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Sulfonamide Directivity Enables Ni-Catalyzed 1,2-Diarylation of Diverse Alkenyl Amines

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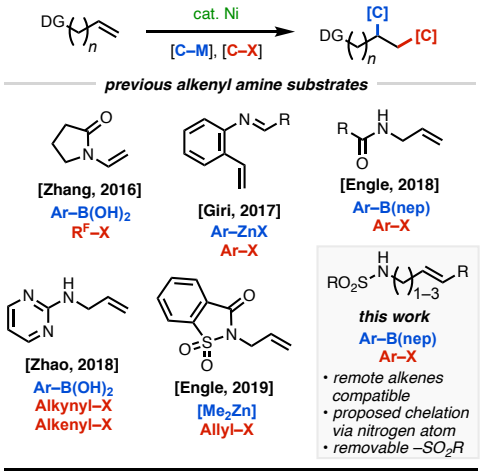
1,2-Diarylation of alkenyl sulfonamides with aryl iodides and aryl boronic esters under nickel catalysis is reported. The developed method tolerates coupling partners with disparate electronic properties and substitution patterns. 1,2- and 1,1-Disubstituted alkenes, as well as alkenes distal from the directing group, are all accommodated. Control experiments are consistent with a N–Ni coordination mode of the directing group, which stands in contrast to earlier reports on amide-directed 1,2-diarylation that involve carbonyl coordination. The synthetic utility of the method arises from the dual function of the sulfonamide as both a directing group and masked amine nucleophile. This is highlighted by various product diversifications where complex amine compounds are synthesized in a two-step sequence of N-functionalization and deprotection of the sulfonyl group.

Sulfonamide Directivity Enables Ni-Catalyzed 1,2-Diarylation of Diverse Alkenyl Amines

Omar Apolinar[a], Van T. Tran[a], Michael A. Schmidt[b], Joseph Derosa[a], and Keary M. Engle[a]*

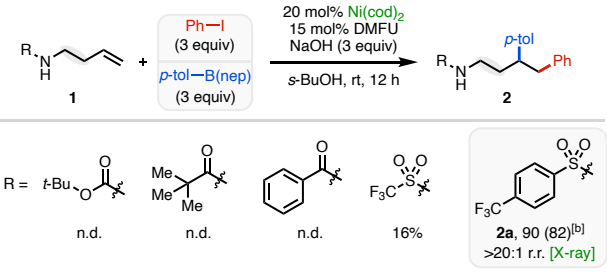
Abstract: 1,2-Diarylation of alkenyl sulfonamides with aryl iodides and aryl boronic esters under nickel catalysis is reported. The developed method tolerates coupling partners with disparate electronic properties and substitution patterns. 1,2- and 1,1-Disubstituted alkenes, as well as alkenes distal from the directing group, are all accommodated. Control experiments are consistent with a N–Ni coordination mode of the directing group, which stands in contrast to earlier reports on amide-directed 1,2-diarylation that involve carbonyl coordination. The synthetic utility of the method arises from the dual function of the sulfonamide as both a directing group and masked amine nucleophile. This is highlighted by various product diversifications where complex amine compounds are synthesized in a two-step sequence of *N*-functionalization and deprotection of the sulfonyl group.

Forging contiguous C–C bonds through 1,2-dicarbofunctionalization of alkenes, also referred to as conjunctive cross-coupling, has blossomed into a vibrant area of catalysis that leverages the unique reactivity of diverse transition metals, including Pd, Ni, Co, Cu, and Fe.[1a-b] In this context, nickel provides unique advantages compared to other transition metals, such as palladium, by having a higher propensity toward oxidative addition and 1,2-migratory insertion steps while being more resilient towards *β*-hydride elimination.[1c] 1,2-Dicarbofunctionalization of alkenyl amine substrates, wherein a protected amine directs key steps in the catalytic cycle, is an attractive approach for selectivity control and offers rapid entry to functionalized alkyl amine product libraries. 1,2-(Fluoroalkyl)arylation and 1,2-diarylation of electronically activated enamides and *ortho*-vinyl aniline derivatives have been reported by Zhang[2a] and Giri[2b], respectively (Scheme 1). More recently the use of a non-removable pyrimidyl auxiliary that facilitates the 1,2-dicarbofunctionalization of non-conjugated terminal alkenes via coordination of Ni with a N(sp^2) atom center was reported by Zhao and coworkers.[2e] Our group has reported the 1,2-diarylation and 1,2-allylmethylation of simple alkenyl amides and *N*-allyl heterocycles, respectively.[3a-b] Ni-catalyzed conjunctive cross-couplings of various classes of non-conjugated alkenes have been reported by other research groups via different mechanistic paradigms.[4] This progress notwithstanding, significant limitations remain in this family of transformations. In particular, existing methods are incompatible with homoallyl and bis-homoallyl amines as well as internal alkenyl amine substrates. Moreover, the directing groups employed in earlier reports are synthetically restrictive in that they cannot be directly employed in further functionalization. The goal of the present study was to identify an amine-based directing group capable of promoting 1,2-diarylation of remote, highly substituted alkenes and engaging in diverse downstream *N*-functionalization chemistry, which



Scheme 1. Previous reports and synopsis of new findings.

Table 1. Optimization of 1,2-diarylation reaction.[a]



entry	deviation from standard conditions	%Yield **2a**[c]
1	no ligand	30
2	*p*-tol-B(OH)$_2$ instead of *p*-tol-B(nep)	54
3	*p*-tol-B(pin) instead of *p*-tol-B(nep)	50
4	Ph-Br instead of Ph-I	n.d.
5	Ni(cod)(DQ), NiCl$_2$, Ni(acac)$_2$, or NiBr$_2$•glyme instead of Ni(cod)$_2$	n.d.
6	conditions from alkenyl amide diarylation[d]	60
7	conditions from alkenyl carboxylate diarylation[e]	n.d.
8	10 mol% Ni(cod)$_2$ instead of 20 mol%	90
9	1.5 equiv of PhI, *p*-tolB(nep), NaOH instead of 3 equiv	90

[a] Reaction conditions: **1a** (0.1 mmol), 0.2 M *s*-BuOH. [b] Values in parentheses are isolated yields. [c] Percentage yield by ^{1}H NMR using CH_2Br_2 as the internal standard; n.d. = not detected. [d] Reaction conditions: 15 mol% Ni(cod)$_2$, 15 mol% dimethylfumarate, 1.5 equiv ArI, 1.5 equiv ArB(nep), 2 equiv NaOH, 0.2 M *i*-BuOH at r.t. [e] Reaction conditions: 15 mol% Ni(cod)$_2$, 2 equiv ArI, 2 equiv ArB(nep), 2 equiv NaOH, 0.1 M *s*-BuOH at 50 °C.

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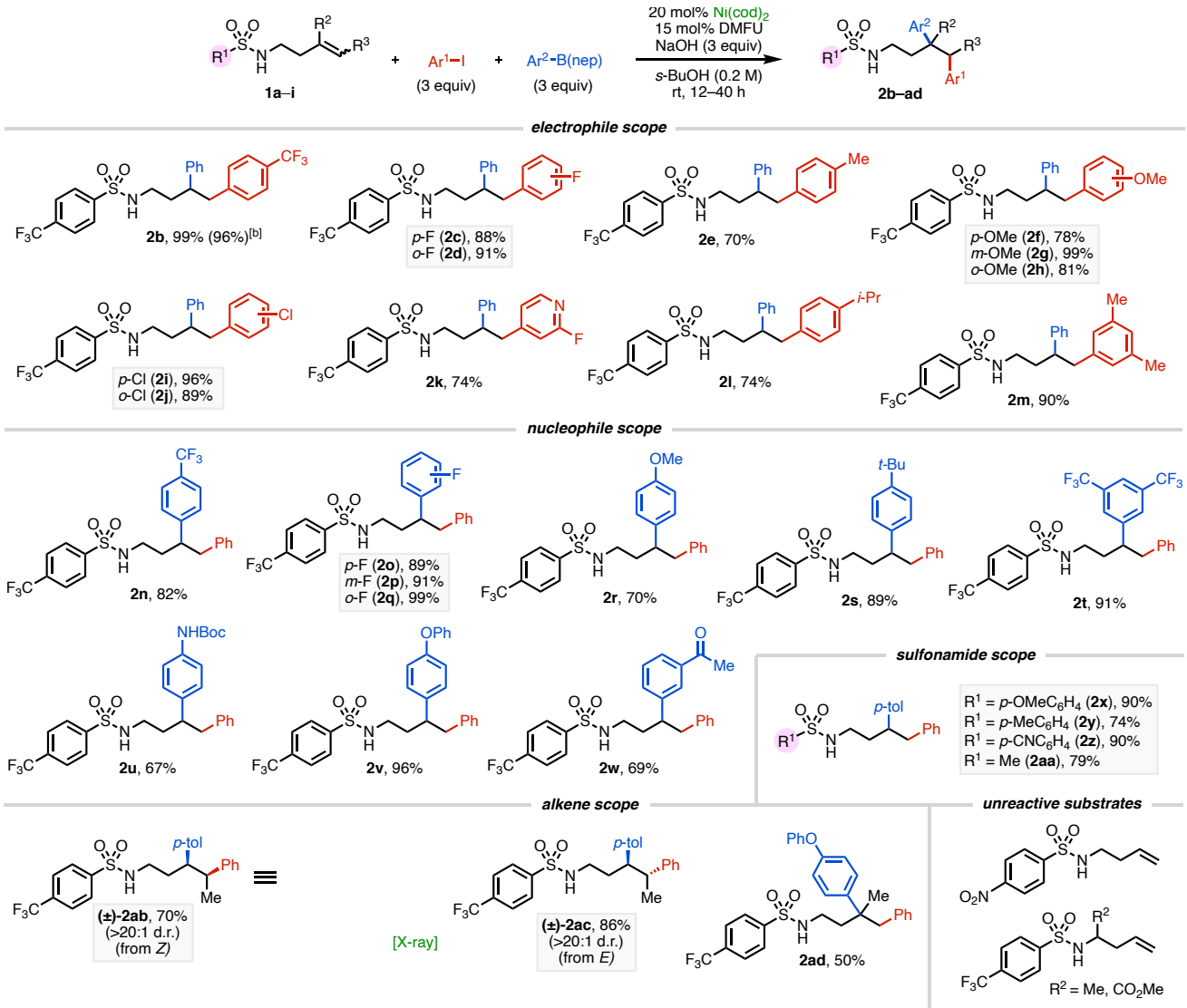
would allow alkenyl amines to act as linchpins in modular synthesis. To this end, herein we report the identification of sulfonamides as uniquely effective and versatile[5,6] directing groups in 1,2-diarylation of alkenes under nickel/dimethyl fumarate (DMFU) catalysis.[7]

To commence the study, we selected iodobenzene and 4-tolylboronic acid neopentyl glycol ester (*p*-tolB(nep)) as model coupling partners and systematically surveyed homoallyl amine substrates bearing different protecting groups. Carbonyl groups that were previously found to direct 1,2-diarylation of allylamine substrates, namely Boc-, Piv-, and Bz-, were ineffective in this case with a more distal alkene. We next turned to sulfonyl protecting groups[6] with the hypothesis that in this case, the nickel catalyst may bind the sulfonamide through nitrogen. Gratifyingly, triflyl-protected homoallyl amine gave the desired product, albeit in low yield. Moving to a less electron-withdrawing aryl sulfonyl group provided 1,2-diarylated product **2a** in excellent yield and regioselectivity, and its connectivity was confirmed by single-crystal X-ray diffraction. While various aryl sulfonamide directing groups were similarly effective (vide infra), the 4-(trifluoromethyl)-phenyl group provided a convenient ^{19}F NMR handle for reaction analysis and was employed for much of the ensuing work. The absence of DMFU and employment of the aryl boronic acid and pinacol ester resulted in diminished yields (Entries 1–3). Bromobenzene was unreactive as an electrophile, and other nickel precatalysts, such as Ni(cod)(DQ), $NiCl_2$, $Ni(acac)_2$, and $NiBr_2$•glyme, were ineffective (Entries 4–5). Under previously published reaction conditions for diarylation of alkenyl amide substrates, lower yield was obtained (Entry 6). No diarylation was observed under conditions for alkenyl carboxylate substrates (Entry 7).[3a,4i] While excellent yields were obtained when lower catalyst loading or equivalents of coupling partners and base were used upon the standard substrate (Entry 8–9), across other examples, higher loading and equivalents gave improved yields.

Next, the scope of electrophilic and nucleophilic aryl coupling partners was investigated (Table 2). Electron-withdrawing groups at the *para* position of the aryl iodides

Table 2. Electrophile, nucleophile, sulfonamide and alkene scope.[a]

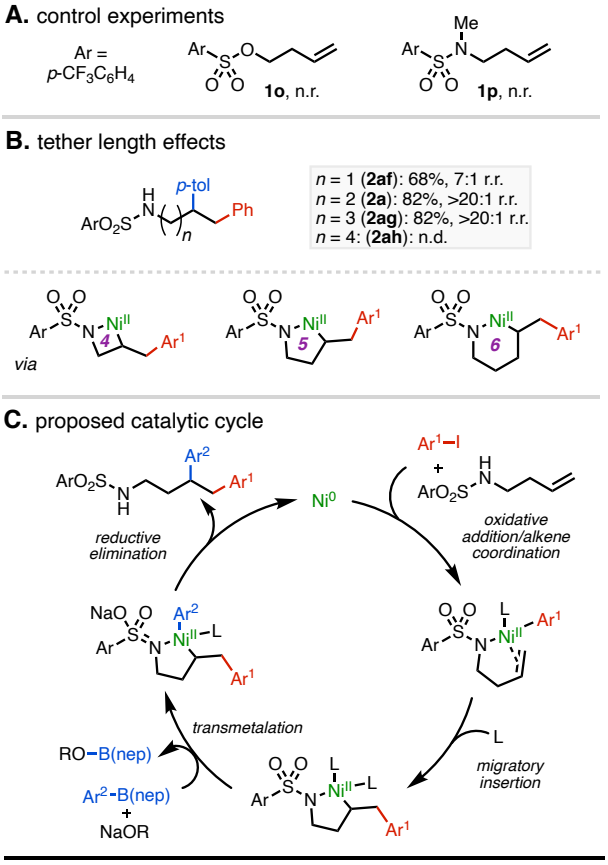


[a] Reactions performed on 0.1 mmol scale. [b] Reactions performed on 1 mmol scale. Percentages represent isolated yields.

afforded the highest product yields (**2b–c**, **2i**), and the product yield decreased with electron-neutral and -donating groups (**2e–f**, **2l**). It is worth noting that product **2b** was synthesized in an excellent yield on a larger scale (1 mmol, 0.48 g isolated). Electron-withdrawing groups on the *meta* position of the aryl iodides gave no 1,2-diarylated product; however, electron-donating groups (**2g**, **2m**) gave 1,2-diarylation in excellent yields. *Ortho*-substituted electron-withdrawing or donating groups on the aryl iodide had little effect on the product yield in comparison to the *para*-substituted examples (**2d**, **2h**, **2j**). Consistent with the previously discussed results, electron-deficient 2-fluoro-4-iodopyridine gave good yield (**2k**). With regards to the nucleophile scope, no apparent trend is observed. Electron-withdrawing and weakly electron-donating groups on the *para* position (**2n–o**, **2s**) gave very good yields. Product yields greatly varied with the use of electron-donating groups on the *para* position ranging from moderate to excellent yields (**2r**, **2u–v**). Aryl boronic esters with electron withdrawing groups on the *meta* and *ortho* positions (**2p**, **2q**, **2t**, **2w**) resulted in moderate to excellent yields as well.

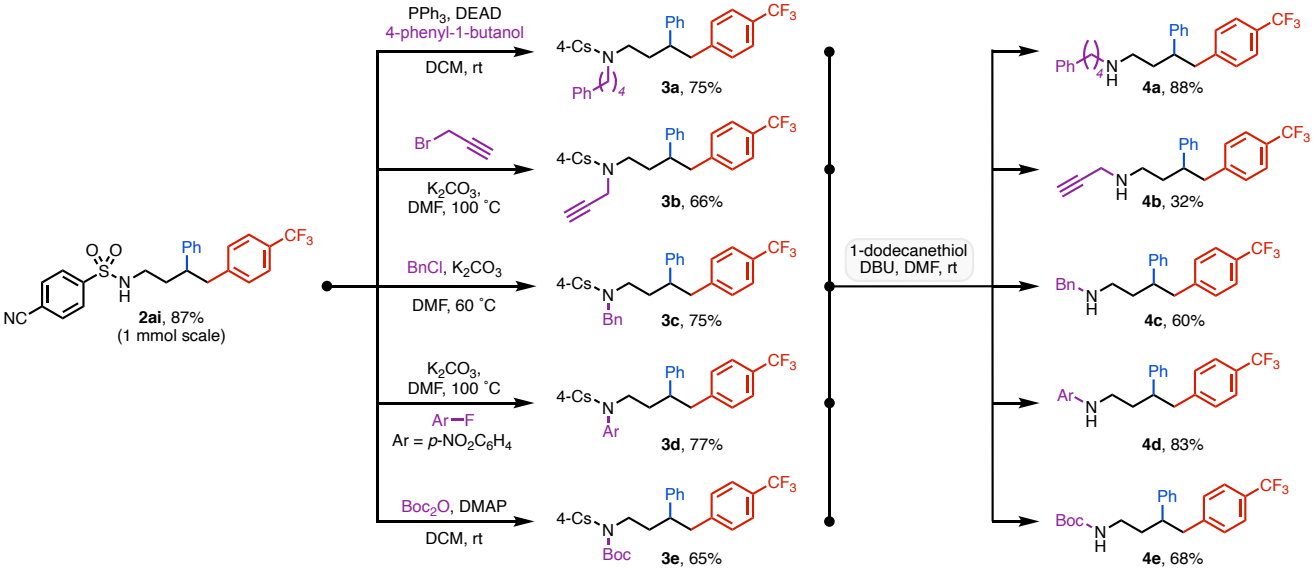
Next, we varied the aryl sulfonyl group by substitution of the trifluoromethyl moiety at the *para*-position and observed good to excellent yields (**2x–z**). Mesyl (Ms) protected homoallyl amine **2aa** is a competent substrate under the reaction conditions. However, product was not detected in the case of a nosyl protecting group, which we attribute to the potential inhibitory effect of nitro groups on Ni catalyst activity.[8] We then examined alkene substrates that are typically challenging in 1,2-diarylation. Pleasingly, (*Z*)- and (*E*)-internal alkenes were well tolerated under the optimized reaction conditions. Diarylated product from a (*Z*)-alkene was obtained in good yield and as a single diastereomer, as confirmed by single-crystal X-ray diffraction (**±-2ab**). The (*E*)-alkene was diarylated in the same fashion, but in a higher yield (**±-2ac**). In addition, a 1,1-disubstituted terminal alkene was found to work moderately well under the reaction conditions (**2ad**). With substitution at the α-position, no conversion was observed.

In a series of control experiments, both homoallyl aryl sulfonate **1o** and *N*-methylated sulfonamide **1p** were subjected to the optimized conditions, which resulted in no product formation (Scheme 2A). This indicates that the N–H moiety is important in the transformation. While we were successful in developing a remote alkene 1,2-diarylation reaction, we were



Scheme 2. (A) Control experiments to test sulfonamide and nitrogen importance. (B) Tether length effects on 1,2-diarylation. (C) Proposed catalytic cycle having directing group with X-type coordination upon migratory insertion.

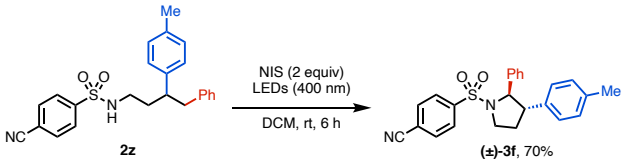
curious about the effect of alkene distance on reactivity (Scheme 2B). When aryl sulfonyl protected allyl amine was subjected to the reaction conditions, diarylated product was obtained in a lower yield and as a 7:1 mixture of regioisomers (**2af**). Reaction of aryl sulfonyl protected pentenyl amine



Scheme 3. Diversification of 1,2-diarylated products as a linchpin technology. Percentages represent isolated yields.

unexpectedly gave the diarylated product in a good yield with excellent regioselectivity (**2ag**). Extension of the alkenyl chain to aryl sulfonyl protected hexenyl amine gave no product. We hypothesize that these alkenyl amine substrates go through 4–6-membered nickelacycles, where a 7-membered nickelacycle is unfavorable.

Although this reaction may proceed via a N–Ni coordination mode,[9] the general catalytic cycle likely follows a similar mechanism as that of alkenyl amide and carboxylate diarylation (Scheme 2C).[3a,4i] The proposed catalytic cycle starts with nickel undergoing oxidative addition into the aryl–iodide bond, followed by alkene coordination of the protected alkenyl amine. Migratory insertion proceeds with the formation of an Ni^{II}(alkyl)(sulfonamido) metallacycle. Subsequent transmetalation affords an Ni^{II}(alkyl)(aryl) species which would finally undergo reductive elimination to give the 1,2-diarylated product. It should be noted that this catalytic cycle may also operate with the sulfonamide directing group as an L-type ligand upon migratory insertion and this pathway cannot be ruled out at this time.



2z **(±)-3f**, 70%

Scheme 4. HLF cyclization of a representative product.

We next envisioned that this method could have synthetic applicability as a linchpin technology where the diarylated products could engage in *N*-functionalization followed by deprotection to form highly functionalized secondary amines that would otherwise be difficult to construct. The 4-cyano-phenyl sulfonyl (4-Cs) protecting group was utilized in scale-up and diversification efforts due to its precedented ease of removal by use of 1-dodecanethiol.[5] With this in mind, we then synthesized diarylated product **2ai** in 87% yield (1 mmol, 0.40 g isolated) (Scheme 3). This product was then subjected to Mitsunobu coupling, propargylation, benzylation, S_NAr, and Boc protection reactions, which proceeded in moderate to good yields providing a diverse set of *N*-functionalized products (**3a–e**). Subsequent treatment with 1-dodecanethiol and DBU led to the removal of the aryl sulfonyl protecting group affording dialkyl, alkyl propargyl, alkyl benzyl, alkyl aryl, and alkyl Boc-protected amines in low to excellent yields (**4a–e**). Lastly, a violet-light-initiated Hofmann–Löffler–Freytag (HLF) cyclization of a representative product, **2z**, furnished 4-Cs-protected pyrrolidine (**±)-3f** in good yield, with the two aryl groups in a *trans* configuration (Scheme 4).[10]

In summary, a Ni-catalyzed 1,2-diarylation of aryl sulfonyl protected alkenyl amines with aryl iodides and aryl boronic esters was developed. This method tolerates electronically varied aryl coupling partners. Electronics on the aryl sulfonyl protecting group is indiscriminate of its directing capabilities with the exception of nosyl substitution. Internal and 1,1-disubstituted alkenes are competent substrates, affording the desired products in moderate to high yields with excellent regio- and diastereoselectivity. Control experiments showed that the free sulfonamide N–H is essential in the reaction. The alkenyl chain length was determined to tolerate dicarbofunctionalization with aryl sulfonyl protected allyl, butenyl, and pentenyl amines. Finally, this methodology may be implemented as a linchpin technology where aryl sulfonyl protected alkenyl amines could engage in 1,2-diarylation, then *N*-functionalization, and lastly deprotection to afford trifunctionalized secondary amines allowing leeway for facile complex amine synthesis.

Experimental Section

General Procedure: To a 1-dram (4 mL) vial equipped with a Teflon-coated magnetic stir bar were added the alkene substrate (0.1 mmol), the appropriate aryl boronic acid neopentylglycol ester (0.3 mmol), the appropriate aryl iodide electrophile (0.3 mmol), and dimethyl fumarate (15 mol%). The vial was then equipped with a septum cap, which was pierced by a 20-gauge needle and introduced into an argon-filled glovebox antechamber. Once transferred inside the glovebox, anhydrous NaOH (0.3 mmol), $Ni(cod)_2$ (20 mol%), and anhydrous sec-butanol (0.5 mL) were added. After stirring for 30 sec, the vial was sealed with a screw-top cap, removed from the glovebox, and left to stir at room temperature for 12 h. After this time, the reaction mixture was diluted with EtOAc (1 mL), poured into a test tube filled with satd. aq. $NaHCO_3$ (10 mL) rinsing with EtOAc (1 mL), and was extracted with EtOAc (3 × 1 mL). The organic layers were combined, and the solvent was removed *in vacuo* to leave a yellow residue, which afforded pure product after preparative thin-layer chromatography (PTLC).

Acknowledgements

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Keywords: alkene • diarylation • nickel • sulfonamide

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SUPPORTING INFORMATION

Table of Contents

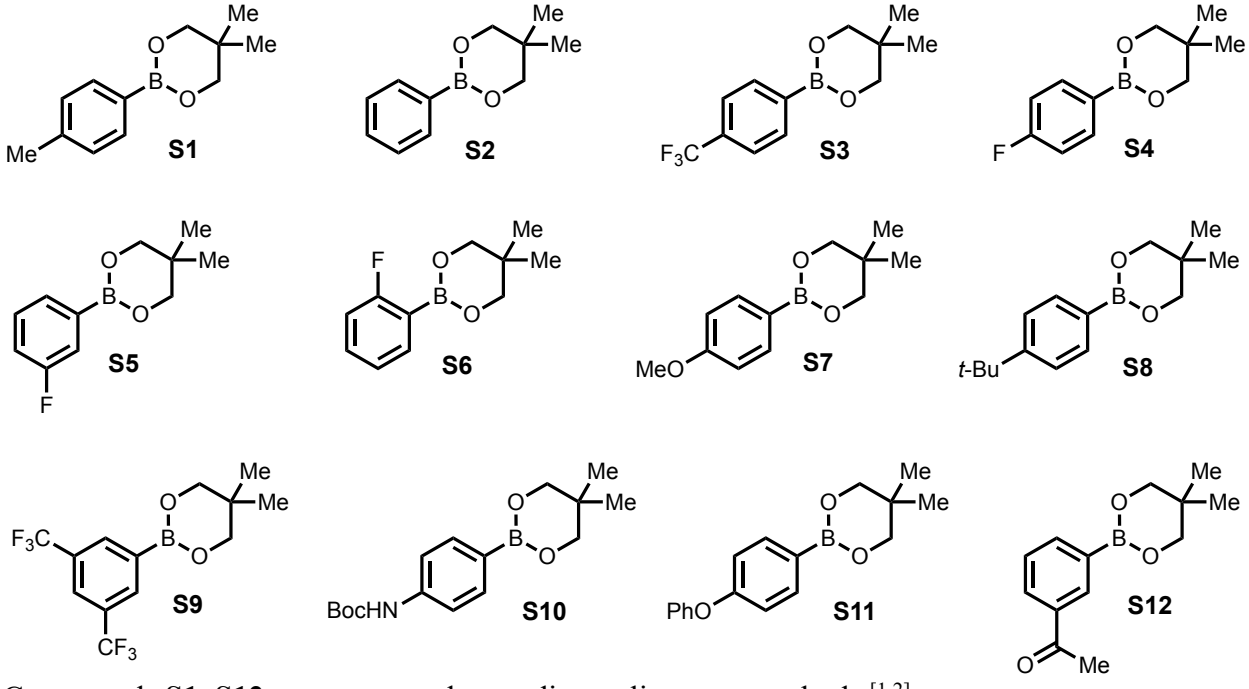
GENERAL INFORMATION

Unless otherwise noted, all materials were used as received from commercial sources without further purification. All aryl iodides, aryl boronic acids, and solvents were purchased from Aldrich, Alfa Aesar, Oakwood, and Combi-Blocks. $Ni(cod)_2$ was purchased from Strem. Loftek LED flood lights were used for photochemical experiments. Teflon-coated magnetic stir bars were soaked in concentrated nitric acid for at least 1 h, washed repeatedly with deionized water then acetone, and air-dried prior to use. In air- or moisture-sensitive reactions, anhydrous solvents from MilliporeSigma or from a Grubbs-type solvent purification system were used. ^{1}H and ^{13}C spectra were recorded with Bruker AV-400, DPX-500 and AV-600 instruments. Spectra were internally referenced to $SiMe_4$ or solvent signals. The following abbreviations (or combinations thereof) were used to explain multiplicities: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septet, and m = multiplet. Mass spectra for new compounds were recorded on an Agilent LC/MSD TOF (for high-resolution samples).

EXPERIMENTAL PROCEDURES

Aryl Boronic Acid Neopentylglycol Ester Synthesis

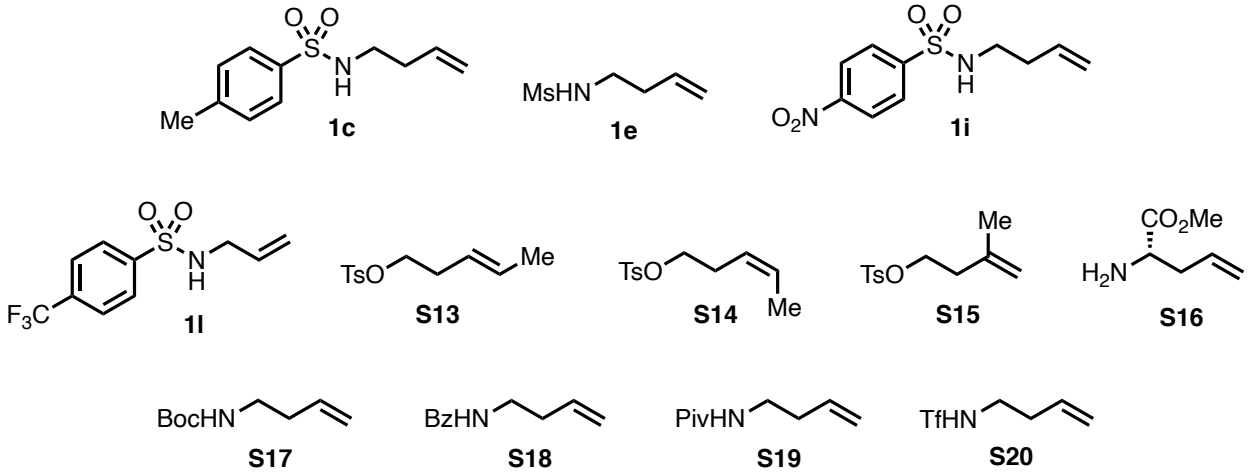
Table S1. Aryl boronic acid neopentylglycol esters (**S1–S12)**.



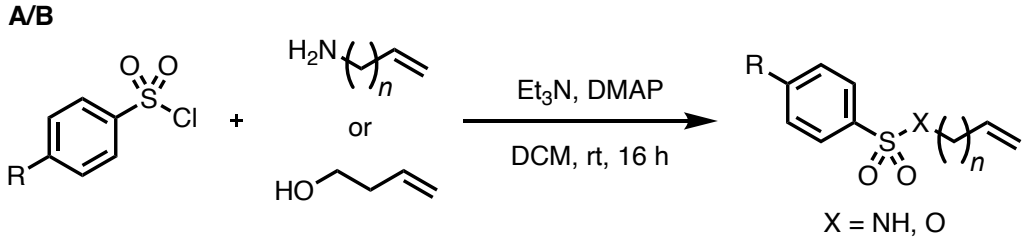
Compounds **S1–S12** were prepared according to literature methods.[1,2]

Alkenyl Sulfonamide and Miscellaneous Substrate Synthesis

Table S2. Starting materials used in this study: alkenyl sulfonamides **1c**, **1e**, **1i,** and **1l**; alkenyl sulfonates **S13–S15**; and alkenyl amine **S16**.



Compounds **1c**,[3] **1e,**[4] **1i**,[5] **1l**,[6] **S13–S15**,[7] **S16**,[8] **S17**,[9] **S18**,[10] **S19**,[11] and **S20**[12] were prepared according to literature methods.

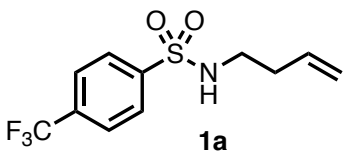


Scheme S1. Synthesis of alkenyl sulfonamides **1a**, **1b**, **1d**, **1k**, and **1o**. These compounds were synthesized using adapted versions of literature procedures describing the preparation of similar compounds.[3,5,6]

General Procedure A: To a 100-mL round-bottom flask equipped with a Teflon-coated magnetic stir bar were added the alkenyl amine (5.0 mmol) and dry DCM (25 mL). The flask was placed in an ice bath, and triethylamine (15.0 mmol) and DMAP (25 mol%) were subsequently added. The reaction mixture was allowed to stir for at least 5 min. Lastly, the appropriate sulfonyl chloride (5.5 mmol) was added, and the reaction mixture was allowed to warm to room temperature and continue stirring for 16 h. After this time, the reaction mixture was transferred to a separatory funnel, washed with 1M HCl (100 mL), and was extracted with DCM (3 × 20 mL). The combined organic layers were then washed with brine (100 mL), dried over Na_2SO_4, and concentrated *in vacuo* to leave a white solid, which afforded pure product after silica gel column chromatography.

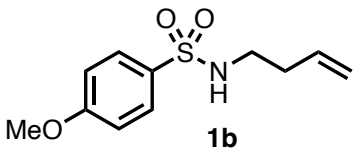
General Procedure B (for small-scale synthesis): To a 10-mL scintillation vial equipped with a Teflon-coated magnetic stir bar were added the alkenyl amine (1.0 mmol) and dry DCM (5 mL). The flask was placed in an ice bath, and triethylamine (3.0 mmol) and DMAP (25 mol%) were subsequently added. The reaction mixture was allowed to stir for at least 5 min. Lastly, the

appropriate sulfonyl chloride (1.1 mmol) was added, and the reaction mixture was allowed to warm to room temperature and continue stirring for 16 h. After this time, the reaction mixture was transferred to a separatory funnel, washed with 1M HCl (5 mL), and extracted with DCM (3 × 1 mL). The combined organic layers were then washed with brine (5 mL), dried over Na_2SO_4, and concentrated *in vacuo* to leave a white solid, which afforded pure product after silica gel column chromatography.



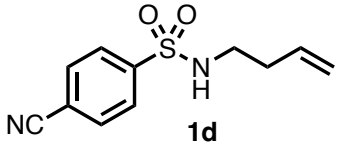
1a

***N*-(but-3-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (1a):** The title compound was prepared from but-3-en-1-amine (356 mg, 5.0 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (1.35 g, 5.5 mmol), according to General Procedure A. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a white solid (995 mg, 71% yield). Characterization data match those reported in the literature.[13]



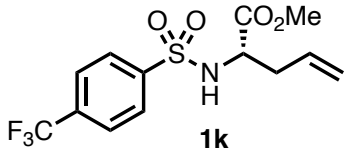
1b

N-(but-3-en-1-yl)-4-methoxybenzenesulfonamide (1b): The title compound was prepared from but-3-en-1-amine (71.1 mg, 1.0 mmol) and 4-methoxybenzenesulfonyl chloride (227 mg, 1.1 mmol), according to General Procedure B. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a colorless oil (190 g, 79% yield). Characterization data match those reported in the literature.[14]



1d

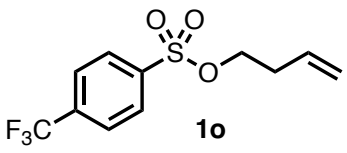
***N*-(but-3-en-1-yl)-4-cyanobenzenesulfonamide (1d):** The title compound was prepared from but-3-en-1-amine (356 mg, 5.0 mmol) and 4-cyanobenzenesulfonyl chloride (1.10 g, 5.5 mmol), according to General Procedure A. Purification using silica gel column chromatography (30% EtOAc in Hexanes) gave the product as a white solid (695 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 2H), 5.62 (ddt, *J* = 17.1, 10.3, 6.9 Hz, 1H), 5.14–5.03 (m, 2H), 4.52 (t, *J* = 6.1 Hz, 1H), 3.09 (q, *J* = 6.4 Hz, 2H), 2.24 (qt, *J* = 6.6, 1.3 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.42, 133.70, 133.00, 127.70, 118.64, 117.32, 116.42, 42.20, 33.70; **HRMS** (ESI-TOF) Calc'd for $C_{11}H_{12}N_2O_2S^+$ [M+H] 237.0698, found 237.0697.



1k

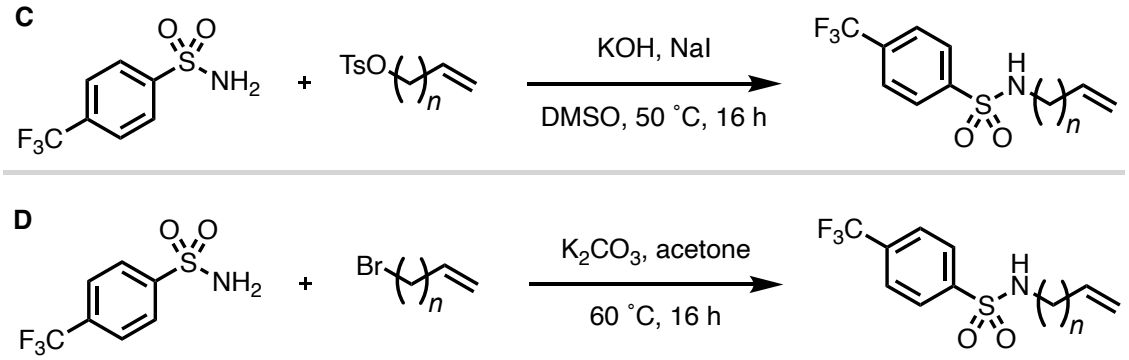
Methyl (*S*)-2-((4-(trifluoromethyl)phenyl)sulfonamido)pent-4-enoate (1k): The title compound was prepared from methyl 2-aminopent-4-enoate (129 mg, 1.0 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (269 mg, 1.1 mmol), according to general procedure B. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a white solid (250 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 5.61 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.21 (d, *J* = 9.0 Hz, 1H), 5.17–5.07 (m, 2H), 4.08 (dt, *J* = 9.0, 5.8 Hz, 1H), 3.54 (s, 3H), 2.53–2.47 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.05, 143.47 (q, *J* = 1.4 Hz), 134.58 (q, *J* = 32.9 Hz), 130.90, 127.77, 126.20 (q, *J* = 3.9 Hz), 123.18 (q, *J* = 273.0 Hz),

120.23, 55.29, 52.59, 37.54; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.40; **HRMS** (ESI-TOF) Calc'd for $C_{13}H_{14}F_3NO_4S^+$ [M+H] 338.0674, found 338.0674.



1o

But-3-en-1-yl 4-(trifluoromethyl)benzenesulfonate (1o): The title compound was prepared from but-3-en-1-ol (71.2 mg, 1.0 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (269 mg, 1.1 mmol), according to General Procedure B. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a yellow oil (48 mg, 17% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 2H), 7.85–7.81 (m, 2H), 5.67 (ddt, J = 16.4, 10.6, 6.7 Hz, 1H), 5.14–5.06 (m, 2H), 4.15 (t, J = 6.7 Hz, 2H), 2.44 (qt, J = 6.7, 1.3 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.81 (q, J = 1.7 Hz), 135.40 (q, J = 33.2 Hz), 132.04, 128.45, 126.42 (q, J = 3.8 Hz), 123.07 (q, J = 272.8 Hz), 118.57, 70.28, 33.13; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.52; **HRMS** (ESI-TOF) Calc'd for $C_{11}H_{11}F_3O_3S^+$ [M+H] 281.0459, found 281.0452.

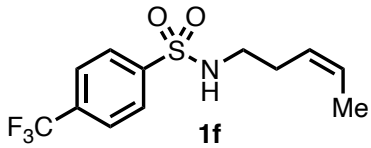


Scheme S2. Synthesis of alkenyl sulfonamides **1f–h**, **1k**, **1m**, and **1n**. These compounds were synthesized using adapted versions of literature procedures describing the preparation of similar compounds.[7-8]

General Procedure C: To a 4-mL dram vial equipped with a Teflon-coated magnetic stir bar were added 4-(trifluoromethyl)benzenesulfonamide (2.3 mmol), finely ground KOH powder (1.3 mmol), and DMSO (1.25 mL). The vial was placed on a heating block and allowed to stir at 50 °C for 2 h. After this time, the vial was cooled to room temperature, and a solution of the appropriate alkenyl tosylate (1.0 mmol) dissolved in DMSO (0.15 mL) was added dropwise, followed by addition of NaI (0.3 mmol) in a single portion. The reaction was allowed to continue at 50 °C for 16 h. After this time, water (10 mL) was added to the vial, and the reaction mixture was extracted with DCM (3 × 1 mL). The combined organic layers were then washed with 10% aqueous solution of NaOH (10 mL) and brine (10 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to leave a white solid, which afforded pure product after silica gel column chromatography.

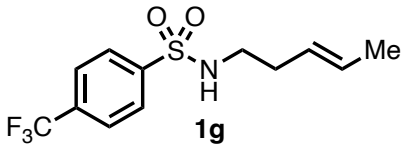
General Procedure D: To a 35-mL bomb flask equipped with a Teflon-coated magnetic stir bar were added 4-(trifluoromethyl)benzenesulfonamide (1 equiv), the appropriate alkenyl bromide (1.1 equiv), K_2CO_3 (2 equiv), and acetone (0.1 M). The flask was placed in an oil bath, and the reaction mixture was allowed to stir at 60 °C for 16 h. After this time, the reaction mixture was

allowed to cool to room temperature and was then filtered over Celite, which was subsequently washed with EtOAc. The filtrate was concentrated *in vacuo* to leave a white solid, which afforded pure product after silica gel column chromatography.



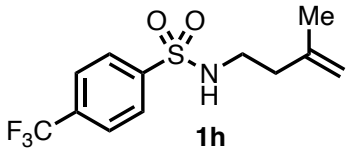
1f

(*Z*)-*N*-(pent-3-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (1f): The title compound was prepared from (*Z*)-pent-3-en-1-yl 4-methylbenzenesulfonate (240 mg, 1.0 mmol) and 4-(trifluoromethyl)benzenesulfonamide (518 mg, 2.3 mmol), according to General Procedure C. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a white solid (50 mg, 17% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 5.66–5.55 (m, 1H), 5.21 (dtd, *J* = 10.9, 7.4, 1.9 Hz, 1H), 4.46 (t, *J* = 6.0 Hz, 1H), 3.04 (q, *J* = 6.5 Hz, 2H), 2.25 (q, *J* = 7.0 Hz, 2H), 1.60–1.56 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.67, 134.37 (q, *J* = 33.1 Hz), 128.10, 127.59, 126.30 (q, *J* = 3.8 Hz), 125.22, 123.27 (q, *J* = 272.4 Hz), 42.77, 27.07, 12.90; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.36; **HRMS** (ESI-TOF) Calc'd for $C_{12}H_{14}F_3NO_2S^+$ [M+H] 294.0776, found 294.0776.



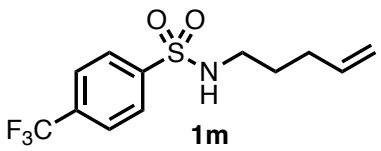
1g

(*E*)-*N*-(pent-3-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (1g): The title compound was prepared from (*E*)-pent-3-en-1-yl 4-methylbenzenesulfonate (240 mg, 1.0 mmol) and 4-(trifluoromethyl)benzenesulfonamide (518 mg, 2.3 mmol), according to General Procedure C. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a white solid (100 mg, 34% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 5.53–5.42 (m, 1H), 5.25–5.15 (m, 1H), 4.47 (t, *J* = 6.3 Hz, 1H), 3.03 (q, *J* = 6.4 Hz, 2H), 2.15 (q, *J* = 6.7 Hz, 2H), 1.63 (dt, *J* = 6.5, 1.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.67 (q, *J* = 1.7 Hz), 134.29 (q, *J* = 33.1 Hz), 129.16, 127.60, 126.29, 126.25 (q, *J* = 3.9, 3.3 Hz), 123.25 (q, *J* = 273.5, 272.9 Hz), 42.76, 32.51, 17.87; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.35; **HRMS** (ESI-TOF) Calc'd for $C_{12}H_{14}F_3NO_2S^+$ [M+H] 294.0776, found 294.0780.



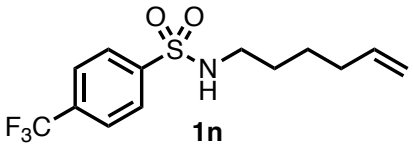
1h

***N*-(3-methylbut-3-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (1h):** The title compound was prepared from 3-methylbut-3-en-1-yl 4-methylbenzenesulfonate (937.2 mg, 3.9 mmol) and 4-(trifluoromethyl)benzenesulfonamide (743.1 mg, 3.3 mmol), according to General Procedure C. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as an off-white solid (194 mg, 22% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 4.82 (t, *J* = 1.6 Hz, 1H), 4.67 (dd, *J* = 1.9, 1.0 Hz, 1H), 4.63 (t, *J* = 5.8 Hz, 1H), 3.12 (td, *J* = 6.7, 5.8 Hz, 2H), 2.18 (td, *J* = 6.7, 1.2 Hz, 2H), 1.62 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.74, 141.29, 134.54 (q, *J* = 33.0 Hz), 127.73, 126.43 (q, *J* = 3.7 Hz), 123.36 (q, *J* = 272.6 Hz), 113.65, 40.69, 37.41, 21.82; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.41; **HRMS** (ESI-TOF) Calc'd for $C_{12}H_{14}F_3NO_2S^+$ [M+H] 294.0776, found 294.0764.



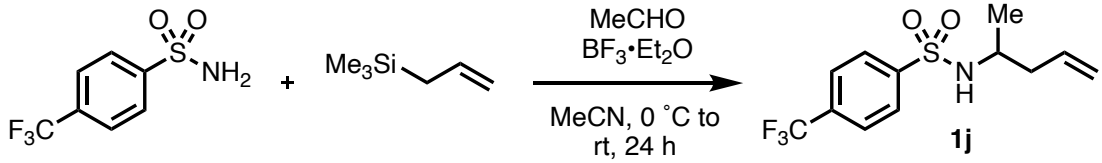
1m

***N*-(pent-4-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (1m):** The title compound was prepared from 4-(trifluoromethyl)benzenesulfonamide (1.13 g, 5.0 mmol), 5-bromopent-1-ene (820 mg, 5.5 mmol), K_2CO_3 (10 mmol) and acetone (5 mL) according to General Procedure D. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a white solid (584.5 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 5.77–5.65 (m, 1H), 5.02–4.94 (m, 2H), 4.44 (t, *J* = 6.4 Hz 1H), 3.06–2.98 (m, 2H), 2.07 (q, *J* = 7.1 Hz, 2H), 1.60 (p, *J* = 7.2 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.66 (q, *J* = 1.4 Hz), 136.96, 134.39 (q, *J* = 33.1 Hz), 127.56, 126.32 (q, *J* = 3.6 Hz), 124.14 (q, *J* = 272.8 Hz), 115.83, 42.72, 30.56, 28.71; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.37; **HRMS** (ESI-TOF) Calc'd for $C_{12}H_{14}F_3NO_2S^+$ [M+H] 294.0776, found 294.0776.



1n

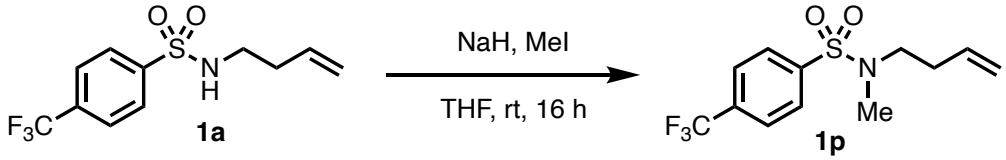
***N*-(hex-5-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (1n):** The title compound was prepared from 4-(trifluoromethyl)benzenesulfonamide (349 mg, 1.55 mmol), 6-bromohex-1-ene (277 mg, 1.7 mmol), K_2CO_3 (3.1 mmol) and acetone (1.7 mL) according to General Procedure D. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a white solid (95 mg, 20% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 5.71 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.00–4.91 (m, 2H), 4.40 (t, *J* = 6.1 Hz, 1H), 3.05–2.97 (m, 2H), 2.01 (q, *J* = 7.1 Hz, 2H), 1.53–1.45 (m, 2H), 1.42–1.32 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.65 (q, *J* = 1.5 Hz), 137.93, 134.34 (q, *J* = 33.1 Hz), 127.57, 126.30 (q, *J* = 3.5 Hz), 123.24 (q, *J* = 272.8 Hz), 115.00, 43.15, 32.99, 28.95, 25.61; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.39; **HRMS** (ESI-TOF) Calc'd for $C_{13}H_{16}F_3NO_2S^+$ [M+H]
308.0932, found 308.0932.



Scheme S3. Synthesis of α-methyl alkenyl sulfonamide **1j**. This compound was synthesized using an adapted version of a literature procedure describing the preparation of a similar compound.[15]

***N*-(pent-4-en-2-yl)-4-(trifluoromethyl)benzenesulfonamide (1j):** To a 4-mL dram vial equipped with a Teflon-coated magnetic stir bar were added acetaldehyde (0.28 mL, 5.0 mmol, 1 equiv), allyltrimethylsilane (0.95 mL, 6.0 mmol, 1.2 equiv), 4-(trifluoromethyl)benzenesulfonamide (1.13 g, 5.0 mmol, 1 equiv), and MeCN (8 mL). The reaction mixture was then cooled to 0 °C, and BF_3•Et_2O (0.62 mL, 5.0 mmol, 1 equiv) was added in one portion. The mixture was stirred for 30 min at 0 °C, then allowed to warm to room temperature and left stirring overnight. After this time, water (100 mL) was added to the vial, and the reaction mixture was extracted with DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 . The combined organic layers were dried over Na_2SO_4, and the solvent was removed *in vacuo*. Purification using silica gel column

chromatography (20% EtOAc in Hexanes) gave the product as a colorless oil (529 mg, 36% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 5.56 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.10–4.99 (m, 2H), 4.64 (d, *J* = 7.7 Hz, 1H), 3.45 (dh, *J* = 7.8, 6.5 Hz, 1H), 2.15 (ddt, *J* = 7.3, 6.2, 1.2 Hz, 2H), 1.11 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.85, 134.42 (q, *J* = 33.0 Hz), 133.13, 127.69, 126.35 (q, *J* = 3.7 Hz), 123.38 (q, *J* = 272.9 Hz), 119.29, 49.73, 41.53, 21.47; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.37; **HRMS** (ESI-TOF) Calc'd for $C_{12}H_{14}F_3NO_2S^+$ [M+H] 294.0776, found 294.0771.

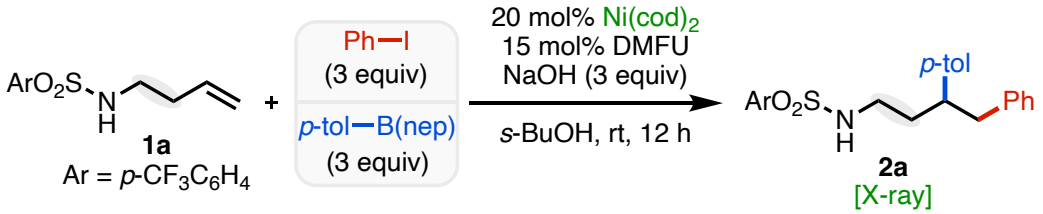


Scheme S4. Synthesis of *N*-methyl alkenyl sulfonamide **1p**. This compound was synthesized using an adapted version of a literature procedure describing the preparation of a similar compound.[16]

***N*-(but-3-en-1-yl)-*N*-methyl-4-(trifluoromethyl)benzenesulfonamide (1p):** To a 1-dram (4 mL) vial equipped with a Teflon-coated magnetic stir bar were added NaH (60% in mineral oil, 12 mg, 0.30 mmol, 0.6 equiv) and THF (1 mL). The vial was submerged in an ice bath, and a solution of the alkenyl sulfonamide **1a** (0.50 mmol, 1 equiv) in THF (2 mL) was subsequently added. The mixture was allowed to stir for at least 10 min, and then MeI (92 mg, 0.65 mmol, 1.3 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 16 h. After this time, the reaction mixture was diluted with sat. aq. NH_4Cl (10 mL) and extracted with EtOAc (3 × 1 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed *in vacuo*. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a colorless oil (75 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 5.75 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.14–5.03 (m, 2H), 3.17–3.09 (m, 2H), 2.79 (s, 3H), 2.32 (tdd, *J* = 8.2, 6.2, 1.4 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.56 (q, *J* = 1.5 Hz), 134.24 (q, *J* = 33.2 Hz), 133.91, 126.24 (q, *J* = 3.8 Hz), 123.27 (q, *J* = 272.7 Hz), 117.46, 49.63, 34.73, 32.29; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.33; **HRMS** (ESI-TOF) Calc'd for $C_{12}H_{14}F_3NO_2S^+$ [M+H] 294.0776, found 294.0779.

Catalyst Loading Experiments for Nickel-Catalyzed 1,2-Diarylation of Alkenes

Table S3. Effect of catalyst loading on product yield. [a]



entry	deviation from standard conditions	%Yield **2a**[b]
1	none	90 (82)[c]
2	10 mol% $Ni(cod)_2$	90
3	5 mol% $Ni(cod)_2$	50
4	2.5 mol% $Ni(cod)_2$	22

[a] Reaction conditions: **1a** (0.1 mmol), *s*-BuOH (0.2 M). [b] Percentages represent ^{1}H NMR yields using CH_2Br_2 as the internal standard. [c] Values in parentheses are isolated yields.

General Procedure for Nickel-Catalyzed 1,2-Diarylation of Alkenes

General Procedure E: To a 1-dram (4 mL) vial equipped with a Teflon-coated magnetic stir bar were added the alkene substrate (0.1 mmol), the appropriate aryl boronic acid neopentylglycol ester (0.3 mmol), the appropriate aryl iodide electrophile (0.3 mmol), and dimethyl fumarate (15 mol%). The vial was then equipped with a septum cap, which was pierced by a 20-gauge needle and introduced into an argon-filled glovebox antechamber. Once transferred inside the glovebox, anhydrous NaOH (0.3 mmol), $Ni(cod)_2$ (20 mol%), and anhydrous sec-butanol (0.5 mL) were added. After stirring for 30 sec, the vial was sealed with a screw-top cap, removed from the glovebox, and left to stir at room temperature for 12 h. After this time, the reaction mixture was diluted with EtOAc (1 mL), poured into test tube filled with sat. aq. $NaHCO_3$ (10 mL), rinsed with EtOAc (1 mL), and extracted with EtOAc (3 × 1 mL). The organic layers were combined, and the solvent was removed *in vacuo* to leave a yellow residue, which afforded pure product after preparative thin-layer chromatography (PTLC).

General Procedure F (for large-scale synthesis of 2b and 2ae): To a 20-mL scintillation vial equipped with a Teflon-coated magnetic stir bar were added **1a** or **1d** (1.0 mmol), phenylboronic acid neopentyl glycol ester **S1** (3.0 mmol), 1-iodo-4-(trifluoromethyl)benzene (3.0 mmol), and dimethyl fumarate (15 mol%) according to General Procedure E. The vial was then introduced into an argon-filled glovebox antechamber. Once transferred inside the glovebox, anhydrous NaOH (3.0 mmol), $Ni(cod)_2$ (20 mol%), and anhydrous sec-butanol (5 mL) were added. After stirring for 30 sec, the vial was removed from the glovebox and left to stir at room temperature for 12–40 h. After this time, the reaction mixture was diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were combined, and the solvent was removed *in vacuo* to leave a yellow or orange residue, which afforded pure product after silica gel column chromatography.

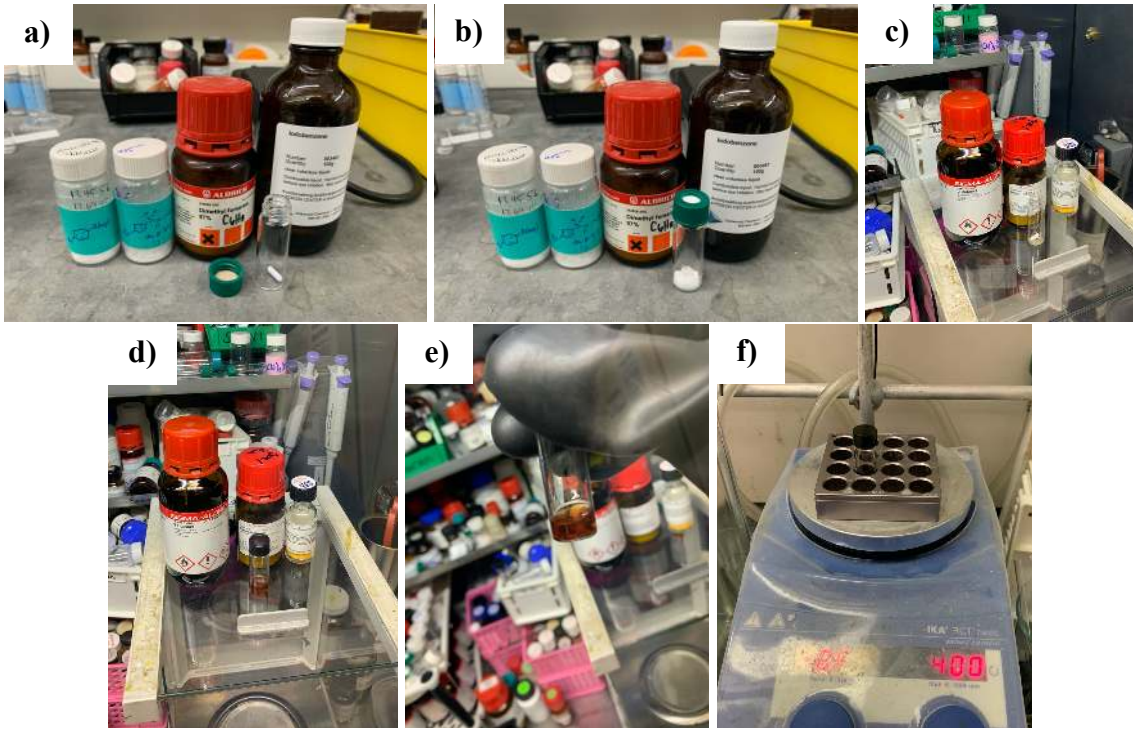
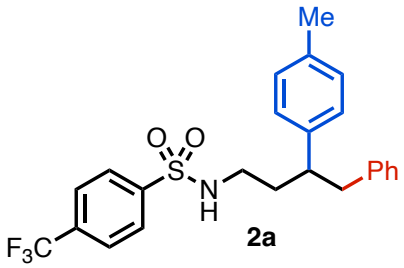
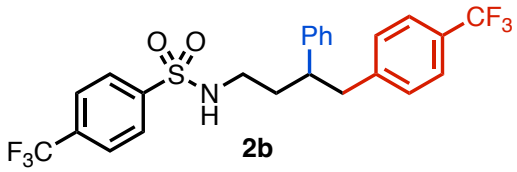


Figure S1: Photographic depiction of reaction setup following general procedure. a) Standard reagents used outside glovebox. b) Addition of reagents outside of the glovebox. c) Reagents used inside glovebox and addition of NaOH and $Ni(cod)_2$. d) Addition of solvent inside of the glovebox and after stirring for 30 sec. e) Closer view of typical color of reaction mixture after 30 sec of stirring in the glovebox. f) Stirring at room temperature outside of glovebox.

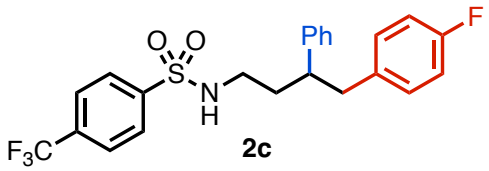


***N*-(4-phenyl-3-(*p*-tolyl)butyl)-4-(trifluoromethyl)benzenesulfonamide (2a):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (36.6 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.21–7.11 (m, 3H), 7.03 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 6.4 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 4.48 (t, J = 6.0 Hz, 1H), 2.89–2.69 (m, 5H), 2.30 (s, 3H), 1.82 (dtd, J = 13.5, 7.6, 3.7 Hz, 1H), 1.71 (dddd, J = 13.5, 10.0, 7.4, 5.5 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.45 (q, J = 1.5 Hz), 140.11, 139.86, 136.26, 134.22 (q, J = 33.1 Hz), 129.35, 129.07, 128.24, 127.51, 127.31, 126.18 (q, J = 3.6 Hz), 126.11, 123.26 (q, J = 272.5 Hz), 44.80, 43.75, 41.63, 34.93, 21.00; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{24}F_3NO_2S^+$ [M+H] 448.1558, found 448.1562; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.30; **X-ray** (single-crystal) Colorless block crystals of X-ray diffraction quality were obtained by vapor diffusion of pentane to a saturated solution of **2a** in benzene (CCDC 2011491).[17]



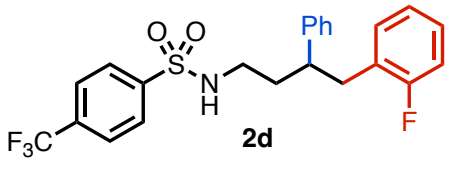
2b

***N*-(3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)-4-(trifluoromethyl)benzenesulfonamide (2b):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-iodo-4-(trifluoromethyl)benzene (82 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a yellow oil (49.4 mg, 99% yield). Additionally, the title compound was also prepared on larger scale from **1a** (279 mg, 1 mmol), phenylboronic acid neopentyl glycol ester **S1** (570 mg, 3 mmol) and 1-iodo-4-(trifluoromethyl)benzene (816 mg, 3 mmol) according to General Procedure F. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a yellow solid (479 mg, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.20 (pt, *J* = 7.4, 1.8 Hz, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.98 (dd, *J* = 7.9, 1.6 Hz, 2H), 4.69 (t, *J* = 6.0 Hz, 1H), 2.91–2.72 (m, 5H), 1.94–1.75 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.76 (q, *J* = 1.4 Hz), 143.32 (q, *J* = 1.4 Hz), 142.31, 134.36 (q, *J* = 33.0 Hz), 129.33, 128.78, 128.45 (q, *J* = 31.5 Hz), 127.49 (d, *J* = 2.2 Hz), 127.00, 126.25 (q, *J* = 3.6 Hz), 125.15 (q, *J* = 271.8 Hz), 125.11 (q, *J* = 3.6 Hz), 124.11 (q, *J* = 273.2 Hz), 115.47, 44.97, 43.35, 41.45, 35.30; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.59, -63.38; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{21}F_6NO_2S^+$ [M+H] 502.1275, found 502.1272.



2c

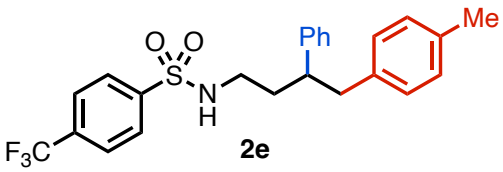
***N*-(4-(4-fluorophenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2c):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-fluoro-4-iodobenzene (67 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (39.6 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.25–7.15 (m, 3H), 7.00–6.95 (m, 2H), 6.91–6.81 (m, 4H), 4.61 (t, *J* = 6.1 Hz, 1H), 2.88–2.71 (m, 5H), 1.92–1.71 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.17, 160.55, 143.37 (q, *J* = 1.4 Hz), 142.75, 135.30 (d, *J* = 3.3 Hz), 134.30 (q, *J* = 33.2 Hz), 130.40 (d, *J* = 7.8 Hz), 128.68, 127.51 (d, *J* = 2.2 Hz), 126.83, 126.24 (q, *J* = 3.7 Hz), 123.23 (q, *J* = 272.8 Hz), 114.96 (d, *J* = 21.1 Hz), 45.34, 42.79, 41.53, 35.10; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.34, -117.31; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{21}F_4NO_2S^+$ [M+H] 452.1307, found 452.1315.



2d

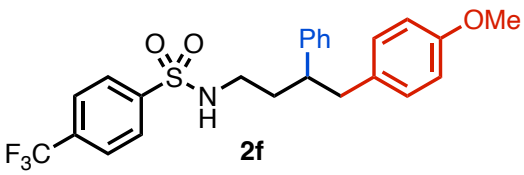
***N*-(4-(2-fluorophenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2d):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-fluoro-2-iodobenzene (67 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (41.1 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.24–7.08 (m, 4H), 7.04–6.98 (m, 2H), 6.91 (dddd, *J* = 15.8, 11.2, 7.8, 1.6 Hz, 3H), 4.60 (s, 1H), 2.92–2.72 (m, 5H), 1.82 (dddd, *J* = 13.0, 7.8, 6.1, 1.9 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 161.94, 160.32, 143.44 (q, *J* = 1.4 Hz), 142.85, 134.25 (q, *J* = 33.0 Hz), 131.38 (d, *J* = 5.0 Hz), 128.67, 127.98 (d, *J* = 8.2 Hz), 127.45 (d, *J* = 15.5 Hz), 126.85, 126.54 (d, *J* = 15.5 Hz), 126.22 (q, *J* = 3.9 Hz), 123.80 (d, *J* = 3.7 Hz), 123.25 (q, *J* = 273.0 Hz), 115.18

(d, J = 22.2 Hz), 43.96, 41.57, 36.68 (d, J = 1.6 Hz), 34.87; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.31, -118.44; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{21}F_4NO_2S^+$ [M+H] 452.1307, found 452.1310.



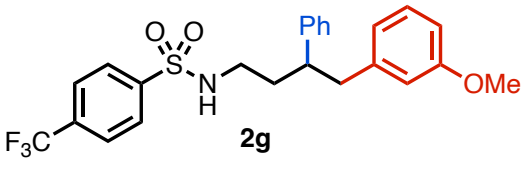
2e

***N*-(3-phenyl-4-(*p*-tolyl)butyl)-4-(trifluoromethyl)benzenesulfonamide (2e):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-iodo-4-methylbenzene (65 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (31 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.26–7.16 (m, 3H), 7.03–6.96 (m, 4H), 6.86 (d, J = 8.0 Hz, 2H), 4.50 (t, J = 5.6 Hz, 1H), 2.87–2.68 (m, 5H), 2.27 (s, 3H), 1.84 (dtd, J = 13.8, 7.7, 3.7 Hz, 1H), 1.73 (dddd, J = 13.5, 9.9, 7.5, 5.5 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.43 (q, J = 1.4 Hz), 143.37, 136.60, 135.62, 134.12 (q, J = 32.5 Hz), 128.95, 128.94, 128.67, 127.51, 127.49, 126.72, 126.20 (q, J = 3.8 Hz), 123.26 (q, J = 272.9 Hz), 45.29, 43.22, 41.62, 34.90, 21.00; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.31; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{24}F_3NO_2S^+$ [M+H] 448.1558, found 448.1556.



2f

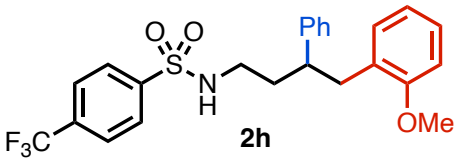
***N*-(4-(4-methoxyphenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2f):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-iodo-4-methoxybenzene (65 mg, 0.3 mmol) according to General Procedure E but with a reaction time of 16 h. Purification using PTLC (20% Acetone in Hexanes) gave the product as a colorless oil (35.8 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.24–7.14 (m, 3H), 7.02–6.97 (m, 2H), 6.90–6.85 (m, 2H), 6.75–6.69 (m, 2H), 4.60 (t, J = 6.0 Hz, 1H), 3.74 (s, 3H), 2.87–2.67 (m, 5H), 1.90–1.79 (m, 1H), 1.74 (dtd, J = 9.9, 8.4, 8.0, 5.9 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.94, 143.42 (q, J = 1.6 Hz), 143.31, 134.21 (q, J = 33.2 Hz), 131.78, 129.99, 128.63, 127.53, 127.51, 126.69, 126.21 (q, J = 3.6 Hz), 123.27 (q, J = 272.6 Hz), 113.62, 55.18, 45.40, 42.75, 41.61, 34.93; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.31; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{24}F_3NO_3S^+$ [M+H] 464.1507, found 464.1502.



2g

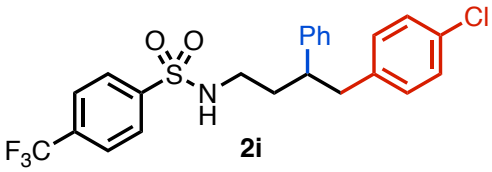
***N*-(4-(3-methoxyphenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2g):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-iodo-3-methoxybenzene (65 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (46 mg, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 7.9 Hz, 2H), 7.25 – 7.15 (m, 3H), 7.10 (t, J = 7.9 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.69 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.58 (dt, J = 7.5, 1.3 Hz, 1H), 6.50 (dd, J = 2.6, 1.6 Hz, 1H), 4.53 (t, J = 6.0 Hz, 1H), 3.70 (s, 3H), 2.88 – 2.70 (m, 5H), 1.86 (dtd, J = 13.9, 7.7, 3.7 Hz, 1H), 1.75 (dddd, J = 13.4, 9.9, 7.4, 5.5 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.45, 143.40

(q, J = 1.4 Hz), 143.22, 141.32, 134.23 (q, J = 33.0 Hz), 129.21, 128.68, 127.50, 126.77, 126.22 (q, J = 3.8 Hz), 123.26 (q, J = 272.5 Hz), 121.47, 114.78, 111.54, 55.09, 45.12, 43.68, 41.59, 34.97; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.31; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{24}F_3NO_3S^+$ [M+H] 464.1507, found 464.1516.



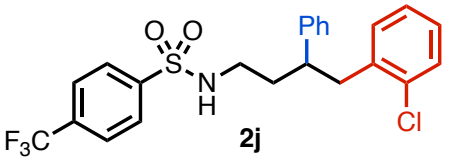
2h

***N*-(4-(2-methoxyphenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2h):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-iodo-3-methoxybenzene (65 mg, 0.3 mmol) according to General Procedure E but with a reaction time of 16 h. Purification using PTLC (20% Acetone in Hexanes) gave the product as a colorless oil (37.3 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.24–7.10 (m, 4H), 7.03–6.97 (m, 2H), 6.81 (ddd, J = 8.2, 2.9, 1.4 Hz, 2H), 6.74 (td, J = 7.3, 1.1 Hz, 1H), 4.62 (t, J = 6.1 Hz, 1H), 3.78 (s, 3H), 2.91–2.71 (m, 5H), 1.87–1.70 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.43, 143.92, 143.54 (q, J = 1.4 Hz), 134.17 (q, J = 32.4 Hz), 130.86, 128.49, 128.14, 127.50, 127.48, 127.46, 126.54, 126.20 (q, J = 3.9 Hz), 123.28 (q, J = 272.6 Hz), 110.32, 55.29, 43.42, 41.68, 37.65, 34.68; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.30; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{24}F_3NO_3S^+$ [M+H] 464.1507, found 464.1501.



2i

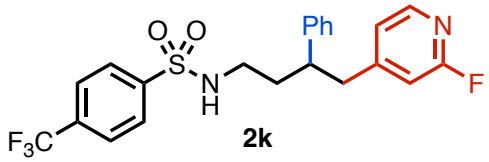
***N*-(4-(4-chlorophenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2i):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-chloro-4-iodobenzene (72 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (44.8 mg, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.24–7.15 (m, 3H), 7.14–7.10 (m, 2H), 7.00–6.94 (m, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.66 (s, 1H), 2.79 (p, J = 5.7, 5.1 Hz, 5H), 1.92–1.72 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.35, 142.60, 138.12, 134.32 (q, J = 33.0 Hz), 131.87, 130.38, 128.72, 128.31, 127.50, 126.89, 126.25 (q, J = 3.6 Hz), 123.23 (q, J = 273.3 Hz), 45.13, 42.93, 41.50, 35.17; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.32; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{21}ClF_3NO_2S^+$ [M+H] 468.1012, found 468.1015.



2j

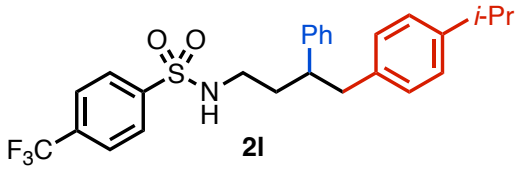
***N*-(4-(2-chlorophenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2j):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-chloro-2-iodobenzene (72 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (43.7 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.28 (dd, J = 7.9, 1.4 Hz, 1H), 7.25–7.16 (m, 3H), 7.08 (td, J = 7.7, 1.8 Hz, 1H), 7.01 (dtd, J = 7.5, 3.4, 2.6, 1.4 Hz, 3H), 6.85 (dd, J = 7.5, 1.8 Hz, 1H), 4.60 (d, J = 5.9 Hz, 1H), 3.01–2.74 (m, 5H), 1.84 (q, J = 7.1 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.45 (q, J = 1.4 Hz), 142.87, 137.28, 134.25 (q, J = 33.3 Hz), 134.05, 131.40, 129.51, 128.69, 127.72,

127.50, 127.42, 126.86, 126.49, 126.22 (q, J = 3.6 Hz), 123.25 (q, J = 273.3 Hz), 43.31, 41.62, 41.27, 34.78; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.30; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{21}ClF_3NO_2S^+$ [M+H] 468.1012, found 468.1009.



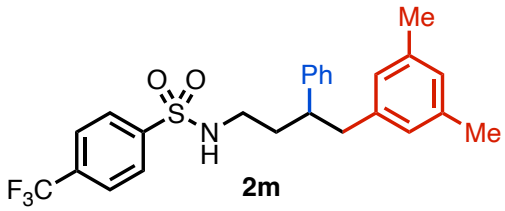
2k

***N*-(3-phenyl-4-(2-(fluoromethyl)pyridin-4-yl)butyl)-4-(trifluoromethyl)benzenesulfonamide (2k):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 4-iodo-2-(trifluoromethyl)pyridine (82 mg, 0.3 mmol) according to General Procedure E but with a reaction time of 16 h. Purification using PTLC (20% Acetone in Hexanes) gave the product as a white solid (33.3 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 5.2 Hz, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.75–7.69 (m, 2H), 7.26–7.17 (m, 3H), 6.99 (dd, J = 7.9, 1.6 Hz, 2H), 6.76 (dt, J = 5.2, 1.7 Hz, 1H), 6.50 (s, 1H), 4.97 (t, J = 6.1 Hz, 1H), 2.96–2.74 (m, 5H), 1.99–1.79 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.28, 164.60, 163.02, 154.83 (d, J = 8.0 Hz), 147.14 (d, J = 15.0 Hz), 143.34 (d, J = 1.1 Hz), 134.36 (q, J = 33.0 Hz), 128.89, 127.45 (d, J = 10.2 Hz), 127.26, 126.27 (q, J = 3.8 Hz), 123.19 (q, J = 273.0 Hz), 122.18 (d, J = 3.8 Hz), 109.76 (d, J = 36.5 Hz), 44.12, 42.55 (d, J = 2.8 Hz), 41.25, 35.60; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.36, -69.31; **HRMS** (ESI-TOF) Calc'd for $C_{22}H_{20}F_4N_2O_2S^+$ [M+H] 453.1260, found 453.1253.



2l

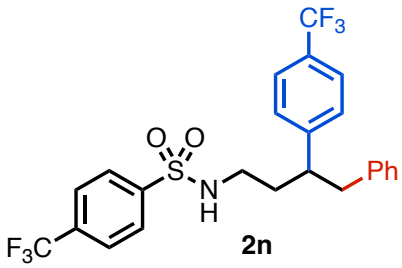
***N*-(4-(4-isopropylphenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2l):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-iodo-4-isopropylbenzene (72 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (35.2 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 9.0 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.26–7.16 (m, 3H), 7.09–7.00 (m, 4H), 6.92 (d, J = 8.1 Hz, 2H), 4.42 (t, J = 6.0 Hz, 1H), 2.89–2.68 (m, 6H), 1.85 (dtd, J = 13.7, 7.7, 3.9 Hz, 1H), 1.73 (dddd, J = 13.5, 9.9, 7.4, 5.6 Hz, 1H), 1.21 (dd, J = 6.9, 0.7 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.71, 143.50, 143.42, 137.01, 134.24 (q, J = 33.2 Hz), 128.97, 128.68, 127.52, 127.48, 126.73, 126.32, 126.21 (q, J = 3.6 Hz), 123.26 (q, J = 272.4 Hz), 45.22, 43.24, 41.63, 34.83, 33.66, 24.02; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.31; **HRMS** (ESI-TOF) Calc'd for $C_{26}H_{28}F_3NO_2S^+$ [M+H] 476.1871, found 476.1863.



2m

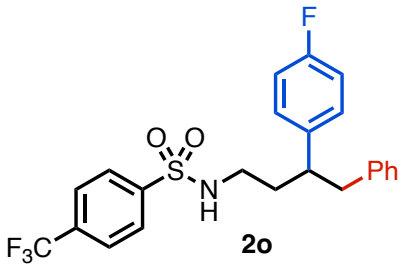
***N*-(4-(3,5-dimethylphenyl)-3-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2m):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), phenylboronic acid neopentyl glycol ester **S2** (57 mg, 0.3 mmol) and 1-iodo-3,5-dimethylbenzene (70 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (41.5 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.27–7.15 (m, 3H), 7.06–7.00 (m, 2H), 6.79 (s, 1H), 6.63 (s, 2H), 4.43 (t, J = 6.0 Hz, 1H), 2.85–2.72 (m, 4H), 2.67 (qd, J = 10.8, 10.2, 5.9 Hz, 1H), 2.23 (s, 6H), 1.83 (dtd, J = 13.9, 7.7, 3.8 Hz, 1H), 1.72 (dddd,

J = 13.5, 10.2, 7.4, 5.6 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.59, 143.39 (q, J = 1.4 Hz), 139.65, 137.72, 134.22 (q, J = 33.2 Hz), 128.67, 127.81, 127.51, 127.45, 126.96, 126.73, 126.18 (q, J = 3.6 Hz), 123.26 (q, J = 273.0 Hz), 45.20, 43.61, 41.66, 34.73, 21.23; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.31; **HRMS** (ESI-TOF) Calc'd for $C_{25}H_{26}F_3NO_2S^+$ [M+H] 462.1715, found 462.1713.



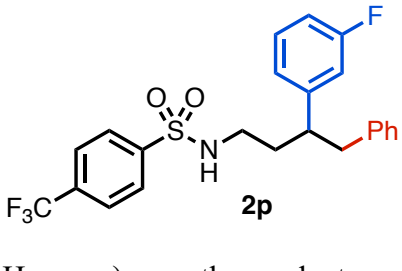
2n

***N*-(4-phenyl-3-(4-(trifluoromethyl)phenyl)butyl)-4-(trifluoromethyl)benzenesulfonamide (2n):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 4-(trifluoromethyl)phenylboronic acid neopentyl glycol ester **S3** (77 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (40.9 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dt, J = 8.1, 0.8 Hz, 2H), 7.71 (dt, J = 8.1, 0.7 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.23–7.11 (m, 5H), 6.98–6.93 (m, 2H), 4.54 (t, J = 6.0 Hz, 1H), 3.00–2.90 (m, 1H), 2.89–2.69 (m, 4H), 1.91 (dtd, J = 13.9, 7.8, 4.5 Hz, 1H), 1.81 (dddd, J = 14.0, 10.3, 7.5, 5.4 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.40 (d, J = 1.1 Hz), 143.28 (d, J = 1.2 Hz), 139.03, 134.43 (q, J = 33.1 Hz), 129.01, 129.00 (q, J = 32.1 Hz), 128.36, 127.93, 127.49, 126.37, 126.29 (q, J = 3.7 Hz), 125.53 (q, J = 3.8 Hz), 124.13 (q, J = 272.0 Hz), 123.19 (q, J = 272.9 Hz), 44.83, 43.34, 41.28, 34.99; **^{19}F NMR** (400 MHz, $CDCl_3$) δ -62.67, -63.40; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{21}F_6NO_2S^+$ [M+H] 502.1275, found 502.1269.



2o

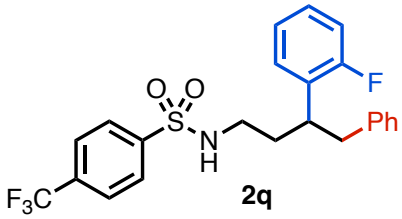
***N*-(3-(4-fluorophenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2o):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 4-fluorophenylboronic acid neopentyl glycol ester **S4** (62 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (40.4 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.20–7.11 (m, 3H), 6.98–6.87 (m, 6H), 4.65 (s, 1H), 2.89–2.69 (m, 5H), 1.86 (dtd, J = 14.1, 7.7, 4.0 Hz, 1H), 1.79–1.68 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.34, 160.72, 143.39 (q, J = 1.4 Hz), 139.43, 138.74 (d, J = 3.3 Hz), 134.34 (q, J = 33.1 Hz), 129.05, 128.91 (d, J = 7.8 Hz), 128.26, 127.50, 126.27 (q, J = 3.7 Hz), 126.21, 123.23 (q, J = 273.1 Hz), 115.41 (d, J = 21.1 Hz), 44.34, 43.76, 41.43, 35.21; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.33, -116.30; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{21}F_4NO_2S^+$ [M+H] 452.1307, found 452.1301.



2p

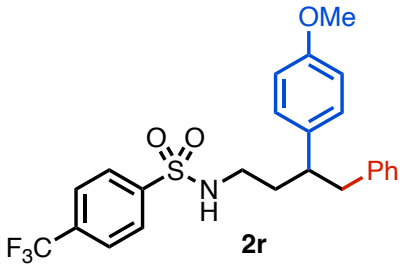
***N*-(3-(3-fluorophenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2p):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 3-fluorophenylboronic acid neopentyl glycol ester **S5** (62 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (41.3 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.21–7.11 (m, 4H), 6.98–6.93 (m, 2H), 6.86 (td, J = 8.3, 2.4 Hz, 1H), 6.78 (dt, J = 7.7, 1.2 Hz, 1H), 6.71 (dt, J = 10.0, 2.1 Hz, 1H), 4.63 (t, J = 6.1

Hz, 1H), 2.90–2.70 (m, 5H), 1.86 (dtd, J = 14.1, 7.8, 3.9 Hz, 1H), 1.80–1.68 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.78, 162.15, 145.89 (d, J = 6.7 Hz), 143.34, 139.24, 134.36 (q, J = 32.9 Hz), 130.12 (d, J = 8.3 Hz), 129.01, 128.32, 127.49, 126.27 (dd, J = 6.5, 3.1 Hz), 123.32 (d, J = 2.8 Hz), 123.22 (q, J = 272.9 Hz), 114.22 (d, J = 21.0 Hz), 113.66 (d, J = 21.1 Hz), 44.93, 43.48, 41.42, 34.97; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.35, -112.90; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{21}F_4NO_2S^+$ [M+H] 452.1307, found 452.1313.



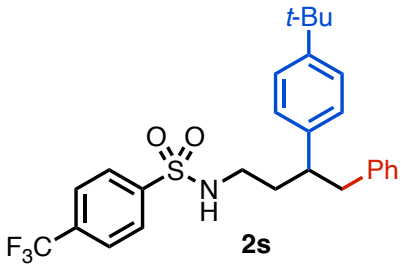
2q

***N*-(3-(2-fluorophenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2q):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 2-fluorophenylboronic acid neopentyl glycol ester **S6** (62 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (41.3 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.24–7.15 (m, 3H), 7.12 (td, J = 8.0, 6.1 Hz, 1H), 7.01–6.96 (m, 2H), 6.81 (td, J = 8.5, 2.6 Hz, 1H), 6.75–6.71 (m, 1H), 6.65 (dt, J = 9.9, 2.1 Hz, 1H), 4.69 (s, 1H), 2.88–2.71 (m, 5H), 1.91–1.72 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.49, 161.86, 143.36 (q, J = 1.4 Hz), 142.65, 142.25 (d, J = 7.2 Hz), 134.30 (q, J = 33.1 Hz), 129.61 (d, J = 8.3 Hz), 128.72, 127.48 (d, J = 7.1 Hz), 126.90, 126.24 (q, J = 3.8 Hz), 124.74 (d, J = 2.7 Hz), 123.24 (q, J = 272.9 Hz), 115.83 (d, J = 21.0 Hz), 113.03 (d, J = 21.0 Hz), 44.99, 43.31 (d, J = 1.8 Hz), 41.49, 35.10; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.33, -63.33, -113.92; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{21}F_4NO_2S^+$ [M+H] 452.1307, found 452.1308.

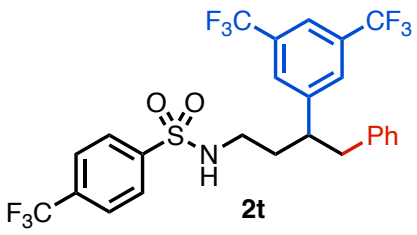


2r

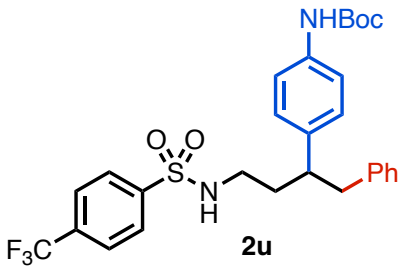
***N*-(3-(4-methoxyphenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2r):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 4-methoxyphenylboronic acid neopentyl glycol ester **S7** (66 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E but with a reaction time of 16 h. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (32.5 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.21–7.10 (m, 3H), 6.98–6.94 (m, 2H), 6.92 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 4.56 (t, J = 6.0 Hz, 1H), 3.76 (s, 3H), 2.87–2.70 (m, 5H), 1.87–1.77 (m, 1H), 1.70 (dddd, J = 13.8, 10.1, 7.3, 5.5 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.28, 143.48 (q, J = 1.4 Hz), 139.84, 135.10, 134.22 (q, J = 33.1 Hz), 129.08, 128.39, 128.22, 127.51, 126.21 (q, J = 3.6 Hz), 126.09, 123.26 (q, J = 273.1 Hz), 114.00, 55.20, 44.37, 43.87, 41.61, 35.13; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.30; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{24}F_3NO_3S^+$ [M+H] 464.1507, found 464.1500.



***N*-(3-(4-(*tert*-butyl)phenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2s):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 4-(*tert*-butyl)phenylboronic acid neopentyl glycol ester **S8** (74 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (43.8 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 7.23–7.12 (m, 3H), 7.02–6.98 (m, 2H), 6.96 (d, J = 8.2 Hz, 2H), 4.44 (t, J = 6.0 Hz, 1H), 2.91–2.85 (m, 1H), 2.85–2.68 (m, 4H), 1.84–1.64 (m, 2H), 1.30 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.66, 143.51 (q, J = 1.3 Hz), 140.27, 139.96, 134.21 (q, J = 33.1 Hz), 129.09, 128.27, 127.52, 127.02, 126.18 (q, J = 3.6 Hz), 126.13, 125.55, 123.26 (q, J = 273.0 Hz), 44.71 (d, J = 1.8 Hz), 43.64, 41.70, 34.75, 34.42, 31.37; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.27; **HRMS** (ESI-TOF) Calc'd for $C_{27}H_{30}F_3NO_2S^+$ [M+H] 490.2028, found 490.2027.

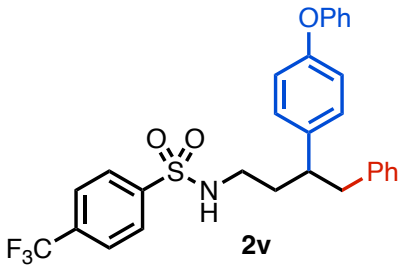


***N*-(3-(3,5-bis(trifluoromethyl)phenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2t):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 3,5-bis(trifluoromethyl)phenylboronic acid neopentyl glycol ester **S9** (98 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (52.1 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dt, J = 8.1, 0.8 Hz, 2H), 7.74–7.68 (m, 3H), 7.47–7.44 (m, 2H), 7.22–7.15 (m, 3H), 6.94–6.89 (m, 2H), 4.88 (t, J = 6.2 Hz, 1H), 3.09 (dtd, J = 9.8, 7.4, 4.9 Hz, 1H), 2.94–2.72 (m, 4H), 1.97 (dtd, J = 14.0, 7.7, 5.0 Hz, 1H), 1.86 (dddd, J = 14.1, 9.9, 7.5, 5.6 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.89, 143.19, 138.20, 134.55 (q, J = 33.2 Hz), 131.73 (q, J = 33.1 Hz), 128.98, 128.49, 127.85 (q, J = 3.9 Hz), 127.45, 126.65, 126.35 (q, J = 3.6 Hz), 123.23 (q, J = 273.0 Hz), 123.14 (q, J = 273.4 Hz) 44.62, 43.22, 41.13, 34.71; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.10, -63.47; **HRMS** (ESI-TOF) Calc'd for $C_{25}H_{20}F_9NO_2S^+$ [M+H] 570.1149, found 570.1149.



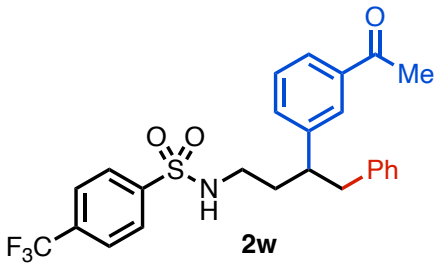
***tert*-butyl (4-(1-phenyl-4-((4-(trifluoromethyl)phenyl)sulfonamido)butan-2-yl)phenyl)carbamate (2u):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), *tert*-butyl(4-phenyl)carbamate boronic acid neopentyl glycol ester **S10** (92 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (37 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.80 (m, 2H), 7.74–7.69 (m, 2H), 7.25–7.12 (m, 5H), 6.96 (ddd, J = 11.5, 7.4, 1.9 Hz, 4H), 6.41 (s, 1H), 4.20 (t, J = 6.1 Hz, 1H), 2.88–2.71 (m, 5H), 1.90–1.80 (m, 1H), 1.73 (td, J = 16.9, 15.7, 8.0 Hz, 1H), 1.52 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.88, 143.43 (q, J = 1.6 Hz), 139.71, 137.70, 136.90, 134.19 (q, J = 33.0 Hz), 129.07, 128.23, 128.00, 127.50, 126.23 (q, J = 3.9 Hz), 126.10, 123.27 (q, J = 273.6 Hz), 118.83, 80.58, 44.56, 43.71, 41.55, 35.09, 28.34;

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.28; **HRMS** (ESI-TOF) Calc'd for $C_{28}H_{31}F_3N_2O_4S^+$ [M+H] 549.2035, found 549.2024.



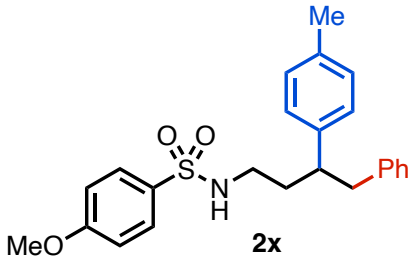
2v

***N*-(3-(4-phenoxyphenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2v):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 4-phenoxyphenyl boronic acid neopentyl glycol ester **S11** (85 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (50.4 mg, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.83 (m, 2H), 7.72–7.68 (m, 2H), 7.36–7.29 (m, 2H), 7.22–7.13 (m, 3H), 7.09 (td, *J* = 7.3, 1.1 Hz, 1H), 7.00–6.94 (m, 6H), 6.91–6.85 (m, 2H), 4.62 (t, *J* = 6.0 Hz, 1H), 2.90–2.72 (m, 5H), 1.84 (dtd, *J* = 15.4, 7.5, 4.6 Hz, 1H), 1.74 (dddd, *J* = 13.1, 9.3, 7.3, 5.3 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.32, 155.84, 143.48, 139.69, 138.09, 134.31 (q, *J* = 33.0 Hz), 129.79, 129.12, 128.77, 128.26, 127.54, 126.28 (q, *J* = 3.8 Hz), 126.19, 123.27, 122.82 (q, *J* = 273.7 Hz), 119.12, 118.74, 44.54, 43.80, 41.62, 35.14; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.26; **HRMS** (ESI-TOF) Calc'd for $C_{29}H_{26}F_3NO_3S^+$ [M+H] 526.1664, found 526.1666.



2w

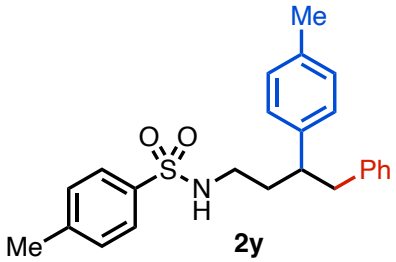
***N*-(3-(3-acetylphenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2w):** The title compound was prepared from **1a** (28 mg, 0.1 mmol), 3-acetylphenyl boronic acid neopentyl glycol ester **S12** (70 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (32.9 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.76 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.72–7.66 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.23 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.21–7.11 (m, 3H), 6.98–6.93 (m, 2H), 4.76 (t, *J* = 6.1 Hz, 1H), 3.02–2.92 (m, 1H), 2.89–2.70 (m, 4H), 2.55 (s, 3H), 1.96–1.77 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.41, 143.43 (q, *J* = 1.4 Hz), 139.24, 137.33, 134.29 (q, *J* = 32.9 Hz), 132.50, 129.07, 128.87, 128.31, 127.47, 127.16, 127.07, 126.29, 126.27 (q, *J* = 3.8 Hz), 123.21 (q, *J* = 272.4 Hz), 44.91, 43.52, 41.44, 34.94, 26.70; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.32; **HRMS** (ESI-TOF) Calc'd for $C_{25}H_{24}F_3NO_3S^+$ [M+H] 476.1507, found 476.1514.



2x

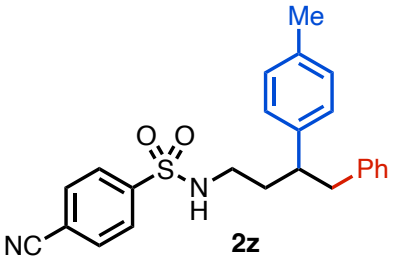
4-methoxy-*N*-(4-phenyl-3-(*p*-tolyl)butyl)benzenesulfonamide (2x): The title compound was prepared from **1c** (24 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (36.9 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.9 Hz, 2H), 7.21–7.10 (m, 3H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 6.6 Hz, 2H), 6.93–6.87 (m, 4H), 4.34 (t, *J* = 6.1 Hz, 1H), 3.84 (s, 3H), 2.86–2.65 (m, 5H), 2.29 (s, 3H), 1.85–1.75 (m, 1H), 1.70 (dqd, *J* = 10.1, 7.4, 5.4 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ

162.76, 140.34, 140.02, 136.01, 131.45, 129.26, 129.18, 129.12, 128.17, 127.42, 125.99, 114.15, 55.61, 44.77, 43.69, 41.48, 35.07, 21.05; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{27}NO_3S^+$ [M+H] 410.1790, found 410.1800.



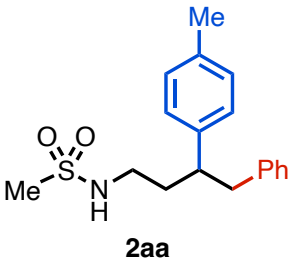
2y

4-methyl-*N*-(4-phenyl-3-(*p*-tolyl)butyl)benzenesulfonamide (2y): The title compound was prepared from **1d** (23 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E but with a reaction time of 16 h. Purification using PTLC (20% Acetone in Hexanes) gave the product as a colorless oil (29 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.24–7.20 (m, 2H), 7.20–7.09 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 6.6 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 4.42 (t, *J* = 6.0 Hz, 1H), 2.85–2.65 (m, 5H), 2.40 (s, 3H), 2.29 (s, 3H), 1.80 (dddd, *J* = 15.3, 7.7, 3.9, 1.9 Hz, 1H), 1.71 (dddd, *J* = 11.6, 8.0, 5.7, 2.1 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.23, 140.33, 140.02, 136.90, 136.01, 129.63, 129.26, 129.12, 128.17, 127.42, 125.98, 44.75, 43.68, 41.52, 35.12, 21.55, 21.06; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{27}NO_2S^+$ [M+H] 394.1841, found 394.1841.



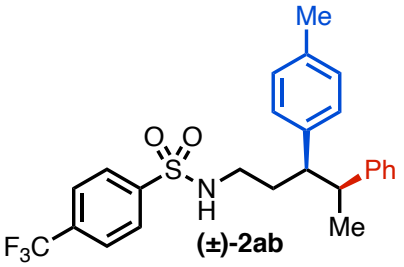
2z

4-cyano-*N*-(4-phenyl-3-(*p*-tolyl)butyl)benzenesulfonamide (2z): The title compound was prepared from **1e** (24 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (37.6 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.23–7.13 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.00–6.96 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.47 (t, *J* = 6.0 Hz, 1H), 2.90–2.69 (m, 5H), 2.31 (s, 3H), 1.86–1.64 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.22, 140.08, 139.80, 136.34, 132.85, 129.40, 129.07, 128.28, 127.58, 127.30, 126.17, 117.37, 116.21, 44.81, 43.77, 41.69, 34.86, 21.06; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{24}N_2O_2S^+$ [M+H] 405.1637, found 405.1638.



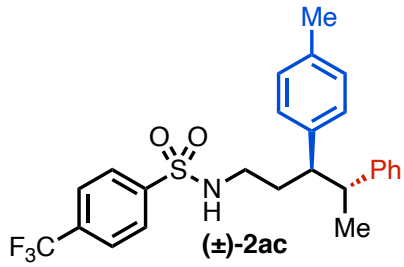
2aa

***N*-(4-phenyl-3-(*p*-tolyl)butyl)methanesulfonamide (2aa):** The title compound was prepared from **1e** (24 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% Acetone in Hexanes) gave the product as a colorless oil (25.2 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24–7.18 (m, 2H), 7.18–7.12 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.07–6.99 (m, 4H), 4.18 (t, *J* = 6.1 Hz, 1H), 3.01–2.79 (m, 5H), 2.74 (s, 3H), 2.31 (s, 3H), 1.97–1.77 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.33, 140.02, 136.26, 129.40, 129.16, 128.26, 127.43, 126.11, 44.93, 43.89, 41.62, 40.08, 35.42, 21.06; **HRMS** (ESI-TOF) Calc'd for $C_{18}H_{23}NO_2S^+$ [M+H] 318.1528, found 318.1533.



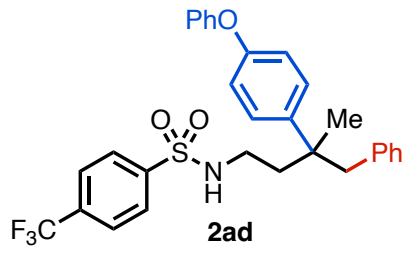
(±)-2ab

***N*-4-phenyl-3-(*p*-tolyl)pentyl)-4-(trifluoromethyl)benzenesulfonamide (2ab):** The title compound was prepared from **1f** (29 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to the General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (32.2 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 7.7 Hz, 2H), 4.03 (s, 1H), 2.74 (p, *J* = 7.0 Hz, 1H), 2.69–2.52 (m, 3H), 2.34 (s, 3H), 1.50 (q, *J* = 7.8, 7.0 Hz, 2H), 0.93 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.92, 143.44, 139.35, 136.35, 134.11 (q, *J* = 33.0 Hz), 129.42, 128.60, 127.86, 127.46, 127.41, 126.40, 126.11 (q, *J* = 3.8 Hz), 123.28 (q, *J* = 272.8 Hz), 50.11, 46.32, 41.82, 34.28, 21.11, 21.02; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.29; **HRMS** (ESI-TOF) Calc'd for $C_{25}H_{26}F_3NO_2S^+$ [M+H] 462.1715, found 462.1713; **X-ray** (single-crystal) Colorless block crystals of X-ray diffraction quality were obtained by vapor diffusion of hexane to a saturated solution of **2ab** in benzene (CCDC 2011492).[17]



(±)-2ac

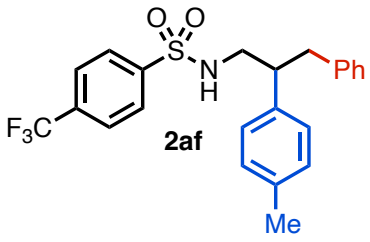
***N*-4-phenyl-3-(*p*-tolyl)pentyl)-4-(trifluoromethyl)benzenesulfonamide (2ac):** The title compound was prepared from **1g** (29 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E but with a reaction time of 16 h. Purification using PTLC (20% Acetone in Hexanes) gave the product as a colorless oil (39.6 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.17–7.07 (m, 3H), 6.95–6.86 (m, 4H), 6.69 (d, *J* = 8.0 Hz, 2H), 4.41 (t, *J* = 6.1 Hz, 1H), 2.97–2.77 (m, 2H), 2.76–2.65 (m, 2H), 2.24 (s, 3H), 1.98 (dtd, *J* = 13.6, 7.9, 3.8 Hz, 1H), 1.75 (dddd, *J* = 13.7, 12.1, 7.4, 5.0 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.62, 143.52 (q, *J* = 1.2 Hz), 138.11, 135.95, 134.22 (q, *J* = 33.1 Hz), 128.82, 128.30, 127.94, 127.84, 127.52, 126.16 (q, *J* = 3.8 Hz), 126.00, 123.25 (q, *J* = 272.6 Hz), 49.46, 45.45, 41.90, 32.07, 20.94, 18.42; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.34; **HRMS** (ESI-TOF) Calc'd for $C_{25}H_{26}F_3NO_2S^+$ [M+H] 462.1715, found 462.1711.



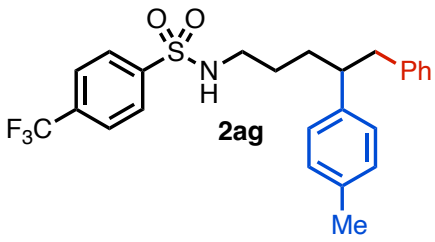
2ad

***N*-(3-methyl-3-(4-phenoxyphenyl)-4-phenylbutyl)-4-(trifluoromethyl)benzenesulfonamide (2ad):** The title compound was prepared from **1h** (29 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E but with a reaction time of 16 h. Purification using PTLC (20% Acetone in Hexanes) gave the product as a colorless oil (27 mg, 50% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.35 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.16–7.09 (m, 4H), 7.09–7.06 (m, 2H), 7.02–6.99 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.73 (dd, *J* = 7.8, 1.8 Hz, 2H), 4.49–4.43 (m, 1H), 2.96–2.89 (m, 1H), 2.86 (d, *J* = 13.2 Hz, 1H), 2.77–2.70 (m,

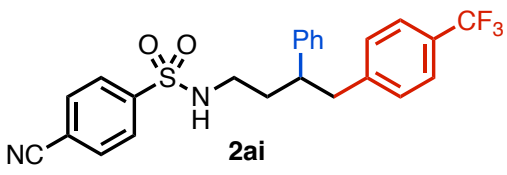
2H), 2.13 (ddd, J = 13.5, 10.6, 5.3 Hz, 1H), 1.75 (ddd, J = 13.5, 10.5, 5.4 Hz, 1H), 1.20 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.30, 155.45, 143.59 (d, J = 1.2 Hz), 140.09, 137.32, 134.34 (q, J = 33.2 Hz), 130.50, 129.79, 127.85, 127.63, 127.53, 126.32, 126.25 (q, J = 3.7 Hz), 123.28, 123.23 (q, J = 272.8 Hz), 118.79, 118.68, 51.08, 41.83, 40.75, 39.73, 23.23; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.28; **HRMS** (ESI-TOF) Calc'd for $C_{30}H_{28}F_3NO_3S^+$ [M+H] 540.1820, found 540.1827.



***N*-(3-phenyl-2-(*p*-tolyl)propyl)-4-(trifluoromethyl)benzenesulfonamide (2af):** The title compound was prepared from **1l** (27 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% Acetone in Hexanes) gave the product as a white solid (29.3 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.24–7.13 (m, 3H), 7.04 (d, J = 7.4 Hz, 2H), 6.97 (d, J = 6.3 Hz, 2H), 6.87 (d, J = 8.1 Hz, 2H), 4.40 (dd, J = 7.8, 4.4 Hz, 1H), 3.29 (ddd, J = 12.6, 7.7, 4.7 Hz, 1H), 3.13–3.03 (m, 1H), 2.94–2.77 (m, 3H), 2.30 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.38 (d, J = 1.2 Hz), 138.95, 137.52, 137.02, 134.21 (q, J = 32.9 Hz), 129.64, 128.93, 127.53, 127.51, 126.40, 126.19 (q, J = 3.6 Hz), 123.28 (q, J = 273.1 Hz), 47.50, 46.97, 40.28, 21.00; **^{19}F NMR** (400 MHz, $CDCl_3$) δ -63.29; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{22}F_3NO_2S^+$ [M+H] 434.1402, found 434.1404.



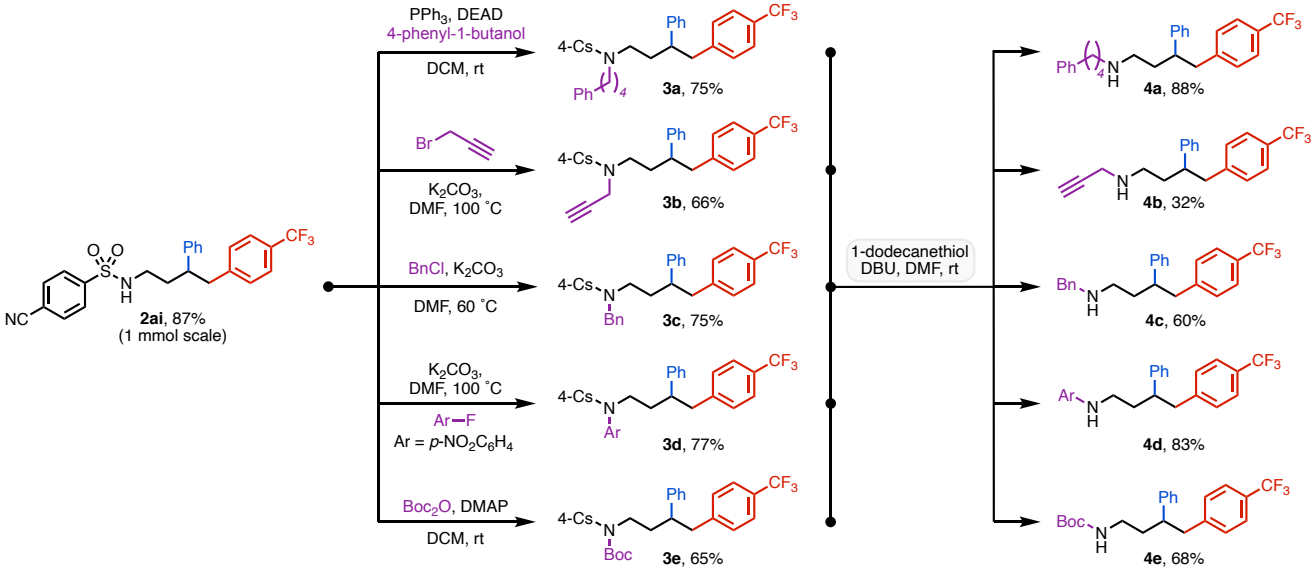
***N*-(5-phenyl-4-(*p*-tolyl)pentyl)-4-(trifluoromethyl)benzenesulfonamide (2ag):** The title compound was prepared from **1m** (29 mg, 0.1 mmol), 4-methylphenylboronic acid neopentyl glycol ester **S1** (61 mg, 0.3 mmol), and iodobenzene (61 mg, 0.3 mmol) according to General Procedure E. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (34 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.22–7.17 (m, 2H), 7.16–7.11 (m, 1H), 7.04 (d, J = 7.8 Hz, 2H), 6.99 (d, J = 6.7 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 4.55 (t, J = 6.1 Hz, 1H), 2.88–2.79 (m, 3H), 2.75 (dd, J = 13.3, 7.5 Hz, 1H), 2.67 (dtd, J = 10.1, 7.2, 4.3 Hz, 1H), 2.29 (s, 3H), 1.65–1.55 (m, 1H), 1.55–1.45 (m, 1H), 1.30–1.19 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.68 (q, J = 1.5 Hz), 135.84, 134.26 (q, J = 33.0 Hz), 129.15, 129.11, 128.17, 127.51, 126.25 (q, J = 3.8 Hz), 125.95, 123.27 (q, J = 273.6 Hz), 47.06, 43.92, 43.27, 32.09, 27.63, 21.01; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.31; **HRMS** (ESI-TOF) Calc'd for $C_{25}H_{26}F_3NO_2S^+$ [M+H] 462.1715, found 462.1722.



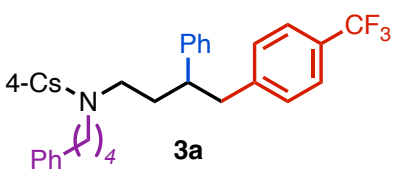
4-cyano-*N*-(3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)benzenesulfonamide (2ai): The title compound was also prepared from **1d** (236 mg, 1 mmol), phenylboronic acid neopentyl glycol ester **S2** (570 mg, 3 mmol) and 1-iodo-4-(trifluoromethyl)benzene (816 mg, 3 mmol) according to General Procedure F. Purification using silica gel column chromatography (20% EtOAc in Hexanes) gave the product as a yellow solid (398 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.29–7.19 (m, 3H), 7.07 (d, J = 7.9 Hz, 2H), 7.01 (d, J = 6.5 Hz,

2H), 4.32 (t, J = 6.1 Hz, 1H), 2.94–2.77 (m, 5H), 1.96–1.77 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.03, 143.80 (d, J = 1.6 Hz), 143.79, 142.34, 132.93, 129.38, 128.78, 128.38 (q, J = 32.3 Hz), 127.59, 127.50, 127.01, 126.98, 125.10 (q, J = 3.6 Hz), 124.28 (q, J = 271.5 Hz), 117.32, 116.28, 44.90, 43.32, 41.48, 35.27; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.59; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{21}F_3N_2O_2S^+$ [M+H] 459.1354, found 459.1346.

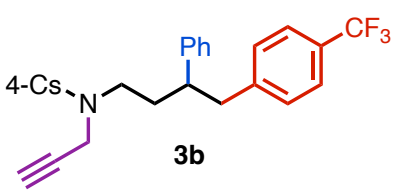
Diversification of 1,2-Diarylation Products



Scheme S6. Diversification of representative product **2ai**.

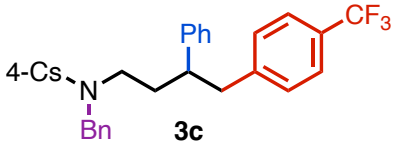


4-cyano-*N*-(3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)-*N*-(4-phenylbutyl)benzenesulfonamide (3a): To a vial containing the starting material **2ai** (398 mg, 0.869 mmol, 1.00 equiv) was added triphenylphosphine (460 mg, 1.737 mmol, 2.00 equiv), 4-phenyl-1-butanol (273 µL, 1.737 mmol, 2.00 equiv), and dichloromethane (4.0 mL). The solution was stirred until homogeneous, then cooled in an ice water bath. A solution of DEAD (40 wt% in toluene, 791 µL, 1.737 mmol, 2.00 equiv) was added dropwise over 40 min. The mixture was warmed to room temperature and stirred for 1 h. The volatiles were removed *in vacuo*, and the crude residue was purified directly by flash column chromatography over silica gel (0 to 20% ethyl acetate in hexanes gradient) to afford the product as a thick, colorless oil (384 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64–7.73 (m, 4H), 7.45 (d, J = 8.1 Hz, 2H), 7.20–7.32 (m, 6H), 7.11 (d, J = 7.1 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 6.8 Hz, 2H), 3.05 (t, J = 7.4 Hz, 2H), 2.86–2.99 m, 3H), 2.74–2.84 (m, 2H), 2.54 (t, J = 7.5 Hz, 2H), 1.84–1.99 (m, 2H), 1.48–1.55 (m, 2H), 1.30–1.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.9, 143.8, 142.6, 141.6, 132.8, 129.4, 128.6, 128.43 (q, J = 32.3 Hz), 128.40, 128.3, 127.6, 127.5, 126.9, 126.0, 125.0 (q, J = 3.7 Hz), 124.2 (q, J = 272 Hz), 117.3, 116.0, 48.3, 46.5, 45.3, 43.4, 35.1, 34.6, 28.0, 27.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3; **HRMS** (ESI) Calc'd for $C_{34}H_{37}F_3N_3O_2S$ $[M+NH_4]^+$ 608.2553, found 608.2567.



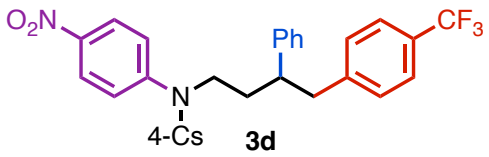
3b

4-cyano-*N*-(3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (3b): To a 1-dram (4 mL) vial equipped with a Teflon-coated magnetic stir bar were added **2ai** (92 mg, 0.20 mmol, 1 equiv), K_2CO_3 (55 mg, 0.40 mmol, 2 equiv), and DMF (330 µL). After stirring for at least 5 min, propargyl bromide (80 wt % in toluene, 38 µL, 0.40 mmol, 2 equiv) was added, and the reaction mixture was left to stir at 100 ˚C under nitrogen for 24 h. After this time, the reaction mixture was cooled, diluted with water (10 mL) and extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4, and concentrated *in vacuo* to leave a yellow residue. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (65.2 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.25–7.19 (m, 1H), 7.13–7.08 (m, 4H), 4.01 (t, *J* = 2.7 Hz, 2H), 3.14–2.84 (m, 5H), 1.99 (td, *J* = 6.8, 3.7 Hz, 2H), 1.93 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.89 (d, *J* = 1.1 Hz), 142.83, 142.75, 132.63, 129.46, 128.66, 128.45 (q, *J* = 32.2 Hz), 128.25, 127.66, 126.89, 125.11 (q, *J* = 4.0 Hz), 124.28 (q, *J* = 271.6 Hz), 117.33, 116.43, 75.72, 74.29, 44.97, 44.85, 43.33, 36.46, 33.14; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.57; **HRMS** (ESI-TOF) Calc'd for $C_{27}H_{23}F_3N_2O_2S^+$ [M+H] 497.1511, found 497.1508.



3c

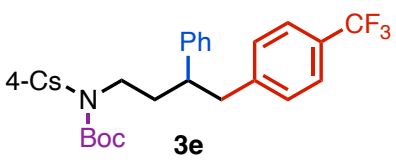
***N*-benzyl-4-cyano-*N*-(3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)benzenesulfonamide (3c):** To a 1-dram (4 mL) vial equipped with a Teflon-coated magnetic stir bar were added a solution of **2ai** (69 mg, 0.15 mmol, 1 equiv) in DMF (200 µL), K_2CO_3 (55 mg, 0.40 mmol, 2 equiv), and 130 µL of DMF. After stirring for at least 5 min, benzyl chloride (51 mg, 0.40 mmol, 2 equiv) was added, and the reaction mixture was left to stir at 60 ˚C under nitrogen for 16 h. After this time, the reaction mixture was cooled, diluted with water (10 mL) and extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4, and the solvent was removed *in vacuo* to leave a colorless residue. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (61.8 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76–7.69 (m, 4H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.25–7.18 (m, 5H), 7.08 (dd, *J* = 7.7, 1.9 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.92–6.87 (m, 2H), 4.28–4.16 (m, 2H), 2.98–2.88 (m, 1H), 2.83 (td, *J* = 9.7, 9.2, 5.0 Hz, 1H), 2.79–2.74 (m, 2H), 2.66–2.56 (m, 1H), 1.80–1.63 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.89, 143.82 (q, *J* = 1.2 Hz), 142.47, 135.41, 132.88, 129.33, 128.71, 128.61, 128.42, 128.32 (q, *J* = 32.3 Hz), 128.18, 127.63, 127.54, 126.81, 125.22, 125.03 (q, *J* = 3.8 Hz), 124.32 (q, *J* = 272.0 Hz), 123.42, 117.33, 116.14, 52.39, 46.72, 45.14, 43.36, 33.93; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.56; **HRMS** (ESI-TOF) Calc'd for $C_{31}H_{27}F_3N_2O_2S^+$ [M+H] 549.1824, found 549.1826.



3d

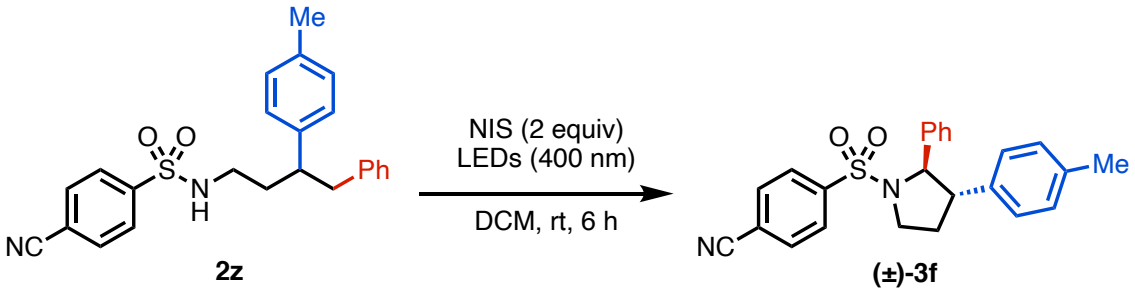
4-cyano-*N*-(4-nitrophenyl)-*N*-(3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)benzenesulfonamide (3d): To a 1-dram (4 mL) vial equipped with a Teflon-coated magnetic stir bar were added **2ai** (92 mg, 0.2 mmol, 1 equiv), K_2CO_3 (55 mg, 0.40 mmol, 2 equiv), and DMF (330 µL). After stirring for at least 5 min, 1-fluoro-4-nitrobenzene (42 mg, 0.30 mmol, 1.5 equiv) was added, and the reaction mixture was left to stir at 100 ˚C under nitrogen for 23 h. After this time, the reaction mixture was cooled, diluted with water (10 mL), and extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4, and

concentrated *in vacuo* to leave a yellow residue. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a yellow solid (88.7 mg, 77% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 (d, J = 8.9 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.29–7.24 (m, 2H), 7.24–7.20 (m, 1H), 7.08–7.00 (m, 6H), 3.55 (dt, J = 13.7, 7.4 Hz, 1H), 3.33 (ddd, J = 13.3, 7.7, 5.3 Hz, 1H), 2.88 (t, J = 1.7 Hz, 3H), 1.91–1.77 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.75, 144.04, 143.76 (q, J = 1.4 Hz), 143.75, 142.43, 141.36, 132.90, 129.37, 128.75, 128.49 (q, J = 32.4 Hz), 128.44, 127.96, 127.58, 127.05, 125.11 (q, J = 3.8 Hz), 124.53, 124.20 (q, J = 271.5 Hz), 116.98, 48.73, 44.93, 43.29, 33.80; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.56; **HRMS** (ESI-TOF) Calc'd for $C_{30}H_{24}F_3N_3O_4S^+$ [M+H] 580.1518, found 580.1523.



3e

***tert*-butyl ((4-cyanophenyl)sulfonyl)(3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)carbamate (4e):** To a 1-dram (4 mL) vial equipped with a Teflon-coated magnetic stir bar were added **2ai** (92 mg, 0.2 mmol), DMAP (2.4 mg, 20 µmol), and DCM (450 µL). After stirring for at least 5 min, di-*tert*-butyl dicarbonate (55 µL, 0.24 mmol, 1.2 equiv) was added, and the reaction mixture was left to stir at room temperature under nitrogen for 23 h. After this time, the reaction was diluted with water (10 mL) and extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4, and concentrated *in vacuo* to leave a colorless residue. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a colorless oil (72.6 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95–7.90 (m, 2H), 7.76 (dd, J = 8.5, 1.6 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.31–7.25 (m, 2H), 7.21 (td, J = 7.3, 1.5 Hz, 1H), 7.12 (t, J = 6.9 Hz, 4H), 3.70–3.56 (m, 2H), 3.05–2.86 (m, 3H), 2.24–2.07 (m, 2H), 1.28 (d, J = 1.5 Hz, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.33, 144.00 (q, J = 1.4 Hz), 142.46, 132.46, 129.46, 128.67, 128.48, 128.38 (q, J = 33.2 Hz), 127.60, 126.89, 125.38, 125.07 (q, J = 4.0 Hz), 124.31 (q, J = 271.6Hz), 117.17, 116.89, 85.08, 46.36, 45.69, 43.64, 35.55, 27.81; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.53; **HRMS** (ESI-TOF) for $C_{29}H_{29}F_3N_2O_4S^+$ [M+H] 559.1878, found 559.1888.



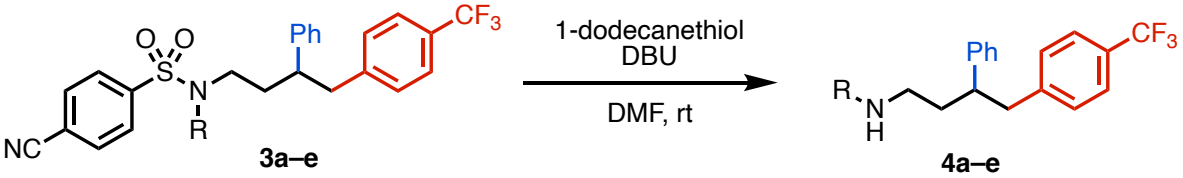
2z **(±)-3f**

Scheme S7. Synthesis of 4-Cs protected pyrrolidine **(±)-3f**. This compound was synthesized using an adapted version of a literature procedure describing the preparation of similar compounds.[18]

4-((2-phenyl-3-(*p*-tolyl)pyrrolidin-1-yl)sulfonyl)benzonitrile ((±)-3f): Inside the glovebox, to a 1-dram (4 mL) vial equipped with a Teflon-coated magnetic stir bar were added **2z** (38.7 mg, 96 µmol, 1 equiv) and NIS (43 mg, 0.19 mmol, 2 equiv). The vial was sealed with a screw-top cap, removed from the glovebox, and anhydrous DCM (2 mL, 0.05 M) was added. The reaction vessel was then irradiated with violet light (400 nm) via LEDs while stirring at room temperature for 6 h. After this time, the reaction mixture was washed with sat. aq. $Na_2S_2O_3$ (5 mL) and $NaHCO_3$ (5

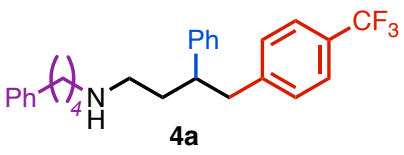
mL) and extracted with DCM (3 × 1 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed *in vacuo* to leave a colorless residue. Purification using PTLC (20% EtOAc in Hexanes) gave the product as a white solid (27.1 mg, 70% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 (s, 4H), 7.23–7.15 (m, 3H), 7.05 (d, J = 6.7 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 6.83 (d, J = 8.1 Hz, 2H), 4.73 (d, J = 6.9 Hz, 1H), 4.02 (ddd, J = 10.4, 7.7, 4.1 Hz, 1H), 3.70 (ddd, J = 10.4, 8.6, 6.4 Hz, 1H), 3.29 (dt, J = 9.0, 6.7 Hz, 1H), 2.31 (s, 3H), 2.27 (ddd, J = 12.8, 6.4, 4.1 Hz, 1H), 2.09 (dtd, J = 12.7, 8.8, 7.8 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.53, 140.50, 136.99, 136.55, 132.43, 129.41, 128.38, 127.65, 127.58, 126.95, 126.85, 117.48, 115.72, 71.21, 54.88, 49.19, 32.02, 21.01; **HRMS** (ESI-TOF) for $C_{24}H_{22}N_2O_2S^+$ [M+H] 403.1480, found 403.1478.

^{1}H-^{1}H NOESY was found to be ambiguous in determining *trans*/*cis* configuration since it is difficult to confidently assign the configuration of substituents of 5-membered rings from $^3J_{H,H}$ values.[19] However, the relative stereochemistry of **(±)-3f** could be assigned based on the ^{1}H spectrum (specifically the chemical shifttt of the α-C(3°)–*H* atom and the J-values of the two benzylic H atoms), as described previously in the literature for 2,3-disubstituted pyrrolidines.[20]



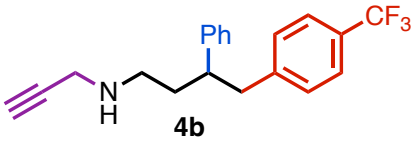
Scheme S8. Synthesis of secondary alkyl amines **4a–e**. These compounds were synthesized using adapted versions of literature procedures describing the preparation of similar compounds.[21]

General Procedure G: A stock solution of 1-dodecanethiol in DMF was degassed by sparging with nitrogen for 20 min. Under a nitrogen atmosphere, the thiol solution was added to **3a–e** in a reaction vessel equipped with a Teflon-coated magnetic stir bar, and the reaction mixture was stirred for 5 min. DBU was then added, at which point a light-yellow color developed, and the reaction mixture was stirred at room temperature for 21–24 h under nitrogen. After this time, the reaction mixture was diluted with water (10 mL) and extracted with EtOAc (×3). The organic layers were combined, and the solvent was removed *in vacuo* to leave an oil, which afforded pure product after silica gel column chromatography or PTLC.



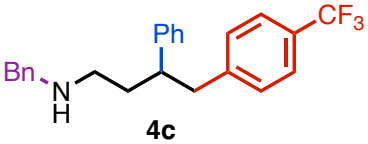
3-phenyl-*N*-(4-phenylbutyl)-4-(4-(trifluoromethyl)phenyl)butan-1-amine (4a): The title compound was prepared from a 0.85 M stock solution of 1-dodecanethiol in DMF (3.25 mL, 2.75 mmol, 5.00 equiv), **3a** (325 mg, 0.550 mmol, 1.0 equiv), and DBU (394 µL, 2.61 mmol, 4.75 equiv) with a reaction time of 24 h according to General Procedure G . After this time, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 10 mL). The crude oil was purified by silica gel column chromatography (0 to 10% MeOH in DCM gradient) to afford the product as a light-tan syrup (206 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.44 (d, J = 8.1 Hz, 2H), 7.23–7.30 (m, 4H), 7.13–7.22 (m, 4H), 7.07–7.13 (m, 4H), 2.84–3.01 (m, 3H), 2.58 (t, J = 7.6 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.39–2.48 (m, 2H), 1.82–1.95 (m, 2H), 1.53–1.64

(m, 2H), 1.42–1.51 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4 (q, *J* = 1.5 Hz), 143.6, 142.3, 129.4, 128.4, 128.3, 128.2, 128.16 (q, *J* = 32.3 Hz), 127.5, 126.5, 125.7, 124.9 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272 Hz), 49.6, 47.8, 45.9, 43.7, 35.7, 35.5, 29.3, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3; **HRMS** (ESI) Calc'd for $C_{27}H_{31}F_3N$ $[M+H]^+$ 426.2403, found 426.2414.



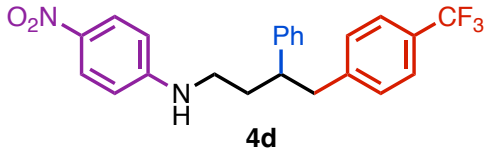
4b

3-phenyl-*N*-(prop-2-yn-1-yl)-4-(4-(trifluoromethyl)phenyl)butan-1-amine (4b): The title compound was prepared from a 1.65 M stock solution of 1-dodecanethiol in DMF (280 µL, 0.46 mmol, 2.7 equiv), **3b** (85 mg, 0.17 mmol, 1 equiv), and DBU (123 µL, 0.815 mmol, 4.75 equiv) with a reaction time of 23 h according to General Procedure G. After this time, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 1 mL). The crude oil was purified by PTLC (20% EtOAc in Hexanes) to afford the product as a yellow oil (18 mg, 32% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.29–7.22 (m, 2H), 7.21–7.15 (m, 1H), 7.13–7.08 (m, 4H), 3.30 (t, *J* = 2.3 Hz, 2H), 2.98–2.90 (m, 3H), 2.52 (t, *J* = 7.3 Hz, 2H), 2.13 (t, *J* = 2.4 Hz, 1H), 1.89–1.81 (m, 2H), 1.24 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.47 (q, *J* = 1.4 Hz), 143.73, 129.42, 128.23 (q, *J* = 32.2 Hz), 127.63, 125.00 (q, *J* = 3.9 Hz), 124.34 (q, *J* = 272.2 Hz), 82.11, 46.70, 45.67, 43.67, 35.64; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.54; **HRMS** (ESI-TOF) Calc'd for $C_{20}H_{20}F_3N^+$ $[M+H]$ 332.1626, found 332.1632.



4c

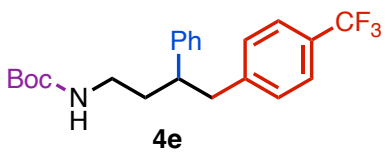
***N*-benzyl-3-phenyl-4-(4-(trifluoromethyl)phenyl)butan-1-amine (4c):** The title compound was prepared from a 1.65 M stock solution of 1-dodecanethiol in DMF (220 µL, 0.36 mmol, 2.8 equiv), **3c** (70 mg, 0.13 mmol, 1 equiv), and DBU (91 µL, 0.61 mmol, 4.75 equiv) with a reaction time of 23 h according to General Procedure G. After this time, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 1 mL). The crude oil was purified by PTLC (20% EtOAc in Hexanes) to afford the product as a colorless oil (29 mg, 60% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.30–7.16 (m, 8H), 7.08 (dd, *J* = 7.1, 1.8 Hz, 4H), 3.64 (q, *J* = 13.1 Hz, 2H), 2.92 (dd, *J* = 7.3, 4.2 Hz, 3H), 2.48 (t, *J* = 7.3 Hz, 2H), 1.93–1.80 (m, 2H), 1.45 (s, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.54 (q, *J* = 1.3 Hz), 143.84, 140.17, 129.42, 128.47, 128.38, 128.20 (q, *J* = 33.4 Hz), 128.09, 127.64, 126.94, 126.48, 124.99 (q, *J* = 3.8 Hz), 124.35 (q, *J* = 271.7Hz), 123.45, 53.94, 47.40, 45.77, 43.70, 35.82; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.52; **HRMS** (ESI-TOF) Calc'd for $C_{24}H_{24}F_3N^+$ $[M+H]$ 384.1939, found 384.1943.



4d

2-nitro-*N*-(3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)aniline (4d): The title compound was prepared from a 1.65 M stock solution of 1-dodecanethiol in DMF (220 µL, 0.36 mmol, 2.7 equiv), **3d** (78 mg, 0.13 mmol. 1 equiv), and DBU (96 µL, 0.64 mmol, 4.75 equiv) with a reaction time of 21 h according to General Procedure G. After this time, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 1 mL). The crude oil was purified by PTLC (20% EtOAc in Hexanes) to afford the product as a yellow oil (46 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.2 Hz, 2H), 7.44 (d, *J* = 7.8

Hz, 2H), 7.34–7.27 (m, 2H), 7.26–7.20 (m, 1H), 7.12 (ddd, J = 7.9, 4.2, 2.5 Hz, 4H), 6.30 (d, J = 9.2 Hz, 2H), 4.39 (t, J = 5.7 Hz, 1H), 3.11–2.89 (m, 5H), 2.07–1.92 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.20, 144.02 (q, J = 1.4 Hz), 142.97, 137.75, 129.40, 128.86, 128.43 (q, J = 32.4 Hz), 127.55, 127.05, 126.38, 125.15 (q, J = 3.7 Hz), 123.40 (q, J = 272.0 Hz), 110.93, 45.81, 43.58, 41.66, 34.71; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.49; **HRMS** (ESI-TOF) Calc'd for $C_{23}H_{21}F_3N_2O_2^+$ [M+H] 415.1633, found 415.1628.



4e

***tert*-butyl (3-phenyl-4-(4-(trifluoromethyl)phenyl)butyl)carbamate (4e):** The title compound was prepared from a 1.65 M stock solution of 1-dodecanethiol in DMF (220 µL, 0.48 mmol, 5 equiv), **3e** (54 mg, 97 µmol, 1 equiv), and DBU (69 µL, 0.46 mmol, 4.75 equiv) with a reaction time of 23 h according to General Procedure G. After this time, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 1 mL). The crude oil was purified by PTLC (20% EtOAc in Hexanes) to afford the product as a colorless oil (26 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.9 Hz, 2H), 7.29–7.22 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.11–7.04 (m, 4H), 4.36 (s, 1H), 3.11–2.75 (m, 5H), 1.87 (ddd, J = 33.1, 14.7, 7.6 Hz, 2H), 1.40 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.85, 144.30 (q, J = 1.4 Hz), 143.27, 129.40, 128.60, 128.28 (q, J = 32.5), 127.58, 126.65, 125.00 (q, J = 4.0 Hz), 124.32 (q, J = 271.9 Hz), 123.42, 79.15, 45.54, 43.34, 38.92, 35.86, 28.39; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.56; **HRMS** (ESI-TOF) Calc'd for $C_{22}H_{26}F_3NO_2^+$ [M+H] 394.1994, found 394.1999.

X-RAY CRYSTALLOGRAPHY

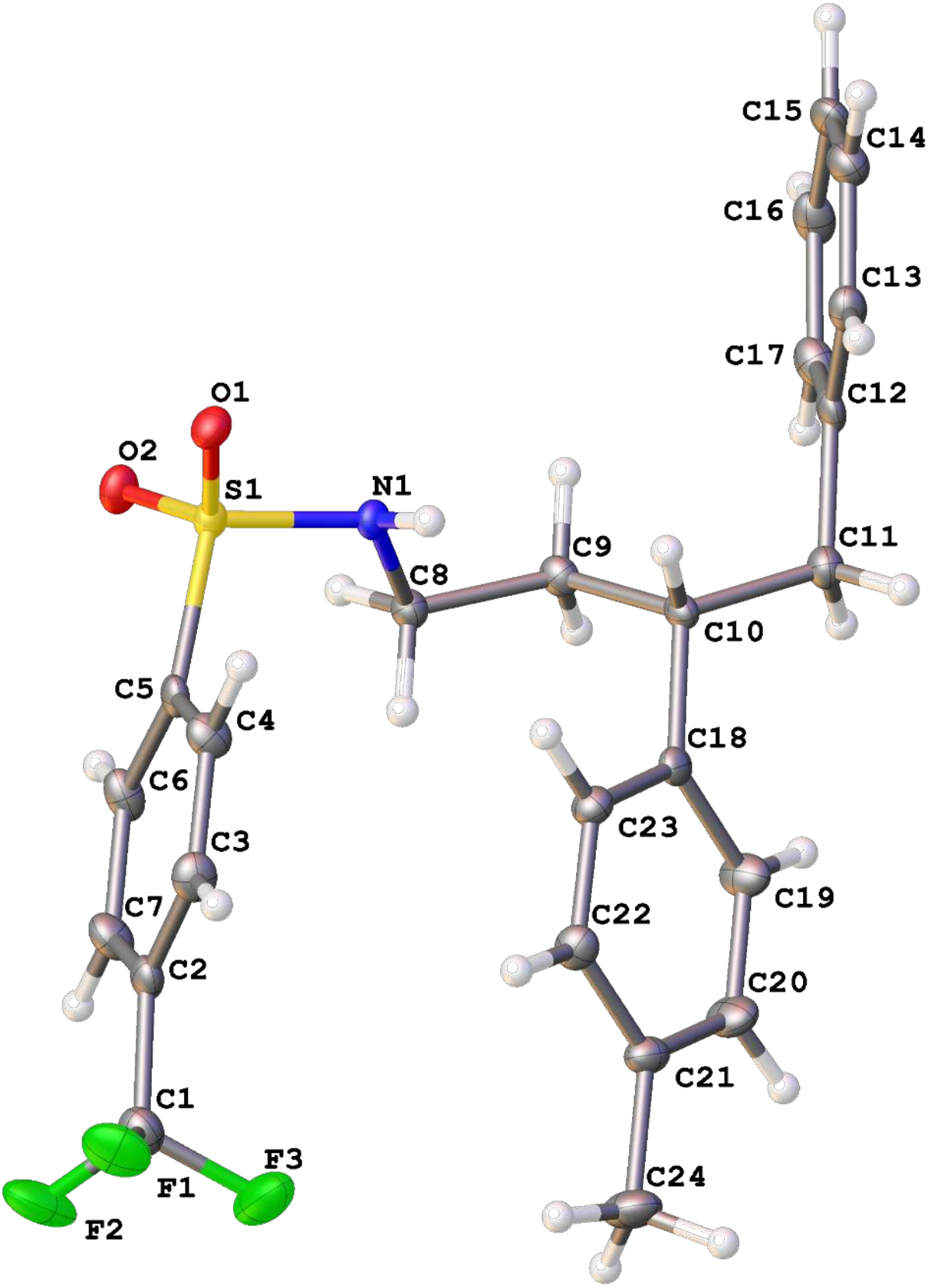


Table S3. Crystal data and structure refinement for **2a**.

Identification code	engle225_a	
Empirical formula	C24 H24 F3 N O2 S	
Formula weight	447.50	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 16.6732(7) Å	α = 90°.
	b = 7.8057(3) Å	β = 103.9000(10)°.
	c = 16.9323(7) Å	γ = 90°.
Volume	2139.14(15) Å^3	
Z	4	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	0.199 mm^{-1}	
F(000)	936	
Crystal size	0.2 x 0.1 x 0.08 mm^3	
Theta range for data collection	2.889 to 25.683°.	
Index ranges	-20<=h<=12, -8<=k<=9, -19<=l<=20	
Reflections collected	12263	
Independent reflections	4067 [R(int) = 0.0298]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.7453 and 0.6625	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4067 / 0 / 284	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0842	
R indices (all data)	R1 = 0.0494, wR2 = 0.0903	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.294 and -0.415 e.Å^{-3}	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3)
for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4474(1)	7626(1)	5195(1)	13(1)
F(1)	6144(1)	7230(2)	9197(1)	33(1)
O(1)	5167(1)	7077(2)	4894(1)	18(1)
N(1)	3813(1)	6070(2)	4996(1)	14(1)
C(1)	5352(1)	7569(2)	8856(1)	23(1)
F(2)	5170(1)	9007(2)	9203(1)	40(1)
O(2)	4045(1)	9173(2)	4903(1)	18(1)
C(2)	5176(1)	7696(2)	7947(1)	17(1)
F(3)	4914(1)	6321(2)	9096(1)	44(1)
C(3)	5644(1)	6737(2)	7529(1)	19(1)
C(4)	5450(1)	6760(2)	6687(1)	18(1)
C(5)	4792(1)	7754(2)	6272(1)	14(1)
C(6)	4333(1)	8748(2)	6684(1)	18(1)
C(7)	4528(1)	8707(2)	7529(1)	20(1)
C(8)	3031(1)	6214(2)	5257(1)	15(1)
C(9)	2451(1)	4767(2)	4898(1)	15(1)
C(10)	2742(1)	2942(2)	5176(1)	14(1)
C(11)	2094(1)	1631(2)	4736(1)	17(1)
C(12)	1944(1)	1742(2)	3818(1)	16(1)
C(13)	2526(1)	1088(2)	3430(1)	18(1)
C(14)	2406(1)	1231(2)	2589(1)	20(1)
C(15)	1716(1)	2046(2)	2130(1)	21(1)
C(16)	1131(1)	2700(2)	2509(1)	21(1)
C(17)	1243(1)	2544(2)	3344(1)	20(1)
C(18)	2944(1)	2794(2)	6097(1)	14(1)
C(19)	2359(1)	2339(3)	6527(1)	22(1)
C(20)	2560(1)	2280(3)	7371(1)	24(1)
C(21)	3344(1)	2726(2)	7823(1)	18(1)
C(22)	3925(1)	3190(2)	7398(1)	18(1)
C(23)	3734(1)	3198(2)	6555(1)	16(1)
C(24)	3563(1)	2678(3)	8742(1)	27(1)

Table S5. Bond lengths [Å] and angles [°] for **2a**.

S(1)-O(1)	1.4351(12)	C(13)-H(13)	0.9500
S(1)-N(1)	1.6211(15)	C(13)-C(14)	1.394(2)
S(1)-O(2)	1.4295(12)	C(14)-H(14)	0.9500
S(1)-C(5)	1.7748(17)	C(14)-C(15)	1.381(2)
F(1)-C(1)	1.334(2)	C(15)-H(15)	0.9500
N(1)-H(1)	0.82(2)	C(15)-C(16)	1.387(3)
N(1)-C(8)	1.477(2)	C(16)-H(16)	0.9500
C(1)-F(2)	1.336(2)	C(16)-C(17)	1.386(2)
C(1)-C(2)	1.499(2)	C(17)-H(17)	0.9500
C(1)-F(3)	1.338(2)	C(18)-C(19)	1.395(2)
C(2)-C(3)	1.391(2)	C(18)-C(23)	1.395(2)
C(2)-C(7)	1.387(2)	C(19)-H(19)	0.9500
C(3)-H(3)	0.9500	C(19)-C(20)	1.388(2)
C(3)-C(4)	1.385(2)	C(20)-H(20)	0.9500
C(4)-H(4)	0.9500	C(20)-C(21)	1.391(2)
C(4)-C(5)	1.389(2)	C(21)-C(22)	1.385(2)
C(5)-C(6)	1.389(2)	C(21)-C(24)	1.512(2)
C(6)-H(6)	0.9500	C(22)-H(22)	0.9500
C(6)-C(7)	1.390(2)	C(22)-C(23)	1.386(2)
C(7)-H(7)	0.9500	C(23)-H(23)	0.9500
C(8)-H(8A)	0.9900	C(24)-H(24A)	0.9800
C(8)-H(8B)	0.9900	C(24)-H(24B)	0.9800
C(8)-C(9)	1.517(2)	C(24)-H(24C)	0.9800
C(9)-H(9A)	0.9900		
C(9)-H(9B)	0.9900	O(1)-S(1)-N(1)	105.58(7)
C(9)-C(10)	1.542(2)	O(1)-S(1)-C(5)	108.34(7)
C(10)-H(10)	1.0000	N(1)-S(1)-C(5)	106.00(7)
C(10)-C(11)	1.544(2)	O(2)-S(1)-O(1)	120.56(7)
C(10)-C(18)	1.520(2)	O(2)-S(1)-N(1)	107.56(7)
C(11)-H(11A)	0.9900	O(2)-S(1)-C(5)	107.93(8)
C(11)-H(11B)	0.9900	S(1)-N(1)-H(1)	110.8(13)
C(11)-C(12)	1.517(2)	C(8)-N(1)-S(1)	119.07(11)
C(12)-C(13)	1.392(2)	C(8)-N(1)-H(1)	116.1(13)
C(12)-C(17)	1.396(2)	F(1)-C(1)-F(2)	106.40(14)

F(1)-C(1)-C(2)	112.80(15)	C(9)-C(10)-C(11)	109.38(13)
F(1)-C(1)-F(3)	106.28(15)	C(11)-C(10)-H(10)	107.5
F(2)-C(1)-C(2)	112.74(15)	C(18)-C(10)-C(9)	111.07(13)
F(2)-C(1)-F(3)	106.23(15)	C(18)-C(10)-H(10)	107.5
F(3)-C(1)-C(2)	111.89(15)	C(18)-C(10)-C(11)	113.63(13)
C(3)-C(2)-C(1)	119.36(16)	C(10)-C(11)-H(11A)	109.1
C(7)-C(2)-C(1)	119.88(15)	C(10)-C(11)-H(11B)	109.1
C(7)-C(2)-C(3)	120.70(16)	H(11A)-C(11)-H(11B)	107.9
C(2)-C(3)-H(3)	120.2	C(12)-C(11)-C(10)	112.32(13)
C(4)-C(3)-C(2)	119.69(16)	C(12)-C(11)-H(11A)	109.1
C(4)-C(3)-H(3)	120.2	C(12)-C(11)-H(11B)	109.1
C(3)-C(4)-H(4)	120.3	C(13)-C(12)-C(11)	120.06(15)
C(3)-C(4)-C(5)	119.34(16)	C(13)-C(12)-C(17)	118.37(16)
C(5)-C(4)-H(4)	120.3	C(17)-C(12)-C(11)	121.53(15)
C(4)-C(5)-S(1)	119.52(13)	C(12)-C(13)-H(13)	119.7
C(4)-C(5)-C(6)	121.35(16)	C(12)-C(13)-C(14)	120.51(16)
C(6)-C(5)-S(1)	118.94(13)	C(14)-C(13)-H(13)	119.7
C(5)-C(6)-H(6)	120.5	C(13)-C(14)-H(14)	119.8
C(5)-C(6)-C(7)	118.96(16)	C(15)-C(14)-C(13)	120.47(16)
C(7)-C(6)-H(6)	120.5	C(15)-C(14)-H(14)	119.8
C(2)-C(7)-C(6)	119.93(16)	C(14)-C(15)-H(15)	120.2
C(2)-C(7)-H(7)	120.0	C(14)-C(15)-C(16)	119.53(16)
C(6)-C(7)-H(7)	120.0	C(16)-C(15)-H(15)	120.2
N(1)-C(8)-H(8A)	109.6	C(15)-C(16)-H(16)	119.9
N(1)-C(8)-H(8B)	109.6	C(17)-C(16)-C(15)	120.14(16)
N(1)-C(8)-C(9)	110.29(13)	C(17)-C(16)-H(16)	119.9
H(8A)-C(8)-H(8B)	108.1	C(12)-C(17)-H(17)	119.5
C(9)-C(8)-H(8A)	109.6	C(16)-C(17)-C(12)	120.96(16)
C(9)-C(8)-H(8B)	109.6	C(16)-C(17)-H(17)	119.5
C(8)-C(9)-H(9A)	108.2	C(19)-C(18)-C(10)	123.01(15)
C(8)-C(9)-H(9B)	108.2	C(19)-C(18)-C(23)	116.97(15)
C(8)-C(9)-C(10)	116.23(13)	C(23)-C(18)-C(10)	119.95(14)
H(9A)-C(9)-H(9B)	107.4	C(18)-C(19)-H(19)	119.4
C(10)-C(9)-H(9A)	108.2	C(20)-C(19)-C(18)	121.18(16)
C(10)-C(9)-H(9B)	108.2	C(20)-C(19)-H(19)	119.4
C(9)-C(10)-H(10)	107.5	C(19)-C(20)-H(20)	119.3

C(19)-C(20)-C(21)	121.47(16)	C(22)-C(23)-C(18)	121.57(15)
C(21)-C(20)-H(20)	119.3	C(22)-C(23)-H(23)	119.2
C(20)-C(21)-C(24)	121.52(16)	C(21)-C(24)-H(24A)	109.5
C(22)-C(21)-C(20)	117.45(15)	C(21)-C(24)-H(24B)	109.5
C(22)-C(21)-C(24)	121.03(16)	C(21)-C(24)-H(24C)	109.5
C(21)-C(22)-H(22)	119.3	H(24A)-C(24)-H(24B)	109.5
C(21)-C(22)-C(23)	121.31(16)	H(24A)-C(24)-H(24C)	109.5
C(23)-C(22)-H(22)	119.3	H(24B)-C(24)-H(24C)	109.5
C(18)-C(23)-H(23)	119.2		

Table S6. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	14(1)	11(1)	14(1)	1(1)	1(1)	-1(1)
F(1)	29(1)	46(1)	20(1)	-3(1)	-7(1)	3(1)
O(1)	18(1)	16(1)	20(1)	2(1)	7(1)	-1(1)
N(1)	15(1)	10(1)	16(1)	0(1)	3(1)	1(1)
C(1)	24(1)	21(1)	20(1)	-2(1)	1(1)	-2(1)
F(2)	62(1)	39(1)	19(1)	-7(1)	7(1)	16(1)
O(2)	19(1)	13(1)	21(1)	4(1)	1(1)	1(1)
C(2)	17(1)	14(1)	17(1)	-2(1)	1(1)	-5(1)
F(3)	53(1)	52(1)	24(1)	8(1)	5(1)	-26(1)
C(3)	16(1)	17(1)	21(1)	2(1)	0(1)	3(1)
C(4)	16(1)	17(1)	20(1)	-1(1)	3(1)	4(1)
C(5)	14(1)	10(1)	16(1)	-2(1)	1(1)	-4(1)
C(6)	15(1)	15(1)	22(1)	-3(1)	-2(1)	2(1)
C(7)	21(1)	18(1)	20(1)	-6(1)	3(1)	2(1)
C(8)	15(1)	14(1)	15(1)	-1(1)	3(1)	0(1)
C(9)	13(1)	16(1)	15(1)	-1(1)	1(1)	-1(1)
C(10)	13(1)	15(1)	13(1)	-3(1)	3(1)	-3(1)
C(11)	18(1)	15(1)	17(1)	-2(1)	4(1)	-3(1)
C(12)	16(1)	12(1)	17(1)	-4(1)	1(1)	-5(1)
C(13)	18(1)	14(1)	19(1)	0(1)	0(1)	-1(1)
C(14)	22(1)	19(1)	20(1)	-4(1)	5(1)	-3(1)
C(15)	27(1)	20(1)	13(1)	-2(1)	0(1)	-7(1)
C(16)	20(1)	18(1)	21(1)	0(1)	-6(1)	-1(1)
C(17)	15(1)	19(1)	24(1)	-5(1)	3(1)	-2(1)
C(18)	17(1)	10(1)	15(1)	-1(1)	5(1)	1(1)
C(19)	16(1)	31(1)	19(1)	-2(1)	4(1)	-5(1)
C(20)	21(1)	32(1)	21(1)	0(1)	11(1)	-6(1)
C(21)	22(1)	18(1)	15(1)	1(1)	6(1)	2(1)
C(22)	14(1)	20(1)	18(1)	1(1)	1(1)	0(1)
C(23)	16(1)	17(1)	16(1)	1(1)	6(1)	0(1)
C(24)	31(1)	36(1)	16(1)	3(1)	7(1)	-3(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2a**.

	x	y	z	U(eq)
H(1)	4048(11)	5140(30)	5075(10)	16
H(3)	6096	6070	7821	23
H(4)	5763	6103	6396	22
H(6)	3894	9446	6393	22
H(7)	4217	9371	7821	24
H(8A)	2766	7328	5076	18
H(8B)	3148	6171	5858	18
H(9A)	2353	4818	4298	18
H(9B)	1914	4969	5034	18
H(10)	3264	2722	4999	16
H(11A)	2284	461	4915	20
H(11B)	1567	1836	4893	20
H(13)	3007	539	3741	21
H(14)	2803	765	2330	24
H(15)	1641	2159	1558	25
H(16)	652	3256	2196	26
H(17)	837	2989	3598	24
H(19)	1812	2064	6236	26
H(20)	2154	1929	7646	29
H(22)	4465	3509	7691	21
H(23)	4152	3486	6283	19
H(24A)	3566	1488	8927	41
H(24B)	3153	3333	8946	41
H(24C)	4111	3183	8950	41

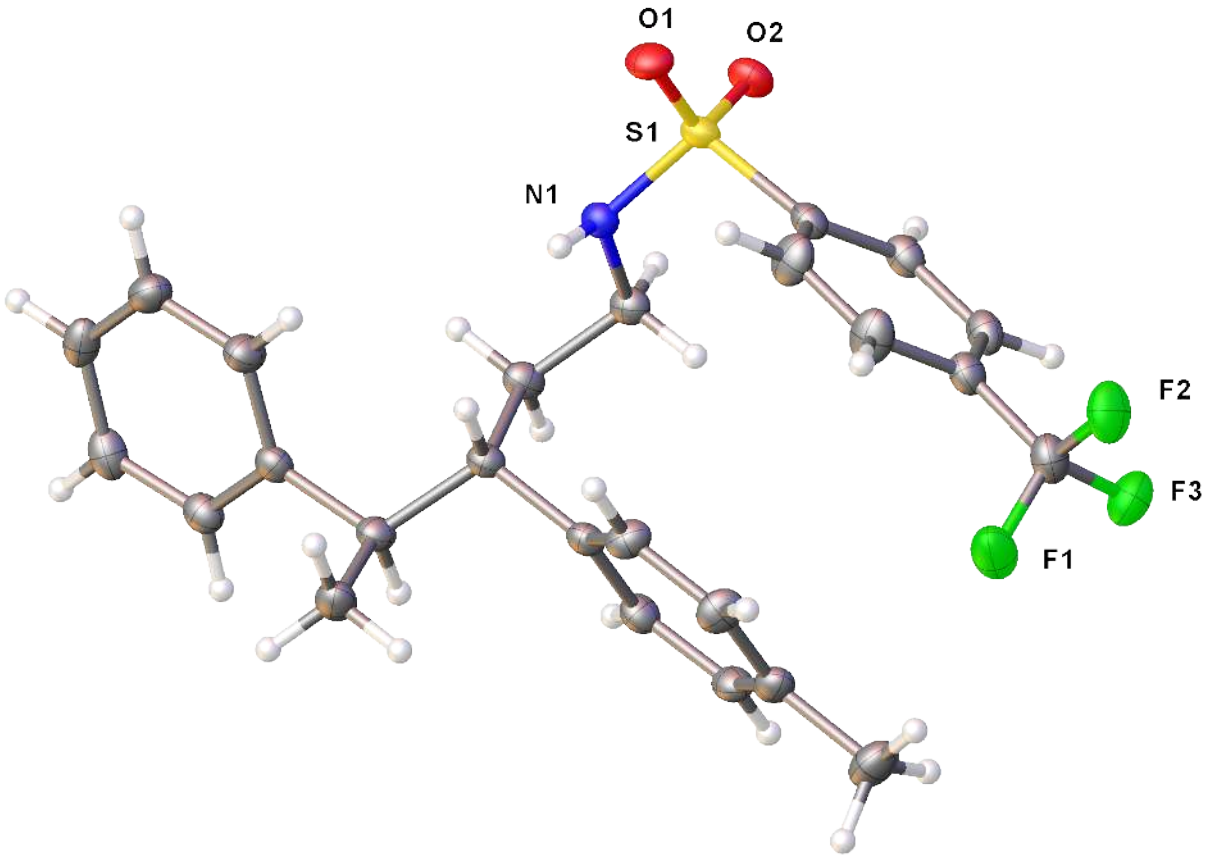

O1
O2
S1
N1
F2
F3
F1

Table S8. Crystal data and structure refinement for **2ab**.

Identification code	engle232	
Empirical formula	C25 H26 F3 N O2 S	
Formula weight	461.53	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 1 21/c 1	
Unit cell dimensions	a = 28.1491(7) Å	α = 90°.
	b = 9.7037(3) Å	β = 123.7560(10)°.
	c = 19.9138(5) Å	γ = 90°.
Volume	4522.4(2) Å^3	
Z	8	
Density (calculated)	1.356 Mg/m^3	
Absorption coefficient	1.682 mm^{-1}	
F(000)	1936	
Crystal size	0.175 x 0.15 x 0.12 mm^3	
Crystal color, habit	colorless block	
Theta range for data collection	3.777 to 69.496°.	
Index ranges	-33<=h<=33, -11<=k<=11, -24<=l<=21	
Reflections collected	32376	
Independent reflections	4121 [R(int) = 0.0375]	
Completeness to theta = 25.242°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7532 and 0.6812	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4121 / 1 / 294	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0341, wR2 = 0.0858	
R indices (all data)	R1 = 0.0391, wR2 = 0.0898	
Largest diff. peak and hole	0.475 and -0.425 e.Å^{-3}	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2ab**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	7594(1)	3876(1)	7240(1)	21(1)
F(1)	5537(1)	2644(1)	3454(1)	43(1)
F(2)	6154(1)	3388(1)	3231(1)	38(1)
F(3)	5611(1)	4821(1)	3324(1)	37(1)
O(1)	8033(1)	2878(1)	7473(1)	29(1)
O(2)	7747(1)	5286(1)	7490(1)	27(1)
N(1)	7218(1)	3352(1)	7574(1)	21(1)
C(1)	6722(1)	4188(2)	7400(1)	22(1)
C(2)	6425(1)	3495(2)	7756(1)	22(1)
C(3)	6140(1)	2117(2)	7351(1)	19(1)
C(4)	5853(1)	1409(2)	7736(1)	22(1)
C(5)	5637(1)	-25(2)	7365(1)	28(1)
C(6)	5713(1)	2313(2)	6451(1)	19(1)
C(7)	5759(1)	1593(2)	5885(1)	24(1)
C(8)	5368(1)	1784(2)	5062(1)	27(1)
C(9)	4920(1)	2714(2)	4772(1)	24(1)
C(10)	4876(1)	3446(2)	5336(1)	24(1)
C(11)	5262(1)	3246(2)	6158(1)	22(1)
C(12)	4489(1)	2930(2)	3880(1)	34(1)
C(13)	6230(1)	1277(2)	8647(1)	21(1)
C(14)	6811(1)	960(2)	9066(1)	26(1)
C(15)	7139(1)	836(2)	9898(1)	29(1)
C(16)	6896(1)	1005(2)	10335(1)	28(1)
C(17)	6316(1)	1284(2)	9928(1)	27(1)
C(18)	5990(1)	1425(2)	9095(1)	23(1)
C(19)	7130(1)	3870(2)	6172(1)	21(1)
C(20)	6844(1)	5059(2)	5763(1)	23(1)
C(21)	6453(1)	5002(2)	4933(1)	24(1)
C(22)	6347(1)	3762(2)	4530(1)	24(1)
C(23)	6641(1)	2575(2)	4942(1)	33(1)
C(24)	7036(1)	2628(2)	5766(1)	31(1)
C(25)	5914(1)	3661(2)	3640(1)	29(1)

Table S10. Bond lengths [Å] and angles [°] for **2ab**.

S(1)-O(1)	1.4283(12)	C(18)-H(18)	0.9500
S(1)-O(2)	1.4380(12)	C(19)-C(20)	1.383(2)
S(1)-N(1)	1.6146(13)	C(19)-C(24)	1.391(2)
S(1)-C(19)	1.7725(16)	C(20)-H(20)	0.9500
F(1)-C(25)	1.343(2)	C(20)-C(21)	1.386(2)
F(2)-C(25)	1.3398(19)	C(21)-H(21)	0.9500
F(3)-C(25)	1.340(2)	C(21)-C(22)	1.384(2)
N(1)-H(1)	0.858(15)	C(22)-C(23)	1.389(2)
N(1)-C(1)	1.4795(19)	C(22)-C(25)	1.496(2)
C(1)-H(1A)	0.9900	C(23)-H(23)	0.9500
C(1)-H(1B)	0.9900	C(23)-C(24)	1.380(3)
C(1)-C(2)	1.521(2)	C(24)-H(24)	0.9500
C(2)-H(2A)	0.9900		
C(2)-H(2B)	0.9900	O(1)-S(1)-O(2)	119.60(7)
C(2)-C(3)	1.537(2)	O(1)-S(1)-N(1)	107.36(7)
C(3)-H(3)	1.0000	O(1)-S(1)-C(19)	108.41(7)
C(3)-C(4)	1.550(2)	O(2)-S(1)-N(1)	107.19(7)
C(3)-C(6)	1.517(2)	O(2)-S(1)-C(19)	107.36(7)
C(4)-H(4)	1.0000	N(1)-S(1)-C(19)	106.17(7)
C(4)-C(5)	1.534(2)	S(1)-N(1)-H(1)	110.6(12)
C(4)-C(13)	1.515(2)	C(1)-N(1)-S(1)	118.70(10)
C(5)-H(5A)	0.9800	C(1)-N(1)-H(1)	116.0(12)
C(5)-H(5B)	0.9800	N(1)-C(1)-H(1A)	109.7
C(5)-H(5C)	0.9800	N(1)-C(1)-H(1B)	109.7
C(6)-C(7)	1.392(2)	N(1)-C(1)-C(2)	109.90(12)
C(6)-C(11)	1.397(2)	H(1A)-C(1)-H(1B)	108.2
C(7)-H(7)	0.9500	C(2)-C(1)-H(1A)	109.7
C(7)-C(8)	1.388(2)	C(2)-C(1)-H(1B)	109.7
C(8)-H(8)	0.9500	C(1)-C(2)-H(2A)	108.8
C(8)-C(9)	1.390(2)	C(1)-C(2)-H(2B)	108.8
C(9)-C(10)	1.391(2)	C(1)-C(2)-C(3)	113.69(12)
C(9)-C(12)	1.508(2)	H(2A)-C(2)-H(2B)	107.7
C(10)-H(10)	0.9500	C(3)-C(2)-H(2A)	108.8
C(10)-C(11)	1.385(2)	C(3)-C(2)-H(2B)	108.8
C(11)-H(11)	0.9500	C(2)-C(3)-H(3)	107.5
C(12)-H(12A)	0.9800	C(2)-C(3)-C(4)	112.92(12)
C(12)-H(12B)	0.9800	C(4)-C(3)-H(3)	107.5
C(12)-H(12C)	0.9800	C(6)-C(3)-C(2)	110.50(12)
C(13)-C(14)	1.398(2)	C(6)-C(3)-H(3)	107.5
C(13)-C(18)	1.394(2)	C(6)-C(3)-C(4)	110.59(12)
C(14)-H(14)	0.9500	C(3)-C(4)-H(4)	107.6
C(14)-C(15)	1.384(2)	C(5)-C(4)-C(3)	109.84(12)
C(15)-H(15)	0.9500	C(5)-C(4)-H(4)	107.6
C(15)-C(16)	1.382(2)	C(13)-C(4)-C(3)	114.82(12)
C(16)-H(16)	0.9500	C(13)-C(4)-H(4)	107.6
C(16)-C(17)	1.385(3)	C(13)-C(4)-C(5)	109.09(13)
C(17)-H(17)	0.9500	C(4)-C(5)-H(5A)	109.5
C(17)-C(18)	1.385(2)	C(4)-C(5)-H(5B)	109.5

C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-C(3)	121.63(13)
C(7)-C(6)-C(11)	117.40(14)
C(11)-C(6)-C(3)	120.97(13)
C(6)-C(7)-H(7)	119.4
C(8)-C(7)-C(6)	121.21(15)
C(8)-C(7)-H(7)	119.4
C(7)-C(8)-H(8)	119.3
C(7)-C(8)-C(9)	121.31(15)
C(9)-C(8)-H(8)	119.3
C(8)-C(9)-C(10)	117.55(15)
C(8)-C(9)-C(12)	122.03(15)
C(10)-C(9)-C(12)	120.42(15)
C(9)-C(10)-H(10)	119.3
C(11)-C(10)-C(9)	121.34(15)
C(11)-C(10)-H(10)	119.3
C(6)-C(11)-H(11)	119.4
C(10)-C(11)-C(6)	121.17(14)
C(10)-C(11)-H(11)	119.4
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(4)	122.75(14)
C(18)-C(13)-C(4)	119.52(14)
C(18)-C(13)-C(14)	117.69(15)
C(13)-C(14)-H(14)	119.6
C(15)-C(14)-C(13)	120.83(15)
C(15)-C(14)-H(14)	119.6
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-C(14)	120.74(16)
C(16)-C(15)-H(15)	119.6
C(15)-C(16)-H(16)	120.4
C(15)-C(16)-C(17)	119.17(15)
C(17)-C(16)-H(16)	120.4
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-C(16)	120.14(15)
C(18)-C(17)-H(17)	119.9
C(13)-C(18)-H(18)	119.3
C(17)-C(18)-C(13)	121.40(15)
C(17)-C(18)-H(18)	119.3
C(20)-C(19)-S(1)	120.22(12)
C(20)-C(19)-C(24)	121.31(15)
C(24)-C(19)-S(1)	118.34(12)
C(19)-C(20)-H(20)	120.5
C(19)-C(20)-C(21)	119.07(14)
C(21)-C(20)-H(20)	120.5
C(20)-C(21)-H(21)	120.1
C(22)-C(21)-C(20)	119.85(14)
C(22)-C(21)-H(21)	120.1
C(21)-C(22)-C(23)	120.86(16)
C(21)-C(22)-C(25)	121.04(15)
C(23)-C(22)-C(25)	118.10(15)
C(22)-C(23)-H(23)	120.2
C(24)-C(23)-C(22)	119.55(15)
C(24)-C(23)-H(23)	120.2
C(19)-C(24)-H(24)	120.3
C(23)-C(24)-C(19)	119.33(15)
C(23)-C(24)-H(24)	120.3
F(1)-C(25)-C(22)	111.92(13)
F(2)-C(25)-F(1)	106.00(14)
F(2)-C(25)-C(22)	112.28(14)
F(3)-C(25)-F(1)	106.78(14)
F(3)-C(25)-F(2)	106.54(13)
F(3)-C(25)-C(22)	112.86(14)

Table S11. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2ab**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	17(1)	20(1)	26(1)	0(1)	11(1)	-3(1)
F(1)	48(1)	45(1)	29(1)	-3(1)	17(1)	-19(1)
F(2)	55(1)	37(1)	33(1)	3(1)	31(1)	6(1)
F(3)	39(1)	37(1)	28(1)	7(1)	16(1)	10(1)
O(1)	19(1)	31(1)	35(1)	2(1)	13(1)	3(1)
O(2)	26(1)	23(1)	33(1)	-4(1)	17(1)	-7(1)
N(1)	20(1)	18(1)	23(1)	0(1)	11(1)	-1(1)
C(1)	22(1)	18(1)	26(1)	-2(1)	13(1)	0(1)
C(2)	23(1)	23(1)	22(1)	-5(1)	14(1)	-3(1)
C(3)	18(1)	19(1)	22(1)	-2(1)	12(1)	-1(1)
C(4)	18(1)	25(1)	23(1)	-1(1)	12(1)	-1(1)
C(5)	27(1)	26(1)	24(1)	-1(1)	11(1)	-7(1)
C(6)	18(1)	17(1)	23(1)	-2(1)	12(1)	-3(1)
C(7)	22(1)	22(1)	25(1)	-3(1)	10(1)	2(1)
C(8)	29(1)	25(1)	23(1)	-6(1)	12(1)	0(1)
C(9)	21(1)	22(1)	24(1)	-1(1)	9(1)	-5(1)
C(10)	18(1)	24(1)	30(1)	3(1)	13(1)	2(1)
C(11)	24(1)	22(1)	27(1)	-1(1)	18(1)	0(1)
C(12)	31(1)	33(1)	25(1)	-1(1)	6(1)	0(1)
C(13)	22(1)	18(1)	24(1)	-2(1)	13(1)	-4(1)
C(14)	22(1)	32(1)	25(1)	0(1)	14(1)	-1(1)
C(15)	23(1)	29(1)	26(1)	1(1)	9(1)	-2(1)
C(16)	38(1)	19(1)	20(1)	-2(1)	12(1)	-5(1)
C(17)	42(1)	19(1)	30(1)	-2(1)	26(1)	-1(1)
C(18)	25(1)	19(1)	29(1)	0(1)	17(1)	0(1)
C(19)	21(1)	19(1)	27(1)	1(1)	16(1)	-2(1)
C(20)	28(1)	17(1)	31(1)	0(1)	20(1)	0(1)
C(21)	29(1)	18(1)	31(1)	5(1)	21(1)	4(1)
C(22)	28(1)	22(1)	27(1)	2(1)	19(1)	0(1)

C(23)	45(1)	18(1)	31(1)	-2(1)	19(1)	2(1)
C(24)	38(1)	18(1)	31(1)	3(1)	16(1)	5(1)
C(25)	37(1)	26(1)	29(1)	2(1)	21(1)	-1(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2ab**.

	x	y	z	U(eq)
H(1)	7163(8)	2479(15)	7507(11)	25
H(1A)	6451	4290	6809	26
H(1B)	6853	5119	7636	26
H(2A)	6130	4128	7703	26
H(2B)	6708	3334	8339	26
H(3)	6447	1486	7424	23
H(4)	5513	1974	7597	26
H(5A)	5962	-599	7483	41
H(5B)	5369	62	6778	41
H(5C)	5443	-453	7595	41
H(7)	6064	958	6065	29
H(8)	5408	1270	4690	33
H(10)	4576	4097	5155	29
H(11)	5218	3751	6529	27
H(12A)	4157	2334	3697	52
H(12B)	4663	2701	3584	52
H(12C)	4366	3896	3781	52
H(14)	6985	829	8775	31
H(15)	7534	632	10173	35
H(16)	7123	932	10907	33
H(17)	6143	1379	10220	33
H(18)	5594	1627	8824	28
H(20)	6915	5901	6046	28
H(21)	6258	5813	4642	29

H(23)	6570	1732	4658	39
H(24)	7241	1824	6054	37

Table S12. Hydrogen bonds for **2ab** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(2)#1	0.858(15)	2.142(15)	2.9811(17)	165.6(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y-1/2,-z+3/2

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[17] CCDC 2011491 (**2a**) and 2011492 (**(±)-2ab**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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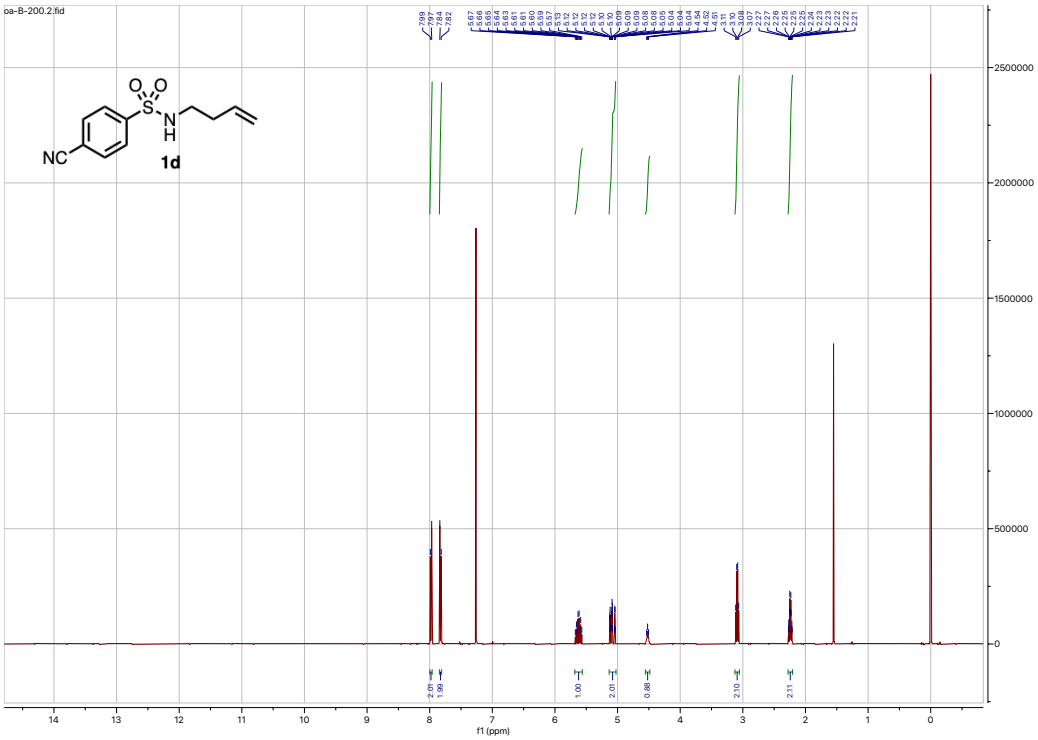
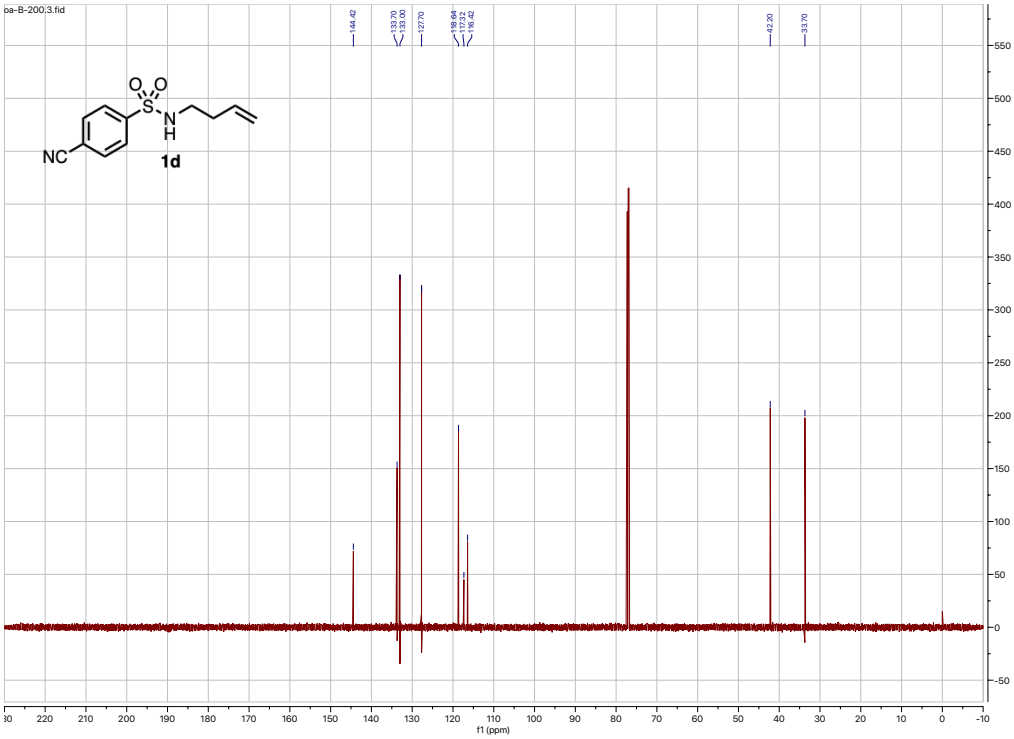
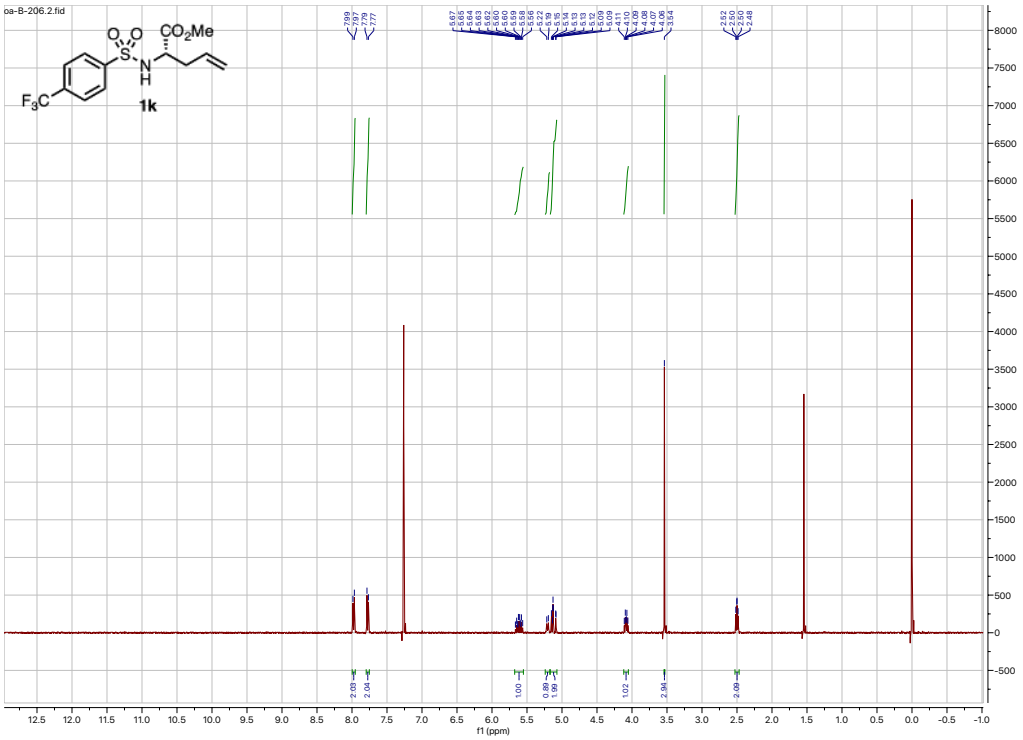
NMR Spectra



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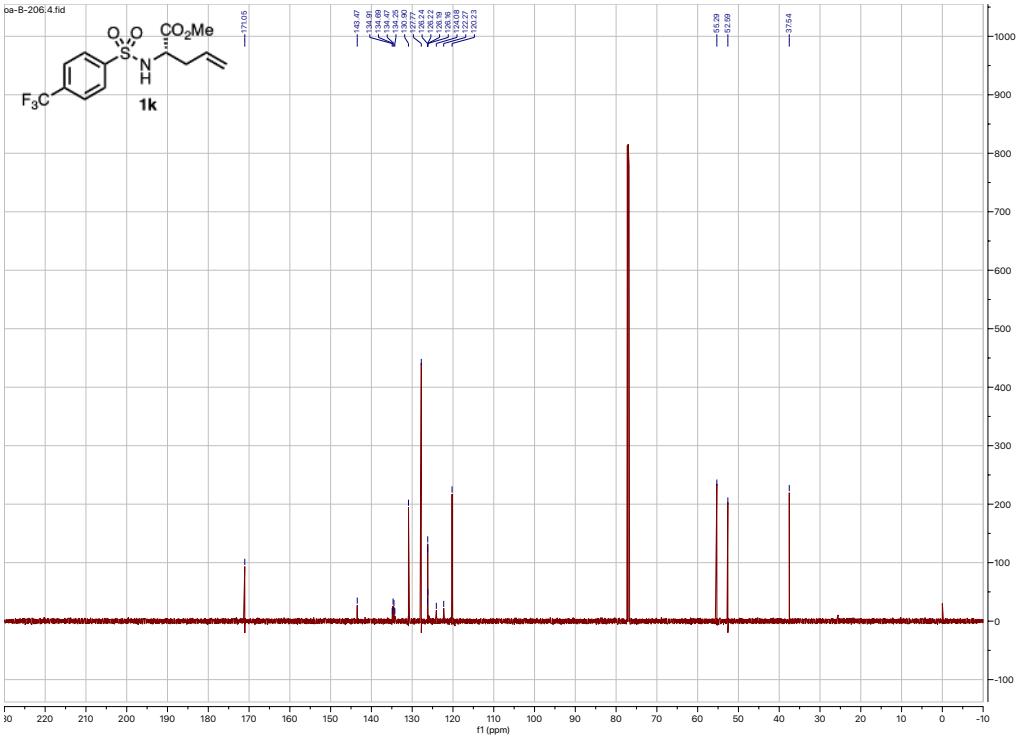
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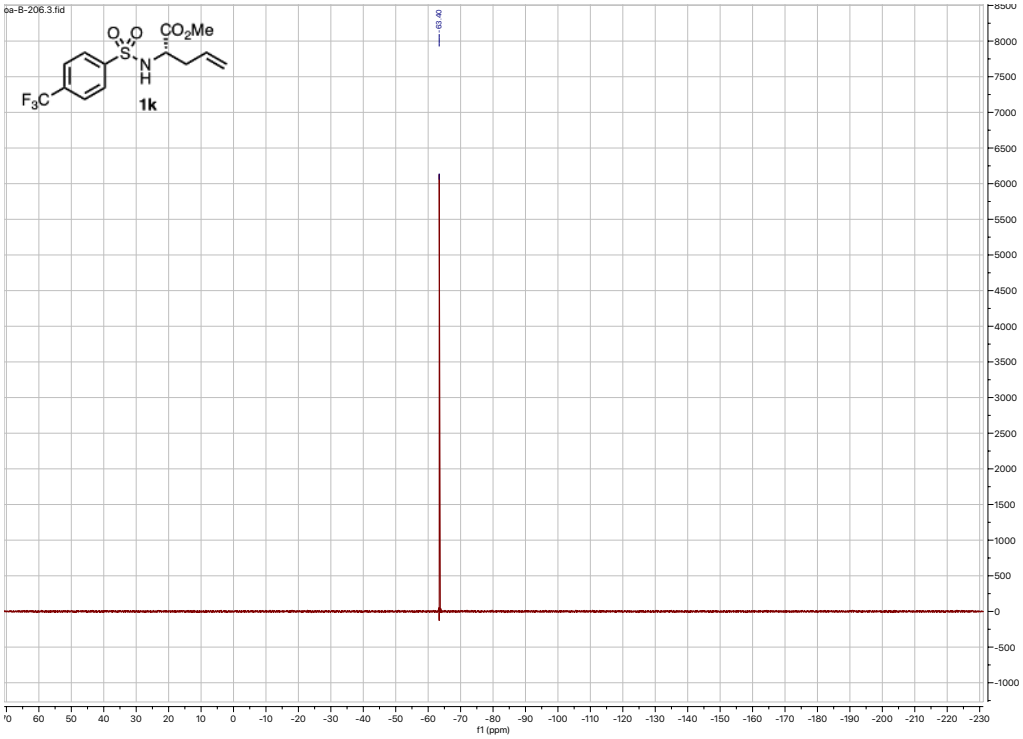
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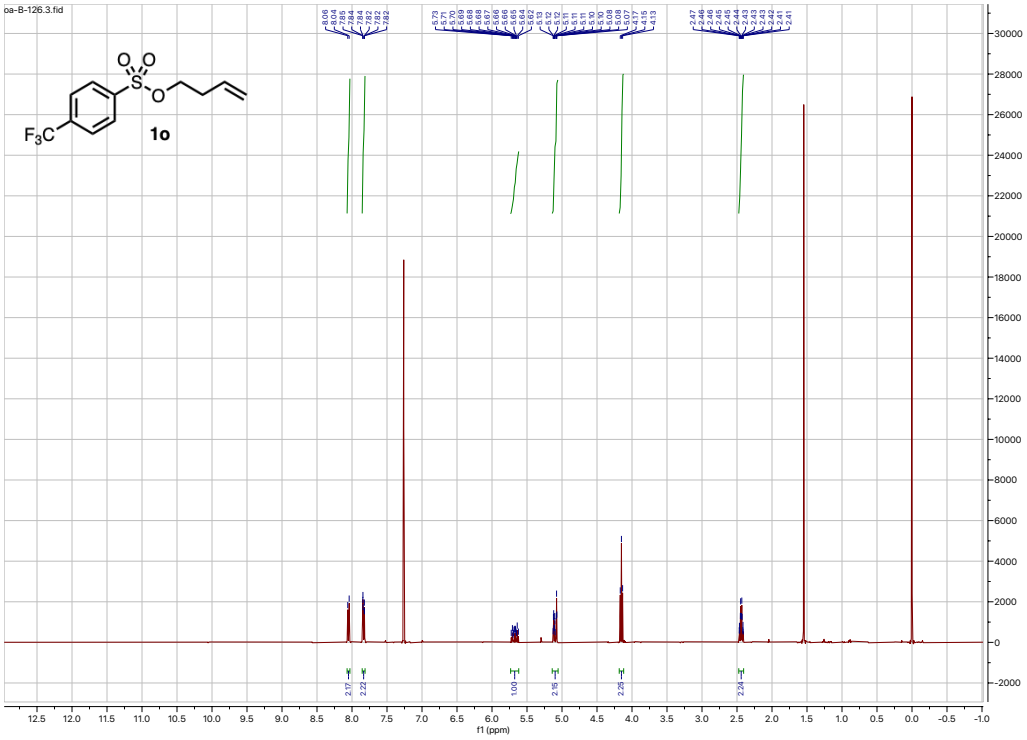
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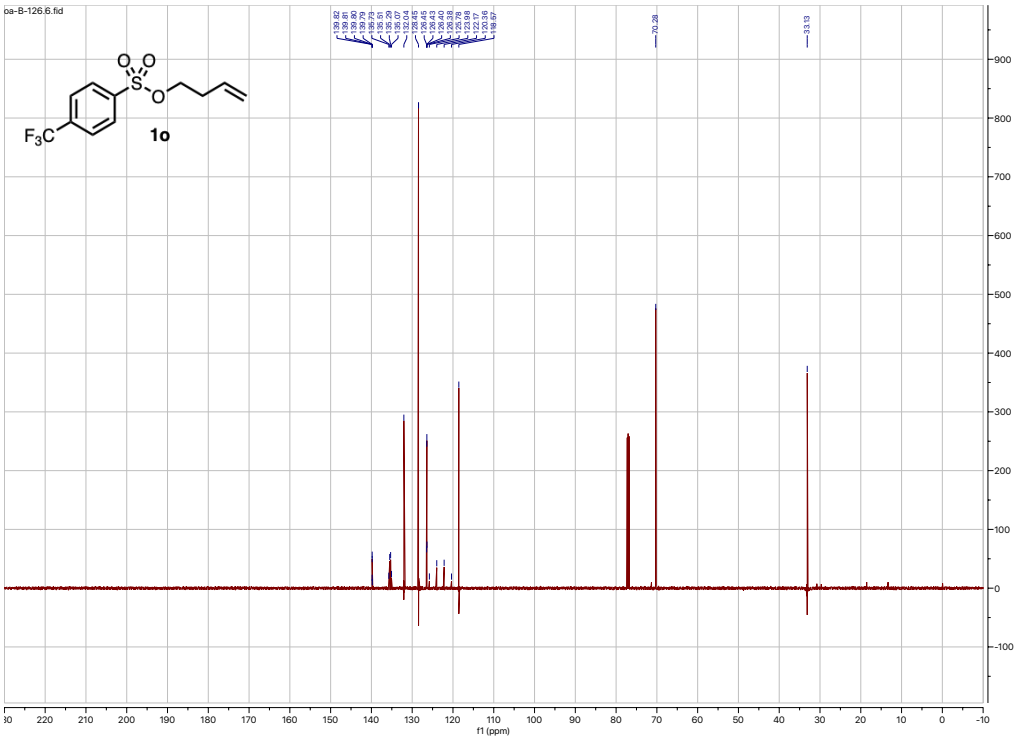
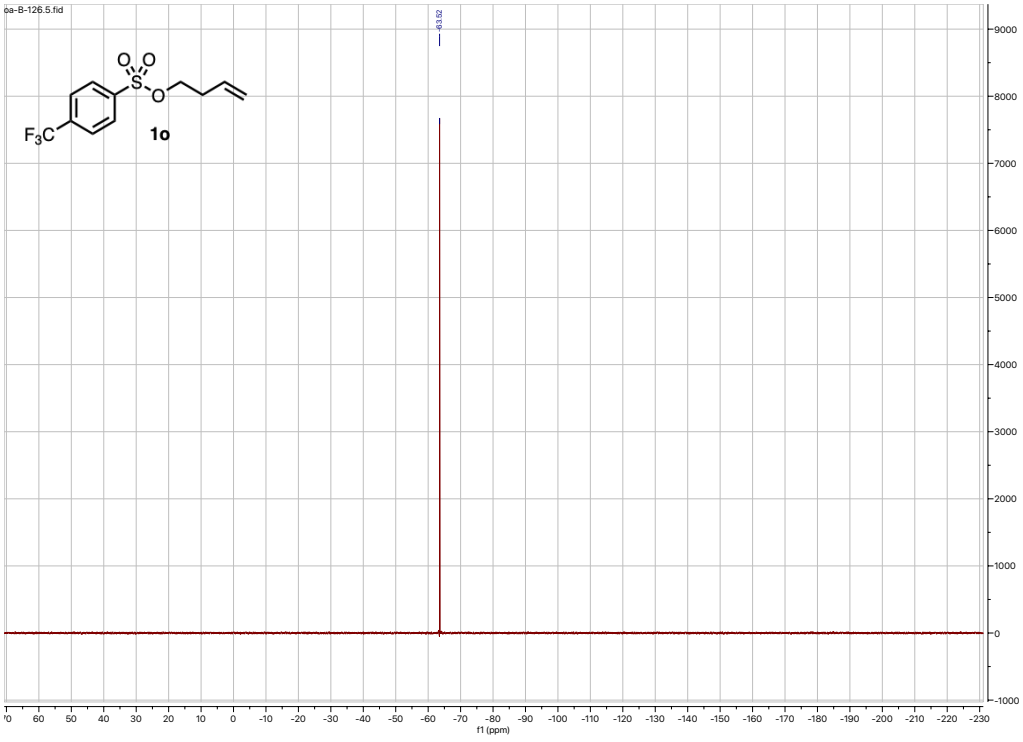
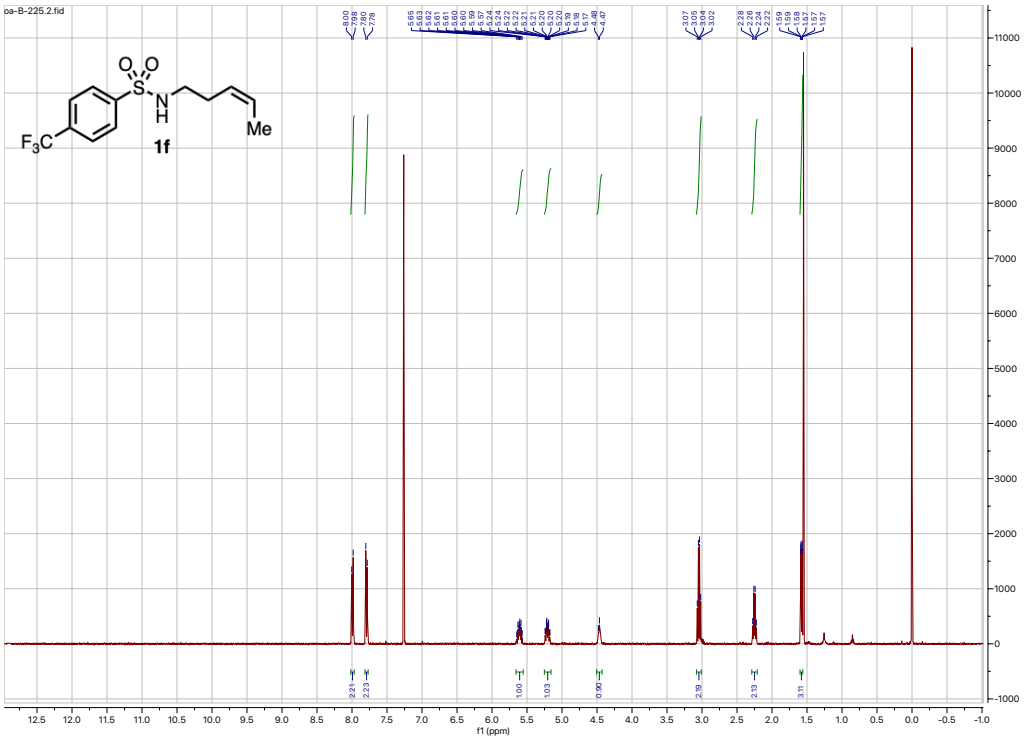
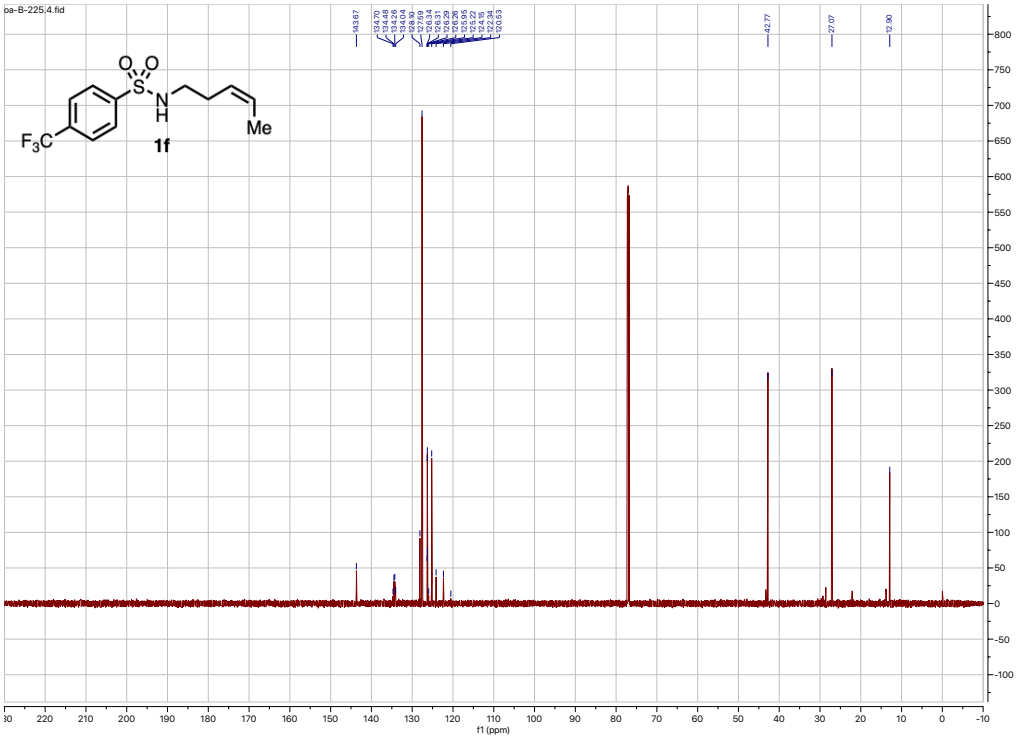
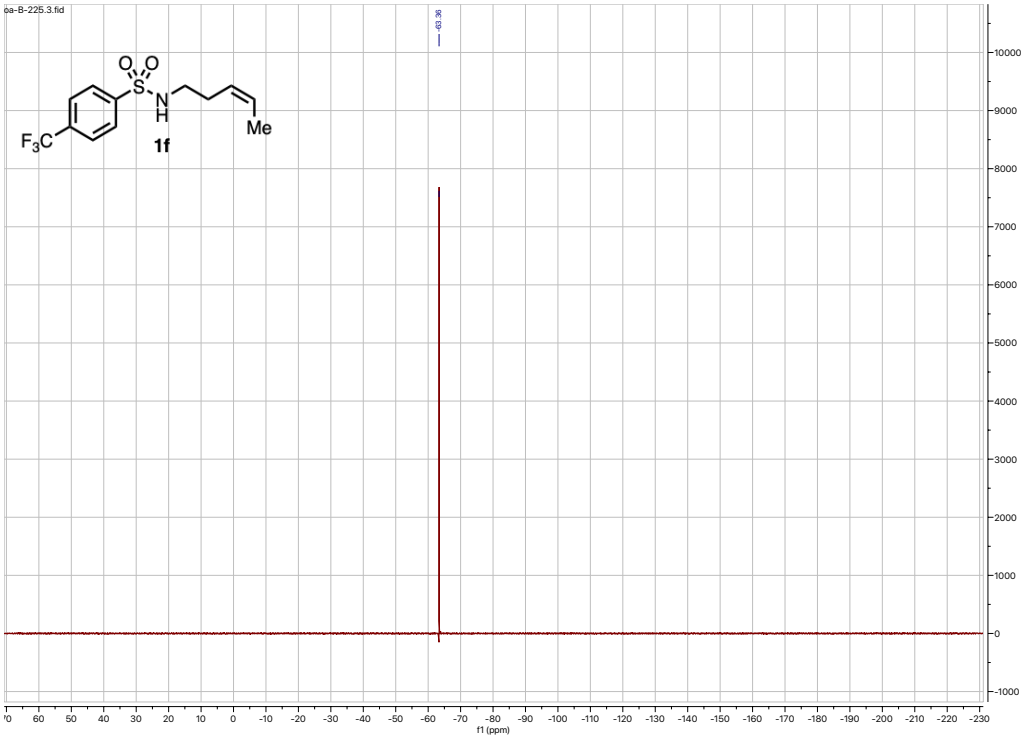
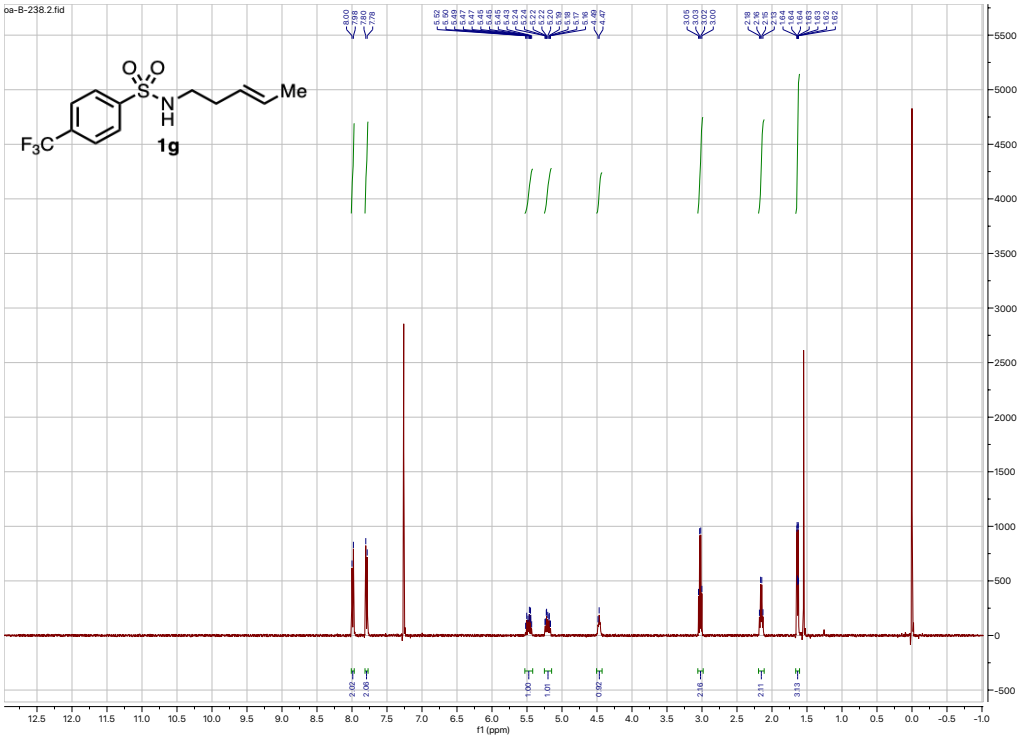

oa-B-126.6.fid
1o
70.28
33.13
f1 (ppm)

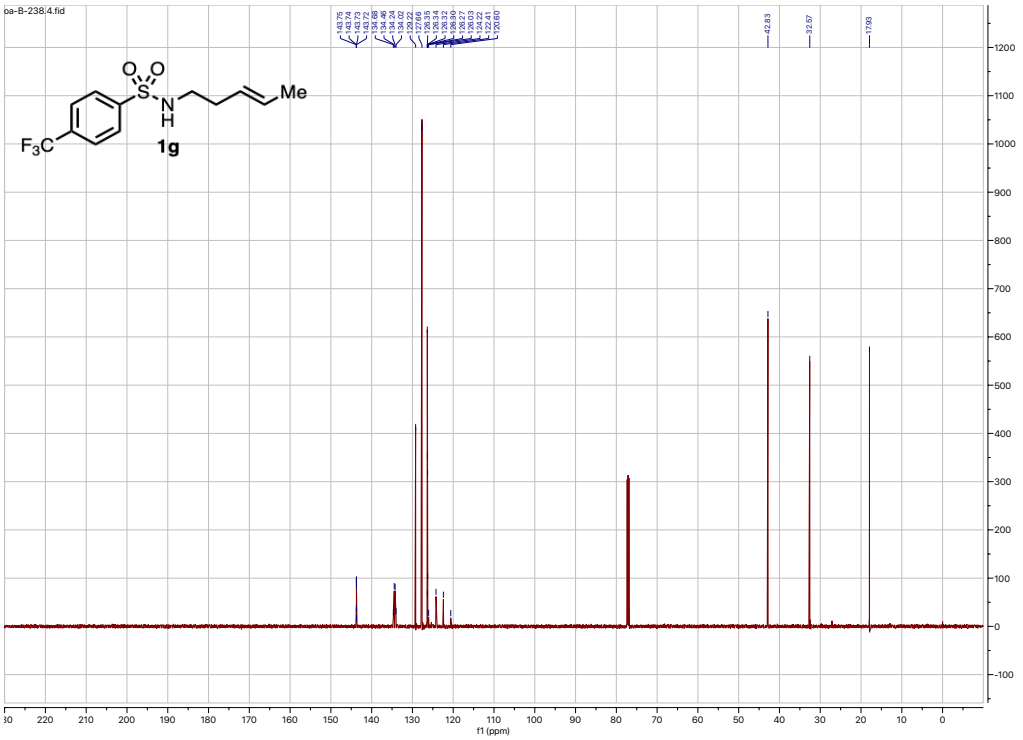

oa-B-126.5.fid
1o
63.92
f1 (ppm)

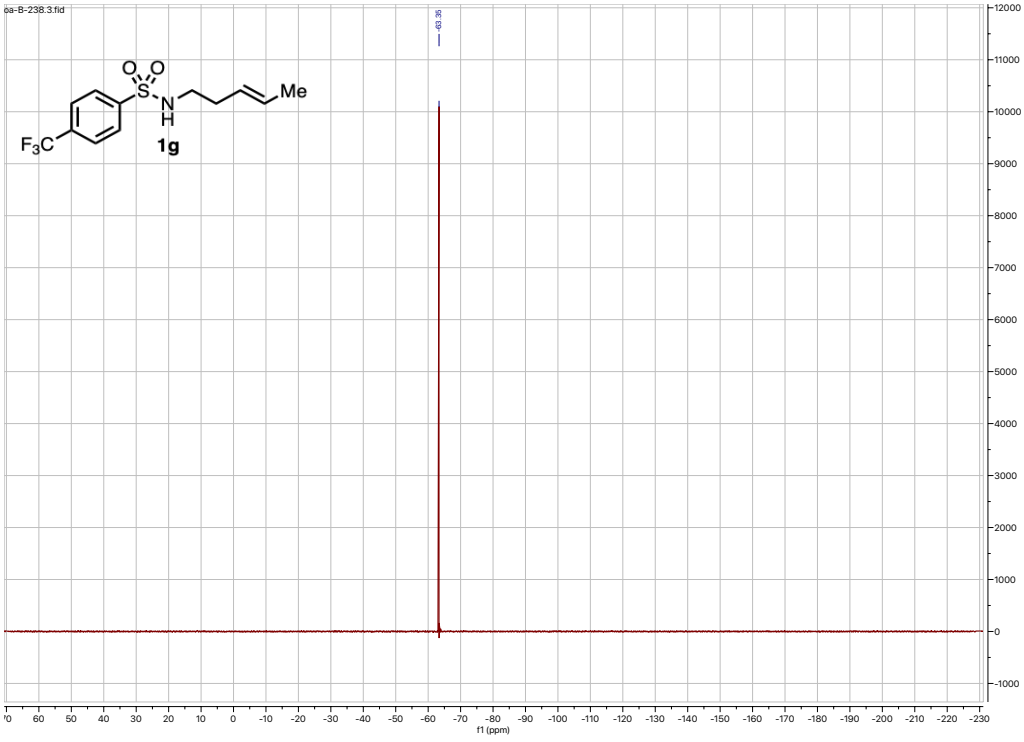

oa-B-225.2.fid
1f
f1 (ppm)


oa-B-225.4.fid
1f
f1 (ppm)


oa-B-225.3.fid
-63.36
1f
F3C
Me
f1 (ppm)


oa-B-238.2.fid
1g
F3C
Me
f1 (ppm)


oa-B-238.4.fid
1g
f1 (ppm)


oa-B-238.3.fid
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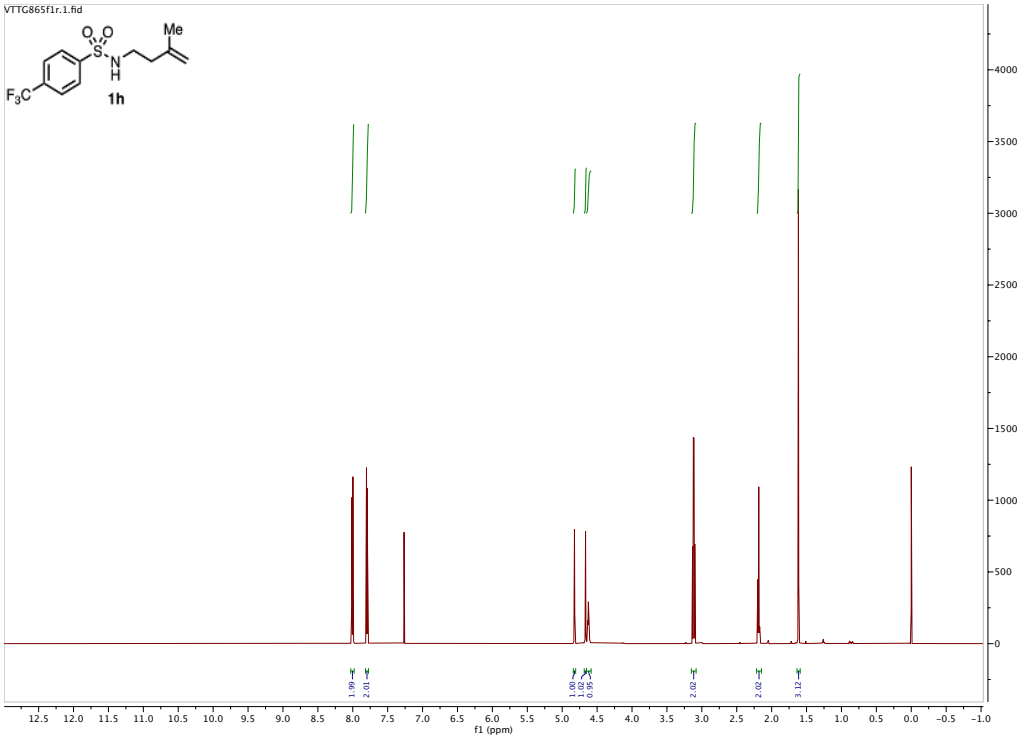
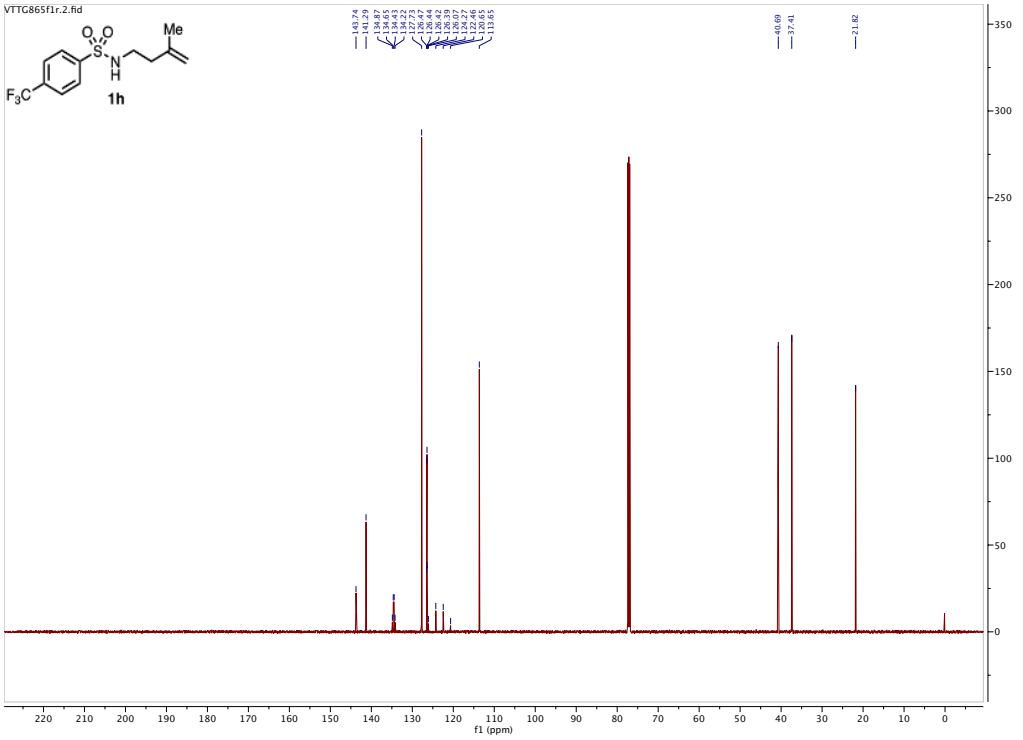
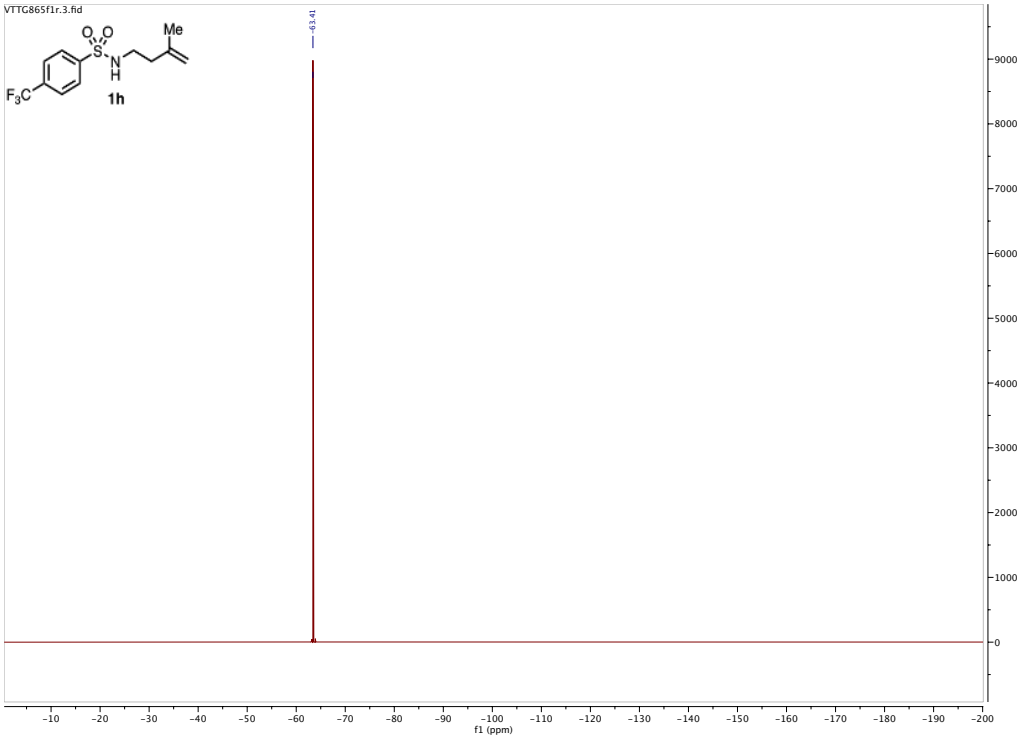
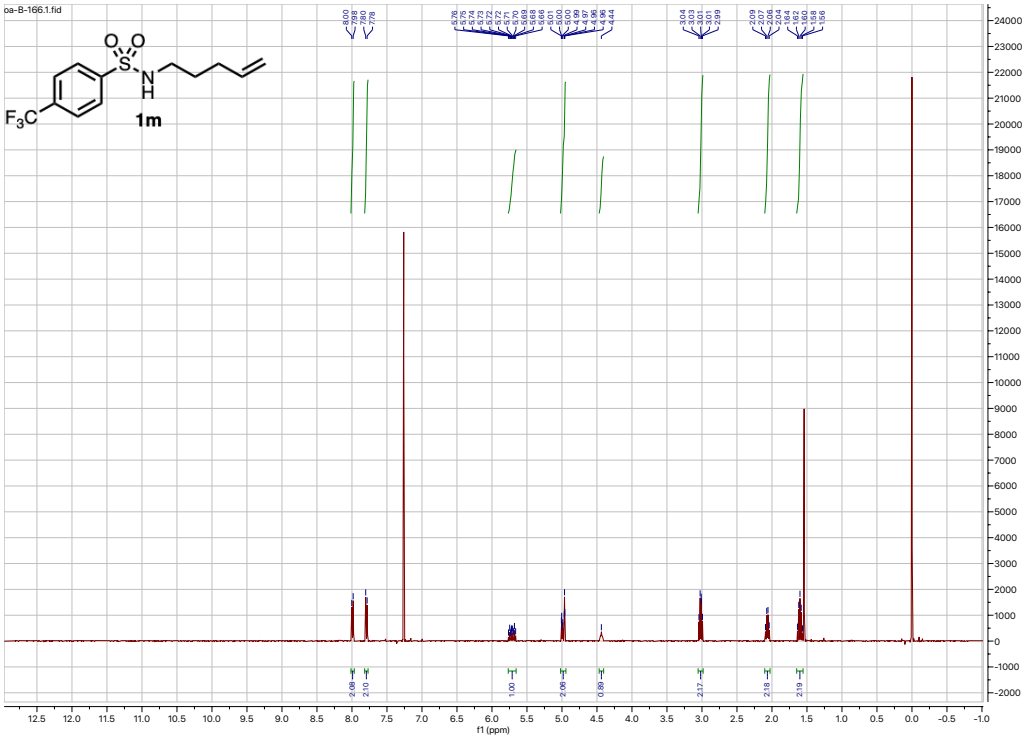
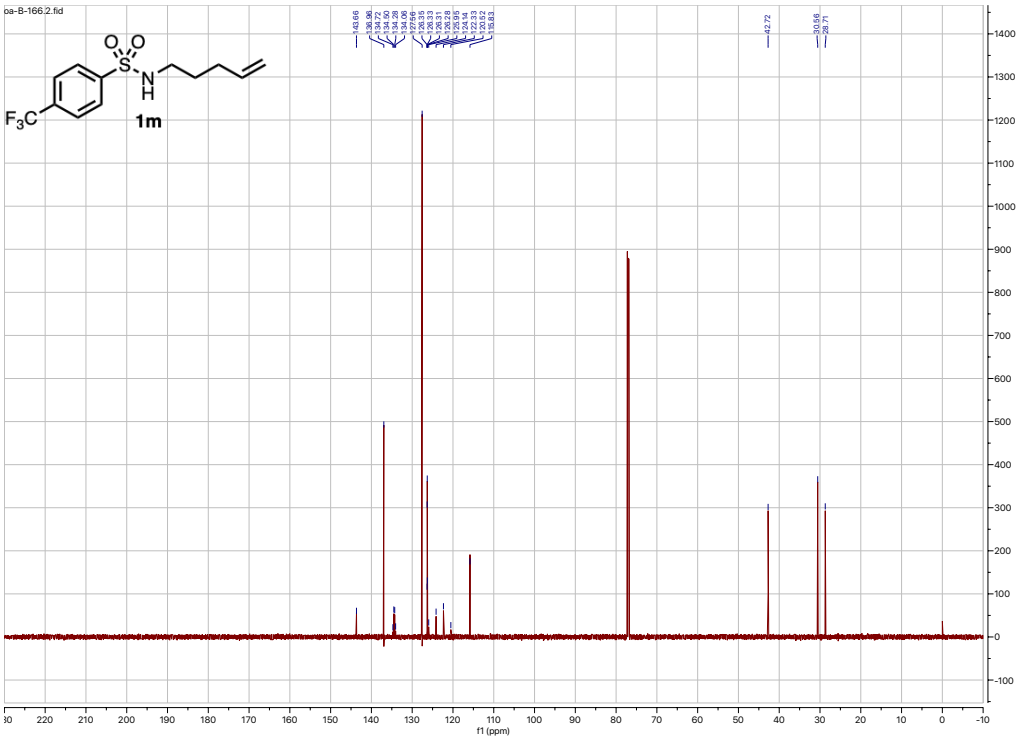
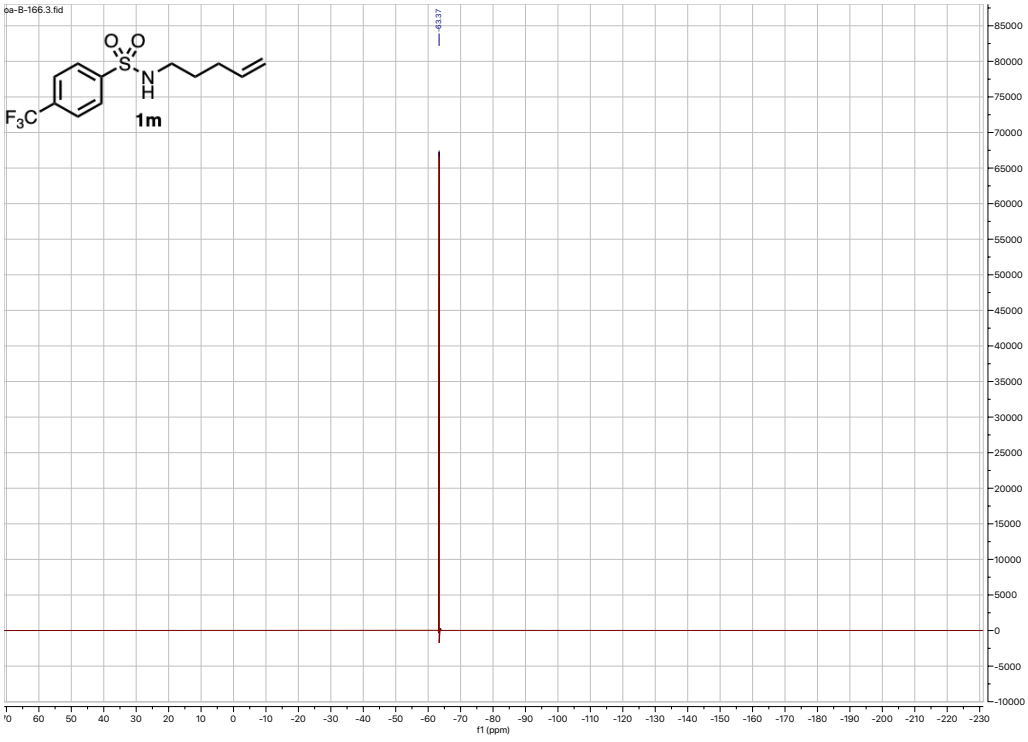

VTTG865f1r.1.fid
1h
f1 (ppm)

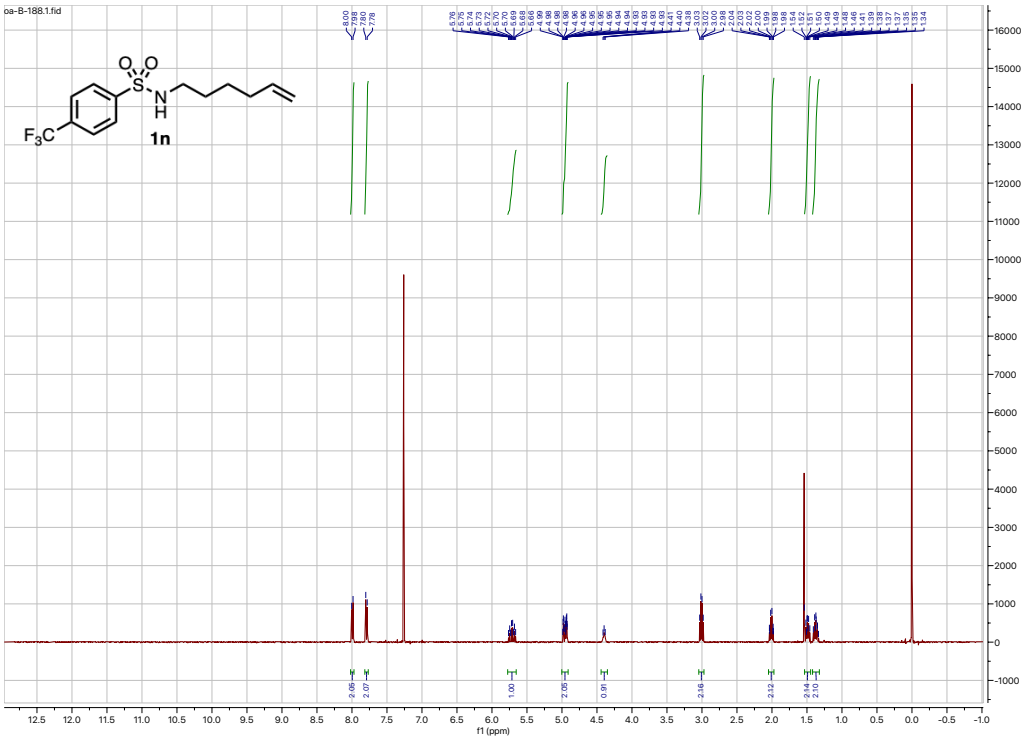

VTTG865f1r.2.fid
1h
f1 (ppm)

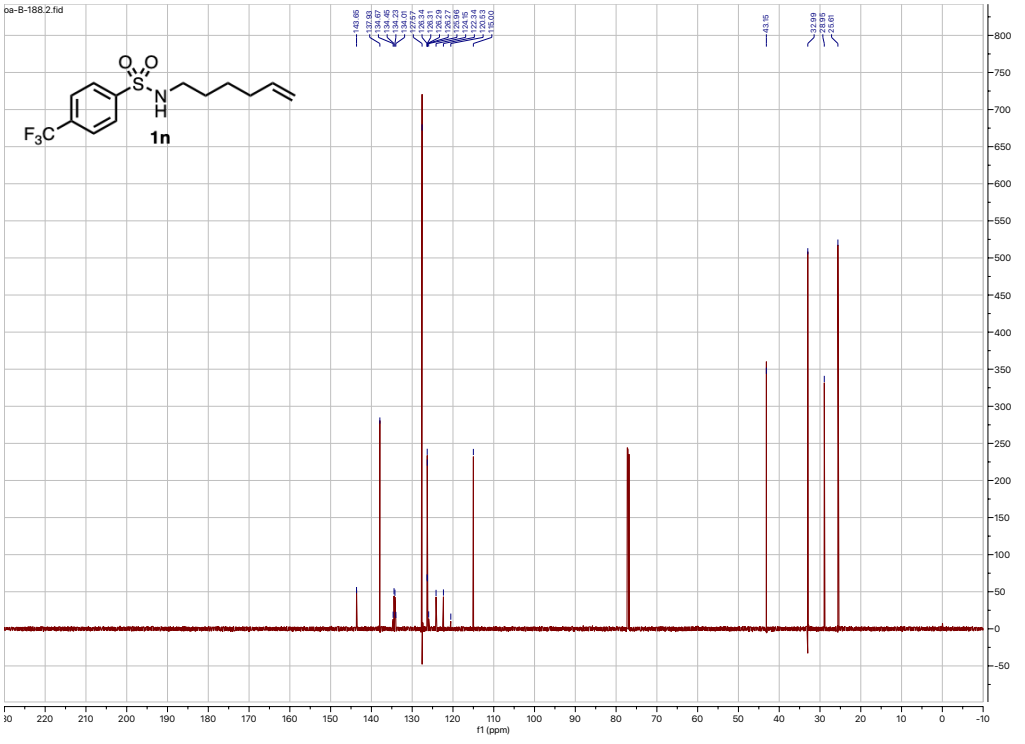

VTTG865f1r.3.fid
Me
1h
F3C
-63.41
f1 (ppm)


oa-B-166.1.fid
1m
F3C
f1 (ppm)


oa-B-166.2.fid
1m
f1 (ppm)


oa-B-166.3.fid
1m
f1 (ppm)


oa-B-188.1.fid
1n
f1 (ppm)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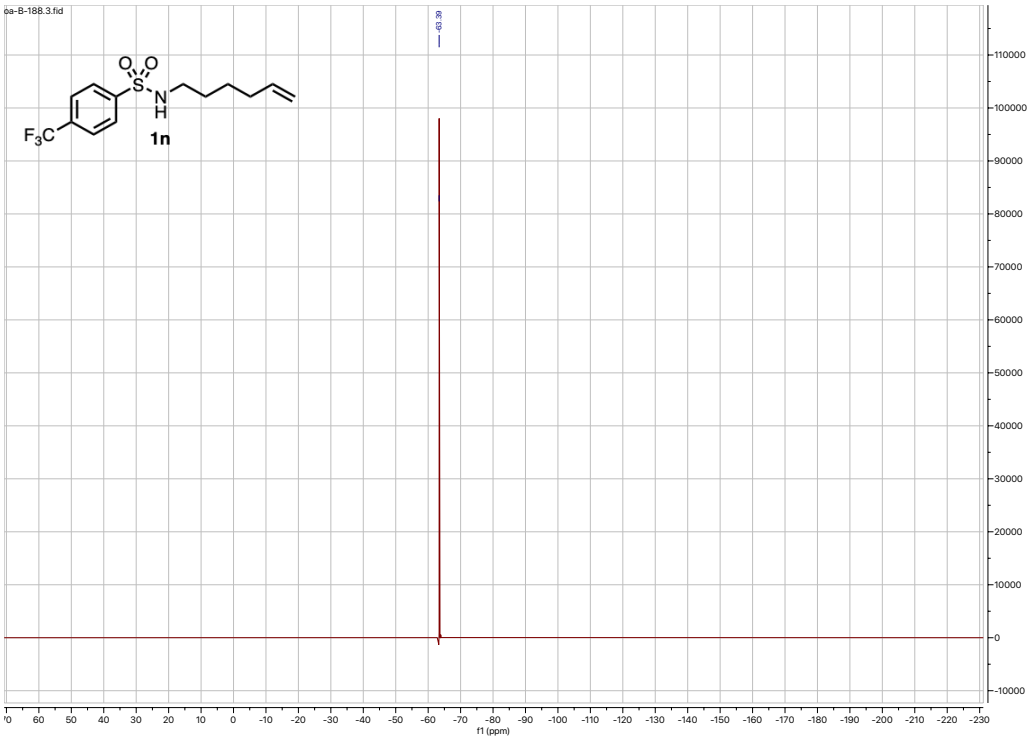
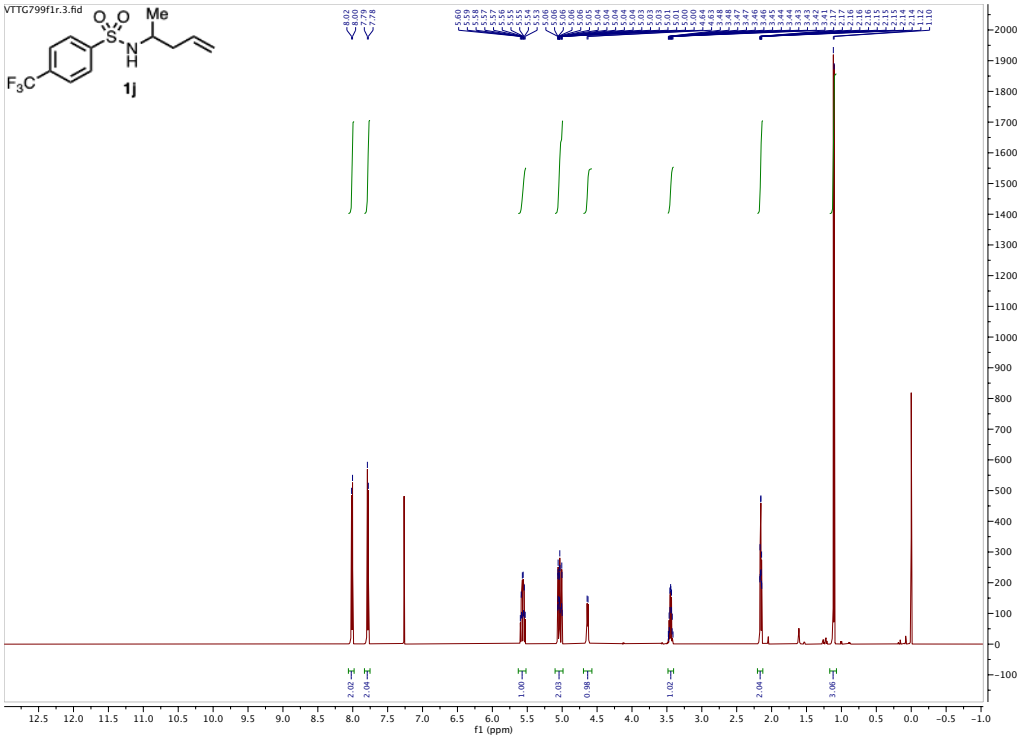
1n
f1 (ppm)


oa-B-188.3.fid
-63.39
1n
f1 (ppm)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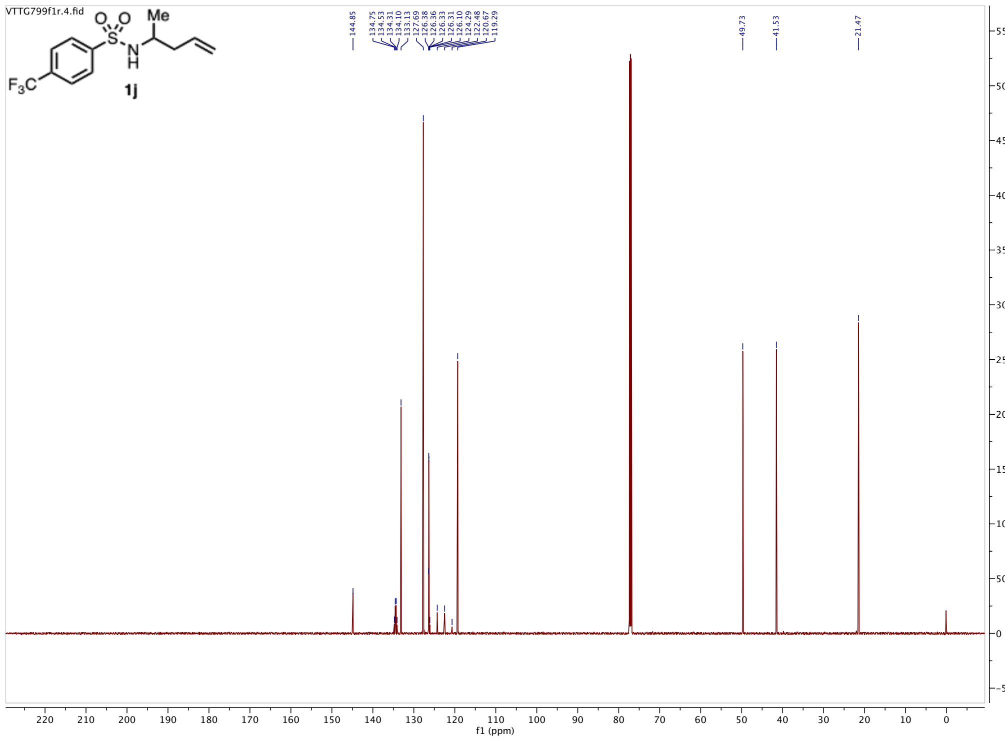
1j
f1 (ppm)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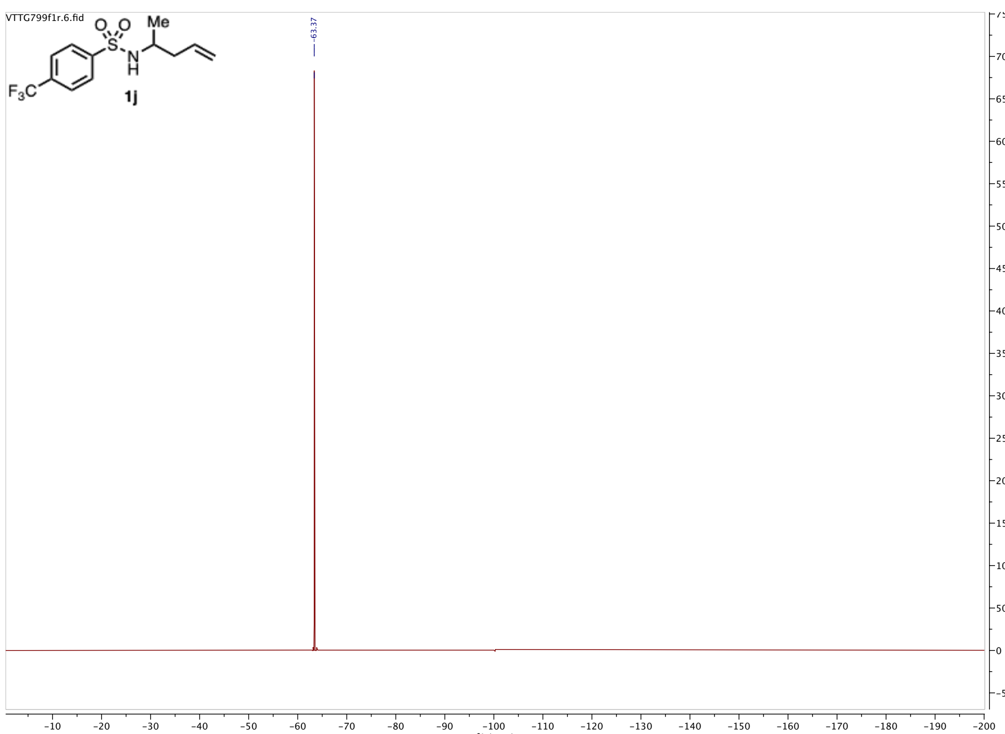
Me
F3C
1j
144.85
134.75
134.53
134.31
134.10
133.13
127.69
126.38
126.36
126.33
126.31
126.10
124.29
122.48
120.67
119.29
49.73
41.53
21.47
f1 (ppm)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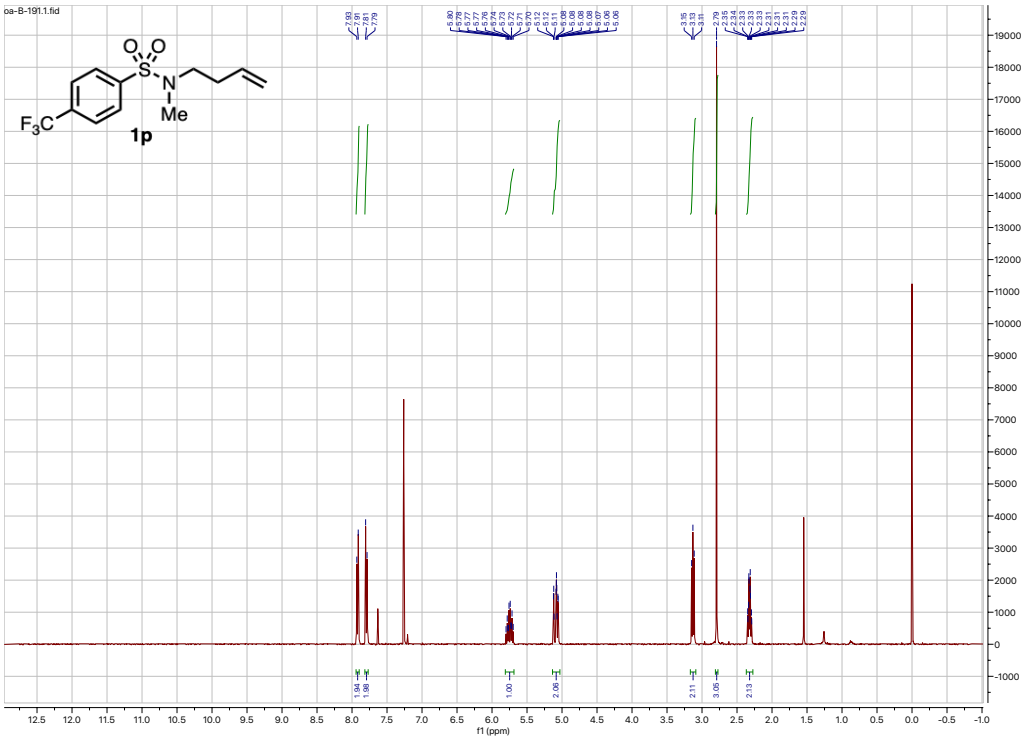
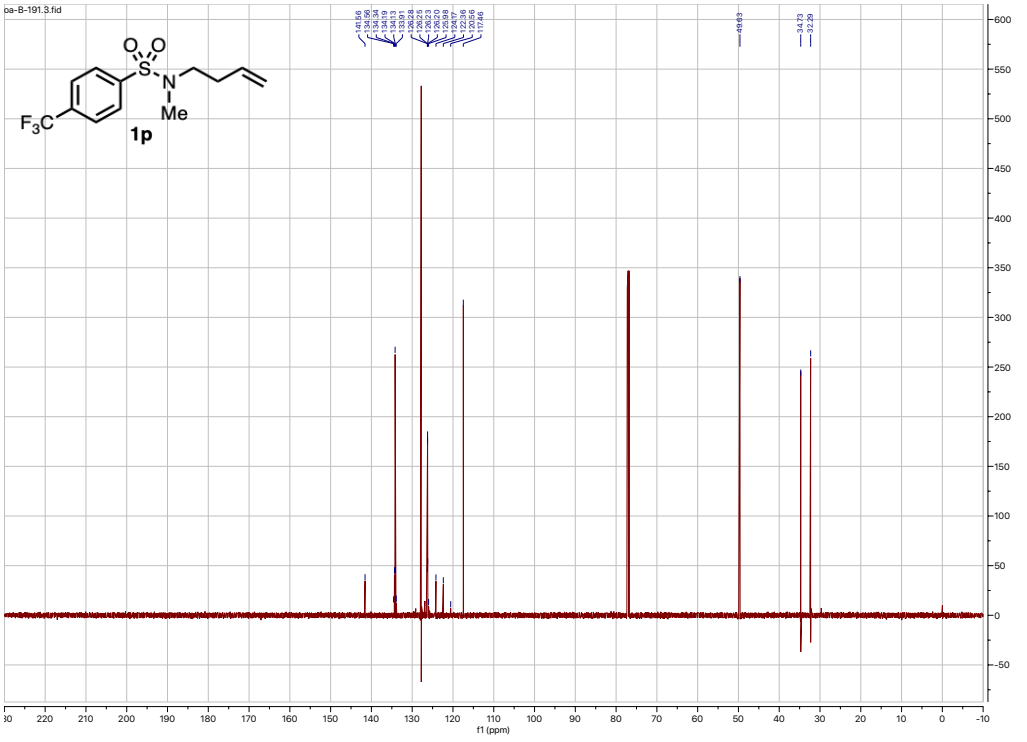
Me
F3C
1j
-63.37
f1 (ppm)


oa-B-191.1.fid
1p
f1 (ppm)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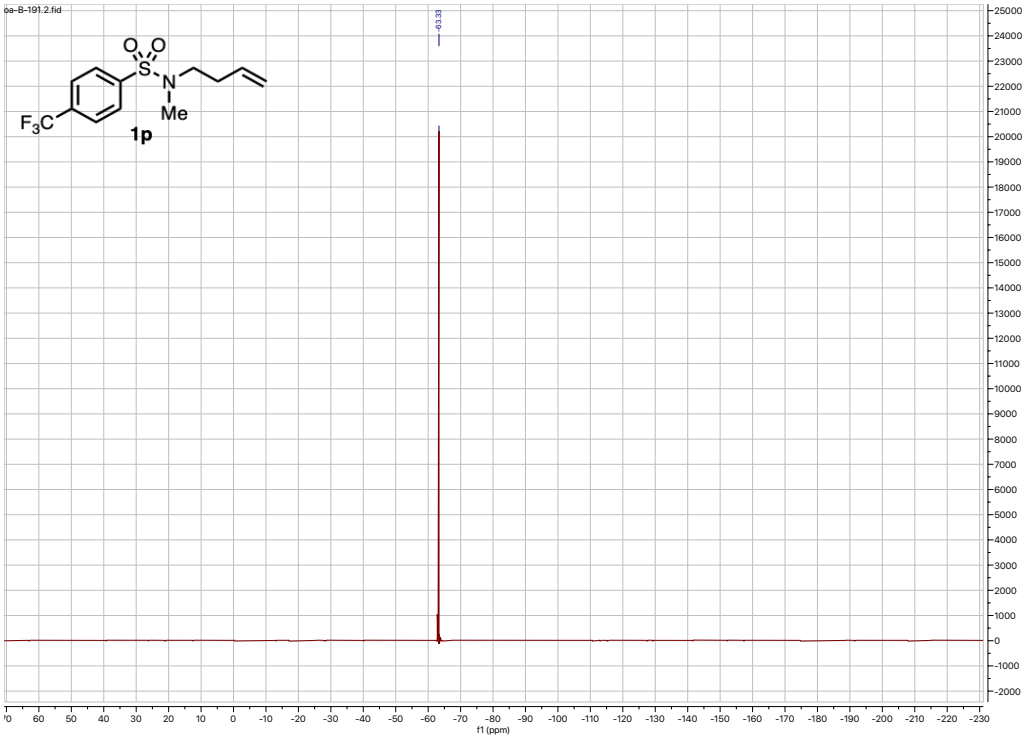
f1 (ppm)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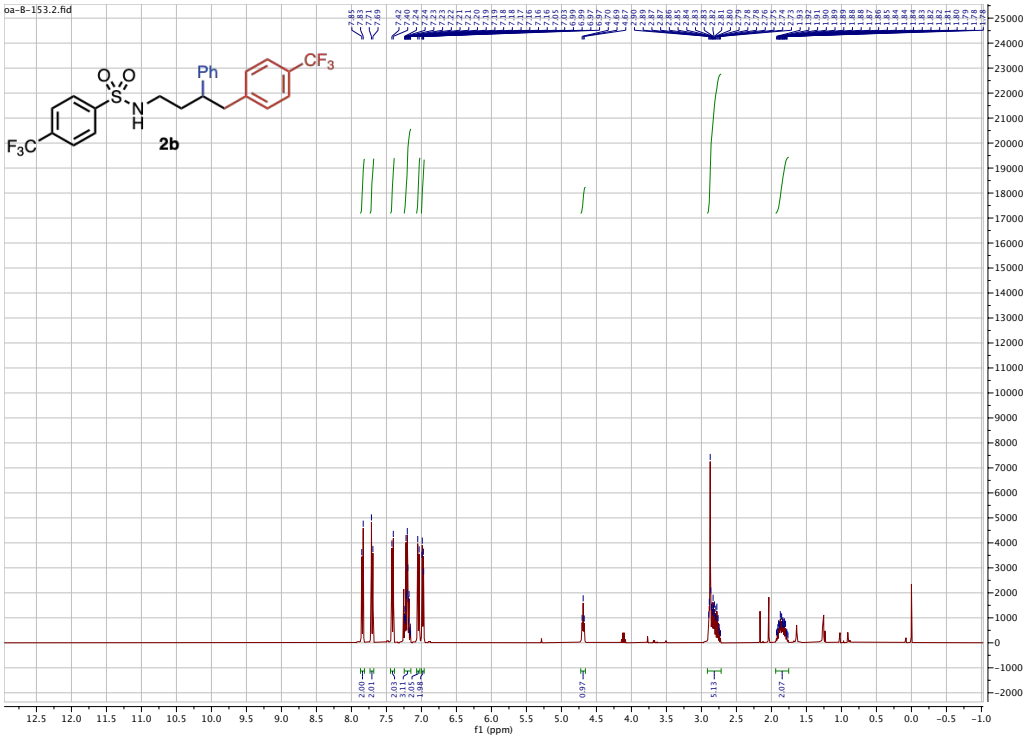
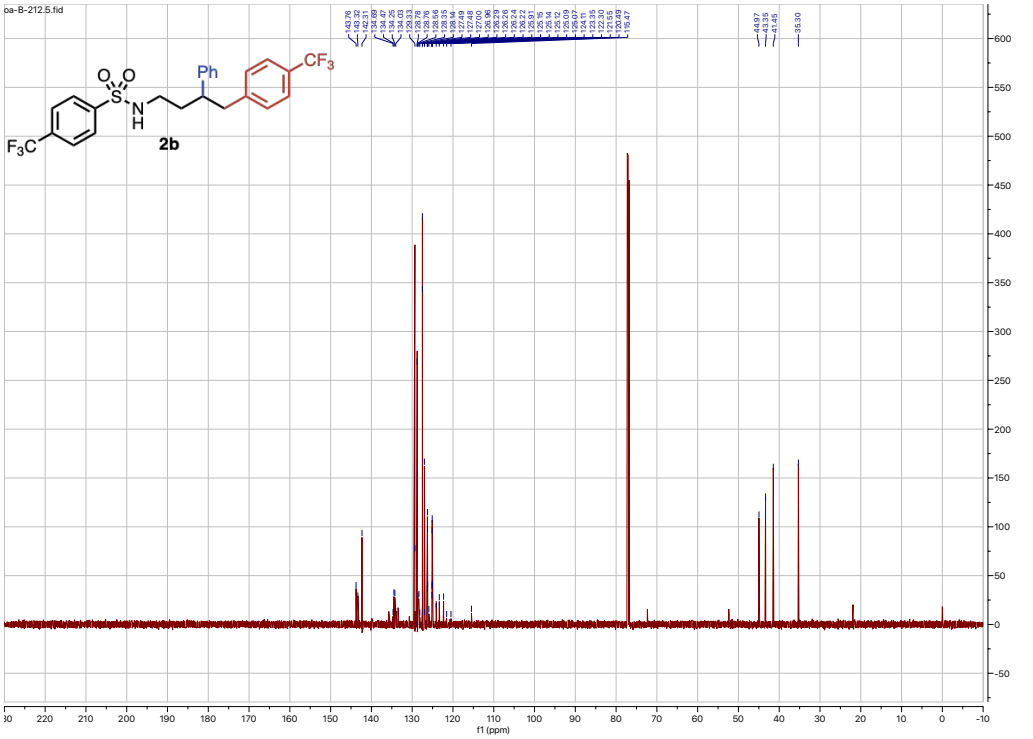
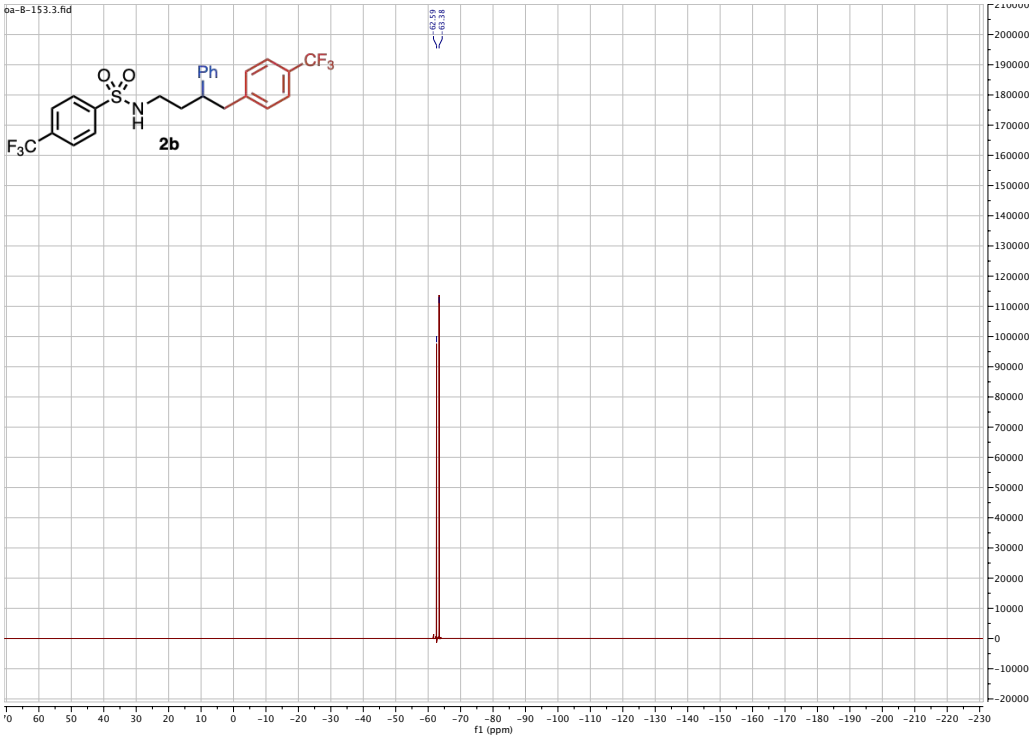
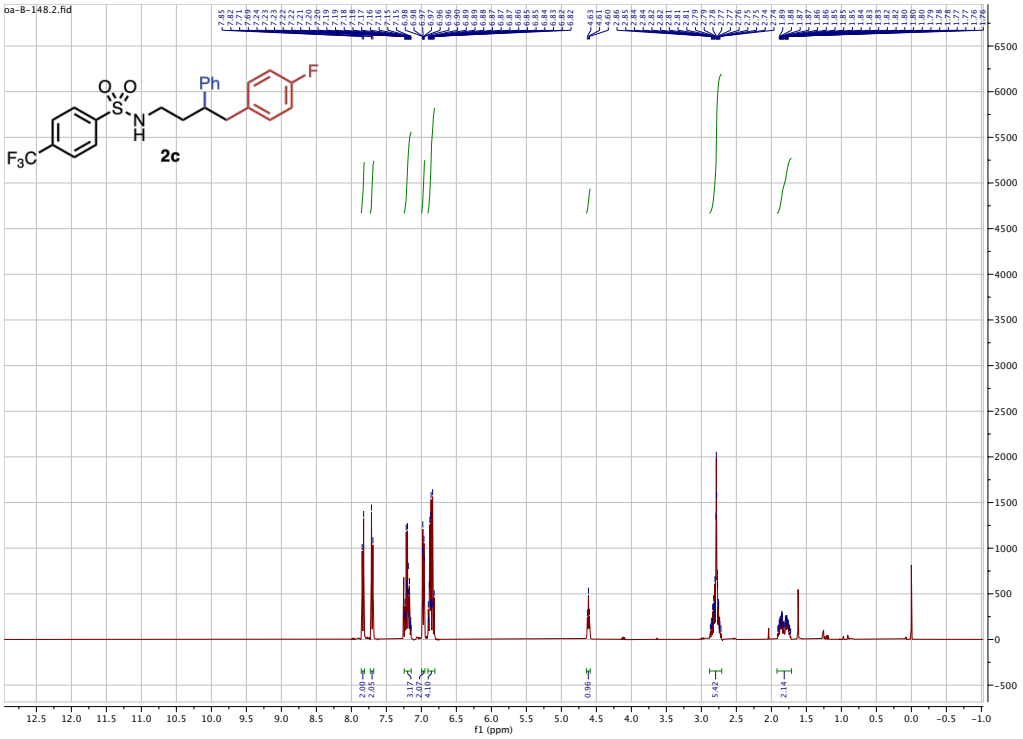
1p
f1 (ppm)


oa-B-153.2.fid
2b
f1 (ppm)


oa-B-212.5.fid
Ph
CF3
F3C
2b
f1 (ppm)


oa-B-153.3.fid
Ph
CF3
F3C
2b
f1 (ppm)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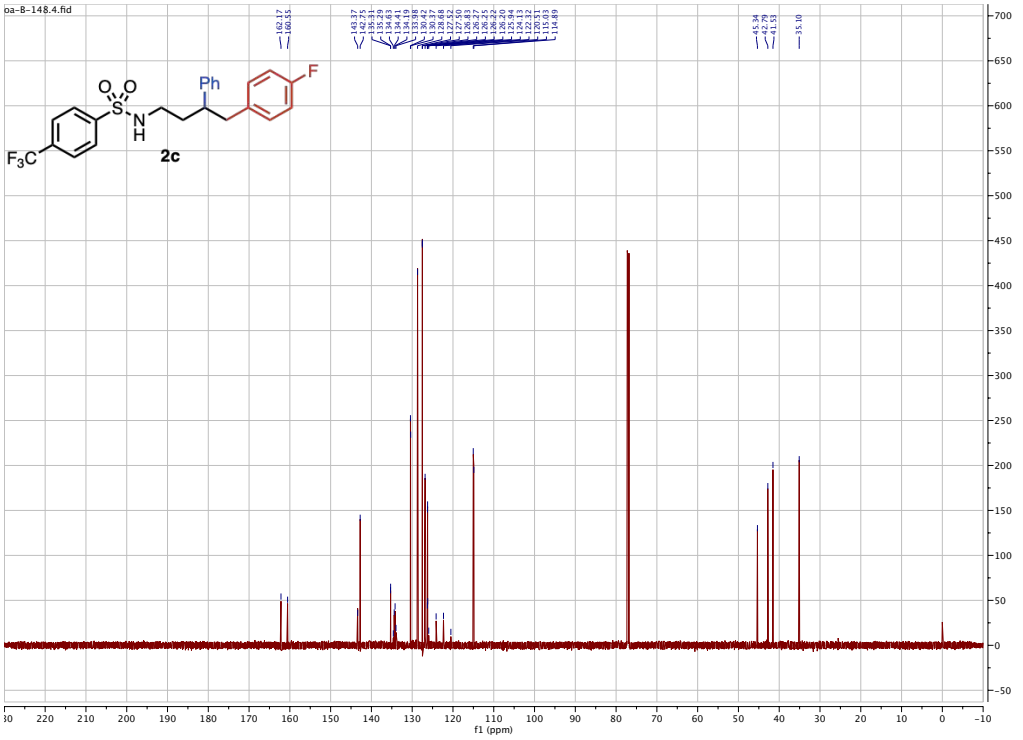
Ph
F
O
O
S
N
H
F3C
2c
f1 (ppm)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Ph
F
O
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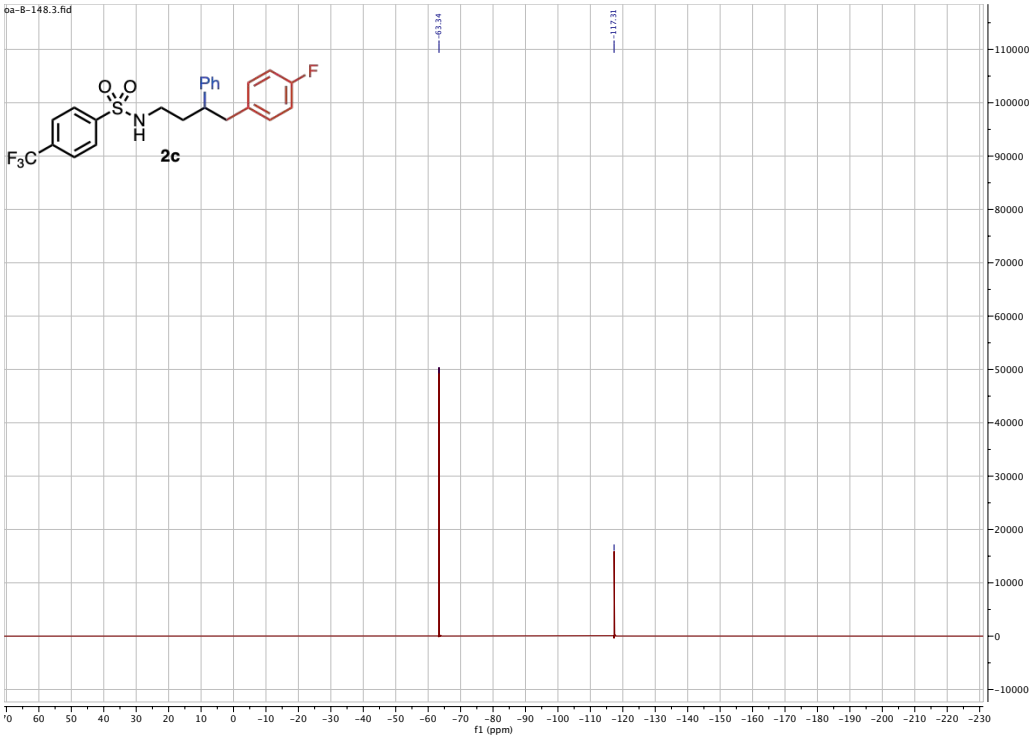
S
N
H
F3C
2c
f1 (ppm)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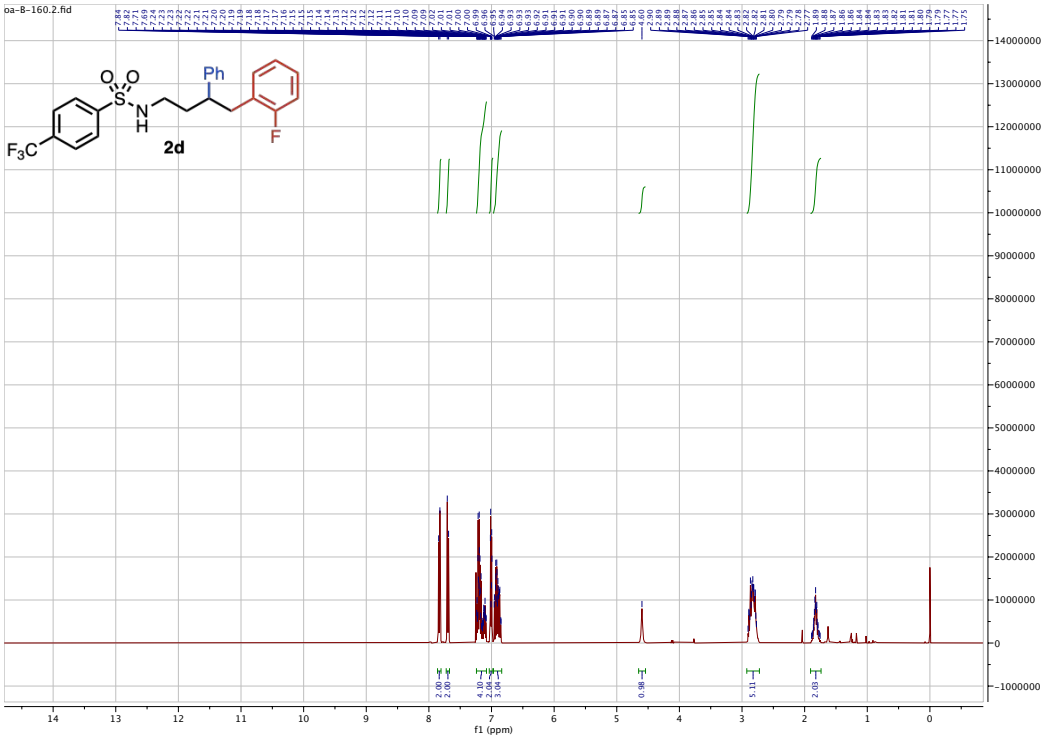
Ph
F
F3C
2c
f1 (ppm)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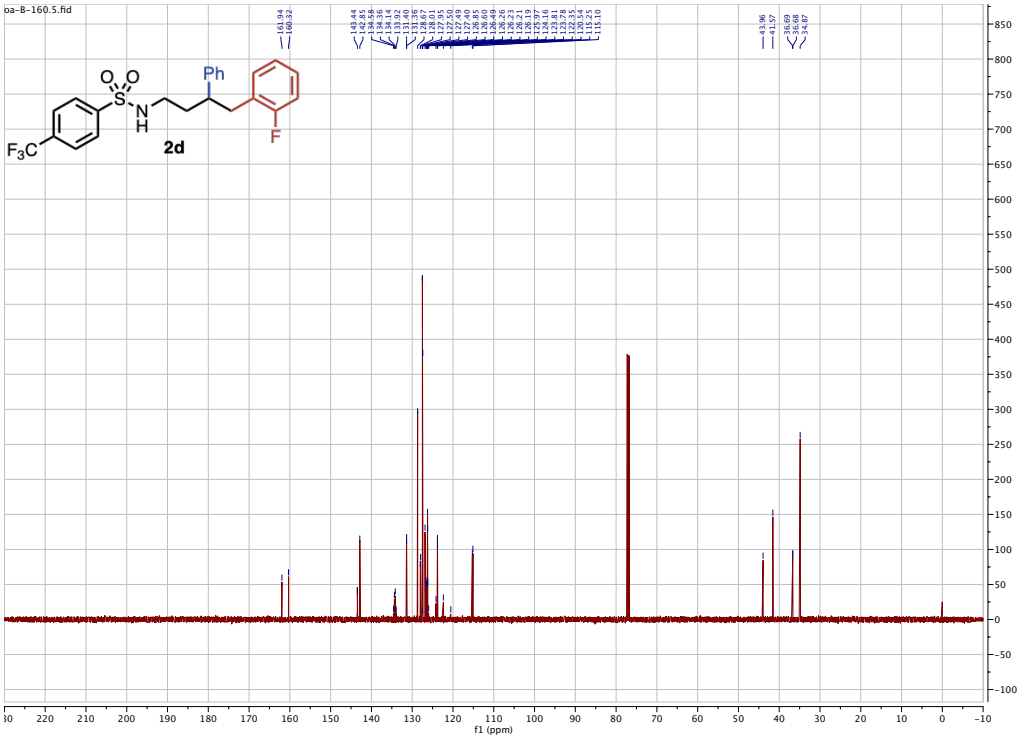
Ph
F
F3C
2d
f1 (ppm)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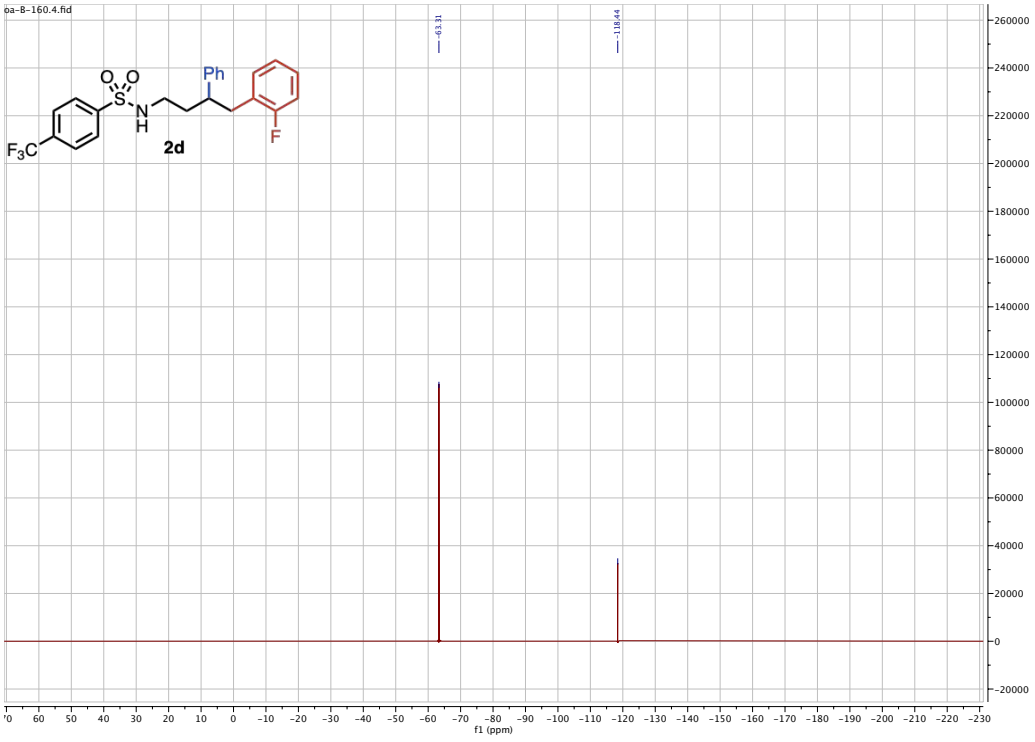
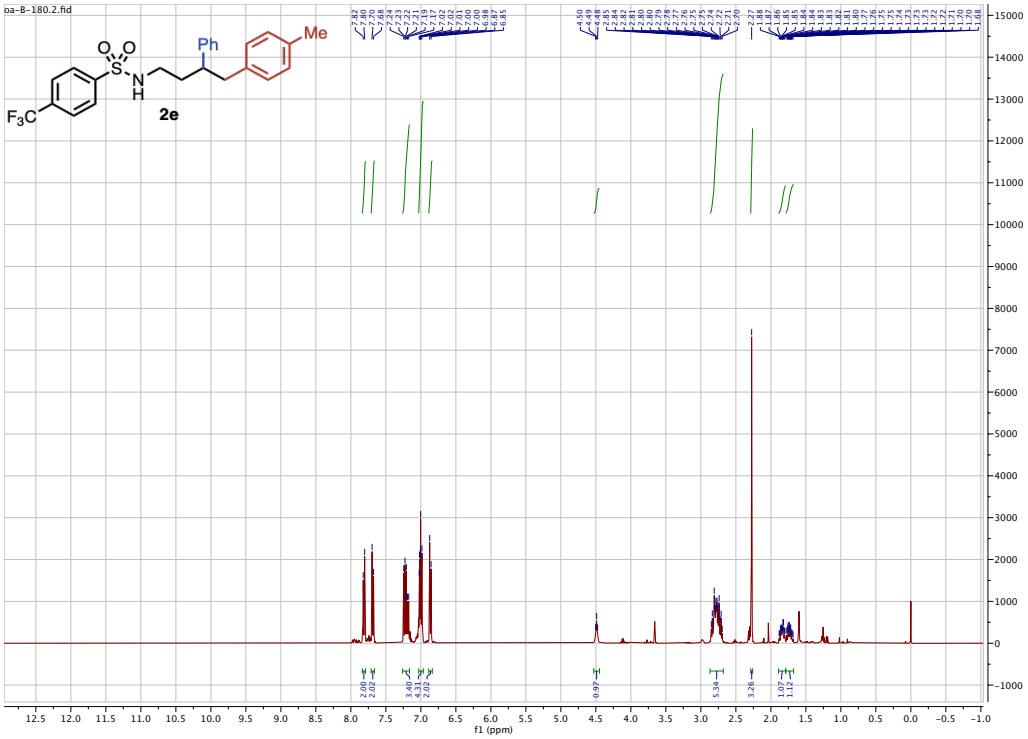
Ph
F
2d
f1 (ppm)


oa-B-160.4.fid
Ph
F
2d
f1 (ppm)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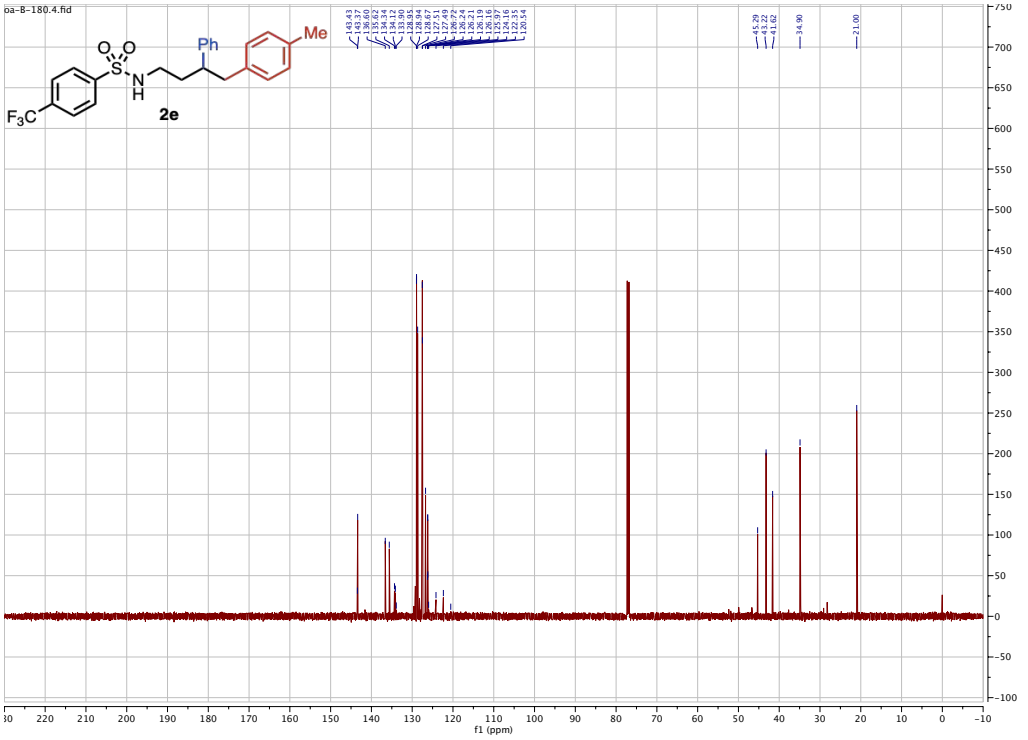
Ph
Me
O
O
S
N
H
F3C
2e
f1 (ppm)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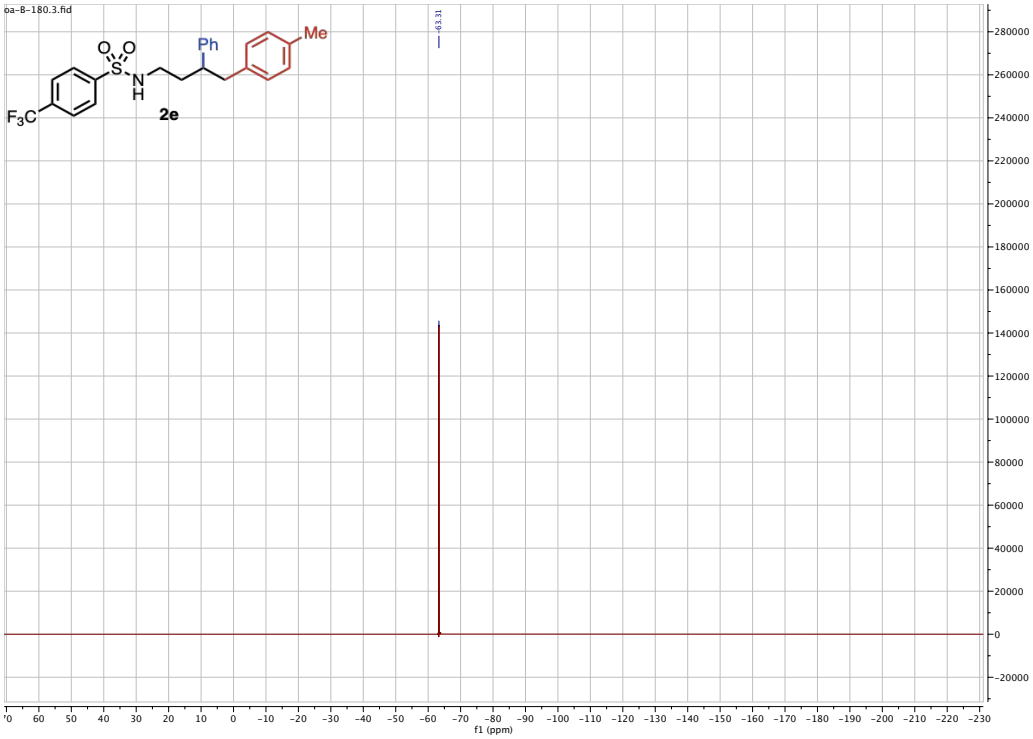
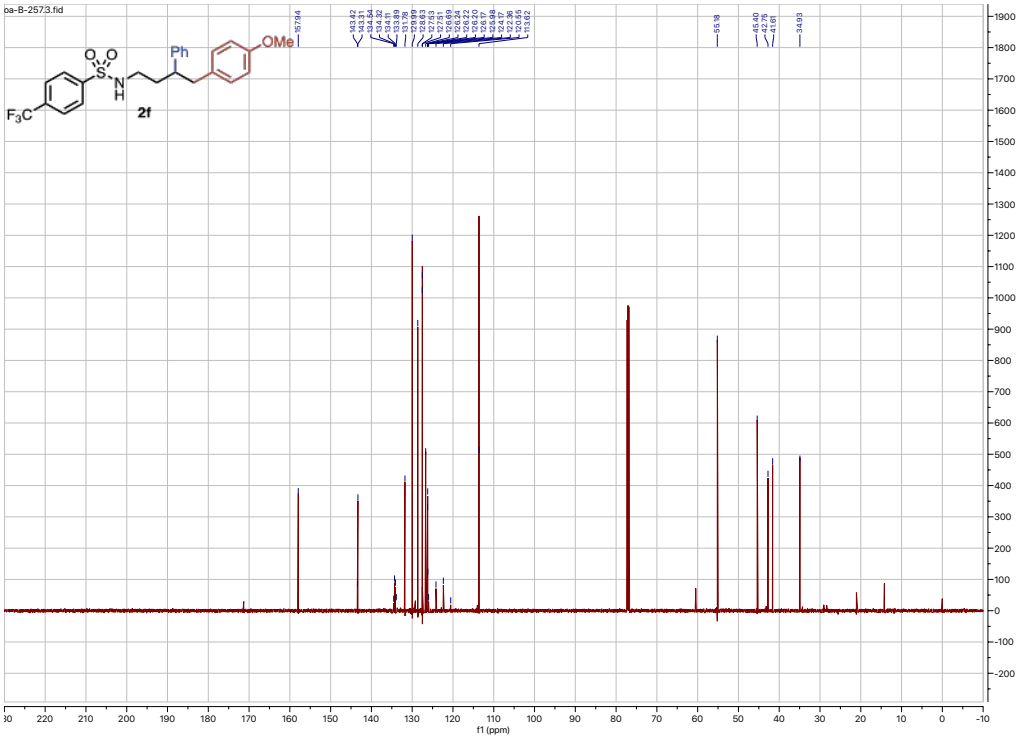
Ph
Me
O
O
S
N
H
F3C
2e
f1 (ppm)


oa-B-180.3.fid
Ph
Me
O
O
S
N
H
F3C
2e
-63.31
f1 (ppm)


oa-B-257.1.fid
Ph
OMe
O
O
S
N
H
F3C
2f
f1 (ppm)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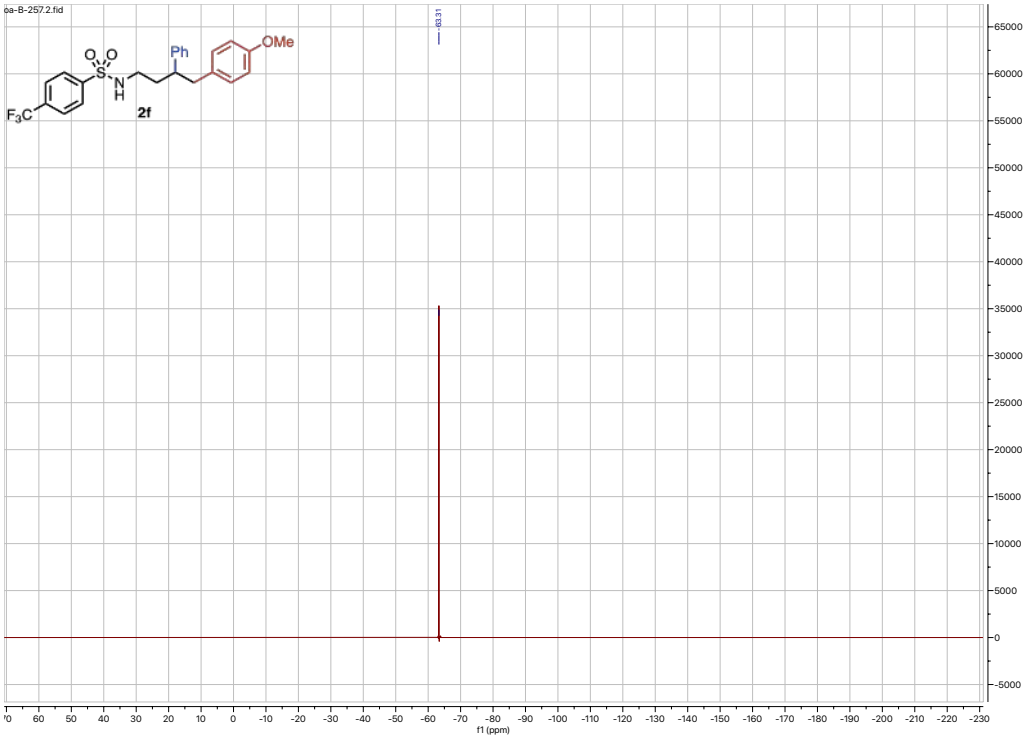
2f
f1 (ppm)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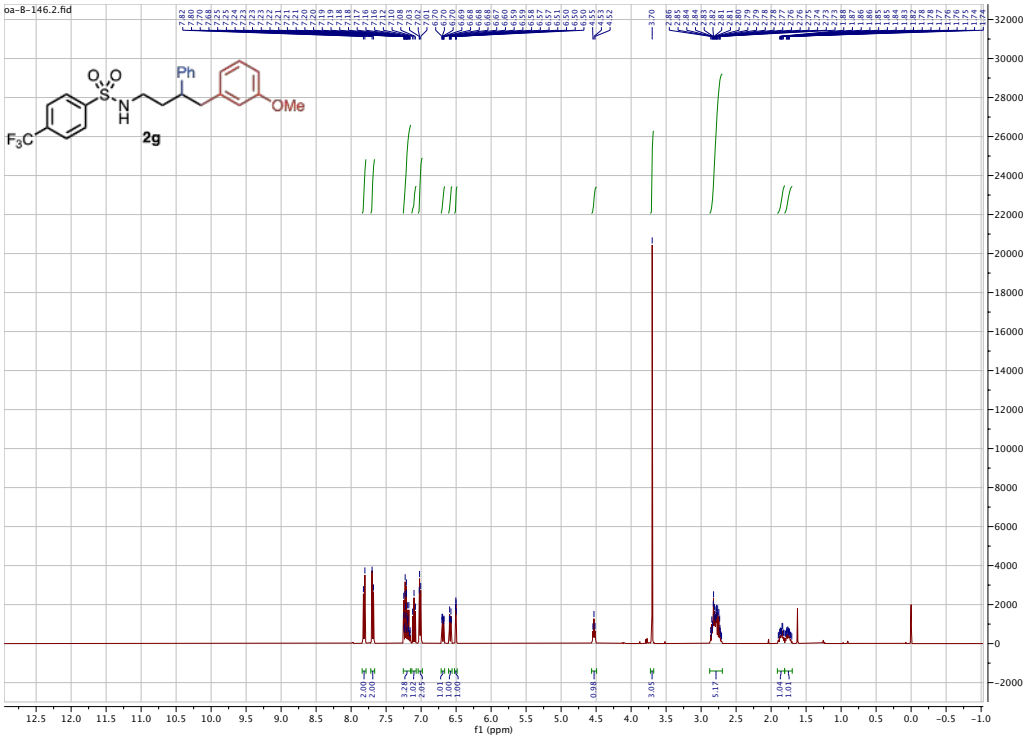
2f
f1 (ppm)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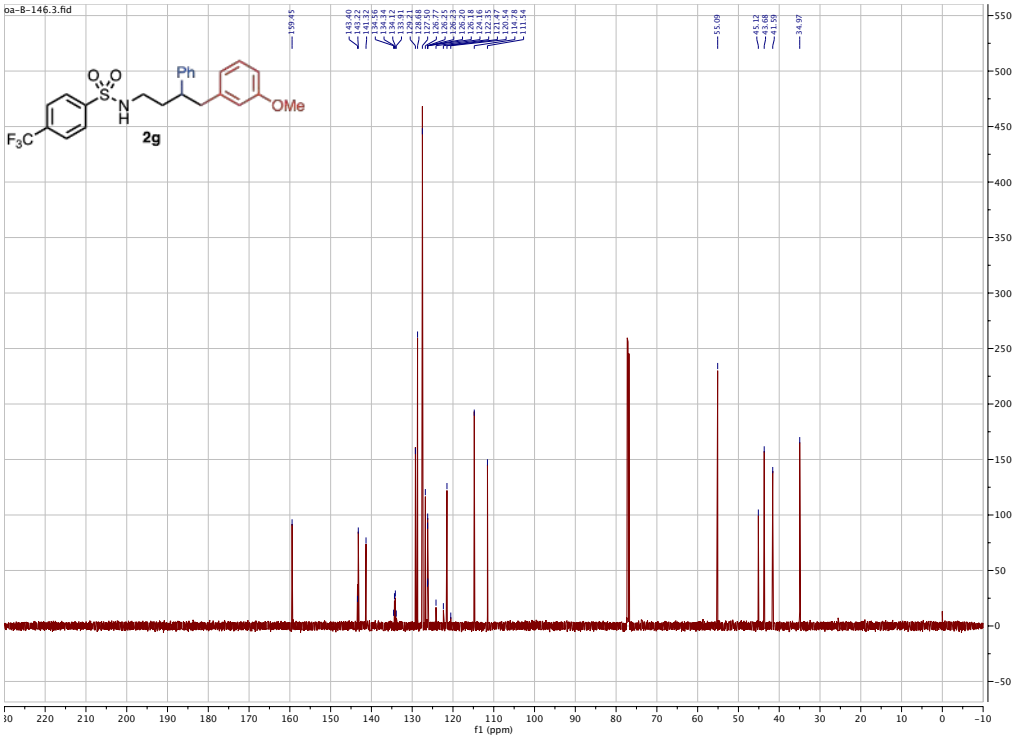
Ph
OMe
F3C
2g
f1 (ppm)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OMe
F3C
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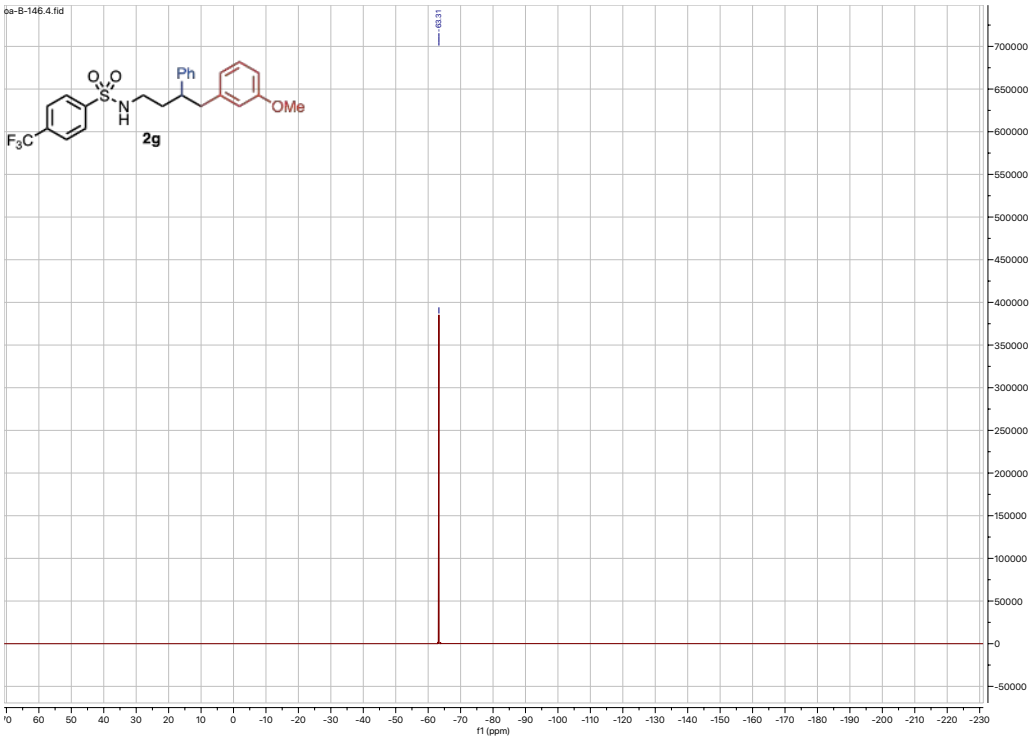
f1 (ppm)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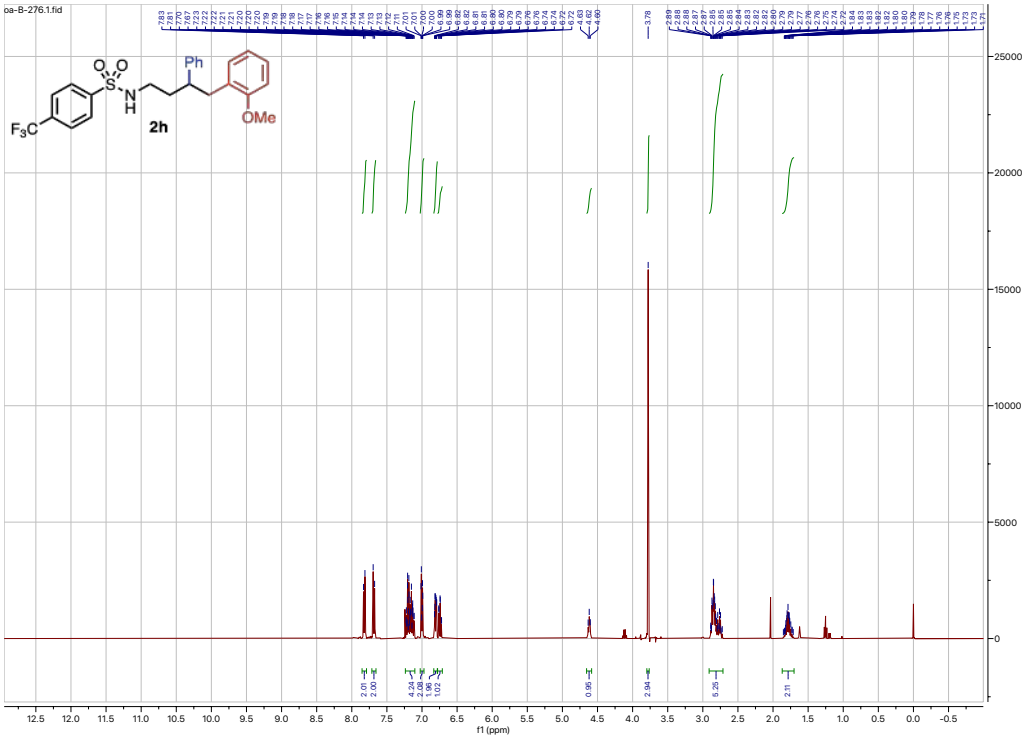
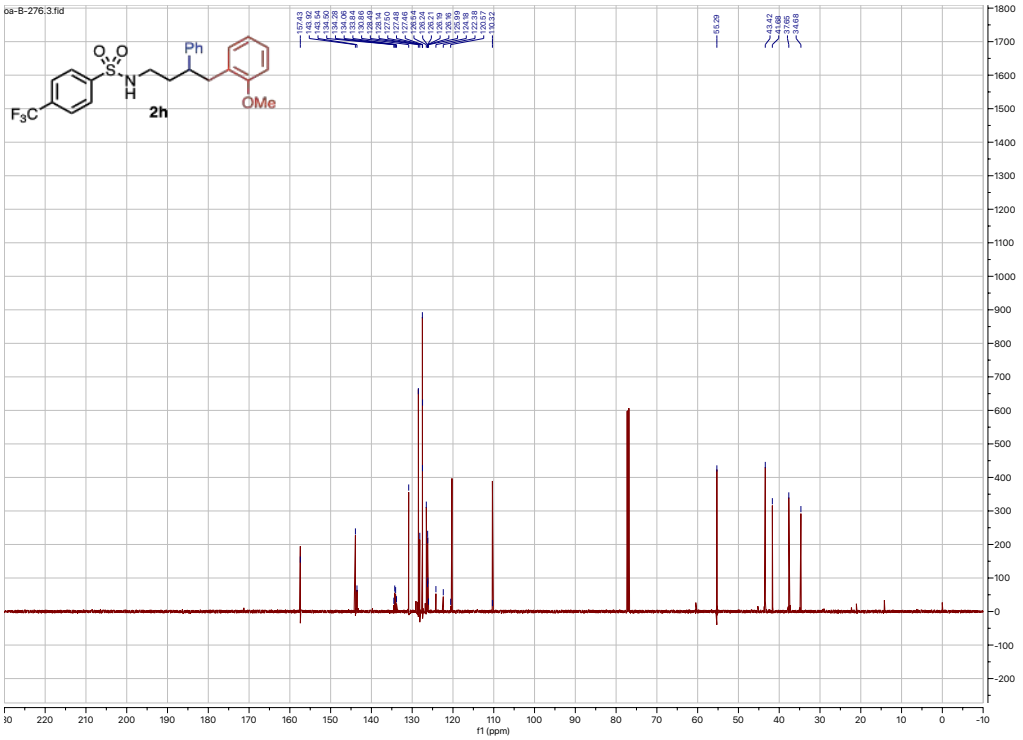
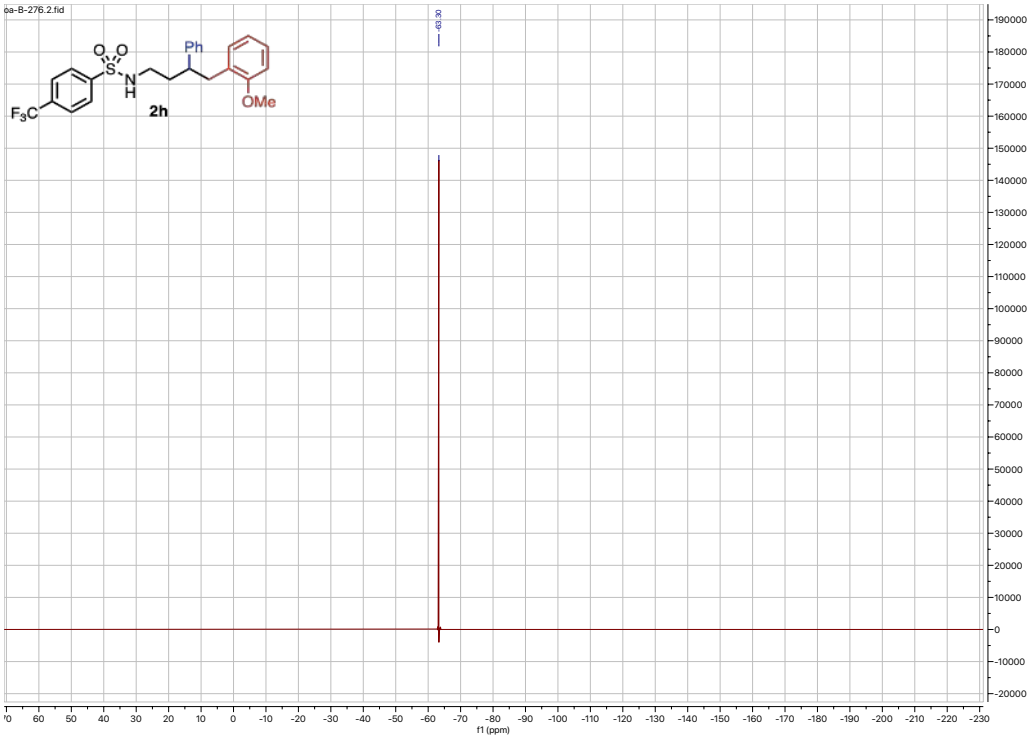
Ph
OMe
F3C
2g
f1 (ppm)


oa-B-276.1.fid
Ph
OMe
F3C
2h
f1 (ppm)


oa-B-276.3.fid
Ph
OMe
F3C
2h
f1 (ppm)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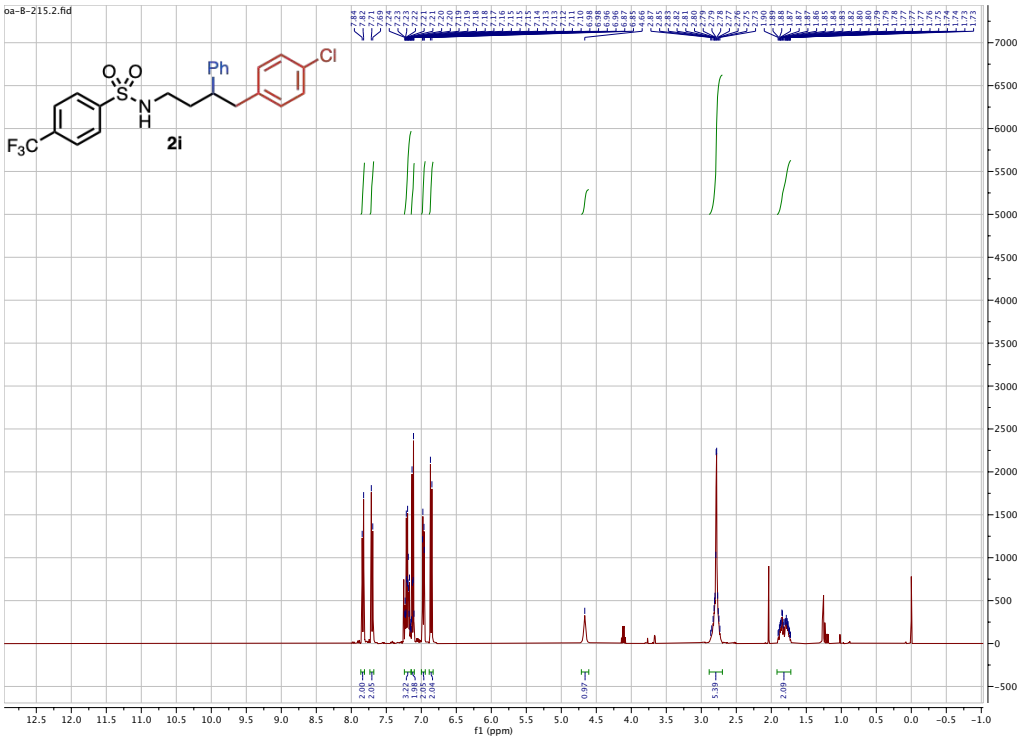
Ph
OMe
F3C
2h
f1 (ppm)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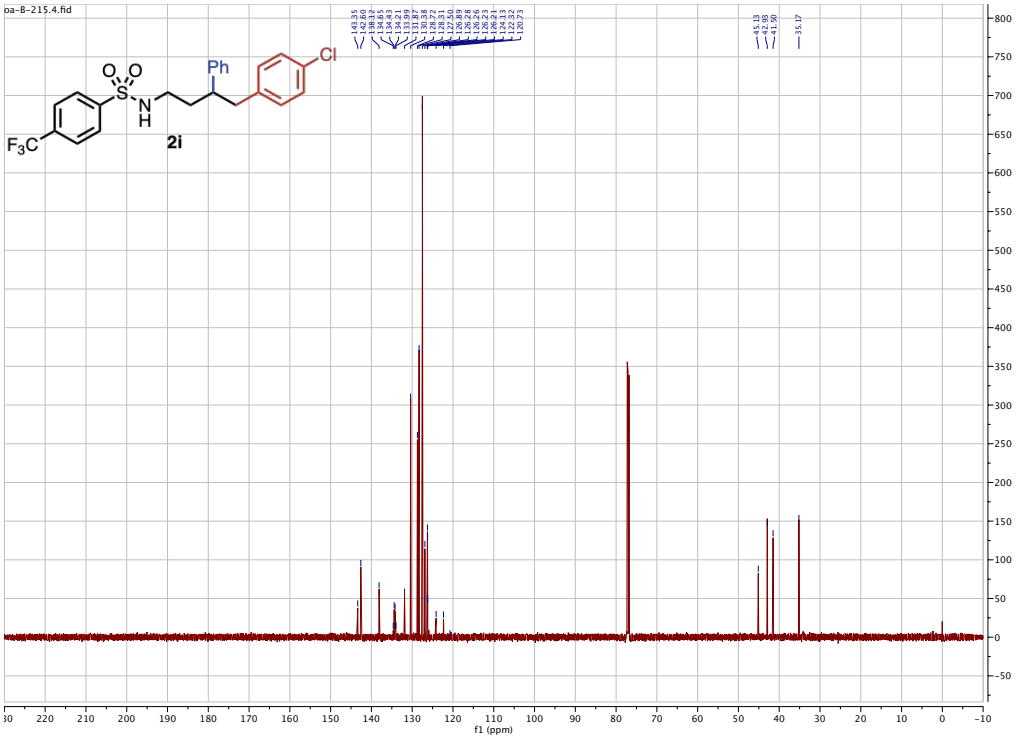
Cl
F3C
2i
f1 (ppm)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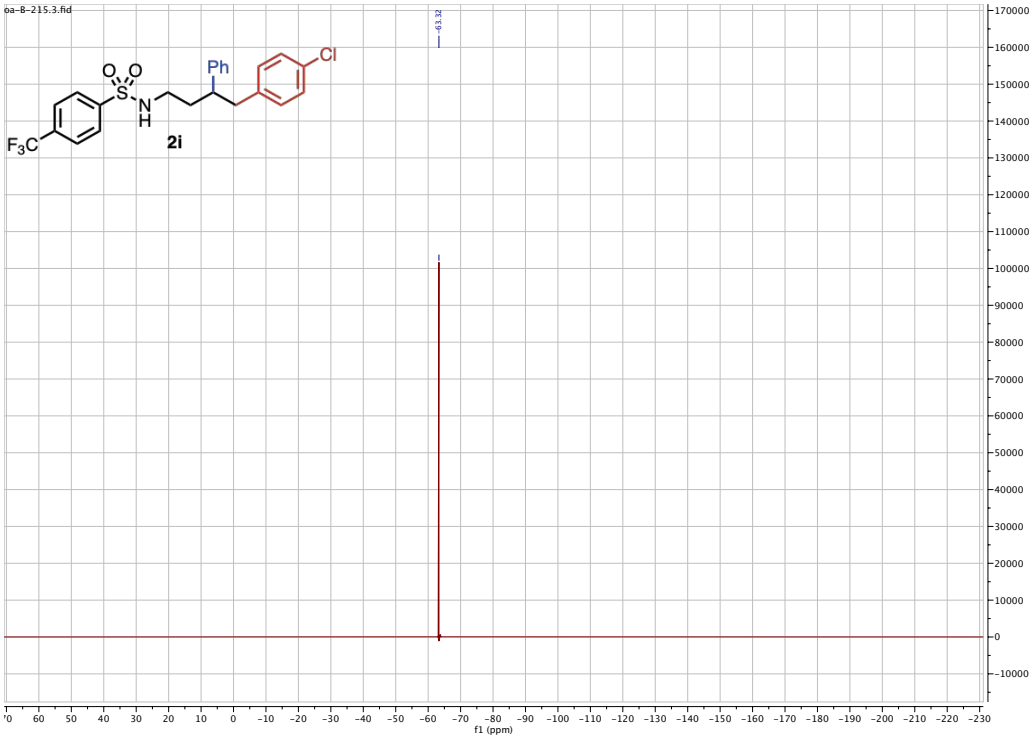
Ph
Cl
F3C
2i
f1 (ppm)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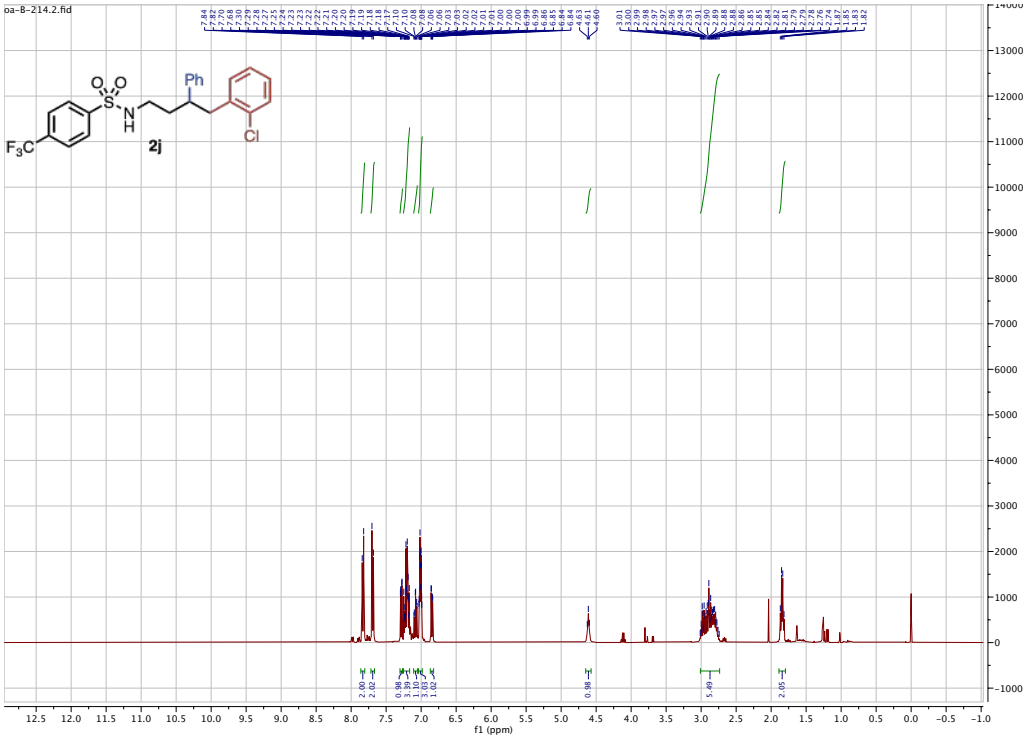
Ph
Cl
O
O
S
N
H
F3C
2i
-63.32
f1 (ppm)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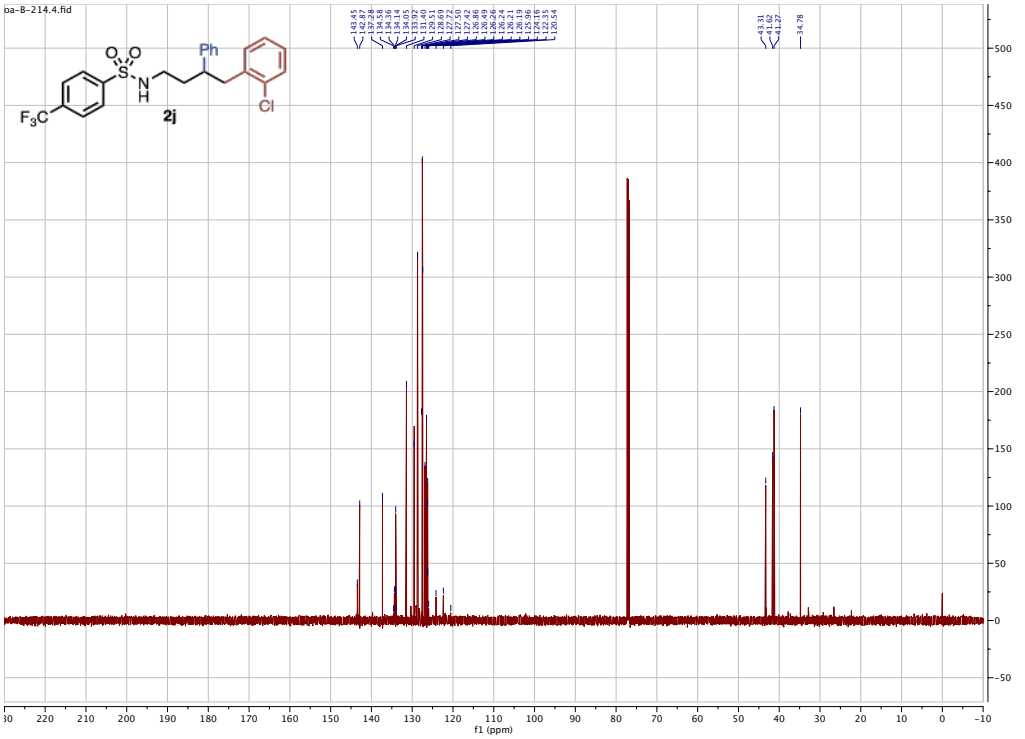
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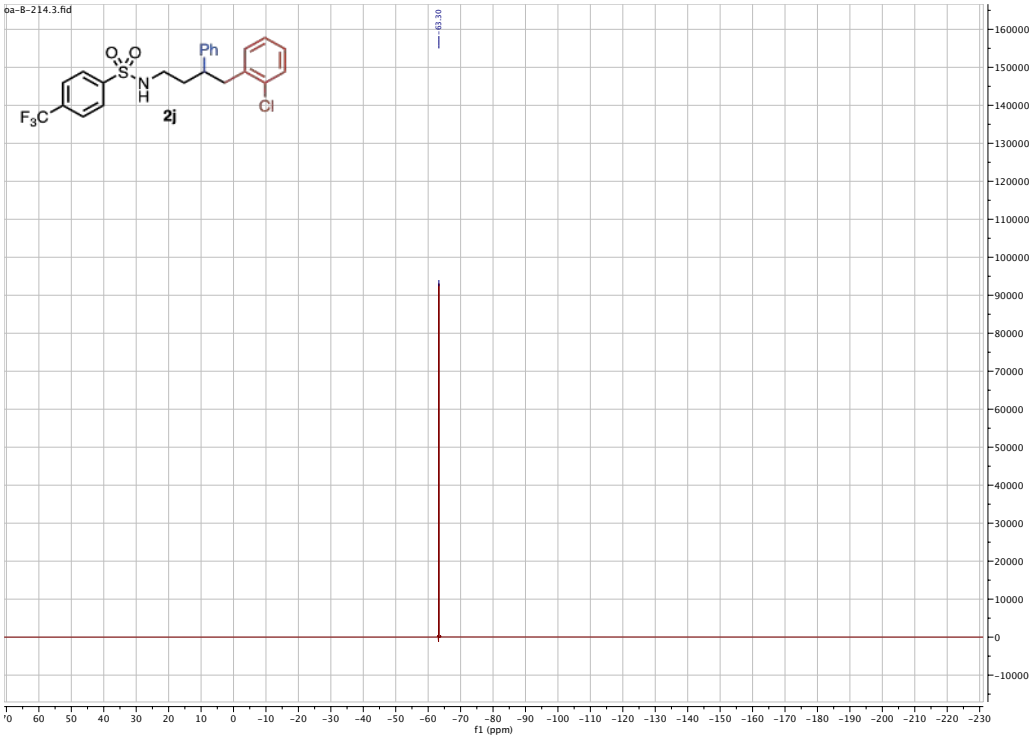
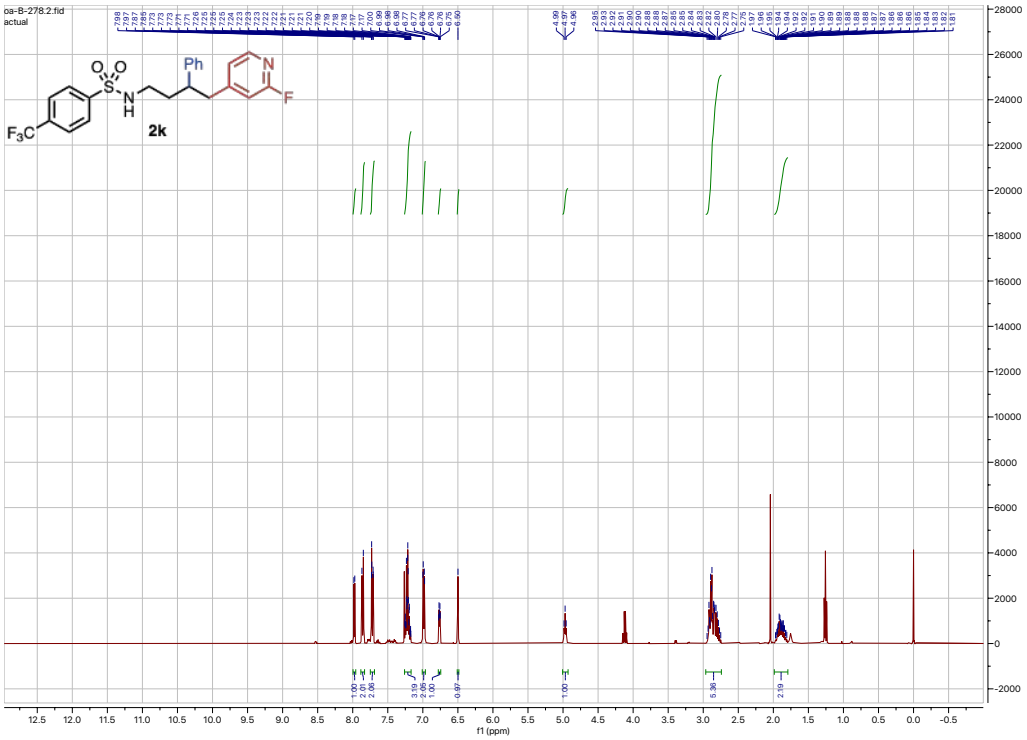
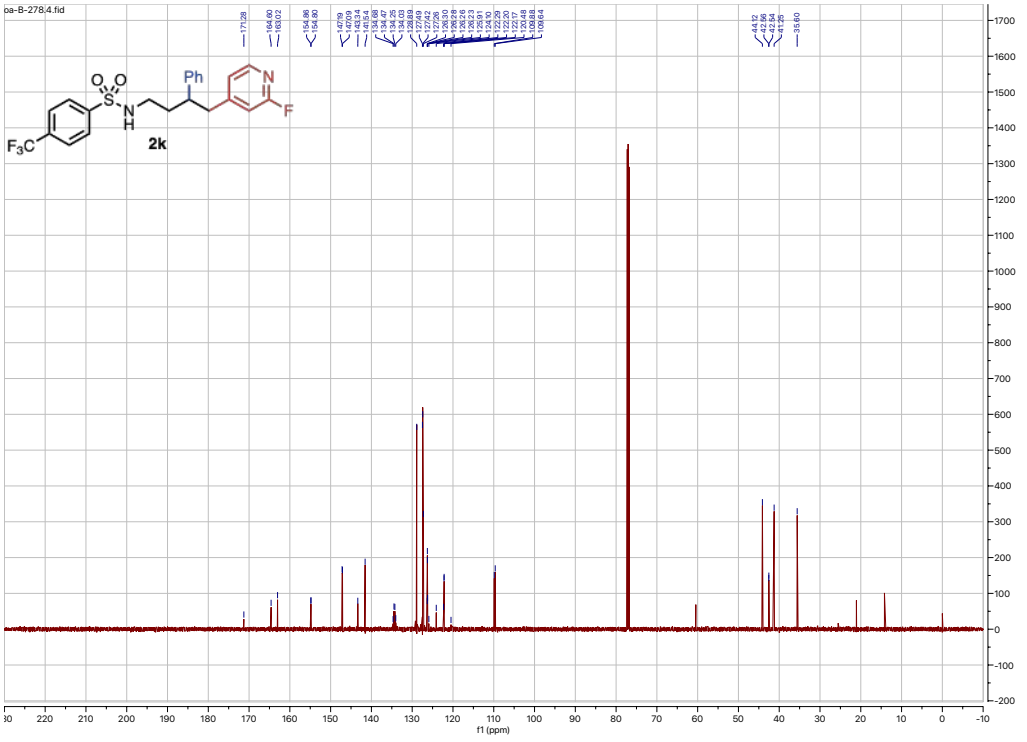
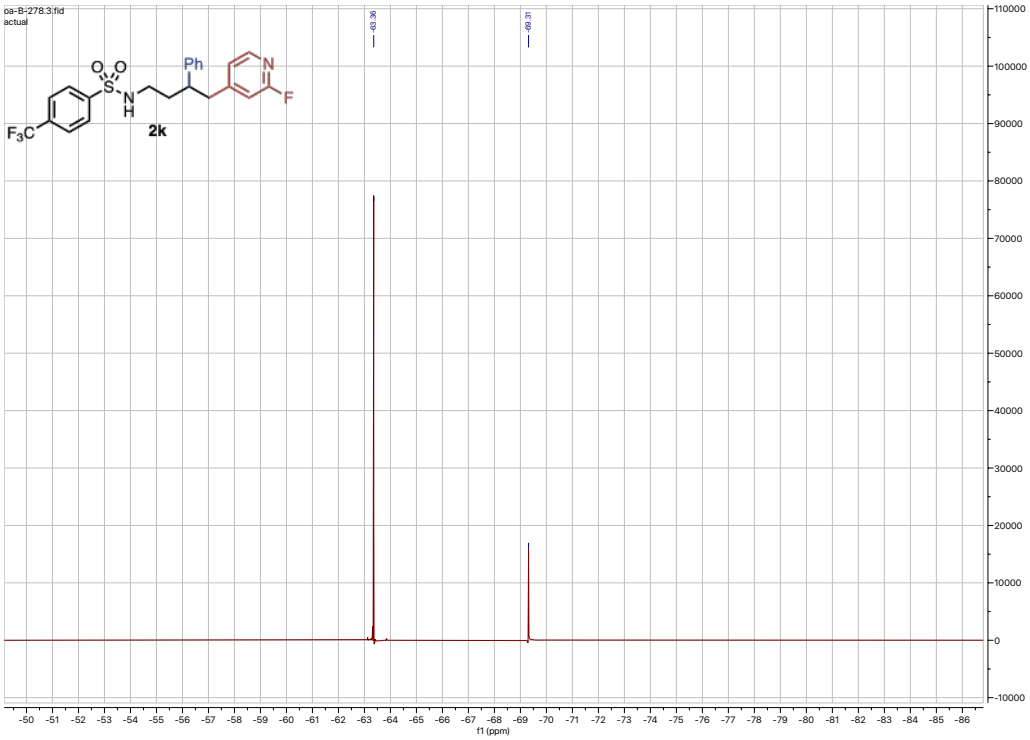
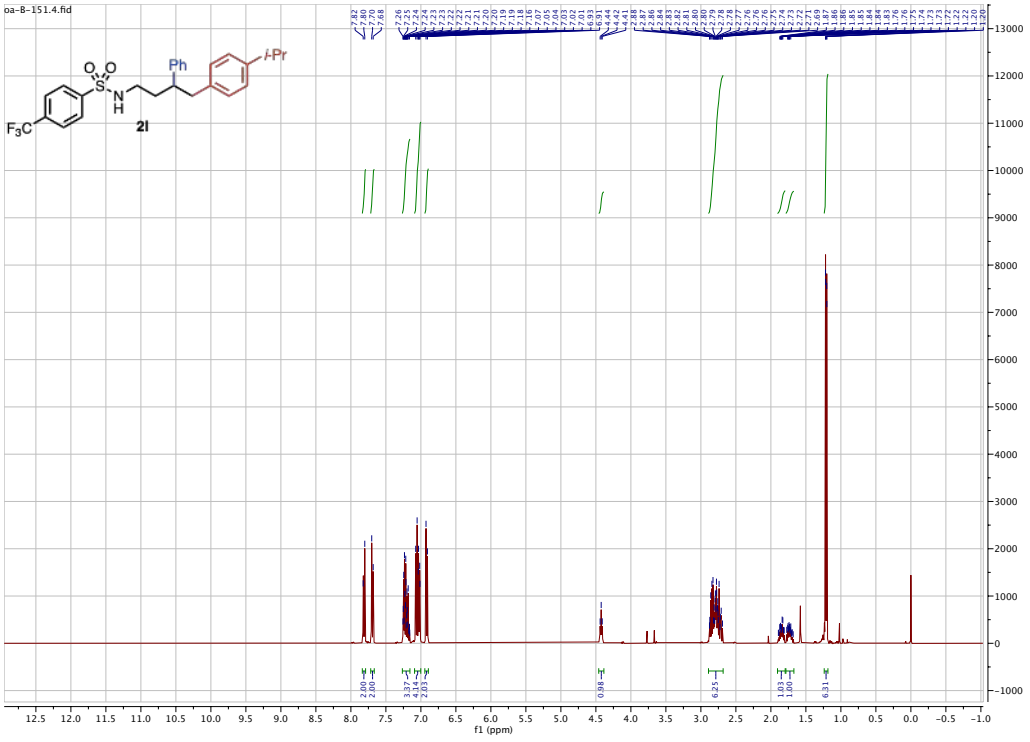
f1 (ppm)

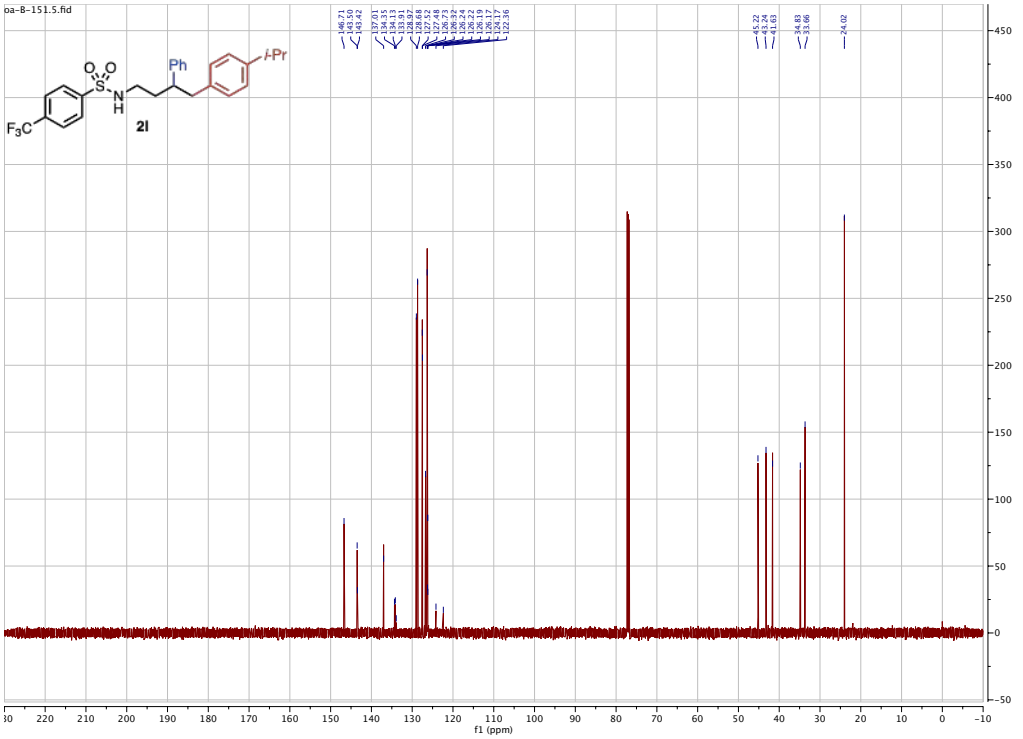

oa-B-214.3.fid
2j
f1 (ppm)

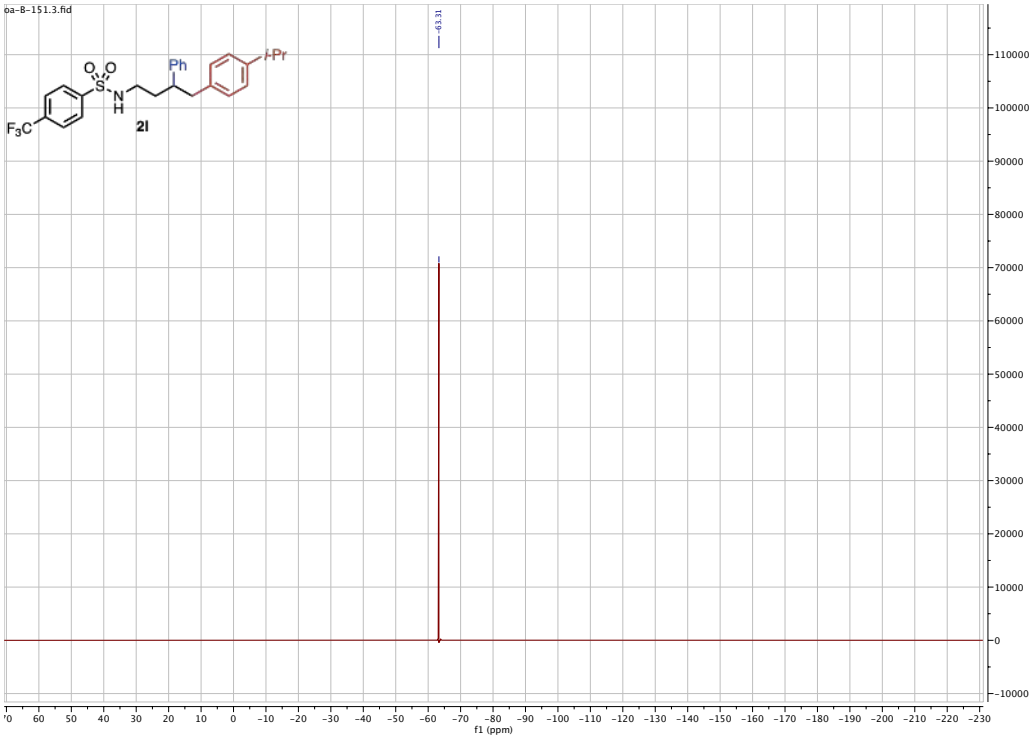

oa-B-278.2.fid
actual
Ph
N
F
O
O
S
N
H
F3C
2k
f1 (ppm)

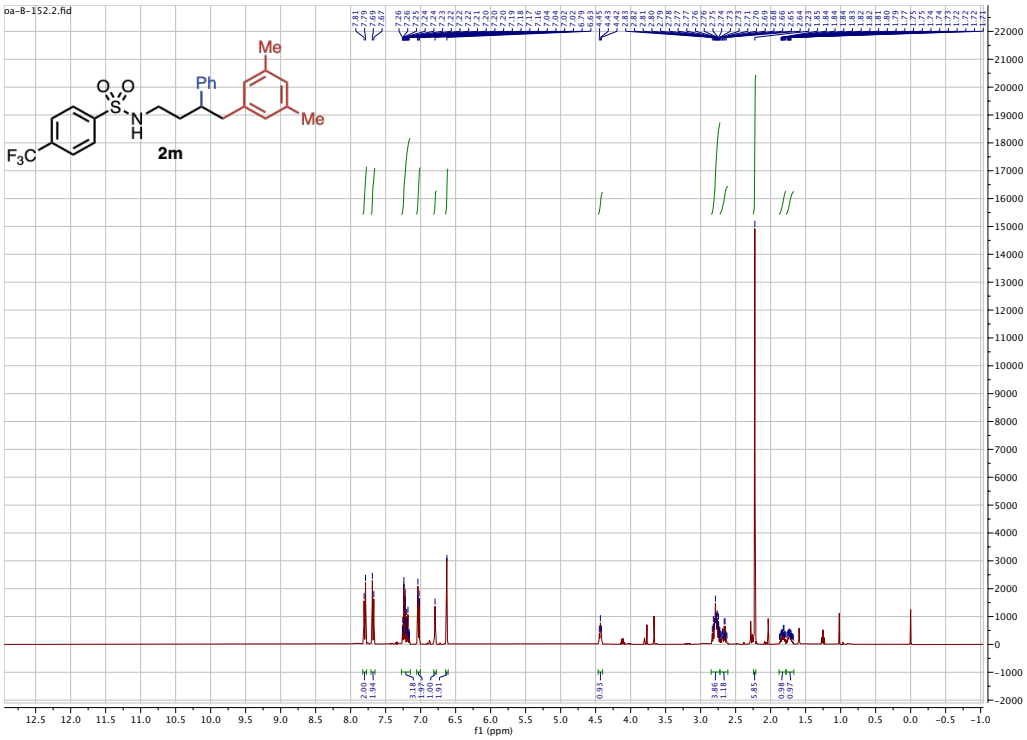

oa-B-278.4.fid
Ph
N
F
O
O
S
N
H
F3C
2k
f1 (ppm)


oa-B-278.3.fid
actual
2k
f1 (ppm)


oa-B-151.4.fid
2l
f1 (ppm)


oa-B-151.5.fid
Ph
i-Pr
F3C
2l
f1 (ppm)


oa-B-151.3.fid
-63.31
Ph
i-Pr
F3C
2l
f1 (ppm)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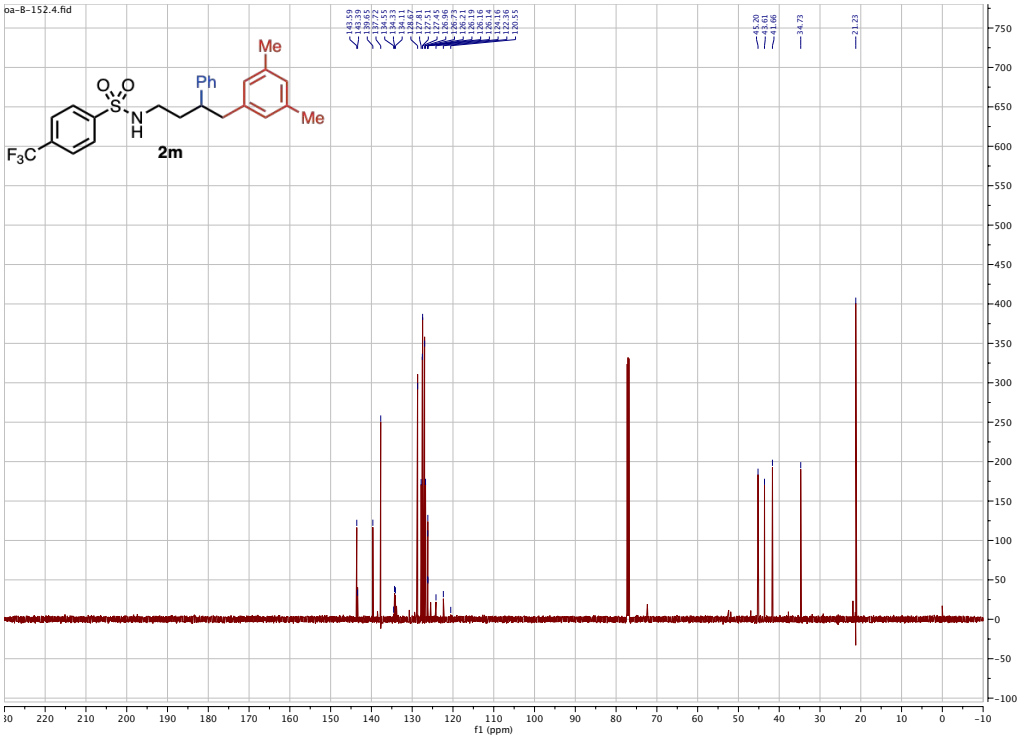
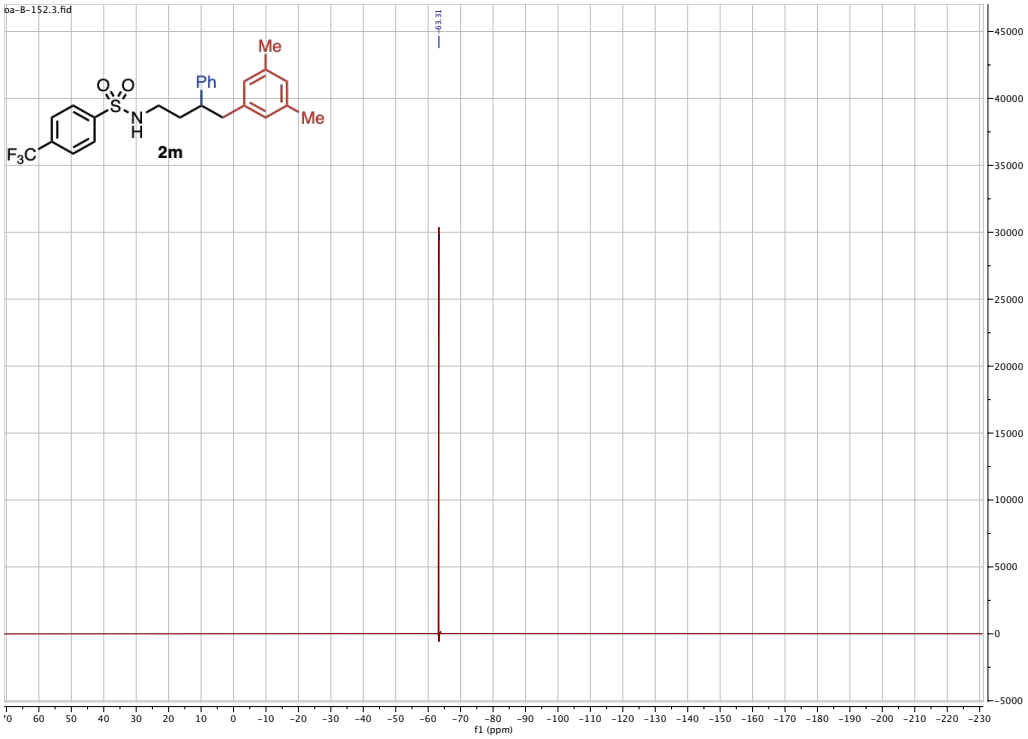
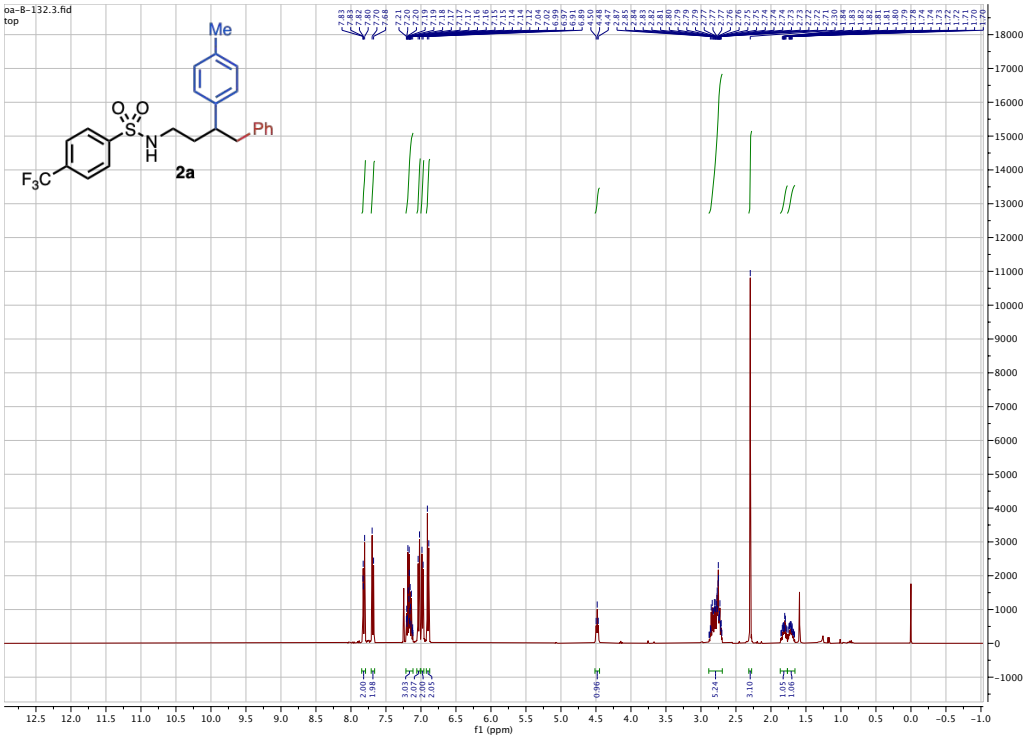
Me
Ph
Me
O
O
S
N
H
F3C
2m
f1 (ppm)


oa-B-152.4.fid
Me
Ph
Me
O
O
S
N
H
F3C
2m
f1 (ppm)


oa-B-152.3.fid
Me
Ph
Me
F3C
2m
f1 (ppm)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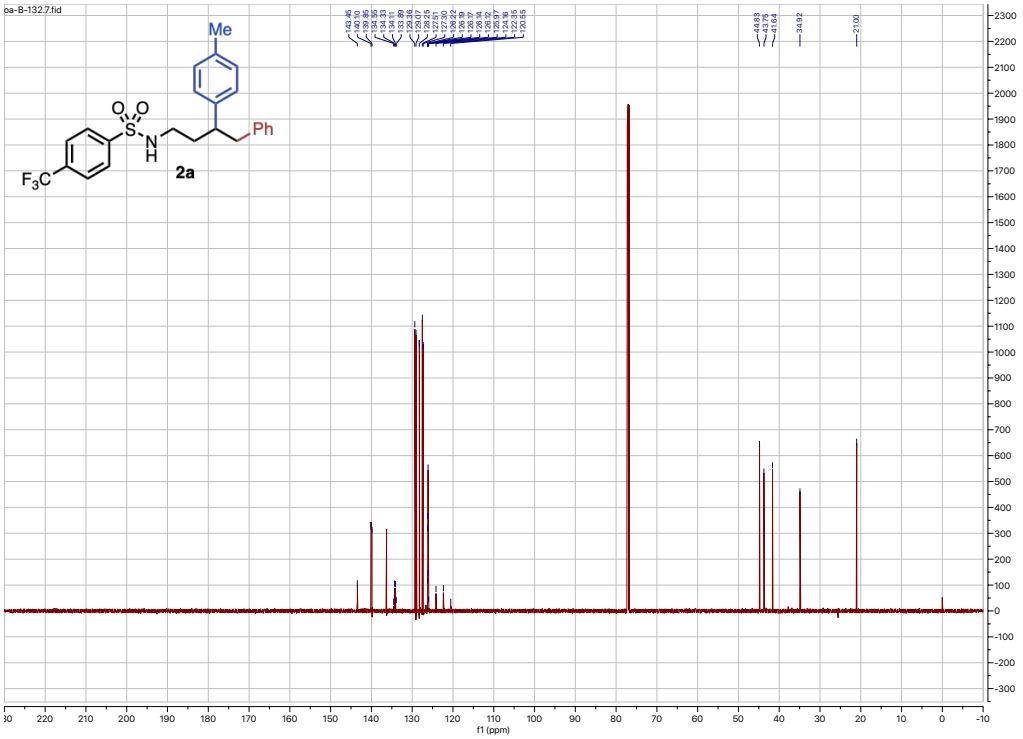
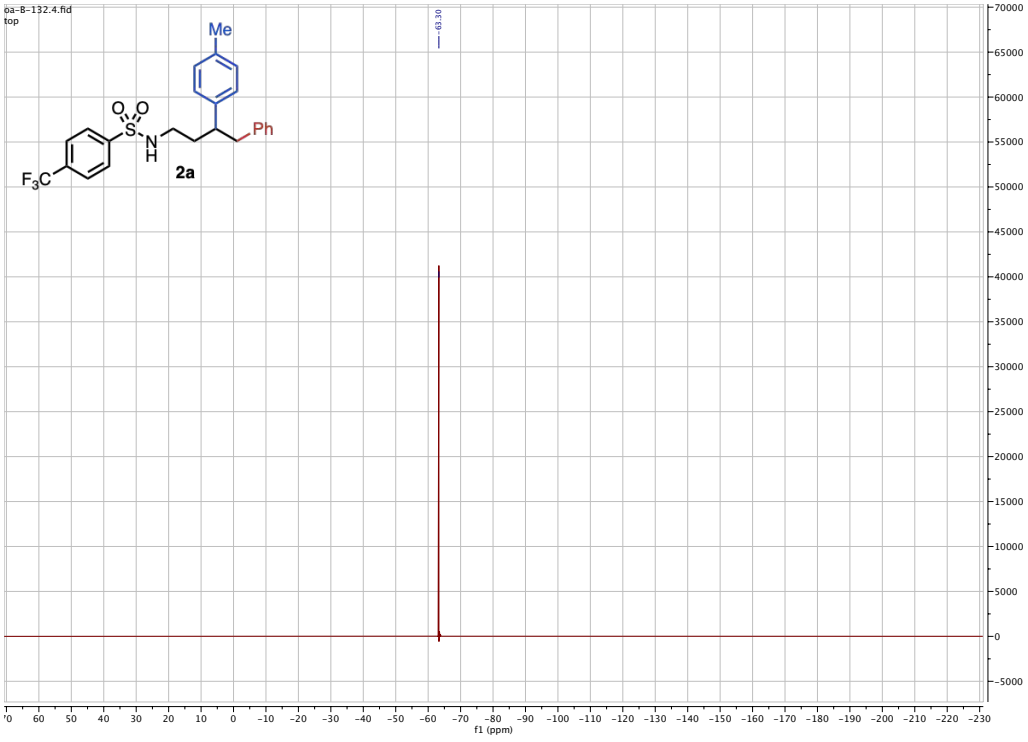
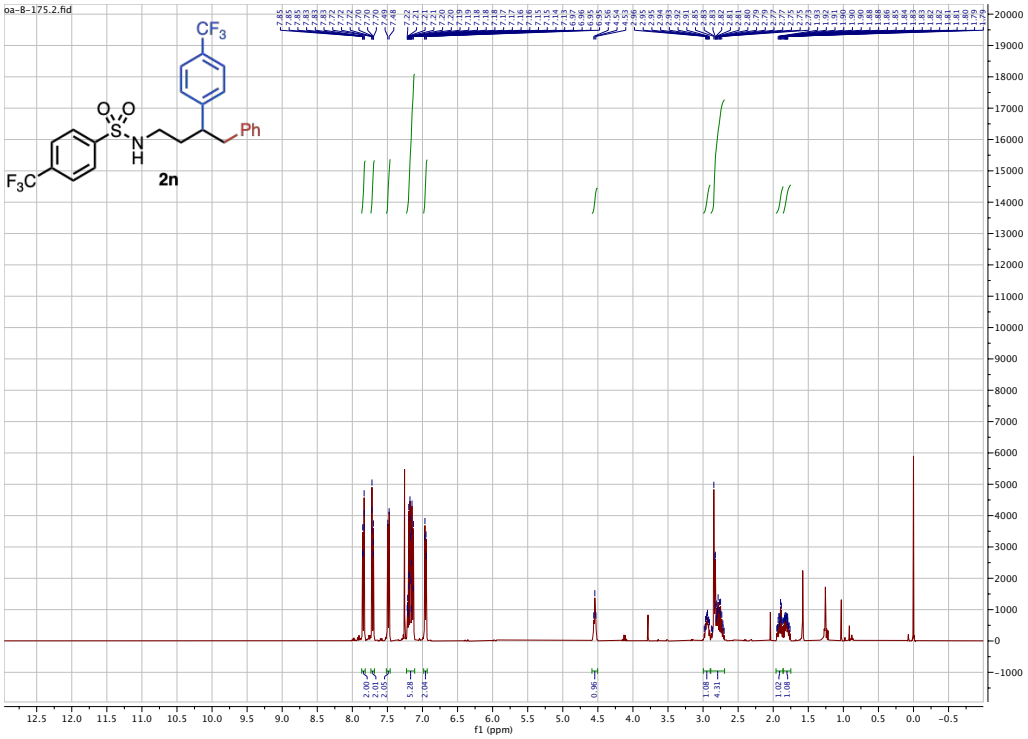
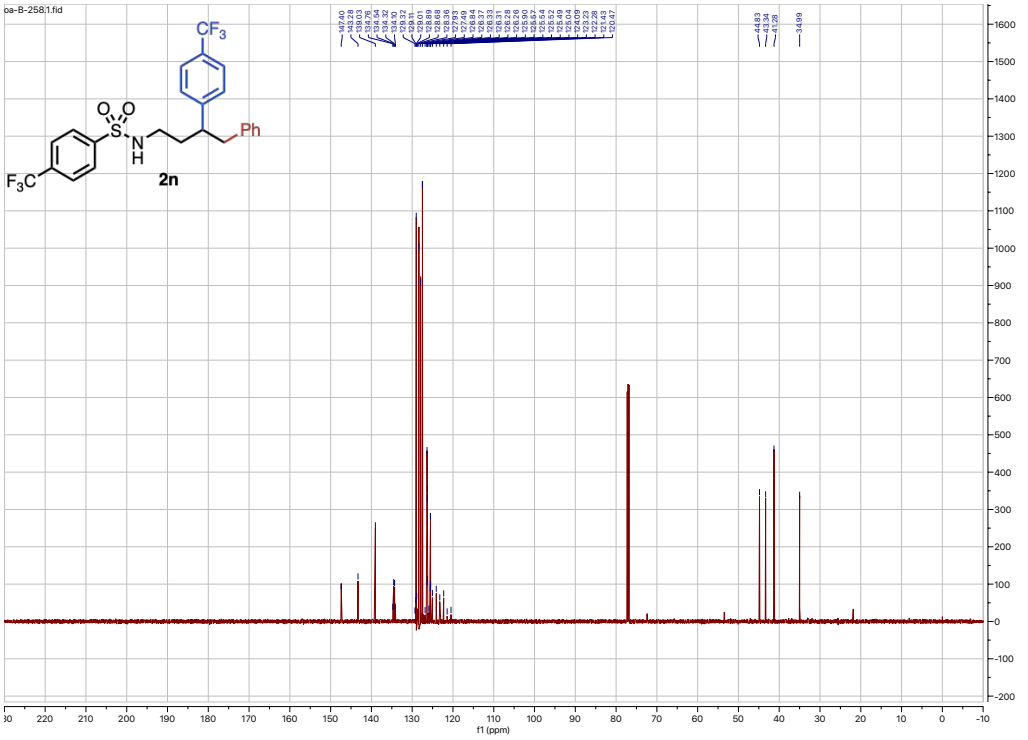
top
Me
Ph
F3C
2a
f1 (ppm)


oa-B-132.7.fid
Me
Ph
2a
f1 (ppm)


oa-B-132.4.fid
top
Me
Ph
2a
f1 (ppm)


oa-B-175.2.fid
CF3
Ph
F3C
2n
f1 (ppm)


oa-B-258.1.fid
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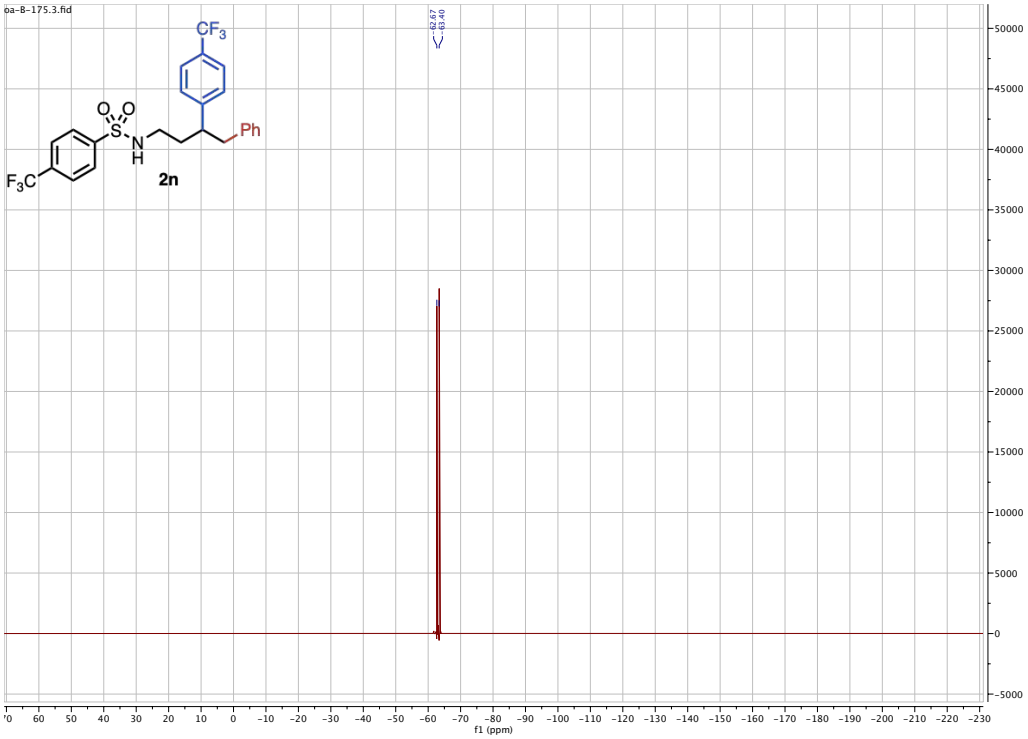
Ph
F3C
2n
f1 (ppm)


oa-B-175.3.fid
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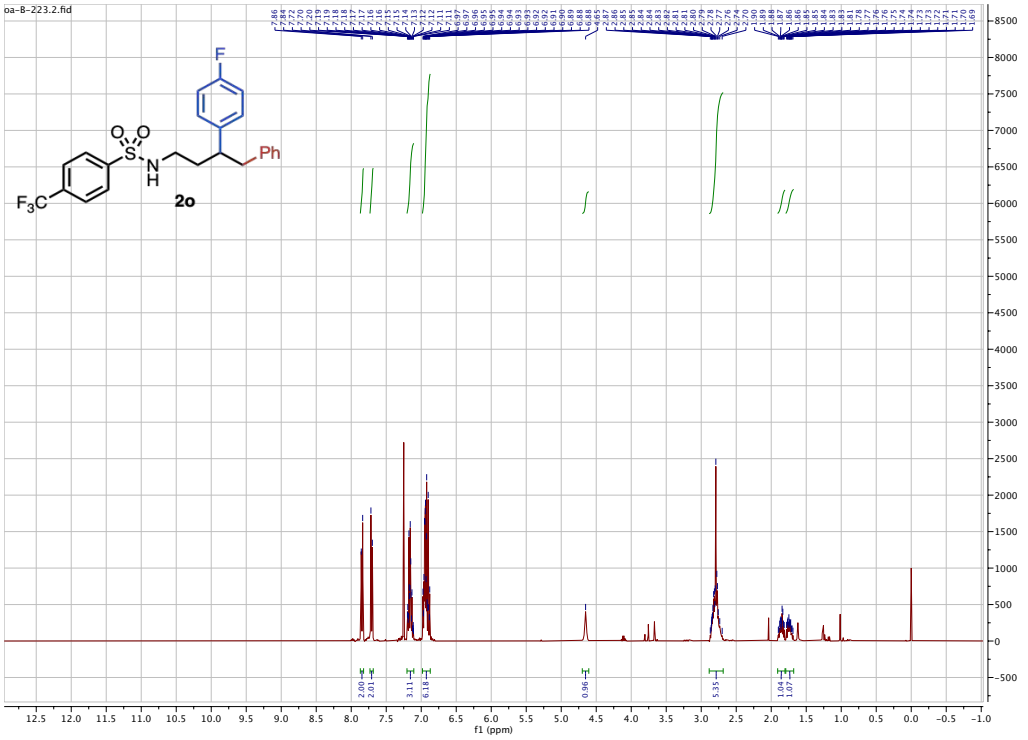
O
O
S
N
H
Ph
F3C
2n
-62.67
-63.40
f1 (ppm)


oa-B-223.2.fid
F
O
O
S
N
H
Ph
F3C
2o
2.00
2.01
3.11
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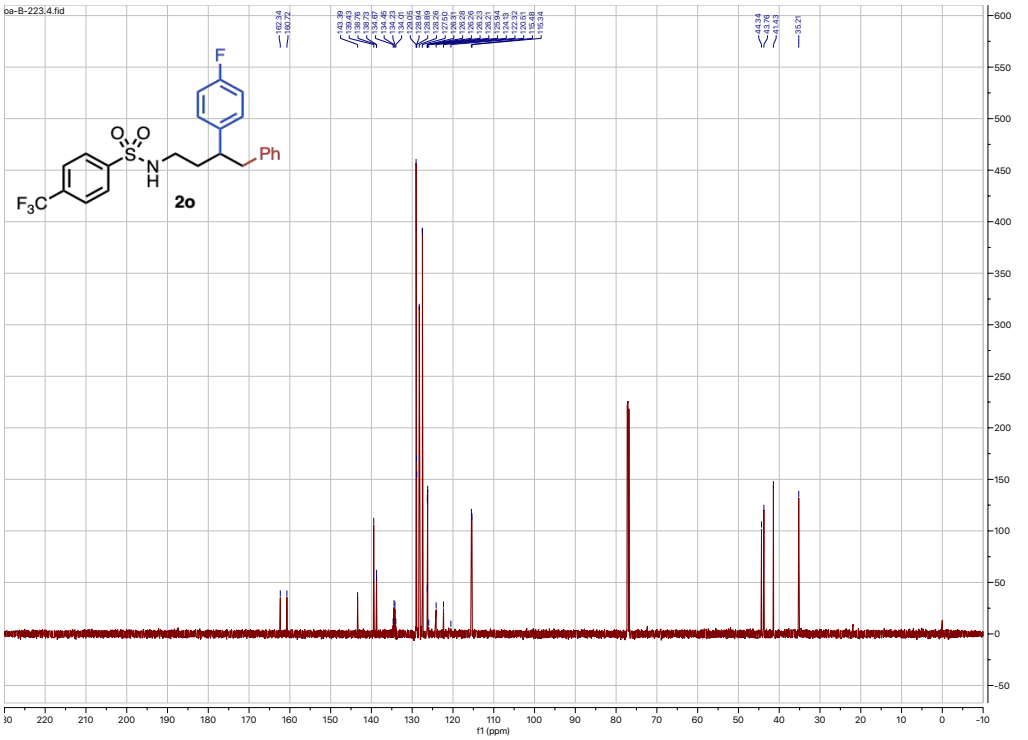
0.96
5.35
1.04
1.07
f1 (ppm)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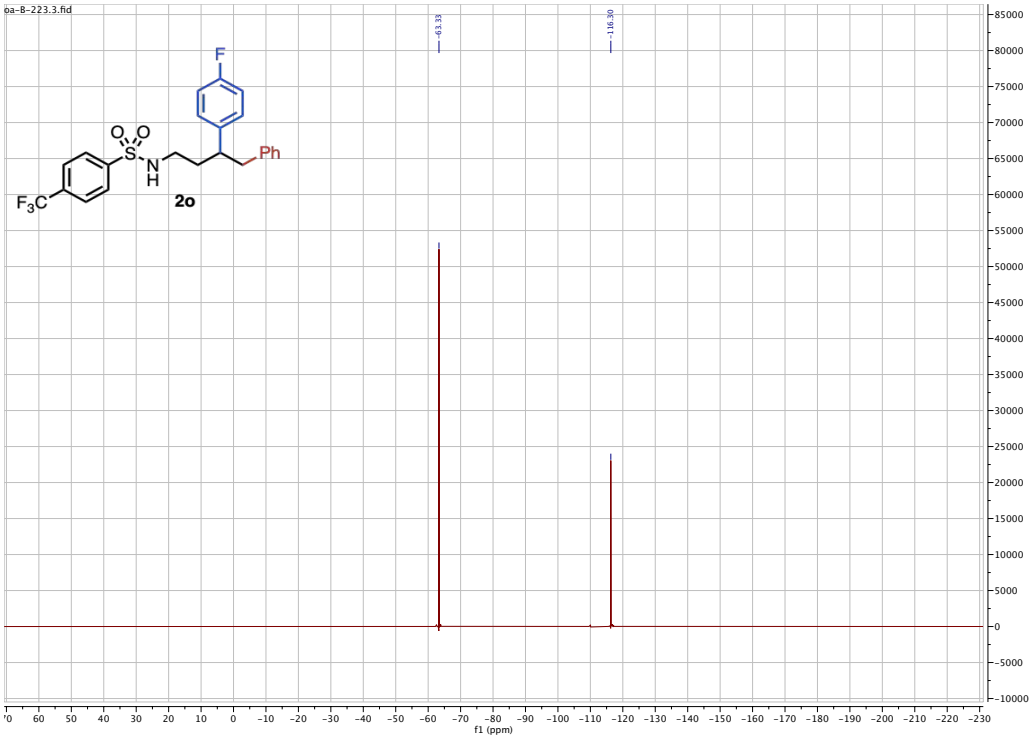
Ph
O
O
S
N
H
F3C
2o
f1 (ppm)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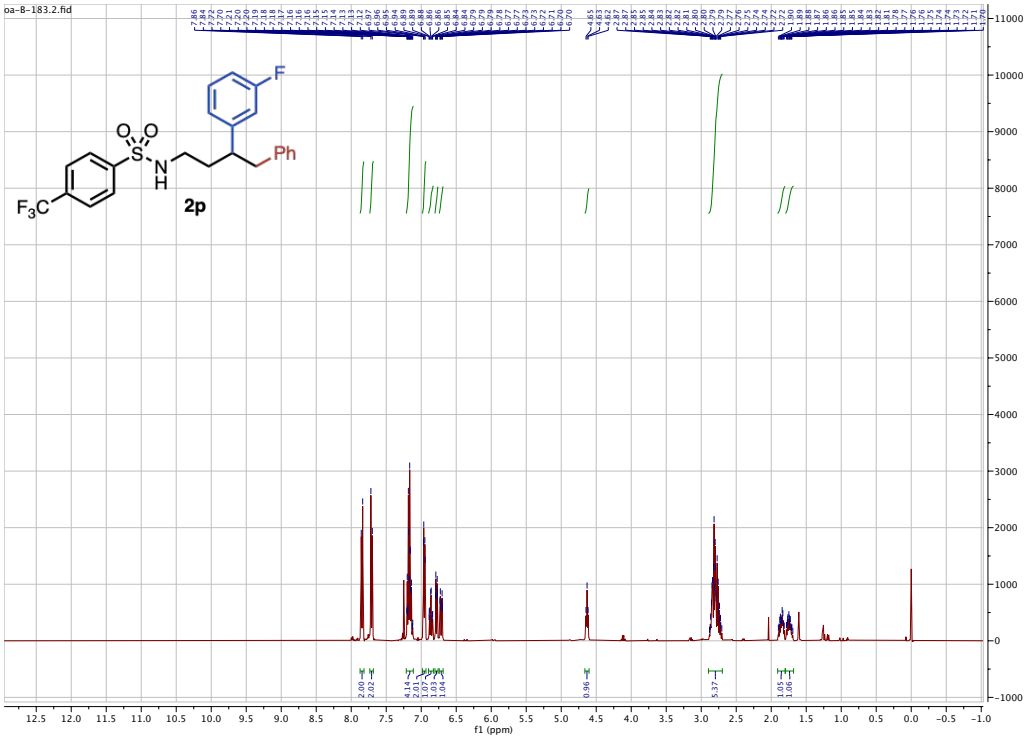
-116.30
F
Ph
O
O
S
N
H
F3C
2o
f1 (ppm)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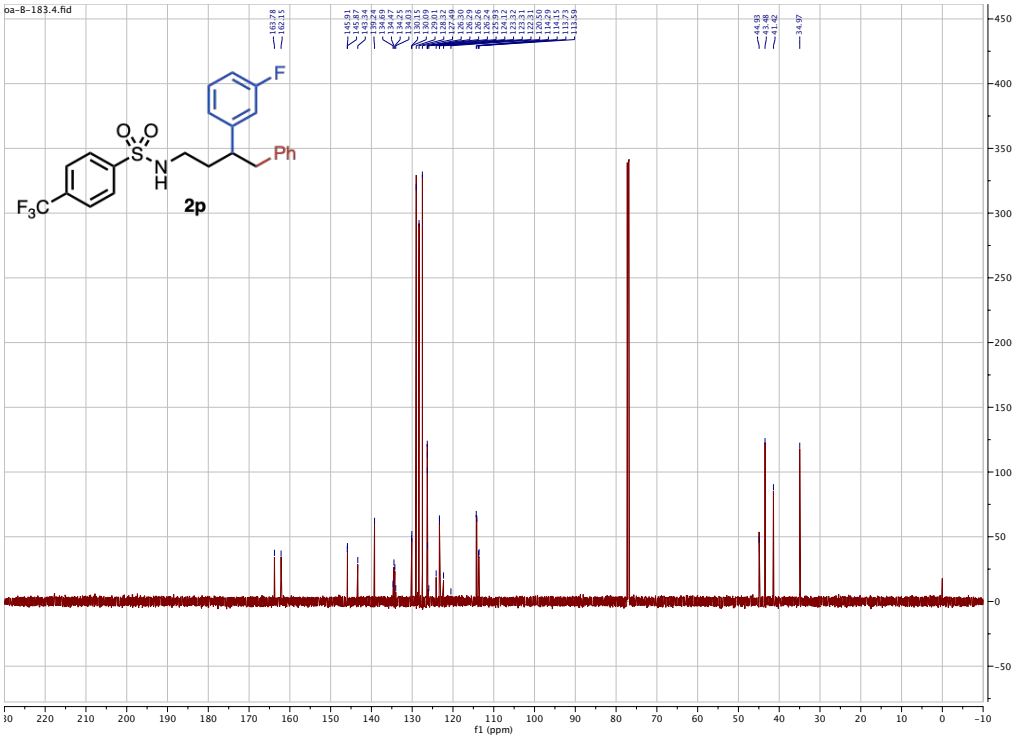
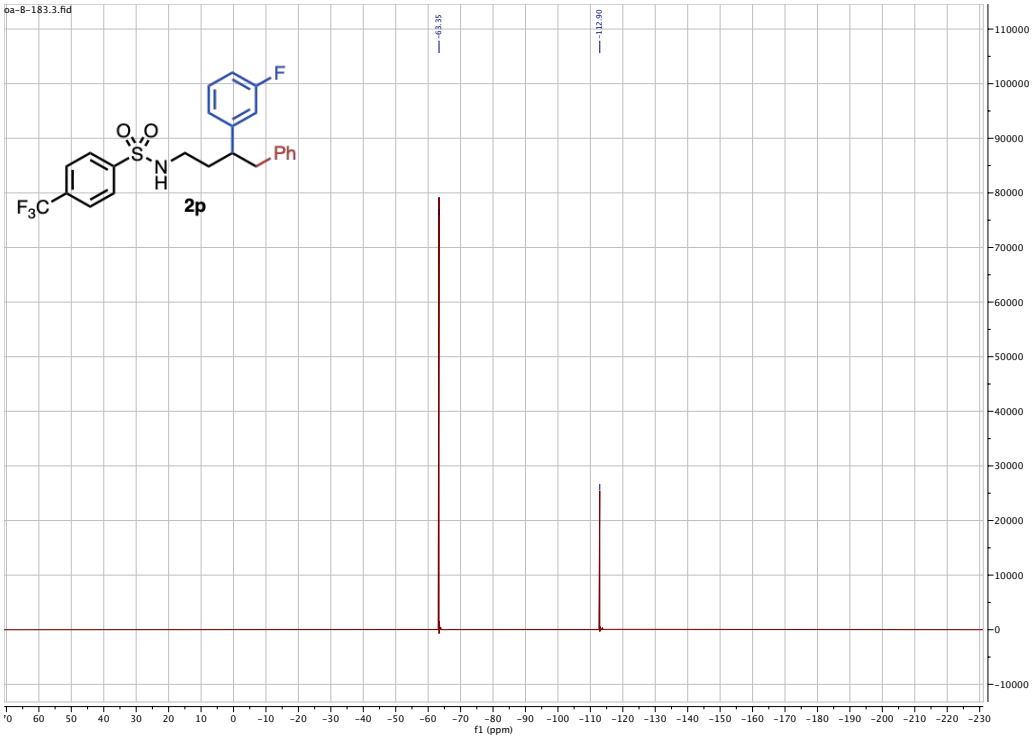
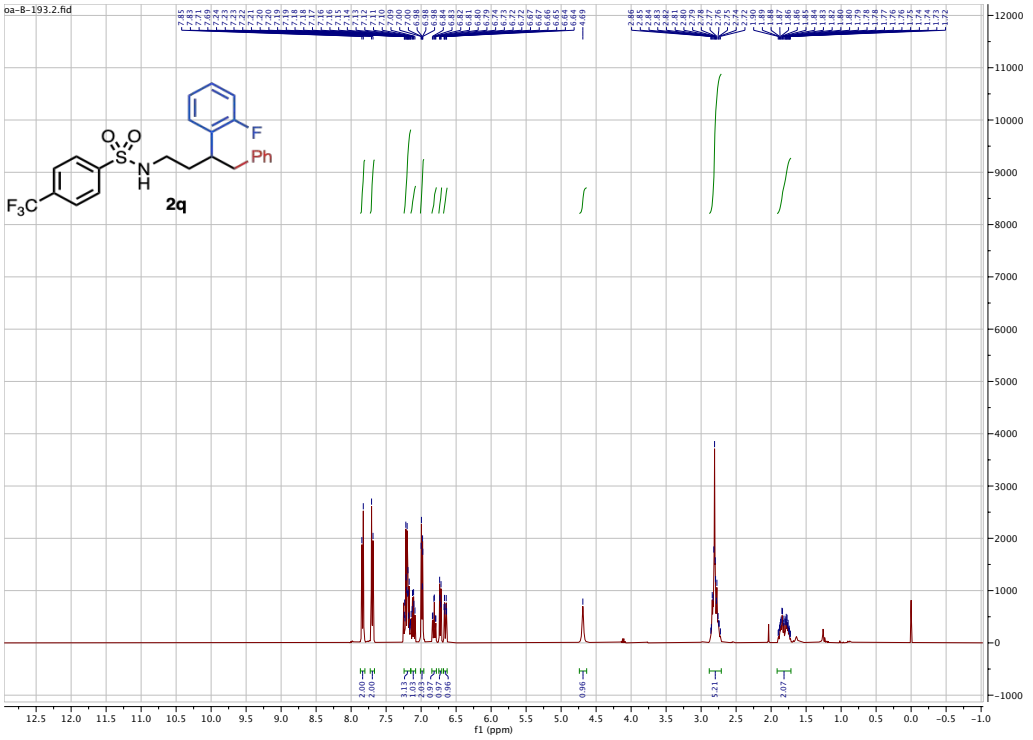
F
Ph
O
O
S
N
H
F3C
2p
f1 (ppm)


oa-B-183.4.fid
F
Ph
O
O
S
N
H
F3C
2p
f1 (ppm)


oa-B-183.3.fid
-63.35
-112.90
F
Ph
O
O
S
N
H
F3C
2p
f1 (ppm)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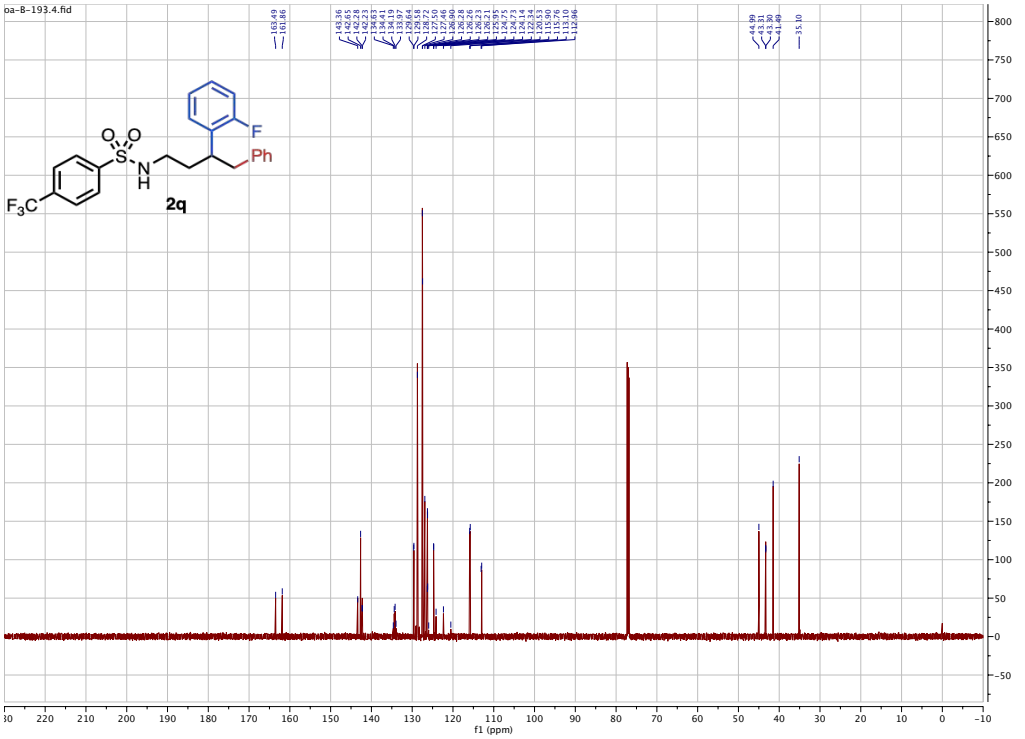
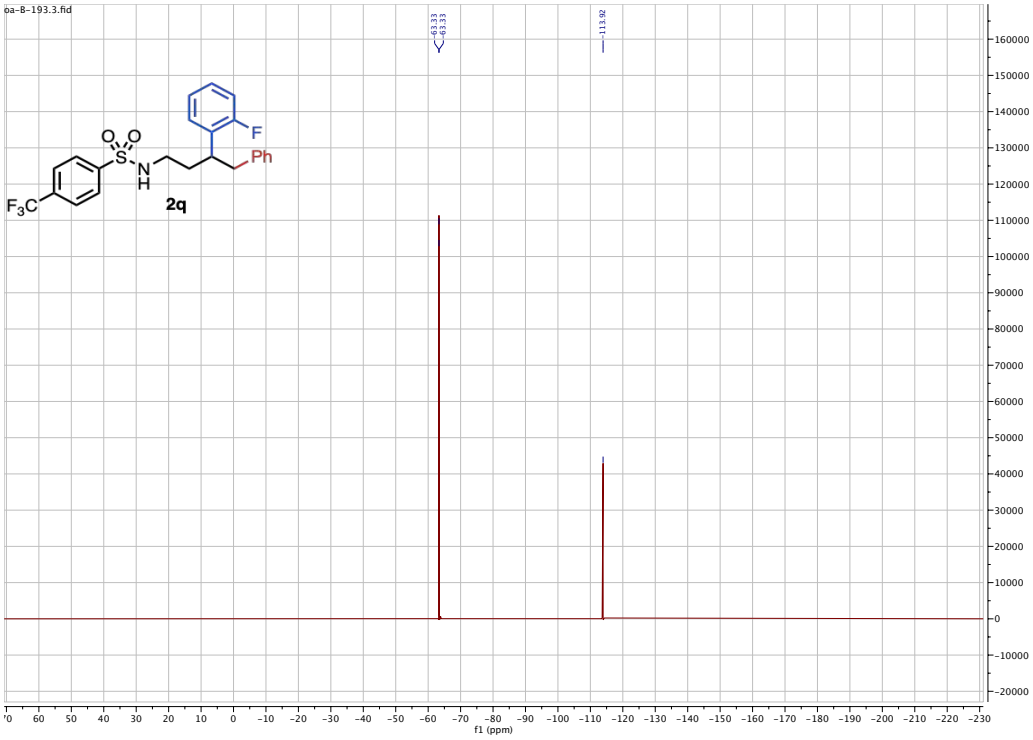
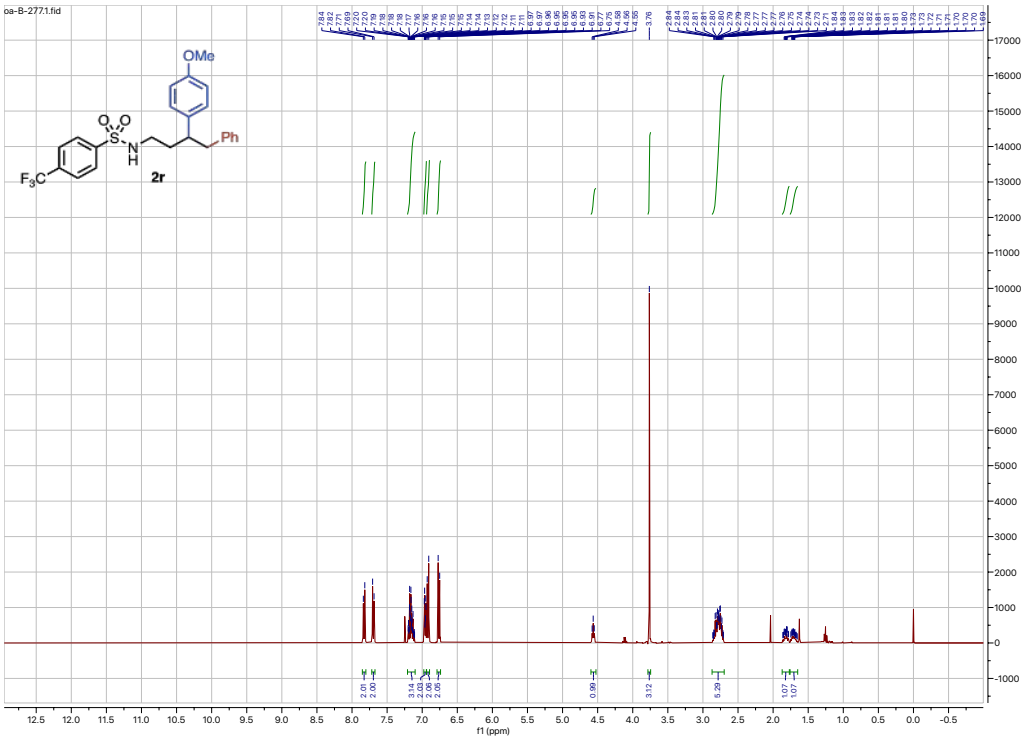
F
Ph
O
O
S
N
H
F3C
2q
f1 (ppm)


oa-B-193.4.fid
2q
f1 (ppm)


oa-B-193.3.fid
2q
f1 (ppm)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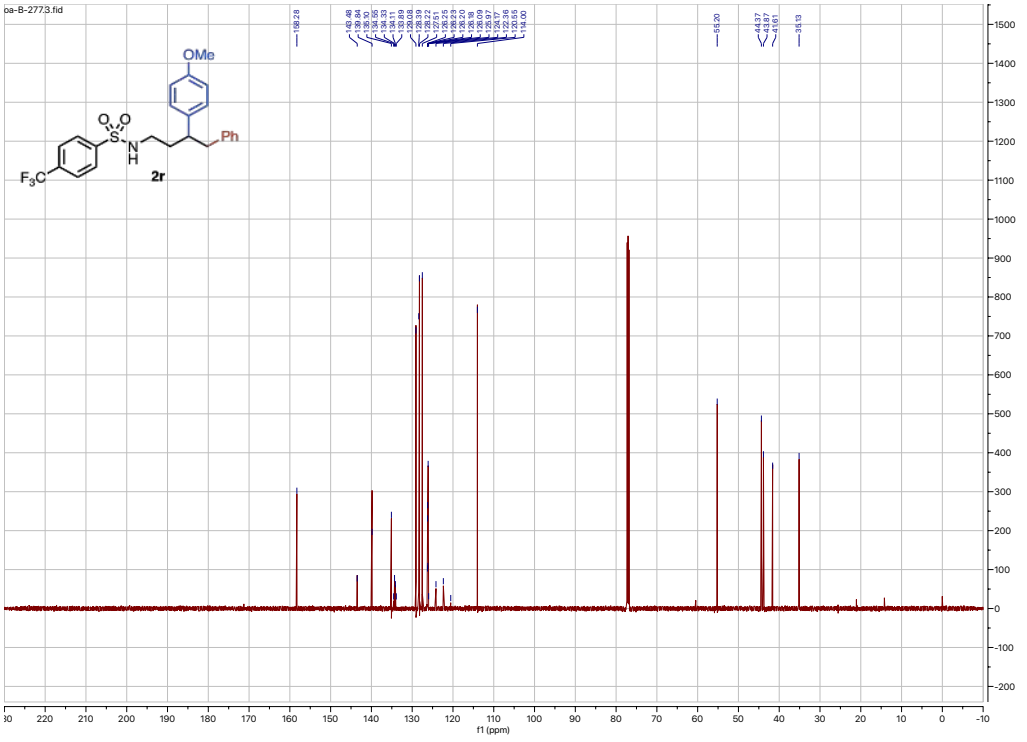
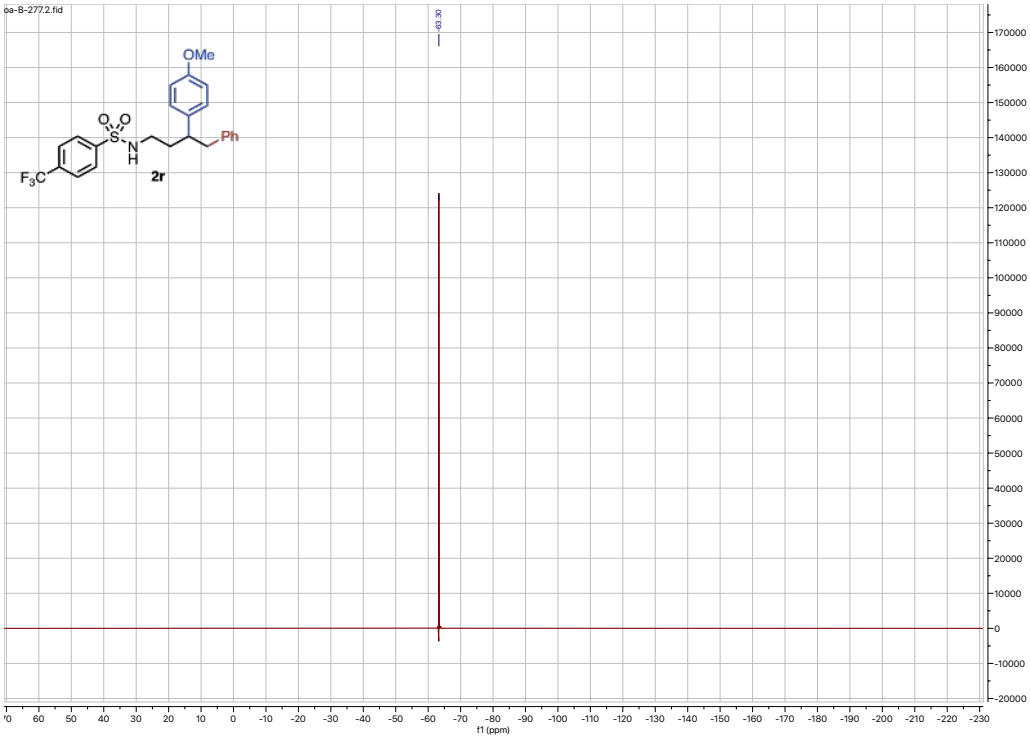
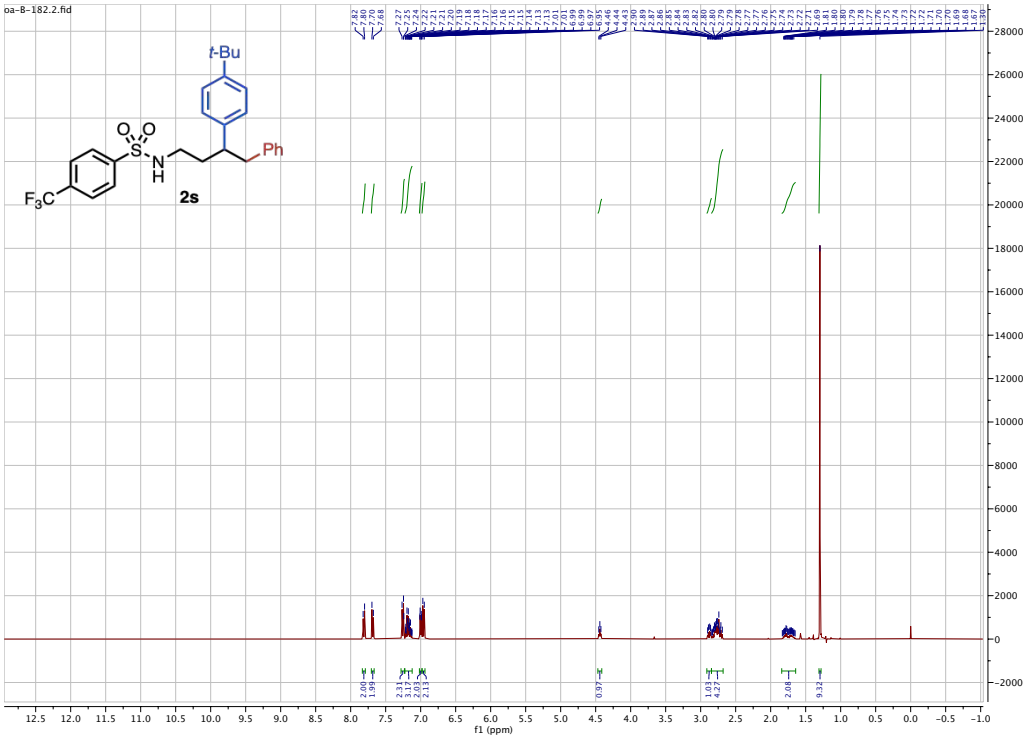
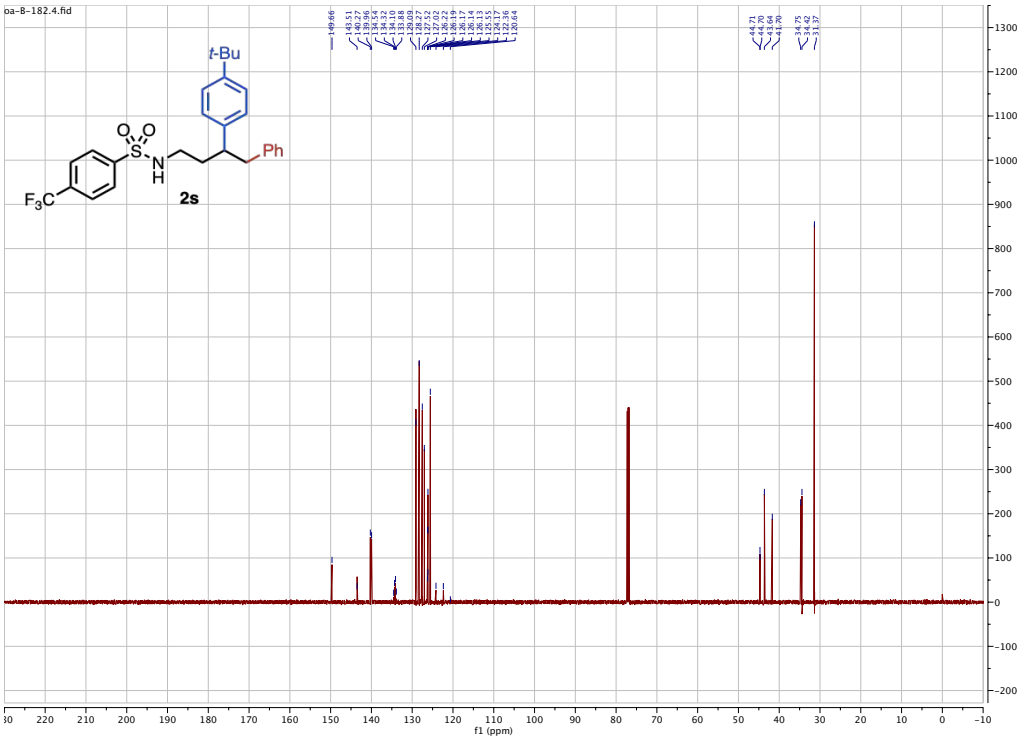
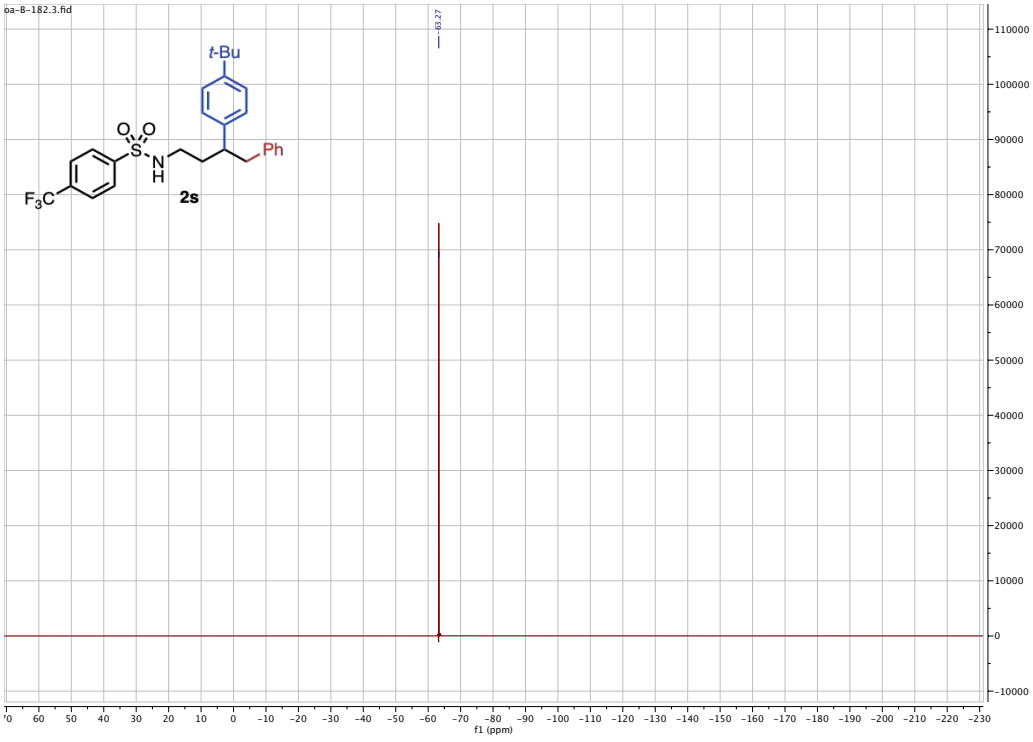
OMe
Ph
F3C
2r
f1 (ppm)

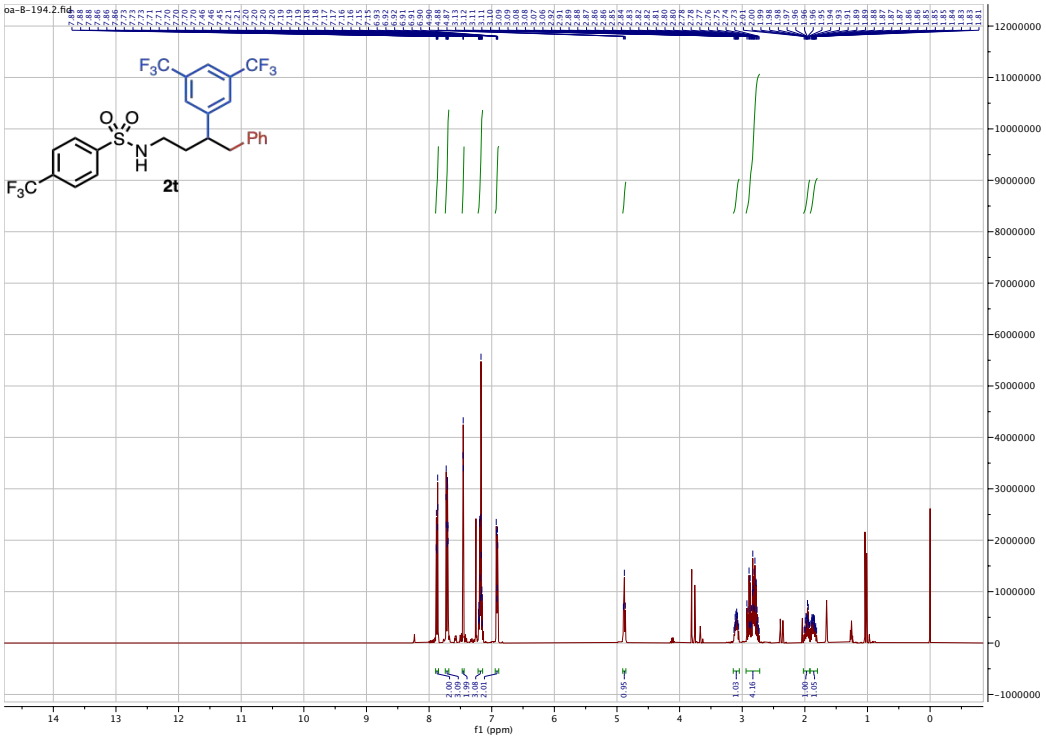

oa-B-277.3.fid
OMe
Ph
F3C
2r
f1 (ppm)

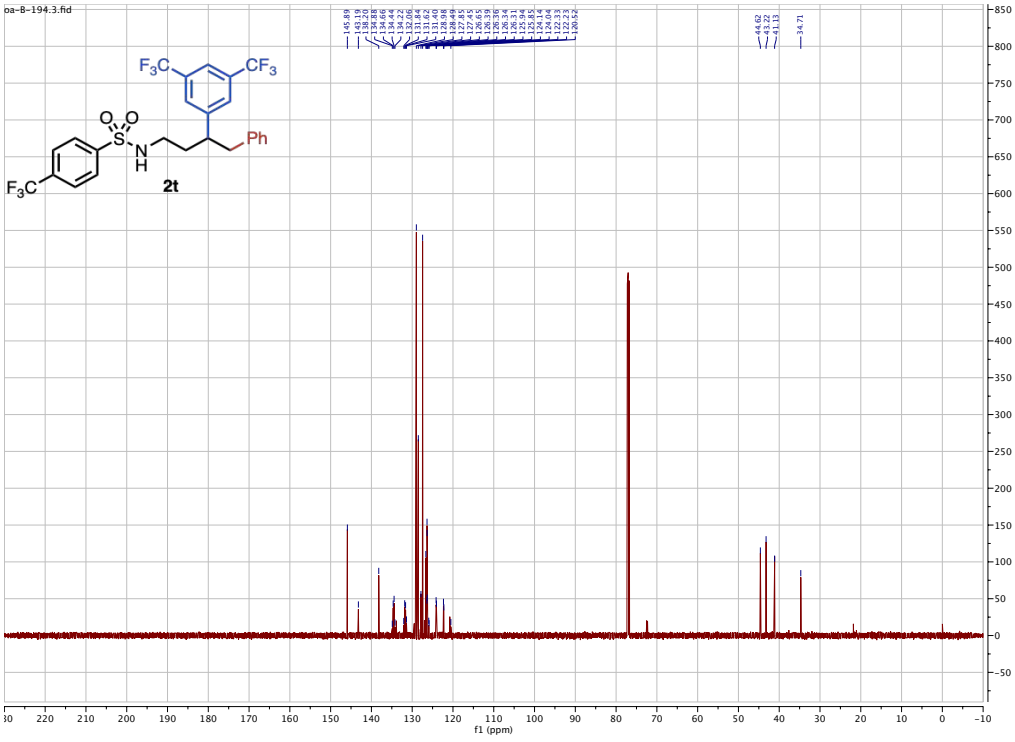

oa-B-277.2.fid
OMe
Ph
F3C
2r
f1 (ppm)


oa-B-182.2.fid
t-Bu
Ph
F3C
2s
f1 (ppm)


oa-B-182.4.fid
t-Bu
Ph
F3C
2s
f1 (ppm)


oa-B-182.3.fid
t-Bu
Ph
F3C
2s
f1 (ppm)


oa-B-194.2.fid
F3C
CF3
Ph
F3C
2t
f1 (ppm)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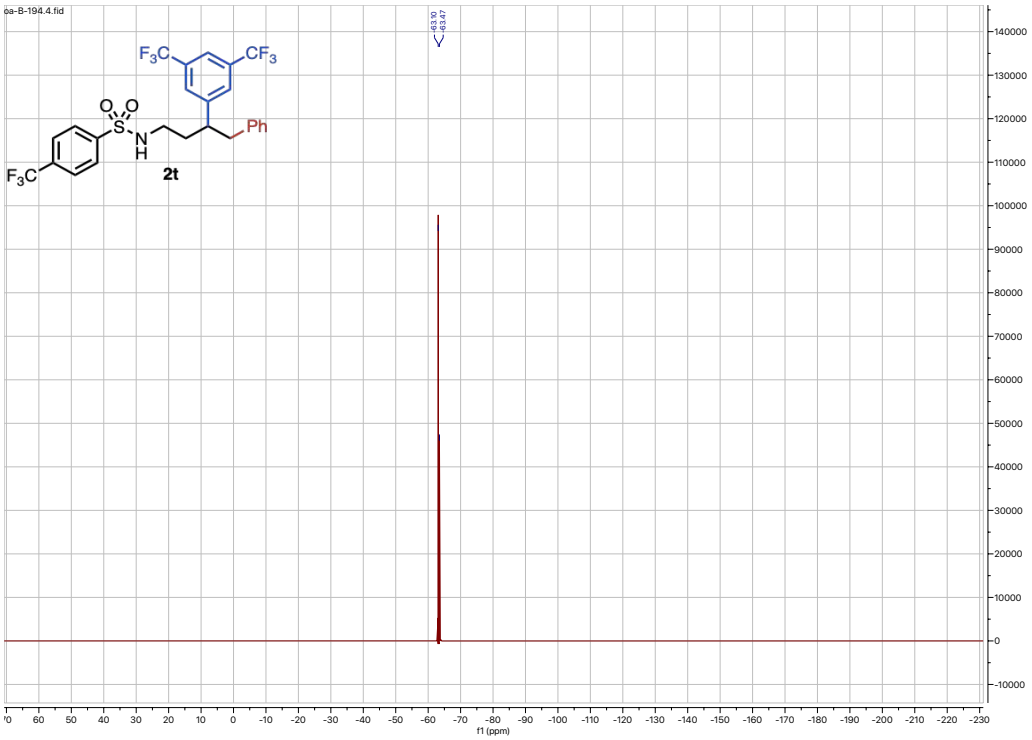
F3C
CF3
Ph
F3C
2t
f1 (ppm)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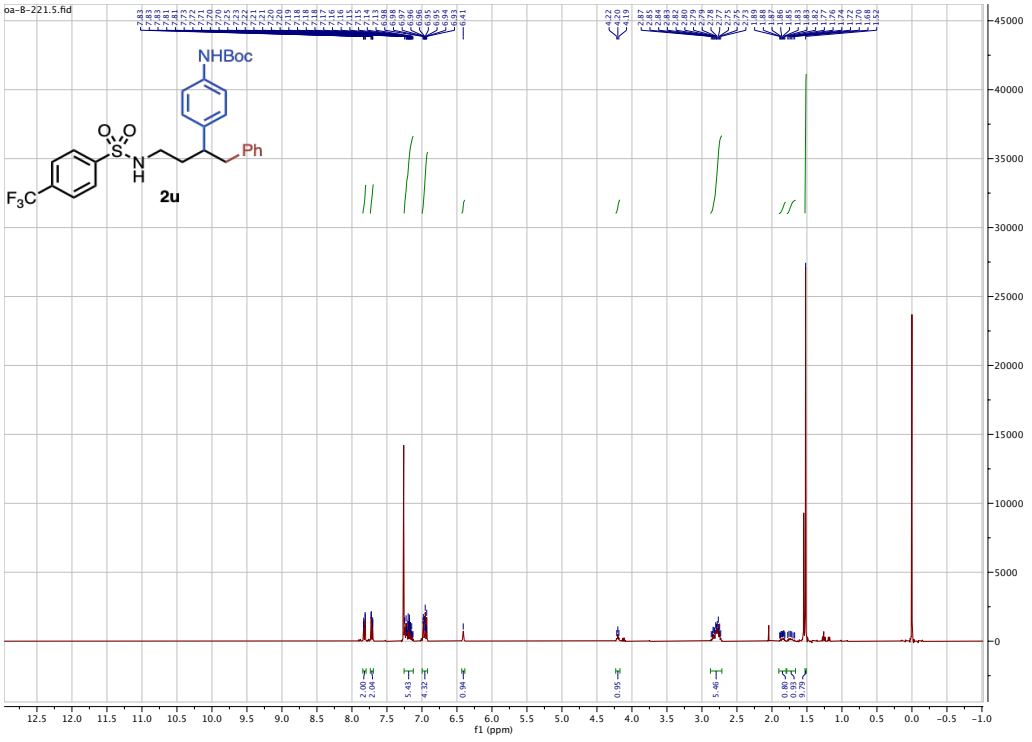
F3C
CF3
Ph
F3C
2t
f1 (ppm)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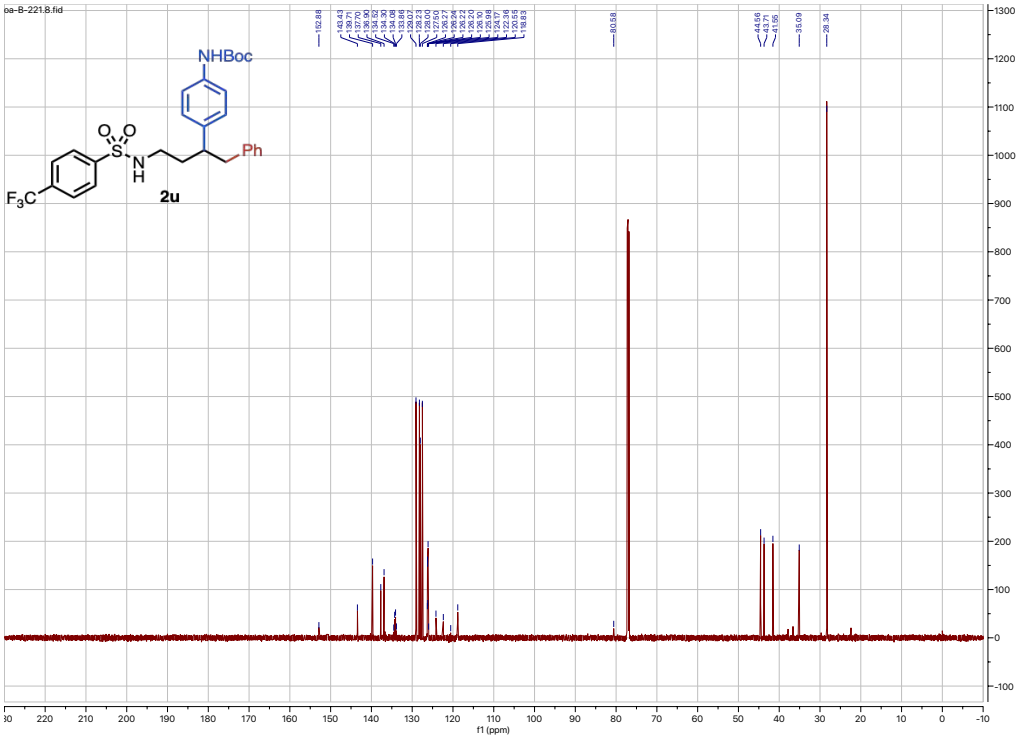
NHBoc
Ph
F3C
2u
f1 (ppm)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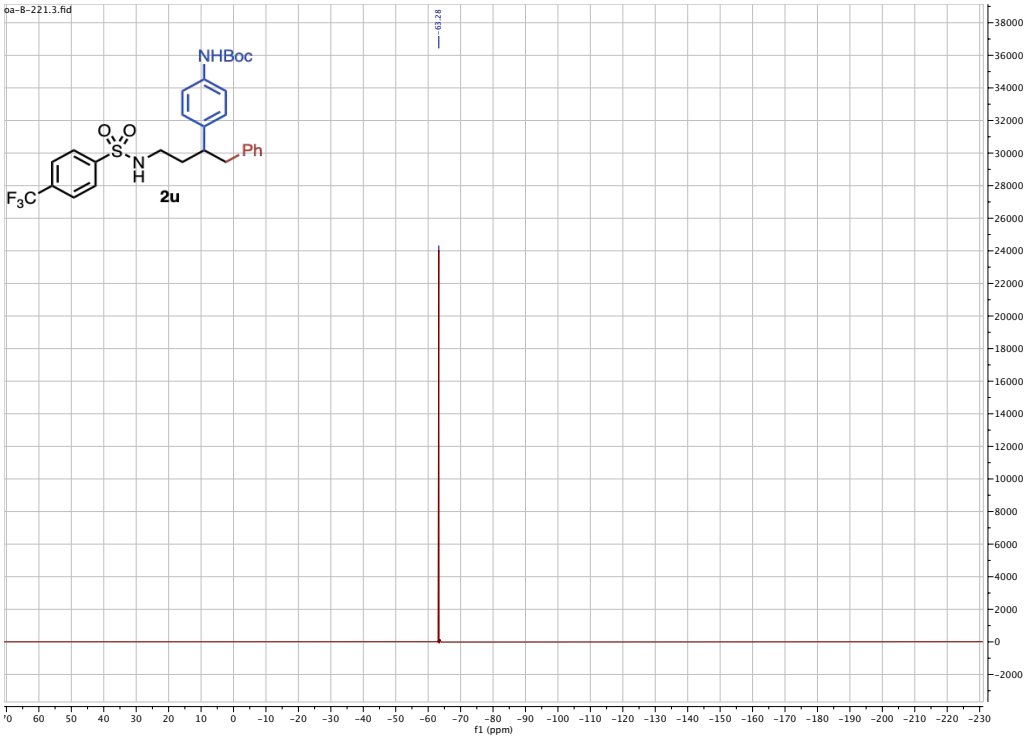
Ph
F3C
2u
f1 (ppm)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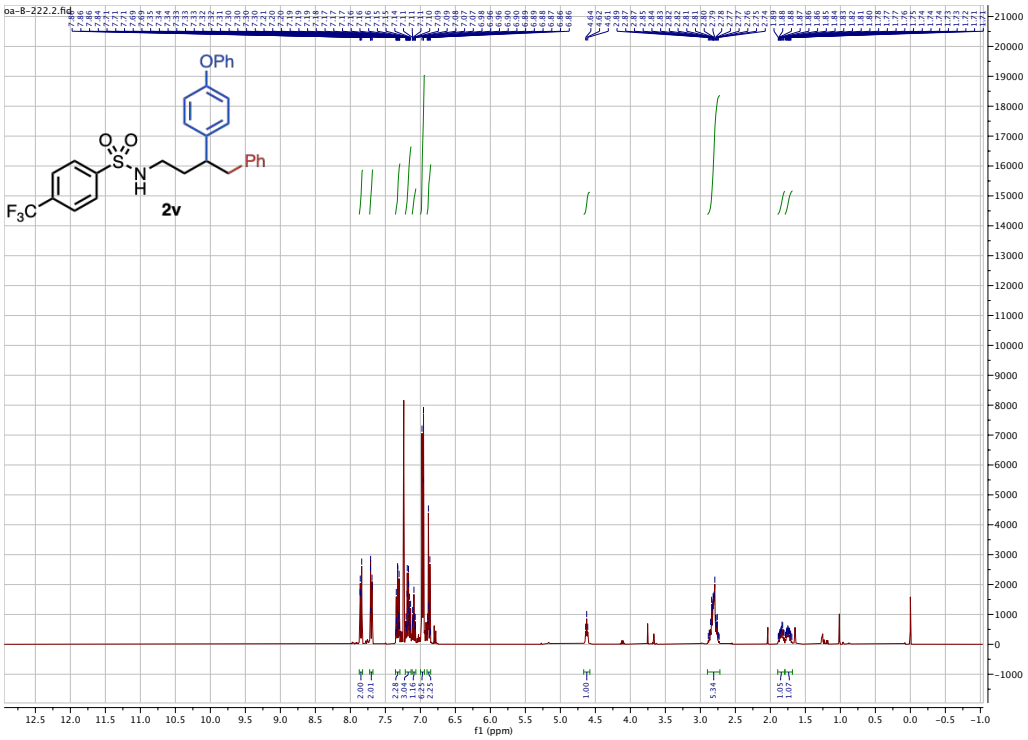
NHBoc
Ph
F3C
2u
f1 (ppm)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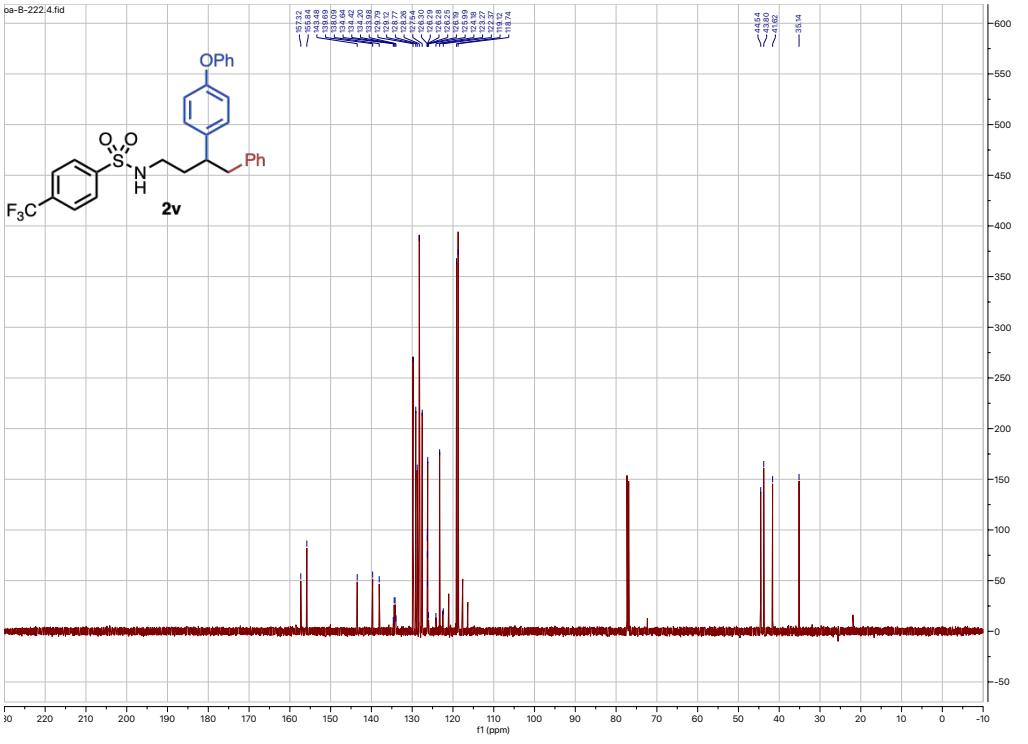
Ph
F3C
2v
f1 (ppm)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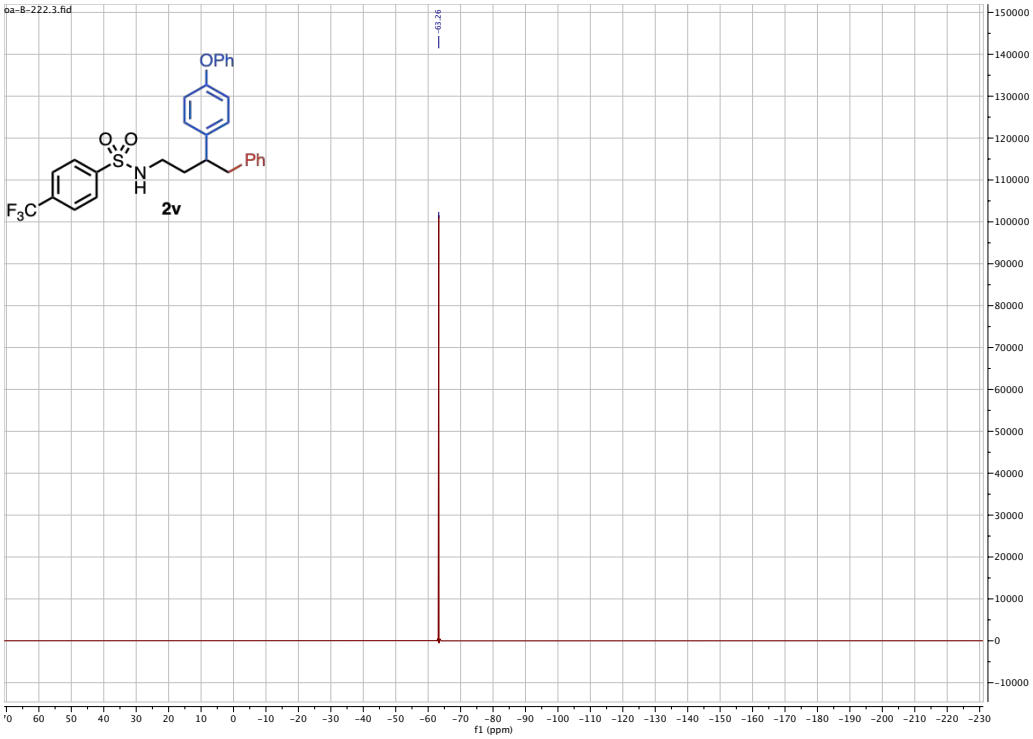
Ph
F3C
2v
f1 (ppm)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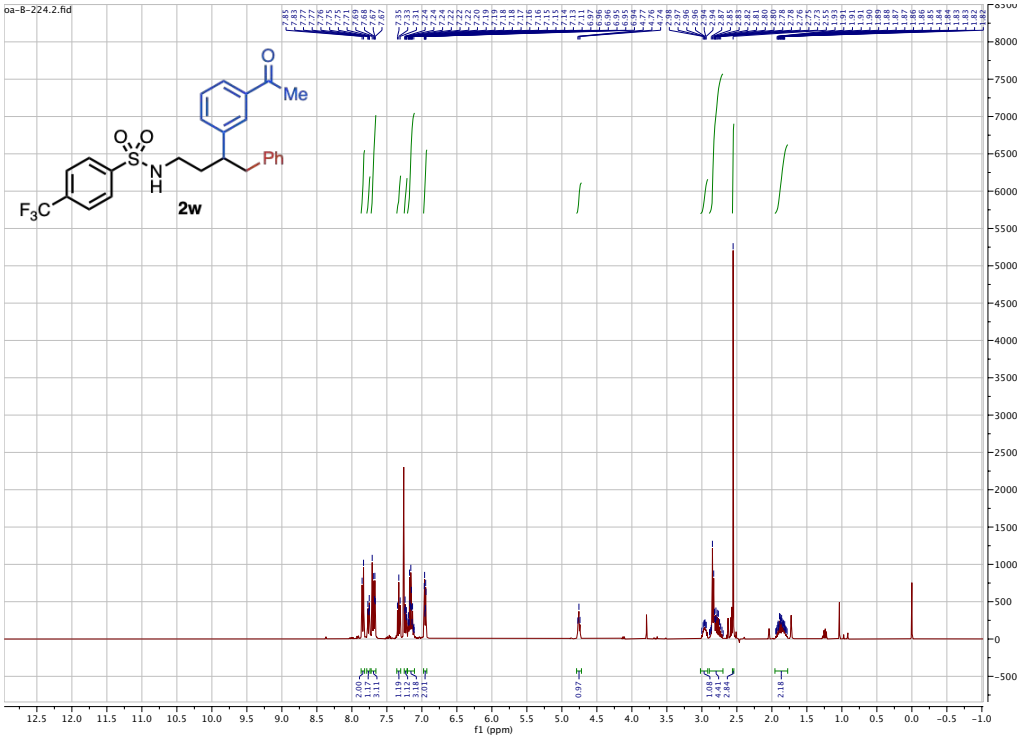
Ph
F3C
2v
f1 (ppm)


oa-B-224.2.fid
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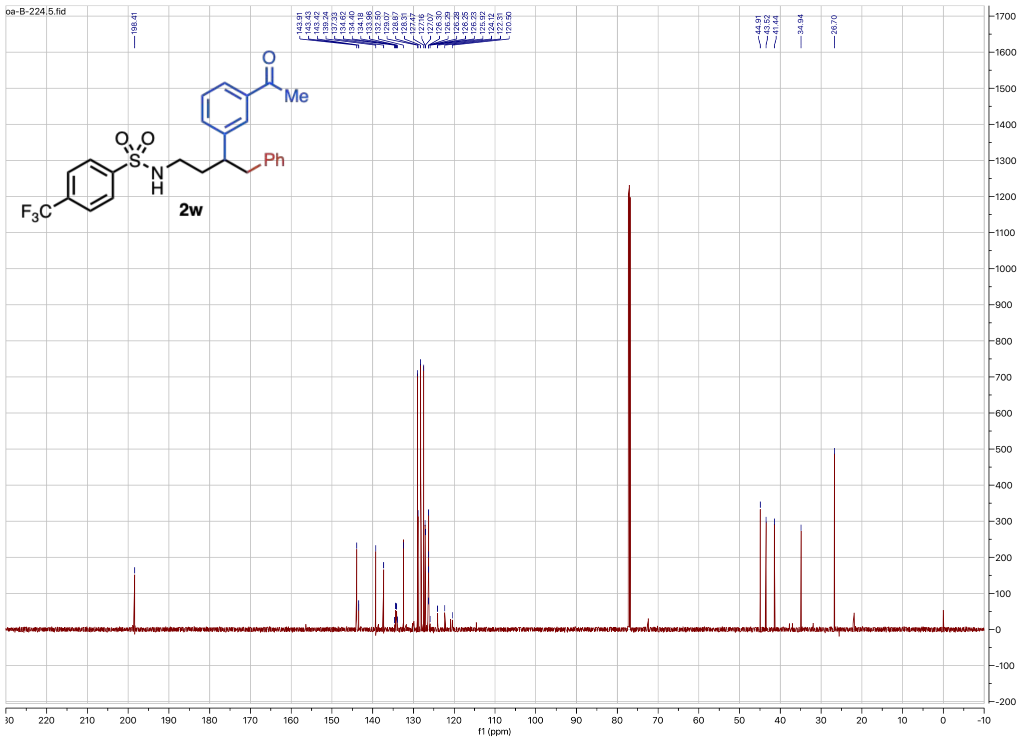
Me
Ph
F3C
2w
f1 (ppm)


oa-B-224.5.fid
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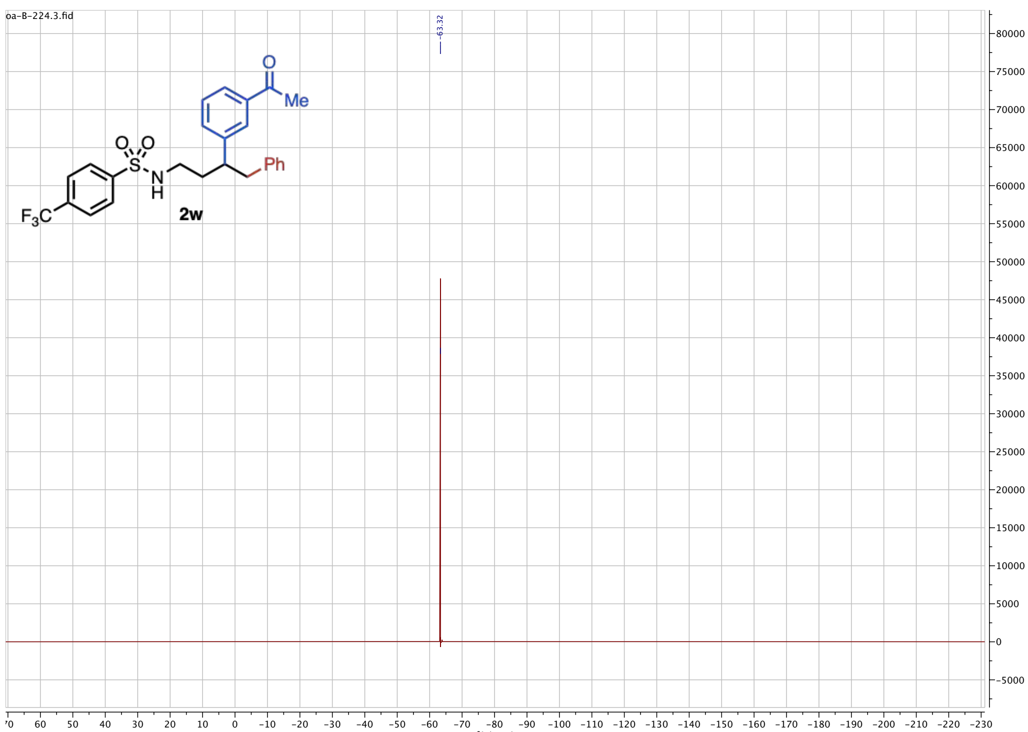
44.01
43.52
41.44
34.94
26.70
Me
Ph
F3C
2w
f1 (ppm)


oa-B-224.3.fid
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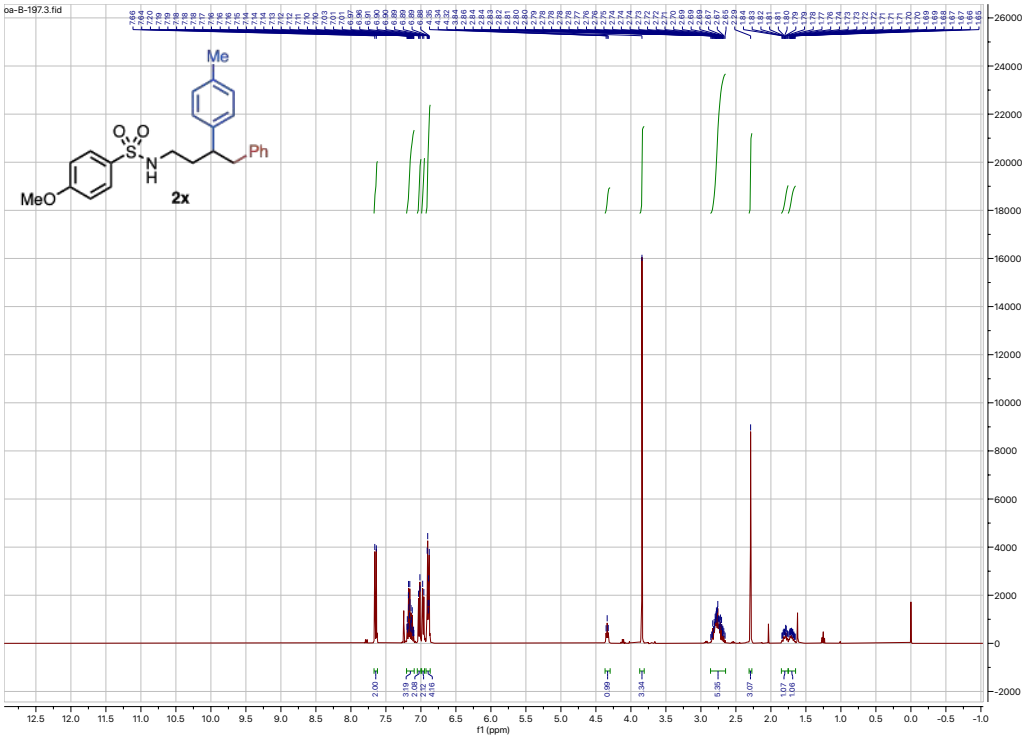
Me
Ph
F3C
2w
f1 (ppm)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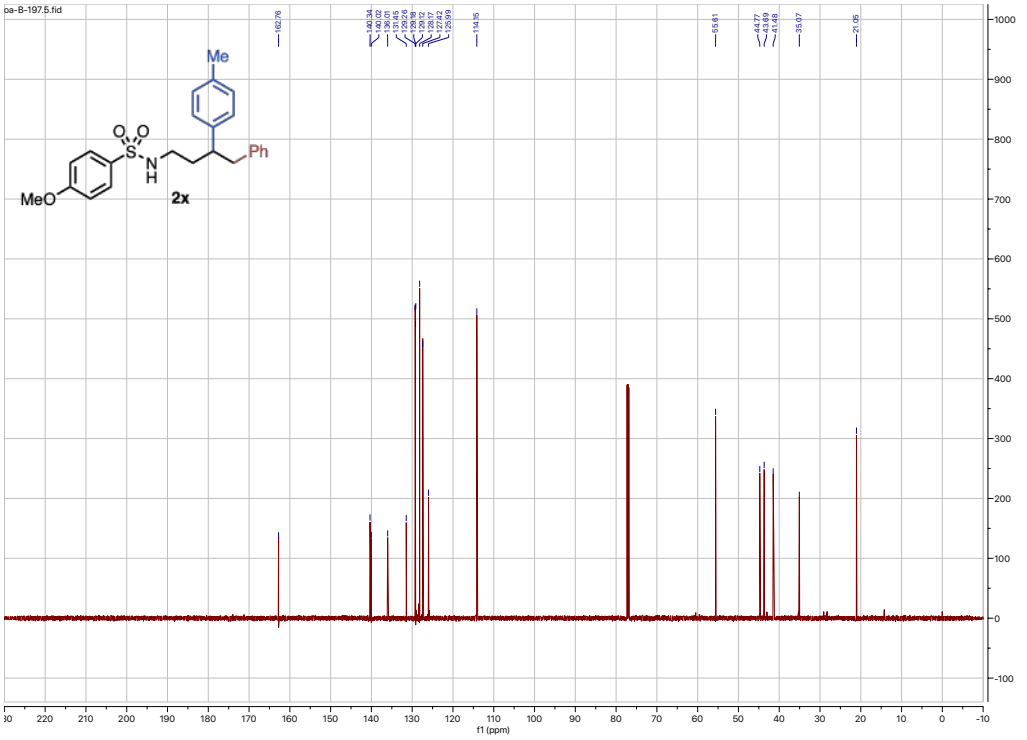
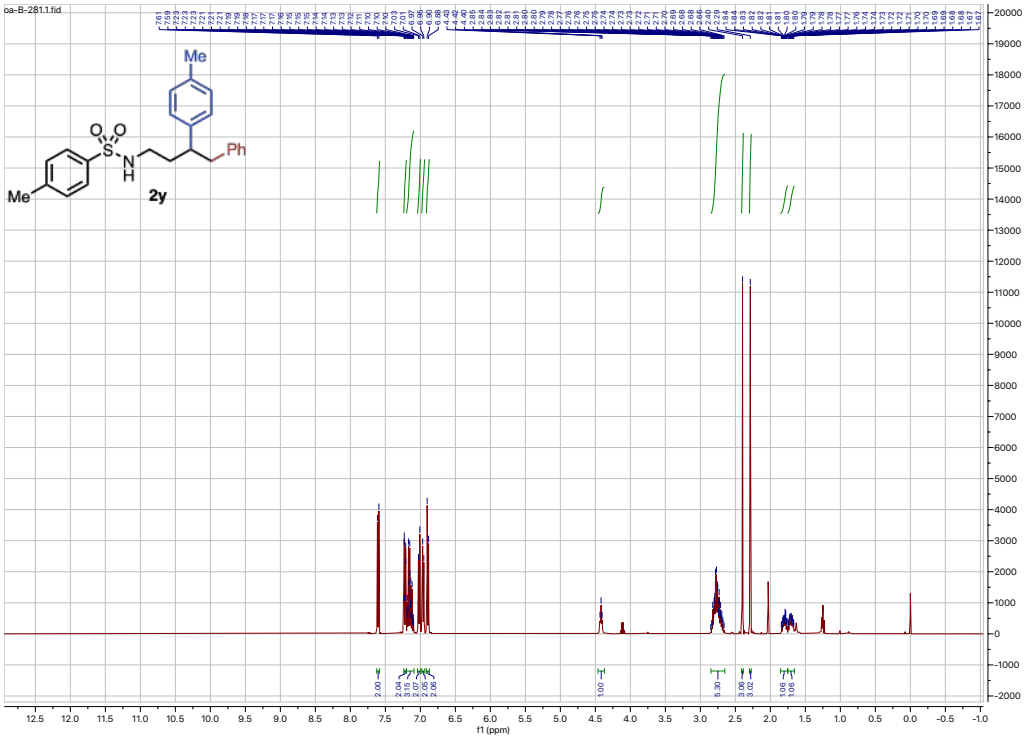
Ph
MeO
2x
f1 (ppm)


oa-B-197.5.fid
Me
Ph
MeO
2x
f1 (ppm)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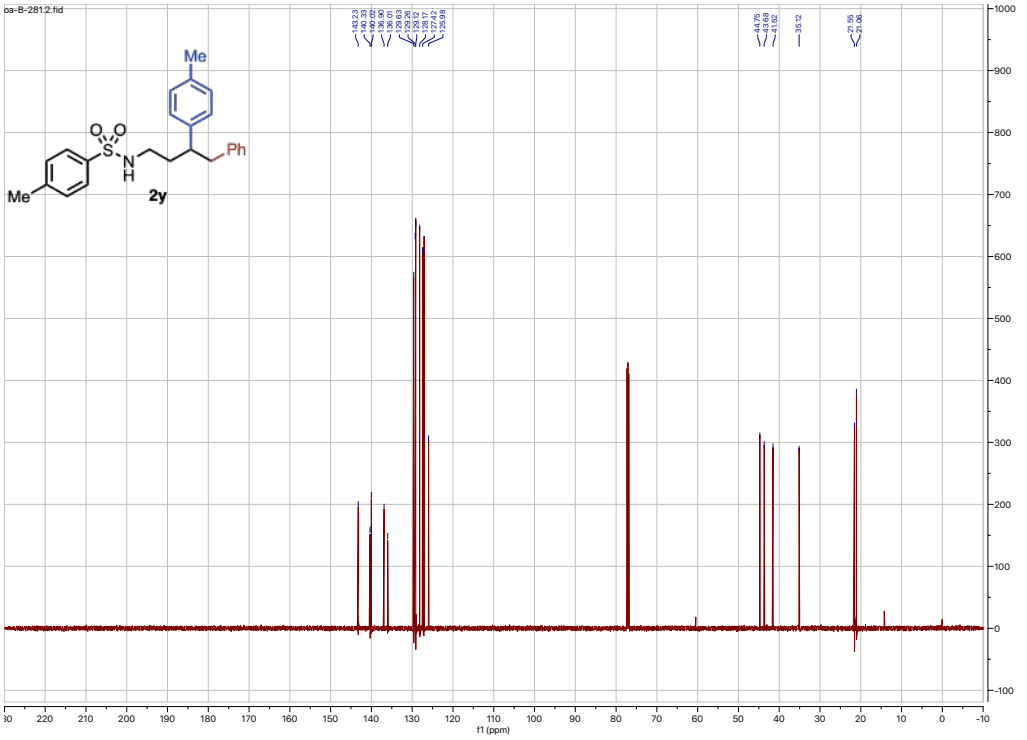
Ph
Me
2y
f1 (ppm)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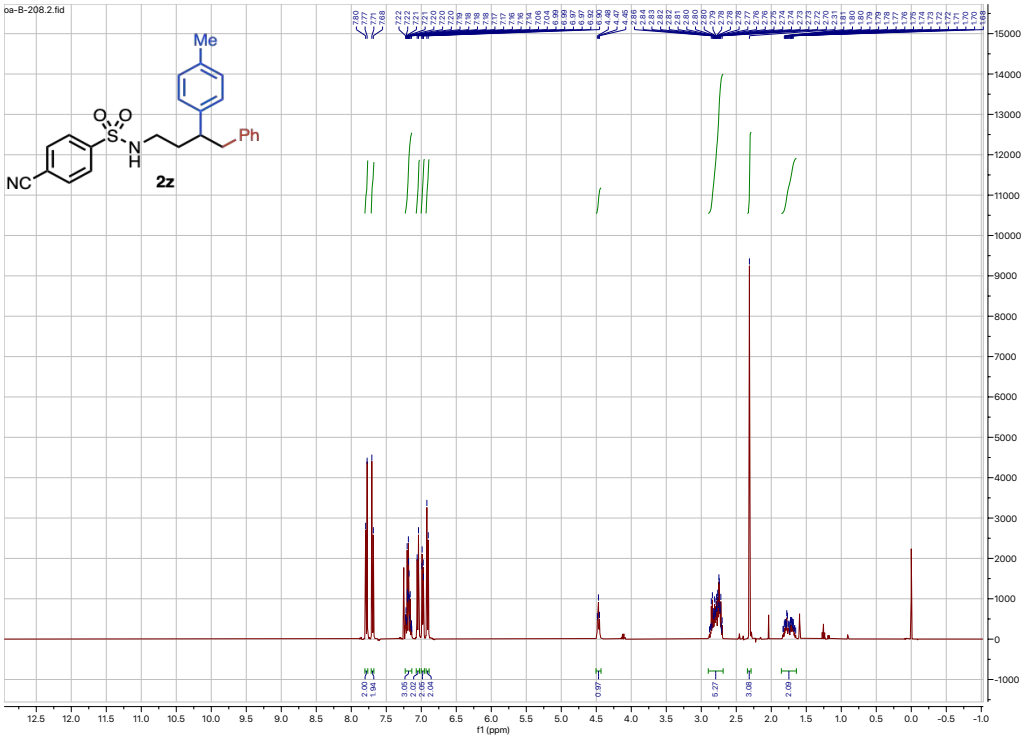
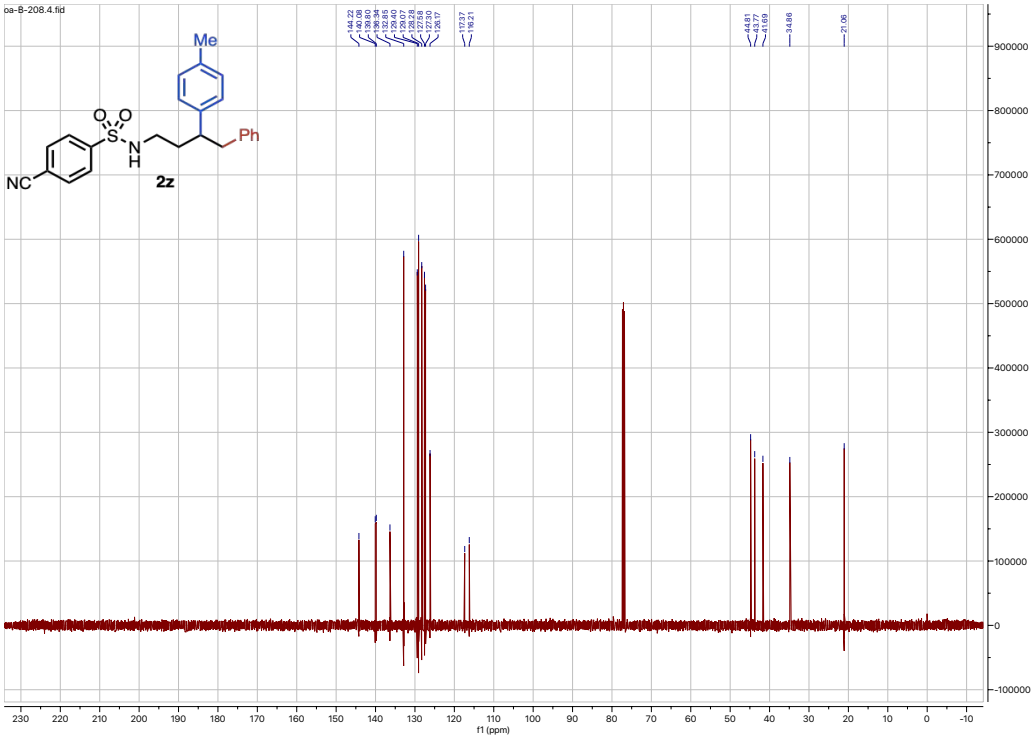
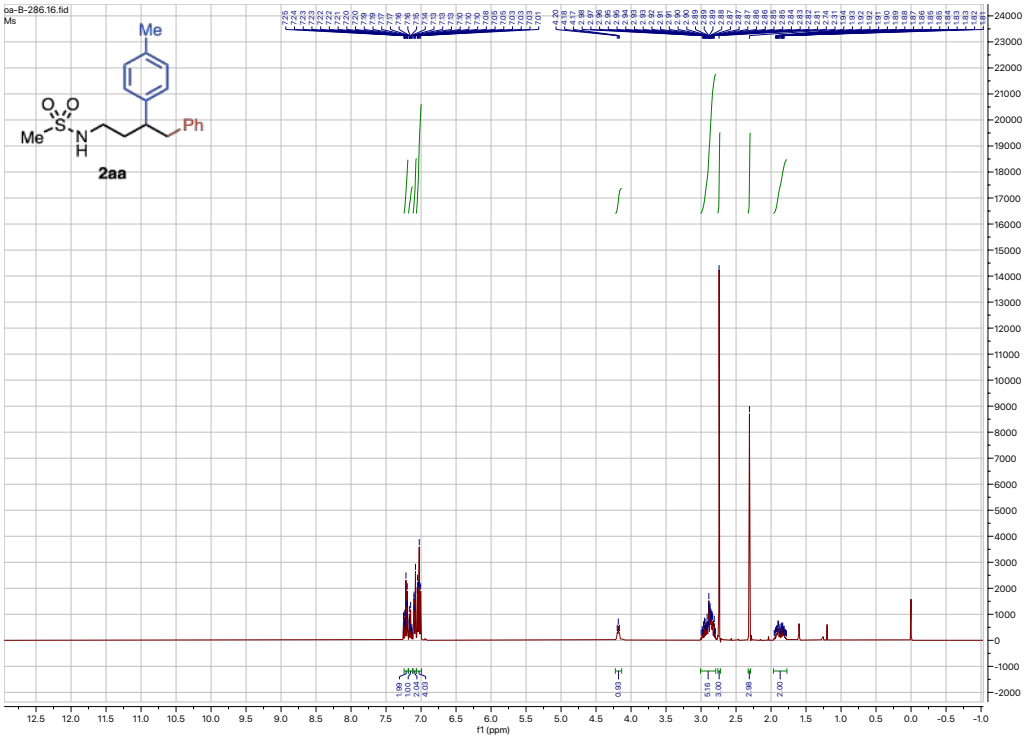
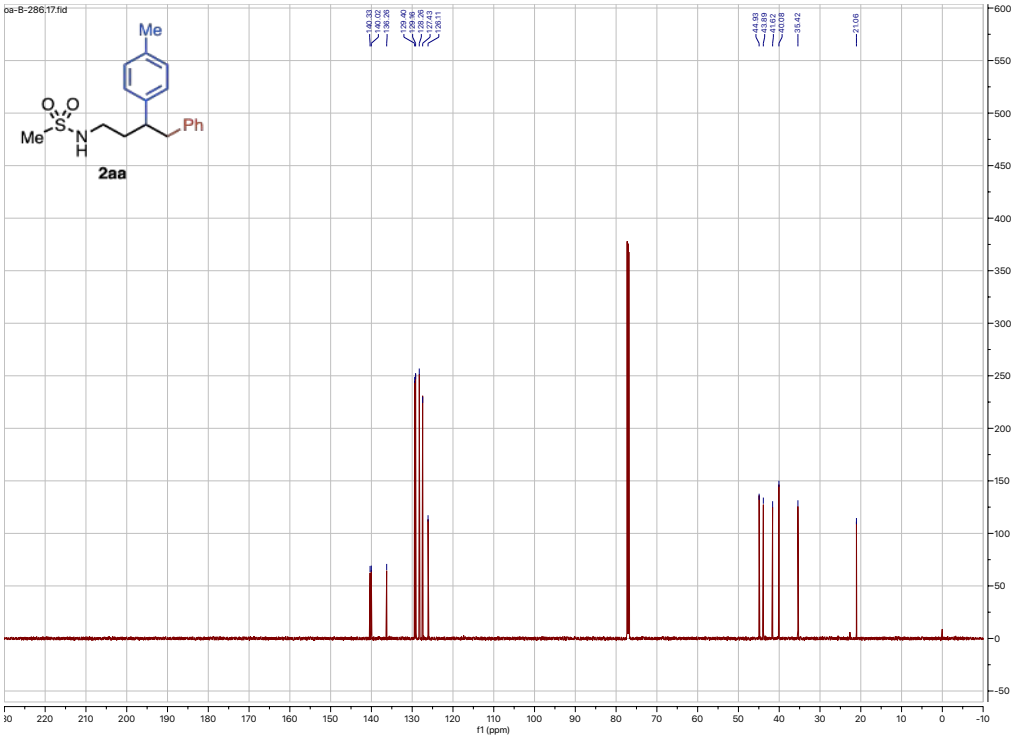
Ph
Me
2y
f1 (ppm)


oa-B-208.2.fid
Me
Ph
NC
2z
f1 (ppm)


oa-B-208.4.fid
Me
Ph
NC
2z
f1 (ppm)


oa-B-286.16.fid
Ms
Me
Me
S
O
O
N
H
Ph
2aa
f1 (ppm)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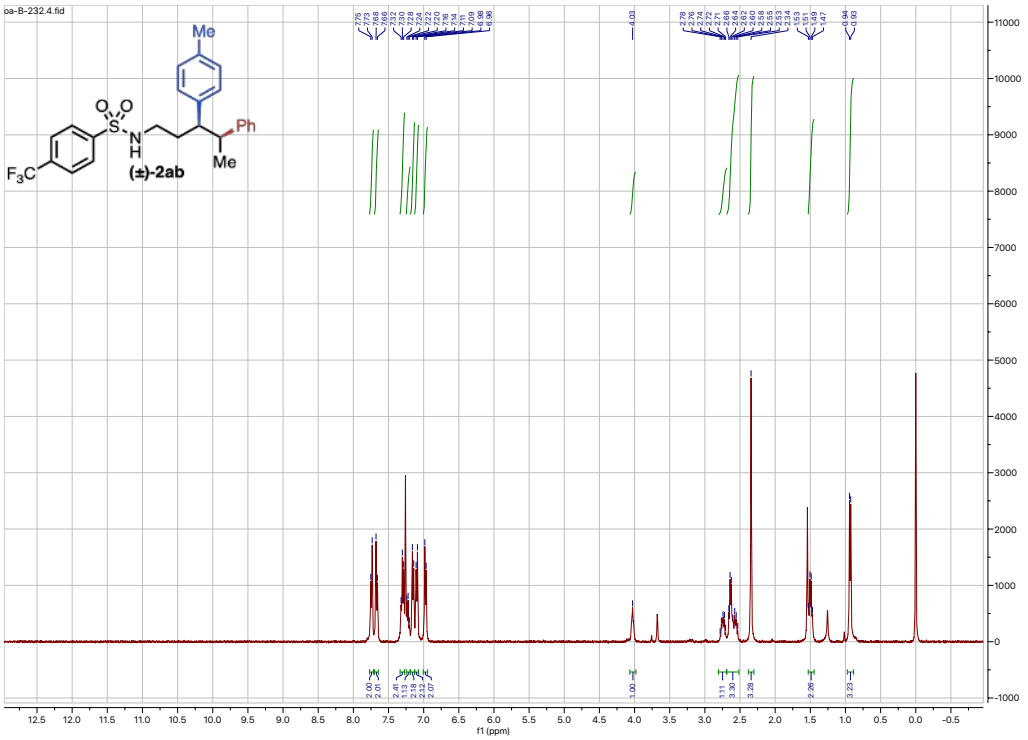
Me
S
O
O
N
H
Ph
2aa
f1 (ppm)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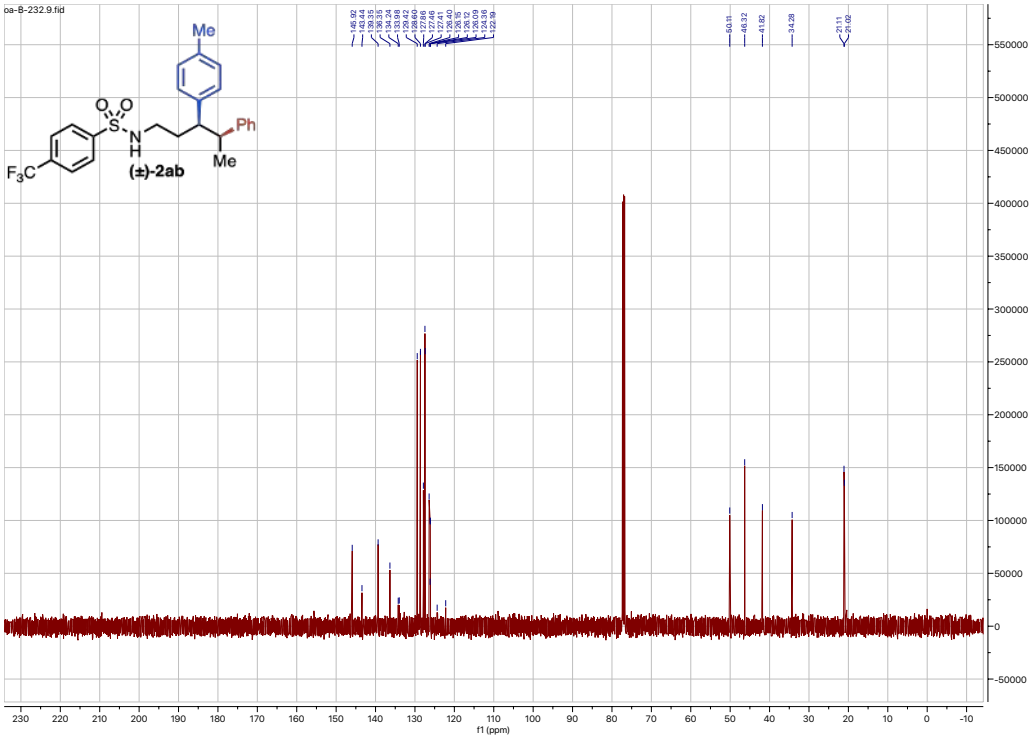
Me
Ph
Me
(±)-2ab
f1 (ppm)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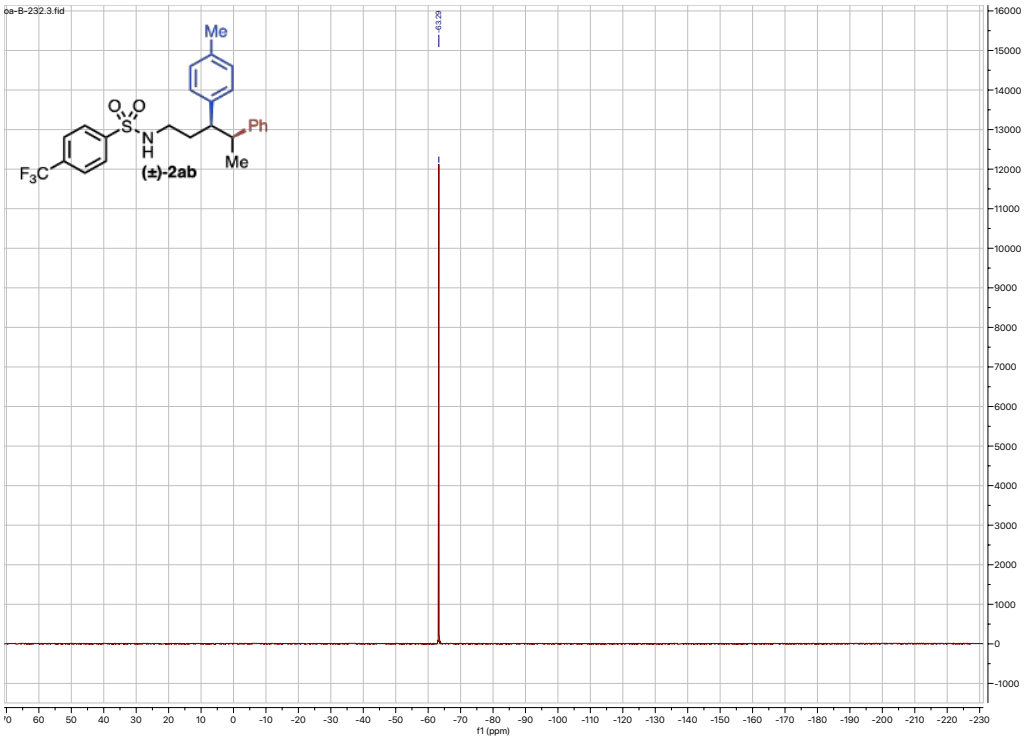
Me
Ph
Me
(±)-2ab
f1 (ppm)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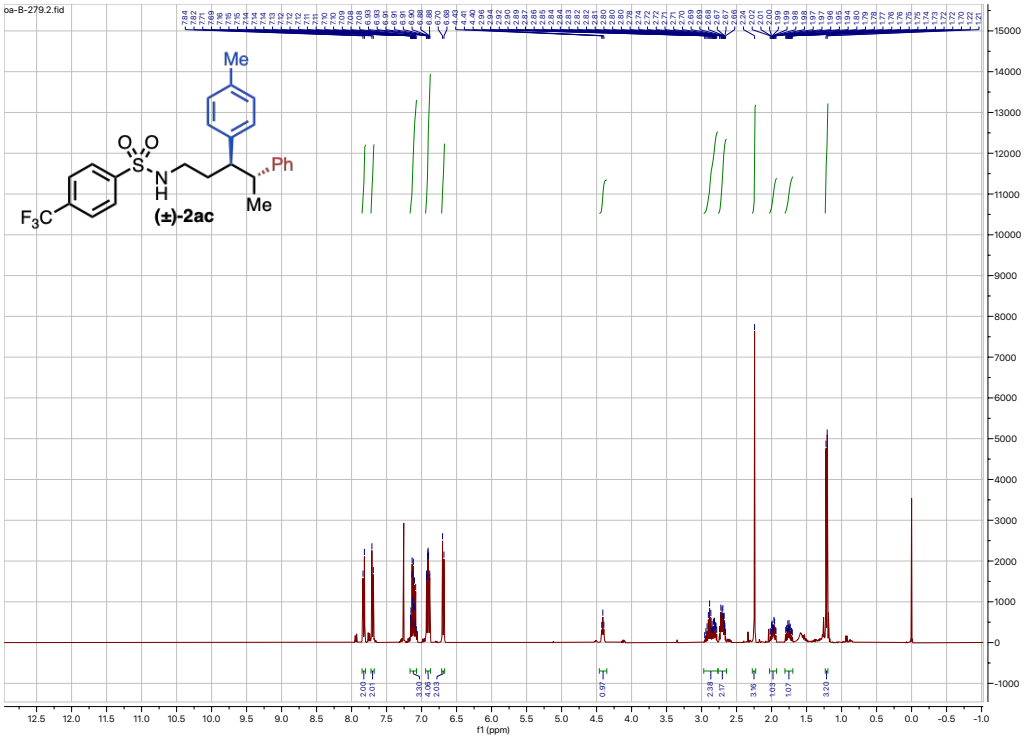
Me
Ph
Me
(±)-2ab
63.29
f1 (ppm)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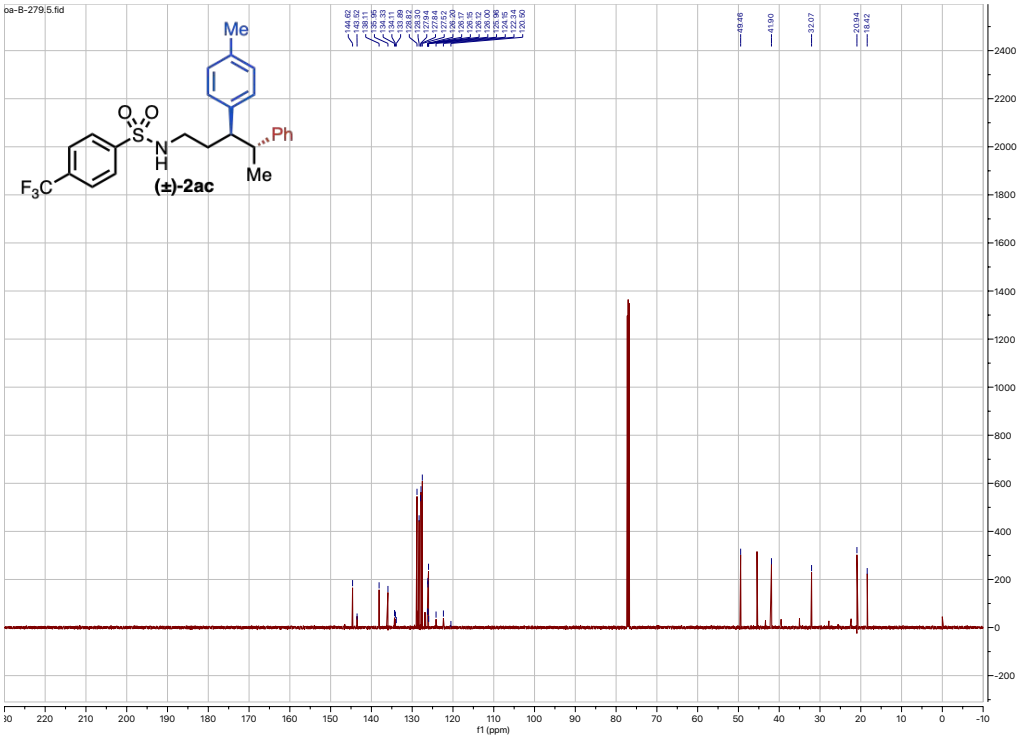
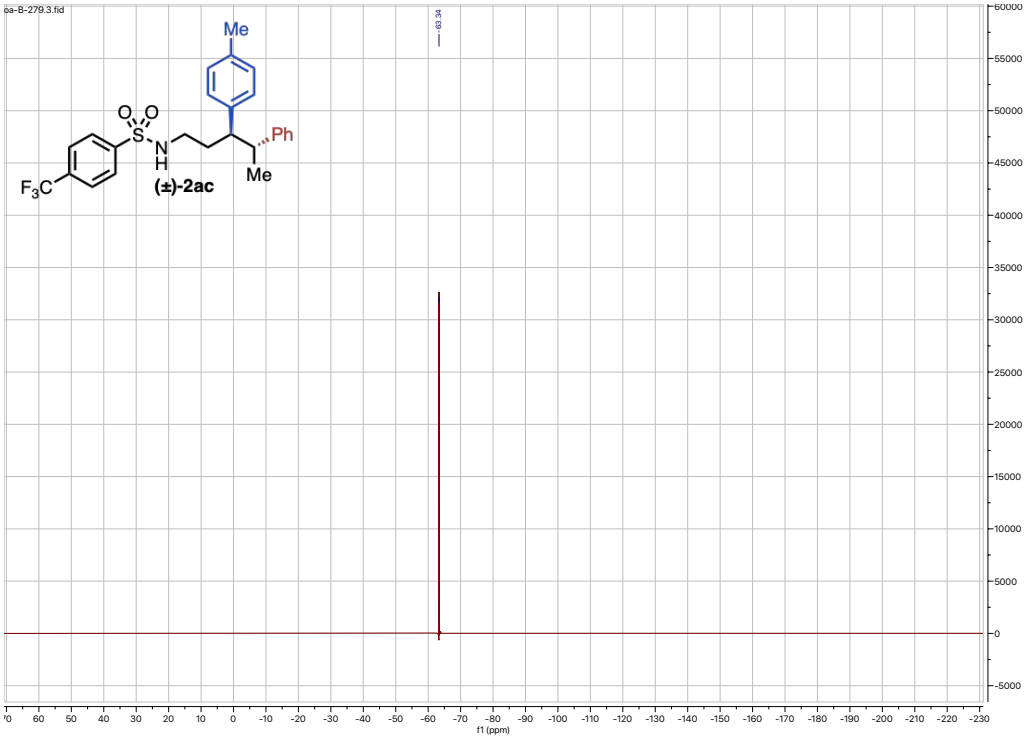
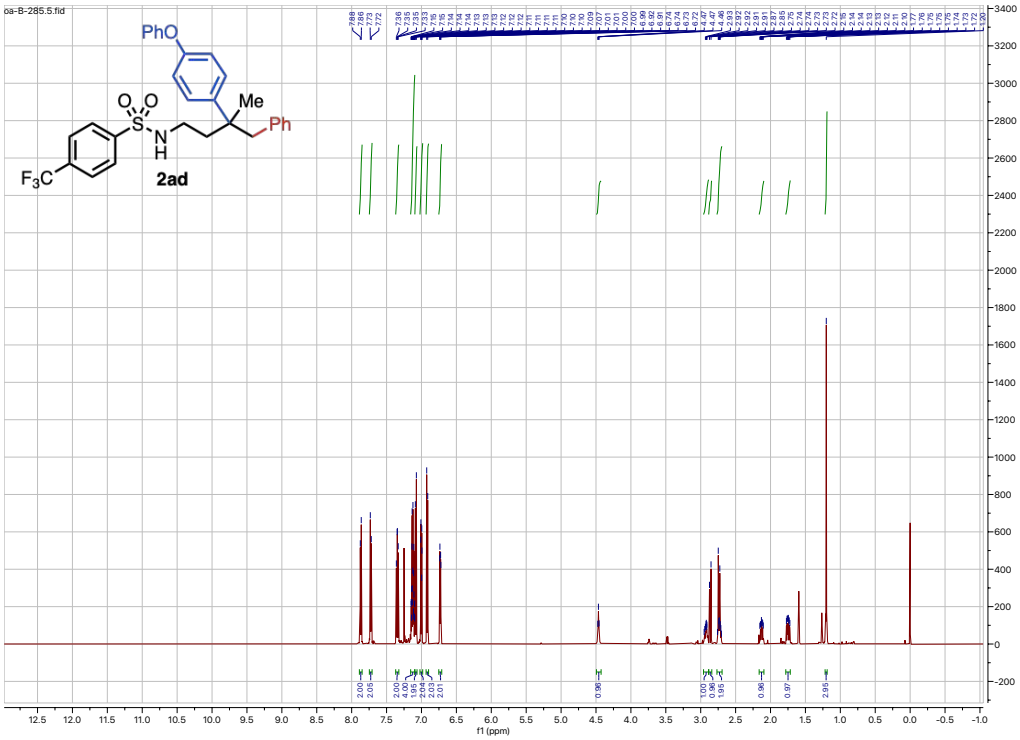
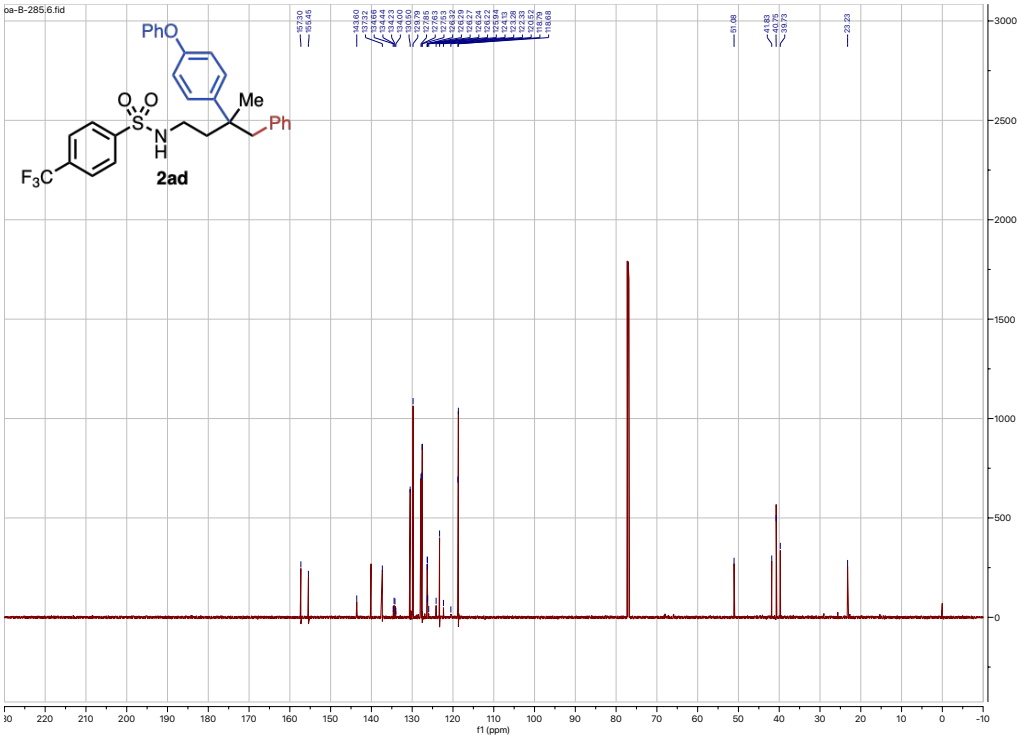
Me
Ph
Me
(±)-2ac
f1 (ppm)


oa-B-279.5.fid
Me
Ph
Me
(±)-2ac
f1 (ppm)


oa-B-279.3.fid
Me
Ph
Me
(±)-2ac
f1 (ppm)


oa-B-285.5.fid
PhO
Me
Ph
O
O
S
N
H
F3C
2ad
f1 (ppm)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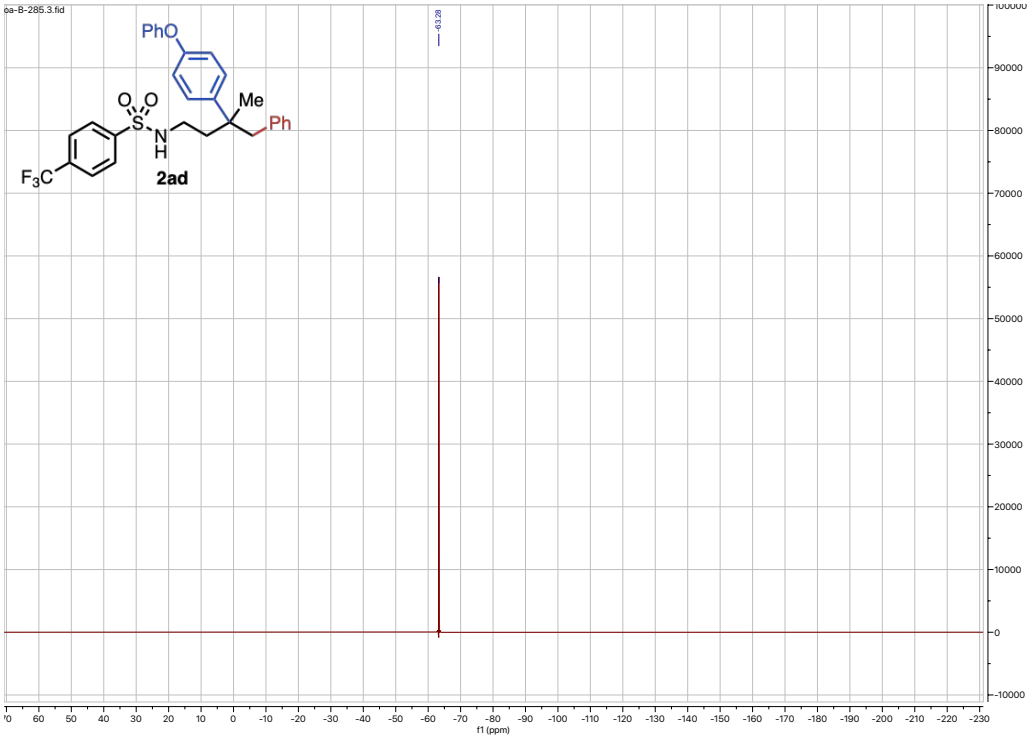
PhO
Me
Ph
O
O
S
N
H
F3C
2ad
f1 (ppm)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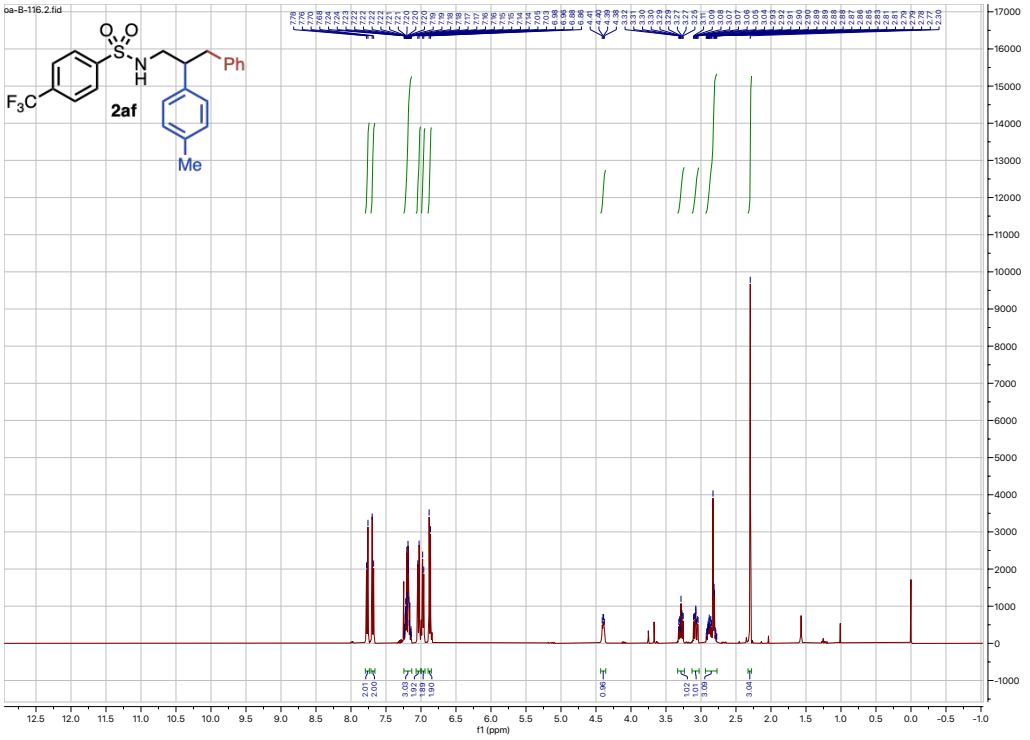
Me
Ph
F3C
2ad
-63.28
f1 (ppm)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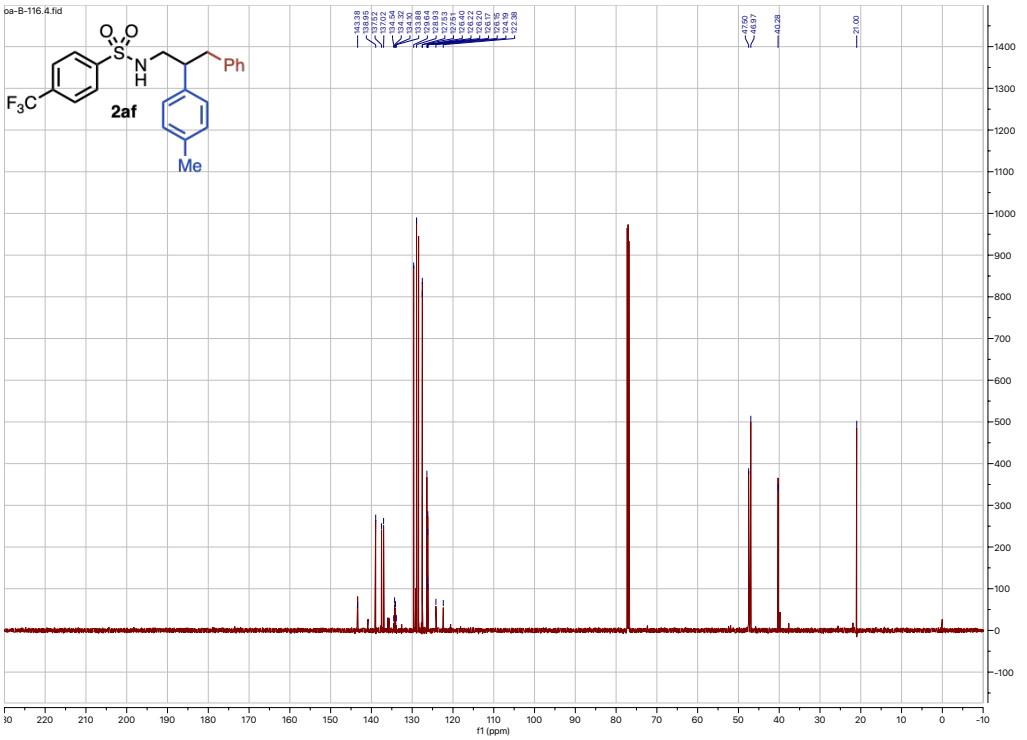
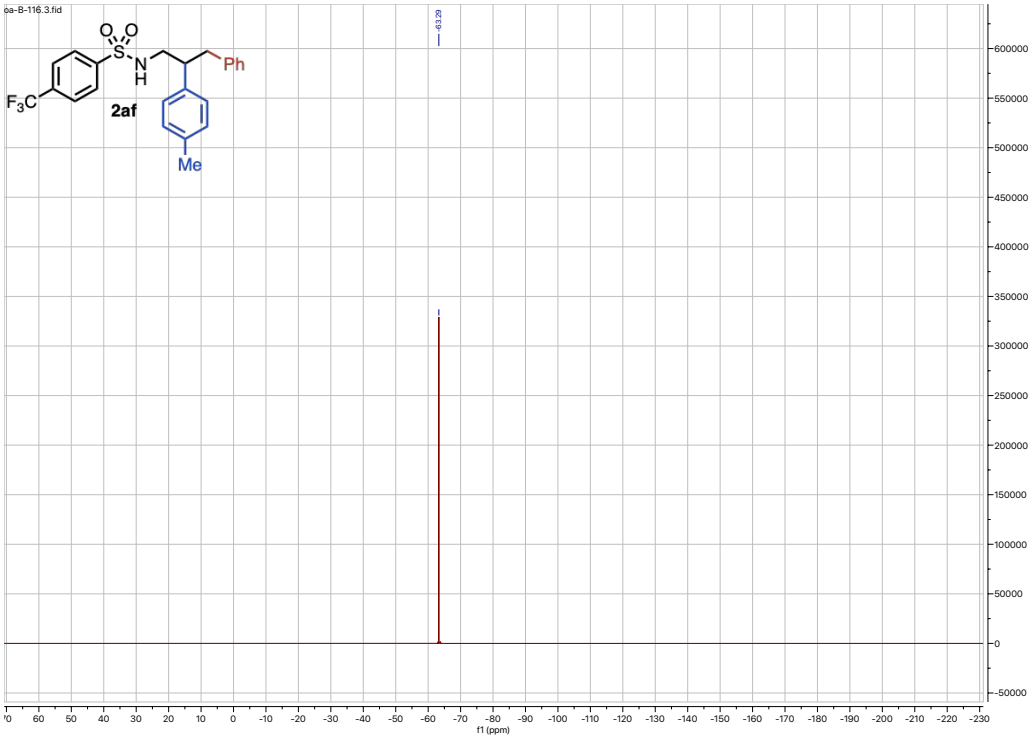
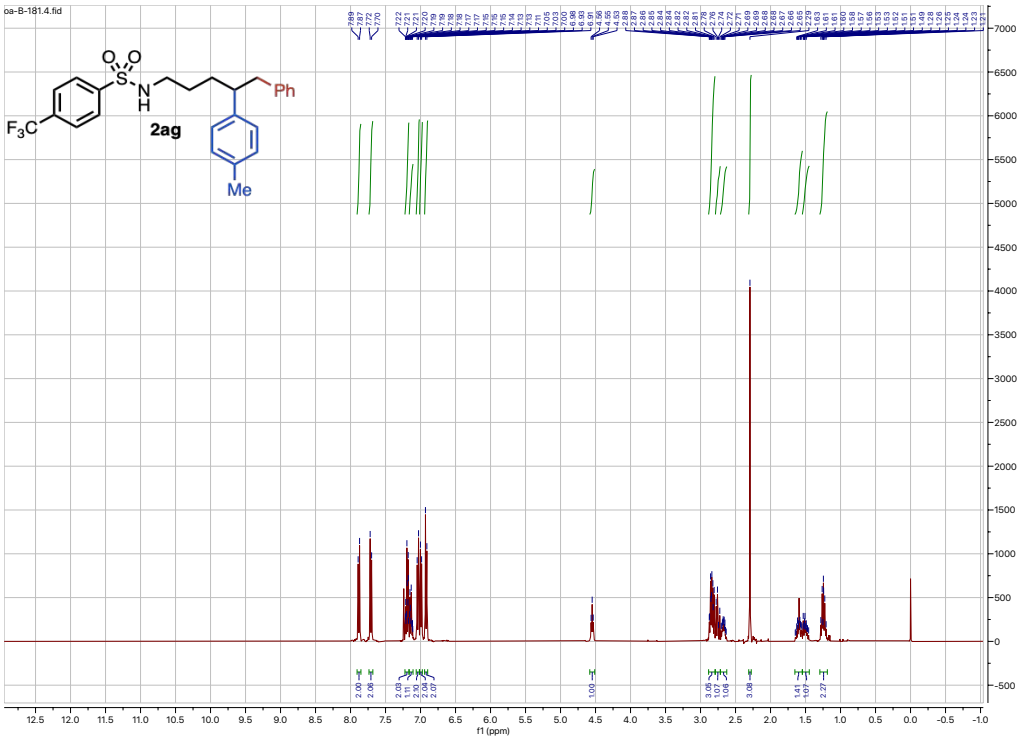
Ph
F3C
2af
Me
f1 (ppm)


oa-B-116.4.fid
2af
Ph
Me
F3C
f1 (ppm)


oa-B-116.3.fid
2af
Ph
Me
F3C
f1 (ppm)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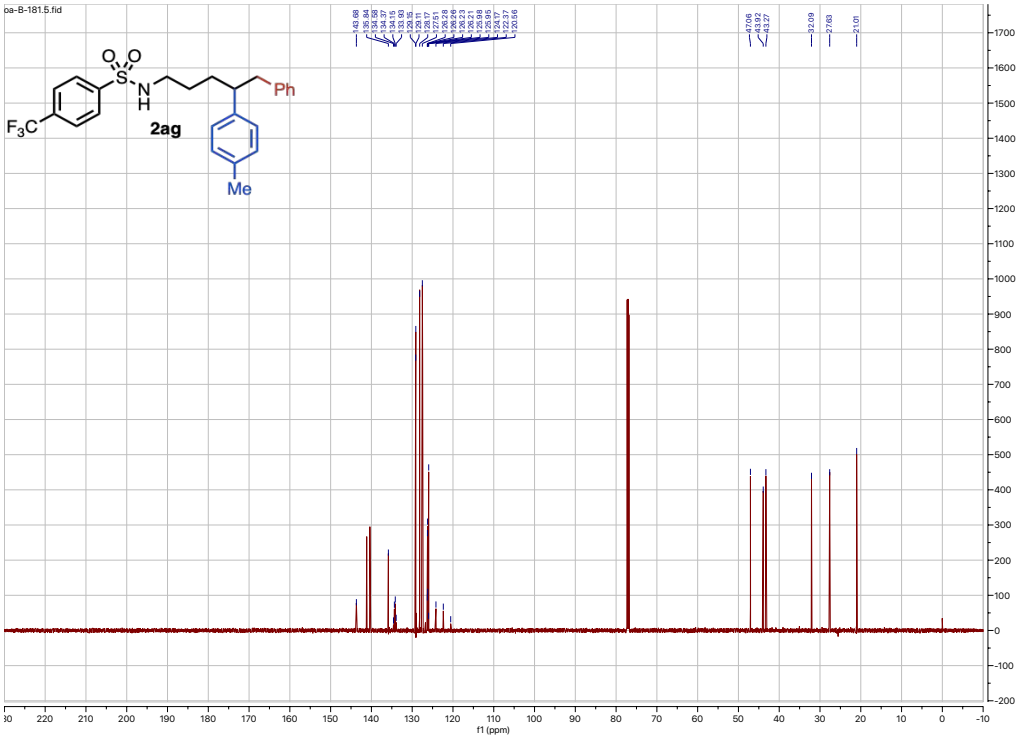
2ag
Ph
Me
F3C
f1 (ppm)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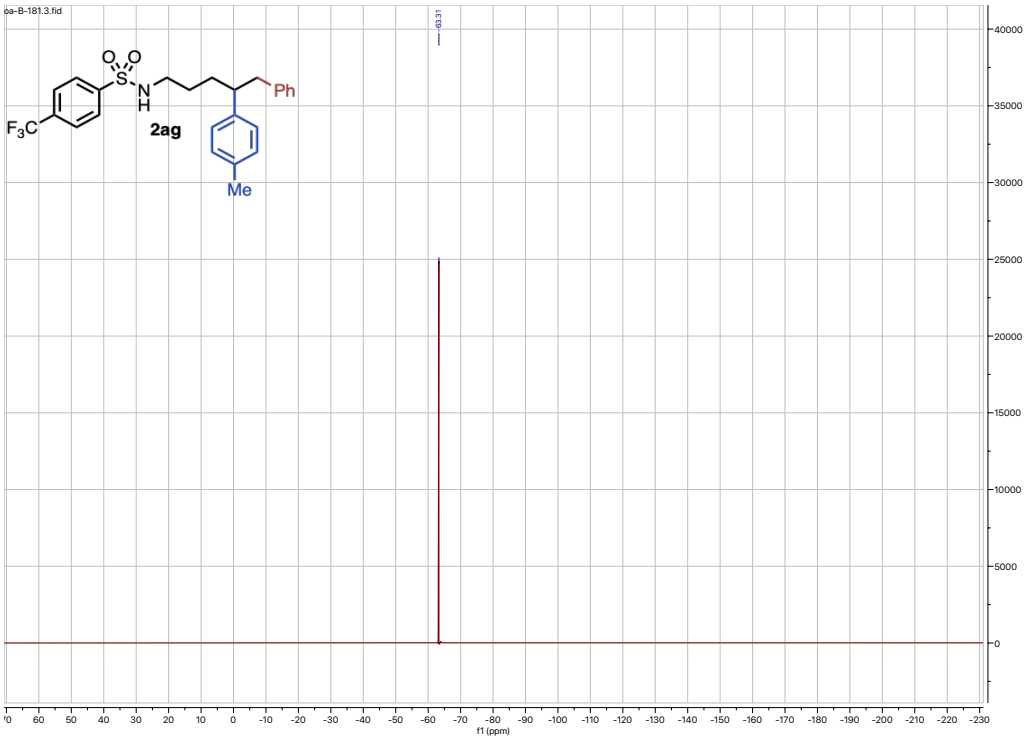
2ag
Ph
Me
F3C
f1 (ppm)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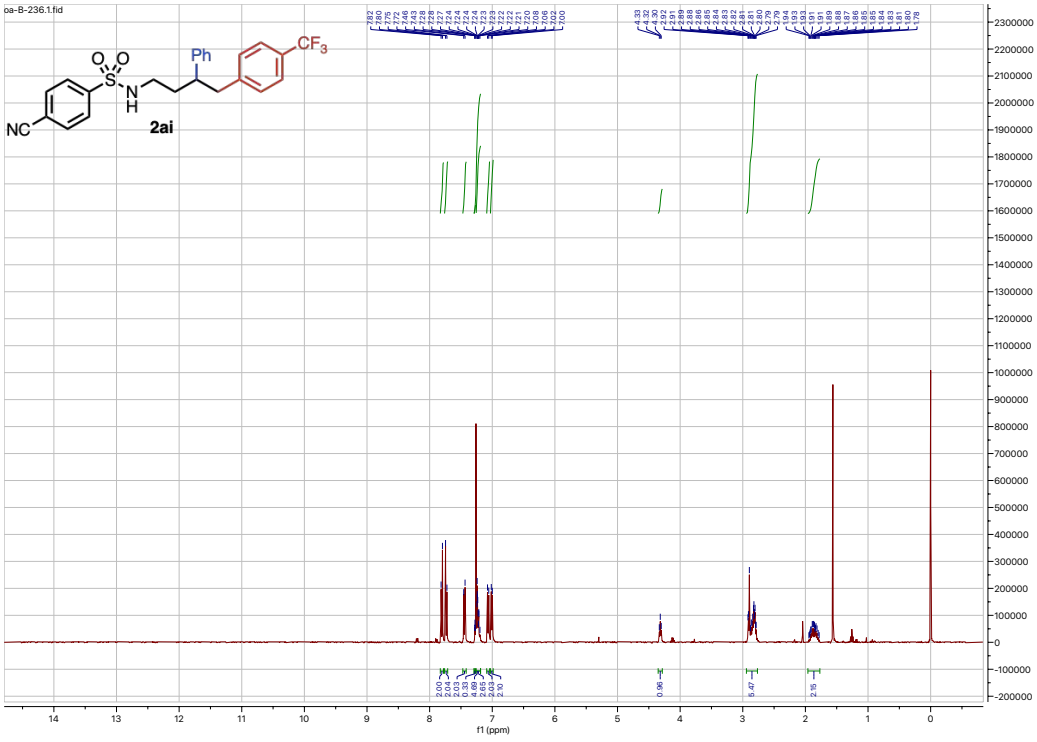
-63.31
2ag
Ph
Me
F3C
f1 (ppm)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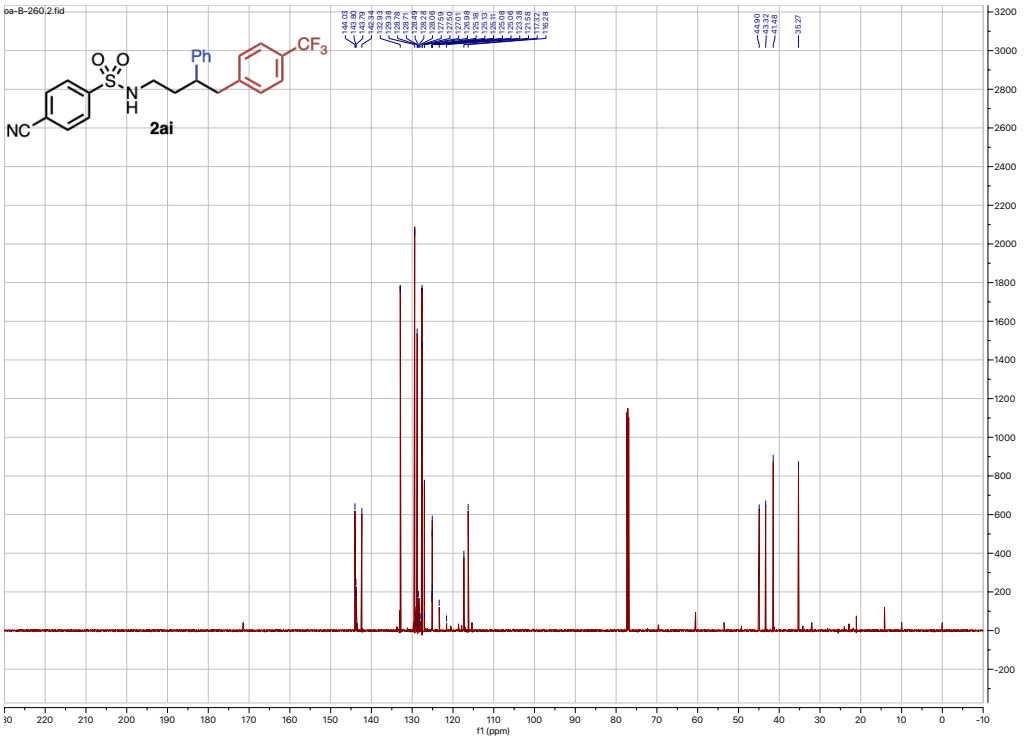
2ai
Ph
CF3
NC
f1 (ppm)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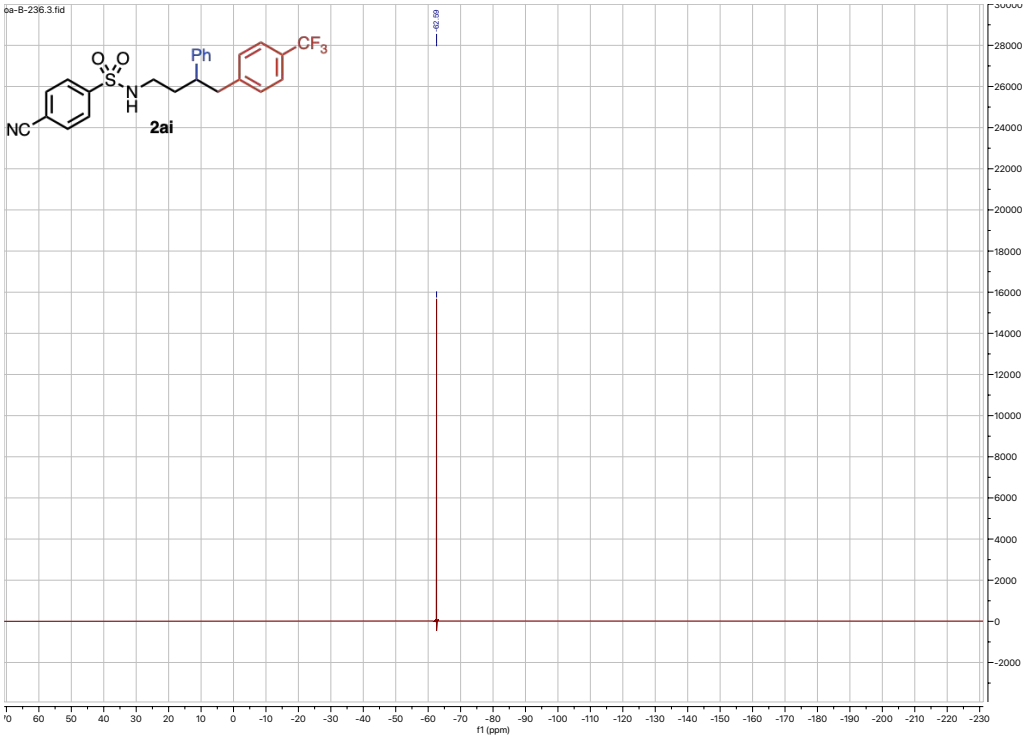
Ph
CF3
NC
2ai
f1 (ppm)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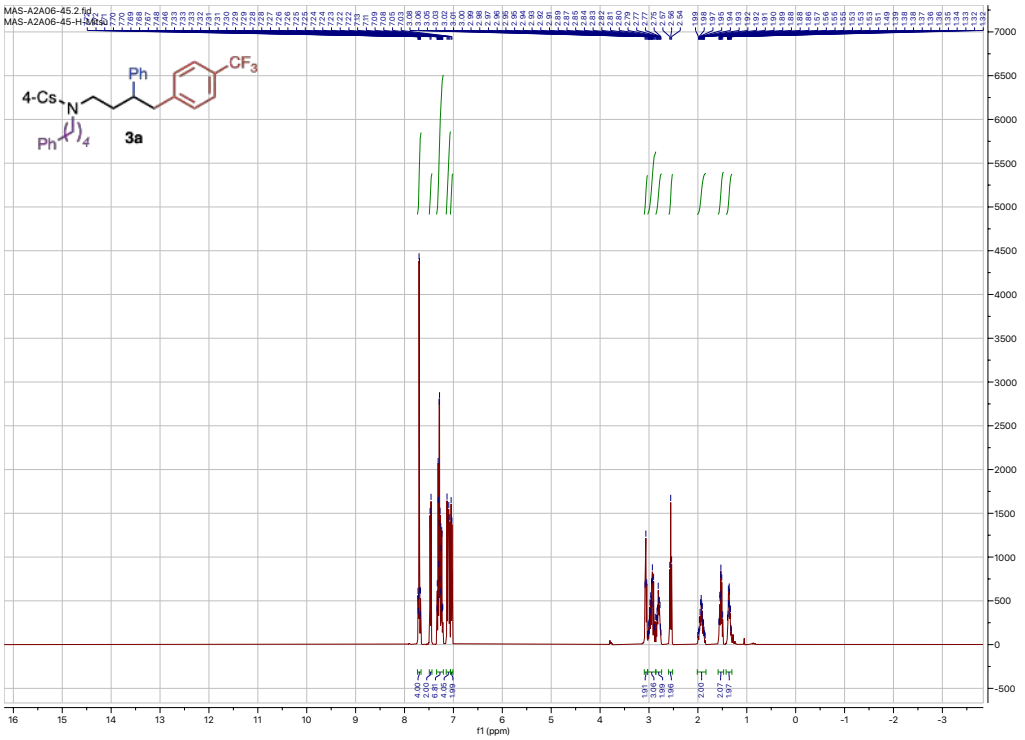
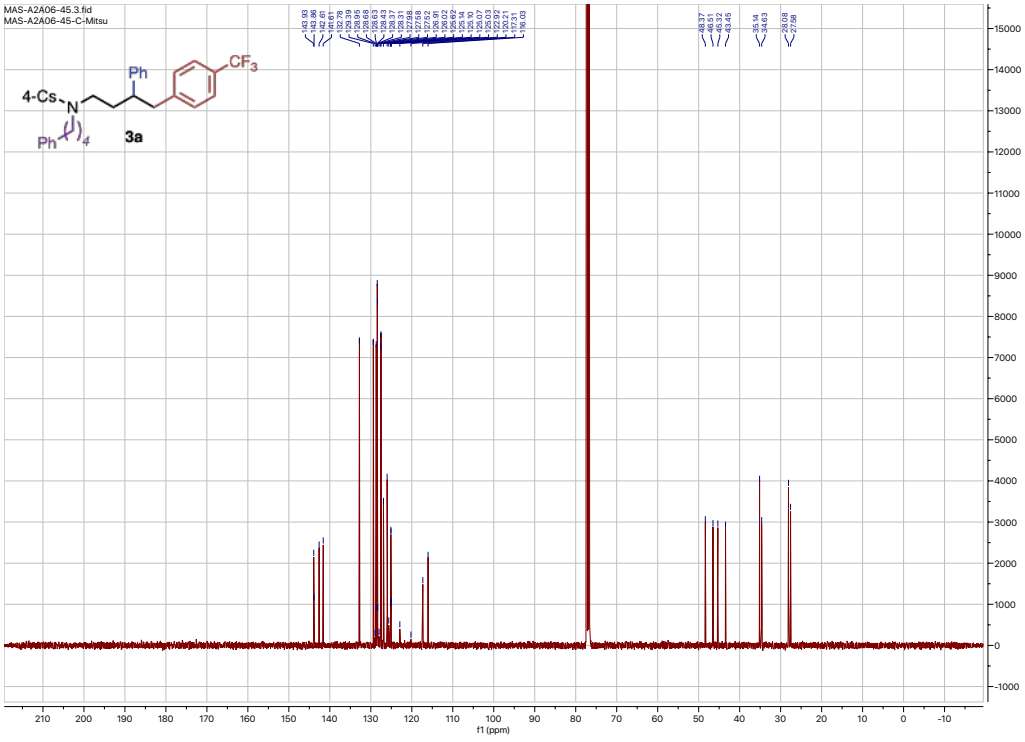
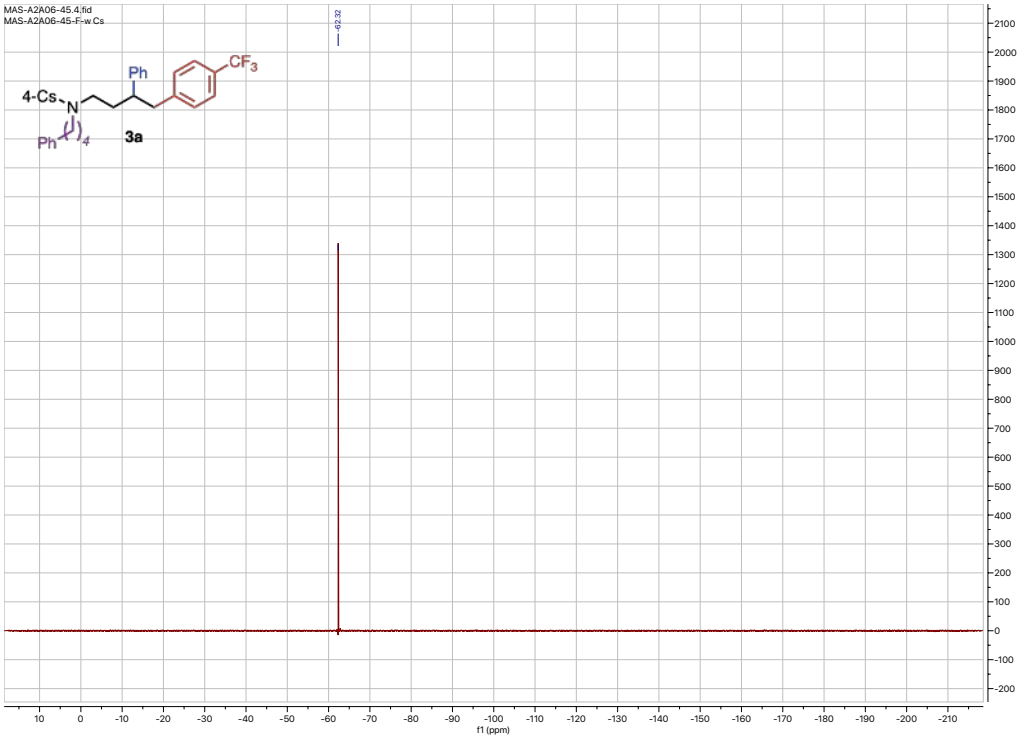
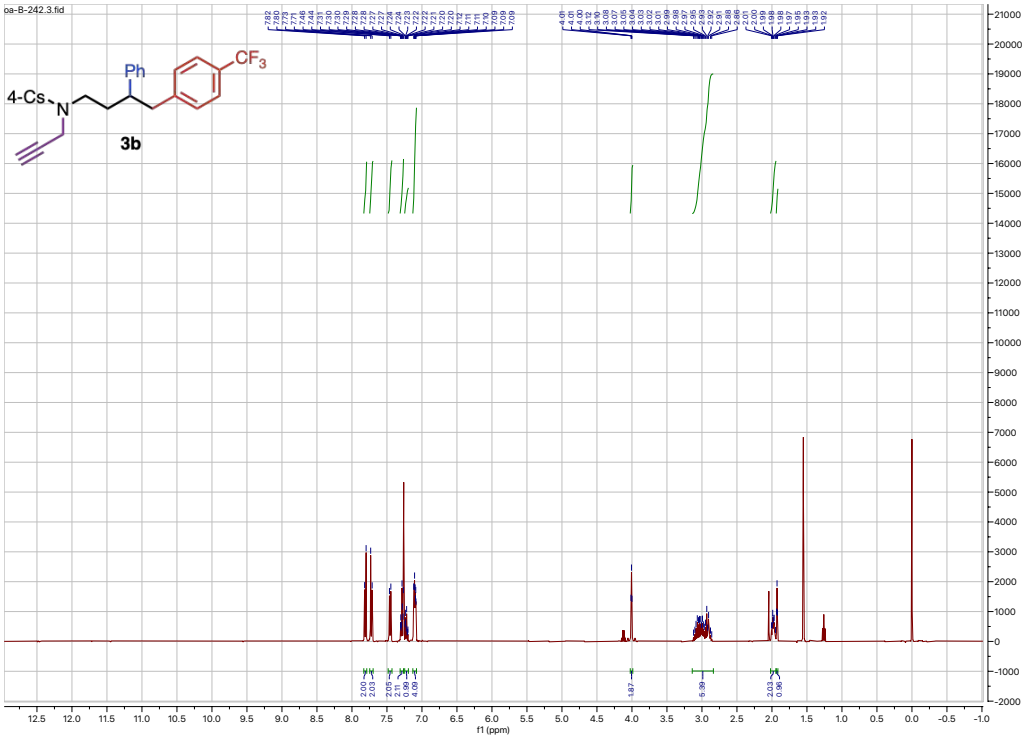
Ph
CF3
NC
2ai
f1 (ppm)


MAS-A2A06-45.2.fid
MAS-A2A06-45-H-Mitsu
4-Cs
N
Ph
Ph
4
CF3
3a
f1 (ppm)


MAS-A2A06-45.3.fid
MAS-A2A06-45-C-Mitsu
4-Cs
N
Ph
Ph
4
CF3
3a
f1 (ppm)


MAS-A2A06-45.4.fid
MAS-A2A06-45-F-w.Cs
-62.32
4-Cs
N
Ph
Ph
4
CF3
3a
f1 (ppm)


oa-B-242.3.fid
4-Cs
N
Ph
CF3
3b
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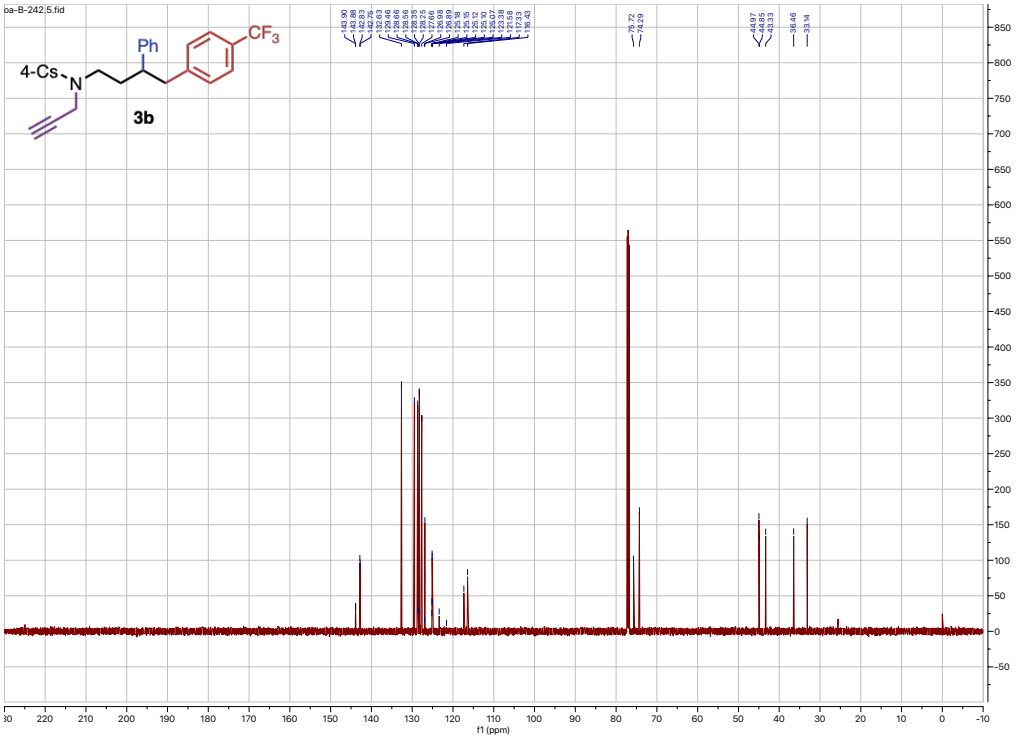
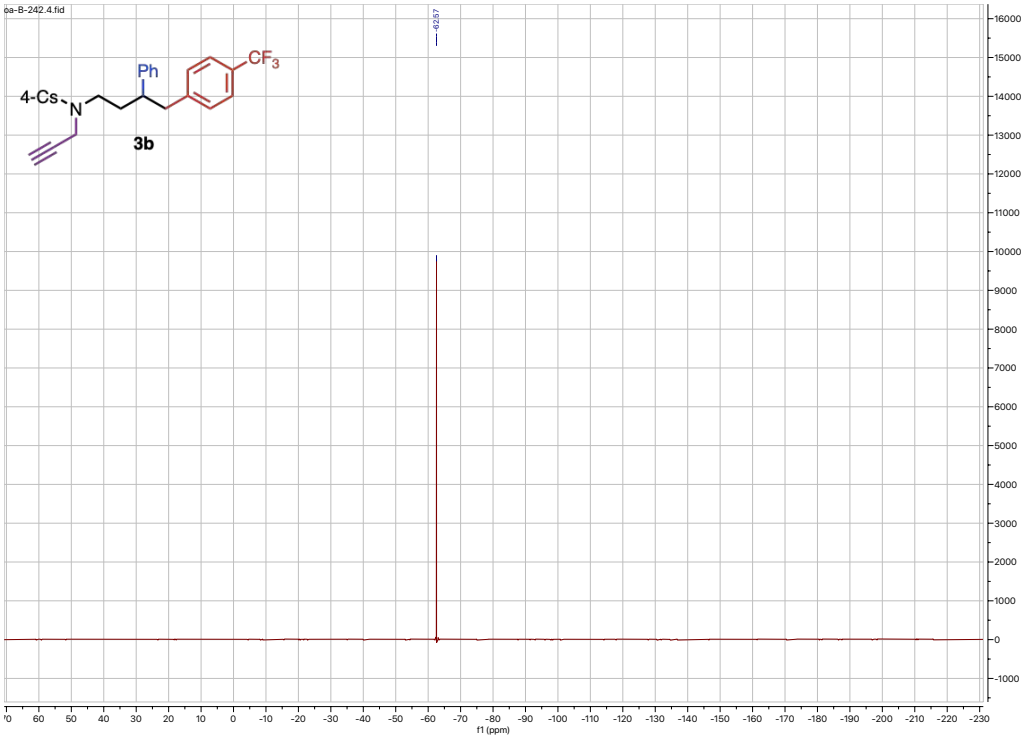
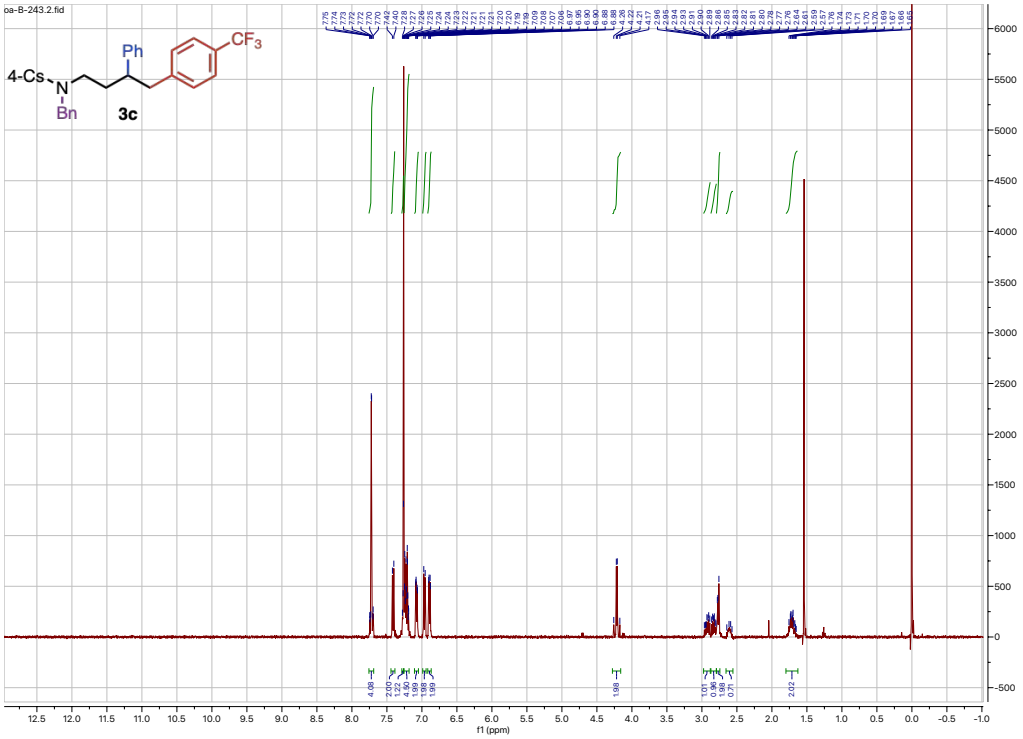
2.03
2.05
3.14
0.99
4.00
4.87
6.99
2.03
0.96
f1 (ppm)


Ph
CF3
4-Cs
N
3b
f1 (ppm)


Ph
CF3
4-Cs
N
3b
f1 (ppm)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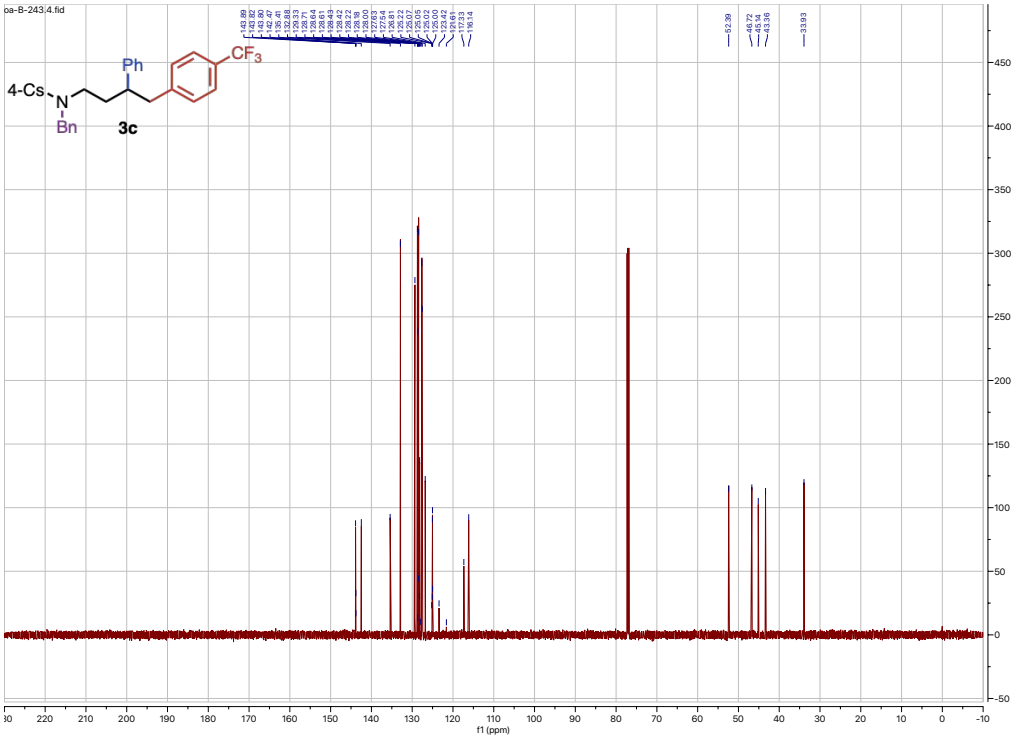
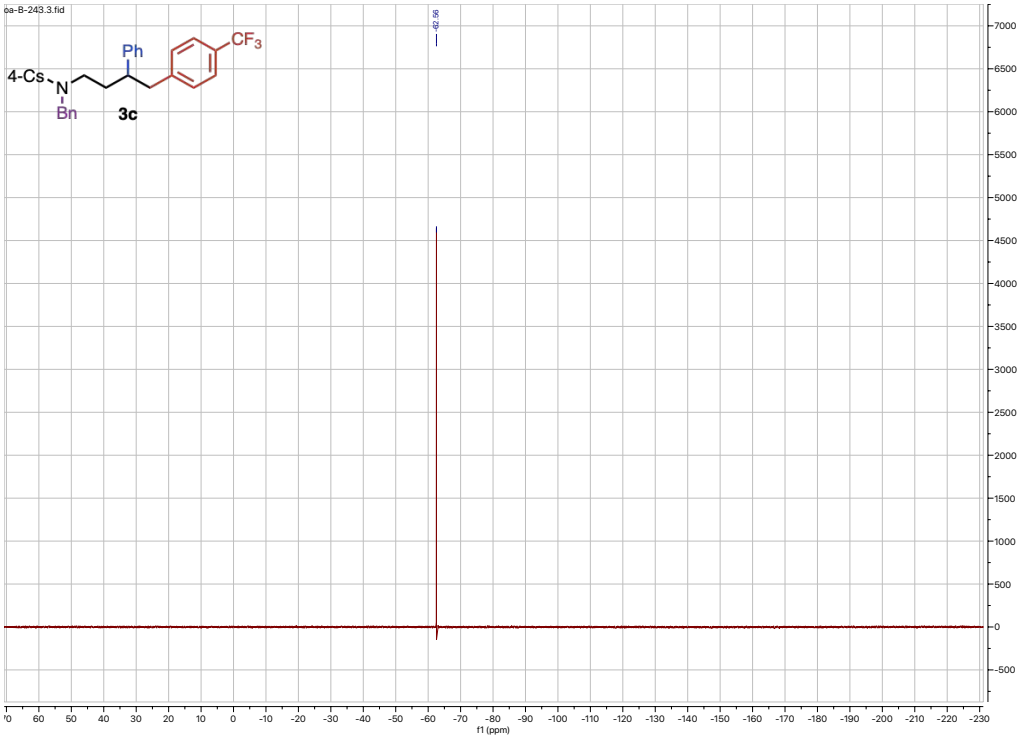
4-Cs
N
Bn
Ph
CF3
3c
f1 (ppm)


oa-B-243\4.fid
4-Cs
N
Bn
Ph
CF3
3c
f1 (ppm)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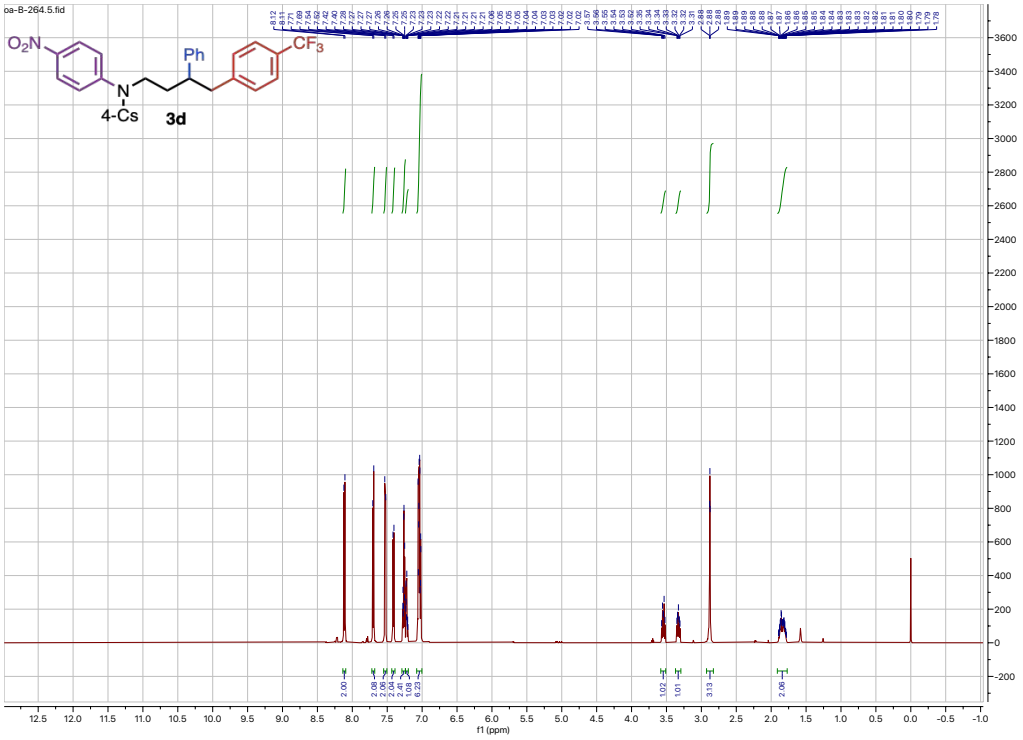
4-Cs
N
Bn
Ph
CF3
3c
f1 (ppm)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O2N
N
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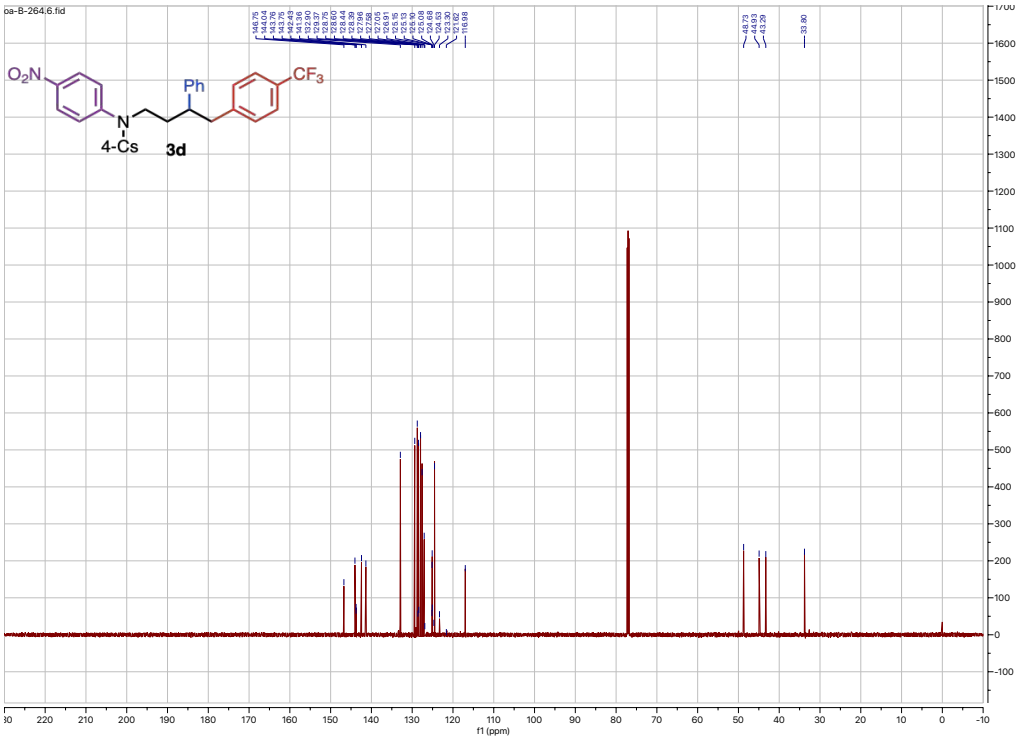
Ph
CF3
3d
f1 (ppm)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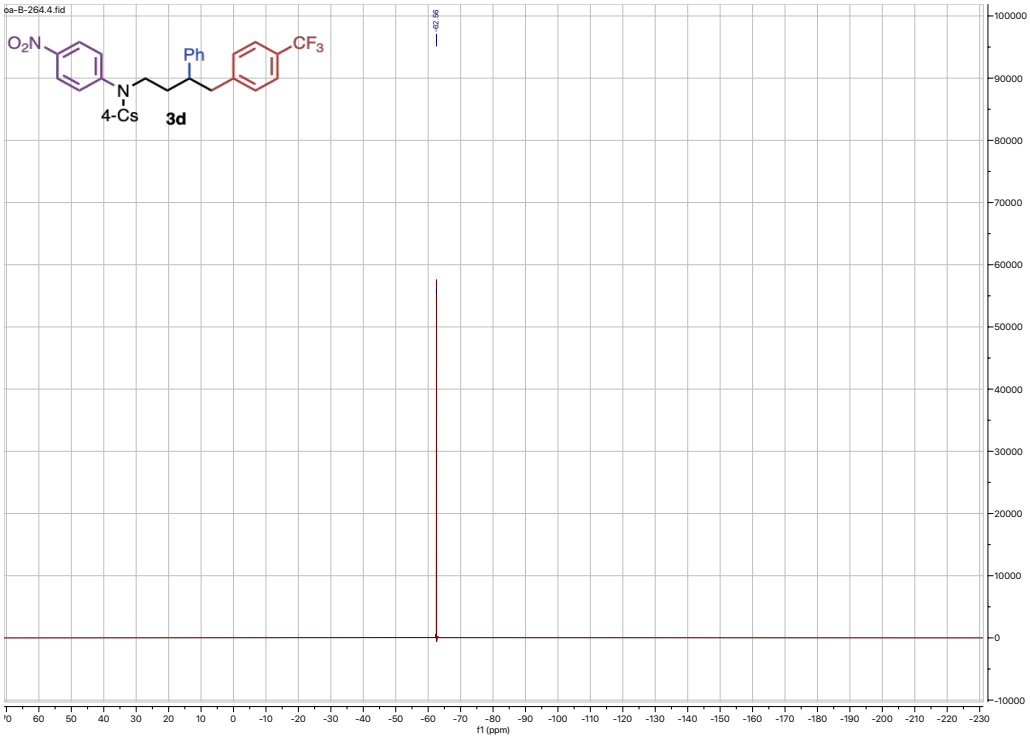
O2N
Ph
CF3
N
4-Cs
3d
f1 (ppm)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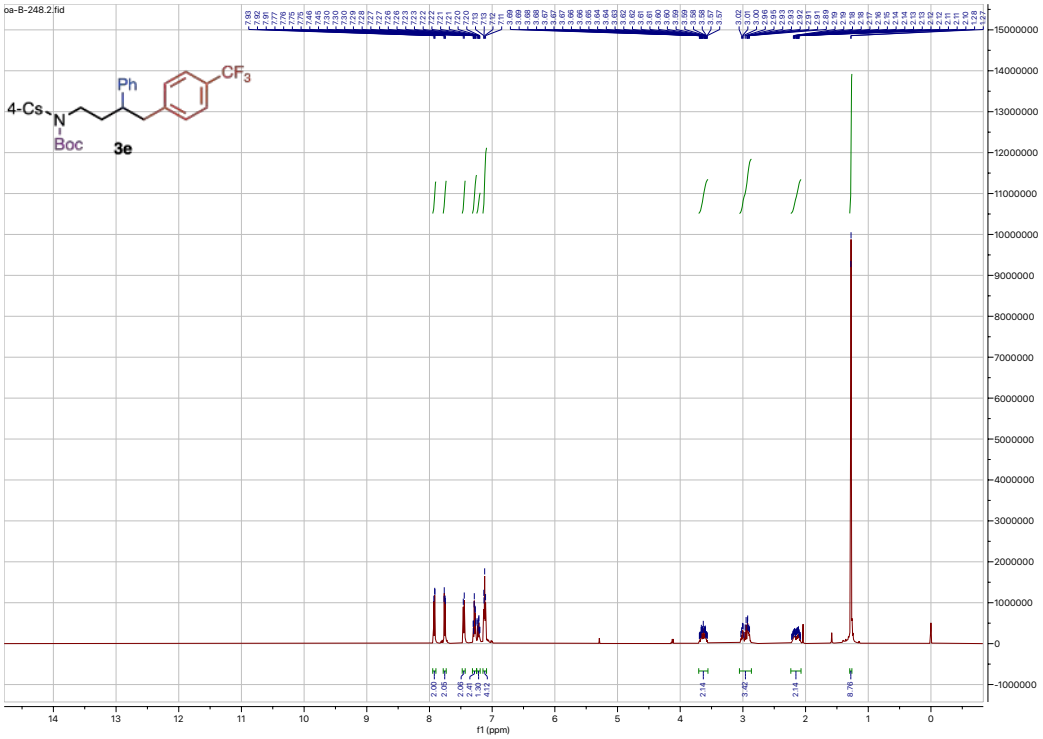
O2N
Ph
CF3
N
4-Cs
3d
f1 (ppm)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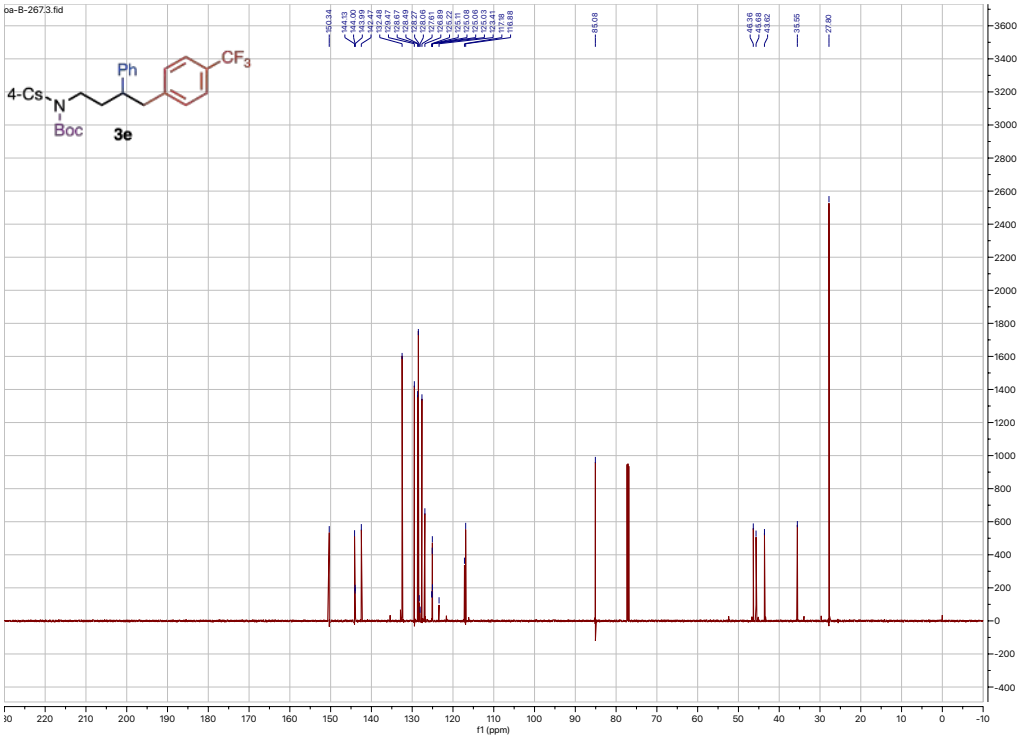
N
Boc
Ph
CF3
3e
f1 (ppm)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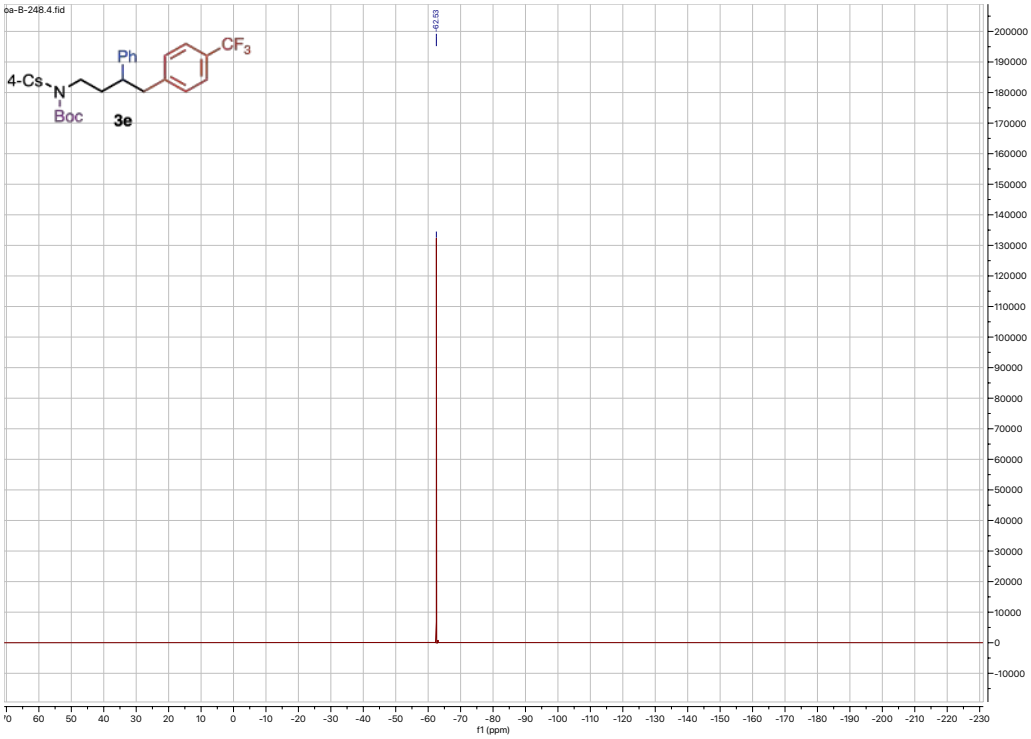
4-Cs
N
Boc
Ph
CF3
3e
f1 (ppm)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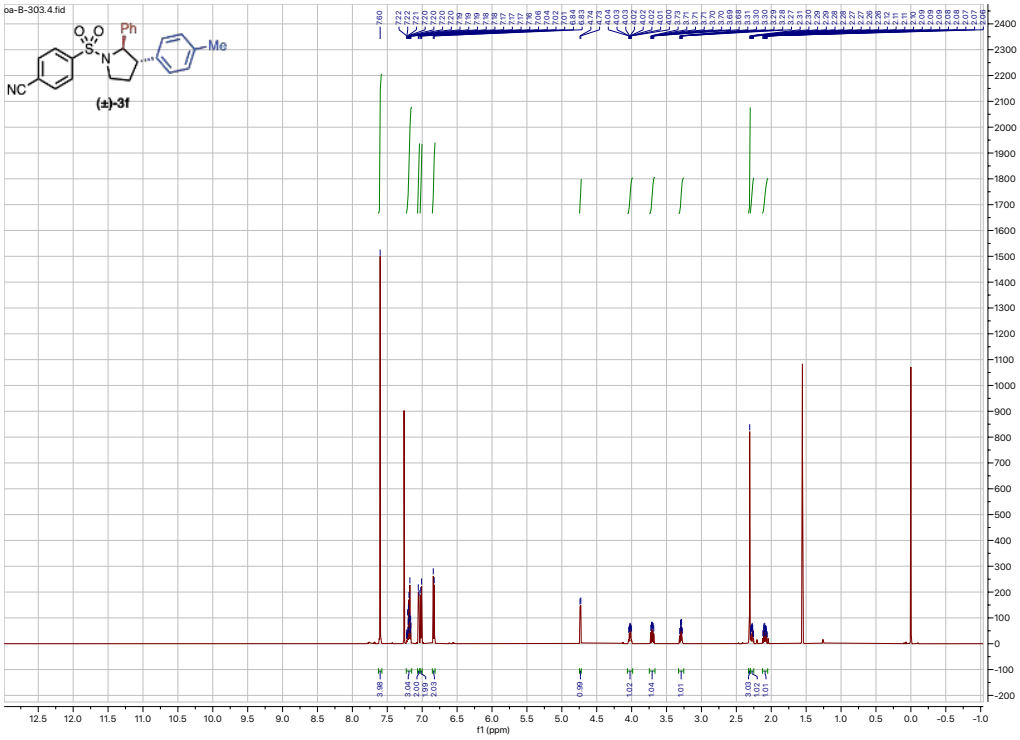
4-Cs
N
Boc
Ph
CF3
3e
-62.53
f1 (ppm)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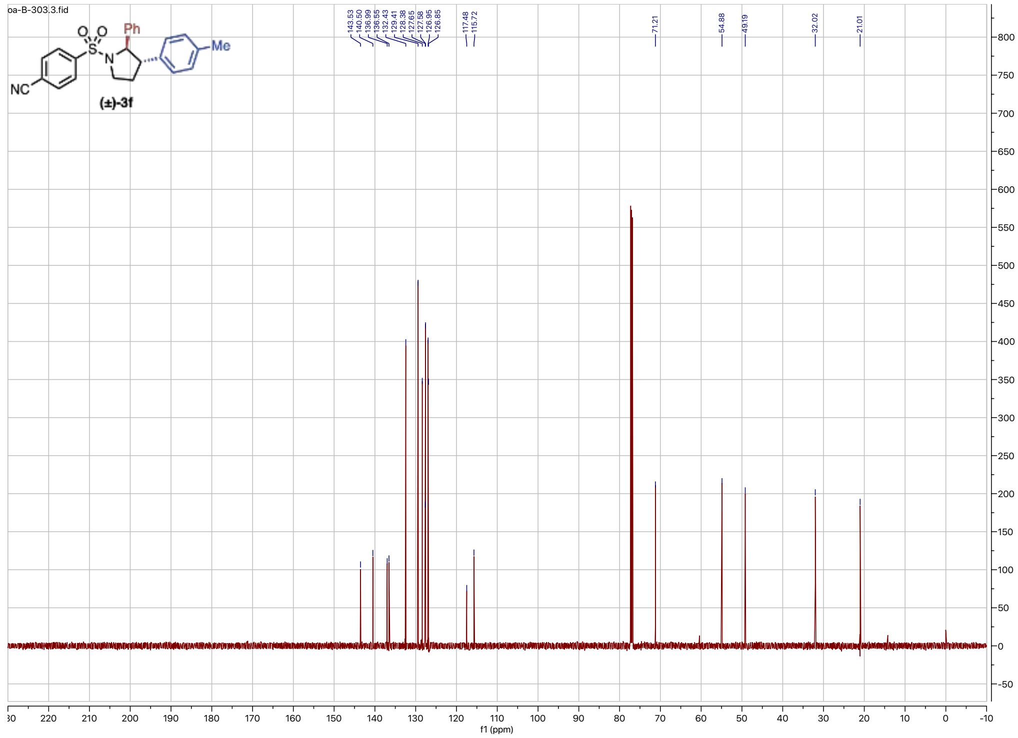
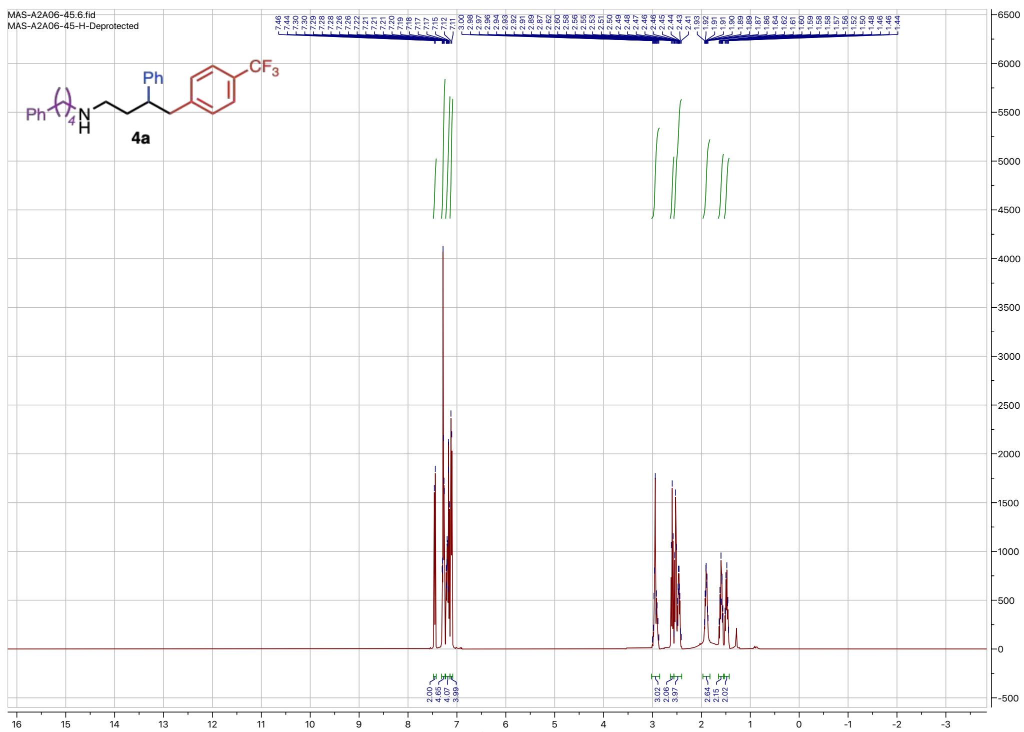
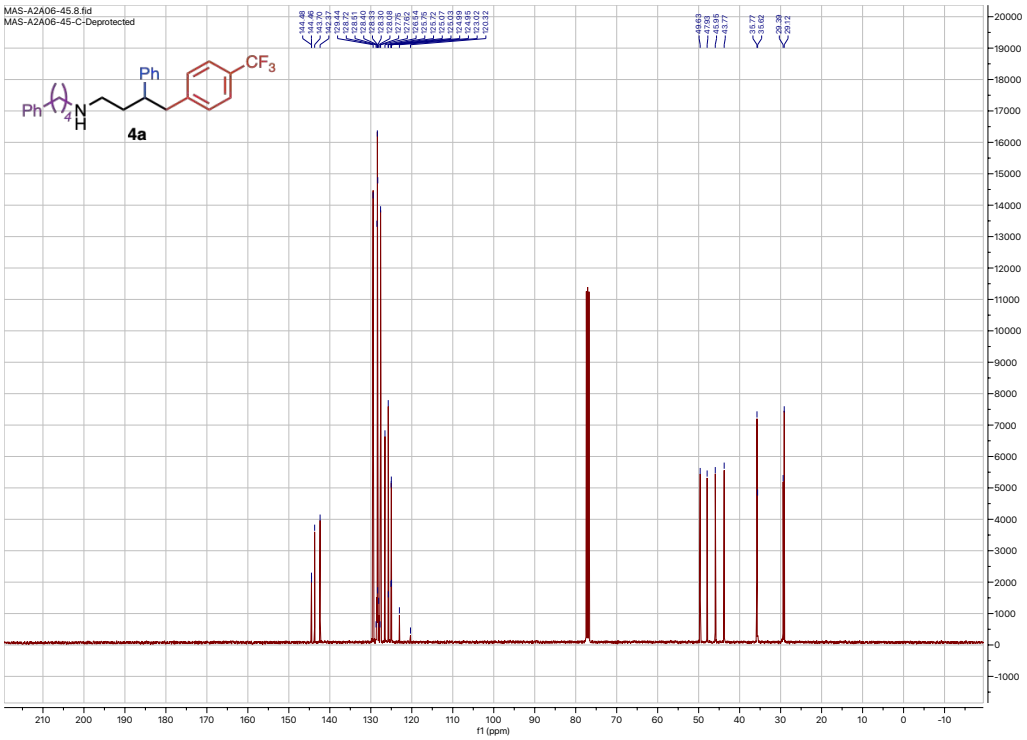
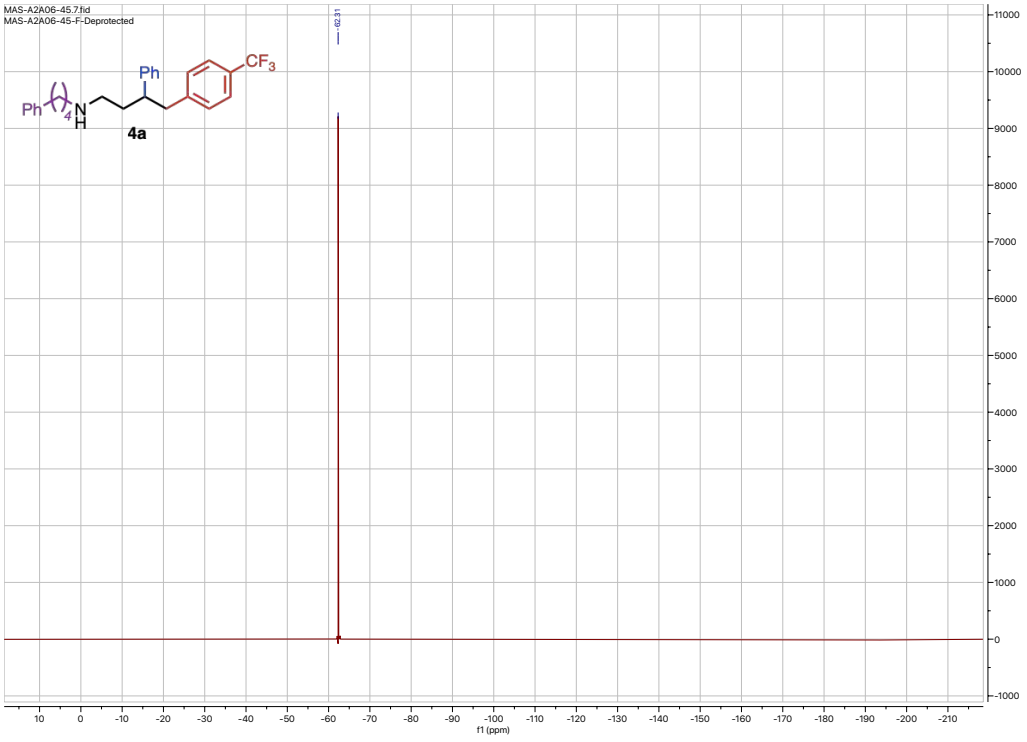
NC
Ph
Me
(±)-3f
f1 (ppm)






MAS-A2A06-45.8.fid
MAS-A2A06-45-C-Deprotected
Ph
CF3
Ph
N
H
4a
f1 (ppm)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MAS-A2A06-45-F-Deprotected
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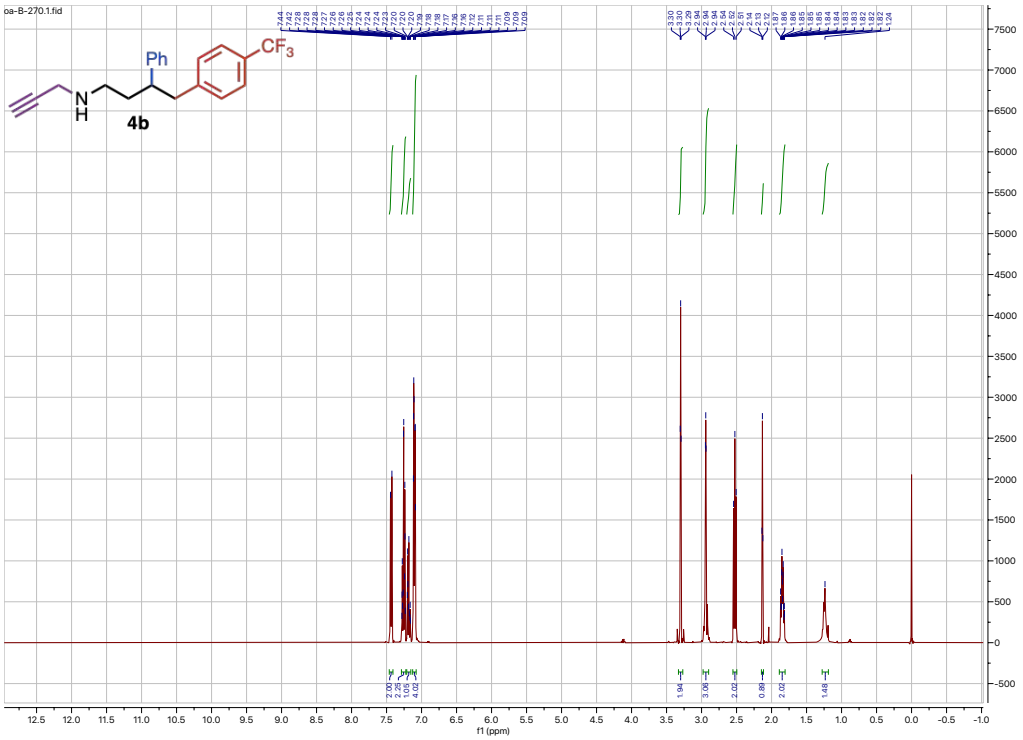
Ph
CF3
Ph
N
H
4a
f1 (ppm)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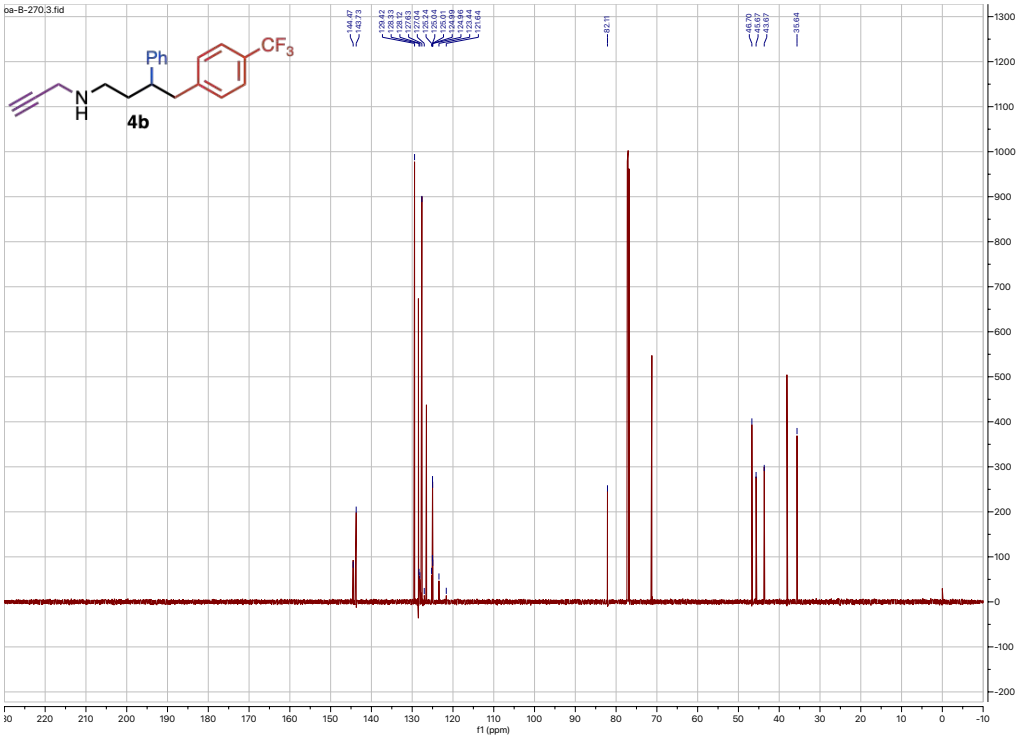
CF3
N
H
4b
f1 (ppm)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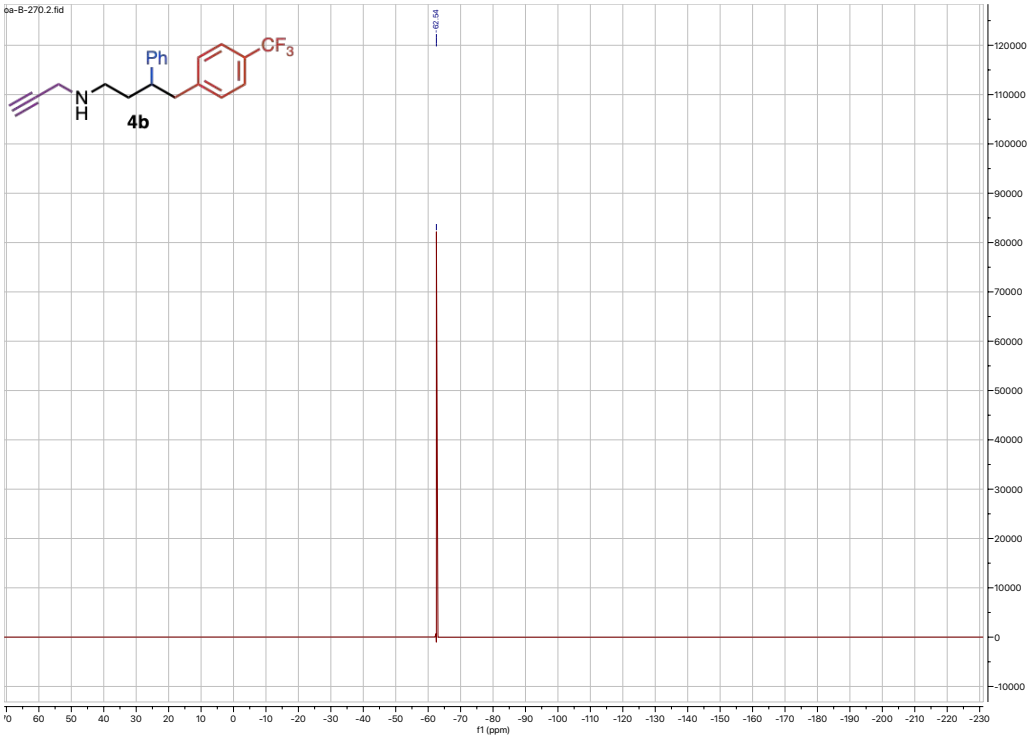
CF3
N
H
4b
f1 (ppm)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Ph
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N
H
4b
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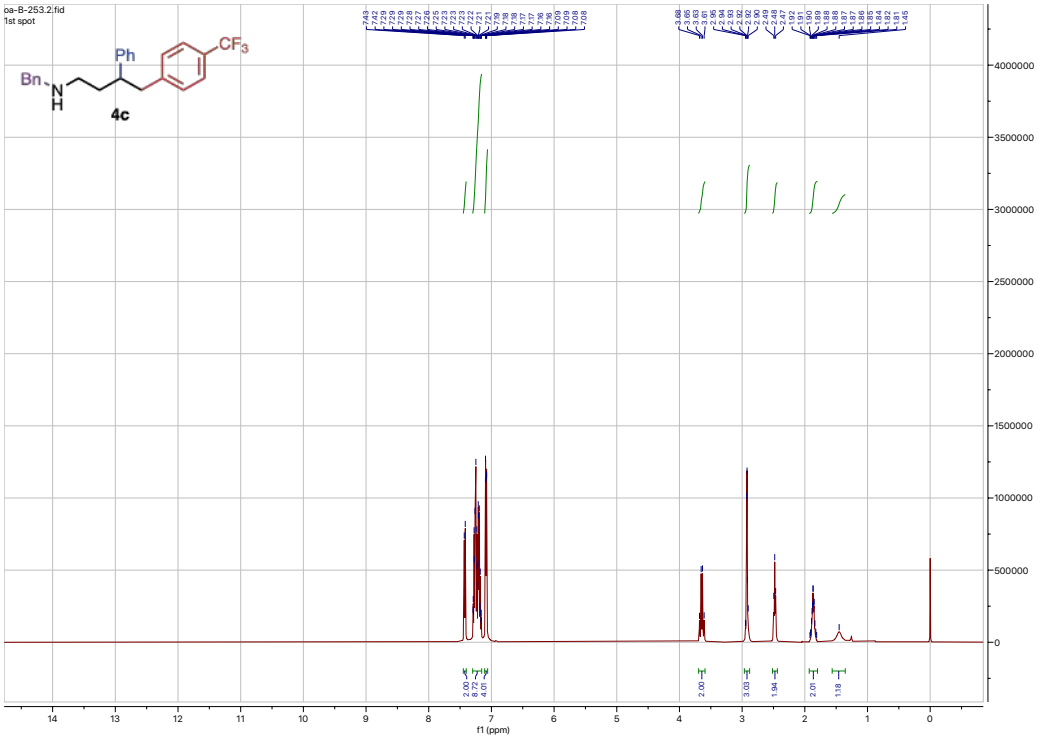
f1 (ppm)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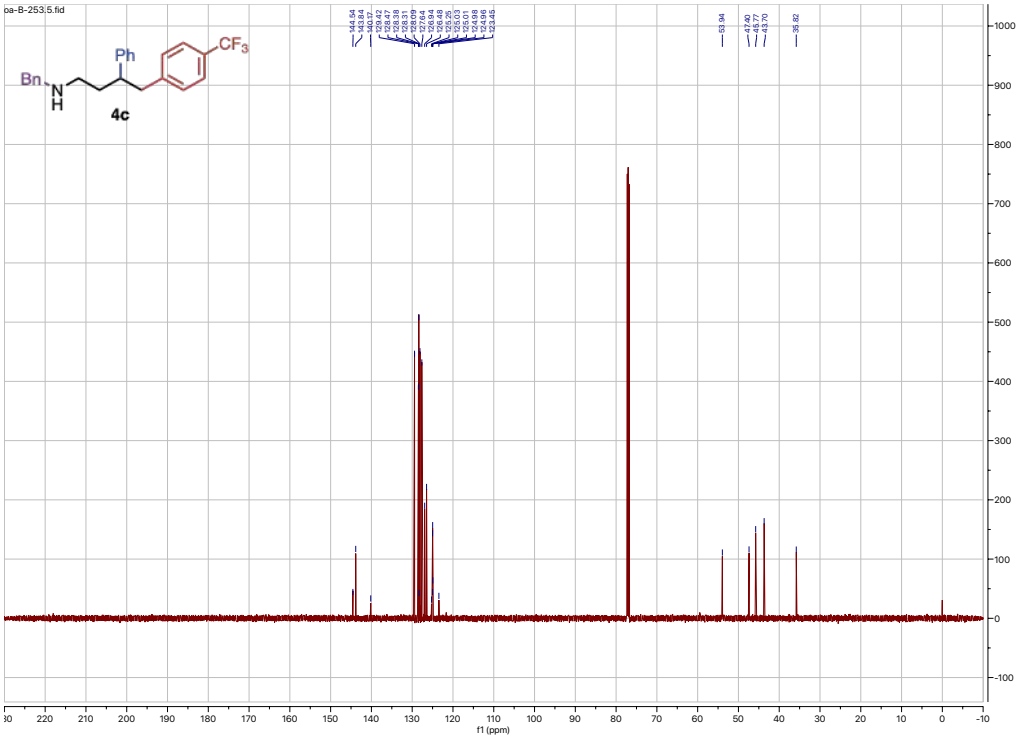
1st spot
Ph
CF3
Bn
N
H
4c
f1 (ppm)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Bn
N
H
Ph
CF3
4c
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143.84
140.07
139.42
138.47
138.31
138.09
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130.94
130.48
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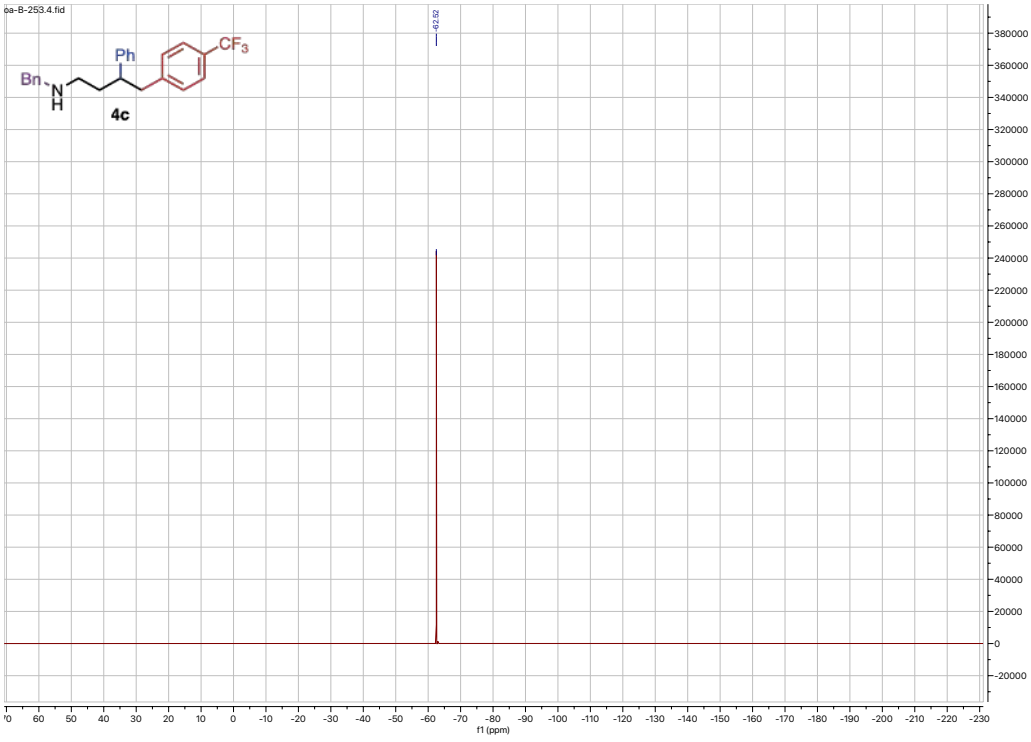
53.94
47.60
45.77
43.70
36.82
f1 (ppm)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H
Ph
CF3
4c
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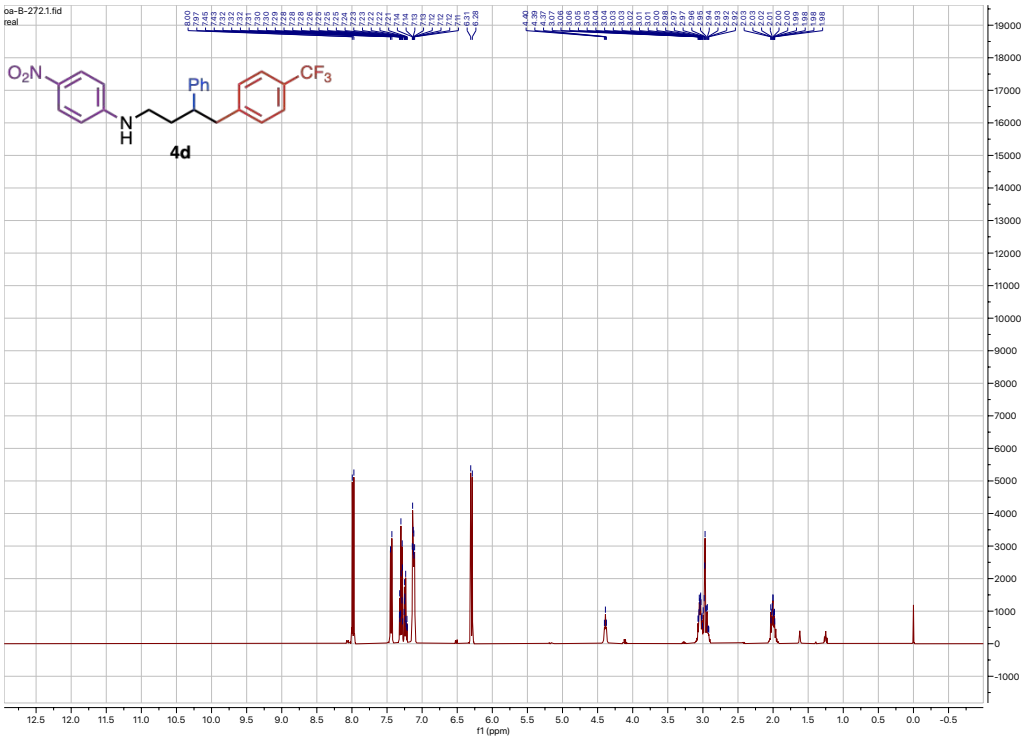
f1 (ppm)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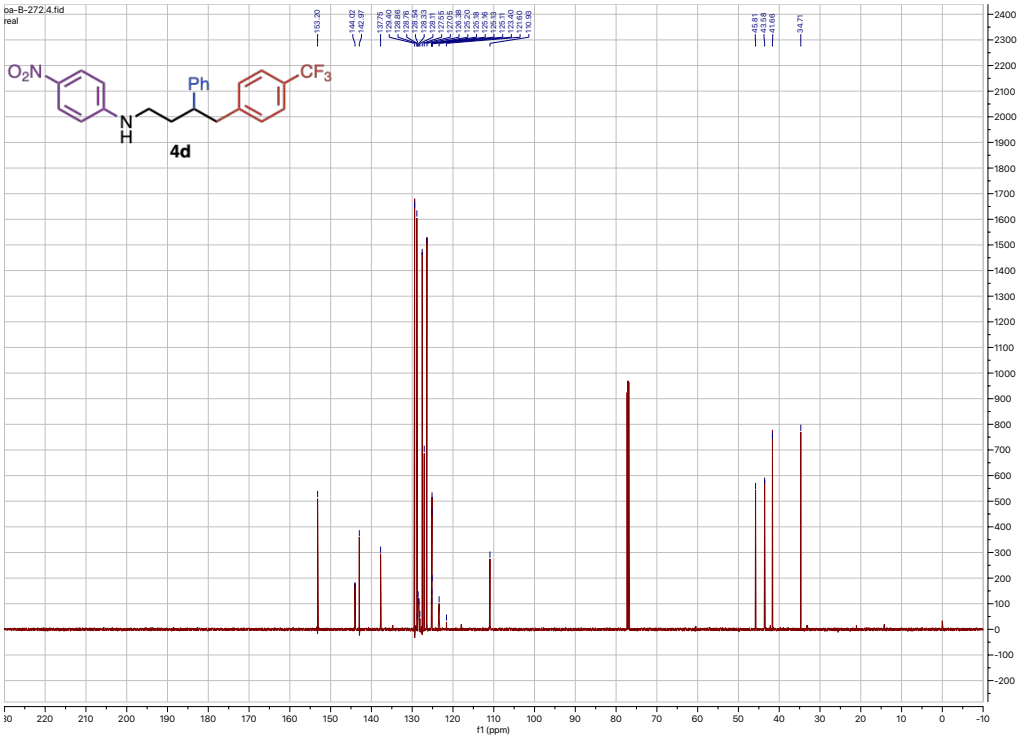
Ph
CF3
N
H
4d
f1 (ppm)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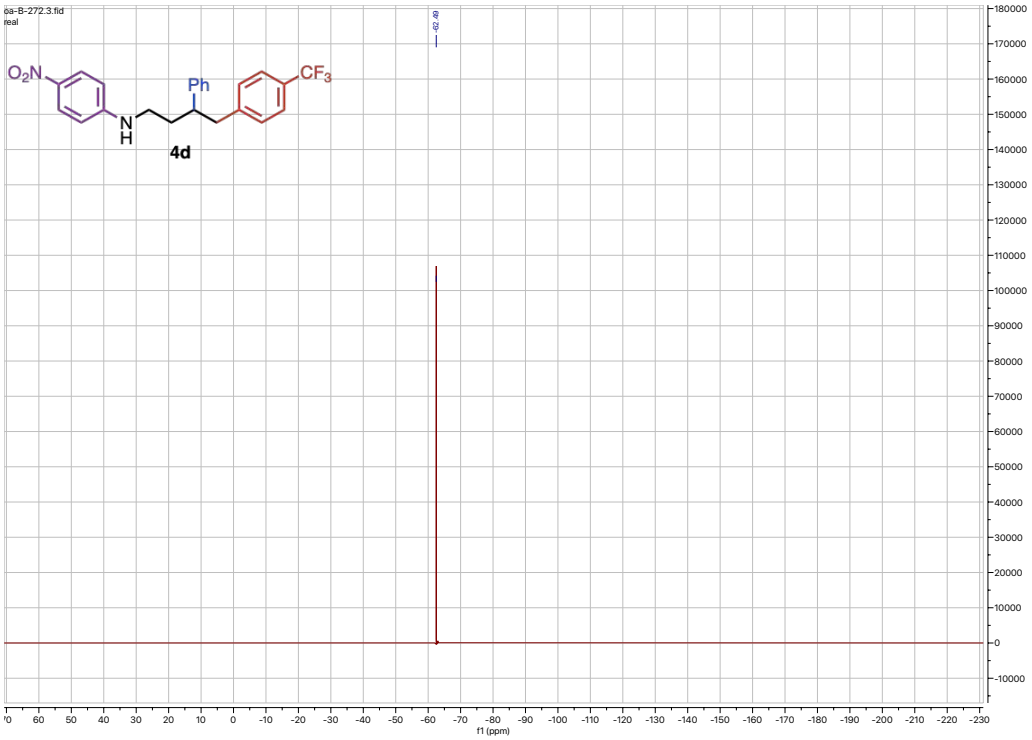
Ph
CF3
N
H
4d
f1 (ppm)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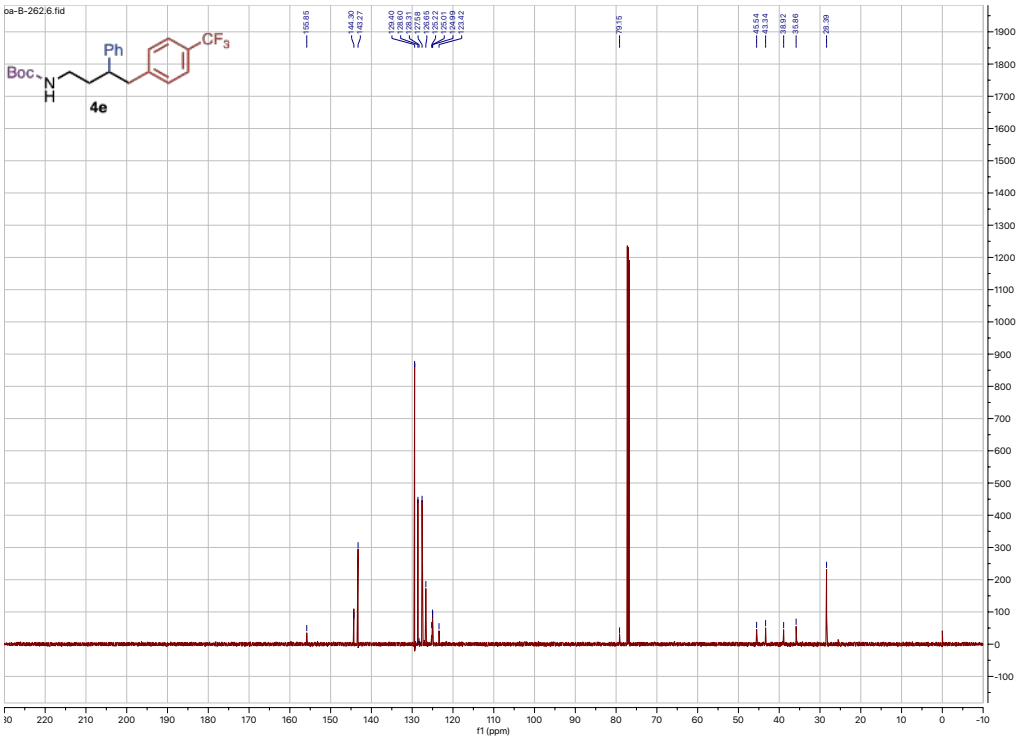
real
O_2N
Ph
CF_3
N
H
4d
f1 (ppm)


oa-B-262.3.fid
Boc
Ph
CF_3
N
H
4e
f1 (ppm)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Boc
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H
Ph
CF3
4e
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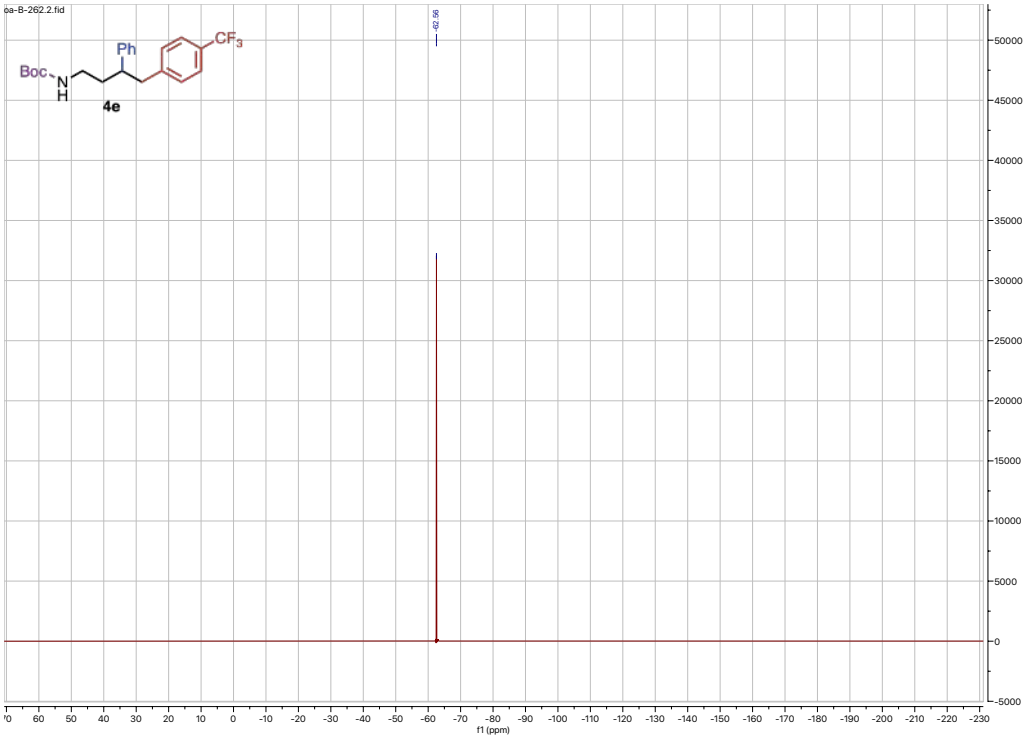
f1 (ppm)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Boc
N
H
Ph
CF3
4e
-62.56
f1 (ppm)

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