**Supporting Information**

# Copper-Catalyzed C–H Fluorination/Functionalization Sequence Enabling Benzylic C–H Cross Coupling with Diverse Nucleophiles

Aristidis Vasilopoulos, Dung L. Golden, Joshua A. Buss, and Shannon S. Stahl*

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue
Madison, WI, 53706, United States

stahl@chem.wisc.edu

## Table of Contents

## I. General Considerations

All reagents were purchased from commercial sources and used as received. Nearly identical performance was observed when using reagents from different commercial sources. Cu salts were purchased from Strem Chemicals and Sigma-Aldrich. C–H substrates and nucleophiles were purchased from Oakwood, Combi-Blocks, Enamine, AK Scientific, TCI America, Ark-Pharm, Ambeed, or Sigma-Aldrich. Nosyl protected amines were synthesized from the corresponding primary amines according to a literature procedure.[1] 3-Phenylpropyl trifluoroacetamide was synthesized according to a literature procedure.[2] NFSI was purchased from Ark-Pharm and Oakwood. Bathophenanthroline and other ligands were purchased from Aldrich, Ambeed, or Strem. The boron reagents were purchased from Sigma-Aldrich, Oakwood, or Combi-Blocks.

All fluorination reaction solids were weighed out on the benchtop, while liquids were added in an inert atmosphere ($N_2$) glovebox. Retention in performance can be obtained by setting up the fluorination reaction on the benchtop with backfilling or sparging of the reaction vessel with $N_2$. The fluorine displacement reactions were all set-up on the benchtop under air. The displacement step can produce catalytic quantities of HF (quenches on the reaction vial), so it is recommended to have ready access to a tube of calcium gluconate in case of accidental exposure to the reaction mixture. $^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on a Bruker Avance III 400 spectrometer at 25 °C ($^1$H 400.1 MHz, $^{13}$C 100.6 MHz, $^{19}$F 376.5 MHz) or a Bruker Avance III 500 spectrometer at 25 °C ($^1$H 500.1 MHz, $^{13}$C 125.7 MHz, $^{19}$F 470.6 MHz), except where noted otherwise, and chemical shifts are reported in parts per million (ppm). NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm ($^1$H) and $CDCl_3$ at 77.16 ppm ($^{13}$C). All $^{19}$F NMR spectra were absolutely referenced to their respective solvent peaks in the $^1$H NMR spectrum. Chromatography was performed using an automated Biotage Isolera® with reusable 25 g Biotage® Sfär Silica HC D cartridges for normal phase or 60 g Biotage® SNAP Ultra C18 cartridges for reversed phase. High-resolution mass spectra were obtained using a Thermo Q Exactive™ Plus via (ASAP-MS) by the mass spectrometry facility at the University of Wisconsin.

## II. General Procedure for Benzylic C–H Fluorination and NMR Quantitation

*Warning: This reaction evolves gas from protonation of $Li_2CO_3$, which is able to pressurize the reaction vial. Be sure to take appropriate safety precautions.*

**Set-up:** On the benchtop, a disposable 4 mL glass vial was charged with $MeB(OH)_2$ (0.6 mmol, 35.9 mg, 2 equiv), $Li_2CO_3$ (0.9 mmol, 66.5 mg, 3 equiv), N-fluorobenzenesulfonimide (NFSI; 0.75 mmol, 236.5 mg, 2.5 equiv), and a Teflon stir bar. The vial was sealed by a PTFE-lined pierceable cap. Bathophenanthroline (BPhen, 0.0216 mmol, 7.2 mg, 0.072 equiv) was weighed into a secondary vial with a Teflon stir bar. Both vials were then transferred to a purging glovebox under $N_2$(g). In the glovebox, CuOAc (0.018 mmol, 2.2 mg, 0.06 equiv) was weighed into the vial containing BPhen. Chlorobenzene (1.8 mL) was added to this vial and the vial is stirred to form a deep red 0.01 M stock solution of copper catalyst. The C–H substrate (0.3 mmol, 1 equiv) was weighed into the vial containing the rest of the reaction components, and then 0.6 mL of the copper catalyst solution was transferred to the reaction vial to give a 0.5 M mixture with a 2 mol% catalyst loading. The solution color changes from red to blue/green. This reaction vial is then removed from the glovebox and set to stir at 45 °C on a stirring hotplate in an aluminum block at 600 rpm for 16 h.

**Work-up:** At the end of the reaction, the mixture often becomes a light blue paste. The cap of the vial is loosened to vent the pressure build-up from the reaction. Dibromomethane (0.3 mmol, 21 µL, 1 equiv) and trifluorotoluene (0.3 mmol, 37 µL, 1 equiv) are then added as $^1$H and $^{19}$F NMR standards, respectively. The mixture is then diluted with $CDCl_3$ (0.6 mL), mixed, and a 30 µL aliquot is taken and filtered over a 1-inch celite plug directly into an NMR tube using $CDCl_3$ (in a few cases, dilution was done with dichloromethane or $CHCl_3$). The amount of benzyl fluoride product is then quantified relative to the two added internal standards. For more information on the quantitation method, see Section VII.

*Reaction tip:*

- The fluorination reaction is highly temperature sensitive, so it is recommended to use a hot plate with a thermocouple.
- For scale up reactions, it may be beneficial to use DCM or acetone as the solvent to improve homogeneity of the reaction.

## III. General Procedure for Catalyzed Benzyl Fluoride Displacement

*Warning: This reaction gradually produces HF, which is seemingly quenched via etching of the inside of the borosilicate vial. This reaction could degrade glass reaction vessels.*

**Set-up:** Following NMR quantitation of the benzyl fluoride product, sodium dithionite (1 equiv with respect to the amount of NFSI used, ~150-250 mg) is added with 100 µL water directly to the reaction vial. The reaction is then stirred for 15 min to quench the remaining NFSI (*warning*: dithionite oxidation results in protonation of remaining $Li_2CO_3$,[3] leading to further pressure build-up). This typically changes the reaction to a red color. The chunky mixture is then filtered over a 3-inch pad of silica or celite into a disposable 15 mL glass vial using dichloromethane as the eluent (silica is preferred if the benzyl fluoride tolerates it). After flushing to a filtrate volume of 5 mL, $MgSO_4$ (3-7 equiv, ~300 mg) is added to the vial and it is allowed to dry for 10 min. Meanwhile, the nucleophile (0.75 mmol, 2.5 equiv) is weighed into another disposable 15 mL glass vial with a Teflon coated stir bar. The benzyl fluoride-containing solution is filtered over a 1-inch celite plug into the 15 mL vial containing the nucleophile, and then 1 mL of additional dichloromethane is used to flush the plug and bring the final reaction volume to 6 mL (0.05 M). The vessel is then sealed with a PTFE-lined pierceable cap and hexafluoroisopropanol (HFIP; 3 mmol, 315 µL, 10 equiv) and/or $BF_3$•$Et_2O$ (0.03 mmol, 3.7 µL, 0.1 equiv) is added to catalyze fluoride displacement. The reaction is stirred overnight. An aliquot of this reaction solution is then taken for $^1$H NMR analysis to determine whether it is complete. Reactions showing incomplete fluoride conversion are subjected to harsher displacement conditions (i.e., heated to 45 °C in an aluminum block on a hotplate or additional $BF_3$•$Et_2O$ is added). The final solution is concentrated on a rotovap and purified using automated flash column chromatography to yield the desired functionalization product.

*Reaction tips:*

- Lewis basic functional groups disrupt fluoride displacement. When using coupling partners with Lewis basic groups, it is typically required to use additional $BF_3$ to enact displacement (>0.25 equiv $BF_3$ is common, *cf.* Substrates **37** and **42**).
- Protonation of Lewis basic groups may also be helpful for enabling displacement reactivity (*cf.* Substrate **31**)

## IV. Procedure for 3 mmol Scale Fluorination/Functionalization Sequence to Prepare 46

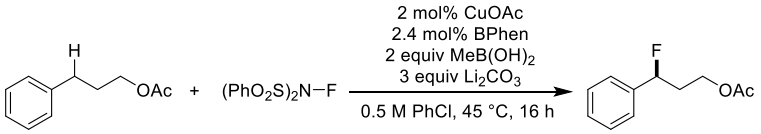
**Fluorination:** On the benchtop, a disposable 20 mL glass vial was charged with $MeB(OH)_2$ (6 mmol, 359 mg, 2 equiv), $Li_2CO_3$ (9 mmol, 665 mg, 3 equiv), NFSI (7.5 mmol, 2.365 g, 2.5 equiv), and a Teflon stir bar. The vial was sealed by a PTFE-lined pierceable cap. Bathophenanthroline (BPhen, 0.072 mmol, 23.9 mg, 0.024 equiv) was weighed into a secondary vial with a Teflon stir bar. Both vials were then transferred to a purging glovebox under $N_2$(g). In the glovebox, CuOAc (0.06 mmol, 7.4 mg, 0.02 equiv) was weighed into the vial containing BPhen followed by addition of chlorobenzene (6 mL, 0.5 M). This solution was allowed to stir for 3 minutes to form a deep red solution. 1-chloro-3-phenylpropane (3 mmol, 429 μL, 1 equiv) was then weighed into the vial containing the rest of the reaction components and the copper catalyst solution was transferred to the reaction vial. The reaction vial was then sealed, removed from the glovebox, and set to stir at 45 °C in an aluminum block on a heated stir plate at 600 rpm for 16 h.

**Functionalization:** The cap was carefully opened to release built-up pressure (the septum may have been pierced with a needle instead). Dibromomethane was then added as an NMR standard (1 mmol, 70.2 μL, 0.33 equiv) and a 50 uL aliquot was taken and filtered over celite with 450 uL $CDCl_3$ directly into an NMR tube for NMR quantitation. To the reaction vial was added sodium dithionite (7.5 mmol, 1.305 g, 2.5 equiv) and water (500 uL) and this mixture was allowed to stir for 10 minutes uncapped. After quenching NFSI, the now chunky red-white mixture was filtered over a 3-inch pad of silica directly into a 250 mL round bottom flask using dichloromethane (54 mL, final concentration of 0.05 M). *p*-Cresol (7.5 mmol, 811 mg, 2.5 equiv) was added to the round bottom flask followed by HFIP (30 mmol, 3.159 mL, 10 equiv) and after initial agitation, the reaction was left to sit at room temperature for 16 h.

**Work-up:** A 100 μL aliquot was taken from the now light gold solution for NMR analysis to detect formation of product and consumption of benzyl fluoride ($^1H$ and $^{19}F$). If any residual fluoride were detected, the vessel would have been warmed to 40 °C on an aluminum block or catalytic $BF_3$•$Et_2O$ would have been added. The reaction was concentrated on the rotovap at 40 °C to remove the solvent (chlorobenzene, dichloromethane, and HFIP) and the concentrated residue was purified by reverse phase chromatography using a 65%→100% MeOH in water gradient. The product fractions were collected and concentrated on the rotovap at 50 °C to yield 445 mg of the desired diarylalkane product **46**, corresponding to 57% yield with respect to the starting C–H substrate).

## V. Screening Tables

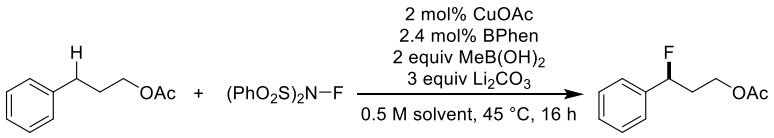
**Table S1.** Control Experiments Table




| entry | control | MB | % SM | % C-N | % C-F($F_2$)[a] |
|---|---|---|---|---|---|
| 1 | No CuOAc | 102 | 102 | -- | -- |
| 2 | No BPhen | 101 | 77 | -- | 24 |
| 3 | No NFSI | 102 | 102 | -- | -- |
| 4 | No $Li_2CO_3$ | 70 | 70 | -- | -- |
| 5 | No $MeB(OH)_2$ | 103 | 103 | -- | -- |
| 6 | Under Air | 66 | 42 | -- | 24 |

[a]Reactions run at 0.2 mmol scale. Calibrated $^1$H NMR yields using mesitylene as an internal standard.

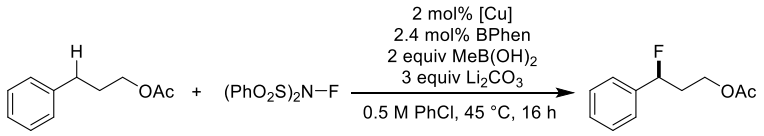
**Table S2.** Solvent Screening Table




| entry | solvent | MB | % SM | % C-N | % C-F($F_2$)[a] |
|---|---|---|---|---|---|
| 1 | DCM | 76 | 9 | -- | 64(3) |
| 2 | DCE | 87 | 16 | -- | 69(2) |
| 3 | MeCN | 25 | 2 | -- | 23 |
| 4 | EtOAc | 80 | 26 | -- | 53(1) |
| **5** | **acetone** | **71** | **--** | **--** | **68(3)** |
| 6 | PhF | 94 | 38 | -- | 55(1) |
| 7 | $PhCF_3$ | 89 | 38 | -- | 50(1) |
| **8** | **PhCl** | **98** | **19** | **--** | **76(3)** |
| 9 | PhCl (0.4 M) | 79 | 7 | -- | 68(4) |
| 10 | PhCl (0.3 M) | 85 | 9 | -- | 72(4) |
| 11 | PhCl (0.2 M) | 77 | 18 | -- | 59 |
| 12 | PhCl (0.1 M) | 77 | 21 | -- | 56 |

[a]Reactions run at 0.2 mmol scale. Calibrated $^1$H NMR yields using mesitylene as an internal standard.

**Table S3.** Cu Salt Screening Table

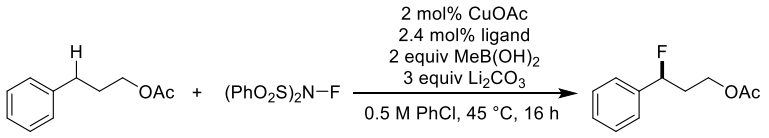



1 equiv 2.0 equiv

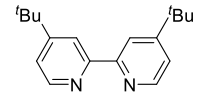
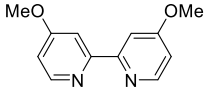
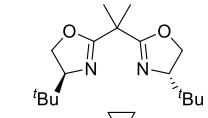
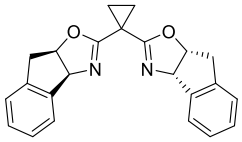
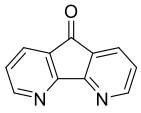
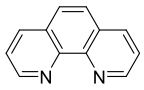
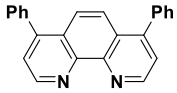
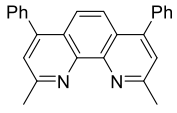
| entry | Cu salt | MB | % SM | % C-N | % C-F($F_2$)[a] |
|---|---|---|---|---|---|
| 1 | CuI•DMS | 74 | 5 | -- | 64(5) |
| 2 | CuBr•DMS | 80 | 9 | -- | 68(3) |
| 3 | CuCl | 88 | 17 | -- | 68(3) |
| **4** | **CuOAc** | **82** | **2** | **--** | **73(7)** |
| 5 | $Cu(MeCN)_4PF_6$ | 94 | 31 | -- | 63 |
| 6 | CuCN | 102 | 92 | -- | 10 |
| 7 | $Cu(OAc)_2$ | 90 | 9 | 5 | 76 |
| 8 | $Cu(OTf)_2$ | 100 | 100 | -- | -- |

[a]Reactions run at 0.2 mmol scale. Calibrated $^1$H NMR yields using mesitylene as an internal standard.

**Table S4.** Ligand Screening Table

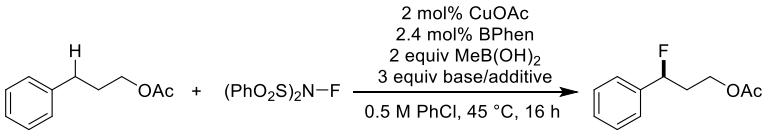



1 equiv 2.0 equiv

| entry | ligand | MB | % SM | % C-N | % C-F($F_2$)[a] |
|---|---|---|---|---|---|
| 1 |  | 93 | 7 | 0 | 81(5) |
| 2 |  | 94 | 37 | 0 | 57 |
| 3* |  | 101 | 56 | 0 | 45 |
| 4* |  | 103 | 46 | 0 | 56(1) |
| 5 |  | 90 | 56 | 0 | 34 |
| 6 |  | 101 | 48 | 0 | 53 |
| **7*** |  | **101** | **19** | **0** | **78(4)** |
| 8 |  | 91 | 29 | 0 | 61(1) |

[a]Reactions run at 0.2 mmol scale. Calibrated $^1$H NMR yields using mesitylene as an internal standard. *In an experiment with 2-(S)-acetoxy-4-phenylbutane, these three ligands formed the fluorinated product with an identical d.r. of 2:1 (avg yield 50%). It is unlikely that enantioselectivity would be observed in fluorination of achiral benzylic substrates when using the chiral ligands in entries 3 or 4.

**Table S5.** Base Screening Table

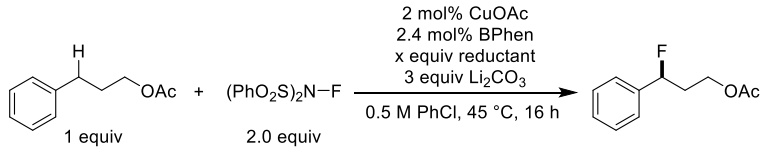



1 equiv 2.0 equiv

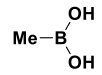
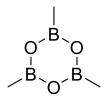
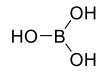
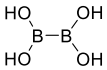
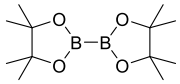
| entry | base/additive | MB | % SM | % C-N | % C-F($F_2$)[a] |
|---|---|---|---|---|---|
| 1 | $K_2CO_3$ | 92 | 75 | -- | 17 |
| 2 | $Na_2CO_3$ | 84 | 30 | -- | 54 |
| 3 | **$Li_2CO_3$** | **97** | **13** | **--** | **78(6)** |
| **4** | LiOAc | 97 | 40 | -- | 57 |
| 5 | $NaHCO_3$ | 70 | 12 | -- | 58 |
| 6 | Li$O^tBu$ | 100 | 100 | -- | -- |
| 7 | LiOTf | 82 | 82 | -- | -- |
| 8 | $K_3PO_4$ | 99 | 99 | -- | -- |

[a]Reactions run at 0.2 mmol scale. Calibrated $^1$H NMR yields using mesitylene as an internal standard.

**Table S6.** Reductant Screening Table

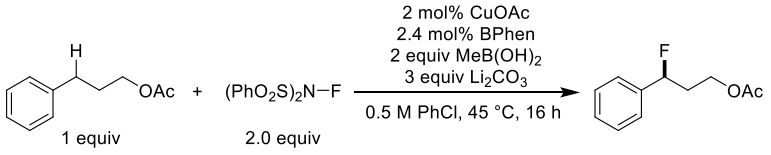



1 equiv 2.0 equiv

| entry | reductant | equiv | MB | % SM | % C-N | % C-F($F_2$)[a] |
|---|---|---|---|---|---|---|
| 1 |  | **2** | **88** | **5** | **--** | **77(6)** |
| 2 |  | 2 | 40 | -- | -- | 37(3) |
| 3 |  | 2 | 103 | 103 | -- | -- |
| 4 |  | 2 | 64 | 10 | -- | 54 |
| 5 |  | 2 | 61 | 9 | -- | 52 |

[a]Reactions run at 0.2 mmol scale. Calibrated $^1$H NMR yields using mesitylene as an internal standard.

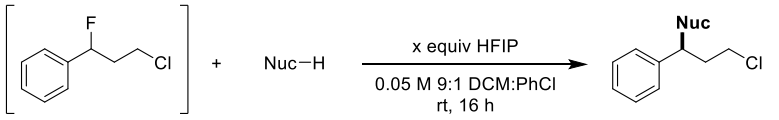
**Table S7.** Reaction Stoichiometry Screening Table

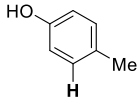



| entry | variation | MB | % SM | % C-N | % C-F($F_2$)[a] |
|---|---|---|---|---|---|
| 1 | standard cond. | 95 | 2 | -- | 80(5) |
| 2 | 35 °C | 93 | 44 | -- | 48(1) |
| 3 | 55 °C | 92 | 3 | -- | 74(10) |
| 4 | 1 equiv. NFSI | 90 | 34 | -- | 52(2) |
| 5 | 3 equiv. NFSI | 98 | 7 | -- | 89(5) |
| 6 | 1 equiv. $Li_2CO_3$ | 95 | 13 | -- | 78(4) |
| 7 | 2 equiv. $Li_2CO_3$ | 93 | 5 | -- | 82(6) |
| 8 | 1 equiv. $MeB(OH)_2$ | 95 | 12 | -- | 79(4) |
| 9 | 2.5 equiv. $MeB(OH)_2$ | 97 | 3 | -- | 87(7) |
| 10 | 1 mol% BPhen | 100 | 12 | -- | 83(5) |
| 11 | 4 mol% BPhen | 103 | 103 | -- | 0 |
| 12 | 1 mol% CuOAc/ 1 mol% BPhen | 96 | 12 | -- | 80(4) |
| 13 | 10 mol% CuOAc/ 10 mol% BPhen | 83 | 13 | -- | 47(3) |
| 14 | 10 mol% CuOAc/ 5 mol% BPhen | 92 | 18 | -- | 63(2) |

[a]Reactions run at 0.2 mmol scale. Calibrated $^1$H NMR yields using mesitylene as an internal standard. Mass balance in this table also accounts for formation of the benzyl ketone.

**Table S8.** HFIP Loading Screening Table



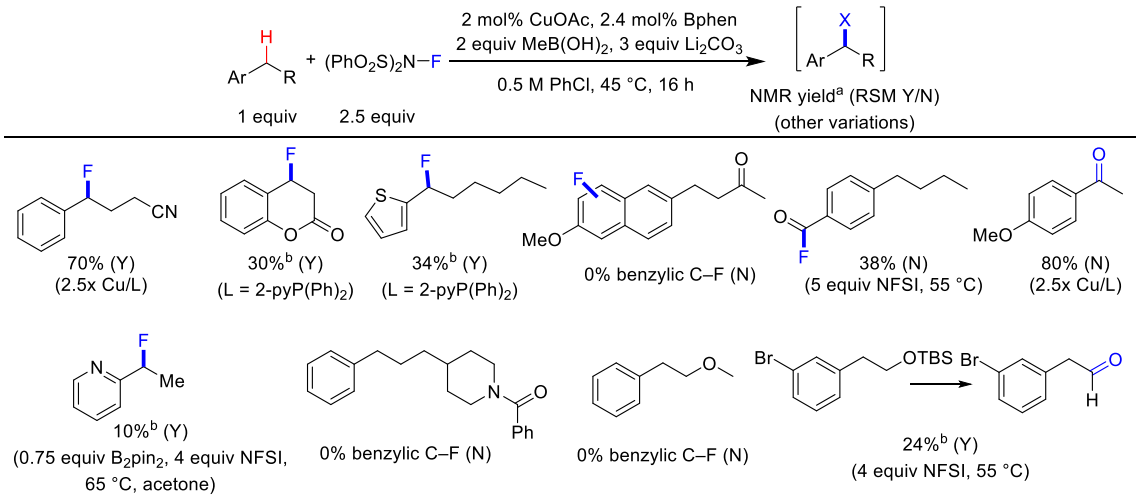

| entry | Nuc–H | equiv HFIP | % SM | % C-Nuc[a] |
|---|---|---|---|---|
| 1 |  | 2 | - | 69 |
| 2 | | **10** | **-** | **100** |
| 3 | | 27 | - | 90 |
| 4 |  | 2 | 100 | **-** |
| 5 | | **10** | **-** | **96** |
| 6 | | 27 | - | 95 |
| 7 |  | 2 | - | 60 |
| 8 | | **10** | **-** | **90** |
| 9 | | 27 | - | 78 |

[a]Reactions run at 0.3 mmol scale. Calibrated $^1$H NMR yields with respect to the benzyl fluoride using $CH_2Br_2$ as an internal standard. HFIP ether product is observed in reactions with 27 equiv HFIP.

## VI. Additional Experiments and Observations

### Less Successful C–H Fluorination Substrates

**Table S9.** Benzylic C–H fluorination results for substrates not included in Scheme 2.



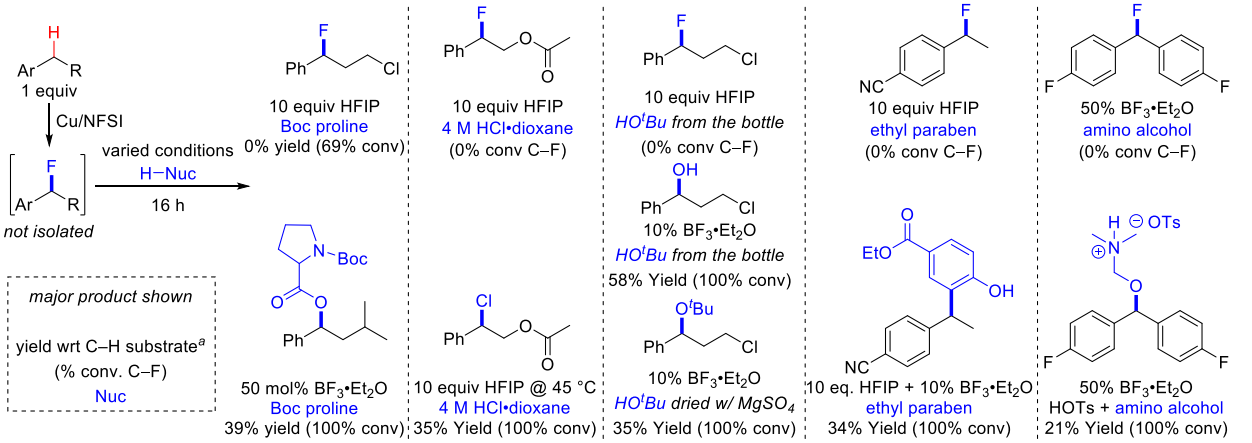

[a]Calibrated $^1$H NMR yields using dibromomethane as the internal standard. Reactions with (Y) indicates that remaining starting material was the major remaining mass balance component. Reactions with (N) indicates that all starting material was consumed. [b]Half Cu/L loading, 1 equiv $B_2pin_2$ no $MeB(OH)_2$

*Discussion:*

The collection of molecules in Table S9 includes products omitted from the manuscript, typically because of low yields and observed deleterious side-reactivity (except for the alkylcyanide substrate, which was omitted because propylbenzene analogs are well-represented in Scheme 2). The lactone substrate suffers from low yield because more forcing conditions result in a competitive dehydrogenation pathway to afford the α,β-unsaturated ester. The thiophene substrate showed very poor mass balance and no product was formed when BPhen was used as the ligand. Nabumetone (the ketone with a naphthalene ring) underwent complete conversion of starting material, but the only fluorination products observed were aryl fluorides. An aryl aldehyde substrate was tested for fluorination, but aldehydic C–H fluorination was observed, which agrees with a recently reported method for acyl fluoride generation.[4] 4-Ethyl anisole oxidation resulted in complete conversion to *p*-methoxy acetophenone. The origin of ketone products likely traces back to C–F displacement by water from $Li_2CO_3$ to form the benzyl alcohol, which is oxidized *in situ* to the ketone ($MeB(OH)_2$ can also serve as a hydroxide source). It is also possible that the more electron-rich substrate oxidizes directly from the benzyl radical to a carbocation in solution, which is trapped by water and oxidized.[5] 2-Ethyl pyridine fluorination resulted in a low yield of heterobenzylic fluoride. The nucleophilic pyridine likely coordinates to an electrophile *in situ*, which deactivates the C–H site to HAT. Ionic chemistries are typically more effective for fluorination of these types of heterobenzylic substrates.[6] Benzylic substrates bearing an amide or ether functionality were not successfully fluorinated despite complete conversion of starting material. It is likely that the weak α-hetero C–H bonds compete for oxidation with the benzylic C–H site under these mildly basic conditions. A benzylic substrate with a TBS-protected alcohol was also tested in the fluorination reaction (92% conversion), but the TBS group is removed *in situ*, leading to an alcohol that is oxidized to an aldehyde (major observed product).

## Observations Regarding Nucleophilic Coupling Partners

**Table S10.** Comparisons between ineffective and effective conditions for forming desired product.

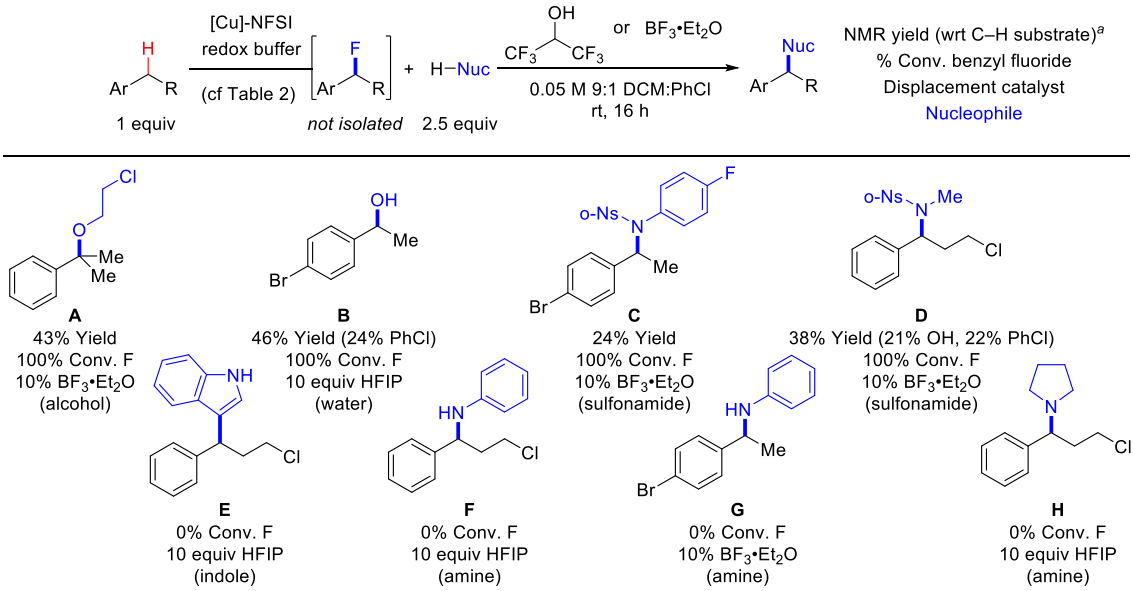



[a]Calibrated $^1$H NMR yields using dibromomethane as the internal standard. Yield calculated based on the starting C–H substrate. 2.5 equiv H–Nuc used, solvent is 9:1 DCM:PhCl at 0.05 M, and reactions run at room temperature unless otherwise noted. Product formation and conversion of starting material is improved from top to bottom.

*Discussion:*

Table S10 shows how changes in conditions could be used to make certain classes of nucleophiles effective for the functionalization reaction. When using Boc proline as the nucleophile, HFIP was not able to catalyze product formation. In general, Lewis basic functional groups like carbamates resulted in obstruction of C–F activation reactivity. For Boc proline, product formation could be enabled by using 50 mol% $BF_3$•$Et_2O$ as the catalyst. 2-Phenethylacetate has a C–F bond that is relatively recalcitrant towards activation (likely due to having an electron withdrawing group at the homobenzylic position). In order to activate the C–F bond for substitution by chloride, the reaction needed to be heated to 45 °C in an aluminum block on a hotplate. If *tert*-butanol is used as the nucleophile for displacement, HFIP does not catalyze displacement and $BF_3$•$Et_2O$ must be used. This may support an $S_N2$-like pathway for displacement under HFIP-catalyzed conditions.[7] If no precautions are taken to remove water when using *tert*-butanol as the nucleophile, the benzyl alcohol is formed as the product. If the reaction is dried with $MgSO_4$ and filtered before $BF_3$•$Et_2O$ is added, the *tert*-butyl ether product is formed instead. In Scheme 3, benzyl fluorides can be displaced by phenols like ethyl paraben in excellent yields when using HFIP as the catalyst. The benzyl fluoride from 4-ethyl benzonitrile is not activated under these conditions. In order to displace this electronically deactivated fluoride, $BF_3$•$Et_2O$ must also be added as a catalyst. This result suggests that electron-deficient aryl rings can stabilize benzyl fluorides. It is possible to protonate Lewis basic groups (like amines), so they do not interfere with C–F activation. This allows an amino alcohol to be used as an effective coupling partner (or a pyridine, cf. **31**). An acid with a DCM-soluble non-nucleophilic counterion should be used to avoid formation of side products (for example, TFA is able to compete for fluoride displacement, so TFA salts should not be used).

**Table S11.** Benzylic C–F displacement results for less effective C–H substrate/nucleophile pairs.




[a]Calibrated $^1$H NMR yields using dibromomethane as the internal standard. Yield calculated based on the starting C–H substrate.

*Discussion:*

Tertiary fluorides can be activated with $BF_3$•$Et_2O$ for trapping by nucleophilic species, albeit the resulting products may have stability issues (the tertiary ether, S11-A, decomposed after 2 days in DCM). For poor nucleophiles like water, it is possible for chlorobenzene to compete in fluoride displacement (S11-B and D). To avoid this issue, the fluorination reaction can be run in DCM. Another issue observed when using water as a nucleophile is that the resulting benzyl alcohol can serve as a nucleophile to form ethereal dimers of the starting material (this led to the relatively low yield of the benzyl alcohol **27** from 6-bromochromane). Ortho-nitro sulfonamide protecting groups can be used to protect primary amines to make competent nucleophiles, but the ortho-nosyl amines tend to have worse reactivity than para-nosyl amines in this reaction (compare S11-C to **43**). Nucleophiles with very Lewis basic groups like amines can completely shut down displacement of the benzyl fluoride (S11-E, F, G, H). It is possible that these groups compete with the fluoride for hydrogen-bond donors and for $BF_3$•$Et_2O$. Efforts to drive these reactions forward with heat (45 °C in an aluminum block on a hotplate) were unsuccessful (testing at higher temperature would need to be done in a different solvent).

## Site Selectivity for Fluorination of Benzylic C–H Bonds

Fluorination reactions were set up under standard conditions (see the general procedure in section II) except 5 equiv of each C–H substrate was employed (160 µL PhMe, 1.5 mmol, 5 equiv; 185 µL PhEt, 1.5 mmol, 5 equiv; 210 µL cumene, 1.5 mmol, 5 equiv). Reactions were worked up in the standard fashion and analyzed via $^{1}H$ and $^{19}F\{^{1}H\}$ NMR spectroscopy. Product yields were determined relative to $^{1}H$ ($CH_2Br_2$, 21 µL, 0.3 mmol, 1 equiv) and $^{19}F$ ($PhCF_3$, 37 µL, 0.3 mmol, 1 equiv) internal standards.

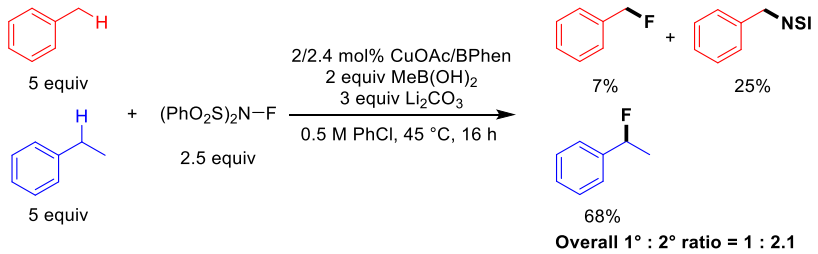



**Figure S1.** Competition experiment for 1° vs. 2° benzylic C–H bond functionalization reactivity.

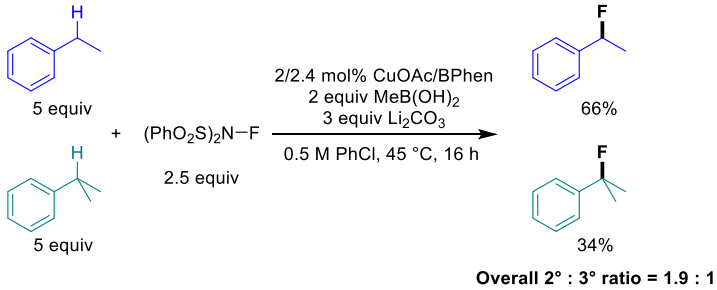
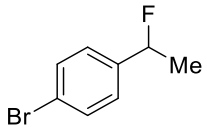



**Figure S2.** Competition experiment for 2° vs. 3° benzylic C–H bond functionalization reactivity.

Similar selectivity preferences have been reported for photochemical benzylic fluorination reactions employing benzophenone and Selectfluor.[8]

## VII. Quantitative $^{1}H$ and $^{19}F$ NMR Spectra for Benzyl Fluoride Products

Processed (phase and baseline corrected) NMR spectra for the crude reaction mixtures of each of the benzyl fluoride products are shown below in red below. Peaks relevant to species of interest (monofluorides, difluorides, and starting material) have been picked, using the multiplet analysis tool in MestreNova. The dark blue overlays show idealized peak curves; inset spectra enlarging important resonances are included where appropriate. See figure captions for additional details.




**(1) 1-bromo-4-(1-fluoroethyl)benzene:** Prepared from 1-bromo-4-ethylbenzene (0.3 mmol, 42 µL, 1.0 equiv) according to the general procedure in section II.
Spectra Available in the Literature (CAS): Yes[9] (159298-87-0)
**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.59 (dq, $^{2}J_{(H,F)}$ = 47.4 Hz, $^{3}J_{(H,H)}$ = 6.4 Hz)
Calibrated $^{1}$H NMR Yield from Benzylic Proton: 81%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -168.05 (dq, $^{2}J_{(H,F)}$ = 48.2 Hz, $^{3}J_{(H,F)}$ = 24.6 Hz)
Calibrated $^{19}$F NMR Yields from Benzyl Fluorides: 86% ($CF_2$ – 11%)

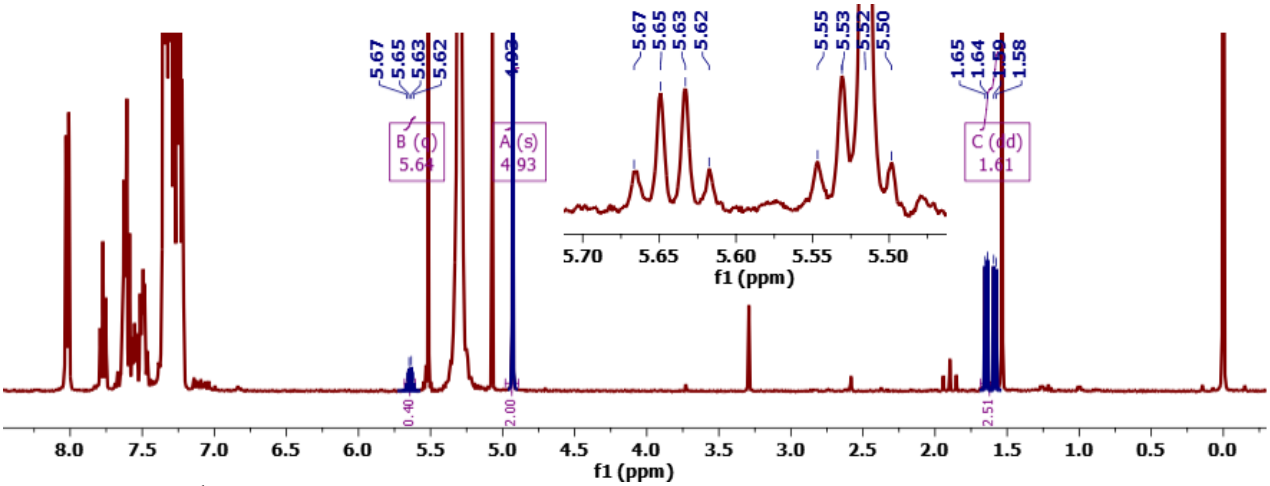



**Figure S3.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.93 ppm). The resolved benzylic and methyl protons are labeled and integrated.

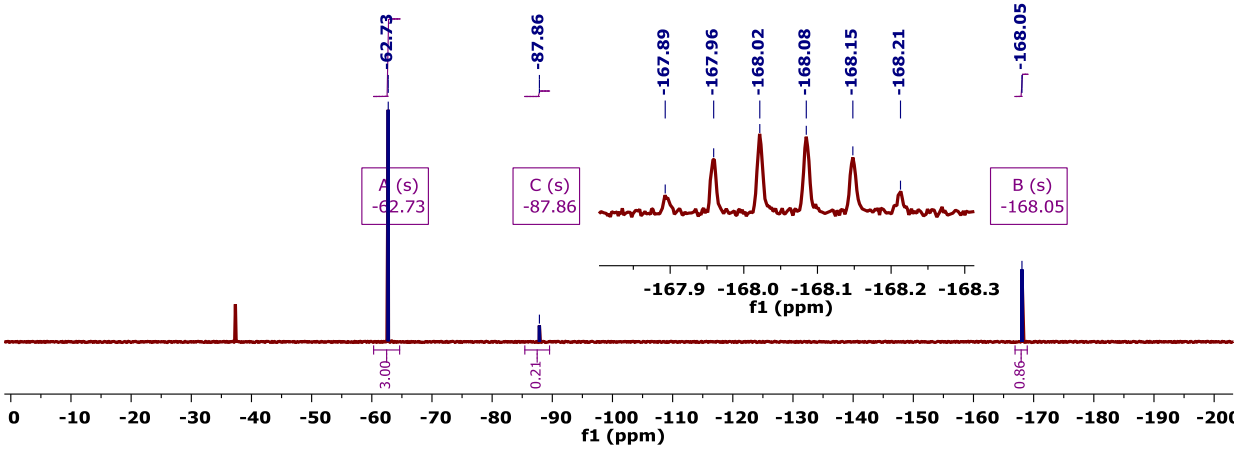
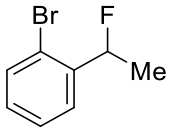



**Figure S4.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.73 ppm). The mono- and di-fluoride (-168.05 and -87.86 ppm, respectively) are labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(2) 1-bromo-2-(1-fluoroethyl)benzene:** Prepared from 1-bromo-2-ethylbenzene (0.3 mmol, 41 µL, 1.0 equiv) according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C.

Spectra Available in the Literature (CAS): Yes[10] (1027513-77-4)

**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.91 (dq, $^2J_{(H,F)}$ = 46.5 Hz, $^3J_{(H,H)}$ = 6.3 Hz)

Calibrated $^1$H NMR Yield from Benzyl Fluoride Methyl Group: 50%

**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -173.76 (dq, $^2J_{(H,F)}$ = 48.3 Hz, $^3J_{(H,F)}$ = 24.4 Hz)

Calibrated $^{19}$F NMR Yields from Benzyl Fluoride: 44%

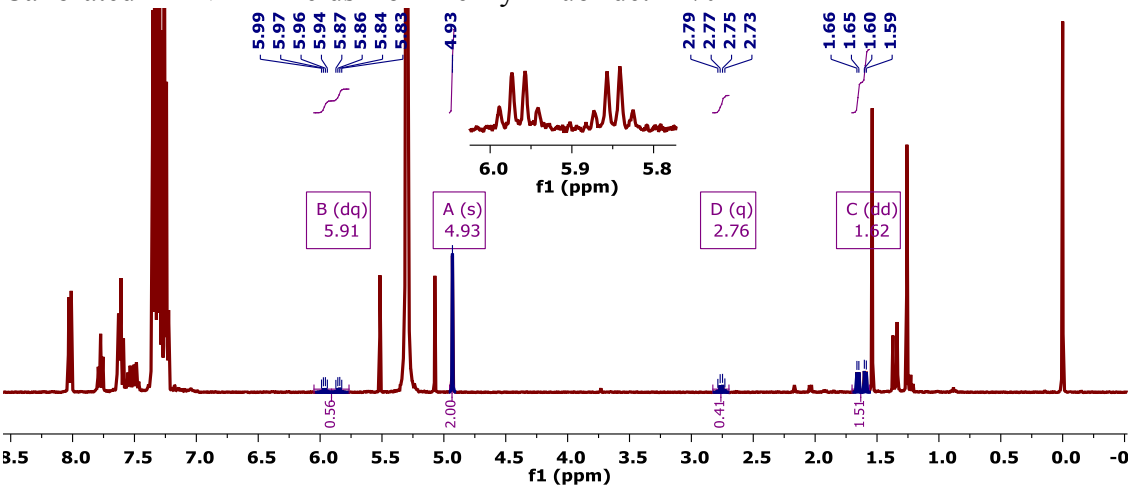



**Figure S5.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.93 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

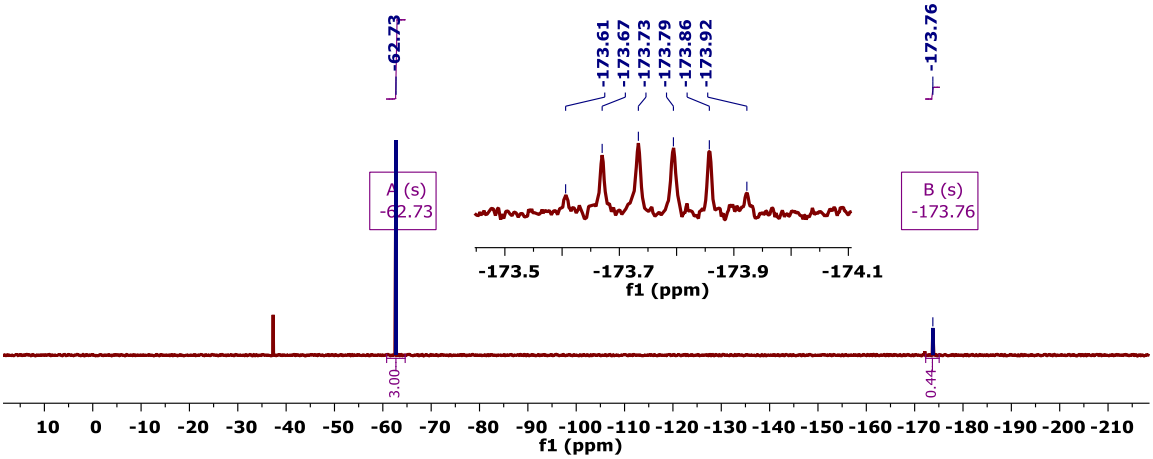
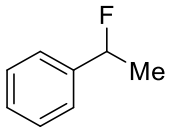



**Figure S6.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.73 ppm). The mono-fluoride (-173. 76 ppm) is labeled and integrated; the inset shows an enlargement of the proton-coupled mono-fluoride.




**(3) (1-fluoroethyl)benzene:** Prepared from ethylbenzene (0.3 mmol, 37 µL, 1.0 equiv) according to the general procedure in section II.
Spectra Available in the Literature (CAS): Yes[11] (7100-97-2)
**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.62 (dq, $^{2}J_{(H,F)}$ = 47.8 Hz, $^{3}J_{(H,H)}$ = 6.5 Hz)
Calibrated $^{1}$H NMR Yield from Benzylic Proton: 67%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -167.02 (dq, $^{2}J_{(H,F)}$ = 47.8 Hz, $^{3}J_{(H,F)}$ = 23.9 Hz)
Calibrated $^{19}$F NMR Yields from Benzyl Fluoride: 64% ($CF_2$ – 11%)

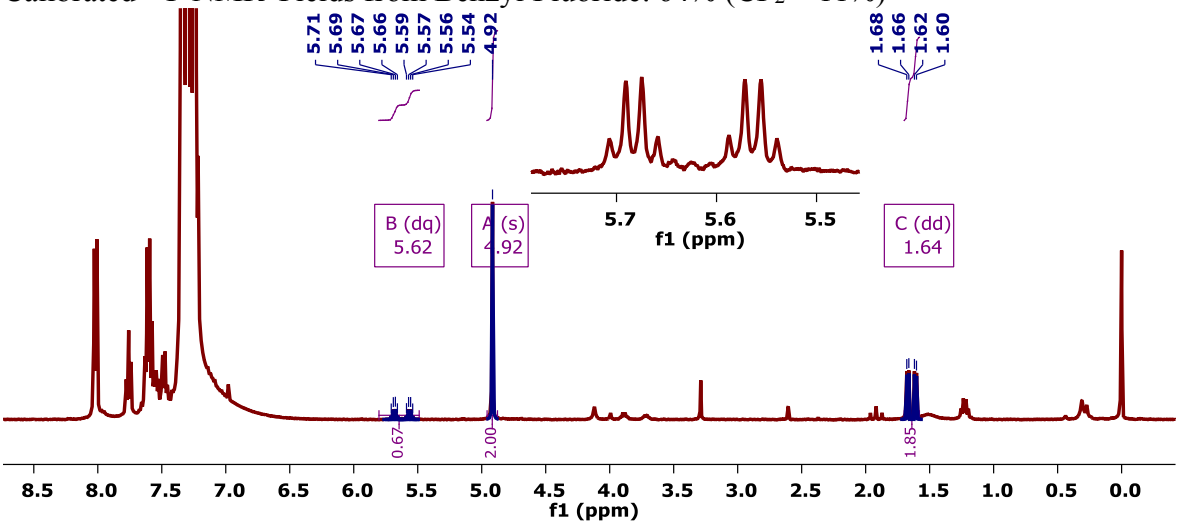



**Figure S7.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.92 ppm). The resolved product benzylic and methyl protons are labeled and integrated.

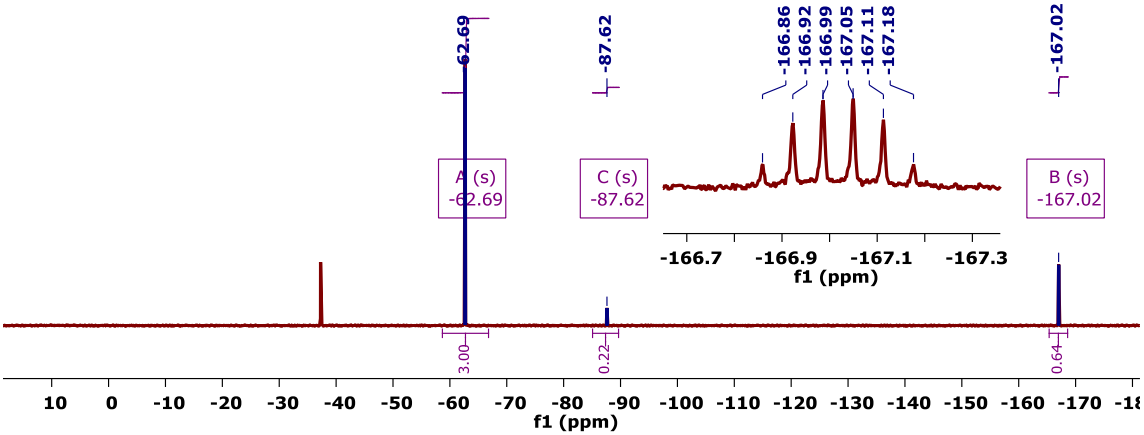
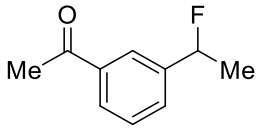



**Figure S8.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.73 ppm). The mono- and di-fluoride (-167.02 and -87.62 ppm, respectively) are labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(4) 1-(3-(1-fluoroethyl)phenyl)ethan-1-one:** Prepared from 1-(3-ethylphenyl)ethan-1-one (0.3 mmol, 49.9 mg, 1.0 equiv) according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C.
Spectra Available in the Literature (CAS): No (1550969-43-1)
**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.61 (dq, $^2J_{(H,F)}$ = 47.5 Hz, $^3J_{(H,H)}$ = 6.5 Hz)
Calibrated $^1$H NMR Yield from Benzyl Fluoride Methyl Group: 83%
**Decoupled Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -168.89 (s)
Calibrated $^{19}$F NMR Yields from Benzyl Fluoride: 75% ($CF_2$ – 20%)

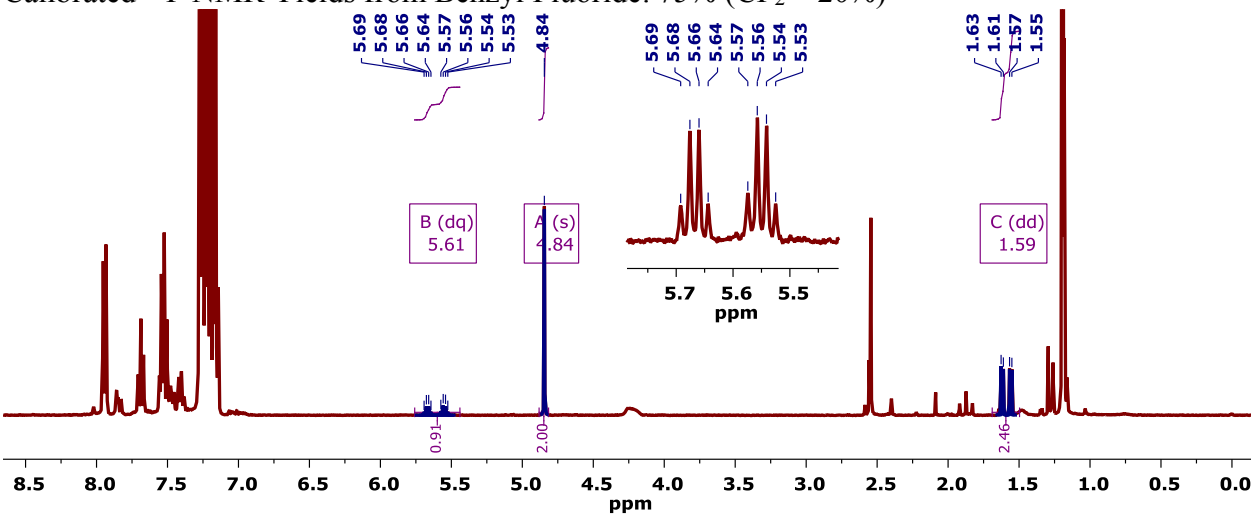



**Figure S9.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.84 ppm). The resolved product benzylic and methyl protons are labeled and integrated.

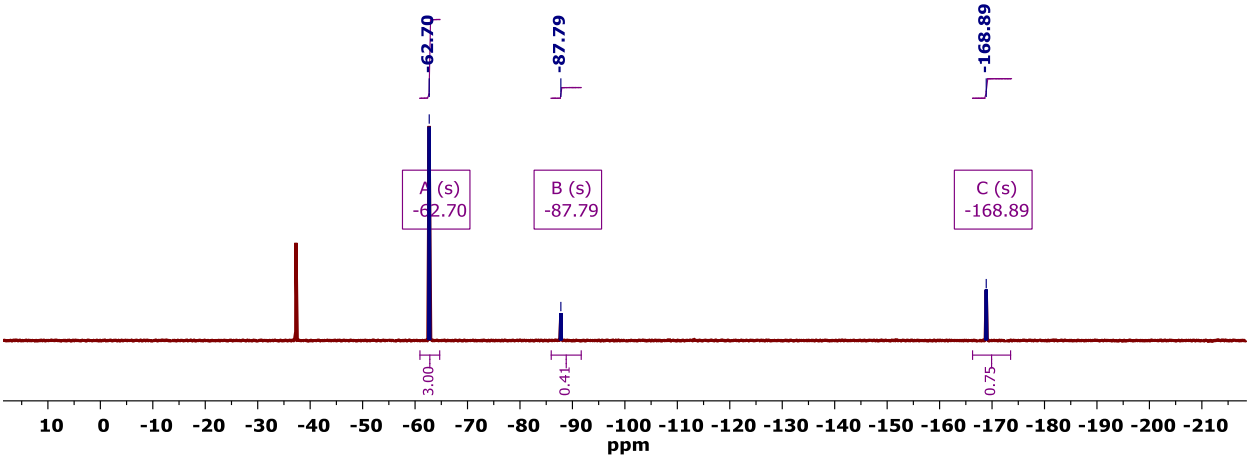
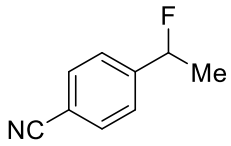



**Figure S10.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.70 ppm). The mono- and di-fluoride (-168.89 and -87.79 ppm, respectively) are labeled and integrated.




**(5) 4-(1-fluoroethyl)benzonitrile:** Prepared from 4-ethylbenzonitrile (0.3 mmol, 41 µL, 1.0 equiv) according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 75 °C.

Spectra Available in the Literature (CAS): Yes[8] (155671-14-0)

**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.70 (dq, $^2J_{(H,F)}$ = 47.4 Hz, $^3J_{(H,H)}$ = 6.5 Hz)

Calibrated $^1$H NMR Yield from Benzyl Fluoride Methyl Group: 56%

**Decoupled Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -172.67 (s)

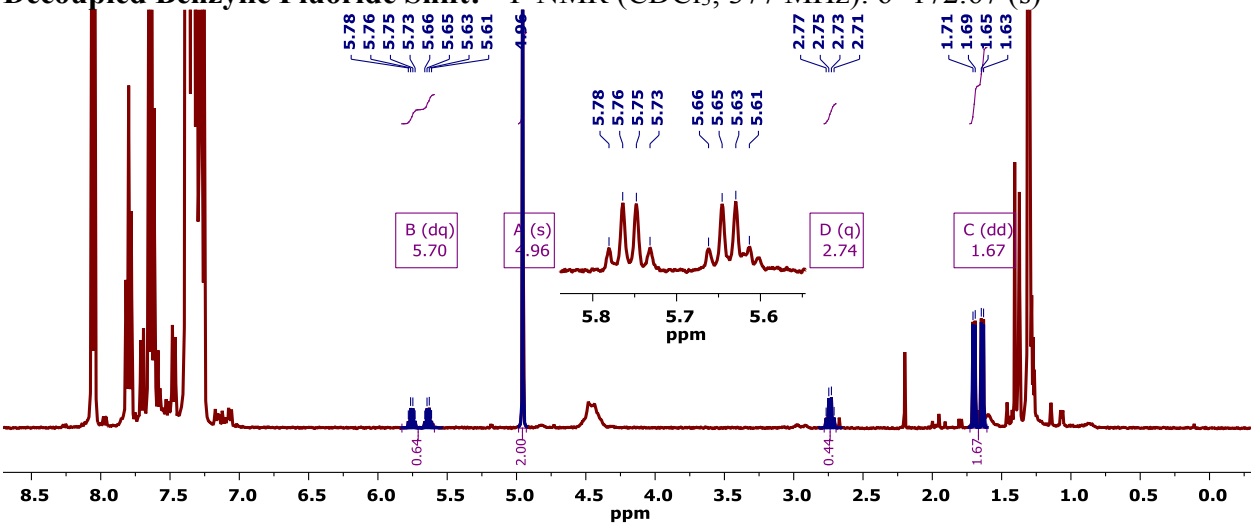



**Figure S11.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.96 ppm). The resolved product benzylic and methyl protons are labeled and integrated. The residual starting material benzylic protons are likewise labeled and integrated.

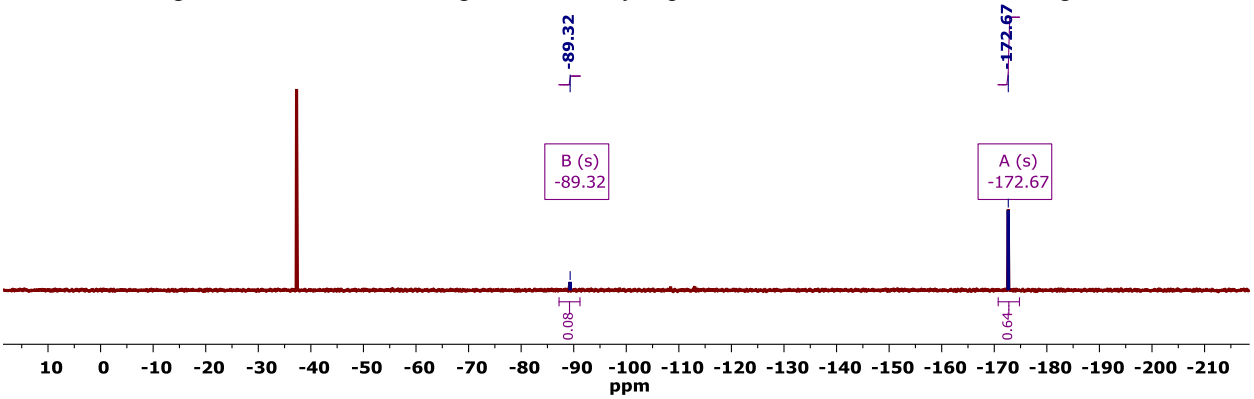
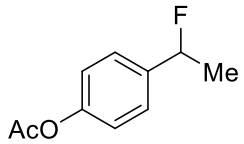



**Figure S12.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture. The mono- and di-fluoride (-172.67 and -89.32 ppm, respectively) are labeled and integrated.




**(6) 4-(1-fluoroethyl)phenyl acetate:** Prepared from 4-ethylphenyl acetate (0.3 mmol, 48 µL, 1.0 equiv) according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C.

Spectra Available in the Literature (CAS): Yes[12] (1487496-31-0)

**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.62 (dq, $^2J_{(H,F)}$ = 47.5 Hz, $^3J_{(H,H)}$ = 6.4 Hz)

Calibrated $^1$H NMR Yield from Benzyl Fluoride Methyl Group: 66%

**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -166.40 (dq, $^2J_{(H,F)}$ = 47.7 Hz, $^3J_{(H,F)}$ = 23.9 Hz)

Calibrated $^{19}$F NMR Yields from Benzyl Fluoride: 63% ($CF_2$ – 7%)

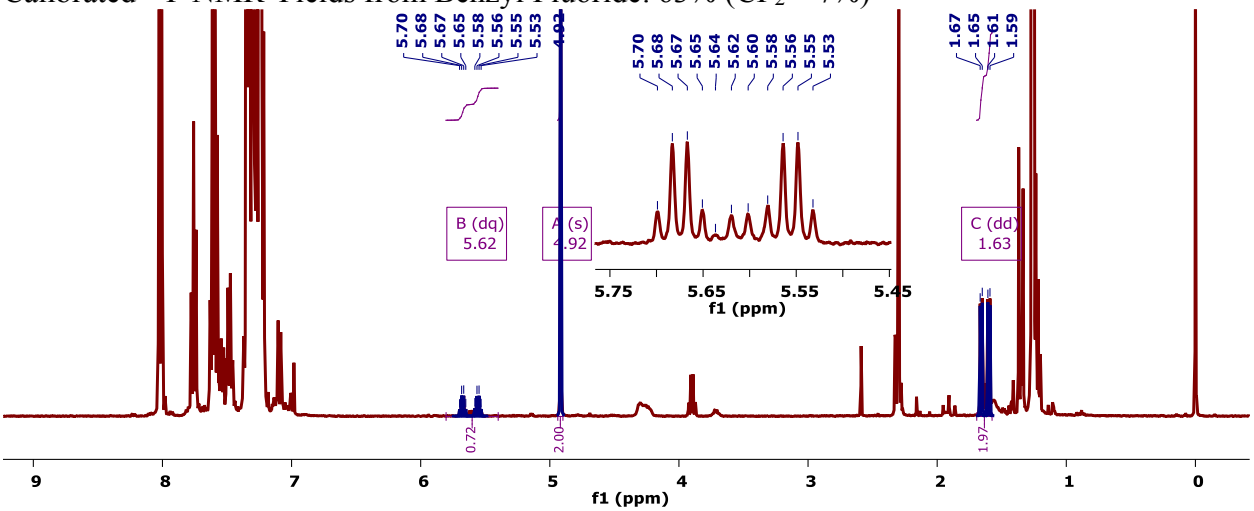



**Figure S13.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.92 ppm). The resolved product benzylic and methyl protons are labeled and integrated.

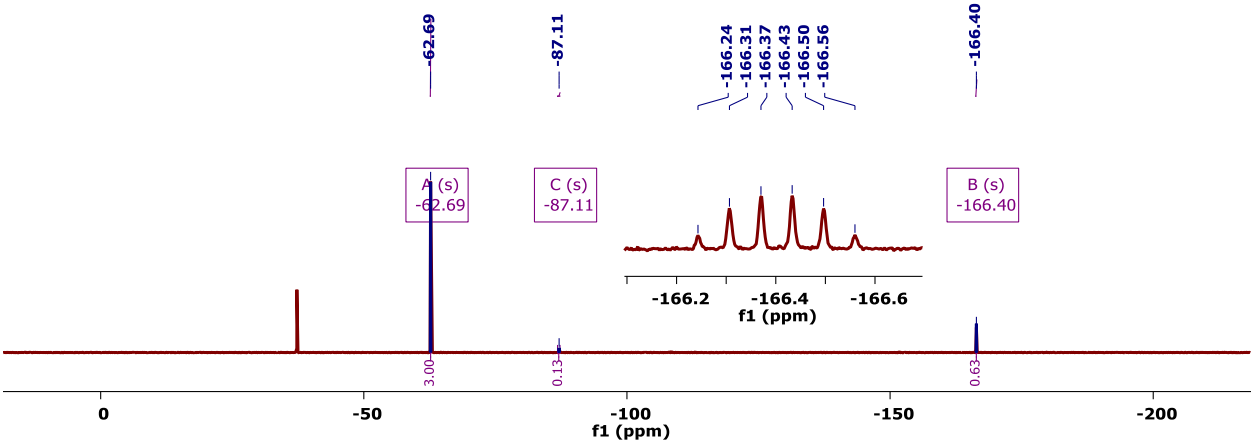
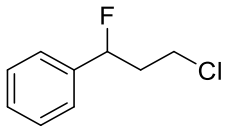



**Figure S14.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.69 ppm). The mono- and di-fluoride (-166.40 and -87.11 ppm, respectively) are labeled and integrated.




**(7) (3-chloro-1-fluoropropyl)benzene:** Prepared from (3-chloropropyl)benzene (0.3 mmol, 45 µL, 1.0 equiv) according to the general procedure in section II. When the reaction was repeated on 3 mmol scale, it was conducted in a 15 mL vial.
Spectra Available in the Literature (CAS): Yes[13] (1487496-36-5)
**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.68 (ddd, $^{2}J_{(H,F)}$ = 47.8 Hz, $^{3}J_{(H,H)}$ = 8.9 & 3.8 Hz)
Calibrated $^{1}$H NMR Yield from Benzyl Proton: 82% (0.3 mmol scale) or 68% (3 mmol scale)
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -179.43 (ddd, $^{2}J_{(H,F)}$ = 46.9 Hz, $^{3}J_{(H,F)}$ = 31.3 & 14.0 Hz)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 75% ($CF_2$ – 5%)

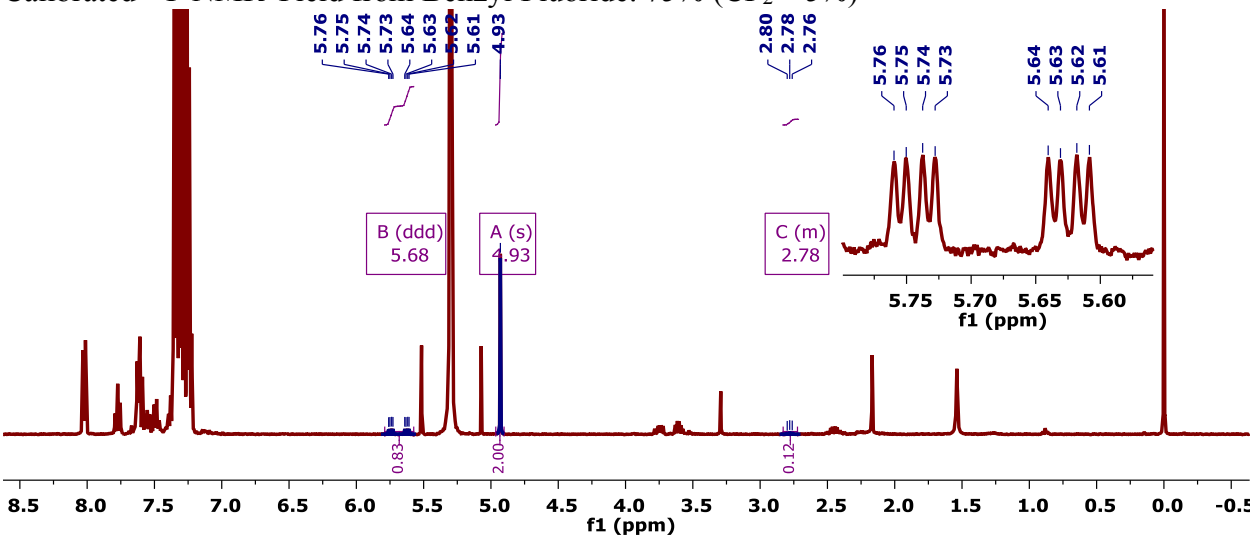



**Figure S15.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.93 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

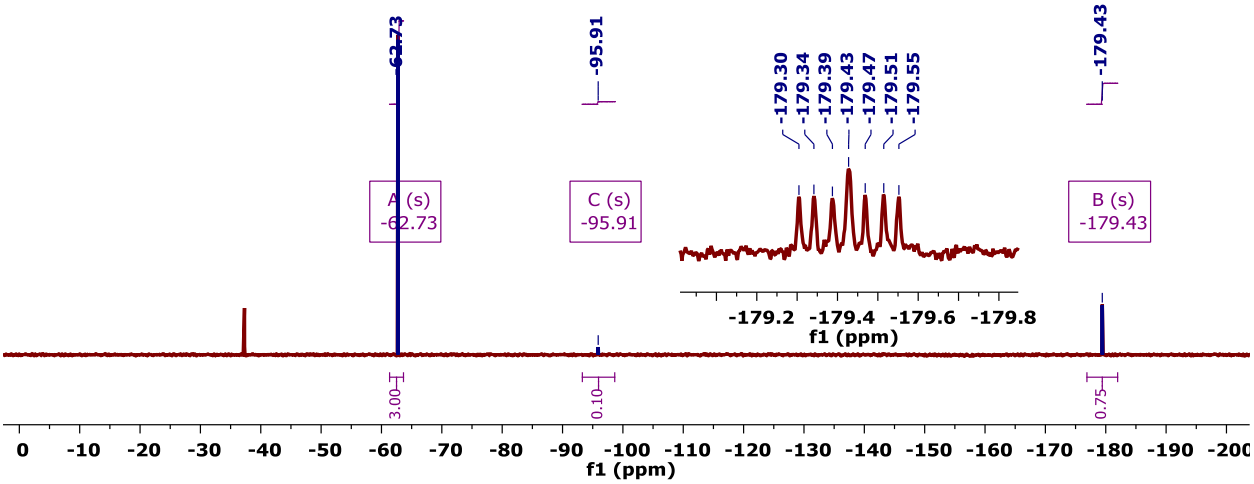
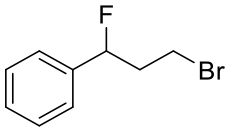



**Figure S16.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.73 ppm). The mono- and di-fluoride (-179.43 and -95.91 ppm, respectively) are labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(8) (3-bromo-1-fluoropropyl)benzene:** Prepared from (3-bromopropyl)benzene (0.3 mmol, 46 µL, 1.0 equiv) according to the general procedure in section II. When the reaction was repeated on 3 mmol scale, it was conducted in a 15 mL vial.
Spectra Available in the Literature (CAS): Yes[11] (1428331-73-0)
**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.66 (ddd, $^{2}J_{(H,F)}$ = 47.7 Hz, $^{3}J_{(H,H)}$ = 8.8 & 3.9 Hz)
Calibrated $^{1}$H NMR Yield from Benzyl Proton: 71% (0.3 mmol scale) or 67% (3 mmol scale)
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -179.33 (ddd, $^{2}J_{(H,F)}$ = 46.9 Hz, $^{3}J_{(H,F)}$ = 31.3 & 14.0 Hz)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 68%

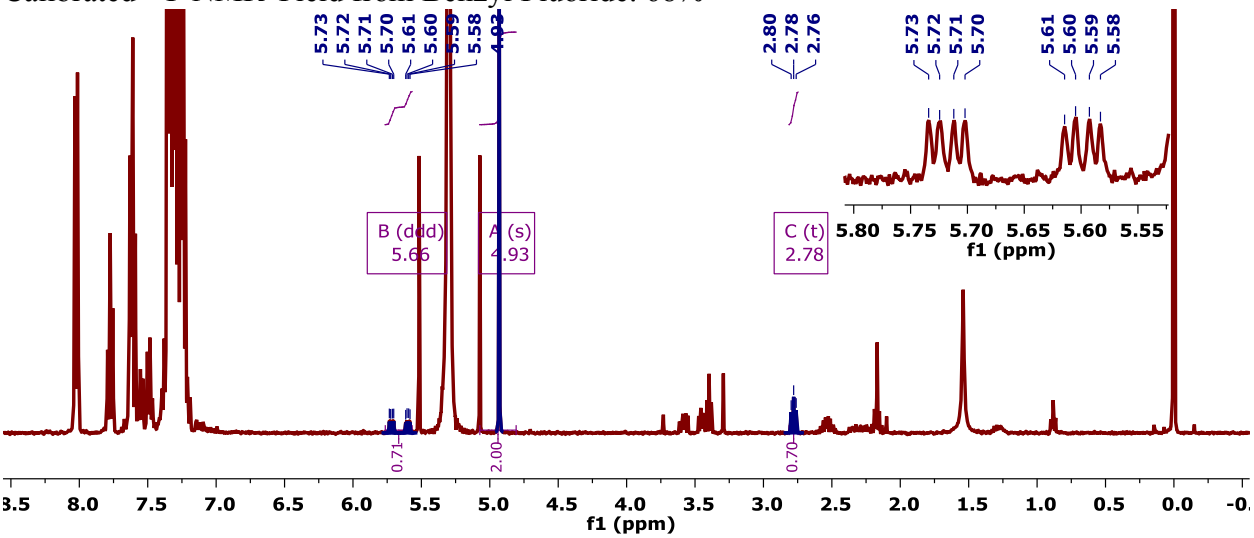



**Figure S17.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.93 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

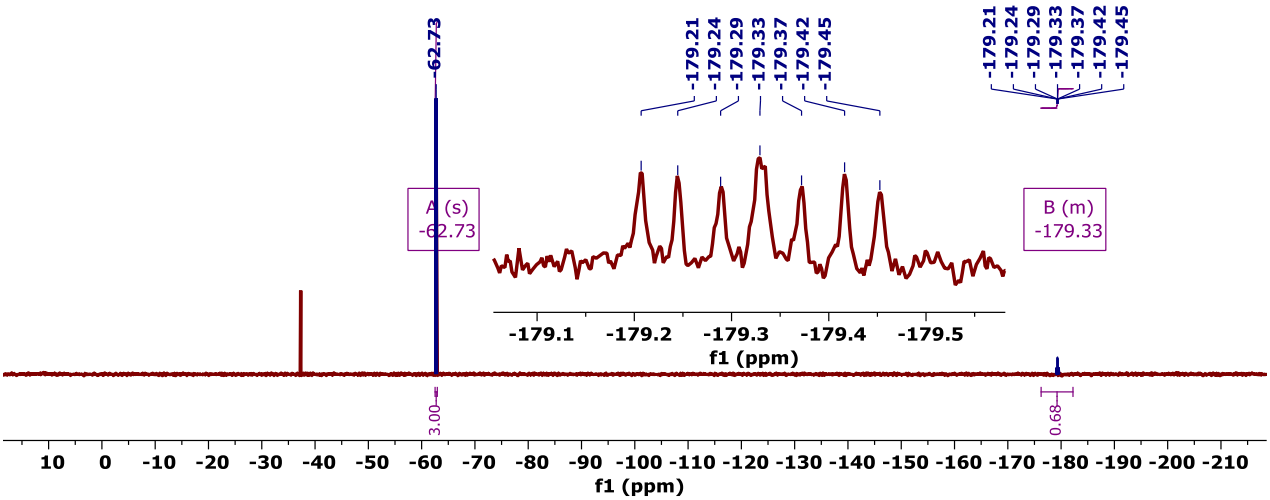
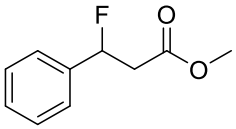



**Figure S18.** Crude $^{19}$F NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.73 ppm). The mono-fluoride (-179.33) is labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(9) Methyl 3-fluoro-3-phenylpropanoate:** Prepared from methyl 3-phenylpropanoate (0.75 mmol, 47 µL, 1.0 equiv) that was formed according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C.
Spectra Available in the Literature (CAS): Yes[8] (188941-05-1)
**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.93 (ddd, $^2J_{(H,F)}$ = 46.9 Hz, $^3J_{(H,H)}$ = 9.2 & 4.1 Hz)
Calibrated $^1$H NMR Yield from Benzyl Proton: 58%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -173.16 (ddd, $^2J_{(H,F)}$ = 46.4 Hz, $^3J_{(H,F)}$ = 32.6 & 13.4 Hz)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 51% ($CF_2$ – 2%)

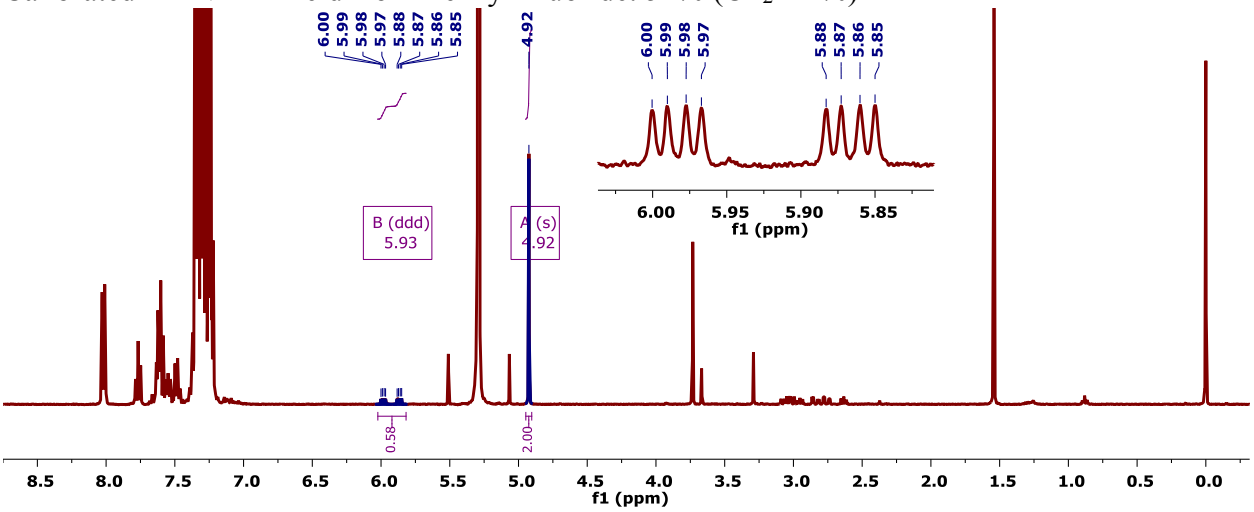



**Figure S19.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.92 ppm). The resolved product benzylic protons are labeled and integrated.

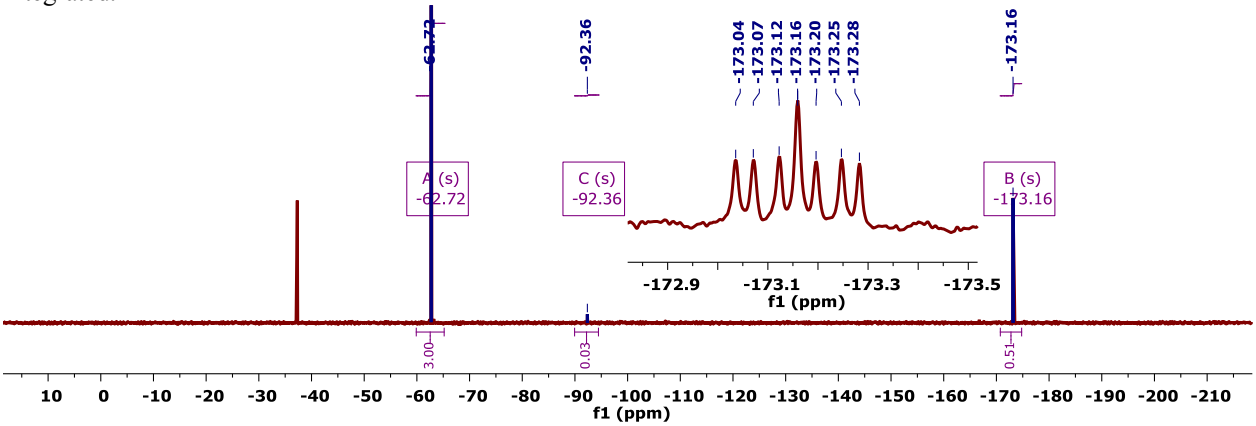
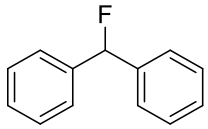



**Figure S20.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.72 ppm). The mono- and di-fluoride (-173.16 and -92.36 ppm, respectively) are labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(10) (fluoromethylene)dibenzene:** Prepared from diphenylmethane (0.3 mmol, 50.5 mg, 1.0 equiv) according to the general procedure in section II.
Spectra Available in the Literature (CAS): Yes[8] (579-55-5)
**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 6.47 (d, $^{2}J_{(H,F)}$ = 47.4 Hz)
Calibrated $^{1}$H NMR Yield from Benzyl Proton: 40%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -166.73 (d, $^{2}J_{(H,F)}$ = 47.5 Hz)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 40%

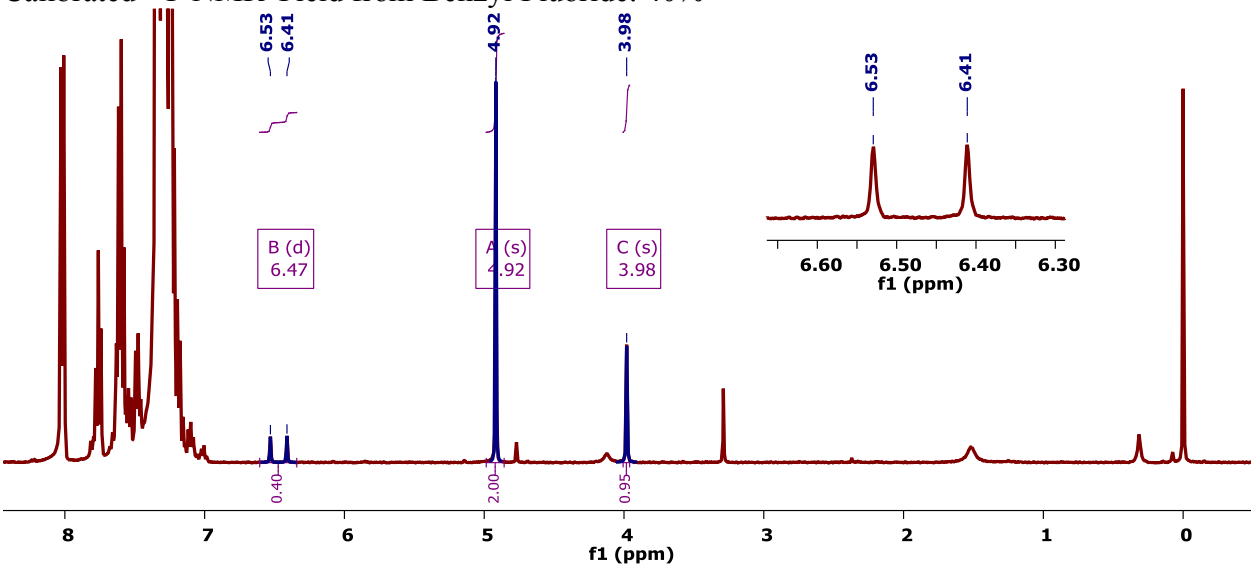



**Figure S21.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.92 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

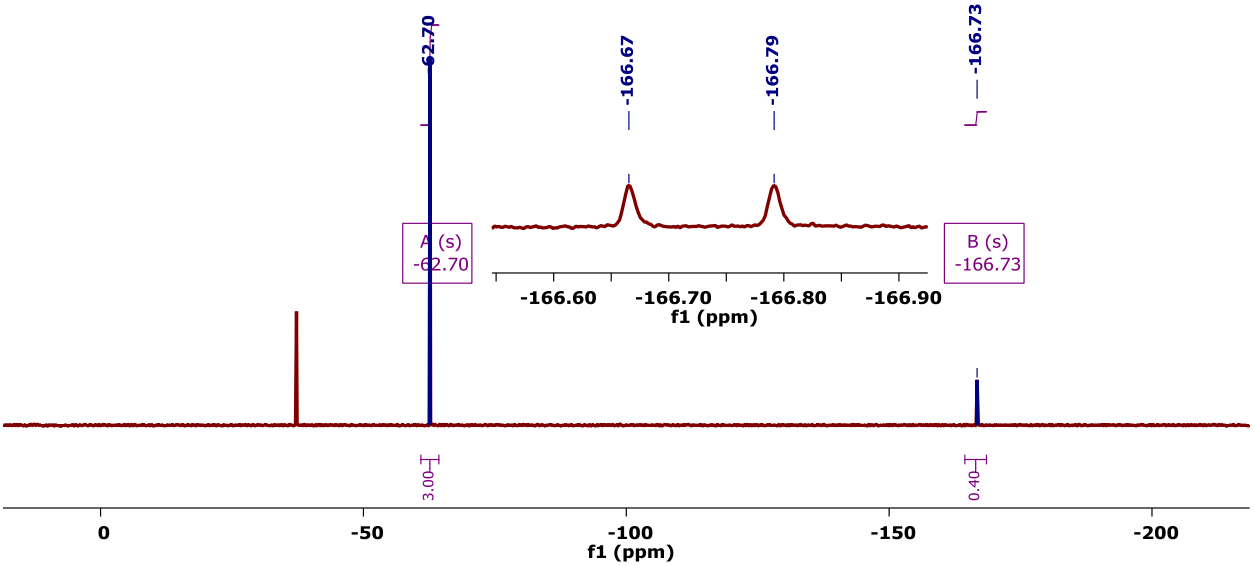
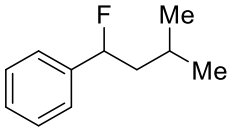



**Figure S22.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.70 ppm). The mono-fluoride (-166.73) is labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(11) (1-fluoro-3-methylbutyl)benzene:** Prepared from isopentylbenzene (0.3 mmol, 52 µL, 1.0 equiv) according to the general procedure in section II.
Spectra Available in the Literature (CAS): No (N/A)
**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.50 (ddd, $^{2}J_{(H,F)}$ = 48.2 Hz, $^{3}J_{(H,H)}$ = 9.2 & 4.3 Hz)
Calibrated $^{1}$H NMR Yield from Benzyl Proton: 70%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -174.31 (ddd, $^{2}J_{(H,F)}$ = 48.4 Hz, $^{3}J_{(H,F)}$ = 33.6 & 14.6 Hz)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 65% ($CF_2$ – 6%)

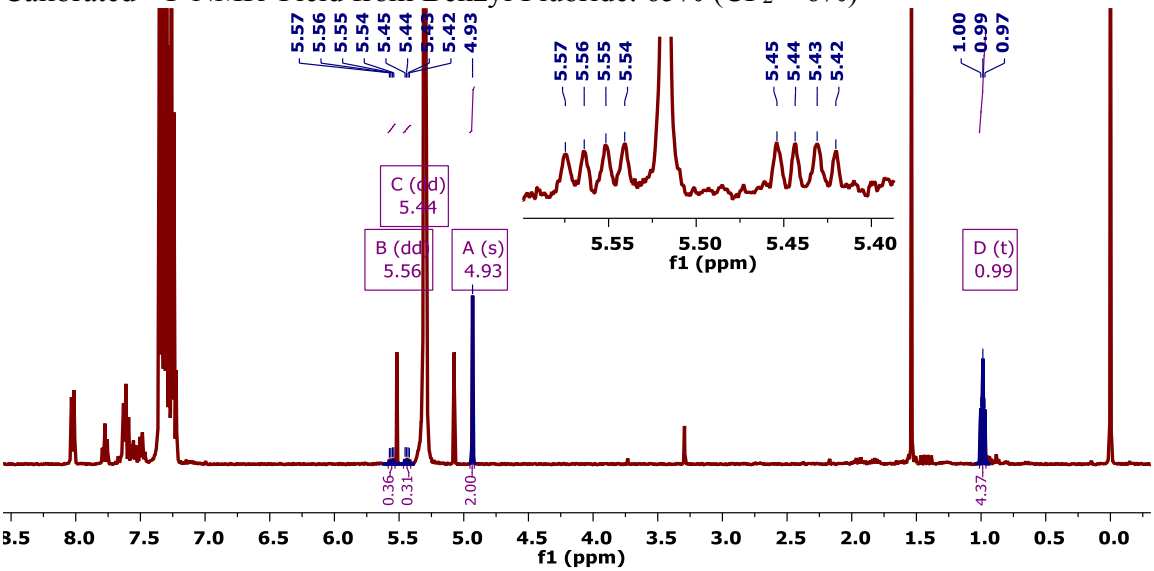



**Figure S23.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.93 ppm). The resolved product benzylic and methyl protons are labeled and integrated.

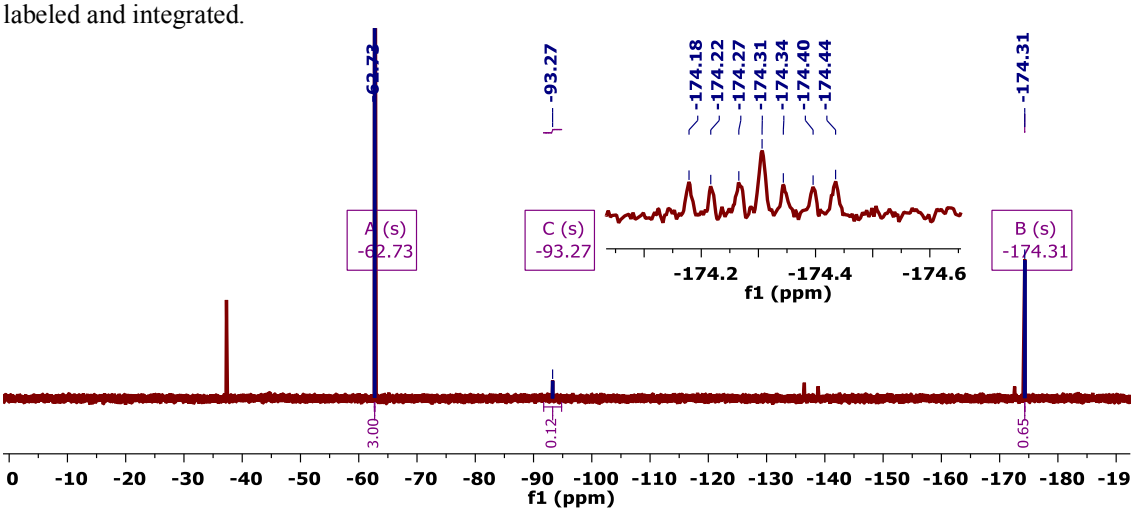
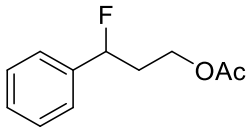



**Figure S24.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.73 ppm). The mono- and di-fluoride (-174.31 and -93.27 ppm, respectively) are labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(12) 3-fluoro-3-phenylpropyl acetate:** Prepared from 3-phenylpropyl acetate (0.3 mmol, 53 µL, 1.0 equiv) according to the general procedure in section II.
Spectra Available in the Literature (CAS): Yes[8] (412026-80-3)
**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.57 (ddd, $^{2}J_{(H,F)}$ = 47.8 Hz, $^{3}J_{(H,H)}$ = 8.8 & 4.3 Hz)
Calibrated $^{1}$H NMR Yield from Benzyl Proton: 79%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -177.40 (ddd, $^{2}J_{(H,F)}$ = 46.1 Hz, $^{3}J_{(H,F)}$ = 30.1 & 15.4 Hz)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 74% ($CF_2$ – 3%)

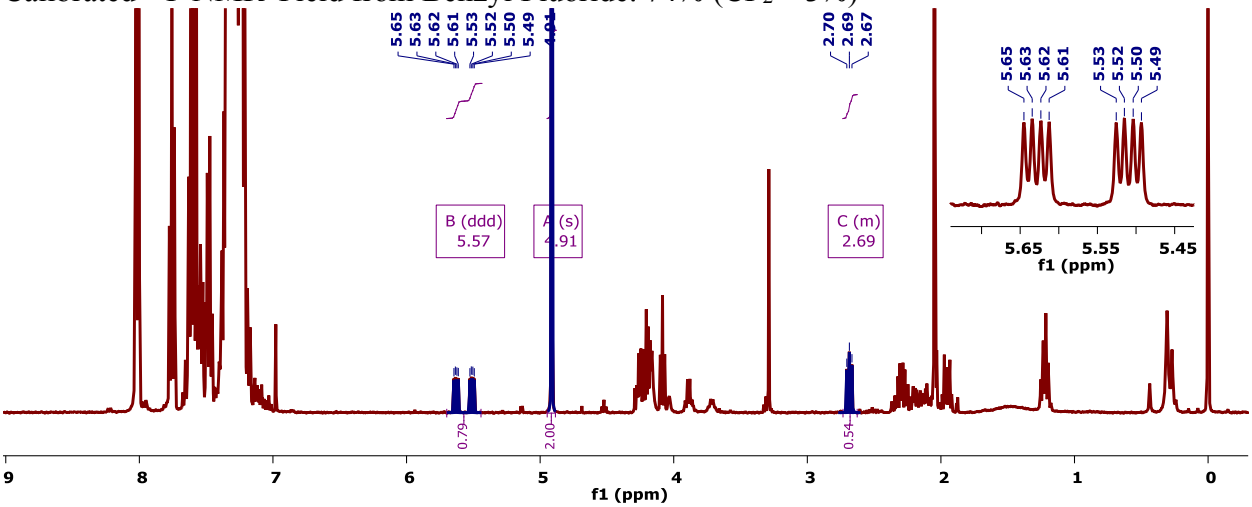



**Figure S25.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.93 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

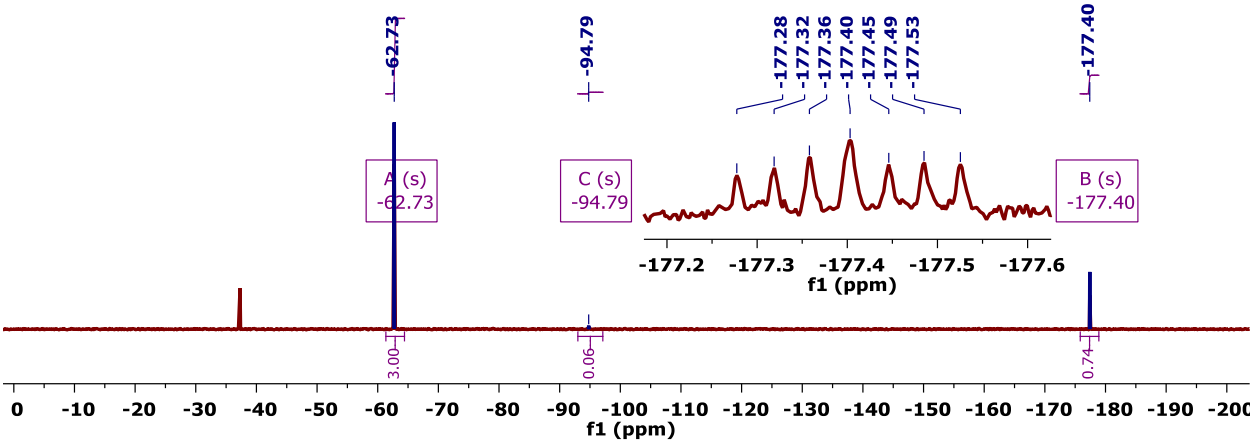
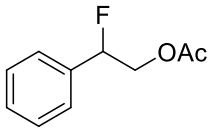



**Figure S26.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.73 ppm). The mono- and di-fluoride (-177.40 and -94.79 ppm, respectively) are labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(13) 2-fluoro-2-phenylethyl acetate:** Prepared from phenethyl acetate (0.3 mmol, 54.6 mg, 1.0 equiv) according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C in acetone.
Spectra Available in the Literature (CAS): Yes[14] (33315-78-5)
**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.58 (ddd, $^2J_{(H,F)}$ = 48.6 Hz, $^3J_{(H,H)}$ = 7.2 & 3.6 Hz)
Calibrated $^1$H NMR Yield from Benzylic Proton: 53%
**Decoupled Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -184.35 (s)

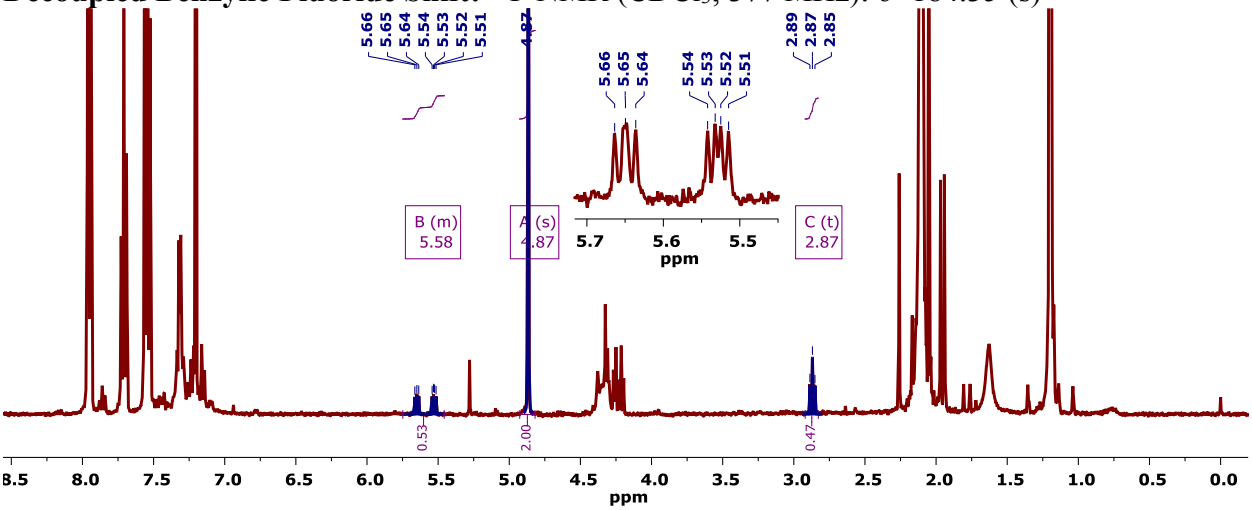



**Figure S27.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.87 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

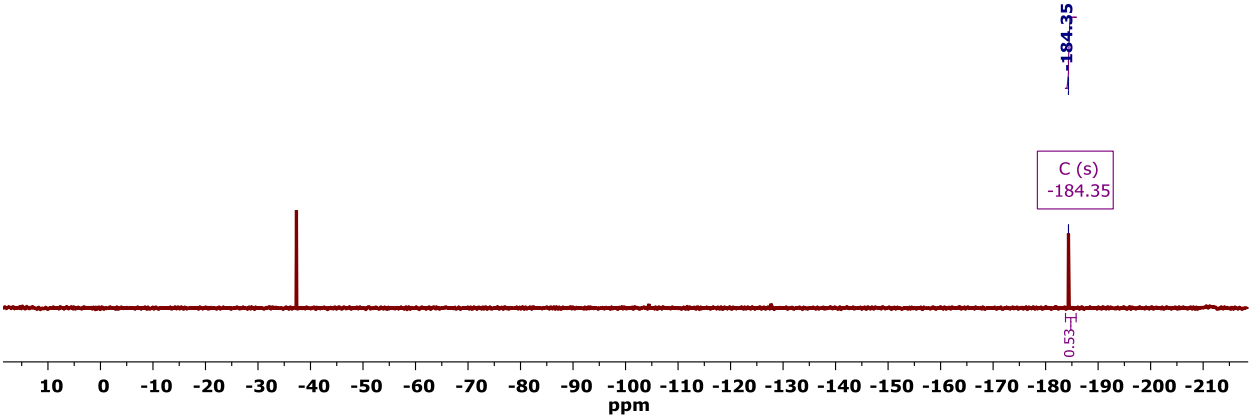
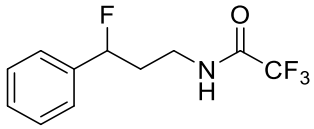



**Figure S28.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture. The mono-fluoride (-184.35) is labeled and integrated.




**(14) 2,2,2-trifluoro-*N*-(3-fluoro-3-phenylpropyl)acetamide:** Prepared from 2,2,2-trifluoro-*N*-(3-phenylpropyl)acetamide (0.3 mmol, 70 mg, 1.0 equiv) according to the general procedure in section II.

Spectra Available in the Literature (CAS): No (N/A)

**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.60 (ddd, $^{2}J_{(H,F)}$ = 48.2 Hz, $^{3}J_{(H,H)}$ = 8.7 & 3.0 Hz)

Calibrated $^{1}$H NMR Yield from Benzyl Proton: 63%

**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -183.75 (ddd, $^{2}J_{(H,F)}$ = 48.0 Hz, $^{3}J_{(H,F)}$ = 30.2 & 17.3 Hz)

Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 63%

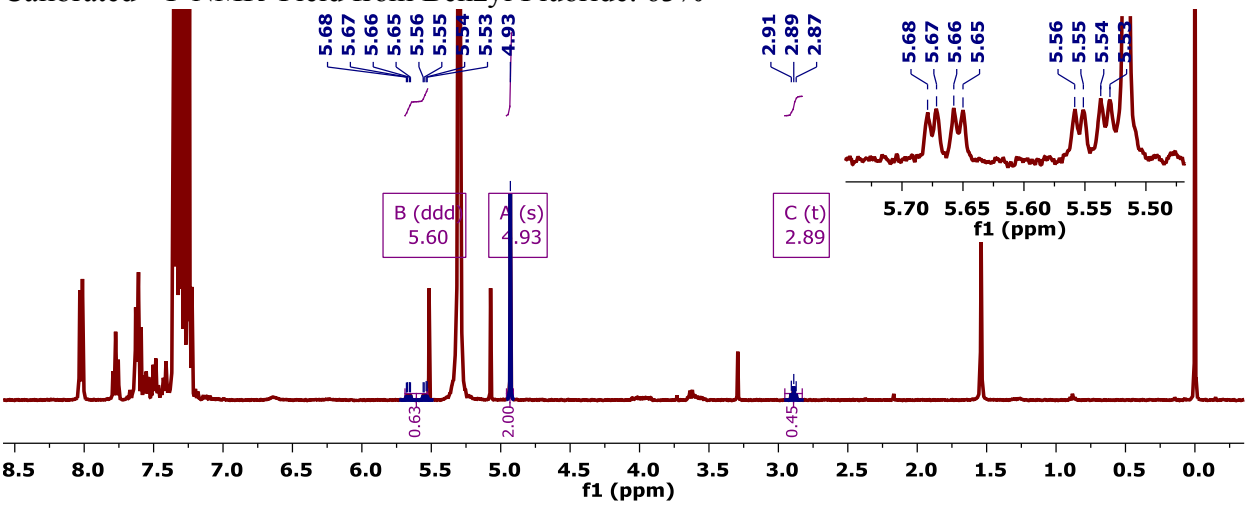



**Figure S29.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.93 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

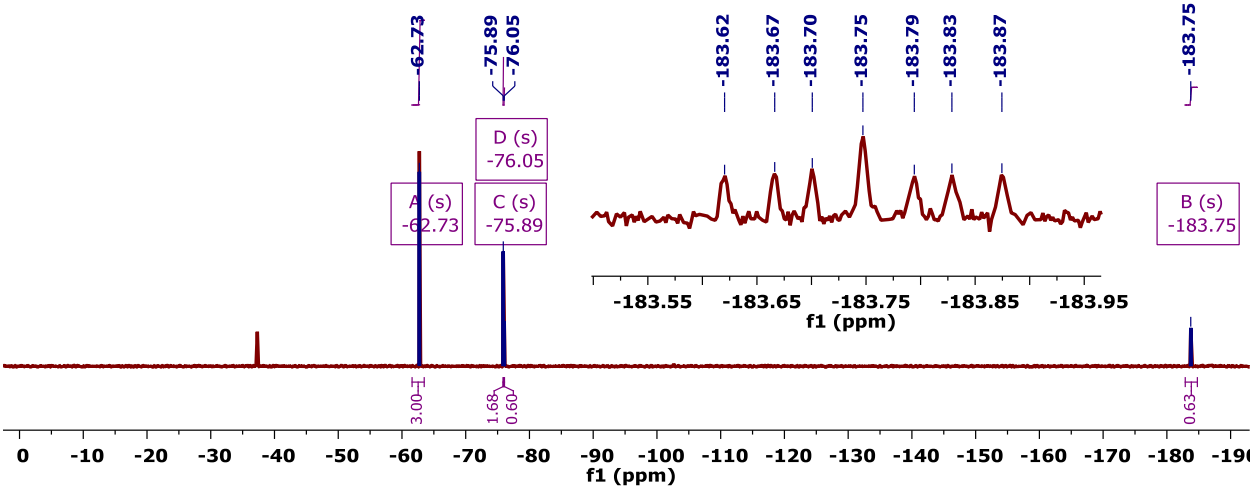
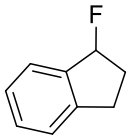



**Figure S30.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.73 ppm). The benzylic fluoride (-183.75 ppm) and $CF_3$ groups (starting material and product) are labeled and integrated; the inset shows an enlargement of the proton-coupled mono-fluoride.




**(15) 1-fluoro-2,3-dihydro-1*H*-indene:** Prepared from indane (0.3 mmol, 37 µL, 1.0 equiv) according to the general procedure in section II with the following variations: 0.5 equiv $MeB(OH)_2$ operating at 35 °C.
Spectra Available in the Literature (CAS): Yes[15] (62393-01-5)
**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.99 (ddd, $^2J_{(H,F)}$ = 58.1 Hz, $^3J_{(H,H)}$ = 6.1 & 2.8 Hz)
Calibrated $^1$H NMR Yield from Benzyl Proton: 60%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -159.91 (dt, $^2J_{(H,F)}$ = 56.3 Hz, $^3J_{(H,F)}$ = 27.2 Hz)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 49%

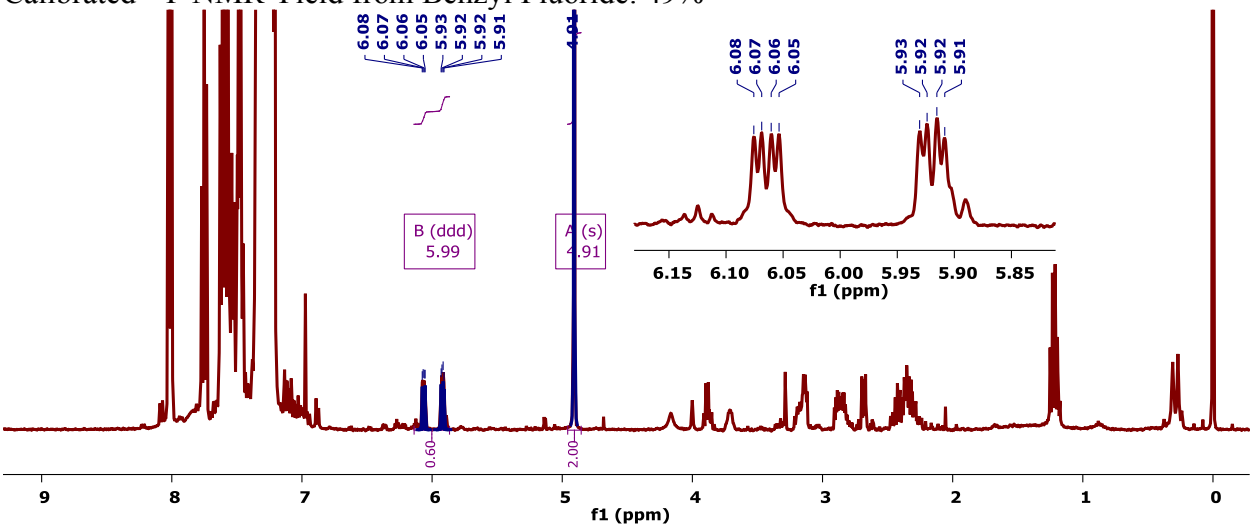



**Figure S31.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.91 ppm). The resolved product benzylic proton is labeled and integrated.

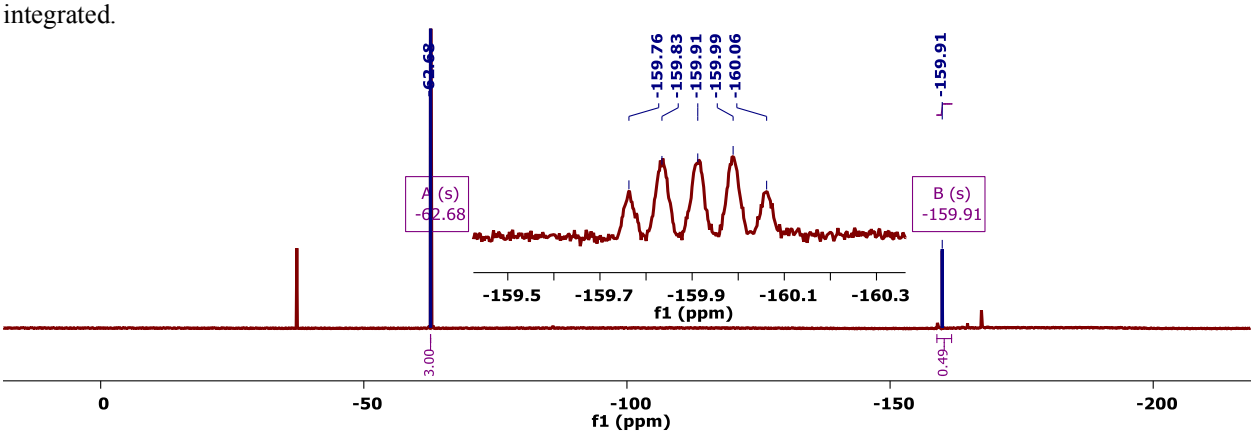
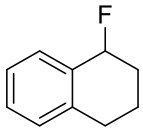



**Figure S32.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.68 ppm). The mono-fluoride (-159.91) is labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(16) 1-fluoro-1,2,3,4-tetrahydronaphthalene:** Prepared from 1,2,3,4-tetrahydronaphthalene (0.3 mmol, 41 µL, 1.0 equiv) according to the general procedure in section II with the following variations: 0.5 equiv $MeB(OH)_2$ operating at 35 °C.
Spectra Available in the Literature (CAS): No (62462-11-7)
**Benzyl Fluoride C–H Shift:** $^{1}H$ NMR ($CDCl_3$, 400 MHz): δ 5.54 (dt, $^{2}J_{(H,F)}$ = 51.8 Hz, $^{3}J_{(H,H)}$ = 3.9 Hz)
Calibrated $^{1}H$ NMR Yield from Benzyl Proton: 61%
**Benzylic Fluoride Shift:** $^{19}F$ NMR ($CDCl_3$, 377 MHz): δ -155.88 (m)
Calibrated $^{19}F$ NMR Yield from Benzyl Fluoride: 57%

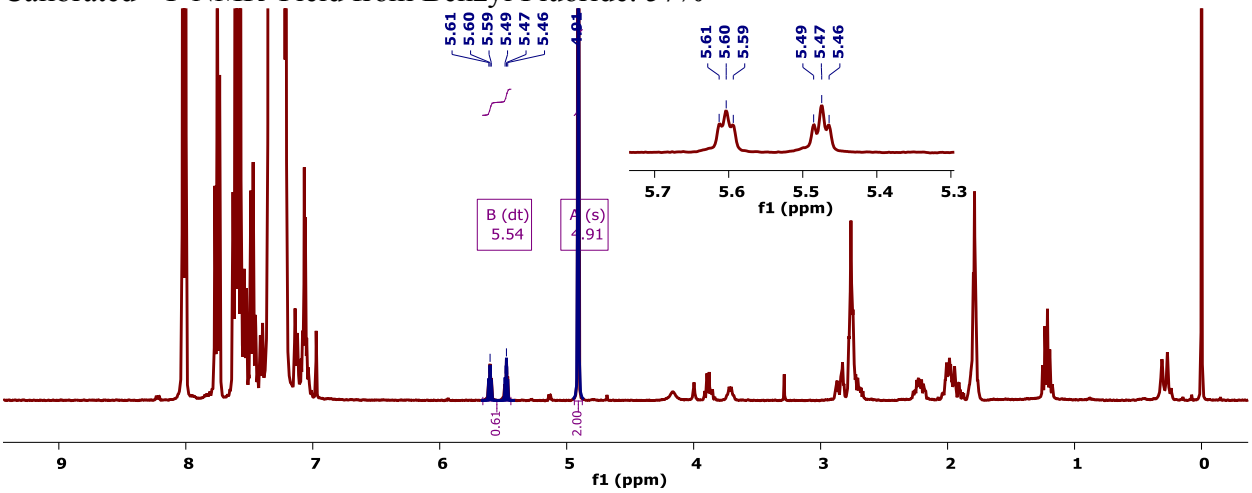



**Figure S33.** Crude $^{1}H$ NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.91 ppm). The resolved product benzylic proton is labeled and integrated.

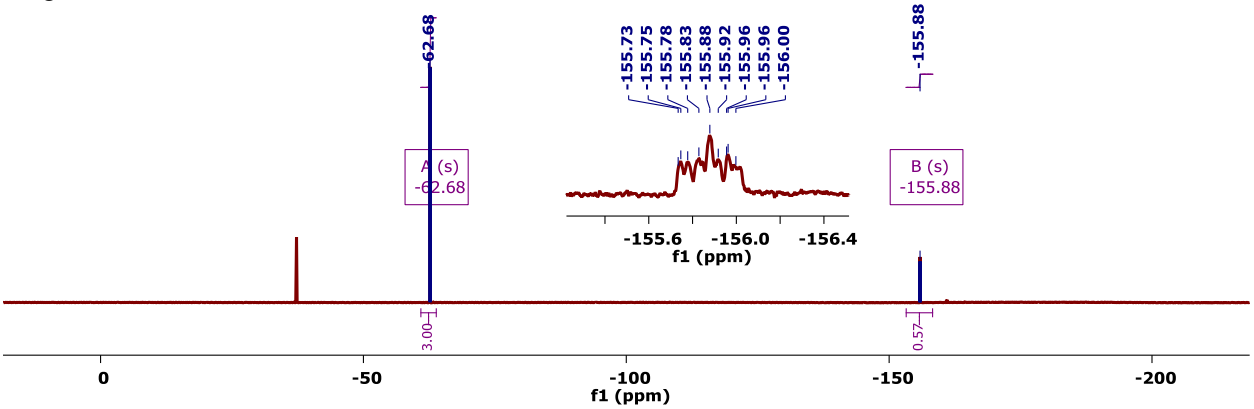
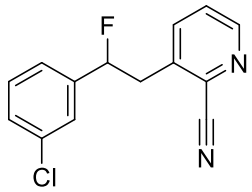



**Figure S34.** Crude $^{19}F\{^{1}H\}$ NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.68 ppm). The mono-fluoride (-155.88) is labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(17) 3-(2-(3-chlorophenyl)-2-fluoroethyl)picolinonitrile:** Prepared from 3-(3-chlorophenethyl)picolinonitrile (0.3 mmol, 73 mg, 1.0 equiv) according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 75 °C.

Spectra Available in the Literature (CAS): No (N/A)

**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.71 (ddd, $^2J_{(H,F)}$ = 53.6 Hz, $^3J_{(H,H)}$ = 5.4 Hz)

Calibrated $^1$H NMR Yield from Benzyl Proton: 45%

**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -178.75 (ddd, $^2J_{(H,F)}$ = 47.9 Hz, $^3J_{(H,F)}$ = 29.9 & 19.0 Hz)

Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 39%

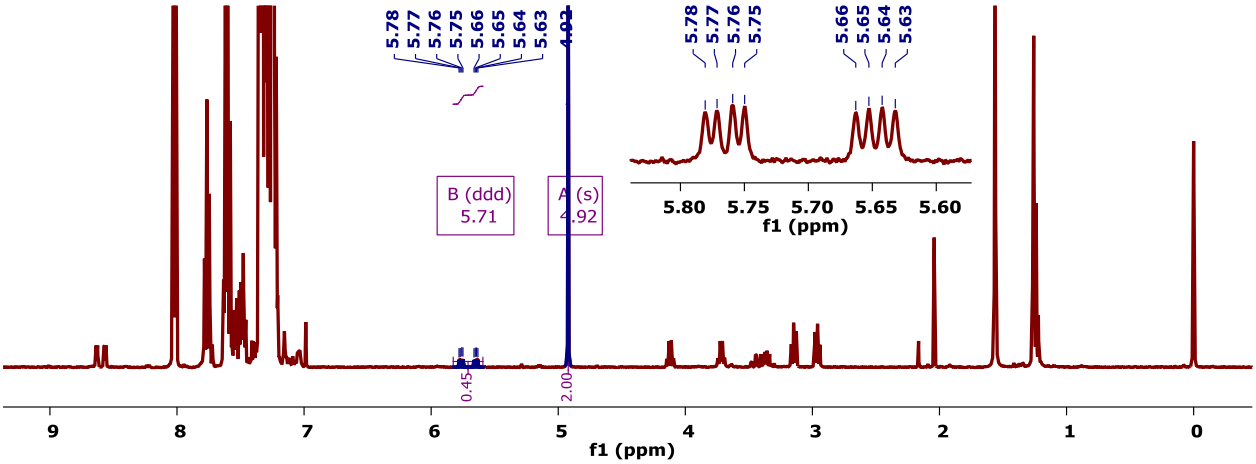



**Figure S35.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.92 ppm). The resolved product benzylic proton is labeled and integrated.

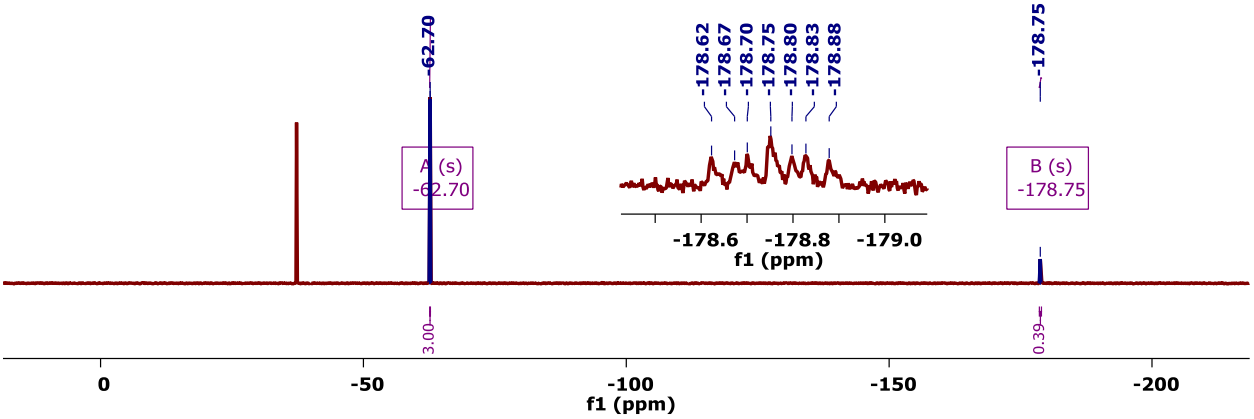
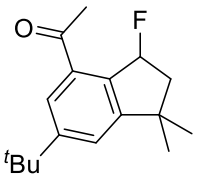



**Figure S36.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.70 ppm). The mono-fluoride (-178.75) is labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(18) 1-(6-(tert-butyl)-3-fluoro-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one:**
Prepared from celestolide (0.3 mmol, 73 mg, 1.0 equiv) according to the general procedure in section II.
Spectra Available in the Literature (CAS): Yes[9] (1500096-10-5)
**Benzyl Fluoride C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 6.45 (dd, $^{2}J_{(H,F)}$ = 53.6 Hz, $^{3}J_{(H,H)}$ = 5.4 Hz)
Calibrated $^{1}$H NMR Yield from Benzyl Proton: 86%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -158.62 (ddd, $^{2}J_{(H,F)}$ = 54.2 Hz, $^{3}J_{(H,F)}$ = 34.1 & 23.5 Hz)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 90% ($CF_2$ – 6%)

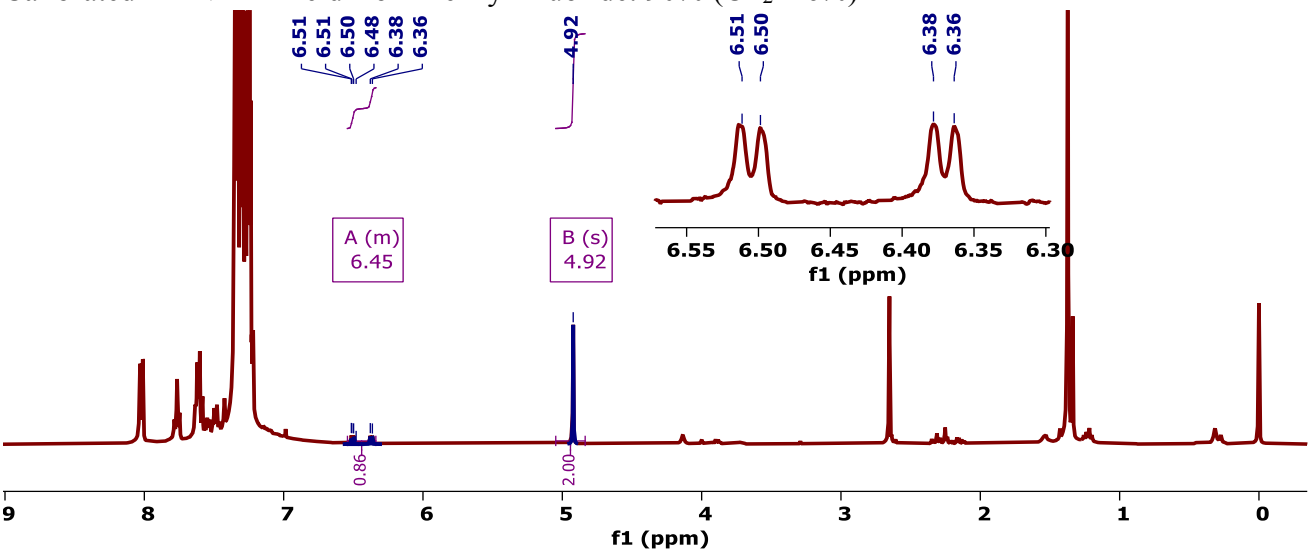



**Figure S37.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.92 ppm). The resolved product benzylic proton is labeled and integrated.

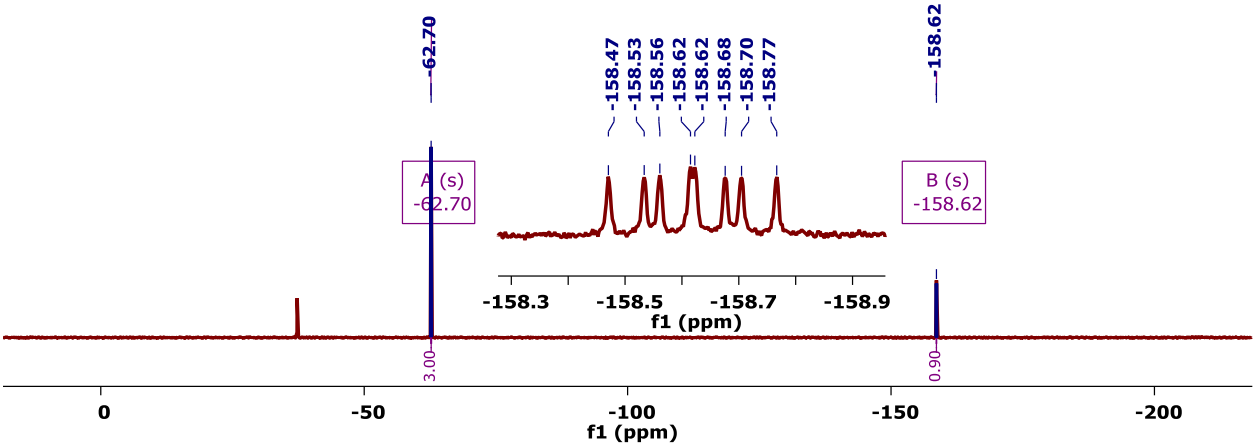
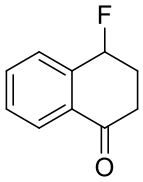



**Figure S38.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.70 ppm). The mono-fluoride (-158.62) is labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(19) 4-fluoro-3,4-dihydronaphthalen-1(*2H*)-one:** Prepared from 1-tetralone (0.3 mmol, 41 µL, 1.0 equiv) formed according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 75 °C in acetone.
Spectra Available in the Literature (CAS): Yes[16] (587853-65-4)
**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.74 (dt, $^2J_{(H,F)}$ = 50.5 Hz, $^3J_{(H,H)}$ = 5.0 Hz)
Calibrated $^1$H NMR Yield from Benzyl Proton: 38%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -170.59 (m)
Calibrated $^{19}$F NMR Yield from Benzyl Fluoride: 44%

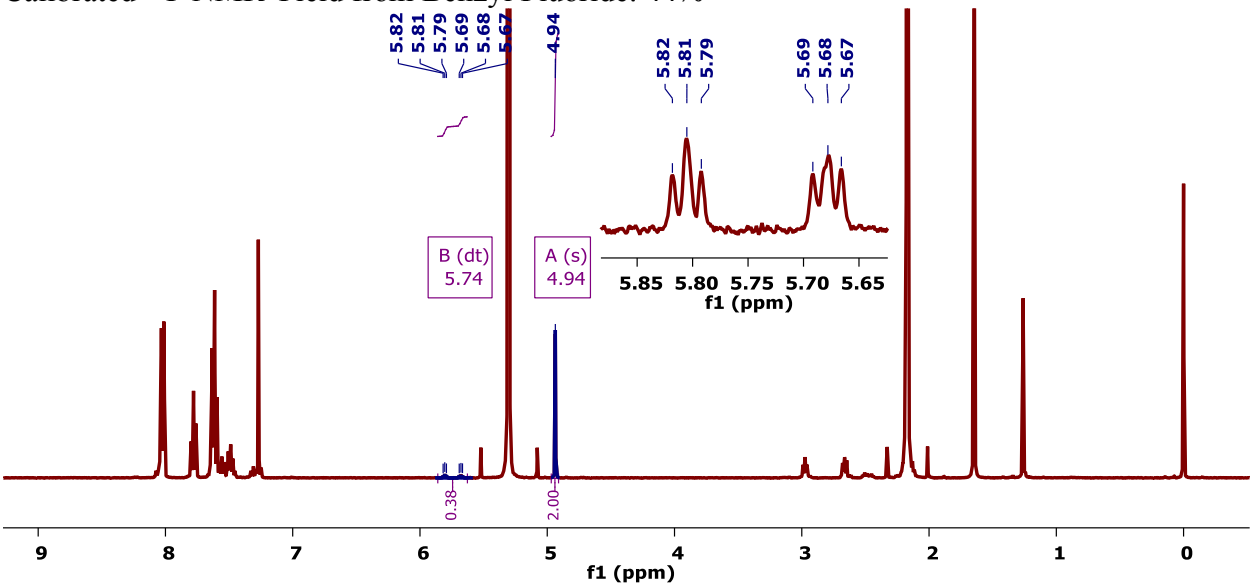



**Figure S39.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.94 ppm). The resolved product benzylic proton is labeled and integrated.

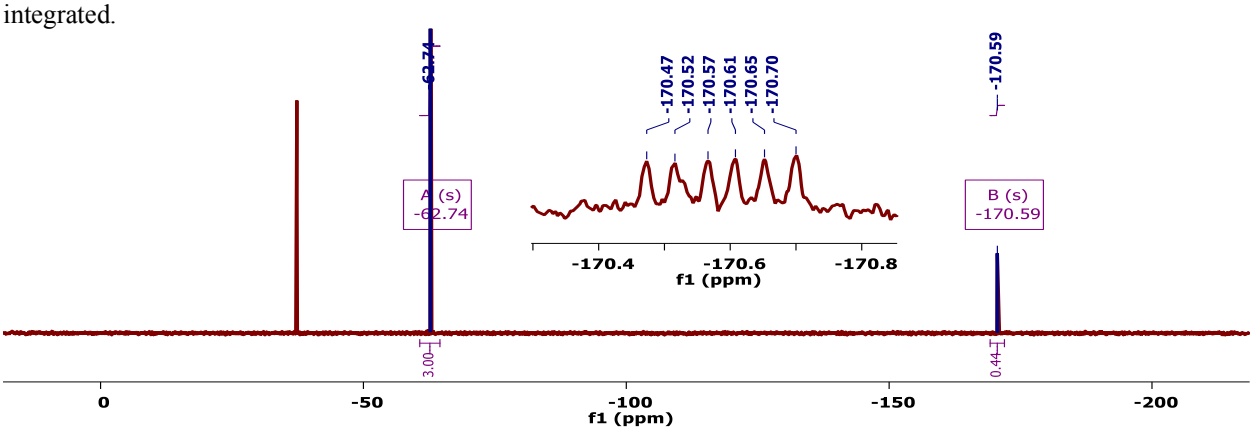
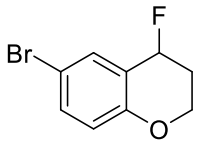



**Figure S40.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.74 ppm). The mono-fluoride (-170.59) is labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(20) 6-bromo-4-fluorochromane:** Prepared from 6-bromochromane (0.3 mmol, 44 µL, 1.0 equiv) according to the general procedure in section II with the following variations: 0.5 equiv $MeB(OH)_2$ operating at 35 °C.
Spectra Available in the Literature (CAS): No (1780938-64-8)
**Benzyl Fluoride C–H Shift:** $^{1}H$ NMR ($CDCl_3$, 400 MHz): δ 5.43 (dt, $^{2}J_{(H,F)}$ = 52.4 Hz, $^{3}J_{(H,H)}$ = 3.4 Hz)
Calibrated $^{1}H$ NMR Yield from Benzylic Proton: 62%
**Benzylic Fluoride Shift:** $^{19}F$ NMR ($CDCl_3$, 377 MHz): δ -153.79 (ddd, $^{2}J_{(H,F)}$ = 50.6 Hz, $^{3}J_{(H,F)}$ = 34.3 & 16.4 Hz)
Calibrated $^{19}F$ NMR Yields from Benzyl Fluoride: 60%

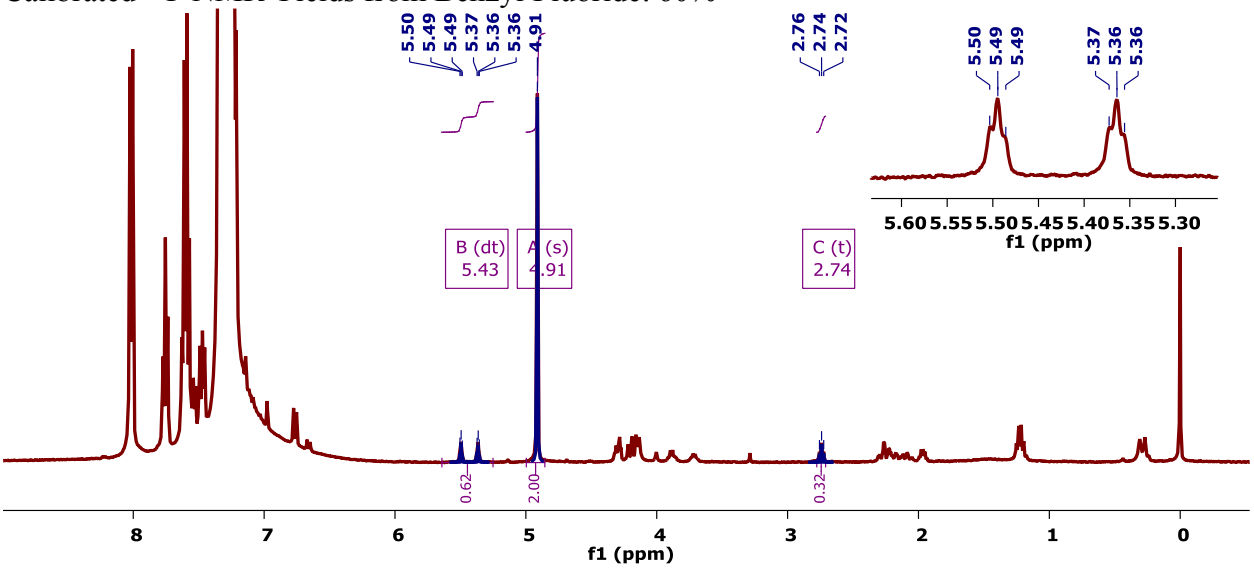



**Figure S41.** Crude $^{1}H$ NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.91 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

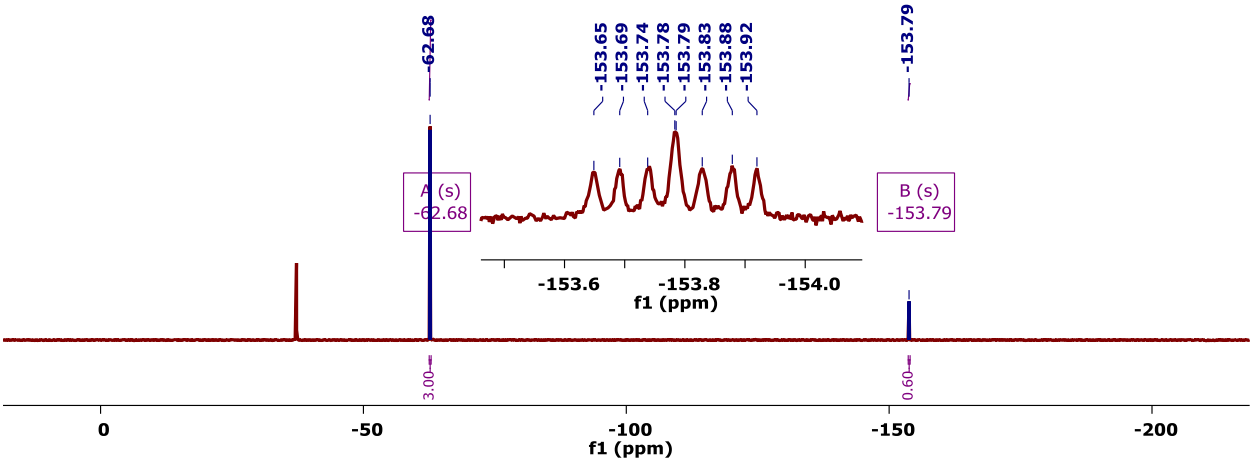
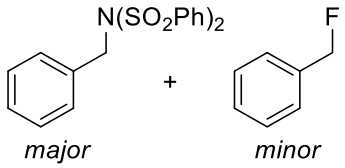



**Figure S42.** Crude $^{19}F\{^{1}H\}$ NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.68 ppm). The mono-fluoride (-153.79) is labeled and integrated. The inset shows an enlargement of the proton-coupled mono-fluoride.




**(21) (fluoromethyl)benzene:** Prepared from toluene (0.3 mmol, 32 µL, 1.0 equiv) according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C in acetone.

Spectra Available in the Literature (CAS): Yes[17] (70869-03-3), Yes[8] (350-50-5)

**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.37 (d, $^2J_{(H,F)}$ = 47.9 Hz)

Calibrated $^1$H NMR Yield from Benzylic Proton(s): 59% (C–N), 12% (C–F), 6% ($C–F_2$)

**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -206.64 (t, $^2J_{(H,F)}$ = 47.3 Hz)

Calibrated $^{19}$F NMR Yields from Benzyl Fluoride(s): 8% (C–F), 8% ($C–F_2$)

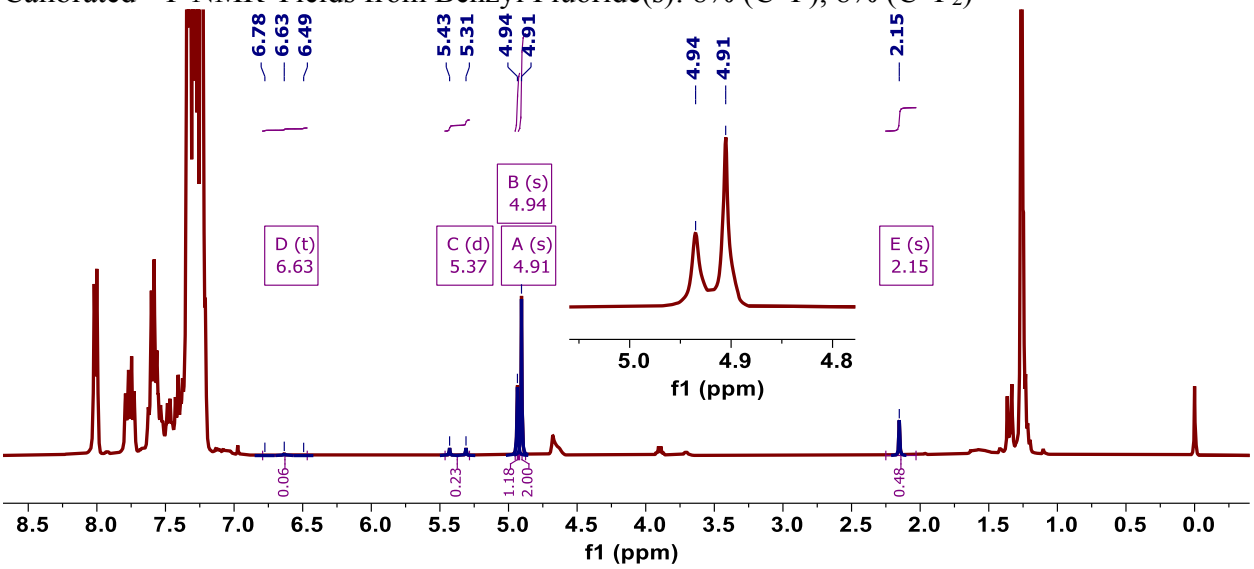



**Figure S43.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.91 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

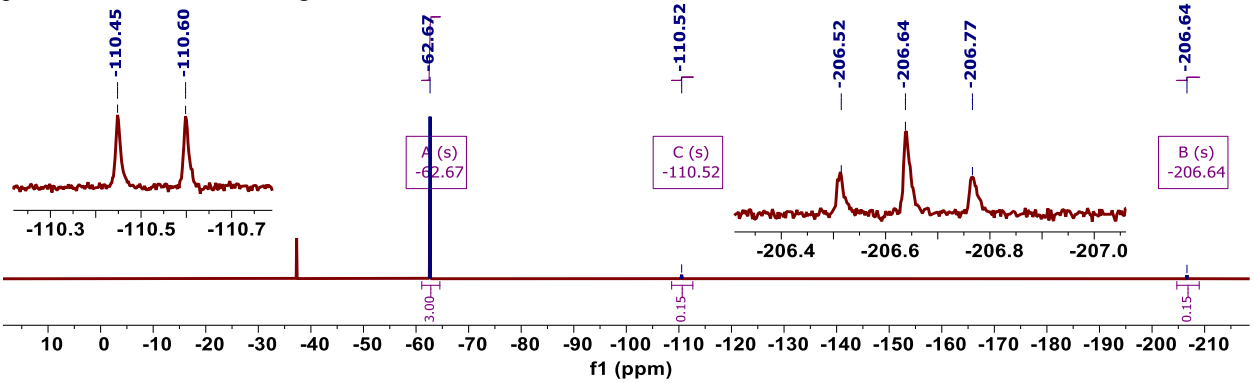
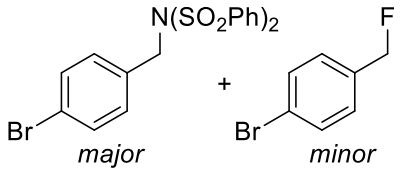



**Figure S44.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.67 ppm). The mono-fluoride (-206.64 ppm) and di-fluoride (-110.52 ppm) are labeled and integrated. The insets show enlargements of the proton-coupled resonances.




**(22) 1-bromo-4-(fluoromethyl)benzene:** Prepared from 4-bromotoluene (0.3 mmol, 37 µL, 1.0 equiv) according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C.

Spectra Available in the Literature (CAS): Yes[17] (1361033-82-0), Yes[14] (459-49-4)

**Benzyl Fluoride C–H Shift:** $^1$H NMR ($CDCl_3$, 400 MHz): δ 5.32 (d, $^2J_{(H,F)}$ = 47.7 Hz)

Calibrated $^1$H NMR Yield from Benzylic Proton(s): 44% (C–N), 8% (C–F), 10% ($C–F_2$)

**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -208.09 (t, $^2J_{(H,F)}$ = 47.7 Hz)

Calibrated $^{19}$F NMR Yields from Benzyl Fluoride: 7% (C–F), 10% ($C–F_2$)

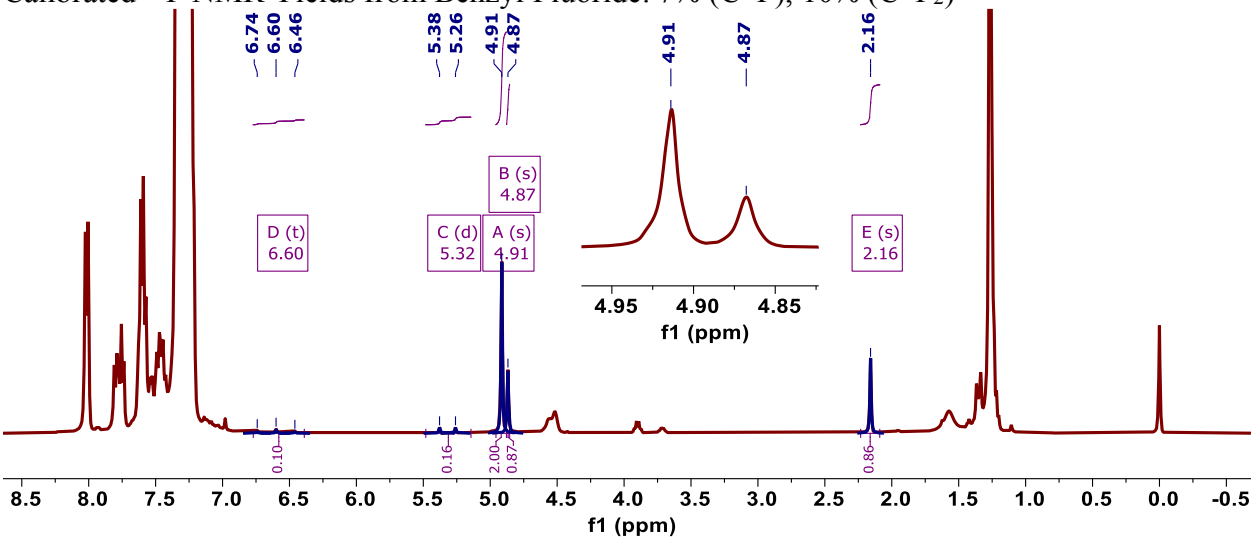



**Figure S45.** Crude $^1$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.91 ppm). The resolved product and starting material benzylic protons are labeled and integrated.

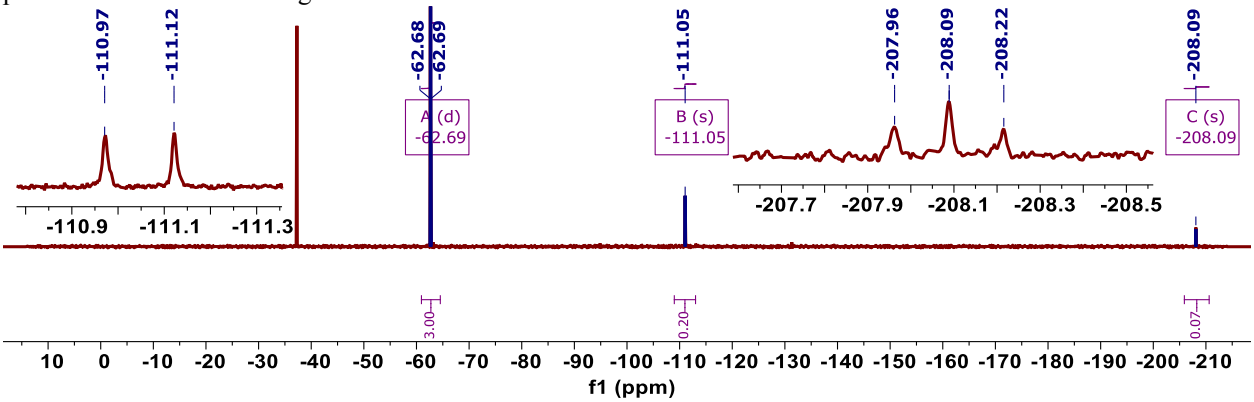
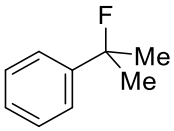



**Figure S46.** Crude $^{19}$F{$^1$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.69 ppm). The mono-fluoride (-208.09 ppm) and the di-fluoride (-111.05 ppm) are labeled and integrated. The insets show enlargements of the proton-coupled resonances.




**(23) (2-fluoropropan-2-yl)benzene:** Prepared from cumene (0.3 mmol, 42 µL, 1.0 equiv) according to the general procedure in section II.
Spectra Available in the Literature (CAS): Yes[8] (74185-81-2)
**Fluoride Product Methyl C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 1.68 (d, $^{3}J_{(H,F)}$ = 21.9 Hz)
Calibrated $^{1}$H NMR Yield from Benzyl Fluoride Methyl Protons: 92%
**Benzylic Fluoride Shift:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -137.39 (hept, $^{3}J_{(H,F)}$ = 21.8 Hz)
Calibrated $^{19}$F NMR Yields from Benzyl Fluoride: 85%

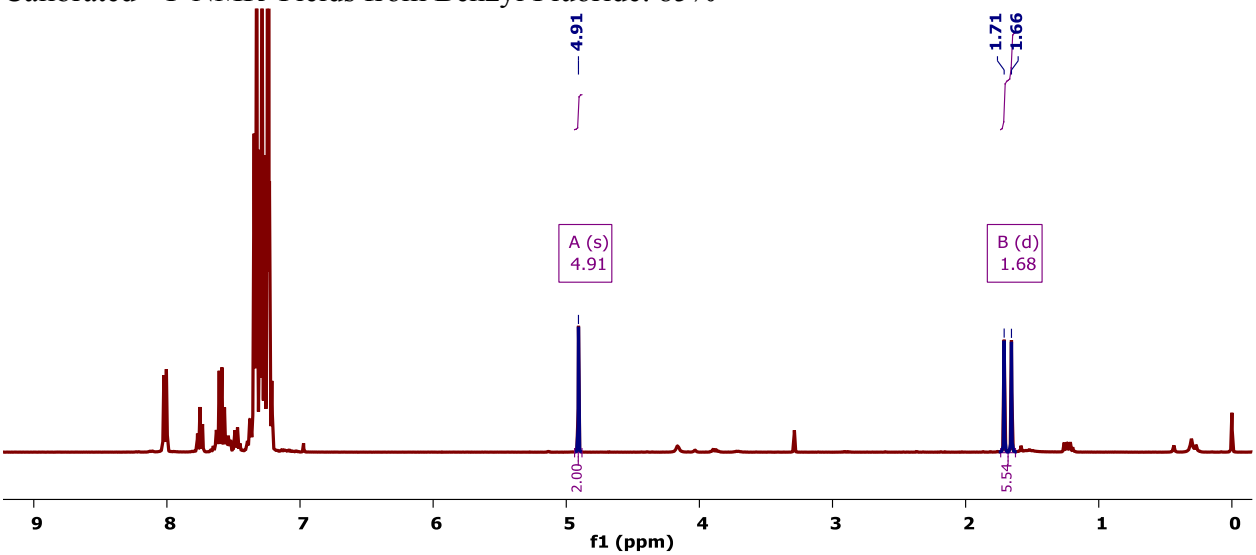



**Figure S47.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.91 ppm). The resolved product aromatic and methyl protons are labeled and integrated.

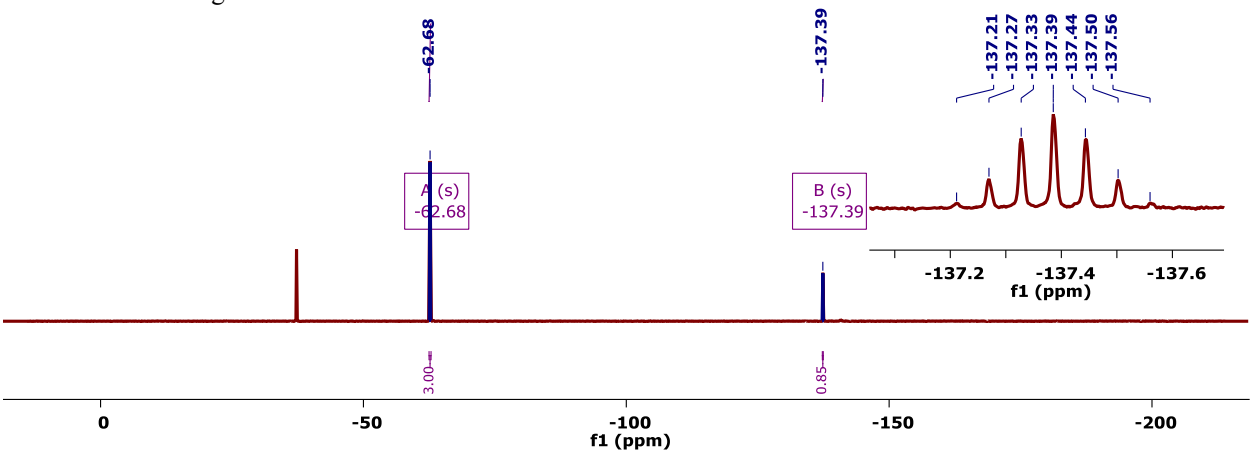
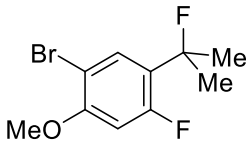



**Figure S48.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.69 ppm). The benzyl-fluoride (-137.39) is labeled and integrated. The inset shows an enlargement of the proton-coupled fluorine resonance.




**(24) 1-bromo-4-fluoro-5-(2-fluoropropan-2-yl)-2-methoxybenzene:** Prepared from 1-bromo-4-fluoro-5-isopropyl-2-methoxybenzene (0.3 mmol, 74 mg, 1.0 equiv) according to the general procedure in section II.

Spectra Available in the Literature (CAS): No (N/A)

**Fluoride Product Aromatic C–H Shift:** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 6.61 (d, $^{3}J_{(H,F)}$ = 12.8 Hz)

Calibrated $^{1}$H NMR Yield from Benzyl Fluoride Aromatic Proton: 84%

**Benzyl Fluoride Product Fluorine Shifts:** $^{19}$F NMR ($CDCl_3$, 377 MHz): δ -112.96 (dt, $^{3}J_{(H,F)}$ = 14.4 Hz, $^{4}J_{(H,F)}$ = 7.6 Hz), -135.16 (hd, $^{3}J_{(H,F)}$ = 22.8 Hz, $^{4}J_{(H,F)}$ = 6.7 Hz)

Calibrated $^{19}$F NMR Yields from Benzyl Fluoride: 82%

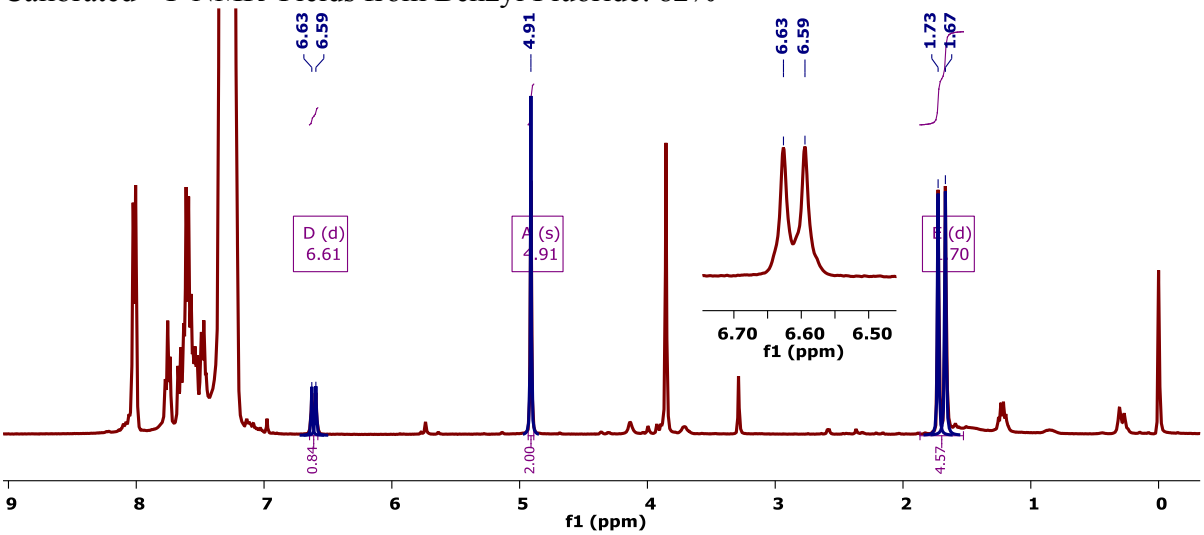



**Figure S49.** Crude $^{1}$H NMR Spectrum ($CDCl_3$, 400 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (21 µL) of $CH_2Br_2$ as an internal standard (4.91 ppm). The resolved product aromatic and methyl protons are labeled and integrated.

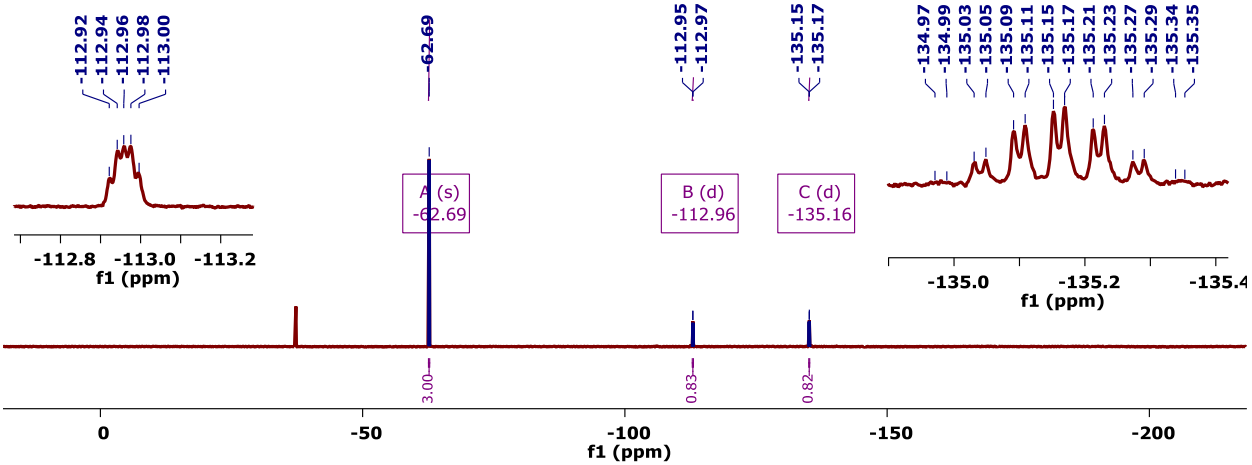
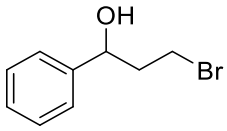
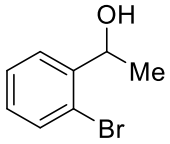



**Figure S50.** Crude $^{19}$F{$^{1}$H} NMR Spectrum ($CDCl_3$, 377 MHz, 25 °C) of the reaction mixture following the addition of 0.3 mmol (37 µL) of $PhCF_3$ as an internal standard (-62.69 ppm). The aryl-fluoride (-112.96) and benzyl-fluoride (-135.16) are labeled and integrated. The inset shows an enlargement of the proton-coupled fluorine resonances.

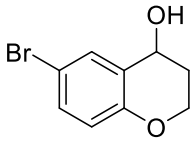
## VIII. Characterization Data for Isolated Cross Coupling Products



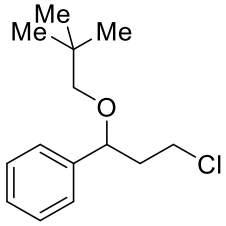

**(25) 3-bromo-1-phenylpropan-1-ol:** Prepared from benzyl fluoride **8** (0.3 mmol scale, 65% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used water (0.75 mmol, 13.5 μL, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 μL, 10 equiv) as the displacement catalyst.
Purification: Normal phase silica gel chromatography was used with a gradient of 0%→10% EtOAc in pentane.
Isolated Yield from Benzyl Fluoride: 64%, 27.4 mg of yellow oil
Spectra Available in the Literature (CAS): Yes[18] (34052-63-6)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.39 – 7.35 (m, 4H), 7.33 – 7.28 (m, 1H), 4.92 (dd, *J* = 8.4, 4.7 Hz, 1H), 3.59 (ddd, *J* = 10.0, 8.2, 6.0 Hz, 1H), 3.42 (dt, *J* = 10.0, 6.1 Hz, 1H), 2.32 (ddt, *J* = 14.3, 8.3, 5.9 Hz, 1H), 2.18 (dddd, *J* = 14.5, 8.2, 6.3, 4.6 Hz, 1H), 2.03 (bs, 1H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 143.6, 128.7, 127.9, 125.8, 72.3, 41.6, 30.2.



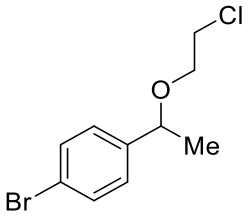

**(26) 1-(2-bromophenyl)ethan-1-ol:** Prepared from benzyl fluoride **2** (0.3 mmol scale, 44% NMR yield) that was formed according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 75 °C. The ensuing displacement step followed the general procedure in section III and used water (0.75 mmol, 13.5 μL, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 μL, 10 equiv) as the displacement catalyst.
Purification: Reverse phase silica gel chromatography was used with a gradient of 50%→85% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 87%, 22.9 mg of colorless oil.
Spectra Available in the Literature (CAS): Yes[19] (5411-56-3)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.60 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 5.24 (q, *J* = 6.4 Hz, 1H), 1.49 (d, *J* = 6.4 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 144.6, 132.7, 128.8, 127.9, 126.7, 121.7, 69.2, 23.6.



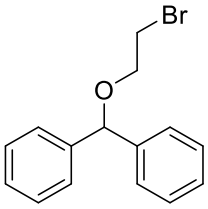

**(27) 6-bromochroman-4-ol:** Prepared from benzyl fluoride **20** (0.3 mmol scale, 57% NMR yield) that was formed according to the general procedure in section II with the following variations: 0.5 equiv $MeB(OH)_2$ operating at 35 °C. The ensuing displacement step followed the general procedure in section III and used water (0.75 mmol, 13.5 µL, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 µL, 10 equiv) as the displacement catalyst.
Purification: Reverse phase silica gel chromatography was used with a gradient of 50%→85% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 34%, 13.1 mg of colorless oil.
Spectra Available in the Literature (CAS): Yes[20] (18385-77-8)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.45 (d, *J* = 2.5 Hz, 1H), 7.28 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 4.76 (t, *J* = 4.3 Hz, 1H), 4.31 – 4.21 (m, 2H), 2.18 – 1.98 (m, 2H), 1.87 (bs, 1H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 153.7, 132.5, 132.1, 126.3, 119.0, 112.4, 63.0, 62.2, 30.6.



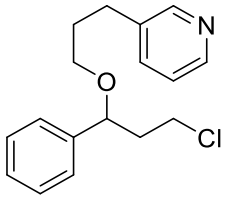

**(28) (3-chloro-1-(neopentyloxy)propyl)benzene:** Prepared from benzyl fluoride **7** (0.3 mmol scale, 76% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used neopentyl alcohol (0.75 mmol, 81.4 µL, 2.5 equiv) as the nucleophile with $BF_3$•$Et_2O$ (0.03 mmol, 3.7 µL, 0.1 equiv) as the displacement catalyst. The nucleophile was dried in 1 mL DCM with $MgSO_4$ prior to use.
Purification: Reverse phase silica gel chromatography was used with a gradient of 70%→100% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 51%, 28.2 mg of light yellow oil.
Spectra Available in the Literature (CAS): No (2173346-35-3)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 3H), 4.42 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.78 (ddd, *J* = 10.6, 8.6, 5.8 Hz, 1H), 3.59 (ddd, *J* = 11.0, 6.4, 5.1 Hz, 1H), 3.03 (d, *J* = 8.5 Hz, 1H), 2.90 (d, *J* = 8.5 Hz, 1H), 2.21 (ddt, *J* = 14.5, 9.2, 5.5 Hz, 1H), 2.00 (dddd, *J* = 14.6, 8.6, 6.4, 4.1 Hz, 1H), 0.91 (s, 9H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 142.3, 128.4, 127.5, 126.4, 79.5, 78.9, 41.9, 41.6, 32.1, 26.7.
**HRMS (ESI) m/z:** $[M-H]^+$ Calcd for $C_{14}H_{20}ClO$ 239.1197; Found 239.1197.




**(29) 1-bromo-4-(1-(2-chloroethoxy)ethyl)benzene:** Prepared from benzyl fluoride **1** (0.3 mmol scale, 74% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used 2-chloroethanol (0.75 mmol, 50.3 µL, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 µL, 10 equiv) as the displacement catalyst.
Purification: Normal phase silica gel chromatography was used with a gradient of 0%→20% EtOAc in pentane.
Isolated Yield from Benzyl Fluoride: 60%, 35.3 mg of colorless amorphous solid.
Spectra Available in the Literature (CAS): No (N/A)
**$^{1}$H NMR** ($CDCl_3$, 500 MHz): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.43 (q, *J* = 6.5 Hz, 1H), 3.62 – 3.53 (m, 4H), 1.44 (d, *J* = 6.5 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 142.4, 131.7, 127.9, 121.4, 77.9, 68.7, 43.0, 23.9.
**HRMS (ESI) m/z:** $[M+NH_4]^+$ Calcd for $C_{10}H_{16}BrClNO$ 280.0098; Found 280.0100.




**(30) ((2-bromoethoxy)methylene)dibenzene:** Prepared from benzyl fluoride **10** (0.3 mmol scale, 46% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used 2-bromoethanol (0.75 mmol, 53.2 µL, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 µL, 10 equiv) as the displacement catalyst.
Purification: Reverse phase silica gel chromatography was used with a gradient of 50%→85% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 80%, 32.3 mg of white solid.
Spectra Available in the Literature (CAS): Yes[21] (91-01-0)
**$^{1}$H NMR** ($CDCl_3$, 500 MHz): δ 7.40 – 7.31 (m, 8H), 7.30 – 7.24 (m, 2H), 5.44 (s, 1H), 3.79 (t, *J* = 6.3 Hz, 2H), 3.53 (t, *J* = 6.2 Hz, 2H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 141.7, 128.4, 127.7, 127.0, 83.9, 68.9, 30.6.




**(31) 3-(3-(3-chloro-1-phenylpropoxy)propyl)pyridine:** Prepared from benzyl fluoride **7** (0.3 mmol scale, 78% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used 3-(3-pyridyl)-1-propanol (0.75 mmol, 43 µL, 2.5 equiv) that was protonated with methanesulfonic acid (0.75 mmol, 48.7 µL, 2.5 equiv) as the nucleophile with both HFIP (3.0 mmol, 315 µL, 10 equiv) and $BF_3$•$Et_2O$ (0.15 mmol, 18.5 µL, 0.5 equiv) as the displacement catalysts. The nucleophile was dried in 1 mL DCM with $MgSO_4$

Purification: An extraction with DCM and sodium bicarbonate was used to remove MsOH and $BF_3$ from pyridine. The organic phase was collected, dried with $MgSO_4$, concentrated on the rotovap and then subjected to chromatography with a gradient of 20%→60% EtOAc in pentane.

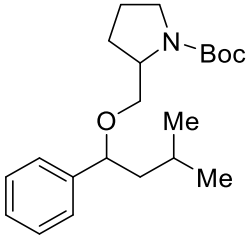
Isolated Yield from Benzyl Fluoride: 36%, 24.1 mg of slightly yellow oil.

Spectra Available in the Literature (CAS): No (N/A)

**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 8.44 (t, *J* = 2.1 Hz, 2H), 7.47 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 3H), 7.19 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.47 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.75 (ddd, *J* = 10.7, 8.5, 5.4 Hz, 1H), 3.54 (dt, *J* = 11.0, 5.7 Hz, 1H), 3.38 (dt, *J* = 9.5, 6.1 Hz, 1H), 3.30 (dt, *J* = 9.5, 6.1 Hz, 1H), 2.76 – 2.61 (m, 2H), 2.25 (ddt, *J* = 14.3, 8.8, 5.5 Hz, 1H), 2.02 (dddd, *J* = 14.4, 8.5, 5.9, 4.6 Hz, 1H), 1.87 (tt, *J* = 8.0, 6.2 Hz, 2H).

**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 149.9, 147.3, 141.7, 137.2, 135.9, 128.6, 127.8, 126.5, 123.3, 78.7, 67.7, 41.7, 41.0, 31.2, 29.6.

**HRMS (ESI) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{21}ClNO$ 290.1306; Found 290.1302.




**(32) *tert*-butyl (2R)-2-((3-methyl-1-phenylbutoxy)methyl)pyrrolidine-1-carboxylate:**
Prepared from benzyl fluoride **11** (0.3 mmol scale, 76% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used N-Boc-DL-prolinol (0.75 mmol, 151 mg, 2.5 equiv) as the nucleophile with $BF_3$•$Et_2O$ (0.15 mmol, 18.5 µL, 0.5 equiv) as the displacement catalyst.

Purification: Silica gel chromatography was used with a gradient of 0%→20% EtOAc in pentane.

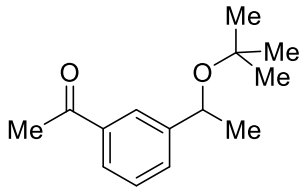
Isolated Yield from Benzyl Fluoride: 49%, 38.8 mg of colorless oil.

Spectra Available in the Literature (CAS): No (N/A)

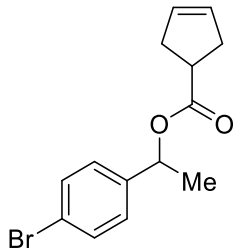
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.34 – 7.29 (m, 2H), 7.28 – 7.23 (m, 3H), 4.34 – 4.16 (m, 1H), 4.04 – 3.73 (m, 1H), 3.43 – 3.01 (m, 4H), 2.06 – 1.85 (m, 3H), 1.86 – 1.65 (m, 4H), 1.47 – 1.42 (m, 2H), 1.44 – 1.31 (m, 9H), 0.96 – 0.85 (m, 6H).

**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 154.4, 143.3, 128.3, 127.3, 126.4, 81.2, 80.6, 79.1, 70.0, 69.6, 68.8, 56.8, 56.5, 47.9, 47.8, 46.7, 46.4, 29.1, 28.5, 24.8, 24.8, 23.2, 23.0, 22.2.

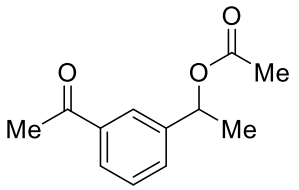
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{21}H_{33}NNaO_3$ 370.2353; Found 370.2348.



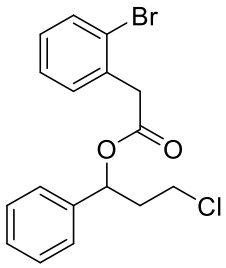

**(33) 1-(3-(1-(*tert*-butoxy)ethyl)phenyl)ethan-1-one:** Prepared from benzyl fluoride **4** (0.3 mmol scale, 80% NMR yield) that was formed according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C. The ensuing displacement step followed the general procedure in section III and used *tert*-butanol (0.75 mmol, 71.7 µL, 2.5 equiv) as the nucleophile with $BF_3$•$Et_2O$ (0.03 mmol, 3.7 µL, 0.1 equiv) as the displacement catalyst. The nucleophile was dried in 1 mL DCM with $MgSO_4$ prior to use.
Purification: Reverse phase silica gel chromatography was used with a gradient of 70%→100% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 66%, 35.5 mg of colorless oil.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.93 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 4.72 (q, *J* = 6.5 Hz, 1H), 2.61 (s, 3H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.16 (s, 9H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 198.3, 148.2, 137.1, 130.4, 128.4, 126.7, 125.3, 83.5, 74.4, 69.5, 28.5, 26.7, 26.6, 25.0.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{14}H_{20}NaO_2$ 243.1356; Found 243.1353.



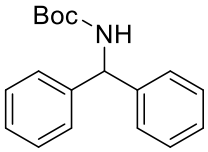

**(34) 1-(4-bromophenyl)ethyl cyclopent-3-ene-1-carboxylate:** Prepared from benzyl fluoride **1** (0.3 mmol scale, 72% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used cyclopent-3-ene-1-carboxylic acid (0.75 mmol, 77.6 µL, 2.5 equiv) as the nucleophile with $BF_3$•$Et_2O$ (0.03 mmol, 3.7 µL, 0.1 equiv) as the displacement catalyst.
Purification: Normal phase silica gel chromatography was used with a gradient of 0%→20% EtOAc in pentane.
Isolated Yield from Benzyl Fluoride: 57%, 36.1 mg of clear, colorless liquid.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.84 (q, *J* = 6.6 Hz, 1H), 5.69 – 5.60 (m, 2H), 3.13 (tt, *J* = 9.0, 7.5 Hz, 1H), 2.73 – 2.54 (m, 4H), 1.51 (d, *J* = 6.7 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 175.2, 140.9, 131.6, 128.9, 127.8, 121.7, 71.5, 41.6, 36.2, 22.1.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{14}H_{15}BrNaO_2$ 317.0148; Found 317.0147.



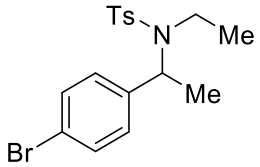

**(35) 1-(3-acetylphenyl)ethyl acetate:** Prepared from benzyl fluoride **4** (0.3 mmol scale, 76% NMR yield) that was formed according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 55 °C. The ensuing displacement step followed the general procedure in section III and used acetic acid (0.75 mmol, 43 µL, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 µL, 10 equiv) as the displacement catalyst.
Purification: Normal phase silica gel chromatography was used with a gradient of 0%→20% EtOAc in pentane.
Isolated Yield from Benzyl Fluoride: 80%, 37.8 mg of colorless oil.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.95 (s, 1H), 7.88 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 5.92 (q, *J* = 6.7 Hz, 1H), 2.62 (s, 3H), 2.09 (s, 3H), 1.56 (d, *J* = 6.7 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 197.8, 170.2, 142.4, 137.4, 130.8, 128.8, 127.9, 125.8, 71.9, 26.7, 22.2, 21.3.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{12}H_{14}NaO_3$ 229.0835; Found 229.0832.



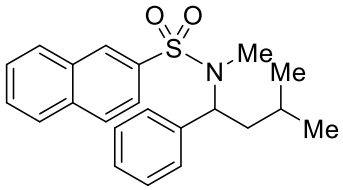

**(36) 3-chloro-1-phenylpropyl 2-(2-bromophenyl)acetate:** Prepared from benzyl fluoride **7** (0.3 mmol scale, 72% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used 2-(2-bromophenyl)acetic acid (0.75 mmol, 161.3 mg, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 µL, 10 equiv) as the displacement catalyst.
Purification: Normal phase silica gel chromatography was used with a gradient of 0%→20% EtOAc in pentane.
Isolated Yield from Benzyl Fluoride: 64%, 50.5 mg of yellow solid.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.23 (m, 7H), 7.15 (ddd, *J* = 8.8, 6.0, 3.0 Hz, 1H), 5.98 (dd, *J* = 8.4, 5.3 Hz, 1H), 3.89 – 3.78 (m, 2H), 3.52 (dt, *J* = 10.9, 7.0 Hz, 1H), 3.43 (dt, *J* = 10.9, 6.4 Hz, 1H), 2.38 (ddt, *J* = 14.5, 8.3, 6.2 Hz, 1H), 2.18 (dtd, *J* = 14.3, 7.1, 5.3 Hz, 1H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 169.5, 139.3, 134.1, 132.8, 131.4, 129.0, 128.6, 128.3, 127.6, 126.4, 125.0, 73.8, 41.9, 40.6, 39.1.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{17}H_{16}BrClNaO_2$ 390.9893; Found 390.9886.



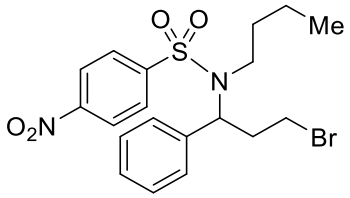

**(37) *tert*-butyl benzhydrylcarbamate:** Prepared from benzyl fluoride **10** (0.3 mmol scale, 44% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used Boc carbamate (0.75 mmol, 87.9 mg, 2.5 equiv) as the nucleophile with $BF_3$•$Et_2O$ (0.15 mmol, 18.5 μL, 0.5 equiv) as the displacement catalyst.
Purification: Normal phase silica gel chromatography was used with a gradient of 0%→20% EtOAc in pentane.
Isolated Yield from Benzyl Fluoride: 70%, 26.2 mg of white solid.
Spectra Available in the Literature (CAS): Yes[22] (21420-61-1)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.35 – 7.30 (m, 4H), 7.29 – 7.22 (m, 6H), 5.92 (bs, 1H), 5.15 (bs, 1H), 1.44 (bs, 9H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 155.0, 142.1, 128.6, 127.3, 127.2, 79.8, 58.4, 28.4.



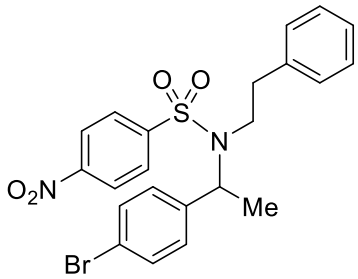

**(38) N-(1-(4-bromophenyl)ethyl)-N-ethyl-4-methylbenzenesulfonamide:** Prepared from benzyl fluoride **1** (0.3 mmol scale, 56% NMR yield) that was formed according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 45 °C with DCM as the solvent instead of PhCl. The ensuing displacement step followed the general procedure in section III and used N-ethyl-4-methylbenzenesulfonamide (0.75 mmol, 149.4 mg, 2.5 equiv) as the nucleophile with $BF_3$.$Et_2O$ (0.03 mmol, 3.7 μL, 0.1 equiv) as the displacement catalyst.
Purification: Reverse phase chromatography was used with a gradient of 65%→100% MeOH in water. Solvent was removed directly on the rotovap at elevated temperatures.
Isolated Yield from Benzyl Fluoride: 78%, 50 mg of white solid.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.73 (d, $J$ = 8.3 Hz, 2H), 7.41 (d, $J$ = 8.5 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.5 Hz, 2H), 5.14 (q, $J$ = 7.1 Hz, 1H), 3.20 – 3.02 (m, $J$ = 7.3 Hz, 2H), 2.44 (s, 3H), 1.37 (d, $J$ = 7.1 Hz, 3H), 0.93 (t, $J$ = 7.1 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 143.1, 139.7, 138.4, 131.4, 129.7, 129.2, 127.1, 121.5, 54.7, 38.9, 21.5, 16.7, 16.6.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{17}H_{20}BrNNaO_2S$ 404.0290; Found 404.0287.



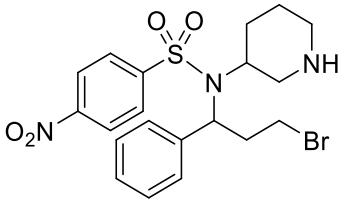
**(39) N-methyl-N-(3-methyl-1-phenylbutyl)naphthalene-2-sulfonamide:** Prepared from benzyl fluoride **11** (0.3 mmol scale, 70% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used N-methyl-2-naphthylsulfonamide (0.75 mmol, 166 mg, 2.5 equiv) as the nucleophile with $BF_3.Et_2O$ (0.03 mmol, 3.7 μL, 0.1 equiv) as the displacement catalyst.
Purification: Normal phase silica gel chromatography was used with a gradient of 0%→20% EtOAc in pentane.
Isolated Yield from Benzyl Fluoride: 82%, 63.1 mg of white solid.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 8.32 (s, 1H), 7.89 (t, *J* = 8.4 Hz, 3H), 7.71 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.66 – 7.55 (m, 2H), 7.28 – 7.21 (m, 5H), 5.29 (dd, *J* = 8.4, 7.0 Hz, 1H), 2.69 (s, 3H), 1.84 – 1.74 (m, 1H), 1.56 – 1.43 (m, 2H), 0.90 (dd, *J* = 13.0, 6.3 Hz, 6H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 138.5, 137.1, 134.6, 132.1, 129.1, 129.1, 128.5, 128.4, 128.4, 128.1, 127.8, 127.7, 127.4, 122.7, 58.2, 39.6, 28.8, 24.8, 22.7, 22.4.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{22}H_{25}NNaO_2S$ 390.1498; Found 390.1495.



**(40) N-(3-bromo-1-phenylpropyl)-N-butyl-4-nitrobenzenesulfonamide:** Prepared from benzyl fluoride **8** (0.3 mmol scale, 67% NMR yield) that was formed according to the general procedure in section II with DCM as the solvent instead of PhCl. The ensuing displacement step followed the general procedure in section III and used N-butyl-4-nitrobenzenesulfonamide (0.75 mmol, 193.7 mg, 2.5 equiv) as the nucleophile with $BF_3.Et_2O$ (0.03 mmol, 3.7 μL, 0.1 equiv) as the displacement catalyst. The nucleophile was dried in 1 mL DCM with $MgSO_4$ prior to use.
Purification: Reverse phase chromatography was used with 65%→100% MeOH in water. Solvent was removed directly on the rotovap at elevated temperatures.
Isolated Yield from Benzyl Fluoride: 62%, 56.3 mg of colorless oil.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 8.26 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.20 – 7.14 (m, 2H), 5.15 (dd, *J* = 8.9, 6.3 Hz, 1H), 3.43 (dt, *J* = 10.3, 6.0 Hz, 1H), 3.26 (ddd, *J* = 10.4, 8.4, 5.9 Hz, 1H), 3.14 (ddd, *J* = 9.8, 6.0, 3.7 Hz, 2H), 2.67 (ddt, *J* = 14.6, 8.9, 5.8 Hz, 1H), 2.37 (dt, *J* = 14.7, 7.3 Hz, 1H), 1.56 – 1.45 (m, 1H), 1.41 – 1.29 (m, 1H), 1.18 (h, *J* = 7.4 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 149.7, 146.8, 136.3, 128.9, 128.7, 128.3, 128.2, 124.1, 60.1, 46.1, 35.3, 32.7, 29.7, 20.1, 13.6.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{19}H_{23}BrN_2NaO_4S$ 477.0454; Found 477.0448.

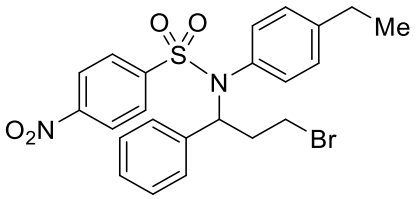


**(41) N-(1-(4-bromophenyl)ethyl)-4-nitro-N-phenethylbenzenesulfonamide:** Prepared from benzyl fluoride **1** (0.3 mmol scale, 83% NMR yield) that was formed according to the general procedure in section II with DCM as the solvent instead of PhCl. The ensuing displacement step followed the general procedure in section III and used N-phenethyl-4-nitrobenzenesulfonamide (0.75 mmol, 229.8 mg, 2.5 equiv) as the nucleophile with $BF_3.Et_2O$ (0.03 mmol, 3.7 µL, 0.1 equiv) as the displacement catalyst. The nucleophile was dried in 1 mL DCM with $MgSO_4$ prior to use.
Purification: Reverse phase chromatography was used with 65%→100% MeOH in water. Solvent was removed directly on the rotovap at elevated temperatures.
Isolated Yield from Benzyl Fluoride: 42%, 51.4 mg of white solid.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.22 – 7.16 (m, 3H), 6.96 (d, *J* = 7.0 Hz, 2H), 5.22 (q, *J* = 7.1 Hz, 1H), 3.31 (ddd, *J* = 14.8, 11.4, 5.5 Hz, 1H), 3.19 (ddd, *J* = 14.8, 11.3, 5.2 Hz, 1H), 2.80 (td, *J* = 12.8, 11.3, 5.5 Hz, 1H), 2.38 (td, *J* = 12.8, 11.3, 5.5 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 149.9, 146.7, 138.5, 138.1, 131.8, 129.2, 128.7, 128.6, 128.2, 126.7, 124.4, 122.3, 55.6, 46.4, 37.6, 16.8.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{22}H_{21}BrN_2NaO_4S$ 511.0298; Found 511.0295.

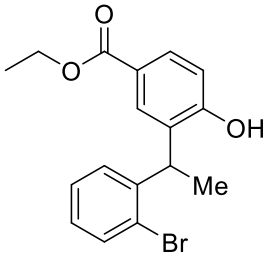


Boc from the Nuc–H piperidine
was removed under displacement conditions

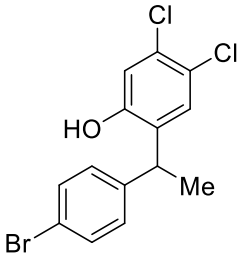
**(42) *tert*-butyl 3-((N-(3-bromo-1-phenylpropyl)-4-nitrophenyl)sulfonamido)piperidine-1-carboxylate:** Prepared from benzyl fluoride **8** (0.3 mmol scale, 63% NMR yield) that was formed according to the general procedure in section II with DCM as the solvent instead of PhCl. The ensuing displacement step followed the general procedure in section III and used 3-((4-nitrophenyl)sulfonamido)-N-Boc-piperidine (0.75 mmol, 289.1 mg, 2.5 equiv) as the nucleophile with $BF_3.Et_2O$ (0.45 mmol, 55.5 µL, 1.5 equiv) as the displacement catalyst.
Purification: Reverse phase chromatography was used with 65%→100% MeOH in water. Solvent was removed directly on the rotovap at elevated temperatures.
Isolated Yield from Benzyl Fluoride: 23%, 21.0 mg of yellow oil.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 8.43 – 8.25 (m, 2H), 8.12 – 7.96 (m, 2H), 7.40 – 7.28 (m, 5H), 5.82 (t, *J* = 6.6 Hz, 1H), 4.90 (bs, 1H), 3.56 – 3.18 (m, 7H), 2.55 – 2.44 (m, 1H), 2.39 – 2.20 (m, 1H), 1.86 – 1.70 (m, 1H), 1.70 – 1.62 (m, 1H), 1.53 – 1.43 (m, 2H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 150.1, 146.5, 139.7, 139.7, 128.8, 128.4, 128.4, 128.3, 126.2, 124.6, 124.6, 75.8, 49.6, 39.6, 39.5, 30.9, 28.7, 28.6, 22.4.
**HRMS (ESI) m/z:** $[M+CO_2+Na]^+$ Calcd for $C_{21}H_{24}BrN_3NaO_6S$ 548.0461; Found 548.0462.



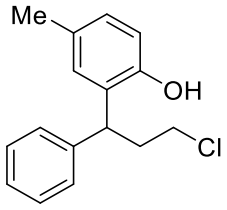
**(43) N-(3-bromo-1-phenylpropyl)-N-(4-ethylphenyl)-4-nitrobenzenesulfonamide:** Prepared from benzyl fluoride **8** (0.3 mmol scale, 68% NMR yield) that was formed according to the general procedure in section II with DCM as the solvent instead of PhCl. The ensuing displacement step followed the general procedure in section III and used N-4-ethylphenyl-4-nitrobenzenesulfonamide (0.75 mmol, 229.8 mg, 2.5 equiv) as the nucleophile with $BF_3$•$Et_2O$ (0.15 mmol, 18.5 μL, 0.5 equiv) as the displacement catalyst. The nucleophile was dried in 1 mL DCM with $MgSO_4$ prior to use.
Purification: Reverse phase chromatography was used with 65%→100% MeOH in water.
Isolated Yield from Benzyl Fluoride: 70%, 72 mg of yellow oil.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.03 (t, *J* = 7.0 Hz, 4H), 6.48 (d, *J* = 7.9 Hz, 2H), 5.74 (t, *J* = 7.6 Hz, 1H), 3.38 (dt, *J* = 10.3, 6.2 Hz, 1H), 3.23 (dt, *J* = 10.3, 7.1 Hz, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.43 – 2.27 (m, 2H), 1.22 (t, *J* = 7.6 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 149.8, 146.5, 145.7, 136.9, 132.3, 131.5, 128.8, 128.7, 128.7, 128.5, 128.4, 123.9, 61.7, 35.7, 29.4, 28.4, 15.1.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{23}H_{23}BrN_2NaO_4S$ 525.0454; Found 525.0452.



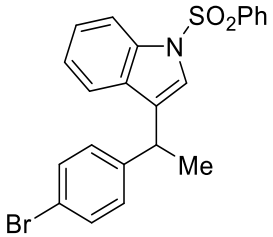
**(44) 3-(1-(2-bromophenyl)ethyl)-4-hydroxy-ethylbenzoate:** Prepared from benzyl fluoride **2** (0.3 mmol scale, 48% NMR yield) that was formed according to the general procedure in section II with the following variations: 1 mol% CuOAc, 1.2 mol% BPhen, 1 equiv $B_2pin_2$ (in place of 2 equiv $MeB(OH)_2$), and 4 equiv NFSI operating at 75 °C. The ensuing displacement step followed the general procedure in section III and used ethyl paraben (0.75 mmol, 124.7 mg, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 μL, 10 equiv) as the displacement catalyst.
Purification: Reverse phase silica gel chromatography was used with a gradient of 50%→85% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 75%, 37.5 mg of colorless oil.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.11 (td, *J* = 7.7, 1.7 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 5.69 (q, *J* = 6.3 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.64 (d, *J* = 6.3 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 166.3, 161.2, 141.4, 132.8, 132.8, 131.5, 129.1, 129.1 128.2, 126.8, 123.0, 121.5, 115.1, 74.9, 60.5, 22.6, 14.3.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{17}H_{17}BrNaO_3$ 371.0253; Found 371.0251.



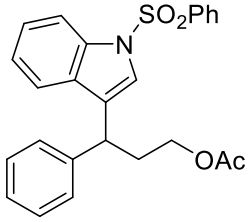

**(45) 2-(1-(4-bromophenyl)ethyl)-4,5-dichlorophenol:** Prepared from benzyl fluoride **1** (0.3 mmol scale, 75% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used 3,4-dichlorophenol (0.75 mmol, 122.3 mg, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 µL, 10 equiv) as the displacement catalyst.
Purification: Reverse phase chromatography was used with a gradient of 65%→100% MeOH in water.
Isolated Yield from Benzyl Fluoride: 83%, 64.3 mg of yellow solid.
Spectra Available in the Literature (CAS): No (N/A)
**$^{1}$H NMR** ($CDCl_3$, 500 MHz): δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.24 (s, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.84 (s, 1H), 4.97 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.3 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 152.1, 143.4, 132.4, 132.4 131.8, 130.5, 129.2, 124.2, 120.5, 117.6, 37.7, 20.6.
**HRMS (ESI) m/z:** $[M-H]^-$ Calcd for $C_{14}H_{10}BrCl_2O$ 342.9298; Found 342.9300.



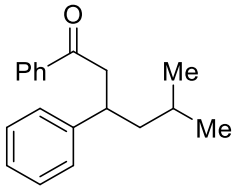

**(46) 2-(3-chloro-1-phenylpropyl)-4-methylphenol:** Prepared from benzyl fluoride **7** (0.3 mmol scale, 77% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used *p*-cresol (0.75 mmol, 81 mg, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 µL, 10 equiv) as the displacement catalyst.
Purification: Reverse phase silica gel chromatography was used with a gradient of 70%→100% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 87%, 52.6 mg of off-white oil.
Isolated Yield from Benzyl Fluoride on 3 mmol Scale (see section IV): 84%, 445 mg of gold oil.
Spectra Available in the Literature (CAS): No (926890-10-0)
**$^{1}$H NMR** ($CDCl_3$, 500 MHz): δ 7.33 – 7.27 (m, 4H), 7.21 (tt, *J* = 5.5, 2.5 Hz, 1H), 7.02 (d, *J* = 2.1 Hz, 1H), 6.91 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.48 (s, 1H), 4.46 (t, *J* = 7.8 Hz, 1H), 3.54 – 3.44 (m, 2H), 2.60 – 2.44 (m, 2H), 2.28 (s, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 151.1, 142.8, 130.2, 129.4, 128.7, 128.6, 128.2, 128.0, 126.7, 116.0, 43.3, 41.4, 37.2, 20.7.
**HRMS (ESI) m/z:** $[M-Cl]^+$ Calcd for $C_{16}H_{17}O$ 225.1274; Found 225.1271.



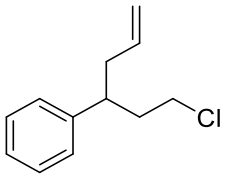

**(47) 3-(1-(4-bromophenyl)ethyl)-1-(phenylsulfonyl)-1H-indole:** Prepared from benzyl fluoride **1** (0.3 mmol scale, 78% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used 1-(phenylsulfonyl)indole (0.75 mmol, 193 mg, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 μL, 10 equiv) as the displacement catalyst.
Purification: Reverse phase silica gel chromatography was used with a gradient of 70%→100% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 78%, 80.4 mg of white solid.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 1.3 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.27 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.15 – 7.07 (m, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 4.18 (q, *J* = 7.6 Hz, 1H), 1.64 (d, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 143.9, 138.2, 135.7, 133.7, 131.6, 130.1, 129.2, 129.0, 127.2, 126.7, 124.8, 123.2, 122.9, 120.2, 120.2, 113.8, 36.4, 21.8.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{22}H_{18}BrNNaO_2S$ 462.0134; Found 462.0131.




**(48) 3-phenyl-3-(1-(phenylsulfonyl)-1H-indol-3-yl)propylacetate:** Prepared from benzyl fluoride **12** (0.3 mmol scale, 76% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used 1-(phenylsulfonyl)indole (0.75 mmol, 193 mg, 2.5 equiv) as the nucleophile with HFIP (3.0 mmol, 315 μL, 10 equiv) as the displacement catalyst.
Purification: Reverse phase silica gel chromatography was used with a gradient of 70%→100% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 50%, 49.5 mg of white solid.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 1.1 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.29 – 7.21 (m, 4H), 7.22 – 7.16 (m, 3H), 7.10 (td, *J* = 7.6, 7.1, 1.0 Hz, 1H), 4.21 – 4.16 (m, 1H), 4.10 – 3.97 (m, 2H), 2.48 (dq, *J* = 13.6, 6.8 Hz, 1H), 2.29 (ddt, *J* = 13.7, 9.0, 6.0 Hz, 1H), 2.03 (s, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 170.9, 142.0, 138.1, 135.6, 133.7, 130.3, 129.2, 128.7, 127.7, 126.9, 126.7, 126.1, 124.9, 123.2, 122.7, 120.1, 113.8, 62.4, 39.2, 34.1, 20.9.
**HRMS (ESI) m/z:** $[M+Na]^+$ Calcd for $C_{25}H_{23}NNaO_4S$ 456.1240; Found 456.1234.




**(49) 5-methyl-1,3-diphenylhexan-1-one:** Prepared from benzyl fluoride **11** (0.3 mmol scale, 70% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used 1-phenyl-1-trimethylsiloxyethylene (0.75 mmol, 153.8 µL, 2.5 equiv) as the nucleophile with $BF_3$•$Et_2O$ (0.03 mmol, 3.7 µL, 0.1 equiv) as the displacement catalyst.
Purification: Normal phase silica gel chromatography was used with a gradient of 0%→20% EtOAc in pentane.
Isolated Yield from Benzyl Fluoride: 68%, 38.3 mg of colorless oil.
Spectra Available in the Literature (CAS): No (N/A)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.89 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.22 (m, 4H), 7.17 (t, *J* = 7.0 Hz, 1H), 3.45 (dtd, *J* = 10.3, 6.9, 4.9 Hz, 1H), 3.31 – 3.13 (m, 2H), 1.66 (ddd, *J* = 13.4, 10.3, 4.7 Hz, 1H), 1.50 (ddd, *J* = 13.7, 9.3, 5.0 Hz, 1H), 1.36 (dpd, *J* = 9.3, 6.6, 4.8 Hz, 1H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 199.1, 144.9, 137.3, 132.8, 128.5, 128.4, 128.0, 127.6, 126.2, 46.5, 45.5, 39.1, 25.4, 23.6, 21.6.
**HRMS (ESI) m/z:** $[M+H]^+$ Calcd for $C_{19}H_{23}O$ 267.1743; Found 267.1740.



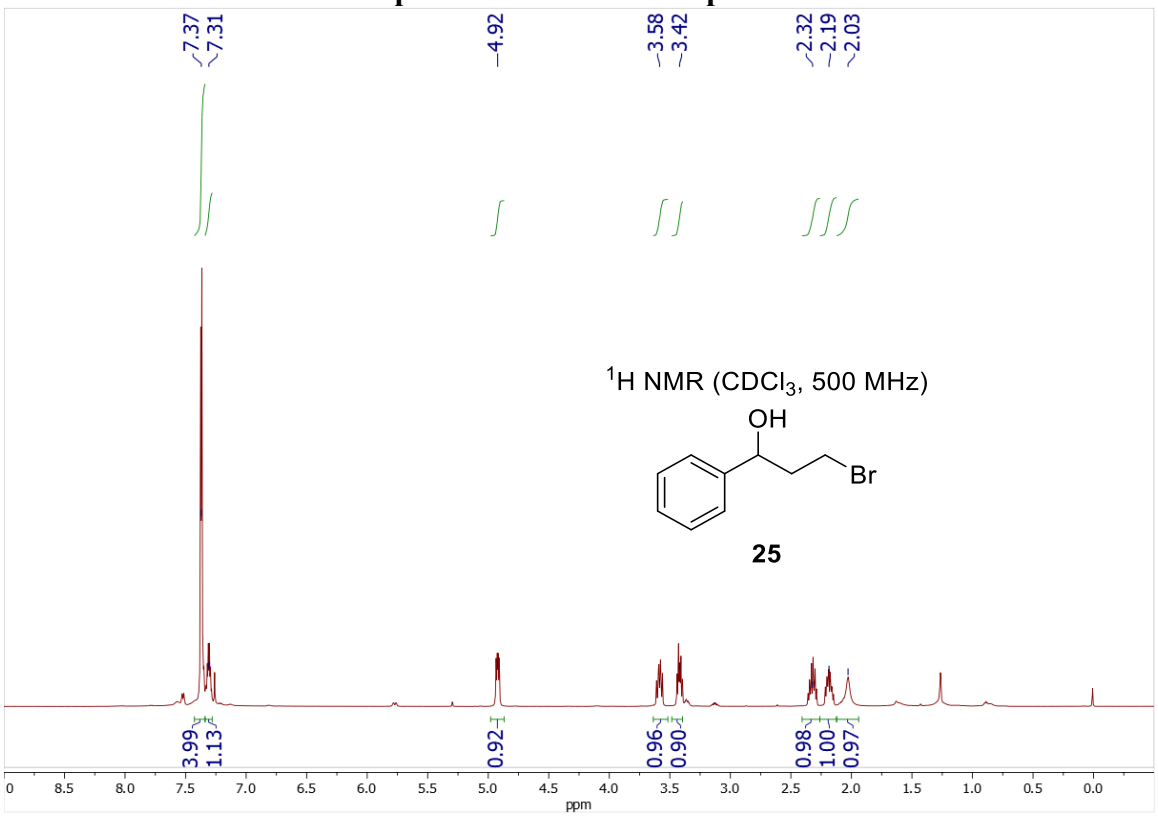

**(50) (1-chlorohex-5-en-3-yl)benzene:** Prepared from benzyl fluoride **7** (0.3 mmol scale, 77% NMR yield) that was formed according to the general procedure in section II. The ensuing displacement step followed the general procedure in section III and used allyltrimethylsilane (0.75 mmol, 119.2 µL, 2.5 equiv) as the nucleophile with both HFIP (3.0 mmol, 315 µL, 10 equiv) and $BF_3$•$Et_2O$ (0.03 mmol, 3.7 µL, 0.1 equiv) as the displacement catalysts.
Purification: Reverse phase silica gel chromatography was used with a gradient of 70%→100% MeOH in water. The product was extracted with 1:1 ether:pentane.
Isolated Yield from Benzyl Fluoride: 43%, 19.2 mg of colorless oil.
Spectra Available in the Literature (CAS): Yes[23] (276254-98-9)
**$^1$H NMR** ($CDCl_3$, 500 MHz): δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 6.7 Hz, 2H), 5.67 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.06 – 4.88 (m, 2H), 3.42 (ddd, *J* = 10.8, 7.1, 4.8 Hz, 1H), 3.26 (ddd, *J* = 10.8, 8.7, 6.5 Hz, 1H), 2.96 – 2.81 (m, 1H), 2.50 – 2.32 (m, 2H), 2.16 (dddd, *J* = 13.4, 8.7, 7.1, 4.4 Hz, 1H), 2.06 – 1.93 (m, 1H).
**$^{13}$C NMR** ($CDCl_3$, 126 MHz): δ 143.3, 136.3, 128.5, 127.6, 126.5, 116.4, 43.1, 42.8, 40.9, 38.6.

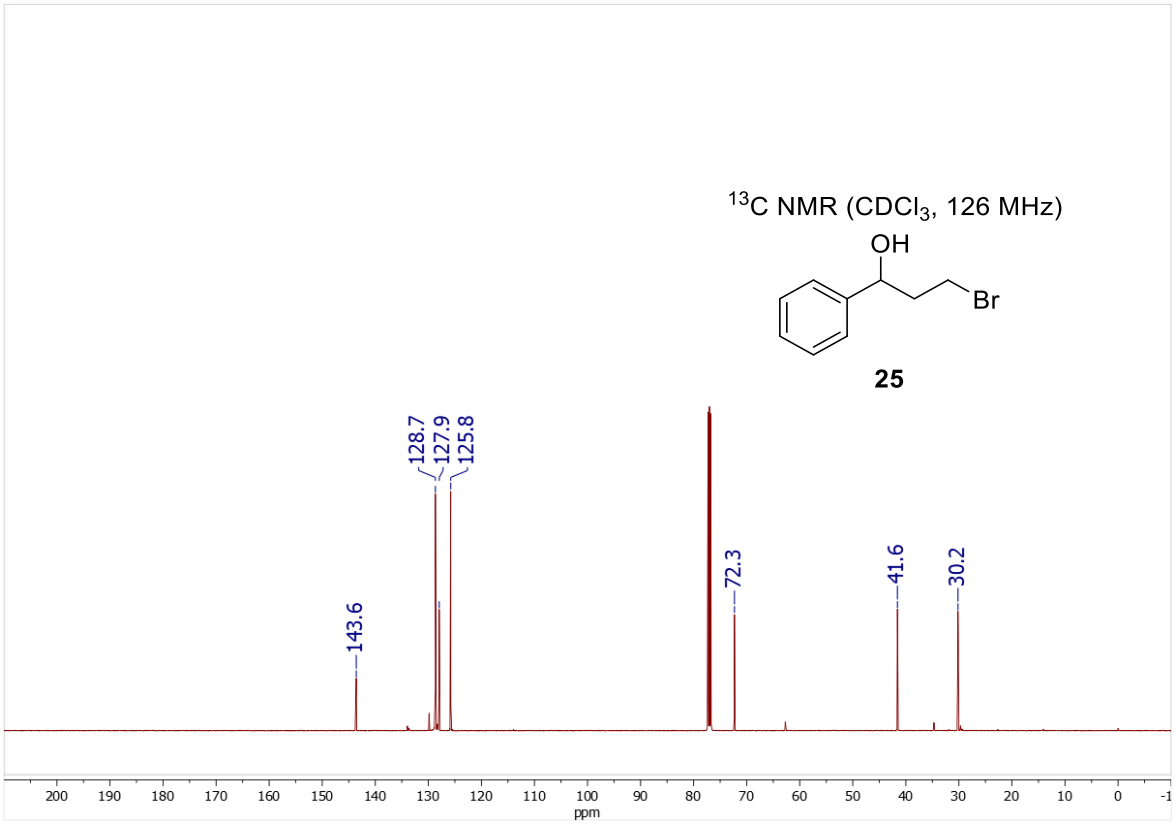
## IX. **References**

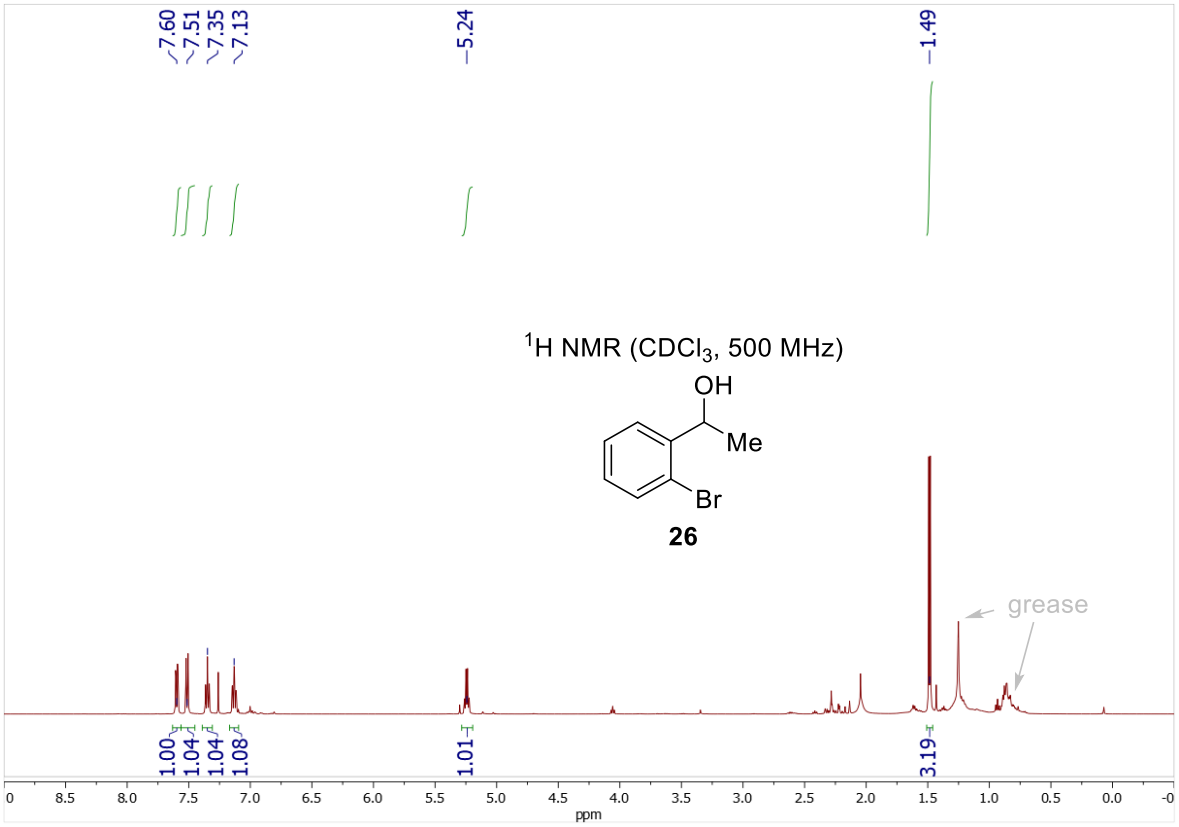

1) Gonçalves, C. R.; Lemmerer, M.; Teskey, C. J.; Adler, P.; Kaiser, D.; Maryasin, B.; González, L.; Maulide, N. A Unified Approach to the Chemoselective α-Functionalization of Amides with Heteroatom Nucleophiles. *J. Am. Chem. Soc.* **2019**, *46*, 18437-18443.
2) Piszel, P. E.; Vasilopoulos, A.; Stahl, S. S. Oxidative Amide Coupling from Functionally Diverse Alcohols and Amines using Aerobic Copper/Nitroxyl Catalysis. *Angew. Chem. Int. Ed.* **2019**, *58*, 12211-12215.
3) Mayhew, S. G. The Redox Potential of Dithionite and SO; from Equilibrium Reactions with Flavodoxins, Methyl Viologen and Hydrogen Plus Hydrogenase. *Eur. J. Biochem.* **1978**, *85*, 535-547.
4) Meanwell, M.; Lehmann, J.; Eichenberger, M.; Martin, R. E.; Britton, R. Synthesis of Acyl Fluorides *via* Photocatalytic Fluorination of Aldehydic C–H Bonds. *Chem. Commun.* **2018**, *54*, 9985-9988.
5) Lee, B. J.; DeGlopper, K. S.; Yoon, T. P. Site-Selective Alkoxylation of Benzylic C–H Bonds by Photoredox Catalysis. *Angew. Chem. Int. Ed.* **2020**, *59*, 197-202.
6) Meanwell, M.; Adluri, B. S.; Yuan, Z.; Newton, J.; Prevost, P.; Nodwell, M. B.; Friesen, C. M.; Schaffer, P.; Martin, R. E.; Britton, R. Direct Heterobenzylic Fluorination, Difluorination and Trifluoromethylthiolation with Dibenzenesulfonamide Derivatives. *Chem. Sci.* **2018**, *9*, 5608-5613.
7) Champagne, P. A.; Pomarole, J.; Thérien, M.-E.; Benhassine, Y.; Beaulieu, S.; Legault, C. Y.; Paquin, J.-F. Enabling Nucleophilic Substitution Reactions of Activated Alkyl Fluorides Through Hydrogen Bonding. *Org. Lett.* **2013**, *15*, 2210-2213.
8) Xia, J.-B.; Zhu, C.; Chen, C. Visible Light-Promoted Metal-Free C–H Activation: Diarylketone-Catalyzed Selective Benzylic Mono- and Difluorination. *J. Am. Chem. Soc.* **2013**, *135*, 17494-17500.
9) Liu, W.; Groves, J.T. Manganese-Catalyzed Oxidative Benzylic C–H Fluorination by Fluoride Ions. *Angew. Chem. Int. Ed.* **2013**, *52*, 6024-6027.
10) Huang, X.; Liu, W.; Ren, H.; Neelamegam, R.; Hooker, J. M.; Groves, J. T. Late Stage Benzylic C–H Fluorination with [$^{18}$F]Fluoride for PET Imaging. *J. Am. Chem. Soc.* **2014**, *136*, 6842-6845.
11) Bloom, S.; Pitts, C. R.; Woltornist, R.; Griswold, A.; Holl, M. G.; Lectka, T. Iron(II)-Catalyzed Benzylic Fluorination. *Org. Lett.* **2013**, *15*, 1722-1724.
12) Nodwell, M. B.; Bagai, A.; Halperin, S. D.; Matin, R. E.; Knust, H.; Britton, R. Direct Photocatalytic Fluorination of Benzylic C–H Bonds with *N*-Fluorobenzenesulfonimide. *Chem. Commun.* **2015**, *51*, 11783-11786.
13) Cantillo, D.; de Frutos, O.; Rincón, J. A.; Mateos, C.; Kappe, C. O. A Continuous-Flow Protocol for Light-Induced Benzylic Fluorinations. *J. Org. Chem.* **2014**, *79*, 8486-8490.
14) Bloom, S.; McCann, M.; Lectka, T. Photocatalyzed Benzylic Fluorination: Shedding "Light" on the Involvement of Electron Transfer. *Org. Lett.* **2014**, *16*, 6338-6341.
15) Sood, D. E.; Champion, S.; Dawson, D. M.; Chabbra, S.; Bode, B. E.; Sutherland, A.; Watson, A. J. B. Deoxyfluorination with $CuF_2$: Enabled by Using a Lewis Base Activating Group. *Angew. Chem. Int. Ed.* **2020**, *59*, 8460-8463.
16) Dinoiu, V.; Fukuhara, T.; Miura, K.; Yoneda, N. Electrochemical Partial Fluorination of Phenylacetic Acids Esters and 1-Tetralone. *J. Fluor. Chem.* **2003**, *121*, 227-231.

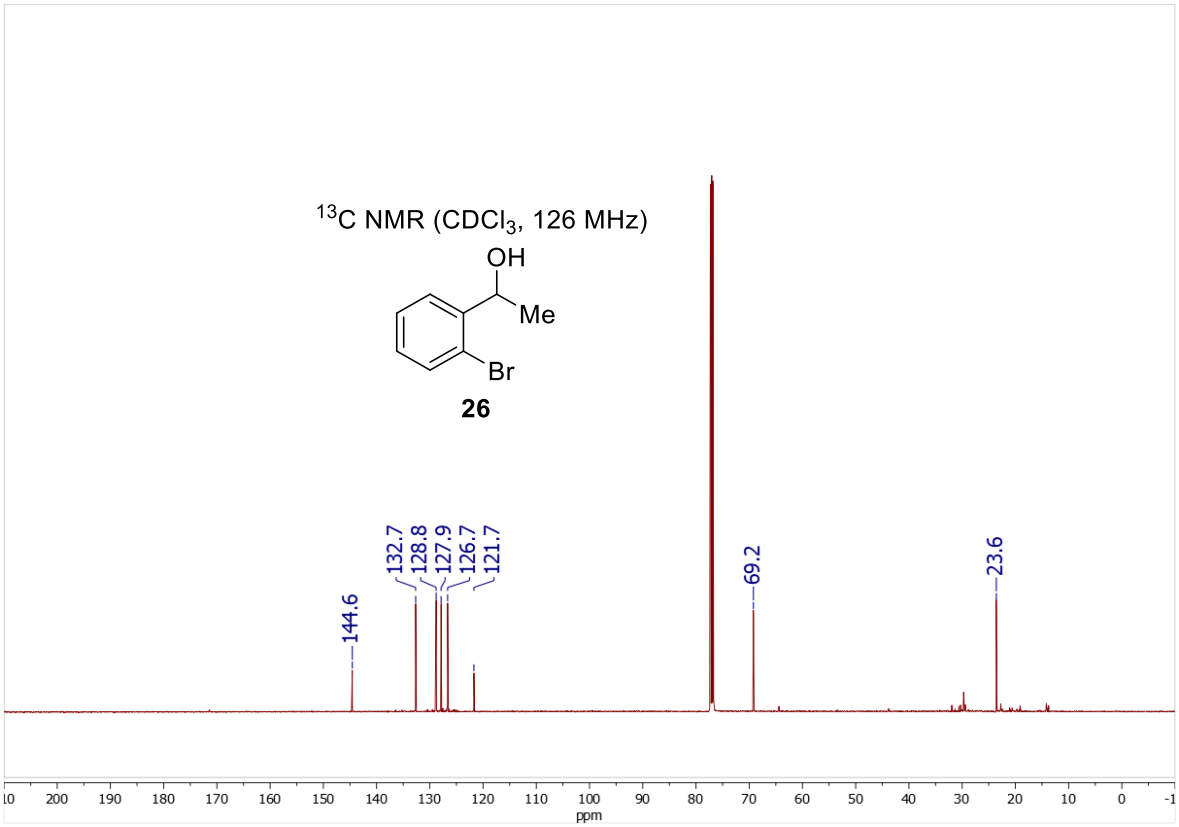
17) Ni, Z.; Zhang, Q.; Xiong, T.; Zheng, Y.; Li, Y.; Zhang, H.; Zhang, J.; Liu, Q. Highly Regioselective Copper-Catalyzed Benzylic C–H Amination by *N*-Fluorobenzenesulfonimide. *Angew. Chem. Int. Ed.* **2012**, *51*, 1244-1247.
18) Trahanovsky, W. S.; Fox, N. S. Oxidation of Organic Compounds with Cerium(IV). XIX. Effect of Alkyl Substitution on the Oxidative Cleavage of Alkylphenylmethanols. *J. Am. Chem. Soc.* **1974**, *96*, 7968-7974.
19) Bosson, J.; Nolan, S. P. N-Heterocyclic Carbene–Ruthenium Complexes for the Racemization of Chiral Alcohols. *J. Org. Chem.* **2010**, *75*, 2039-2043.
20) Ramadas, S.; Krupadanam, G. L. D. Enantioselective Acylation of Chroman-4-ols Catalyzed by Lipase from *Pseudomonas Cepecia* (Amano PS). *Tetrahedron: Asymmetry* **1997**, *8*, 3059-3066.
21) Darwish, K. M.; Salama, I.; Mostafa, S.; Gomaa, M. S.; Khafagy, E.-S.; Helal, M. A. Synthesis, Biological Evaluation, and Molecular Docking Investigation of Benzhydrol- and Indole-Based Dual PPAR-γ/FFAR1 Agonists. *Bioorg. Med. Chem. Lett.* **2018**, *28*, 1595-1602.
22) Dastbaravardeh, N.; Schnürch, M.; Mihovilovic, M. D. Ruthenium(0)-Catalyzed $sp^3$ C–H Bond Arylation of Benzylic Amines Using Arylboronates. *Org. Lett.* **2012**, *14*, 1930-1933.
23) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. Direct Substitution of the Hydroxy Group in Alcohols with Silyl Nucleophiles Catalyzed by Indium Trichloride. *Angew. Chem. Int. Ed.* **2004**, *43*, 1414-1416.

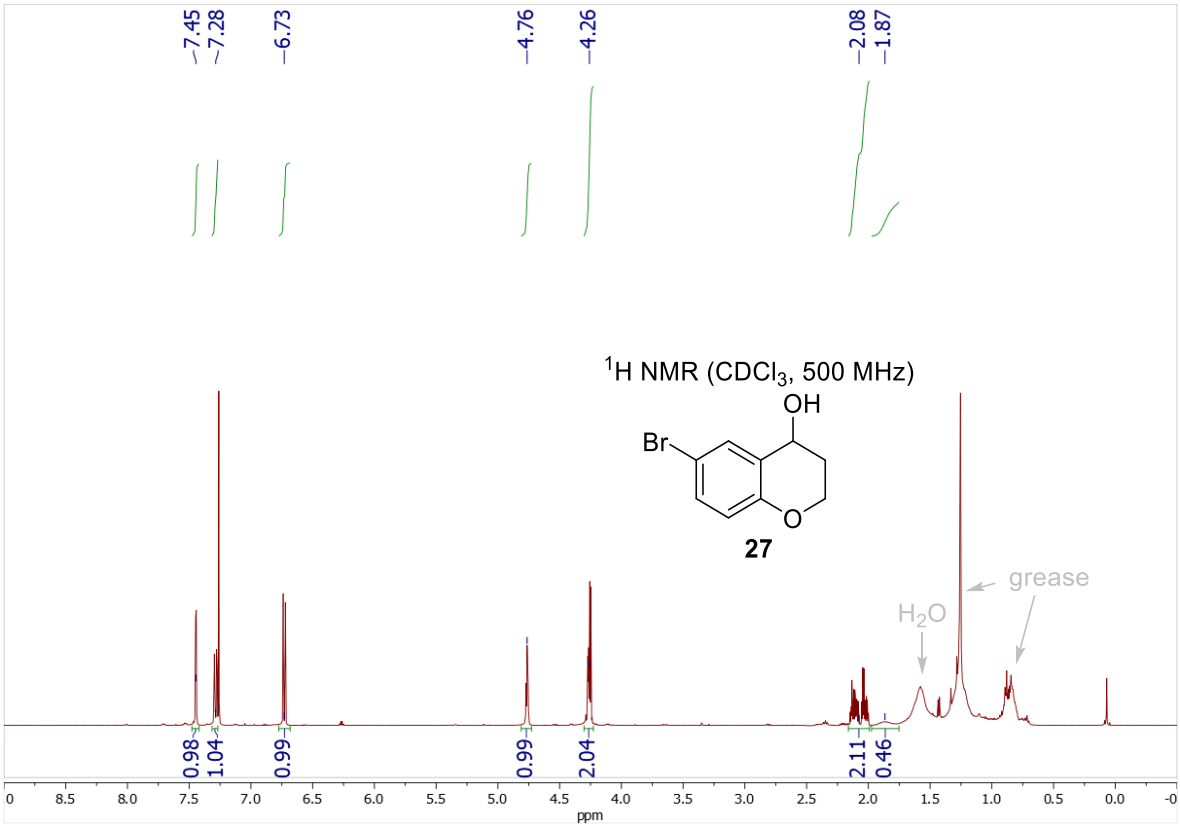
## X. $^{1}$H NMR and $^{13}$C NMR Spectra of Isolated Compounds

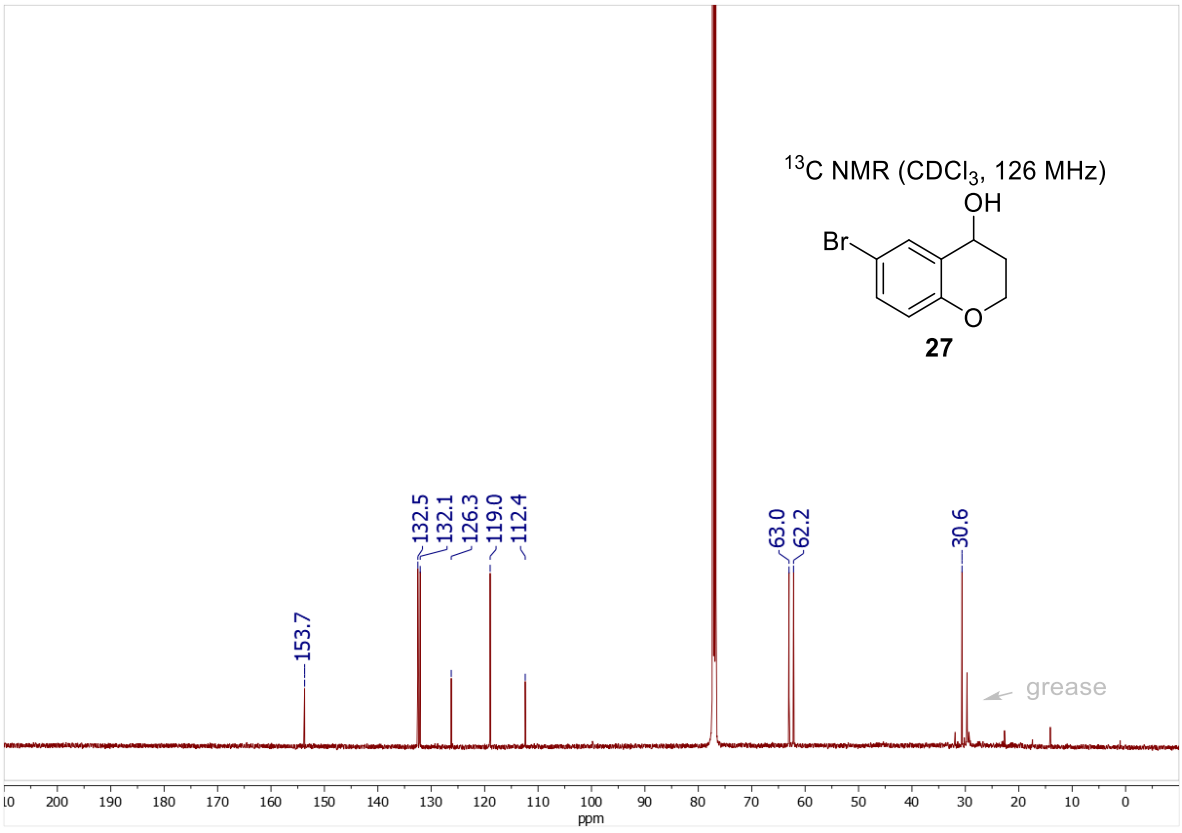


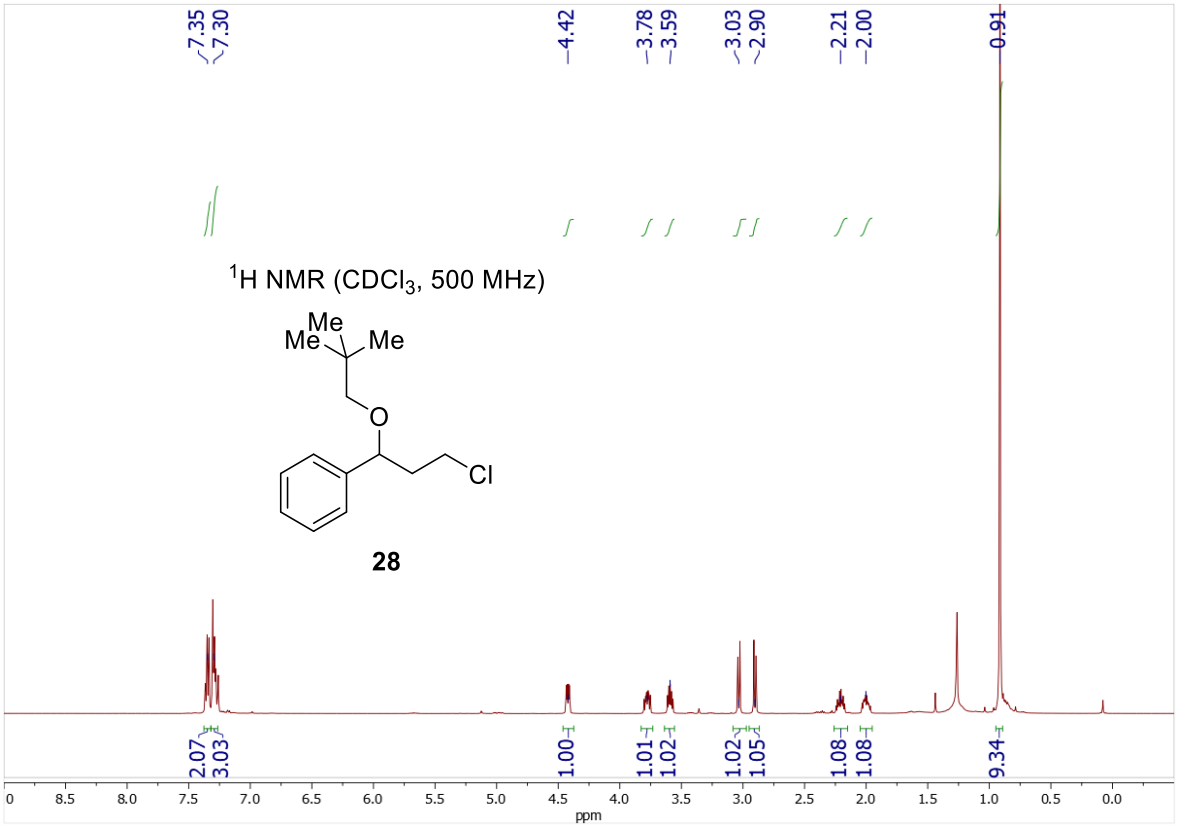



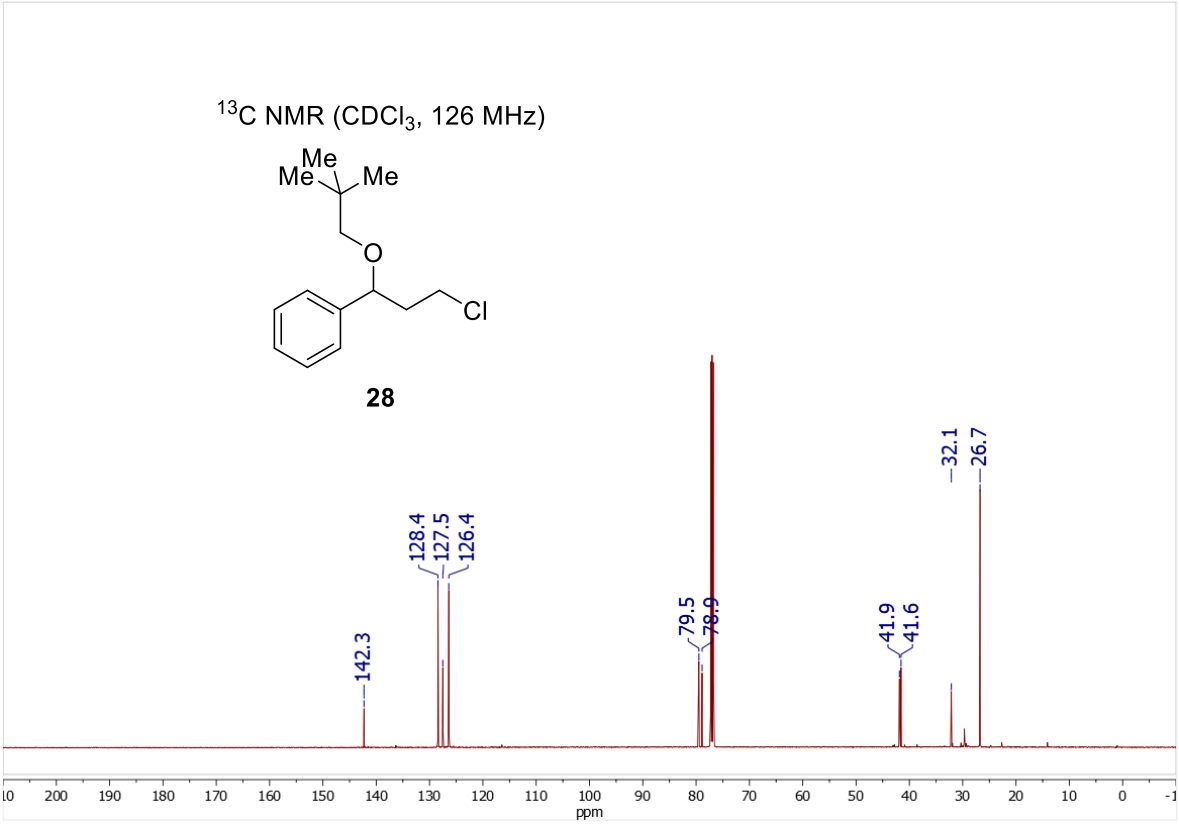

7.60
7.51
7.35
7.13
5.24
1.49
1H NMR (CDCl3, 500 MHz)
OH
Me
Br
26
grease
1.00
1.04
1.04
1.08
1.01
3.19
ppm

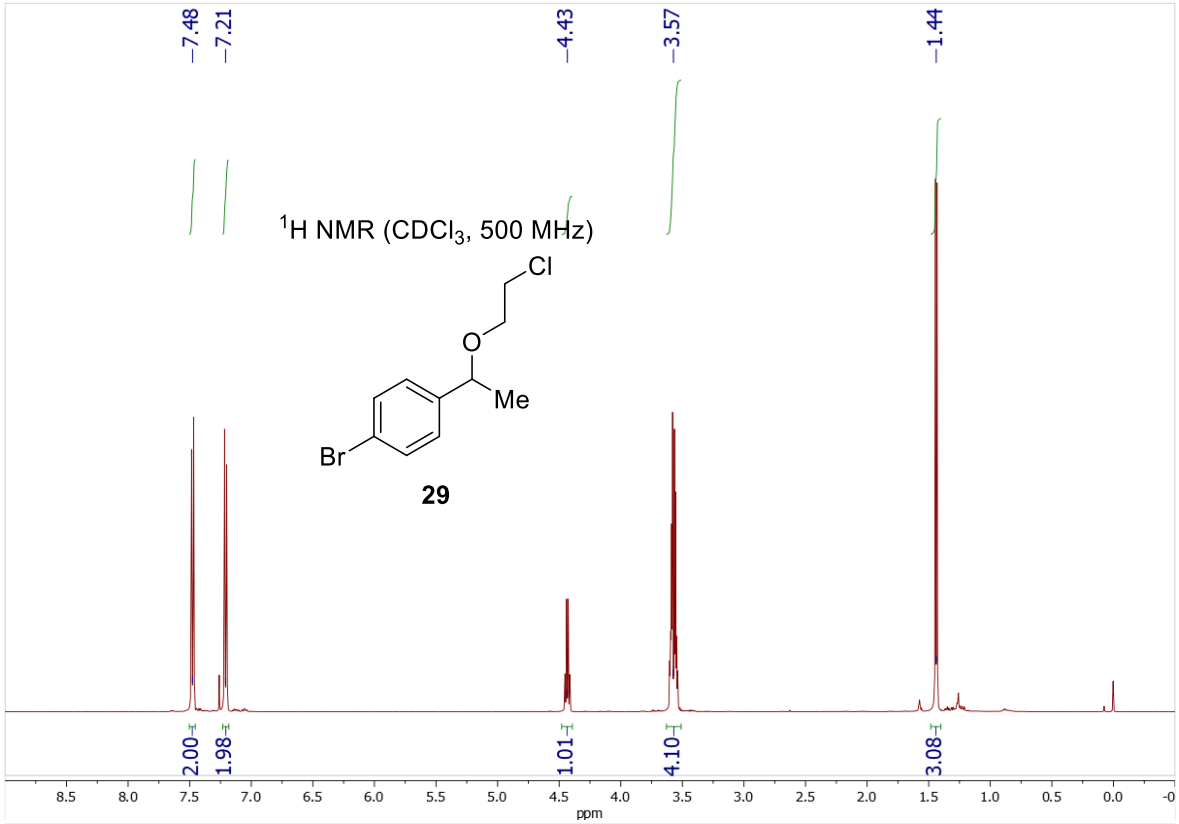

13C NMR (CDCl3, 126 MHz)
OH
Me
Br
26
144.6
132.7
128.8
127.9
126.7
121.7
69.2
23.6
ppm

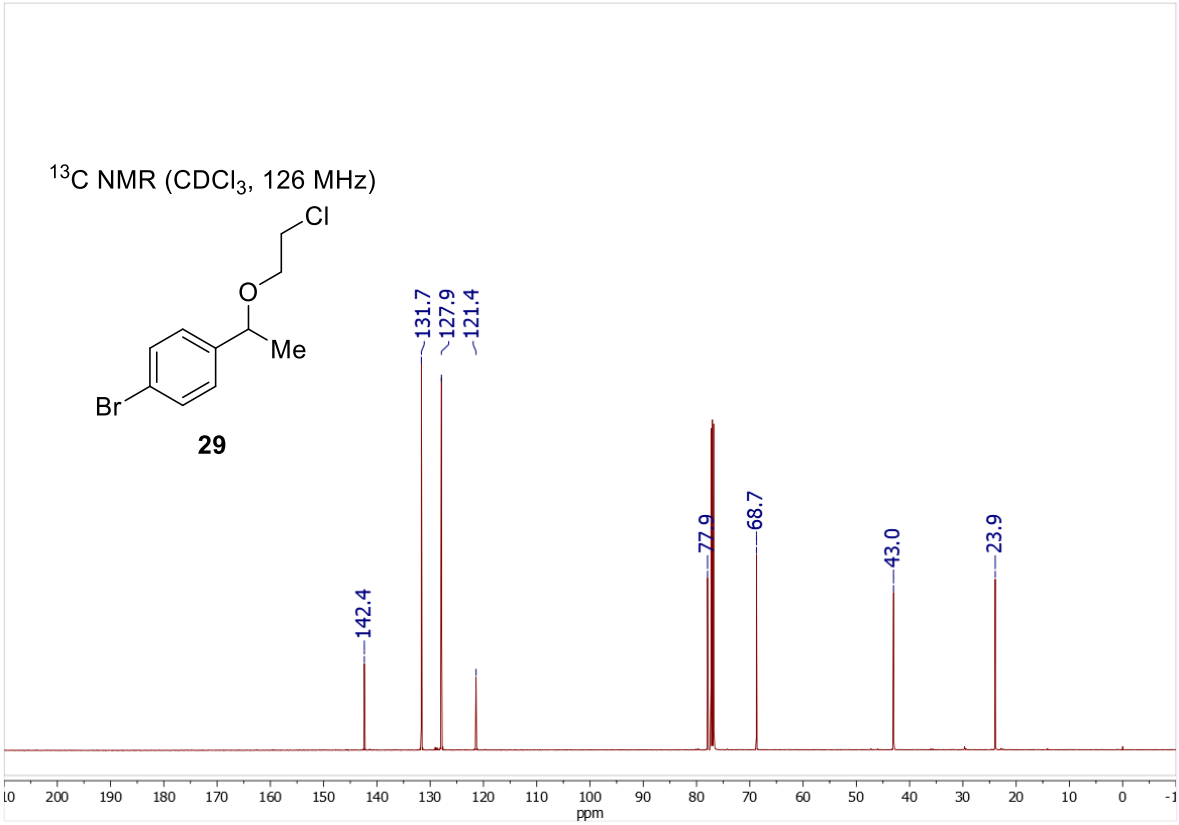

7.45
7.28
6.73
4.76
4.26
2.08
1.87
$^{1}$H NMR ($CDCl_3$, 500 MHz)
OH
Br
O
27
grease
$H_2O$
0.98
1.04
0.99
0.99
2.04
2.11
0.46
ppm

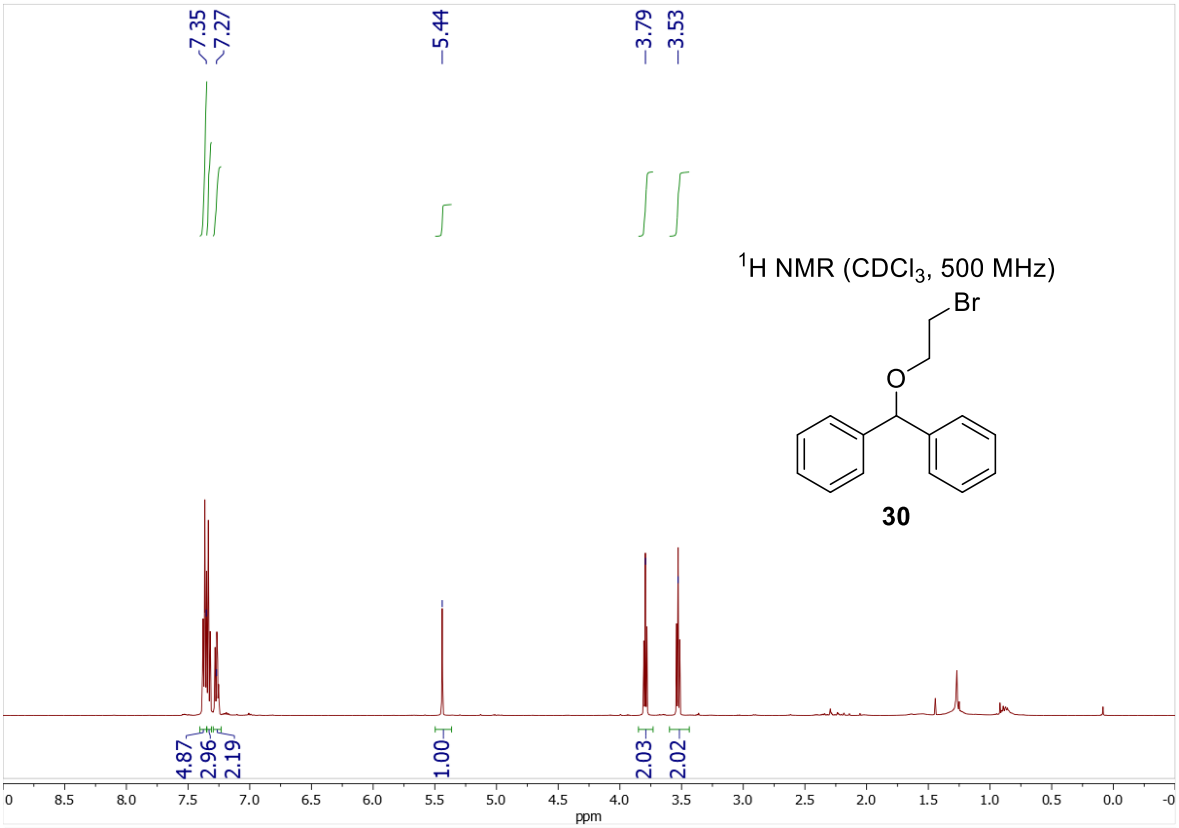

$^{13}$C NMR ($CDCl_3$, 126 MHz)
OH
Br
O
27
153.7
132.5
132.1
126.3
119.0
112.4
63.0
62.2
30.6
grease
ppm

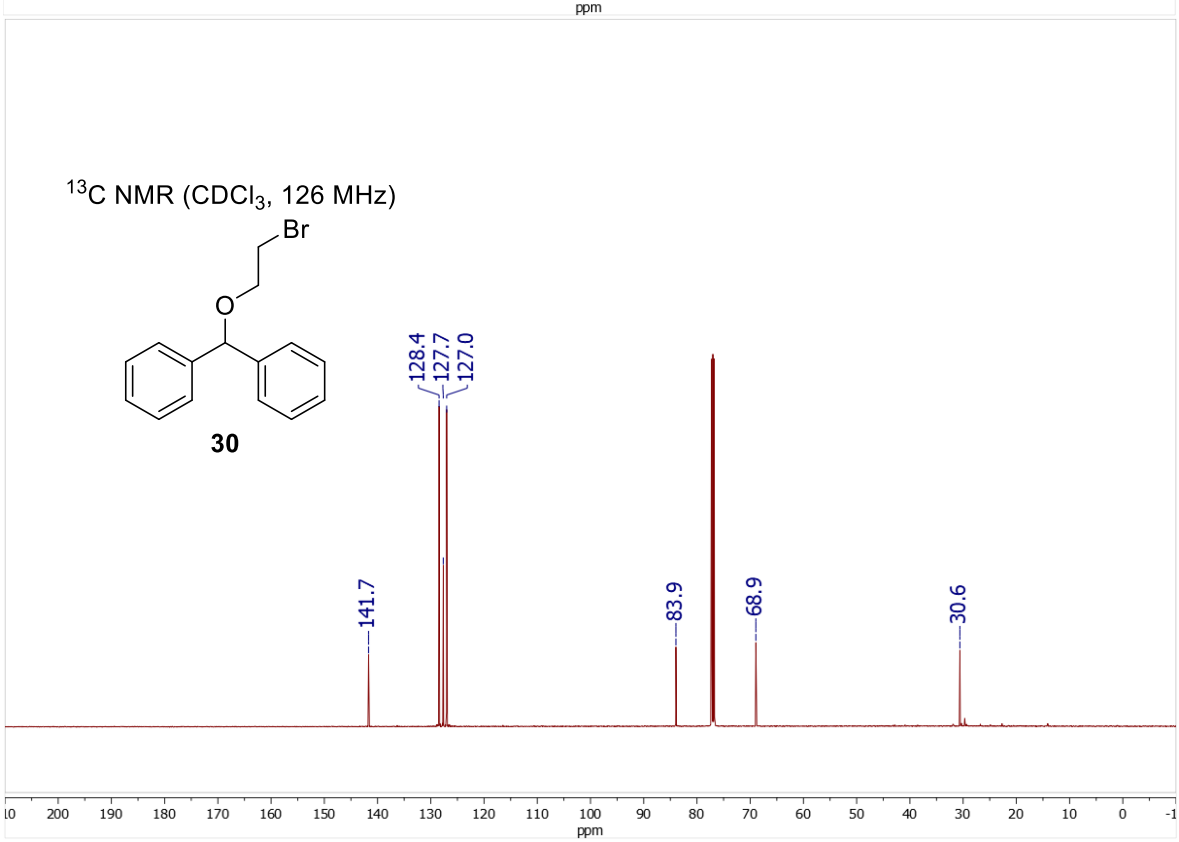

7.35
7.30
4.42
3.78
3.59
3.03
2.90
2.21
2.00
0.91
1H NMR (CDCl3, 500 MHz)
Me
Me
Me
O
Cl
28
2.07
3.03
1.00
1.01
1.02
1.02
1.05
1.08
1.08
9.34
ppm

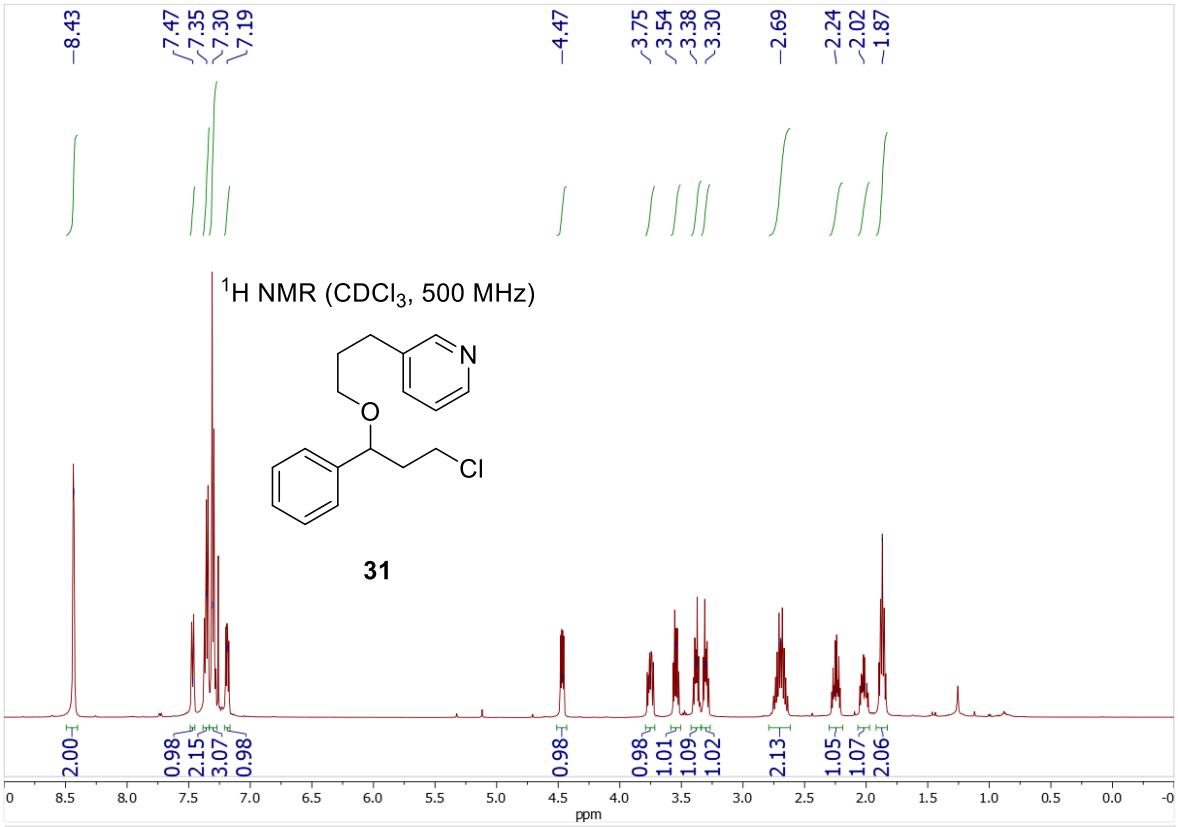

13C NMR (CDCl3, 126 MHz)
Me
Me
Me
O
Cl
28
142.3
128.4
127.5
126.4
79.5
78.9
41.9
41.6
32.1
26.7
ppm

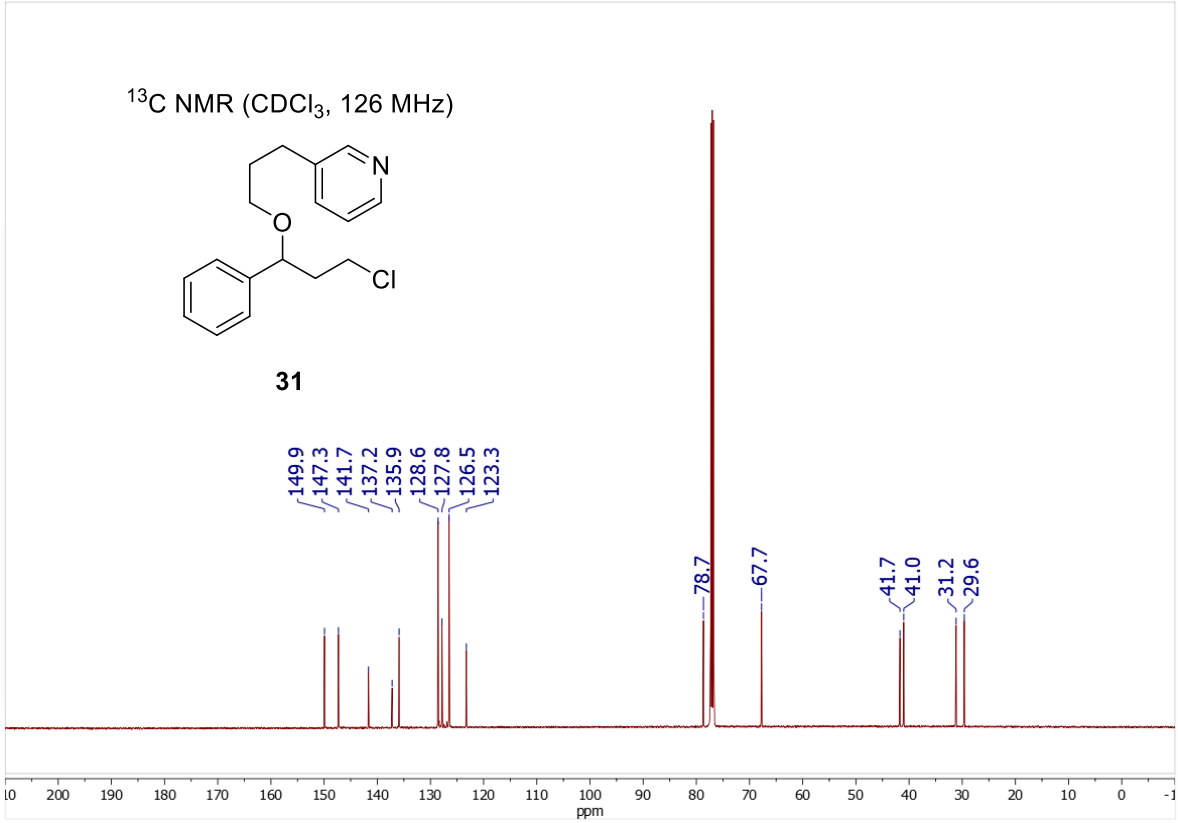

7.48
7.21
4.43
3.57
1.44
$^1$H NMR ($CDCl_3$, 500 MHz)
Cl
O
Me
Br
29
2.00
1.98
1.01
4.10
3.08
ppm

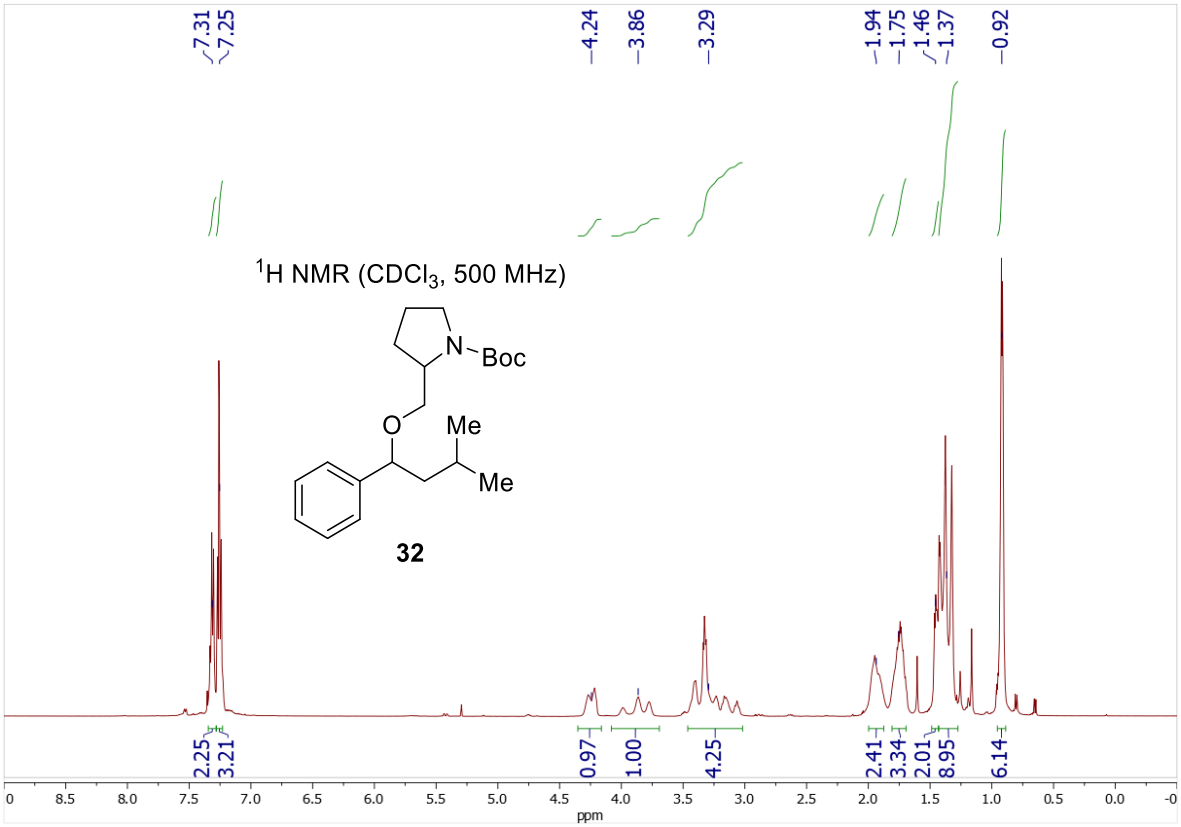

$^{13}$C NMR ($CDCl_3$, 126 MHz)
Cl
O
Me
Br
29
142.4
131.7
127.9
121.4
77.9
68.7
43.0
23.9
ppm


7.35
7.27
5.44
3.79
3.53
$^1$H NMR ($CDCl_3$, 500 MHz)
Br
O
30
4.87
2.96
2.19
1.00
2.03
2.02
ppm

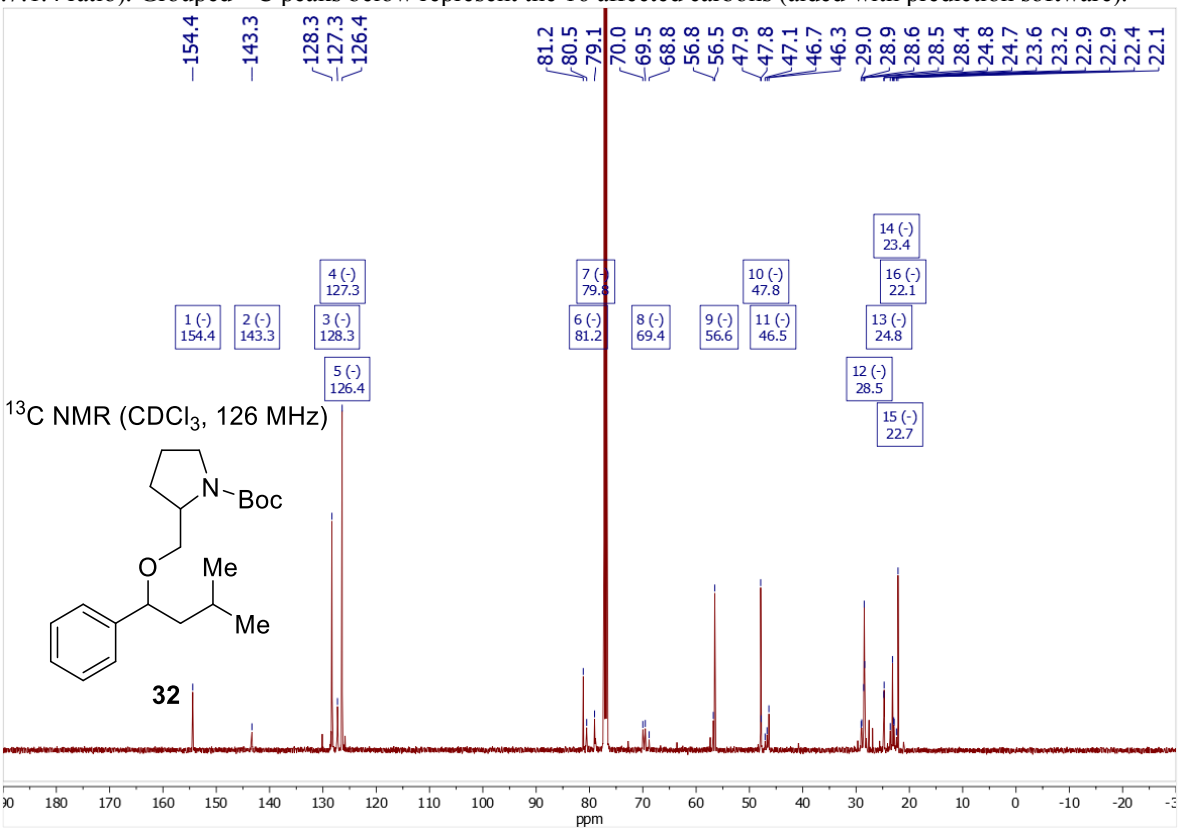

$^{13}$C NMR ($CDCl_3$, 126 MHz)
Br
O
30
128.4
127.7
127.0
141.7
83.9
68.9
30.6
ppm

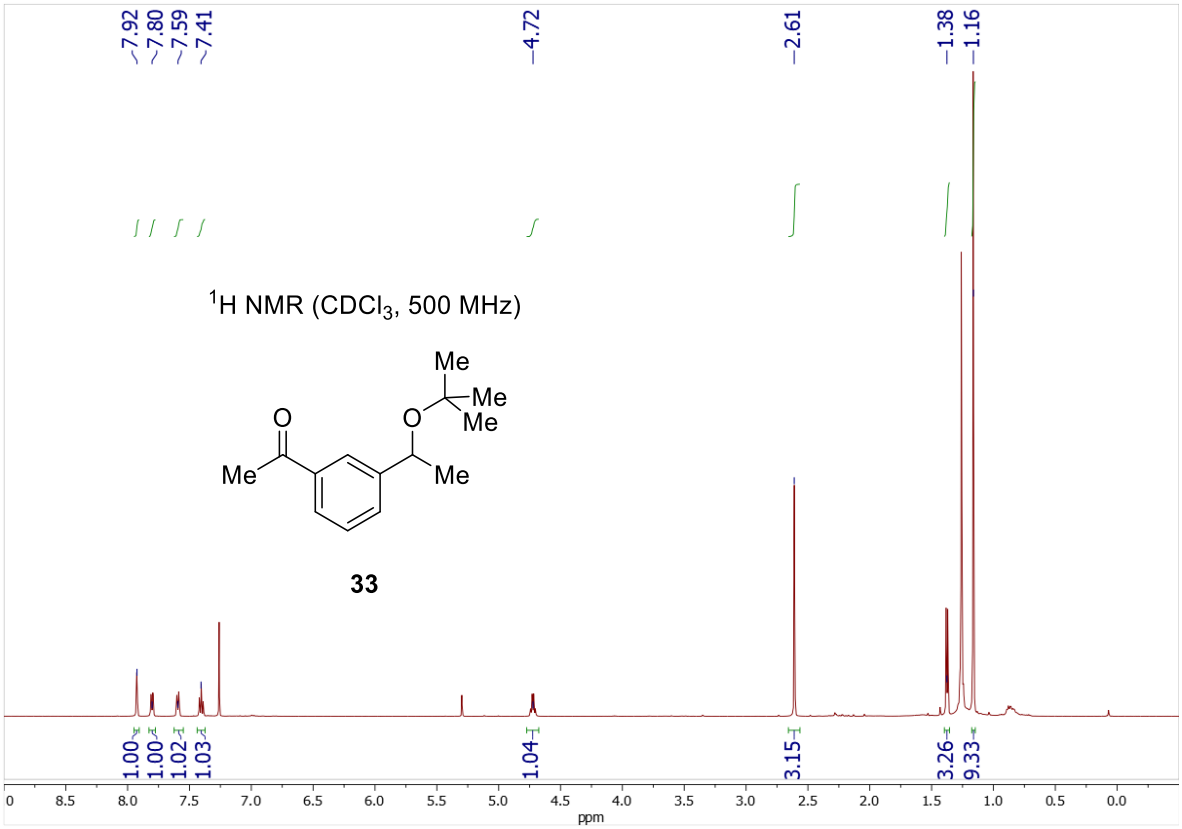

8.43
7.47
7.35
7.30
7.19
4.47
3.75
3.54
3.38
3.30
2.69
2.24
2.02
1.87
$^1$H NMR ($CDCl_3$, 500 MHz)
N
O
Cl
31
2.00
0.98
2.15
3.07
0.98
0.98
0.98
1.01
1.09
1.02
2.13
1.05
1.07
2.06
ppm


$^{13}$C NMR ($CDCl_3$, 126 MHz)
N
O
Cl
31
149.9
147.3
141.7
137.2
135.9
128.6
127.8
126.5
123.3
78.7
67.7
41.7
41.0
31.2
29.6
ppm

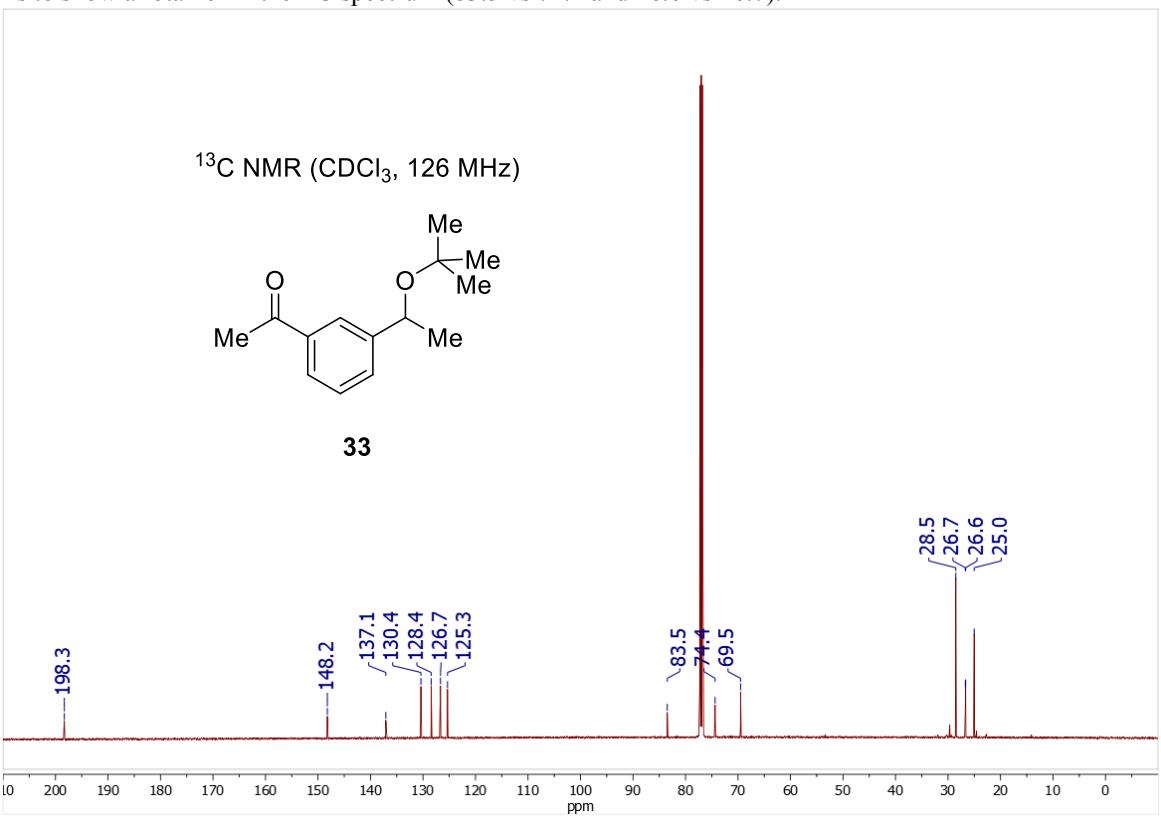


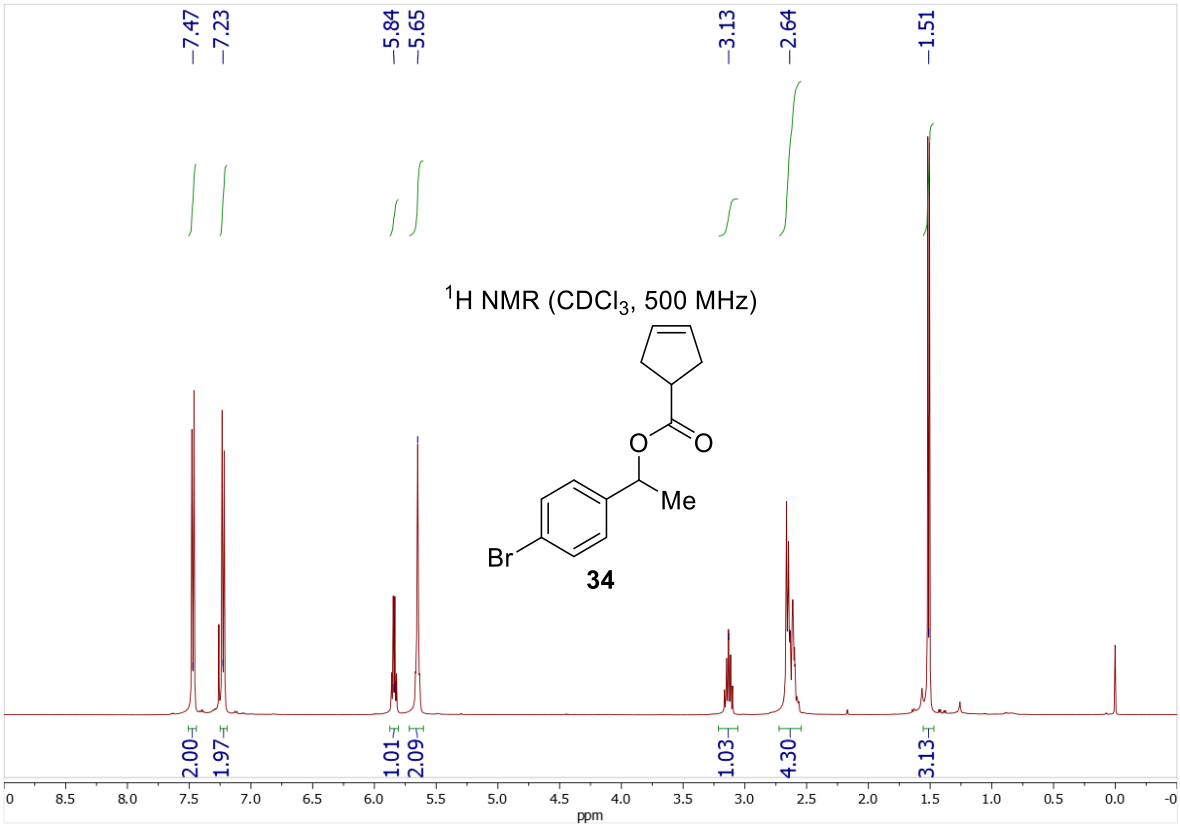

A combination of diastereomers and Boc rotamers make these spectra complex (*tert*-butyl peak above is 3 peaks with 1:1.7:1.4 ratio). Grouped $^{13}$C peaks below represent the 16 affected carbons (aided with prediction software).

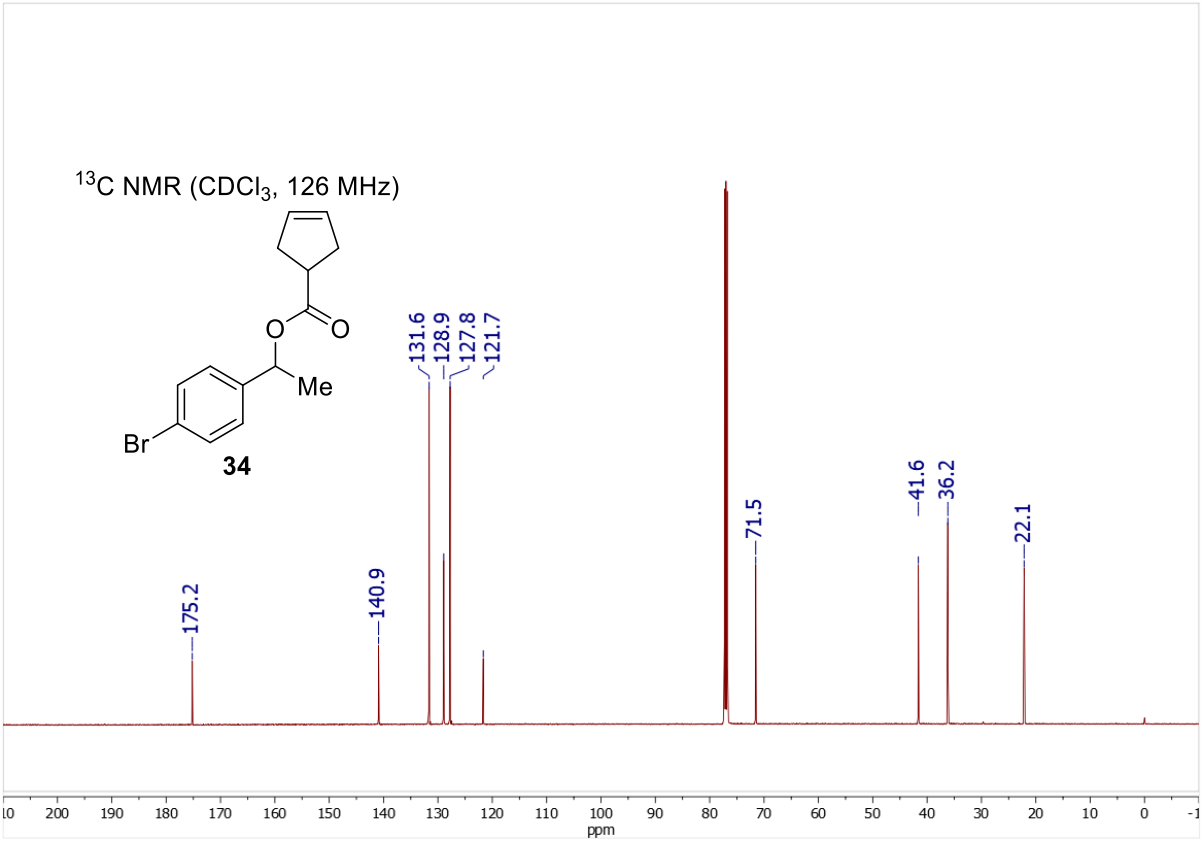


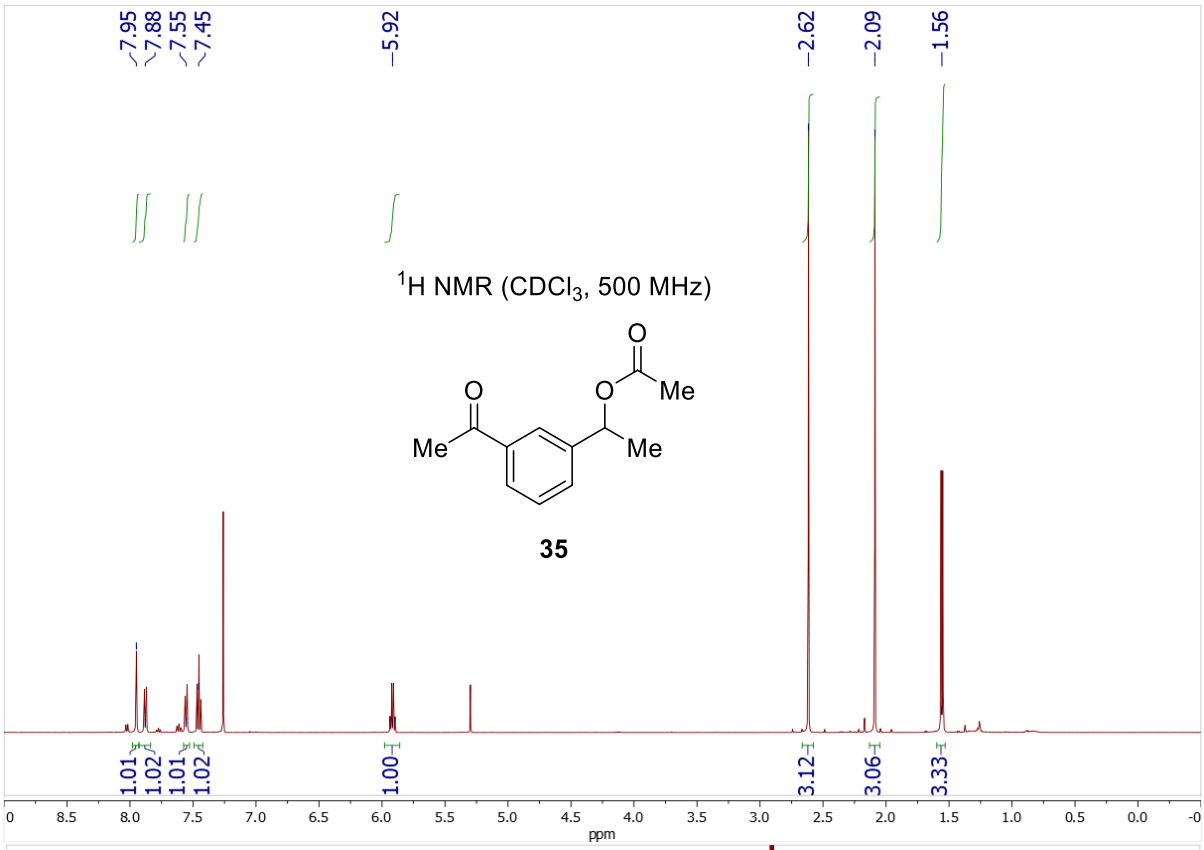


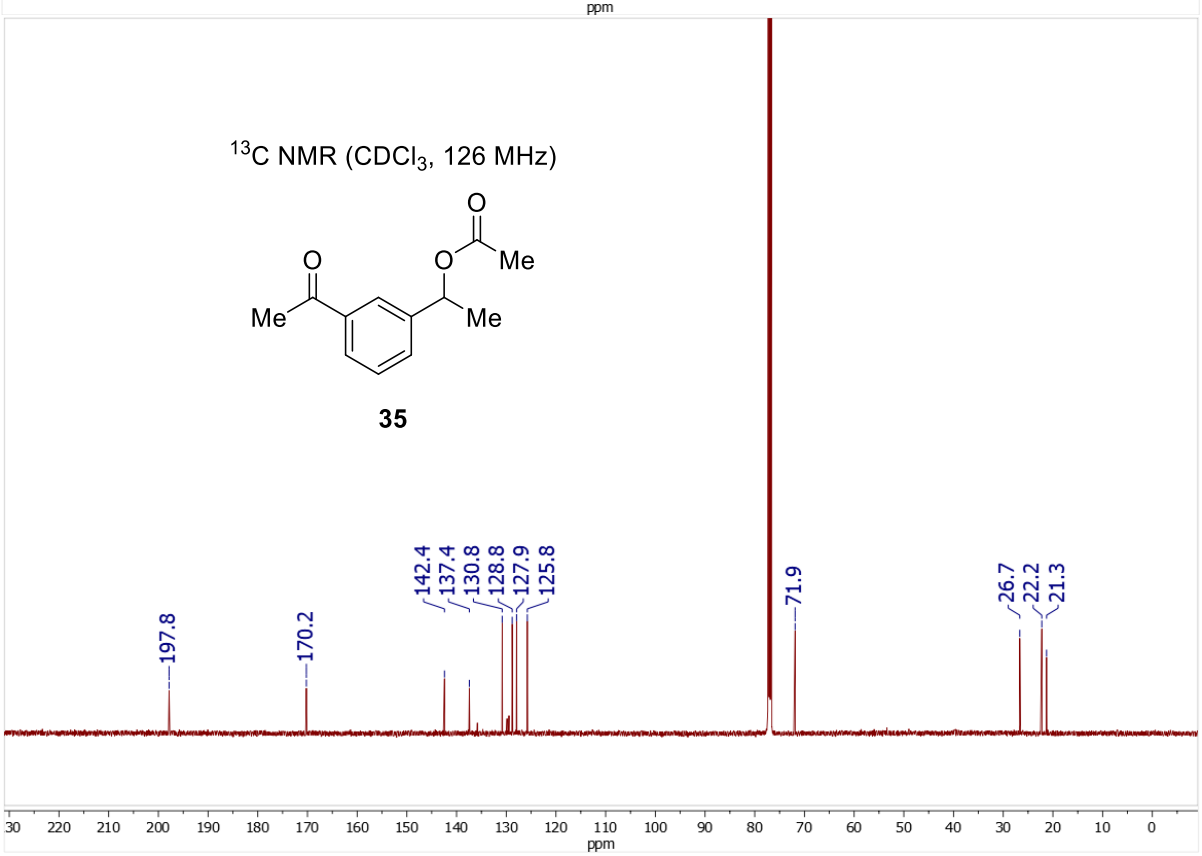

Seems to show a rotamer in the $^{13}C$ spectrum (83.5 vs 74.4 and 26.6 vs 26.7):

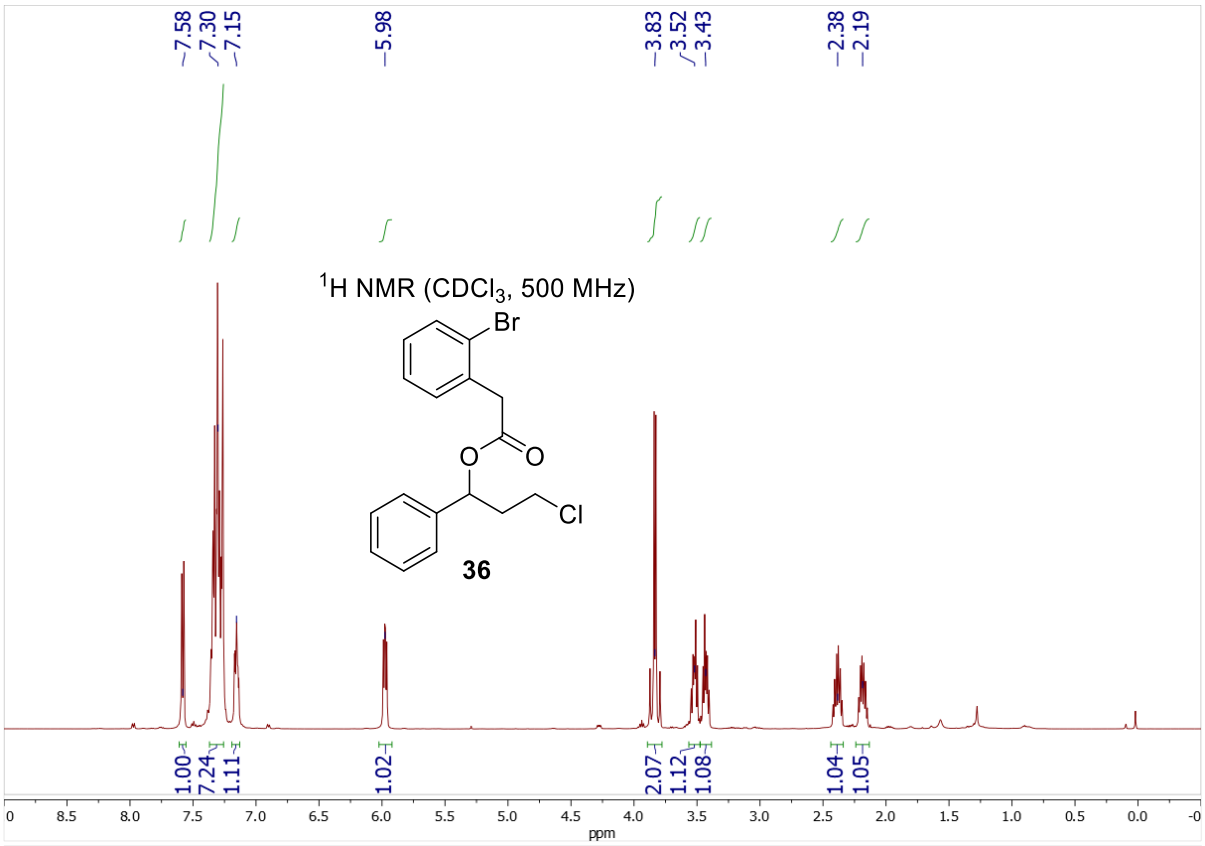


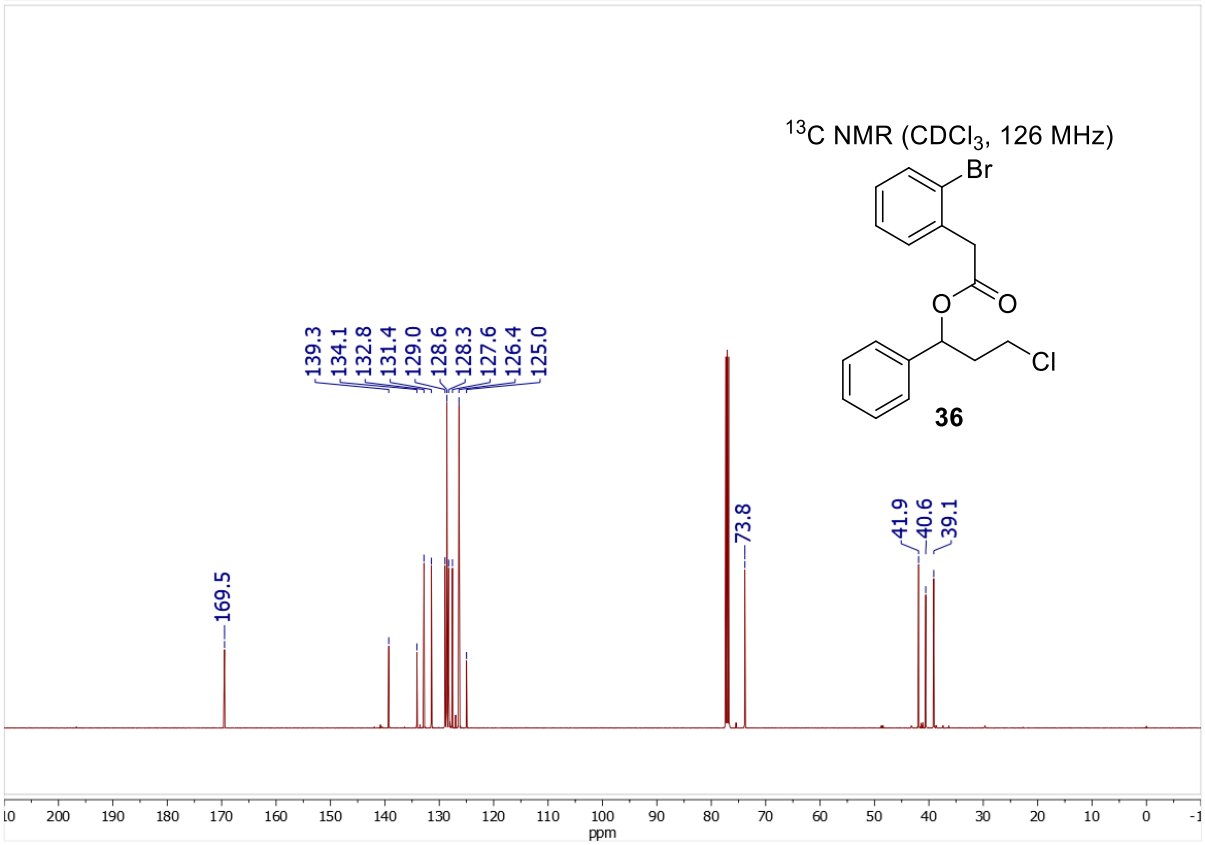

7.47
7.23
5.84
5.65
3.13
2.64
1.51
1H NMR (CDCl3, 500 MHz)
O
O
Me
Br
34
2.00
1.97
1.01
2.09
1.03
4.30
3.13
ppm

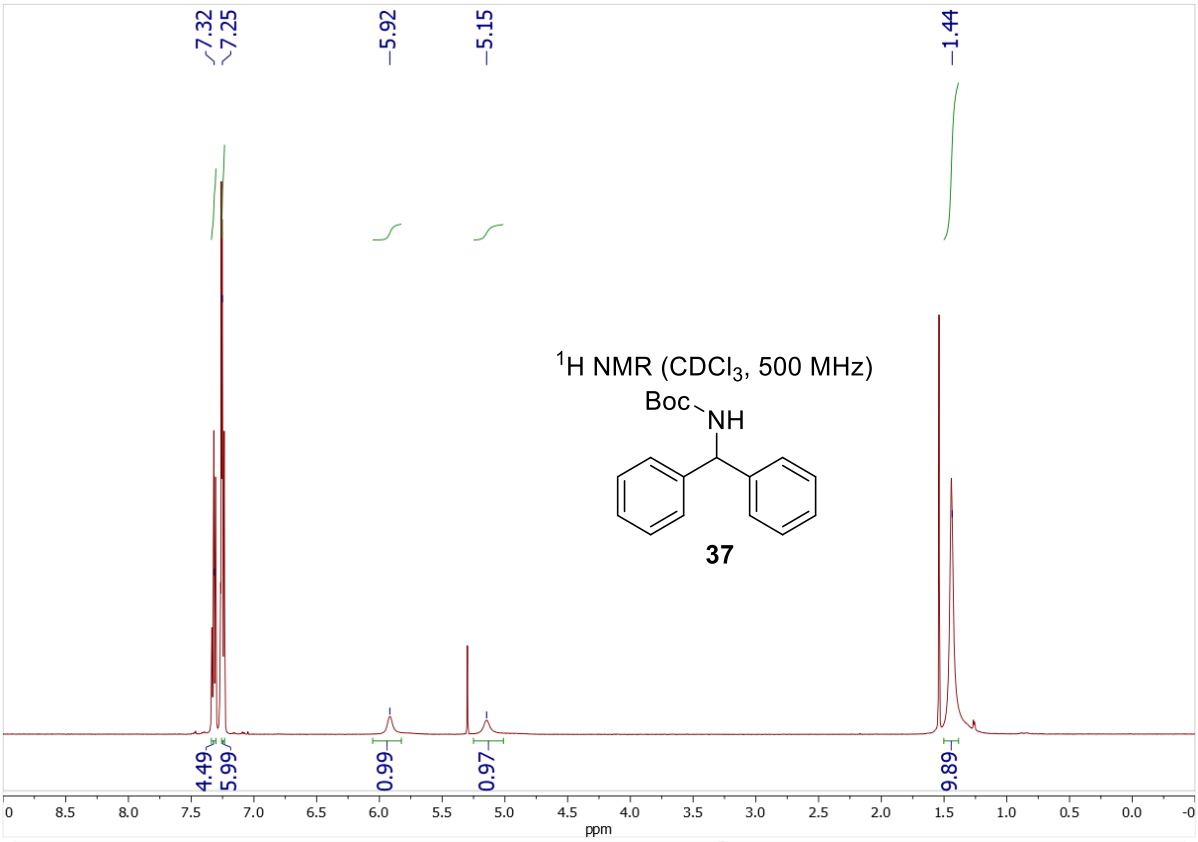

13C NMR (CDCl3, 126 MHz)
O
O
Me
Br
34
131.6
128.9
127.8
121.7
175.2
140.9
71.5
41.6
36.2
22.1
ppm

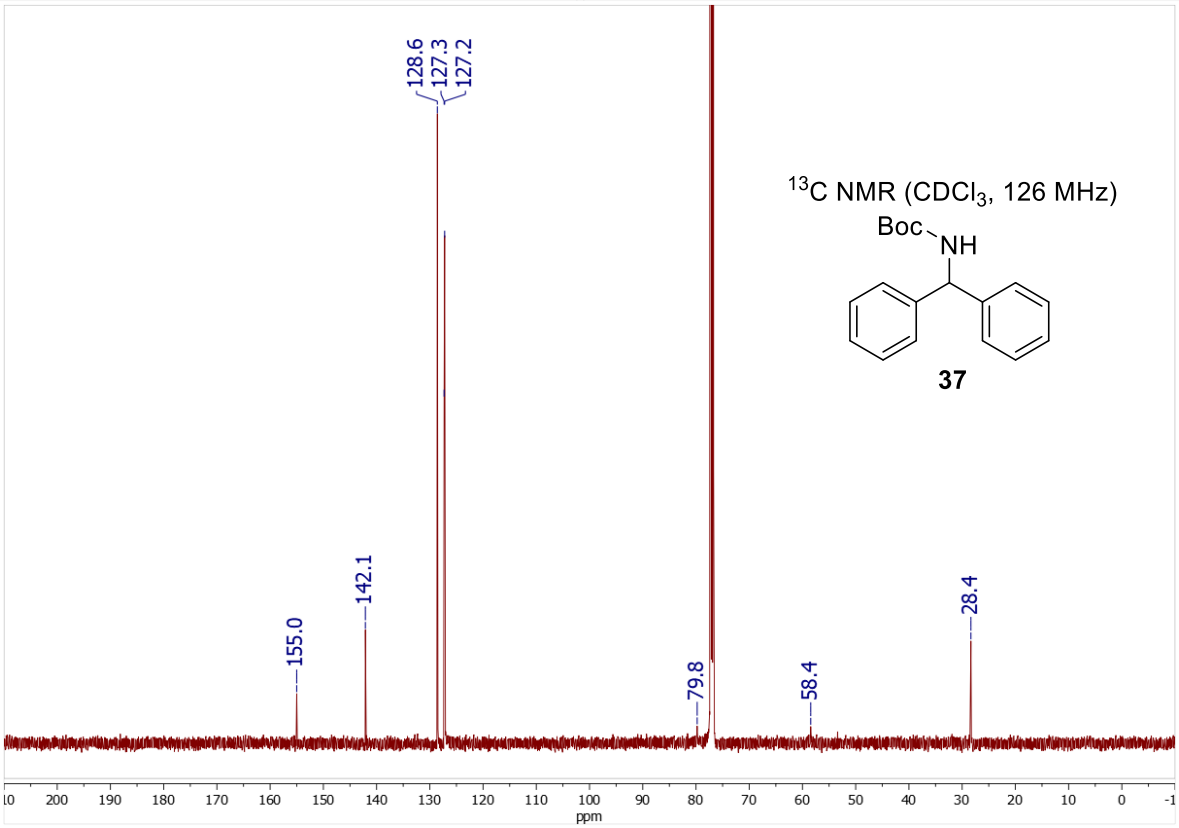

7.95
7.88
7.55
7.45
5.92
2.62
2.09
1.56
$^1$H NMR ($CDCl_3$, 500 MHz)
O
O
Me
O
Me
Me
35
1.01
1.02
1.01
1.02
1.00
3.12
3.06
3.33
ppm

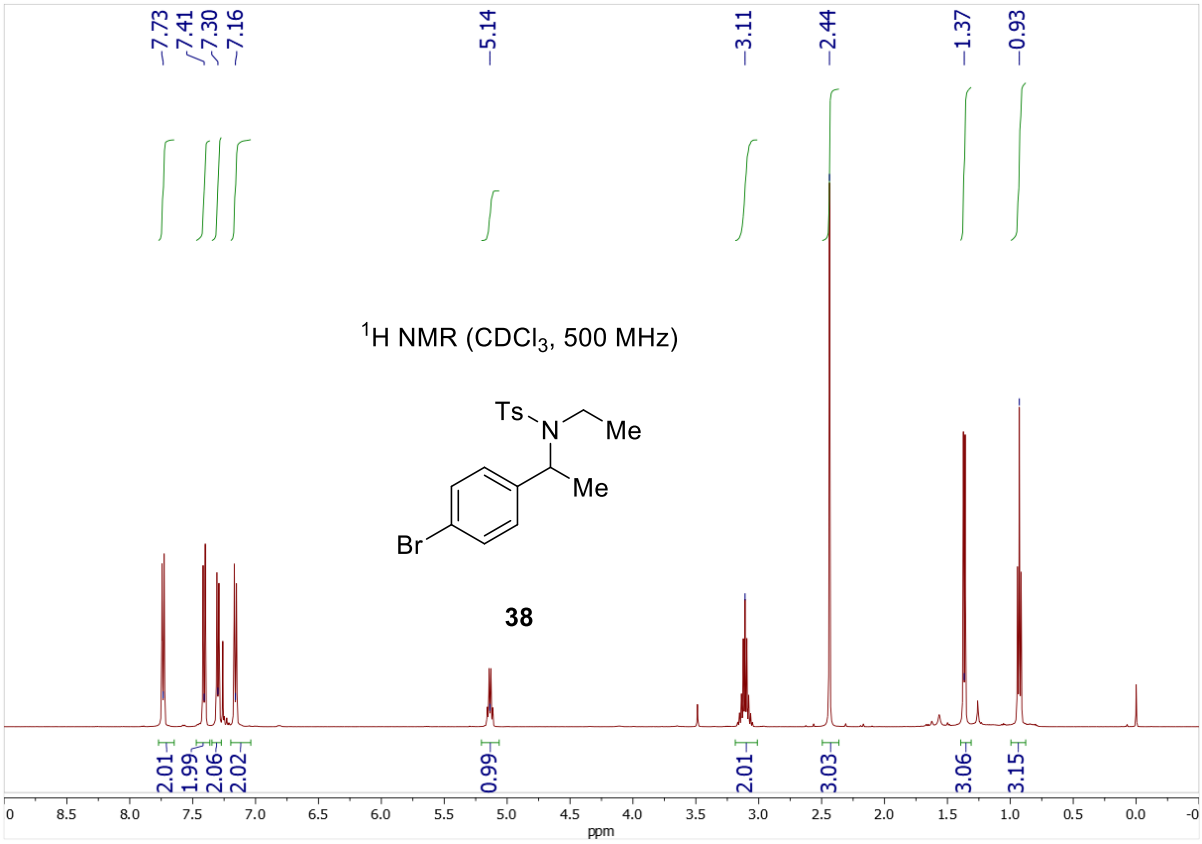

$^{13}$C NMR ($CDCl_3$, 126 MHz)
O
O
Me
O
Me
Me
35
197.8
170.2
142.4
137.4
130.8
128.8
127.9
125.8
71.9
26.7
22.2
21.3
ppm

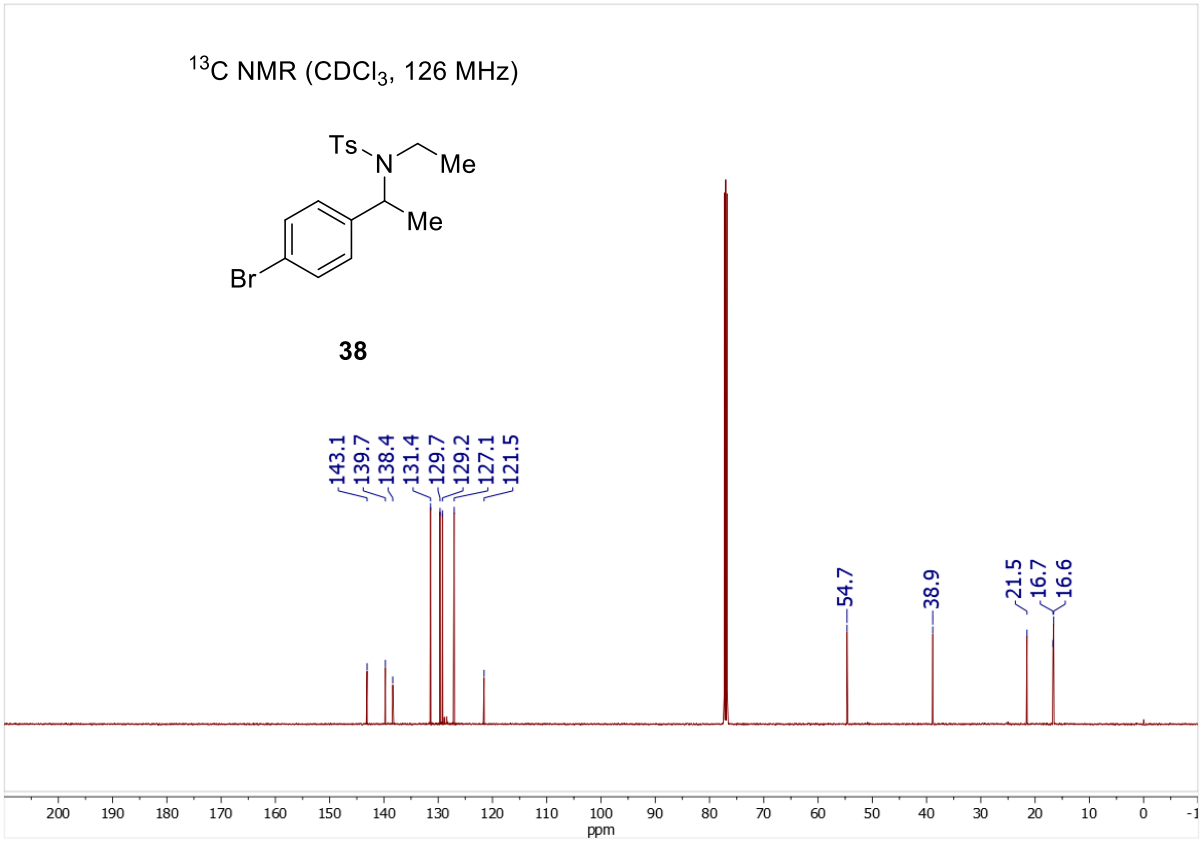

7.58
7.30
7.15
5.98
3.83
3.52
3.43
2.38
2.19
$^1$H NMR ($CDCl_3$, 500 MHz)
Br
O
O
Cl
36
1.00
7.24
1.11
1.02
2.07
1.12
1.08
1.04
1.05
ppm

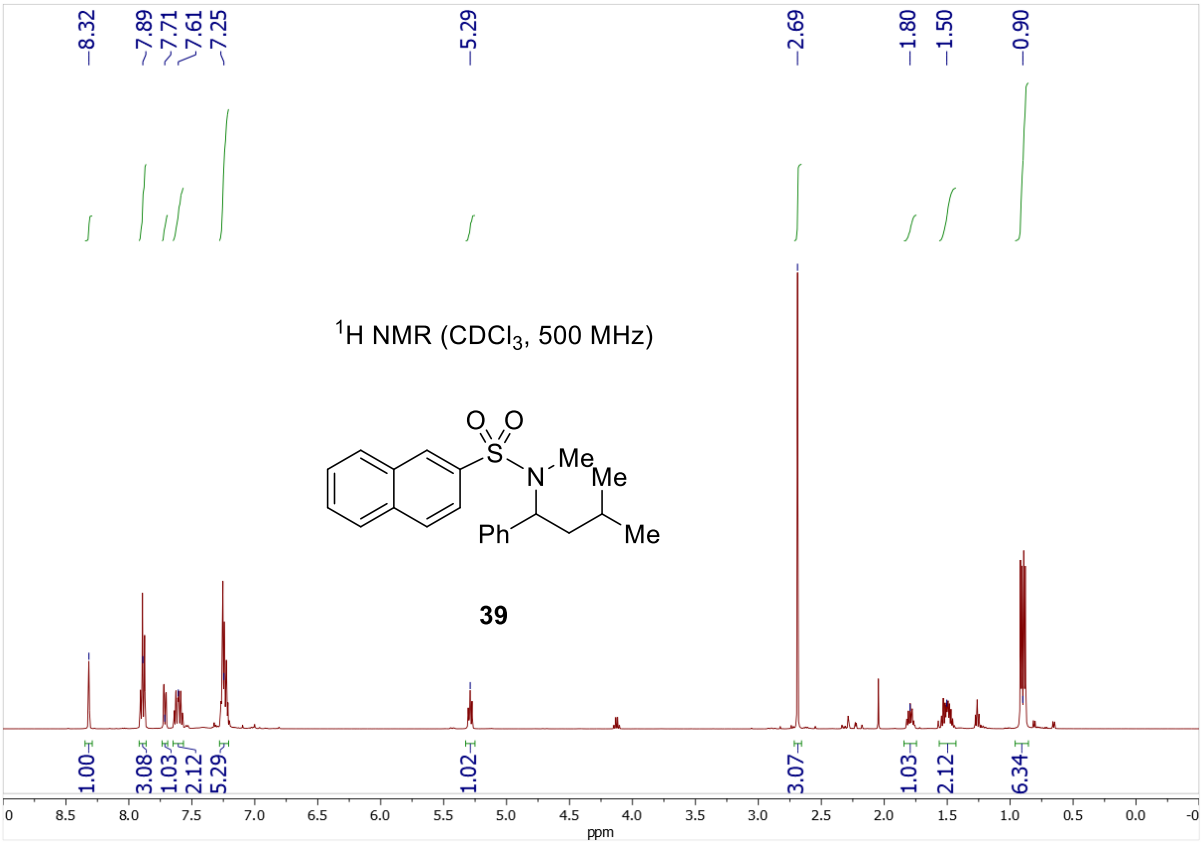

$^{13}$C NMR ($CDCl_3$, 126 MHz)
Br
O
O
Cl
36
139.3
134.1
132.8
131.4
129.0
128.6
128.3
127.6
126.4
125.0
169.5
73.8
41.9
40.6
39.1
ppm

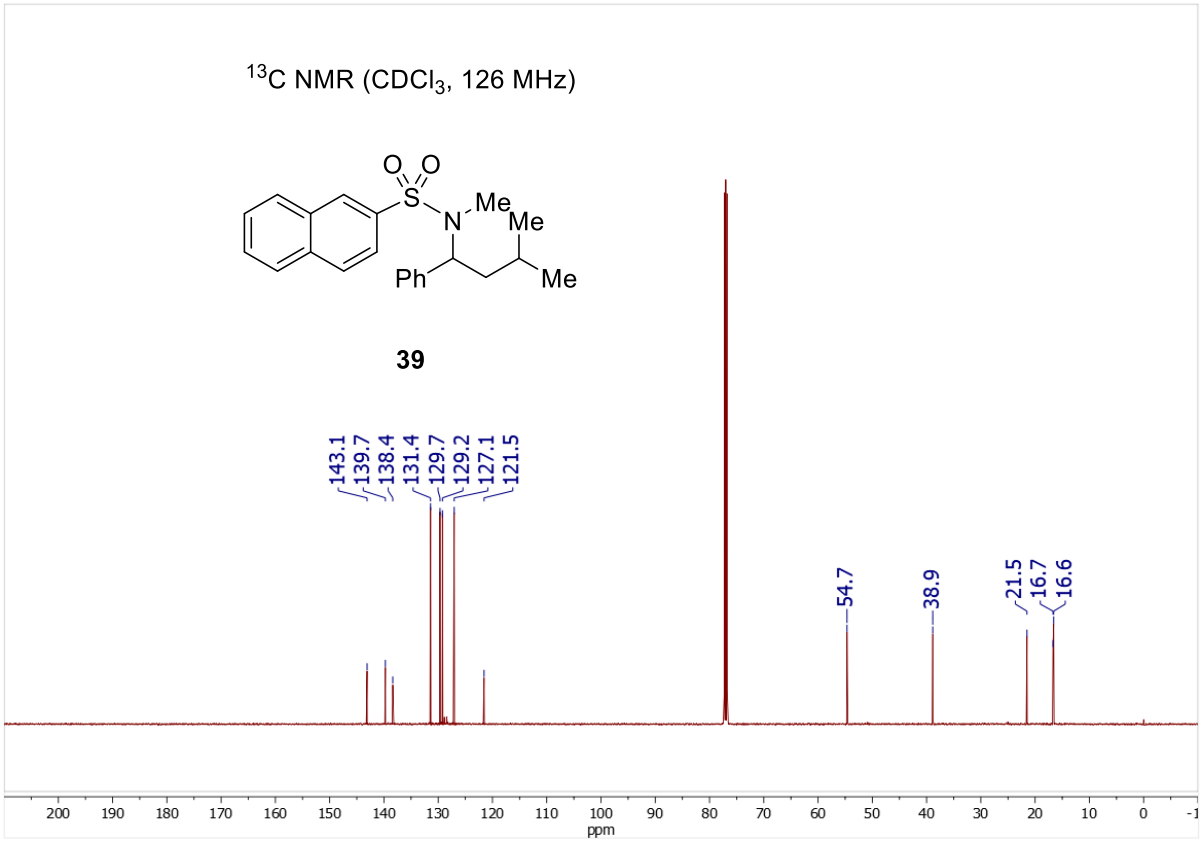

7.32
7.25
5.92
5.15
1.44
4.49
5.99
0.99
0.97
9.89
ppm
$^1$H NMR ($CDCl_3$, 500 MHz)
Boc
NH
37

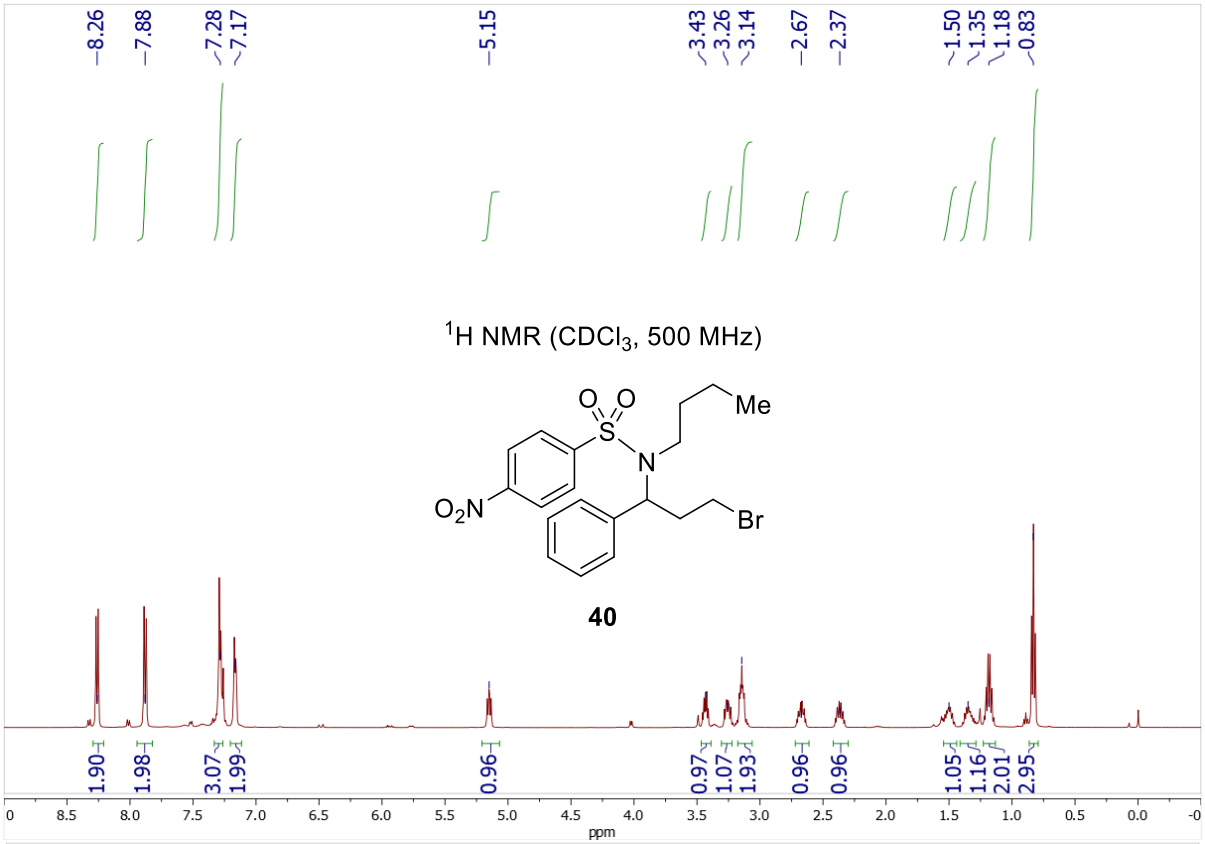

128.6
127.3
127.2
155.0
142.1
79.8
58.4
28.4
ppm
$^{13}$C NMR ($CDCl_3$, 126 MHz)
Boc
NH
37

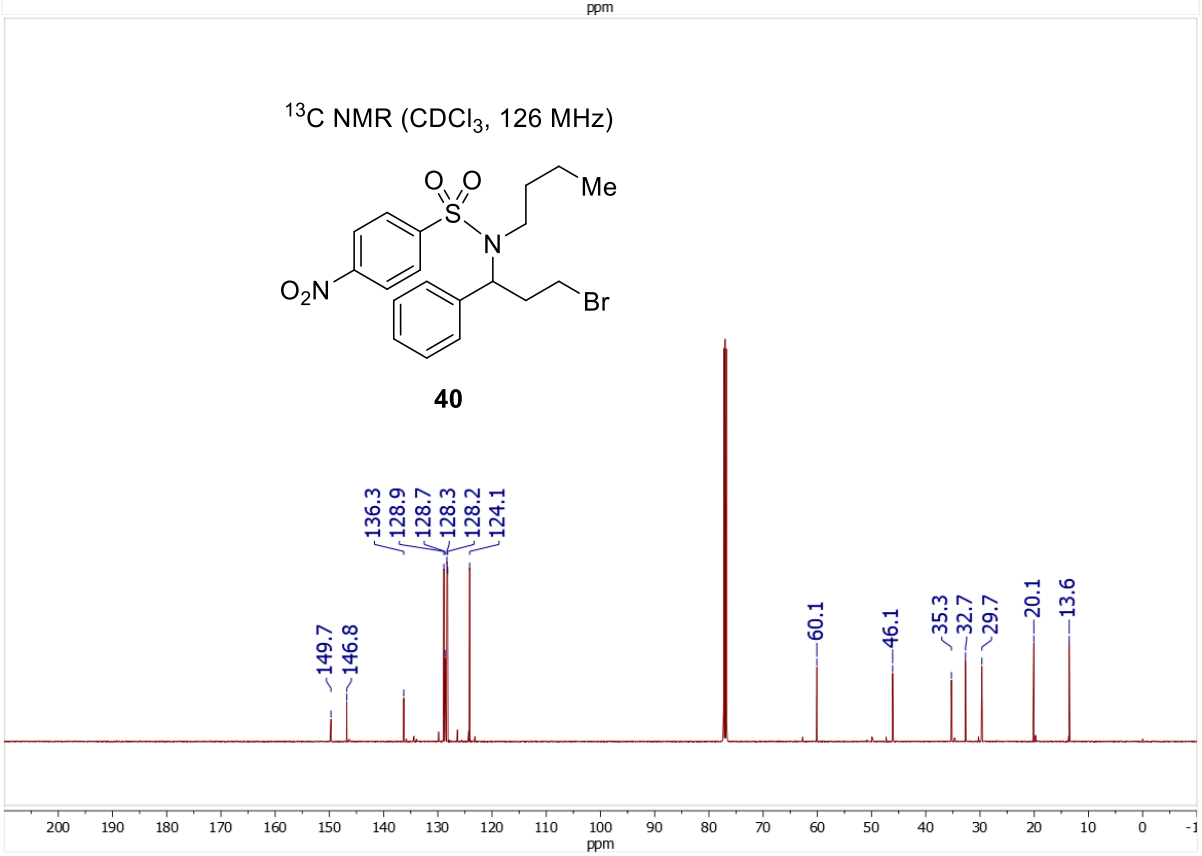

7.73
7.41
7.30
7.16
5.14
3.11
2.44
1.37
0.93
$^1$H NMR ($CDCl_3$, 500 MHz)
Ts
N
Me
Me
Br
38
2.01
1.99
2.06
2.02
0.99
2.01
3.03
3.06
3.15
ppm

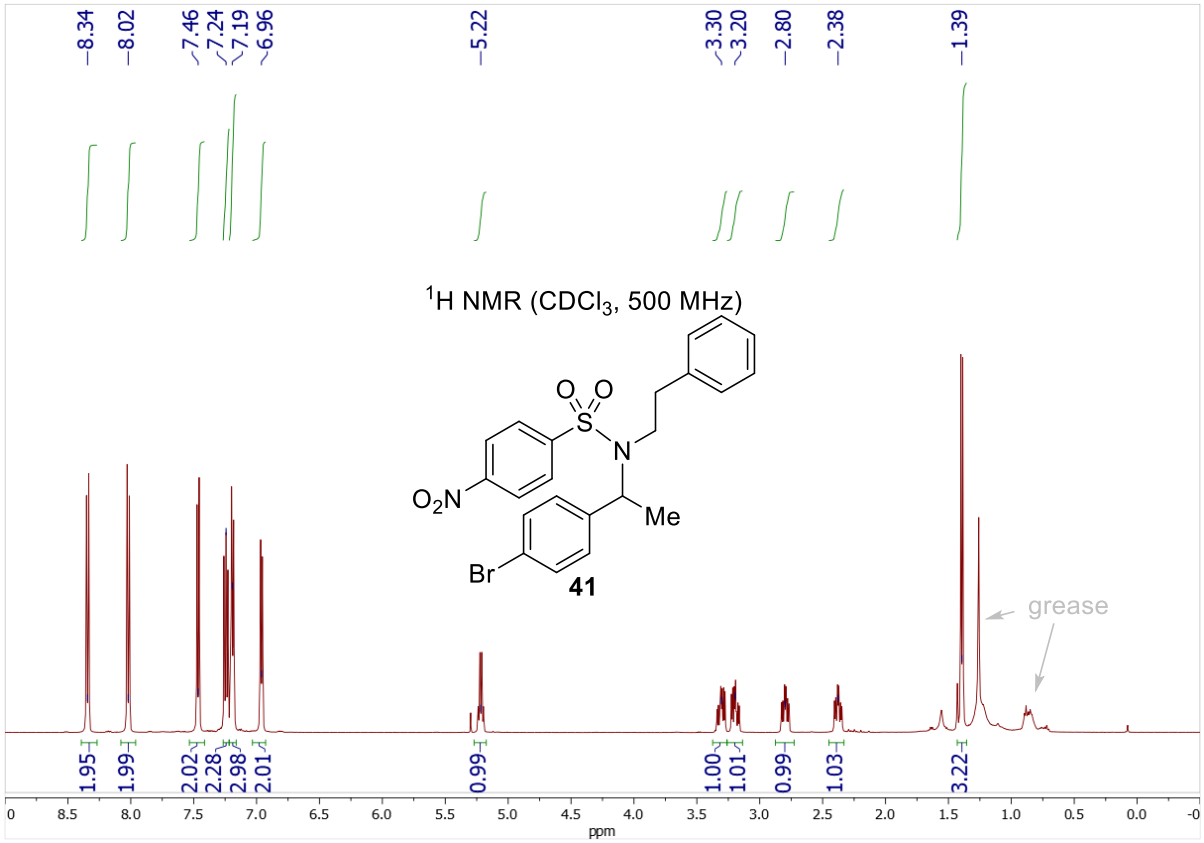

$^{13}$C NMR ($CDCl_3$, 126 MHz)
Ts
N
Me
Me
Br
38
143.1
139.7
138.4
131.4
129.7
129.2
127.1
121.5
54.7
38.9
21.5
16.7
16.6
ppm

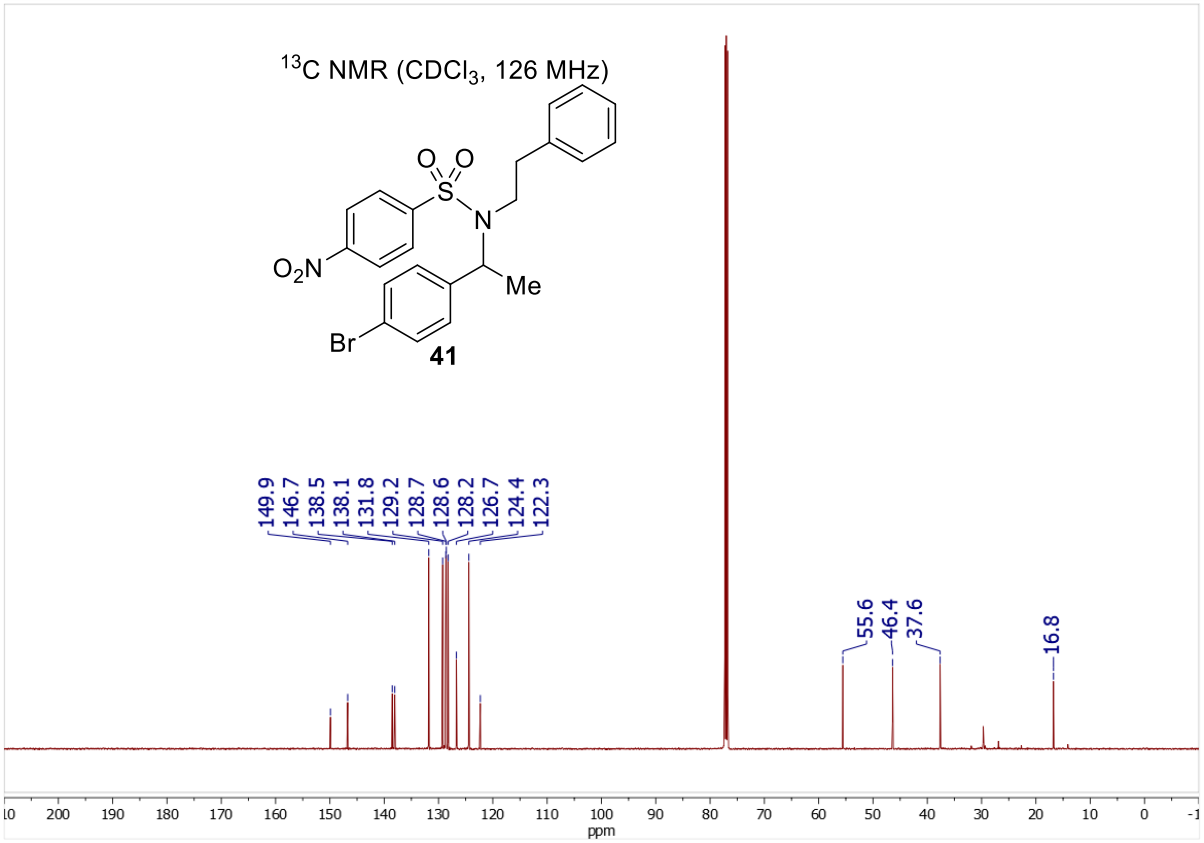

8.32
7.89
7.71
7.61
7.25
5.29
2.69
1.80
1.50
0.90
$^1$H NMR ($CDCl_3$, 500 MHz)
O
O
S
N
Me
Me
Ph
Me
39
1.00
3.08
1.03
2.12
5.29
1.02
3.07
1.03
2.12
6.34
ppm

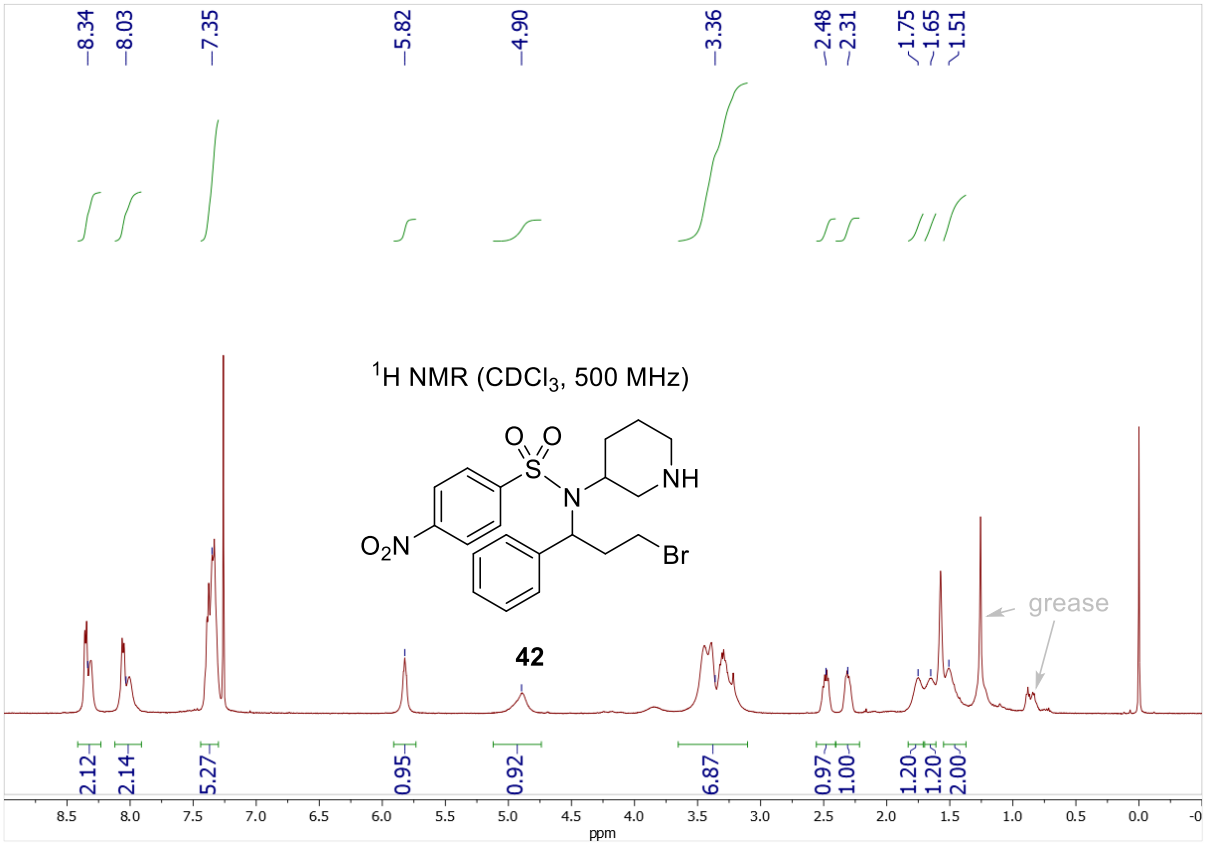

$^{13}$C NMR ($CDCl_3$, 126 MHz)
O
O
S
N
Me
Me
Ph
Me
39
143.1
139.7
138.4
131.4
129.7
129.2
127.1
121.5
54.7
38.9
21.5
16.7
16.6
ppm


8.26
7.88
7.28
7.17
5.15
3.43
3.26
3.14
2.67
2.37
1.50
1.35
1.18
0.83
1H NMR (CDCl3, 500 MHz)
Me
O
O
S
N
O2N
Br
40
1.90
1.98
3.07
1.99
0.96
0.97
1.07
1.93
0.96
0.96
1.05
1.16
2.01
2.95
ppm

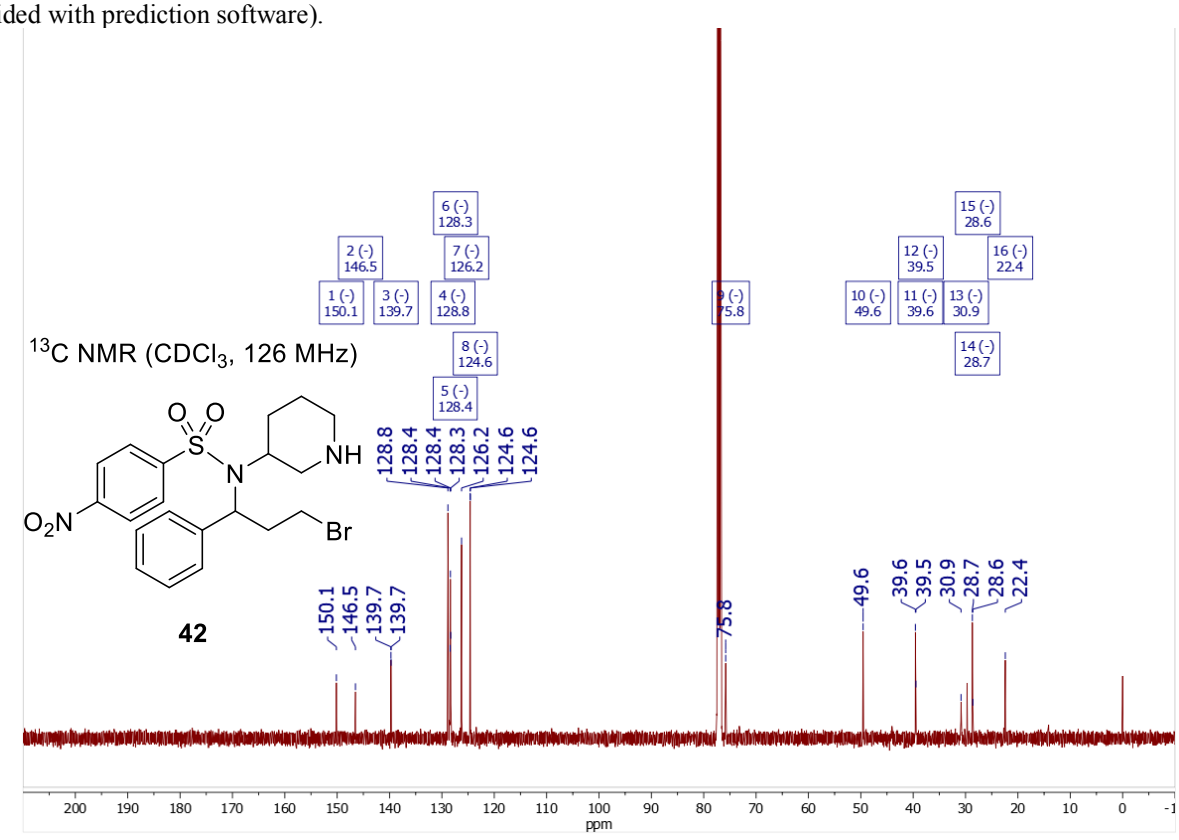

13C NMR (CDCl3, 126 MHz)
Me
O
O
S
N
O2N
Br
40
136.3
128.9
128.7
128.3
128.2
124.1
149.7
146.8
60.1
46.1
35.3
32.7
29.7
20.1
13.6
ppm

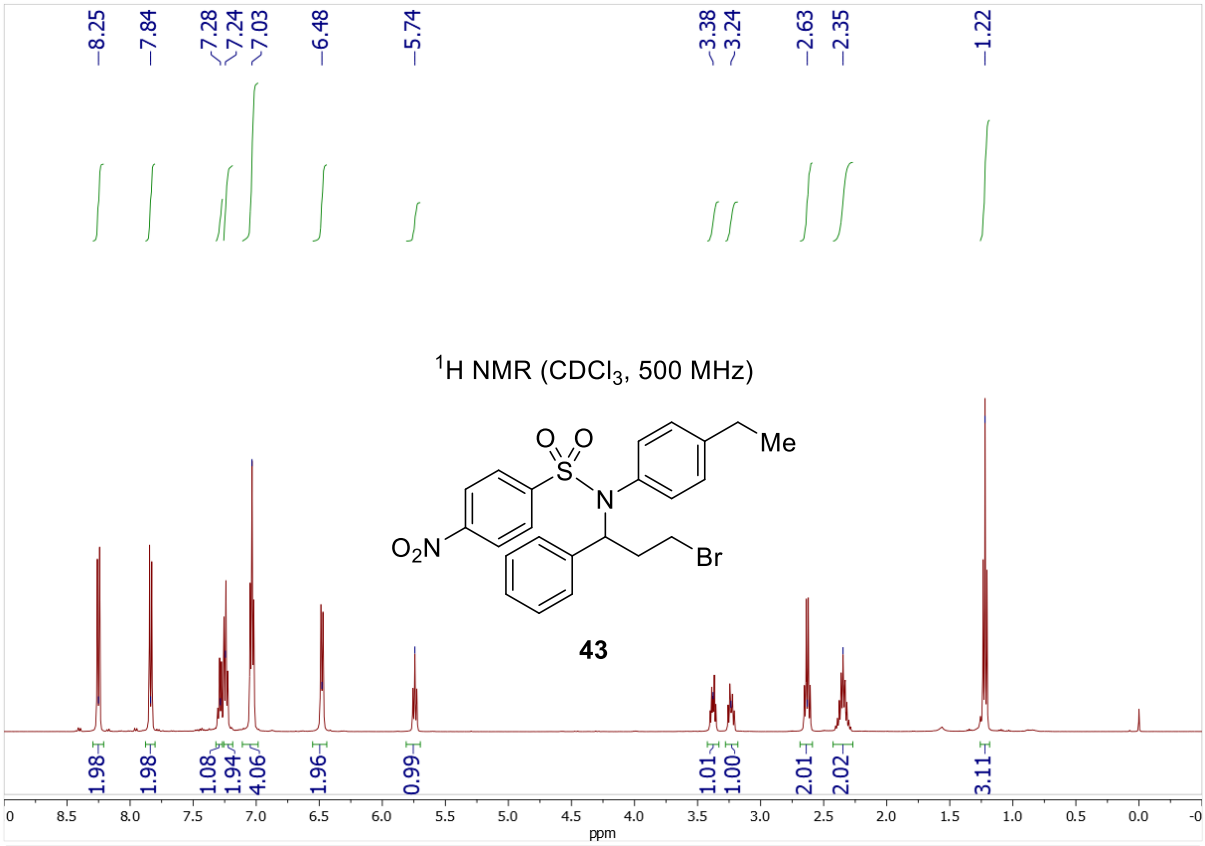

8.34
8.02
7.46
7.24
7.19
6.96
5.22
3.30
3.20
2.80
2.38
1.39
1H NMR (CDCl3, 500 MHz)
O2N
Me
Br
41
grease
1.95
1.99
2.02
2.28
2.98
2.01
0.99
1.00
1.01
0.99
1.03
3.22
ppm

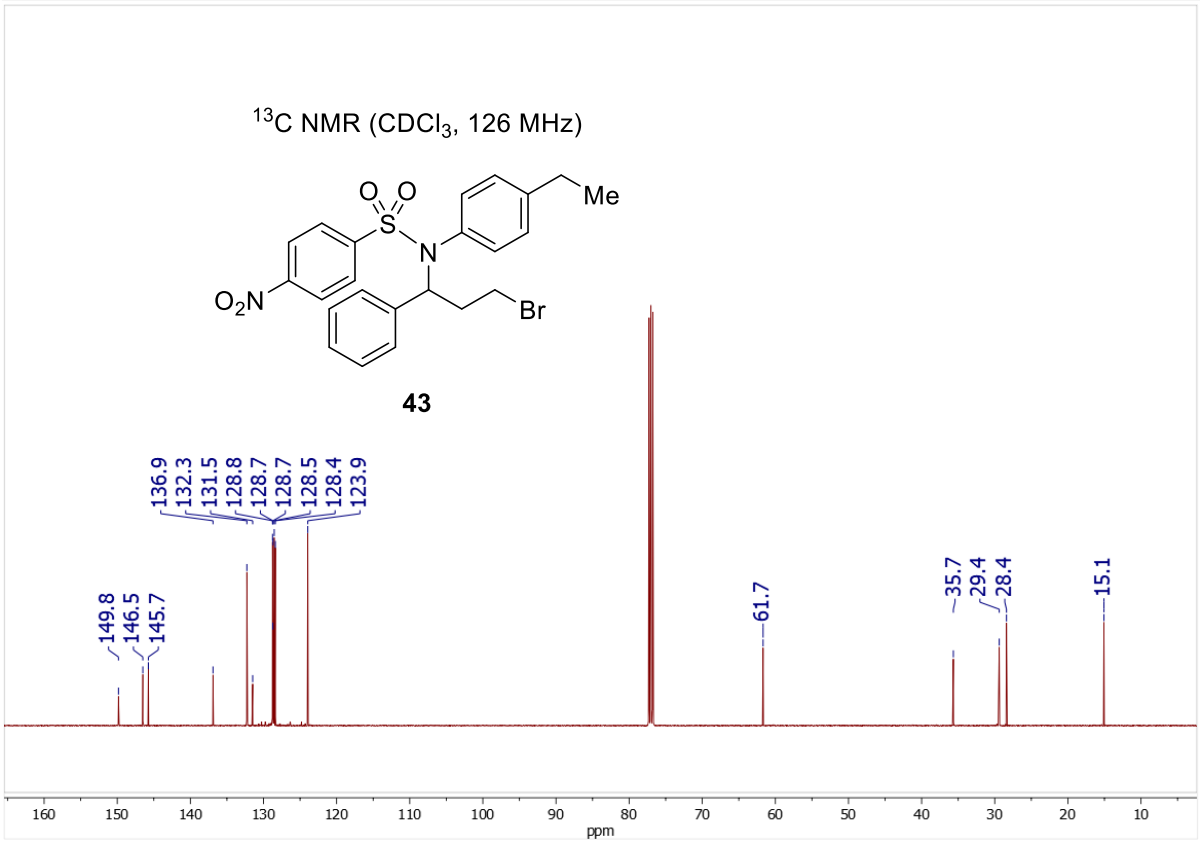

13C NMR (CDCl3, 126 MHz)
O2N
Me
Br
41
149.9
146.7
138.5
138.1
131.8
129.2
128.7
128.6
128.2
126.7
124.4
122.3
55.6
46.4
37.6
16.8
ppm

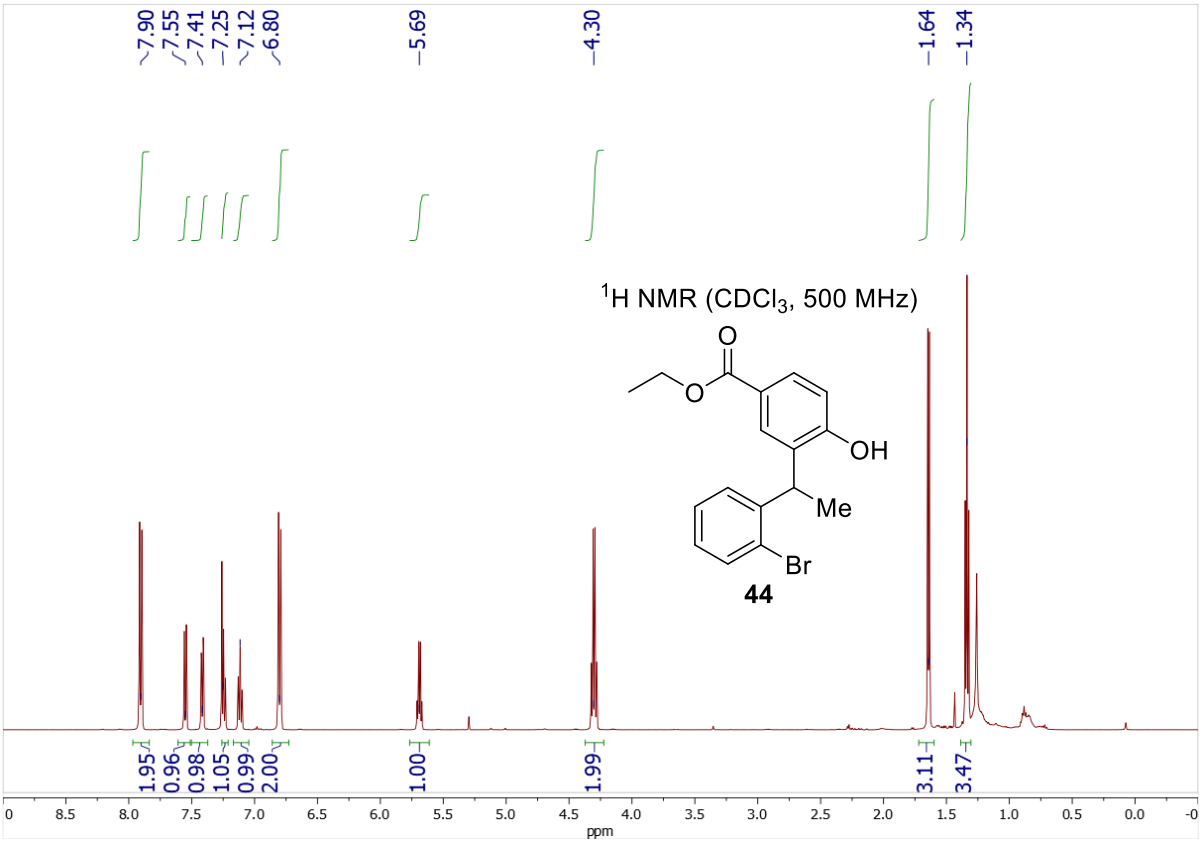


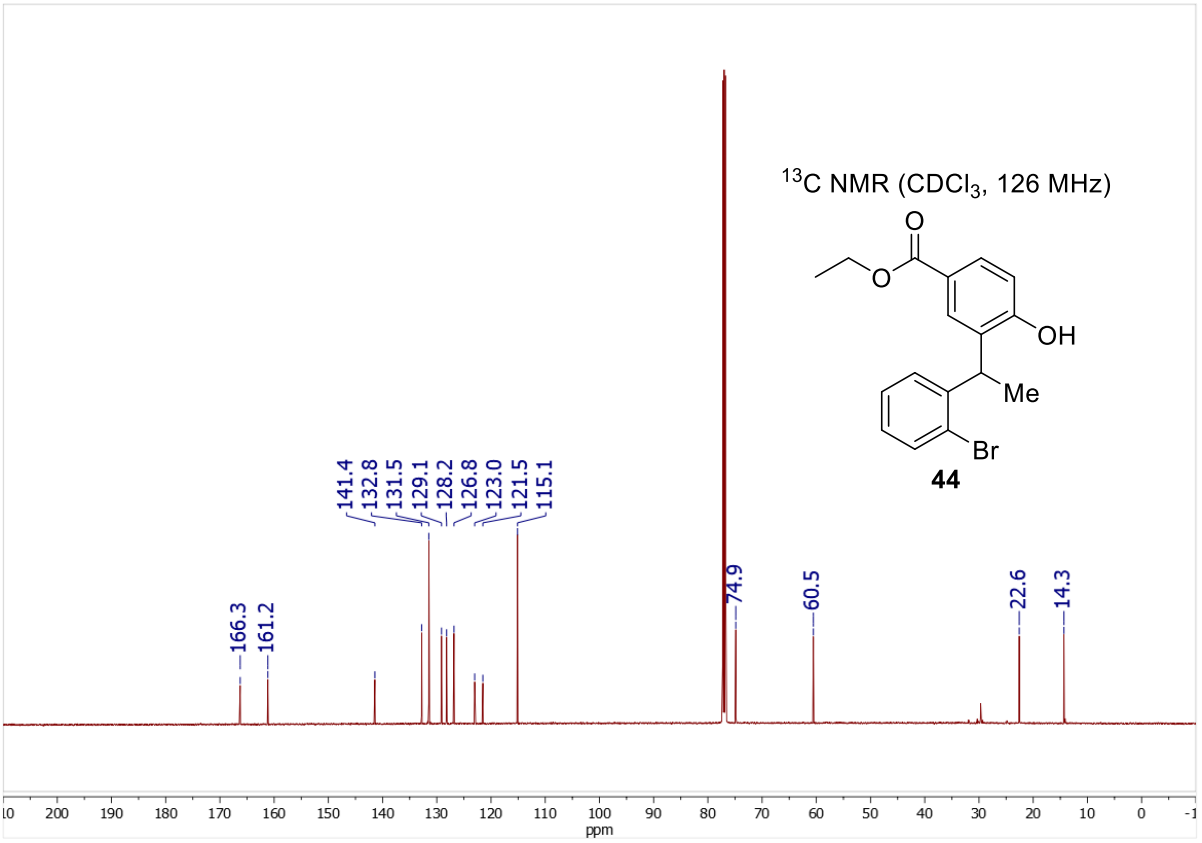

Diastereomers make these spectra complex. Diastereomeric $^{13}$C peaks are grouped below within the numbered boxes (aided with prediction software).

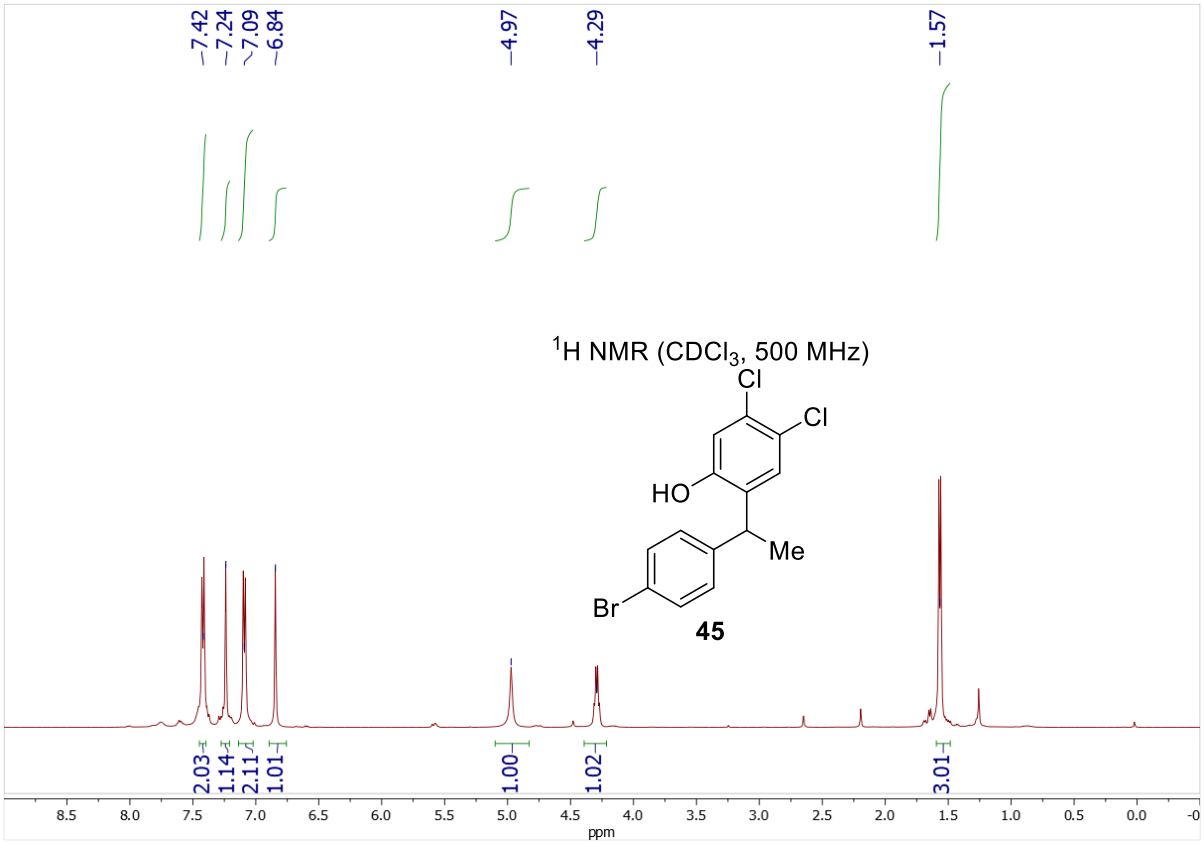


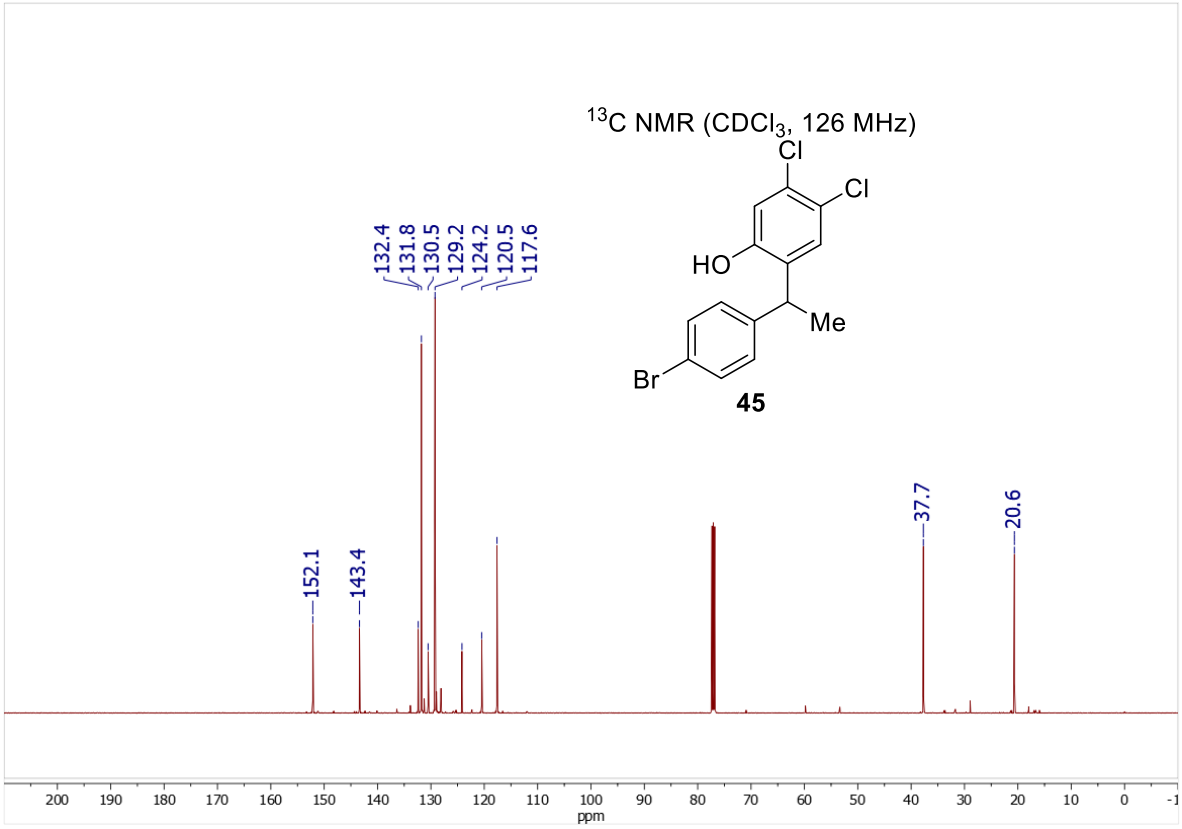

8.25
7.84
7.28
7.24
7.03
6.48
5.74
3.38
3.24
2.63
2.35
1.22
1H NMR (CDCl3, 500 MHz)
Me
O2N
Br
43
1.98
1.98
1.08
1.94
4.06
1.96
0.99
1.01
1.00
2.01
2.02
3.11
ppm

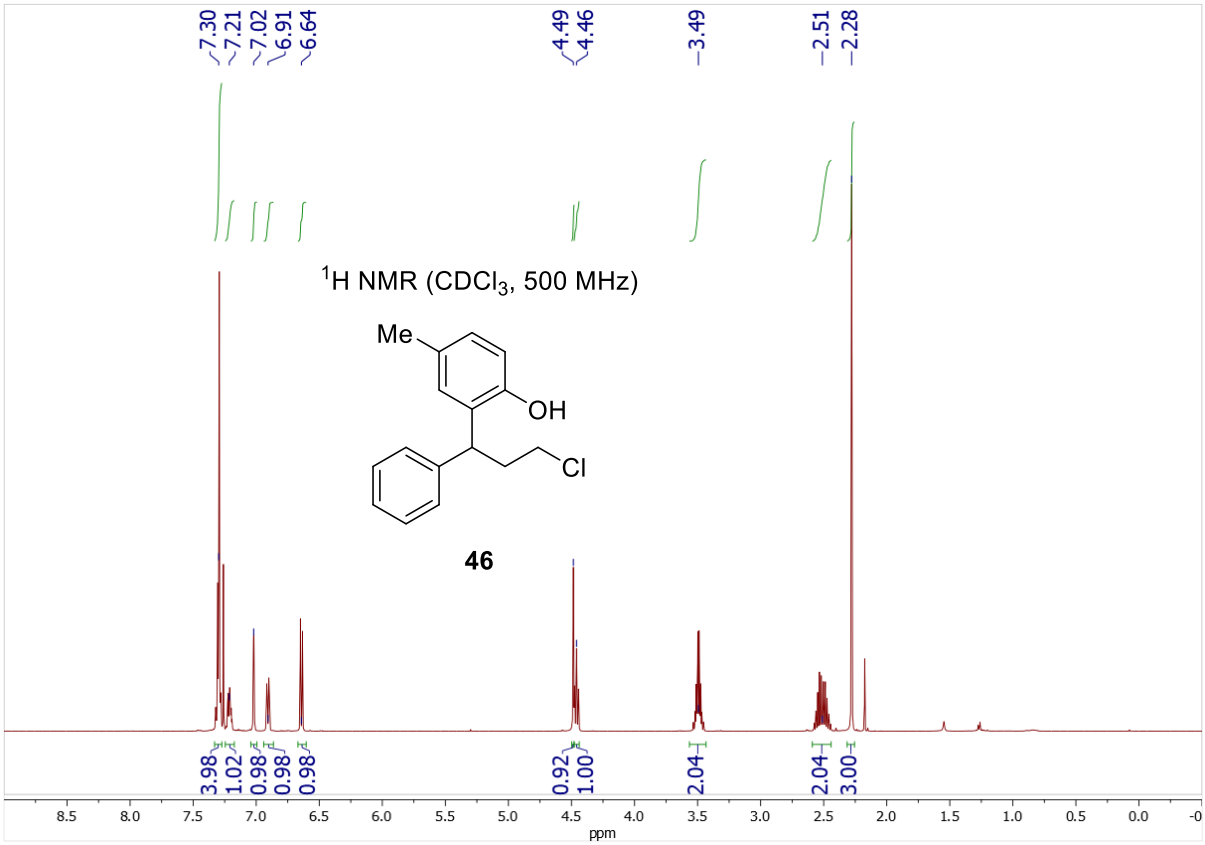

13C NMR (CDCl3, 126 MHz)
Me
O2N
Br
43
136.9
132.3
131.5
128.8
128.7
128.7
128.5
128.4
123.9
149.8
146.5
145.7
61.7
35.7
29.4
28.4
15.1
ppm

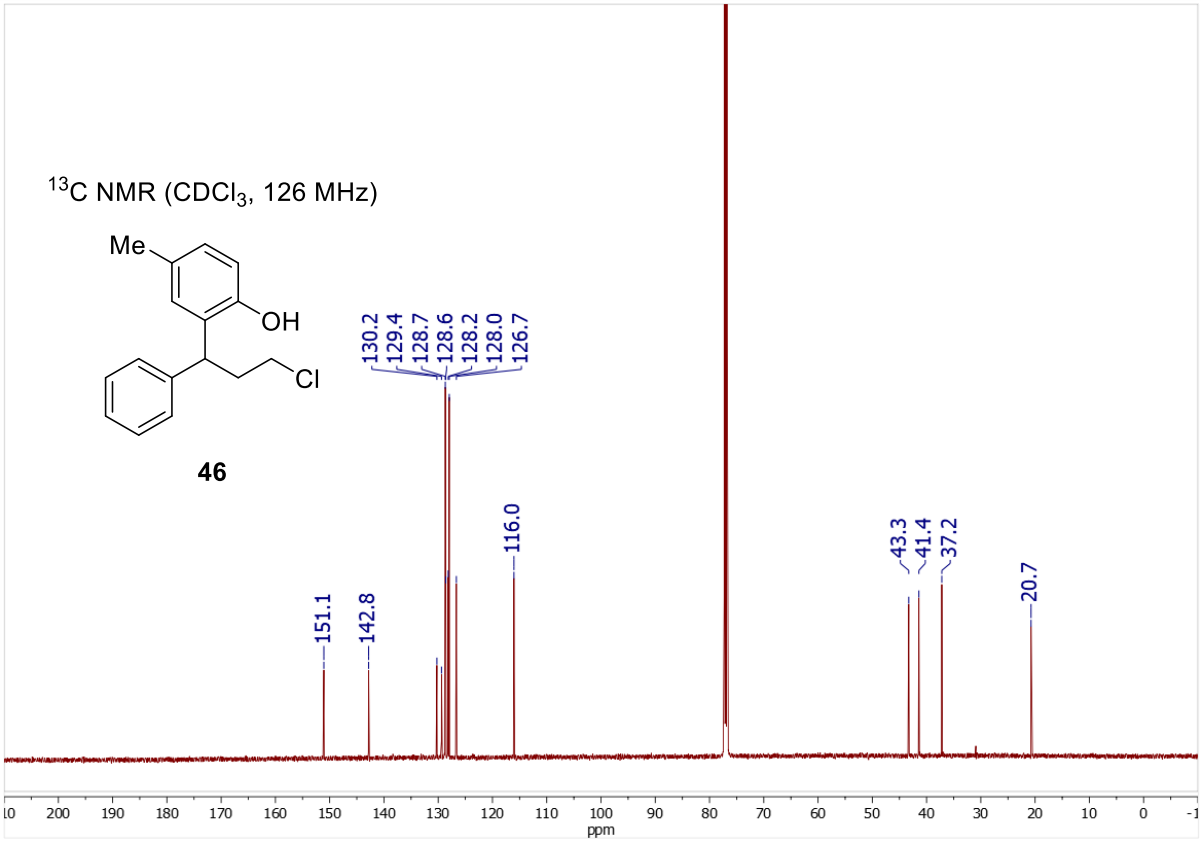

7.90
7.55
7.41
7.25
7.12
6.80
5.69
4.30
1.64
1.34
1H NMR (CDCl3, 500 MHz)
O
O
OH
Me
Br
44
1.95
0.96
0.98
1.05
0.99
2.00
1.00
1.99
3.11
3.47
ppm

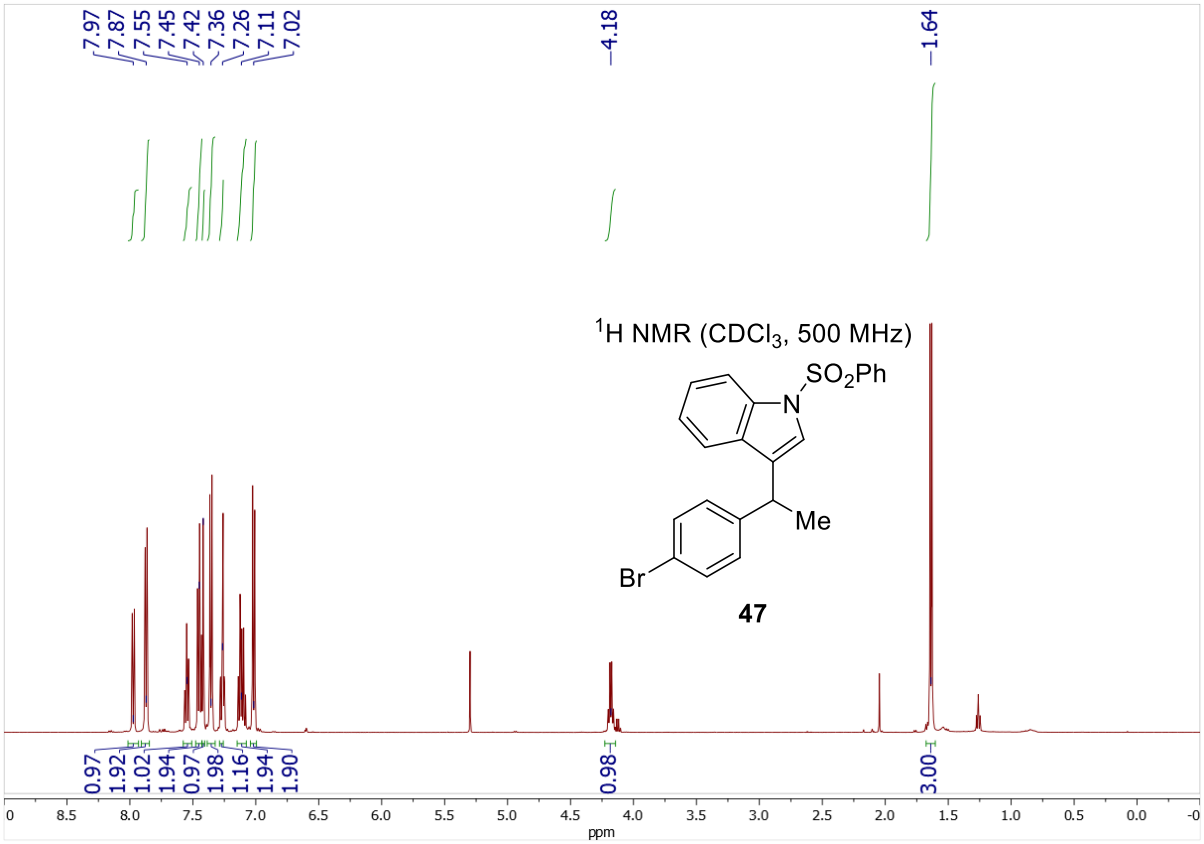

13C NMR (CDCl3, 126 MHz)
O
O
OH
Me
Br
44
141.4
132.8
131.5
129.1
128.2
126.8
123.0
121.5
115.1
166.3
161.2
74.9
60.5
22.6
14.3
ppm

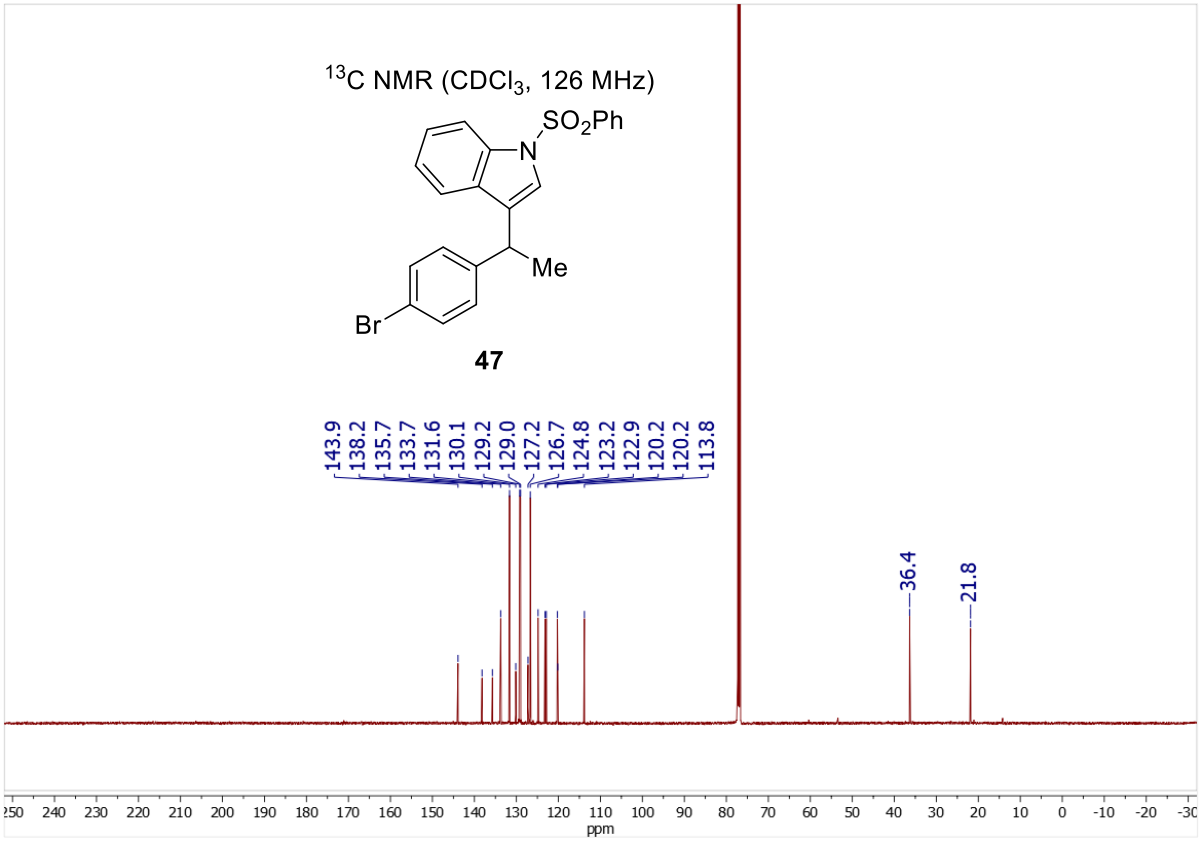

7.42
7.24
7.09
6.84
4.97
4.29
1.57
$^1$H NMR (CDCl$_3$, 500 MHz)
Cl
Cl
HO
Me
Br
45
2.03
1.14
2.11
1.01
1.00
1.02
3.01
ppm

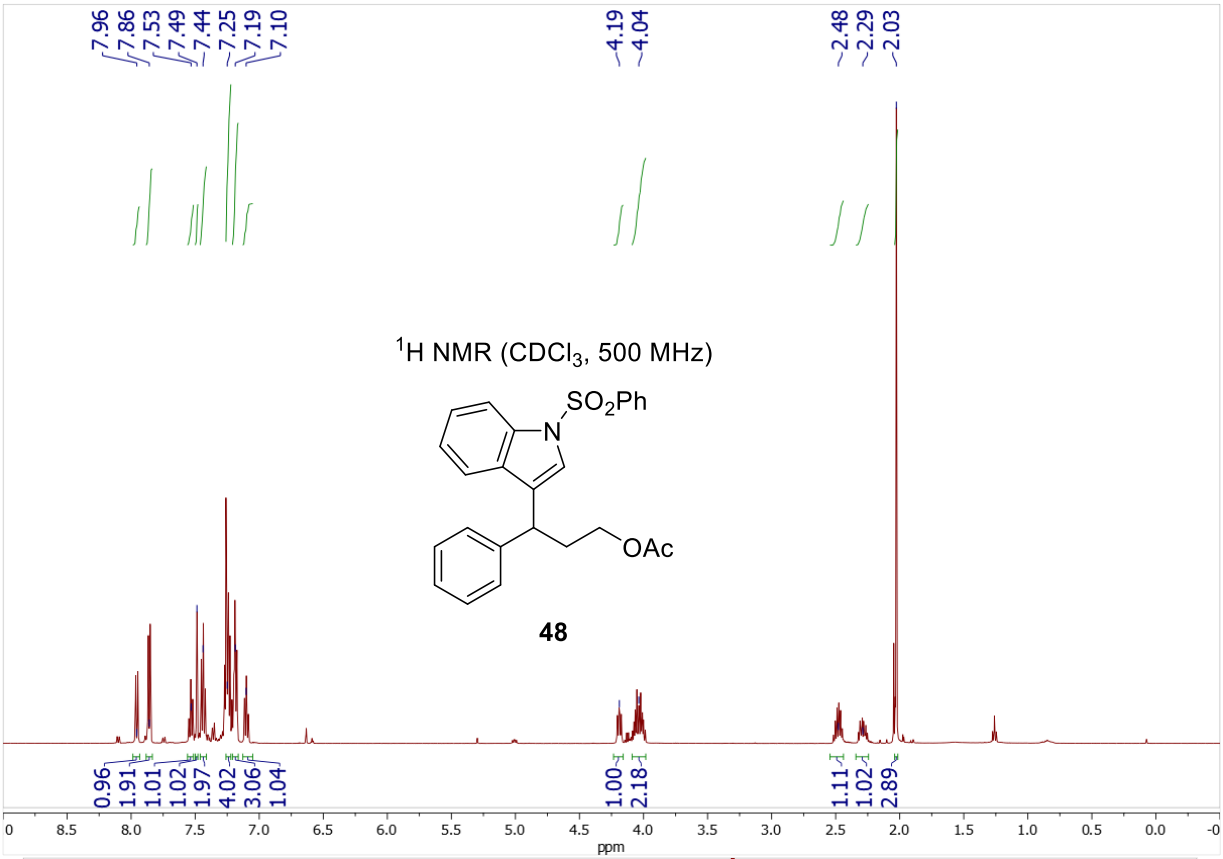

$^{13}$C NMR (CDCl$_3$, 126 MHz)
132.4
131.8
130.5
129.2
124.2
120.5
117.6
152.1
143.4
37.7
20.6
Cl
Cl
HO
Me
Br
45
ppm

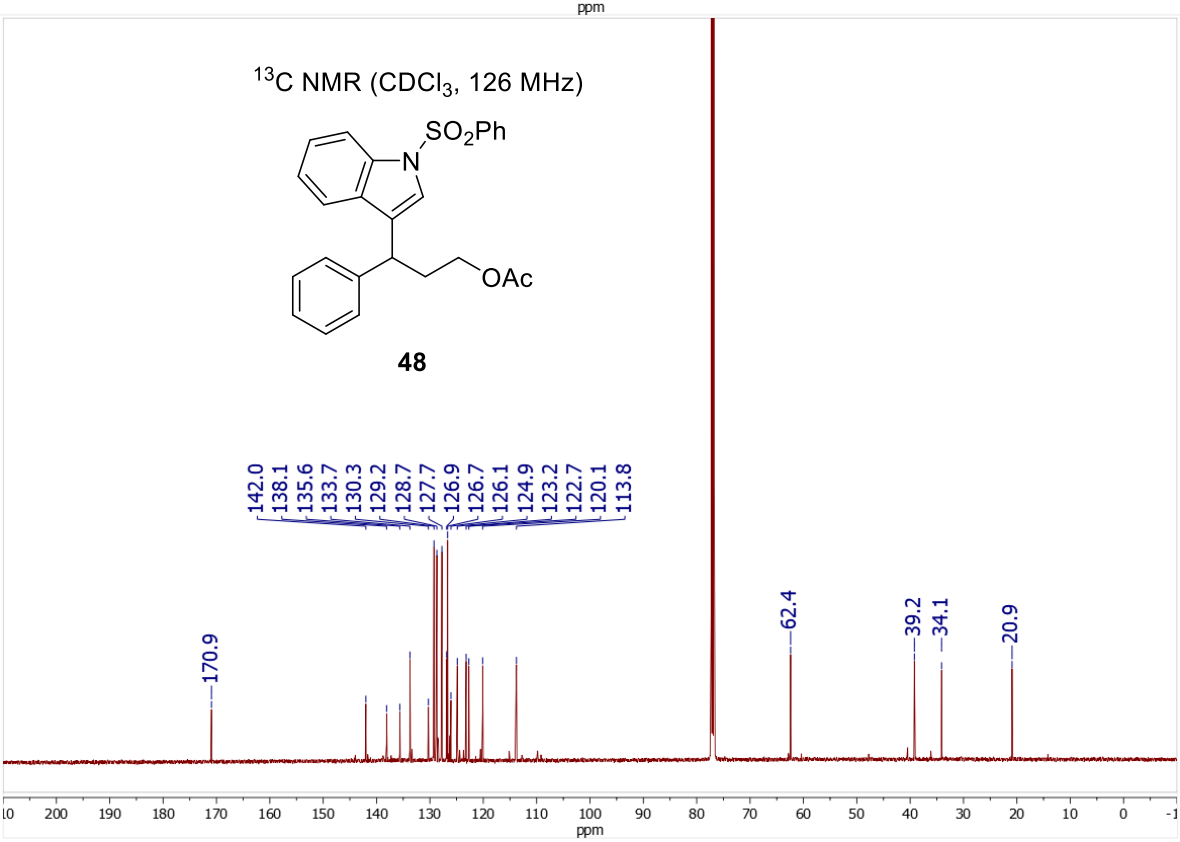

7.30
7.21
7.02
6.91
6.64
4.49
4.46
3.49
2.51
2.28
$^1$H NMR ($CDCl_3$, 500 MHz)
Me
OH
Cl
46
3.98
1.02
0.98
0.98
0.98
0.92
1.00
2.04
2.04
3.00
ppm

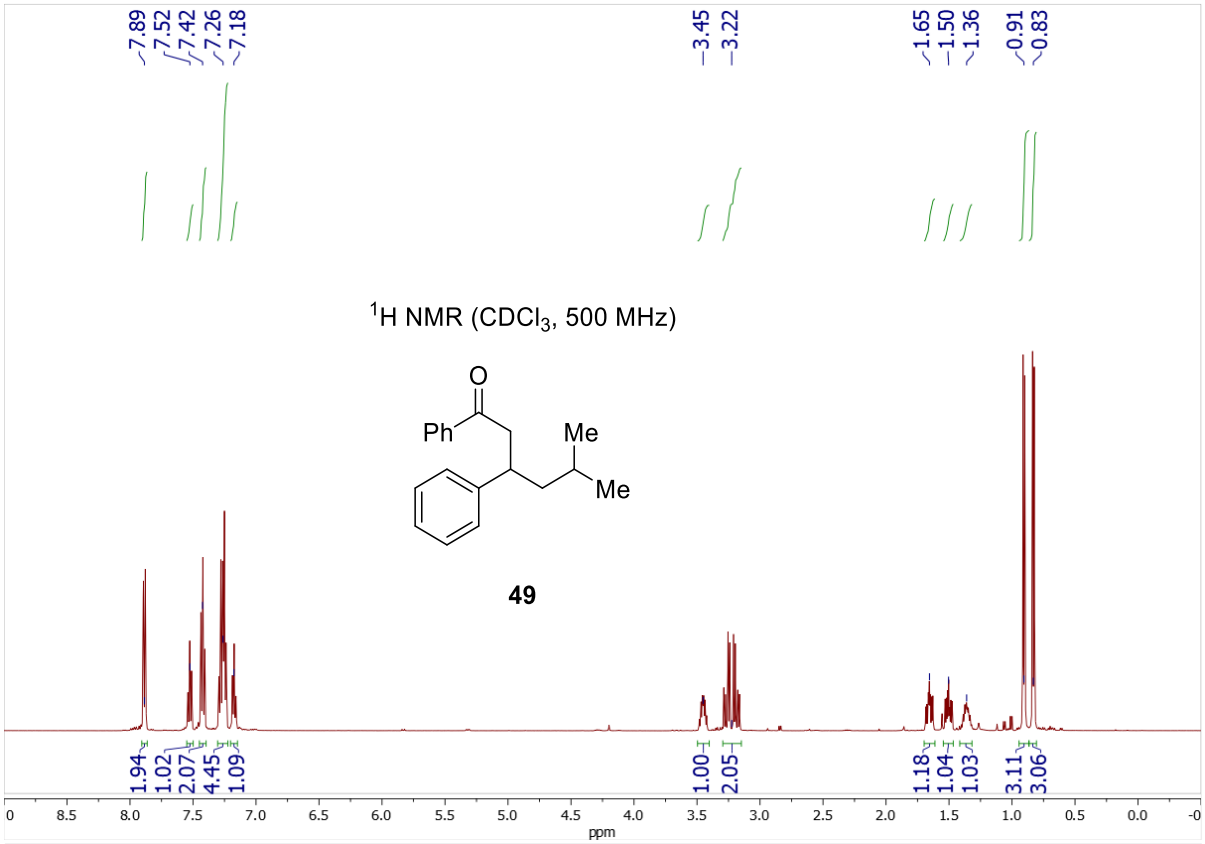

$^{13}$C NMR ($CDCl_3$, 126 MHz)
Me
OH
Cl
46
130.2
129.4
128.7
128.6
128.2
128.0
126.7
151.1
142.8
116.0
43.3
41.4
37.2
20.7
ppm

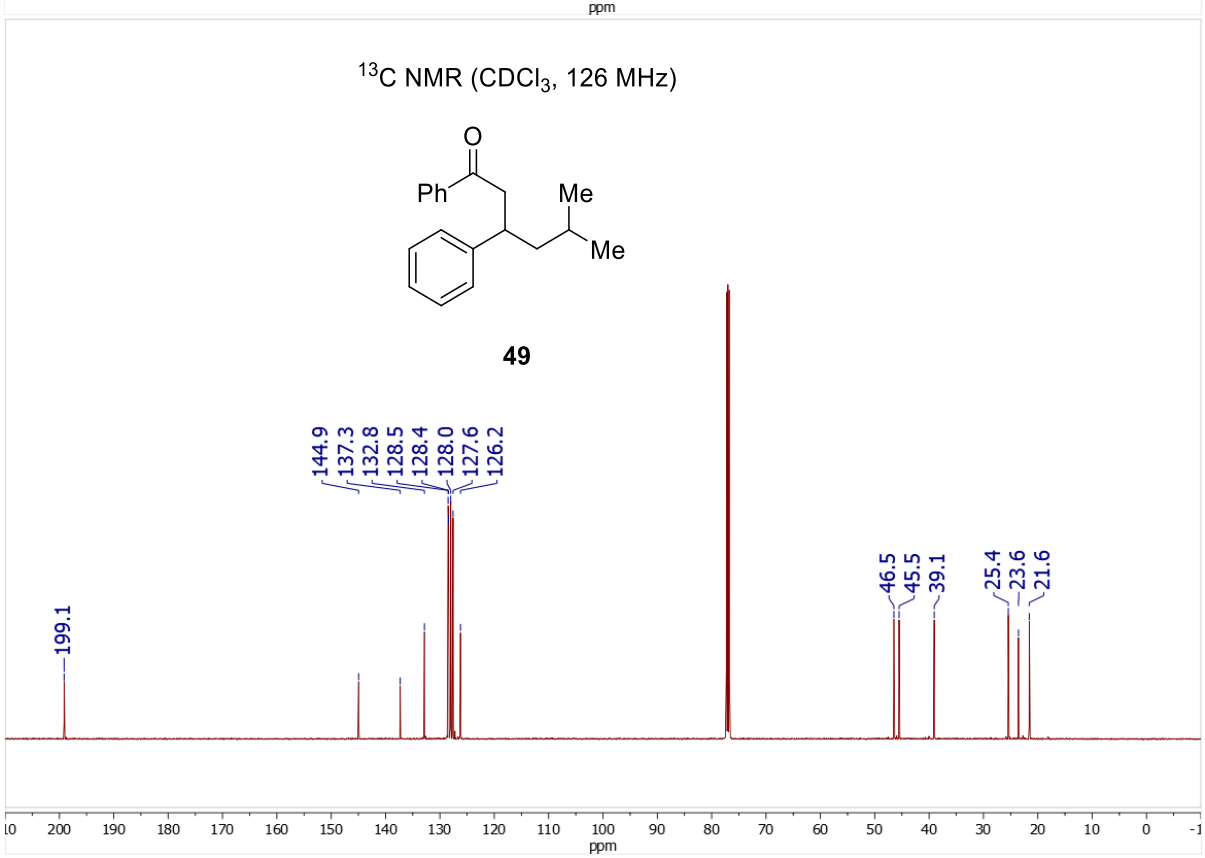

7.97
7.87
7.55
7.45
7.42
7.36
7.26
7.11
7.02
4.18
1.64
$^1$H NMR (CDCl$_3$, 500 MHz)
SO$_2$Ph
N
Me
Br
47
0.97
1.92
1.02
1.94
0.97
1.98
1.16
1.94
1.90
0.98
3.00
ppm

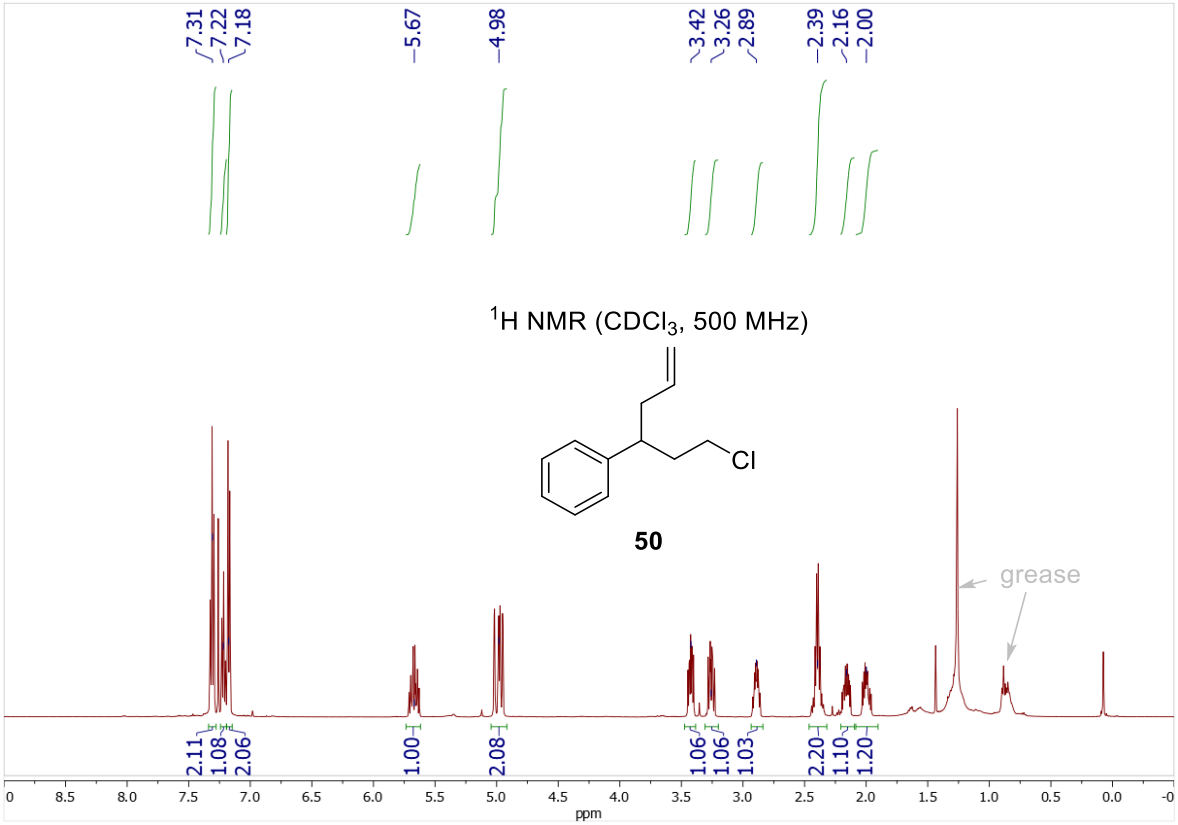

$^{13}$C NMR (CDCl$_3$, 126 MHz)
SO$_2$Ph
N
Me
Br
47
143.9
138.2
135.7
133.7
131.6
130.1
129.2
129.0
127.2
126.7
124.8
123.2
122.9
120.2
120.2
113.8
36.4
21.8
ppm

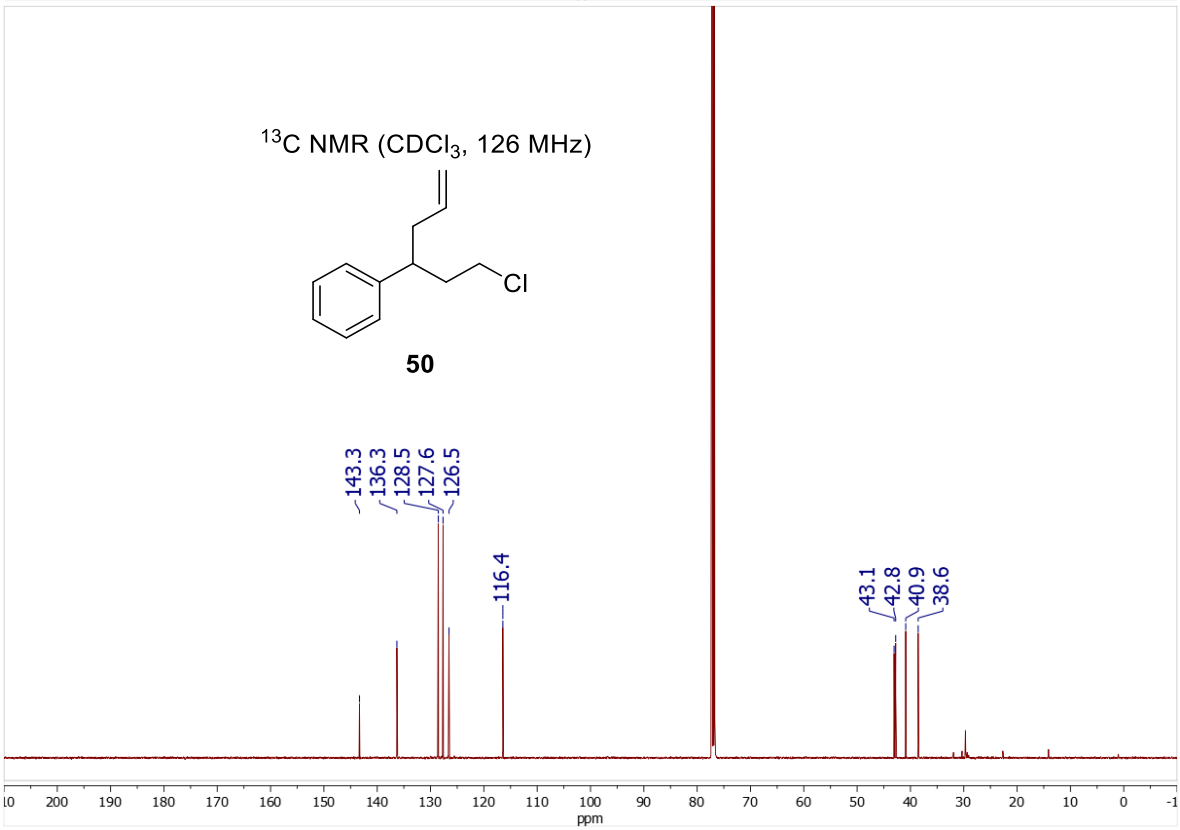

7.96
7.86
7.53
7.49
7.44
7.25
7.19
7.10
4.19
4.04
2.48
2.29
2.03
1H NMR (CDCl3, 500 MHz)
SO2Ph
N
OAc
48
0.96
1.91
1.01
1.02
1.97
4.02
3.06
1.04
1.00
2.18
1.11
1.02
2.89
ppm


13C NMR (CDCl3, 126 MHz)
SO2Ph
N
OAc
48
142.0
138.1
135.6
133.7
130.3
129.2
128.7
127.7
126.9
126.7
126.1
124.9
123.2
122.7
120.1
113.8
170.9
62.4
39.2
34.1
20.9
ppm


7.89
7.52
7.42
7.26
7.18
3.45
3.22
1.65
1.50
1.36
0.91
0.83
1H NMR (CDCl3, 500 MHz)
O
Ph
Me
Me
49
1.94
1.02
2.07
4.45
1.09
1.00
2.05
1.18
1.04
1.03
3.11
3.06
ppm


13C NMR (CDCl3, 126 MHz)
O
Ph
Me
Me
49
144.9
137.3
132.8
128.5
128.4
128.0
127.6
126.2
199.1
46.5
45.5
39.1
25.4
23.6
21.6
ppm


7.31
7.22
7.18
5.67
4.98
3.42
3.26
2.89
2.39
2.16
2.00
1H NMR (CDCl3, 500 MHz)
Cl
50
grease
2.11
1.08
2.06
1.00
2.08
1.06
1.06
1.03
2.20
1.10
1.20
ppm


13C NMR (CDCl3, 126 MHz)
Cl
50
143.3
136.3
128.5
127.6
126.5
116.4
43.1
42.8
40.9
38.6
ppm