Supplementary Information

Cation Radical-Mediated Semi-Pinacol and n+2 Ring Expansions Mediated by Organic Photoredox Catalysis

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General Reagent Information

All reagents were purchased from commercial suppliers and were used as received unless otherwise indicated. Anhydrous acetonitrile (MeCN), dichloromethane (DCM), diethyl ether, and tetrahydrofuran (THF) were obtained by running degassed solvents through stainless steel columns packed with drying agents in a laboratory-built solvent purification system.

General Analytical Information

Thin layer chromatography was performed on SiliaPlate silica gel plates (thickness: 250 μm) obtained from Siliacycle Inc. and 254 nm UV light was used as the visualizing agent. All chromatographic separations were performed via flash chromatography using either SiliaFlash P60 silica gel (40-63 μm) or R60 fine silica gel (20-45 μm) as specified in the individual synthetic procedures herein.

Proton, carbon, fluorine, and two-dimensional nuclear magnetic resonance (NMR) spectra (^{1}H, ^{13}C, ^{19}F, COSY, HSQC, HMBC, NOESY) were obtained using the following spectrometers: Bruker Avance NEO 400 MHz (^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz, ^{19}F NMR at 376 MHz), Bruker Avance NEO 600 MHz (^{1}H NMR at 600 MHz, ^{13}C NMR at 151 MHz) Bruker Avance Narrow-bore magnet 400 MHz (^{1}H NMR at 400 MHz, 13C NMR at 101 MHz, ^{19}F at 376 MHz), Bruker Avance III 500 MHz (^{1}H NMR at 500 MHz, 13C NMR at 126 MHz), and Bruker Avance III 600 MHz (^{1}H NMR at 600 MHz, 13C NMR at 151 MHz). All spectra were recorded in CDCl3 unless otherwise noted. Processing of spectra was performed using MestreNova (version 14.1.2) and were referenced utilizing residual undeuterated solvent as the internal reference (i.e. for the case of $CDCl_3$, $CHCl_3$ was used with values of δ = 7.26 for ^{1}H NMR and δ = 77.16 for ^{13}C NMR). In cases where NMR-based yields are reported, hexamethyldisiloxane (HMDSO) was used as an internal standard with the singlet representing the eighteen protons from the six degenerate methyl groups being used for integration. Data are reported in terms of chemical shift, multiplicities, and integration. The following abbreviations are used to describe multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddt = doublet of doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet.

High-resolution mass spectra (HRMS) were obtained using a Thermo Scientific LTQ-FT mass spectrometer with electrospray ionization (ESI) in positive or negative mode.

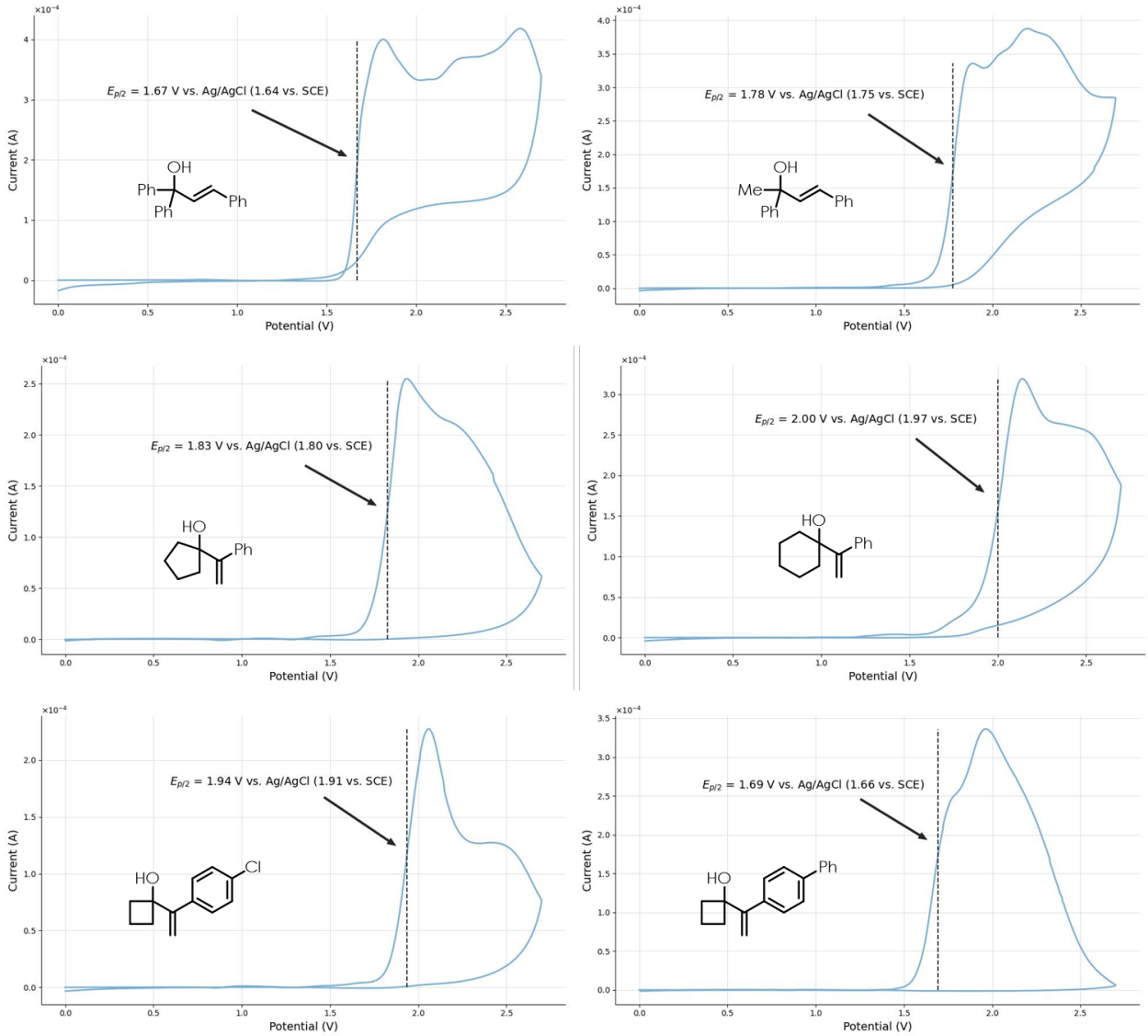
General Photoreactor Information

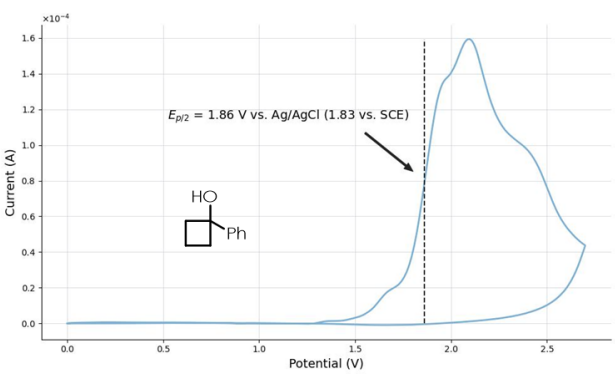
All photochemical reactions presented in the substrate scope (Scheme 5 in the main text) were conducted using a SynLED parallel photoreactor purchased from Sigma-Aldrich (Product # Z744080) which contain 16 wells suitable for 2 dram vials and uses 450 nm LEDs as the irradiation source. The temperature of the SynLED was measured using a thermocouple and was found to be between 25 and 35 °C when in use. For the continuous flow and batch setups, along with several entries in the optimization tables, 456 nm PR160L Kessil lamps were used. For entries in the optimization tables in which photochemical reactions were conducted at low temperatures, a NesLab CB-80 cryobath chiller equipped with a SynLED was used to maintain a temperature of approximately 5 °C.

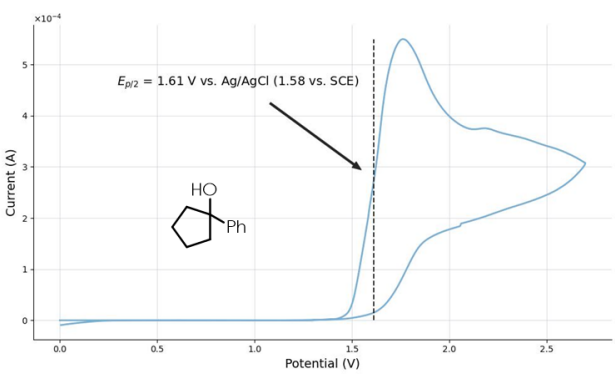
Electrochemistry Methods and Measurements

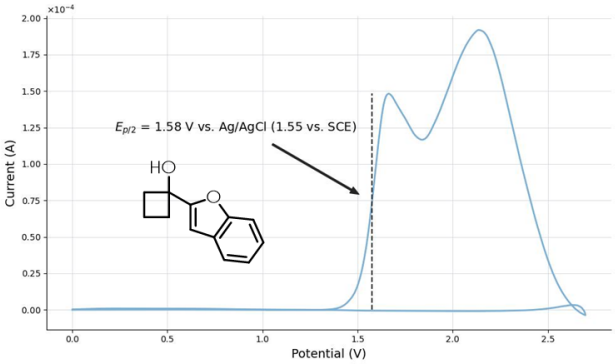
Cyclic Voltammetry

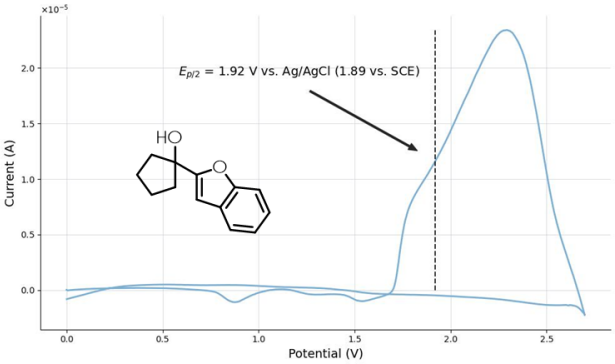
Oxidation potentials were obtained via cyclic voltammetry using a Pine Instruments WaveNow potentiostat with a standard three electrode setup: working (glassy carbon), reference (Ag/AgCl in 3 M NaCl), and counter (platinum wire). All samples were prepared as a 5 mM solution of substrate in anhydrous, degassed acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (nBu$_4$NPF$_6$) as a supporting electrolyte. Measurements were taken using a scan rate of 100 mV/s from an initial potential of 0 V to a vertex potential of 2.7 V. The cyclic voltammograms were then processed using an in-house Python script which subtracted a background scan from the experimental data, located the maximum current (C_p), and determined the oxidation potential ($E_{p/2}$) by taking half of the maximum current ($C_{p/2}$). This potential (vs. Ag/AgCl) was then referenced to SCE by subtracting 0.03 V. Values for a range of the starting materials from this study, along with several additional relevant substrates are shown below.

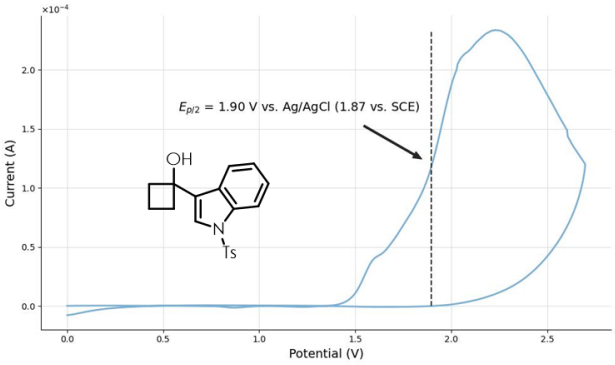


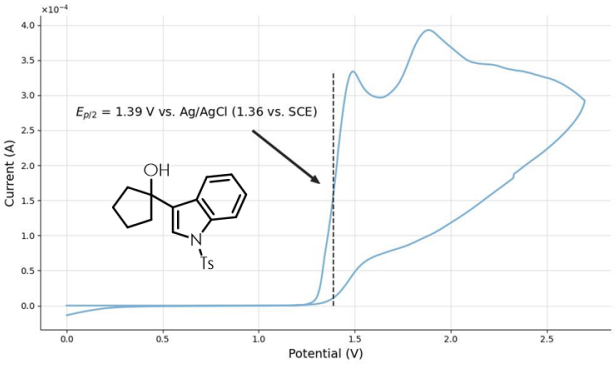

$E_{p/2}$ = 1.86 V vs. Ag/AgCl (1.83 vs. SCE)
HO
Ph
Current (A)
Potential (V)

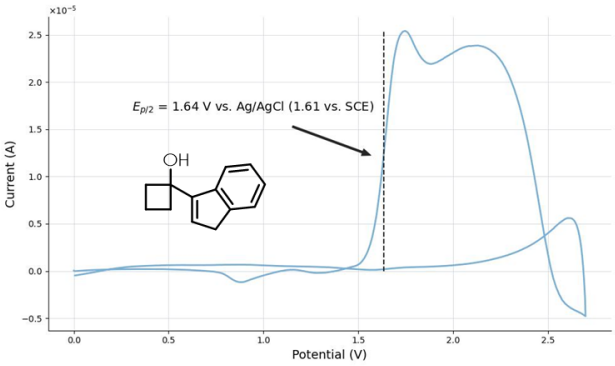

$E_{p/2}$ = 1.61 V vs. Ag/AgCl (1.58 vs. SCE)
HO
Ph
Current (A)
Potential (V)

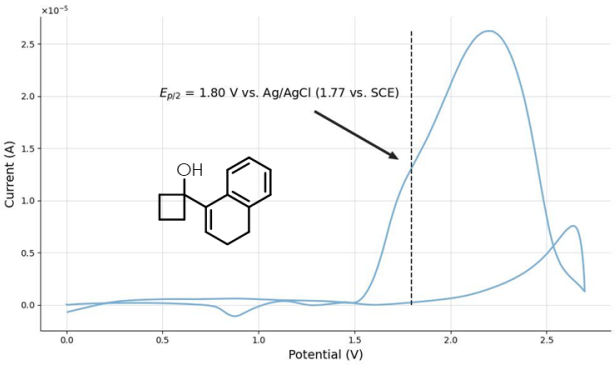

$E_{p/2}$ = 1.58 V vs. Ag/AgCl (1.55 vs. SCE)
HO
O
Current (A)
Potential (V)


$E_{p/2}$ = 1.92 V vs. Ag/AgCl (1.89 vs. SCE)
HO
O
Current (A)
Potential (V)


$E_{p/2}$ = 1.90 V vs. Ag/AgCl (1.87 vs. SCE)
OH
N
Ts
Current (A)
Potential (V)

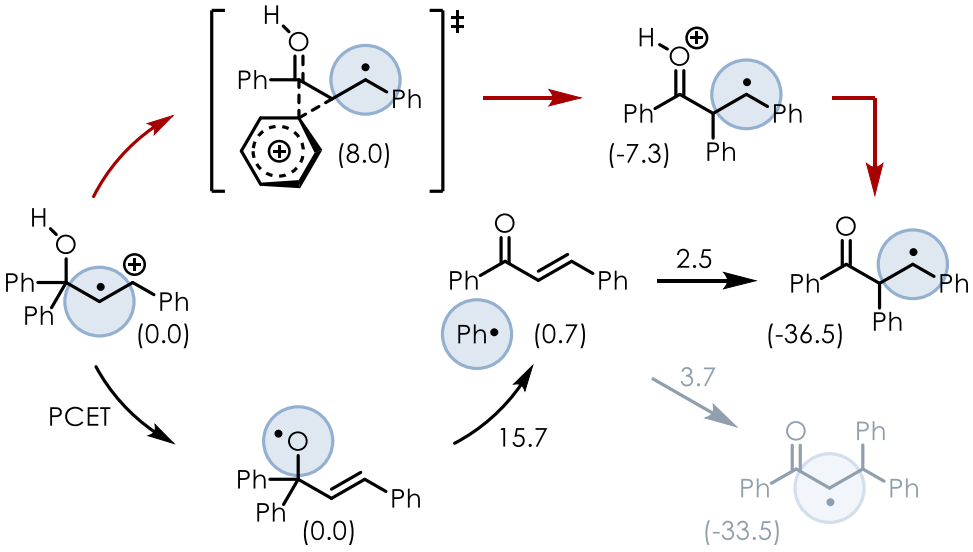

$E_{p/2}$ = 1.39 V vs. Ag/AgCl (1.36 vs. SCE)
OH
N
Ts
Current (A)
Potential (V)


$E_{p/2}$ = 1.64 V vs. Ag/AgCl (1.61 vs. SCE)
OH
Current (A)
Potential (V)

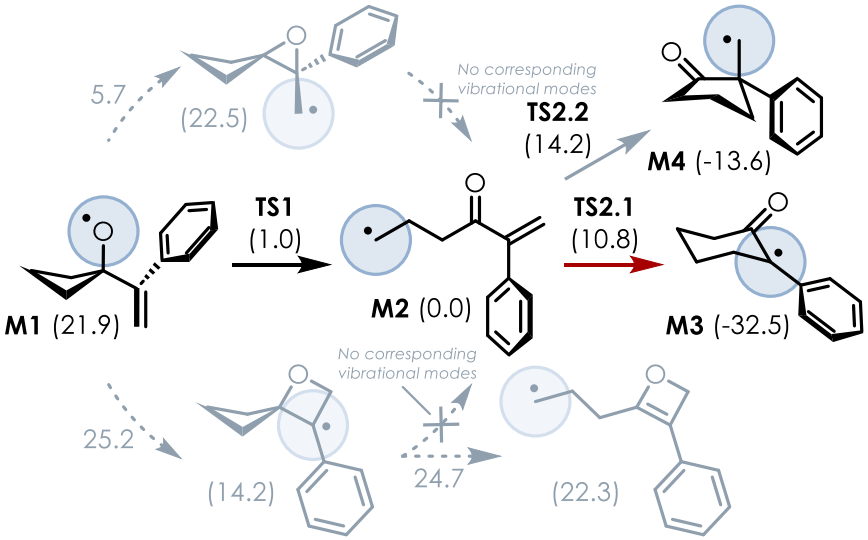

$E_{p/2}$ = 1.80 V vs. Ag/AgCl (1.77 vs. SCE)
OH
Current (A)
Potential (V)

Computational Studies

Mechanistic Studies for Reactions A and B



Scheme S1 Possible reaction pathways for reaction A. (Red arrows) Lowest energy pathway proceeding through a concerted semi-pinacol-like transition state with $\Delta G^{\ddagger}$ = 8.0 kcal/mol. (Black arrows) PCET pathway and subsequent phenyl radical expulsion with $\Delta G^{\ddagger}$ = 15.7 kcal/mol followed by 1,3-addition with $\Delta G^{\ddagger}$ = 2.5 kcal/mol to yield the 1,2-phenyl migration product with ΔG = -36.5 kcal/mol. (Grey arrow) 1,4-addition of the phenyl radical with $\Delta G^{\ddagger}$ = 3.7 kcal/mol and ΔG = -33.5 kcal/mol.



Scheme S2 Possible reaction pathways for reaction B. (Black arrow) PCET pathway from alkoxy radical to cyclobutane-scissioned primary radical with the methyl radical set to 0.0 kcal/mol and $\Delta G^{\ddagger}$ = 1.0 kcal/mol for the cleavage. (Red arrow) 6-*endo-trig* cyclization pathway with $\Delta G^{\ddagger}$ = 10.8 kcal/mol and ΔG = -32.5 kcal/mol. (Grey solid arrow) 5-*exo-trig* cyclization pathway with $\Delta G^{\ddagger}$ = 14.2 kcal/mol and ΔG = -13.6 kcal/mol. (Grey dotted arrows) Pathways for interaction of the alkoxy radical with the neighboring styrene, yielding either an epoxide or an oxetane.

Energy Calculations

Input structures for the compounds in Schemes S1 and S2 were created using GaussView[1] and then submitted to the CREST (Conformer Rotamer Ensemble Sampling Tool) ensemble generation program[2–4] using the GFN2-xTB method,[5] the default ensemble sorting parameters (energy window = 6.0 kcal/mol; energy threshold = 0.05 kcal/mol; root mean square deviation threshold = 0.125 Å), and the analytical linearized Poisson-Boltzmann (ALPB) implicit solvation model[6] with acetonitrile as the solvent. Geometry optimization and frequency calculations (omitting Raman intensities) were then carried out using Gaussian 16[7] for each conformer at the wB97XD/Def2TZVP level of theory[8–10] (which includes empirical dispersion corrections using Grimme's D2 model) with solvation modeled using the self-consistent reaction field (SCFR) approach and the conductor-like polarizable continuum model (CPCM)[11,12] with acetonitrile as the solvent. Screening of the resulting frequency calculations indicated that no imaginary frequencies were obtained, indicating that the geometries corresponded to ground state structures. Boltzmann weights were then calculated using Equation S1 where P_i is the weight that each conformer I contributes to the total energy, E_i is the energy in kcal/mol relative to the other conformers in the ensemble, R is the gas constant (1.9872 x 10^{-3} kcal • K^{-1} • mol^{-1}), and T is the temperature (298 K).

Equation S1 Boltzmann equation.

$$P_i = \frac{e^{-E_i/RT}}{\sum_i e^{-E_i/RT}}$$

Transition states geometries, frequencies, and energies were then computed at the same level of theory using Gaussian's quadratic synchronous transit (QST2 and QST3; 2 point and 3 points, respectively) transition state search methods[13] using the lowest energy conformer of the relevant starting materials computed above as a starting geometry. The obtained structures were then verified as saddle points by the observation of a single negative vibrational frequency corresponding to the vibrational mode associated with bond breaking/formation along with IRC[14] calculations to confirm that the transition states led to and from the appropriate products and starting materials, respectively.

Spin Density and Percent Buried Volume Calculations

Spin densities were then calculated using the lowest energy conformation of each intermediate along with the transition state structures at the same level of theory mentioned above using Gaussian 16.[7] The spin densities for all non-hydrogen atoms were then extracted from the Gaussian output files and normalized using Equation S2 where the spin density for each atom is divided by the sum of the spin densities of all non-hydrogen atoms. The atom with the highest normalized fractional spin density along with it's associated atom label was then recorded for each structure.

Equation S2 Spin density normalization.

$$Normalized\ Spin_i = \frac{|Spin\ Density_i|}{\sum_j |Spin\ Density_j|}$$

Percent buried volumes for the atoms with the highest fraction spin density in each structure were then calculated using the Paton group's DBSTEP (DFT-based Steric Parameters) Python-based tool[15] and recorded. A summary of all the relevant values presented in this section are summarized in Table S1 below.

Reaction B	Conformer Generation			Boltzmann-averaged Energies			Spin Density		% Buried volume
Entry	Charge/Multiplicity	# of conformers	Lowest E Conf	E (Hartrees)	E (kcal/mol)	Erel (kcal/mol)	Atom	Fraction	
SM	0 1	12	2	-540.7149767	-339303.5143	-	-	-	-
SM_radcat	1 2	9	1	-540.4819083	-339157.2618	-	C14	0.26956	40.68
Orad	0 2	5	1	-540.0576307	-338891.0238	21.89	O11	0.68574	44.36
Orad_to_MeRad	0 2	-	-	-540.056053	-338890.0338	22.88	C4	0.46382	43.39
MeRad	0 2	33	7	-540.0925217	-338912.9182	0.00	C2	0.89037	27.71
MeRad_to_P1rad	0 2	-	-	-540.075339	-338902.1359	10.78	C12	0.44589	59.06
P1rad	0 2	7	1	-540.1443116	-338945.4168	-32.50	C12	0.38637	58.69
P1	0 1	12	2	-540.7758664	-339341.7231	-	-	-	-
MeRad_to_P2rad	0 2	-	-	-540.06992	-338898.7354	14.18	C13	0.79648	45.15
P2rad	0 2	5	4	-540.1142569	-338926.5573	-13.64	C13	0.88511	45.72
P2	0 1	6	1	-540.7720724	-339339.3424	-	-	-	-
Orad_to_epoxideRad	0 2	-	-	-540.048512	-338885.3017	27.62	C13	0.6508	40.42
epoxideRad	0 2	1	1	-540.056752	-338890.4724	22.45	C13	0.73026	39.71
Orad_to_oxetaneRad	0 2	-	-	-540.017447	-338865.8081	47.11	C4	0.37726	44.58
oxetaneRad	0 2	1	1	-540.069934	-338898.7442	14.17	C12	0.34521	57.64
oxetaneRad_to_oxetaneCleaveRad	0 2	-	-	-540.030568	-338874.0417	38.88	C12	0.352234	57.33
oxetaneCleaveRad	0 2	8	2	-540.0569983	-338890.6269	22.29	C2	0.8833	27.8

Table S1 Calculated values for reaction B using descriptive names in the Entry column. (Conformer Generation column) Charge and multiplicity for each species, the number of conformers generated by CREST and used for subsequent calculations, and the conformer number of the lowest energy conformer. (Boltzmann-Averaged Energies column) Energies in Hartrees, kcal/mol, and kcal/mol set relative to the primary radical. (Spin Density column) Atom with highest fractional spin density (highlighted as blue circles in Figure 3 and Scheme S2), and corresponding fractional spin density on that atom. (% Buried Volume column) Calculated percent buried volume at the atom with the highest fractional spin density.

Reaction Trajectory Plot

Using the values obtained above (Table S1), a three-dimensional plot of the 5-*exo-trig* and 6-*endo-trig* reaction trajectories was then constructed using Matplotlib to compare the reaction pathways depicted in Scheme S2. The plot is shown in Figure S1 with relative energy in kcal/mol on the z-axis, maximum fractional spin density on the y-axis, and percent buried volume at the atom of maximum fractional spin density on the x-axis.

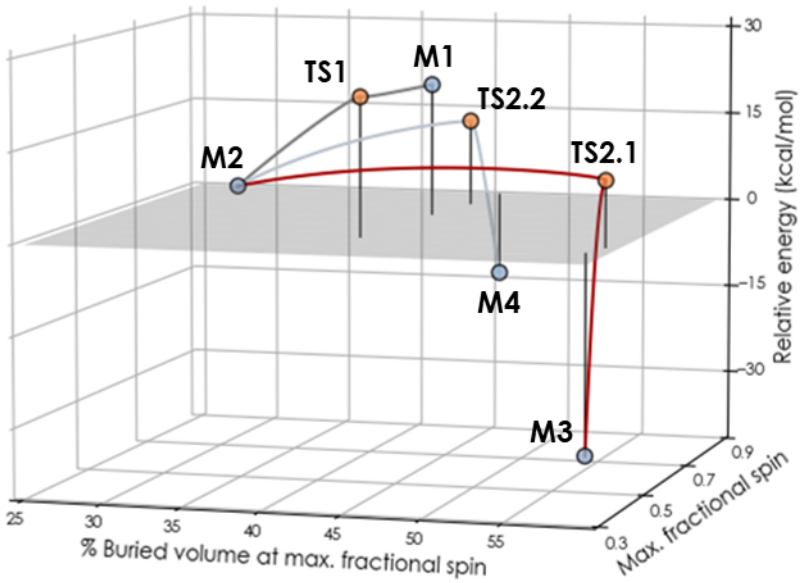
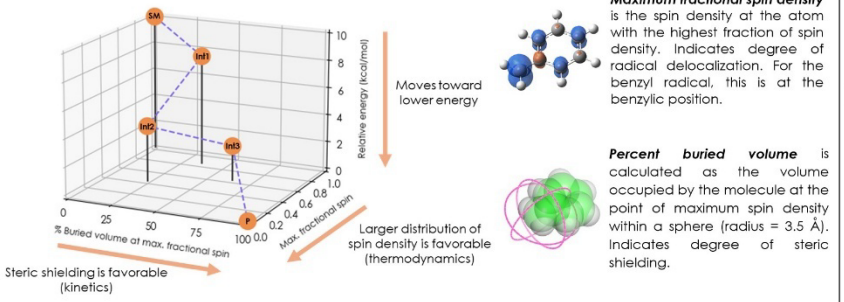


Figure S1 Three-dimensional plot of potential reaction pathways (black lines – cleavage of cyclobutane alkoxy radical to primary radical; red lines – 6-*endo-trig*; grey lines – 5-*exo-trig*); E vs. Max. fractional spin density vs. % Buried volume at max. fractional spin density. The xy plane at z = 0 is plotted such that the energy of the primary radical is set to zero.

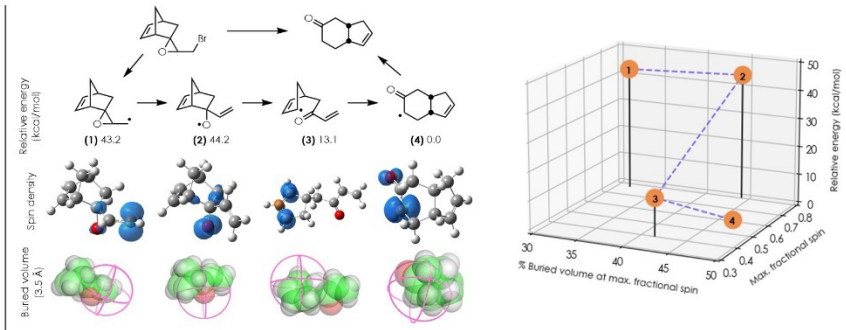
Comparison of Reaction Pathways to Other Radical Pathways

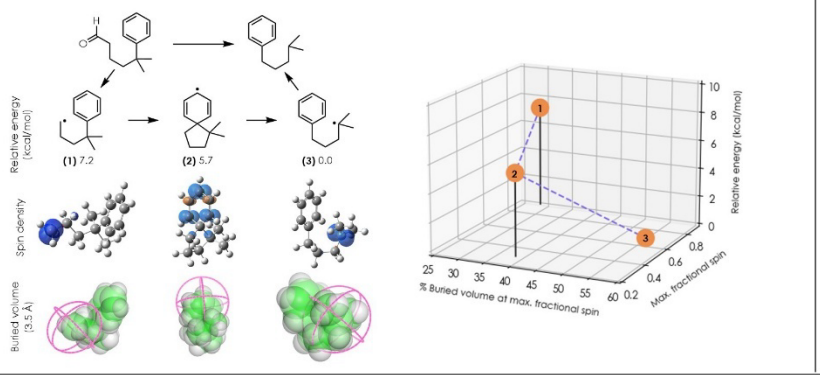
To gain insight into the favorability of the mechanistic pathways proposed above, we sought to compare the 5-*exo* and 6-*endo*-*trig* trajectories to trajectories computed for known radical reaction mechanisms. The data set used is summarized in Figure S2, which includes a visual overview of the physical meaning of maximum fractional spin density and percent buried volume (top left corner) along with nine known radical mechanisms and their respective trajectories. These trajectories were calculated as described above at the M06-2X/Def2TZVP level of theory[10,16] with water as the solvent using the SCFR approach and the SMD (Solvation Model based on Density)[17] model – values used in Paton's studies from which this quantitative method of assessing radical reactions was derived.[15]

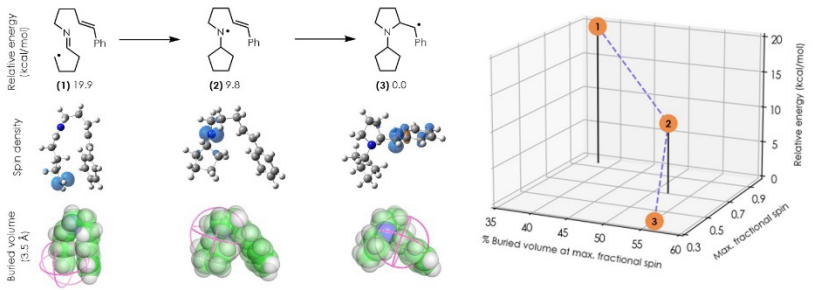


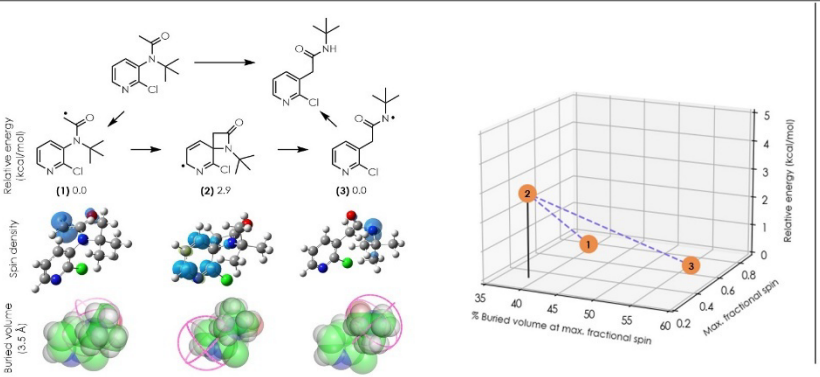
Maximum fractional spin density is the spin density at the atom with the highest fraction of spin density. Indicates degree of radical delocalization. For the benzyl radical, this is at the benzylic position.

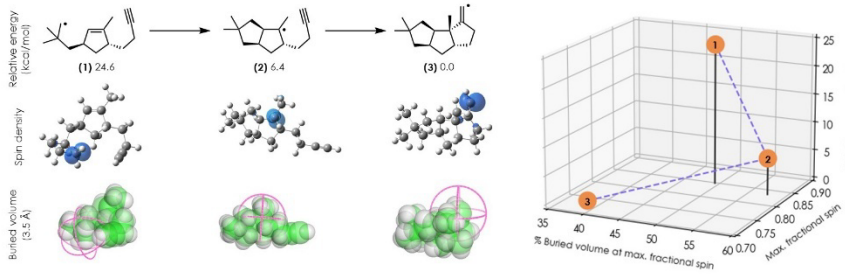
Percent buried volume is calculated as the volume occupied by the molecule at the point of maximum spin density within a sphere (radius = 3.5 Å). Indicates degree of steric shielding.











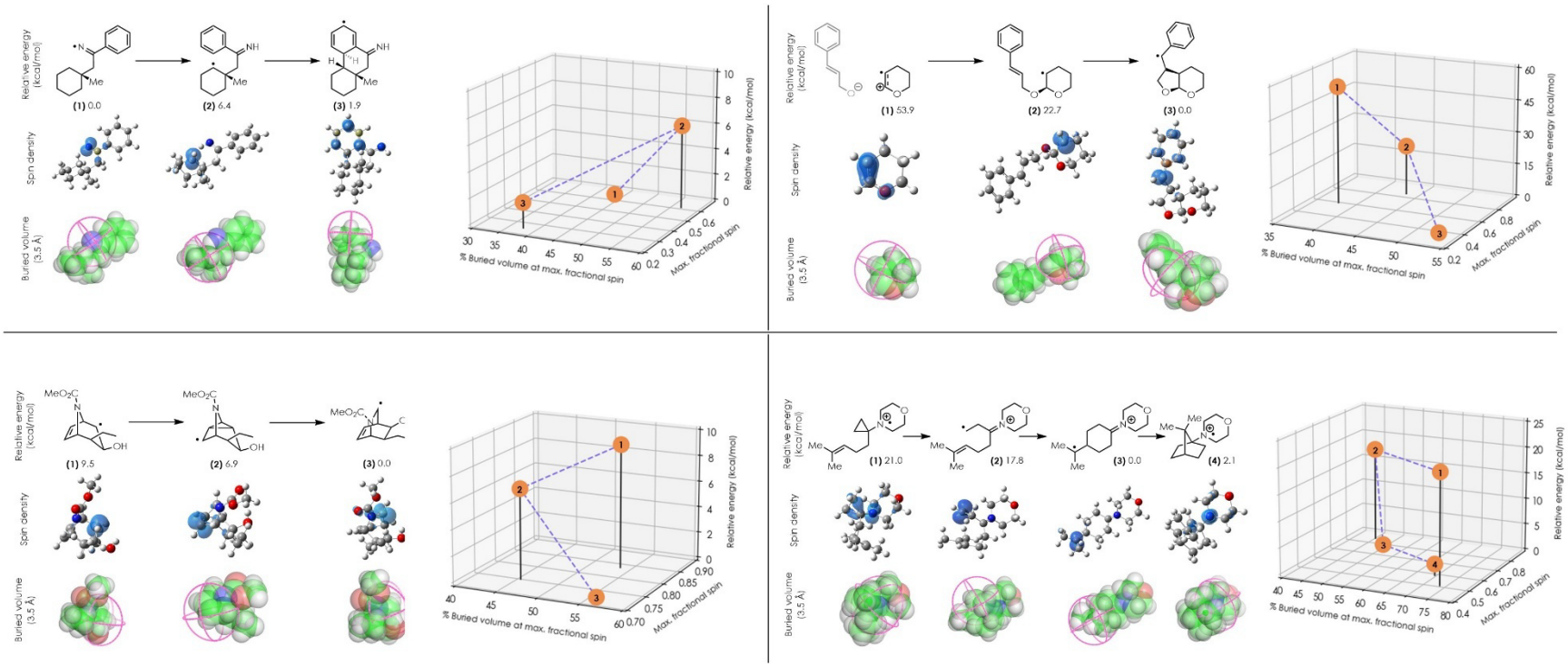


Figure S2 Summary of known productive radical reaction pathways plotted as energy (z-axis), maximum fractional spin density (y-axis), and percent buried volume at the atom of maximum fractional spin density (x-axis). (Top left) Visual overview of the physical meaning of maximum fractional spin density and percent buried volume. Each reaction shows the associated 3D plot along with the reaction scheme (top), plot of spin density (middle), and a representation of the buried volume where the pink sphere represents the volume used for the calculation (pink).

Analysis of the dataset was conducted by comparing the reaction trajectories to that of an ideal radical reaction trajectory in which the path followed would be one that flows toward more thermodynamically stable intermediates (decrease in energy; z-axis), intermediates in which the fractional spin density is less localized on single atoms and more dispersed via conjugation etc. (decrease in maximum fractional spin density; y-axis), and intermediates in which the radical species are more sterically shielded (increase in percent buried volume at the site of maximum fractional spin density; x-axis). Based on this trend, a favorable reaction trajectory – increasing buried volume (x), decreasing spin density (y), and decreasing relative energy (z) – can be represented by the vector ⟨+1, -1, -1⟩ as shown in Figure S3.

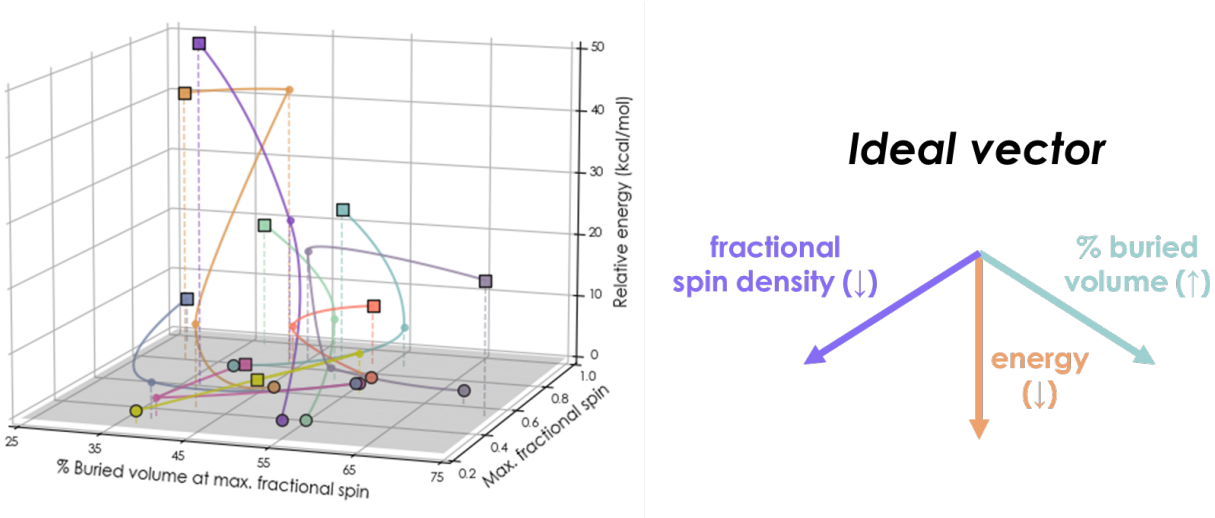


Figure S3 Analysis of the reaction trajectories for the radical reactions shown in Figure S2. (Left) Overlayed plot of relative energy in kcal/mol vs. maximum fractional spin density, vs. percent buried volume at the atom with maximum fractional spin density. Squares outlined in black represent the start of the trajectory, whereas circles outlined in black represent the end. Intermediate points are represented by small circles with no black outline. (Right) A depiction of a vector representing the ideal direction a trajectory should follow to minimize energy, distribute spin density, and sterically shield the radical.

The reactions in the dataset were then analyzed using equations S3 through S7 and averaged to yield the values provided in Table S2. The cosine similarity corresponds to the directional alignment of the reaction trajectory along the ideal vector, the projection magnitude represents how far the trajectory moves in that direction, and the Δ buried volume, Δ max fractional spin density, and Δ relative energy represent the change in the respective values.

Equation S3 Cosine similarity to reference direction. $$\cos(\theta) = \frac{v \cdot r_{ref}}{\|v\|}$$

Equation S4 Projection magnitude. $$\text{projection} = v \cdot r_{ref}$$

Equation S5 Change in buried volume. $$\Delta\text{BV} = x_{final} - x_{initial}$$

Equation S6 Change in max fractional spin density. $$\Delta\text{SD} = y_{final} - y_{initial}$$

Equation S7 Change in relative energy. $$\Delta\text{E} = z_{final} - z_{initial}$$

Trajectory Analysis	
Average cosine similarity to ideal vector [↑ buried, ↓ spin, ↓ energy]	+0.48
Average projection magnitude toward ideal direction	+15.91
Average Δ % buried volume at max. frac. Spin	+7.88
Average Δ max. frac. Spin	-0.20
Average Δ relative energy	-19.47

Table S2 Analysis of radical reaction pathways shown in Figure S2 using the equations above.

With these values now calculated for the test dataset, we then calculated the same values for the proposed 5-*exo-trig* and 6-*endo-trig* pathways both to see how they compared between each other and to see how their favorability ranked against the dataset. The values were normalized and compared relative to the dataset averages. These values are shown in Table S3 and a radar plot of the 6-*endo-trig* pathway (red) compared to the 5-*exo-trig* pathway (grey) is shown in Figure S4, overlayed on circles where 1x represents the average values calculated for the reactions in our test dataset.

Trajectory Analysis (5-exo-trig vs. 6-endo-trig) Normalized vs. dataset average	5-exo-trig	6-endo-trig
Average cosine similarity to ideal vector [↑ buried, ↓ spin, ↓ energy]	1.25	1.49
Average projection magnitude toward ideal direction	1.33	2.00
Average Δ % buried volume at max. frac. spin	0.17	1.82
Average Δ max. frac. spin	0.00	1.50
Average Δ relative energy	1.82	2.00

Table S3 Analysis of 5-*exo-trig* vs. 6-*endo-trig* reaction pathways using the equations above – normalized and compared to the test dataset.

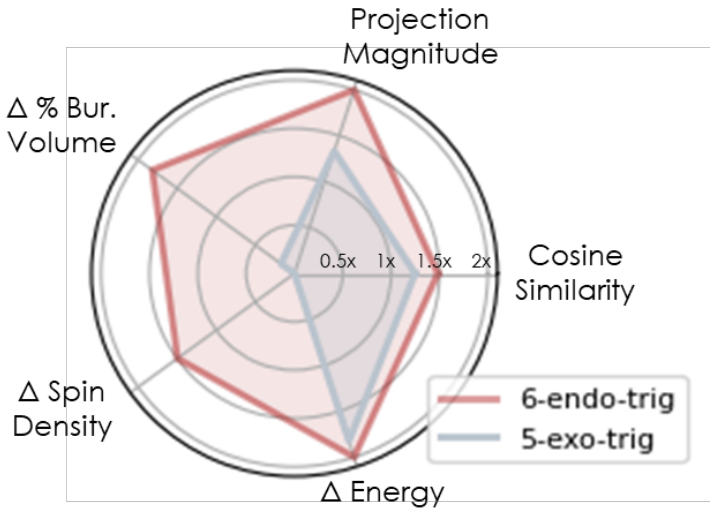
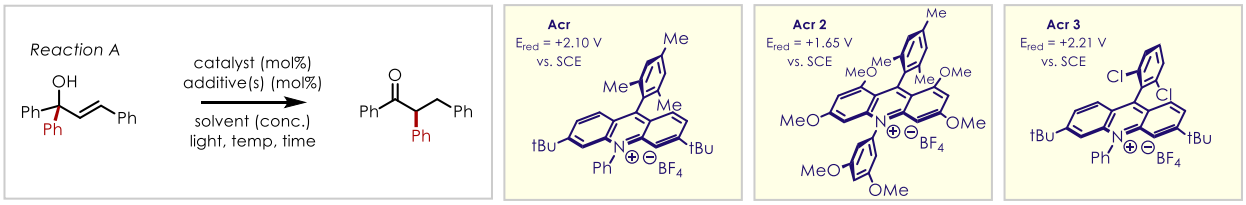


Figure S4 Radar plot of the data from Table S3 where red represents the 6-*endo-trig* pathway, grey the 5-*exo-trig* pathway and the circles labeled 0.5x, 1x, 1.5x, and 2x represent the values calculated from the dataset in Figure S2 and summarized in Table S2.

Optimization Tables

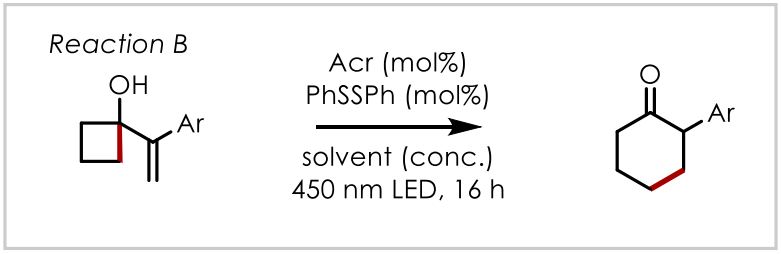
Reaction A Optimization Table

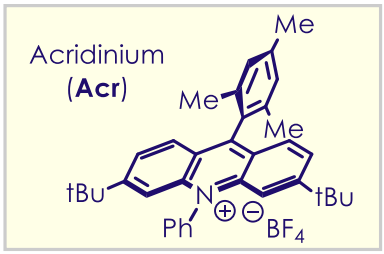


Conditions	Catalyst	Catalyst mol%	Additive	Additive mol%	Additive 2	Additive 2 mol%	Solvent	Conc. (mM)	LED (nm)	Temp (°C)	Time (h)	% Yield / Result
Initial hit	Acr	5	PhSSPh	10	-	-	DCE	150	450	25-35	24	12
Controls	-	-	-	-	-	-	DCE	150	-	25-35	24	NR
	-	-	-	-	-	-	DCE	150	450	25-35	24	NR
	Acr	5	-	-	-	-	DCE	150	-	25-35	24	NR
	Acr	5	PhSSPh	-	-	-	DCE	150	-	25-35	24	no P
	Acr	5	-	-	-	-	DCE	150	450	25-35	24	no P
	-	-	PhSSPh	10	-	-	DCE	150	450	25-35	24	no P
Low temp	Acr	5	PhSSPh	10	-	-	DCE	150	450	5	24	trace P
Solvent screen	Acr	5	PhSSPh	10	-	-	DCM	150	450	25-35	24	+ side products
	Acr	5	PhSSPh	10	-	-	MeCN	150	450	25-35	24	27
Conc. screen	Acr	5	PhSSPh	10	-	-	MeCN	600	450	25-35	24	30
	Acr	5	PhSSPh	10	-	-	MeCN	300	450	25-35	24	32
	Acr	5	PhSSPh	10	-	-	MeCN	150	450	25-35	24	32
	Acr	5	PhSSPh	10	-	-	MeCN	75	450	25-35	24	39
	Acr	5	PhSSPh	10	-	-	MeCN	40	450	25-35	24	37
	Acr	5	PhSSPh	10	-	-	MeCN	20	450	25-35	24	40
	Acr	5	PhSSPh	10	-	-	MeCN	15	450	25-35	24	47
	Acr	5	PhSSPh	10	-	-	MeCN	10	450	25-35	24	50
Time / additive equiv.	Acr	5	PhSSPh	10	-	-	MeCN	10	450	25-35	3	15
	Acr	5	PhSSPh	10	-	-	MeCN	10	450	25-35	6	25
	Acr	5	PhSSPh	20	-	-	MeCN	10	450	25-35	3	22
	Acr	5	PhSSPh	20	-	-	MeCN	10	450	25-35	6	27
Catalyst screen	Acr 2	5	PhSSPh	10	-	-	MeCN	10	450	25-35	24	+ side products
	Acr 3	5	PhSSPh	10	-	-	MeCN	10	450	25-35	24	3.8
Additive screen	Acr	5	PhSH	10	-	-	MeCN	10	450	25-35	24	+ side products
	Acr	5	phenyl malononitrile	10	-	-	MeCN	10	450	25-35	24	+ side products
	Acr	5	PhSSPh	10	2,6-lutidine	10	MeCN	10	450	25-35	24	35
	Acr	5	PhSSPh	10	2,6-lutidine	10	MeCN	10	450	25-35	24	32

Table S4 Optimization table for the cation radical-mediated semi-pinacol (CRM-SP) reaction.

Reaction B Optimization Table

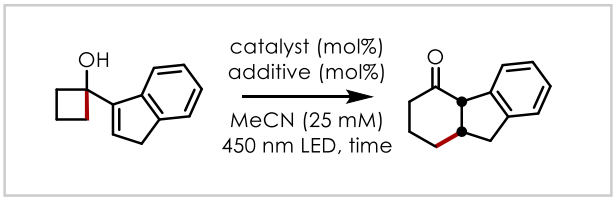


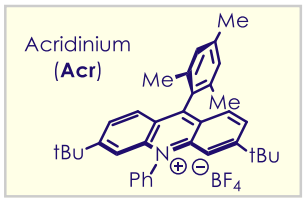


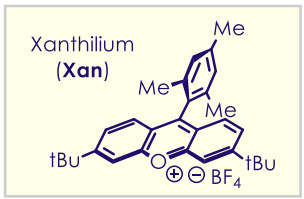
Conditions	Acr mol%	PhSSPh mol%	Solvent	Conc. (mM)	LED (nm)	Sparge	% Yield
Initial hit	5	10	MeCN	25	450	Ar	45
Controls	-	10	MeCN (anh)	25	450	Ar	0
	-	10	MeCN (anh)	25	450	Ar	0
	5	-	MeCN (anh)	25	450	Ar	13
	5	10	MeCN (anh)	25	-	Ar	0
	5	10	MeCN (anh)	25	450	-	0
Solvent screen	5	10	DCE	25	450	Ar	18
	5	10	DCM	25	450	Ar	31
	5	10	TFE	25	450	Ar	0
	5	10	TFT	25	450	Ar	41
	5	10	MeCN (anh)	25	450	Ar	91
Conc. screen	5	10	MeCN (anh)	50	450	Ar	84
	5	10	MeCN (anh)	100	450	Ar	85
	5	10	MeCN (anh)	200	450	Ar	77
Additive equiv. screen	5	5	MeCN (anh)	25	450	Ar	95
	5	15	MeCN (anh)	25	450	Ar	85
	5	30	MeCN (anh)	25	450	Ar	92
	5	50	MeCN (anh)	25	450	Ar	75

Table S5 Optimization for the n+2 ring expansion reaction.

Reaction B Indene Substrate Optimization Table



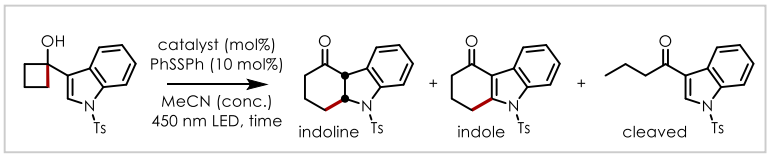


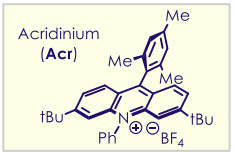


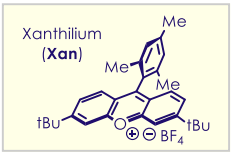
Entry #	Catalyst	Catalyst mol%	Additive	Additive mol%	time (h)	% Yield product
1	Acr	5	PhSSPh	5	6	33
2	Acr	5	PhSSPh	5	16	24
3	Acr	5	PhSSPh	10	16	21
4	Xan	5	PhSSPh	5	16	23
5	Xan	5	PhSSPh	5	48	38
6	Xan	10	PhSSPh	10	48	47
7	Xan	10	TRIP-SH	10	24	29

Table S6 Optimization for the n+2 ring expansion of the indene-based substrate.

Reaction B Indole Substrate Optimization Table



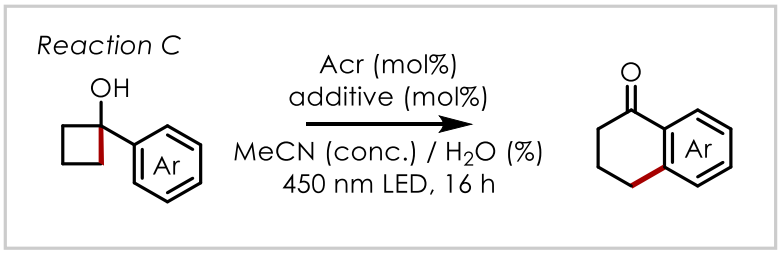


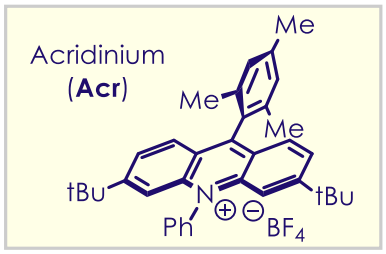


Entry #	Catalyst	Catalyst mol%	PhSSPh mol%	[MeCN] (mM)	time (h)	% Yield Indoline	Indole	Cleaved	SM	Total	Indoline vs. Side Products
1	Acr	5	5	25	6	12	9	9	64	94	0.67
2	Acr	5	5	25	24	25	10	25	20	80	0.71
3	Xan	10	10	25	6	-	-	-	85	85	-
4	Xan	5	5	25	24	9	-	-	58	67	-
5	Acr	10	5	25	24	28	14	16	-	58	0.93
6	Acr	10	10	25	24	23	10	28	-	61	0.61
7	Acr	20	20	25	24	20	8	18	-	46	0.77
8	Acr	10	10	50	24	40	9	13	-	62	1.82
9	Acr	5	10	50	24	29	13	39	-	81	0.56
10	Acr	5	20	50	24	23	12	34	-	69	0.50
11	Acr	10	20	50	24	35	11	17	-	63	1.25
12	Acr	10	40	50	24	29	17	15	-	61	0.91
13	Acr	10	10	100	24	40	17	16	-	73	1.21
14	Acr	10	10	200	24	40	17	8	-	65	1.60
15	Acr	20	20	50	24	30	15	8	-	53	1.30
16	Acr	10	10	50	48	0	60	10	-	70	0.00

Table S7 Optimization of the n+2 ring expansion for the N-tosyl indole substrate.

Reaction C Optimization table





	Entry	Acr mol%	$K_2S_2O_8$ equiv.	PhSSPh mol%	[MeCN] (mM)	Sparge	LED (nm)	% H_2O	Yields (%) Tetralone	Cleaved	SM	Total	Ratio Tetralone/Cleaved
	1	5	-	5	25	Ar	450	-	-	trace	-	-	-
	2	5	2	-	25	Ar	450	-	8.0	-	11.0	19.0	-
	3	5	2	-	25	Ar	450	5	16.0	8.0	26.0	50.0	2.0
	4	5	-	-	25	O_2	450	-	-	-	-	-	-
	5	5	2	-	25	Ar	450	25	15.2	5.3	16.2	36.7	2.9
	6	5	-	-	25	Ar	450	25	3.6	2.9	51.2	57.7	1.2
	7	5	2	-	25	Ar	450	-	8.8	7.0	52.0	67.8	1.3
	8	20	2	-	25	Ar	450	25	24.8	14.6	9.6	49.0	1.7
	9	5	2	-	100	Ar	450	25	7.5	7.6	0.5	15.6	1.0
Controls	10	-	-	-	25	Ar	-	25	-	-	quant.	-	-
Controls	11	-	-	-	25	Ar	450	25	-	-	quant.	-	-
Controls	12	20	-	-	25	Ar	-	25	-	trace	>99	-	-
Controls	13	20	2	-	25	Ar	-	25	-	-	quant.	-	-
Controls	14	20	-	-	25	Ar	450	25	-	trace	>99	-	-
Controls	15	-	2	-	25	Ar	450	25	-	-	quant.	-	-

Table S8 Optimization of the n+2 ring expansion with rearomatization.

Unsuccessful Substrates

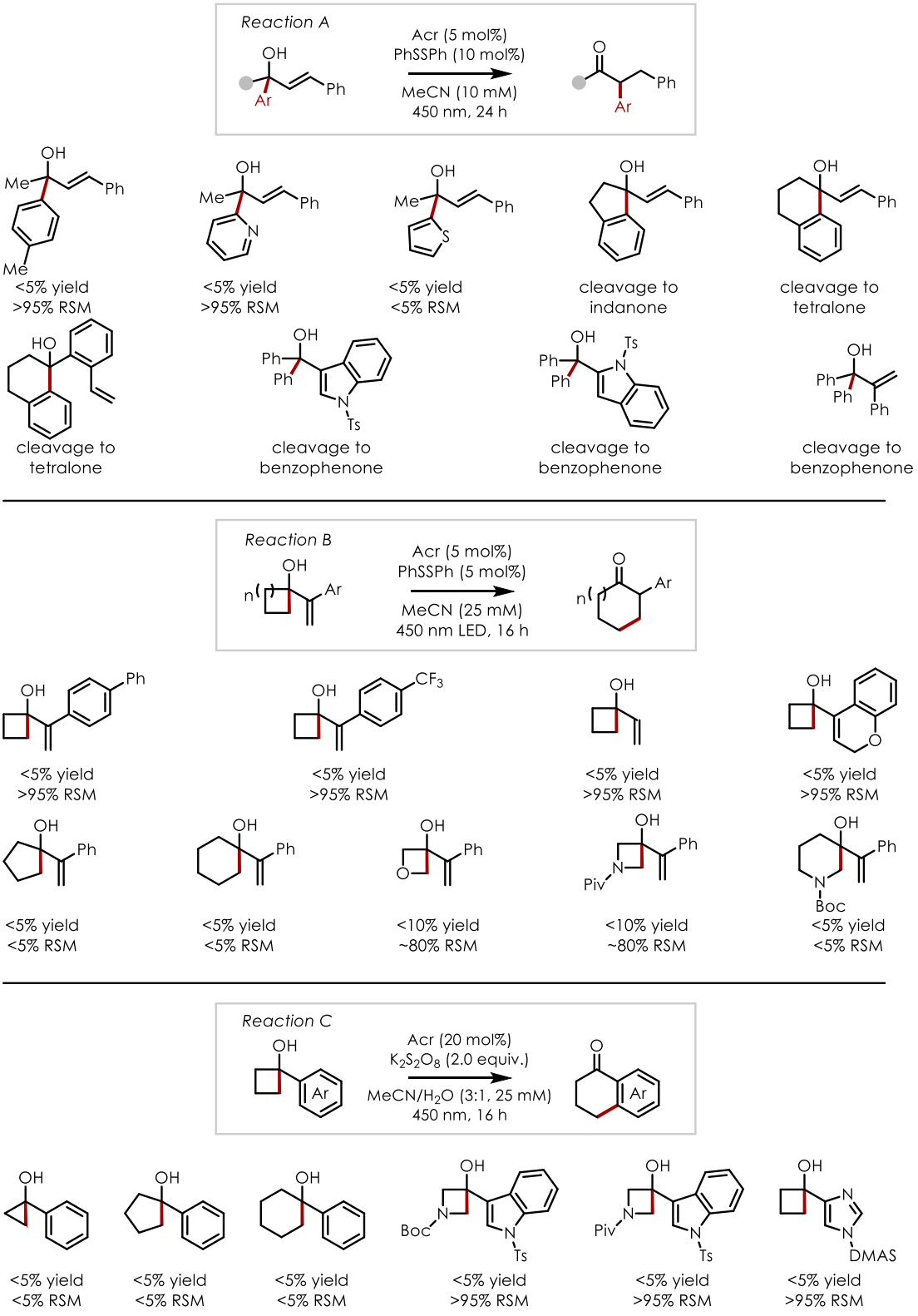


Figure S5 Unsuccessful substrates for reactions A, B, and C with desired migrating bond highlighted in red and experimental observations noted below each compound.

Batch Reaction Information

Batch reaction procedure (gram scale)

To a flame-dried 250 mL oval-shaped recovery flask containing a magnetic stir bar was added 1-(1-phenylvinyl)cyclobutan-1-ol (1.00 g, 5.74 mmol, 1.0 equiv.), 3,6-di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (165 mg, 0.29 mmol, 5 mol%), and diphenyl disulfide (63 mg, 0.29 mmol, 5 mol%). Acetonitrile (115 mL, 0.05 M) was added and the flask was sealed with a rubber septum. The reaction was then sparged with argon for 30 minutes and further sealed with parafilm and electrical tape. Two 456 nm Kessil lamps were placed approximately 4 cm from the flask on opposing sides and a fan was pointed toward the reaction vessel at a distance of approximately 15 cm (Figure S6). The reaction was then stirred vigorously under irradiation by the Kessil lamps for 20 hours, after which thin layer chromatography revealed complete consumption of starting material. The crude reaction mixture was then concentrated en vacuo and purified by column chromatography (silica: 40-63 μm; 0 to 10% ethyl acetate in hexanes) to afford **5** (615 mg; 3.6 mmol; 62% yield) as a crystalline white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[18]

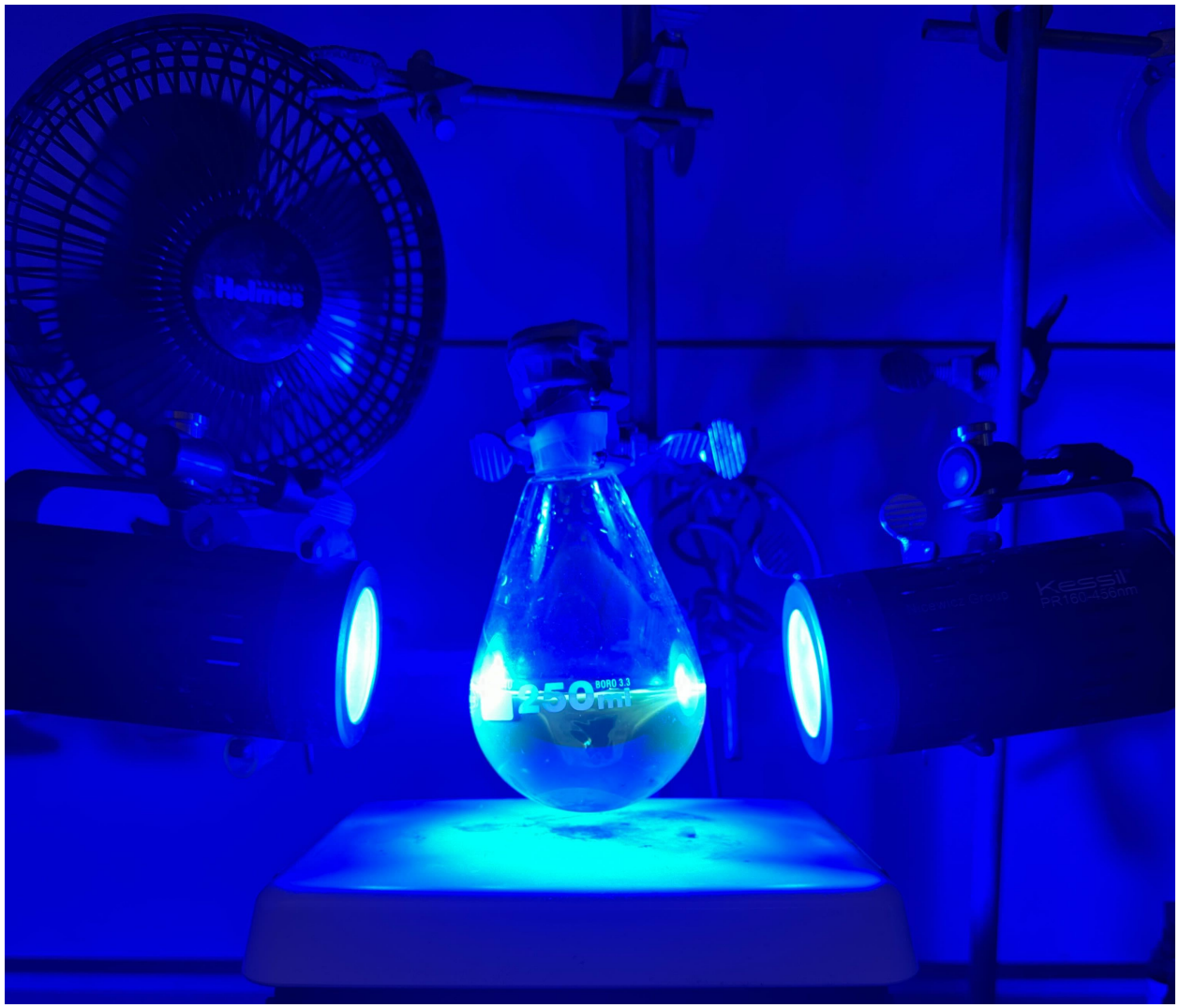


Figure S6 Bach reaction setup highlighting the placement of the 456 nm Kessil lamps, stir plate, and fan. Not pictured is a protective shield to contain the irradiation.

Continuous Flow Reaction Information

Continuous flow setup diagram

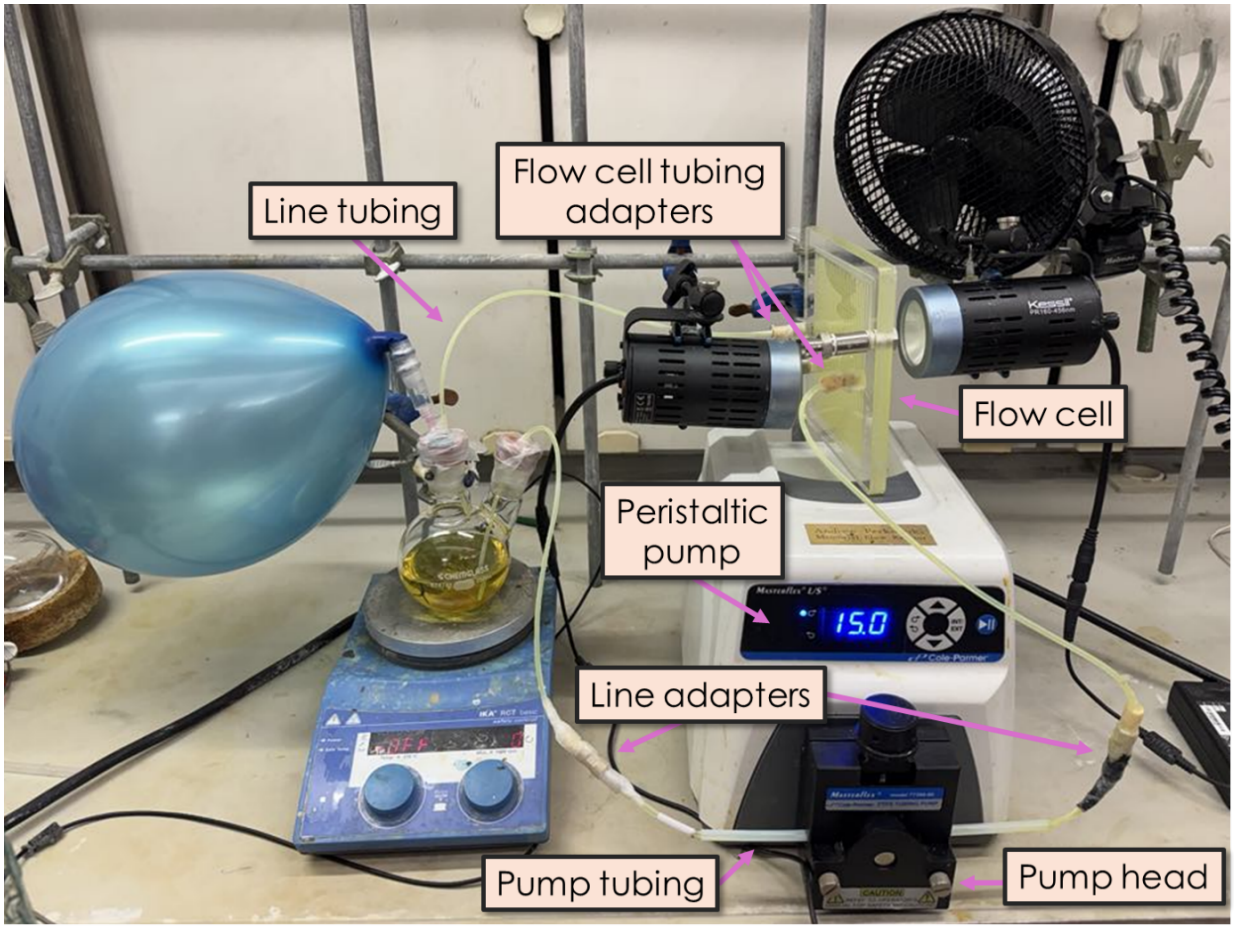


Figure S7 Diagram of continuous flow setup with key parts labeled.

List of flow equipment

- Flow cell: Little Things Factory Gmbh XXL-ST-02 Microreactor
- Peristaltic pump: Masterflex L/S Precision Variable-Speed Console Drive (Cole-Parmer # 76403-054)
- Pump head: Masterflex L/S Rigid PTFE-Tubing Pump Head (Cole-Parmer # EW-77390-00)
- Pump tubing: Masterflex PTFE-Tubing 4 mm O.D. (Cole-Parmer # EW-77390-50)
- Line tubing: PTFE Tubing 1/16” I.D., 1/8” O.D. (Cole-Parmer # WU-06605-27)
- Flow cell tubing adapters: 1/4-28 flangeless fitting/ferrule for 1/8" O.D. tubing (Sigma-Aldrich SUPELCO # 58686)
- Line adapters: 4MM PTFE Male NPT Compression Adapter (Cole-Parmer # WU-31321-62) and 1/8” O.D. to 1/8” PTFE Female NPT Compression Adapter (Cole-Parmer # EW31320-50)

Analytical description of the continuous flow system

Table S9 shows the relevant physical parameters of the flow cell along with the associated analytical descriptions and the equations used for their calculation. The flow rate was measured in triplicate by recording the volume dispensed by the pump over the course of one minute. Of particular note is the residence time of 6.47 minutes which indicates that each portion of the reaction mixture spends 6.47 minutes passing through the flow cell and being irradiated by the LEDs over the course of a single cycle. From this value it can be calculated that it takes ~15 cycles for the entire volume (115 mL for 1.0 g scale) of the reaction mixture to pass through the flow cell and that over the course of 16 hours, the entire reaction mixture passes through the flow cell ~10 times. This leads to a total time of exposure to irradiation in the flow cell of 63 minutes for each portion of the reaction mixture.

Continuous Flow - 1.0 g Scale	
Cell volume (mL)	7.50
Flow rate (ml/min)	1.16
Reaction time (min)	960
Total volume (mL)	115.00
Residence time (min)	6.47
Cycle time (min)	99.14
Processed volume (mL)	1113.60
Reactor turnovers	148.48
Number of cycles for total volume	15.33
Total number of cycles	9.68
Total solution exposure (min)	63

Equation S8 $t_{residence} = \frac{V_{cell}}{FR}$

Equation S9 $t_{cycle} = \frac{V_{tot}}{FR}$

Equation S10 $V_{proc} = FR \times t_{reaction}$

Equation S11 $reactor\ turnovers = \frac{V_{proc}}{V_{cell}}$

Equation S12 $\#\ of\ cycles\ for\ V_{tot} = \frac{V_{tot}}{V_{cell}}$

Equation S13 $\#\ of\ cycles = \frac{t_{reaction}}{t_{cycle}}$

Equation S14 $t_{exposure} = t_{residence} \times \#\ of\ cycles$

Table S9 Flow cell parameters, analytical description of the flow system, and relevant equations for calculation of the descriptors.

Continuous flow procedure (gram scale)

Pre-reaction washing / sparging: Without attaching the reaction flask, the continuous flow synthesis system was set up as shown above. The inlet and outlet tubing was then connected to a flame-dried 250 mL round bottom flask containing 100 mL anhydrous acetonitrile through a hole punctured in the septum. An argon balloon and a vent needle were then attached to the round bottom flask and the pump was turned on with a speed of 100 rpm. This pre-reaction sparging procedure was conducted for one hour before each run.

Reaction setup: To a flame-dried 250 mL two-necked round bottom flask was added 1-(1-phenylvinyl)cyclobutan-1-ol (1.00 g; 5.74 mmol; 1.0 equiv.), 1,2-diphenyldisulfane (63 mg; 287 µmol; 5 mol%), and 3,6-di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (165 mg; 287 µmol; 5 mol%) followed by the addition of an argon balloon attached via a 6 inch needle. 115 mL anhydrous acetonitrile (0.05 M in 1-(1-phenylvinyl)cyclobutan-1-ol) was then added to the reaction mixture and the 6-inch needle was lowered into the solvent, followed by the attachment of a vent needle. The reaction mixture was sparged in this manner for 20 minutes. Next, the pump was turned off and the outlet of the pre-reaction sparging solution was removed and attached to the reaction flask. After ensuring connection, the pump was turned back on and the remaining sparging solution was removed by visually inspecting as the yellow reaction mixture proceeded through the flow cell. Upon reaching the end of the flow cell, the pump was again turned off and the inlet tubing from the sparging solution was removed and inserted into the reaction flask. The degassing procedure was then repeated – this time with the reaction mixture – for 30 minutes before turning on the 456 nm LEDs. After this time, the vent needle was removed, the argon needle raised above the solvent level, and the pump speed reduced to 15 rpm. A protective shield was placed over the

irradiated portion, also ensuring that the reaction flask itself was not irradiated, and the LED Kessil lamps were turned on. The reaction was then allowed to proceed for 16 hours, after which TLC revealed the complete consumption of starting material. The lights and the pump were then turned off and the outlet tubing was removed and submerged in an Erlenmeyer flask containing acetonitrile. The pump was then turned on and an excess of acetonitrile was used to flush the contents of the flow cell into the reaction flask. After disconnecting the flask from the flow system, the solvent was then removed via rotary evaporation and the crude reaction purified by column chromatography (silica: 40-63 μm; 0 to 10% ethyl acetate in hexanes) to afford **5** (477 mg; 2.8 mmol; 48% yield) as a crystalline white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[18]

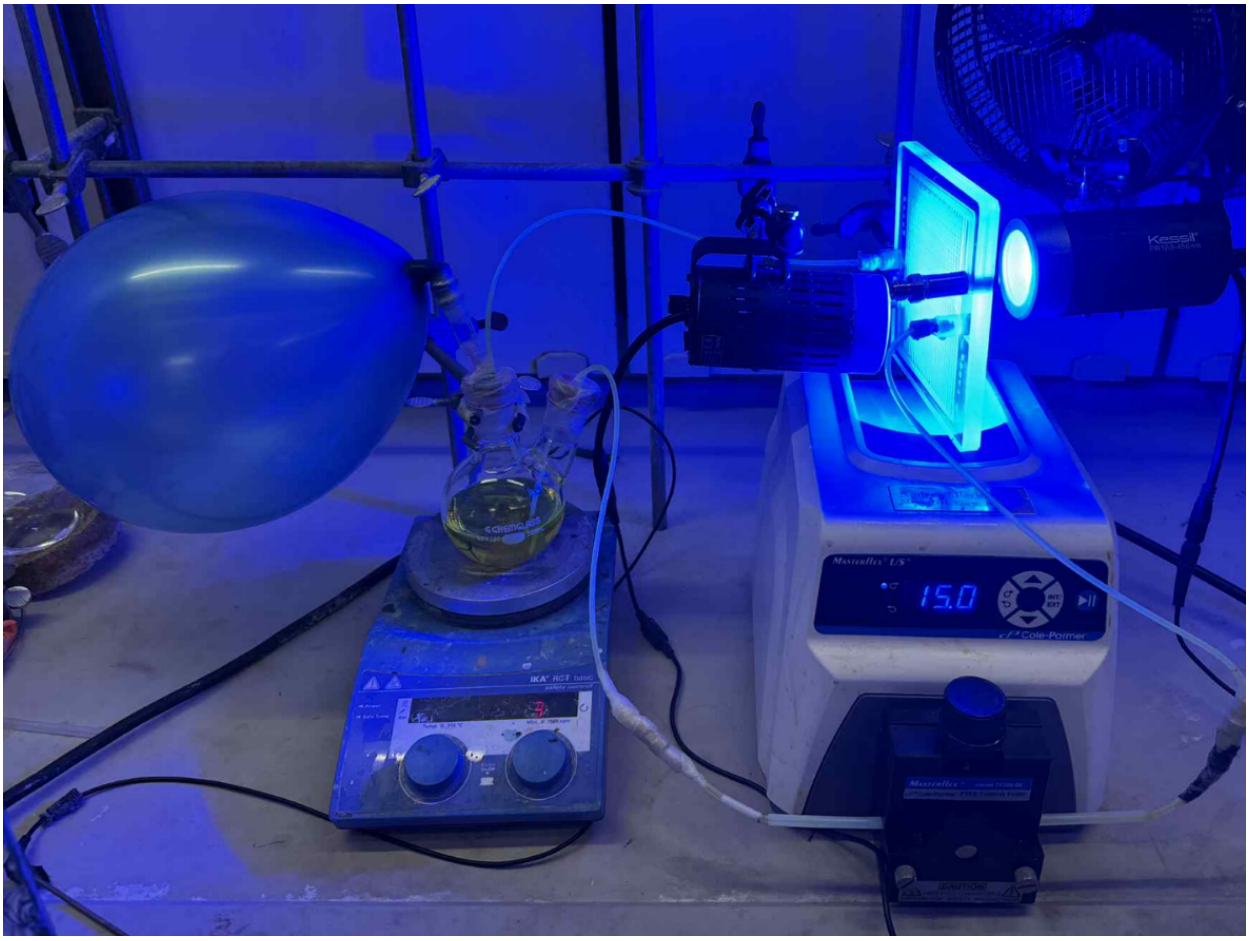
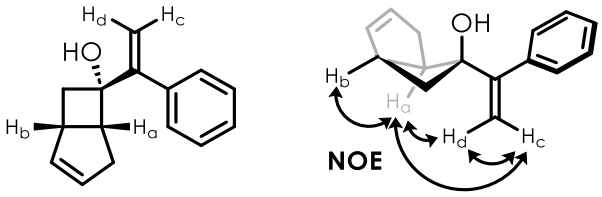


Figure S8 Continuous flow setup highlighting the placement of the LED lamps. The protective shield is not shown and should be placed over the Kessil lamps, ensuring that the reaction flask doesn't receive irradiation. Kessil lamps are offset to provide full coverage of the flow cell.

Stereochemistry Assignment

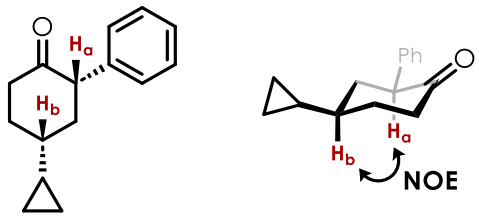
Compound S16



Proton	∂ (ppm)	m (apparent)	J (Hz)	NOE
H_a	3.29	ddq	8.7, 7.3, 1.4	**NOE to H_b, H_c, and H_d**
H_b	3.09	m	n/a	**NOE to H_a**
H_c	5.36	d	0.9	**NOE to H_a**
H_d	5.35	d	0.9	**NOE to H_c**

Table S10 An NOE between H_a and H_b suggests a cis ring fusion. Additionally, the NOE between H_a and $H_{c/d}$ suggest a trans relationship between the styrene and the ring fusion.

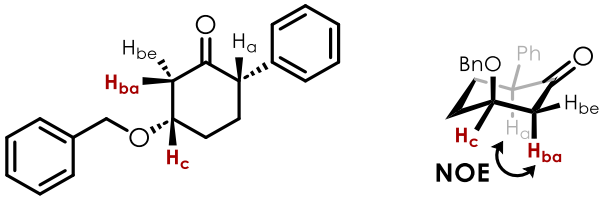
Compound S36



Proton	∂ (ppm)	m (apparent)	J (Hz)	NOE
H_a	3.58	dd	**13.4**, 5.4	**NOE to H_b**
H_b	2.26	ddt	**13.5**, 6.1, 3.1	**NOE to H_a**

Table S11 A cis stereochemical relationship between the phenyl and cyclopropyl substituents is suggested due to the large J Values for both H_a and H_b as well as the presence of an NOE between H_a and H_b.

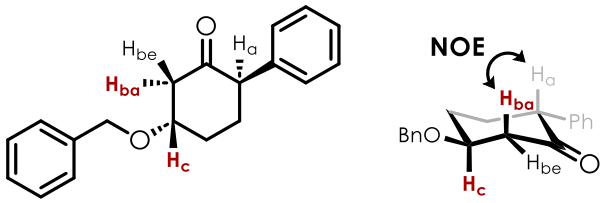
Compound 11 Diastereomer 2 (major)



Proton	∂ (ppm)	m (apparent)	J (Hz)	NOE
H_a	3.59	dd	12.1, 5.7	**NOE to H_{ba}**
H_{ba}	2.62	dd	14.3, 3.4	**NOE to H_a**
H_{be}	2.86	ddd	14.3, 3.9, 2.3	n/a
H_c	4.16	p	3.6	n/a

Table S12 A *cis* stereochemical relationship between the Ph and OBn substituents is suggested by the presence of axial-axial NOE interactions between H_a and H_{ba} and the lack of a large coupling constant between H_c and H_{ba} as found in **11** Diastereomer 1.

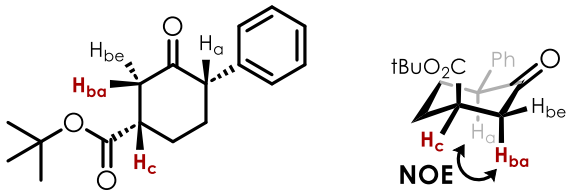
Compound 11 Diastereomer 1 (minor)



Proton	∂ (ppm)	m (apparent)	J (Hz)	NOE
H_a	3.58	dd	11.4, 5.7	**NOE to H_{ba}**
H_{ba}	2.59	ddd	13.3, **10.4**, 1.2	**NOE to H_a**
H_{be}	2.97	ddd	13.3, 4.6, 2.0	n/a
H_c	3.80	tt	**9.8**, 4.4	n/a

Table S13 A *trans* stereochemical relationship between the Ph and OBn substituents is suggested by the presence of axial-axial NOE interactions between H_a and H_{ba} and a large coupling constant between H_c and H_{ba}.

Compound 13 Diastereomer 2 (major)



Proton	∂ (ppm)	m (apparent)	J (Hz)	NOE
H_a	3.54	dd	9.9, 5.7	**1D NOE to H_{ba}**
H_{ba}	2.49	ddd	14.8, 5.6, 1.1	**1D NOE to H_a**
H_{be}	2.73	ddd	14.8, 5.1, 1.4	n/a
H_c	3.02	td	5.8, 3.2	n/a

Table S14 A *cis* stereochemical relationship between the Ph and Boc substituents is suggested by the presence of axial-axial NOE interactions between H_a and H_{ba} and the lack of a large coupling constant between H_c and H_{ba}.

Compound 13 Diastereomer 1 (minor)

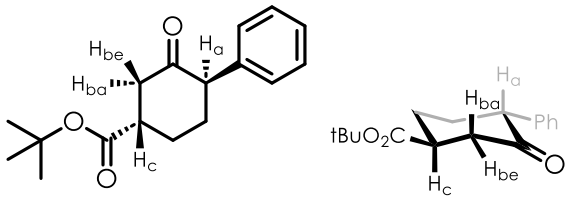
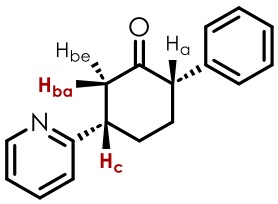
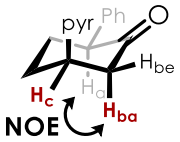


Table S15 A *trans* stereochemical relationship between the Ph and CO_2tBu substituents was inferred by consideration of the interactions found in **13** Diastereomer 2.

Compound 15

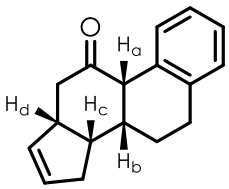


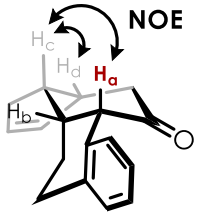


Proton	∂ (ppm)	m (apparent)	J (Hz)	NOE
H_a	3.74	dd	12.6, 5.5	**1D NOE to H_{ba}**
H_{ba}	3.02	td	13.3, 1.1	**1D NOE to H_a**
H_{be}	2.72	ddd	13.6, 4.2, 1.4	n/a
H_c	3.38 – 3.24	m	n/a	n/a

Table S16 A *cis* stereochemical relationship between the Ph and pyridine substituents is suggested by the presence of axial-axial NOE interactions between H_a and H_{ba} and the lack of a large coupling constant between H_c and H_{ba}.

Compound 20





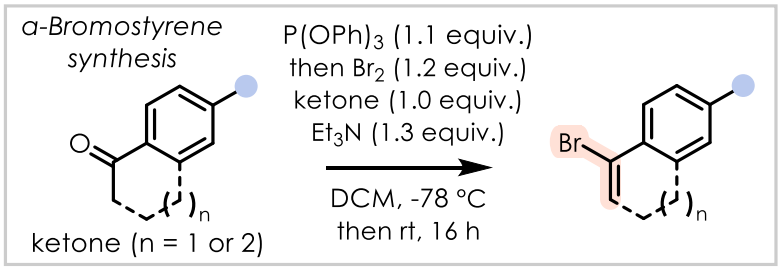
Proton	∂ (ppm)	m (apparent)	J (Hz)	NOE
H_a	3.56	d	**5.6**	**NOE to H_c**
H_b	2.39	m	n/a	
H_c	2.81	ddt	8.5, 6.1, 4.3	**NOE to H_a and H_d**
H_d	3.26	dddt	10.7, 7.1,4.7, 2.3	**NOE to H_c**

Table S17 A strong NOE is observed between H_c and H_d. Additionally, an NOE between H_C and H_A is observed via 1D NOE at 3.58ppm. This NOE information in conjunction with the small J value for H_a indicates the all cis configuration depicted.

Synthetic Methods and Characterization Data

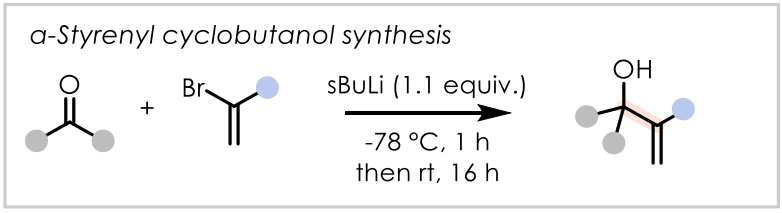
General Procedures

General Procedure for the Synthesis of α-bromostyrene derivatives



A flame dried flask equipped with a magnetic stir bar was purged with argon and charged with triphenyl phosphite (1.1 equiv.) along with dichloromethane (0.3 M).The reaction was cooled to -78 °C and bromine (1.2 equiv.) was added dropwise, resulting in an orange-colored solution. The corresponding benzylic ketone (1.0 equiv.) was added dropwise (if liquid), or portion wise (if solid) followed by the dropwise addition of triethylamine (1.3 equiv.) and the reaction was allowed to warm to room temperature and stirred for an additional 16 hours. After this period, the reaction was refluxed for 2 hours and quenched with sodium sulfite. The organic layer was then separated and washed with saturated sodium thiosulfate (aq.), 1 M hydrochloric acid, saturated sodium bicarbonate (aq.), water, and saturated sodium chloride (aq.). The organic layer was then dried over sodium sulfate, the solids filtered off, and the solvent removed via rotary evaporation. The product was further purified using column chromatography, the conditions of which are specified with their respective entries.

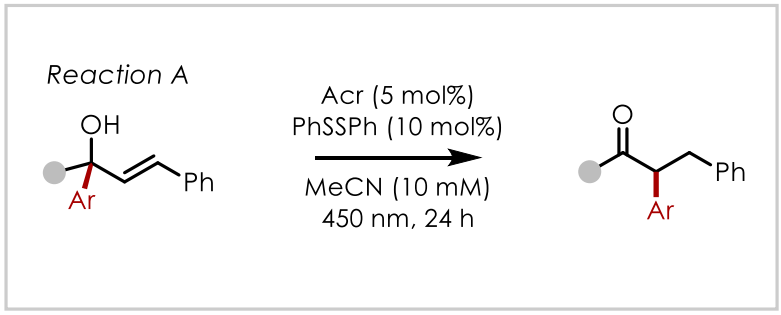
General Procedure for the Synthesis of α-Styrenyl Cyclobutanols

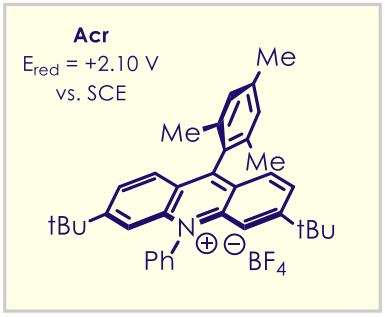


A flame dried flask equipped with a magnetic stir bar was purged with argon and charged with the corresponding alpha-bromostyrene derivative (1.0 equiv.) in diethyl ether (0.1 M). The reaction was cooled to -78 °C and freshly titrated *sec*-butyllithium (1.1 equiv.) was added dropwise. The reaction was allowed

to stir for 1 hour at -78 °C, followed by the dropwise addition of the corresponding cyclobutanone (1.5 equiv.). In the case of cyclobutanones that were solid, the compound was dissolved in a minimal amount of tetrahydrofuran before being added dropwise to the reaction mixture. The reaction was then allowed to warm to room temperature and stirred for an additional 16 hours, after which the reaction was quenched with saturated ammonium chloride solution followed by extraction using ethyl acetate (3x). The combined organic layers were then washed with brine, dried over sodium sulfate, the solids filtered off, and the solvent removed via rotary evaporation to yield the crude product. The product was further purified using column chromatography, the conditions of which are specified with their respective entries.

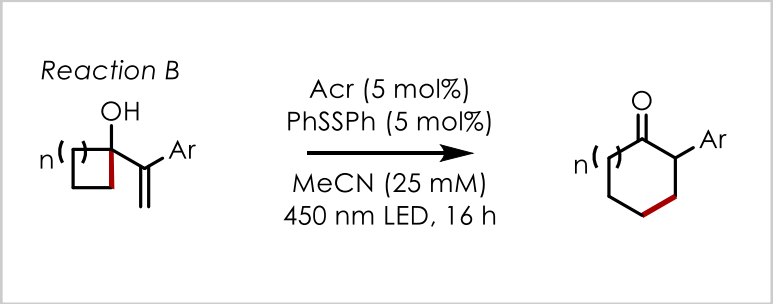
General Procedure for Reaction A

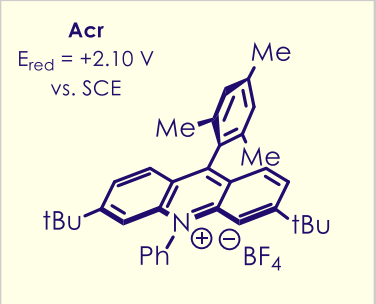




The equivalents of reagents are as listed here unless otherwise stated in the individual entries. The relevant tertiary alcohol (0.05 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of diphenyl disulfide (1.10 mg; 5 µmol; 10 mol%) and photocatalyst **Acr** (1.45 mg; 2.5 µmol; 5 mol%). Anhydrous acetonitrile (5 mL; 10 mM in tertiary alcohol) was then added and the reaction mixture was sparged with argon for 10 minutes, and further sealed with electrical tape and parafilm. The vial was then placed in a SynLED well (450 nm) and stirred for 24 hours. After this time, the solvent was removed by rotary evaporation and the resulting mixture was purified by column chromatography. The eluant used is specified for each individual entry. For isolated yields, four 0.05 mmol reactions were combined for a total of 0.2 mmol. For percent conversions, NMR yields were recorded by combining two 0.05 mmol reactions – for a total of 0.1 mmol – and adding 9.4 µL hexamethyldisiloxane standard.

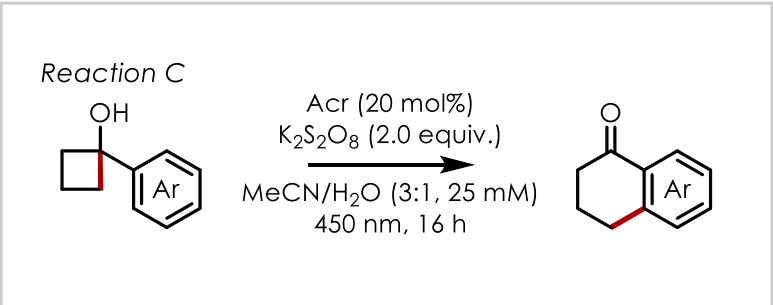
General Procedure for Reaction B

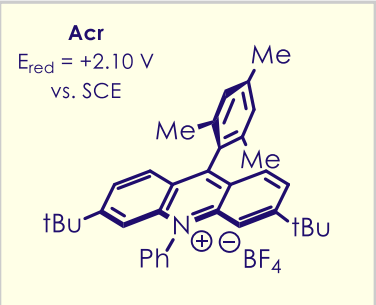




The equivalents of reagents are as listed here unless otherwise stated in the individual entries. The relevant cyclobutanol (0.1 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of diphenyl disulfide (1.10 mg; 5 µmol; 5 mol%) and photocatalyst **Acr** (2.90 mg; 5 µmol; 5 mol%). Anhydrous acetonitrile (4 mL; 25 mM in cyclobutanol starting material) was then added and the reaction mixture was sparged with argon for 10 minutes. The vial was further sealed with electrical tape and parafilm, then placed in a SynLED well (450 nm) and stirred for 16 hours. After this time, the solvent was removed by rotary evaporation and the resulting mixture was purified by column chromatography. The eluant used is specified for each individual entry. For isolated yields, two 0.1 mmol reactions were combined for a total of 0.2 mmol. For percent conversions, NMR yields were recorded using the individual 0.1 mmol reactions and adding 9.4 µL hexamethyldisiloxane standard.

General Procedure for Reaction C

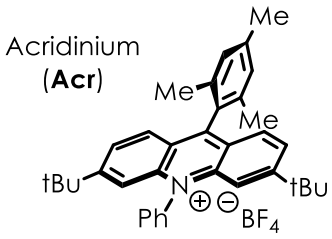




The equivalents of reagents are as listed here unless otherwise stated in the individual entries. The relevant cyclobutanol (0.1 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of potassium persulfate (54.1 mg; 0.2 mmol; 2.0 equiv.) and photocatalyst **Acr** (11.48 mg; 20 µmol; 20 mol%). A 3:1 mixture of acetonitrile (3 mL) and DI water (1 mL) was then added (overall

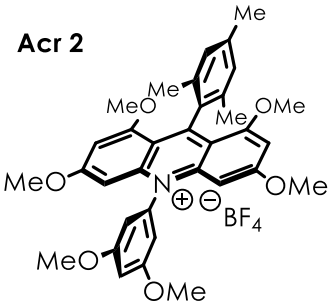
concentration: 25 mM in cyclobutanol starting material) and the reaction mixture was sparged with argon for 10 minutes. The reaction vessel was further sealed with electrical tape and parafilm. The vial was then placed in a SynLED well (450 nm) and stirred for 16 hours. After this time, the solvent was removed by rotary evaporation and the resulting mixture was purified by column chromatography. The eluant used is specified for each individual entry. For isolated yields, two 0.1 mmol reactions were combined for a total of 0.2 mmol. For percent conversions, NMR yields were recorded using the individual 0.1 mmol reactions and adding 9.4 μL hexamethyldisiloxane standard.

Preparation of Photoredox Catalysts



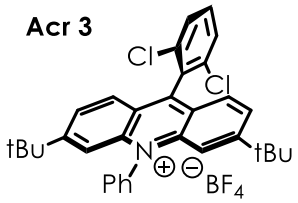
3,6-di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (Acr): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[19]

Reference: A. R. White, L. Wang and D. A. Nicewicz, *Synlett*, 2019, **30**, 827–832. DOI: 10.1055/s-0037-1611744



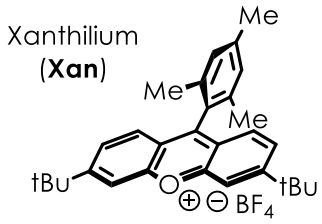
10-(3,5-dimethoxyphenyl)-9-mesityl-1,3,6,8-tetramethoxyacridin-10-ium tetrafluoroborate (Acr-2): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[19]

Reference: A. R. White, L. Wang and D. A. Nicewicz, *Synlett*, 2019, **30**, 827–832. DOI: 10.1055/s-0037-1611744



3,6-di-tert-butyl-9-(2,6-dichlorophenyl)-10-phenylacridin-10-ium tetrafluoroborate (Acr-3): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[19]

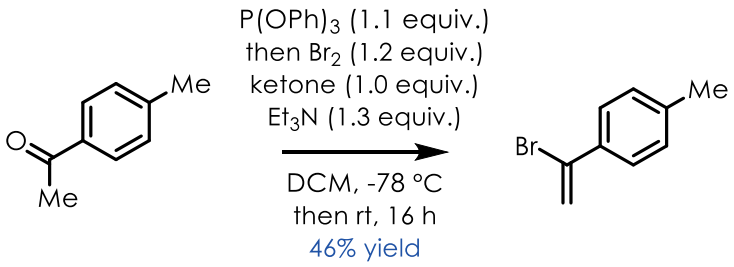
Reference: A. R. White, L. Wang and D. A. Nicewicz, *Synlett*, 2019, **30**, 827–832. DOI: 10.1055/s-0037-1611744



3,6-di-tert-butyl-9-mesitylxanthylium tetrafluoroborate (Xan): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[19]

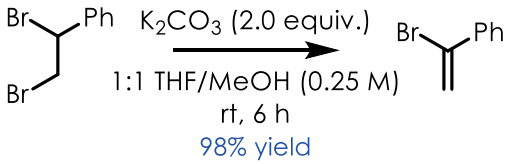
Reference: A. R. White, L. Wang and D. A. Nicewicz, *Synlett*, 2019, **30**, 827–832. DOI: 10.1055/s-0037-1611744

Preparation of Miscellaneous Starting Materials



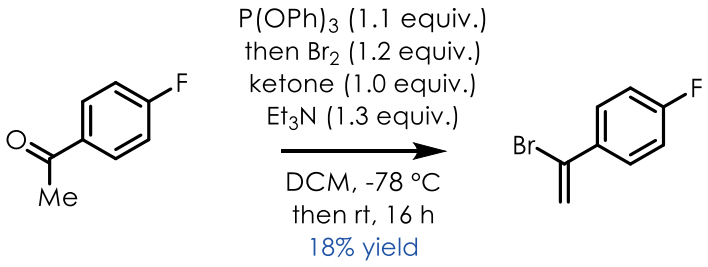
1-(1-bromovinyl)-4-methylbenzene (S4.1): Prepared according to the General Procedure for the Synthesis of α-Bromostyrene Derivatives on a 25 mmol scale. Purified by column chromatography (silica: 40-63 μm; 100% hexanes) to afford **S4.1** (2.3 g; 11.7 mmol; 46% yield) after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[20]

Reference: K. L. Wilson, J. Murray, C. Jamieson and A. J. B. Watson, *Synlett*, 2017, **29**, 650–654. DOI: 10.1055/s-0036-1589143



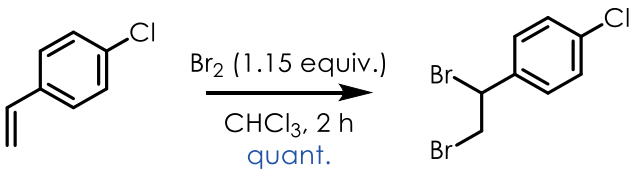
(1-bromovinyl)benzene (S5.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[21]

Reference: D. L. Cain, C. McLaughlin, J. J. Molloy, C. Carpenter-Warren, N. A. Anderson and A. J. B. Watson, *Synlett*, 2018, **30**, 787–791. DOI: 10.1055/s-0037-1611228



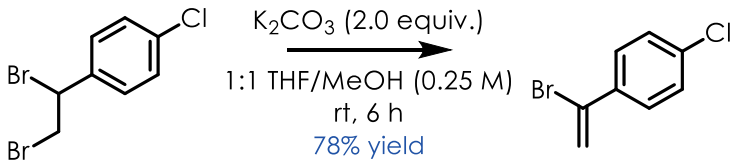
1-(1-bromovinyl)-4-fluorobenzene (S6.1): Prepared according to the General Procedure for the Synthesis of α-Bromostyrene Derivatives on a 20 mmol scale. Purified by column chromatography (silica: 40-63 μm; 100% hexanes) to afford **S6.1** (710 mg; 3.5 mmol; 18% yield) after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[22]

Reference: D. Shen, D. Cao, R. Zhang, P. Bai and Z. Liu, *Org. Biomol. Chem.*, 2024, **22**, 4062–4066. DOI: 10.1039/D4OB00608A



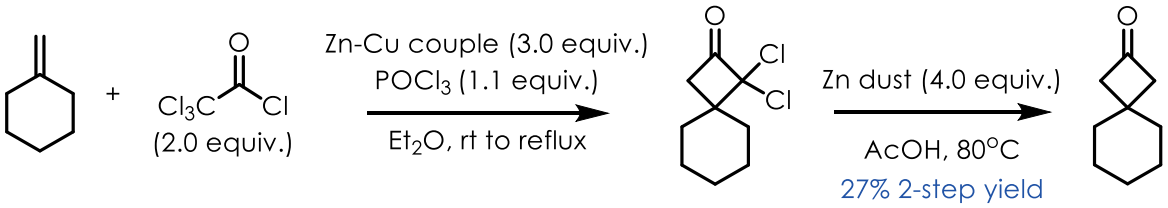
1-chloro-4-(1,2-dibromoethyl)benzene (S7.2): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[20]

Reference: K. L. Wilson, J. Murray, C. Jamieson and A. J. B. Watson, *Synlett*, 2017, **29**, 650–654. DOI: 10.1055/s-0036-1589143



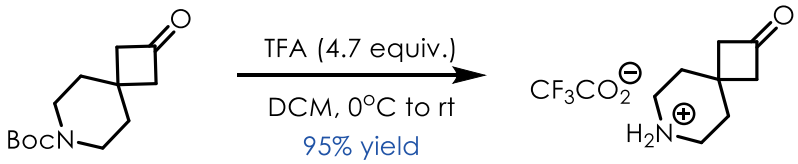
1-(1-bromovinyl)-4-chlorobenzene (S7.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[20]

Reference: K. L. Wilson, J. Murray, C. Jamieson and A. J. B. Watson, *Synlett*, 2017, **29**, 650–654. DOI: 10.1055/s-0036-1589143

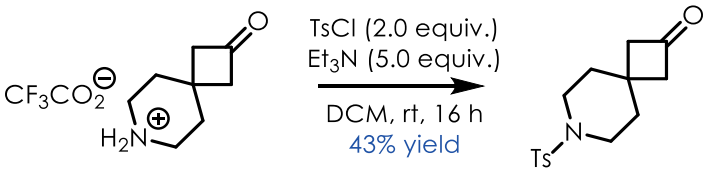


Spiro[3.5]nonan-2-one (S8.1): Prepared according to a known literature procedure.[23] Spectral data were found to be in agreement with those reported in the literature.[24]

References: H. Zhang, X. Lv, H. Yu, Z. Bai, G. Chen and G. He, *Org. Lett.*, 2021, **23**, 3620–3625. DOI: 10.1021/acs.orglett.1c01007. I. Tomiya, Y. Wu and K. Hyodo, *Adv. Synth. Catal.*, 2024, **366**, 1606–1614. DOI: 10.1002/adsc.202301421.

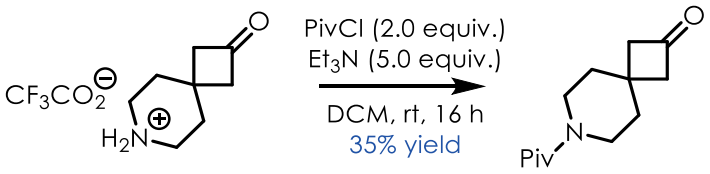


2-oxo-7-azaspiro[3.5]nonan-7-ium 2,2,2-trifluoroacetate (S9.2): To a 100 mL round bottom flask charged with a magnetic stir bar were added tert-butyl 2-oxo-7-azaspiro[3.5]nonane-7-carboxylate, (2.0 g, 8.4 mmol, 1 equiv.) and dichloromethane (30 mL 0.25 M). The reaction was cooled to 0 °C and trifluoroacetic acid was added dropwise (3.0 mL, 39 mmol, 4.7 equiv.). The reaction was allowed to warm to room temperature overnight. The stir bar was removed and the reaction was concentrated en vacuo to yield product **S9.2** as a yellow oil and used crude without additional purification. (2.0 g, 95%)



7-tosyl-7-azaspiro[3.5]nonan-2-one (S9.1): To a stirred solution of 2-oxo-7-azaspiro[3.5]nonan-7-ium 2,2,2-trifluoroacetate (1.6 g; 6.3 mmol; 1.0 equiv.) in dichloromethane (25 mL; 0.21 M) was added tosyl chloride (2.4 g; 12.6 mmol; 2.0 equiv.) followed by the dropwise addition of triethylamine (4.4 mL; 32 mmol; 5.0 equiv.). The reaction was allowed to stir for 16 hours, after which the reaction was quenched with saturated ammonium chloride (aq.). The aqueous layer was extracted with an additional three rounds of dichloromethane and the combined organic layers were then washed with water and saturated sodium chloride (aq.). The organic layer was then dried over sodium sulfate, filtered, and concentrated via rotary evaporation. The resulting crude reaction mixture was then purified by column chromatography (silica: 40-63 µm; gradient: 0 to 50% ethyl acetate in hexanes) to afford **S9.1** (800 mg; 2.7 mmol; 45%) as an off-white solid after being subjected to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[25]

Reference: K. Murai, H. Komatsu, R. Nagao and H. Fujioka, *Org. Lett.*, 2012, **14**, 772–775. DOI: 10.1021/ol203313n

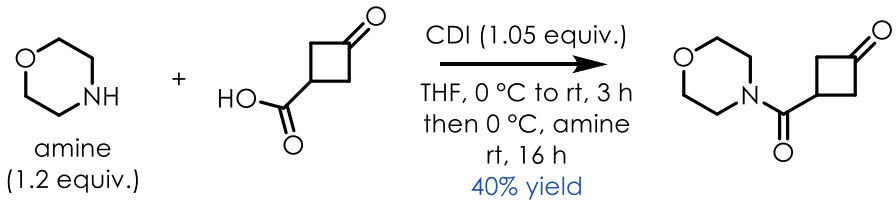


7-pivaloyl-7-azaspiro[3.5]nonan-2-one (S10.1): To a stirred solution of 2-oxo-7-azaspiro[3.5]nonan-7-ium 2,2,2-trifluoroacetate (1.6 g; 6.3 mmol; 1.0 equiv.) in dichloromethane (25 mL; 0.21 M) was added pivaloyl chloride (1.6 mL; 12.6 mmol; 2.0 equiv.) followed by the dropwise addition of triethylamine (4.4 mL; 32 mmol; 5.0 equiv.). The reaction was allowed to stir for 16 hours, after which the reaction was quenched with saturated ammonium chloride (aq.). The aqueous layer was extracted with an additional three rounds of dichloromethane, and the combined organic layers were then washed with water and saturated sodium chloride (aq.). The organic layer was then dried over sodium sulfate, filtered, and concentrated via rotary evaporation. The resulting crude reaction mixture was then purified by column chromatography (silica: 40-63 μm; gradient: 0 to 50% ethyl acetate in hexanes) to afford **S10.1** (500 mg; 2.2 mmol; 35%) as an off-white solid after being subjected to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.60 (t, *J* = 5.5 Hz, 4H), 2.83 (s, 4H), 1.73 (t, *J* = 5.6 Hz, 4H), 1.28 (s, 9H).

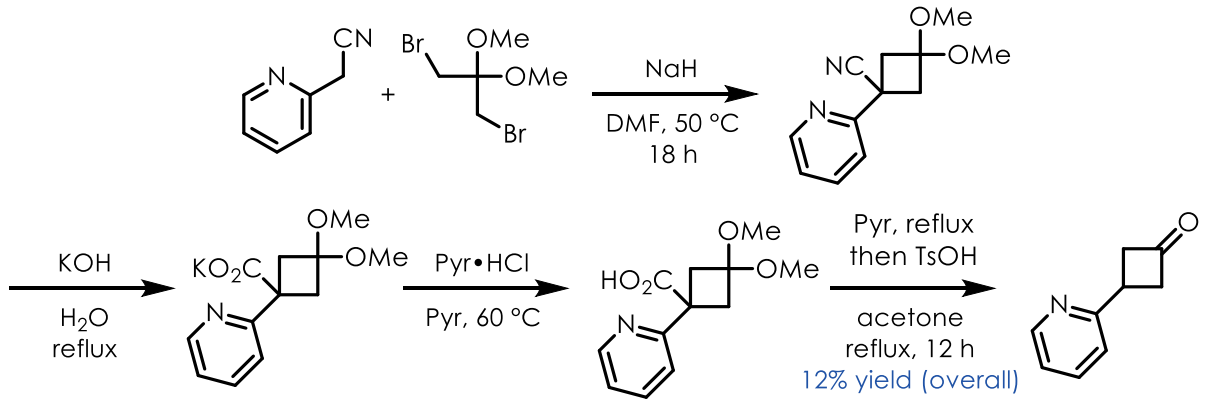
^{13}C NMR (151 MHz, $CDCl_3$): δ 206.4, 176.5, 56.7, 43.4, 38.9, 37.1, 29.6, 28.5.

HRMS (m/z): calculated for $C_{13}H_{22}NO$ $[M+H]^+$ 224.1645, found 224.1648.



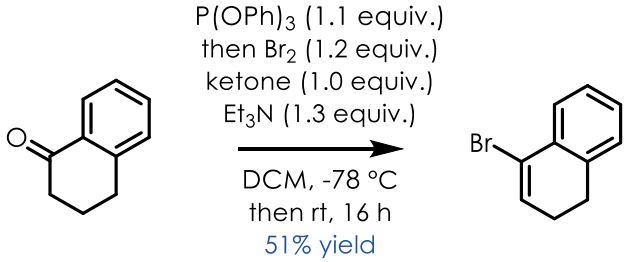
3-(morpholine-4-carbonyl)cyclobutan-1-one (S14.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[26]

Reference: K. J. Woelk, K. Dhake, N. D. Schley and D. C. Leitch, *Chem. Commun.*, 2023, **59**, 13847–13850. DOI: 10.1039/D3CC04234K



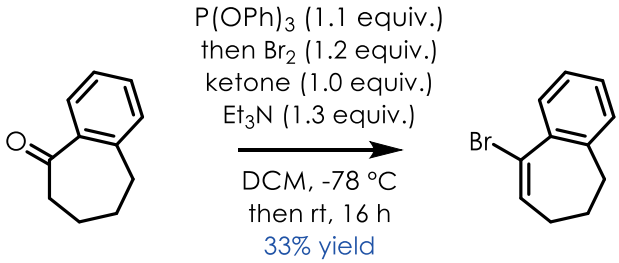
3-(pyridin-2-yl)cyclobutan-1-one (S15.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[27]

Reference: O. P. Demchuk, O. V. Hryshchuk, B. V. Vashchenko, D. S. Radchenko, V. O. Kovtunenko, I. V. Komarov and O. O. Grygorenko, *Eur. J. Org. Chem.*, 2019, **2019**, 5937–5949. DOI: 10.1002/ejoc.201901001



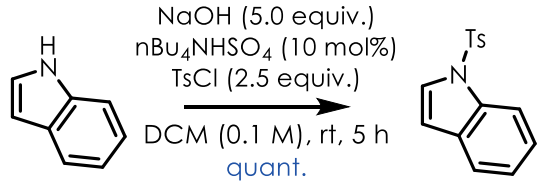
4-bromo-1,2-dihydronaphthalene (S18.1): Prepared according to the General Procedure for the Synthesis of α-Bromostyrene Derivatives on a 30 mmol scale. Purified by column chromatography (silica: 40-63 μm; 100% hexanes) to afford **S18.1** (3.2 g; 15.3 mmol; 51% yield) after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[28]

Reference: P. Woźnicki and M. Stankevič, *Eur. J. Org. Chem.*, 2021, **2021**, 3484–3491. DOI: 10.1002/ejoc.202100456



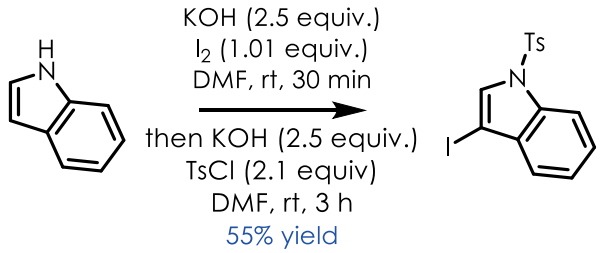
9-bromo-6,7-dihydro-5H-benzo[7]annulene (S19.1): Prepared according to the General Procedure for the Synthesis of α-Bromostyrene Derivatives on a 15 mmol scale. Purified by column chromatography (silica: 40-63 μm; 100% hexanes) to afford **S19.1** (1.1 g; 4.9 mmol; 33% yield) after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[29]

Reference: J. L. Hofstra, K. E. Poremba, A. M. Shimozono and S. E. Reisman, *Angew. Chem.*, 2019, **131**, 15043–15047. DOI: 10.1002/ange.201906815



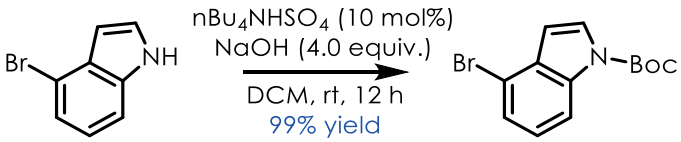
1-tosyl-1H-indole (S21.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[30]

Reference: A. Leclair, Q. Wang and J. Zhu, *ACS Catal.*, 2022, **12**, 1209–1215. DOI: 10.1021/acscatal.1c05621



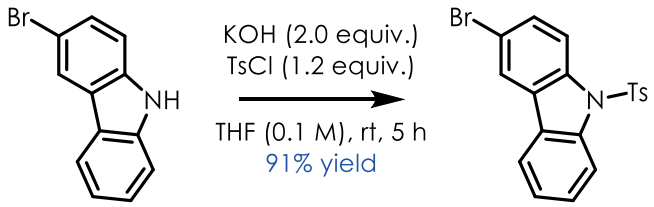
3-iodo-1-tosyl-1H-indole (S22.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[31]

Reference: K. Mitsudo, P. Thansandote, T. Wilhelm, B. Mariampillai and M. Lautens, *Org. Lett.*, 2006, **8**, 3939–3942. DOI: 10.1021/ol061373t



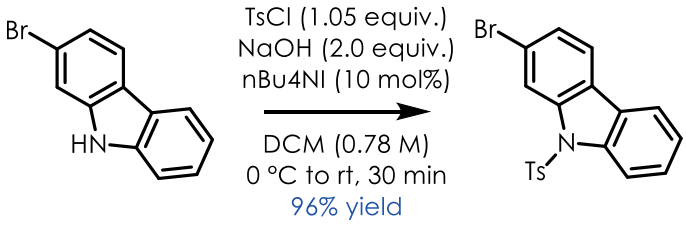
3-iodo-1-tosyl-1H-indole (S24.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[32]

Reference: S. Pandit, V. K. Pandey, A. S. Adhikari, S. Kumar, A. K. Maurya, R. Kant and N. Majumdar, *J. Org. Chem.*, 2023, **88**, 97–105. DOI: 10.1021/acs.joc.2c01869



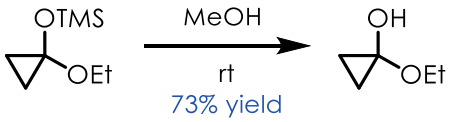
3-bromo-9-tosyl-9H-carbazole (S25.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[33]

References Y. Xu, C. Gao, J. Andréasson and M. Grøtli, *Org. Lett.*, 2018, **20**, 4875–4879. DOI: 10.1021/acs.orglett.8b02014



2-bromo-9-tosyl-9H-carbazole (S26.1): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[34]

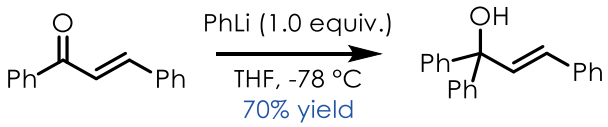
Reference R. Murmu, S. Kundu, M. Majhi, S. Pal, A. Mondal and A. Bisai, *Chem. Commun.*, 2024, **60**, 9737–9740. DOI: 10.1039/D4CC03070B



1-ethoxycyclopropan-1-ol (S32.1): Prepared according to a known literature procedure on a 10 mmol scale. Spectral data were found to be in agreement with those reported in the literature.[35]

Reference: P. A. Wender, A. J. Dyckman, C. O. Husfeld and M. J. C. Scanio, *Org. Lett.*, 2000, **2**, 1609–1611. DOI: 10.1021/ol0058691

Preparation of Tertiary Alcohol Starting Materials



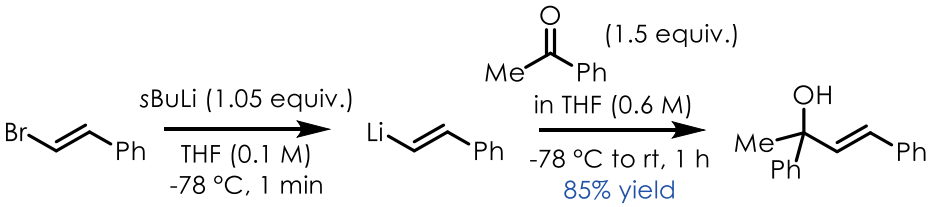
(E)-1,1,3-triphenylprop-2-en-1-ol (S1): Prepared according to a known literature procedure.[36] Spectral data were found to be in agreement with those reported in the literature.[37]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 – 7.42 (m, 5H), 7.38 – 7.24 (m, 10H), 6.85 (d, *J* = 15.9 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 2.48 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.1, 136.8, 135.3, 129.3, 128.7, 128.4, 127.9, 127.5, 127.1, 126.8, 79.5.

$E_{p/2}$ = 1.67 V vs. Ag/AgCl (1.64 V vs. SCE).

References: A.-M. Carroll, M. McCarthy, P. M. Lacey, C. P. Saunders, D. J. Connolly, A. Farrell, B. V. Rokade, R. Goddard, P. Fristrup, P.-O. Norrby and P. J. Guiry, *Tetrahedron*, 2020, **76**, 130780. DOI: 10.1016/j.tet.2019.130780. S. Liu, X. Zeng and B. Xu, *Asian J. Org. Chem.*, 2017, **6**, 507–511. DOI: 10.1002/ajoc.201700091



(E)-2,4-diphenylbut-3-en-2-ol (S2): To a flame-dried flask was added acetophenone (0.48 mL; 4.1 mmol; 1.5 equiv.) and anhydrous tetrahydrofuran (7 mL; 0.6 M in acetophenone). A separate solution of (E)-(2-bromovinyl)benzene (0.35 mL; 2.7 mmol; 1.0 equiv.) in tetrahydrofuran (27 mL; 0.1 M in (E)-(2-bromovinyl)benzene) was prepared and cooled to -78 °C, followed by the addition of sec-*butyl*-lithium (1.2 M in cyclohexane - 2.4 mL; 2.9 mmol; 1.05 equiv.). To this second solution was added the acetophenone solution, dropwise at -78 °C, followed by a 10-minute period of stirring at this temperature before removing the flask from the dry ice bath and allowing to warm to room temperature over the course of 1 hour. The reaction mixture was then quenched with a saturated ammonium chloride solution (aq.) and extracted with additional diethyl ether. The water layer was extracted three times with ether and the combined organic layers then washed with water, followed by a saturated sodium chloride solution (aq.). The organic layer was then dried over sodium sulfate and the solvent removed by rotary evaporation. The crude reaction

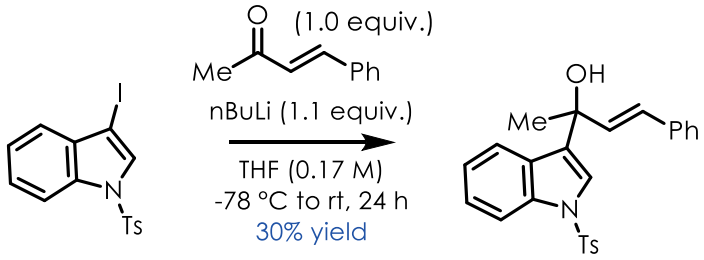
mixture was then purified by column chromatography (silica: 40-63 µm; gradient: 0 to 20% ethyl acetate in hexanes) to afford **S2** (0.52 g; 2.3 mmol; 85% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[37]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.1 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.37 – 7.25 (m, 4H), 6.69 (d, *J* = 16.1 Hz, 1H), 6.55 (d, *J* = 16.1 Hz, 1H), 2.06 (s, 1H), 1.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 136.8, 136.5, 128.7, 128.5, 127.8, 127.8, 127.2, 126.7, 125.4, 74.8, 29.9.

$E_{p/2}$ = 1.77 V vs. Ag/AgCl (1.74 V vs. SCE).

Reference: S. Liu, X. Zeng and B. Xu, *Asian J. Org. Chem.*, 2017, **6**, 507–511. DOI: 10.1002/ajoc.201700091

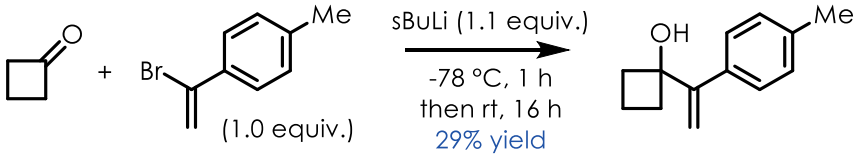


4-phenyl-3-(1-tosyl-1H-indol-3-yl)butan-2-one (S3): To a flame-dried round bottom flask was added C3-iodo-indole **S3.1** (1.36 g; 3.42 mmol) and tetrahydrofuran (13.7 mL). The flask was cooled to -78 °C followed by the addition of n-butyllithium (2.4 M in hexanes; 1.57 mL; 3.77 mmol; 1.1 equiv.) and the reaction mixture was allowed to stir for 30 minutes at that temperature. A solution of (E)-4-phenylbut-3-en-2-one (501 mg; 3.42 mmol; 1.0 equiv.) in tetrahydrofuran (6.85 mL) was then added dropwise at -78 °C, stirred for an additional 10 minutes at that temperature, and then slowly warmed to room temperature. After 1 hour at room temperature, the reaction was quenched with saturated ammonium chloride (aq.) and extracted with ethyl acetate. The organic layer was then washed with saturated sodium chloride (aq.), dried over sodium sulfate, and concentrated via rotary evaporation. The crude reaction mixture was then purified by column chromatography (silica: 40-63 µm; gradient: 5 to 10% ethyl acetate in hexanes) to afford **S3** (421 mg; 1.01 mmol; 30% yield) as an off-white solid after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.57 (s, 1H), 7.38 – 7.27 (m, 5H), 7.25 – 7.15 (m, 4H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.1, 136.6, 135.9, 135.3, 134.6, 130.1, 128.9, 128.7, 128.7, 128.2, 127.9, 127.0, 126.8, 124.8, 123.3, 122.6, 122.0, 113.8, 72.2, 29.2, 21.7.

HRMS (m/z): calculated for $C_{25}H_{23}NO_3Na$ $[M+Na]^+$ 440,1291, found 440.1288.

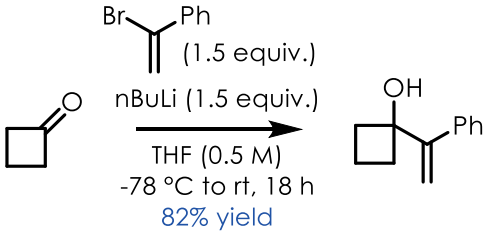


1-(1-(p-tolyl)vinyl)cyclobutan-1-ol (S4): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 6.3 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **S4** (350 mg; 1.8 mmol; 29% yield) as a yellow oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[38]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.35 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.33 (s, 2H), 2.52 – 2.44 (m, 2H), 2.35 (s, 3H), 2.25 (tdd, *J* = 9.4, 6.8, 2.9 Hz, 2H), 1.98 (dtt, *J* = 11.3, 9.3, 5.7 Hz, 1H), 1.91 (s, 1H), 1.63 (dtt, *J* = 11.0, 8.8, 6.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.2, 137.3, 136.1, 128.9, 127.5, 112.1, 78.1, 35.7, 21.1, 13.4, 13.4.

Reference: Y. Shen, H.-J. Jiang, J. Yu and L.-Z. Gong, *J. Org. Chem.*, 2024, **89**, 15341–15351. DOI: 10.1021/acs.joc.4c01872



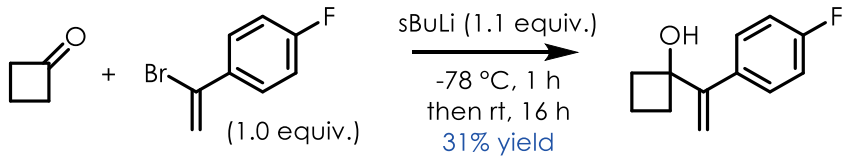
1-(1-phenylvinyl)cyclobutan-1-ol (S5): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[39]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 – 7.46 (m, 2H), 7.36 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 5.38 (d, *J* = 0.9 Hz, 1H), 5.36 (d, *J* = 0.9 Hz, 1H), 2.53 – 2.44 (m, 2H), 2.30 – 2.21 (m, 2H), 2.07 (s, 1H), 1.99 (dtt, *J* = 11.3, 9.4, 5.7 Hz, 1H), 1.64 (dtt, *J* = 11.1, 8.9, 6.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.5, 139.2, 128.3, 127.7, 127.6, 112.9, 78.2, 35.8, 13.5.

$E_{p/2}$ = 1.88 V vs. Ag/AgCl (1.85 V vs. SCE).

Reference: M. S. Dhak, D. Arunprasath, S. P. Argent and J. D. Cuthbertson, *Chem. – Eur. J.*, 2023, **29**, e202300922. DOI: 10.1002/chem.202300922



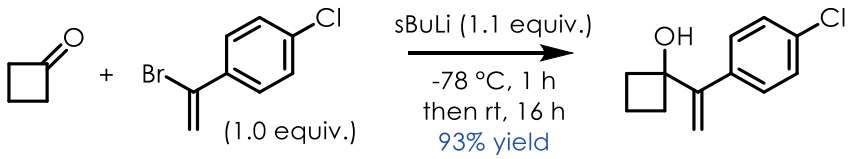
1-(1-(4-fluorophenyl)vinyl)cyclobutan-1-ol (S6): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 12.4 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **S6** (750 mg; 3.9 mmol; 29% yield) as a yellow oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[40]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.46 (m, 2H), 7.07 – 7.00 (m, 2H), 5.38 (d, *J* = 0.8 Hz, 1H), 5.35 (d, *J* = 0.8 Hz, 1H), 2.54 – 2.42 (m, 2H), 2.31 – 2.20 (m, 2H), 2.02 (dddt, *J* = 15.0, 11.3, 9.5, 4.9 Hz, 1H), 1.89 (s, 1H), 1.65 (dtt, *J* = 11.1, 8.9, 6.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.5 (d, *J* = 246.4 Hz), 151.5, 135.2 (d, *J* = 3.3 Hz), 129.4 (d, *J* = 7.7 Hz), 115.1 (d, *J* = 21.1 Hz), 113.0, 78.2, 35.7, 13.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.07 (tt, J = 8.9, 5.5 Hz).

Reference: T. Zheng, R. Chen, J. Huang, T. P. Gonçalves, K.-W. Huang and Y.-Y. Yeung, *Chem*, 2023, **9**, 1255–1269. DOI: 10.1016/j.chempr.2023.01.016



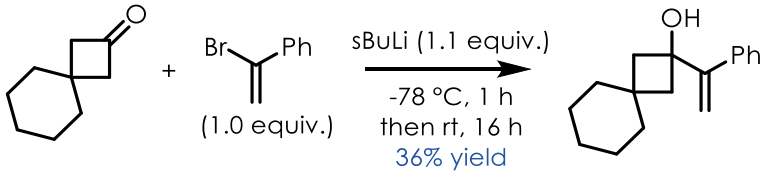
1-(1-(4-chlorophenyl)vinyl)cyclobutan-1-ol (S7): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 4.6 mmol scale. Purified by column chromatography (silica: 40-

63 µm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **S7** (890 mg; 4.3 mmol; 93% yield) as a yellow oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[38]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 – 7.41 (m, 2H), 7.29 (dt, *J* = 8.7, 2.2 Hz, 2H), 5.38 (d, *J* = 1.8 Hz, 1H), 5.37 – 5.35 (m, 1H), 2.43 (dddt, *J* = 10.2, 7.3, 4.7, 1.3 Hz, 2H), 2.27 – 2.18 (m, 2H), 2.02 – 1.92 (m, 1H), 1.86 (d, *J* = 2.0 Hz, 1H), 1.62 (dttd, *J* = 11.0, 9.0, 6.6, 2.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 151.5, 137.6, 133.5, 129.1, 128.4, 113.5, 78.1, 35.8, 13.5.

Reference: Y. Shen, H.-J. Jiang, J. Yu and L.-Z. Gong, *J. Org. Chem.*, 2024, **89**, 15341–15351. DOI: 10.1021/acs.joc.4c01872

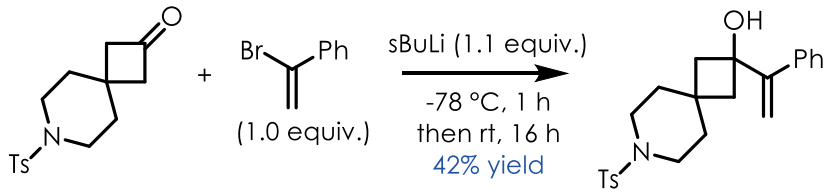


2-(1-phenylvinyl)spiro[3.5]nonan-2-ol (S8): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 2.4 mmol scale. Purified by column chromatography (silica: 40-63 µm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **S8** (210 mg; 0.87 mmol; 36% yield) as a white solid after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 – 7.43 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 5.36 – 5.34 (m, 2H), 2.30 – 2.22 (m, 2H), 2.11 – 2.01 (m, 2H), 1.81 (s, 1H), 1.69 – 1.62 (m, 2H), 1.47 – 1.39 (m, 2H), 1.37 – 1.29 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.4, 139.2, 128.3, 127.7, 127.6, 113.2, 73.8, 46.2, 39.3, 38.9, 31.5, 26.0, 23.2, 23.0.

HRMS (m/z): calculated for $C_{17}H_{22}O$ $[M+Na]^+$ 265.1563, found 265.1566.



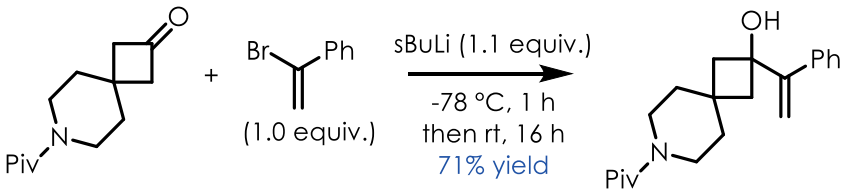
2-(1-phenylvinyl)-7-tosyl-7-azaspiro[3.5]nonan-2-ol (S9): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 2.2 mmol scale. Purified by column chromatography

(silica: 40-63 μm; gradient: 0 to 25% ethyl acetate in hexanes) to afford **S9** (360 mg; 0.91 mmol; 42% yield) as a crystalline white solid after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.58 (m, 2H), 7.48 – 7.40 (m, 2H), 7.34 – 7.27 (m, 5H), 5.34 (s, 1H), 5.27 (d, *J* = 0.7 Hz, 1H), 2.95 (t, *J* = 5.6 Hz, 2H), 2.84 (t, J = 5.6 Hz, 2H), 2.43 (s, 3H), 2.22 – 2.11 (m, 2H), 2.04 – 1.97 (m, 2H), 1.90 (dd, *J* = 6.4, 4.8 Hz, 2H), 1.82 (s, 1H), 1.57 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.8, 143.5, 138.6, 133.4, 129.8, 128.4, 127.9, 127.8, 127.5, 113.5, 73.7, 44.9, 43.4, 43.3, 37.4, 37.3, 29.4, 21.7.

HRMS (m/z): calculated for $C_{23}H_{28}NO_3S$ $[M+H]^+$ 398.1784, found 398.1789.

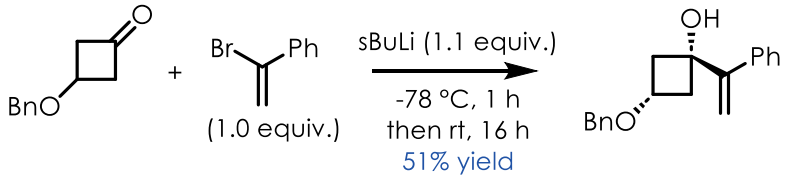


1-(2-hydroxy-2-(1-phenylvinyl)-7-azaspiro[3.5]nonan-7-yl)-2,2-dimethylpropan-1-one (S10): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 1.9 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 50% ethyl acetate in hexanes) to afford **S10** (450 mg; 1.4 mmol; 71% yield) as a colorless oil after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.45 (m, 2H), 7.36 – 7.28 (m, 3H), 5.38 (d, *J* = 0.8 Hz, 1H), 5.35 (d, *J* = 0.8 Hz, 1H), 3.58 – 3.51 (m, 2H), 3.48 – 3.41 (m, 2H), 2.38 – 2.27 (m, 2H), 2.18 – 2.11 (m, 2H), 1.94 (s, 1H), 1.82 – 1.77 (m, 2H), 1.49 – 1.42 (m, 2H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.4, 154.0, 138.8, 128.4, 127.8, 127.6, 113.5, 73.8, 45.3, 42.5, 42.4, 38.8, 38.5, 38.3, 30.4, 28.6.

HRMS (m/z): calculated for $C_{21}H_{30}NO_2$ $[M+H]^+$ 328.2271, found 328.2272.



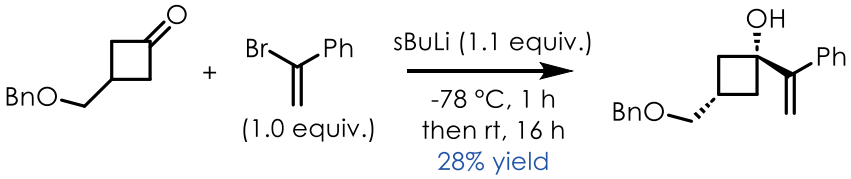
(1s,3s)-3-(benzyloxy)-1-(1-phenylvinyl)cyclobutan-1-ol (S11): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 2.2 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **S11** (310 mg; 1.1

mmol; 51% yield) as a yellow oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[41]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 – 7.46 (m, 2H), 7.39 – 7.27 (m, 8H), 5.37 (d, *J* = 1.5 Hz, 2H), 4.43 (s, 2H), 3.72 (p, *J* = 6.6 Hz, 1H), 2.86 (ddt, *J* = 13.6, 6.1, 3.8 Hz, 2H), 2.34 (ddt, *J* = 13.6, 6.2, 3.7 Hz, 2H), 2.25 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 151.8, 139.0, 138.2, 128.7, 128.6, 128.4, 128.0, 127.8, 127.8, 113.8, 71.3, 70.6, 65.8, 44.1.

Reference: L. Song, Y. Zhou, H. Liang, H. Li, Y. Lai, H. Yao, R. Lin and R. Tong, *J. Org. Chem.*, 2023, **88**, 504–512. DOI: 10.1021/acs.joc.2c02496

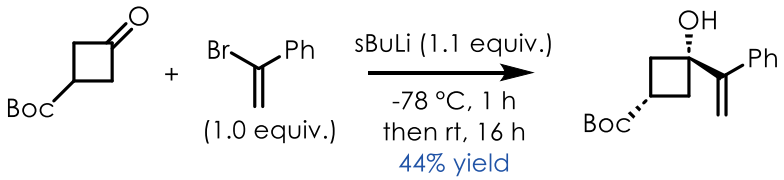


(1s,3s)-3-((benzyloxy)methyl)-1-(1-phenylvinyl)cyclobutan-1-ol (S12): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 5.5 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **S12** (450 mg; 1.5 mmol; 28% yield) as a yellow oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[41]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.45 (m, 2H), 7.38 – 7.27 (m, 8H), 5.39 (d, *J* = 0.9 Hz, 1H), 5.38 (d, *J* = 0.9 Hz, 1H), 4.58 (s, 2H), 3.56 (d, J = 4.9 Hz, 2H), 3.17 (s, 1H), 2.77 – 2.59 (m, 2H), 2.31 – 2.16 (m, 1H), 2.16 – 2.06 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 139.4, 138.3, 128.6, 128.2, 127.9, 127.9, 127.7, 127.6, 113.4, 74.9, 73.9, 73.4, 39.2, 26.6.

Reference: L. Song, Y. Zhou, H. Liang, H. Li, Y. Lai, H. Yao, R. Lin and R. Tong, *J. Org. Chem.*, 2023, **88**, 504–512. DOI: 10.1021/acs.joc.2c02496



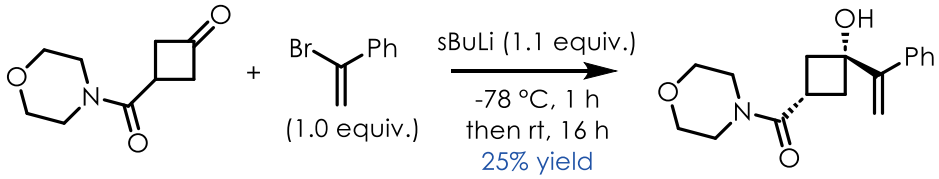
tert-butyl (1s,3s)-3-hydroxy-3-(1-phenylvinyl)cyclobutane-1-carboxylate (S13): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 5.5 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **S13** (660 mg; 2.4 mmol; 44% yield) as a yellow oil after subjection to high vacuum. Relative stereochemistry assigned by analogy.[41]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 – 7.46 (m, 2H), 7.32 (tt, *J* = 6.6, 1.1 Hz, 2H), 7.31 – 7.27 (m, 1H), 5.41 (d, *J* = 0.7 Hz, 1H), 5.39 (d, *J* = 0.7 Hz, 1H), 3.14 (s, 1H), 2.77 – 2.70 (m, 2H), 2.68 – 2.62 (m, 1H), 2.47 – 2.42 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 175.9, 151.5, 138.9, 128.3, 127.7, 127.7, 113.7, 80.9, 74.7, 39.5, 31.4, 28.2.

HRMS (m/z): calculated for $C_{17}H_{22}O_3$ $[M+Na]^+$ 297.1461, found 297.1465.

Reference: L. Song, Y. Zhou, H. Liang, H. Li, Y. Lai, H. Yao, R. Lin and R. Tong, *J. Org. Chem.*, 2023, **88**, 504–512. DOI: 10.1021/acs.joc.2c02496



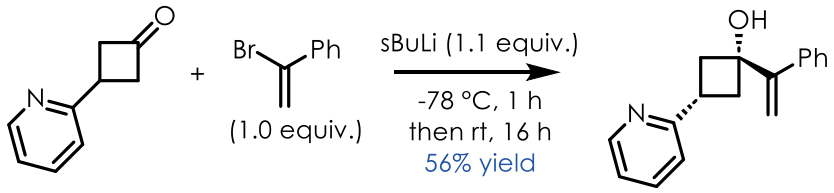
((1s,3s)-3-hydroxy-3-(1-phenylvinyl)cyclobutyl)(morpholino)methanone (S14): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 4.1 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 60% ethyl acetate in hexanes) to afford **S14** (300 mg; 1.0 mmol; 25% yield) as a viscous colorless oil after subjection to high vacuum. Relative stereochemistry assigned by analogy.[41]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.28 (m, 3H), 5.44 (s, 1H), 5.41 (s, 1H), 3.87 (s, 1H), 3.66 (m, 6H), 3.37 (t, *J* = 4.7 Hz, 2H), 2.97 – 2.85 (m, 1H), 2.73 (dd, *J* = 12.1, 8.8 Hz, 2H), 2.61 – 2.50 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 174.1, 151.5, 138.8, 128.2, 127.6, 127.6, 113.5, 74.7, 66.9, 66.7, 45.9, 42.4, 39.3, 28.4.

HRMS (m/z): calculated for $C_{17}H_{21}NO_3$ $[M+H]^+$ 288.1594, found 288.1596.

Reference: L. Song, Y. Zhou, H. Liang, H. Li, Y. Lai, H. Yao, R. Lin and R. Tong, *J. Org. Chem.*, 2023, **88**, 504–512. DOI: 10.1021/acs.joc.2c02496



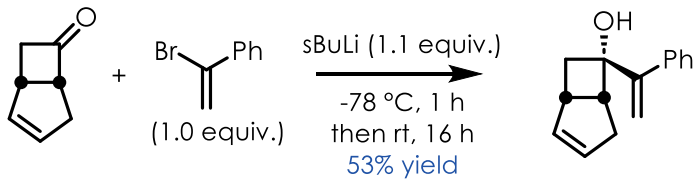
(1s,3s)-1-(1-phenylvinyl)-3-(pyridin-2-yl)cyclobutan-1-ol (S15): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 2.5 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 60% ethyl acetate in hexanes) to afford **S15** (350 mg; 1.4 mmol; 56% yield) as a waxy yellow solid after subjection to high vacuum. Relative stereochemistry assigned by analogy.[41]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (dt, *J* = 4.4, 1.6 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.37 – 7.26 (m, 3H), 7.19 – 7.14 (m, 2H), 7.12 (s, 1H), 5.41 (d, *J* = 1.0 Hz, 1H), 5.38 (d, *J* = 1.0 Hz, 1H), 3.36 (tt, *J* = 9.1, 3.8 Hz, 1H), 3.08 – 2.97 (m, 2H), 2.46 – 2.38 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.2, 152.9, 149.3, 139.7, 137.0, 128.1, 127.7, 127.4, 122.8, 121.6, 113.1, 76.2, 42.6, 34.8.

HRMS (m/z): calculated for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383, found 252.1387.

Reference: L. Song, Y. Zhou, H. Liang, H. Li, Y. Lai, H. Yao, R. Lin and R. Tong, *J. Org. Chem.*, 2023, **88**, 504–512. DOI: 10.1021/acs.joc.2c02496

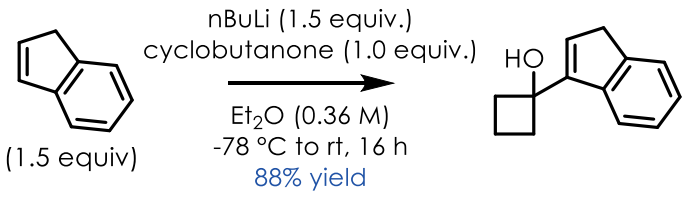


(1S,5R,6S)-6-(1-phenylvinyl)bicyclo[3.2.0]hept-2-en-6-ol (S16): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 5.5 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **S16** (620 mg; 2.9 mmol; 53% yield) as a waxy yellow solid after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 5.95 – 5.86 (m, 2H), 5.36 (d, *J* = 0.9 Hz, 1H), 5.35 (d, *J* = 0.9 Hz, 1H), 3.29 (ddq, *J* = 8.8, 7.3, 1.4 Hz, 1H), 3.09 – 2.98 (m, 1H), 2.86 – 2.76 (m, 2H), 2.55 – 2.45 (m, 1H), 2.06 (s, 1H), 1.97 (ddd, *J* = 13.1, 3.5, 1.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.0, 139.6, 135.4, 132.8, 128.2, 127.8, 127.5, 113.8, 77.8, 46.1, 42.5, 39.3, 33.3.

HRMS (m/z): calculated for $C_{15}H_{16}O$ $[M+Na]^+$ 235.1093, found 235.1098.



1-(1H-inden-3-yl)cyclobutan-1-ol (S17): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[42]

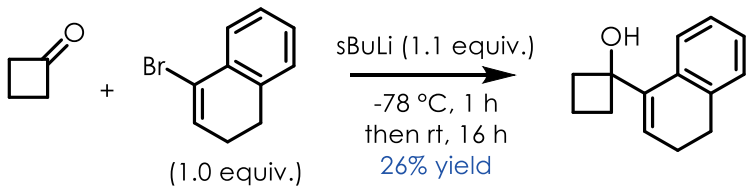
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.48 (s, 1H), 3.41 (d, *J* = 2.4 Hz, 2H), 2.63 – 2.54 (m, 2H), 2.39 (qd, *J* = 9.4, 2.5 Hz, 2H), 2.10 (s, 1H), 1.96 – 1.87 (m, 1H), 1.68 – 1.57 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.4, 145.2, 142.8, 128.3, 126.1, 124.9, 124.1, 121.7, 74.1, 37.7, 35.7, 13.4.

$E_{p/2}$ = 1.64 V vs. Ag/AgCl (1.61 V vs. SCE).

Reference: F. Romanov-Michailidis, L. Guénée and A. Alexakis, *Org. Lett.*, 2013, **15**, 5890–5893.

DOI: 10.1021/ol402981z

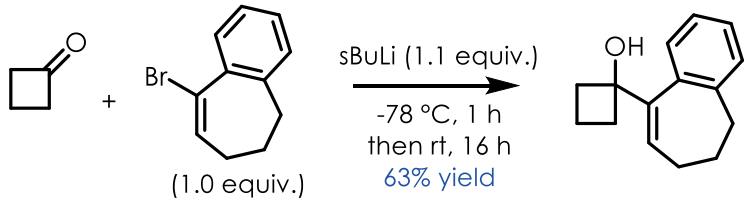


1-(3,4-dihydronaphthalen-1-yl)cyclobutan-1-ol (S18): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 7.2 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **S18** (370 mg; 1.9 mmol; 26% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[40]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.22 – 7.10 (m, 3H), 6.19 (t, *J* = 4.6 Hz, 1H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.55 (dtd, *J* = 13.7, 5.1, 2.9 Hz, 2H), 2.39 – 2.28 (m, 4H), 2.04 – 1.93 (m, 2H), 1.67 – 1.56 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 139.7, 137.6, 132.3, 128.0, 126.9, 126.2, 125.5, 125.4, 77.6, 35.9, 28.4, 23.3, 14.0.

Reference: T. Zheng, R. Chen, J. Huang, T. P. Gonçalves, K.-W. Huang and Y.-Y. Yeung, *Chem*, 2023, **9**, 1255–1269. DOI: 10.1016/j.chempr.2023.01.016

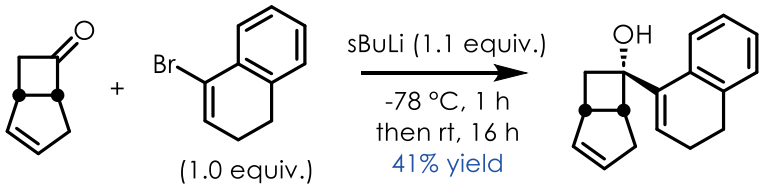


1-(6,7-dihydro-5H-benzo[7]annulen-9-yl)cyclobutan-1-ol (S19): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 5.5 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **S19** (450 mg; 2.1 mmol; 63% yield) as a waxy white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[43]

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.53 – 7.47 (m, 1H), 7.24 – 7.13 (m, 3H), 6.31 (t, *J* = 7.3 Hz, 1H), 2.53 (t, *J* = 7.1 Hz, 2H), 2.44 – 2.34 (m, 2H), 2.21 – 2.12 (m, 2H), 2.09 (p, *J* = 7.2 Hz, 2H), 2.02 – 1.88 (m, 2H), 1.84 (q, *J* = 7.3 Hz, 2H), 1.61 – 1.55 (m, 1H).

^{13}C NMR (151 MHz, CD_2Cl_2): δ 145.7, 142.2, 138.9, 129.2, 127.5, 127.1, 126.7, 126.0, 78.8, 36.5, 34.6, 32.5, 24.7, 13.9.

Reference: F. Romanov-Michailidis, M. Romanova-Michaelides, M. Pupier and A. Alexakis, *Chem. – Eur. J.*, 2015, **21**, 5561–5583. DOI: 10.1002/chem.201406133

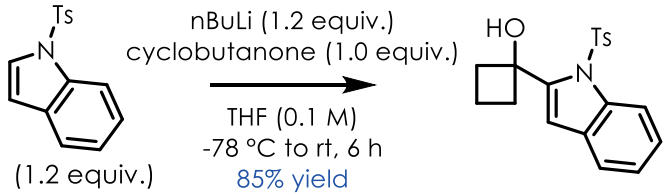


(1S,5R,6S)-6-(3,4-dihydronaphthalen-1-yl)bicyclo[3.2.0]hept-2-en-6-ol (S20): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols on a 7.2 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **S20** (700 mg; 3.0 mmol; 41% yield) as a waxy yellow solid after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 – 7.46 (m, 1H), 7.22 – 7.13 (m, 3H), 6.21 (t, *J* = 4.7 Hz, 1H), 5.98 – 5.93 (m, 2H), 3.39 (tq, *J* = 9.0, 1.5 Hz, 1H), 3.09 – 3.04 (m, 1H), 3.01 – 2.89 (m, 2H), 2.79 – 2.73 (m, 2H), 2.61 (ddt, *J* = 17.9, 9.0, 1.8 Hz, 1H), 2.37 – 2.29 (m, 2H), 2.11 (ddd, *J* = 13.1, 3.8, 1.2 Hz, 1H), 2.06 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.6, 137.5, 135.4, 132.6, 132.4, 127.8, 126.7, 126.2, 126.1, 125.3, 76.9, 45.6, 42.9, 39.5, 33.4, 28.4, 23.3.

HRMS (m/z): calculated for $C_{17}H_{18}O$ $[M+H]^+$ 261.1250, found 261.1254.

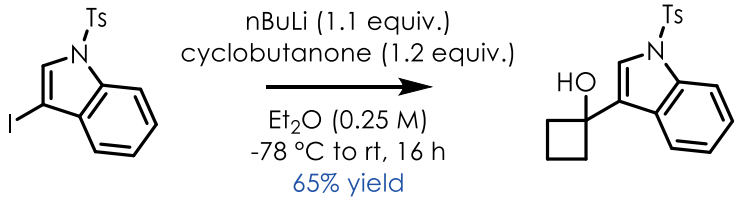


1-(1-tosyl-1H-indol-2-yl)cyclobutan-1-ol (S21): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[44]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.55 – 7.46 (m, 1H), 7.28 – 7.17 (m, 4H), 6.76 (d, *J* = 0.9 Hz, 1H), 2.75 – 2.65 (m, 2H), 2.61 – 2.49 (m, 2H), 2.35 (s, 3H), 2.20 – 2.01 (m, 1H), 1.76 (dtt, *J* = 11.0, 8.9, 7.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.9, 145.0, 137.5, 136.0, 129.9, 128.8, 126.6, 125.1, 123.9, 121.3, 114.8, 110.0, 73.2, 36.5, 21.7, 14.4.

Reference: A. Sandvoß and J. M. Wahl, *Org. Lett.*, 2023, **25**, 5795–5799. DOI: 10.1021/acs.orglett.3c02048



1-(1-tosyl-1H-indol-3-yl)cyclobutan-1-ol (S22): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[45]

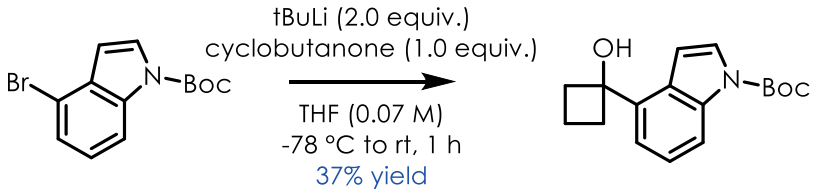
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.54 (s, 1H), 7.34 – 7.28 (t, *J* = 7.3 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 2.72 (s, 1H),

2.54 – 2.46 (m, 2H), 2.38 (qd, *J* = 9.4, 2.5 Hz, 2H), 2.29 (s, 3H), 1.87 (dtt, *J* = 11.2, 9.5, 3.8 Hz, 1H), 1.61 (dp, *J* = 11.1, 8.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.0, 135.9, 135.1, 129.9, 128.9, 126.9, 126.8, 124.8, 123.1, 122.2, 121.6, 113.7, 72.7, 36.4, 21.5, 13.2.

$E_{p/2}$ = 1.90 V vs. Ag/AgCl (1.87 V vs. SCE).

Reference: P. Natho, A. B. Rouse, J. L. Greenfield, L. A. Allen, A. J. White, Z. Yang and P. J. Parsons, *Tetrahedron*, 2020, **76**, 131636. DOI: 10.1016/j.tet.2020.131636

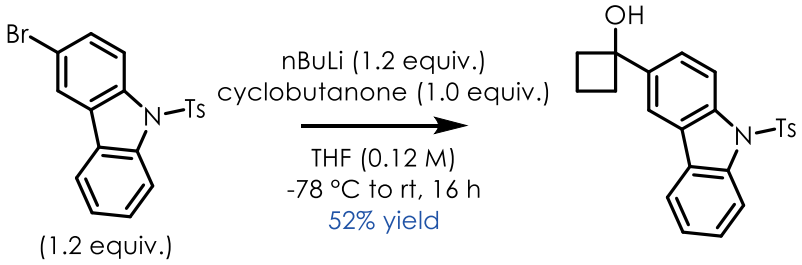


tert-butyl 4-(1-hydroxycyclobutyl)-1H-indole-1-carboxylate (S24): A stirred solution of tert-butyl 1H-indole-1-carboxylate **S24.1** (1.33 g; 4.50 mmol; 1.0 equiv.) in THF (45 mL; 0.1 M in **S24.1**) was cooled to -78 °C. t-Butyl lithium (5.3 mL of a 1.7M solution in pentanes; 8.99 mmol; 2.0 equiv.) was then added dropwise and the solution was stirred at -78 °C for 20 minutes. A solution of cyclobutanone (336 µL; 4.50 mmol; 1.0 equiv.) in THF (20 mL; 22 mM in cyclobutanone) was added dropwise and stirred for an additional hour. The reaction was then warmed to room temperature (25 °C) over the course of 30 minutes before quenching the reaction with saturated ammonium chloride solution (aq.). The reaction was diluted with ethyl acetate and the organic layer was washed with saturated sodium chloride (aq.; 3x). The organic layer was dried over sodium sulfate, filtered and concentrated via rotary evaporation. The resulting crude reaction mixture was then purified by column chromatography (silica: 40-63 µm; 20% ethyl acetate in hexanes) to afford **S24** (478.5 mg; 4.5 mmol; 37%) as a yellow oil after being subjected to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.61 (s, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 3.7 Hz, 1H), 2.76 – 2.69 (m, 2H), 2.53 – 2.44 (m, 2H), 2.21 (s, 1H), 2.10 – 2.01 (m, 1H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.8, 137.5, 136.2, 128.3, 125.6, 123.8, 118.7, 115.1, 107.2, 83.9, 77.6, 36.2, 28.3, 13.8.

HRMS (m/z): calculated for $C_{17}H_{21}NO_3$ $[M+Na]^+$ 310.1413, found 310.1412.

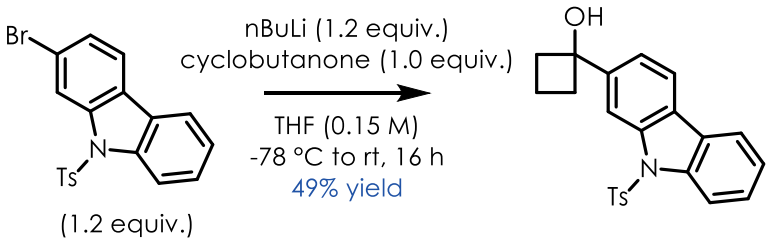


1-(9-tosyl-9H-carbazol-3-yl)cyclobutan-1-ol (S25): Tosyl-protected 3-bromocarbazole **S25.1** (500 mg; 1.25 mmol; 1.2 equiv.) was dissolved in tetrahydrofuran (5.6 mL; 0.22 M in **S25.1**) and cooled to -78 °C. n-Butyl lithium (0.5 mL of a 2.5 M solution in hexanes; 1.25 mmol; 1.2 equiv.) was then added dropwise and the solution was stirred at -78 °C for 1 hour. A solution of cyclobutanone (78 µL; 1.04 mmol; 1.0 equiv.) in tetrahydrofuran (5 mL) was then added dropwise and the reaction was slowly warmed to room temperature and stirred for 16 hours. The reaction was then quenched with a saturated ammonium chloride solution (aq.) and the resulting water layer extracted with ethyl acetate three times. The combined organic layers were dried over sodium sulfate, which was then removed by filtration. The solvent was then removed via rotary evaporation and the crude product purified by column chromatography (silica: 40-63 µm; gradient: 0 to 30% ethyl acetate in hexanes) to afford **S25** (212 mg; 545 µmol; 52%) as an off-white solid after being subjected to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (t, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.48 (td, 1H), 7.40 – 7.29 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.71 – 2.58 (m, 2H), 2.50 – 2.38 (m, 2H), 2.24 (s, 3H), 2.17 – 1.99 (m, 1H), 1.82 – 1.64 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.0, 142.2, 138.8, 137.6, 135.0, 129.8, 127.5, 126.6, 126.5, 126.4, 124.8, 124.0, 120.1, 116.5, 115.2, 115.1, 77.2, 37.3, 21.6, 13.2.

HRMS (m/z): calculated for $C_{23}H_{21}NO_3S$ $[M+H]^+$ 414.1134, found 414.1130.



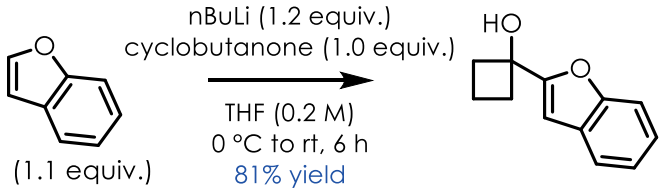
1-(9-tosyl-9H-carbazol-2-yl)cyclobutan-1-ol (S26): Tosyl-protected 2-bromocarbazole **S26.1** (1.00 g; 2.50 mmol; 1.2 equiv.) was dissolved in tetrahydrofuran (11.4 mL; 0.22 M in **S26.1**) and cooled to -78 °C.

n-Butyl lithium (1.0 mL of a 2.5 M solution in hexanes; 2.50 mmol; 1.2 equiv.) was then added dropwise and the solution was stirred at -78 °C for 1 hour. A solution of cyclobutanone (156 µL; 1.04 mmol; 1.0 equiv.) in tetrahydrofuran (5 mL) was then added dropwise and the reaction was slowly warmed to room temperature and stirred for 16 hours. The reaction was then quenched with a saturated ammonium chloride solution (aq.) and the resulting water layer extracted with ethyl acetate three times. The combined organic layers were dried over sodium sulfate, which was then removed by filtration. The solvent was then removed via rotary evaporation and the crude product purified by column chromatography (silica: 40-63 µm; gradient: 0 to 30% ethyl acetate in hexanes) to afford **S26** (403 mg; 2.08 mmol; 49%) as an off-white solid after being subjected to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 1.1 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 7.6, 2.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.52 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.48 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.36 (td, *J* = 7.4, 1.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 2.73 – 2.62 (m, 2H), 2.55 – 2.43 (m, 2H), 2.26 (s, 3H), 2.17 – 2.05 (m, 1H), 2.00 (s, 1H), 1.87 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.2, 145.1, 138.9, 138.6, 135.1, 129.8, 127.4, 126.6, 126.2, 125.6, 124.1, 121.4, 120.1, 120.1, 115.3, 111.8, 77.6, 37.4, 21.6, 13.3.

HRMS (m/z): calculated for $C_{23}H_{21}NO_3S$ $[M+Na]^+$ 414.1134, found 414.1131.



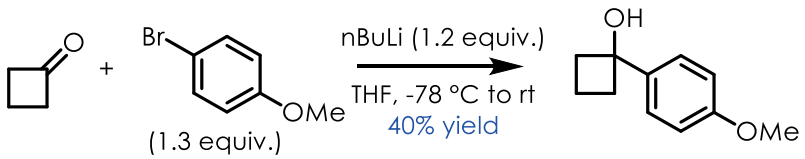
1-(benzofuran-2-yl)cyclobutan-1-ol (S27): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[46]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.28 (td, *J* = 8.3, 7.8, 1.4 Hz, 1H), 7.23 (td, *J* = 7.4, 1.0 Hz, 1H), 6.67 (d, *J* = 1.0 Hz, 1H), 2.67 – 2.59 (m, 2H), 2.54 (s, 1H), 2.46 – 2.37 (m, 2H), 2.01 – 1.92 (m, 1H), 1.80 (dp, J = 11.4, 8.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.8, 155.2, 128.3, 124.3, 122.9, 121.2, 111.4, 101.6, 72.8, 35.7, 13.0.

$E_{p/2}$ = 1.58 V vs. Ag/AgCl (1.55 V vs. SCE).

Reference: Y. Sun, X. Huang, X. Li, F. Luo, L. Zhang, M. Chen, S. Zheng and B. Peng, *Adv. Synth. Catal.*, 2018, **360**, 1082–1087. DOI: 10.1002/adsc.201701237

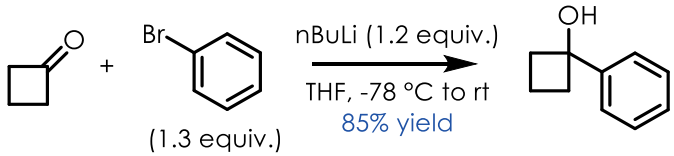


1-(4-methoxyphenyl)cyclobutan-1-ol (S28): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[47]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.32 (s, 3H), 2.36 – 2.30 (m, 2H), 2.25 – 2.12 (m, 2H), 1.85 – 1.82 (m, 1H), 1.56 – 148 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 139.0, 126.1, 113.7, 76.0, 54.5, 37.2, 13.0.

Reference: A. Petti, P. Natho, K. Lam and P. J. Parsons, *Eur. J. Org. Chem.*, 2021, **2021**, 854–858. DOI: 10.1002/ejoc.202001535



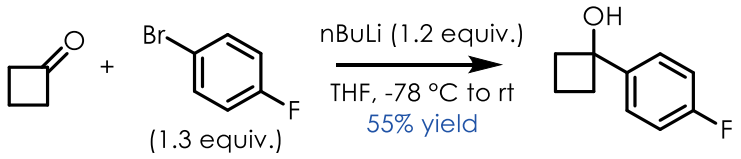
1-phenylcyclobutan-1-ol (S29): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[47]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.50 (m, 2H), 7.42 – 7.35 (m, 2H), 7.32 – 7.26 (m, 1H), 2.62 – 2.54 (m, 2H), 2.42 – 2.33 (m, 2H), 2.08 – 1.98 (m, 2H), 1.66 – 1.74 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.4, 128.6, 127.4, 125.1, 77.2, 36.9, 13.1.

$E_{p/2}$ = 1.86 V vs. Ag/AgCl (1.83 V vs. SCE).

Reference: A. Petti, P. Natho, K. Lam and P. J. Parsons, *Eur. J. Org. Chem.*, 2021, **2021**, 854–858. DOI: 10.1002/ejoc.202001535



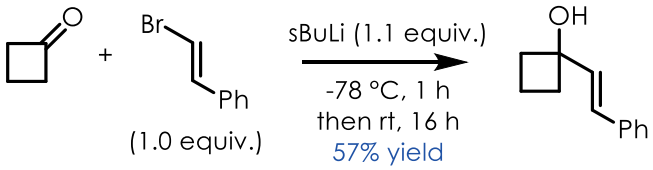
1-(4-fluorophenyl)cyclobutan-1-ol (S30): Prepared according to a known literature procedure. Spectral data were found to be in agreement with those reported in the literature.[47]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.39 (m, 2H), 7.08 – 6.97 (m, 2H), 2.58 – 2.43 (m, 2H), 2.39 – 2.27 (m, 2H), 2.05 – 1.91 (m, 2H), 1.73 – 1.58 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.0 (d, J = 245.2 Hz), 142.2 (d, J = 3.3 Hz), 126.9 (d, J = 8.4 Hz), 115.2 (d, J = 21.1 Hz), 76.6, 37.0, 13.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.7.

Reference: A. Petti, P. Natho, K. Lam and P. J. Parsons, *Eur. J. Org. Chem.*, 2021, **2021**, 854–858. DOI: 10.1002/ejoc.202001535

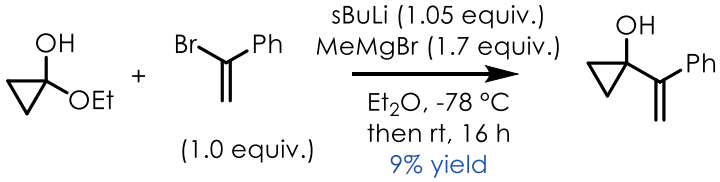


(E)-1-styrylcyclobutan-1-ol (S31): Prepared according to the General Procedure for the Synthesis of α-Styrenyl Cyclobutanols using β-bromostyrene (as opposed to α-bromostyrene) on a 7.1 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **S31** (700 mg; 4.0 mmol; 57% yield) as a colorless oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[48]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 – 7.39 (m, 2H), 7.38 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 2.40 – 2.30 (m, 2H), 2.30 – 2.22 (m, 2H), 2.05 (s, 1H), 1.89 (dtt, *J* = 11.3, 9.6, 4.0 Hz, 1H), 1.70 (dp, *J* = 11.3, 8.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 137.0, 134.1, 128.7, 128.7, 127.6, 127.6, 126.9, 126.6, 75.3, 36.6, 12.4.

Reference R.-Y. Zhang, L.-Y. Xi, L. Shi, X.-Z. Zhang, S.-Y. Chen and X.-Q. Yu, *Org. Lett.*, 2016, **18**, 4024–4027. DOI: 10.1021/acs.orglett.6b01856



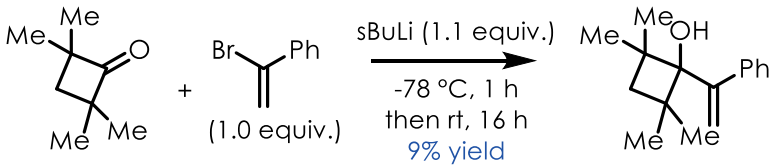
1-(1-phenylvinyl)cyclopropan-1-ol (S32): A flame dried flask equipped with a magnetic stir bar was first backfilled with argon, followed by the addition of anhydrous diethyl ether (20 mL; 0.23 M) and α-bromostyrene (1.35 g; 7.4 mmol; 1.0 equiv.). The reaction was cooled to -78 °C and freshly titrated s-

butyllithium (1.22 M; 6.35 mL; 7.7 mmol; 1.05 equiv.) was added dropwise and allowed to react for 1 hour. During this time, a separate flame dried flask equipped with a magnetic stir bar was charged with anhydrous diethyl ether (10 mL) along with 1-ethoxycyclopropan-1-ol (1.05 g; 10.3 mmol; 1.4 equiv.). The second flask was also cooled to -78 °C followed by the dropwise addition of methylmagnesium bromide (3.0 M; 4.2 mL; 12.5 mmol; 1.7 equiv.). After stirring for 30 minutes at -78 °C, the contents were transferred to the flask containing α-bromostyrene dropwise via syringe, after which the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was then quenched with saturated ammonium chloride solution (aq.), extracted with ethyl acetate, washed with saturated sodium chloride solution (aq.), and dried over sodium sulfate. The organic layer was then filtered and concentrated via rotary evaporation. The crude product was then purified via column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to yield **S32** (100 mg; 0.6 mmol; 9% yield) as a yellow oil after being subjected to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[49]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 – 7.57 (m, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.29 (m, 1H), 5.35 (d, *J* = 1.1 Hz, 1H), 5.29 (d, *J* = 1.1 Hz, 1H), 1.11 – 1.07 (m, 2H), 0.96 – 0.91 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 149.2, 139.0, 128.5, 128.0, 127.3, 112.5, 57.8, 14.0.

Reference: X. Shu, M. Zhang, Y. He, H. Frei and F. D. Toste, *J. Am. Chem. Soc.*, 2014, **136**, 5844–5847. DOI: 10.1021/ja500716j

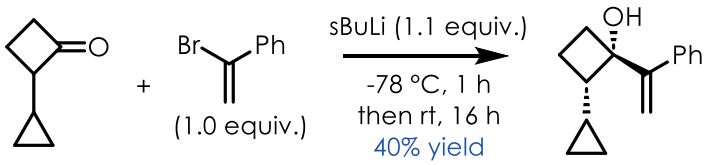


2,2,4,4-tetramethyl-1-(1-phenylvinyl)cyclobutan-1-ol (S34): Compound **S34** was prepared according to the General Procedure for the Synthesis of α-Styryl Cyclobutanols on a 4.50 mmol scale. Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **S34** (90 mg; 0.39 mmol; 9% yield) as a yellow oil after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.30 – 7.24 (m, 3H), 5.22 (d, *J* = 1.3 Hz, 1H), 5.18 (d, *J* = 1.3 Hz, 1H), 1.78 – 1.74 (m, 2H), 1.45 – 1.38 (m, 1H), 1.13 (s, 6H), 1.07 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 142.6, 127.9, 127.9, 127.2, 116.9, 83.7, 47.6, 39.7, 28.6, 25.8.

HRMS (m/z): calculated for $C_{16}H_{22}O$ $[M+H]^+$ 231.1743, found 231.1743.



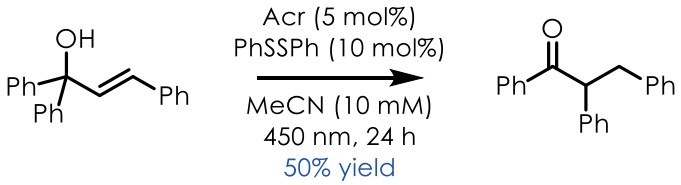
2-cyclopropyl-1-(1-phenylvinyl)cyclobutan-1-ol (S36): Compound **S36** was prepared according to the General Procedure for the Synthesis of α-Styryl Cyclobutanols on a 2.05 mmol scale. (Using only 1.15 equivalent of 2-cyclopropylcyclobutanone.) Purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **S36** (175 mg; 0.82 mmol; 40% yield) as a yellow oil after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.35 – 7.27 (m, 3H), 5.33 (d, *J* = 1.1 Hz, 1H), 5.24 (d, *J* = 1.1 Hz, 1H), 2.28 – 2.13 (m, 3H), 2.11 – 2.01 (m, 1H), 1.76 (td, *J* = 8.3, 5.8 Hz, 2H), 0.97 (qt, *J* = 8.2, 5.1 Hz, 1H), 0.55– 0.42 (m, 2H), 0.27 – 0.19 (m, 1H), 0.08 – -0.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 140.1, 128.1, 128.0, 127.4, 113.1, 79.9, 48.0, 32.7, 19.8, 9.6, 3.3, 2.2.

HRMS (m/z): calculated for $C_{15}H_{18}O$ $[M+Na]^+$ 237.1250, found 237.1248.

Synthesis of Rearrangement Products

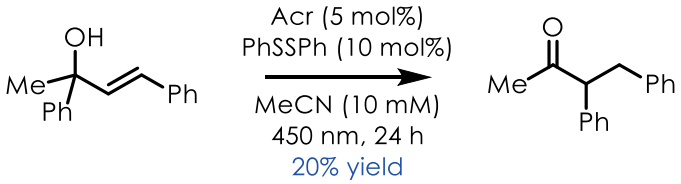


1,2,3-triphenylpropan-1-one (1): Compound **1** was prepared according to General Procedure for Reaction A beginning with tertiary alcohol **S1** (14.0 mg; 0.05 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 2.5% ethyl acetate in hexanes) to afford **1** (28.8 mg; 101 μmol; 50% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[50]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 – 7.88 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.26 – 7.18 (m, 7H), 7.16 – 7.11 (m, 3H), 4.81 (t, *J* = 7.3 Hz, 1H), 3.57 (dd, *J* = 13.8, 7.5 Hz, 1H), 3.07 (dd, *J* = 13.8, 7.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.4, 139.9, 139.2, 136.9, 133.0, 129.3, 128.8, 128.6, 128.4, 128.4, 128.3, 127.3, 126.3, 56.1, 40.3.

Reference T. Zhang, K. Wang, Y. Ke, Y. Tang, L. Liu, T. Huang, C. Li, Z. Tang and T. Chen, *Org. Biomol. Chem.*, 2021, **19**, 8237–8240. DOI: 10.1039/D1OB01468D

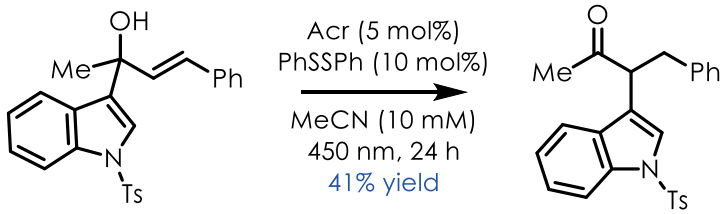


3,4-diphenylbutan-2-one (2): Compound **2** was prepared according to the General Procedure for Reaction A beginning with tertiary alcohol **S2** (11.2 mg; 0.05 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 2.5% ethyl acetate in hexanes) to afford **2** (9.0 mg; 40 μmol; 20% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[51]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.12 (m, 5H), 7.05 (d, *J* = 6.7 Hz, 2H), 3.92 (t, *J* = 7.4 Hz, 1H), 3.43 (dd, *J* = 13.9, 7.5 Hz, 1H), 2.90 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.03 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.6, 139.7, 138.5, 129.0, 128.9, 128.4, 128.2, 127.4, 126.1, 61.6, 38.4, 29.6.

Reference: D. Méndez-Sánchez, J. Mangas-Sánchez, E. Busto, V. Gotor and V. Gotor-Fernández, *Adv. Synth. Catal.*, 2016, **358**, 122–131. DOI: 10.1002/adsc.201500801

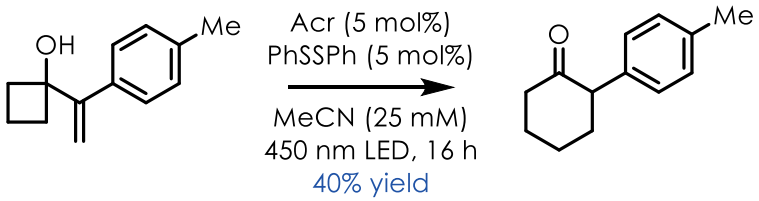


4-phenyl-3-(1-tosyl-1H-indol-3-yl)butan-2-one (3): Compound **3** was prepared according to the General Procedure for Reaction A beginning with tertiary alcohol **S3** (20.9 mg; 0.05 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 5 to 10% ethyl acetate in hexanes) to afford **3** (34.2 mg; 82 μmol; 41% yield) as an off-white solid after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.37 (s, 1H), 7.35 – 7.28 (m, 1H), 7.25 – 7.18 (m, 3H), 7.16 – 7.12 (m, 3H), 7.02 – 6.93 (m, 2H), 4.11 – 4.03 (t, *J* = 8.1 Hz, 1H), 3.41 (dd, *J* = 13.9, 6.9 Hz, 1H), 3.03 (dd, *J* = 13.9, 8.1 Hz, 1H), 2.36 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.3, 145.1, 139.3, 135.4, 135.1, 130.0, 129.6, 128.9, 128.5, 126.9, 126.4, 125.2, 124.8, 123.6, 119.9, 119.4, 114.0, 52.8, 36.8, 29.0, 21.7.

HRMS (m/z): calculated for $C_{25}H_{23}NO_3S$ $[M+Na]^+$ 440.1291, found 440.1287.



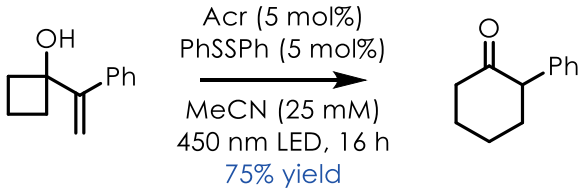
2-(p-tolyl)cyclohexan-1-one (4): Compound **4** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S4** (18.8 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 10%

ethyl acetate in hexanes) to afford **4** (15 mg; 80 µmol; 40% yield) as a yellow oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[52]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.15 (d, *J* = 7.8 Hz, 2H), 7.06 – 7.01 (m, 2H), 3.58 (dd, *J* = 12.2, 5.4 Hz, 1H), 2.53 (dtd, *J* = 13.7, 4.0, 1.4 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.34 (s, 3H), 2.30 – 2.21 (m, 1H), 2.15 (ttd, *J* = 6.4, 3.7, 1.1 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.83 (tdd, *J* = 11.8, 9.1, 5.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.7, 136.6, 135.8, 129.2, 128.5, 57.2, 42.3, 35.2, 28.0, 25.5, 21.2.

Reference: J. Löffler, N. Kaiser, D. Knyszek, F. Krischer, M. Jörges, K.-S. Feichtner and V. H. Gessner, *Angew. Chem. Int. Ed.*, 2024, **63**, e202408947. DOI: 10.1002/anie.202408947

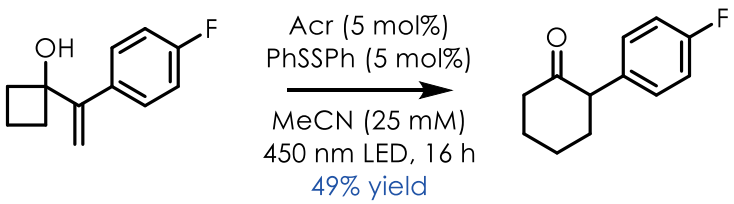


2-phenylcyclohexan-1-one (5): Compound **5** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S5** (17.4 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 µm; gradient: 0 to 5% ethyl acetate in hexanes) to afford **5** (26.1 mg; 150 µmol; 75% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[18]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.1 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 3.62 (dd, *J* = 12.1, 5.3 Hz, 1H), 2.59 – 2.40 (m, 2H), 2.34 – 2.23 (m, 1H), 2.21 – 2.11 (m, 1H), 2.10 – 1.96 (m, 2H), 1.92 – 1.74 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.4, 138.9, 128.7, 128.5, 127.0, 57.5, 42.3, 35.2, 27.9, 25.5.

Reference: M. Shibuya, M. Tomizawa, Y. Sasano and Y. Iwabuchi, *J. Org. Chem.*, 2009, **74**, 4619–4622. DOI: 10.1021/jo900486w



2-(4-fluorophenyl)cyclohexan-1-one (6): Compound **6** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S6** (19.2 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale,

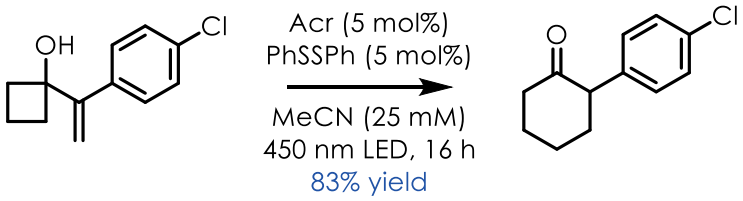
the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **6** (19 mg; 99 μmol; 49% yield) as a yellow oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[53]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12 – 7.06 (m, 2H), 7.05 – 6.97 (m, 2H), 3.60 (dd, *J* = 12.3, 5.4 Hz, 1H), 2.60 – 2.39 (m, 2H), 2.26 (ddd, *J* = 15.5, 5.9, 2.9 Hz, 1H), 2.17 (td, *J* = 5.9, 3.6 Hz, 1H), 2.05 – 1.91 (m, 2H), 1.89 – 1.74 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.3, 161.9 (d, J = 244.8 Hz), 134.6 (d, J = 3.3 Hz), 130.2 (d, J = 7.8 Hz), 115.3 (d, J = 21.2 Hz), 56.8, 42.4, 38.1, 35.6, 28.0, 25.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.97 – -116.11 (m).

Reference: B. Mandal, S. Mandal, S. Halder and D. Adhikari, *Chem. Commun.*, 2024, **60**, 5852–5855. DOI: 10.1039/D4CC01287A

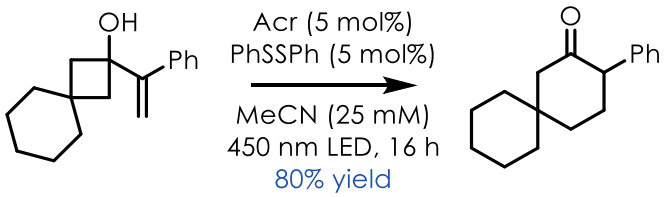


2-(4-chlorophenyl)cyclohexan-1-one (7): Compound **7** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S7** (20.9 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **7** (35 mg; 167 μmol; 83% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[53]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 2H), 7.09 – 7.05 (m, 2H), 3.59 (dd, *J* = 12.5, 5.4 Hz, 1H), 2.53 (dddd, *J* = 15.2, 4.2, 3.3, 1.4 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.26 (dddd, *J* = 13.4, 6.0, 3.6, 2.4 Hz, 1H), 2.17 (tq, *J* = 9.3, 3.1 Hz, 1H), 2.03 – 1.93 (m, 2H), 1.87 – 1.76 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.9, 137.3, 132.8, 130.1, 128.6, 56.9, 42.3, 35.4, 27.9, 25.5.

Reference: B. Mandal, S. Mandal, S. Halder and D. Adhikari, *Chem. Commun.*, 2024, **60**, 5852–5855. DOI: 10.1039/D4CC01287A

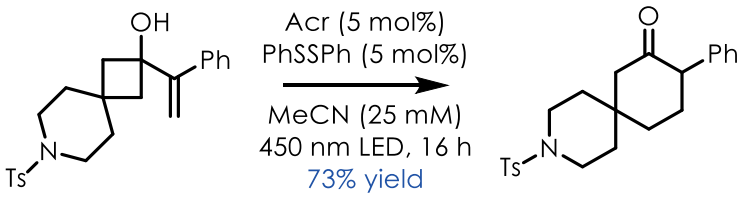


3-phenylspiro[5.5]undecan-2-one (8): Compound **8** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S8** (24.2 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 15% ethyl acetate in hexanes) to afford **8** (39 mg; 161 μmol; 80% yield) as a white solid after subjection to high vacuum.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.26 (tt, *J* = 6.6, 1.4 Hz, 1H), 7.17 – 7.11 (m, 2H), 3.55 (dd, *J* = 11.0, 7.3 Hz, 1H), 2.50 (dd, *J* = 13.1, 2.4 Hz, 1H), 2.26 (d, *J* = 13.1 Hz, 1H), 2.18 – 2.09 (m, 2H), 1.96 (dq, *J* = 14.0, 3.3 Hz, 1H), 1.69 (ddd, *J* = 13.8, 10.9, 5.7 Hz, 1H), 1.57 – 1.36 (m, 10H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 210.1, 138.9, 128.7, 128.5, 127.0, 57.0, 52.8, 40.1, 39.5, 35.7, 33.8, 30.1, 26.3, 21.8, 21.5.

HRMS (m/z): calculated for $C_{17}H_{23}O$ $[M+H]^+$ 243.1743, found 243.1744.

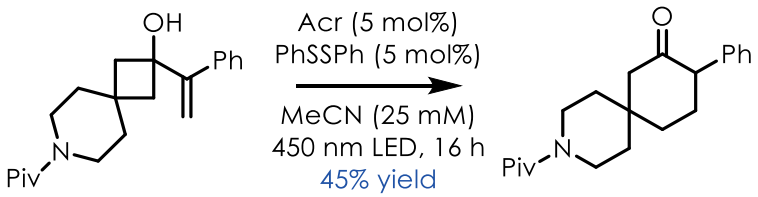


9-phenyl-3-tosyl-3-azaspiro[5.5]undecan-8-one (9): Compound **9** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S9** (39.8 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 50% ethyl acetate in hexanes) to afford **9** (58 mg; 146 μmol; 73% yield) as a white solid after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 – 7.62 (m, 2H), 7.36 – 7.29 (m, 4H), 7.28 – 7.21 (m, 1H), 7.13 – 7.06 (m, 2H), 3.54 (dd, *J* = 11.8, 6.2 Hz, 1H), 3.33 – 3.20 (m, 2H), 2.85 – 2.74 (m, 2H), 2.45 (s, 3H), 2.38 (dd, *J* = 13.4, 2.1 Hz, 1H), 2.21 – 2.15 (m, 1H), 2.15 – 2.01 (m, 2H), 1.81 – 1.67 (m, 3H), 1.67 – 1.57 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 208.9, 143.8, 138.1, 133.1, 129.9, 128.6, 128.6, 127.8, 127.2, 56.7, 50.0, 41.9, 38.2, 37.3, 37.3, 36.2, 32.7, 29.6, 21.7.

HRMS (m/z): calculated for $C_{23}H_{27}NO_3S$ $[M+Na]^+$ 420.1604, found 420.1597.

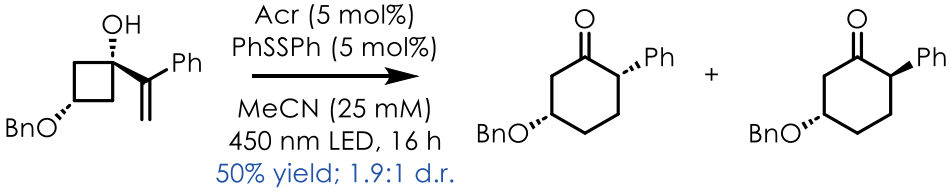


9-phenyl-3-pivaloyl-3-azaspiro[5.5]undecan-8-one (10): Compound **10** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S10** (32.8 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 µm; gradient: 0 to 50% ethyl acetate in hexanes) to afford **10** (30 mg; 916 µmol; 45% yield) as a yellow oil after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.3 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.15 – 7.09 (m, 2H), 3.76 (dddd, *J* = 18.5, 11.1, 8.6, 4.7 Hz, 2H), 3.61 (dd, *J* = 11.6, 6.5 Hz, 1H), 3.54 – 3.39 (m, 2H), 2.59 (dd, *J* = 13.2, 2.3 Hz, 1H), 2.34 (d, *J* = 13.2 Hz, 1H), 2.26 – 2.07 (m, 2H), 1.95 (dq, *J* = 13.8, 3.5 Hz, 1H), 1.80 (ddd, *J* = 13.8, 11.9, 4.7 Hz, 1H), 1.62 – 1.41 (m, 4H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 209.1, 176.4, 138.2, 128.6, 128.6, 127.2, 56.8, 51.2, 41.2, 40.8, 39.0, 38.8, 38.4, 35.9, 33.6, 29.7, 28.5.

HRMS (m/z): calculated for $C_{21}H_{30}NO_2$ $[M+H]^+$ 328.2271, found 328.2268.



(2S,5R)-5-(benzyloxy)-2-phenylcyclohexan-1-one (11): Compound **11** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S11** (28.0 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 µm; gradient: 0 to 15% ethyl acetate in hexanes) to afford two diastereomers of **11** (*cis*: 18 mg; 64 µmol; 32% / *trans*: 10 mg; 36 µmol; 18%) as yellow oils after subjection to high vacuum.

***Cis*-11**

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.27 (m, 8H), 7.19 – 7.14 (m, 2H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.16 (p, *J* = 3.6 Hz, 1H), 3.59 (dd, *J* = 12.1, 5.7 Hz, 1H), 2.86 (ddd, *J* = 14.3, 3.9, 2.3 Hz,

1H), 2.62 (dd, *J* = 14.3, 3.4 Hz, 1H), 2.47 (qd, *J* = 12.6, 3.7 Hz, 1H), 2.24 (dqd, *J* = 13.9, 3.8, 2.3 Hz, 1H), 2.10 (dddd, *J* = 14.6, 7.5, 3.9, 1.1 Hz, 1H), 1.97 (tdd, *J* = 12.6, 4.1, 2.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 208.1, 138.7, 138.4, 128.8, 128.5, 128.5, 127.7, 127.6, 127.1, 76.0, 70.0, 57.3, 46.5, 29.6, 29.3.

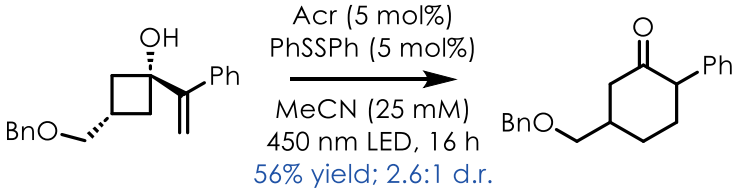
HRMS (m/z): calculated for $C_{19}H_{20}O_2$ $[M+Na]^+$ 303.1356, found 303.1352.

***Trans*-11**

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (q, *J* = 4.1 Hz, 4H), 7.35 – 7.29 (m, 3H), 7.28 – 7.26 (m, 1H), 7.14 – 7.09 (m, 2H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 3.80 (tt, *J* = 9.8, 4.4 Hz, 1H), 3.58 (dd, *J* = 11.4, 5.7 Hz, 1H), 2.97 (ddd, *J* = 13.3, 4.6, 2.0 Hz, 1H), 2.59 (ddd, *J* = 13.3, 10.4, 1.2 Hz, 1H), 2.38 (ddq, *J* = 9.4, 4.3, 1.9 Hz, 1H), 2.32 – 2.23 (m, 1H), 1.96 – 1.81 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.3, 138.2, 138.1, 128.7, 128.6, 128.6, 127.9, 127.8, 127.3, 76.8, 70.6, 56.3, 48.5, 31.3, 28.6.

HRMS (m/z): calculated for $C_{19}H_{20}O_2$ $[M+Na]^+$ 303.1356, found 303.1351.

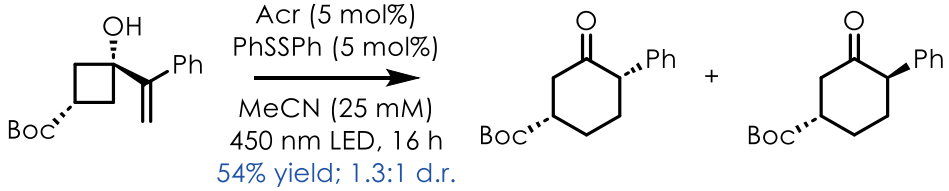


(2S,5R)-5-((benzyloxy)methyl)-2-phenylcyclohexan-1-one (12): Compound **12** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S12** (29.4 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 20% ethyl acetate in hexanes) to afford **12** as an inseparable mixture of diastereomers (33 mg; 112 μmol; 56%; 2.6:1 d.r.) as a yellow oil after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 – 7.27 (m, 27H), 7.26 – 7.21 (m, 2H), 7.18 – 7.09 (m, 8H), 4.59 – 4.44 (m, 8H), 3.64 (dd, *J* = 8.6, 5.9 Hz, 3H), 3.60 – 3.54 (m, 1H), 3.45 (dd, *J* = 5.5, 1.6 Hz, 2H), 3.42 (d, *J* = 6.3 Hz, 6H), 2.60 (ddd, *J* = 13.4, 4.0, 2.0 Hz, 1H), 2.57 – 2.51 (m, 3H), 2.43 (dtd, *J* = 10.8, 6.4, 4.5 Hz, 3H), 2.40 – 2.27 (m, 8H), 2.27 – 2.21 (m, 0H), 2.15 – 2.07 (m, 4H), 2.04 – 1.86 (m, 7H), 1.71 (tdd, *J* = 13.2, 11.8, 3.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.5, 209.4, 138.7, 138.5, 138.4, 138.3, 128.8, 128.7, 128.6, 128.5, 128.5, 128.1, 127.8, 127.8, 127.7, 127.1, 127.0, 74.5, 73.4, 73.3, 73.2, 57.3, 55.8, 45.5, 43.7, 40.6, 38.3, 34.0, 29.9, 29.2, 26.1.

HRMS (m/z): calculated for $C_{20}H_{23}O_2$ $[M+H]^+$ 295.1693, found 295.1696.



tert-butyl (1R,4S)-3-oxo-4-phenylcyclohexane-1-carboxylate (13): Compound **13** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S13** (27.4 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 35% ethyl acetate in hexanes) to afford two diastereomers of **13** (*trans*: 18 mg; 66 μmol; 30% / *cis*: 13 mg; 47 μmol; 24%) as white solids after subjection to high vacuum.

***Cis*-13**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H), 7.19 – 7.13 (m, 2H), 3.54 (dd, J = 9.9, 5.7 Hz, 1H), 3.02 (td, *J* = 5.8, 3.2 Hz, 1H), 2.73 (ddd, *J* = 14.8, 5.1, 1.4 Hz, 1H), 2.49 (ddd, *J* = 14.8, 5.6, 1.1 Hz, 1H), 2.32 – 2.01 (m, 4H), 1.47 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 208.0, 173.4, 138.7, 128.7, 128.4, 127.1, 81.4, 56.2, 43.7, 42.5, 30.7, 28.2, 26.8.

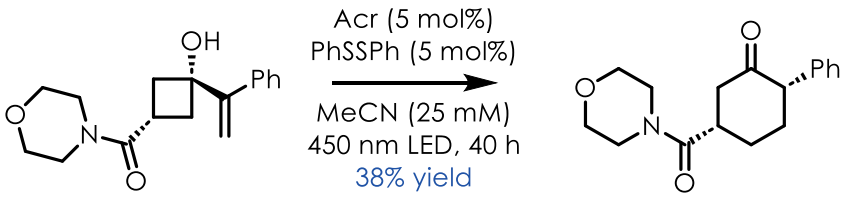
HRMS (m/z): calculated for $C_{17}H_{22}O_3$ $[M+Na]^+$ 297.1461, found 297.1459.

***Trans*-13**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.14 – 7.08 (m, 2H), 3.59 (dd, *J* = 12.3, 5.4 Hz, 1H), 2.83 – 2.73 (m, 1H), 2.72 – 2.61 (m, 2H), 2.37 – 2.30 (m, 1H), 2.27 (dtd, *J* = 10.1, 3.5, 1.7 Hz, 1H), 2.11 – 1.87 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 208.2, 172.8, 138.3, 128.7, 128.5, 127.3, 81.2, 56.9, 45.4, 44.1, 33.5, 28.6, 28.2.

HRMS (m/z): calculated for $C_{17}H_{22}O_3$ $[M+Na]^+$ 297.1461, found 297.1458.

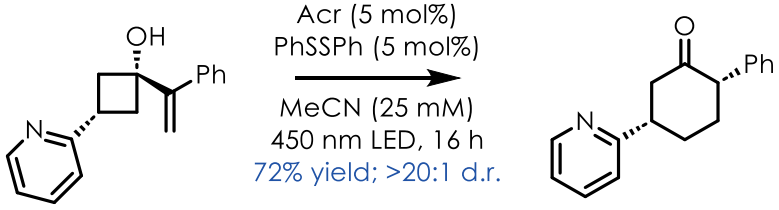


(2S,5R)-5-(morpholine-4-carbonyl)-2-phenylcyclohexan-1-one (14): Compound **14** was prepared according to a modified version of General Procedure for Reaction B in which the reaction was run for 40 hours, beginning with cyclobutanol **S14** (28.7 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 30% acetone in hexanes) to afford **14**, of which only a single diastereomer was isolated (22 mg; 77 μmol; 38%) as an off-white solid after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.12 (dd, *J* = 7.1, 1.8 Hz, 2H), 3.73 – 3.62 (m, 7H), 3.53 (t, *J* = 4.8 Hz, 2H), 3.16 – 3.04 (m, 1H), 2.96 – 2.85 (m, 1H), 2.51 (ddd, *J* = 13.9, 4.1, 2.0 Hz, 1H), 2.37 (ddt, *J* = 12.6, 6.5, 3.1 Hz, 1H), 2.23 – 1.95 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 208.6, 171.6, 138.1, 128.7, 128.5, 127.3, 67.0, 66.9, 56.9, 46.1, 44.6, 42.4, 41.3, 33.8, 28.8.

HRMS (m/z): calculated for $C_{17}H_{22}NO_3$ $[M+H]^+$ 288.1594, found 288.1597.



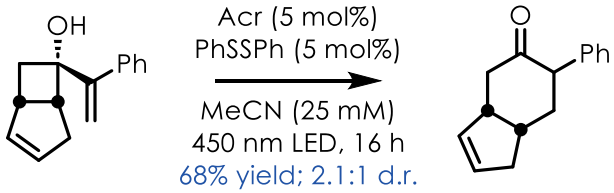
(2S,5R)-2-phenyl-5-(pyridin-2-yl)cyclohexan-1-one (15): Compound **15** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S15** (25.1 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 30% ethyl acetate in hexanes) to afford **15**, of which only a single diastereomer was isolated (36 mg; 143 μmol; 72%; >20:1 d.r.) as an off-white solid after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (dd, *J* = 5.3, 1.9 Hz, 1H), 7.66 (td, *J* = 7.7, 1.9 Hz, 1H), 7.36 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.18 (dq, *J* = 7.3, 1.3 Hz, 4H), 3.74 (dd, *J* = 12.6, 5.5 Hz, 1H), 3.38 – 3.24

(m, 1H), 3.02 (td, *J* = 13.3, 1.1 Hz, 1H), 2.74 (ddd, *J* = 13.6, 4.2, 1.4 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.29 – 2.07 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.4, 162.6, 149.7, 138.6, 136.9, 128.9, 128.5, 127.2, 122.1, 121.8, 57.1, 47.7, 47.7, 34.3, 32.5.

HRMS (m/z): calculated for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383, found 252.1381.

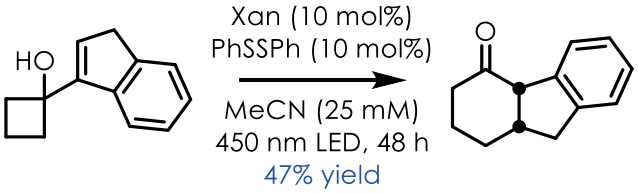


(3aR,7aS)-6-phenyl-1,3a,4,6,7,7a-hexahydro-5H-inden-5-one (16): Compound **16** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S16** (21.2 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 35% diethyl ether in hexanes) to afford **16** as an inseparable mixture of diastereomers (29 mg; 137 μmol; 68%; 2.1:1 d.r.) as a yellow oil after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 9H), 7.27 – 7.21 (m, 5H), 7.19 – 7.12 (m, 8H), 5.82 (dq, *J* = 4.5, 2.3 Hz, 1H), 5.77 (dp, *J* = 4.6, 2.3 Hz, 3H), 5.66 (dq, *J* = 6.0, 2.2 Hz, 3H), 5.60 (dt, *J* = 6.2, 2.3 Hz, 1H), 3.46 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.44 – 3.37 (m, 3H), 3.34 (ddp, *J* = 7.9, 5.2, 2.7 Hz, 1H), 3.20 (dddt, *J* = 11.1, 8.7, 6.4, 2.4 Hz, 3H), 2.89 – 2.71 (m, 7H), 2.71 – 2.59 (m, 5H), 2.55 – 2.47 (m, 3H), 2.47 – 2.25 (m, 4H), 2.23 – 2.08 (m, 9H), 1.99 (dt, J = 14.0, 4.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 213.0, 212.6, 139.9, 139.6, 134.3, 133.0, 131.2, 129.9, 128.7, 128.6, 128.3, 128.1, 127.0, 126.9, 55.2, 51.4, 43.8, 43.7, 43.0, 42.8, 40.0, 39.9, 35.9, 35.5, 35.3, 32.2.

HRMS (m/z): calculated for $C_{15}H_{16}O$ $[M+Na]^+$ 235.1093, found 235.1092.



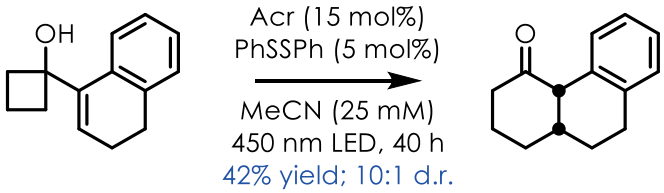
(4aS,9aS)-1,2,3,4a,9,9a-hexahydro-4H-fluoren-4-one (17): Cyclobutanol **S17** (18.6 mg; 0.1 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of diphenyl disulfide (10 mol%; 2.18 mg; 0.01 mmol) and photocatalyst **Xan** (10 mol%; 4.96 mg; 0.01 mmol). Anhydrous

acetonitrile (25 mM in **S17**; 4 mL) was then added and the reaction mixture was sparged with argon for 10 minutes. The vial was then placed in a SynLED well (450 nm) and stirred for 48 hours. After this time, the solvent was removed by rotary evaporation and the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 2.5% ethyl acetate in hexanes). For isolated yields, two 0.1 mmol reactions were combined – for a total of 0.2 mmol – which, after purification, afforded **17** (17.6 mg; 94 μmol; 47% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[54]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 1H), 7.25 – 7.16 (m, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 3.85 (d, *J* = 7.1 Hz, 1H), 3.08 (dd, *J* = 15.6, 6.9 Hz, 1H), 3.00 – 2.90 (m, 1H), 2.70 (dd, *J* = 15.6, 2.2 Hz, 1H), 2.39 (dt, *J* = 15.5, 4.4 Hz, 1H), 2.25 (ddd, *J* = 15.5, 11.9, 5.4 Hz, 1H), 1.94 – 1.88 (m, 1H), 1.87 – 1.81 (m, 1H), 1.80 – 1.69 (m, 1H), 1.48 – 1.39 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 211.4, 143.0, 140.3, 127.5, 126.8, 125.4, 124.4, 58.7, 42.3, 39.6, 38.9, 28.0, 23.6.

Reference: T. Iwama and V. H. Rawal, *Org. Lett.*, 2006, **8**, 5725–5728. DOI: 10.1021/ol062093g

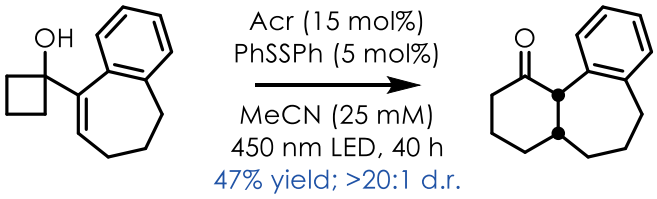


(4aS,10aS)-2,3,4a,9,10,10a-hexahydrophenanthren-4(1H)-one (18): C yclobutanol **S18** (20.0 mg; 0.1 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of diphenyl disulfide (1.1 mg; 0.005 mmol; 5 mol%) and photocatalyst **Acr** (8.6 mg; 0.015 mmol; 15 mol%). Anhydrous acetonitrile (25 mM in **S18**; 4 mL) was then added and the reaction mixture was sparged with argon for 10 minutes. The vial was then placed in a SynLED well (450 nm) and stirred for 40 hours. After this time, the solvent was removed by rotary evaporation and the resulting crude mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 10% ethyl acetate in hexanes). For isolated yields, two 0.1 mmol reactions were combined – for a total of 0.2 mmol – which, after purification, afforded **18** (17.0 mg; 85 μmol; 42% yield; 10:1 d.r.) as a yellow oil after subjection to high vacuum. Relative stereochemistry is in agreement with those reported in the literature.[55]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.18 (td, *J* = 7.2, 1.5 Hz, 1H), 7.15 – 7.11 (m, 2H), 6.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 3.73 (d, *J* = 5.4 Hz, 1H), 2.93 (dt, *J* = 17.2, 6.3 Hz, 1H), 2.81 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.50 (tdt, *J* = 8.9, 6.6, 3.8 Hz, 1H), 2.40 (t, *J* = 6.5 Hz, 2H), 2.03 – 1.87 (m, 3H), 1.84 – 1.69 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 211.9, 136.1, 132.9, 129.8, 129.5, 126.9, 125.9, 55.6, 40.7, 37.8, 28.5, 27.5, 26.1, 24.6.

Reference: H. W. Thompson and D. J. Long, *J. Org. Chem.*, 1988, **53**, 4201–4209. DOI: 10.1021/jo00253a009

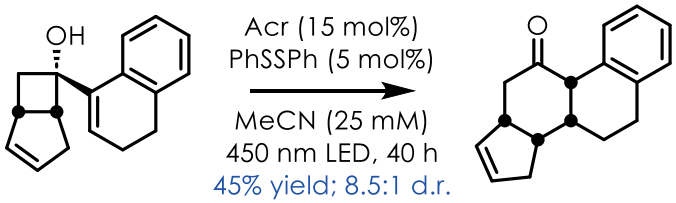


(4aR,11bS)-2,3,4,4a,5,6,7,11b-octahydro-1H-dibenzo[a,c][7]annulen-1-one (19): Cyclobutanol **S19** (21.4 mg; 0.1 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of diphenyl disulfide (1.1 mg; 0.005 mmol; 5 mol%) and photocatalyst **Acr** (8.6 mg; 0.015 mmol; 15 mol%). Anhydrous acetonitrile (25 mM in **S19**; 4 mL) was then added and the reaction mixture was sparged with argon for 10 minutes. The vial was then placed in a SynLED well (450 nm) and stirred for 40 hours. After this time, the solvent was removed by rotary evaporation and the resulting crude mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 10% diethyl ether in hexanes). Analysis of the crude reaction mixture by ^{1}H NMR indicated a d.r. of 5.2:1. For isolated yields, two 0.1 mmol reactions were combined – for a total of 0.2 mmol – which, after purification, afforded **19** (20.0 mg; 93 μmol; 47% yield; >20:1 d.r.) as a yellow oil after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.05 (m, 3H), 6.98 – 6.91 (m, 1H), 3.96 (d, *J* = 4.0 Hz, 1H), 2.81 (ddd, *J* = 14.1, 11.9, 1.9 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.56 – 2.36 (m, 3H), 2.23 – 2.08 (m, 2H), 2.06 – 1.90 (m, 2H), 1.85 – 1.65 (m, 3H), 1.47 – 1.32 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.7, 144.3, 137.3, 131.3, 130.4, 127.4, 126.0, 65.3, 42.5, 42.0, 37.0, 34.2, 33.6, 27.7, 22.7.

HRMS (m/z): calculated for $C_{15}H_{19}O$ $[M+H]^+$ 215.1430, found 215.1433.

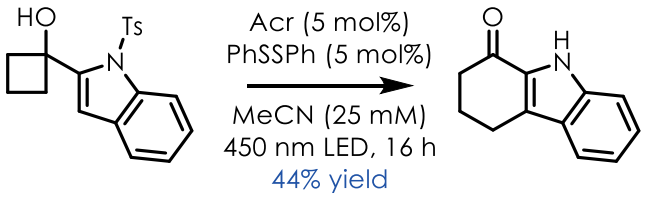


(8R,9S,13S,14R)-6,7,8,9,12,13,14,15-octahydro-11H-cyclopenta[a]phenanthren-11-one (20): Cyclobutanol **S20** (23.8 mg; 0.1 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of diphenyl disulfide (1.1 mg; 0.005 mmol; 5 mol%) and photocatalyst **Acr** (8.6 mg; 0.015 mmol; 15 mol%). Anhydrous acetonitrile (25 mM in **S20**; 4 mL) was then added and the reaction mixture was sparged with argon for 10 minutes. The vial was then placed in a SynLED well (450 nm) and stirred for 40 hours. After this time, the solvent was removed by rotary evaporation and the resulting crude mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 15% diethyl ether in hexanes). For isolated yields, two 0.1 mmol reactions were combined – for a total of 0.2 mmol – which, after purification, afforded **20** (21.0 mg; 88 μmol; 45% yield; 8.5:1 d.r.) as a white solid after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 1H), 7.18 – 7.13 (m, 2H), 7.08 (dd, *J* = 5.3, 3.6 Hz, 1H), 5.81 – 5.77 (m, 1H), 5.66 (dq, *J* = 6.0, 2.1 Hz, 1H), 3.56 (d, *J* = 5.6 Hz, 1H), 3.26 (dddt, *J* = 10.7, 7.1, 4.7, 2.3 Hz, 1H), 2.87 (ddd, *J* = 16.9, 5.6, 2.9 Hz, 1H), 2.81 (ddt, *J* = 8.5, 6.1, 4.3 Hz, 1H), 2.72 (ddt, *J* = 17.0, 11.2, 5.7 Hz, 1H), 2.66 – 2.56 (m, 2H), 2.46 (dd, *J* = 15.9, 9.0 Hz, 1H), 2.41 – 2.33 (m, 2H), 1.93 (ddtd, *J* = 13.7, 6.0, 2.9, 1.6 Hz, 1H), 1.52 – 1.44 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 211.7, 136.7, 134.1, 133.4, 130.8, 130.4, 129.0, 126.9, 125.6, 53.3, 43.8, 41.5, 39.2, 38.9, 35.7, 29.9, 24.1.

HRMS (m/z): calculated for $C_{17}H_{19}O$ $[M+H]^+$ 239.1430, found 239.1433.



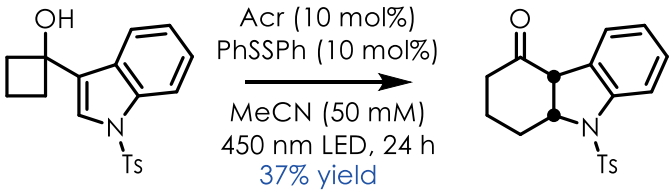
2,3,4,9-tetrahydro-1H-carbazol-1-one (21): Compound **21** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S21** (34.1 mg; 0.1 mmol). For isolated yields at a 0.2

mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 30% ethyl acetate in hexanes) to afford **21** as (16.4 mg; 88 μmol; 44%) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[56]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.16 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 3.02 (t, *J* = 6.1 Hz, 2H), 2.67 (dd, *J* = 7.3, 5.6 Hz, 2H), 2.28 (p, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.5, 137.9, 131.4, 129.6, 127.2, 126.0, 121.5, 120.5, 112.6, 38.4, 25.1, 21.5.

Reference: D. Bansal, P. Sivaganesan, C. Elanchezhian, G. Nataraj, M. K. Das and S. Chaudhuri, *Chem. – Asian J.*, 2025, **20**, e202500246. DOI: 10.1002/asia.202500246

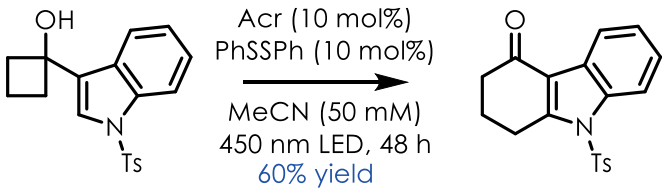


(4aR,9aR)-9-tosyl-1,2,3,4a,9,9a-hexahydro-4H-carbazol-4-one (22): Cyclobutanol **S22** (34.1 mg; 0.1 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of diphenyl disulfide (10 mol%; 2.18 mg; 0.01 mmol) and photocatalyst **Acr** (5.74 mg; 10 mol%; 0.01 mmol). Anhydrous acetonitrile (50 mM in **S22**; 2 mL) was then added and the reaction mixture was sparged with argon for 10 minutes. The vial was then placed in a SynLED well (450 nm) and stirred for 24 hours. After this time, the solvent was removed by rotary evaporation and the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 2.5% ethyl acetate in hexanes). For isolated yields, two 0.1 mmol reactions were combined – for a total of 0.2 mmol – which, after purification, afforded **22** (25.0 mg; 74 μmol; 37% yield) as a white solid after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.30 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.07 (td, *J* = 7.5, 0.9 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 4.62 (td, *J* = 8.8, 5.9 Hz, 1H), 3.54 (d, *J* = 8.8 Hz, 1H), 2.42 – 2.36 (m, 1H), 2.36 (s, 3H), 2.28 – 2.19 (m, 2H), 1.96 – 1.83 (m, 2H), 1.70 – 1.60 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 207.8, 144.4, 141.5, 135.4, 130.0, 129.9, 129.3, 126.9, 125.5, 124.5, 118.1, 64.1, 54.3, 38.6, 29.8, 21.7, 19.0.

HRMS (m/z): calculated for $C_{19}H_{19}NO_3S$ $[M+Na]^+$ 364.0978, found 364.0983.

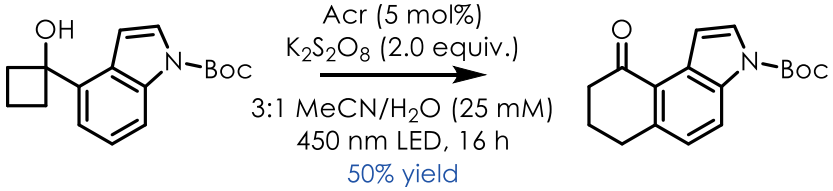


9-tosyl-1,2,3,9-tetrahydro-4H-carbazol-4-one (23): Cyclobutanol **S22** (34.1 mg; 0.1 mmol) was added to a flame-dried 2-dram vial equipped with a magnetic stir bar, followed by the addition of diphenyl disulfide (10 mol%; 2.18 mg; 0.01 mmol) and photocatalyst **Acr** (10 mol%; 5.74 mg; 0.01 mmol). Anhydrous acetonitrile (50 mM in **S22**; 2 mL) was then added and the reaction mixture was sparged with argon for 10 minutes. The vial was then placed in a SynLED well (450 nm) and stirred for 48 hours. After this time, the solvent was removed by rotary evaporation and the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 2.5% ethyl acetate in hexanes). For isolated yields, two 0.1 mmol reactions were combined – for a total of 0.2 mmol – which, after purification, afforded **23** (41.0 mg; 121 μmol; 60% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[57]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28-8.23 (m, 1H), 8.20-8.13 (m, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.40-7.30 (m, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 3.33 (t, *J* = 6.2 Hz, 2H), 2.56 (t, *J* = 6.2 Hz, 2H), 2.38 (s, 3H), 2.28-2.18 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 195.1, 150.9, 145.8, 135.9, 135.5, 130.2, 126.6, 125.8, 125.4, 124.9, 121.9, 118.0, 113.9, 37.9, 24.6, 23.2, 21.7.

Reference: A. Krishnan and S. Kamaraj, *J. Org. Chem.*, 2023, **88**, 16315–16329. DOI: 10.1021/acs.joc.3c01810



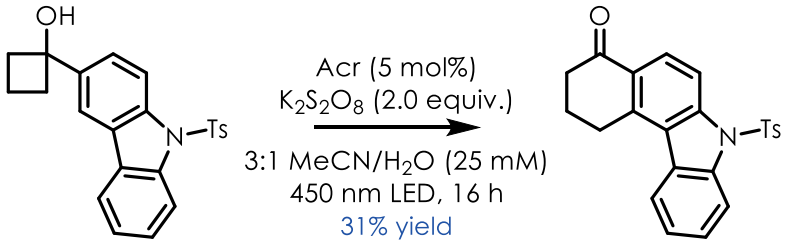
tert-butyl 9-oxo-6,7,8,9-tetrahydro-3H-benzo[e]indole-3-carboxylate (24): Compound **24** was prepared according to the General Procedure for Reaction C beginning with cyclobutanol **S24** (28.7 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography

(silica: 40-63 μm; gradient: 1 to 2.5% ethyl acetate in hexanes) to afford **24** (28.6 mg; 100 μmol; 50% yield) as a white solid after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 3.6 Hz, 1H), 7.56 (d, *J* = 3.6 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 3.05 (t, *J* = 6.1 Hz, 2H), 2.70 (t, *J* = 6.6 Hz, 2H), 2.17 (p, *J* = 6.3 Hz, 2H), 1.67 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 149.6, 141.0, 134.8, 129.4, 128.6, 124.8, 124.5, 120.4, 108.7, 84.2, 40.1, 30.1, 28.3, 23.9.

HRMS (m/z): calculated for $C_{17}H_{19}NO_3$ $[M+1]^+$ 286.1438, found 286.1438.

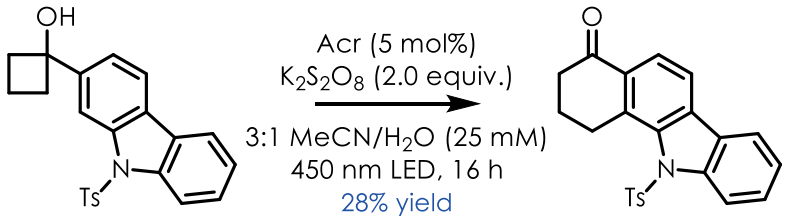


7-tosyl-1,2,3,7-tetrahydro-4H-benzo[c]carbazol-4-one (25): Compound **25** was prepared according to the General Procedure for Reaction C beginning with cyclobutanol **S25** (39.1 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **25** (24.0 mg; 62 μmol; 31% yield) as a white solid after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.9 Hz, 1H), 8.24 (d, *J* = 8.9 Hz, 1H), 8.07 (d, *J* = 7.1 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.54 (t, *J* = 8.6 Hz, 1H), 7.42 (t, *J* = 8.2 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.45 (t, *J* = 6.2 Hz, 2H), 2.73 (dd, *J* = 8.0, 5.4 Hz, 2H), 2.34 – 2.28 (m, 2H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.7, 145.5, 141.5, 140.4, 138.9, 135.0, 130.0, 129.1, 127.4, 126.7, 126.7, 126.4, 124.3, 123.8, 122.9, 115.2, 113.2, 38.4, 27.7, 22.7, 21.7.

HRMS (m/z): calculated for $C_{23}H_{19}NO_3S$ $[M+H]^+$ 390.1158, found 390.1140.

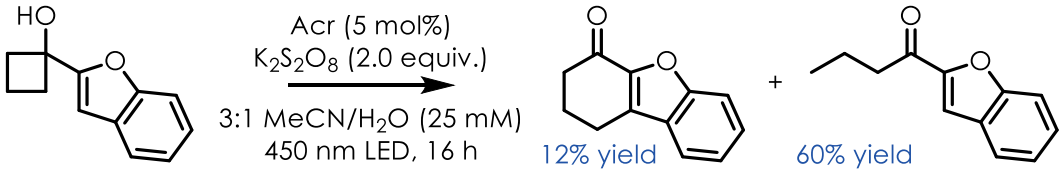


7-tosyl-1,2,3,7-tetrahydro-4H-benzo[c]carbazol-4-one (26): Compound **26** was prepared according to the General Procedure for Reaction C beginning with cyclobutanol **S26** (39.1 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **26** (22.0 mg; 56 μmol; 28% yield) as a white solid after subjection to high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.46 (td, *J* = 8.5, 7.9, 1.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.61 (t, *J* = 5.9 Hz, 2H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.19 (s, 3H), 2.08 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.8, 144.7, 143.2, 139.7, 138.5, 135.3, 132.8, 131.7, 129.2, 128.9, 128.5, 127.1, 126.1, 126.1, 120.6, 120.0, 117.9, 39.1, 29.8, 23.9, 21.6.

HRMS (m/z): calculated for $C_{23}H_{19}NO_3S$ $[M+H]^+$ 390.1158, found 390.1137.

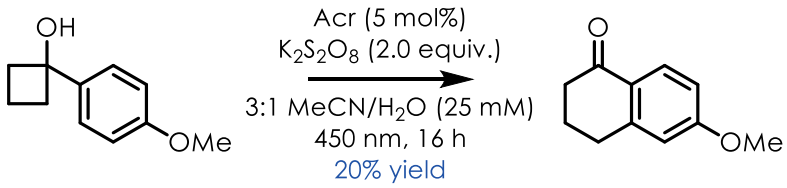


2,3-dihydrodibenzo[b,d]furan-4(1H)-one (27): Compound **27** was prepared according to the General Procedure for Reaction C beginning with cyclobutanol **S27** (18.8 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **27** (4.5 mg; 24 μmol; 12% yield) as a white film after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[58]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.55 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.36 – 7.40 (m), 3.00 (t, J = 6.2 Hz, 2H), 2.74 (t, J = 6.2 Hz, 2H), 2.31 – 2.38 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 188.0, 155.4, 147.2, 134.2, 128.6, 125.9, 123.2, 121.3, 112.4, 38.1, 23.6, 20.9

Reference: J. Yu, H. Zhao, S. Liang, X. Bao and C. Zhu, *Org. Biomol. Chem.*, 2015, **13**, 7924–7927. DOI: 10.1039/C5OB01222H

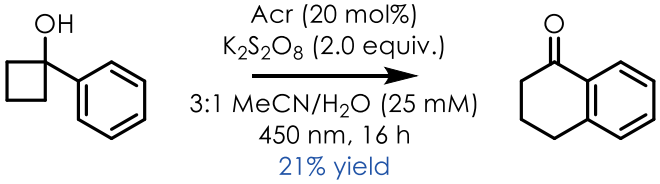


6-methoxy-3,4-dihydronaphthalen-1(2H)-one (28): Compound **28** was prepared according to the General Procedure for Reaction C beginning with cyclobutanol **S28** (17.8 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **28** as (7.1 mg; 40 μmol; 20%) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[58]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.72 (d, *J* = 2.8 Hz, 1H), 3.87 (s, 3H), 2.94 (t, *J* = 6.1 Hz, 2H), 2.63 (t, *J* = 6.5 Hz, 2H), 2.13 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.4, 163.6, 147.1, 129.7, 126.4, 113.1, 112.7, 55.5, 39.0, 30.3, 23.5.

Reference: J. Yu, H. Zhao, S. Liang, X. Bao and C. Zhu, *Org. Biomol. Chem.*, 2015, **13**, 7924–7927. DOI: 10.1039/C5OB01222H



3,4-dihydronaphthalen-1(2H)-one (29): Compound **29** was prepared according to a modified version of General Procedure for Reaction C using 20 mol% acridinium beginning with cyclobutanol **S29** (14.8 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **29** (6.1 mg; 42 μmol; 21%) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[58]

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.47 (td, *J* = 7.4, 1.5 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.25 (s, 1H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.66 (t, *J* = 6.4 Hz, 2H), 2.15 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.6, 144.6, 133.6, 132.8, 128.9, 127.3, 126.8, 39.3, 29.9, 23.4.

Reference: J. Yu, H. Zhao, S. Liang, X. Bao and C. Zhu, *Org. Biomol. Chem.*, 2015, **13**, 7924–7927. DOI: 10.1039/C5OB01222H

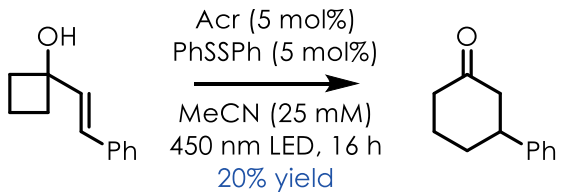
6-fluoro-3,4-dihydronaphthalen-1(2H)-one (30): Compound **30** was prepared according to the General Procedure for Reaction C beginning with cyclobutanol **S30** (16.6 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (silica: 40-63 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **30** as (6.56 mg; 40 μmol; 20%) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[58]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 8.6, 6.0 Hz, 1H), 6.96 (td, *J* = 8.6, 2.6 Hz, 1H), 6.91 (dd, *J* = 9.2, 2.6 Hz, 1H), 2.94 (t, *J* = 6.1 Hz, 2H), 2.64 (t, *J* = 6.4 Hz, 2H), 2.12 (p, *J* = 6.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.1, 165.8 (d, *J* = 255.4 Hz), 147.6 (d, *J* = 9.1 Hz), 130.4 (d, *J* = 9.8 Hz), 129.4 (d, *J* = 2.5 Hz), 115.2 (d, *J* = 21.4 Hz), 114.4 (d, *J* = 22.2 Hz), 38.9, 30.0 (d, *J* = 1.8 Hz), 23.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -104.8.

Reference: J. Yu, H. Zhao, S. Liang, X. Bao and C. Zhu, *Org. Biomol. Chem.*, 2015, **13**, 7924–7927. DOI: 10.1039/C5OB01222H



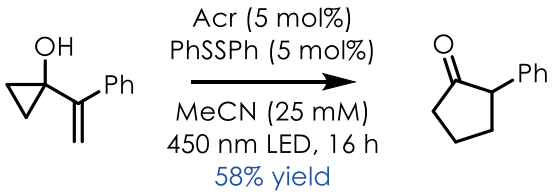
3-phenylcyclohexan-1-one (31): Compound **31** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S31** (17.4 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **31** (6 mg; 0.04 mmol; 20% yield) as a white solid after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[59]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.26 – 7.21 (m, 3H), 3.01 (tt, *J* = 11.9, 3.9 Hz, 1H), 2.60 (ddt, *J* = 14.0, 4.2, 2.0 Hz, 1H), 2.53 (ddd, *J* = 13.9, 12.5, 1.1 Hz, 1H), 2.46 (dddt, *J* = 14.3, 4.8,

3.3, 1.8 Hz, 1H), 2.42 – 2.36 (m, 1H), 2.16 (ddq, *J* = 13.2, 6.7, 3.1 Hz, 1H), 2.09 (dqd, *J* = 12.1, 3.2, 1.4 Hz, 1H), 1.90 – 1.73 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 211.2, 144.5, 128.8, 126.8, 126.7, 49.1, 44.9, 41.3, 32.9, 25.7.

Reference: S. Ikemoto, S. Muratsugu, T. Koitaya, Y. Tsuji, M. Das, K. Yoshizawa, F. Glorius and M. Tada, *J. Am. Chem. Soc.*, 2023, **145**, 1497–1504. DOI: 10.1021/jacs.2c07290

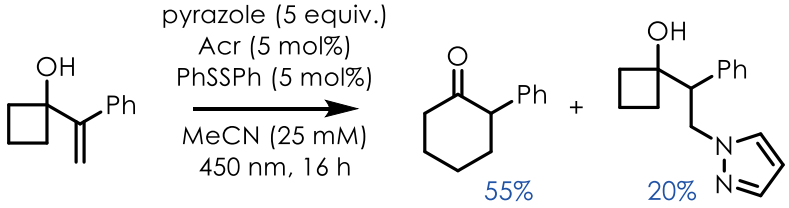


2-phenylcyclopentan-1-one (32): Compound **32** was prepared according to the General Procedure for Reaction B beginning with cyclobutanol **S32** (16.0 mg; 0.1 mmol). For isolated yields at a 0.2 mmol scale, the crude reaction mixture was purified by column chromatography (fine silica: 20-45 µm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **32** (16 mg; 94 µmol; 47% yield) as a yellow oil after subjection to high vacuum. Spectral data were found to be in agreement with those reported in the literature.[60]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.17 (m, 2H), 3.37 – 3.28 (m, 1H), 2.57 – 2.42 (m, 2H), 2.30 (ddd, *J* = 18.9, 10.7, 8.7 Hz, 1H), 2.23 – 2.05 (m, 2H), 2.02 – 1.84 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 218.4, 138.5, 128.7, 128.3, 127.0, 55.5, 38.6, 31.9, 21.0.

Reference: Á. Gutiérrez-Bonet, A. Flores-Gaspar and R. Martin, *J. Am. Chem. Soc.*, 2013, **135**, 12576–12579. DOI: 10.1021/ja4068707



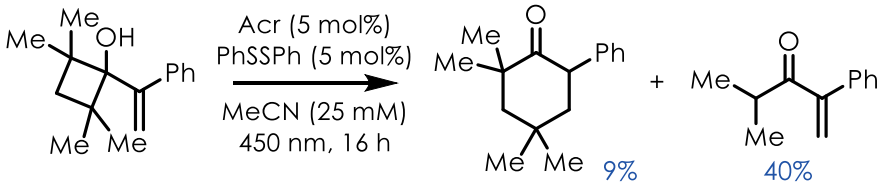
1-(1-phenyl-2-(1H-pyrazol-1-yl)ethyl)cyclobutan-1-ol (33): Compound **33** was prepared according to the General Procedure for Reaction B, with 5 equivalents of added pyrazole, beginning with cyclobutanol **S5** (17.4 mg; 0.1 mmol). The crude reaction mixture was purified by column chromatography (silica: 40-63 µm;

gradient: 0 to 15% ethyl acetate in hexanes) to afford **33** (20% ^{1}H NMR Yield) as a volatile yellow oil after subjection to high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 1.9 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.28 (ddd, *J* = 7.5, 6.6, 1.3 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.18 – 7.16 (m, 1H), 6.12 (t, *J* = 2.1 Hz, 1H), 4.64 (dd, *J* = 14.1, 7.6 Hz, 1H), 4.43 (dd, *J* = 14.1, 7.4 Hz, 1H), 3.37 (t, *J* = 7.5 Hz, 1H), 3.15 (s, 1H), 1.95 – 1.70 (m, 5H), 1.60 – 1.53 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 139.0, 130.1, 129.0, 128.4, 127.1, 105.3, 76.5, 54.0, 53.1, 36.1, 35.0, 12.8.

HRMS (m/z): calculated for $C_{15}H_{18}N_2O$ $[M+H]^+$ 243.1492, found 243.1492.

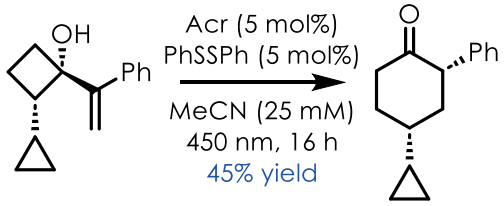


4-methyl-2-phenylpent-1-en-3-one (35): Compound **35** was prepared according to the General Procedure for Reaction B, beginning with cyclobutanol **S34** (23.0 mg; 0.1 mmol). The crude reaction mixture was purified by column chromatography (fine silica: 25-40 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **35** (40% ^{1}H NMR yield) as a yellow oil which is volatile under high vacuum. Spectral data were found to be in agreement with those reported in the literature.[61]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.30 (d, *J* = 7.4 Hz, 2H), 6.00 – 5.97 (m, 1H), 5.85 (d, *J* = 1.5 Hz, 1H), 3.22 (hept, *J* = 7.0 Hz, 1H), 1.14 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.0, 149.2, 137.5, 128.3, 128.1, 128.1, 122.7, 36.8, 18.7.

Reference: Gembus, V.; Bonnect, J.-J.; Janin, F.; Bohn, P.; Levacher, V.; Brière, J.-F. *Org. Biomol. Chem.* 2010, ***8***, 3287-3293. DOI: 10.1039/C004704J



4-cyclopropyl-2-phenylcyclohexan-1-one (36): Compound **36** was prepared according to the General Procedure for Reaction B, beginning with cyclobutanol **S36** (21.4 mg; 0.1 mmol). The crude reaction mixture

was purified by column chromatography (fine silica: 25-40 μm; gradient: 0 to 10% ethyl acetate in hexanes) to afford **36** (45% ^{1}H NMR yield) as a yellow oil which is volatile under high vacuum.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.28 – 7.21 (m, 1H), 7.18 – 7.08 (m, 2H), 3.58 (dd, *J* = 13.4, 5.4 Hz, 1H), 2.54 (ddd, *J* = 14.0, 4.8, 2.7 Hz, 1H), 2.47 (tdd, *J* = 13.9, 6.0, 1.1 Hz, 1H), 2.37 (ddt, *J* = 13.2, 5.4, 3.3 Hz, 1H), 2.26 (ddt, *J* = 13.5, 6.1, 3.1 Hz, 1H), 1.89 (td, *J* = 13.3, 11.9 Hz, 1H), 1.70 (tdd, *J* = 13.5, 12.0, 4.8 Hz, 1H), 1.21 (tdt, *J* = 12.1, 8.8, 3.6 Hz, 1H), 0.59 (qt, *J* = 8.2, 4.9 Hz, 1H), 0.54 – 0.41 (m, 2H), 0.17 (dddd, *J* = 11.9, 9.7, 8.4, 4.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.5, 138.9, 128.8, 128.5, 127.1, 56.8, 42.8, 41.7, 41.6, 33.6, 16.5, 3.7, 3.6.

HRMS (m/z): calculated for $C_{15}H_{18}O$ $[M+Na]^+$ 237.1250, found 237.1248.

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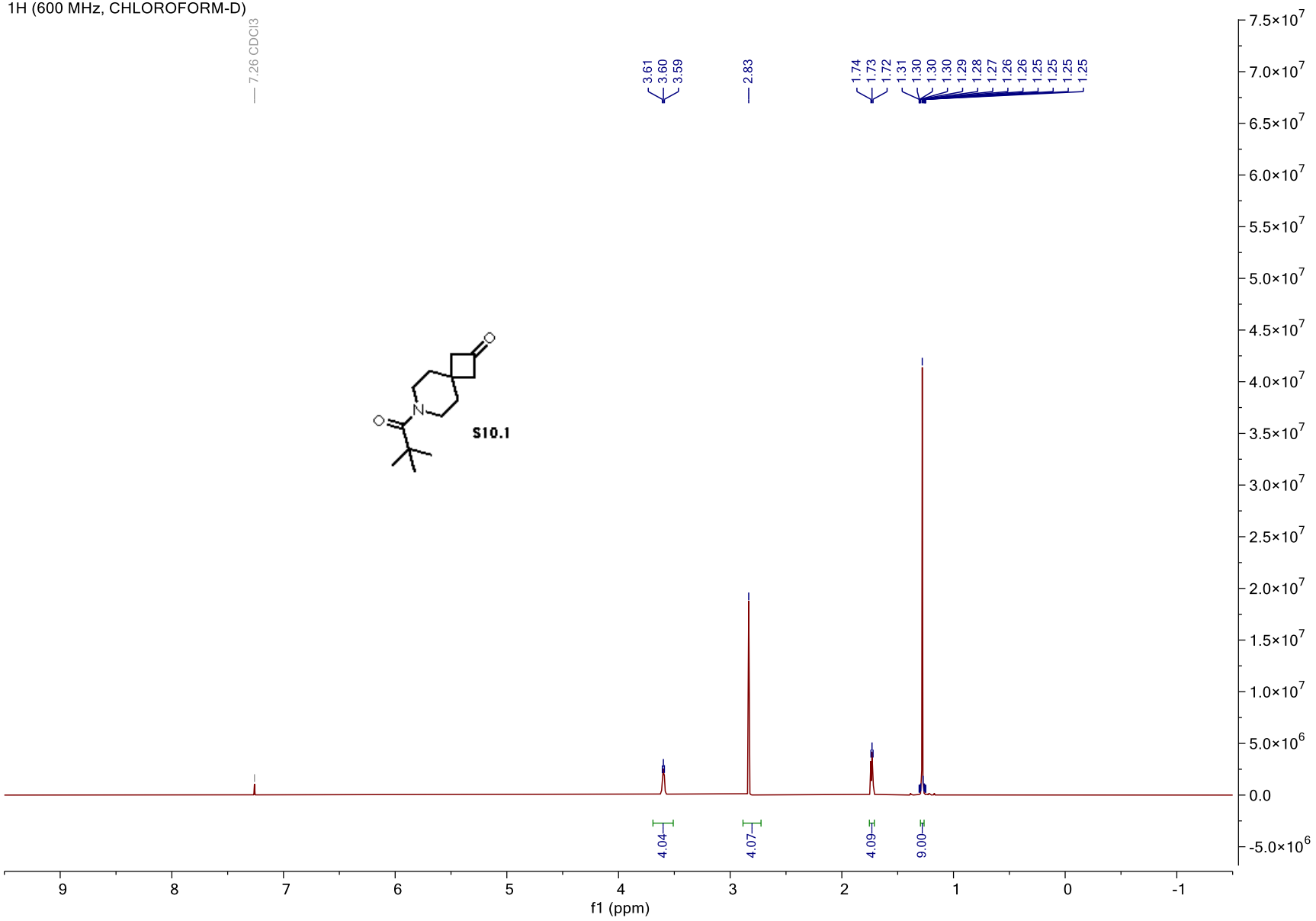
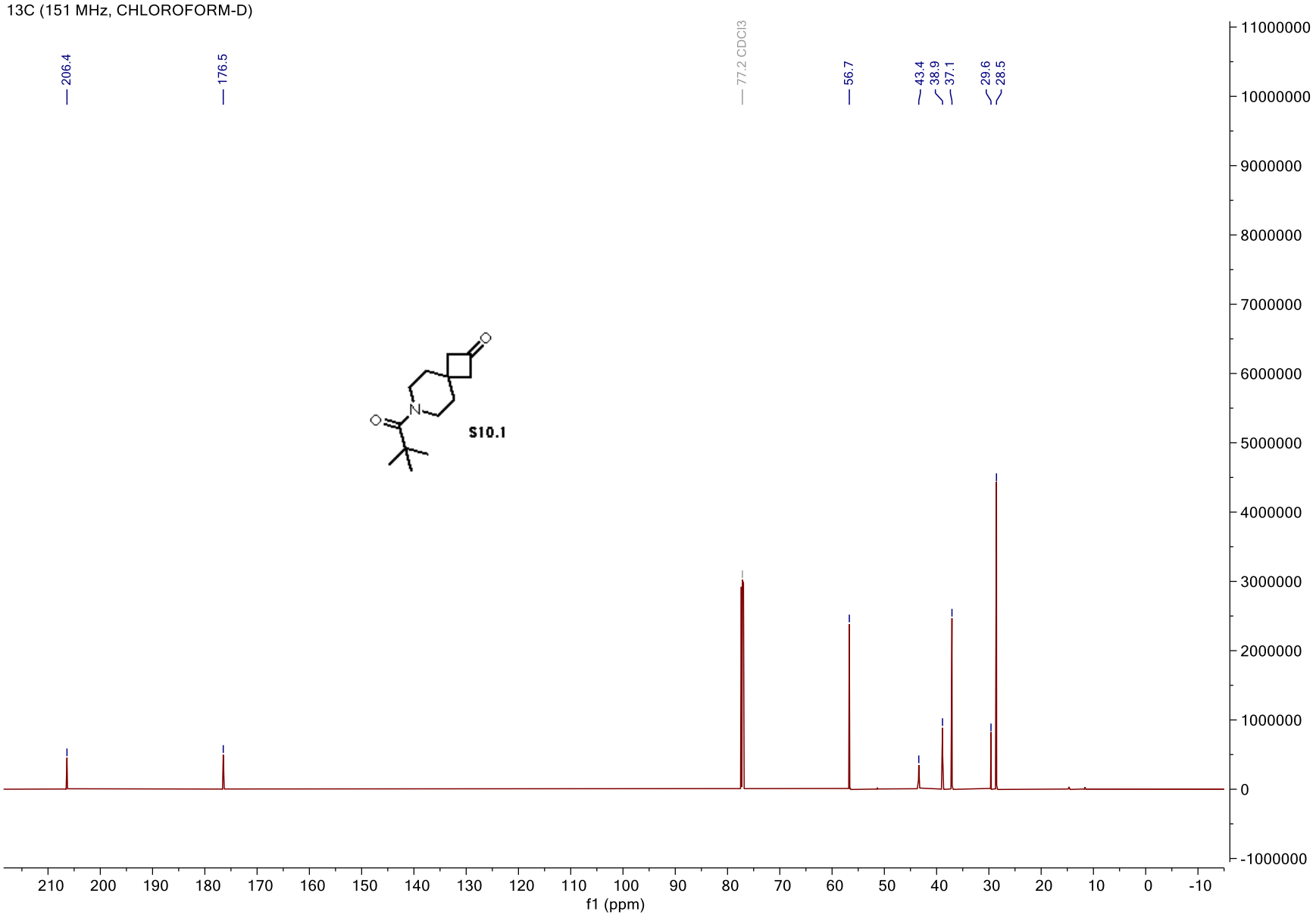
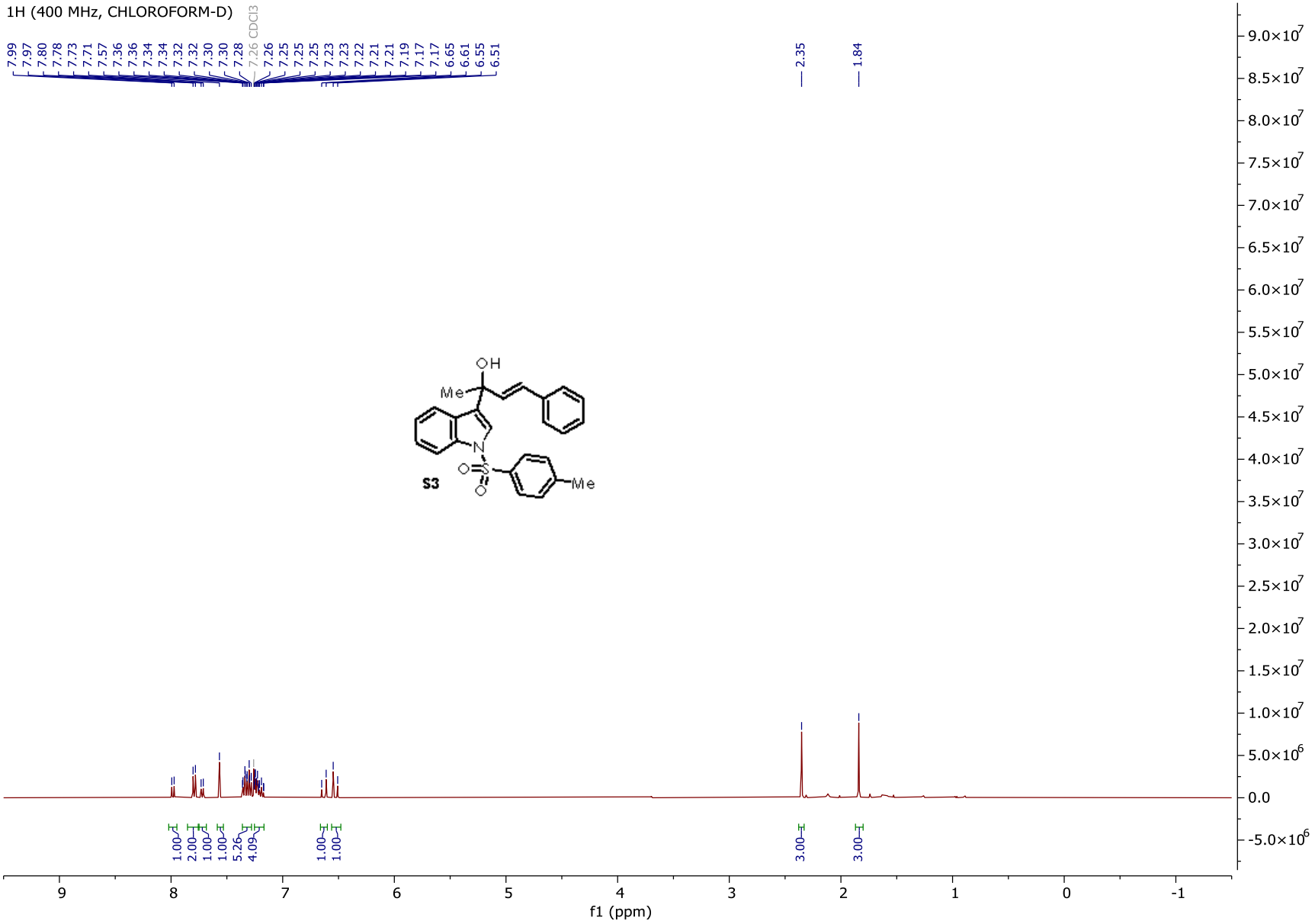
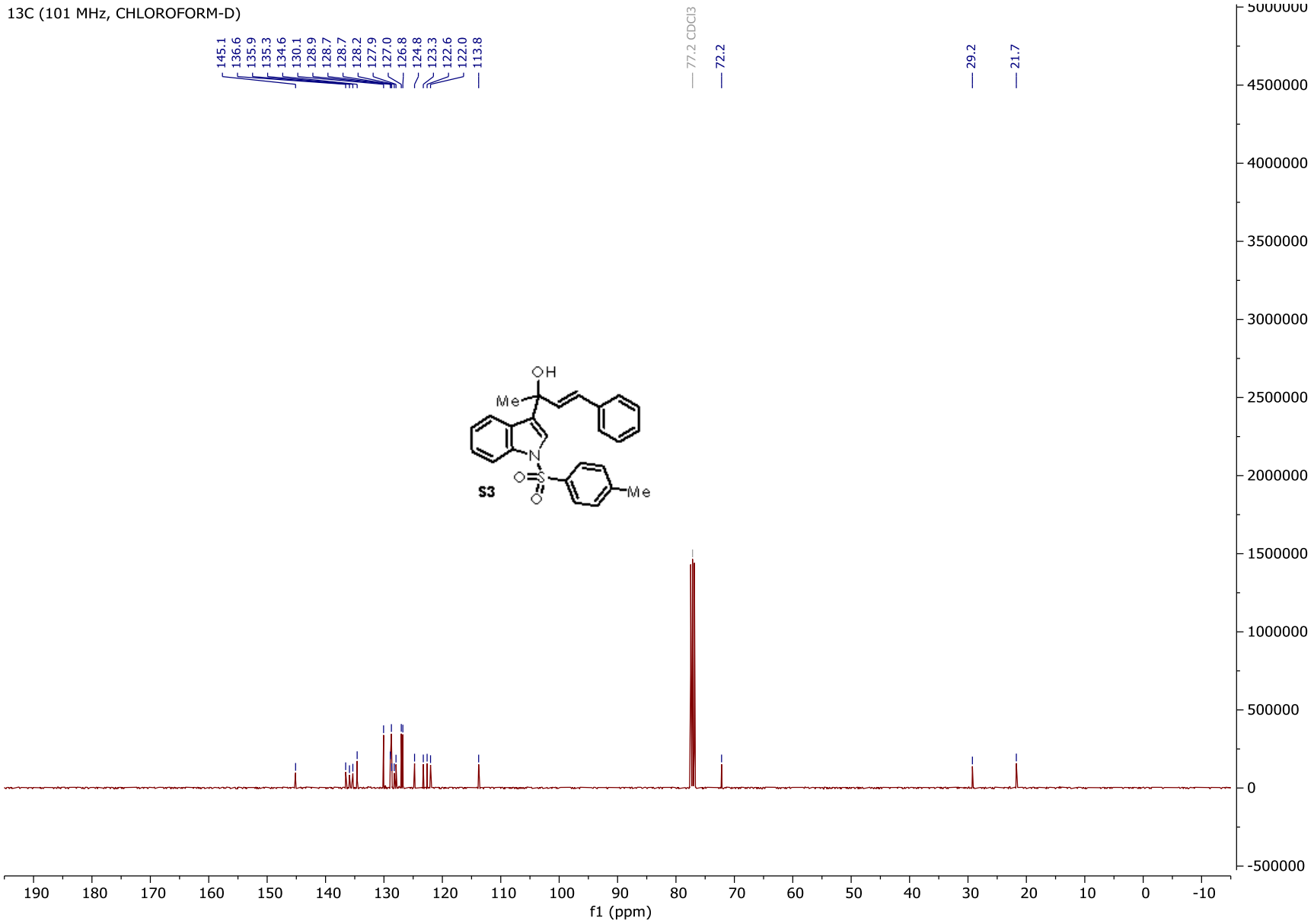
^{1}H and ^{13}C NMR Spectra

1H (600 MHz, CHLOROFORM-D)

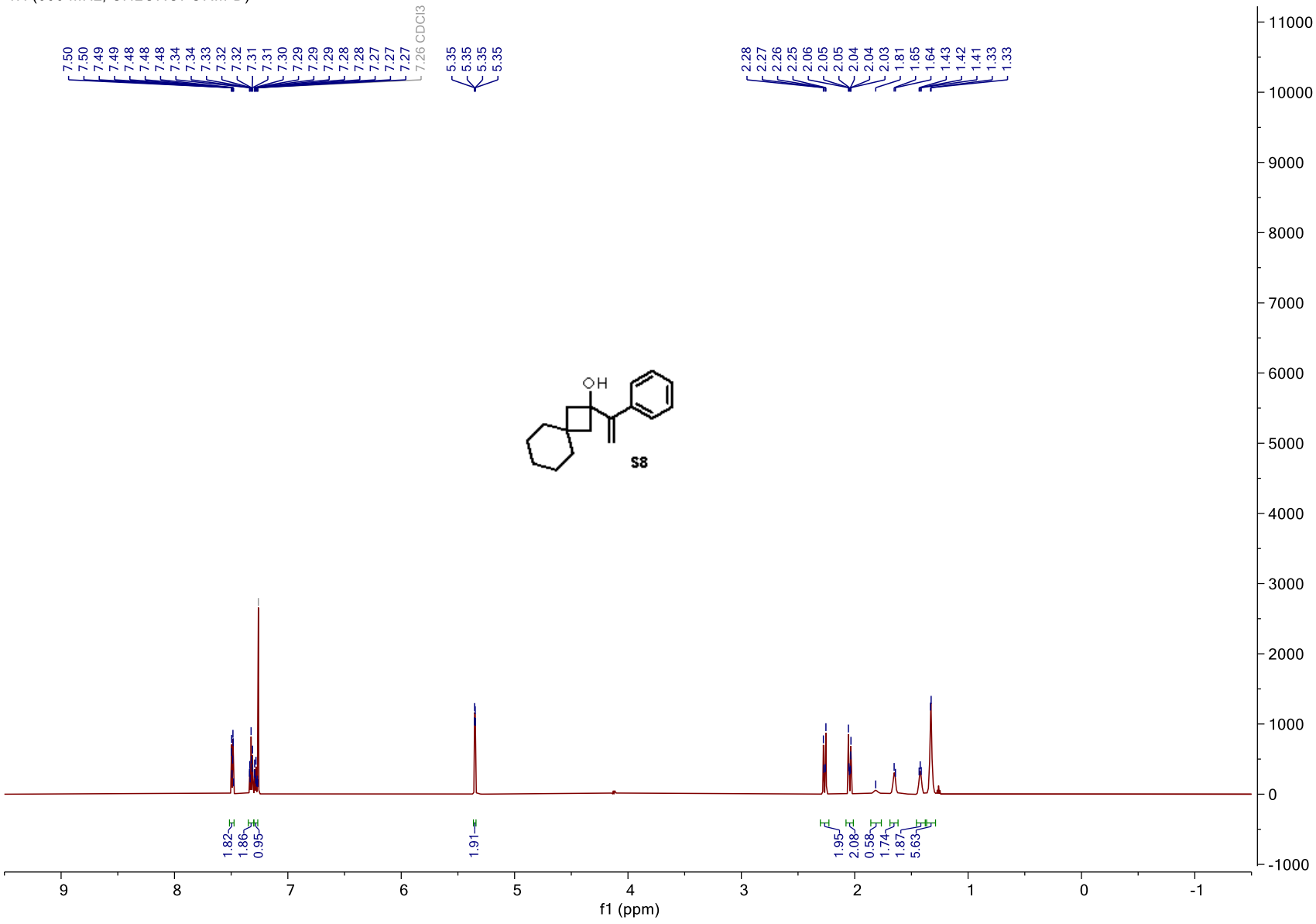


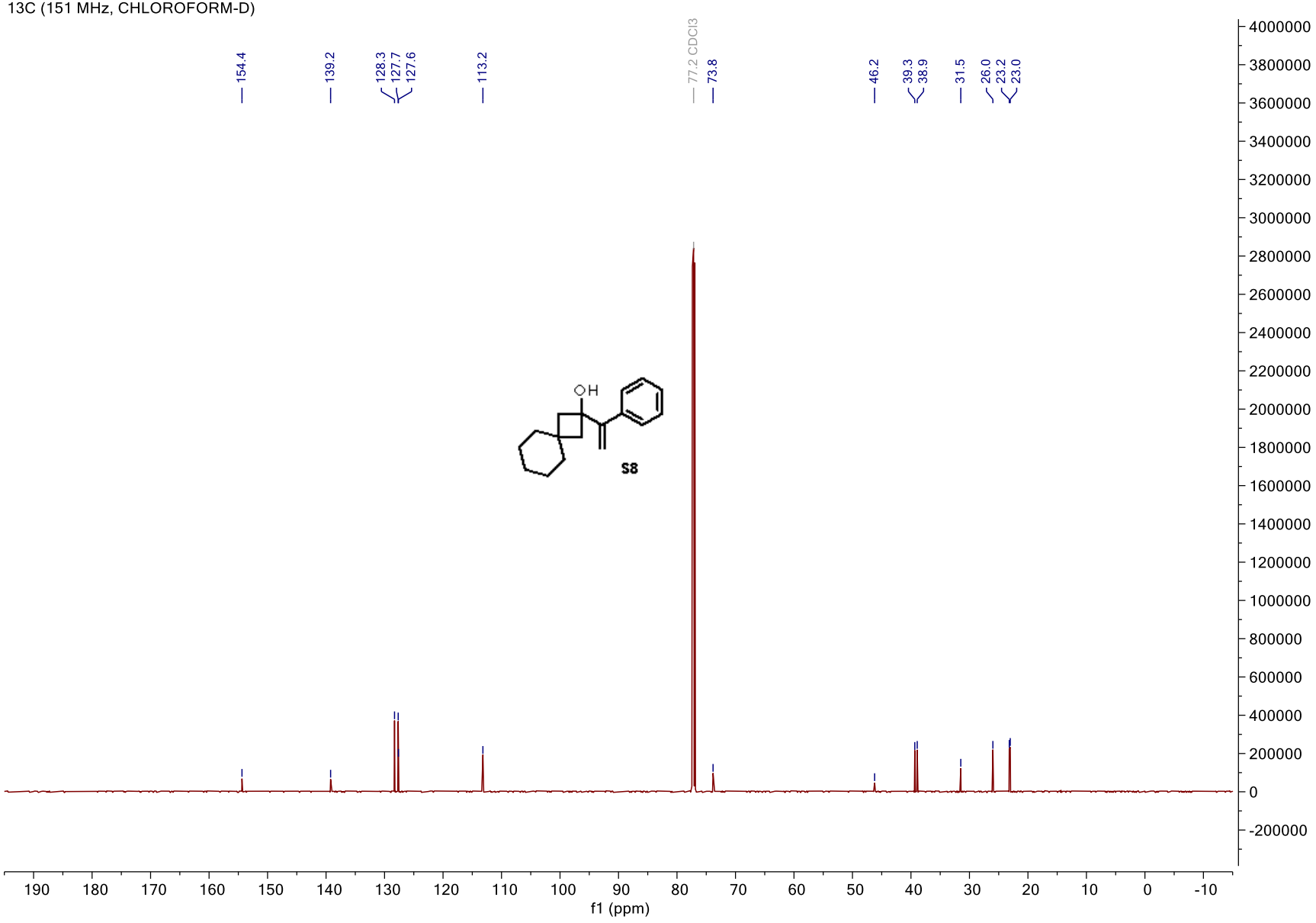

13C (151 MHz, CHLOROFORM-D)
206.4
176.5
77.2 CDCl3
56.7
43.4
38.9
37.1
29.6
28.5
S10.1
f1 (ppm)


1H (400 MHz, CHLOROFORM-D)
7.99
7.97
7.80
7.78
7.73
7.71
7.57
7.36
7.34
7.34
7.32
7.30
7.28
7.26 CDCl3
7.26
7.25
7.25
7.25
7.23
7.23
7.22
7.21
7.21
7.19
7.17
7.17
6.65
6.61
6.55
6.51
2.35
1.84
OH
Me
N
S
O
O
S3
Me
1.00
2.00
1.00
5.26
4.09
1.00
1.00
3.00
3.00
f1 (ppm)

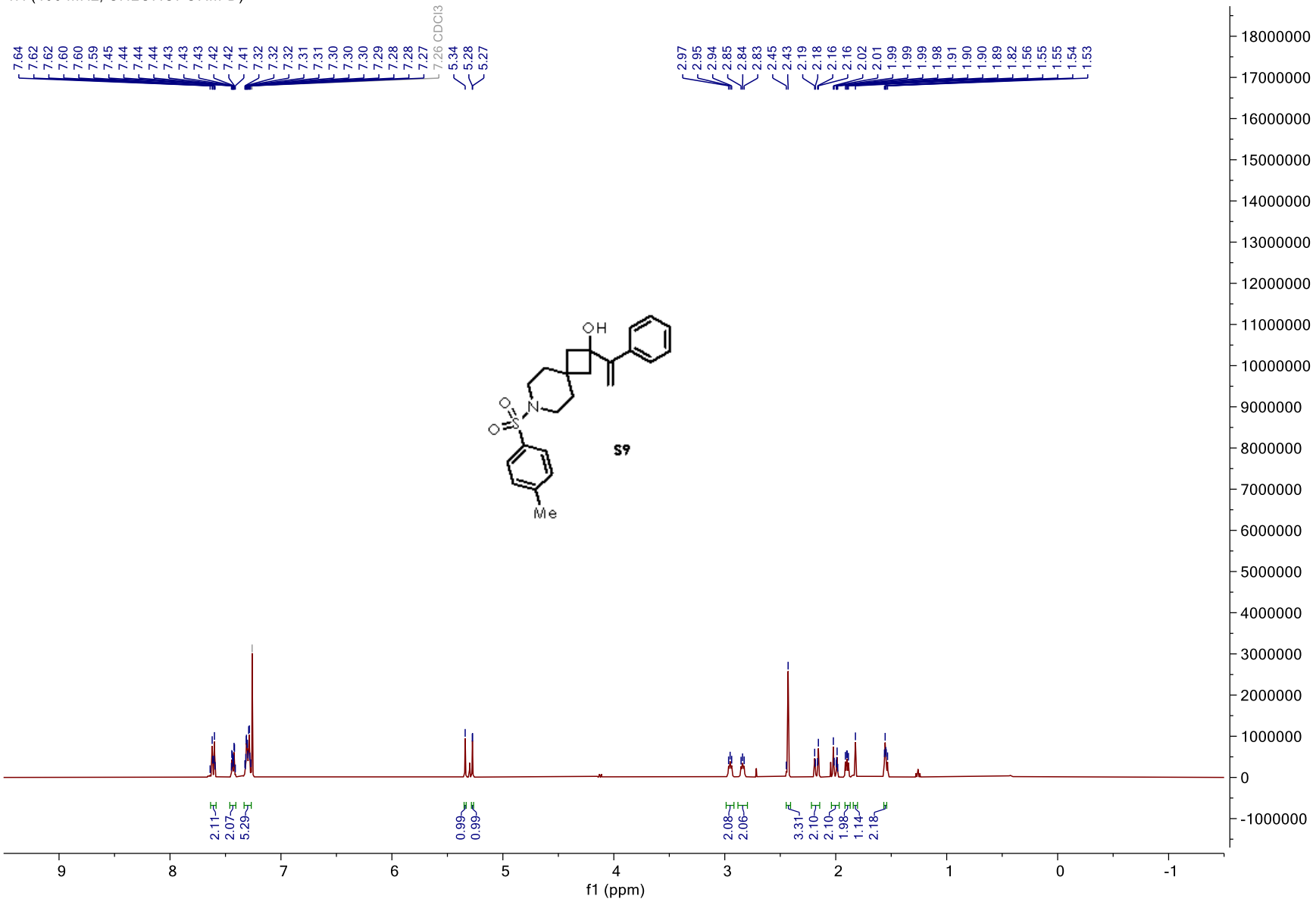

13C (101 MHz, CHLOROFORM-D)
145.1
136.6
135.9
135.3
134.6
130.1
128.9
128.7
128.7
128.2
127.9
127.0
126.8
124.8
123.3
122.6
122.0
113.8
77.2 CDCl3
72.2
29.2
21.7
OH
Me
N
S
Me
S3
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

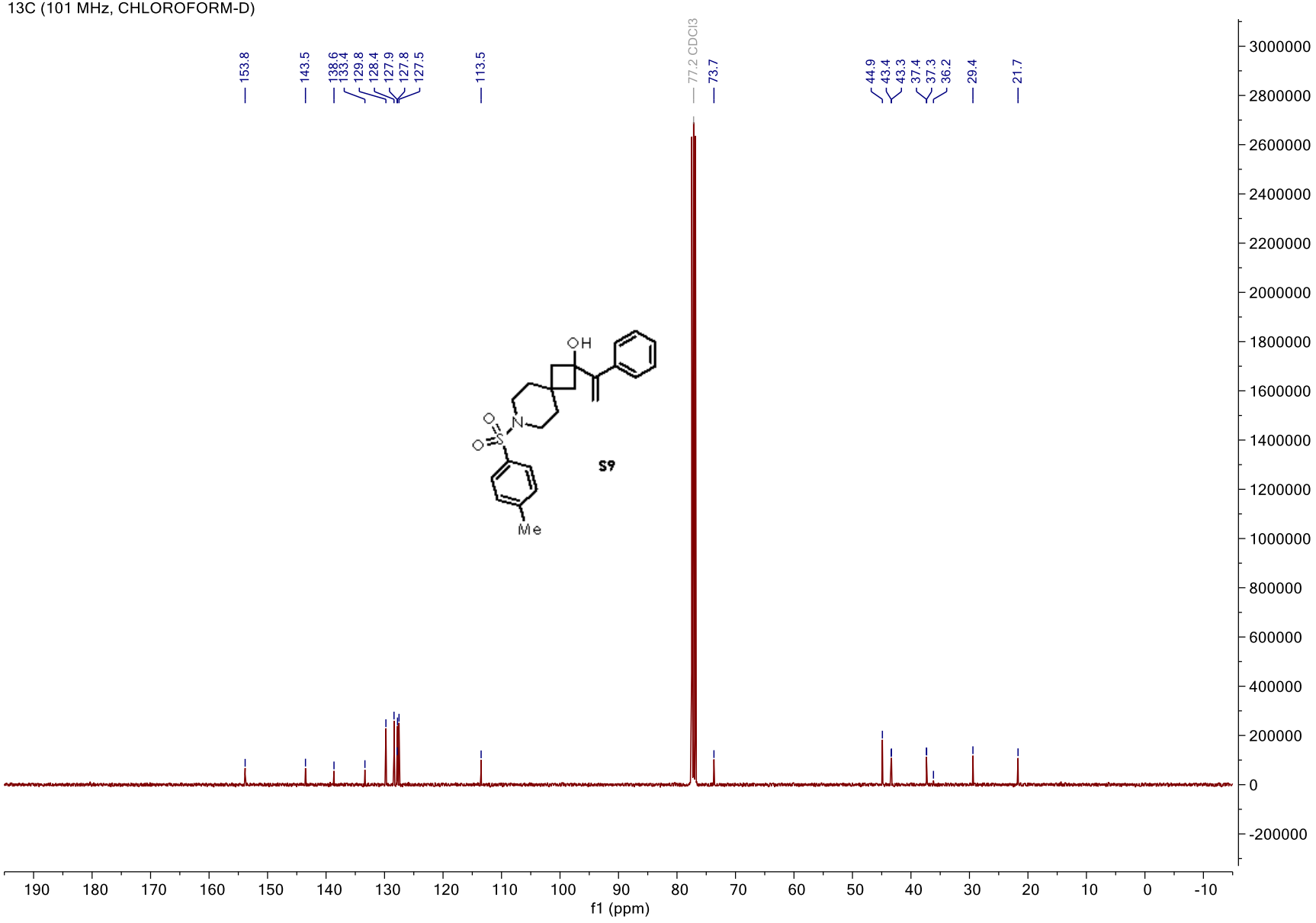
1H (600 MHz, CHLOROFORM-D)

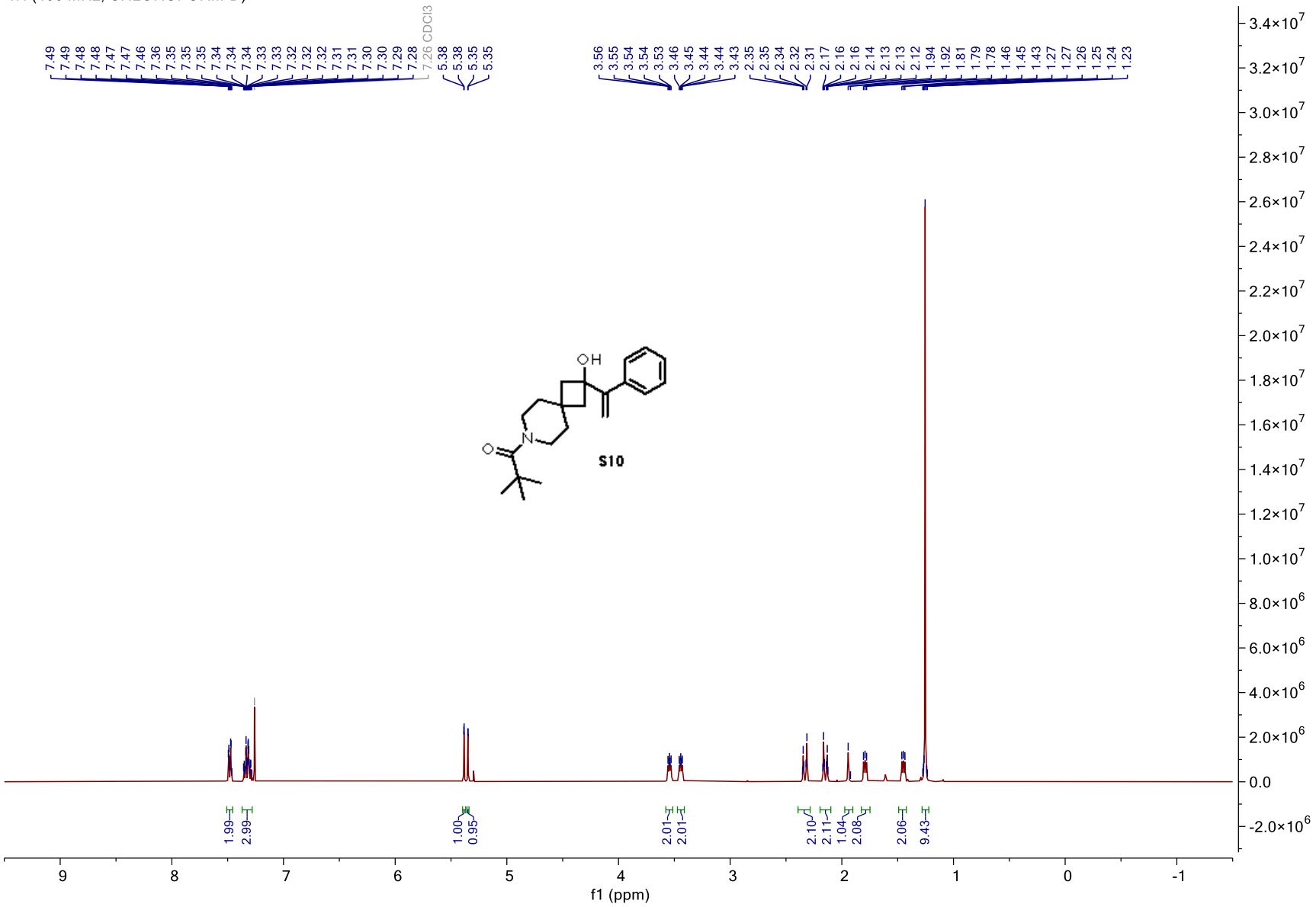


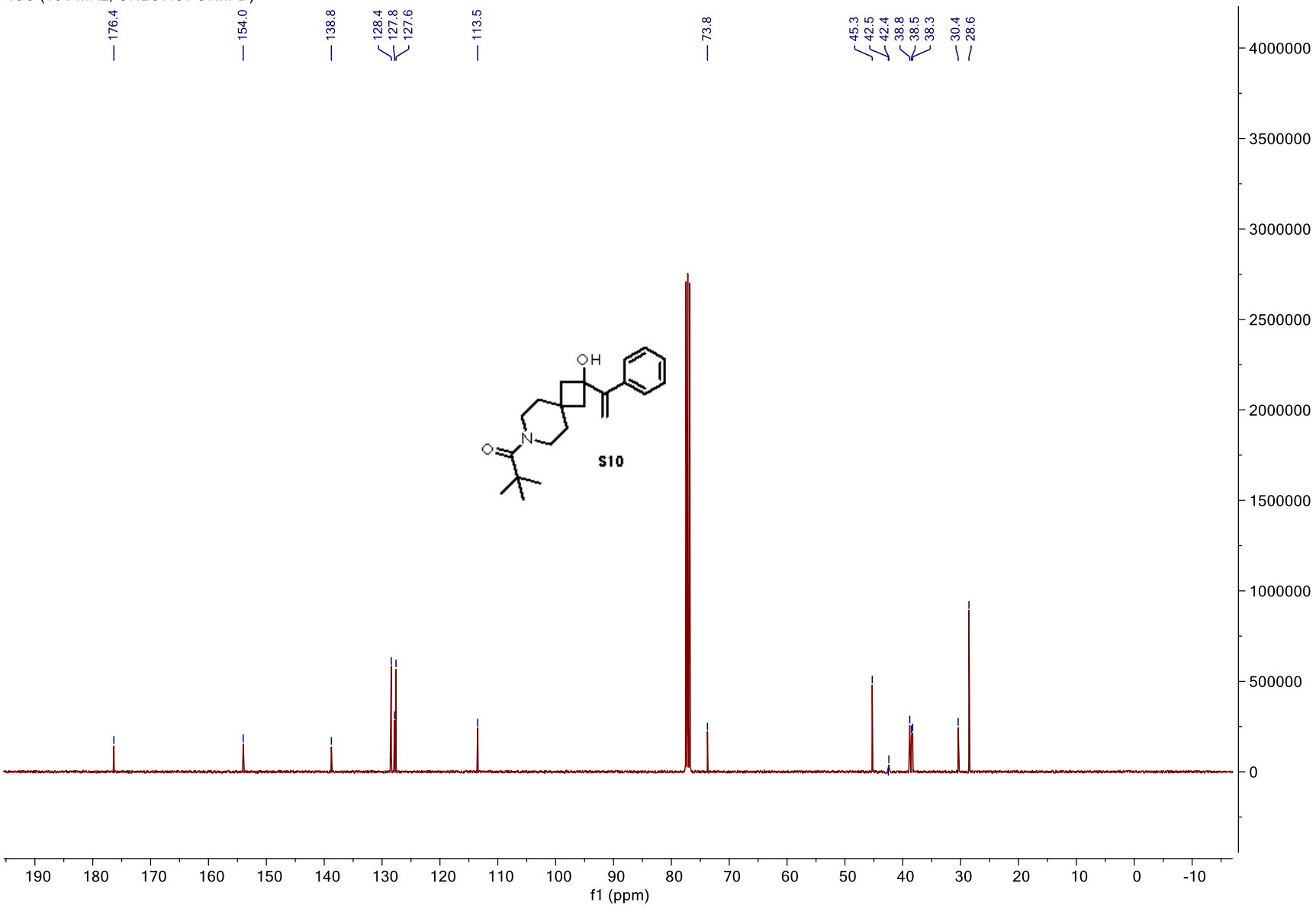

13C (151 MHz, CHLOROFORM-D)
154.4
139.2
128.3
127.7
127.6
113.2
77.2 CDCl3
73.8
46.2
39.3
38.9
31.5
26.0
23.2
23.0
OH
S8
f1 (ppm)

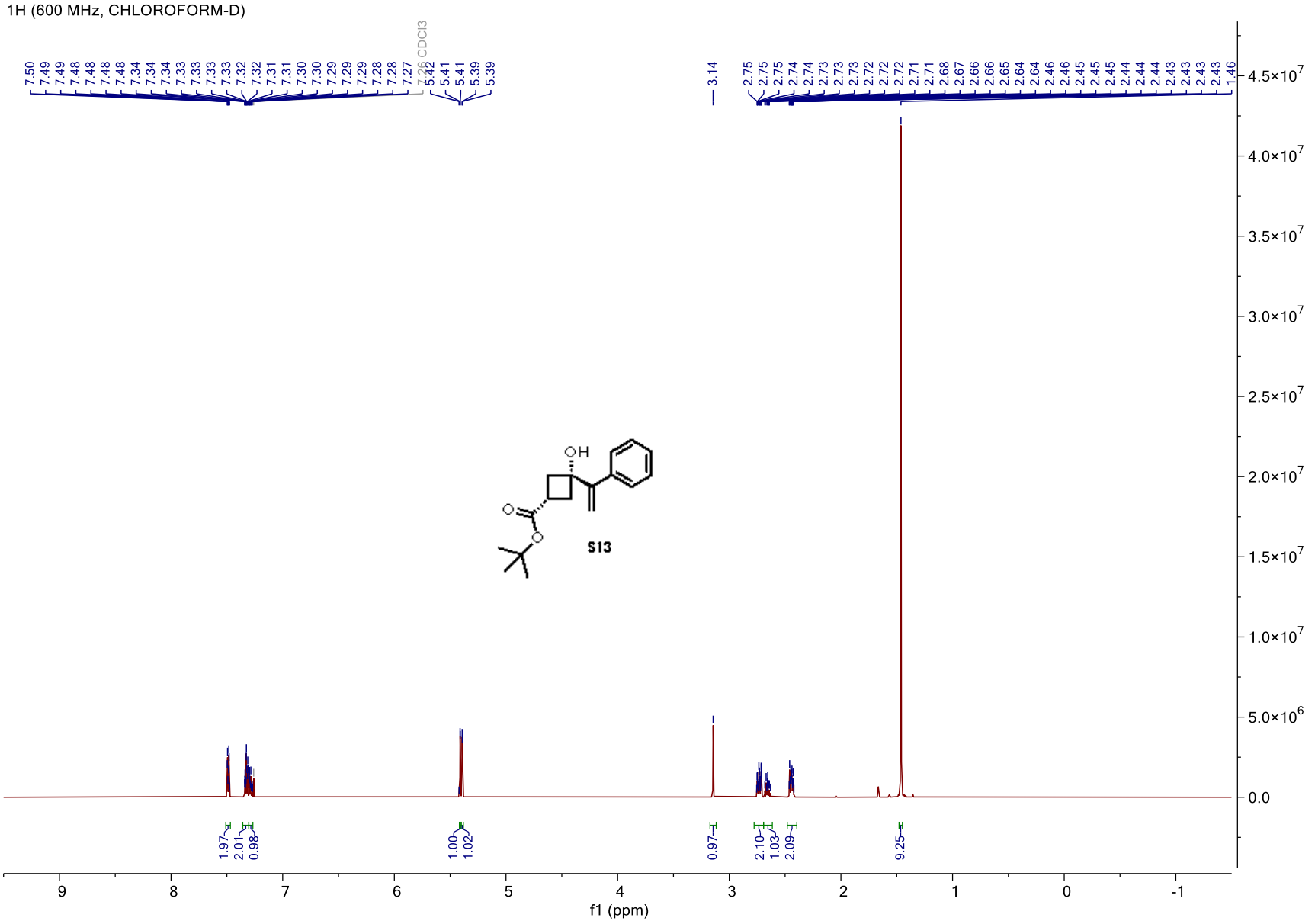
1H (400 MHz, CHLOROFORM-D)

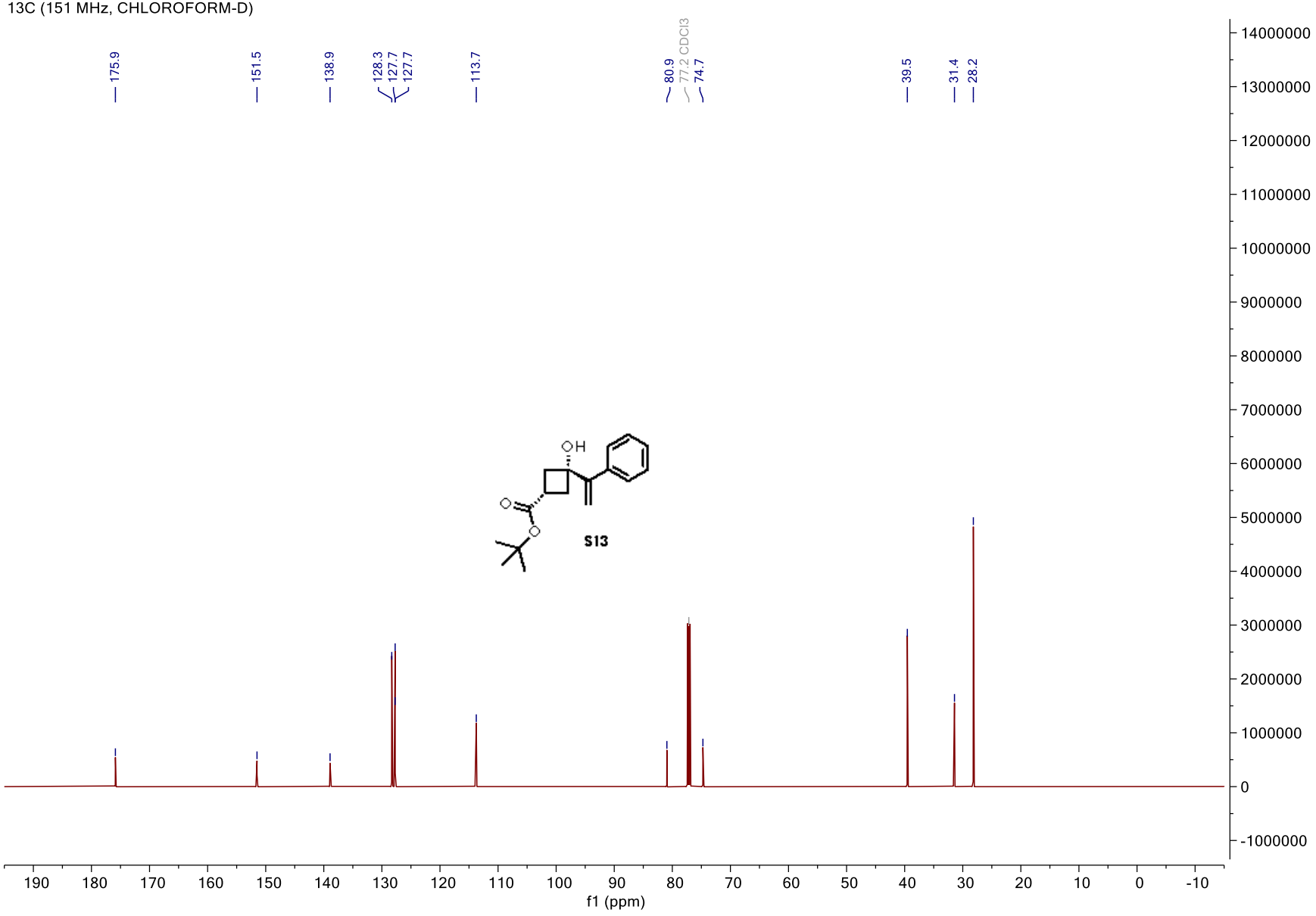



13C (101 MHz, CHLOROFORM-D)
153.8
143.5
138.6
133.4
129.8
128.4
127.9
127.8
127.5
113.5
77.2 CDCl3
73.7
44.9
43.4
43.3
37.4
37.3
36.2
29.4
21.7
OH
N
S
Me
S9
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

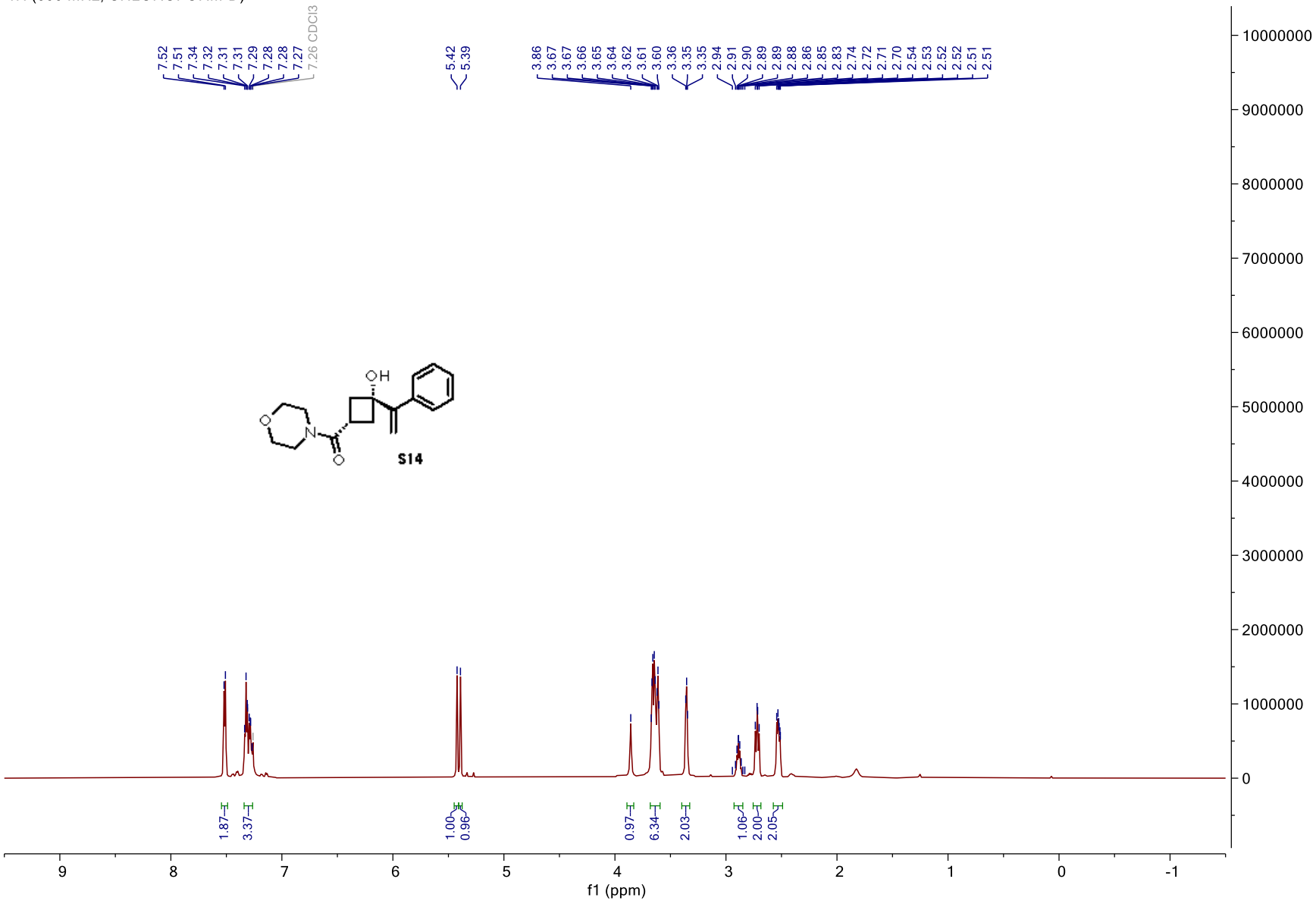

1H (400 MHz, CHLOROFORM-D)
7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.26 CDCl3 5.38 5.38 5.35 5.35 5.35
3.56 3.55 3.54 3.54 3.53 3.46 3.45 3.44 3.44 3.43 2.35 2.35 2.34 2.32 2.31 2.17 2.16 2.16 2.14 2.13 2.13 2.12 1.94 1.92 1.81 1.79 1.78 1.46 1.45 1.43 1.27 1.27 1.26 1.25 1.24 1.23
OH
N
O
S10
3.4×10^7
3.2×10^7
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
1.99 2.99 1.00 0.95 2.01 2.01 2.10 2.11 1.04 2.08 2.06 9.43
9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

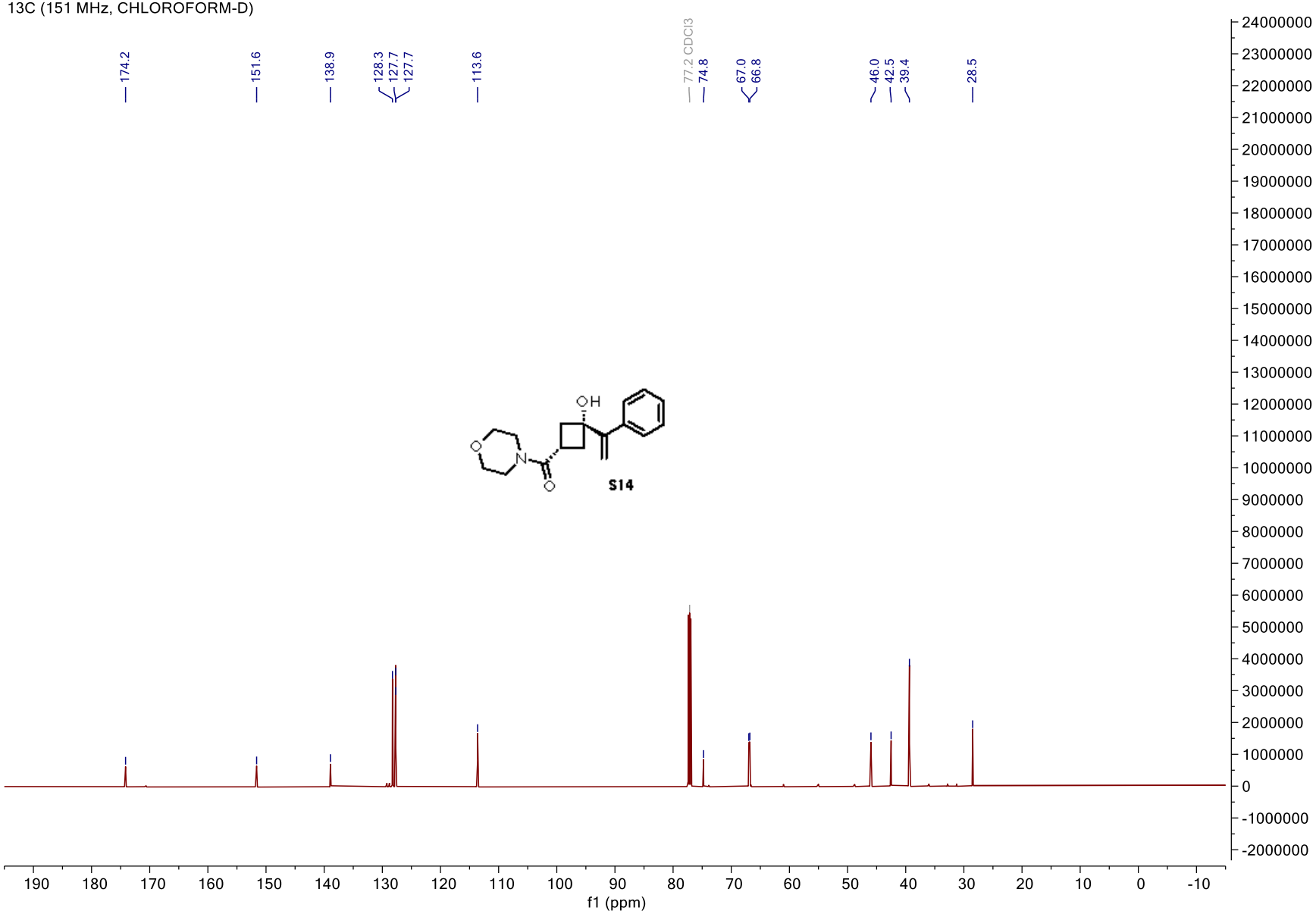

13C (101 MHz, CHLOROFORM-D)
176.4
154.0
138.8
128.4
127.8
127.6
113.5
73.8
45.3
42.5
42.4
38.8
38.5
38.3
30.4
28.6
OH
N
O
S10
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

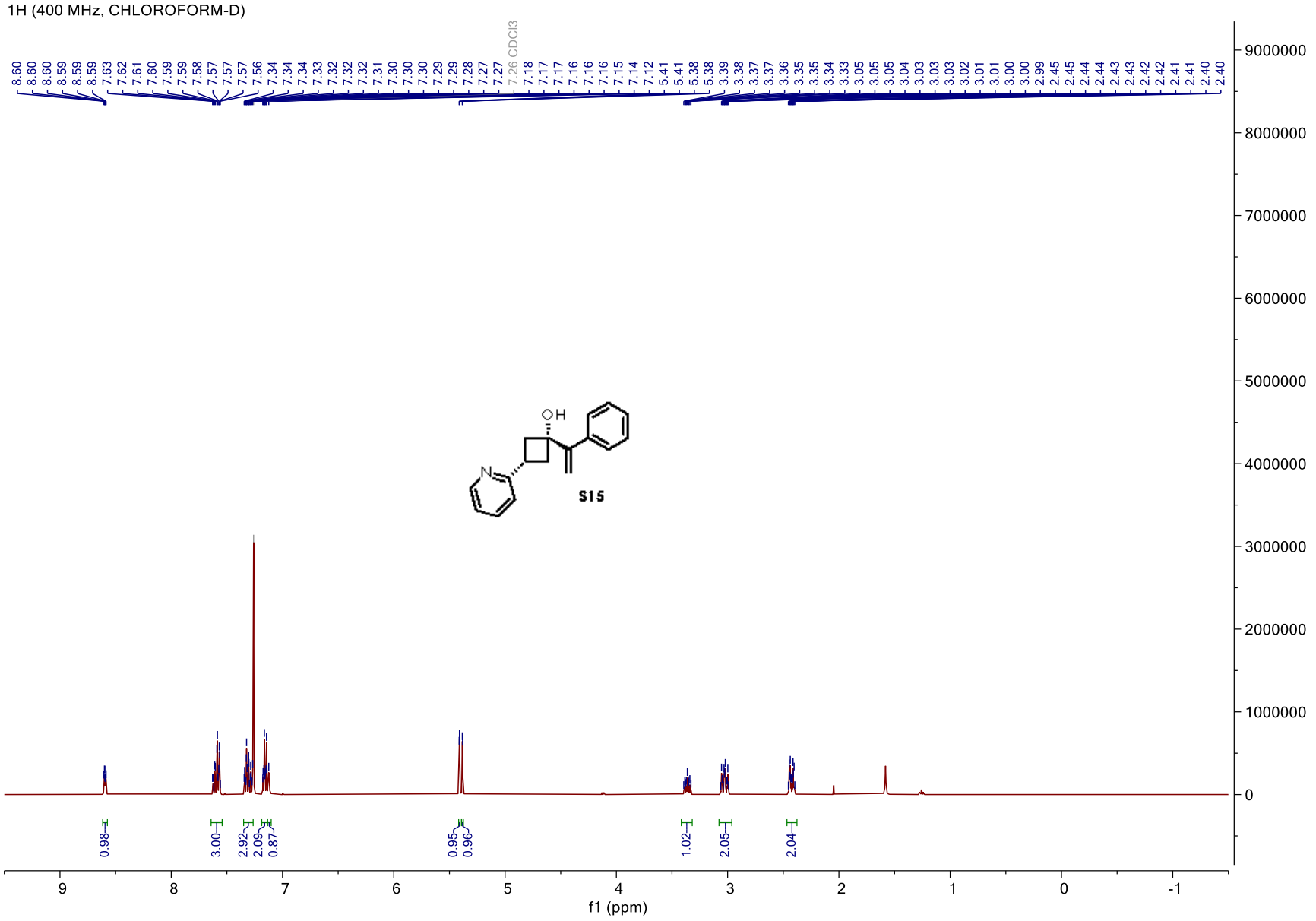

1H (600 MHz, CHLOROFORM-D)
7.50 7.49 7.49 7.48 7.48 7.48 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.27
7.26 CDCl3
5.42 5.41 5.41 5.39 5.39
3.14
2.75 2.75 2.75 2.74 2.74 2.73 2.73 2.72 2.72 2.72 2.71 2.71 2.68 2.67 2.66 2.66 2.65 2.64 2.64 2.46 2.46 2.45 2.45 2.44 2.44 2.44 2.43 2.43 2.43 2.43 1.46
OH
S13
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
1.97 2.01 0.98 1.00 1.02 0.97 2.10 1.03 2.09 9.25
9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


13C (151 MHz, CHLOROFORM-D)
175.9
151.5
138.9
128.3
127.7
127.7
113.7
80.9
77.2 CDCl3
74.7
39.5
31.4
28.2
OH
S13
f1 (ppm)

1H (600 MHz, CHLOROFORM-D)




13C (151 MHz, CHLOROFORM-D)
174.2
151.6
138.9
128.3
127.7
127.7
113.6
77.2 CDCl3
74.8
67.0
66.8
46.0
42.5
39.4
28.5
OH
N
O
O
S14
f1 (ppm)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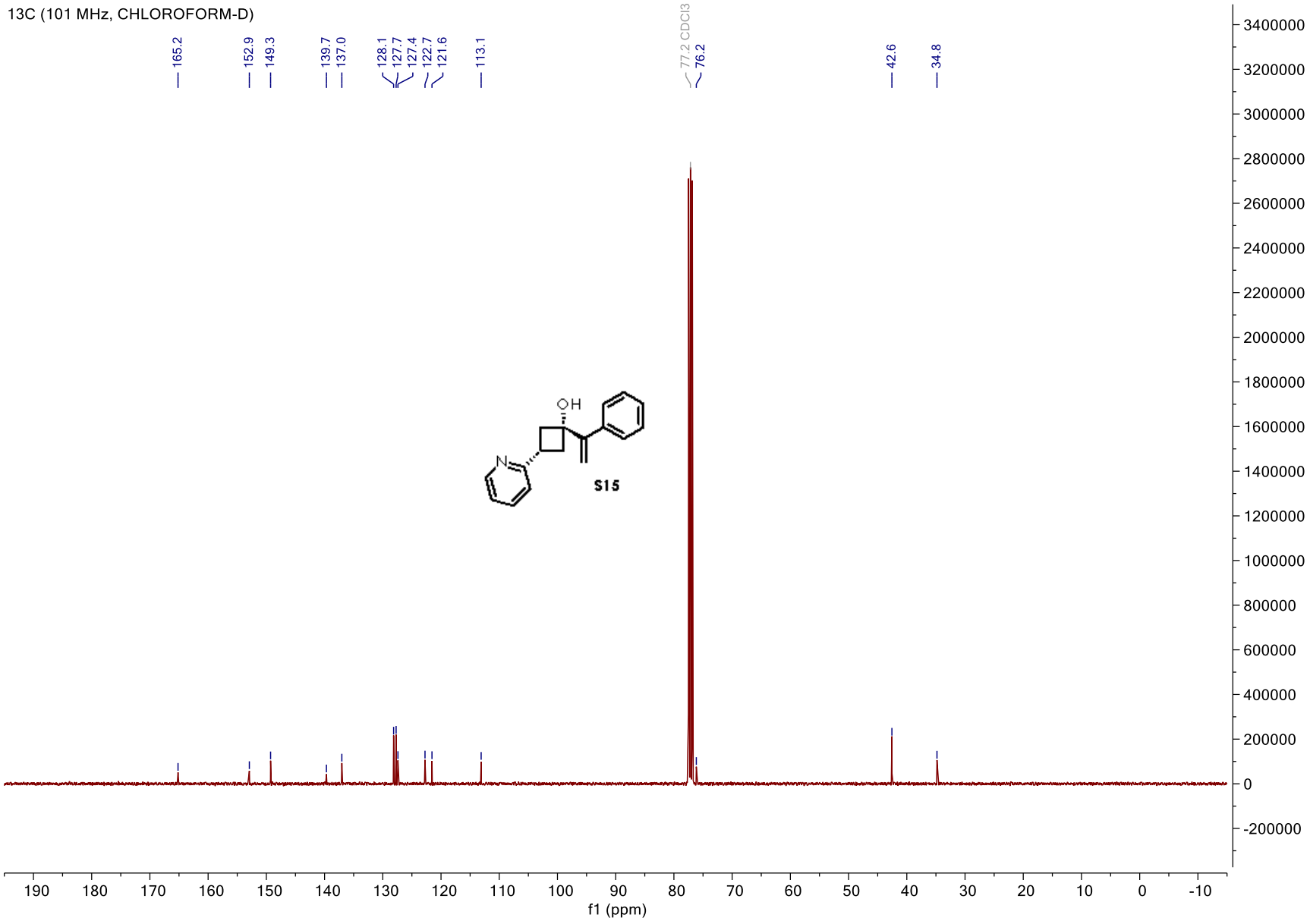
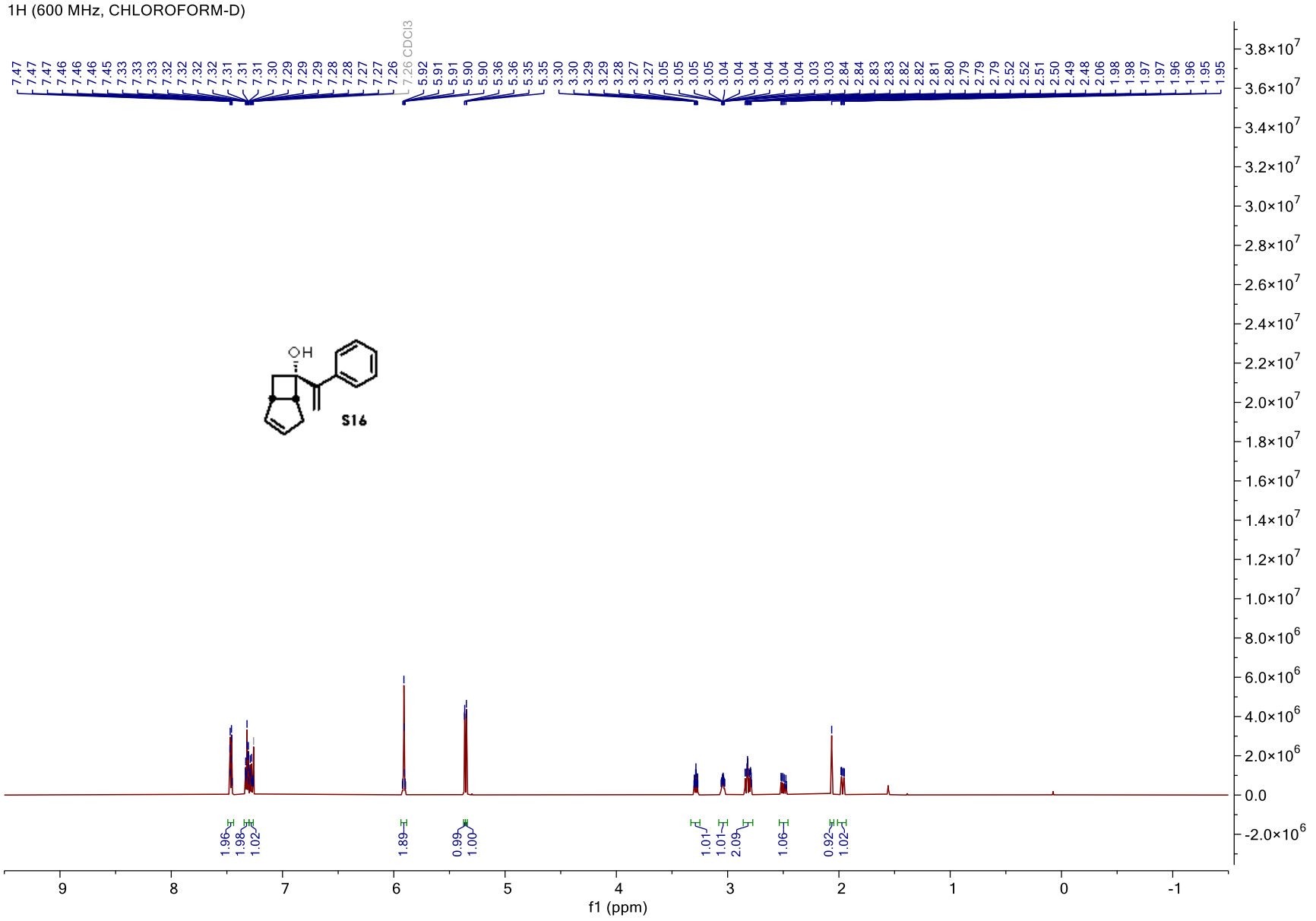
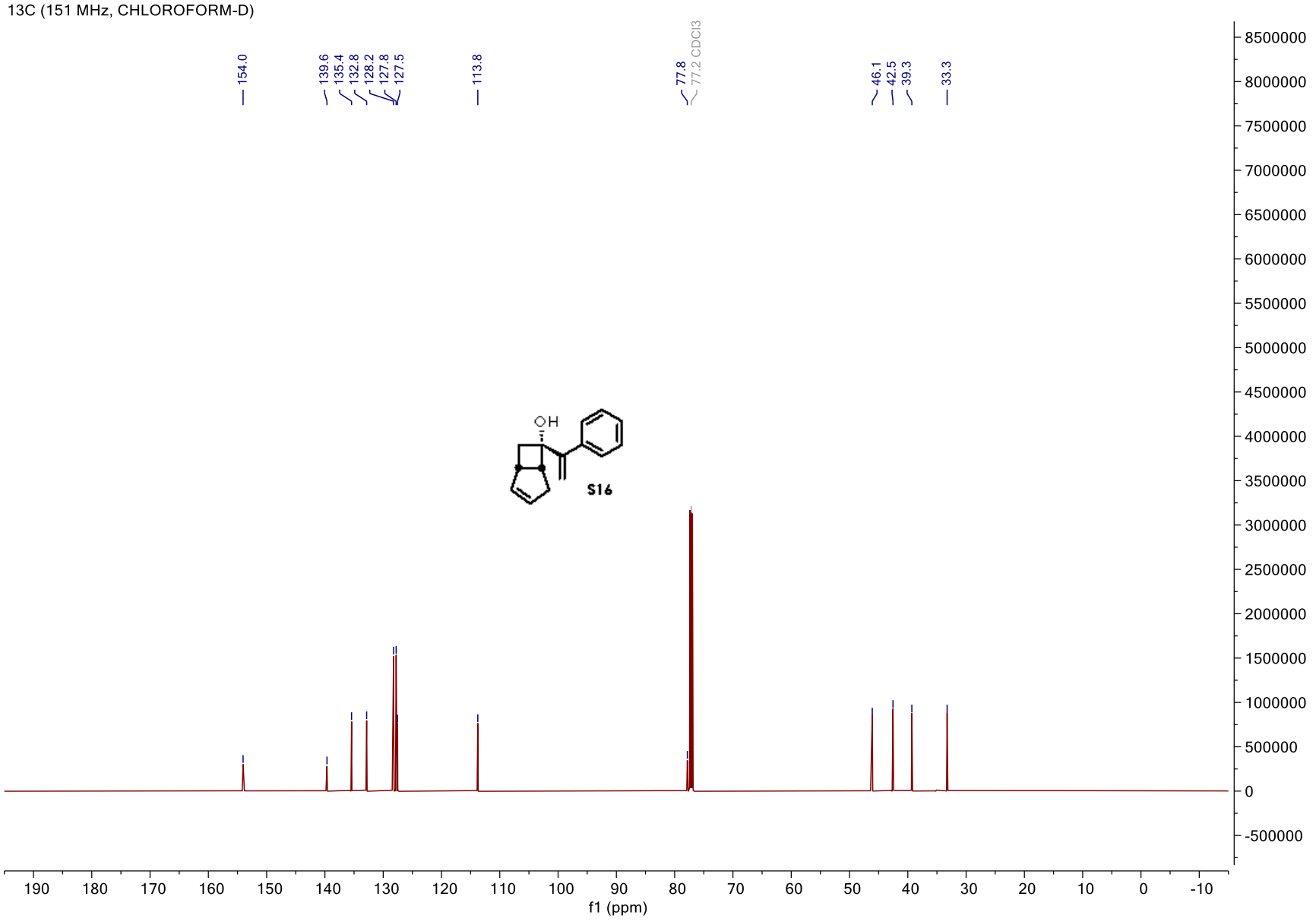
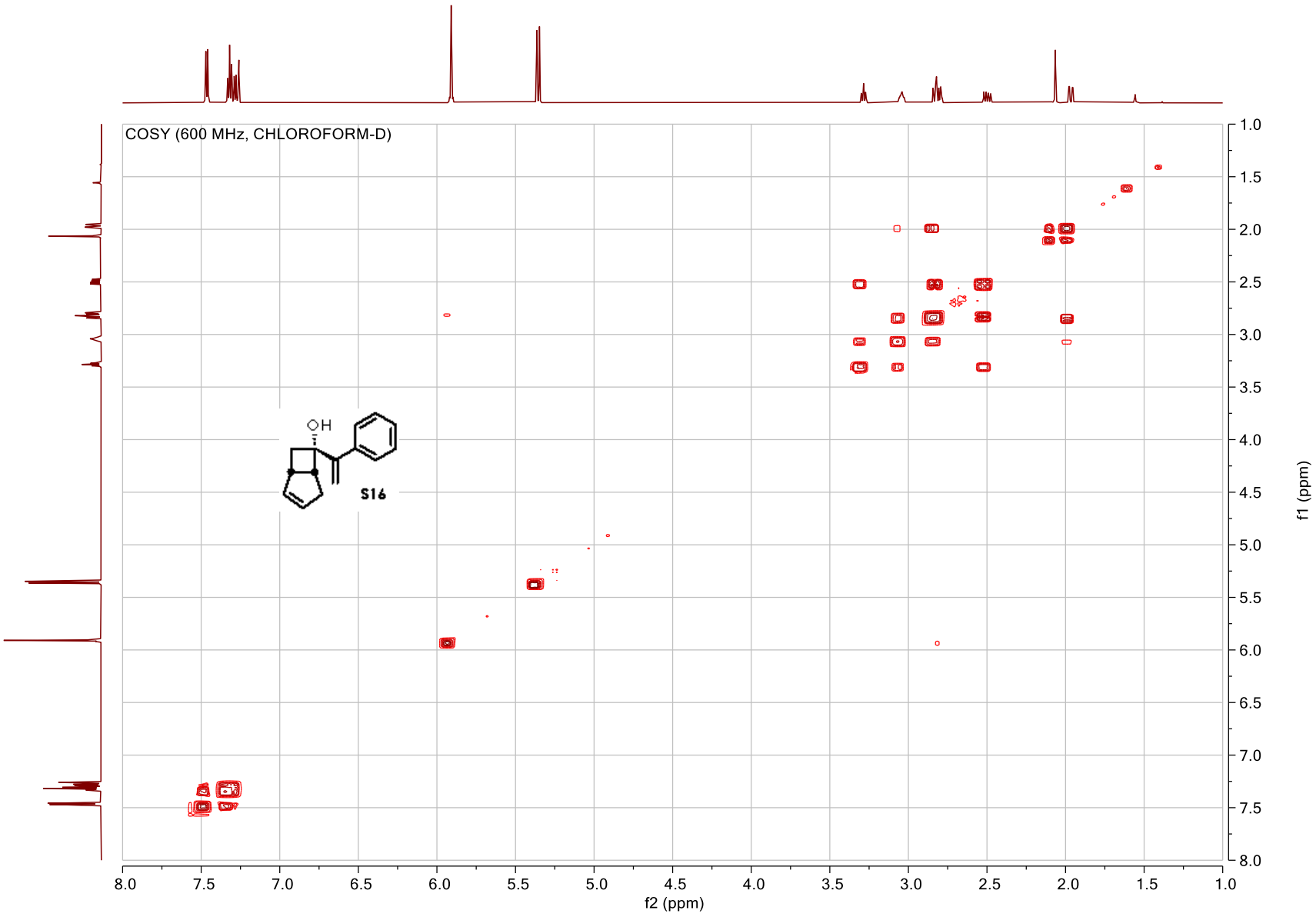
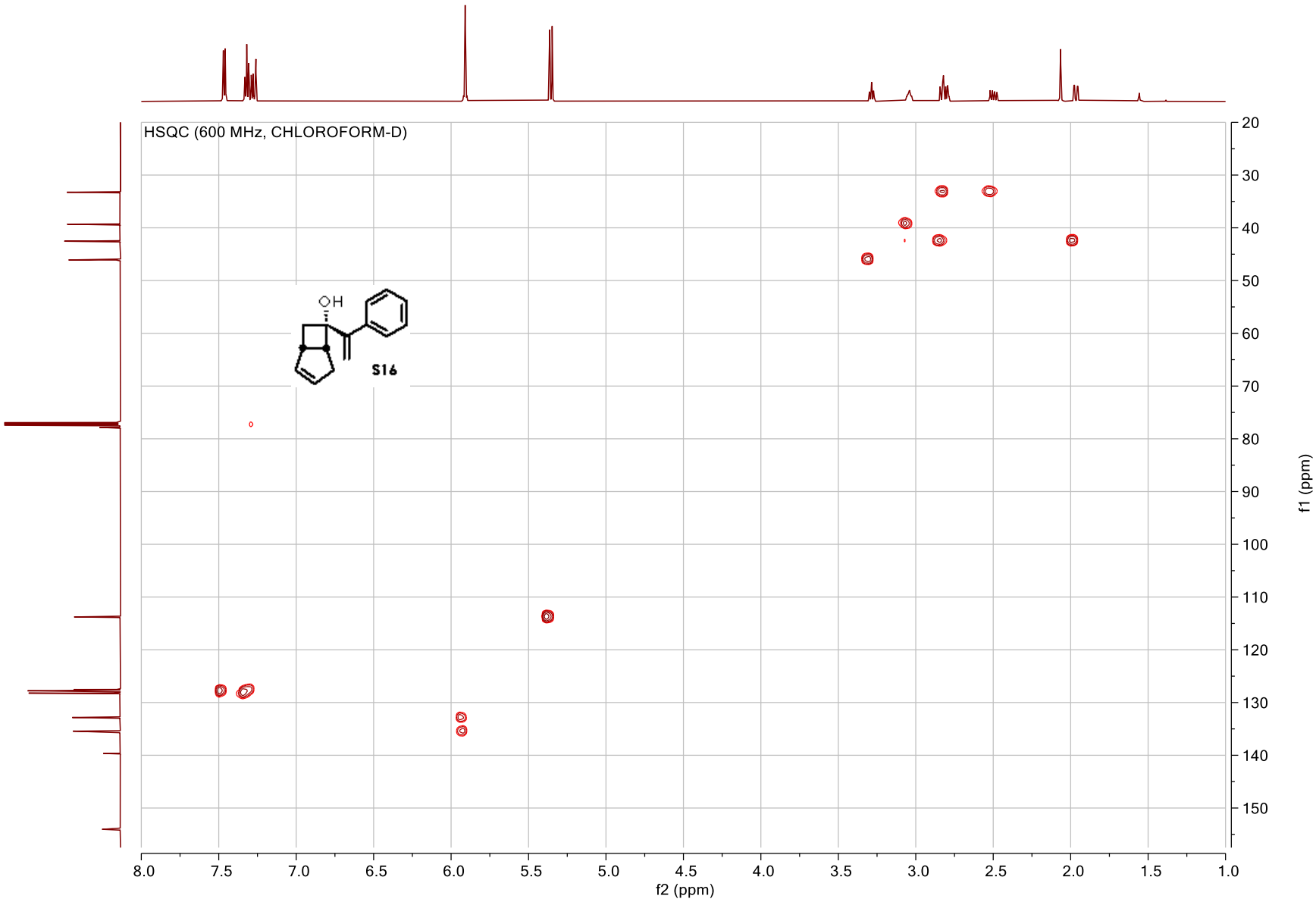
7.26 CDCl3
S15
f1 (ppm)

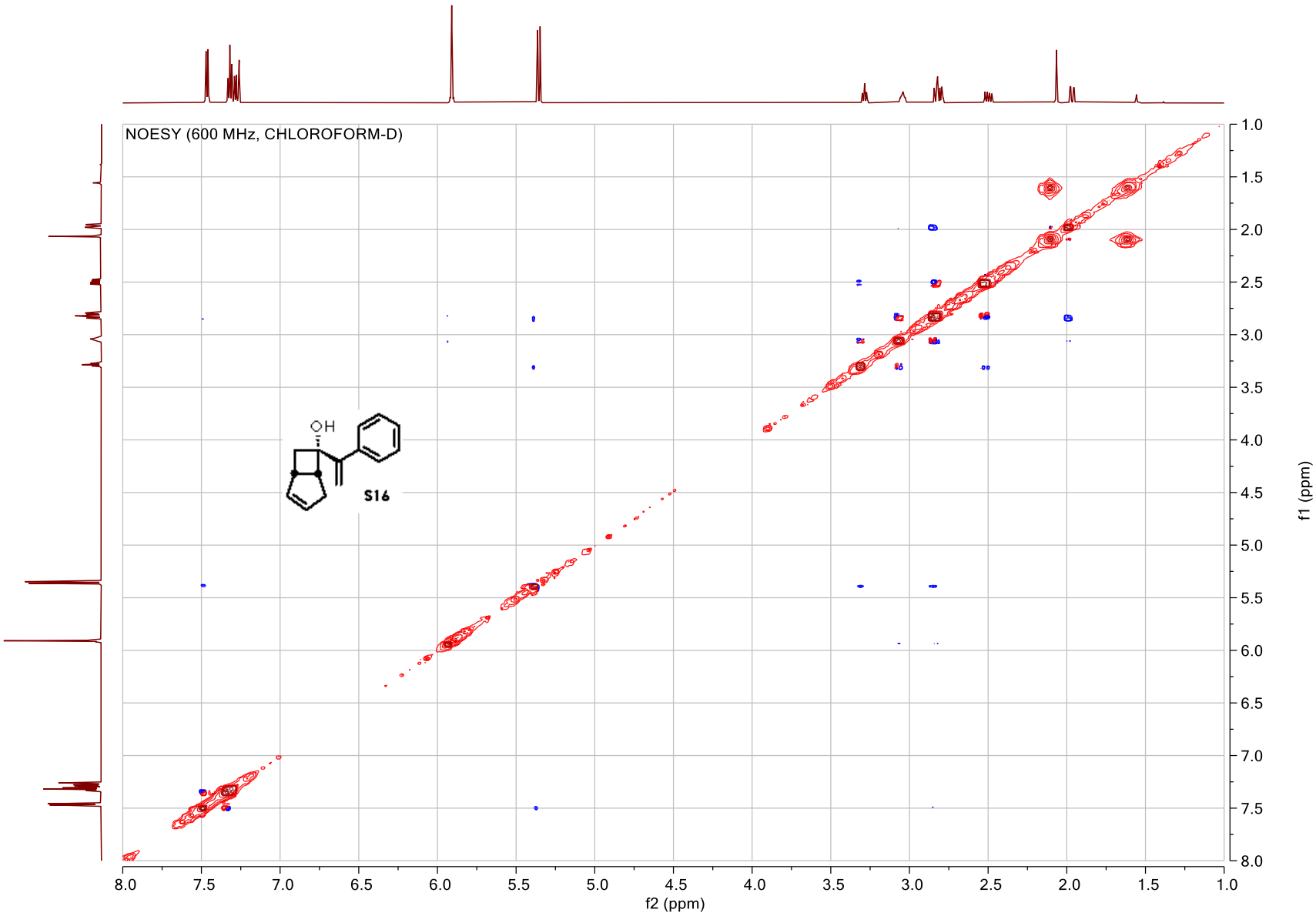

13C (101 MHz, CHLOROFORM-D)
165.2
152.9
149.3
139.7
137.0
128.1
127.7
127.4
122.7
121.6
113.1
77.2 CDCl3
76.2
42.6
34.8
OH
N
S15
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

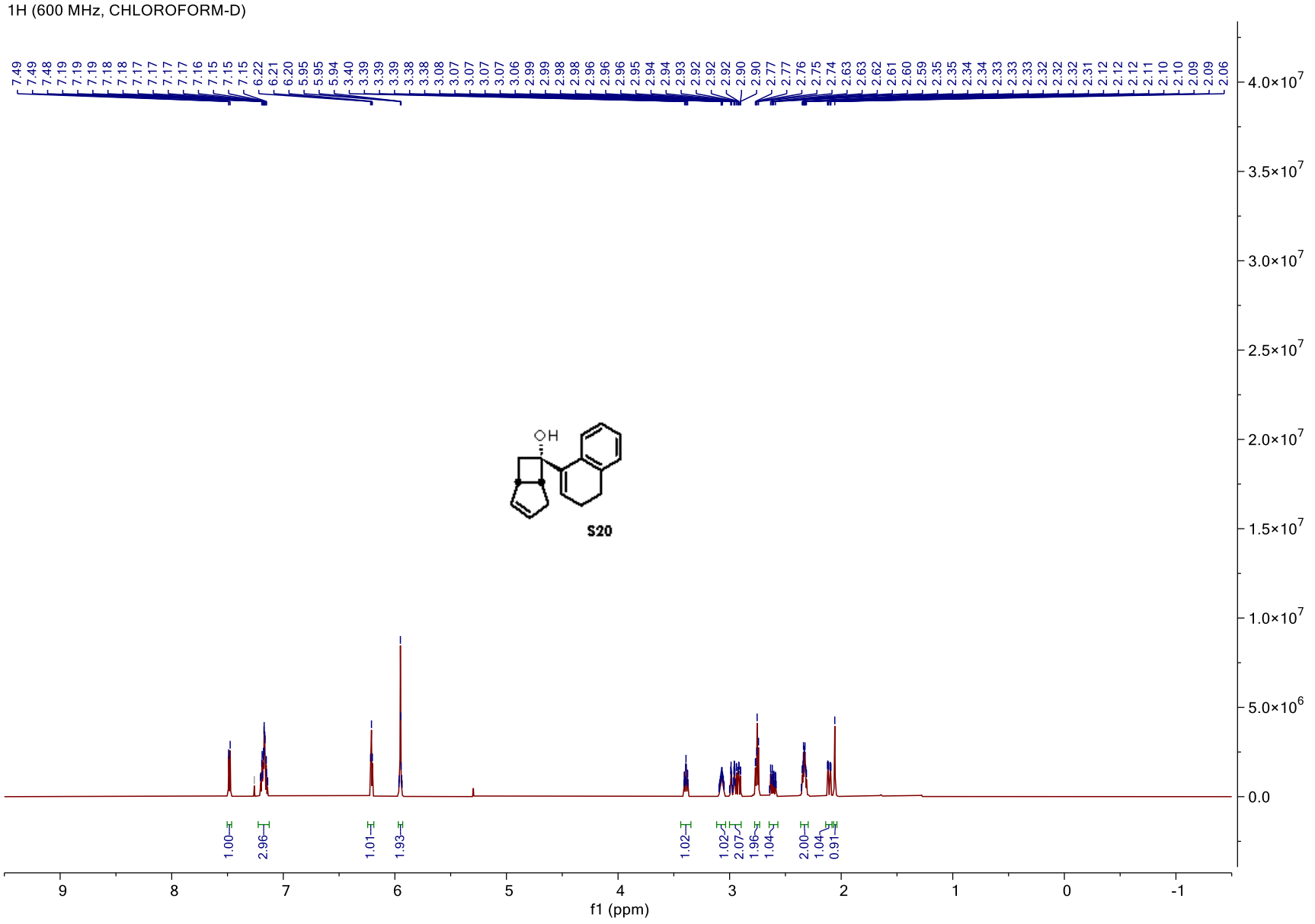

1H (600 MHz, CHLOROFORM-D)
7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 CDCl3 5.92 5.91 5.91 5.90 5.90 5.36 5.36 5.35 5.35 3.30 3.30 3.29 3.29 3.28 3.27 3.27 3.05 3.05 3.05 3.04 3.04 3.04 3.04 3.04 3.03 3.03 2.84 2.84 2.83 2.83 2.82 2.82 2.81 2.80 2.79 2.79 2.79 2.52 2.52 2.51 2.50 2.49 2.48 2.06 1.98 1.98 1.97 1.97 1.96 1.96 1.95 1.95
OH
S16
3.8×10^7
3.6×10^7
3.4×10^7
3.2×10^7
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
1.96 1.98 1.02 1.89 0.99 1.00 1.01 1.01 2.09 1.06 0.92 1.02
9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


13C (151 MHz, CHLOROFORM-D)
154.0
139.6
135.4
132.8
128.2
127.8
127.5
113.8
77.8
77.2 CDCl3
46.1
42.5
39.3
33.3
S16
f1 (ppm)

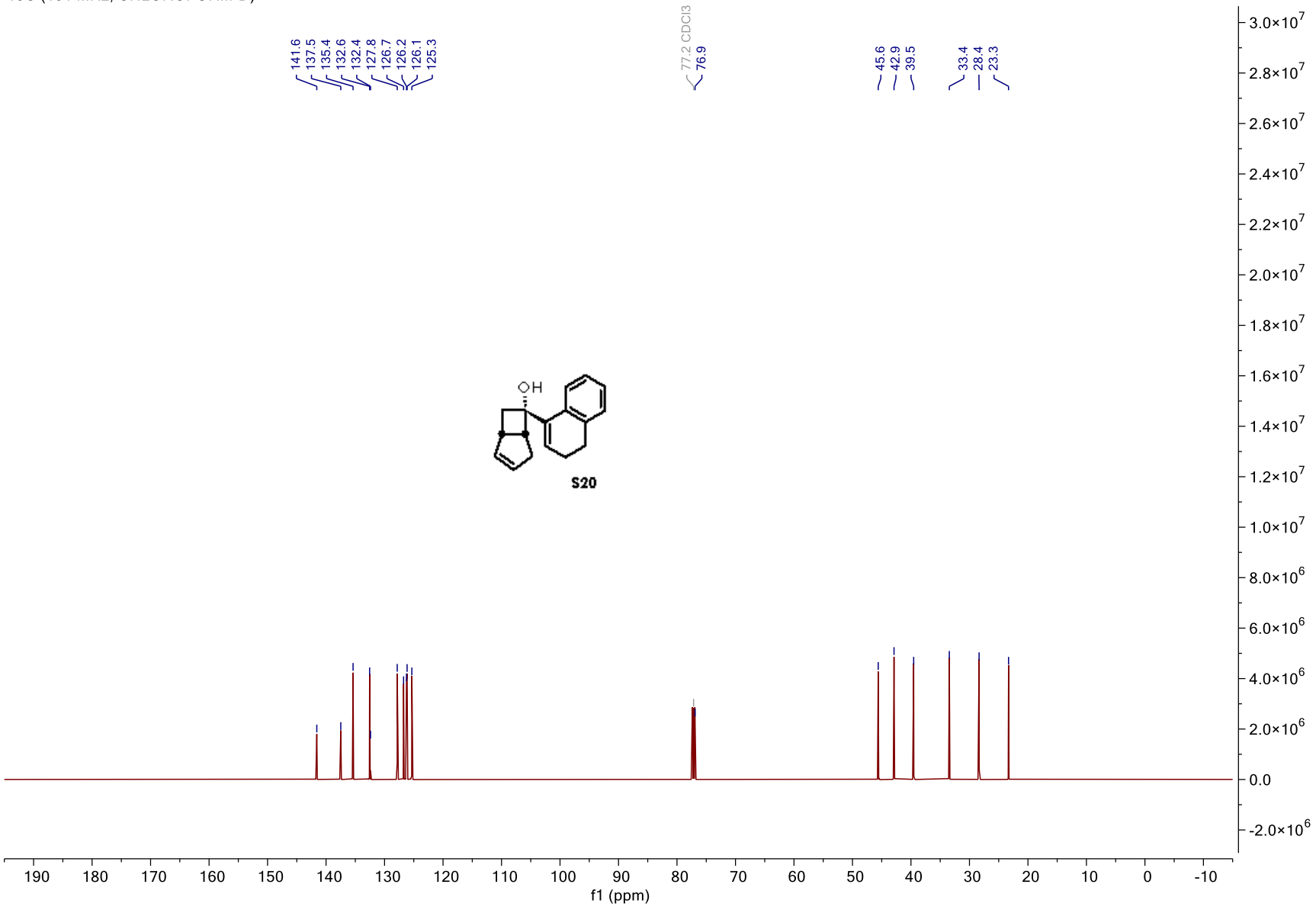

COSY (600 MHz, CHLOROFORM-D)
OH
S16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)

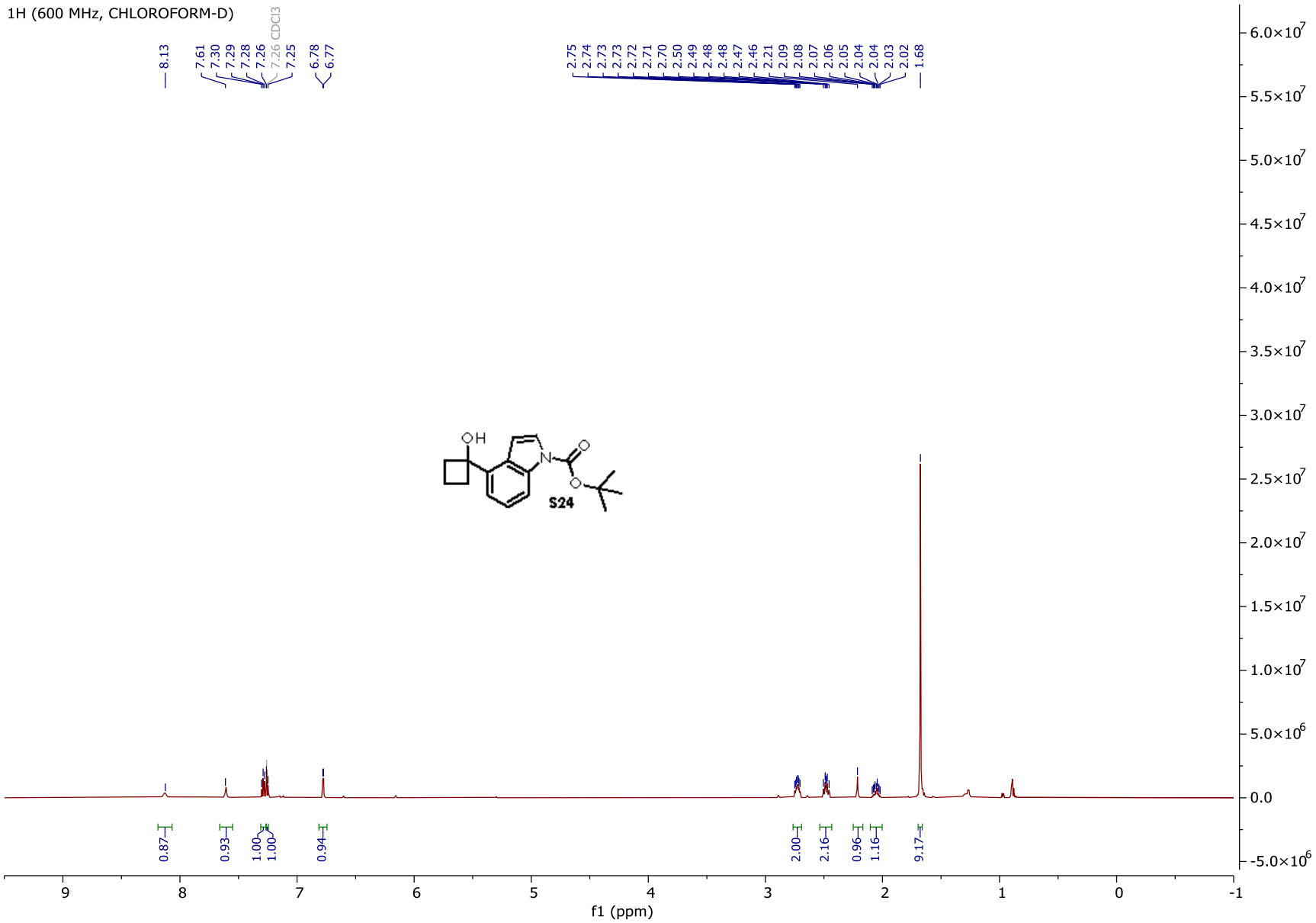

HSQC (600 MHz, CHLOROFORM-D)
OH
S16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

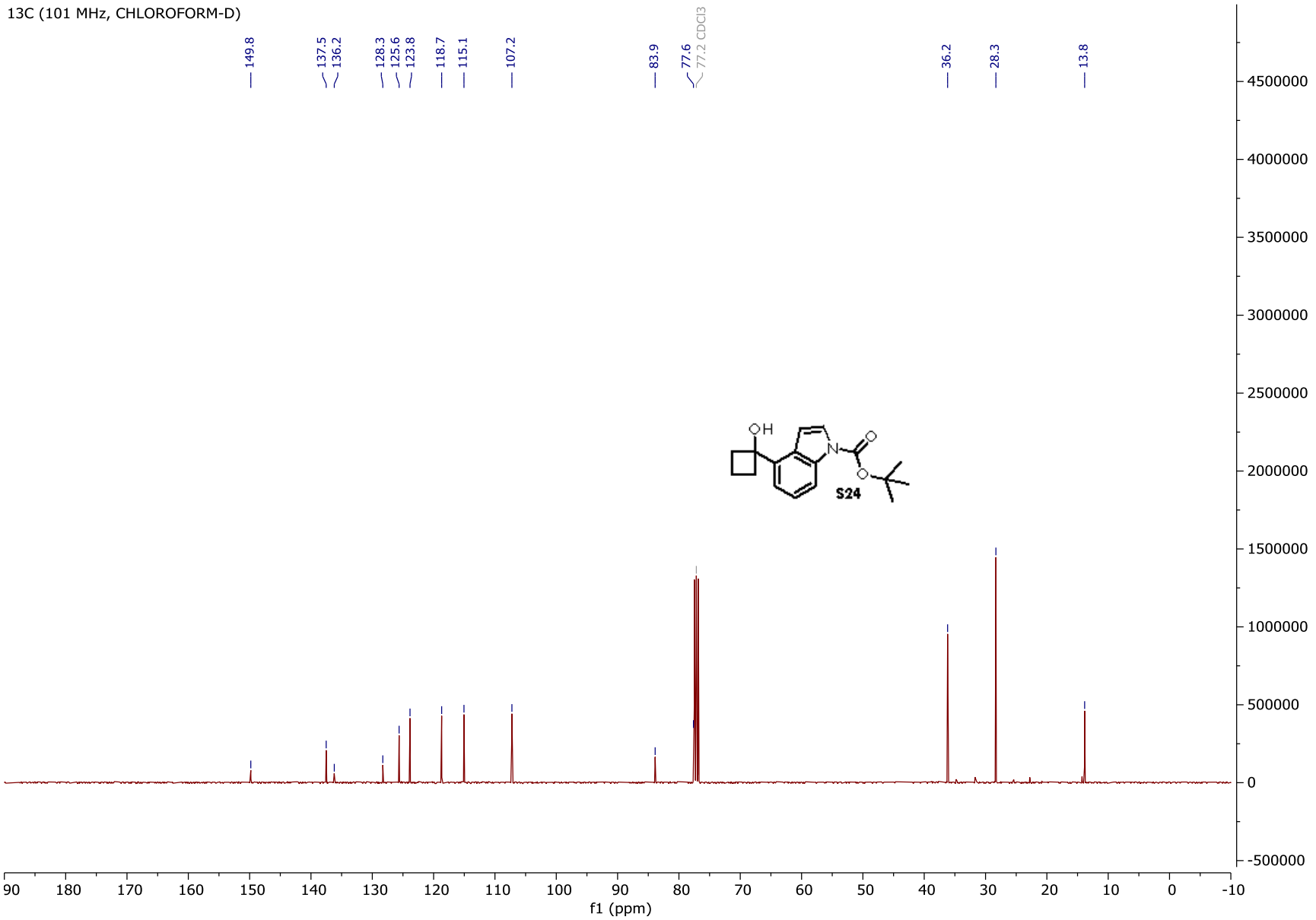

NOESY (600 MHz, CHLOROFORM-D)
OH
S16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)

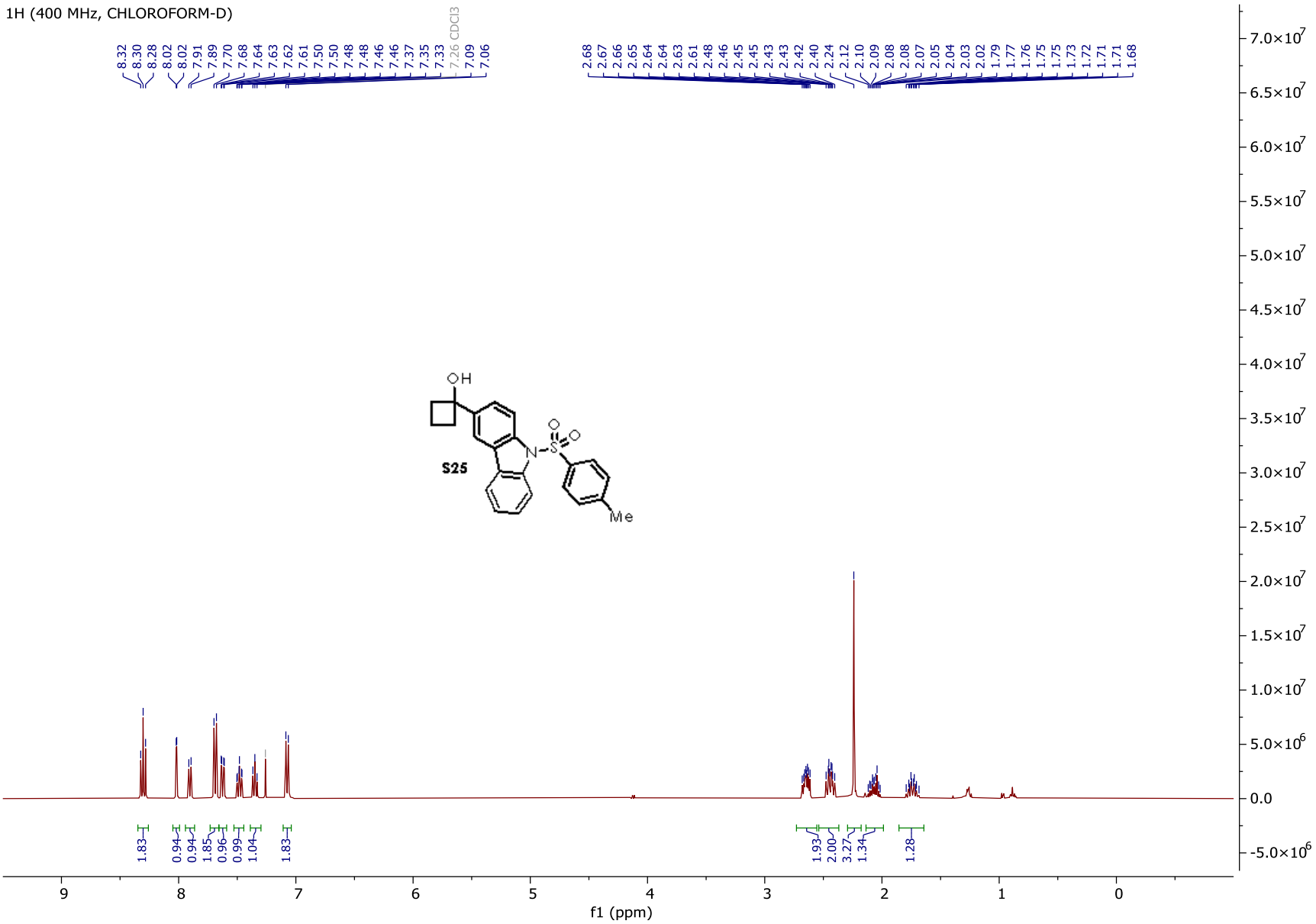

1H (600 MHz, CHLOROFORM-D)
7.49 7.49 7.48 7.19 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.17 7.16 7.15 7.15 7.15 6.22 6.21 6.20 5.95 5.95 5.94 3.40 3.39 3.39 3.39 3.38 3.38 3.08 3.07 3.07 3.07 3.07 3.06 2.99 2.99 2.98 2.98 2.96 2.96 2.96 2.95 2.94 2.94 2.93 2.92 2.92 2.92 2.90 2.90 2.77 2.77 2.76 2.75 2.74 2.63 2.63 2.62 2.61 2.60 2.59 2.35 2.35 2.34 2.34 2.33 2.33 2.33 2.32 2.32 2.32 2.31 2.12 2.12 2.12 2.11 2.10 2.10 2.09 2.09 2.06
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
OH
S20
1.00 2.96 1.01 1.93 1.02 1.02 2.07 1.96 1.04 2.00 1.04 0.91
9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

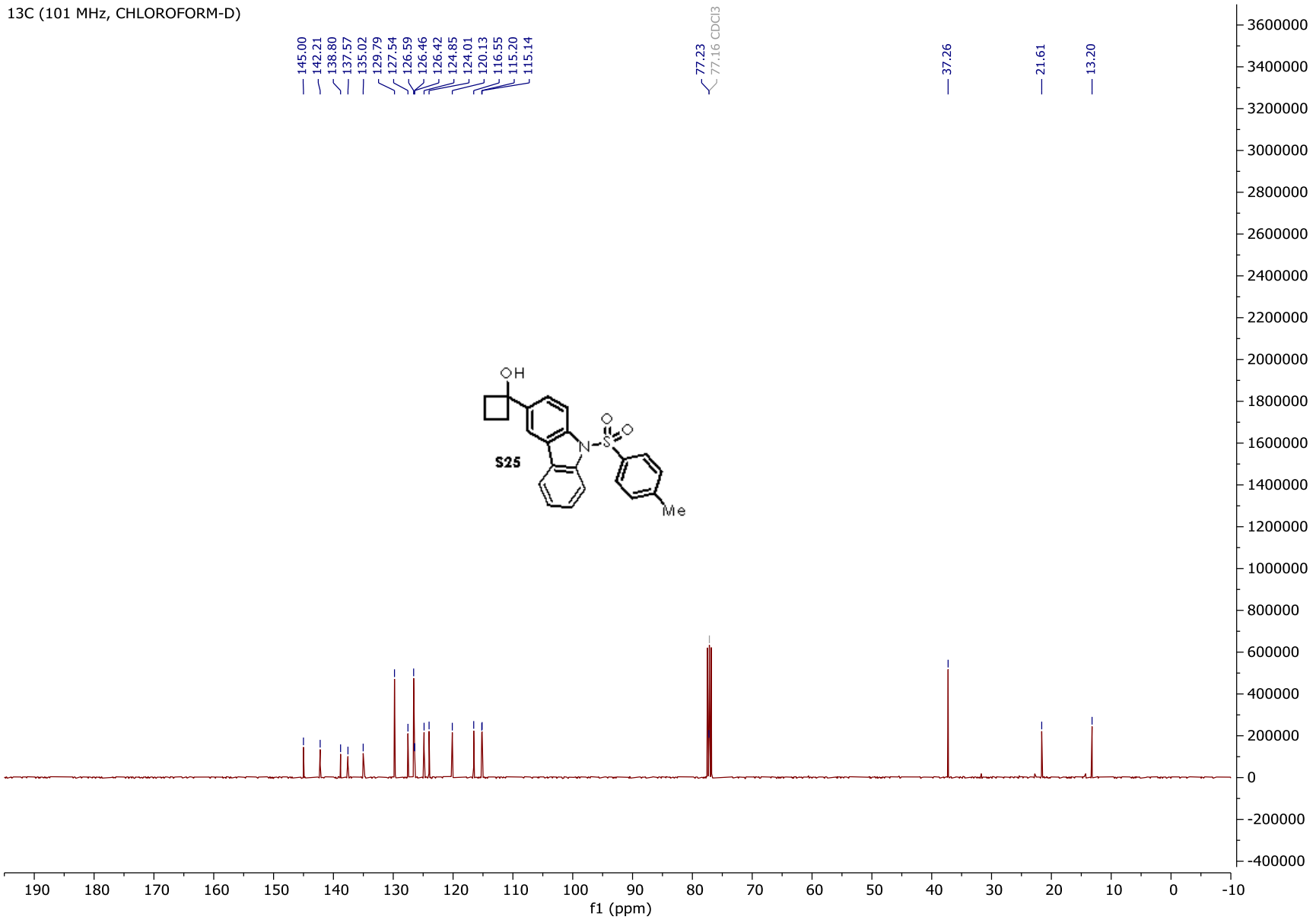
13C (151 MHz, CHLOROFORM-D)

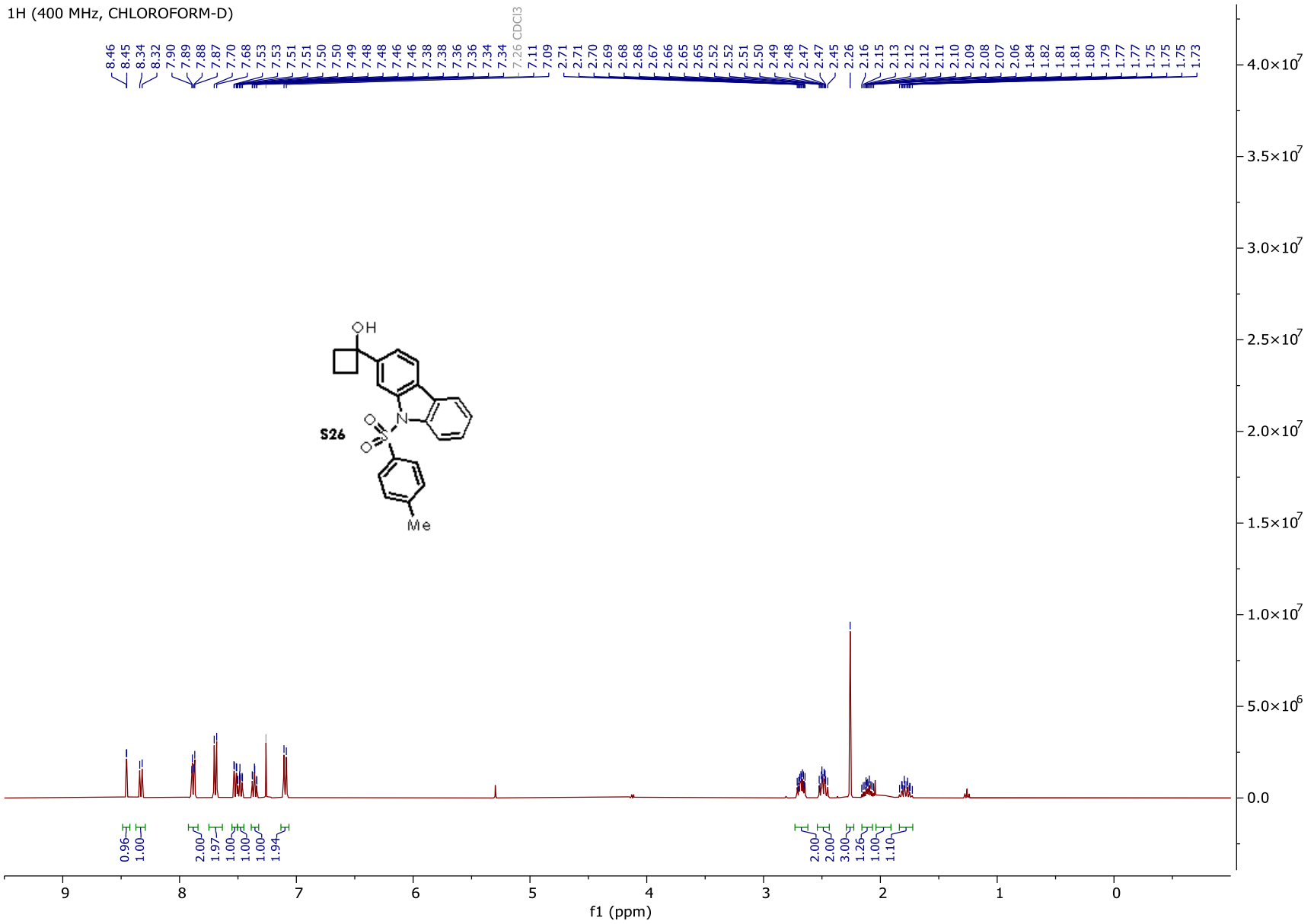


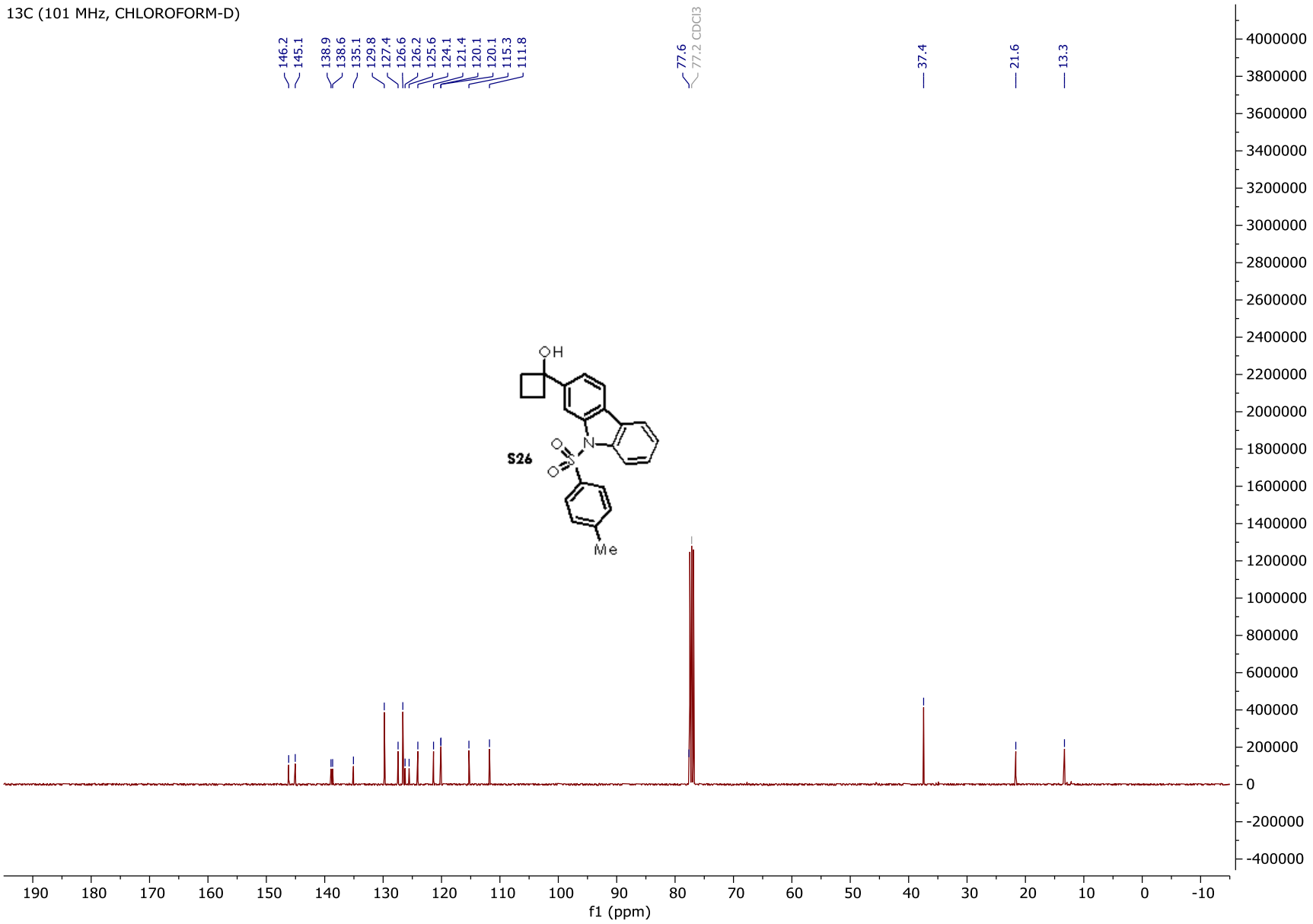

1H (600 MHz, CHLOROFORM-D)
8.13
7.61
7.30
7.29
7.28
7.26
7.26 CDCl3
7.25
6.78
6.77
2.75
2.74
2.73
2.73
2.72
2.71
2.70
2.50
2.49
2.48
2.48
2.47
2.46
2.21
2.09
2.08
2.07
2.06
2.05
2.04
2.04
2.03
2.02
1.68
OH
N
O
O
S24
0.87
0.93
1.00
1.00
0.94
2.00
2.16
0.96
1.16
9.17
f1 (ppm)

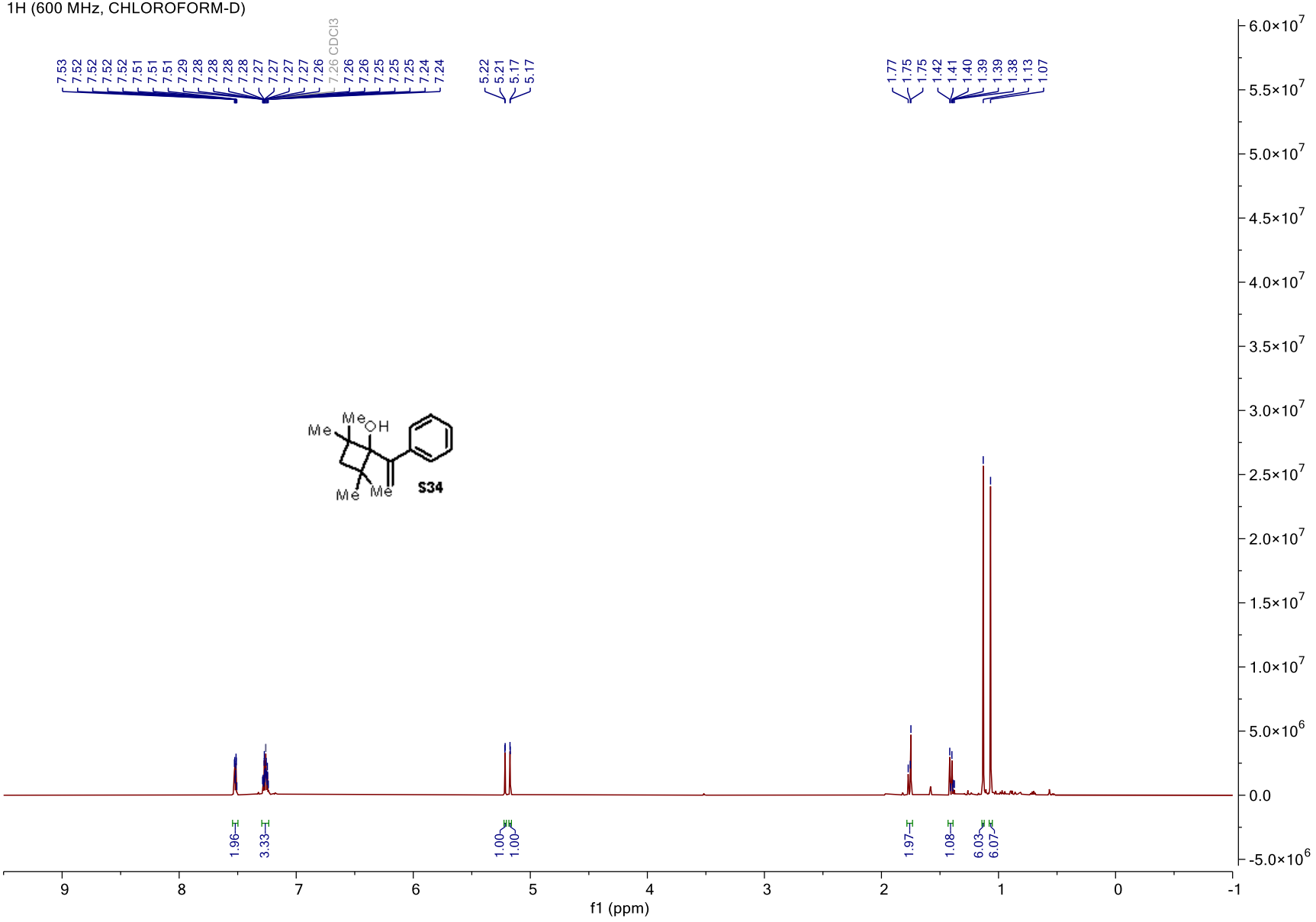

13C (101 MHz, CHLOROFORM-D)
149.8
137.5
136.2
128.3
125.6
123.8
118.7
115.1
107.2
83.9
77.6
77.2 CDCl3
36.2
28.3
13.8
OH
N
O
O
S24
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1H (400 MHz, CHLOROFORM-D)
8.32
8.30
8.28
8.02
8.02
7.91
7.89
7.70
7.68
7.64
7.63
7.62
7.61
7.50
7.50
7.48
7.48
7.46
7.46
7.37
7.35
7.33
7.26 CDCl3
7.09
7.06
2.68
2.67
2.66
2.65
2.64
2.64
2.63
2.61
2.48
2.46
2.45
2.45
2.43
2.43
2.42
2.40
2.24
2.12
2.10
2.09
2.08
2.08
2.07
2.05
2.04
2.03
2.02
1.79
1.77
1.76
1.75
1.75
1.73
1.72
1.71
1.71
1.68
OH
S25
N
S
O
O
Me
1.83
0.94
0.94
1.85
0.96
0.99
1.04
1.83
1.93
2.00
3.27
1.34
1.28
f1 (ppm)

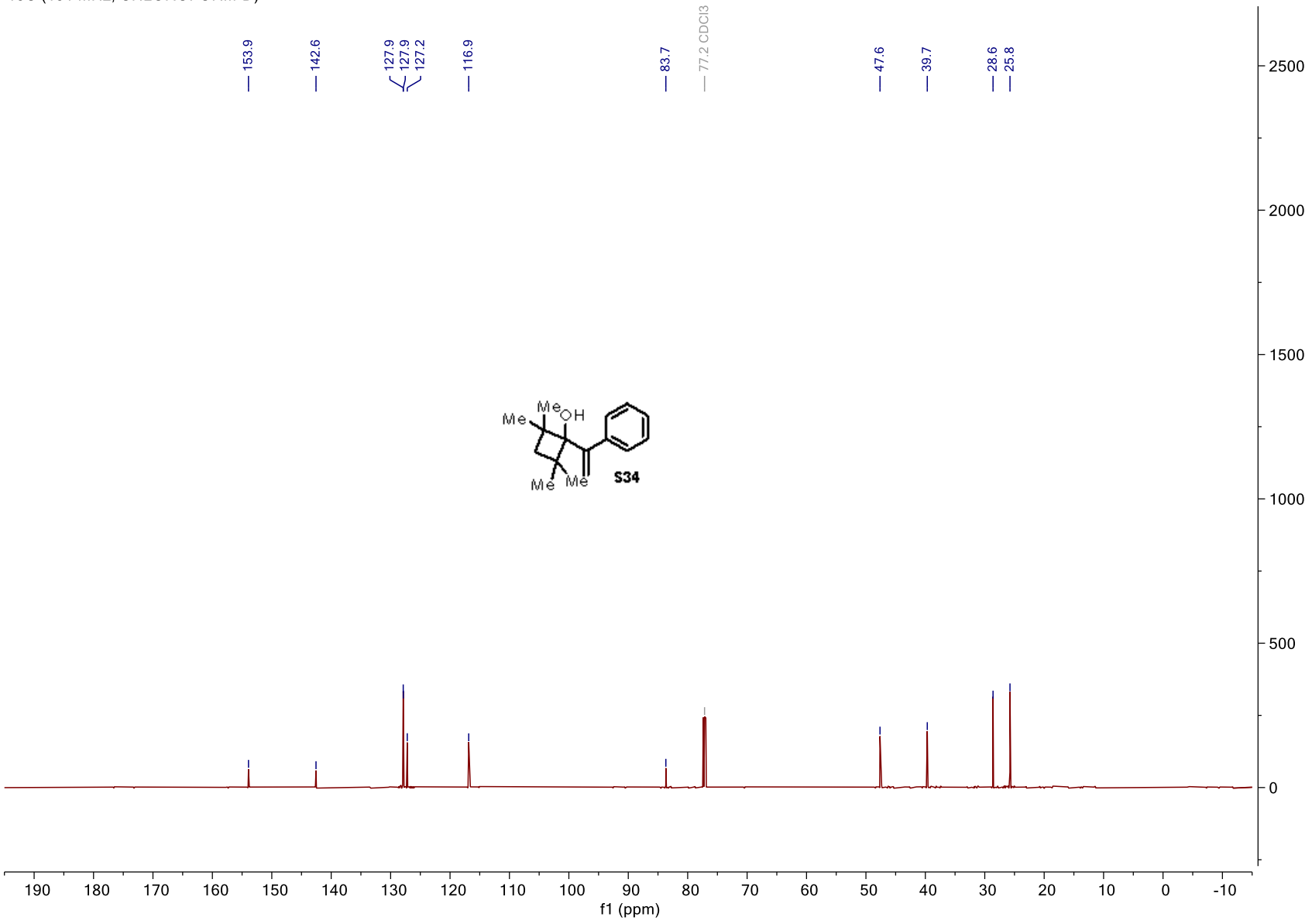

13C (101 MHz, CHLOROFORM-D)
145.00
142.21
138.80
137.57
135.02
129.79
127.54
126.59
126.46
126.42
124.85
124.01
120.13
116.55
115.20
115.14
77.23
77.16 CDCl3
37.26
21.61
13.20
OH
S25
N
S
O
O
Me
f1 (ppm)

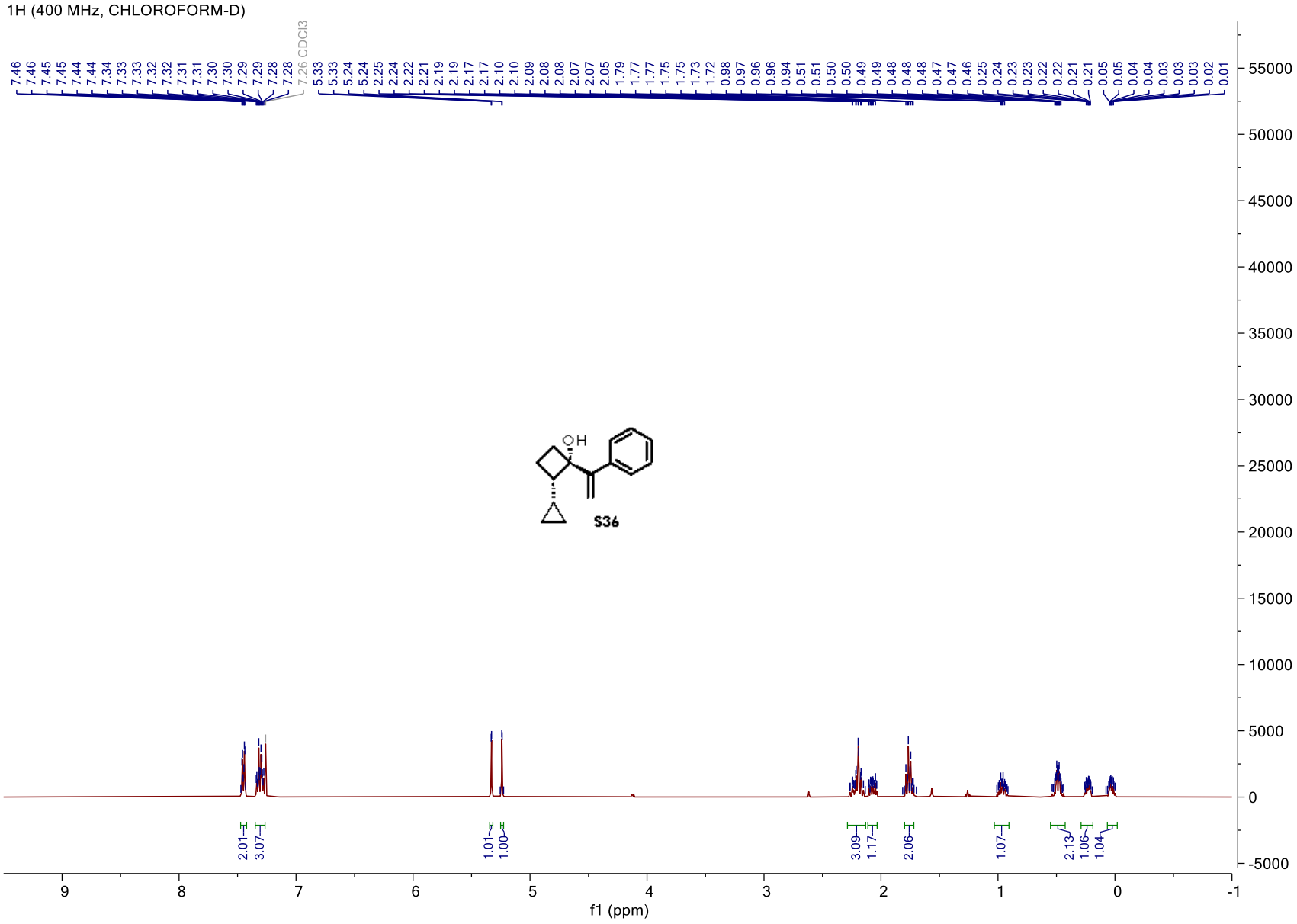

1H (400 MHz, CHLOROFORM-D)
8.46 8.45 8.34 8.32 7.90 7.89 7.88 7.87 7.70 7.68 7.53 7.53 7.51 7.51 7.50 7.50 7.49 7.48 7.48 7.46 7.46 7.38 7.38 7.36 7.36 7.34 7.34 7.26 CDCl3 7.11 7.09 2.71 2.71 2.70 2.69 2.68 2.68 2.67 2.66 2.65 2.65 2.52 2.52 2.51 2.50 2.49 2.48 2.47 2.47 2.45 2.26 2.16 2.15 2.13 2.12 2.12 2.11 2.10 2.09 2.08 2.07 2.06 1.84 1.82 1.81 1.81 1.80 1.79 1.77 1.77 1.75 1.75 1.73
OH
N
S
O
O
S26
Me
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
0.96 1.00 2.00 1.97 1.00 1.00 1.00 1.94 2.00 2.00 3.00 1.26 1.00 1.10
9 8 7 6 5 4 3 2 1 0
f1 (ppm)

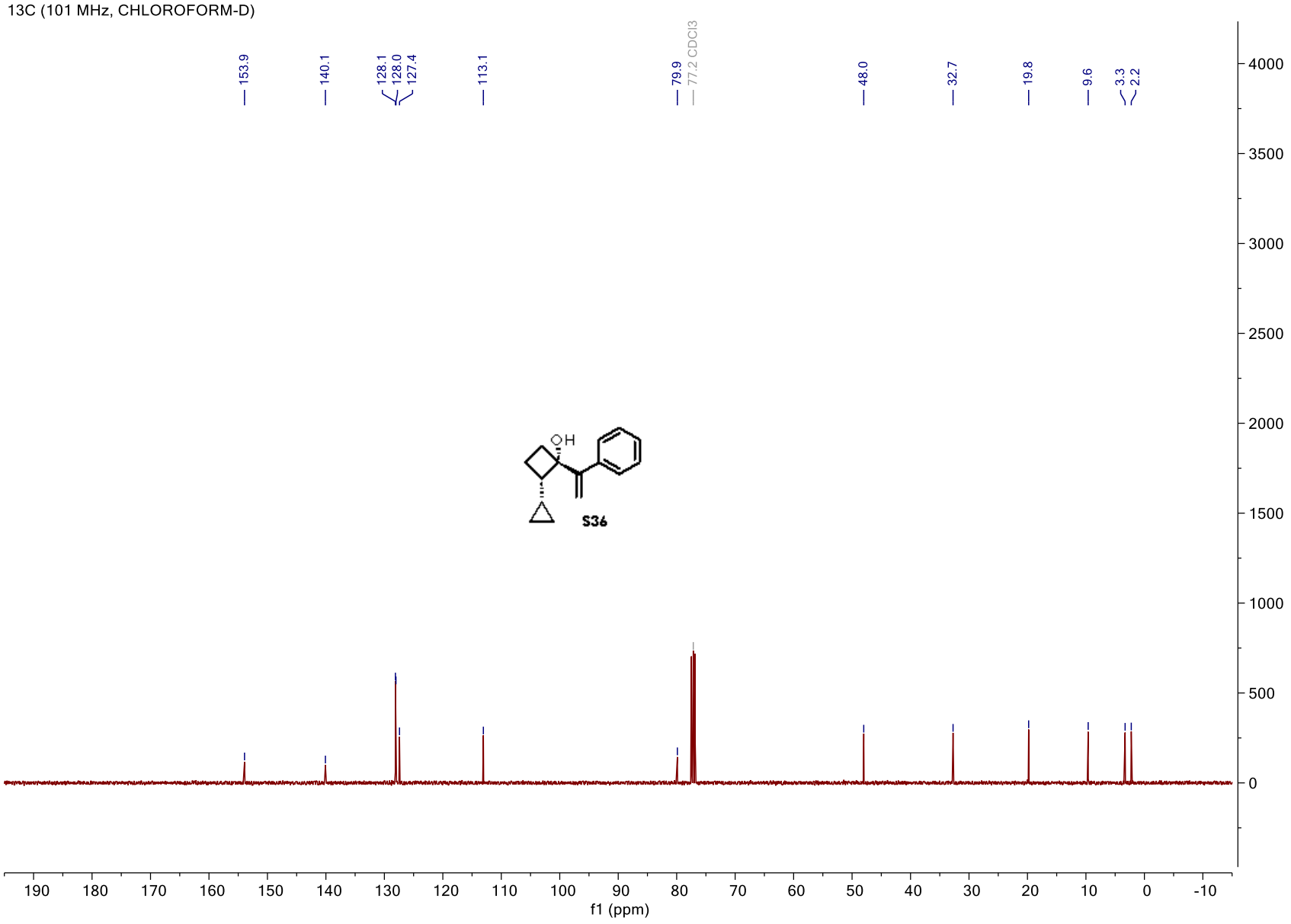

13C (101 MHz, CHLOROFORM-D)
146.2
145.1
138.9
138.6
135.1
129.8
127.4
126.6
126.2
125.6
124.1
121.4
120.1
115.3
111.8
77.6
77.2 CDCl3
37.4
21.6
13.3
OH
N
S
O
O
Me
S26
4000000
3800000
3600000
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
-400000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

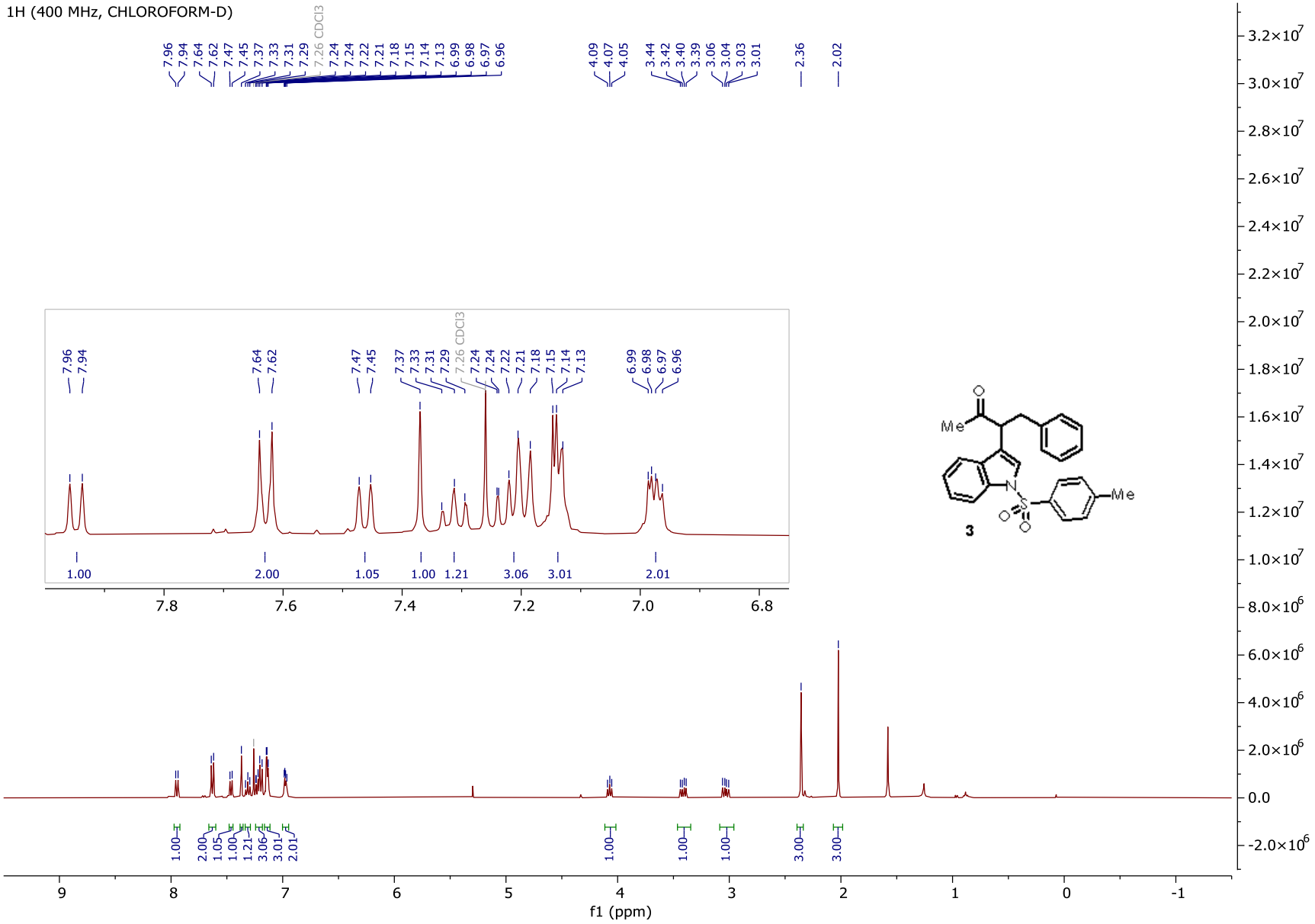

1H (600 MHz, CHLOROFORM-D)
7.53 7.52 7.52 7.52 7.52 7.51 7.51 7.51 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.27 7.26 7.26 CDCl3 7.26 7.25 7.25 7.25 7.24 7.24
5.22 5.21 5.17 5.17
1.77 1.75 1.75 1.42 1.41 1.40 1.39 1.39 1.38 1.13 1.07
Me
OH
Me
Me
Me
S34
1.96
3.33
1.00
1.00
1.97
1.08
6.03
6.07
f1 (ppm)

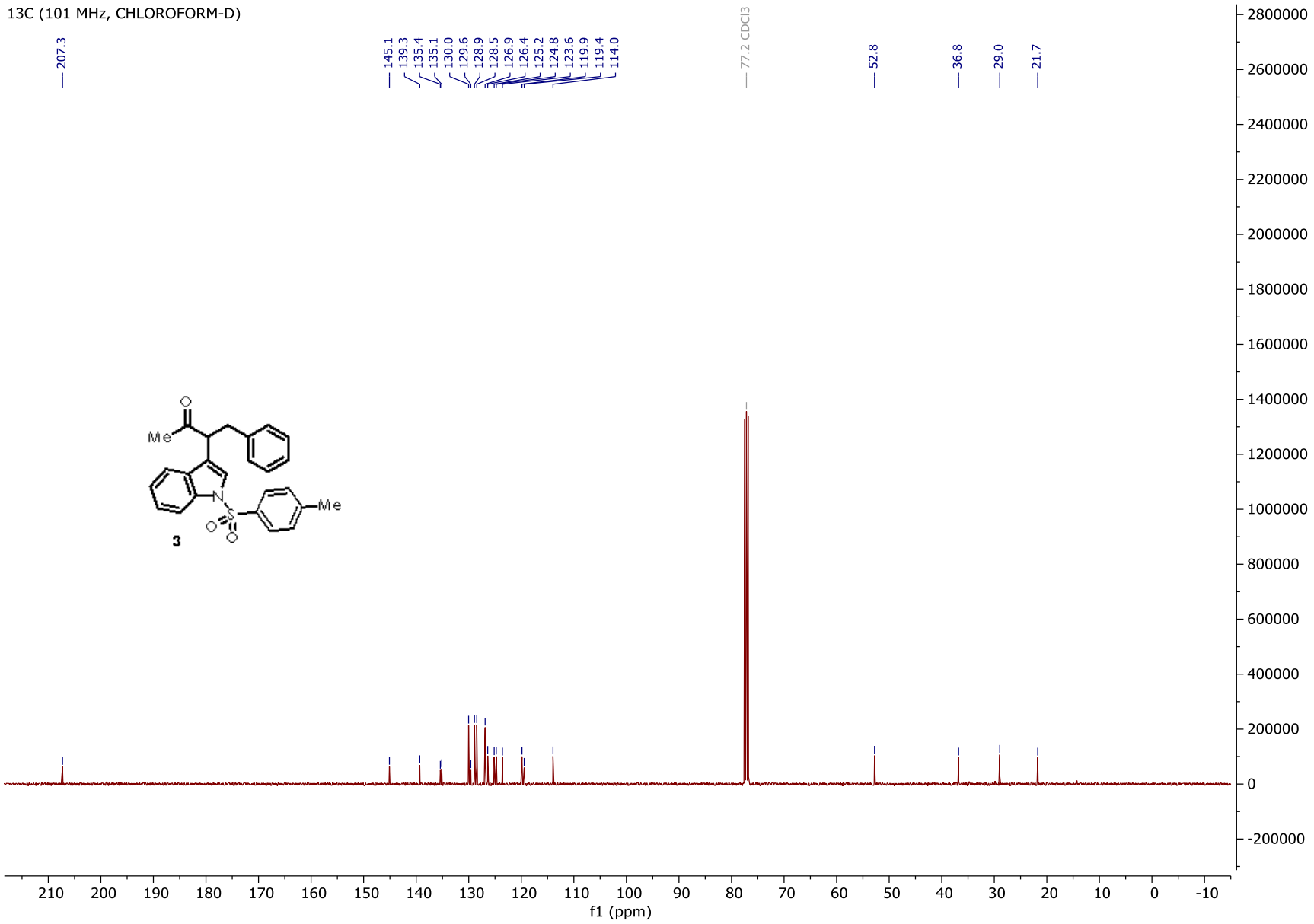
13C (151 MHz, CHLOROFORM-D)

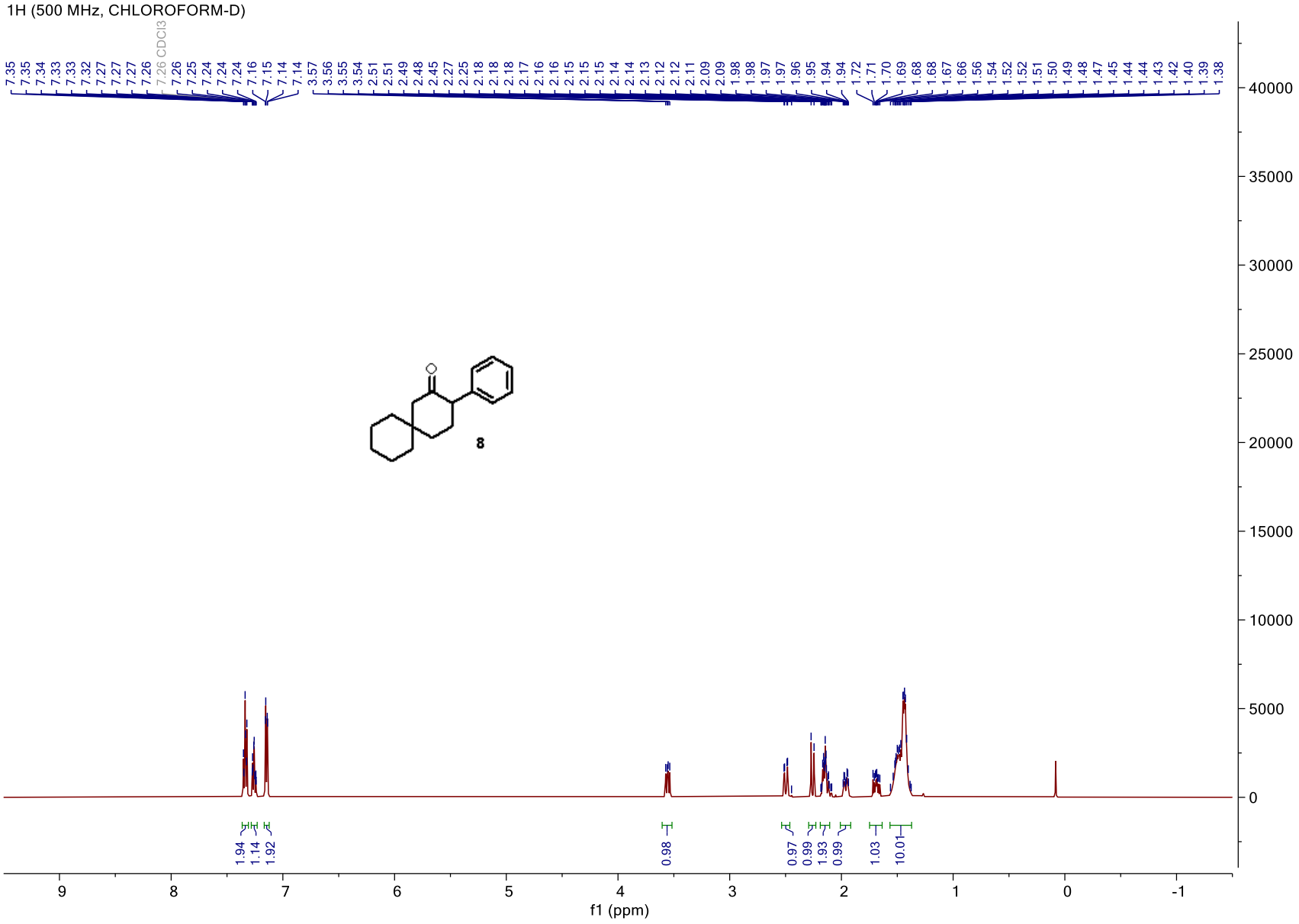



1H (400 MHz, CHLOROFORM-D)
7.26 CDCl3
OH
S36
f1 (ppm)

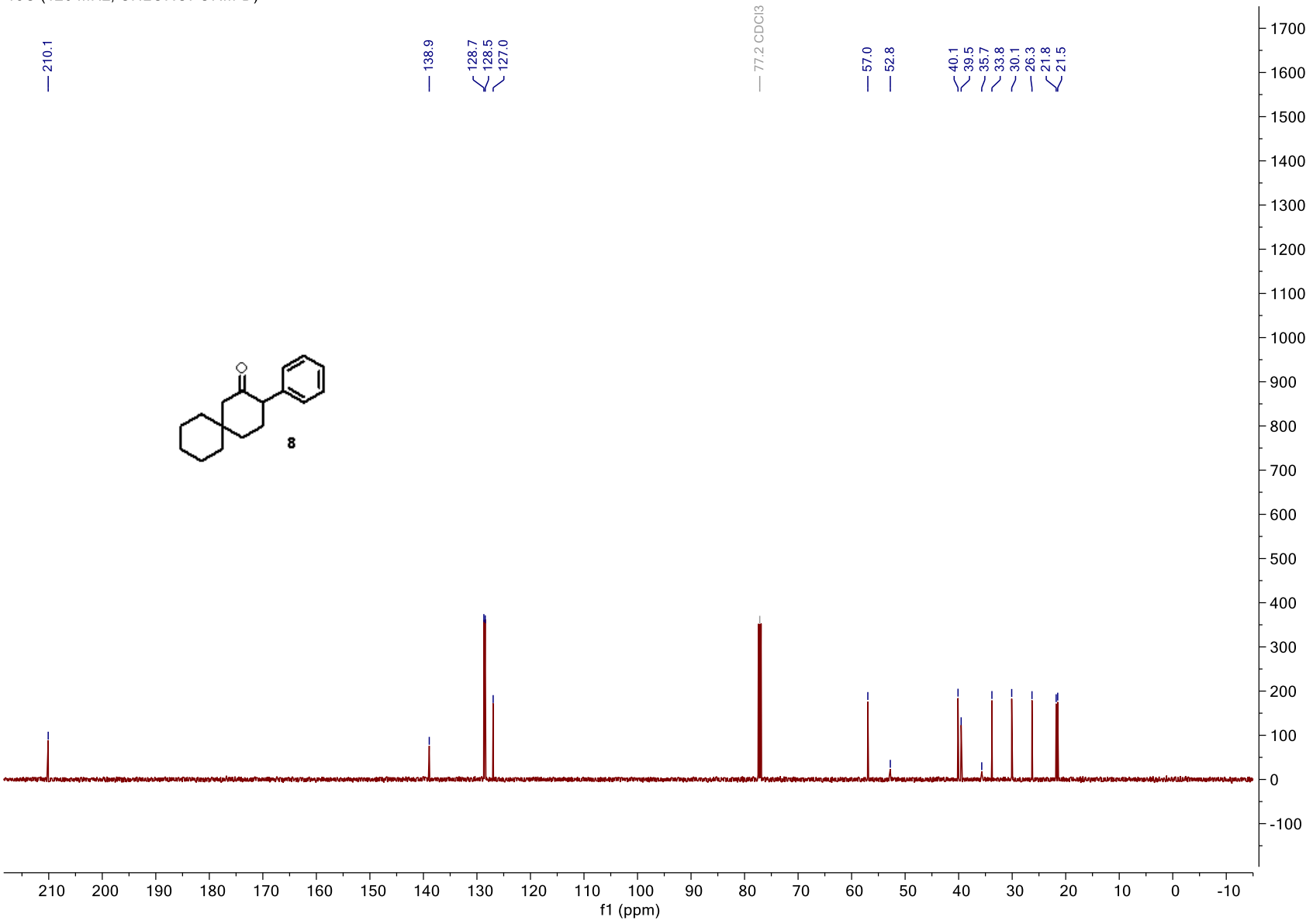

13C (101 MHz, CHLOROFORM-D)
153.9
140.1
128.1
128.0
127.4
113.1
79.9
77.2 CDCl3
48.0
32.7
19.8
9.6
3.3
2.2
OH
S36
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

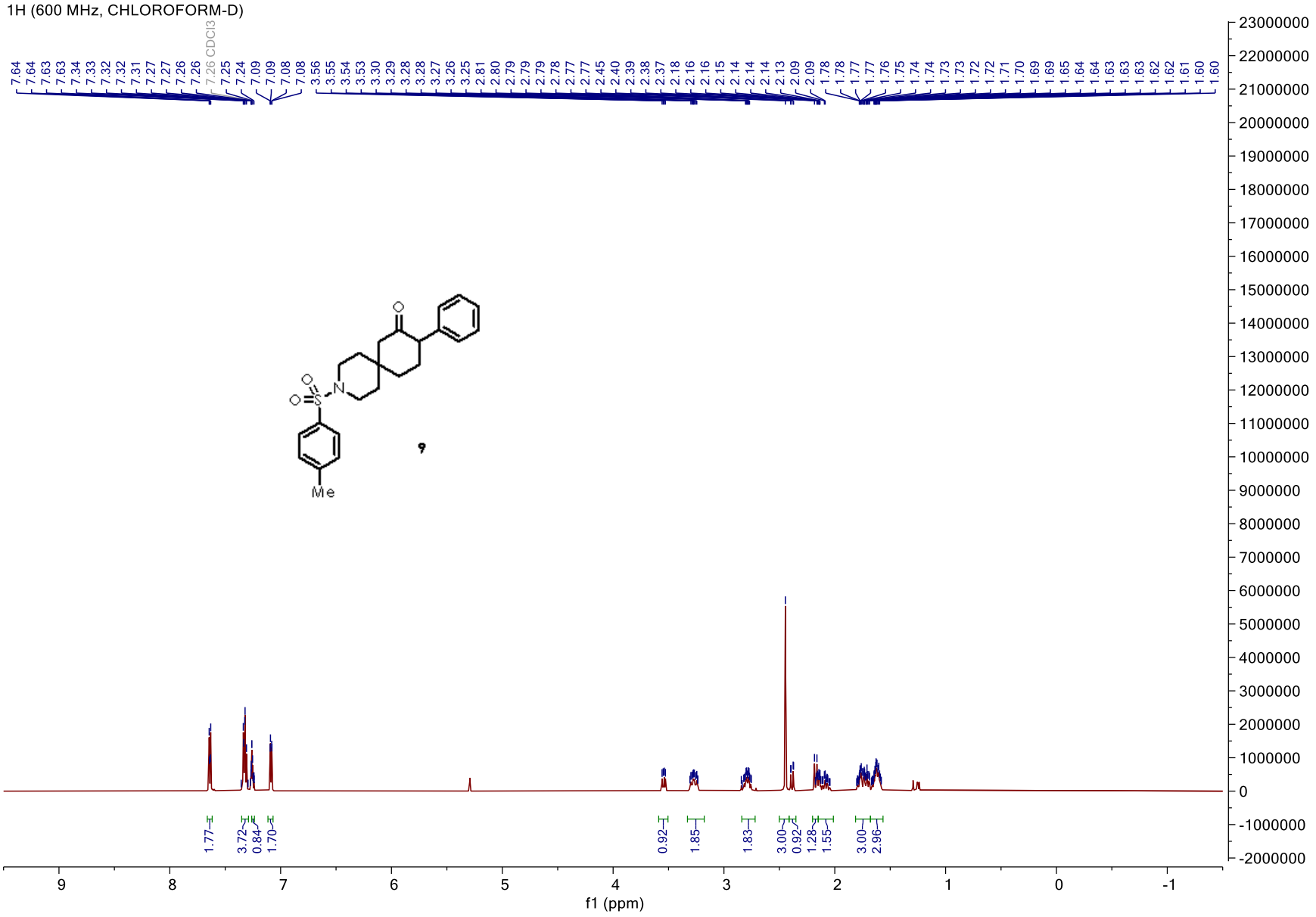

1H (400 MHz, CHLOROFORM-D)
7.96 7.94 7.64 7.62 7.47 7.45 7.37 7.33 7.31 7.29 7.26 CDCl3 7.24 7.24 7.22 7.21 7.18 7.15 7.14 7.13 6.99 6.98 6.97 6.96
4.09 4.07 4.05 3.44 3.42 3.40 3.39 3.06 3.04 3.03 3.01 2.36 2.02
1.00 2.00 1.05 1.00 1.21 3.06 3.01 2.01
1.00 2.00 1.05 1.00 1.21 3.06 3.01 2.01 1.00 1.00 1.00 3.00 3.00
f1 (ppm)
Me
Me
3


13C (101 MHz, CHLOROFORM-D)
207.3
145.1
139.3
135.4
135.1
130.0
129.6
128.9
128.5
126.9
126.4
125.2
124.8
123.6
119.9
119.4
114.0
77.2 CDCl3
52.8
36.8
29.0
21.7
Me
N
S
Me
3
f1 (ppm)

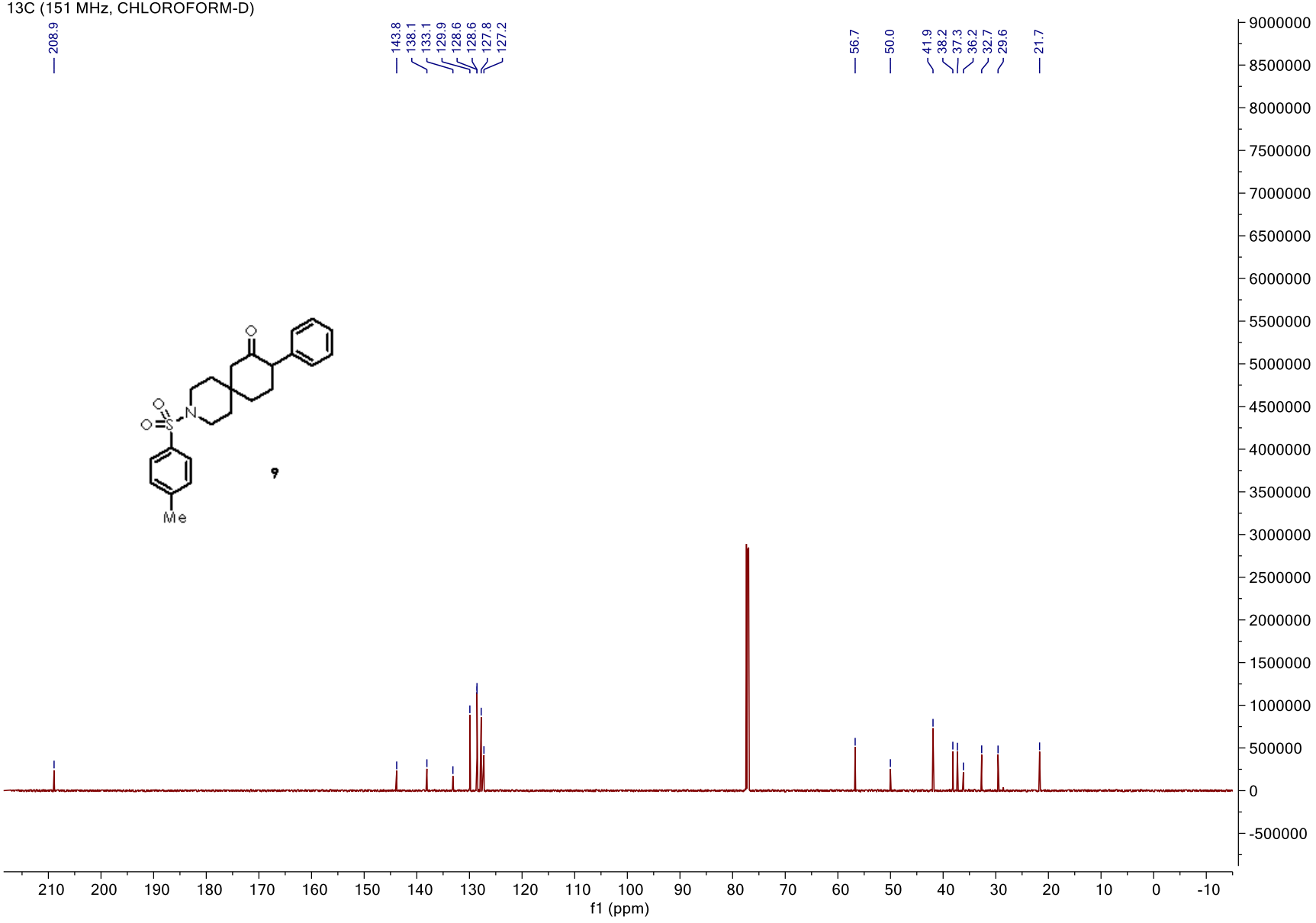

1H (500 MHz, CHLOROFORM-D)
7.35 7.35 7.34 7.33 7.33 7.32 7.27 7.27 7.27 7.26 7.26 CDCl3 7.26 7.25 7.24 7.24 7.24 7.16 7.15 7.14 7.14
3.57 3.56 3.55 3.54 2.51 2.51 2.49 2.48 2.45 2.27 2.25 2.18 2.18 2.17 2.16 2.16 2.15 2.15 2.15 2.14 2.14 2.13 2.12 2.12 2.11 2.09 2.09 1.98 1.98 1.97 1.97 1.96 1.95 1.94 1.94 1.72 1.71 1.70 1.69 1.68 1.68 1.67 1.66 1.56 1.54 1.52 1.52 1.51 1.50 1.49 1.48 1.47 1.45 1.44 1.44 1.43 1.42 1.40 1.39 1.38
8
1.94
1.14
1.92
0.98
0.97
0.99
1.93
0.99
1.03
10.01
f1 (ppm)

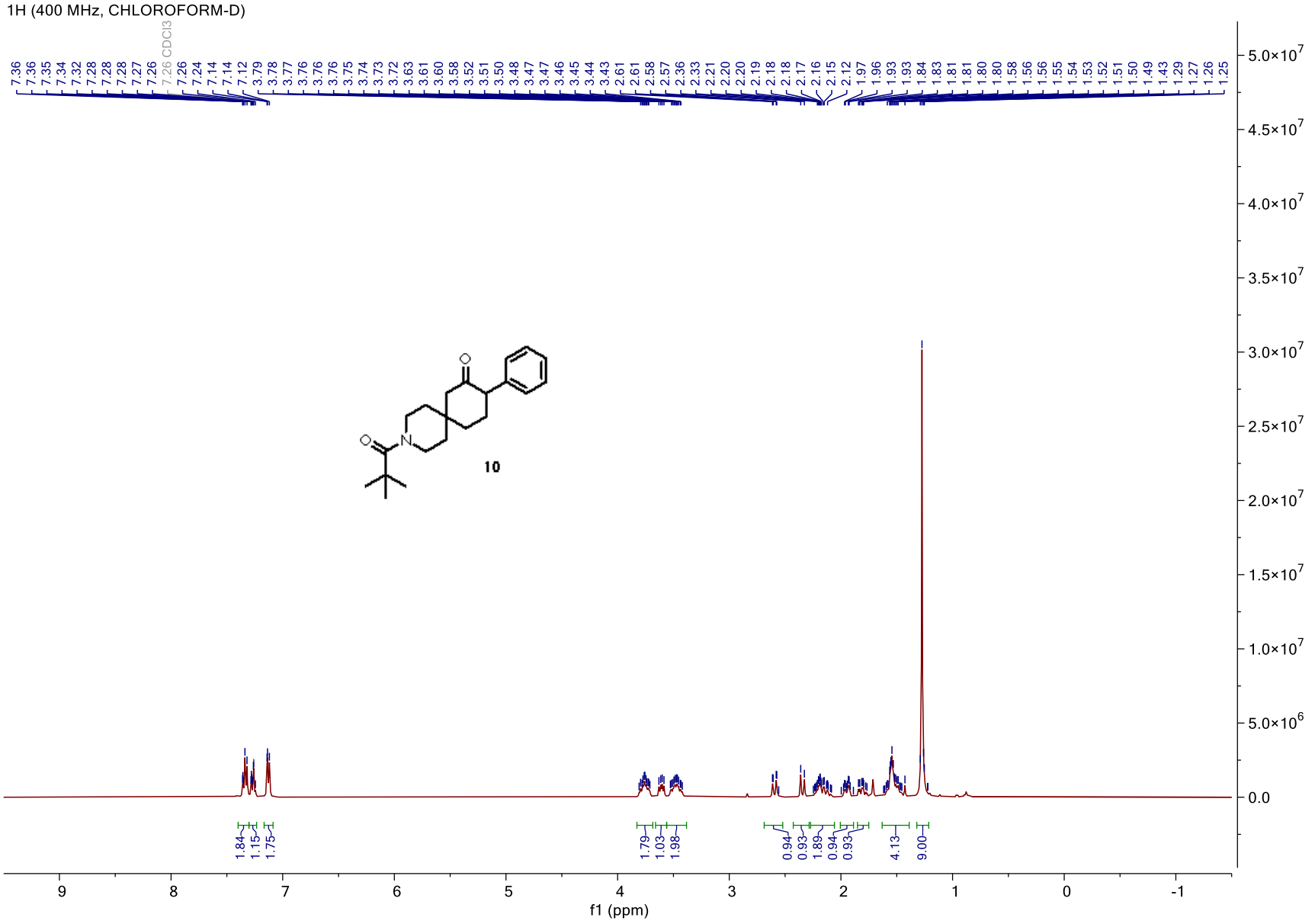
13C (126 MHz, CHLOROFORM-D)



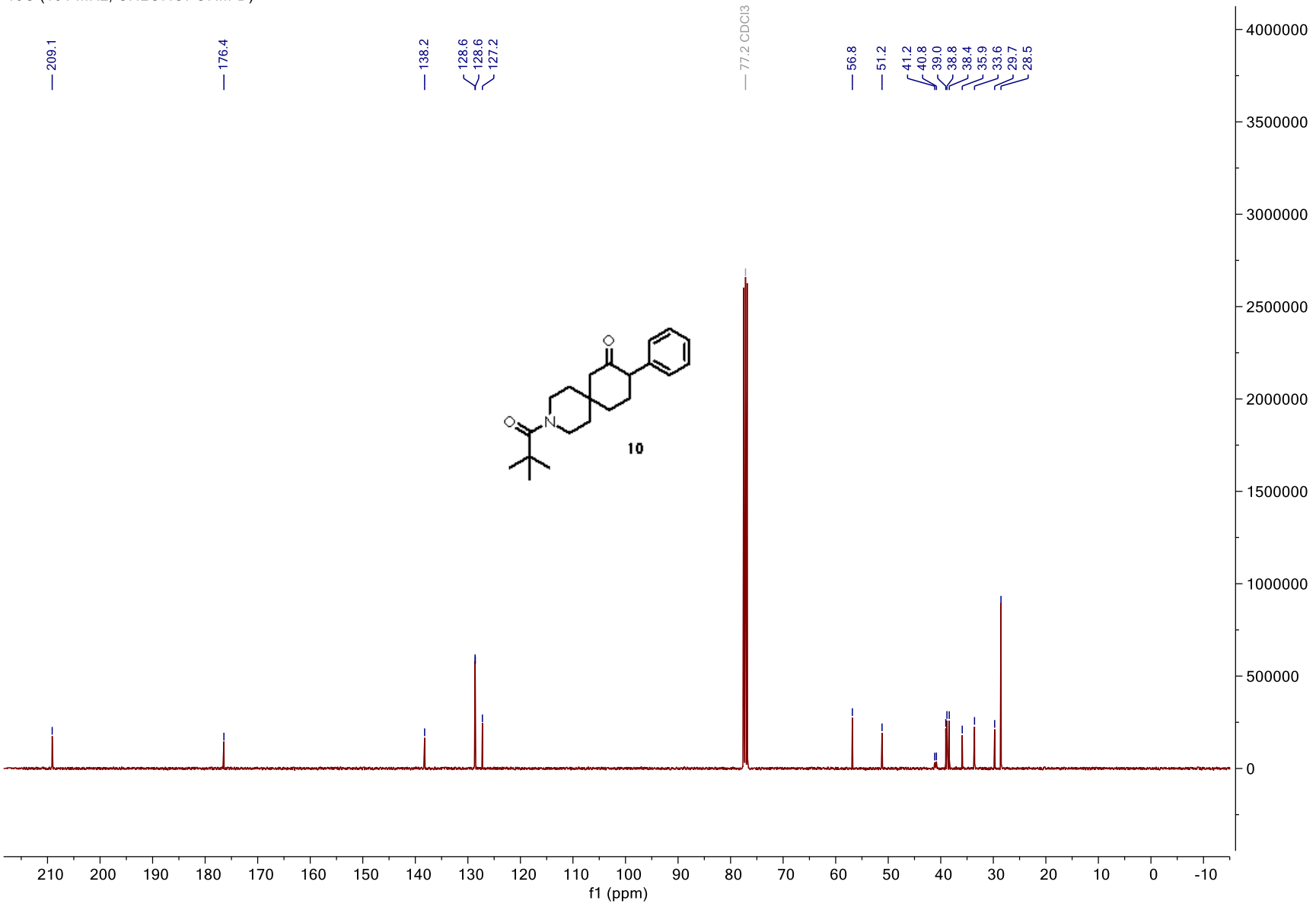

1H (600 MHz, CHLOROFORM-D)
7.64 7.64 7.63 7.63 7.34 7.33 7.32 7.32 7.31 7.27 7.27 7.26 7.26 7.26 CDCl3 7.25 7.24 7.09 7.09 7.08 7.08
3.56 3.55 3.54 3.53 3.30 3.29 3.28 3.28 3.27 3.26 3.25 2.81 2.80 2.79 2.79 2.79 2.78 2.77 2.77 2.45 2.40 2.39 2.38 2.37 2.18 2.16 2.16 2.15 2.14 2.14 2.14 2.13 2.09 2.09 1.78 1.78 1.77 1.77 1.76 1.75 1.74 1.74 1.73 1.73 1.72 1.72 1.71 1.70 1.69 1.69 1.65 1.64 1.64 1.63 1.63 1.63 1.62 1.62 1.61 1.60 1.60
Me
9
1.77 3.72 0.84 1.70 0.92 1.85 1.83 3.00 0.92 1.28 1.55 3.00 2.96
f1 (ppm)

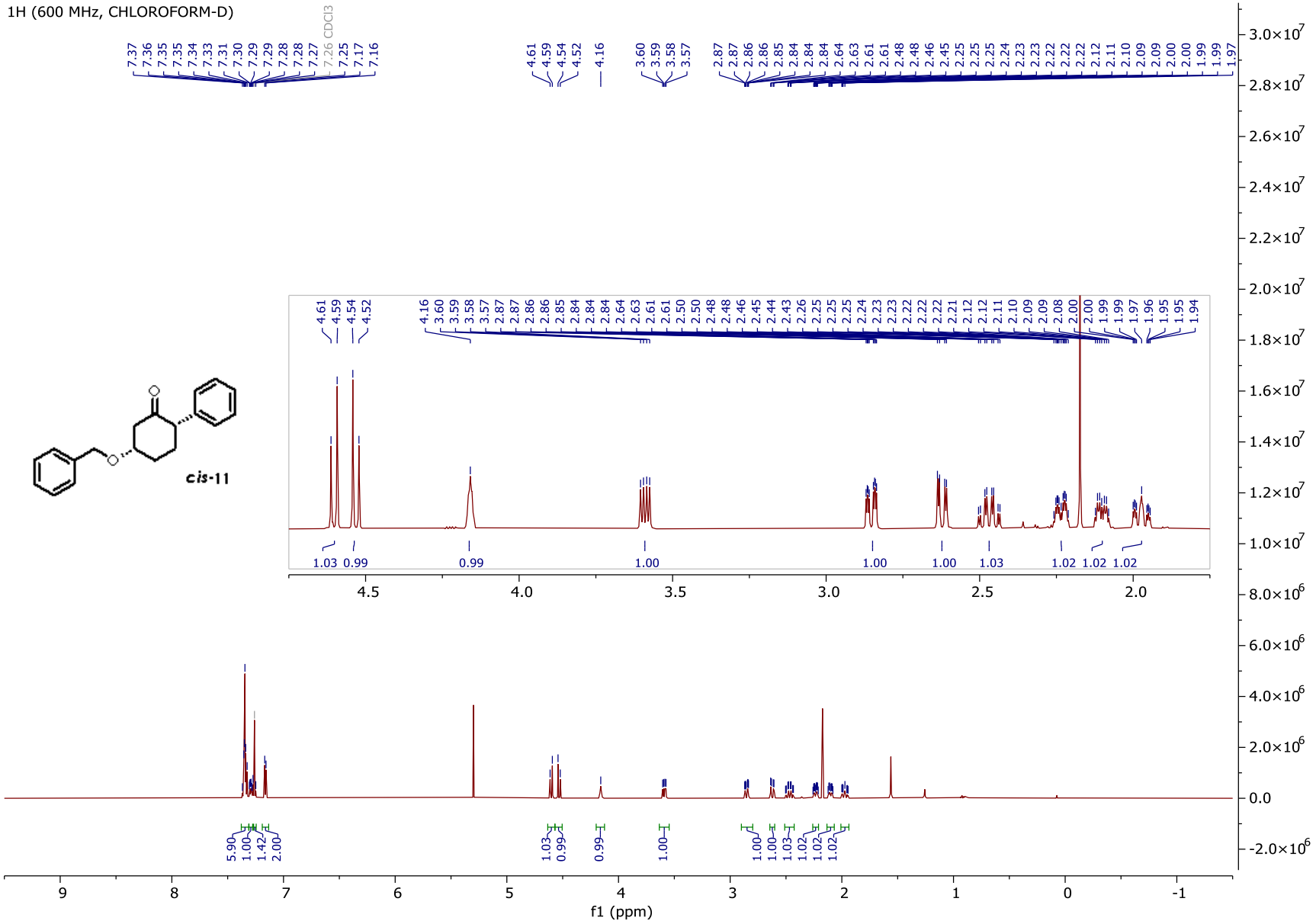
13C (151 MHz, CHLOROFORM-D)

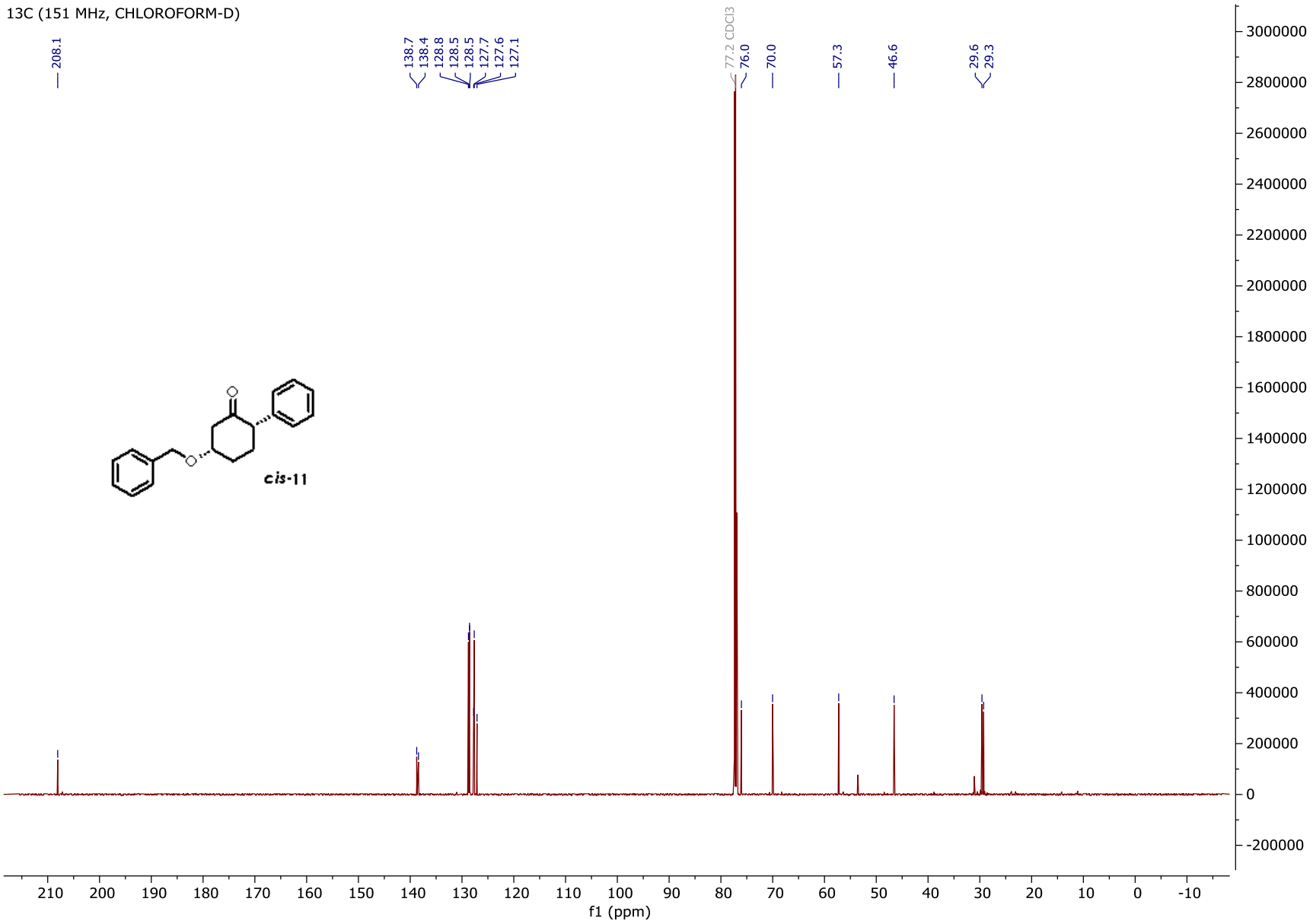


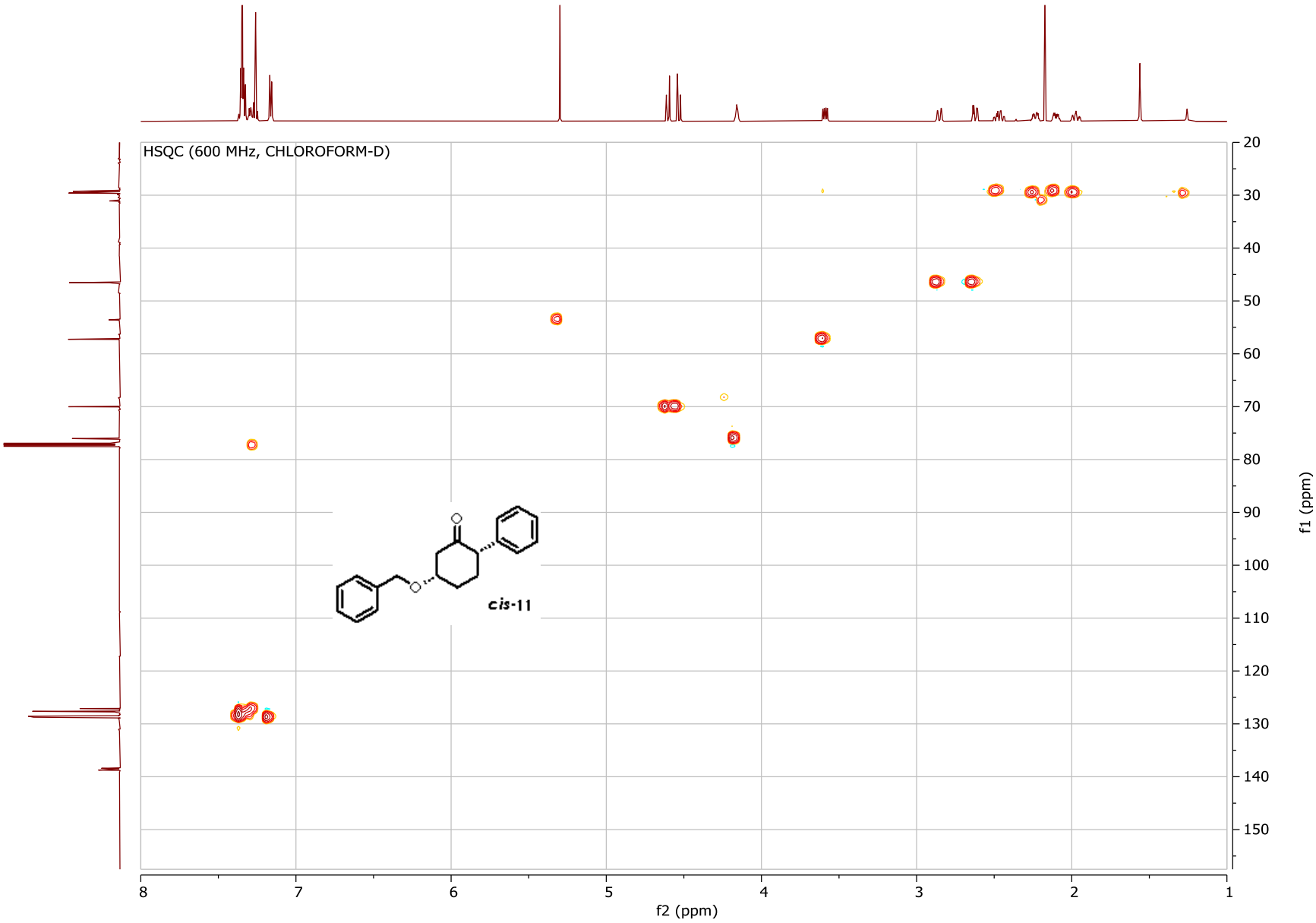

1H (400 MHz, CHLOROFORM-D)
7.36 7.36 7.35 7.34 7.32 7.28 7.28 7.28 7.27 7.26 7.26 CDCl3 7.26 7.24 7.14 7.14 7.12 3.79 3.78 3.77 3.76 3.76 3.76 3.75 3.74 3.73 3.72 3.63 3.61 3.60 3.58 3.52 3.51 3.50 3.48 3.47 3.47 3.46 3.45 3.44 3.43 2.61 2.61 2.58 2.57 2.36 2.33 2.21 2.20 2.20 2.19 2.18 2.18 2.17 2.16 2.15 2.12 1.97 1.96 1.93 1.93 1.84 1.83 1.81 1.81 1.80 1.80 1.58 1.56 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.43 1.29 1.27 1.26 1.25
10
1.84 1.15 1.75 1.79 1.03 1.98 0.94 0.93 1.89 0.94 0.93 4.13 9.00
f1 (ppm)

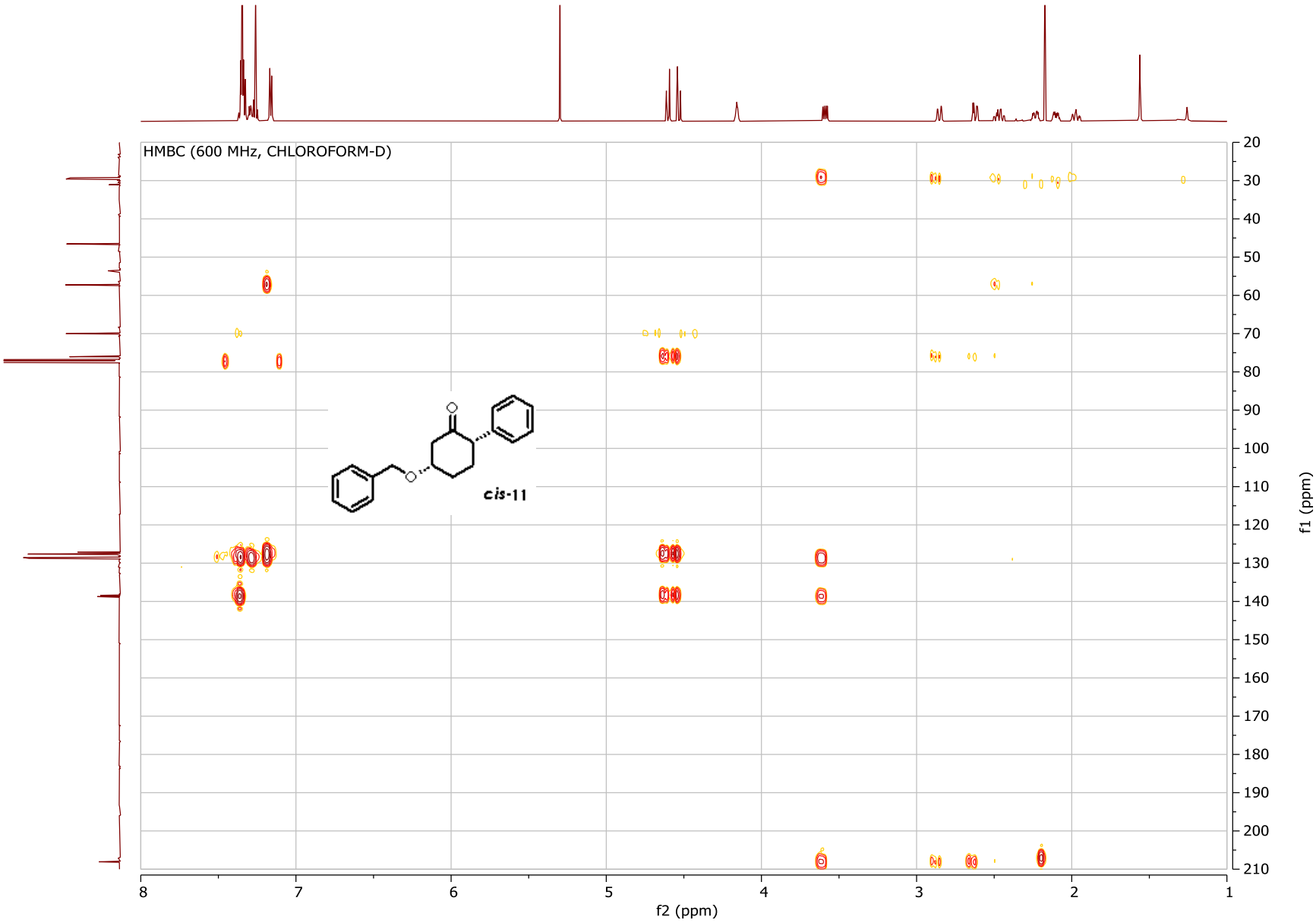
13C (101 MHz, CHLOROFORM-D)

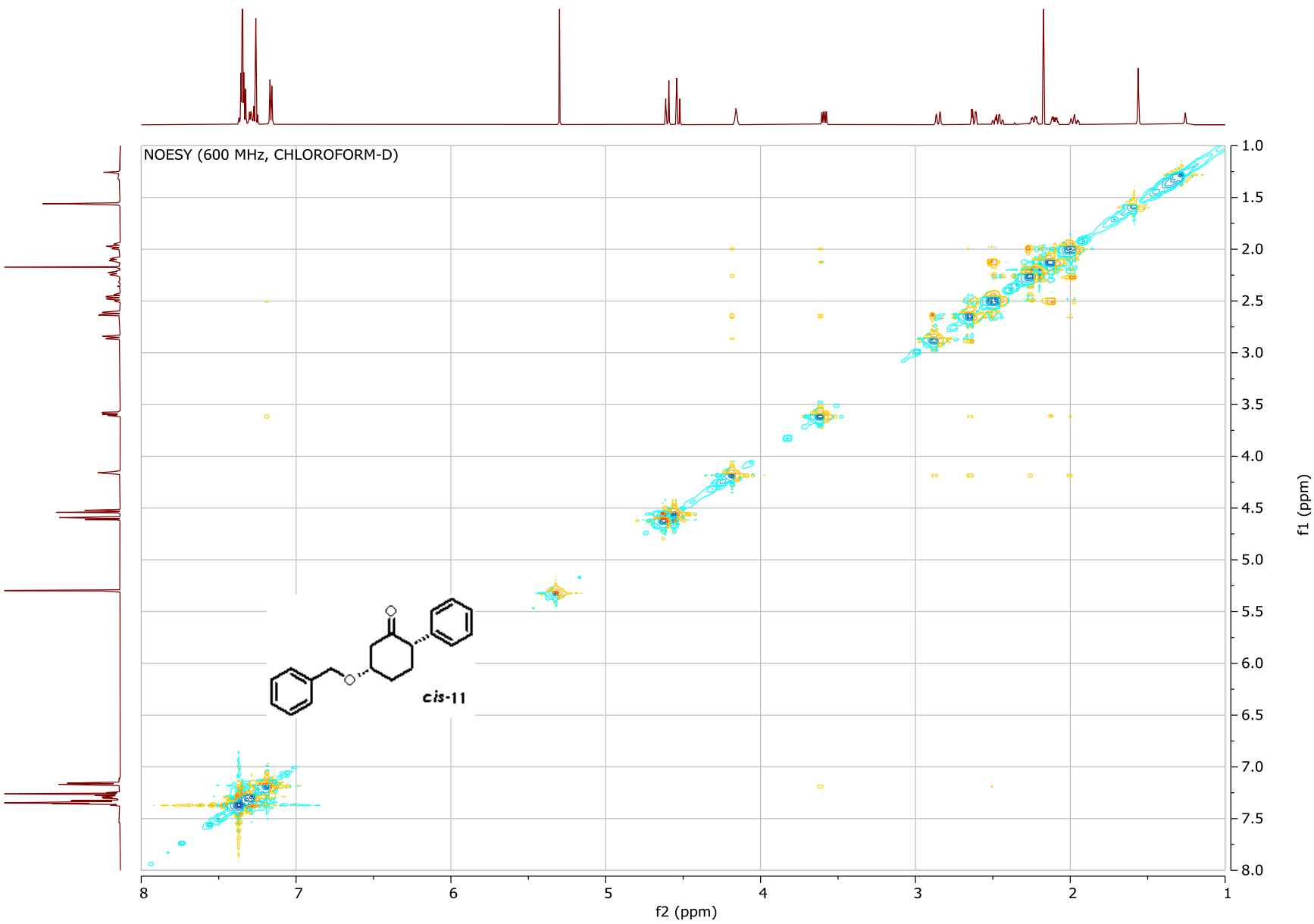


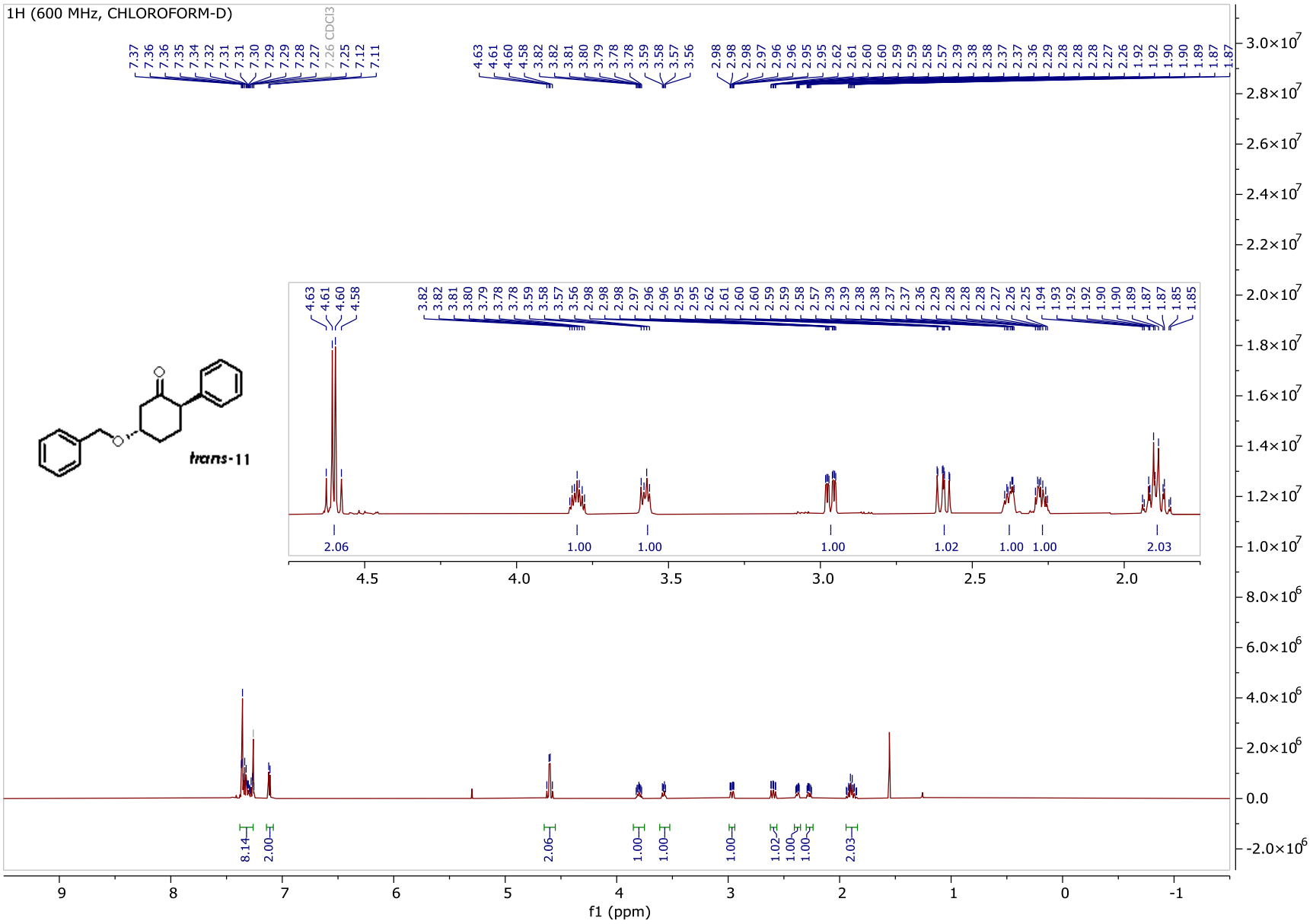

1H (600 MHz, CHLOROFORM-D)
cis-11
f1 (ppm)

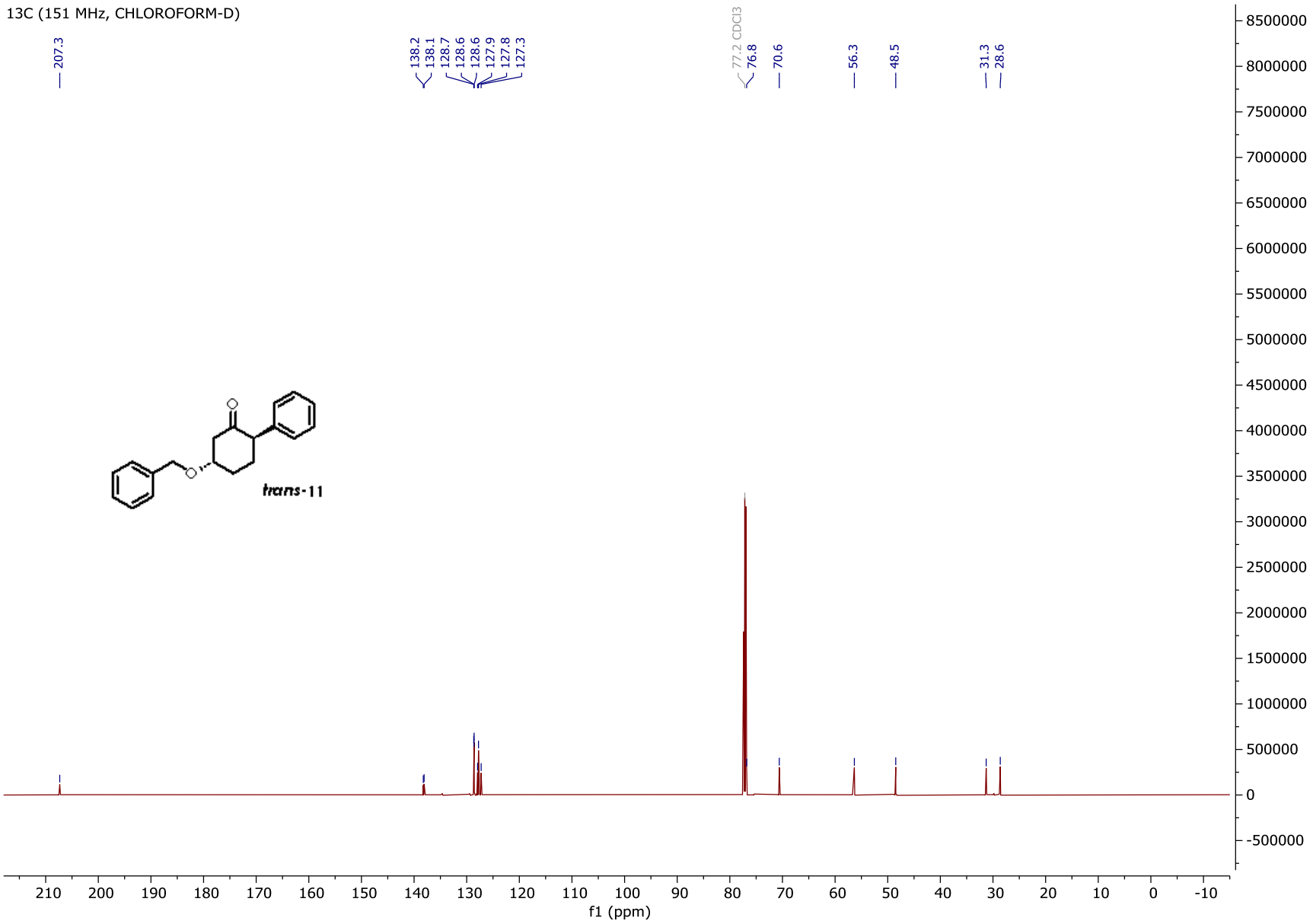

13C (151 MHz, CHLOROFORM-D)
208.1
138.7
138.4
128.8
128.5
128.5
127.7
127.6
127.1
77.2 CDCl3
76.0
70.0
57.3
46.6
29.6
29.3
cis-11
f1 (ppm)

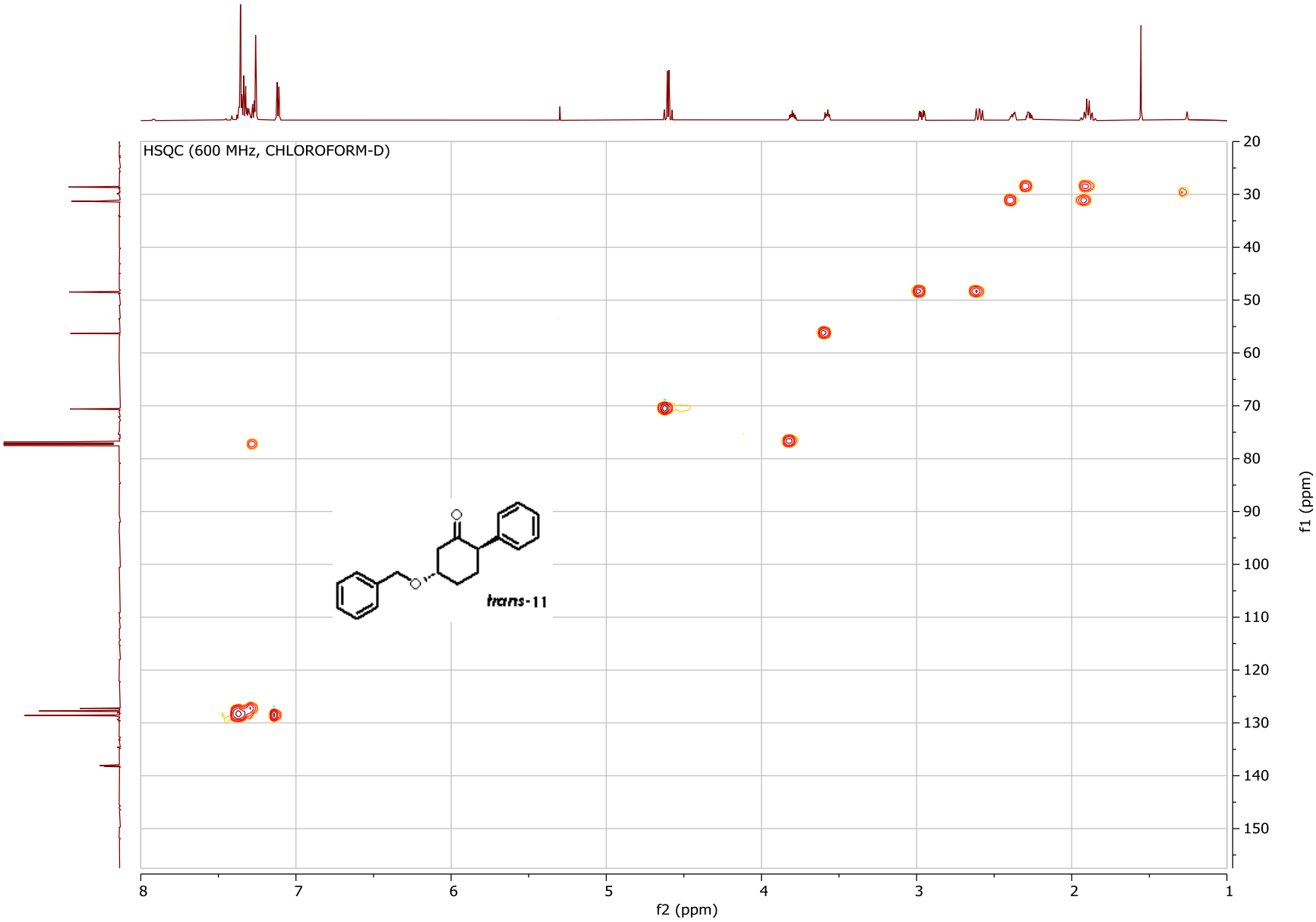

HSQC (600 MHz, CHLOROFORM-D)
cis-11
f2 (ppm)
f1 (ppm)
8
7
6
5
4
3
2
1
20
30
40
50
60
70
80
90
100
110
120
130
140
150

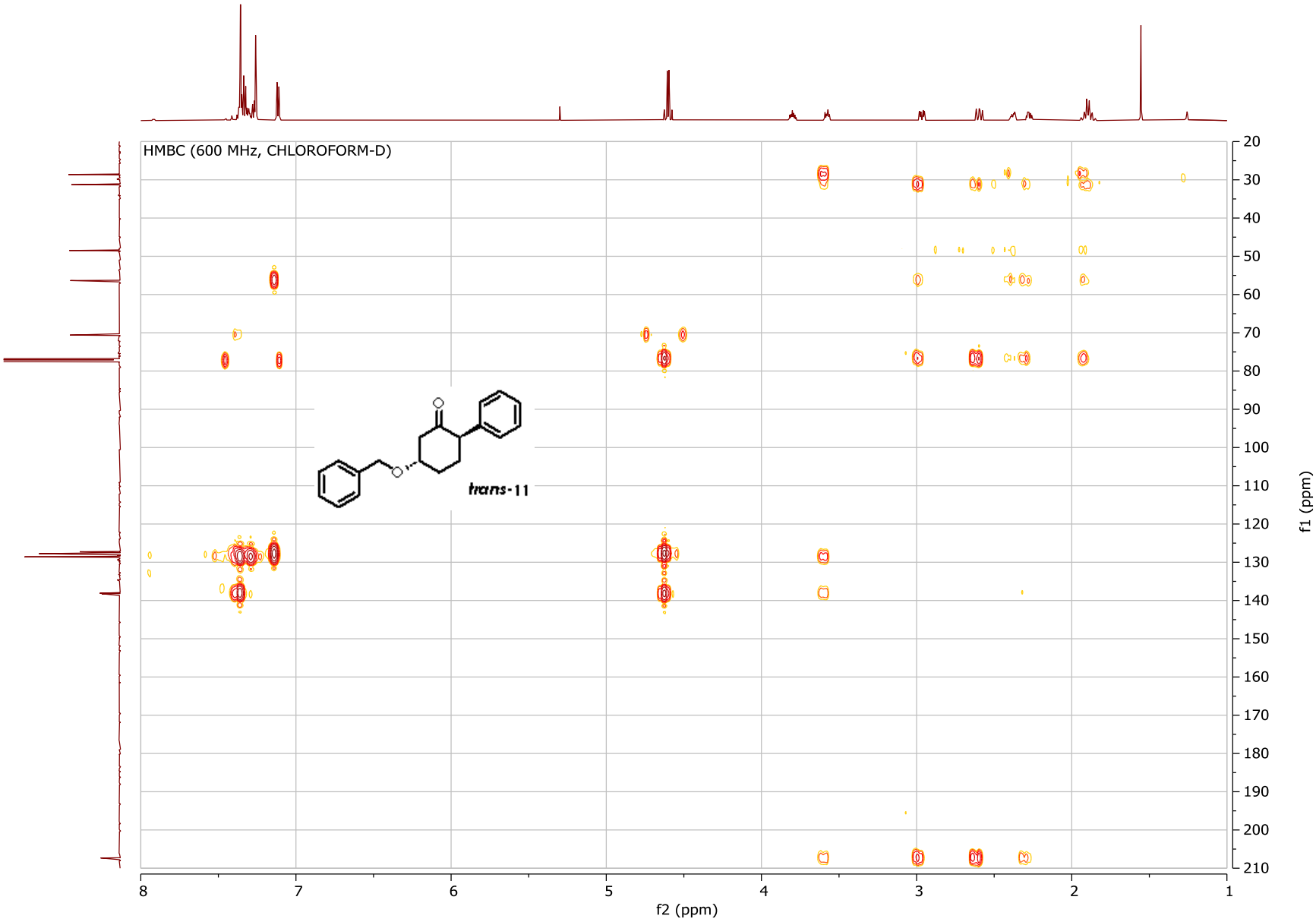

HMBC (600 MHz, CHLOROFORM-D)
cis-11
f2 (ppm)
f1 (ppm)

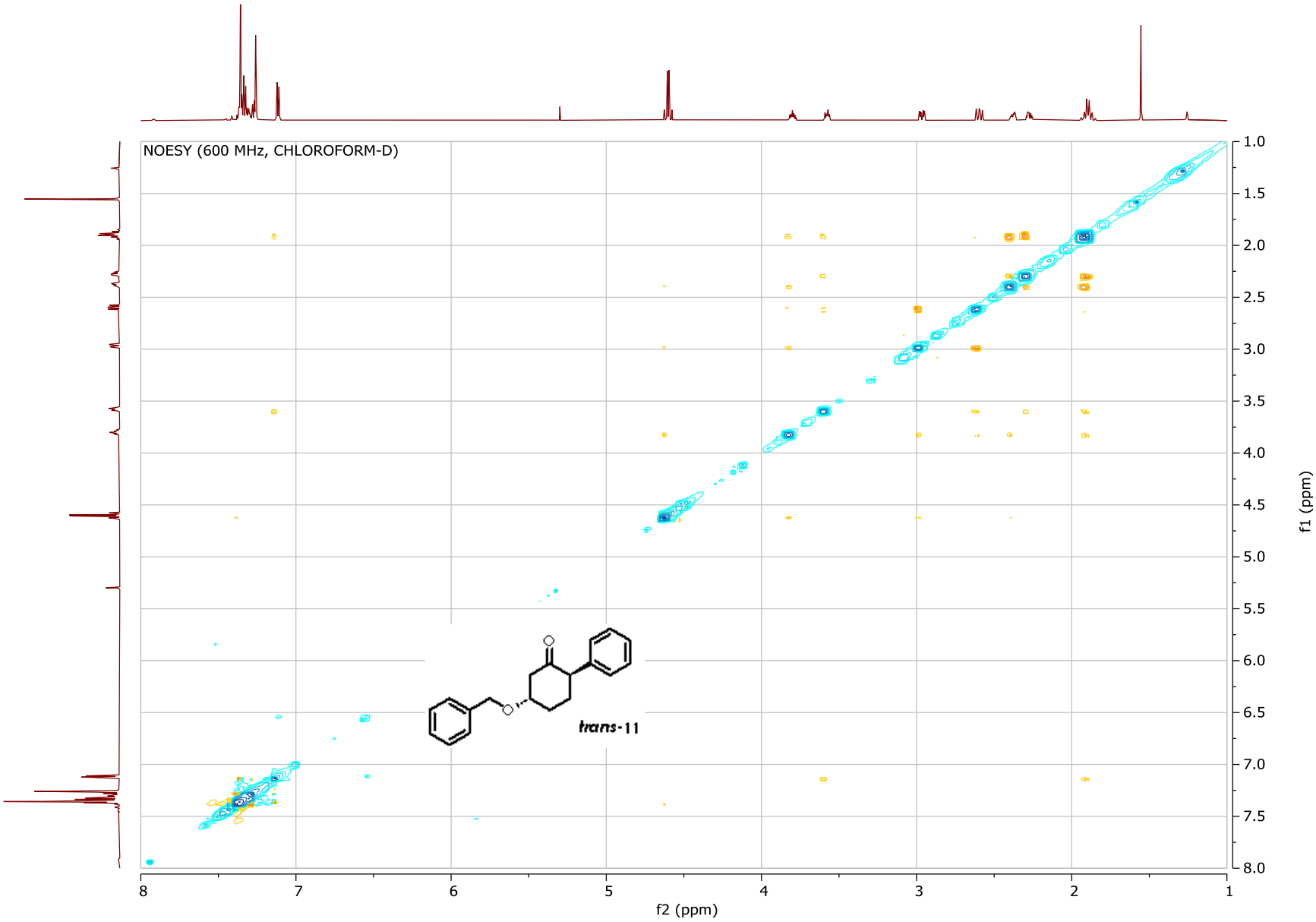

NOESY (600 MHz, CHLOROFORM-D)
cis-11
f2 (ppm)
f1 (ppm)
8
7
6
5
4
3
2
1
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

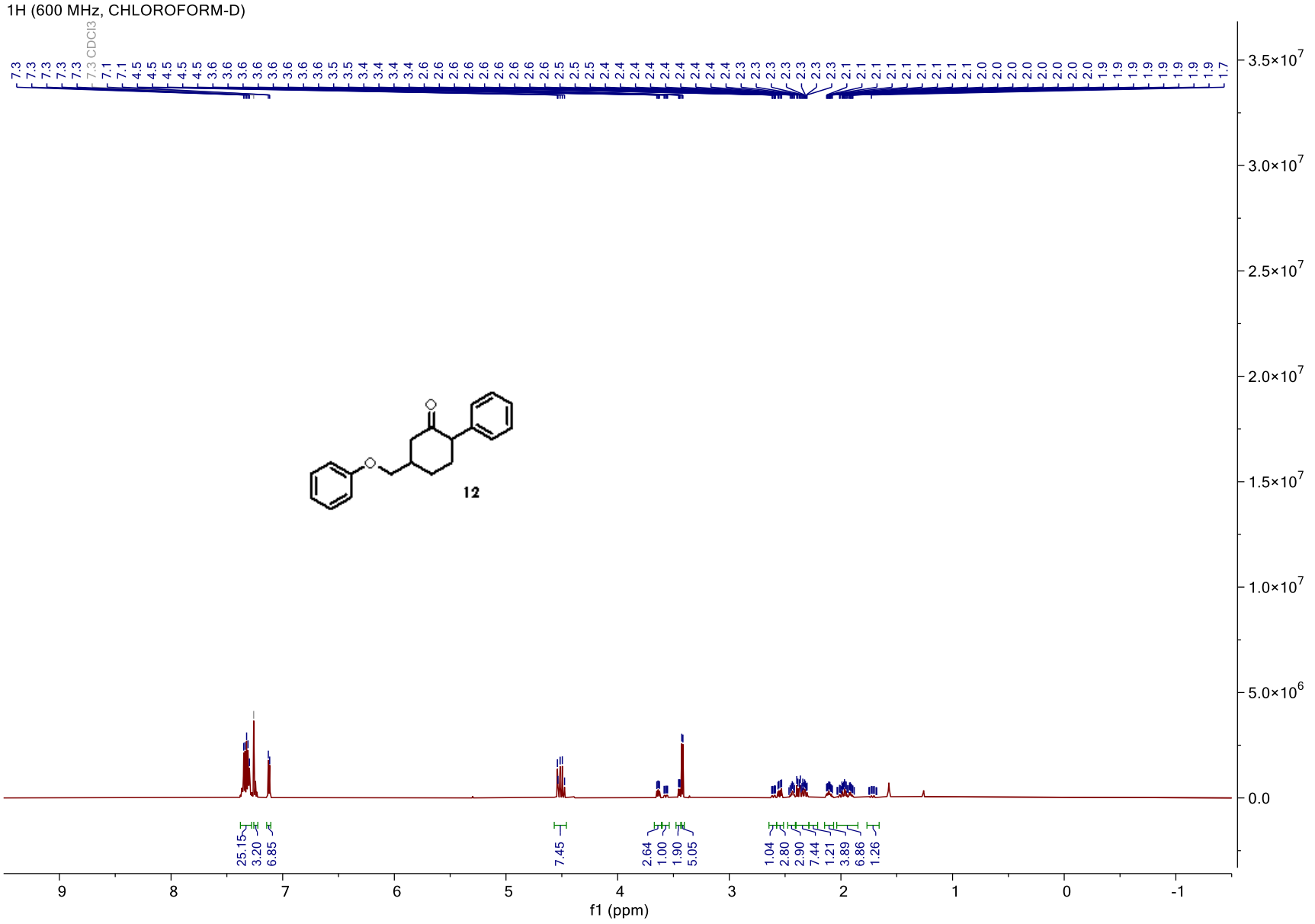

1H (600 MHz, CHLOROFORM-D)
trans-11
f1 (ppm)


13C (151 MHz, CHLOROFORM-D)
207.3
138.2
138.1
128.7
128.6
128.6
127.9
127.8
127.3
77.2 CDCl3
76.8
70.6
56.3
48.5
31.3
28.6
trans-11
f1 (ppm)

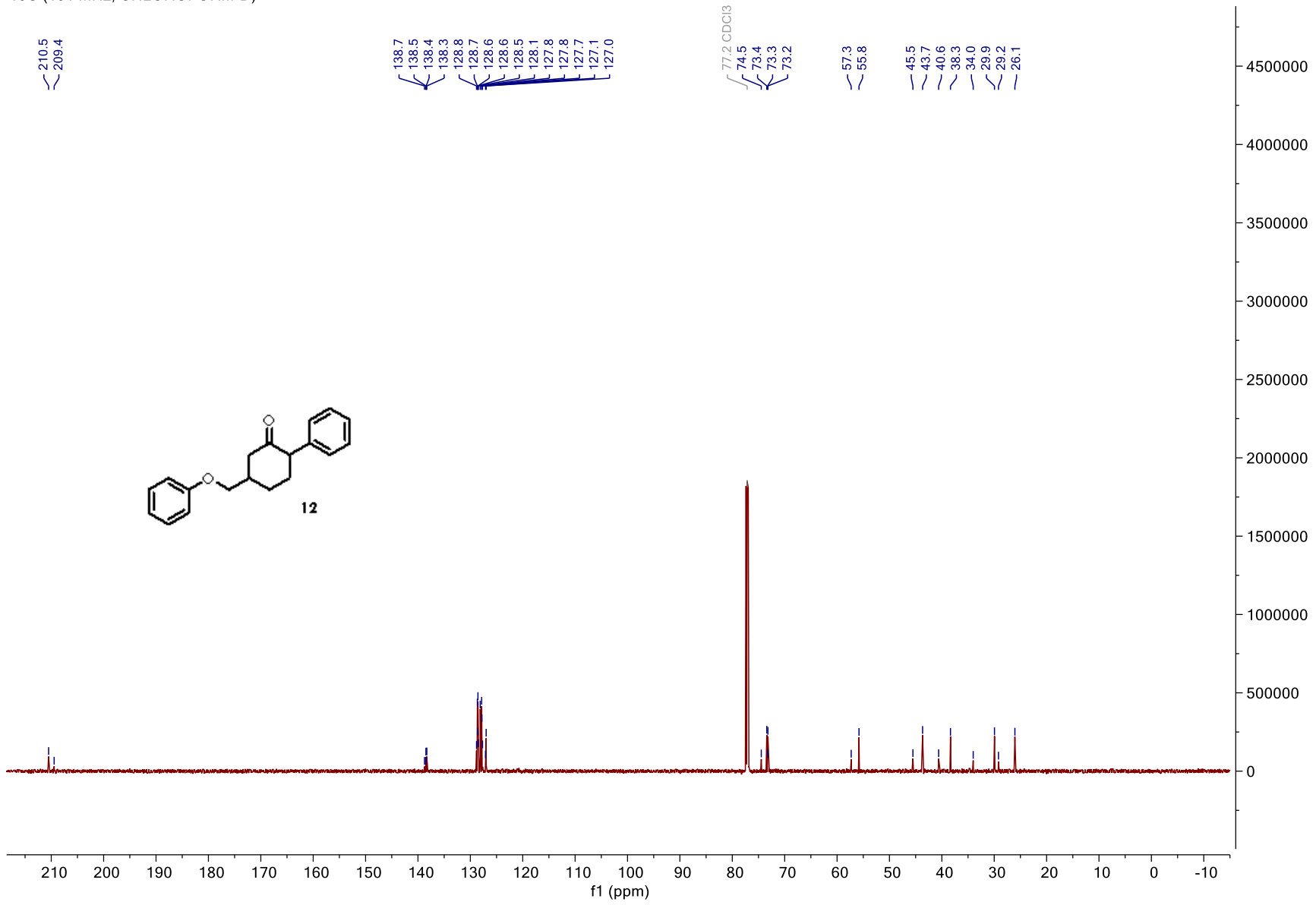

HSQC (600 MHz, CHLOROFORM-D)
trans-11
f2 (ppm)
f1 (ppm)
8
7
6
5
4
3
2
1
20
30
40
50
60
70
80
90
100
110
120
130
140
150

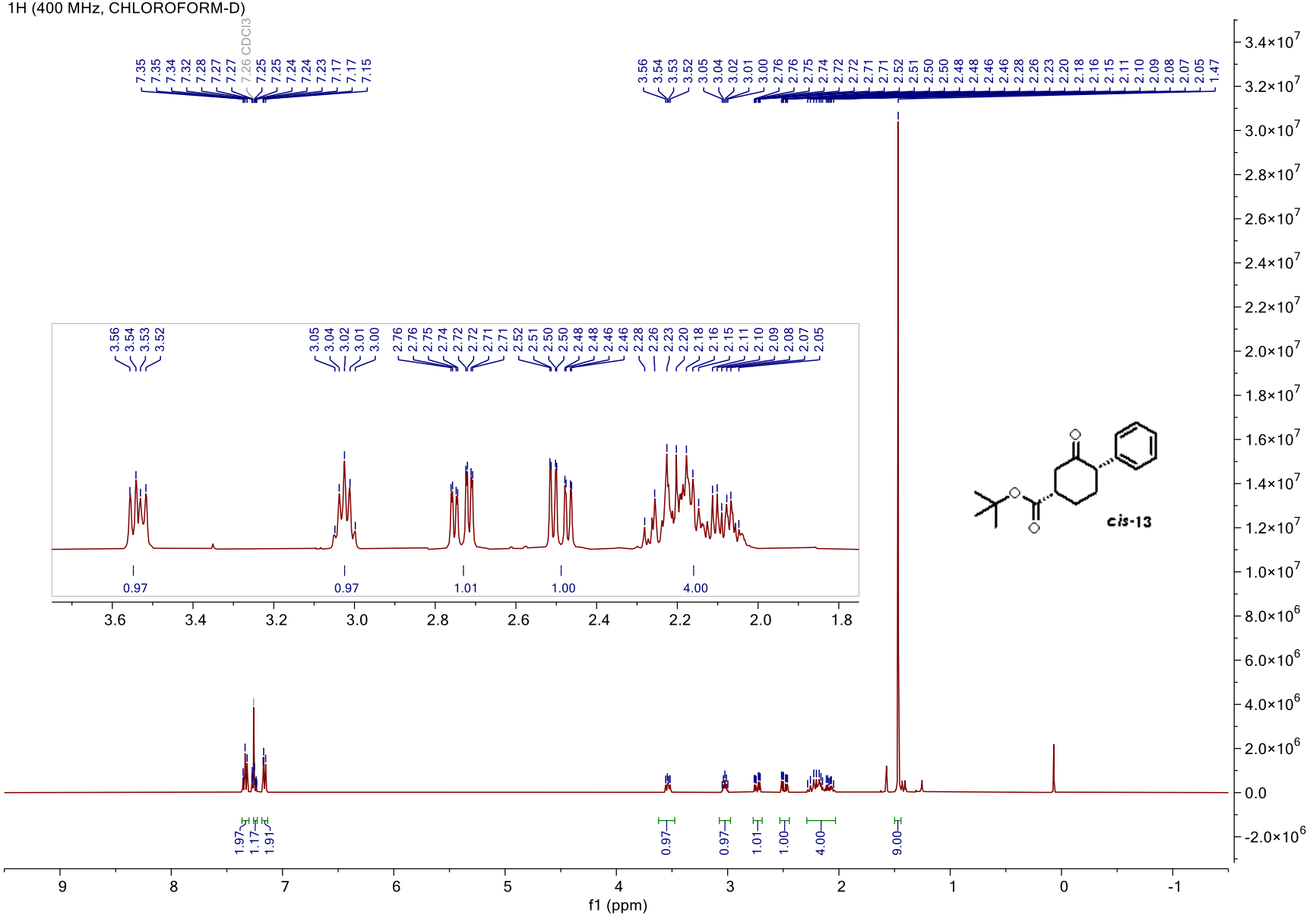

HMBC (600 MHz, CHLOROFORM-D)
trans-11
f2 (ppm)
f1 (ppm)
8
7
6
5
4
3
2
1
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210


NOESY (600 MHz, CHLOROFORM-D)
trans-11
f2 (ppm)
f1 (ppm)
8
7
6
5
4
3
2
1
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

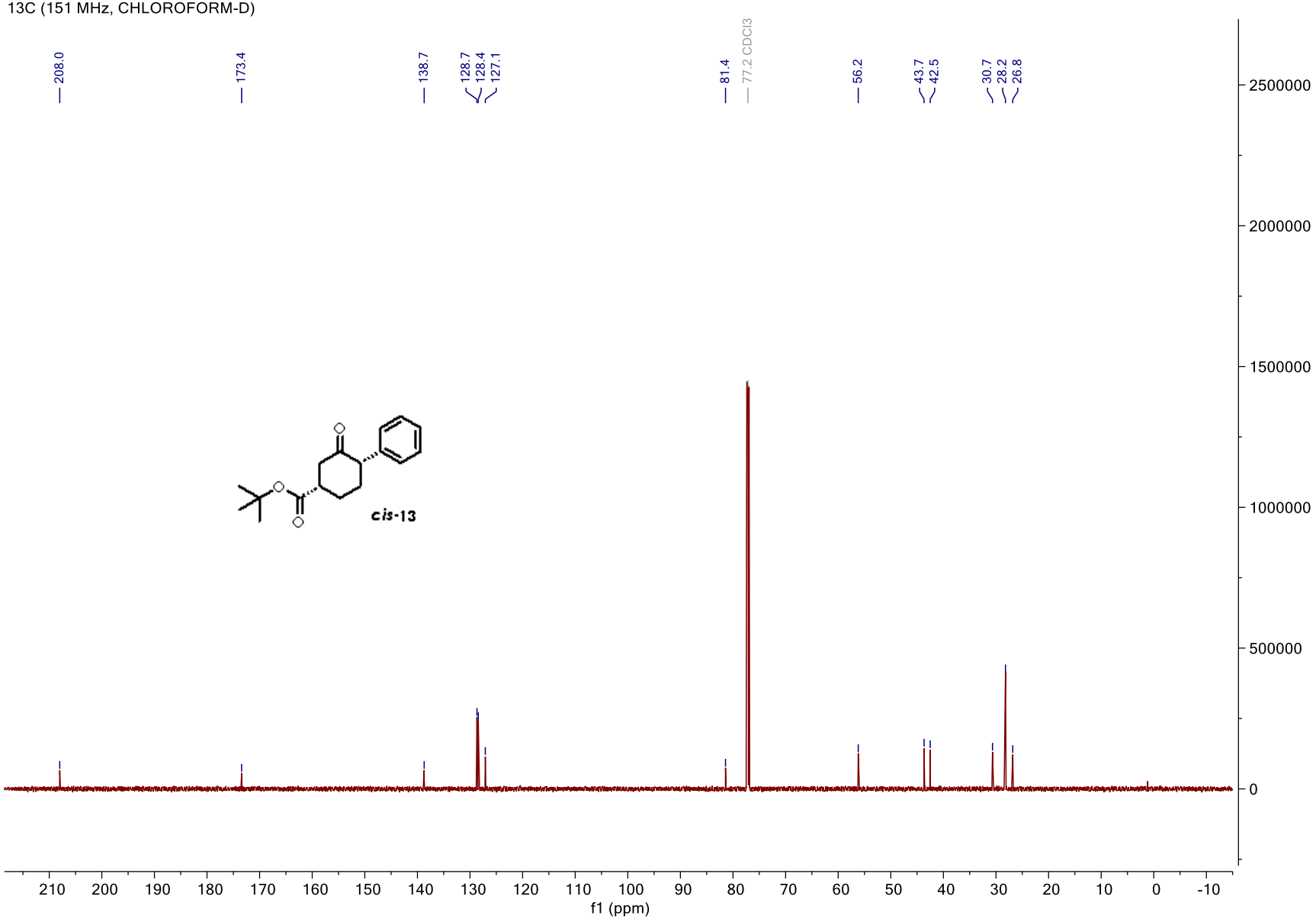

1H (600 MHz, CHLOROFORM-D)
7.3 CDCl3
12
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
25.15
3.20
6.85
7.45
2.64
1.00
1.90
5.05
1.04
2.80
2.90
7.44
1.21
3.89
6.86
1.26
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

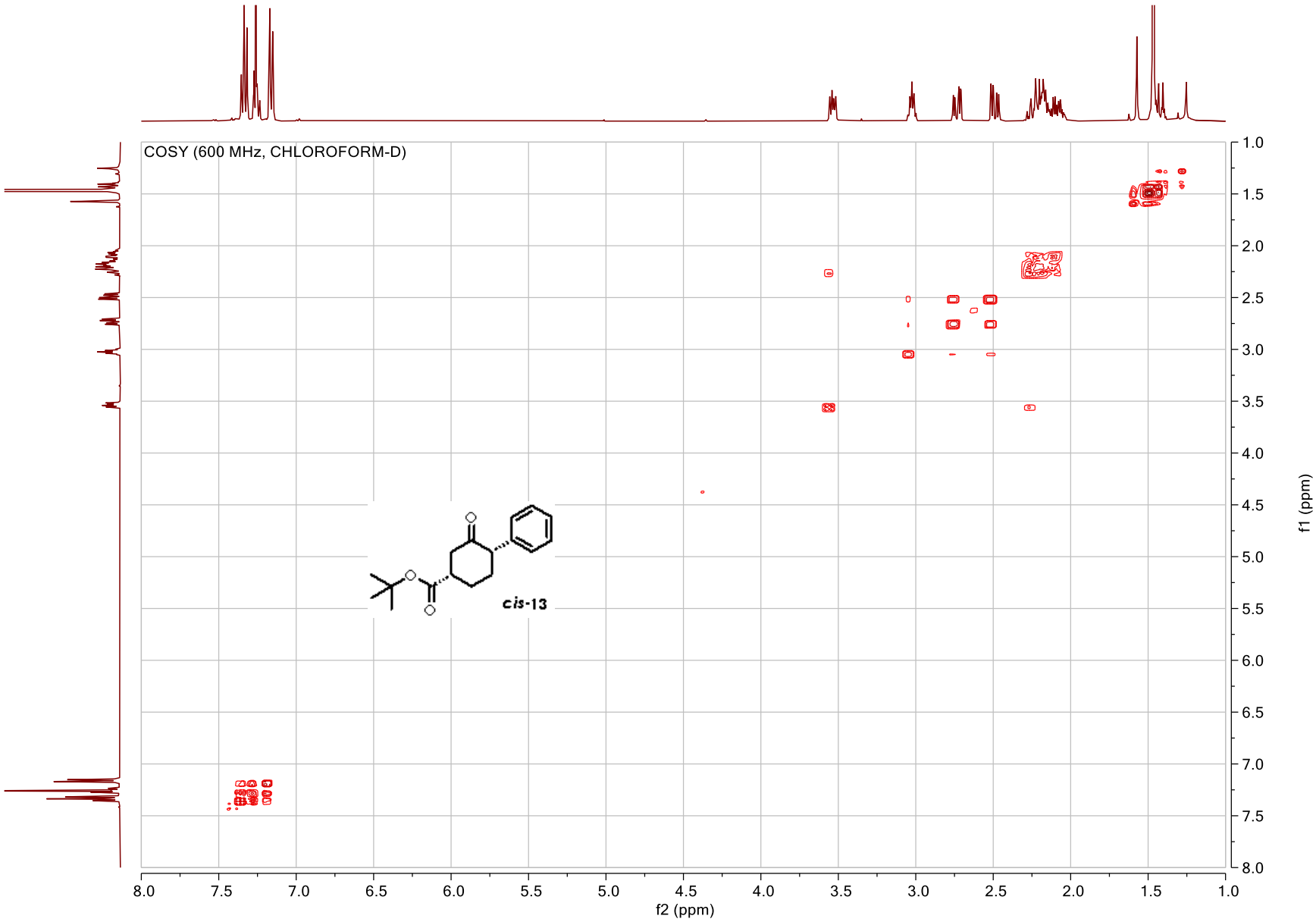
13C (151 MHz, CHLOROFORM-D)

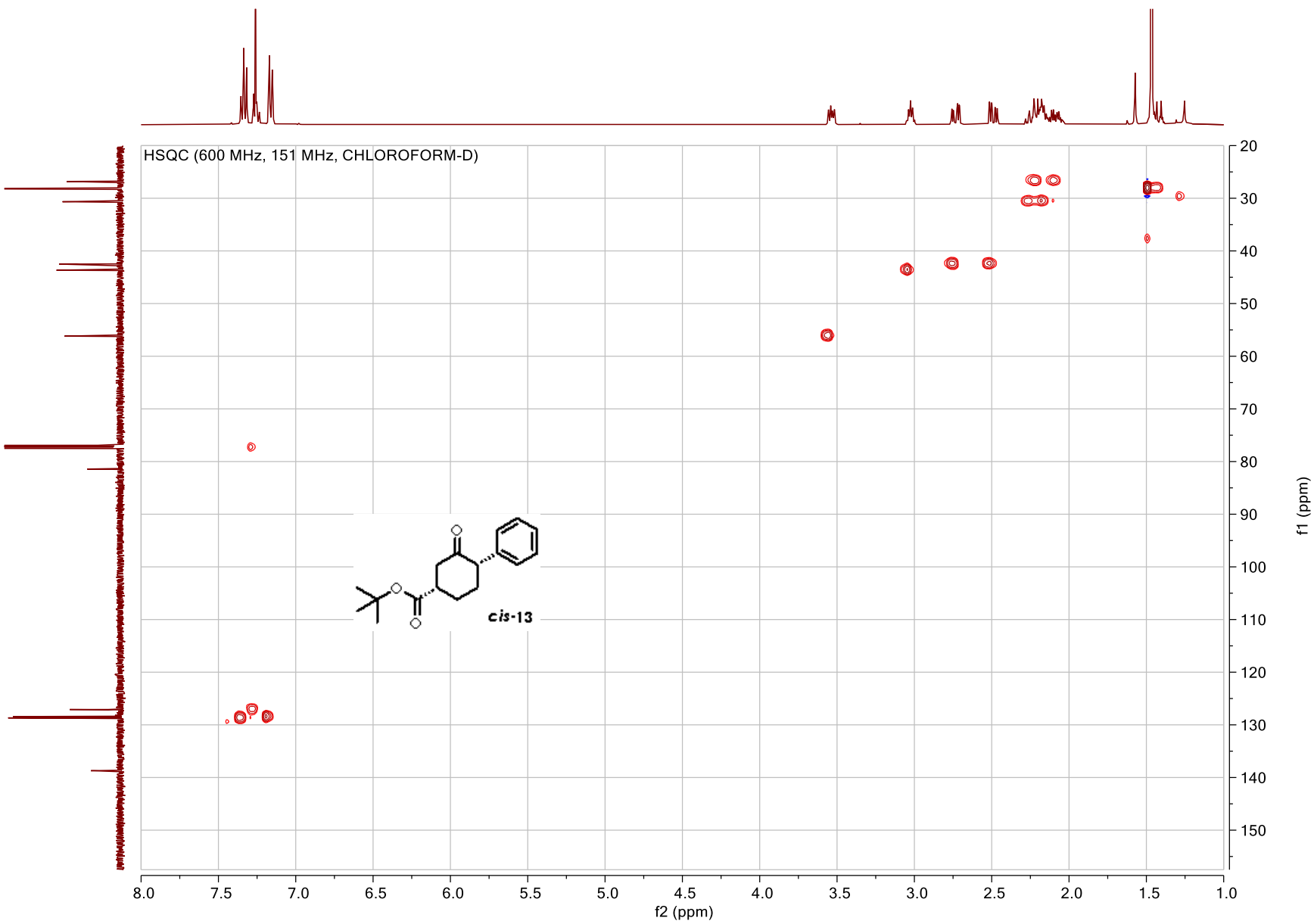


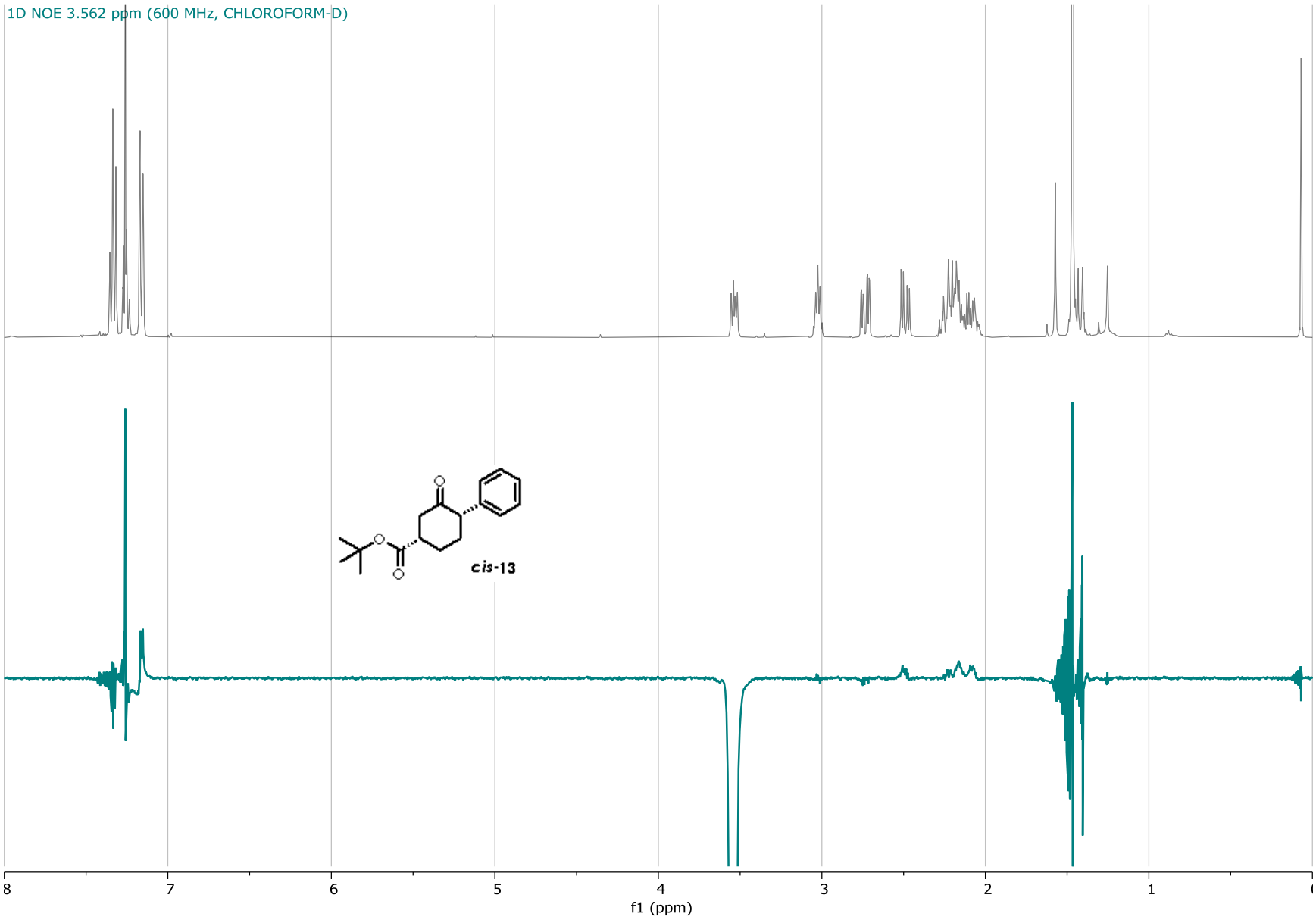

1H (400 MHz, CHLOROFORM-D)
7.26 CDCl3
cis-13
0.97
0.97
1.01
1.00
4.00
1.97
1.17
1.91
0.97
0.97
1.01
1.00
4.00
9.00
f1 (ppm)

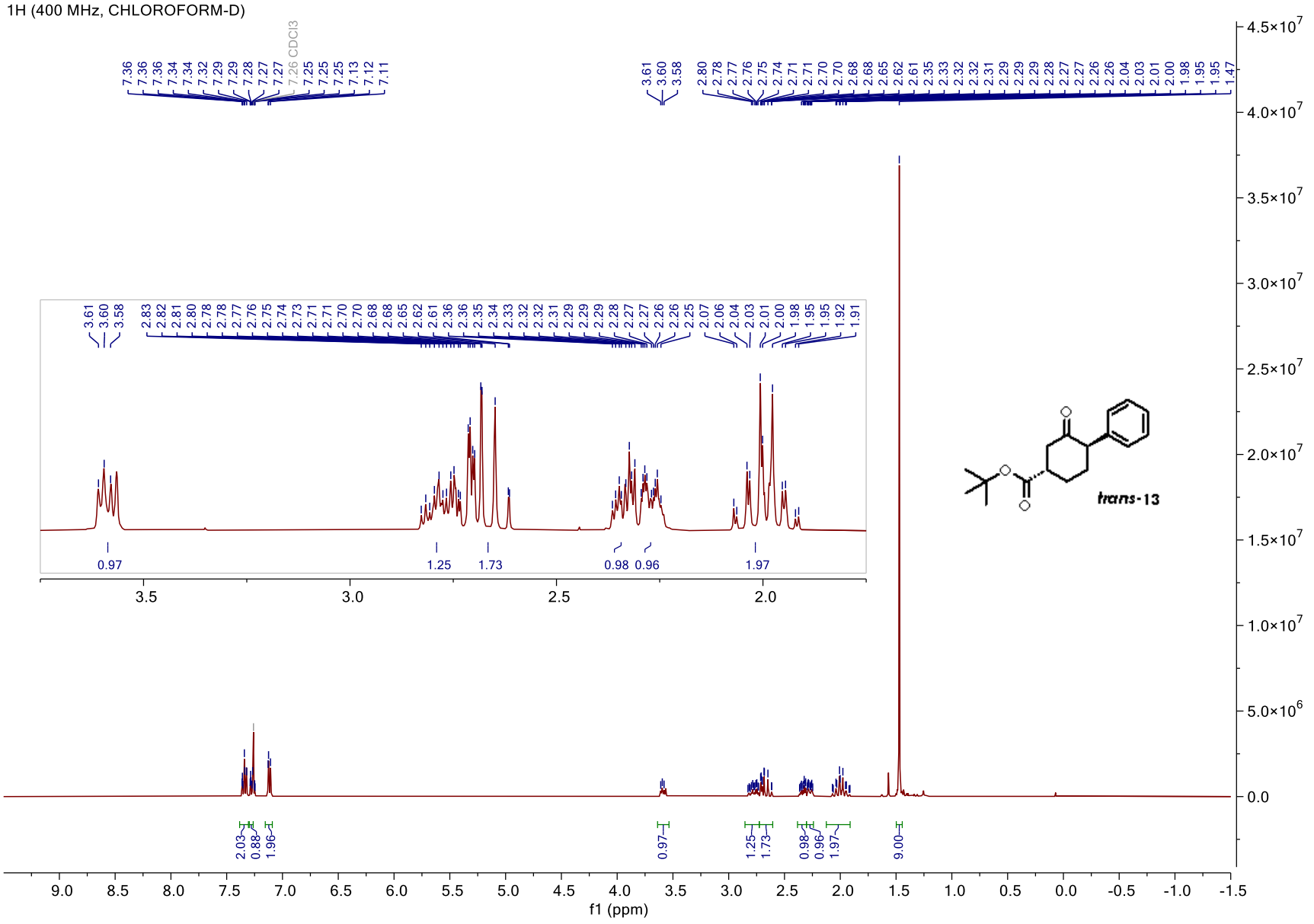
13C (151 MHz, CHLOROFORM-D)

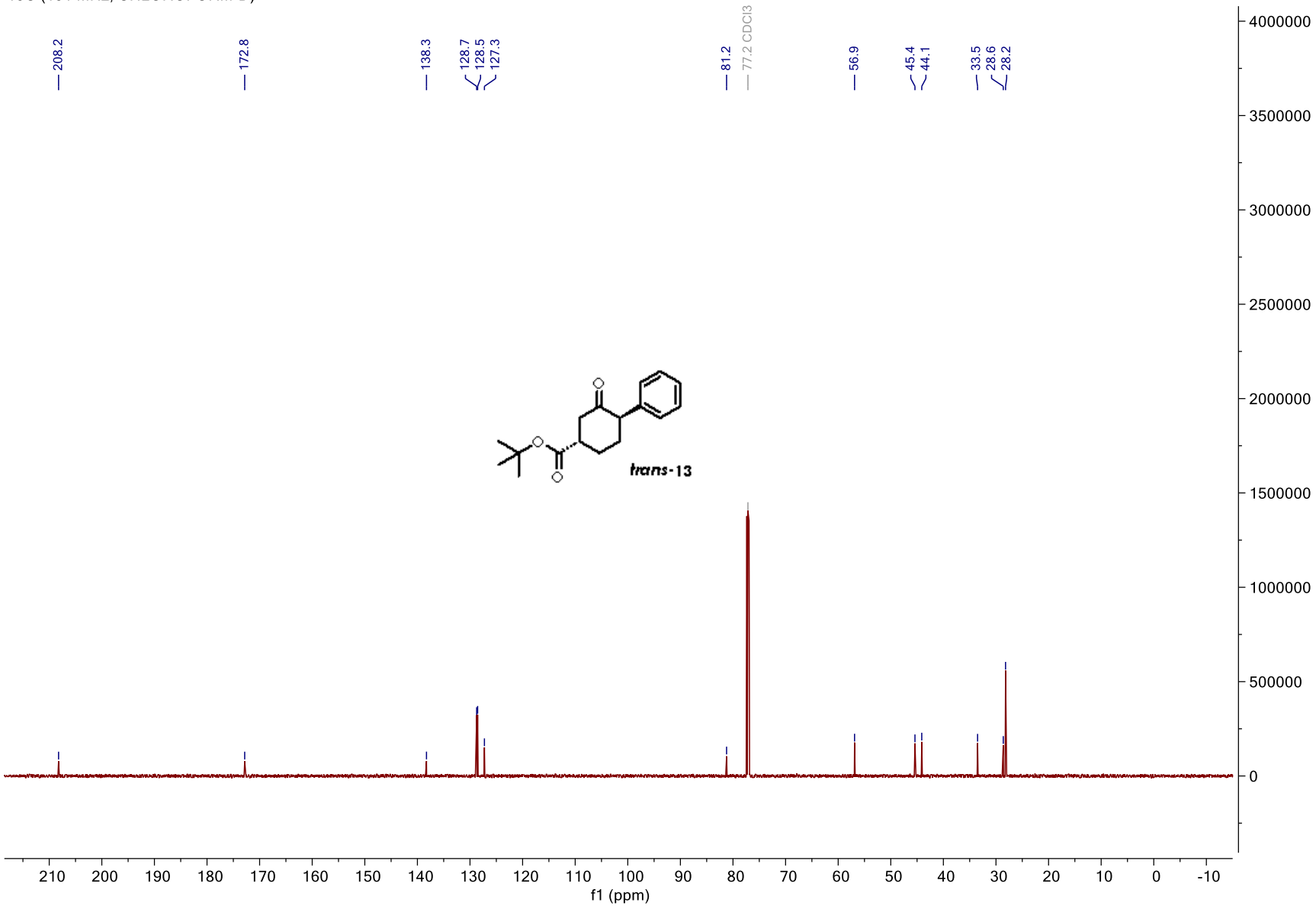


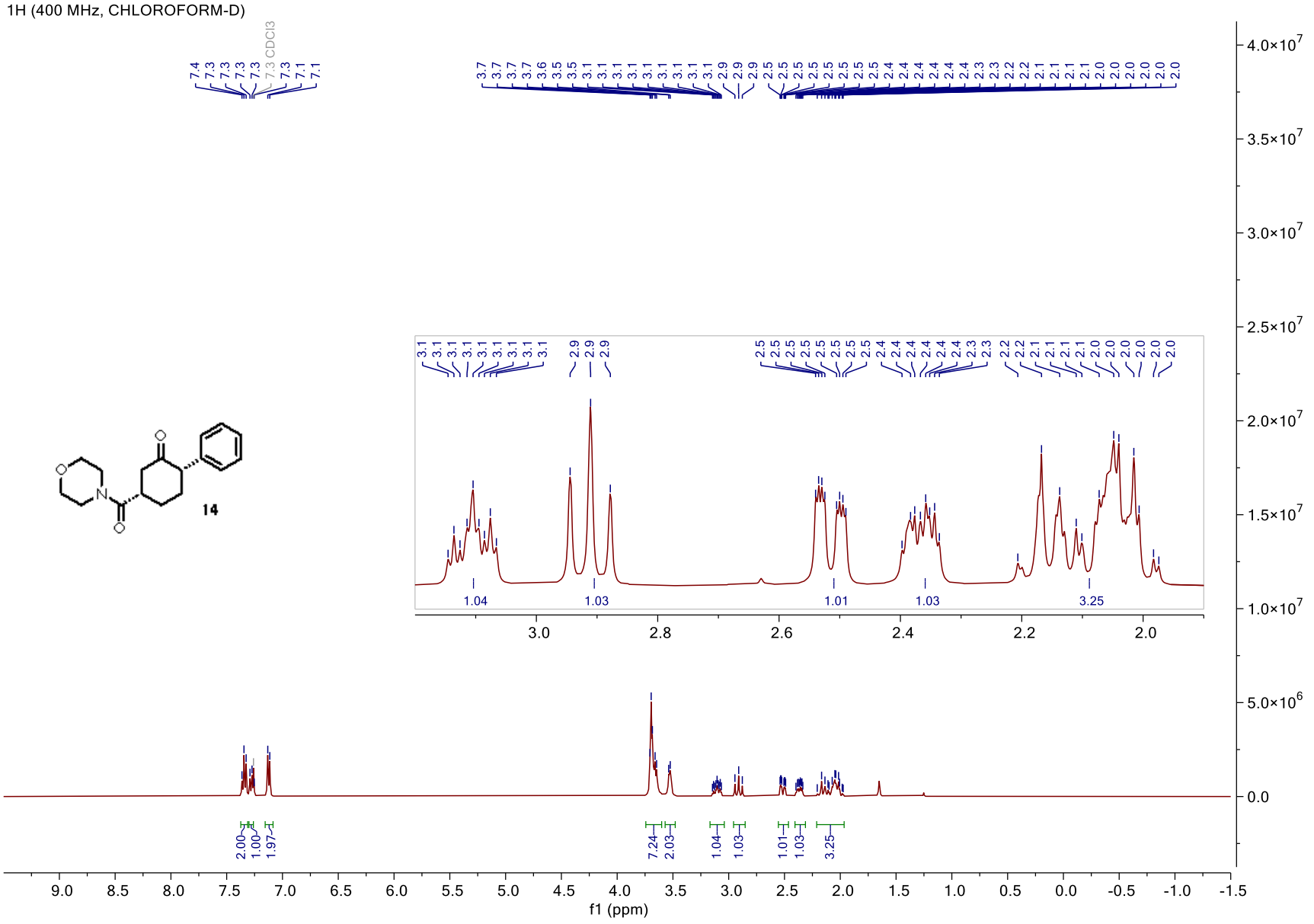

COSY (600 MHz, CHLOROFORM-D)
cis-13
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


HSQC (600 MHz, 151 MHz, CHLOROFORM-D)
cis-13
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
20
30
40
50
60
70
80
90
100
110
120
130
140
150

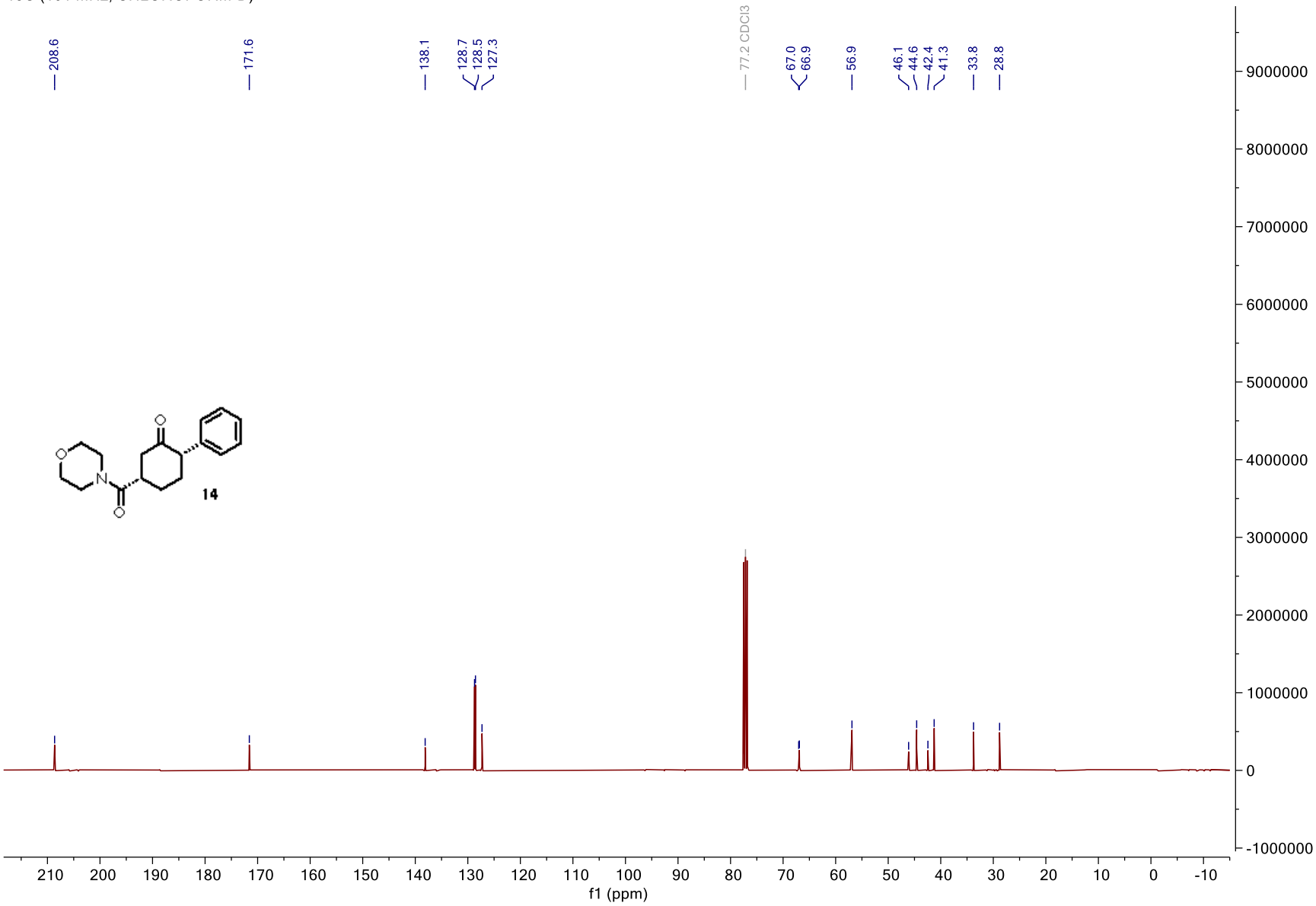

1D NOE 3.562 ppm (600 MHz, CHLOROFORM-D)
cis-13
8
7
6
5
4
3
2
1
f1 (ppm)

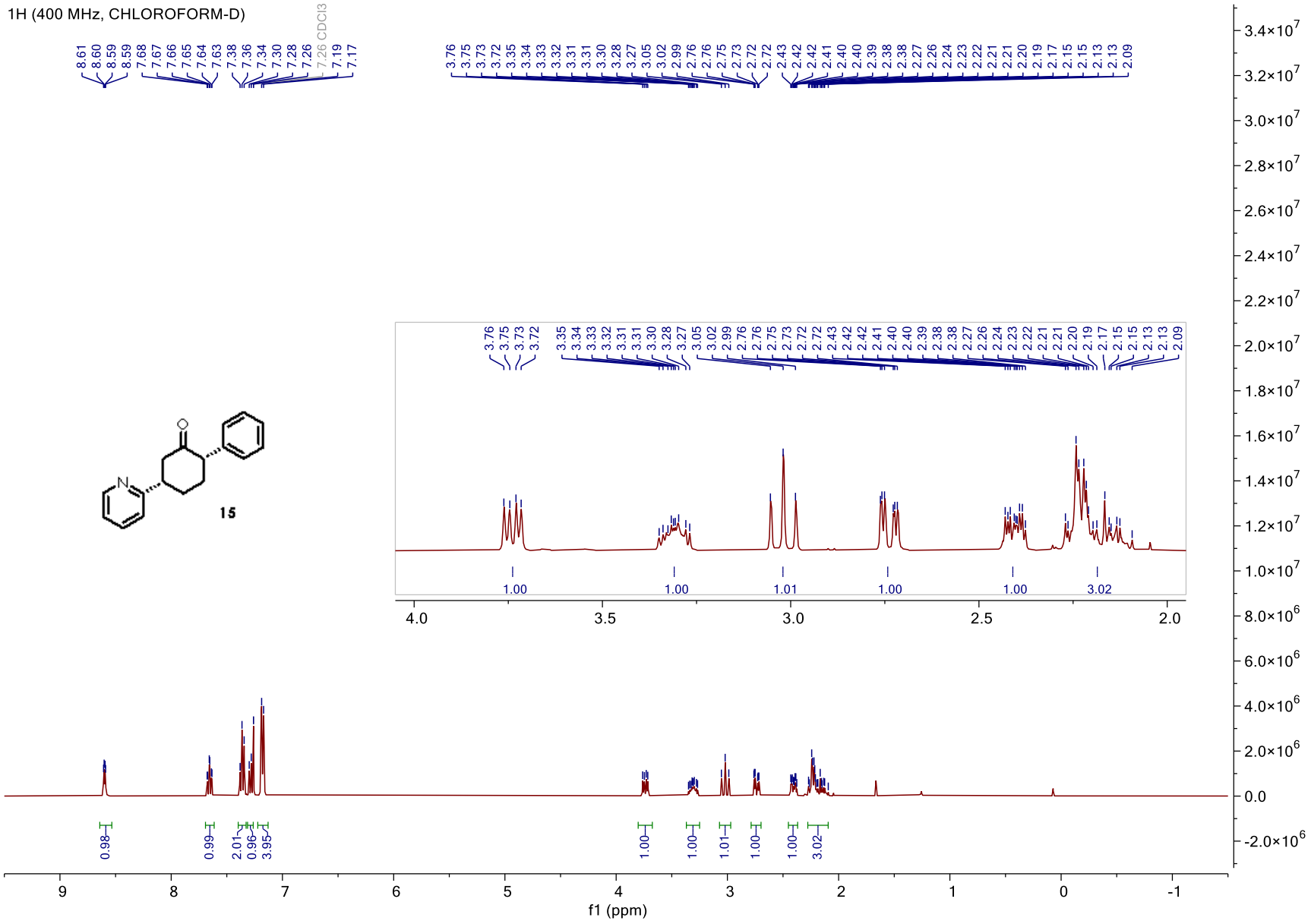

1H (400 MHz, CHLOROFORM-D)
7.26 CDCl3
trans-13
f1 (ppm)

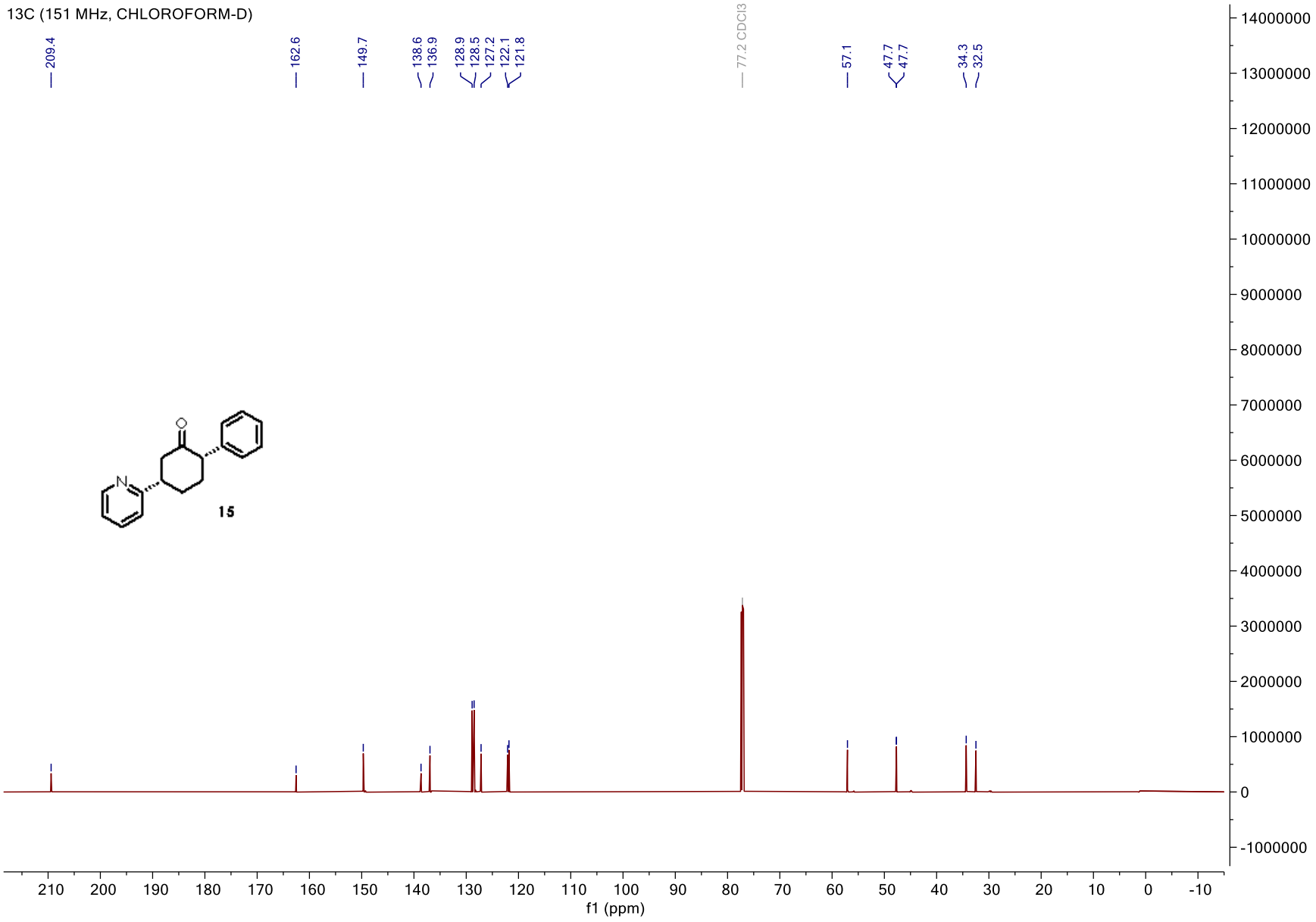

13C (151 MHz, CHLOROFORM-D)
208.2
172.8
138.3
128.7
128.5
127.3
81.2
77.2 CDCl3
56.9
45.4
44.1
33.5
28.6
28.2
trans-13
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

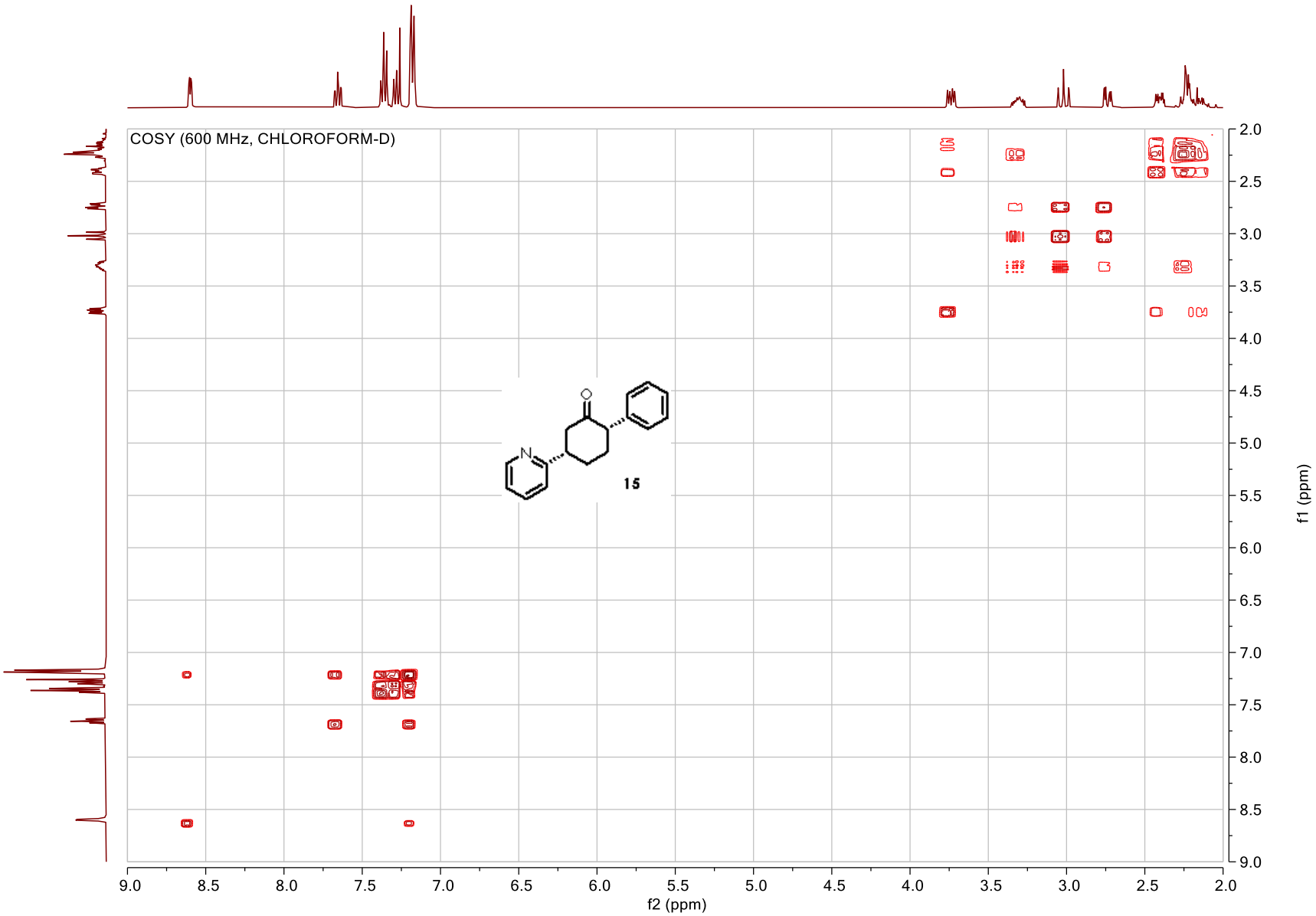

1H (400 MHz, CHLOROFORM-D)
7.3 CDCl3
14
1.04
1.03
1.01
1.03
3.25
2.00
1.00
1.97
7.24
2.03
1.04
1.03
1.01
1.03
3.25
f1 (ppm)

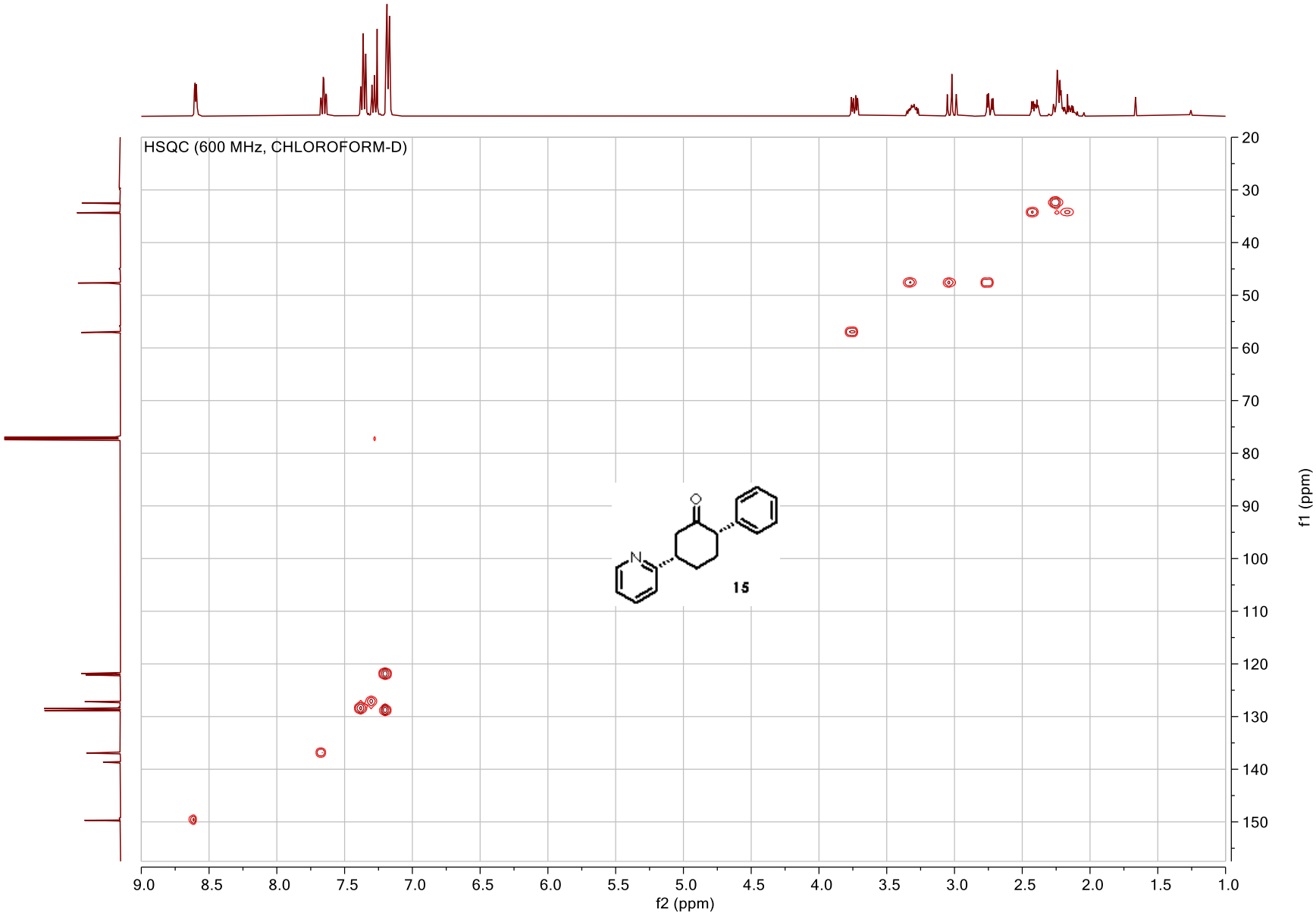
13C (101 MHz, CHLOROFORM-D)

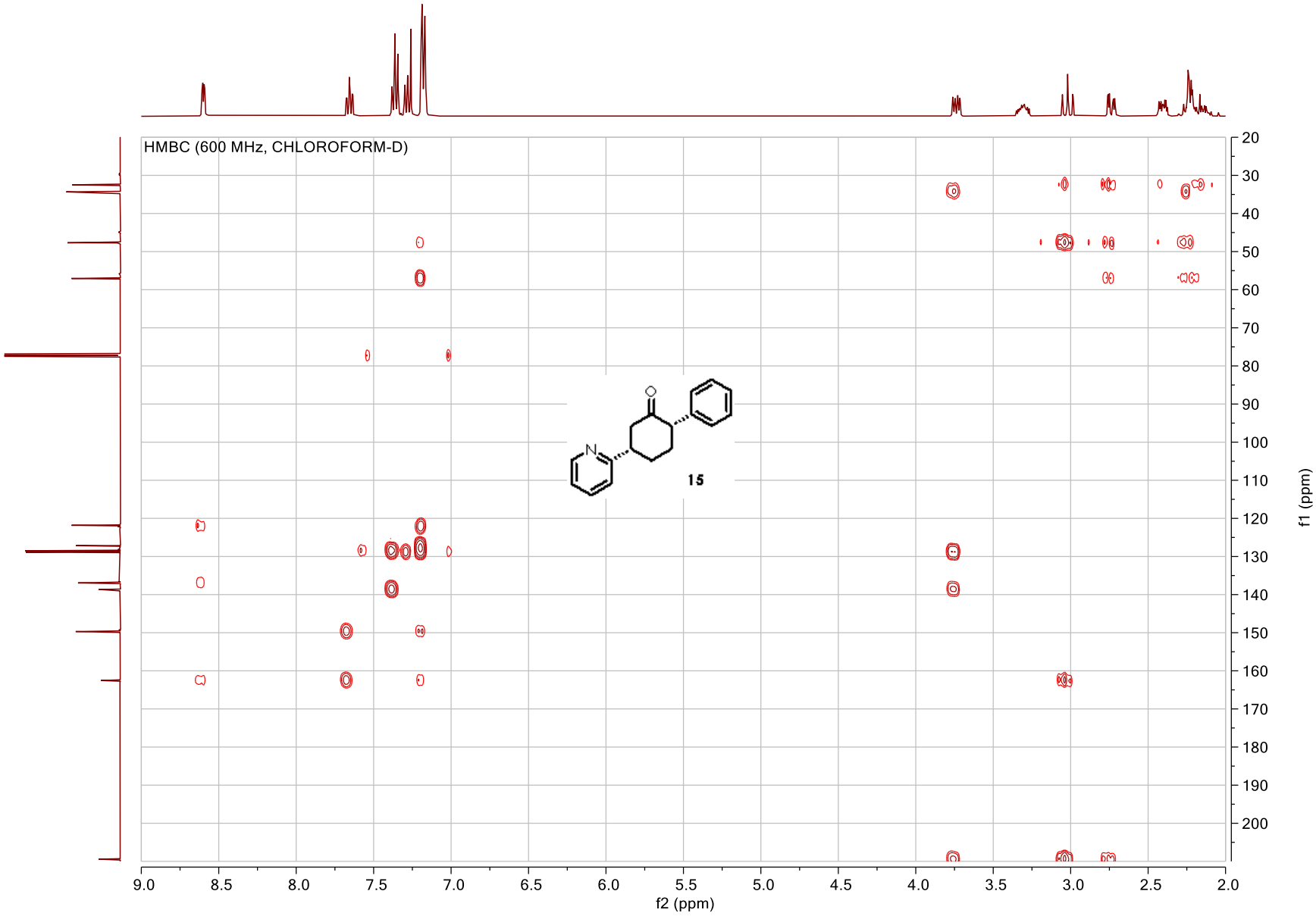


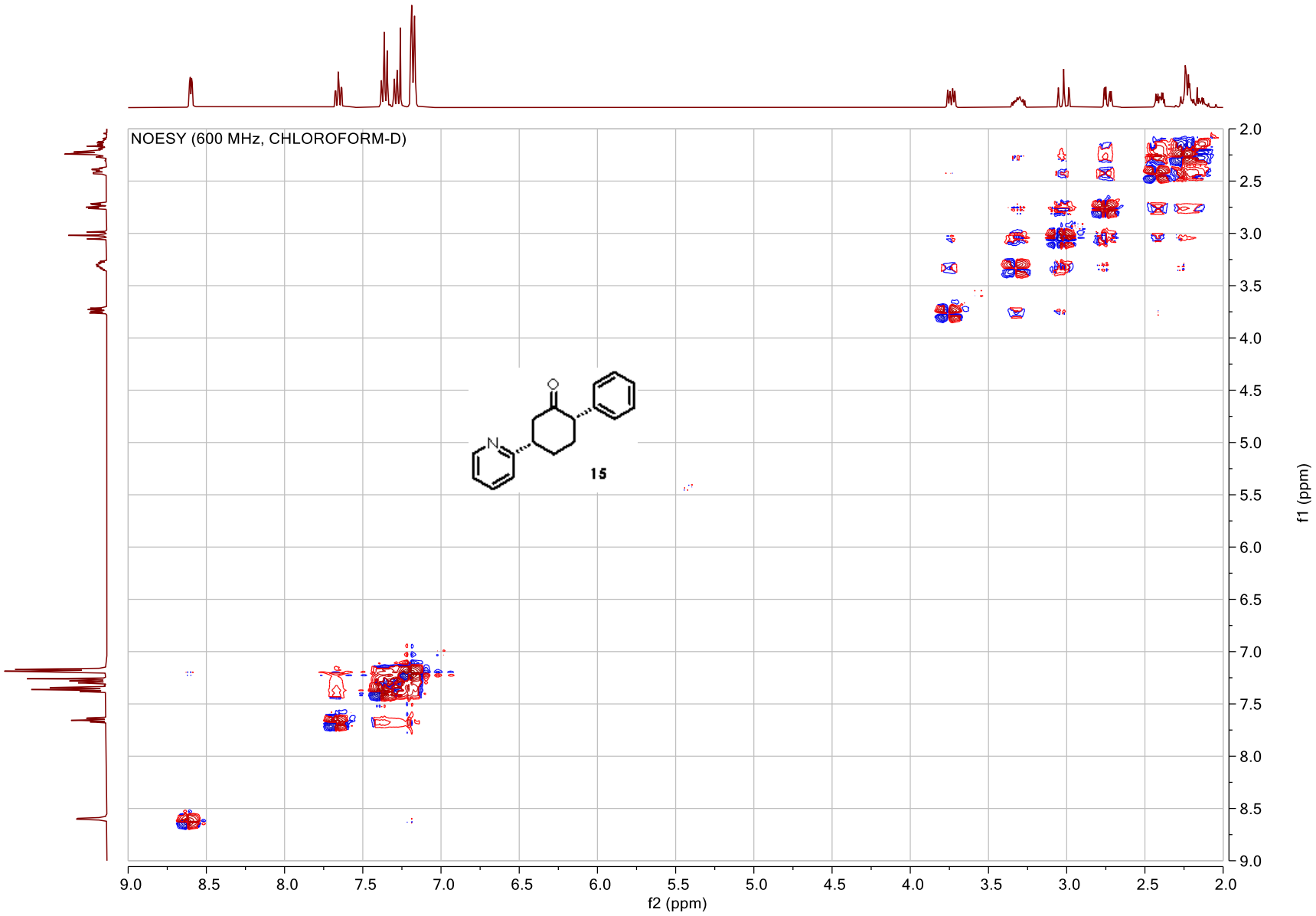

1H (400 MHz, CHLOROFORM-D)
15
f1 (ppm)

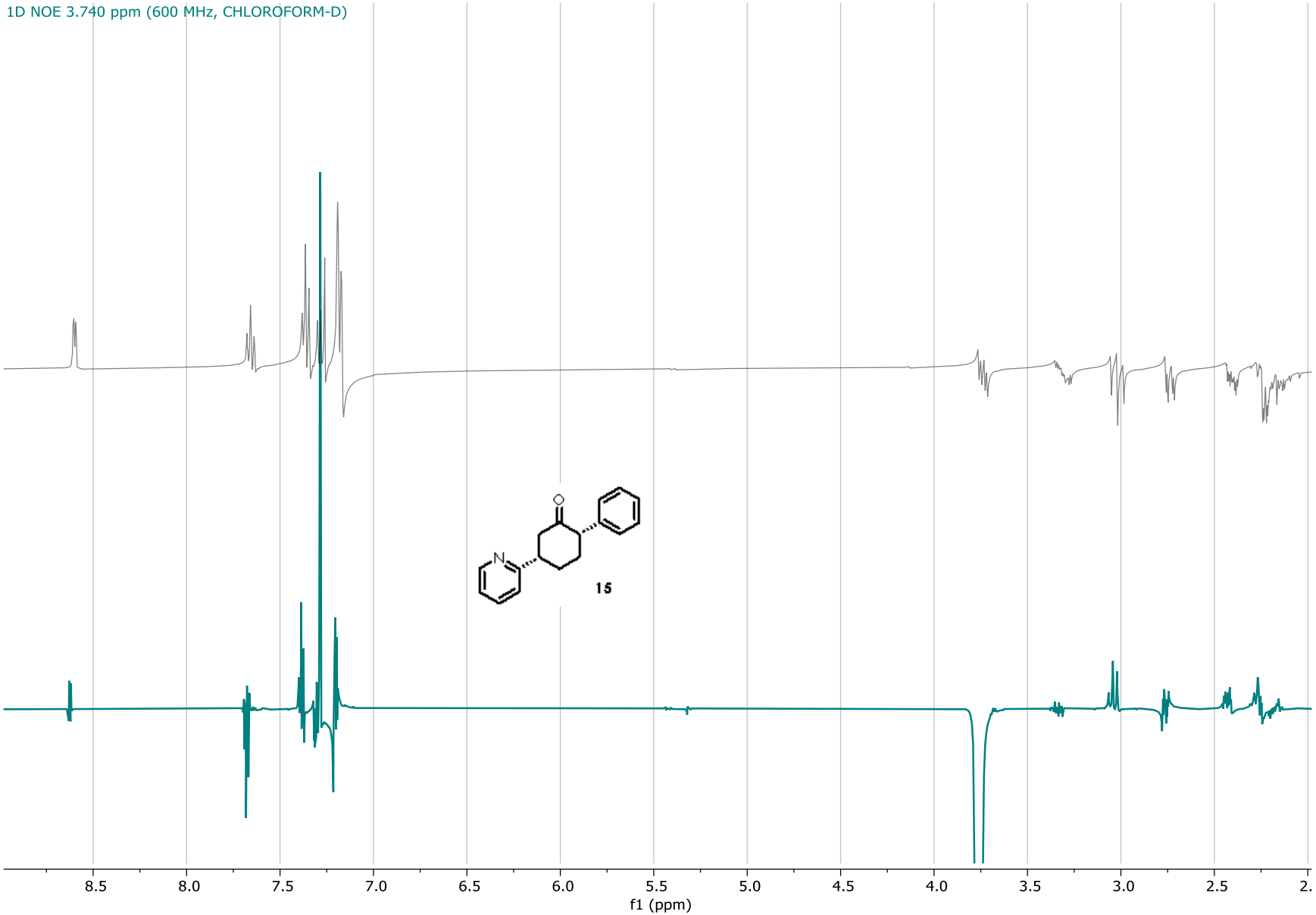

13C (151 MHz, CHLOROFORM-D)
209.4
162.6
149.7
138.6
136.9
128.9
128.5
127.2
122.1
121.8
77.2 CDCl3
57.1
47.7
47.7
34.3
32.5
15
f1 (ppm)

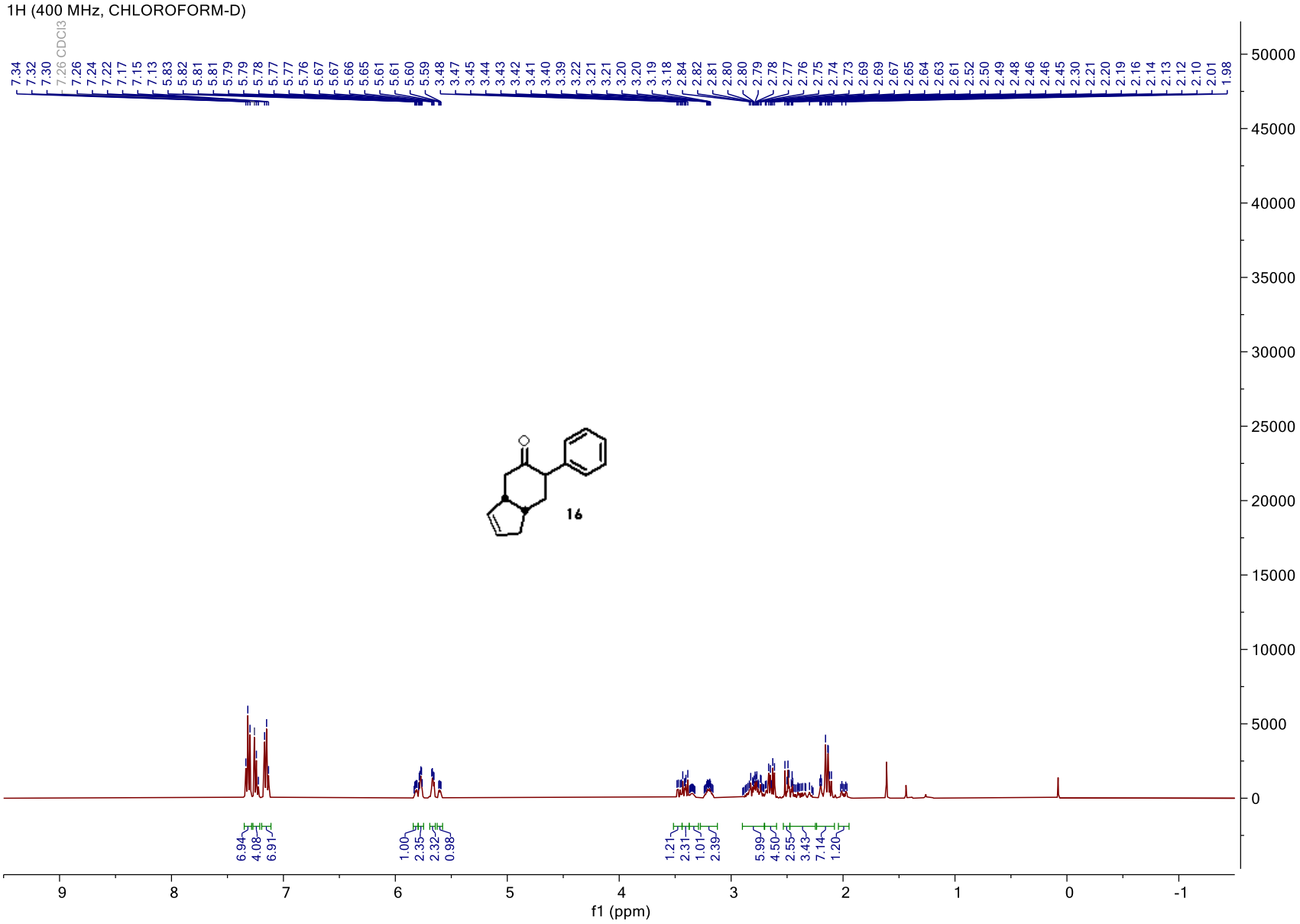

COSY (600 MHz, CHLOROFORM-D)
15
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0


HSQC (600 MHz, CHLOROFORM-D)
15
f2 (ppm)
f1 (ppm)

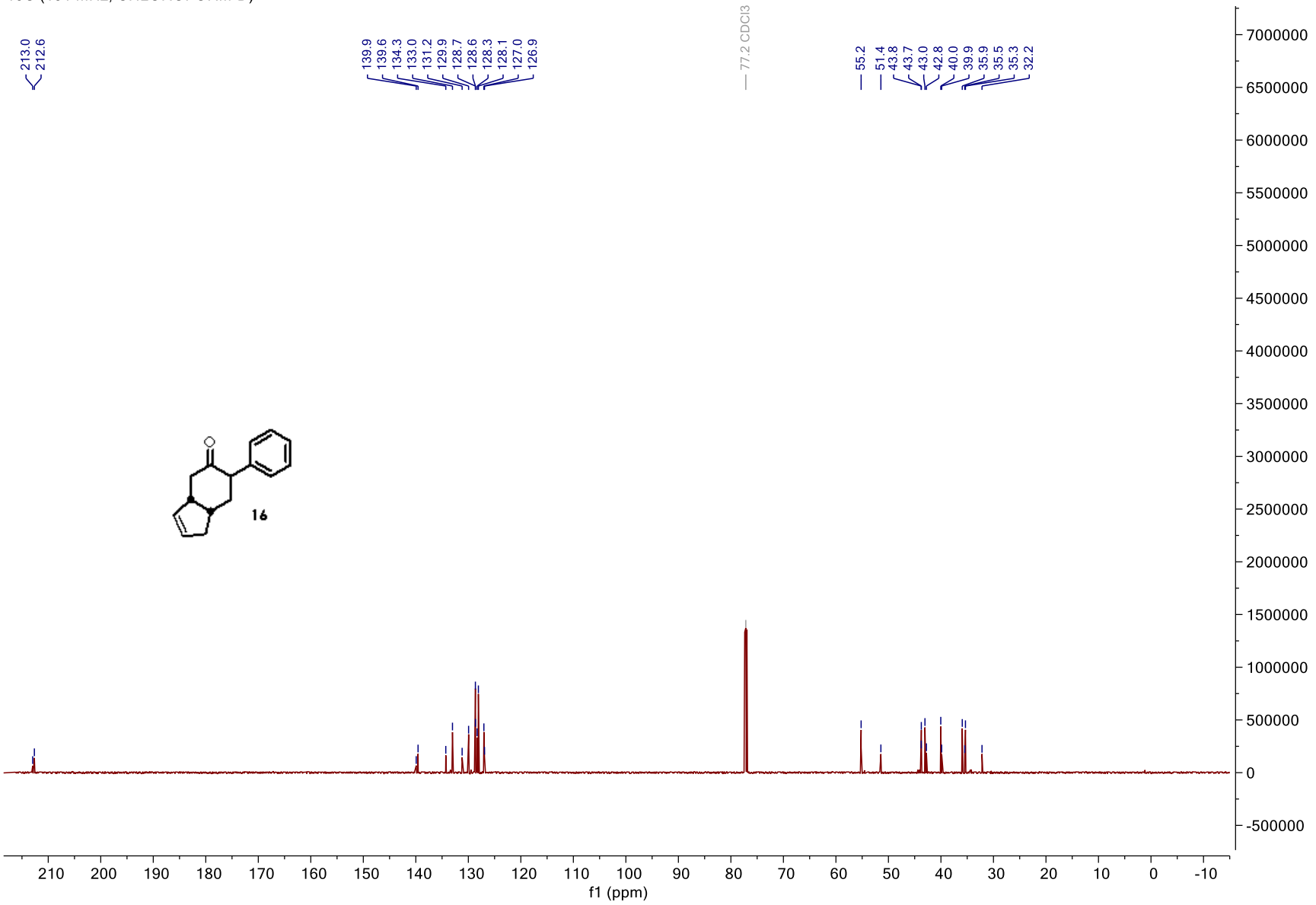

HMBC (600 MHz, CHLOROFORM-D)
15
f2 (ppm)
f1 (ppm)

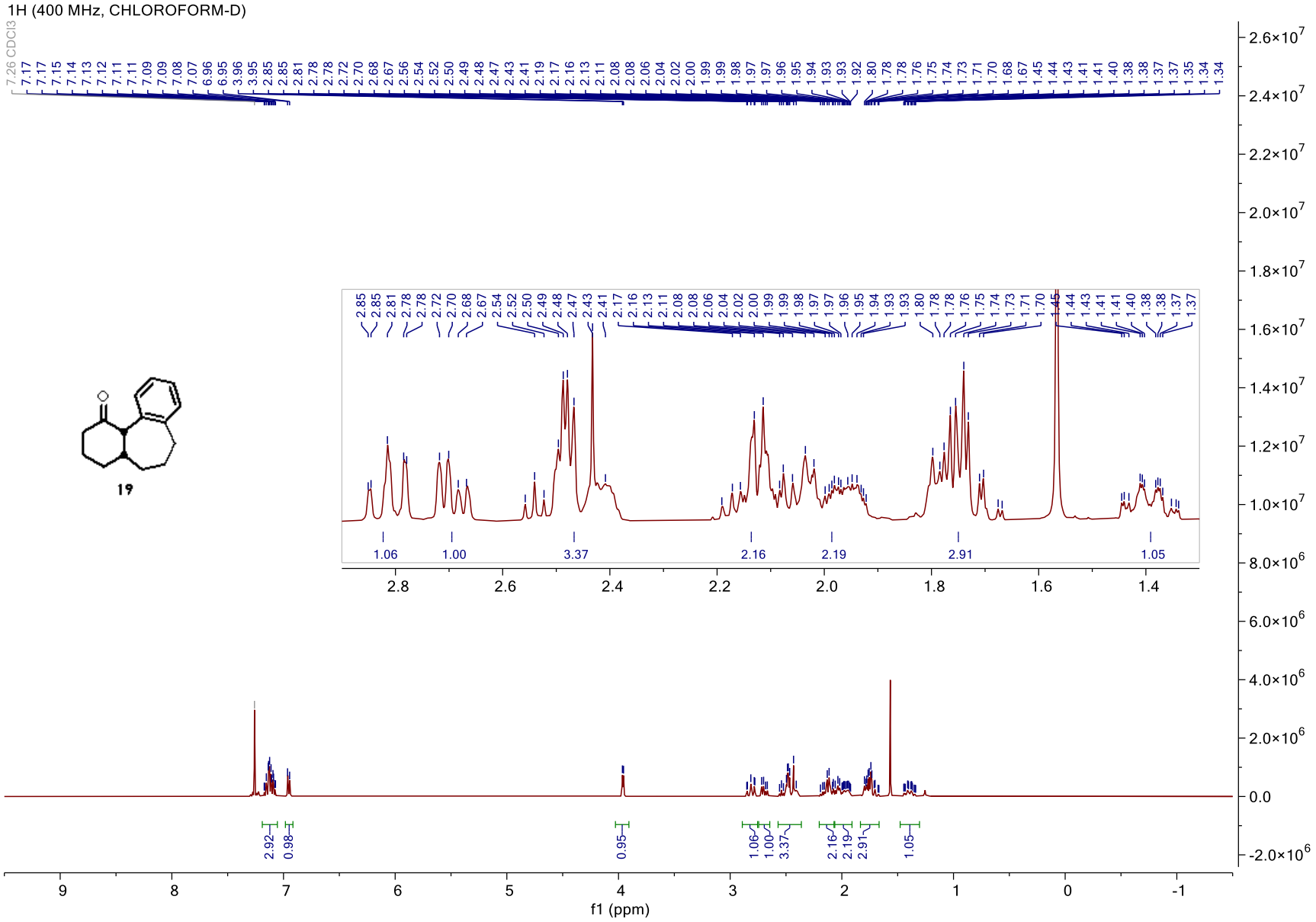

NOESY (600 MHz, CHLOROFORM-D)
15
f2 (ppm)
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0


1D NOE 3.740 ppm (600 MHz, CHLOROFORM-D)
N
15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.
f1 (ppm)

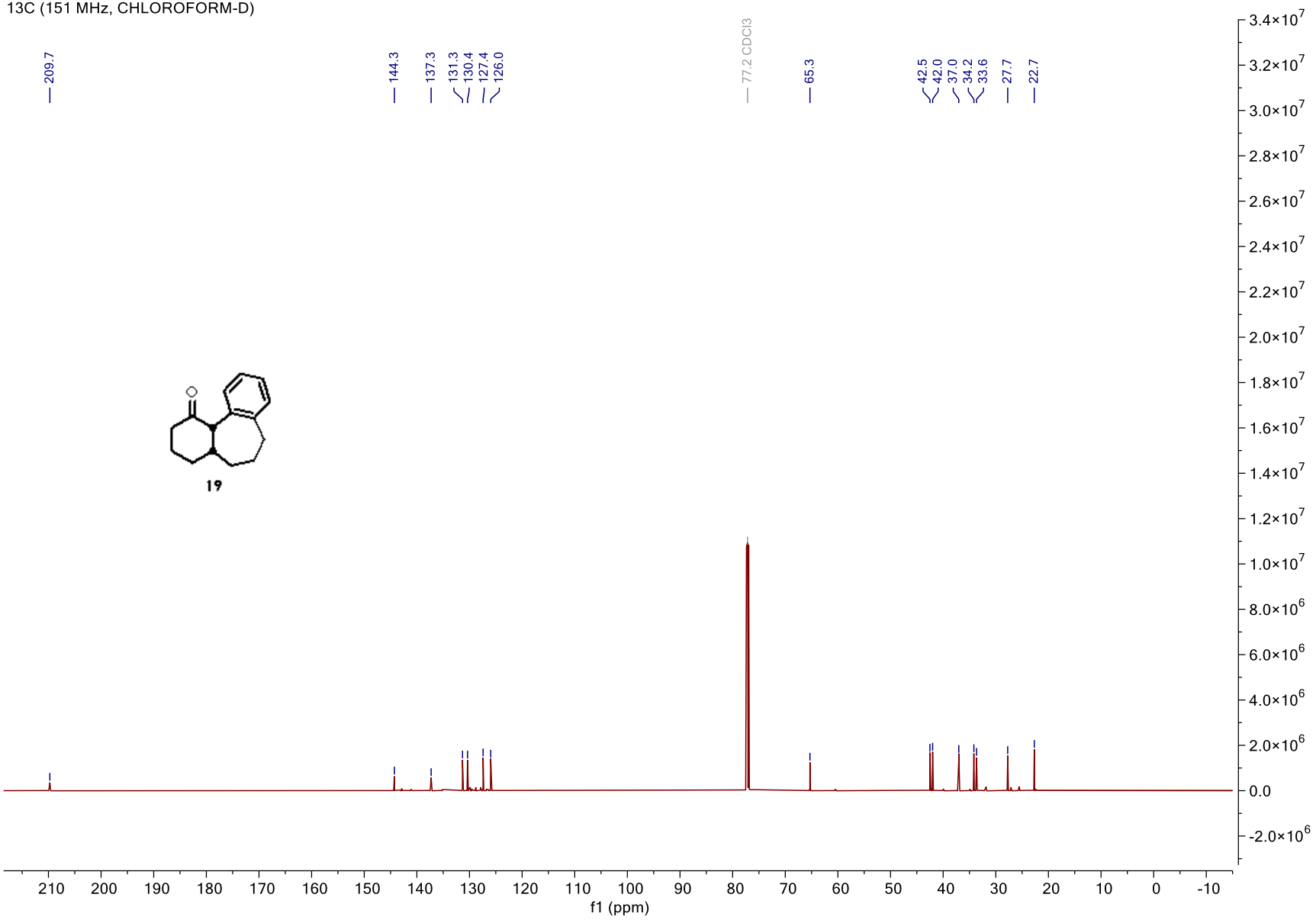

1H (400 MHz, CHLOROFORM-D)
7.34 7.32 7.30 7.26 CDCl3 7.26 7.24 7.22 7.17 7.15 7.13 5.83 5.82 5.81 5.81 5.79 5.79 5.78 5.77 5.77 5.76 5.67 5.67 5.66 5.65 5.61 5.61 5.60 5.59 3.48 3.47 3.45 3.44 3.43 3.42 3.41 3.40 3.39 3.22 3.21 3.21 3.20 3.20 3.19 3.18 2.84 2.82 2.81 2.80 2.80 2.79 2.78 2.77 2.76 2.75 2.74 2.73 2.69 2.69 2.67 2.65 2.64 2.63 2.61 2.52 2.50 2.49 2.48 2.46 2.46 2.45 2.30 2.21 2.20 2.19 2.16 2.14 2.13 2.12 2.10 2.01 1.98
16
6.94 4.08 6.91 1.00 2.35 2.32 0.98 1.21 2.31 1.01 2.39 5.99 4.50 2.55 3.43 7.14 1.20
f1 (ppm)

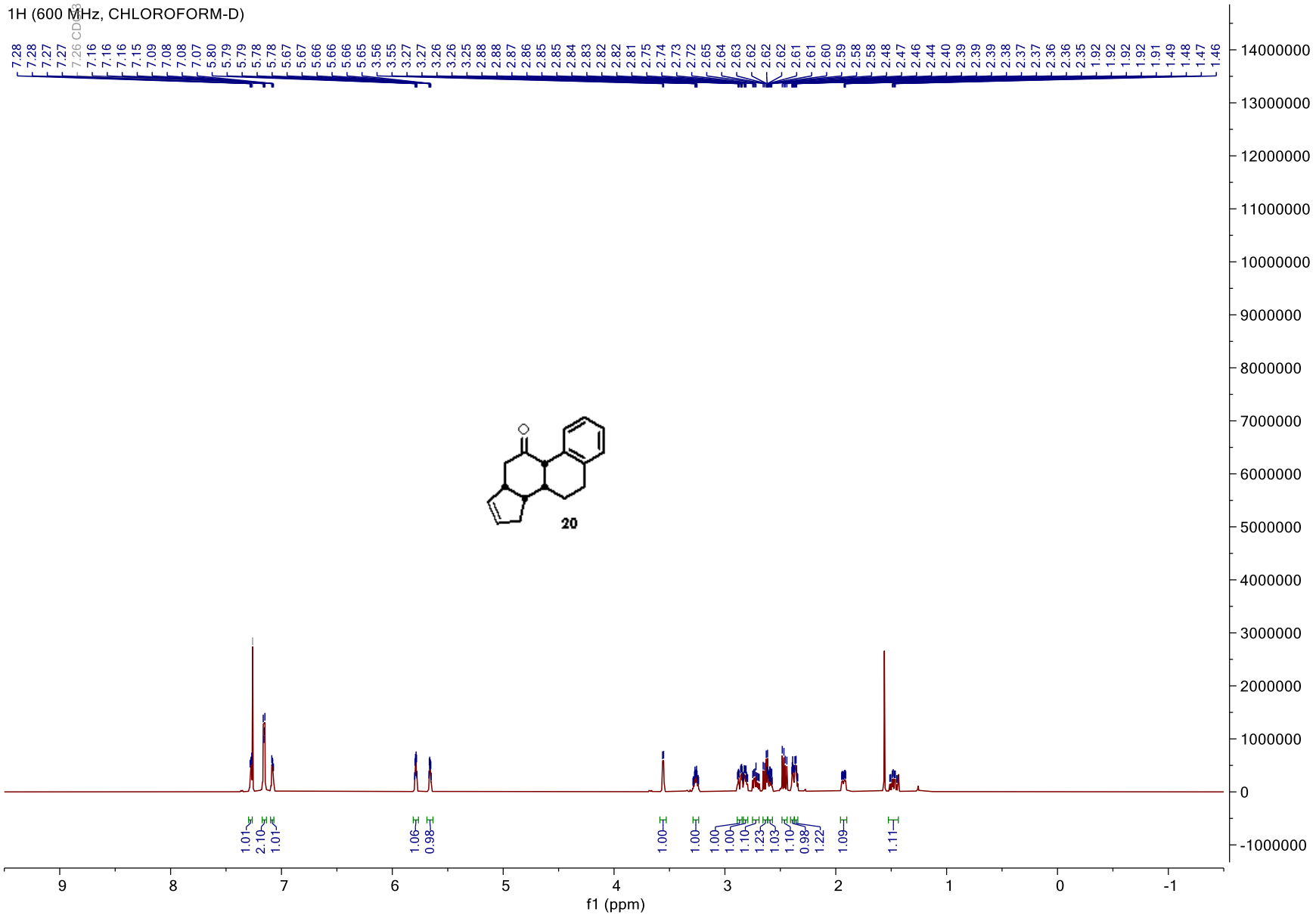
13C (151 MHz, CHLOROFORM-D)

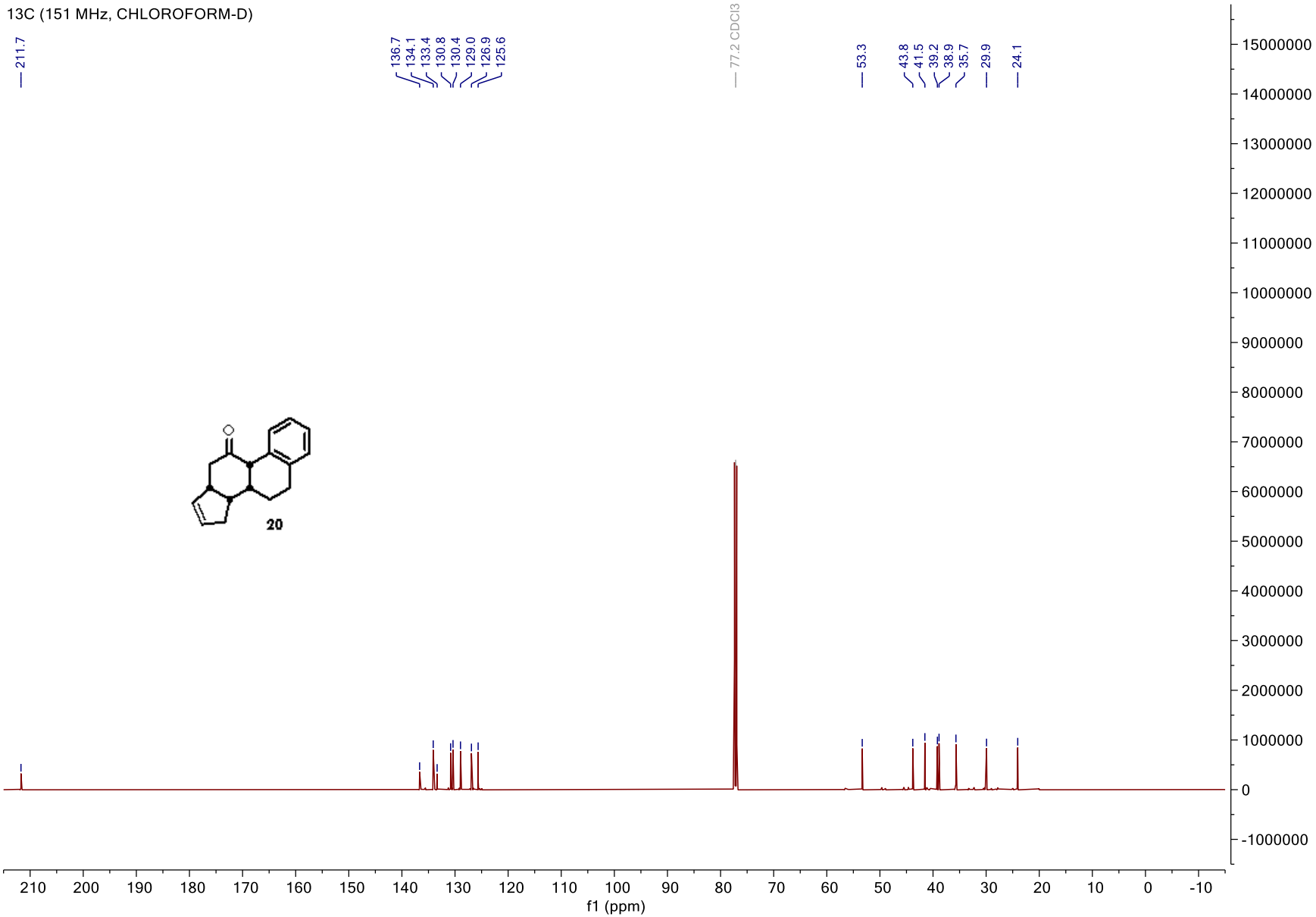


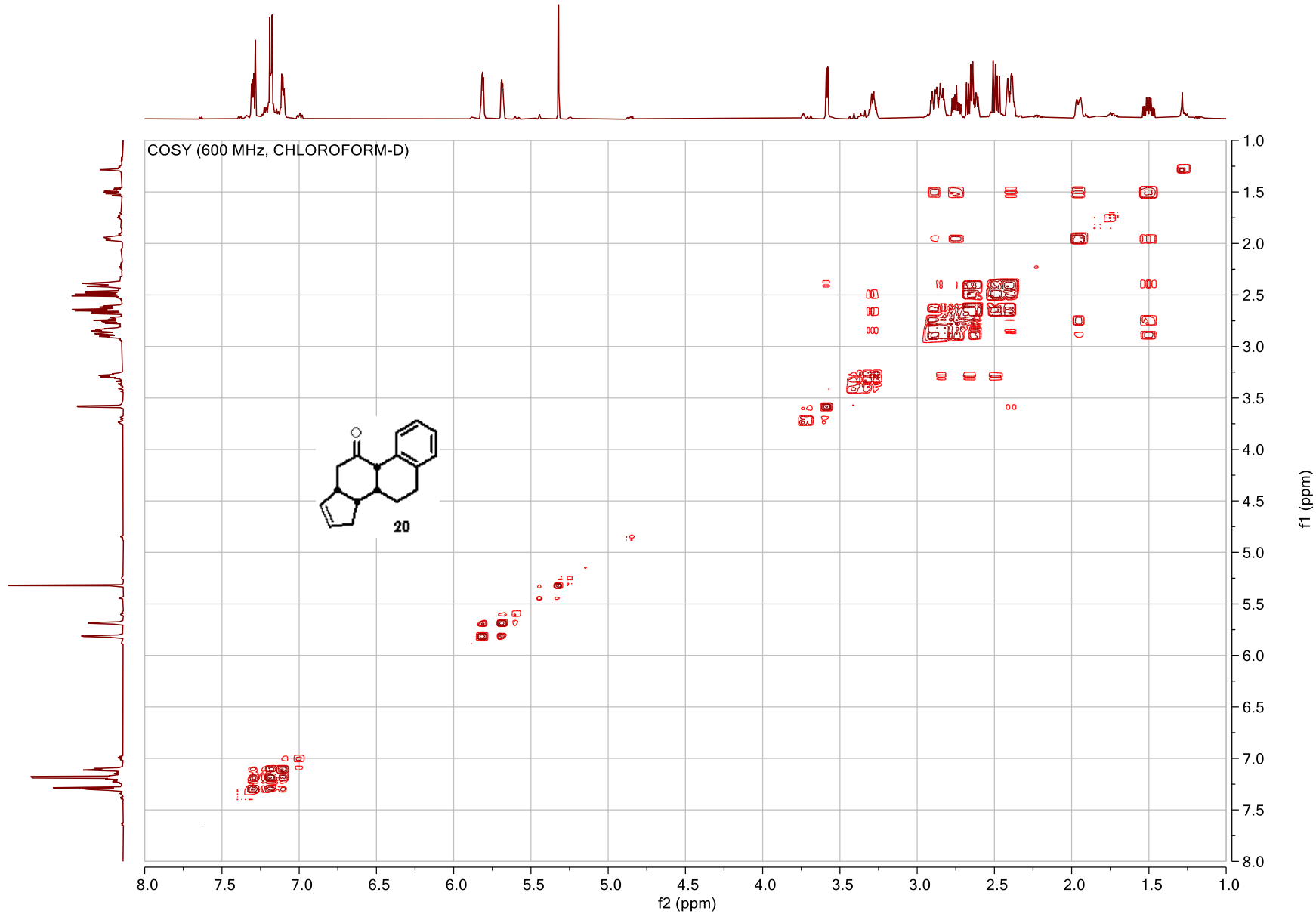

1H (400 MHz, CHLOROFORM-D)
7.26 CDCl3
19
1.06
1.00
3.37
2.16
2.19
2.91
1.05
2.92
0.98
0.95
1.06
1.00
3.37
2.16
2.19
2.91
1.05
f1 (ppm)

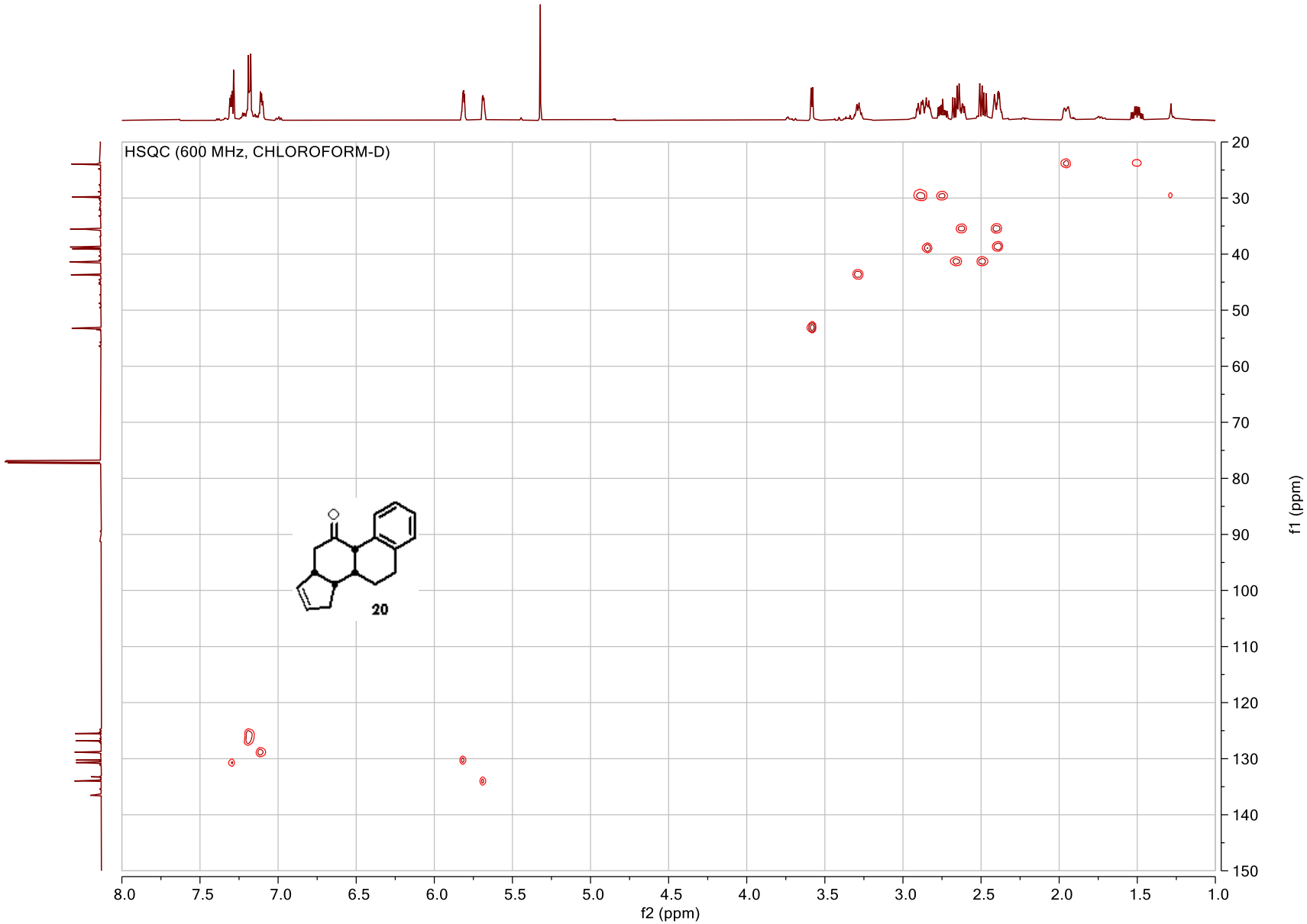
13C (151 MHz, CHLOROFORM-D)

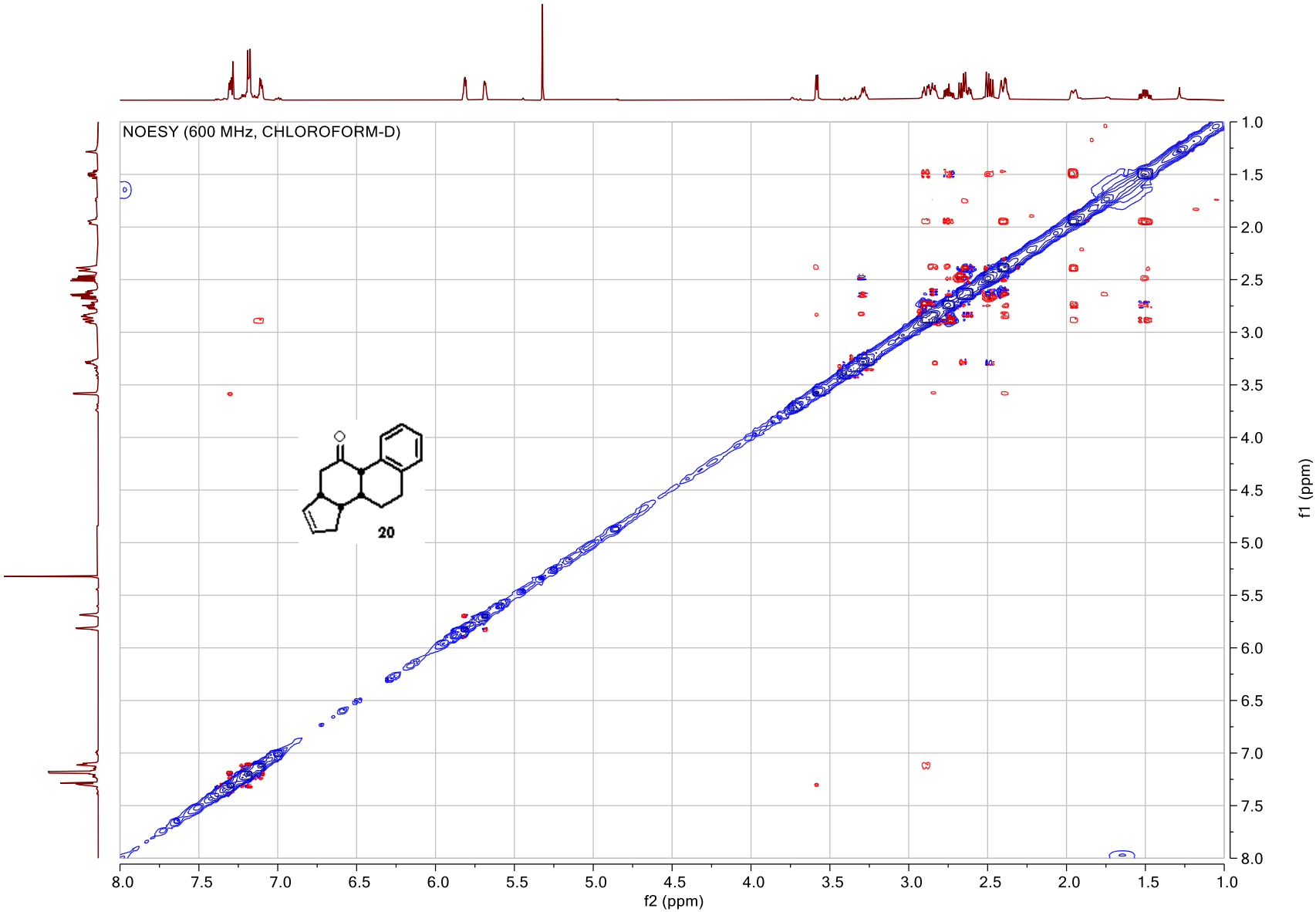


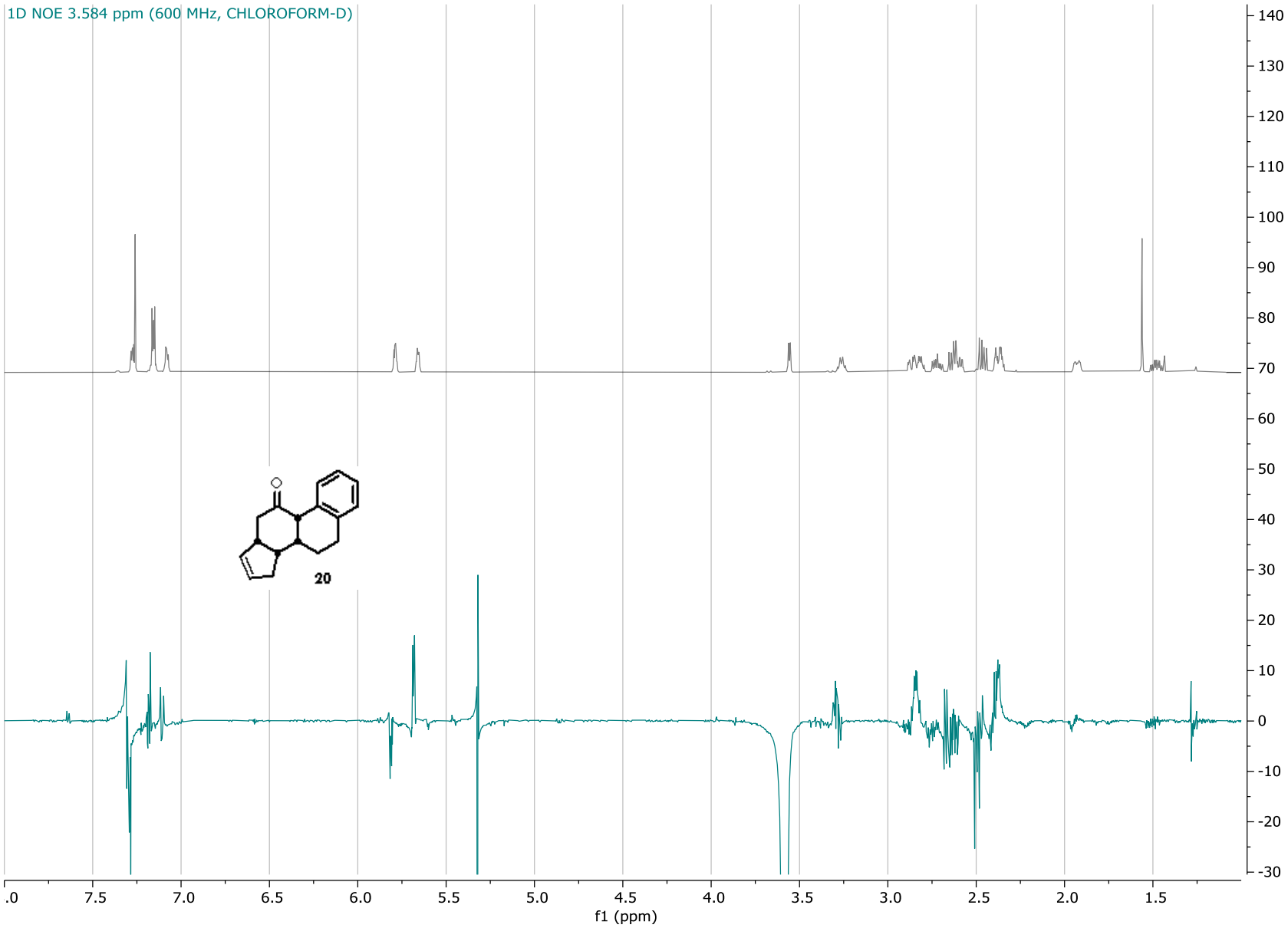

1H (600 MHz, CHLOROFORM-D)
7.26 CDCl3
20
f1 (ppm)

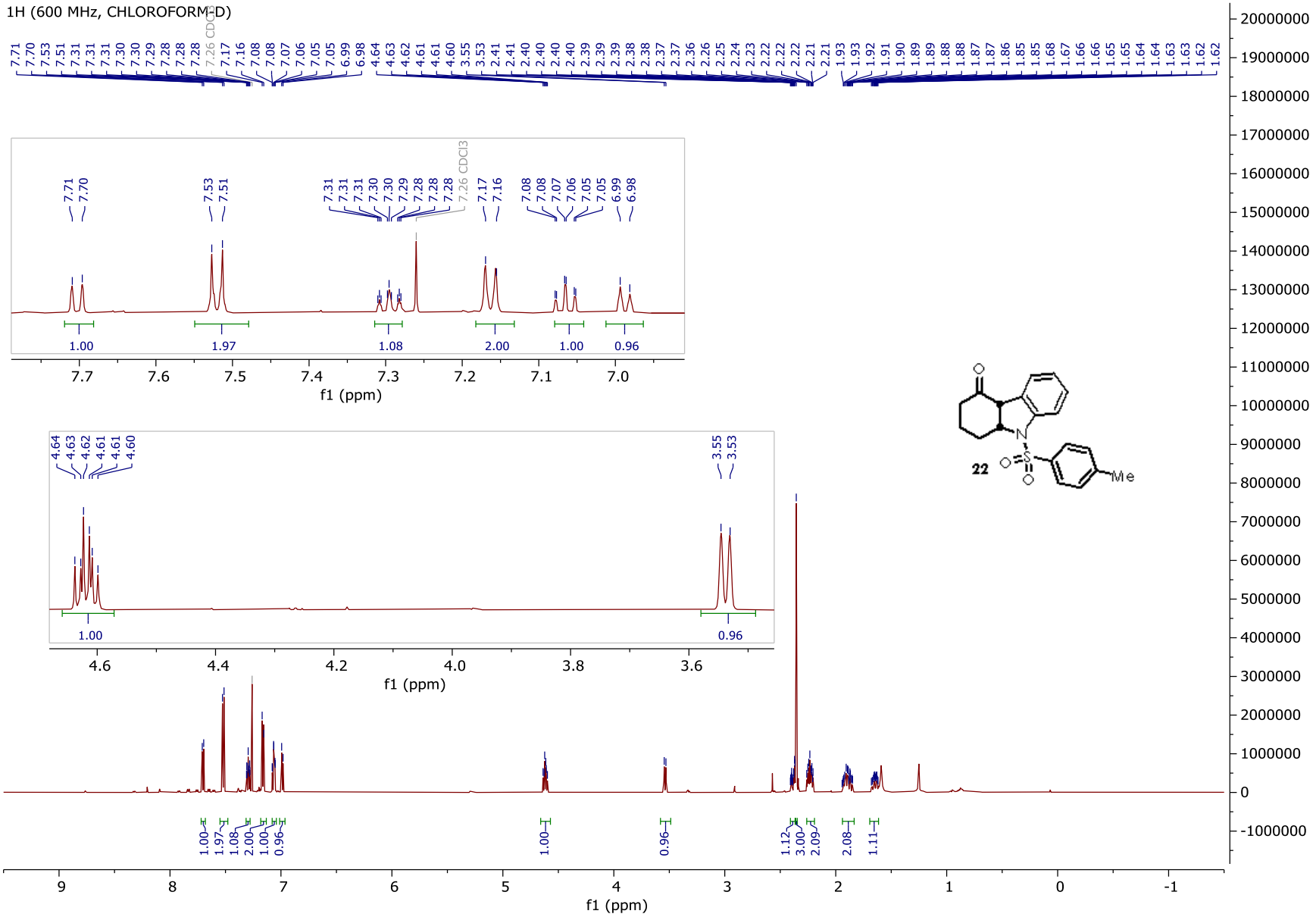

13C (151 MHz, CHLOROFORM-D)
211.7
136.7
134.1
133.4
130.8
130.4
129.0
126.9
125.6
77.2 CDCl3
53.3
43.8
41.5
39.2
38.9
35.7
29.9
24.1
20
f1 (ppm)

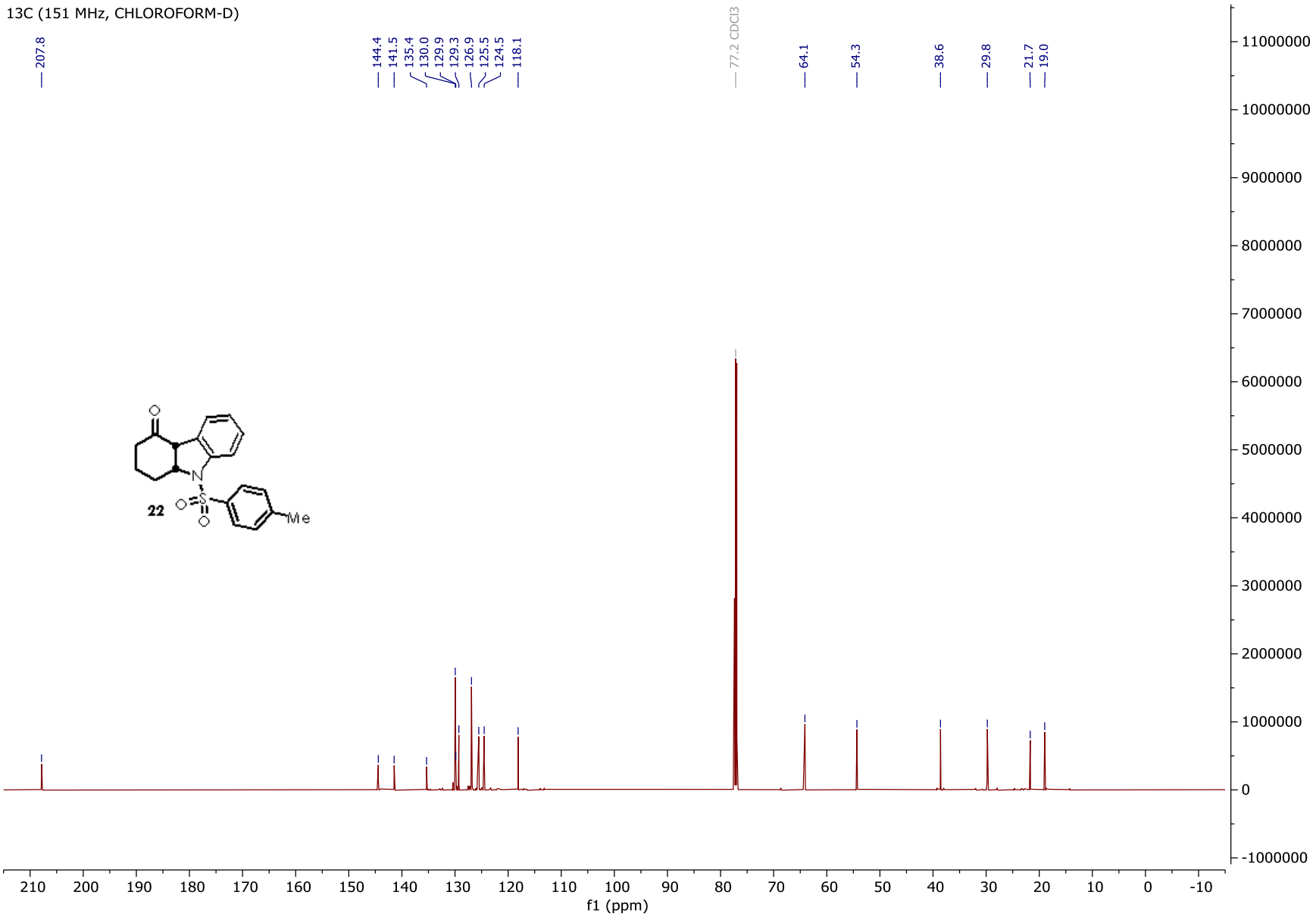

COSY (600 MHz, CHLOROFORM-D)
20
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

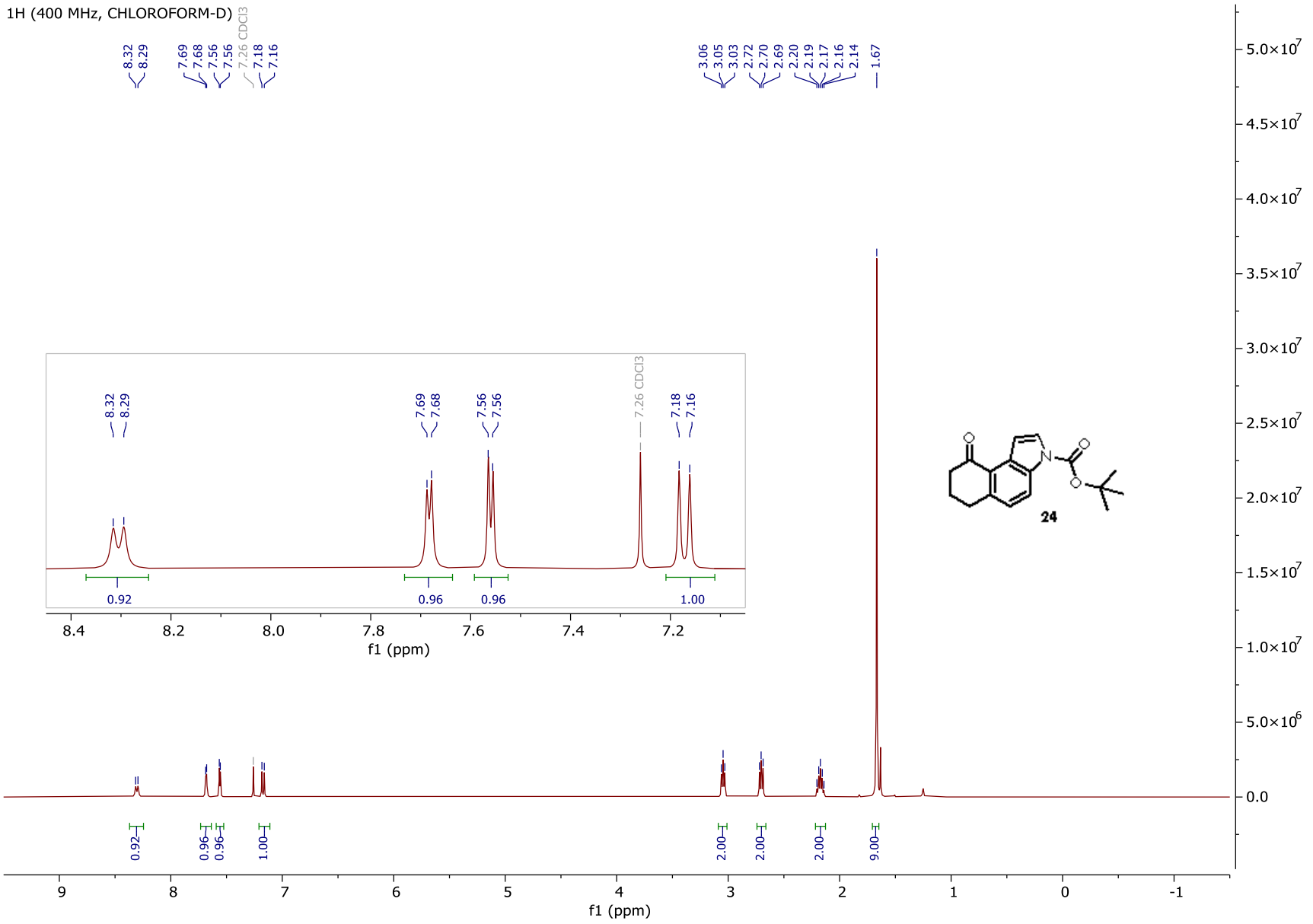

HSQC (600 MHz, CHLOROFORM-D)
20
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
20
30
40
50
60
70
80
90
100
110
120
130
140
150

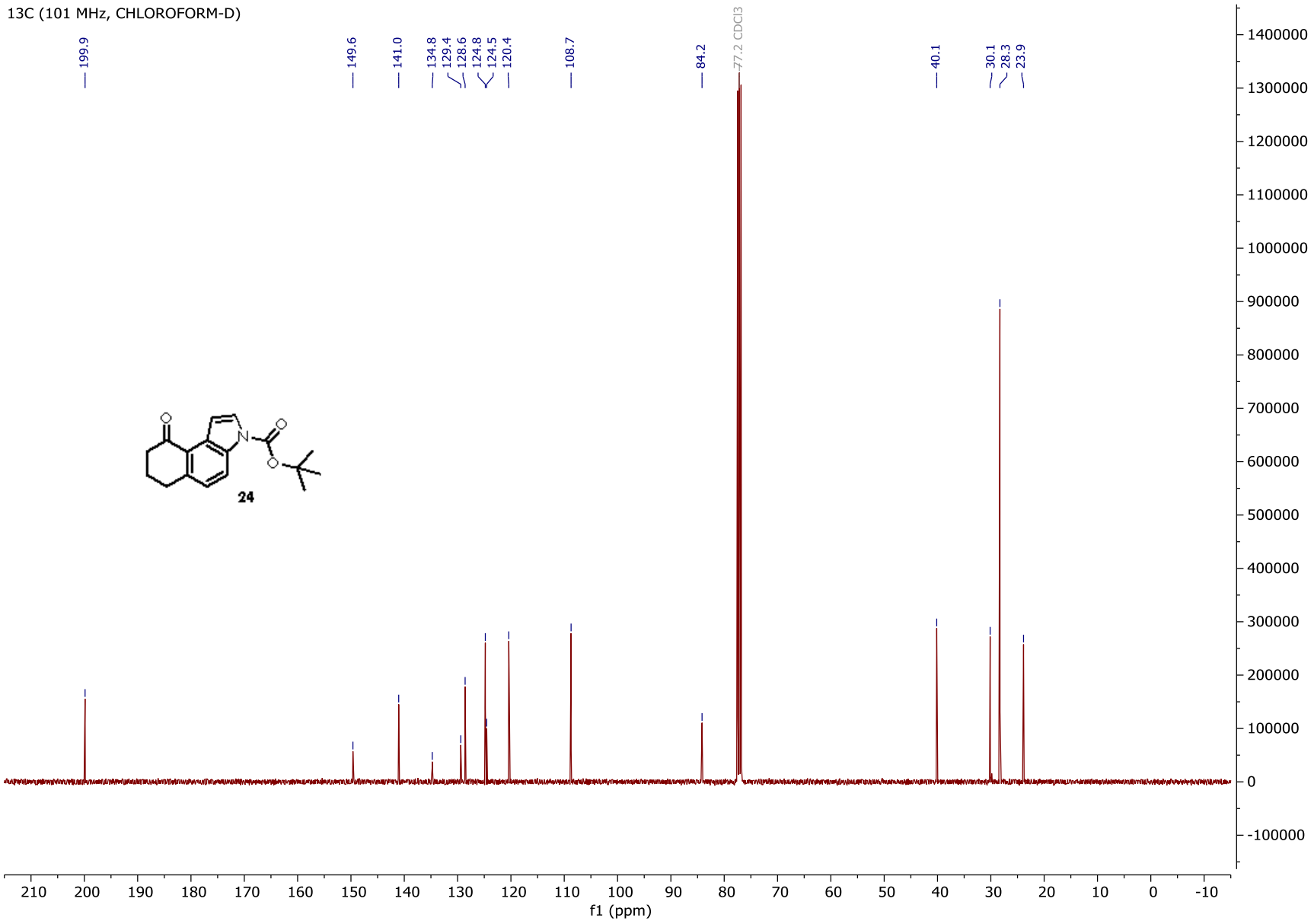

NOESY (600 MHz, CHLOROFORM-D)
20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

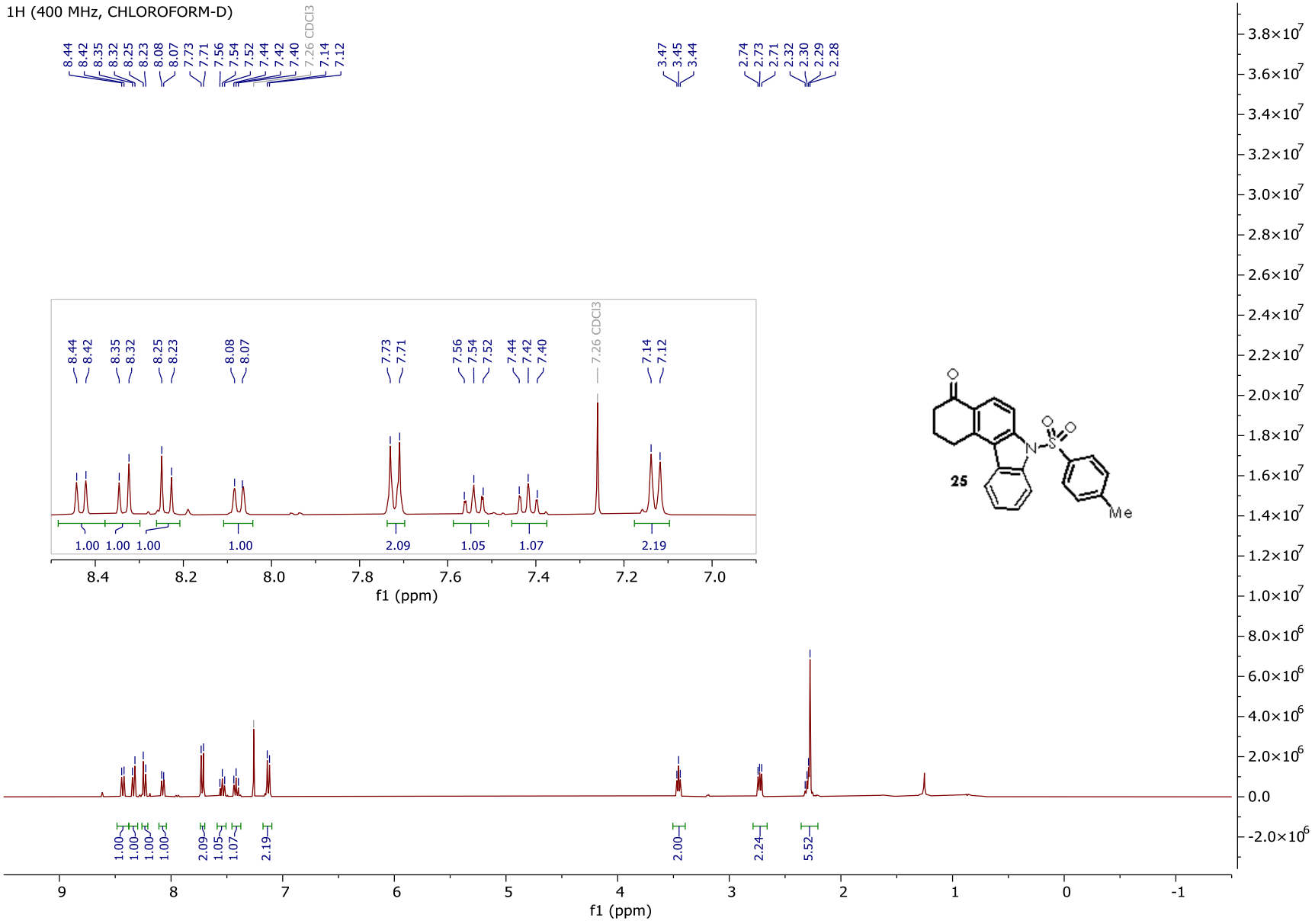

1D NOE 3.584 ppm (600 MHz, CHLOROFORM-D)
20
f1 (ppm)

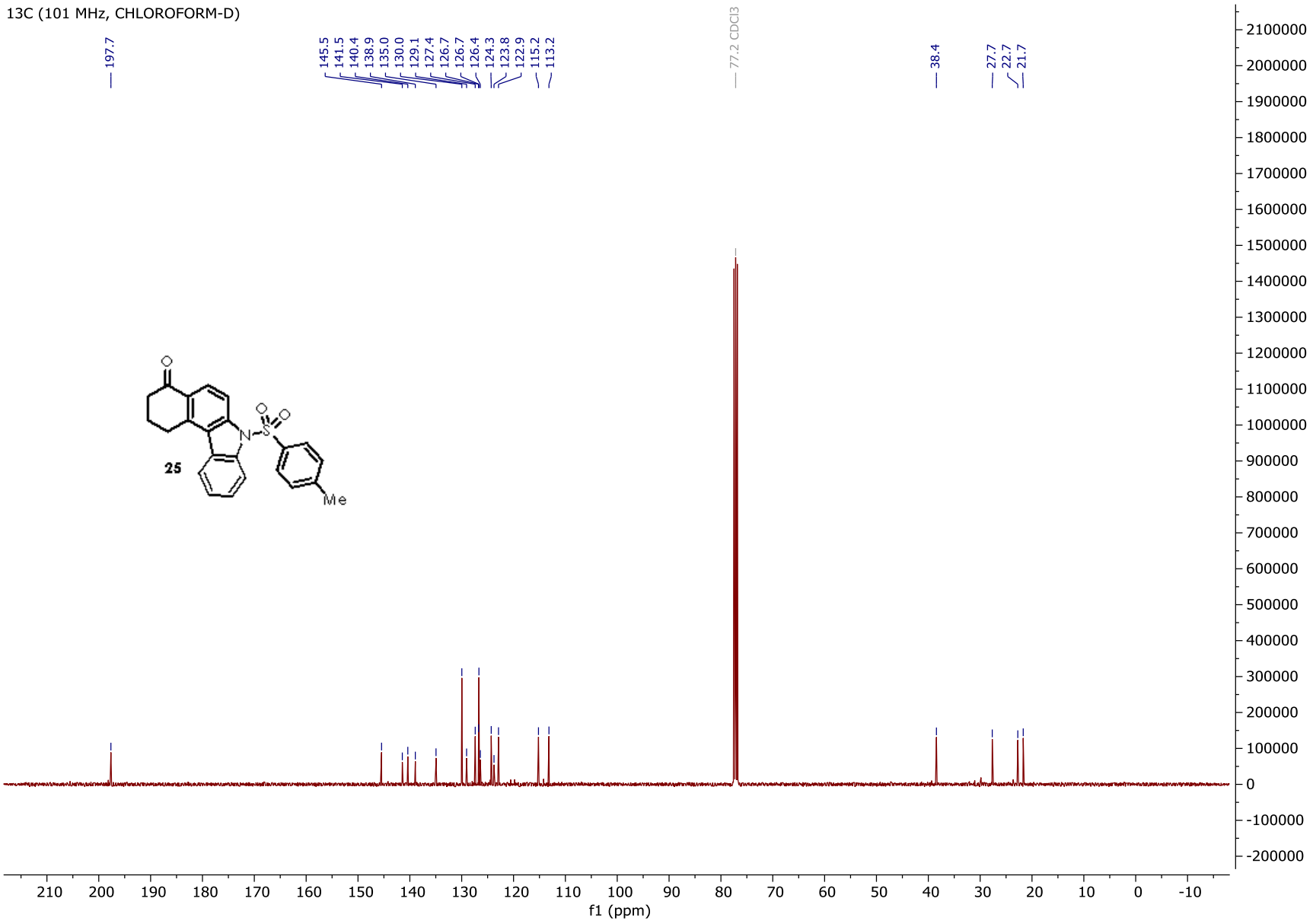

1H (600 MHz, CHLOROFORM-D)
7.26 CDCl3
1.00
1.97
1.08
2.00
1.00
0.96
f1 (ppm)
22
Me
1.00
0.96
1.00
0.96
1.12
3.00
2.09
2.08
1.11
f1 (ppm)

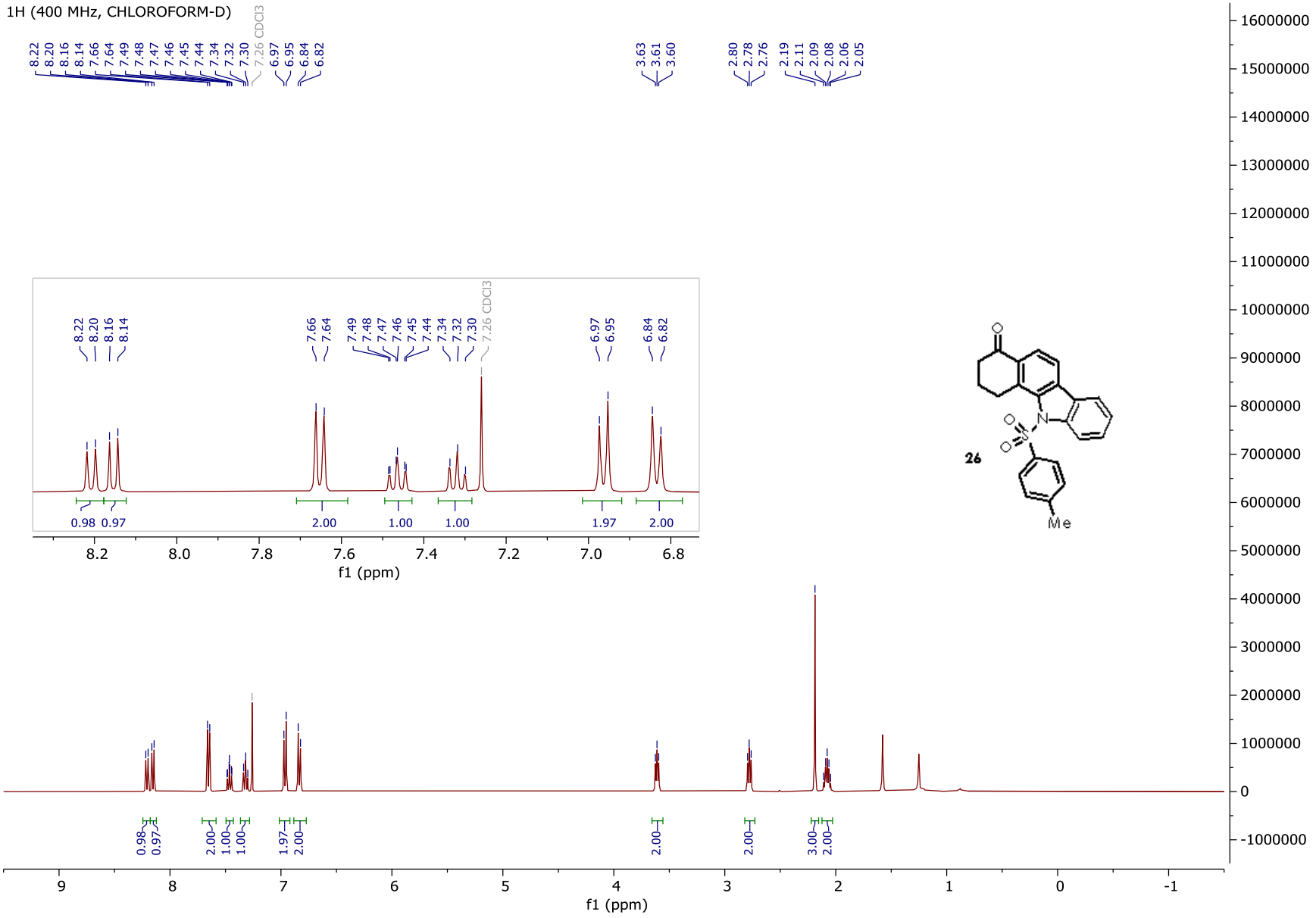

13C (151 MHz, CHLOROFORM-D)
207.8
144.4
141.5
135.4
130.0
129.9
129.3
126.9
125.5
124.5
118.1
77.2 CDCl3
64.1
54.3
38.6
29.8
21.7
19.0
22
Me
f1 (ppm)

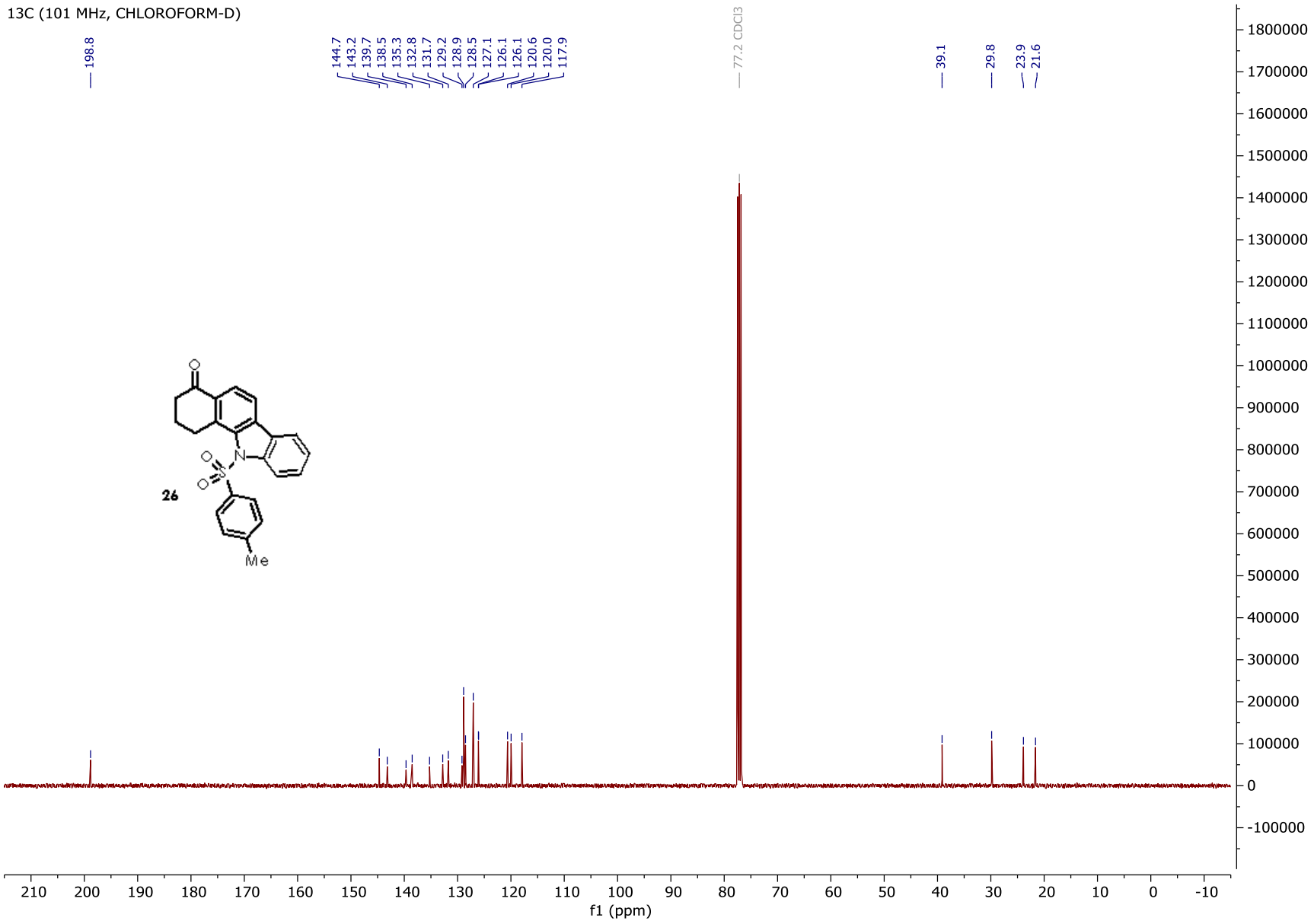

1H (400 MHz, CHLOROFORM-D)
8.32
8.29
7.69
7.68
7.56
7.56
7.26 CDCl3
7.18
7.16
3.06
3.05
3.03
2.72
2.70
2.69
2.20
2.19
2.17
2.16
2.14
1.67
0.92
0.96
0.96
1.00
f1 (ppm)
2.00
2.00
2.00
9.00
24

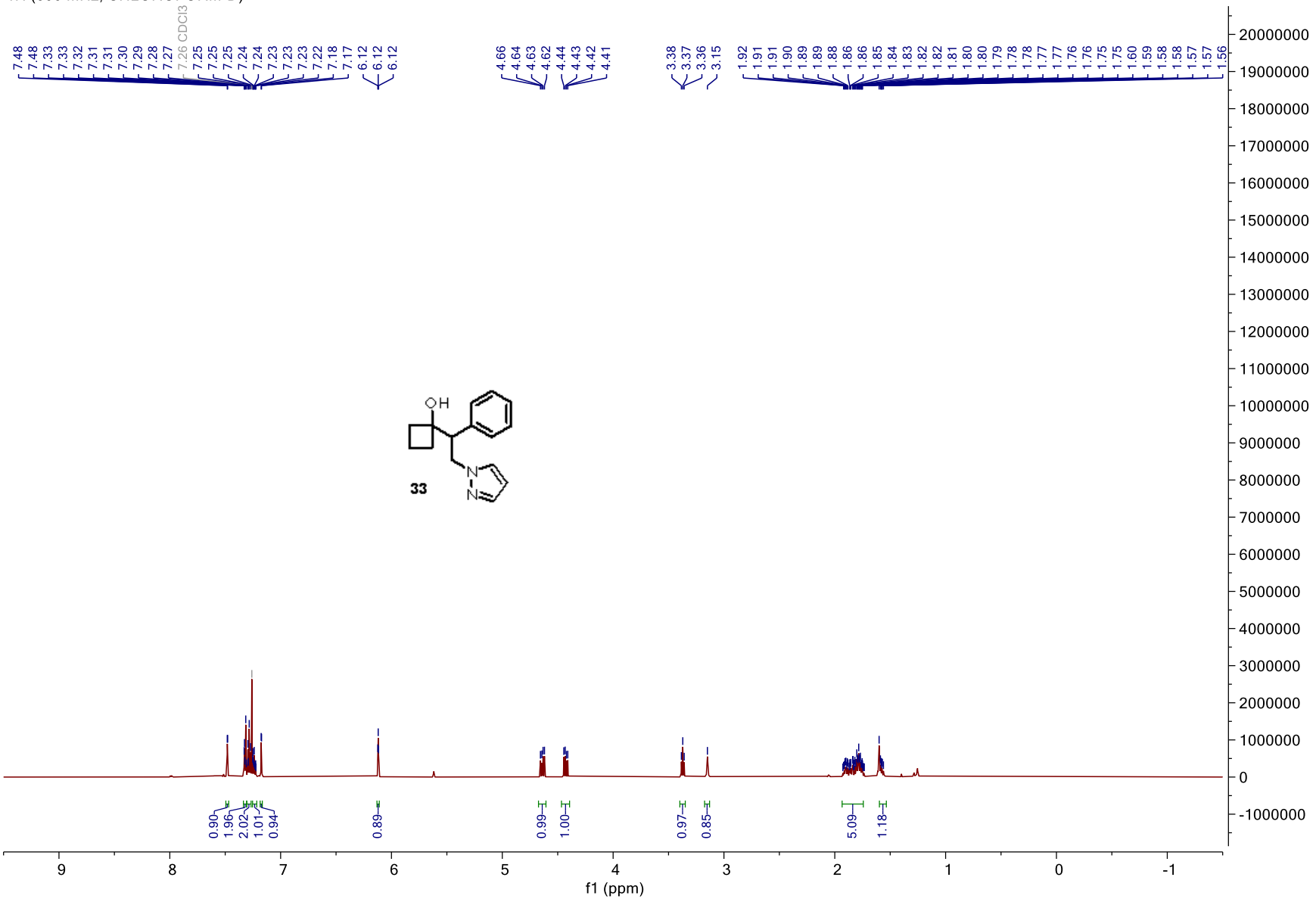

13C (101 MHz, CHLOROFORM-D)
199.9
149.6
141.0
134.8
129.4
128.6
124.8
124.5
120.4
108.7
84.2
77.2 CDCl3
40.1
30.1
28.3
23.9
24
f1 (ppm)


1H (400 MHz, CHLOROFORM-D)
8.44
8.42
8.35
8.32
8.25
8.23
8.08
8.07
7.73
7.71
7.56
7.54
7.52
7.44
7.42
7.40
7.26 CDCl3
7.14
7.12
3.47
3.45
3.44
2.74
2.73
2.71
2.32
2.30
2.29
2.28
1.00 1.00 1.00 1.00 2.09 1.05 1.07 2.19
f1 (ppm)
25
Me
1.00 1.00 1.00 1.00 2.09 1.05 1.07 2.19 2.00 2.24 5.52
f1 (ppm)

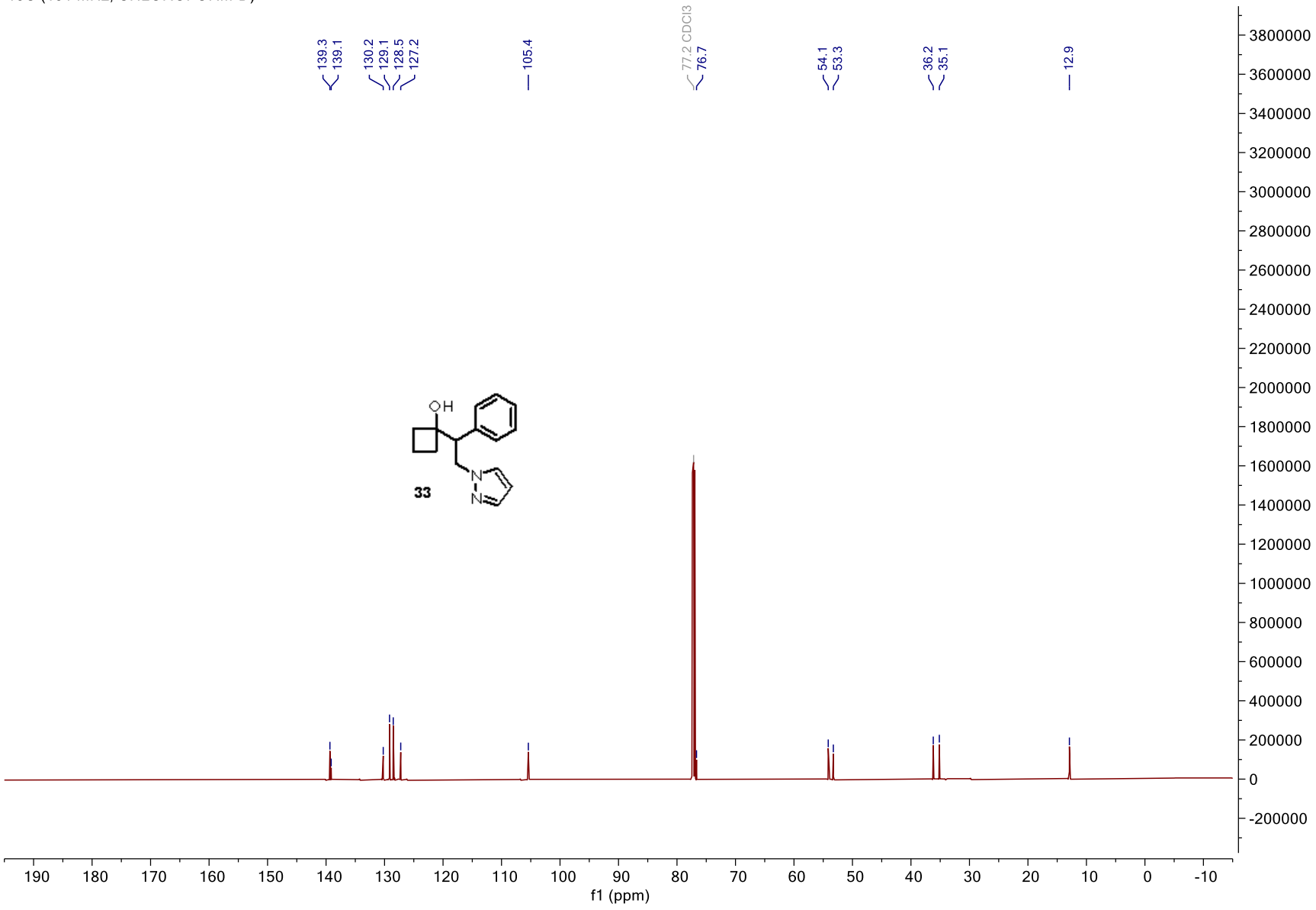

13C (101 MHz, CHLOROFORM-D)
197.7
145.5
141.5
140.4
138.9
135.0
130.0
129.1
127.4
126.7
126.7
126.4
124.3
123.8
122.9
115.2
113.2
77.2 CDCl3
38.4
27.7
22.7
21.7
25
Me
f1 (ppm)

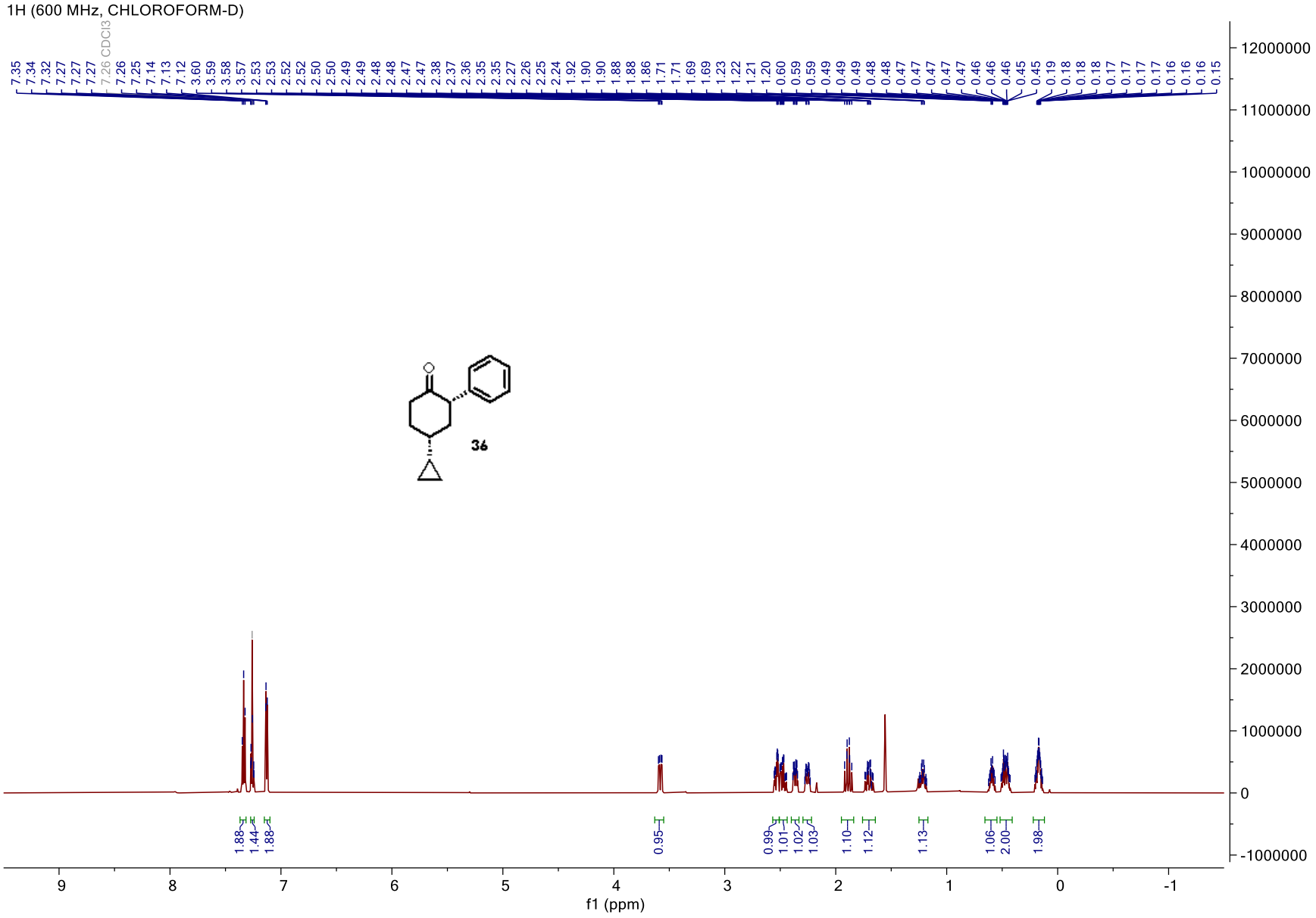

1H (400 MHz, CHLOROFORM-D)
8.22
8.20
8.16
8.14
7.66
7.64
7.49
7.48
7.47
7.46
7.45
7.44
7.34
7.32
7.30
7.26 CDCl3
6.97
6.95
6.84
6.82
3.63
3.61
3.60
2.80
2.78
2.76
2.19
2.11
2.09
2.08
2.06
2.05
0.98 0.97
2.00
1.00
1.00
1.97
2.00
f1 (ppm)
26
Me

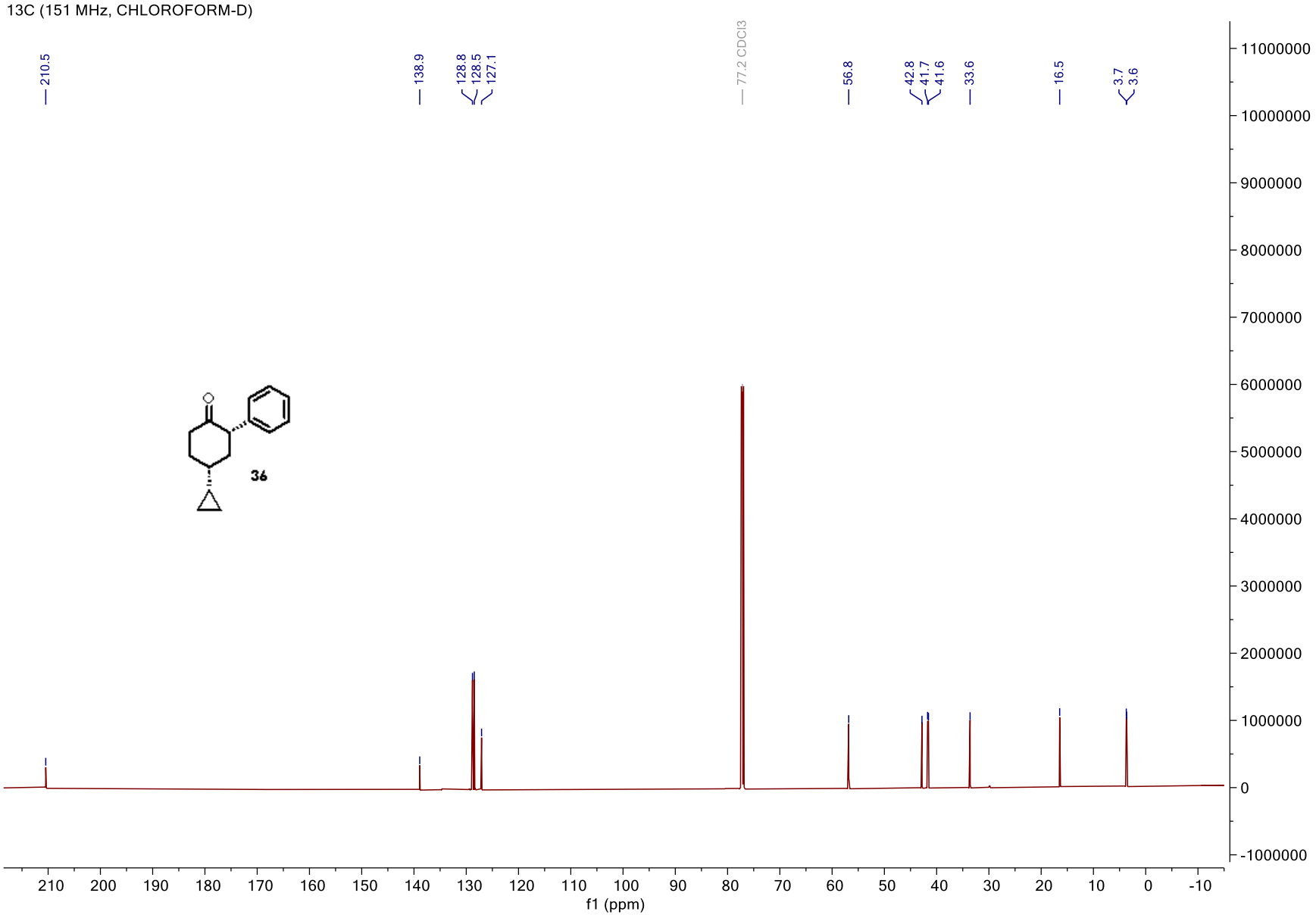

13C (101 MHz, CHLOROFORM-D)
198.8
144.7
143.2
139.7
138.5
135.3
132.8
131.7
129.2
128.9
128.5
127.1
126.1
126.1
120.6
120.0
117.9
77.2 CDCl3
39.1
29.8
23.9
21.6
26
Me
f1 (ppm)

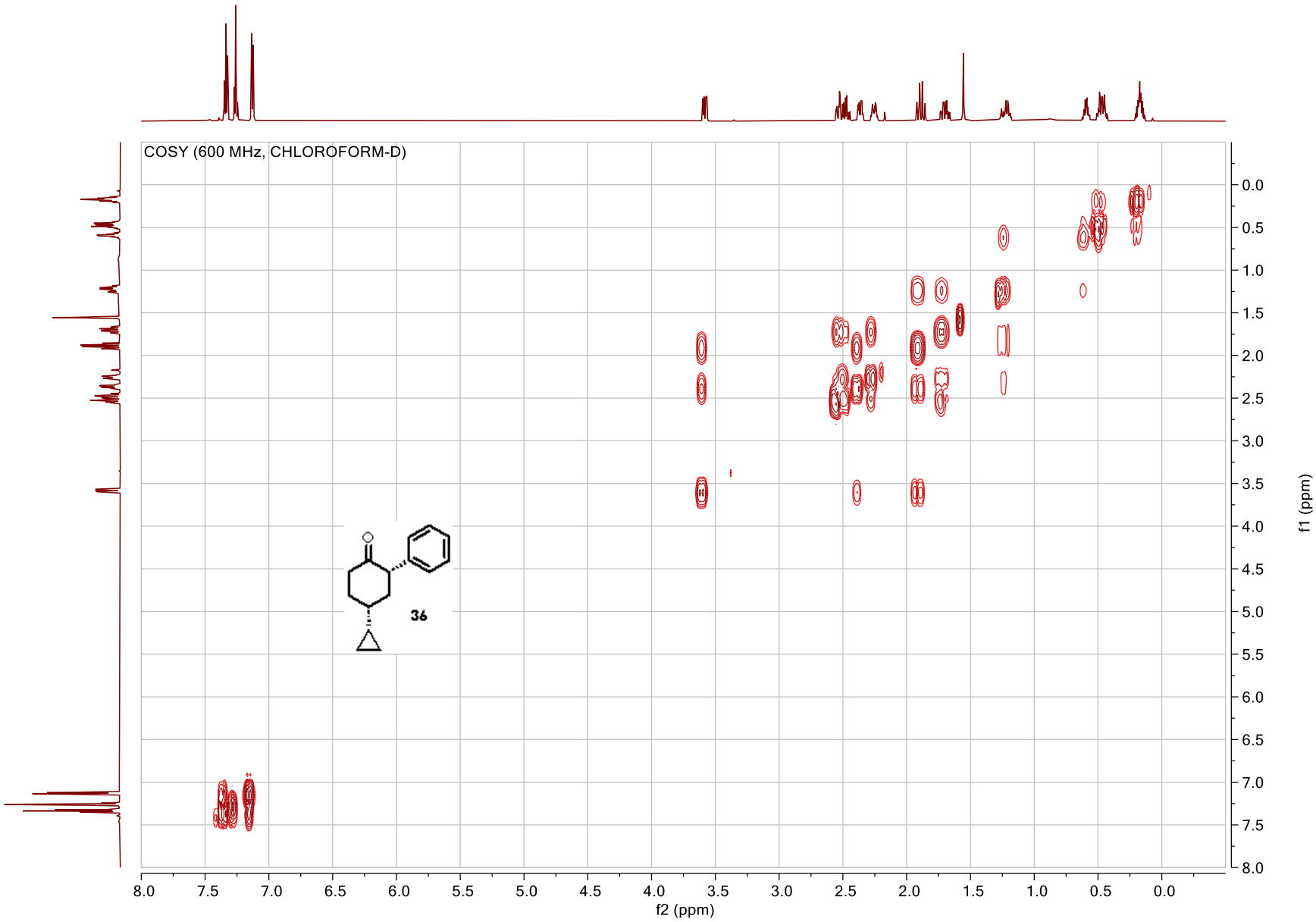

1H (600 MHz, CHLOROFORM-D)
7.48 7.48 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.26 CDCl3 7.25 7.25 7.25 7.24 7.24 7.23 7.23 7.22 7.18 7.17 6.12 6.12 6.12
4.66 4.64 4.63 4.62 4.44 4.43 4.42 4.41
3.38 3.37 3.36 3.15
1.92 1.91 1.91 1.90 1.89 1.89 1.88 1.86 1.86 1.85 1.84 1.83 1.82 1.82 1.81 1.80 1.80 1.79 1.78 1.78 1.77 1.77 1.76 1.75 1.75 1.60 1.59 1.58 1.58 1.57 1.57 1.56
OH
N
N
33
0.90 1.96 2.02 1.01 0.94 0.89 0.99 1.00 0.97 0.85 5.09 1.18
f1 (ppm)

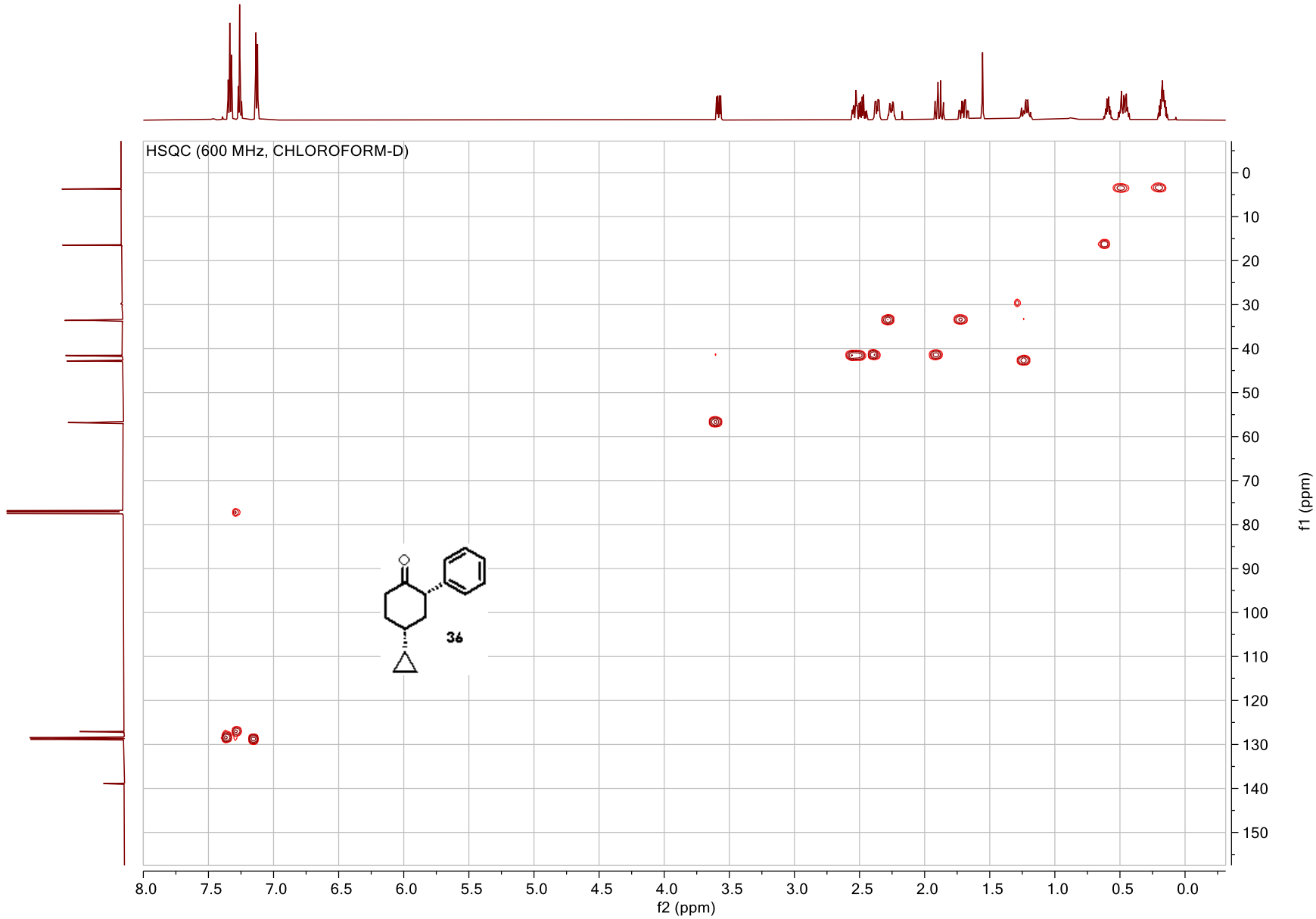
13C (151 MHz, CHLOROFORM-D)

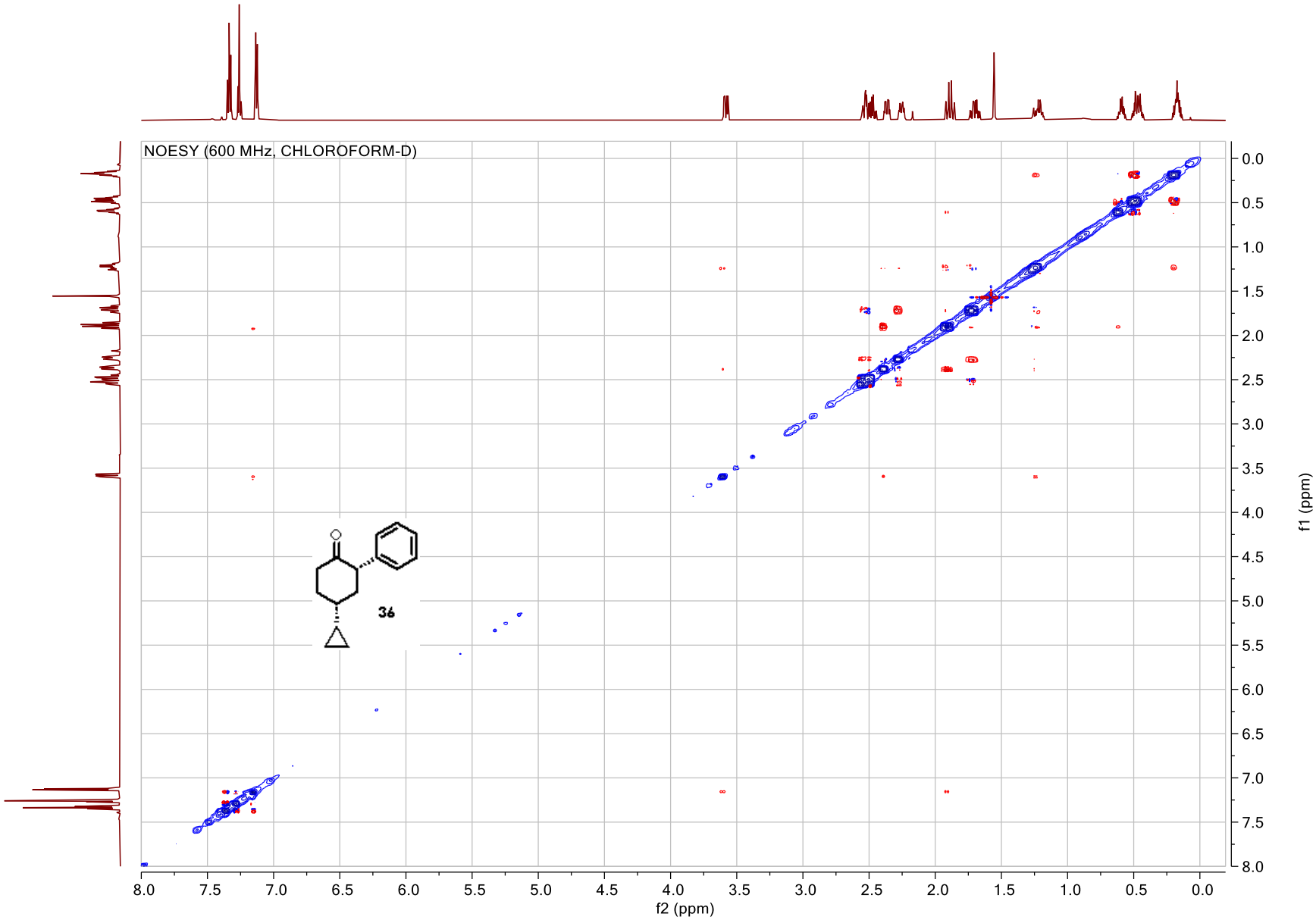



1H (600 MHz, CHLOROFORM-D)
7.35 7.34 7.32 7.27 7.27 7.27 7.26 CDCl3 7.26 7.25 7.14 7.13 7.12 3.60 3.59 3.58 3.57 2.53 2.53 2.52 2.52 2.50 2.50 2.49 2.49 2.48 2.48 2.47 2.47 2.38 2.37 2.36 2.35 2.35 2.27 2.26 2.25 2.24 1.92 1.90 1.90 1.88 1.88 1.86 1.71 1.71 1.69 1.69 1.23 1.22 1.21 1.20 0.60 0.59 0.59 0.49 0.49 0.49 0.48 0.48 0.47 0.47 0.47 0.47 0.46 0.46 0.46 0.45 0.45 0.19 0.18 0.18 0.17 0.17 0.17 0.17 0.16 0.16 0.16 0.15
36
1.88 1.44 1.88 0.95 0.99 1.01 1.02 1.03 1.10 1.12 1.13 1.06 2.00 1.98
f1 (ppm)


13C (151 MHz, CHLOROFORM-D)
210.5
138.9
128.8
128.5
127.1
77.2 CDCl3
56.8
42.8
41.7
41.6
33.6
16.5
3.7
3.6
36
f1 (ppm)


COSY (600 MHz, CHLOROFORM-D)
36
f2 (ppm)
f1 (ppm)


HSQC (600 MHz, CHLOROFORM-D)
36
f2 (ppm)
f1 (ppm)


NOESY (600 MHz, CHLOROFORM-D)
36
f2 (ppm)
f1 (ppm)