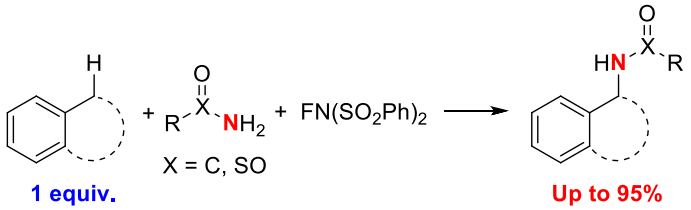
Non-Directed, Copper Catalyzed Benzylic C-H Amination Avoiding Substrate Excess

Anqi Wang,[†] Cristina C. DeOliveira,[†] and Marion H. Emmert[†‡]*

[†]Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, U.S.A.

[‡]Current Address: Process Research & Development, MRL, Merck & Co. Inc, 770 Sumneytown Pike, West Point, PA, 19486, U.S.A.

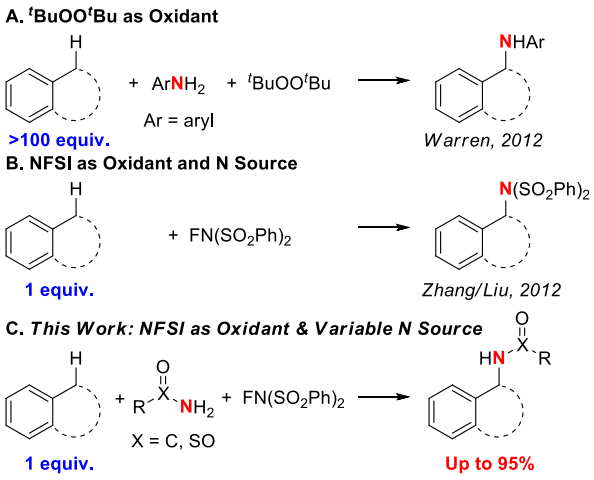


ABSTRACT: We report the development of a benzylic C-H amination protocol that addresses two common drawbacks in non-directed, intermolecular benzylic C-H aminations: (i) the need to use an excess of substrate and (ii) the limitation to only introduce one type of nitrogen source. Key to this discovery is the use of the strong oxidant *N*-fluorobenzenesulfonimide (NFSI) in combination with a Cu/diimine ligand catalyst system. The established conditions allow to lower the C-H substrate loading to 1.0 equivalent and provide up to 95% yield of C-H amination product. Furthermore, sulfonamides and benzamides can be employed as nitrogen sources, resulting in access to a diverse product scope.

Efficiently converting C-H bonds into other functional groups in organic molecules has been of prime interest to the synthetic community in the last decades.[1-6] The most prominent approach to achieve this goal, so-called directed or chelate-assisted C-H functionalization, has established the use of directing groups that lead a catalyst to a specific C-H bond.[7-9] This directed C-H bond attack provides access to many sites within complex targets that are otherwise difficult to modify at late stages of a synthesis.

In comparison to the vast knowledge that has been created for these directed reactions, non-chelate-assisted C-H functionalizations are underdeveloped.[10,11] This is likely due to several fundamental barriers to access such reactivity: (i) The non-directed cleavage of C-H bonds is often kinetically challenging. Therefore, such transformations frequently require an excess of substrate, making them less synthetically useful. (ii) Due to the significant strength and high pK_a's of C-H bonds, many reagents used in oxidative C-H functionalizations are highly reactive and can thus lead to side reactions. In combination with slow C-H bond cleavage, this can cause low selectivities, therefore also favoring conditions with high substrate loadings.

Due to these challenges, it is not surprising that many benzylic C-H amination protocols that do not proceed through chelate-assistance require an excess of substrate.[12-17] Among those examples is a recent protocol developed in our group that employs a Cu-based catalyst system and protected hydroxylamines as reagents.[18] Based on detailed mechanistic studies, we speculated that departure from the hydroxylamine scaffold towards a combination of oxidant and N source should be effective with the same catalyst system. Examples of such systems have been reported by Warren and coworkers, using ^{t}BuOO^{t}Bu as oxidant.[13,15] We were further inspired by an example of benzylic C-H cyanation employing *N*-fluorobenzenesulfonimide (NFSI) published by Stahl, Liu, and co-workers.[19] NFSI has further been employed as oxidant and N source in a Cu catalyzed C-H amination that is selective for primary benzylic C-H bonds and introduces the -N(SO$_2$PH)$_2$ group (Scheme 1B).[20]

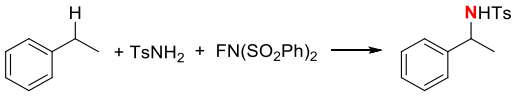


Scheme 1. Previous and herein reported Cu catalyzed, benzylic, non-directed C-H aminations.

As the latter example is strongly limited with regards to synthetic applications, we reasoned that the introduction of an external nucleophile in combination with NFSI may provide variability for the direct synthesis of protected benzylic amines (Scheme 1C). This manuscript describes the development and scope of the resulting methodology.

Optimizations with 1 equivalent of ethylbenzene as substrate (for all details, see the SI) led to the identification of conditions, which afforded the amination product $PhCHNHTsCH_3$ in excellent yield (95%; Table 1, entry 1). In contrast to the prior reactivity established with NFSI (Scheme 1B),[20] it was crucial to perform the reaction under a nitrogen atmosphere; the presence of air resulted in a significantly diminished yield (64%; entry 2). Both the Cu catalyst and the oxidant were required for reactivity, as illustrated by 0% yield in their absences (entries 3 and 4). Interestingly, only slightly diminished loadings of NFSI or $TsNH_2$ (2 equiv.) resulted in noticeably lower yields (68% and 63%, respectively; entries 5 and 6).

Table 1. Selected Optimization and Background Studies.



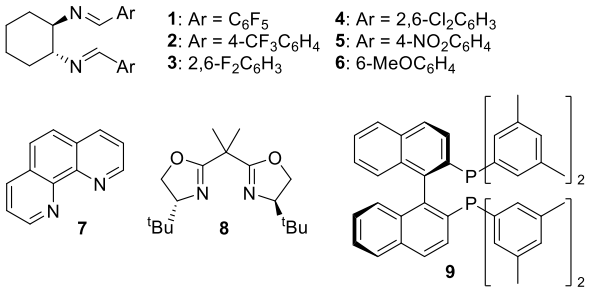
Entry	Changes to Standard Conditions[a]	Yield[b]
1	**None**	**95%**
2	air atmosphere	64%
3	no Cu catalyst precursor	0%
4	No NFSI	0%
5	2 equiv. NFSI	68%
6	2 equiv. $TsNH_2$	63%
7	MeCN as solvent	57%
8	C_6H_6 as solvent	73%
9	1,2-dichloroethane as solvent	92%
10	$Cu(OTf)_2$ instead of $Cu(BF_4)_2{\cdot}6H_2O$	7%
11	Ligand **2** instead of **1**	72%
12	Ligand **3** instead of **1**	76%
13	Ligand **4** instead of **1**	72%
14	Ligand **5** instead of **1**	57%
15	Ligand **6** instead of **1**	32%
16	Ligand **7** instead of **1**	62%
17	Ligand **8** instead of **1**	69%
18	Ligand **9** instead of **1**	82%
19	No ligand	75%

[a]Standard Conditions: $Cu(BF_4)_2{\cdot}6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **1** (6.0 mg, 12.6 µmol, 10.0 mol%), $TsNH_2$ (64.2 mg, 0.375 mmol, 3.00 equiv.), NFSI (118.3 mg, 0.375 mmol, 3.00 equiv.), ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $PhCF_3$ (1.5 mL), 110 °C, 48 h, N_2. [b]Yields were determined by quantitative, crude ^1H NMR using ClH_2CCHCl_2 as internal standard. All yields are shown as averages of at least two catalytic runs.

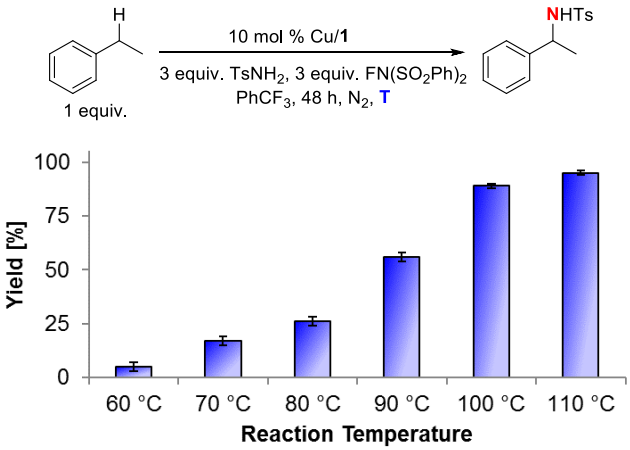
Similarly, use of different solvents than trifluorotoluene also resulted in diminished yields (entries 7 to 9), with 1,2-dichloroethane performing best among the alternative solvents (92%). Furthermore, the identity of the Cu catalyst precursor was shown to be important: Using $Cu(OTf)_2$ instead of $Cu(BF_4)_2{\cdot}6H_2O$ reduced the product yield to only 7% (Table 1, entry 10).

Interestingly, C-H amination reactivity was observed regardless of the identity of the used diimine ligand: Employing the electron-deficient ligands **2**, **3**, and **4** (Scheme 2) afforded 72 to 76% yield (entries 11 to 13). Using the NO_2-substituted ligand **5**, which has shown high activity in combination with Cu catalysts and Chloramine-T as oxidant,[21] afforded only 57% yield (entry 14), while an electron-rich diimine ligand (**6**) resulted in even lower yield (32%; entry 15) than the reaction in the absence of any added ligand (75%, entry 19). These observations suggest that a relatively electron-poor Cu species is important to promote reactivity. In agreement with this hypothesis, electron-rich ligands **7** and **8** that are frequently used in the literature in combination with Cu catalyst precursors provide mediocre yields in C-H amination (62% and 69%, respectively; entries 16/17). Interestingly, the BINAP-derivative **9** is the only other tested ligand than **1** that affords higher yields (82%; entry 18) than the reaction in the absence of ligand.

Finally, a comparison of product yields at difference temperatures (Scheme 3) further suggests that the highest C-H amination reactivities are obtained above 100 °C.



Scheme 2. Ligands Used in Reaction Optimization.

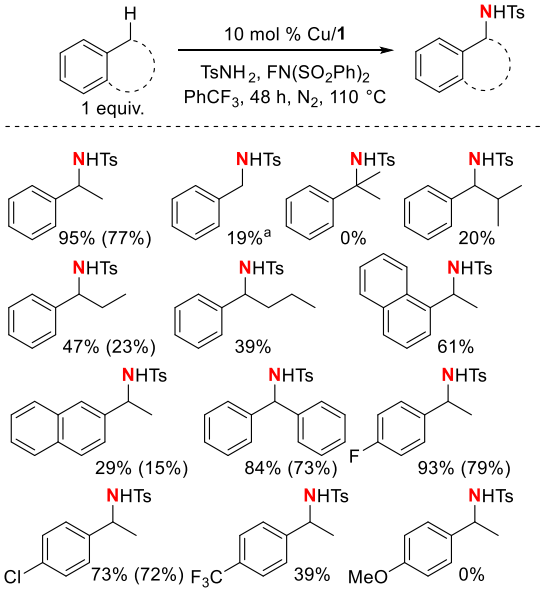


Scheme 3. Temperature Study.

With the optimized conditions in hand, we turned our attention to exploring the scope of alkyl arenes (Scheme 4). Substrates with only primary or tertiary benzylic C-H bonds provided lower reactivity: The C-H amination of toluene only afforded 19% of C-H amination product (together with 24% of $PhCH_2N(SO_2Ph)_2$), while no product was observed in reactions employing cumene as the substrate. C-H amination of isobutyl benzene only proceeded in 20% yield. The latter observations with cumene and isobutyl benzene as substrate imply that the observed reactivity is not only governed by free radical stabilities but is also influenced by the sterics in the immediate surrounding of the benzylic C-H bond.

n-Propyl benzene and *n*-butyl benzene both afforded mediocre yields of product (47% and 39%, respectively). Interestingly, 1-ethyl naphthalene showed much higher reactivity (61%) than 2-ethyl naphthalene (29%), which may be attributable to the different stabilities of the respective radical intermediates. Diphenylmethane underwent C-H amination in high yield (84%), further pointing towards the importance of stabilizing potential radical intermediates.

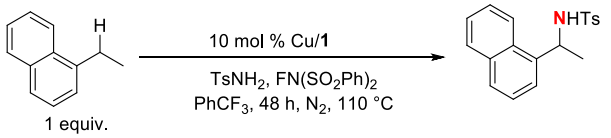
Finally, electron-withdrawing and electron-neutral substituents (F, Cl, CF_3) on the ethyl benzene core were tolerated, resulting in 93%, 73%, and 39% yield of C-H amination product. In contrast, 4-methoxyethylbenzene did not afford any distinguishable product under the standard reaction conditions. Generally, the isolated yields (shown in brackets in Scheme 4) are in the same range as the crude yields, but occasionally ~20% lower due to challenges separating the product from $(PhSO_2)_2NH$, the side product of oxidation.



Scheme 4. Benzylic CH Substrate Scope. Yields were determined by quantitative, crude ^{1}H NMR using ClH_2CCHCl_2 as internal standard. Yields are shown as averages of at least two catalytic runs. Isolated yields are shown in brackets. [a]24% of $PhCH_2N(SO_2Ph)_2$ were also formed.

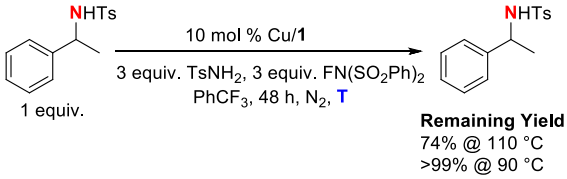
Motivated by the variability of yields, we focused on gaining a better understanding of limiting factors in the reaction. We thus performed a series of experiments geared at elucidating potential catalyst decomposition (Scheme 5). 1-Ethyl naphthalene was chosen as substrate, due to the mediocre (61%) yields obtained under standard reaction conditions. To test for catalyst decomposition, we added another batch of catalyst into the mixture after 48 h, followed by another 48 h of reaction time. Similarly, oxidant decomposition was tested by charging with a second batch of oxidant.

Surprisingly, *both reactions afforded significantly lower yields* (22% and 8%, respectively) than the original 61% after 48 h; recharging both catalyst and NFSI resulted in 14% yield. These data imply that the product of C-H amination is not stable under the standard reaction conditions. To test if product decomposition is a limiting factor, we subjected $PhCHNHTsCH_3$ to standard reaction conditions (Scheme 6). Only 74% of $PhCHNHTsCH_3$ were remaining after 48 h, supporting that product decomposition occurs 110 °C. Gratifyingly, no decomposition was observed when the reaction was performed at 90 °C (>99% $PhCHNHTsCH_3$ after 48 h).

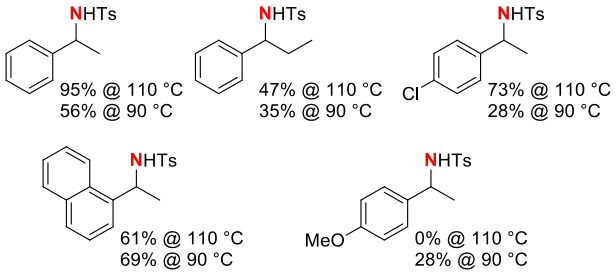


Yield	Conditions
61%	Standard conditions
22%	Added 10 mol % Cu/**1** after 48 h & reacted for 48 h
14%	Added 10 mol % Cu/**1** + 3 equiv. NFSI after 48 h & reacted for 48 h
8%	Added 3 equiv. NFSI after 48 h & reacted for 48 h

Scheme 5. Test for Catalyst or Oxidant Decomposition.



Scheme 6. Product Decomposition Study.

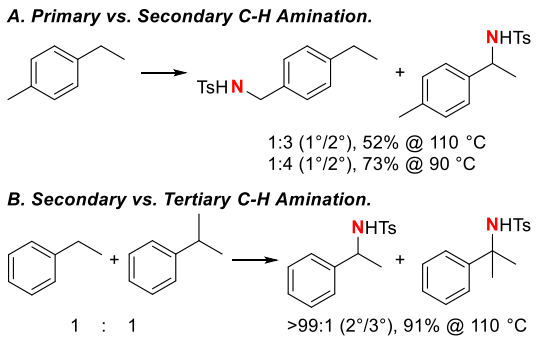


Scheme 7. Comparison of Selected Product Yields at 90 and 110 °C.

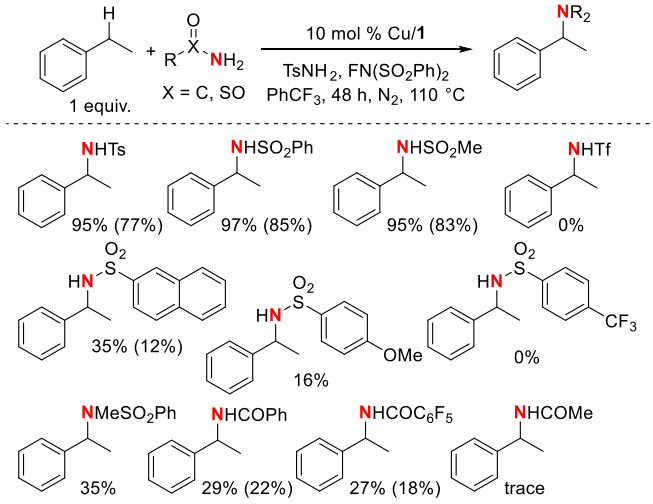
Encouraged by this result, we performed C-H aminations of several benzylic substrates at 90 °C; all chosen substrates had not shown quantitative yields under standard conditions (Scheme 7). The obtained yields suggest that product decomposition does not seem to be a major factor in limiting yields for most simple alkylbenzenes (ethyl benzene, n-propyl benzene,

and 4-chloroethyl benzene shown in Scheme 7; for more examples, see the SI); all these substrates showed decreased yields at 90 °C. In contrast, 1-ethyl naphthalene showed improved yields under these conditions (69% vs. 61%). Most excitingly, the yield with 4-methoxyethyl benzene was raised from 0% to 28% by lowering the temperature to 90 °C. This suggests that C-H amination occurs with 4-methoxyethyl benzene at 110 °C, but that the product is unstable under standard reaction conditions and thus not observed.

We then investigated if different reaction temperatures influence the site selectivity of C-H amination in addition to influencing product stability. To this end, we subjected 4-ethyltoluene to reaction conditions at 110 °C and at 90 °C (Scheme 8A). The reaction at the lower temperature provided both higher product yields (73% vs. 52%) and higher selectivity (1:4 vs. 1:3) compared to the reaction outcome at 110 °C. This suggests that (i) product decomposition is an important factor at 110 °C and (ii) that lower temperature favors site selectivity for C-H amination of secondary C-H bonds with lower bond dissociation energies than primary C-H bonds.



Scheme 8. Selectivity Studies. A. Primary vs. Secondary C-H Amination at 110 and 90 °C. B. Secondary vs. Tertiary C-H Amination at 110 °C.



Scheme 9. Nitrogen Source Scope. Yields were determined by quantitative, crude ^{1}H NMR using ClH_2CCHCl_2 as internal standard. Yields are shown as averages of at least two catalytic runs. Isolated yields are shown in brackets.

In contrast to this effect on primary vs. secondary C-H amination, amination is completely selective for transformation of secondary C-H bonds vs. tertiary C-H bonds (Scheme 8B). This implies that the reaction mechanism is unlikely to proceed through free radical intermediates, as at least small amounts of tertiary C-H amination would be excepted in that case.

Next, we explored the scope of introducible N sources (Scheme 9). Generally, all reactions with electron-neutral (H_2NSO_2R, R = *p*-tol, Ph, naphthyl; 95%, 97%, 35%) and electron-rich sulfonamides (H_2NSO_2R, R = Me, *p*-C_6H_4OMe; 95%, 16%) formed the respective benzylic C-H amination product, while electron-poor sulfonamides (H_2NSO_2R, R = CF_3, *p*-$C_6H_4CF_3$) were unreactive. In contrast to previous work with this catalyst system,[18] reactivity to the C-H amination product was also observed with secondary sulfonamides ($HNMeSO_2Ph$; 35%) and, most excitingly, benzamides as N source (H_2NCOPh, 29%; $H_2NCOC_6F_5$, 27%). With acetamide, only traces (<1%) of product were observed. Isolated yields generally aligned with the yields measured by quantitative ^{1}H NMR.

Several experimental studies were performed to gain insight into the reaction mechanism of the protocol. KIE studies with a 1:1 mixture of toluene and toluene-d_8 as substrate resulted in an equimolar mixture of deuterated and non-deuterated C-H amination product, implying a kinetic isotope effect (KIE) of 1.0. This suggests that C-H bond scission in the developed reaction occurs after the rate-determining step and that C-H bond cleavage is fast in comparison to other reaction steps. The obtained KIE value is further distinctly differentiated from KIEs observed in similar Cu catalyzed C-H functionalizations, such as Stahl and Liu's C-H cyanation (KIE = 3.5) via radical relay reactivity,[19] Warren's C-H amination employing a Cu(nacnac) catalyst system (KIE = 70),[13] or Liu's Cu catalyzed C-H amination with NFSI that is selective for primary benzylic C-H amination (KIE = 4.0).[20]

A series of radical trapping experiments with TEMPO, $BrCCl_3$, and air did not provide further insight into the operating reaction mechanism (for details see the SI). In all cases, substrate consumption seemed to be unaffected by the employed additives, while yields were lowered. As such, a radical relay as in Stahl and Liu's C-H cyanation[19] seems unlikely, while other mechanisms could not be excluded based on the available data.

Overall, this manuscript summarizes the development of a reaction protocol that addresses two common drawbacks in non-directed, intermolecular benzylic C-H aminations: (i) the need to use an excess of substrate and (ii) the limitation to only introduce one type of nitrogen source. The strong oxidant *N*-fluorobenzenesulfonimide (NFSI) in combination with a Cu/diimine ligand catalyst system are important to achieve this reactivity and allow low substrate loadings of 1.0 equivalent. Under these conditions, up to 97% yield of C-H amination product can be obtained. Excitingly, the use of both sulfonamides and benzamides as nitrogen sources is tolerated. The ability to introduce various protected amine groups suggests (in agreement with findings by Warren and co-workers)[12-15] that combinations of nitrogen sources and oxidants in Cu catalyzed benzylic C-H aminations are synthetically more versatile with respect to their product scope than approaches employing electrophilic amination reagents, such as Chloramine-T,[21-23] protected hydroxylamines,[18] or reagents derived from iodosoarenes (e.g. PhI=NTs).

ASSOCIATED CONTENT

Experimental procedures, spectroscopic data, and detailed optimization data (PDF) are attached to this manuscript.

AUTHOR INFORMATION

Corresponding Author

* mhemmert@wpi.edu; marion.emmert@merck.com; @EmmertLab

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Supporting Information

Non-Directed, Copper Catalyzed Benzylic C-H Amination Avoiding Substrate Excess

Anqi Wang,[†] Cristina C. DeOliveira,[†] and Marion H. Emmert[†‡]*

[†]Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, U.S.A.

[‡]Current Address: Process Research & Development, MRL, Merck & Co. Inc, 770 Sumneytown Pike, West Point, PA, 19486, U.S.A.

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Materials and Methods

All reagents and solvents were used as received unless noted otherwise. All reagents were obtained commercially unless otherwise noted.

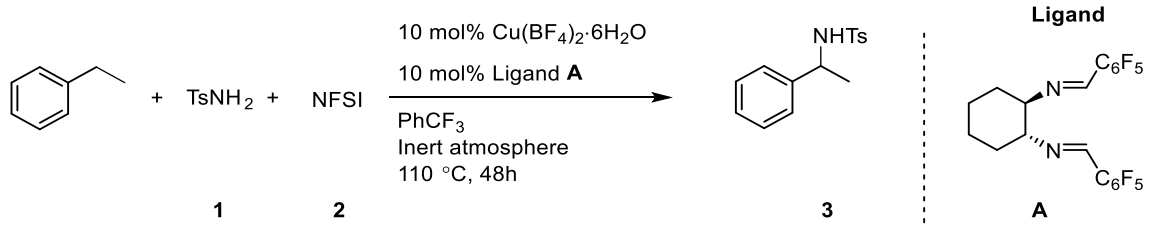
Stirbars used in catalytic reactions were cleaned with aqua regia for at least 3 h upon gentle stirring, rinsed with copious amounts of water, and dried in an oven at 120 °C prior to use. Yields are reported as average yields of at least 2 experiments. The reported error is the standard deviation of at least two replicate trials.

All catalytic experiments were set up in a Vigor glovebox kept under a dry nitrogen atmosphere unless otherwise noted. Upon sealing the reaction vials in the glovebox, catalytic reaction mixtures were removed from the glovebox and heated on pre-heated vial plates.

All NMR experiments were carried out on a Bruker BioSpin 500MHz Avance III Digital NMR spectrometer. All quantitative ^{1}H NMR measurements were performed using an adjusted method (15 s relaxation time, NS = 32) with 1,1,2-trichloroethane as internal standard. All NMR spectra were recorded at room temperature unless otherwise noted.

GC-MS analyses were performed on an Agilent 5975C instrument using a 19091S-433 (HP-5MS; 30 m, 0.25 mm i.d., 0.25 μm df) column. The identities of all products were verified by comparison of the obtained data with NMR and GC-MS data of original samples.

Representative Procedure for Catalytic Benzylic Amination Reactions



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), p-Toluenesulfonamide (64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.), ethylbenezene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.) and 1.5 mL benzotrifluoride were added in this sequence to a 4 mL scintillation vial, equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After stirring the mixture vigorously for the dedicated reaction time, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure (rotary evaporator). 1,1,2-trichloroethane (20.0 µL, 28.8 mg, 215.9 mmol) was added into the reaction vial as NMR standard following the addidtion of 1.0 mL $CDCl_3$. The resulting mixture was filtered through Celite. The filtrate was used directly for quantitative ^1H NMR measurements (as shown in Figure S1) to determine the yield of product **3** by measuring the ratio of integrals for the benzylic proton of **3** (peak at 4.53 ppm) and the proton of 1,1,2-trichloroethane at 5.79 ppm.

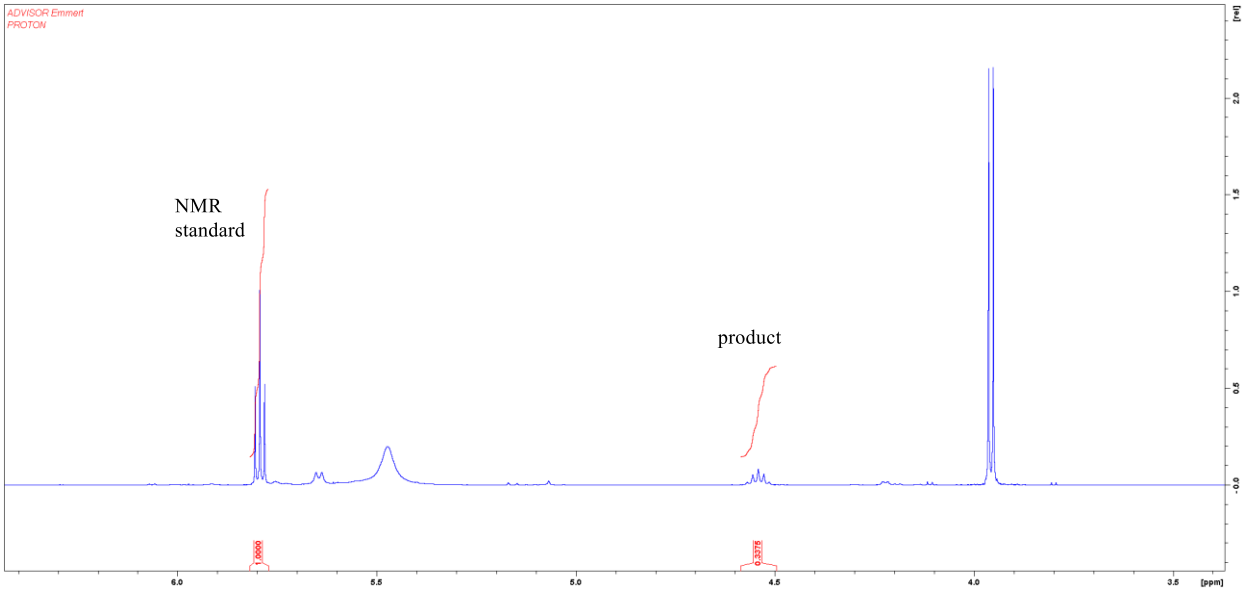
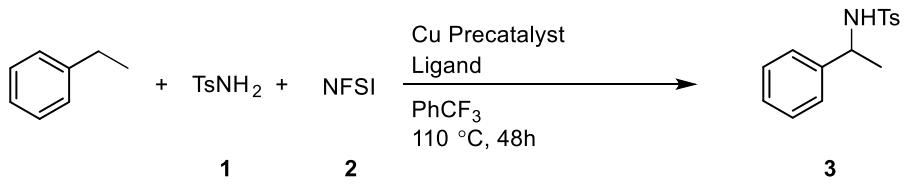


Figure S1. NMR Example for Yield Analysis of Product

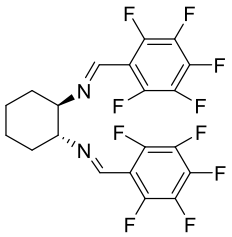
Reaction Optimization

Table S1. Reaction Optimization. Conditions: Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), amination reagent **1** (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL benzotrifluoride 110 °C, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

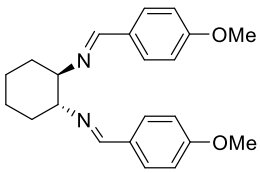


1 **2** **3**

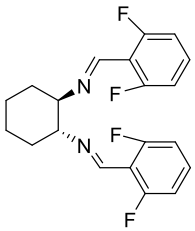
Entry	Copper precatalyst	Ligand	NFSI	Atmosphere	NMR Yield of **3**
1	-	-	Yes	air	0 ± 0
2	-	-	3.00 equiv	nitrogen	0 ± 0
3	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	-	3.00 equiv	air	51 ± 2
4	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	**A** (10 mol%)	3.00 equiv	air	64 ± 2
5	-	-	**No NFSI**	nitrogen	0 ± 0
6	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	-	3.00 equiv	nitrogen	75 ± 1
7	CuCl (10 mol%)	-	3.00 equiv	nitrogen	65 ± 2
8	CuBr (10 mol%)	-	3.00 equiv	nitrogen	0 ± 0
9	$CuCl_2$ (10 mol%)	-	3.00 equiv	nitrogen	68 ± 1
10	$[Cu(MeCN)_4]PF_6$ (10 mol%)	-	3.00 equiv	nitrogen	73 ± 1
11	$Cu(OAc)_2$ (10 mol%)	-	3.00 equiv	nitrogen	63 ± 2
12	$Cu(OTf)_2$ (10 mol%)	-	3.00 equiv	nitrogen	7 ± 0
13	CuOTf·0.5toluene (10 mol%)	-	3.00 equiv	nitrogen	41 ± 1
14	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	**A** (10 mol%)	3.00 equiv	nitrogen	95 ± 2
15	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	**B** (10 mol%)	3.00 equiv	nitrogen	32 ± 2
16	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	**C** (10 mol%)	3.00 equiv	nitrogen	76 ± 2
17	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	**D** (10 mol%)	3.00 equiv	nitrogen	72 ± 2
18	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	**E** (10 mol%)	3.00 equiv	nitrogen	57 ± 1
19	$Cu(BF_4)_2{\cdot}6H_2O$ (10 mol%)	**F** (10 mol%)	3.00 equiv	nitrogen	72 ± 1



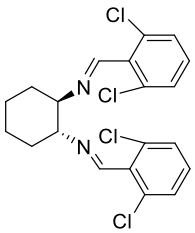
A



B



C



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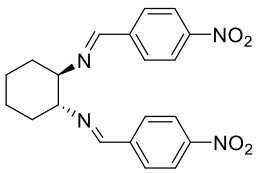

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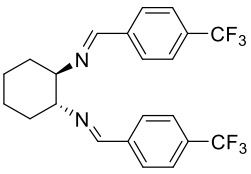
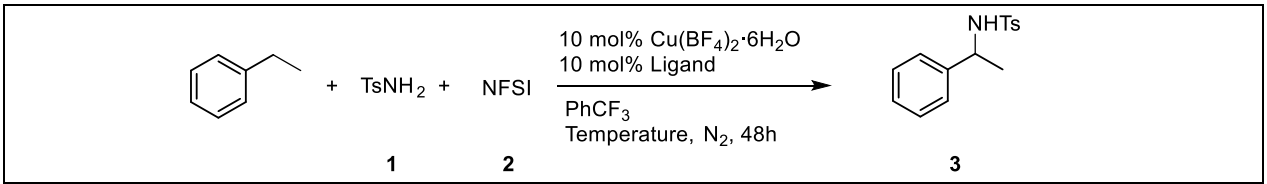


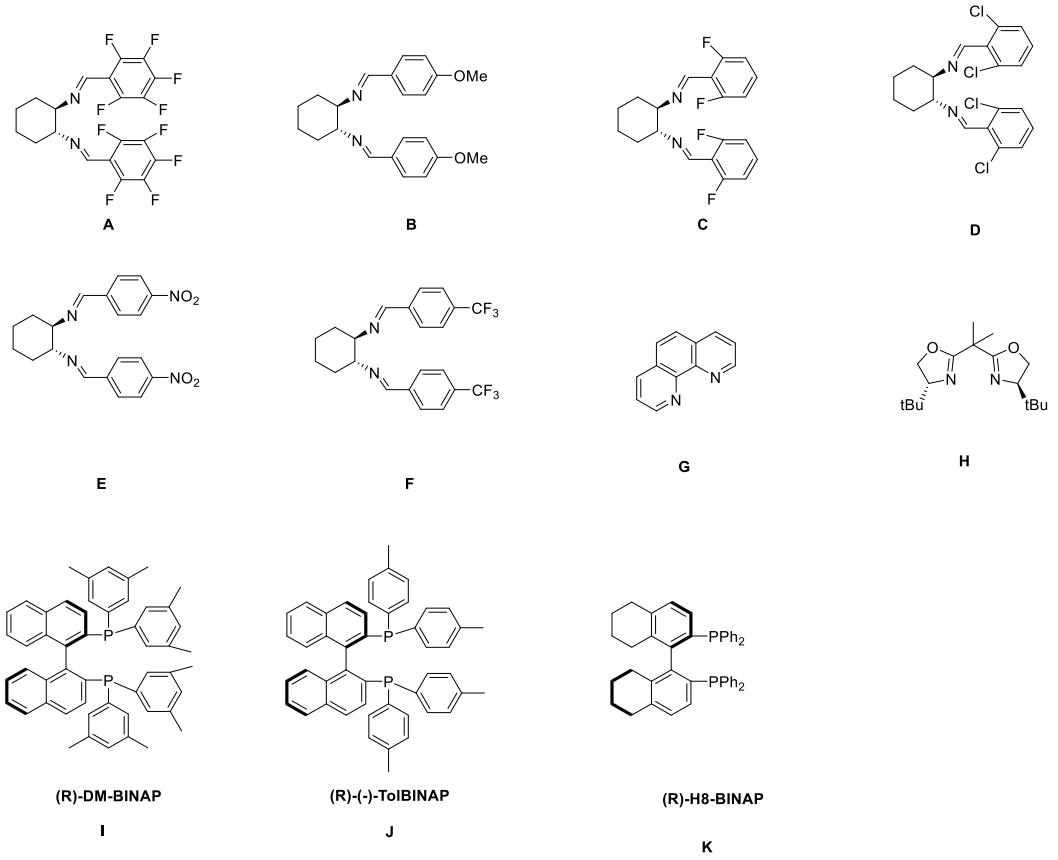
F

Ligand Study

Table S2. Ligand Study@ 90 °C and 110 °C. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand (12.6 µmol, 10.0 mol%), amination reagent **1** (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL benzotrifluoride 110 °C, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

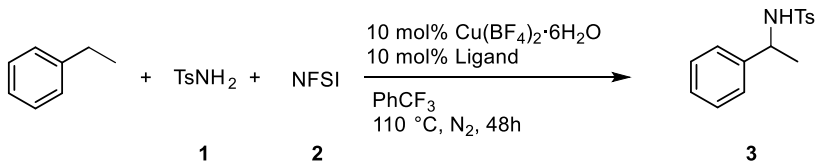


Entry	Ligand	Yield% @**90 °C**	Yield% @**110 °C**
1	**A**	16 ± 1	95 ± 2
2	**B**	8 ± 2	32 ± 2
3	**C**	17 ± 1	76 ± 2
4	**D**	17 ± 2	72 ± 2
5	**E**	11 ± 2	57 ± 1
6	**F**	21 ± 2	71 ± 1
7	**G**	n/a	62 ± 2
8	**H**	n/a	69 ± 2
9	**I**	n/a	82 ± 1
10	**J**	n/a	13 ± 2
11	**K**	n/a	25 ± 1



Optimization of Amine and NFSI

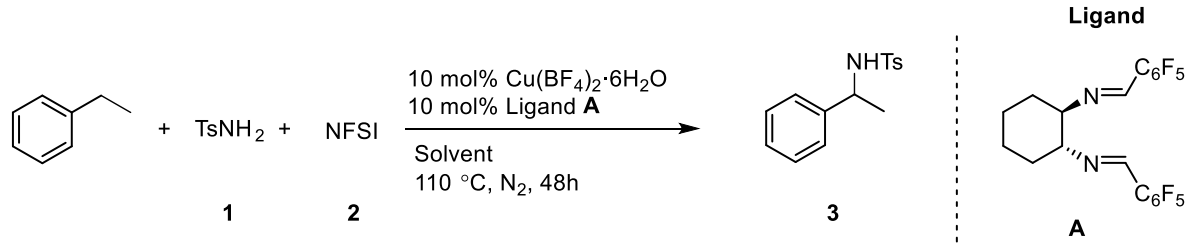
Table S3. Optimization of Amine and NFSI. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2{\cdot}6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand (12.6 µmol, 10.0 mol%), amination reagent **1**, *N*-Fluorobenzenesulfonimide and 1.5 mL benzotrifluoride 110 °C, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.



Entry	Equivalent of $TsNH_2$	Equivalent of NFSI	Yield% of **3**
1	1	1	37 ± 2
2	1	2	42 ± 1
3	1	3	44 ± 2
4	2	1	51 ±2
5	2	2	59 ± 2
6	2	3	63 ± 2
7	3	1	52 ± 1
8	3	2	68 ± 1
9	3	3	95 ± 2

Solvent Study

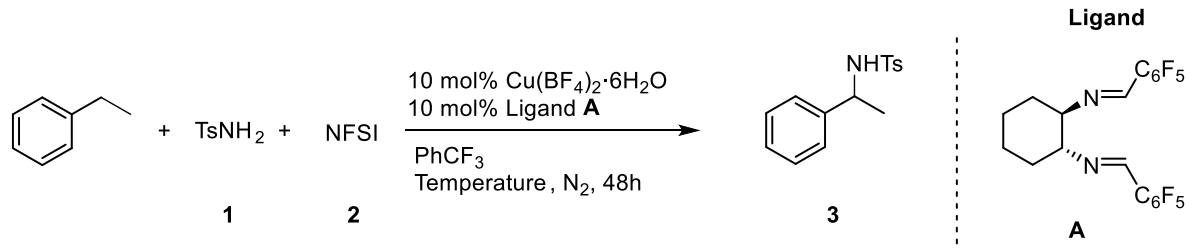
Table S4. Solvent Study. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), amination reagent **1** (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL solvent, 110 °C, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.



Entry	Solvent	Yield% of Product **3**
1	MeCN	57 ± 1
2	1, 2-dichloroehthane	92 ± 2
3	PhBr	64 ± 2
4	PhCN	23 ± 2
5	PhCF3	95 ± 1
6	Benzene	73 ± 1

Temperature Study

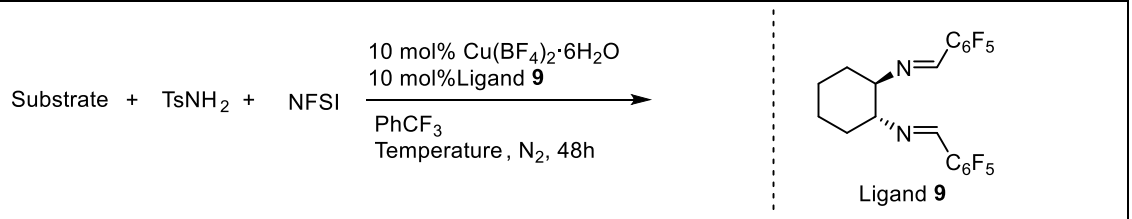
Table S5. Temperature Study. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), amination reagent **1** (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL solvent, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

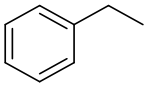
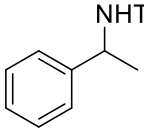
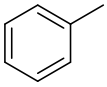
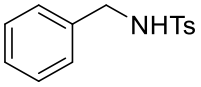
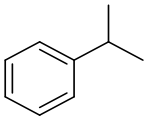
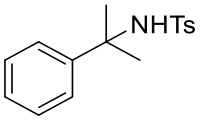
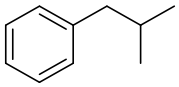
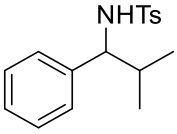
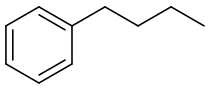
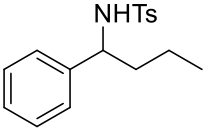
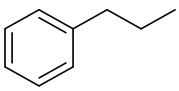
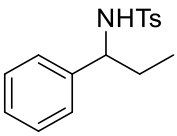


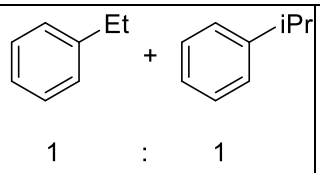
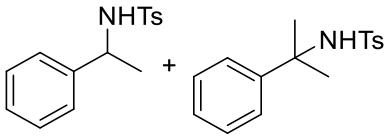
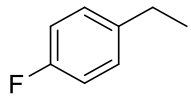
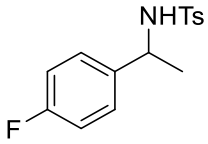
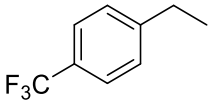
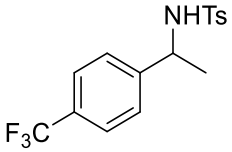
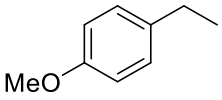
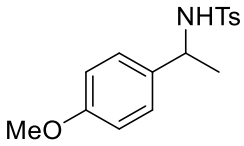
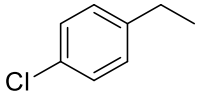
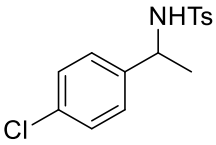
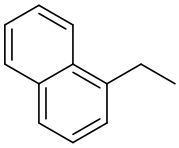
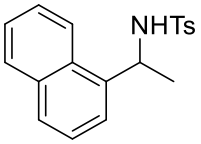
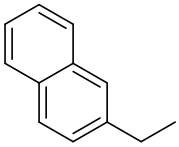
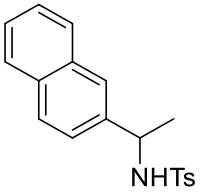
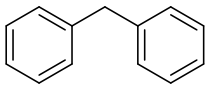
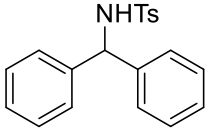
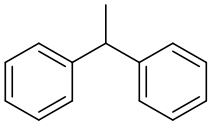
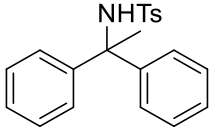
Entry	Temperature	Yield% of Product **3**
1	110 °C	95 ± 1
2	100 °C	89 ± 1
3	90 °C	56 ± 2
4	80 °C	26 ± 2
5	70 °C	17 ± 2
6	60 °C	5 ± 2

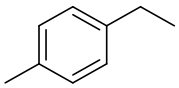
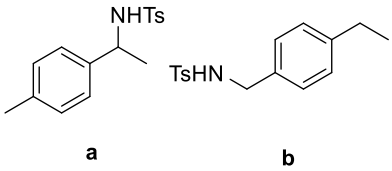
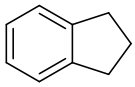
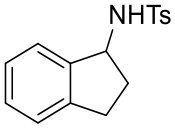
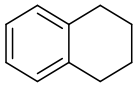
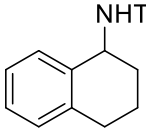
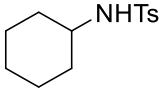
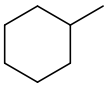
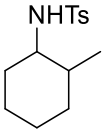
Substrate Scope

Table S6. Substrate Scope. Substrate (0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), amination reagent **1** (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL $PhCF_3$, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.



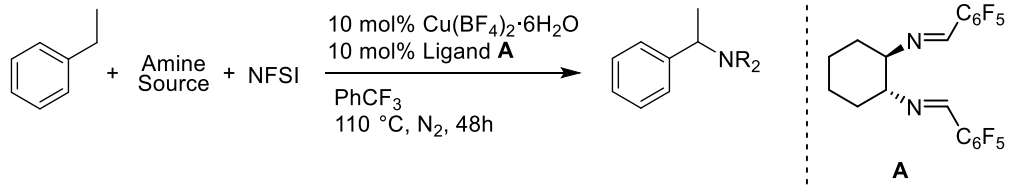
Entry	Substrate	Product	NMR Yield @90 °C	NMR Yield @110 °C (Isolated Yield)	Remaining substrate @110 °C
1			56 ± 2	95± 2 (77%)	3 ± 1
2			7 ± 2	19 ± 2	Not detected due to low boiling point of substrate and sample preparation via vacuum evaporation
3			Not performed	0 ± 0	47 ± 3*
4			0 ± 0	20 ± 1	56 ± 3*
5			32 ± 2	39 ± 2	24 ± 4*
6			35 ± 2	47 ± 2 (23%)	21 ± 2*

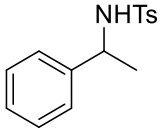
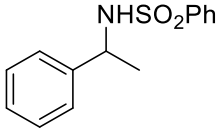
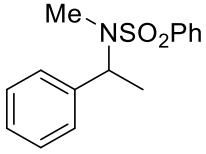
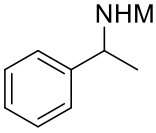
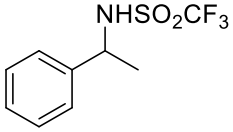
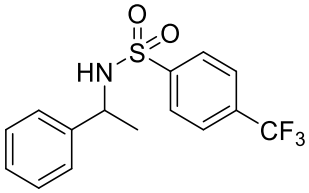
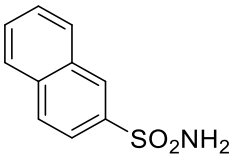
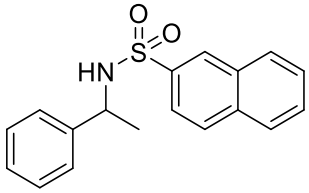
7			Not performed	91 ± 2 & 0 ± 0	Not determined
8			Not performed	93 ± 2 (79%)	8 ± 1
9			Not performed	39 ± 2	60 ± 4
10			28 ± 3	0 ± 0	9 ± 6*
11			28 ± 2	73 ± 2 (72%)	30 ± 2
12			69 ± 1	61 ± 1	4 ± 3*
13			24 ± 1	29 ± 0 (15%)	8 ± 1*
14			Not performed	74 ± 1 (73%)	23 ± 2
15			Not performed	Not detected	98% (with ligand) 98% (without ligand)

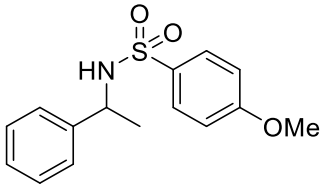
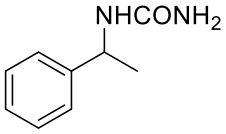
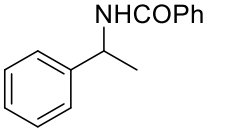
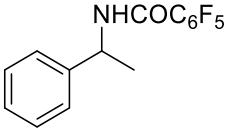
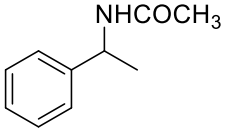
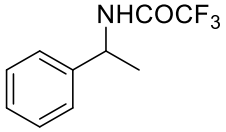
16			**a** 59 ± 2 **b** 14± 1	**a** 40 ± 1 **b** 12 ± 1	Unable to determine (low substrate boiling point)
17			0 ± 0	0 ± 0	0%
18			0 ± 0	0 ± 0	0%
19			Trace in GCMS	Trace in GCMS	Unable to determine (low substrate boiling point)
20			Not performed	Trace in GCMS	Unable to determine (low substrate boiling point)
*Mass balances are low, likely due to the volatility of the starting material.					

Amine Scope

Table S7. Amine Scope. Ethylbenzene (0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), amine (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL $PhCF_3$, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

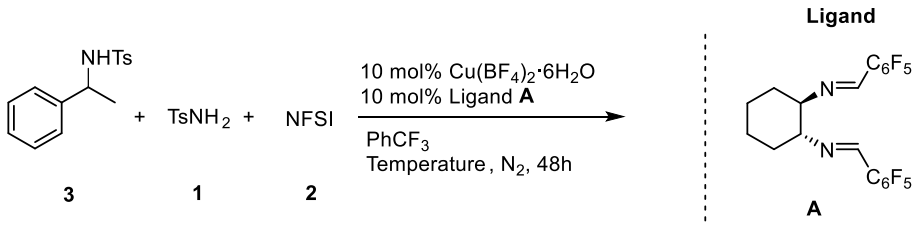


Entry	Amine Source	Product	Yield%@90 °C	Yield%@110 °C (Isolated)
1	$TsNH_2$		n/a	95 ± 2 (77%)
2	$PhSO_2NH_2$		n/a	97 ± 2 (85%)
3	$PhSO_2NHMe$		17 ± 1	35 ± 1 (29%)
4	$MsNH_2$		n/a	95 ± 2 (83%)
5	$CF_3SO_2NH_2$		n/a	0 ± 0
6	p-$CF_3PhSO_2NH_2$		0 ± 0	0 ± 0
7			6 ± 1	35 ± 1(12%)

8	p-MeO-$PhSO_2NH_2$		n/a	16 ± 1
9	Urea		n/a	0 ± 0
10	$PhCONH_2$		18 ± 1	29 ± 2 (22%)
11	$C_6F_5CONH_2$		18 ± 1	27 ± 2 (18%)
12	CH_3CONH_2		n/a	Trace in GC-MS (But difficult to quantify by NMR due to low quantity)
13	CF_3CONH_2		n/a	0 ± 0

Study of Product Decomposition

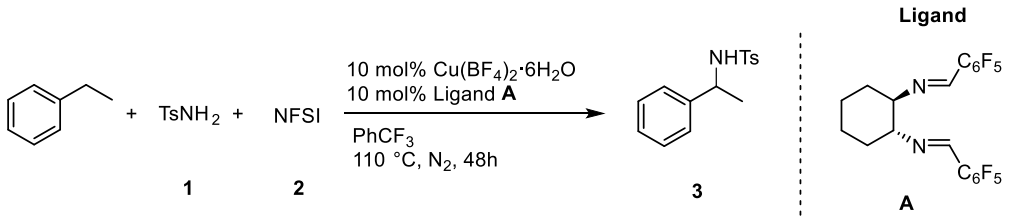
Table S8. Study of Product Decomposition. N-(1-phenylethyl)-p-toluenesulfonamide (34.4 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), amination reagent **1** (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL $PhCF_3$, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.



Entry	Temperature	Percent of **3** Left
1	90 °C	100 ± 2
2	110 °C	74 ± 1

Solvent Volume Study

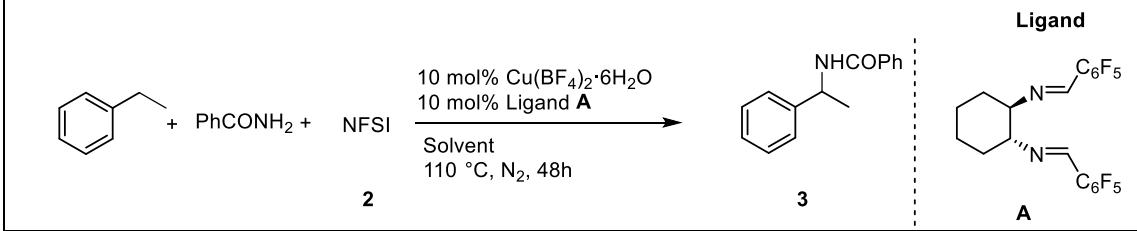
Table S9. Solvent Volume Study. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), amination reagent **1** (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and benzotrifluoride, 110 °C, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.



Entry	Volume of $PhCF_3$	Percent of **3** Left
1	0.5 mL	84 ± 2
2	1.0 mL	84 ± 1
3	1.5 mL	95 ± 2
4	2.0 mL	76 ± 1

Solvent Study for $PhCONH_2$ Reactions

Table S10. Solvent Study. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), $PhCONH_2$ (45.4 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL solvent, 110 °C, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

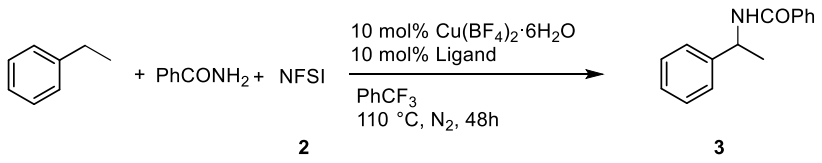


2 **3** **A**

Entry	Solvent	Yield% of Product **3**
1	MeCN	0 ± 0
2	1, 2-dichloroehthane	0 ± 0
3	PhBr	0 ± 0
4	PhCN	0 ± 0
5	PhCF3	29 ± 2
6	1, 1, 2-trichloroethane	10 ± 1
7	Benzene	0 ± 0

Optimization of Amine and NFSI for $PhCONH_2$ Reactions

Table S11. Optimization of Amine and NFSI. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand (12.6 µmol, 10.0 mol%), $PhCONH_2$, *N*-Fluorobenzenesulfonimide and 1.5 mL benzotrifluoride 110 °C, 48 h. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

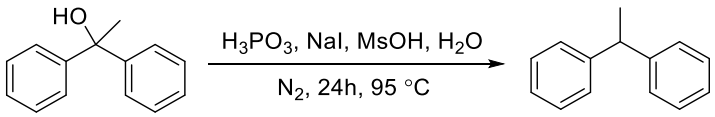


2 **3**

Entry	Equivalent of $TsNH_2$	Equivalent of NFSI	Yield% of **3**
1	1	1	17 ± 2
2	1	2	17 ± 2
3	1	3	16 ± 2
4	2	1	23 ± 1
5	2	2	28 ± 2
6	2	3	26 ± 1
7	3	1	21 ± 1
8	3	2	28 ± 1
9	3	3	29 ± 2

Synthesis of Substrate

Ethane-1,1-diyldibenzene



The title compound was synthesized in analogy to a literature known procedure[1].

A 20 mL scintillation vial equipped with a Teflon-coated stir bar was charged with 1,1-diphenylethanol (0.91 g, 5.0 mmol, 1.0 equiv.), sodium iodide (225 mg, 1.5 mmol, 0.3 equiv.), and concentrated phosphoric acid (615 mg, 7.5 mmol, 1.5 equiv.). The vial was flushed with N_2 and charged with 1.7 mL of H_2O and 3.3 mL of methanesulfonic acid. The reaction mixture was heated to 95 °C for 24 h. Upon completion, the reaction was cooled to room temperature and washed with 10 mL H_2O. The aqueous layer was extracted with EtOAc (2 × 15 mL) and the organic layers were combined. The solvent of the mixture was removed under reduced pressure to afford the crude product, which was purified on silica using hexane as eluent to afford the product as a colorless oil (630 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.44–7.28 (m, 10H; Ar-H), 4.28 (q, 1H), 1.78 (d, 3H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 146.5 (s), 128.5 (s), 127.8 (s), 126.1 (s), 44.9 (s), 22.0 (s);

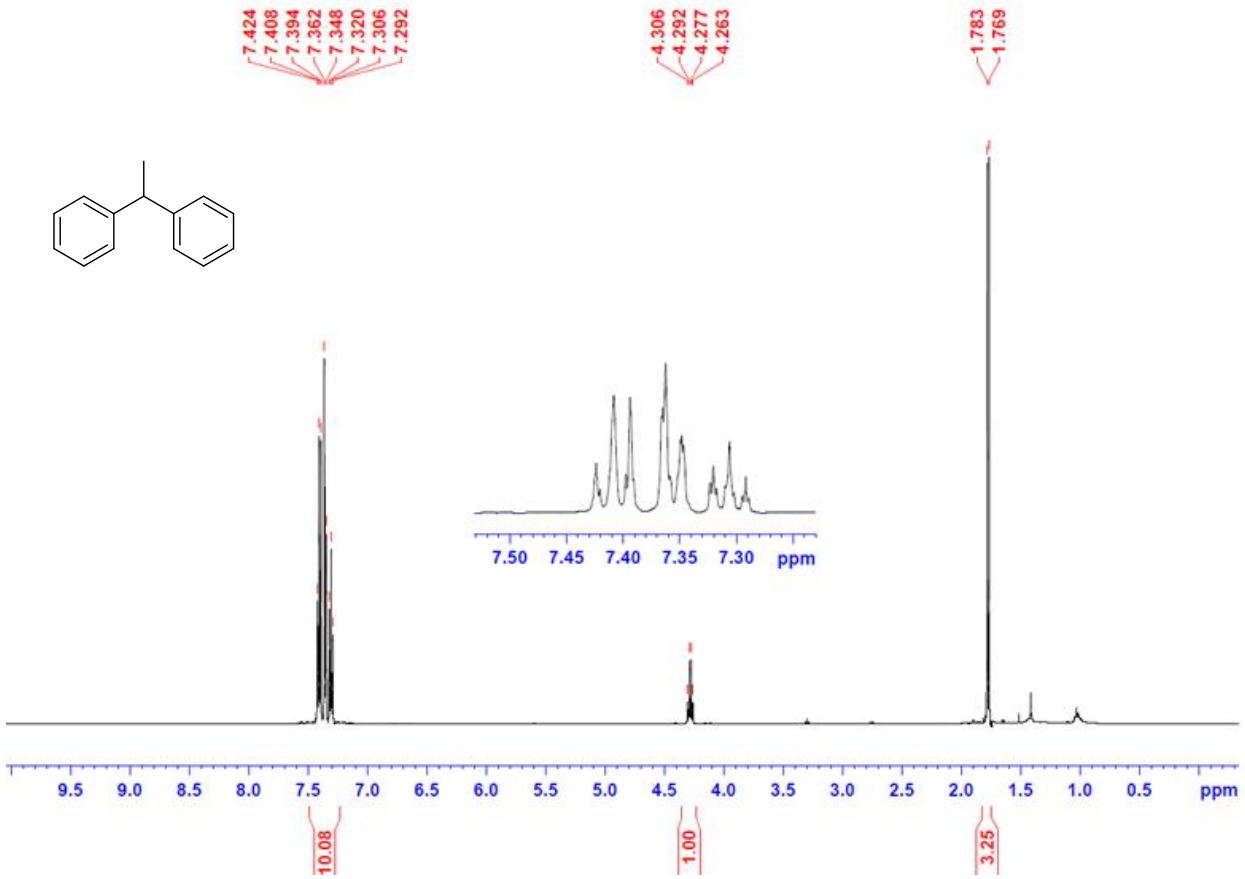


Figure S2. ^{1}H NMR of Ethane-1,1-diyldibenzene in $CDCl_3$.

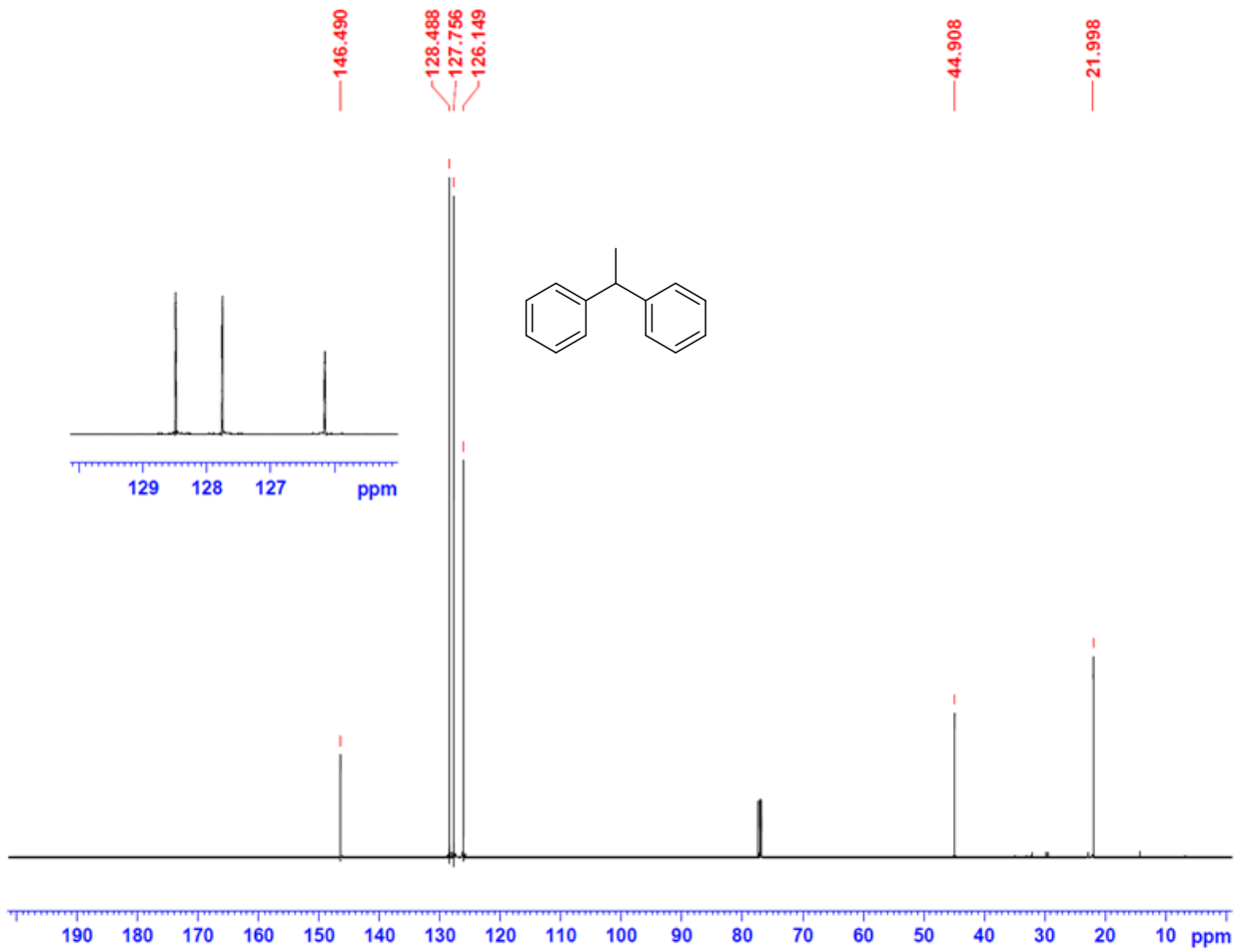
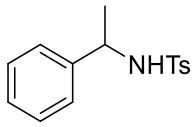


Figure S3. ^{13}C NMR of Ethane-1,1-diyldibenzene in $CDCl_3$.

Isolation of Selected Products from Catalytic Reactions

4-Methyl-N-(1-phenylethyl)benzenesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), $TsNH_2$ (324 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and ethylbenzene (78 µL, 66.4 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ was added to mixture, which was then filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product. Purification was performed by column chromatography on silica using ethyl acetate/hexane (1:4) as eluent. 133 mg (77% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the reported spectra.[2]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.76 (d, 2H; Ar-H), 7.30 (d, 2H; Ar-H), 7.17-7.38 (m, 5H; Ar-H), 4.79 (br t, 1H; NH), 4.11 (d, 2H; -C*H*$_2$Ph), 2.43(s, 3H; C*H*$_3$PhSO$_2$-);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 143.6 (s), 137.0 (s), 136.4 (s), 129.9 (s), 128.8 (s), 128.0 (s), 128.0 (s), 127.3 (s), 47.4 (s), 21.7 (s);

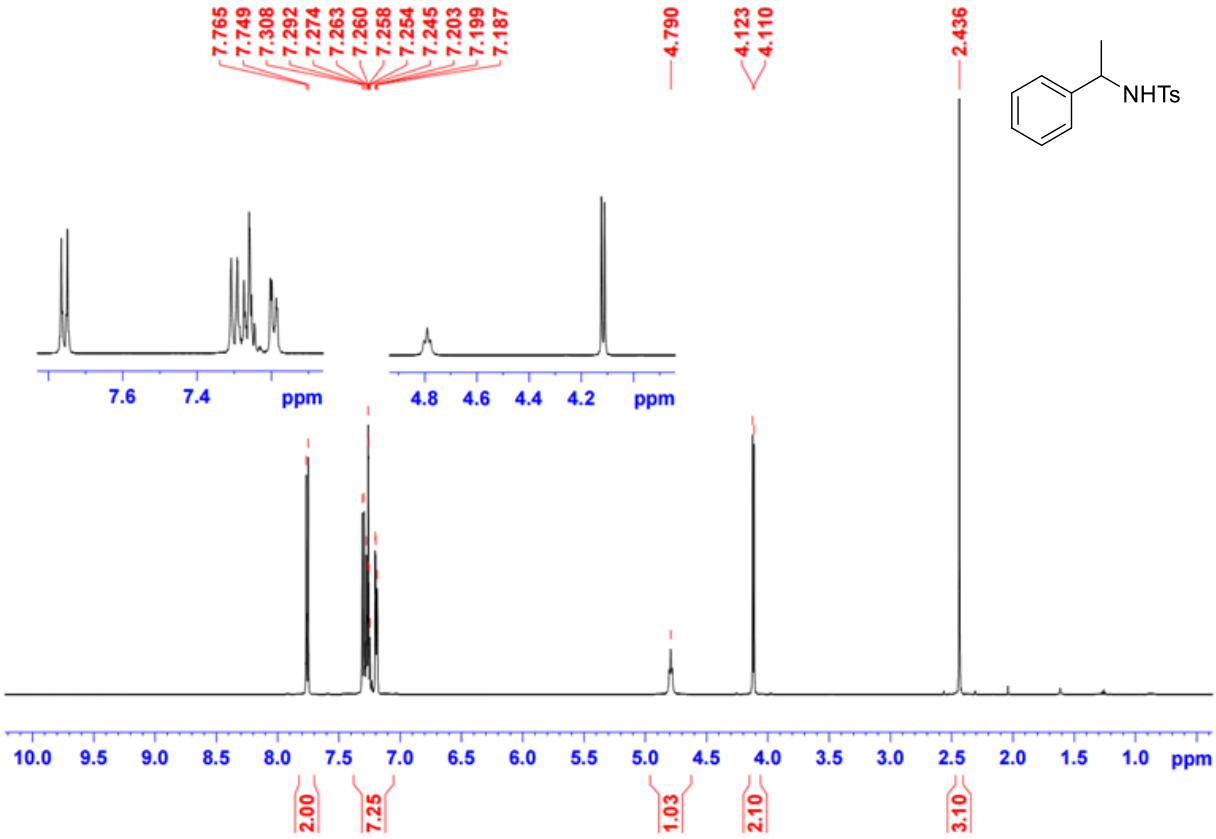


Figure S4. ^{1}H NMR of *N*-Benzyl-4-methylbenzenesulfonamide in $CDCl_3$.

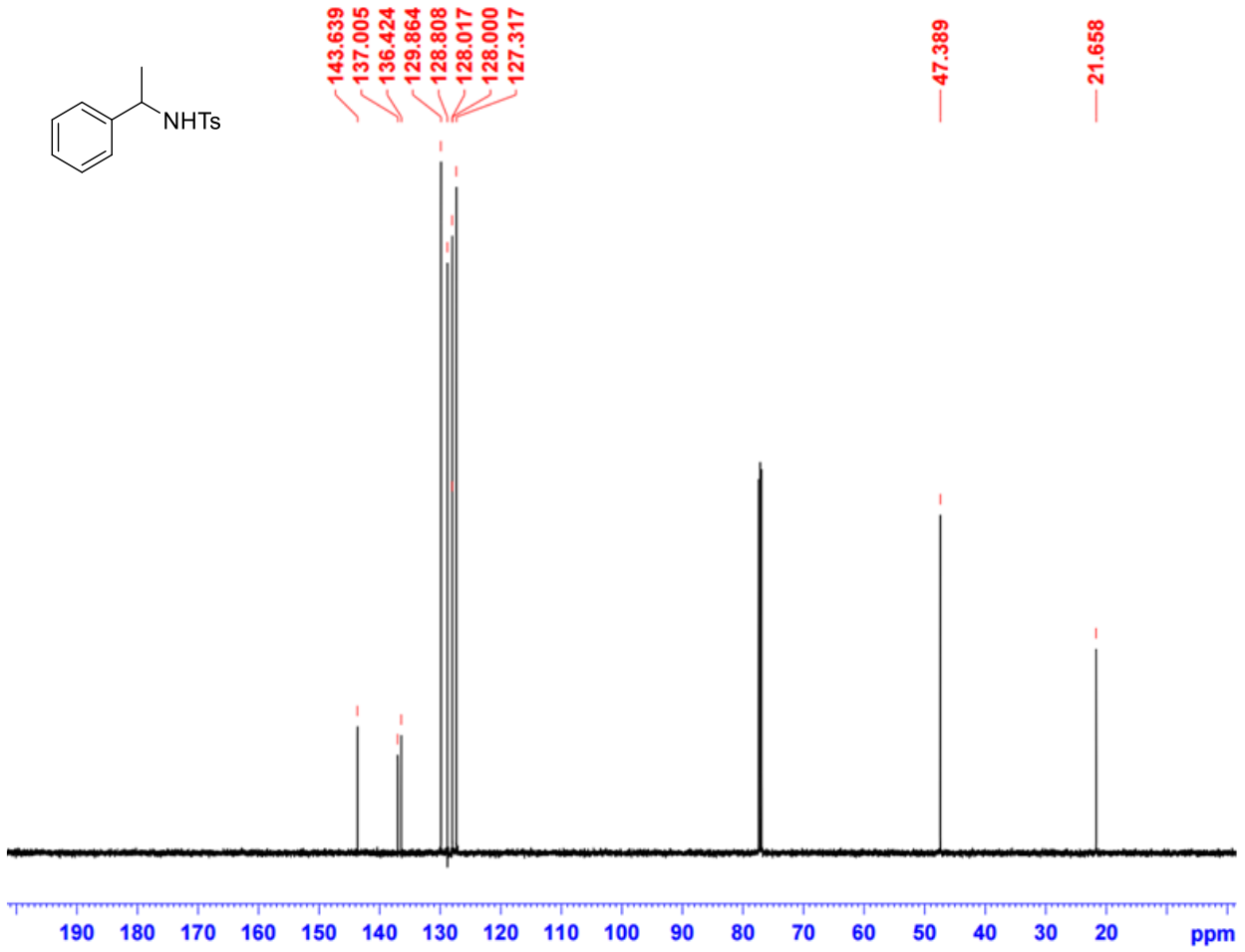
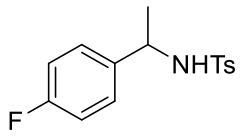


Figure S5. ^{13}C NMR of *N*-Benzyl-4-methylbenzenesulfonamide in $CDCl_3$.

N-(1-(4-Fluorophenyl)ethyl)-4-methylbenzenesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), $TsNH_2$ (324 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and 1-ethyl-4-fluorobenzene (79 µL, 77.6 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ was added into the mixture, which was then filtered through a Celite plug. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent. 145 mg (79% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the reported spectra.[2]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.60 (2H, d), 7.16 (2H, d), 7.07 (2H, m), 6.83 (2H, m), 5.57 (1H, d, NH), 4.44 (1H, quintet), 2.37 (3H, s), 1.36 (3H, d);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 163.0 (s), 161.0 (s), 143.3 (s), 138.1 (d), 137.7 (s), 129.5 (s), 127.9 (d), 127.1 (s), 115.3 (d), 53.1 (s), 23.6 (s), 21.5 (s);

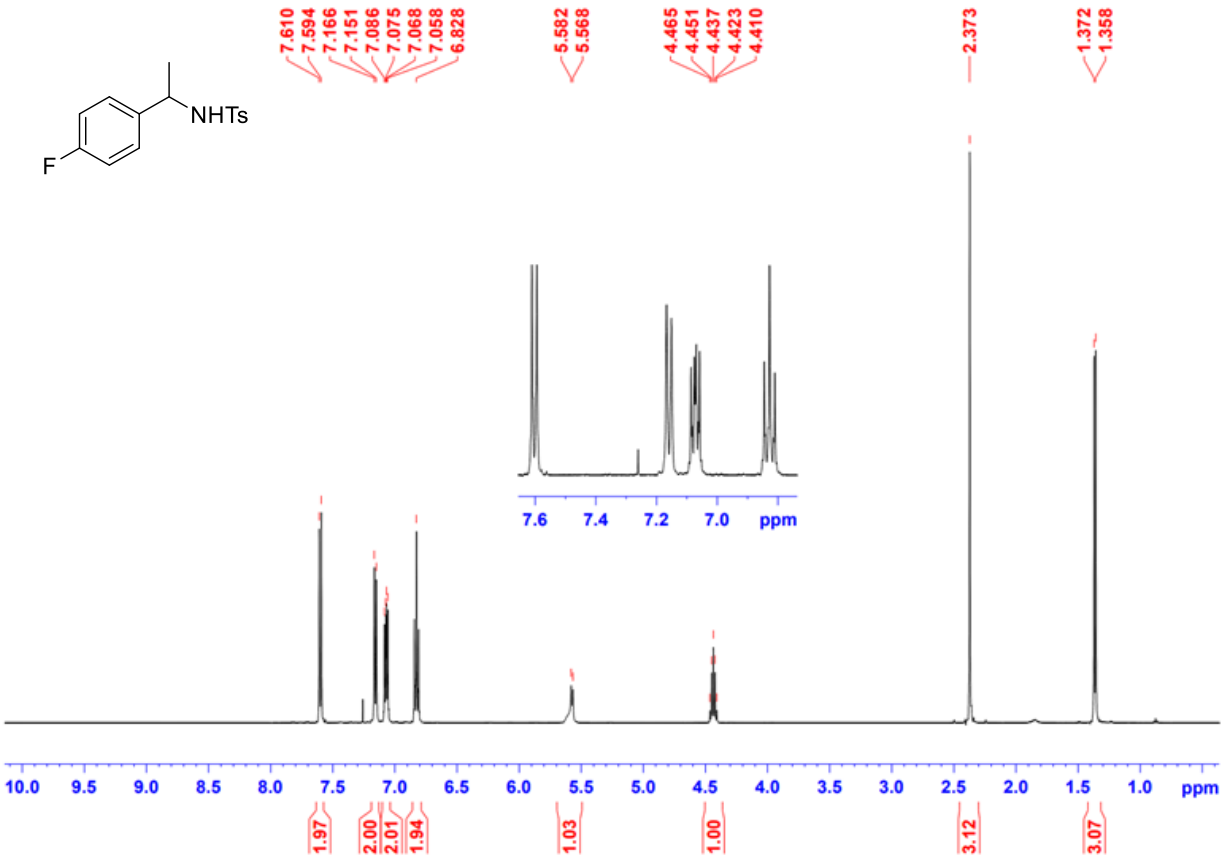


Figure S6. ^{1}H NMR of N-(1-(4-Fluorophenyl)ethyl)-4-methylbenzenesulfonamide in $CDCl_3$.

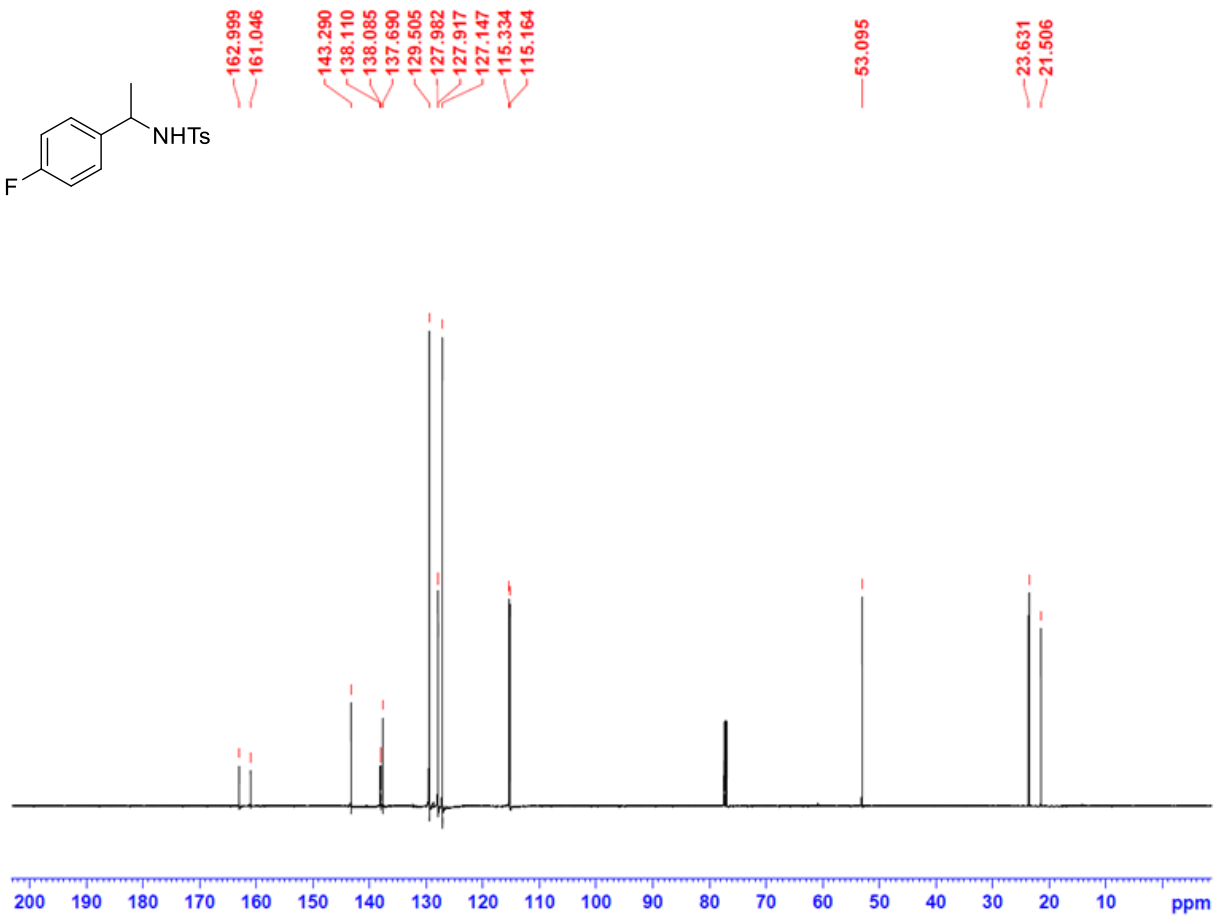
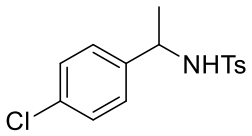


Figure S7. ^{13}C NMR of N-(1-(4-Fluorophenyl)ethyl)-4-methylbenzenesulfonamide in $CDCl_3$.

N-(1-(4-Chlorophenyl)ethyl)-4-methylbenzenesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), $TsNH_2$ (324 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and 1-ethyl-4-chlorobenzene (90 µL, 87.9 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent. 139 mg (72% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the literature reported spectra.[2]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.58 (2H, d), 7.14 (2H, d), 7.09 (2H, d), 7.03 (2H, d), 5.76 (1H, d, NH), 4.42 (1H, quintet), 2.38 (3H, s), 1.35 (3H, d);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 143.3 (s), 140.8 (s), 137.5 (s), 133.0 (s), 129.5 (s), 128.5 (s), 127.7 (s), 127.1 (s), 53.1 (s), 23.4 (s), 21.5 (s);

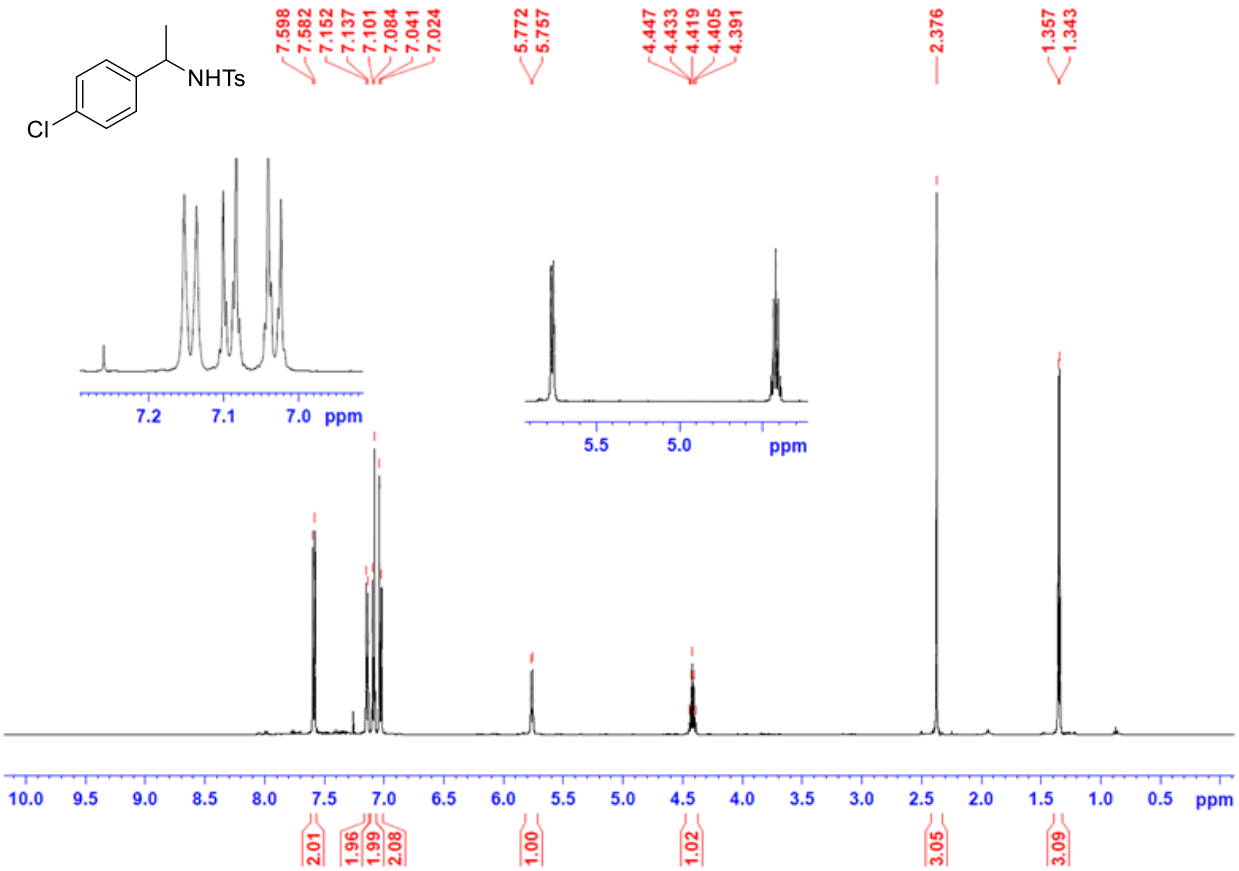


Figure S8. ^{1}H NMR of N-(1-(4-Chlorophenyl)ethyl)-4-methylbenzenesulfonamide in $CDCl_3$.

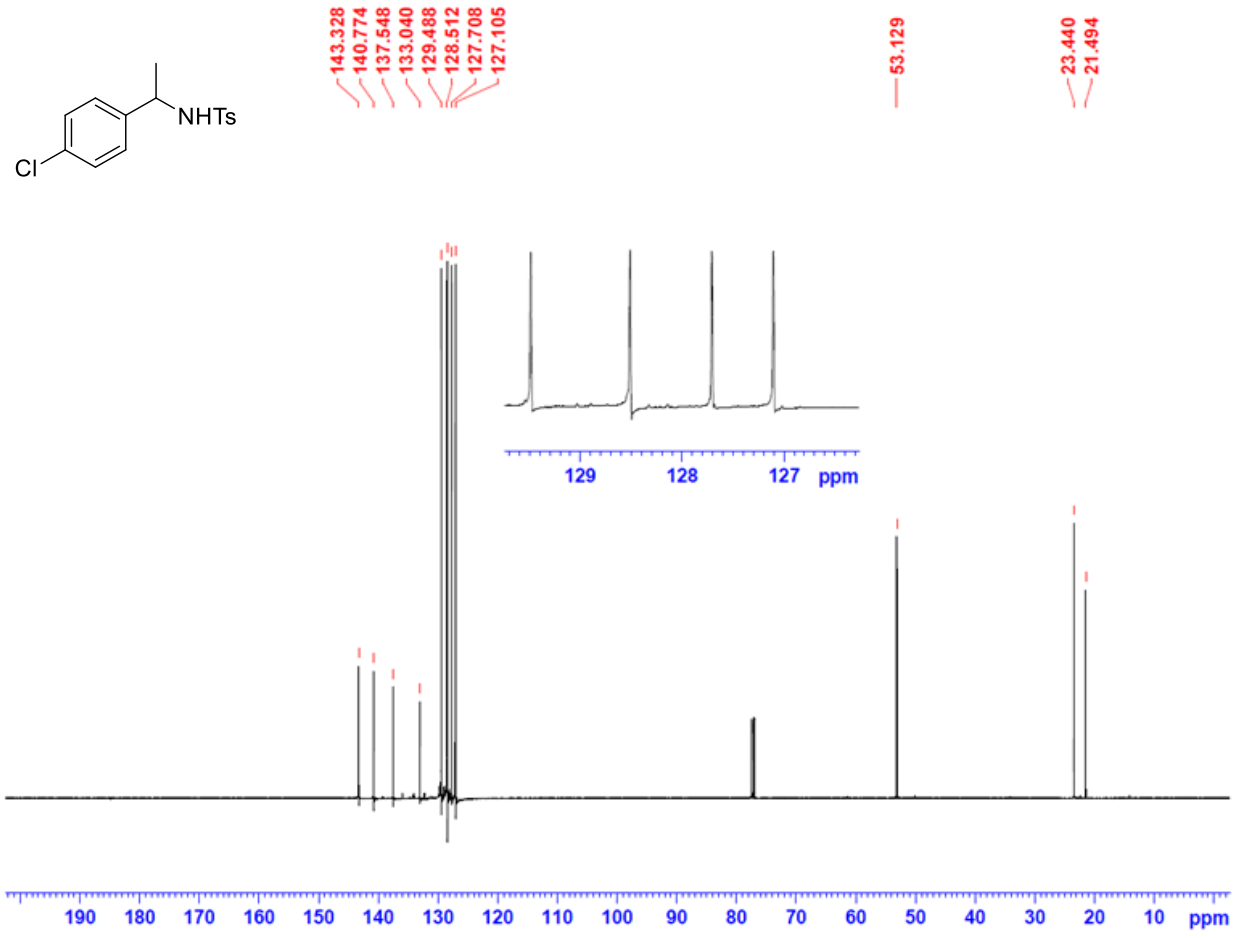
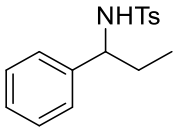


Figure S9. ^{13}C NMR of N-(1-(4-Chlorophenyl)ethyl)-4-methylbenzenesulfonamide in $CDCl_3$.

4-Methyl-N-(1-phenylpropyl)benzenesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), $TsNH_2$ (324 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and n-propylbenzene (88 µL, 75.1 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent. 41 mg (23% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the literature reported spectra.[3]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = δ 7.53 (d, 2 H), 7.18-7.13 (m, 3 H), 7.11 (d, 2 H), 7.03-6.97 (m, 2 H), 4.74 (d, 1 H), 4.19 (q, 1 H), 2.35 (s, 3 H), 1.87-1.65 (m, 2 H), 0.78 (t, 3 H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 143.1 (s), 140.8 (s), 137.9 (s), 129.4 (s), 128.6 (s), 127.5 (s), 127.2 (s), 126.7 (s), 60.0 (s), 30.7 (s), 21.6 (s), 10.6 (s);

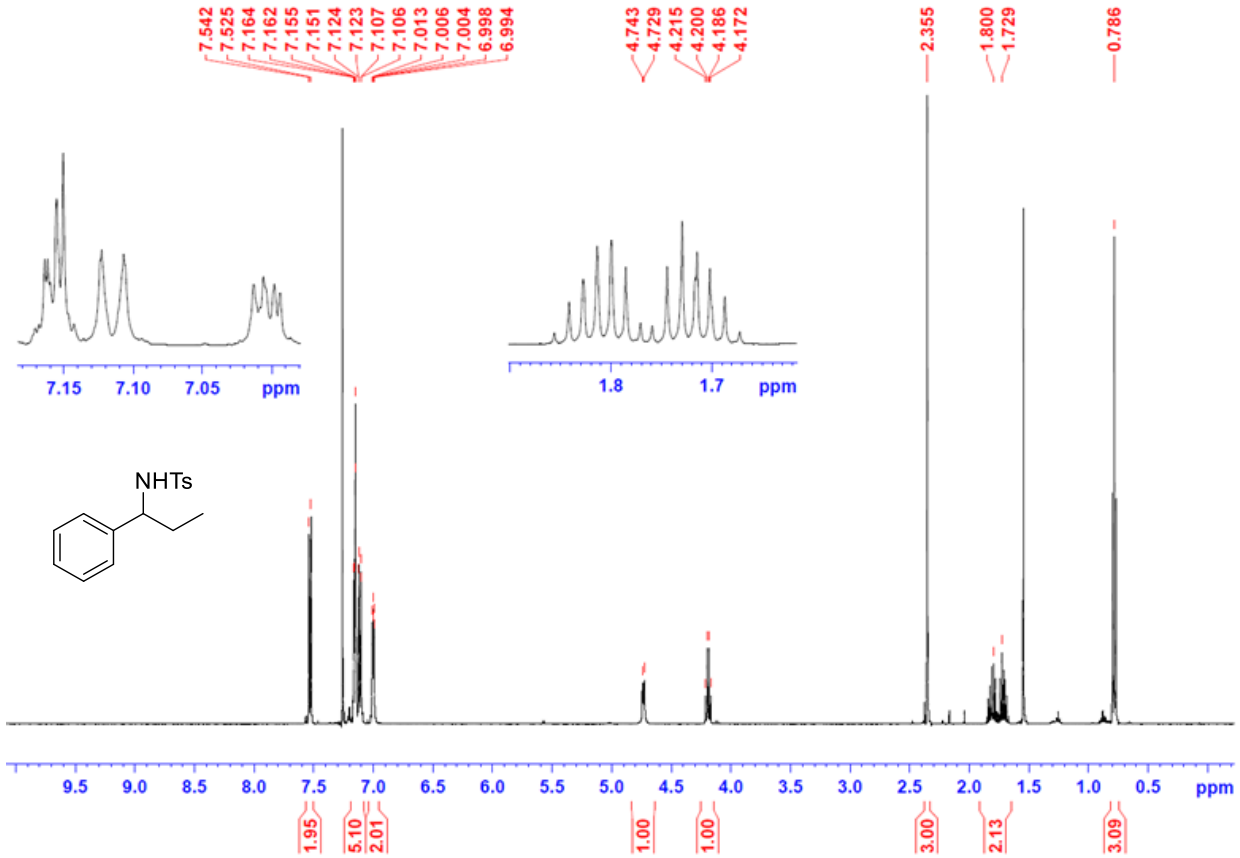


Figure S10. ^{1}H NMR of 4-Methyl-N-(1-phenylpropyl)benzenesulfonamide in $CDCl_3$.

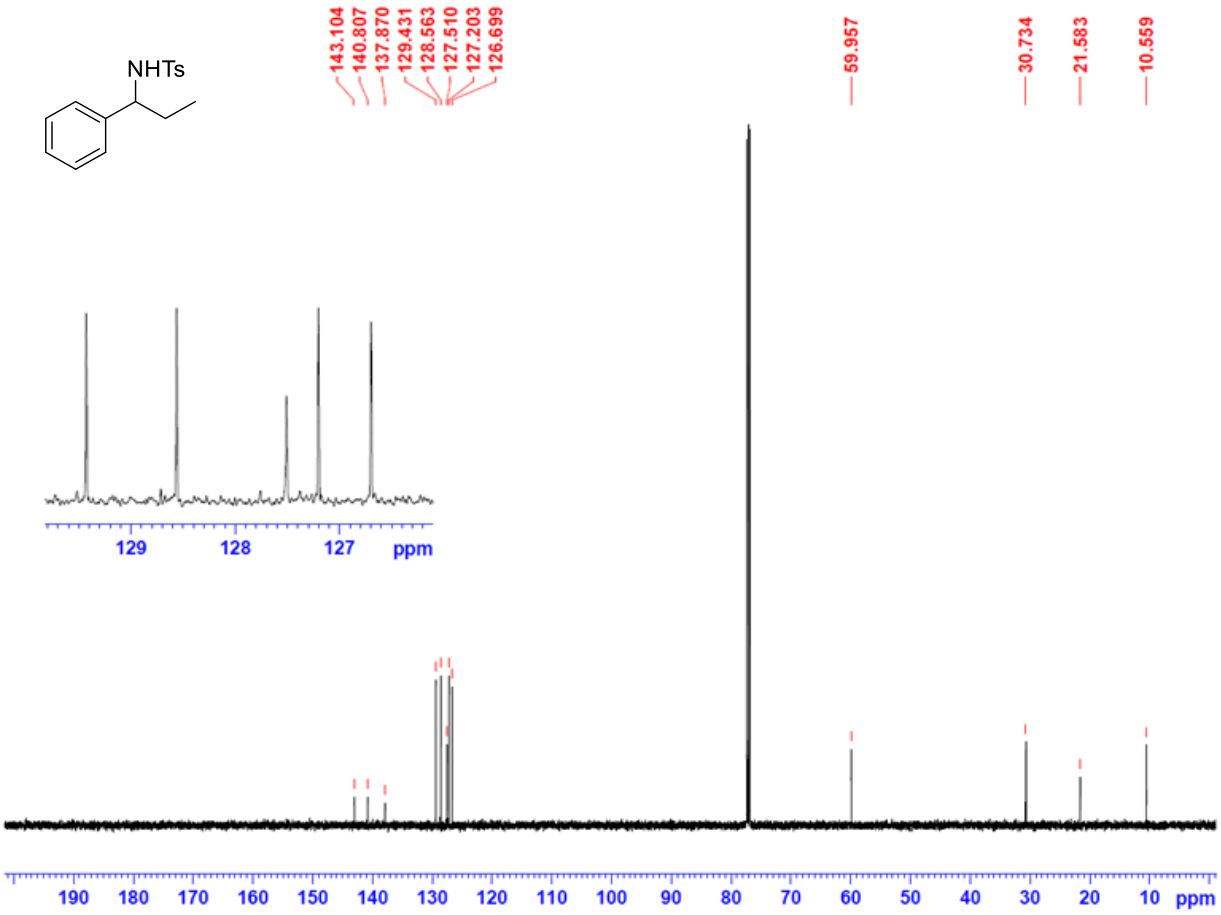
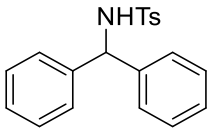


Figure S11. ^{13}C NMR of 4-Methyl-N-(1-phenylpropyl)benzenesulfonamide in $CDCl_3$.

N-Benzhydryl-4-methylbenzenesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), $TsNH_2$ (324 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and diphenylmethane (104 µL, 105.1 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent. 154 mg (73% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the literature reported spectra.[4]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.56 (d, 2H), 7.24 - 7.17(m, 6H), 7.13 (d, 2H), 7.12 – 7.08 (s, 4H), 5.57 (d, 1H), 5.09 (d, 1H), 2.39 (s, 3H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 143.3 (s), 140.7 (s), 137.5 (s), 129.5 (s), 128.7 (s), 127.7 (s), 127.5 (s), 127.4 (s), 61.5 (s), 21.5 (s);

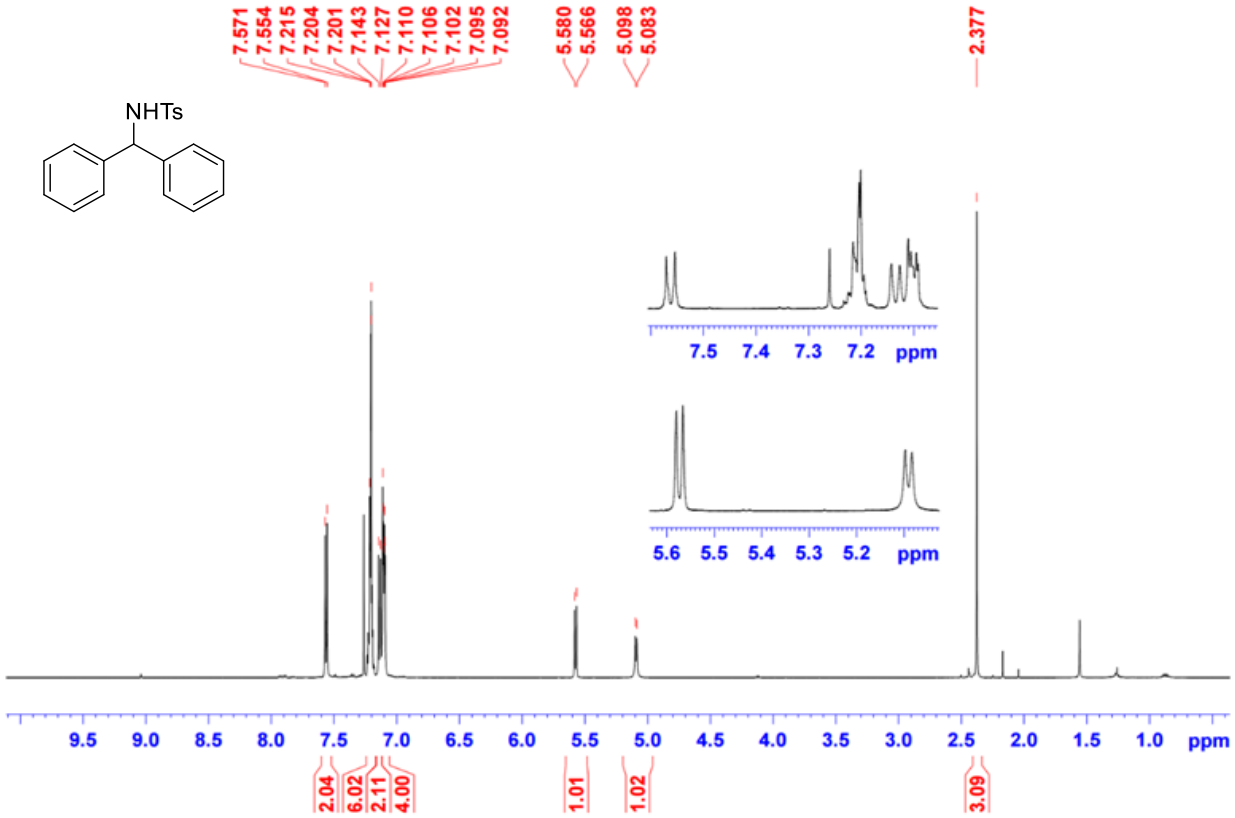


Figure S12. ^{1}H NMR of N-benzhydryl-4-methylbenzenesulfonamide in $CDCl_3$.

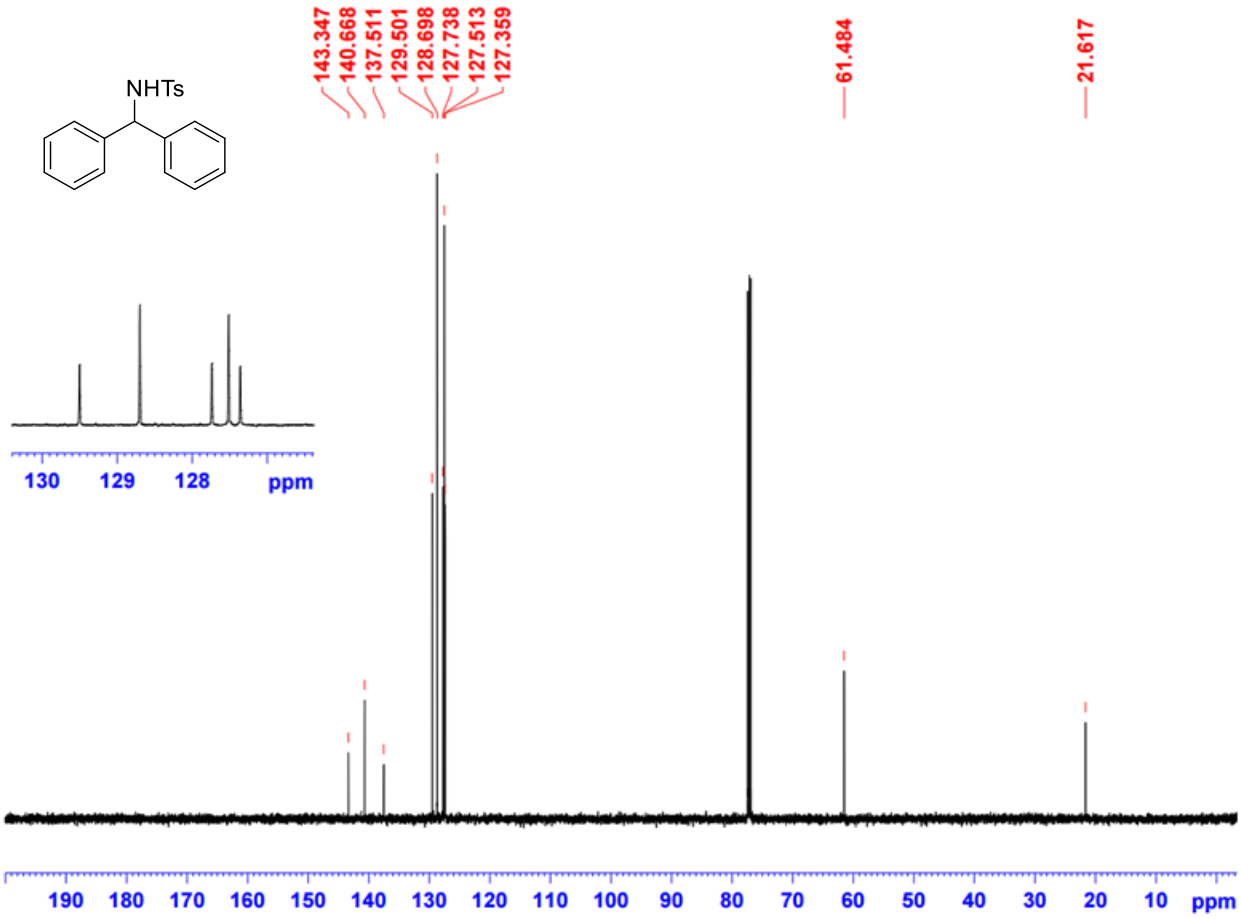
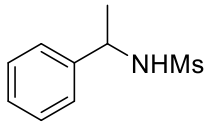


Figure S13. ^{13}C NMR of N-benzhydryl-4-methylbenzenesulfonamide in $CDCl_3$.

N-(1-Phenylethyl)methanesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), $MsNH_2$ (178 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and ethylbenzene (80 µL, 13.3 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ was added into reaction mixture, followed by a filtration through a Celite plug. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/ hexane (1:4) as eluent. 105 mg (83% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the literature reported spectra.[5]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.42-7.26 (m, 5H), 5.68 (d, 1H); 4.65 (p, 1H), 2.62 (s, 3H), 1.54 (d, 3H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 142.7 (s), 128.8 (s), 127.7 (s), 126.2 (s), 53.7 (s), 41.5 (s), 23.9 (s);

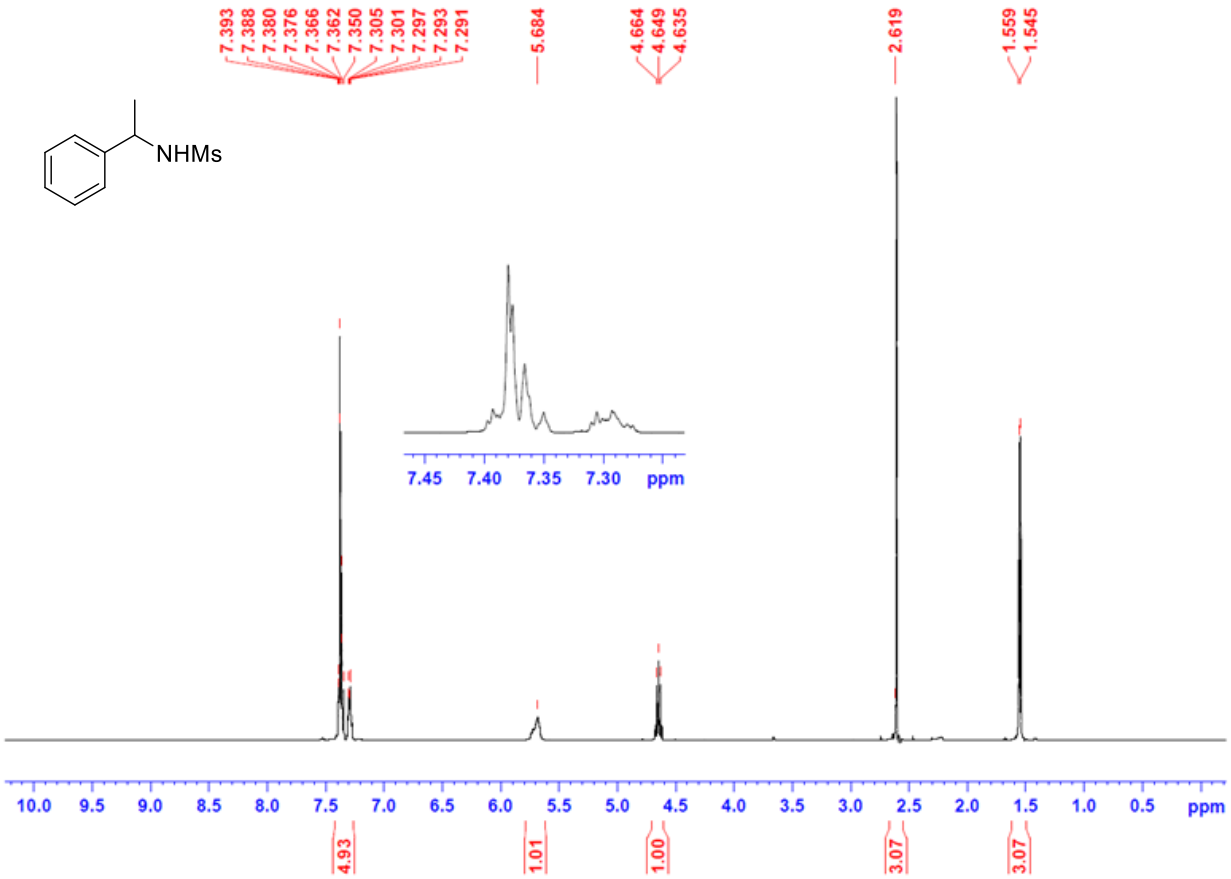


Figure S14. ^{1}H NMR of N-(1-Phenylethyl)methanesulfonamide in $CDCl_3$.

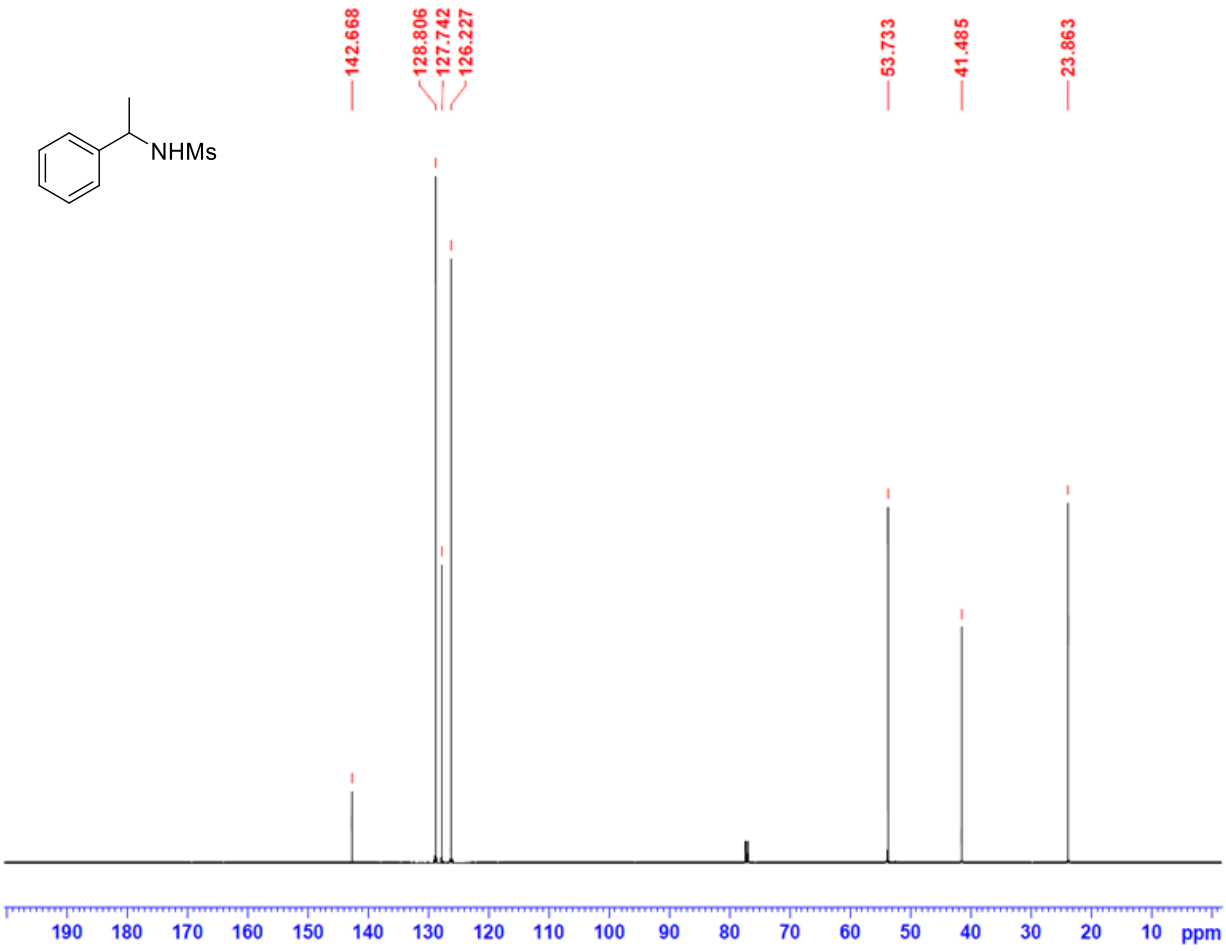
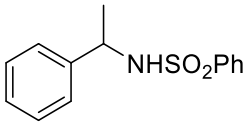


Figure S15. ^{13}C NMR of N-(1-Phenylethyl)methanesulfonamide in $CDCl_3$.

N-(1-phenylethyl)benzenesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), Benzenesulfonamide (296 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and ethylbenzene (80 µL, 13.3 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/hexane (1:4) as eluent. 141 mg (85% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the literature reported spectra.[5]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.75-7.71 (m, 2H), 7.47 (td, J = 6.4, 1H), 7.39-7.32 (m, 2H), 7.20−7.06 (m, 5H), 5.44 (d, 1H), 4.50 (p, 1H), 1.42 (d, 3H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 142.0 (s), 140.8 (s), 132.4 (s), 128.9 (s), 128.6 (s), 127.5 (s), 127.1 (s), 126.2 (s), 53.8 (s), 23.7 (s);

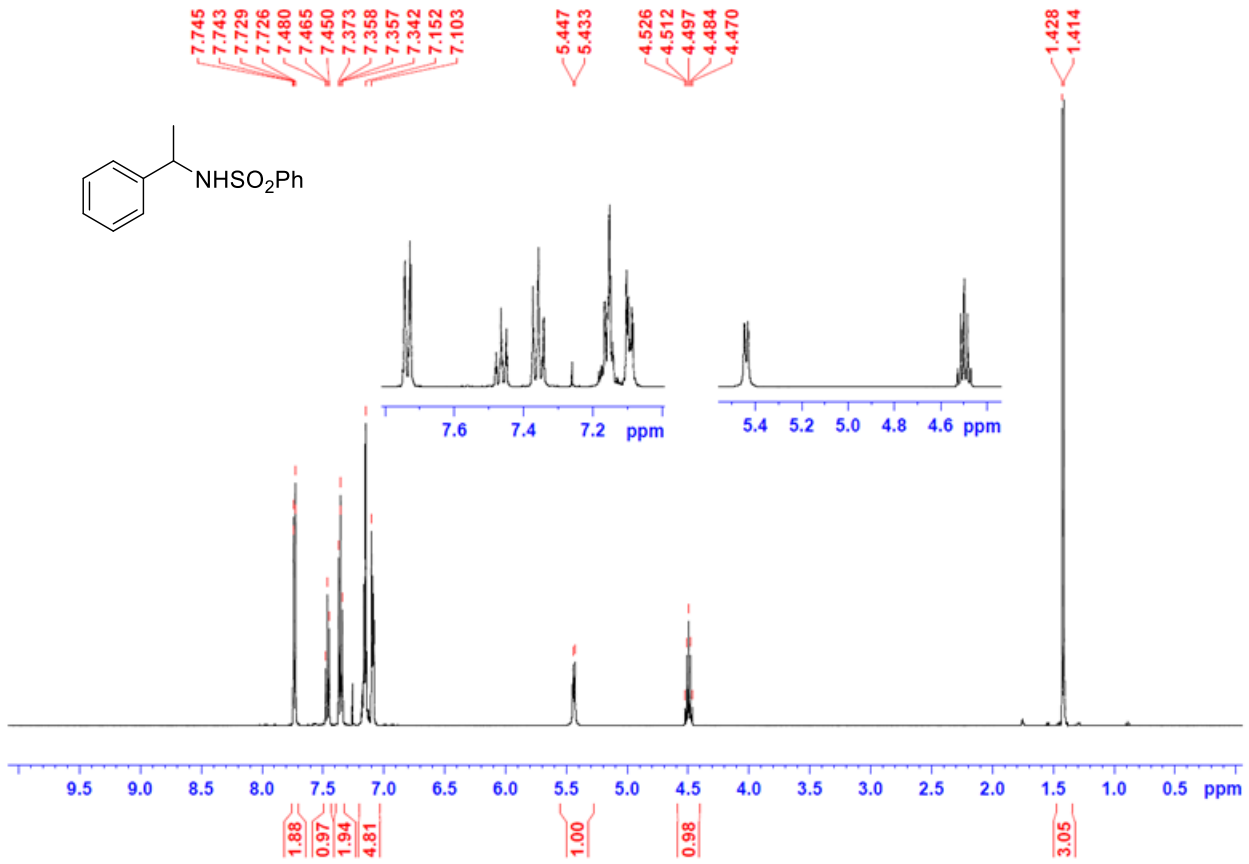


Figure S16. ^{1}H NMR of N-(1-phenylethyl)benzenesulfonamide in $CDCl_3$.

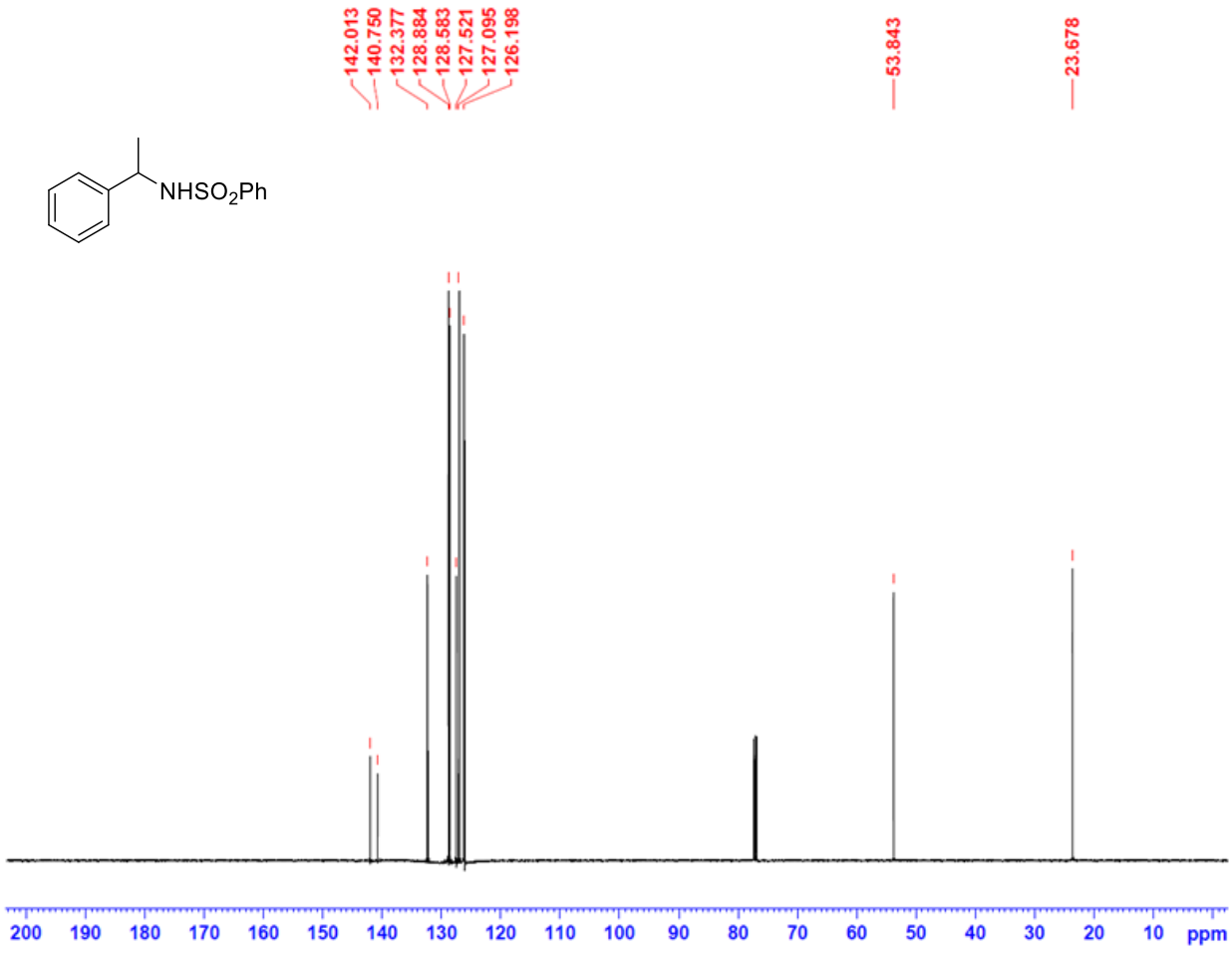
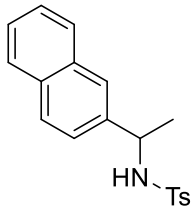


Figure S17. ^{13}C NMR of N-(1-phenylethyl)benzenesulfonamide in $CDCl_3$.

4-Methyl-N-(1-(naphthalen-2-yl)ethyl)benzenesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), $TsNH_2$ (324 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and 2-ethylnaphthalene (99 µL, 97.6 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/ hexane (1:4) as eluent. 30 mg (15% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the literature reported spectra.[6]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.74 (t, 1H), 7.65 (d, 2H), 7.58 (d, 2H), 7.40-7.49 (m, 3H), 7.22 (d, 1H), 7.00 (d, 2H), 5.43(d, 1H), 4.64 (dt, 1H), 2.22 (s, 3H), 1.50 (d, 3H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 143.1 (s), 139.2 (s), 137.7 (s), 133.2 (s), 132.8 (s), 129.4 (s), 128.5 (s), 127.9 (s), 127.6 (s), 127.2 (s), 126.2 (s), 126.0(s), 125.2 (s), 124.2 (s), 54.0 (s), 23.5 (s), 21.3 (s);

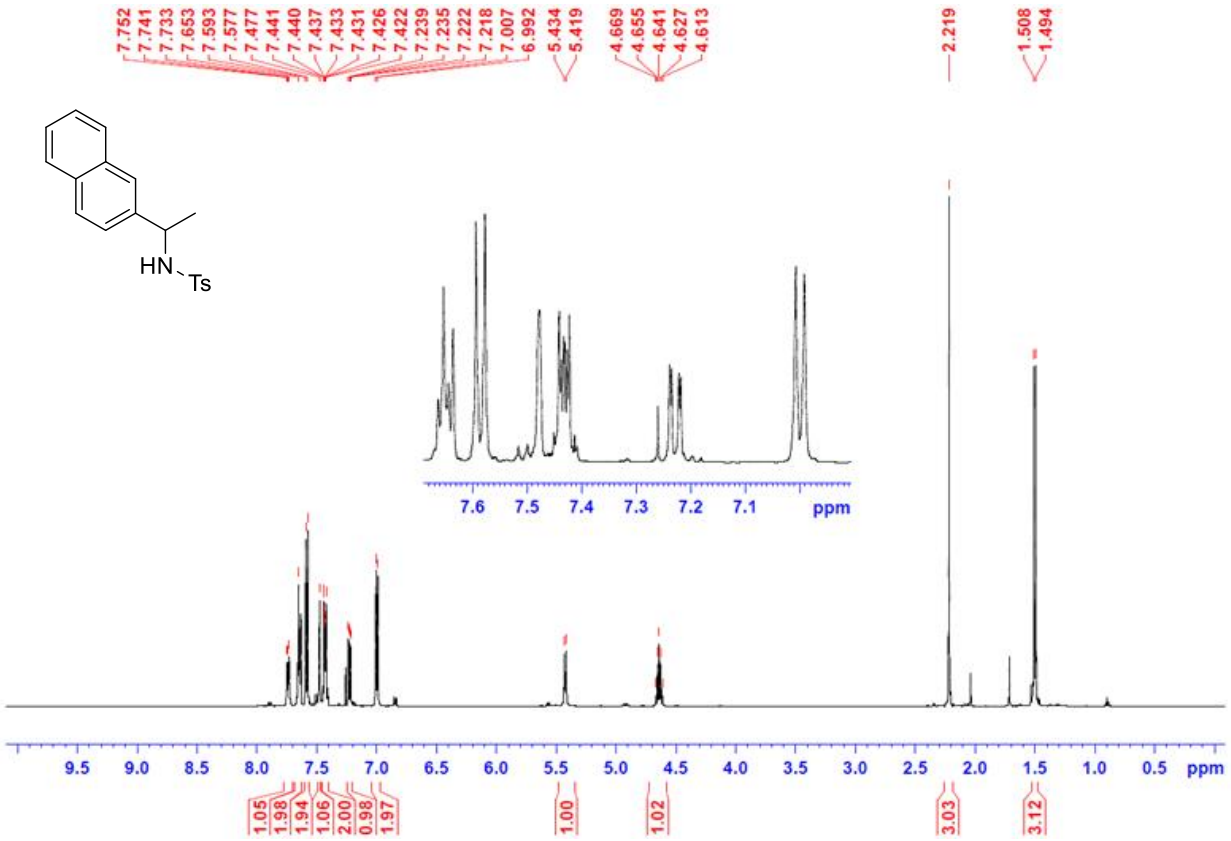


Figure S18. ^{1}H NMR of 4-Methyl-N-(1-(naphthalen-2-yl)ethyl)benzenesulfonamide in $CDCl_3$.

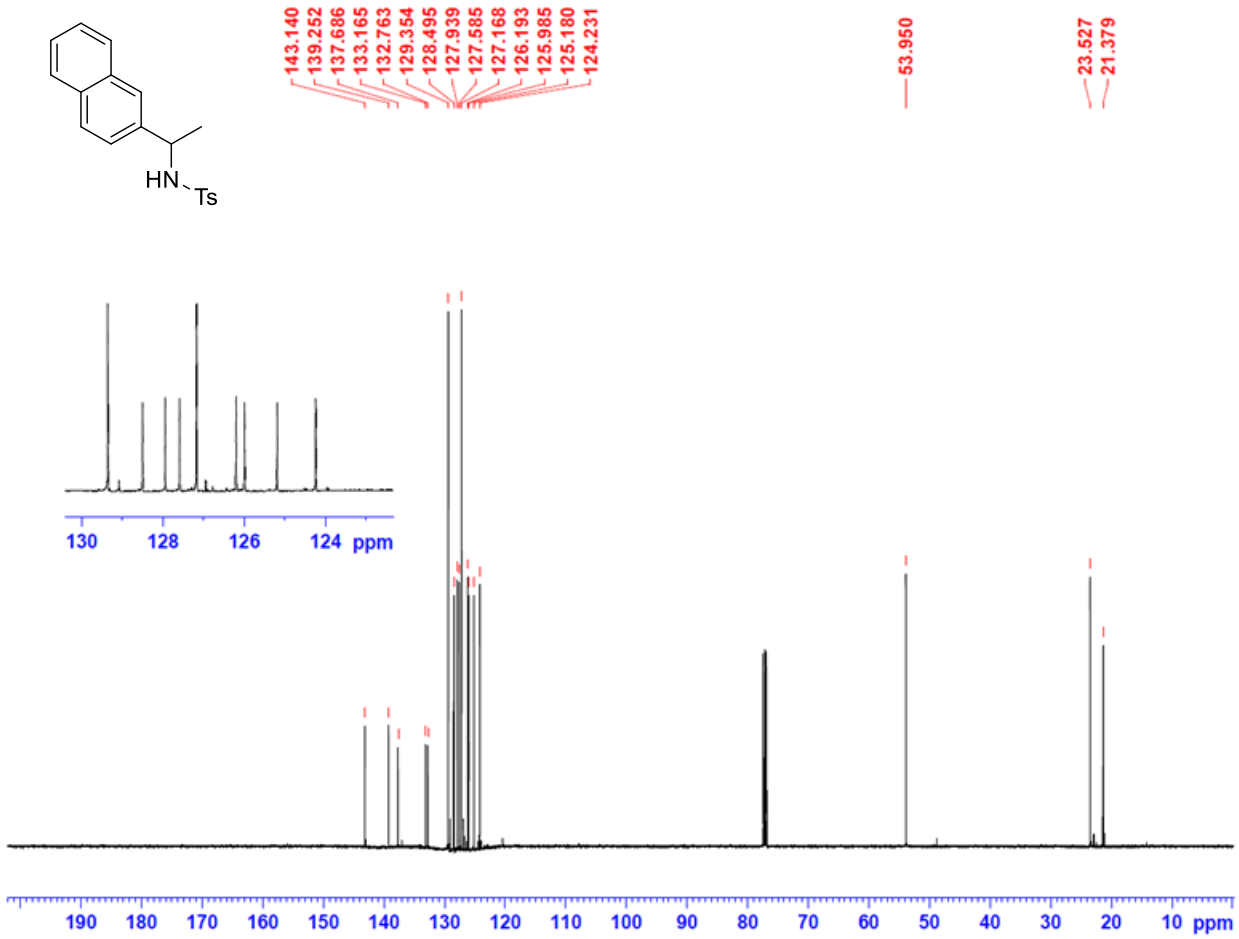
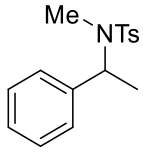


Figure S19. ^{13}C NMR of 4-Methyl-N-(1-(naphthalen-2-yl)ethyl)benzenesulfonamide in $CDCl_3$.

N,4-Dimethyl-N-(1-phenylethyl)benzenesulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), N,4-dimethylbenzenesulfonamide (347 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and ethylbenzene (80 µL, 13.3 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/ hexane (1:4) as eluent. 52 mg (29% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the literature reported spectra.[5]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.74 (dt, 2H), 7.33-7.21 (m, 7H), 5.29 (q, 1H), 2.57 (s, 3H), 2.44 (s, 3H), 1.29 (d, 3H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 143.2 (s), 140.0 (s), 137.4 (s), 129.8 (s), 128.5 (s), 127.6 (s), 127.4 (s), 127.2 (s), 54.8 (s), 28.5 (s), 21.6 (s), 15.3 (s);

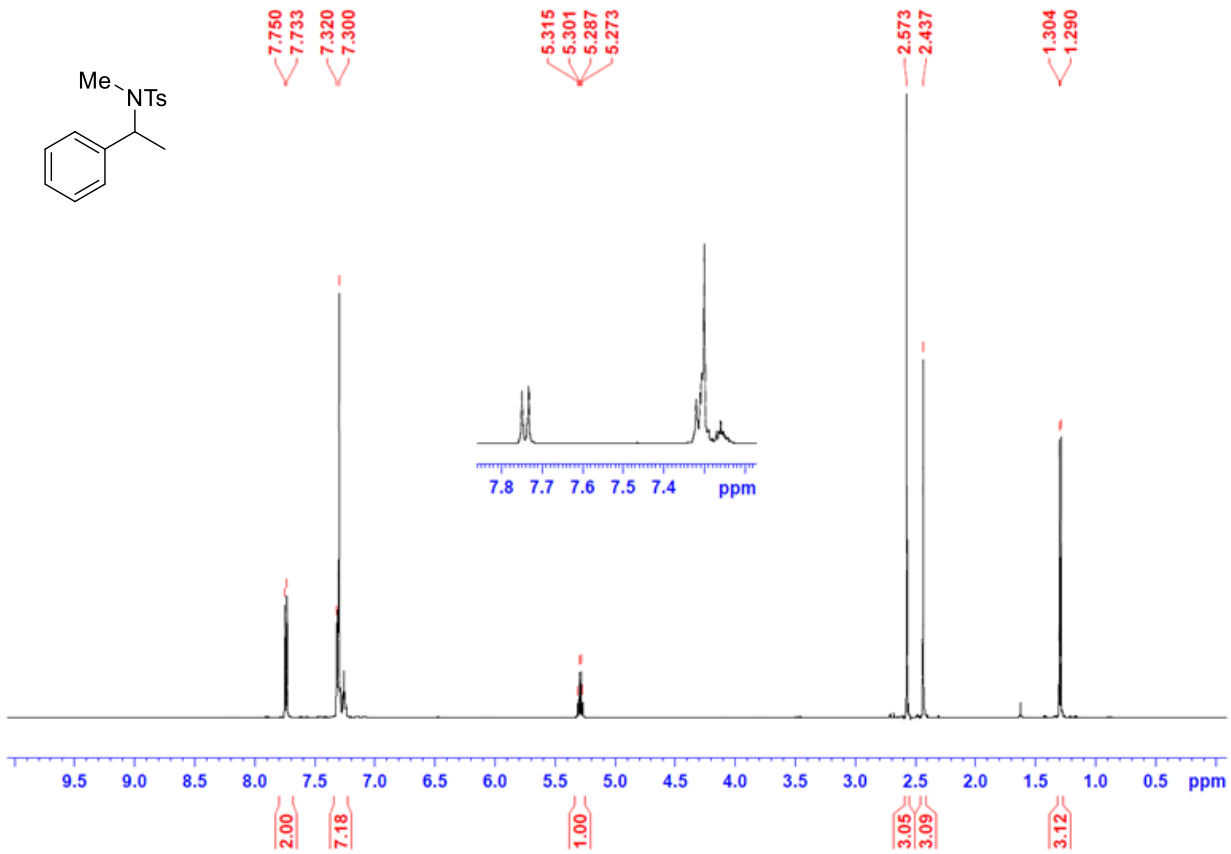


Figure S20. ^{1}H NMR of N,4-Dimethyl-N-(1-phenylethyl)benzenesulfonamide in $CDCl_3$.

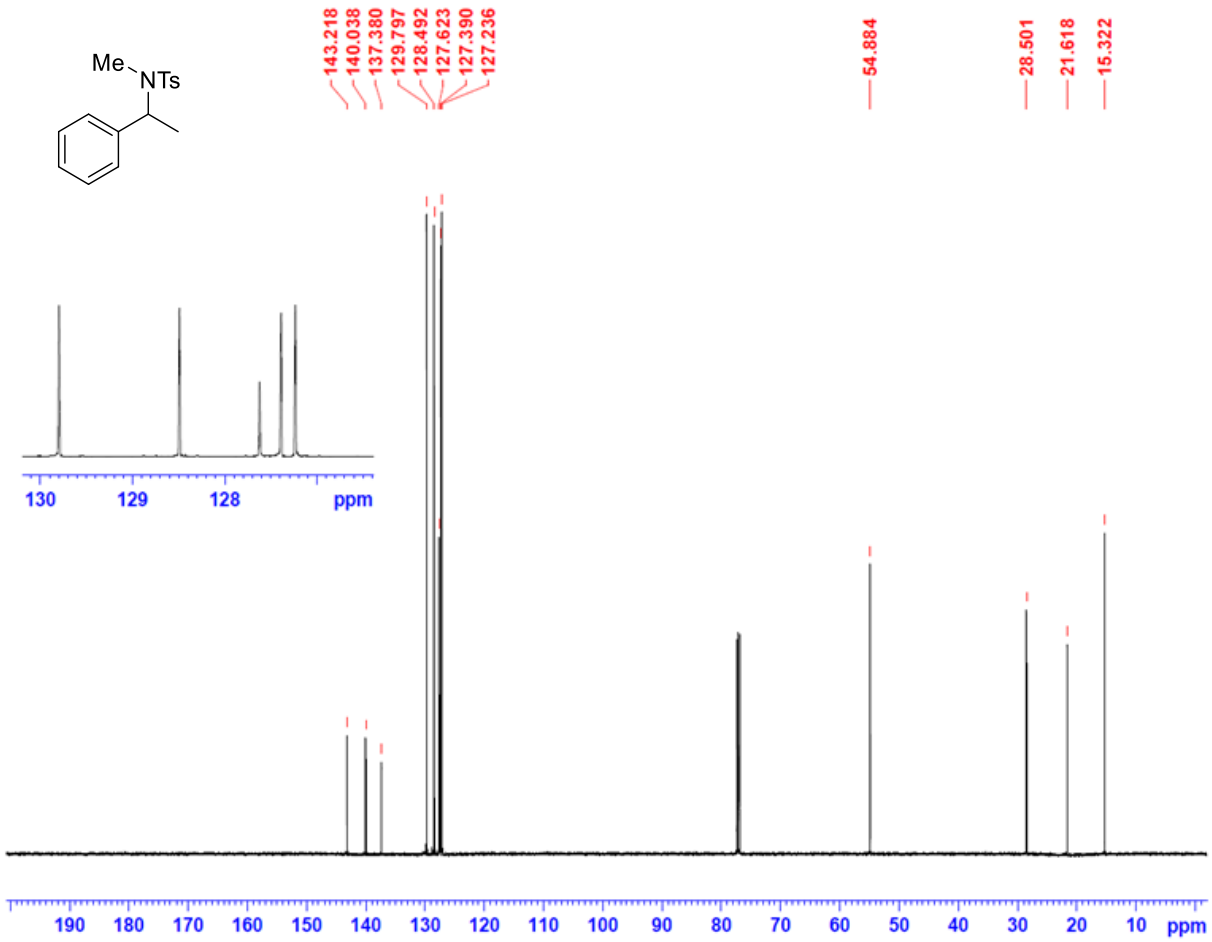
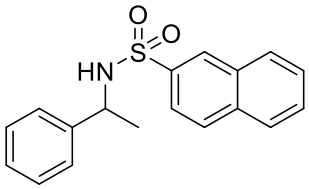


Figure S21. ^{13}C NMR of N,4-Dimethyl-N-(1-phenylethyl)benzenesulfonamide in $CDCl_3$.

N-(1-Phenylethyl)naphthalene-2-sulfonamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), N-(1-Phenylethyl)naphthalene-2-sulfonamide (389 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and ethylbenzene (80 µL, 13.3 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/ hexane (1:4) as eluent. 23 mg (12% yield) of pure title compound was obtained as white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 8.26 (d, 1H), 7.89-7.82 (m, 3H), 7.69 (dd, 1H), 7.65-7.55 (m, 2H), 7.14-7.04 (m, 5H), 4.74 (d, 1H), 4.54 (q, 1H), 4.64 (dt, 1H) 1.45 (d, 3H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 141.8 (s), 137.5 (s), 134.8 (s), 132.2 (s), 129.4 (s), 128.8 (s), 128.7 (s), 128.6 (s), 128.0 (s), 127.7 (s), 127.5 (s), 126.2 (s), 122.4 (s),53.9 (s), 23.7 (s);

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3274 (s), 3059 (s), 3031 (s), 2977 (s), 2932 (s), 2873 (s), 1658 (s), 1592 (s), 1539 (s), 1494 (s), 1454 (s), 1427 (s), 1379 (s), 1321 (s), 1272 (s), 1245 (s), 1207 (s), 1155 (s), 1131 (s), 1120 (s), 1075 (s), 1019 (s), 966 (s), 907 (s), 865 (s), 816 (s), 762 (s), 749 (s), 699 (s), 662 (s), 643 (s), 619 (s);

HRMS: calcd. for $C_{18}H_{18}NO_2S$, $[M+H]^+$: 312.1058, found: 312.1042;

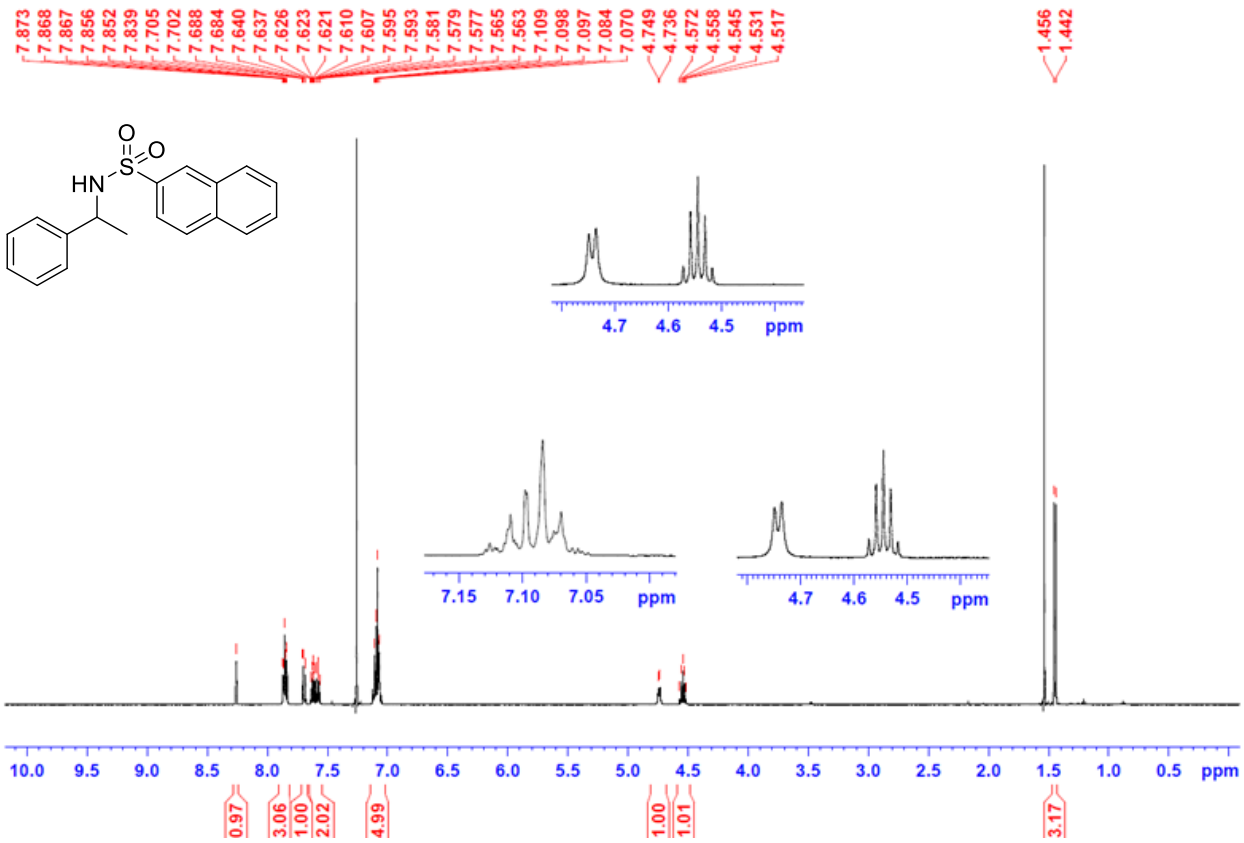


Figure S22. ^{1}H NMR of N-(1-Phenylethyl)naphthalene-2-sulfonamide in $CDCl_3$.

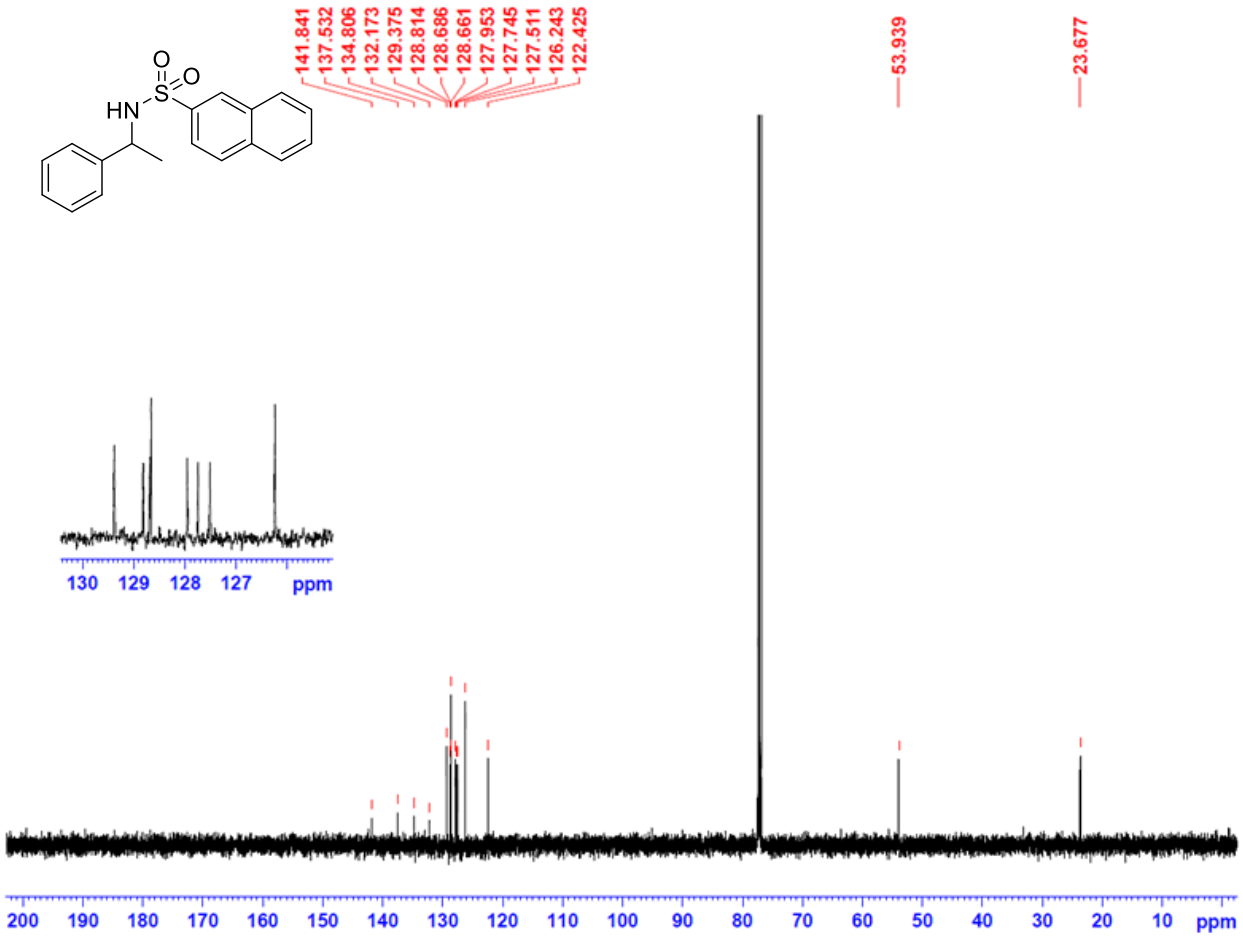
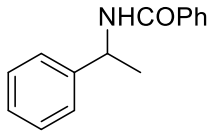


Figure S23. ^{13}**C NMR of N-(1-Phenylethyl)naphthalene-2-sulfonamide in** $CDCl_3$**.**

N-(1-Phenylethyl)benzamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), benzamide (227 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and ethylbenzene (80 µL, 13.3 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/ petroleum ether (1:9 to 1:1) as eluent. 31 mg (22% yield) of pure title compound was obtained. The ^1H and ^{13}C NMR match the literature reported spectra.[7]

^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.77 (d, 2H), 7.53-7.19 (m, 8H), 6.35 (d, br, 1H), 5.34 (q, 1H), 1.61 (d, 3H)

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 166.7 (s), 143.3 (s), 134.8 (s), 131.6 (s), 128.9 (s), 128.7 (s), 127.6 (s), 127.1 (s), 126.4 (s), 49.4 (s), 21.9 (s)；

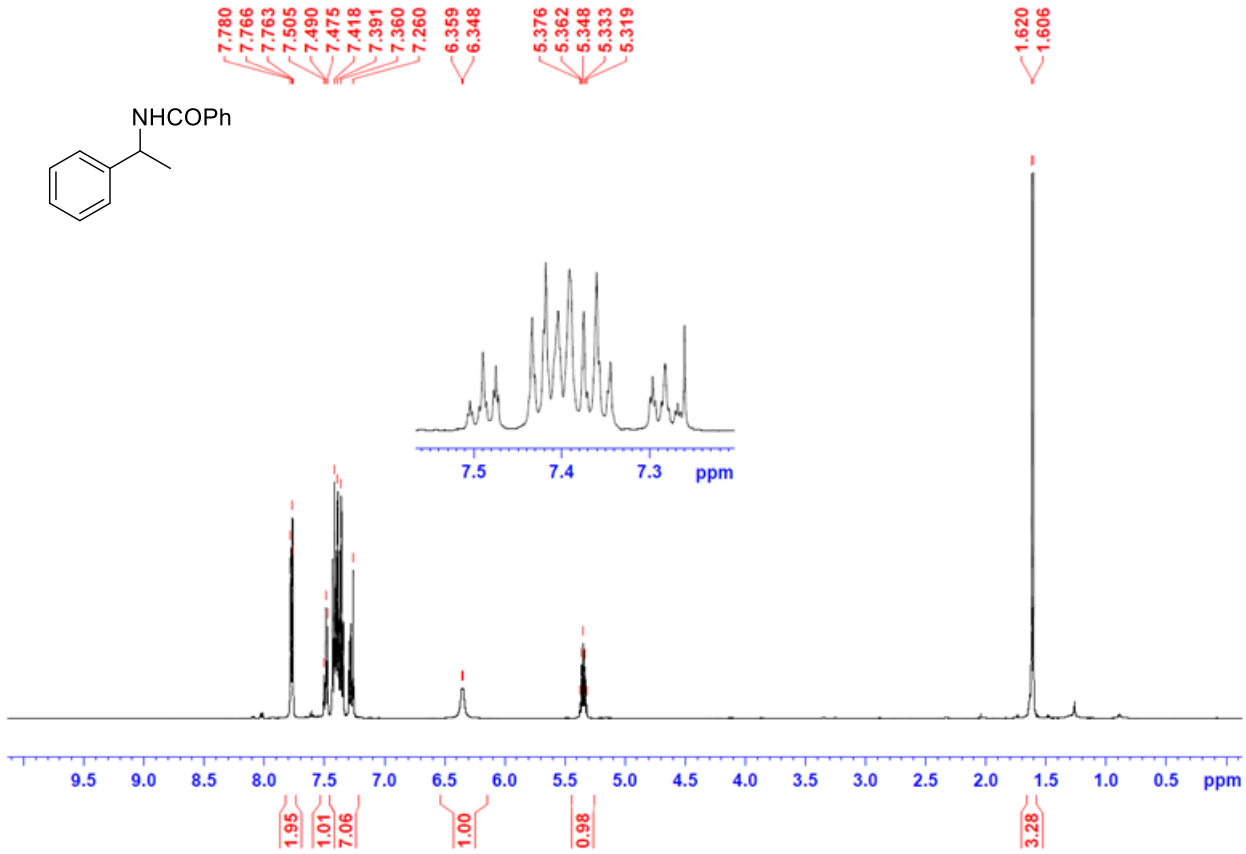


Figure S24. ^{1}H NMR of N-(1-Phenylethyl)benzamide in $CDCl_3$.

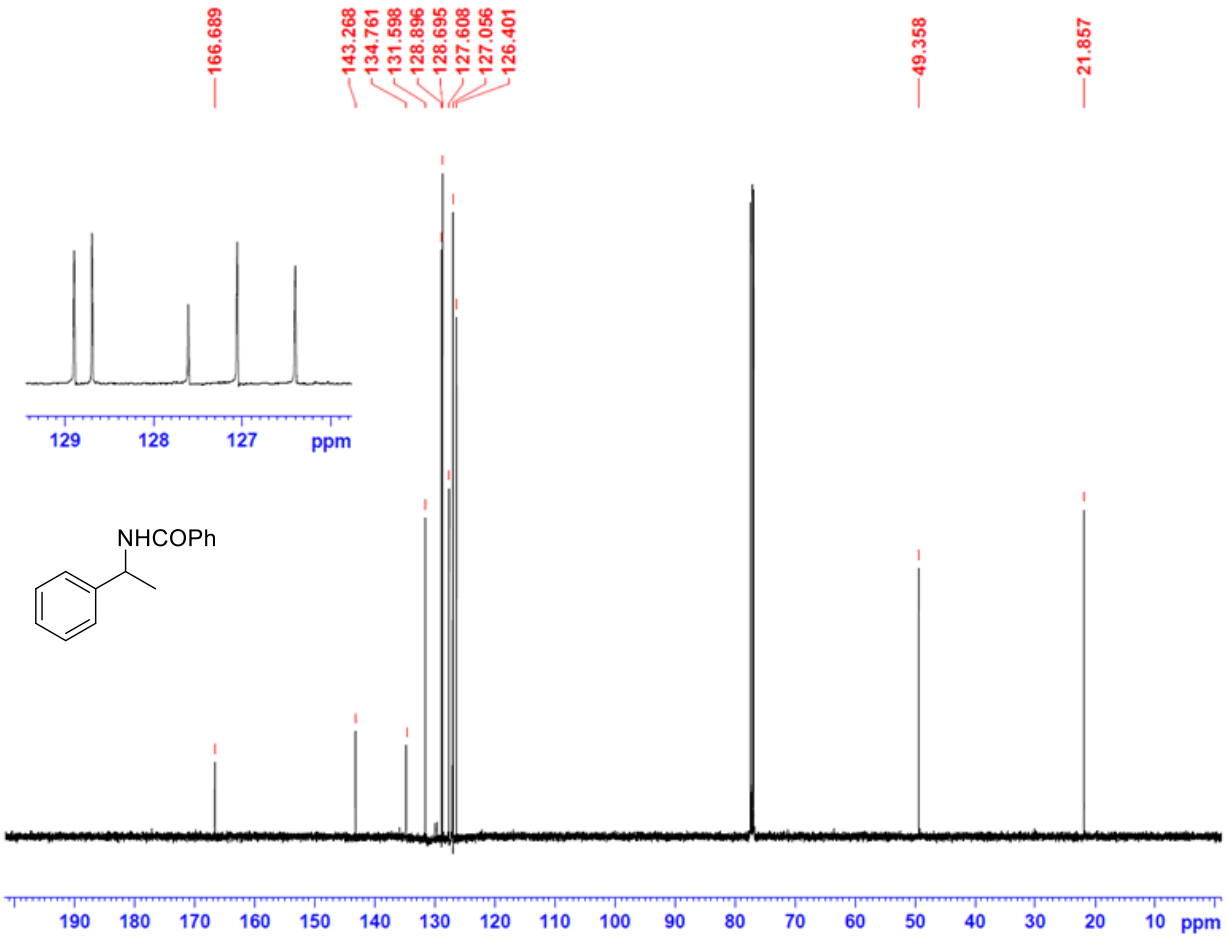
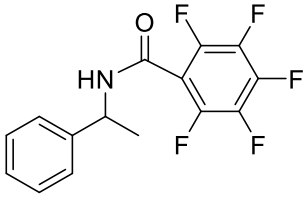


Figure S25. ^{13}C NMR of N-(1-Phenylethyl)benzamide in $CDCl_3$.

2,3,4,5,6-Pentafluoro-N-(1-phenylethyl)benzamide



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), 2,3,4,5,6-pentafluorobenzamide (396 mg, 1.88 mmol, 3.00 equiv), *N*-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) and ethylbenzene (80 µL, 13.3 mg, 0.625 mmol, 1.00 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was concentrated under vacuum (rotary evaporator) to yield the crude product which was purified by column chromatography using ethyl acetate/petroleum ether (1:9 to 1:1) as eluent. 35 mg (18% yield) of pure title compound was obtained.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 7.39-7.26 (m, 5H), 6.37 (d, 1H), 5.27 (q, 1H), 1.59 (d, 3H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 156.6 (s), 145.2 (m), 143.3 (m), 141.9 (s), 141.4 (m), 138.8 (m), 136.7 (m), 129.0 (s), 127.9 (s), 126.2 (s), 111.7 (m), 50.1 (s), 21.6 (s);

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3349 (s), 3076 (s), 3037 (s), 2993 (s), 2362 (s), 2324 (s), 1655 (s), 1538 (s), 1514 (s), 1486 (s), 1450 (s), 1407 (s), 1381 (s), 1323 (s), 1308 (s), 1282 (s), 1248 (s), 1214 (s), 1130 (s), 1117 (s), 1092 (s), 1032 (s), 1017 (s), 992 (s), 947 (s), 907 (s), 809 (s), 791 (s), 764 (s), 734 (s), 698 (s), 649 (s), 614 (s);

HRMS: calcd. for $C_{15}H_{11}F_5NO$ $[M+H]^+$: 316.0761, found: 316.0740

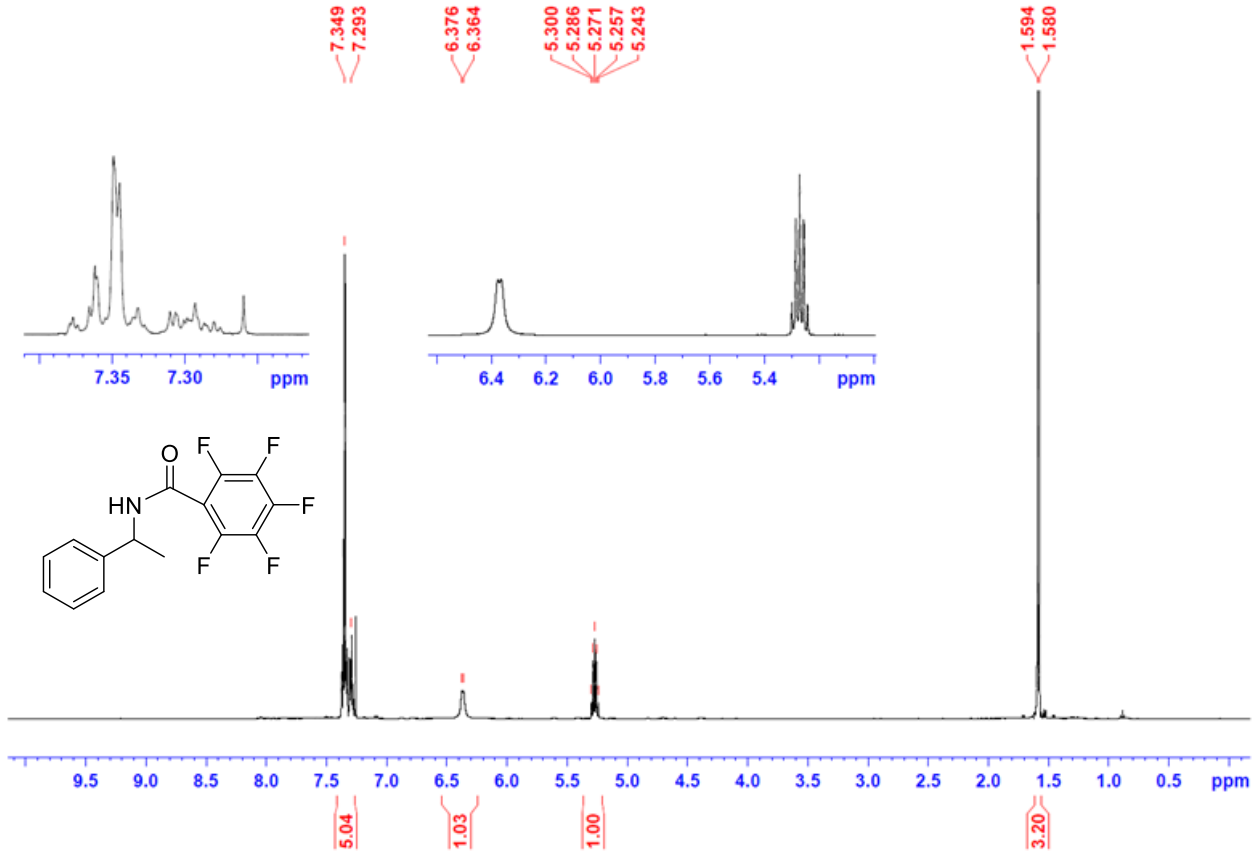


Figure S26. ^{1}H NMR of 2,3,4,5,6-Pentafluoro-N-(1-phenylethyl)benzamide in $CDCl_3$.

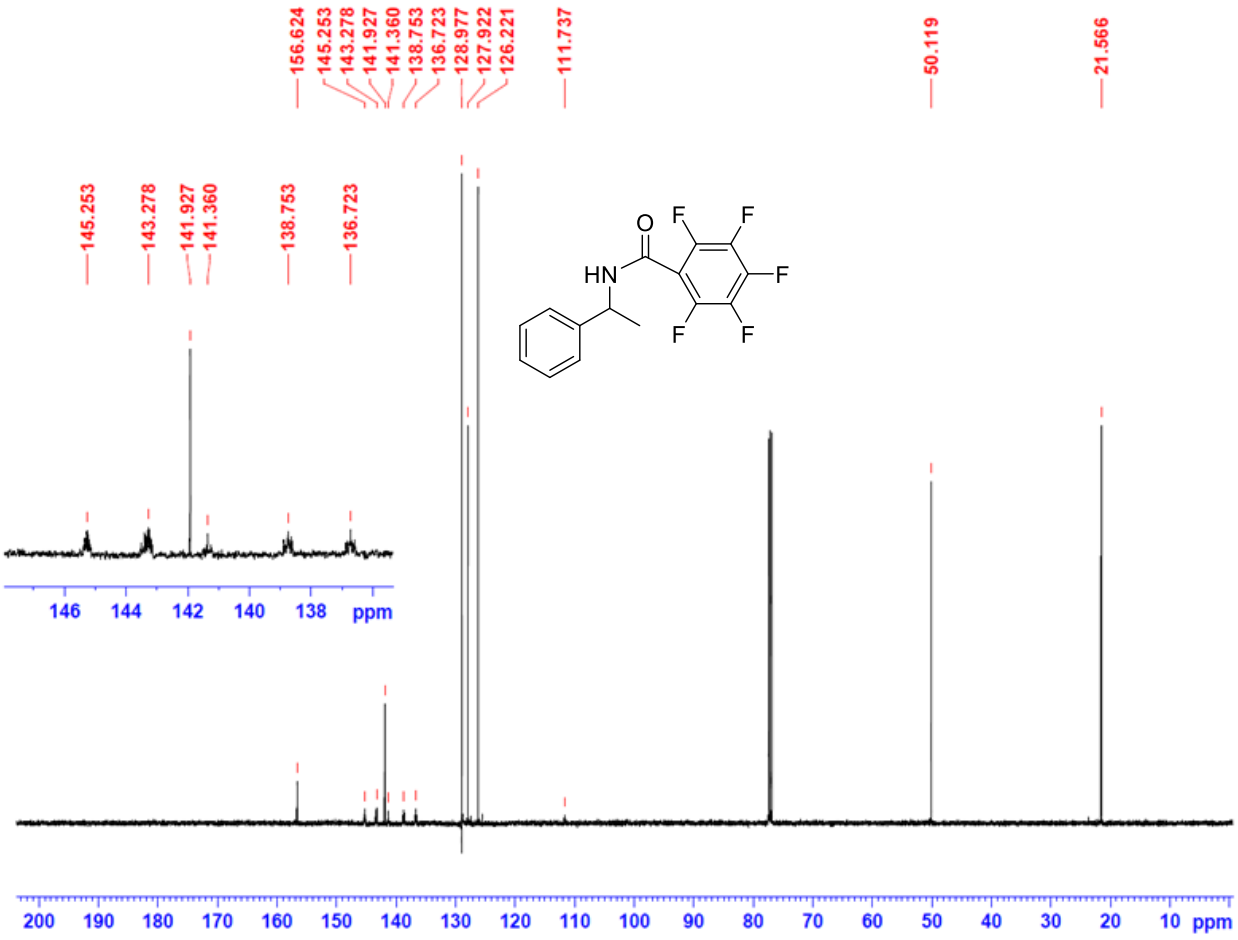
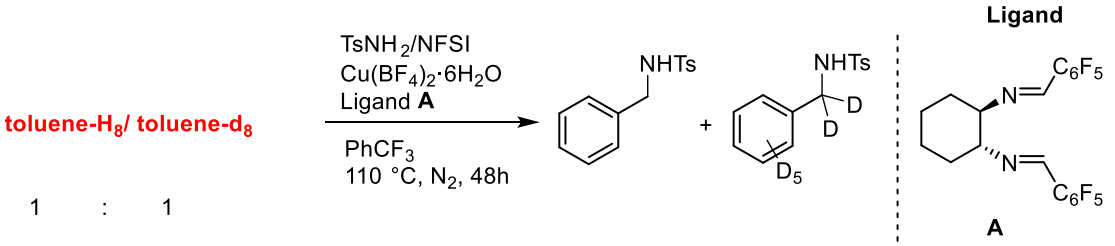


Figure S27. ^{13}C NMR of 2,3,4,5,6-Pentafluoro-N-(1-phenylethyl)benzamide in $CDCl_3$.

KIE Experiment



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (23.0 mg, 63.0 µmol, 10.0 mol%), ligand **A** (30.0 mg, 63 µmol, 10.0 mol%), $TsNH_2$ (324 mg, 1.88 mmol, 3.00 equiv), N-Fluorobenzenesulfonimide (593 mg, 1.88 mmol, 3.00 equiv) toluene (36 µL, 31.3 mg, 0.313 mmol, 0.50 equiv.) and toluene-d_8 (36 µL, 33.8mg, 0.313 mmol, 0.50 equiv.) were added in this sequence to a 20 mL scintillation vial equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. 15 mL $CHCl_3$ and 2 g $CaCO_3$ were added into the mixture and the resulting suspension was filtered through Celite. The filtrate was analyzed for GC-MS. The kinetic isotope effect (KIE) was calculated to $k_H/k_D \approx 1.0$ using the intensity of peaks m/z 106 and m/z 107 (products with only C-H bonds) over the intensity of peaks m/z 113, 114, and 115 (products with only C-D bonds; see Table S12).

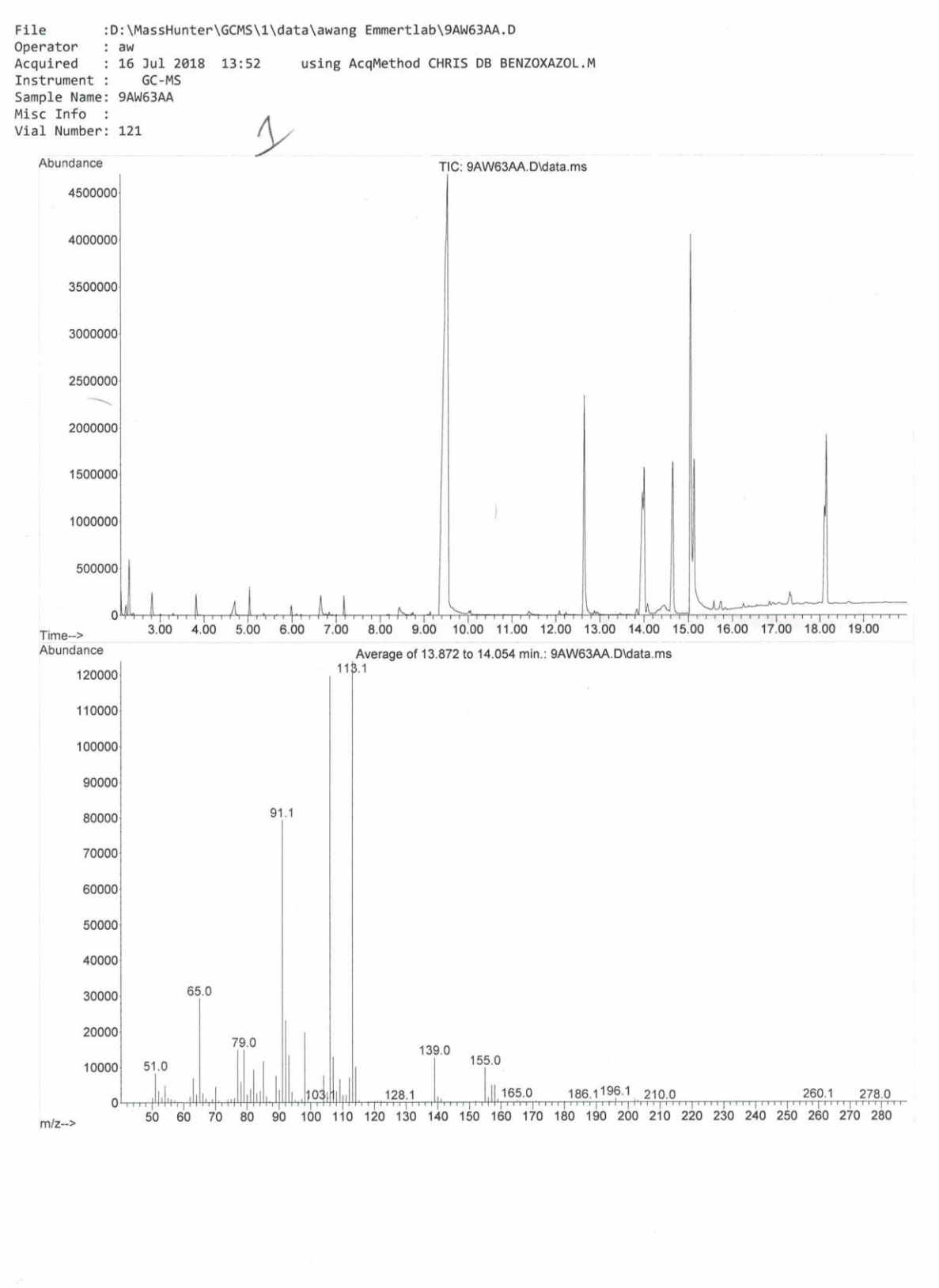


Figure S28. GC-MS Spectrum of KIE Experiment

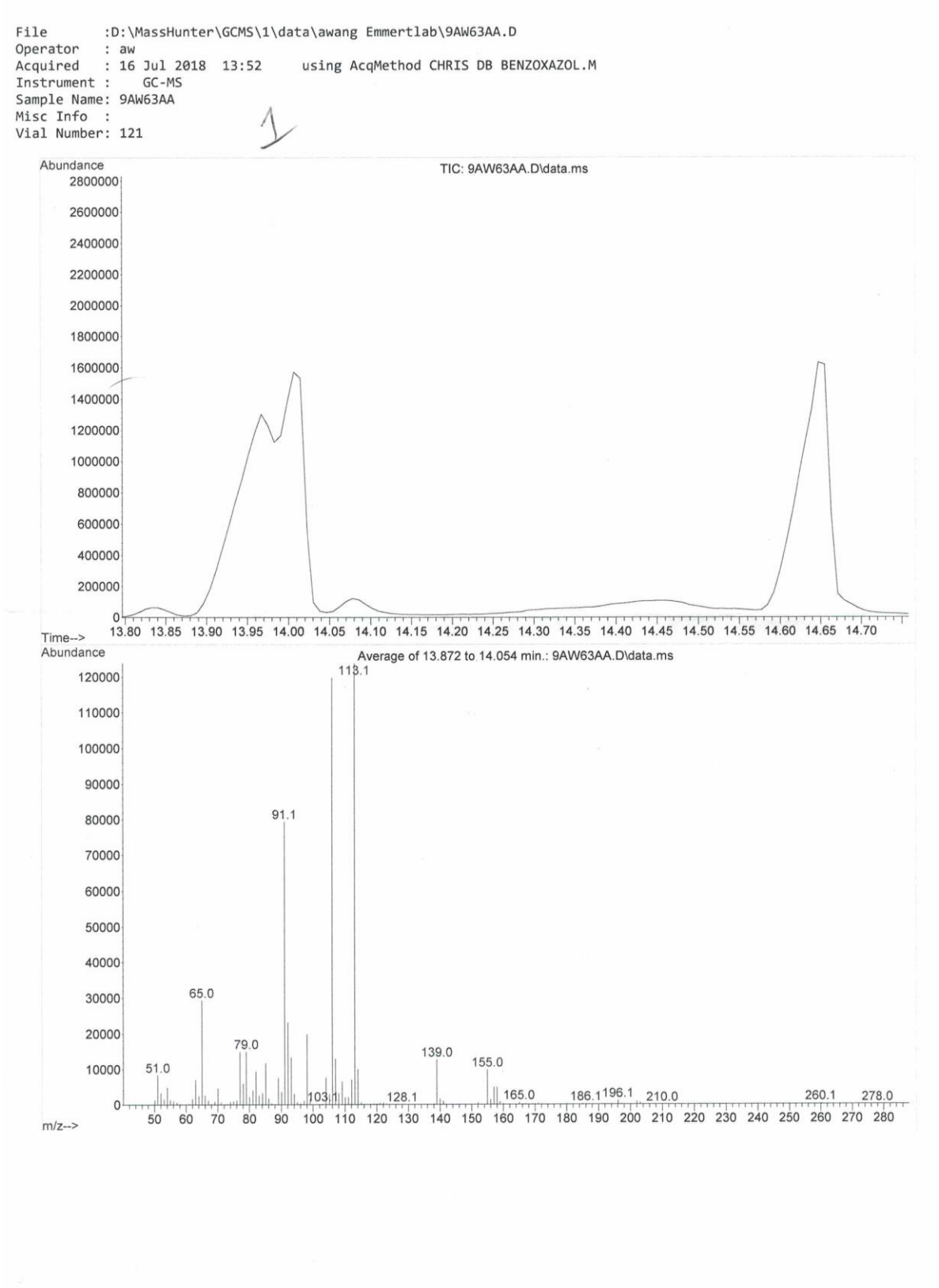
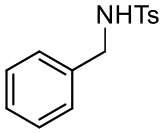
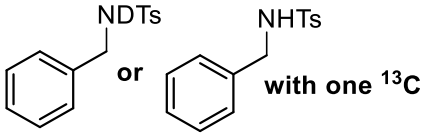
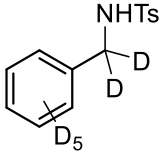
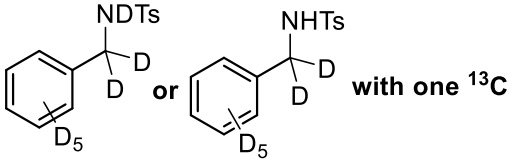
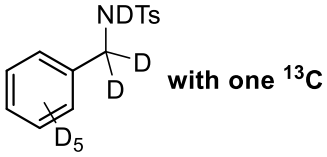


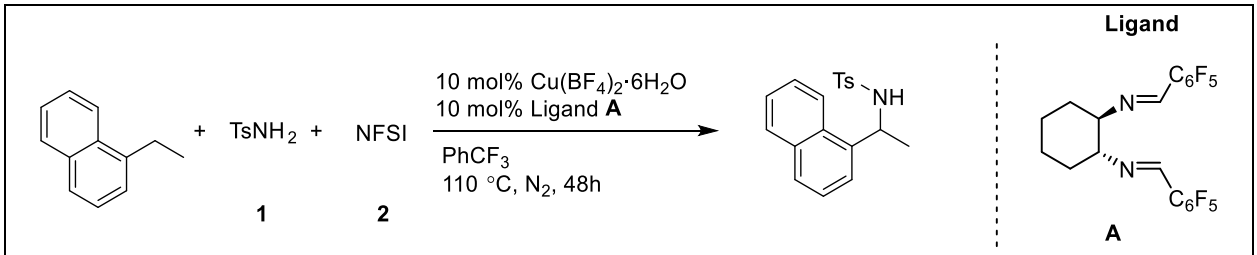
Figure SS29. GC-MS Spectrum KIE Experiment (Zoom in View)

Table S12. Structures and EIMS Abundance of Reaction Products Incorporating Different Isotopes (H vs. D; ^{12}C vs. ^{13}C).

Structure	m/z	Abundance	Total for deuterated/non-deuterated product
	106	119806	132800
	107	12994	
	113	123920	134651
	114	10138	
	115	593	

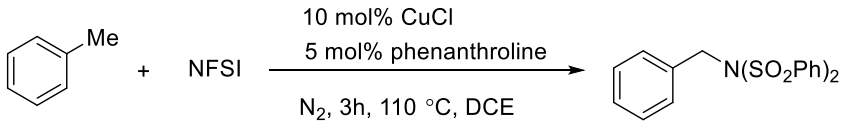
Decomposition Study of 1-Ethylnaphthalene

Table S13. 1-Ethylnaphthalene (0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), amination reagent **1** (p-Toluenesulfonamide, 64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118.3 mg, 0.375 mmol, 3.00 equiv.) and 1.5 mL $PhCF_3$, 48 h. Another batch of chemicals were added to run for another 48 hours before stopping the reaction for work out, unless noted as nothing. The reactions were prepared according to the Representative Procedure for Catalytic Benzylic Amination Reactions.



After 48h add	Yield%
Nothing added	61 ± 1
10 mol% Cu/Ligand	22 ± 2
10 mol% Cu/Ligand, 3 eq NFSI	14 ± 6
3 eq NFSI	8 ± 5

Synthesis of NFSI Amination Product of Toluene



The title compound was synthesized in analogy to a literature known procedure[8].

A 20 mL scintillation vial equipped with a Teflon-coated stir bar was charged with toluene (0.212 mL, 2 mmol, 1.0 equiv.), CuCl (19.80 mg, 0.20 mmol, 10 mol%), NFSI (693.0 mg, 2.20 mmol 1.1 equiv.), 1,10-phenanthroline (9.90 mg, 0.05 mmol, 5 mol%) and 6.0 mL DCE. The reaction mixture was stirred at 110 °C for 3 h. Upon completion, the reaction was cooled to room temperature and quenched by addition of 10 mL H_2O. The mixture was then extracted with 3 × 10 mL CH_2Cl_2. The combined organic extracts were washed with 10 mL sat. aqueous $NaHCO_3$ solution and 10 mL brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford a brown solid. The crude product was purified by recrystallization from EtOAc/hexane to afford a white solid (488 mg, 63%).

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 4.94 (s, 2H), 7.20-7.29 (m, 3H), 7.35-7.40 (m, 2H), 7.40-7.45 (m, 4H), 7.54-7.60 (m, 2H), 7.76-7.80 (m, 4H);

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 52.6 (s), 128.3 (s), 128.6 (s), 128.9 (s), 128.4 (s), 133.7 (s), 134.6 (s), 140.2 (s);

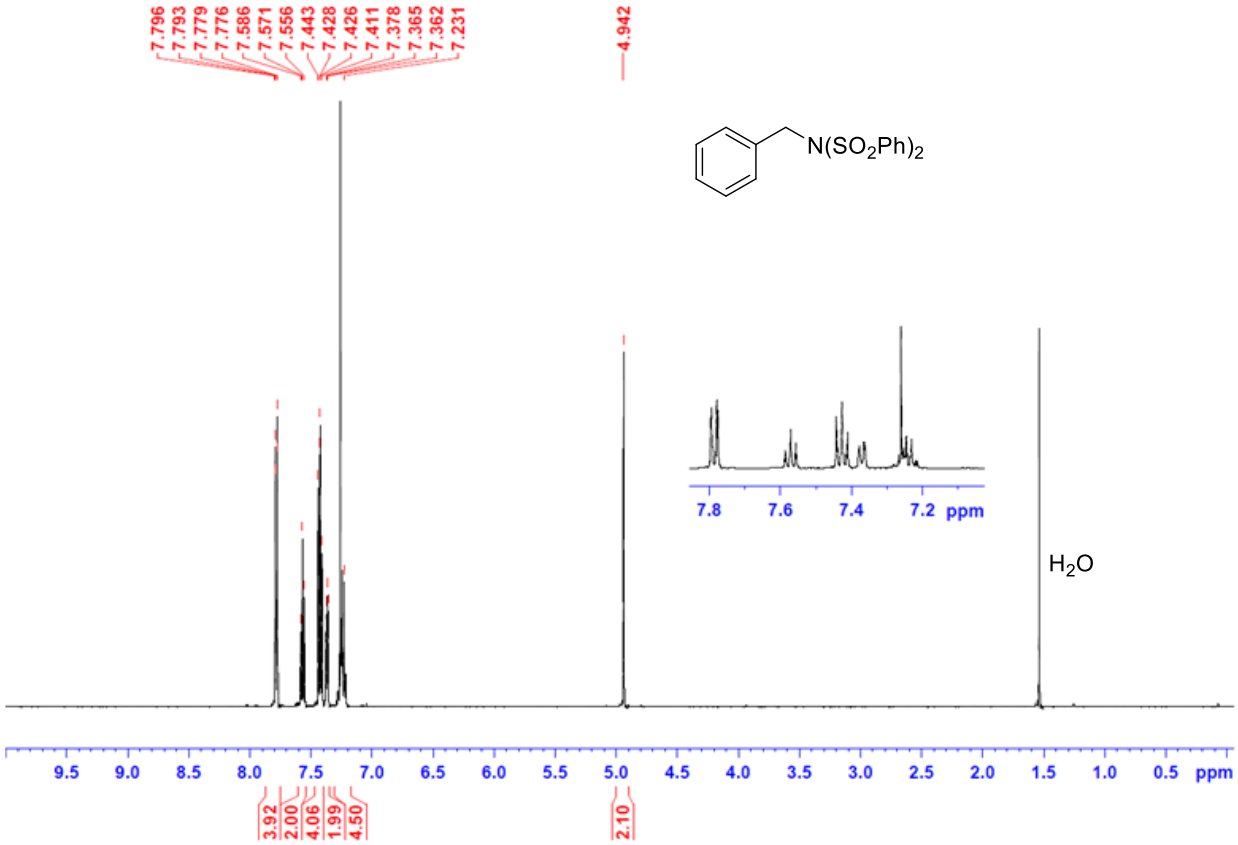


Figure S30. ^{1}H NMR of *N*-Benzyl-*N*-(phenylsulfonyl)benzenesulfonamide in $CDCl_3$.

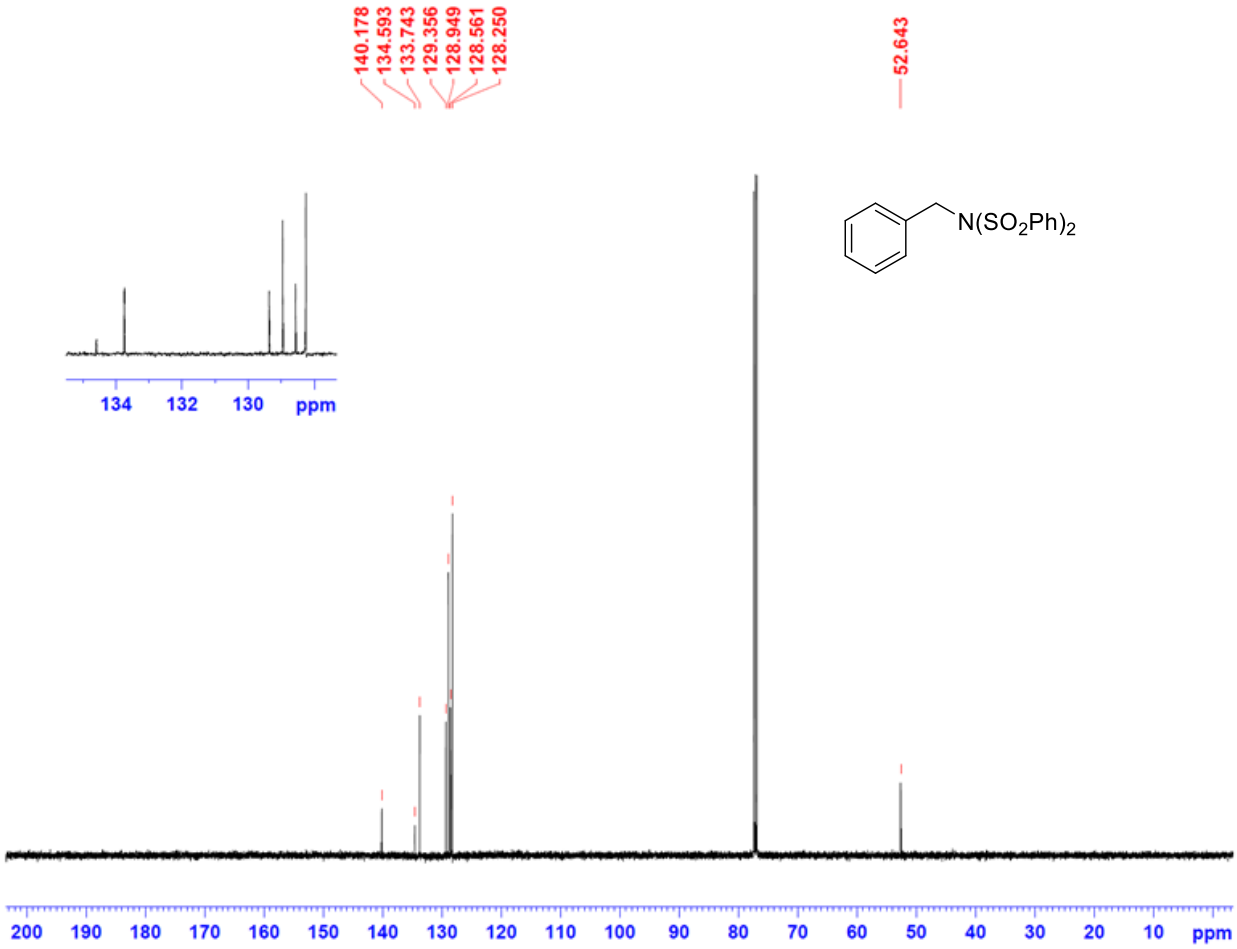
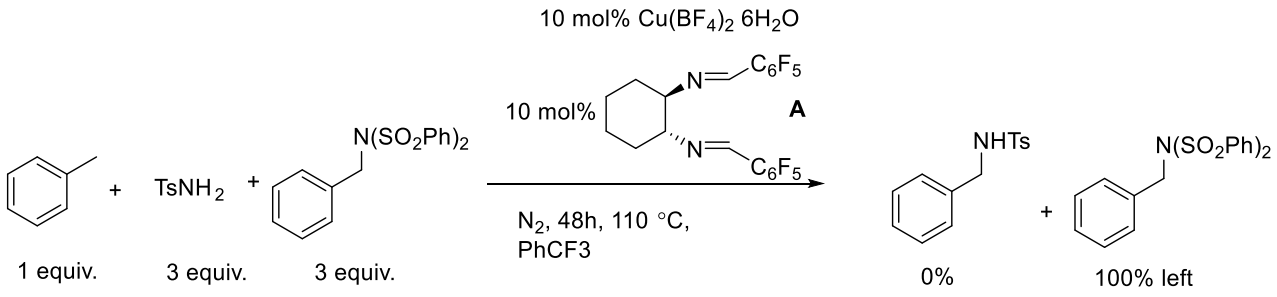


Figure S31. ^{13}C NMR of *N*-Benzyl-*N*-(phenylsulfonyl)benzenesulfonamide in $CDCl_3$.

Catalytic reaction in the presences of NFSI amination product of toluene [$PhCH_2(NSO_2Ph)_2$]

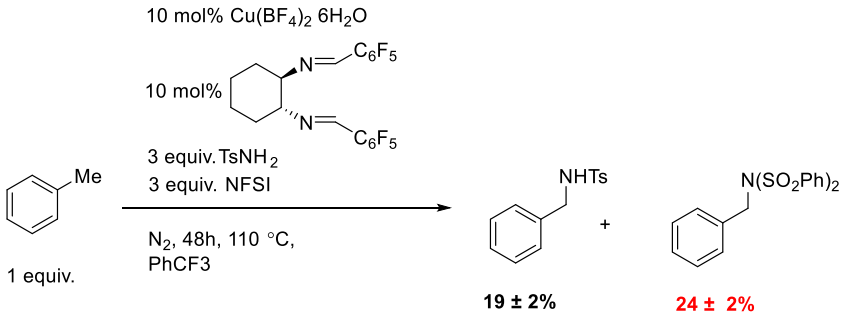
The following reaction was performed to gain insight into the viability of $PhCH_2(NSO_2Ph)_2$ being an intermediate rather than a side product.



Procedure: In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), p-toluenesulfonamide (64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-benzyl-*N*-(phenylsulfonyl)benzenesulfonamide (145.1 mg, 0.375 mmol, 3.00 equiv.), toluene (14.0 µL, 0.125 mmol, 1.00 equiv.), and 1.5 mL benzotrifluoride were added in this sequence to a 4 mL scintillation vial, equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate upon vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure (rotary evaporator). 1.0 mL $CDCl_3$ was added into the reaction vial, followed by addition of 1,1,2-trichloroethane (20.0 µL, 28.8 mg, 215.9 mmol) as NMR standard. The resulting mixture was filtered through Celite. ^1H NMR analysis showed that 100% $PhCH_2(NSO_2Ph)_2$ remained in the reaction mixture and that no amination product of toluene was formed. This result was supported by GCMS analysis.

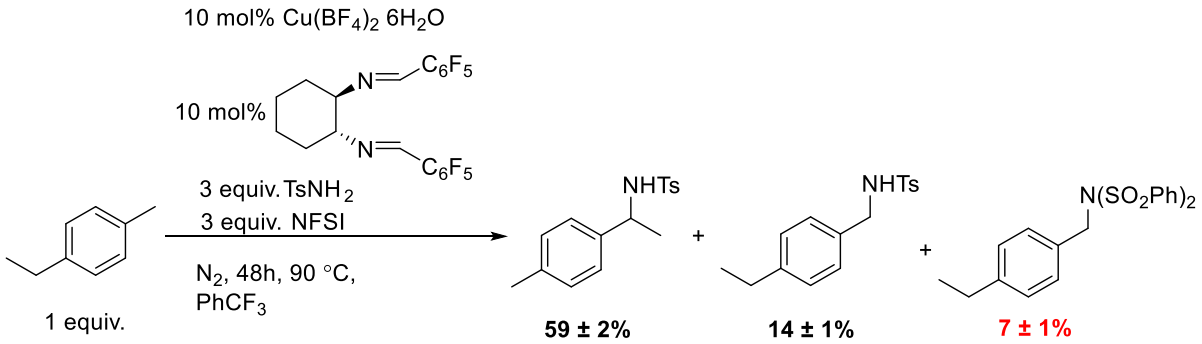
Analysis of Side Products

Reaction of Toluene



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), p-toluenesulfonamide (64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-benzyl-*N*-(phenylsulfonyl)benzenesulfonamide (145.1 mg, 0.375 mmol, 3.00 equiv.), toluene (14.0 µL, 0.125 mmol, 1.00 equiv.), and 1.5 mL benzotrifluoride were added in this sequence to a 4 mL scintillation vial, equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate upon vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure (rotary evaporator). 1.0 mL $CDCl_3$ was added into the reaction vial, followed by addition of 1,1,2-trichloroethane (20.0 µL, 28.8 mg, 215.9 mmol) as NMR standard. The resulting mixture was filtered through Celite. ^1H NMR analysis showed that 24% of side product $PhCH_2(NSO_2Ph)_2$ and 19% of BnNHTs was formed. This result was supported by GCMS analysis.

Reaction of 4-Ethyltoluene

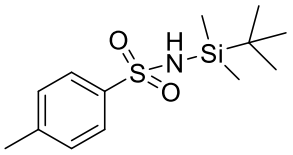


In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), p-toluenesulfonamide (64.2 mg, 0.375 mmol, 3.00 equiv.), *N*-benzyl-*N*-(phenylsulfonyl)benzenesulfonamide (145.1 mg, 0.375 mmol, 3.00 equiv.), 4-ethyltoluene (16.0 µL, 0.125 mmol, 1.00 equiv.), and 1.5 mL benzotrifluoride were added in this sequence to a 4 mL scintillation vial, equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 90 °C on a pre-heated vial plate upon vigorous stirring (1500 rpm). After 48 h, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure (rotary evaporator). 1.0 mL $CDCl_3$ was added into the reaction vial, followed by addition of 1,1,2-trichloroethane (20.0 µL, 28.8 mg, 215.9 mmol) as NMR standard. The resulting mixture was filtered through Celite.

^1H NMR analysis showed 7% 4-$EtPhCH_2(NSO_2Ph)_2$, 59% of the secondary C-H amination product, and 14% of primary C-H amination product. This result was supported by GCMS analysis.

TsNHTBS as Potential Amination Reagent

Preparation of TsNHTBS



N-(*tert*-butyldimethylsilyl)-4-methylbenzenesulfonamide

The title compound was synthesized in analogy to a literature-known procedure[9]:

At room temperature, 4-methylbenzenesulfonamide (5.70 g, 33.0 mmol, 1.00 equiv.) was dissolved in dry THF (40 mL) in a round bottom flask following with the addition of trimethylamine (10.5 mL, 72.4 mmol, 2.20 equiv.) under N_2. The mixture was cooled to 0 °C. A solution of tert-butyldimethylsilyl chloride (6.44 g, 41.3 mmol, 1.25 equiv) in toluene (7.4 mL) was added dropwise into the reaction. The mixture was allowed to warm up to room temperature and stirred for 2 h, then stirred at 50 °C for 48 h. The reaction mixture was then cooled to 25 °C and the solid was removed by filtration and washed with Et_2O (2 x 50 mL). The organic phases were combined and the solvent was removed under reduced pressure overnight to obtain an off-white solid crude product. The pure title compound was obtained by washing off impurities using distilled hexane (6.8 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ [ppm] =) δ 7.72–7.77 (m, 2H), 7.24–7.30 (m, 2H), 4.26 (s, 1H), 2.42 (s, 3H), 0.89 (s, 3H), 0.90 (s, 9H), 0.22 (s, 6H)

^{13}C (NMR 125 MHz, $CDCl_3$, 25 ºC): δ [ppm] = 142.8 (s), 141.1 (s), 129.6 (s), 126.3 (s), 25.9 (s), 21.6 (s), 17.4 (s), -4.3 (s);

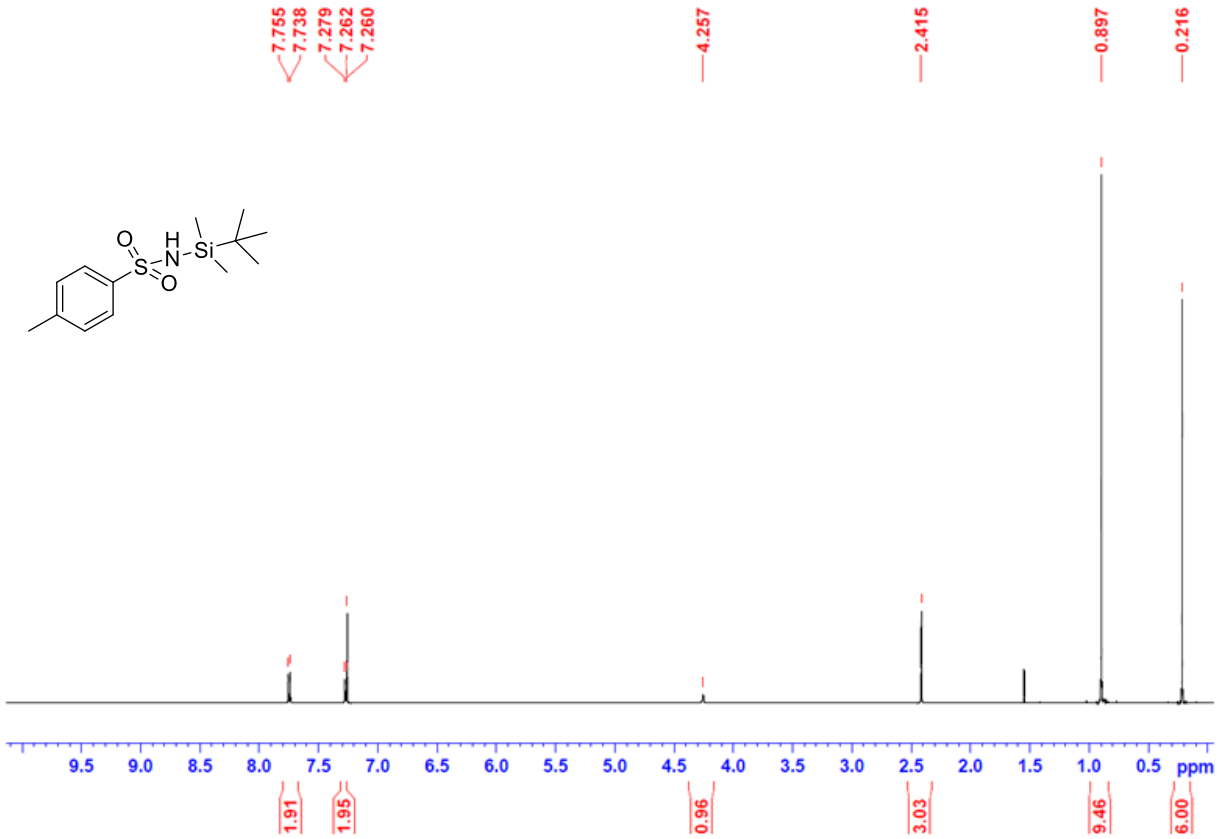


Figure S32. ^{1}H NMR of TsNHTBS in $CDCl_3$.

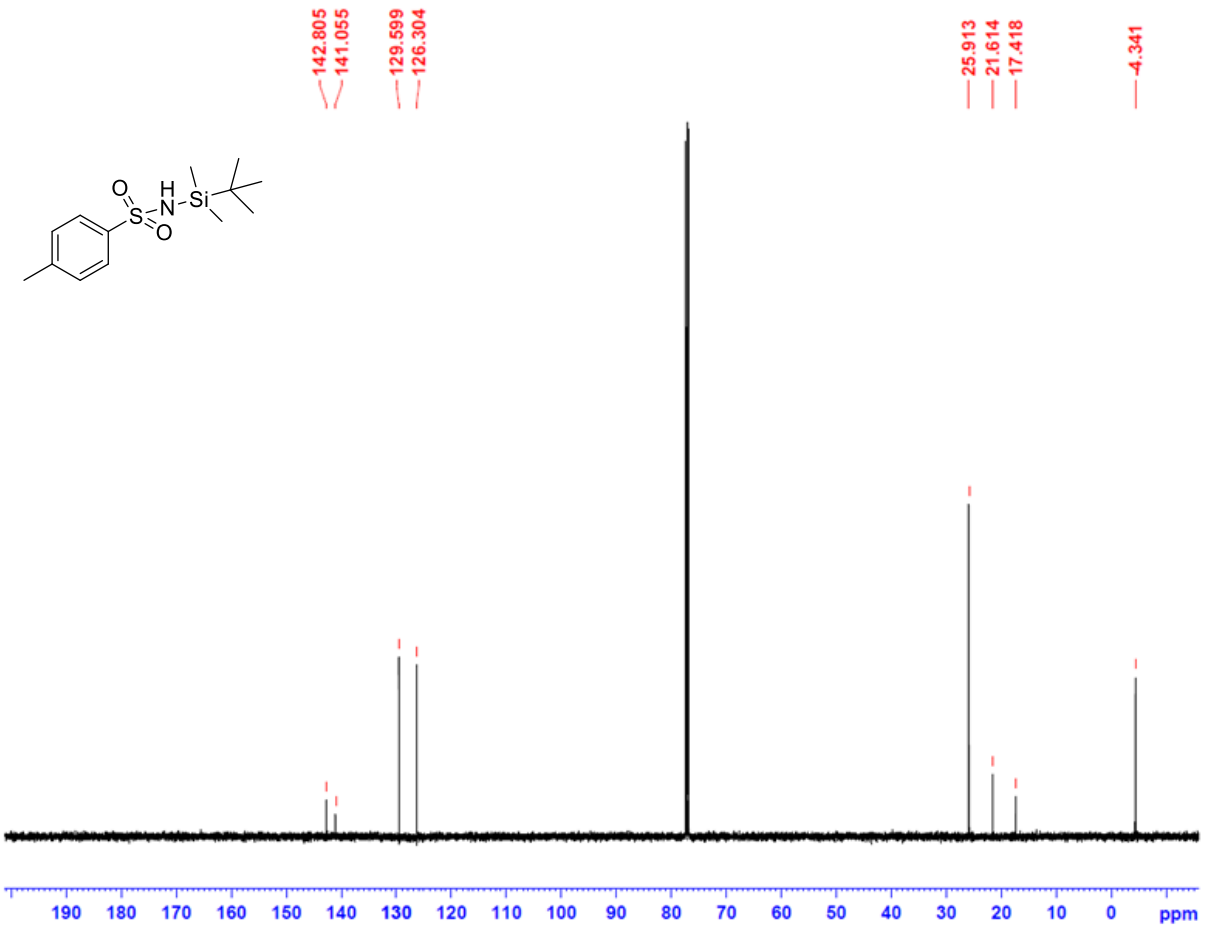
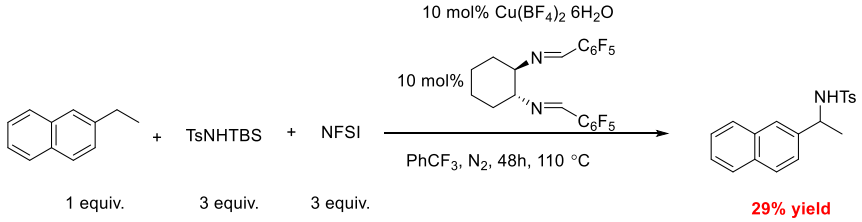


Figure S33. ^{13}C NMR of TsNHTBS in $CDCl_3$.

Catalytic Reactions with TsNHTBS



In a glovebox, $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (6.0 mg, 12.6 µmol, 10.0 mol%), TsNHTBS (107 mg, 0.375 mmol, 3.00 equiv.), NFSI (118 mg, 0.375 mmol, 3.00 equiv.), 2-ethylnaphathlene (20 µL, 19.5 mg, 0.125 mmol, 1.00 equiv.) and 1.5 mL benzotrifluoride were added in this sequence to a 4 mL scintillation vial, equipped with a Teflon-coated stir bar. The vial was sealed with a Teflon-lined vial cap and heated to 110 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After stirring the mixture vigorously for the dedicated reaction time, the vial was taken off the heating block and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure (rotary evaporator). 1,1,2-trichloroethane (20.0 µL, 28.8 mg, 215.9 mmol) was added into the reaction vial as NMR standard followed by addition of 1.0 mL $CDCl_3$. The resulting mixture was filtered through Celite. The filtrate was analyzed by quantitative ^1H NMR and GC-MS.

The low (29%) yield (compared with 61% yield under standard conditions) suggests that sequestering fluoride in the reaction mixture does not contribute to product formation.

Radical Trap Experiments

TEMPO

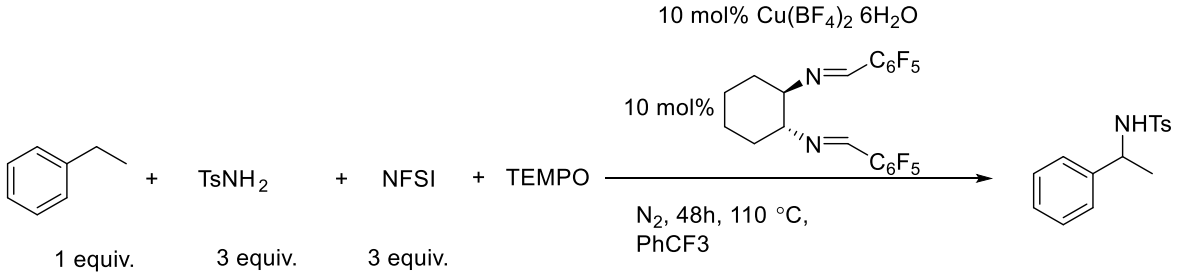


Table S14. TEMPO Experiments. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (12.6 µmol, 10.0 mol%), amination reagent **1**, (64.7 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118 mg, 0.375 mmol, 3.00 equiv.) TEMPO and 1.5 mL benzotrifluoride 110 °C, 48 h. The reactions were prepared for GC-MS and NMR analysis according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

TEMPO	**Yield of Amination product**	**TEMPO Adduct**	**Remaining Substrate**
10 mol%	48.4%	Not detected	6.1%
100 mol%	0%	Not detected	0%
400 mol%	0%	Not detected	0%

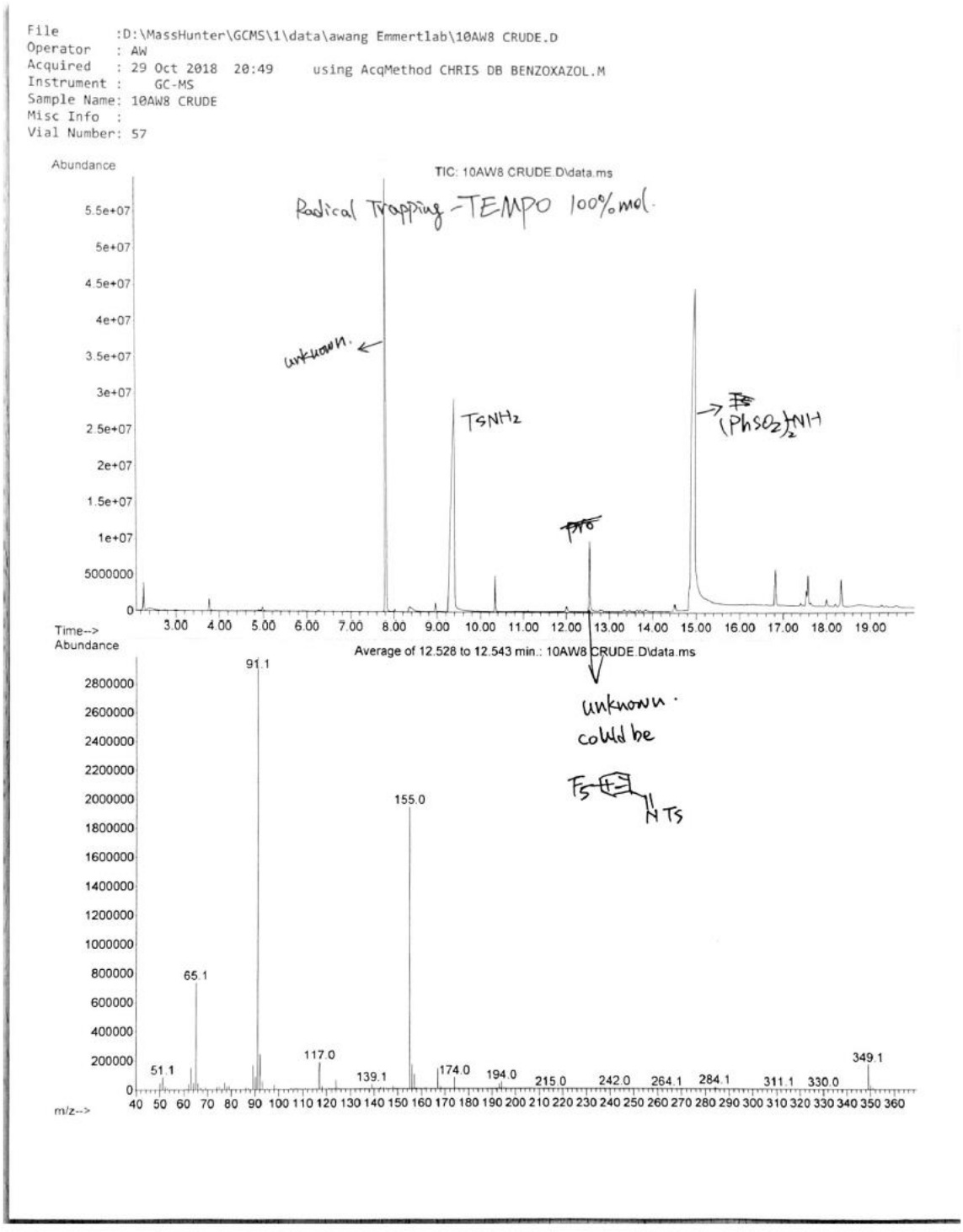


Figure S34. A GC-MS Spectrum for a 48 h Radical Trapping Experiment using TEMPO

BrCCl₃

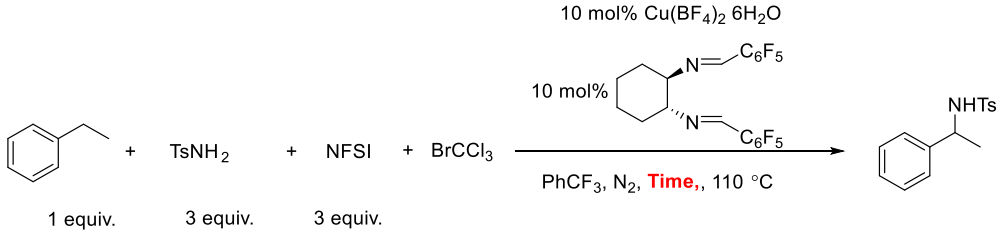


Table S15. $BrCCl_3$ Experiments. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand **A** (12.6 µmol, 10.0 mol%), amination reagent **1**, (64.7 mg, 0.375 mmol, 3.00 equiv.), N-Fluorobenzenesulfonimide (118 mg, 0.375 mmol, 3.00 equiv.) $BrCCl_3$ and 1.5 mL benzotrifluoride 110 °C. The reactions were prepared for GC-MS and NMR analysis according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

Amount of $BrCCl_3$	Reaction Time	NMR Yield of Amination Product	Bromination Product	Remaining Substrate by NMR
10 mol%	15 min	8.6%	Not detected	90.6%
100 mol%	15 min	10.6%	Not detected	86.3%
400 mol%	15 min	18.4%	Not detected	78.3%
10 mol%	1 h	38.3%	Not detected	37.9%
100 mol%	1 h	51.2%	Not detected	13.9%
400 mol%	1 h	61.3%	Not detected	10.8%
10 mol%	48 h	74.3%	Not detected	5.2%
100 mol%	48 h	70.4%	Not detected	3.2%
400 mol%	48 h	51.8%	Not detected	0%

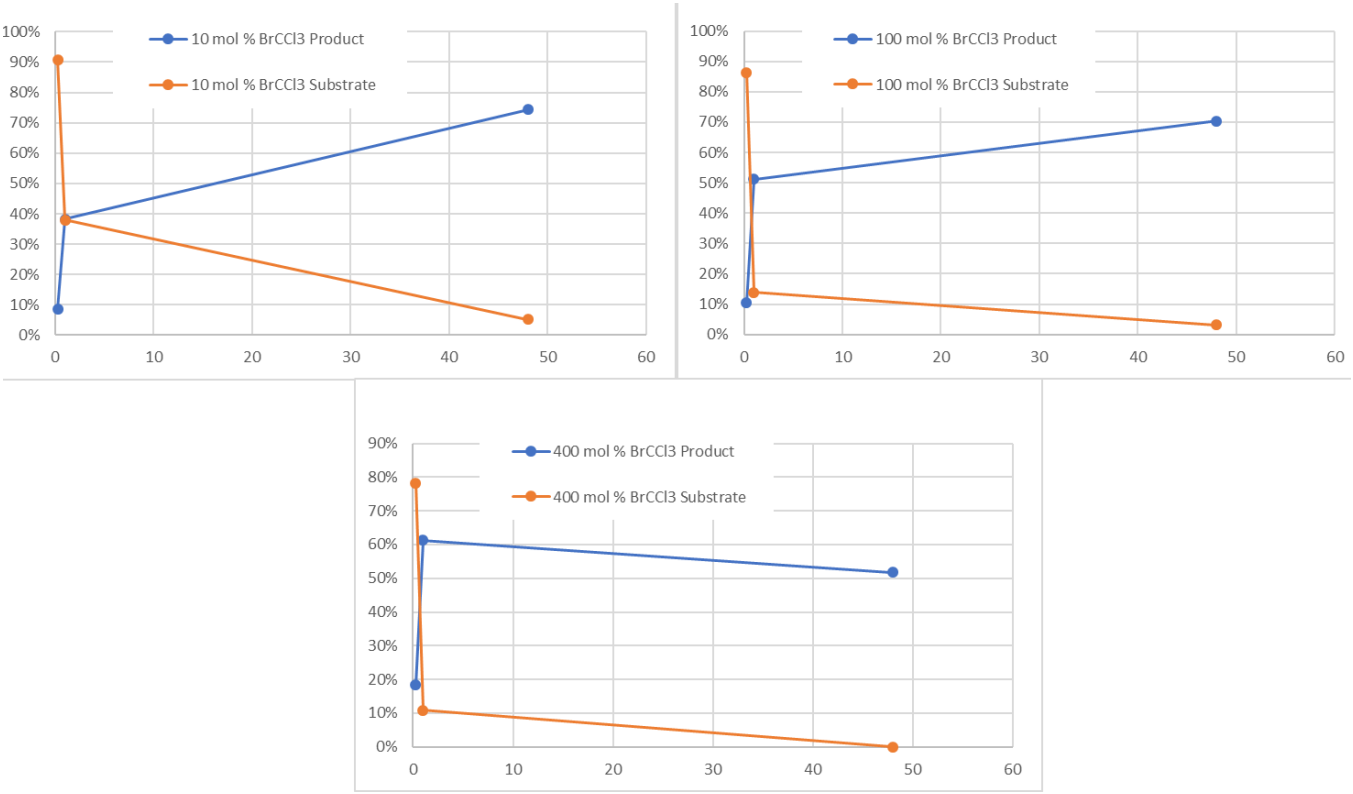


Figure S35. Time courses of reactions with different amounts of $BrCCl_3$ added.

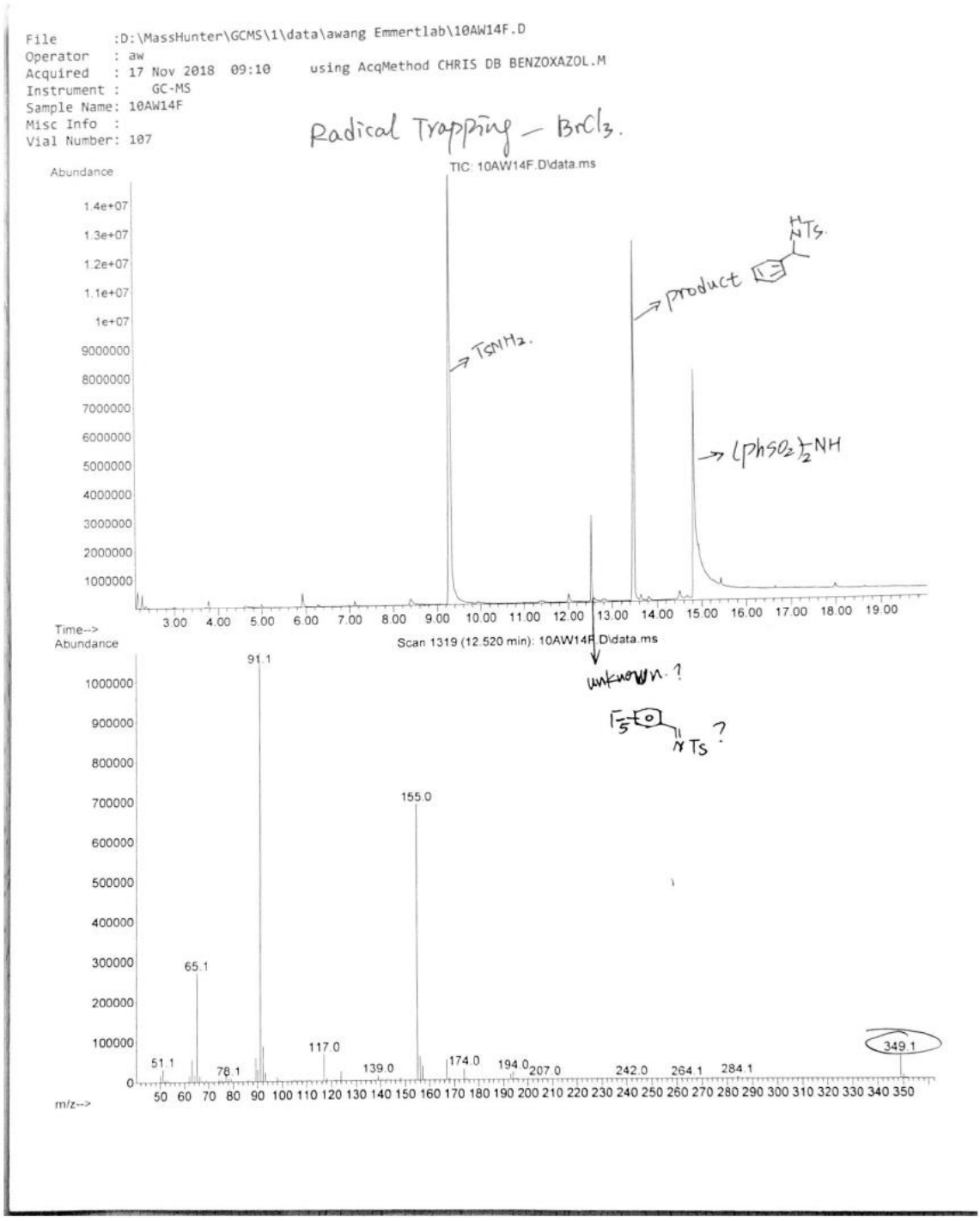


Figure S36. A GC-MS Spectrum for a 48 h Radical Trapping Experiment using $BrCCl_3$ showing no new compound formed.

Reaction in Air

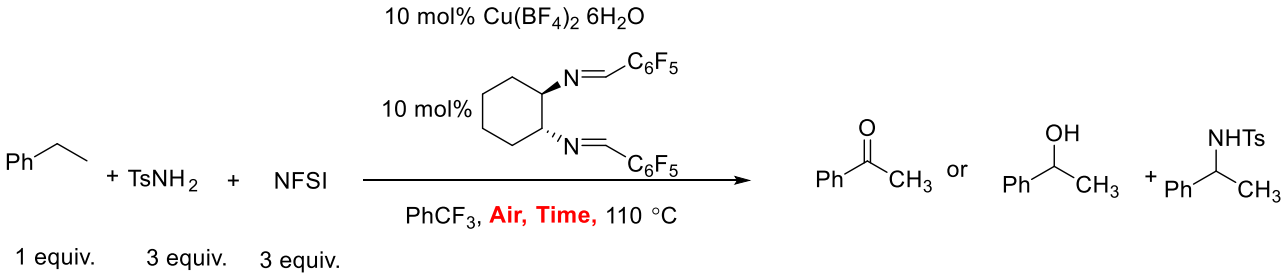


Table S16. Air Experiments. Ethylbenzene (16.0 µL, 13.3 mg, 0.125 mmol, 1.00 equiv.), $Cu(BF_4)_2 \cdot 6H_2O$ (4.6 mg, 12.6 µmol, 10.0 mol%), ligand A (12.6 µmol, 10.0 mol%), amination reagent 1, (64.7 mg, 0.375 mmol, 3.00 equiv.), *N*-Fluorobenzenesulfonimide (118 mg, 0.375 mmol, 3.00 equiv.) TEMPO and 1.5 mL benzotrifluoride 110 °C, 48 h under air. The reactions were prepared for GC-MS and NMR analysis according to the Representative Procedure for Catalytic Benzylic Amination Reactions.

Reaction Time	Oxidation Product (alcohol or ketone)	NMR Yield of Amination Product	Remaining Substrate
15 min	Not detected	5.8%	94.7%
1 h	Not detected	28.8%	9.8%
48 h	Not detected	60.3%	10.4%

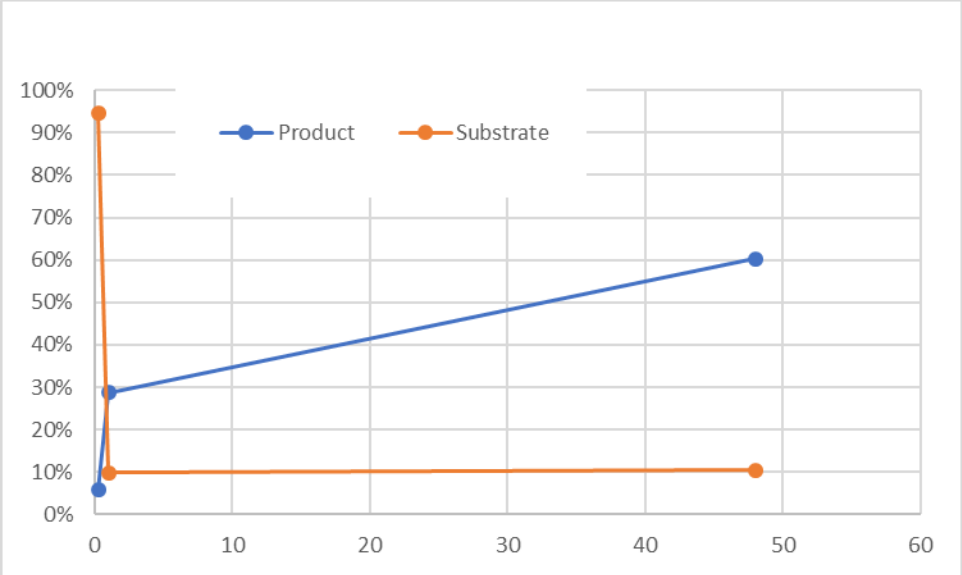


Figure S37. Time Course of Reaction in Air.

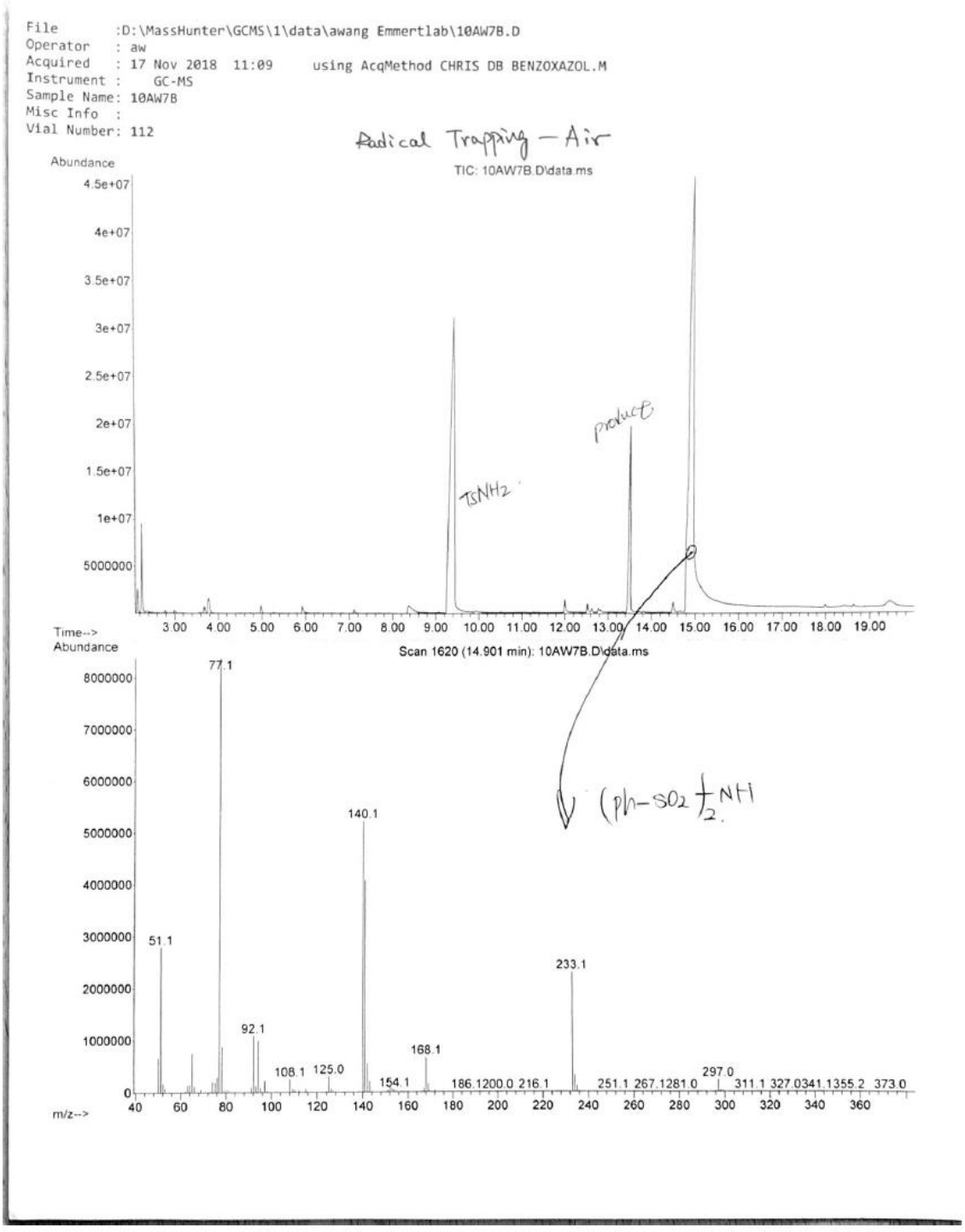


Figure S38. A GC-MS Spectrum for a reaction in air after 48 h, showing no new product.

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