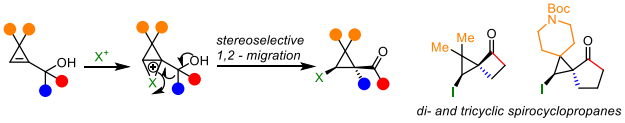
Semipinacol Rearrangement of Cyclopropenylcarbinols for the Synthesis of Highly Substituted Cyclopropanes

Vladyslav Smyrnov and Jerome Waser*

Laboratory of Catalysis and Organic Synthesis, Institut des Sciences et Ingénierie Chimique, Ecole Polytechnique Fédérale de Lausanne, CH-1015, Lausanne, Switzerland.

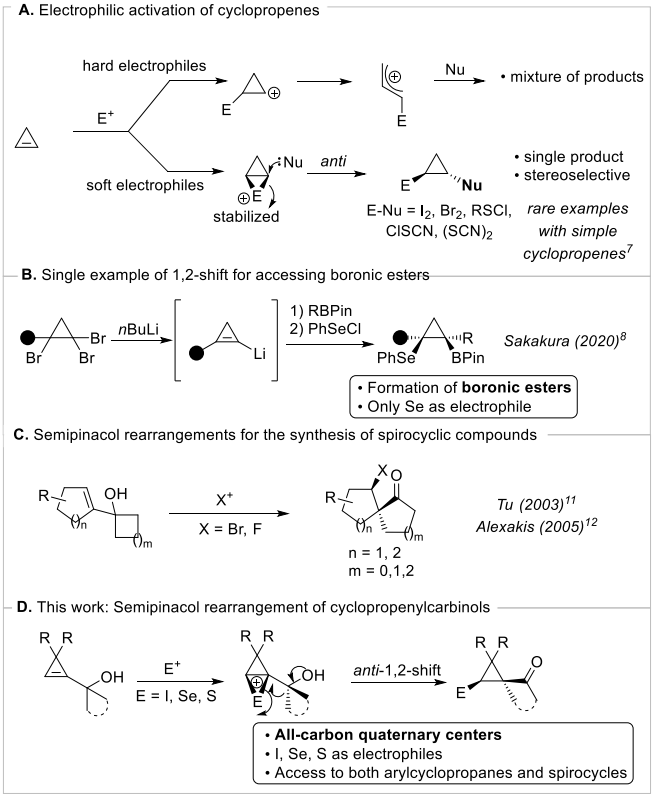


ABSTRACT: An electrophile-induced semipinacol rearrangement of cyclopropenylcarbinols is reported. This transformation gives access to various polyfunctionalized cyclopropanes under mild metal-free conditions. The scope of the reaction includes iodine, sulfur and selenium electrophiles, aryl and strained ring migrating groups, and diverse substitution patterns on the cyclopropene. The reaction is particularly efficient for the synthesis of small ring-containing spirocycles, which are important rigid three-dimensional building blocks for medicinal chemistry.

Since their discovery, cyclopropanes have attracted the attention of chemists due to their unique bonding properties, their ring strain, and their rigid conformation.[1] In addition, cyclopropanes are present in numerous bioactive compounds, including both natural products and synthetic molecules.[2] Nevertheless, polysubstituted cyclopropanes are difficult to access.[3] One successful approach relies on the functionalization of cyclopropenes via carbo- or heterometallation of the double bond, which allows the simultaneous introduction of two substituents on the three-membered ring in a stereoselective fashion.[4,5] In contrast, the electrophilic activation of the cyclopropene double bond is less developed. One of the reasons for that is the instability of the cyclopropyl cation, which readily undergoes electrocyclic ring-opening to form an allyl cation (Scheme 1A).[6] To avoid this side reaction, the formation of three-membered *onium* cations with soft electrophiles has two advantages: it stabilizes the ring system and promotes at the same time *anti* stereoselective addition of the nucleophile. Despite the high potential of this approach, there was only rare examples of simple transformations like dihalogenation, chlorosulfenylation, and thiocyanation proceeding with a very narrow scope (usually 2-3 examples) until 2020.[7] In 2020, Sakakura and coworkers described an electrophile-induced *anti*-selective 1,2-boronate migration of *in situ* generated cyclopropenylboronates, resulting in functionalized substituted cyclopropyl boronates (Scheme 1B).[8] This study was limited to the use of phenylselenyl chloride as an electrophile and resulted in a boron-substituted carbon center. To the best of our knowledge, no electrophilic approach has been reported so far for the formation of quaternary all-carbon centers on cyclopropanes.

In this context, semipinacol-type rearrangements enable the synthesis of β – functionalized ketones bearing quaternary stereocenters.[9] In particular, the electrophilic activation of cyclic alkenes in β position to an alcohol gives access to spirocycles (Scheme 1C), which are important in medicinal chemistry.[10] However, this strategy has been only rarely used. In 2003, Tu and co-workers developed a halonium-induced semipinacol rearrangement and reported one example each of [5,5] and [6,6] spirocycles.[11] Enantioselective halogenative semi-pinacol rearrangements giving access to [4-6,6] spirocycles fused to benzene rings were developed by Alexakis and co-workers.[12] In addition, reactions proceeding via cleavage of weak sigma bonds have been also reported to access spirocycles.[13,14] However, to the best of our knowledge, there is no report of a semipinacol rearrangement on cyclopropenes to access spirocyclic systems.

Scheme 1. a) Electrophilic activation of cyclopropenes. b) 1,2-Shift on boron. c) Semipinacol rearrangements for the synthesis of spirocyclic compounds. d) Semipinacol rearrangement of cyclopropenylcarbinols

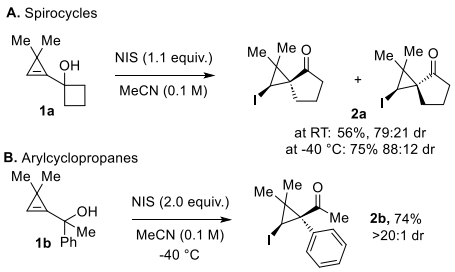


In this work, we report the first example of semipinacol-type rearrangements of cyclopropenylcarbinols by electrophilic activation of the double bond giving access to all-carbon quaternary centers (Scheme 1D). This transformation results in the formation of complex functionalized cyclopropyl ketone products, versatile building blocks for further transformations[15] that are difficult to access via classical methods such as the Corey-Chaykovsky reaction.[16] The transformation is efficient

for the generation of di- and tri-spirocyclic compounds, containing cyclopropanes and cyclobutanes.

We chose substrate **1a** as model compound (Scheme 2), as cyclobutanol derivatives readily undergo semipinacol rearrangements due to the release of ring strain [9c,17] and 3,3-dimethylcyclopropenylcarbinols are easily accessed through the addition of 3,3-dimethylcyclopropenyllithium reagents to ketones.[18] The latter can be accessed in two steps (cyclopropanation with bromoform and elimination/metalation) from broadly available brominated alkenes. Furthermore, the *gem*–dimethyl group can be found in bioactive compounds.[19] In an initial screening of electrophiles (See SI for details), a successful iodination, 1,2-carbon shift was obtained when using NIS (Scheme 1A). In accordance with our hypothesis of migration on an onium species, the major diastereoisomer resulted from an *anti*-selective migration. The minor diastereoisomer may arise from partial formation of a carbocation intermediate. The obtained cyclopropyl iodides represent versatile building blocks for subsequent modification.[20,21] Lowering the temperature to -40 °C gave spirocyclic product **2a** in 75% yield and 88:12 *dr*. Aryl groups are known to have a high migratory aptitude in pinacol-type reactions.[22] Starting from alcohol **1b**, the corresponding product **2b** was obtained in 74% yield and excellent *dr*, indicating that only the onium pathway is taken in this case. Further attempts to achieve migration of alkenyl, or less-migration prone tertiary alkyl, and primary alkyl groups led only to a complex mixture of products (See SI for details). Nevertheless, our semi-pinacol approach gave access to two of the most important classes of cyclopropanes: spirocyclic derivatives and arylcyclopropanes.[23]

Scheme 2. a) Synthesis of spirocycles. b) Synthesis of arylcyclopropanes



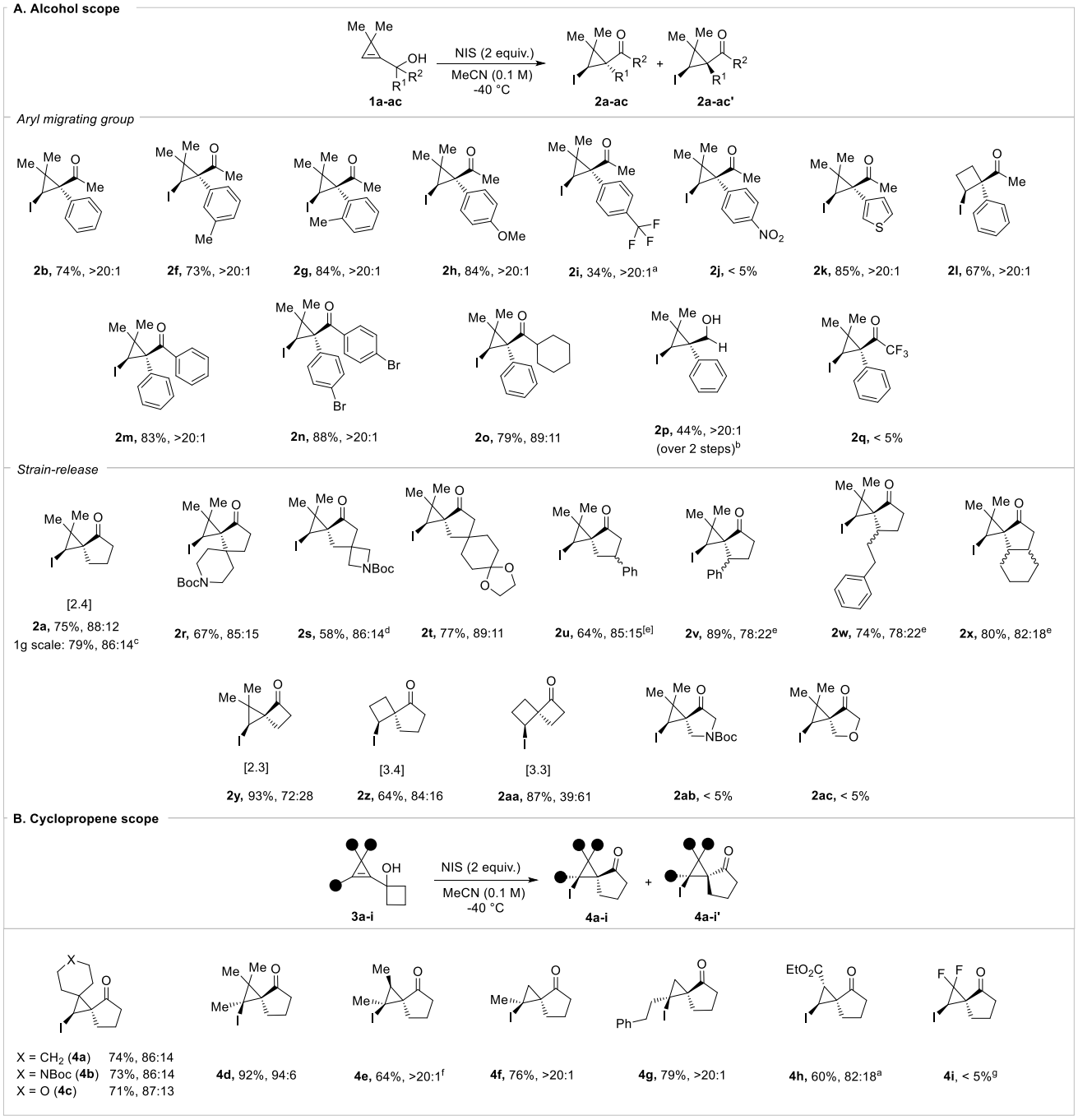
To investigate the scope of the reaction, a selection of cyclopropenes **1f-q** bearing different aryl substituents was prepared[18] (Scheme 3A). *Meta*- and *ortho*-tolyl substituted cyclopropanes **2f** and **2g** were obtained in 73 and 84% yield. The electron-rich *p*-methoxyphenyl group migrated well to give **2h**. Even the electron-poor *p*-trifluoromethylphenyl substituted cyclopropane **2i** could be obtained in 34% yield when the reaction was performed at -20 °C in $MeNO_2$. The more electron-poor *p*-nitrophenyl group failed to undergo migration (**2j**). Thiophene could also migrate giving product **2k** in 85% yield. A cyclobutene derivative resulted in **2l**. The non-migrating group could also be varied. Products **2m** and **2n** with R^2 = Ar were obtained in 83% and 88% yield. When R^2 = cyclohexyl **2o** was formed in 79% yield. An aldehyde product was formed from secondary benzylic alcohol **1p** (R^1 = Ph, R^2 = H) and reduced to alcohol **2p** to facilitate isolation. An electron-withdrawing trifluoromethyl group prevented the reaction to occur at low temperature (**2q**), leading to re-isolation of the starting material. At higher temperature degradation was observed.

We then examined the strain-release semipinacol rearrangement. The reaction of 2,2-disubstituted cyclobutanol **1r**, bearing a protected amine, resulted in migration of the more substituted carbon, forming **2r** in 67% yield and 85:15 *dr*. 3,3–Disubstituted cyclobutanols **1s** and **1t** gave iodides **2s** and **2t**. Monosubstituted cyclobutanols with alkyl and aryl substituents (**1u-w**) were also suitable substrates for the reaction. The more substituted carbon atom migrated exclusively with good *anti* selectivity, but the relative configuration at the migrating center was not controlled. The reaction of fused cyclobutanol **1x** gave tricyclic product **2x** in 80% yield. Finally, these conditions allowed access to spirocyclic systems containing different small ring sizes. Starting from cyclopropanol **1y** [2.3]-spirocyclic **2y** was formed. Cyclobutene derivatives **1z** and **1aa** were readily transformed to the corresponding [3.n] spirocyclic building blocks **2z** and **2aa**. The heterocyclic analogs **2ab** and **2ac** of [2.3]-spirocycles could not be obtained.

We then explored the influence of the substituents on the cyclopropene ring (Scheme 3B). We synthesized cyclopropenes **3a-i** bearing a cyclobutanol fragment.[18] Tricyclic iodides **4a-c** were formed in 71-74% yield from cyclopropenes **3a-c**. Tetrasubstituted cyclopropene **3d** gave hexasubstituted cyclopropane **4d** bearing 3 contiguous quaternary centers. The reaction of methyl substituted cyclopropene **3e** results in product **4e** with high diastereoselectivity. Iodides **4f** and **4g** were formed from 3-unsubstituted cyclopropenes in good yields with excellent diastereoselectivity. Ester-bearing product **4h** could be synthesized using more forcing conditions. Product **4i** could not be obtained from the difluorocyclopropene **3i**.

We then examined other electrophiles in the semipinacol rearrangement (Scheme 4). We were pleased to see that the Ph_2S_2 + SO_2Cl_2 system for *in situ* generation of PhSCl[24] was suitable for a sulfenylative semipinacol rearrangement. The use of a TBS-protected alcohol led to a better yield and *dr* (See SI for optimization details). The sulfenylated spirocyclic ketone **6a** was obtained in 82% yield as a single diastereoisomer. The same conditions also worked well for a selenylative semipinacol rearrangement using PhSeCl, giving product **7a** in 84% yield. When using SCNCl generated *in situ* from chlorobenziodoxolone and trimethylsilyl isothiocyanate,[25] the corresponding ketothiocyanate **8a** was obtained in 89% yield, albeit in poor *dr*. The lower *dr* may be explained by the lower stability of the cyclic episulfonium ion, which is destabilized by the electron-withdrawing CN group, leading to increased formation of the free carbocation. The chalcogenative semipinacol rearrangements were then performed on different substrates to give [2.3]-spirobicyclohexane derivatives **6-8** bearing -SPh, -SePh, and -SCN functionalities. The migration of the aryl group was observed for **7c** and **8c**. Finally, the less reactive substrate **5d** could be transformed into compound **6d** when the reaction was performed at -40 °C.

Scheme 3. a) Alcohol scope of the semipinacol rearrangement. b) Cyclopropene scope of the semipinacol rearrangement.

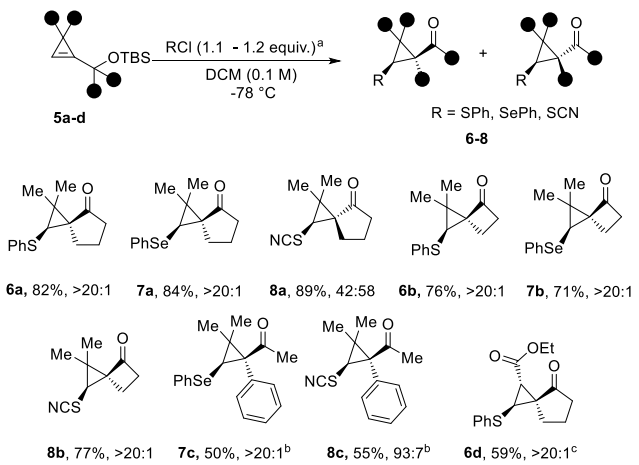


[a]The reaction was performed in $MeNO_2$ (0.1 M) at -20 °C. [b]The crude aldehyde was reduced using $NaBH_4$ (2 equiv.) in MeOH. [c]1.1 equiv. of NIS was used. [d]The reaction was performed in 1:1 mixture of MeCN and $MeNO_2$ (0.1 M). [e]The indicated *dr* corresponds to the relative configuration of the cyclopropane ring substituents; the configuration of the other stereocenters is not controlled (a *dr* between 1:1 and 1:1.5 was observed). [f]The indicated *dr* corresponds to the relative configuration of the centers bearing the electrophile and the migrating group. For the relative configuration of the other methyl group the *dr* is 82:18 (the major diastereoisomer is drawn). [g]The TBS protected alcohol was used as the starting material.

To demonstrate the versatility of the obtained polyfunctional building blocks, we investigated product modifications. Several examples of stereoretentive transition metal-catalyzed couplings of cyclopropyl iodides have been reported.[26] Sonogashira-type coupling of **4h** with phenylacetylene can be achieved using the conditions developed by Cossy and coworkers,[24c] resulting in the formation of product **9** with complete stereoretention. Arylation of iodide **4h** can be achieved via a Suzuki coupling, forming product **10** in 72% yield. The reduction of **2a** using L-Selectride resulted in the formation of **11** as a

single diastereoisomer. Methylation of the lithium enolate obtained from **2a** through the addition of LHMDS led to the formation of **12** as a mixture of diastereoisomers. Treatment of compound **11** with an excess of *t*BuLi resulted in the formation of dilithiated intermediate **I**.[20b] Quenching of **I** with NH_4Cl gave compound **13**. Trapping of **I** with CO_2, followed by acidic work-up, resulted in the formation of tricyclic lactone **14**. Finally, 1,2 addition of **I** to benzophenone gave alcohol **15**.

Scheme 4. Scope of electrophiles



[a]Reaction conditions. For R = SPh: Ph_2S_2 (0.7 equiv.), SO_2Cl_2 (0.6 equiv.); For R = SePh: PhSeCl (1.1 equiv.); for R = SCN: 1-chloro-1,2-benziodoxol-3-(1*H*)-one (1.2 equiv.), TMSNCS (1.2 equiv.). [b]The non-protected alcohol starting material was used. [c]The reaction was performed at -40 °C

In conclusion, we have reported the first examples of electrophile-induced semipinacol rearrangements on cyclopropenes. The transformation can be used for the stereoselective synthesis of polyfunctionalized cyclopropanes bearing all-carbon quaternary centers using soft electrophiles, such as I^+, PhS^+, $PhSe^+$, and NCS^+. The 1,2-migration was achieved in the case of aryl-substituted alcohols, cyclopropanols, and cyclobutanols. Moreover, the transformation was extended to cyclobutenes, giving rise to functionalized cyclobutanes. Thus, we could obtain the full range of [m.n]-spirocyclic ring systems with m = 2, 3 and n = 3, 4. Our work demonstrates the high synthetic potential of the electrophilic activation of cyclopropenes as an underdeveloped strategy for synthesizing complex cyclopropanes.

ASSOCIATED CONTENT

Supporting Information

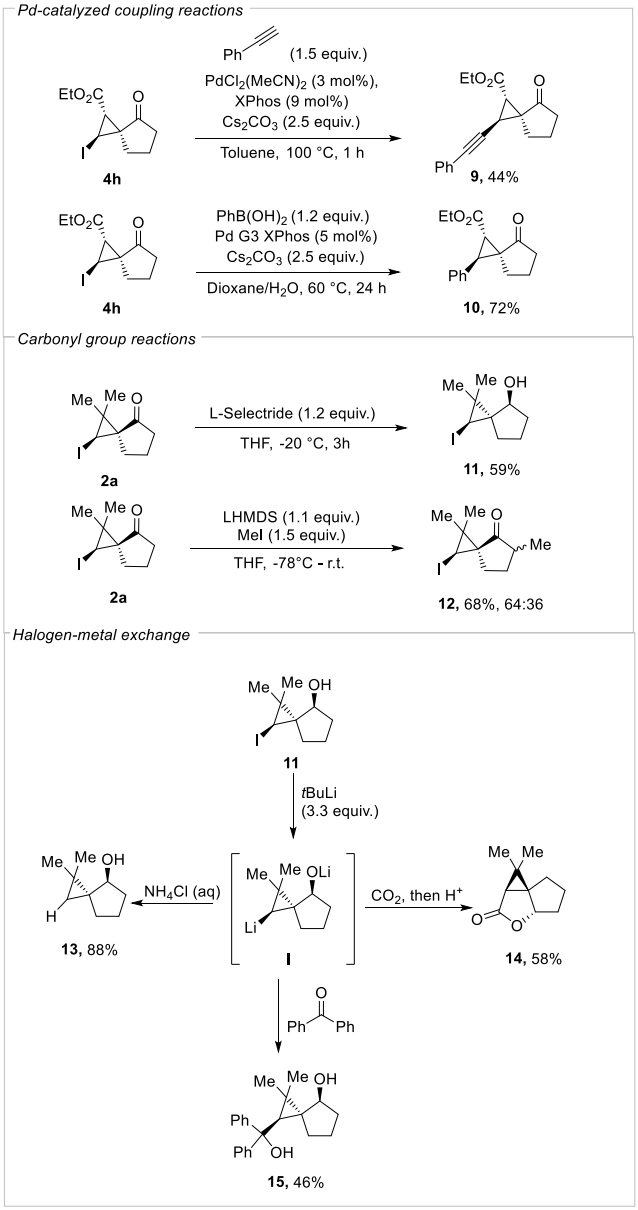
The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures and analytical data for all new compounds; copy of NMR spectra (PDF).

AUTHOR INFORMATION

Corresponding Author

Jerome Waser - Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne, Switzerland. orcid.org/0000-0002-4570-914X; Email: jerome.waser@epfl.ch

Scheme 5. Product modifications (see SI for experimental details)



Authors

Vladyslav Smyrnov - Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne, Switzerland. https://orcid.org/0000-0001-7180-0337

Author Contributions

V.S. discovered and optimized the reaction, performed scope investigations and products modification, and prepared the experimental parts and first draft of the manuscript. J. W. supervised the project, edited the manuscript and proofread the experimental part.

Notes

The authors declare no competing financial interest.

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(22) They are 323'561 reported arylcyclopropanes, 11 of them are approved drugs. There are already 16737 reported [3,5] spirocycles, and the interest for such compounds continues to increase (ref. 10). Source: reaxys search performed on 13.05.2023.
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Supporting Information

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General information

The NMR spectra were recorded on a Brucker DPX-400 spectrometer at 400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F. The chemical shift (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents (chloroform-*d* - 7.26 ppm ^{1}H NMR and 77.12 ppm ^{13}C NMR; methylene chloride-d_2 5.32 ppm ^{1}H NMR and 53.8 ppm ^{13}C NMR; acetonitrile-d_3 1.92 ppm ^{1}H NMR and 1.4 and 118.7 ppm ^{13}C NMR; benzene-d_6 7.16 ppm ^{1}H NMR and 128.06 ppm ^{13}C NMR). ^{13}C and ^{19}F spectra have been measured using broadband {1H} decoupling. Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet or massive; bs, broad signal). Infrared spectra of selected compounds were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm^{-1} (w = weak, m = medium, s = strong, br = broad). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. The raw data obtained from the Q-TOF Waters instrument does not take into account the mass of the electron for the ion, the obtained raw data has been therefore corrected by removing the mass of the electron (5 mDa). Mass spectrometry for CEC reactions was performed on UPLC-MS system consisting of a Waters Acquity UPLC and a Waters VION IMS QTOF. Samples were analyzed using Waters Acquity-I-UPLC Classsystem (Waters Corporation, Milford, MA, USA) coupled with a Waters Vion IMS-QTof Mass Spectrometer equipped with LockSpray. The instrument was controlled by Waters UNIFI 1.9.4 (3.1.0, Waters Corporation, Milford, MA, USA). Yields of isolated products refer to materials of >95% purity as determined by ^{1}H NMR unless stated otherwise.

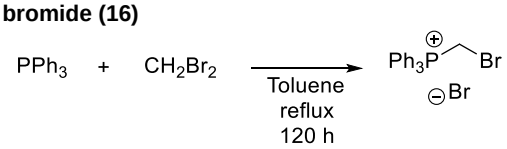
The authors are indebted to the team of the research support service of ISIC at EPFL, particularly to the NMR, X-Ray, and the High Resolution Mass Spectrometry Units.

General procedures. All reactions were carried out under air unless stated otherwise. Synthesis grade solvents were used as purchased; anhydrous solvents (THF, Et_2O, Toluene, and DCM) were taken from a commercial SPS solvent dispenser (H_2O content < 10 ppm, *Karl-Fischer* titration). Chromatographic purification of products was accomplished using Biotage Isolera Spektra One with pre-packaged silica cartridges purchased from Buchi, models: Sepacore or GraceResolve (4 g, 12 g, 25 g, 40 g, 80 g, 120 g). For thin layer chromatography (TLC) analysis throughout this work, Pre-coated TLC sheets ALUGRAM® Xtra SIL G/UV_{254} were employed, using UV light as the visualizing agent and basic aqueous potassium permanganate ($KMnO_4$) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Materials. Most of the starting materials used in this study are commercial and were purchased in the highest purity available from Sigma-Aldrich, Fluka, Alfa Aesar, and Fluorochem and used as received, without further purifications.

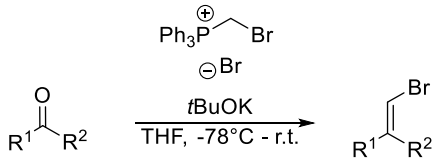
Synthesis of the Starting Materials

(Bromomethyl)triphenylphosphonium bromide (16)



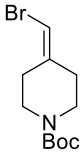
A solution of triphenylphosphine (50.00 g, 190.6 mmol, 1 equiv.) and dibromomethane (29.7 mL, 427 mmol, 2.25 equiv.) in toluene (425 mL) was heated at reflux for 120 h. The reaction mixture was allowed to stay at 0°C for 1h and filtered. The precipitate was washed with toluene (30 mL and pentane (50 mL), dried under vacuum to give (bromomethyl)triphenylphosphonium bromide (**16**) (67.3 g, 154 mmol, 81% yield) as an off-white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 6H, Ar*H*), 7.79 (ddd, *J* = 7.4, 6.4, 1.7 Hz, 3H, Ar*H*), 7.68 (ddd, *J* = 9.0, 7.1, 3.7 Hz, 6H, Ar*H*), 5.82 (d, *J* = 5.9 Hz, 2H, CH_2).
Spectral data were consistent with the values reported in the literature.[1]

General procedure 1 (GP1). Wittig reaction for the preparation of bromoalkenes



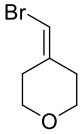
Under N_2 atmosphere: To a solution of (bromomethyl)triphenylphosphonium bromide (11.3 g, 26.0 mmol, 1.30 equiv.) in THF (80 mL), cooled to -78°C, potassium *tert*-butoxide (2.92 g, 26.0 mmol, 1.3 equiv.) was added. The reaction mixture was stirred at that temperature for 1 h. The ketone (20 mmol, 1 equiv.) was added, the reaction mixture was stirred at r.t. overnight. Water (100 mL) was added; the mixture was extracted with Et_2O (2x100 mL). The combined organic layers were washed with brine (70 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by flash chromatography.

***tert*-Butyl 4-(bromomethylene)piperidine-1-carboxylate (17a)**



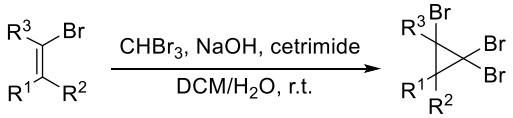
Following the GP1, starting from *tert*-butyl 4-oxopiperidine-1-carboxylate, the title compound was obtained after a purification by flash chromatography (Et_2O/Pentane, gradient 2-20% Et_2O) as a white solid (5.17 g, 18.7 mmol, 94% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.99 (s, 1H, C=C*H*), 3.40 (m, 4H, 2xCH_2N), 2.38 (m, 2H, CH_2), 2.23 (m, 2 H, CH_2), 1.47 (s, 9 H, C(CH_3)$_3$).
Spectral data was consistent with the values reported in literature.[2]

4-(Bromomethylene)tetrahydro-2H-pyran (17b)



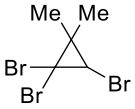
Following the GP1, starting from tetrahydro-4H-pyran-4-one, the title compound was obtained after a purification by flash chromatography (Et_2O/Pentane, gradient 1-10% Et_2O) as a colorless oil (2.46 g, 13.9 mmol, 69% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (s, 1H, C=C*H*), 3.58-3.78 (m, 4H, 2xCH_2O), 2.20-2.52 (m, 4H, 2xCH_2).
Spectral data was consistent with the values reported in literature.[3]

General procedure 2 (GP2). Dibromocyclopropanation of bromoalkenes



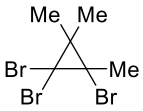
To a solution of alkenylbromide (1 equiv.), cetrimide (0.1 equiv.) and bromoform (2.7 equiv.) in DCM (0.25 mL per 1 mmol of bromoalkene) a 50% w/w NaOH solution (0.2 mL per 1 mmol of bromoalkene) was added dropwise. The resulting solution was vigorously stirred for 24-120 h at r.t. The reaction mixture was diluted with water and DCM. The layers were separated, the aqueous layer was extracted with DCM. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. This crude can be optionally dissolved in pentane and filtered through a pad of silica gel, followed by concentration of pentane under vacuum. The crude was purified by vacuum distillation, column chromatography or recrystallization.

1,1,3-Tribromo-2,2-dimethylcyclopropane (18a)



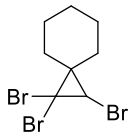
Following the GP2 (reaction time – 24 h), starting from 1-bromo-2-methylprop-1-ene (14.6 g, 108 mmol) the title compound was obtained after filtration through a small pad of silica gel (Pentane) and a purification by vacuum distillation (15 mbar, 70-80°C) as a colorless oil (23.4 g, 76.3 mmol, 70% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47 (s, 1H, C*H*), 1.51 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$).
Spectral data was consistent with the values reported in literature.[4]

1,1,2-Tribromo-2,3,3-trimethylcyclopropane (18b)



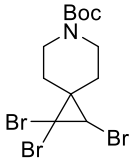
Following the GP2 (reaction time – 72 h), starting from 2-bromo-3-methylbut-2-ene (6.50 g, 43.6 mmol) the title compound was obtained after filtration through a small pad of silica gel (Pentane) and a purification by recrystallization from EtOH (1 mL/g) as a white solid (6.62 g, 20.6 mmol, 47% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H, C*H*$_3$), 1.54 (3, 3H, C*H*$_3$), 1.39 (s, 3H, C*H*$_3$).
Spectral data was consistent with the values reported in literature.[5]

1,1,2-Tribromospiro[2.5]octane (18c)



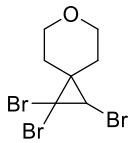
Following the GP2 (reaction time – 120 h), starting from (bromomethylene)cyclohexane (1.27 g, 7.27 mmol) the title compound was obtained after filtration through a small pad of silica gel (Pentane) and a purification by flash chromatography (Pentane) as a colorless oil (2.14 g, 6.18 mmol, 85% yield).
Rf (Pentane) = 0.9.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 1H, C*H*), 1.94 – 1.41 (m, 10H, 5xC*H*$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 42.9, 41.8, 35.9, 35.1, 32.8, 25.2, 24.7, 24.2.
IR (ν_{max}, cm^{-1}) 3029 (w), 2930 (s), 2855 (s), 1446 (s), 1344 (w), 1276 (m), 1245 (m), 1220 (w), 1010 (m), 953 (w), 878 (w), 828 (w), 793 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M - Br]^+$ Calcd for $C_8H_{11}{}^{79}Br_2{}^+$ 264.9228; Found 264.9225.

***tert*-Butyl 1,1,2-tribromo-6-azaspiro[2.5]octane-6-carboxylate (18d)**



Following the GP2 (reaction time – 120 h), starting from tert-butyl 4-(bromomethylene)piperidine-1-carboxylate **17a** (2.76 g, 10.0 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a white solid (2.41 g, 5.38 mmol, 54% yield).
Rf (10% Et_2O/Pentane) = 0.55.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 – 3.52 (m, 2H, 2xC*H*HN), 3.47 (s, 1H, C*H*), 3.46 – 3.34 (m, 2H, 2xCH*H*N), 1.94 (ddd, *J* = 12.3, 8.1, 3.8 Hz, 1H, CH*H*CH$_2$N), 1.88 – 1.68 (m, 3H, CH*H*CH$_2$N, 2xC*H*HCH$_2$N), 1.47 (s, 9H, C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 80.0, 42.1 (br), 40.8, 40.5, 35.3, 33.7, 32.3, 28.4.
IR (ν_{max}, cm^{-1}) 2976 (m), 2926 (w), 2864 (w), 1689 (s), 1418 (s), 1366 (m), 1242 (s), 1166 (s), 1123 (s), 1023 (m), 952 (m), 863 (m), 798 (m), 769 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}{}^{79}Br_3NNaO_2{}^+$ 467.8780; Found 467.8781.

1,1,2-Tribromo-6-oxaspiro[2.5]octane (18e)

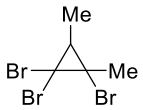


Following the GP2 (reaction time – 120 h), starting from 4-(bromomethylene)tetrahydro-2H-pyran **17b** (1.77 g, 10.0 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (2.07 g, 5.93 mmol, 59% yield).

Rf (10% Et_2O/Pentane) = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (dddd, *J* = 21.7, 11.7, 5.9, 3.8 Hz, 2H, 2xC*H*HO), 3.64 (tdd, *J* = 11.8, 8.2, 3.1 Hz, 2H, 2xCH*H*O), 3.48 (s, 1H, C*H*), 2.05 (ddd, *J* = 12.8, 8.5, 3.8 Hz, 1H, CH*H*CH_2O), 1.89 (ddd, *J* = 12.7, 8.2, 3.8 Hz, 1H, CH*H*CH_2O), 1.80 – 1.70 (m, 2H, 2x C*H*HCH_2O).
^{13}C NMR (101 MHz, $CDCl_3$) δ 66.1, 66.1, 41.2, 40.7, 36.0, 33.2, 32.9.
IR (ν_{max}, cm^{-1}) 3029 (w), 2962 (m), 2918 (m), 2845 (m), 1464 (w), 1440 (m), 1387 (w), 1257 (m), 1213 (w), 1185 (w), 1105 (s), 1031 (m), 1011 (m), 962 (m), 871 (w), 842 (m), 799 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_7H_{10}{}^{79}Br_3O^+$ 346.8276; Found 346.8272.

1,1,2-Tribromo-2,3-dimethylcyclopropane (18f)

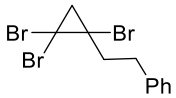


Following the GP2 (reaction time – 72 h), starting from 2-bromobut-2-ene (mixture of *E* and *Z* isomer) (1.35 g, 10.0 mmol) the title compound (mixture of diastereomers, *cis*:*trans* 1.35:1) was obtained after filtration through a small pad of silica gel (Pentane) and a purification by chromatography (Pentane) as a colorless oil (1.89 g, 6.16 mmol, 62% yield).
Trans-isomer:
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.09 (s, 3H, C*H*$_3$), 1.39 (q, *J* = 6.3 Hz, 1H, C*H*), 1.31 (d, *J* = 6.3 Hz, 3H, C*H*$_3$CH).
Cis-isomer:
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.94 (q, *J* = 6.6 Hz, 1H, C*H*), 1.85 (s, 3H, C*H*$_3$), 1.21 (d, *J* = 6.6 Hz, 3H, C*H*$_3$CH).
Spectral data was consistent with the values reported in literature.[6]

1,1,2-Tribromo-2-methylcyclopropane (18g)

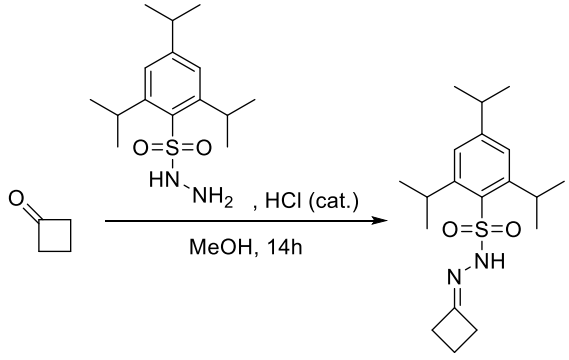
Following the GP2 (reaction time – 24 h), starting from 2-bromoprop-1-ene (1.21 g, 10.0 mmol) the title compound was obtained after filtration through a small pad of silica gel (Pentane) and a purification by vacuum distillation (10-11 mbar, 57-65°C) as a colorless oil (1.66 g, 5.67 mmol, 57% yield).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.08 (s, 3H, C*H*$_3$), 1.99-1.97 (d, *J* = 9.2 Hz, 1H, C*H*H), 1.86-1.83 (d, *J* = 9.2 Hz, 1H, CH*H*).
Spectral data was consistent with the values reported in literature.[6]

(2-(1,2,2-Tribromocyclopropyl)ethyl)benzene (18h)



Following the GP2 (reaction time – 24 h), starting from (3-bromobut-3-en-1-yl)benzene[7] (0.95 g, 4.5 mmol) the title compound was obtained after filtration through a small pad of silica gel (Pentane) and a purification by chromatography (Pentane) as a colorless oil (0.91 g, 2.4 mmol, 53% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.35 (m, 5H, Ar*H*), 2.86–3.16 (m, 2H, C*H*$_2$Ph), 2.16–2.47 (m, 2H, C*H*$_2$$CH_2$Ph), 1.92 (dd, 1H, *J* = 9.4, 0.6 Hz, C*H*H), 1.73 (d, 1H, *J* = 9.4 Hz, CH*H*).
Spectral data was consistent with the values reported in literature.[8]

N'-Cyclobutylidene-2,4,6-triisopropylbenzenesulfonohydrazide



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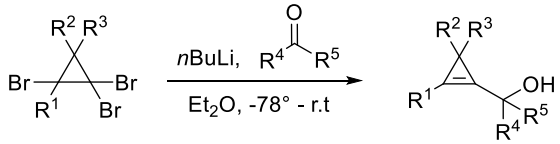
To a solution of cyclobutanone (1.25 g, 17.8 mmol, 1.00 equiv.) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (5.32 g, 17.8 mmol, 1.00 equiv.) in MeOH (20 mL) two drops of aqueous HCl (36% w/w) were added. A white precipitate started to appear. The reaction mixture was kept in the freezer (-20 °C) overnight. The mixture was filtered, the precipitate was washed with cold MeOH and dried under vacuum to give N'-cyclobutylidene-2,4,6-triisopropylbenzenesulfonohydrazide **21** (4.85 g, 13.8 mmol, 78% yield) as an amorphous white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 2H, Ar*H*), 6.99 (br s, 1H, N*H*), 4.20 (hept, *J* = 6.8 Hz, 2H, 2xC*H*$(CH_3)_2$), 2.96 – 2.83 (m, 3H, C*H*$_2$ & C*H*$(CH_3)_2$), 2.82 – 2.72 (m, 2H, C*H*$_2$), 2.06 – 1.94 (m, 2H, C*H*$_2$), 1.26 (m, 18H, 6xC*H*$_3$).

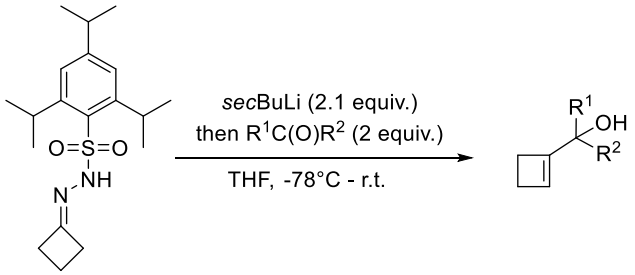
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 153.2, 151.3, 131.2, 123.9, 34.2, 34.1, 31.5, 29.9, 24.8, 23.6, 13.7.
IR (ν_{max}, cm^{-1}) 3245 (m), 2962 (s), 2930 (m), 2871 (m), 1782 (w), 1667 (w), 1600 (m), 1566 (w), 1462 (m), 1426 (m), 1385 (m), 1364 (m), 1324 (m), 1259 (w), 1159 (s), 1034 (m), 910 (m), 883 (m), 734 (s).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{31}N_2O_2S^+$ 351.2101; Found 351.2090.

General procedure 3 (GP3). Synthesis of cyclopropenylcarbinols



Under N_2 atmosphere: To a solution of tribromide (1 equiv.) in Et_2O (3 mL/mmol of tribromide), cooled to -78 °C, a solution of *n*BuLi (2.5 M in hexanes, 1.9 equiv.) was added dropwise. The reaction mixture was warmed to -20 °C and stirred at that temperature for 1 h. After that, the mixture was cooled to -50 °C, ketone (0.8 equiv.) was added in one portion. The reaction mixture was stirred at r.t. for 2 h. Water (2 mL/mmol of tribromide) was added. The layers were separated, the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. The crude product was purified by column chromatography.

General procedure 4 (GP4). Shapiro reaction of cyclobutanone trisylhydrazone for the synthesis of cyclobutenylcarbinols



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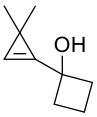
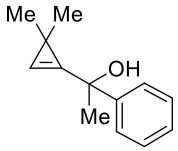
Under N_2 atmosphere: To a solution of N'-cyclobutylidene-2,4,6-triisopropylbenzenesulfonohydrazide (1 equiv.) in THF (4 mL/mmol of hydrazone), cooled to -78 °C, a solution of *sec*-BuLi (1.4 M in cyclohexane, 2.1 equiv.) was added dropwise. The reaction mixture was stirred at -78 °C fro 15 min, then at -20 °C for 45 min. Then, the mixture was cooled to -78 °C, followed by addition of the ketone (2 equiv.). The reaction mixture was stirred at r.t. for 1 h. Water was added, the mixture was extracted with Et_2O (2x). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product. This crude was purified by column chromatography.

1-(3,3-Dimethylcycloprop-1-en-1-yl)cyclobutan-1-ol (1a)



Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (5.80 g, 18.9 mmol) and cyclobutanone (1.06 g, 15.1 mmol) the title compound was obtained after a purification by chromatography (gradient 3-30% Et_2O/Pentane) as a light-yellow oil (1.83 g, 13.2 mmol, 88% yield).
Rf (15% Et_2O/Pentane) = 0.27.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H, C=C*H*), 2.42 – 2.22 (m, 4H, 2xCH_2), 2.17 (s, 1H, O*H*), 1.90 – 1.69 (m, 2H, CH_2), 1.31 – 1.21 (s, 6H, 2xCH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 111.5, 74.2, 36.6, 27.4, 21.6, 12.3.
IR (ν_{max}, cm^{-1}) 2926 (s), 2854 (m), 1461 (m), 1363 (m), 1246 (m), 1156 (m), 1120 (m), 1020 (m), 945 (m), 791 (m), 717 (m).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_9H_{15}O^+$ 139.1117; Found 139.1116.

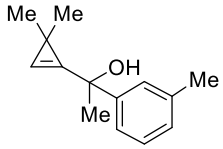
1-(3,3-Dimethylcycloprop-1-en-1-yl)-1-phenylethan-1-ol (1b)



Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (3.07 g, 10.0 mmol) and acetophenone (961.2 mg, 8.000 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (1.29 g, 6.85 mmol, 86% yield).
^{1}H NMR (300 MHz, $CDCl_3$): 7.56 - 7.54 (m, 2H, Ar*H*), 7.39 - 7.28 (m, 3H, Ar*H*), 7.04 (s, 1H, C=C*H*), 2.85 (br s, 1H, O*H*), 1.75 (s, 3H, ArC(OH)CH_3), 1.25 (s, 3H, CH_3CCH_3), 1.19 (s, 3H, CH_3CCH_3).

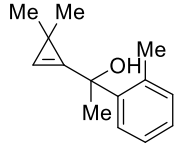
Spectral data was consistent with the values reported in literature.[9]

1-(3,3-Dimethylcycloprop-1-en-1-yl)-1-(m-tolyl)ethan-1-ol (1f)



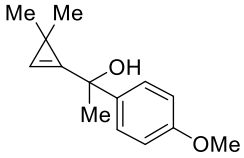
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 1-(m-tolyl)ethan-1-one (537 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (718 mg, 3.55 mmol, 89% yield).
Rf (10% Et_2O/Pentane) = 0.61.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 1.9 Hz, 1H, Ar*H*), 7.33 – 7.28 (m, 1H, Ar*H*), 7.23 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.08 (d, *J* = 7.4 Hz, 1H, Ar*H*), 7.01 (s, 1H, C=C*H*), 2.37 (s, 3H, ArC*H*$_3$), 2.13 (s, 1H, O*H*), 1.72 (s, 3H, ArC(OH)C*H*$_3$), 1.23 (s, 3H, C*H*$_3$CCH$_3$), 1.18 (s, 3H, CH$_3$CC*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 140.1, 137.8, 128.1, 127.9, 125.6, 122.0, 113.3, 74.5, 30.0, 27.6, 27.5, 22.6, 21.6.
IR (ν_{max}, cm^{-1}) 3370 (s), 2965 (s), 2928 (s), 2859 (s), 1606 (m), 1455 (m), 1366 (s), 1278 (m), 1177 (m), 1083 (m), 937 (m), 787 (s).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O^+$ 203.1430; Found 203.1437.

1-(3,3-Dimethylcycloprop-1-en-1-yl)-1-(o-tolyl)ethan-1-ol (1g)



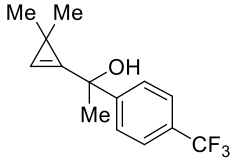
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 1-(o-tolyl)ethan-1-one (537 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (691 mg, 3.42 mmol, 85% yield).
Rf (10% Et_2O/Pentane) = 0.66.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 1H, Ar*H*), 7.18 (m, 3H, Ar*H*), 6.96 (s, 1H, C=C*H*), 2.50 (s, 3H, ArC*H*$_3$), 2.06 (s, 1H, O*H*), 1.83 (s, 3H, ArC(OH)C*H*$_3$), 1.20 (s, 3H, C*H*$_3$CCH$_3$), 1.11 (s, 3H, CH$_3$CC*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 138.7, 136.4, 132.3, 127.5, 125.6, 125.4, 113.2, 74.9, 28.5, 27.4, 27.1, 22.3, 21.6.
IR (ν_{max}, cm^{-1}) 3404 (m), 2964 (m), 2935 (m), 2859 (m), 1455 (m), 1364 (m), 1277 (w), 1181 (m), 1089 (m), 1051 (m), 906 (m), 759 (s), 730 (s).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O^+$ 203.1430; Found 203.1437.

1-(3,3-Dimethylcycloprop-1-en-1-yl)-1-(4-methoxyphenyl)ethan-1-ol (1h)



Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 1-(4-methoxyphenyl)ethan-1-one (600.7 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (736 mg, 3.38 mmol, 84% yield).
Rf (10% Et_2O/Pentane) = 0.25.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H, Ar*H*), 7.02 (s, 1H, C=C*H*), 6.95 – 6.87 (m, 2H, Ar*H*), 3.83 (s, 3H, OC*H*$_3$), 2.14 (s, 1H, O*H*), 1.74 (s, 3H, ArC(OH)C*H*$_3$), 1.24 (s, 3H, C*H*$_3$CCH$_3$), 1.19 (s, 3H, CH$_3$CC*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 140.1, 137.6, 126.2, 113.5, 113.0, 74.1, 55.3, 29.9, 27.6, 27.5, 22.5.
IR (ν_{max}, cm^{-1}) 3465 (m), 2964 (m), 2934 (m), 2858 (m), 2838 (m), 1611 (m), 1511 (s), 1458 (m), 1365 (m), 1301 (m), 1246 (s), 1178 (s), 1091 (m), 1034 (s), 834 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_2^+$ 219.1380; Found 219.1369.

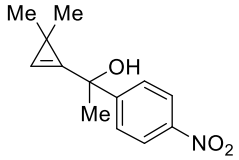
1-(3,3-Dimethylcycloprop-1-en-1-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (1i)



Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 1-(4-(trifluoromethyl)phenyl)ethan-1-one (753 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as an amorphous white solid (923 mg, 3.38 mmol, 84% yield).
Rf (10% Et_2O/Pentane) = 0.51.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.61 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.07 (s, 1H, C=C*H*), 2.19 (s, 1H, O*H*), 1.73 (s, 3H, ArC(OH)C*H*$_3$), 1.22 (s, 3H, C*H*$_3$CCH$_3$), 1.18 (s, 3H, CH$_3$CC*H*$_3$).

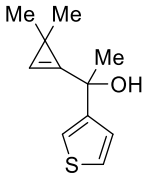
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 139.5, 129.4 (q, *J* = 32.5 Hz), 125.4, 125.2 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272 Hz), 114.3, 74.2, 30.2, 27.6, 27.4, 22.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4.
IR (v_{max}, cm^{-1}) 3412 (w), 2968 (w), 2937 (w), 2862 (w), 1451 (w), 1411 (w), 1368 (m), 1325 (s), 1166 (s), 1125 (s), 1073 (s), 1017 (m), 844 (m), 734 (w).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}F_3O^+$ 257.1148; Found 257.1157.

1-(3,3-dimethylcycloprop-1-en-1-yl)-1-(4-nitrophenyl)ethan-1-ol (1j)



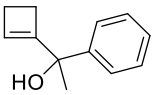
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 1-(4-nitrophenyl)ethan-1-one (660 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 5-50% Et_2O/Pentane) as an amorphous white solid (632 mg, 3.38 mmol, 68% yield).
Rf (25% Et_2O/Pentane) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.15 (m, 2H, Ar*H*), 7.74 – 7.66 (m, 2H, Ar*H*), 7.11 (s, 1H, C=C*H*), 2.24 (s, 1H, O*H*), 1.75 (s, 3H, ArC(OH)C*H*$_3$), 1.22 (s, 3H, C*H*$_3$CCH$_3$), 1.18 (s, 3H, CH$_3$CC*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 147.1, 139.1, 126.0, 123.5, 114.9, 74.2, 30.2, 27.6, 27.4, 23.1.
IR (v_{max}, cm^{-1}) 3420 (w), 2972 (m), 1744 (w), 1603 (m), 1520 (s), 1450 (m), 1346 (s), 1271 (w), 1224 (w), 1083 (s), 856 (s)
HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{15}NNaO_3^+$ 256.0944; Found 256.0936.

1-(3,3-Dimethylcycloprop-1-en-1-yl)-1-(thiophen-3-yl)ethan-1-ol (1k)



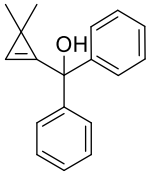
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 1-(thiophen-3-yl)ethan-1-one (505 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 4-40% Et_2O/Pentane) as a yellow oil (575 mg, 2.96 mmol, 74% yield).
Rf (20% Et_2O/Pentane) = 0.8.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H, Ar*H*), 7.12 (dd, *J* = 4.9, 1.5 Hz, 1H, Ar*H*), 7.01 (s, 1H, C=C*H*), 2.21 (s, 1H, O*H*), 1.74 (s, 3H, ArC(OH)C*H*$_3$), 1.22 (s, 3H, C*H*$_3$CCH$_3$), 1.17 (s, 3H, CH$_3$CC*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 139.5, 125.9, 125.9, 119.9, 113.2, 72.7, 29.3, 27.6, 22.5. (one carbon is not resolved).
IR (v_{max}, cm^{-1}) 3403 (m), 2965 (m), 2931 (m), 2856 (m), 1449 (m), 1366 (m), 1235 (m), 1181 (m), 1083 (m), 857 (m), 788 (s), 730 (s).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{15}OS^+$ 195.0838; Found 195.0841.

1-(Cyclobut-1-en-1-yl)-1-phenylethan-1-ol (1l)



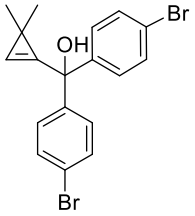
Following the GP4, starting from N'-cyclobutylidene-2,4,6-triisopropylbenzenesulfonohydrazide (1.05 g, 3.00 mmol, 1.00 equiv.) and acetophenone (721 mg, 6.00 mmol, 2.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 3-30% EtOAc/Pentane) as a yellow oil (169 mg, 0.970 mmol, 32% yield).
Rf (15% Et_2O/Pentane) = 0.56.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H, Ar*H*), 7.34 (m, 2H, Ar*H*), 7.26 (m, 1H, Ar*H*), 5.88 (s, 1H, C=C*H*), 2.55 – 2.39 (m, 2H, C*H*$_2$), 2.33 (t, *J* = 3.3 Hz, 2H, C*H*$_2$), 1.91 (s, 1H, O*H*), 1.65 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 145.4, 128.1, 127.9, 126.9, 125.1, 73.5, 28.1, 28.0, 25.3.
IR (v_{max}, cm^{-1}) 3393 (m), 2957 (m), 2921 (m), 2840 (w), 1680 (w), 1447 (m), 1364 (m), 1266 (m), 1173 (w), 1073 (m), 902 (m), 763 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H_{-1}]^+$ Calcd for $C_{12}H_{13}O^+$ 173.0961; Found 173.0957.

(3,3-Dimethylcycloprop-1-en-1-yl)diphenylmethanol (1m)



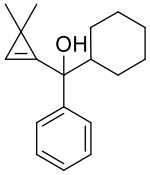
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and benzophenone (729 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 3-30% Et_2O/Pentane) as a yellow oil (911 mg, 3.64 mmol, 91% yield).
^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 4H, Ar*H*), 7.36 – 7.29 (m, 4H, Ar*H*), 7.28 – 7.22 (m, 3H, C=*CH* & Ar*H*), 2.52 (s, 1H, O*H*), 1.17 (s, 6H, 2xC*H*$_3$).
Spectral data was consistent with the values reported in literature.[10]

Bis(4-bromophenyl)(3,3-dimethylcycloprop-1-en-1-yl)methanol (1n)



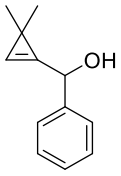
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and bis(4-bromophenyl)methanone (1.36 g, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (1.23 g, 3.01 mmol, 75% yield).
Rf (10% Et_2O/Pentane) = 0.75.
^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 4H, Ar*H*), 7.38 – 7.32 (m, 4H, Ar*H*), 7.29 (s, 1H, C=C*H*), 2.53 (s, 1H, O*H*), 1.18 (s, 6H, 2xC*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 138.7, 131.4, 128.2, 121.8, 117.2, 78.0, 27.4, 23.6.
IR (ν_{max}, cm^{-1}) 3462 (m), 2964 (m), 2936 (m), 2858 (m), 1483 (s), 1396 (m), 1365 (m), 1328 (m), 1275 (m), 1181 (m), 1160 (m), 1072 (s), 1011 (s), 904 (m), 813 (s), 734 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H_{-1}]^+$ Calcd for $C_{18}H_{15}{}^{79}Br_2O^+$ 404.9484; Found 404.9467.

Cyclohexyl(3,3-dimethylcycloprop-1-en-1-yl)(phenyl)methanol (1o)



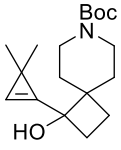
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and cyclohexyl(phenyl)methanone (753 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a yellow oil (831 mg, 3.24 mmol, 81% yield).
Rf (5% Et_2O/Pentane) = 0.52.
^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H, Ar*H*), 7.33 (dd, *J* = 8.4, 6.7 Hz, 2H, Ar*H*), 7.28 – 7.22 (m, 1H, Ar*H*), 7.10 (s, 1H, C=C*H*), 2.01 (s, 1H, O*H*), 1.93 – 1.66 (m, 4H, *CH* &*CH*$_2$), 1.64 – 1.58 (m, 1H, C*H*$_2$), 1.57 – 1.46 (m, 1H, C*H*$_2$), 1.28 – 0.95 (m, 5H, C*H*$_2$), 1.24 (s, 3H, C*H*$_3$), 1.17 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.0, 127.7, 126.8, 126.0, 115.1, 79.9, 48.0, 28.0, 27.4, 27.3, 27.0, 26.5, 26.5, 26.4, 22.1.
IR (ν_{max}, cm^{-1}) 3462 (m), 2928 (s), 2853 (s), 1447 (m), 1364 (m), 1318 (m), 1274 (m), 1177 (m), 1065 (m), 983 (m), 762 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H_{-1}]^+$ Calcd for $C_{18}H_{23}O^+$ 255.1743; Found 255.1743.

(3,3-Dimethylcycloprop-1-en-1-yl)(phenyl)methanol (1p)



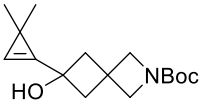
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and benzaldehyde (424 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (562 mg, 3.23 mmol, 81% yield).
^1H NMR (400 MHz, $CDCl_3$) δ 7.35- 7.22 (m, 5H, Ar*H*), 7.06 (s, 1H, C=C*H*), 5.64 (s, 1H, C*H*), 2.58 (s, br, 1H, O*H*), 1.15 (s, 3H, C*H*$_3$), 1.00 (s, 3H, C*H*$_3$).
Spectral data was consistent with the values reported in literature.[11]

***tert*-Butyl 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-hydroxy-7-azaspiro[3.5]nonane-7-carboxylate (1r)**



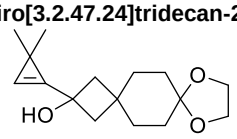
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (401 mg, 1.31 mmol) and *tert*-butyl 1-oxo-7-azaspiro[3.5]nonane-7-carboxylate (250 mg, 1.05 mmol) the title compound was obtained after a purification by chromatography (gradient 10-80% Et_2O/Pentane) as an amorphous white solid (273 mg, 0.88 mmol, 85% yield).
Rf (40% Et_2O/Pentane) = 0.53.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H, C=C*H*), 3.92 (m, 1H, CH_2N), 3.75 (m, 1H, CH_2N), 3.05 (dt, *J* = 13.8, 7.1 Hz, 1H, CH_2N), 2.90 (m, 1H, CH_2N), 2.28 – 2.20 (m, 2H, CH_2), 1.86 (s, 1H, O*H*), 1.84 – 1.73 (m, 3H, CH_2), 1.60 (m, 1H, CH_2), 1.53-1.44 (m, 11H, C(CH_3)$_3$ & CH_2), 1.30 (s, 3H, CH_3), 1.24 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$):
Major rotamer:
δ 154.9, 137.2, 115.8, 79.3, 77.9, 46.8, 40.6 (2C), 34.3, 32.0, 30.9, 28.5, 28.5, 27.8, 24.3, 21.8.
Minor rotamer:
δ 77.6, 45.6, 35.2, 30.7, 25.3, 23.9, 23.3, 14.2. (other peaks are not resolved).
IR (v_{max}, cm^{-1}) 3431 (m), 2966 (m), 2936 (m), 2859 (m), 1670 (s), 1428 (s), 1366 (m), 1245 (s), 1171 (s), 1146 (s), 971 (m), 863 (w), 767 (w).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{29}NNaO_3^+$ 330.2040; Found 330.2039.

***tert*-Butyl 6-(3,3-dimethylcycloprop-1-en-1-yl)-6-hydroxy-2-azaspiro[3.3]heptane-2-carboxylate (1s)**



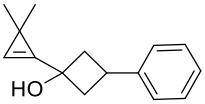
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and *tert*-butyl 6-oxo-2-azaspiro[3.3]heptane-2-carboxylate (845 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 15-100% Et_2O/Pentane) as an amorphous white solid (1.10 g, 3.24 mmol, 98% yield).
Rf (60% Et_2O/Pentane) =0.44.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H, C=C*H*), 3.97 (s, 2H, CH_2N), 3.94 (s, 2H, CH_2N), 2.62 – 2.51 (m, 2H, CH_2), 2.54 – 2.44 (m, 2H, CH_2), 2.09 (s, 1H, O*H*), 1.43 (s, 9H, C(CH_3)$_3$), 1.25 (s, 6H, 2xCH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 137.8, 113.3, 79.5, 69.1, 61.6, 46.8, 29.4, 28.4, 27.5, 22.4.
IR (v_{max}, cm^{-1}) 3401 (m), 2967 (m), 2930 (m), 2878 (m), 1674 (s), 1418 (s), 1366 (s), 1245 (m), 1166 (s), 1054 (s), 932 (w), 856 (w), 770 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{25}NNaO_3^+$ 302.1727; Found 302.1722.

2-(3,3-Dimethylcycloprop-1-en-1-yl)-8,11-dioxadispiro[3.2.47.24]tridecan-2-ol (1t)



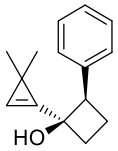
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 8,11-dioxadispiro[3.2.47.24]tridecan-2-one[13] (785 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 6-60% Et_2O/Pentane) as an amorphous white solid (658 mg, 3.24 mmol, 62% yield).
Rf (30% Et_2O/Pentane) = 0.24.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.93 (s, 1H, C=C*H*), 3.89 (s, 4H, 2xOCH_2), 2.27 – 2.19 (m, 2H, CH_2), 2.12 – 1.98 (m, 3H, CH_2 & O*H*), 1.74 (dd, *J* = 7.9, 4.7 Hz, 2H, CH_2), 1.70 – 1.62 (m, 2H, CH_2), 1.61 – 1.55 (m, 4H, CH_2), 1.23 (s, 6H, 2xCH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 112.0, 108.5, 69.2, 64.2, 45.5, 37.0, 35.0, 31.6, 31.3, 30.2, 27.5, 22.3.
IR (v_{max}, cm^{-1}) 3441 (w), 2928 (s), 2858 (m), 1449 (m), 1368 (m), 1269 (m), 1231 (m), 1162 (m), 1094 (s), 1037 (m), 975 (w), 931 (m), 882 (w), 719 (w).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{25}O_3^+$ 265.1798; Found 265.1798.

1-(3,3-Dimethylcycloprop-1-en-1-yl)-3-phenylcyclobutan-1-ol (1u)



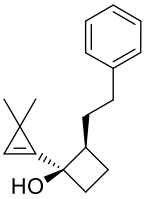
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (656 mg, 2.14 mmol) and 2-phenethylcyclobutan-1-one (250 mg, 1.71 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a mixture of diasteromers (ca 10:1, *cis* isomer is major), amorphous white solid (274 mg, 1.28 mmol, 75% yield).
Rf (10% Et_2O/Pentane) = 0.16.
Major isomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 5H, Ar*H*), 7.08 (s, 1H, C=C*H*), 3.27 (m, 1H, ArC*H*), 2.75 (m, 2H, CH_2), 2.64 – 2.44 (m, 2H, CH_2), 2.30 (s, 1H, O*H*), 1.36 (s, 6H, 2x CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 137.8, 128.4, 126.7, 126.2, 112.0, 70.4, 44.1, 30.3, 27.5, 21.9.
IR (v_{max}, cm^{-1}) 3337 (m), 3065 (w), 3028 (m), 2964 (m), 2934 (s), 2856 (m), 1496 (m), 1452 (m), 1368 (m), 1242 (s), 1181 (m), 1129 (m), 1098 (m), 1022 (w), 961 (w), 752 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O^+$ 215.1430; Found 215.1424.
Stereoselectivity of addition was deduced based on the previous reports of addition of carbon-based nucleophiles to this ketone.[12]

***cis*-1-(3,3-Dimethylcycloprop-1-en-1-yl)-2-phenylcyclobutan-1-ol (1v)**



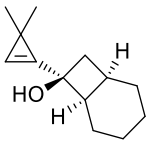
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 2-phenylcyclobutan-1-one[13] (584 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a light-yellow oil (390 mg, 1.82 mmol, 45% yield).
Rf (5% Et_2O/Pentane) = 0.25.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 2H, Ar*H*), 7.25 (m, 3H, Ar*H*), 7.02 (s, 1H, C=C*H*), 3.79 (t, *J* = 8.7 Hz, 1H, ArC*H*), 2.73 – 2.50 (m, 1H, CH_2), 2.49 – 2.38 (m, 1H, CH_2), 2.33 – 2.07 (m, 2H, CH_2), 1.70 (d, *J* = 1.2 Hz, 1H, O*H*), 1.34 (s, 3H, CH_3), 1.29 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.7, 128.5, 128.2, 127.0, 113.5, 76.9, 49.9, 32.5, 27.7, 27.6, 21.5, 20.7.
IR (v_{max}, cm^{-1}) 3431 (m), 3061 (w), 3029 (w), 2956 (m), 2858 (m), 1496 (w), 1453 (m), 1364 (m), 1267 (w), 1230 (w), 1182 (w), 1116 (w), 981 (w).
HRMS (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_{15}H_{17}^+$ 197.1325; Found 197.1325.
Stereoselectivity of addition was deduced based on the previous reports of addition of carbon-based nucleophiles to this ketone.[14]

***cis*-1-(3,3-Dimethylcycloprop-1-en-1-yl)-2-phenethylcyclobutan-1-ol (1w)**



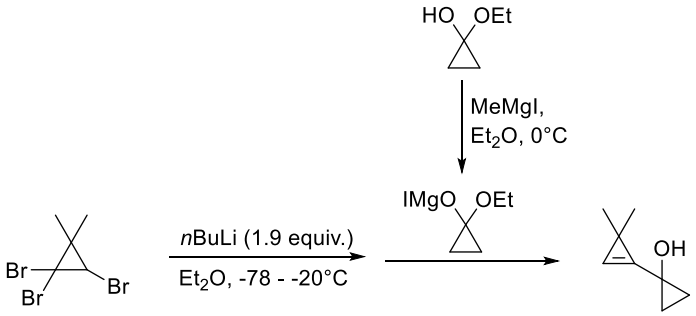
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and 2-phenethylcyclobutan-1-one[13] (697 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a yellow oil (633 mg, 2.61 mmol, 65% yield).
Rf (5% Et_2O/Pentane) = 0.28.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (m, 2H, Ar*H*), 7.18 (m, 3H, Ar*H*), 6.93 (s, 1H, C=C*H*), 2.59 (m, 2H, ArCH_2), 2.51 – 2.39 (m, 1H, C*H*), 2.32 – 2.15 (m, 2H, CH_2), 2.07 – 1.91 (m, 2H, CH_2), 1.87 – 1.74 (m, 2H, CH_2), 1.74 – 1.62 (m, 1H, CH_2), 1.24 (s, 3H, CH_3), 1.21 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 138.3, 128.4, 128.3, 125.7, 111.6, 75.3, 45.0, 33.6, 33.4, 31.2, 27.5, 21.5, 20.7 (one carbon is not resolved).
IR (v_{max}, cm^{-1}) 3409 (m), 3027 (m), 2936 (s), 2856 (m), 1497 (m), 1451 (m), 1364 (m), 1267 (w), 1235 (w), 1180 (m), 1116 (m), 982 (w).
HRMS (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_{17}H_{21}^+$ 225.1638; Found 225.1635.
Stereoselectivity of addition was deduced based on the previous reports of addition of carbon-based nucleophiles to this ketone.[15]

***rel*-(1R,6R,7R)-7-(3,3-Dimethylcycloprop-1-en-1-yl)bicyclo[4.2.0]octan-7-ol (1x)**



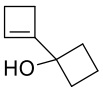
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and bicyclo[4.2.0]octan-7-one[16] (497 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as an amorphous white solid (537 mg, 2.79 mmol, 70% yield).
Rf (10% Et_2O/Pentane) = 0.67.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H, C=C*H*), 2.45 – 2.21 (m, 3H, CH_2 & C*H*), 2.11 (m, 1H, C*H*), 1.96 (s, 1H, O*H*), 1.90 – 1.76 (m, 1H, CH_2), 1.76 – 1.66 (m, 2H, CH_2), 1.65 – 1.30 (m, 4H, CH_2), 1.28 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.18 – 1.02 (m, 1H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 110.9, 72.6, 43.5, 37.1, 27.6, 27.5, 25.8, 23.7, 22.7, 21.8, 21.7, 21.3.
IR (v_{max}, cm^{-1}) 3345 (m), 2932 (s), 2855 (m), 1451 (m), 1364 (m), 1229 (m), 1156 (m), 1076 (m), 1027 (w), 975 (w), 717 (m)-
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M - H]^+$ Calcd for $C_{13}H_{19}O^+$ 191.1430; Found 191.1430.
Stereoselectivity of addition was deduced based on the previous reports of addition of carbon-based nucleophiles to this ketone.[17]

3',3'-Dimethyl-[1,1'-bi(cyclopropan)]-1'-en-1-ol (1y)



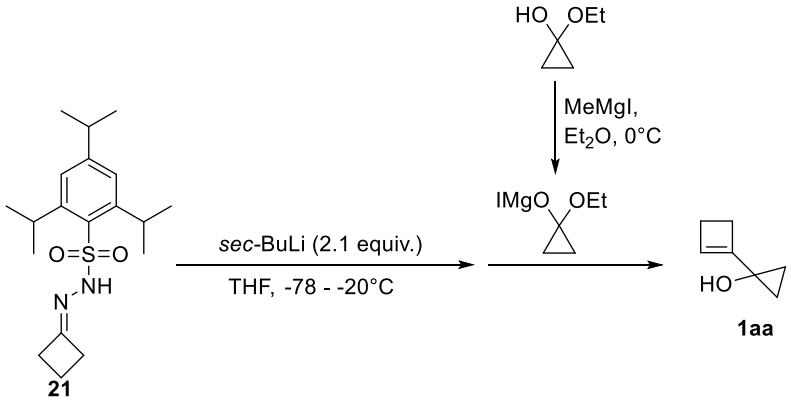
Under N_2 atmosphere: To a solution of 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (3.07 g, 10.0 mmol, 1.00 equiv.) in Et_2O (30 mL), cooled to -78 °C, a solution of *n*BuLi (2.5M in hexanes, 7.6mL, 1.90 equiv.) was added dropwise. The reaction mixture was warmed to -20 °C and stirred at that temperature for 1 h. Concurrently, in a separate flask, to a solution of 1-ethoxycyclopropan-1-ol[18] (817 mg, 8.00 mmol, 0.8 equiv.) in Et_2O, cooled to 0 °C, a solution of MeMgI (3 M in Et_2O, 2.66 mL, 8.00 mmol, 0.80 equiv.) was added dropwise. The mixture was stirred for 10 min at 0 °C. The above cyclopropenyllithium solution was transferred into the second flask with the syringe. The reaction mixture was stirred at r.t. overnight. Water (20 mL) was added. The layers were separated, the aqueous layer was extracted with Et_2O (20 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. This crude was purified by column chromatography (gradient 3-24% Et_2O/Pentane) to give 3',3'-dimethyl-[1,1'-bi(cyclopropan)]-1'-en-1-ol **1y** (297 mg, 2.39 mmol, 30% yield) as a light-yellow oil.
Rf (10% Et_2O/Pentane) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H, C=C*H*), 2.35 (s, 1H, O*H*), 1.26 – 1.19 (m, 2H, CH_2), 1.15 (s, 6H, 2xCH_3), 1.00 – 0.92 (m, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 111.0, 53.7, 27.1, 21.0, 16.4.
IR (ν_{max}, cm^{-1}) 3294 (m), 2962 (m), 2932 (s), 2858 (m), 1764 (m), 1451 (m), 1413 (m), 1364 (m), 1249 (s), 1020 (m), 979 (s), 867 (w), 838 (m).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_8H_{13}O^+$ 125.0961; Found 125.0956.

[1,1'-Bi(cyclobutan)]-1'-en-1-ol (1z)



Following the GP4, starting from N'-cyclobutylidene-2,4,6-triisopropylbenzenesulfonohydrazide **21** (351 mg, 1.00 mmol, 1.00 equiv.) and cyclobutanone (140 mg, 2.00 mmol, 2.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 4-40% Et_2O/Pentane) as a yellow oil (45 mg, 0.36 mmol, 36% yield).
Rf (20% Et_2O/Pentane) = 0.44.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (s, 1H, C=C*H*), 2.60 – 2.54 (m, 2H, CH_2), 2.39 – 2.33 (m, 2H, CH_2), 2.27 (m, 2H, CH_2), 2.11 (m, 2H, CH_2), 1.88 – 1.70 (m, 2H, CH_2 & O*H*), 1.63 – 1.47 (m, 1H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 126.0, 73.4, 34.8, 27.5, 25.4, 12.4.
IR (ν_{max}, cm^{-1}) 3349 (m), 2939 (s), 2871 (m), 2842 (m), 1714 (m), 1670 (m), 1246 (s), 1141 (s), 1076 (m), 961 (w), 903 (w), 857 (m), 752 (w).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_8H_{12}O^+$ 124.0883; Found 124.0880.

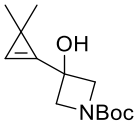
1-(Cyclobut-1-en-1-yl)cyclopropan-1-ol (1aa)



Under N_2 atmosphere: To a solution of N'-cyclobutylidene-2,4,6-triisopropylbenzenesulfonohydrazide **21** (1.51 g, 4.31 mmol, 1.00 equiv.) in THF (12 mL), cooled to -78 °C, a solution of *sec*-BuLi (1.4 M in cyclohexane, 6.46 mL, 9.05 mmol, 2.10 equiv.) was added dropwise. The reaction mixture was stirred at -78 °C for 15 min, then at -20 °C for 45 min. Concurrently, in a separate flask, to a solution of 1-ethoxycyclopropan-1-ol[14] (397 mg, 3.88 mmol, 0.90 equiv.) in Et_2O, cooled to 0 °C, a solution of MeMgI (3 M in Et_2O, 1.29 mL, 3.88 mmol, 0.90 equiv.) was added dropwise. The mixture was stirred for 10 min at 0 °C. The above cyclobutenyllithium solution was

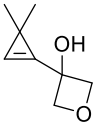
transferred into the second flask with the syringe. The reaction mixture was stirred at r.t. overnight. Water (20 mL) was added. The layers were separated, the aqueous layer was extracted with Et_2O (20 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product. This crude was purified by column chromatography (gradient 4-40% Et_2O/Pentane) to give 1-(cyclobut-1-en-1-yl)cyclopropan-1-ol **1aa** (69 mg, 0.62 mmol, 16% yield) as a yellow oil.
Rf (20% Et_2O/Pentane) = 0.54.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (s, 1H, C=C*H*), 2.39 – 2.28 (m, 4H, C*H*$_2$), 2.05 (s, 1H, O*H*), 1.01 – 0.92 (m, 2H, C*H*$_2$), 0.85 – 0.75 (m, 2H, C*H*$_2$).
Spectral data was consistent with the values reported in literature.[19]

***tert*-Butyl 3-(3,3-dimethylcycloprop-1-en-1-yl)-3-hydroxyazetidine-1-carboxylate (1ab)**



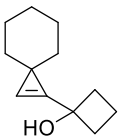
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and oxetan-3-one (288 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 10-100% Et_2O/Pentane) as an amorphous white solid (853 mg, 3.56 mmol, 89% yield).
Rf (50% Et_2O/Pentane) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H, C=C*H*), 4.07 (s, 4H, C*H*$_2$N), 2.37 (s, 1H, O*H*), 1.46 (s, 9H, C(C*H*$_3$)$_3$), 1.26 (s, 6H, C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 135.4, 116.0, 79.9, 68.7, 62.2, 28.4, 27.3, 22.5.
IR (ν_{max}, cm^{-1}) 3359 (m), 2973 (s), 1757 (w), 1675 (s), 1413 (s), 1367 (s), 1249 (m), 1159 (s), 1073 (s), 856 (m), 772 (m).
HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{21}NNaO_3^+$ 262.1414; Found 262.1406.

3-(3,3-Dimethylcycloprop-1-en-1-yl)oxetan-3-ol (1ac)



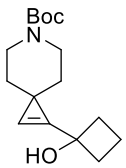
Following the GP3, starting from 1,1,3-tribromo-2,2-dimethylcyclopropane **18a** (1.53 g, 5.00 mmol) and tert-butyl 3-oxoazetidine-1-carboxylate (685 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 10-100% Et_2O/Pentane) as an amorphous white solid (486 mg, 3.56 mmol, 89% yield).
Rf (50% Et_2O/Pentane) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H, C=C*H*), 4.82 (d, *J* = 7.1 Hz, 2H, C*H*$_2$O), 4.74 (d, *J* = 6.5 Hz, 2H, C*H*$_2$O), 2.40 (s, 1H, O*H*), 1.30 (s, 6H, C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8, 116.3, 83.1, 73.3, 27.3, 22.4.
IR (ν_{max}, cm^{-1}) 3377 (m), 2962 (s), 2878 (s), 1757 (m), 1452 (m), 1372 (m), 1318 (m), 1269 (m), 1234 (m), 1137 (m), 1044 (m), 974 (s), 917 (m), 857 (m), 725 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_8H_{13}O_2^+$ 141.0910; Found 141.0910.

1-(Spiro[2.5]oct-1-en-1-yl)cyclobutan-1-ol (3a)



Following the GP3, starting from 1,1,2-tribromospiro[2.5]octane **18c** (1.73 g, 5.00 mmol) and cyclobutanone (280 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 3-30% Et_2O/Pentane) as an amorphous white solid (627 mg, 3.52 mmol, 88% yield).
Rf (15% Et_2O/Pentane) = 0.36.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 1H, C=C*H*), 2.39 – 2.20 (m, 4H, C*H*$_2$), 2.10 (s, 1H, O*H*), 1.89 – 1.69 (m, 2H, C*H*$_2$), 1.66 – 1.43 (m, 8H, C*H*$_2$), 1.43 – 1.35 (m, 2H, C*H*$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 111.1, 73.7, 38.9, 36.3, 29.6, 26.9, 26.7, 12.4.
IR (ν_{max}, cm^{-1}) 3335 (m), 2986 (m), 2925 (s), 2850 (m), 1443 (m), 1249 (m), 1163 (m), 1116 (m), 961 (w), 716 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}O^+$ 179.1430; Found 179.1430.

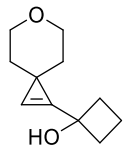
***tert*-Butyl 1-(1-hydroxycyclobutyl)-6-azaspiro[2.5]oct-1-ene-6-carboxylate (3b)**



Following the GP3, starting from *tert*-butyl 1,1,2-tribromo-6-azaspiro[2.5]octane-6-carboxylate **18d** (896 mg, 2.00 mmol) and cyclobutanone (112 mg, 1.60 mmol) the title compound was obtained after a purification by chromatography (gradient 7-60% Et_2O/Pentane) as an amorphous white solid (299 mg, 1.07 mmol, 54% yield).
Rf (25% Et_2O/Pentane) = 0.17.

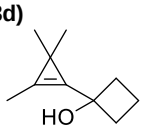
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H, C=C*H*), 3.71 – 3.63 (m, 2H, CH_2N), 3.33 (m, 2H, CH_2N), 2.32 (m, 2H, CH_2), 2.29 – 2.16 (m, 2H, CH_2), 2.11 (s, 1H, O*H*), 1.96 – 1.79 (m, 1H, CH_2), 1.78 – 1.63 (m, 3H, CH_2), 1.47 (s, 9H, C(CH_3)$_3$), 1.45 – 1.33 (m, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 138.0, 109.9, 79.3, 73.4, 44.7, 37.8, 36.4, 28.5, 27.3, 12.4.
IR (v_{max}, cm^{-1}) 3430 (w), 2980 (m), 2939 (m), 1666 (s), 1476 (m), 1426 (s), 1366 (m), 1242 (s), 1167 (s), 1113 (s), 989 (m), 961 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{25}NNaO_3^+$ 302.1727; Found 302.1724.

1-(6-Oxaspiro[2.5]oct-1-en-1-yl)cyclobutan-1-ol (3c)



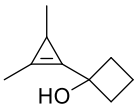
Following the GP3, starting from 1,1,2-tribromo-6-oxaspiro[2.5]octane **18e** (1.74 g, 5.00 mmol) and cyclobutanone (280 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 8-80% Et_2O/Pentane) as an amorphous white solid (502 mg, 2.79 mmol, 70% yield).
Rf (40% Et_2O/Pentane) = 0.31.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H, C=C*H*), 3.84 (m, 2H, CH_2O), 3.74 (m, 2H, CH_2O), 2.48 – 2.29 (m, 2H, CH_2), 2.26 (m, 2H, CH_2), 2.11 (s, 1H, O*H*), 1.93 – 1.70 (m, 4H, CH_2), 1.44 (m, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 109.8, 73.4, 68.7, 38.9, 36.4, 26.4, 12.4.
IR (v_{max}, cm^{-1}) 3393 (m), 2937 (s), 2846 (m), 1429 (m), 1383 (m), 1307 (m), 1246 (m), 1234 (m), 1159 (s), 1094 (s), 1004 (m), 964 (m), 838 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H_{-1}O_{-1}]^+$ Calcd for $C_{11}H_{15}O^+$ 163.1117; Found 163.1115.

1-(2,3,3-Trimethylcycloprop-1-en-1-yl)cyclobutan-1-ol (3d)



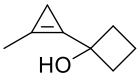
Following the GP3, starting from 1,1,2-tribromo-2,3,3-trimethylcyclopropane **18b** (1.60 g, 5.00 mmol) and cyclobutanone (280 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 3-30% Et_2O/Pentane) as an amorphous white solid (481 mg, 3.16 mmol, 79% yield).
Rf (15% Et_2O/Pentane) = 0.39.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (m, 4H, CH_2), 2.04 (s, 3H, CH_3), 2.02 (s, 1H, O*H*), 1.84 – 1.61 (m, 2H, CH_2), 1.18 (s, 6H, 2x CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 126.3, 119.7, 74.4, 36.9, 25.7, 21.9, 12.4, 8.6.
IR (v_{max}, cm^{-1}) 3324 (s), 2940 (s), 2854 (s), 1861 (w), 1440 (s), 1364 (m), 1274 (m), 1246 (s), 1177 (m), 1141 (s), 1106 (s), 958 (m), 824 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H_{-1}]^+$ Calcd for $C_{10}H_{15}O^+$ 151.1117; Found 151.1117.

1-(2,3-Dimethylcycloprop-1-en-1-yl)cyclobutan-1-ol (3e)



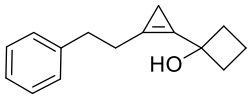
Following the GP3, starting from 1,1,2-tribromo-2,3-dimethylcyclopropane **18f** (1.53 g, 5.00 mmol) and cyclobutanone (280 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a colorless oil (486 mg, 3.52 mmol, 88% yield).
Rf (10% Et_2O/Pentane) = 0.38.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 – 2.19 (m, 4H, CH_2), 2.09 (s, 3H, CH_3), 2.04 (s, 1H, O*H*), 1.90 – 1.66 (m, 2H, CH_2), 1.62 (q, *J* = 4.6 Hz, 1H, C*H*), 1.09 (d, *J* = 4.5 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 120.7, 114.4, 73.5, 36.6, 36.4, 20.6, 16.1, 12.5, 9.9.
IR (v_{max}, cm^{-1}) 3312 (m), 2987 (m), 2942 (s), 2914 (m), 2889 (m), 2854 (m), 1863 (m), 1441 (m), 1424 (m), 1370 (m), 1349 (m), 1245 (s), 1133 (s), 1091 (m), 958 (m), 814 (m).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_9H_{15}O^+$ 139.1117; Found 139.1116.

1-(2-Methylcycloprop-1-en-1-yl)cyclobutan-1-ol (3f)



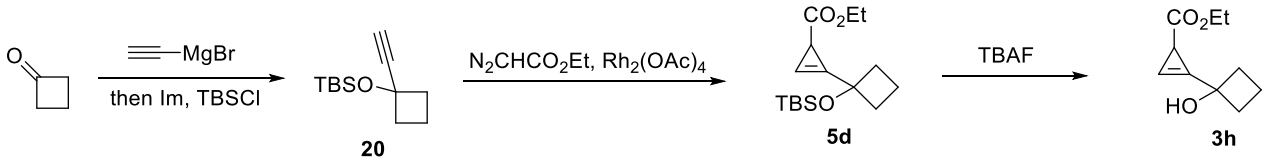
Following the GP3, starting from 1,1,2-tribromo-2-methylcyclopropane **18g** (1.46 g, 5.00 mmol) and cyclobutanone (280 mg, 4.00 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (213 mg, 1.72 mmol, 43% yield).
Rf (10% Et_2O/Pentane) = 0.18.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 – 2.20 (m, 4H, CH_2), 2.17 (s, 3H, CH_3), 2.11 (s, 1H, O*H*), 1.89 – 1.60 (m, 2H, CH_2), 1.07 (s, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 112.6, 107.0, 72.5, 36.0, 12.6, 11.2, 8.5.
IR (v_{max}, cm^{-1}) 3331 (m), 2970 (s), 2940 (s), 2865 (s), 1874 (w), 1443 (m), 1256 (m), 1132 (s), 1025 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_8H_{13}O^+$ 125.0961; Found 125.0960.

1-(2-Phenethylcycloprop-1-en-1-yl)cyclobutan-1-ol (3g)



Following the GP3, starting from (2-(1,2,2-tribromocyclopropyl)ethyl)benzene **18h** (913 mg, 2.38 mmol) and cyclobutanone (133 mg, 1.90 mmol) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (350 mg, 1.63 mmol, 86% yield).
Rf (10% Et_2O/Pentane) = 0.22.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H, Ar*H*), 7.26 – 7.19 (m, 3H, Ar*H*), 2.94 (m, 2H, ArCH_2), 2.89 – 2.81 (m, 2H, CH_2), 2.30 – 2.16 (m, 4H, CH_2), 1.82 (s, 1H, O*H*), 1.81 – 1.71 (m, 1H, CH_2), 1.62 (m, 1H, CH_2), 1.10 (s, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 128.4, 128.3, 126.1, 113.3, 109.8, 72.4, 35.8, 33.4, 27.5, 12.5, 8.0.
IR (ν_{max}, cm^{-1}) 3341 (m), 2942 (s), 2866 (s), 1868 (w), 1496 (m), 1451 (m), 1245 (s), 1133 (s), 1067 (s), 1011 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O^+$ 215.1430; Found 215.1427.

Ethyl 2-(1-hydroxycyclobutyl)cycloprop-2-ene-1-carboxylate (3h)



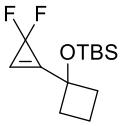
Under N_2 atmosphere: To a solution of ethynylmagnesium bromide (0.5 M in THF, 200 mL, 100 mmol, 1.30 equiv.), cooled to 0 °C, cyclobutanone (5.40 g, 76.9 mmol, 1.00 equiv.) was added dropwise. The reaction mixture was stirred at r.t. for 2 h. Saturated aqueous NH_4Cl (100 mL) was added. The mixture was extracted with Et_2O (2x100 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give 1-ethynylcyclobutan-1-ol (6.88 g, 71.6 mmol, 93% yield) as a brown oil. This product was used without further purification.
To the solution of 1-ethynylcyclobutan-1-ol (6.88 g, 71.6 mmol, 1.00 equiv.) in DCM (250 mL) imidazole (6.35 g, 93.1 mmol, 1.30 equiv.) was added, followed by *tert*-butyldimethylsilyl chloride (15.5 g, 85.9 mmol, 1.20 equiv.) in DCM (20 mL). The reaction mixture was stirred at r.t. overnight. Saturated aqueous $NaHCO_3$ (100 mL) was added. The layers were separated, the aqueous layer was extracted with DCM (50 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. This crude was purified by column chromatography (Pentane), to give *tert*-butyl(1-ethynylcyclobutoxy)dimethylsilane **20** (15.1 g, 72.0 mmol, 100% yield) as a colorless oil.
Rf (Pentane) = 0.77.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 1H, C*H*), 2.39 (m, 2H, CH_2), 2.22 (m, 2H, CH_2), 1.87 – 1.66 (m, 2H, CH_2), 0.89 (s, 9H, C(CH_3)$_3$), 0.14 (s, 6H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 88.5, 71.0, 68.2, 40.1, 25.7, 17.8, 12.9, -3.5.
IR (ν_{max}, cm^{-1}) 2957 (m), 2933 (m), 2888 (w), 2859 (m), 2114 (w), 1468 (w), 1249 (s), 1168 (m), 1140 (s), 990 (m), 913 (w), 877 (m), 835 (s), 776 (s).
HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{23}OSi^+$ 211.1513; Found 211.1523.

Under N_2 atmosphere: To a suspension of rhodium (II) acetate dimer (8.84 mg, 0.0200 mmol, 0.01 equiv.) in *tert*-butyl(1-ethynylcyclobutoxy)dimethylsilane (1.26 g, 6.00 mmol, 3 equiv.) a solution of ethyl diazoacetate (228 mg, 2.00 mmol, 1.00 equiv.) in DCM (8 mL) was added dropwise over 10 h using syringe pump. The reaction mixture was stirred for another 4 h. The reaction mixture was filtered through a short pad of silica gel (1cm). The sorbent was washed with DCM (20 mL). The mother liquor was concentrated under vacuum to give the crude product. This crude was purified by column chromatography (gradient 1-10% Et_2O/Pentane) to give ethyl 2-(1-((*tert*-butyldimethylsilyl)oxy)cyclobutyl)cycloprop-2-ene-1-carboxylate **5d** (329 mg, 1.11 mmol, 55% yield).
Rf (5% Et_2O/Pentane) = 0.49.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (d, *J* = 1.4 Hz, 1H, C=C*H*), 4.15 (qd, *J* = 7.1, 2.5 Hz, 2H, OCH_2), 2.40 (d, *J* = 1.5 Hz, 1H, C*H*), 2.38 – 2.25 (m, 4H, CH_2), 1.81 – 1.66 (m, 2H, CH_2), 1.25 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 0.90 (s, 9H, C(CH_3)$_3$), 0.09 (s, 3H, SiCH_3), 0.08 (s, 3H, SiCH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 119.0, 94.2, 73.5, 60.3, 37.5, 37.0, 25.7, 21.9, 17.9, 14.4, 13.1, -3.2, -3.3.
IR (ν_{max}, cm^{-1}) 2956 (m), 2896 (w), 2863 (m), 1726 (s), 1469 (w), 1368 (w), 1338 (m), 1256 (s), 1181 (s), 1146 (s), 1033 (m), 992 (m), 838 (s), 779 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{29}O_3Si^+$ 297.1880; Found 297.1880.

To a solution of ethyl 2-(1-((*tert*-butyldimethylsilyl)oxy)cyclobutyl)cycloprop-2-ene-1-carboxylate (1.00 g, 3.37 mmol, 1.00 equiv.) in THF (10 mL) a solution of TBAF (1 M in THF, 3.54 mL, 3.54 mmol, 1.05 equiv.) was added. The reaction mixture was stirred at r.t. for 2 h. Water (10 mL) was added. The mixture was extracted with Et_2O (2x10 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under vacuum to give crude product. This crude was purified by column chromatography (gradient 8-80% Et_2O/Pentane) to give ethyl 2-(1-hydroxycyclobutyl)cycloprop-2-ene-1-carboxylate **3h** (449 mg, 2.46 mmol, 73% yield) as a yellow oil.
Rf (40% Et_2O/Pentane) = 0.22.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, *J* = 1.4 Hz, 1H, C=C*H*), 4.16 (qd, *J* = 7.1, 4.0 Hz, 2H, OCH_2), 2.50 (s, 1H, O*H*), 2.48 – 2.40 (m, 2H, CH_2), 2.38 – 2.27 (m, 3H, CH_2), 1.83 (m, 1H, C*H*), 1.70 (m, 1H, CH_2), 1.27 (t, *J* = 7.1 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 118.2, 94.9, 71.8, 60.6, 35.9, 35.5, 21.1, 14.3, 12.5.

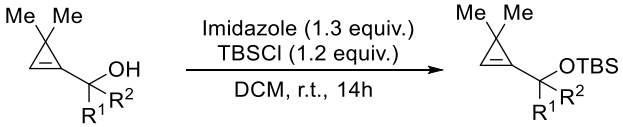
IR (v_{max}, cm^{-1}) 3420 (m), 2989 (m), 2940 (m), 2879 (w), 1833 (m), 1772 (m), 1698 (s), 1381 (m), 1260 (s), 1195 (s), 1112 (s), 1026 (m), 957 (m), 741 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}NaO_3^+$ 205.0835; Found 205.0831.

***tert*-Butyl(1-(3,3-difluorocycloprop-1-en-1-yl)cyclobutoxy)dimethylsilane (3i)**



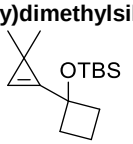
Under N_2 atmosphere: A solution of NaI (525 mg, 3.50 mmol, 0.350 equiv.) and *tert*-butyl(1-ethynylcyclobutoxy)dimethylsilane **20** (2.10 g, 10.0 mmol, 1.00 equiv.) in THF (15 mL) was heated to reflux. CF_3SiMe_3 (4.98 g, 35.0 mmol, 3.50 equiv.) was added dropwise over 12–16 h at this temperature. The reaction mixture was heated for another 4 hours. The solvent was evaporated under vacuum, the residue was diluted with CH_2Cl_2 (50 mL), the precipitate was filtered off, and the combined filtrates were evaporated under vacuum to give crude product. This crude was purified by column chromatography (Pentane) to give *tert*-Butyl(1-(3,3-difluorocycloprop-1-en-1-yl)cyclobutoxy)dimethylsilane **3i** (1.15 g, 4.42 mmol, 44% yield) as a red oil.
Rf (Pentane) = 0.26.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 2.0 Hz, 1H, C=C*H*), 2.44 – 2.29 (m, 4H, CH_2), 1.92 – 1.77 (m, 2H, CH_2), 0.91 (s, 9H, C(CH_3)$_3$), 0.09 (s, 6H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5 (t, *J* = 10.7 Hz), 114.0 (t, *J* = 11.8 Hz), 102.3 (t, *J* = 269.9 Hz), 72.9, 37.9, 25.6, 17.8, 12.5, -3.2.
IR (v_{max}, cm^{-1}) 2961 (m), 2934 (m), 2859 (m), 1720 (w), 1473 (m), 1310 (s), 1265 (s), 1161 (s), 1033 (s), 996 (m), 973 (m), 910 (m), 883 (m), 835 (s), 777 (s).
HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{22}F_2NaOSi^+$ 283.1300; Found 283.1287.

General procedure 5 (GP5). TBS protection of cyclopropenylcarbinols



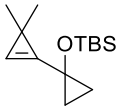
To a solution of alcohol (1 equiv.) in DCM (5 mL/mmol of alcohol) imidazole (1.3 equiv.) was added, followed by solution of *tert*-butyldimethylsilyl chloride (1.2 equiv.) in DCM (1mL/mmol of alcohol). The reaction mixture was stirred at r.t. overnight. Saturated aqueous $NaHCO_3$ was added. The layers were separated, the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. This crude was purified by column chromatography.

tert-Butyl(1-(3,3-dimethylcycloprop-1-en-1-yl)cyclobutoxy)dimethylsilane (5a)



Following the GP5, starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)cyclobutan-1-ol **1a** (735 mg, 5.32 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (Pentane) as a colorless oil (962 mg, 3.81 mmol, 72% yield).
Rf (Pentane) = 0.66.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H, C=C*H*), 2.42 – 2.25 (m, 2H, CH_2), 2.21 (m, 2H, CH_2), 1.82 – 1.69 (m, 2H, CH_2), 1.25 (s, 6H, 2xCH_3), 0.91 (s, 9H, C(CH_3)$_3$), 0.06 (s, 6H, 2xSiCH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 111.0, 75.8, 38.0, 27.5, 25.9, 21.5, 18.0, 12.8, -3.0.
IR (v_{max}, cm^{-1}) 2957 (m), 2935 (m), 2889 (m), 2858 (m), 1753 (w), 1468 (m), 1363 (w), 1253 (s), 1175 (s), 1141 (s), 997 (s), 900 (s), 836 (s), 777 (s).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{29}OSi^+$ 253.1982; Found 253.1989.

***tert*-Butyl((3',3'-dimethyl-[1,1'-bi(cyclopropan)]-1'-en-1-yl)oxy)dimethylsilane (5b)**



Following the GP5, starting from 3',3'-dimethyl-[1,1'-bi(cyclopropan)]-1'-en-1-ol **1y** (240 mg, 1.95 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (Pentane) as a colorless oil (352 mg, 1.47 mmol, 76% yield).
Rf (Pentane) = 0.67.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 1H, C=C*H*), 1.16 – 1.07 (m, 8H, 2x CH_3 & CH_2), 0.92 (m, 2H, CH_2), 0.87 (s, 9H, C(CH_3)$_3$), 0.13 (s, 6H, 2xSiCH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 110.7, 54.7, 27.1, 25.7, 20.8, 17.7, 16.9, -3.7.
IR (v_{max}, cm^{-1}) 2959 (m), 2933 (m), 2859 (m), 1472 (w), 1363 (w), 1255 (s), 1040 (s), 886 (m), 838 (s), 779 (s).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{27}OSi^+$ 239.1826; Found 239.1827.

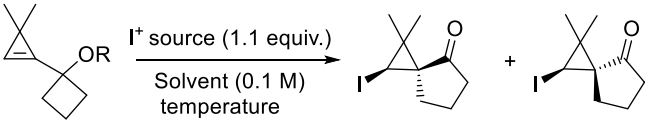
Optimization studies

Reaction of 1a with diverse electrophiles.[a]

Entry	Reagent	X	Yield	dr[b]
1	CSA	H	-	-
2	Selectfluor	F	-	-
3	NBS	Br	-	-
4	PhSCl	PhS	53	67:33
5	NIS	I	56	79:21

All reactions were run starting from 0.2 mmol of cyclopropene. The reagent (1.1 – 1.2 equiv.) was added to a solution of **1a** (0.20 mmol, 1.0 equiv.) in DCM or MeCN (0.1 M). The reaction was stirred at rt until **1a** was consumed (TLC). The reaction mixture was concentrated and analyzed by ^{1}H NMR.

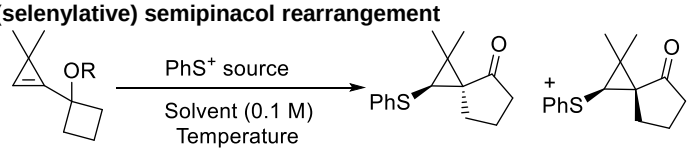
Optimization of iodinative semipinacol rearrangement



All reactions were run starting from 0.2 mmol of cyclopropene. After competion of the reaction (checked by TLC), the reaction mixture was filtered through a pad of silica gel and concentrated under vacuum. Then, NMR yield and *dr* were measured using $CDCl_3$ as a solvent and CH_2Br_2 as an internal standard by integration of C*H*I peaks (2.94 ppm – major isomer, 3.39 ppm - minor isomer)

I^+ source	R	Solvent	Temperature	NMR yield	dr
NIS	H	MeCN	0°C	56%	79:21
NIS	H	MeCN	-20°C	72%	85:15
NIS	H	MeCN	-40°C	80%	88:12
PhthNI	H	MeCN	-40°C	74%	88:12
$I(coll)_2PF_6$	H	MeCN	-40°C	77%	83:17
NIS	TMS	MeCN	-40°C	50%	79:21
NIS	TBS	MeCN	-40°C	65%	72:28
NIS	H	Acetone	-78°C	78%	82:18
NIS	H	$MeNO_2$	-20°C	80%	86:14
NIS (1 equiv.)	H	MeCN	-40°C	70%	88:12

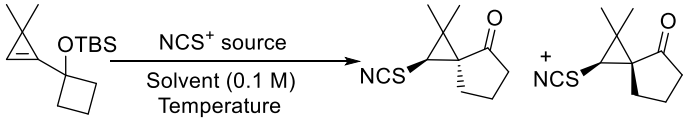
Optimization of sulfenylative (selenylative) semipinacol rearrangement

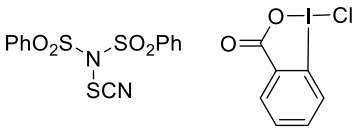


All reactions were run starting from 0.2 mmol of cyclopropene. After completion of the reaction (checked by TLC), the reaction mixture was concentrated under vacuum. Then, NMR yield and *dr* were measured using $CDCl_3$ as a solvent and CH_2Br_2 as an internal standard by integration of C*H*S peaks (2.49 ppm – major isomer, 2.89 ppm – minor isomer)

PhS$^+$ source	R	Solvent	Temperature	NMR yield	dr
PhSCl (1.1 equiv.)	H	MeCN	20°C	56%	67:33
Ph_2S_2 (0.7 equiv.) + SO_2Cl_2 (0.6 equiv.)	H	MeCN	-40°C	65%	91:9
Ph_2S_2 (0.7 equiv.) + SO_2Cl_2 (0.6 equiv.)	TMS	MeCN	-40°C	69%	97:3
Ph_2S_2 (0.7 equiv.) + SO_2Cl_2 (0.6 equiv.)	TBS	MeCN	-40°C	71%	98:2
Ph_2S_2 (0.7 equiv.) + SO_2Cl_2 (0.6 equiv.)	TBS	DCM	-78°C	88%	95:5
Ph_2S_2 (0.7 equiv.) + SO_2Cl_2 (0.6 equiv.)	TBS	Acetone	-78°C	43%	95:5
Ph_2S_2 (0.7 equiv.) + SO_2Cl_2 (0.6 equiv.)	TBS	$MeNO_2$	-20°C	44%	77:23
PhSeCl (1.1 equiv.)	TBS	DCM	-78°C	89%	>99:1

Optimization of thiocyanative semipinacol rearrangement



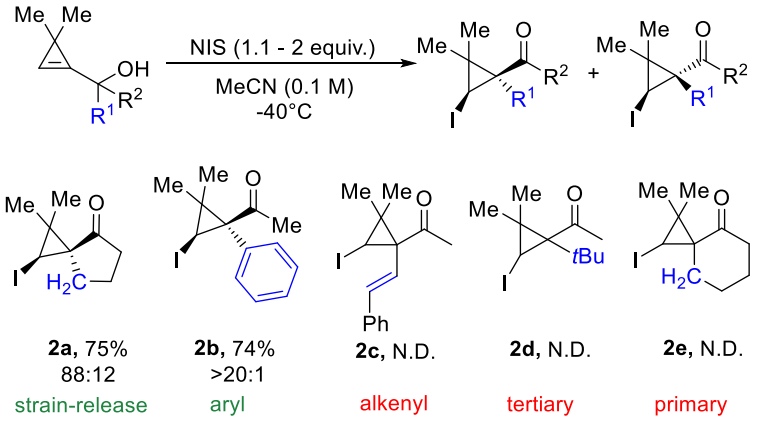


A B

All reactions were run starting from 0.2 mmol of cyclopropene. After completion of the reaction (checked by TLC), the reaction mixture was filtered through a pad of silica gel and concentrated under vacuum. Then, NMR yield and *dr* were measured using $CDCl_3$ as a solvent and CH_2Br_2 as an internal standard by integration of C*H*S peaks (3.03 ppm – major iomer, 2.64 ppm – minor isomer)

NCS$^+$ source	Solvent	Temperature	NMR yield	dr
A + AcCl (1.3 equiv.)	DCM	-78°C to r.t.	25%	40:60
A + AcCl (1.3 equiv.)	MeCN	-40°C to r.t.	57%	46:54
B + TMSNCS (1.2 equiv.)	DCM	-78°C	84%	42:58
B + TMSNCS (1.2 equiv.)	MeCN	-40°C	54%	39:61
B + TMSNCS (1.2 equiv.)	AcMe	-78°C	-	-
B+ TMSNCS (1.2 equiv.)	$CHCl_3$	-60°C	20%	66:34

Examination of diverse migrating groups in the iodinative semipinacol rearrangement



Comments on unsuccessful reactions:

Substrate **2c**:

Full conversion was observed after 2 h of reaction with NIS (2 euiv.) at -40°C. During the standard workup procedure (extraction), the organic layer became very dark. Upon concentration, black oil was obtained that show very complex mixture of unidentifiable products by ^{1}H NMR. Similar behavior was observed when other cyclopropyl iodides made in this study were heated over 40-50°C for a prolonged time. Therefore, we can conclude that the product of alkenyl group migration posess even lower thermal stability and is impossible to isolate.

Substrate **2d**:

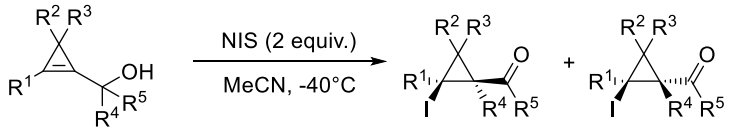
Full conversion was observed after 14 h of reaction with NIS (2 euiv.) at -40°C. After standard workup, ^{1}H NMR analysis of the crude showed the mixture of products with a variety of peaks in the region 4.8 – 6.9 ppm. We assumed that electrocyclic ring-opening took place giving mixtures of alkene products. No product peak could be seen (typically ca 2.9 ppm for CH-I), therefore no isolation was done.

Substrate **2e**:

Same as **2d** but the reaction time is lower (3h).

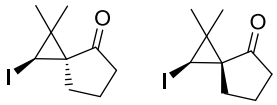
Electrophile-induced semipinacol rearrangement of cyclopropenylcarbinols

General procedure 6 (GP6). Iodinative semipinacol rearrangement of cyclopropenylcarbinols.



To a solution of alcohol (0.30 mmol, 1.00 equiv.) in MeCN (3 mL), cooled to -40 °C, N-iodosuccinimide (0.60 mmol, 2.00 equiv.) was added all at once. The reaction mixture was stirred at -40 °C until all the alcohol was consumed (checked by TLC). The reaction mixture was poored into saturated aqueous $Na_2S_2O_3$ (10 mL), extracted with Et_2O (2x10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum to give the crude product. At this point, NMR analysis of the crude mixture was taken to estimate the *dr* value by integration of C*H*I peaks. Only one diastereoisomer was formed if the *dr* was not specified. The crude product was purified by column chromatography.

***rel*-(2S,3S)-2-Iodo-1,1-dimethylspiro[2.4]heptan-4-one and *rel*-(2S,3R)-2-iodo-1,1-dimethylspiro[2.4]heptan-4-one (2a and 2a')**



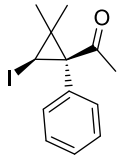
The title compounds were prepared, following the GP6 (1.1 equiv. of NIS was used), starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)cyclobutan-1-ol **1a** (41.5 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 88:12 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 3-30% Et_2O/Pentane) to give **2a** (52.1 mg, 0.20 mmol, 66% yield) and **2a'** (7.1 mg, 0.027 mmol, 9% yield) as yellow oils. Total yield – 75%.

A gram scale experiment with 1-(3,3-dimethylcycloprop-1-en-1-yl)cyclobutan-1-ol **1a** (1.00 g, 7.24 mmol, 1.00 equiv.) was also accomplished using the same procedure. The *dr* value was determined to be 86:14 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 3-30% Et_2O/Pentane) to give **2a** (1.31 g, 4.96 mmol, 69% yield) and **2a'** (209 mg, 0.791 mmol, 11% yield) as yellow oils. Total yield - 79%.

Characterization data of **2a**:
Rf (15% Et_2O/Pentane) = 0.39.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (s, 1H, C*H*), 2.45 – 2.29 (m, 2H, C*H*$_2$), 2.27 – 2.17 (m, 1H, C*H*$_2$), 1.99 – 1.83 (m, 3H, C*H*$_2$), 1.27 (s, 3H, C*H*$_3$), 1.24 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 40.8, 37.5, 31.9, 31.9, 23.4, 20.3, 20.1, 15.1.
IR (ν_{max}, cm^{-1}) 2957 (m), 2871 (m), 1721 (s), 1457 (m), 1356 (m), 1263 (m), 1166 (m), 1040 (m), 830 (w).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_9H_{14}IO^+$ 265.0084; Found 265.0095.

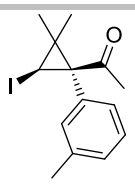
Characterization data of **2a'**:
Rf (10% Et_2O/Pentane) = 0.83.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 1H, C*H*), 2.50 – 2.25 (m, 2H, C*H*$_2$), 2.12 – 1.99 (m, 1H, C*H*$_2$), 1.98 – 1.89 (m, 2H, C*H*$_2$), 1.85 – 1.75 (m, 1H, C*H*$_2$), 1.32 (s, 3H, C*H*$_3$), 1.16 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 215.6, 40.4, 40.2, 33.2, 31.5, 24.5, 20.4, 19.2, 18.5.
IR (ν_{max}, cm^{-1}) 2953 (m), 2873 (w), 1721 (s), 1461 (w), 1408 (w), 1356 (w), 1224 (m), 1166 (s), 1105 (m), 1029 (w), 983 (w), 838 (w).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_9H_{14}IO^+$ 265.0084; Found 265.0095.
The relative configuration of the major diastereomer was assigned based on NOESY experiments.

***rel*-1-((1S,3S)-3-Iodo-2,2-dimethyl-1-phenylcyclopropyl)ethan-1-one (2b)**



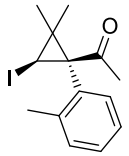
Following the GP6, starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-phenylethan-1-ol **1b** (56.5 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a yellow oil (70 mg, 0.22 mmol, 74% yield).
Rf (5% Et_2O/Pentane) = 0.53.
^{1}H NMR (400 MHz, C_6D_6) δ 7.02 – 6.90 (m, 5H, Ar*H*), 2.86 (s, 1H, C*H*), 1.96 (s, 3H, C*H*$_3$C(O)R), 1.51 (s, 3H, C*H*$_3$), 0.60 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, C_6D_6) δ 201.0, 137.4, 129.4, 128.6, 127.4, 49.3, 28.0, 27.7, 24.9, 23.4, 9.3.
IR (ν_{max}, cm^{-1}) 3234 (m), 2928 (m), 2858 (m), 1954 (w), 1865 (w), 1706 (s), 1618 (m), 1451 (m), 1330 (m), 1238 (m), 1159 (m), 1095 (w), 988 (w), 812 (s).
HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{15}INaO^+$ 337.0060; Found 337.0059.
The relative sterochemistry was confirmed by NOESY experiment.

***rel*-1-((1S,3S)-3-iodo-2,2-dimethyl-1-(m-tolyl)cyclopropyl)ethan-1-one (2f)**



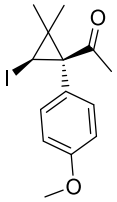
Following the GP6, starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-(m-tolyl)ethan-1-ol **1f** (60.7 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 0-6% Et_2O/Pentane) as a yellow oil (72 mg, 0.22 mmol, 73% yield).
Rf (5% Et_2O/Pentane) = 0.89.
^{1}H NMR (400 MHz, C_6D_6) δ 7.03 – 6.91 (m, 2H, Ar*H*), 6.83 (m, 2H, Ar*H*), 2.93 (s, 1H, C*H*), 2.01 (s, 6H, ArC*H*$_3$ & C*H*$_3$C(O)R), 1.53 (s, 3H, C*H*$_3$), 0.65 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, C_6D_6) δ 201.1, 138.3, 137.3, 130.0, 128.7, 128.3, 126.6, 49.4, 27.9, 27.7, 25.1, 23.4, 20.9, 9.4.
IR (ν_{max}, cm^{-1}) 2961 (m), 2924 (m), 2867 (w), 1706 (s), 1605 (m), 1455 (m), 1354 (m), 1235 (m), 988 (w), 817 (w), 788 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: [M + H]$^+$ Calcd for $C_{14}H_{18}IO^+$ 329.0397; Found 329.0394.
The relative configuration was assigned by analogy to compound **2b**.

***rel*-1-((1S,3S)-3-iodo-2,2-dimethyl-1-(o-tolyl)cyclopropyl)ethan-1-one (2g)**



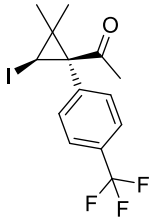
Following the GP6, starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-(o-tolyl)ethan-1-ol **1g** (60.7 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 0-6% Et_2O/Pentane) as a yellow oil (82 mg, 0.25 mmol, 84% yield).
Rf (5% Et_2O/Pentane) = 0.79.
The rotation around one of the C-C bonds is slow on NMR timescale. Therefore two sets of peaks are observed in NMR, which correspond to two rotamers (mixture ca 3.5:1 in CD_2Cl_2 at r.t.). Upon consecutive selective excitation of 2 C*H*I signals (3.25 ppm (major) and 2.94 ppm (minor)) under 1D NOE experiment conditions nearly identical spectra were observed. Therefore, both signals correspond to the same proton (but to different rotamers).
Major rotamer:
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.28 (m, 1H, Ar*H*), 7.28 – 7.13 (m, 3H, Ar*H*), 3.25 (s, 1H, C*H*), 2.25 (s, 3H, ArC*H*$_3$), 1.99 (s, 3H, C*H*$_3$C(O)R), 1.53 (s, 3H, C*H*$_3$), 0.87 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 202.9, 139.2, 136.6, 130.6, 129.9, 127.8, 126.6, 48.4, 29.4, 28.6, 23.8, 22.7, 19.1, 10.6.
Minor rotamer:
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.28 (m, 1H, Ar*H*), 7.28 – 7.13 (m, 3H, Ar*H*), 2.94 (s, 1H, C*H*), 2.35 (s, 3H, ArC*H*$_3$), 2.02 (s, 3H, C*H*$_3$C(O)R), 1.32 (s, 3H, C*H*$_3$), 1.19 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 201.6, 139.7, 135.9, 131.8, 131.5, 127.7, 125.5, 45.8, 29.8, 29.6, 24.5, 23.9, 20.5, 14.0.
IR (ν_{max}, cm^{-1}) 3062 (w), 3015 (m), 2953 (m), 2921 (m), 2870 (w), 1705 (s), 1487 (m), 1455 (m), 1353 (m), 1237 (m), 1212 (m), 1159 (m), 1119 (w), 988 (w), 748 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: [M + H]$^+$ Calcd for $C_{14}H_{18}IO^+$ 329.0397; Found 329.0394.
The relative configuration was assigned by analogy to compound **2b**..

***rel*-1-((1S,3S)-3-Iodo-1-(4-methoxyphenyl)-2,2-dimethylcyclopropyl)ethan-1-one (2h)**



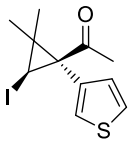
Following the GP6, starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-(4-methoxyphenyl)ethan-1-ol **1h** (65.5 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as an amorphous white solid (87 mg, 0.25 mmol, 84% yield).
Rf (5% Et_2O/Pentane) = 0.57.
^{1}H NMR (400 MHz, C_6D_6) δ 6.97 – 6.83 (m, 2H, Ar*H*), 6.71 – 6.57 (m, 2H, Ar*H*), 3.28 (s, 3H, OC*H*$_3$), 2.88 (s, 1H, C*H*), 2.02 (s, 3H, C*H*$_3$C(O)R), 1.52 (s, 3H, C*H*$_3$), 0.68 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, C_6D_6) δ 201.2, 159.2, 130.5, 129.0, 114.2, 54.5, 48.7, 27.9, 27.6, 25.0, 23.4, 9.7.
IR (ν_{max}, cm^{-1}) 2957 (m), 1737 (m), 1701 (s), 1608 (m), 1509 (s), 1458 (m), 1353 (m), 1293 (m), 1241 (s), 1173 (m), 1116 (m), 1033 (m), 828 (m).
HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{17}INaO_2^+$ 367.0165; Found 367.0167.
The relative configuration was assigned by analogy to compound **2b**.

***rel*-1-((1S,3S)-3-Iodo-2,2-dimethyl-1-(4-(trifluoromethyl)phenyl)cyclopropyl)ethan-1-one (2i)**



Following the GP6 ($MeNO_2$ was used instead of MeCN, temperature was -20 °C), starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol **1i** (76.9 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 0-6% Et_2O/Pentane) as a yellow oil (39 mg, 0.10 mmol, 34% yield).
Rf (5% Et_2O/Pentane) = 0.93.
^{1}H NMR (400 MHz, C_6D_6) δ 7.25 – 7.20 (m, 2H, Ar*H*), 6.81 – 6.74 (m, 2H, Ar*H*), 2.70 (s, 1H, C*H*), 1.84 (s, 3H, C*H*$_3$C(O)R), 1.44 (s, 3H, C*H*$_3$), 0.45 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, C_6D_6) δ 200.1, 141.4, 129.8, 129.50 (q, *J* = 32.6 Hz), 125.5 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 272Hz), 48.9, 28.3, 27.8, 24.7, 23.3, 8.6.
^{19}F NMR (376 MHz, C_6D_6) δ -62.3.
IR (v_{max}, cm^{-1}) 2962 (w), 2928 (w), 2874 (w), 1707 (m), 1617 (w), 1410 (w), 1326 (s), 1240 (m), 1166 (s), 1127 (s), 1069 (m), 1019 (w), 835 (w).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}F_3IO^+$ 383.0114; Found 383.0111.
The relative configuration was assigned by analogy to compound **2b**.

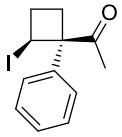
***rel*-1-((1S,3S)-3-Iodo-2,2-dimethyl-1-(thiophen-3-yl)cyclopropyl)ethan-1-one (2k)**



Molecular Weight: 320.19

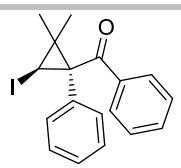
Following the GP6, starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-(m-tolyl)ethan-1-ol **1k** (58.3 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a yellow oil (82 mg, 0.26 mmol, 85% yield).
Rf (5% Et_2O/Pentane) = 0.80.
^{1}H NMR (400 MHz, C_6D_6) δ 6.72 (m, 1H, Ar*H*), 6.57 (m, 1H, Ar*H*), 6.47 (m, 1H, Ar*H*), 2.82 (s, 1H, C*H*), 1.96 (s, 3H, C*H*$_3$C(O)R)), 1.46 (s, 3H, C*H*$_3$), 0.64 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, C_6D_6) δ 200.7, 137.9, 128.2, 126.1, 123.8, 44.8, 28.4, 27.8, 24.7, 22.9, 9.6.
R (v_{max}, cm^{-1}) 2954 (m), 2925 (m), 2867 (m), 1707 (s), 1453 (m), 1353 (m), 1331 (s), 1238 (m), 812 (s), 785 (s).
HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}IOS^+$ 320.9805; Found 336.0968.
The relative configuration was assigned by analogy to compound **2b**.

***rel*-1-((1R,2S)-2-Iodo-1-phenylcyclobutyl)ethan-1-one (2l)**



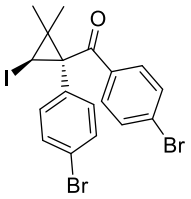
Following the GP6, starting from 1-(cyclobut-1-en-1-yl)-1-phenylethan-1-ol **1l** (52.3 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a light-yellow oil (61 mg, 0.20 mmol, 67% yield).
Rf (10% Et_2O/Pentane) = 0.75.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.35 (m, 2H, Ar*H*), 7.35 – 7.26 (m, 1H, Ar*H*), 7.26 – 7.18 (m, 2H, Ar*H*), 4.93 (dd, *J* = 9.6, 8.3 Hz, 1H, C*H*), 3.14 (td, *J* = 9.9, 3.4 Hz, 1H, C*H*$_2$), 2.64 – 2.45 (m, 2H C*H*$_2$), 2.23 (td, *J* = 10.1, 8.4 Hz, 1H, C*H*$_2$), 1.98 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 206.0, 143.8, 128.8, 127.3, 125.3, 63.9, 31.8, 31.2, 27.5, 20.2.
IR (v_{max}, cm^{-1}) 2988 (m), 2950 (m), 1705 (s), 1494 (m), 1447 (m), 1353 (m), 1243 (m), 1212 (m), 1186 (m), 1148 (m), 1080 (m), 820 (m), 760 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}IO^+$ 301.0084; Found 301.0079.
The relative configuration was assigned by analogy to compound **2b**.

***rel*-((1S,3S)-3-Iodo-2,2-dimethyl-1-phenylcyclopropyl)(phenyl)methanone (2m)**



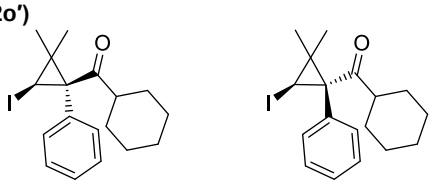
Following the GP6, starting from (3,3-dimethylcycloprop-1-en-1-yl)diphenylmethanol **1m** (75.1 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a yellow oil (94 mg, 0.25 mmol, 83% yield).
Rf (5% Et_2O/Pentane) = 0.73.
^1H NMR (400 MHz, CD_2Cl_2) δ 8.07 – 7.99 (m, 2H, Ar*H*), 7.53 – 7.43 (m, 3H, Ar*H*), 7.39 (m, 2H, Ar*H*), 7.32 (m, 2H, Ar*H*), 7.25 – 7.19 (m, 1H, Ar*H*), 3.69 (s, 1H, C*H*), 1.45 (s, 3H, CH_3), 0.98 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 194.4, 137.2, 134.7, 132.8, 130.4, 129.1, 128.7, 128.1, 127.3, 46.2, 27.5, 26.7, 22.8, 10.1.
IR (ν_{max}, cm^{-1}) 3059 (w), 2957 (w), 2925 (w), 2867 (w), 1667 (s), 1597 (m), 1447 (m), 1263 (m), 1172 (w), 987 (w), 790 (w), 738 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}IO^+$ 377.0397; Found 377.0388.
The relative configuration was assigned by analogy to compound **2b**.

***rel*-(4-Bromophenyl)((1S,3S)-1-(4-bromophenyl)-3-iodo-2,2-dimethylcyclopropyl)methanone (2n)**



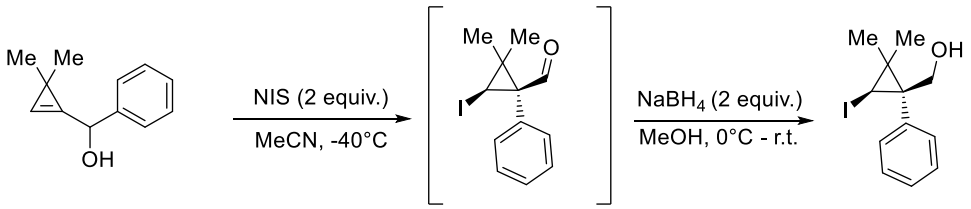
Following the GP6, starting from bis(4-bromophenyl)(3,3-dimethylcycloprop-1-en-1-yl)methanol **1n** (122 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 0-6% Et_2O/Pentane) as an amorphous white solid (0.14 g, 0.26 mmol, 88% yield).
Rf (5% Et_2O/Pentane) = 0.82.
^1H NMR (400 MHz, C_6D_6) δ 7.75 – 7.66 (m, 2H, Ar*H*), 7.14 (m, 2H, Ar*H*), 7.10 – 7.02 (m, 2H, Ar*H*), 6.79 – 6.68 (m, 2H, Ar*H*), 3.10 (s, 1H, C*H*), 1.49 (s, 3H, CH_3), 0.58 (s, 3H, CH_3).
^{13}C NMR (101 MHz, C_6D_6) δ 192.5, 136.0, 133.2, 131.9, 131.9, 131.4, 130.4, 128.0, 121.5, 45.4, 27.5, 26.6, 22.5, 9.1.
IR (ν_{max}, cm^{-1}) 2957 (m), 2924 (m), 2867 (m), 1671 (s), 1583 (s), 1487 (s), 1394 (s), 1278 (s), 1250 (s), 1072 (s), 1010 (s), 986 (s), 814 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}{}^{79}Br_2IO^+$ 532.8607; Found 532.8587.
The relative configuration was assigned by analogy to compound **2b**.

***rel*-Cyclohexyl((1S,3S)-3-iodo-2,2-dimethyl-1-phenylcyclopropyl)methanone and *rel*-cyclohexyl((1R,3S)-3-iodo-2,2-dimethyl-1-phenylcyclopropyl)methanone (2o and 2o')**



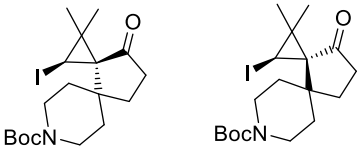
Following the GP6, starting from cyclohexyl(3,3-dimethylcycloprop-1-en-1-yl)(phenyl)methanol (76.9 mg, 0.300 mmol, 1.00 equiv.) the title compounds were obtained after a purification by chromatography (gradient 0-4% Et_2O/Pentane) as a mixture in a ratio 89:11 as a yellow oil (91 mg, 0.24 mmol, 79% yield).
Rf (2% Et_2O/Pentane) = 0.83.
Major diastereomer **2l**:
^1H NMR (400 MHz, CD_2Cl_2) δ 7.53 – 7.06 (m, 5H, Ar*H*), 3.25 (s, 1H, C*H*I), 2.72 (m, 1H, RC(O)C*H*), 1.83 (m, 1H, CH_2), 1.71 – 1.43 (m, 3H, CH_2), 1.34 (s, 3H, CH_3), 1.27 (m, 1H, CH_2), 1.18 – 0.96 (m, 5H, CH_2), 0.91 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 208.5, 137.7, 129.8, 128.6, 127.6, 49.3, 49.3, 31.4, 28.9, 28.0, 25.9, 25.7, 25.4, 25.1, 23.5, 10.4.
Minor diastereomer **2l'**:
^1H NMR (400 MHz, CD_2Cl_2) δ 3.93 (s, 1H, C*H*I), 2.47 – 2.30 (m, 1H, RC(O)C*H*). Other peaks are not resolved from the peaks of major diastereomer.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 208.7, 136.2, 132.3, 128.2, 127.7, 48.9, 48.6, 31.3, 29.7, 29.0, 28.4, 26.6, 25.7, 20.9, 13.0. (one carbon is not resolved)
IR (ν_{max}, cm^{-1}) 2925 (s), 2854 (m), 1696 (s), 1493 (m), 1447 (m), 1364 (m), 1313 (m), 1245 (m), 1190 (m), 1149 (m), 1108 (m), 1078 (w), 993 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}IO^+$ 383.0866; Found 383.0856.
The relative configuration of the major diastereomer was assigned based on 1D NOE experiment.

***rel*-((1S,3S)-3-Iodo-2,2-dimethyl-1-phenylcyclopropyl)methanol (2p)**



To a solution of (3,3-dimethylcycloprop-1-en-1-yl)(phenyl)methanol **1p** (52.3 mg, 0.300 mmol, 1.00 equiv.) in MeCN (3 mL), cooled to -40°C N-iodosuccinimide (0.13 g, 0.60 mmol, 2.0 equiv.) was added all at once. The reaction mixture was stirred at -40 °C for 14 h. The reaction mixture was poored into saturated aqueous $Na_2S_2O_3$ (10 mL), extracted with Et_2O (2x10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum until ca 1/3 of initial volume remained. The resulting solution was diluted with MeOH (15 mL) and cooled to 0 °C. $NaBH_4$ (22.7 mg, 0.600 mmol, 2.00 equiv.) was added at 0 °C. The reaction mixture was stirred at r.t. for 2 h, then concentrated under vacuum, diluted with water (10 mL) and extracted with Et_2O (2x10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting crude was purified by column chromatography (gradient 3-30% Et_2O/Pentane) to give *rel*-((1S,3S)-3-iodo-2,2-dimethyl-1-phenylcyclopropyl)methanol **2p** (40 mg, 0.13 mmol, 44% yield) as a yellow oil.
Rf (15% Et_2O/Pentane) = 0.46.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.41 – 7.31 (m, 2H, Ar*H*), 7.30 – 7.21 (m, 3H, Ar*H*), 3.95 (d, *J* = 11.8 Hz, 1H, OC*H*$_2$), 3.79 (d, *J* = 11.8 Hz, 1H, OC*H*$_2$), 3.10 (s, 1H, C*H*), 1.32 (s, 3H, C*H*$_3$), 0.90 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 139.7, 129.8, 128.4, 126.9, 69.4, 38.3, 24.9, 24.0, 21.9, 13.9.
IR (ν_{max}, cm^{-1}) 3411 (m), 3059 (w), 3024 (m), 2952 (m), 2926 (m), 2872 (m), 1493 (m), 1447 (m), 1374 (m), 1241 (m), 1182 (w), 1138 (m), 1030 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H_{-1}]^+$ Calcd for $C_{12}H_{14}IO^+$ 301.0084; Found 301.0076.
The relative configuration was assigned by analogy to compound **2b**.

***rel-tert*-Butyl (2S,3S)-2-iodo-1,1-dimethyl-12-oxo-7-azadispiro[2.0.54.33]dodecane-7-carboxylate and *rel-tert*-butyl (2S,3R)-2-iodo-1,1-dimethyl-12-oxo-7-azadispiro[2.0.54.33]dodecane-7-carboxylate (2r and 2r′)**

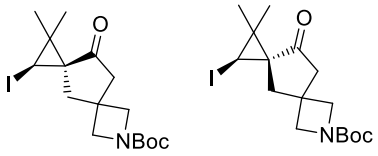


The title compounds were prepared, following the GP6, starting from *tert*-butyl 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-hydroxy-7-azaspiro[3.5]nonane-7-carboxylate **1r** (92.2 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 85:15 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 6-50% Et_2O/Pentane) to give **2r** (81 mg, 0.19 mmol, 62% yield) and **2r′** (6.40 mg, 0.015 mmol, 5% yield) as yellow oils. Total yield – 67%.

Characterization data of **2r**:
Rf (25% Et_2O/Pentane) = 0.64.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.84 (dt, *J* = 13.4, 4.8 Hz, 1H, C*H*$_2$N), 3.75 (dt, *J* = 13.5, 4.8 Hz, 1H, C*H*$_2$N), 3.13 – 3.01 (m, 2H, C*H*$_2$N), 2.99 (s, 1H, C*H*), 2.27 – 2.11 (m, 1H, C*H*$_2$), 1.95 – 1.75 (m, 3H, C*H*$_2$), 1.65 (ddd, *J* = 13.5, 10.3, 4.3 Hz, 1H, C*H*$_2$), 1.55 (ddd, *J* = 14.1, 10.0, 4.1 Hz, 1H, C*H*$_2$), 1.42 (s, 9H, C(C*H*$_3$)$_3$), 1.33 (m, 2H, C*H*$_2$), 1.27 (s, 3H, C*H*$_3$), 1.19 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 214.6, 154.5, 79.1, 49.4, 40.4 (br), 39.7 (br), 37.2, 32.2, 31.4 (br, C), 31.0, 28.1, 27.3, 23.0, 20.0, 15.6. (one carbon is not resolved).
IR (ν_{max}, cm^{-1}) 2973 (m), 2867 (m), 1685 (s), 1421 (s), 1364 (m), 1249 (s), 1152 (s), 1102 (m), 986 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{28}INNaO_3^+$ 456.1006; Found 456.1013.

Characterization data of **2r′**:
Rf (25% Et_2O/Pentane) = 0.78.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.84 (dt, *J* = 13.2, 4.9 Hz, 1H, C*H*$_2$N), 3.68 (dt, *J* = 13.5, 5.0 Hz, 1H, C*H*$_2$N), 3.41 (s, 1H, C*H*), 3.18 – 3.04 (m, 2H, C*H*$_2$N), 2.07 – 1.80 (m, 3H, C*H*$_2$), 1.75 (ddd, *J* = 11.2, 7.5, 4.3 Hz, 1H, C*H*$_2$), 1.67 (ddd, *J* = 14.0, 10.0, 4.3 Hz, 1H, C*H*$_2$N), 1.51 (m, 1H, C*H*$_2$), 1.45 – 1.29 (m, 11H, C*H*$_2$ & C(C*H*$_3$)$_3$), 1.25 (s, 3H, C*H*$_3$), 1.15 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 216.8, 154.5, 79.1, 49.3, 40.5 (br), 39.8, 39.4 (br), 33.2, 31.5 (br), 31.2, 31.0 (br), 28.1, 26.9, 24.1, 19.2, 18.4.
IR (ν_{max}, cm^{-1}) 2949 (m), 2871 (w), 1693 (s), 1424 (s), 1366 (m), 1253 (s), 1171 (s), 1101 (m), 986 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{28}INNaO_3^+$ 456.1006; Found 456.1005.
The relative configuration was assigned by analogy to compound **2a**.

***rel-tert*-butyl (2S,3S)-2-Iodo-1,1-dimethyl-10-oxo-7-azadispiro[2.1.35.23]decane-7-carboxylate and *rel-tert*-butyl (2S,3R)-2-iodo-1,1-dimethyl-10-oxo-7-azadispiro[2.1.35.23]decane-7-carboxylate (2s and 2s′)**

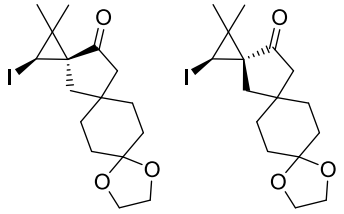


The title compounds were prepared, following the GP6 (1:1 mixture of MeCN:$MeNO_2$ was used as the solvent), starting from *tert*-butyl 6-(3,3-dimethylcycloprop-1-en-1-yl)-6-hydroxy-2-azaspiro[3.3]heptane-2-carboxylate **1s** (83.8 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 86:14 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 5-50% EtOAc/Pentane) to give **2s** (64 mg, 0.16 mmol, 53% yield) and **2s′** (6.50 mg, 0.016 mmol, 5% yield) as yellow oils. Total yield – 58%.

Characterization data of **2s**:
Rf (30% EtOAc/Pentane) = 0.76.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.87 – 3.75 (m, 4H, CH_2N), 2.99 (s, 1H, C*H*), 2.56 (d, *J* = 1.9 Hz, 2H, CH_2), 2.41 (d, *J* = 13.4 Hz, 1H, CH_2), 2.14 (d, *J* = 13.4 Hz, 1H, CH_2), 1.41 (s, 9H, C(CH_3)$_3$), 1.28 (s, 3H, CH_3), 1.20 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 209.6, 156.1, 79.3, 59.2 (br, 2C), 51.3, 42.3, 38.1, 35.3, 31.9, 28.1, 23.3, 19.7, 14.2.
IR (ν_{max}, cm^{-1}) 2977 (m), 2872 (m), 1725 (s), 1695 (s), 1402 (s), 1256 (m), 1131 (s), 1040 (m), 956 (m), 772 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{24}INNaO_3^+$ 428.0693; Found 428.0694.

Characterization data of **2s′**:
Rf (30% EtOAc/Pentane) = 0.83.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.92 – 3.76 (m, 4H, CH_2N), 3.39 (s, 1H, C*H*), 2.67 – 2.52 (m, 2H, CH_2), 2.22 (d, *J* = 13.7 Hz, 1H, CH_2), 2.07 (d, *J* = 13.7 Hz, 2H, CH_2), 1.42 (s, 9H, C(CH_3)$_3$), 1.30 (s, 3H, CH_3), 1.17 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.7, 156.2, 79.3, 59.5 (br, 2C), 51.4, 41.9, 41.0, 35.5, 33.4, 28.1, 24.5, 18.1, 18.1.
IR (ν_{max}, cm^{-1}) 2930 (m), 2872 (m), 1699 (s), 1402 (s), 1148 (s), 1031 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{24}INNaO_3^+$ 428.0693; Found 428.0691.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-(2S,3S)-2-iodo-1,1-dimethyl-9,12-dioxatrispiro[2.1.2.48.25.23]hexadecan-16-one and *rel*-(2S,3R)-2-iodo-1,1-dimethyl-9,12-dioxatrispiro[2.1.2.48.25.23]hexadecan-16-one (2t and 2t′)**

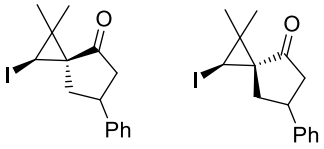


The title compounds were prepared, following the GP6, starting from 2-(3,3-dimethylcycloprop-1-en-1-yl)-8,11-dioxadispiro[3.2.47.24]tridecan-2-ol **1t** (79.3 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 89:11 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 3-30% Et_2O/Pentane) to give **2t** (83 mg, 0.21 mmol, 71% yield) as an amorphous white solid and **2t′** (6.5 mg, 0.018 mmol, 6% yield) as colorless oil. Total yield – 77%.

Characterization data of **2t**:
Rf (15% Et_2O/Pentane) = 0.19.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.90 (s, 4H, OCH_2), 2.93 (s, 1H, C*H*), 2.26 (s, 2H, CH_2), 2.11 (d, *J* = 13.3 Hz, 1H, CH_2), 1.81 (d, *J* = 13.3 Hz, 1H, CH_2), 1.72 – 1.50 (m, 8H, CH_2), 1.23 (s, 3H, CH_3), 1.19 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.8, 108.2, 64.2, 52.0, 42.8, 37.2, 36.5, 34.1, 33.9, 31.7, 31.6, 23.3, 19.7, 15.6. (two carbons are not resolved).
IR (ν_{max}, cm^{-1}) 2927 (m), 2878 (m), 1721 (s), 1444 (m), 1372 (m), 1270 (m), 1159 (s), 1099 (s), 1037 (s), 946 (m), 889 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{23}INaO_3^+$ 413.0584; Found 413.0579.

Characterization data of **2t′**:
Rf (15% Et_2O/Pentane) = 0.23.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.95 (s, 4H, OCH_2), 3.43 (s, 1H, C*H*), 2.36 (dd, *J* = 17.5, 0.9 Hz, 1H, CH_2), 2.32 – 2.23 (m, 1H, CH_2), 1.94 (d, *J* = 13.6 Hz, 1H, CH_2), 1.84 – 1.62 (m, 9H, CH_2), 1.32 (s, 3H, CH_3), 1.17 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 214.0, 108.3, 64.2, 40.2, 37.1, 34.4, 33.7, 32.8, 31.7, 31.6, 30.6, 30.1, 24.4, 19.0, 18.0. (one carbon is not resolved).
IR (ν_{max}, cm^{-1}) 2928 (s), 1718 (s), 1448 (m), 1372 (m), 1225 (m), 1173 (m), 1102 (m), 1038 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{24}IO_3^+$ 391.0765; Found 391.0766.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-(2S,3S)-2-Iodo-1,1-dimethyl-6-phenylspiro[2.4]heptan-4-one and *rel*-(2S,3R)-2-iodo-1,1-dimethyl-6-phenylspiro[2.4]heptan-4-one (2u and 2u′)**



The title compounds were prepared, following the GP6, starting from *rel*-(1s,3s)-1-(3,3-dimethylcycloprop-1-en-1-yl)-3-phenylcyclobutan-1-ol **1u** (64.3 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 85:15 by the integration of the crude ^{1}H NMR spectrum (two *cis* isomers were isolated (*dr* 1.43:1). The crude material was purified by column chromatography (gradient 1-10% Et_2O/Pentane) to give **2u$_1$** (32 mg, 0.095 mmol, 32% yield) as a yellow oil, **2u$_2$** (23 mg, 0.069 mmol, 23% yield) as a yellow oil and **2u′** (8.8 mg, 0.027 mmol, 9% yield) as a colorless oil. Total yield – 64%.

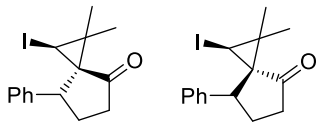
Characterization data of **2u$_1$**:
Rf (5% Et_2O/Pentane) = 0.44.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.38 – 7.29 (m, 2H, Ar*H*), 7.27 – 7.19 (m, 3H, Ar*H*), 3.38 (tt, *J* = 9.0, 7.2 Hz, 1H, ArC*H*), 2.96 (s, 1H, C*H*I), 2.78 (ddd, *J* = 17.8, 7.7, 1.5 Hz, 1H, CH_2), 2.59 – 2.46 (m, 2H, CH_2), 2.11 (dd, *J* = 13.3, 8.9 Hz, 1H, CH_2), 1.32 (s, 3H, CH_3), 1.25 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.1, 143.4, 128.6, 126.7, 126.6, 47.7, 39.3, 38.9, 37.7, 32.6, 22.8, 20.1, 14.9.
IR (ν_{max}, cm^{-1}) 3028 (w), 2957 (m), 2918 (m), 2867 (w), 1728 (s), 1456 (m), 1357 (m), 1235 (m), 1163 (m), 1107 (m), 1040 (w), 760 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}IO^+$ 341.0397; Found 341.0387.

Characterization data of **2u$_2$**:
Rf (5% Et_2O/Pentane) = 0.49.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.34 (m, 2H, Ar*H*), 7.25 (m, 3H, Ar*H*), 3.56 – 3.40 (m, 1H, ArC*H*), 3.04 (s, 1H, C*H*I), 2.71 (ddd, *J* = 17.4, 7.5, 1.5 Hz, 1H, CH_2), 2.61 (dd, *J* = 17.4, 10.3 Hz, 1H, CH_2), 2.38 (dd, *J* = 13.2, 9.4 Hz, 1H, CH_2), 2.27 (ddd, *J* = 13.2, 6.9, 1.4 Hz, 1H, CH_2), 1.25 (s, 3H, CH_3), 1.13 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.2, 143.1, 128.6, 128.6, 126.6, 47.4, 40.6, 38.9, 37.8, 31.7, 23.0, 19.6, 15.0.
IR (ν_{max}, cm^{-1}) 3033 (w), 2955 (m), 2919 (m), 2869 (w), 1723 (s), 1455 (m), 1356 (m), 1232 (m), 1158 (m), 1108 (w), 1032 (m), 760 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}IO^+$ 341.0397; Found 341.0387.

Characterization data of **2u′**:
Rf (5% Et_2O/Pentane) = 0.58.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.41 – 7.32 (m, 2H, Ar*H*), 7.31 – 7.21 (m, 3H, Ar*H*), 3.53 – 3.39 (m, 2H, ArC*H* & C*H*I), 2.78 (ddd, *J* = 18.1, 8.0, 1.6 Hz, 1H, CH_2), 2.47 (dd, *J* = 18.1, 10.4 Hz, 1H, CH_2), 2.35 (ddd, *J* = 13.3, 6.7, 1.7 Hz, 1H, CH_2), 1.94 (dd, *J* = 13.3, 10.3 Hz, 1H, CH_2), 1.34 (s, 3H, CH_3), 1.27 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 213.4, 143.3, 128.6, 126.8, 126.7, 47.0, 41.8, 39.7, 39.0, 33.6, 24.0, 18.5, 16.7.
IR (ν_{max}, cm^{-1}) 3029 (w), 2956 (w), 2914 (w), 2872 (w), 1721 (s), 1455 (w), 1359 (w), 1225 (m), 1170 (m), 1105 (w).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}IO^+$ 341.0397; Found 341.0387.

The relative configuration (cyclopropane ring sterochemistry) was assigned by analogy to compound **2a**. The relative configuration of carbon atom bearing a phenyl substituent was not assigned.

***rel*-(2S,3S)-2-iodo-1,1-dimethyl-7-phenylspiro[2.4]heptan-4-one and *rel*-(2S,3R)-2-iodo-1,1-dimethyl-7-phenylspiro[2.4]heptan-4-one (2v and 2v′)**



The title compounds were prepared, following the GP6, starting from *rel*-(1S,2S)-1-(3,3-dimethylcycloprop-1-en-1-yl)-2-phenylcyclobutan-1-ol **1v** (64.3 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 78:22 by the integration of the crude ^{1}H NMR spectrum (two *cis* isomers were isolated (*dr* 2.1:1). The crude material was purified by column chromatography (gradient 1-10% Et_2O/Pentane) to give **2v$_1$** (46 mg, 0.13 mmol, 45% yield) as a yellow oil, **2v$_2$** (26 mg, 0.075 mmol, 25% yield) as an amorphous white solid and **2v′** (19 mg, 0.057 mmol, 19% yield) as a colorless oil. Total yield – 89%.

Characterization data of **2v$_1$**:
Rf (5% Et_2O/Pentane) = 0.25.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.34 (m, 2H, Ar*H*), 7.26 – 7.21 (m, 1H, Ar*H*), 7.18 – 7.11 (m, 2H, Ar*H*), 3.59 – 3.48 (m, 1H, ArC*H*), 2.78 (s, 1H, C*H*I), 2.53 – 2.28 (m, 3H, CH_2), 1.98 – 1.83 (m, 1H, CH_2), 1.29 (s, 3H, CH_3), 1.22 (s, 3H, CH_3).
^{13}C NMR (101 MHz, C_6D_6) δ 209.7, 143.9, 128.7, 128.3, 126.6, 47.3, 40.5, 38.0, 34.2, 30.4, 21.8, 20.5, 13.8.
IR (ν_{max}, cm^{-1}) 2956 (m), 2928 (m), 2872 (w), 1725 (s), 1607 (w), 1455 (m), 1375 (w), 1260 (w), 1237 (w), 1165 (m), 1047 (w), 767 (w).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}IO^+$ 341.0397; Found 341.0388.

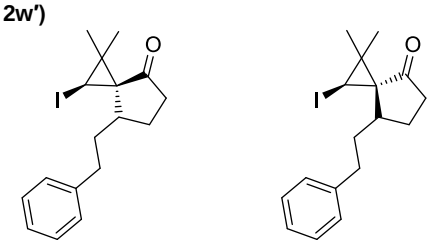
Characterization data of **2v$_2$**:
Rf (5% Et_2O/Pentane) = 0.43.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.31 (m, 2H, Ar*H*), 7.27 – 7.20 (m, 1H, Ar*H*), 7.18 – 7.11 (m, 2H, Ar*H*), 3.40 (d, *J* = 6.2 Hz, 1H, ArC*H*), 3.17 (s, 1H, C*H*I), 2.48 – 2.29 (m, 2H, CH_2), 2.28 – 2.14 (m, 1H, CH_2), 1.99 – 1.86 (m, 1H, CH_2), 1.46 (s, 3H, CH_3), 0.91 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 213.7, 143.9, 128.5, 127.0, 126.4, 51.2, 42.6, 36.7, 30.9, 29.5, 24.3, 19.9, 15.6.
IR (ν_{max}, cm^{-1}) 2957 (m), 2928 (m), 2871 (w), 1724 (s), 1453 (m), 1369 (m), 1233 (m), 1151 (m), 1044 (w), 1027 (w), 802 (w), 755 (m).

HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}IO^+$ 341.0397; Found 341.0398.

Characterization data of **2v′**:
Rf (5% Et_2O/Pentane) = 0.38.
^1H NMR (400 MHz, CD_2Cl_2) δ 7.34 – 7.27 (m, 2H, Ar*H*), 7.26 – 7.20 (m, 1H, Ar*H*), 7.17 – 7.12 (m, 2H, Ar*H*), 3.53 (s, 1H, C*H*I), 3.51 – 3.46 (m, 1H, ArC*H*), 2.34 – 2.16 (m, 3H, CH_2), 2.08 – 1.98 (m, 1H, CH_2), 1.42 (s, 3H, CH_3), 1.24 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 214.3, 141.5, 128.3, 127.9, 126.3, 46.2, 45.3, 35.5, 33.4, 30.7, 24.0, 19.1, 10.4.
IR (ν_{max}, cm^{-1}) 2954 (m), 2927 (m), 2871 (w), 1721 (s), 1458 (m), 1361 (m), 1235 (m), 1177 (m), 1102 (m), 863 (w), 802 (w), 748 (m).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}IO^+$ 341.0397; Found 341.0394.

The relative configuration (cyclopropane ring sterochemistry) was assigned by analogy to compound **2a**. The relative configuration of the carbon atom bearing a phenyl substituent was not assigned.

***rel*-(2S,3S)-2-Iodo-1,1-dimethyl-7-phenethylspiro[2.4]heptan-4-one and *rel*-(2S,3R)-2-iodo-1,1-dimethyl-7-phenethylspiro[2.4]heptan-4-one (2w and 2w′)**



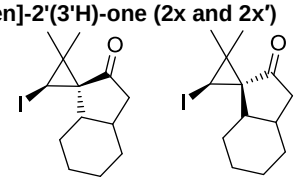
The title compounds were prepared, following the GP6, starting from *rel*-(1S,2R)-1-(3,3-dimethylcycloprop-1-en-1-yl)-2-phenethylcyclobutan-1-ol **1w** (72.3 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 78:22 by the integration of the crude
^1H NMR spectrum (two *cis* isomers were isolated). The crude material was purified by column chromatography (gradient 1-10% Et_2O/Pentane) to give **2w$_1$** (47 mg, 0.13 mmol, 42% yield) as a yellow oil, **2w$_2$** (18 mg, 0.048 mmol, 16% yield) as a yellow oil and **2w′** (18 mg, 0.048 mmol, 16% yield) as a yellow oil. Total yield - 74%.

Characterization data of **2w$_1$**:
Rf (5% Et_2O/Pentane) = 0.2.
^1H NMR (400 MHz, C_6D_6) δ 7.25 – 7.14 (m, 2H, Ar*H*), 7.13 – 7.04 (m, 1H, Ar*H*), 7.05 – 6.93 (m, 2H, Ar*H*), 2.73 (s, 1H, C*H*I), 2.44 (ddd, *J* = 14.2, 9.6, 4.9 Hz, 1H, C*H*), 2.22 (ddd, *J* = 13.8, 9.4, 7.3 Hz, 1H, CH_2), 2.06 (dt, *J* = 18.0, 9.0 Hz, 1H, CH_2), 1.92 (ddd, *J* = 18.2, 9.0, 4.7 Hz, 1H, CH_2), 1.73 (ddt, *J* = 10.6, 7.2, 3.7 Hz, 1H, CH_2), 1.53 – 1.32 (m, 2H, CH_2), 1.31 – 1.14 (m, 5H, CH_2 & CH_3), 0.72 (s, 3H, CH_3).
^{13}C NMR (101 MHz, C_6D_6) δ 209.8, 141.6, 128.4, 128.3, 126.0, 41.4, 39.0, 37.6, 33.5, 33.2, 32.2, 24.3, 21.6, 20.6, 10.3.
IR (ν_{max}, cm^{-1}) 3065 (w), 3026 (w), 2930 (m), 2869 (w), 1725 (m), 1620 (w), 1455 (m), 1330 (m), 1163 (m), 813 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}INaO^+$ 391.0529; Found 391.0528.

Characterization data of **2w$_2$**:
Rf (5% Et_2O/Pentane) = 0.3.
^1H NMR (400 MHz, CD_2Cl_2) δ 7.32 – 7.21 (m, 2H, Ar*H*), 7.21 – 7.10 (m, 3H, Ar*H*), 2.87 (s, 1H, C*H*I), 2.78 (ddd, *J* = 14.2, 9.6, 5.0 Hz, 1H, C*H*), 2.55 (ddd, *J* = 13.7, 9.3, 7.4 Hz, 1H, CH_2), 2.47 – 2.31 (m, 1H, CH_2), 2.31 – 2.15 (m, 1H, CH_2), 2.15 – 1.89 (m, 3H, CH_2), 1.85 – 1.73 (m, 1H, CH_2), 1.71 – 1.60 (m, 1H, CH_2), 1.36 (s, 3H, CH_3), 1.23 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 213.5, 141.7, 128.4 (2C), 125.9, 45.1, 44.8, 36.5, 33.9, 33.3, 29.7, 24.1, 22.7, 20.4, 14.7.
IR (ν_{max}, cm^{-1}) 3025 (m), 2951 (m), 2925 (m), 2863 (m), 1726 (s), 1496 (w), 1455 (m), 1370 (m), 1260 (w), 1224 (m), 1150 (m), 1030 (w), 954 (w), 745 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}INaO^+$ 391.0529; Found 391.0515.

Characterization data of **2w′**:
Rf (5% Et_2O/Pentane) = 0.29.
^1H NMR (400 MHz, CD_2Cl_2) δ 7.33 – 7.13 (m, 5H, Ar*H*), 3.26 (s, 1H, C*H*I), 2.79 (ddd, *J* = 13.7, 10.5, 4.8 Hz, 1H, C*H*), 2.63 (ddd, *J* = 13.7, 10.0, 6.6 Hz, 1H, CH_2), 2.45 – 2.06 (m, 5H, CH_2), 1.92 – 1.75 (m, 1H, CH_2), 1.53 – 1.38 (m, 1H, CH_2), 1.27 (s, 3H, CH_3), 1.09 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 213.5, 142.0, 128.4, 128.3, 125.8, 46.6, 40.0, 35.7, 33.8, 32.0, 29.4, 24.2, 23.6, 19.2, 9.1.
IR (ν_{max}, cm^{-1}) 3025 (w), 2950 (m), 2925 (m), 2868 (m), 1722 (s), 1455 (m), 1372 (m), 1231 (m), 1170 (m), 1105 (w), 1033 (w), 743 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}INaO^+$ 391.0529; Found 391.0515.
The relative configuration (cyclopropane ring sterochemistry) was assigned by analogy to compound **2a**. The relative configuration of the carbon atom bearing an phenethyl substituent was not assigned.

***rel*-(1S,3S)-3-Iodo-2,2-dimethylhexahydrospiro[cyclopropane-1,1'-inden]-2'(3'H)-one and *rel*-(1S,3R)-3-iodo-2,2-dimethylhexahydrospiro[cyclopropane-1,1'-inden]-2'(3'H)-one (2x and 2x′)**



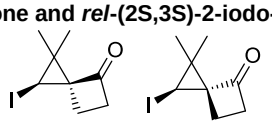
The title compounds were prepared, following the GP6, starting from *rel*-(1R,6R,7S)-7-(3,3-dimethylcycloprop-1-en-1-yl)bicyclo[4.2.0]octan-7-ol **1x** (57.7 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 82:18 by the integration of the crude
^{1}H NMR spectrum (two *cis* isomers were observed, *dr* 2.57:1). The crude material was purified by column chromatography (gradient 1-6% Et_2O/Pentane) to give **2x$_1$** (45 mg, 0.14 mmol, 47% yield) as an amorphous white solid and unseparable mixture of **2x$_2$** and **2x′** (*dr* 57:43, 31 mg, 0.10 mmol, 33% yield) as a yellow oil. Total yield – 80%.

Characterization data of **2x$_1$**:
Rf (3% Et_2O/Pentane) = 0.26.
^{1}H NMR (400 MHz, C_6D_6) δ 2.66 (s, 1H, C*H*I), 2.06 (dd, *J* = 17.6, 10.9 Hz, 1H, CH_2), 1.90 (dd, *J* = 17.7, 7.9 Hz, 1H, CH_2), 1.82 – 1.68 (m, 1H, C*H*), 1.58 (m, 1H, C*H*), 1.43 – 0.72 (m, 14H, CH_2 & CH_3).
^{13}C NMR (101 MHz, C_6D_6) δ 209.8, 43.1, 41.6, 40.2, 33.3, 31.6, 26.6, 25.3, 24.3, 21.9, 20.7, 20.6, 9.5.
IR (ν_{max}, cm^{-1}) 2926 (s), 2855 (m), 1721 (s), 1455 (m), 1358 (m), 1263 (m), 1231 (w), 1170 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{19}INaO^+$ 341.0373; Found 341.0370.

Characterization data of **2x$_2$** and **2x′**:
Rf (3% Et_2O/Pentane) = 0.38.
^{1}H NMR (400 MHz, CD_2Cl_2) (peaks are reported as they are seen in spectrum, the peaks that are surely correspond to 2 are reported in *italic,* the peaks that are surely correspond to 3 are reported in **bold**) δ **3.20 (s, 0.43H,** C*H*I**)**, *2.95 (s, 0.56H,* C*HI)*, 2.57 – 2.40 (m, 1.15H), 2.30 (m, 1.56H), 2.19 – 2.02 (m, 1.58H), *1.92 (m, 0.6H)*, 1.86 – 1.47 (m, 5.51H), 1.47 – 1.31 (m, 3.12H), 1.32 – 1.11 (m, 5.21H), **1.09 (s, 1.41H)**, *1.07 – 0.92 (m, 0.59H).*
^{13}C NMR (101 MHz, CD_2Cl_2) of **2x$_2$**: δ 213.8, 46.9, 46.3, 40.3, 32.4, 29.7, 26.4, 26.1, 25.0, 24.5, 20.5, 19.7, 14.5.
^{13}C NMR (101 MHz, CD_2Cl_2) of **2x′**: δ 214.1, 48.9, 41.3, 39.3, 34.0, 31.4, 26.6, 24.4, 23.9, 22.7, 20.2, 19.3, 7.9.
IR (ν_{max}, cm^{-1}) 2923 (s), 2854 (m), 1724 (s), 1451 (m), 1368 (m), 1229 (m), 1148 (m), 1080 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{19}INaO^+$ 341.0373; Found 341.0376.

The relative configuration (cyclopropane ring sterochemistry) was assigned by analogy to compound **2a**. The relative configuration of the fused rings junction was not assigned.

***rel*-(2S,3S)-2-Iodo-1,1-dimethylspiro[2.3]hexan-4-one and *rel*-(2S,3S)-2-iodo-1,1-dimethylspiro[2.3]hexan-4-one (2y and 2y′)**

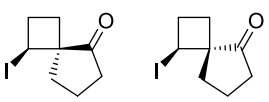


The title compounds were prepared, following the GP6, starting from 3',3'-dimethyl-[1,1'-bi(cyclopropan)]-1'-en-1-ol **1y** (37.3 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 72:28 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 1-10% Et_2O/Pentane) to give 1 (51 mg, 0.20 mmol, 67% yield) as a yellow oil and 2 (19 mg, 0.078 mmol, 26% yield) as a yellow oil. Total yield – 93%.

Characterization data of **2y**:
Rf (5% Et_2O/Pentane) = 0.33.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.07 – 2.85 (m, 3H, C*H*I & CH_2), 2.25 (ddd, *J* = 11.5, 9.4, 6.0 Hz, 1H, CH_2), 2.06 (ddd, *J* = 11.5, 9.4, 5.8 Hz, 1H, CH_2), 1.27 (s, 3H, CH_3), 1.25 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 208.2, 51.0, 44.3, 32.7, 22.4, 21.4, 18.7, 10.9.
IR (ν_{max}, cm^{-1}) 2954 (m), 2926 (m), 2869 (w), 1757 (s), 1447 (m), 1374 (m), 1210 (m), 1160 (m), 1097 (m), 1075 (m), 1026 (s), 977 (m), 831 (w).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_8H_{12}IO^+$ 250.9927; Found 250.9925.

Characterization data of **2y′**:
Rf (5% Et_2O/Pentane) = 0.33.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.35 (s, 1H, C*H*), 3.06 – 2.86 (m, 2H, CH_2), 2.09 (ddd, *J* = 11.7, 9.0, 6.3 Hz, 1H, CH_2), 1.85 (ddd, *J* = 11.7, 8.9, 6.8 Hz, 1H, CH_2), 1.35 (s, 3H, CH_3), 1.19 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 210.0, 52.6, 42.7, 33.5, 24.0, 20.2, 19.9, 15.7.
IR (ν_{max}, cm^{-1}) 2979 (m), 2953 (m), 2932 (m), 2867 (w), 1761 (s), 1451 (w), 1372 (m), 1203 (m), 1158 (s), 1094 (s), 1026 (m), 987 (w).
HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_8H_{12}IO^+$ 250.9927; Found 250.9926.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-(1S,4S)-1-Iodospiro[3.4]octan-5-one and *rel*-(1S,4R)-1-iodospiro[3.4]octan-5-one (2z and 2z′)**

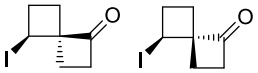


The title compounds were prepared, following the GP6, starting from [1,1'-bi(cyclobutan)]-1'-en-1-ol **2z** (37.3 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 84:16 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 2-20% Et_2O/Pentane) to give **2z** (42 mg, 0.17 mmol, 56% yield) as a yellow oil and **2z′** (5.9 mg, 0.024 mmol, 8% yield) (the compound was not obtained in the pure form, the yield was estimated from the ^{1}H NMR) as a yellow oil. Total yield – 64%.

Characterization data of **2z**:
Rf (10% Et_2O/Pentane) = 0.47.
^1H NMR (400 MHz, CD_2Cl_2) δ 4.41 (dd, *J* = 9.9, 8.3 Hz, 1H, C*H*), 2.56 (dq, *J* = 11.3, 10.0 Hz, 1H, CH_2), 2.47 – 2.24 (m, 3H, CH_2), 2.20 – 1.88 (m, 5H, CH_2), 1.87 – 1.74 (m, 1H, CH_2).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 218.1, 57.6, 37.2, 36.7, 30.0, 29.5, 21.3, 18.3.¨
IR (v_{max}, cm^{-1}) 2949 (m), 1734 (s), 1446 (w), 1402 (w), 1248 (m), 1166 (m), 1078 (m), 1048 (m), 820 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_8H_{12}IO^+$ 250.9927; Found 250.9923.

Characterization data of **2z′**:
Rf (10% Et_2O/Pentane) = 0.5.
^1H NMR (400 MHz, CD_2Cl_2) δ 4.88 – 4.79 (m, 1H, C*H*), 2.56 (dtd, *J* = 11.5, 8.1, 3.4 Hz, 1H, CH_2), 2.43 (dq, *J* = 11.6, 9.4 Hz, 1H, CH_2), 2.29 – 2.05 (m, 5H, CH_2), 2.04 – 1.92 (m, 2H, CH_2), 1.80 (dqd, *J* = 12.8, 8.5, 6.5 Hz, 1H, CH_2).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 217.0, 55.9, 37.3, 37.0, 31.7, 30.5, 23.2, 18.6.
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_8H_{12}IO^+$ 250.9927; Found 250.9924.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-(4S,5S)-5-Iodospiro[3.3]heptan-1-one and *rel*-(4S,5R)-5-iodospiro[3.3]heptan-1-one (2aa and 2aa′)**

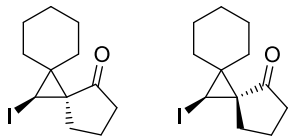


The title compounds were prepared, following the GP6, starting from 1-(cyclobut-1-en-1-yl)cyclopropan-1-ol **1aa** (33.1 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 39:61 by the integration of the crude ^1H NMR spectrum. The crude material was purified by column chromatography (gradient 2-20% Et_2O/Pentane) to give **2aa** (27 mg, 0.11 mmol, 38% yield) as a light-yellow oil and **2aa′** (35 mg, 0.15 mmol, 50% yield) as a light-yellow oil. Total yield – 87%.

Characterization data of **2aa**:
Rf (10% Et_2O/Pentane) = 0.44.
^1H NMR (400 MHz, CD_2Cl_2) δ 4.48 – 4.38 (m, 1H, C*H*), 3.07 (ddd, *J* = 17.9, 10.8, 8.0 Hz, 1H, CH_2), 2.81 (ddd, *J* = 17.9, 9.7, 6.4 Hz, 1H, CH_2), 2.55 – 2.35 (m, 3H, CH_2), 2.26 – 2.11 (m, 1H, CH_2), 2.08 – 1.91 (m, 2H, CH_2).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 210.0, 71.1, 43.2, 31.0, 30.1, 22.4, 18.0.
IR (v_{max}, cm^{-1}) 2949 (m), 1779 (s), 1391 (w), 1238 (m), 1055 (s).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_7H_{10}IO^+$ 236.9771; Found 236.9768.

Characterization data of **2aa′**:
Rf (10% Et_2O/Pentane) = 0.56.
^1H NMR (400 MHz, CD_2Cl_2) δ 4.79 (td, *J* = 7.0, 1.8 Hz, 1H, C*H*), 2.93 (ddd, *J* = 17.3, 10.2, 7.0 Hz, 1H, CH_2), 2.82 (ddd, *J* = 17.8, 10.5, 7.0 Hz, 1H, CH_2), 2.66 – 2.50 (m, 1H, CH_2), 2.52 – 2.21 (m, 4H, CH_2), 2.12 (ddd, *J* = 12.0, 10.2, 7.0 Hz, 1H, CH_2).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 207.6, 68.9, 41.9, 30.3, 29.6, 27.8, 24.6.
IR (v_{max}, cm^{-1}) 2979 (m), 2944 (m), 1779 (s), 1431 (w), 1392 (w), 1260 (w), 1239 (w), 1165 (w), 1058 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_7H_{10}IO^+$ 236.9771; Found 236.9768.
The relative configuration was assigned based on NOESY experiments.

***rel*-(5S,12S)-12-Iododispiro[4.0.5^6.1^5]dodecan-1-one and *rel*-(5S,12R)-12-iododispiro[4.0.5^6.1^5]dodecan-1-one (4a and 4a′)**



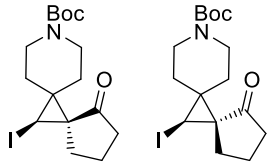
The title compounds were prepared, following the GP6, starting from 1-(spiro[2.5]oct-1-en-1-yl)cyclobutan-1-ol **3a** (53.5 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 86:14 by the integration of the crude ^1H NMR spectrum. The crude material was purified by column chromatography (gradient 1-10% Et_2O/Pentane) to give **4a** (60 mg, 0.20 mmol, 65% yield) as a yellow oil and **4a′** (8 mg, 0.03 mmol, 9% yield) as a colorless oil. Total yield – 74%.

Characterization data of **4a**:
Rf (5% Et_2O/Pentane) = 0.35.
^1H NMR (400 MHz, CD_2Cl_2) δ 2.94 (s, 1H, C*H*), 2.43 – 2.14 (m, 3H, CH_2), 2.00 – 1.84 (m, 3H, CH_2), 1.74 (m, 1H, CH_2), 1.69 – 1.38 (m, 8H, CH_2), 1.15 (m, 1H, CH_2).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 212.6, 40.7, 38.3, 37.4, 33.5, 30.8, 29.0, 25.8, 25.6, 25.0, 20.5, 13.6.
IR (v_{max}, cm^{-1}) 2924 (s), 2852 (m), 1725 (s), 1447 (m), 1408 (m), 1332 (m), 1256 (m), 1231 (m), 1138 (m), 1087 (m), 829 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{12}H_{18}IO^+$ 305.0397; Found 305.0397.

Characterization data of **4a′**:
Rf (5% Et_2O/Pentane) = 0.49.
^1H NMR (400 MHz, CD_2Cl_2) δ 3.33 (s, 1H, C*H*), 2.44 – 2.22 (m, 2H, CH_2), 2.09 – 1.90 (m, 3H, CH_2), 1.86 – 1.58 (m, 4H, CH_2), 1.59 – 1.34 (m, 6H, CH_2), 1.20 (m, 1H, CH_2).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 215.1, 40.3, 39.9, 39.3, 33.9, 30.7, 28.2, 25.8, 25.8, 24.8, 20.5, 17.1.
IR (v_{max}, cm^{-1}) 2926 (s), 2853 (m), 1725 (s), 1449 (m), 1404 (w), 1321 (w), 1256 (m), 1217 (m), 1195 (m), 1148 (m), 1080 (w), 1038 (w), 838 (w).

HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{12}H_{18}IO^+$ 305.0397; Found 305.0397.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-*tert*-Butyl (5S,12S)-12-iodo-1-oxo-9-azadispiro[4.0.56.15]dodecane-9-carboxylate and *rel*-*tert*-butyl (5S,12R)-12-iodo-1-oxo-9-azadispiro[4.0.56.15]dodecane-9-carboxylate (4b and 4b′)**

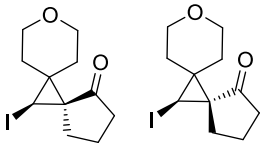


The title compounds were prepared, following the GP6, starting from *tert*-butyl 1-(1-hydroxycyclobutyl)-6-azaspiro[2.5]oct-1-ene-6-carboxylate **3b** (83.8 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 86:14 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 5-50% Et_2O/Pentane) to give **4b** (77 mg, 0.19 mmol, 64% yield) as a light-yellow oil and **4b′** (12 mg, 0.030 mmol, 10% yield) as a colorless oil. Total yield – 73%.

Characterization data of **4b**:
Rf (25% Et_2O/Pentane) = 0.32.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.48 (ddd, *J* = 13.3, 6.9, 4.0 Hz, 1H, C*H*$_2$N), 3.41 – 3.27 (m, 2H, C*H*$_2$N), 3.22 (ddd, *J* = 13.4, 6.7, 3.9 Hz, 1H, C*H*$_2$N), 2.98 (s, 1H, C*H*), 2.52 – 2.26 (m, 2H, C*H*$_2$), 2.25 – 2.12 (m, 1H, C*H*$_2$), 2.06 – 1.79 (m, 4H, C*H*$_2$), 1.72 (ddd, *J* = 13.9, 8.2, 4.0 Hz, 2H, C*H*$_2$), 1.56 – 1.44 (m, 1H, C*H*$_2$), 1.42 (s, 9H, C(C*H*$_3$)$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 212.4, 154.5, 79.2, 42.9 (br), 40.6, 37.0, 35.7, 33.1 (br), 31.0, 28.6 (br), 28.1, 20.4, 11.3. one carbon is not resolved.
IR (ν_{max}, cm^{-1}) 2973 (m), 2916 (m), 2860 (m), 1721 (s), 1685 (s), 1418 (s), 1365 (m), 1239 (s), 1166 (s), 1130 (s), 1010 (m), 976 (m), 955 (m), 865 (w), 826 (m), 769 (w).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{24}INNaO_3^+$ 428.0693; Found 428.0695.

Characterization data of **4b′**:
Rf (25% Et_2O/Pentane) = 0.39.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.48 – 3.22 (m, 5H, 2xC*H*$_2$N and C*H*), 2.44 – 2.26 (m, 2H, C*H*$_2$), 2.11 – 1.93 (m, 3H, C*H*$_2$), 1.92 – 1.80 (m, 2H, C*H*$_2$), 1.82 – 1.69 (m, 1H, C*H*$_2$), 1.59 (ddd, *J* = 14.2, 7.9, 4.5 Hz, 1H, C*H*$_2$), 1.42 (m, 10H, C*H*$_2$ & C(C*H*$_3$)$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 215.1, 154.9, 79.7, 42.4 (br), 40.4, 40.1, 37.2, 33.4, 31.1, 28.6 (br), 28.5, 20.8, 15.5.
IR (ν_{max}, cm^{-1}) 2975 (m), 2920 (m), 2862 (m), 1722 (s), 1692 (s), 1421 (s), 1366 (m), 1242 (s), 1170 (s), 982 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{24}INNaO_3^+$ 428.0693; Found 428.0695.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-(5S,12S)-12-Iodo-9-oxadispiro[4.0.56.15]dodecan-1-one and *rel*-(5S,12R)-12-iodo-9-oxadispiro[4.0.56.15]dodecan-1-one (4c and 4c′)**

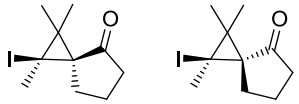


The title compounds were prepared, following the GP6, starting from 1-(6-oxaspiro[2.5]oct-1-en-1-yl)cyclobutan-1-ol **3c** (54.1 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 87:13 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 8-80% EtOAc/Pentane) to give **4c** (58 mg, 0.19 mmol, 63% yield) as an amorphous white solid and **4c′** (7.7 mg, 0.025 mmol, 8% yield) as a light-yellow oil. Total yield – 71%

Characterization data of **4c**:
Rf (40% Et_2O/Pentane) = 0.41.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.64 (m, 3H, C*H*$_2$O), 3.47 (ddd, *J* = 11.5, 5.8, 3.8 Hz, 1H, C*H*$_2$O), 2.99 (s, 1H, C*H*), 2.44 – 2.25 (m, 2H, C*H*$_2$), 2.19 (m, 1H, C*H*$_2$), 2.02 – 1.72 (m, 6H, C*H*$_2$), 1.49 (dt, *J* = 13.6, 4.6 Hz, 1H, C*H*$_2$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 212.4, 66.8, 66.7, 40.6, 37.0, 35.1, 33.9, 30.8, 29.7, 20.4, 11.6.
IR (ν_{max}, cm^{-1}) 2957 (m), 2911 (m), 2842 (m), 1718 (s), 1370 (m), 1227 (m), 1105 (s), 1010 (m), 979 (m), 827 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{11}H_{16}IO_2^+$ 307.0190; Found 307.0184.

Characterization data of **4c′**:
Rf (40% Et_2O/Pentane) = 0.54
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.65 – 3.40 (m, 4H, C*H*$_2$O), 3.28 (s, 1H, C*H*), 2.37 – 2.18 (m, 2H, C*H*$_2$), 1.98 – 1.66 (m, 6H, C*H*$_2$), 1.57 (ddd, *J* = 13.9, 7.7, 4.2 Hz, 1H, C*H*$_2$), 1.40 (dddd, *J* = 13.8, 5.3, 3.6, 1.3 Hz, 1H, C*H*$_2$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 214.7, 67.2, 66.2, 39.9, 39.8, 36.2, 33.8, 30.6, 29.4, 20.4, 15.4.
IR (ν_{max}, cm^{-1}) 2961 (m), 2918 (m), 2845 (m), 1720 (s), 1243 (m), 1218 (m), 1153 (m), 1102 (s), 1011 (w), 989 (w), 837 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{11}H_{16}IO_2^+$ 307.0190; Found 307.0186.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-(1S,3S)-1-Iodo-1,2,2-trimethylspiro[2.4]heptan-4-one and *rel*-(1S,3R)-1-iodo-1,2,2-trimethylspiro[2.4]heptan-4-one (4d and 4d′)**

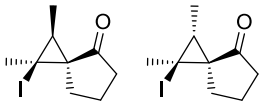


The title compounds were prepared, following the GP6, starting from 1-(2,3,3-trimethylcycloprop-1-en-1-yl)cyclobutan-1-ol **3d** (46.6 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 94:6 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 2-20% Et_2O/Pentane) to give **4d** (71 mg, 0.25 mmol, 85% yield) as an amorphous white solid and **4d′** (6.20 mg, 0.021 mmol, 7% yield) as a light-yellow oil. Total yield – 92%.

Characterization data of **4d**:
Rf (10% Et_2O/Pentane) = 0.51.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.24 (ddd, *J* = 8.6, 6.8, 1.8 Hz, 2H, CH_2), 2.02 (s, 3H, CH_3), 1.98 – 1.89 (m, 2H, CH_2), 1.86 – 1.61 (m, 2H, CH_2), 1.23 (s, 3H, CH_3), 1.07 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 212.3, 41.1, 40.6, 35.3, 30.2, 29.0, 27.7, 25.2, 19.8, 16.8.
IR (ν_{max}, cm^{-1}) 2957 (s), 2879 (m), 1717 (s), 1458 (m), 1375 (m), 1155 (m), 1112 (s), 1056 (s), 831 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{15}INaO^+$ 301.0060; Found 301.0072.

Characterization data of **4d′**:
Rf (10% Et_2O/Pentane) = 0.76.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.50 – 2.23 (m, 5H, CH_2 & CH_3), 2.17 (dt, *J* = 14.0, 7.2 Hz, 1H, CH_2), 2.03 (dt, *J* = 13.2, 6.4 Hz, 1H, CH_2), 1.94 – 1.77 (m, 2H, CH_2), 1.31 (s, 3H, CH_3), 1.28 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 214.2, 41.8, 41.4, 41.3, 37.5, 36.0, 29.4, 26.3, 20.2, 13.6.
IR (ν_{max}, cm^{-1}) 2927 (s), 2860 (m), 1720 (s), 1455 (m), 1375 (m), 1187 (m), 1166 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{10}H_{16}IO^+$ 279.0240; Found 279.0241.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-(1S, 2R, 3S)-1-Iodo-1,2-dimethylspiro[2.4]heptan-4-one and *rel*-(1S, 2S, 3S)-1-iodo-1,2-dimethylspiro[2.4]heptan-4-one (4e and 4e′)**

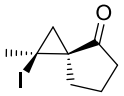


The title compounds were prepared, following the GP6, starting from 1-(2,3-dimethylcycloprop-1-en-1-yl)cyclobutan-1-ol **3e** (41.5 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 82:18 by the integration of the crude ^{1}H NMR spectrum (*$CHCH_3$ center). The crude material was purified by column chromatography (gradient 1-10% Et_2O/Pentane) to give **4e** (42 mg, 0.16 mmol, 53% yield) as a yellow oil and **4e′** (9 mg, 0.03 mmol, 11% yield) as a yellow oil. Total yield – 64%.

Characterization data of **4e**:
Rf (5% Et_2O/Pentane) = 0.63.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.41 – 2.20 (m, 3H, CH_2), 2.13 (s, 3H, CH_3), 1.98 – 1.76 (m, 3H, CH_2), 1.14 (d, *J* = 6.3 Hz, 3H, CH_3), 0.90 (q, *J* = 6.2 Hz, 1H, C*H*).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 212.3, 41.2, 38.6, 38.2, 33.1, 32.5, 24.4, 20.0, 14.9.
IR (ν_{max}, cm^{-1}) 2963 (m), 2924 (m), 2867 (m), 1725 (s), 1375 (m), 1324 (m), 1130 (s), 1058 (m), 831 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_9H_{13}INaO^+$ 286.9903; Found 286.9899.

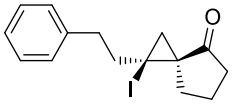
Characterization data of **4e′**:
Rf (5% Et_2O/Pentane) = 0.48
^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.46 – 2.28 (m, 2H, CH_2), 2.07 – 1.82 (m, 7H, CH_2 & CH_3), 1.77 (q, *J* = 6.6 Hz, 1H, C*H*), 1.01 (d, *J* = 6.5 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 213.2, 39.7, 39.2, 35.8, 26.0, 24.2, 20.1, 15.5, 8.0.
IR (ν_{max}, cm^{-1}) 2968 (m), 2927 (m), 2870 (m), 1729 (s), 1389 (m), 1156 (s), 1065 (m), 828 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_9H_{13}INaO^+$ 286.9903; Found 286.9892.
The relative configuration was assigned by 1D NOE experiments.

***rel*-(1S,3S)-1-iodo-1-methylspiro[2.4]heptan-4-one (4f)**



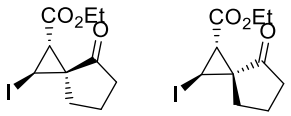
Following the GP6, starting from 1-(2-methylcycloprop-1-en-1-yl)cyclobutan-1-ol **3f** (37.2 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as an amorphous light-yellow solid (57 mg, 0.23 mmol, 76% yield).
Rf (10% Et_2O/Pentane) = 0.32.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.46 – 2.19 (m, 3H, CH_2), 2.04 (s, 3H, CH_3), 2.01 – 1.88 (m, 3H, CH_2), 1.50 (d, *J* = 5.5 Hz, 1H, CH_2), 1.12 (d, *J* = 5.5 Hz, 1H, CH_2).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 213.1, 39.1, 37.0, 33.5, 32.1, 28.7, 20.1, 9.6.
IR (ν_{max}, cm^{-1}) 2968 (m), 2924 (w), 2865 (w), 1729 (s), 1451 (w), 1418 (w), 1343 (m), 1244 (m), 1159 (s), 1119 (s), 1069 (m), 1038 (m), 817 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_8H_{12}IO^+$ 250.9927; Found 250.9927.

***rel*-(1S,3S)-1-Iodo-1-phenethylspiro[2.4]heptan-4-one (4g)**



Following the GP6, starting from 1-(2-phenethylcycloprop-1-en-1-yl)cyclobutan-1-ol **3g** (64.3 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a light-yellow oil (80 mg, 0.24 mmol, 79% yield).
Rf (10% Et_2O/Pentane) = 0.25.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.34 – 7.16 (m, 5H, Ar*H*), 3.00 – 2.88 (m, 2H, CH_2), 2.49 – 2.21 (m, 3H, CH_2), 2.08 – 1.89 (m, 5H, CH_2), 1.53 (d, *J* = 5.6 Hz, 1H, CH_2), 1.12 (d, *J* = 5.6 Hz, 1H, CH_2).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 212.7, 141.0, 128.6, 128.5, 126.1, 44.9, 39.3, 37.3, 36.2, 32.4, 29.1, 20.3, 18.9.
IR (ν_{max}, cm^{-1}) 2969 (m), 1728 (s), 1495 (m), 1453 (m), 1412 (m), 1339 (m), 1241 (m), 1154 (s), 1059 (m), 751 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}IO^+$ 341.0397; Found 341.0392.
The relative configuration was assigned by analogy to compound **2a**.

***rel*-Ethyl (1S,2S,3S)-2-iodo-4-oxospiro[2.4]heptane-1-carboxylate and ethyl (1S,2S,3R)-2-iodo-4-oxospiro[2.4]heptane-1-carboxylate (4h and 4h')**



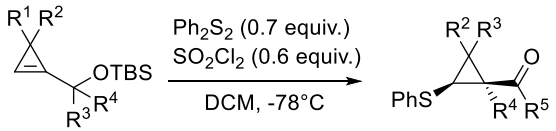
The title compounds were prepared, following the GP6 (in $MeNO_2$ at -20°C), starting from ethyl 2-(1-((*tert*-butyldimethylsilyl)oxy)cyclobutyl)cycloprop-2-ene-1-carboxylate **5d** (88.9 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 69:31 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 2-20% Et_2O/Pentane) to give **4h** (49 mg, 0.16 mmol, 53% yield) as a colorless oil and **4h'** (23 mg, 0.075 mmol, 25% yield) as a colorless oil. Total yield – 78%.

Alternatively, the title compounds were prepared, following the GP6 (in $MeNO_2$ at -20°C), starting from ethyl 2-(1-hydroxycyclobutyl)cycloprop-2-ene-1-carboxylate **3h** (54.7 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 82:18 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 2-20% Et_2O/Pentane) to give **4h** (46 mg, 0.15 mmol, 50% yield) as a colorless oil and **4h'** (8.7 mg, 0.027 mmol, 9% yield) as a colorless oil. Total yield – 60%.

Characterization data of **4h**:
Rf (10% Et_2O/Pentane) = 0.24.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.14 (qd, *J* = 7.1, 1.9 Hz, 2H, OCH_2), 3.29 (d, *J* = 6.0 Hz, 1H, C*H*I), 2.60 – 2.31 (m, 3H, CH_2 & C*H*CO_2Et), 2.31 – 2.14 (m, 2H, CH_2), 2.07 – 1.94 (m, 2H, CH_2), 1.25 (t, *J* = 7.1 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 210.9, 168.7, 61.4, 39.7, 38.8, 36.3, 29.4, 20.5, 14.0, -4.8.
IR (ν_{max}, cm^{-1}) 2975 (w), 2874 (w), 1725 (s), 1406 (m), 1319 (m), 1267 (s), 1194 (s), 1150 (s), 1090 (m), 1033 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{13}INaO_3^+$ 330.9802; Found 330.9801.
The relative configuration was assigned by analogy with previously described experiments.

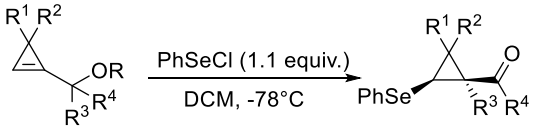
Characterization data of **4h'**:
Rf (10% Et_2O/Pentane) = 0.16.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.10 (qd, *J* = 7.2, 1.1 Hz, 2H, OCH_2), 3.57 (d, *J* = 6.3 Hz, 1H, C*H*I), 2.53 – 2.32 (m, 2H, CH_2), 2.29 (d, *J* = 6.3 Hz, 1H, C*H*CO_2Et), 2.18 – 1.97 (m, 4H, CH_2), 1.22 (t, *J* = 7.1 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.5, 166.6, 61.3, 41.7, 39.7, 39.4, 35.1, 20.2, 13.9, -1.7.
IR (ν_{max}, cm^{-1}) 2982 (w), 1739 (s), 1407 (m), 1239 (s), 1201 (m), 1154 (m), 1098 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{13}INaO_3^+$ 330.9802; Found 330.9801.
The relative configuration was assigned by analogy to compound **2a**.

General procedure 7 (GP7). Sulfenylative semipinacol rearrangement



Under N_2 atmosphere: To a solution of phenyl disulfide (46 mg, 0.21 mmol, 0.70 equiv.) in DCM (2.5 mL) sulfuryl dichloride (14.5 µL, 0.180 mmol, 0.600 equiv.) was added. The reaction mixture was stirred for 30 min, then cooled to -78 °C. A solution of cyclopropene (0.30 mmol, 1.00 equiv.) in DCM (0.5 mL) was added. The reaction mixture was stirred at -78 °C until full consumption of the starting cyclopropene (checked by TLC). The mixture was poured into saturated aqueous $NaHCO_3$ (10 mL), extracted with DCM (2x10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude material was purified by column chromatography.

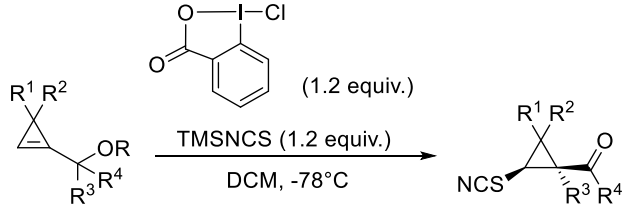
General procedure 8 (GP8). Selenylative semipinacol rearrangement



R = TBS, H

To a solution of cyclopropene (0.30 mmol, 1.00 equiv.) in DCM (3 mL), cooled to -78 °C, PhSeCl (63.2 mg, 0.330 mmol, 1.10 equiv.) was added. The reaction mixture was stirred at -78 °C until full consumption of the starting cyclopropene (checked by TLC). The mixture was poured into saturated aqueous $NaHCO_3$ (10 mL) and extracted with DCM (2x10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude material was purified by column chromatography.

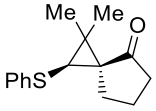
General procedure 9 (GP9). Thiocyanative semipinacol rearrangement.



R = TBS, H

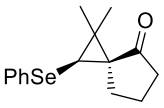
Under N_2 atmosphere: To a solution of 1-chloro-1λ^3-benzo[d][1,2]iodaoxol-3(1H)-one (102 mg, 0.360 mmol, 1.20 equiv.) in DCM (2.5 mL) trimethylsilyl isothiocyanate (50.7 µL, 0.360 mmol, 1.20 equiv.) was added. The reaction mixture was stirred for 30 min, then cooled to -78 °C. A solution of cyclopropene (0.30 mmol, 1.00 equiv.) in DCM (0.5 mL) was added. The reaction mixture was stirred at -78 °C until full consumption of the starting cyclopropene (checked by TLC). The mixture was poured into saturated aqueous $NaHCO_3$ (10 mL) and extracted with DCM (2x10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude material was purified by column chromatography.

***rel*-(2S,3S)-1,1-Dimethyl-2-(phenylthio)spiro[2.4]heptan-4-one (6a)**



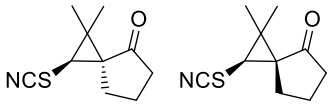
Following the GP7, starting from *tert*-butyl(1-(3,3-dimethylcycloprop-1-en-1-yl)cyclobutoxy)dimethylsilane **5a** (75.7 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% EtOAc/Pentane) as a light-yellow solid (61 mg, 0.25 mmol, 82% yield).
Rf (5% EtOAc/Pentane) = 0.56.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.31 – 7.24 (m, 2H, Ar*H*), 7.23 – 7.18 (m, 2H, Ar*H*), 7.16 – 7.09 (m, 1H, Ar*H*), 2.49 (s, 1H, C*H*), 2.37 – 2.15 (m, 3H, CH_2), 2.05 – 1.87 (m, 3H, CH_2), 1.35 (s, 3H, CH_3), 1.34 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 213.3, 138.5, 128.8, 127.0, 125.0, 44.2, 40.7, 40.6, 33.3, 31.7, 23.9, 20.7, 14.8.
IR (ν_{max}, cm^{-1}) 3066 (w), 2957 (m), 2871 (m), 1720 (s), 1584 (m), 1478 (m), 1372 (m), 1266 (m), 1167 (m), 1040 (m), 832 (w), 739 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}NaOS^+$ 269.0971; Found 269.0975.
The relative configuration was assigned by NOESY experiment.

***rel*-(2S,3S)-1,1-Dimethyl-2-(phenylselanyl)spiro[2.4]heptan-4-one (7a)**



Following the GP8, starting from *tert*-butyl(1-(3,3-dimethylcycloprop-1-en-1-yl)cyclobutoxy)dimethylsilane **5a** (75.7 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% EtOAc/Pentane) as a yellow oil (74 mg, 0.25 mmol, 84% yield).
Rf (5% EtOAc/Pentane) = 0.6.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H, Ar*H*), 7.21 – 7.09 (m, 3H, Ar*H*), 2.44 (s, 1H, C*H*), 2.30 – 2.12 (m, 3H, CH_2), 1.98 – 1.79 (m, 3H, CH_2), 1.28 (s, 3H, CH_3), 1.26 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 215.1, 132.5, 131.5, 129.0, 126.3, 41.1, 40.7, 40.3, 33.0, 31.2, 24.1, 21.0, 16.9.
IR (ν_{max}, cm^{-1}) 3064 (w), 2954 (m), 2871 (m), 1717 (s), 1579 (m), 1476 (m), 1371 (m), 1266 (m), 1166 (m), 1040 (m), 831 (m), 736 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}NaOSe^+$ 317.0415; Found 317.0421.
The relative configuration was assigned by analogy to compound **6a**.

***rel*-(2S,3S)-1,1-Dimethyl-2-thiocyanatospiro[2.4]heptan-4-one and *rel*-(2S,3R)-1,1-dimethyl-2-thiocyanatospiro[2.4]heptan-4-one (8a and 8a′)**

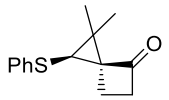


The title compounds were prepared, following the GP9, starting from *tert*-butyl(1-(3,3-dimethylcycloprop-1-en-1-yl)cyclobutoxy)dimethylsilane **5a** (75.7 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 42:58 by the integration of the crude ^{1}H NMR spectrum. The crude material was purified by column chromatography (gradient 2-20% EtOAc/Pentane) to give **8a** (22 mg, 0.11 mmol, 37% yield) as a yellow oil and **8a′** (30 mg, 0.15 mmol, 51% yield) as a yellow oil. Total yield – 89%.

Characterization data of **8a**:
Rf (10% EtOAc/Pentane) = 0.44.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (s, 1H, C*H*), 2.42 – 2.28 (m, 2H, CH_2), 2.30 – 2.14 (m, 1H, CH_2), 2.12 – 1.89 (m, 3H, CH_2), 1.34 (s, 3H, CH_3), 1.29 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 213.9, 113.4, 41.7, 40.4, 40.1, 33.1, 30.4, 23.3, 20.8, 14.8.
IR (ν_{max}, cm^{-1}) 2960 (m), 2928 (m), 2876 (w), 2157 (m), 1721 (s), 1455 (w), 1363 (m), 1250 (m), 1171 (m), 1109 (m), 1038 (w), 835 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{13}NNaOS^+$ 218.0610; Found 218.0608.

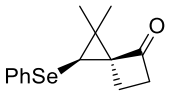
Characterization data of **8a′**:
Rf (10% EtOAc/Pentane) = 0.56.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 (s, 1H, C*H*), 2.38 (t, *J* = 7.3 Hz, 2H, CH_2), 2.18 – 2.11 (m, 2H, CH_2), 2.11 – 1.97 (m, 2H, CH_2), 1.30 (s, 3H, CH_3), 1.25 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.3, 111.3, 42.4, 39.7, 39.0, 34.0, 26.1, 21.1, 19.1, 18.4.
IR (ν_{max}, cm^{-1}) 2962 (m), 2926 (m), 2874 (m), 2154 (m), 1722 (s), 1461 (m), 1375 (m), 1267 (m), 1172 (m), 1109 (w), 1044 (m), 961 (w), 915 (w), 833 (w), 740 (w).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{13}NNaOS^+$ 218.0610; Found 218.0607.
The relative configurations were assigned by NOESY experiments.

***rel*-(2S,3S)-1,1-dimethyl-2-(phenylthio)spiro[2.3]hexan-4-one (6b)**



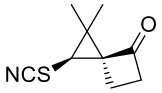
Following the GP7, starting from *tert*-butyl((3',3'-dimethyl-[1,1'-bi(cyclopropan)]-1'-en-1-yl)oxy)dimethylsilane **5b** (71.5 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a light-yellow oil (53 mg, 0.23 mmol, 76% yield).
Rf (5% Et_2O/Pentane) = 0.45.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.19 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.13 – 7.01 (m, 3H, Ar*H*), 2.93 – 2.72 (m, 3H, CH_2 & C*H*), 1.98 (ddd, *J* = 11.6, 9.4, 5.8 Hz, 1H, CH_2), 1.88 (ddd, *J* = 11.6, 9.0, 5.9 Hz, 1H, CH_2), 1.31 (s, 3H, CH_3), 1.14 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.3, 136.9, 129.0, 126.0, 125.2, 54.7, 43.4, 39.9, 34.7, 21.2, 17.8, 15.3.
IR (ν_{max}, cm^{-1}) 3061 (w), 2980 (m), 2952 (m), 2870 (w), 1758 (s), 1583 (m), 1480 (m), 1441 (m), 1373 (m), 1227 (m), 1150 (m), 1100 (s), 1027 (m), 983 (w), 738 (s).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}OS^+$ 233.0995; Found 233.0995.
The relative configuration was assigned by analogy to compound **6a**.

***rel*-(2S,3S)-1,1-Dimethyl-2-(phenylselanyl)spiro[2.3]hexan-4-one (7b)**



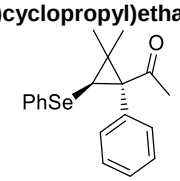
Following the GP8, starting from *tert*-butyl((3',3'-dimethyl-[1,1'-bi(cyclopropan)]-1'-en-1-yl)oxy)dimethylsilane **5b** (71.5 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a light-yellow oil (59 mg, 0.21 mmol, 71% yield).
Rf (5% Et_2O/Pentane) = 0.45.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.33 (m, 2H, Ar*H*), 7.29 – 7.24 (m, 2H, Ar*H*), 7.21 (m, 1H, Ar*H*), 3.09 (s, 1H, C*H*), 2.96 (ddd, *J* = 17.3, 9.5, 6.0 Hz, 1H, CH_2), 2.86 (ddd, *J* = 17.3, 9.2, 5.7 Hz, 1H, CH_2), 2.11 (ddd, *J* = 11.4, 9.4, 5.7 Hz, 1H, CH_2), 1.98 (ddd, *J* = 11.4, 9.2, 6.0 Hz, 1H, CH_2), 1.41 (s, 3H, CH_3), 1.26 (s, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.6, 130.9, 129.7, 129.2, 126.2, 43.3, 37.1, 34.5, 21.4, 19.7, 16.7.
IR (ν_{max}, cm^{-1}) 3058 (w), 2979 (m), 2952 (m), 2870 (w), 1756 (s), 1579 (w), 1477 (m), 1440 (m), 1375 (m), 1216 (m), 1152 (m), 1094 (s), 1074 (m), 1025 (m), 983 (w), 735 (s).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}OSe^+$ 281.0439; Found 281.0438.
The relative configuration was assigned by analogy to compound **6a**.

***rel*-(2S,3S)-1,1-Dimethyl-2-thiocyanatospiro[2.3]hexan-4-one (8b)**



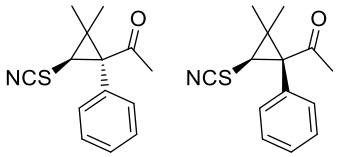
Following the GP8, starting from *tert*-butyl((3',3'-dimethyl-[1,1'-bi(cyclopropan)]-1'-en-1-yl)oxy)dimethylsilane **5b** (71.5 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a light-yellow oil (42 mg, 0.23 mmol, 77% yield).
Rf (10% Et_2O/Pentane) = 0.29.
^1H NMR (400 MHz, CD_2Cl_2) δ 3.09 – 3.01 (m, 3H, C*H*$_2$ & C*H*), 2.32 – 2.13 (m, 2H, C*H*$_2$), 1.32 (s, 3H, C*H*$_3$), 1.29 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 208.6, 110.9, 53.9, 44.0, 37.4, 34.2, 20.5, 17.7, 15.2.
IR (ν_{max}, cm^{-1}) 2982 (m), 2931 (m), 2883 (w), 2157 (m), 1765 (s), 1451 (w), 1377 (m), 1231 (m), 1160 (m), 1100 (s), 1032 (m).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_9H_{11}NNaOS^+$ 204.0454; Found 204.0453.

***rel*-1-((1S,3S)-2,2-Dimethyl-1-phenyl-3-(phenylselanyl)cyclopropyl)ethan-1-one (7c)**



Following the GP8, starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-phenylethan-1-ol **1b** (56.5 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 1-10% Et_2O/Pentane) as a colorless oil (52 mg, 0.15 mmol, 50% yield).
Rf (5% Et_2O/Pentane) = 0.45.
^1H NMR (400 MHz, CD_2Cl_2) δ 7.51 – 7.16 (m, 10H, Ar*H*), 2.77 (s, 1H, C*H*), 2.06 (s, 3H, RC(O)C*H*$_3$), 1.35 (s, 3H, C*H*$_3$), 1.20 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 204.4, 138.3, 133.9, 130.6, 130.6, 129.0, 128.6, 127.6, 126.0, 51.1, 36.0, 29.7, 29.5, 24.8, 19.1.
IR (ν_{max}, cm^{-1}) 3058 (m), 3022 (w), 2976 (m), 2950 (m), 2927 (m), 2867 (w), 1696 (s), 1579 (m), 1476 (m), 1440 (m), 1356 (m), 1216 (m), 1108 (m), 1024 (m), 736 (s).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}OSe^+$ 345.0752; Found 345.0753.
The relative configuration was assigned by analogy to compound **6a**.

***rel*-1-((1S,3S)-2,2-Dimethyl-1-phenyl-3-thiocyanatocyclopropyl)ethan-1-one and *rel*-1-((1S,3R)-2,2-dimethyl-1-phenyl-3-thiocyanatocyclopropyl)ethan-1-one (8c and 8c′)**

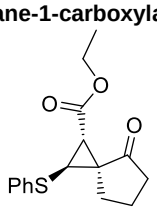


The title compounds were prepared, following the GP9, starting from 1-(3,3-dimethylcycloprop-1-en-1-yl)-1-phenylethan-1-ol **1b** (56.5 mg, 0.300 mmol, 1.00 equiv.). The *dr* value was determined to be 93:7 by the integration of the crude ^1H NMR spectrum. The crude material was purified by column chromatography (gradient 2-20% Et_2O/Pentane) to give inseparable mixture of **8c** and **8c′** (96:4) (41 mg, 0.17 mmol, 55% yield) as a colorless oil.

Characterization data of **8c**:
Rf (10% Et_2O/Pentane) = 0.34.
^1H NMR (400 MHz, CD_2Cl_2) δ 7.46 – 7.31 (m, 5H, Ar*H*), 2.87 (s, 1H, C*H*), 2.07 (s, 3H, RC(O)C*H*$_3$), 1.40 (s, 3H, C*H*$_3$), 1.17 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 204.7, 136.1, 130.5, 128.9, 128.3, 114.6, 50.6, 39.8, 30.6, 29.0, 23.9, 17.2.
IR (ν_{max}, cm^{-1}) 3061 (w), 3029 (w), 2981 (w), 2961 (w), 2931 (w), 2874 (w), 2154 (m), 1696 (s), 1447 (m), 1359 (m), 1271 (m), 1220 (m), 1190 (m), 1112 (m), 1024 (w), 989 (w), 952 (w), 761 (m).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{15}NNaOS^+$ 268.0767; Found 268.0766.

Characterization data of **8c′**:
Rf (10% Et_2O/Pentane) = 0.34.
^1H NMR (400 MHz, CD_2Cl_2) δ 7.46 – 7.31 (m, 3H, Ar*H*), 7.23 (dd, *J* = 7.9, 1.7 Hz, 2H, Ar*H*), 3.58 (s, 1H, C*H*), 1.96 (s, 3H, RC(O)C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.29 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 202.8, 133.2, 131.4, 129.2, 128.6, 111.8, 51.1, 34.6, 32.3, 29.2, 20.7, 19.7.
IR (ν_{max}, cm^{-1}) 3061 (w), 3029 (w), 2981 (w), 2961 (w), 2931 (w), 2874 (w), 2154 (m), 1696 (s), 1447 (m), 1359 (m), 1271 (m), 1220 (m), 1190 (m), 1112 (m), 1024 (w), 989 (w), 952 (w), 761 (m).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{15}NNaOS^+$ 268.0767; Found 268.0766.
The relative configuration was assigned by analogy to compound **6a**.

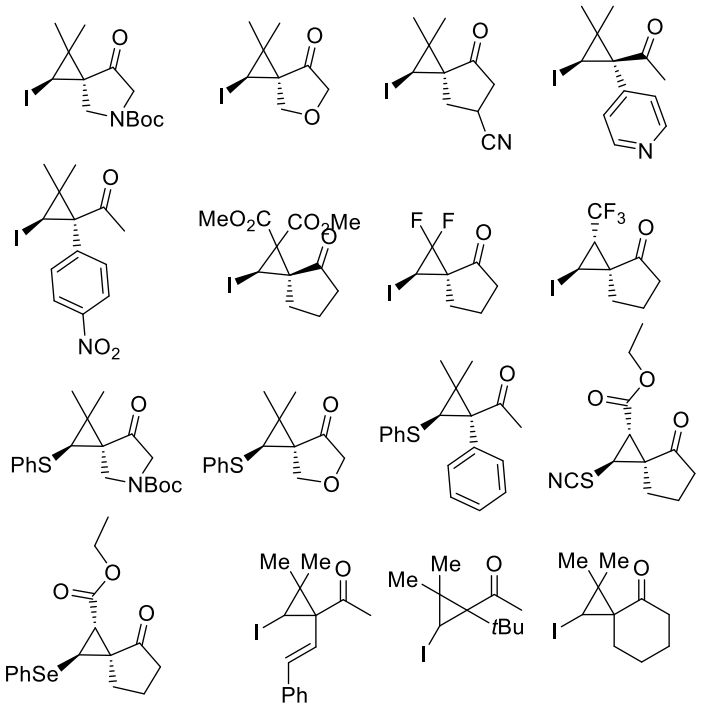
***rel*-Ethyl (1S,2S,3S)-4-oxo-2-(phenylthio)spiro[2.4]heptane-1-carboxylate (6d)**



Following the GP7 (the reaction was run at -40 °C instead of -78 °C), starting from ethyl 2-(1-((*tert*-butyldimethylsilyl)oxy)cyclobutyl)cycloprop-2-ene-1-carboxylate **5d** (88.9 mg, 0.300 mmol, 1.00 equiv.) the title compound was obtained after a purification by chromatography (gradient 2-20% Et_2O/Pentane) as a yellow oil (52 mg, 0.18 mmol, 59% yield).
Rf (10% Et_2O/Pentane) = 0.16.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.32 – 7.15 (m, 5H, Ar*H*), 4.17 (qd, *J* = 7.1, 2.4 Hz, 2H, OCH_2), 3.22 (d, *J* = 6.0 Hz, 1H, C*H*S), 2.53 (d, *J* = 6.0 Hz, 1H, C*H*CO_2Et), 2.35 – 2.11 (m, 4H, CH_2), 2.10 – 1.97 (m, 1H, CH_2), 1.95 – 1.76 (m, 1H, CH_2), 1.26 (t, *J* = 7.1 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 210.4, 169.1, 136.6, 129.0, 128.6, 126.3, 61.3, 42.7, 38.8, 37.4, 34.5, 29.9, 20.6, 14.0.
IR (ν_{max}, cm^{-1}) 2977 (m), 2936 (w), 2879 (w), 1725 (s), 1583 (w), 1478 (m), 1409 (m), 1321 (m), 1264 (s), 1206 (s), 1166 (s), 1092 (m), 1029 (m), 842 (w), 742 (m).
HRMS (Sicrit plasma/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}O_3S^+$ 291.1049; Found 291.1049.
The relative configuration was assigned by analogy to compound **6a**.

Unsuccessful examples

During the exploration of the scope of the transformations we encountered several unsuccessful examples, that are summarized in Scheme S1. The reaction is sensitive to variations of electron density of both cyclopropene double bond and migrating group. In particular, electron-withdrawing substituents on the aliphatic carbon of the cyclopropene ring or on the migrating group can prevent the reaction ot occur.

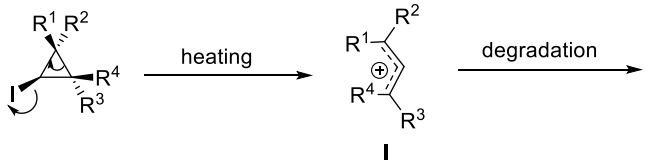


Scheme S1

Stability of the products

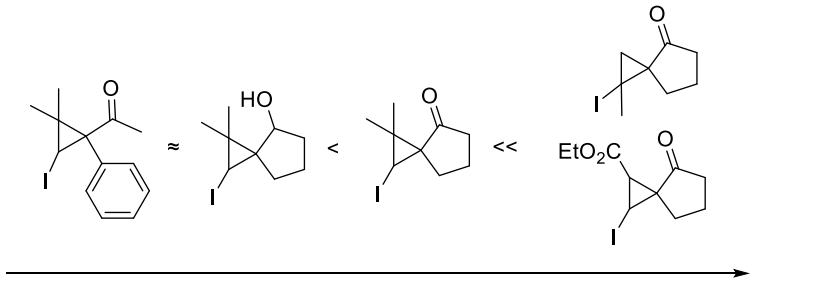
It should be noted that some of the synthesized products posess limited stability. Polysubstituted iodocyclopropanes are unstable under heating, producing unidentifiable black polymer-like residues. The instability can be explained by a concerted ionization of the C-I bond/electrocyclic ring-opening of the cyclopropane ring, followed by degradation processes (Scheme S2A). The speculative stability order, based on experimental observations is presented in Scheme S2B , and corresponds to the inverted order of the stability of cation **I** . We recommend to avoid temperatures higher than 30 °C during all manipulations needed for isolation of the compounds structurally similar to the left three compounds from Scheme Xb. We also recommend storage of such compounds at -20°C.

a) Degradation of polysubstituted iodocyclopropanes:



I

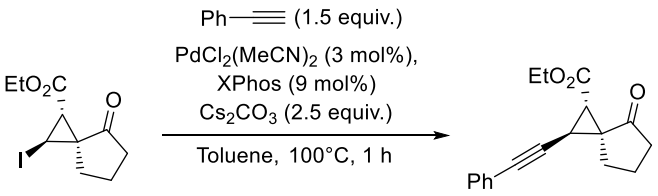
b) Speculative relative stability of iodocyclopropanes:



Scheme S2

Product modifications

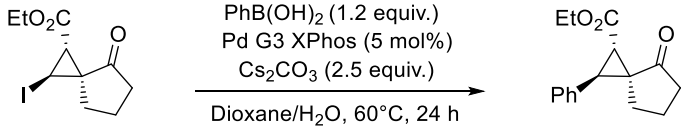
***rel*-Ethyl (1S,2R,3S)-4-oxo-2-(phenylethynyl)spiro[2.4]heptane-1-carboxylate (9)**



Under N_2 atmosphere: According to a reported procedure,[16] a reaction tube was charged with $PdCl_2(MeCN)_2$ (1.58 mg, 6.00 µmol, 3 mol %), X-Phos (8.54 mg, 18.0 µmol, 9 mol %), Cs_2CO_3 (163 mg, 0.500 mmol, 2.50 equiv) and *rel*-ethyl (1S,2S,3S)-2-iodo-4-oxospiro[2.4]heptane-1-carboxylate **4h** (61.6 mg, 0.200 mmol) in toluene (1 mL). The resulting mixture was heated to 100 °C. Phenylacetylene (33.6 µL, 0.300 mmol, 1.50 equiv) was added. After a total duration of 1 h heating at 100 °C, the reaction mixture was cooled to rt and filtered through a pad of Celite (EtOAc). The filtrate was then concentrated under reduced pressure and the residue was purified by flash chromatography (2-20% Et_2O/Pentane) to afford *rel*-ethyl (1S,2R,3S)-4-oxo-2-(phenylethynyl)spiro[2.4]heptane-1-carboxylate **9** (25 mg, 0.088 mmol, 44% yield) as an orange oil.

Rf (10% Et_2O/Pentane) = 0.21.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 2H, Ar*H*), 7.21 – 7.11 (m, 3H, Ar*H*), 4.09 (qd, *J* = 7.1, 3.9 Hz, 2H, OCH_2), 2.58 (d, *J* = 6.1 Hz, 1H, C*H*), 2.46 – 2.35 (m, 2H, CH_2 & C*H*), 2.32 – 2.12 (m, 2H, C*H*), 2.10 – 1.92 (m, 3H, CH_2), 1.19 (t, *J* = 7.1 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 169.3, 131.8, 128.2, 128.1, 122.9, 84.4, 82.1, 61.3, 42.9, 38.8, 34.2, 29.2, 25.0, 20.7, 14.3.
IR (ν_{max}, cm^{-1}) 2983 (m), 2904 (m), 2361 (w), 1728 (s), 1411 (w), 1324 (m), 1267 (m), 1213 (s), 1171 (s), 1090 (m), 1038 (m), 759 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}NaO_3^+$ 305.1148; Found 305.1155.

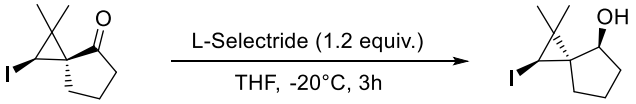
***rel*-Ethyl (1S,2R,3S)-4-oxo-2-phenylspiro[2.4]heptane-1-carboxylate (10)**



Under N_2 atmosphere: A reaction tube was charged with Pd G3 XPhos (8.46 mg, 0.0100 mmol, 5.00 mol%), Cs_2CO_3 (163 mg, 0.500 mmol, 2.50 equiv.), and $PhB(OH)_2$ (29.3 mg, 0.240 mmol, 1.2 equiv.). A solution of *rel*-ethyl (1S,2S,3S)-2-iodo-4-oxospiro[2.4]heptane-1-carboxylate **4h** (61.6 mg, 0.200 mmol) in dioxane (1 mL) was added, followed by water (0.2 mL). The reaction mixture was heated at 60 °C for 24 h. The reaction mixture was cooled to rt and filtered through a pad of Celite (EtOAc). The filtrate was then concentrated under reduced pressure and the residue was purified by flash chromatography (2-20% Et_2O/Pentane) to afford *rel*-ethyl (1S,2R,3S)-4-oxo-2-phenylspiro[2.4]heptane-1-carboxylate **10** (37 mg, 0.22 mmol, 72% yield) as a yellow oil.

Rf (10% Et_2O/Pentane) = 0.21.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H, Ar*H*), 7.23 – 7.16 (m, 3H, Ar*H*), 4.21 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.13 (d, *J* = 6.9 Hz, 1H, C*H*), 2.94 (d, *J* = 6.9 Hz, 1H, C*H*), 2.42 – 1.99 (m, 6H, CH_2), 1.31 (t, *J* = 7.1 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.0, 170.6, 134.1, 128.8, 128.1, 127.2, 61.1, 44.3, 41.9, 39.0, 31.8, 30.5, 21.0, 14.3.
IR (ν_{max}, cm^{-1}) 2982 (m), 2903 (w), 2876 (w), 1723 (s), 1450 (m), 1321 (m), 1267 (m), 1224 (m), 1200 (m), 1165 (s), 1098 (m), 1044 (m), 844 (w), 741 (w)-
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}NaO_3^+$ 281.1148; Found 281.1151.

***rel*-(2S,3S,4S)-2-Iodo-1,1-dimethylspiro[2.4]heptan-4-ol (11)**



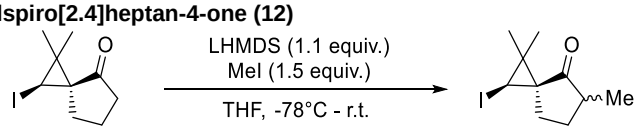
Under N_2 atmosphere: To a solution of *rel*-(2S,3S)-2-iodo-1,1-dimethylspiro[2.4]heptan-4-one **2a** (1.00 g, 3.79 mmol, 1.00 equiv.) in THF (20 mL), cooled to -20 °C, a solution of L-Selectride (1.00 M in THF, 4.54 mL, 4.54 mmol, 1.20 equiv.) was added dropwise. The resulting mixture was stirred at -20 °C for 3 h. Saturated aqueous NH_4Cl (20 mL) was added and the reaction mixture was extracted with Et_2O (2x50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting crude was purified by column chromatography (gradient 2-20% Et_2O/Pentane) to give *rel*-(2S,3S,4S)-2-iodo-1,1-dimethylspiro[2.4]heptan-4-ol **11** (590 mg, 2.22 mmol, 59% yield) as an orange oil.

Rf (10% Et_2O/Pentane) = 0.55.
^{1}H NMR (400 MHz, C_6D_6) δ 3.93 (m, 1H, HOC*H*), 2.40 (t, *J* = 2.1 Hz, 1H, C*H*I), 2.18 (s, 1H, O*H*), 2.12 – 1.97 (m, 1H, CH_2), 1.90 (ddd, *J* = 13.2, 8.0, 2.8 Hz, 1H, CH_2), 1.77 (ddd, *J* = 13.1, 10.0, 6.3 Hz, 1H, CH_2), 1.46 (ddtt, *J* = 18.0, 8.7, 6.1, 2.7 Hz, 1H, CH_2), 1.33 (dddd, *J* = 18.9, 9.5, 4.4, 1.8 Hz, 1H, CH_2), 1.19 (ddd, *J* = 13.3, 8.6, 4.8 Hz, 1H, CH_2), 0.99 (s, 3H, CH_3), 0.66 (s, 3H, CH_3).
^{13}C NMR (101 MHz, C_6D_6) δ 76.7, 40.0, 33.6, 26.9, 24.1, 23.1, 23.1, 21.2, 12.6.
IR (ν_{max}, cm^{-1}) 3235 (m), 2976 (s), 2904 (m), 1617 (m), 1451 (m), 1392 (m), 1328 (m), 1070 (m), 812 (s).

HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + H_{-1}]^+$ Calcd for $C_9H_{14}IO^+$ 265.0084; Found 265.0084.

The relative configuration was assigned by 1D NOE experiment.

***rel*-(2S,3S)-2-Iodo-1,1,5-trimethylspiro[2.4]heptan-4-one (12)**

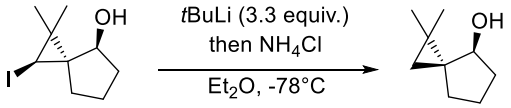


Under N_2 atmosphere: To a solution of *rel*-(2S,3S)-2-iodo-1,1-dimethylspiro[2.4]heptan-4-one **2b** (132 mg, 0.500 mmol, 1.00 equiv.) in THF (2 mL), cooled to -78 °C a solution of LHMDS (1.00 M in THF, 0.55 mL, 0.55 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was stirred at -78 °C for 30 min. MeI (106 mg, 0.750 mmol, 1.50 equiv.) was added and the reaction mixture was stirred at rt overnight. Saturated aqueous NH_4Cl (5 mL) was added and the reaction mixture was extracted with Et_2O (2x5 mL). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting crude was purified by column chromatography (gradient 1-10% Et_2O/Pentane) to give *rel*-(2S,3S)-2-iodo-1,1,5-trimethylspiro[2.4]heptan-4-one **12** (95 mg, 0.34 mmol, 68% yield) as a yellow oil (inseparable mixture of diastereomers (64:36 dr)).

Rf (5% Et_2O/Pentane) = 0.5.
^{1}H NMR (400 MHz, CD_2Cl_2) ((peaks are reported as they are seen in spectrum, the peaks that are surely correspond to major diastereomer are reported in *italic,* the peaks that are surely correspond to minor diastereomer are reported in **bold**) δ **2.98 (s, 0.33H,** C*H***)**, *2.95 (s, 0.58H,* C*H)*, 2.38 – 2.02 (m, 3H), *1.90 (ddd, J = 13.3, 10.5, 6.9 Hz, 0.67H)*, **1.81 – 1.70 (m, 0.37H)**, **1.56 – 1.45 (m, 0.36H)**, *1.38 (dtd, J = 12.5, 10.8, 7.2 Hz, 0.77H)*, *1.27 (s, 2.04H)*, **1.24 (s, 1.04H)**, **1.21 (s, 1.09H)**, *1.17 (s, 1.89H)*, 1.05 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, CD_2Cl_2) (major diastereomer) δ 214.2, 45.7, 37.4, 32.5, 29.4, 28.5, 22.9, 20.2, 15.1, 14.7.
^{13}C NMR (101 MHz, CD_2Cl_2) (minor diatereomer) δ 213.9, 45.9, 37.3, 30.9, 30.4, 29.1, 23.1, 19.6, 16.1, 13.9.
IR (ν_{max}, cm^{-1}) 2961 (m), 2929 (m), 2868 (m), 1721 (s), 1455 (m), 1372 (m), 1357 (m), 1238 (m), 1159 (m), 1109 (m), 1002 (m), 898 (w).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{15}INaO^+$ 301.0060; Found 301.0060.

Relative configuration of the major/minor diastereomer was not assigned.

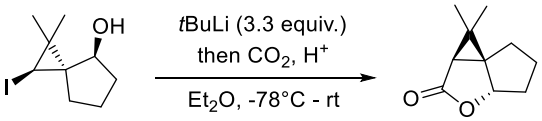
***rel*-(3S,4S)-1,1-Dimethylspiro[2.4]heptan-4-ol (13)**



Under N_2 atmosphere: To a solution of *t*BuLi (1.70 M in pentane, 0.53 mL, 0.91 mmol, 3.3 equiv.) in Et_2O (1.5 mL), cooled to -78 °C, a solution of *rel*-(2S,3S,4S)-2-iodo-1,1-dimethylspiro[2.4]heptan-4-ol **11** (73.1 mg, 0.270 mmol, 1.00 equiv.) in Et_2O (1.5 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 30 min. Saturated aqueous NH_4Cl (5 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting crude was purified by column chromatography (gradient 2-20% Et_2O/Pentane) to give *rel*-(3S,4S)-1,1-dimethylspiro[2.4]heptan-4-ol **13** (34 mg, 0.24 mmol, 88% yield) as a colorless oil.

Rf (10% Et_2O/Pentane) = 0.29.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (dd, *J* = 4.9, 2.9 Hz, 1H, C*H*), 1.90 – 1.68 (m, 4H, CH_2), 1.67 – 1.58 (m, 1H, CH_2), 1.57 – 1.48 (m, 1H, CH_2), 1.23 – 1.18 (br s, 1H, O*H*), 1.08 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 0.59 (d, *J* = 4.3 Hz, 1H, CH_2), 0.19 (d, *J* = 4.3 Hz, 1H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 73.1, 36.4, 36.1, 30.3, 22.4, 21.7, 21.7, 21.4, 19.1.
IR (ν_{max}, cm^{-1}) 3433 (w), 2972 (m), 2870 (w), 1069 (w), 910 (s), 730 (s).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_9H_{15}^+$ 123.1168; Found 123.1169.

***rel*-(1aS,3aS,6aS)-1,1-Dimethylhexahydro-2H-cyclopenta[b]cyclopropa[c]furan-2-one (14)**

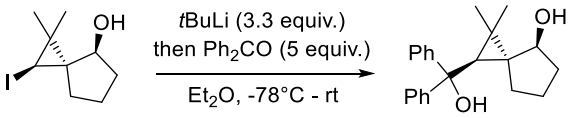


Under N_2 atmosphere: To a solution of *t*BuLi (1.70 M in pentane, 0.58 mL, 0.99 mmol, 3.3 equiv.) in Et_2O (1.5 mL), cooled to -78 °C, a solution of *rel*-(2S,3S,4S)-2-iodo-1,1-dimethylspiro[2.4]heptan-4-ol **11** (79.8 mg, 0.300 mmol, 1.00 equiv.) in Et_2O (1.5 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 30 min. Dry CO_2 was bubbled through the solution during 30 min. The reaction mixture was stirred at r.t under 1 atm of CO_2 overnight. 1 N HCl (5 mL) was added and the reaction mixture was stirred for 15 min. The layers were separated and the aqueous layer was extracted with Et_2O (5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting crude product was purified by column chromatography (gradient 4-40% Et_2O/Pentane) to give *rel*-(1aS,3aS,6aS)-1,1-dimethylhexahydro-2H-cyclopenta[b]cyclopropa[c]furan-2-one **14** (29 mg, 0.17 mmol, 58% yield) as an orange oil.

Rf (20% Et_2O/Pentane) = 0.49.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (dd, *J* = 7.4, 5.0 Hz, 1H, OC*H*), 2.23 – 2.08 (m, 1H, CH_2), 2.01 – 1.80 (m, 3H, CH_2), 1.78 – 1.67 (m, 2H, CH_2), 1.61 (s, 1H, C*H*), 1.20 (s, 3H, CH_3), 1.19 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 81.8, 46.7, 36.7, 33.6, 27.8, 26.9, 22.9, 22.8, 16.8.

IR (v_{max}, cm^{-1}) 2967 (m), 2873 (m), 1758 (s), 1451 (w), 1380 (w), 1352 (w), 1260 (w), 1181 (m), 1141 (m), 1112 (m), 1052 (s), 982 (m), 915 (w.)
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{14}NaO_2^+$ 189.0886; Found 189.0890.

***rel*-(2S,3S,4S)-2-(Hydroxydiphenylmethyl)-1,1-dimethylspiro[2.4]heptan-4-ol (15)**



Under N_2 atmosphere: To a solution of *t*BuLi (1.70 M in pentane, 0.58 mL, 0.99 mmol, 3.3 equiv.) in Et_2O (1.5 mL), cooled to -78 °C, a solution of *rel*-(2S,3S,4S)-2-iodo-1,1-dimethylspiro[2.4]heptan-4-ol **11** (79.8 mg, 0.300 mmol, 1.00 equiv.) in Et_2O (1.5 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 30 min. A solution of benzophenone (273 mg, 1.50 mmol, 5.00 equiv.) in Et_2O (2 mL) was added dropwise. The reaction mixture was stirred at rt overnight. Saturated aqueous NH_4Cl (5 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting crude product was purified by column chromatography (gradient 4-40% Et_2O/Pentane) to give *rel*-(2S,3S,4S)-2-(hydroxydiphenylmethyl)-1,1-dimethylspiro[2.4]heptan-4-ol **15** (44.8 mg, 0.136 mmol, 46% yield) as a yellow oil.

Rf (20% Et_2O/Pentane) = 0.59.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 4H, Ar*H*), 7.35 – 7.14 (m, 6H, Ar*H*), 4.75 (s, 1H, O*H*), 4.38 (s, 1H, HOC*H*), 2.08 – 1.87 (m, 3H, CH_2 & C*H*), 1.85 – 1.76 (m, 3H, CH_2 & O*H*), 1.72 – 1.62 (m, 2H, CH_2), 1.01 (s, 3H, CH_3), 0.99 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 147.8, 128.2, 127.6, 126.7, 126.5, 126.2, 126.0, 77.5, 75.1, 43.6, 39.2, 36.6, 31.1, 24.7, 23.9, 22.5, 16.8.
IR (v_{max}, cm^{-1}) 3349 (m), 3058 (m), 2968 (m), 2908 (m), 2867 (m), 1447 (m), 1375 (m), 1069 (m), 1000 (m), 908 (m), 734 (s).
HRMS (Nanochip-based ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{26}NaO_2^+$ 345.1825; Found 345.1825.

References

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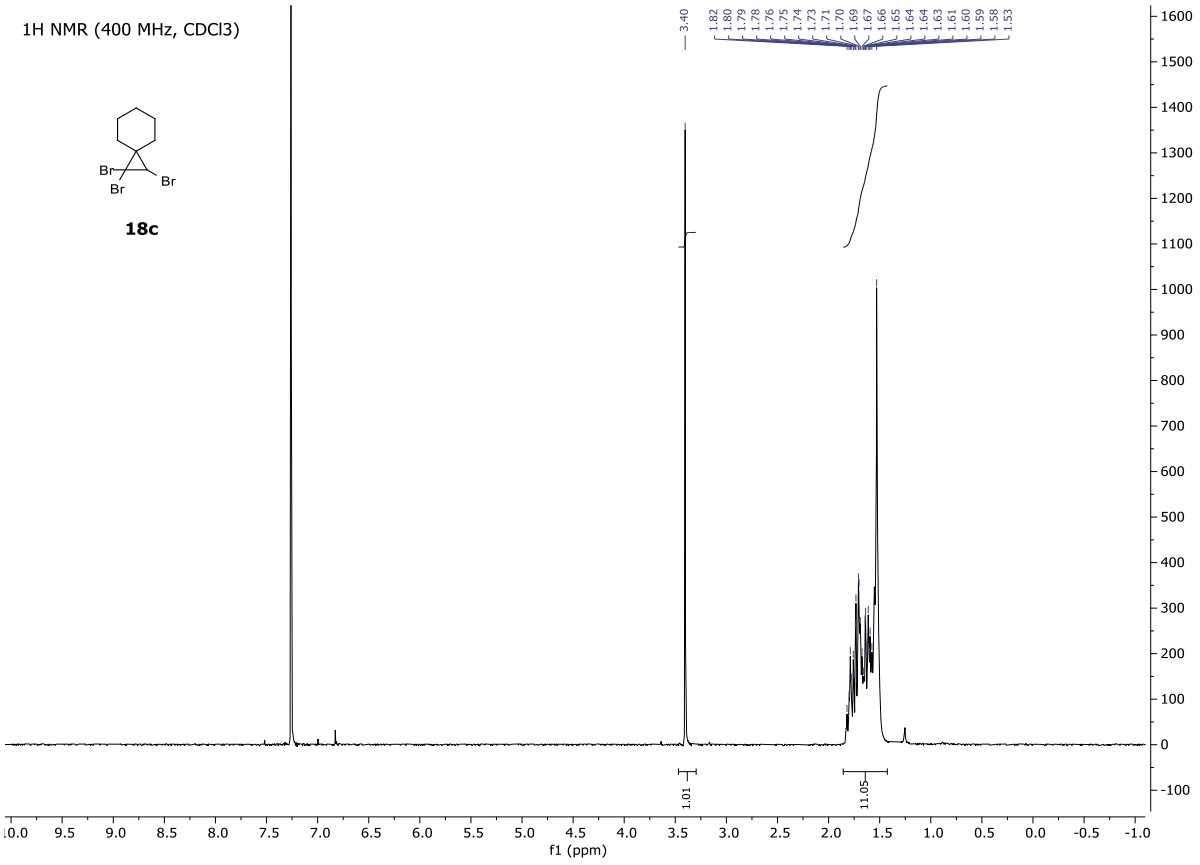
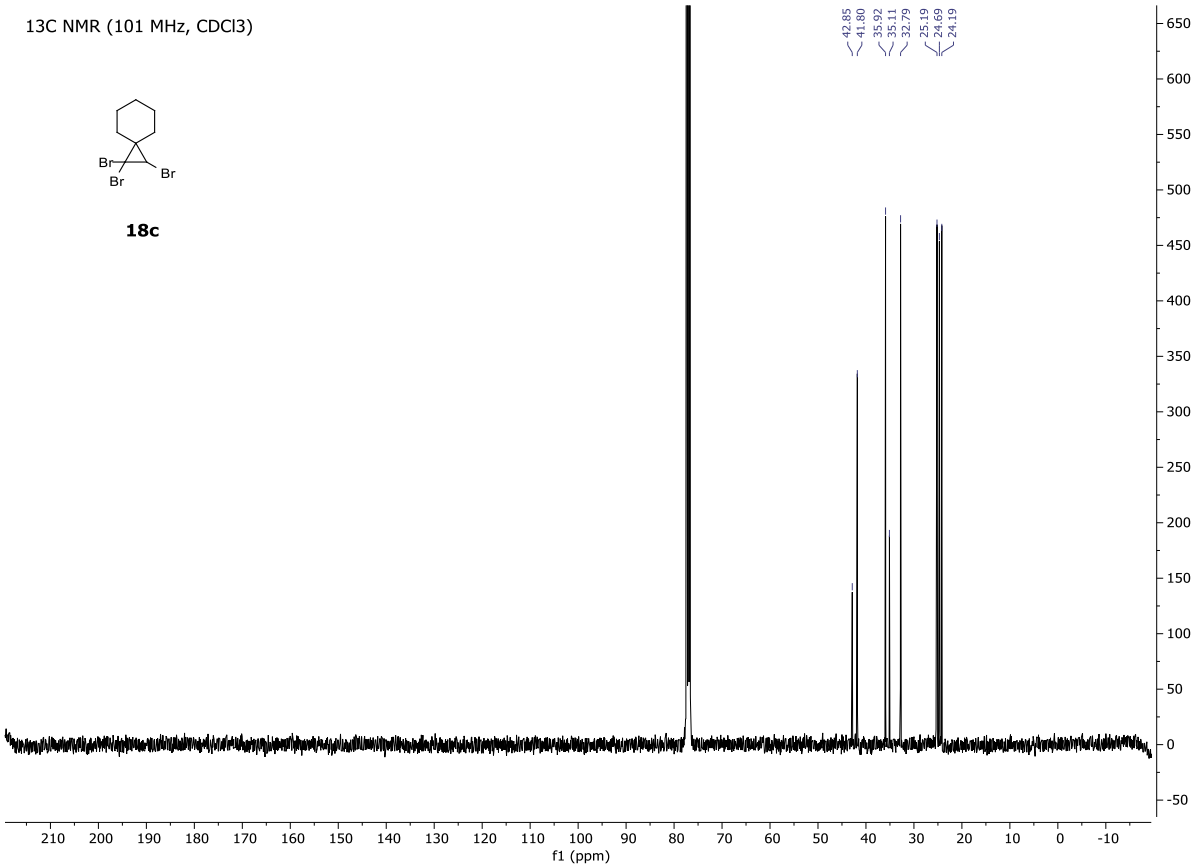
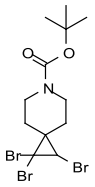
NMR spectra.


1H NMR (400 MHz, CDCl3)
Br
Br
Br
18c
3.40
1.82
1.80
1.79
1.78
1.76
1.75
1.74
1.73
1.71
1.70
1.69
1.67
1.66
1.65
1.64
1.64
1.63
1.61
1.60
1.59
1.58
1.53
1.01
11.05
f1 (ppm)


13C NMR (101 MHz, CDCl3)
Br
Br
Br
18c
42.85
41.80
35.92
35.11
32.79
25.19
24.69
24.19
f1 (ppm)

1H NMR (400 MHz, CDCl3)



18d

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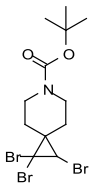

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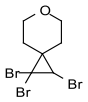
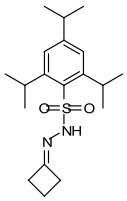


18e

13C NMR (101 MHz, CDCl3)

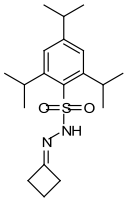
18e

1H NMR (400 MHz, CDCl3)



21

13C NMR (101 MHz, CDCl3)



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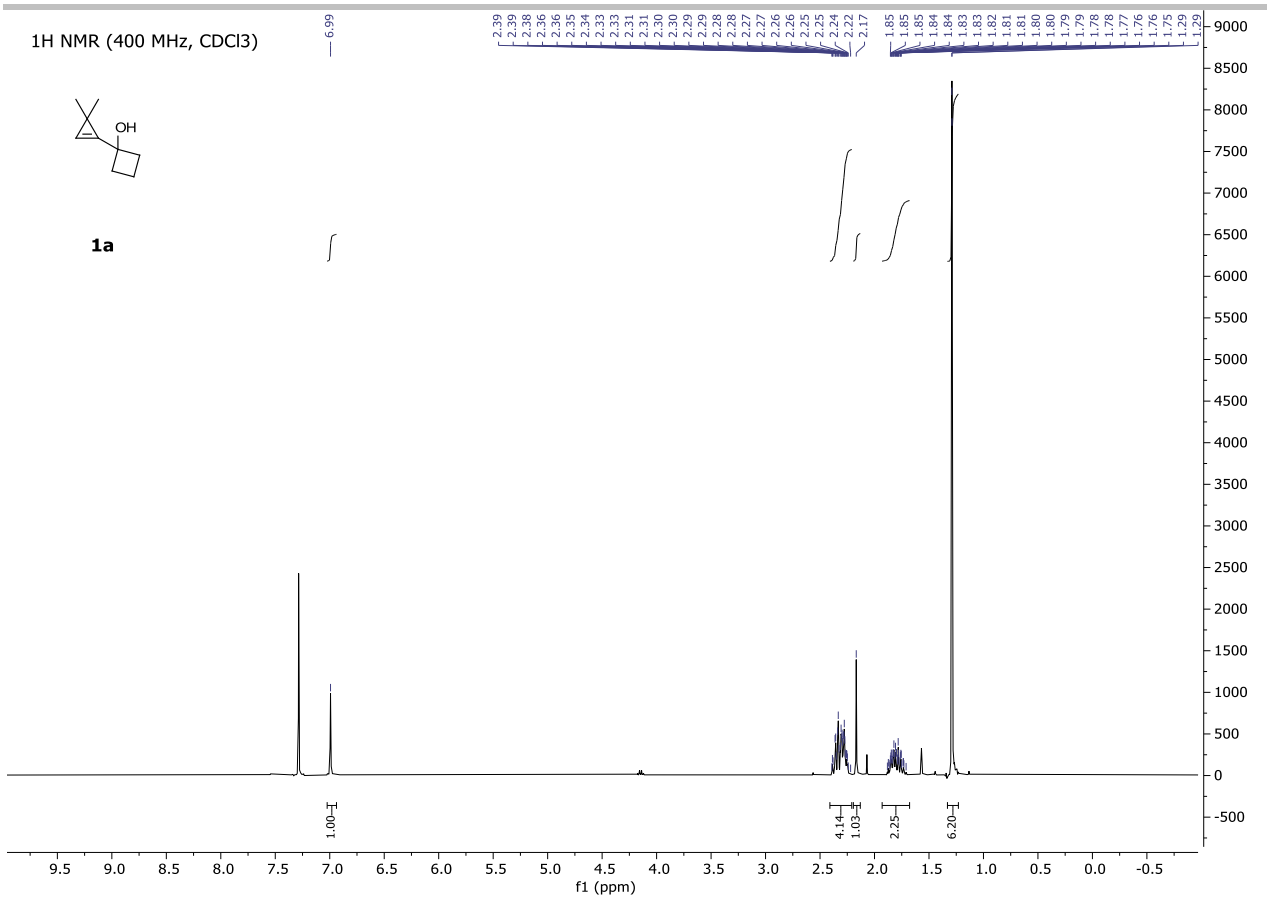
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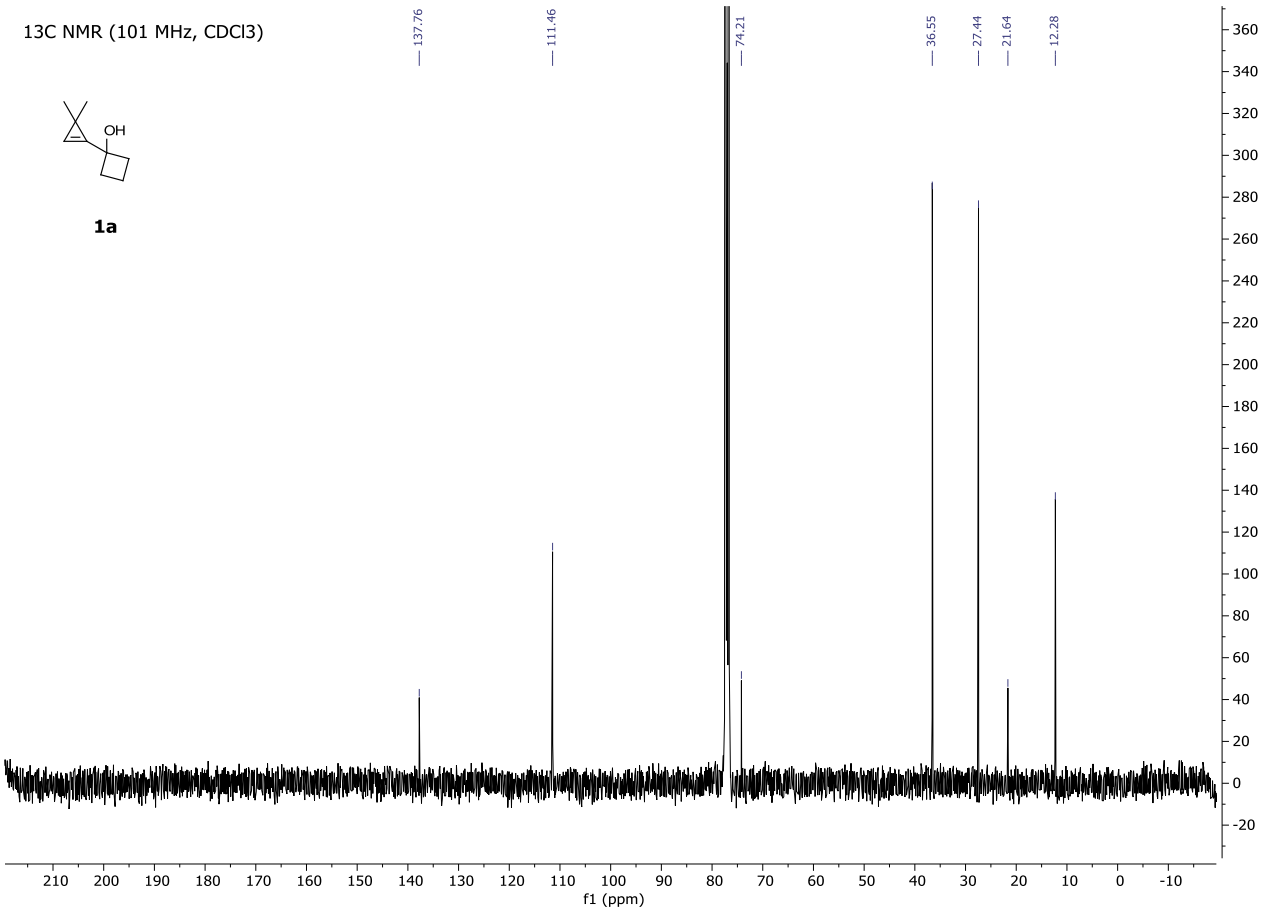
OH
1a
f1 (ppm)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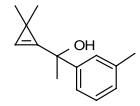
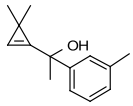
OH
1a
137.76
111.46
74.21
36.55
27.44
21.64
12.28
f1 (ppm)

1H NMR (400 MHz, CDCl3)

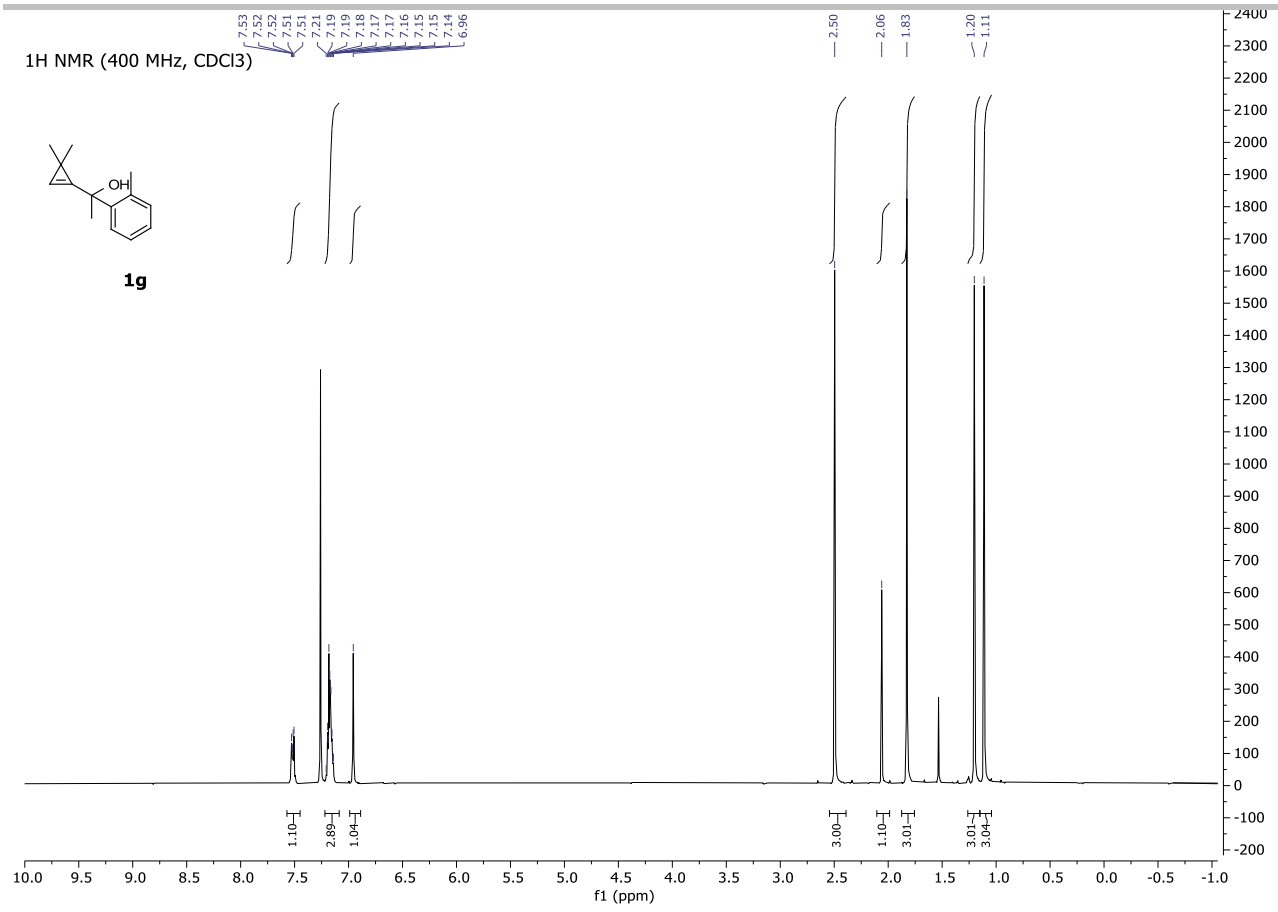


1f

13C NMR (101 MHz, CDCl3)



1f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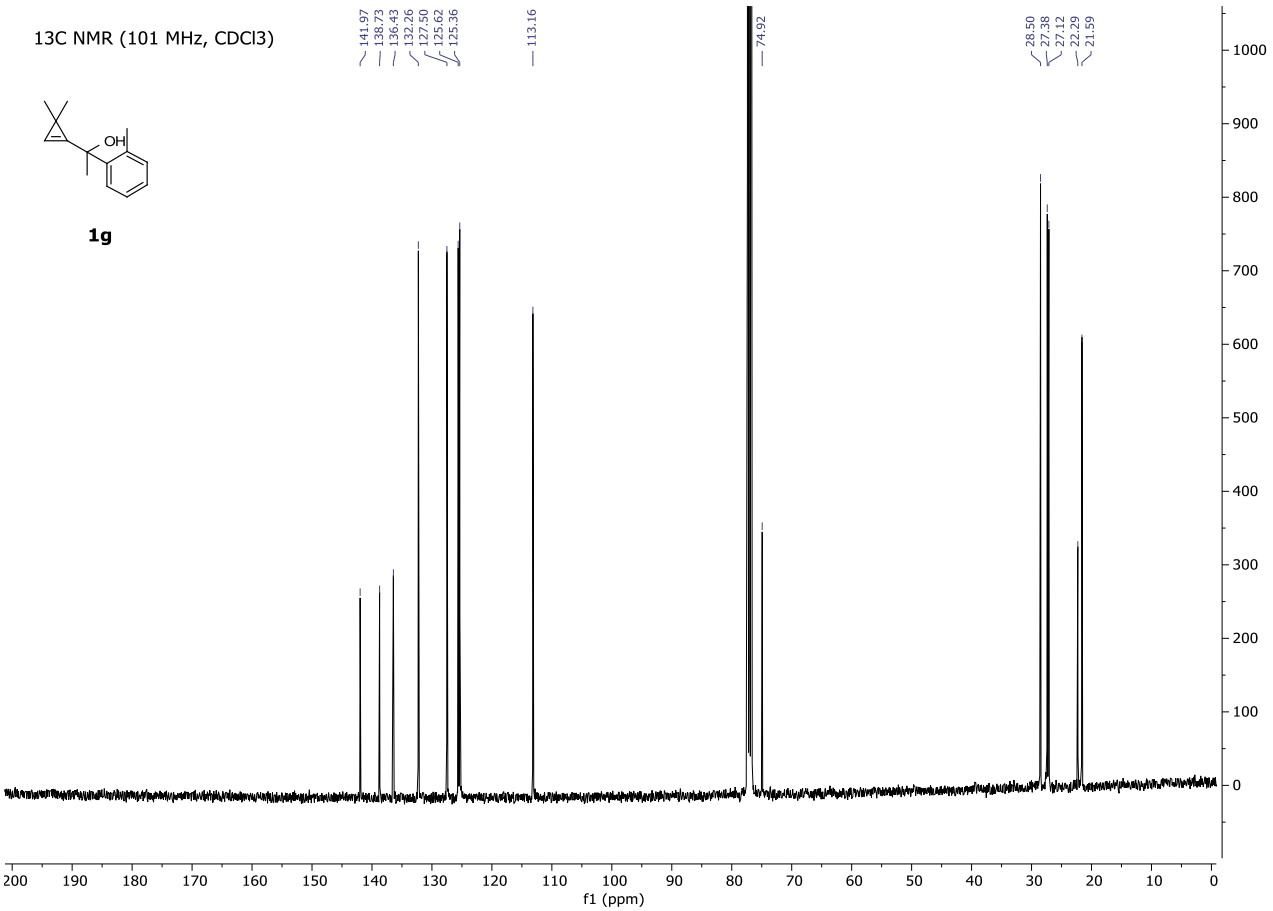
OH
1g
7.53
7.52
7.52
7.51
7.51
7.21
7.19
7.19
7.18
7.17
7.16
7.15
7.15
7.14
6.96
2.50
2.06
1.83
1.20
1.11
1.10
2.89
1.04
3.00
1.10
3.01
3.01
3.04
f1 (ppm)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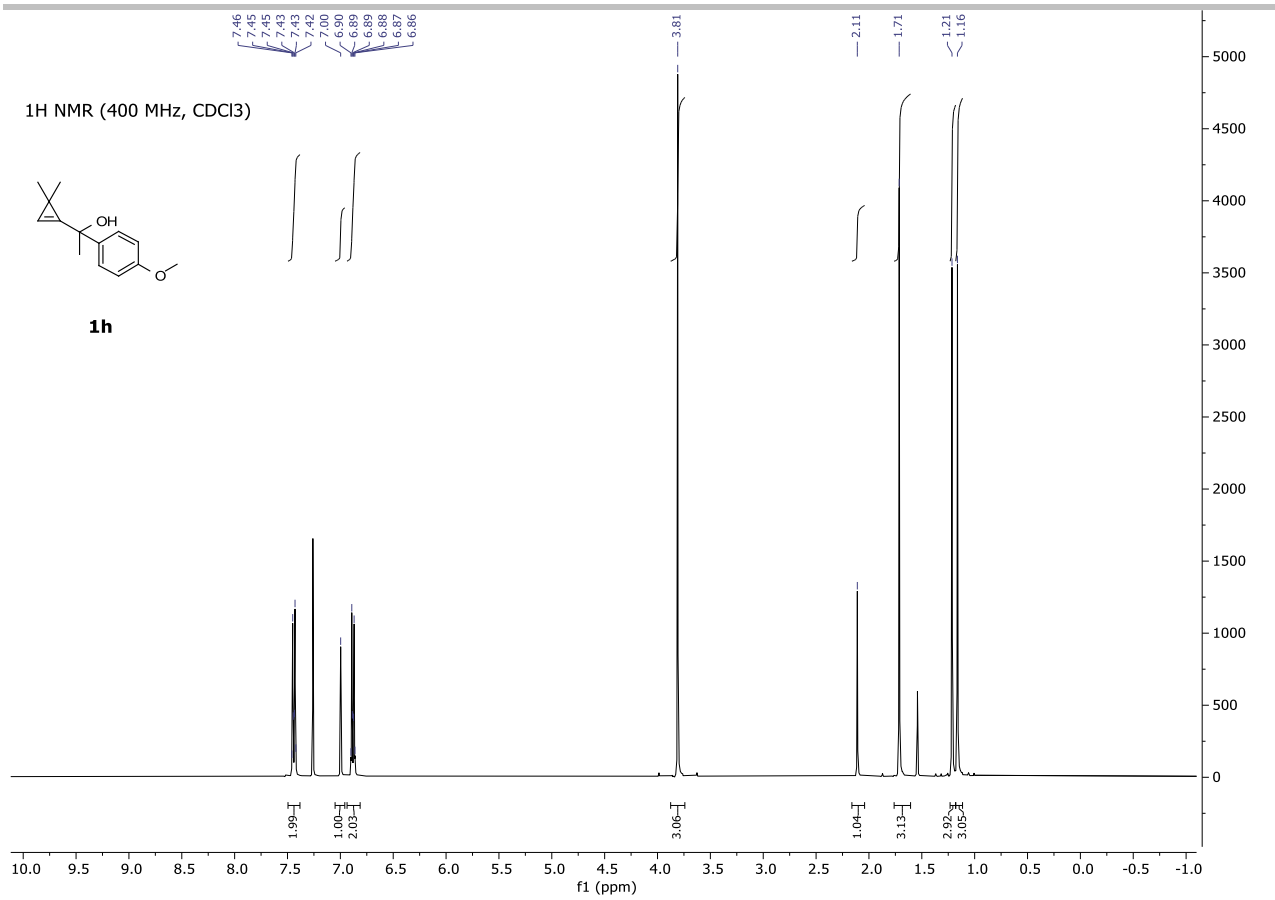
OH
1g
141.97
138.73
136.43
132.26
127.50
125.62
125.36
113.16
74.92
28.50
27.38
27.12
22.29
21.59
f1 (ppm)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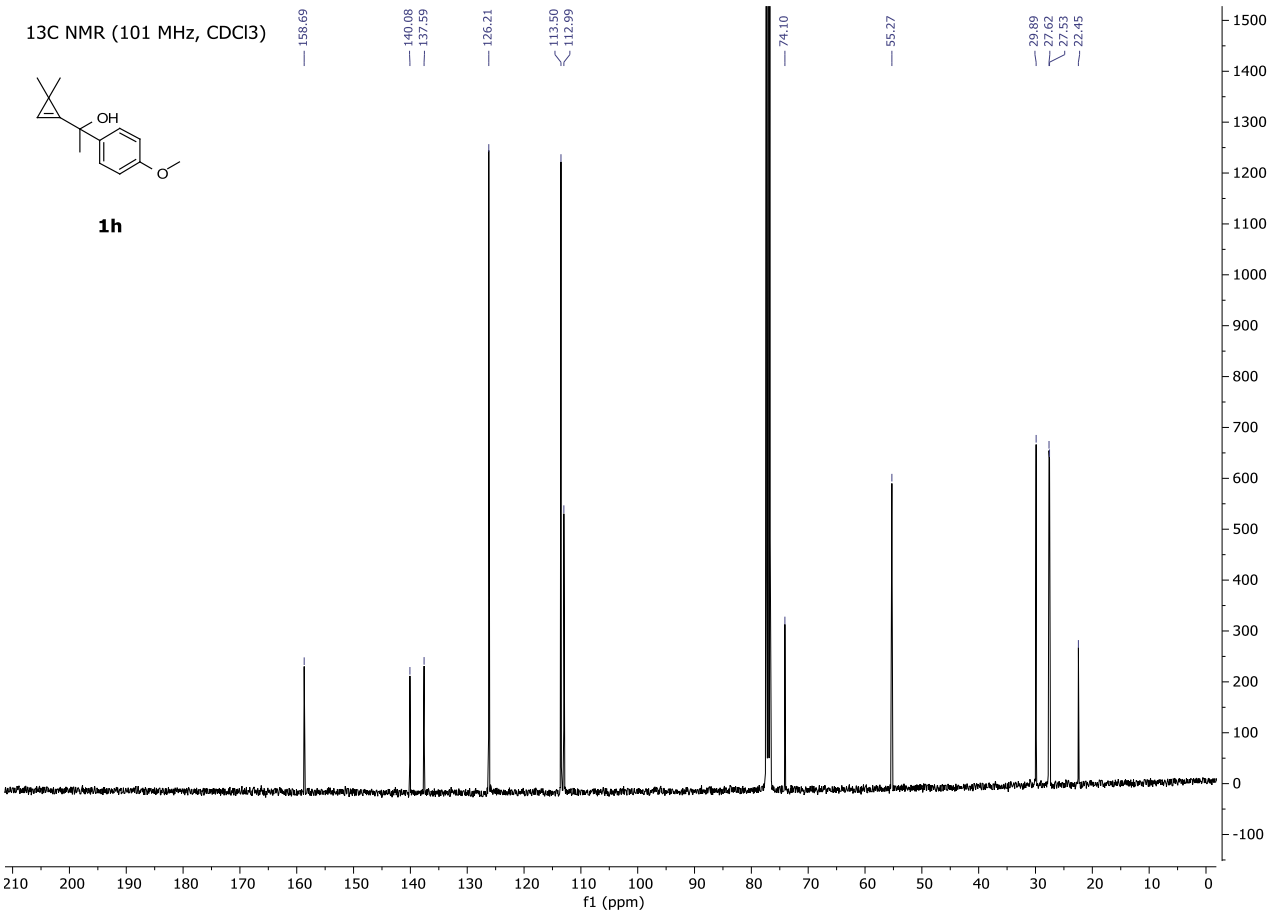
OH
O
1h
7.46
7.45
7.45
7.43
7.43
7.42
7.00
6.90
6.89
6.89
6.88
6.87
6.86
3.81
2.11
1.71
1.21
1.16
1.99
1.00
2.03
3.06
1.04
3.13
2.92
3.05
f1 (ppm)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OH
O
1h
158.69
140.08
137.59
126.21
113.50
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74.10
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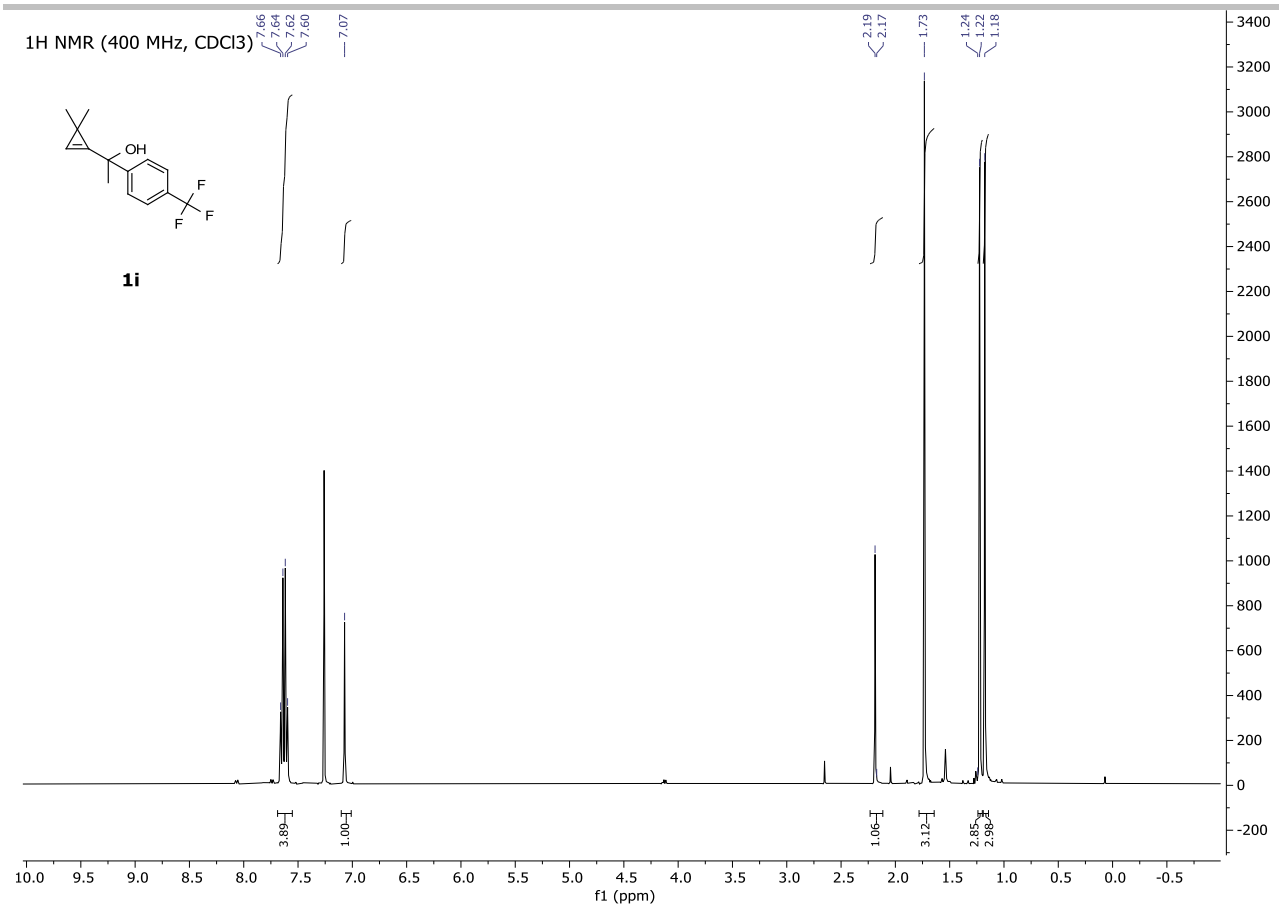
29.89
27.62
27.53
22.45
f1 (ppm)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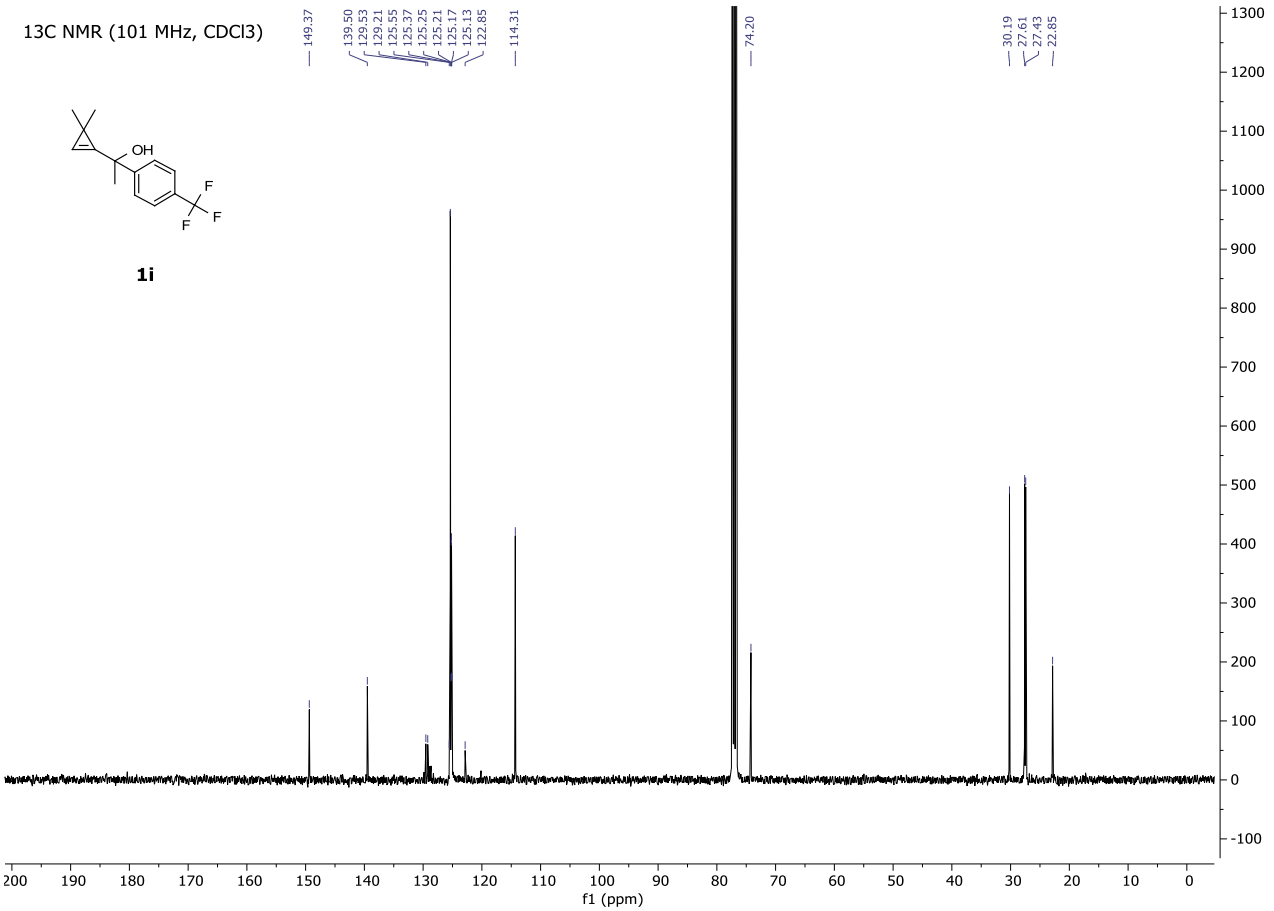
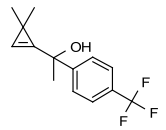
7.66
7.64
7.62
7.60
7.07
2.19
2.17
1.73
1.24
1.22
1.18
OH
F
F
F
1i
3.89
1.00
1.06
3.12
2.85
2.98
f1 (ppm)

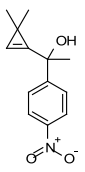

13C NMR (101 MHz, CDCl3)
149.37
139.50
129.53
129.21
125.55
125.37
125.25
125.21
125.17
125.13
122.85
114.31
74.20
30.19
27.61
27.43
22.85
OH
F
F
F
1i
f1 (ppm)

19F NMR (376 MHz, CDCl3)

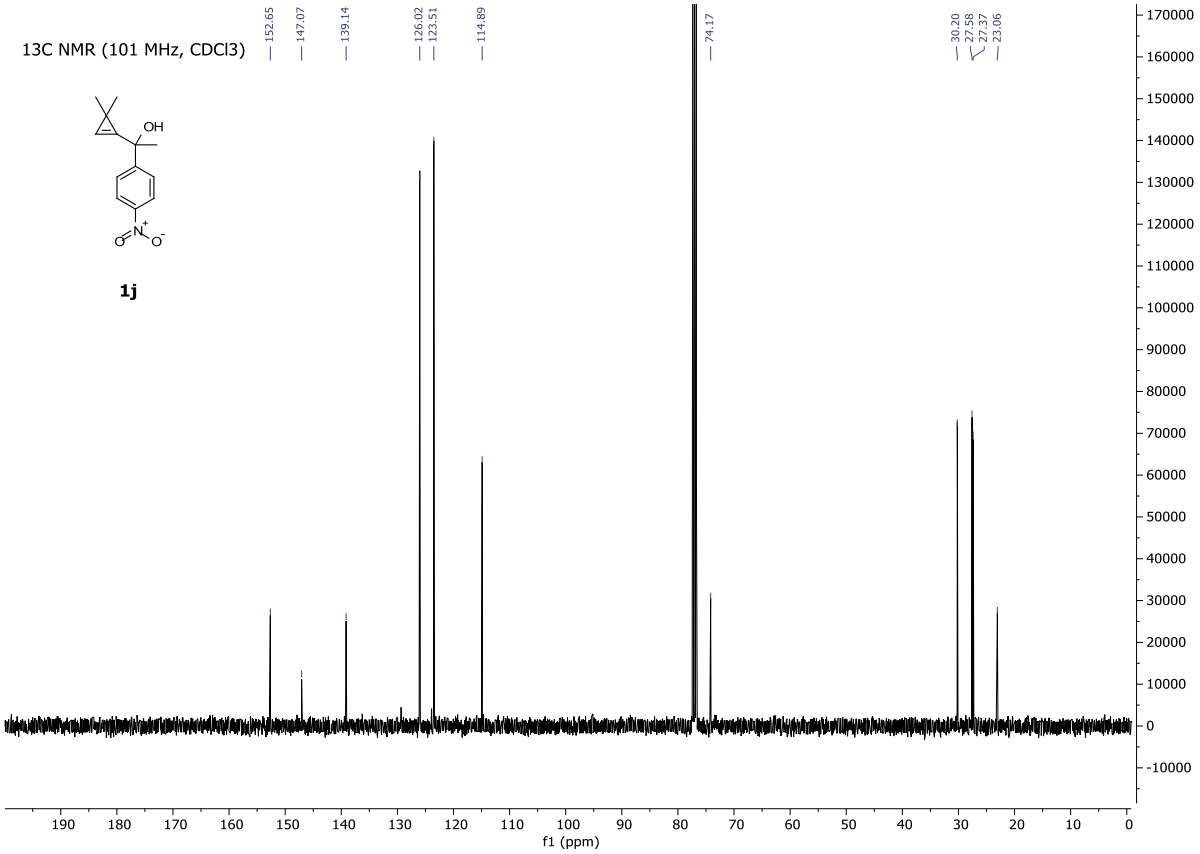


1i

1H NMR (400 MHz, CDCl3)



1j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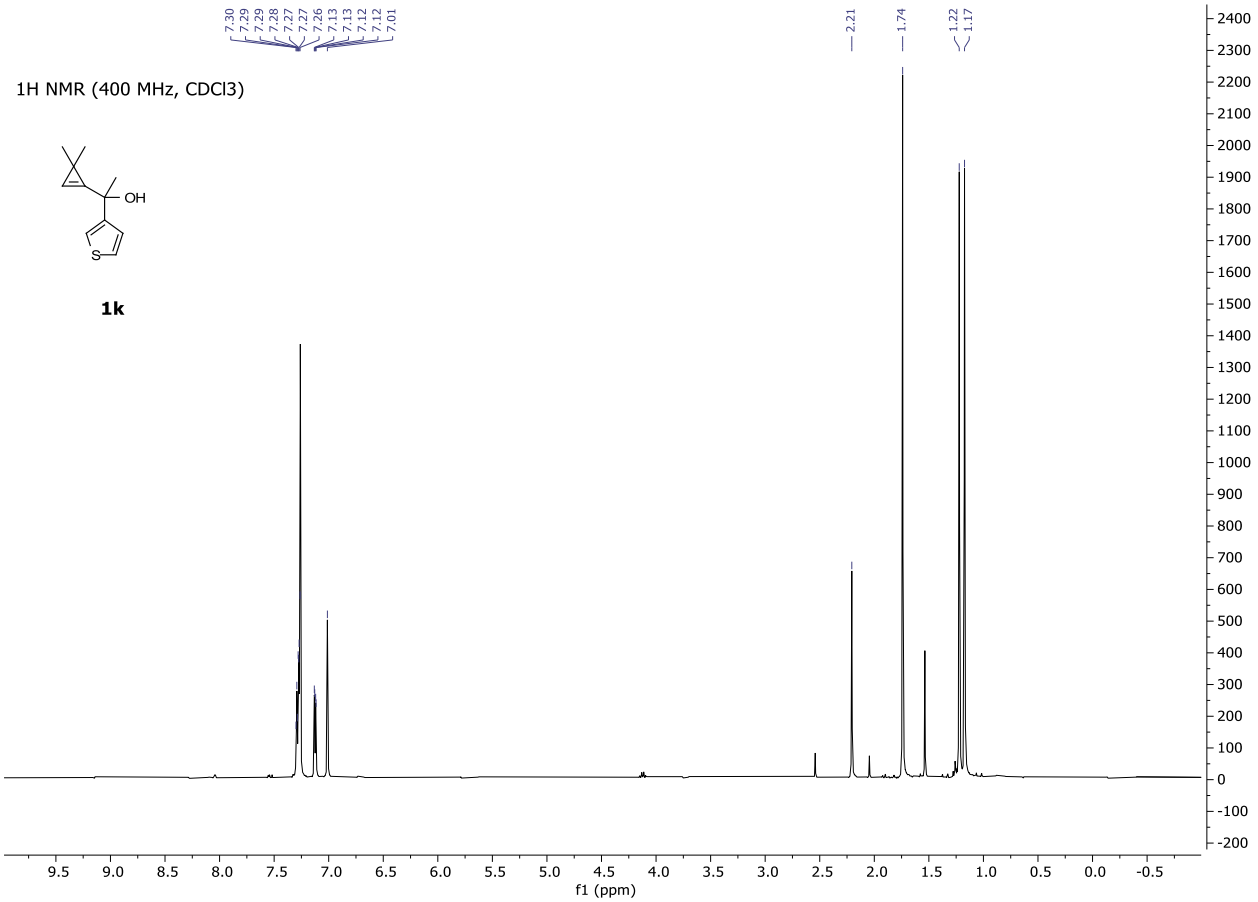
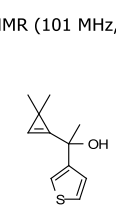
152.65
147.07
139.14
126.02
123.51
114.89
74.17
30.20
27.58
27.37
23.06
OH
1j
f1 (ppm)


1H NMR (400 MHz, CDCl3)
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.13
7.13
7.12
7.12
7.01
2.21
1.74
1.22
1.17
OH
S
1k
f1 (ppm)

13C NMR (101 MHz, CDCl3)



1k

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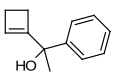
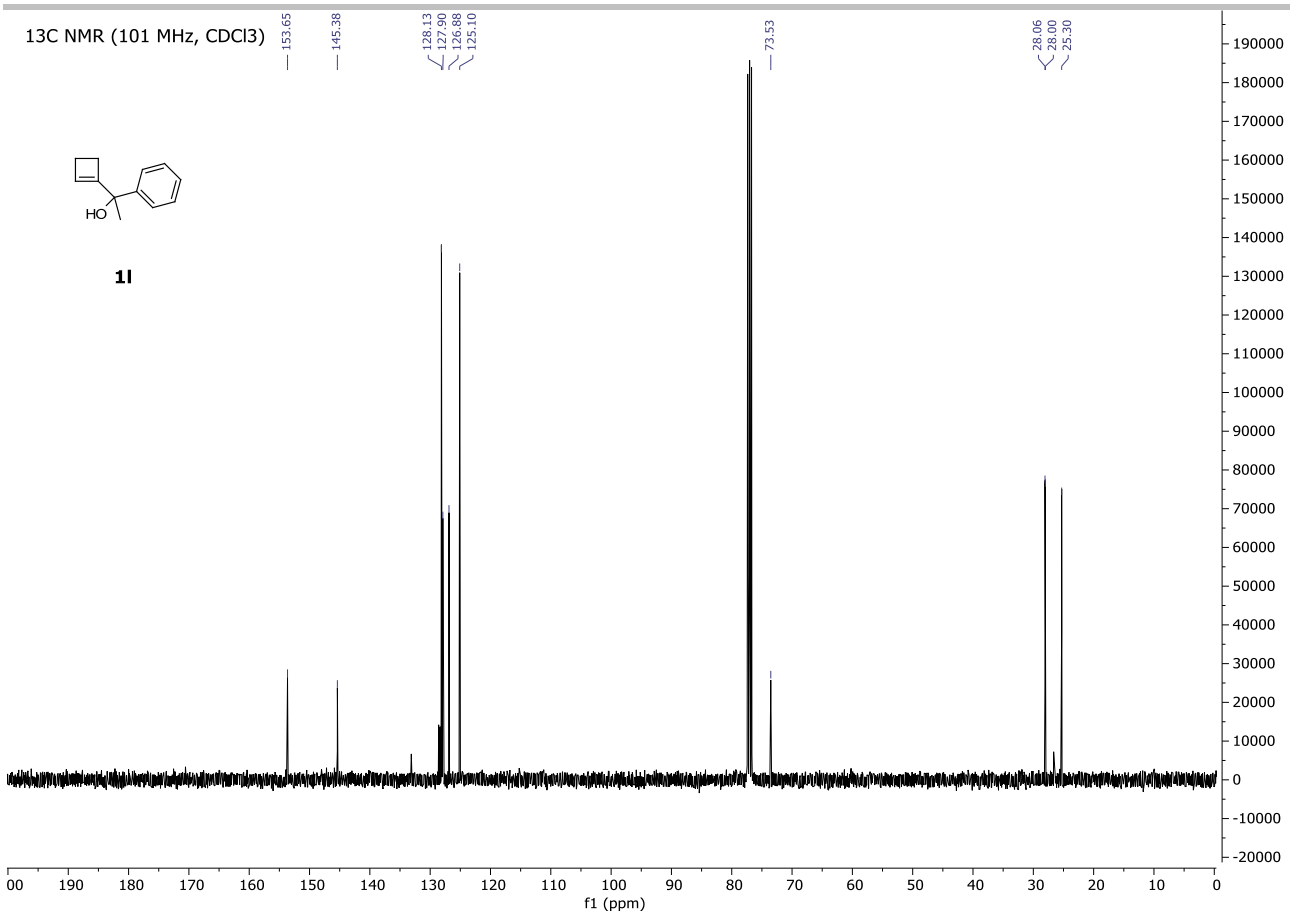


1l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153.65
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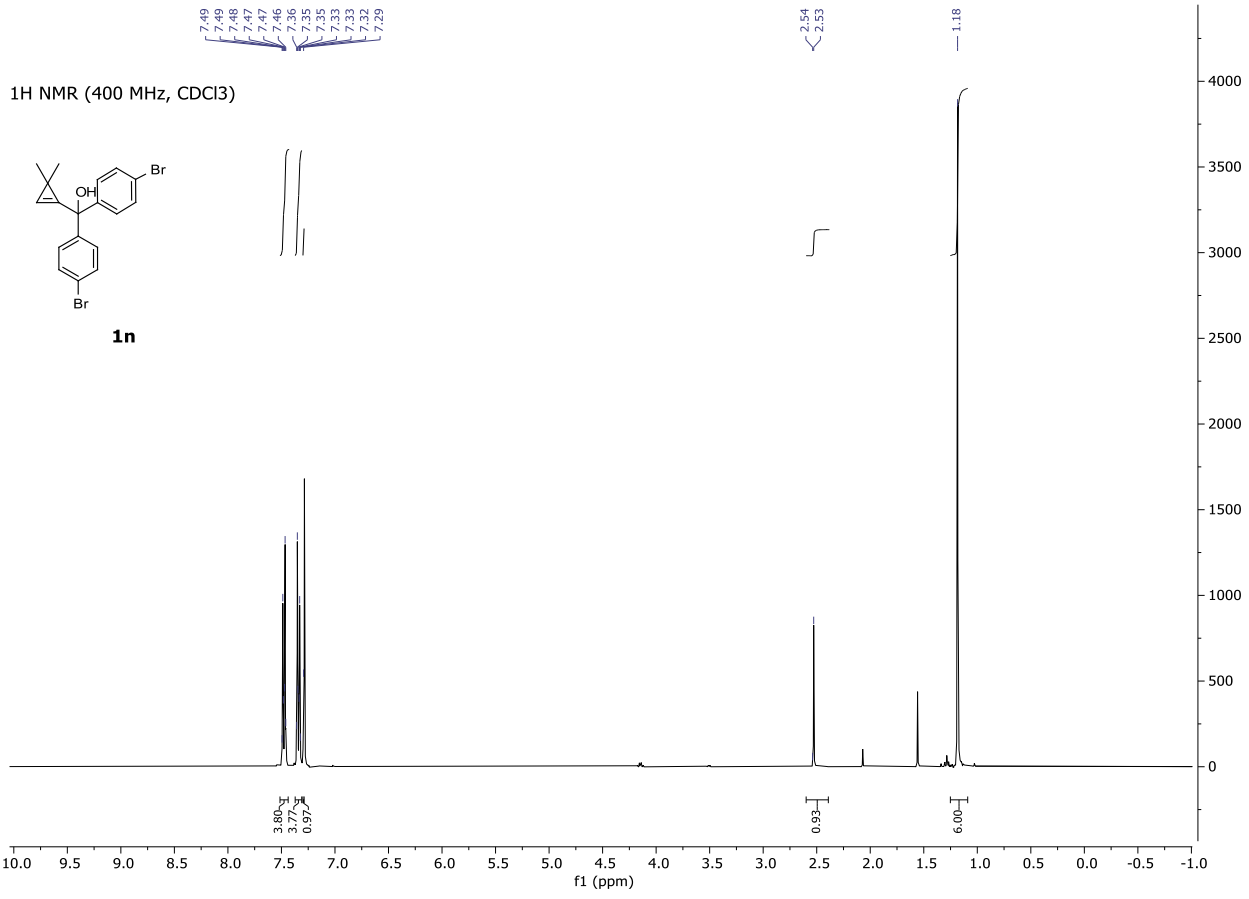
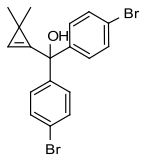
127.90
126.88
125.10
73.53
28.06
28.00
25.30
HO
1l
f1 (ppm)


1H NMR (400 MHz, CDCl3)
7.49
7.49
7.48
7.47
7.47
7.46
7.36
7.35
7.35
7.33
7.33
7.32
7.29
2.54
2.53
1.18
OH
Br
Br
1n
3.80
3.77
0.97
0.93
6.00
f1 (ppm)

13C NMR (101 MHz, CDCl3)



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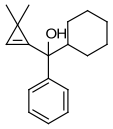

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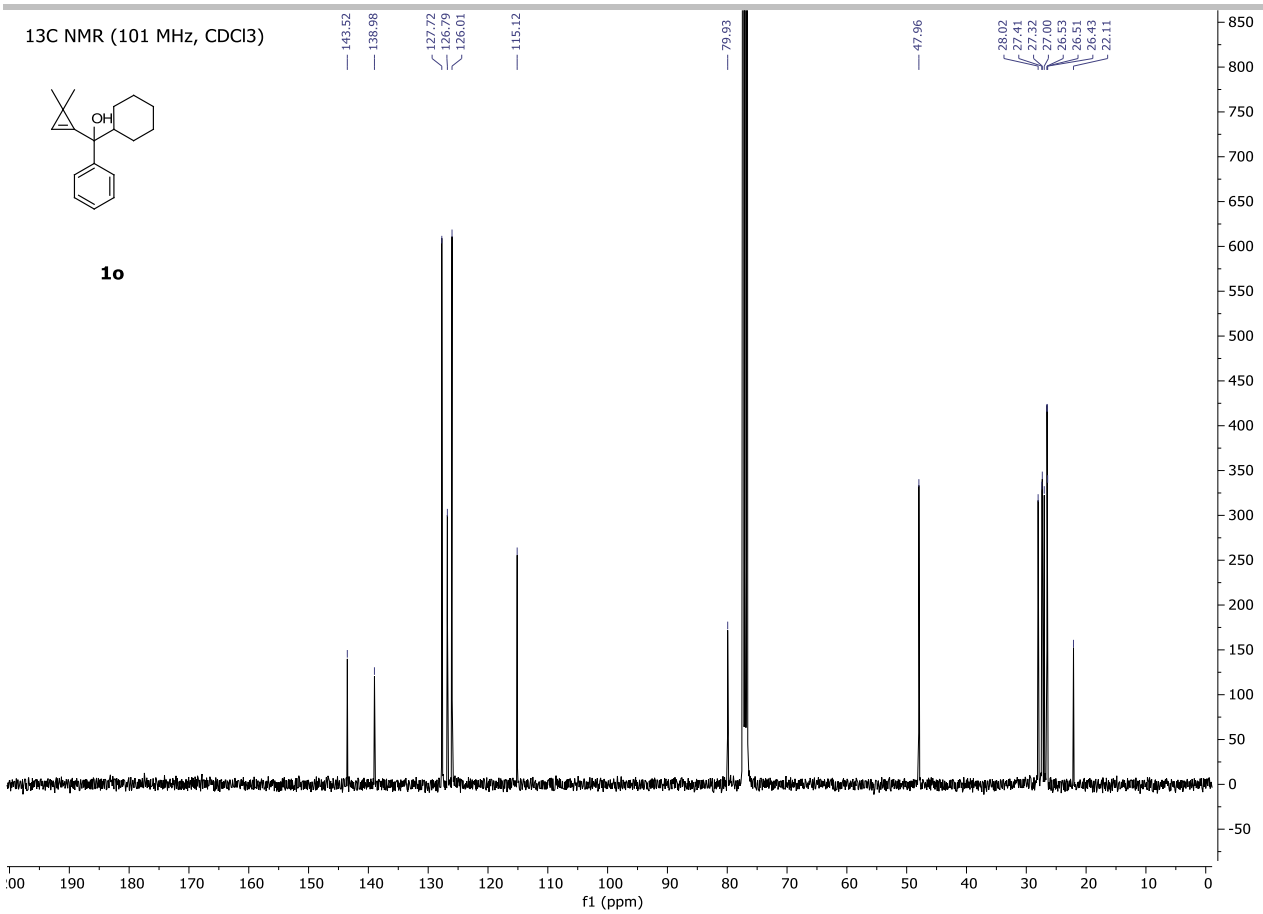
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143.52
138.98
127.72
126.79
126.01
115.12
79.93
47.96
28.02
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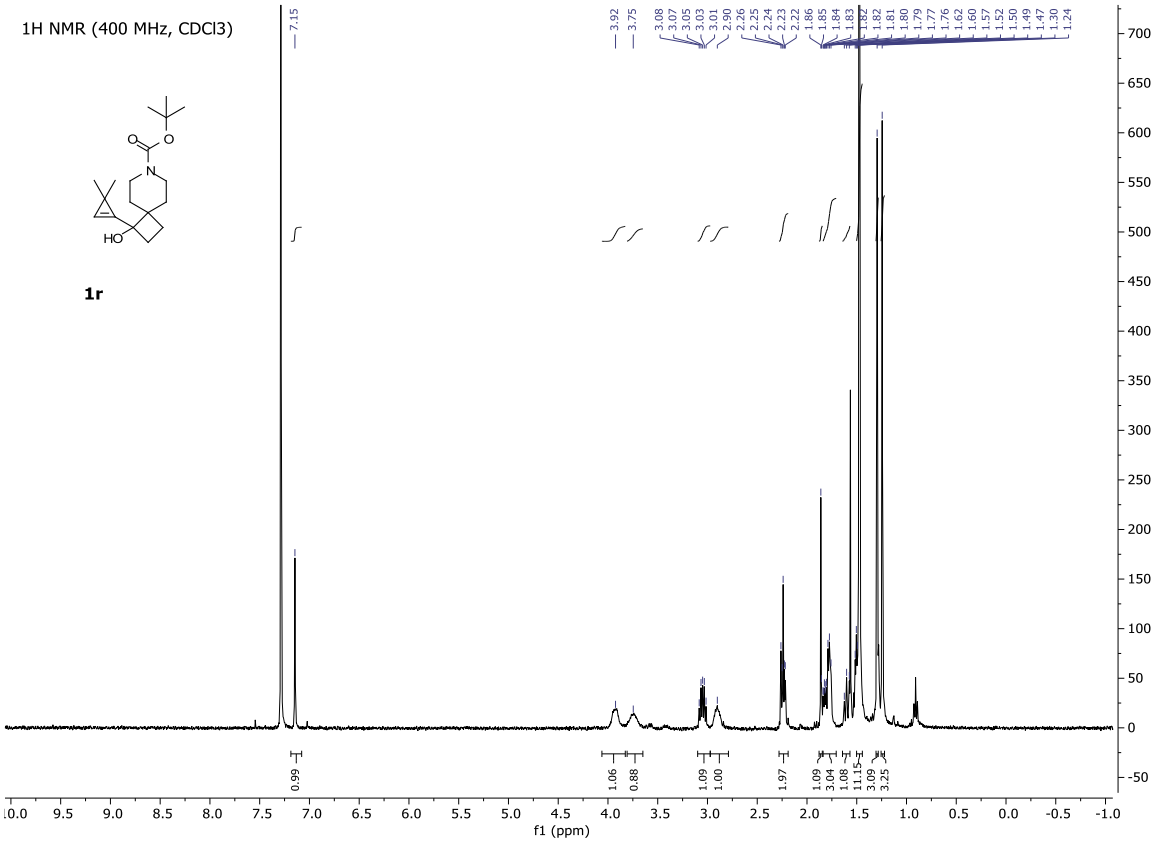
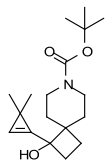
26.51
26.43
22.11
OH
1o
f1 (ppm)


1H NMR (400 MHz, CDCl3)
7.15
3.92
3.75
3.08
3.07
3.05
3.03
3.01
2.90
2.26
2.25
2.24
2.23
2.22
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.77
1.76
1.62
1.60
1.57
1.52
1.50
1.49
1.47
1.30
1.24
O
O
N
HO
1r
0.99
1.06
0.88
1.09
1.00
1.97
1.09
3.04
1.08
11.15
3.09
3.25
f1 (ppm)

13C NMR (101 MHz, CDCl3)



1r

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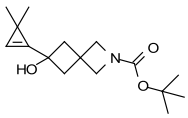

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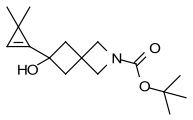

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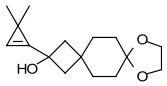

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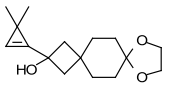

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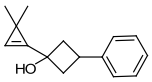

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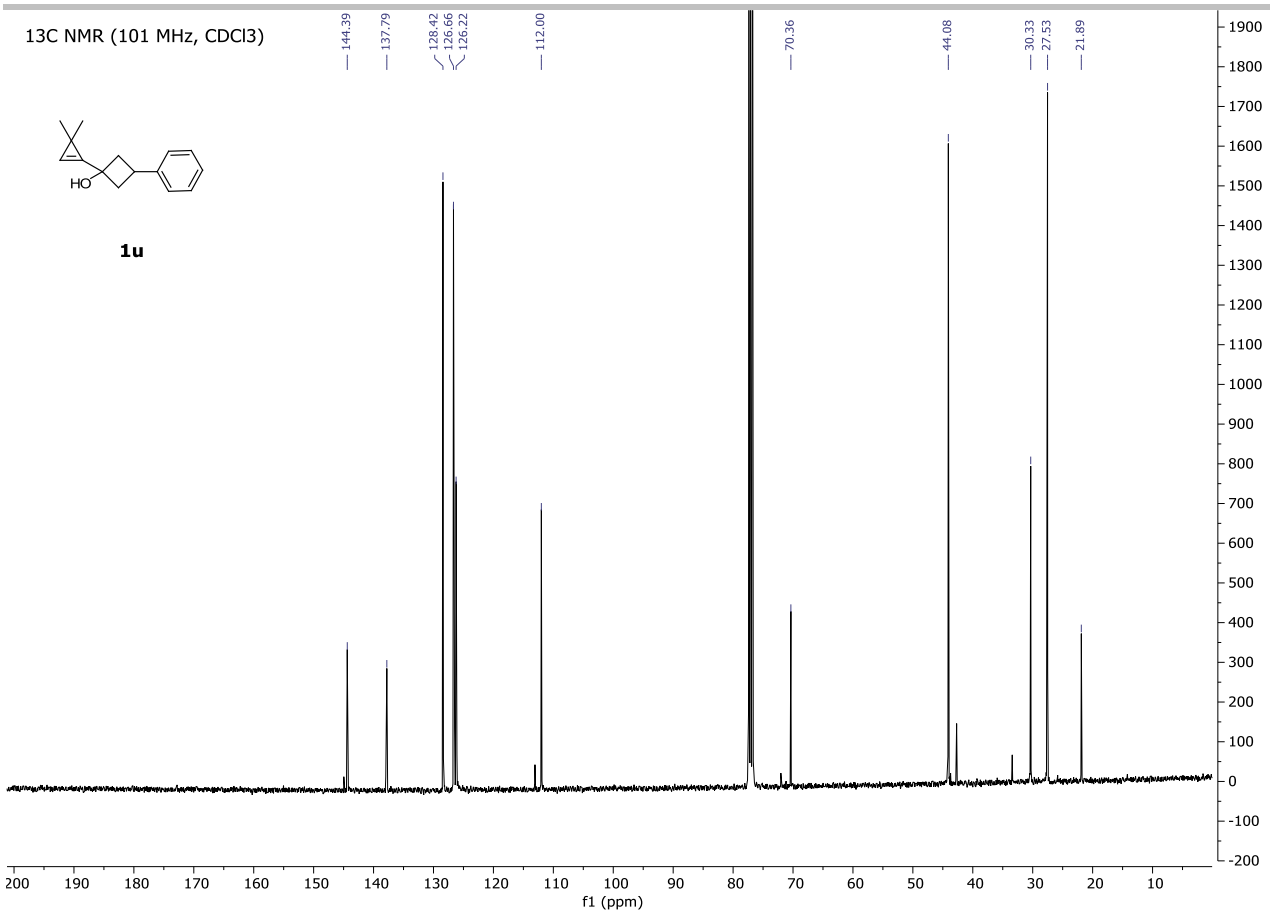
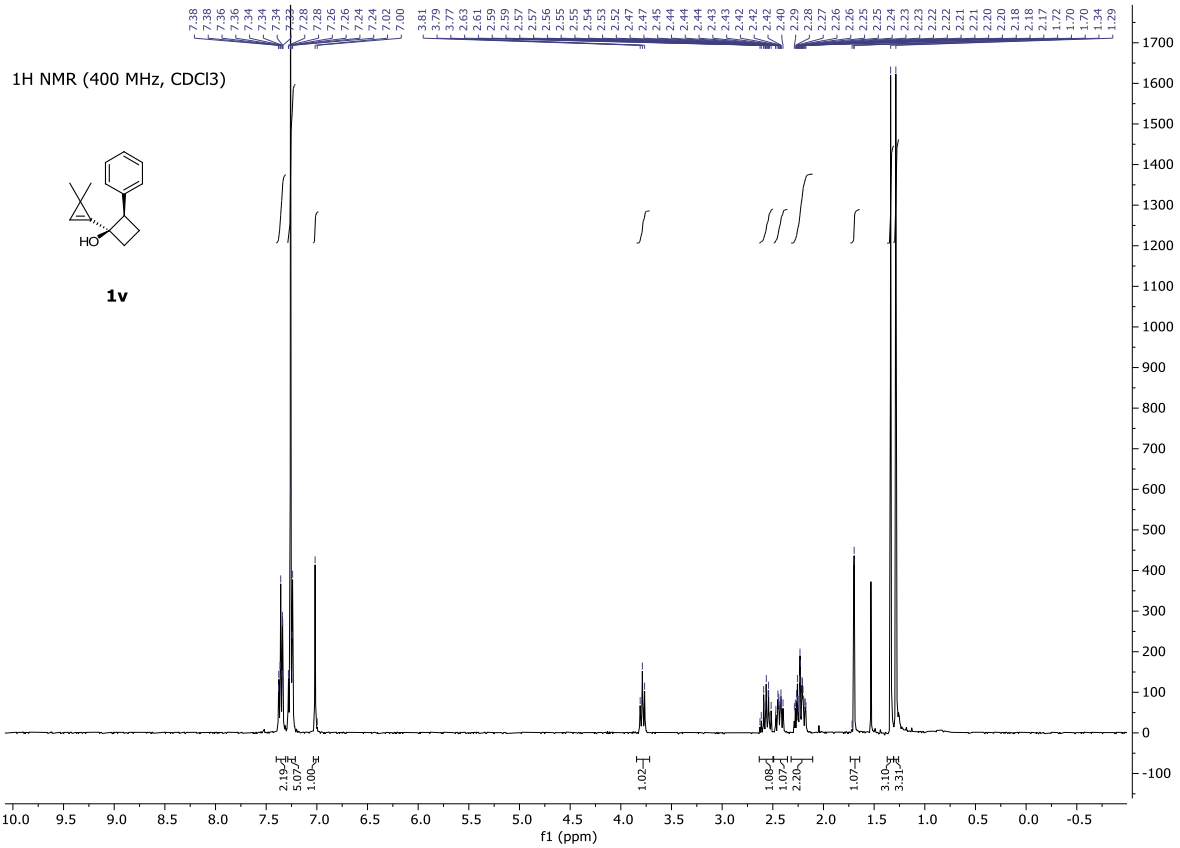
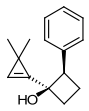

13C NMR (101 MHz, CDCl3)
144.39
137.79
128.42
126.66
126.22
112.00
70.36
44.08
30.33
27.53
21.89
HO
1u
f1 (ppm)

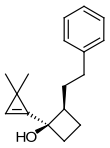

1H NMR (400 MHz, CDCl3)
HO
1v
f1 (ppm)

13C NMR (101 MHz, CDCl3)



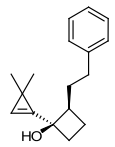
1v

1H NMR (400 MHz, CDCl3)



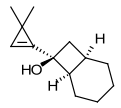
1w

13C NMR (101 MHz, CDCl3)



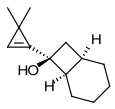
1w

1H NMR (400 MHz, CDCl3)



1x

13C NMR (101 MHz, CDCl3)



1x

1H NMR (400 MHz, CDCl3)

1z

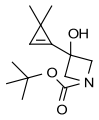
13C NMR (101 MHz, CDCl3)

1z

1H NMR (400 MHz, CDCl3)

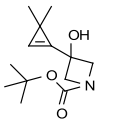
1aa

1H NMR (400 MHz, CDCl3)



1ab

13C NMR (101 MHz, CDCl3)



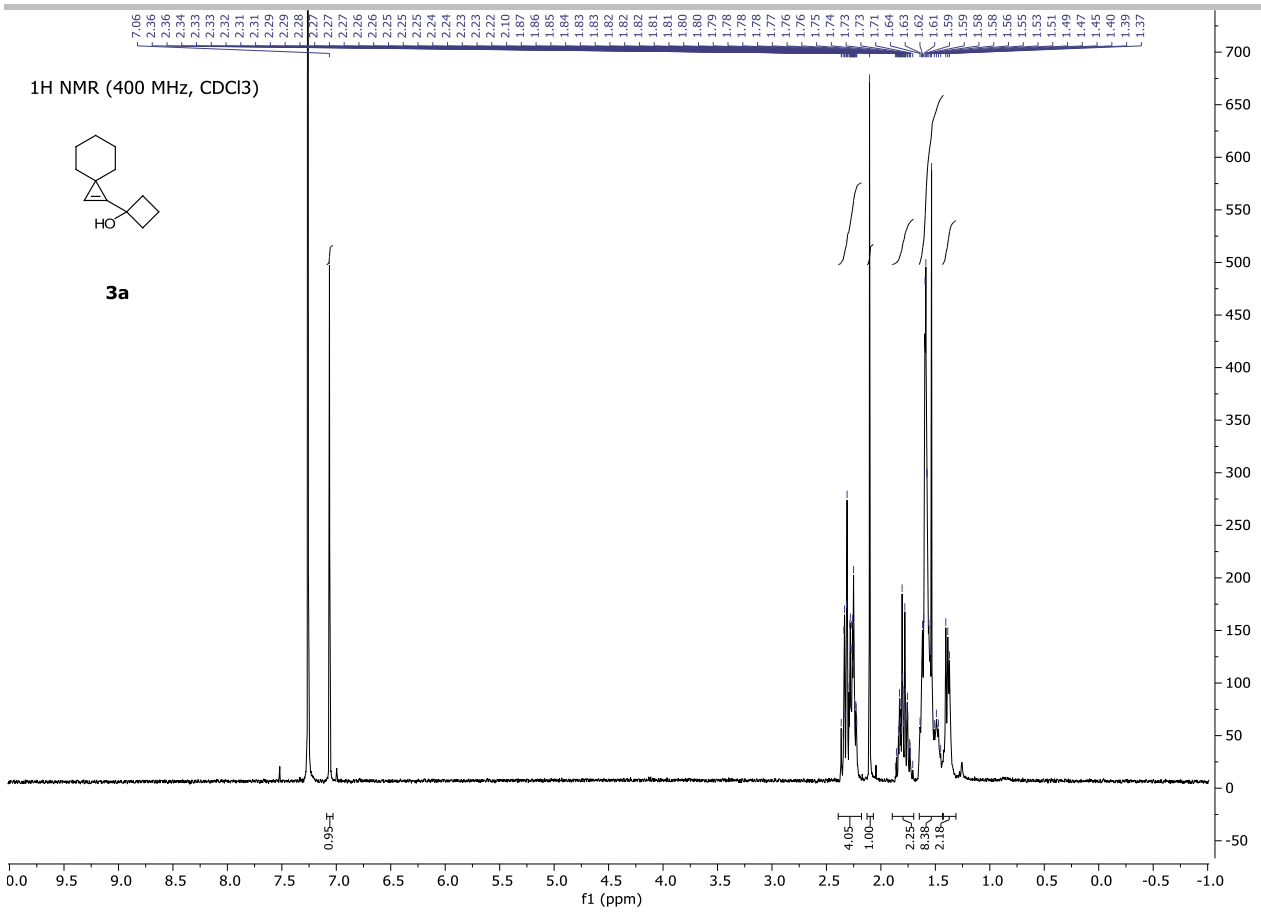
1ab

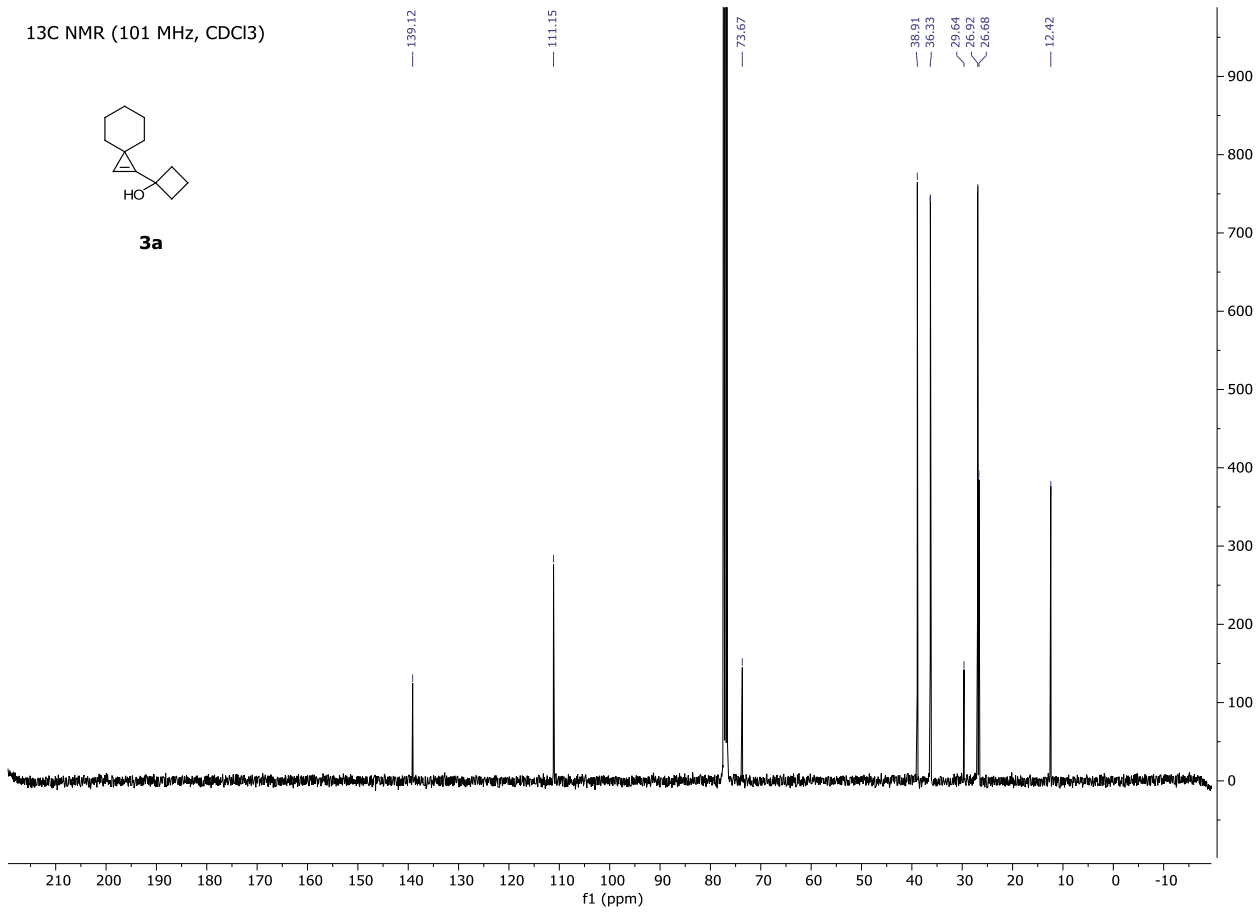
1H NMR (400 MHz, CDCl3)

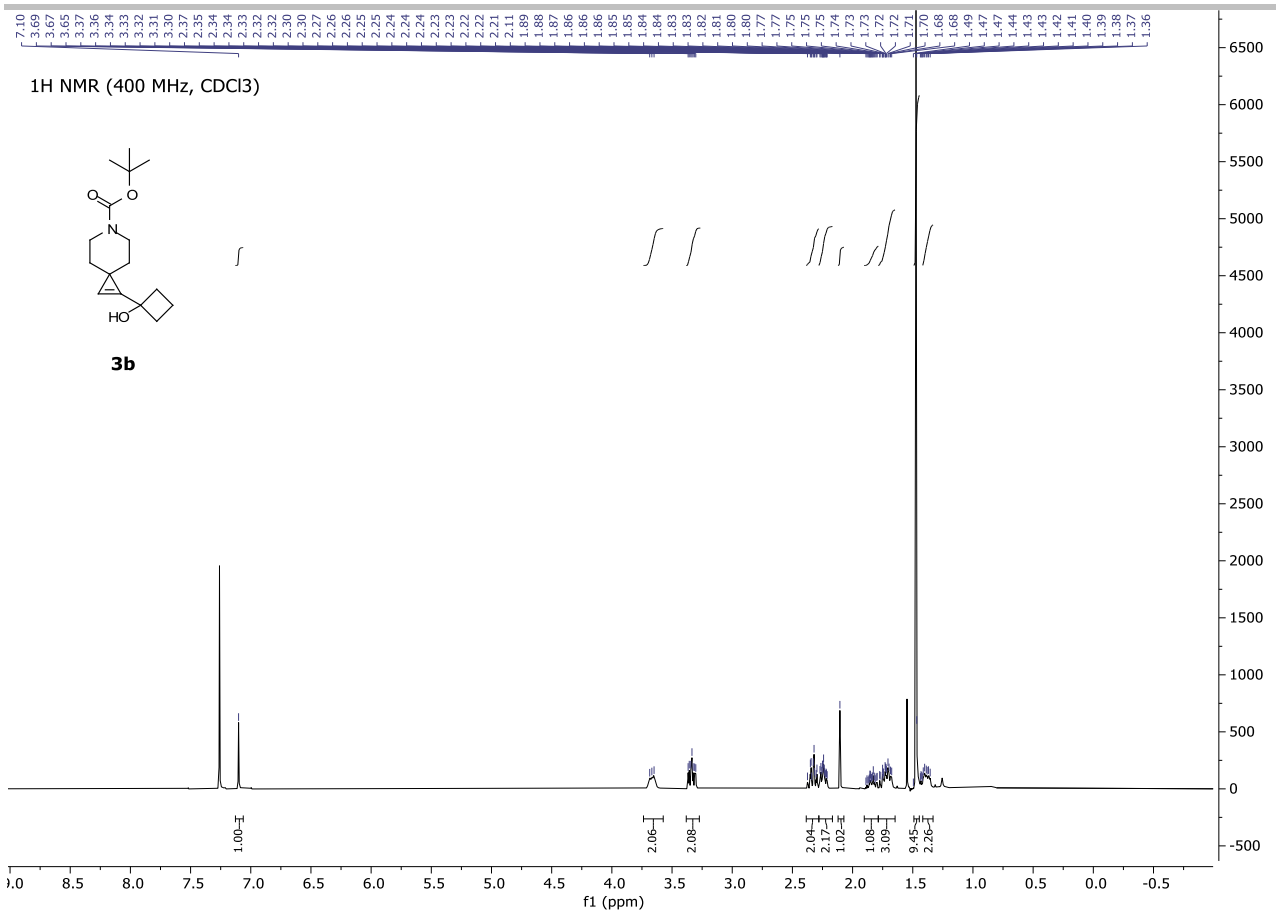
1ac

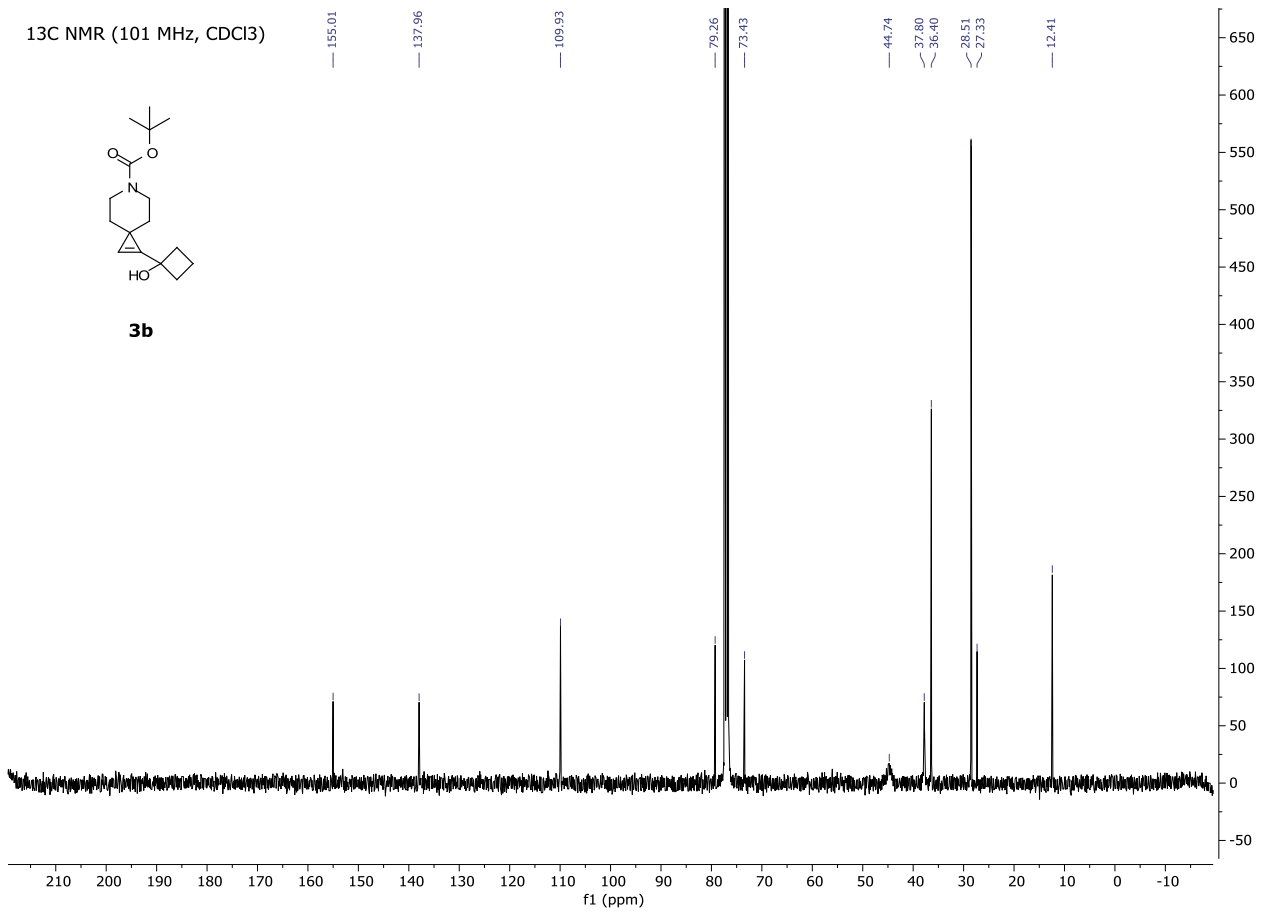
13C NMR (101 MHz, CDCl3)

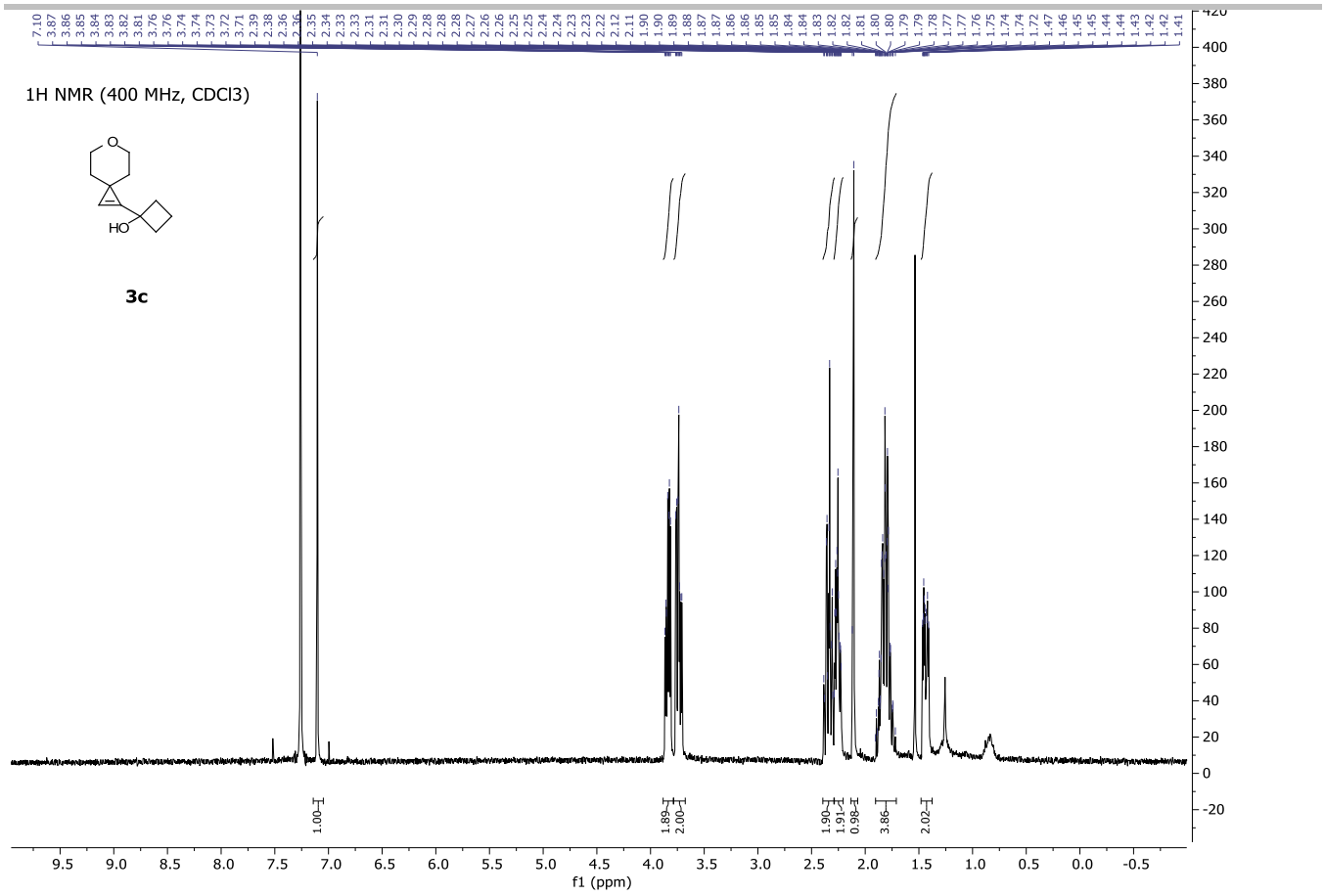
1ac

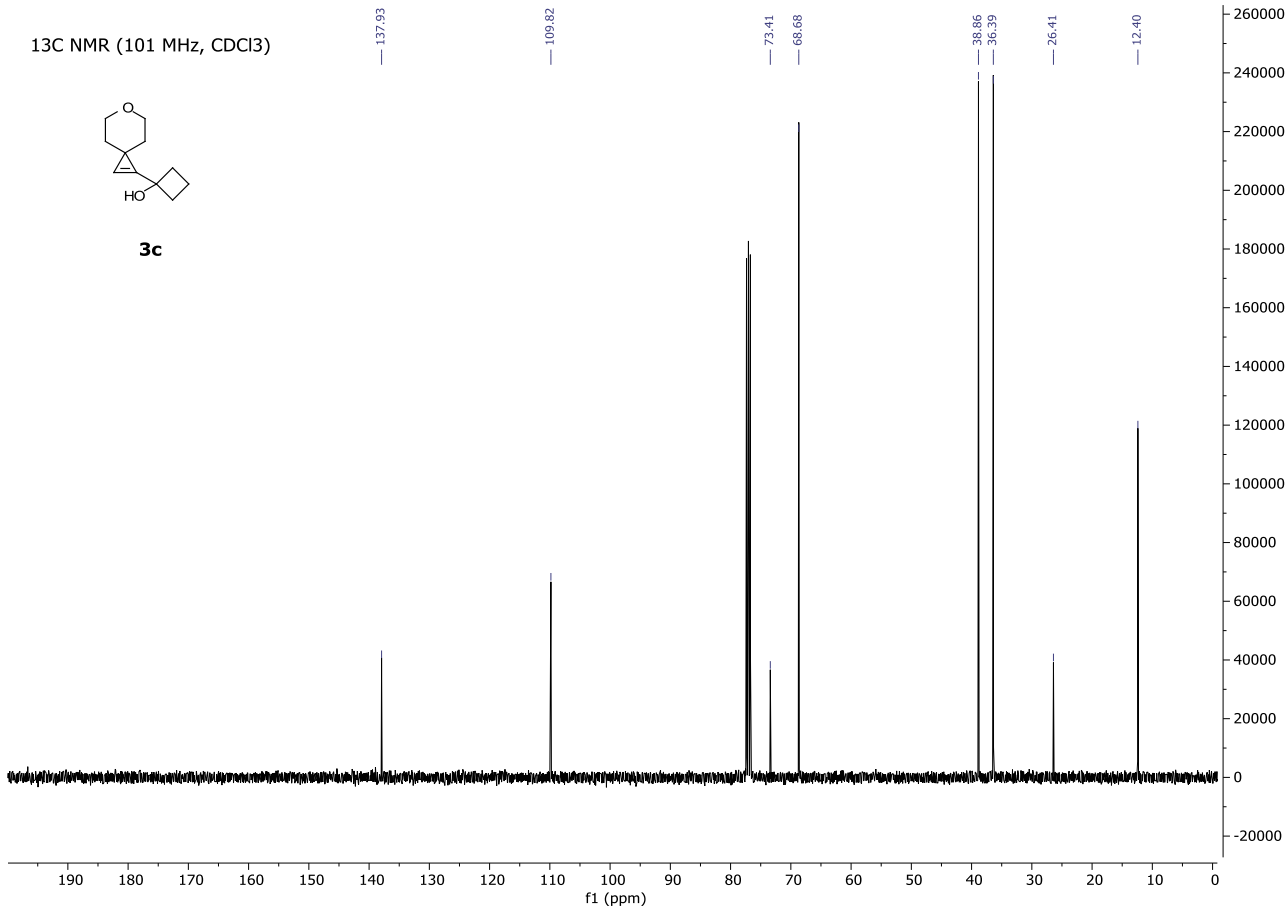

1H NMR (400 MHz, CDCl3)
HO
3a
f1 (ppm)

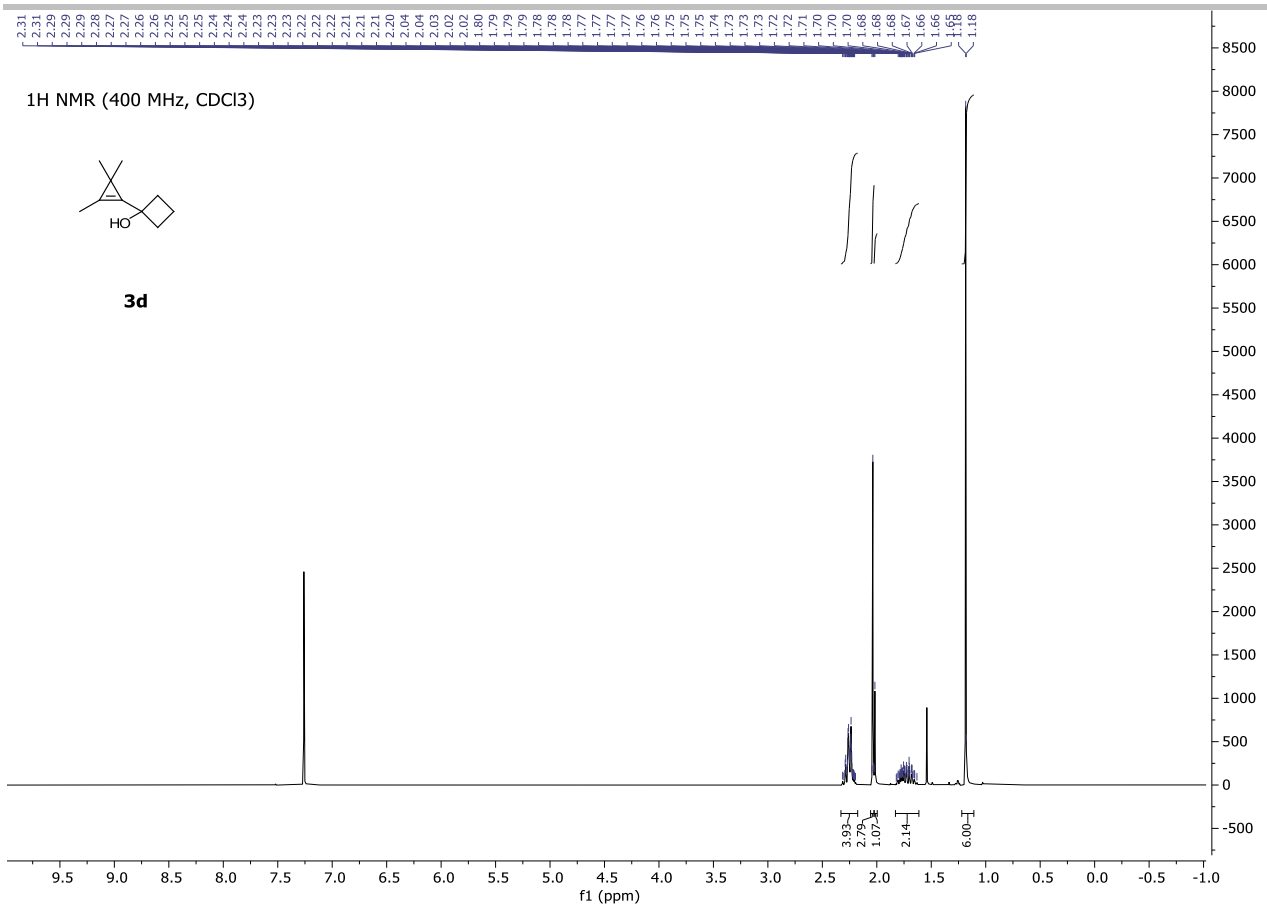

13C NMR (101 MHz, CDCl3)
HO
3a
139.12
111.15
73.67
38.91
36.33
29.64
26.92
26.68
12.42
f1 (ppm)

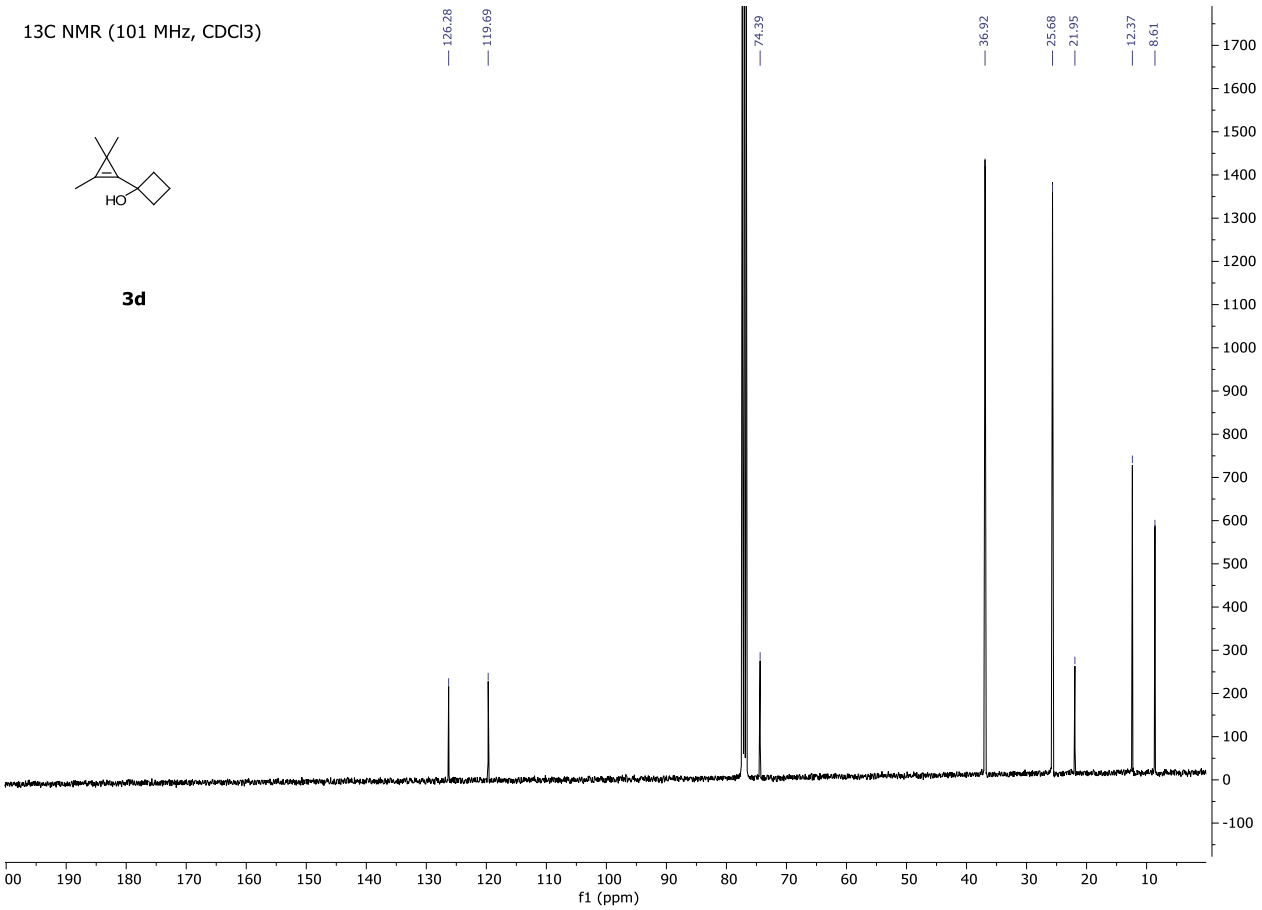

1H NMR (400 MHz, CDCl3)
3b
f1 (ppm)


13C NMR (101 MHz, CDCl3)
155.01
137.96
109.93
79.26
73.43
44.74
37.80
36.40
28.51
27.33
12.41
3b
f1 (ppm)

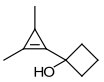

1H NMR (400 MHz, CDCl3)
HO
3c
f1 (ppm)


13C NMR (101 MHz, CDCl3)
HO
3c
137.93
109.82
73.41
68.68
38.86
36.39
26.41
12.40
f1 (ppm)


1H NMR (400 MHz, CDCl3)
HO
3d
3.93
2.79
1.07
2.14
6.00
f1 (ppm)

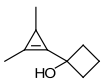

13C NMR (101 MHz, CDCl3)
126.28
119.69
74.39
36.92
25.68
21.95
12.37
8.61
HO
3d
f1 (ppm)

1H NMR (400 MHz, CDCl3)



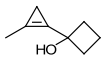
3e

13C NMR (101 MHz, CDCl3)



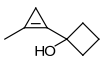
3e

1H NMR (400 MHz, CDCl3)

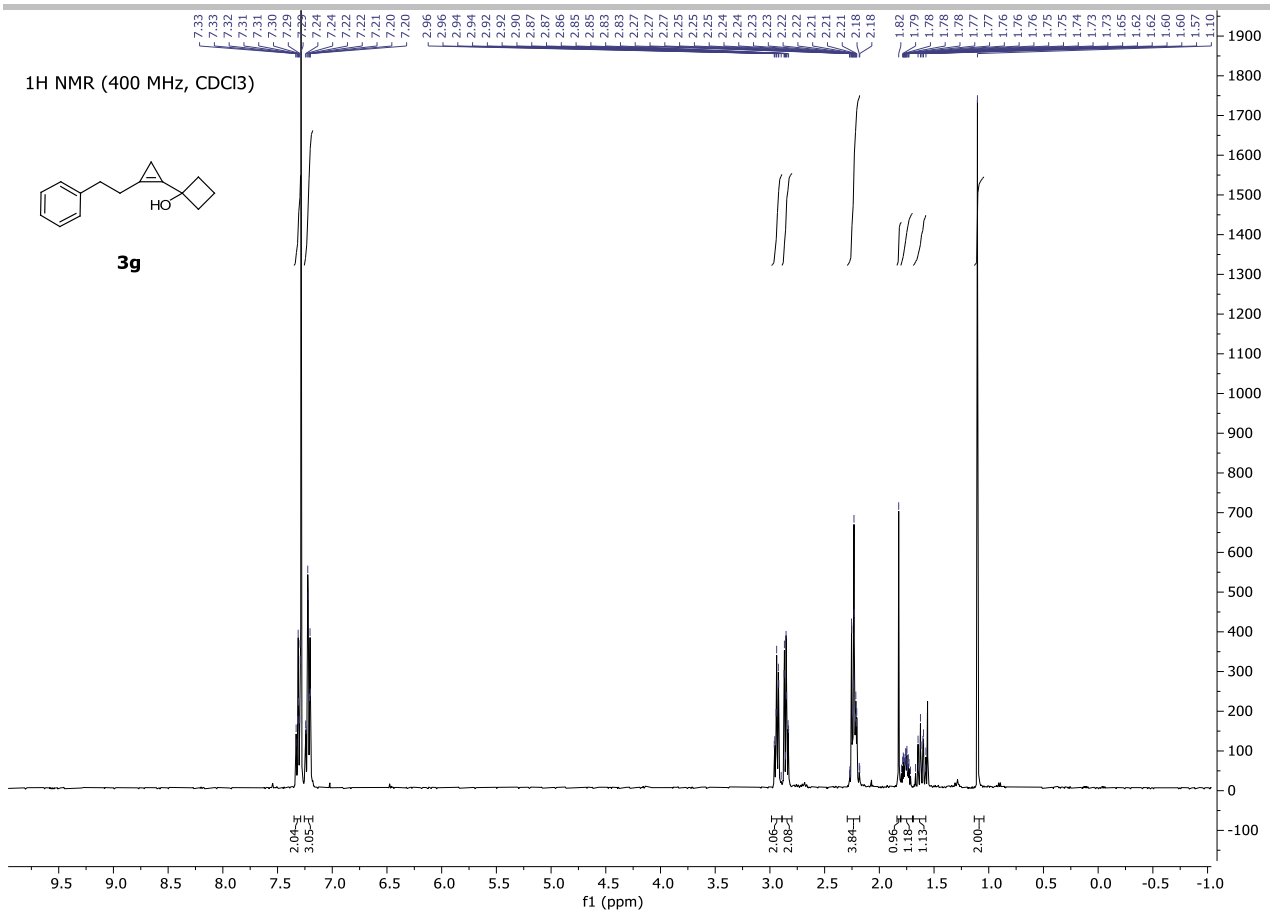


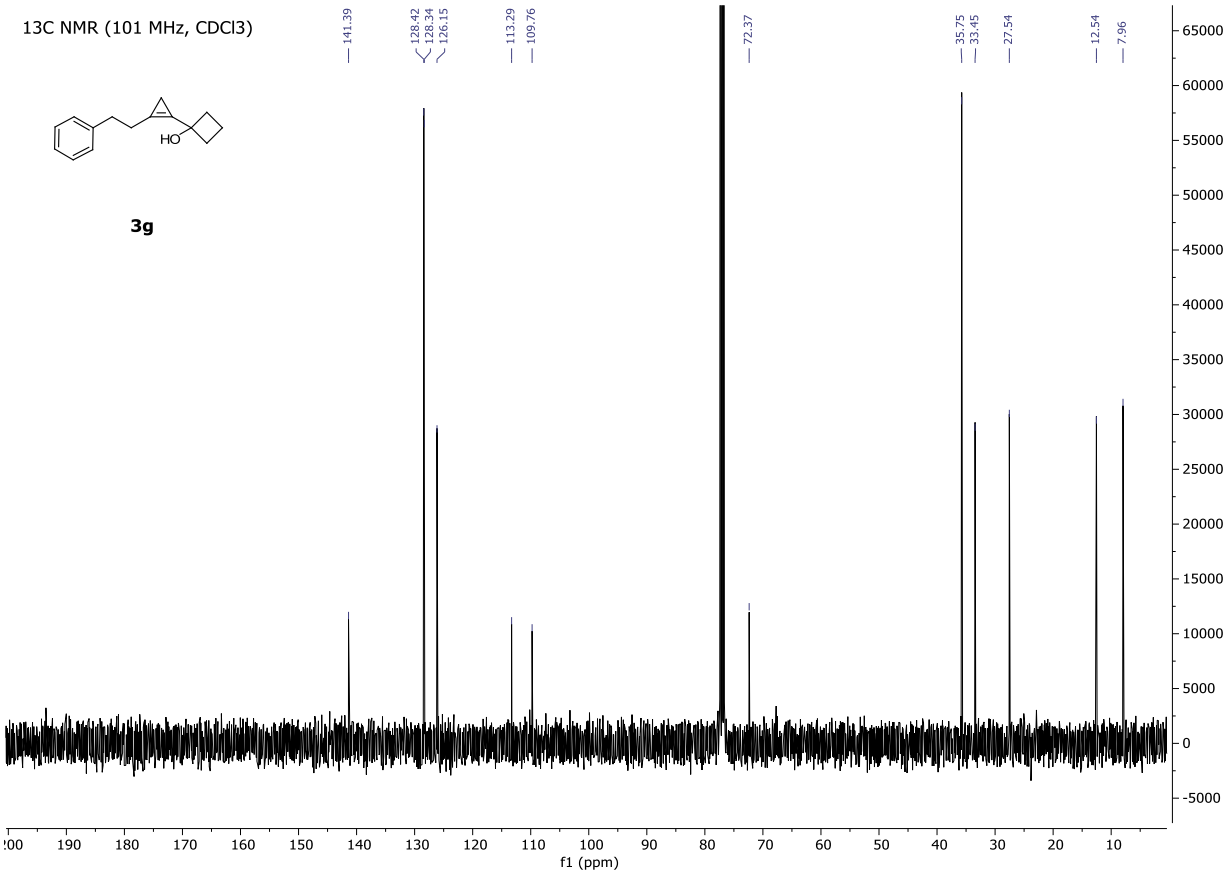
3f

13C NMR (101 MHz, CDCl3)

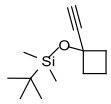


3f


1H NMR (400 MHz, CDCl3)
HO
3g
f1 (ppm)

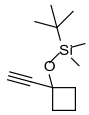

13C NMR (101 MHz, CDCl3)
HO
3g
f1 (ppm)

1H NMR (400 MHz, CDCl3)



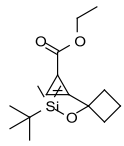
20

13C NMR (101 MHz, CDCl3)



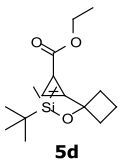
20

1H NMR (400 MHz, CDCl3)

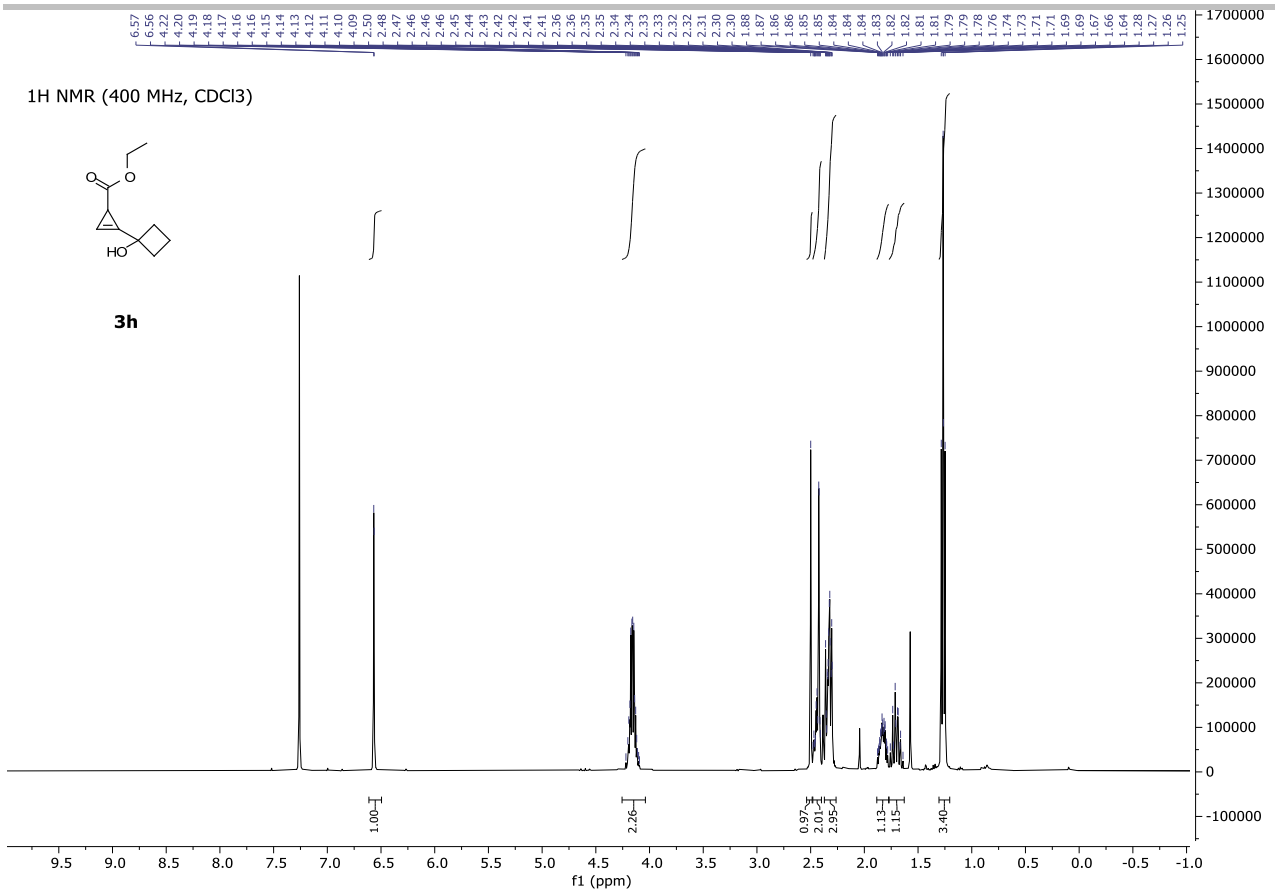


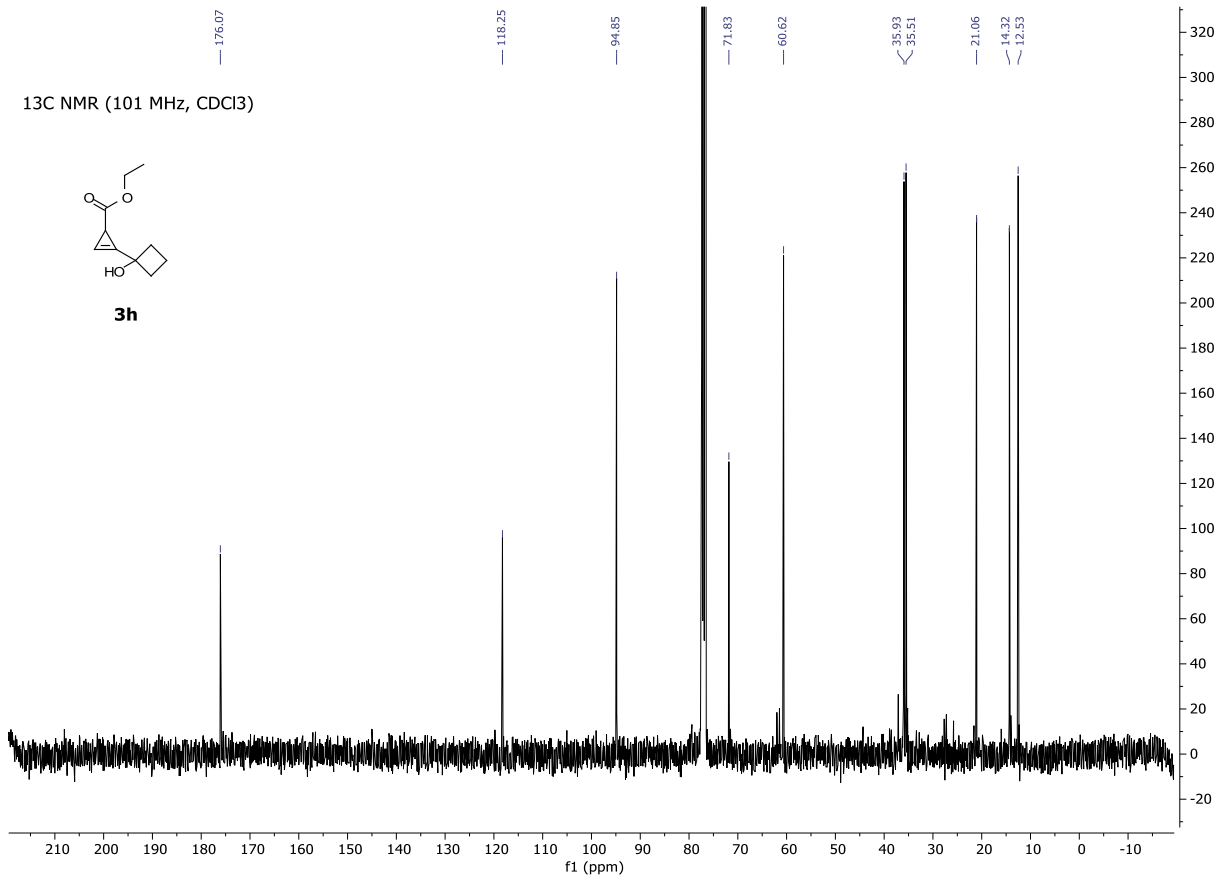
5d

13C NMR (101 MHz, CDCl3)

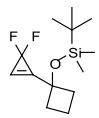


5d


1H NMR (400 MHz, CDCl3)
3h
f1 (ppm)

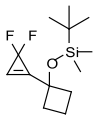

13C NMR (101 MHz, CDCl3)
3h
f1 (ppm)

1H NMR (400 MHz, CDCl3)



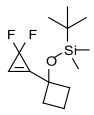
3i

13C NMR (101 MHz, CDCl3)



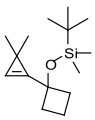
3i

19F NMR (376 MHz, CDCl3)



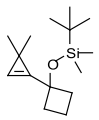
3i

1H NMR (400 MHz, CDCl3)



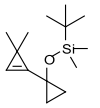
5a

13C NMR (101 MHz, CDCl3)



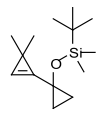
5a

1H NMR (400 MHz, CDCl3)



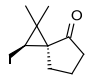
5b

13C NMR (101 MHz, CDCl3)

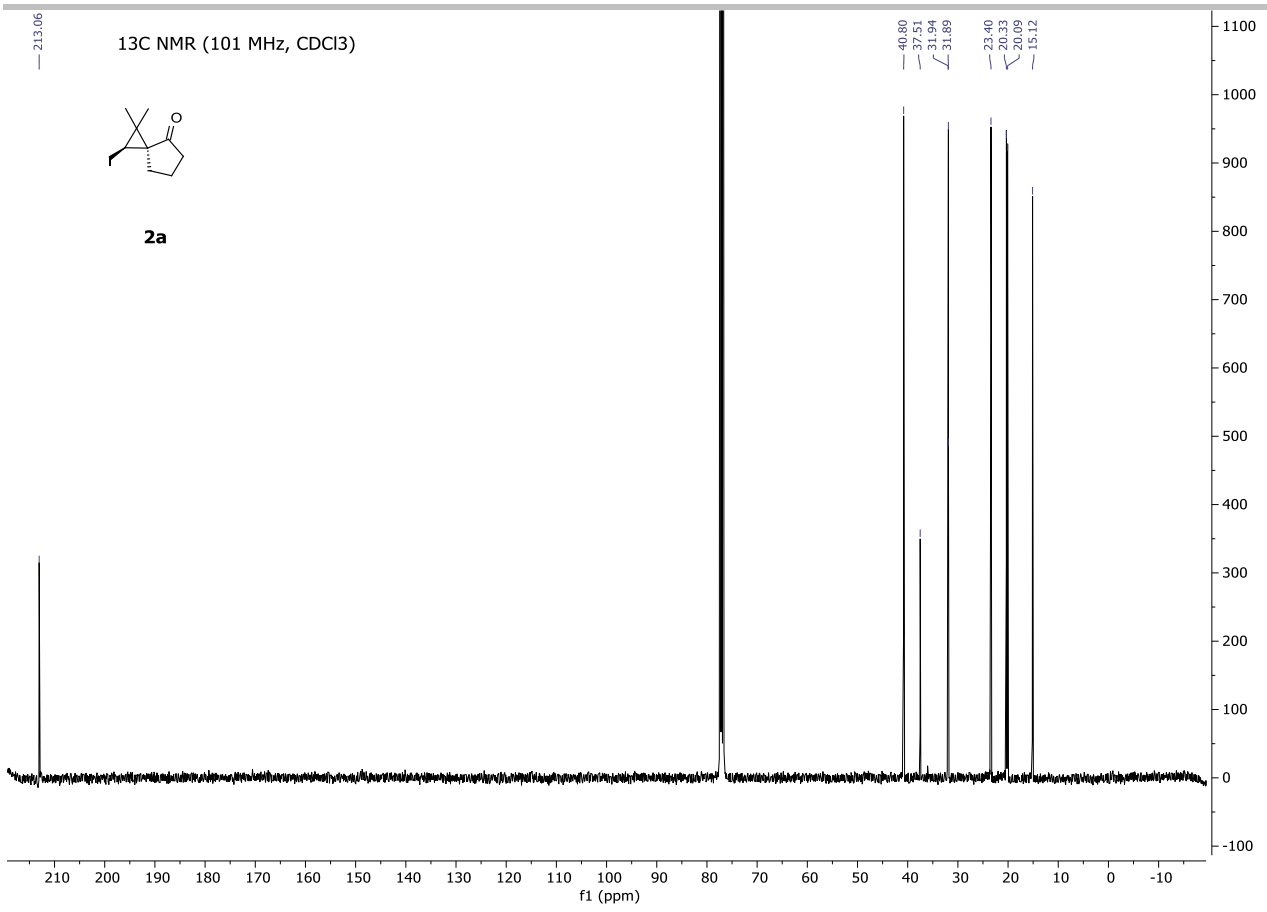


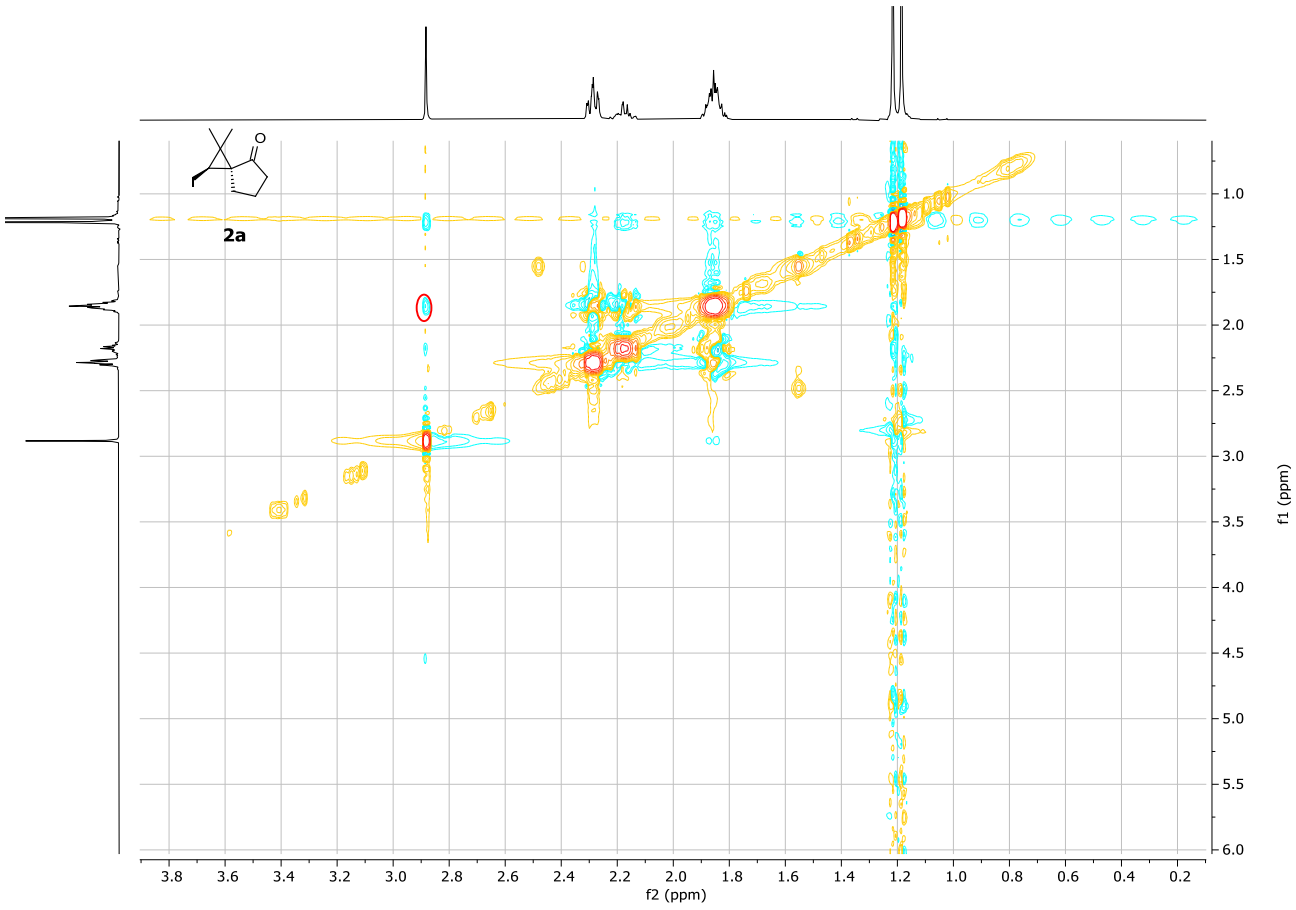
5b

1H NMR (400 MHz, CDCl3)



2a


13C NMR (101 MHz, CDCl3)
213.06
40.80
37.51
31.94
31.89
23.40
20.33
20.09
15.12
2a
f1 (ppm)

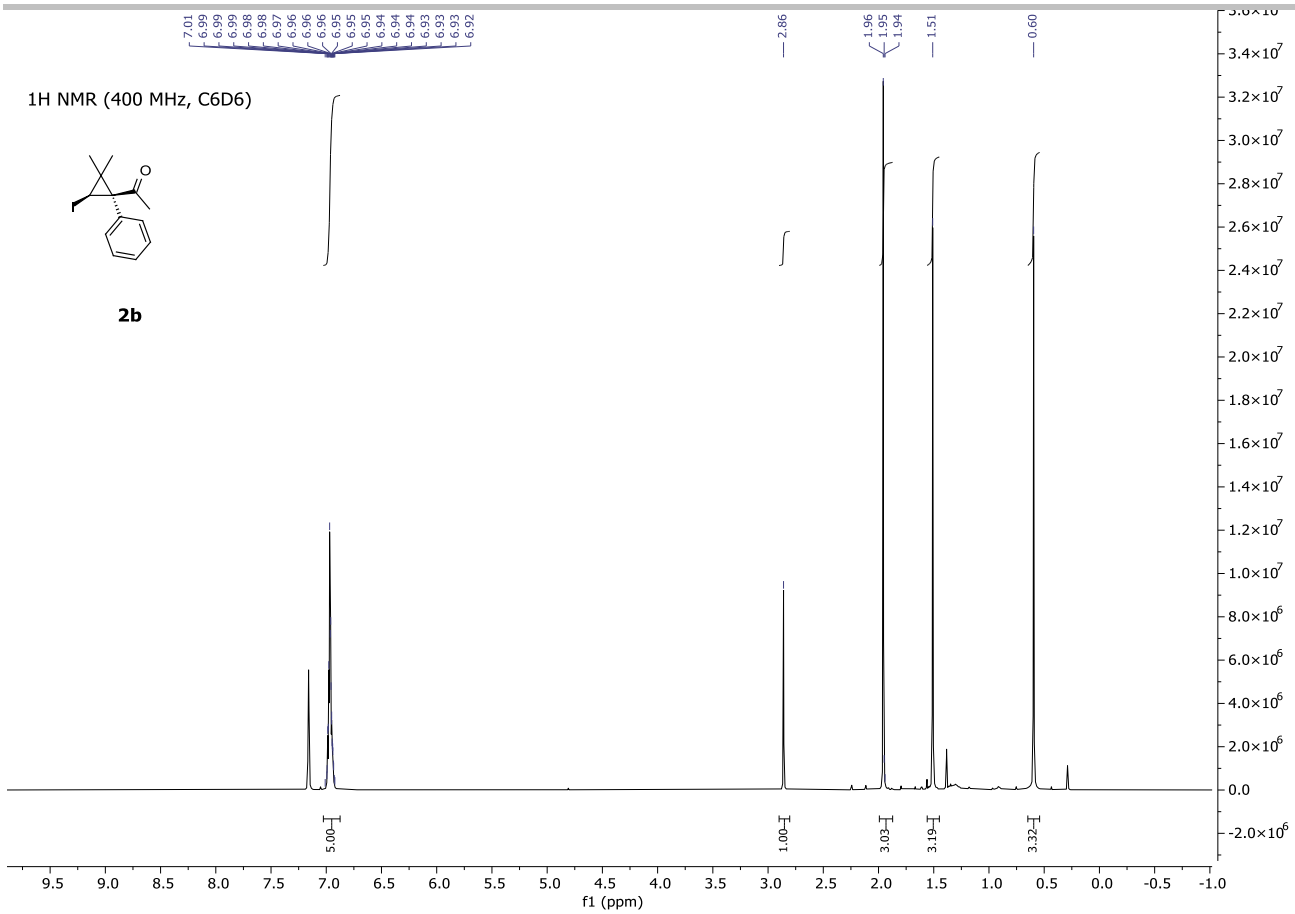

2a
f2 (ppm)
f1 (ppm)

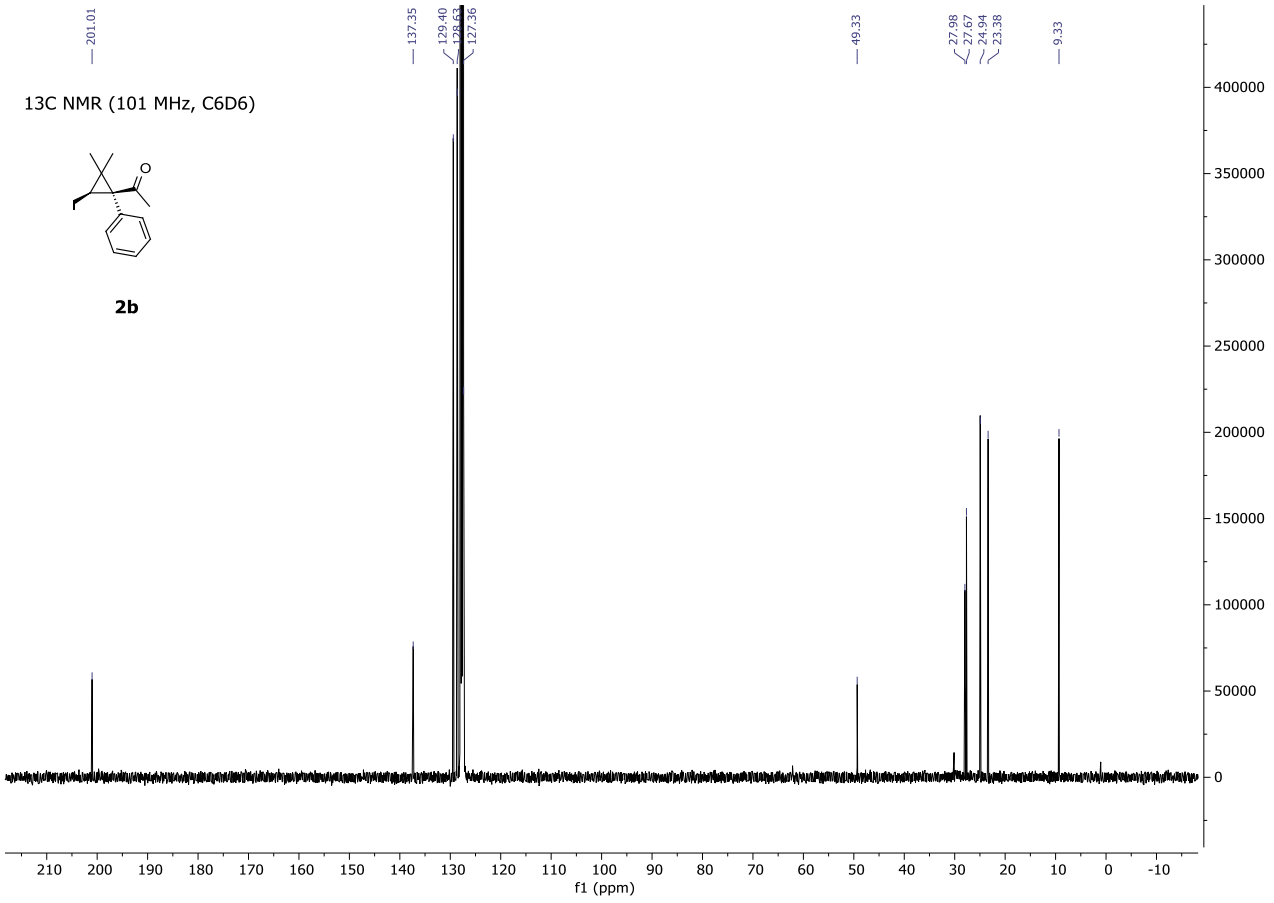
1H NMR (400 MHz, CDCl3)

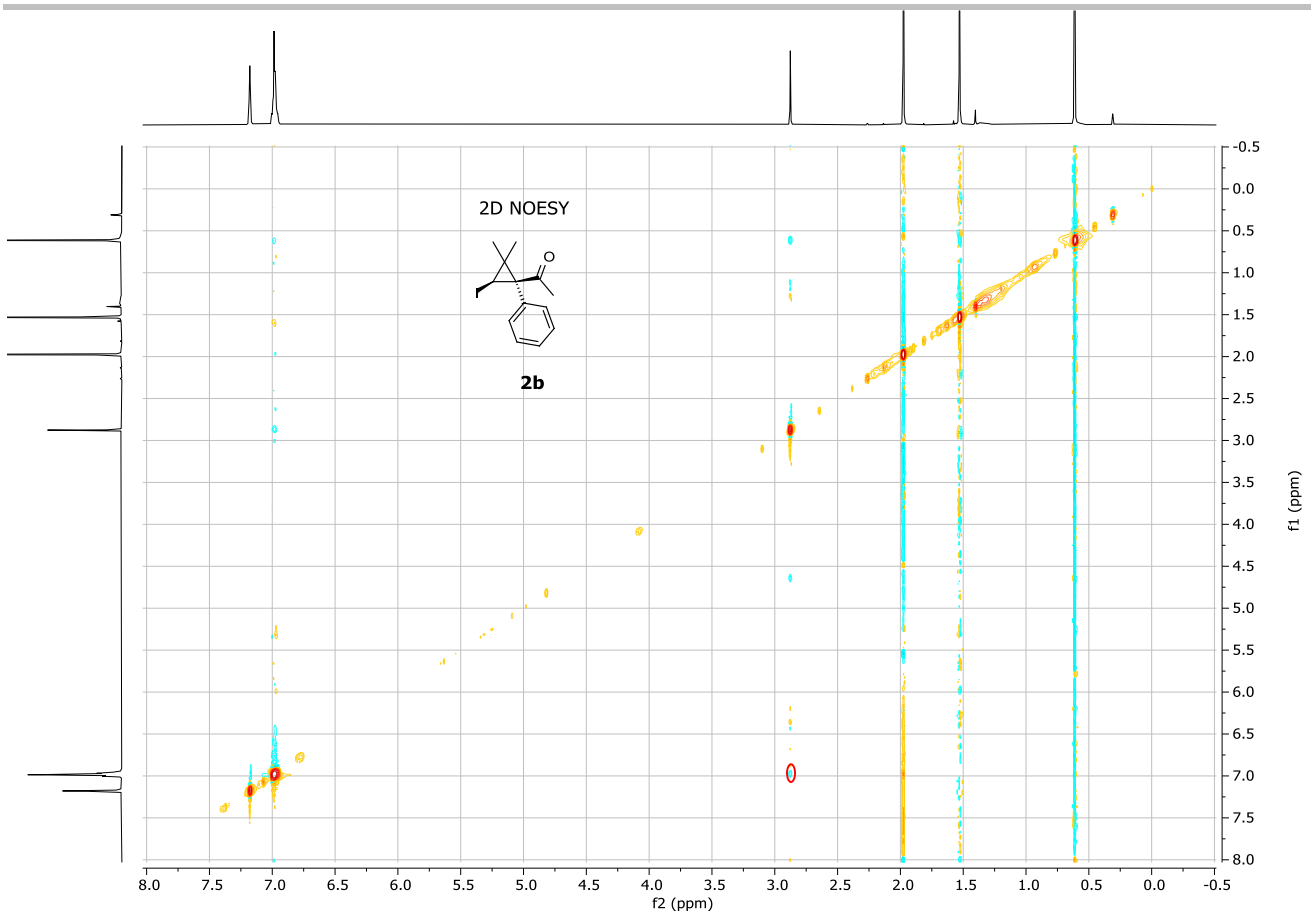
2a'

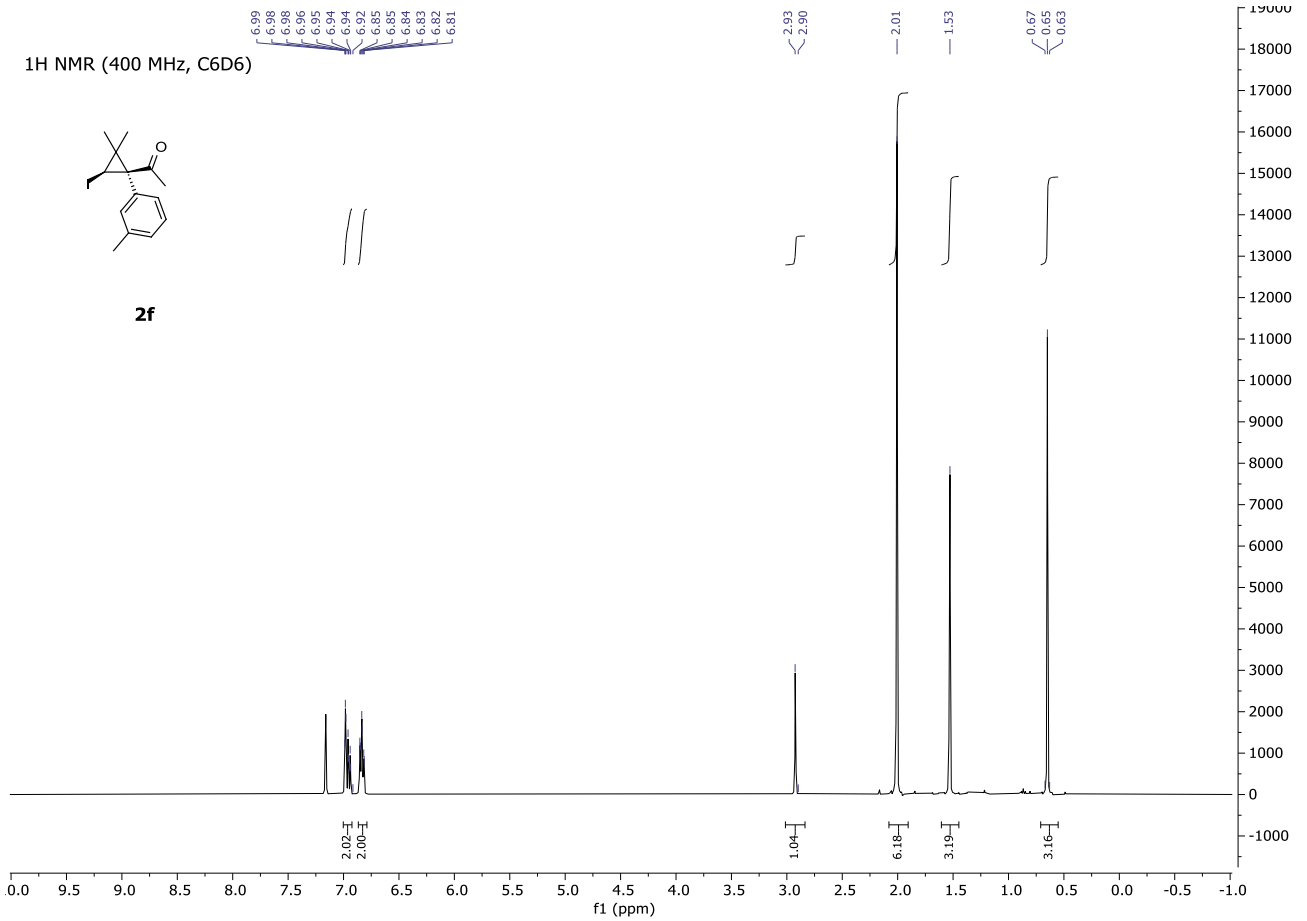
13C NMR (101 MHz, CDCl3)

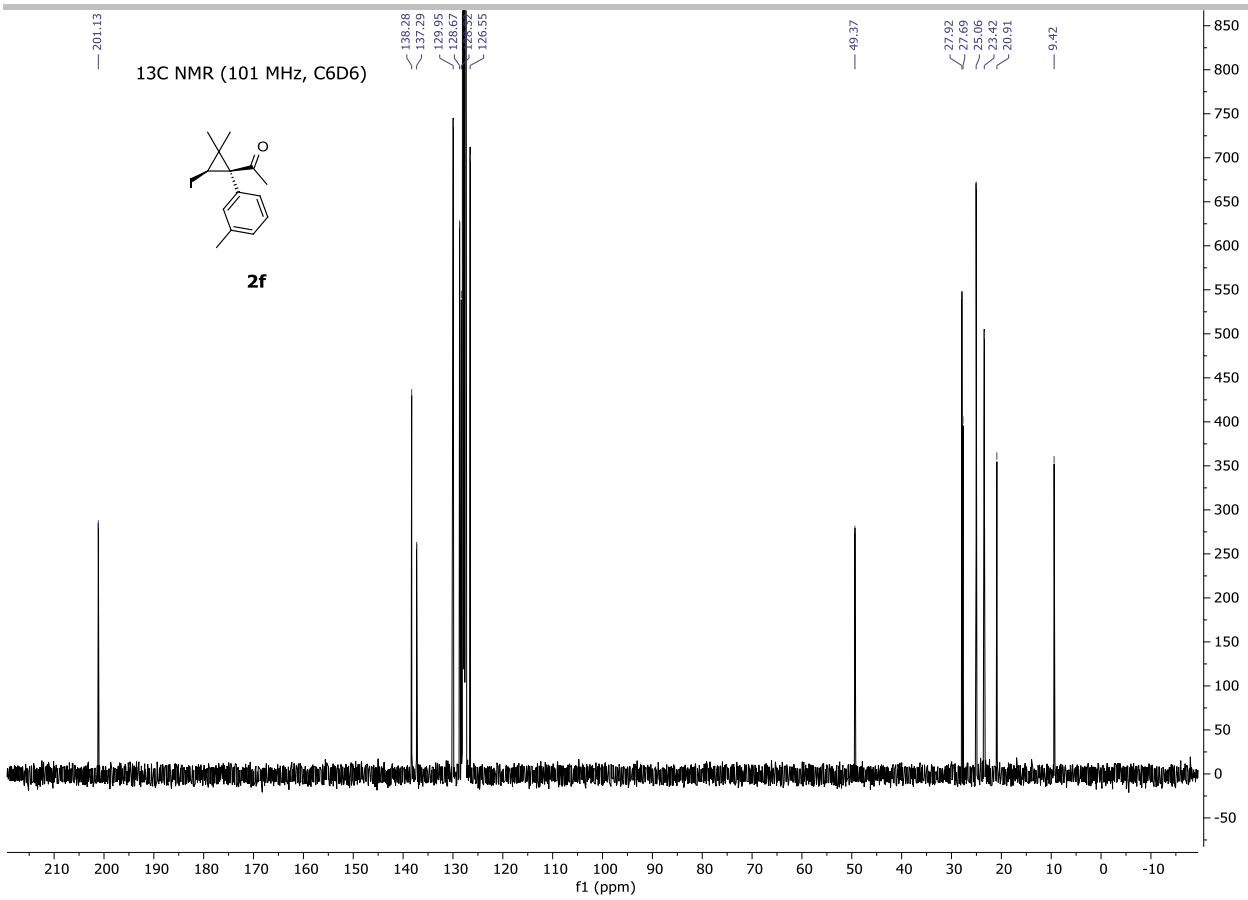
2a'


1H NMR (400 MHz, C6D6)
2b
7.01
6.99
6.99
6.99
6.99
6.98
6.98
6.97
6.96
6.96
6.96
6.95
6.95
6.95
6.94
6.94
6.94
6.93
6.93
6.93
6.92
2.86
1.96
1.95
1.94
1.51
0.60
5.00
1.00
3.03
3.19
3.32
f1 (ppm)

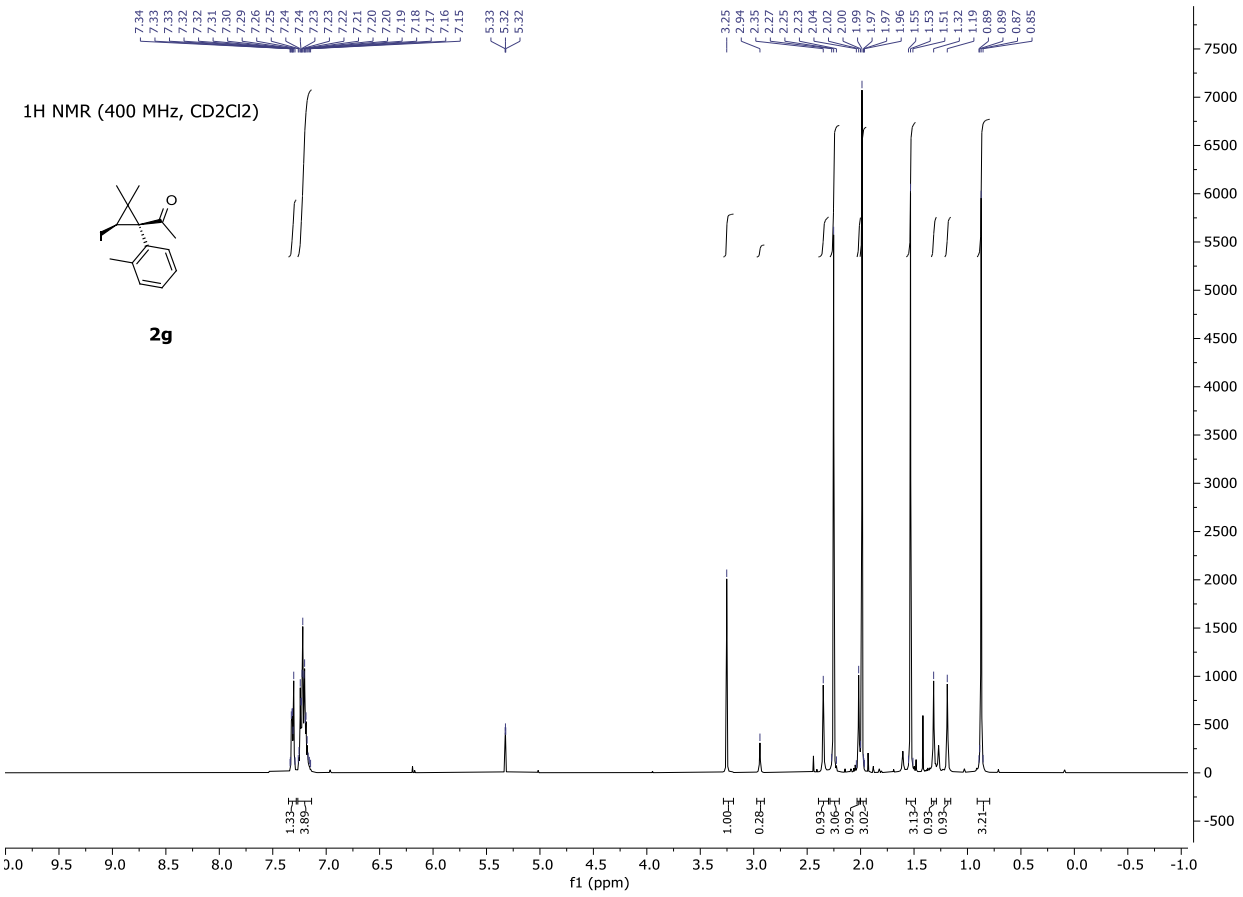

13C NMR (101 MHz, C6D6)
2b
201.01
137.35
129.40
128.63
127.36
49.33
27.98
27.67
24.94
23.38
9.33
f1 (ppm)


2D NOESY
2b
f2 (ppm)
f1 (ppm)

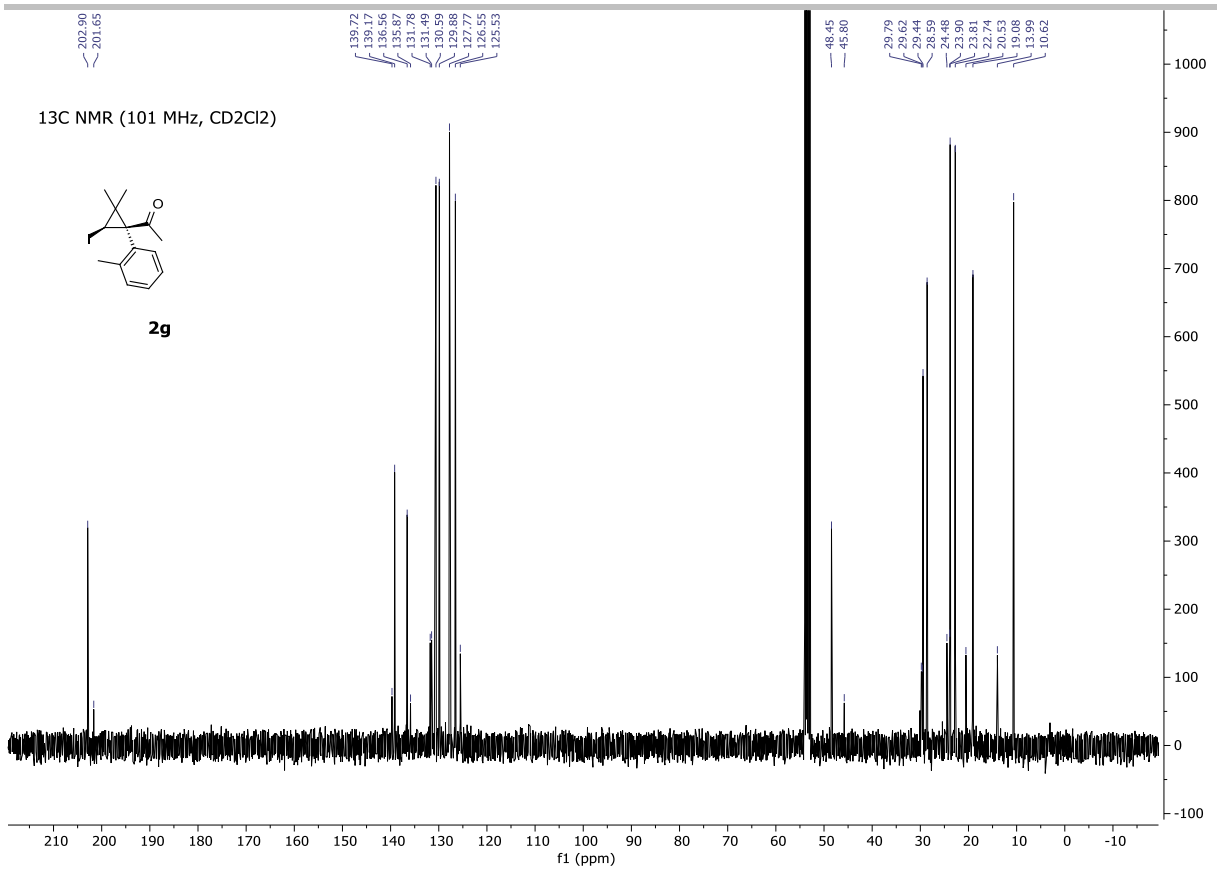

1H NMR (400 MHz, C6D6)
2f
f1 (ppm)

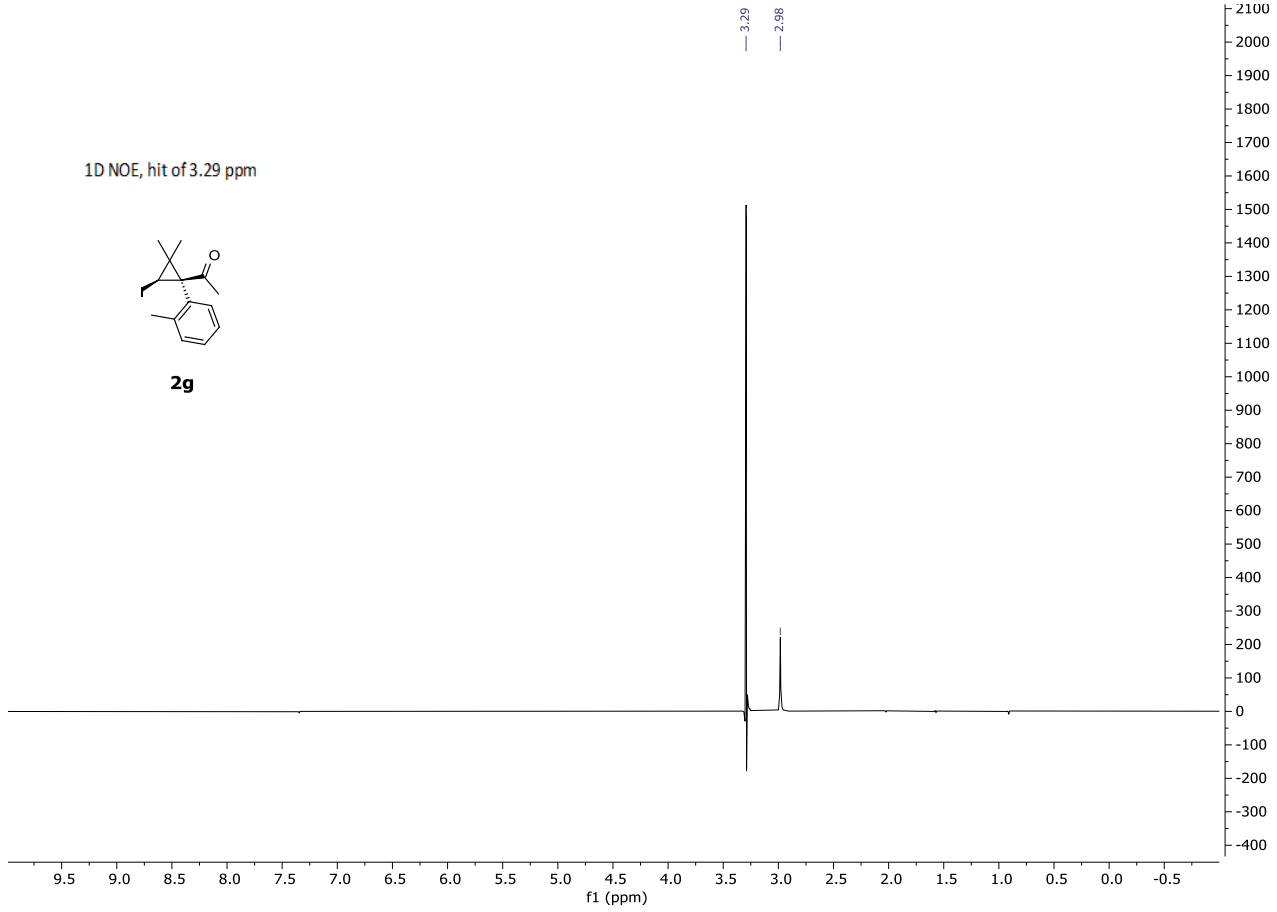

13C NMR (101 MHz, C6D6)
201.13
138.28
137.29
129.95
128.67
126.55
49.37
27.92
27.69
25.06
23.42
20.91
9.42
f1 (ppm)

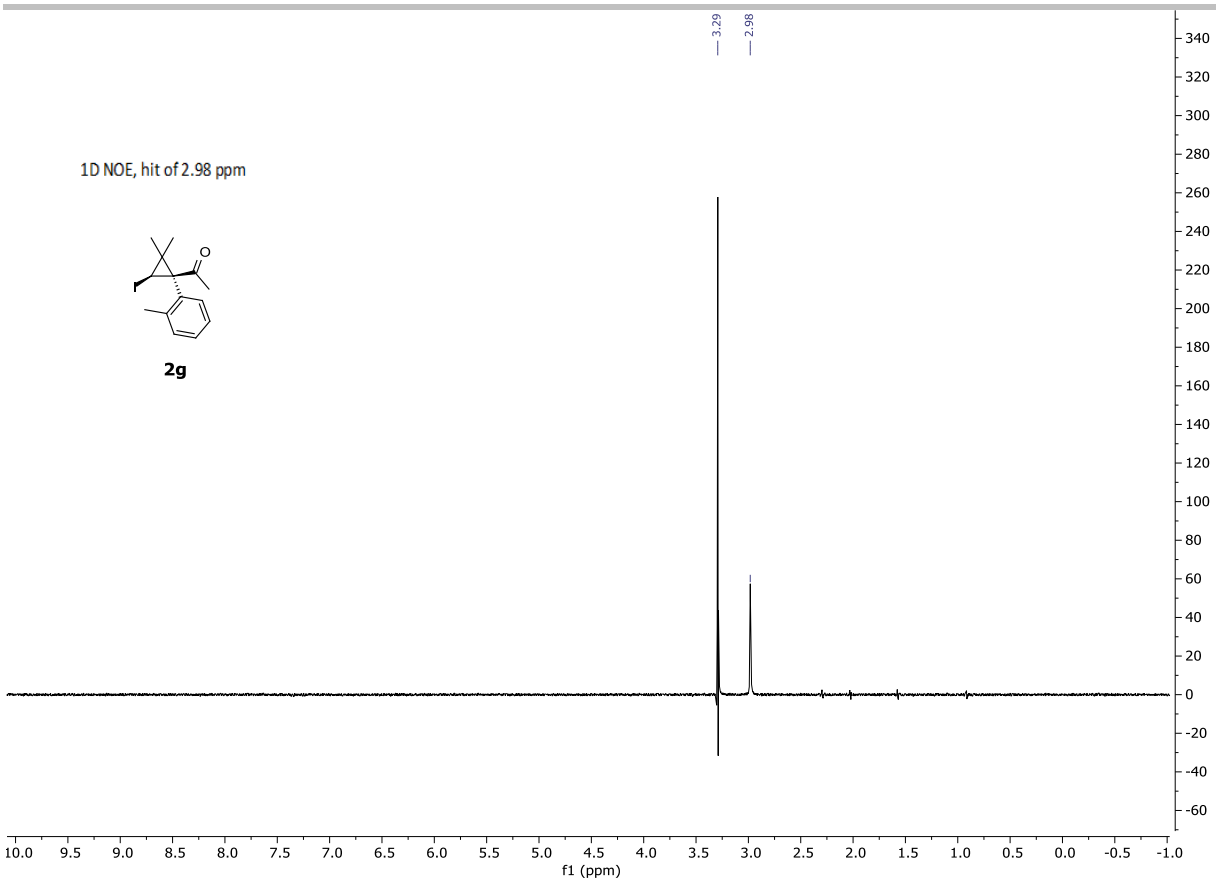
2f

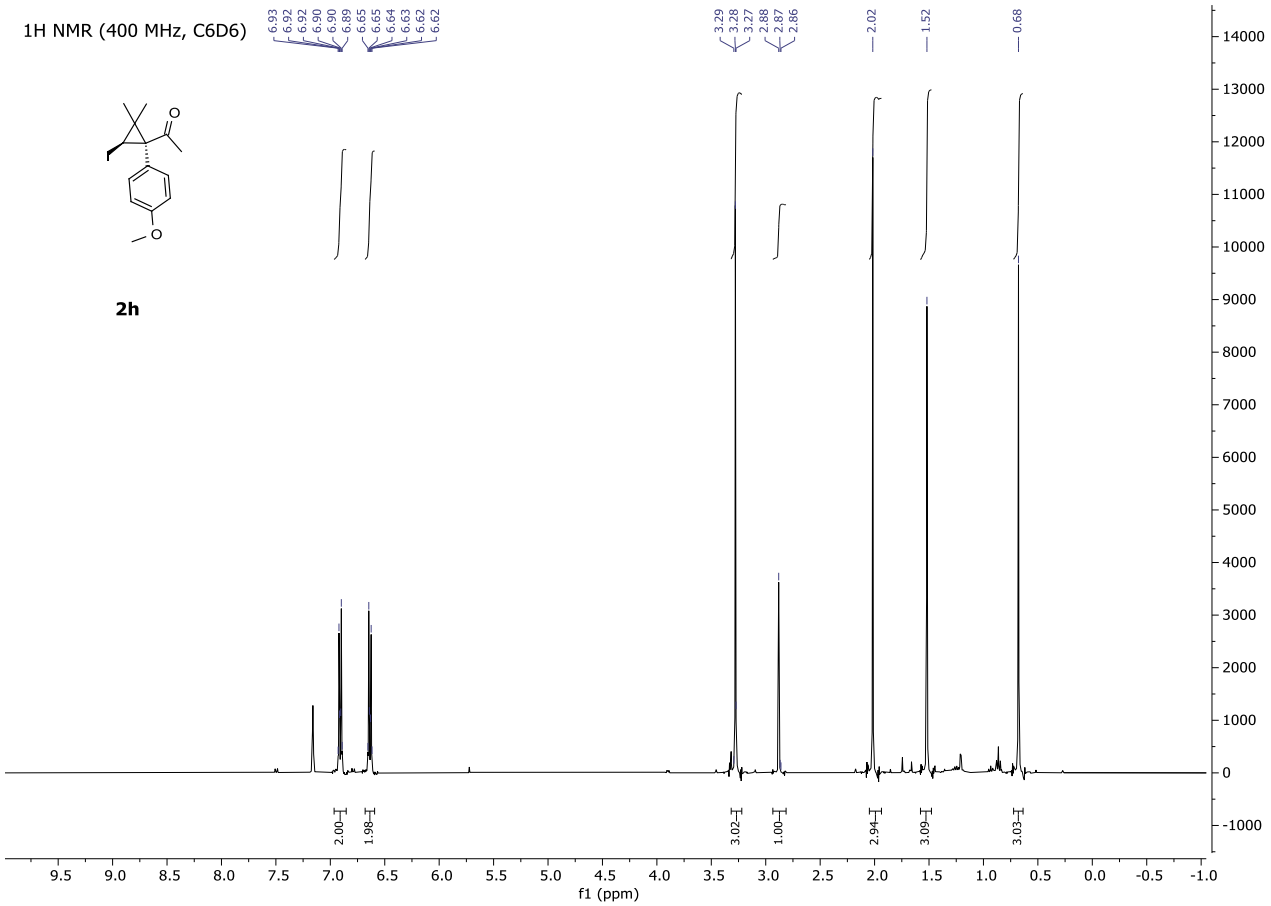

1H NMR (400 MHz, CD2Cl2)
f1 (ppm)

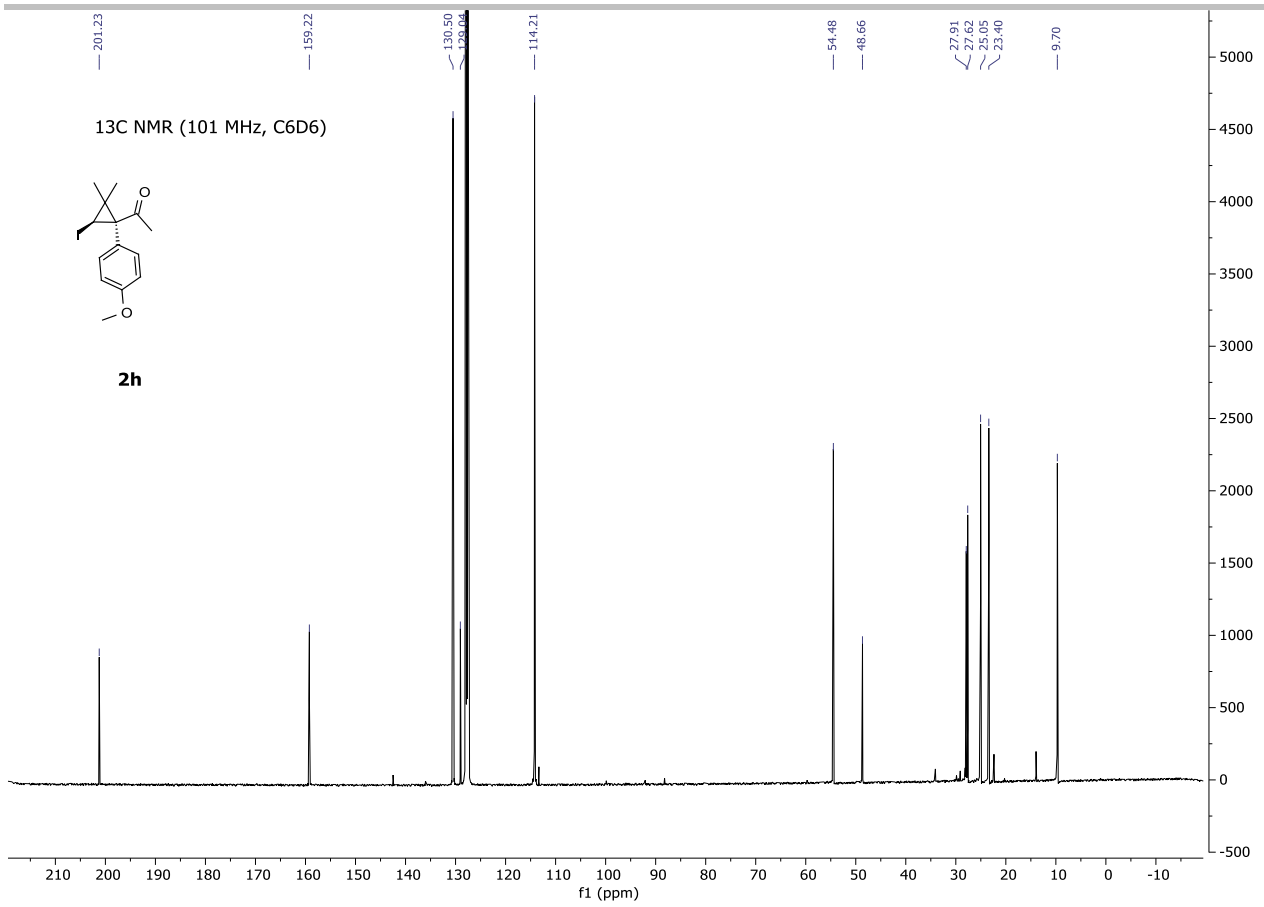
2g


13C NMR (101 MHz, CD2Cl2)
2g
f1 (ppm)

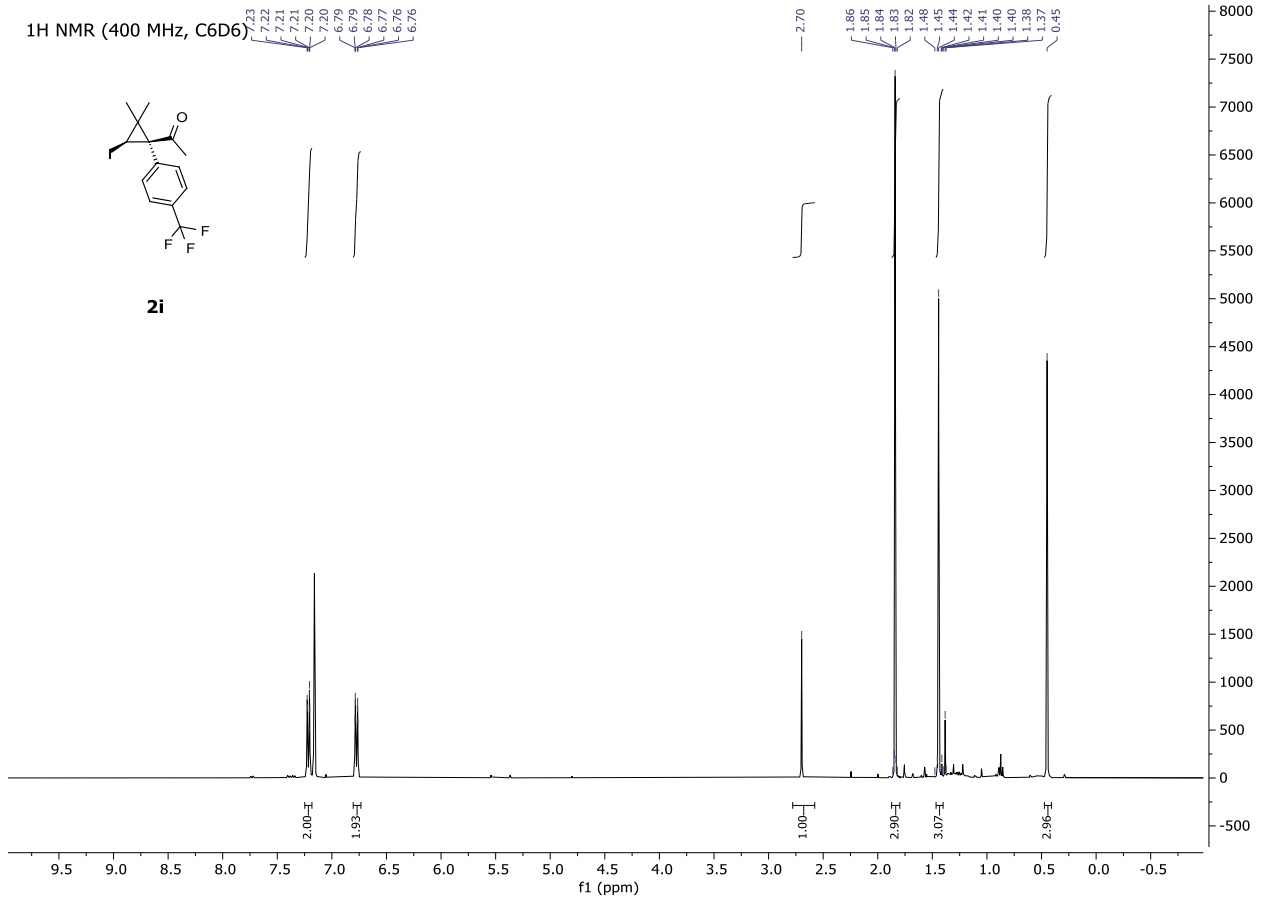

1D NOE, hit of 3.29 ppm
2g
f1 (ppm)


3.29
2.98
1D NOE, hit of 2.98 ppm
O
2g
f1 (ppm)

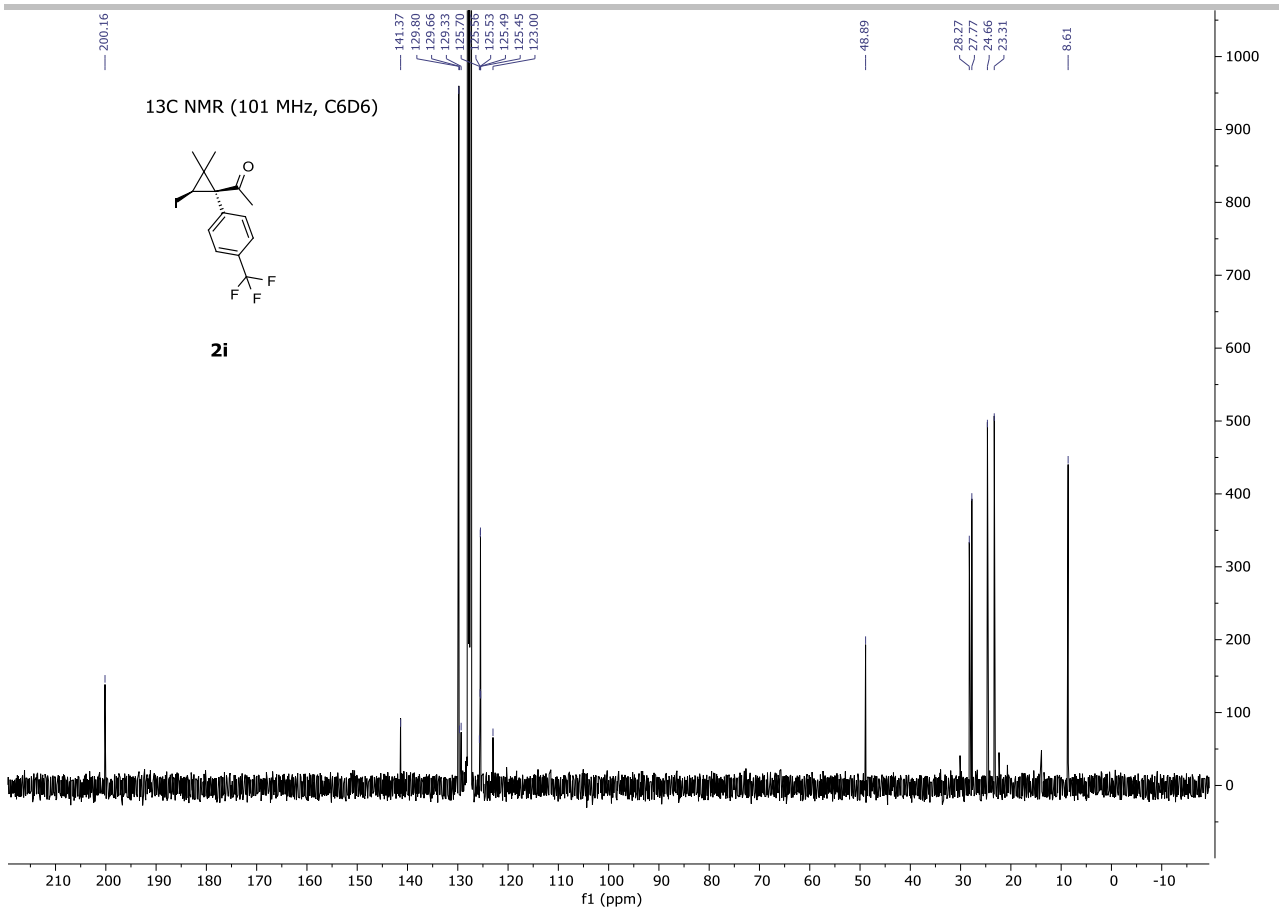

1H NMR (400 MHz, C6D6)
6.93
6.92
6.92
6.90
6.90
6.89
6.65
6.65
6.64
6.63
6.62
6.62
3.29
3.28
3.27
2.88
2.87
2.86
2.02
1.52
0.68
O
O
2h
2.00
1.98
3.02
1.00
2.94
3.09
3.03
f1 (ppm)

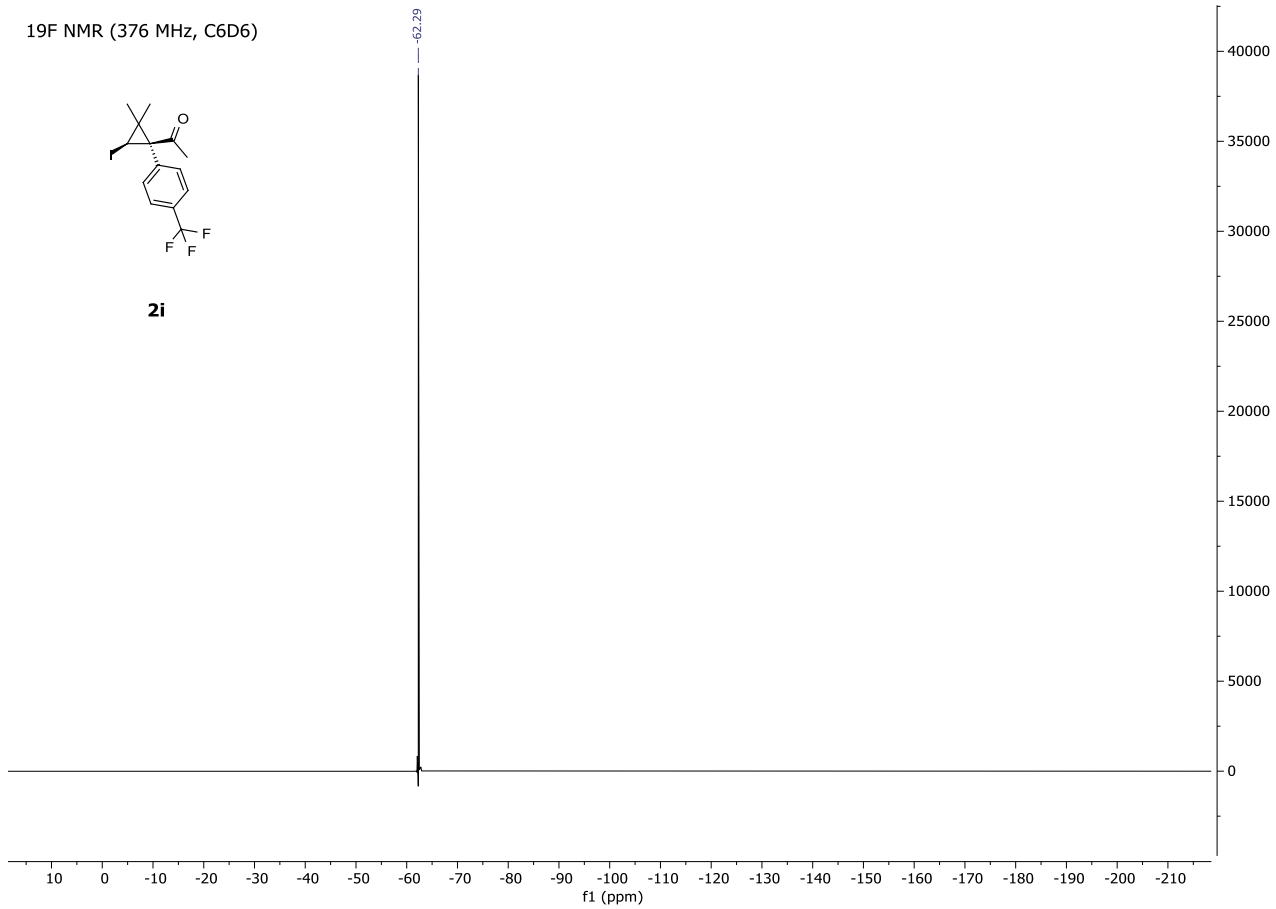

13C NMR (101 MHz, C6D6)
201.23
159.22
130.50
129.04
114.21
54.48
48.66
27.91
27.62
25.05
23.40
9.70
f1 (ppm)

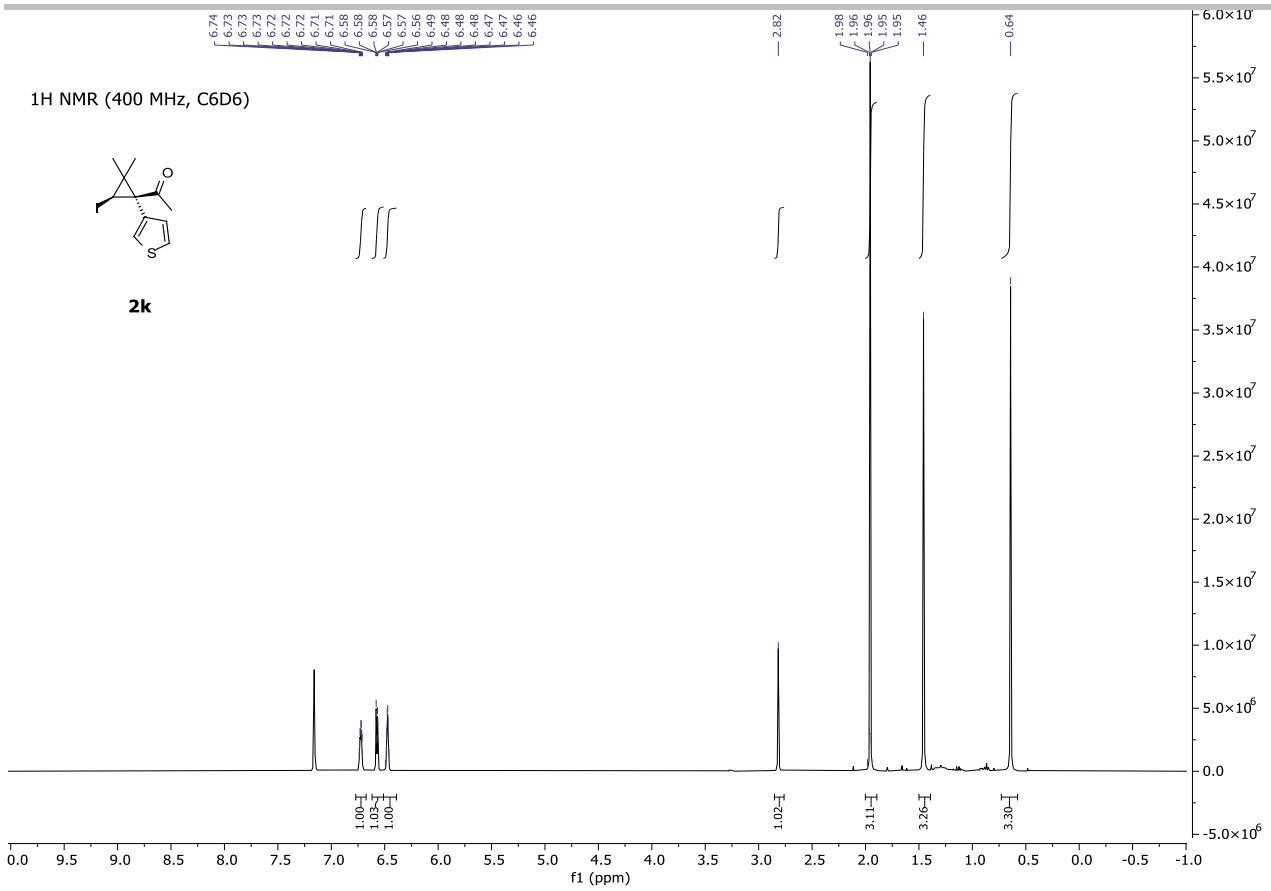
2h

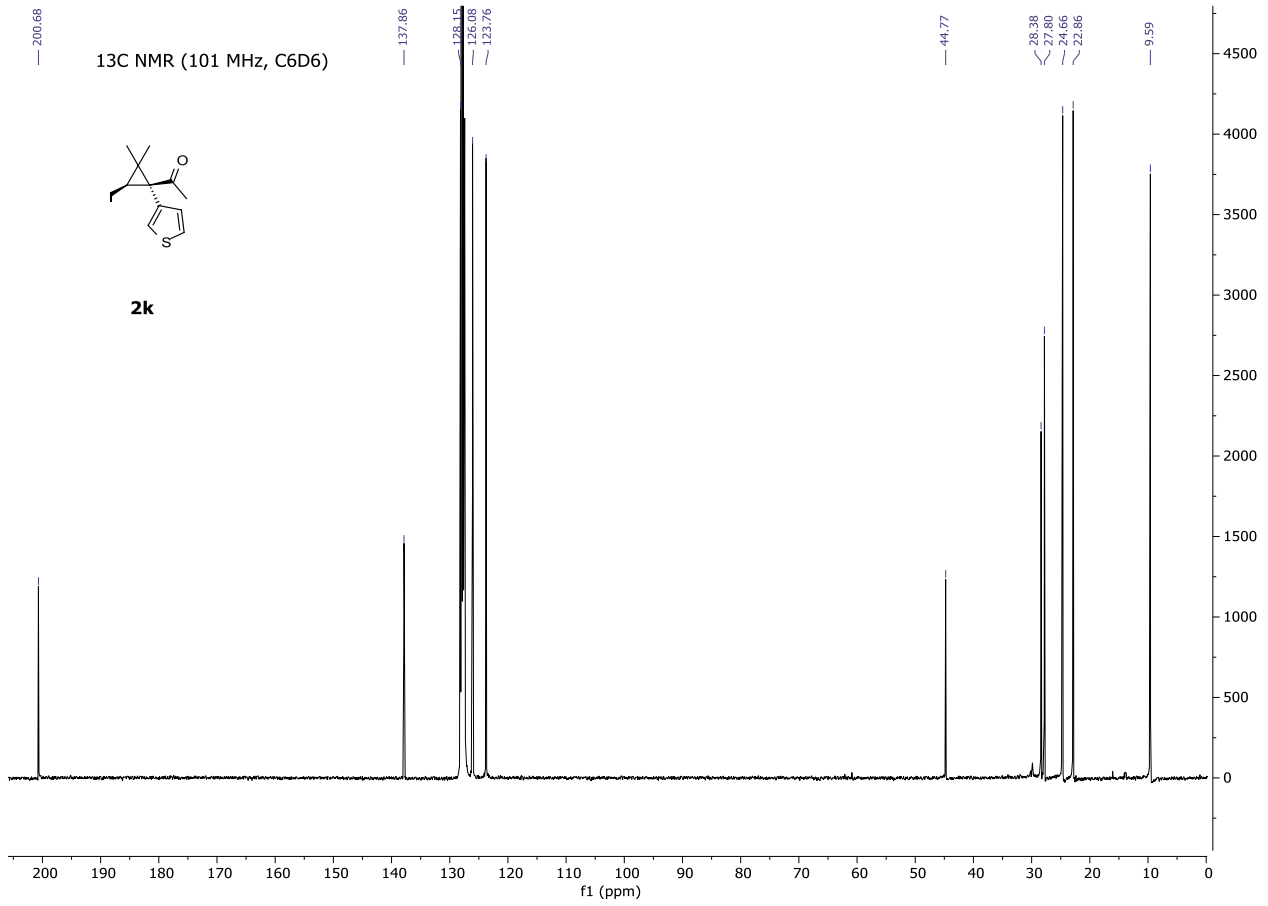

1H NMR (400 MHz, C6D6)
7.23
7.22
7.21
7.21
7.20
7.20
6.79
6.79
6.78
6.77
6.76
6.76
2.70
1.86
1.85
1.84
1.83
1.82
1.48
1.45
1.44
1.42
1.41
1.40
1.40
1.38
1.37
0.45
2.00
1.93
1.00
2.90
3.07
2.96
f1 (ppm)

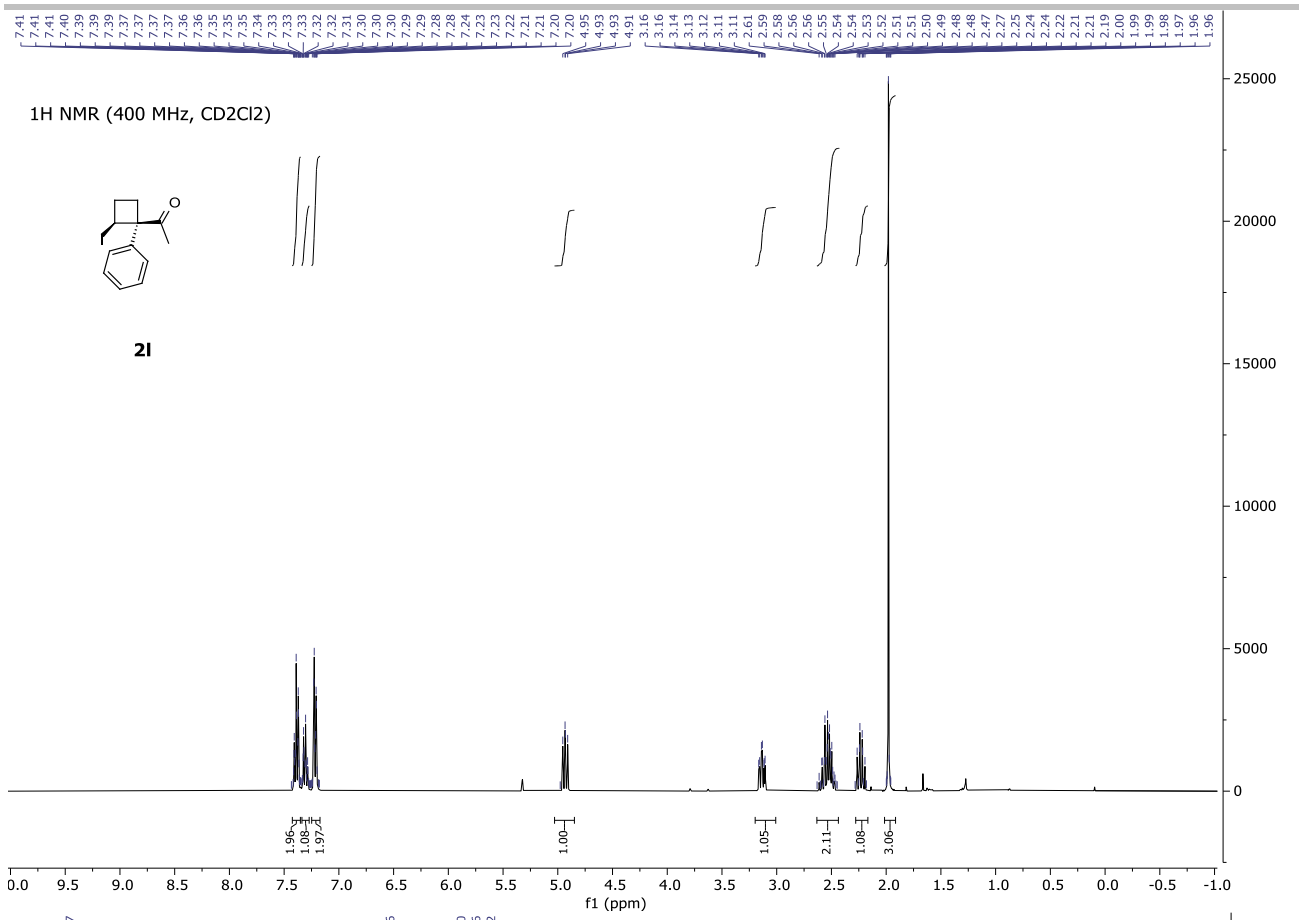
2i

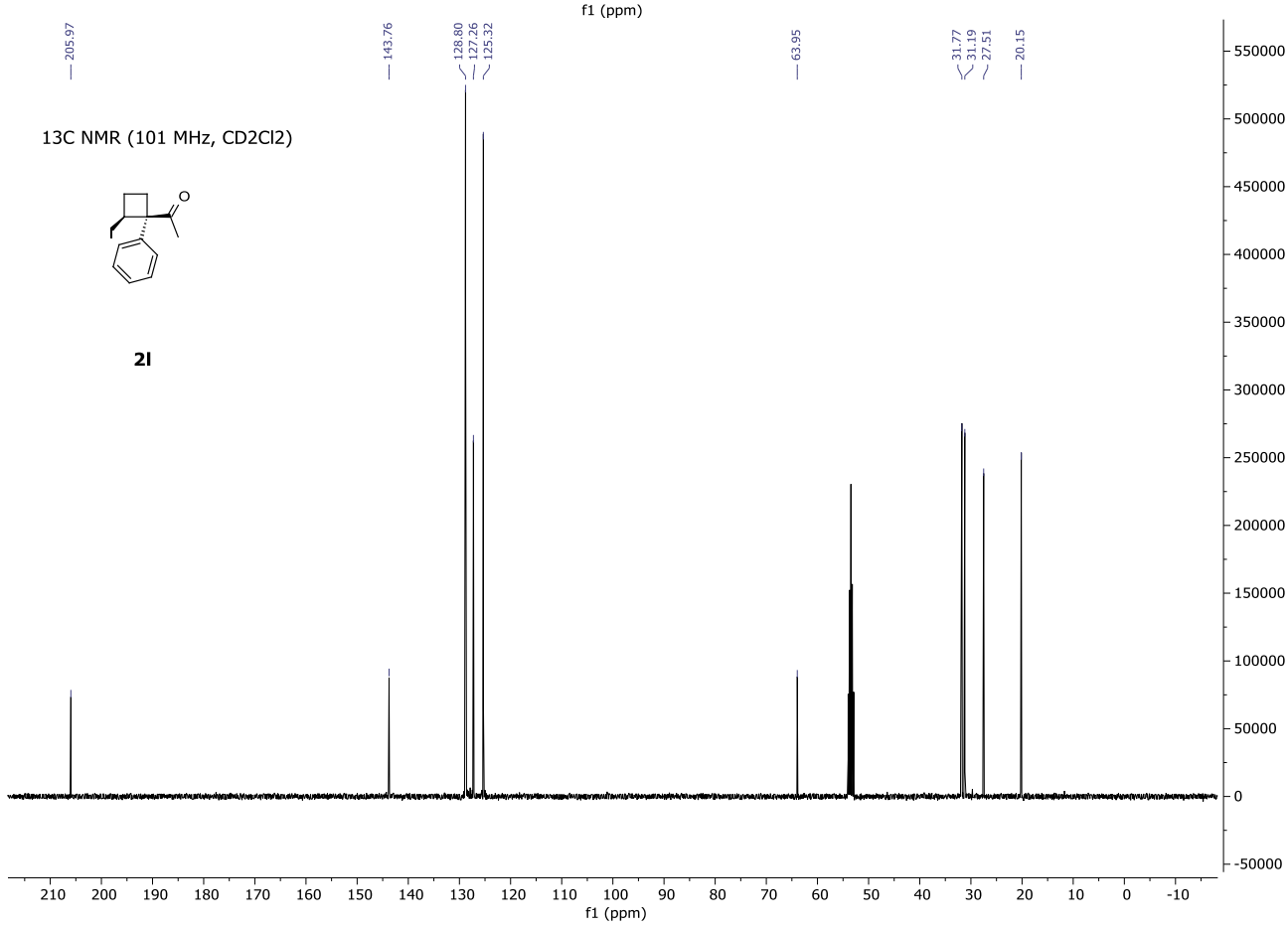

13C NMR (101 MHz, C6D6)
2i
200.16
141.37
129.80
129.66
129.33
125.70
125.56
125.53
125.49
125.45
123.00
48.89
28.27
27.77
24.66
23.31
8.61
f1 (ppm)

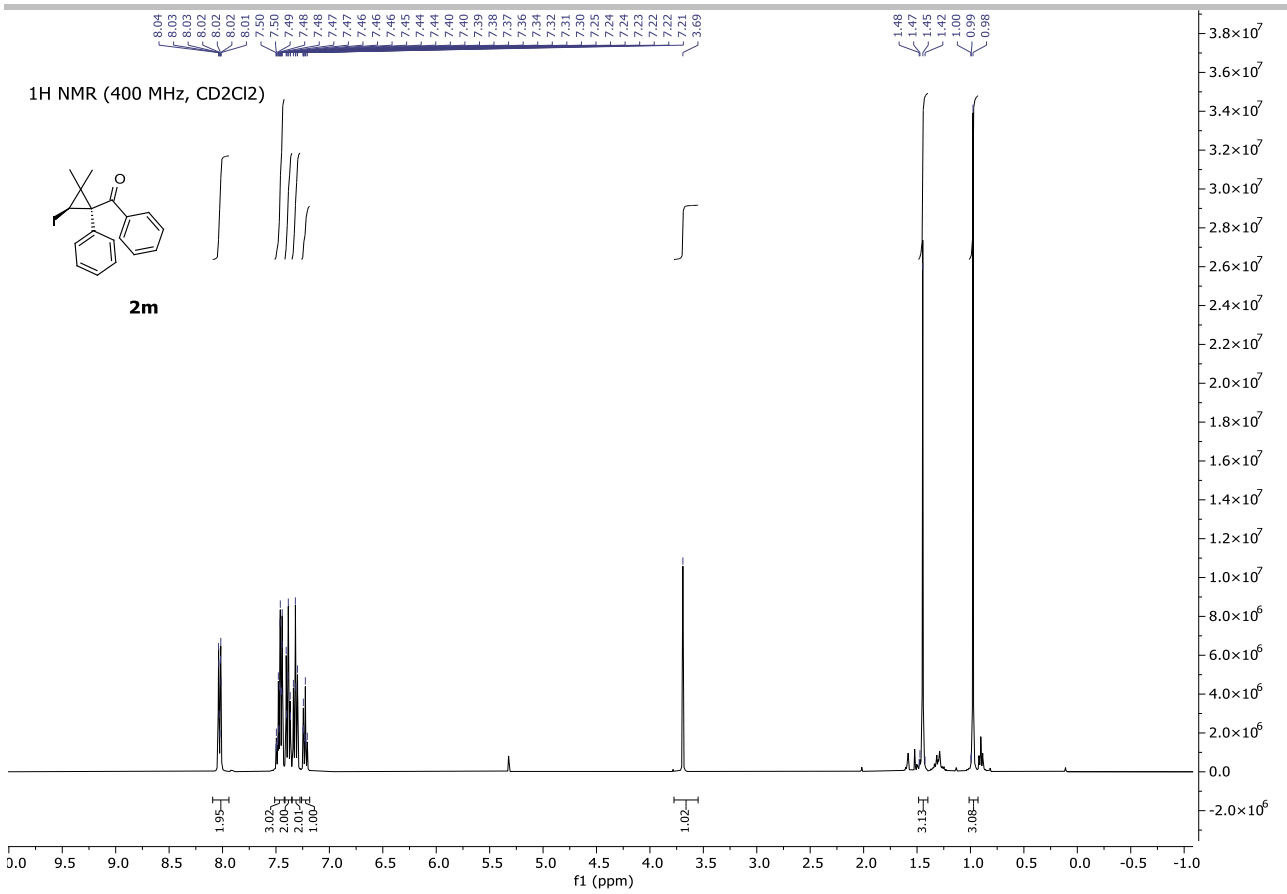

19F NMR (376 MHz, C6D6)
2i
-62.29
f1 (ppm)

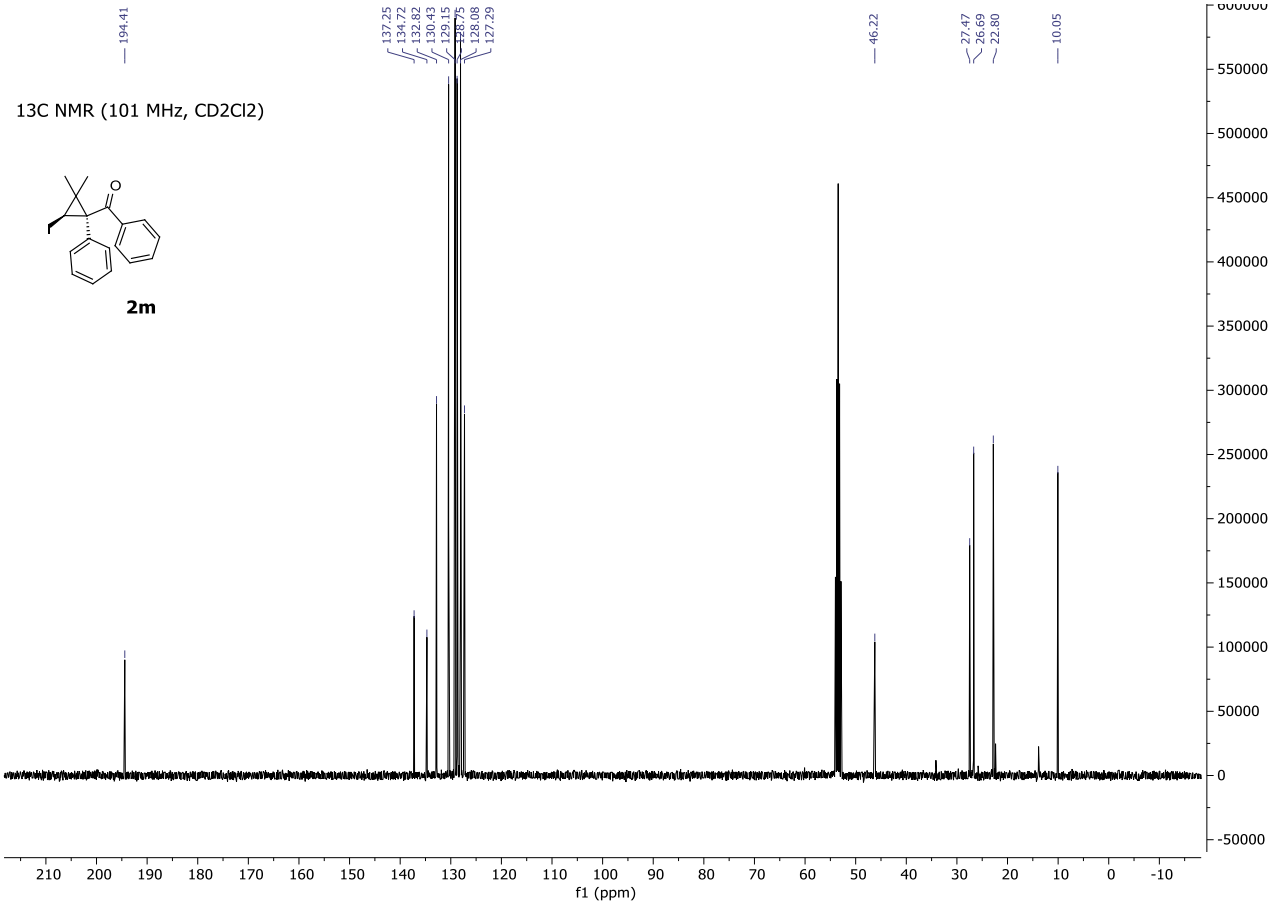

1H NMR (400 MHz, C6D6)
2k
f1 (ppm)

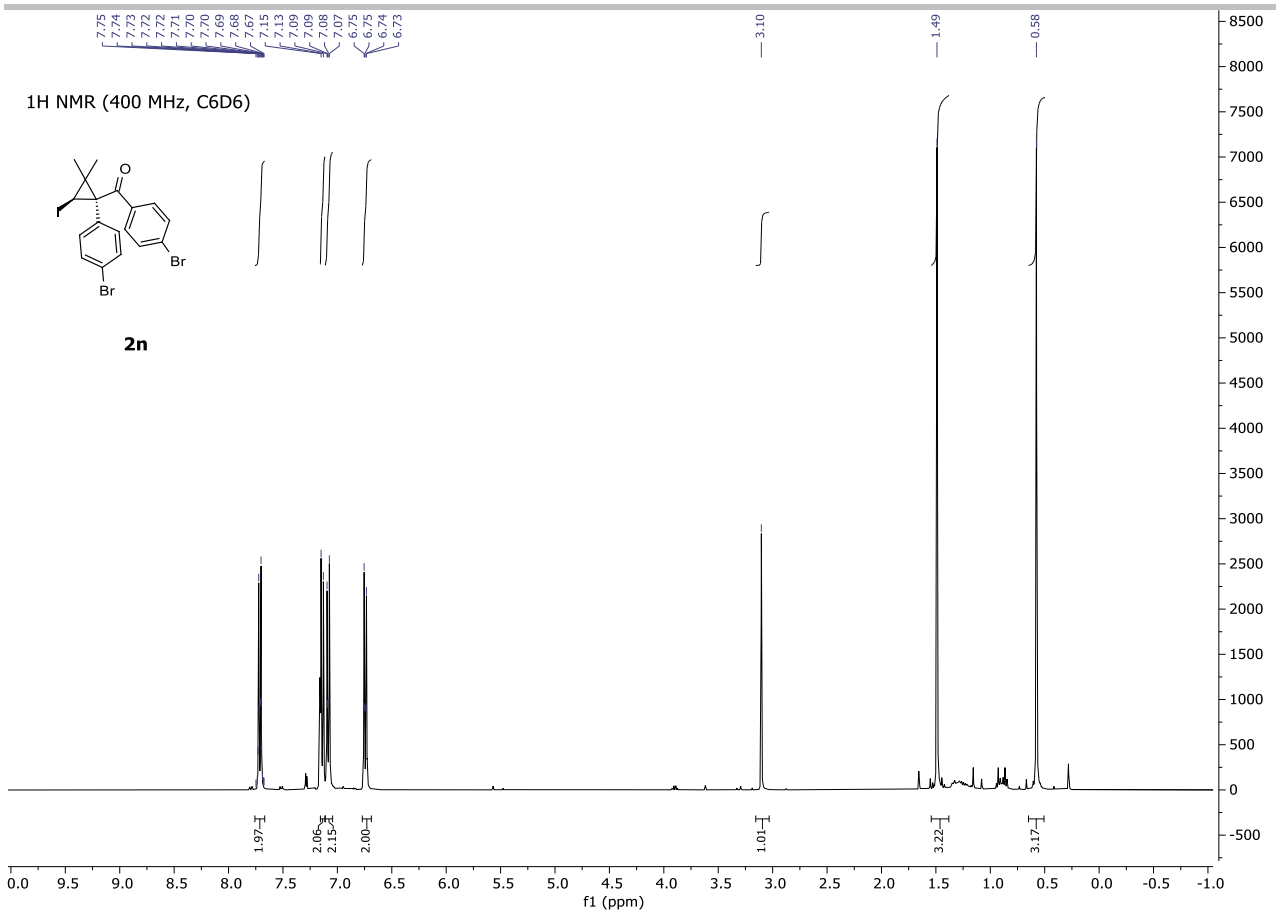

13C NMR (101 MHz, C6D6)
2k
f1 (ppm)

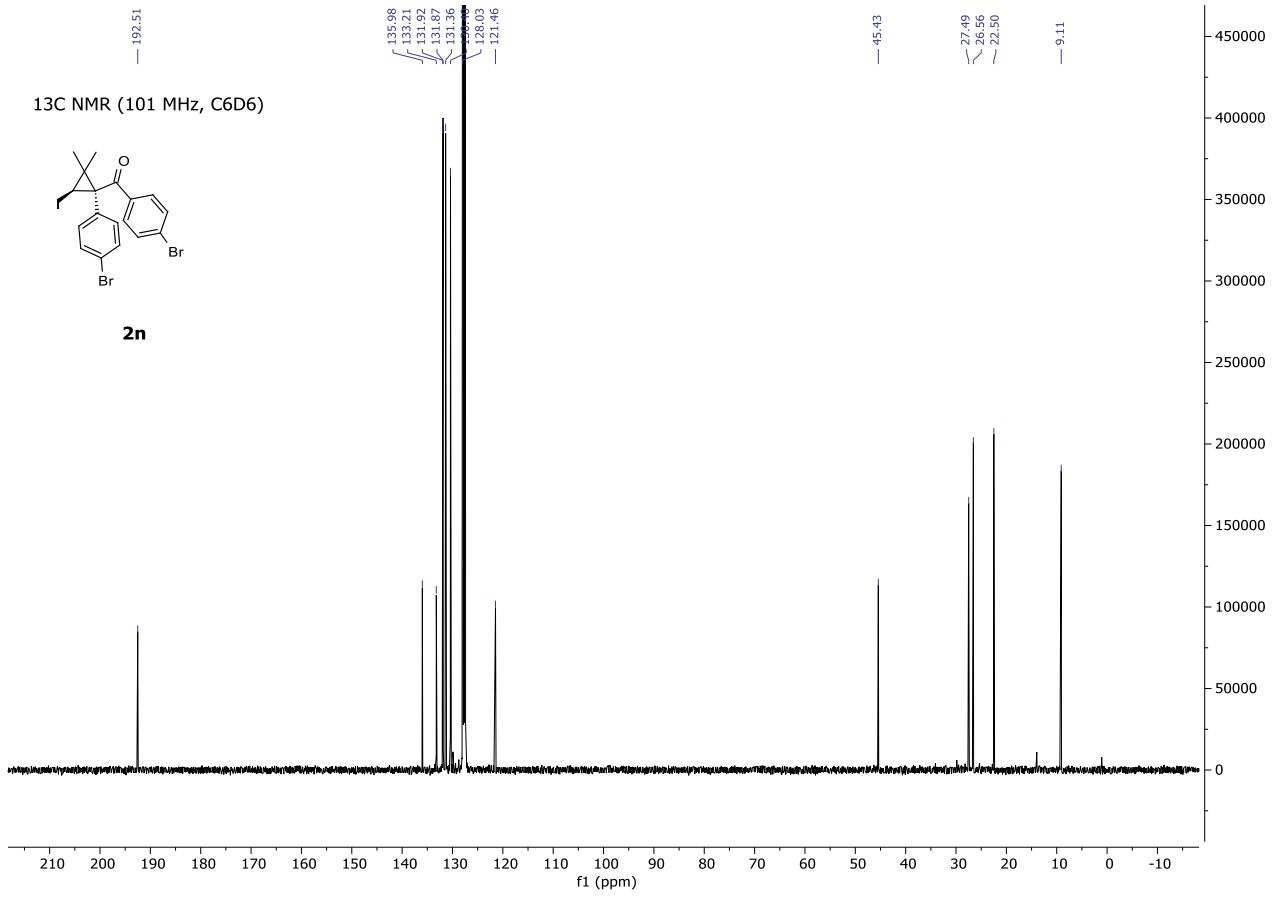

1H NMR (400 MHz, CD2Cl2)
2l
f1 (ppm)

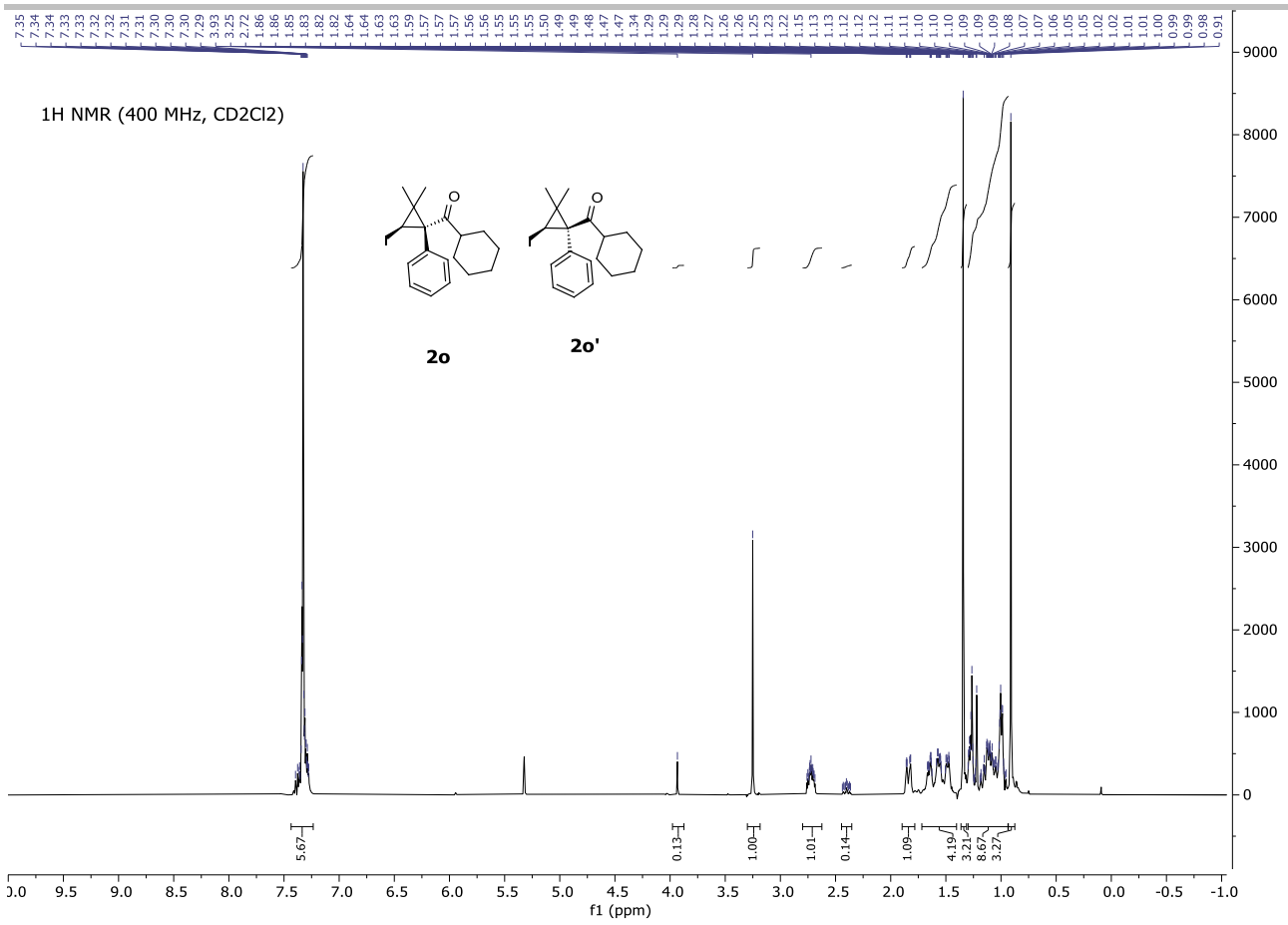

13C NMR (101 MHz, CD2Cl2)
2l
205.97
143.76
128.80
127.26
125.32
63.95
31.77
31.19
27.51
20.15
f1 (ppm)

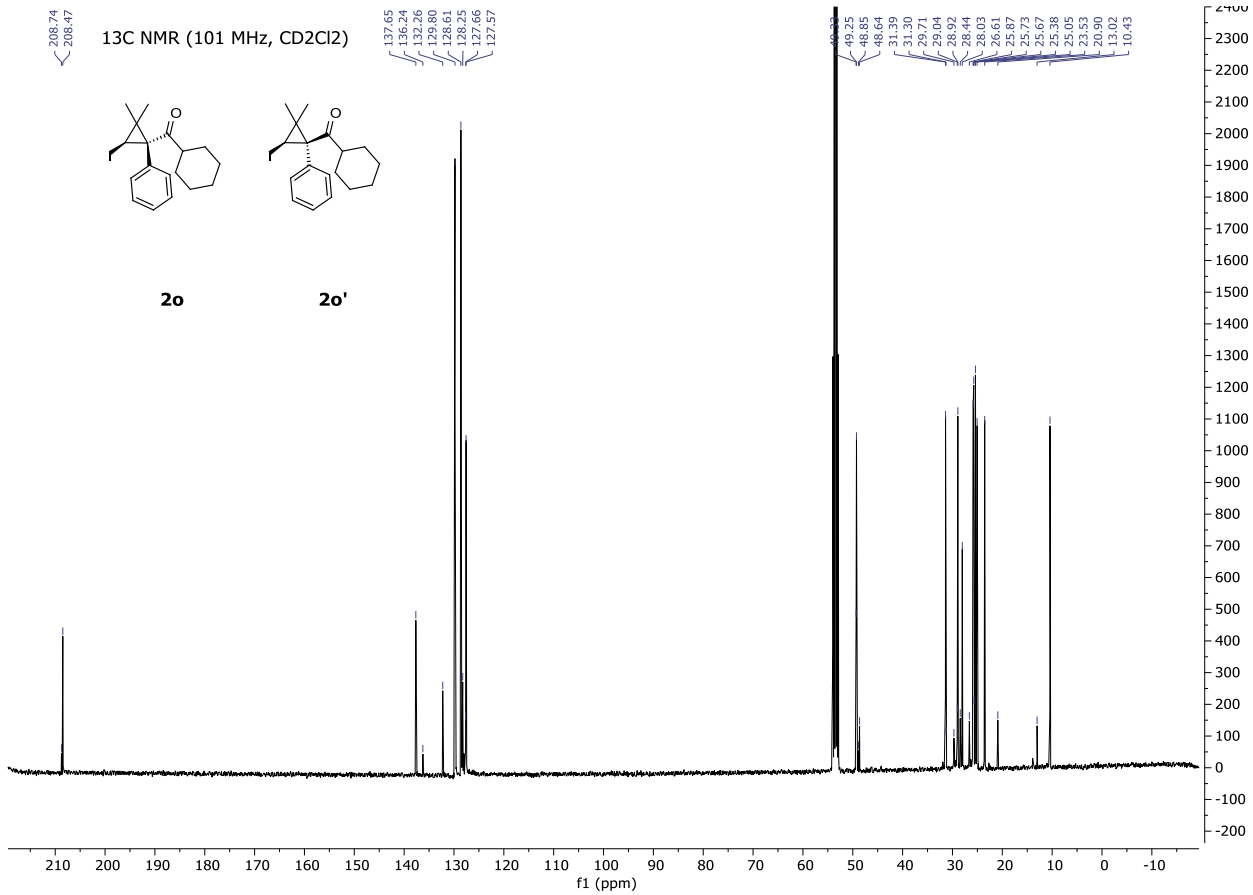

1H NMR (400 MHz, CD2Cl2)
2m
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
2m
f1 (ppm)

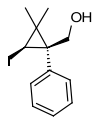

1H NMR (400 MHz, C6D6)
Br
Br
2n
7.75
7.74
7.73
7.72
7.72
7.71
7.70
7.70
7.69
7.68
7.67
7.15
7.13
7.09
7.09
7.08
7.07
6.75
6.74
6.73
3.10
1.49
0.58
1.97
2.06
2.15
2.00
1.01
3.22
3.17
f1 (ppm)


13C NMR (101 MHz, C6D6)
Br
Br
2n
192.51
135.98
133.21
131.92
131.87
131.36
128.03
121.46
45.43
27.49
26.56
22.50
9.11
f1 (ppm)


1H NMR (400 MHz, CD2Cl2)
2o
2o'
f1 (ppm)

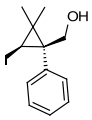

13C NMR (101 MHz, CD2Cl2)
2o
2o'
f1 (ppm)

1H NMR (400 MHz, CD2Cl2)

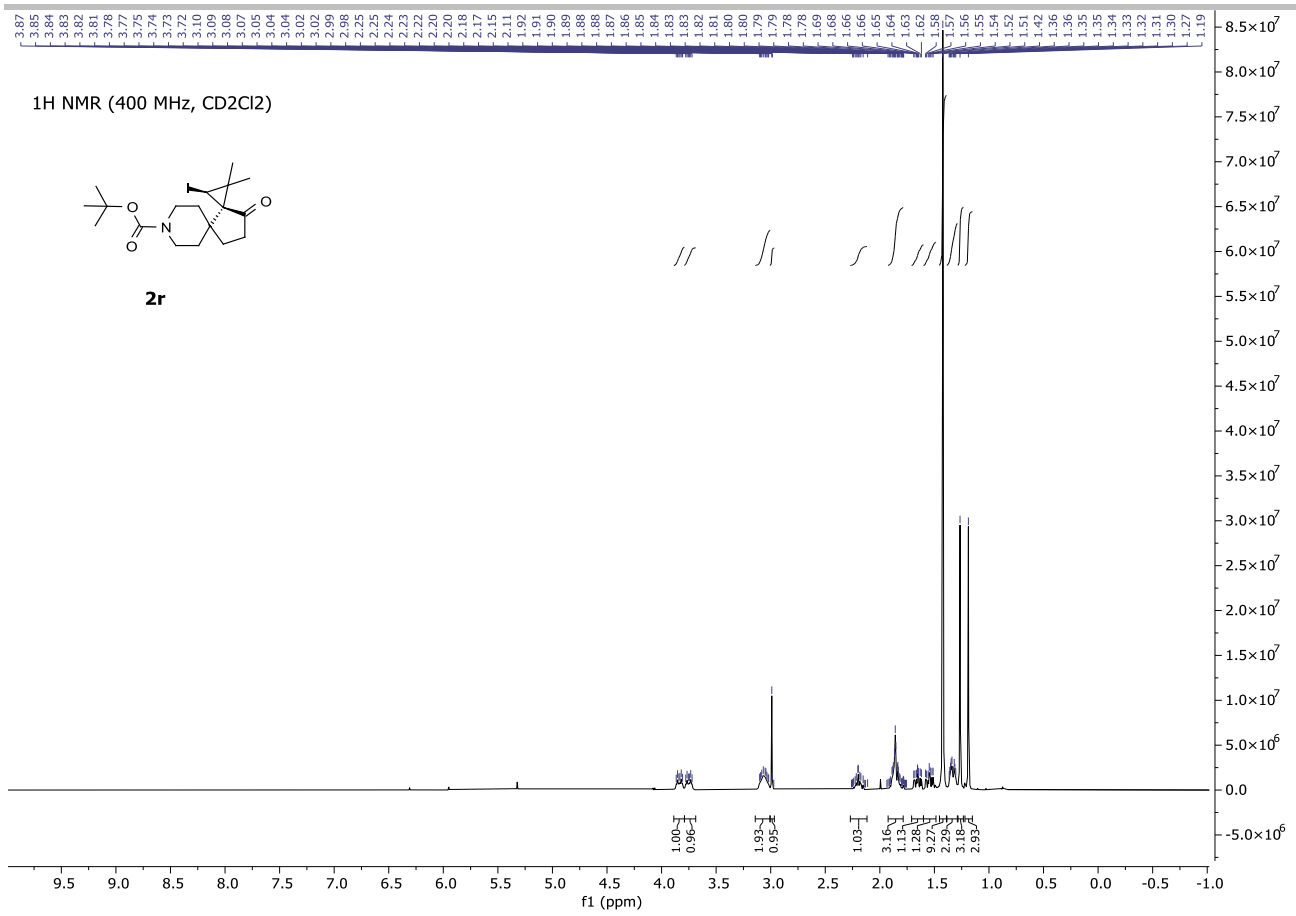


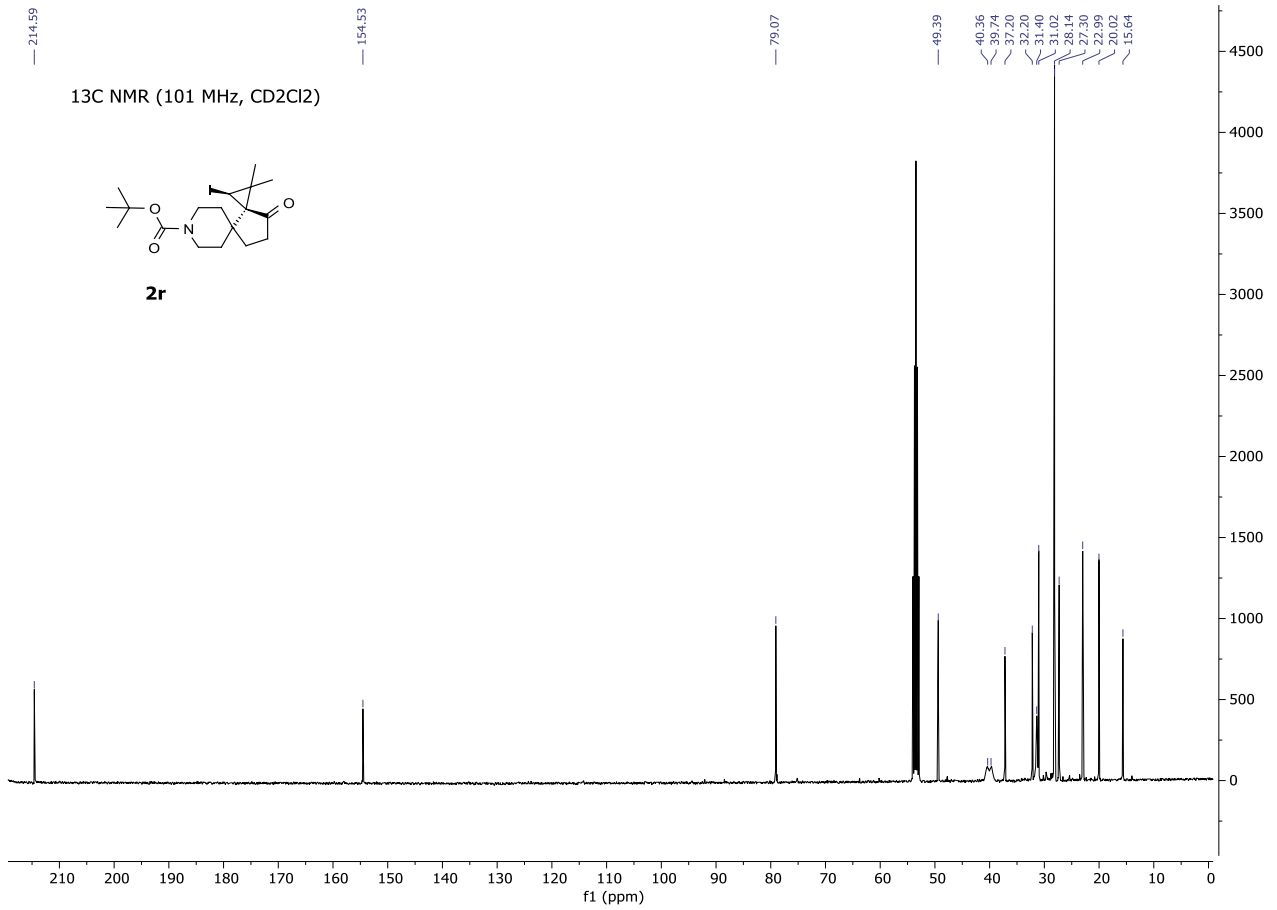
2p

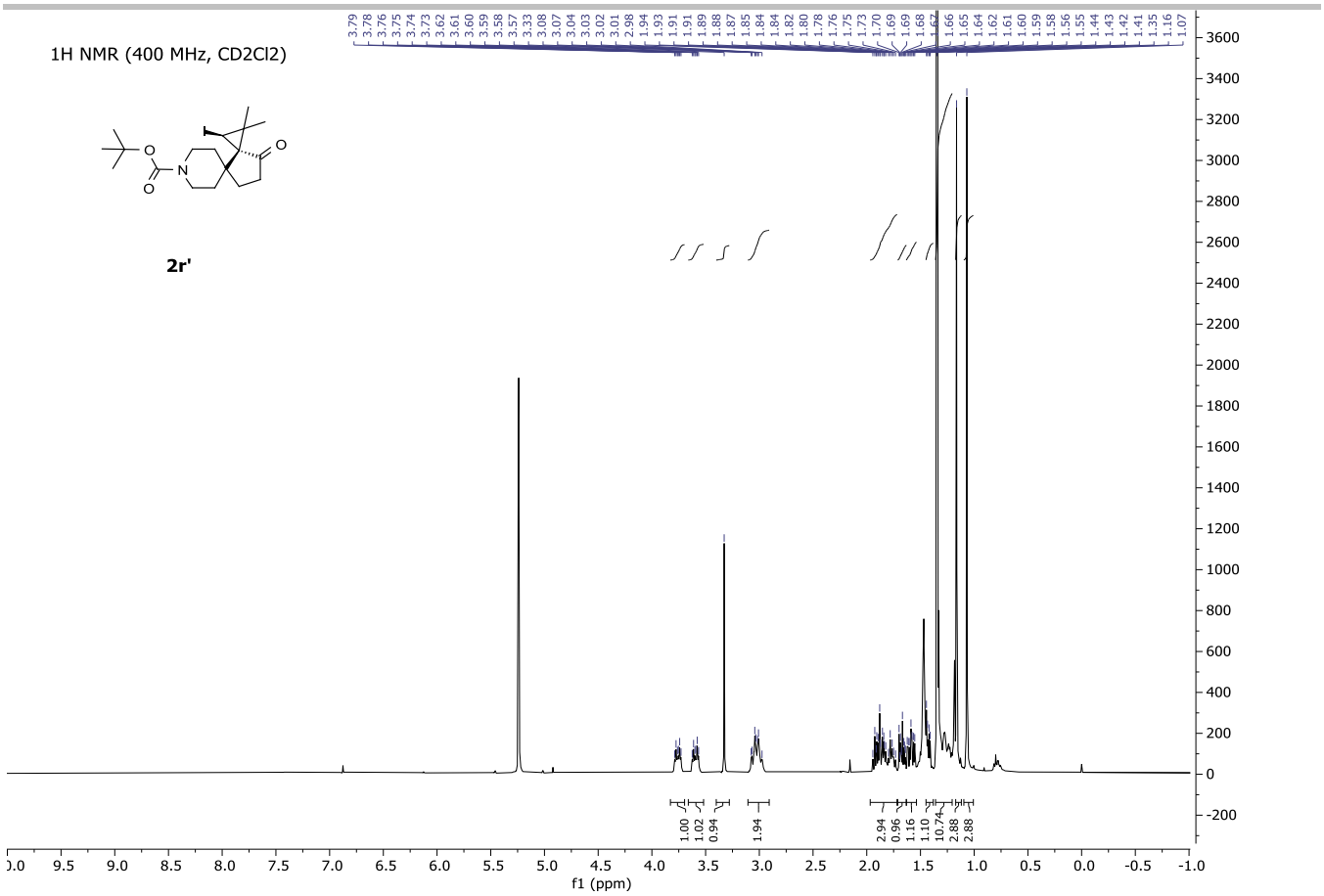
13C NMR (101 MHz, CD2Cl2)

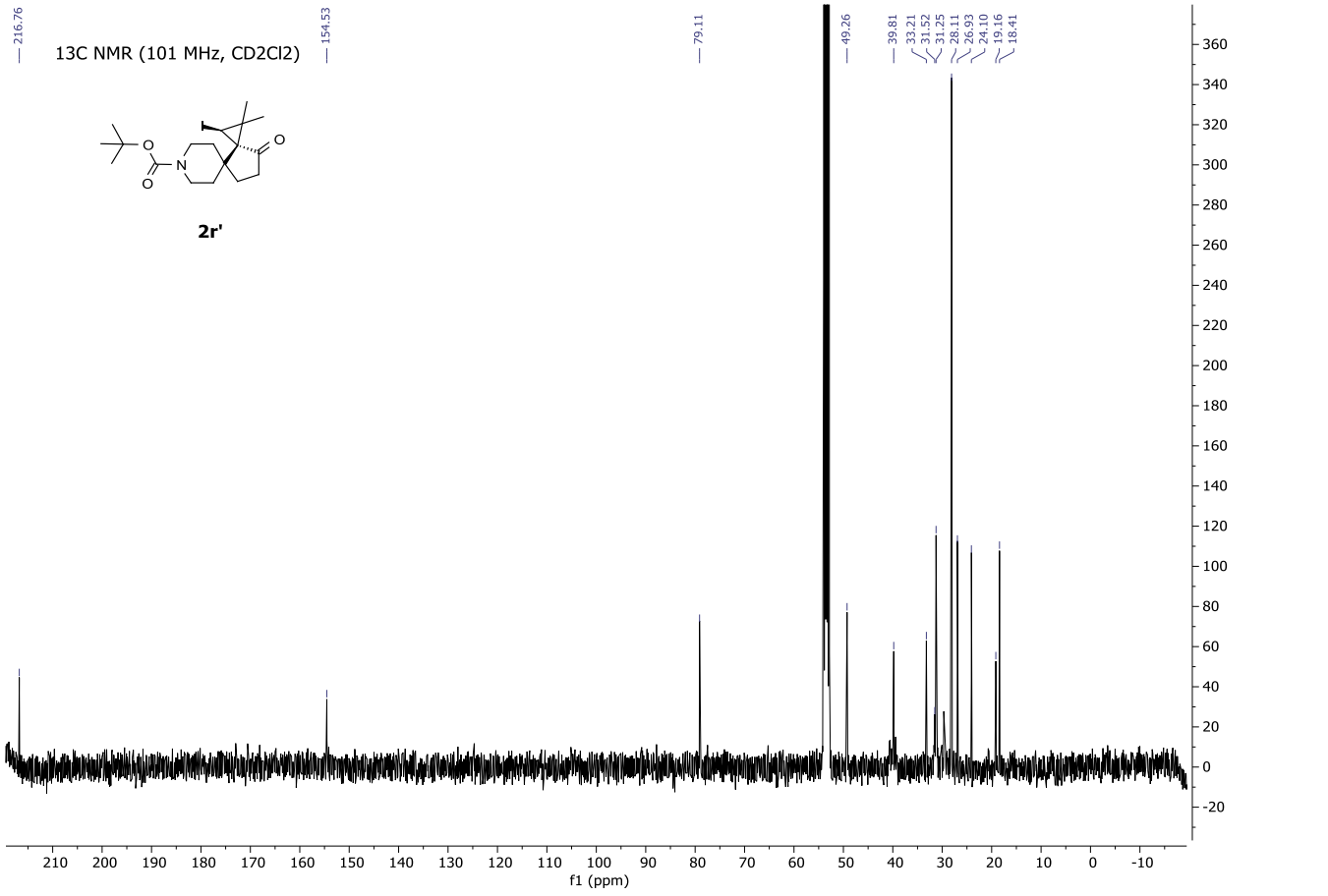


2p

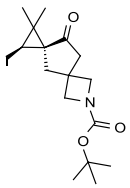

1H NMR (400 MHz, CD2Cl2)
2r
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
2r
f1 (ppm)


1H NMR (400 MHz, CD2Cl2)
2r'
f1 (ppm)

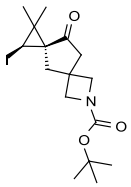

13C NMR (101 MHz, CD2Cl2)
2r'
f1 (ppm)

1H NMR (400 MHz, CD2Cl2)



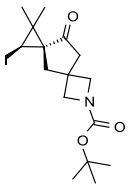
2s

13C NMR (101 MHz, CD2Cl2)



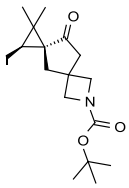
2s

1H NMR (400 MHz, CD2Cl2)



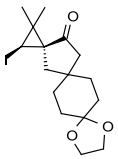
2s'

13C NMR (101 MHz, CD2Cl2)



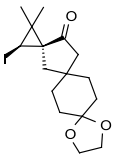
2s'

1H NMR (400 MHz, CDCl3)



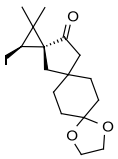
2t

13C NMR (101 MHz, CD2Cl2)



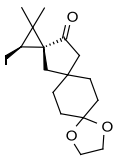
2t

1H NMR (400 MHz, CD2Cl2)

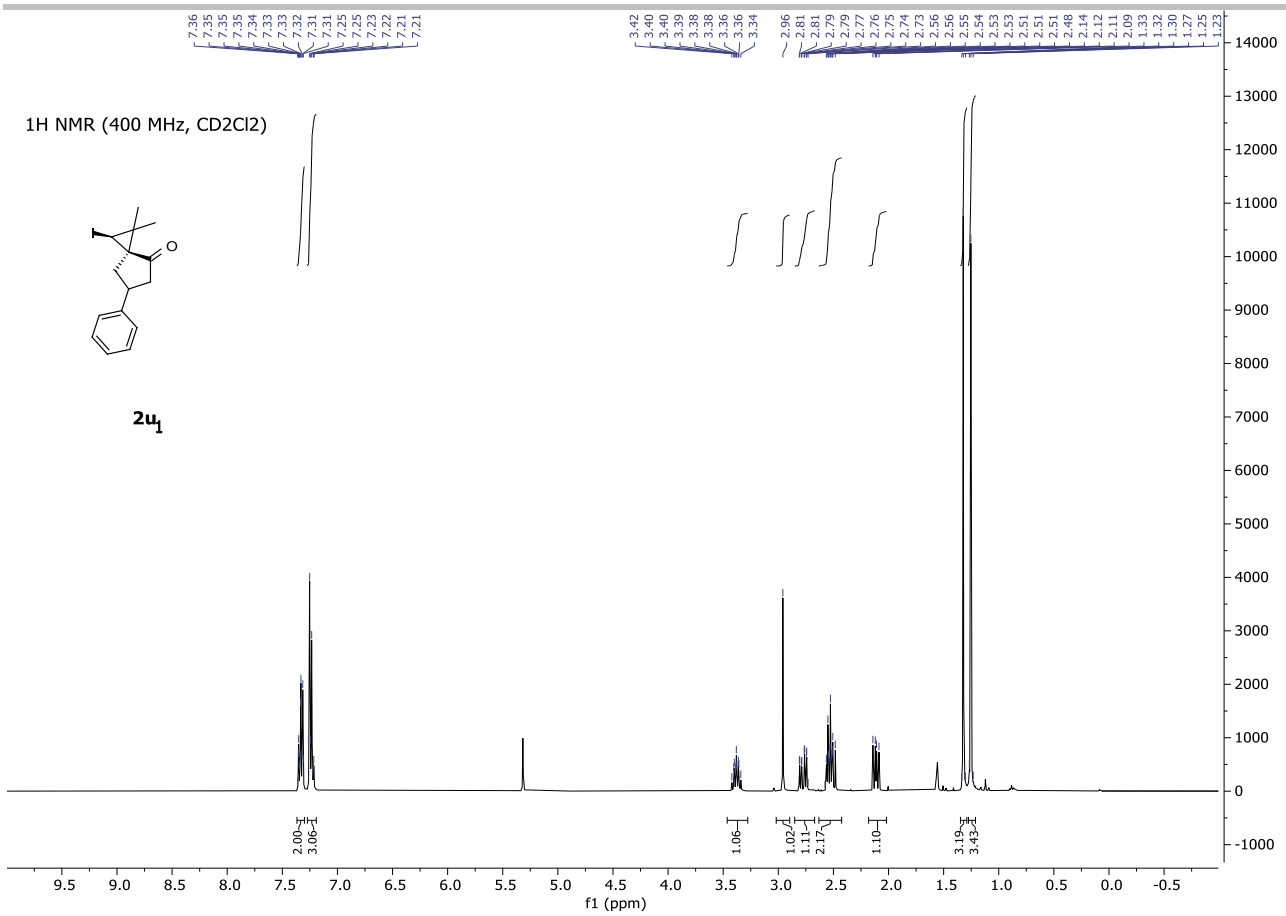


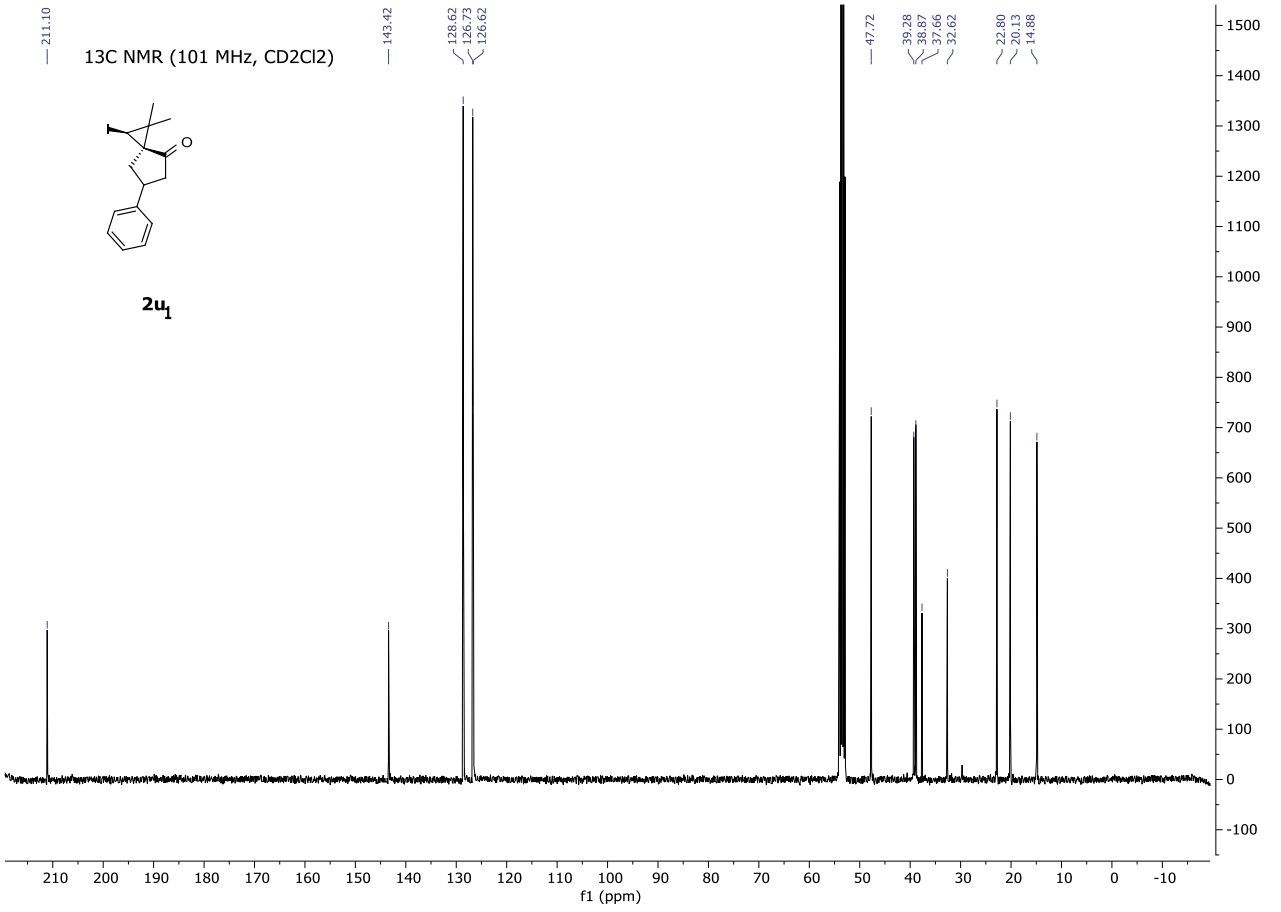
2t'

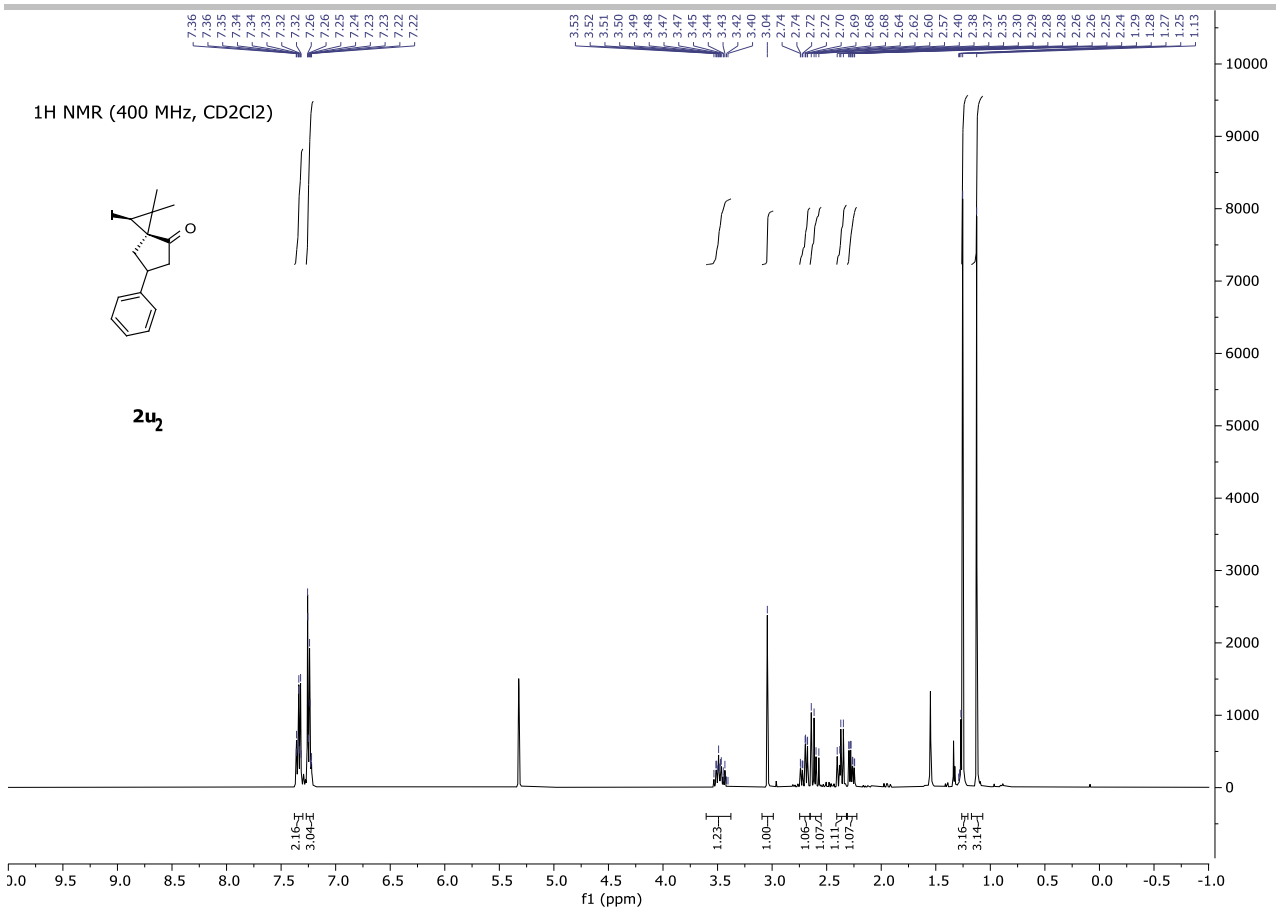
13C NMR (101 MHz, CD2Cl2)



2t'


1H NMR (400 MHz, CD2Cl2)
2u1
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
2u1
f1 (ppm)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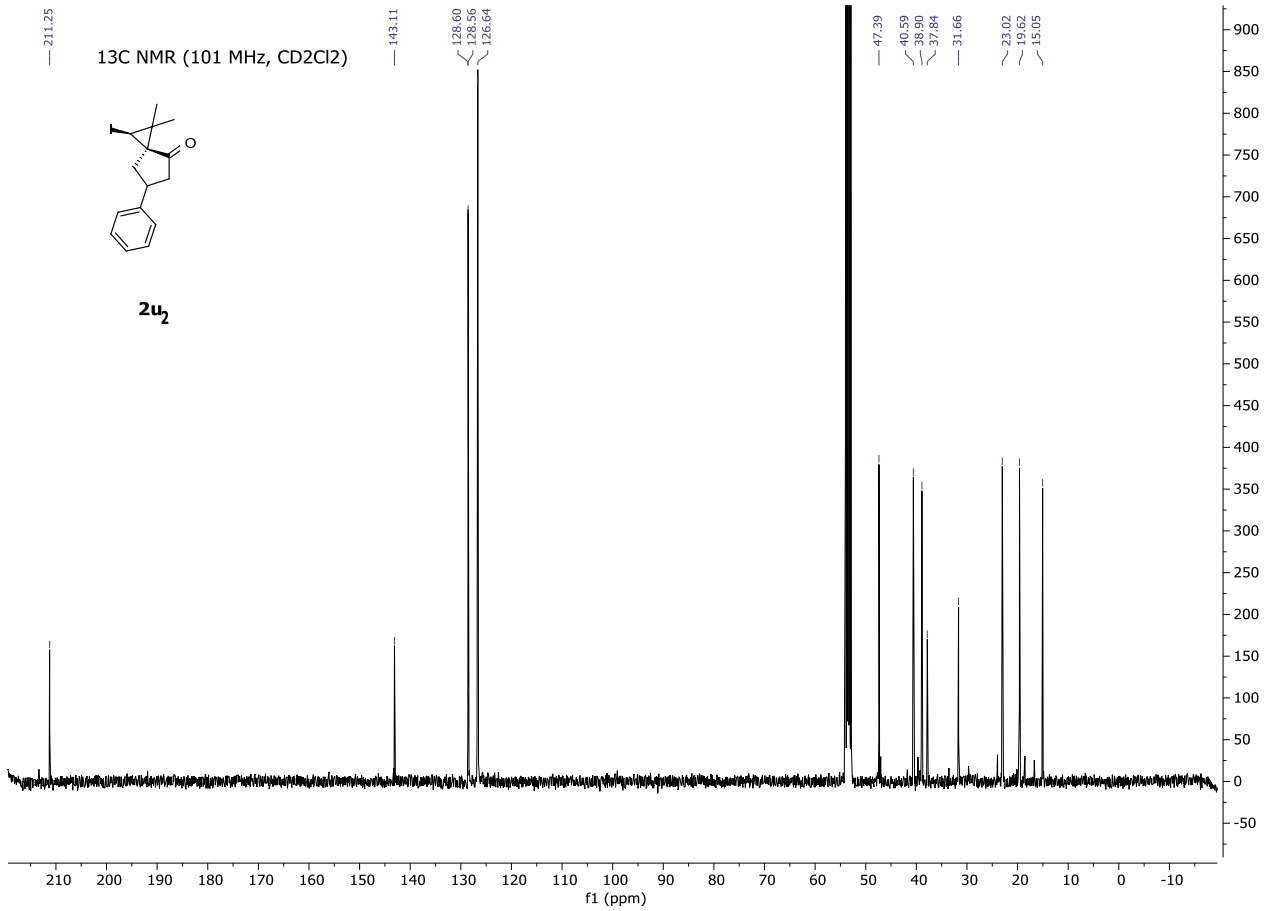
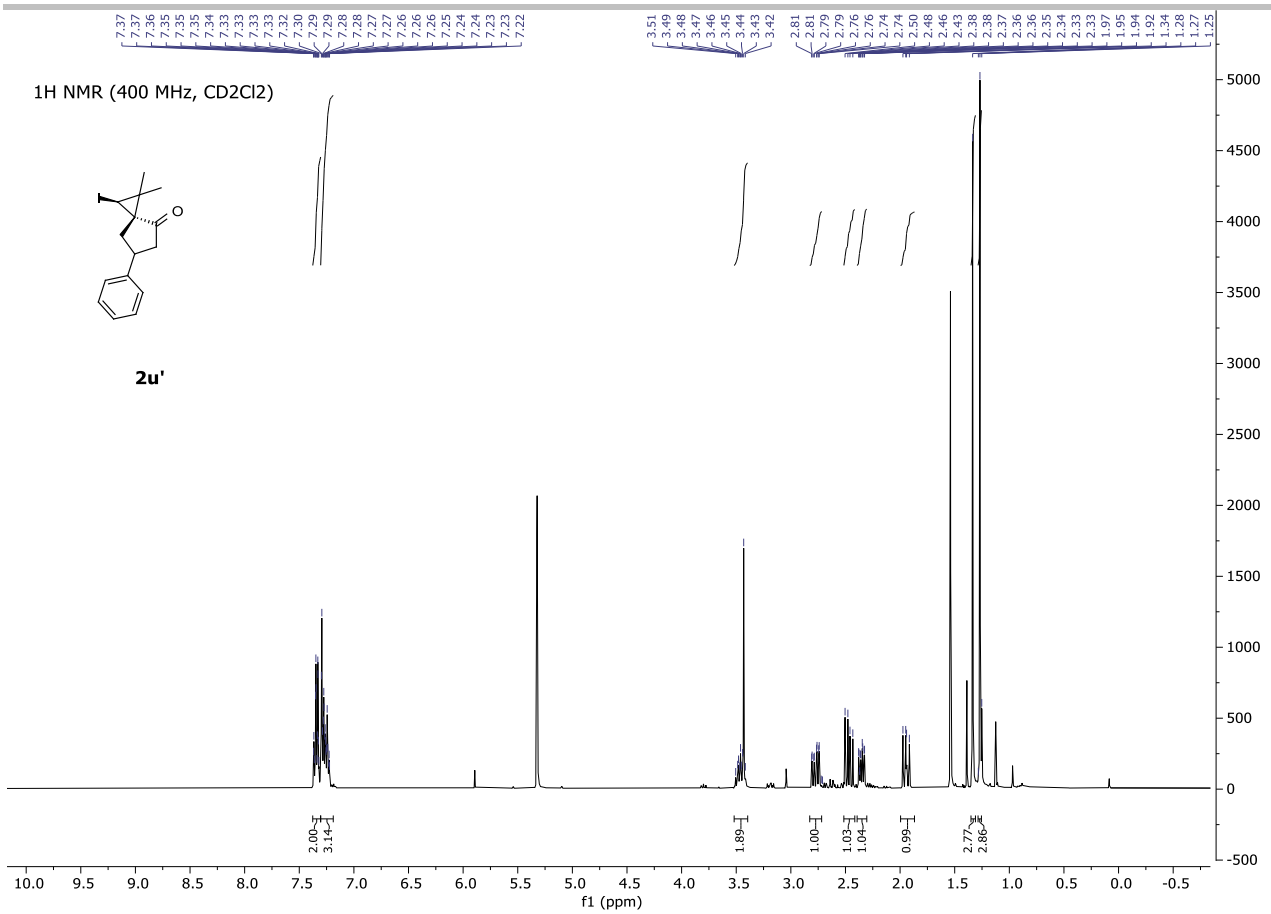
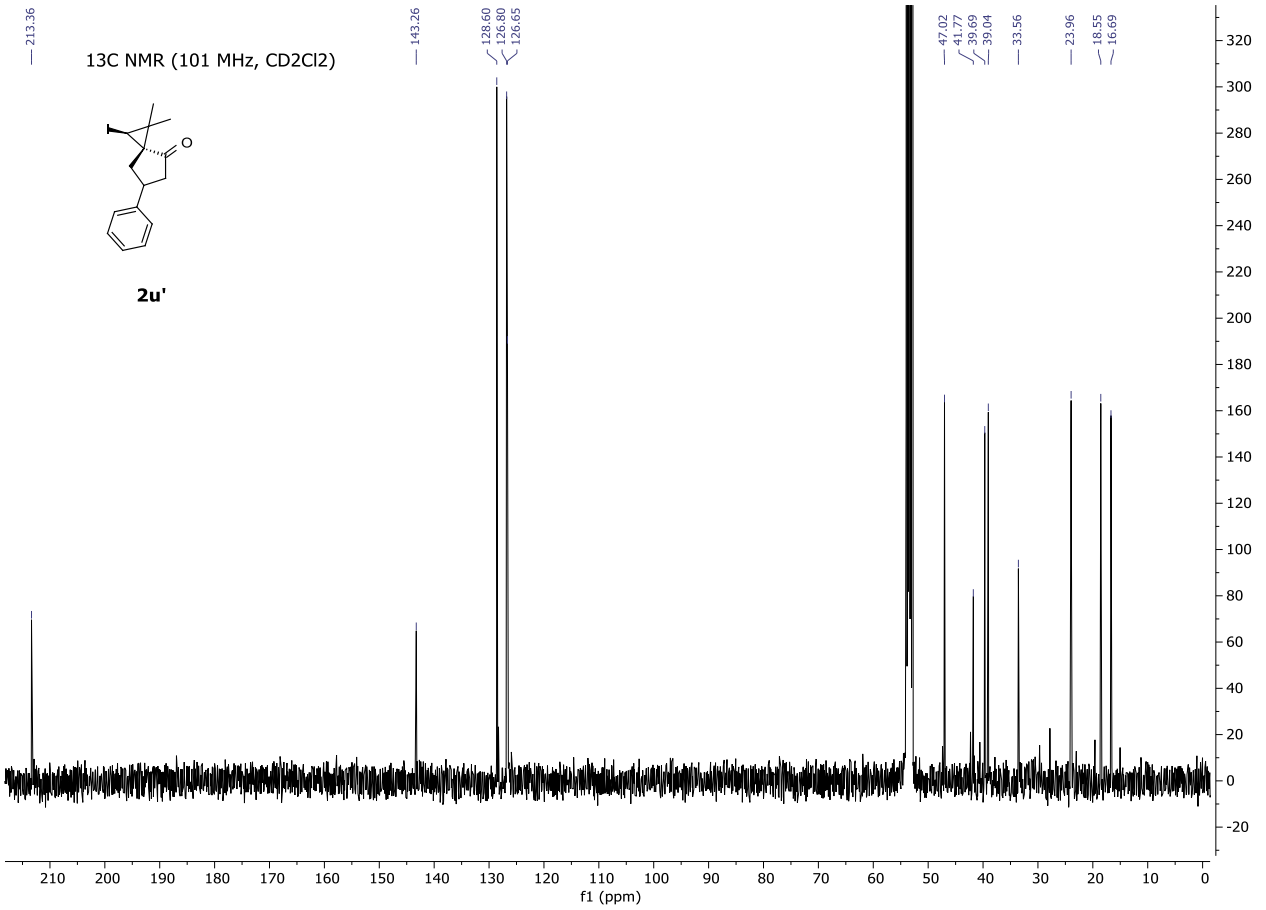
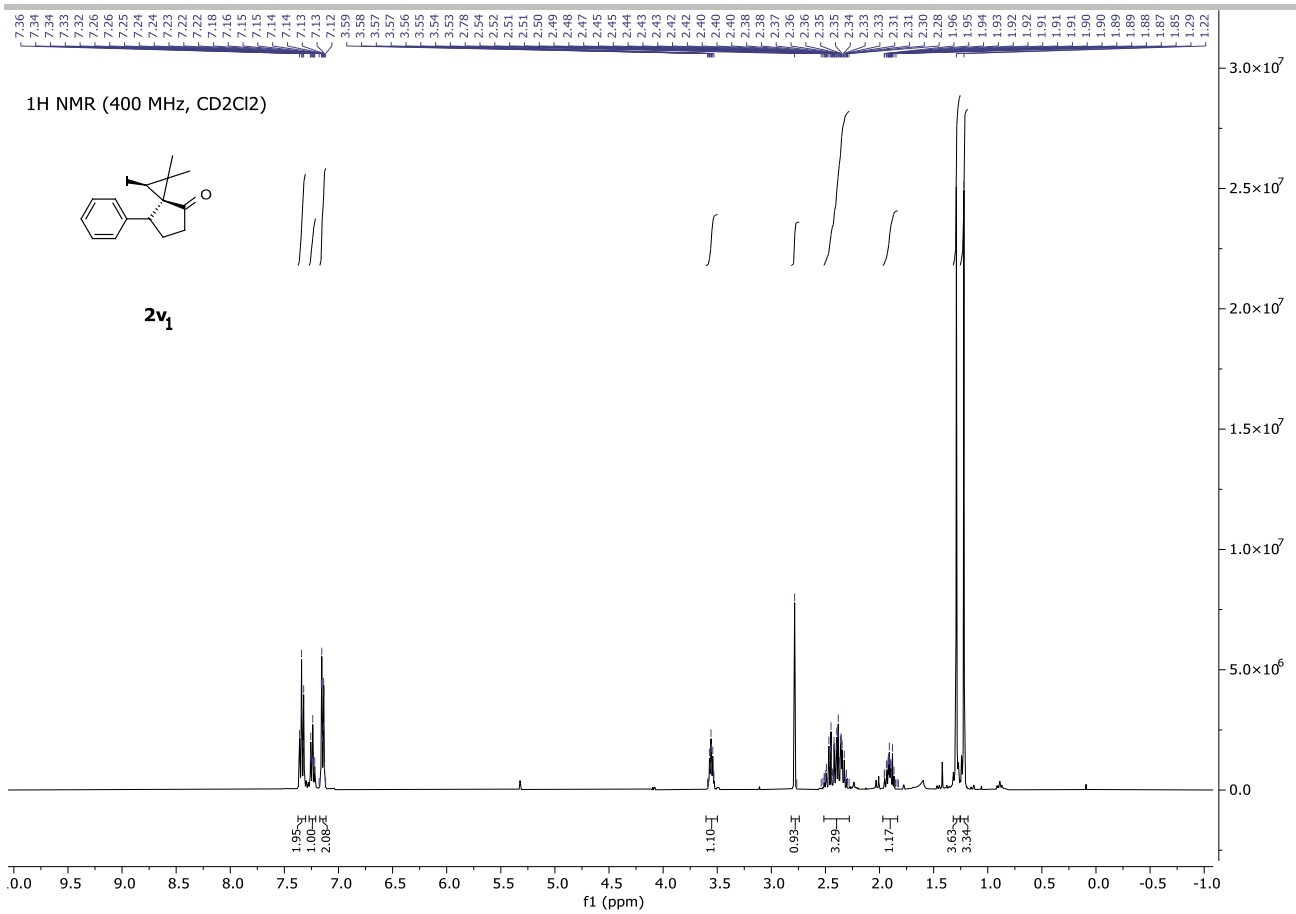
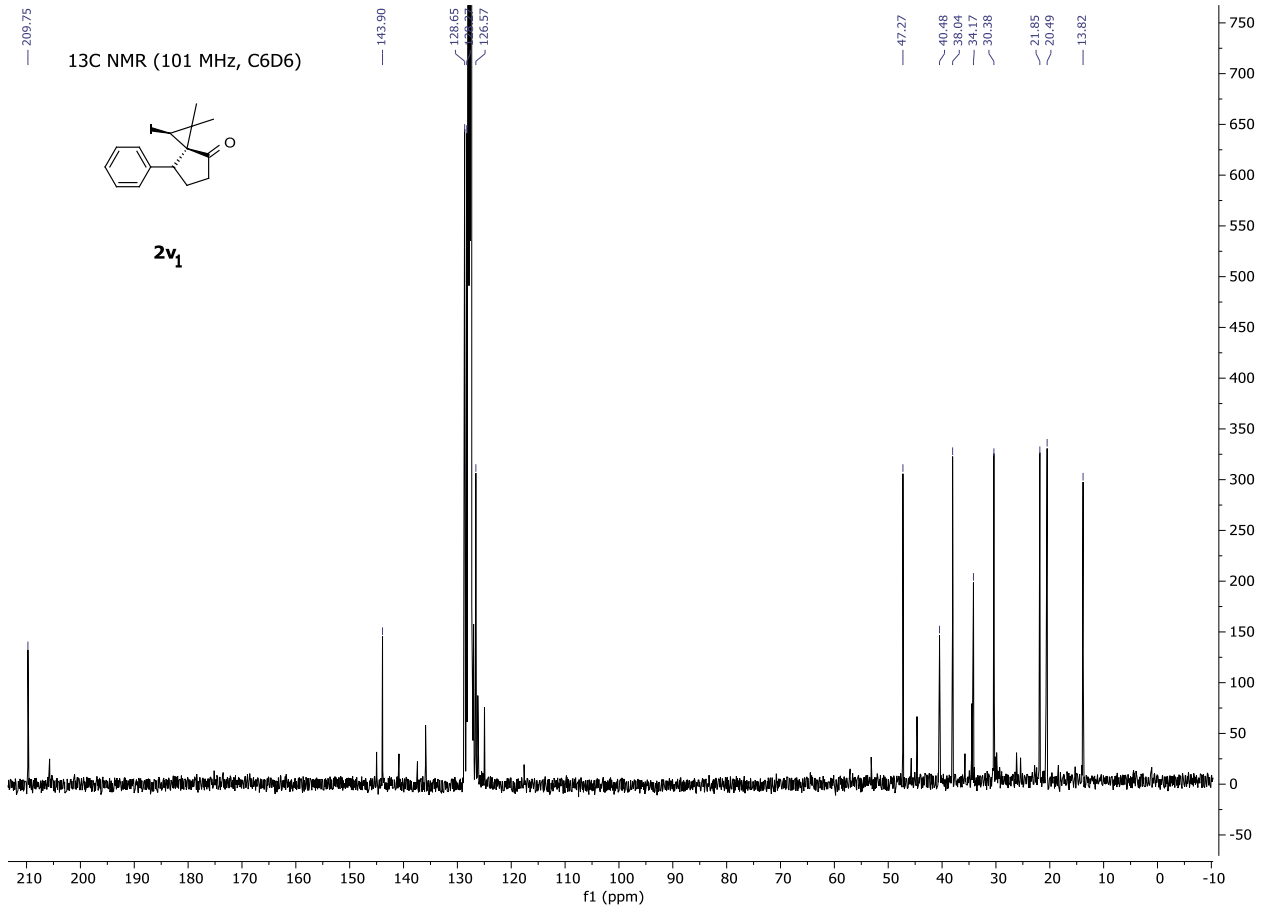
2u2
f1 (ppm)

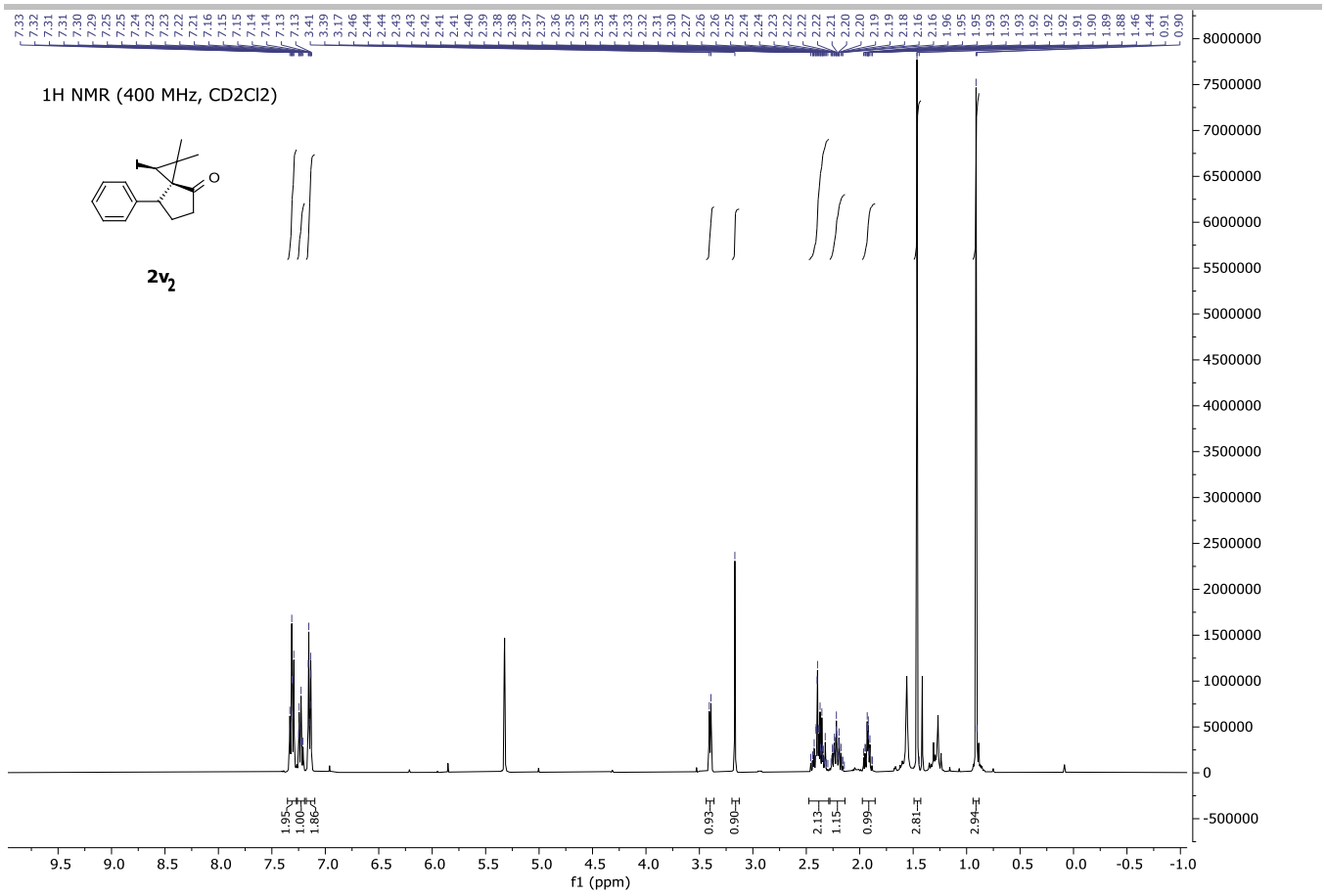

13C NMR (101 MHz, CD2Cl2)
2u2
f1 (ppm)

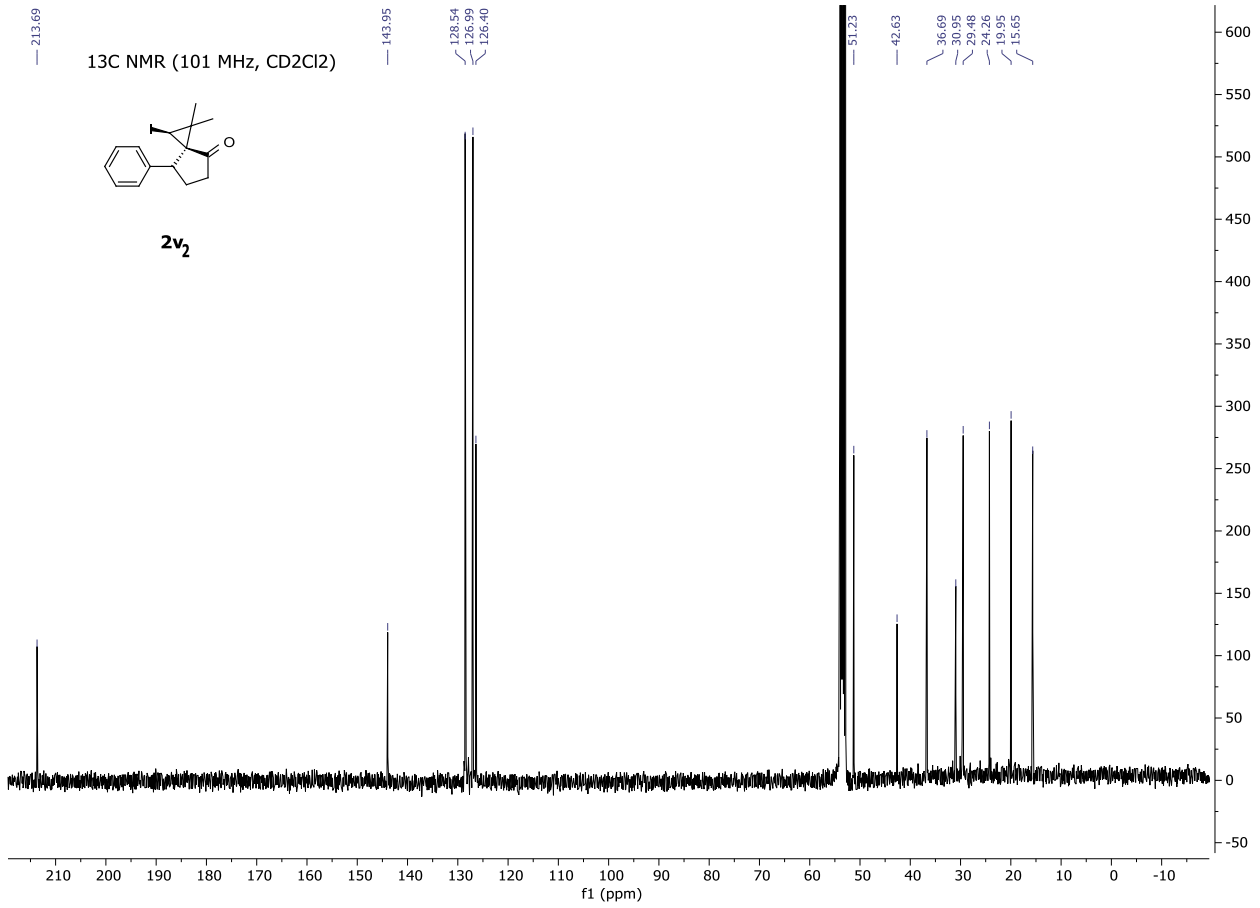

1H NMR (400 MHz, CD2Cl2)
2u'
f1 (ppm)

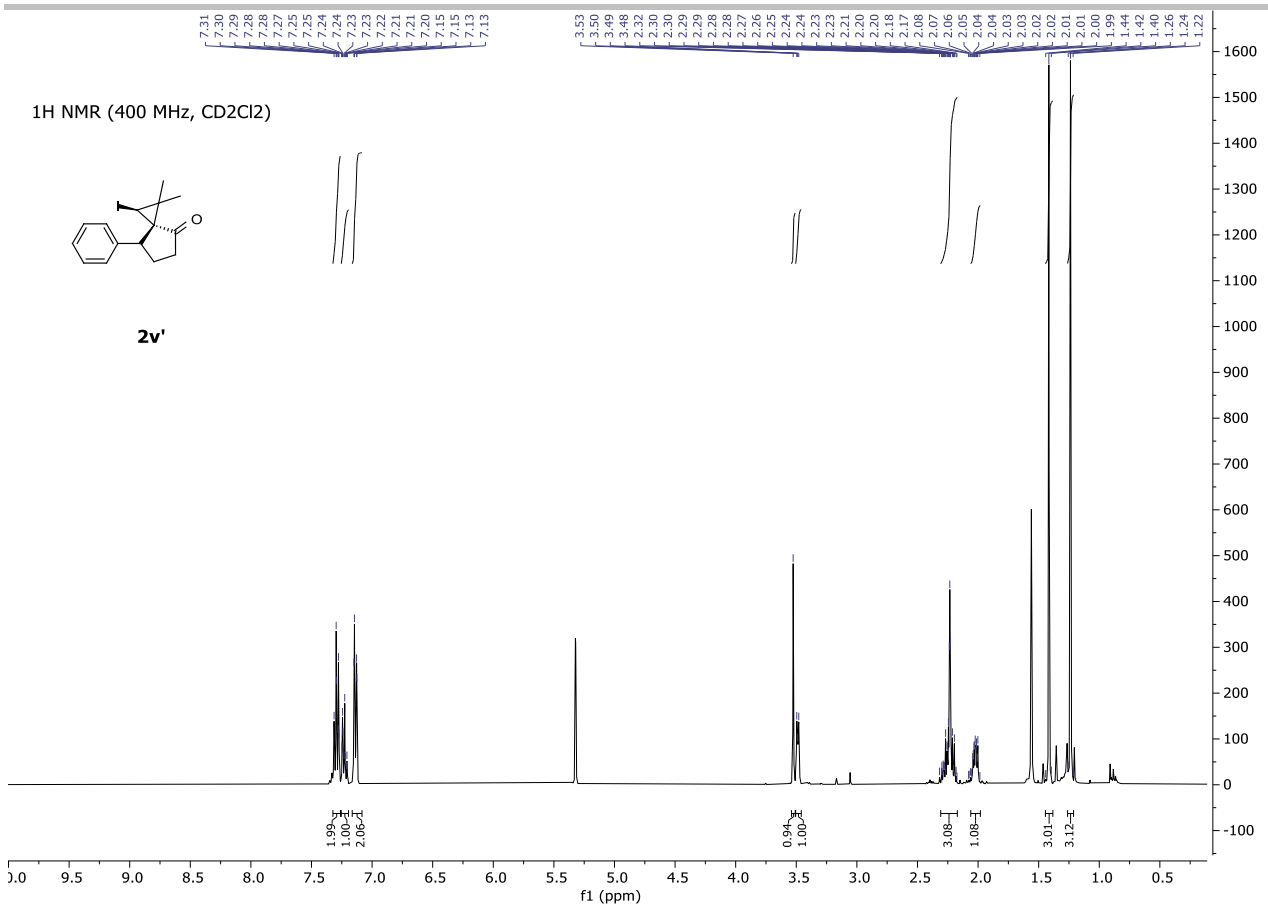

13C NMR (101 MHz, CD2Cl2)
2u'
f1 (ppm)

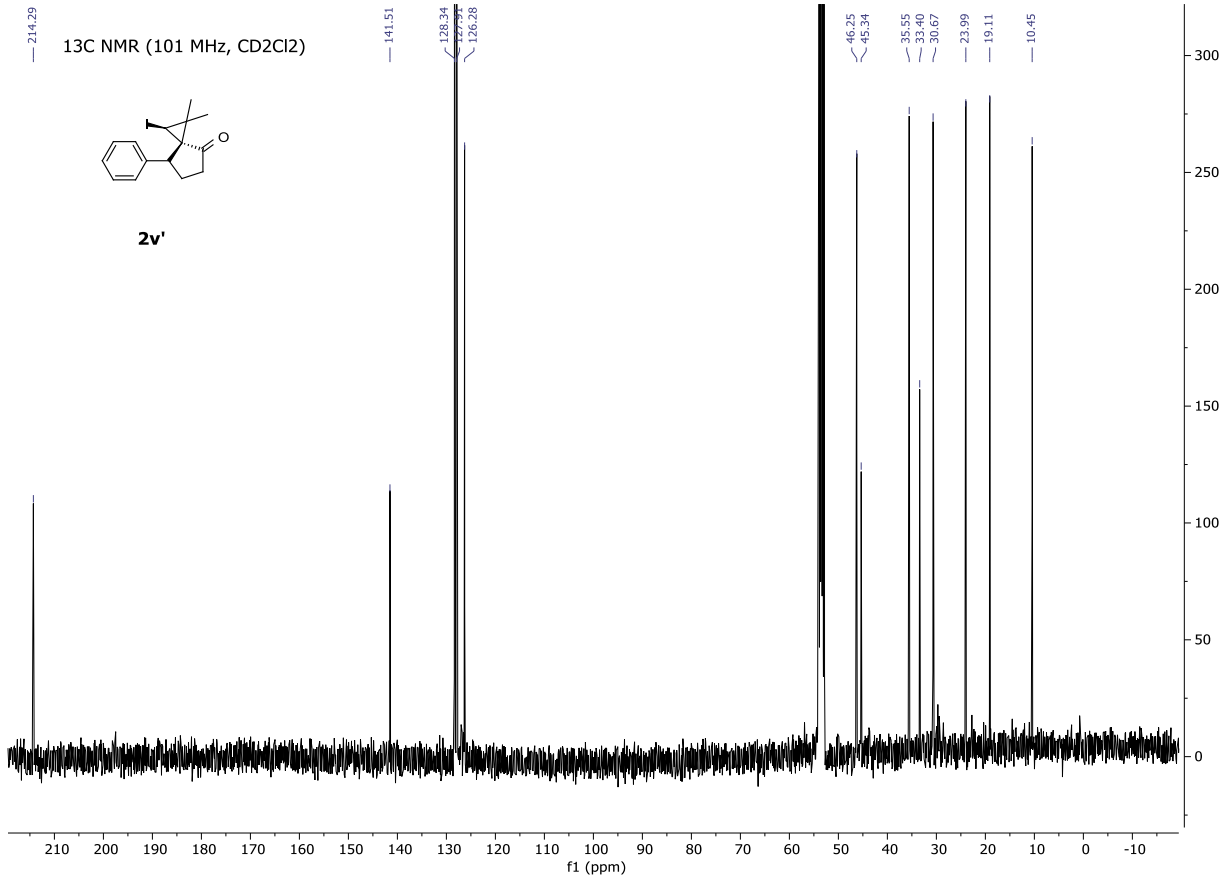

1H NMR (400 MHz, CD2Cl2)
O
2v1
f1 (ppm)

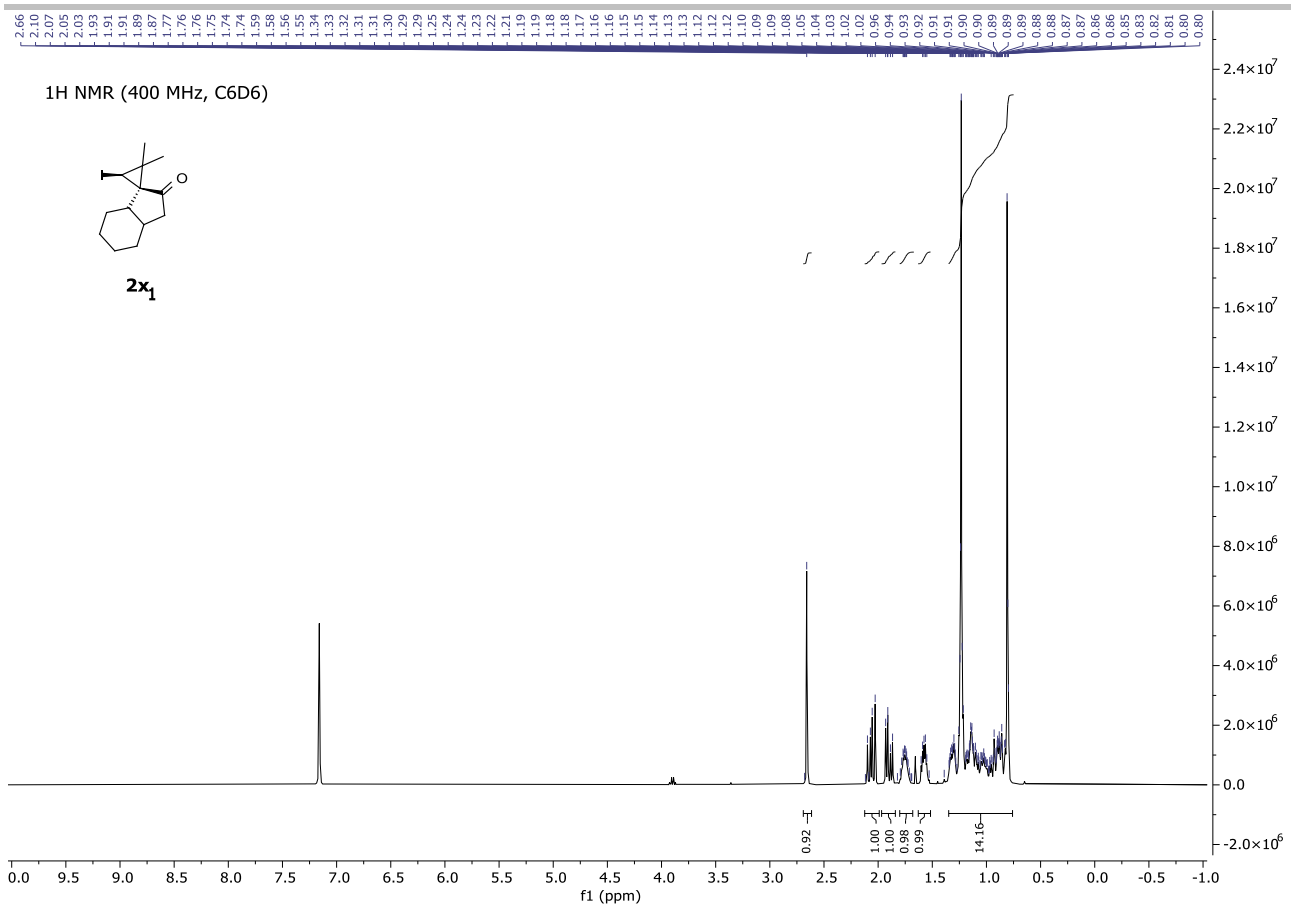

13C NMR (101 MHz, C6D6)
O
2v1
f1 (ppm)

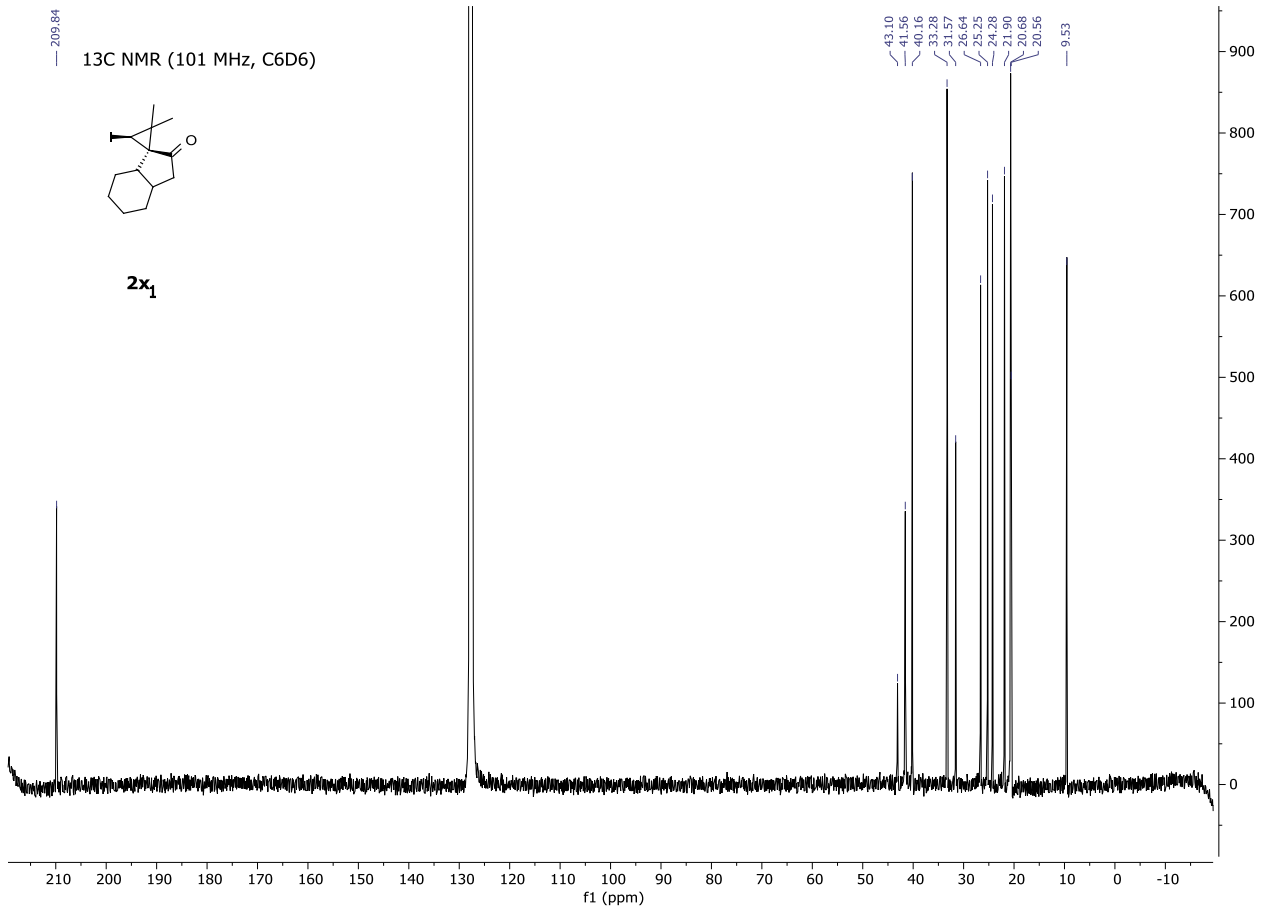

1H NMR (400 MHz, CD2Cl2)
O
2v2
f1 (ppm)

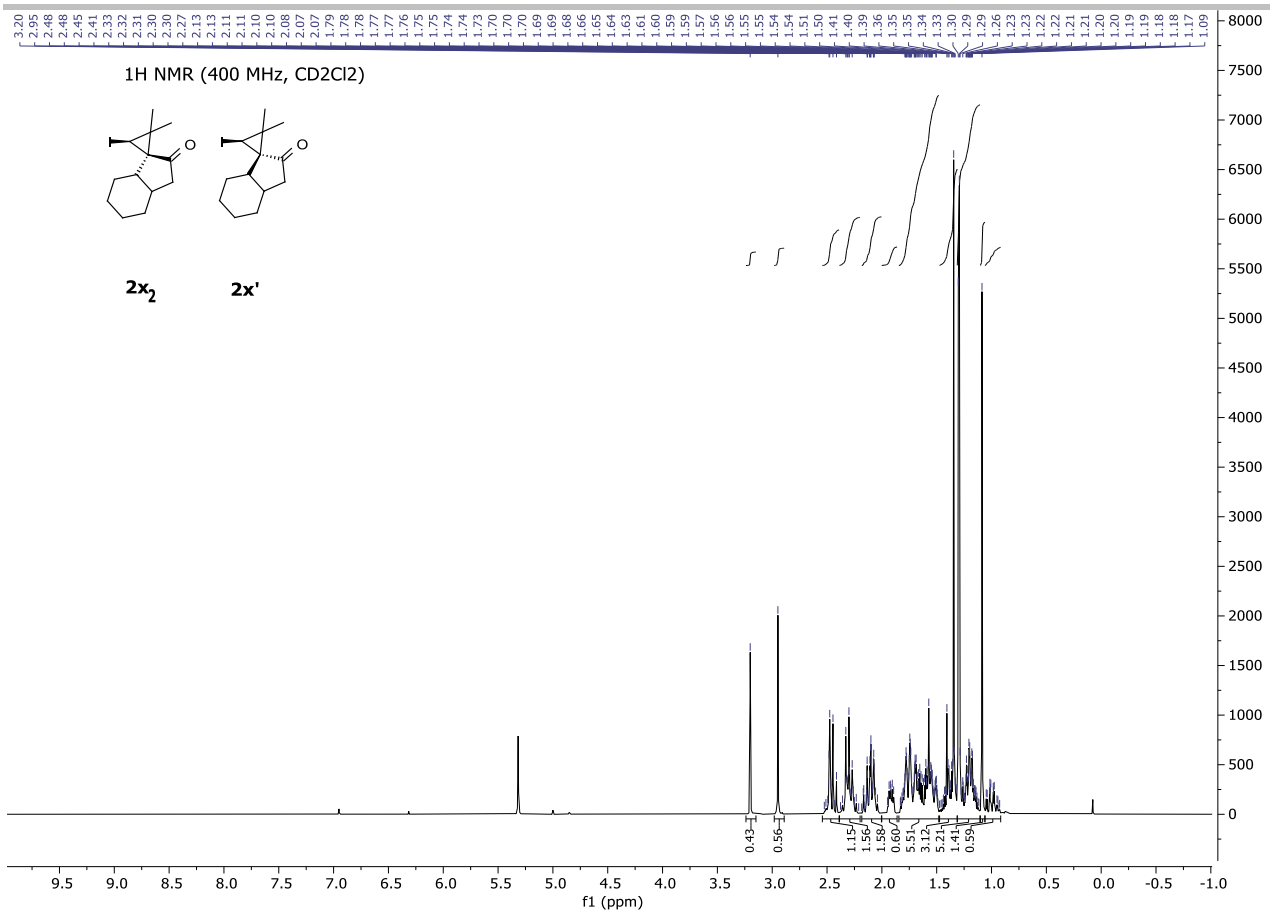

213.69
143.95
128.54
126.99
126.40
51.23
42.63
36.69
30.95
29.48
24.26
19.95
15.65
13C NMR (101 MHz, CD2Cl2)
O
2v2
f1 (ppm)

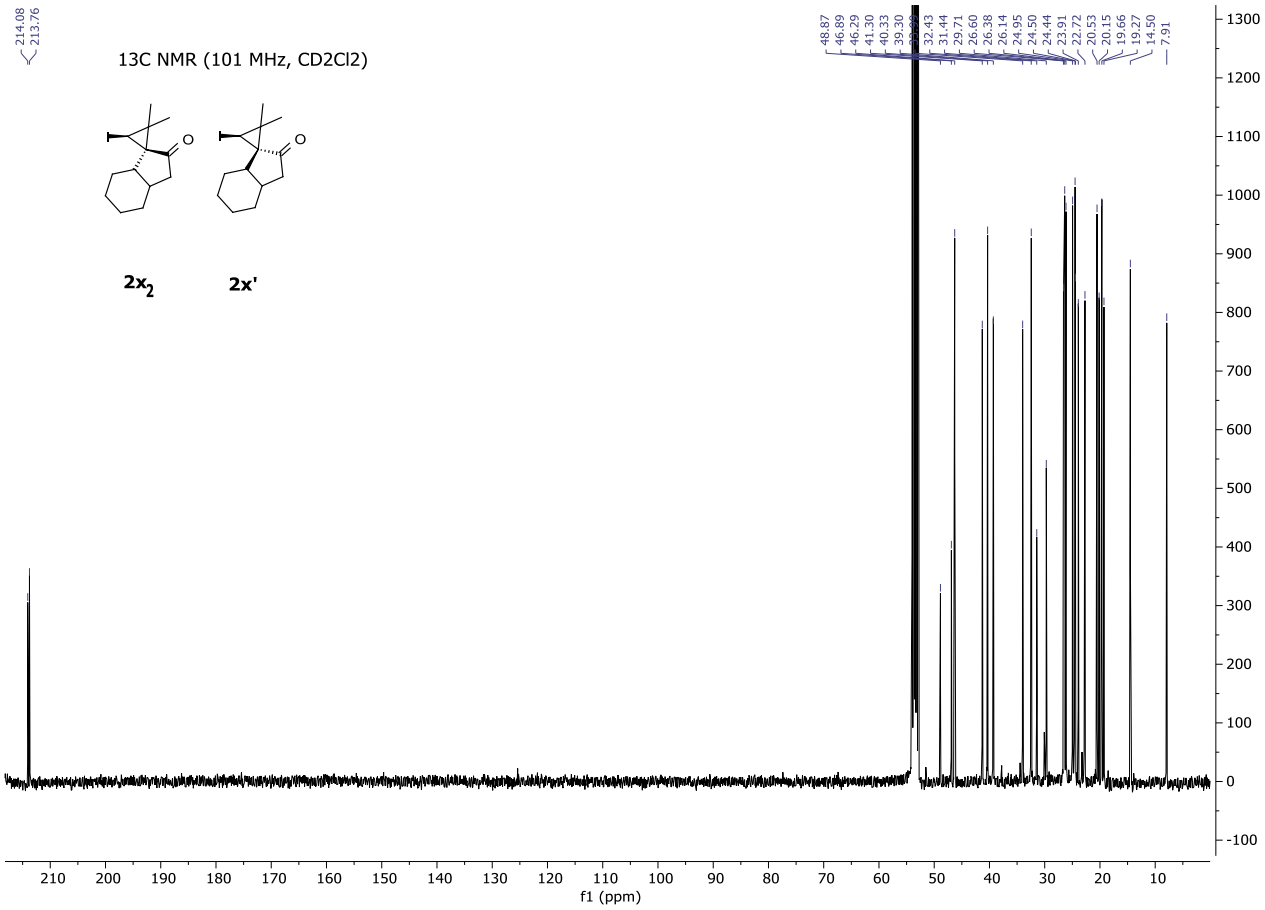

1H NMR (400 MHz, CD2Cl2)
2v'
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
2v'
f1 (ppm)


1H NMR (400 MHz, C6D6)
O
2x1
f1 (ppm)


209.84
13C NMR (101 MHz, C6D6)
O
2x1
43.10
41.56
40.16
33.28
31.57
26.64
25.25
24.28
21.90
20.68
20.56
9.53
f1 (ppm)


1H NMR (400 MHz, CD2Cl2)
2x2
2x'
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
2x2
2x'
f1 (ppm)

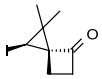
1H NMR (400 MHz, CD2Cl2)

2y

13C NMR (101 MHz, CD2Cl2)

2y

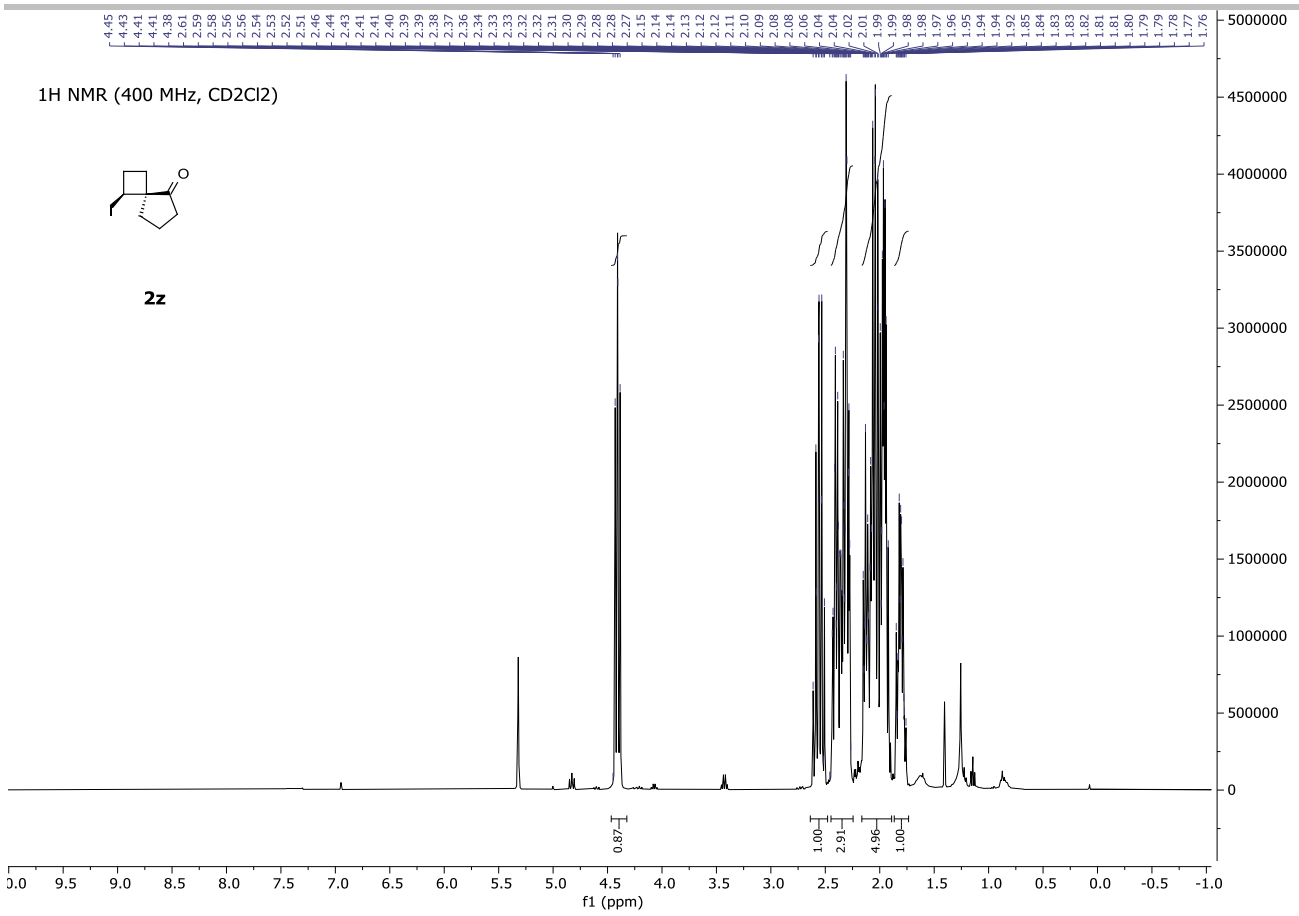
1H NMR (400 MHz, CD2Cl2)

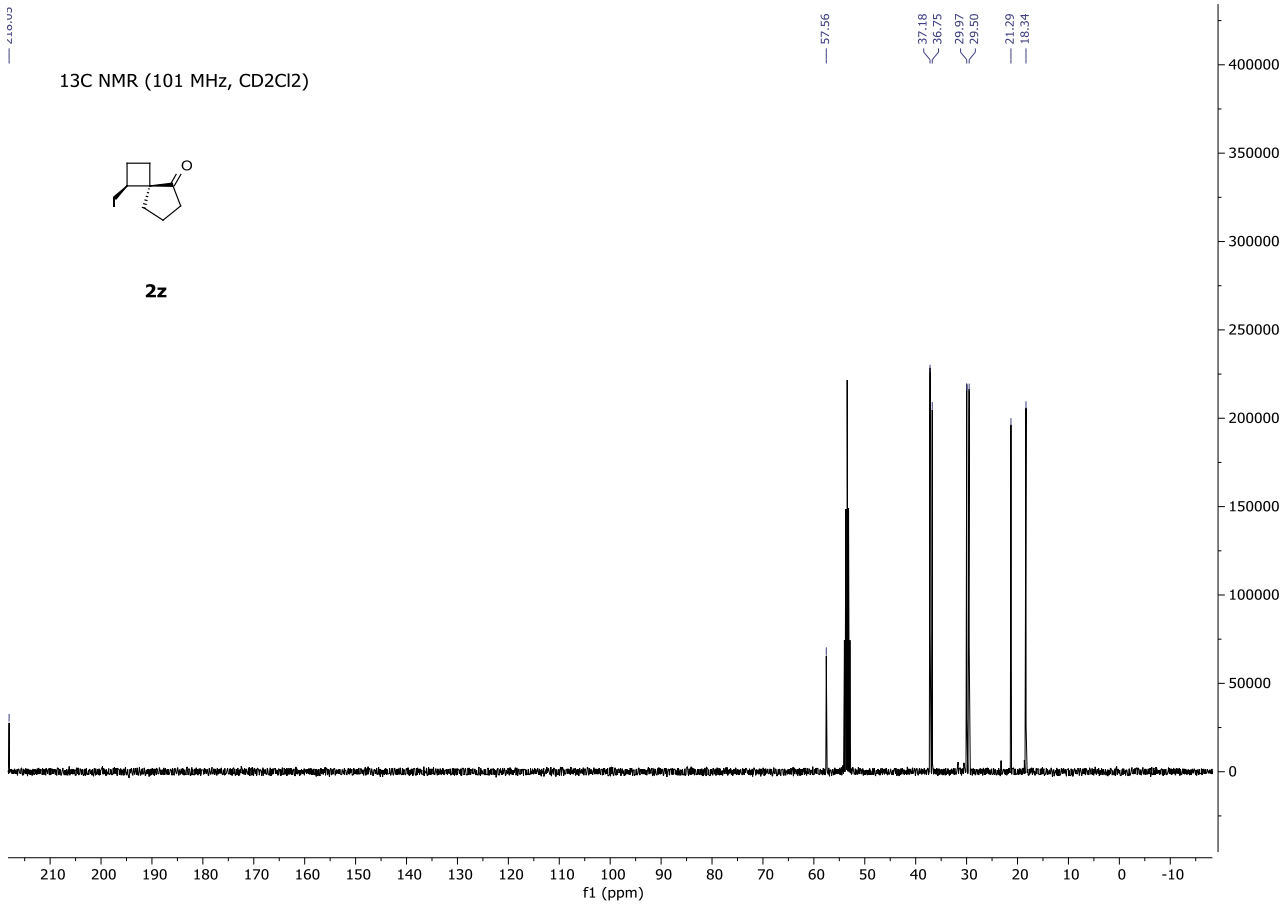


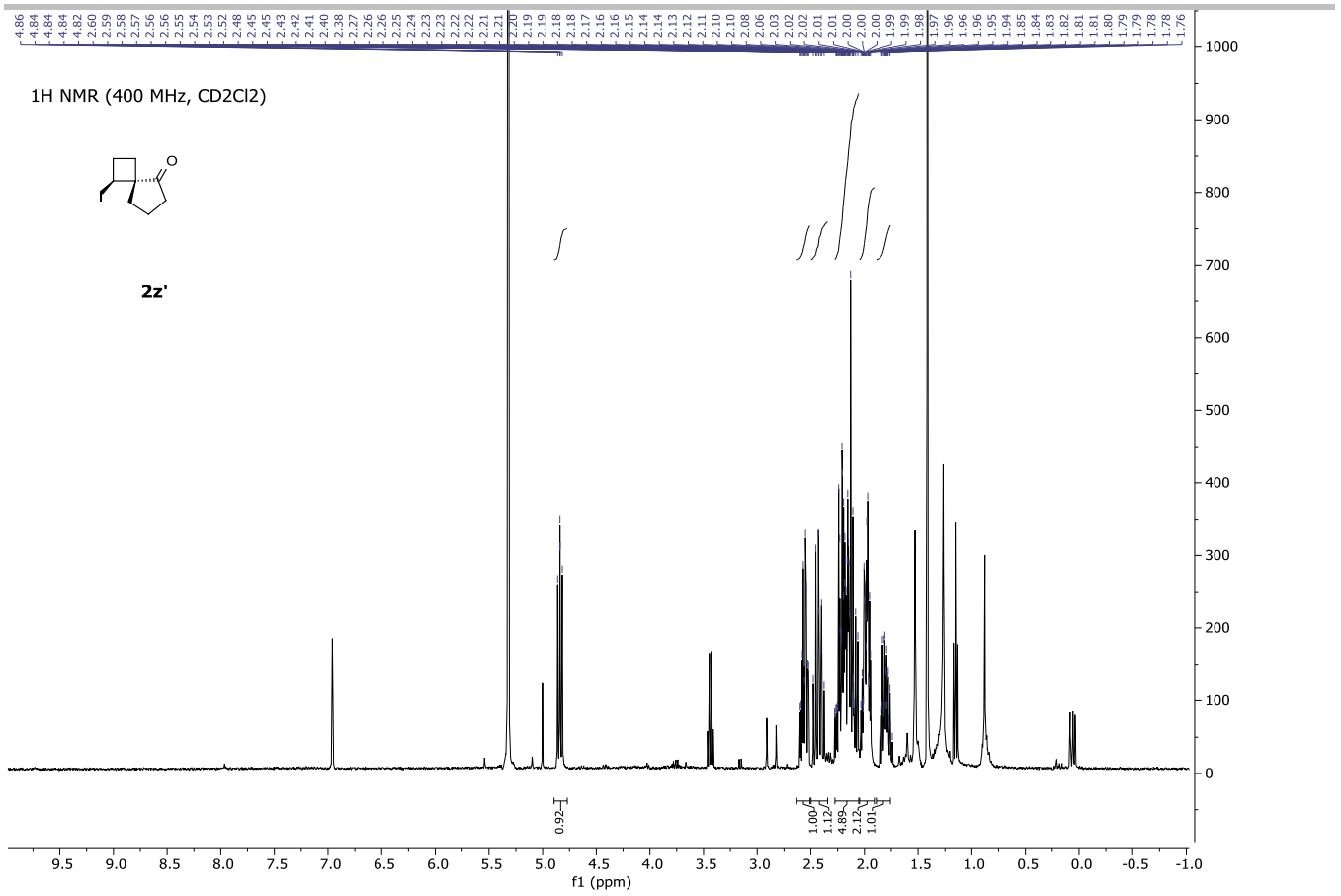
2y'

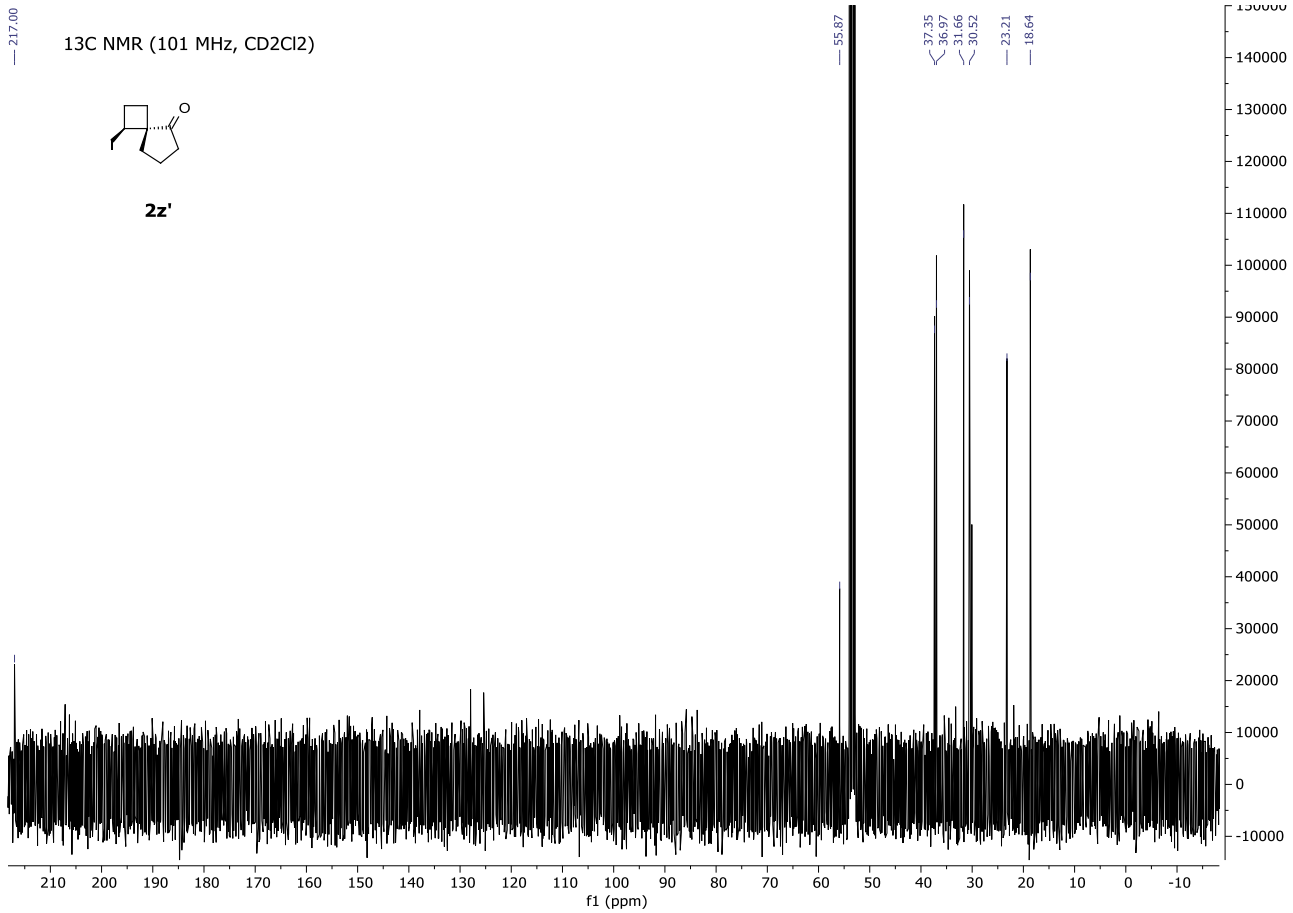
13C NMR (101 MHz, CD2Cl2)

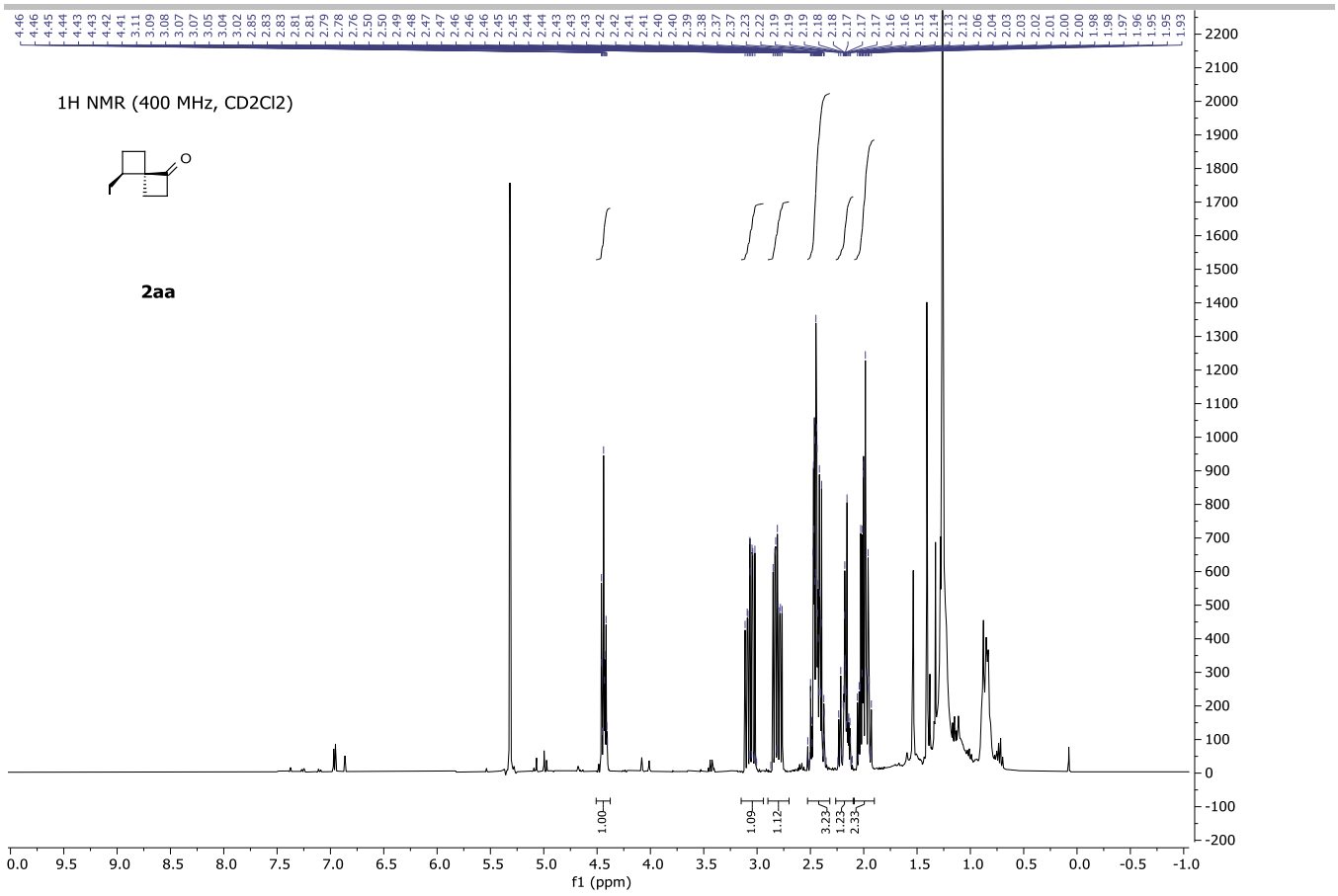
2y'

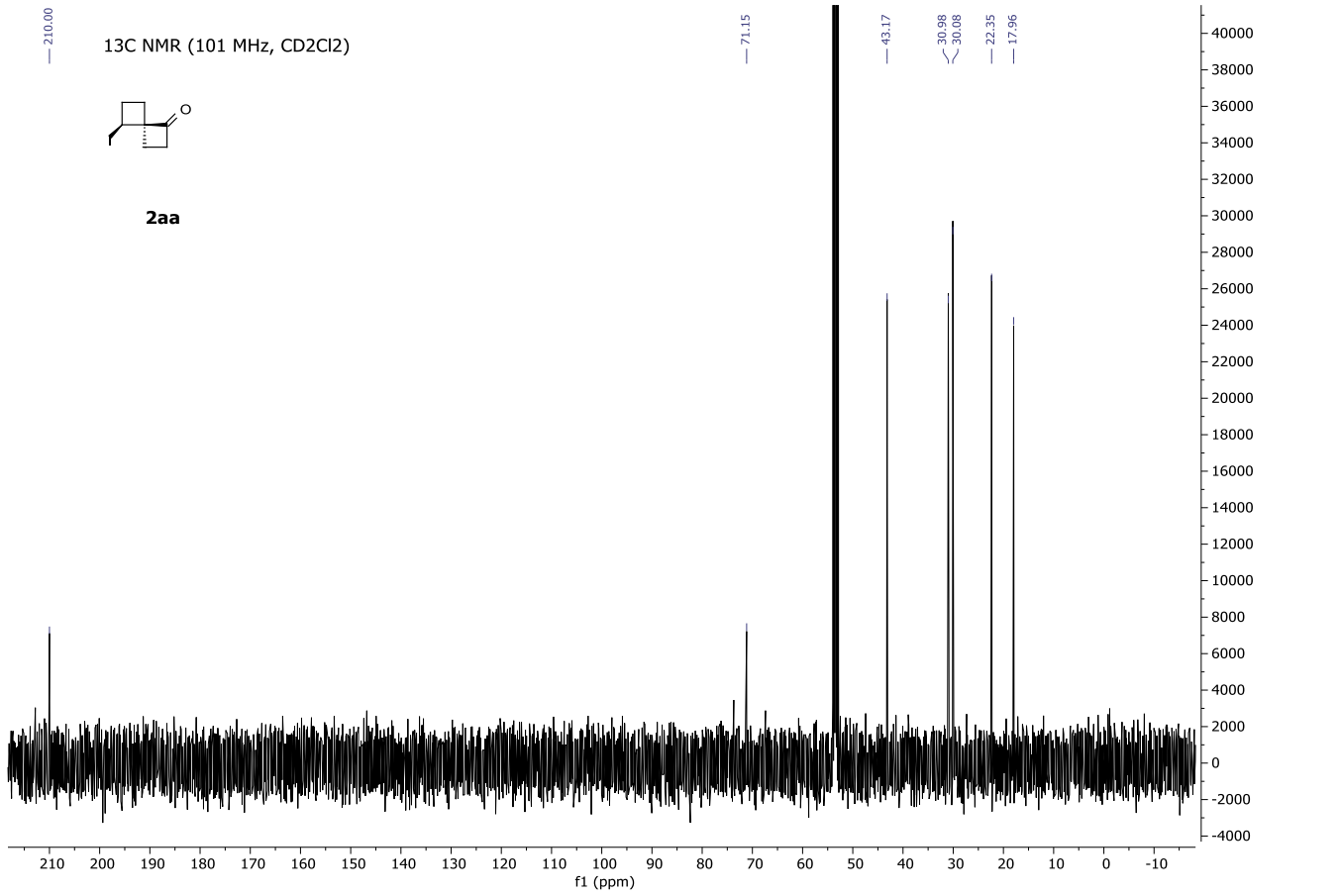

1H NMR (400 MHz, CD2Cl2)
2z
f1 (ppm)

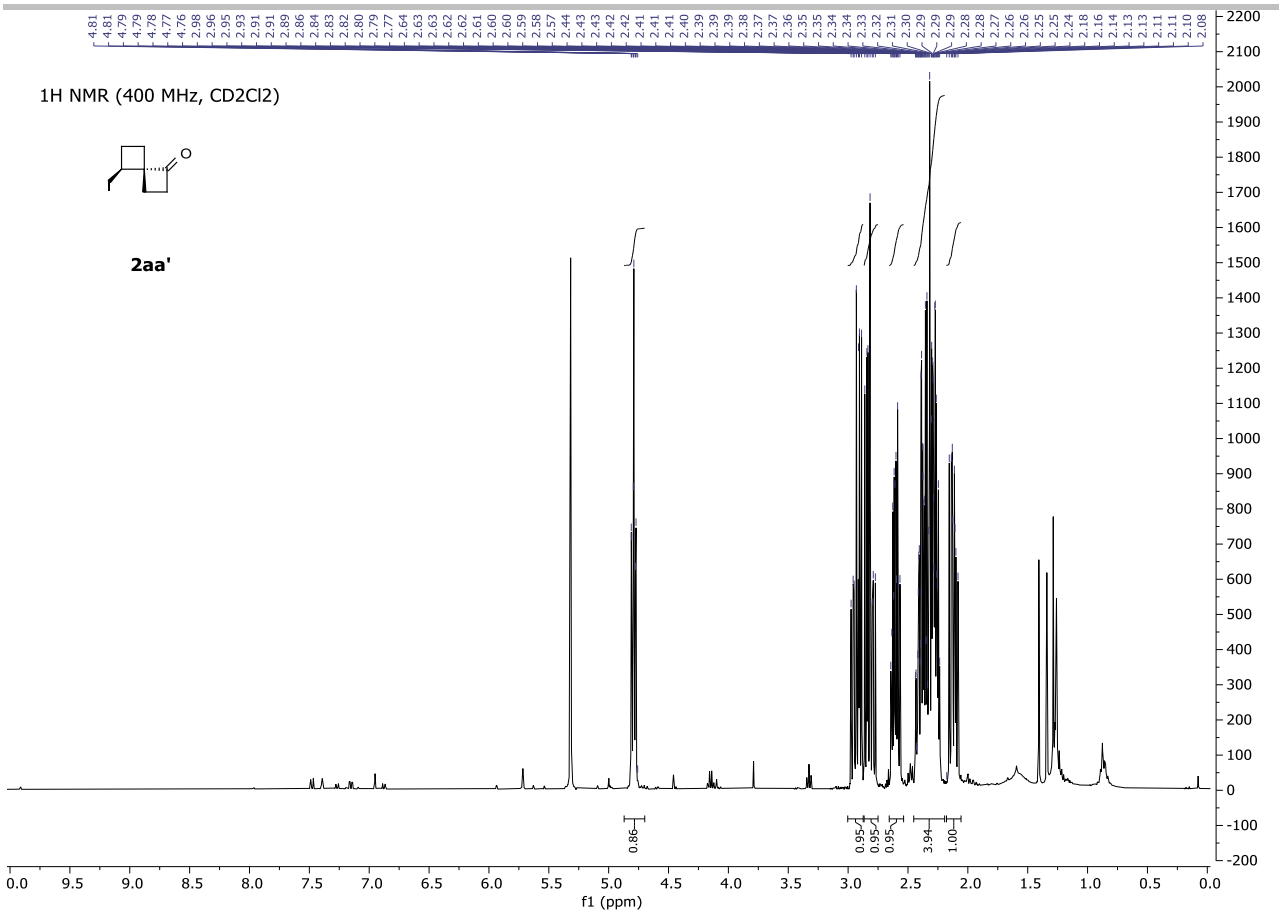

13C NMR (101 MHz, CD2Cl2)
2z
57.56
37.18
36.75
29.97
29.50
21.29
18.34
f1 (ppm)

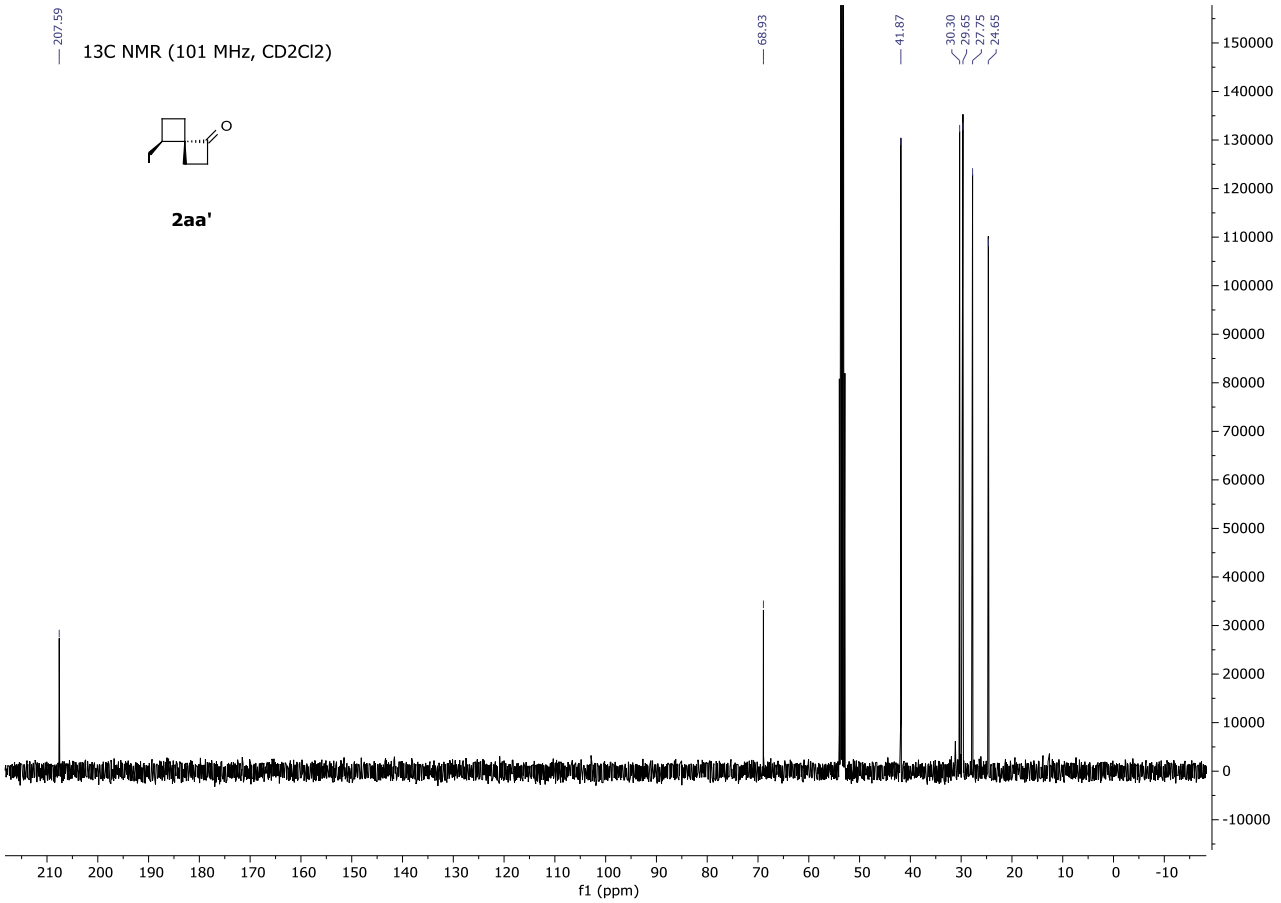

1H NMR (400 MHz, CD2Cl2)
2z'
f1 (ppm)

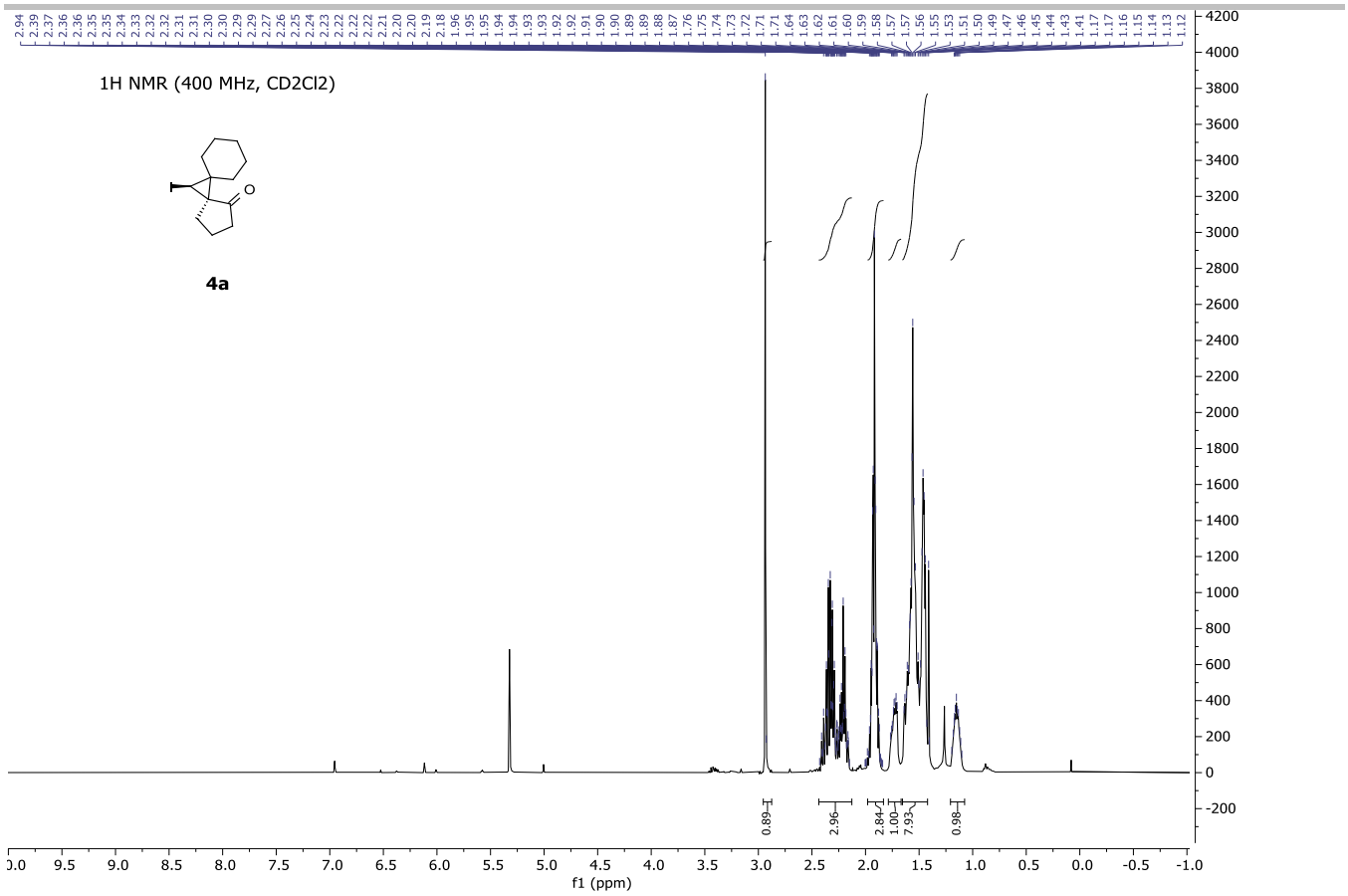

13C NMR (101 MHz, CD2Cl2)
2z'
217.00
55.87
37.35
36.97
31.66
30.52
23.21
18.64
f1 (ppm)

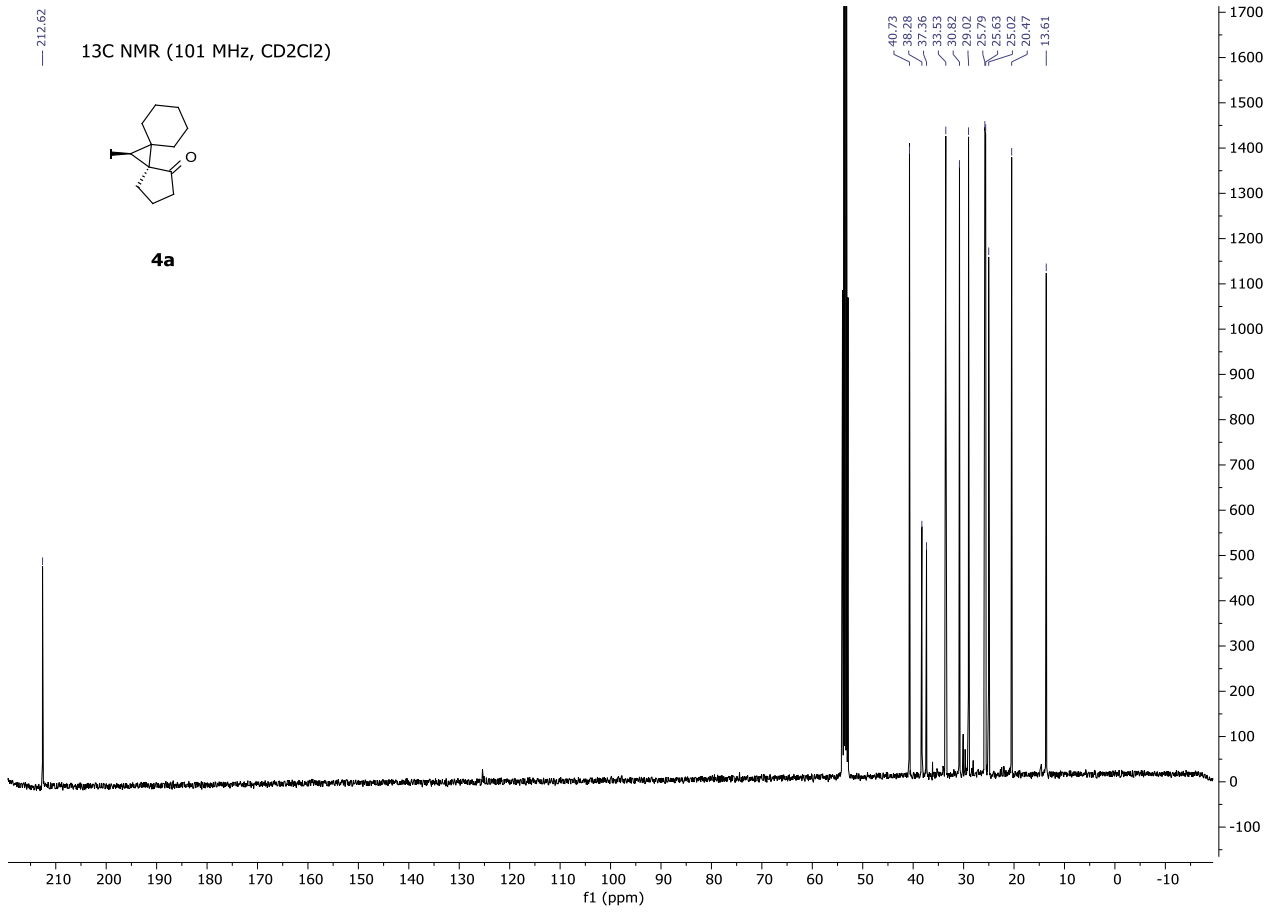

1H NMR (400 MHz, CD2Cl2)
2aa
f1 (ppm)

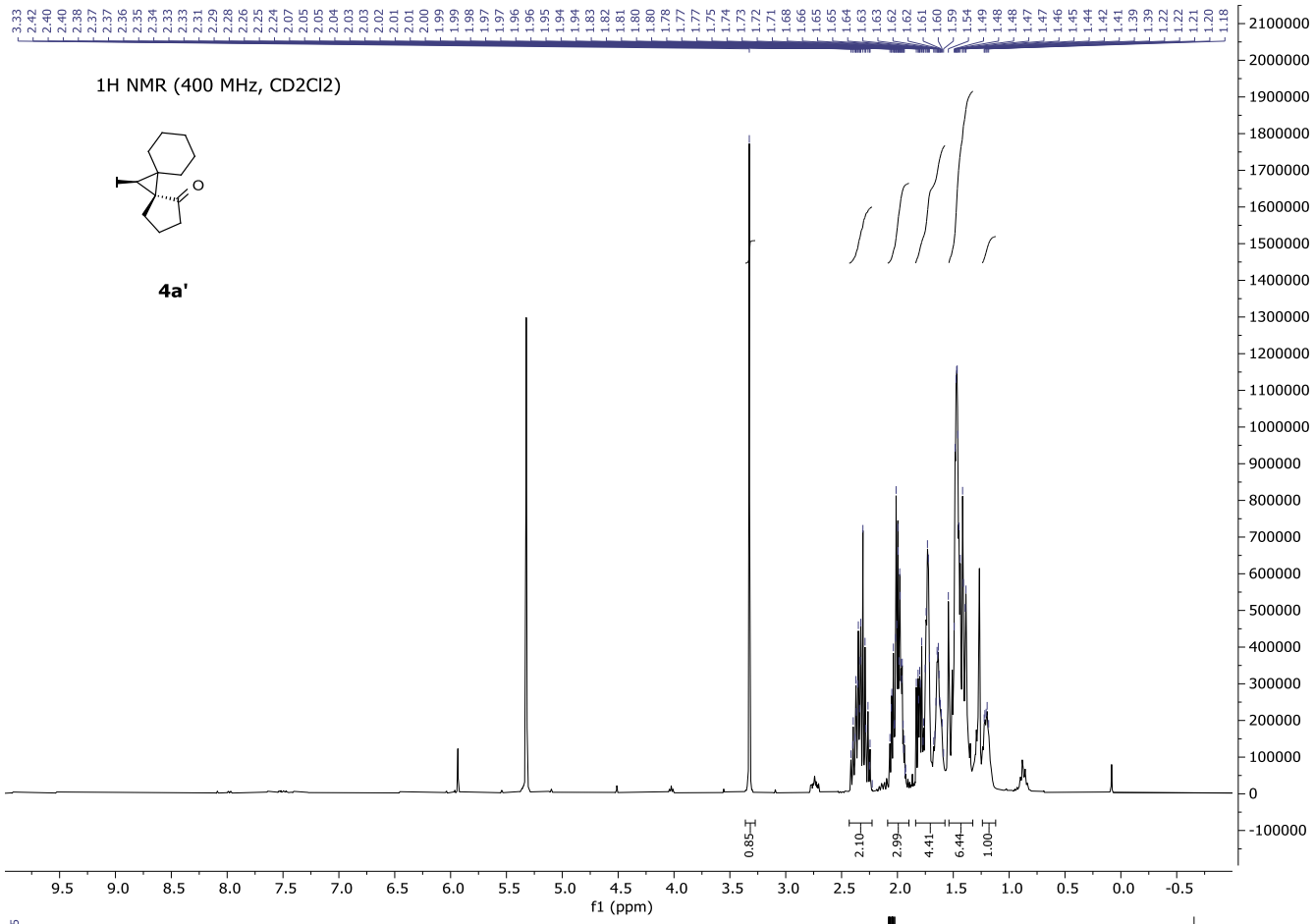

13C NMR (101 MHz, CD2Cl2)
2aa
210.00
71.15
43.17
30.98
30.08
22.35
17.96
f1 (ppm)

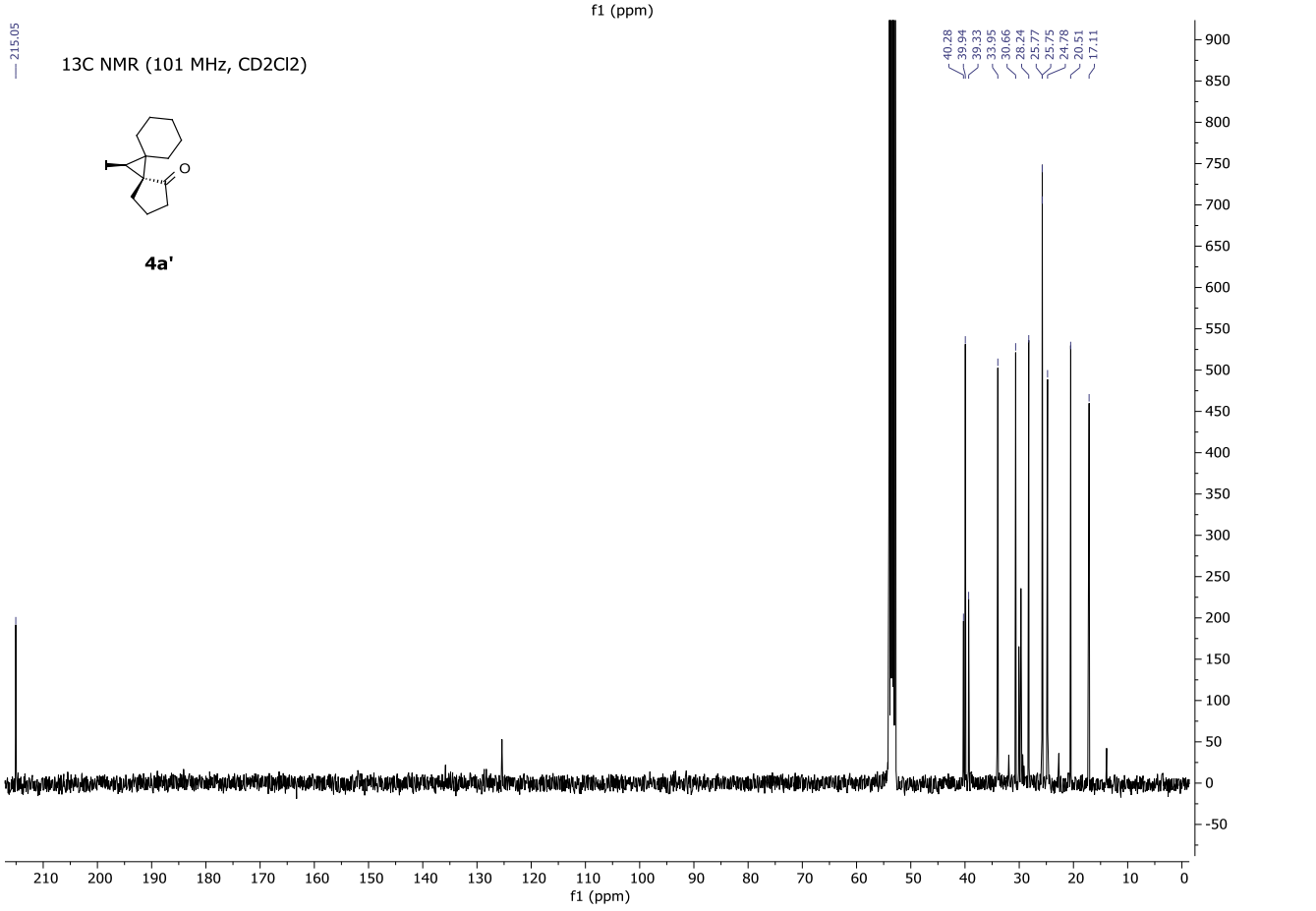

1H NMR (400 MHz, CD2Cl2)
2aa'
f1 (ppm)

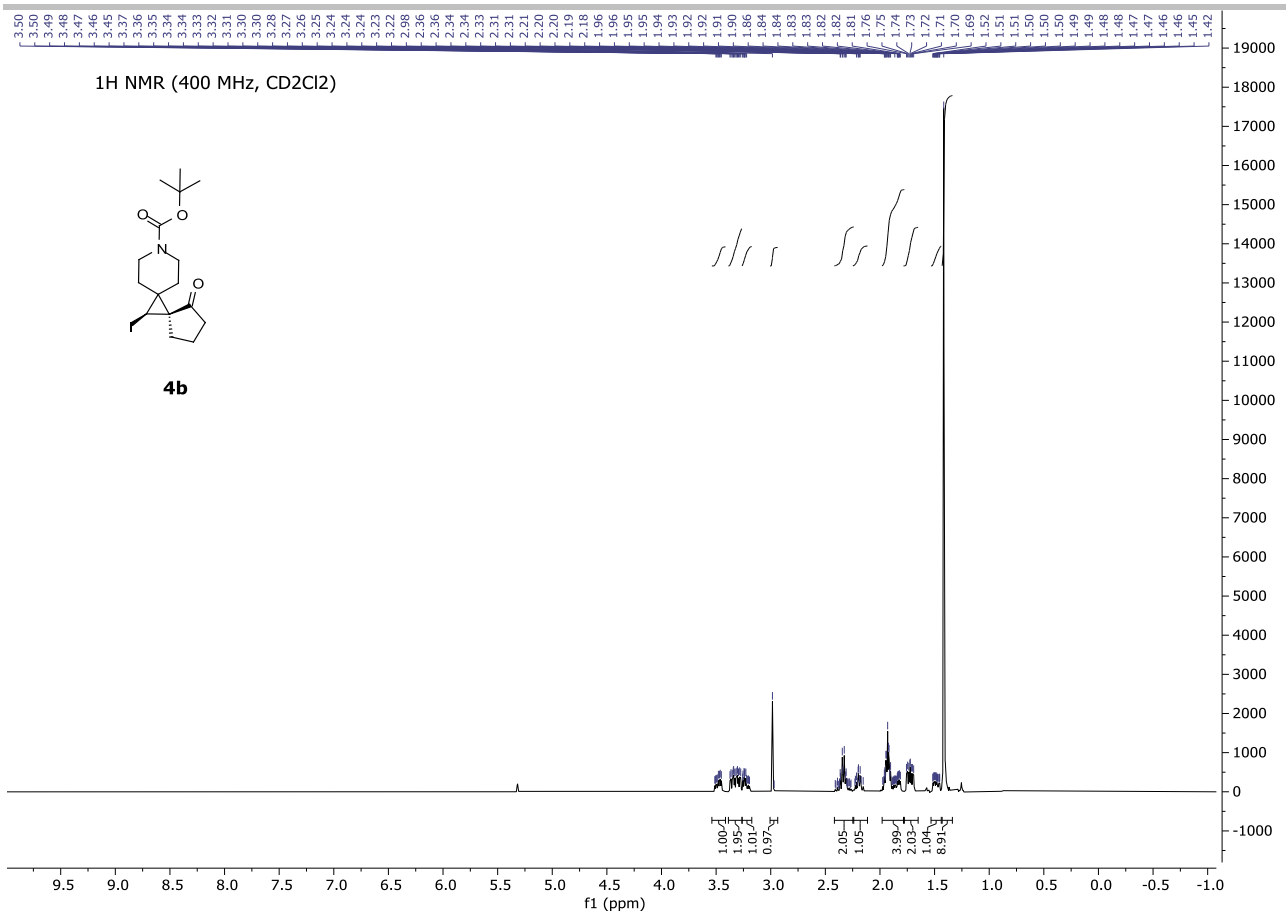

13C NMR (101 MHz, CD2Cl2)
2aa'
207.59
68.93
41.87
30.30
29.65
27.75
24.65
f1 (ppm)

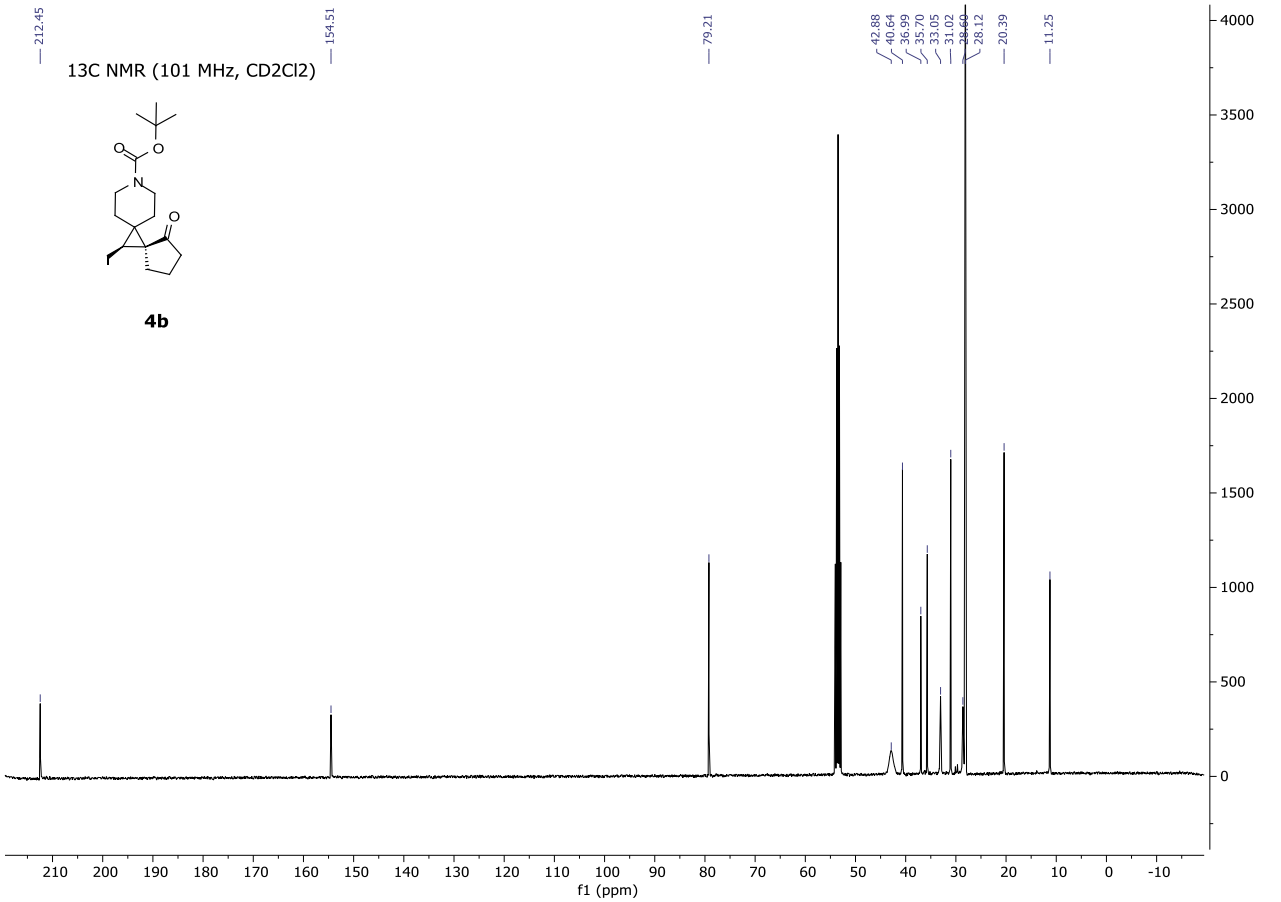

1H NMR (400 MHz, CD2Cl2)
4a
f1 (ppm)

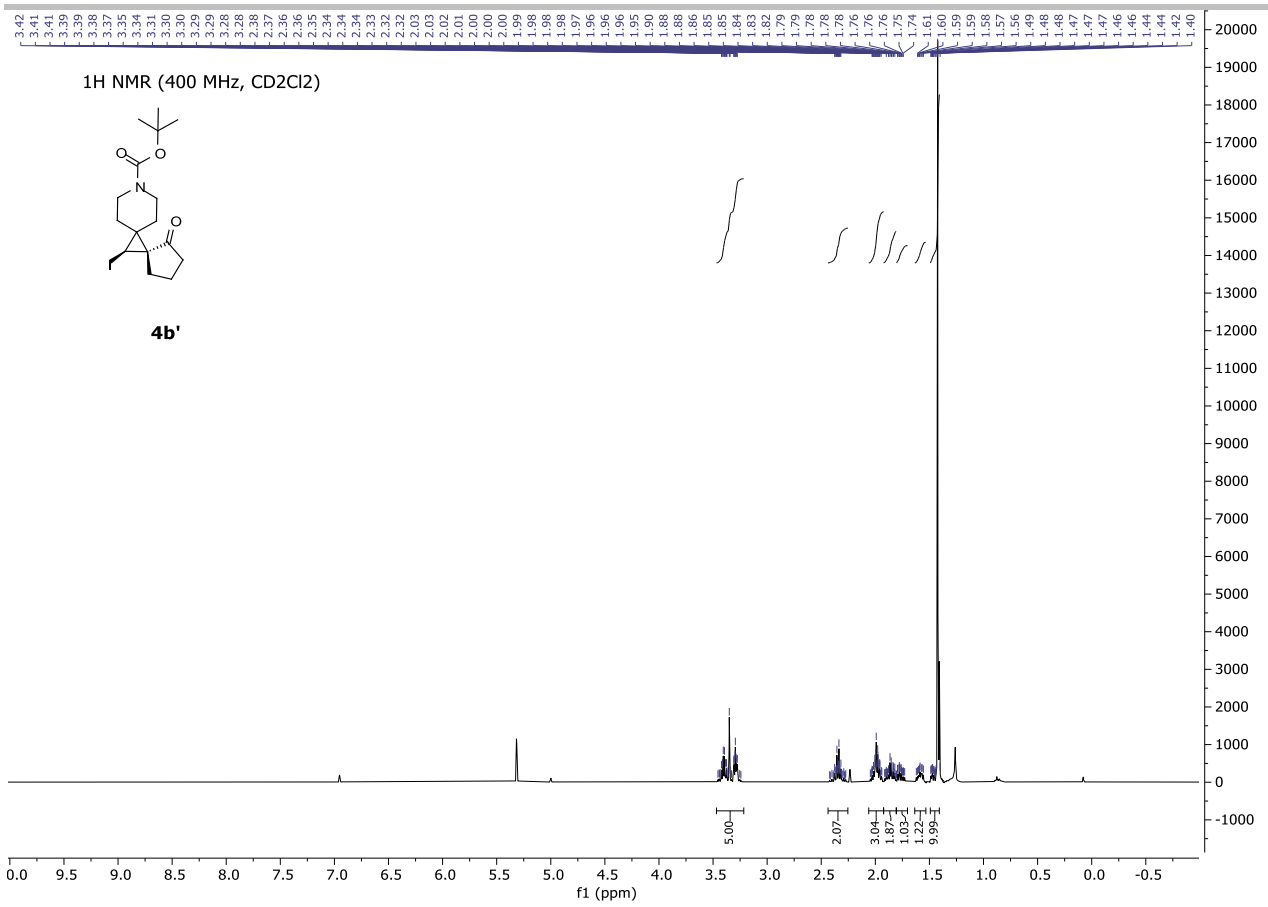

13C NMR (101 MHz, CD2Cl2)
4a
f1 (ppm)

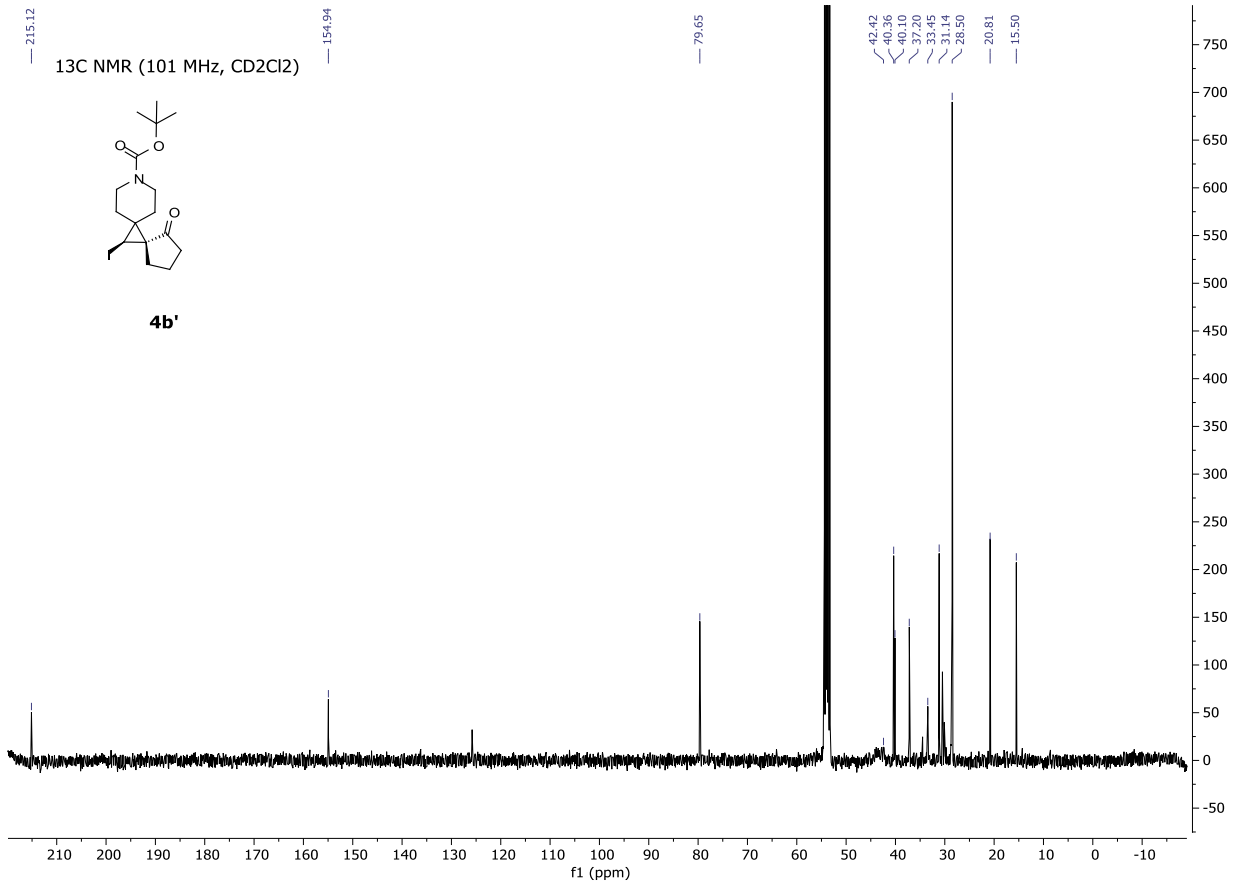

1H NMR (400 MHz, CD2Cl2)
4a'
f1 (ppm)

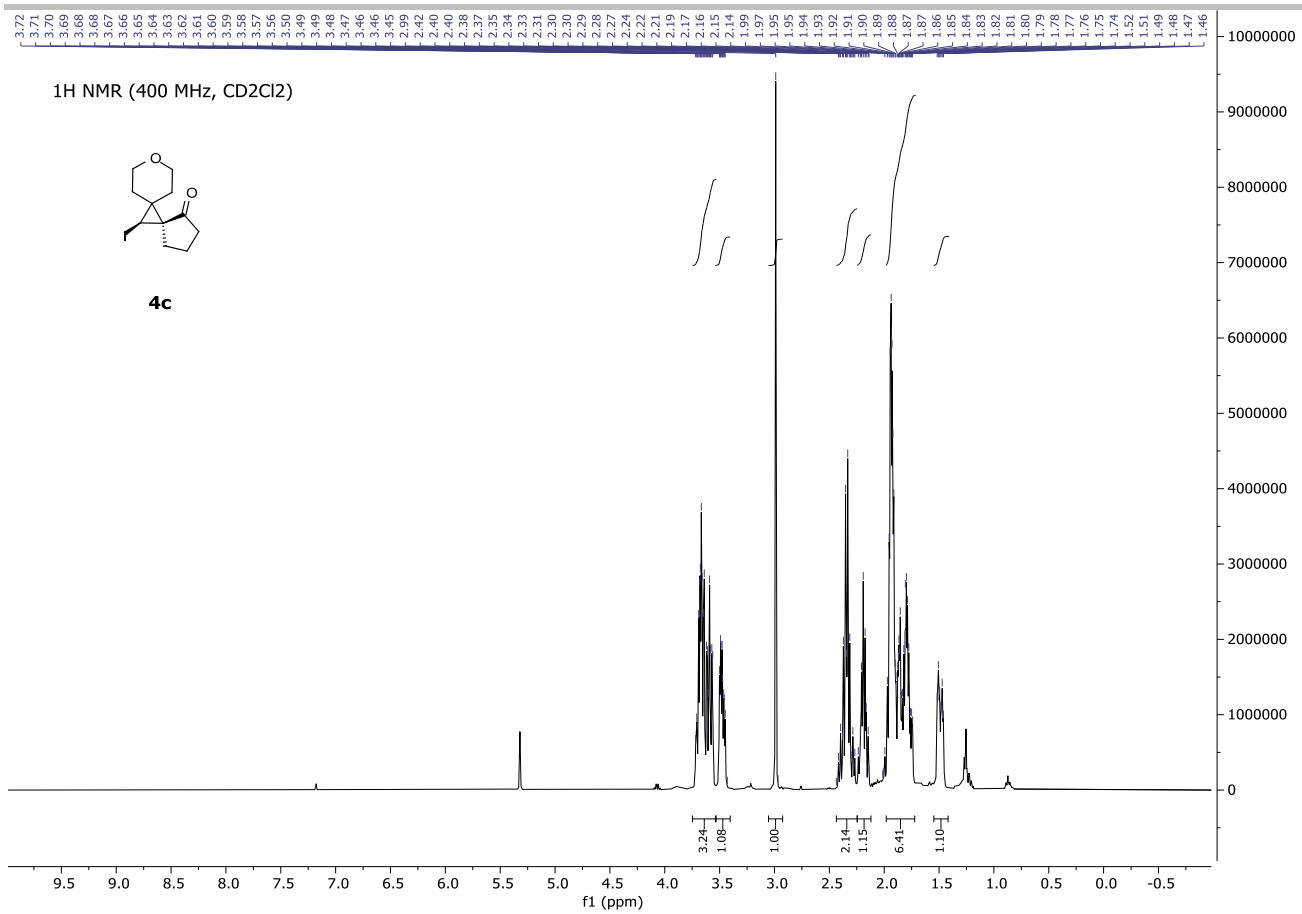

13C NMR (101 MHz, CD2Cl2)
4a'
f1 (ppm)

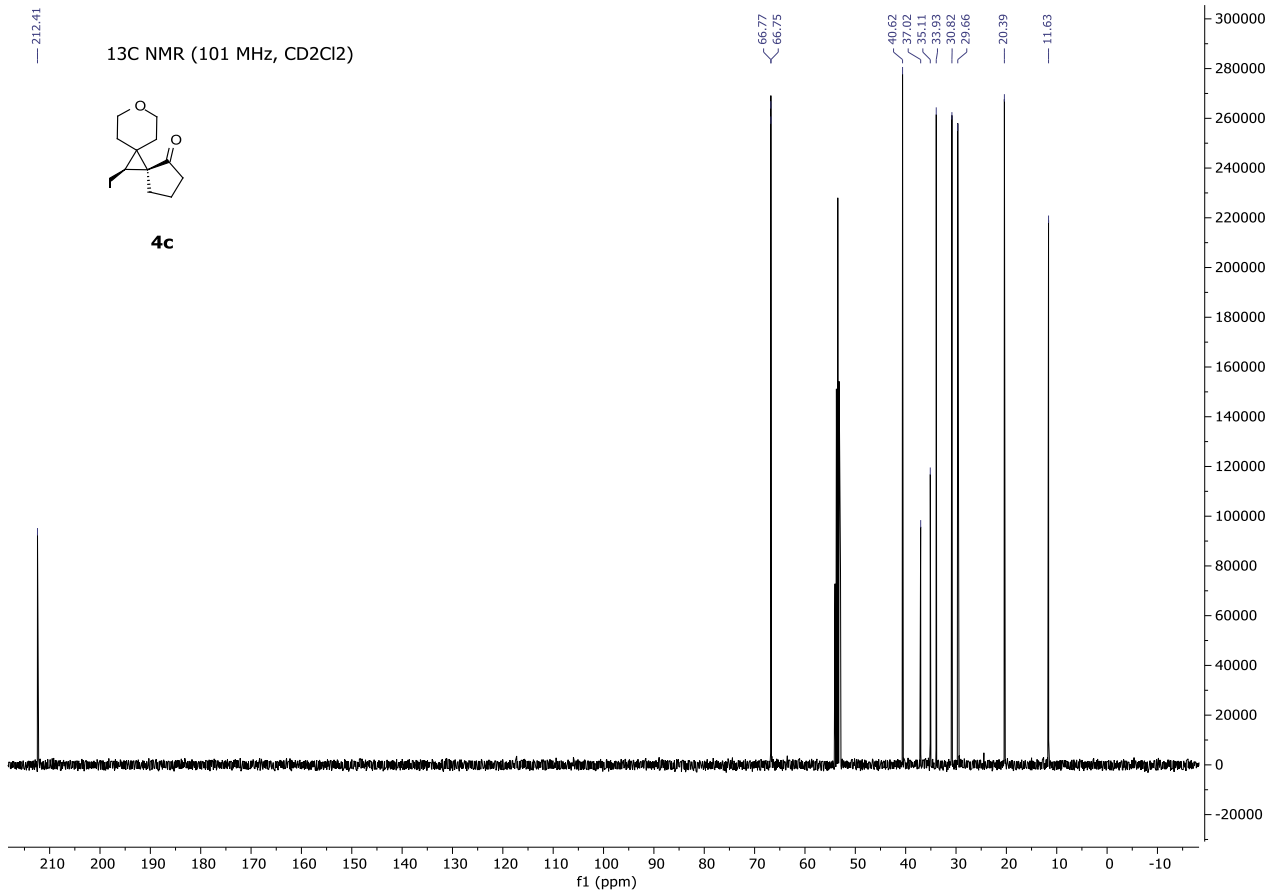

1H NMR (400 MHz, CD2Cl2)
4b
f1 (ppm)

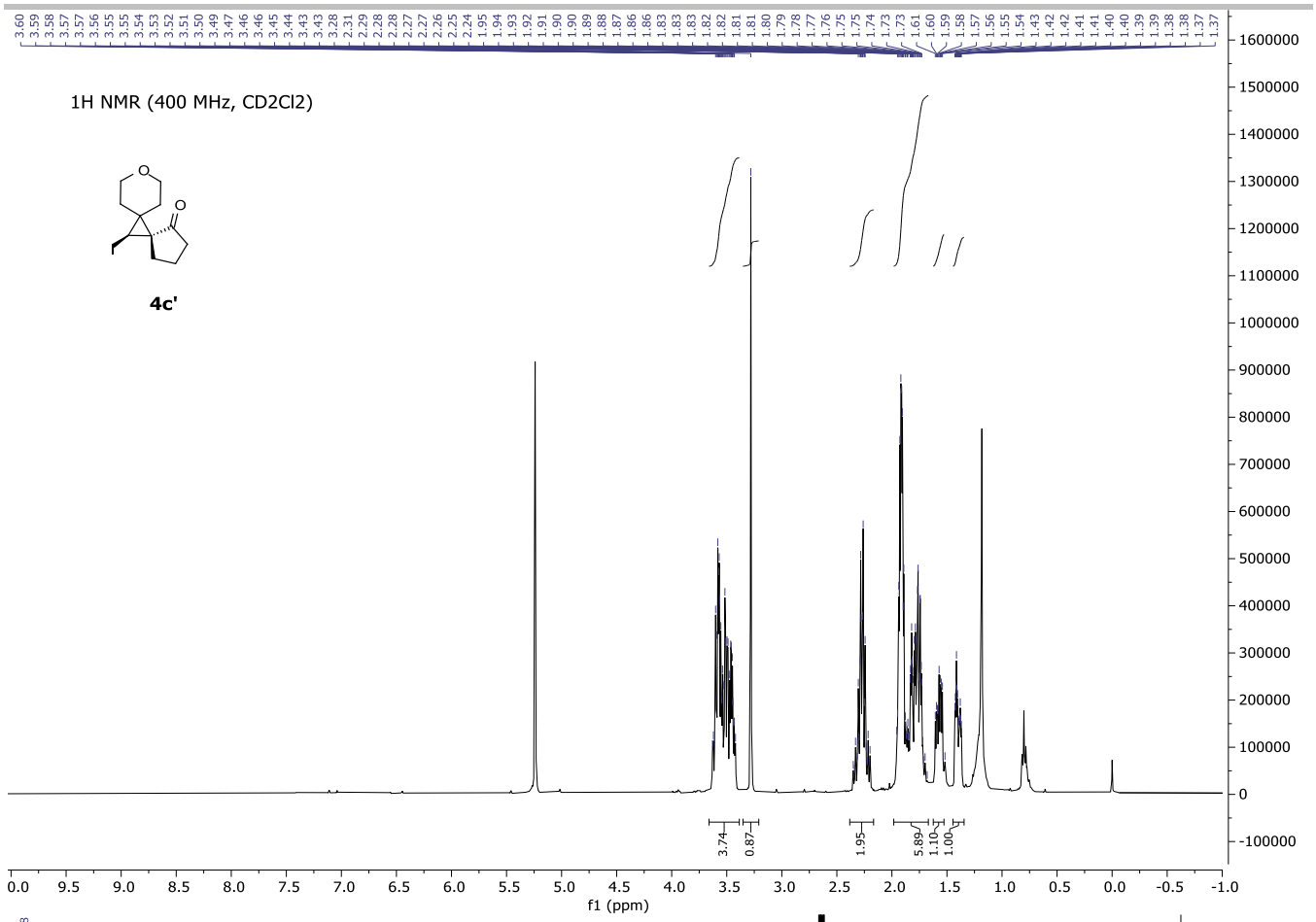

13C NMR (101 MHz, CD2Cl2)
4b
212.45
154.51
79.21
42.88
40.64
36.99
35.70
33.05
31.02
28.60
28.12
20.39
11.25
f1 (ppm)

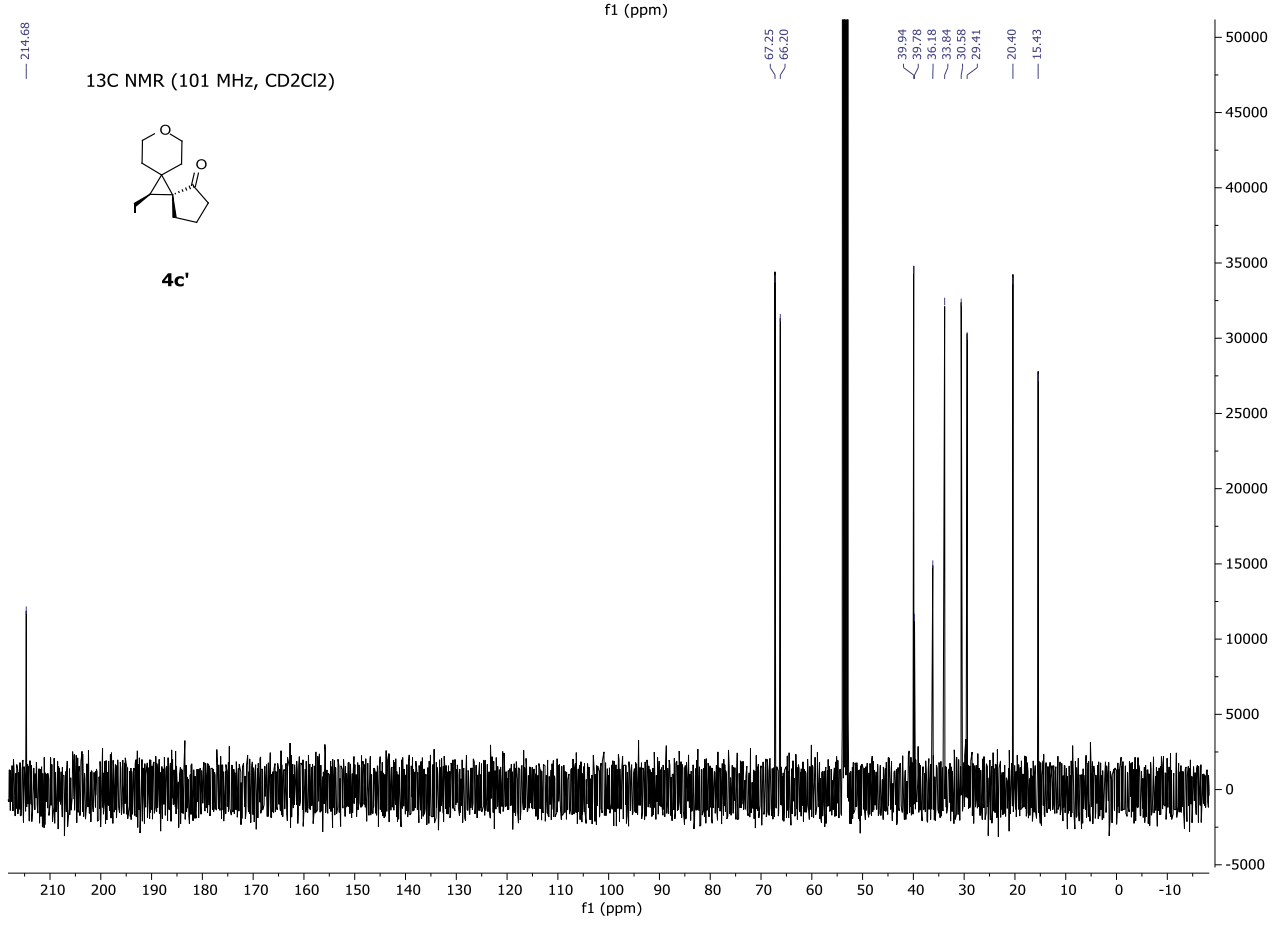

1H NMR (400 MHz, CD2Cl2)
4b'
5.00
2.07
3.04
1.87
1.03
1.22
9.99
f1 (ppm)

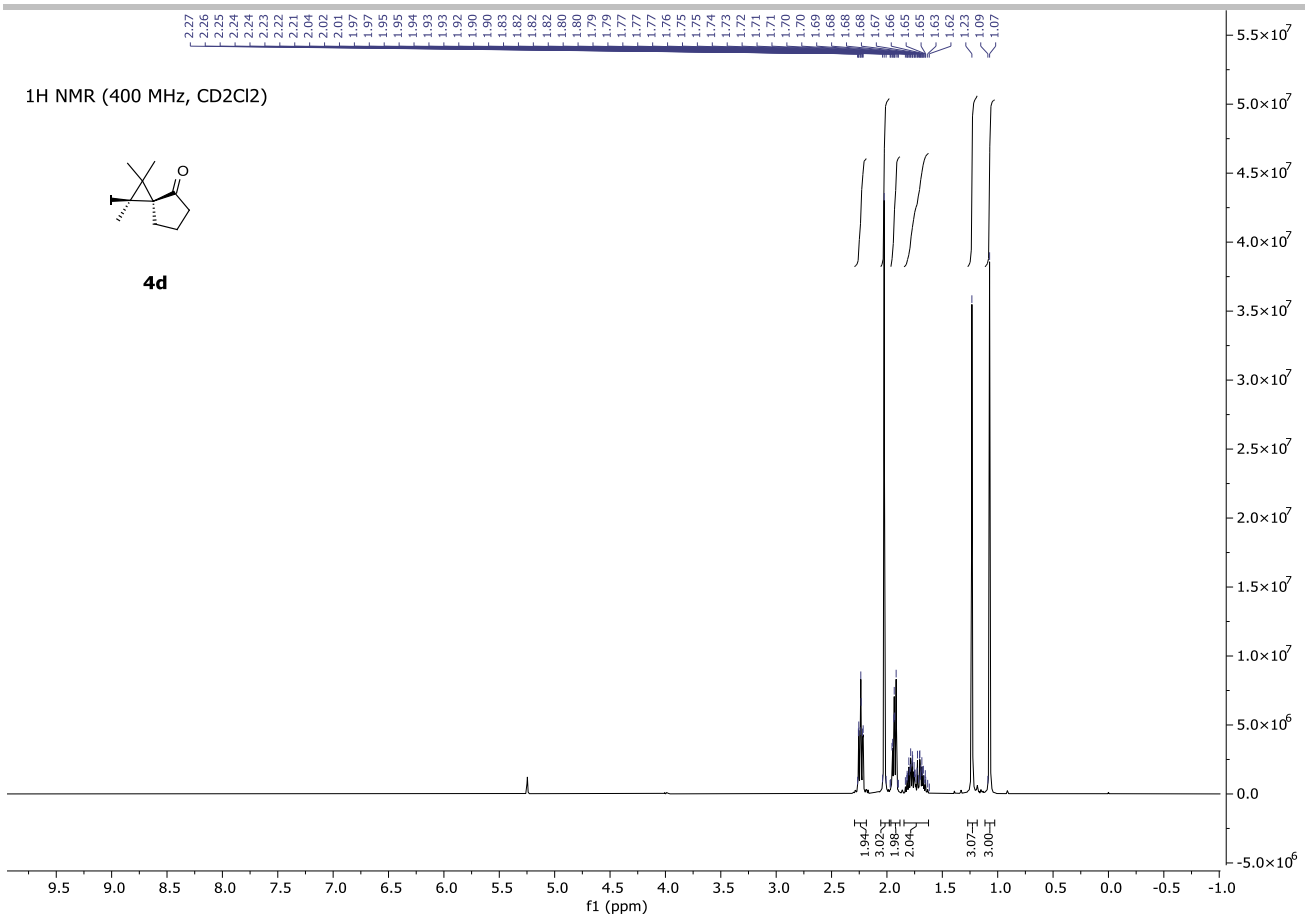

215.12
154.94
79.65
42.42
40.36
40.10
37.20
33.45
31.14
28.50
20.81
15.50
13C NMR (101 MHz, CD2Cl2)
4b'
f1 (ppm)

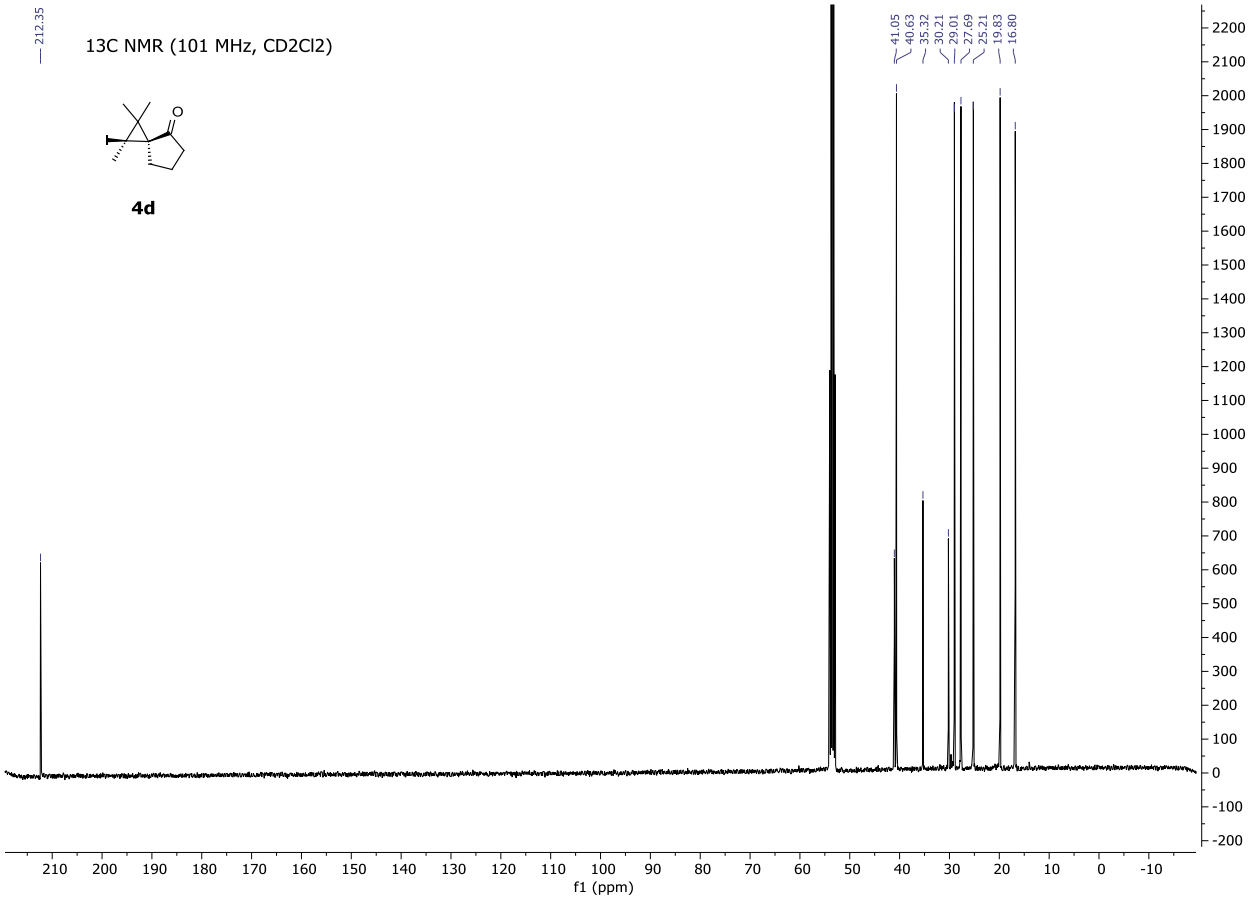

1H NMR (400 MHz, CD2Cl2)
4c
f1 (ppm)

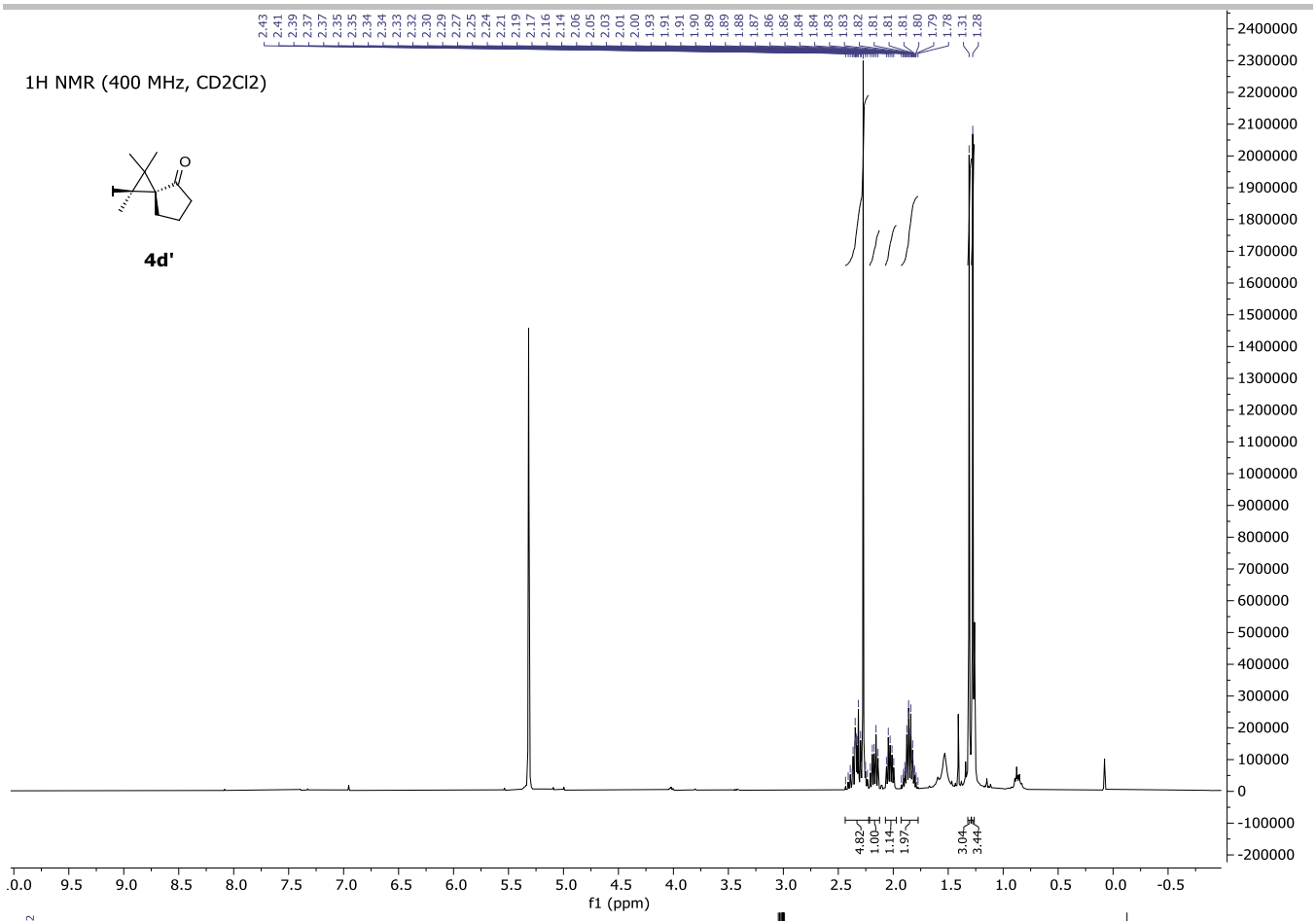

13C NMR (101 MHz, CD2Cl2)
4c
f1 (ppm)

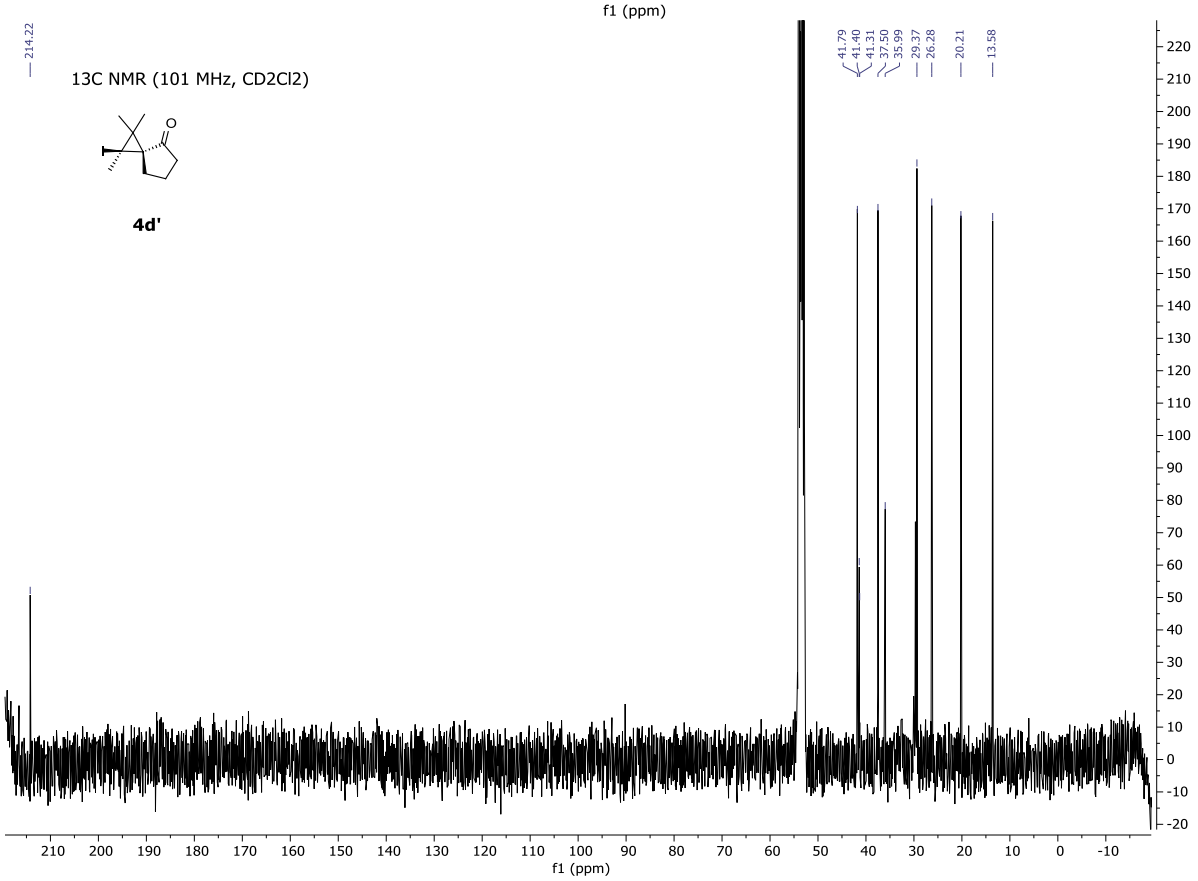

1H NMR (400 MHz, CD2Cl2)
4c'
3.74
0.87
1.95
5.89
1.10
1.00
f1 (ppm)

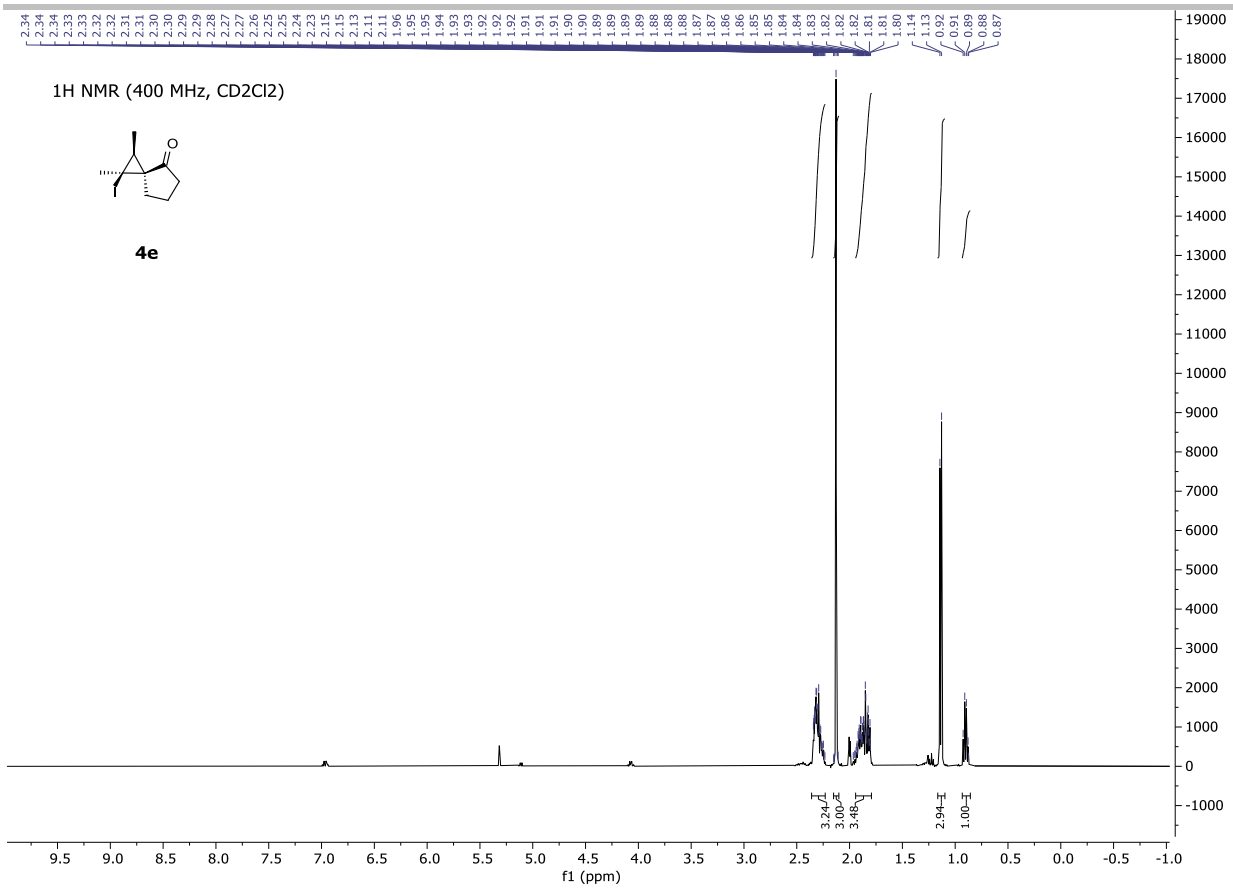

214.68
67.25
66.20
39.94
39.78
36.18
33.84
30.58
29.41
20.40
15.43
13C NMR (101 MHz, CD2Cl2)
4c'
f1 (ppm)

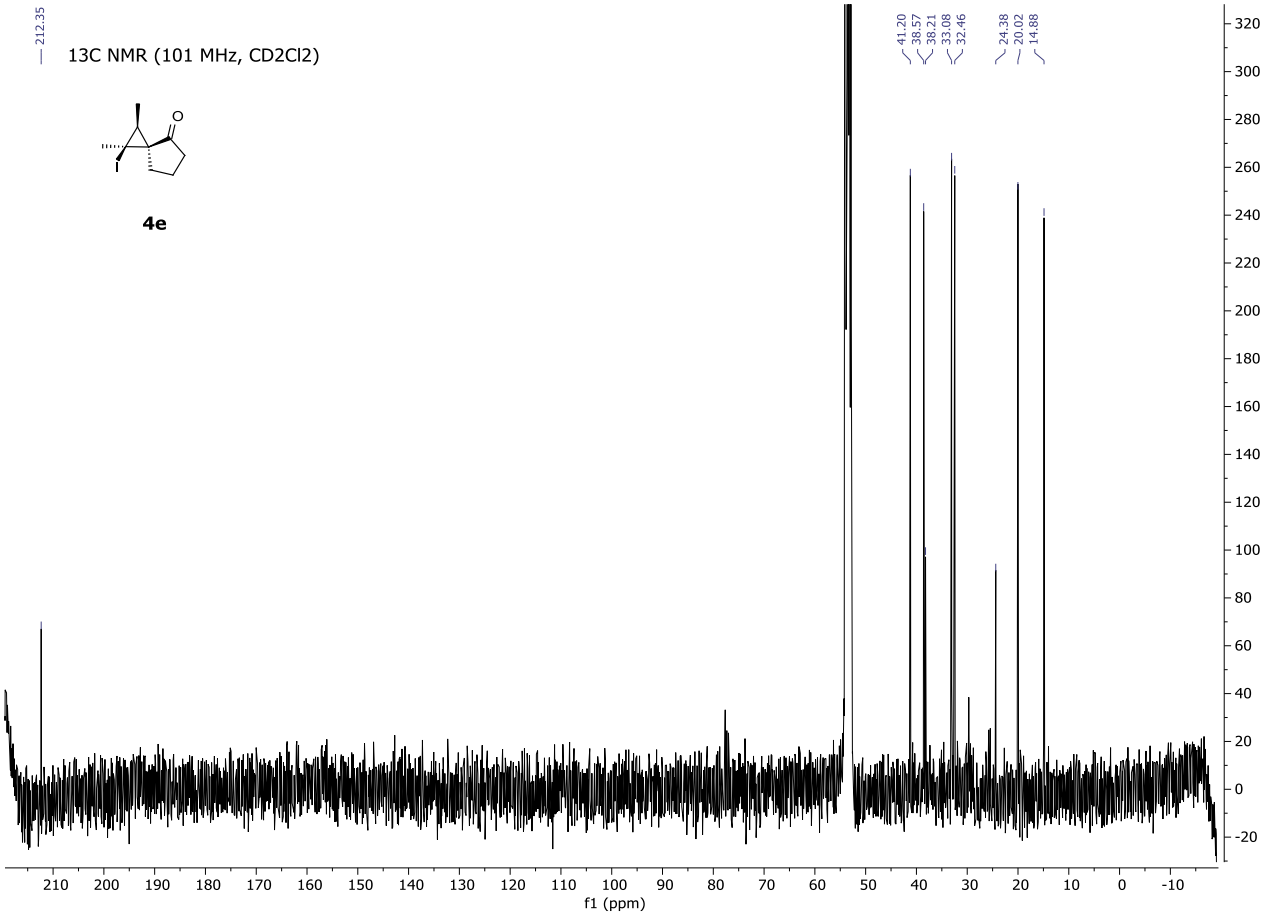

1H NMR (400 MHz, CD2Cl2)
4d
f1 (ppm)

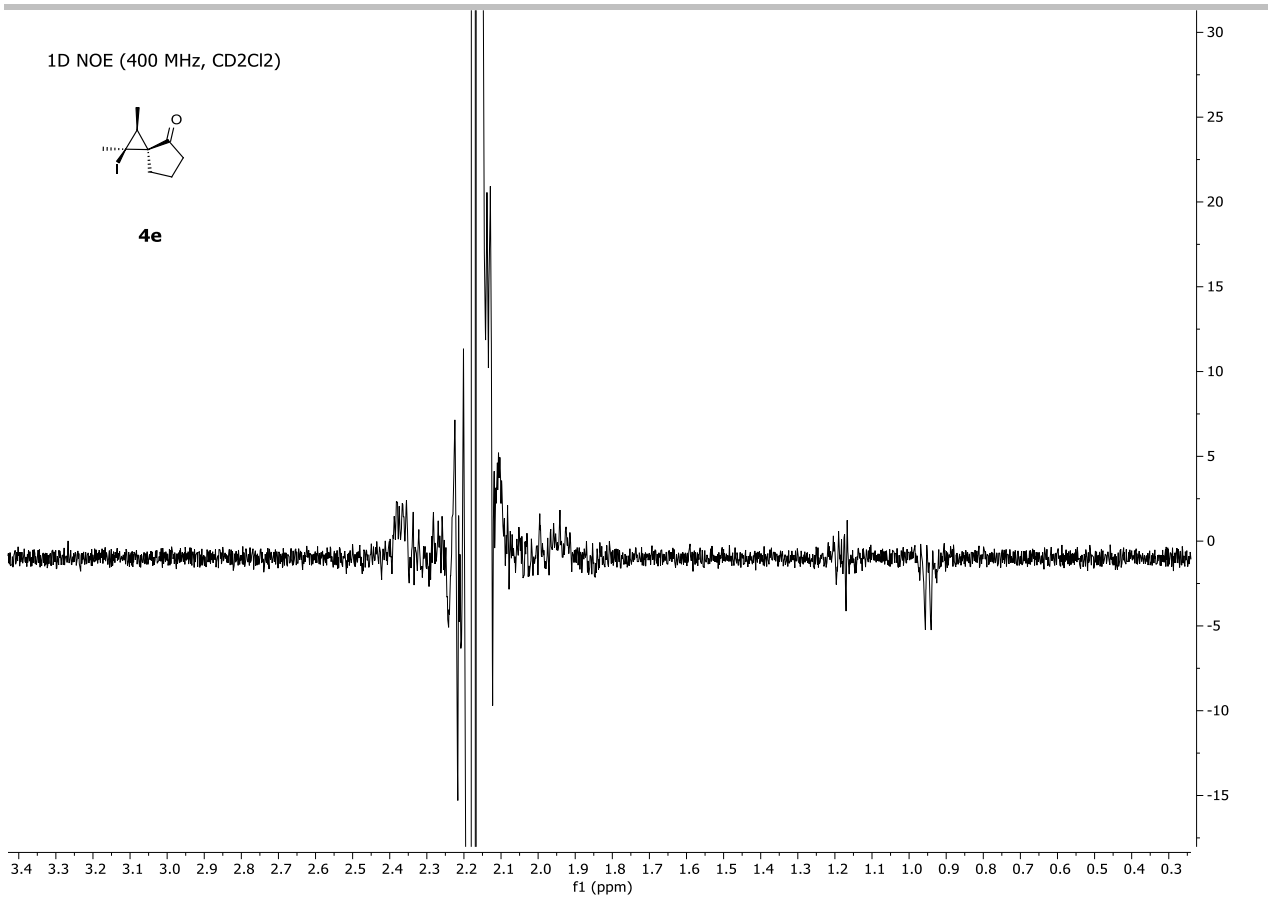

13C NMR (101 MHz, CD2Cl2)
4d
f1 (ppm)

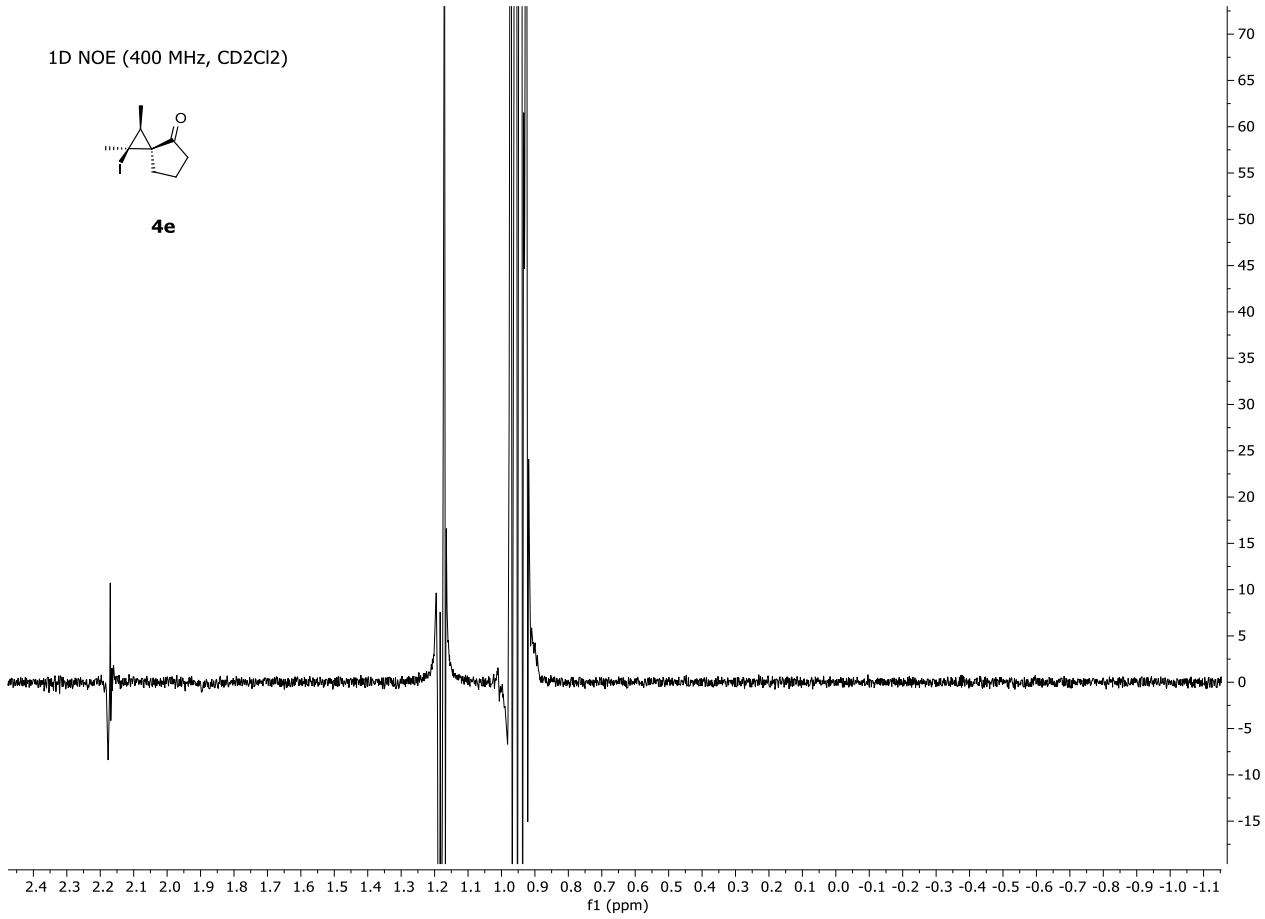

1H NMR (400 MHz, CD2Cl2)
4d'
f1 (ppm)

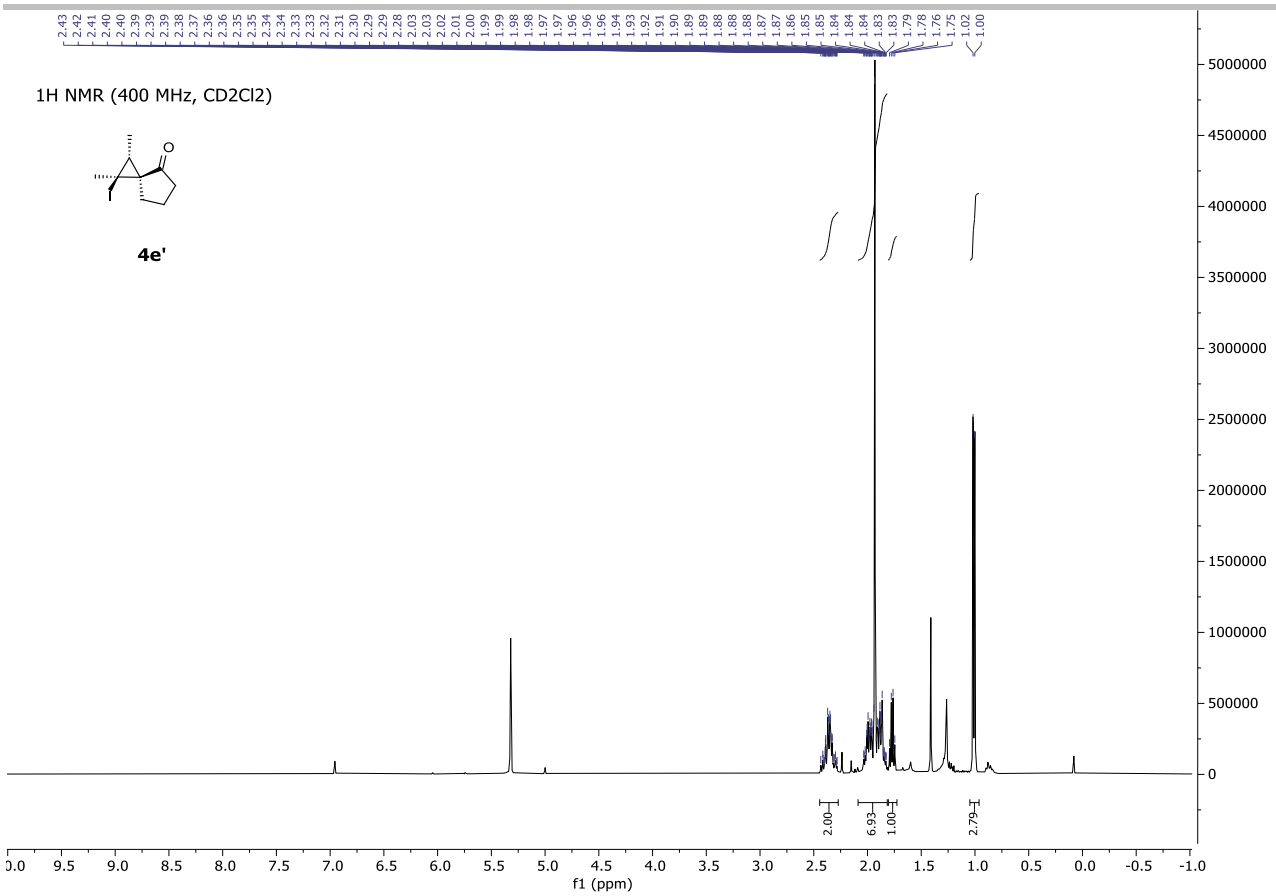

13C NMR (101 MHz, CD2Cl2)
4d'
f1 (ppm)

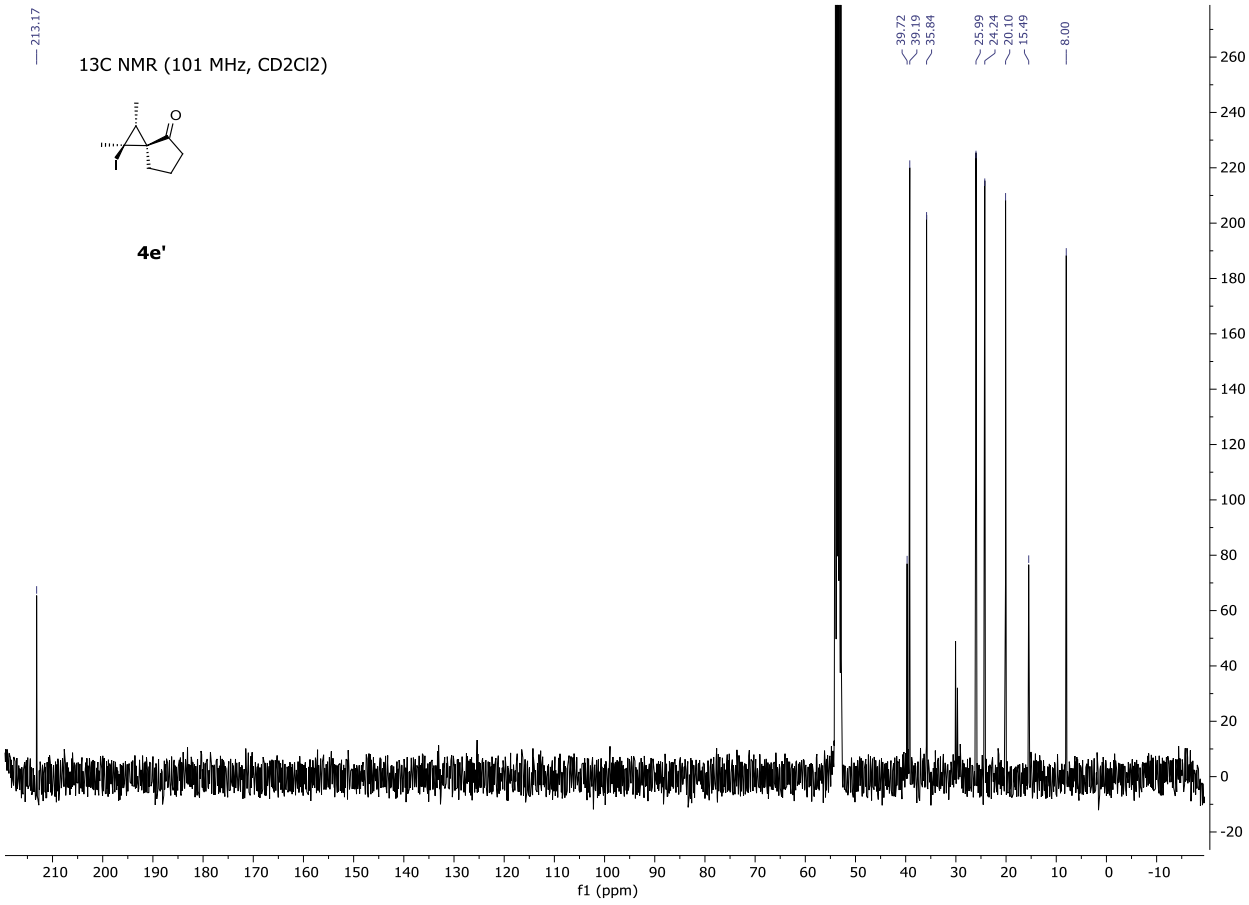

1H NMR (400 MHz, CD2Cl2)
4e
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
212.35
41.20
38.57
38.21
33.08
32.46
24.38
20.02
14.88
4e
f1 (ppm)


1D NOE (400 MHz, CD2Cl2)
O
4e
30 25 20 15 10 5 0 -5 -10 -15
3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3
f1 (ppm)


1D NOE (400 MHz, CD2Cl2)
O
4e
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1 -0.2 -0.3 -0.4 -0.5 -0.6 -0.7 -0.8 -0.9 -1.0 -1.1
f1 (ppm)


1H NMR (400 MHz, CD2Cl2)
4e'
f1 (ppm)

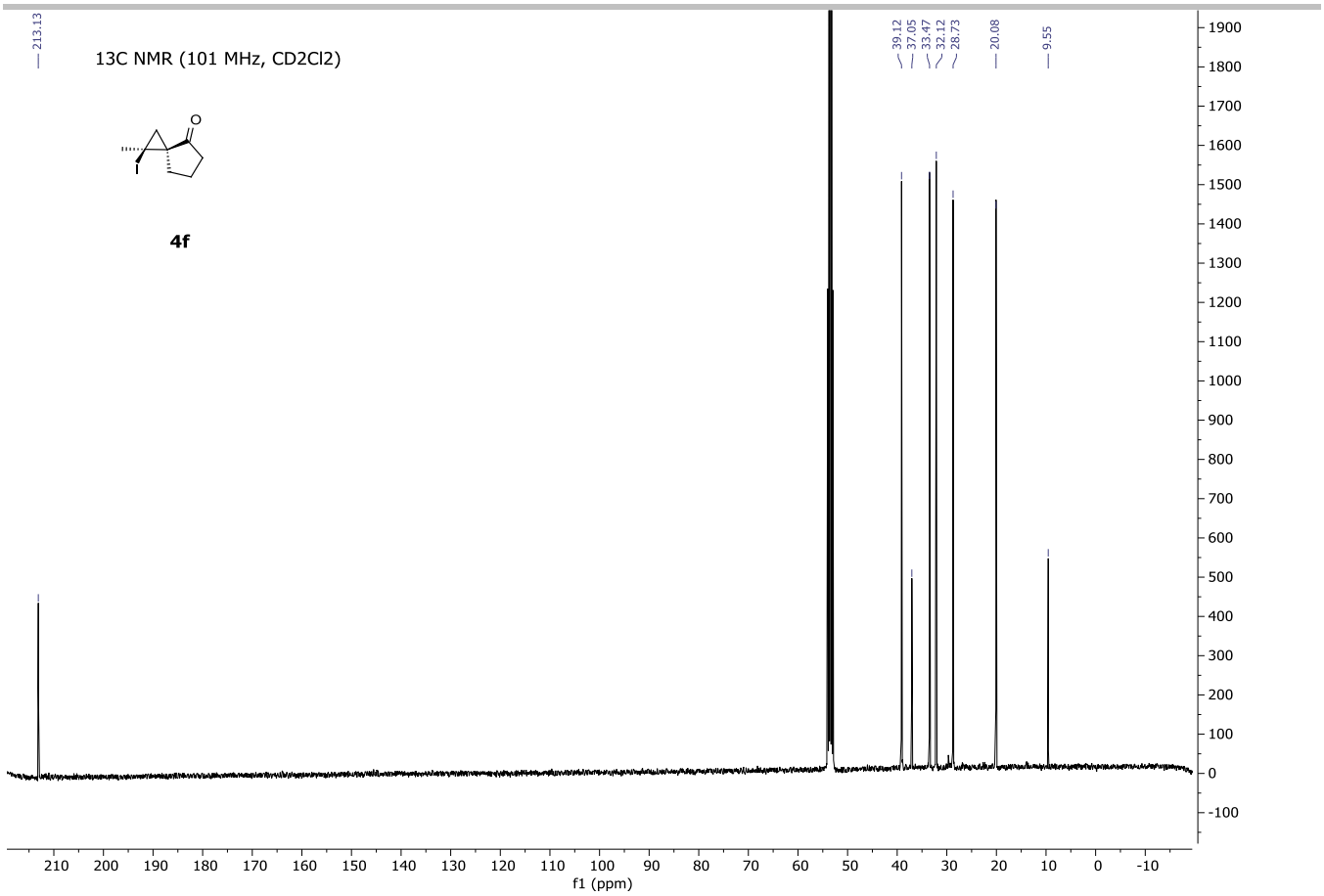

13C NMR (101 MHz, CD2Cl2)
4e'
f1 (ppm)

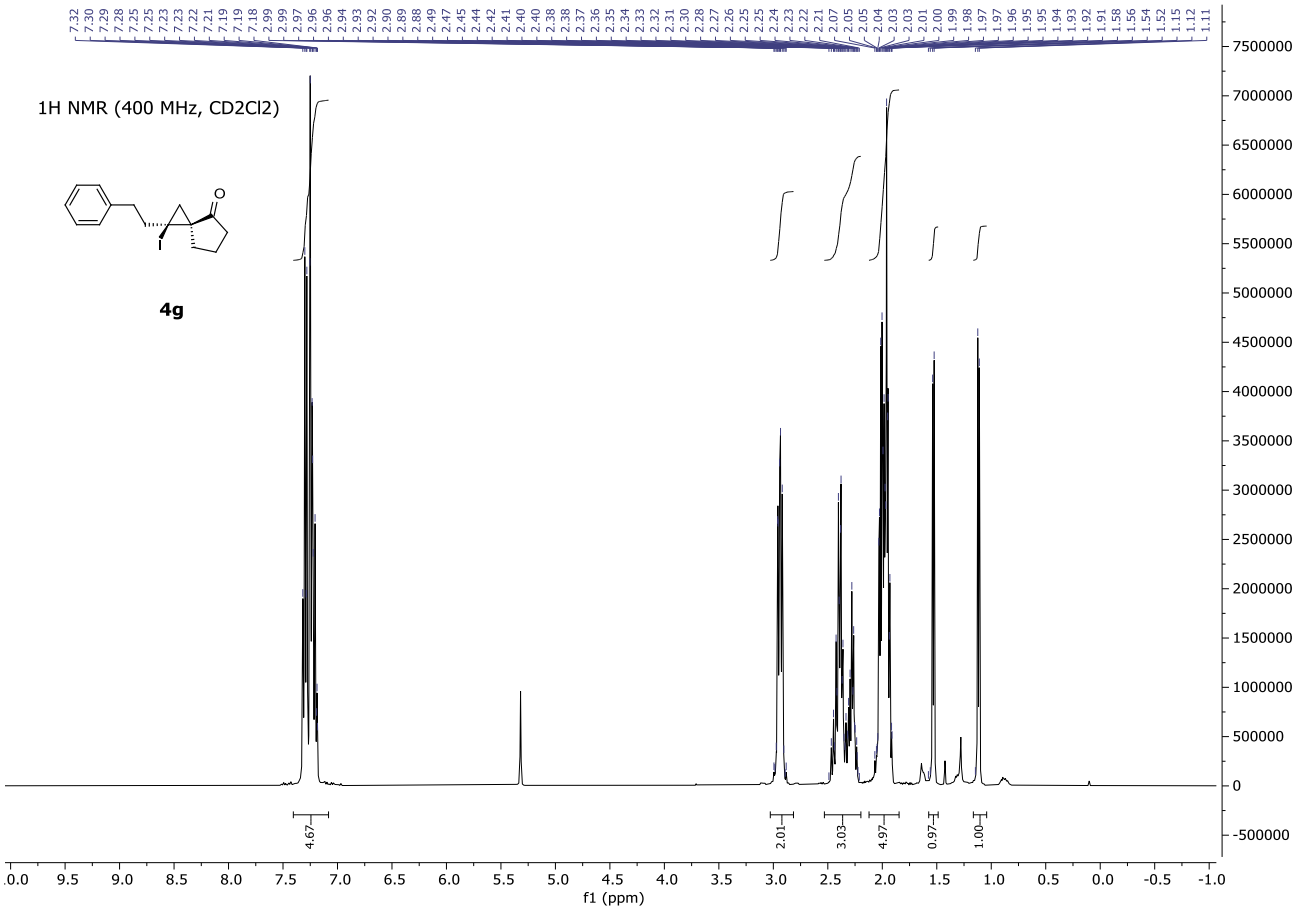
1D NOE (400 MHz, CD2Cl2)

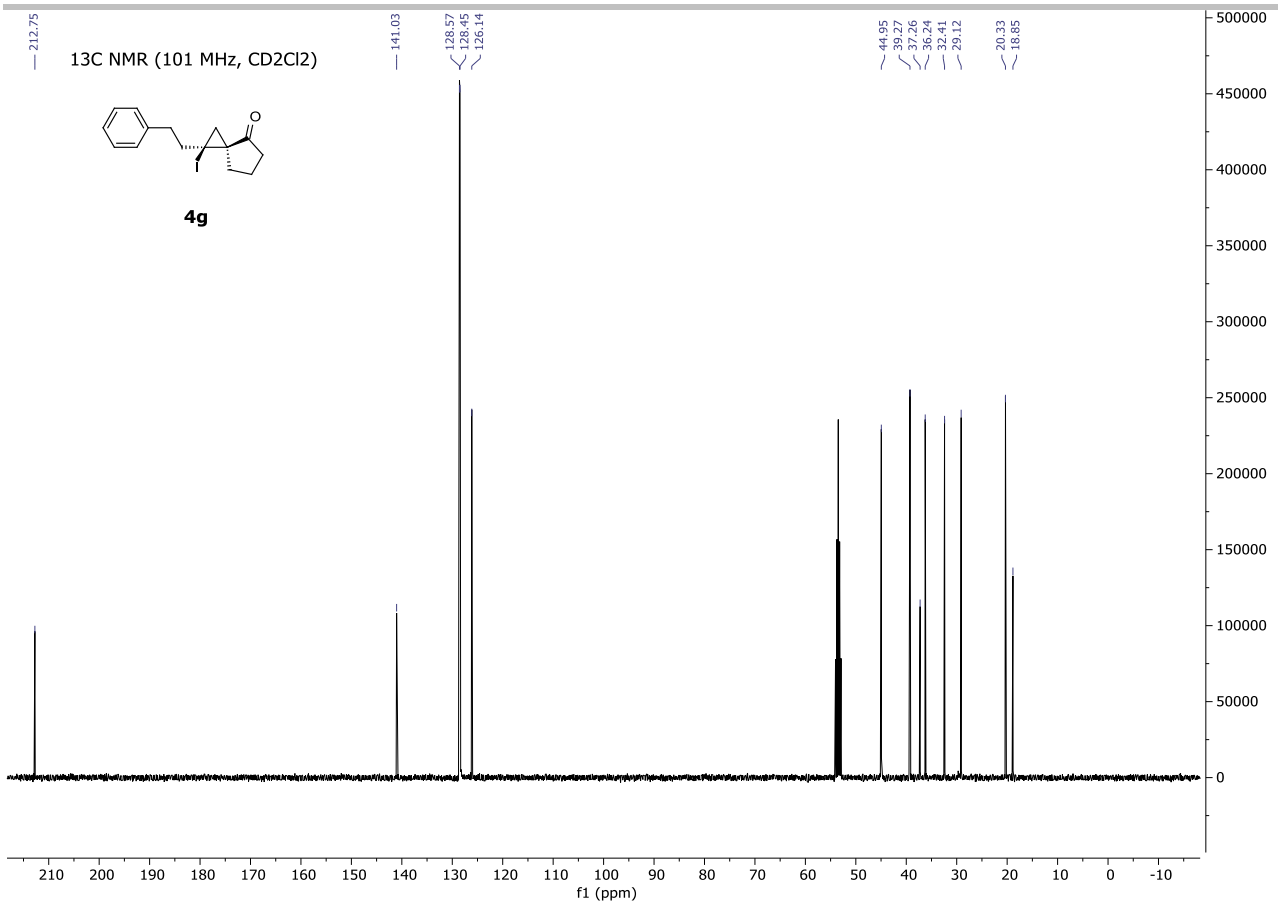
4e'

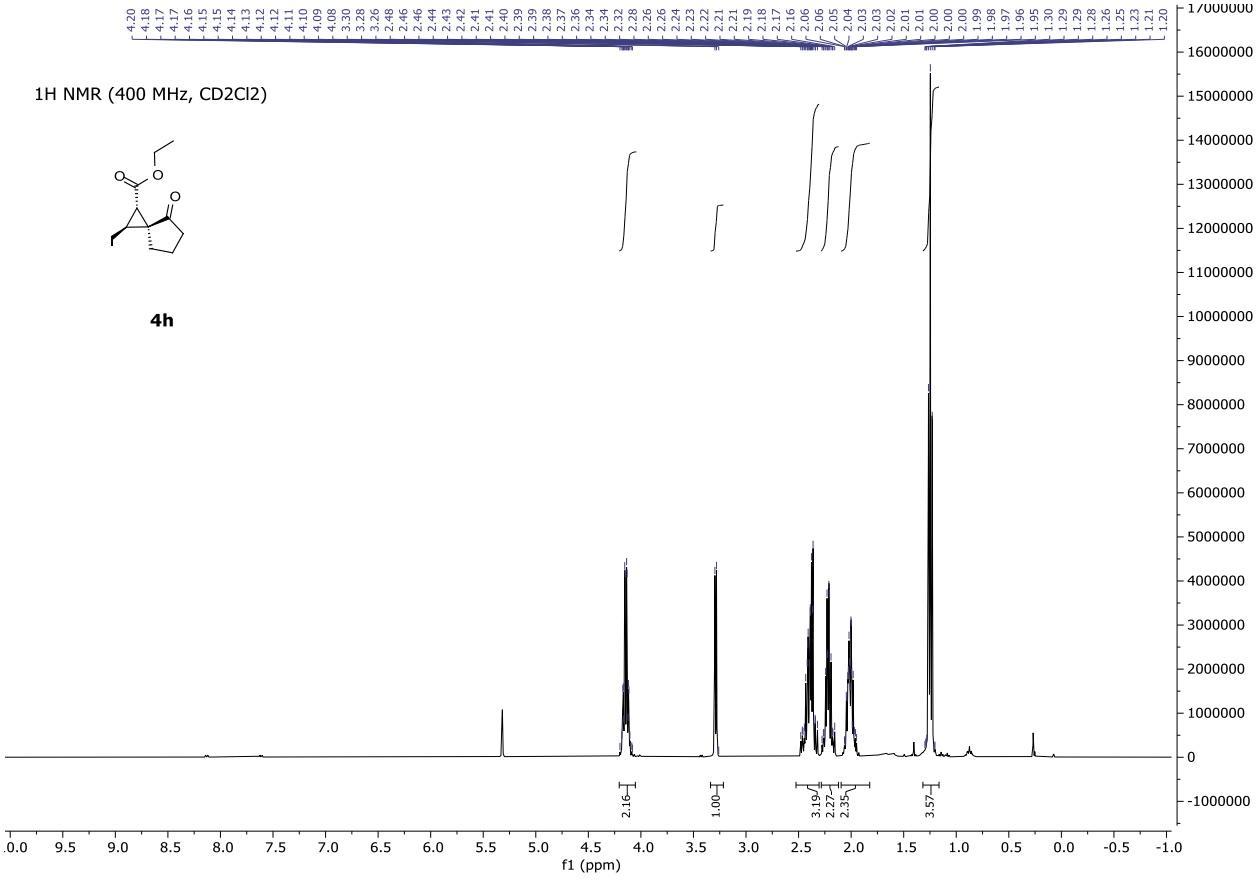
1H NMR (400 MHz, CD2Cl2)

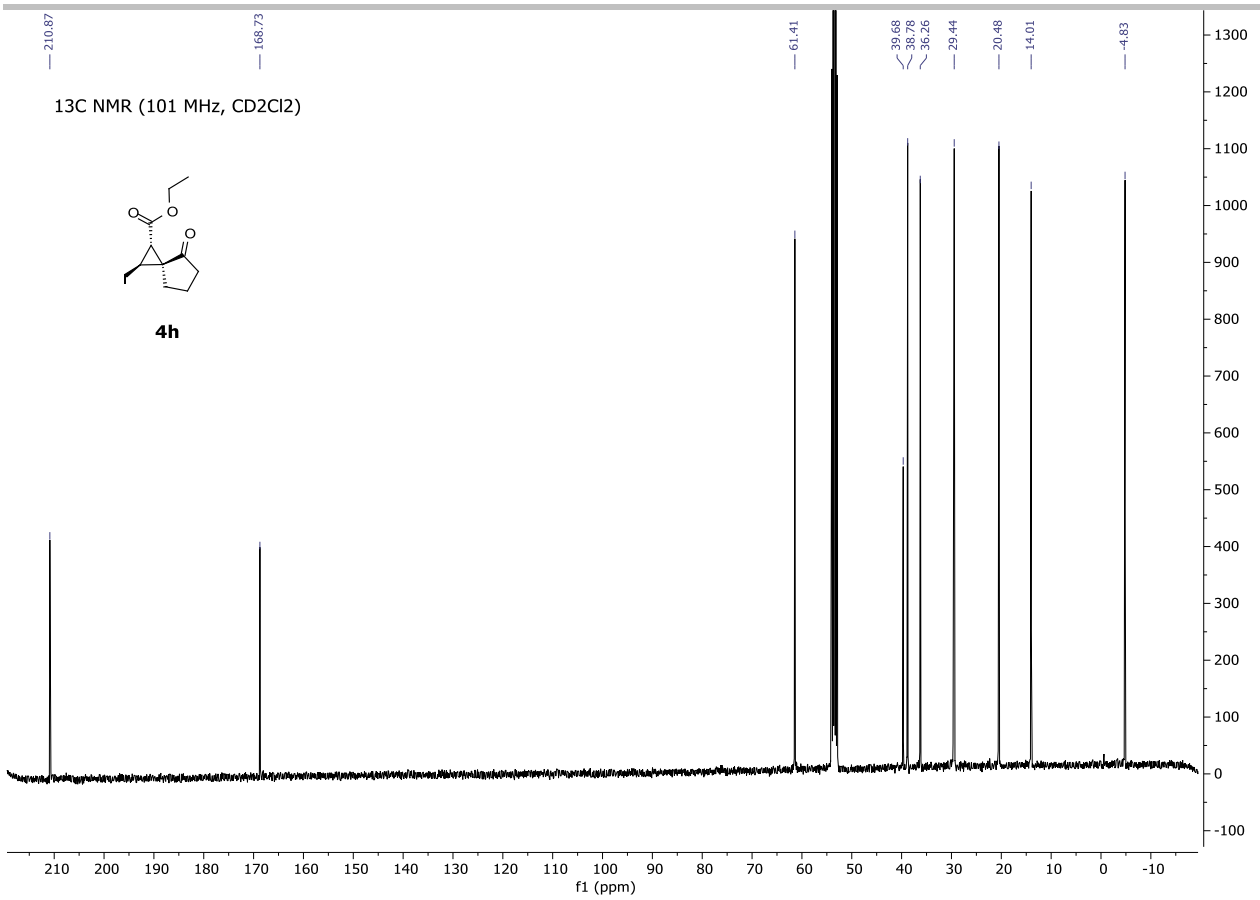
4f


213.13
39.12
37.05
33.47
32.12
28.73
20.08
9.55
13C NMR (101 MHz, CD2Cl2)
O
4f
f1 (ppm)

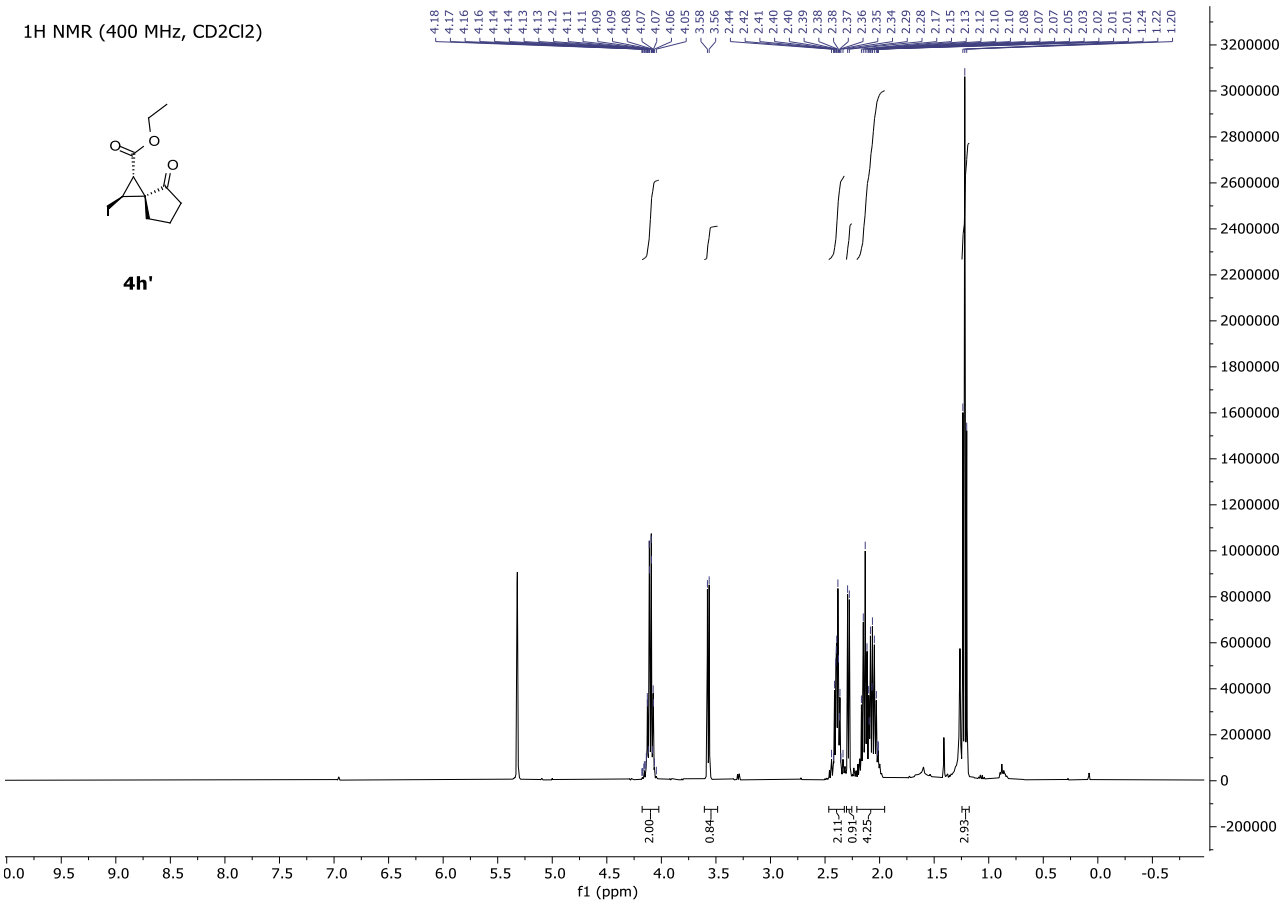

1H NMR (400 MHz, CD2Cl2)
O
4g
4.67
2.01
3.03
4.97
0.97
1.00
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
212.75
141.03
128.57
128.45
126.14
44.95
39.27
37.26
36.24
32.41
29.12
20.33
18.85
4g
f1 (ppm)

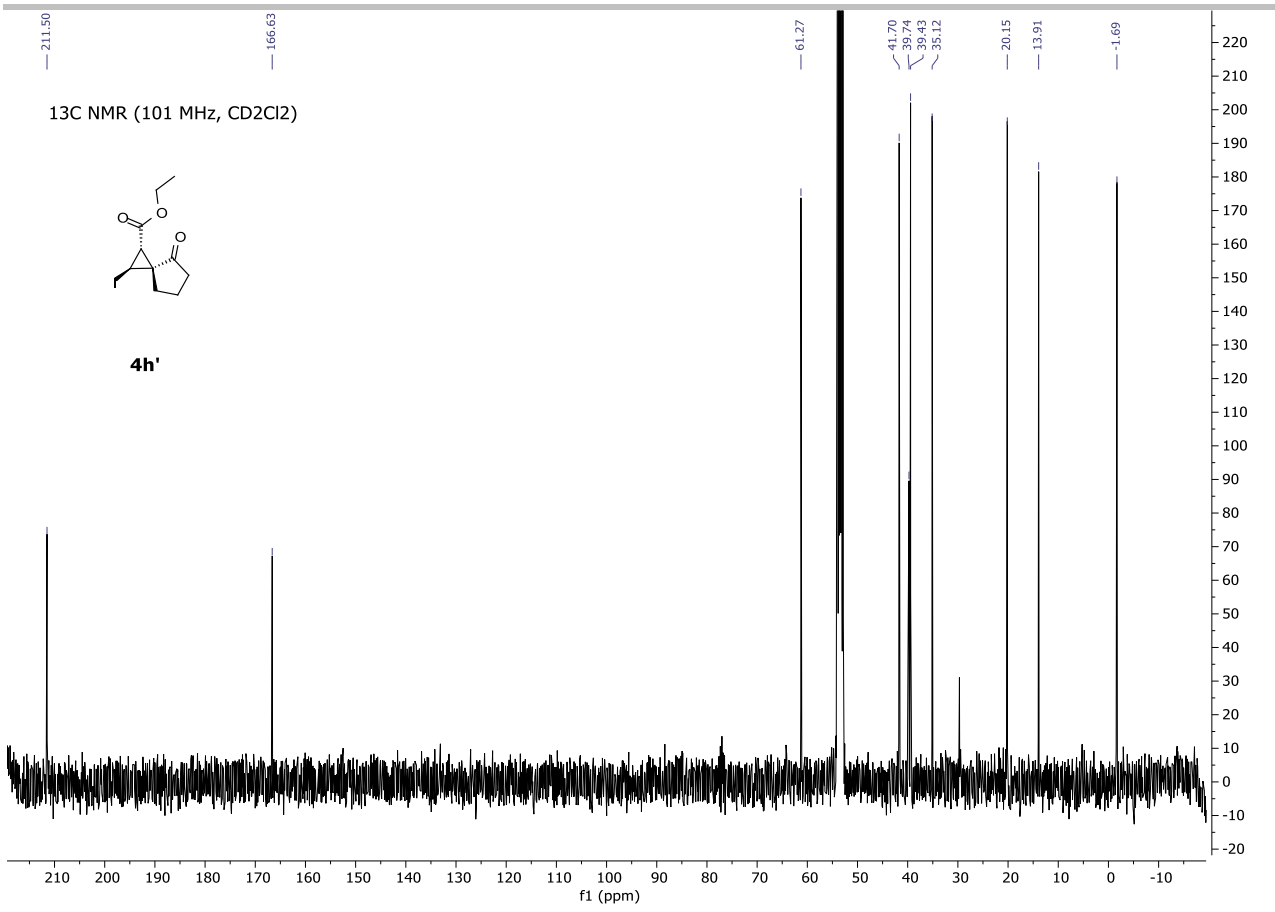

1H NMR (400 MHz, CD2Cl2)
4h
2.16
1.00
3.19
2.27
2.35
3.57
f1 (ppm)

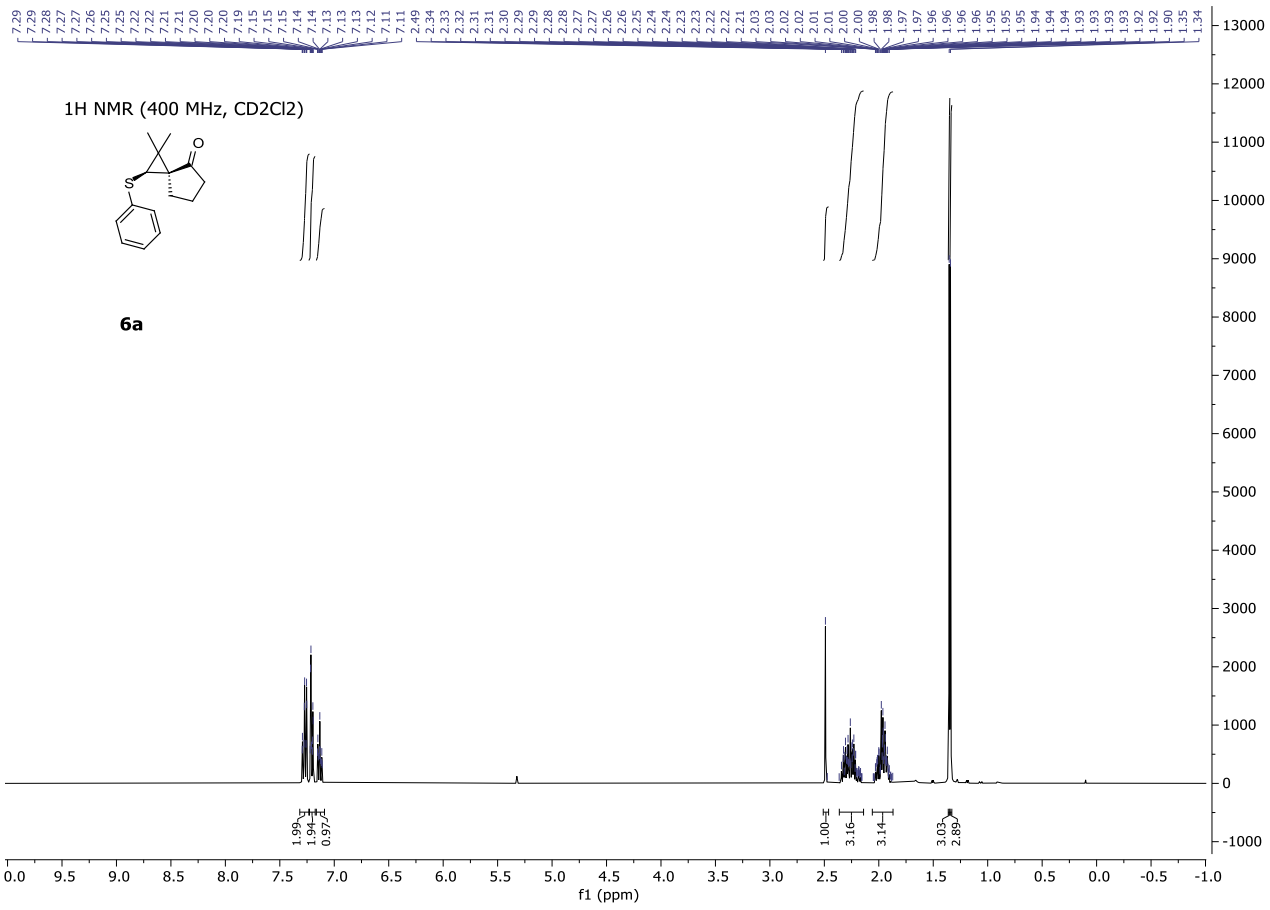

13C NMR (101 MHz, CD2Cl2)
210.87
168.73
61.41
39.68
38.78
36.26
29.44
20.48
14.01
-4.83
f1 (ppm)

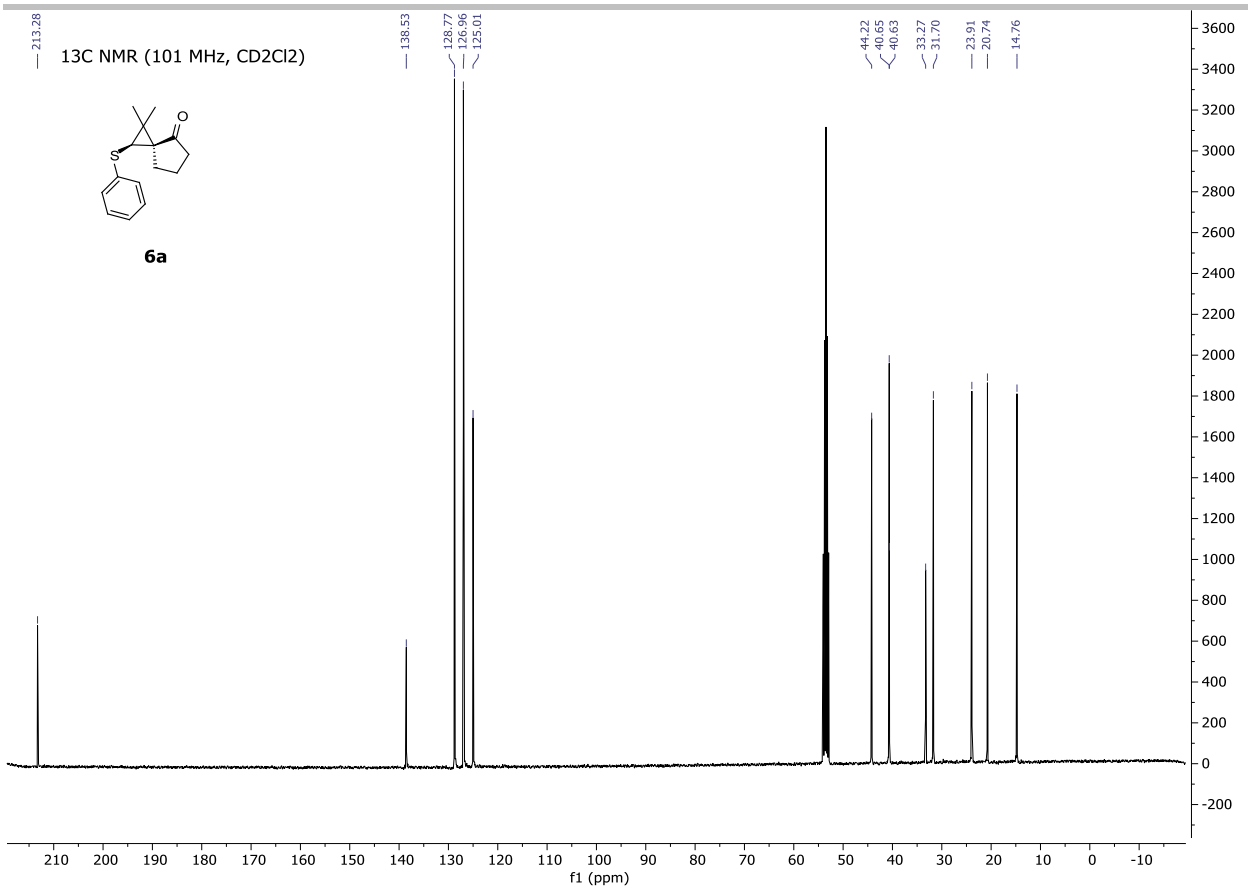
4h

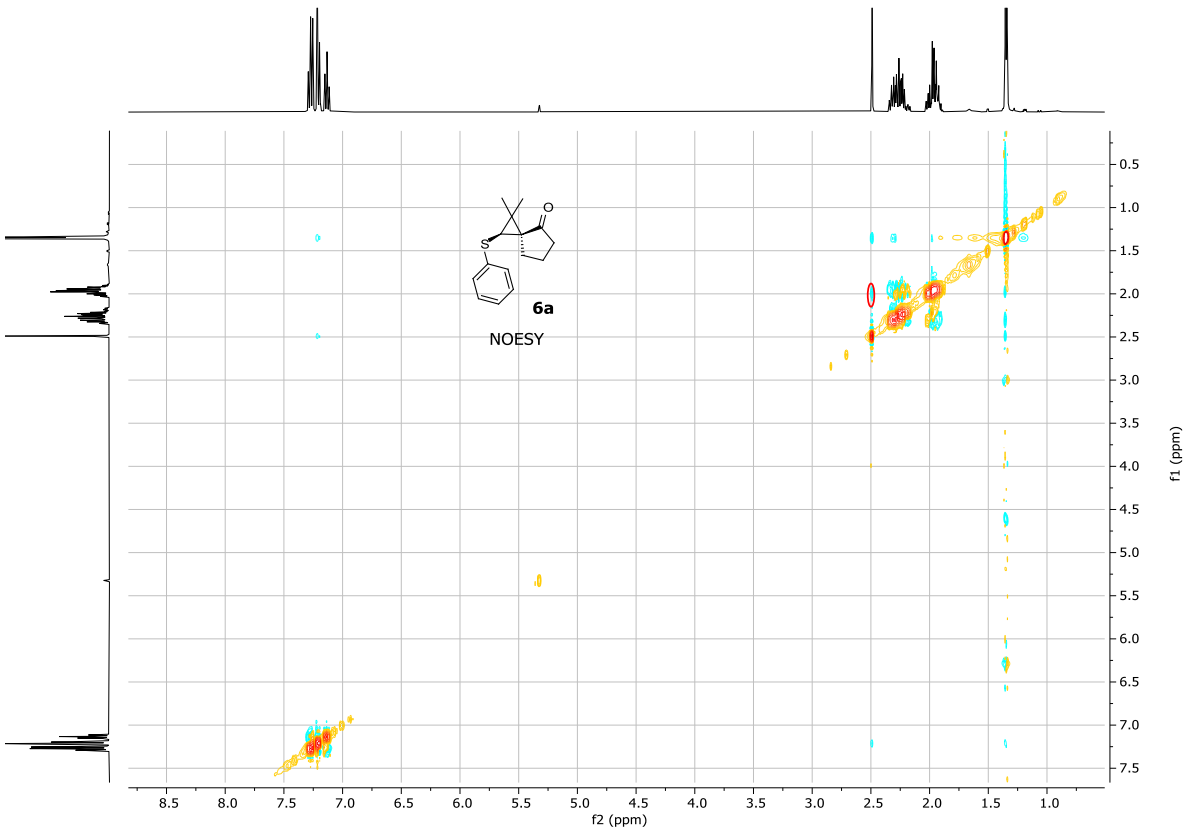

1H NMR (400 MHz, CD2Cl2)
2.00
0.84
2.11
0.91
4.25
2.93
f1 (ppm)

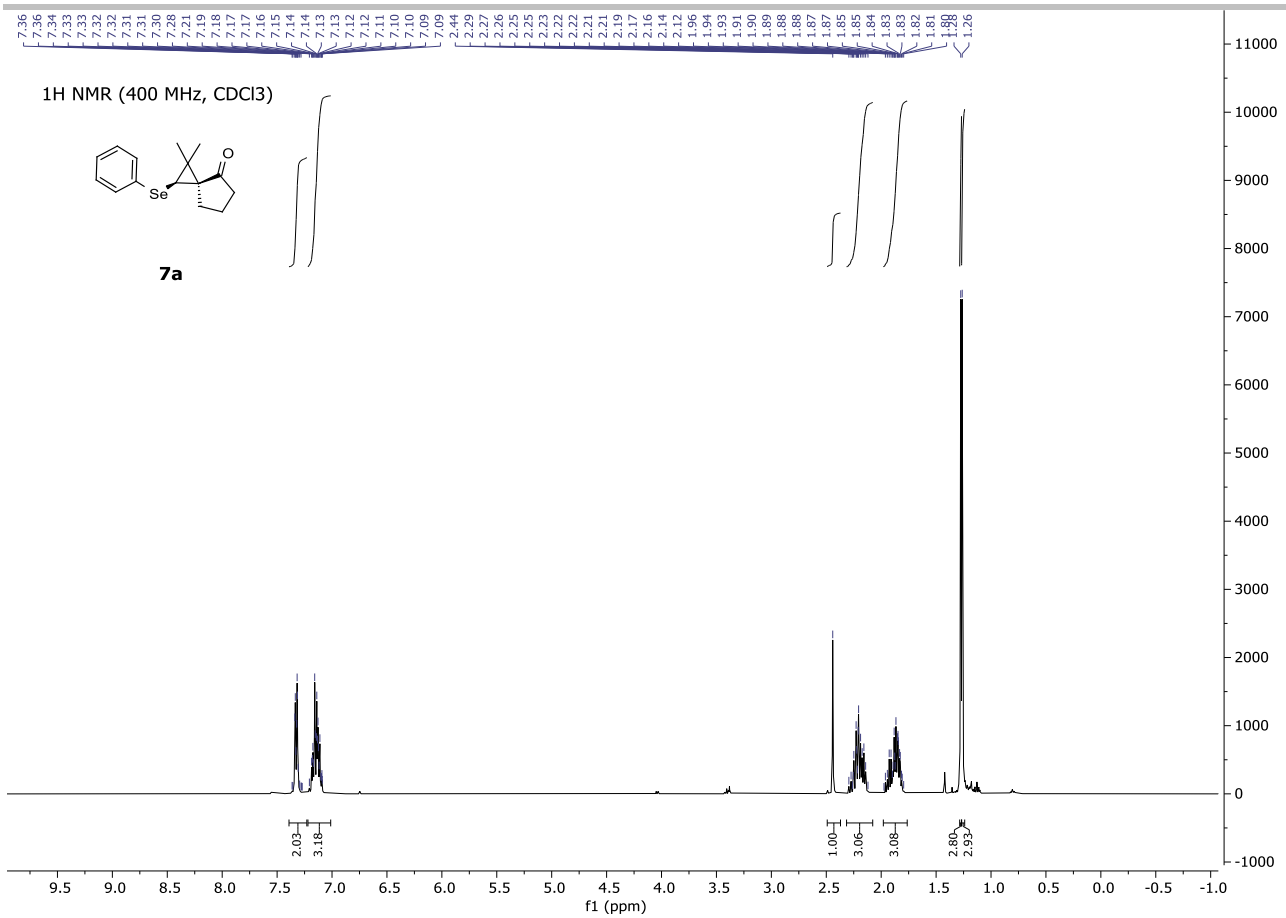
4h'

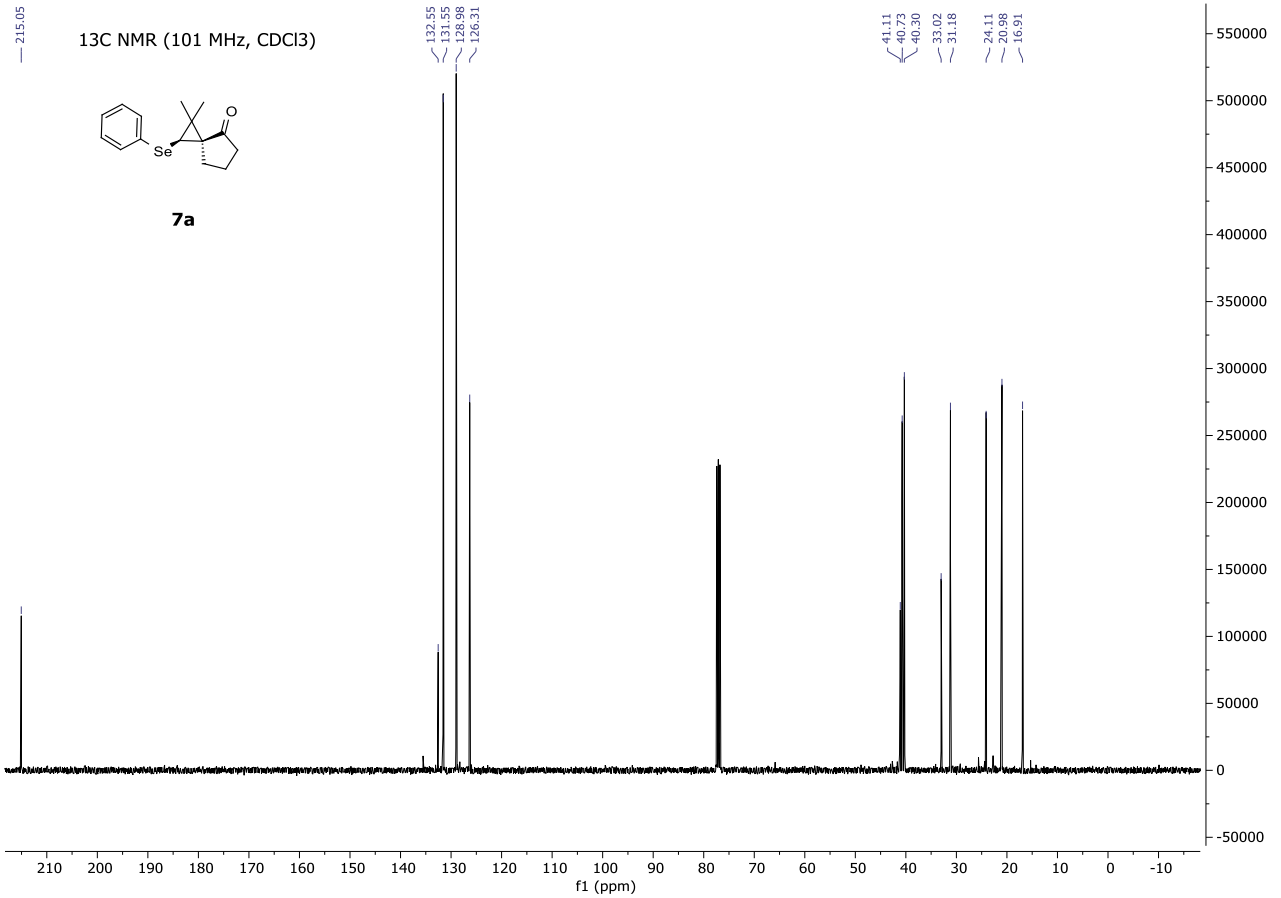

211.50
166.63
61.27
41.70
39.74
39.43
35.12
20.15
13.91
-1.69
13C NMR (101 MHz, CD2Cl2)
4h'
f1 (ppm)

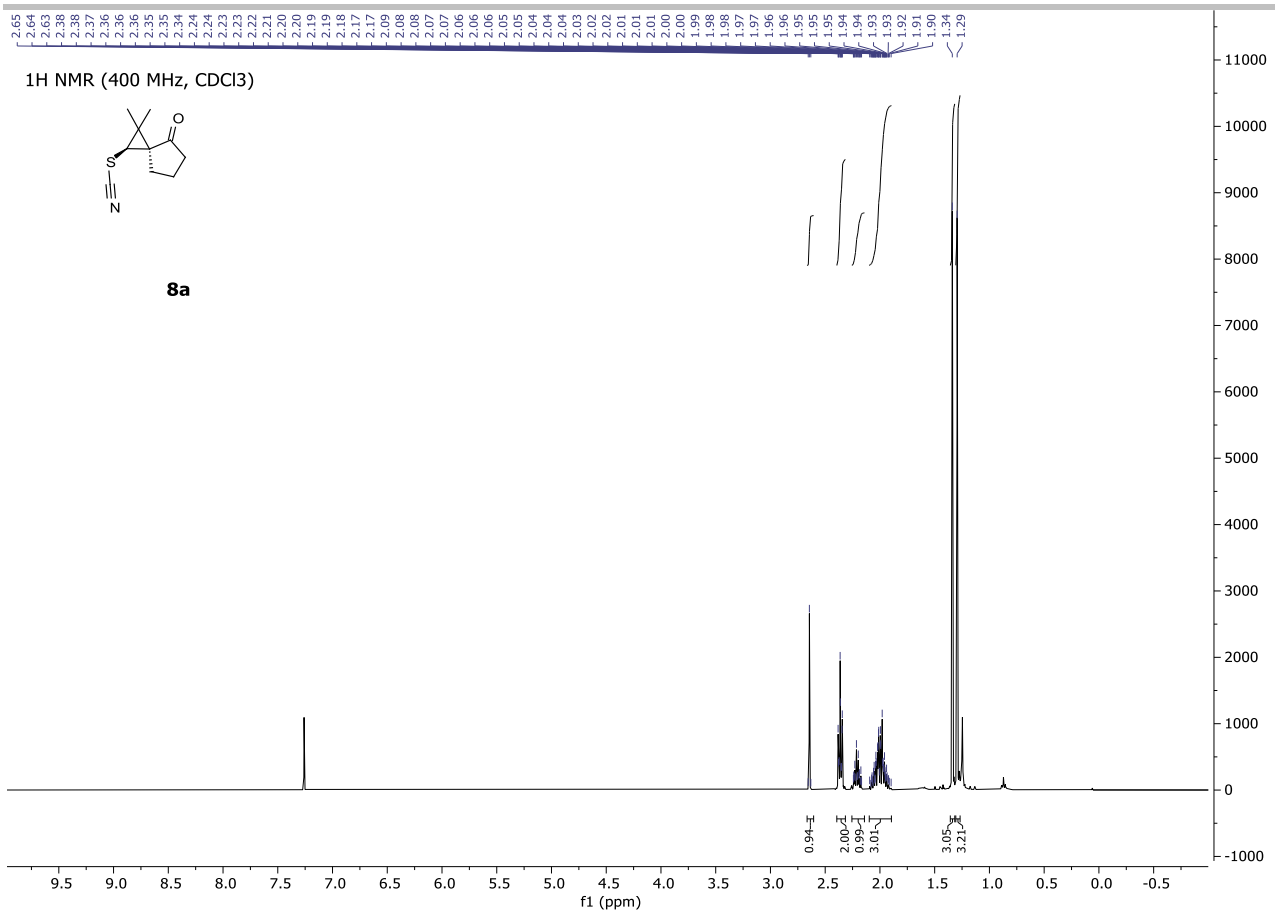

1H NMR (400 MHz, CD2Cl2)
6a
1.99
1.94
0.97
1.00
3.16
3.14
3.03
2.89
f1 (ppm)

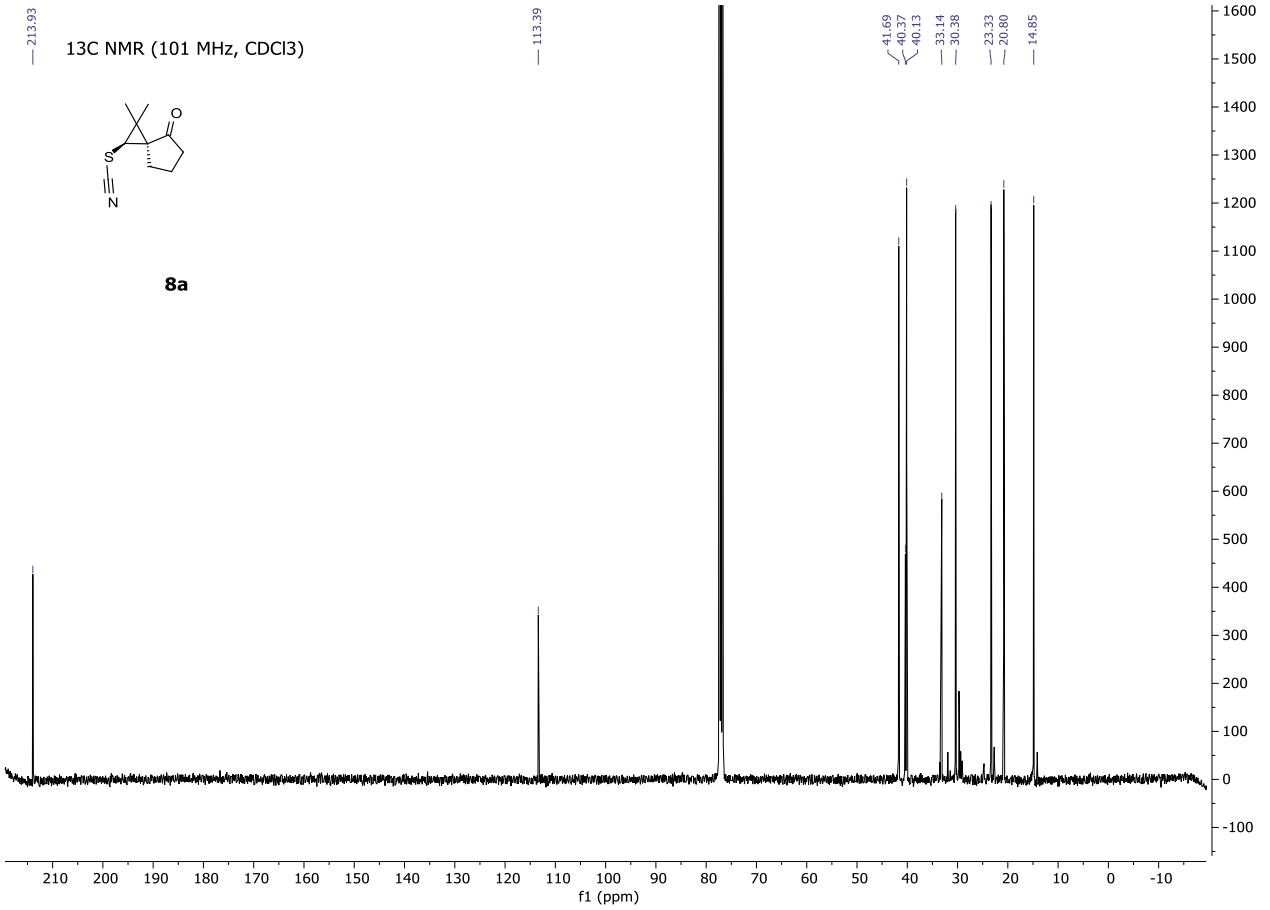

13C NMR (101 MHz, CD2Cl2)
213.28
138.53
128.77
126.96
125.01
44.22
40.65
40.63
33.27
31.70
23.91
20.74
14.76
6a
f1 (ppm)


6a
NOESY
f2 (ppm)
f1 (ppm)

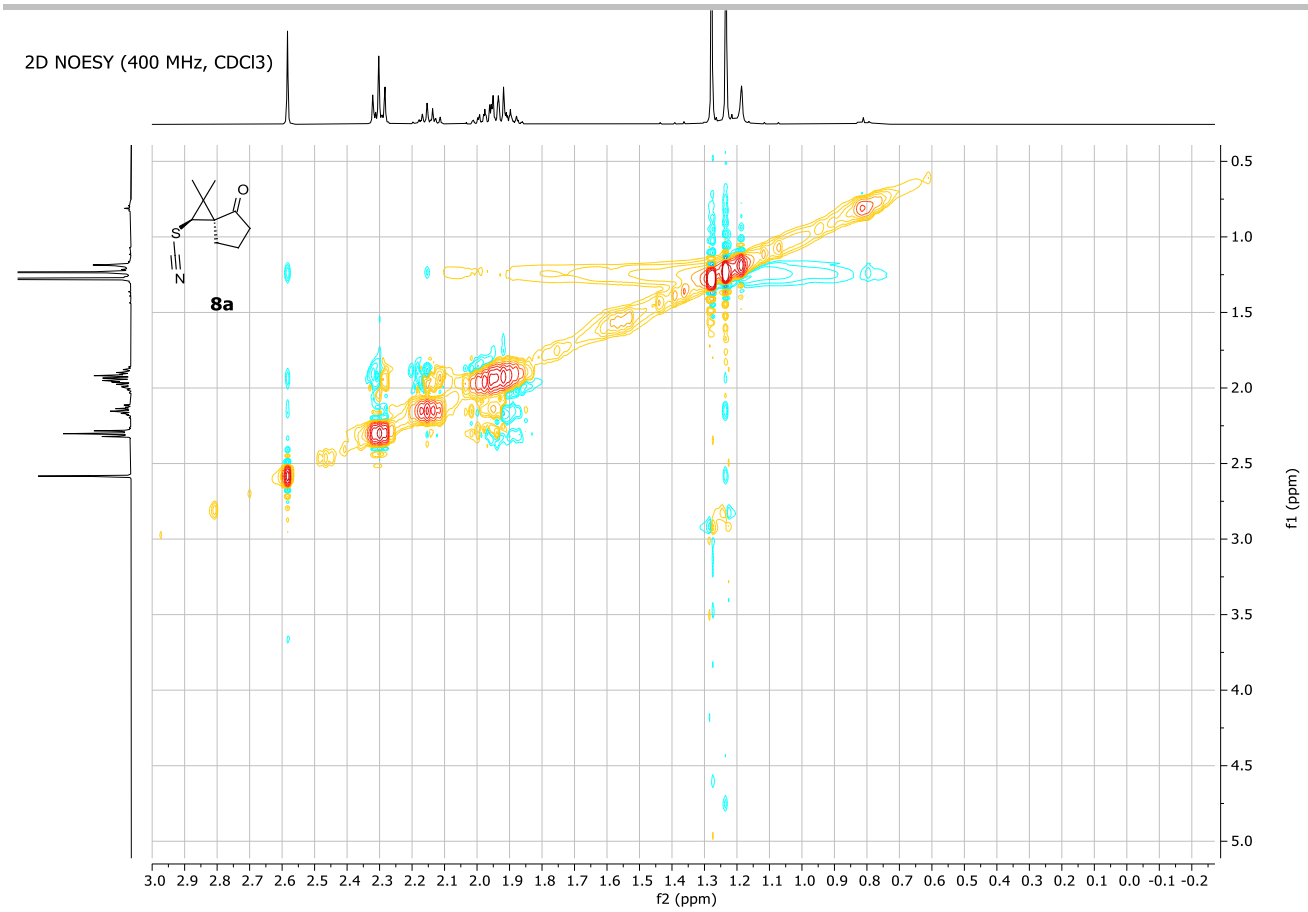

1H NMR (400 MHz, CDCl3)
Se
O
7a
f1 (ppm)


13C NMR (101 MHz, CDCl3)
Se
O
7a
f1 (ppm)

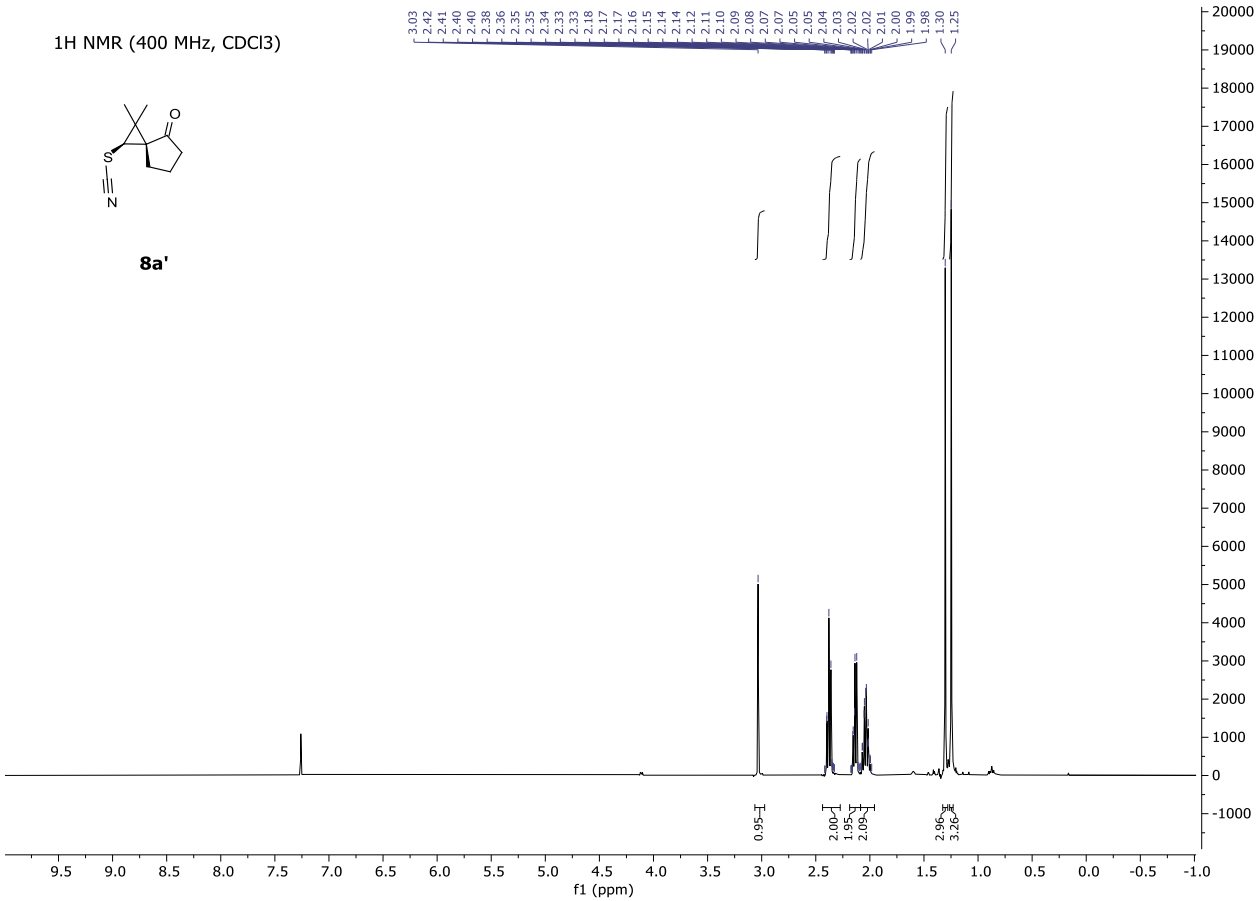

1H NMR (400 MHz, CDCl3)
8a
f1 (ppm)

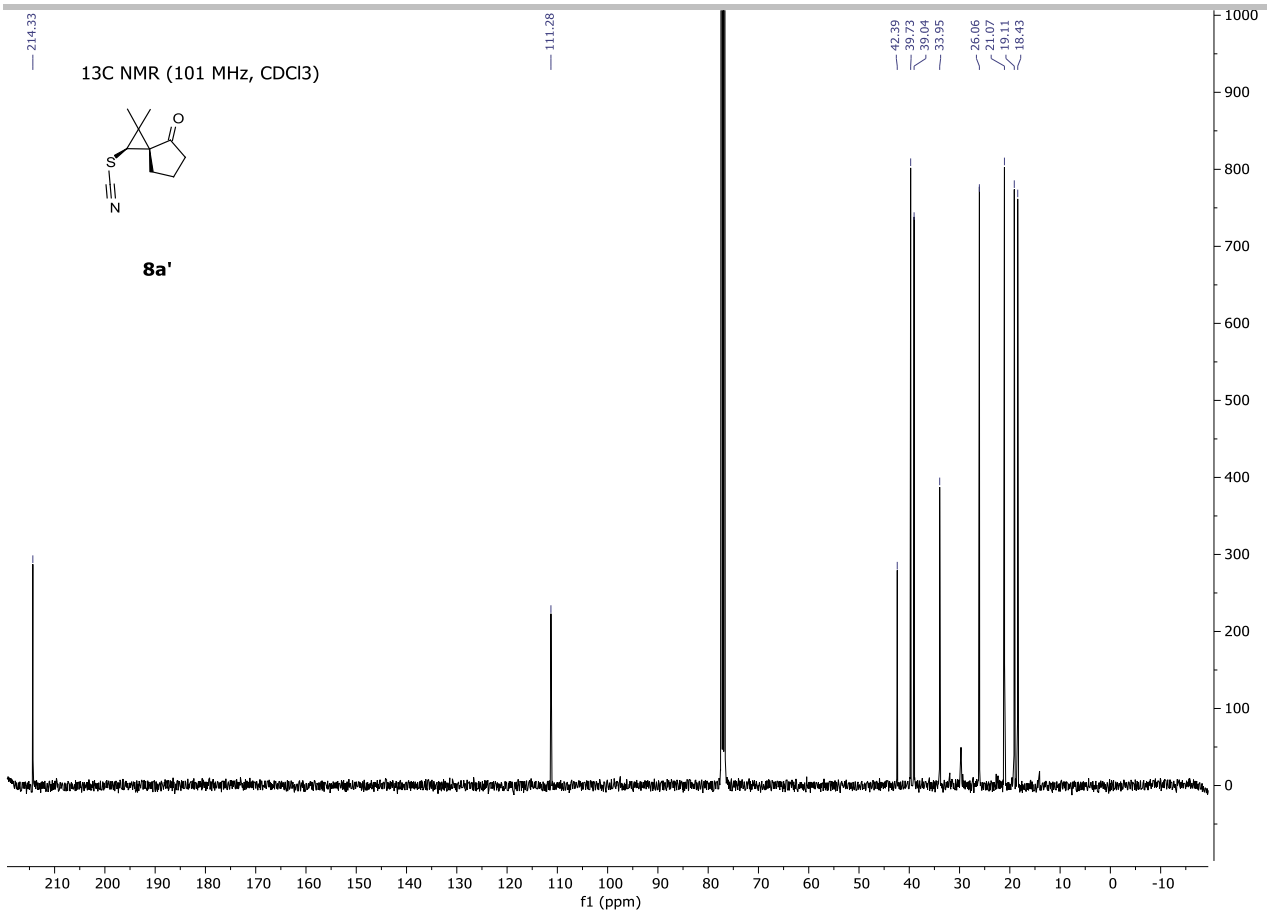

13C NMR (101 MHz, CDCl3)
8a
f1 (ppm)

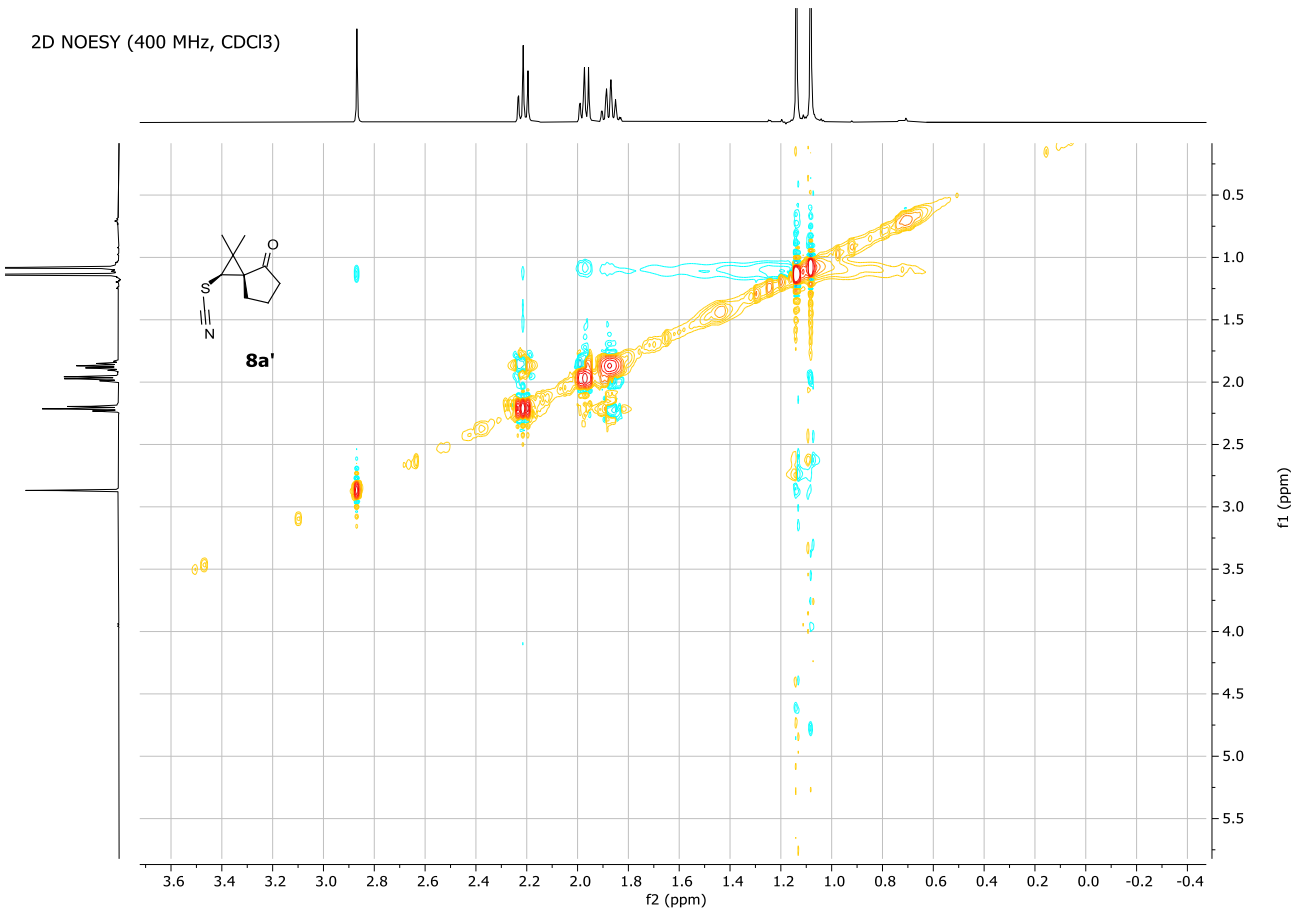
2D NOESY (400 MHz, CDCl3)



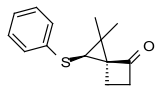
1H NMR (400 MHz, CDCl3)




13C NMR (101 MHz, CDCl3)
214.33
111.28
42.39
39.73
39.04
33.95
26.06
21.07
19.11
18.43
8a'
f1 (ppm)

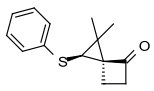

2D NOESY (400 MHz, CDCl3)
8a'
f2 (ppm)
f1 (ppm)

1H NMR (400 MHz, CD_2Cl_2)

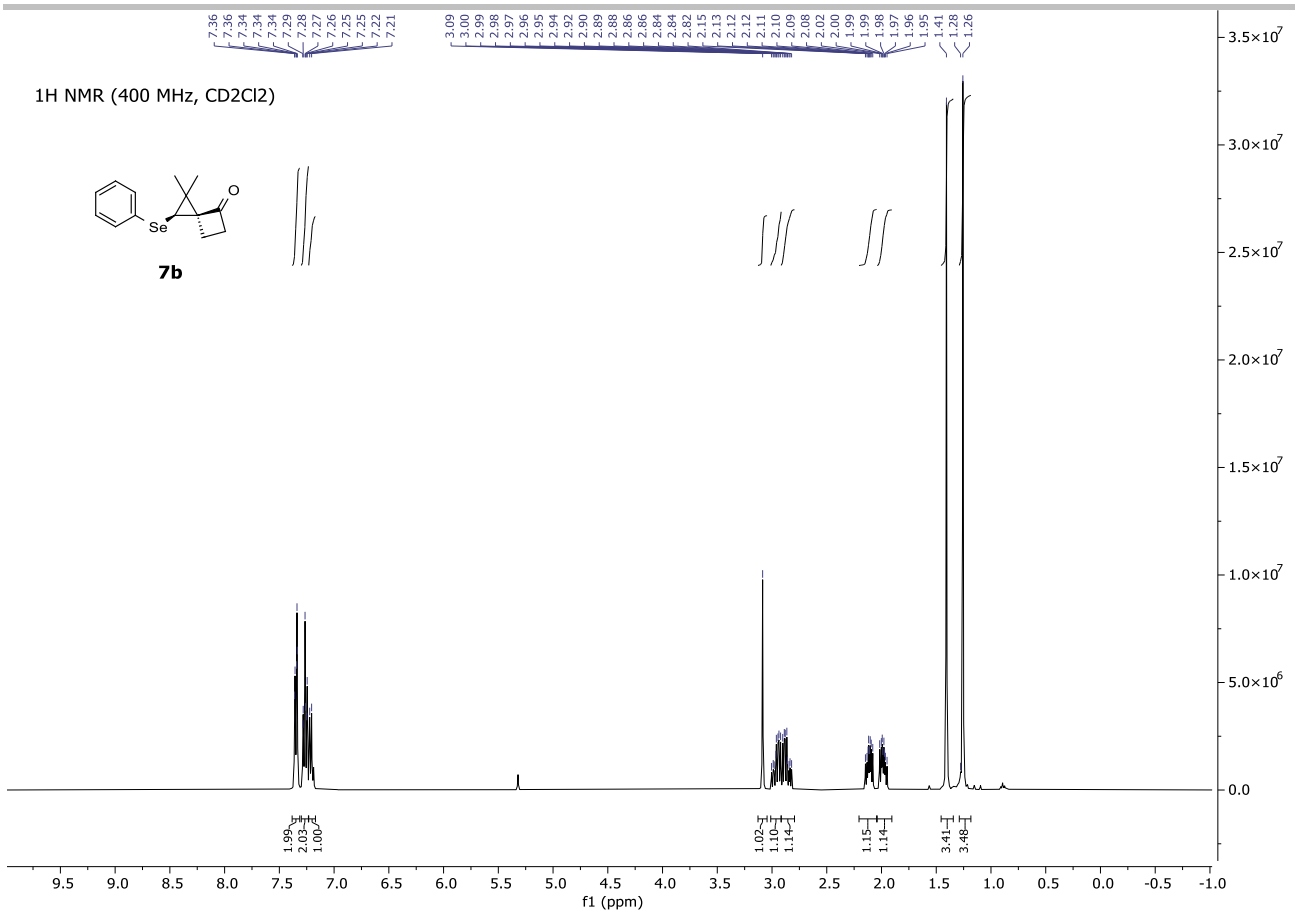


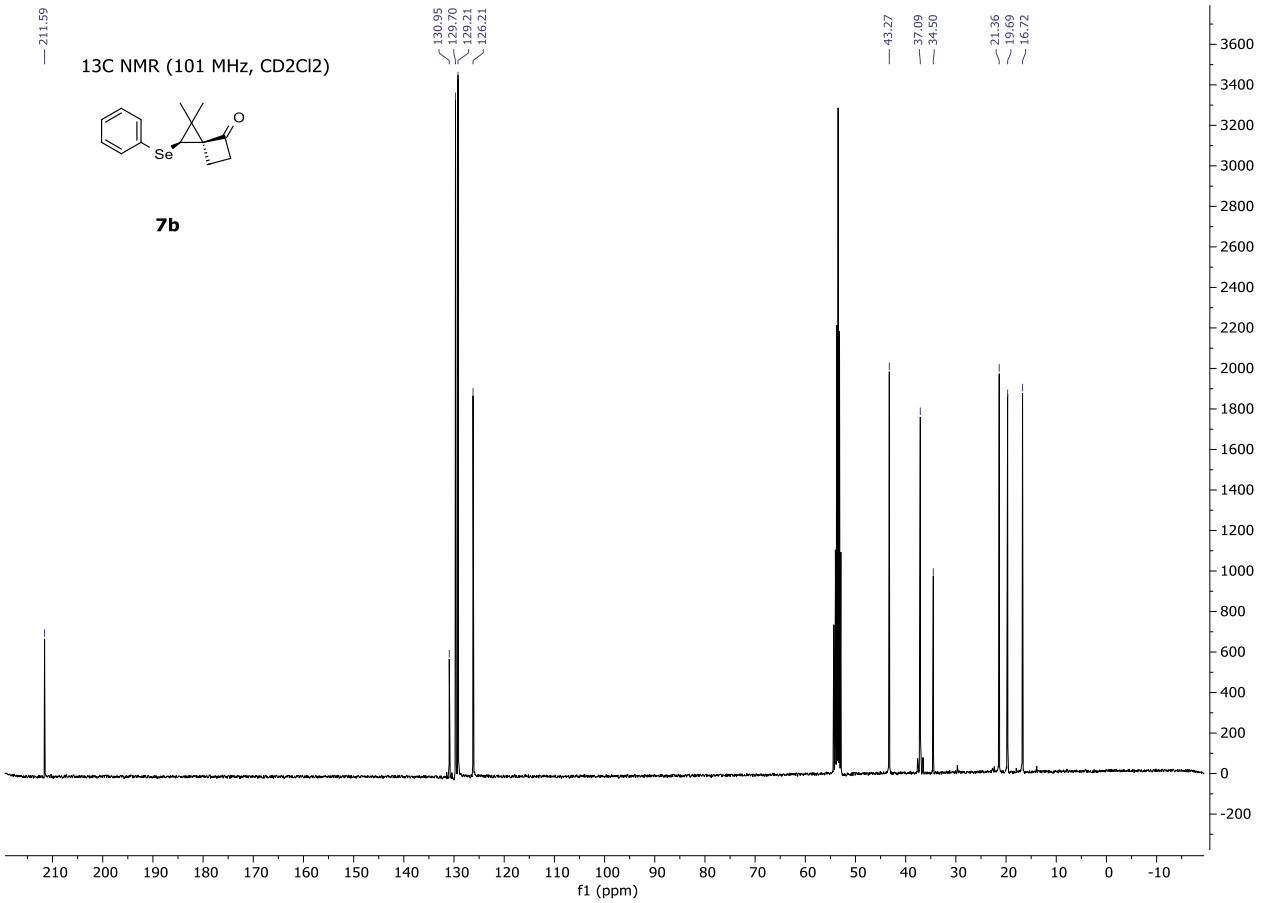
6b

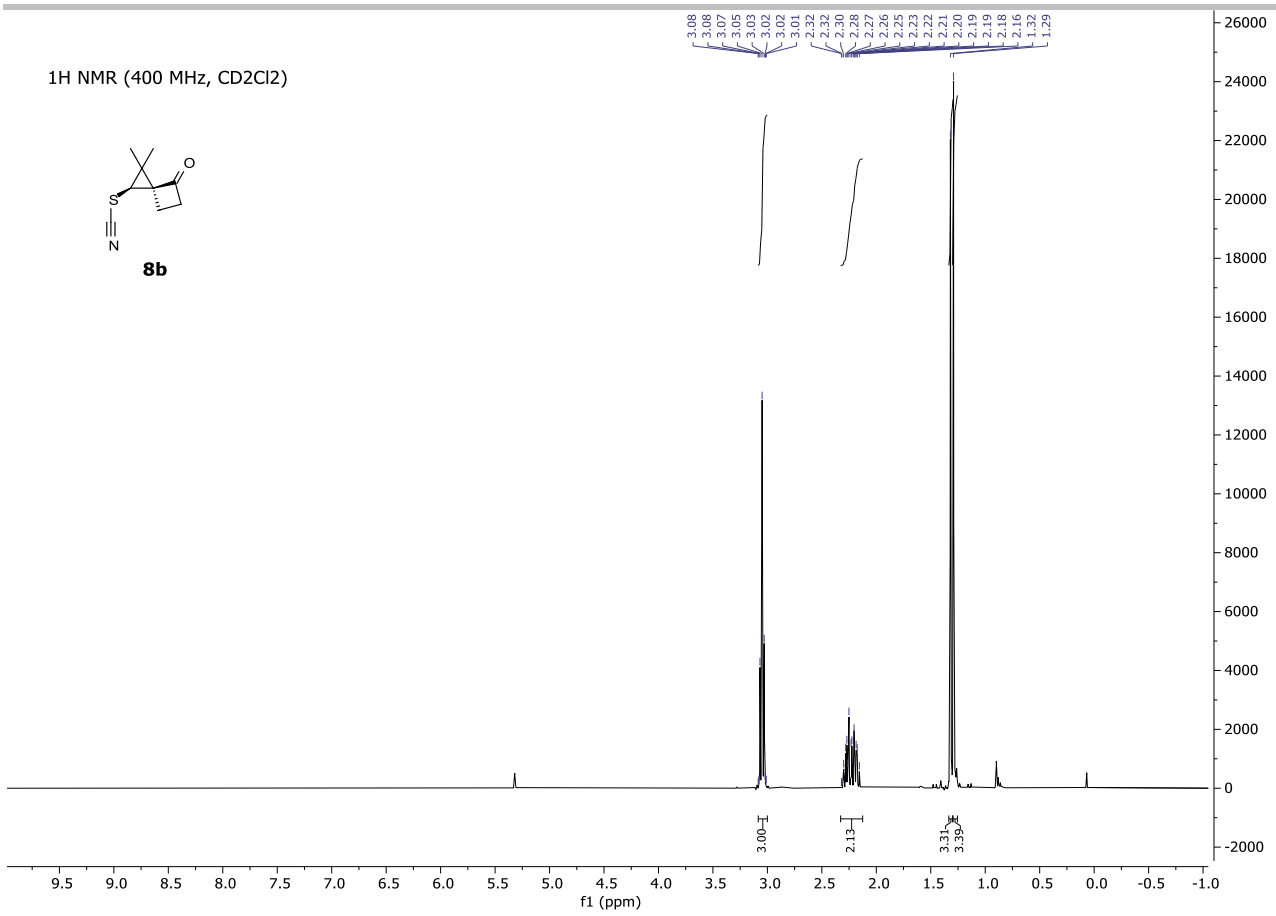
13C NMR (101 MHz, CD_2Cl_2)

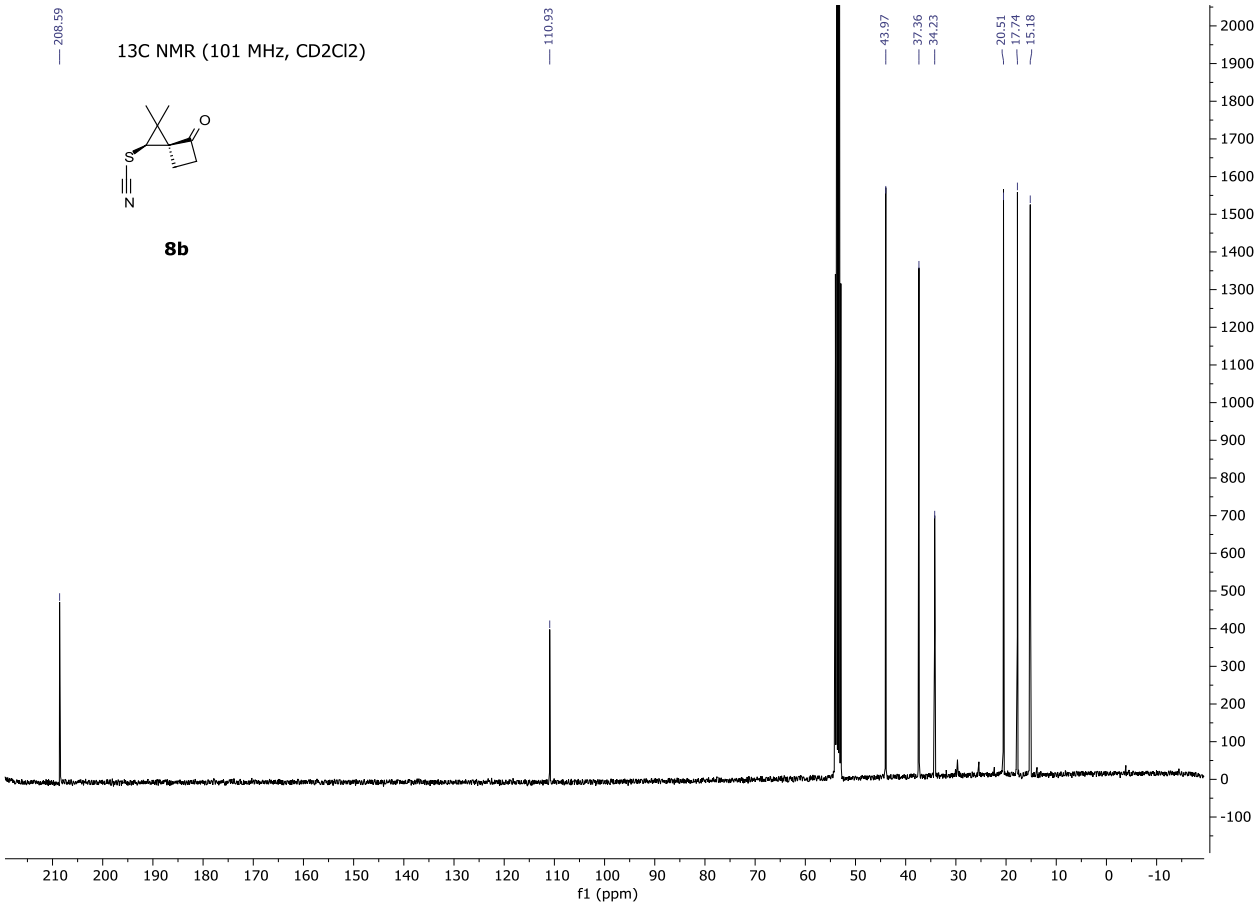


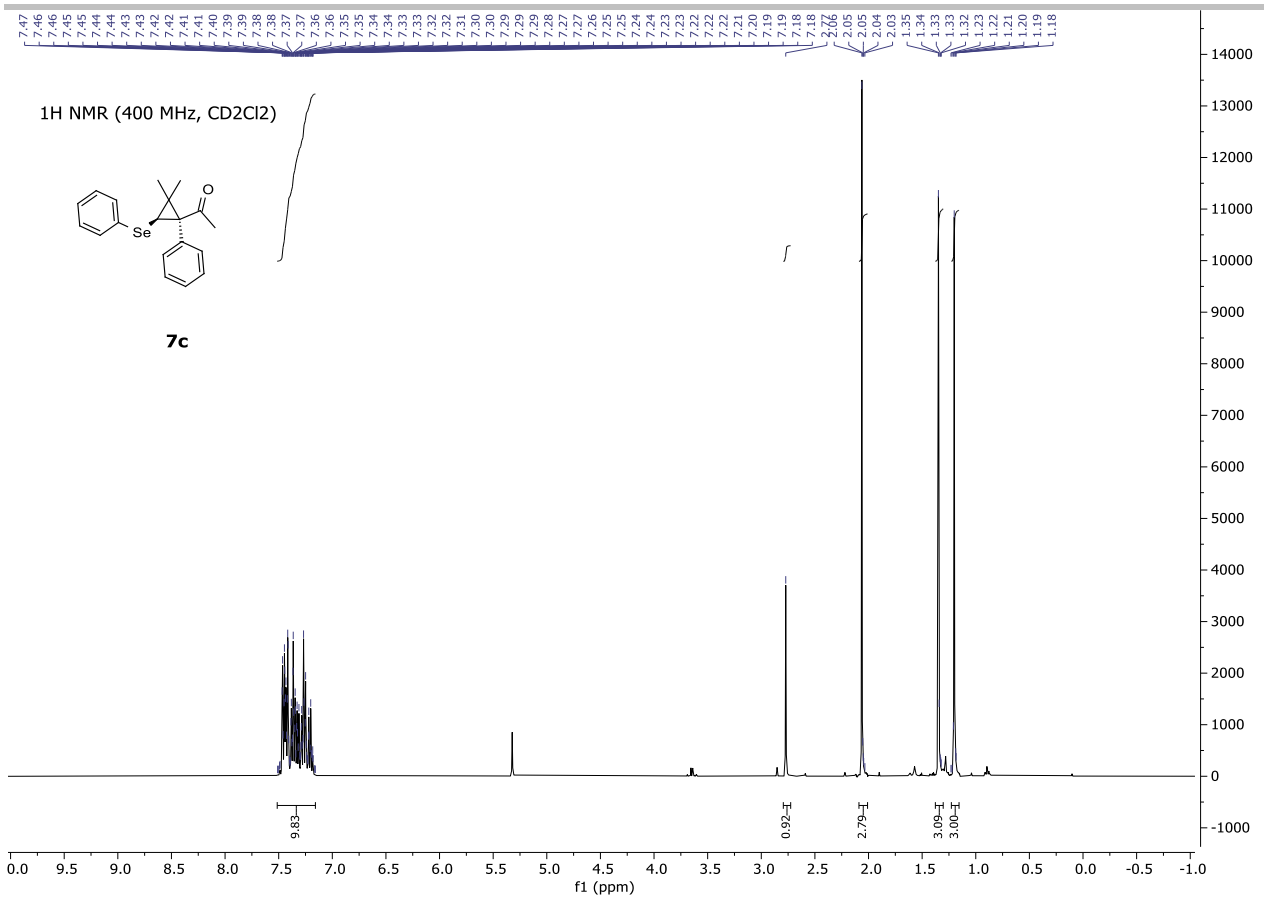
6b

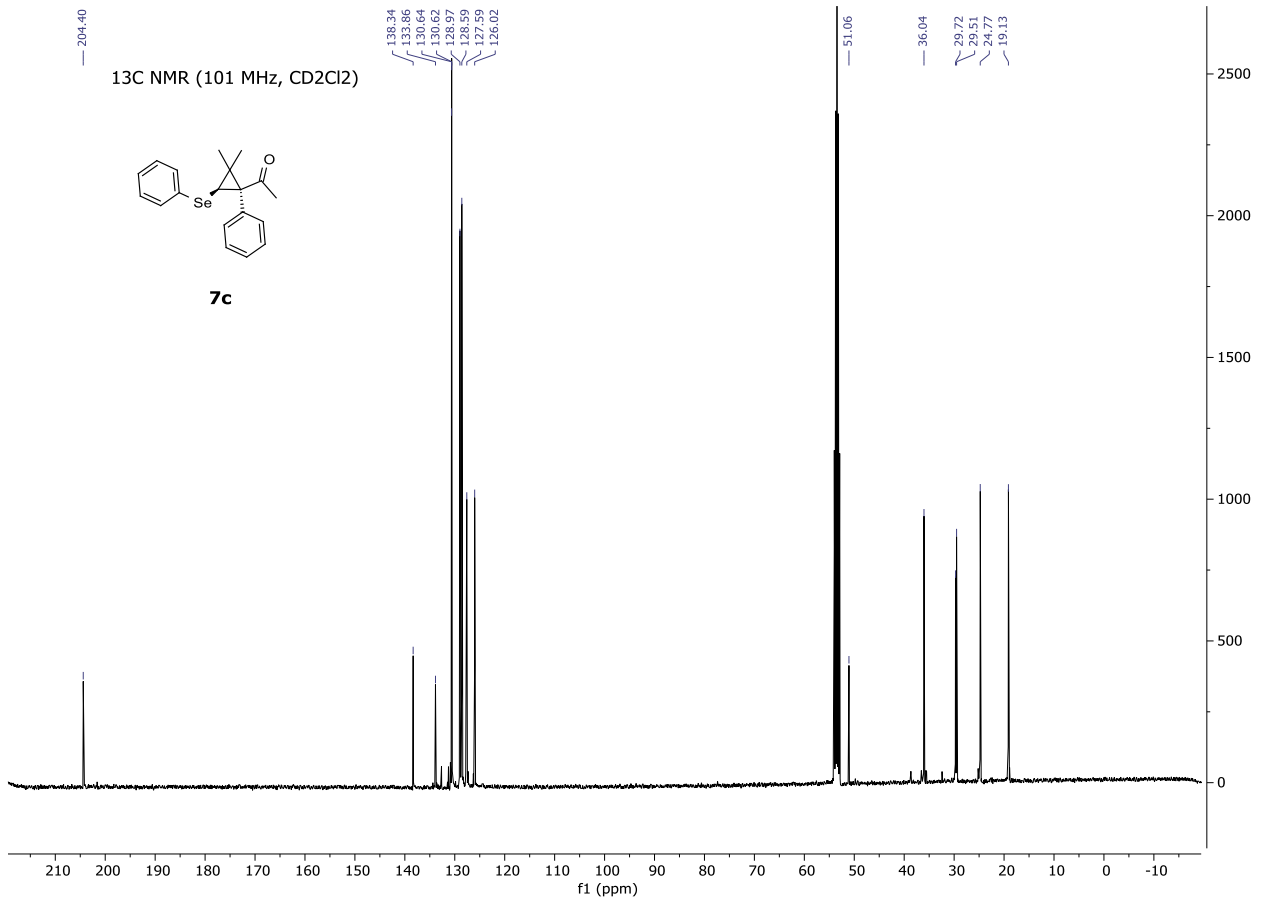

1H NMR (400 MHz, CD2Cl2)
7b
f1 (ppm)

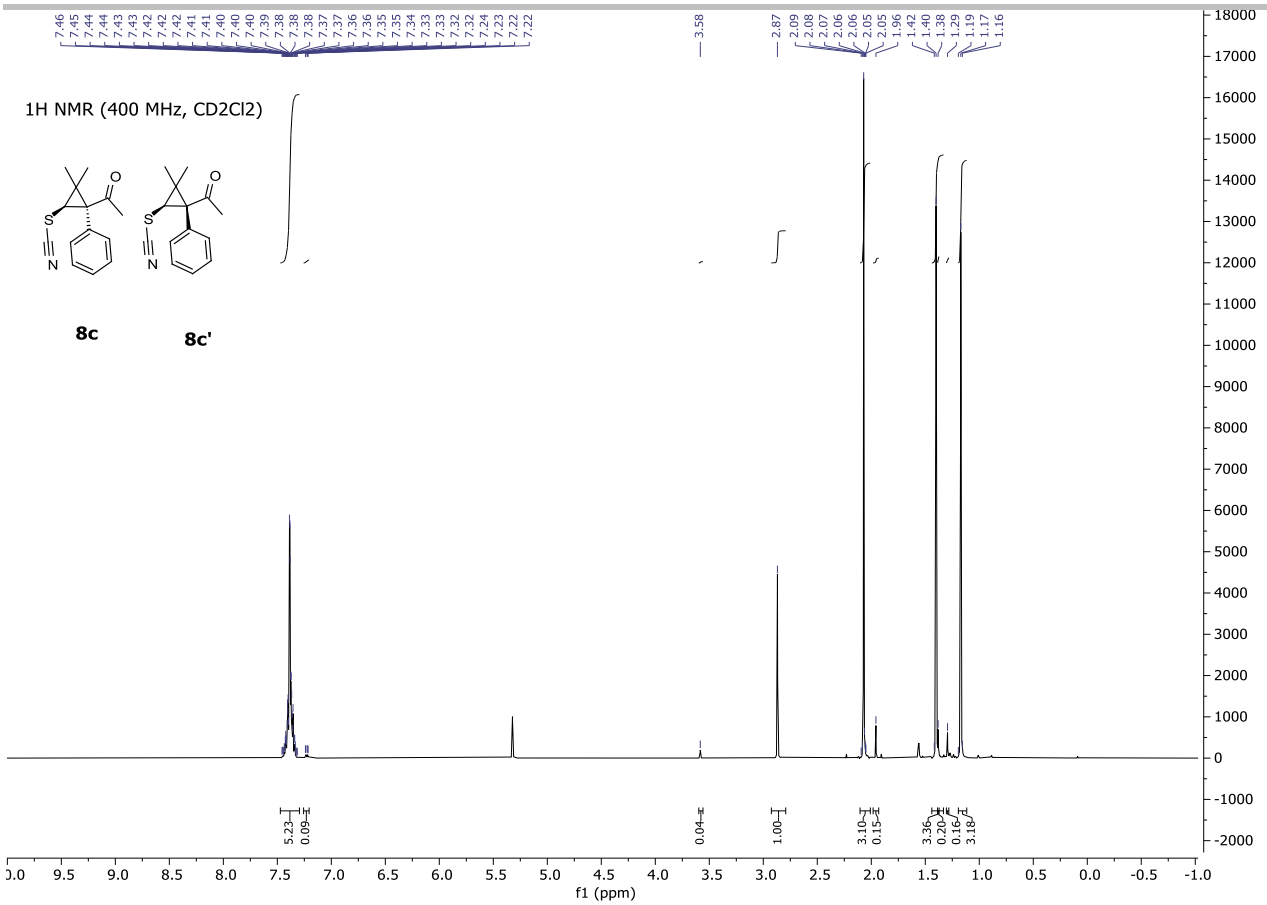

13C NMR (101 MHz, CD2Cl2)
7b
f1 (ppm)

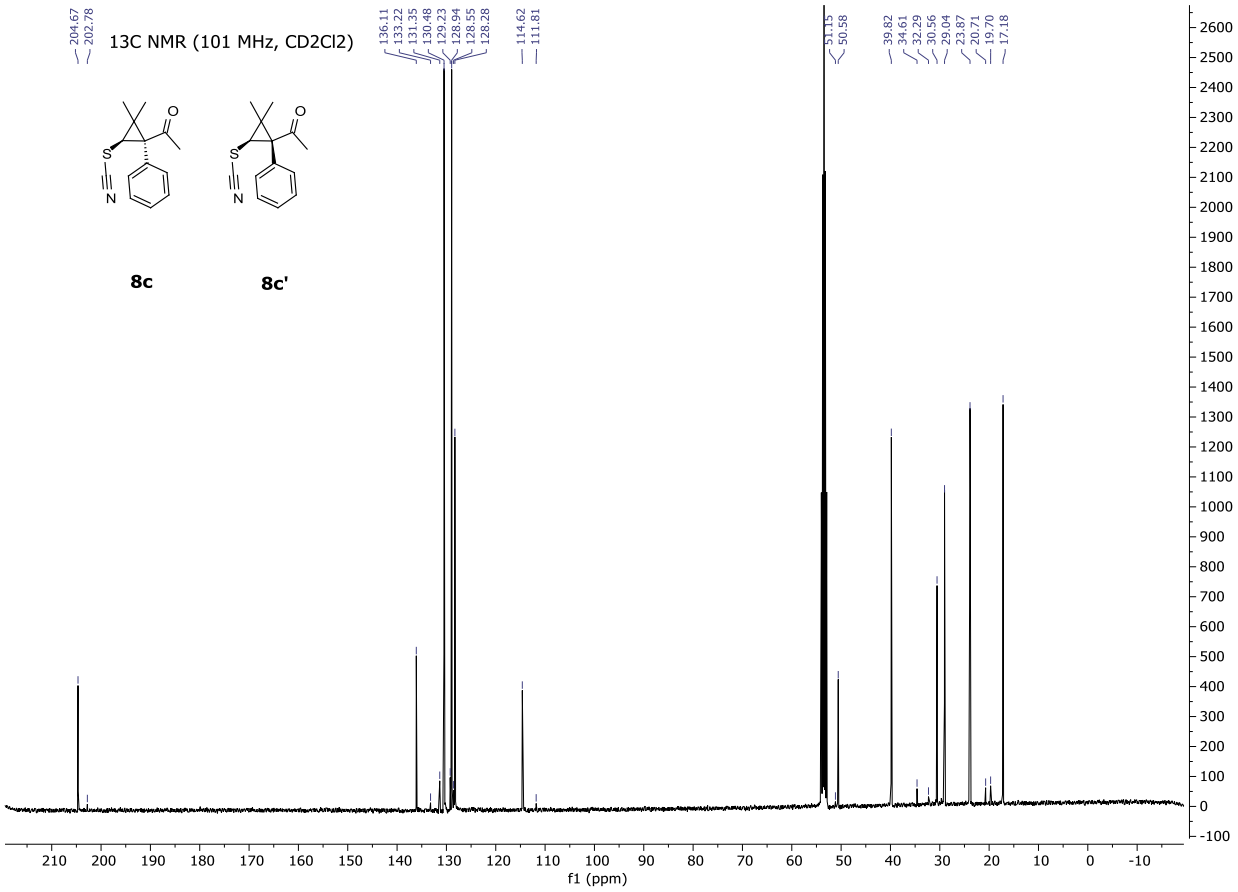

1H NMR (400 MHz, CD2Cl2)
8b
f1 (ppm)

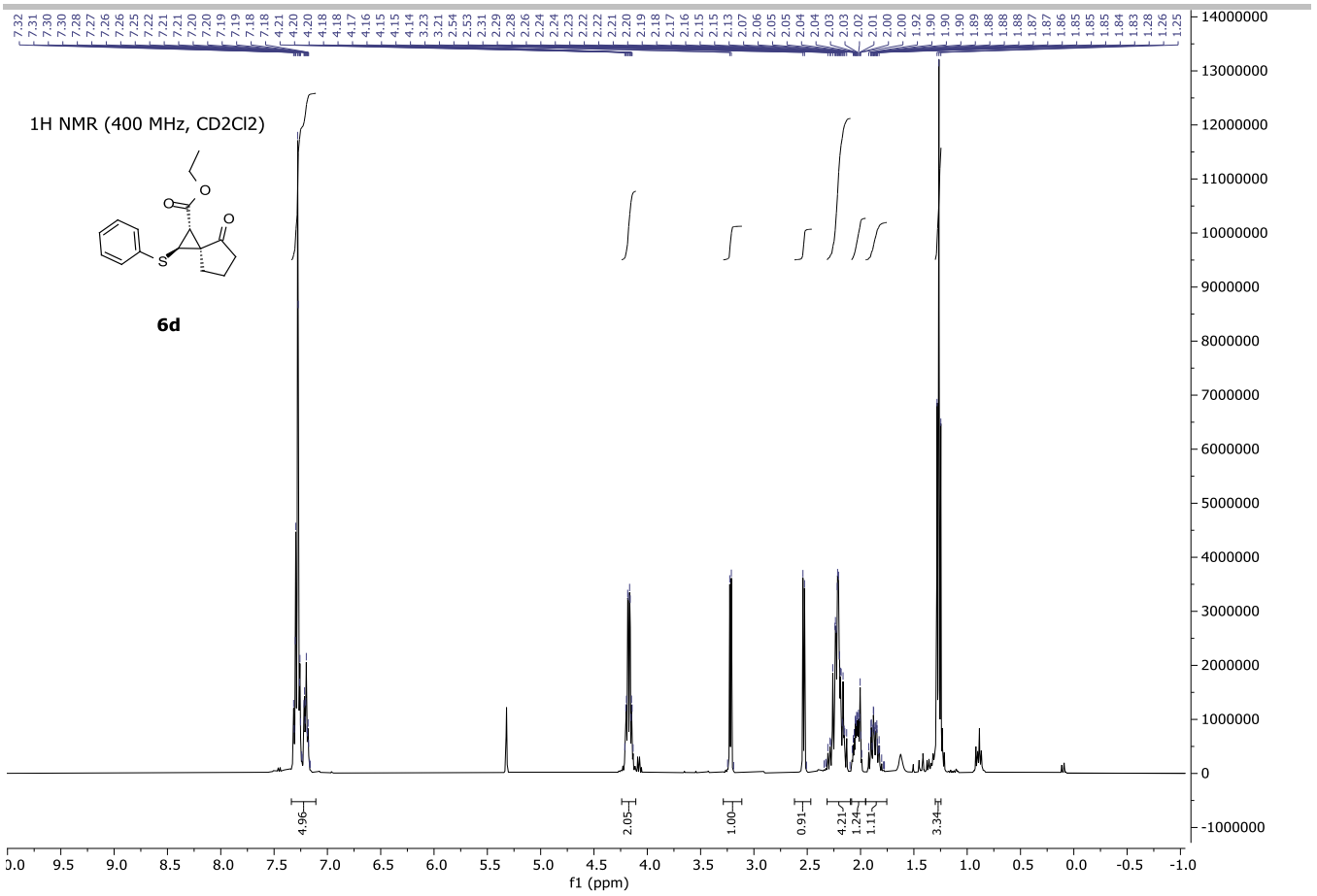

13C NMR (101 MHz, CD2Cl2)
8b
f1 (ppm)

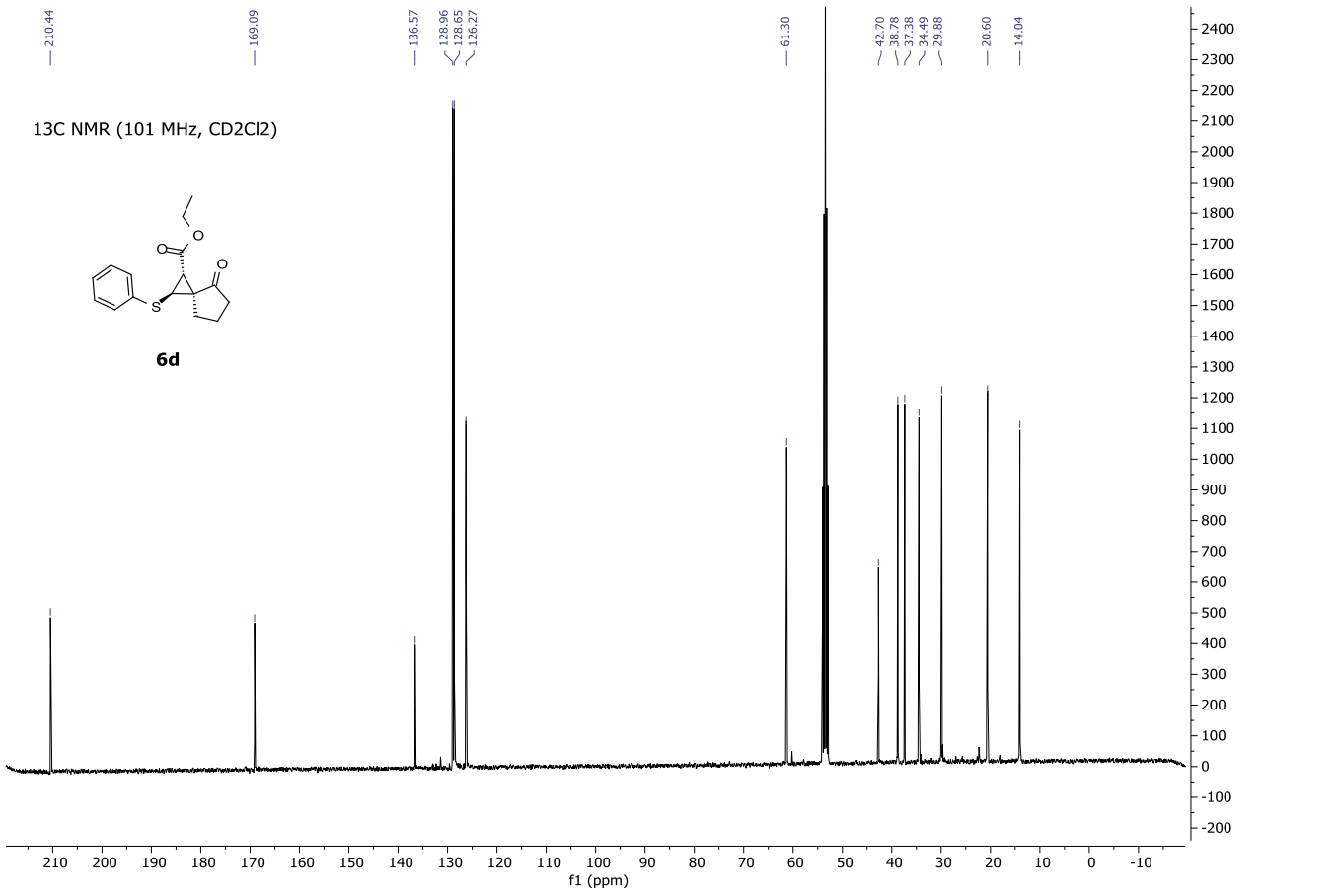

1H NMR (400 MHz, CD2Cl2)
7c
f1 (ppm)

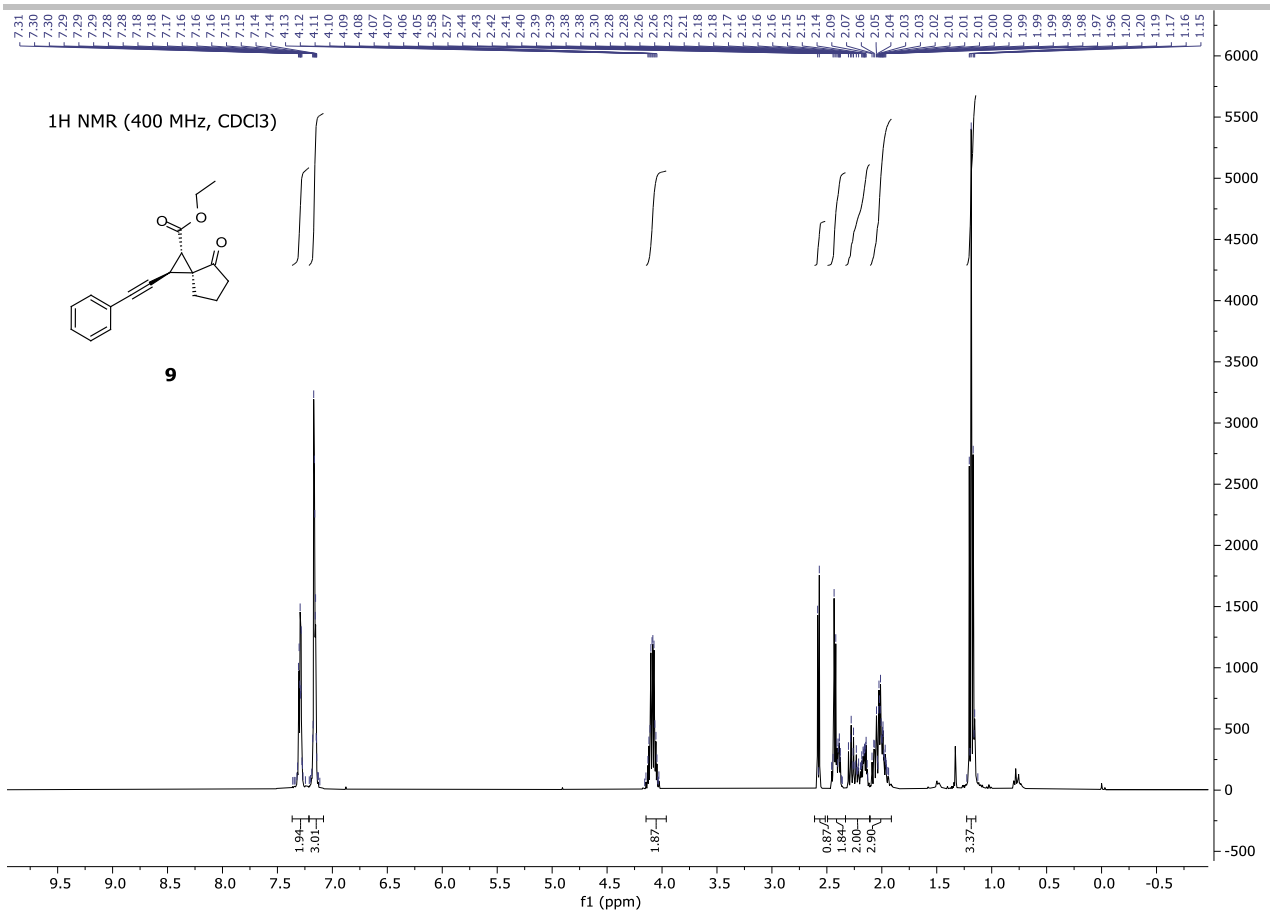

13C NMR (101 MHz, CD2Cl2)
7c
f1 (ppm)

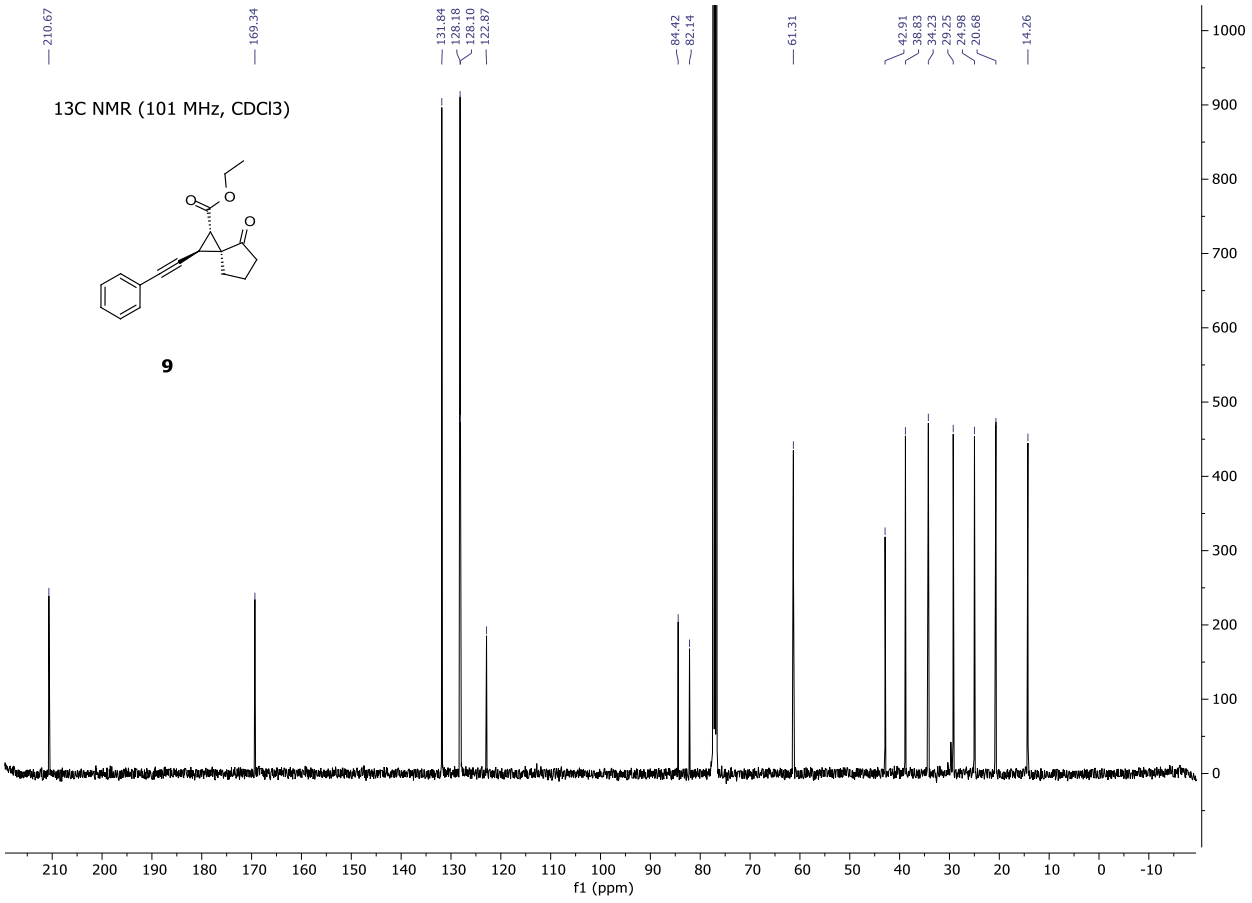

1H NMR (400 MHz, CD2Cl2)
8c
8c'
f1 (ppm)

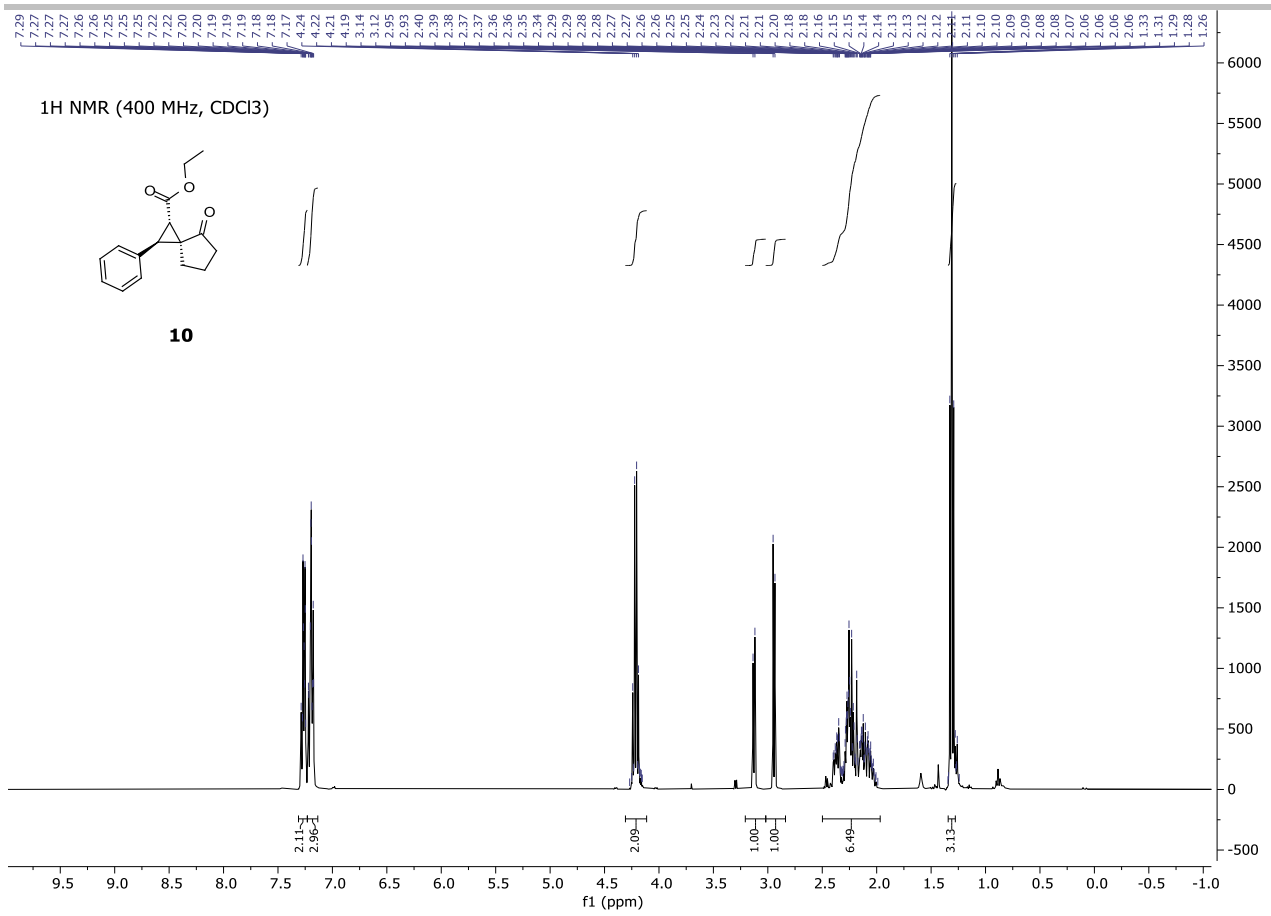

13C NMR (101 MHz, CD2Cl2)
8c
8c'
f1 (ppm)

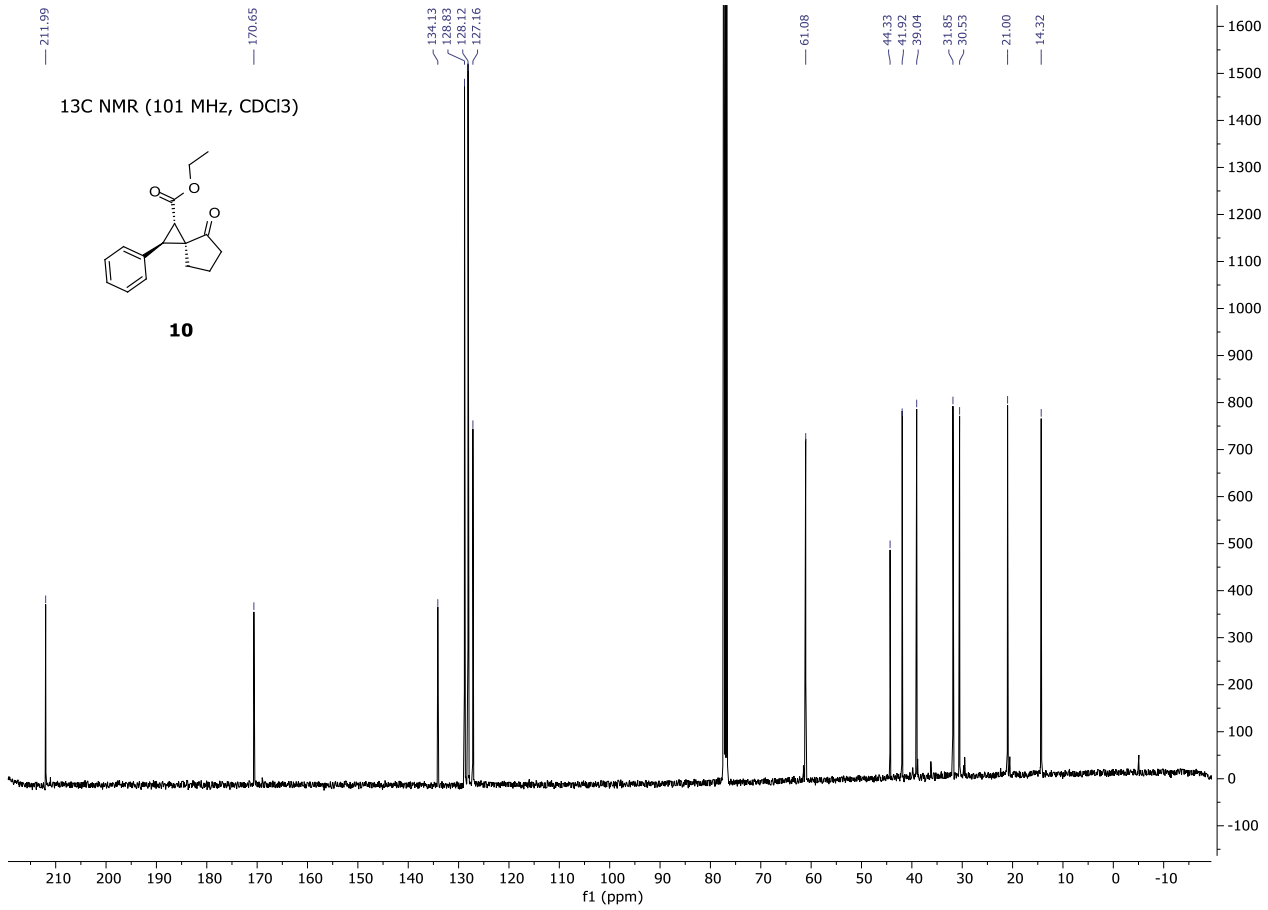

1H NMR (400 MHz, CD2Cl2)
6d
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
6d
f1 (ppm)


1H NMR (400 MHz, CDCl3)
9
f1 (ppm)


13C NMR (101 MHz, CDCl3)
9
f1 (ppm)


1H NMR (400 MHz, CDCl3)
10
f1 (ppm)


13C NMR (101 MHz, CDCl3)
10
211.99
170.65
134.13
128.83
128.12
127.16
61.08
44.33
41.92
39.04
31.85
30.53
21.00
14.32
f1 (ppm)

1H NMR (400 MHz, C6D6)

11

13C NMR (101 MHz, C6D6)

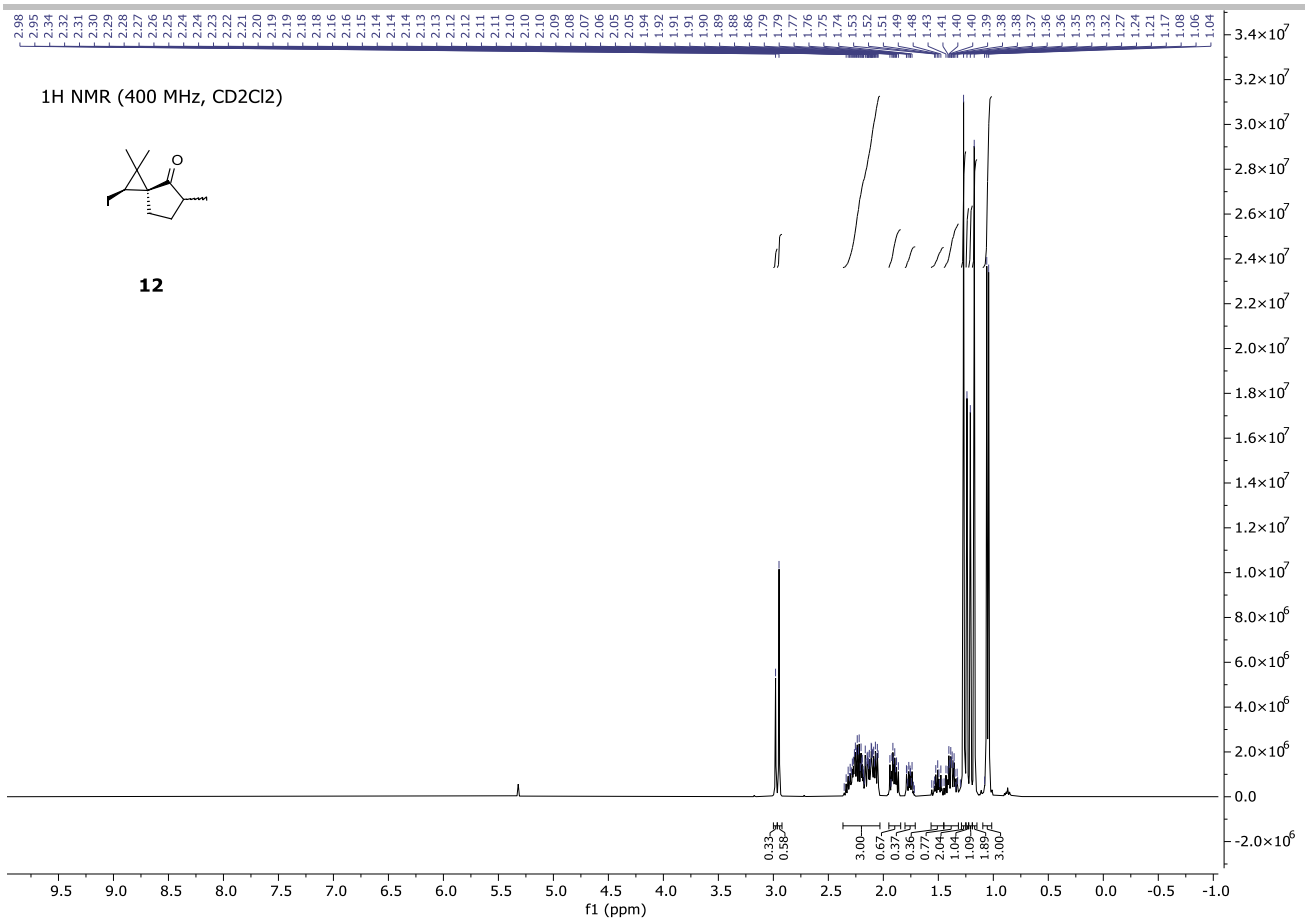
11

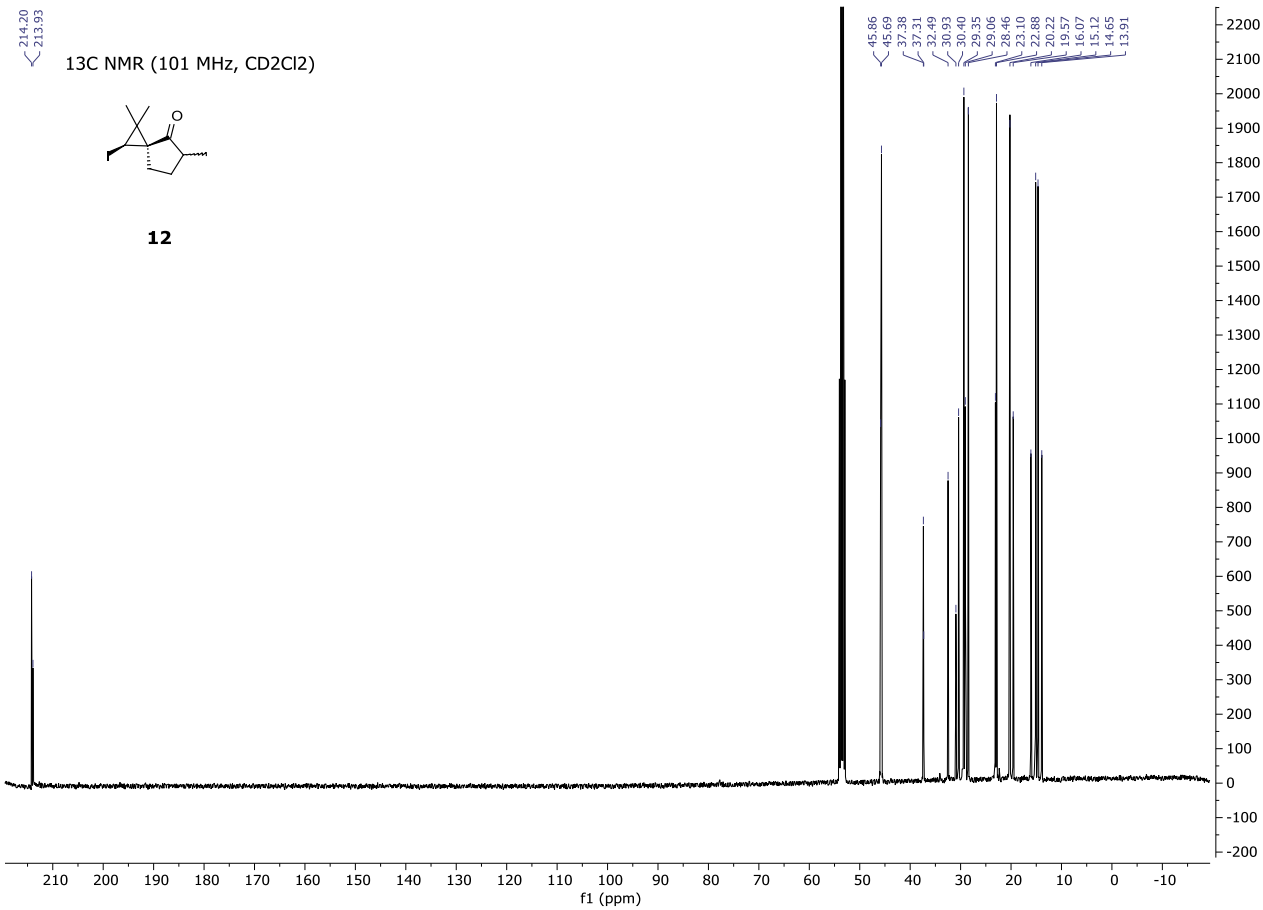
1H NMR (400 MHz, CD2Cl2)

11

1D NOE (400 MHz, CD2Cl2)

11


1H NMR (400 MHz, CD2Cl2)
12
f1 (ppm)


13C NMR (101 MHz, CD2Cl2)
12
f1 (ppm)

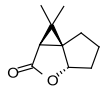
1H NMR (400 MHz, CDCl3)

13

13C NMR (101 MHz, CDCl3)

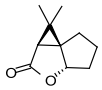
13

1H NMR (400 MHz, CDCl3)



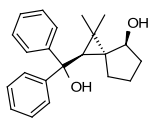
14

13C NMR (101 MHz, CDCl3)



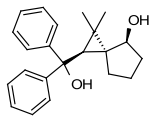
14

1H NMR (400 MHz, CDCl3)



15

13C NMR (101 MHz, CDCl3)



15