1,3,2-Diazaphospholene-Catalyzed Reductive Cyclizations of Organohalides

Johannes Klett, Dr. Łukasz Woźniak and Prof. Dr. Nicolai Cramer*[a]

[a] J. Klett, Dr. Ł. Woźniak, Prof. Dr. N. Cramer
Institute of Chemical Sciences and Engineering (ISIC)
EPFL SB ISIC LCSA, BCH 4305
1015 Lausanne (Switzerland)
E-mail: nicolai.cramer@epfl.ch
Homepage: https://www.epfl.ch/labs/lcsa/

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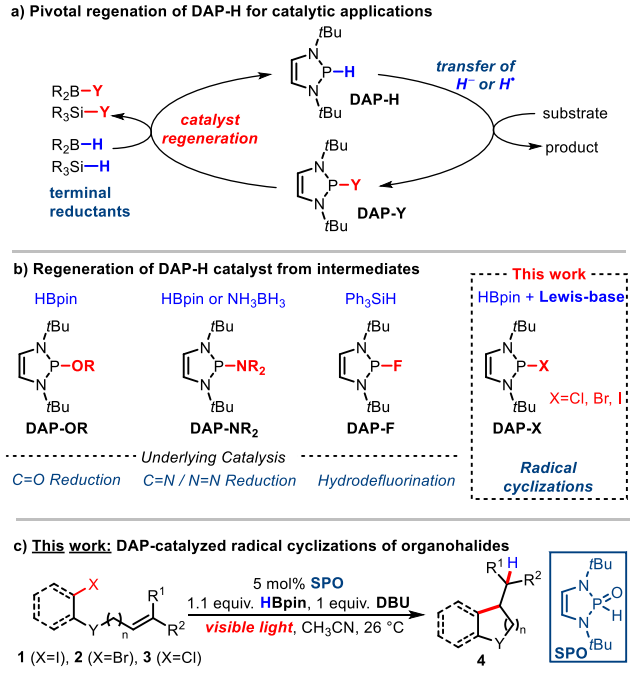
Abstract: 1,3,2-diazaphospholenes hydrides (DAP-Hs) are highly nucleophilic organic hydrides serving as main-group catalysts for a range of attractive transformations. DAP hydrides can act as stoichiometric hydrogen atom transfer agents in radical reactions. Herein, we report a DAP-catalyzed reductive radical cyclization of a broad range of aryl and alkyl halides under mild conditions. The pivotal DAP catalyst turnover was achieved by a DBU-assisted *σ*-bond metathesis between the formed DAP halide and HBpin rapidly regenerating DAP-H. The transformation is significantly accelerated by irradiation with visible light. Mechanistic investigations indicate that visible light irradiation leads to the formation of DAP dimers which are in equilibrium with the DAP radicals accelerating the cyclization. The direct use of $(DAP)_2$ enabled a catalytic protocol in the absence of light.

Discovered in the 1980s, 1,3,2-diazaphospholenes (**DAPs**)[1] represent a class of electron-rich heterocycles with a great application potential as versatile main-group catalysts.[2] For, instance, diazaphospholene hydrides (**DAP-Hs**) are powerful nucleophiles and weakly basic organic hydride donors.[3] They are very capable to reduce carbonyl compounds[4] and in conjugate fashion *α,β*-unsaturated amides,[5] esters,[5b,6] ketones[5] and acids.[7] A *σ*-bond metathesis between the alkoxy-substituted **DAPs** and pinacol borane (HBpin) regenerating **DAP-H** rendered these processes catalytic.[4] Reports by Kinjo and Speed utilized metathesis between the P–N and B–H bonds employing HBpin and ammonia borane to enable catalytic reductions of azobenzenes[8] and imines.[5b,9] Cheng *et al.* demonstrated the cleavage of the P–F bond in **DAP** fluorides by phenylsilane enabling hydrodefluorination of trifluoromethyl alkenes[10] and polyfluoro arenes.[11] The reactivity of **DAP-Hs** is not limited to the two electron transfer processes.[12] These electron-rich heterocycles can engage in reductions of alkyl and aryl halides[13] and *α*-carboxy ketones[14] *via* radical pathways. However, radical processes that can use catalytic amounts of **DAPs** are very scarce. A single report of deoxygenation of *α*-carboxy ketones employs diazaphosphinane as catalyst and AIBN as an initiator.[14] It capitalizes on the *σ*-bond metathesis between the P–O and B–H bonds for the catalyst's regeneration. In contrast to the **DAP-F**, the related halide bearing **DAP-X** (X= I, Br, Cl) do not undergo a *σ*-bond metathesis with borane or silane reagents. This represent a relevant reactivity gap hampering the closure of catalytic cycles. To exploit the full potential of **DAPs** in radical chemistry with organohalides, it is essential to render the transformations catalytic.

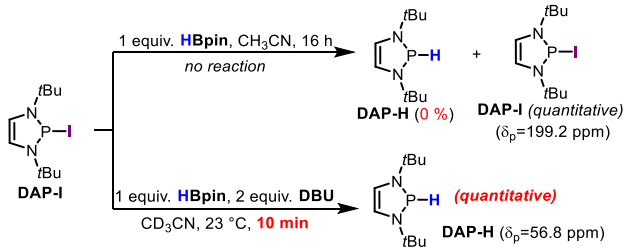
Radical cyclizations of organohalides across olefins are highly useful transformations to access diverse cyclic skeletons.[15] Typically, reductive cyclization of organohalides operating by radical mechanism require stoichiometric amounts of toxic organostannanes[16] and radical initiators such as e.g. AIBN[17] or Et_3B/O_2.[18] Advances in photochemical methods provided some alternatives including the use of metal- and organic photocatalysts[19] as well as electron-donor reagents.[20] The high affinity of **DAPs** towards organohalides makes them very attractive for activating this broad compounds class.[21] Speed demonstrated the functionalization of organo iodides and bromides.[22] However, catalytic variants of these processes remain so far elusive. A rapid and efficient regeneration of the **DAP-H** from **DAP-X** under mild conditions would be an essential gateway to catalytic transformations with organohalide substrate. Herein, we report an efficient Lewis-base promoted regeneration of **DAP-H** from **DAP-X** and its application for reductive radical cyclizations of aryl and alkyl halides under catalytic conditions.



Scheme 1. a) **DAPs** in catalysis: Regeneration of **DAP-H** to close catalytic cycles. b) Landscape of reduction options for **DAP-Y** into **DAP-H** and the underlying catalytic processes c) **DAP**-catalyzed reductive radical cyclization of organohalides.

To explore the ways to close the catalytic cycle, we first investigated the possibility to reliably regenerate the pivotal **DAP-H** species from the formed **DAP-I** of the stoichiometric process. Mixing **DAP-I** and HBpin in CD_3CN does not lead to any

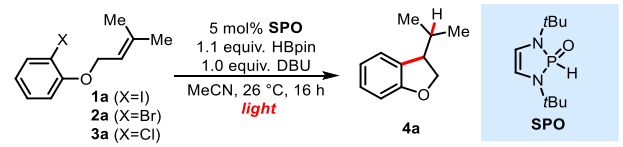
meaning formation of **DAP-H** after 16 h (Scheme 2). We hypothesized that activation of the borane by a suitable Lewis base[23] could facilitate the *σ*-bond metathesis between the **DAP-I** and HBpin. To our delight, adding DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to the **DAP-I**/HBpin mixture in CD_3CN triggered the quantitative generation of **DAP-H** in less than ten minutes. DMAP or *N*-methyl imidazole were as well competent (see SI for details).



Scheme 2. Fast regeneration of **DAP-H** with the DBU/HBpin system.

With the rapid **DAP-H** regeneration from **DAP-X** solved by the DBU-assisted *σ*-bond metathesis, we turned our efforts towards a fully catalytic transformation for the cyclization of aryl iodide **1a** and aryl bromide **2a** (Table 1, for a comprehensive optimization study, see SI). Employing 5 mol% of the robust and conveniently usable secondary phosphine oxide **SPO**[24] as the pre-catalyst in combination with the HBpin/DBU mixture in MeCN, gave cyclization product **4a** in 23 % yield (entry 1). This corresponds to over four catalyst turnovers. During our optimization studies, we noticed that the reaction rate and progress is highly sensitive to light. While still taking place under the careful exclusion of light (entry 2), the yield of **4a** almost quadrupled when irradiating the reaction mixture with white LEDs (entry 3). This effect was even more pronounced with aryl bromide **2a**. However, no reaction took place in the absence of light (entry 4). The use of white LEDs restored some reactivity giving **4a** in 12% yield (entry 5). Switching to a more powerful a Kessil lamp (427 nm) allowed to increase the yield of **4a** to 91% (entry 6). Control experiments omitting **SPO**, DBU and HBpin showed their indispensable role in the transformation (entries 7-9). Aryl chloride **3a** did not react under the current conditions (entry 10).

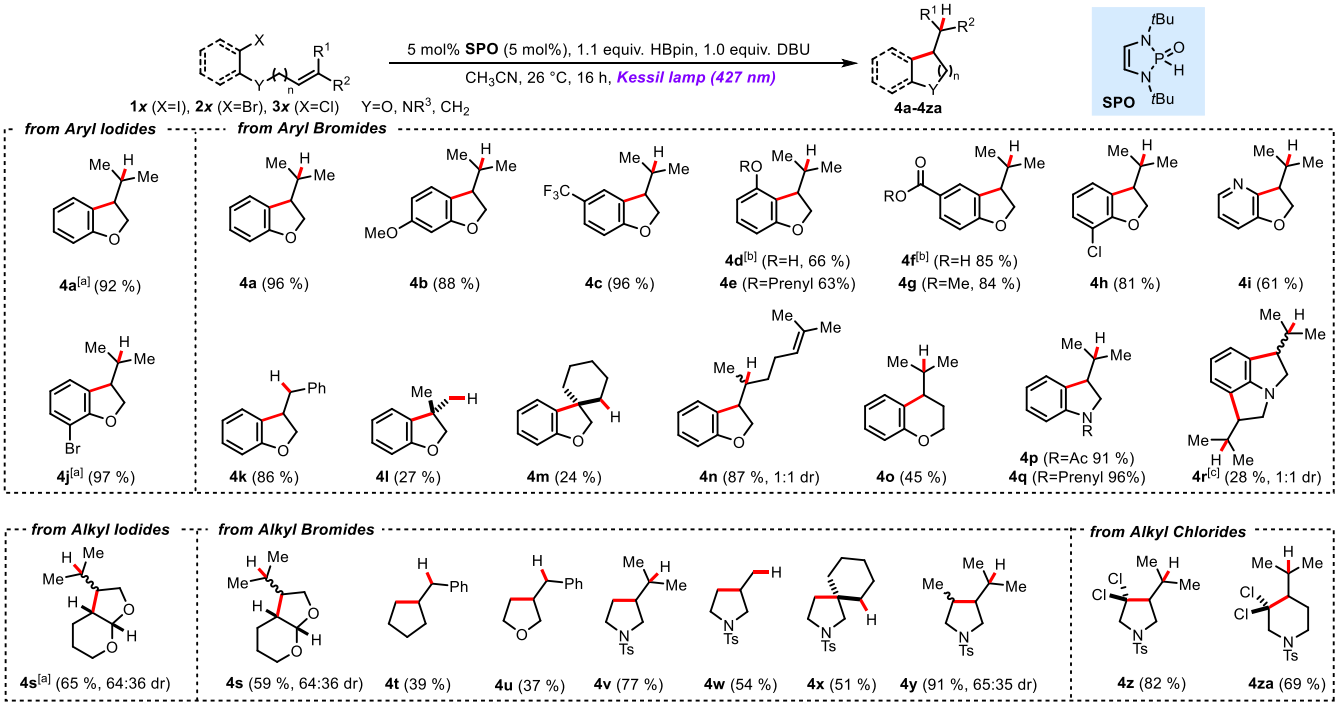
Table 1. Optimization of the **DAP**-catalysed cyclization of **1-2a**.[a]



entry	substrate	light	% yield[b]
1	**1a**	ambient	23
2	**1a**	*exclusion of light*	19
3	**1a**	white LEDs	89
4	**2a**	*exclusion of light*	0
5	**2a**	white LEDs	12
6	**2a**	Kessil lamp (427 nm)	91
7[c]	**2a**	Kessil lamp (427 nm)	0
8[d]	**2a**	Kessil lamp (427 nm)	5
9[e]	**2a**	Kessil lamp (427 nm)	0
10	**3a**	Kessil lamp (427 nm)	0

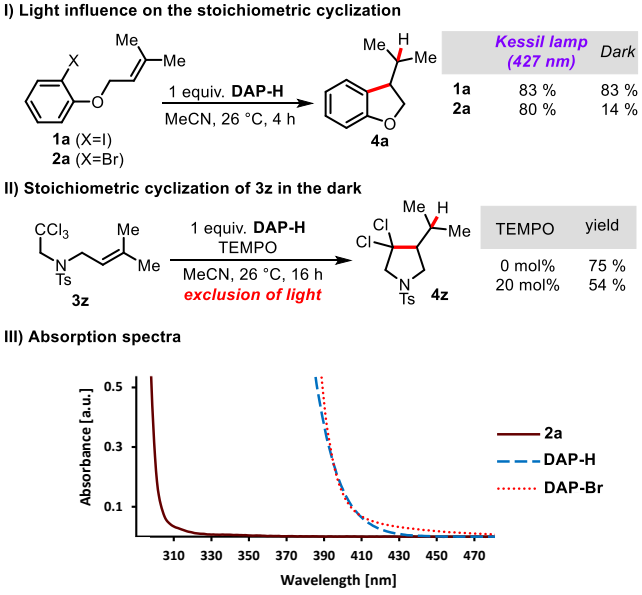
[a] Conditions: 0.1 mmol **1a**, 5 µmol **SPO**, 0.11 mmol HBpin, 0.1 mmol DBU, 0.1 M (0.8 M for **2a** and **3a**) in MeCN at 26 °C for 16 h, [a] Yields determined by ^{1}H-NMR with an internal standard; [c] no **SPO** [d] no DBU; [d] no HBpin.

Next, we evaluated the scope of the **DAP**-catalyzed reductive cyclization of a broad set of substituted aryl halide substrates (Scheme 3). Dihydrobenzofurane **4a** was isolated in excellent yields (92 % from **1a** and 96 % from **2a**). The transformation is tolerant to potential reactive functional groups like methyl esters, free phenols and carboxylic acids reliably delivering products **4b**-**4g**. Notably, a switch from the Kessil lamp (427 nm) to white LEDs allowed for a selective cyclization originating from the aryl iodide moiety of **1j** *in the presence* of the adjacent bromide substituent in 97 % yield. Along the same lines, the reaction of aryl bromide **2h** cleanly proceeded in the presence of an adjacent chloride moiety under standard conditions. The reaction of the bromo pyridine **2i** cyclized to product **4i** without **DAP**-catalyzed reduction of its pyridine core.[25] Aryl bromides bearing different alkenyl tethers reacted well. For instance, styrene **2k** underwent cyclization in 86 % yield. The nature of the olefin acceptor portion was as well modifiable (**4l**-**4n**). Substrates which pass through 1° or 2° alkyl radical intermediates reacted in reduced yields (**4l** and **4m**). Besides the formation of the five-membered rings, the process enabled the 6-exo-trig cyclizations as demonstrated for 4-isopropylchromane **4o**. Aniline substrates were readily converted into functionalized indolines **4p**-**4r**. Next, we explored the potential of alkyl halide substrates for the cyclization. In this respect, iodo acetals **1s** and bromo **2s** smoothly reacted providing bicyclic product **4s**. Primary alkyl bromides **2u** and **2t** cyclized to the corresponding tetrahydrofuran **4u** and cyclopentane **4t** in moderate yields. The cyclization of substituted alkenyl amines led to pyrrolidines **4v**-**4w** in good yield. A secondary alkyl bromide analogue formed disubstituted pyrrolidine **4y** in 91% yield and 65:35 *dr*. Noteworthy, substrates bearing a trichloroalkyl group engaged in the transformation providing dichloro-substituted pyrrolidine **4z** and piperidine **4za** in 82% and 69% yield, respectively.



Scheme 3: Scope of the **DAP**-catalyzed cyclization of organohalides. Conditions: 0.20 mmol **1*x*-3*x***, 10 µmol **SPO**, 0.22 mmol HBpin, 0.20 mmol DBU in MeCN (**1*x***=0.2 M, **2*x*-3*x***=0.8 M) in MeCN at 26 °C for 16 h. [a] white LEDs instead of the Kessil lamp 427 nm. [b] 2.5 equiv. HBpin. [c] 10 mol% **SPO**, 2.2 equiv. HBpin and 2.0 equiv. DBU.

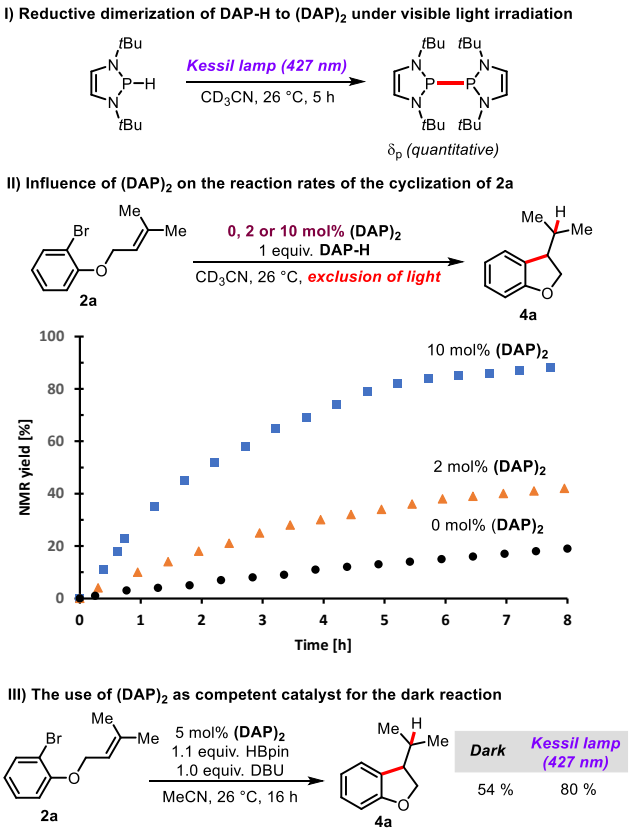
We next conducted mechanistic investigations to better understand the effect the light plays in this transformation. The stoichiometric reactions indicate that the cyclizations of **1a** and **2a** take as well place in the dark. However, irradiation by a Kessil lamp (427 nm) accelerates the transformations (Scheme 4). In contrast, the catalytic reaction with substrate **2a** occurs only under irradiation. Aryl bromide **2a** still cyclized to **4a** in the dark, albeit with poor efficiency. The direct reaction of **DAP-H** and CCl_4 does not require activation by strong light sources affording **DAP-Cl** and a mixture of chloromethanes CH_mCl_{4-m} (m=0-3).[21b] This P–H/C–Cl bond metathesis proceeds eventually through a radical mechanism. Substrate **3z** was exposed to 1 equiv. of **DAP–H** under exclusion of light yielding 75 % of product **4z**. Attempts to inhibit the hypothesized radical mechanism by the addition of 20 mol% TEMPO were futile. TEMPO rapidly reacts with **DAP-H** and after consumption of all added TEMPO, the remaining amount of **DAP-H** produced **4z** in 54 % yield. To gain mechanistic insight of the light-enhanced reaction, we first identified which species absorb light in the visible spectrum. The absorption spectra of **DAPs** and **2a** indicates that only **DAP-H** and **DAP-Br** absorb light at wavelengths above 400 nm, which is an emission tail of the Kessil lamp (427 nm). No ground state associations between the **DAPs** and **2a** were found (see SI). Based on this information, two scenarios in which visible light accelerates the cyclization of **2a** are plausible. In scenario I, a photoexcitation of **DAP-H** triggers a SET from the excited **DAP-H*** to **2a**. Scenario II involves a photoexcitation of **DAP-H** leading to a 1,3,2-diazaphospholene radical (**DAP•**). On the basis of electrochemical and spectroscopic measurements, we estimated the redox potential of the excited **DAP-H*** is -3.14 V (*vs.* Fc^+/Fc in MeCN), indicating that a SET between **DAP-H*** and **2a** (E_{red} **2a**/**2a**$^{\bullet-}$=-3.36 V *vs.* Fc^+/Fc in MeCN) is endergonic (see SI for details). Next, we examined the generation of **DAP•** radical species by excitation of **DAP-H**. We hypothesized that visible light from the Kessil lamp (427 nm) could trigger a reductive dimerization of **DAP-H**. This was previously reported by Gudat *et al.* using UV light from a medium-pressure Hg-lamp.[26] The resulting **(DAP)$_2$** species, described as a weakly *σ*-bonded dimer, would dissociate in solution to give the persistent 7π-radical **DAP•** species.[27] Indeed, ^{31}P-NMR analysis confirmed formation of **(DAP)$_2$** from **DAP-H** upon irradiation by a Kessil lamp (427 nm) (Scheme 5). This evidence supports the suggestion of an initiation of a radical chain process through the immediacy of **(DAP)$_2$**.



Scheme 4. Evaluation of the light influence or TEMPO on the cyclization efficiency and absorption spectra of the reaction components.

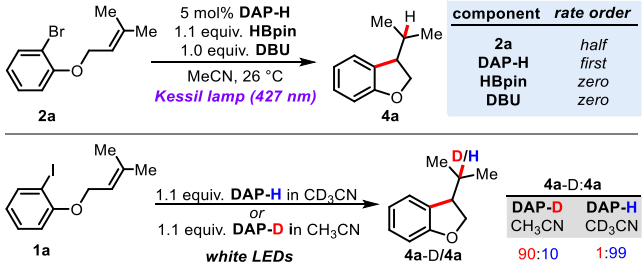
Next, we tested the influence of **(DAP)$_2$** on the cyclizations reaction rate of **2a** with one equivalent of **DAP-H** in the dark.

Notably, already 2 mol% of **(DAP)$_2$** remarkably accelerates the cyclization. This observation clearly supports the outlined scenario II. Both findings let to the hypothesis that an exchange of the **SPO** catalyst by **(DAP)$_2$** would enable a *catalytic* process *without* the visible light activation. Remarkably, 5 mol% **(DAP)$_2$** promoted a catalytic reaction in the absence of light forming **4a** in 54 % yield.



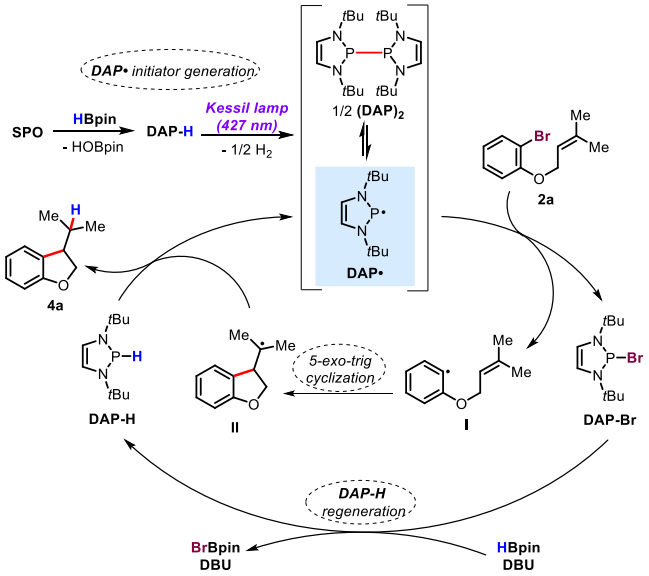
Scheme 5. Illustration of the role of **(DAP)$_2$** in the **DAP**-catalyzed cyclizations.

Further mechanistic experiments comprised initial-rate kinetic studies of the model reaction across a range of concentrations for each reaction component under visible light irradiation (see SI for details). A first-order dependence was inferred for **DAP-H** and a half order for substrate **2a**, supporting a radical chain mechanism. The zeroth-order dependence on the concentration of HBpin and of DBU indicate that the regeneration of the **DAP-H** is not a turnover limiting step. Moreover, the reaction rates increase with the increasing light intensity (see SI). Deuterium labelling studies with **1a** using **DAP-D** in CH_3CN or **DAP-H** in CD_3CN confirm the origin of the hydrogen atom of **4a** from the catalyst.



Scheme 6. Initial-rate kinetics for the **DAP**-catalyzed cyclization and deuterium labelling studies.

Taking all mechanistic experiments into account, the catalytic cycle can be portrayed (Scheme 7). With **SPO** as the pre-catalyst, the process is initiated by the reduction with HBpin forming **DAP-H**. Visible light irradiation converts **DAP-H** to **(DAP)$_2$**. The dissociation equilibrium of **(DAP)$_2$** into two molecules of **DAP•** initiates a radical chain process by bromine atom abstraction from **2a**.[28] The resulting aryl radical **I** adds across the C=C bond in a 5-exo-trig fashion forming radical species **II**. In turn, **II** abstracts the hydrogen atom from **DAP-H** delivering product **4a** and **DAP•**. Enabled by DBU, **DAP-Br** is converted back to **DAP-H** with HBpin. Employing **(DAP)$_2$** as catalyst allows entering the catalytic cycle bypassing the light activation step. However, the reduced yield of the **(DAP)$_2$**-catalyzed reaction in the dark indicates that light can heal the catalytic cycle by regeneration **DAP•** after radical chain terminations.



Scheme 7. Proposed mechanism of the **DAP**-catalyzed cyclization of organohalides.

In summary, we developed a **DAP**-catalyzed reductive radical cyclization of organohalides. The **DAP** catalyst turnover was achieved by implementation of a DBU-assisted *σ*-bond metathesis between **DAP-X** (X=I, Br, Cl) and HBpin providing a fast regeneration of **DAP-H**. The transformation is significantly accelerated by the irradiation with visible light. The developed process allowed the efficient reductive cyclizations of a broad range of aryl and alkyl halides under mild and convenient conditions. Detailed mechanistic investigations revealed that visible light leads to the formation of **(DAP)$_2$** which is in equilibrium with **DAP•** accelerating the cyclization. The direct use **(DAP)$_2$** enabled a catalytic protocol in the absence of light. These findings will serve as blueprint and accelerator for the further developments of **DAP**-catalyzed radical processes.

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Keywords: DAP Catalysis • Phosphorous • Cyclization • Radical Chemistry

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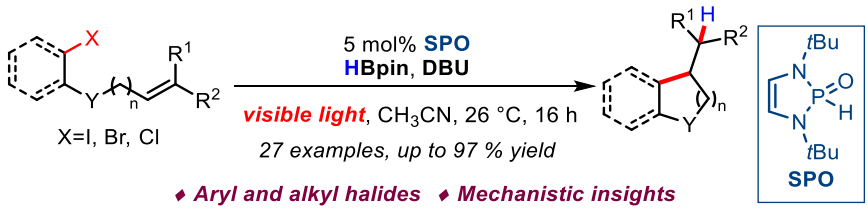
[28] An alternative mechanism involving SET from **DAP•** (E_{red} **DAP**$^{+}$/ **DAP•** = -1.76 V *vs.* Fc^{+}/Fc in MeCN)) to **2a** (E_{red} **2a/2a**$^{\bullet-}$ = -3.36 V *vs.* Fc^{+}/Fc in MeCN) is thermodynamically prohibited (see SI for details).



*J. Klett, Ł. Woźniak, N. Cramer**

[Page No. – Page No. 1,3,2-Diazaphospholene-Catalyzed Reductive Cyclizations of Organohalides

1,3,2-diazaphospholenes hydrides (DAP-H) are shown as efficient catalysts for reductive radical cyclization of aryl and alkyl halides under mild conditions and accelerated by irradiation with visible light. The pivotal DAP catalyst turnover was achieved by a DBU-assisted *σ*-bond metathesis between the formed DAP halide and HBpin rapidly regenerating DAP-H.

Supporting Information

1,3,2-Diazaphospholene-Catalyzed Reductive Cyclizations of Organohalides

Johannes Klett, Dr. Łukasz Woźniak and Prof. Dr. Nicolai Cramer*

Table of Contents

1. Experimental Procedures 2
1.1 General and Materials 2
1.2 Condition Screening 5
1.3 Mechanistic Investigations 6
1.3.1 Cyclic Voltammetry 6
1.3.2 UV/VIS measurements 10
1.3.3 Formation of DAP-H from DAP-I with DBU as an Activator 13
1.3.4 Kinetic Investigations 15
1.3.5 Deuterated experiments 22
1.3.6 Formation of $(DAP)_2$ from DAP-H under Irradiation 24
1.3.7 Attempts to inhibit the reductive cyclization by TEMPO 25
1.4 DAP Synthesis 26
1.5 Substrate Synthesis 31
1.6 Intramolecular Reductive Cyclization 55
1.7 Non-working Substrates 68
2. References 69
3. NMR Spectra 71

1. Experimental Procedures

1.1 General and Materials

Experimental Techniques

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring inside a glove box or using Schlenk technique, unless otherwise indicated. Chemicals were used as obtained from the suppliers unless otherwise indicated.

Drying, Degassing and Purification of Solvents

CH_2Cl_2, THF and MeCN were purified by an Innovative Technology Solvent Delivery System. *n*-Hexane was distilled over CaH_2 under nitrogen atmosphere. Before being transferred into a nitrogen-filled glove box to be stored over 4 Å molecular sieves, all solvents were degassed *via* freeze-pump-thaw technique. 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) was distilled over CaH_2 under nitrogen atmosphere, degassed *via* freeze-pump-thaw technique and stored inside the glovebox.

Flash Chromatography

Flash chromatography was performed with SiliaFlash silica gel P60 (40-63 μm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F_{254}). Compounds were either visualized under UV-light at 254 nm and/or by dipping the plates in $KMnO_4$ stain: ($KMnO_4$ (3.0 g), Na_2CO_3 (20 g), aq NaOH solution (5 wt %, 5.0 mL) in H_2O (300 mL)) or Vanillin stain: vanillin (10 g) and H_2SO_4 (conc., 1 mL) in EtOH (250 mL)) followed by heating.

NMR Spectroscopy

^{1}H NMR data was acquired on a Bruker *AVANCE400* (400 MHz), Bruker *DRX-400* (400 MHz) or Bruker *AVANCEIII-400* (400 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to incompletely deuterated $CDCl_3$ (s, 7.26 ppm), C_6D_6 (s, 7.16 ppm), or CD_3CN (quint, 1.94 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; hept, hepted; m, multiplet; br, broad. Proton-decoupled ^{13}C NMR data were acquired on a Bruker *AVANCE400* (101 MHz), Bruker *DRX-400* (101 MHz) or Bruker *AVANCEIII-400* (101 MHz). Chemical shifts are reported in ppm relative to $CDCl_3$ (77.16 ppm) or C_6D_6 (128.06 ppm).^{31}P NMR data was acquired on a Bruker *AVANCE400* (162 MHz) spectrometer. ^{19}F NMR data was acquired on a Bruker *AVANCE400* (376 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and were referenced using the Ξ-scales with 85% H_3PO_4 (Ξ=40.480747 MHz, ^{31}P) and CCl_3F (Ξ=94.094011 MHz, ^{19}F) as secondary references.

Cyclic Voltammetry

Cyclic voltammetry data was acquired on a BioLogic SP-150 Potentiostat. Bu_4NPF_6 was recrystalized from EtOH and dried in vacuo prior use. All measurements were performed under nitrogen atmosphere inside a glovebox. Supporting electrolyte: Bu_4NPF_6 (0.1 M in MeCN), working electrode: glassy carbon disc (⌀=0.3 mm), counter electrode platinum wire, reference electrode: 0.1 M $AgNO_3$/Ag (in 0.1 M Bu_4NPF_6-MeCN), scanrate: 100 mV/s, analyte concentration: 10 mM. All spectra are referenced against the ferrocene/ferrocene$^+$ couple as an internal standard.

UV/VIS Spectroscopy

UV/VIS data was acquired on an Agilent Cary 60 UV-Vis. All measurements were performed in an oven-dried, sealable quartz glass cuvette, which was charged inside and nitrogen-filled glovebox with the analytes and solvent. The concentration of the analytes was c = 0.04 M in MeCN.

Infrared Spectroscopy

Infrared (IR) data was recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). The intensity of the absorbance frequencies is indicated with: (w), weak, (m), medium; (s), strong and (br), broad.

Melting Points

Melting points (Mp) were measured on a Büchi Melting Point B-540 and are uncorrected.

Mass Spectrometry

HRMS ESI measurements were performed by an Agilent LC-MS TOF and XEVO G2-S QTOF mass spectrometers. APPI/LTQ-Orbitrap-FT-MS analyses were performed on a Thermo Orbitrap Elite and LTQ Orbitrap FTMS instrument. High resolution mass values are given in m/z.

Irradiation Setups

a) The setup for the irradiation with white LEDs consisted of a photoreactor made out of a metal drum (h=26 cm, ⌀=14 cm), in which white LED stripes from Ledxon were attached. On top of the drum, a fan was installed. For irradiation of a vial, it was hold in a beaker on a stirring plate and the drum was placed over the stirring plate. The distance between the LEDs and the reaction vial was 6 cm. The reaction chamber was cooled by the fan.

b) The setup for the irradiation with the Kessil PR-160 lamps (427 and 390 nm), consisted of the specific lamp, a stirring plate, a clamp to hold the vial in place and a fan. To ensure efficient cooling two tubes, connected to a compressed air outlet, were directly pointed to the reaction vial. The distance between the Kessil lamps and the reaction vial was 2 cm. For all irradiation setups, thermo-coupled experiments showed a constant reaction temperature of 26 °C.

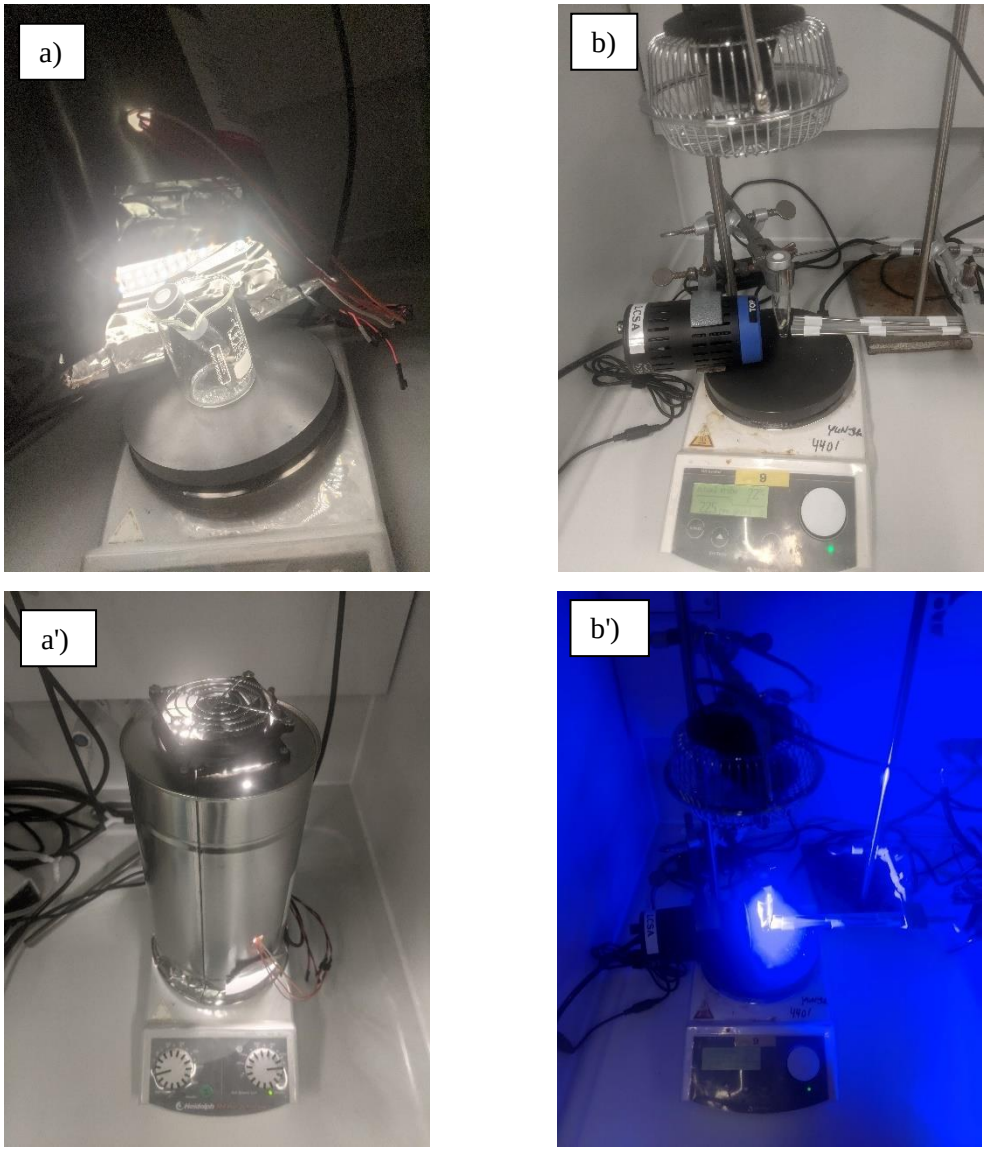


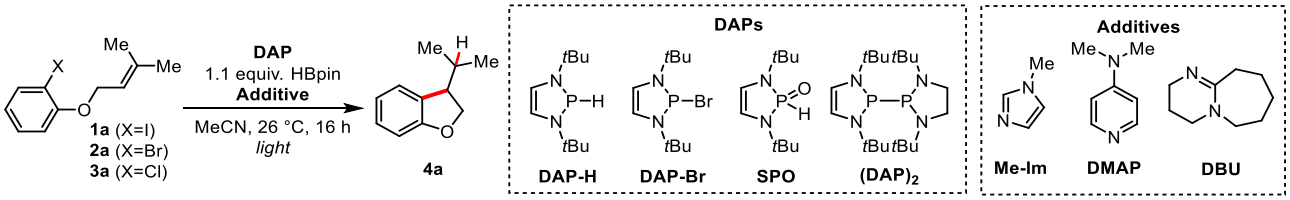
Figure S1: Setup for the irradiation with white LEDs: a) view into the photoreactor, a') closed reactor. Setup for the irradiation with Kessil lamps (390 nm and 427 nm): without b) and with irradiation b').

1.2 Condition Screening

General Procedure A:

A 1 mL microwave vial, equipped with a stir bar was charged with 10 µmol substrate and transferred into the glovebox. MeCN was added, followed by the additive, **DAP** and 110 µmol HBpin. The vial was capped, removed from the glovebox and irradiated for 16 h at rt. Volatiles were removed under reduced pressure and the residue was directly subjected to ^{1}H NMR analysis.

Table S1: Condition Screening for **DAP** catalyzed reductive Cyclizations of **1-3a**.[a]



Entry	substrate	DAP [mol%]	Additive (equiv.)	light	Conv. [%][b]	Yield [%][b]
1[c,d]	**1a**	**DAP-H** [150]	-	ambient	100	80
2[c,d]	**1a**	**DAP-H** [150]	-	exclusion of light	100	80
3[e]	**1a**	**DAP-H** [100]	-	exclusion of light	84	83
3[e]	**1a**	**DAP-H** [100]	-	Kessil lamp (427 nm)	95	83
4	**1a**	**DAP-Br** [10]	**Me-Im** (2.0)	white LEDs	47	40
5	**1a**	**DAP-Br** [10]	**DMAP** (2.0)	white LEDs	100	80
6	**1a**	**DAP-Br** [10]	**DBU** (2.0)	white LEDs	100	86
7	**1a**	**DAP-Br** [10]	**DBU** (2.0)	white LEDs	100	84
8[f]	**1a**	**SPO** [10]	**DBU** (1.0)	white LEDs	100	75
9	**1a**	**SPO** [5]	**DBU** (1.0)	white LEDs	100	89
10	**1a**	**SPO** [5]	**DBU** (1.0)	ambient	39	23
11	**1a**	**SPO** [5]	**DBU** (1.0)	exclusion of light	27	19
12	**2a**	**SPO** [5]	**DBU** (1.0)	white LEDs	13	12
13	**2a**	**SPO** [5]	**DBU** (1.0)	Kessil lamp (427 nm)	76	70
14[g]	**2a**	**SPO** [5]	**DBU** (1.0)	Kessil lamp (427 nm)	100	91
15[g]	**2a**	**SPO** [5]	-	Kessil lamp (427 nm)	6	5
16[g]	**2a**	-	**DBU** (1.0)	Kessil lamp (427 nm)	0	0
17[c,g]	**2a**	**SPO** [5]	**DBU** (1.0)	Kessil lamp (427 nm)	0	0
18[c,g]	**2a**	**DAP-H** [100]	-	exclusion of light	38	37
19[c,g]	**2a**	**DAP-H** [100]	-	exclusion of light	14	13
20[c,g]	**2a**	**DAP-H** [100]	-	Kessil lamp (427 nm)	84	80
21[g]	**2a**	**SPO** [5]	**DBU** (1.0)	exclusion of light	6	5
22[g]	**2a**	**(DAP)$_2$** [5]	**DBU** (1.0)	Kessil lamp (427 nm)	100	80
23[c,g]	**2a**	**(DAP)$_2$** [5]	**DAP-H** (1.0)	exclusion of light	91	78
24[g]	**2a**	**(DAP)$_2$** [5]	**DBU** (1.0)	exclusion of light	59	54
25[g]	**2a**	**(DAP)$_2$** [2.5]	**DBU** (1.0)	exclusion of light	41	41
26[g]	**2a**	**(DAP)$_2$** [5]	-	exclusion of light	6	5
27[c,g]	**2a**	**(DAP)$_2$** [5]	**SPO** (1.0)	exclusion of light	0	0
28[c,g]	**2a**	**(DAP)$_2$** [5]	**SPO** (1.0), **DBU** (1.0)	exclusion of light	0	0
29[c,g]	**2a**	**(DAP)$_2$** [5]	**SPO** (1.0), **DBU** (1.0)	Kessil lamp (427 nm)	0	0

30[g]	**3a**	**SPO** [5]	**DBU** (1.0)	Kessil lamp (427 nm)	0	0

[a] GP A; conditions: 100 µmol **1a-3a**, 2.5-150 µmol ***DAP***, 110 µmol HBpin, 100-200 µmol *additive* in MeCN (0.1 M) at 26 °C for 16 h. [b] Determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as an internal standard. [c] no HBpin. [d] 2 h reaction time. [e] 4 h reaction time. [f] 0.33 equiv. $PhSiH_3$ instead of HBpin. [g] c(substrate)=0.8 M in MeCN.

1.3 Mechanistic Investigations

1.3.1 Cyclic Voltammetry

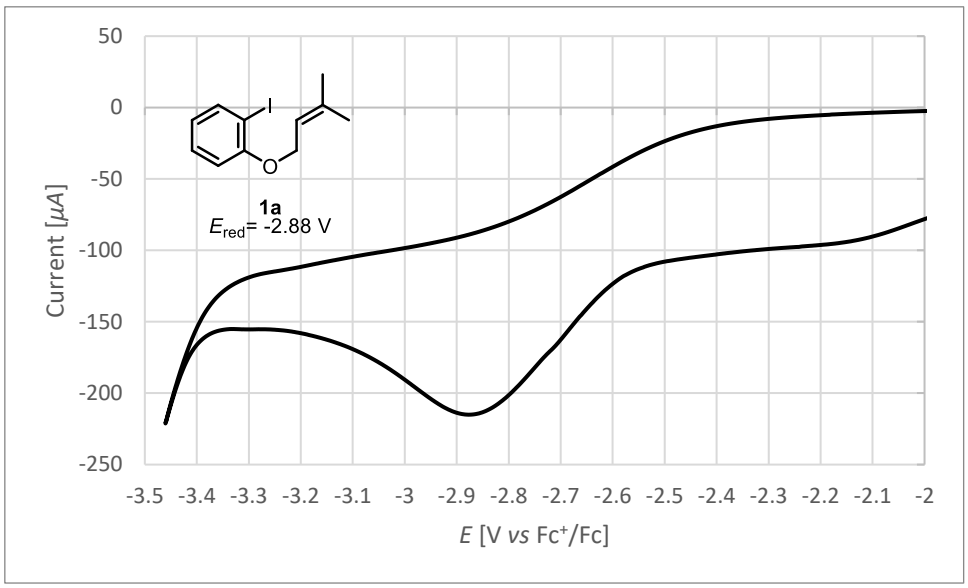


Figure S2: Cyclic voltammetry of substrate **1a**. The irreversible reduction peak potential E_{red} was determined to be at -2.88 V.

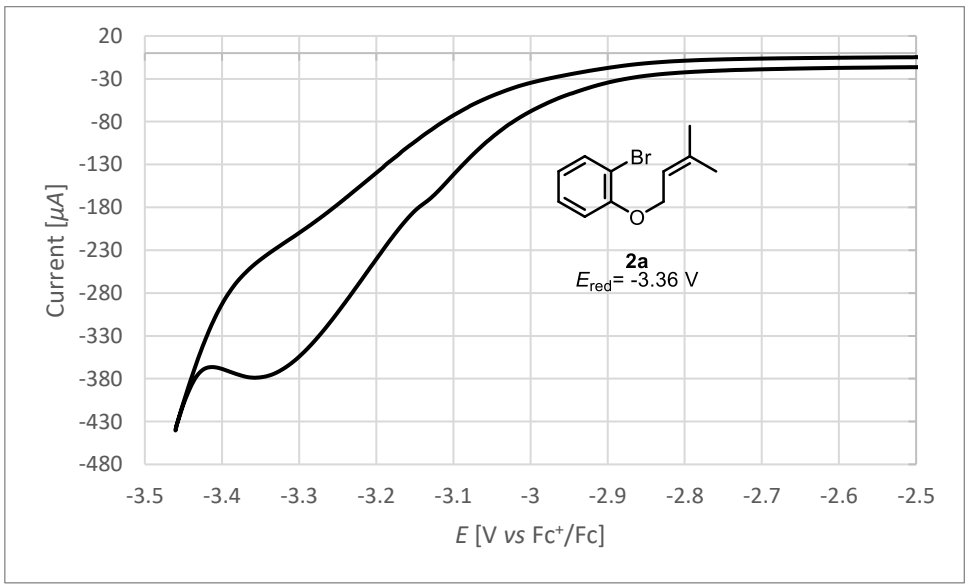


Figure S3: Cyclic voltammetry of substrate **2a**. The irreversible reduction peak potential E_{red} was determined to be at -3.36 V.

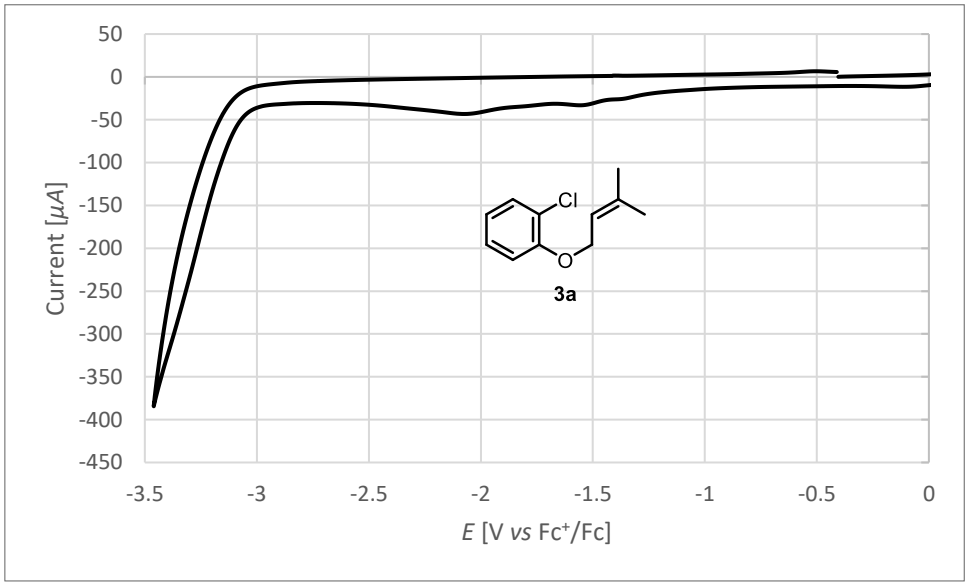


Figure S4: Cyclic voltammetry of substrate **3a**. Its reduction peak was found to be outside the solvent window.

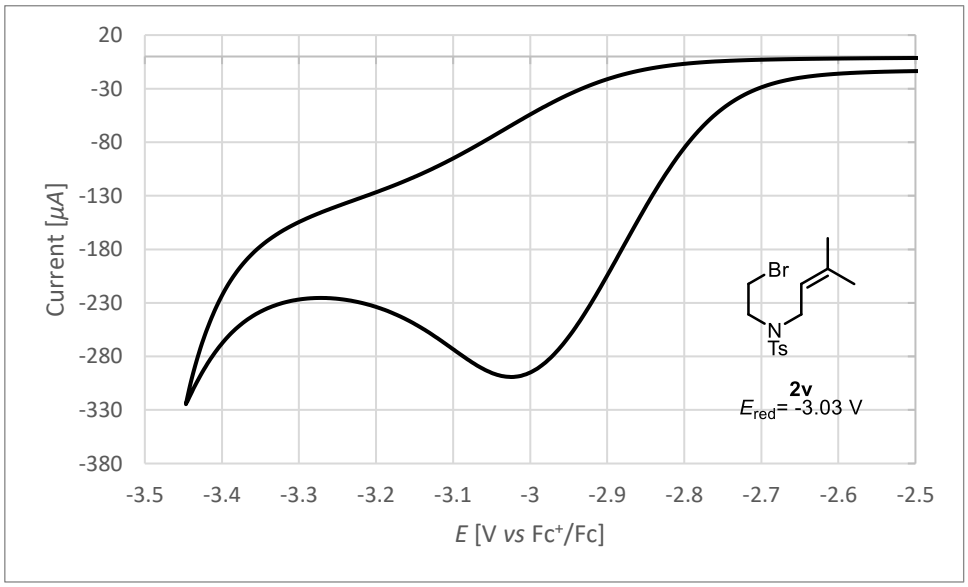


Figure S5: Cyclic voltammetry of substrate **2v**. The irreversible reduction peak potential E_{red} was determined to be at -3.03 V.

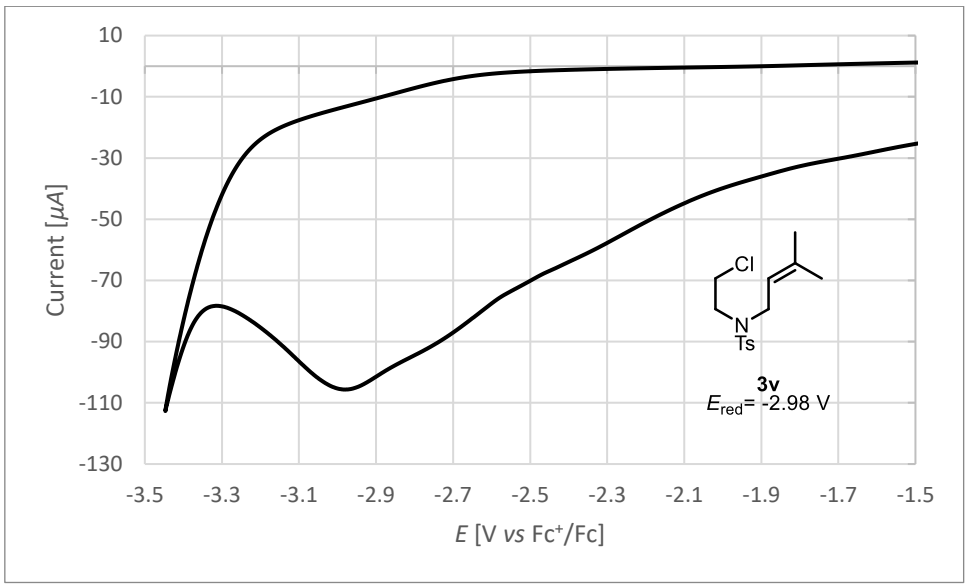


Figure S6: Cyclic voltammetry of substrate **3v**. The irreversible reduction peak potential E_p^{red} was determined to be at -2.98 V.

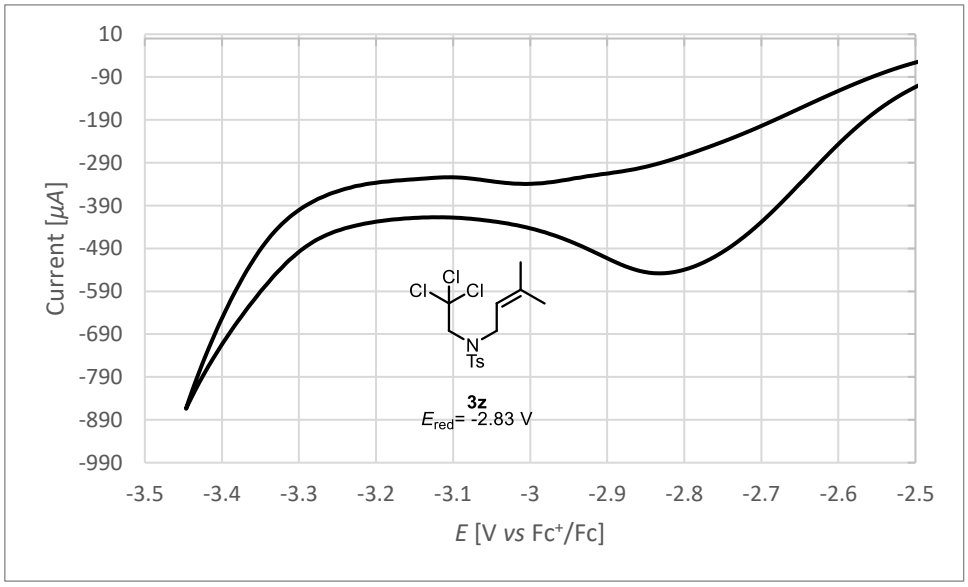


Figure S7: Cyclic voltammetry of substrate **3z**. The irreversible reduction peak potential E_{red} was determined to be at -2.83 V.

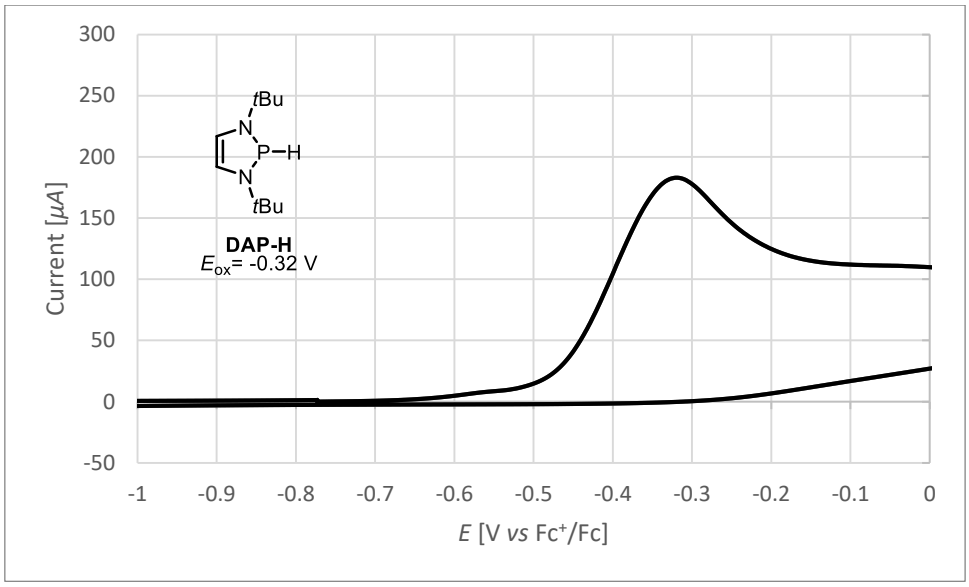


Figure S8: Cyclic voltammetry of **DAP-H**. The irreversible oxidation peak potential E_{ox} was determined to be at -0.32 V.

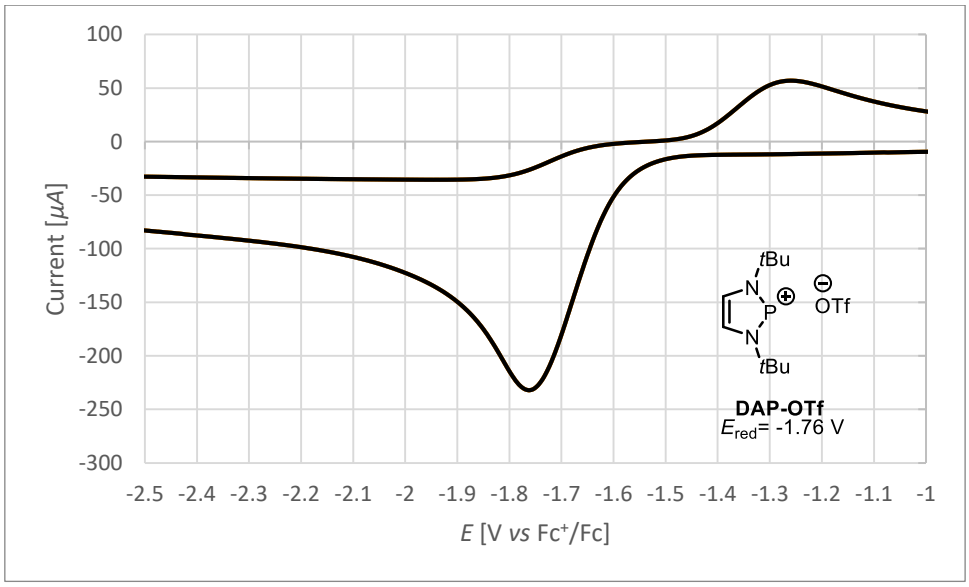


Figure S9: Cyclic voltammetry of **DAP-OTf**. The irreversible reduction peak potential E_{red} was determined to be at -1.76 V.

1.3.2 UV/VIS measurements

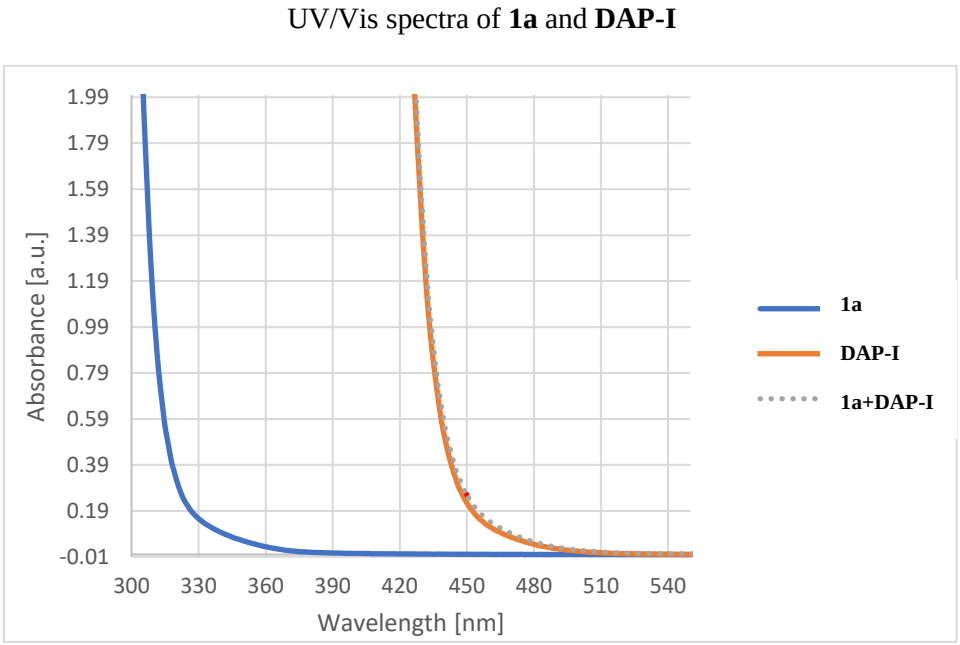


Figure S10: UV-Vis absorption spectra of **1a** (blue, full line), **DAP-I** (orange, dashed line) and a mixture of **1a** and **DAP-I** (grey, dotted line). Analyte concentration: 0.04 M in MeCN. No formation of an EDA complex was observed.

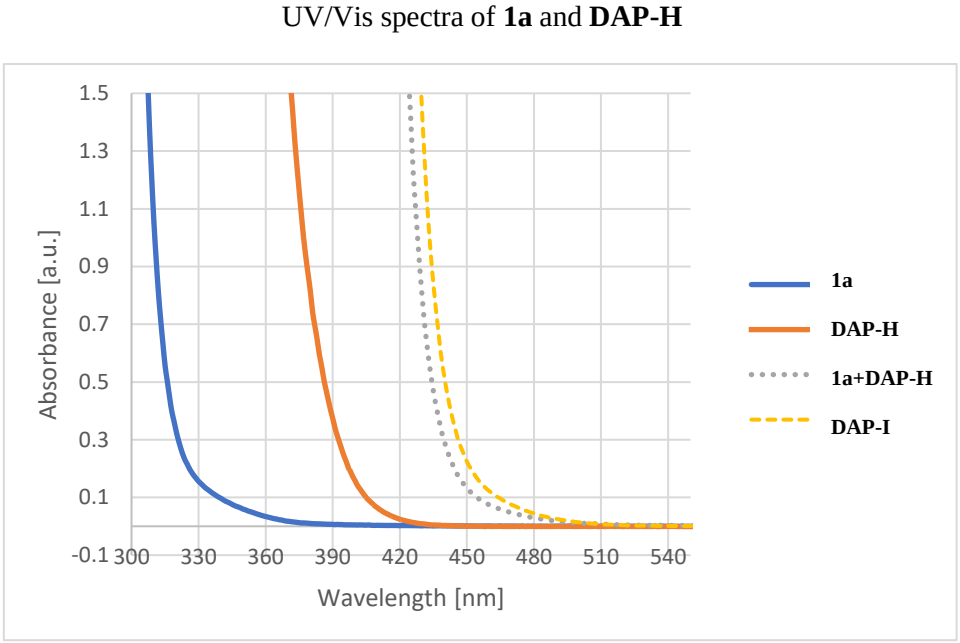


Figure S11: UV-Vis absorption spectra of **1a** (blue, full line)**, DAP-H** (orange, dashed line), a mixture of **1a** and **DAP-H** (grey, dotted line) and **DAP-I** (yellow, long dashed line). Analyte concentration: 0.04 M in MeCN. Rapid reaction of **1a** and **DAP-H** resulting in formation of **DAP-I** was observed.

UV/Vis spectra of **2a** and **DAP-Br**

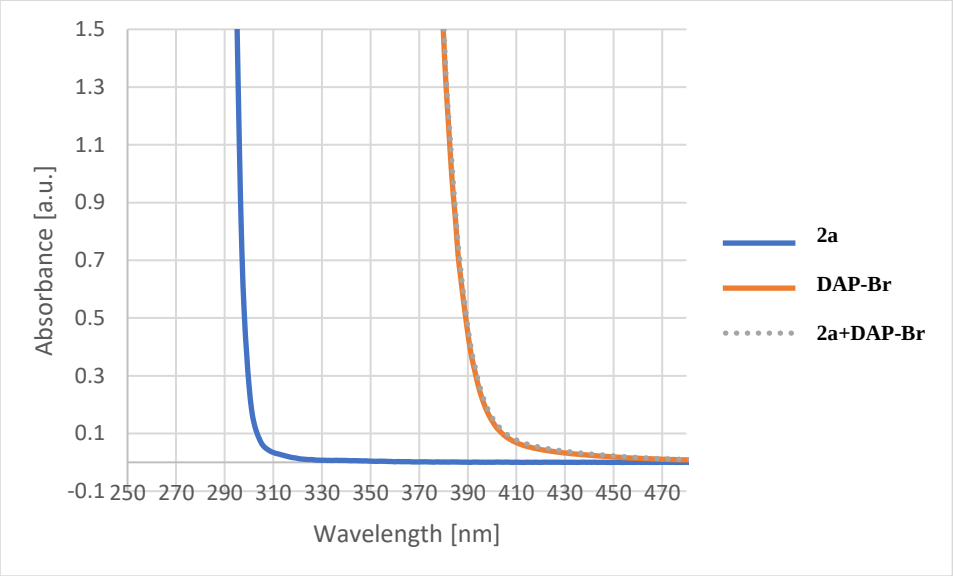


Figure S12: UV-Vis absorption spectra of **2a** (blue, full line)**, DAP-Br** (orange, dashed line) and a mixture of **2a** and **DAP-Br** (grey, dotted line). Analyte concentration: 0.04 M in MeCN. No formation of an EDA complex was observed.

UV/Vis spectra of **2a** and **DAP-H**

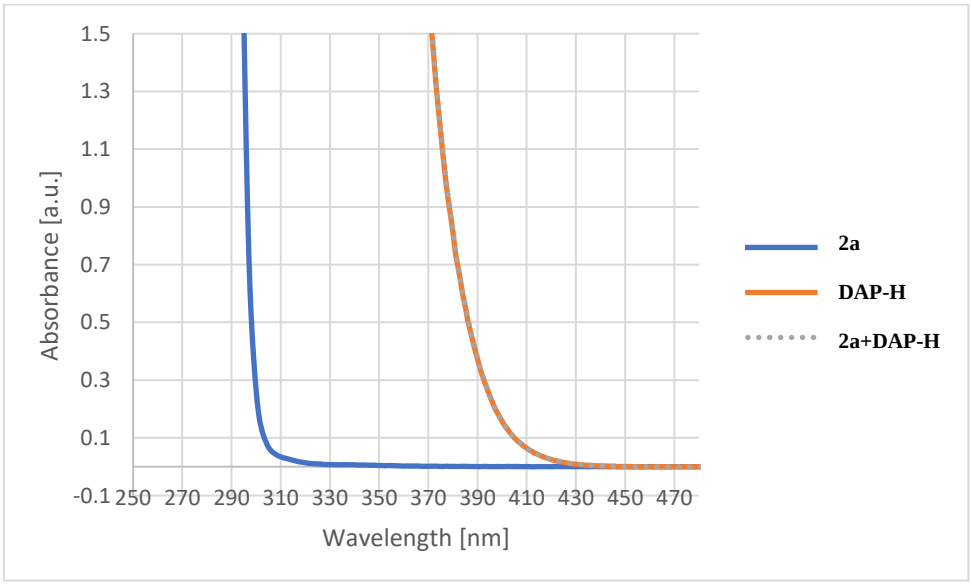


Figure S13: UV-Vis absorption spectra of **2a** (blue, full line)**, DAP-H** (orange, dashed line) and a mixture of **2a** and **DAP-H** (grey, dotted line). Analyte concentration: 0.04 M in MeCN. No formation of an EDA complex was observed.

Estimation of Excited State Oxidation Potential of **DAP-H**.

The estimated excited state oxidation potential E^0 (**DAP-H**$^+$/**DAP-H***) was calculated according to equation (1)[1,2]:

$$E^0\ (\textbf{DAP-H}^+/\textbf{DAP-H}^*) = E^0(\textbf{DAP-H}^+/\textbf{DAP-H}) - E_{00}(\textbf{DAP-H}^*/\textbf{DAP-H}) \quad (1)$$

Since the electrochemical oxidation of **DAP-H** was irreversible (see Figure S8), the irreversible peak potential E_{ox} was used for E^0(**DAP-H**$^+$/**DAP-H**). E_{00}(**DAP-H***/**DAP-H**), which is the excited state energy of the **DAP-H**, was estimated spectroscopically from the position of the long wavelength tail of the absorption spectrum (see Figure **S14**) recorded in MeCN, the same solvent used for the electrochemical analysis.

For **DAP-H**, E_{ox} was measured to be – 0.32 V, which provides E^0(**DAP-H**$^+$/**DAP-H**) = – 0.32 V. The position of the long wavelength tail of the absorption spectrum corresponds to 440 nm, which translates into an E_{00}(**DAP-H***/**DAP-H**) of 2.82 eV.

$$E^0\ (\textbf{DAP-H}^+/\textbf{DAP-H}^*) = -0.32\ \text{V} - 2.82\ \text{V} = -3.14\ \text{V}$$

The estimated excited state oxidation potential E^0 (**DAP-H**$^+$/**DAP-H***) = – 3.14 V shows the SET from **DAP-H*** to substrate **1a** (E_{red} = – 2.88 V) to be exergonic and for **2b** (E_{red} = – 3.36 V) to be endergonic.

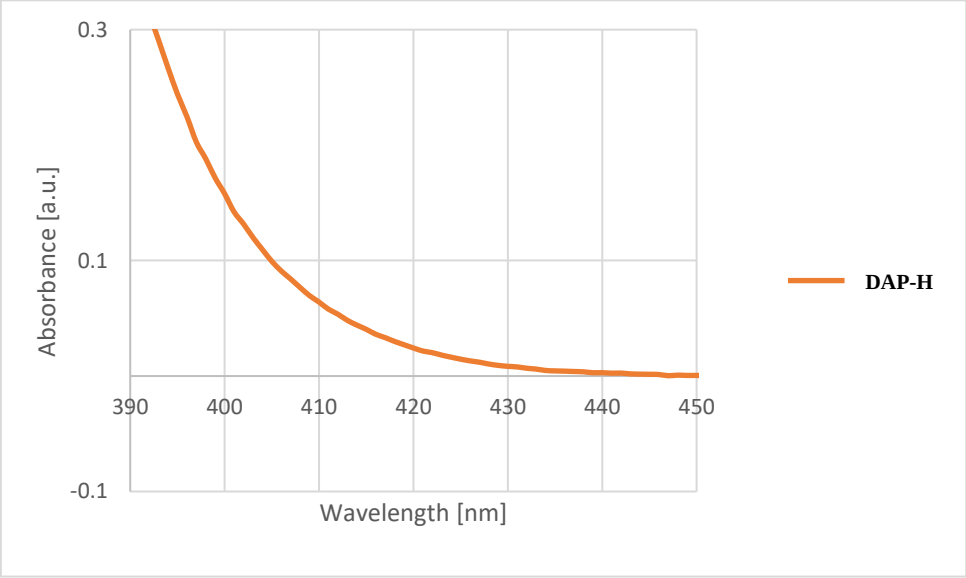
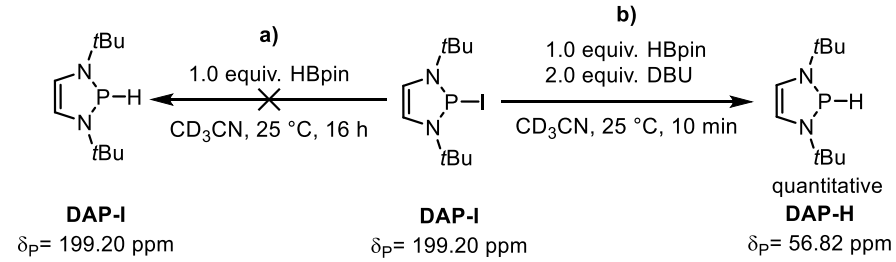


Figure S14: Zoom of the UV/Vis absorption spectra of **DAP-H** depicted in Figure S13. Analyte concentration: 0.04 M in MeCN. The long wavelength tail of the absorption of **DAP-H** was determined to be at 440 nm.

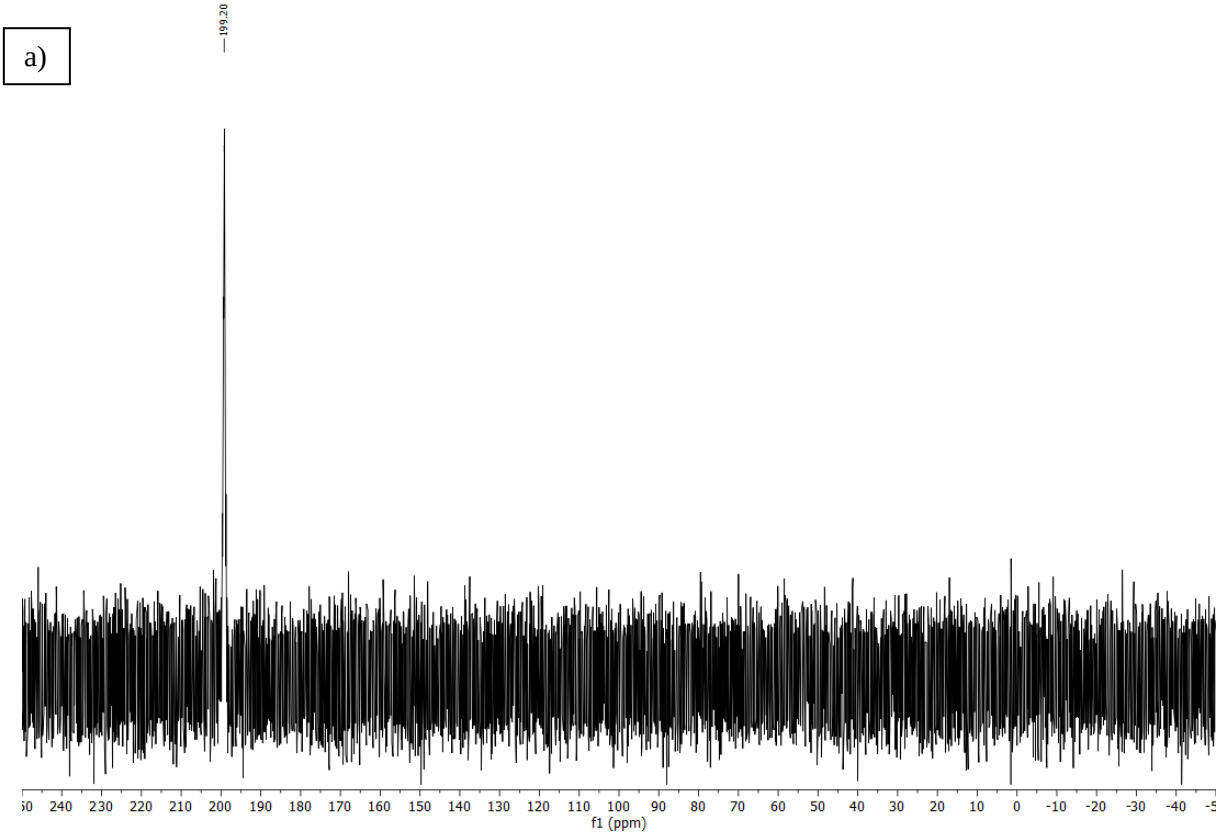
1.3.3 Formation of DAP-H from DAP-I with DBU as an Activator



A dried J-Young NMR tube was charged with a solution of **DAP-I** (8.00 mg, 24.5 µmol, 1.00 equiv.) and HBpin (3.56 µL, 3.14 mg, 24.5 µmol, 1.00 equiv.) in CD_3CN (0.7 mL) inside the glovebox. The tube was sealed and submitted to NMR analysis. No reaction towards **DAP-H** was observed, even after 16 h. **DAP-I** was the only detectable species in ^{31}P NMR at δ = 199.20 ppm (Figure S15 a).

A dried J-Young NMR tube was charged with a solution of **DAP-I** (16.3 mg, 50.0 µmol, 1.00 equiv.), DBU (14.9 µL, 15.2 mg, 100 µmol, 2.00 equiv.) and HBpin (7.25 µL, 6.40 mg, 50.0 µmol, 1.00 equiv.) in CD_3CN (1.0 mL) inside the glovebox. The tube was sealed and submitted to NMR analysis. In ^{31}P NMR, rapid conversion of **DAP-I** to **DAP-H** as the only detectable species at δ = 56.79 ppm was observed (Figure S15 b).

a)



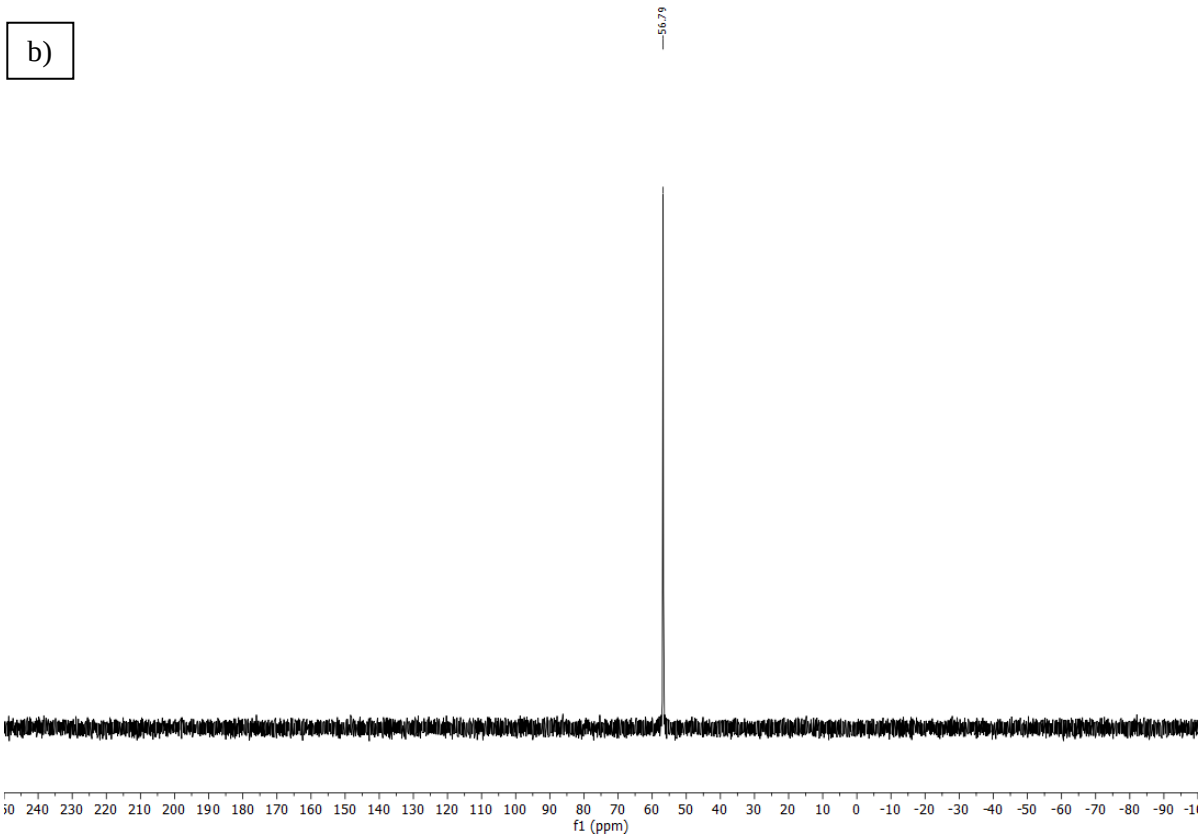
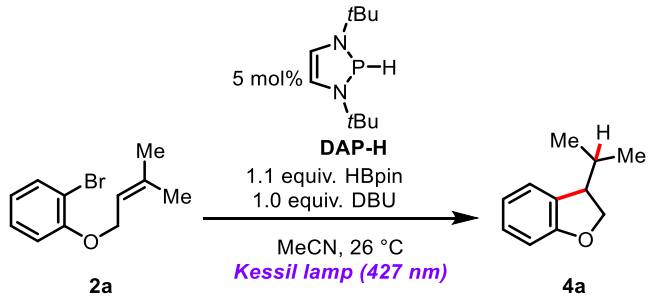


Figure S15: ^{31}P NMR spectra of: a) a mixture of **DAP-I** (1.00 equiv.) and HBpin (1.00 equiv.) in CD_3CN and b) **DAP-I** (1.00 equiv.), DBU (2.00 equiv.) and HBpin (1.00 equiv.) in CD_3CN.

1.3.4 Kinetic Investigations



General procedure B

A flame dried 10 ml microwave vial was charged with substrate **2a** (120.6 mg, 0.5 mmol, 1 equiv.) and 1,3,5-trimethoxybenzene NMR standard (28.0 mg, 0.166 mmol, 0.33 equiv.) under air and the vial was introduced inside the glovebox. Next, dry and degassed MeCN (0.625 ml), DBU (76.1 mg, 75.0 µL, 0.50 mmol, 1.00 equiv.), HBpin (70.4 mg, 80.0 µL, 0.55 mmol, 1.10 equiv.) and **DAP-H** (5.0 mg, 0.025 mmol, 0.05 equiv.) were added. The tube was sealed and stirred under the irradiation of a Kessil lamp (427 nm). Samples of 50 µL of this mixture were taken under a nitrogen atmosphere at specific times. The solvent was evaporated and the samples were analyzed by ^{1}H NMR.

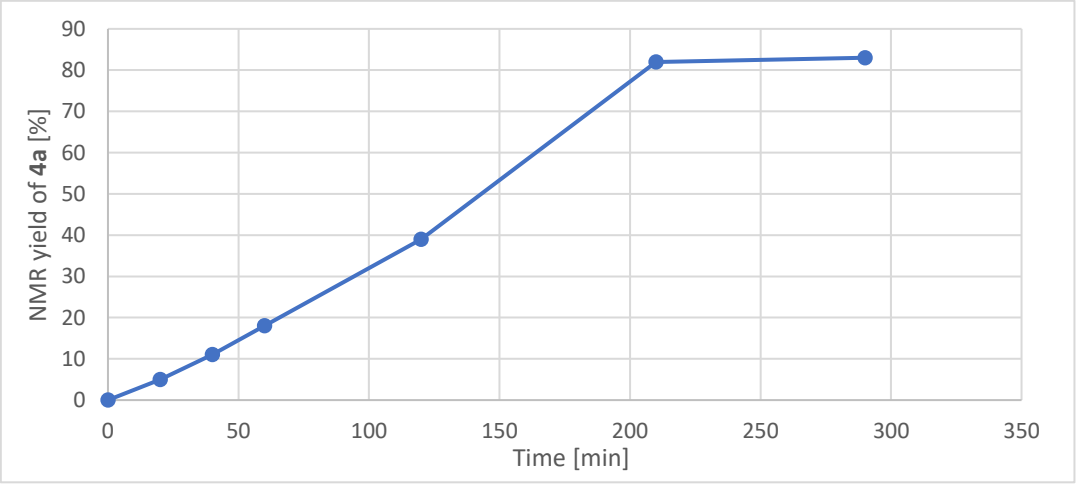
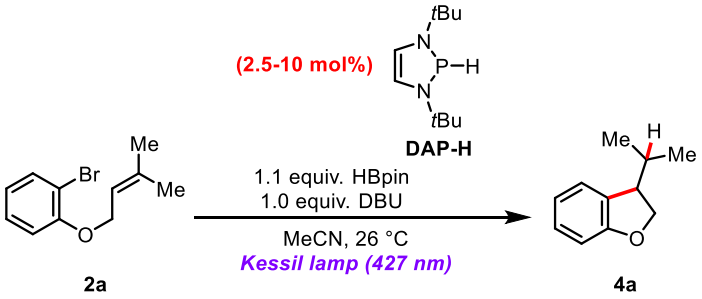


Figure S16: Reaction profile of **DAP** catalyzed cyclization of **2a**.

The reaction shows a linear kinetic behavior at the initial stage of the reaction and no substantial induction period is observed.

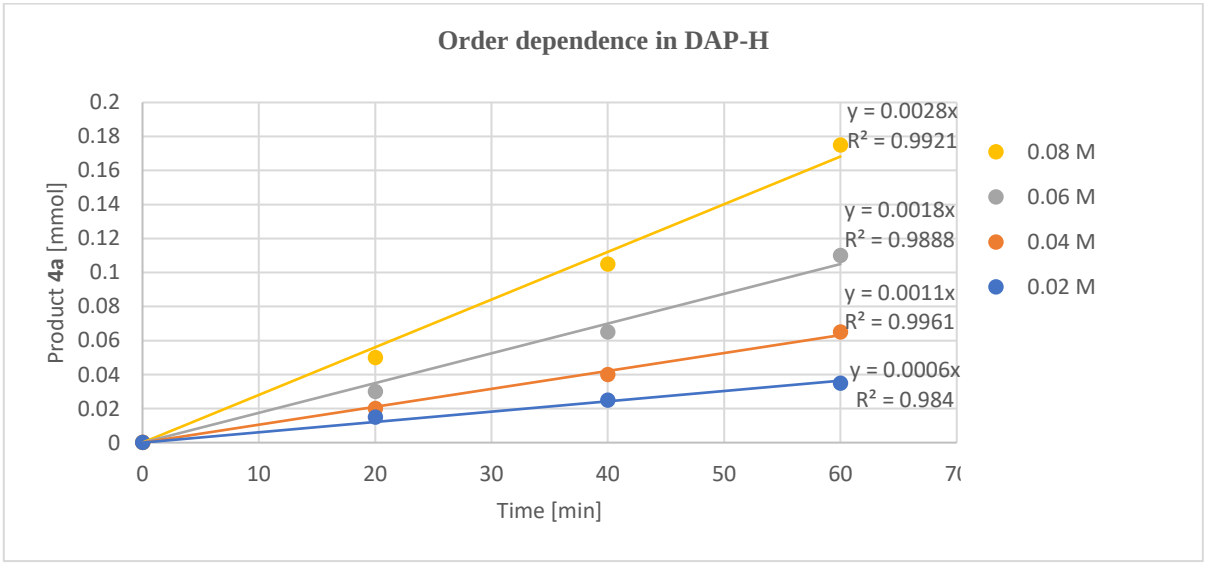
Order dependence in catalyst **DAP-H**



2a 4a

GP B was used with the following modifications: The amount of **DAP-H** (2.5 - 10 mg, 0.0125 - 0.010 mmol, 0.025 - 0.100 equiv.) was varied.

a)



b)

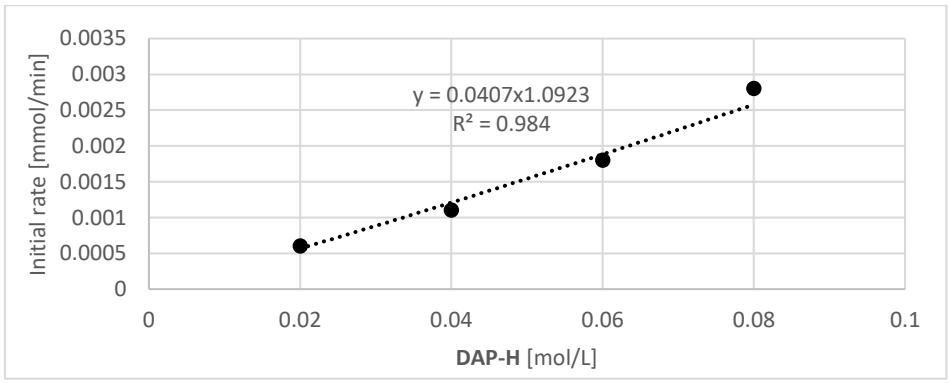
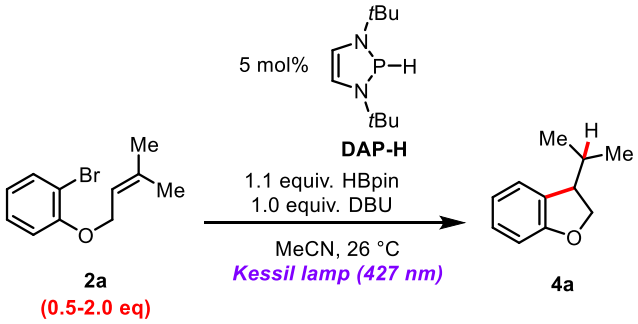


Figure S17: a) Reaction profiles at different initial concentrations of **DAP-H** showing a first-order dependence in **DAP-H**. Rate constants calculated from the slope of the plots. [2a] = 0.8 M; [DBU] = 0.8 M; [HBpin] = 0.88 M; [**DAP-H**] = 0.02 M (blue line), [**DAP-H**] = 0.04 M (orange line), [**DAP-H**] = 0.06 M (grey line), [**DAP-H**] = 0.08 M (blue line). b) Plot of initial rate (mmol/min) versus **DAP-H** (mmol) with fit to $y = ax^b$ where, y= Δ[[4a]/Δ[t, x= [**DAP-H**], b = reaction order.

Order dependence in substrate **2a**



GP B was used with the following modifications: The amount of **2a** (60.0 – 242 mg, 0.25 – 1.00 mmol, 0.50 – 2.00 equiv.) was varied.

a)

b)

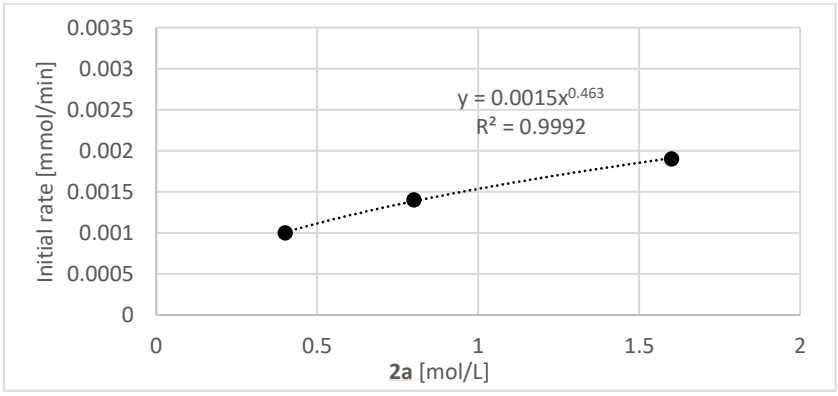
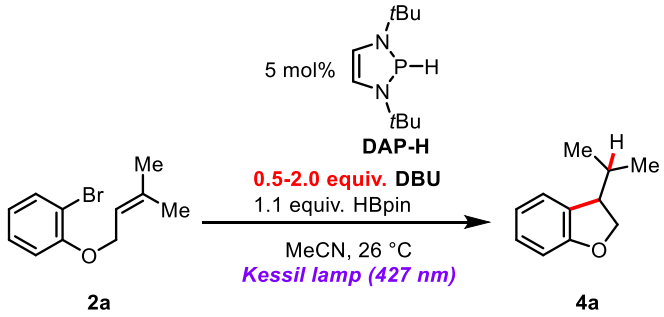


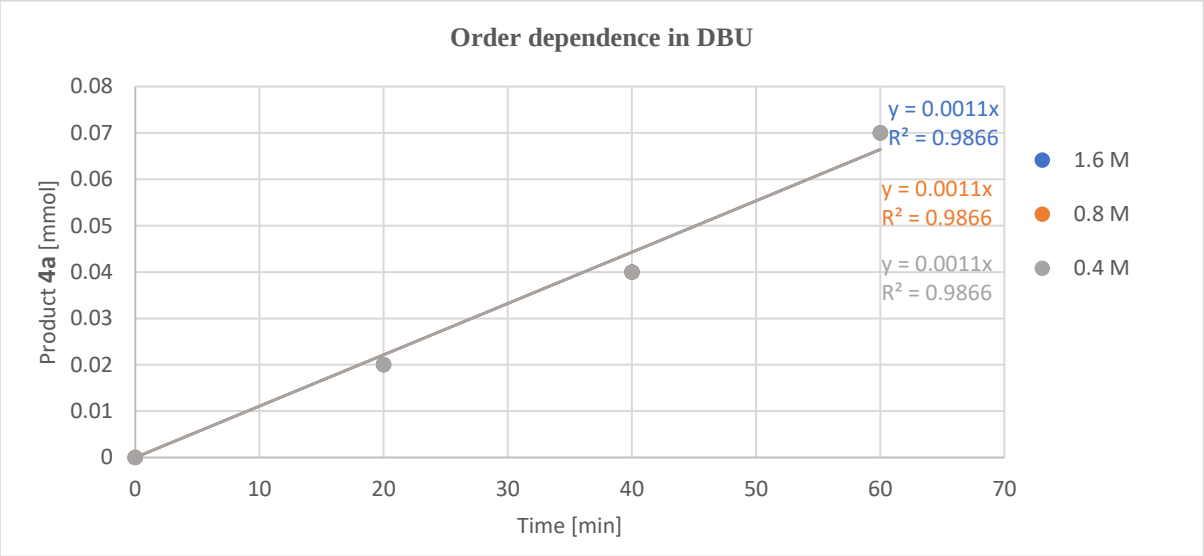
Figure S18: a) Reaction profiles at different initial concentrations of **2a** showing a half-order dependence in **2a**. Rate constants calculated from the slope of the plots. [DBU] = 0.8 M; [HBpin] = 0.88 M; [DAP-H] = 0.04 M; [**2a**] = 0.40 M; (grey line), [**2a**] = 0.8 M; (orange line), [**2a**]= 1.6 M; (blue line). b) Plot of initial rate (mmol/min) versus 1 (mmol) with fit to $y = ax^b$ where, y = Δ[4a]/ Δ[t, x = [**2a**], b = reaction order.

Order dependence in **DBU**



GP B was used with the following modifications: The amount of **DBU** (38.0 – 152 mg, 38.0 – 151 µL, 0.25 – 1.00 mmol, 0.5 – 2.0 equiv.) was varied.

a)



b)

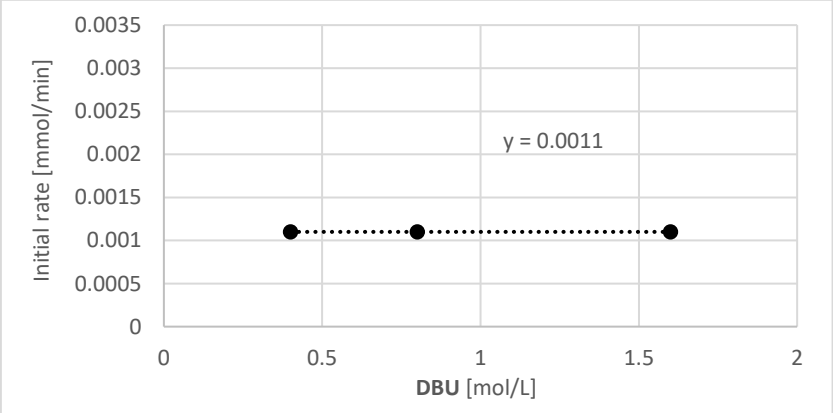
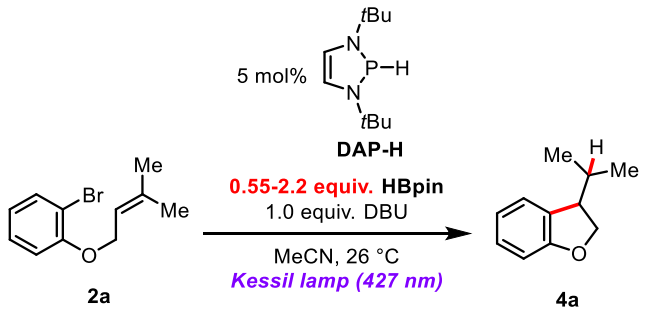


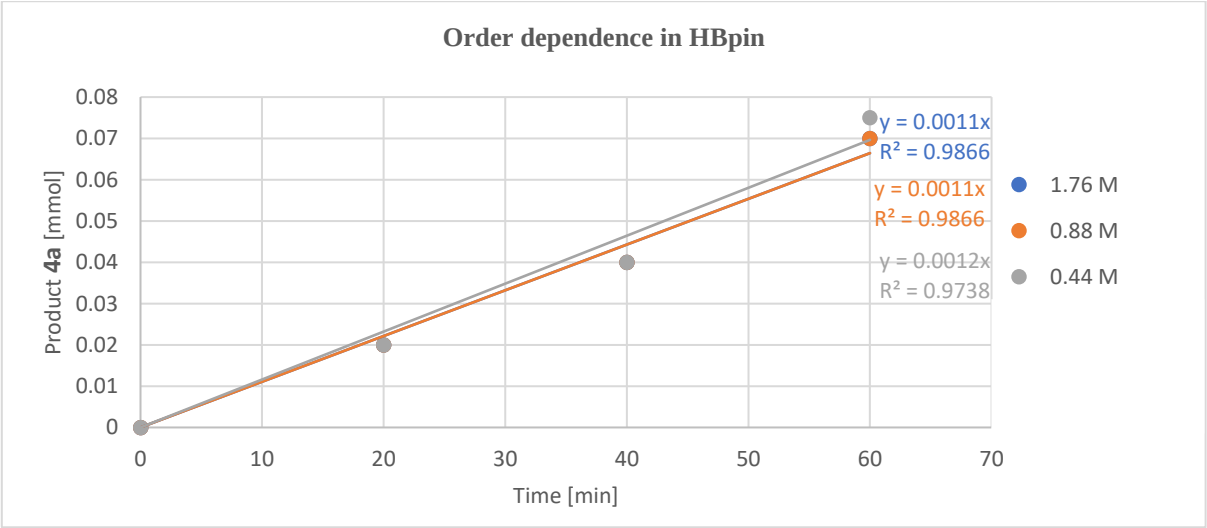
Figure S19: a) Reaction profiles at different initial concentrations of **DBU** showing a zero-order dependence in **DBU**. Rate constants calculated from the slope of the plots. [2a] = 0.8 M; [HBpin] = 0.88 M; [DAP-H] = 0.04 M; [**DBU**]= 0.40 M (grey line), [**DBU**]= 0.8 M; (orange line), [**DBU**]= 1.6 M; (blue line). b) Plot of initial rate (mmol/min) versus **DBU** (mmol) with fit to $y = ax^b$ where, y = Δ [4a]/Δt, x = [**DBU**], b = reaction order.

Order dependence in **HBpin**



GP B was used with the following modifications: The amount of **HBpin** (35.0 – 141 mg, 40.0 – 160 µL, 0.275 – 1.10 mmol, 0.55 – 2.20 equiv.) was varied.

a)



b)

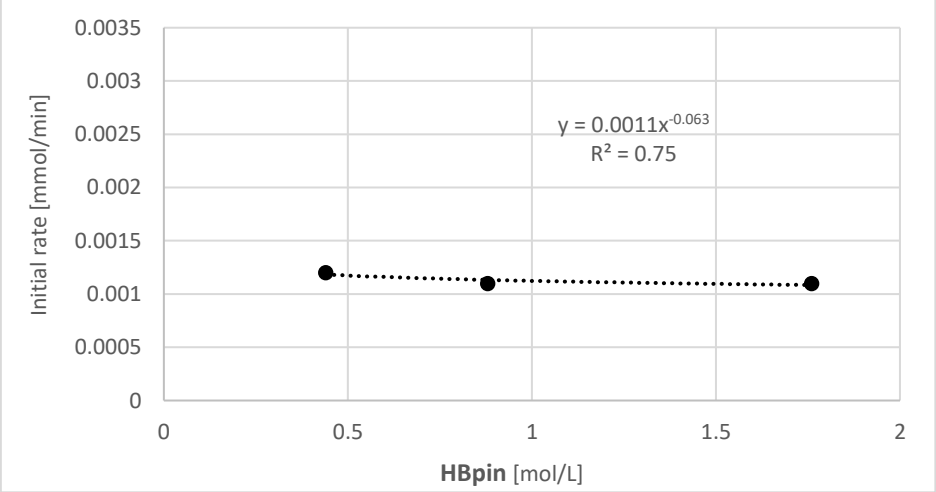
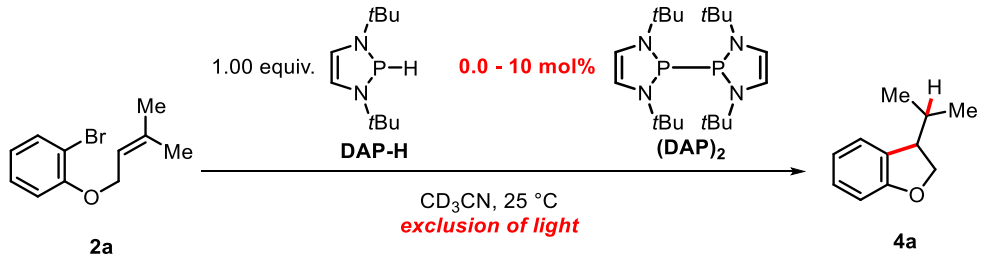


Figure S20: a) Reaction profiles at different initial concentrations of **HBpin** showing a zero-order dependence in **HBpin**. Rate constants calculated from the slope of the plots. [2a] = 0.80 M; [DBU] = 0.8 M; [DAP-H] = 0.04 M; [**HBpin**] = 0.44 M (grey line), [**HBpin**] = 0.88 M; (orange line), [**HBpin**] = 1.76 M; (blue line). b) Plot of initial rate (mmol/min) versus **HBpin** (mmol) with fit to $y = ax^b$ where, y = Δ[4a]/Δt, x= [**HBpin**], b = reaction order.

Effect of the **(DAP)$_2$** additive on the stoichiometric reaction



A dried J-Young NMR tube was charged with substrate **2a** (120.6 mg, 0.50 mmol, 1.00 equiv.) and 1,3,5-trimethoxybenzene (28.0 mg, 0.17 mmol, 0.33 equiv.) under air and the tube was introduced inside the glovebox. Next, dry and degassed CD_3CN (0.625 ml) was added followed by addition of **DAP-H** (100 mg, 0.50 mmol, 1.00 equiv.) and **(DAP)$_2$** (0.0 – 10 mol%) under exclusion of light. The tube sealed and the reaction progress was monitored by ^{1}H NMR.

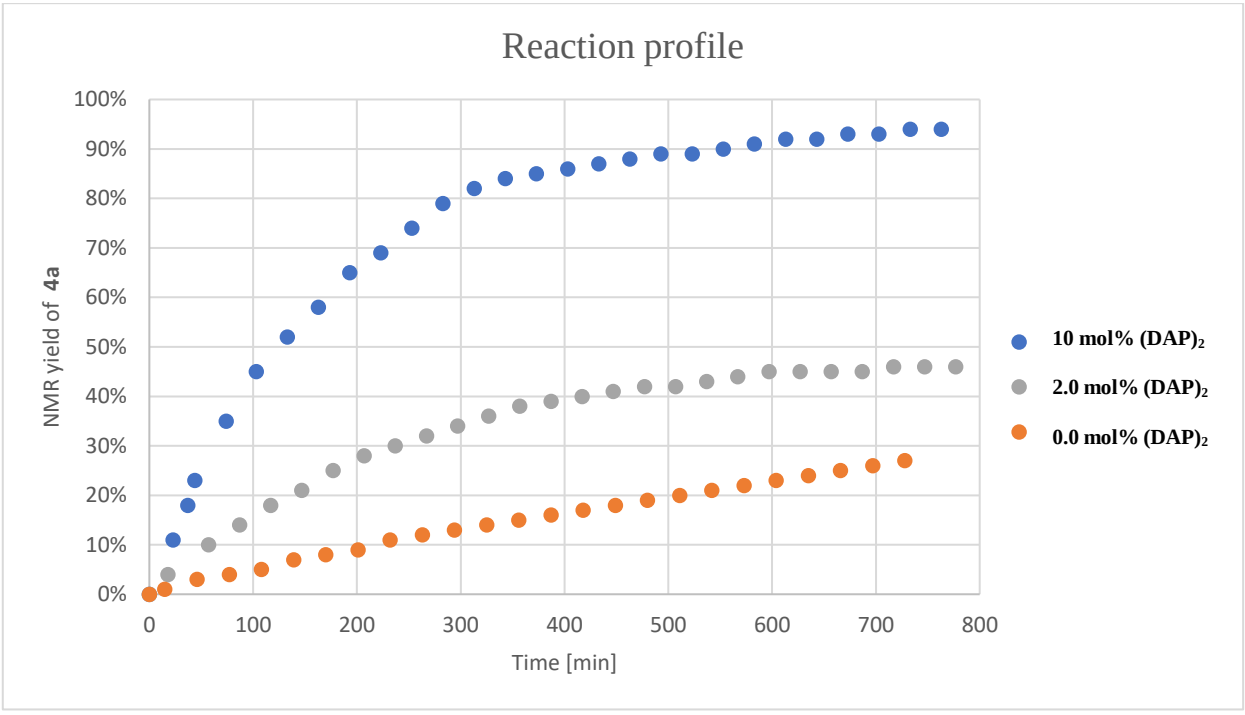
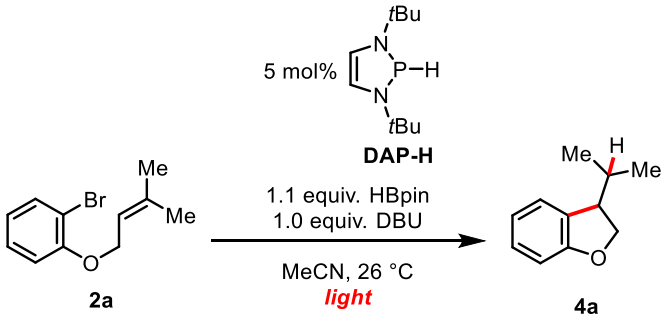


Figure S21: Reaction profiles with different amounts of **(DAP)$_2$**. [**2a**] = 0.8 M; [**DAP-H**]= 0.8 M; **(DAP)$_2$** = 0.0 mol%; (orange line), **(DAP)$_2$** = 2.0 mol%; (grey line), **(DAP)$_2$** = 10 mol%; (blue line).

Dependance in light.



GP B was used with the following modifications: The power of the light source was varied.

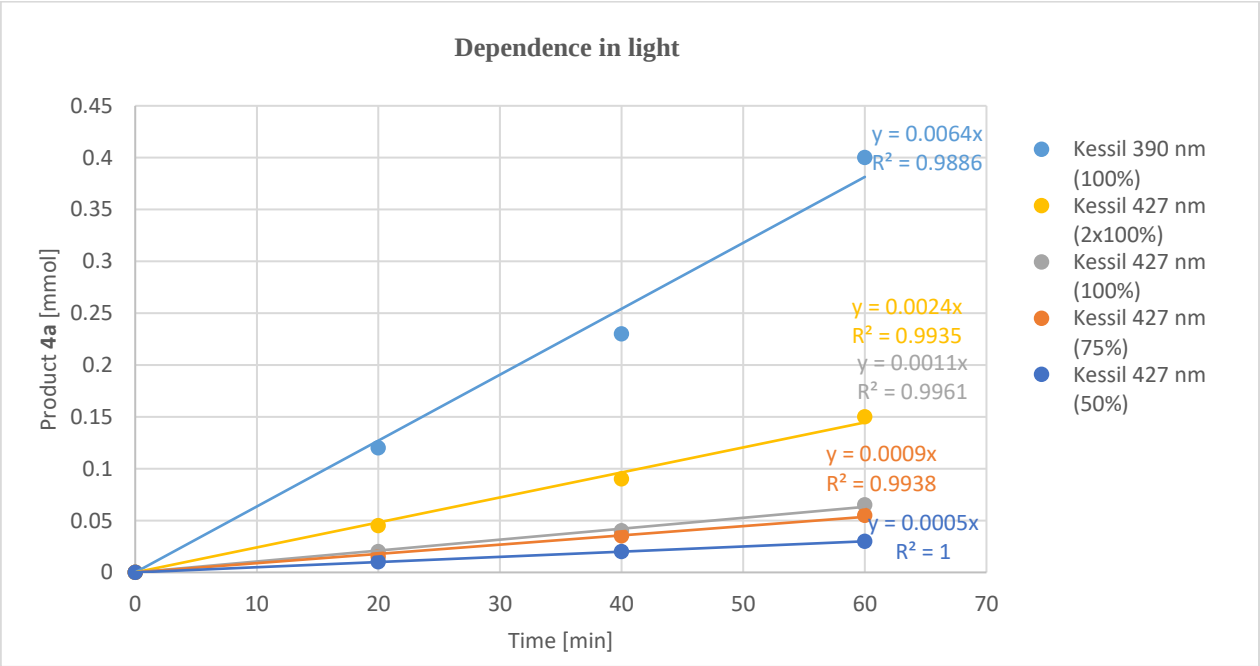
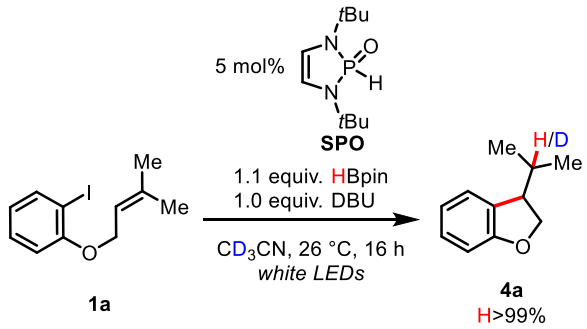


Figure S22: Reaction profiles at different irradiance. [**2a**] = 0.8 M; [DBU] = 0.8 M; [**DAP-H**]= 0.04; [HBpin] = 0.88 M. Kessil lamp (427 nm) 50% power (dark blue line), Kessil lamp (427 nm) 75% power (orange line), Kessil lamp (427 nm) 100% power (grey line), 2×Kessil lamp (427 nm) 100% power (yellow line), Kessil lamp (390 nm) 100% power (light blue line).

1.3.5 Deuterated experiments

Exclusion of HAT from the Solvent



A stirred mixture of **1a** (28.8 mg, 100 µmol, 1.00 equiv.), **SPO** (1.08 mg, 5.00 µmol, 0.05 equiv.), DBU (15.2 mg, 100 µmol, 1.00 equiv.) and HBpin (14.1 mg, 110 µmol, 1.10 equiv.) in CD_3CN (1 mL) was irradiated with white LEDs for 16 h. Volatiles were removed under reduced pressure and the residue was purified by flash chromatography (*n*-pentane:EA=40:1) to afford **4a** as a colorless oil. A H incorporation greater than 99% was determined by ^1H NMR.

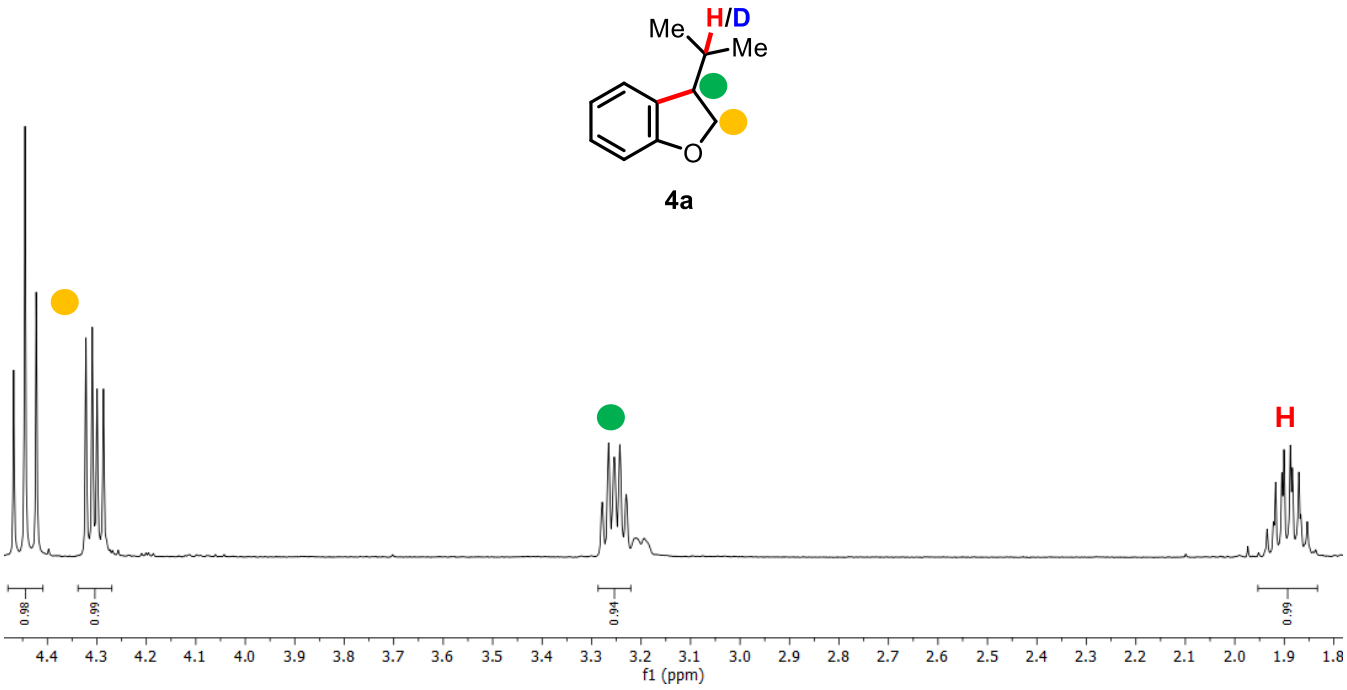
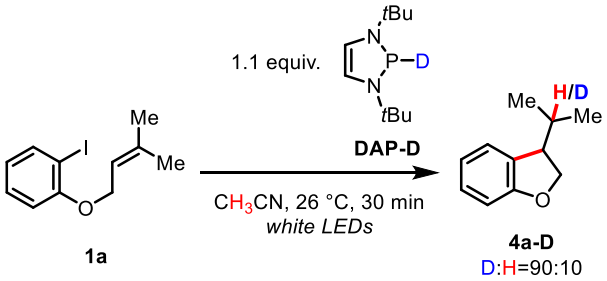


Figure S23: Zoom of the ^1H NMR spectra of isolated **4a**.

Proof of possible HAT from a DAP species



A stirred mixture of **1a** (57.6 mg, 0.20 mmol, 1.00 equiv.) and **DAP-D** (44.3 mg, 0.22 mmol, 1.10 equiv.) in MeCN (2 mL) was irradiated with white LEDs for 30 min. Volatiles were removed under reduced pressure and the residue was purified by flash chromatography (*n*-pentane:EA=40:1) to afford **4a-D** as a colorless oil. An incorporation of D:H = 90:10 was determined by ^{1}H NMR.

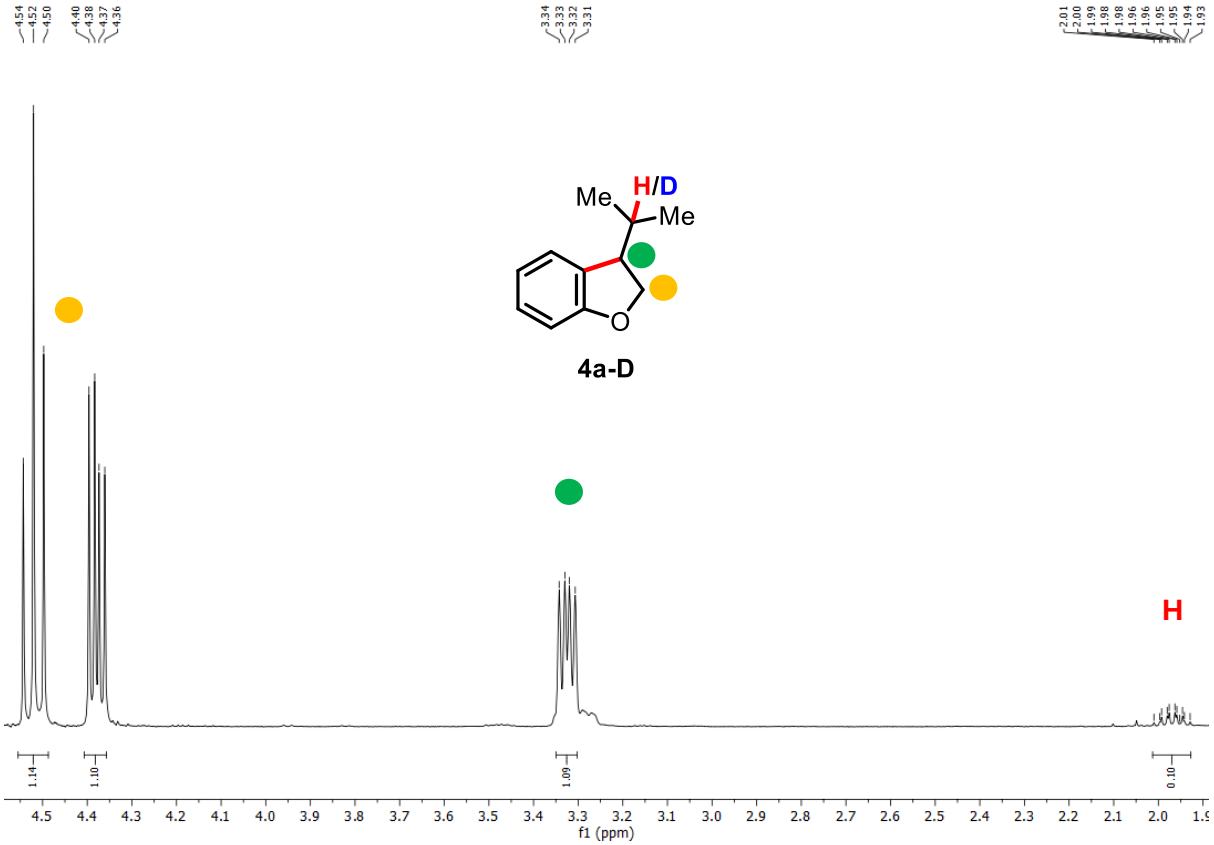
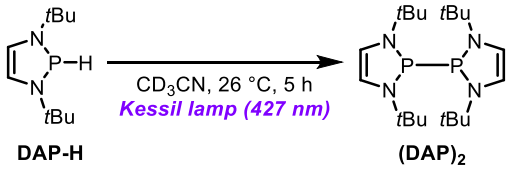


Figure S24: Zoom of the ^{1}H NMR spectra of isolated **4a-D**.

1.3.6 Formation of $(DAP)_2$ from DAP-H under Irradiation



A dried J-Young NMR tube was charged with a solution of **DAP-H** (10 mg, 50 µmol) in CD_3CN (0.5 mL) inside the glovebox. The tube was sealed and submitted to NMR analysis. In ^{31}P NMR, only **DAP-H** was detected at δ = 56.86 ppm (Figure S25a). The tube was irradiated with a Kessil lamp (427 nm) for 5 h. After irradiation, a solid precipitate was observed, presumably **$(DAP)_2$**, which was found to be poorly soluble in MeCN and CD_3CN. ^{31}P NMR analysis showed complete conversion of **DAP-H** and the new signal at δ = 78.20 ppm corresponded to **$(DAP)_2$** (**Figure S25**Figure S25 b).

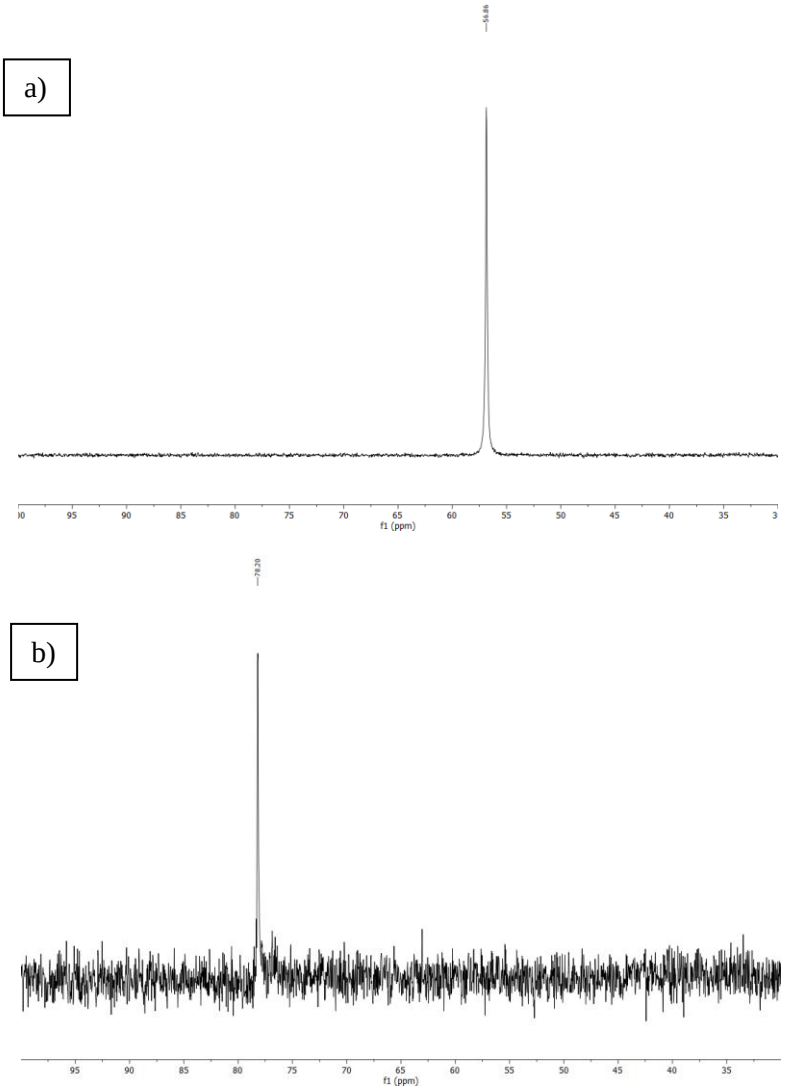
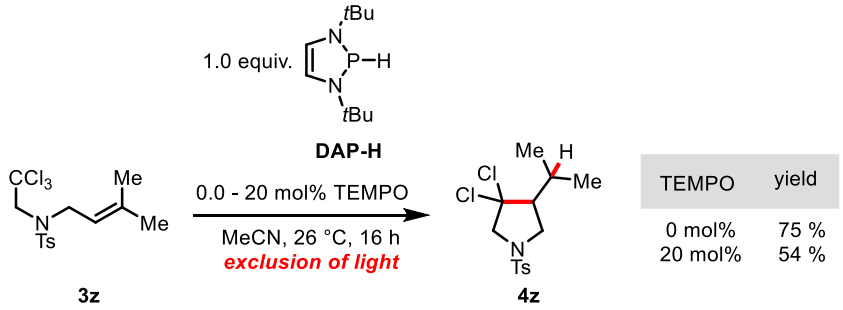


Figure S25: ^{31}P NMR spectra of a solution of **DAP-H** in CD_3CN a) before and b) after irradiation with Kessil lamp (427 nm) to access **$(DAP)_2$**.

1.3.7 Attempts to inhibit the reductive cyclization by TEMPO

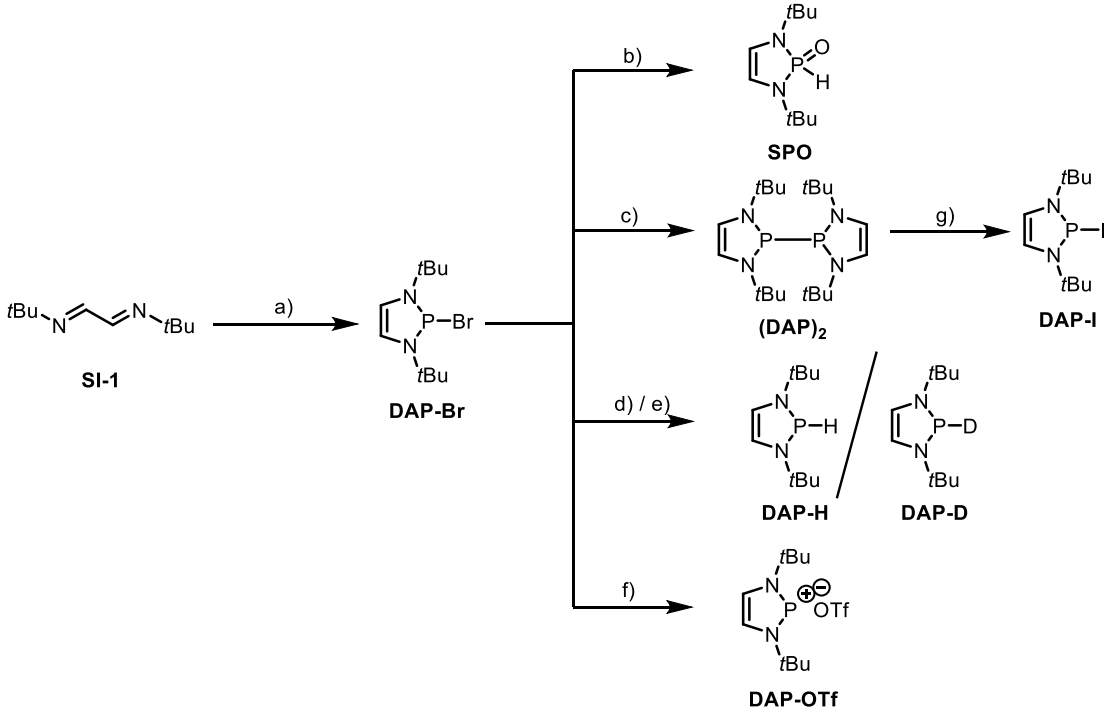


Two separate 1 mL microwave vial, equipped with a stir bar were charged with **3z** (37.1 mg, 100 µmol, 1.00 equiv.), to one vial was added (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (3.13 mg, 20 µmol, 0.20 equiv.) and both vials were transferred into the glovebox. MeCN (125 µL) was added, followed by **DAP-H** (20.0 Mg, 100 µmol, 1.00 equiv.) under strict exclusion of light. The vials were capped and the reaction mixtures were stirred for 16 h at 26 °C. Volatiles were removed under reduced pressure and the residue was directly subjected to ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

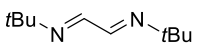
Note: **DAP-H** reacts rapidly with TEMPO, thus inhibition of hypothesized radical intermediates could not be observed.

1.4 DAP Synthesis

General Overview



N[1], *N*[2]-Di-*tert*-butylethane-1,2-diimine (SI-1)



SI-1

To a stirred solution of oxaldehyde (2.90 g, 20.0 mmol, 1.00 equiv.) in H_2O (20 w-%) was added *tert*-butylamine (2.09 mL, 1.46 g, 20.0 mmol, 2.00 equiv.) at 0°C under air. Instantly a white precipitate formed and the reaction mixture solidified. The mixture was sonicated for 15 min. The solid was filtered, washed several times with H_2O, dissolved in CH_2Cl_2 (20 mL) and dried over Na_2SO_4. All volatiles were removed under reduced pressure to afford **SI-1** (1.19 g, 7.04 mmol, 70 %) as a white solid with a wet appearance, which was used in the next step without further purification.

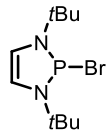
*Analytical data of **SI-1**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 2H), 1.26 (s, 18H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 58.4, 29.5 ppm.

All spectroscopic data corresponded to the reported literature values.[3]

2-Bromo-1,3-di-*tert*-butyl-2,3-dihydro-1H-1,3,2-diazaphosphole (DAP-Br)



DAP-Br

a) To a stirred solution of diimine **SI-1** (505 mg, 3.00 mmol, 1.00 equiv.) in dry Et_2O (5 mL) was added cyclohexene (912 µL, 739 mg, 9.00 mmol, 3.00 equiv.), followed by PBr_3 (285 µL, 812 mg, 3.00 mmol, 1.00 equiv.) at rt. The mixture was stirred for 20 h at rt and all volatiles were removed in vacuo. The solid residue was transferred into the glovebox, filtered, and washed with Et_2O to afford the title compound (623 mg, 2.23 mmol, 74 %) as a faint yellow powder.

*Analytical data of **DAP-Br**:*

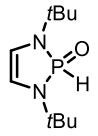
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (s, 2H), 1.73 (s, 19H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.3 (d, J = 7.2 Hz), 59.3 (d, J = 7.4 Hz), 30.3 (d, J = 10.0 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 185.89 ppm.

All spectroscopic data corresponded to the reported literature values.[4]

1,3-Di-*tert*-butyl-1,3-dihydro-1,3,2-diazaphosphole 2-oxide (SPO)



SPO

b) **SPO** was synthesized according to a known procedure.[5] To a stirred solution of **DAP-Br** (500 mg, 1.79 mmol, 1.00 equiv.) in CH_2Cl_2 (5 mL) was added NEt_3 (250 µL, 181 mg, 1.79 mmol, 1.00 equiv.) at rt. The resulting mixture was stirred for 5 min and quenched by the addition of H_2O (10 mL). After stirring for 1 h, the reaction mixture was extracted with CH_2Cl_2 (2 × 15 mL). Organic layers were dried over Na_2SO_4 and all volatiles were removed under reduced pressure to afford the title compound (349 mg, 1.61 mmol, 90 %) as an ivory solid.

*Analytical data of **SPO**:*

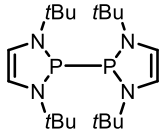
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (dt, J = 646.9, 1.8 Hz, 1H), 5.95 (dd, J = 16.0, 1.7 Hz, 2H), 1.43 (s, 18H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.6 (d, J = 10.2 Hz), 53.6 (d, J = 4.3 Hz), 30.2 (d, J = 4.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 3.36 ppm.

All spectroscopic data corresponded to the reported literature values.[5]

1,1',3,3'-Tetra-*tert*-butyl-1,1',3,3'-tetrahydro-2,2'-bi(1,3,2-diazaphosphole) $(DAP)_2$



$(DAP)_2$

c) **$(DAP)_2$** was synthesized according to a known procedure.[6] To a stirred suspension of **DAP-Br** (4.02 g, 14.4 mmol, 1.00 equiv.) and Mg (turnings, 1.05 g, 43.2 mmol, 3.00 equiv.) in dry THF (12 mL) inside a Schlenk flask, was added iodine (366 mg, 1.44 mmol, 0.10 equiv.) at rt. The mixture was stirred for 4 h and all volatiles were removed in vacuo. The flask was transferred into the glovebox and the residue was suspended in *n*-pentane (20 mL). The resulting mixture was filtered over celite and the remaining solid was washed with *n*-pentane (2 × 20 mL). All volatiles were removed in vacuo to afford the title compound (2.55 g, 6.41 mmol, 44 %) as an off-white solid.

*Analytical data of **$(DAP)_2$**:*

^{1}H NMR (400 MHz, C_6D_6): δ = 5.94 (t, *J* = 1.9 Hz, 4H), 1.26 (s, 36H) ppm.

^{13}C NMR (100 MHz, C_6D_6): δ = 121.3, 54.2 (t, *J* = 7.7 Hz), 30.3 (t, *J* = 4.0 Hz) ppm.

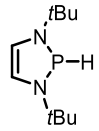
^{31}P NMR (162 MHz, C_6D_6): δ = 79.86 ppm.

^{1}H NMR (400 MHz, CD_3CN): δ = 5.95 (t, *J* = 2.0 Hz, 4H), 1.18 (s, 36H) ppm.

^{31}P NMR (162 MHz, CD_3CN): δ = 78.20 ppm.

All spectroscopic data (acquired in C_6D_6) corresponded to the reported literature values.[6]

1,3-Di-*tert*-butyl-2,3-dihydro-1H-1,3,2-diazaphosphole (DAP-H)



DAP-H

d) To a stirred suspension of **DAP-Br** (2.70 g, 10.0 mmol, 1.00 equiv.) in dry and degassed THF (70 mL) inside a Schlenk flask was added $LiAlH_4$ (1.25 mL, 2.4 M in THF, 114 mg, 3.00 mmol, 0.30 equiv.) at – 78 °C. The mixture was stirred for 30 min at – 78 °C. The cooling bath was removed and the mixture was stirred for further 2 h. All volatiles were removed in vacuo and the flask was transferred into the glovebox. The residue was suspended in *n*-hexane (15 mL) and filtered over celite. The remaining residue inside the flask was washed with additional *n*-hexane (2 × 20 mL). Volatiles were removed in vacuo to afford a yellow oil. Distillation (1 mbar, 73 °C) afforded the title compound (1.19 g, 5.94 mmol, 59%) as a faint yellow liquid.

*Analytical data of **DAP-H**:*

^{1}H NMR (400 MHz, C_6D_6): δ = 6.16 (d, *J* = 184.2 Hz, 1H), 6.00 (d, *J* = 3.9 Hz, 2H), 1.16 (s, 18H) ppm.

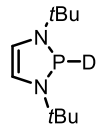
^{31}P NMR (162 MHz, C_6D_6): δ = 57.49 ppm.

^{1}H NMR (400 MHz, CD_3CN): δ = 6.08 (d, *J* = 4.0 Hz, 2H), 1.21 (d, *J* = 1.0 Hz, 18H) ppm.

^{31}P NMR (162 MHz, CD_3CN): δ = 56.81 ppm.

All spectroscopic data in C_6D_6[7] and CD_3CN[8] corresponded to the reported literature values.

1,3-Di-*tert*-butyl-2,3-dihydro-1H-1,3,2-diazaphosphole-2-d (DAP-D)



DAP-D

e) A solution of $LiAlD_4$ was prepared by a modified literature procedure[9]:

Inside the glovebox, LiD (186 mg, 20.6 mmol, 2.06 equiv.) and $LiAlD_4$ (23.6 mg, 0.56 mmol, 0.06 equiv.) were thoroughly ground separately and suspended in Et_2O (2 mL). Under stirring, a solution of $AlCl_3$ (500 mg, 3.75 mmol, 0.38 equiv.) in Et_2O (5 mL) was added dropwise. The reaction was stirred for further 30 min and filtered over a short plug of celite. This solution of $LiAlD_4$ was used without further analysis or purification in the next step.

Outside the glovebox, the prior obtained solution of $LiAlD_4$ in Et_2O was added to a stirred solution of **DAP-Br** (2.79 g, 10.0 mmol, 1.00 equiv.) in THF (70 mL) inside a Schlenk tube at – 78 °C. The mixture was stirred for further 30 min at this temperature and was allowed to reach rt, at which the stirring was continued for additional 2 h. All volatiles were removed in vacuo and the Schlenk tube was transferred into the glovebox. The yellow residue was suspended in *n*-hexane (15 mL), filtered over celite and washed with *n*-hexane (2×15 mL). The volatiles were removed in vacuo and the remaining yellow liquid residue was distilled under reduced pressure (0.08 mbar, 70 °C) to afford the title compound as a highly air and moisture sensitive, faint yellow liquid (657 mg, 3.28 mmol, 33%, D incorporation > 95%)

*Analytical data of **DAP-D**:*

^{1}H NMR (400 MHz, C_6D_6): δ = 6.00 (d, J = 4.0 Hz, 2H), 1.16 (d, J = 1.0 Hz, 18H) ppm.

^{13}C NMR (101 MHz, C_6D_6): δ = 121.1 (d, J = 6.8 Hz), 53.7 (d, J = 13.5 Hz), 29.7 (d, J = 8.8 Hz) ppm.

^{31}P NMR (162 MHz, C_6D_6): δ = 55.84 – 55.47 (m) ppm.

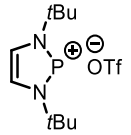
^{1}H NMR (400 MHz, CD_3CN): δ = 6.08 (d, J = 4.0 Hz, 2H), 1.21 (d, J = 1.0 Hz, 18H) ppm.

^{13}C NMR (101 MHz, CD_3CN): δ = 121.5 (d, J = 7.1 Hz), 54.2 (d, J = 12.2 Hz), 29.8 (d, J = 8.9 Hz) ppm.

^{31}P NMR (162 MHz, CD_3CN): δ = 55.94 ppm.

HRMS (ESI): calcd. for $[C_{10}H_{20}{}^2HN_2P]^+$, $[M]^+$: 201.1500; found: 201.1508.

1,3-Di-*tert*-butyl-1,3-dihydro-2H-1,3,2-diazaphosphol-2-yl trifluoromethanesulfonate (DAP-OTf)



DAP-OTf

f) To a stirred solution of **DAP-Br** (1.00 g, 3.58 mmol, 1.00 equiv.) in dry and degassed THF (30 mL) was added trimethylsilyl trifluoromethanesulfonate (647 µL, 796 mg, 3.58 mmol, 1.00 equiv.) at rt. The yellow solution turned immediately colorless and precipitation was observed. The mixture was stirred for 2 h and the precipitate was removed by filtration over celite. All volatiles were removed in vacuo to afford **DAP-OTf** (1.03 g, 2.95 mmol, 82%) as a white solid.

*Analytical data of **DAP-OTf**:*

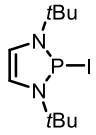
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 2 H), 1.80 (d, J = 1.9 Hz, 18H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.9 (d, J = 3.6 Hz), 62.8 (d, J = 7.6 Hz), 31.4 (d, J = 9.4 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 202.10 ppm.

All spectroscopic data in corresponded to the reported literature values.[10]

1,3-Di-tert-butyl-2-iodo-2,3-dihydro-1H-1,3,2-diazaphosphole (DAP-I)



DAP-I

g) To a stirred suspension of **$(DAP)_2$** (797 mg, 2.00 mmol, 1.00 equiv.) in MeCN (6 mL) was added iodobenzene (223 µL, 408 mg, 1.00 mmol, 1.00 equiv.) at rt. The mixture was stirred for 2 h and all volatiles were removed in vacuo. The bright yellow solid residue was washed with *n*-pentane and dried in vacuo to afford **DAP-I** (608 mg, 1.86 mmol, 93 %) as a bright yellow solid.

*Analytical data of **DAP-I**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 2H), 1.75 (d, J = 2.0 Hz, 19H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.9 (d, J = 6.5 Hz), 60.1 (d, J = 7.1 Hz), 29.8 (d, J = 9.6 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 194.35 ppm.

^{1}H NMR (400 MHz, CD_3CN): δ = 7.84 (d, J = 3.3 Hz, 2H), 1.71 (d, J = 2.0 Hz, 20H) ppm.

^{31}P NMR (162 MHz, CD_3CN): δ = 199.31 ppm.

All spectroscopic data (acquired in $CDCl_3$) corresponded to the reported literature values.[6]

1.5 Substrate Synthesis

General Procedure C:

Without exclusion of moisture or oxygen. To a stirred suspension of K_2CO_3 (2.00 – 3.00 equiv.) and alcohol (1.00 equiv.) in DMF (0.5 M) was added alkyl halide (1.1 – 1.3 equiv.) at rt. The reaction was stirred for 16 h and diluted with H_2O (2 mL per mmol alcohol) and aq. NaOH (2 M, 2 mL per mmol alcohol). The mixture was extracted with EtOAc or *n*-pentane (3×) and the combined organic layers were washed with sat. aq. $Na_2S_2O_3$, followed by brine. After drying over Na_2SO_4, all volatiles were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2, *n*-pentane:EtOAc).

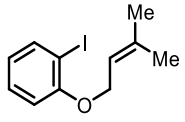
General Procedure D:

A stirred suspension of amide (1.00 equiv.), K_2CO_3 (2.00 equiv.), KI (10 mol%) and alkyl bromide (1.30 equiv.) in acetone (0.5 M) was heated to 60 °C. After 18 h, the mixture was cooled to rt, diluted with H_2O (10 mL per mmol amide) and extracted with Et_2O (3 × 10 mL per mmol amide). After drying the combined organic layers over Na_2SO_4, all volatiles were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2, *n*-pentane:EtOAc).

General Procedure E:

To a stirred solution of PPh_3 (3.00 equiv.) in dry THF (0.5 M) was added CBr_4 (3.00 equiv.) at 0 °C. The resulting mixture was stirred for 5 min, followed by the addition of alcohol (1.00 equiv., dissolved in 1-2 mL dry THF). The reaction was allowed to reach rt, stirred for 18 h and quenched by the addition of H_2O (20 mL per mmol alcohol). The mixture was extracted with CH_2Cl_2 (3 × 20 mL per mmol alcohol), combined organic layers were dried over $MgSO_4$ and all volatiles were removed under reduced pressure. Purification of the residue by flash chromatography (SiO_2, *n*-pentane:EtOAc) afforded the desired products.

1-Iodo-2-((3-methylbut-2-en-1-yl)oxy)benzene (1a)



1a

Synthesized according to GP C from 2-iodophenol (1.10 g, 5.00 mmol, 1.00 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.00 equiv.) and 1-bromo-3-methylbut-2-ene (654 µL, 820 mg, 5.50 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **1a** (1.25 g, 4.35 mmol, 87%) as a colourless liquid.

*Analytical data of **1a**:*

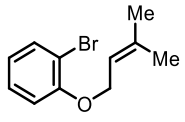
TLC (SiO_2): R_f (*n*-pentane: EtOAc = 40:1) = 0.43

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.32 – 7.23 (m, 1H), 6.83 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.70 (td, *J* = 7.6, 1.4 Hz, 1H), 5.54 – 5.49 (m, 1H), 4.59 (d, *J* = 6.5 Hz, 2H), 1.80 (s, 3H), 1.75 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.6, 139.6, 138.1, 129.5, 122.6, 119.7, 112.8, 87.1, 66.4, 25.9, 18.5 ppm.

All spectroscopic data corresponded to the reported literature values.[6]

1-Bromo-2-((3-methylbut-2-en-1-yl)oxy)benzene (2a)



2a

Synthesized according to GP C from 2-bromophenol (1.59 mL, 2.56 g, 15.0 mmol, 1.11 equiv.), K_2CO_3 (6.22 g, 45.0 mmol, 3.33 equiv.) and 1-bromo-3-methylbut-2-ene (1.58 mL, 2.01 g, 13.5 mmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **2a** (2.79 g, 11.6 mmol, 86%) as a colourless liquid.

*Analytical data of **2a**:*

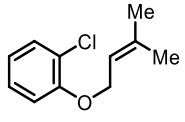
TLC (SiO_2): R_f (*n*-pentane: EtOAc = 40:1) = 0.42

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.29 – 7.20 (m, 1H), 6.91 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.82 (td, *J* = 7.6, 1.4 Hz, 1H), 5.56 – 5.46 (m, 1H), 4.60 (d, *J* = 6.5 Hz, 2H), 1.80 (s, 3H), 1.75 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.4, 138.2, 133.5, 128.5, 121.9, 119.6, 113.9, 112.6, 66.3, 26.0, 18.5 ppm.

All spectroscopic data corresponded to the reported literature values.[11]

1-Chloro-2-((3-methylbut-2-en-1-yl)oxy)benzene (3a)



3a

Synthesized according to GP C from 2-chlorophenol (3.36 µL, 424 mg, 3.30 mmol, 1.10 equiv.), K_2CO_3 (1.24 g, 9.00 mmol, 3.00 equiv.) and 1-bromo-3-methylbut-2-ene (352 µL, 447 mg, 3.00 mmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **3a** (506 mg, 2.57 mmol, 86%) as a colourless liquid.

*Analytical data of **3a**:*

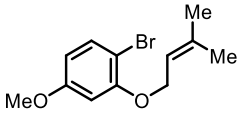
TLC (SiO_2): R_f (*n*-pentane: EtOAc = 40:1) = 0.42

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.36 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.24 – 7.15 (m, 1H), 6.93 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.93 – 6.84 (m, 1H), 5.56 – 5.47 (m, 1H), 4.60 (d, *J* = 6.6 Hz, 2H), 1.79 (s, 3H), 1.75 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.5, 138.4, 130.4, 127.7, 123.2, 121.4, 119.6, 114.0, 66.2, 26.0, 18.4 ppm.

All spectroscopic data corresponded to the reported literature values.[12]

1-Bromo-4-methoxy-2-((3-methylbut-2-en-1-yl)oxy)benzene (2b)



2b

Synthesized according to GP C from 2-bromo-5-methoxyphenol (374 µL, 609 mg, 3.00 mmol, 1.00 equiv.), K_2CO_3 (1.24 g, 9.00 mmol, 3.00 equiv.) and 1-bromo-3-methylbut-2-ene (387µL, 492 mg, 3.30 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1) afforded **2b** (650 mg, 2.40 mmol, 80%) as a colourless liquid.

*Analytical data of **2b**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 20:1) = 0.48

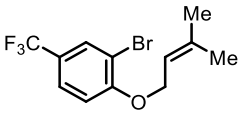
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 3.0 Hz, 1H), 6.89 – 6.75 (m, 2H), 5.54 – 5.45 (m, 1H), 4.52 (d, *J* = 7.0 Hz, 2H), 3.76 (s, 3H), 1.78 (s, 3H), 1.72 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.3, 149.8, 138.2, 119.9, 118.9, 115.7, 113.8, 113.3, 67.3, 56.0, 26.0, 18.4 ppm.

IR (ATR): 2968 (w), 2935 (w), 1491 (s), 1440 (w) 1273 (m), 1212 (s), 1039 (s), 996 (w), 757 (w) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{12}H_{15}BrO_2+H]^+$, $[M+H]^+$: 271.0328; found: 271.0325.

2-Bromo-1-((3-methylbut-2-en-1-yl)oxy)-4-(trifluoromethyl)benzene (2c)



2c

Synthesized according to GP C from 2-bromo-4-(trifluoromethyl)phenol (723 mg, 3.00 mmol, 1.00 equiv.), K_2CO_3 (1.24 g, 9.00 mmol, 3.00 equiv.) and 1-bromo-3-methylbut-2-ene (387µL, 492 mg, 3.30 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **2c** (649 mg, 2.01 mmol, 70%) as a colourless liquid.

*Analytical data of **2c**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.64

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 1.9 Hz, 1H), 7.55 – 7.47 (m, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 5.53 – 5.44 (m, 1H), 4.65 (d, *J* = 6.5 Hz, 2H), 1.80 (s, 3H), 1.76 (s, 3H) ppm.

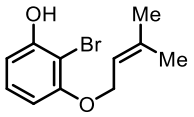
^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.9, 139.2, 130.7 (q, $^3J_{FC}$ = 3.8 Hz), 125.9 (q, $^3J_{FC}$ = 3.9 Hz), 123.8 (q, $^2J_{FC}$ = 33.2 Hz), 123.7 (q, $^1J_{FC}$ = 271.6 Hz), 118.7, 112.9, 112.5, 66.5, 26.0, 18.5 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ = – 61.67 ppm.

IR (ATR): 2974 (w), 1607 (m), 1502 (m), 1322 (s), 1267 (s), 1117 (s), 1079 (s), 1047 (s), 980 (m), 813 (m), 686 (w), 618 (w) cm^{-1}.

HRMS (APPI/LTQ- Orbitrap): calcd. for $[C_{12}H_{12}BrF_3O]^+$, $[M]^+$: 308.0018; found: 308.0015.

2-Bromo-3-((3-methylbut-2-en-1-yl)oxy)phenol (2d)



2d

Synthesized according to GP C from 2-bromobenzene-1,3-diol (1.13 g, 6.00 mmol, 1.00 equiv.), K_2CO_3 (2.49 g, 18.0 mmol, 3.00 equiv.) and 1-bromo-3-methylbut-2-ene (1.04 mL, 1.34 g, 9.00 mmol, 1.50 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1 – 10:1) afforded **2d** (434 mg, 1.69 mmol, 56%) as a white solid.

*Analytical data of **2d**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.37

Mp: 34.3 – 36.7 °C.

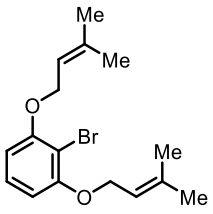
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (t, *J* = 8.3 Hz, 1H), 6.67 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.48 (dd, *J* = 8.3, 1.3 Hz, 1H), 5.62 (s, 1H), 5.55 – 5.46 (m, 1H), 4.58 (d, *J* = 6.5 Hz, 2H), 1.80 (s, 3H), 1.75 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.0, 153.6, 138.4, 128.7, 119.5, 108.5, 105.3, 100.8, 66.4, 26.0, 18.5 ppm.

IR (ATR): 3493 (br), 2931 (w), 2913 (w), 1592 (s), 1459 (s), 1266 (m), 1195 (s), 1053 (s), 766 (s) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{11}H_{13}BrO_2]^+$, $[M]^+$: 256.0093; found: 256.0090.

2-Bromo-1,3-bis((3-methylbut-2-en-1-yl)oxy)benzene (2e)



2e

The title compound was isolated during the synthesis of 2-Bromo-3-((3-methylbut-2-en-1-yl)oxy)phenol (**2d**) following GP C. Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1 – 10:1) afforded **2e** (527 mg, 1.62 mmol, 54%) as a white solid.

*Analytical data of **2e**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.70

Mp: 86.2 – 89.3 °C.

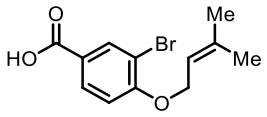
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 2H), 5.57 – 5.44 (m, 2H), 4.59 (dt, *J* = 6.5, 1.0 Hz, 4H), 1.78 (s, 6H), 1.74 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.8 (2C), 138.0 (2C), 128.0, 119.8 (2C), 106.4 (2C), 102.6, 66.5 (2C), 26.0 (2C), 18.5 (2C) ppm.

IR (ATR): 2973 (w), 2913 (w), 1589 (m), 1458 (s), 1382 (m), 1252 (m), 1234 (m), 1074 (s), 1036 (m), 760 (m) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{16}H_{22}BrO_2+H]^+$, $[M+H]^+$: 325.0798; found: 325.0790.

3-Bromo-4-((3-methylbut-2-en-1-yl)oxy)benzoic acid (2f)



2f

To a stirred solution of methyl 3-bromo-4-((3-methylbut-2-en-1-yl)oxy)benzoate (**2g**) (299 mg, 1.00 mmol, 1.00 equiv.) in THF/MeOH (1:1, 4 mL) was added NaOH (44 mg, 1.10 mmol, 1.10 equiv.) dissolved in H_2O (1 mL). The resulting mixture was heated to 60 °C for 19 h. After the reaction was cooled to rt, aq. HCl (1 M, 10 mL) were added, and the resulting mixture was extracted with EtOAc (3 × 15 mL). Combined organic layers were dried over Na_2SO4 and all volatiles were removed under reduced pressure to afford the title compound **2f** (276 mg, 968 µmol, 97%) as a white solid.

*Analytical data of **2f**:*

Mp: 155.8 – 157.9 °C.

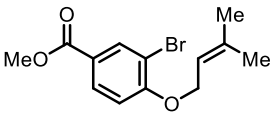
^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.98 (br s, 1H), 8.30 (d, *J* = 2.1 Hz, 1H), 8.02 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 5.54 – 5.46 (m, 1H), 4.68 (d, *J* = 6.6 Hz, 2H), 1.81 (s, 3H), 1.77 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 159.8, 139.3, 135.7, 131.3, 122.6, 118.7, 112.5, 112.2, 66.5, 26.0, 18.6 ppm.

IR (ATR): 2913 (br), 1678 (s), 1596 (s), 1427 (m), 1318 (m), 1274 (s), 1046 (w), 802 (m) cm^{-1}.

HRMS (ESI): calcd. for $[C_{12}H_{13}BrO_3-H]^-$, $[M-H]^-$: 282.9975; found: 282.9972.

Methyl 3-bromo-4-((3-methylbut-2-en-1-yl)oxy)benzoate (2g)



2g

Synthesized according to GP C from 3-bromo-4-hydroxybenzoate (693 mg, 3.00 mmol, 1.00 equiv.), K_2CO_3 (415 mg, 3.00 mmol, 1.00 equiv.) and 1-bromo-3-methylbut-2-ene (387µL, 492 mg, 3.30 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1) afforded **2g** (639 mg, 2.14 mmol, 71%) as a white solid.

*Analytical data of **2g**:*

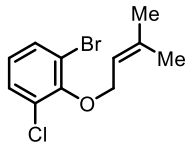
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 20:1) = 0.27

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 2.1 Hz, 1H), 7.95 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 5.54 – 5.44 (m, 1H), 4.66 (d, *J* = 6.5 Hz, 2H), 3.89 (s, 3H), 1.80 (s, 3H), 1.76 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.9, 159.0, 139.0, 135.0, 130.6, 123.6, 118.8, 112.4, 112.1, 66.4, 52.3, 26.0, 18.5 ppm.

All spectroscopic data corresponded to the reported literature values.[12]

1-Bromo-3-chloro-2-((3-methylbut-2-en-1-yl)oxy)benzene (2h)



2h

Synthesized according to GP C from 2-bromo-6-chlorophenol (622 mg, 3.00 mmol, 1.00 equiv.), K_2CO_3 (1.24 g, 9.00 mmol, 3.00 equiv.) and 1-bromo-3-methylbut-2-ene (387 µL, 492 mg, 3.30 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **2h** (103 mg, 281 µmol, 84%) as a colourless oil.

*Analytical data of **2h**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.64

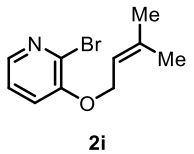
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.33 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 5.69 – 5.59 (m, 1H), 4.55 (dt, *J* = 7.4, 0.8 Hz, 2H), 1.80 (s, 3H), 1.75 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.5, 139.9, 132.0, 129.8, 129.8, 125.7, 119.5, 119.3, 70.1, 26.0, 18.2 ppm.

IR (ATR): 2930 (br), 1674 (w), 1559 (w), 1435 (s), 1379 (m), 1240 (s), 1068 (w), 946 (s), 766 (s), 752 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{11}H_{12}BrClO+Na]^+$, $[M+Na]^+$: 296.9652; found: 296.9663.

2-Bromo-3-((3-methylbut-2-en-1-yl)oxy)pyridine (2i)



2i

Synthesized according to GP C from 2-bromopyridin-3-ol (522 mg, 3.00 mmol, 1.00 equiv.), K_2CO_3 (1.24 g, 9.00 mmol, 3.00 equiv.) and 1-bromo-3-methylbut-2-ene (387µL, 492 mg, 3.30 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **2i** (580 mg, 2.40 mmol, 80%) as a colourless liquid.

*Analytical data of **2i**:*

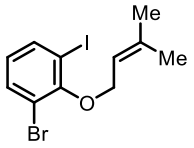
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.26

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.22 – 7.14 (m, 1H), 7.12 (dd, *J* = 8.1, 1.6 Hz, 1H), 5.51 – 5.40 (m, 1H), 4.61 (d, *J* = 6.6 Hz, 2H), 1.79 (s, 3H), 1.75 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.4, 141.3, 139.3, 133.4, 123.4, 120.3, 118.7, 66.3, 25.9, 18.5 ppm.

All spectroscopic data corresponded to the reported literature values.[12]

1-Bromo-3-iodo-2-((3-methylbut-2-en-1-yl)oxy)benzene (1j)



1j

To a stirred solution of 2-bromo-6-iodophenol (100 mg, 335 µmol, 1.00 equiv.), triphenylphosphane (87.7 mg, 335 µmol, 1.00 equiv.) and 3-methylbut-2-en-1-ol (40.8 µL, 34.6 mg, 401 µmol, 1.20 equiv.) in THF (2 mL) was added

DIAD (65.7 µL, 67.6 mg, 335 µmol, 1.00 equiv.) at rt. The resulting mixture was heated to 80 °C for 18 h. The reaction was cooled to rt and all volatiles were removed under reduced pressure. Purification of the residue by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **1j** (103 mg, 281 µmol, 84%) as a colourless oil.

*Analytical data of **1j**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.34

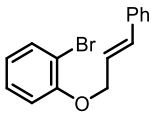
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.70 (t, *J* = 7.9 Hz, 1H), 5.73 – 5.63 (m, 1H), 4.53 (d, *J* = 7.3 Hz, 2H), 1.82 (s, 3H), 1.79 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.7, 139.8, 138.8, 133.9, 127.1, 119.6, 117.5, 93.4, 70.2, 26.0, 18.5 ppm.

IR (ATR): 2930 (br), 1550 (w), 1429 (s), 1378 (m), 1234 (m), 1068 (w), 945 (s), 766 (s), 703 (s) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{11}H_{12}BrIO]^+$, $[M]^+$: 365.9111; found: 365.9106.

(*E*)-1-Bromo-2-(cinnamyloxy)benzene (2k)



2k

Synthesized according to GP C from 2-bromophenol (531 µL, 865 mg, 5.00 mmol, 1.00 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 3.00 equiv.) and [(*E*)-3-bromoprop-1-enyl]benzene (1.08 g, 5.50 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1 – 20:1) afforded **2k** (2.79 g, 11.6 mmol, 86%) as a colourless oil.

*Analytical data of **2k**:*

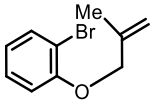
TLC (SiO_2): R_f (*n*-pentane: EtOAc = 40:1) = 0.35

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.23 (m, 2H), 6.96 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.85 (td, *J* = 7.6, 1.4 Hz, 1H), 6.79 (dt, *J* = 15.9, 1.7 Hz, 1H), 6.43 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.79 (dd, *J* = 5.6, 1.6 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.2, 136.5, 133.6, 133.2, 128.8, 128.6, 128.1, 126.8, 124.1, 122.3, 114.0, 112.6, 69.9 ppm.

All spectroscopic data corresponded to the reported literature values.[13]

1-Bromo-2-((2-methylallyl)oxy)benzene (2l)



2l

Synthesized according to GP C from 2-bromophenol (318 µL, 519 mg, 3.00 mmol, 1.00 equiv.), K_2CO_3 (1.24 g, 9.00 mmol, 3.00 equiv.) and 3-bromo-2-methylprop-1-ene (332 µL, 446 mg, 3.30 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **2l** (676 mg, 2.98 mmol, 99%) as a colourless liquid.

*Analytical data of **2l**:*

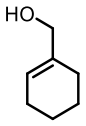
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.42

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.9, 1H), 7.28 – 7.19 (m, 1H), 6.89 (d, J = 8.3, 1H), 6.83 (t, J = 7.6, 1H), 5.20 – 5.14 (m, 1H), 5.05 – 4.96 (m, 1H), 4.50 (s, 2H), 1.86 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.1, 140.4, 133.5, 128.5, 122.0, 113.6, 113.0, 112.4, 72.6, 19.5 ppm.

All spectroscopic data corresponded to the reported literature values.[14]

Cyclohex-1-en-1-ylmethanol (SI-2)



SI-2

To a stirred solution of $LiAlH_4$ (1.14 g, 12.5 mL, 30.0 mmol, 2.40 M in THF, 3.00 equiv.) was added a solution of cyclohexene-1-carboxylic acid (1.26 g, 10.0 mmol, 1.00 equiv.) in Et_2O (25 mL) dropwise at 0 °C. The mixture was stirred for 3 h and quenched by the careful addition of H_2O (10 mL). Aq. NaOH (2 M, 30 mL), EtOAc (30 mL) and CH_2Cl_2 (50 mL) was added. Filtration over a pad of celite, allowed to separate the layers. The organic layer was dried over Na_2SO_4, volatiles were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1 – 3:1) to afford **SI-2** (780 mg, 6.95 mmol, 70 %) as a faint yellow liquid.

*Analytical data of **SI-2**:*

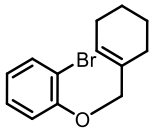
TLC (SiO_2): R_f (*n*-pentane: EtOAc = 10:1) = 0.20

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71 – 5.64 (m, 1H), 3.97 (s, 2H), 2.07 – 1.96 (m, 4H), 1.71 – 1.52 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.7, 123.2, 67.8, 25.7, 25.1, 22.7, 22.6 ppm.

All spectroscopic data corresponded to the reported literature values.[15]

1-Bromo-2-(cyclohex-1-en-1-ylmethoxy)benzene (2m)



2m

To a stirred solution of cyclohexen-1-ylmethanol (**SI-2**) (123 mg, 1.10 mmol, 1.10 equiv.uiv) in dry Et_2O (5 mL) was added PBr_3 (104 µL, 298 mg, 1.10 mmol, 1.10 equiv.) at 0 °C. The reaction mixture was stirred for 1 h and carefully quenched by the addition of sat. aq. NH_4Cl (5 mL). The layers were separated and the organic layer, containing the corresponding bromide, was directly used in GP C with 2-bromophenol (116 µL, 173 mg, 1.00 mmol, 1.00 equiv.) and K_2CO_3 (415 mg, 3.00 mmol, 3.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **2m** (92 mg, 344 µmol, 34%) as a colourless oil.

*Analytical data of **2m**:*

TLC (SiO_2): R_f (*n*-pentane: EtOAc = 40:1) = 0.50

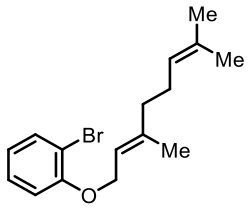
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.4, 1.6 Hz, 1H), 6.90 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.82 (td, *J* = 7.6, 1.4 Hz, 1H), 5.89 – 5.82 (m, 1H), 4.44 (s, 2H), 2.16 – 2.03 (m, 4H), 1.76 – 1.65 (m, 2H), 1.65 – 1.57 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.4, 133.4, 133.4, 128.4, 125.6, 121.9, 113.8, 112.5, 73.7, 25.8, 25.1, 22.5, 22.4 ppm.

IR (ATR): 2926 (m), 1585 (w), 1478 (s), 1442 (m), 1291 (s), 1247 (s), 1049 (m), 1030 (s), 999 (m), 745 (s) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{13}H_{15}BrO+H]^+$, $[M+H]^+$: 267.0379; found: 267.0377.

(*E*)-1-Bromo-2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)benzene (2n)



2n

To a stirred solution of (3*E*)-4,8-dimethylnona-3,7-dien-1-ol (989 µL, 879 mg, 5.23 mmol, 1.10 equiv.) in dry Et2O (13 mL) was added tribromophosphane (1.48 g, 519 µL, 5.46 mmol, 1.15 equiv.) at 0 °C and exclusion of light. The mixture was stirred for 15 min and quenched by the careful addition of sat. aq. NH_4Cl (13 mL). Layers were separated and the organic layer, containing the corresponding alkyl bromide, was directly used in GP C to synthesize **2n** from 2-bromophenol (548 µL, 822 mg, 4.75 mmol, 1.00 equiv.) and K_2CO_3 (2.63 g, 19.0 mmol, 4.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 1:0 – 40:1) afforded the title compound (985 mg, 3.19 mmol, 67%) as a colourless liquid.

*Analytical data of **2n**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.43

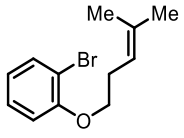
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.28 – 7.19 (m, 1H), 6.90 (dd, J = 8.2, 1.4 Hz, 1H), 6.82 (td, J = 7.6, 1.4 Hz, 1H), 5.54 – 5.47 (m, 1H), 5.13 – 5.05 (m, 1H), 4.63 (d, J = 6.4 Hz, 2H), 2.18 – 2.03 (m, 4H), 1.74 (s, 3H), 1.67 (s, 3H), 1.61 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.4, 141.3, 133.5, 132.0, 128.4, 123.9, 121.9, 119.5, 114.0, 112.6, 66.4, 39.7, 26.4, 25.8, 17.9, 16.9 ppm.

IR (ATR): 2917 (m), 1586 (w), 1477 (s), 1442 (m), 1276 (m), 1235 (m), 1031 (m), 994 (m), 746 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{21}BrO+Na]^+$, $[M+Na]^+$: 331.0668; found: 331.0667.

1-Bromo-2-((4-methylpent-3-en-1-yl)oxy)benzene (2o)



2o

Synthesized according to GP C from 2-bromophenol (265 µL, 433 mg, 2.50 mmol, 1.49 equiv.), K_2CO_3 (1.04 g, 7.5 mmol, 4.47 equiv.) and 5-bromo-2-methylpent-2-ene (255 µL, 274 mg, 1.68 mmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 1:0 – 40:1) afforded **2o** (256 mg, 1.00 mmol, 60%) as a colourless liquid.

*Analytical data of **2o**:*

TLC (SiO_2): R_f (*n*-pentane: EtOAc = 40:1) = 0.50

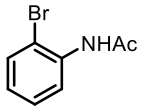
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.28 – 7.19 (m, 1H), 6.88 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.81 (td, *J* = 7.6, 1.4 Hz, 1H), 5.29 – 5.19 (m, 1H), 3.99 (t, *J* = 7.1 Hz, 2H), 2.59 – 2.49 (m, 2H), 1.74 (s, 3H), 1.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.5, 134.8, 133.5, 128.5, 121.8, 119.4, 113.4, 112.4, 77.5, 77.2, 76.8, 68.9, 28.3, 26.0, 18.0 ppm.

IR (ATR): 2989 (w), 2916 (w), 2877 (w), 1586 (w), 1481 (m), 1442 (m), 1293 (m), 1247 (s), 1051 (s), 1030 (s), 745 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{12}H_{15}BrO+Na]^+$, $[M+Na]^+$: 277.0198; found: 277.0199.

***N*-(2-Bromophenyl)acetamide (SI-3)**



SI-3

To a stirred solution of 2-bromoaniline (1.72 g, 10.0 mmol, 1.00 equiv.uiv) and DMAP (61.1 mg, 500 µmol, 5mol%) in $CHCl_3$ (40 mL) was Ac_2O (945 µL 1.02 g, 10.0 mmol, 1.00 equiv.uiv) dropwise. The mixture was refluxed for 3 h, cooled down to rt and washed with H_2O (40 mL). The organic layer was dried over $MgSO_4$ and all volatiles were removed under reduced pressure. Purification of the residue by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1) afforded **SI-3** (1.91 g, 8.93 mmol, 89%) as a white solid.

*Analytical data of **SI-3**:*

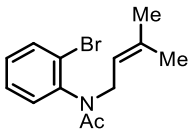
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.43

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 8.2 Hz, 1H), 7.60 (br s, 1H), 7.53 (d, *J* = 8.1Hz, 1H), 7.34 – 7.28 (m, 1H), 7.03 – 6.94 (m, 1H), 2.24 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.4, 135.8, 132.3, 128.5, 125.3, 122.1, 113.3, 25.0 ppm.

All spectroscopic data corresponded to the reported literature values.[16]

***N*-(2-Bromophenyl)-*N*-(3-methylbut-2-en-1-yl)acetamide (2p)**



2p

To a stirred solution of *N*-(2-bromophenyl)acetamide (**SI-3**) (642 mg, 3.00 mmol, 1.00 equiv.) in THF (9 mL) was added sodium hydride (120 mg, 3.00 mmol, 1.00 equiv.) (60 wt% in mineral oil) at 0 °C. The mixture was stirred for 5 min and 1-bromo-3-methylbut-2-ene (387 µL, 492 mg, 3.30 mmol, 1.10 equiv.) was added. The reaction was allowed to reach rt, stirred for further 5 h and quenched by the addition of H_2O (10 mL). The resulting mixture was extracted with EtOAc (3 × 15 mL). Combined organic layers were dried over Na_2SO_4 and all volatiles were removed under reduced pressure. Purification of the residue by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1) afforded **2p** (778 mg, 2.76 mmol, 92%) as a colourless liquid.

*Analytical data of **2p**:*

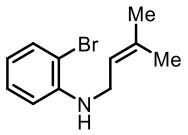
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.50

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.34 (td, *J* = 7.6, 1.5 Hz, 1H), 7.22 (td, *J* = 7.8, 1.7 Hz, 1H), 7.17 (dd, *J* = 7.7, 1.7 Hz, 1H), 5.28 – 5.18 (m, 1H), 4.73 – 4.63 (m, 1H), 3.81 (dd, *J* = 14.5, 8.2 Hz, 1H), 1.79 (s, 3H), 1.64 (s, 3H), 1.39 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.0, 141.6, 137.0, 133.8, 131.3, 129.7, 128.5, 124.2, 118.9, 45.3, 25.8, 22.6, 17.6 ppm.

All spectroscopic data corresponded to the reported literature values.[12]

2-Bromo-*N*-(3-methylbut-2-en-1-yl)aniline (SI-4)



SI-4

To a stirred solution of 2-bromoaniline (516 mg, 3.00 mmol, 1.00 equiv.) in dry THF (10 mL) was added LDA (1.50 mL, 3.00 mmol, 2.00 M in THF, 1.00 equiv.) at –78 °C. After 5 min, 1-bromo-3-methylbut-2-ene (312 µL, 402 mg, 2.70 mmol, 0.900 equiv.) was added dropwise. The reaction was allowed to warm to rt and quenched by the addition of aq. sat. NH_4Cl (10 mL). Layers were separated and the aqueous layer was extracted with *n*-pentane (3 × 20 mL). Combined organic layers were dried over Na_2SO_4 and all volatiles were removed under reduced pressure. Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **SI-4** (581 mg, 2.42 mmol, 81%) as a colourless oil.

*Analytical data of **SI-4**:*

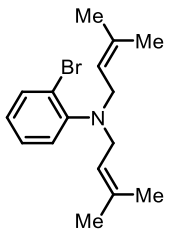
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.54

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, J = 7.8, 1.5 Hz, 1H), 7.21 – 7.15 (m, 1H), 6.63 (dd, J = 8.2, 1.5 Hz, 1H), 6.57 (td, J = 7.6, 1.5 Hz, 1H), 5.39 – 5.30 (m, 1H), 4.24 (br s, 1H), 3.77 – 3.71 (m, 2H), 1.78 (s, 3H), 1.74 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.2, 136.3, 132.5, 128.6, 121.2, 117.7, 111.5, 109.8, 42.0, 25.9, 18.2 ppm.

All spectroscopic data corresponded to the reported literature values.[17]

2-Bromo-*N*,*N*-bis(3-methylbut-2-en-1-yl)aniline (2q)



2q

Synthesized according to GP C from 2-bromo-*N*-(3-methylbut-2-en-1-yl)aniline (**SI-4**) (240 mg, 1.00 mmol, 1.00 equiv.), K_2CO_3 (276 mg, 2.00 mmol, 2.00 equiv.) and 1-bromo-3-methylbut-2-ene (127 µL, 164 mg, 1.10 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **2q** (239 mg, 775 µmol, 78%) as a colourless oil.

*Analytical data of **2q**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.54

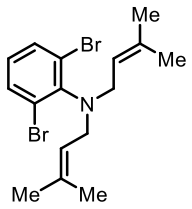
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.21 (ddd, *J* = 8.4, 7.3, 1.6 Hz, 1H), 6.98 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.87 (td, *J* = 7.6, 1.6 Hz, 1H), 5.25 – 5.16 (m, 2H), 3.63 (d, *J* = 7.5 Hz, 4H), 1.68 (s, 6H), 1.60 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.8, 134.8 (2C), 133.8, 127.5, 124.0, 123.9, 121.5 (2C), 121.3, 50.4 (2C), 25.9 (2C), 18.1 (2C) ppm.

IR (ATR): 2969 (m), 2926 (m), 2812 (m), 1583 (w), 1473 (s), 1376 (m), 1226 (w), 1089 (m), 1026 (s), 753 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{22}BrN+H]^+$, $[M+H]^+$: 308.1008; found: 308.1017.

2,6-Dibromo-*N*,*N*-bis(3-methylbut-2-en-1-yl)aniline (2r)



2r

Synthesized according to GP C from 2,6-dibromoanilline (753 mg, 3.00 mmol, 1.00 equiv.), K_2CO_3 (2.07 g, 15.0 mmol, 5.00 equiv.) and 3-bromo-2-methylprop-1-ene (809 µL, 1.04 g, 6.30 mmol, 2.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 1:0 – 20:1) afforded **2r** (391 mg, 1.01 mmol, 34%) as a colourless liquid.

*Analytical data of **2r**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.89

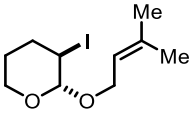
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 7.9 Hz, 1H), 5.34 – 5.25 (m, 2H), 3.74 (d, *J* = 6.9, 4H), 1.66 (s, 6H), 1.59 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.6, 134.1 (2C), 132.9 (2C), 127.7 (2C), 127.2, 122.8 (2C), 49.9 (2C), 26.0 (2C), 17.9 (2C) ppm.

IR (ATR): 2969 (w), 2911 (m), 1672 (w), 1544 (m), 1424 (s), 1375 (m), 1189 (w), 1133 (w), 925 (w), 843 (w), 769 (s), 715 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{21}Br_2N+H]^+$, $[M+H]^+$: 386.0114; found: 386.0120.

3-Iodo-2-((3-methylbut-2-en-1-yl)oxy)tetrahydro-2H-pyran (1s)



1s

Synthesized according to a literature known procedure.[18] To a stirred solution of 3-methylbut-2-en-1-ol (1.02 mL, 861 mg, 10.0 mmol, 1.00 equiv.) and 3,4-dihydro-2H-pyran (998 µL, 925 mg, 11.0 mmol, 1.10 equiv.) in dry CH_2Cl_2 (10 mL) was added 1-iodopyrrolidine-2,5-dione (2.25 g, 10.0 mmol, 1.00 equiv.) at – 30 °C. The reaction was stirred for 3 h, diluted with CH_2Cl_2 (20 mL), washed with H_2O (20 mL), aq. $Na_2S_2O_3$ (10%, 20 mL), brine

(20 mL) and dried over Na_2SO_4. Volatiles were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) to afford **1s** (2.68 g, 9.03 mmol, 90%) as a colourless oil.

*Analytical data of **1s**:*

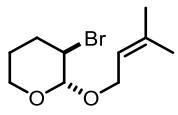
TLC (SiO_2): R_f (*n*-pentane: EtOAc = 10:1) = 0.58

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41 – 5.32 (m, 1H), 4.65 (d, *J* = 5.4 Hz, 1H), 4.22 (dd, *J* = 11.6, 6.6 Hz, 1H), 4.14 – 4.02 (m, 2H), 4.04 – 3.94 (m, 1H), 3.58 (ddd, *J* = 11.2, 7.4, 3.5 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.06 – 1.97 (m, 1H), 1.80 – 1.72 (m, 1H), 1.76 (s, 3H), 1.69 (s, 3H), 1.63 – 1.52 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.2, 120.2, 101.5, 64.7, 63.6, 33.0, 29.8, 26.0, 25.7, 18.2 ppm.

All spectroscopic data corresponded to the reported literature values.[18]

3-Bromo-2-((3-methylbut-2-en-1-yl)oxy)tetrahydro-2H-pyran (2s)



2s

To a stirred solution of 3-methylbut-2-en-1-ol (508 µL, 431 mg, 5.00 mmol, 1.00 equiv.) and 3,4-dihydro-2H-pyran (499 µL, 463 mg, 5.50 mmol, 1.10 equiv.) in CH_2Cl_2 (5 mL) was added 1-bromopyrrolidine-2,5-dione (890 mg, 5.00 mmol, 1.00 equiv.) at 0 °C. The mixture was stirred for 22 h at rt, followed by the addition of CH_2Cl_2 (10 mL). The organic layer was washed with H_2O (15 mL), aq. $Na_2S_2O_3$ (10%, 20 mL), brine (20 mL) and dried over Na_2SO_4. Volatiles were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) to afford **2s** (905 mg, 3.63 mmol, 73 %) as a colourless oil.

*Analytical data of **2s**:*

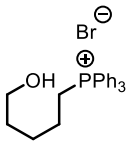
TLC (SiO_2): R_f (*n*-pentane: EtOAc = 10:1) = 0.70

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.40 – 5.31 (m, 1H), 4.63 (d, *J* = 4.4 Hz, 1H), 4.28 – 4.17 (m, 2H), 4.07 (dd, *J* = 11.8, 7.6 Hz, 1H), 3.98 (dt, J = 6.6, 4.3 Hz, 1H), 3.98 – 3.88 (m, 1H), 3.63 – 3.53 (m, 1H), 2.45 – 2.34 (m, 1H), 2.02 – 1.86 (m, 2H), 1.76 (s, 3H), 1.69 (s, 3H), 1.58 – 1.46 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.3, 120.2, 100.1, 64.5, 62.6, 49.8, 30.3, 26.0, 23.5, 18.2 ppm.

All spectroscopic data corresponded to the reported literature values.[19]

(5-Hydroxypentyl)triphenylphosphonium bromide (SI-5)



SI-5

Prepared according to the literature procedure.[20] A stirred suspension of PPh_3 (4.46 g, 17.0 mmol, 1.00 equiv.), 5-bromopentan-1-ol (2.84 g, 17.0 mmol, 1.00 equiv.) and K_2CO_3 (2.35 g, 17.0 mmol, 1.00 equiv.) in MeCN (15 mL) was heated to reflux for 4 h. The reaction mixture was cooled to rt, filtered, and treated with Et_2O (150 mL) upon which a white gum precipitated. The solvents were decanted off and the remaining residue was washed with Et_2O (50 mL). The gum was dried in vacuo to afford **SI-5** (2.55 g, 5.95 mmol, 35%) as a white solid.

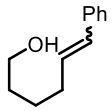
*Analytical data of **SI-5**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 – 7.67 (m, 15H), 3.77 – 3.68 (m, 4H), 3.15 (br s, 1H), 1.81 – 1.63 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.2, 135.1, 130.7, 130.6, 119.0, 61.8, 31.1, 27.2, 27.0, 23.1, 22.6 ppm.

All spectroscopic data corresponded to the reported literature values.[21]

(*E*/*Z*)-6-Phenylhex-5-en-1-ol (SI-6)



SI-6

Prepared according to the literature procedure.[22] To a stirred suspension of (5-hydroxypentyl) triphenylphosphonium bromide (**SI-5**) (2.15 g, 5.00 mmol, 1.00 equiv.) in dry THF (7.5 mL) was added *n*BuLi (6.25 mL, 1.60 M in *n*-hexane, 641 mg, 10.0 mmol, 2.00 equiv.) at 0 °C. A red coloured suspension was obtained, to which a solution of benzaldehyde (531 µL, 557 mg, 5.25 mmol, 1.05 equiv.) in dry THF (4 mL) was added dropwise. After 5 min the red colour vanished and an ivory, thick suspension was obtained. The mixture stirred for 4 h at rt and was poured into a mixture of H_2O (25 mL) and EtOAc (25 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (1 × 10 mL). Combined organic layers were washed with brine (1 × 15 mL) and dried over Na2SO4. All volatiles were removed under reduced pressure and purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1) afforded **SI-6** (415 mg, 2.36 mmol, 47%, *E*:*Z*=79:21) as a faint yellow oil.

*Analytical data of **SI-6**:*

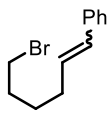
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.45

^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-isomer**: δ = 7.39 – 7.17 (m, 5H), 6.47 – 6.36 (m, 1H), 6.22 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.26 (qd, *J* = 7.1, 1.4 Hz, 2H), 1.70 – 1.49 (m, 4H), 1.33 (br s, 1H); **(*Z*)-isomer:** δ = 7.39 – 7.17 (m, 5H), 6.47 – 6.36 (m, 1H), 5.66 (dt, J = 11.7, 7.2 Hz, 1H), 3.63 (t, J = 6.4 Hz, 2H), 2.37 (qd, J = 7.2, 1.8 Hz, 2H), 1.70 – 1.49 (m, 4H), 1.33 (s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.9, 137.8, 132.8, 130.7, 130.3, 129.3, 128.9, 128.6, 127.1, 126.7, 126.1, 63.0, 62.9, 32.9, 32.5, 32.4, 28.6, 26.2, 25.6 ppm.

All spectroscopic data corresponded to the reported literature values.[22,23]

(*E*/*Z*)-(6-Bromohex-1-en-1-yl)benzene (2t)



2t

Prepared according to the literature procedure.[22] A solution of PPh_3 (628 mg, 2.39 mmol, 1.05 equiv.) in dry CH_2Cl_2 (3 mL) was slowly added to a solution of (*E*/*Z*)-6-phenylhex-5-en-1-ol (402 mg, 2.28 mmol, 1.00 equiv.) and CBr_4 (832 mg, 2.51 mmol, 1.10 equiv.) in dry CH_2Cl_2 (11 mL) at rt. The reaction mixture was stirred for 22 h and quenched by the addition of H_2O (5 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL),

combined organic layers were dried over $MgSO_4$ and all volatiles were removed under reduced pressure. Purification by flash chromatography (SiO_2, petroleum ether) afforded **2t** (419 mg, 1.75 mmol, 77%, *E*:*Z*=78:22) as a colourless liquid.

*Analytical data of **2t**:*

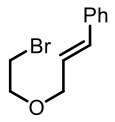
TLC (SiO_2): R_f (petroleum ether) = 0.21

^{1}H NMR (400 MHz, $CDCl_3$): **(*E*)-isomer**: δ = 7.37 – 7.17 (m, 5H), 6.45 – 6.36 (m, 1H), 6.20 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.44 (t, *J* = 6.8 Hz, 2H), 2.26 (qd, *J* = 7.3, 1.4 Hz, 2H), 2.00 – 1.85 (m, 2H), 1.72 – 1.57 (m, 2H); **(*Z*)-isomer:** δ = 7.38 – 7.16 (m, 5H), 6.46 (d, *J* = 11.7 Hz, 1H), 5.65 (dt, *J* = 11.7, 7.2 Hz, 1H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.37 (qd, *J* = 7.4, 1.9 Hz, 2H), 2.00 – 1.85 (m, 2H), 1.71 – 1.56 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ =137.8, 132.2, 130.6, 130.1, 129.6, 128.9, 128.7, 128.3, 127.1, 126.7, 126.1, 33.9, 33.8, 32.4, 32.4, 32.2, 28.5, 28.0, 27.8 ppm.

All spectroscopic data corresponded to the reported literature values.[22]

(*E*)-(3-(2-Bromoethoxy)prop-1-en-1-yl)benzene (2u)



2u

Prepared according to the literature procedure.[24] To a stirred solution of 2-bromoethanol (355 µL, 625 mg, 5.00 mmol, 1.00 equiv.) in dry THF (2.5 mL) was added $ZnEt_2$ (2.50 mL, 1.00 M in THF, 309 mg, 2.50 mmol, 0.500 equiv.) dropwise at rt. The mixture was stirred for 15 min, and [(*E*)-3-phenylprop-2-enyl] acetate (881 mg, 5.00 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (289 mg, 250 µmol, 5 mol%) were added. The resulting mixture was stirred for 3 h and all volatiles were removed under reduced pressure. Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1) afforded **2u** (692 mg, 2.87 mmol, 57%) as a colourless liquid.

*Analytical data of **2u**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 20:1) = 0.57

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.38 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 6.63 (d, *J* = 15.8 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.23 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.82 (t, *J* = 6.2 Hz, 2H), 3.51 (t, *J* = 6.2 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.6, 133.1, 128.7, 128.0, 126.7, 125.6, 71.9, 70.1, 30.6 ppm.

All spectroscopic data corresponded to the reported literature values.[24]

***N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (SI-7)**

SI-7

A solution of 2-aminoethanol (2.40 mL, 2.44 g, 40.0 mmol, 1.00 equiv.) and TsCl (7.63 g, 40.0 mmol, 1.00 equiv.) in CH_2Cl_2 (100 mL) was stirred for 10 min at 0 °C, followed by the dropwise addition of NEt_3 (5.58 mL, 4.05 g, 40.0 mmol, 1.00 equiv.). The rection was stirred for 6 h at rt and washed with H_2O (3 × 100 mL) and brine (100

mL). The organic layer was dried over Na_2SO_4 and all volatiles were removed under reduced pressure to afford the title compound **SI-7** (5.65 g, 26.2 mmol, 66%) as a white solid, which was used in the next step without further purification.

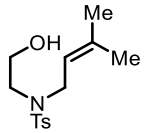
*Analytical data of **SI-7**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 3H), 5.06 (br s, 1H), 3.69 (d, J = 4.8 Hz, 2H), 3.09 (d, J = 5.2 Hz, 2H), 2.43 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143., 136.8, 129.9 (2C), 127.3 (2C), 61.5, 45.2, 21.7 ppm.

All spectroscopic data corresponded to the reported literature values.[25]

_N_-(2-Hydroxyethyl)-4-methyl-_N_-(3-methylbut-2-en-1-yl)benzenesulfonamide (SI-8)



SI-8

Synthesized according to GP D from *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**SI-7**) (1.08 g, 5.00 mmol, 1.00 equiv.), K_2CO_3 (1.38 g, 10.0 mmol, 2.00 equiv.), KI (83 mg, 500 µmol, 5 mol%) and 1-bromo-3-methylbut-2-ene (847 µL, 1.08 g, 6.50 mmol, 1.30 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1 – 1:1) afforded **SI-8** (1.22 g, 4.31 mmol, 86%) as a colourless oil.

*Analytical data of **SI-8**:*

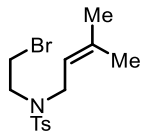
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.22

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 5.07 – 4.98 (m, 1H), 3.83 (d, J = 7.1 Hz, 2H), 3.72 (m, 2H), 3.20 (t, J = 5.3 Hz, 2H), 2.43 (s, 3H), 2.26 (br s, 1H), 1.67 (s, 3H), 1.62 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.6, 137.7, 136.5, 129.8 (2C), 127.5 (2C), 119.0, 61.4, 49.9, 47.2, 25.9, 21.7, 18.0 ppm.

All spectroscopic data corresponded to the reported literature values.[26]

_N_-(2-Bromoethyl)-4-methyl-_N_-(3-methylbut-2-en-1-yl)benzenesulfonamide (2v)



2v

Synthesized according to GP E from *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**SI-8**) (567 mg, 2.00 mmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **2v** (614 mg, 1.77 mmol, 89%) as a colourless oil.

*Analytical data of **2v**:*

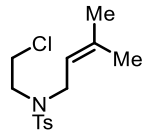
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.42

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.06 – 4.98 (m, 1H), 3.80 (d, J = 7.2 Hz, 2H), 3.49 – 3.33 (m, 4H), 2.43 (s, 3H), 1.69 (s, 3H), 1.63 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.7, 138.2, 136.6, 129.9 (2C), 127.4 (2C), 118.8, 49.0, 46.9, 29.8, 26.0, 21.7, 18.0 ppm.

All spectroscopic data corresponded to the reported literature values.[26]

N-(2-Chloroethyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (3v)



3v

Synthesized according to GP E from PPh_3 (787 mg, 3.00 mmol, 3.00 equiv.), CCl_4 (290 µL, 461 mg, 3.00 mmol, 3.00 equiv.) and *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**SI-8**) (283 mg, 1.00 mmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **3v** (76 mg, 251 µmol, 25%) as a colourless oil.

*Analytical data of **3v**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.35

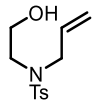
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.06 – 4.97 (m, 1H), 3.81 (d, *J* = 7.2 Hz, 2H), 3.61 (dd, *J* = 8.1, 6.9 Hz, 2H), 3.33 (dd, *J* = 8.1, 6.8 Hz, 2H), 2.44 (s, 3H), 1.69 (s, 3H), 1.63 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.6, 138.2, 136.7, 129.9 (2C), 127.4 (2C), 118.8, 48.8, 47.0, 42.2, 26.0, 21.7, 18.0 ppm.

IR (ATR): 2971 (m), 2919 (m), 1451 (w), 1342 (m), 1158 (s), 1091 (m), 723 (m), 653 (m), 549 (m) cm^{-1}.

HRMS (ESI): calcd. for $[C_{14}H_{20}ClNO_2S+Na]^+$, $[M+Na]^+$: 324.0795; found: 324.0794.

N-Allyl-*N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (SI-9)



SI-9

Synthesized according to GP D from *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**SI-7**) (646 g, 3.00 mmol, 1.00 equiv.), K_2CO_3 (829 mg, 6.00 mmol, 2.00 equiv.), KI (50 mg, 300 µmol, 10 mol%) and 3-bromoprop-1-ene (337 µL, 427 mg, 3.90 mmol, 1.30 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1 – 1:1) afforded **SI-9** (734 mg, 2.88 mmol, 96%) as a colourless oil.

*Analytical data of **SI-9**:*

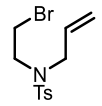
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.22

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.74 – 5.62 (m, 1H), 5.22 – 5.15 (m, 2H), 3.85 (d, *J* = 6.4 Hz, 2H), 3.73 (q, *J* = 5.5 Hz, 2H), 3.24 (t, J = 5.4 Hz, 2H), 2.43 (s, 3H), 2.27 – 2.18 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.7, 136.3, 133.2, 123.0 (2C), 127.4 (2C), 119.5, 61.3, 52.4, 49.9, 21.7 ppm.

All spectroscopic data corresponded to the reported literature values.[27]

_N_-Allyl-_N_-(2-bromoethyl)-4-methylbenzenesulfonamide (2w)



2w

Synthesized according to GP E from *N*-allyl-*N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**SI-9**) (511 mg, 2.00 mmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **2w** (367 mg, 1.15 mmol, 58%) as a faint yellow oil.

*Analytical data of **2w**:*

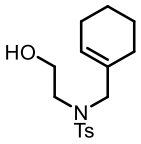
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.33

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.72 – 5.62 (m, 1H), 5.21 (dq, *J* = 6.4, 1.3 Hz, 1H), 5.18 (t, *J* = 1.3 Hz, 1H), 3.81 (d, *J* = 6.5 Hz, 2H), 3.50 – 3.39 (m, 4H), 2.44 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.9, 136.4, 133.0, 130.0 (2C), 127.3 (2C), 119.8, 52.2, 49.1, 29.4, 21.7 ppm.

All spectroscopic data corresponded to the reported literature values.[27]

_N_-(Cyclohex-1-en-1-ylmethyl)-_N_-(2-hydroxyethyl)-4-methylbenzenesulfonamide (SI-10)



SI-10

To a stirred solution of cyclohexen-1-ylmethanol (**SI-2**) (280 mg, 2.50 mmol, 1.00 equiv.) in dry Et_2O (12 mL) was added PBr_3 (119 µL, 338 mg, 1.25 mmol, 0.50 equiv.) at 0 °C. The reaction mixture was stirred for 2 h and added to aq. sat. K_2CO_3 (10 mL). Layers were separated and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic layers were dried over $MgSO_4$, and all volatiles were removed under reduced pressure to afford crude 1-(bromomethyl)cyclohex-1-ene which was directly used in GP C with *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**SI-7**) (503 mg, 2.50 mmol, 1.00 equiv.) and K_2CO_3 (1.04 g, 7.50 mmol, 3.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1) afforded **SI-10** (302 mg, 976 µmol, 39%) as a colourless oil.

*Analytical data of **SI-10**:*

TLC (SiO_2): R_f (*n*-pentane: EtOAc = 3:1) = 0.63

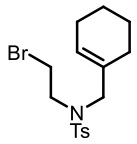
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.62 – 5.56 (m, 1H), 3.67 (dd, *J* = 11.1, 5.6 Hz, 4H), 3.16 (t, *J* = 5.4 Hz, 2H), 2.43 (s, 3H), 2.37 – 2.29 (m, 1H), 2.03 – 1.93 (m, 4H), 1.64 – 1.51 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.6, 136.1, 133.4, 129.9 (2C), 127.5 (2C), 127.2, 61.5, 57.0, 50.5, 26.1, 25.4, 22.5, 22.3, 21.7 ppm.

IR (ATR): 3517 (br), 2926 (m), 1446 (w), 1307 (m), 1158 (s), 655 (m), 549 (m) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{23}NO_3S+Na]^+$, $[M+Na]^+$: 332.1291; found: 332.1292.

_N_-(2-Bromoethyl)-_N_-(cyclohex-1-en-1-ylmethyl)-4-methylbenzenesulfonamide (2x)



2x

Synthesized according to GP E from _N_-(cyclohex-1-en-1-ylmethyl)-_N_-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**SI-10**) (250 mg, 808 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, _n_-pentane:EtOAc = 10:1) afforded **2x** (214 mg, 574 µmol, 71%) as a white solid.

*Analytical data of **2x**:*

TLC (SiO_2): R_f (_n_-pentane: EtOAc = 3:1) = 0.48

Mp: 69.2 – 70.4 °C.

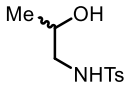
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 5.65 – 5.58 (m, 1H), 3.62 (s, 2H), 3.43 – 3.29 (m, 4H), 2.43 (s, 3H), 2.05 – 1.92 (m, 4H), 1.67 – 1.51 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.7, 136.4, 133.2, 129.9 (2C), 127.7, 127.3 (2C), 56.5, 49.5, 29.4, 26.1, 25.4, 22.6, 22.3, 21.7 ppm.

IR (ATR): 2927 (m), 1447 (w), 1340 (s), 1160 (s), 1091 (w), 932 (w), 549 (m) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{22}BrNOS+H]^+$, $[M+H]^+$: 372.0627; found: 372.0627.

(±)-_N_-(2-Hydroxypropyl)-4-methylbenzenesulfonamide (SI-11)



SI-11

A solution of 1-aminopropan-2-ol (3.10 mL, 3.00 g, 40.0 mmol, 1.00 equiv.) and TsCl (7.63 g, 40.0 mmol, 1.00 equiv.) in CH_2Cl_2 (100 mL) was stirred for 10 min at 0 °C, followed by the dropwise addition of NEt_3 (5.58 mL, 4.05 g, 40.0 mmol, 1.00 equiv.). The reaction was stirred for 18 h at rt and washed with H_2O (3 × 100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4 and all volatiles were removed under reduced pressure to afford the title compound **SI-11** (7.30 g, 31.8 mmol, 80%) as a white solid, which was used in the next step without further purification.

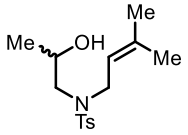
*Analytical data of **SI-11**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 4.88 (s, 1H), 3.97 – 3.84 (m, 1H), 3.11 – 3.00 (m, 1H), 2.77 (dd, J = 13.1, 8.1 Hz, 1H), 2.43 (s, 3H), 1.91 (s, 1H), 1.16 (d, J = 6.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.7, 136.8, 129.9 (2C), 127.2 (2C), 66.7, 50.1, 21.7, 20.9 ppm.

All spectroscopic data corresponded to the reported literature values.[25]

(±)-*N*-(2-Hydroxypropyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (SI-12)



SI-12

Synthesized according to GP D from *N*-(2-hydroxypropyl)-4-methylbenzenesulfonamide (**SI-11**) (688 g, 3.00 mmol, 1.00 equiv.), K_2CO_3 (829 mg, 6.00 mmol, 2.00 equiv.), KI (50 mg, 300 µmol, 10 mol%) and 3-bromoprop-1-ene (337 µL, 427 mg, 3.90 mmol, 1.30 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1) afforded **SI-12** (651 mg, 2.19 mmol, 73%) as a colourless oil.

*Analytical data of **SI-12**:*

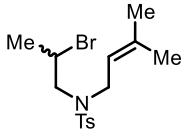
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.42

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 5.05 – 4.95 (m, 1H), 4.05 – 3.92 (m, 1H), 3.84 (d, *J* = 7.1 Hz, 2H), 3.05 (dd, *J* = 14.6, 8.6 Hz, 1H), 2.93 (dd, *J* = 14.6, 3.1 Hz, 1H), 2.60 (br s, 1H), 2.43 (s, 3H), 1.66 (s, 2H), 1.61 (s, 3H), 1.14 (d, *J* = 6.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.6, 137.7, 136.5, 129.8 (2C), 127.5 (2C), 118.9, 66.4, 55.3, 47.6, 25.9, 21.7, 20.5, 17.9 ppm.

All spectroscopic data corresponded to the reported literature values.[12]

(±)-*N*-(2-Bromopropyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (2y)



2y

Synthesized according to GP E from *N*-(2-hydroxypropyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (**SI-12**) (297 mg, 1.00 mmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **2y** (270 mg, 749 µmol, 75%) as a colourless gum.

*Analytical data of **2y**:*

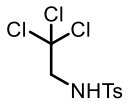
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.55

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 4.98 – 4.88 (m, 1H), 4.35 – 4.20 (m, 1H), 3.93 – 3.72 (m, 2H), 3.38 (dd, *J* = 14.5, 8.4 Hz, 1H), 3.29 (dd, *J* = 14.6, 6.1 Hz, 1H), 2.43 (s, 3H), 1.72 (d, *J* = 6.7 Hz, 3H), 1.65 (s, 3H), 1.62 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.6, 137.9, 136.5, 129.8 (2C), 127.5 (2C), 118.6, 55.3, 47.4, 47.3, 25.9, 23.5, 21.7, 17.9 ppm.

All spectroscopic data corresponded to the reported literature values.[12]

4-Methyl-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (SI-13)



SI-13

A solution of 2,2,2-trichloroethan-1-amine[28] (6.12 mL, 5.94 g, 40.0 mmol, 1.00 equiv.) and TsCl (7.63 g, 40.0 mmol, 1.00 equiv.) in CH_2Cl_2 (100 mL) was stirred for 10 min at 0 °C, followed by the dropwise addition of NEt_3 (5.58 mL, 4.05 g, 40.0 mmol, 1.00 equiv.). The rection was stirred for 17 h at rt and washed with H_2O (3 × 100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4 and all volatiles were removed under reduced pressure to afford a brown solid, which was purified in a first step by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1 – 3:1) to afford an off white solid. Recrystallization from EtOAc at –33 °C afforded **SI-13** (5.86 g, 19.4 mmol, 48%) as a white solid.

*Analytical data of **SI-13**:*

TLC (SiO_2): R_f (*n*-pentane: EtOAc = 10:1) = 0.17

Mp: 140.1 – 141.8 °C.

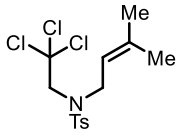
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.30 (t, *J* = 7.0 Hz, 1H), 3.97 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.3, 137.4, 130.0 (2C), 127.2 (2C), 96.9, 61.2, 21.7 ppm.

IR (ATR): 3255 (br), 2972 (m), 2901 (m), 1447 (w), 1324 (m), 1158 (s), 1046 (s), 877 (m), 707 (m), 534 (m) cm^{-1}.

HRMS (ESI): calcd. for $[C_9H_{10}Cl_3NO_2S+H]^+$, $[M+H]^+$: 301.9571; found: 301.9569.

4-Methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (3z)



3z

Synthesized according to GP C from 4-methyl-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (**SI-13**) (908 mg, 3.00 mmol, 1.00 equiv.), K_2CO_3 (1.24 g, 9.00 mmol, 3.00 equiv.) and 3-bromo-2-methylprop-1-ene (332 µL, 446 mg, 3.30 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **3z** (1.03 g, 2.78 mmol, 93%) as a white solid.

*Analytical data of **3z**:*

TLC (SiO_2): R_f (*n*-pentane: EtOAc = 10:1) = 0.59

Mp: 68.8 – 69.8 °C.

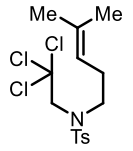
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 – 7.75 (m, 2H), 7.32 – 7.30 (m, 2H), 4.87 – 4.79 (m, 1H), 4.28 (s, 2H), 4.15 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.0, 138.9, 137.4, 129.8 (2C), 127.9 (2C), 118.1, 98.7, 62.6, 47.3, 26.1, 21.7, 18.1 ppm.

IR (ATR): 2926 (w), 1447 (w), 1340 (m), 1160 (s), 1092 (m), 907 (s), 814 (s), 732 (s), 546 (m) cm^{-1}.

HRMS (ESI): calcd. for $[C_{14}H_{18}Cl_3NO_2S+Na]^+$, $[M+Na]^+$: 392.0016; found: 392. 0016.

4-Methyl-*N*-(4-methylpent-3-en-1-yl)-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (3za)



3za

Synthesized according to GP C from 4-methyl-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (**SI-13**) (605 mg, 2.00 mmol, 1.00 equiv.), K_2CO_3 (829 mg, 6.00 mmol, 3.00 equiv.) and 5-bromo-2-methylpent-2-ene (295 µL, 359 mg, 2.20 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **3za** (474 mg, 1.23 mmol, 62%) as a white solid.

*Analytical data of **3za**:*

TLC (SiO_2): R_f (*n*-pentane: EtOAc = 10:1) = 0.52

Mp: 67.7 – 69.9 °C.

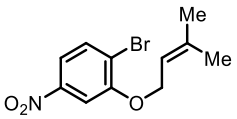
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 – 7.70 (m, 2H), 7.36 – 7.29 (m, 2H), 4.89 – 4.80 (m, 1H), 4.30 (s, 2H), 3.41 – 3.32 (m, 2H), 2.44 (s, 3H), 2.37 – 2.26 (m, 2H), 1.63 (s, 3H), 1.55 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.0, 136.8, 135.0, 129.9 (2C), 127.7 (2C), 119.5, 98.4, 64.4, 49.0, 26.9, 25.8, 21.7, 17.9 ppm.

IR (ATR): 2971 (w), 2922 (w), 1598 (w), 1342 (s), 1162 (s), 1092 (m), 923 (m), 815 (m), 727 (s), 653 (m), 548 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{15}H_{20}Cl_3NO_2S+H]^+$, $[M+H]^+$: 384.0353; found: 384. 0362.

1-Bromo-2-((3-methylbut-2-en-1-yl)oxy)-4-nitrobenzene (SI-14)



SI-14

Synthesized according to GP C from 2-bromo-5-nitrophenol (323 µL, 527 mg, 2.42 mmol, 1.00 equiv.), K_2CO_3 (1.00 g, 7.25 mmol, 3.00 equiv.) and 1-bromo-3-methylbut-2-ene (312 µL, 396 mg, 2.66 mmol, 1.10 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1) afforded **SI-14** (599 mg, 2.09 mmol, 87%) as an off white solid.

*Analytical data of **SI-14**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 20:1) = 0.57

Mp: 65.8 – 67.7 °C.

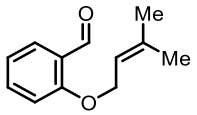
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 – 7.67 (m, 3H), 5.55 – 5.40 (m, 1H), 4.70 (d, *J* = 6.7 Hz, 2H), 1.84 – 1.78 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.8, 148.1, 140.0, 133.7, 120.3, 118.2, 116.5, 108.0, 66.9, 26.0, 18.6 ppm.

IR (ATR): 2970 (w), 2914 (w), 1569 (w), 1512 (s), 1473 (w), 1352 (m) 1262 (m), 1038 (m), 987 (s), 864 (m), 736 (s) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{11}H_{12}BrNO_3]^+$, $[M]^+$: 284.9995; found: 284.9988.

2-((3-Methylbut-2-en-1-yl)oxy)benzaldehyde (SI-15)



SI-15

To a stirred solution of 3-methylbut-2-en-1-ol (2.23 mL, 1.89 g, 22.0 mmol, 1.10 equiv.) in dry Et_2O (11 mL) was added PBr_3 (2.09 mL, 5.96 g, 22.0 mmol, 1.10 equiv.) at 0 °C. The mixture was stirred for 1 h until TLC control showed complete consumption of the alcohol. The reaction mixture was carefully quenched by the addition of sat. aq. NH_4Cl (15 mL) and the layers were separated. The organic layer, containing the corresponding bromide, was directly used in GP C with 2-hydroxybenzaldehyde (2.09 mL, 2.44 g, 20.0 mmol, 1.00 equiv.) and K_2CO_3 (11.1 g, 80.0 mmol, 4.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **SI-15** (3.03 g, 15.9 mmol, 80%) as a yellow liquid.

*Analytical data of **SI-15**:*

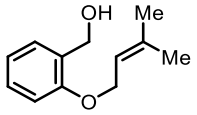
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.56

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.50 (s, 1H), 7.83 (dd, J = 7.7, 1.9 Hz, 1H), 7.52 (ddd, J = 8.4, 7.3, 1.9 Hz, 1H), 7.05 – 6.95 (m, 2H), 5.54 – 5.46 (m, 1H), 4.64 (d, J = 6.3 Hz, 2H), 1.81 (s, 3H), 1.76 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.2, 161.5, 138.9, 135.9, 128.4, 125.3, 120.7, 119.1, 113.1, 65.6, 25.9, 18.4 ppm.

All spectroscopic data corresponded to the reported literature values.[29]

(2-((3-Methylbut-2-en-1-yl)oxy)phenyl)methanol (SI-16)



SI-16

To a stirred solution of 2-(3-methylbut-2-enoxy)benzaldehyde (**SI-15**) (1.04 g, 5.48 mmol, 1.00 equiv.) in dry MeOH (20 mL) was added $NaBH_4$ (207 mg, 5.48 mmol, 1.00 equiv.) at 0 °C. The reaction mixture was allowed to reach rt and stirred for 18 h, followed by the addition of EtOAc (20 mL) and sat. aq. NH_4Cl (20 mL). The resulting mixture was extracted with EtOAc (2 × 20 mL). Combined organic layers were dried over Na_2SO_4, volatiles were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1) to afford **SI-16** (942 mg, 4.90 mmol, 89%) as a colourless liquid.

*Analytical data of **SI-16**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.78

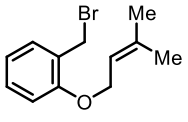
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.21 (m, 2H), 6.98 – 6.86 (m, 2H), 5.53 – 5.44 (m, 1H), 4.69 (d, J = 6.4 Hz, 2H), 4.57 (d, J = 6.6 Hz, 2H), 2.49 (t, J = 6.6 Hz, 1H), 1.80 (s, 3H), 1.74 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.0, 138.4, 129.5, 129.0, 128.9, 120.7, 119.7, 111.6, 65.1, 62.7, 25.9, 18.4 ppm.

IR (ATR): 3385 (br), 2972 (w), 2914 (m), 1602 (m), 1490 (m), 1454 (s), 1382 (w), 1232 (s), 1043 (m), 1003 (s), 751 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{12}H_{16}O_2+Na]^+$, $[M+Na]^+$: 215.1043; found: 215.1041.

1-(Bromomethyl)-2-((3-methylbut-2-en-1-yl)oxy)benzene (SI-17)



SI-17

Synthesized according to GP E from (2-((3-methylbut-2-en-1-yl)oxy)phenyl)methanol (**SI-16**) (385 mg, 2.00 mmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:CH_2Cl_2 = 8:1) afforded **SI-17** (145 mg, 568 µmol, 28%) as a colourless oil.

*Analytical data of **SI-17**:*

TLC (SiO_2): R_f (*n*-pentane: CH_2Cl_2 = 8:1) = 0.30

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.31 – 7.22 (m, 1H), 6.96 – 6.85 (m, 2H), 5.56 – 5.47 (m, 1H), 4.63 – 4.57 (m, 2H), 4.59 (s, 2H), 1.80 (s, 3H), 1.76 (s, 3H) ppm.

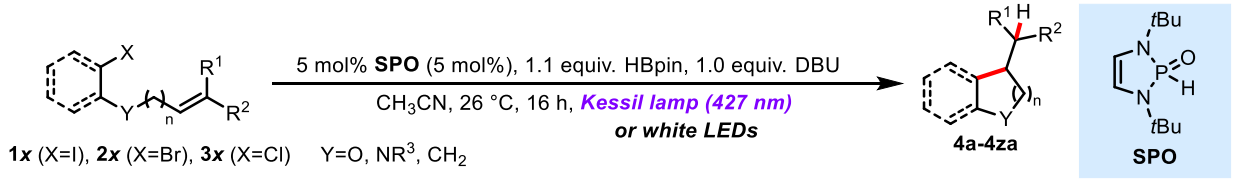
^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.9, 137.9, 131.1, 130.2, 126.6, 120.7, 119.9, 112.5, 65.5, 29.4, 25.9, 18.5 ppm.

IR (ATR): 2973 (s), 2912 (m), 1601 (m), 1491 (s), 1455 (s), 1230 (s), 1047 (m), 1001 (m), 751 (s), 607 (w) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{12}H_{15}BrO]^+$, $[M]^+$: 254.0301; found: 254.0298.

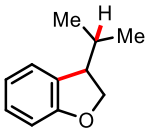
1.6 Intramolecular Reductive Cyclization

General Procedure F:



An oven-dried microwave vial, equipped with a stir bar was charged with the aryl or alkyl halide (200 µmol, 1.00 equiv.) and transferred into the glovebox. MeCN (0.2 M for iodides; 0.8 M for bromides and chlorides) was added, followed by DBU (30.0 µL, 30.5 mg, 200 µmol, 1.00 equiv.), **SPO** (43.3 µL, as a 50 mg/mL MeCN stock solution, 2.16 mg, 10.0 µmol, 5 mol%) and HBpin (32.0 µL, 28.2 mg, 220 µmol, 1.10 equiv.), unless otherwise stated. The vial was closed, removed from the glovebox, and irradiated (for iodides: white LEDs; for bromides and chlorides: Kessil lamp 427 nm) for 16 h at 26 °C. Volatiles were removed under reduced pressure and the residue was purified by flash chromatography (SiO_2, *n*-pentane:EtOAc).

3-Isopropyl-2,3-dihydrobenzofuran (4a)



4a

Synthesized according to GP F (white LEDs) from 1-iodo-2-((3-methylbut-2-en-1-yl)oxy)benzene (**1a**) (57.6 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4a** (30 mg, 184 µmol, 92%) as a colourless liquid.

Synthesized according to GP F (Kessil lamp 427 nm) from 1-bromo-2-((3-methylbut-2-en-1-yl)oxy)benzene (**2a**) (48.2 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4a** (31 mg, 191 µmol, 96%) as a colourless liquid.

*Analytical data of **4a**:*

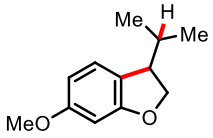
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.43

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 – 7.15 (m, 1H), 7.17 – 7.08 (m, 1H), 6.85 (td, *J* = 7.4, 1.0 Hz, 1H), 6.81 – 6.74 (m, 1H), 4.52 (t, *J* = 9.1 Hz, 1H), 4.38 (dd, *J* = 9.0, 5.1 Hz, 1H), 3.38 – 3.28 (m, 1H), 2.05 – 1.89 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.5, 129.6, 128.3, 125.2, 120.2, 109.5, 74.0, 48.3, 31.8, 20.0, 18.6 ppm.

All spectroscopic data corresponded to the reported literature values.[30]

3-Isopropyl-6-methoxy-2,3-dihydrobenzofuran (4b)



4b

Synthesized according to GP F (Kessil lamp 427 nm) from 1-bromo-4-methoxy-2-((3-methylbut-2-en-1-yl)oxy)benzene (**2b**) (54.2 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4b** (34 mg, 177 µmol, 88%) as a colourless liquid.

*Analytical data of **4b**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.29

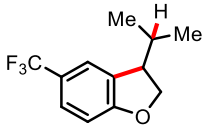
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 – 6.74 (m, 1H), 6.69 – 6.64 (m, 2H), 4.50 (t, *J* = 9.0 Hz, 1H), 4.36 (dd, *J* = 9.0, 5.2 Hz, 1H), 3.76 (s, 3H), 3.35 – 3.25 (m, 1H), 2.03 – 1.90 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.7, 154.0, 130.7, 112.9, 111.7, 109.2, 74.2, 56.2, 48.7, 31.7, 20.0, 18.5 ppm.

IR (ATR): 2957 (m), 2901 (w), 1603 (w), 1487 (s), 1464 (m), 1274 (m), 1216 (m), 1194 (m), 1179 (m), 1034 (m), 959 (m), 804 (m), 713 (w) cm^{-1}.

HRMS (ESI): calcd. for $[C_{12}H_{16}O_2+H]^+$, $[M+H]^+$: 193.1223; found: 193.1199.

3-Isopropyl-5-(trifluoromethyl)-2,3-dihydrobenzofuran (4c)



4c

Synthesized according to GP F (Kessil lamp 427 nm) from 2-bromo-1-((3-methylbut-2-en-1-yl)oxy)-(trifluoromethyl)benzene (**2c**). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4c** (44 mg, 0.19 mmol, 96%) as a colourless liquid.

*Analytical data of **4c**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.36

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 – 7.36 (m, 2H), 6.85 – 6.78 (m, 1H), 4.60 (t, *J* = 9.3 Hz, 1H), 4.46 (dd, *J* = 9.2, 5.2 Hz, 1H), 3.37 (dt, *J* = 9.5, 5.1 Hz, 1H), 1.99 (heptd, *J* = 6.8, 4.9 Hz, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm.

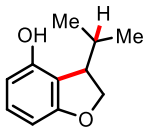
^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.2, 130.5, 126.3 (q, $^3J_{FC}$ = 3.9 Hz), 124.8 (q, $^1J_{FC}$ = 271.0 Hz), 122.7 (q, $^2J_{FC}$ = 32.2 Hz), 122.4 (q, $^3J_{FC}$ = 3.9 Hz), 109.5, 74.8, 47.8, 31.8, 19.8, 18.5 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ = – 60.96 ppm.

IR (ATR): 2963 (w), 1619 (2), 1499 (w), 1317 (s), 1154 (s), 1108 (s), 1057 (m), 956 (w), 824 (m), 662 (w) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{12}H_{13}F_3O]^+$, $[M]^+$: 230.0913; found: 230.0913.

3-Isopropyl-2,3-dihydrobenzofuran-4-ol (4d)



4d

Synthesized according to GP F (Kessil lamp 427 nm) from 2-bromo-3-((3-methylbut-2-en-1-yl)oxy)phenol (**2d**) (46.0 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1) afforded **4d** (21 mg, 118 µmol, 66%) as a colourless gum.

*Analytical data of **4d**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 20:1) = 0.12

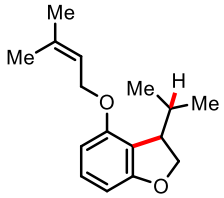
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (td, *J* = 8.0, 0.6 Hz, 1H), 6.43 – 6.36 (m, 1H), 6.28 (dd, *J* = 8.1, 0.8 Hz, 1H), 4.67 (s, 1H), 4.48 – 4.41 (m, 2H), 3.54 – 3.45 (m, 1H), 2.25 (heptd, *J* = 6.9, 4.1 Hz, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.2, 153.0, 129.4, 115.3, 107.9, 102.6, 73.1, 46.5, 29.9, 20.8, 17.3 ppm.

IR (ATR): 3401 (br), 2958 (m), 1611 (m), 1458 (s), 1280 (m), 1014 (s), 949 (w), 784 (w) cm^{-1}.

HRMS (ESI): calcd. for $[C_{11}H_{14}O_2+H]^+$, $[M+H]^+$: 179.1067; found: 179.1061.

3-Isopropyl-4-((3-methylbut-2-en-1-yl)oxy)-2,3-dihydrobenzofuran (4e)



4e

Synthesized according to GP F (Kessil lamp 427 nm) from 2-bromo-1,3-bis((3-methylbut-2-en-1-yl)oxy)benzene (**2e**) (65.1 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4e** (31 mg, 126 µmol, 63%) as a colourless oil.

*Analytical data of **4e**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.26

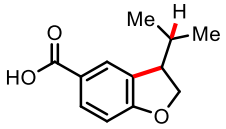
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 – 7.02 (m, 1H), 6.42 (dd, *J* = 8.1, 3.6 Hz, 2H), 5.51 – 5.42 (m, 1H), 4.61 – 4.48 (m, 2H), 4.46 – 4.39 (m, 2H), 3.56 – 3.47 (m, 1H), 2.31 (heptd, *J* = 6.9, 3.9 Hz, 1H), 1.79 (s, 3H), 1.73 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.7, 156.5, 137.3, 129.1, 120.3, 117.0, 104.3, 102.7, 72.8, 65.0, 46.8, 29.2, 25.9, 20.9, 18.4, 17.0 ppm.

IR (ATR): 2957 (m), 1605 (m), 1453 (m), 1269 (m), 1252 (m), 1058 (s), 782 (w), 745 (w) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{22}O_2+H]^+$, $[M+H]^+$: 247.1693; found: 247.1697.

3-Isopropyl-2,3-dihydrobenzofuran-5-carboxylic acid (4f)



4f

Synthesized according to GP F (Kessil lamp 427 nm) from 3-bromo-4-((3-methylbut-2-en-1-yl)oxy)benzoic acid (**2f**) (57.0 mg, 200 µmol, 1.00 equiv.) and HBpin (72.5 µL, 64.0 mg, 500 µmol, 2.50 equiv.). After 16 h, all volatiles were remove under reduced pressure and the residue was washed with *n*-pentane to afford **4f** (35 mg, 170 µmol, 85%) as a white solid.

*Analytical data of **4f**:*

TLC (SiO_2): R_f (*n*-pentane:Et_2O = 1:1) = 0.40

Mp: 142.1 – 143.7 °C.

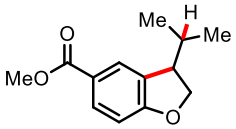
^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.28 (br s, 1H), 8.03 – 7.89 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.63 (t, *J* = 9.3 Hz, 1H), 4.48 (dd, *J* = 9.3, 5.2 Hz, 1H), 3.44 – 3.34 (m, 1H), 2.05 – 1.97 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1, 165.5, 132.3, 130.3, 127.7, 121.6, 109.4, 75.2, 47.5, 31.8, 19.8, 18.3 ppm.

IR (ATR): 3641 (w), 2967 (m), 1678 (s), 1607 (m), 1411 (m), 1296 (m), 1245 (m), 1052 (w), 952 (w) cm^{-1}.

HRMS (ESI): calcd. for $[C_{12}H_{14}O_3+H]^+$, $[M+H]^+$: 207.1016; found: 207.1010.

Methyl 3-isopropyl-2,3-dihydrobenzofuran-5-carboxylate (4g)



4g

Synthesized according to GP F (Kessil lamp 427 nm) from methyl 3-bromo-4-((3-methylbut-2-en-1-yl)oxy)benzoate (**2g**) (59.8 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4g** (37 mg, 168 µmol, 84%) as a white solid.

*Analytical data of **4g**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.19

Mp: 50.2 – 52.1 °C.

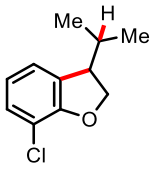
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.85 (m, 2H), 6.79 – 6.75 (m, 1H), 4.59 (t, *J* = 9.3 Hz, 1H), 4.45 (dd, *J* = 9.2, 5.2 Hz, 1H), 3.87 (s, 3H), 3.40 – 3.33 (m, 1H), 1.99 (heptd, *J* = 6.8, 4.9 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.2, 164.7, 131.4, 130.0, 127.0, 122.5, 109.2, 75.0, 51.9, 47.6, 31.7, 19.8, 18.3 ppm.

IR (ATR): 2957 (m), 1710 (s), 1608 (m), 1491 (m), 1437 (m), 1256 (s), 1157 (m), 1108 (s), 952 (s), 834 (w), 767 (m), 667 (w) cm^{-1}.

HRMS (ESI): calcd. for $[C_{13}H_{16}O_3+H]^+$, $[M+H]^+$: 221.1172; found: 221.1142.

7-Chloro-3-isopropyl-2,3-dihydrobenzofuran (4h)



4h

Synthesized according to GP F (Kessil lamp 427 nm) from 1-bromo-3-chloro-2-((3-methylbut-2-en-1-yl)oxy)benzene (**2h**) (55.1 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 1:0 – 40:1) afforded **4h** (32 mg, 162 µmol, 81%) as a colourless oil.

*Analytical data of **4h**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.36

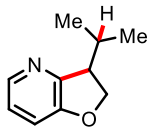
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.79 (dd, *J* = 8.0, 7.4 Hz, 1H), 4.62 (t, *J* = 9.2 Hz, 1H), 4.48 (dd, *J* = 9.2, 5.3 Hz, 1H), 3.41 (dtt, *J* = 9.3, 5.3, 0.9 Hz, 1H), 1.98 (heptd, *J* = 6.9, 5.0 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.3, 131.4, 128.6, 123.5, 121.3, 115.1, 74.7, 49.0, 31.8, 19.9, 18.5 ppm.

IR (ATR): 2961 (s), 2901 (m), 1605 (w), 1449 (s), 1220 (m), 1076 (m), 1055 (m), 955 (m), 889 (w) cm^{-1}.

HRMS (APPI/LTQ-Orbitrap): calcd. for $[C_{11}H_{13}ClO]^+$, $[M]^+$: 196.0649; found: 196.0647.

3-Isopropyl-2,3-dihydrofuro[3,2-b]pyridine (4i)



4i

Synthesized according to GP F (Kessil lamp 427 nm) from 2-bromo-3-((3-methylbut-2-en-1-yl)oxy)pyridine (**2i**) (48.4 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 3:1) afforded **4i** (20 mg, 123 µmol, 61%) as a colourless oil.

*Analytical data of **4i**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.63

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (dd, *J* = 3.8, 2.4 Hz, 1H), 7.02 – 6.97 (m, 2H), 4.62 (t, *J* = 9.4 Hz, 1H), 4.46 (dd, *J* = 9.3, 5.8 Hz, 1H), 3.43 – 3.34 (m, 1H), 2.21 (heptd, *J* = 6.9, 4.8 Hz, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H) ppm.

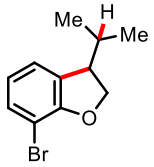
^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.2, 153.1, 141.6, 122.4, 115.6, 73.3, 48.1, 31.0, 20.2, 18.0 ppm.

IR (ATR): 2958 (m), 1575 (w), 1426 (s), 1261 (m), 1157 (w), 1103 (w), 945 (s), 783 (m) cm^{-1}.

HRMS (ESI): calcd. for $[C_{10}H_{13}NO+H]^+$, $[M+H]^+$: 164.1070; found: 164.1065.

All spectroscopic data corresponded to the reported literature values.[31]

7-Bromo-3-isopropyl-2,3-dihydrobenzofuran (4j)



4j

Synthesized according to GP F (white LEDs) from 1-bromo-3-iodo-2-((3-methylbut-2-en-1-yl)oxy)benzene (**1j**) (70.4 mg, 191 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4j** (45 mg, 186 µmol, 97%) as a colourless oil.

*Analytical data of **4j**:*

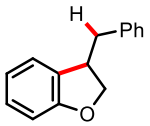
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.37

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.73 (dd, *J* = 8.0, 7.3 Hz, 1H), 4.62 (t, *J* = 9.2 Hz, 1H), 4.47 (dd, *J* = 9.2, 5.4 Hz, 1H), 3.44 (dtt, *J* = 9.3, 5.3, 0.9 Hz, 1H), 1.98 (heptd, *J* = 6.8, 4.9 Hz, 1H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.7, 131.4, 131.1, 124.2, 121.7, 102.7, 74.4, 49.2, 31.8, 19.9, 18.5 ppm.

All spectroscopic data corresponded to the reported literature values.[32]

3-Benzyl-2,3-dihydrobenzofuran (4k)



4k

Synthesized according to GP F (KESSIL lamp) from (*E*)-1-bromo-2-(cinnamyloxy)benzene (**2k**) (57.8 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4k** (36 mg, 171 µmol, 86%) as a colourless oil.

*Analytical data of **4k**:*

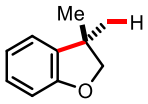
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.26

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.28 (m, 2H), 7.30 – 7.21 (m, 1H), 7.24 – 7.17 (m, 2H), 7.19 – 7.10 (m, 1H), 7.02 – 6.95 (m, 1H), 6.87 – 6.78 (m, 2H), 4.54 (t, *J* = 8.9 Hz, 1H), 4.30 (dd, *J* = 8.9, 6.0 Hz, 1H), 3.77 (tt, *J* = 8.9, 6.1 Hz, 1H), 3.08 (dd, *J* = 13.8, 6.4 Hz, 1H), 2.86 (dd, *J* = 13.8, 8.9 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.1, 139.3, 130.4, 129.1, 128.7, 128.5, 126.6, 124.7, 120.4, 109.8, 76.5, 43.6, 41.2 ppm.

All spectroscopic data corresponded to the reported literature values.[30]

3,3-Dimethyl-2,3-dihydrobenzofuran (4l)



4l

Synthesized according to GP F (Kessil lamp 427 nm) from 1-bromo-2-((2-methylallyl)oxy)benzene (**2l**) (45.4 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4l** (8 mg, 54.0 µmol, 27%) as a colourless oil.

*Analytical data of **4l**:*

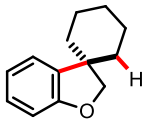
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.52

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 – 7.07 (m, 2H), 6.93 – 6.84 (m, 1H), 6.83 – 6.76 (m, 1H), 4.23 (s, 2H), 1.35 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.3, 136.7, 128.0, 122.4, 120.7, 109.8, 84.5, 42.0, 27.7 (2C) ppm.

All spectroscopic data corresponded to the reported literature values.[33]

***2H*-spiro[benzofuran-3,1'-cyclohexane] (4m)**



4m

Synthesized according to GP F (Kessil lamp 427 nm) from 1-bromo-2-(cyclohex-1-en-1-ylmethoxy)benzene (**2m**) (51.0 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 1:0 – 40:1) afforded **4m** (9 mg, 47 µmol, 24%) as a colourless liquid.

*Analytical data of **4m**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.65

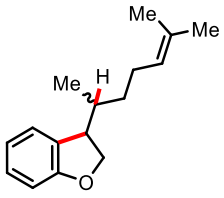
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 – 7.07 (m, 2H), 6.87 (td, *J* = 7.4, 1.0 Hz, 1H), 6.82 – 6.75 (m, 1H), 4.36 (s, 2H), 1.82 – 1.58 (m, 7H), 1.40 – 1.31 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.4, 136.4, 128.2, 123.0, 120.5, 109.8, 81.1, 46.3, 36.9 (2C), 25.6, 23.5 (2C) ppm.

IR (ATR): 2925 (s), 2852 (m), 1599 (w), 1479 (s), 1449 (m), 1228 (s), 977 (s) 749 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{13}H_{16}O]^+$, $[M]^+$: 188.1196; found: 188.1194.

3-(6-Methylhept-5-en-2-yl)-2,3-dihydrobenzofuran (4n)



4n

Synthesized according to GP F (Kessil lamp 427 nm) from (*E*)-1-bromo-2-((3,7-dimethylocta-2,6-dien-1-yl)oxy)benzene (**2n**) (61.9 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4n** (40 mg, 173 µmol, 87%) as a colourless oil (*d.r.* = 50:50).

*Analytical data of **4n**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.41

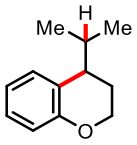
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 – 7.07 (m, 2H), 6.89 – 6.80 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.15 – 5.01 (m, 1H), 4.55 (t, *J* = 9.2 Hz, 1/2H), 4.50 (t, *J* = 9.3 Hz, 1/2H), 4.36 (ddd, J = 9.0, 6.9, 5.4 Hz, 1H), 3.50 (dt, *J* = 9.7, 4.9 Hz, 1/2H), 3.42 (dt, *J* = 9.5, 4.8 Hz, 1/2H), 2.14 – 1.73 (m, 3H), 1.70 (s, 3/2H), 1.68 (s, 3/2H), 1.62 (s, 3/2H), 1.59 (s, 3/2H), 1.51 – 1.31 (m, 1H), 1.32 – 1.14 (m, 1H), 0.89 (d, J = 6.8 Hz, 3/2H), 0.81 (d, J = 6.9 Hz, 3/2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.77, 160.52, 131.84, 131.78, 129.85, 128.98, 128.27, 128.19, 125.40, 124.78, 124.50, 124.41, 120.31, 120.17, 109.47, 109.42, 74.86, 73.04, 47.29, 46.75, 36.54, 36.03, 34.73, 33.31, 25.98, 25.92, 25.89, 25.85, 17.86, 17.82, 16.44, 14.94 ppm.

IR (ATR): 2963 (m), 2914 (m), 1595 (m), 1483 (s), 1459 (m), 1229 (s), 958 (w), 749 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{22}O+H]^+$, $[M+H]^+$: 231.1743; found: 231.1738

4-Isopropylchromane (4o)



4o

Synthesized according to GP F (Kessil lamp 427 nm) from 1-bromo-2-((4-methylpent-3-en-1-yl)oxy)benzene (**2o**) (51.0 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4o** (16 mg, 91 µmol, 45%) as a colourless liquid.

*Analytical data of **4o**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 1:0 – 40:1) = 0.47

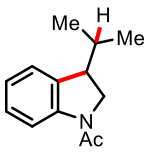
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 – 7.12 (m, 1H), 7.13 – 7.04 (m, 1H), 6.86 (td, *J* = 7.5, 1.4 Hz, 1H), 6.80 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.27 (ddd, *J* = 10.7, 6.1, 4.5 Hz, 1H), 4.15 – 4.08 (m, 1H), 2.73 (q, *J* = 6.5 Hz, 1H), 2.32 – 2.14 (m, 1H), 1.92 (tdd, *J* = 6.2, 4.3, 2.2 Hz, 2H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.2, 129.0, 127.2, 125.8, 120.1, 116.9, 65.0, 39.8, 30.7, 23.0, 21.2, 17.6 ppm.

IR (ATR): 2958 (s), 2871 (m), 1580 (w), 1488 (s), 1451 (m), 1223 (s), 1068 (s), 752 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{12}H_{16}O]^+$, $[M]^+$: 176.1196; found: 176.1195.

1-(3-Isopropylindolin-1-yl)ethan-1-one (4p)



4p

Synthesized according to GP F (Kessil lamp 427) from *N*-(2-bromophenyl)-*N*-(3-methylbut-2-en-1-yl)acetamide (**2p**) (56.4 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 1:1) afforded **4p** (37 mg, 182 µmol, 91%) as a colourless oil.

*Analytical data of **4p**:*

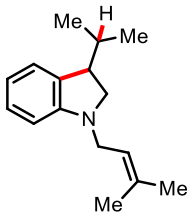
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 1:1) = 0.59

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.13 (m, 2H), 7.02 (td, *J* = 7.5, 1.1 Hz, 1H), 4.00 (t, *J* = 10.2 Hz, 1H), 3.79 (dd, *J* = 10.6, 5.0 Hz, 1H), 3.35 (dt, *J* = 9.6, 4.7 Hz, 1H), 2.24 (s, 3H), 2.13 – 1.99 (m, 1H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.7, 143.3, 133.9, 128.0, 124.5, 123.6, 116.9, 51.3, 46.1, 32.0, 24.4, 20.2, 17.5 ppm.

All spectroscopic data corresponded to the reported literature values.[34]

3-Isopropyl-1-(3-methylbut-2-en-1-yl)indoline (4q)



4q

Synthesized according to GP F (Kessil lamp 427) from 2-bromo-*N*,*N*-bis(3-methylbut-2-en-1-yl)aniline (**2q**) (61.7 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1) afforded **4q** (44 mg, 191 µmol, 96%) as a colourless liquid.

*Analytical data of **4q**:*

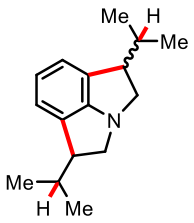
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.32

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 – 7.02 (m, 2H), 6.64 (td, *J* = 7.4, 1.0 Hz, 1H), 6.48 (dd, *J* = 8.2, 1.0 Hz, 1H), 5.32 – 5.23 (m, 1H), 3.71 – 3.64 (m, 2H), 3.41 – 3.29 (m, 1H), 3.19 – 3.05 (m, 2H), 2.10 – 1.96 (m, 1H), 1.75 (s, 3H), 1.72 (s, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.9, 135.3, 132.9, 127.5, 124.6, 120.4, 117.1, 107.2, 55.2, 47.0, 46.6, 30.8, 25.9, 20.7, 18.9, 18.1 ppm.

All spectroscopic data corresponded to the reported literature values.[35]

1,5-Diisopropyl-1,2,4,5-tetrahydropyrrolo[3,2,1-hi]indole (4r)



4r

Synthesized according to GP F (Kessil lamp 427 nm) from 2,6-dibromo-*N*,*N*-bis(3-methylbut-2-en-1-yl)aniline (**2r**) (77.4 mg, 200 µmol, 1.00 equiv.), DBU (59.7 µL, 60.9 mg, 400 µmol, 2.00 equiv.), **SPO** (86.6 µL, 50 mg/mL

in MeCN stock solution, 4.33 mg, 20 µmol, 10 mol%) and HBpin (63.8 µL. 56.3 mg, 440 µmol, 2.20 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 40:1 – 20:1) afforded **4r** (13 mg, 56 µmol, 28%) as a faint yellow oil (*d.r.* = 1:1).

*Analytical data of **4r**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 40:1) = 0.22

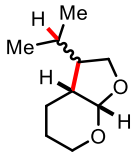
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96 (d, *J* = 7.3 Hz, 2H), 6.63 (td, *J* = 7.3, 2.3 Hz, 1H), 3.44 – 3.21 (m, 4H), 3.03 (dd, *J* = 8.6, 6.5 Hz, 1H), 2.92 (dd, *J* = 8.4, 7.0 Hz, 1H), 1.99 (dpd, *J* = 13.5, 6.8, 2.4 Hz, 2H), 1.08 (d, *J* = 4.3 Hz, 3H), 1.07 (d, *J* = 4.3 Hz, 3H), 0.99 (d, *J* = 5.0 Hz, 3H), 0.97 (d, *J* = 5.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.6, 126.1, 126.0, 123.0, 122.9, 119.6, 62.0, 61.9, 55.6, 55.5, 30.9, 30.9, 21.0, 20.9, 20.9, 20.8 ppm.

IR (ATR): 2956 (s), 2869 (m), 2818 (w), 1585 (m), 1487 (m), 1450 (m), 1047 (w), 749 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{23}N+H]^+$, $[M+H]^+$: 230.1903; found: 230.1909.

3-Isopropylhexahydro-4H-furo[2,3-b]pyran (4s)



4s

Synthesized according to GP F (white LEDs) from 3-iodo-2-((3-methylbut-2-en-1-yl)oxy)tetrahydro-2H-pyran (**1s**) (59.2 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **4s** (22.0 mg, 129 µmol, 65%) as a colourless oil (*cis*/*trans* = 64:36).

Synthesized according to GP F (Kessil lamp 427 nm) from 3-bromo-2-((3-methylbut-2-en-1-yl)oxy)tetrahydro-2H-pyran (**2s**) (49.8 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **4s** (20.0 mg, 118 µmol, 59%) as a colourless oil (*cis*/*trans*[36]= 64:36).

*Analytical data of **4s**:*

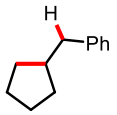
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 3:1) = 0.58

^{1}H NMR (400 MHz, $CDCl_3$): ***cis***: δ = 5.29 (d, *J* = 3.2 Hz, 1H), 3.94 (t, *J* = 7.8 Hz, 1H), 3.71 – 3.62 (m, 3H), 1.96 – 1.82 (m, 2H), 1.71 – 1.54 (m, 4H), 1.42 – 1.32 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H) ppm. ***trans***: δ = 4.99 (d, *J* = 3.6 Hz, 1H), 4.18 (t, *J* = 8.6 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.67 – 3.61 (m, 1H), 3.46 – 3.39 (m, 1H), 2.15 – 2.06 (m, 1H), 1.90 – 1.76 (m, 3H), 1.71 – 1.54 (m, 2H), 1.42 – 1.32 (m, 1H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): ***cis***: δ = 102.3, 69.2, 60.9, 49.1, 35.9, 26.5, 23.5, 21.9, 21.2, 19.0 ppm. ***trans***: δ = 102.7, 71.3, 64.5, 44.5, 41.5, 30.3, 23.7, 21.7, 20.9, 19.7 ppm.

All spectroscopic data corresponded to the reported literature values.[36–38]

(Cyclopentylmethyl)benzene (4t)



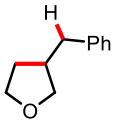
4t

Synthesized according to GP F (Kessil lamp 427 nm) from [(*E*)-6-bromohex-1-enyl]benzene (47.8 mg, 200 µmol, 1.00 equiv.) **2t**. Purification by flash chromatography (SiO2, n-pentane:EtOAc = 40:1) afforded an inseparable mixture of **4t** and **2t**. The mixture was analysed by qualitative NMR analysis with 1,3,5-trimethoxybenzene as internal standard to determine the NMR yield for **4t** to be 39%. The characteristic product signals matched those reported in literature.[39]

*Analytical data of **4t**:*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 2.61 (d, *J* = 7.4 Hz, 2H), 2.15 – 2.03 (m, 1H), 1.75 – 1.67 (m, 2H), 1.66 – 1.59 (m, 2H), 1.59 – 1.45 (m, 2H), 1.27 – 1.13 (m, 2H) ppm.

3-Benzyltetrahydrofuran (4u)



4u

Synthesized according to GP F (Kessil lamp 427 nm) from (*E*)-(3-(2-bromoethoxy)prop-1-en-1-yl)benzene (48.2 mg, 200 µmol, 1.00 equiv.) (**2u**). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1) afforded **4u** (12.0 mg, 74.0 µmol, 37%) as a colourless oil.

*Analytical data of **4u**:*

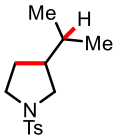
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 6:1) = 0.33

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 3.91 (td, *J* = 8.2, 5.0 Hz, 1H), 3.84 (dd, *J* = 8.4, 6.9 Hz, 1H), 3.76 (dt, *J* = 8.4, 7.4 Hz, 1H), 3.47 (dd, *J* = 8.4, 6.6 Hz, 1H), 2.70 (dd, *J* = 7.7, 2.2 Hz, 2H), 2.52 (hept, *J* = 7.1 Hz, 1H), 2.00 (dtd, *J* = 12.5, 7.6, 5.0 Hz, 1H), 1.70 – 1.57 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.9, 128.8 (2C), 128.6 (2C), 126.2, 73.5, 68.0, 41.1, 39.5, 32.3 ppm.

All spectroscopic data corresponded to the reported literature values.[40]

3-Isopropyl-1-tosylpyrrolidine (4v)



4v

Synthesized according to GP F (Kessil lamp 427 nm) from *N*-(2-bromoethyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (**2v**) (69.3 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **4v** (41.0 mg, 153 µmol, 77%) as a colourless oil.

*Analytical data of **4v**:*

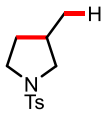
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.31

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.44 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.36 (ddd, *J* = 9.7, 8.5, 2.3 Hz, 1H), 3.14 (td, *J* = 9.9, 6.8 Hz, 1H), 2.77 (t, *J* = 9.6 Hz, 1H), 2.42 (s, 3H), 1.95 – 1.85 (m, 1H), 1.74 – 1.62 (m, 1H), 1.41 – 1.29 (m, 2H), 0.84 (d, *J* = 1.1 Hz, 3H), 0.82 (d, *J* = 1.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.4, 134.0, 129.7 (2C), 127.6 (2C), 52.2, 48.2, 46.5, 31.9, 30.1, 21.6, 21.4, 21.1 ppm.

All spectroscopic data corresponded to the reported literature values.[40]

3-Methyl-1-tosylpyrrolidine (4w)



4w

Synthesized according to GP F (Kessil lamp 427 nm) from *N*-allyl-*N*-(2-bromoethyl)-4-methylbenzenesulfonamide (**2w**) (63.7 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 6:1) afforded **4w** (26.0 mg, 109 µmol, 54%) as a white solid.

*Analytical data of **4w**:*

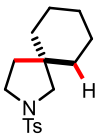
TLC (SiO_2): R_f (*n*-pentane:Et_2O = 6:1) = 0.33

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.42 (dd, *J* = 9.7, 7.1 Hz, 1H), 3.34 (ddd, *J* = 9.9, 8.2, 4.1 Hz, 1H), 3.22 (ddd, *J* = 9.8, 8.2, 7.2 Hz, 1H), 2.75 (dd, *J* = 9.7, 7.8 Hz, 1H), 2.43 (s, 3H), 2.18 – 2.05 (m, 1H), 1.96 – 1.84 (m, 1H), 1.35 (dq, *J* = 12.3, 8.4 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.4, 134.2, 129.7 (2C), 127.7 (2C), 54.9, 47.8, 33.5, 33.4, 21.7, 17.8 ppm.

All spectroscopic data corresponded to the reported literature values.[41]

2-Tosyl-2-azaspiro[4.5]decane (4x)



4x

Synthesized according to GP F (Kessil lamp 427 nm) from *N*-(cyclohex-1-en-1-ylmethyl)-*N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**2x**) (74.5 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **4x** (30.0 mg, 102 µmol, 51%) as a colourless oil.

*Analytical data of **4x**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.28

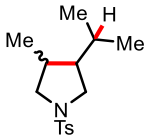
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 3.25 (t, *J* = 7.1 Hz, 2H), 3.04 (s, 2H), 2.42 (s, 3H), 1.64 – 1.51 (m, 2H), 1.43 – 1.17 (m, 10H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3, 134.0, 129.7 (2C), 127.6 (2C), 57.9, 46.5, 42.6, 37.1, 35.5, 26.0, 23.4, 21.7 ppm.

IR (ATR): 2922 (m), 2853 (w), 1450 (m), 1342 (s), 1158 (s), 1095 (s), 816 (w), 662 (s), 588 (s), 545 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{16}H_{23}NO_2+H]^+$, $[M+H]^+$: 294.1528; found: 294.1506.

3-Isopropyl-4-methyl-1-tosylpyrrolidine (4y)



4y

Synthesized according to GP F (Kessil lamp 427 nm) from (±)-*N*-(2-hydroxypropyl)-4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (**2y**) (72.1 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **4y** (51.0 mg, 181 µmol, 91%) as a colourless oil (*d.r.* = 65:35).

*Analytical data of **4y**:*

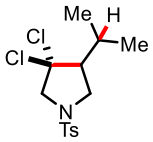
TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.29

^{1}H NMR (400 MHz, $CDCl_3$): **major**: δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 3.41 (dd, *J* = 9.5, 7.7 Hz, 1H), 3.29 (dd, *J* = 9.9, 5.7 Hz, 1H), 3.15 (d, *J* = 9.7 Hz, 1H), 2.87 (dd, *J* = 11.2, 9.7 Hz, 1H), 2.42 (s, 3H), 2.23 – 2.11 (m, 1H), 1.65 – 1.52 (m, 1H), 1.49 – 1.38 (m, 1H), 0.82 (t, *J* = 6.7 Hz, 6H), 0.62 (d, *J* = 7.0 Hz, 3H) ppm. **minor**: δ = 7.69 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 9.2 Hz, 2H), 3.42 (d, *J* = 9.5 Hz, 1H), 3.36 – 3.27 (m, 1H), 2.92 (dd, *J* = 10.0, 8.8 Hz, 1H), 2.72 (dd, *J* = 9.6, 8.3 Hz, 1H), 2.42 (s, 3H), 1.93 – 1.80 (m, 1H), 1.67 – 1.57 (m, 1H), 1.49 – 1.42 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.4, 143.3, 134.5, 133.6, 129.7, 127.7, 127.4, 56.1, 55.5, 52.0, 50.3, 50.1, 49.8, 36.0, 34.0, 28.8, 27.4, 21.9, 21.6, 21.5, 21.1, 18.5, 17.7, 13.0 ppm.

All spectroscopic data corresponded to the reported literature values.[42]

3,3-Dichloro-4-isopropyl-1-tosylpyrrolidine (4z)



4z

Synthesized according to GP F (Kessil lamp 427 nm) from 4-methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (**3z**) (74.1 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 20:1) afforded **4z** (55.0 mg, 163 µmol, 82%) as a white solid.

*Analytical data of **4z**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 20:1) = 0.19

Mp: 135.5 – 136.2 °C.

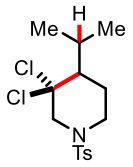
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.11 (d, *J* = 11.9 Hz, 1H), 3.89 (d, *J* = 11.8 Hz, 1H), 3.69 (dd, *J* = 9.6, 7.9 Hz, 1H), 3.05 (dd, *J* = 10.5, 9.6 Hz, 1H), 2.44 (s, 3H), 2.30 – 2.15 (m, 1H), 1.99 – 1.84 (m, 1H), 1.15 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.1, 134.0, 129.9 (2C), 127.7 (2C), 87.8, 66.7, 59.1, 51.2, 29.6, 21.8 (2C), 21.2 ppm.

IR (ATR): 2966 (m), 1351 (m), 1167 (s), 1064 (m), 814 (w), 665 (s), 595 (m), 549 (m) cm^{-1}.

HRMS (ESI): calcd. for $[C_{14}H_{19}Cl_2NO_2S+H]^+$, $[M+H]^+$: 336.0586; found: 336.0560.

3,3-Dichloro-4-isopropyl-1-tosylpiperidine (4za)



4za

Synthesized according to GP F (Kessil lamp 427 nm) from 4-methyl-*N*-(4-methylpent-3-en-1-yl)-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (**3za**) (77.0 mg, 200 µmol, 1.00 equiv.). Purification by flash chromatography (SiO_2, *n*-pentane:EtOAc = 10:1) afforded **4za** (48.0 mg, 137 µmol, 69%) as a white solid.

*Analytical data of **4za**:*

TLC (SiO_2): R_f (*n*-pentane:EtOAc = 10:1) = 0.33

Mp: 131.6 – 133.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.27 (dd, *J* = 12.5, 2.2 Hz, 1H), 3.89 (ddt, *J* = 11.8, 4.6, 2.3 Hz, 1H), 2.82 (d, *J* = 12.5 Hz, 1H), 2.44 (s, 3H), 2.46 – 2.36 (m, 1H), 2.34 (td, *J* = 12.1, 2.8 Hz, 1H), 1.90 – 1.74 (m, 1H), 1.68 – 1.56 (m, 2H), 0.98 (d, *J* = 4.5 Hz, 3H), 0.96 (d, *J* = 4.7 Hz, 3H) ppm.

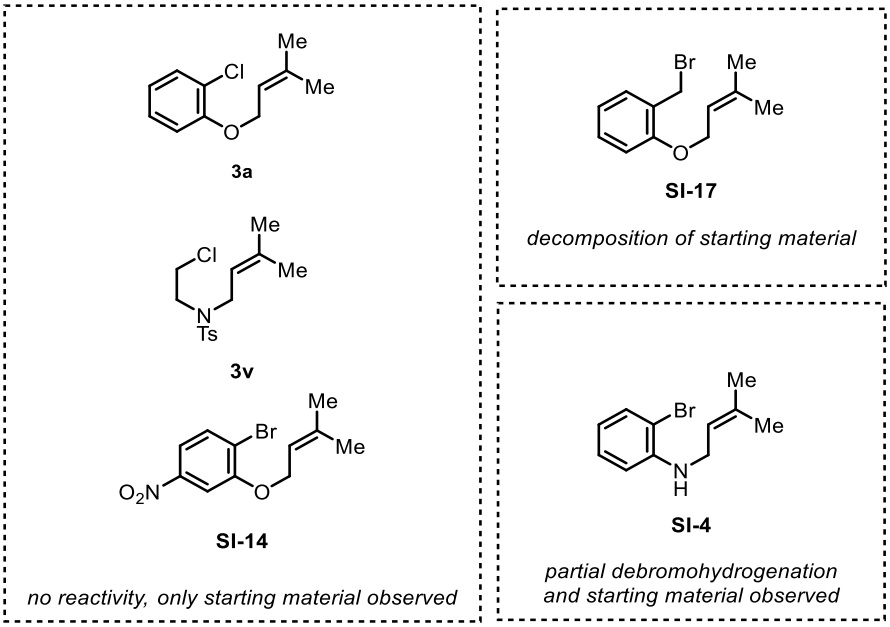
^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.1, 134.0, 130.0, 127.7, 90.9, 62.0, 55.5, 46.3, 27.7, 24.2, 24.0, 21.7, 18.3 ppm.

IR (ATR): 2961 (w), 1391 (m), 1262 (w), 1162 (s), 1091 (m), 946 (m), 815 (m), 743 (s), 654 (s), 548 (s) cm^{-1}.

HRMS (ESI): calcd. for $[C_{15}H_{21}Cl_2NO_2S+H]^+$, $[M+H]^+$: 350.0743; found: 350.0749.

1.7 Non-working Substrates

Following compounds were used in GP F. However, no desired intramolecular cyclization reaction was observed.



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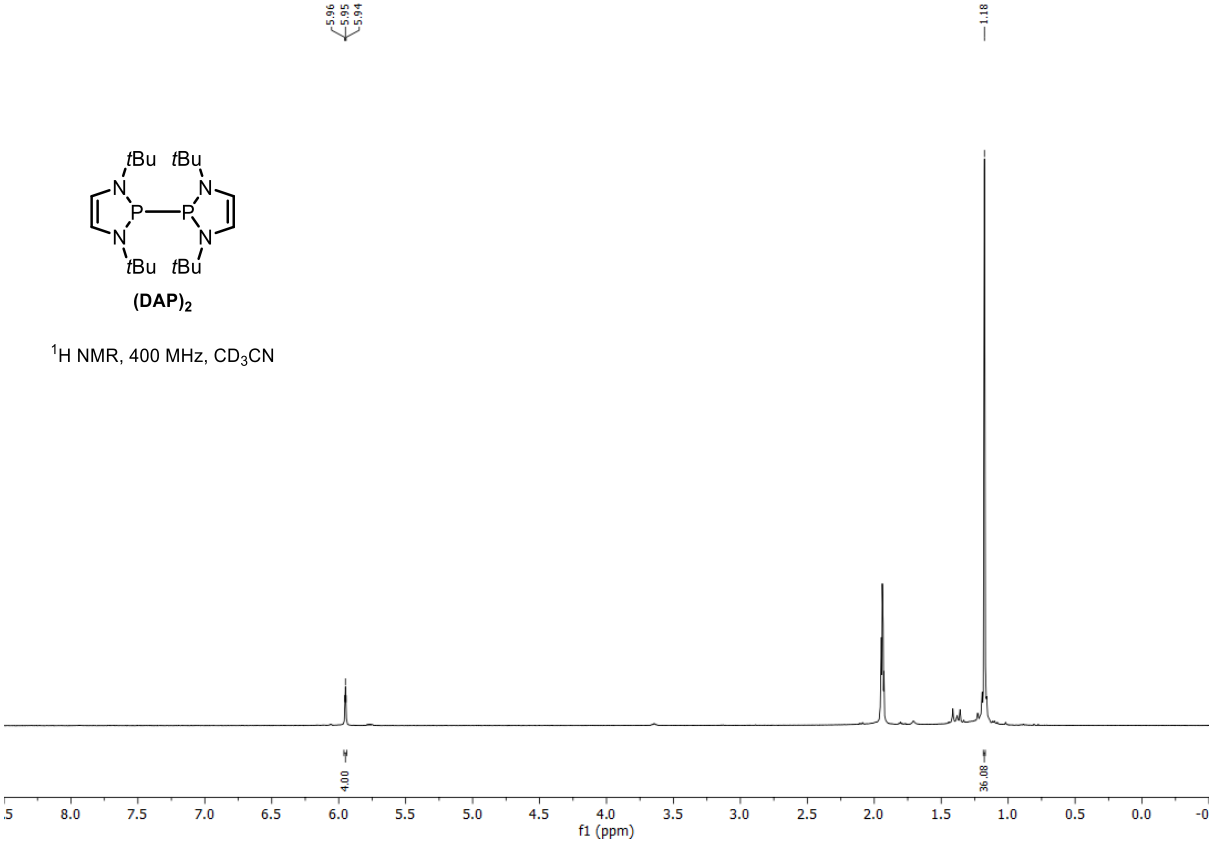
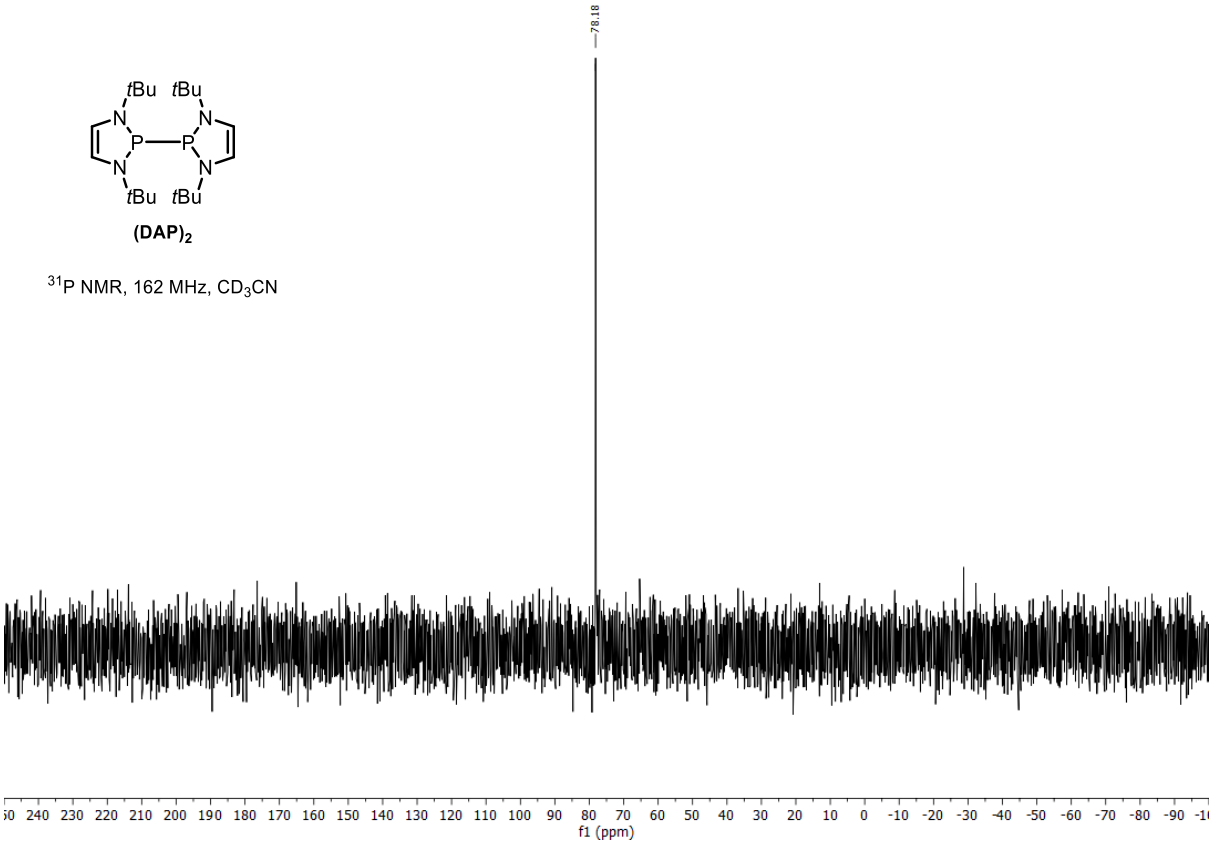
3. NMR Spectra



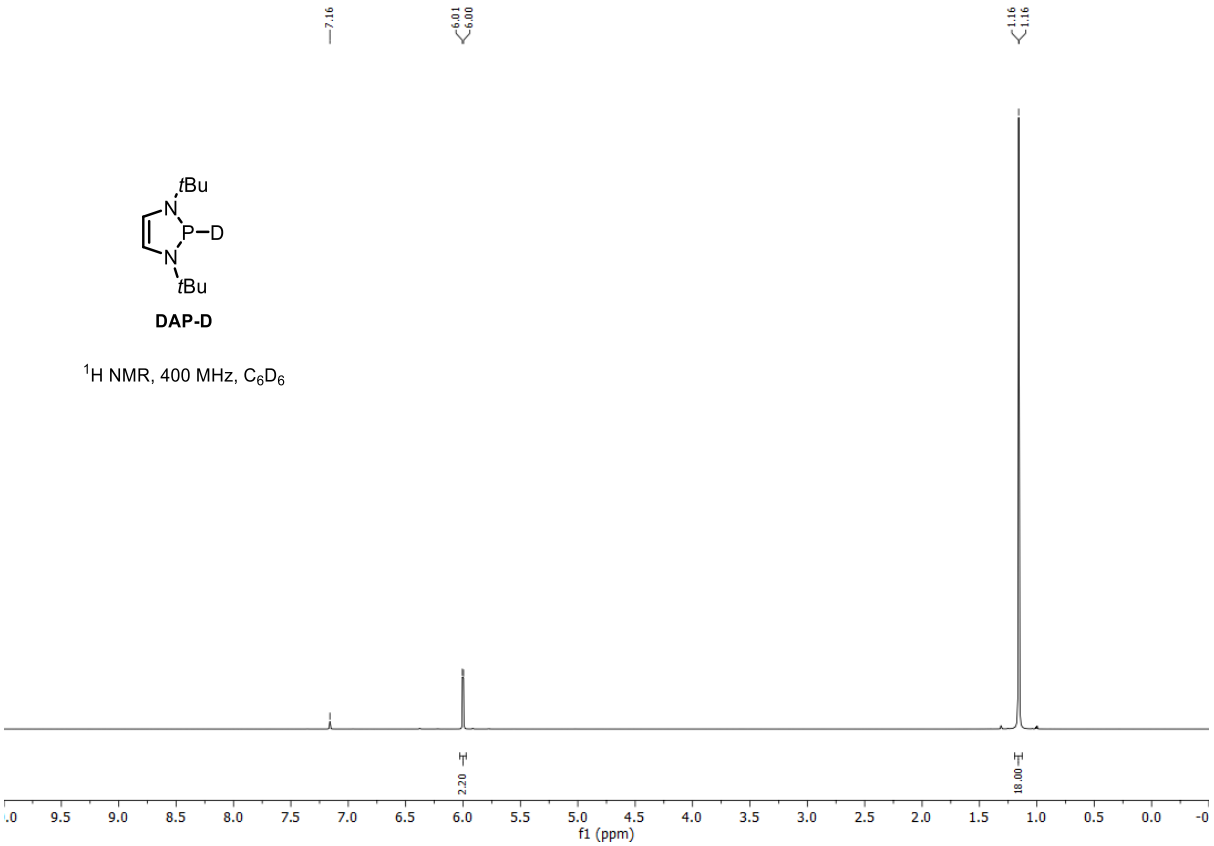
(DAP)$_2$

^{1}H NMR, 400 MHz, CD_3CN



(DAP)$_2$

^{31}P NMR, 162 MHz, CD_3CN



DAP-D

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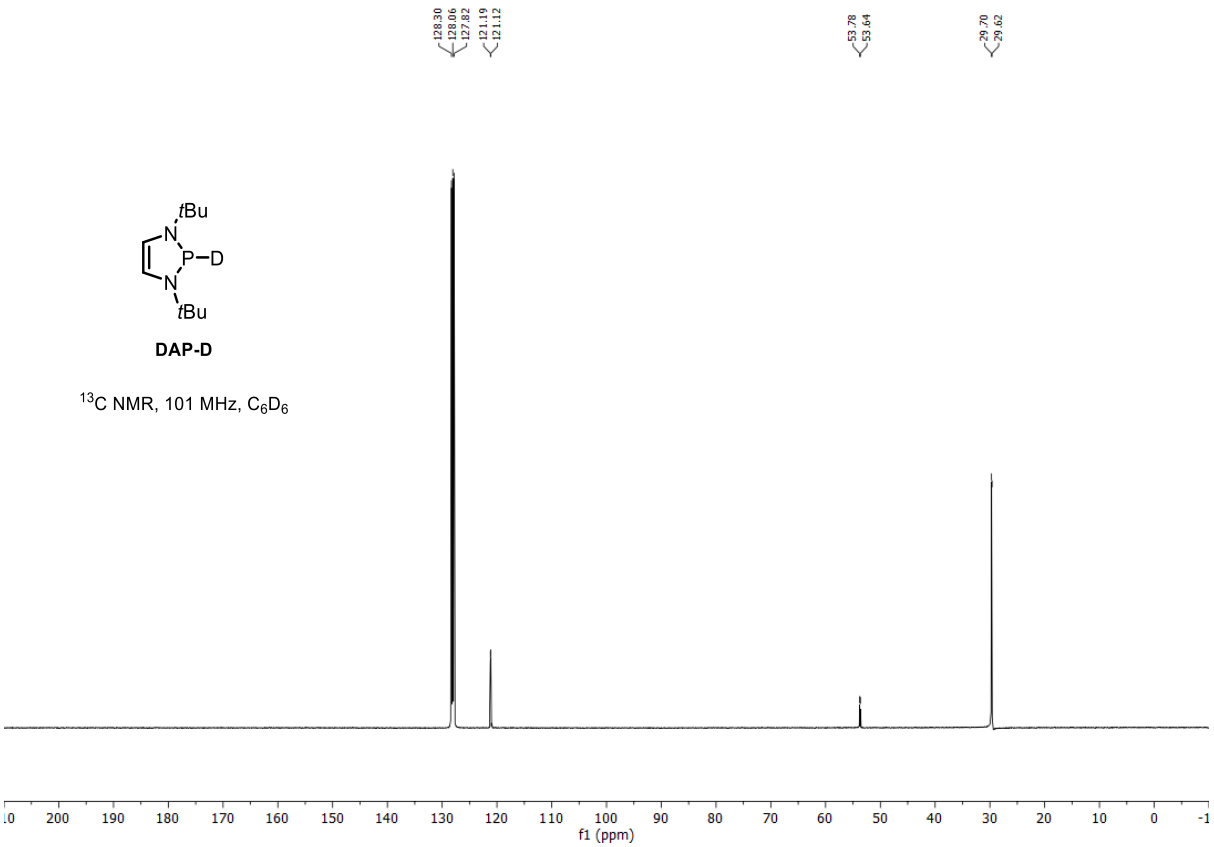
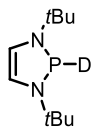


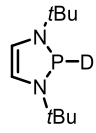
DAP-D

^{13}C NMR, 101 MHz, C_6D_6



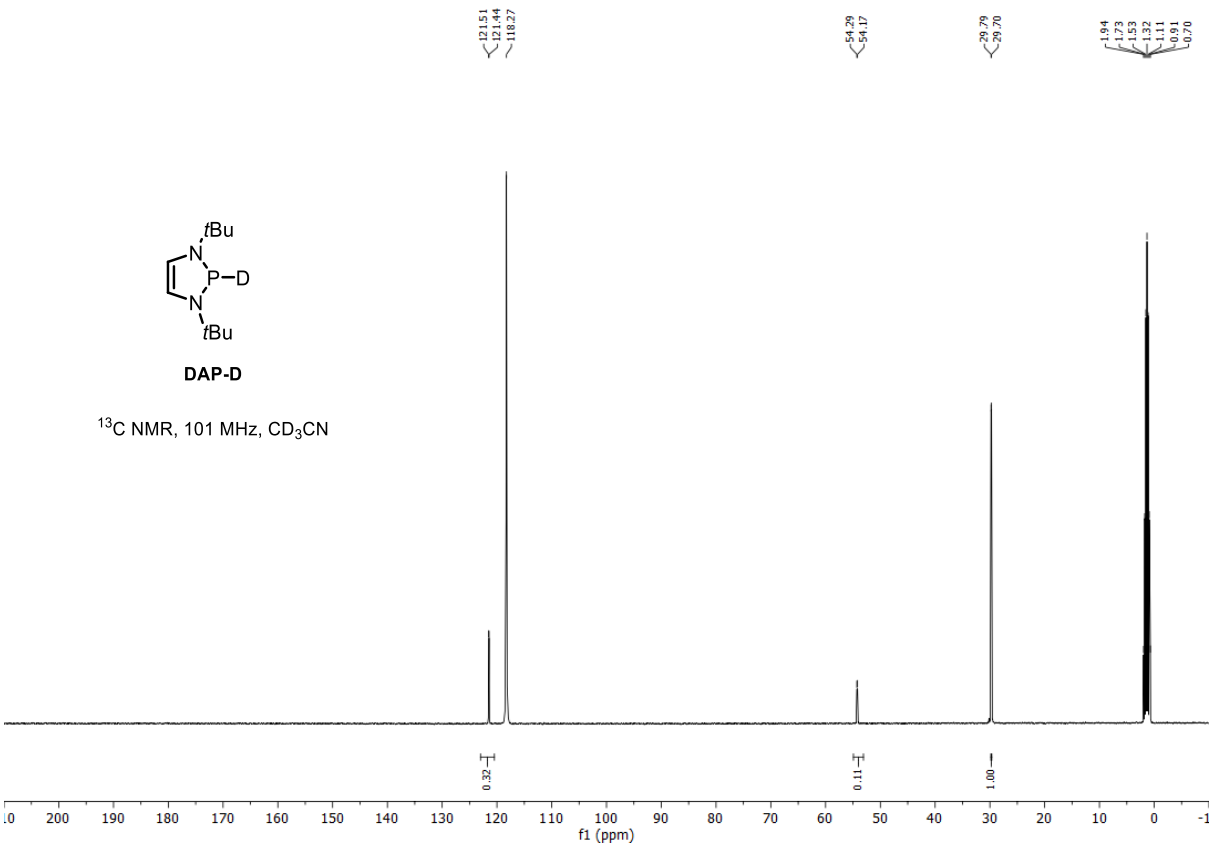
DAP-D

^{31}P NMR, 162 MHz, C_6D_6



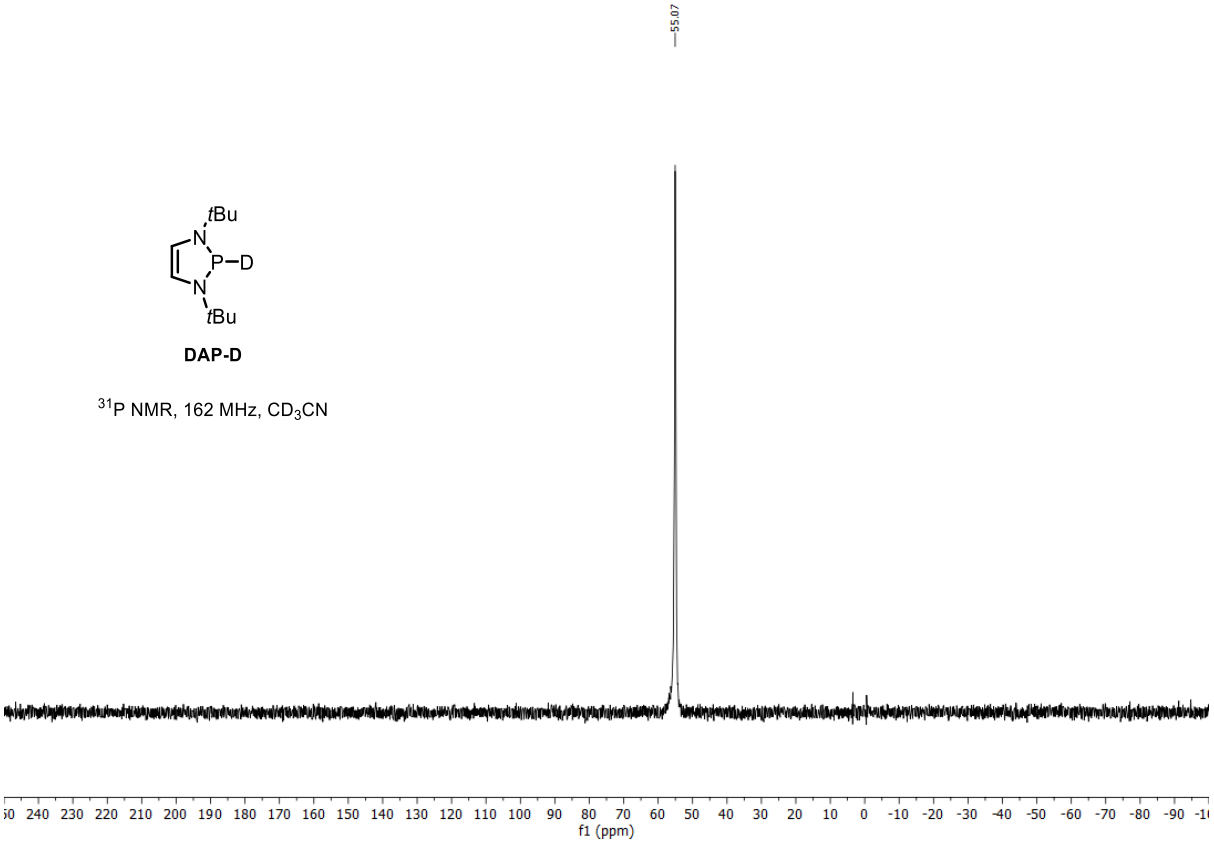
DAP-D

^{1}H NMR, 400 MHz, CD_3CN



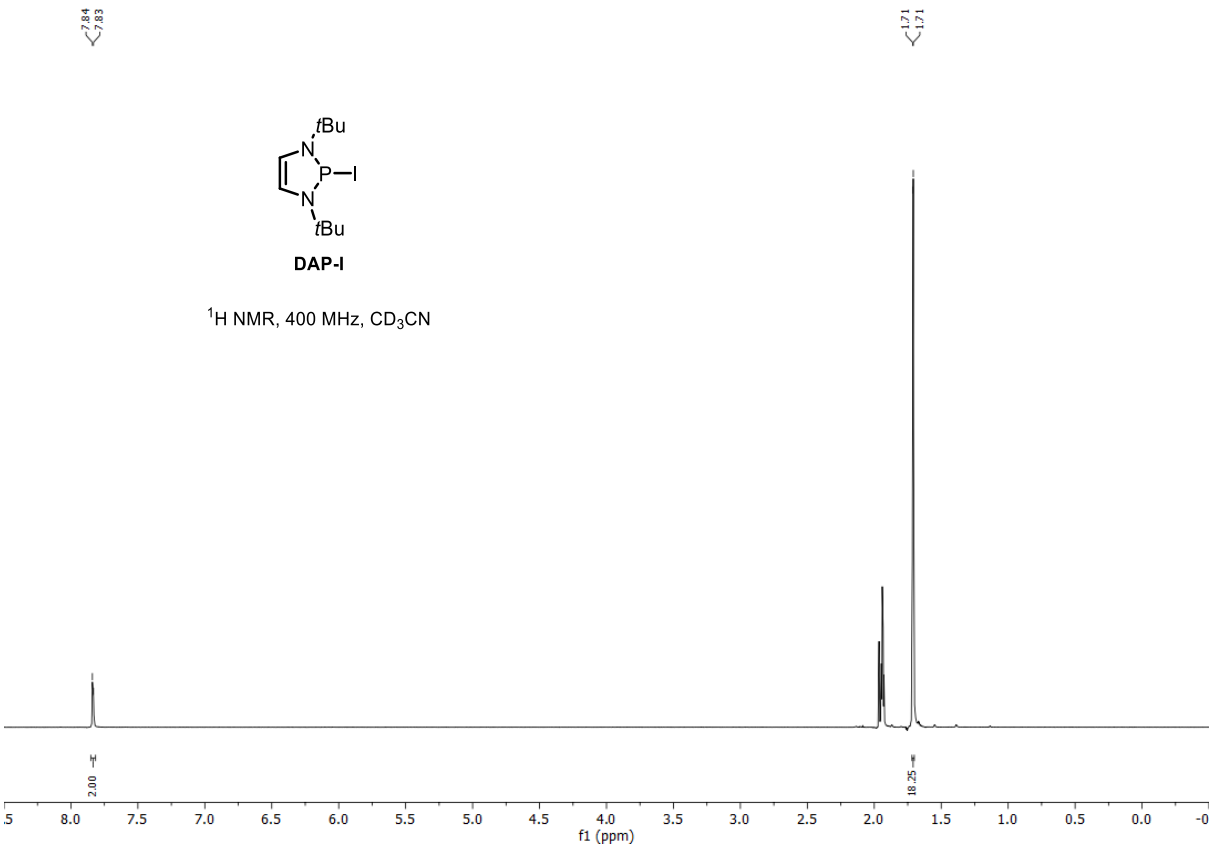
DAP-D

^{13}C NMR, 101 MHz, CD_3CN



DAP-D

^{31}P NMR, 162 MHz, CD_3CN



DAP-I

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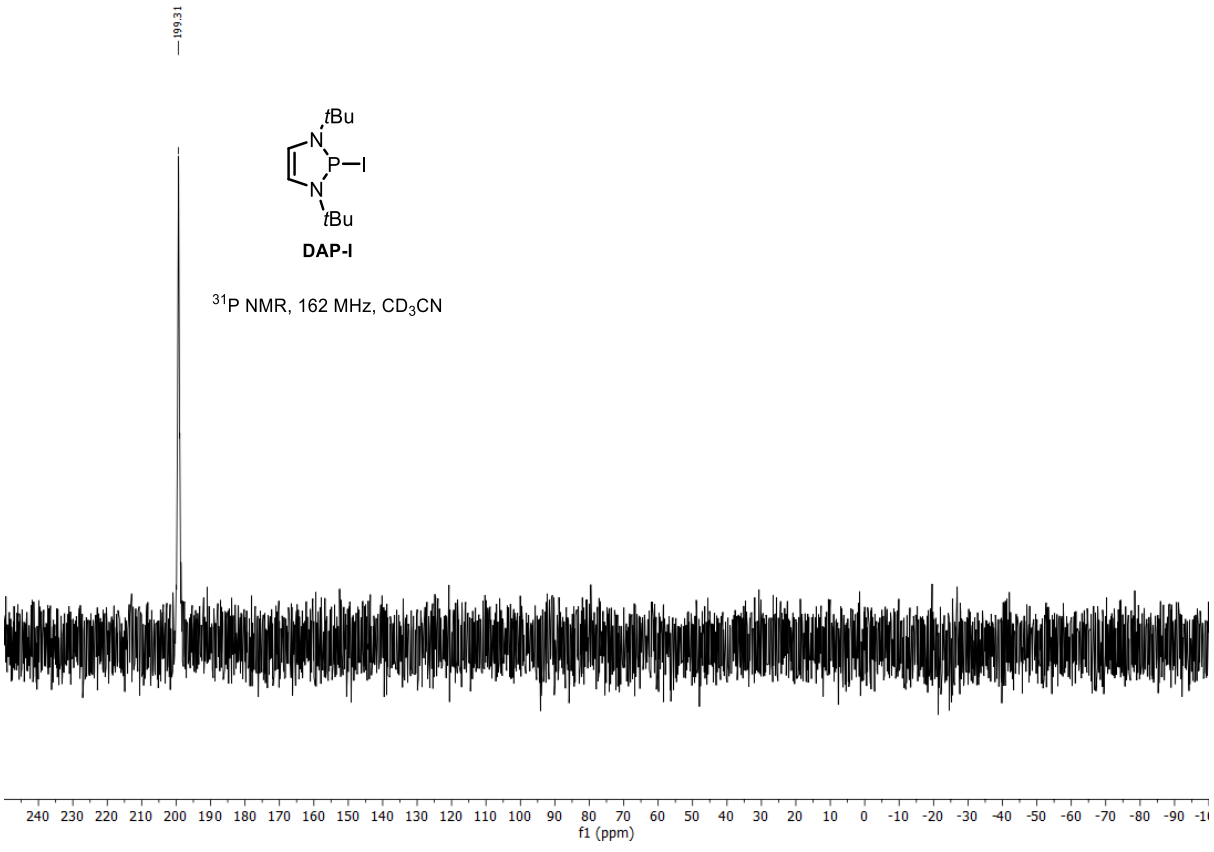
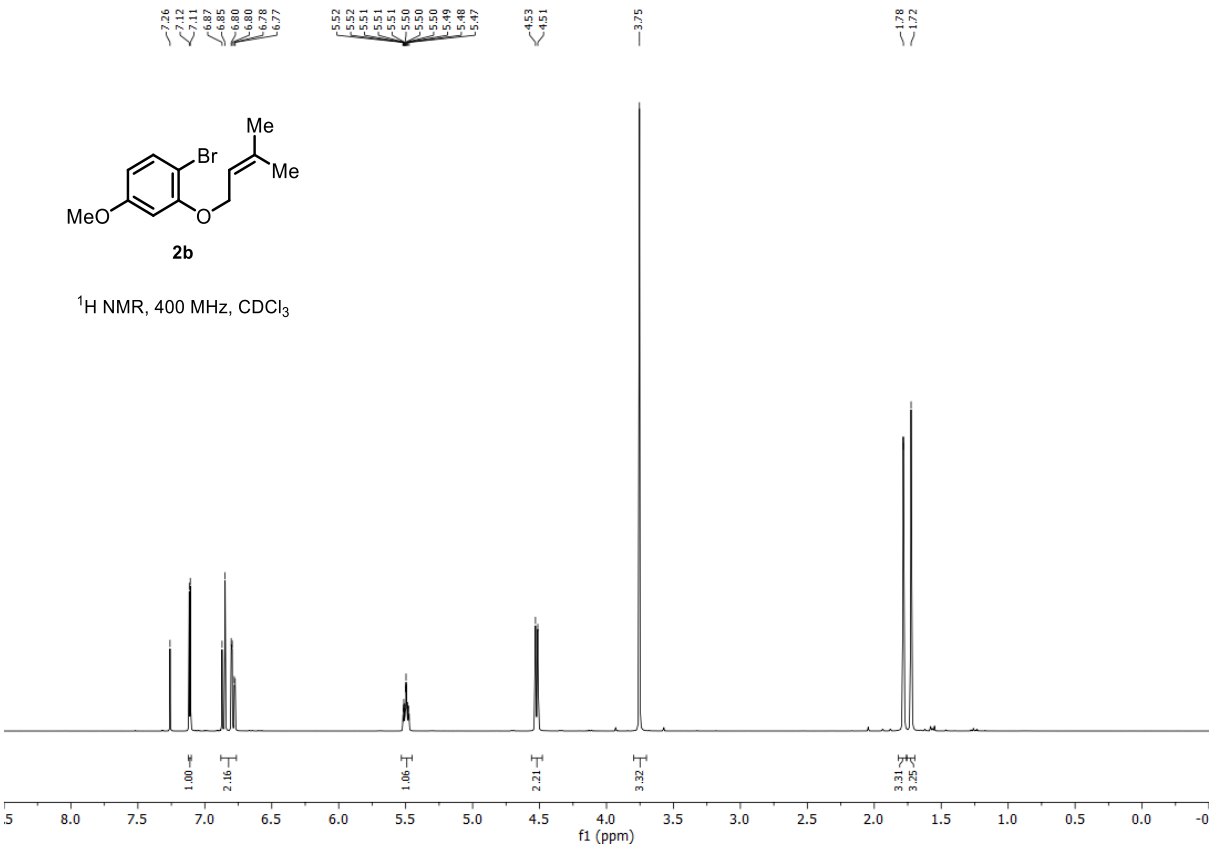
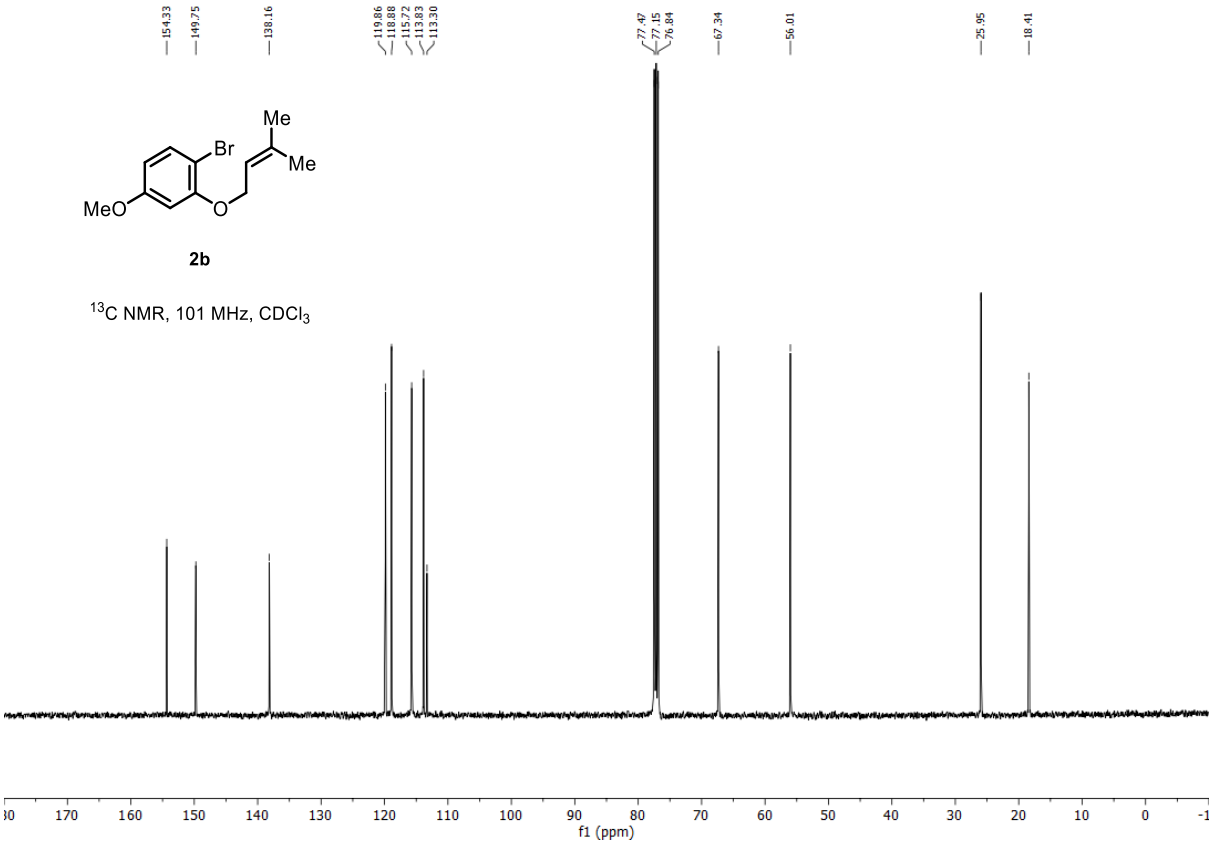
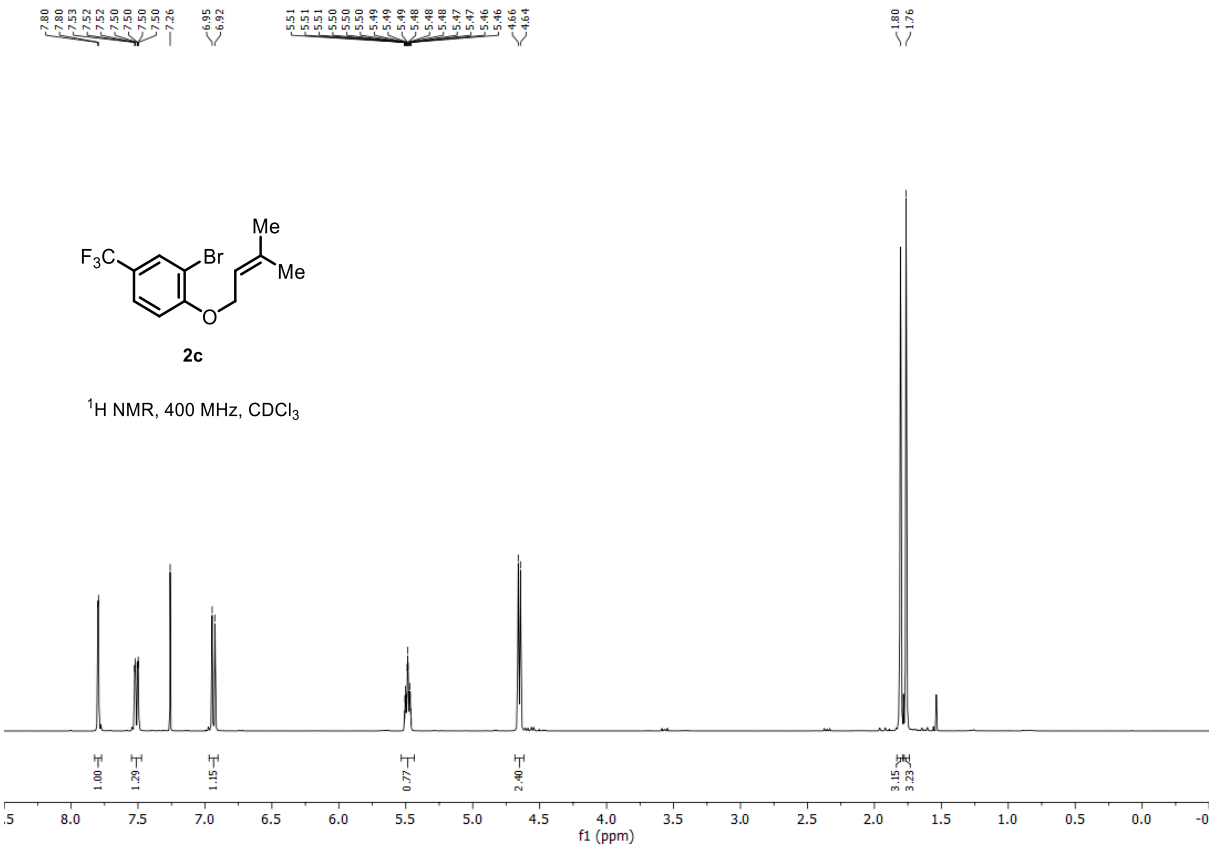


DAP-I

^{31}P NMR, 162 MHz, CD_3CN

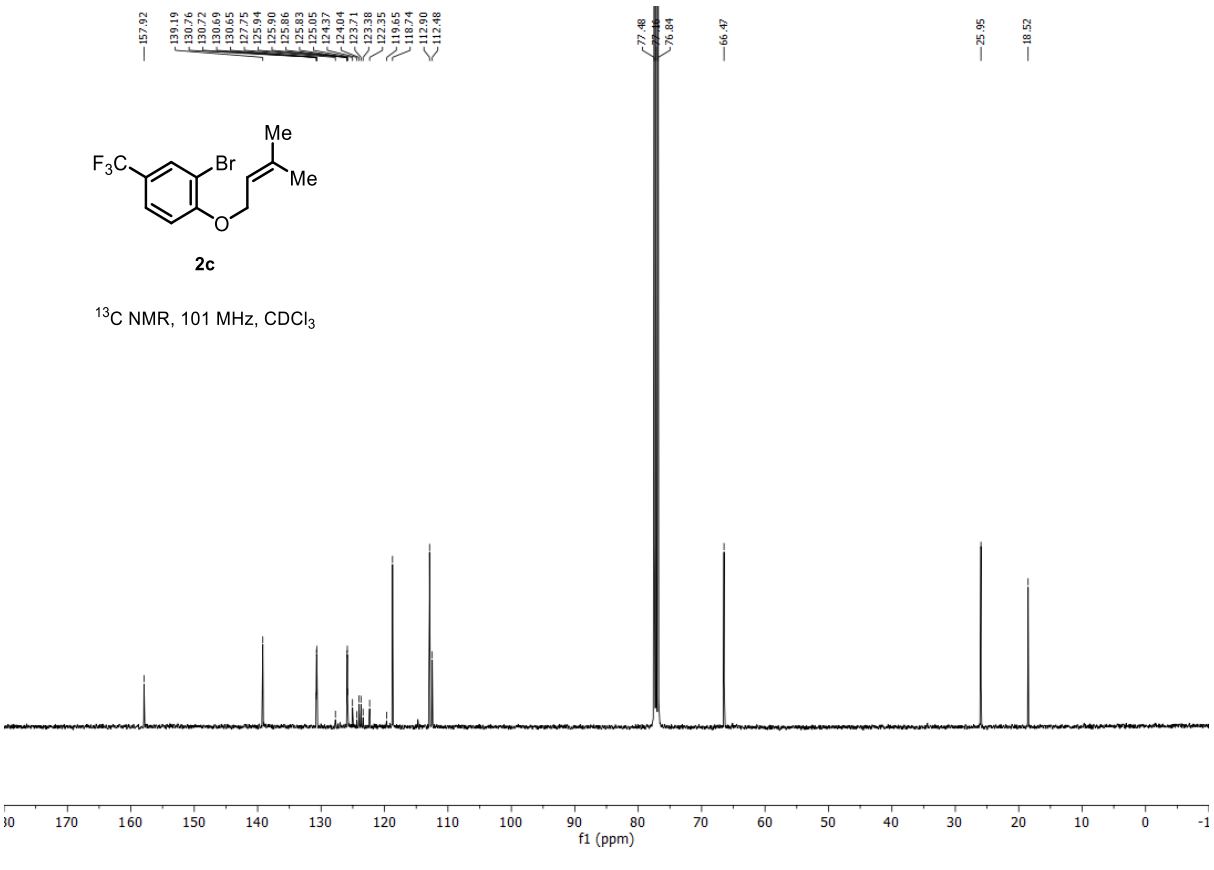

Me
Br
Me
MeO
O
2b
1H NMR, 400 MHz, CDCl3
f1 (ppm)


Me
Br
Me
MeO
O
2b
13C NMR, 101 MHz, CDCl3
f1 (ppm)



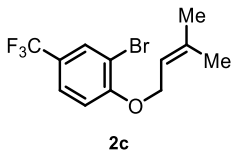
2c

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



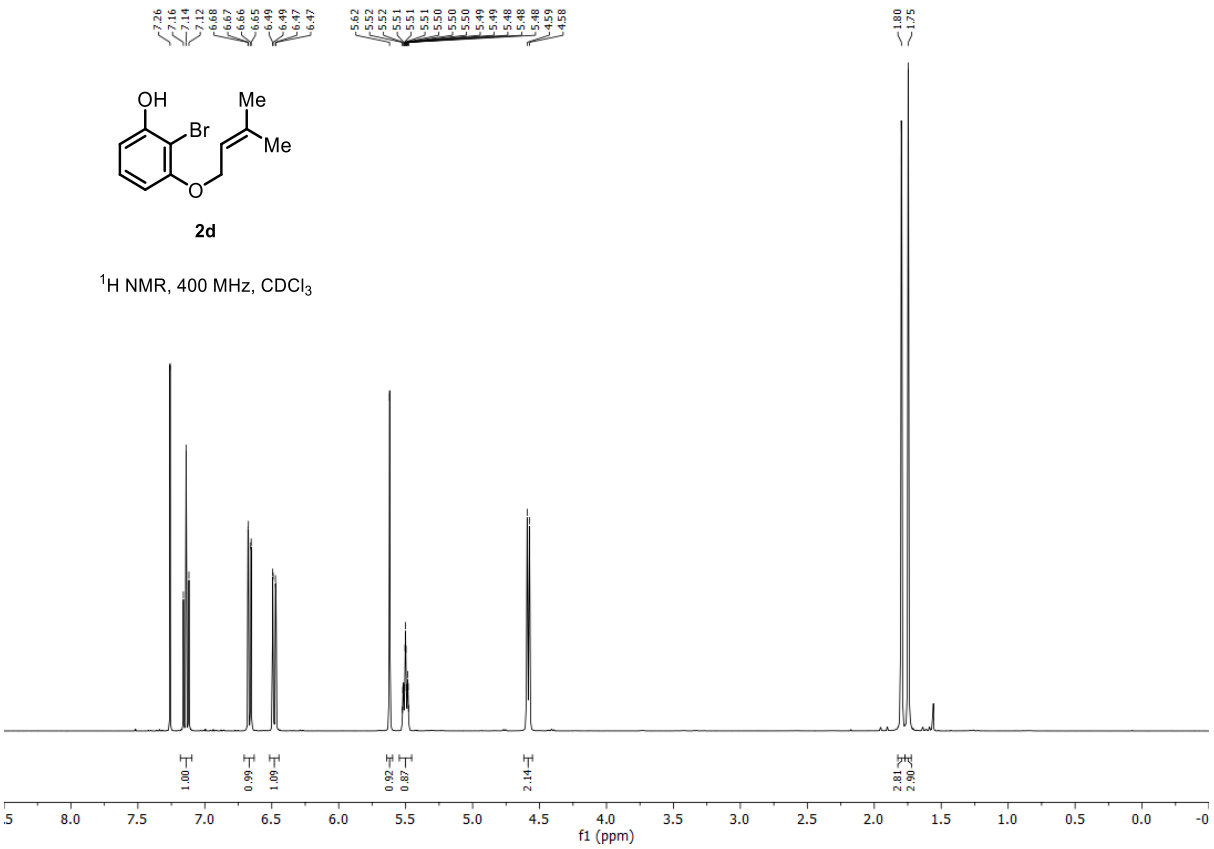
2c

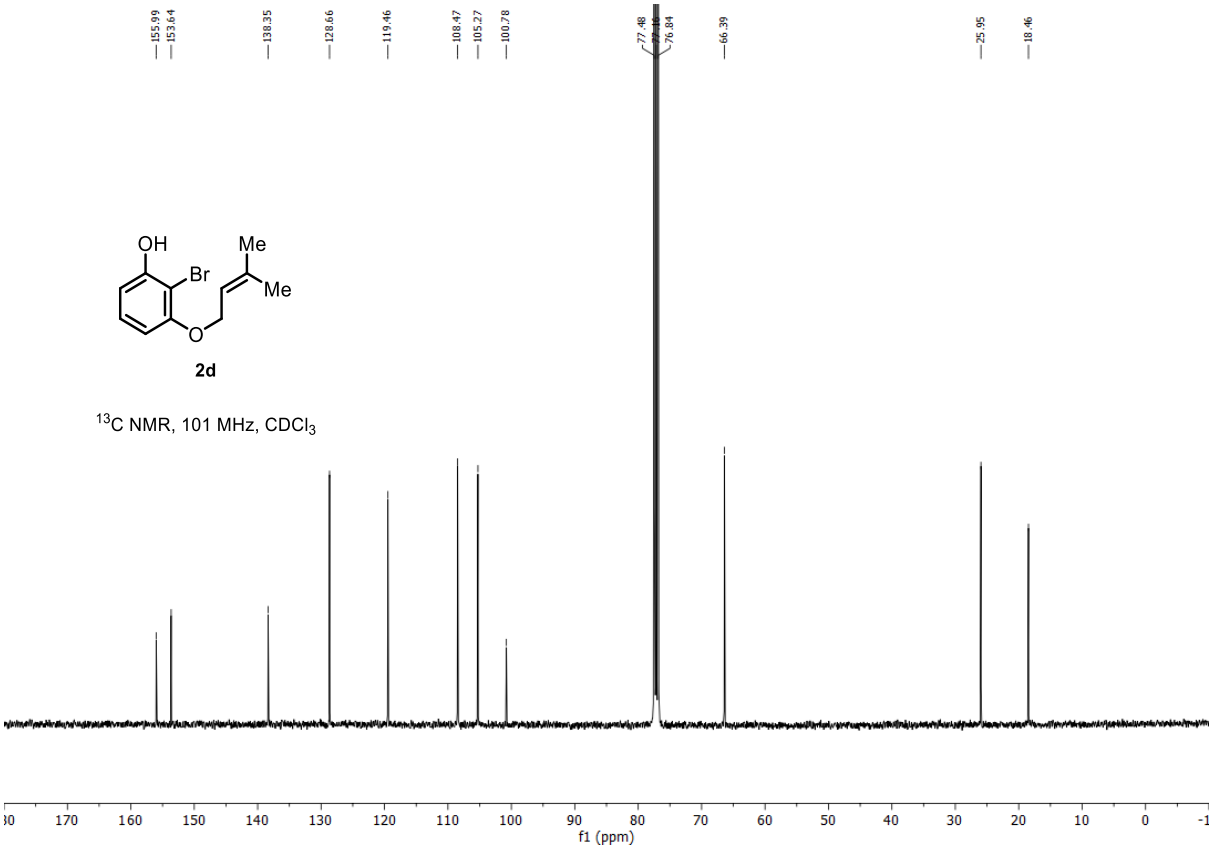
^{13}C NMR, 101 MHz, $CDCl_3$

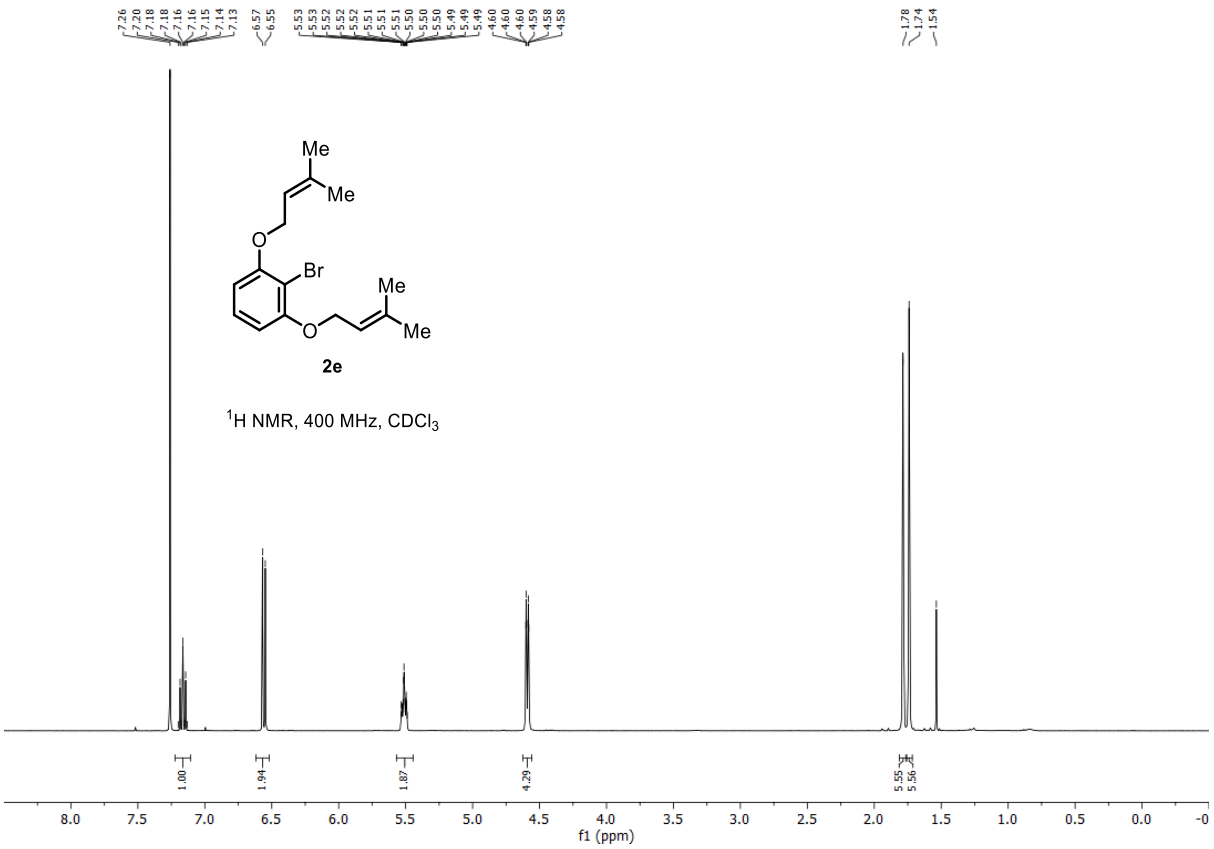


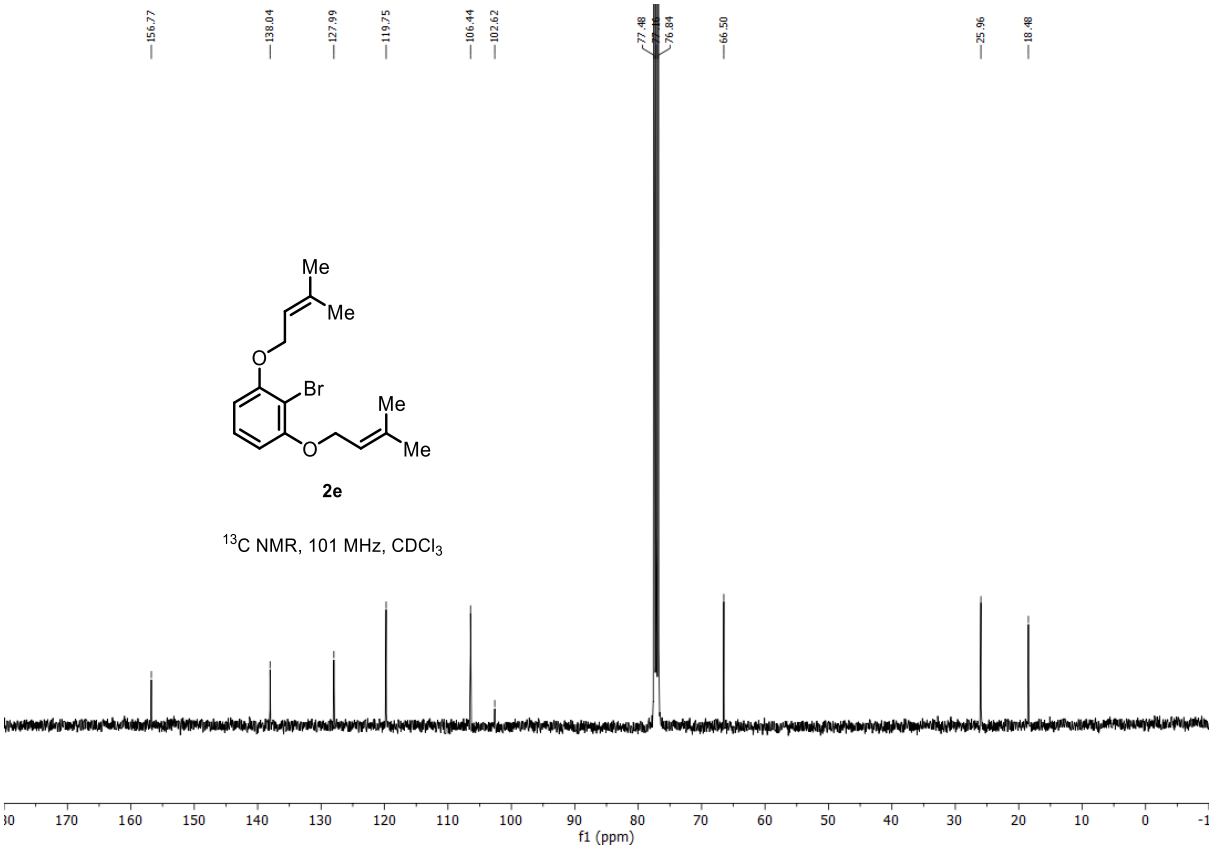
2c

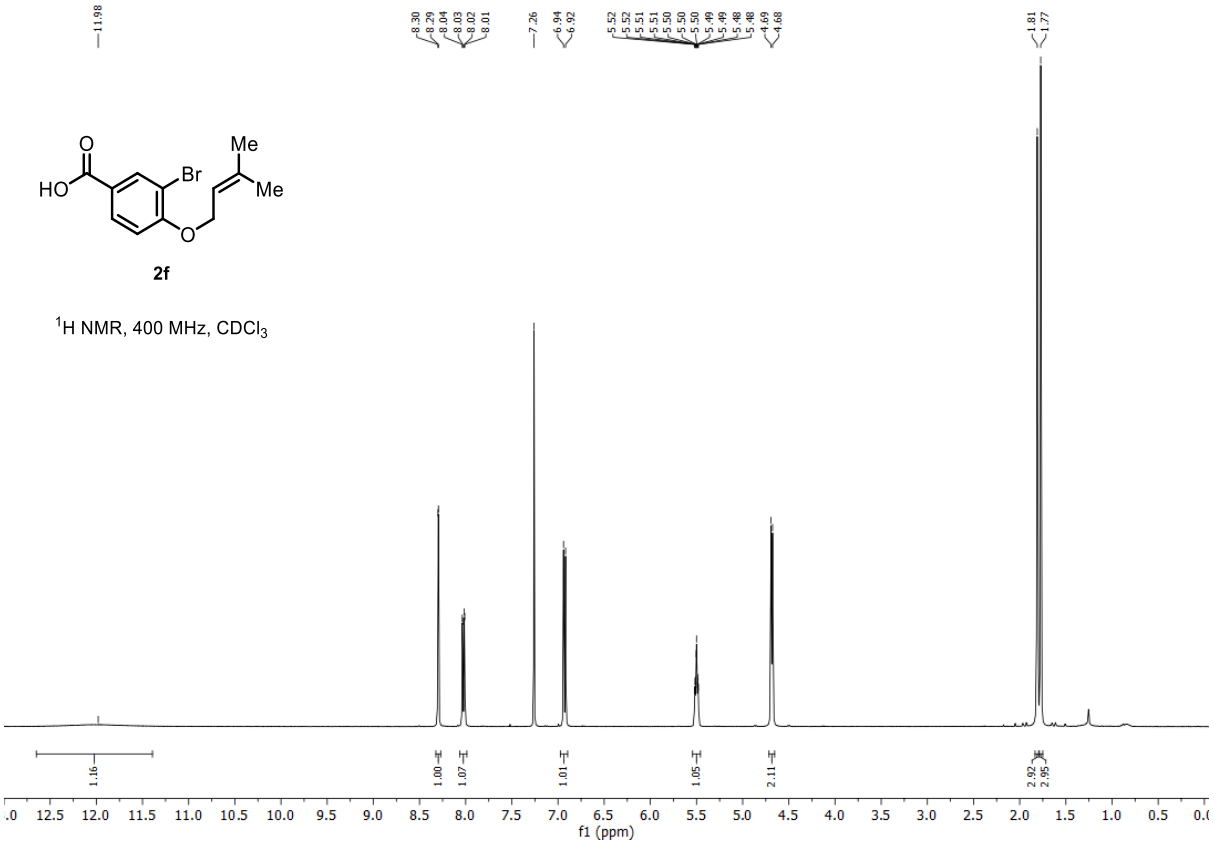
^{19}F NMR, 376 MHz, $CDCl_3$


OH
Br
O
Me
Me
2d
1H NMR, 400 MHz, CDCl3
f1 (ppm)


OH
Br
O
Me
Me
2d
13C NMR, 101 MHz, CDCl3
f1 (ppm)

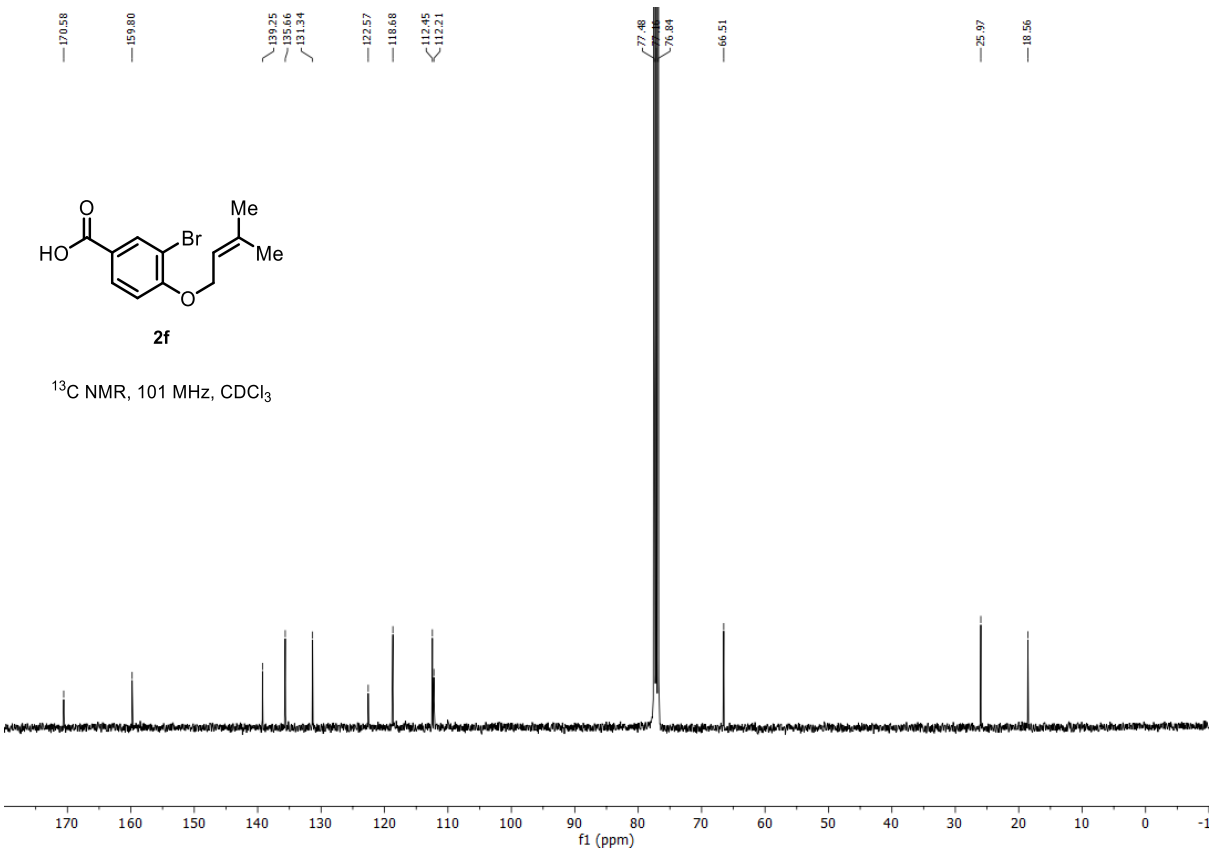

Me
Me
O
Br
Me
O
Me
2e
1H NMR, 400 MHz, CDCl3
f1 (ppm)


Me
Me
O
Br
Me
O
Me
2e
13C NMR, 101 MHz, CDCl3
f1 (ppm)



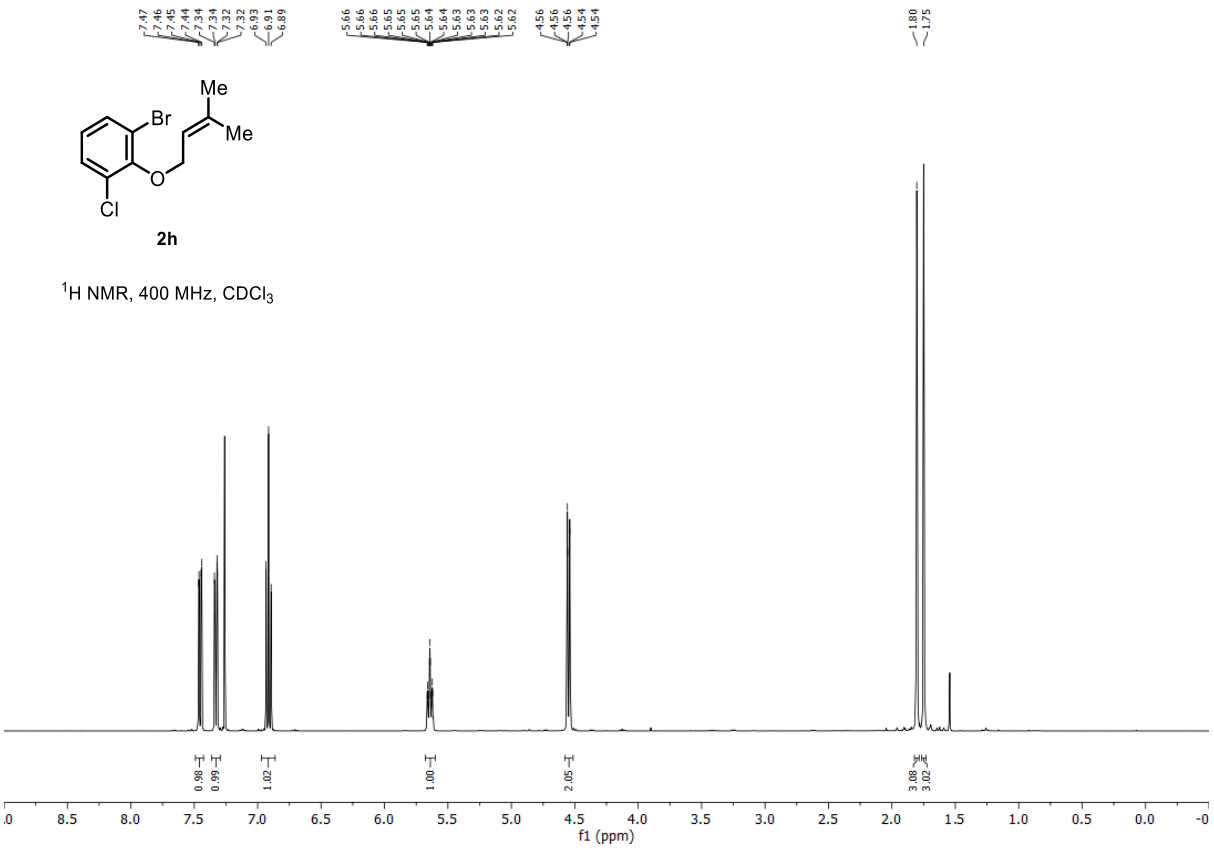
2f

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



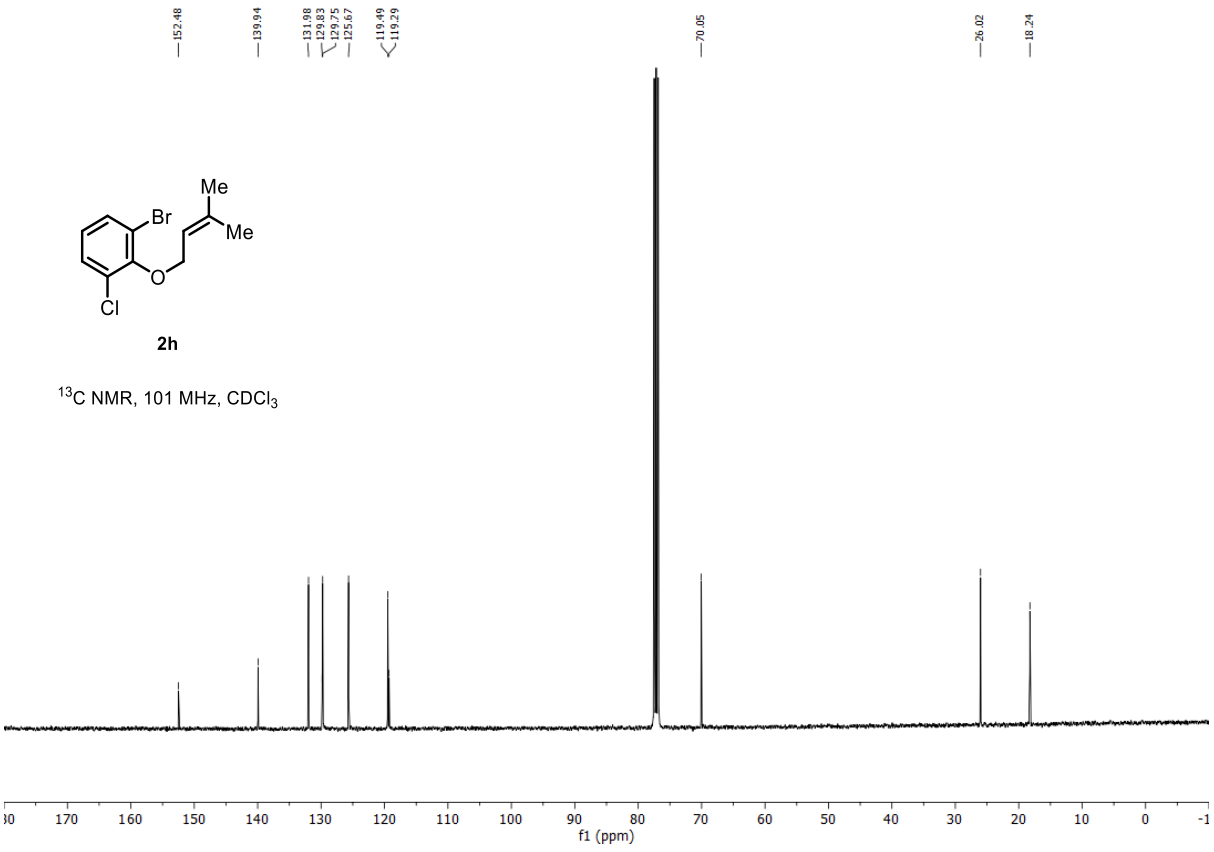
2f

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



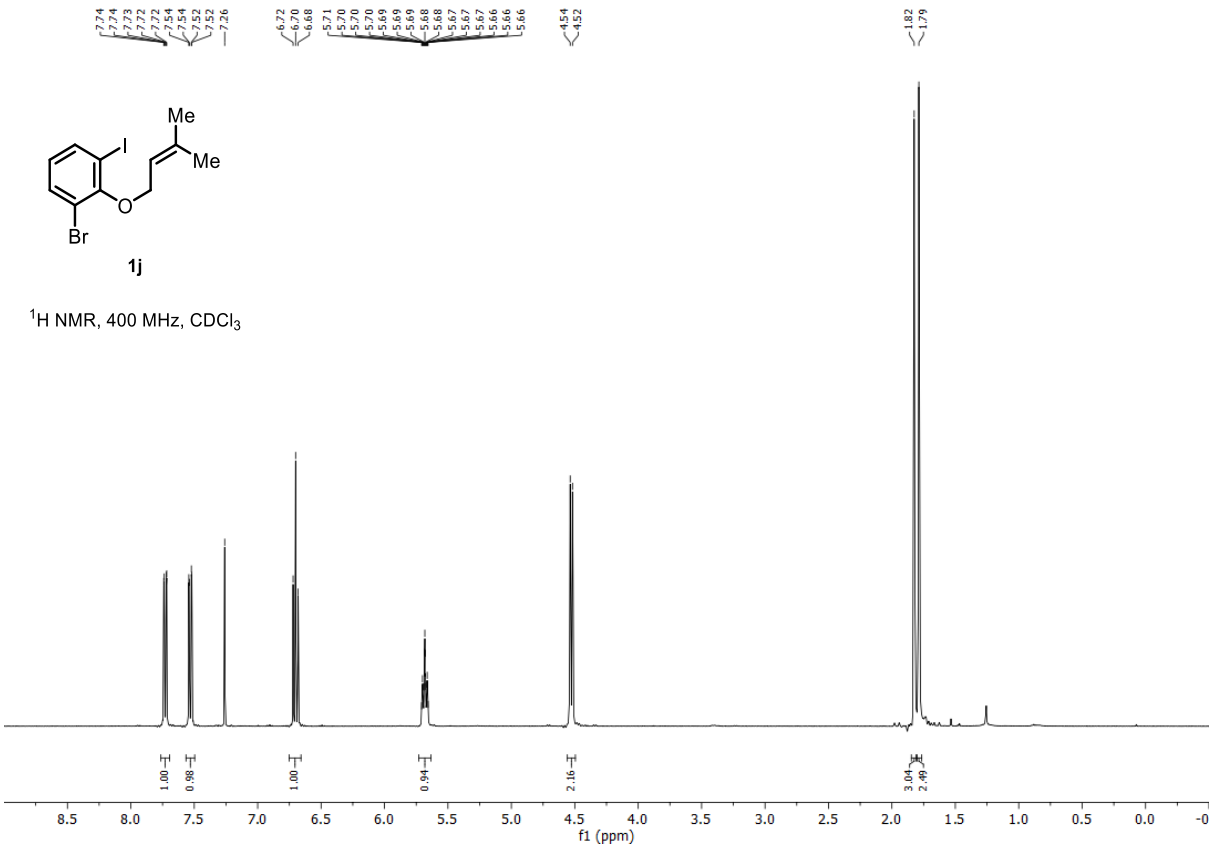
2h

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



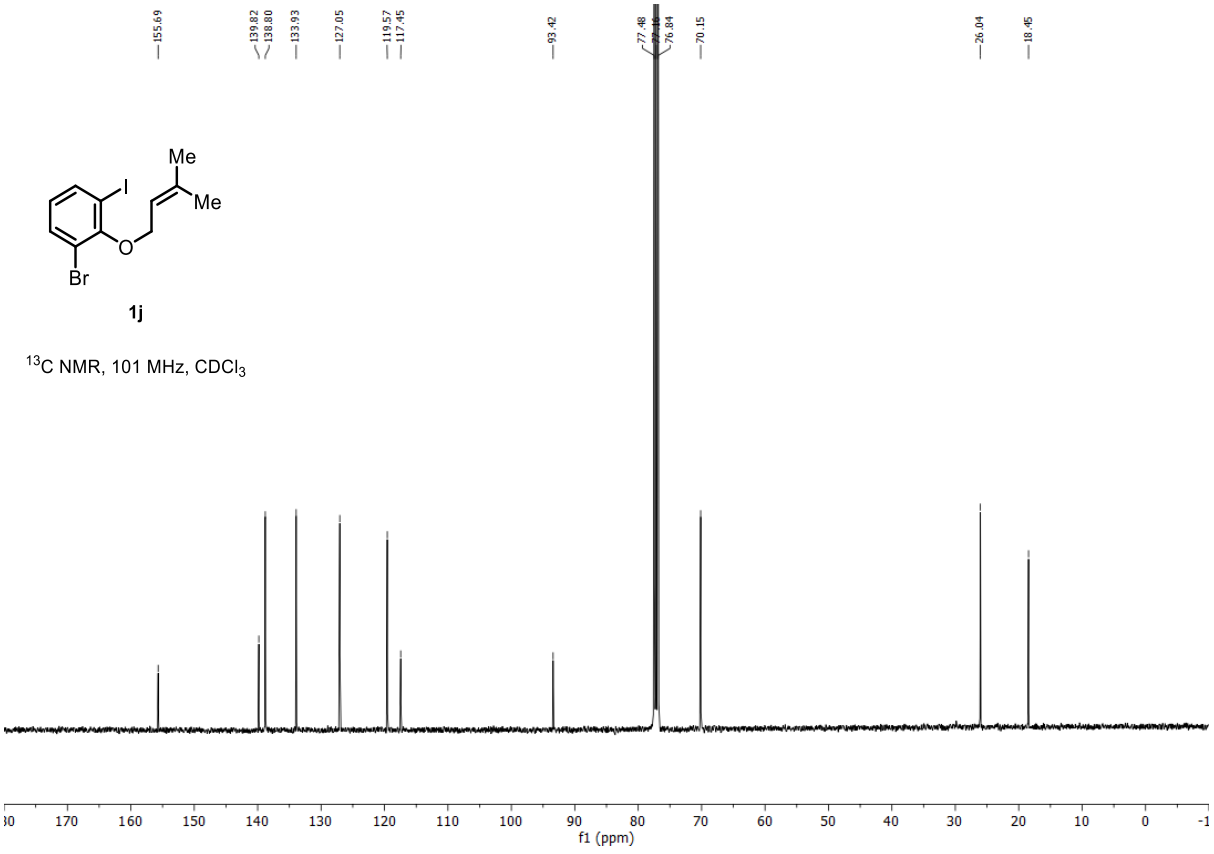
2h

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



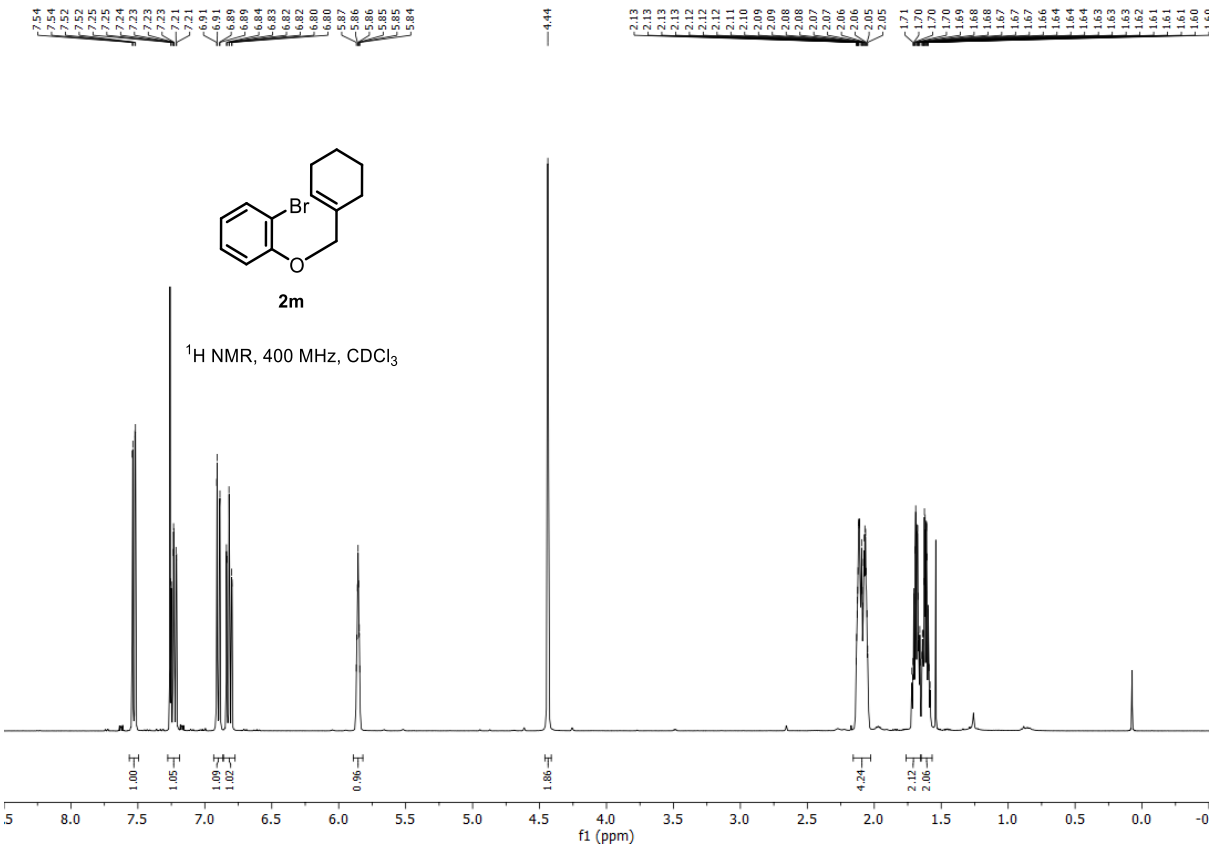
1j

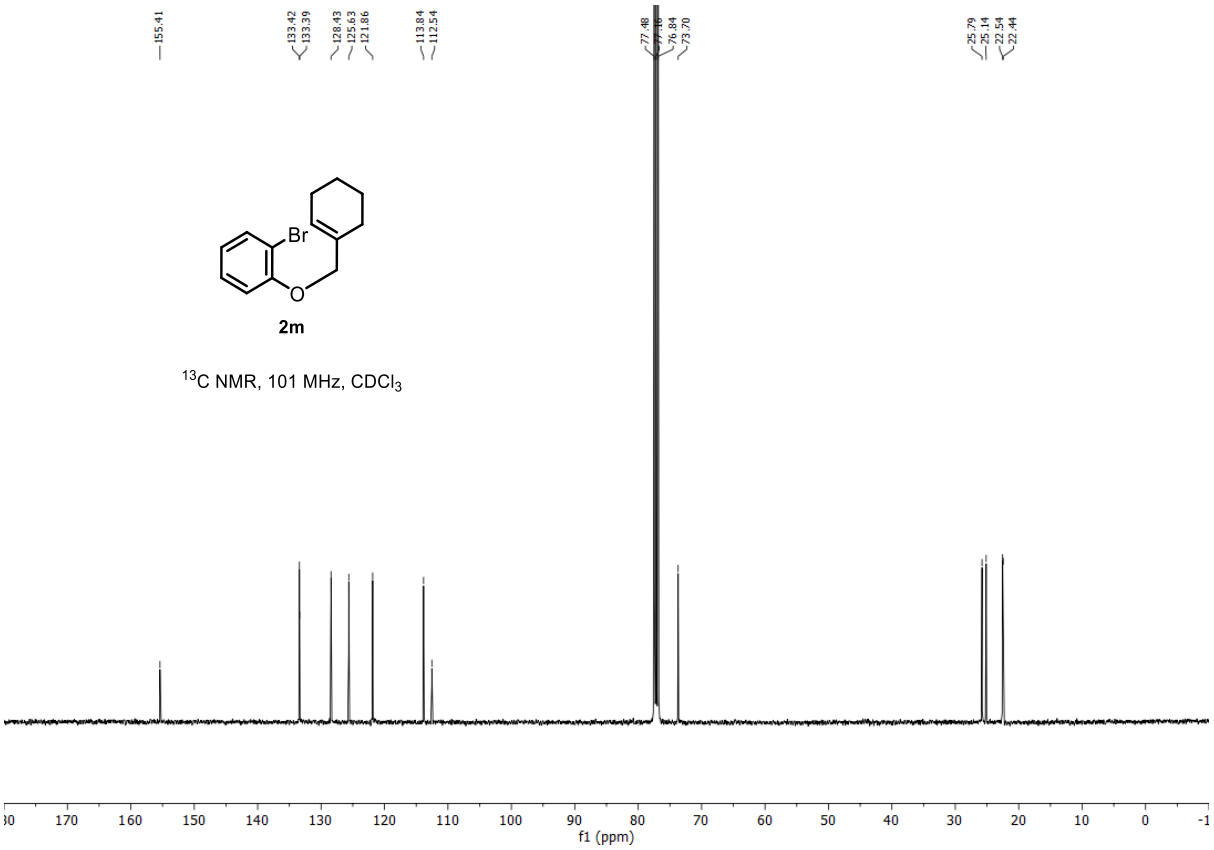
^{1}H NMR, 400 MHz, $CDCl_3$

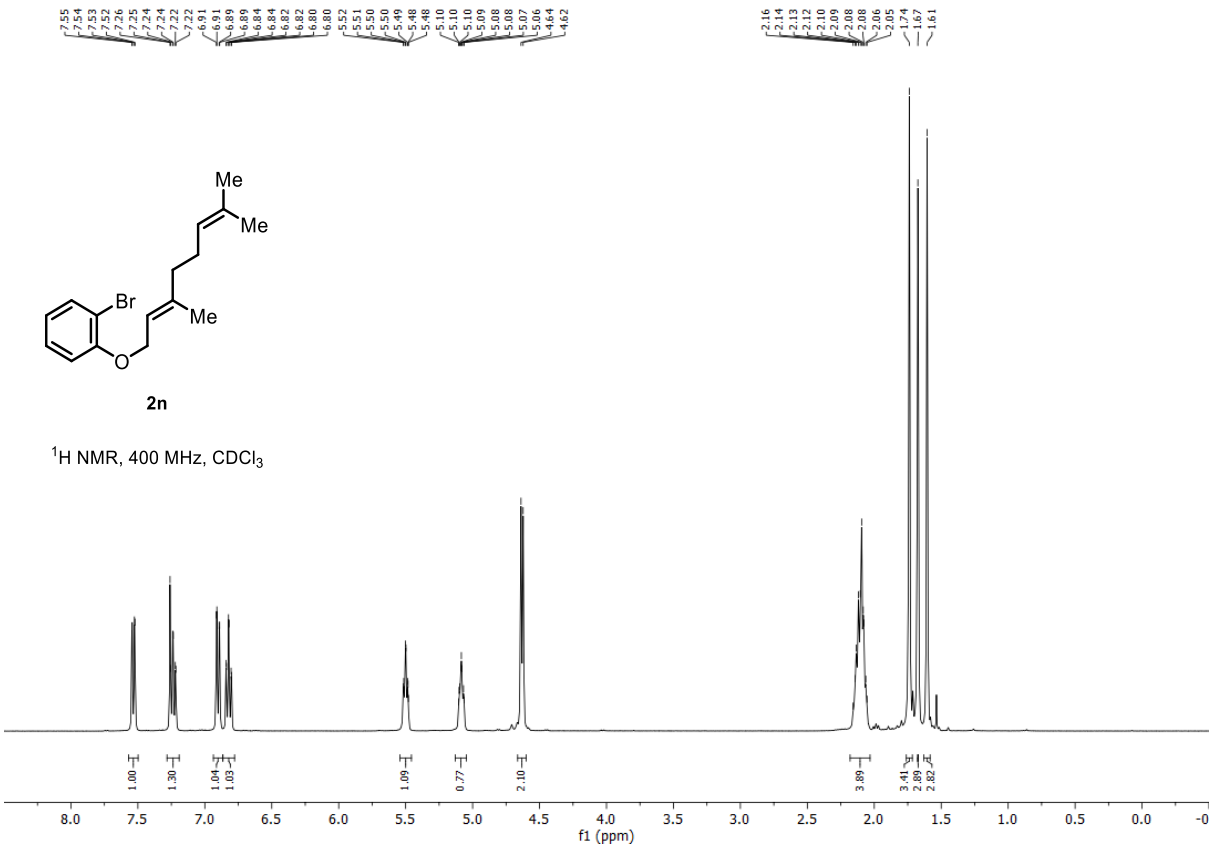


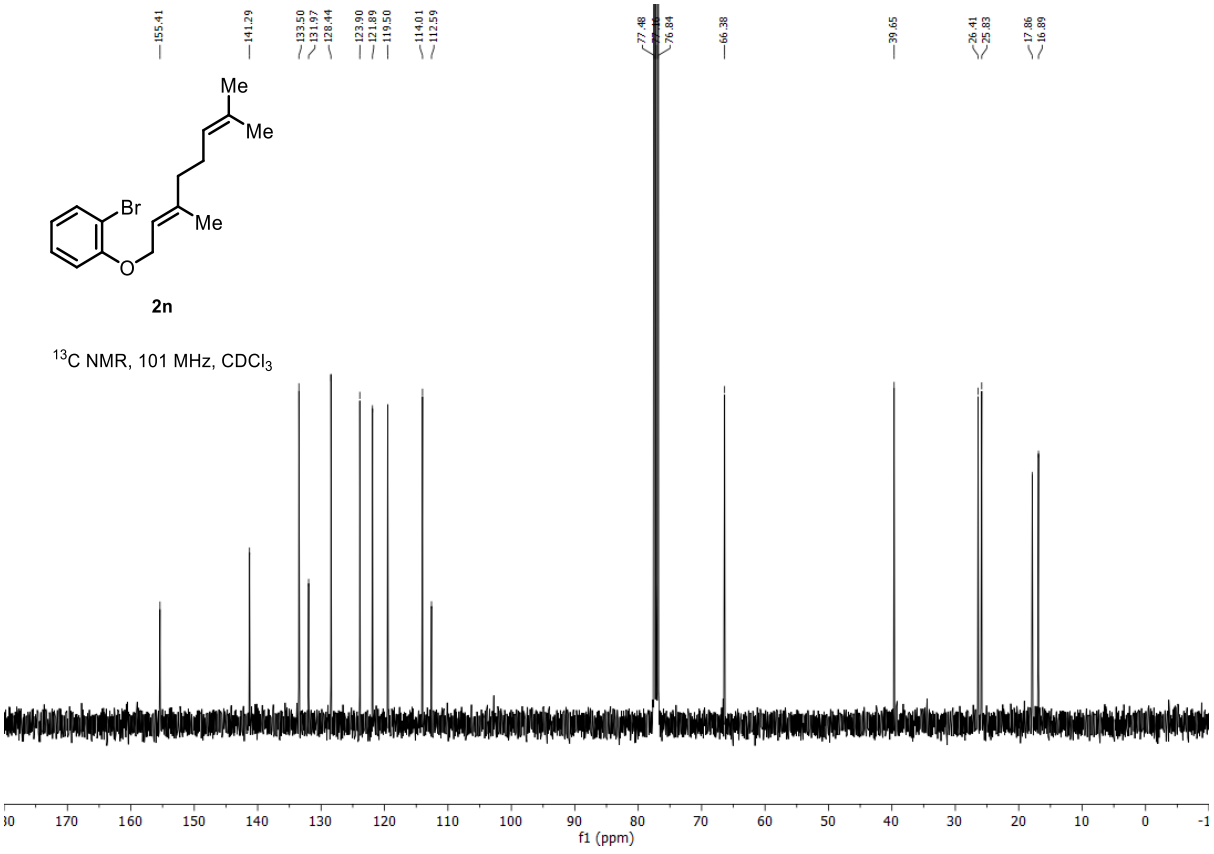
1j

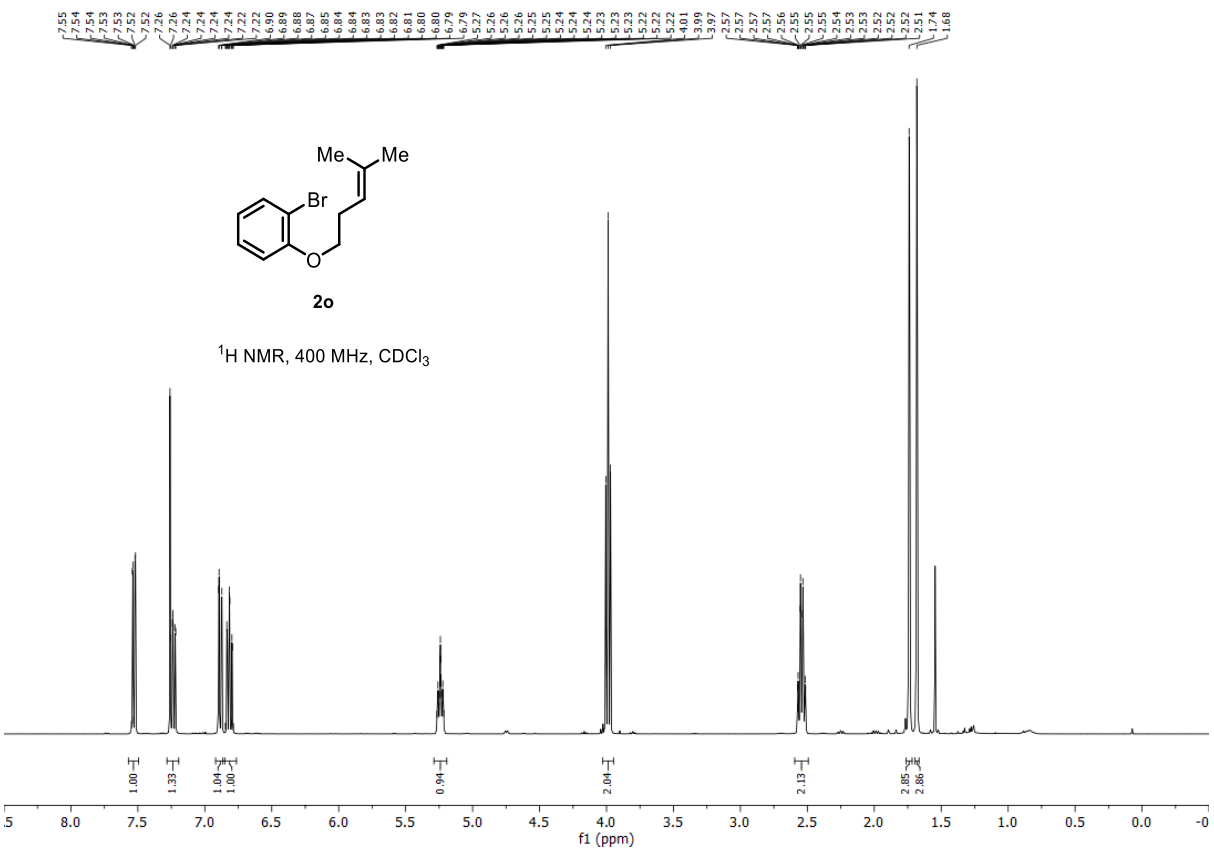
^{13}C NMR, 101 MHz, $CDCl_3$

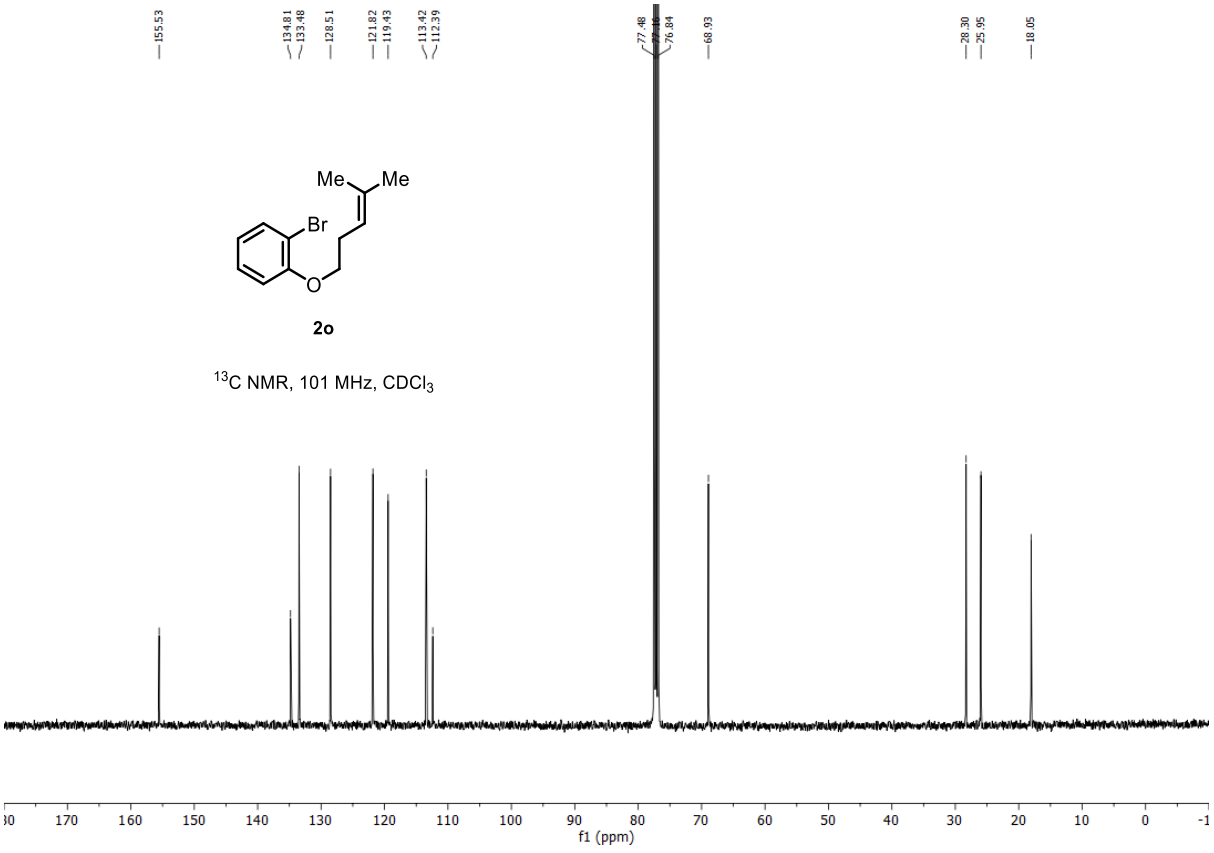

Br
O
2m
1H NMR, 400 MHz, CDCl3
1.00
1.05
1.09
1.02
0.96
1.86
4.24
2.12
2.06
f1 (ppm)

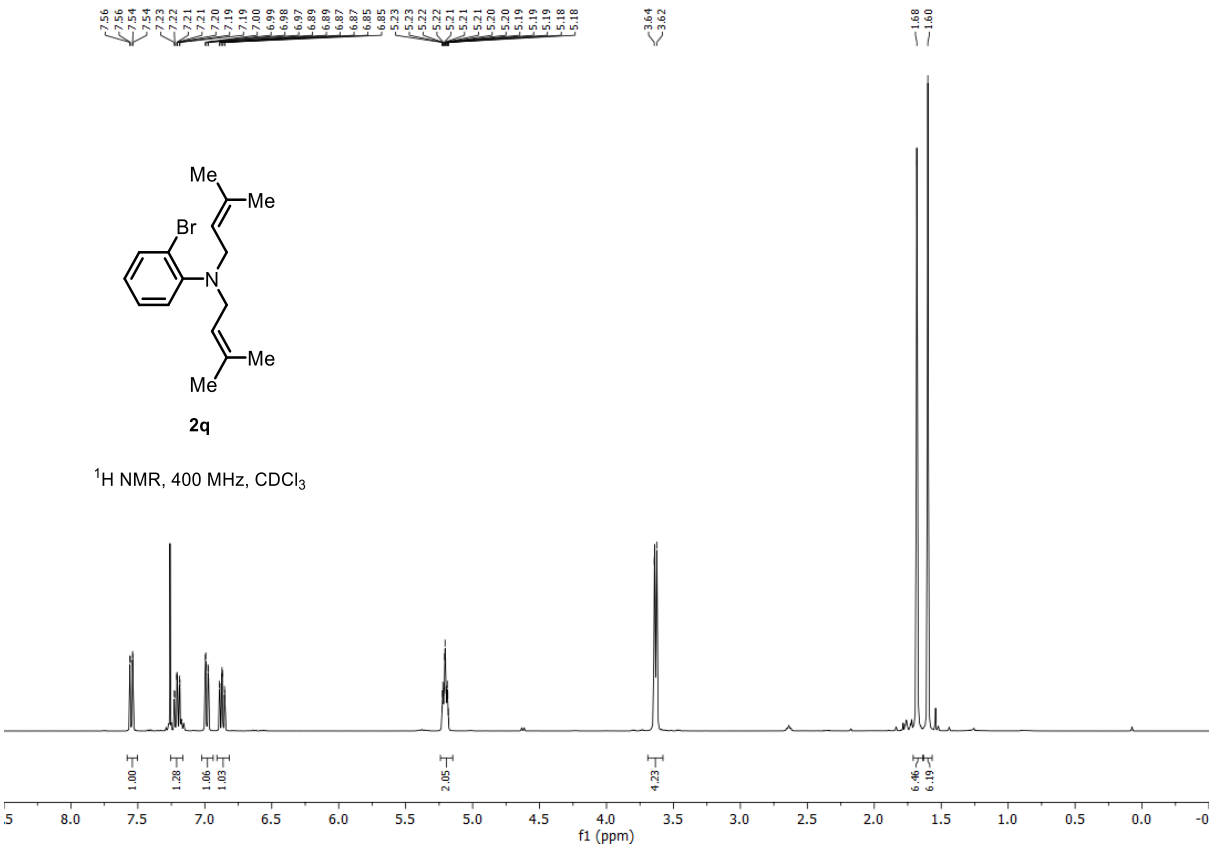

155.41
133.42
133.39
128.43
125.63
121.86
113.84
112.54
77.48
77.16
76.84
73.70
25.79
25.14
22.54
22.44
Br
O
2m
13C NMR, 101 MHz, CDCl3
f1 (ppm)

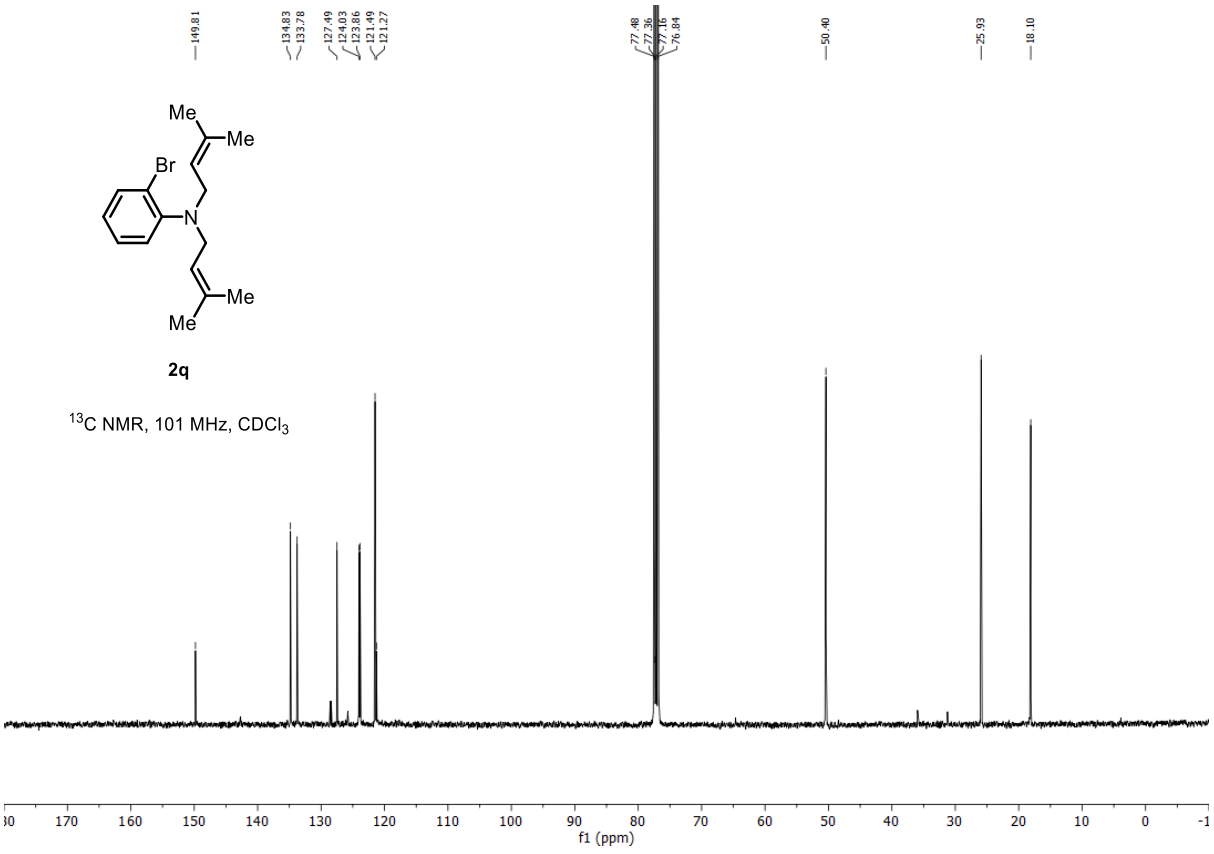

Me
Me
Br
Me
O
2n
1H NMR, 400 MHz, CDCl3
f1 (ppm)

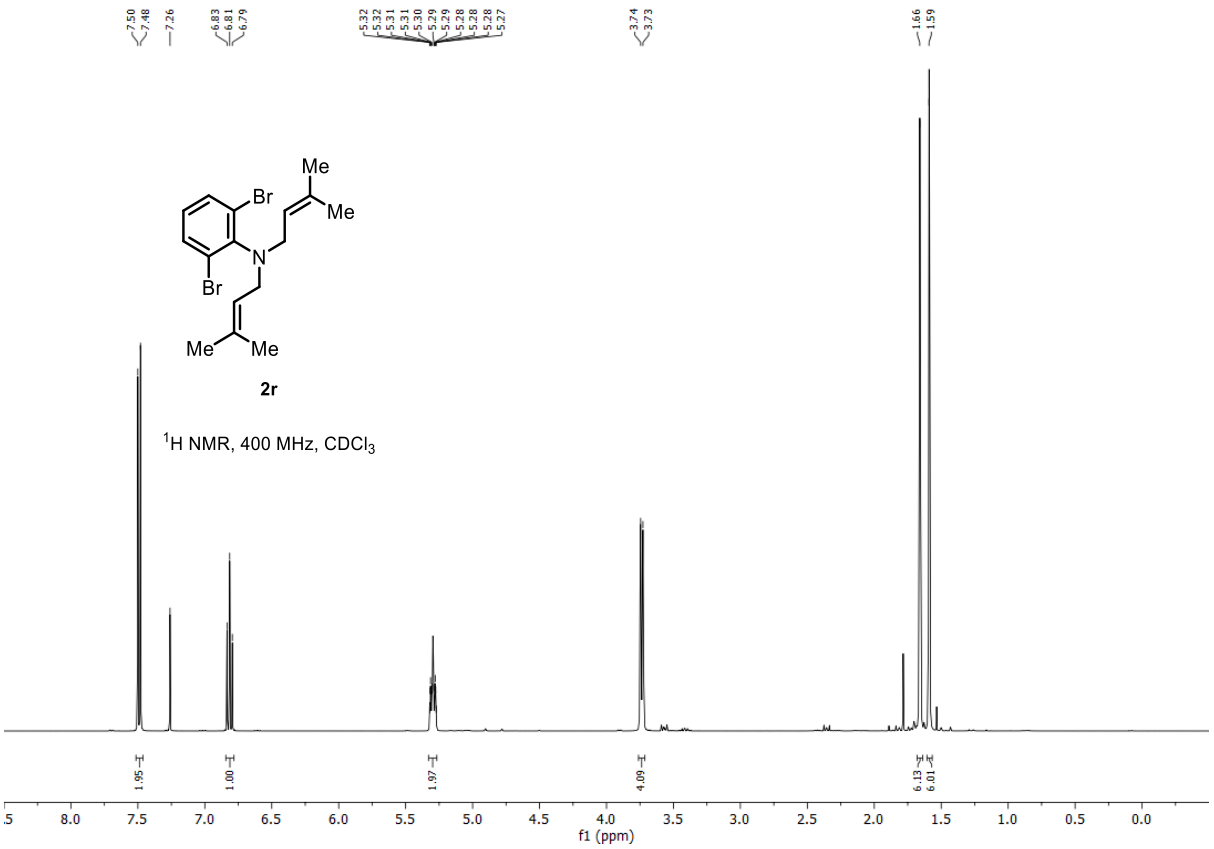

Me
Me
Br
Me
O
2n
13C NMR, 101 MHz, CDCl3
f1 (ppm)

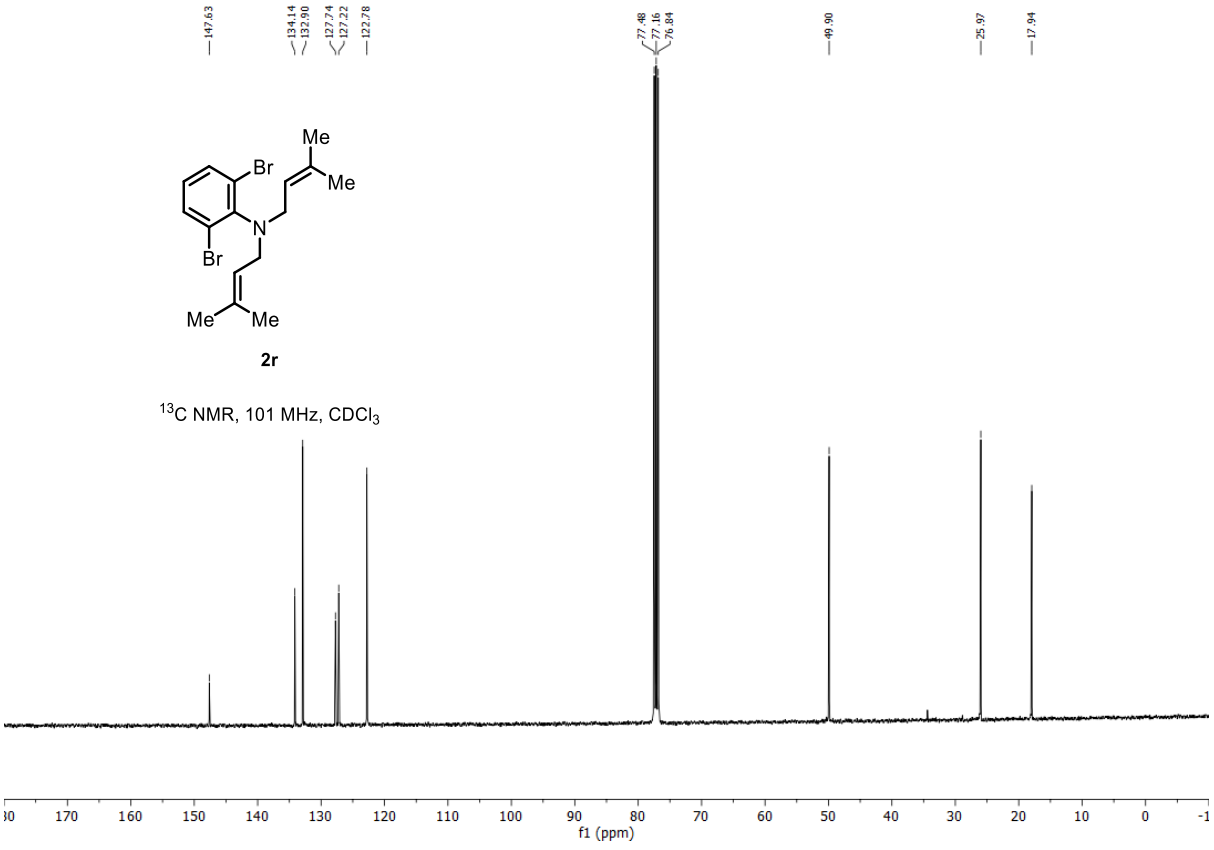

Me
Me
Br
O
2o
^{1}H NMR, 400 MHz, $CDCl_3$
f1 (ppm)

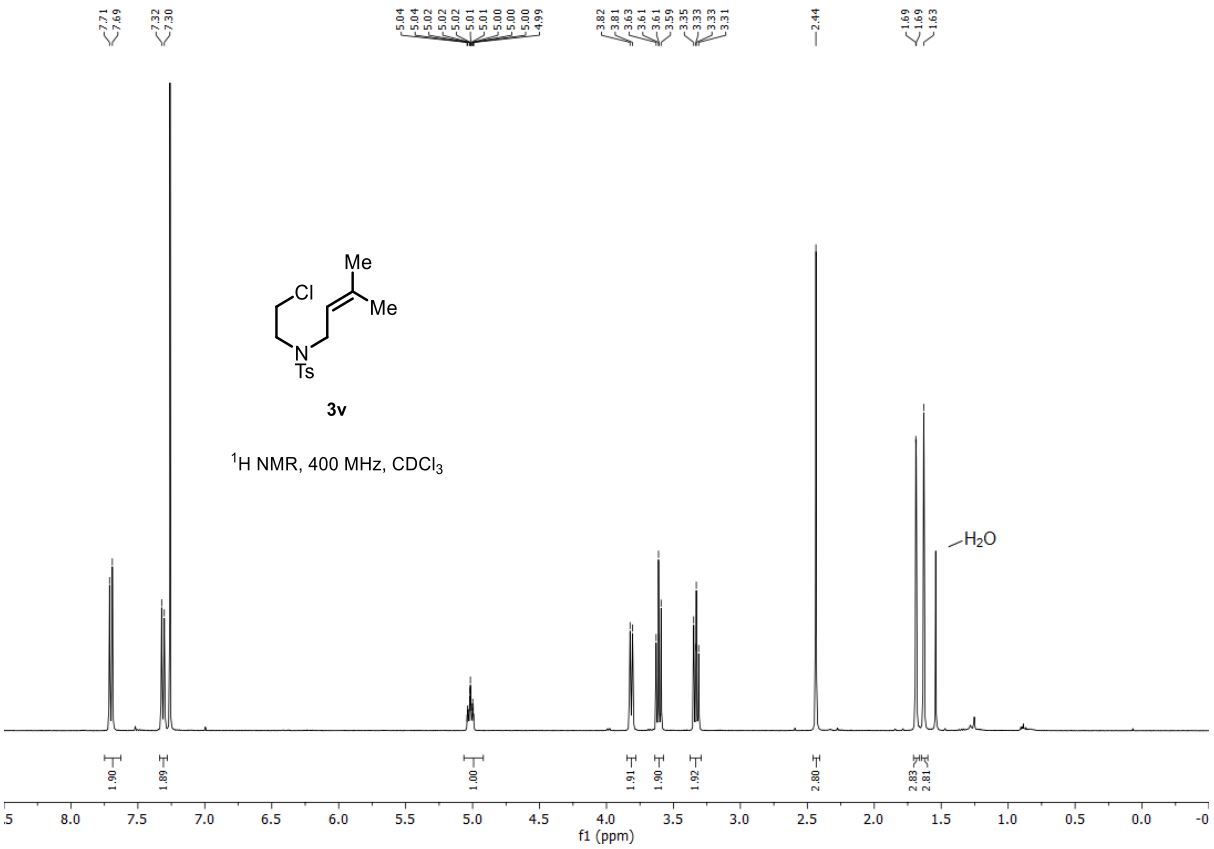

Me
Me
Br
O
2o
^{13}C NMR, 101 MHz, $CDCl_3$
f1 (ppm)

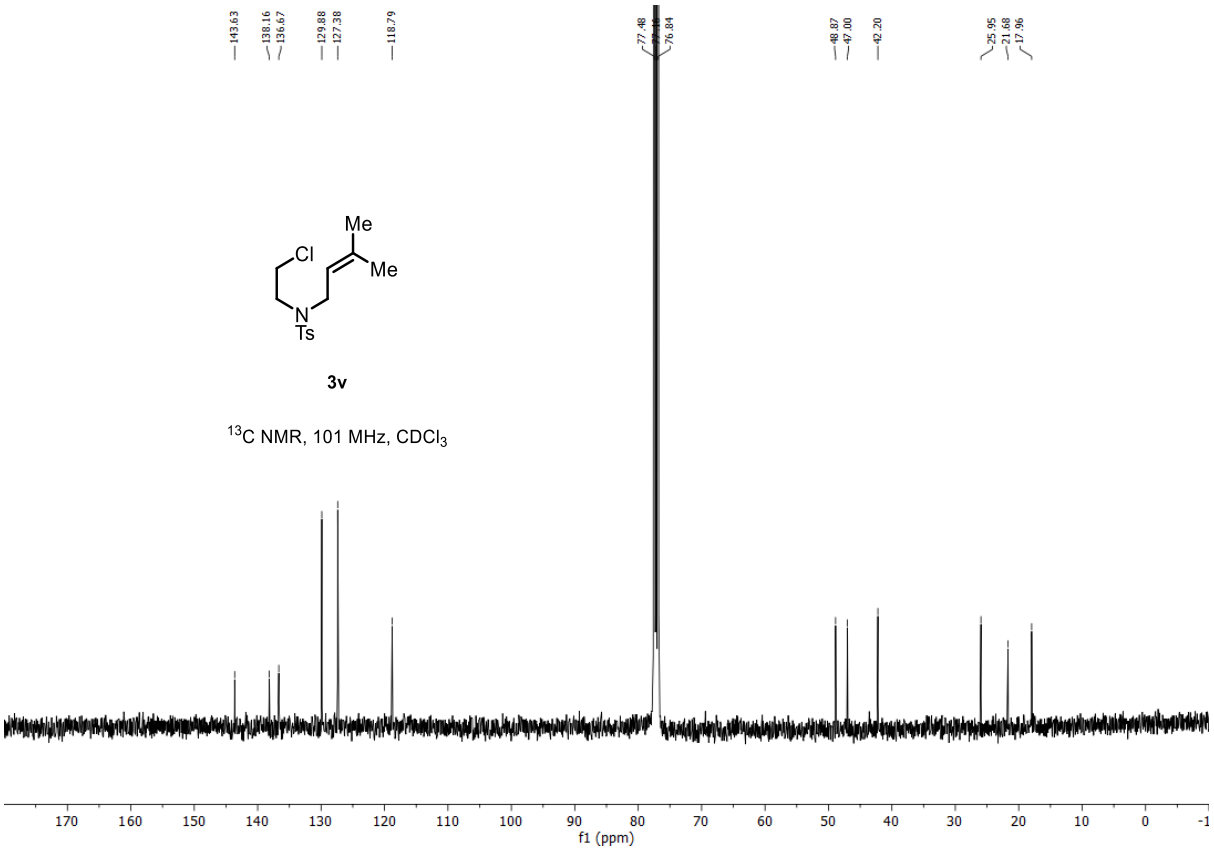

Me
Me
Br
N
Me
Me
2q
1H NMR, 400 MHz, CDCl3
f1 (ppm)

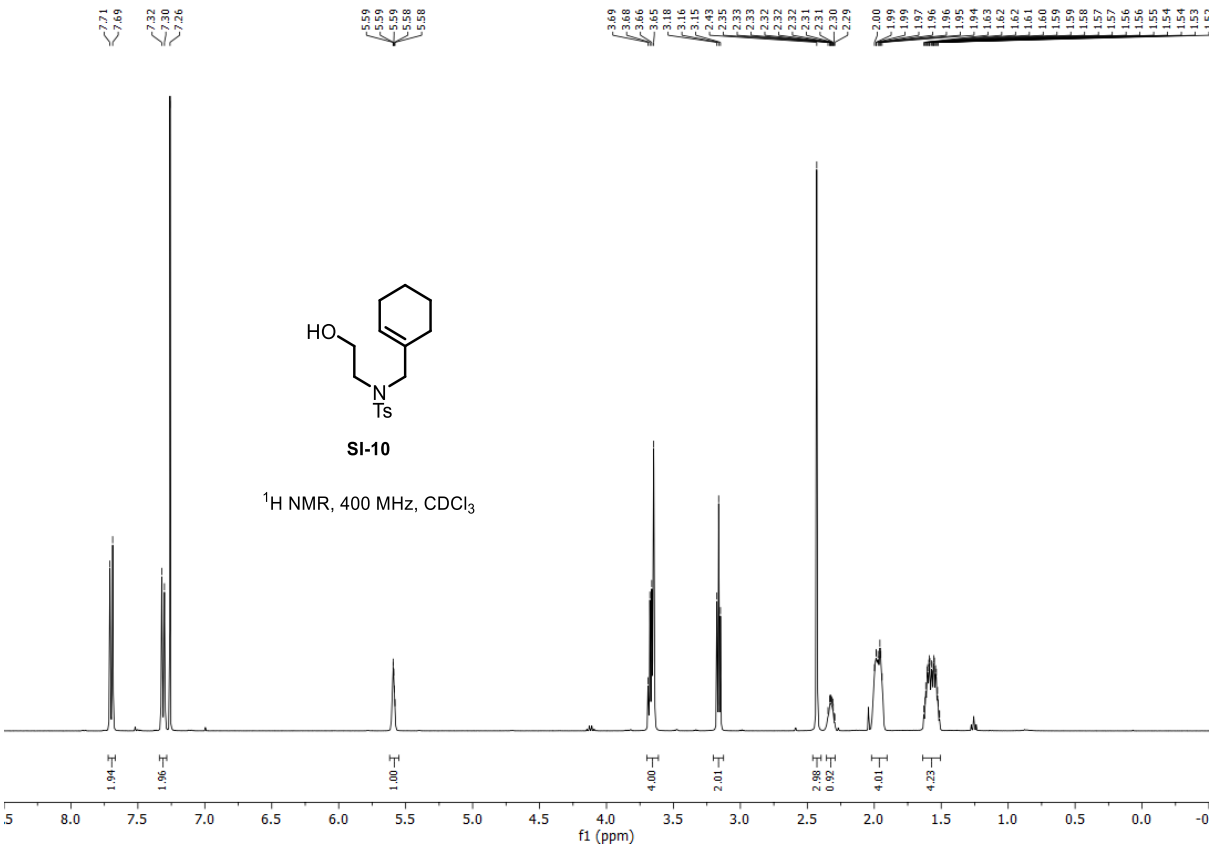

Me
Me
Br
N
Me
Me
2q
13C NMR, 101 MHz, CDCl3
f1 (ppm)

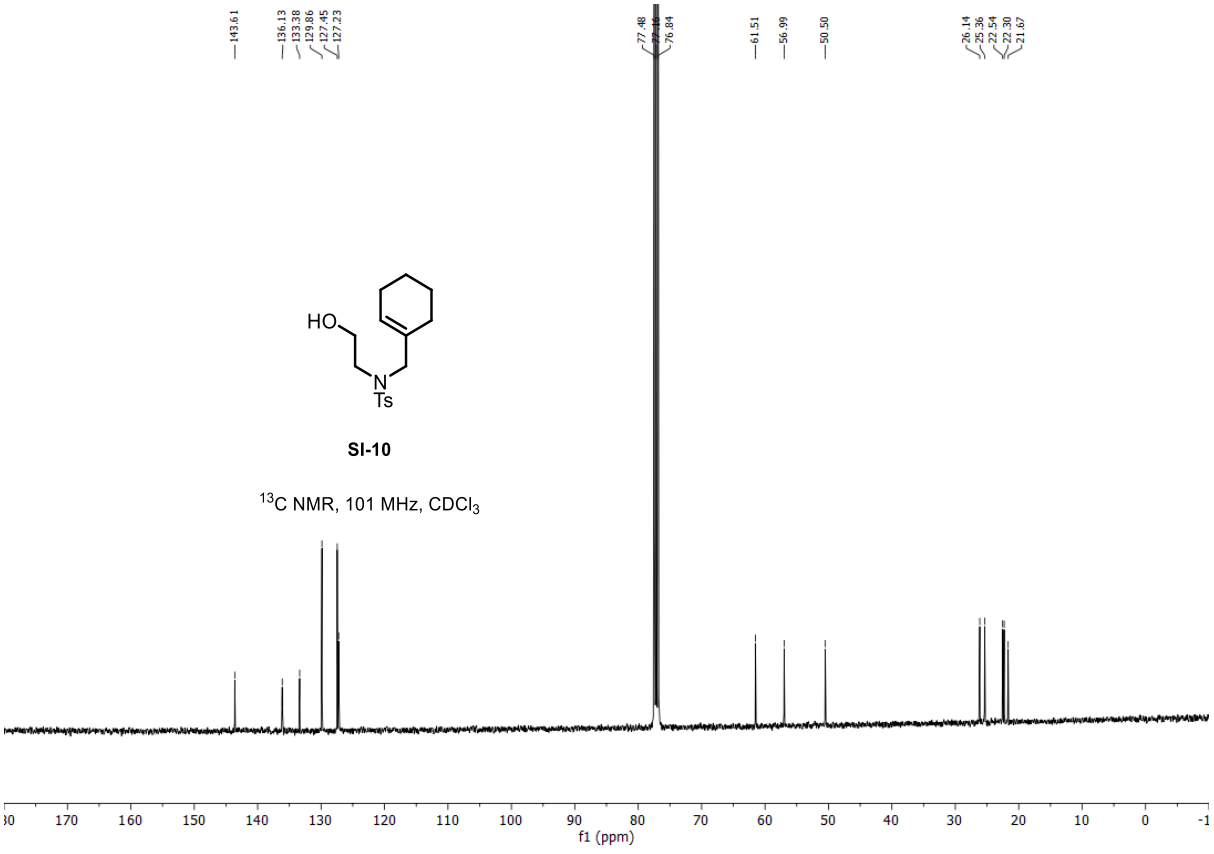

Me
Br
Me
N
Br
Me
Me
2r
1H NMR, 400 MHz, CDCl3
f1 (ppm)

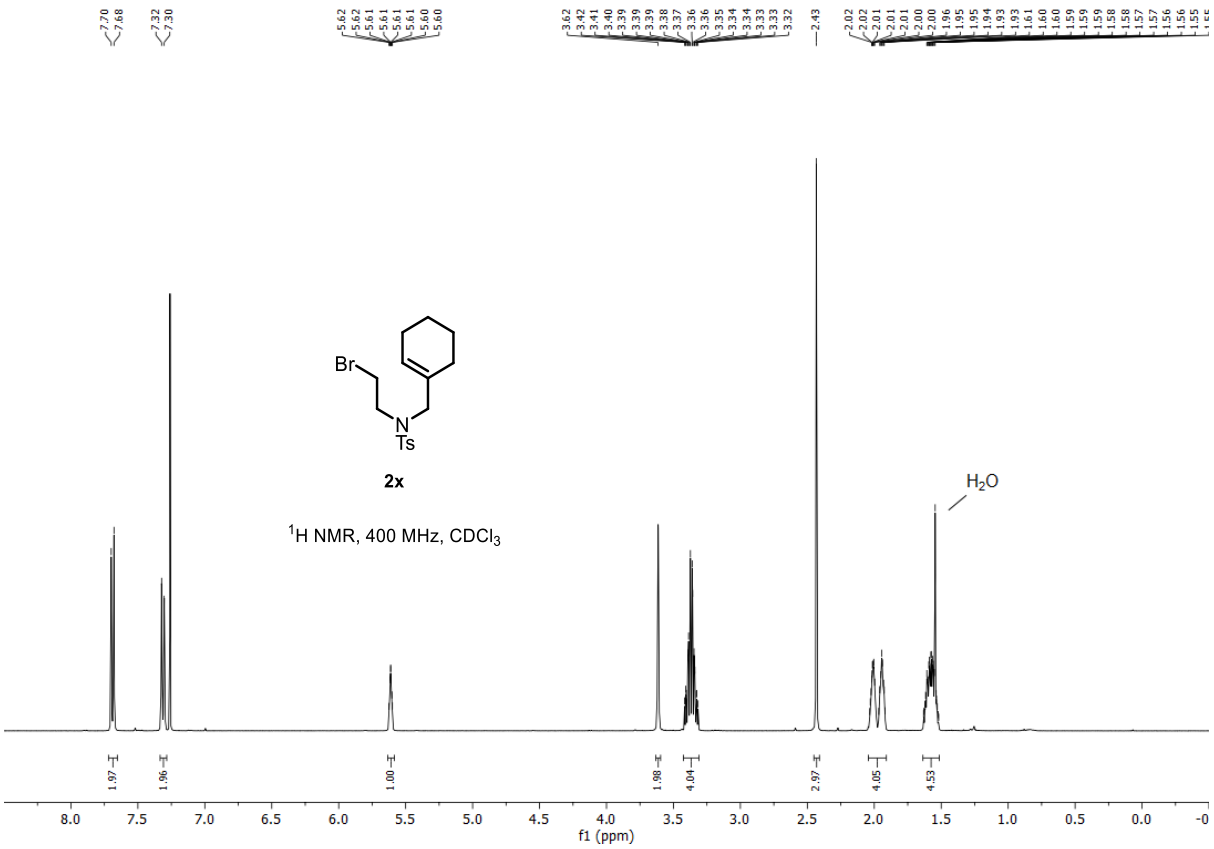

Me
Br
Me
N
Br
Me
Me
2r
13C NMR, 101 MHz, CDCl3
f1 (ppm)

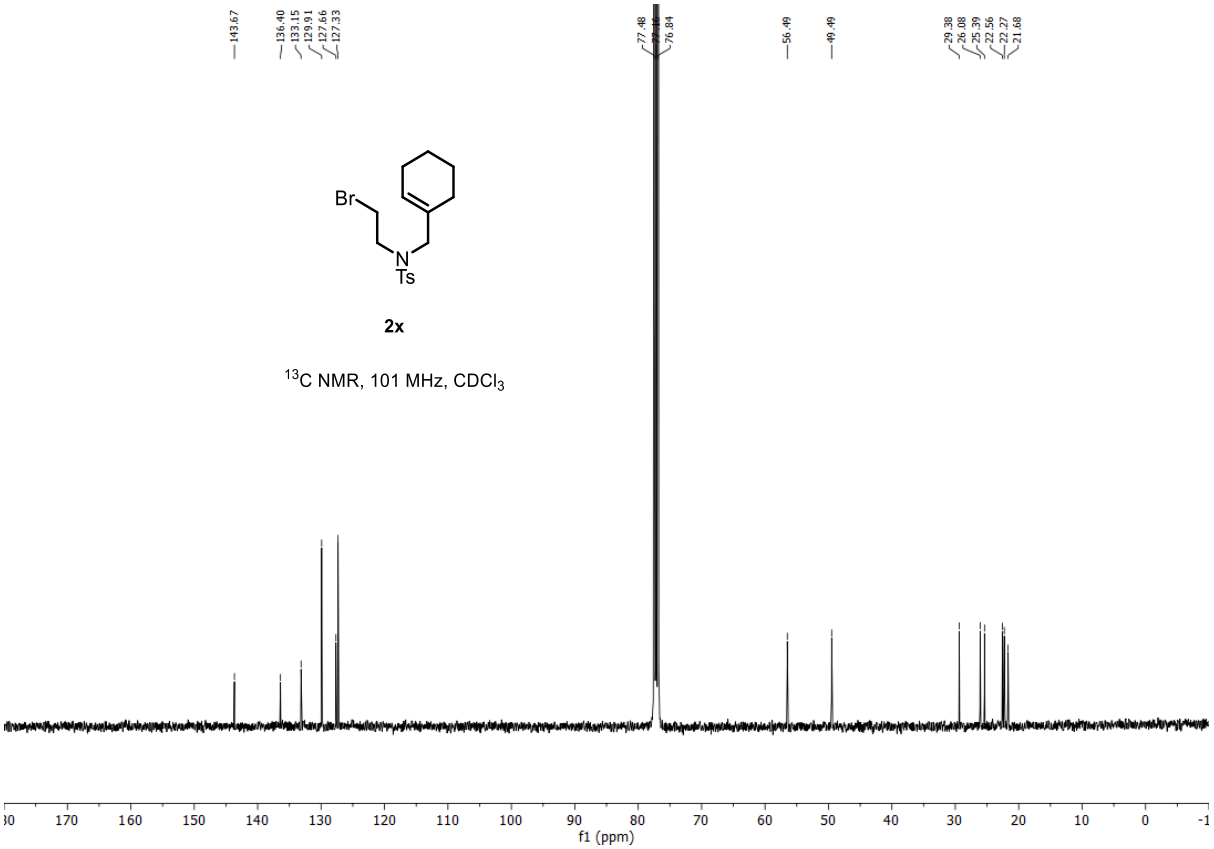

Me
Cl
Me
N
Ts
3v
^{1}H NMR, 400 MHz, $CDCl_3$
H_2O
f1 (ppm)

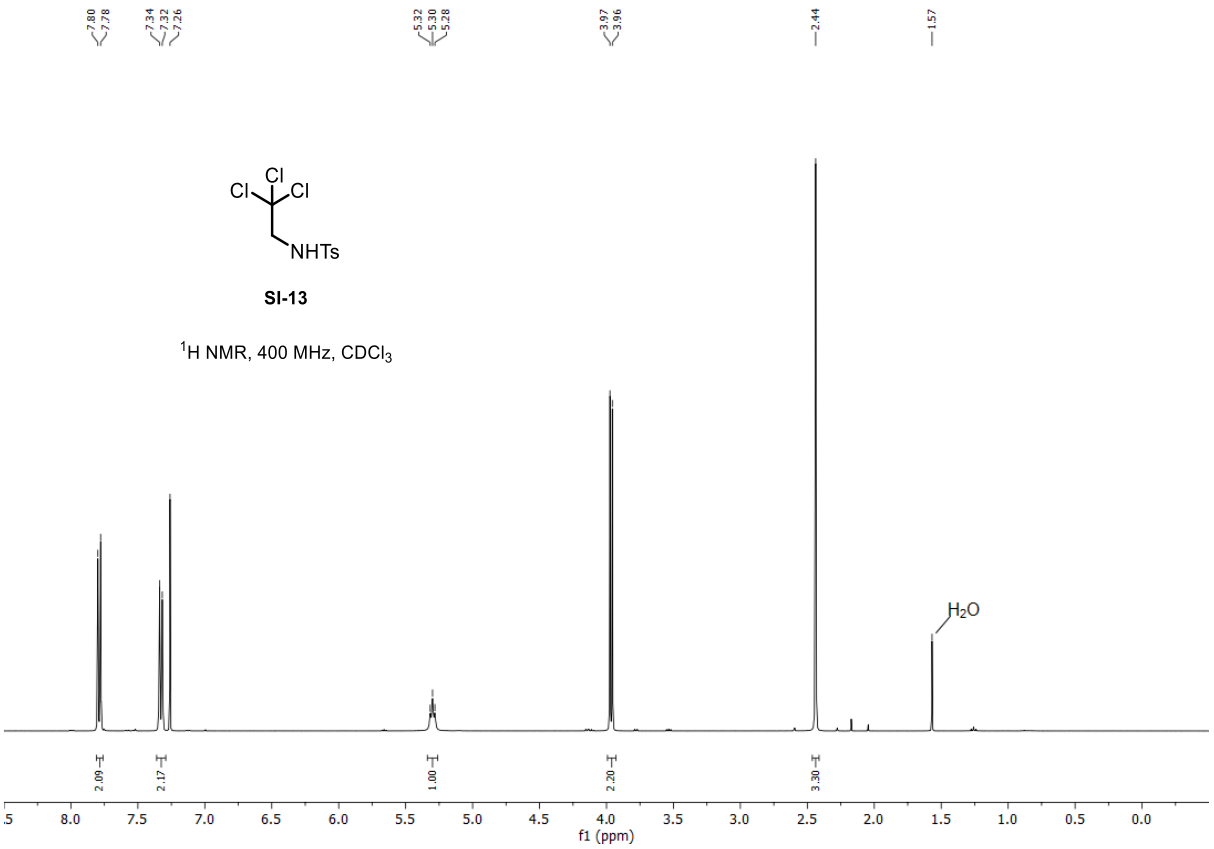

Me
Cl
Me
N
Ts
3v
^{13}C NMR, 101 MHz, $CDCl_3$
f1 (ppm)


HO
N
Ts
SI-10
1H NMR, 400 MHz, CDCl3
f1 (ppm)


HO
N
Ts
SI-10
13C NMR, 101 MHz, CDCl3
f1 (ppm)

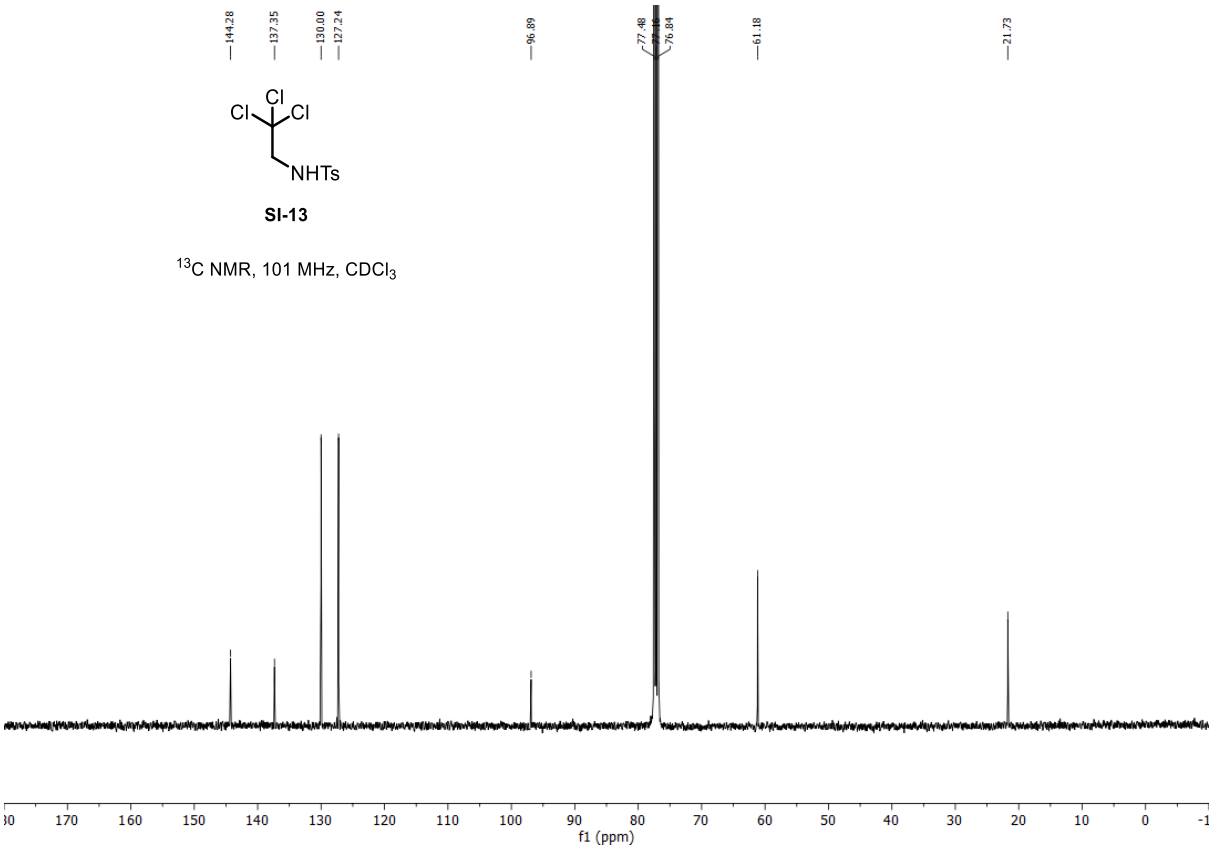

Br
N
Ts
2x
^{1}H NMR, 400 MHz, CDCl$_3$
H$_2$O
f1 (ppm)


Br
N
Ts
2x
^{13}C NMR, 101 MHz, CDCl$_3$
f1 (ppm)



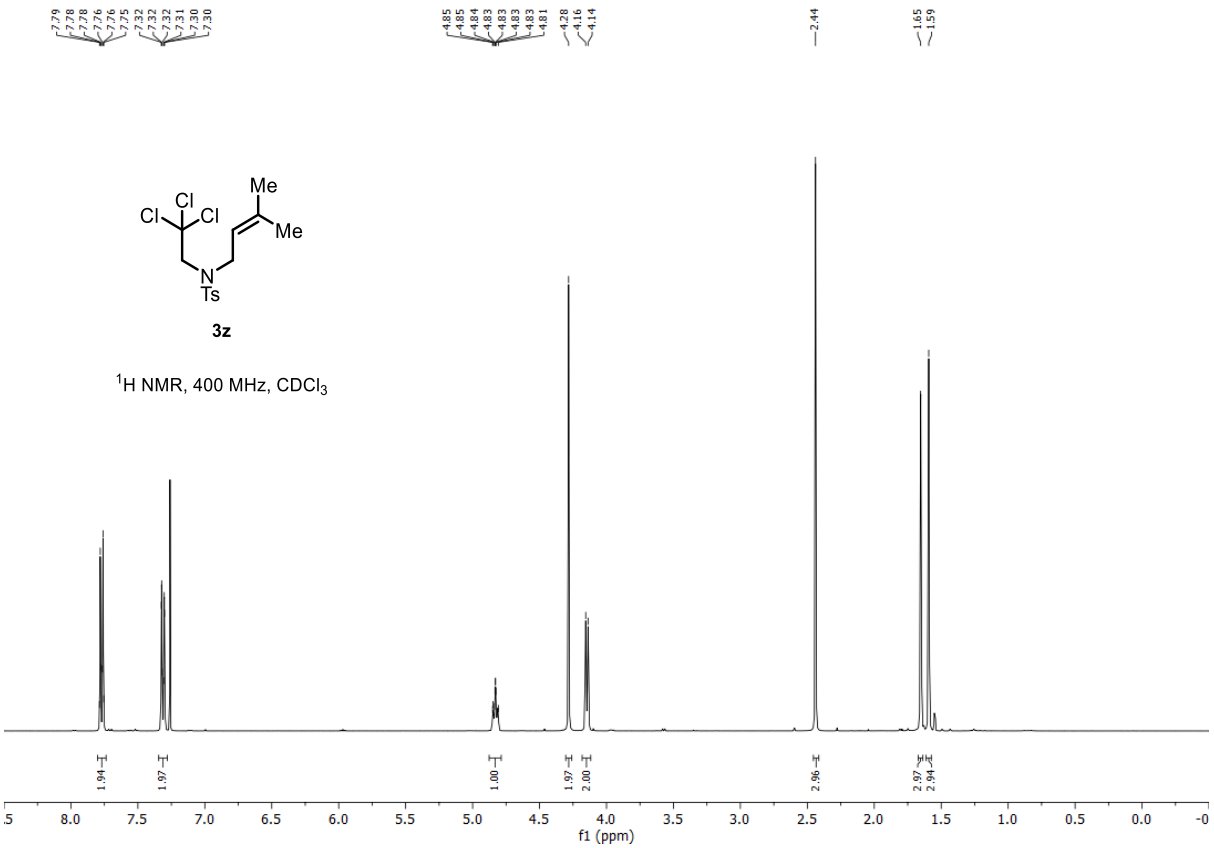
SI-13

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



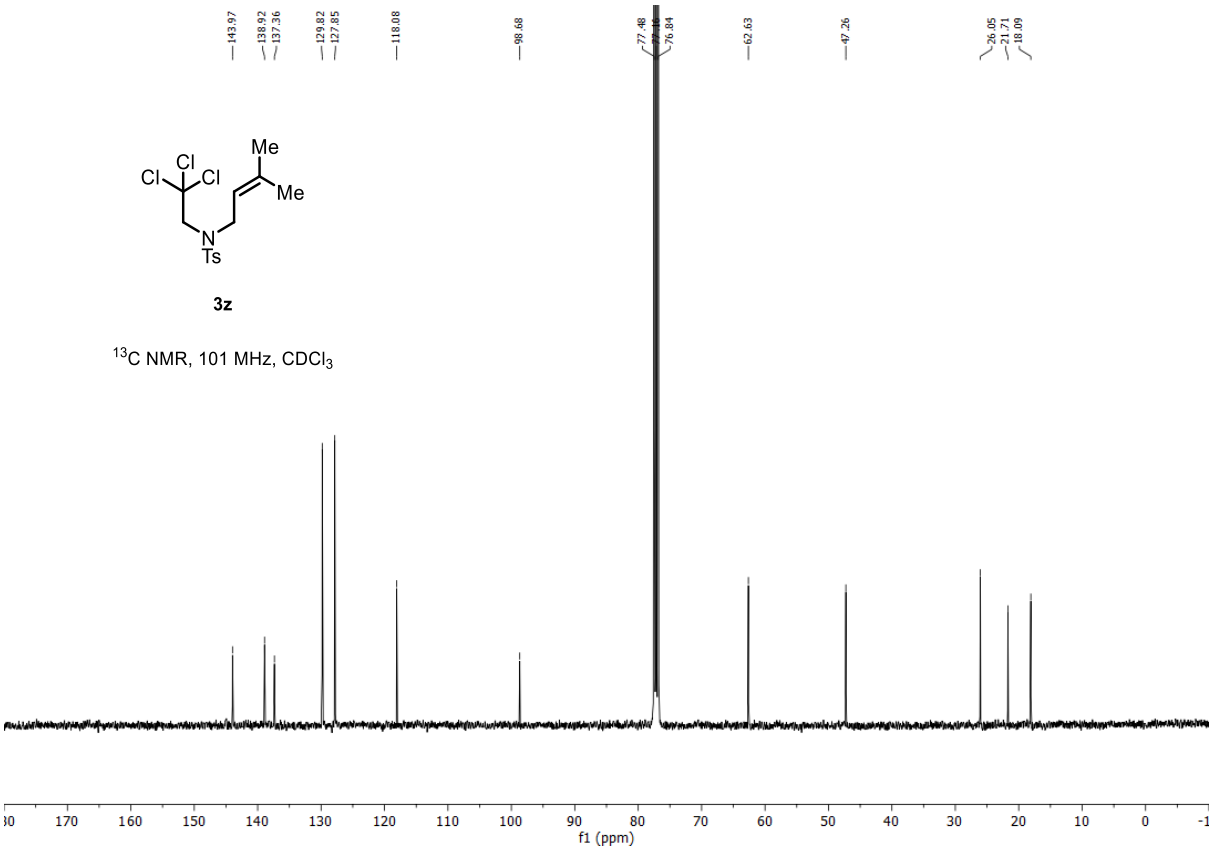
SI-13

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



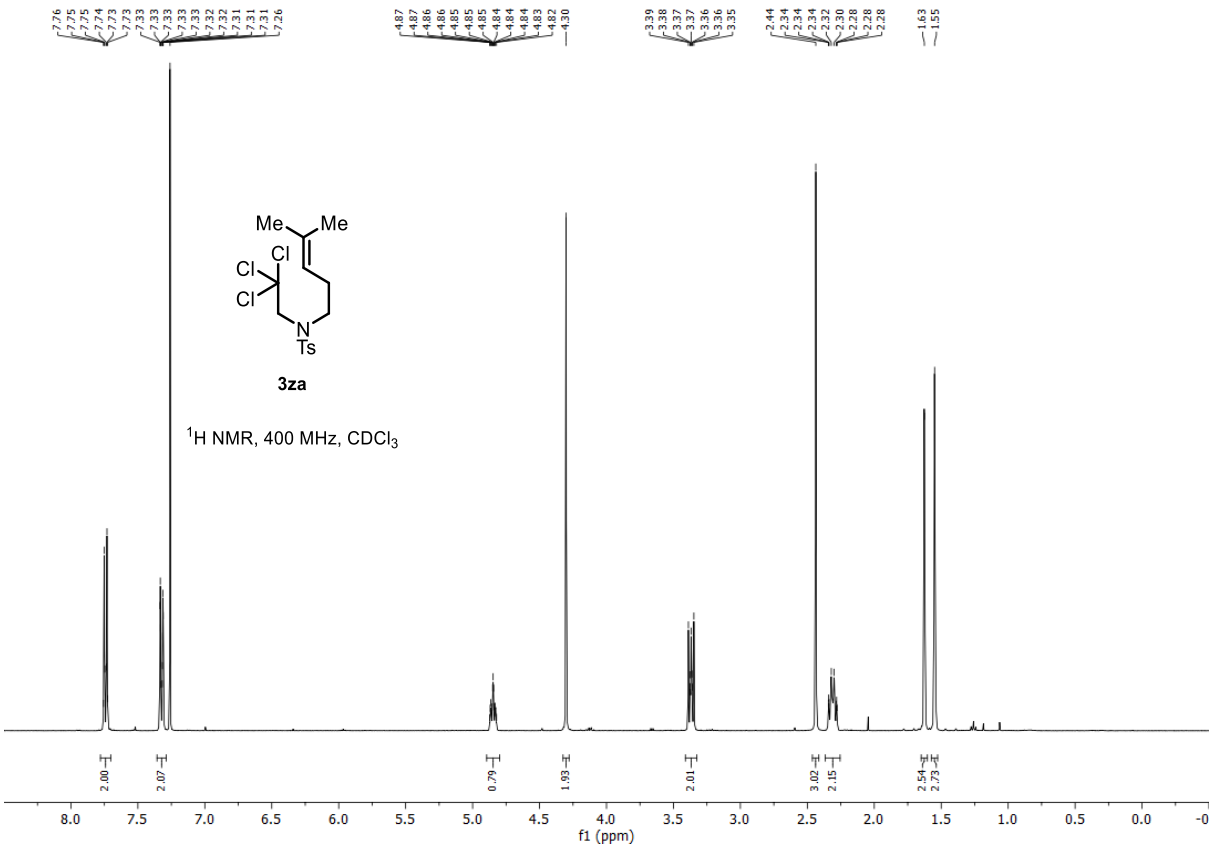
3z

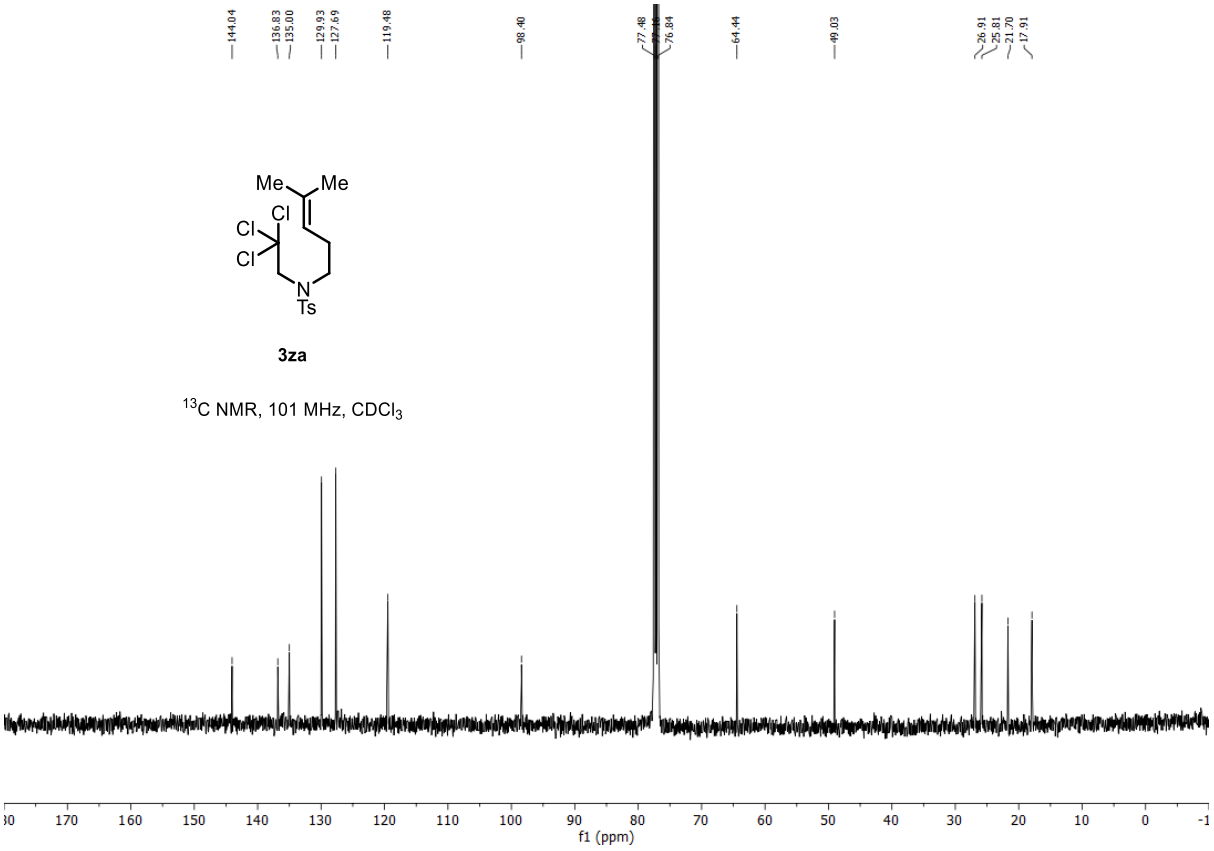
^{1}H NMR, 400 MHz, $CDCl_3$

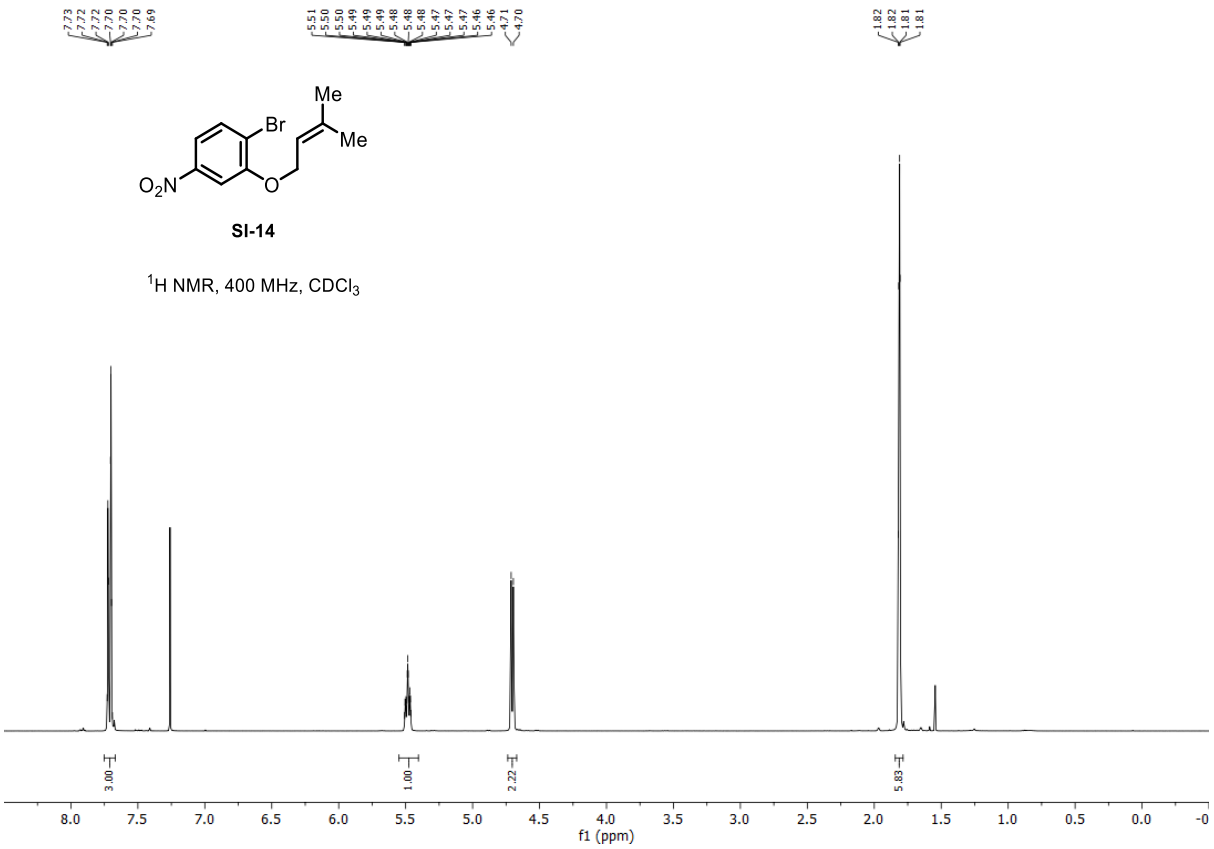


3z

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

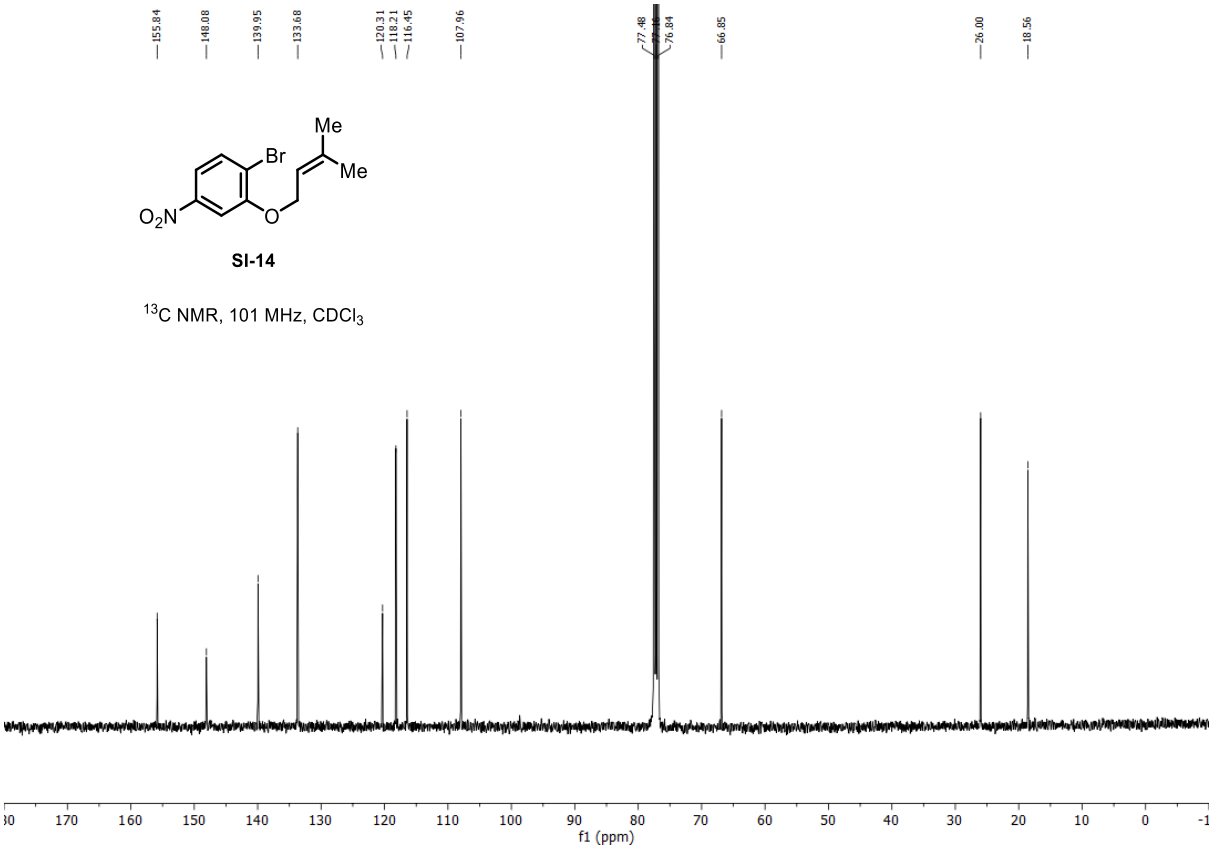

Me
Me
Cl
Cl
Cl
N
Ts
3za
^{1}H NMR, 400 MHz, $CDCl_3$
f1 (ppm)


Me
Me
Cl
Cl
Cl
N
Ts
3za
^{13}C NMR, 101 MHz, $CDCl_3$
f1 (ppm)



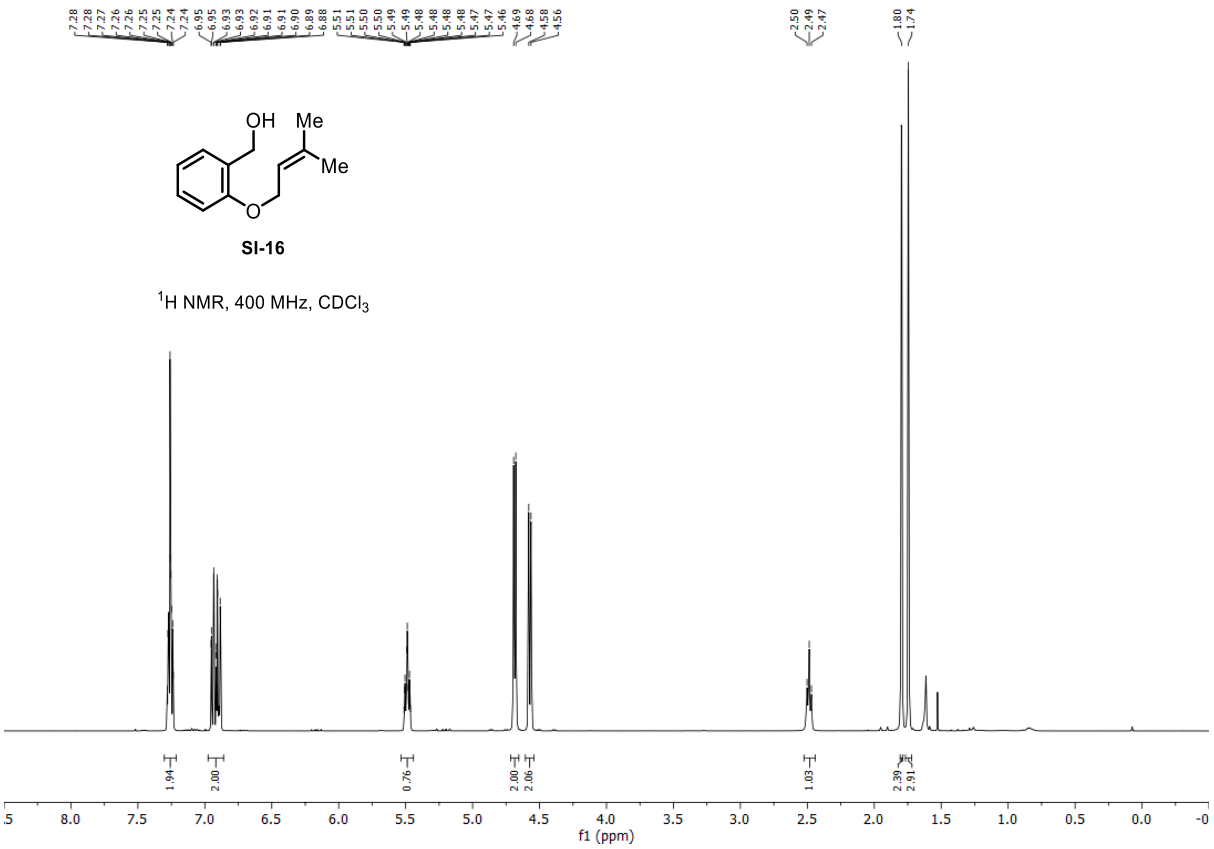
SI-14

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



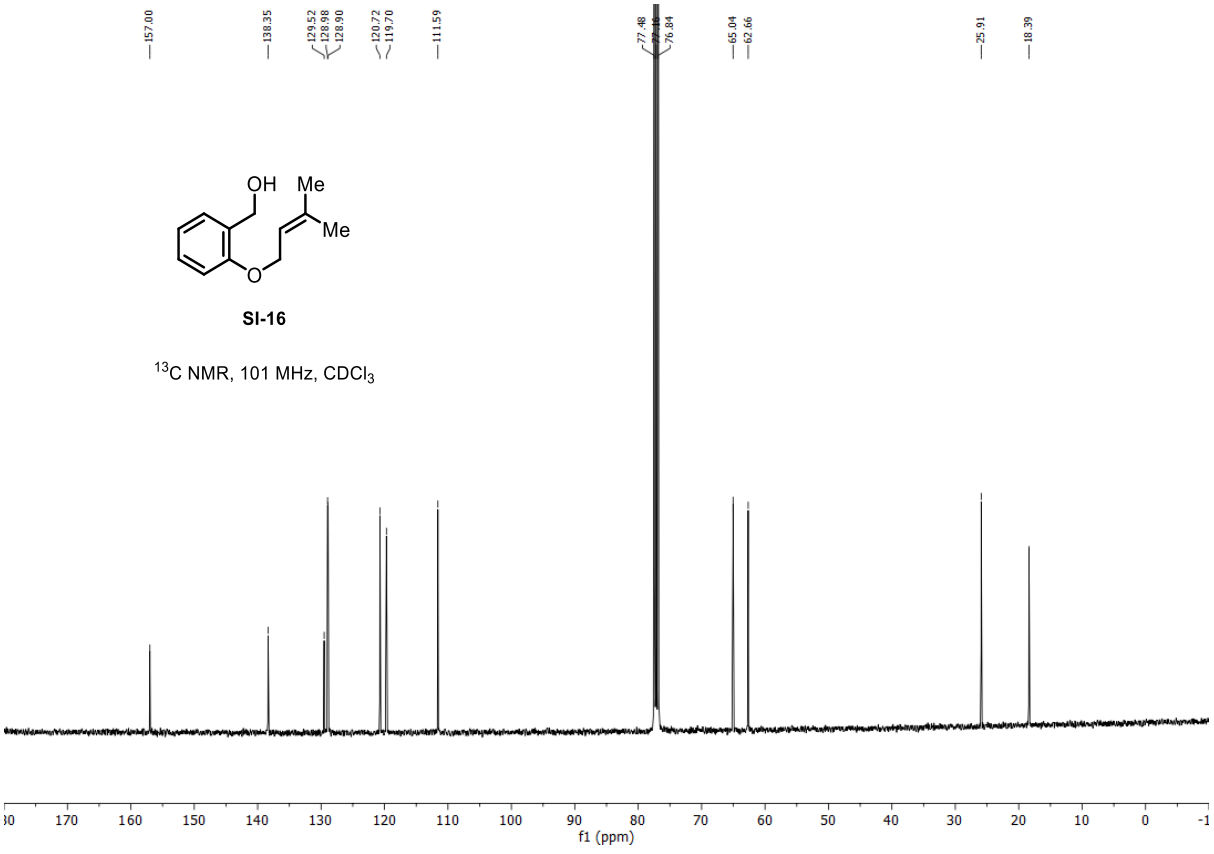
SI-14

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



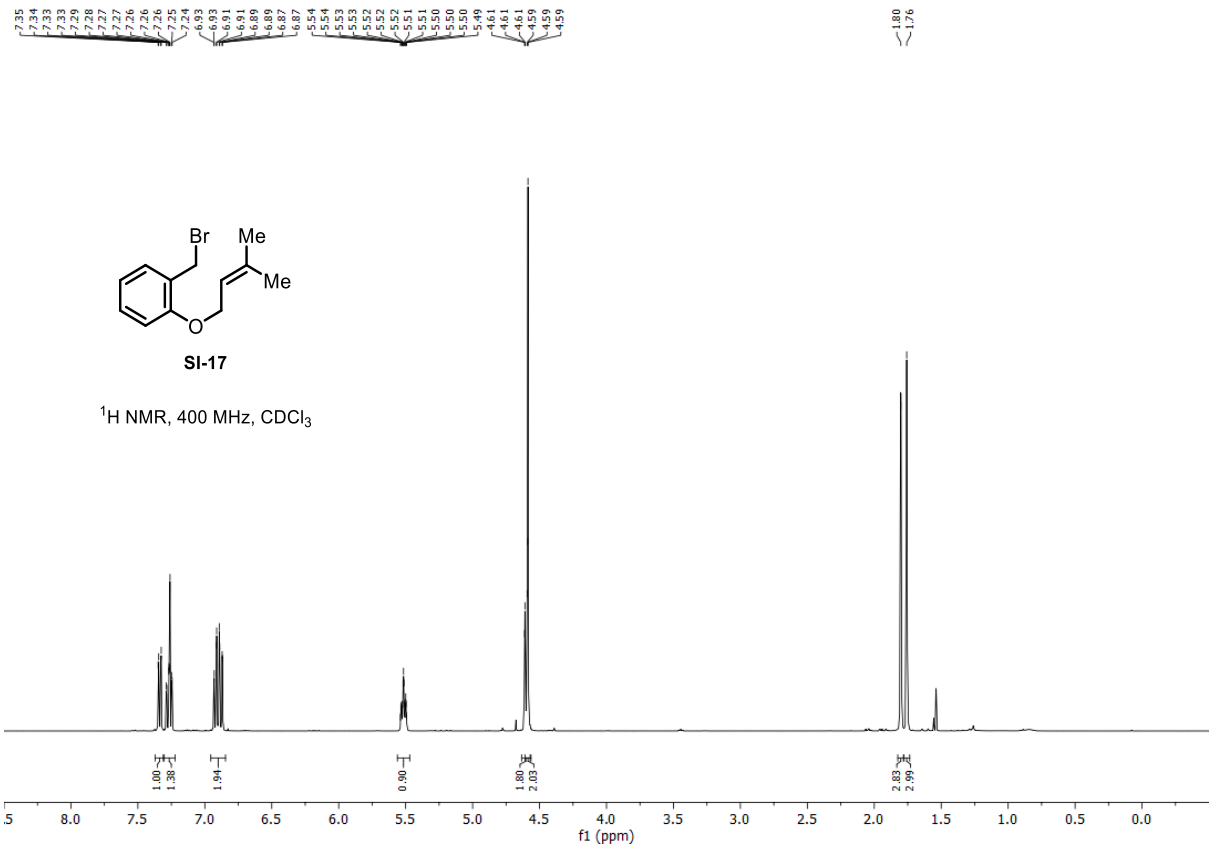
SI-16

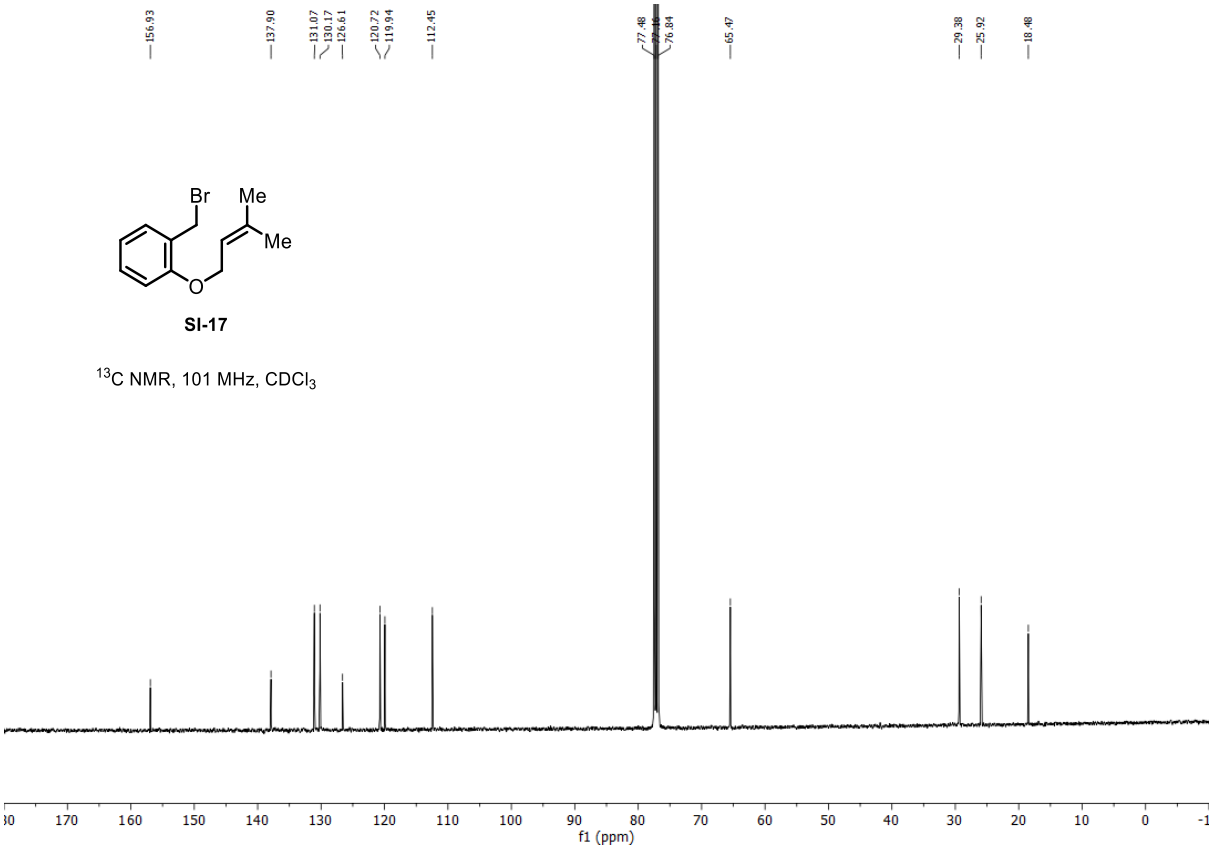
^{1}H NMR, 400 MHz, $CDCl_3$

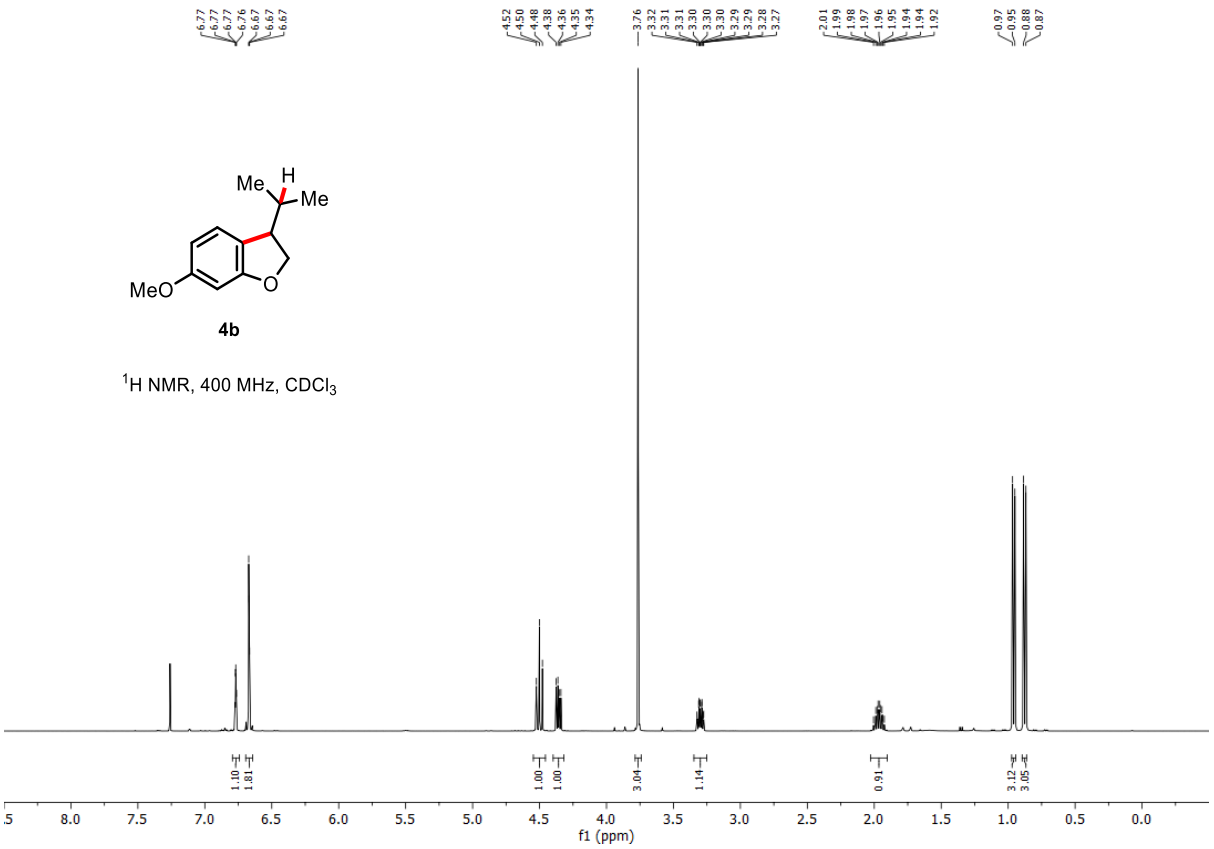


SI-16

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

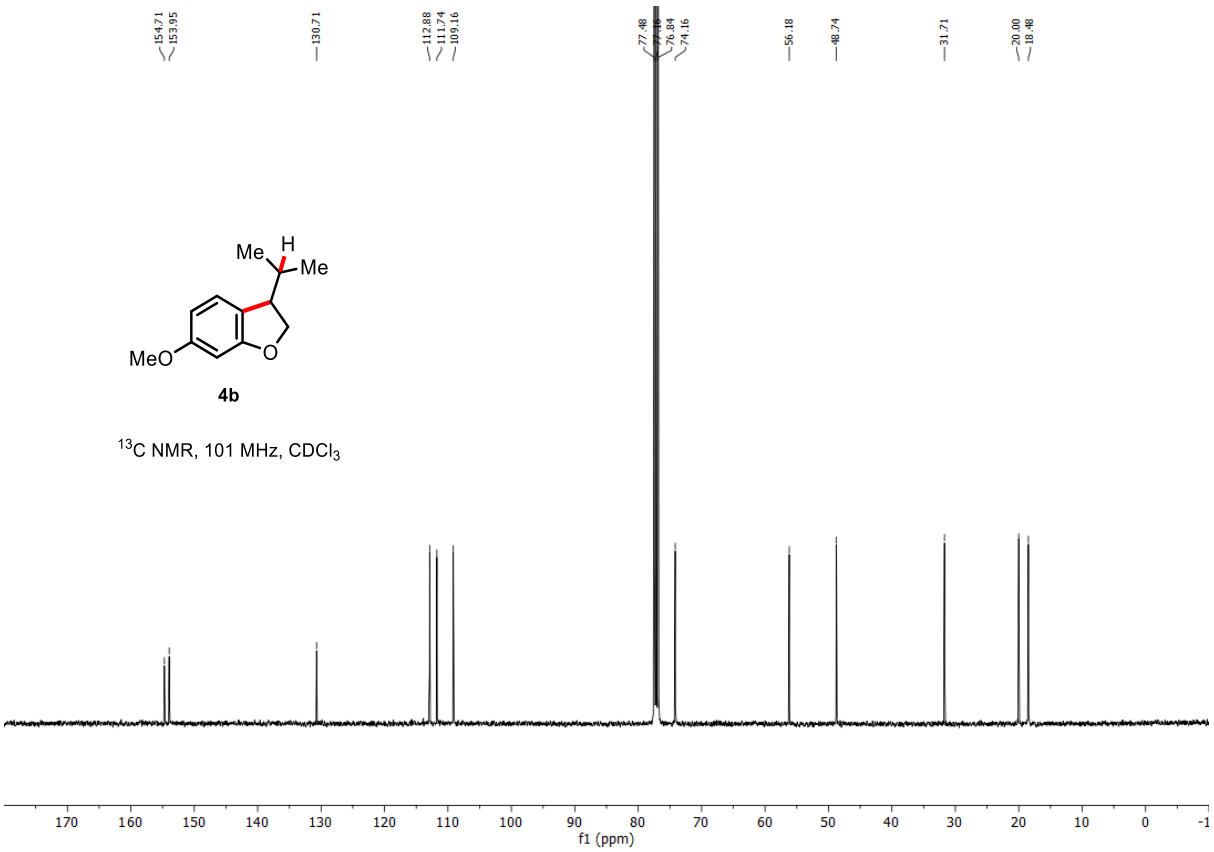

Br
Me
Me
O
SI-17
1H NMR, 400 MHz, CDCl3
f1 (ppm)


Br
Me
Me
O
SI-17
13C NMR, 101 MHz, CDCl3
f1 (ppm)



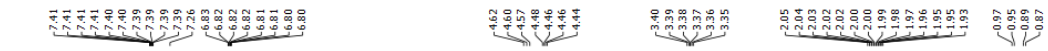
4b

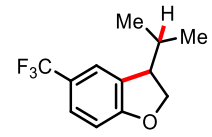
^{1}H NMR, 400 MHz, $CDCl_3$



4b

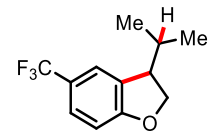
^{13}C NMR, 101 MHz, $CDCl_3$





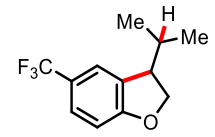
4c

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



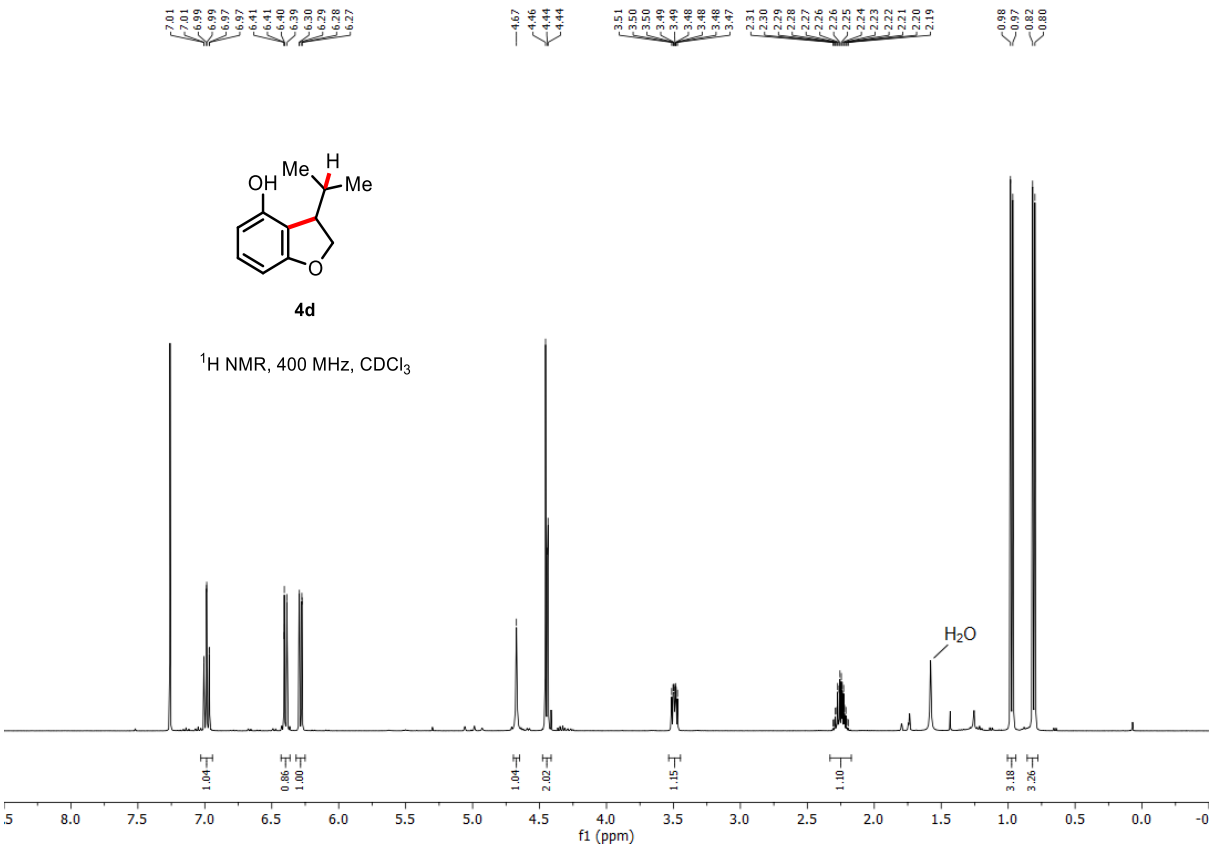
4c

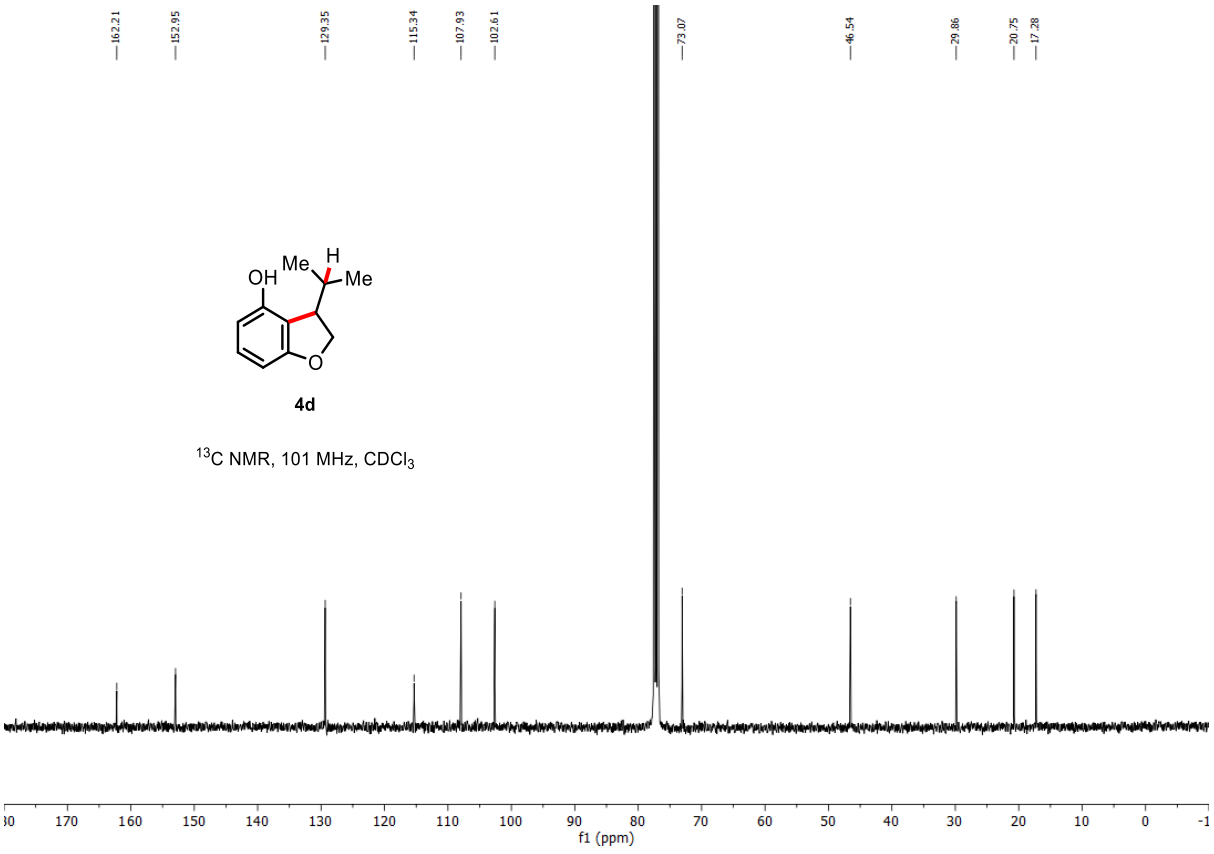
^{13}C NMR, 101 MHz, $CDCl_3$

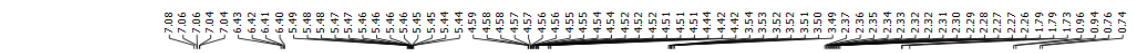


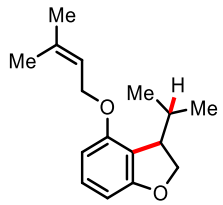
4c

^{19}F NMR, 376 MHz, $CDCl_3$


OH
Me
H
Me
O
4d
^{1}H NMR, 400 MHz, $CDCl_3$
H_2O
f1 (ppm)

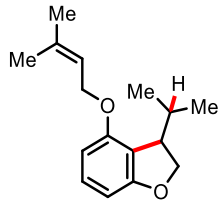

OH
Me
H
Me
O
4d
^{13}C NMR, 101 MHz, $CDCl_3$
f1 (ppm)





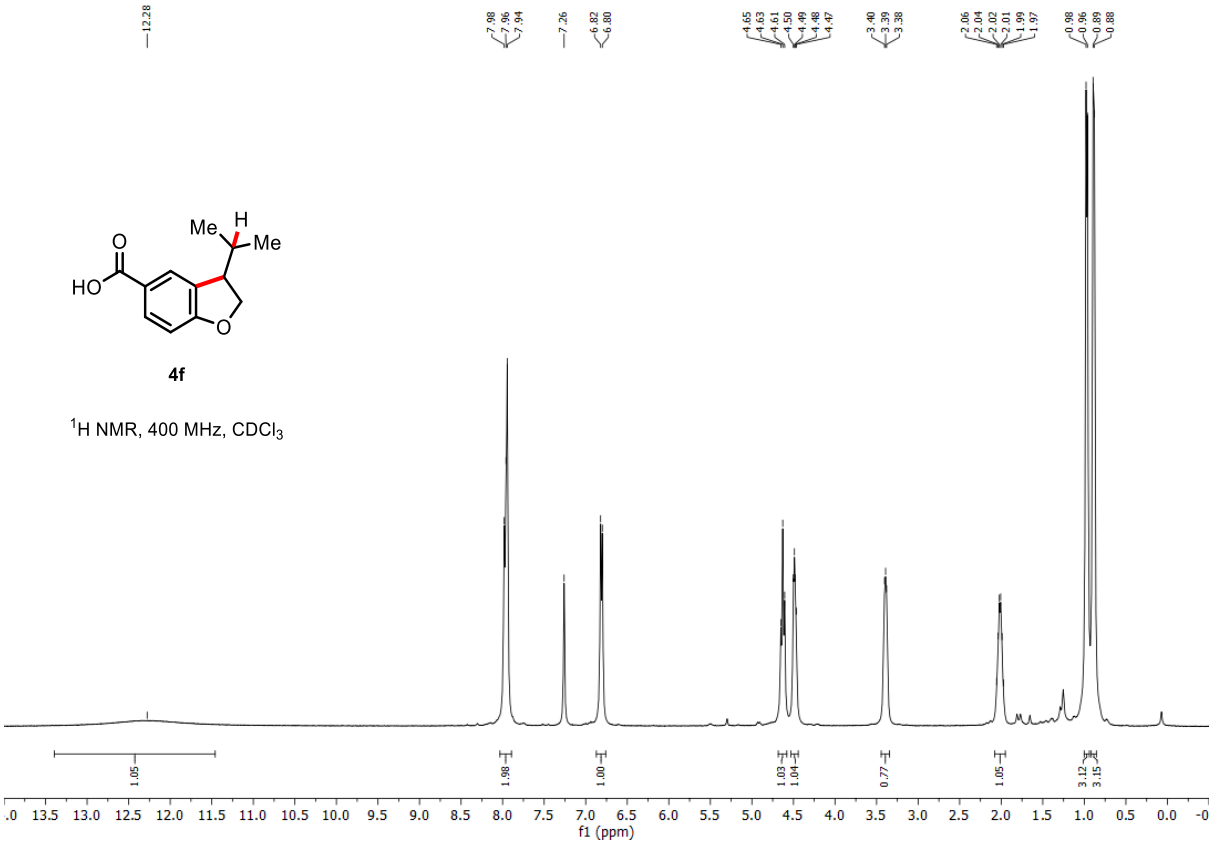
4e

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



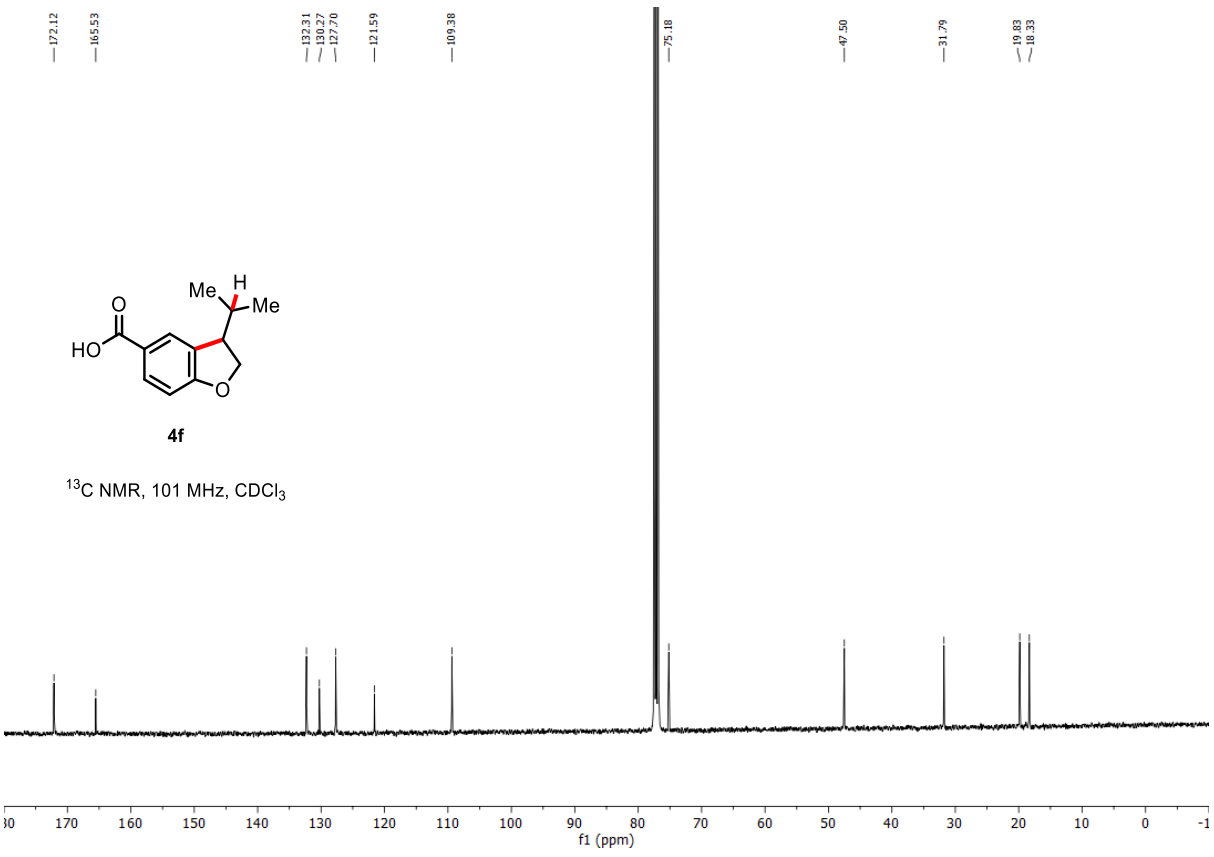
4e

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



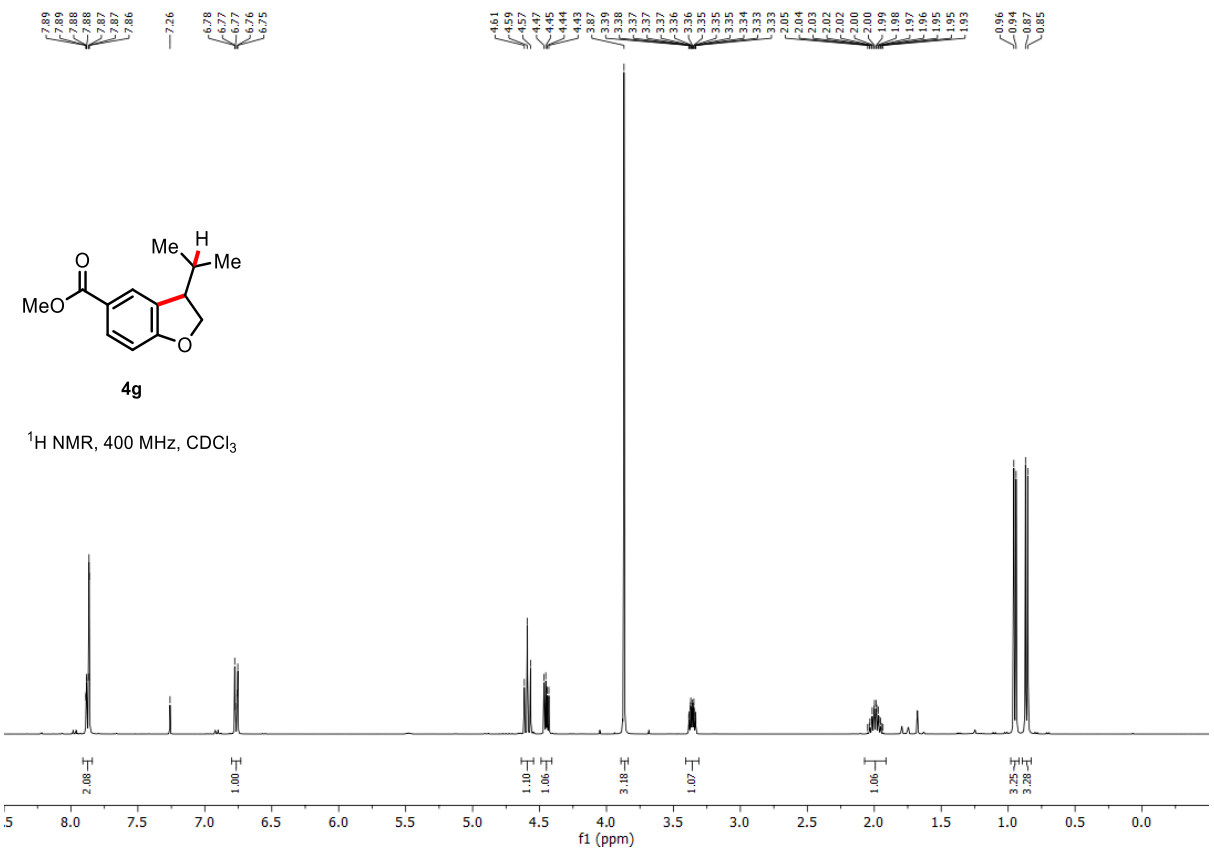
4f

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



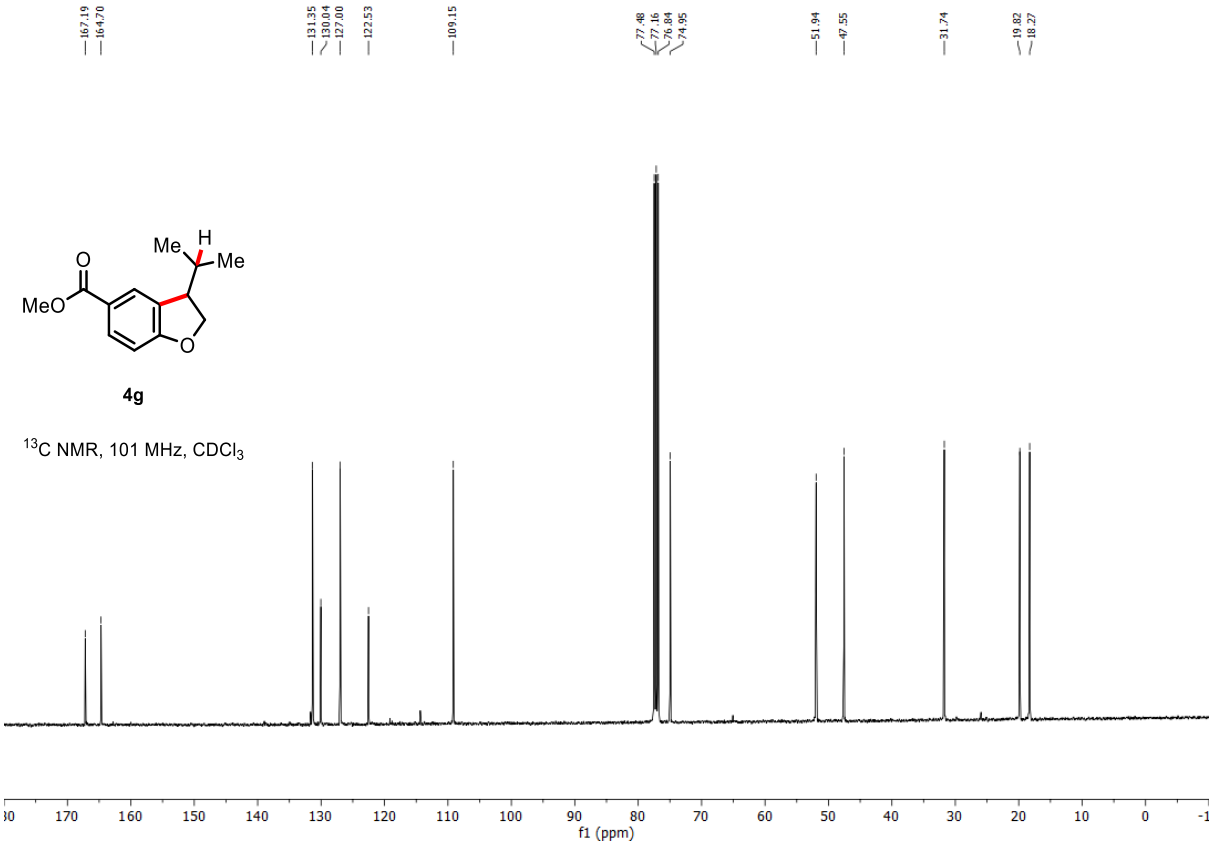
4f

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



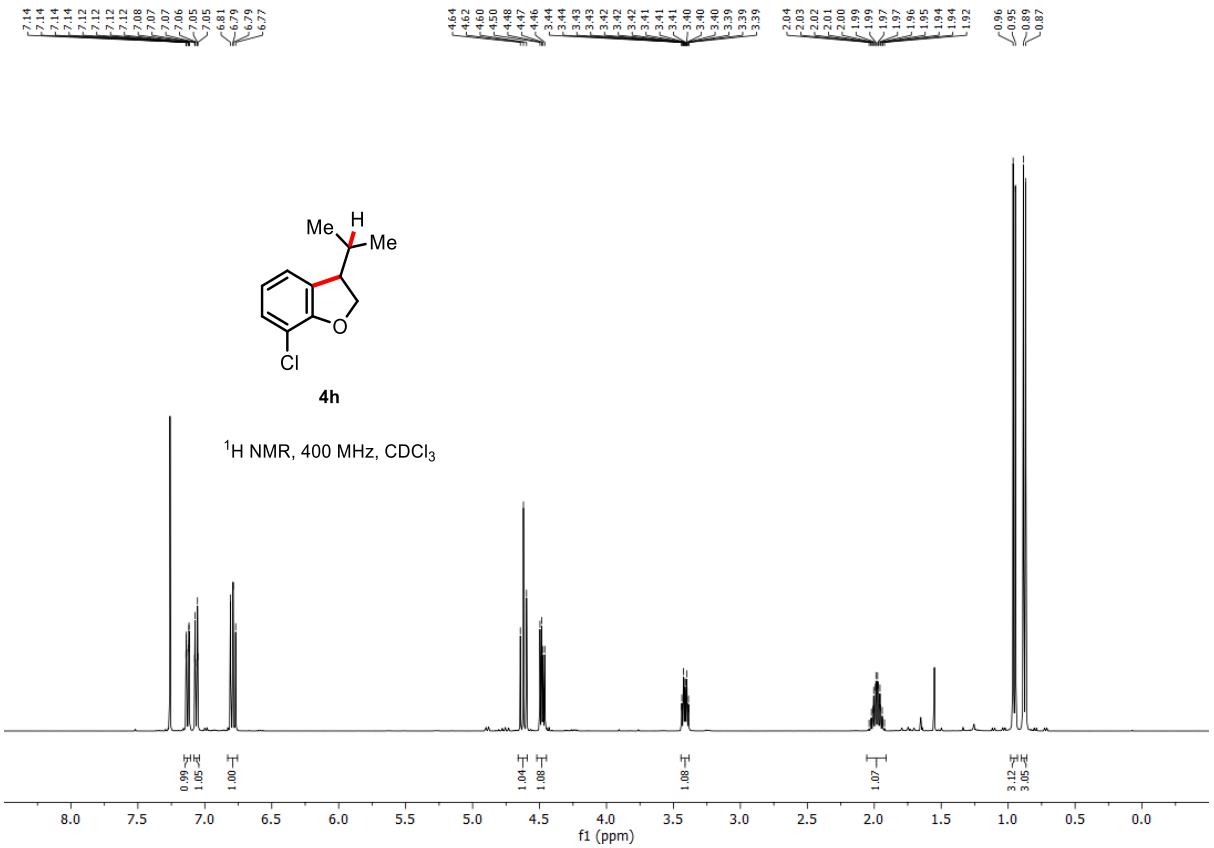
4g

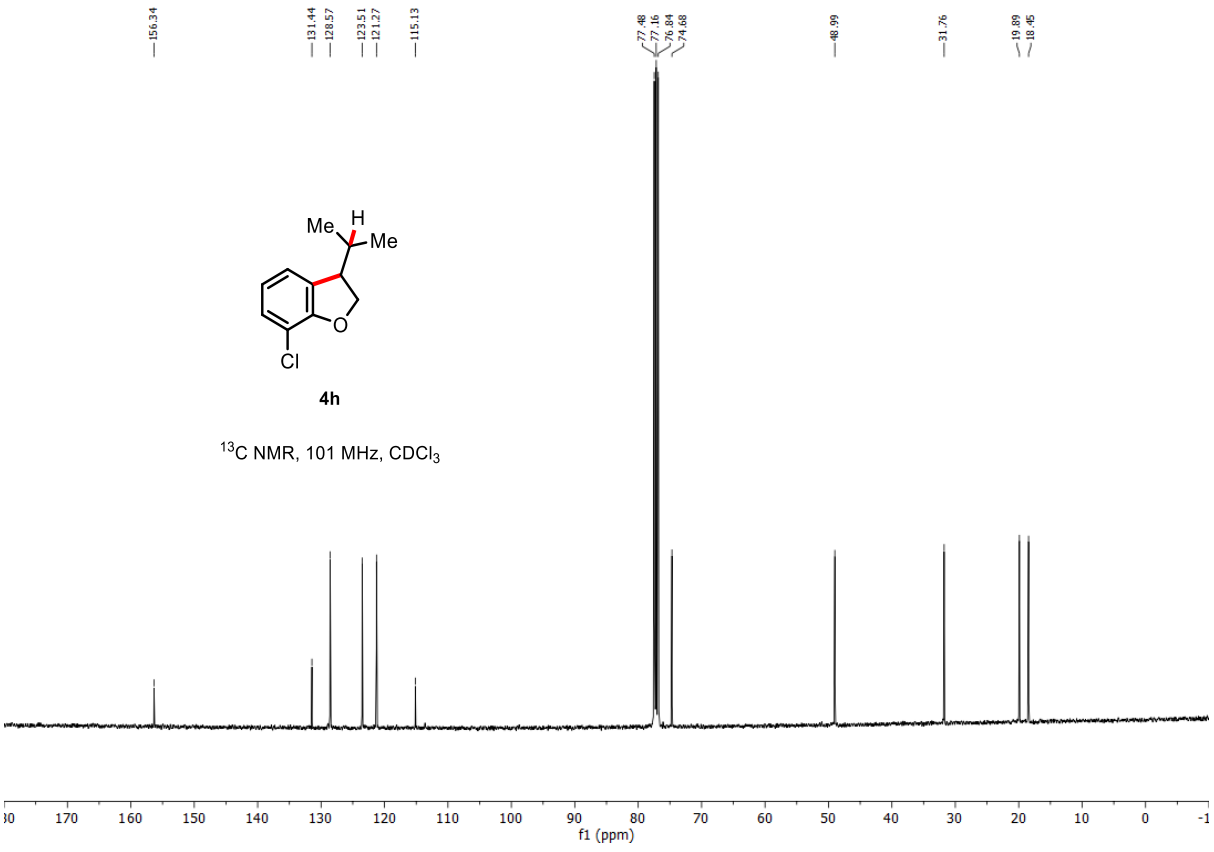
^{1}H NMR, 400 MHz, $CDCl_3$

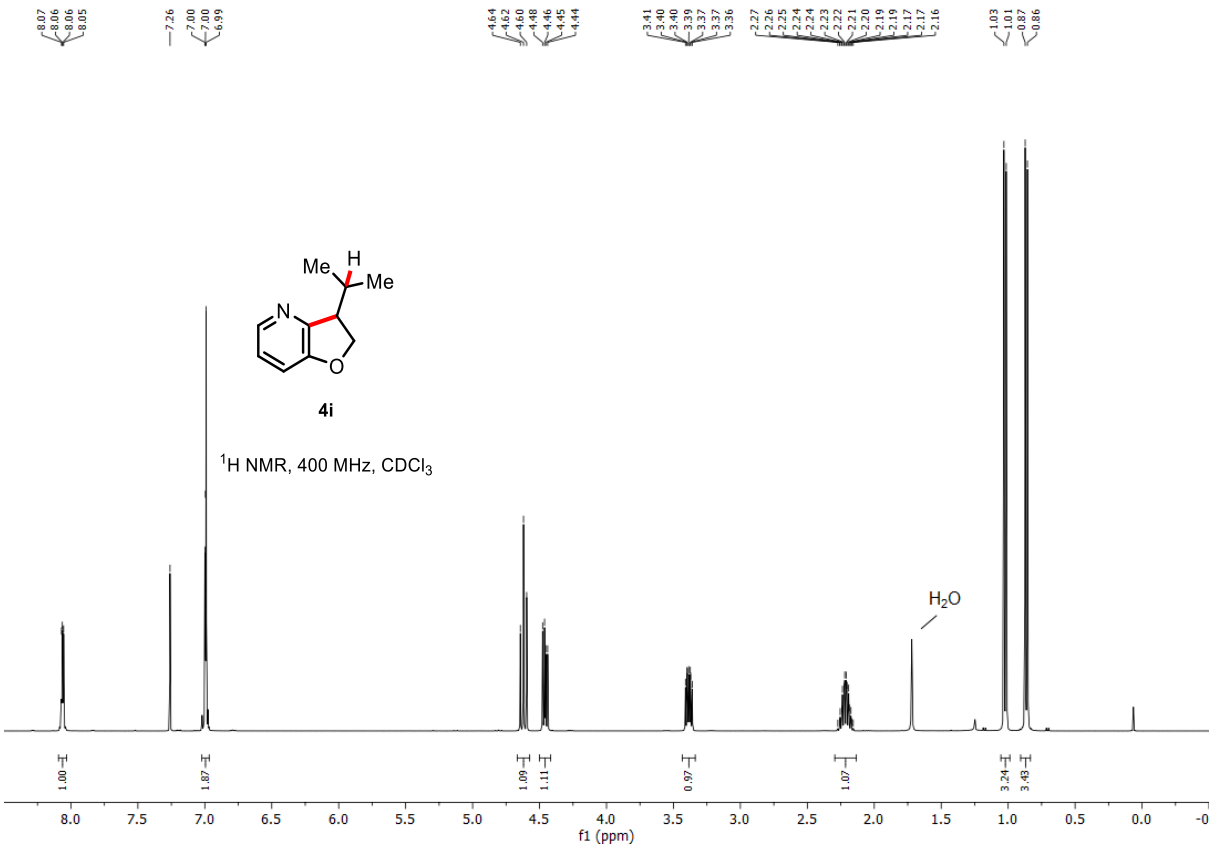


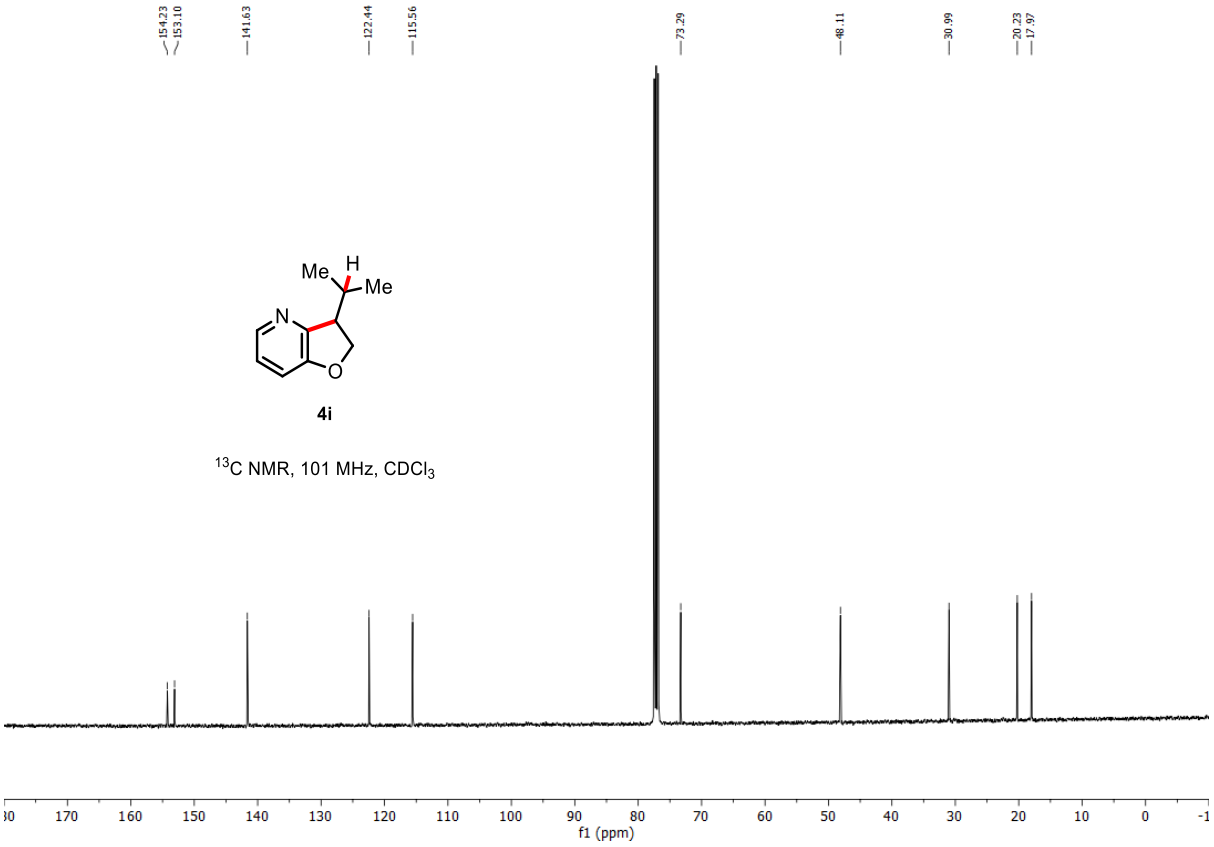
4g

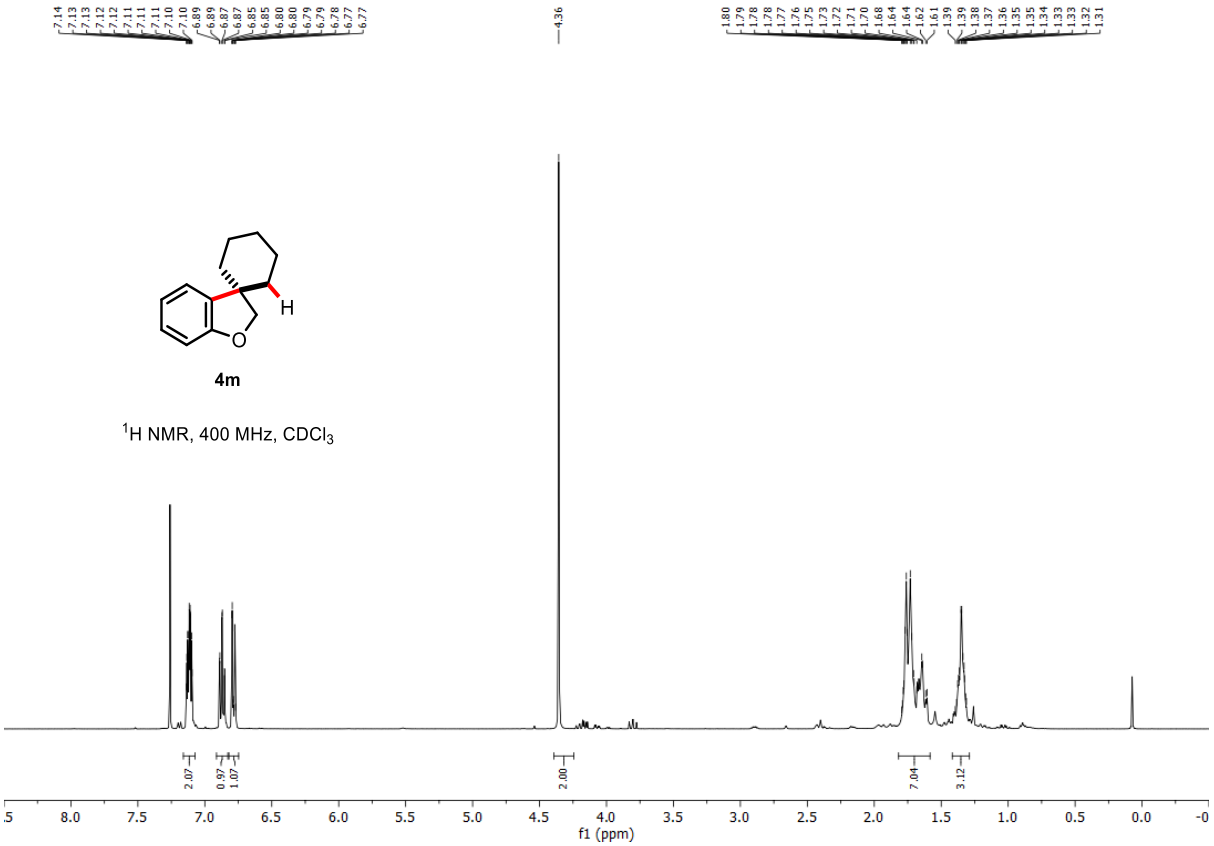
^{13}C NMR, 101 MHz, $CDCl_3$


Me
H
Me
O
Cl
4h
^{1}H NMR, 400 MHz, $CDCl_3$
f1 (ppm)


Me
H
Me
O
Cl
4h
^{13}C NMR, 101 MHz, $CDCl_3$
f1 (ppm)

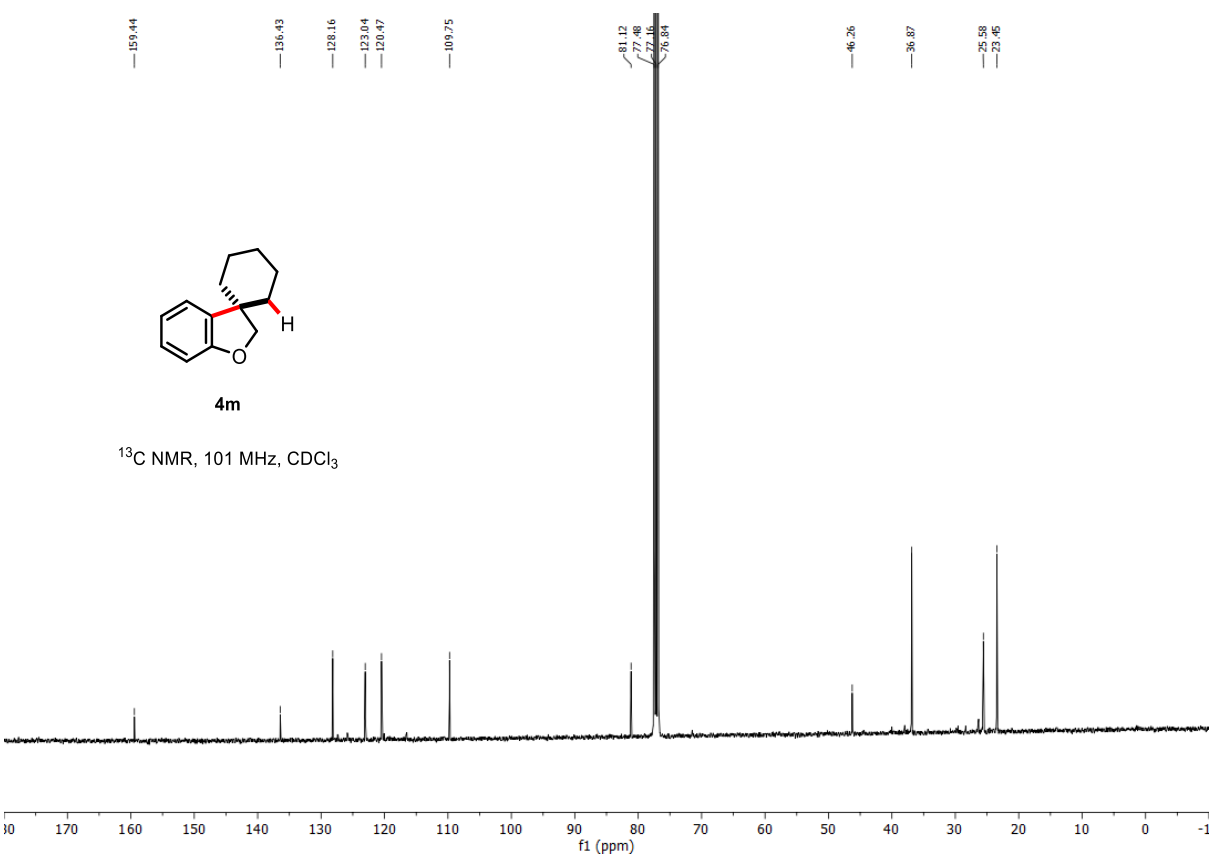

Me
H
Me
N
O
4i
^{1}H NMR, 400 MHz, $CDCl_3$
H_2O
f1 (ppm)


Me
H
Me
N
O
4i
^{13}C NMR, 101 MHz, $CDCl_3$
f1 (ppm)



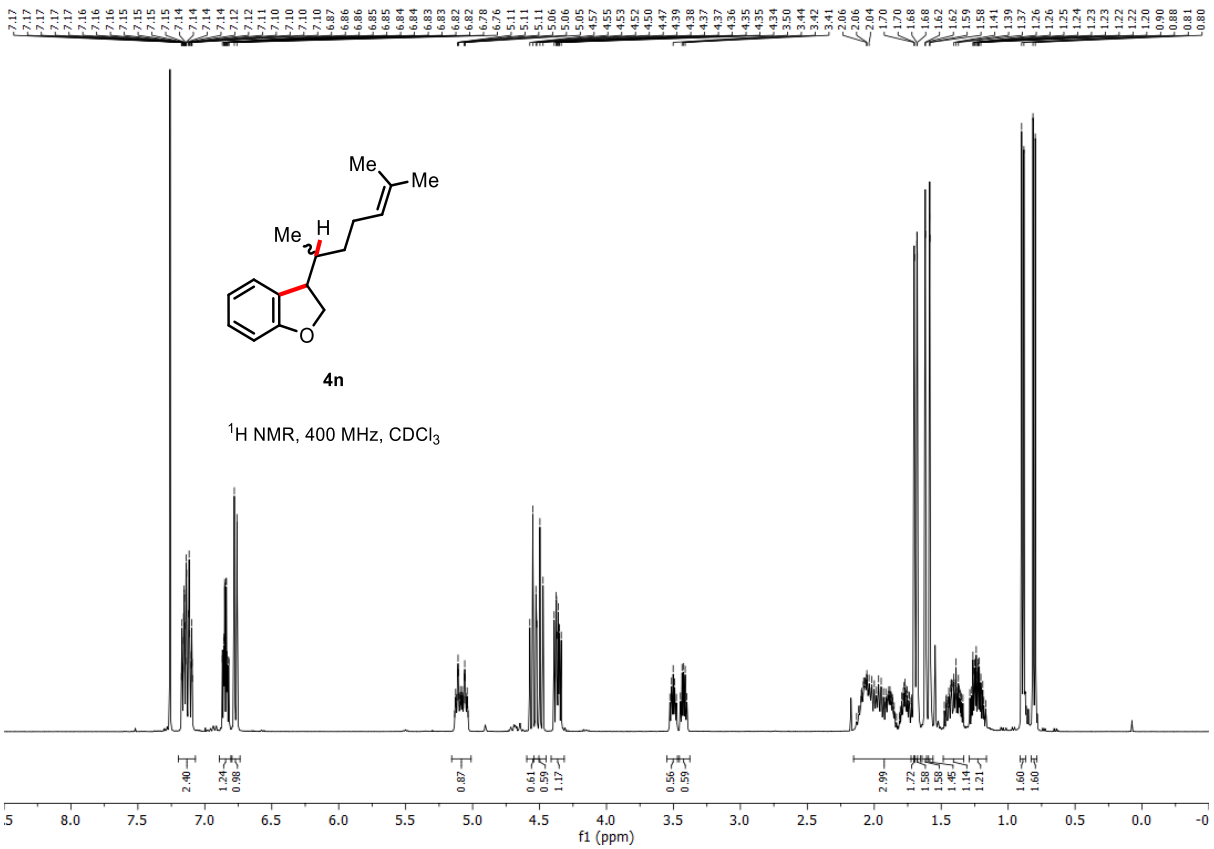
4m

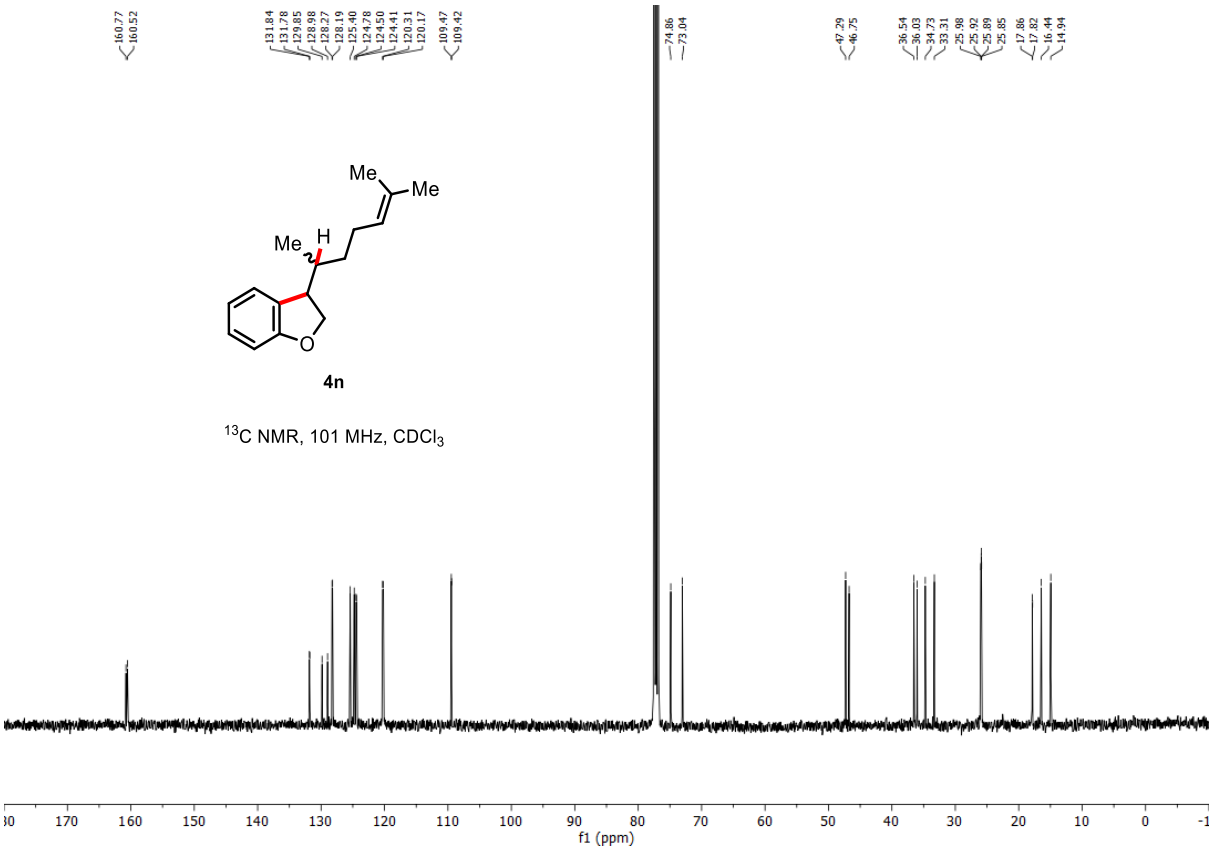
^{1}H NMR, 400 MHz, $CDCl_3$

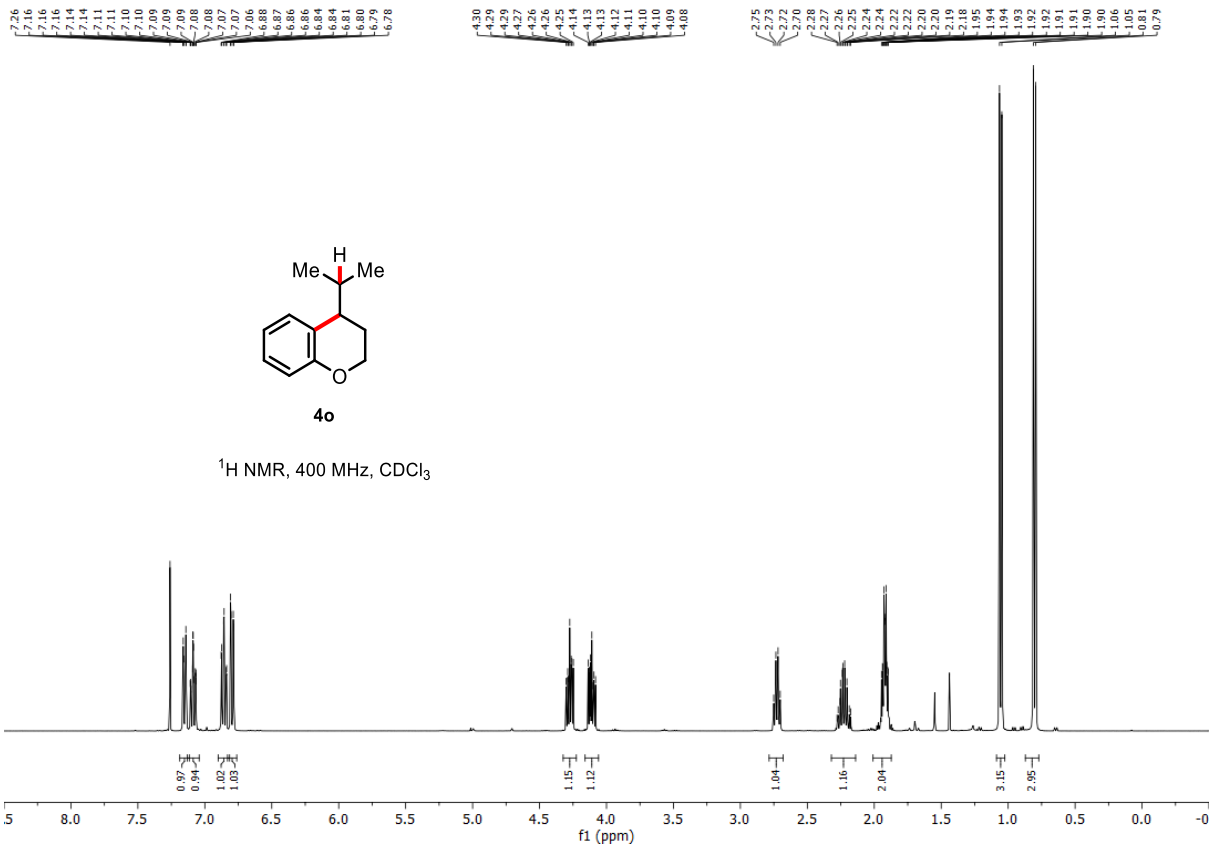


4m

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

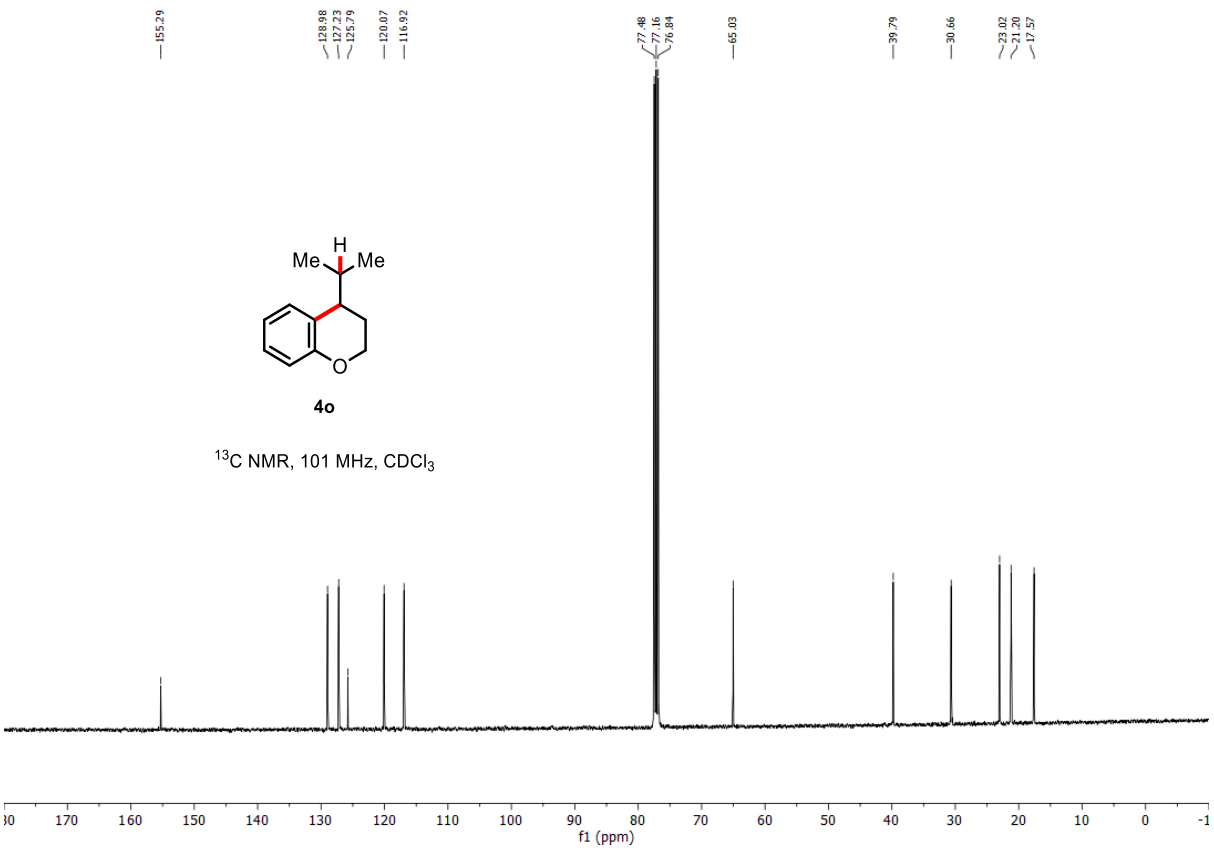

Me
Me
Me
H
O
4n
^{1}H NMR, 400 MHz, $CDCl_3$
f1 (ppm)


Me
Me
Me
H
O
4n
^{13}C NMR, 101 MHz, $CDCl_3$
f1 (ppm)



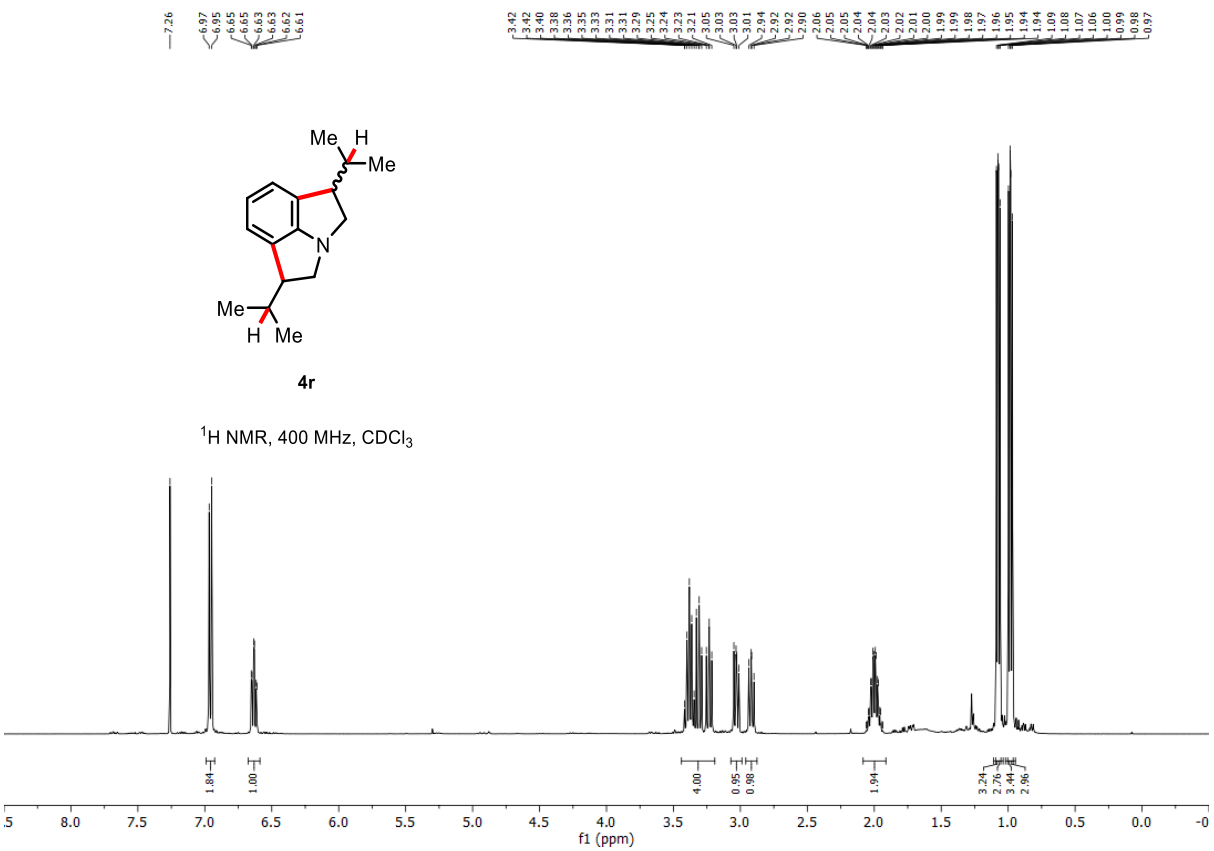
4o

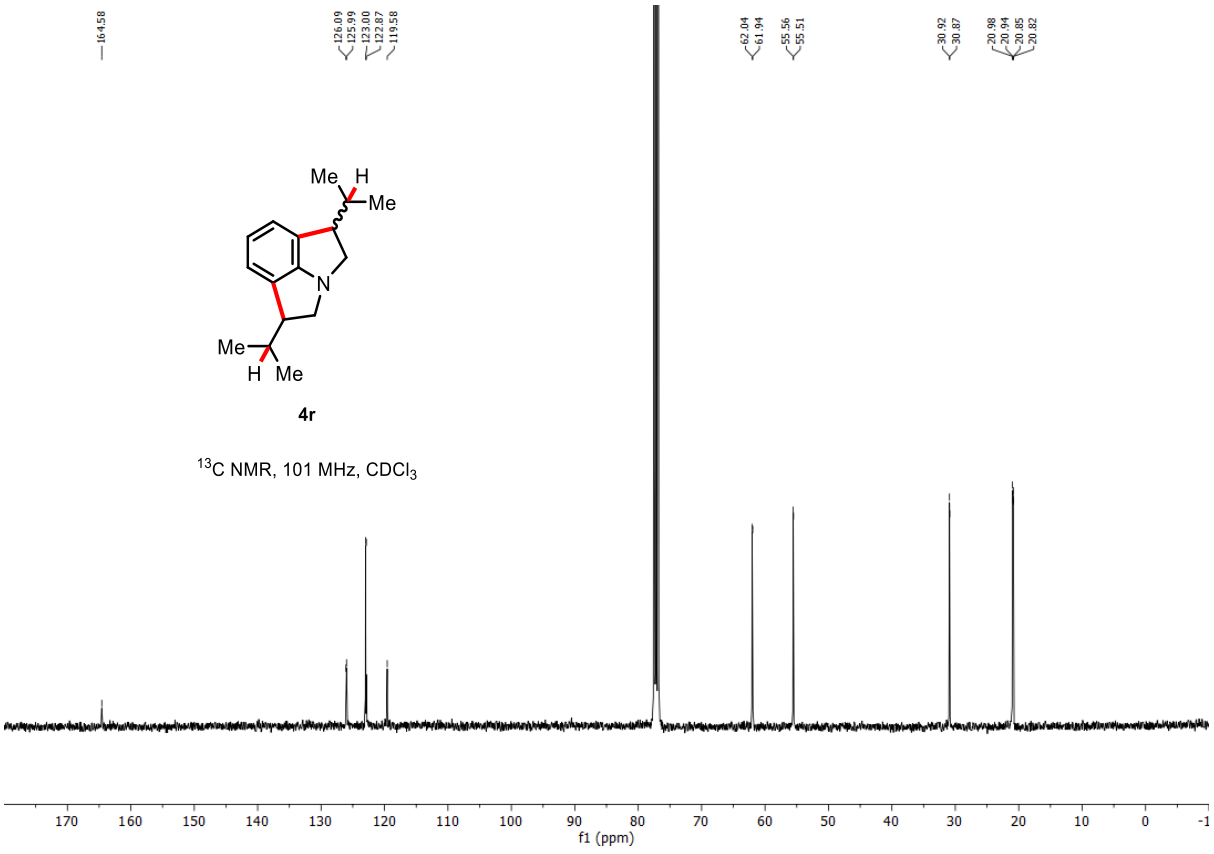
^{1}H NMR, 400 MHz, $CDCl_3$

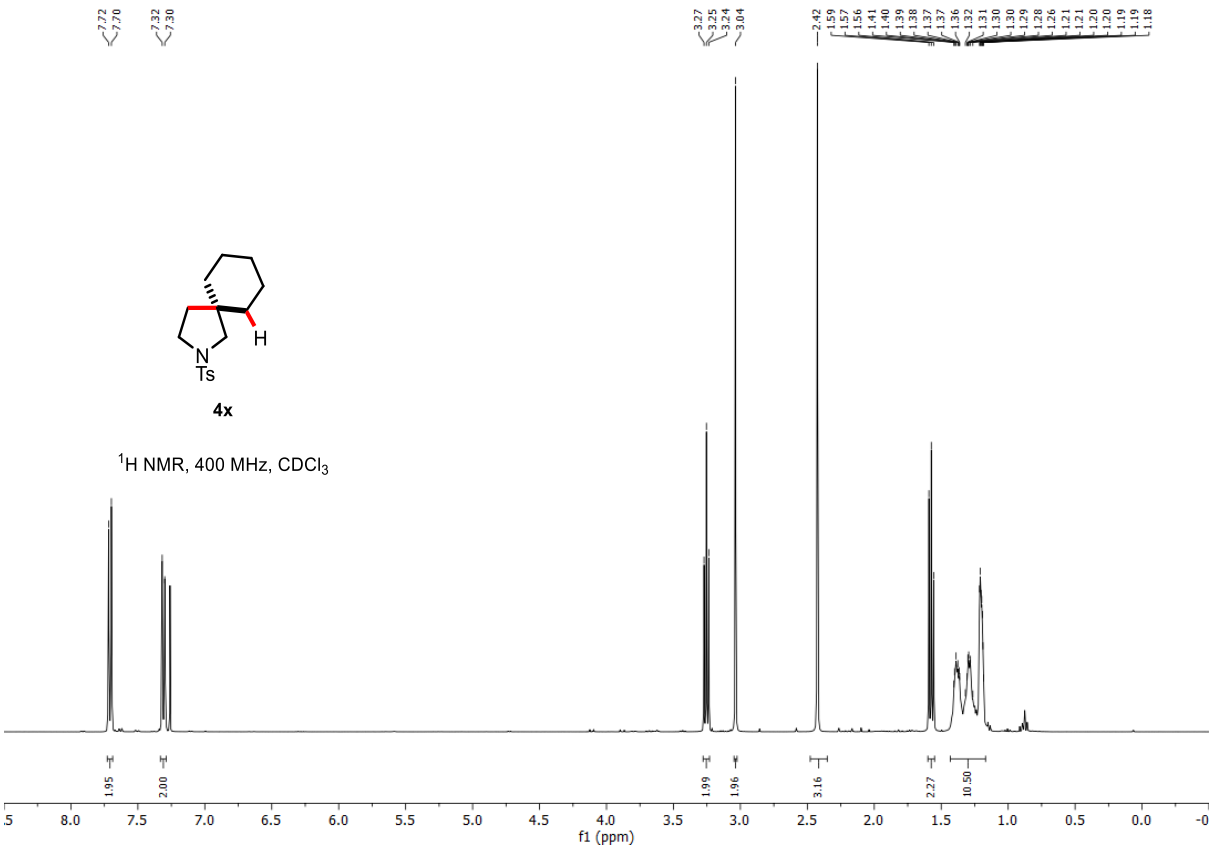


4o

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

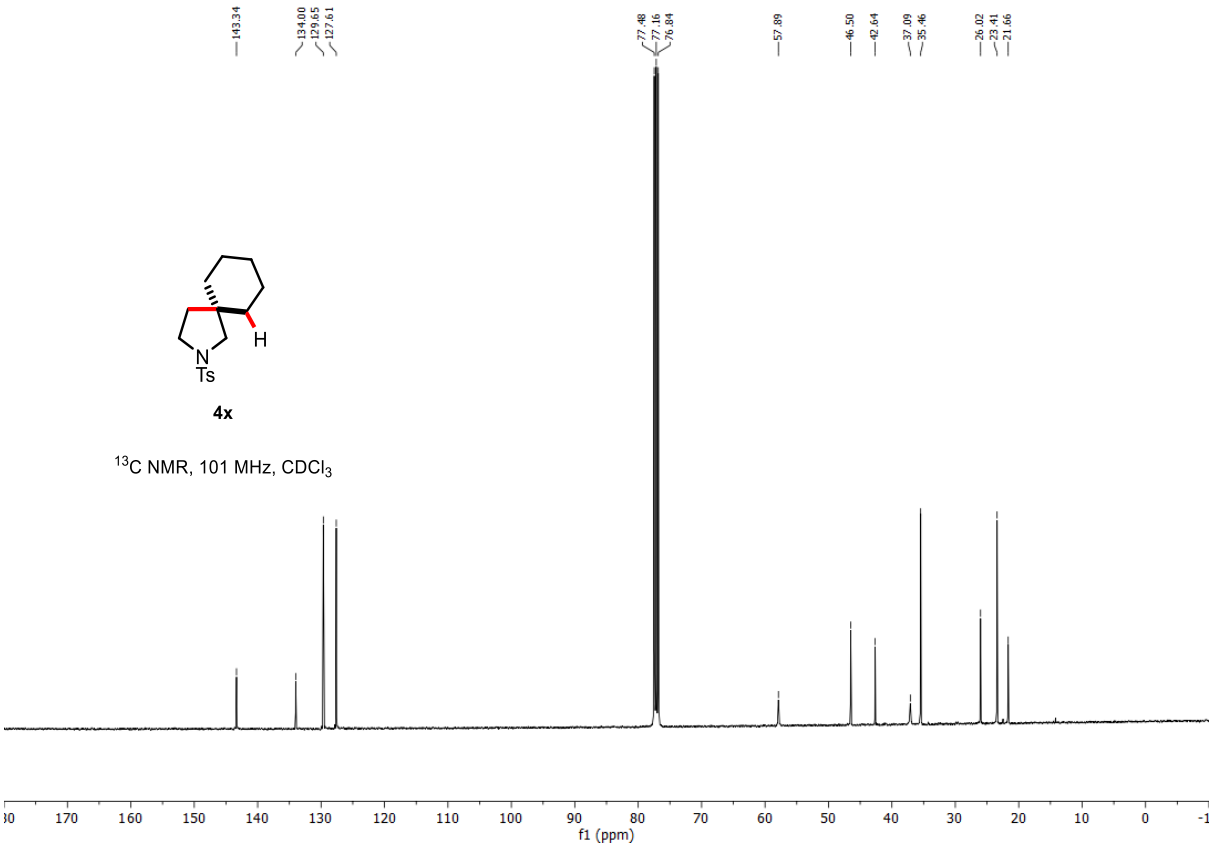

Me H
Me
N
Me
H Me
4r
1H NMR, 400 MHz, CDCl3
f1 (ppm)


Me H
Me
N
Me
H Me
4r
13C NMR, 101 MHz, CDCl3
f1 (ppm)



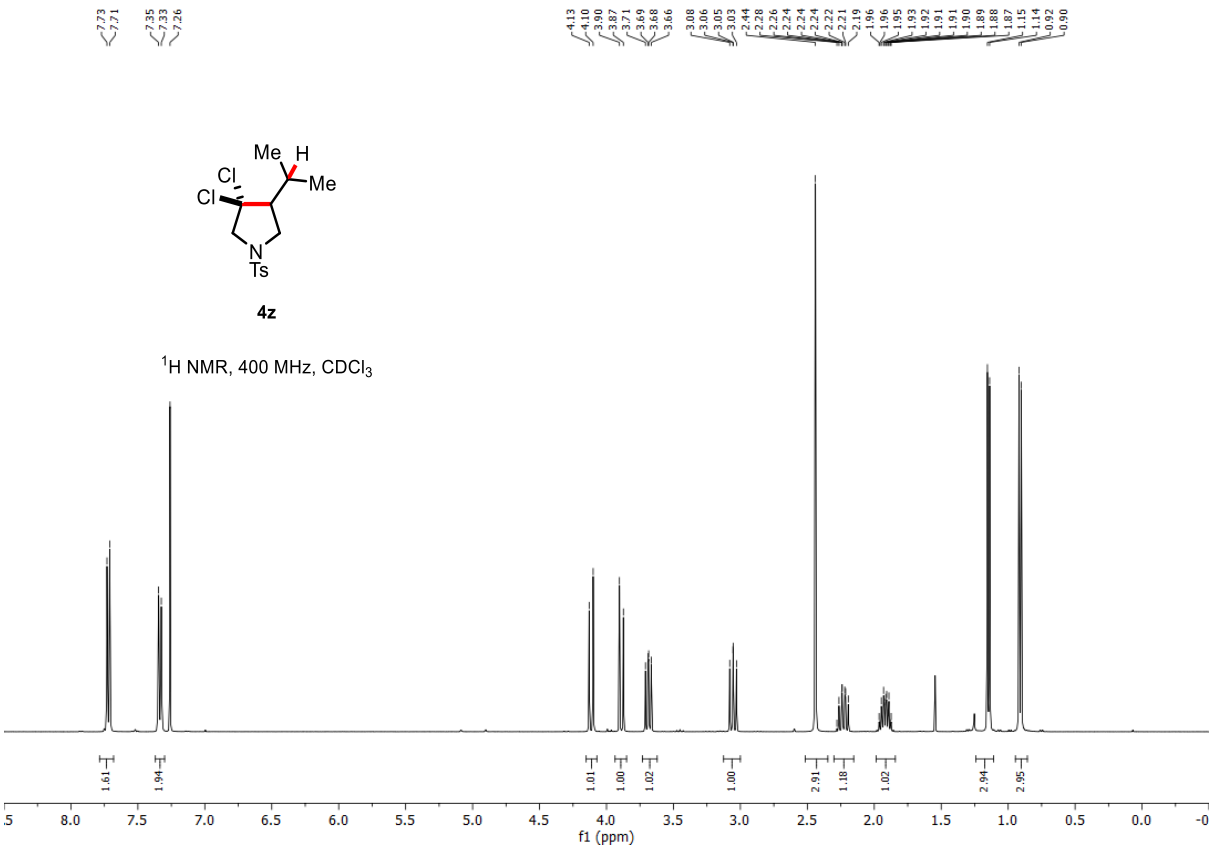
4x

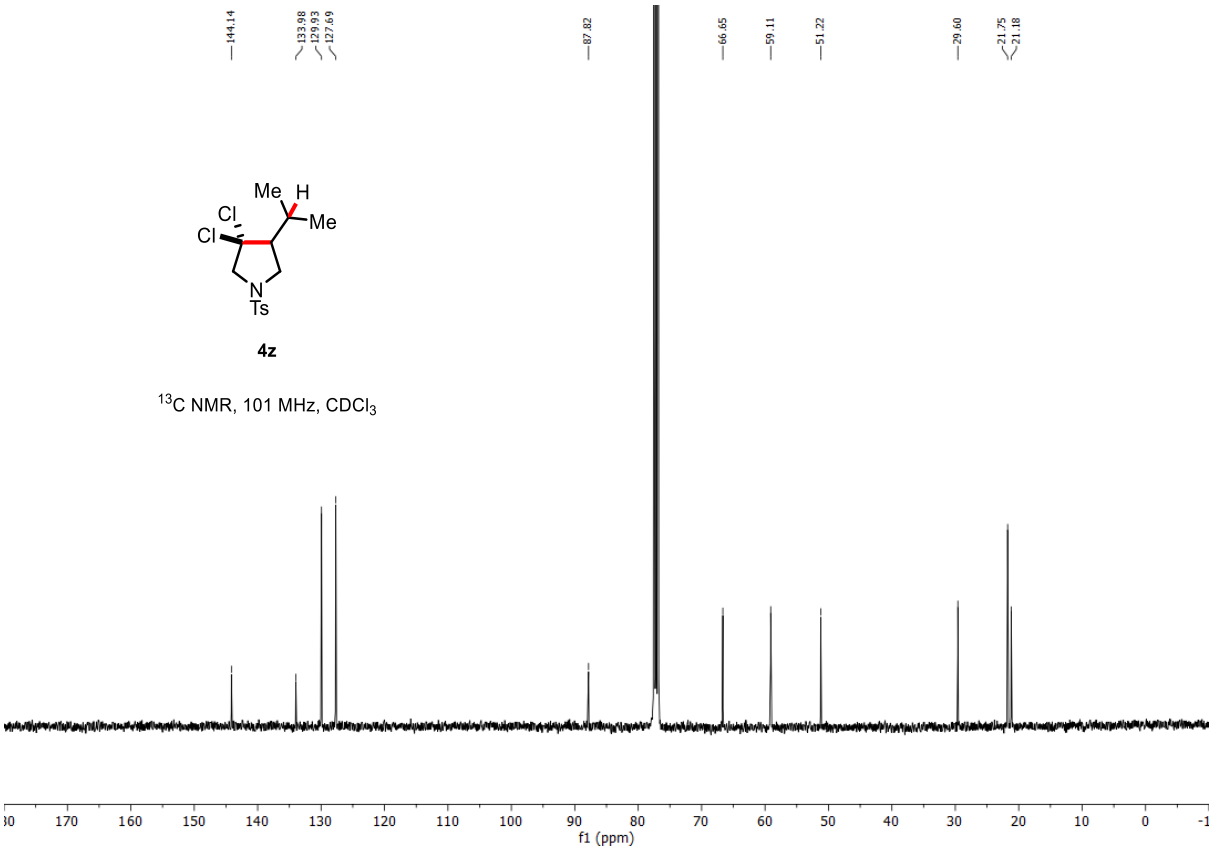
^{1}H NMR, 400 MHz, $CDCl_3$

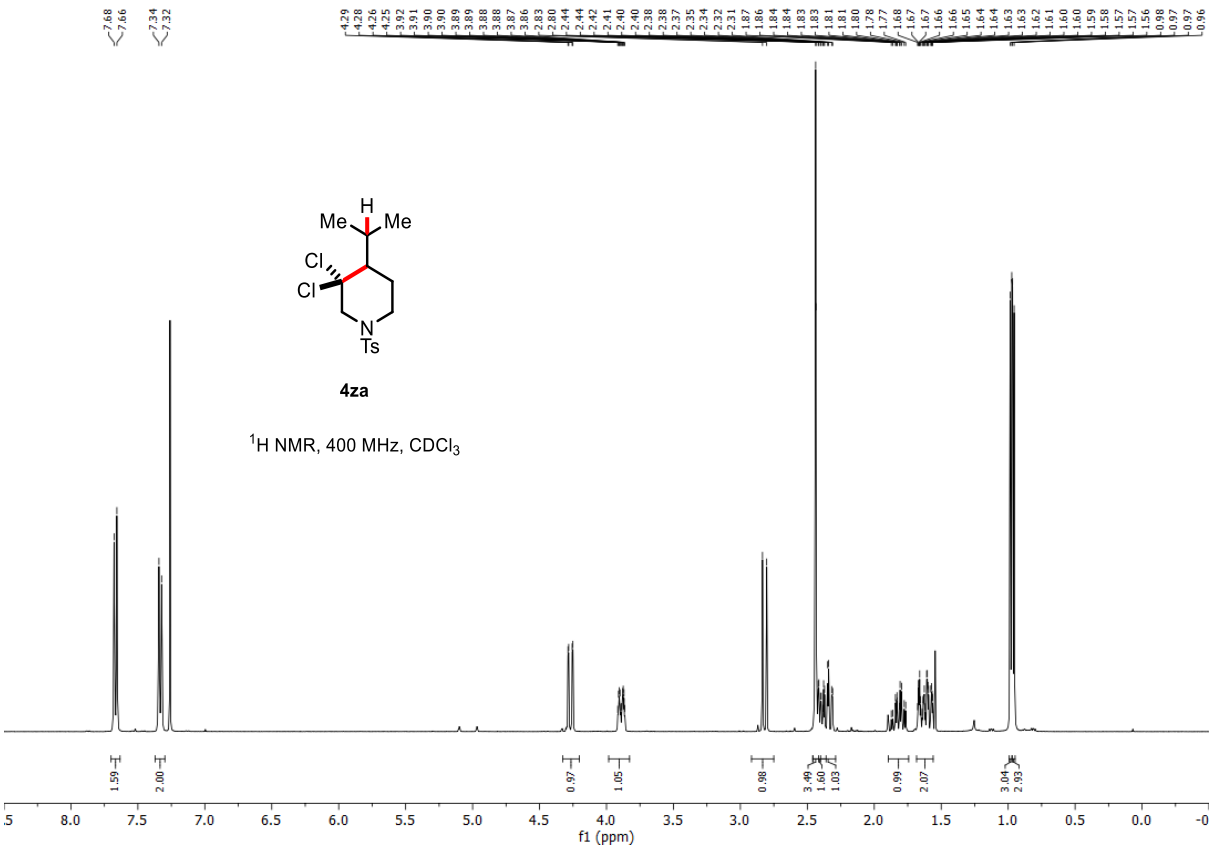


4x

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

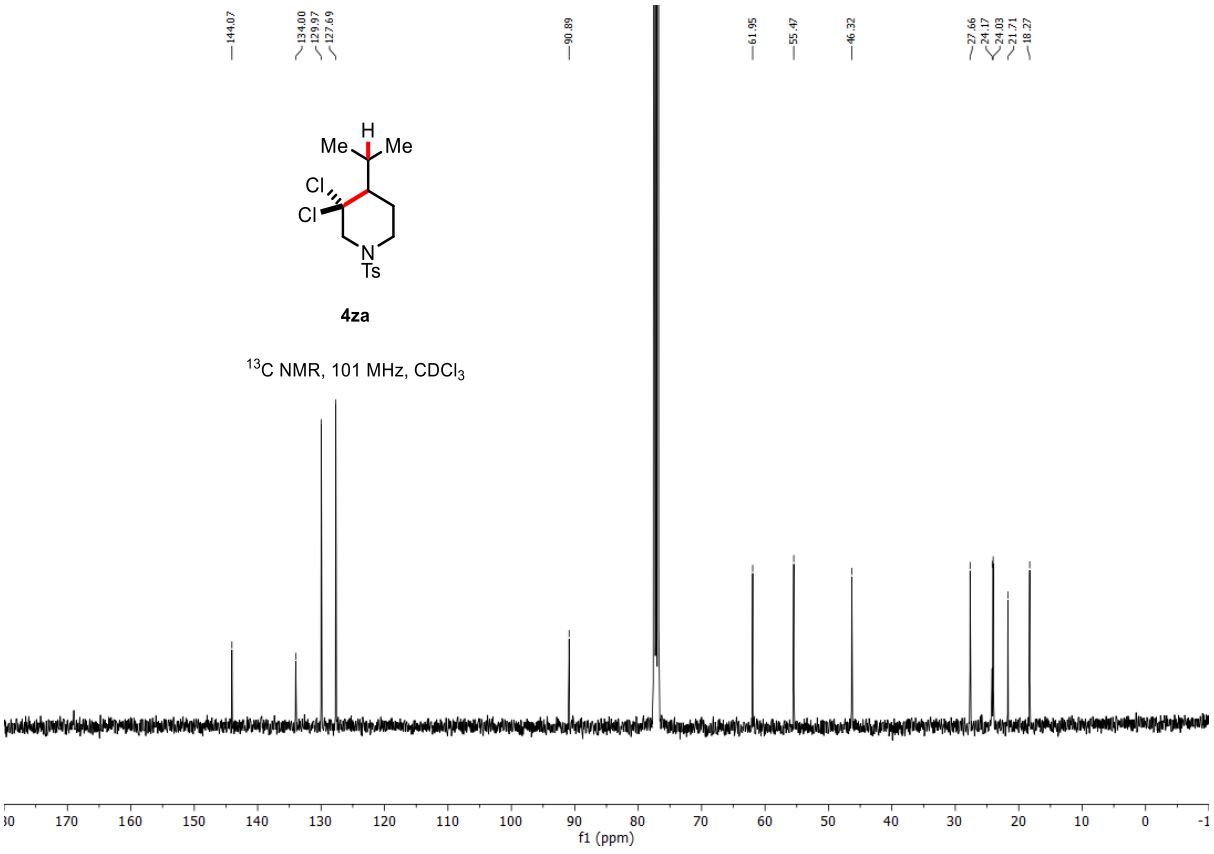

Me H
Cl
Cl
Me
N
Ts
4z
1H NMR, 400 MHz, CDCl3
f1 (ppm)


Me H
Cl
Cl
Me
N
Ts
4z
13C NMR, 101 MHz, CDCl3
f1 (ppm)



4za

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



4za

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