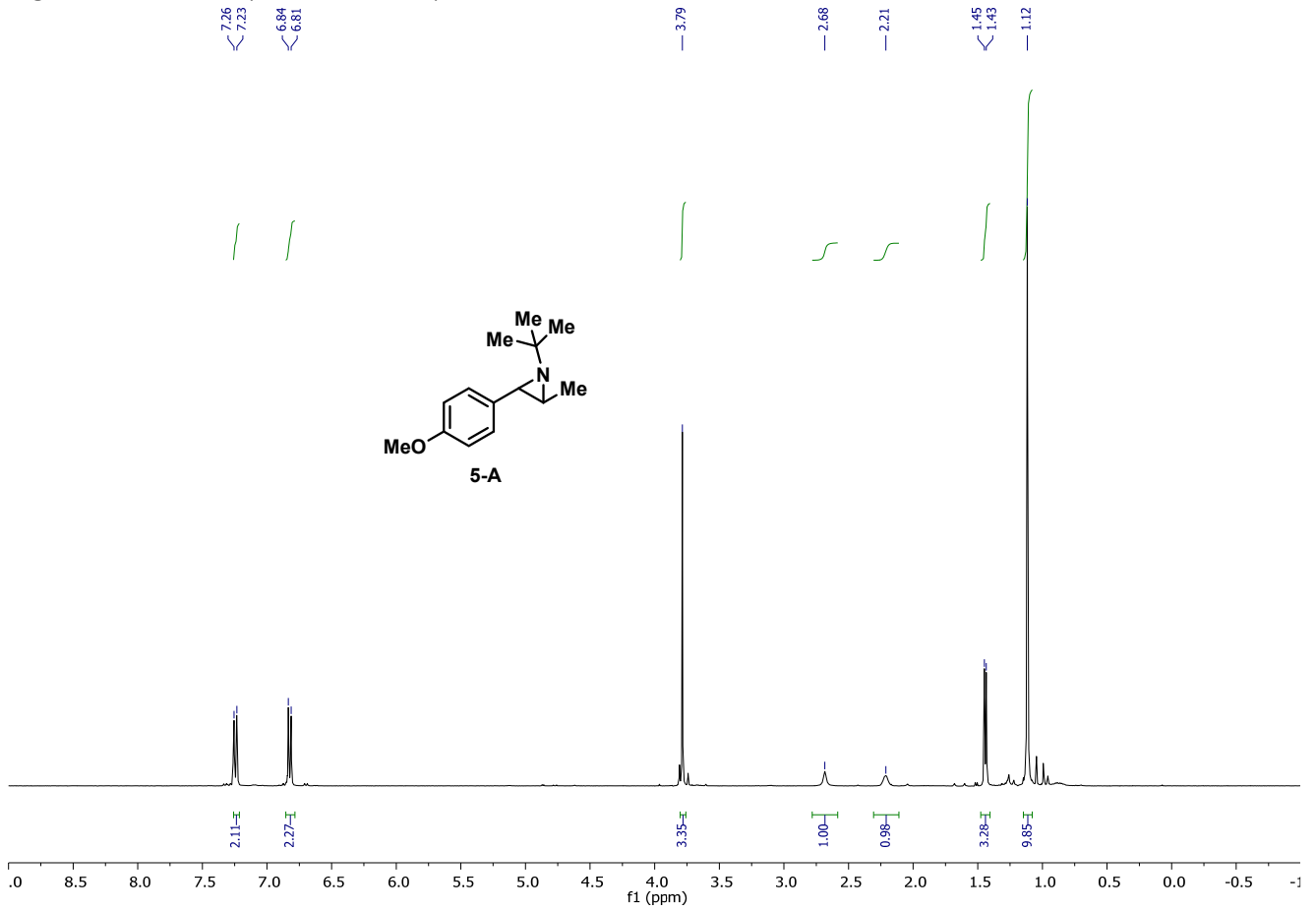


Figure S36. ^{13}C NMR (101 MHz, CDCl_3) of **5-A**

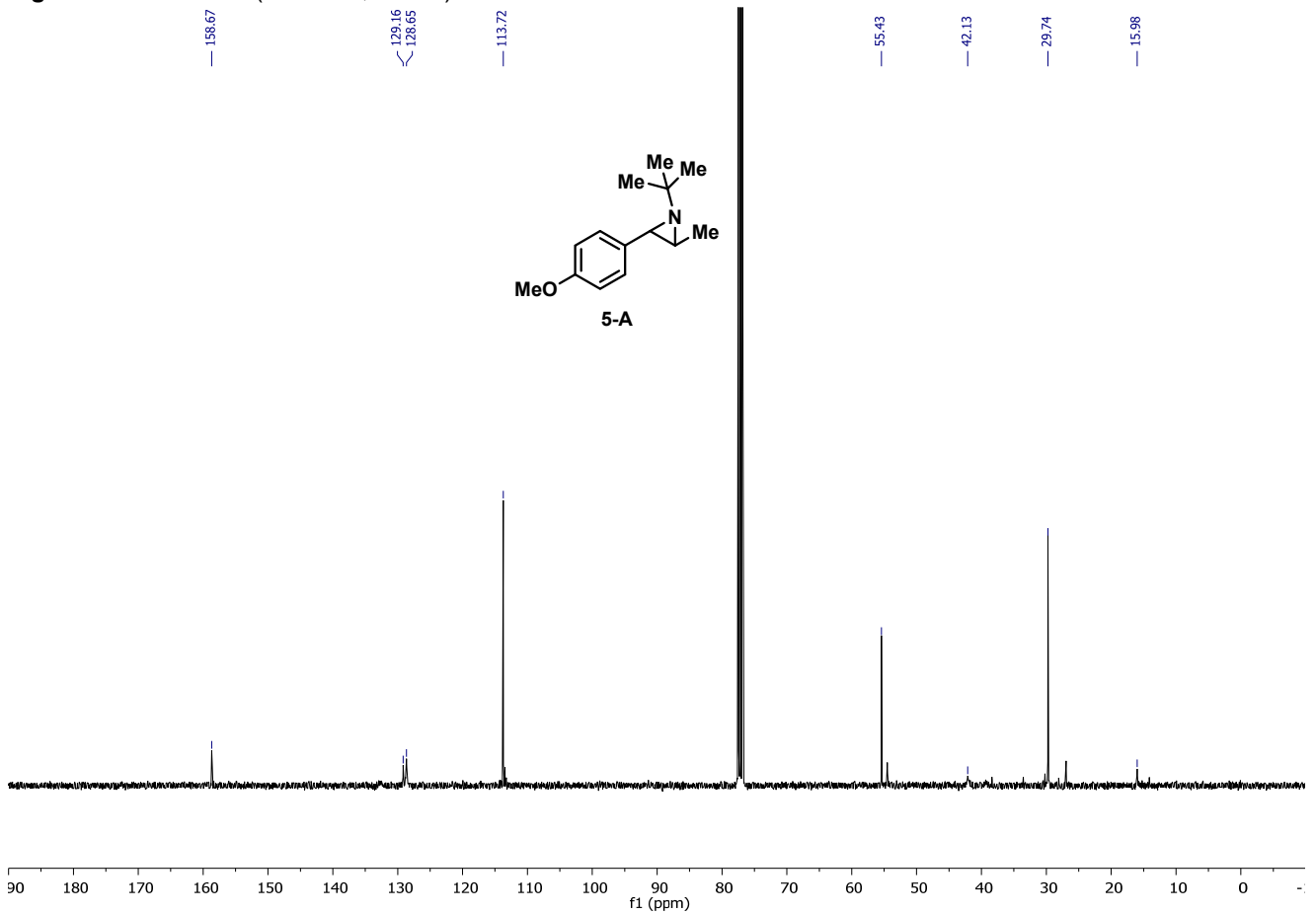


Figure S37. ¹H NMR (400 MHz, CD₃OD) of 5-B

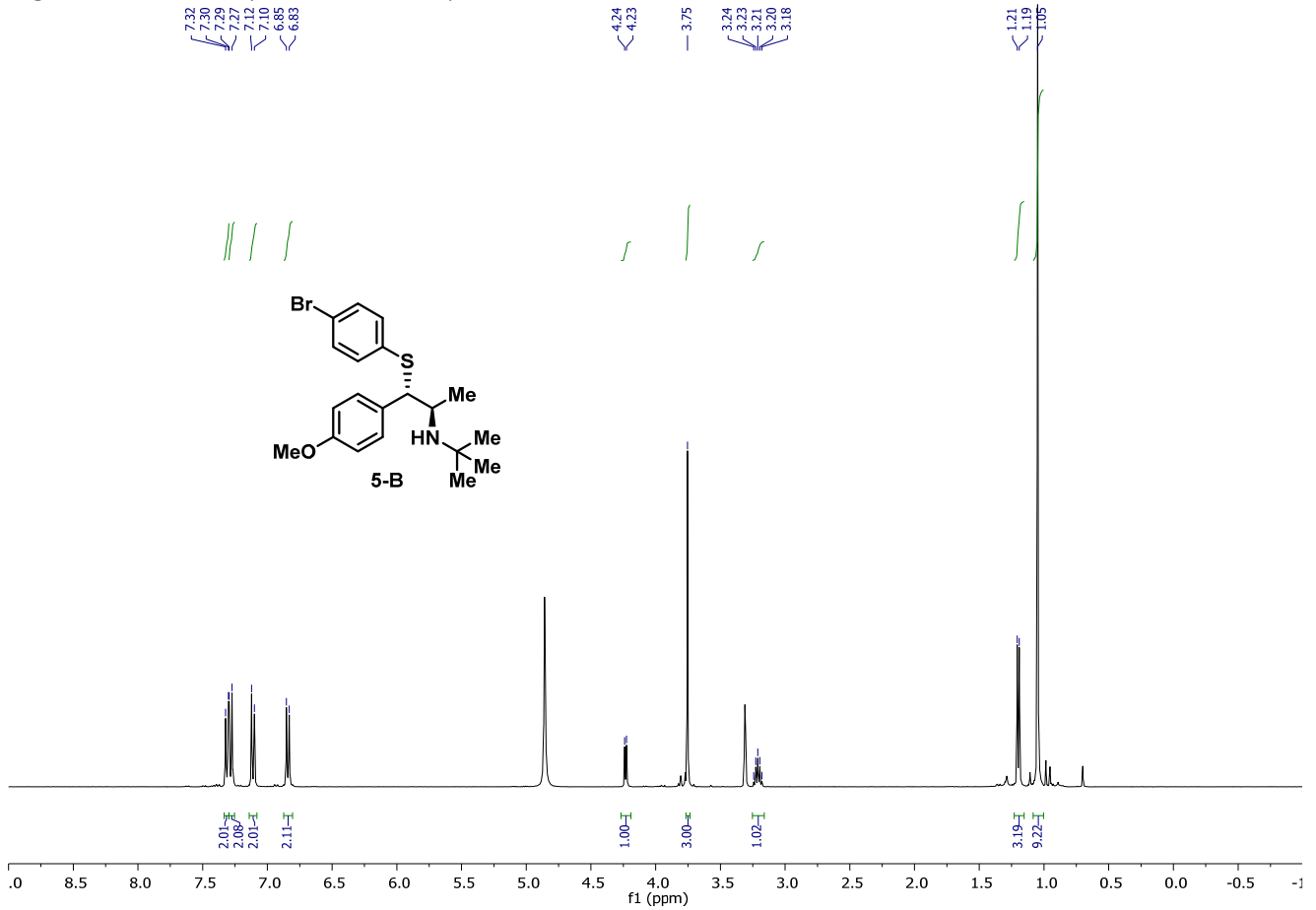


Figure S38. ¹³C NMR (101 MHz, CD₃OD) of 5-B

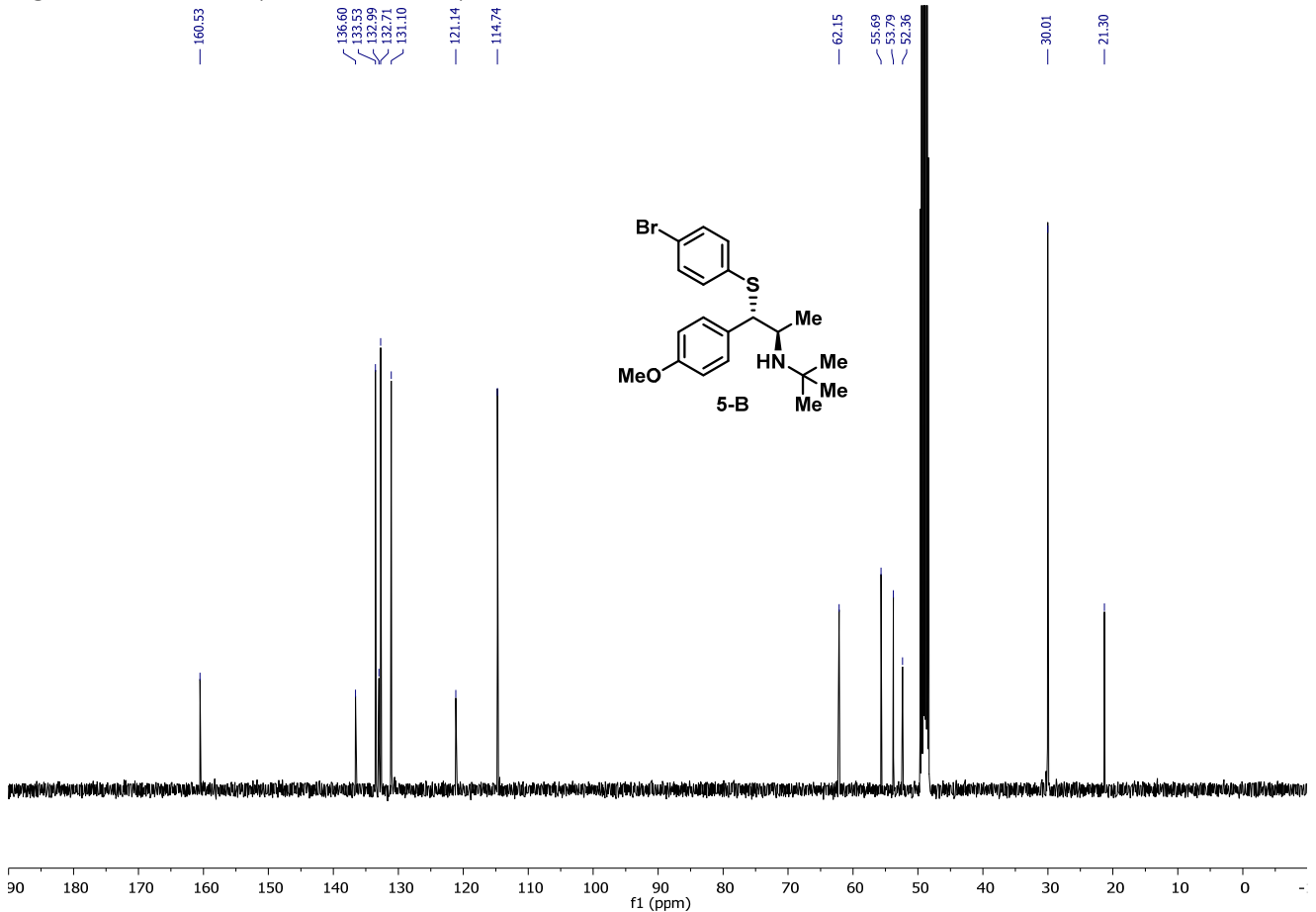


Figure S39. ¹H NMR (400 MHz, CD₃OD) of 6-A

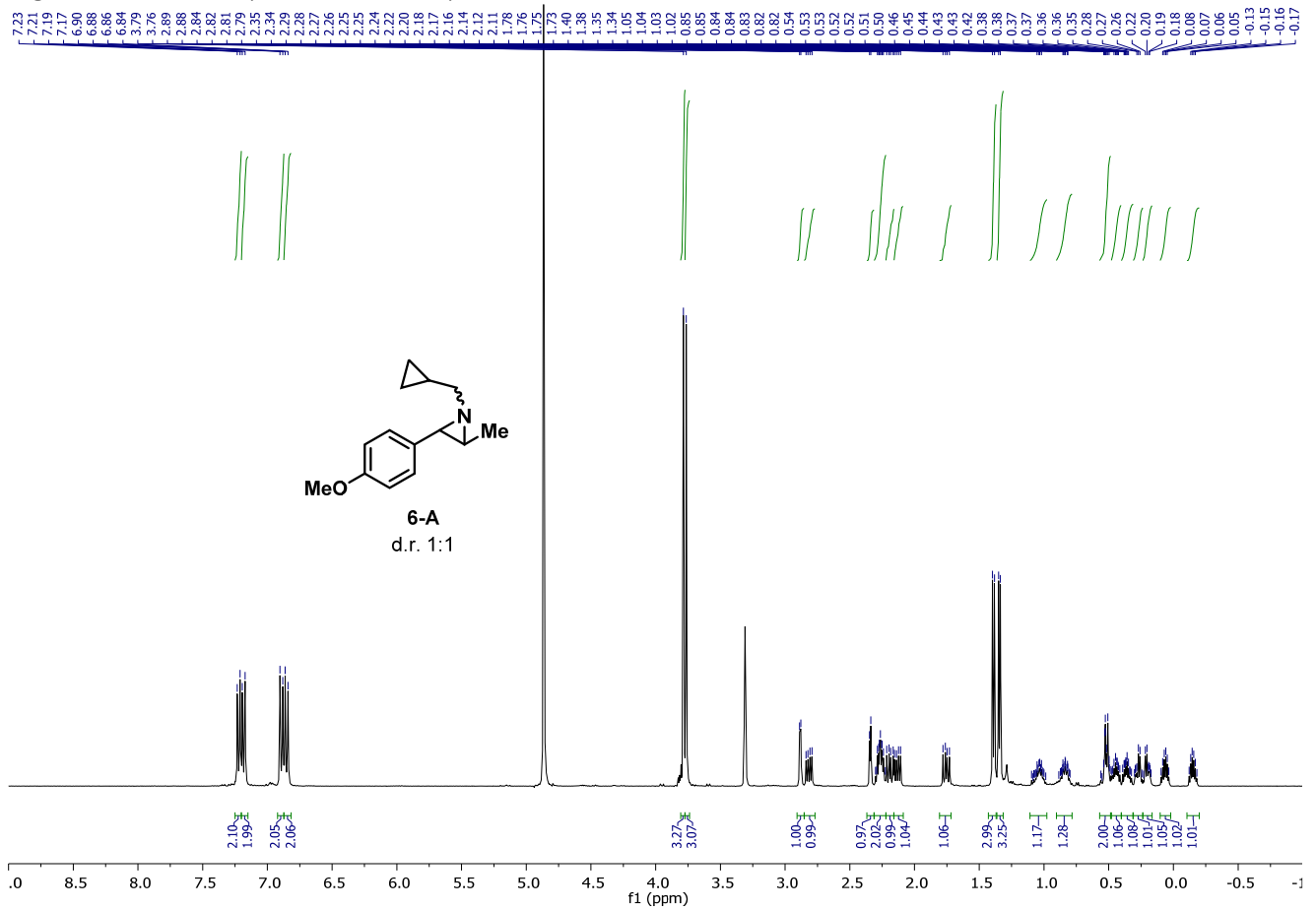


Figure S40. ¹³C NMR (101 MHz, CD₃OD) of 6-A

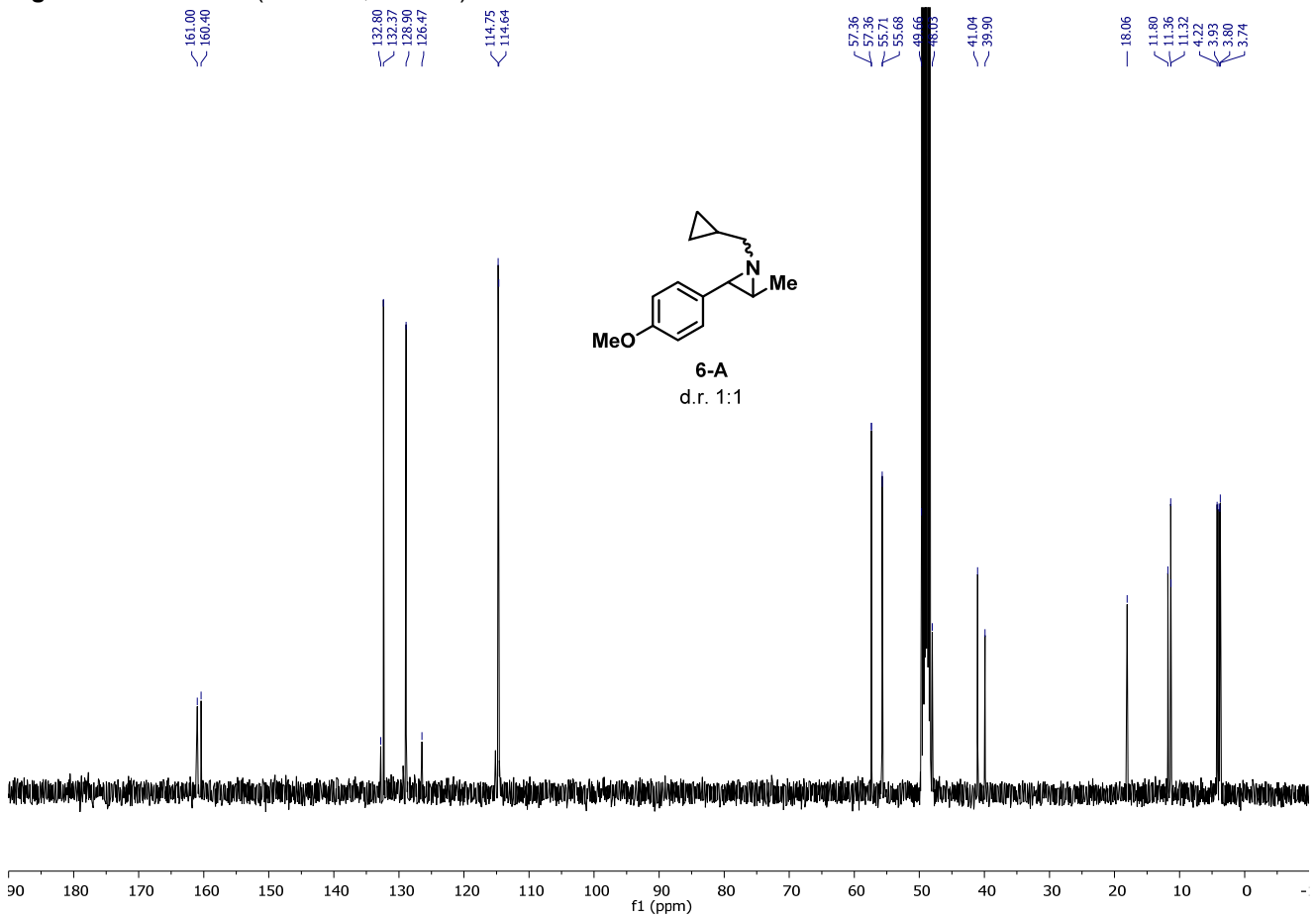


Figure S41. ¹H NMR (400 MHz, CD₃OD) of 6-B

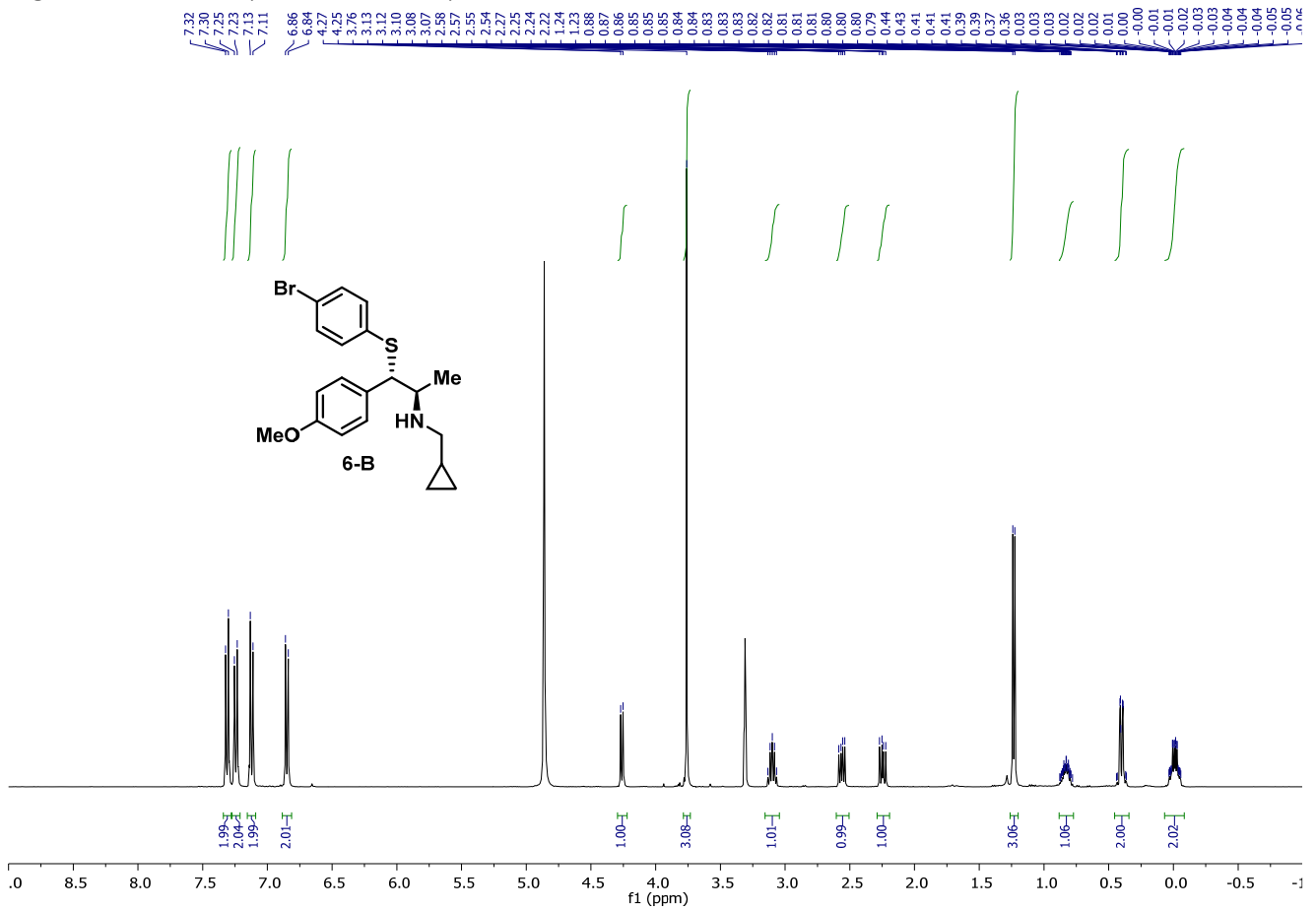


Figure S42. ¹³C NMR (101 MHz, CD₃OD) of 6-B

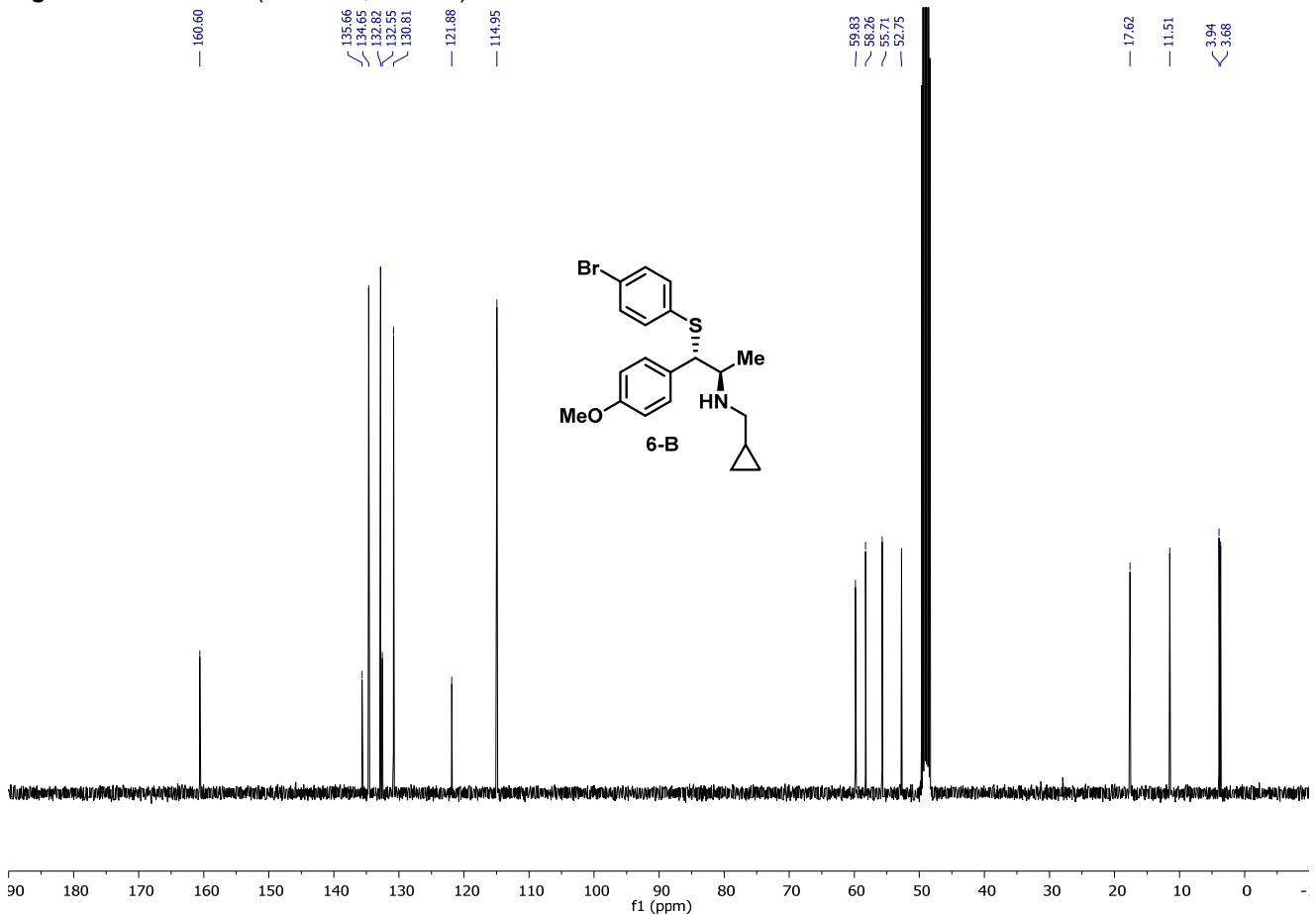


Figure S43. ¹H NMR (400 MHz, CD₃OD) of 7-B

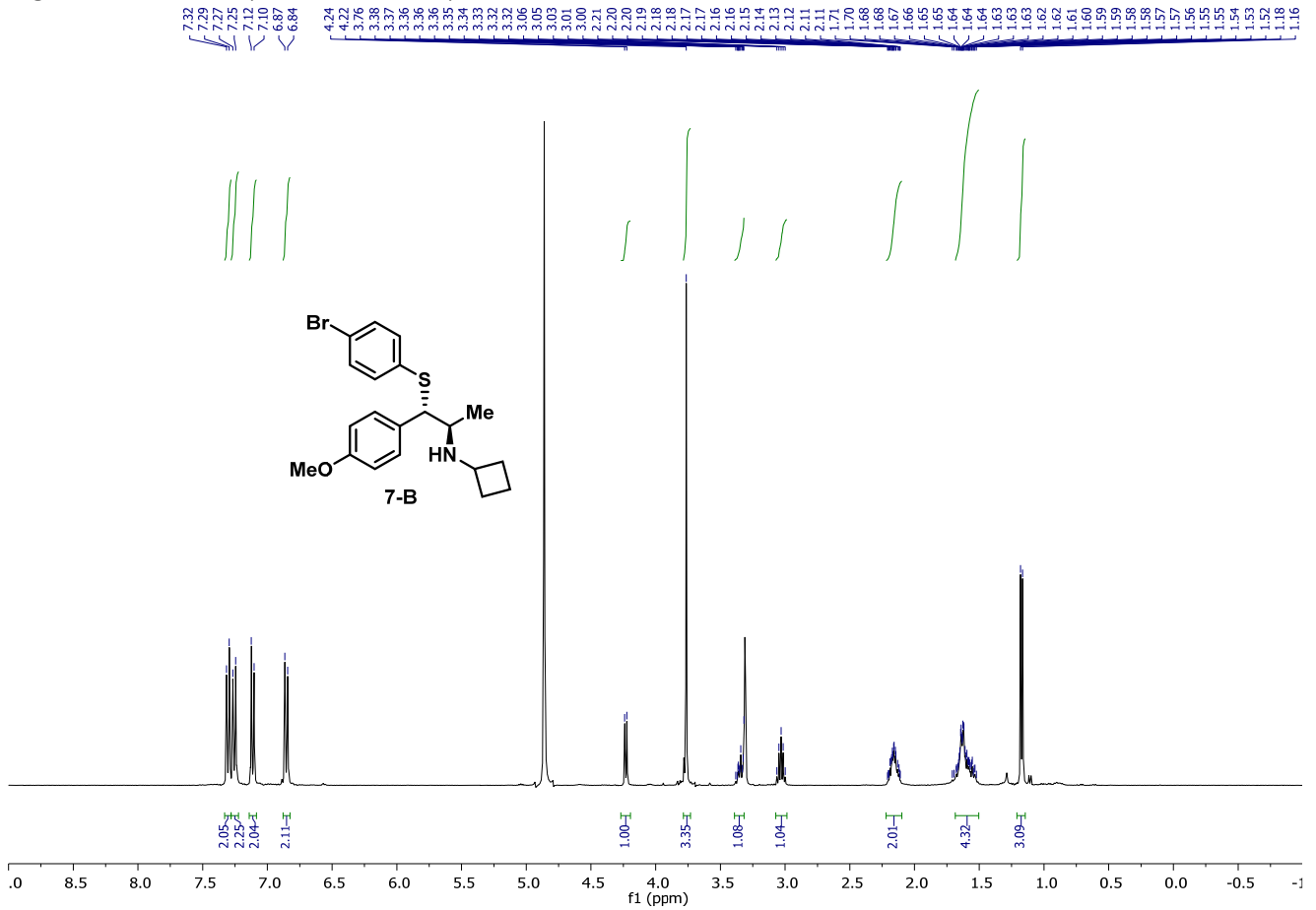


Figure S44. ¹³C NMR (101 MHz, CD₃OD) of 7-B

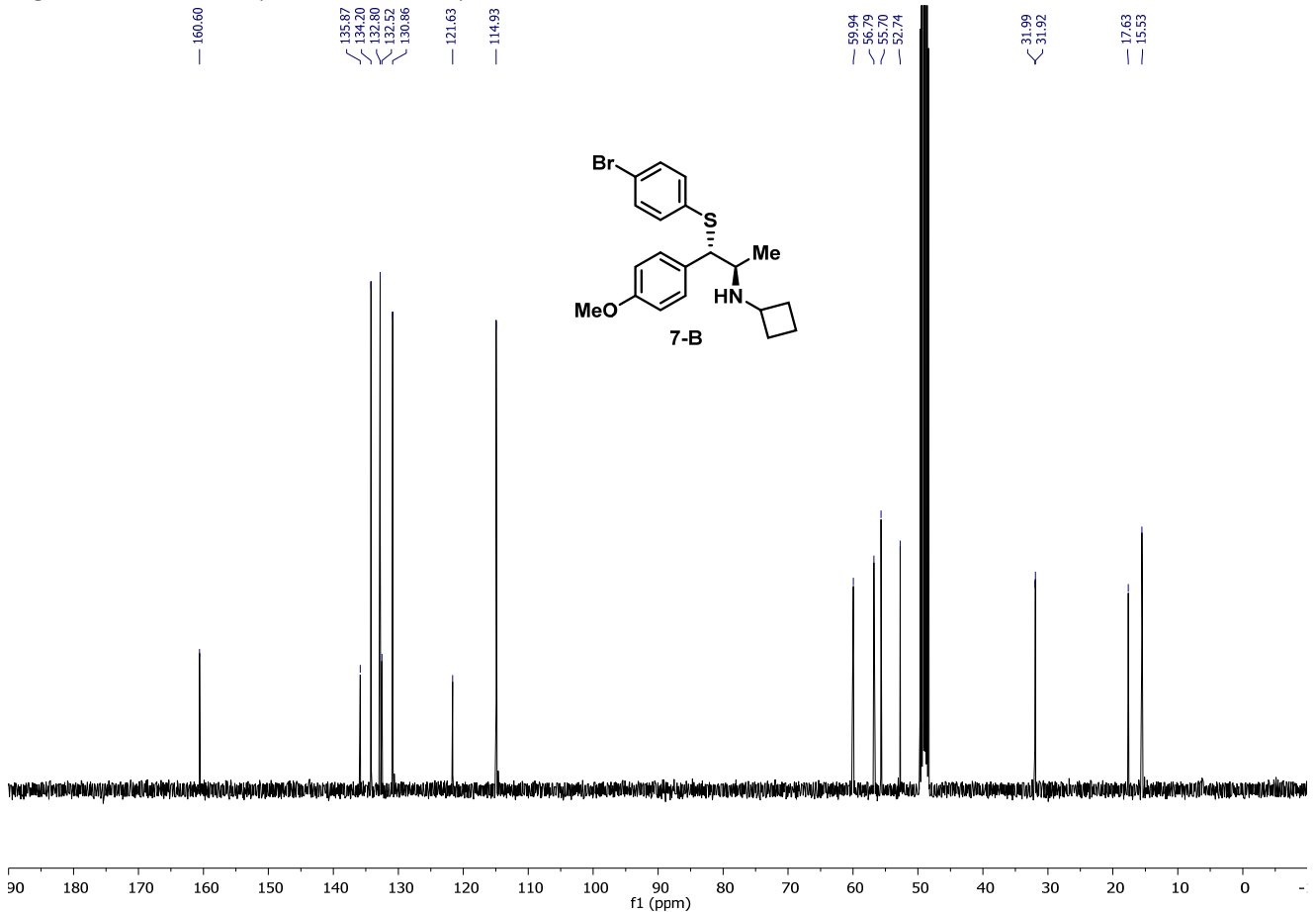


Figure S45. ¹H NMR (400 MHz, CD₃OD) of 8-A

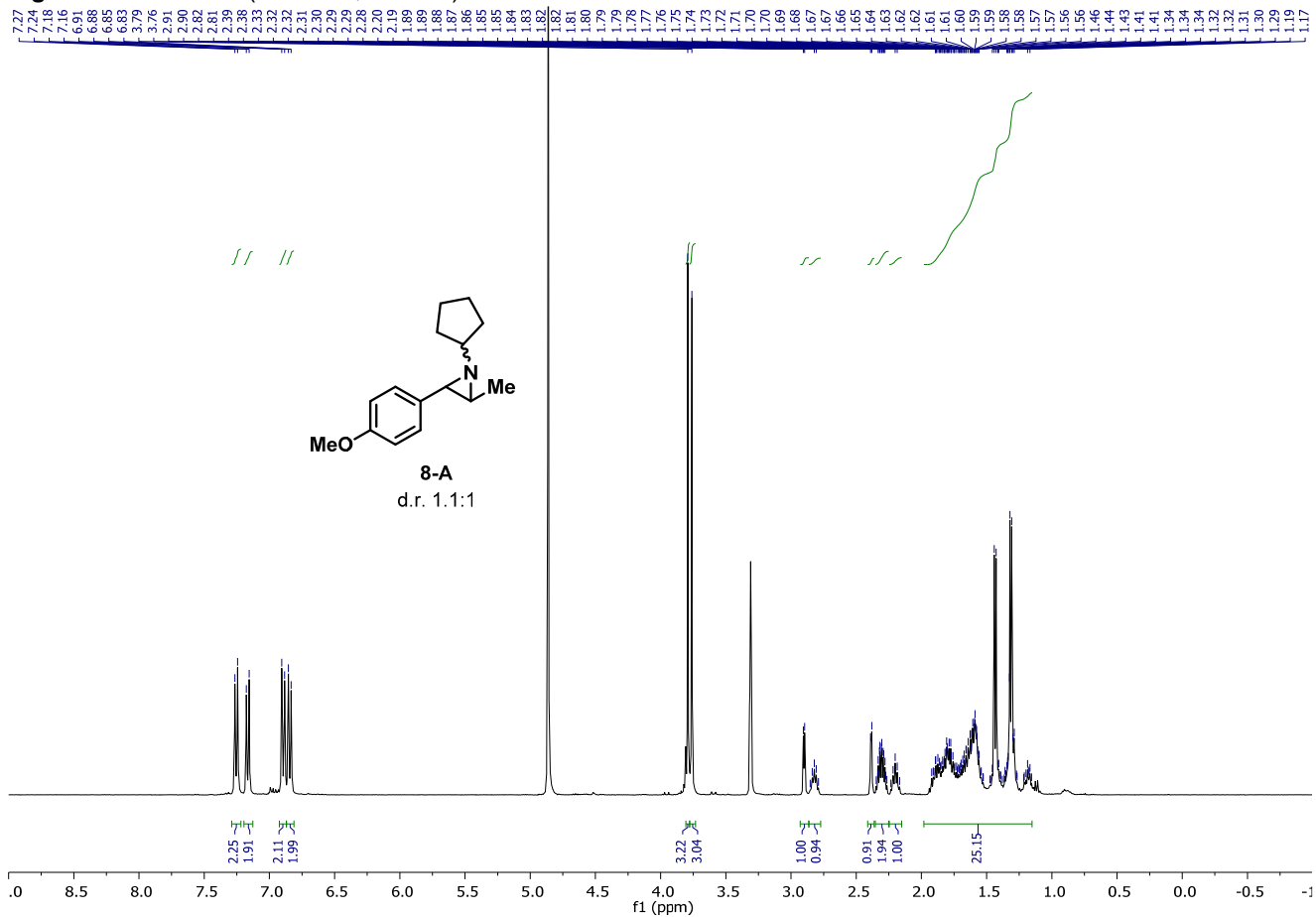


Figure S46. ¹³C NMR (101 MHz, CD₃OD) of 8-A

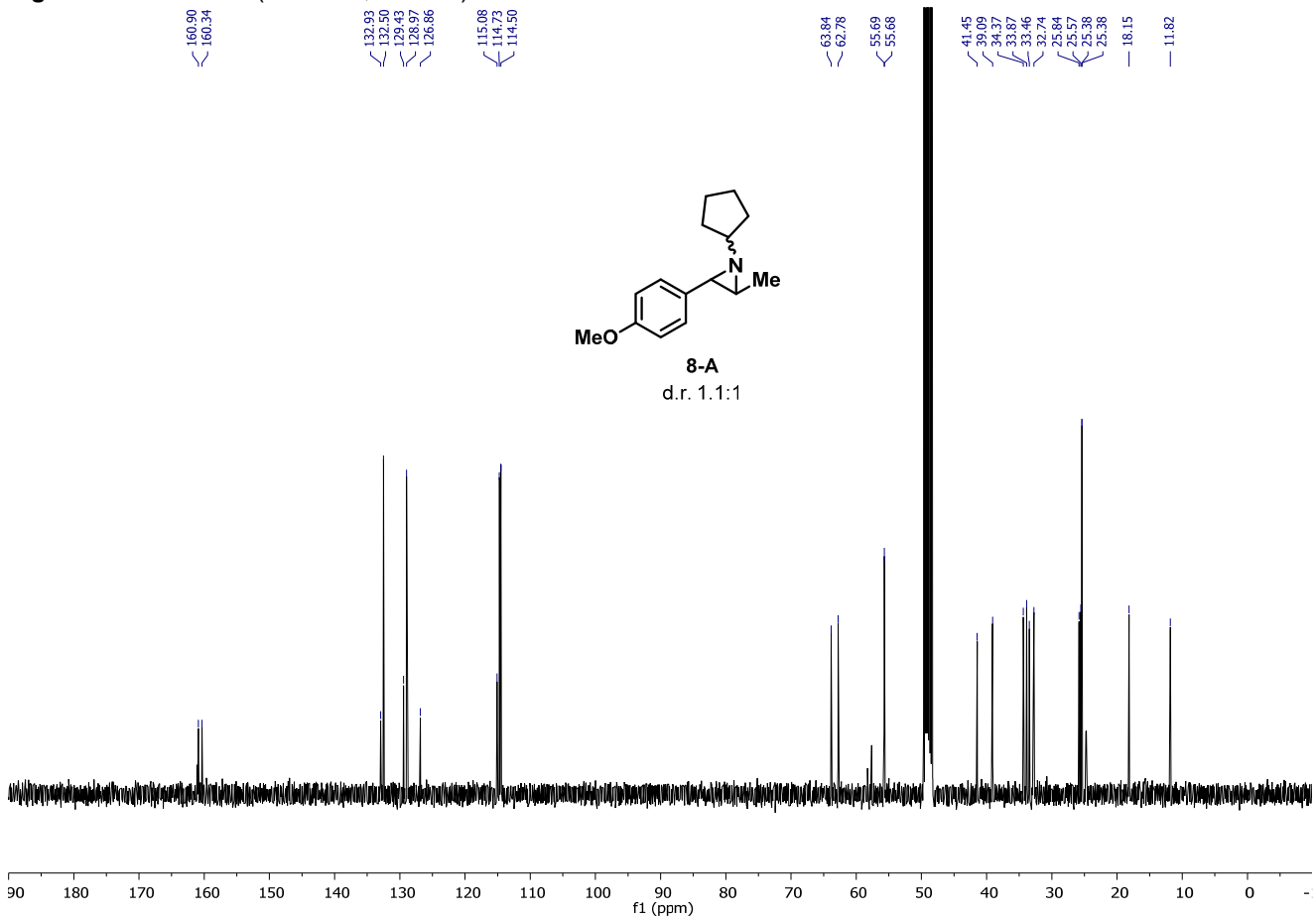


Figure S47. ¹H NMR (400 MHz, CD₃OD) of 8-B

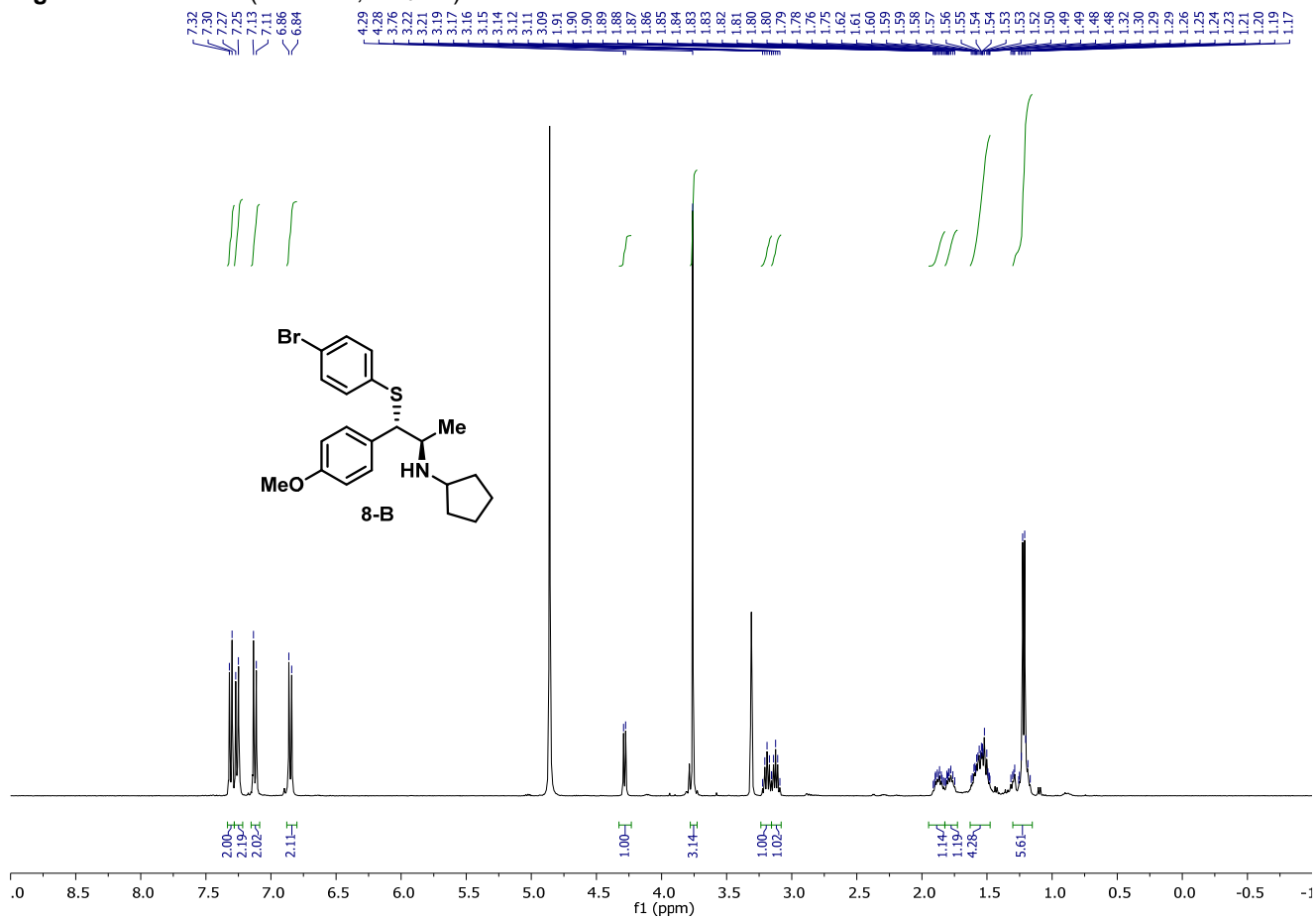


Figure S48. ¹³C NMR (101 MHz, CD₃OD) of 8-B

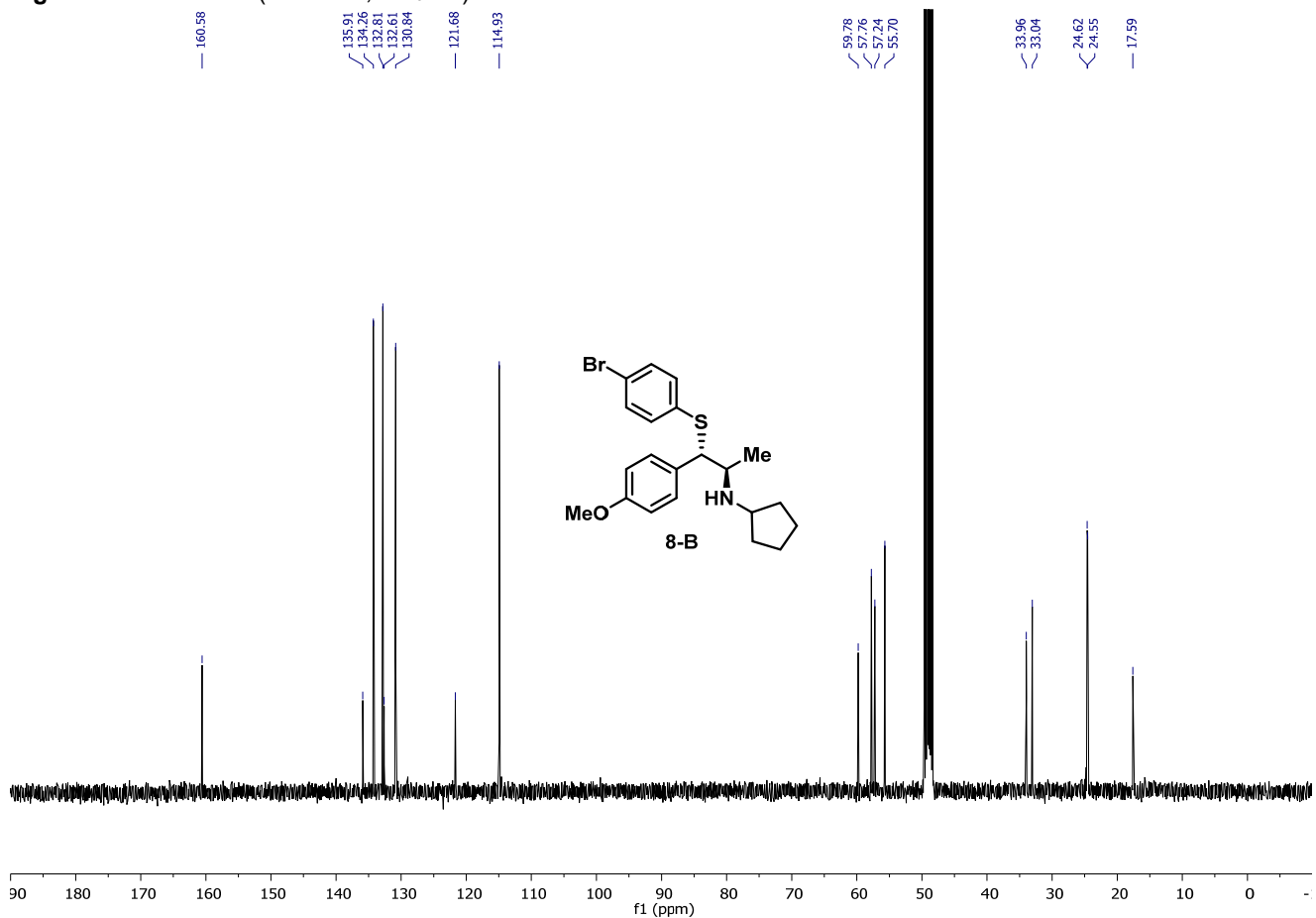


Figure S49. ¹H NMR (400 MHz, CD₃OD) of 9-A

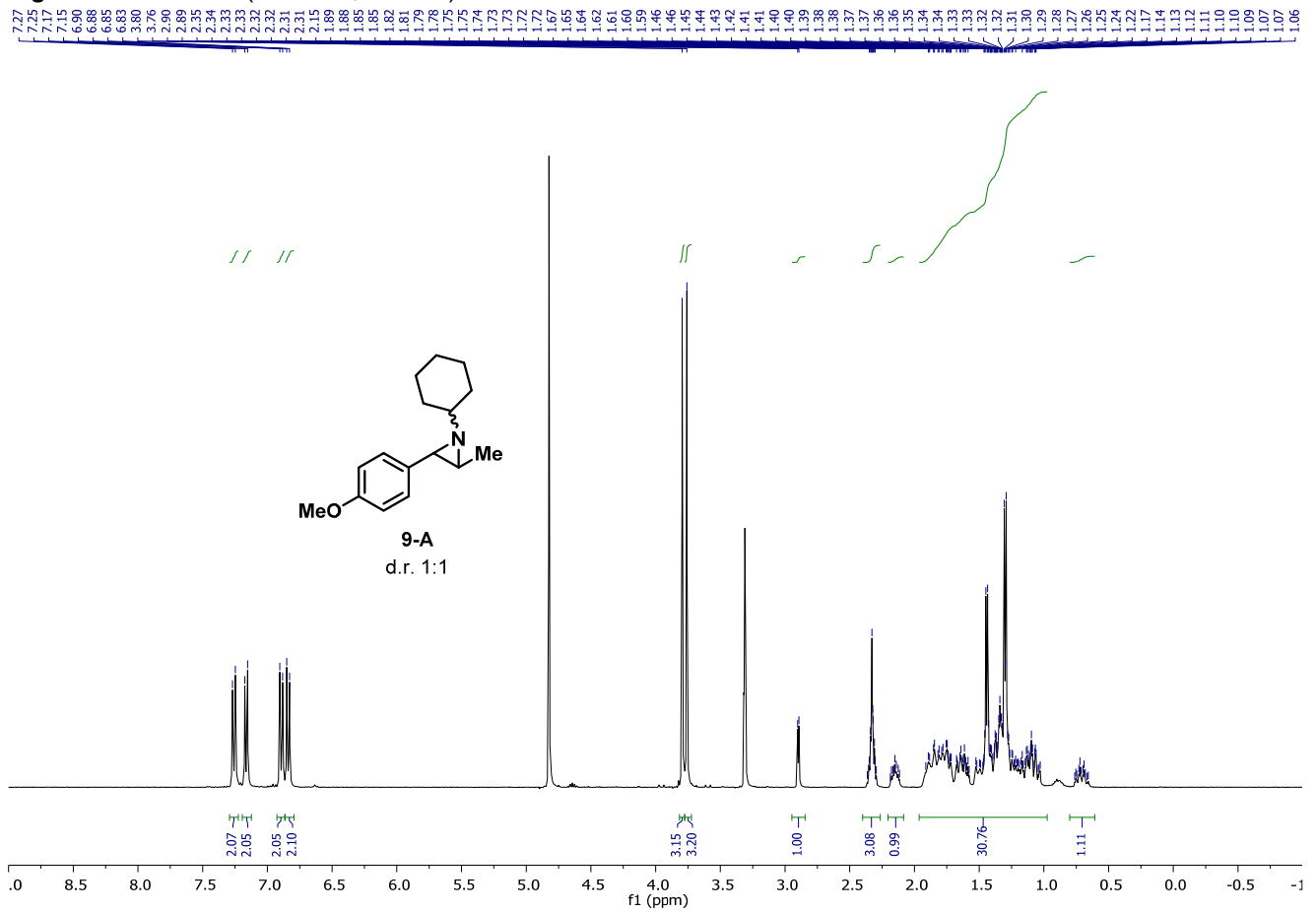


Figure S50. ¹³C NMR (101 MHz, CD₃OD) of 9-A

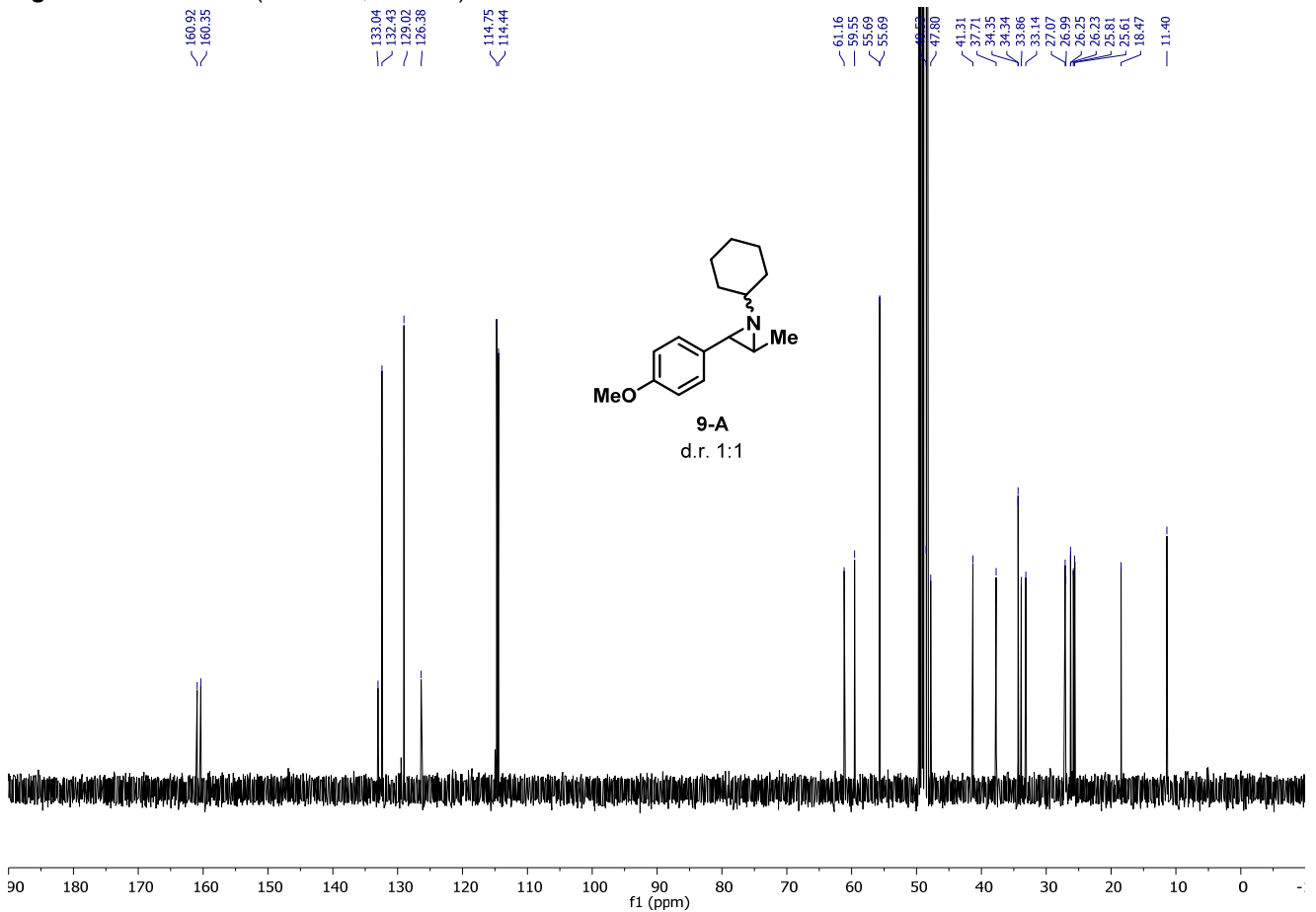


Figure S51. ¹H NMR (400 MHz, CD₃OD) of 9-B

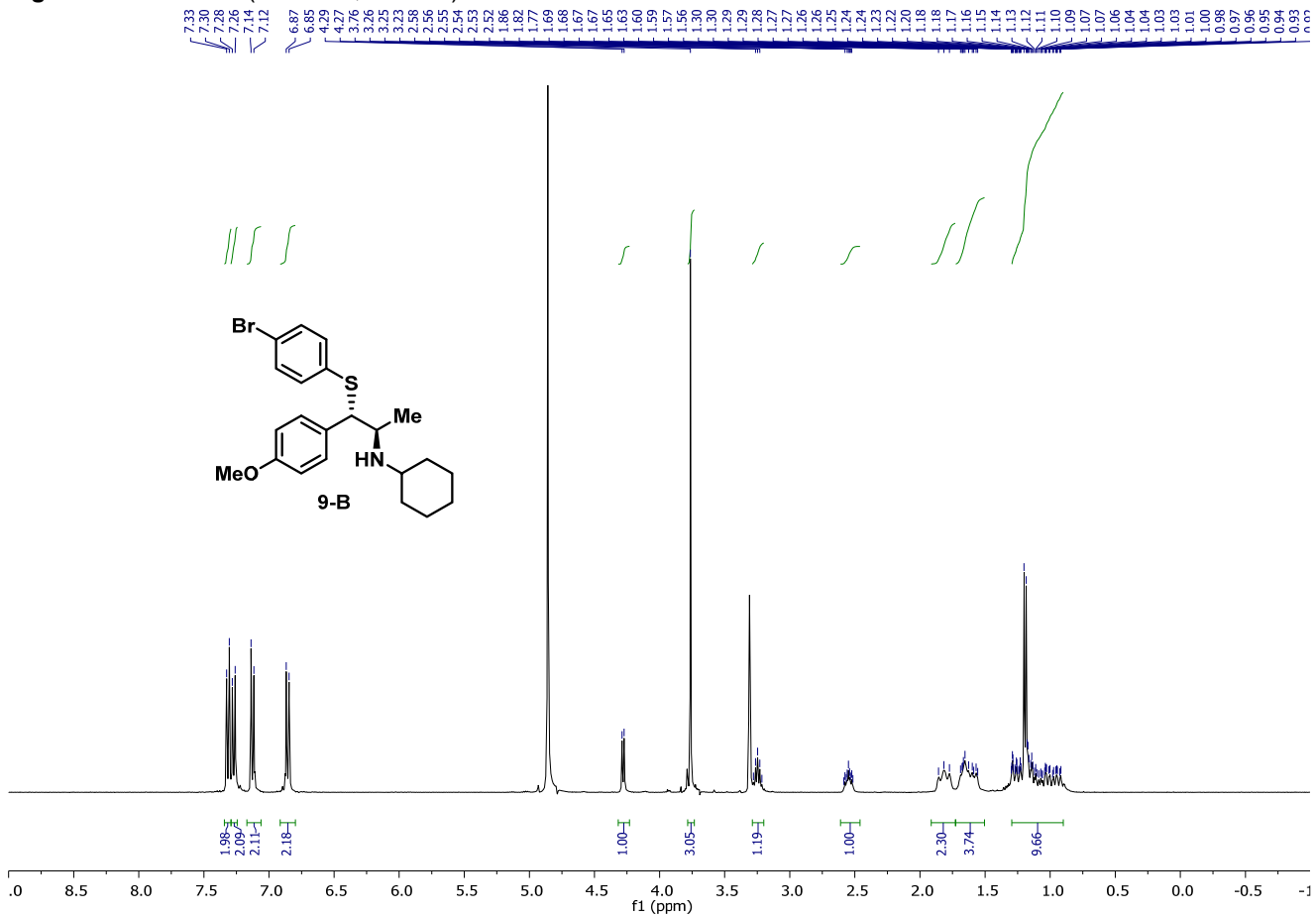


Figure S52. ¹³C NMR (101 MHz, CD₃OD) of 9-B

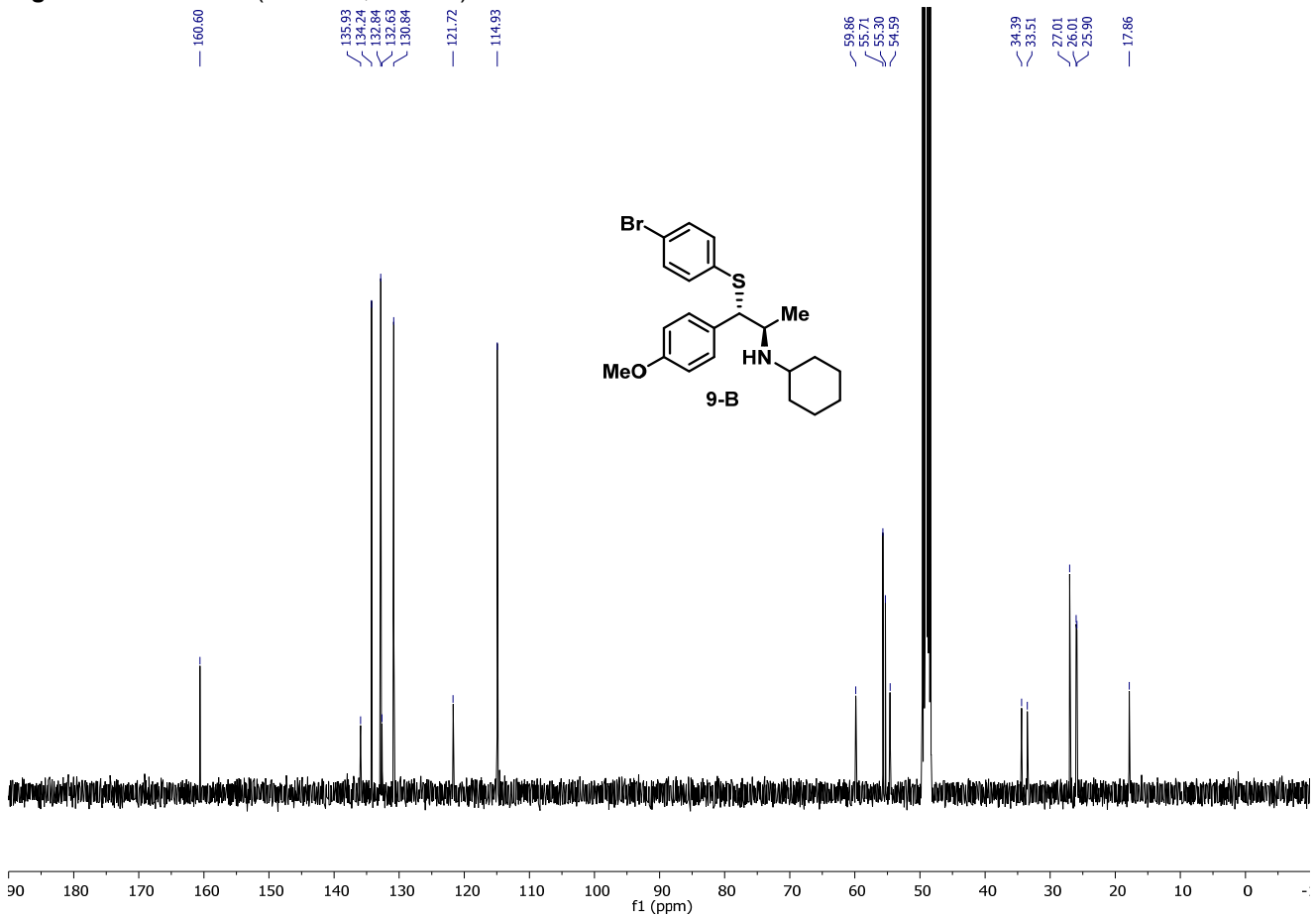


Figure S53. ¹H NMR (400 MHz, CD₃OD) of 10-B

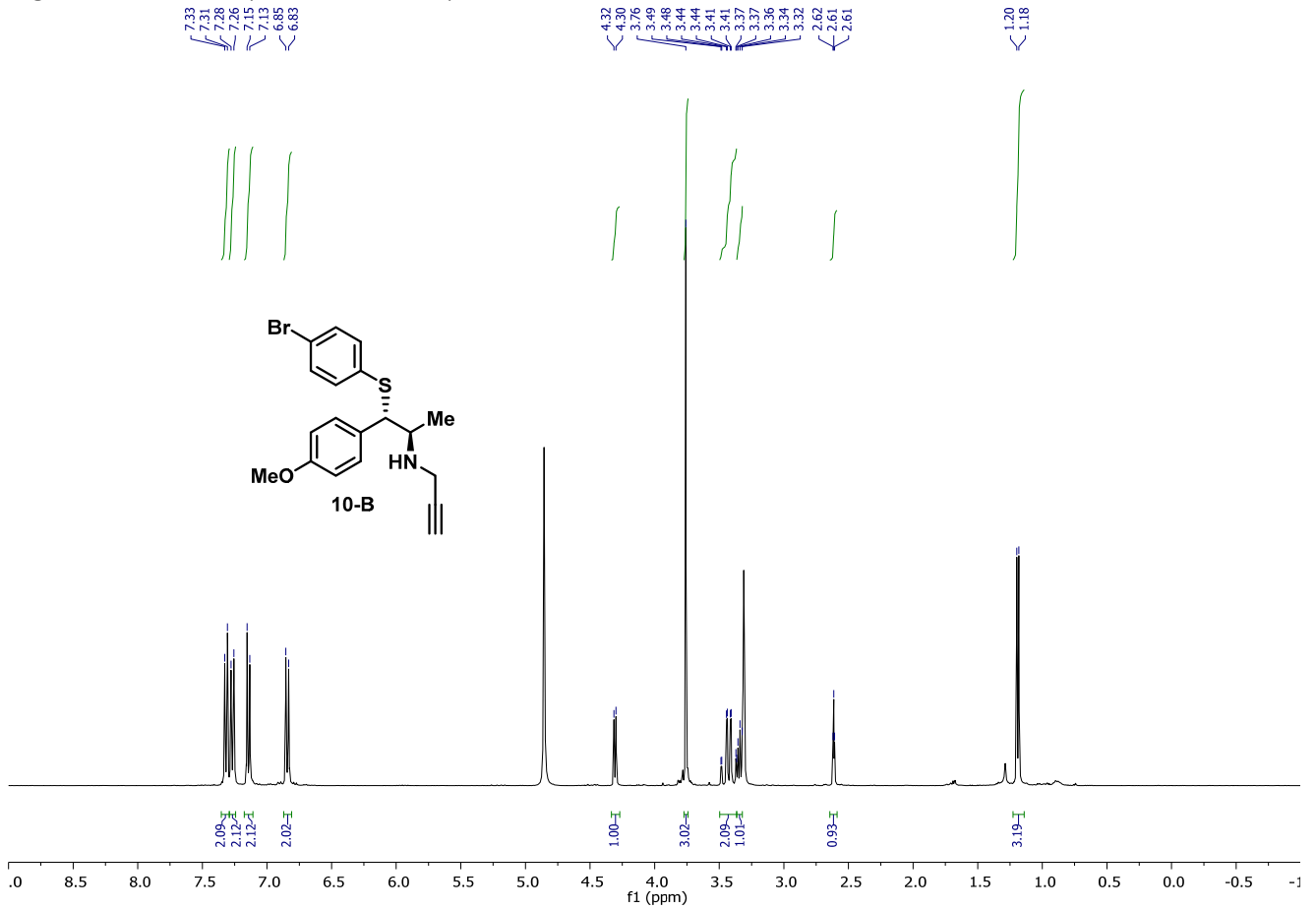


Figure S54. ¹³C NMR (101 MHz, CD₃OD) of 10-B

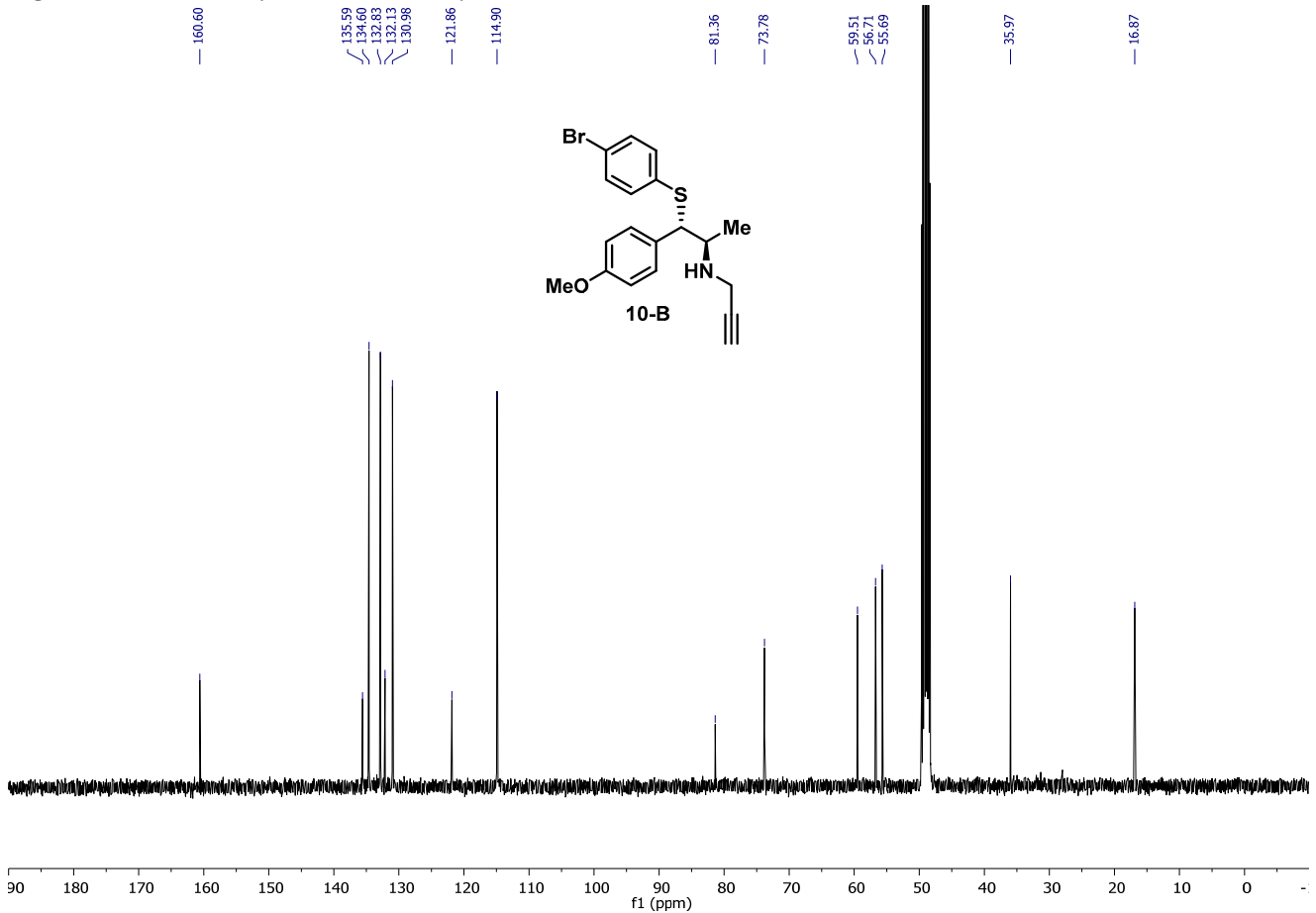


Figure S55. ¹H NMR (400 MHz, CD₃OD) of 11-A

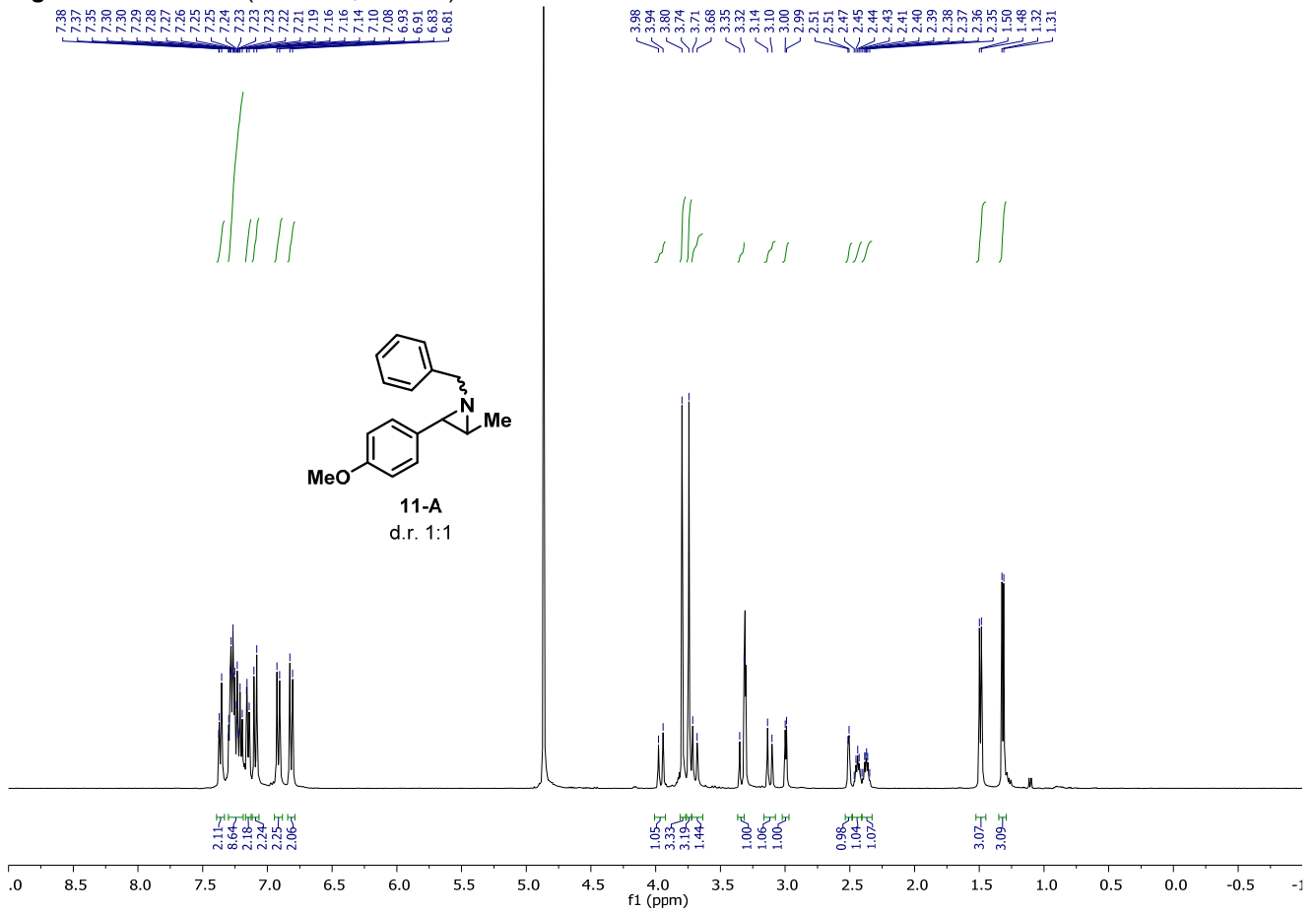


Figure S56. ¹³C NMR (101 MHz, CD₃OD) of 11-A

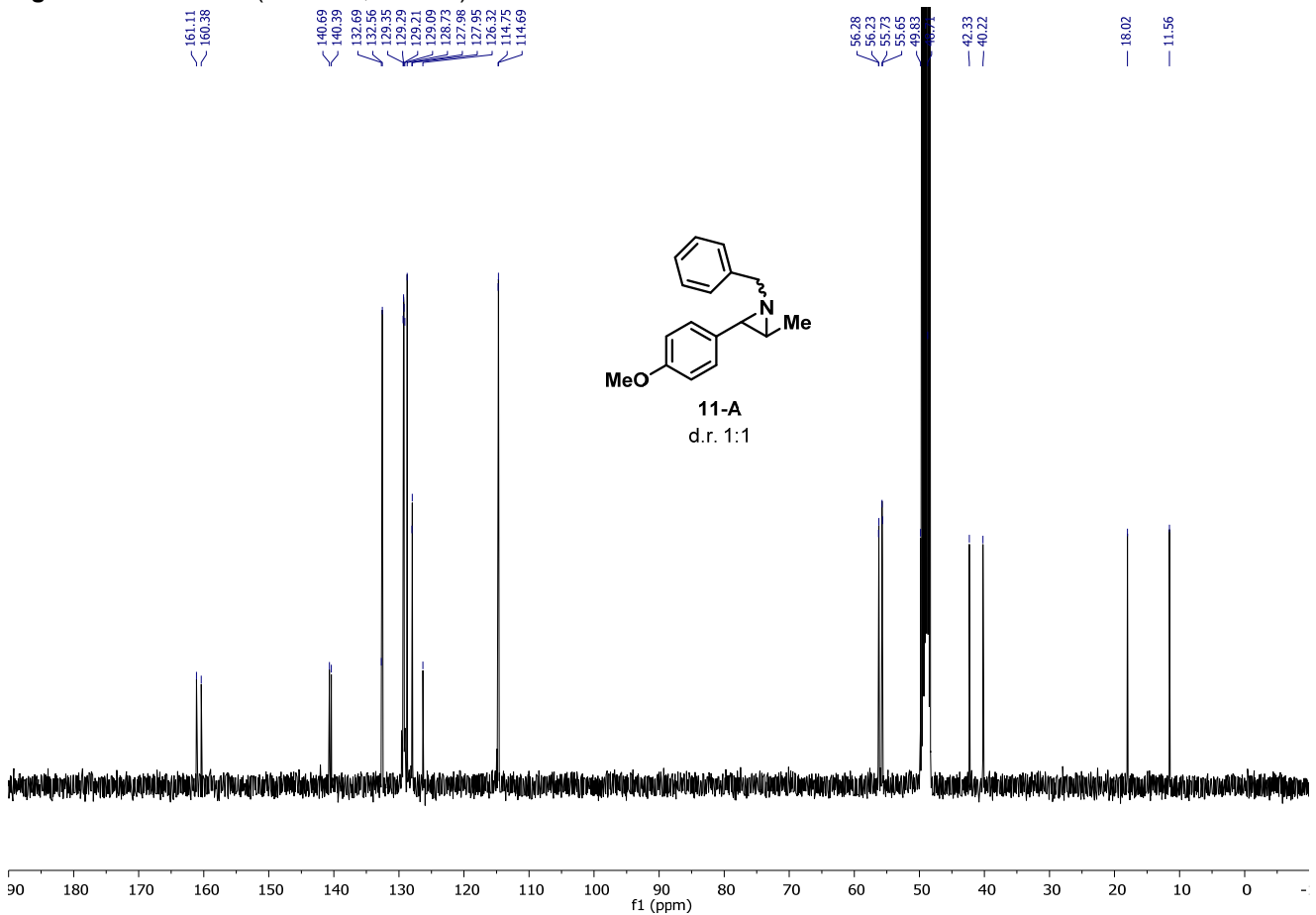


Figure S57. ¹H NMR (400 MHz, CD₃OD) of 11-B

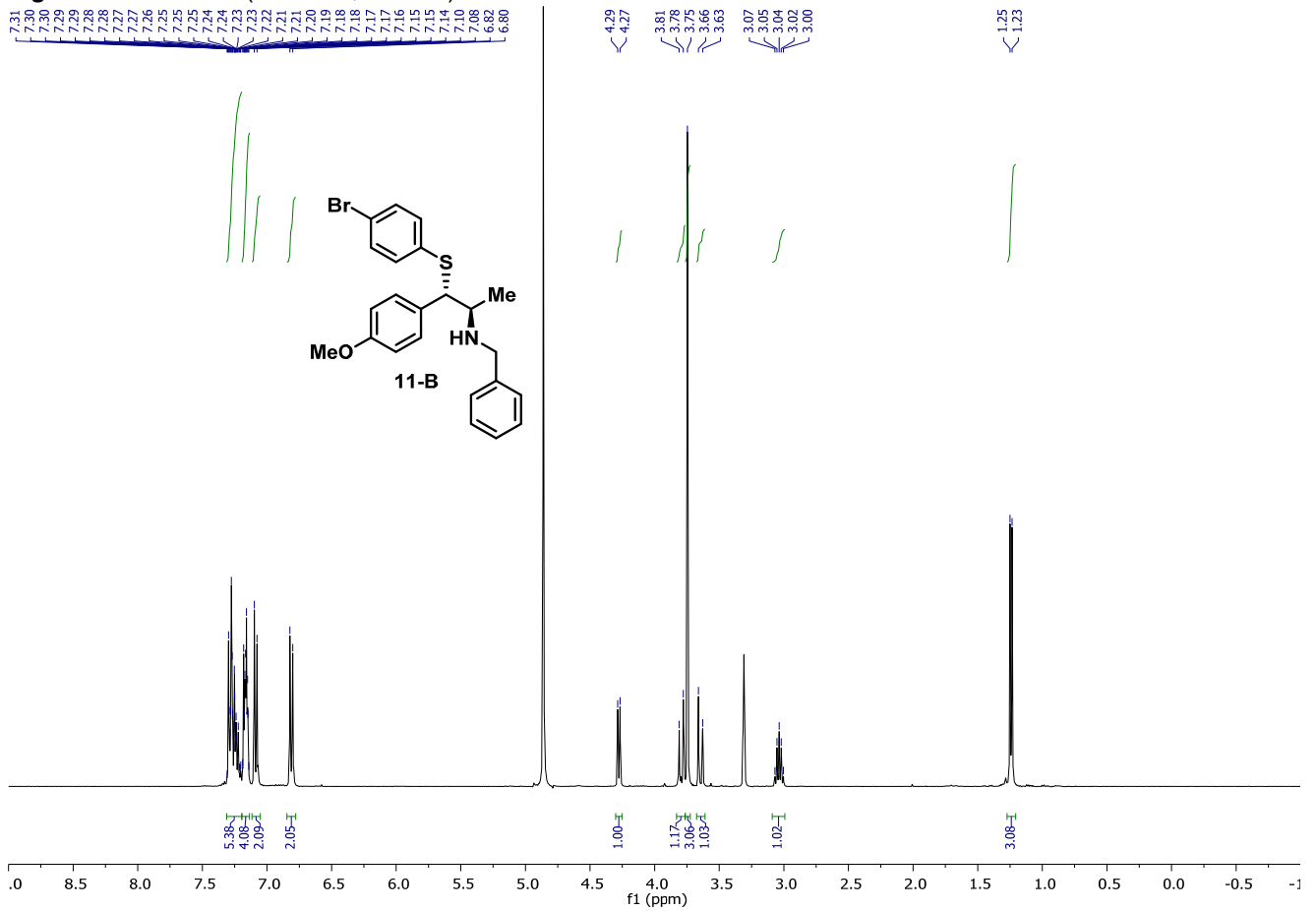


Figure S58. ¹³C NMR (101 MHz, CD₃OD) of 11-B

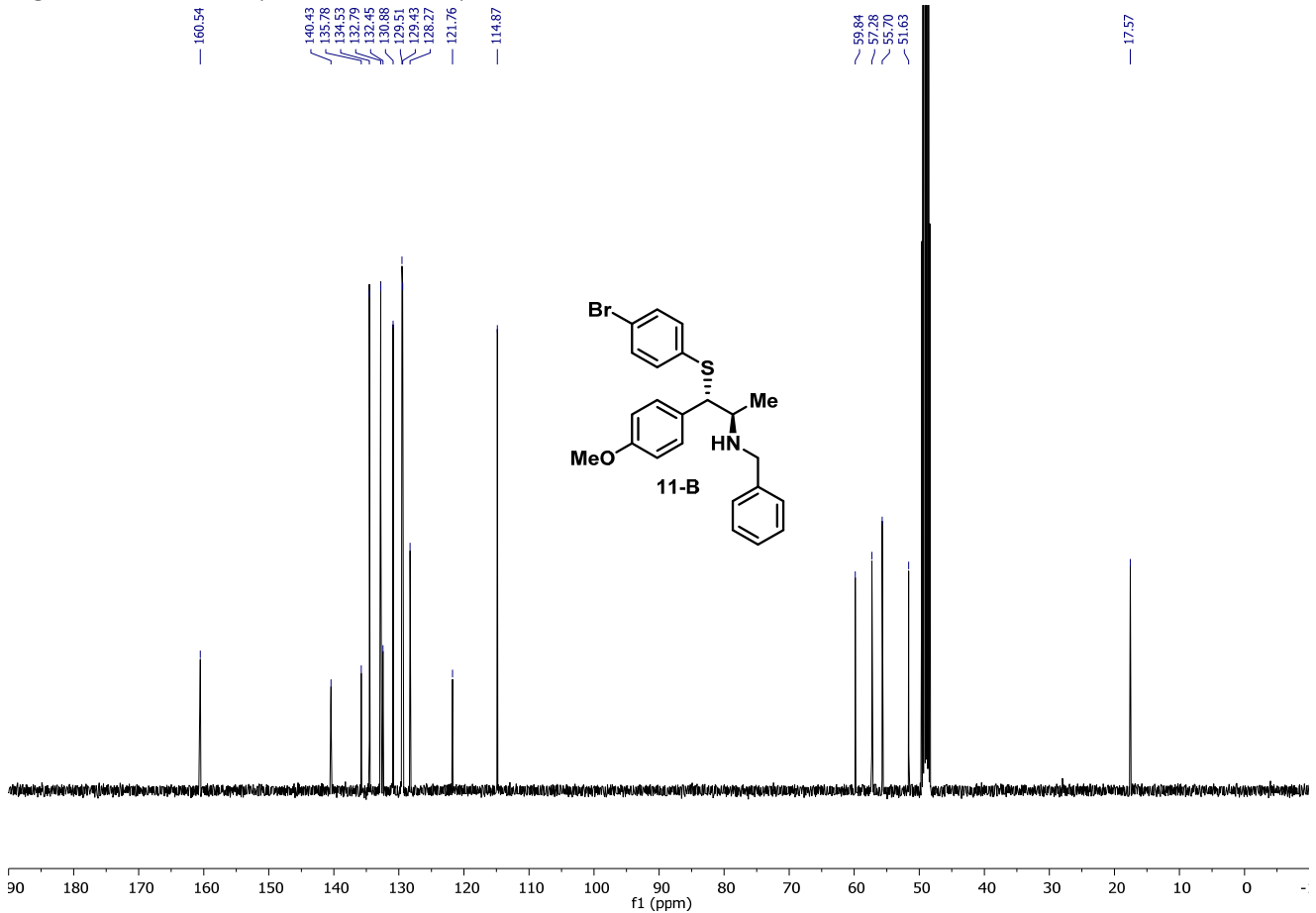


Figure S59. ¹H NMR (400 MHz, CD₃OD) of 12-A

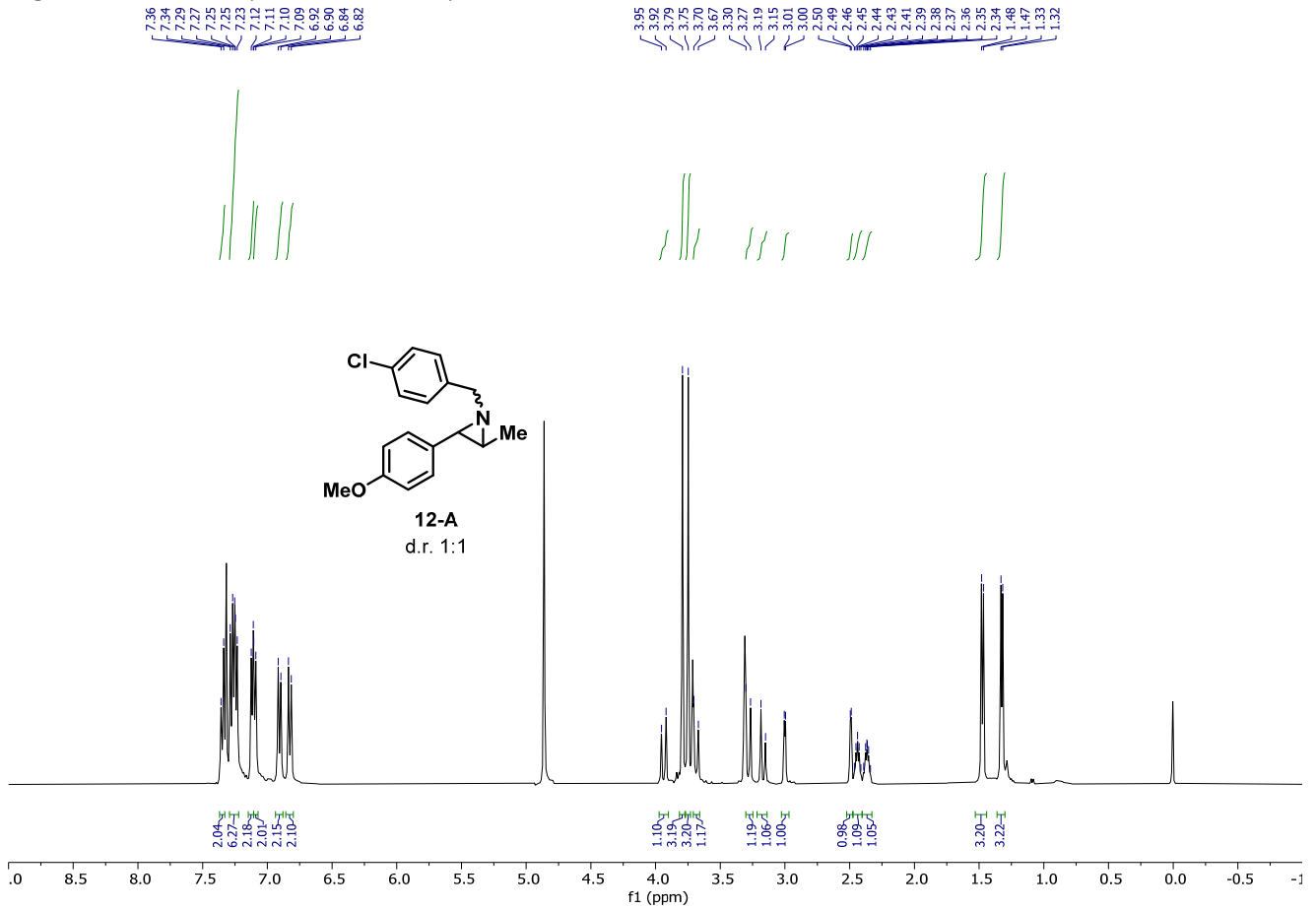


Figure S60. ¹³C NMR (101 MHz, CD₃OD) of 12-A

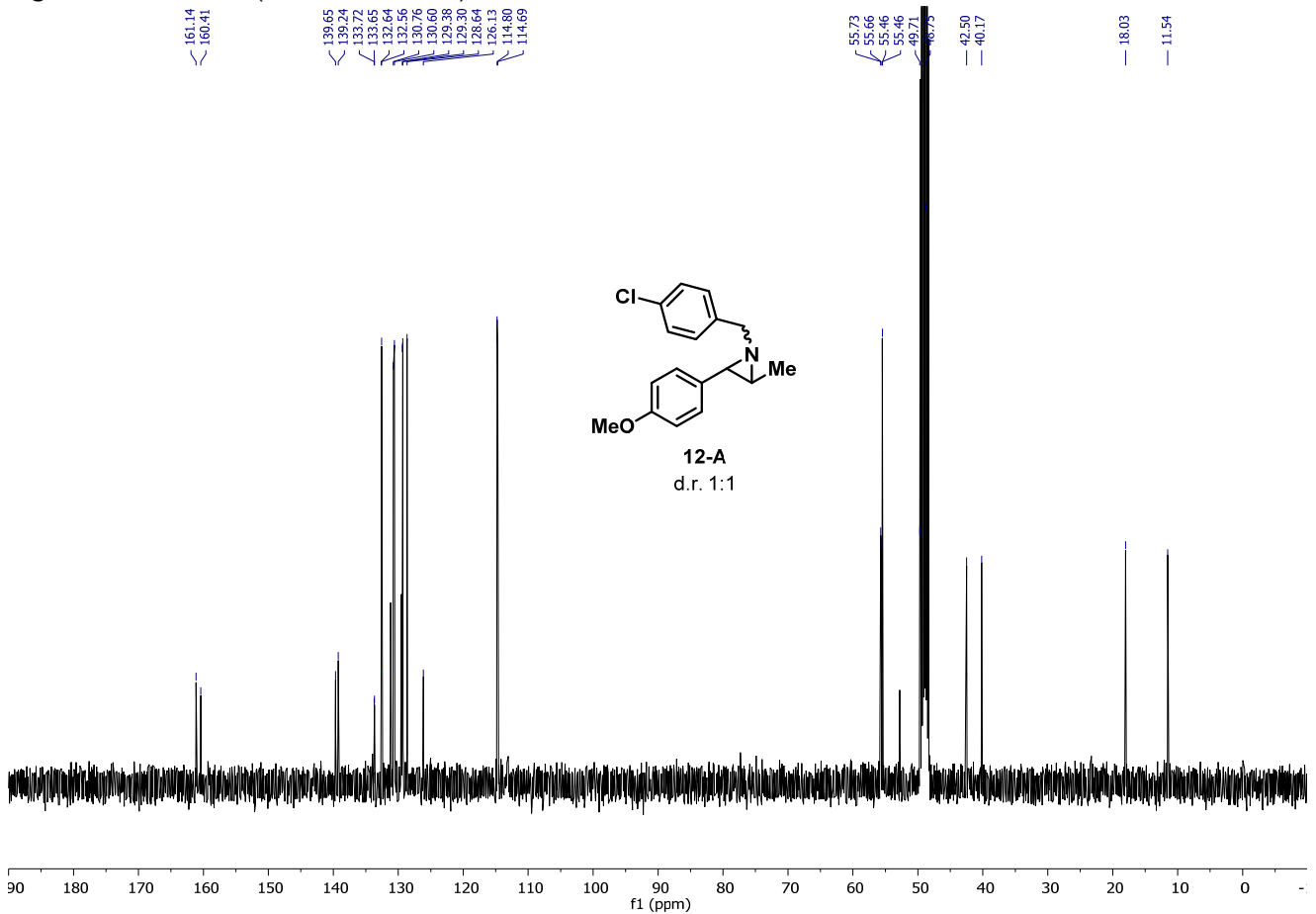


Figure S61. ¹H NMR (400 MHz, CD₃OD) of 12-B

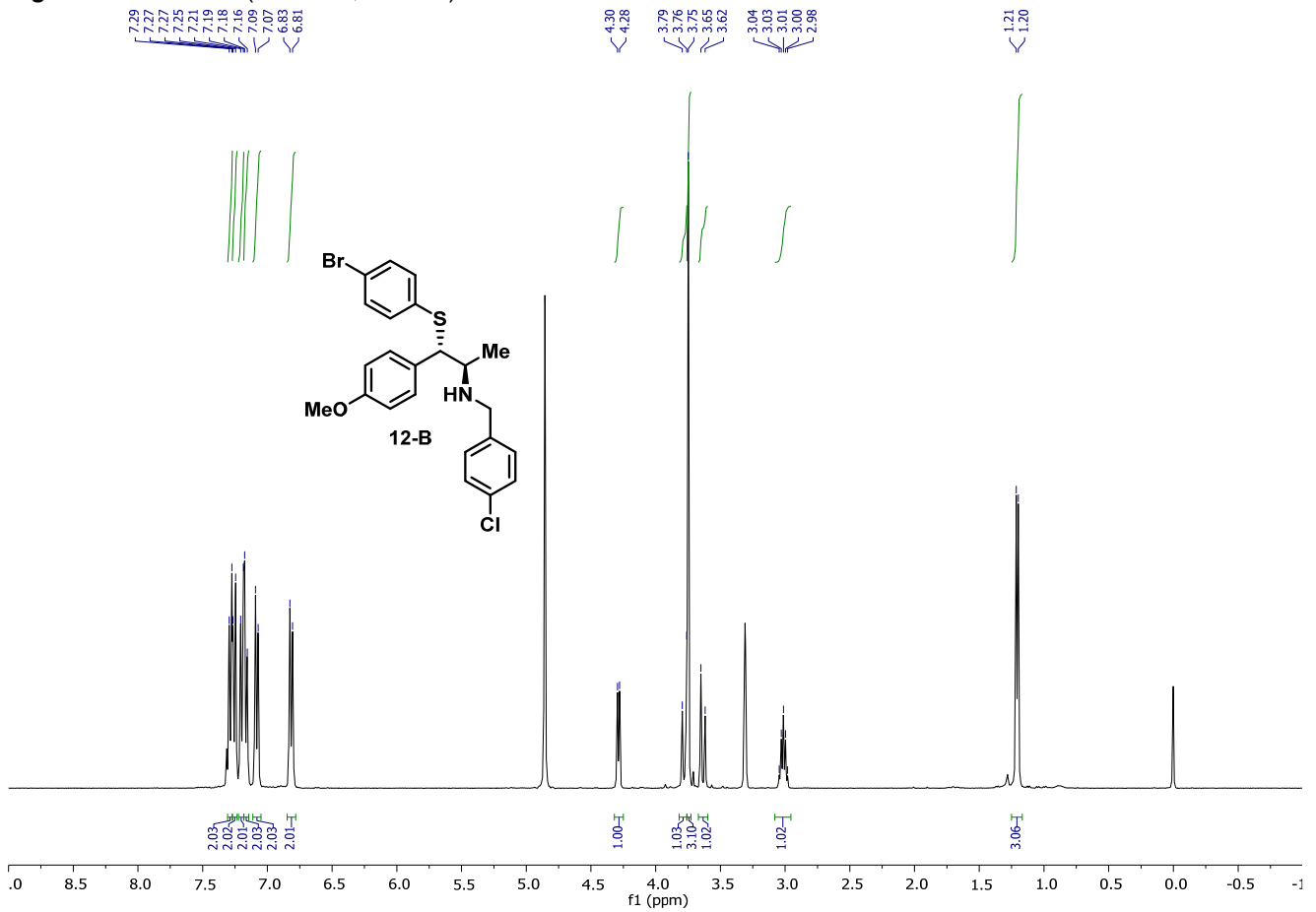


Figure S62. ¹³C NMR (101 MHz, CD₃OD) of 12-B

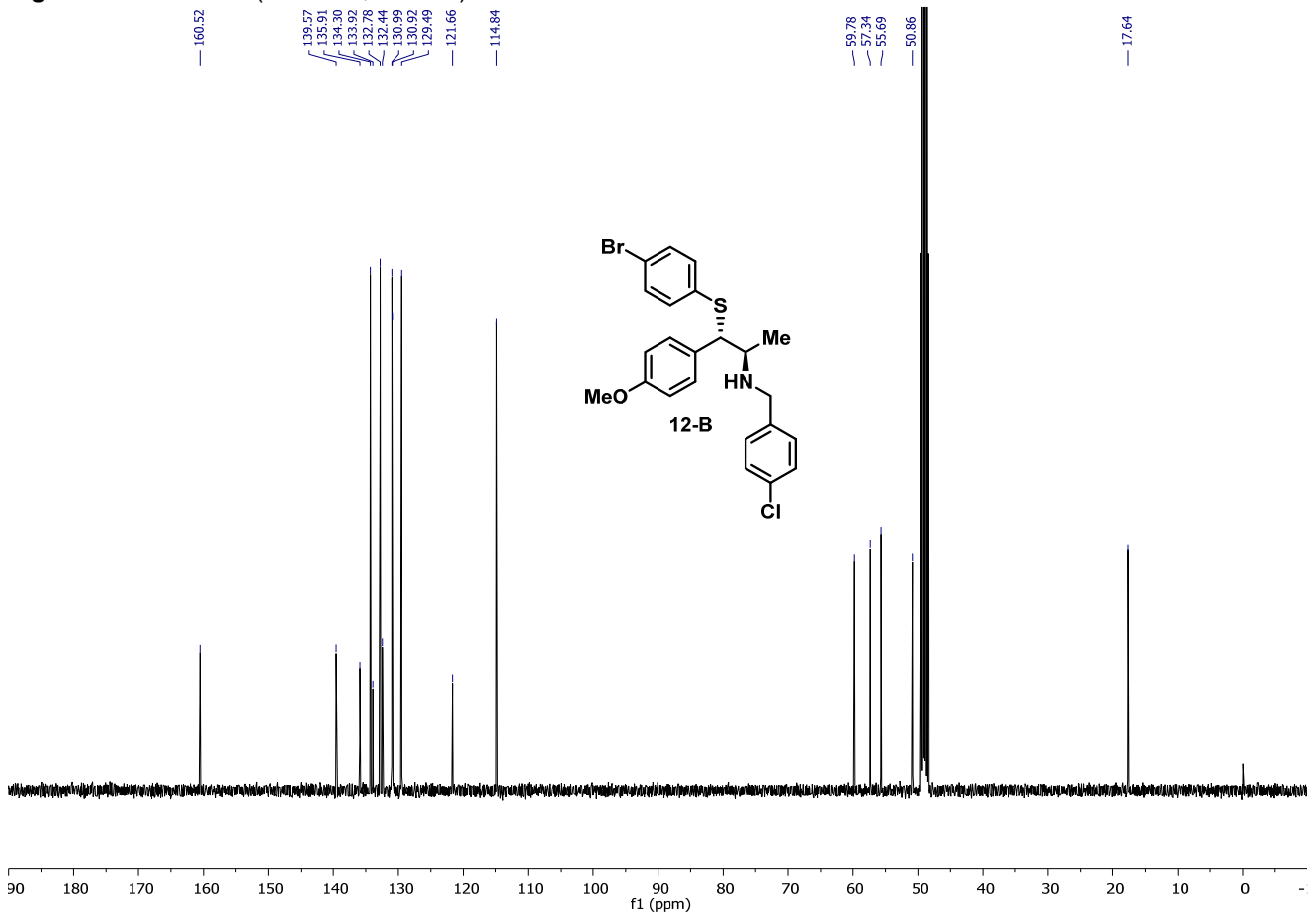


Figure S63. ¹H NMR (400 MHz, CD₃OD) of first *trans*-isomer 13-A

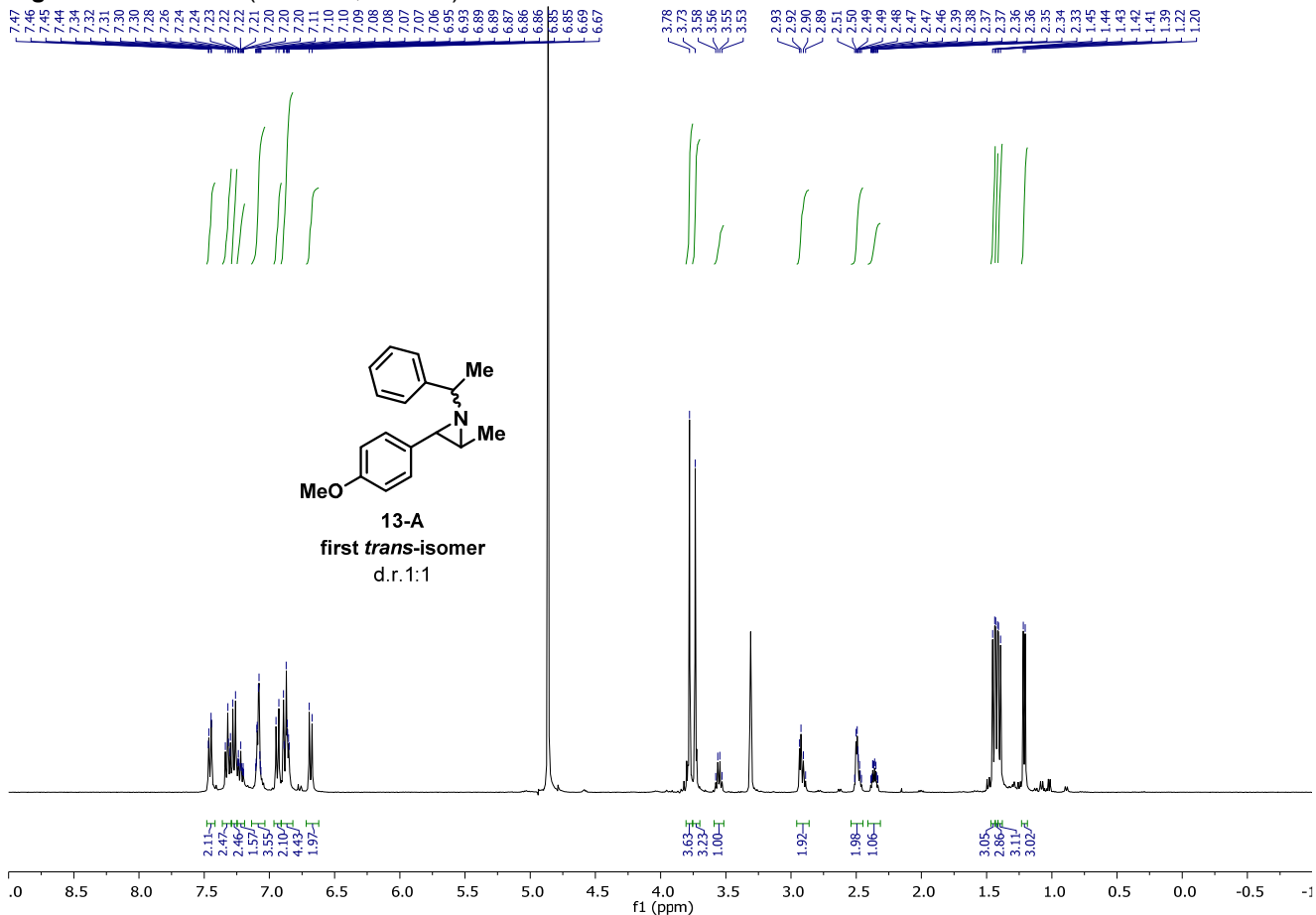


Figure S67. ¹³C NMR (101 MHz, CD₃OD) of first *trans*-isomer 13-A

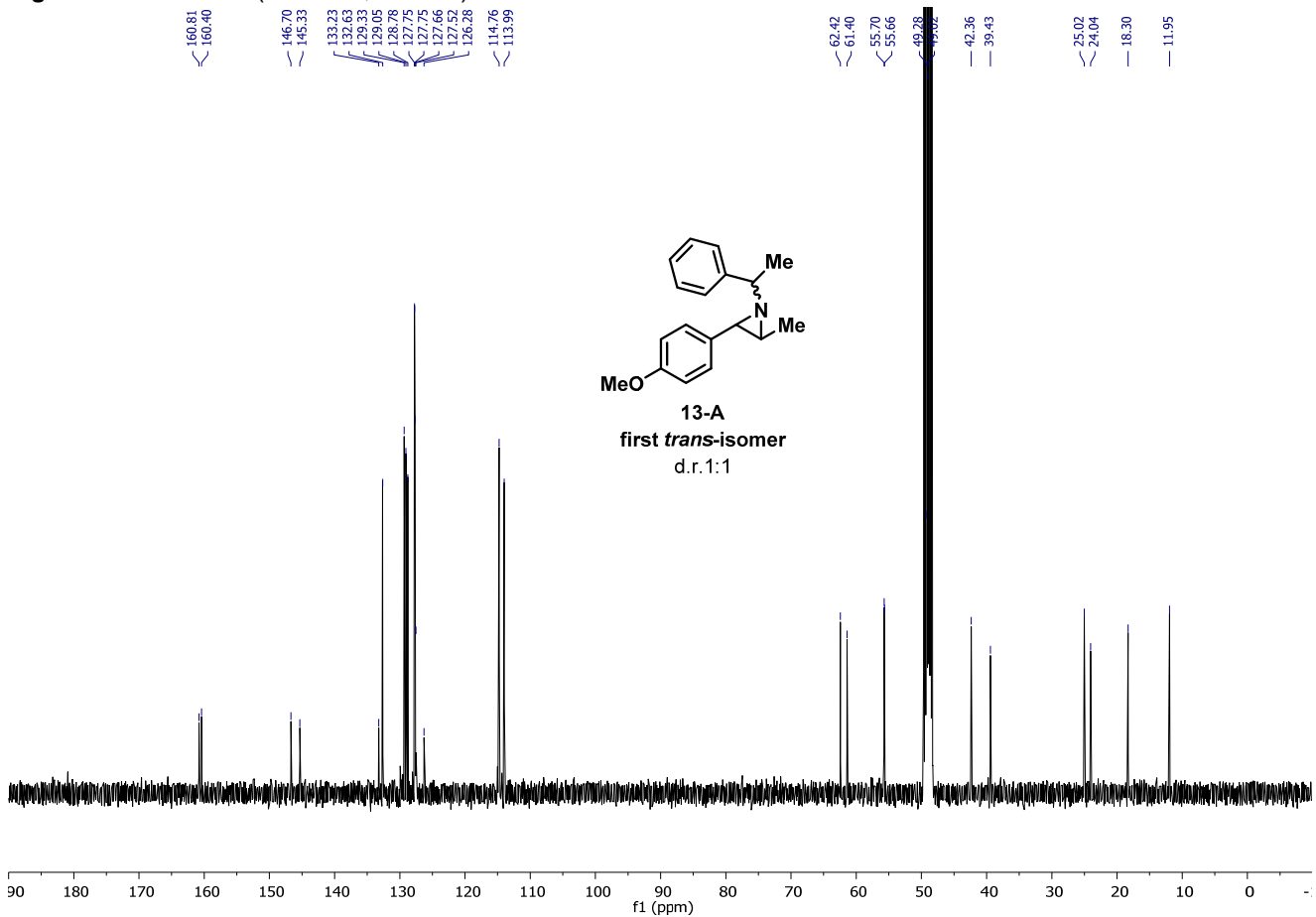


Figure S68. ¹H NMR (400 MHz, CD₃OD) of second *trans*-isomer 13-A

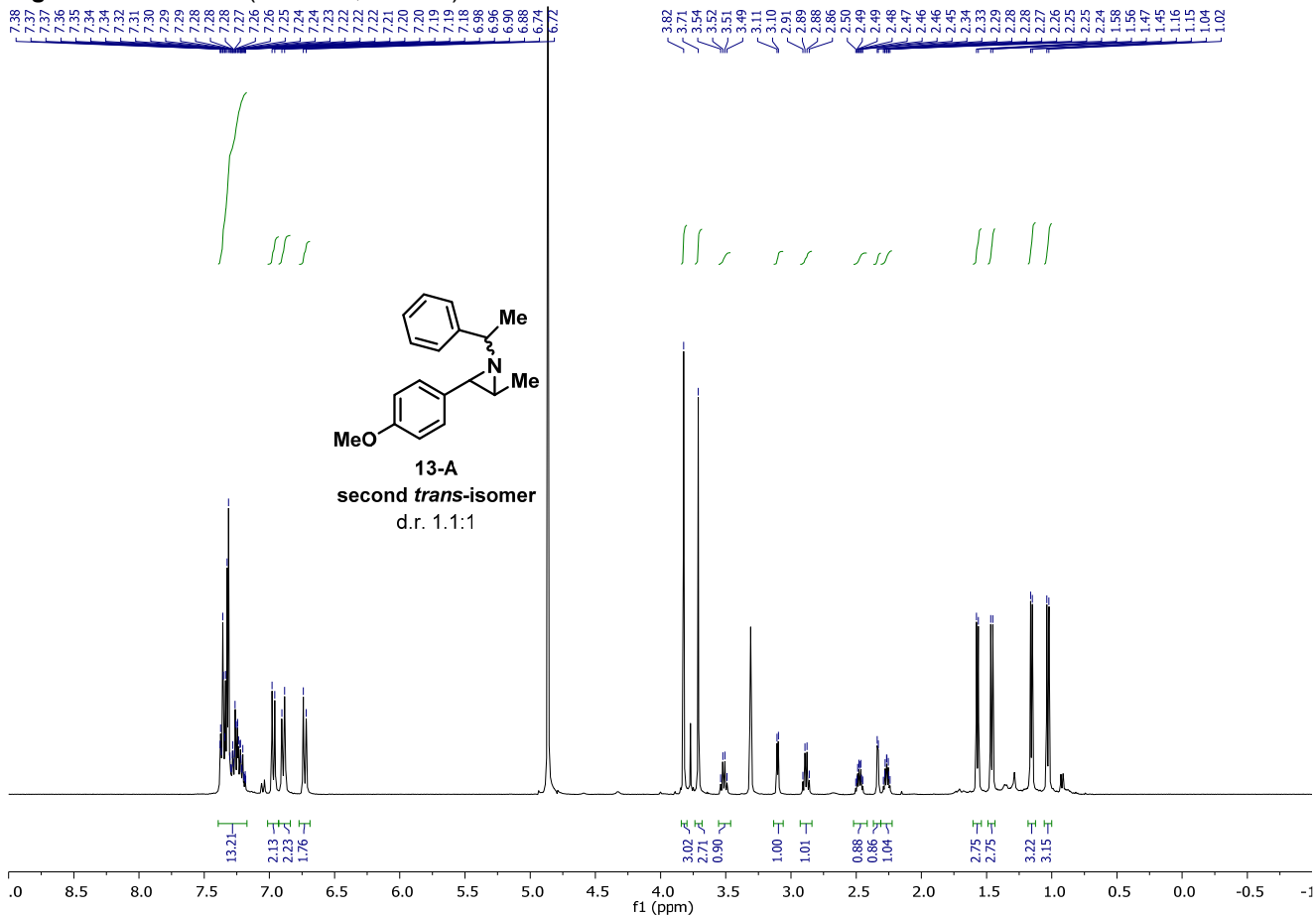


Figure S69. ¹³C NMR (101 MHz, CD₃OD) of second *trans*-isomer 13-A

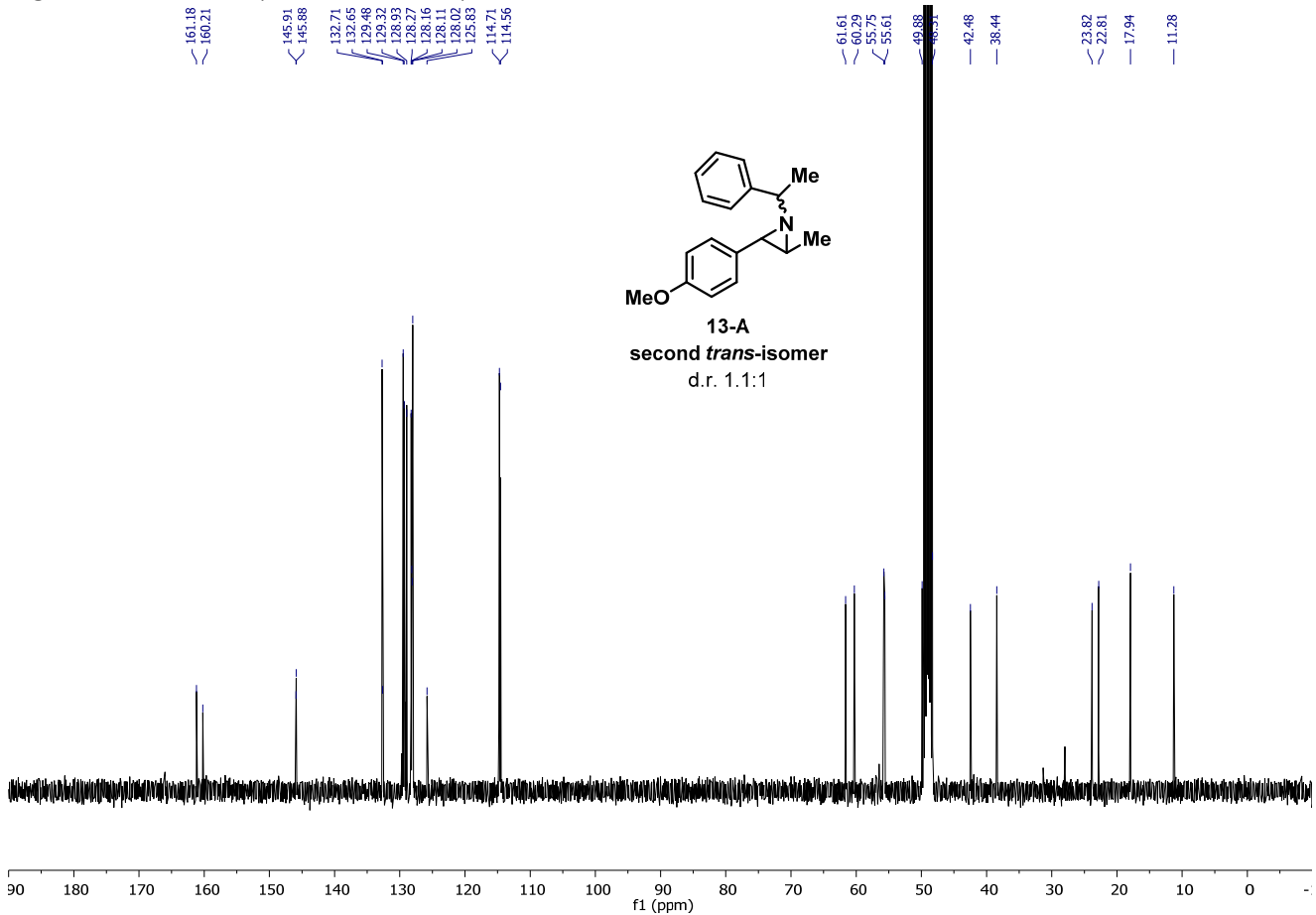


Figure S70. ¹H NMR (400 MHz, CD₃OD) of first *anti*-isomer 13-B

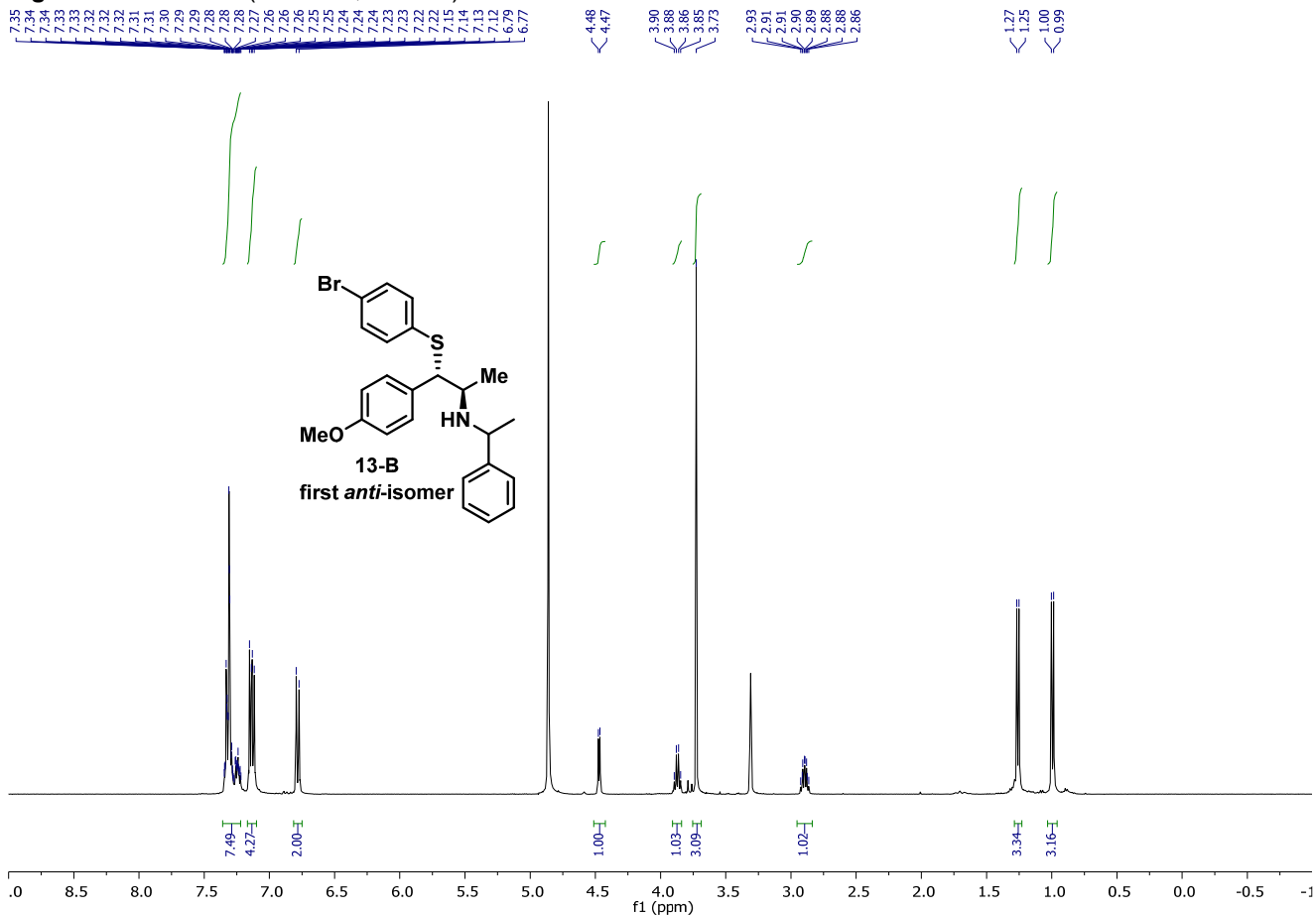


Figure S71. ¹³C NMR (101 MHz, CD₃OD) of first *anti*-isomer 13-B

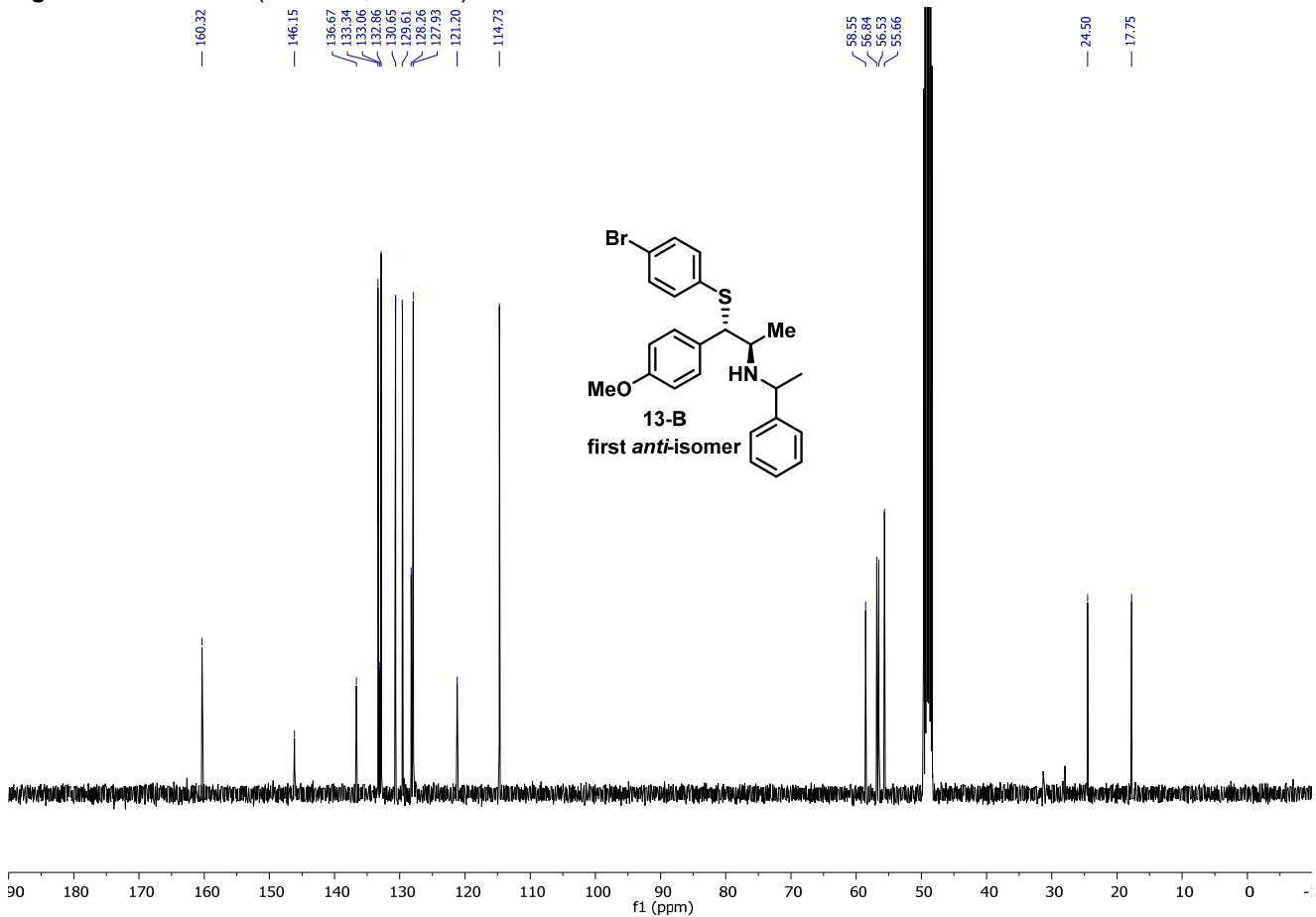


Figure S72. ¹H NMR (400 MHz, CD₃OD) of second *anti*-isomer 13-B

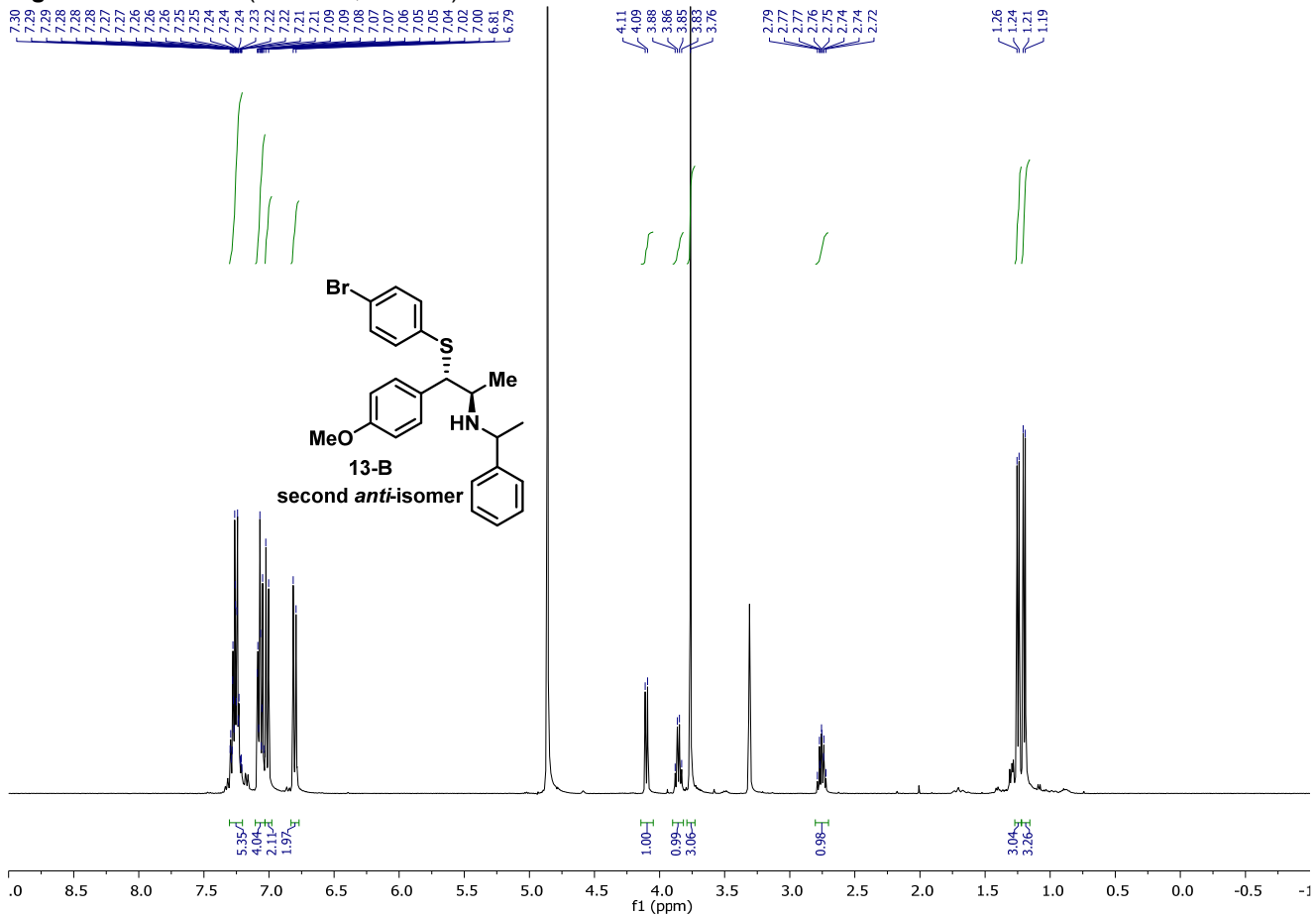


Figure S73. ¹³C NMR (101 MHz, CD₃OD) of second *anti*-isomer 13-B

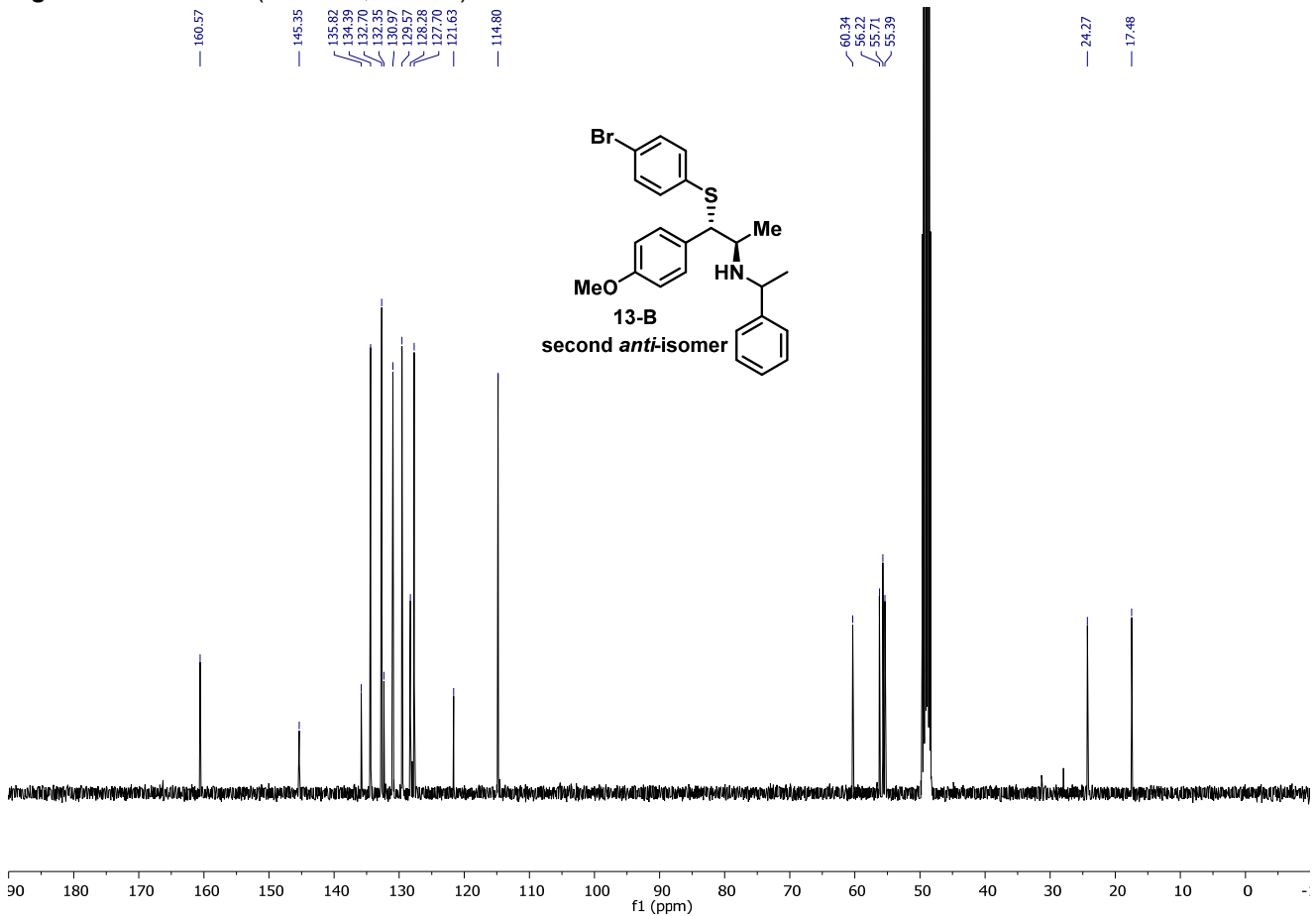


Figure S74. ¹H NMR (400 MHz, CD₃OD) of 14-B

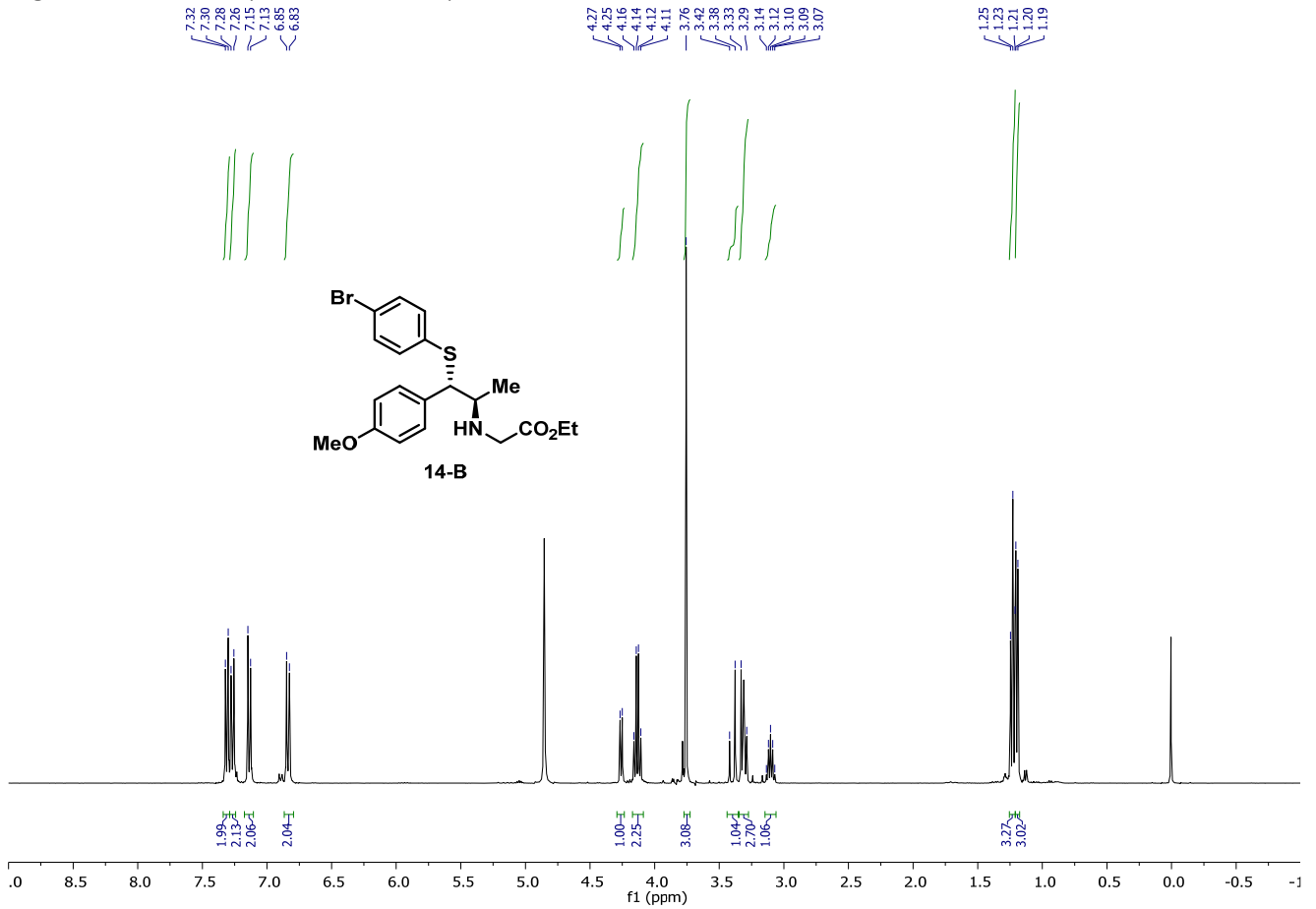


Figure S75. ¹³C NMR (101 MHz, CD₃OD) of 14-B

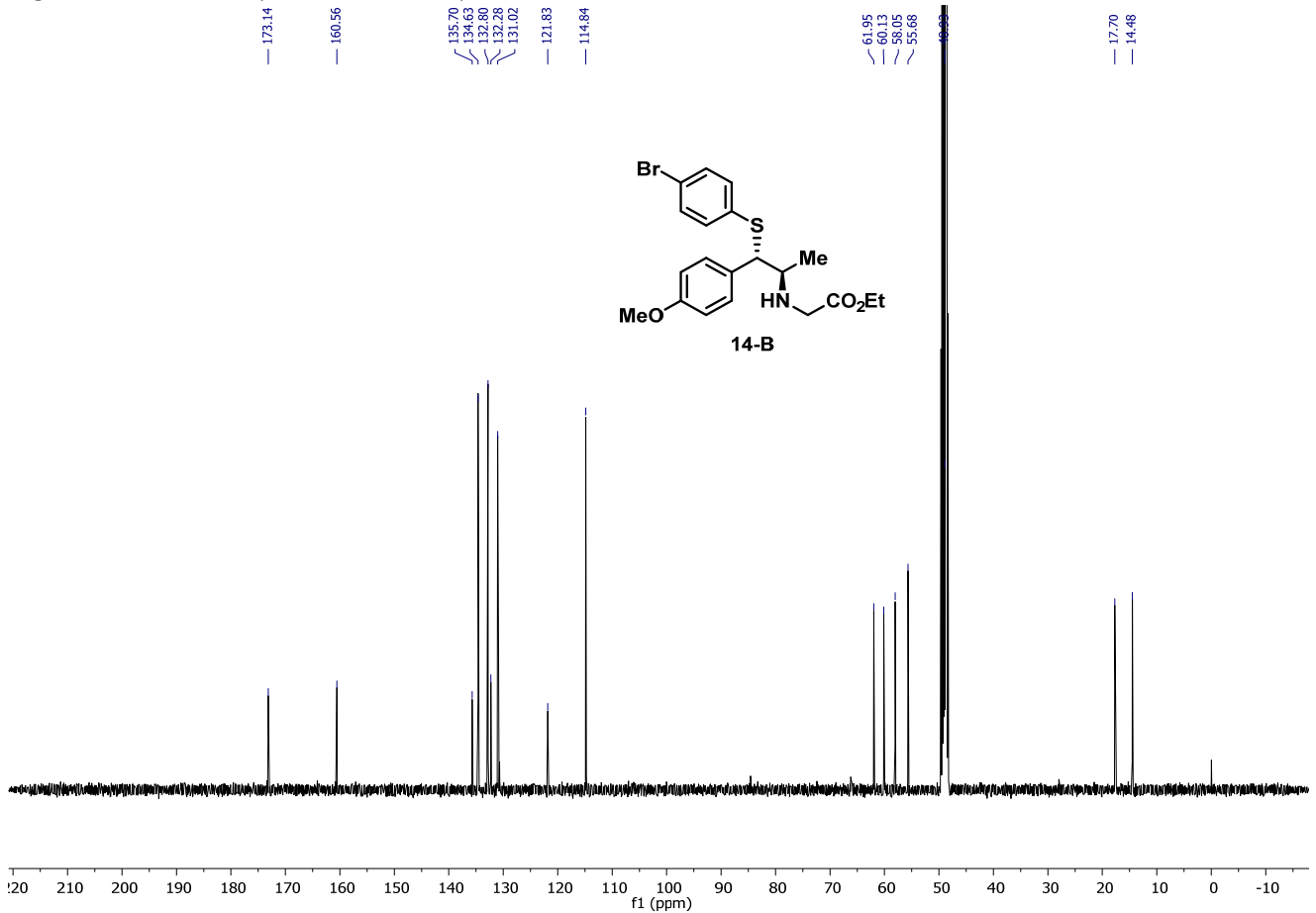


Figure S76. ¹H NMR (400 MHz, CD₃OD) of first *anti*-isomer 15-B

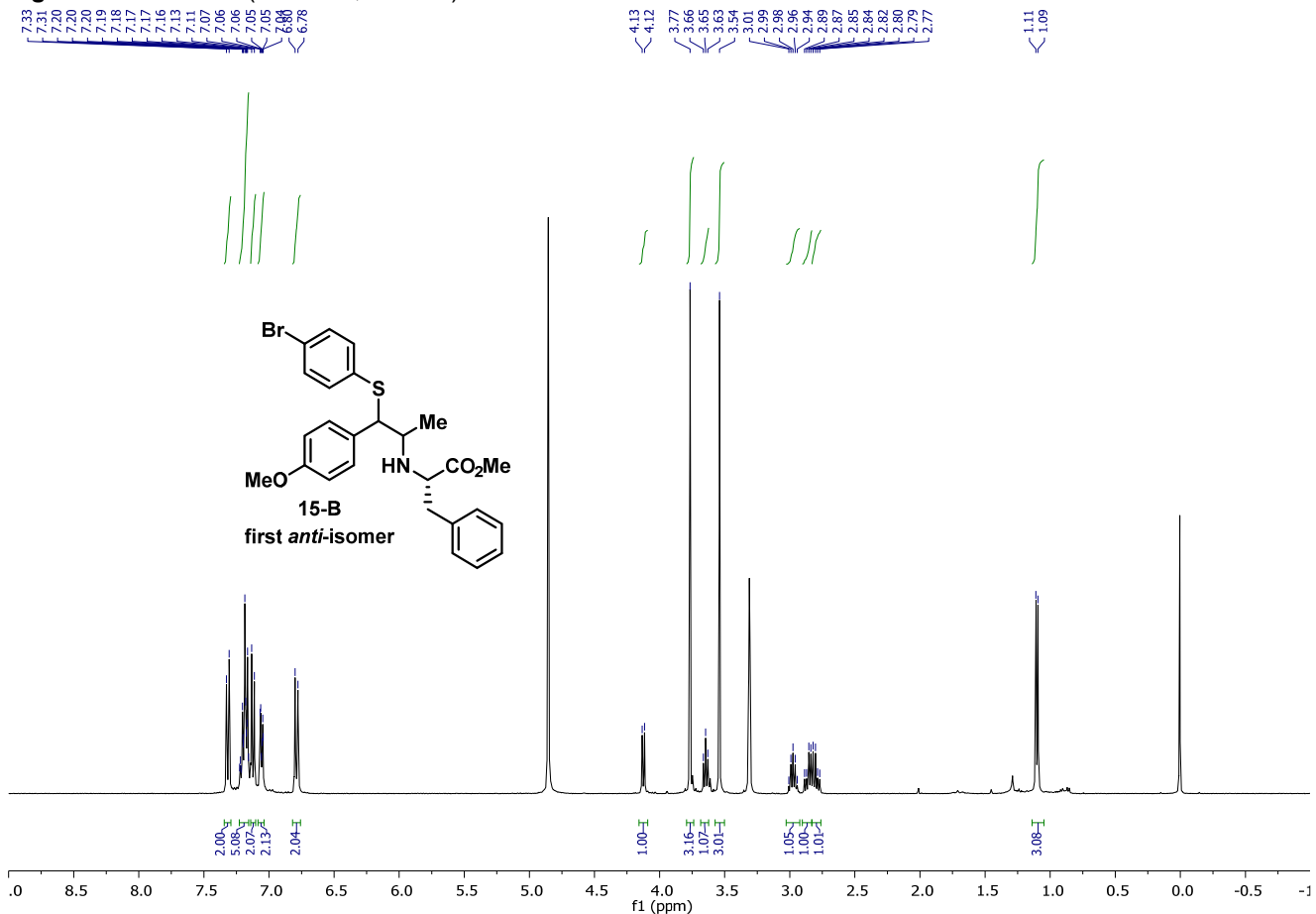


Figure S77. ¹³C NMR (101 MHz, CD₃OD) of first *anti*-isomer 15-B

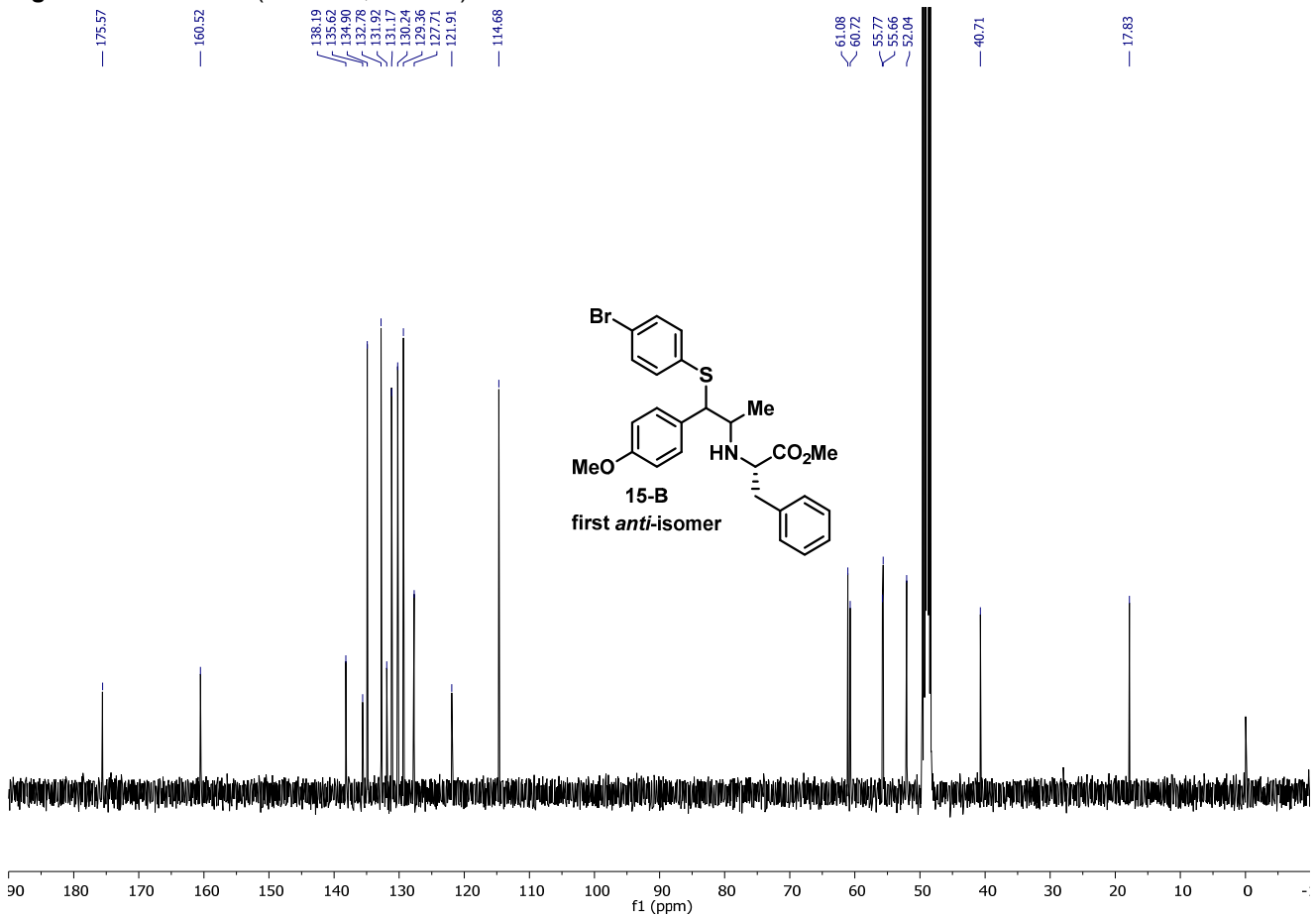


Figure S78. ¹H NMR (400 MHz, CD₃OD) of second *anti*-isomer 15-B

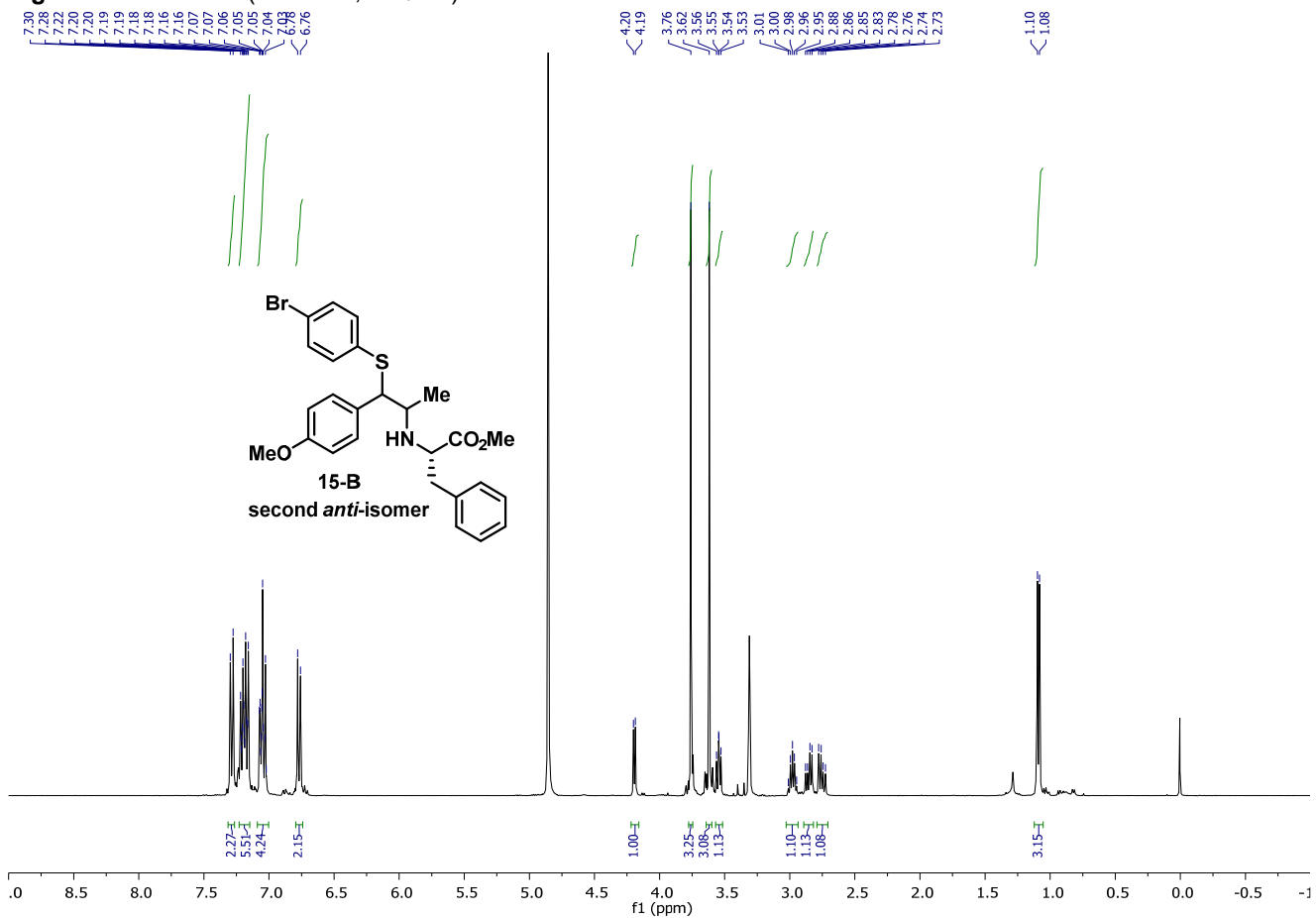


Figure S79. ¹³C NMR (101 MHz, CD₃OD) of second *anti*-isomer 15-B

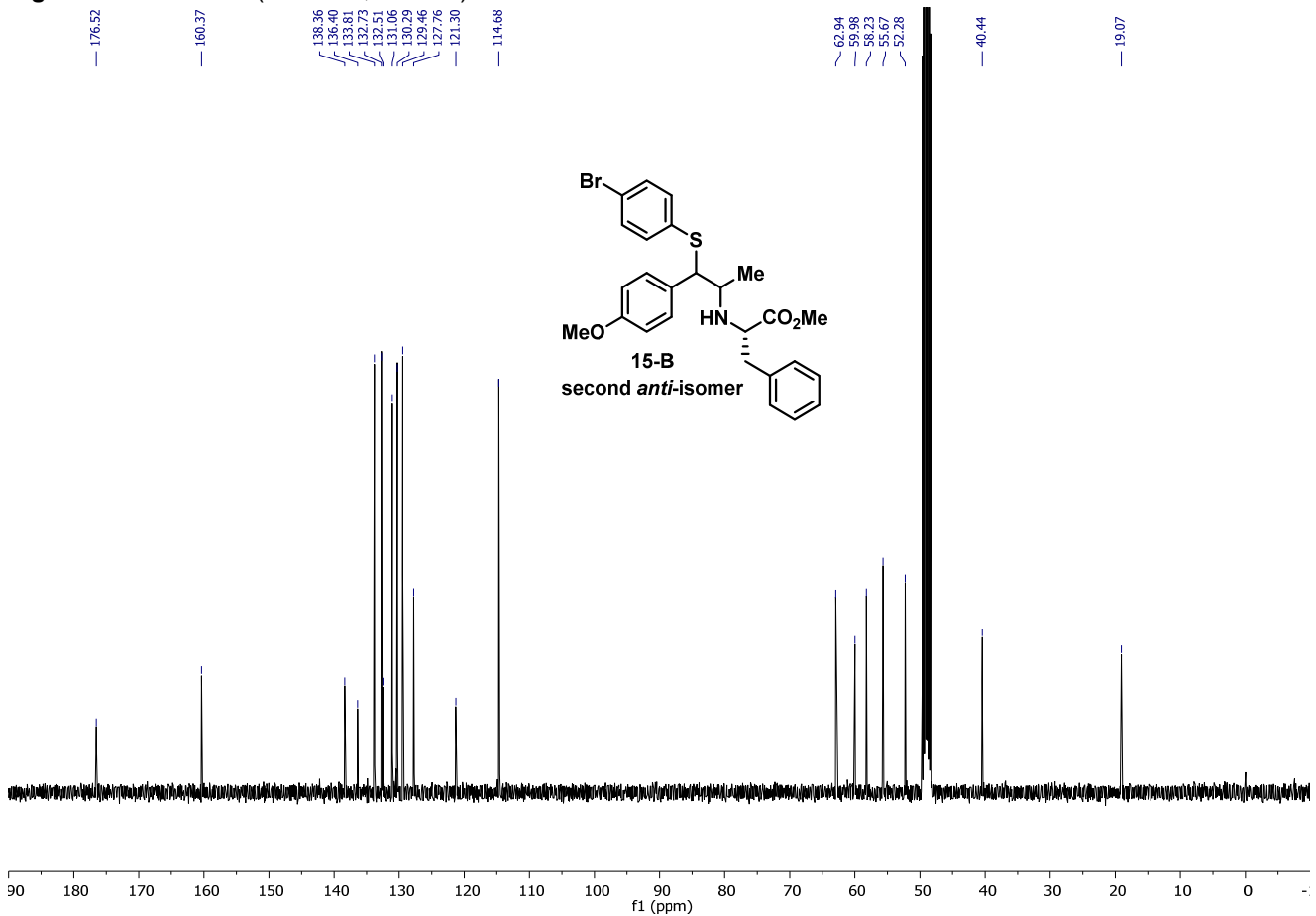


Figure S80. ¹H NMR (400 MHz, CD₃OD) of 16-A

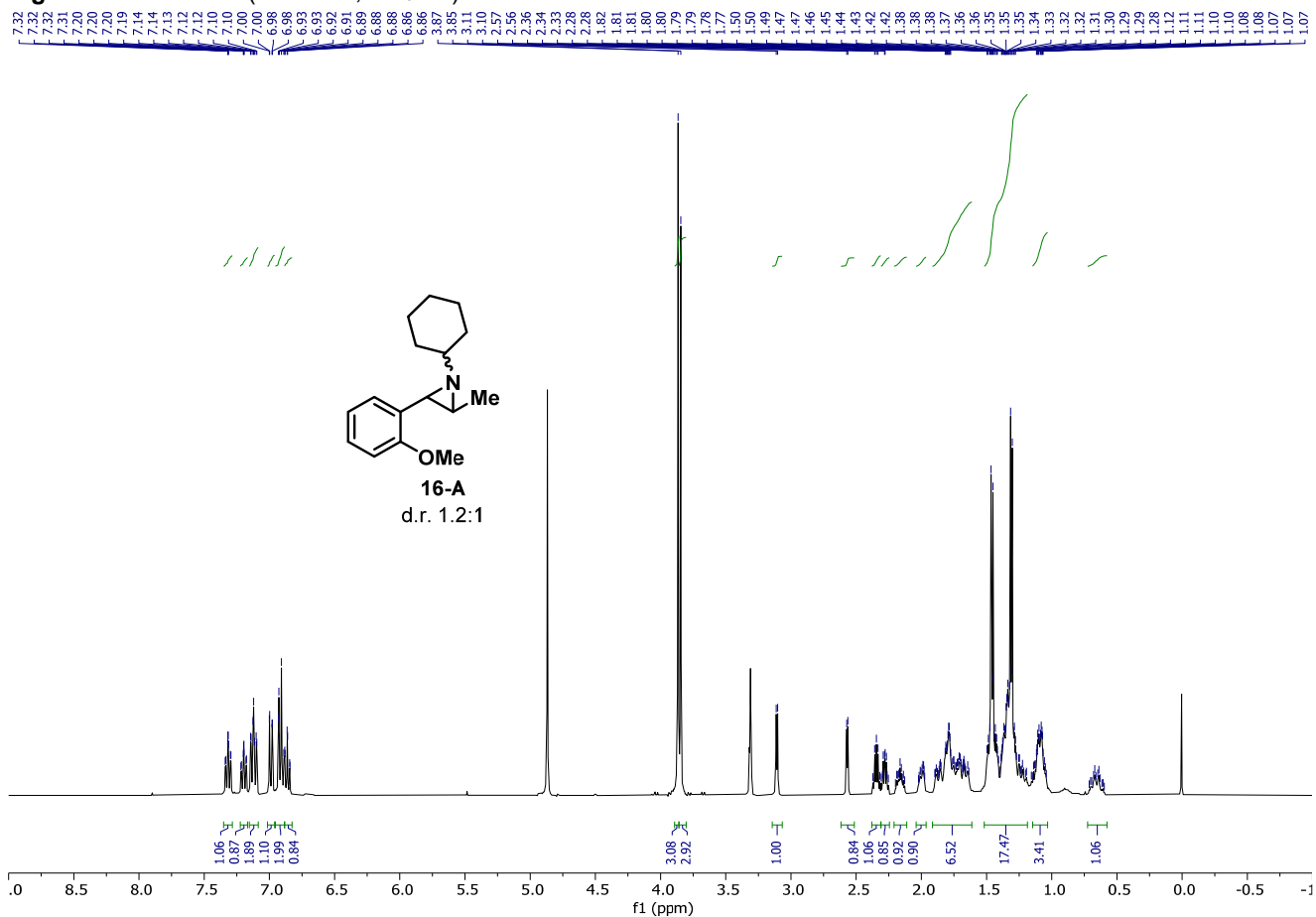


Figure S81. ¹³C NMR (101 MHz, CD₃OD) of 16-A

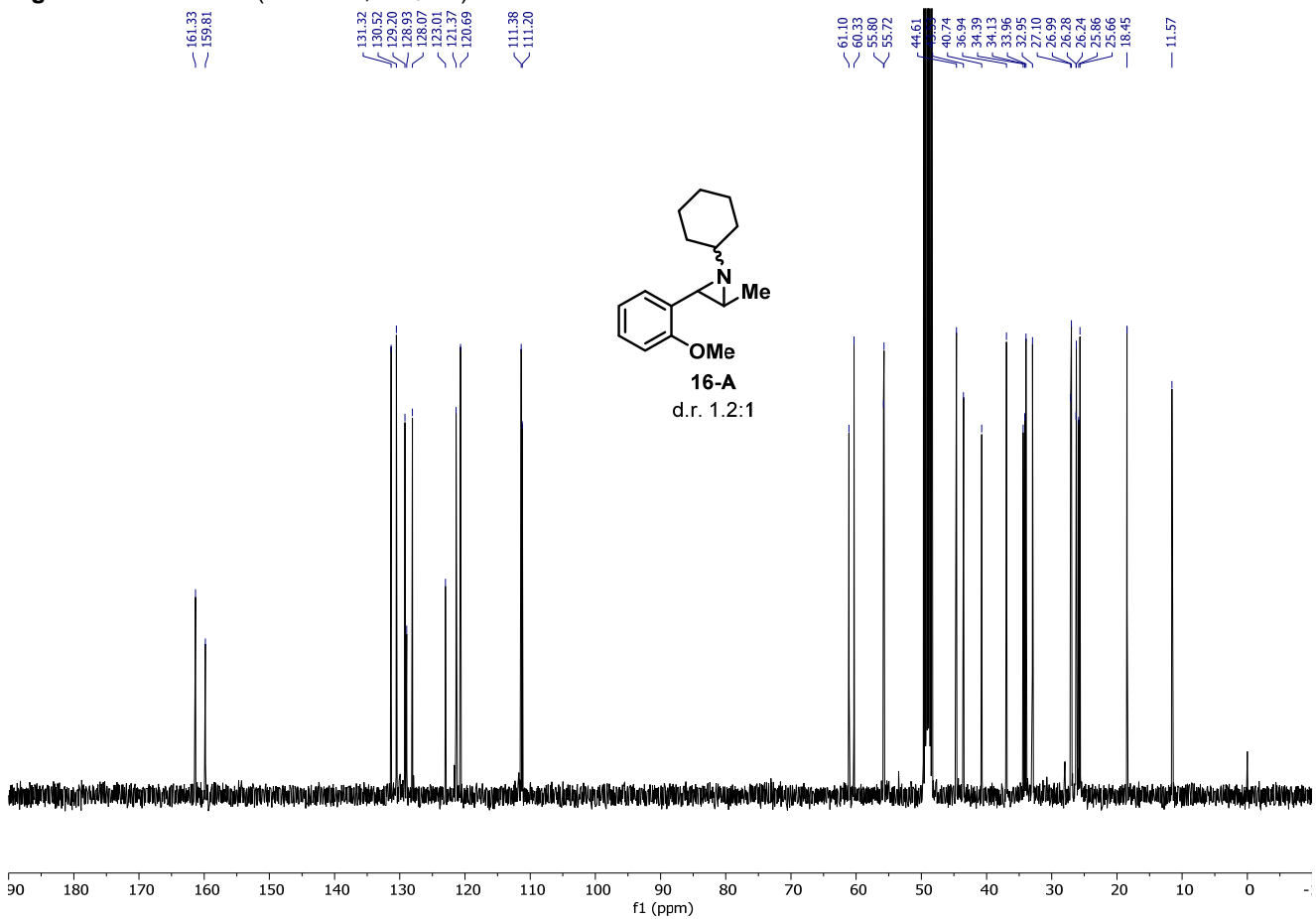


Figure S82. ¹H NMR (400 MHz, CD₃OD) of 17-B

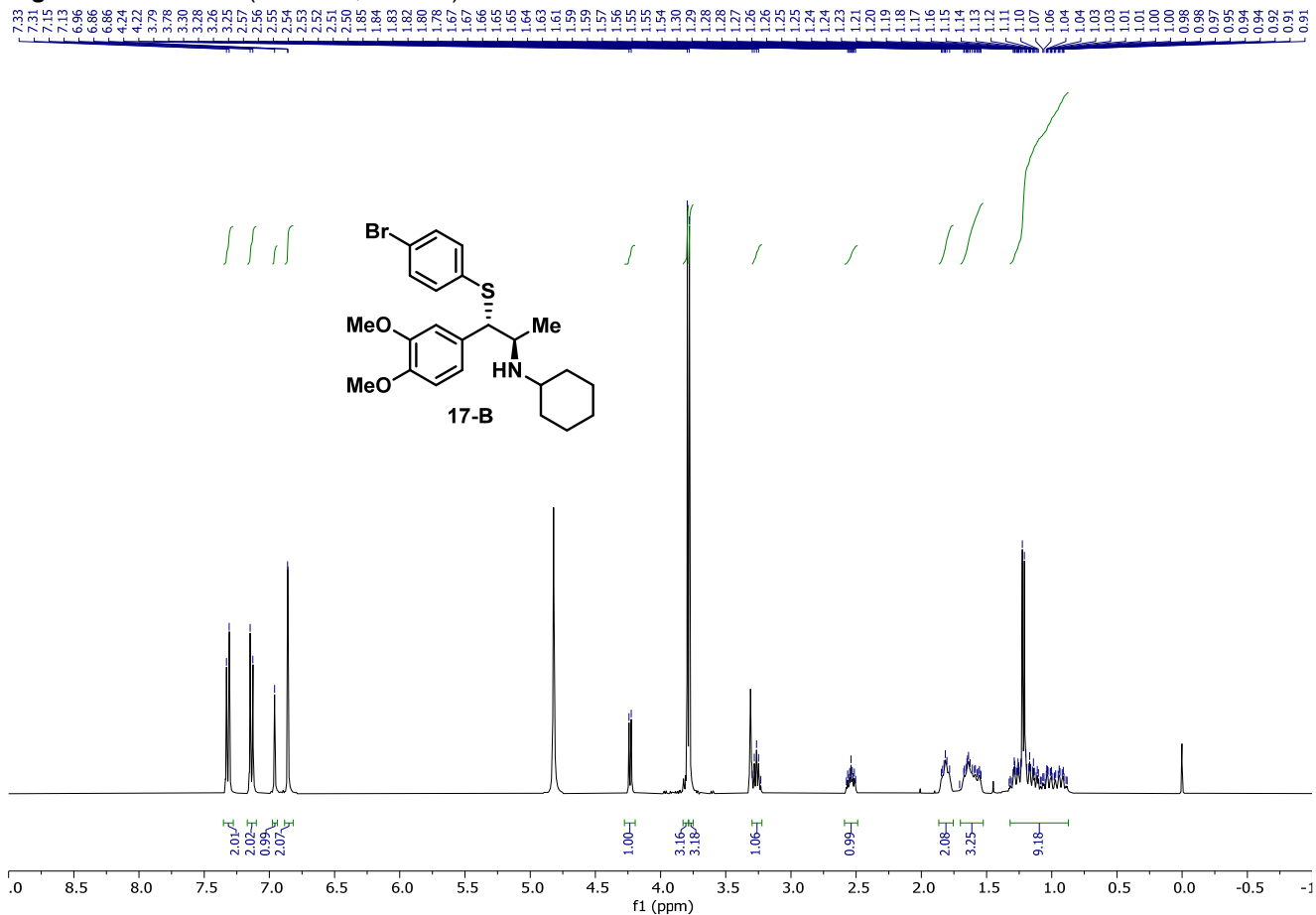


Figure S83. ¹³C NMR (101 MHz, CD₃OD) of 17-B

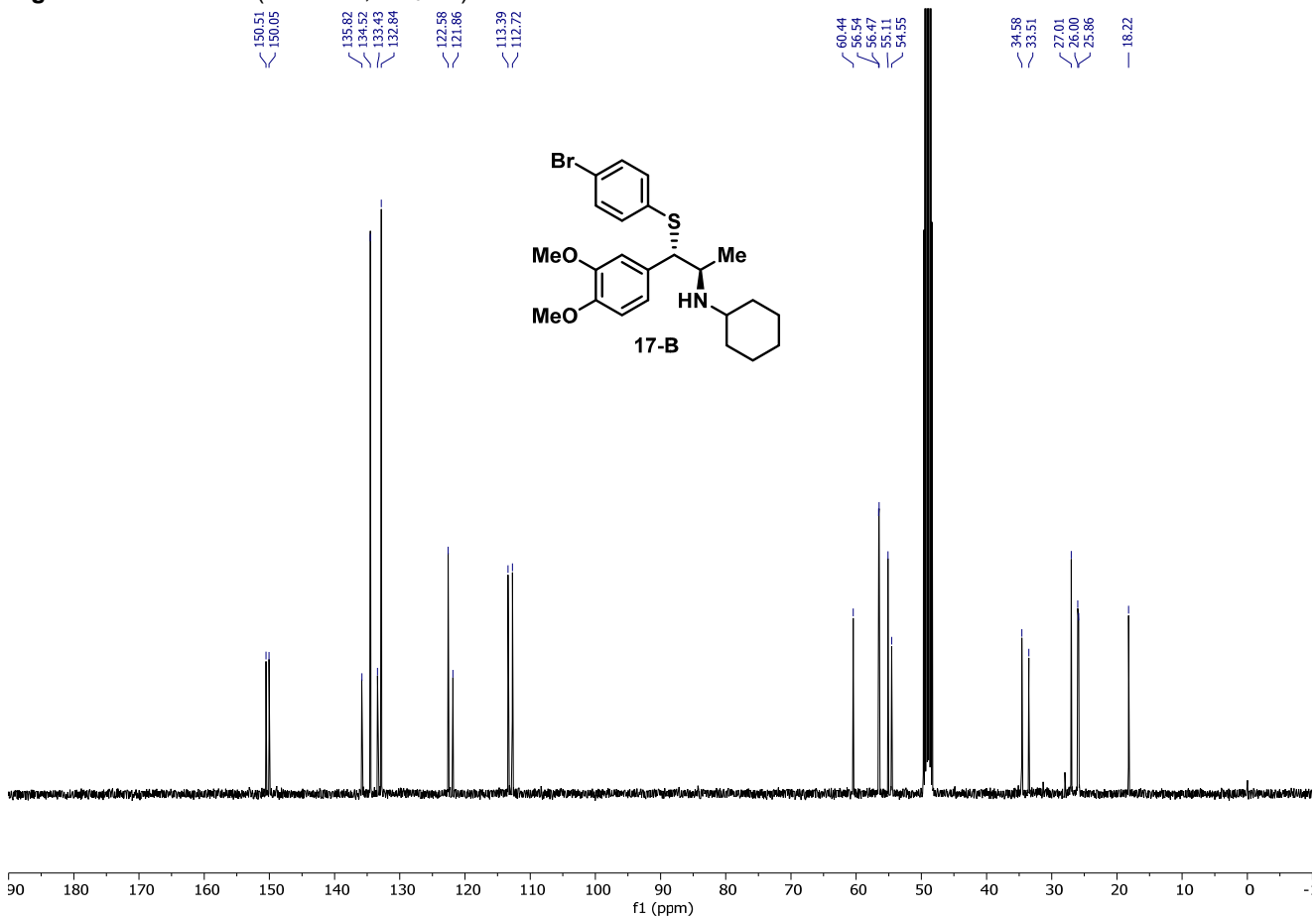


Figure S84. ¹H NMR (400 MHz, CD₃OD) of 18-B

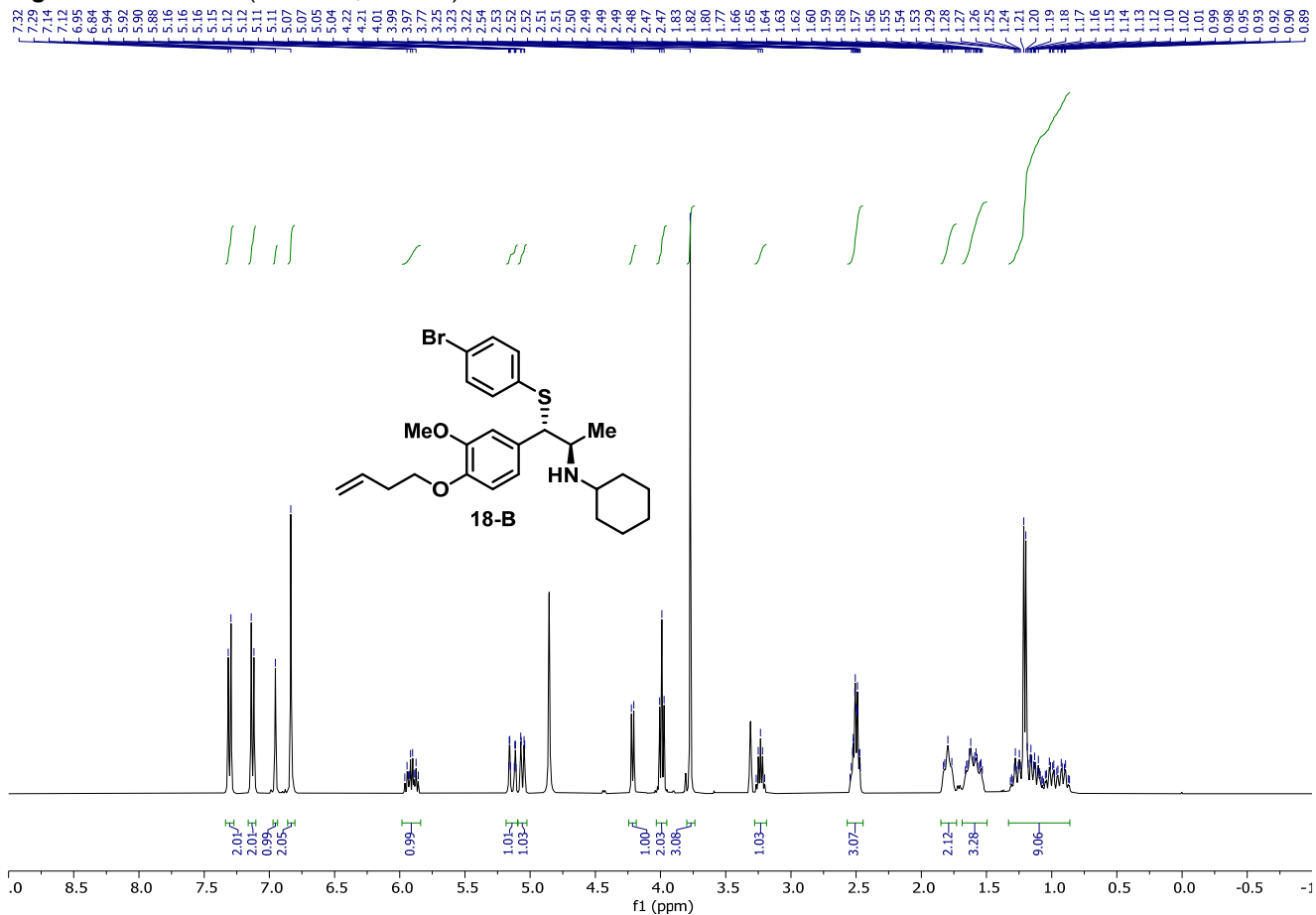


Figure S85. ¹³C NMR (101 MHz, CD₃OD) of 18-B

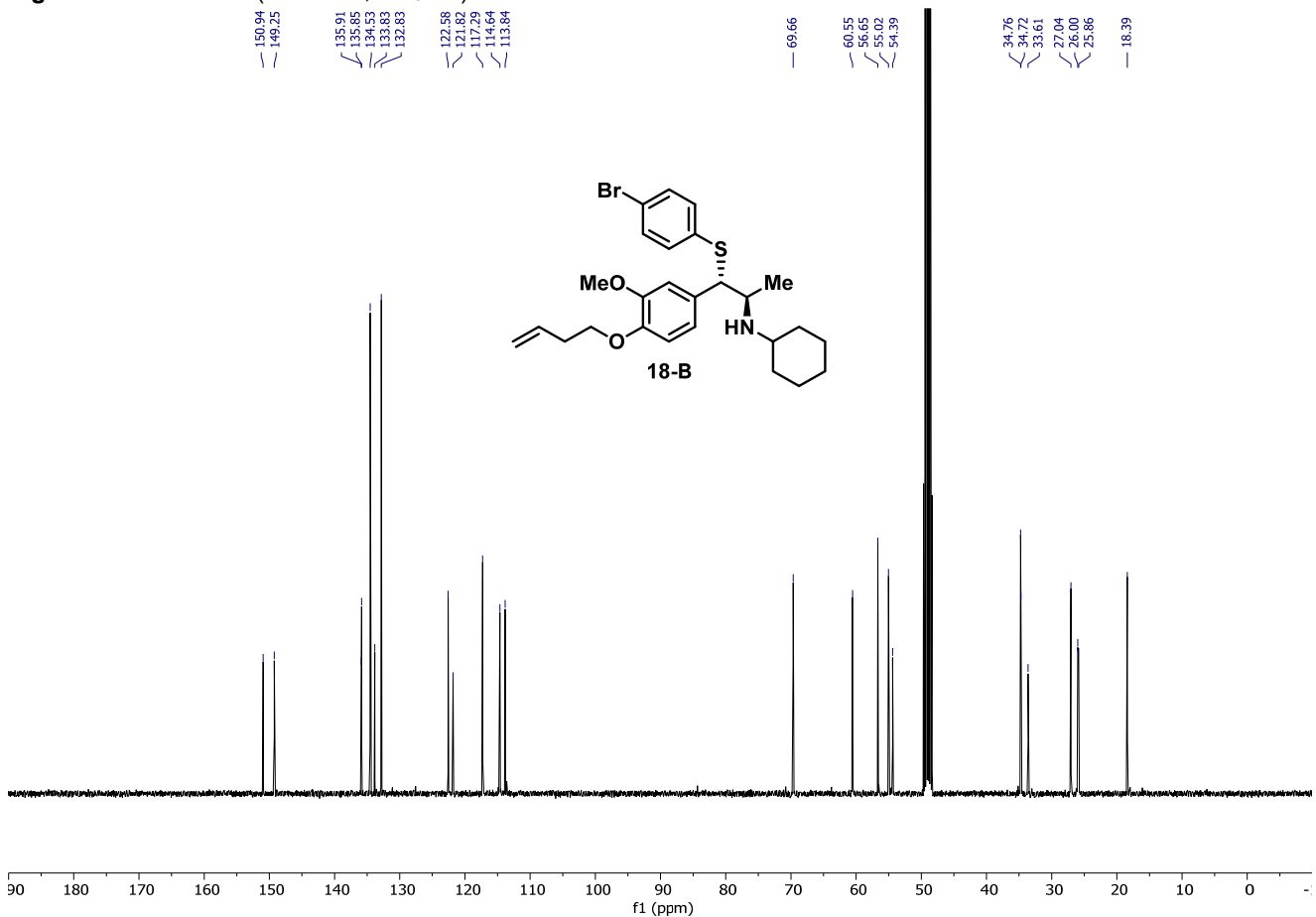


Figure S86. ¹H NMR (400 MHz, CD₃OD) of 19-A

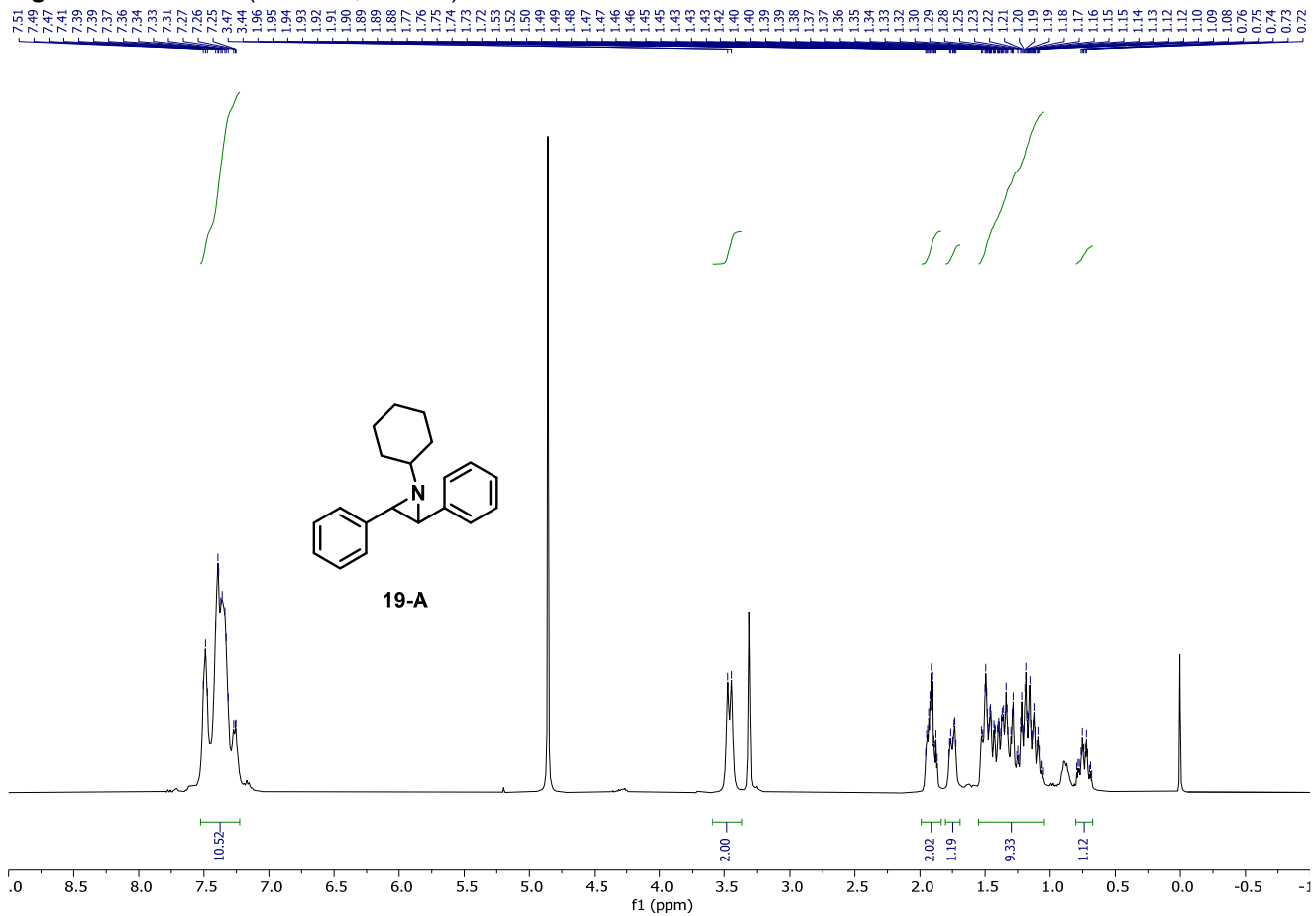


Figure S87. ¹³C NMR (101 MHz, CD₃OD) of 19-A

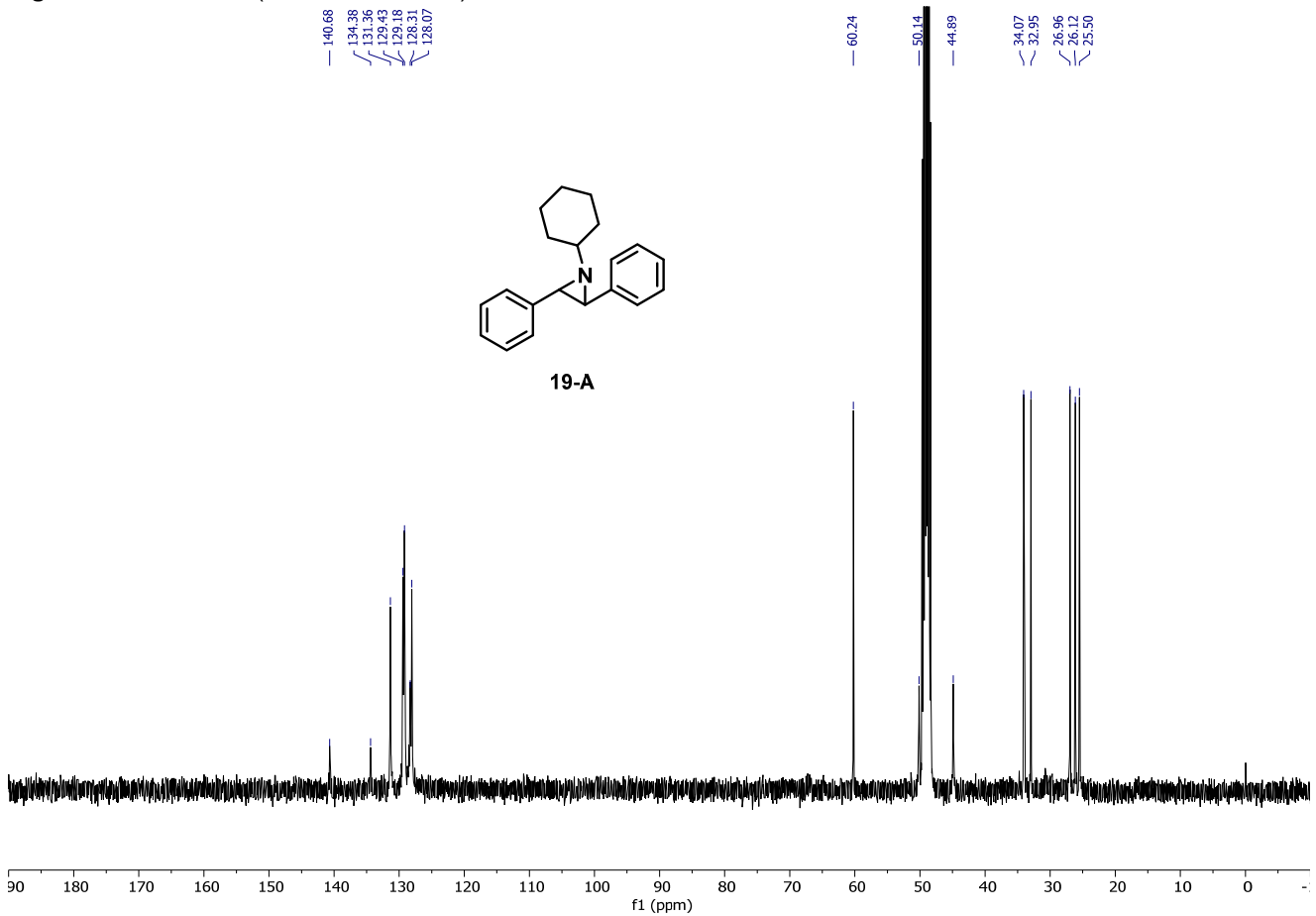


Figure S88. ¹H NMR (400 MHz, CD₃OD) of 20-A

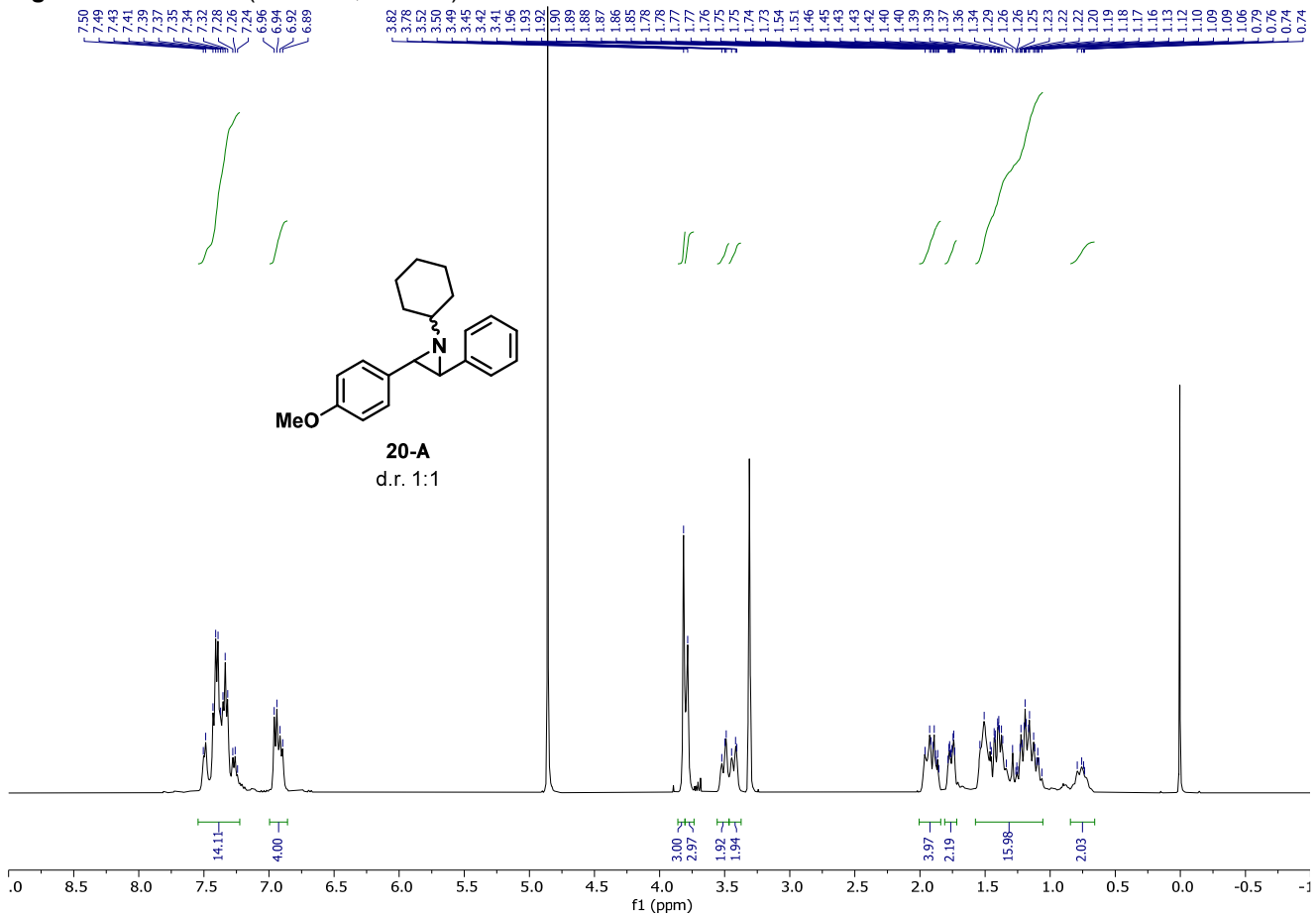


Figure S89. ¹³C NMR (101 MHz, CD₃OD) of 20-A

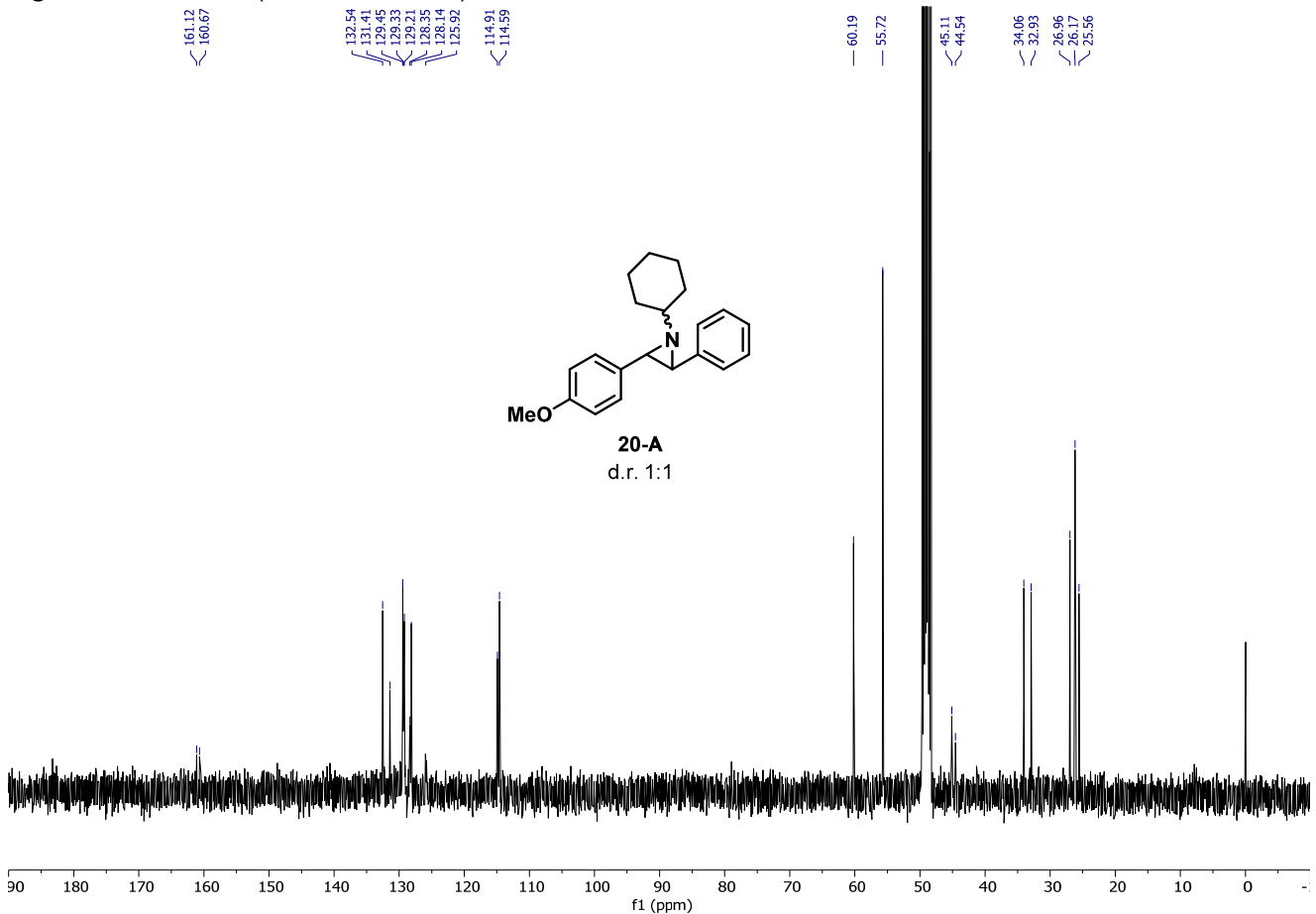


Figure S90. ¹H NMR (400 MHz, CD₃OD) of 21-A

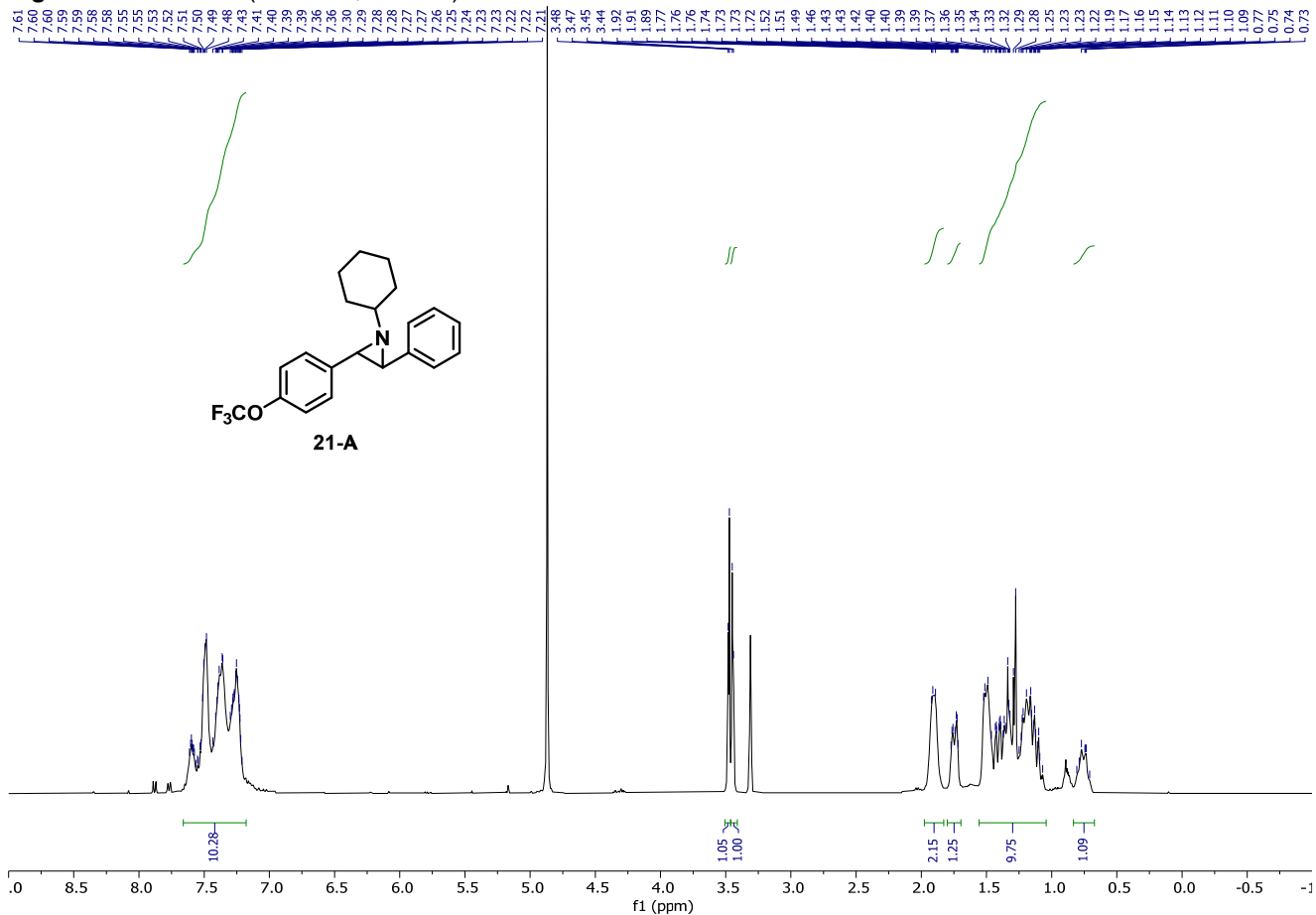


Figure S91. ¹³C NMR (101 MHz, CD₃OD) of 21-A

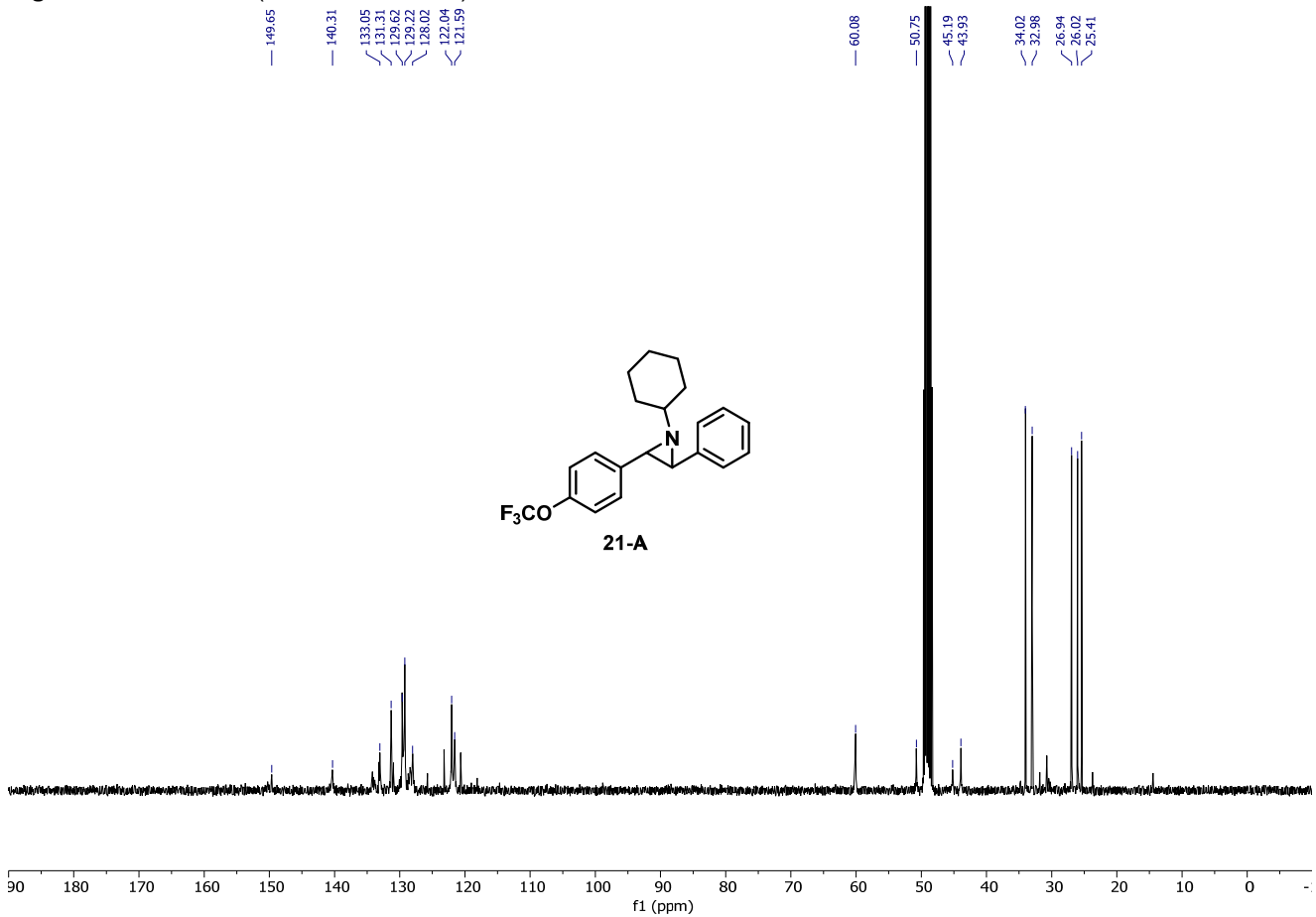


Figure S92. ^{19}F NMR (376 MHz, CD_3OD) of 21-A

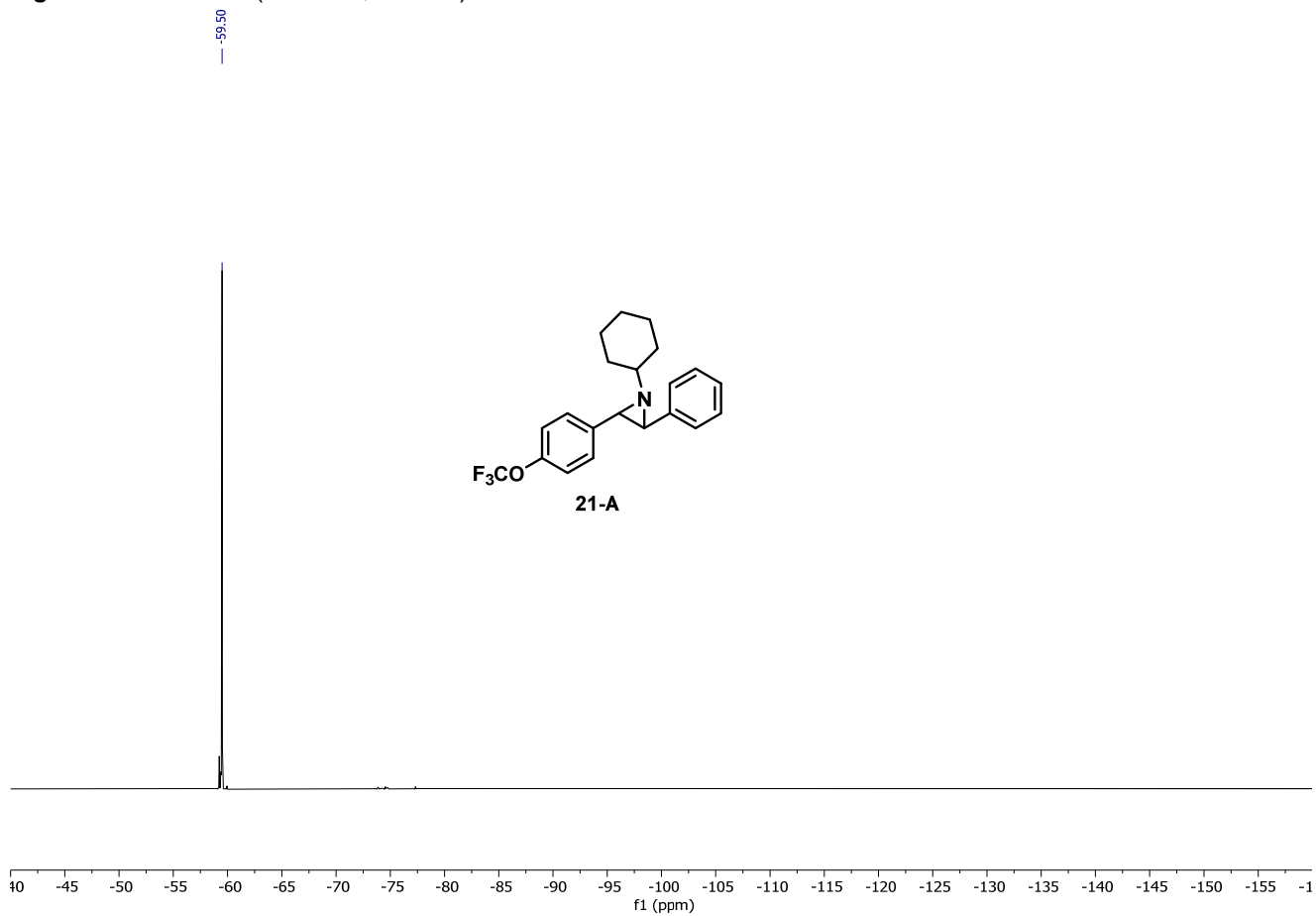


Figure S93. ¹H NMR (400 MHz, CD₃OD) of 22-A

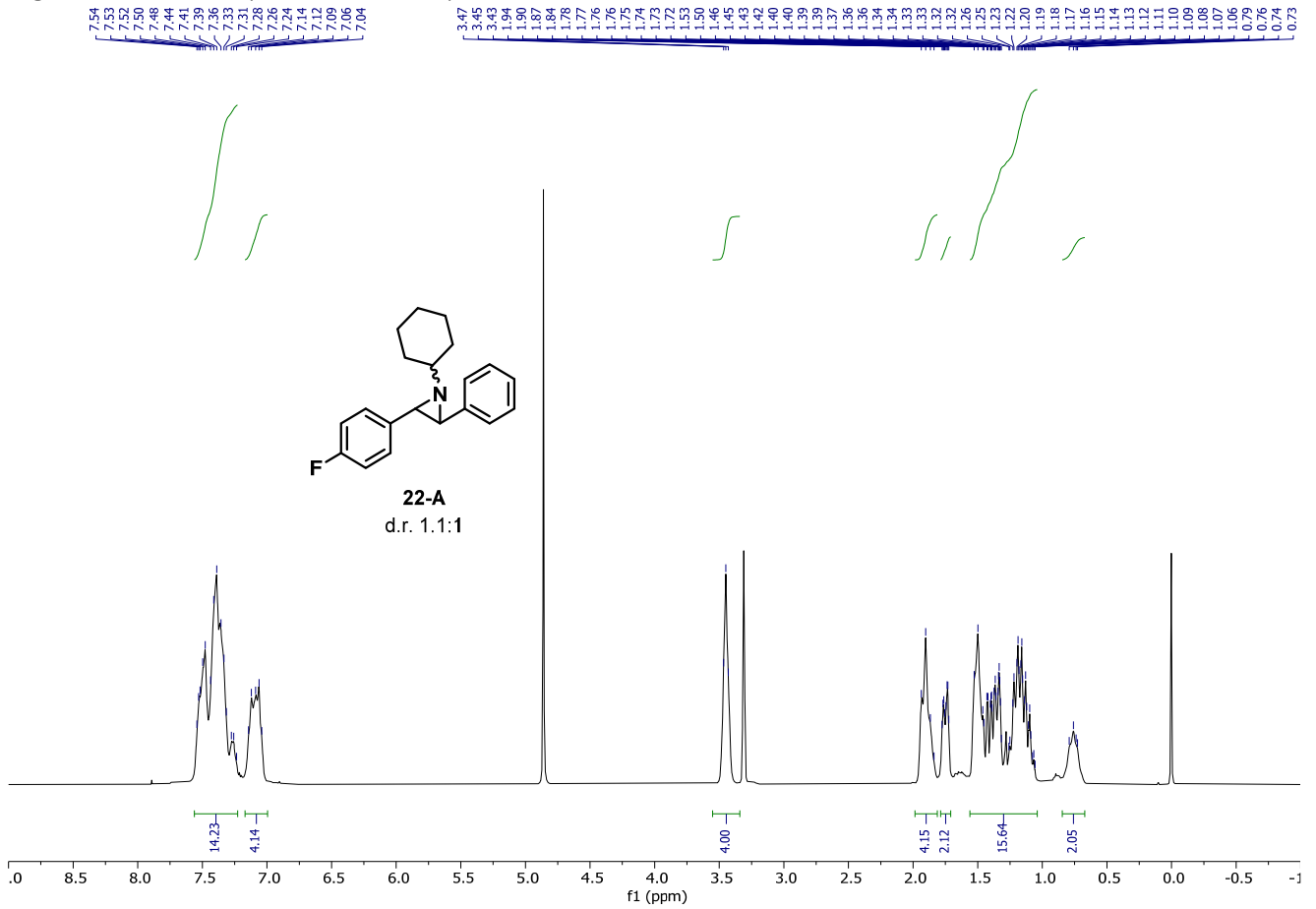


Figure S94. ¹³C NMR (101 MHz, CD₃OD) of 22-A

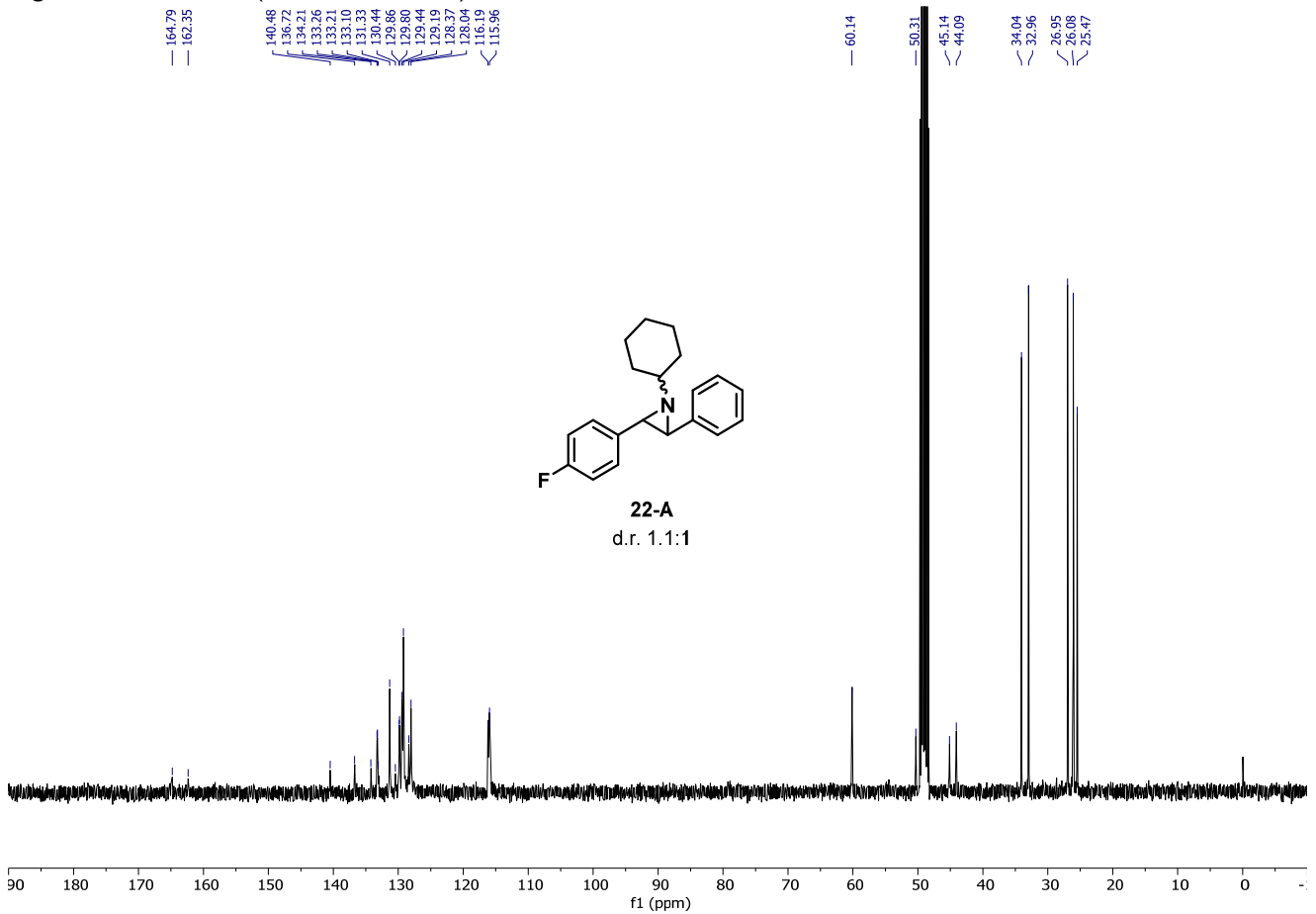


Figure S95. ^{19}F NMR (376 MHz, CD_3OD) of **22-A**

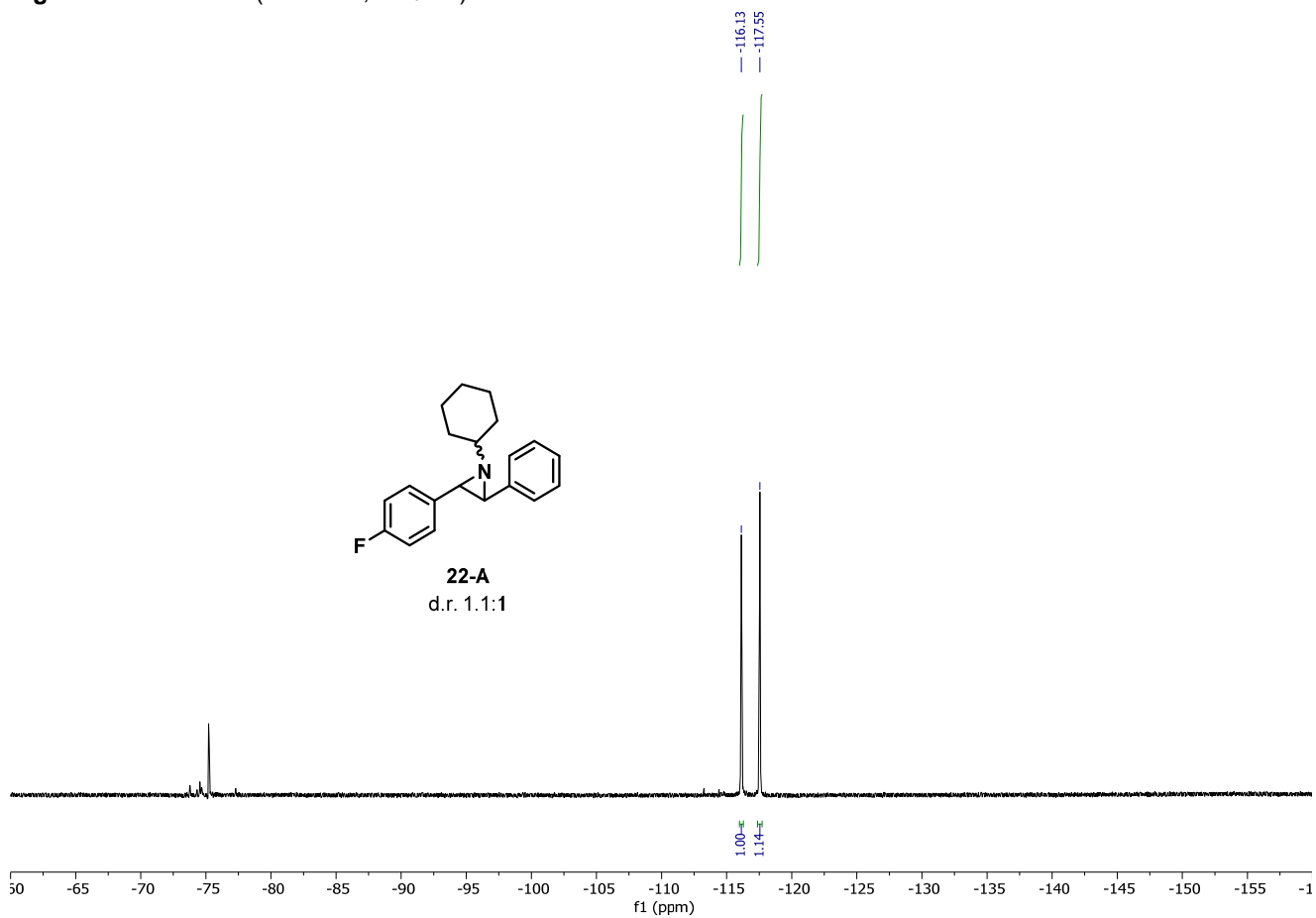


Figure S96. ¹H NMR (400 MHz, CD₃OD) of 23-A

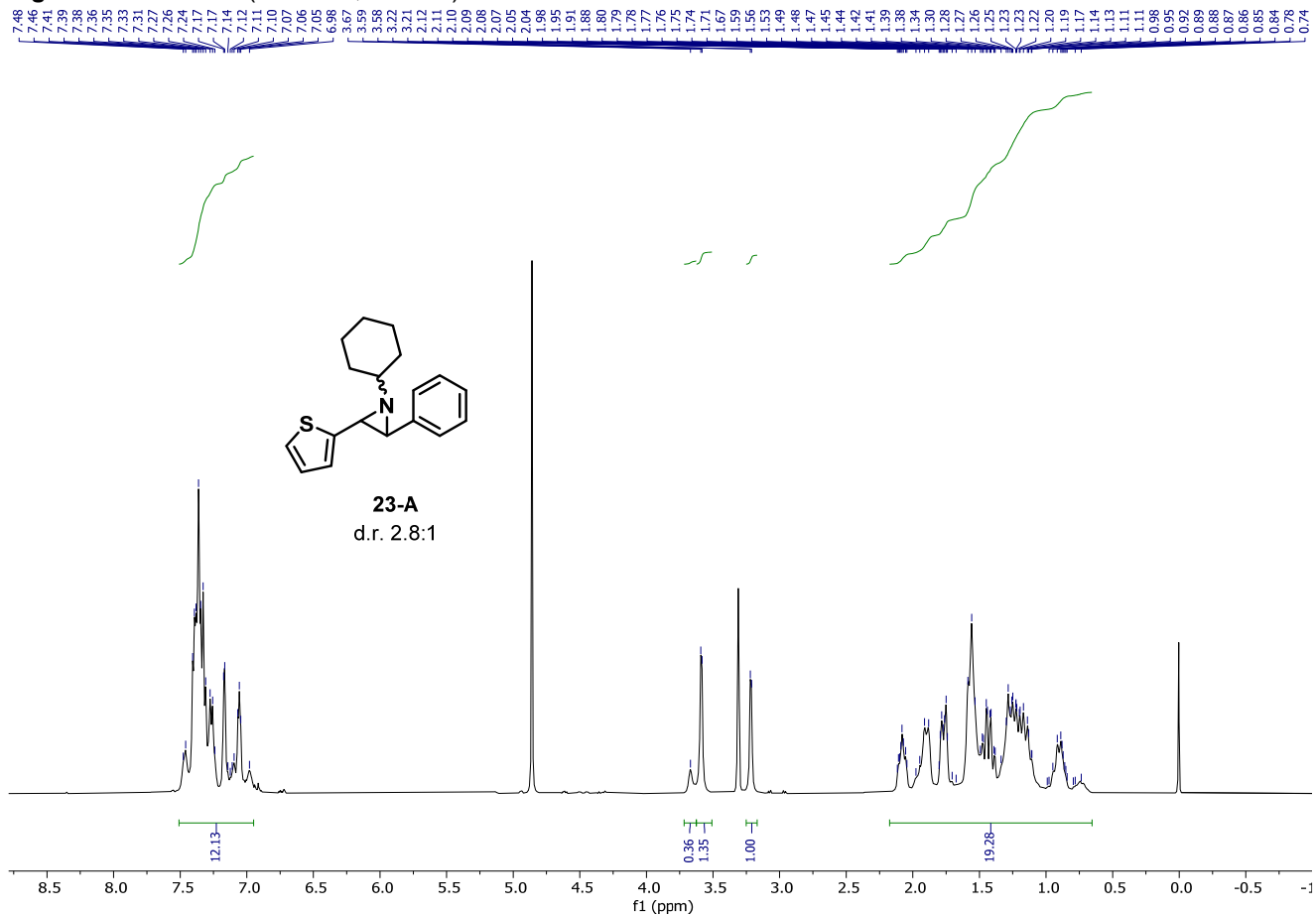


Figure S97. ¹³C NMR (101 MHz, CD₃OD) of 23-A

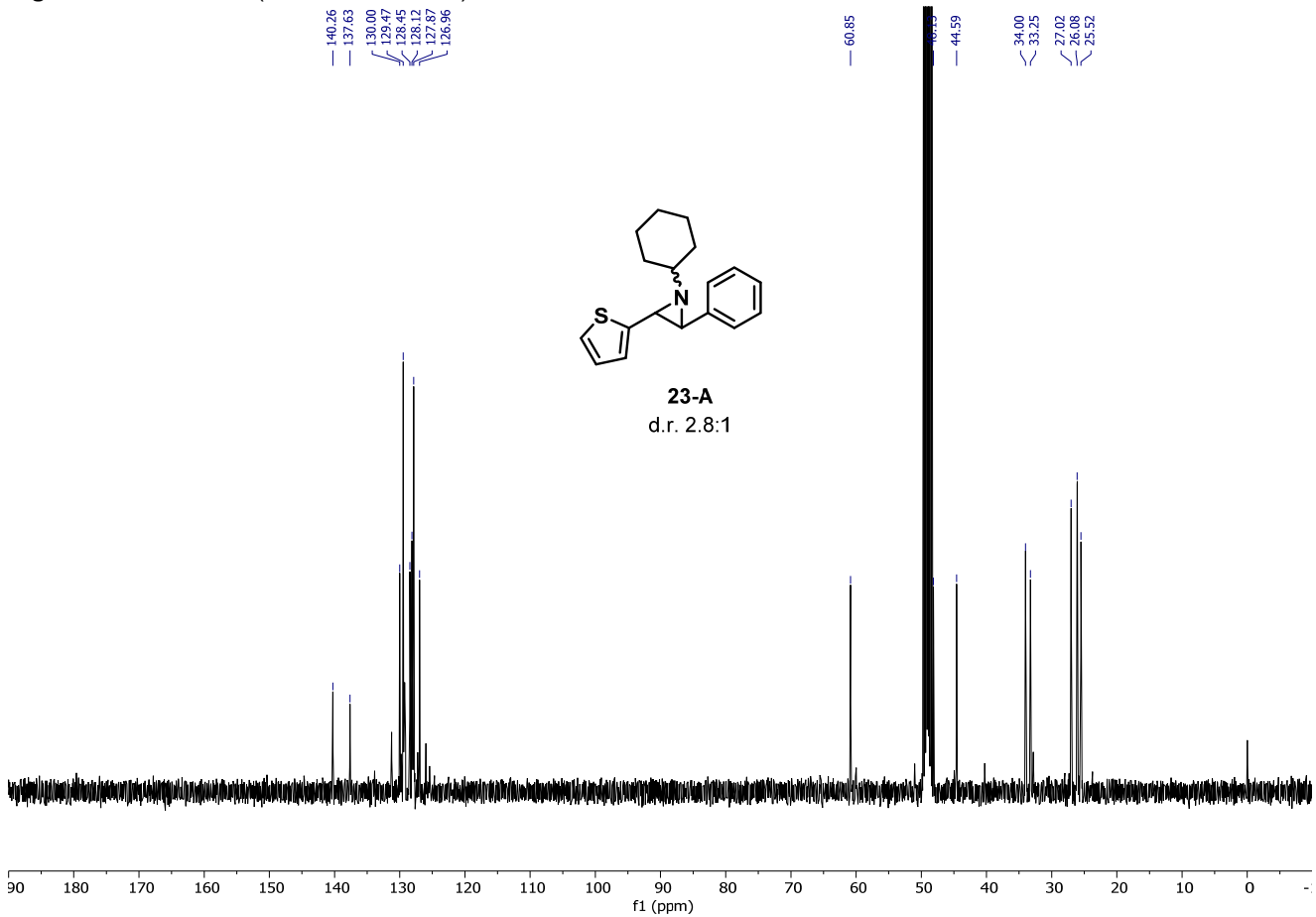


Figure S98. ¹H NMR (400 MHz, CD₃OD) of 24-A

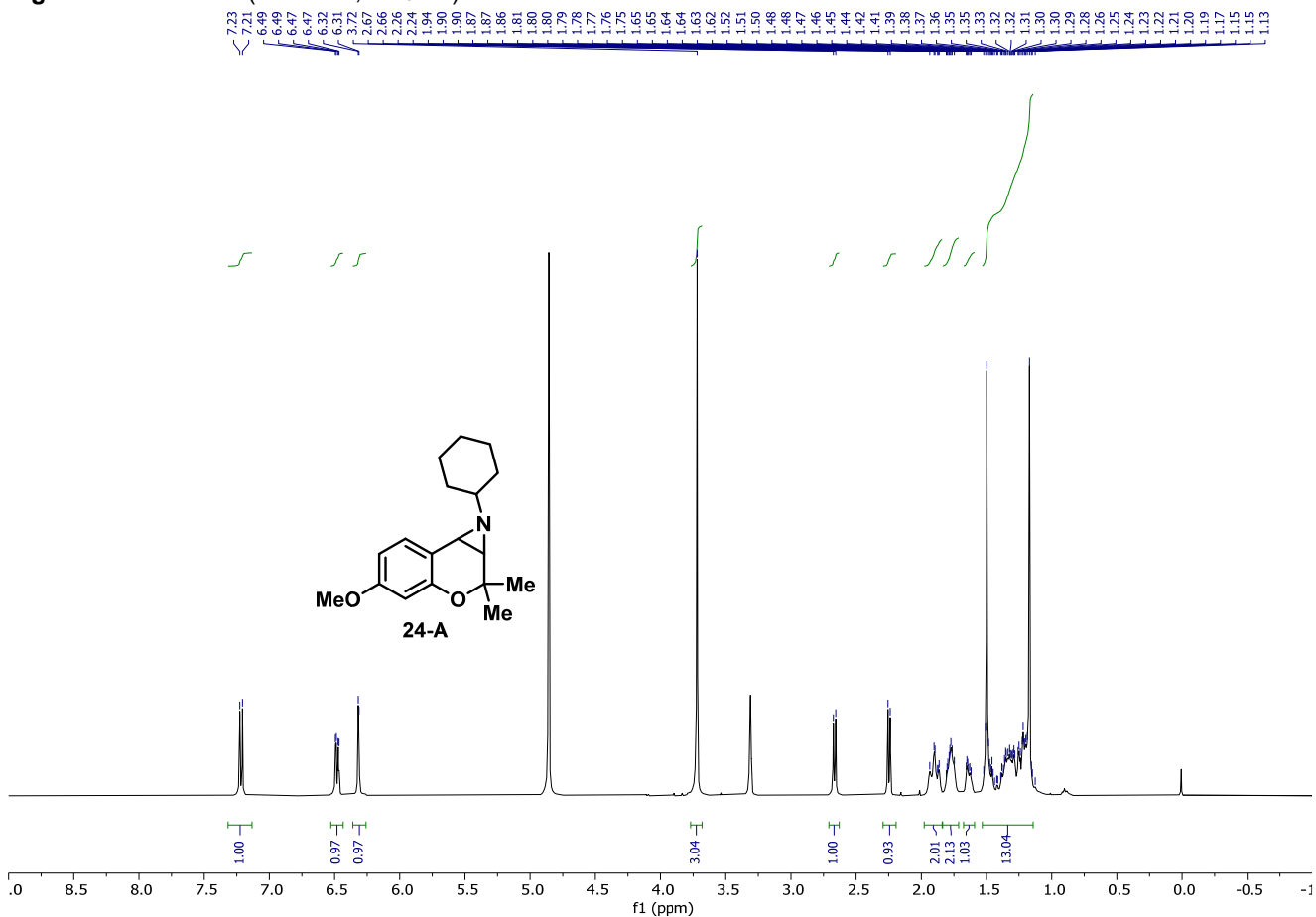


Figure S99. ¹³C NMR (101 MHz, CD₃OD) of 24-A

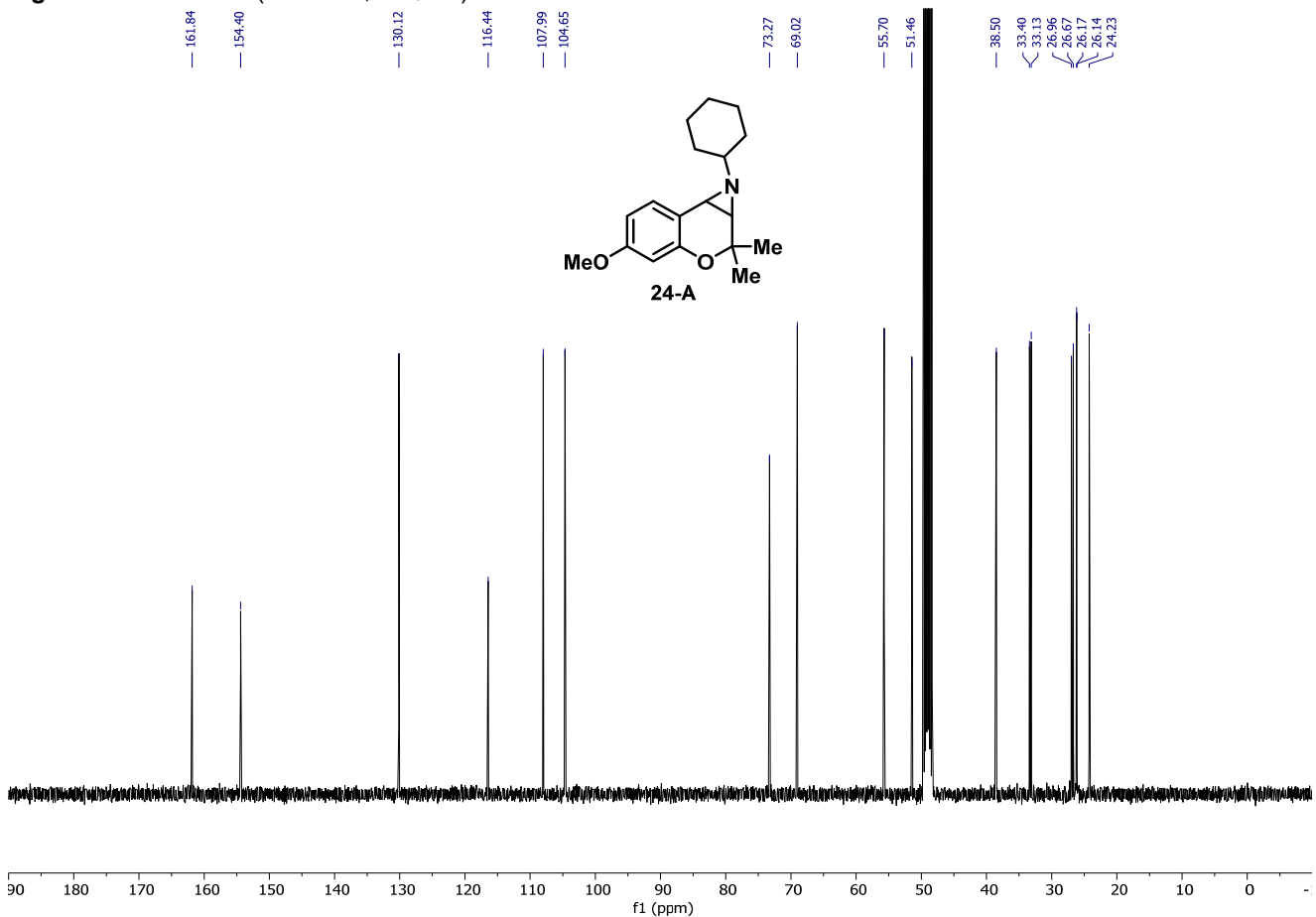


Figure S100. ¹H NMR (400 MHz, CD₃OD) of 25-A

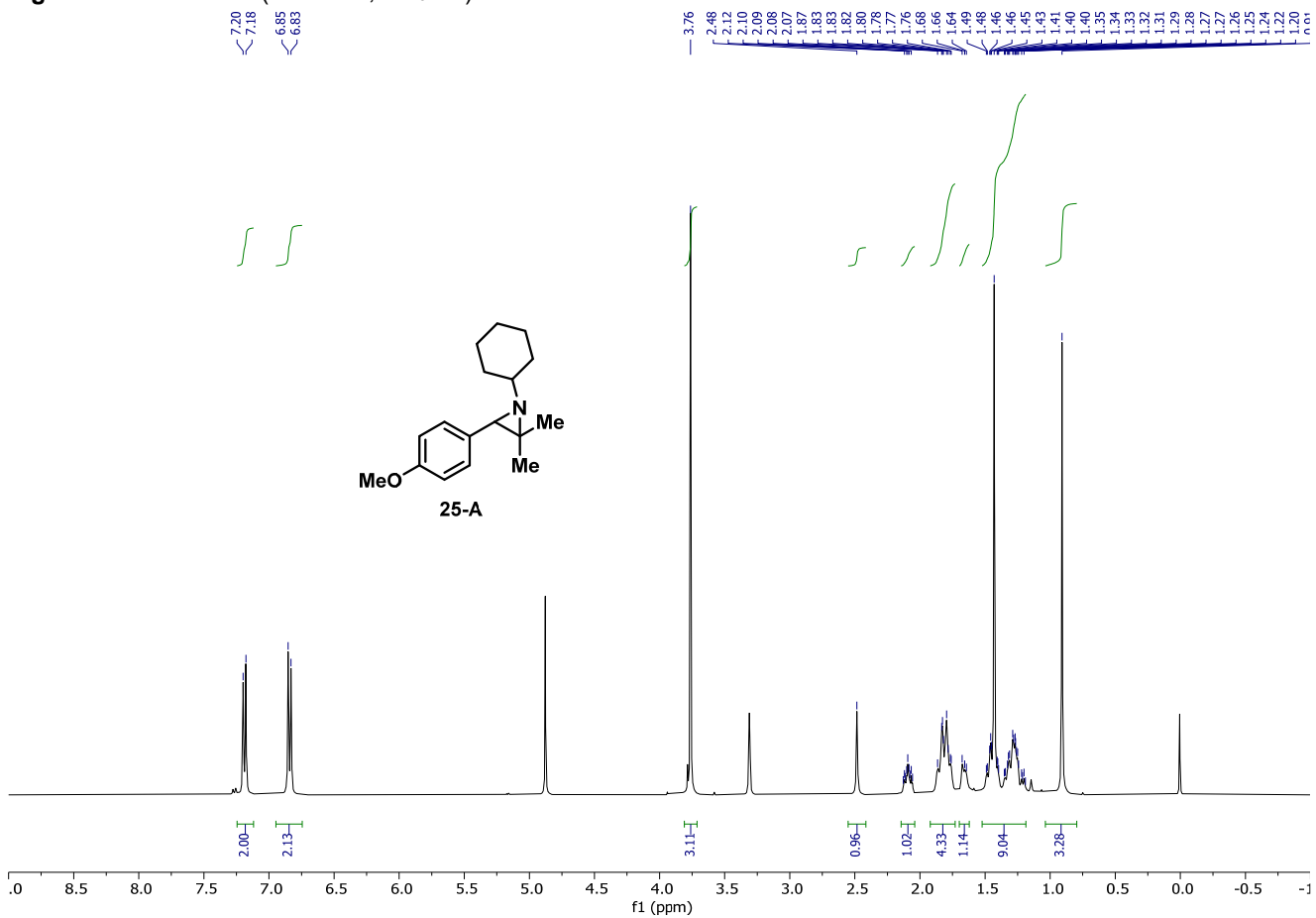


Figure S101. ¹³C NMR (101 MHz, CD₃OD) of 25-A

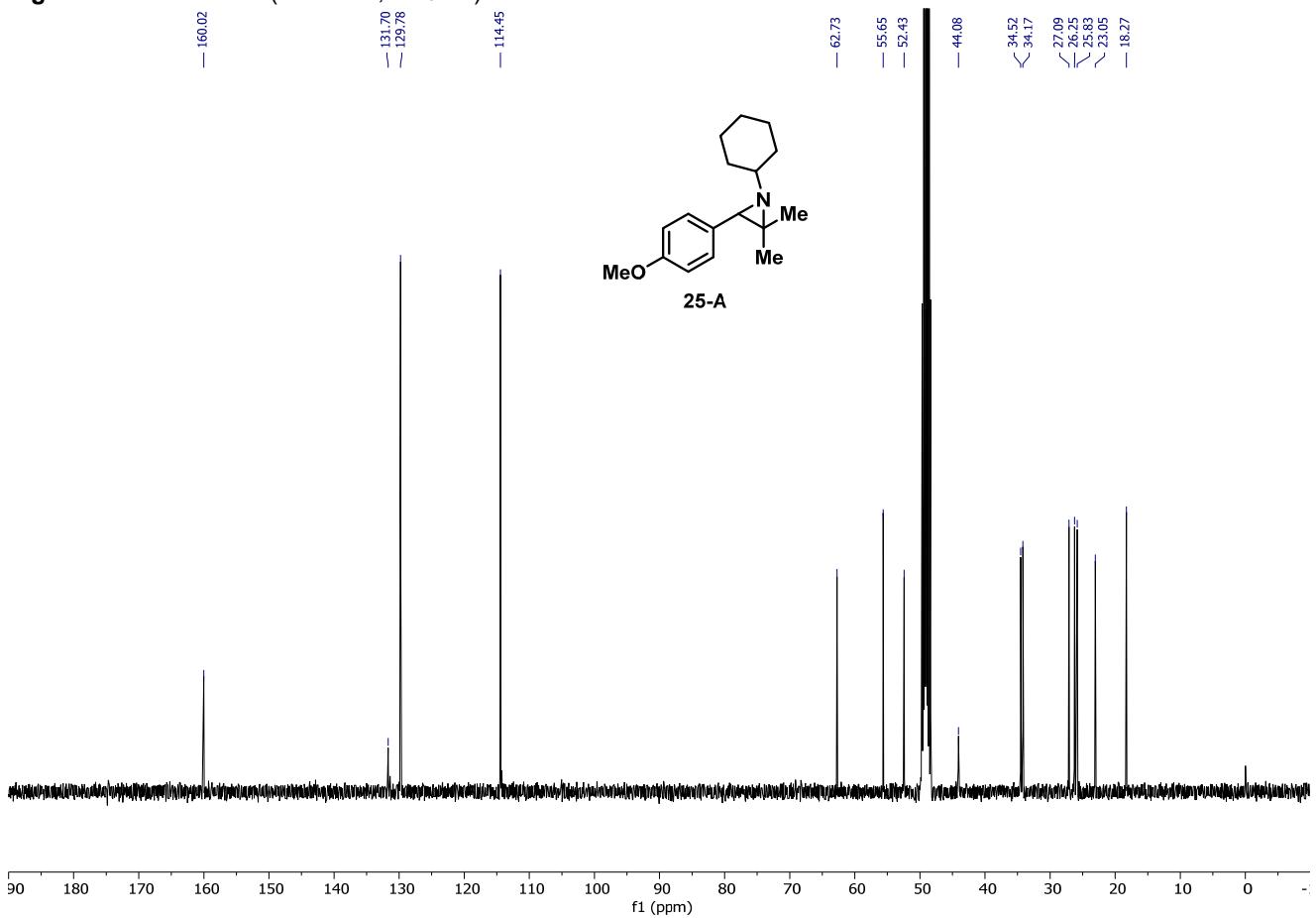


Figure S102. ¹H NMR (400 MHz, CD₃OD) of 26-A

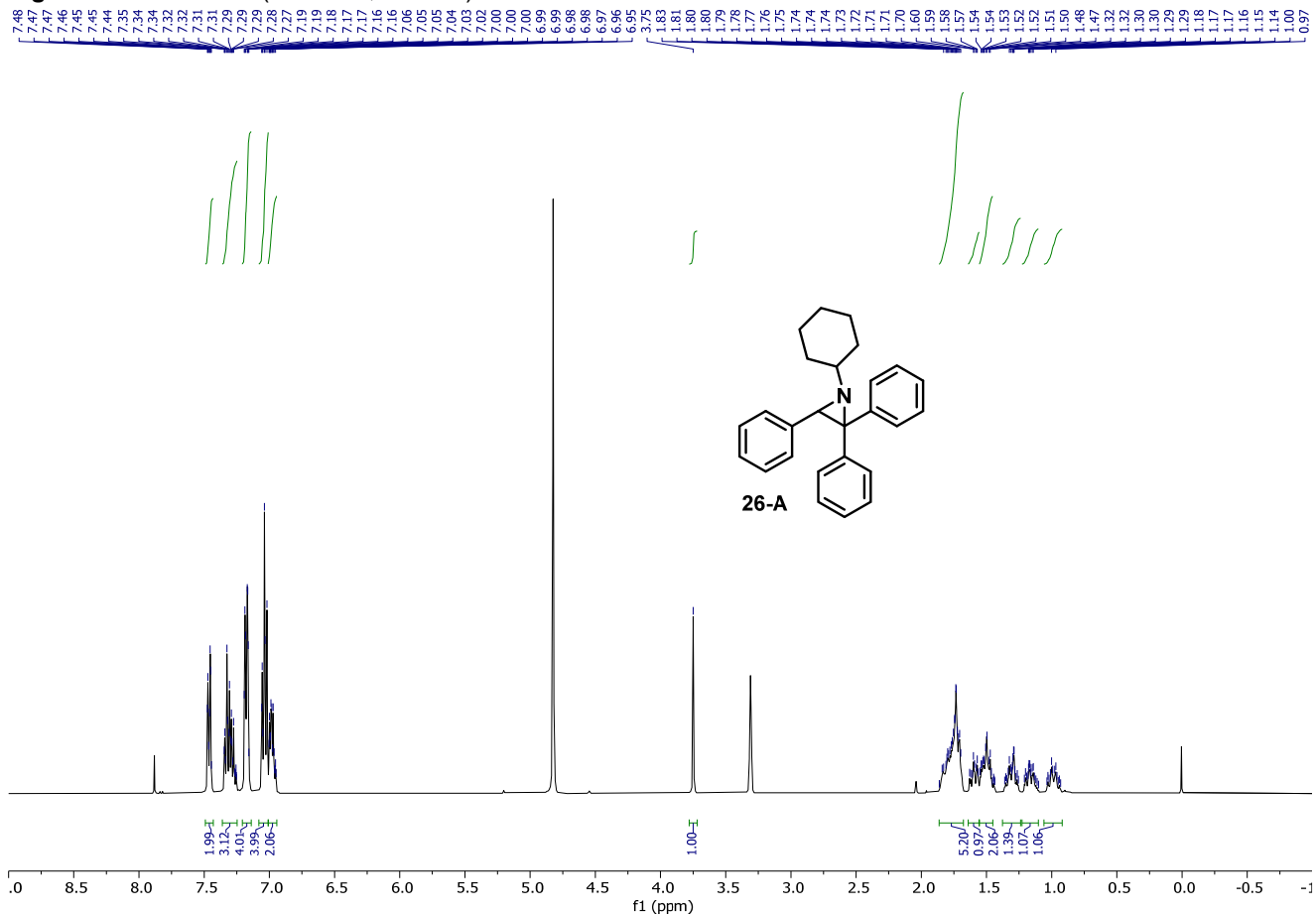


Figure S103. ¹³C NMR (101 MHz, CD₃OD) of 26-A

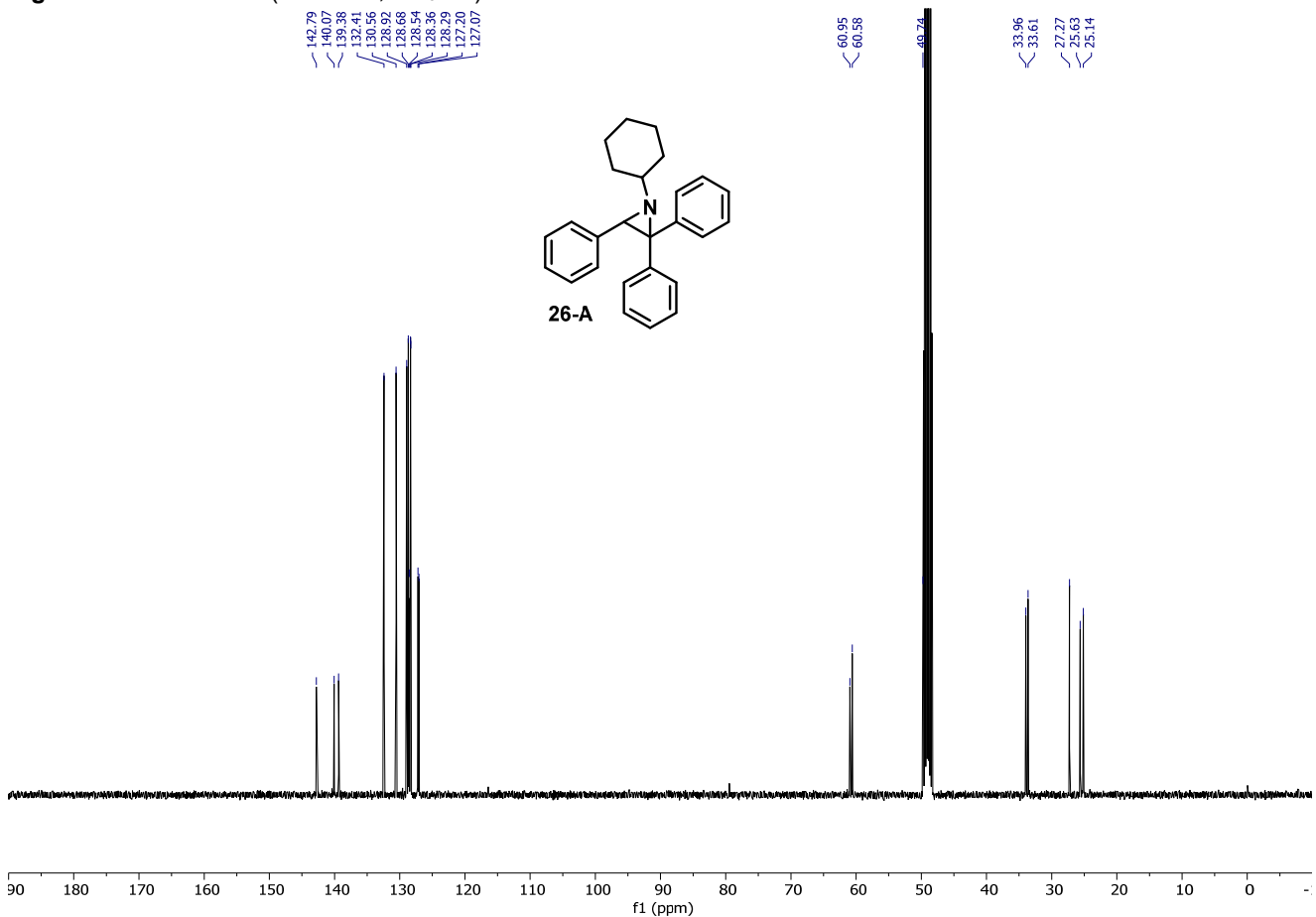


Figure S104. ¹H NMR (400 MHz, CD₃Cl) of 27-A

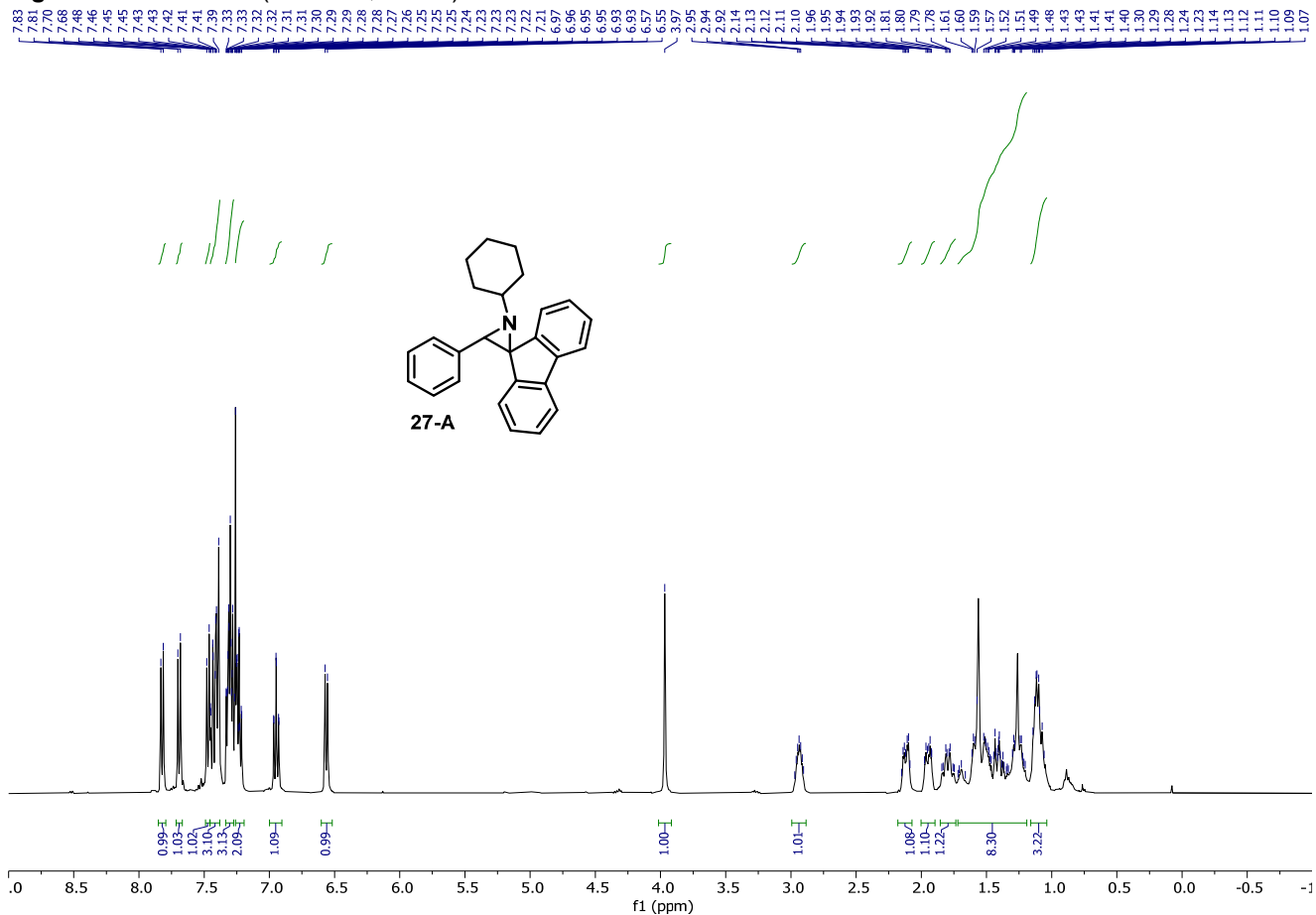


Figure S105. ¹³C NMR (101 MHz, CD₃Cl) of 27-A

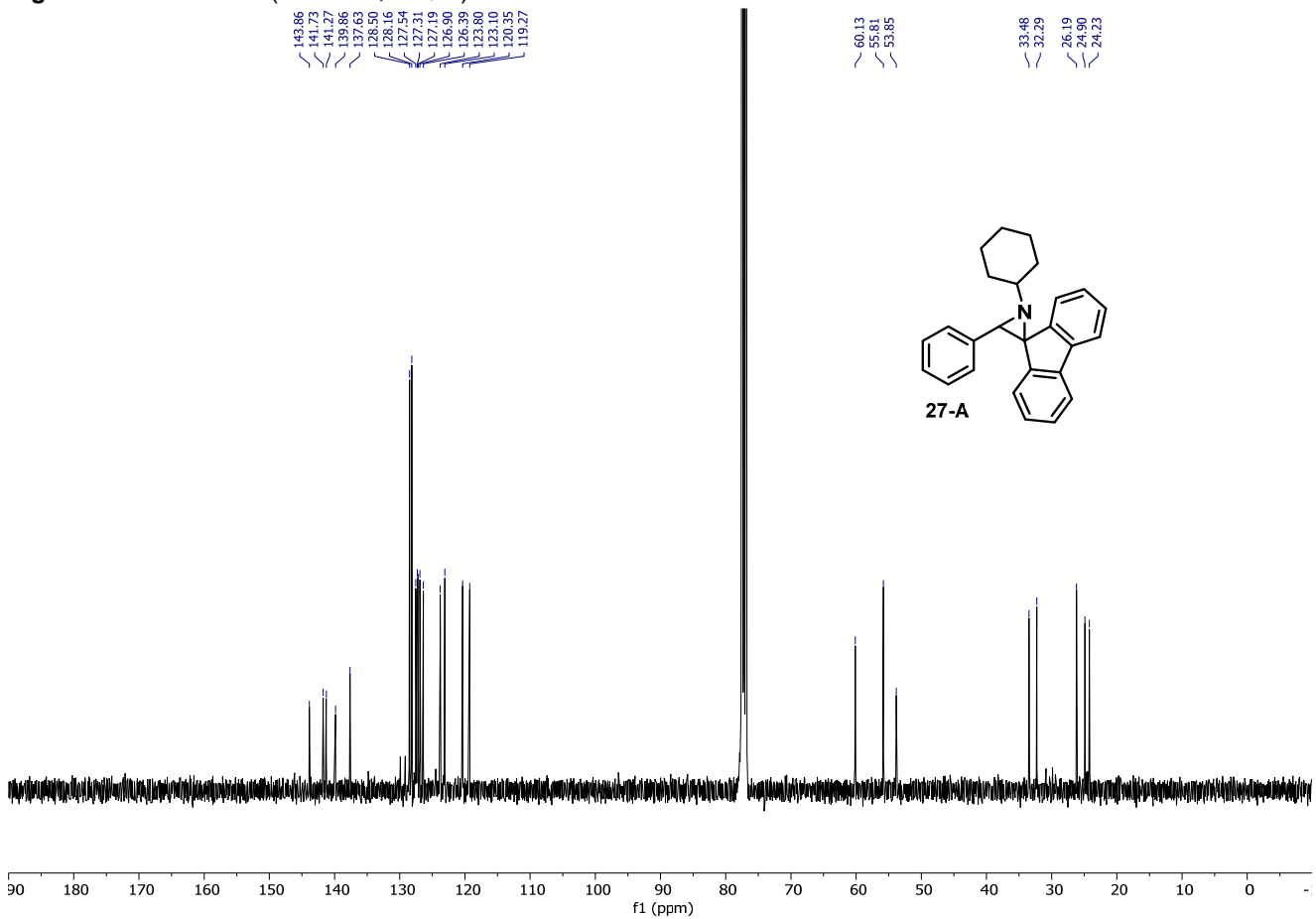


Figure S106. ¹H NMR (400 MHz, CD₃OD) of 28-A

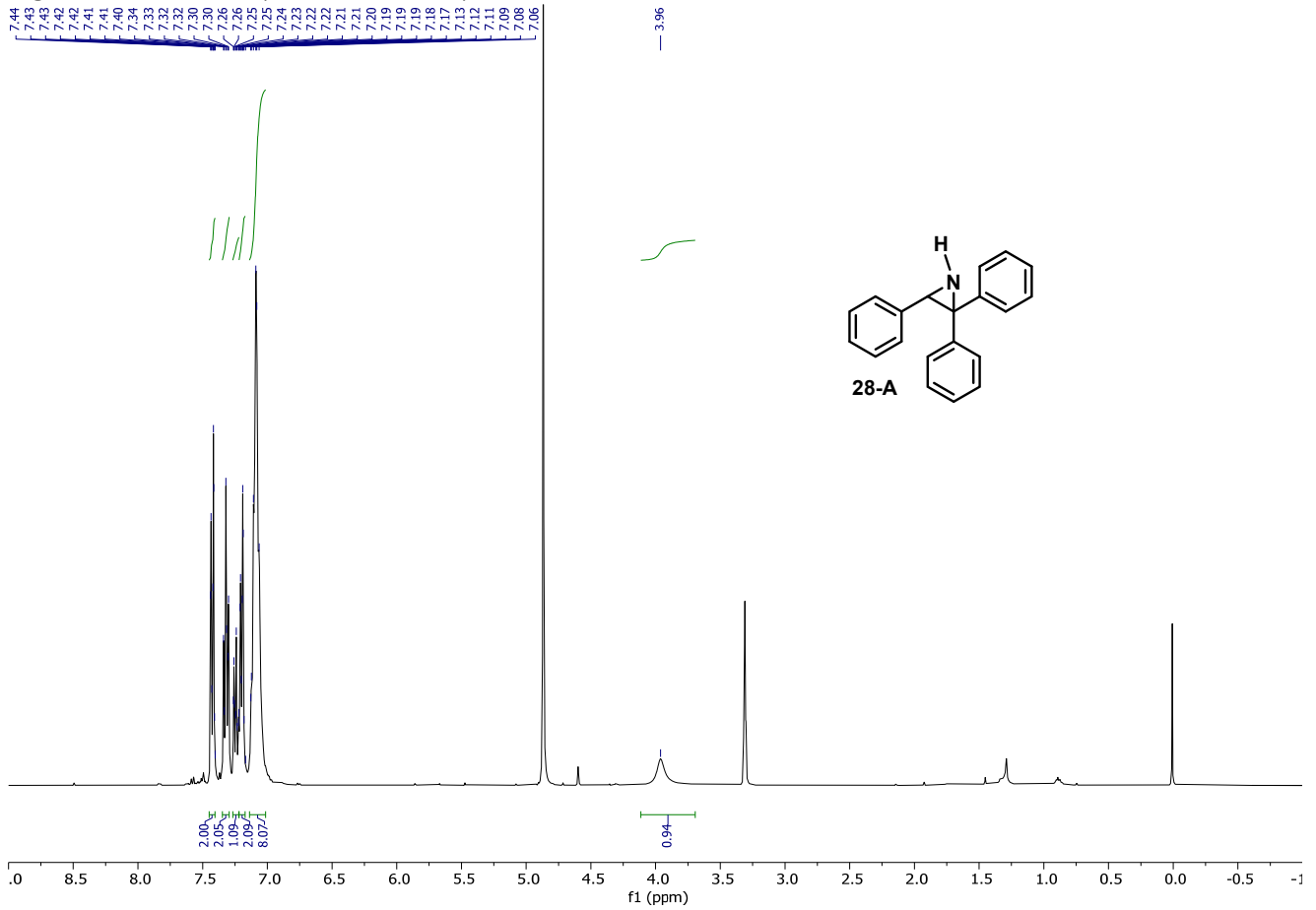


Figure S107. ¹³C NMR (101 MHz, CD₃OD) of 28-A

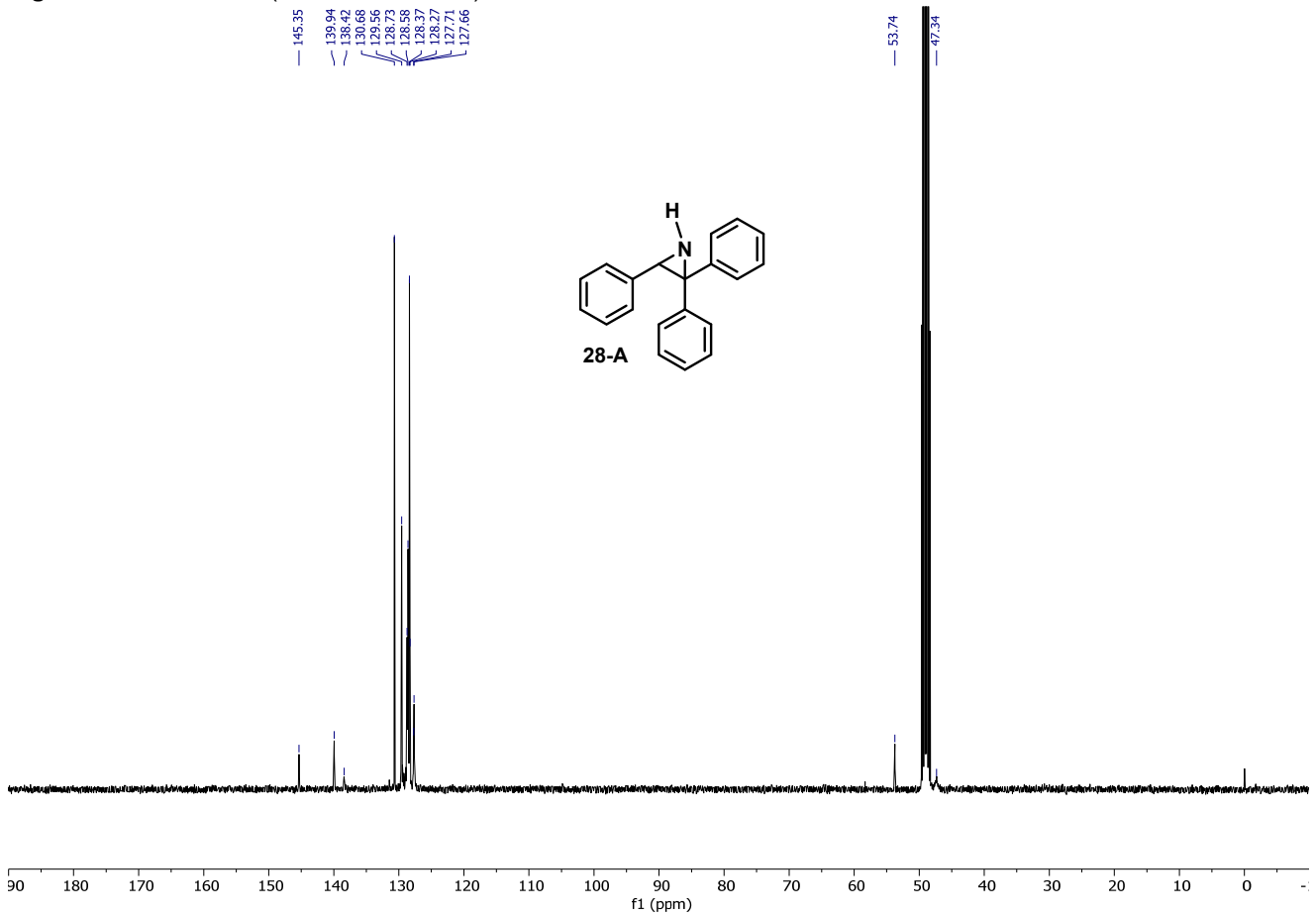


Figure S108. ¹H NMR (400 MHz, CD₃OD) of 4-C

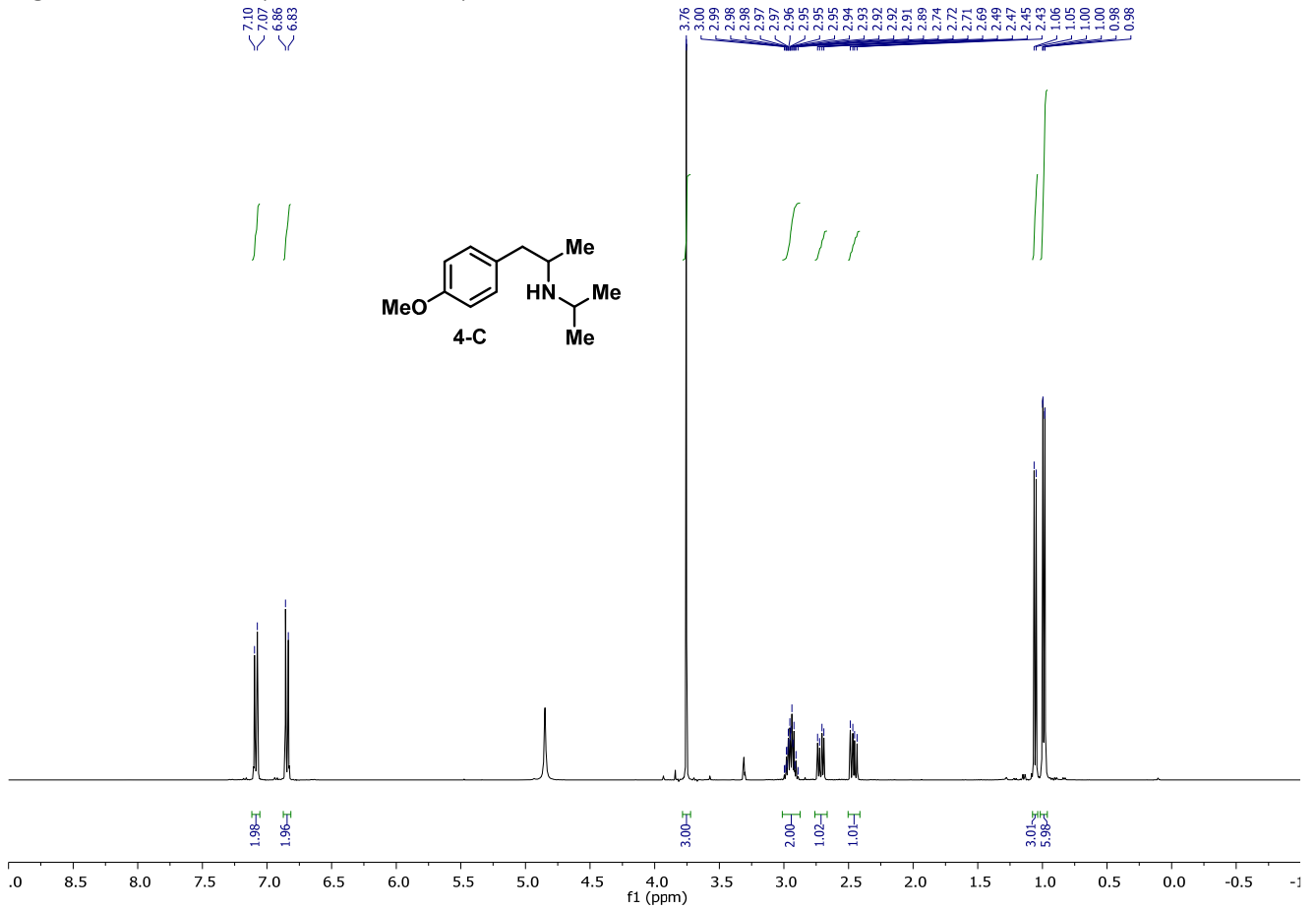


Figure S109. ¹³C NMR (101 MHz, CD₃OD) of 4-C

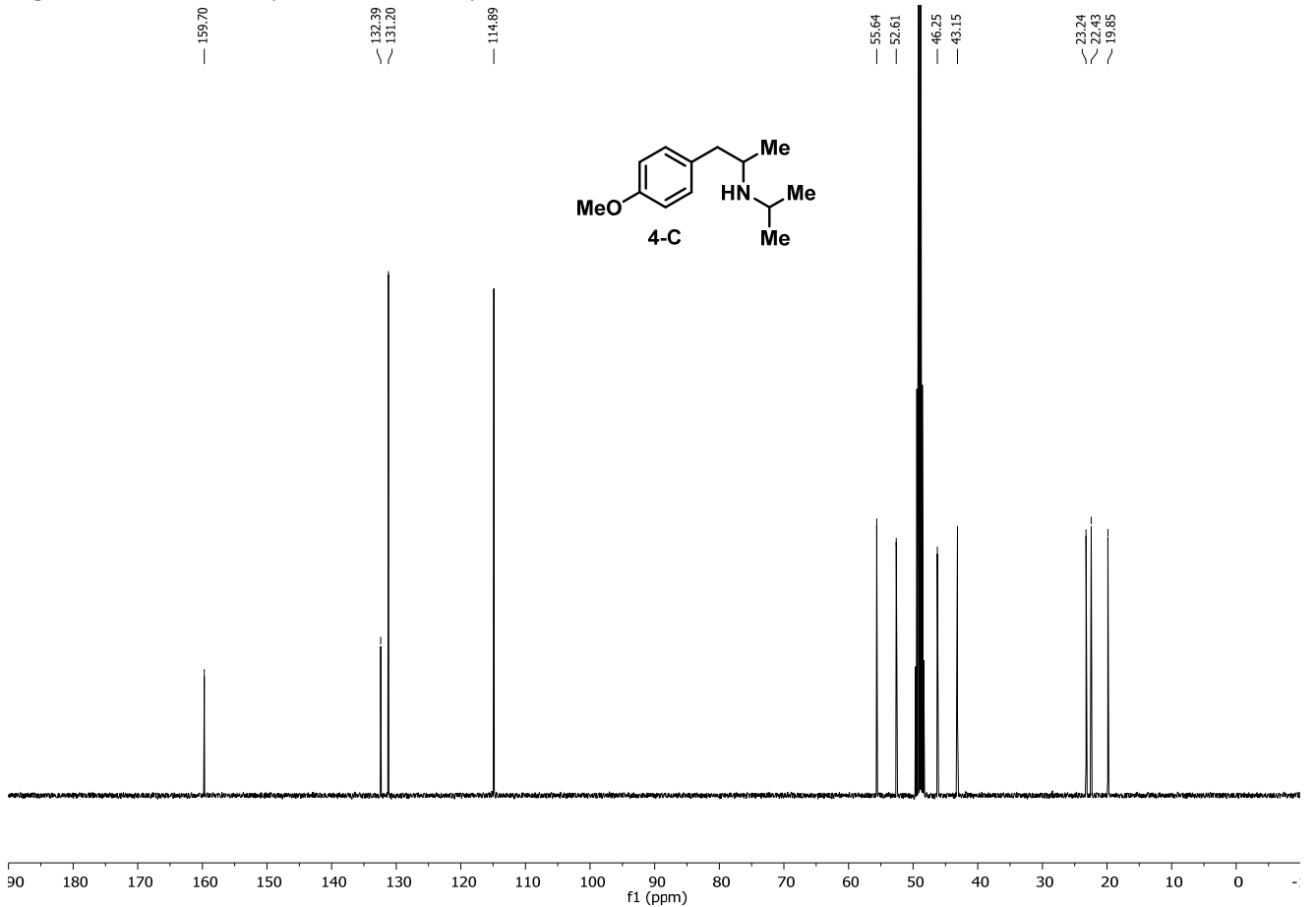


Figure S110. ¹H NMR (400 MHz, CD₃OD) of 9-C

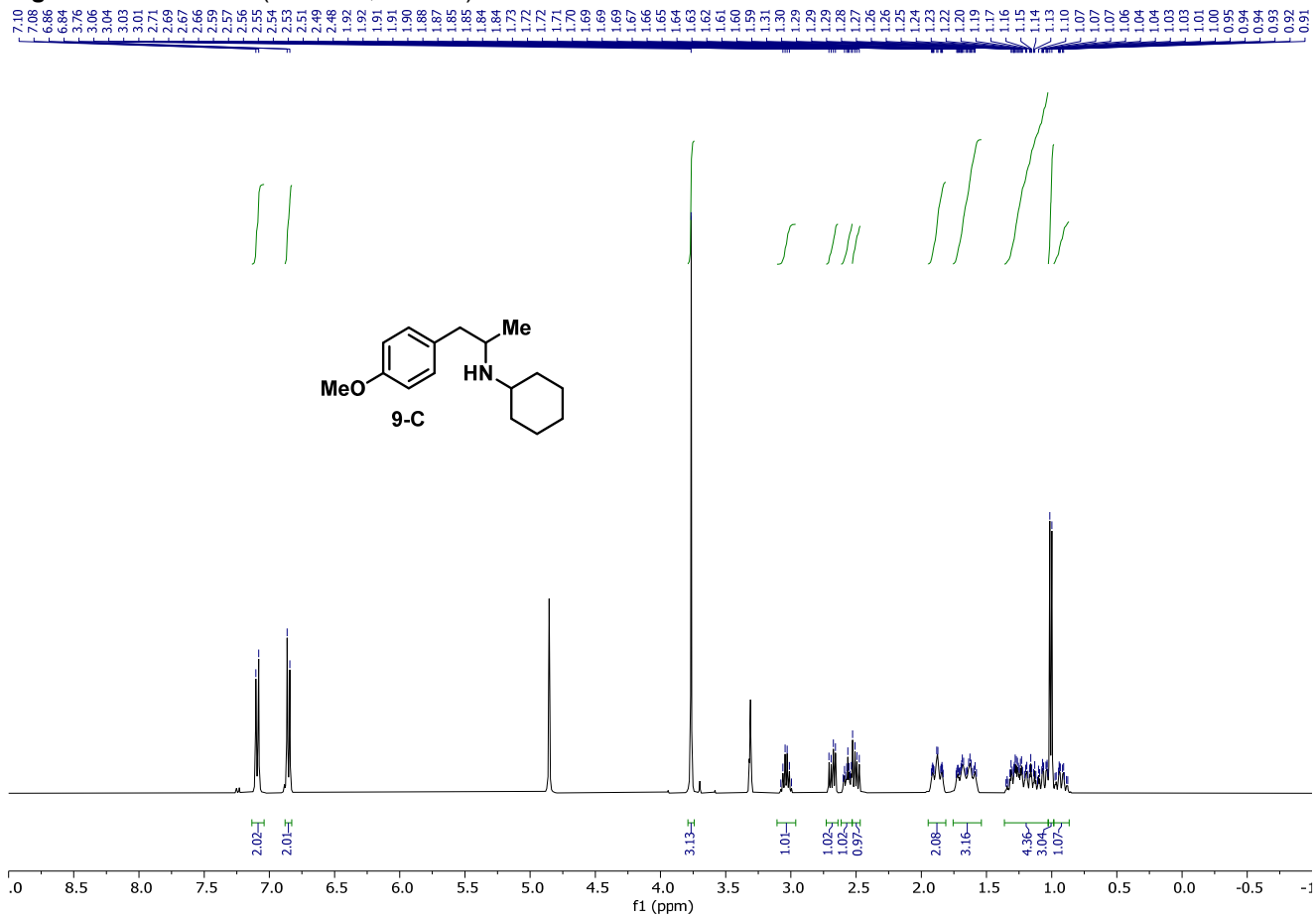


Figure S112. ¹³C NMR (101 MHz, CD₃OD) of 9-C

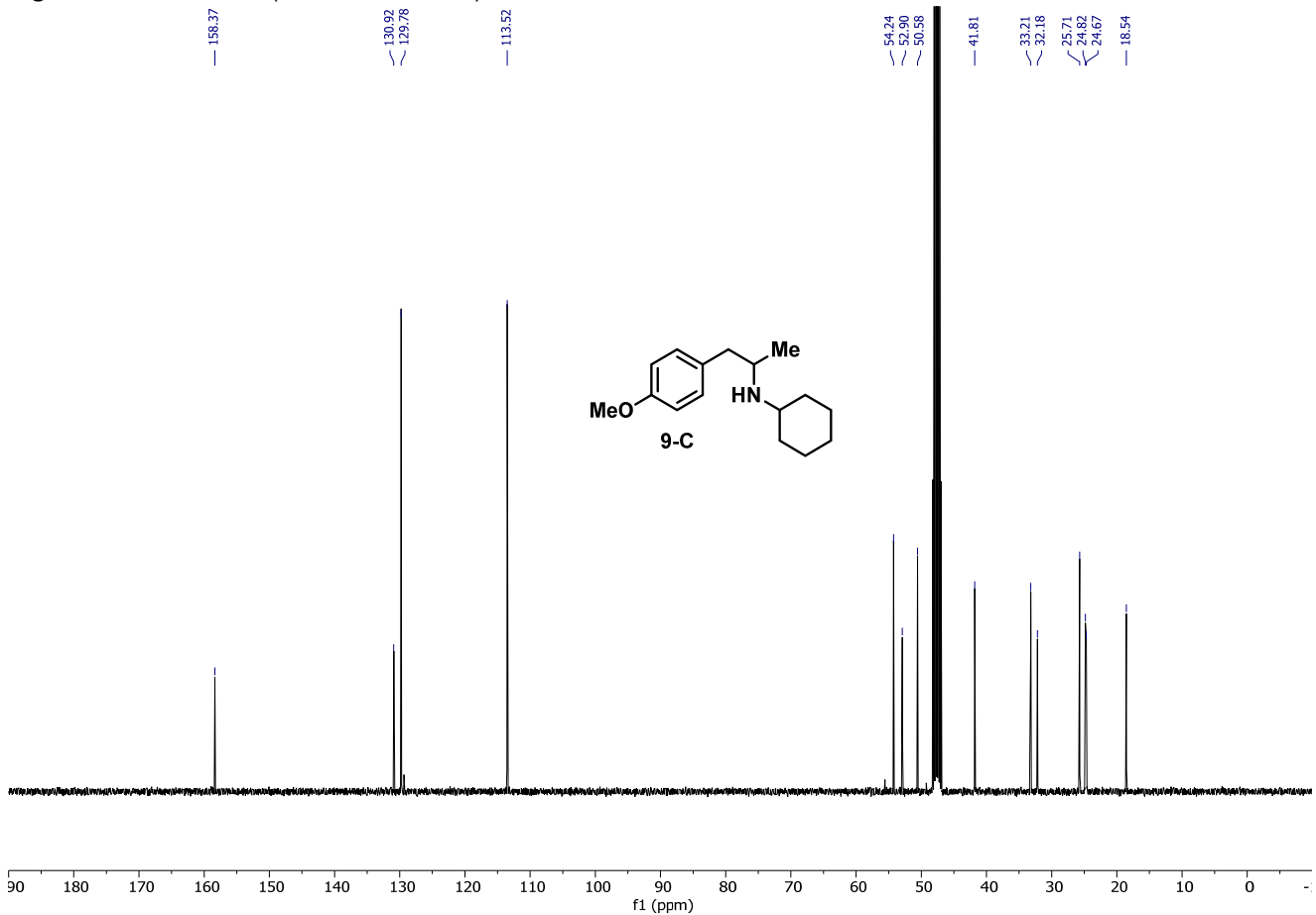


Figure S113. ¹H NMR (400 MHz, CD₃OD) of 11-C

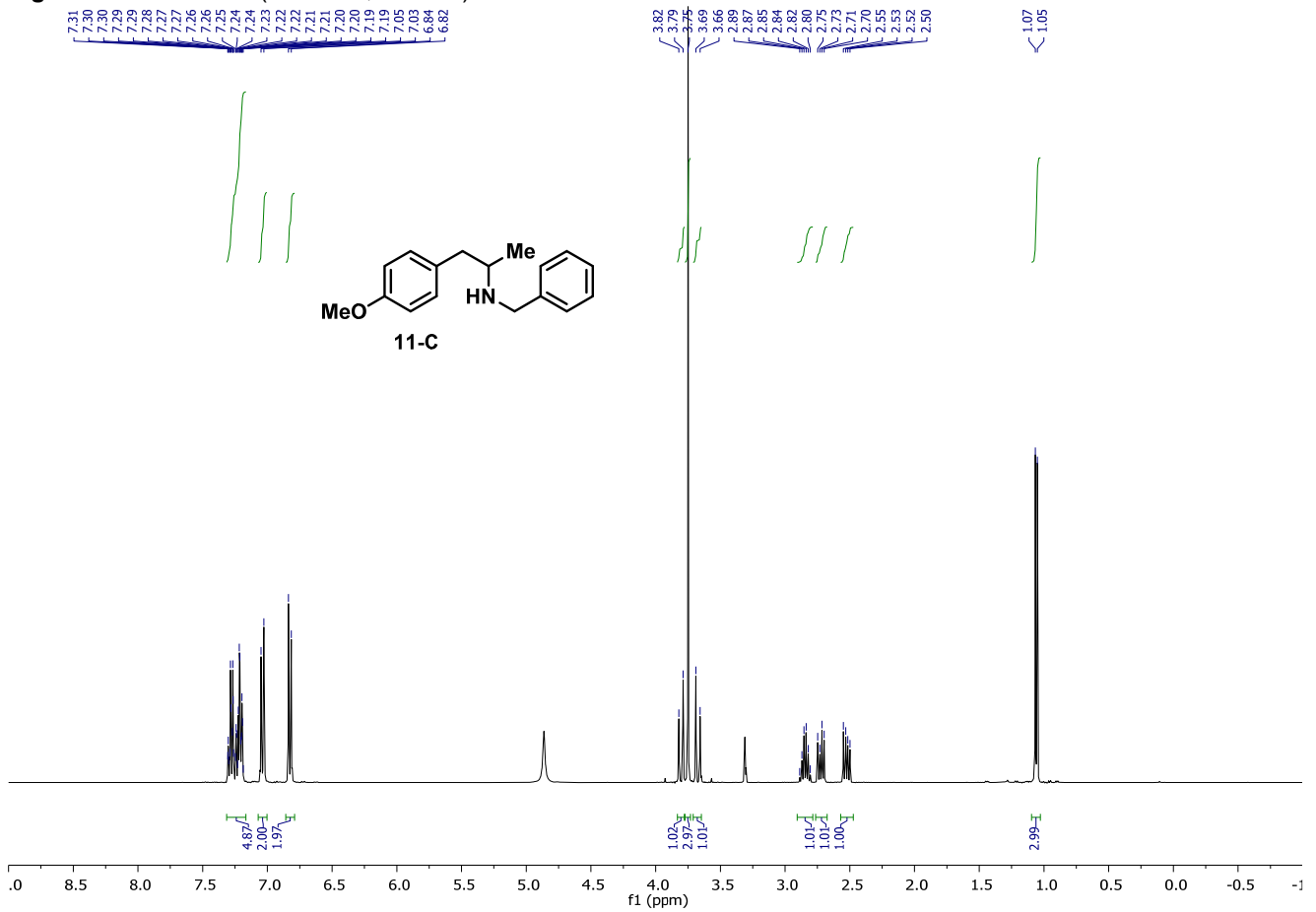


Figure S114. ¹³C NMR (101 MHz, CD₃OD) of 11-C

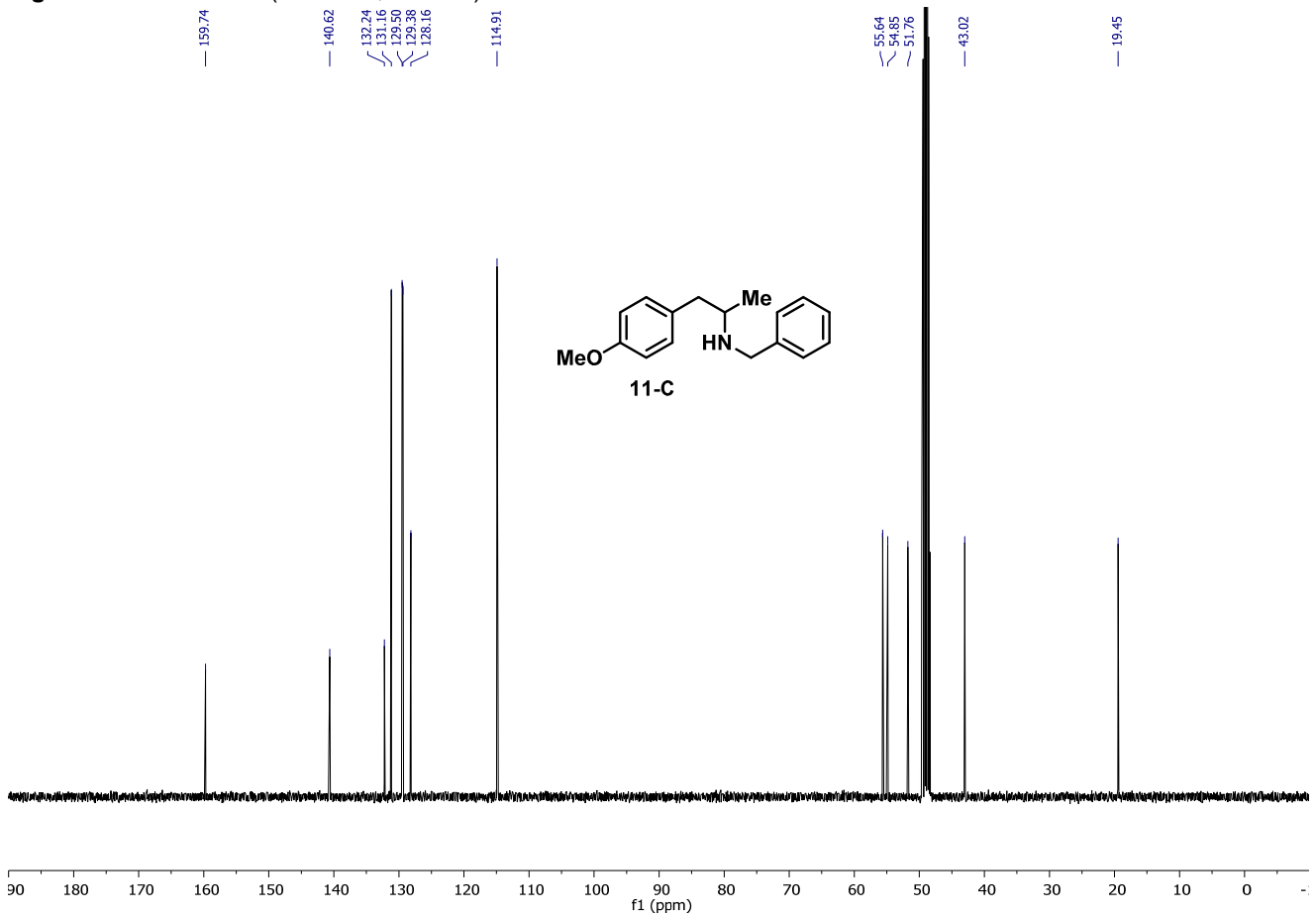


Figure S115. ¹H NMR (400 MHz, CD₃OD) of 29-C

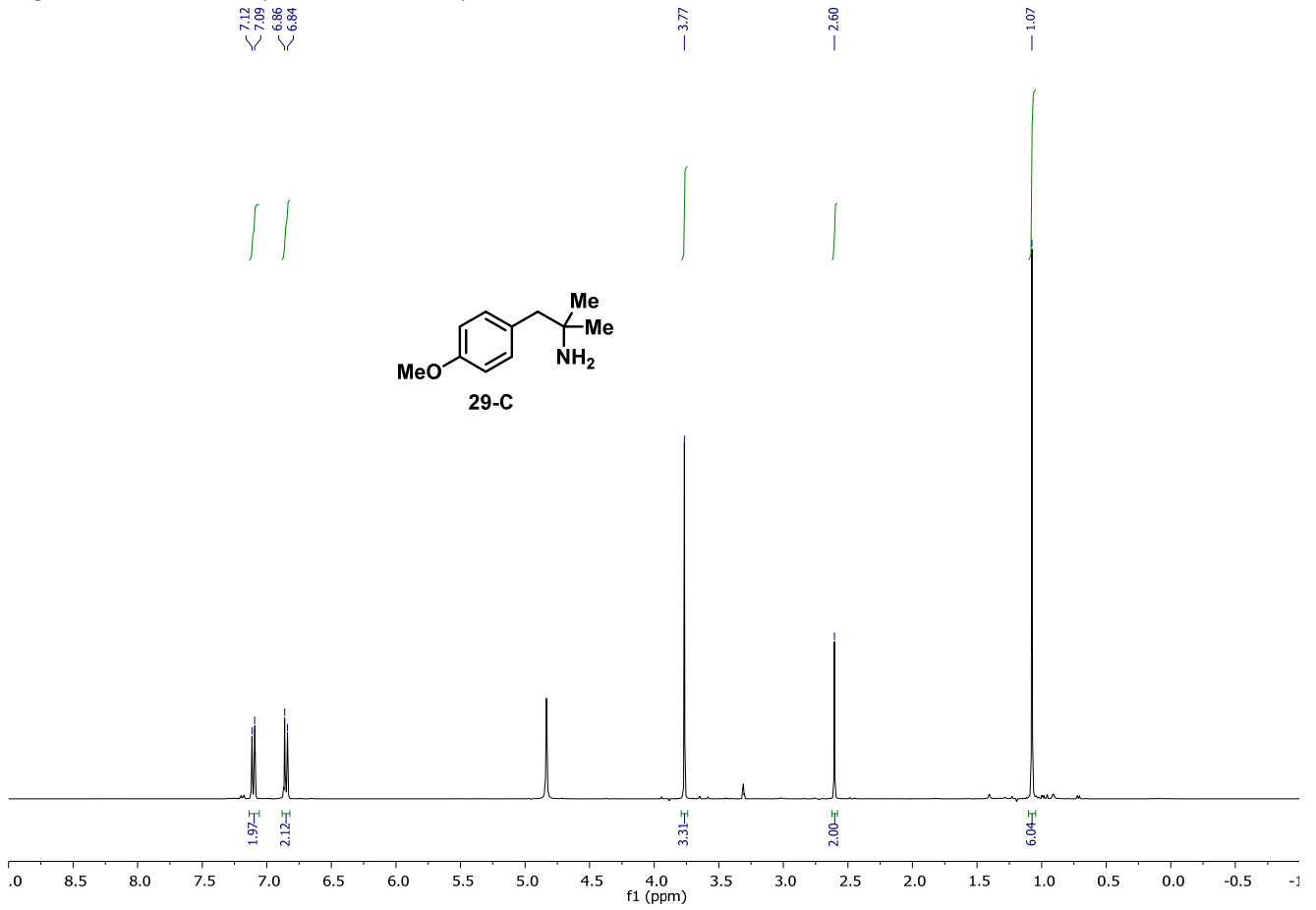


Figure S116. ¹³C NMR (101 MHz, CD₃OD) of 29-C

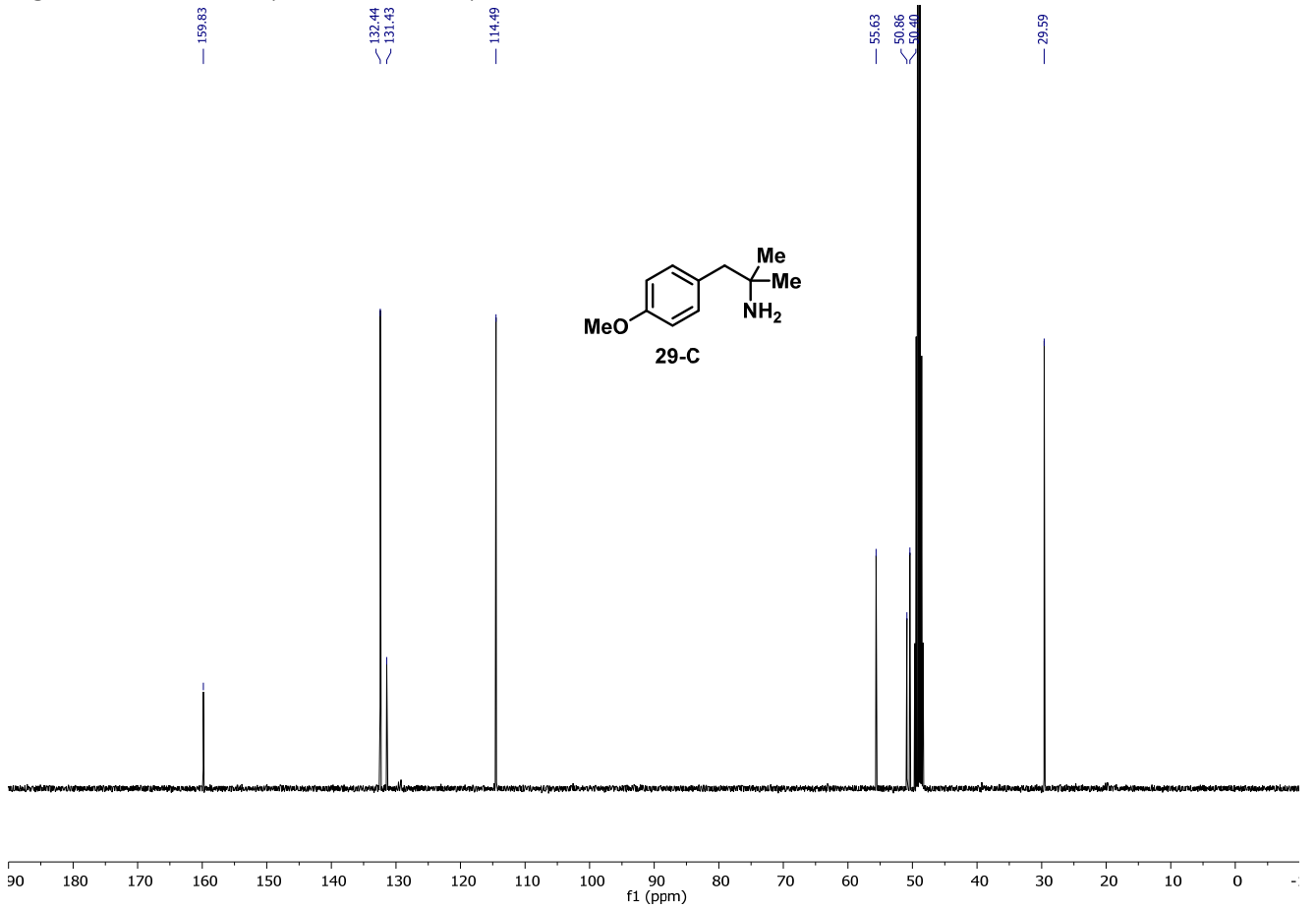


Figure S117. ¹H NMR (400 MHz, CD₃OD) of 31-C

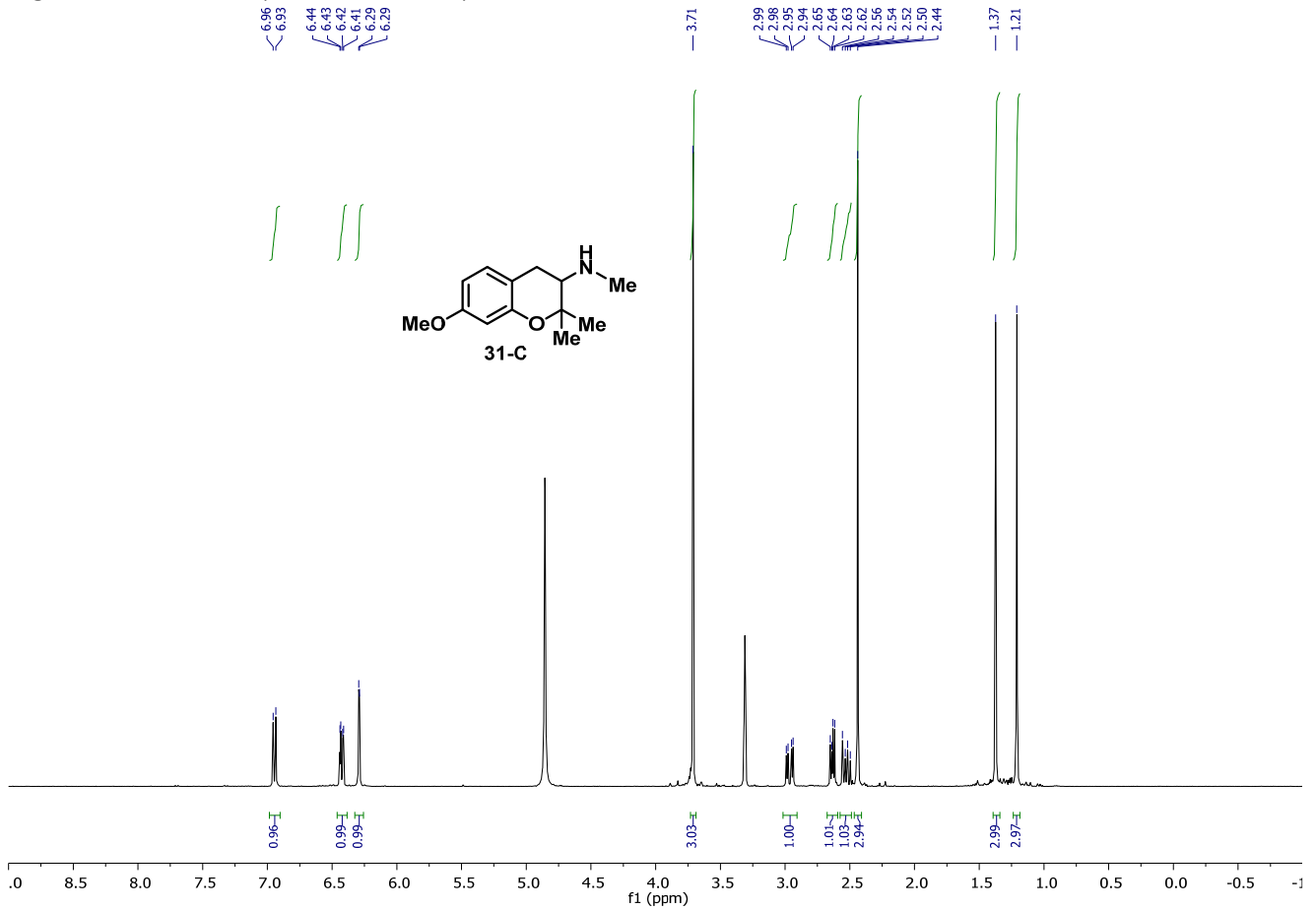


Figure S118. ¹³C NMR (101 MHz, CD₃OD) of 31-C

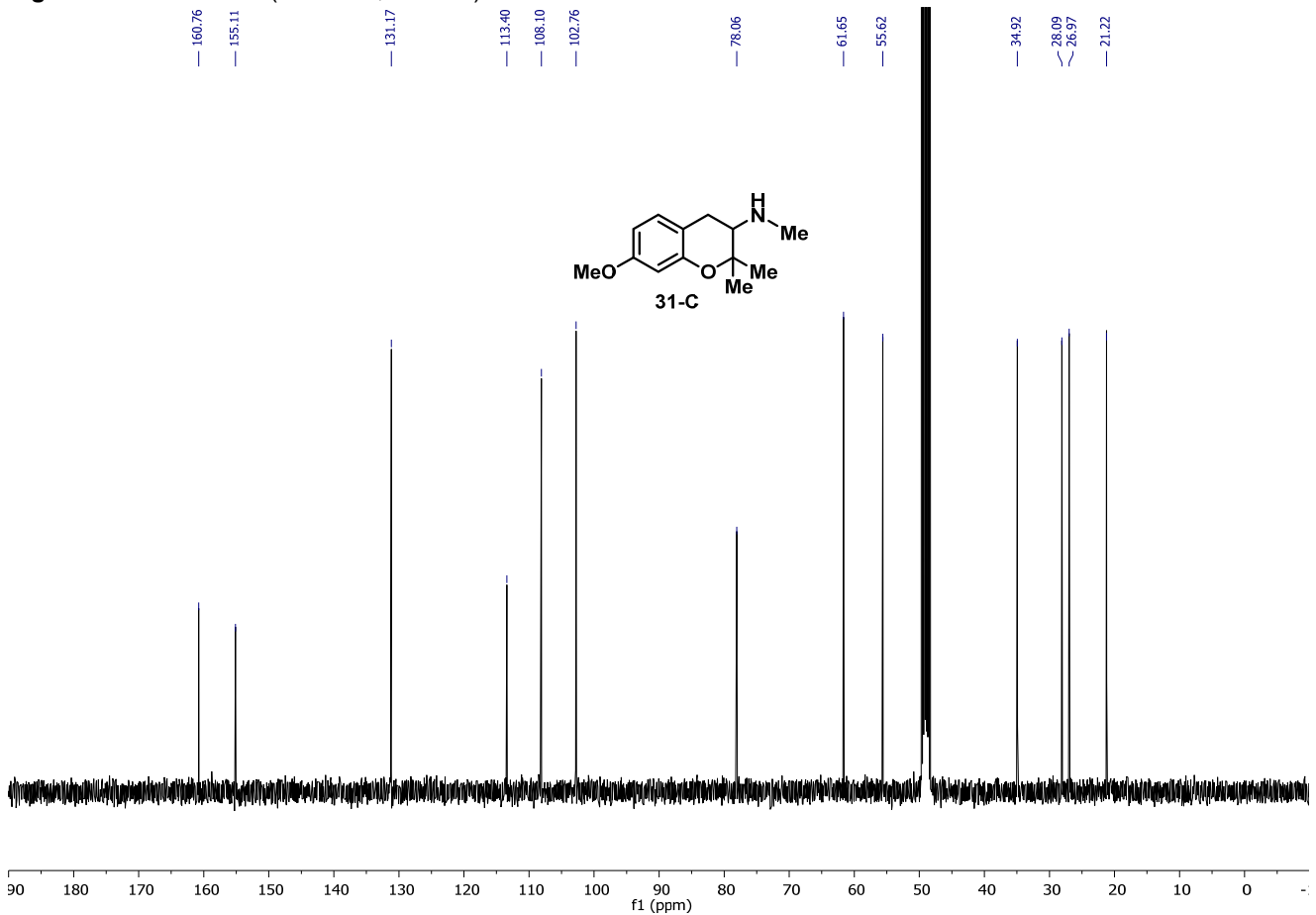


Figure S119. ¹H NMR (400 MHz, CD₃OD) of 24-C

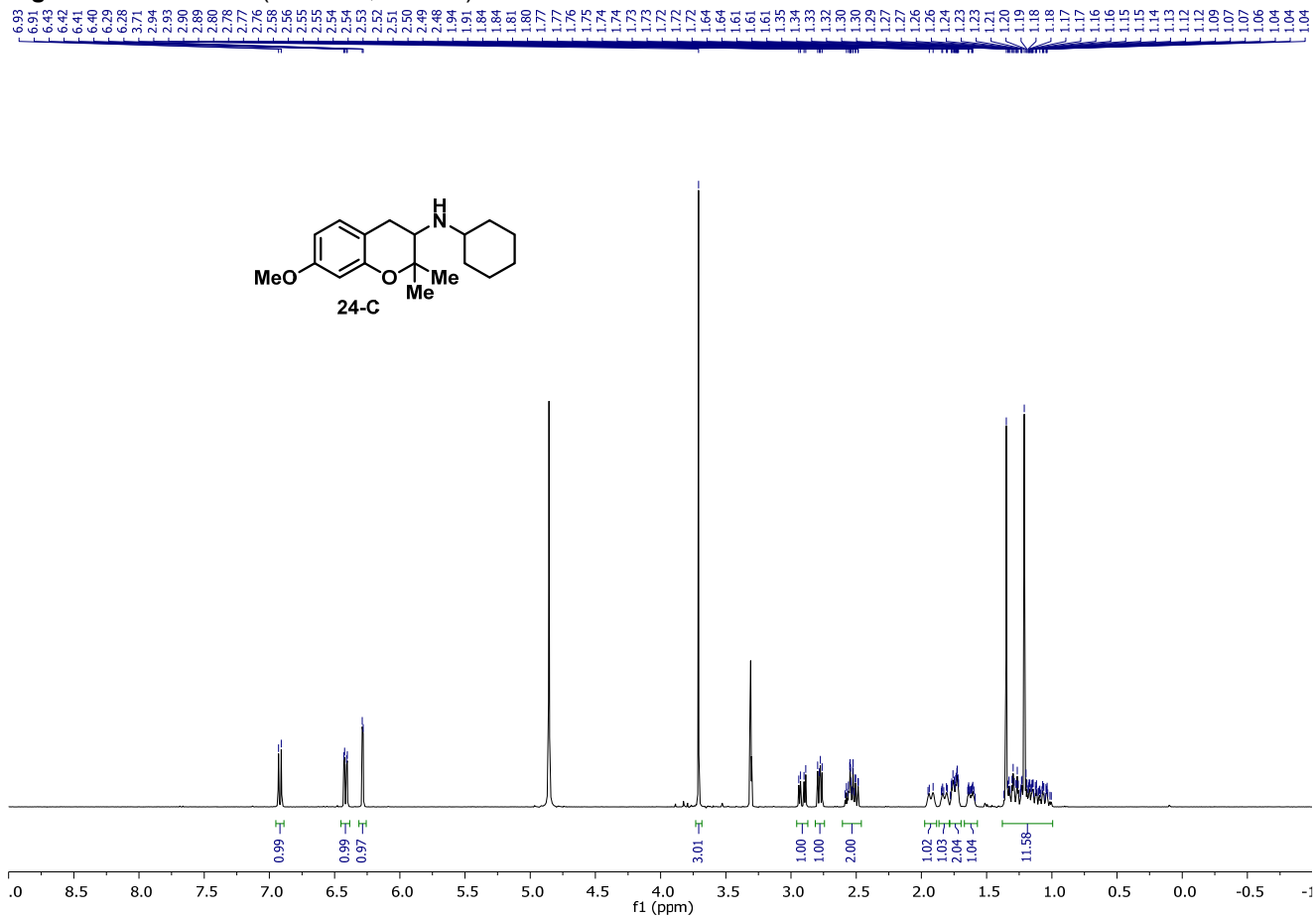
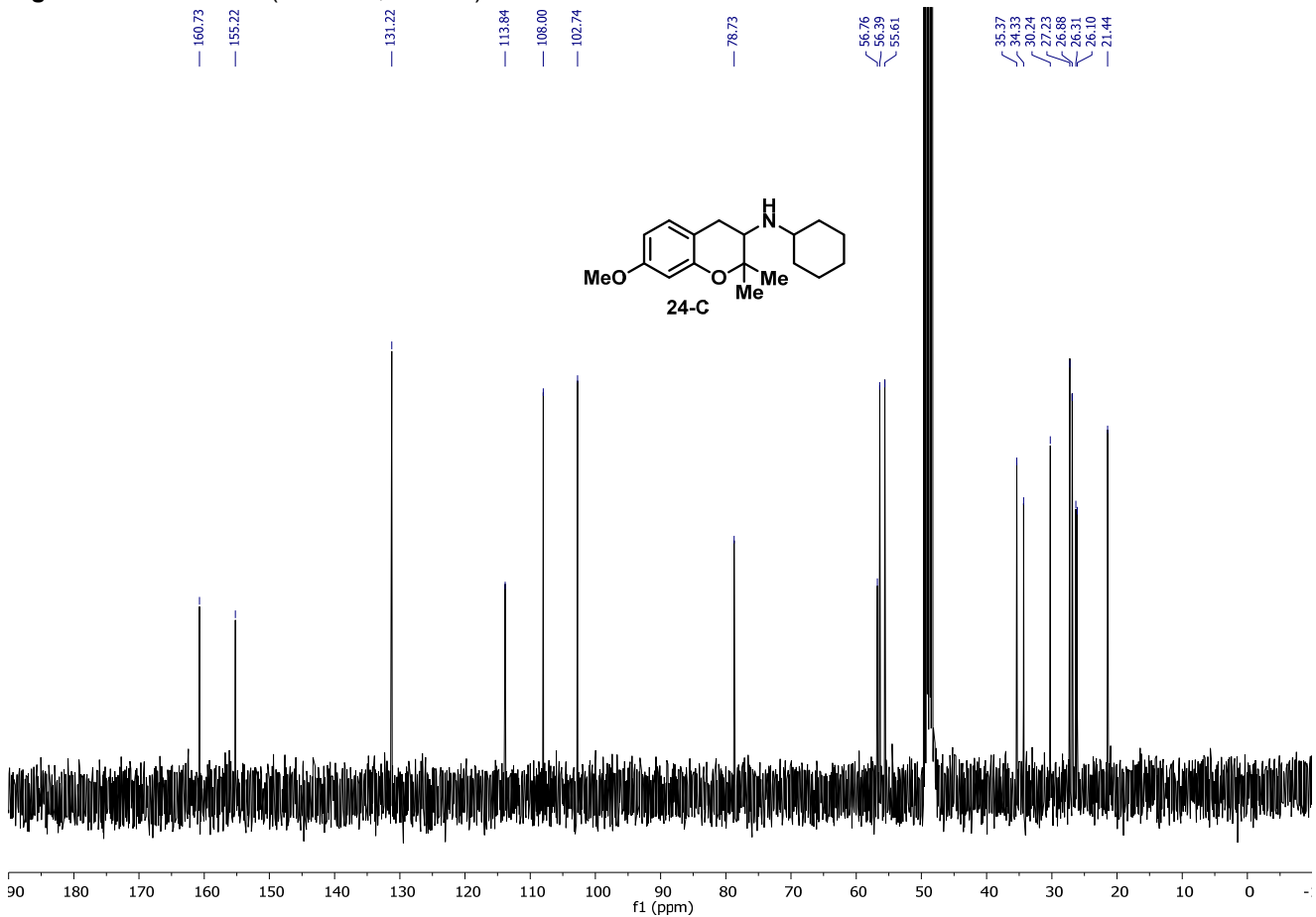
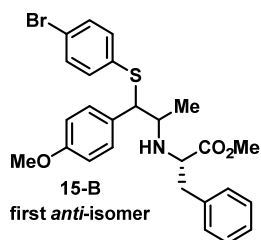


Figure S120. ¹³C NMR (101 MHz, CD₃OD) of 24-C

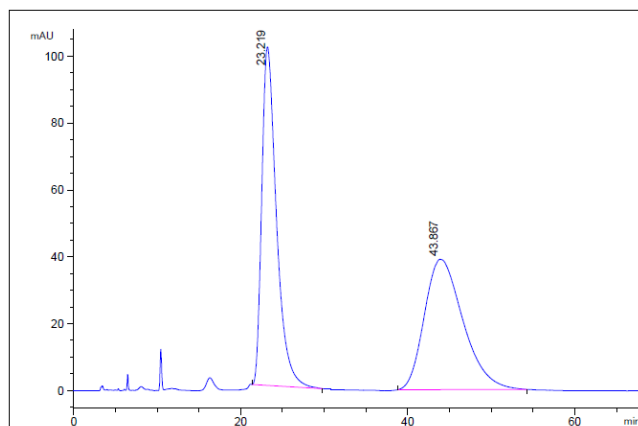


3. Chiral HPLC



Chiralcel OJ-H column, hexane/iPrOH 90:10, flow rate 1 mL/min, 25°C, $\lambda = 265$ nm

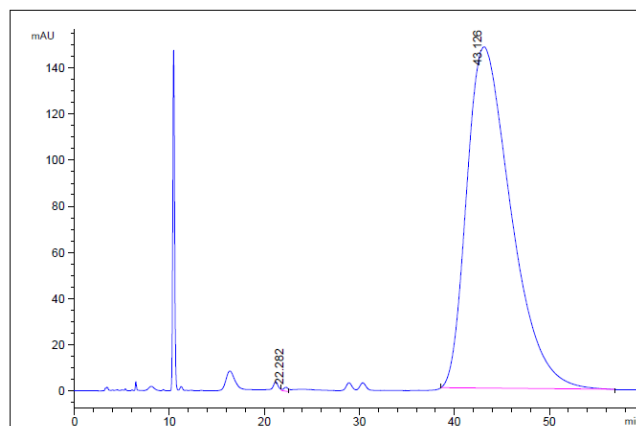
Chiral HPLC of racemic first *anti*-isomer 15-B



Signal 1: VWD1 A, Wavelength=265 nm

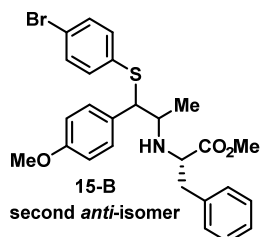
Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	23.219	BB	1.813	12349.408	49.568	
2	43.867	BB	3.794	12564.585	50.432	

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



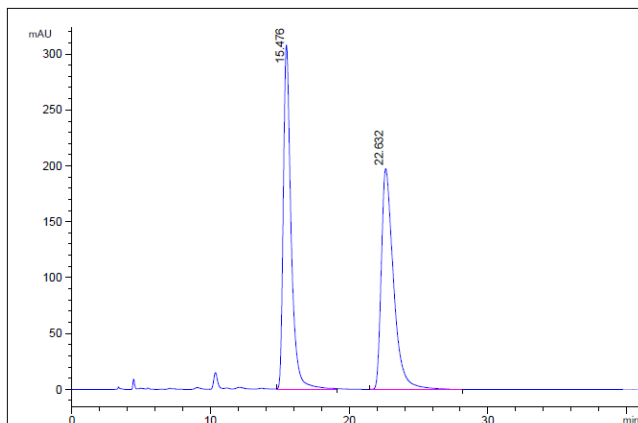
Signal 1: VWD1 A, Wavelength=265 nm

Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	22.282	MM	0.548	57.286	0.120	
2	43.128	BB	3.941	47866.309	99.880	



Chiralcel OD-H column, hexane/iPrOH 98:2, flow rate 1 mL/min, 25°C, $\lambda = 265$ nm

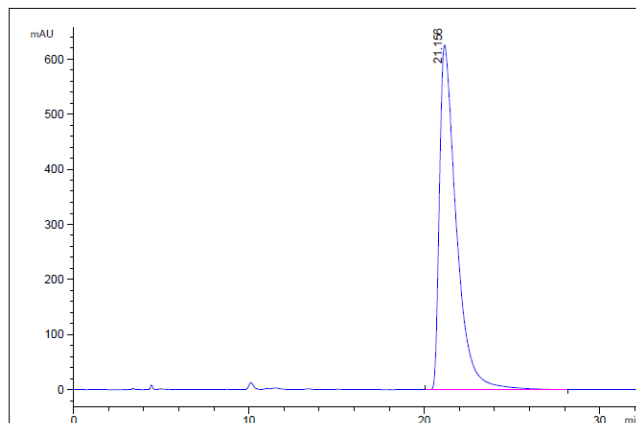
Chiral HPLC of racemic second *anti*-isomer 15-B



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	

III. Supplemental References

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