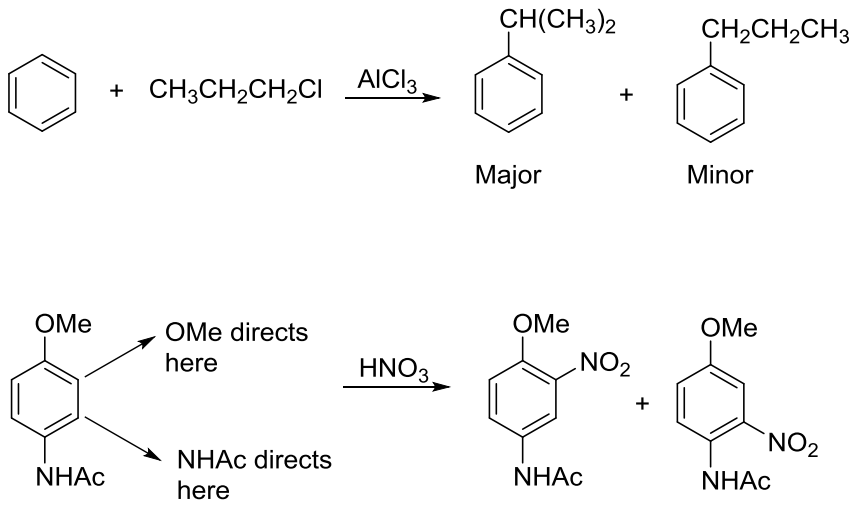
Chapter II

Base-mediated [3+3] benzannulation reactions of bis-sulfonyl propenes and Morita-Baylis-Hillman (MBH) bromides for the synthesis of highly substituted arenes

2.1. Introduction

Substituted arene units are widely prevalent in organic chemistry and are routinely found as the core unit of many natural products and synthetic molecules.[1] The arene scaffold constitute an excellent building block as it can be conveniently transformed into various desired target molecules. Organic chemists strive continuously to develop methods to synthesize arenes. Generally, substituted arenes are constructed by stepwise introduction of functional group via electrophilic aromatic substitution reactions.[2] Friedel-Crafts reaction is a well established and one of the oldest among such methods.[3] This reaction has wide application for synthesis of mono-substituted arenes while regioselective synthesis of di-, tri- and tetra-substituted arenes often becomes challenging via aromatic substitution reactions. The directing effect of groups present on aryl ring decides the regiochemical outcome of the reaction and may prevent the formation of a desired regioisomer. The structural rearrangement of electrophile (carbocation) generated during the course of electrophilic substitution reaction can lead to the formation of unwanted side-products. Electron withdrawing groups on the arene ring deactivate them and bulky substituents repel the approach of electrophiles thereby making such electrophilic substitutions problematic. Some examples of above mentioned problems complicate the outcomes of aromatic electrophilic substitutions are depicted in scheme 1.



Scheme 1: Regiochemical control challenges in electrophilic aromatic substitution

Modern synthetic methods such as transition metal mediated cross-coupling reactions[4] and directed metallation reactions[5] address these issues significantly. These methods, however, employ arenes preinstalled with groups which become involved in coupling reaction. Most of the reactive groups on such pre-functionalised arene are introduced via aromatic substitution reaction. Their synthesis, especially when a poly-substituted arene is required, again faces the same issues described above.

An alternative approach of arene construction is highly desirable to overcome these issues. *Benzannulation reactions*, where the union of two acyclic precursors affords an arene product address above-mentioned aspects to some extent. This method has become a powerful tool for the synthesis of arenes due to its many favorable virtues. Dotz reaction[6] and Danheiser benzannulation[7] are important and well known transformations that demonstrate the potential of this strategy in organic synthesis. In a benzannulation reaction the acyclic precursor can be of various sizes and type, the assembly of two or more components may be catalyzed or mediated by metal

complexes, acids, bases or light. The combination of two, three or more acyclic building blocks may result in an efficient synthesis of arenes. Different varieties of benzannulation reactions are developed and can be classified into various categories depending on the number of carbon atoms contributed by each of acyclic building block to final product, such as [3+3], [4+2], [5+1], [2+2+2], *etc*. Benzannulation reactions of the [3+3] class are more pertinent to work presented in this chapter.[8] Elegant applications of this strategy in the total synthesis of arene containing natural products reveal the power of this method.[9] A detailed discussion on benzannulation reactions may be found in chapter 1.

In the following passages, a novel [3+3] benzannulation reaction of Morita-Baylis-Hillman bromides and unsaturated sulfones that affords tetra-substituted bis-sulfonylarenes is described. To present the results in context, a brief overview of arysulfones is presented in following sections.

2.2. Aryl sulfones

Arylsulfones are important synthetic targets owing to their synthetic utility and favorable properties.[10] A number of aryl sulfones exhibit biological activities such as inhibitory activities against various enzymes.[11] In addition, some arylsulfones shows excellent coordinating properties,[12] which enhances their demand. The anti-leprosy drug dapsone and the anti- ischemic agent cariporide are important aryl sulfones in pharmacology. Some important aryl sulfones are depicted in figure 1.

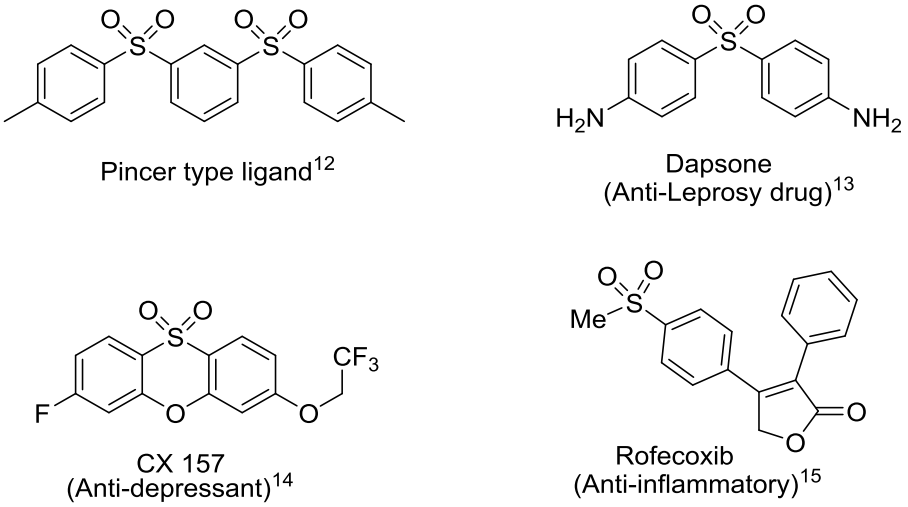


Figure 1: Some important biological active aryl sulfones

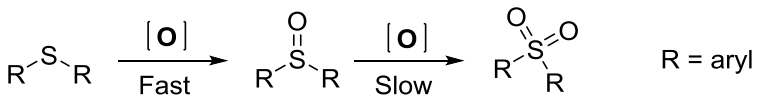
As a consequence, a number of methods have been developed for their synthesis and a few selected methods are presented below.

2.3. Synthesis of aryl sulfones

Commonly used methods for synthesis of aryl sulfones are, (i) oxidation of aryl sulfides,[16] (ii) sulfonylation of arenes[17] and (iii) coupling of sulfinates with aryl halides or tosylates.[18] Each of these three methods are described with examples in the following sections.

2.3.1. Oxidation of aryl sulfides

A general route for synthesis of aryl sulfones involves oxidation of corresponding aryl sulfides. Peroxyacids and peroxides are the common oxidants used for oxidation of sulfides and sulfoxide into sulfones. A general approach for oxidation of sulfides is described in scheme 2.

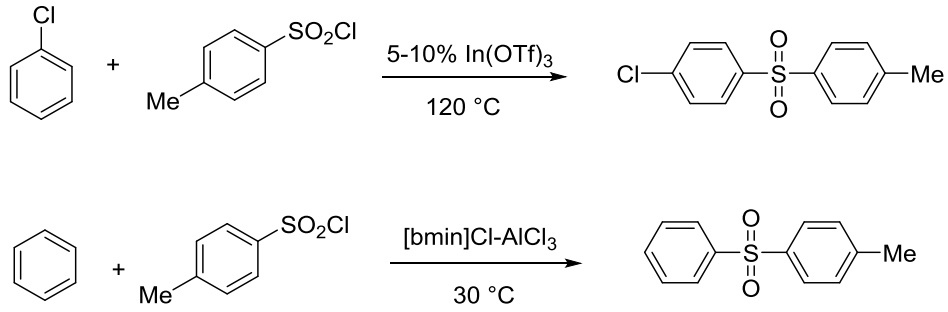


Scheme 2: General method for oxidation of sulfides into sulfones

Initially, sulfides are oxidized to sulfoxides which can be further oxidized to sulfones. Some other reagents such as potassium permanganate, osmium tetraoxide and HOF.CH_3CN complex are also effective in oxidation of sulfides into sulfones.

2.3.2. Sulfonylation of arenes by sulfonyl chlorides

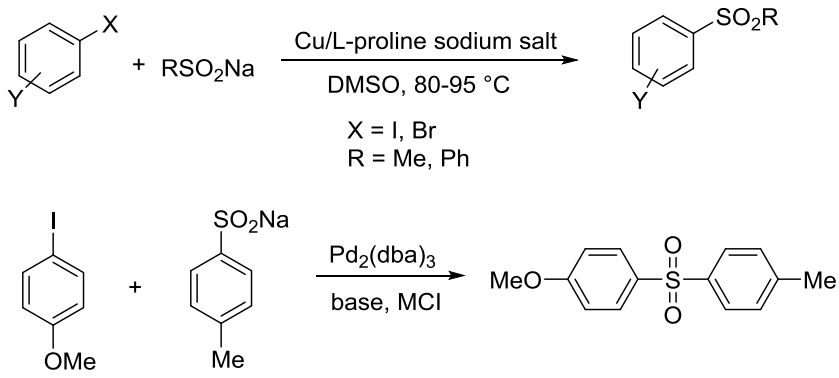
Arenes undergo sulfonylation by sulfonyl chloride in presence of Lewis acids. Both activated and deactivated arenes are reactive towards sulfonylation reaction and generate the corresponding aryl sulfones. Two examples of Lewis acid-mediated sulfonylation reactions of arenes with *p*- toluenesulfonyl chloride are depicted in scheme 3.



Scheme 3: Synthesis of aryl sulfones *via* sulfonylation

2.3.3. Coupling of sulfinates with aryl halides

Metal mediated coupling of aryl halides with sodium salt of sulfinic acids affords aryl sulfones in good yields (scheme 4). Symmetrical and unsymmetrical aryl sulfones can be synthesized *via* this coupling reaction.

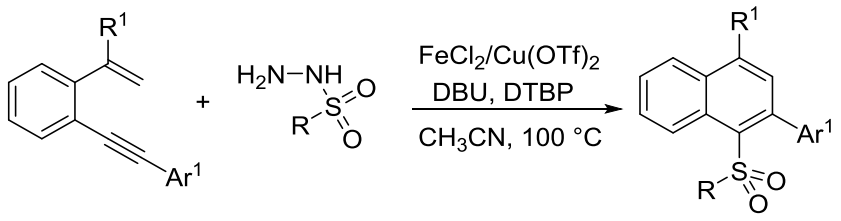


Scheme 4: Synthesis of aryl sulfones via coupling of sodium sulfinate salt with aryl halides

It is notable that in all of the above mentioned methods, pre-functionalised arenes are used for sulfonylation that affords a number of simple aryl sulfones, however, synthesis of more substituted aryl sulfones would be difficult by using these methods. For such substituted sulfones, the di-, tri-, and tetra-substituted arene building blocks are not readily available. In addition, the already present functionalities on arene building blocks may interfere with regiochemistry and reactivity of sulfonylation reaction. *Benzannulation approach* for synthesis of aryl sulfones may address some of these challenges. This approach, however, has been applied only rarely and the available examples are presented below.

2.4. Synthesis of aryl sulfones via benzannulation reactions

An acyclic sulfone moiety can be converted into arene *via* annulation reaction with another suitable precursor. The acyclic sulfone precursor may be prepared by nucleophilic displacement reaction of leaving group by aryl sodium sulfinate salt. Unlike other methods, in benzannulation strategy the sulfone group is introduced on the arene ring as it is formed. The innate simplicity and verstility of this approach make it a promising strategy for synthesis of aryl sulfones. For example, Fe-Cu co-catalyzed oxidative benzannulation of enynes and sulfonyl hydrazides afforded sulfonyl naphthalene derivatives (Scheme 5) [19]

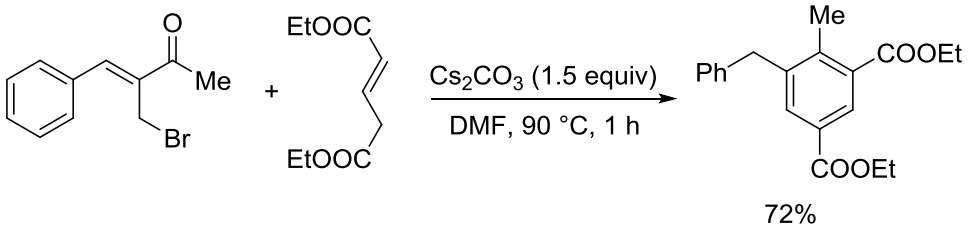


Scheme 5: Synthesis of aryl sulfones via benzannulation reaction of enynes and sulfonyl hydrazides

2.5. Statement of the problem

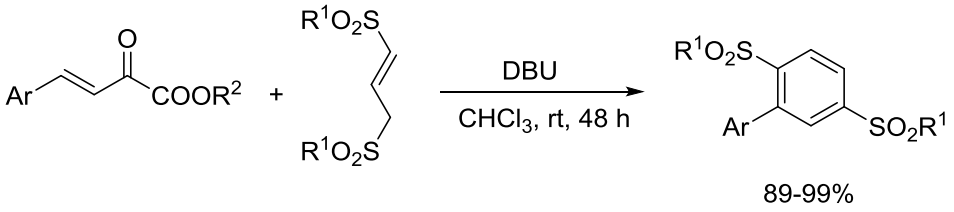
It is worth noting that a highly substituted arene with deactivating groups can be readily synthesized via benzannulation method, however, the introduction of more than one electron withdrawing group is much difficult via electrophilic substitution reaction. Additionally, the regiochemical outcome in electrophilic substitution reactions is determined by the group present on arene ring. As consequences of above discussion, a benzannulation approach for synthesis of highly functionalized sulfonyl arenes appears highly attractive. Our investigations towards this end, led to the development of a convenient and regioselective method for the rapid synthesis of biarylmethanes from simple precursors.

Kim and co-workers in 2013 described a base mediated [3+3] benzannulation reaction of Morita-Baylis-Hillman (MBH) adducts and glutacnoates to afford poly-substituted arene derivatives bearing 1,3-dicarboxylates group (Scheme 6).[20] The MBH adduct contains three electrophilic centers, and the reaction is initiated by displacement of allylic bromide in MBH adduct by nucleophilic end of the 1,3-dicarboxylate anion.



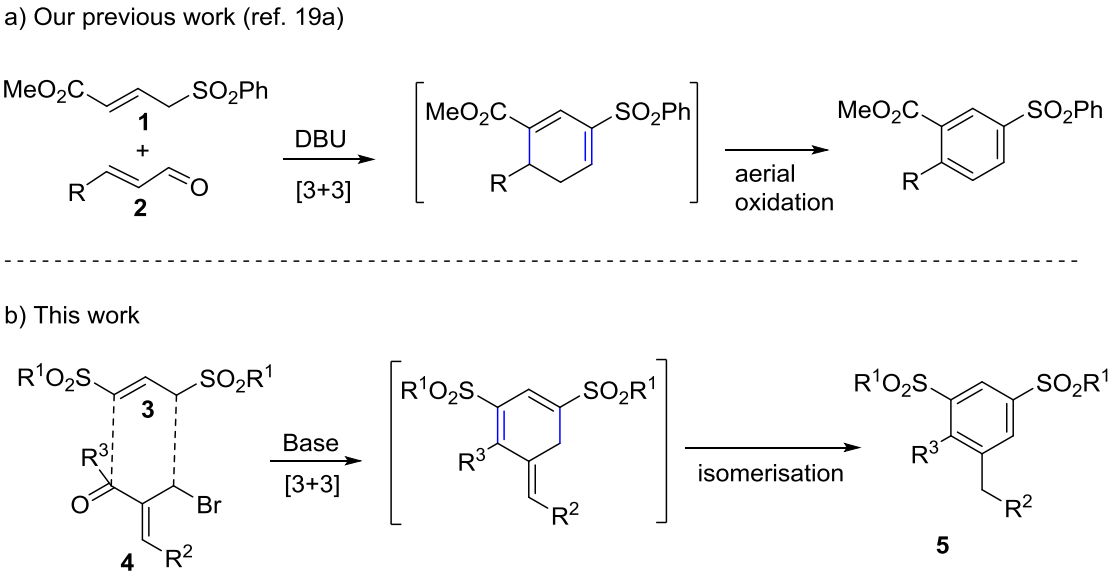
Scheme 6: [3+3] benzannulation of MBH bromide and glutaconates

In 2018 Zhang, Yan and co-workers reported a facile synthesis of aryl sulfones via a base mediated [3+3] benzannulation reaction of 1,3-bis(sulfonyl)propene and β,γ-unsaturated α-ketoester (Scheme 7).[21]



Scheme 7: [3+3] benzannulation of β,γ-unsaturated α-ketoesters and 1,3-bis(sulfonyl)propene

Recently, our group developed an aerial oxidative, [3+3] benzannulation reaction mediated by base that afforded aryl sulfones from 4-sulfonyl crotonates **1** (a bis-nucleophile) and α,β-unsaturated aldehydes and ketones **2** (a 1,3-bis-electrophile) (Scheme 8a).[19a] We surmised that the benzannulation reaction of sulfone bearing symmetric 1,3-bis-nucleophile and a suitable electrophile partner could potentially afford substituted bis-sulfonylarenes (Scheme 8b). For this, we selected Morita-Baylis-Hillman adduct-derived bromide **4** as 3-atom bis-electrophilic building block and 1,3-bis-sulfonylpropene **3** as the bis-nucleophile.



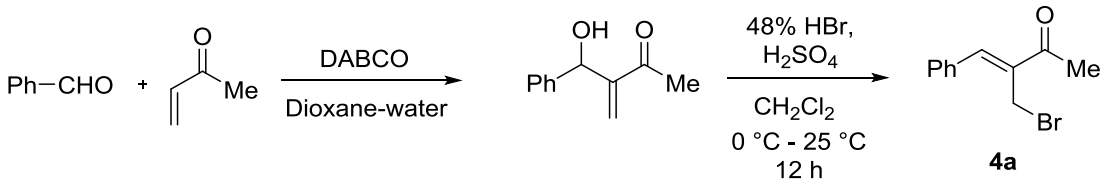
Scheme 8: (a) Benzannulation of enals and bis-sulfonylpropene (b) the present work

Indeed, the MBH bromide **4** incorporates three different electrophilic centers and it was interesting to test its reactivity and regiochemical preferences in a reaction with bis-

nucleophiles **3**. Additional impetus for the exploration came from the easy availability of both the 3-carbon building blocks.

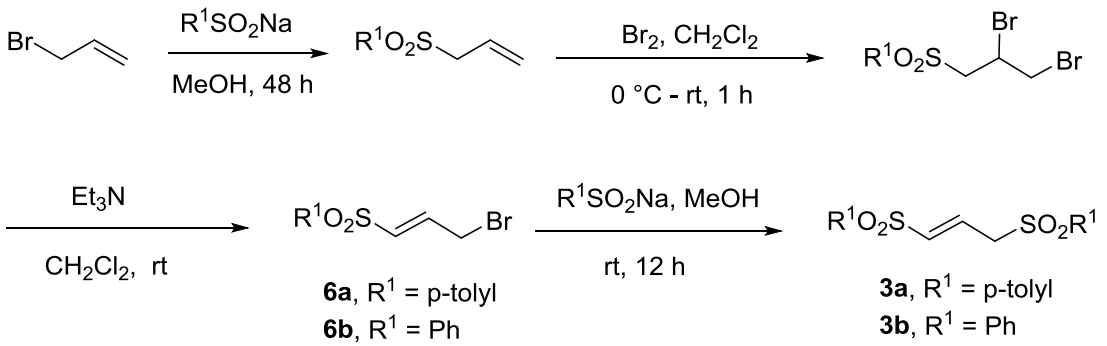
2.6. Results and discussion

In order to test the feasibility of the proposed benzannulation reaction, the required MBH bromide **4a** was prepared from the reaction of benzaldehyde with methyl vinyl ketone in presence of DABCO and followed by bromination with HBr as reported earlier (Scheme 9).[22]



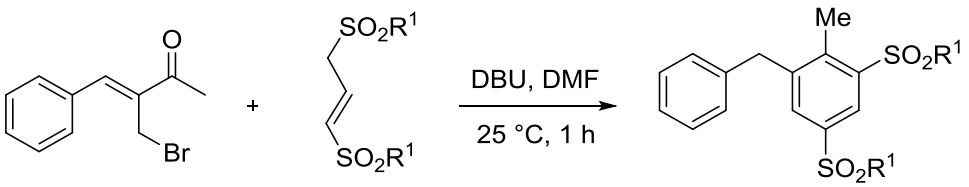
Scheme 9: Preparation of MBH bromide **4a**

The nucleophilic partners, 1,3-bistoluenelsulfonylpropene **3a** and 1,3-bisphenylsulfonylprpopene **3b** were easily prepared via a nucleophilic displacement reaction from the corresponding known bromides **6a, 6b**.[23] These, in turn were assembled from allyl bromide via substitution-bromination-elimination sequence (Scheme 10).



Scheme 10: Preparation of 1,3-bis-arylsulfonylprpopenes **6a-b** from allyl bromide

Once both the reaction partners **4a** and **3a** were at hand, we started our investigations by their union in a benzannulation reaction. Initially, **4a** and **3a** were treated under the conditions of our previously reported benzannulation protocol.[19a] Pleasingly, an aromatic product incorporating both the arenesulfonyl groups was obtained which was assigned the structure **5aa** (Scheme 10). The structure of benzannulated product was assigned on the basis of spectroscopic analysis. The product was isolated as a white crystalline product. The ^{1}H NMR spectrum of **5aa** exhibited a singlet at δ 3.99 (2H) indicating the presence of a methylene group incorporated between two benzene rings. Another singlet at δ 2.35 corresponding to three protons was assigned to methyl group, attached to arene product. Two different doublets at δ 8.63 (d, J = 2.0Hz, 1H) and δ 7.87 (d, J = 2.0, 1H) was assigned to two mutually coupled protons on newly formed arene. Other aliphatic and aromatic hydrogen signals indicated the attachment of tosyl group to benzannulated product. In ^{13}C NMR spectrum signals at δ 39.7 and δ 16.3 confirmed the presence of benzylic methylene and methyl groups in product **5aa**, respectively. All other peaks and other characterization data were also in agreement with the assigned structure (Scheme 11).



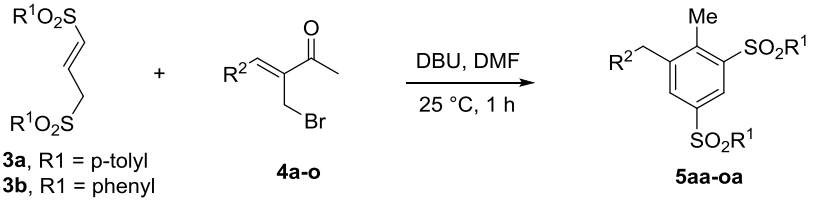
4a **3a**, R^1 = *p*-tolyl **5aa**, 74%

Scheme 11: Benzannulation reaction of **4a** and **3a**

The facile formation of a tetra-substitutes arene from two acyclic precursors prompted us to explore the generality and scope of the benzannulation reaction. For further investigations towards this end, a number of MBH bromides were prepared by

following same method as described in Scheme 8. All of these MBH bromides were then treated with 1,3-bis-arylsulfonyl propene **3a** and **3b** under the optimal conditions of benzannulation reaction. The results are presented in table 1.

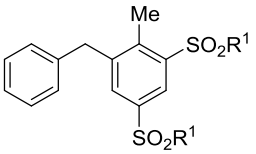
Table 1: Substrate scope of benzannulation reaction[a]



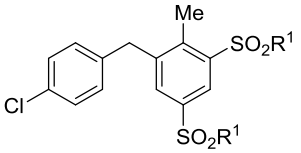
3a, R1 = p-tolyl
3b, R1 = phenyl

4a-o

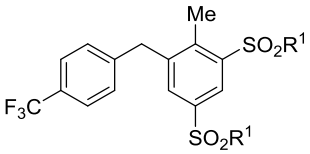
5aa-oa



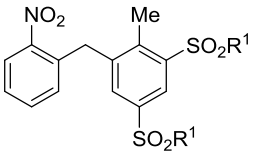
5aa, R^1 = p-tolyl, 74%
5ab, R^1 = phenyl, 75%



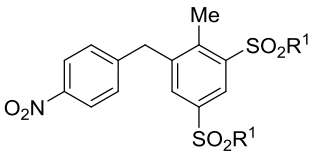
5ba, R^1 = p-tolyl, 71%
5bb, R^1 = phenyl, 74%



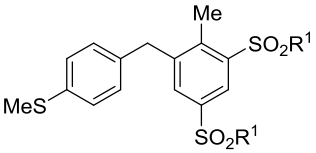
5ca, R^1 = p-tolyl, 66%
5cb, R^1 = phenyl, 69%



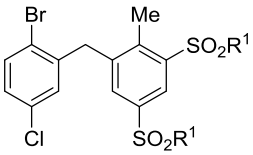
5da, R^1 = p-tolyl, 58%



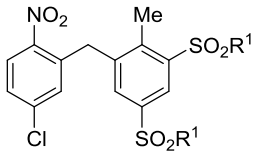
5ea, R^1 = p-tolyl, 56%



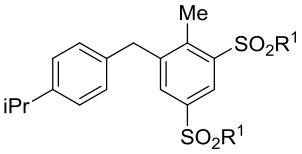
5fa, R^1 = p-tolyl, 78%



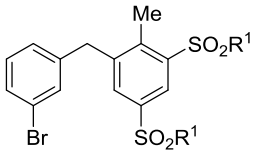
5ga, R^1 = p-tolyl, 67%



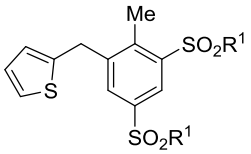
5ha, R^1 = p-tolyl, 62%



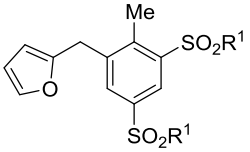
5ia,R^1 = p-tolyl, 75%



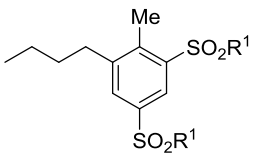
5ja, R^1 = p-tolyl, 73%
5jb, R^1 = phenyl, 76%



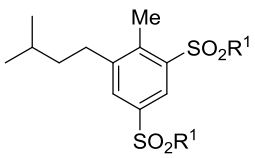
5ka, R^1 = p-tolyl, 72%
5kb, R^1 = phenyl, 74%



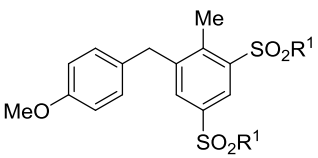
5la, R^1 = p-tolyl, 69%
5lb, R^1 = phenyl, 71%



5ma, R^1 = p-tolyl, 72%



5na, R^1 = p-tolyl, 73%

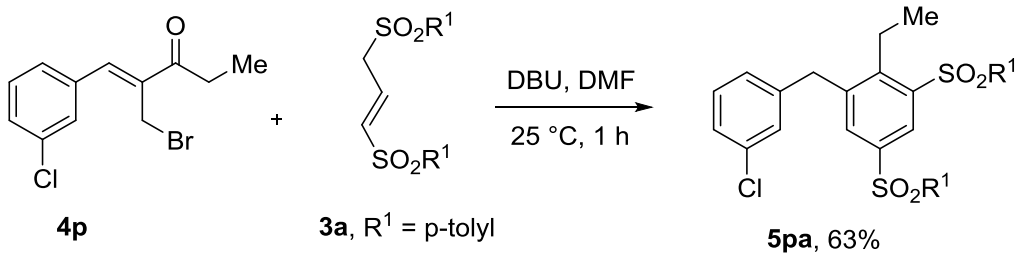


5oa,R^1 = p-tolyl, 82%

[a]reaction conditions: **4** (0.3mmol), **3** (0.33mmol), DBU (0.45mmol), DMF (5ml), 1 h, 25 °C

A variety of MBH adducts **4a-4o** derived from different substituted aldehydes were employed in study reacted smoothly and afforded corresponding tetra-substituted bis-sulfonylarenes **5aa-5oa**. It may be noted that, different groups such as nitro, trifluromethyl, chloro, thiomethyl and bromo can be easily incorporated in biarylmethane products. Electron rich MBH bromide such as *p*-methoxyphenyl ring was also tolerated in the benzannulation reaction. Heteroaryl rings such as thiophene- and furan-bearing biarymethane products (**5ka, 5kb, 5la and 5lb**) may also be synthesized *via* this method. It is worth noting that the reaction is not limited to aryl substrates, alkyl group bearing MBH bromide reacted smoothly to generate corresponding arene **5ma** and **5na**. We tested the scalability of the reaction with 1 g of MBH bromide **4j** and pleasingly, the desired product **5ja** was isolated in 71% yield.

The benzannulation reaction was then tested with an MBH bromide **4p** derived from ethyl vinyl ketone. The treatment of **4p** with **3a** under the conditions of benzannulation reaction afforded ethyl-substituted bis-sulfonylarene **5pa** (Scheme 12).

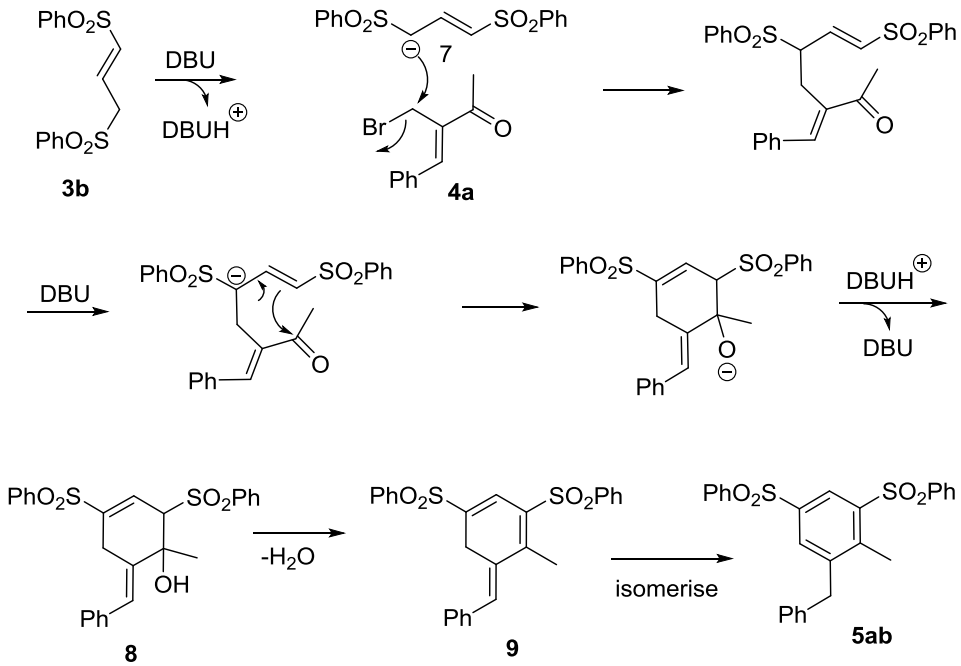


Scheme 12: Benzannulation reaction with MBH bromide derived from ethyl vinyl ketone

It is noteworthy that all the bis-sulfonylarene products are novel molecules. Their synthesis by conventional methods would not be trivial. Additionally, the bis-sulfonylarene products **5aa-5pa** may assume special importance in view of utility as pincer-type ligands.[12]

2.7. Plausible mechanism for benzannulation reaction

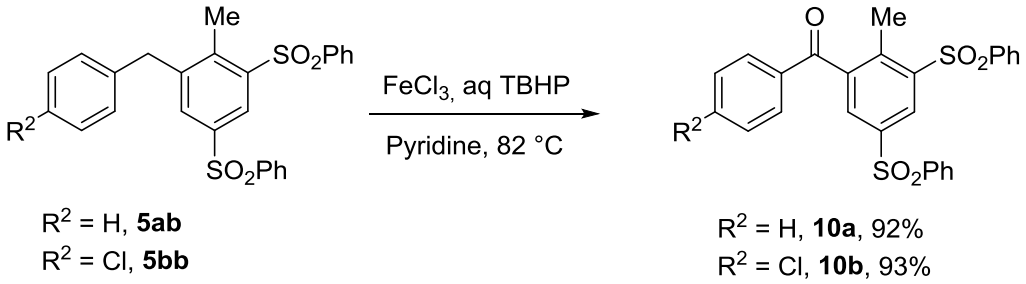
A mechanistic proposal depicted in scheme 12 may be advanced to explain the formation of arene products **5**. Initially, DBU deprotonates 1,3-bisphenylsulfonylprpopene **3b** to afford a stabilized carbanion **7**. This carbanion may interact with MBH bromide **4a** at three different electrophilic sites. These are: (i) 1,2- addition at carbonyl group (ii) 1,4-addition conjugate to the carbonyl group or, (iii) displacement of allylic bromide. It is presumable that the bromine containing carbon is least hindered electrophilic site in MBH bromide **4a** and carbanion **7** displaces bromide in **4a**. It is also noteworthy that the allylic bromide is considered as an activated electrophile in nucleophilic substitution reactions. Further deprotonation and intramolecular cyclisation forms cyclohexenol derivative **8**. It is presumable that intramolecular 1,2-addition of the carbanion to enone moiety is favored over Michael addition due to high steric demands. Dehydration of carbinol **8** then produces cyclohexadiene derivative **9**. The cyclohexadiene readily undergoes isomerisation via [1,3]-H shift to furnish the aromatic product **5ab** (Scheme 13).



Scheme 13: Plausible mechanism of benzannulation reaction

2.8. Synthetic modification of biarylmethane derivatives

The biarylmethane products are amenable to further synthetic modifications. Benzylic oxidation[24] of biarymethanes by *tert*-butyl hydroperoxide (TBHP) and $FeCl_3$ afforded corresponding benzophenone derivatives in excellent yields (Scheme 14). It is important to note that oxidation proceeds selectively at methylene group and methyl group present on phenyl ring was unaffected. Importantly, similar substituted benzophenones are highly sought-after targets for applications in medicinal chemistry, UV-blocking agents and photocatalysis.



R^2 = H, **5ab**
R^2 = Cl, **5bb**

R^2 = H, **10a**, 92%
R^2 = Cl, **10b**, 93%

Scheme 14: Benzophenone synthesis via site-selective oxidation of biarylmethanes

2.9. Conclusion

In conclusion, a [3+3] benzannulation reaction of two readily available, acyclic precursors viz., 1,3-bissulfonyl propenes and MBH-bromides to afford highly substituted bis-sulfonyl arenes has been developed. The newly formed phenyl ring contains two arenesulfonyl groups which are difficult to introduce by other methods. The benzannulation reaction developed here is metal free, mediated by base (DBU) and proceeds at room temperature to generate a highly substituted product. The biarylmethane derivatives can be readily converted into corresponding benzophenone derivatives *via* site-selective oxidation by TBHP and $FeCl_3$. It is presumable that the present benzannulation reaction may find application as a valuable and powerful synthetic tool for the construction of highly substituted arenes.

2.10. Experimental section

General information

All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ solvent at ambient temperature, chemical shift δ are given in ppm on a scale downfield from tetramethylsilane (TMS), and the coupling constant *J* are in Hz. The signal patterns are indicated as follows: s, Singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet; brs = broad). FTIR spectra were recorded as neat. Melting points were recorded on an electrothermal apparatus and are uncorrected. All solvents and reagents were used without further purification unless specified otherwise. Technical grade petroleum ether and ethyl acetate used for column chromatography were distilled prior to use. Column chromatography was carried out using silica gel (60-120 mesh and 100-200 mesh) packed in glass columns. All reactions were performed in oven-dried glassware with magnetic stirring. TLC analysis was performed on 60 F_{254} silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining by $KMnO_4$. High-resolution mass spectra were recorded with q-TOF electrospray mass spectrometer. All purchased chemicals were used as received.

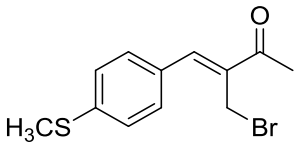
Preparatiom of MBH adduct

In a RB flask a solution of aldehyde (5.0 mmol) and methyl vinyl ketone or ethyl vinyl ketone (7.5 mmol) in 20 ml of 1,4-dioxane-water (1:1, v/v) was stirred at room temperature in presence of DABCO (2 mmol). The reaction progress was monitored by TLC. Upon completion the reaction, mixture was diluted with water and extracted with ether (3×20 ml). The organic layer was washed with brine, dried over sodium sulfate and solvent was evaporated by using rotavapour. The crude product was purified by column charomatography on silica gel using ethyl acetate-petroleum ether as eluent to give desired MBH adduct.

Preparation of MBH bromides 4a-4p[22]

In a RB flask a solution of MBH adduct in DCM (3ml/mmol) kept at 0 ˚C, to this 48% HBr solution (0.4ml/mmol of MBH adduct) was added dropwise. Then, conc. H_2SO_4 (0.3ml/mmol of MBH adduct) was added and stirred overnight at room temperature. The reaction mixture was diluted with water and extracted with DCM (3×10ml). The combined organic layer was dried over sodium sulfate and solvent was evaporated by using rotavapour. The pure product MBH bromide was isolated after column charomatography on silica gel using ethyl acetate-petroleum ether as eluent.

Spectroscopic data for novel MBH bromides



4f, (Z)-3-(bromomethyl)-4-(4-(methylthio)phenyl)but-3-en-2-one

Colorless crystal, 558 mg, 87% (from 500 mg of MBH adduct)

R_f = 0.8 (20% ethyl acetate in hexanes)

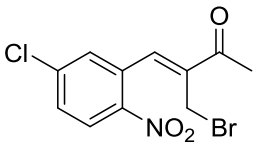
Melting point: 93-94 ˚C

IR (KBr) υ**max**: 2922, 2852, 1657, 1614, 1587, 1489, cm^{-1}

^{1}H NMR (400 MHz, CDCl3) δ 7.58 (s, 1H), 7.55(d, *J* = 8.4Hz, 2H), 7.32(d, *J* = 8.4Hz, 2H), 4.38(s, 2H), 2.53 (s, 3H), 2.50(s, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 197.1, 142.6, 142.5, 142.0, 136.3, 130.4, 125.8, 25.9, 25.4, 15.0

HRMS calcd for $C_{12}H_{13}BrOS$ (M+H) 284.9949; found 284.9949.



4h, (Z)-3-(bromomethyl)-4-(5-chloro-2-nitrophenyl)but-3-en-2-one

Pale yellow solid, 553 mg, 89% (from 500 mg of MBH adduct)

R_f = 0.6 (20% ethyl acetate in hexanes)

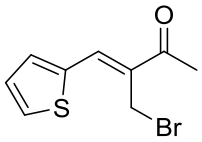
Melting point: 108-109 ˚C

IR (KBr) υ**max**: 1676, 1599, 1560, 1523, 1464, 1427, 1338, 906, 813, 679, 526 cm^{-1}

^{1}H NMR (400 MHz, CDCl3) δ 8.21(d, *J* = 8.8Hz, 1H), 7.88(s, 1H), 7.75(d, *J* = 2.2Hz, 1H), 7.57 (dd, *J* = 8.8, 2.2Hz, 1H), 4.06(s, 2H), 2.53 (s, 3H).

^{13}C NMR (100 MHz, CDCl3) δ 196.4, 145.3, 140.9, 138.6, 138.2, 132.2, 130.3, 129.9, 127.0, 26.2, 23.6

HRMS calcd for $C_{11}H_9BrClNO_3$ (M+H) 317.9533; found 317.9544



4k, (Z)-3-(bromomethyl)-4-(thiophen-2-yl)but-3-en-2-one

Yellow solid, 531 mg, 79% (from 500 mg of MBH adduct)

R_f = 0.7 (20% ethyl acetate in hexanes)

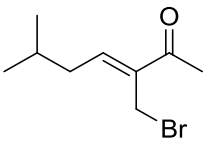
Melting point: 129-131 ˚C

IR (KBr) υ_{max}: 2922, 1659, 1603, 1414, 1203, 700 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.68 (dd, *J* = 5.2, 0.4 Hz, 1H), 7.51 (dd, *J* = 3.6, 0.4 Hz, 1H), 7.20 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.55 (s, 2H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 137.1, 135.5, 134.1, 133.6, 132.6, 128.3, 25.8, 25.0

HRMS calcd for $C_9H_{10}BrOS$ (M+H) 244.9636; found 244.9636.



4n, (Z)-3-(bromomethyl)-6-methylhept-3-en-2-one

Pale Yellow oil, 505 mg, 72% (from 500 mg of MBH adduct)

R_f = 0.7 (20% ethyl acetate in hexanes)

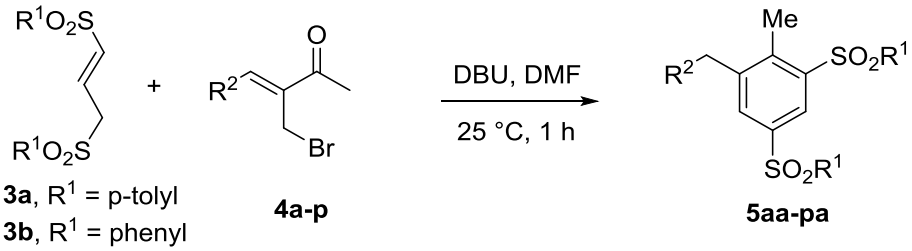
IR (KBr) υ_{max}: 2957, 1670, 1462, 412 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (t, J = 7.5Hz, 1H), 4.16 (s, 2H), 2.33 (s, 3H), 2.25–2.21 (m, 2H), 1.87–1.79 (m, 1H), 0.96 (d, J = 6.7Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 147.7, 139.0, 38.3, 28.3, 25.6, 22.8, 22.7

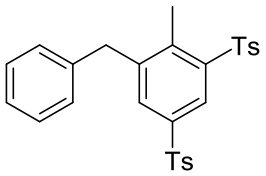
HRMS calcd for $C_9H_{16}BrO$ (M+H) 219.0385; found 219.0379.

General procedure for the DBU-mediated benzannulation reaction



DBU (0.45 mmol) was added to a solution of MBH bromide **4a-p** (0.30 mmol) and 1,3-bissulfonylpropene **3a-b** (0.33 mmol) in DMF (5 mL). The reaction mixture was stirred at 25 ˚C for 1h. After completion of the reaction, 10 mL deionized water was added and the solution was extracted with ethylacetate (3×10 mL). The combined organic layers were washed with brine, dried over sodium sulfate and the solvent was evaporated off on a rotavpor under reduced pressure. The residue was subjected to column charomatography on silica gel using petroleum ether-ethyl acetate as eluent to afford analytically pure sample of the product.

Spectroscopic data for the products 5aa-5pa



5aa, 4,4'-(5-benzyl-4-methyl-1,3-phenylenedisulfonyl)bis(methylbenzene)

White solid, 110 mg, 75%

R_f = 0.6 (20% ethyl acetate in hexanes)

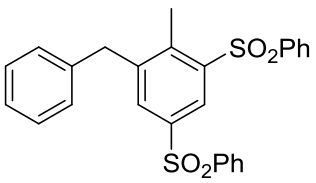
Melting point: 189-191 ˚C

IR (KBr) υ_{max}: 3082, 2926, 1591, 1492, 1442, 1319, 1294, 1147, 540 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 2.0, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.33–7.29 (m, 4H), 7.27–7.20 (m, 3H), 6.94 (d, *J* = 6.5Hz, 2H), 4.00 (s, 2H), 2.43 (s, 6H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.7, 142.3, 141.9, 140.3, 137.9, 137.7, 137.4, 133.2, 130.2, 130.0, 128.9, 128.6, 128.0, 127.9, 126.9, 39.7, 21.7, 16.3

HRMS calcd for $C_{28}H_{27}O_4S_2$ (M+H) 491.1351; found 491.1346.



5ab, (5-benzyl-4-methyl-1, 3-phenylenedisulfonyl)dibenzene

White solid, 108 mg, 75%

R_f = 0.6 (20% ethyl acetate in hexanes)

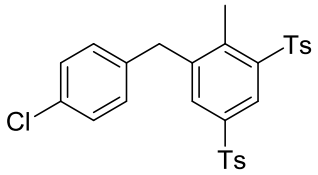
Melting point: 160-162 ˚C

IR (KBr) υ_{max}: 3086, 3059, 1583, 1496, 1446, 1315, 1147, 835, 567 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.0 Hz, 1H), 7.92 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.89 (d, *J* = 2.0, 1H), 7.82 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.61 (t, *J* = 7.2, 2H), 7.65–7.48 (m, 4H), 7.28–7.17 (m, 3H), 6.94 (d, *J* = 6.8Hz, 2H), 4.00 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.7, 141.6, 140.9, 140.3, 140.0, 137.6, 133.8, 133.5, 129.6, 129.4, 129.0, 128.5, 127.9, 127.1, 126.9, 39.7, 16.4.

HRMS calcd for $C_{26}H_{23}O_4S_2$ (M+H) 463.1038; found 463.1049.



5ba, 4,4'-[5-(4-chlorobenzyl)-4-methyl-1,3-phenylenedisulfonyl]bis(methylbenzene)

White solid, 112 mg, 71%

R_f = 0.6 (20% ethyl acetate in hexanes)

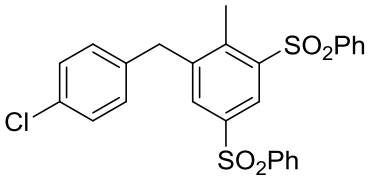
Melting point: 192-194 ˚C

IR (KBr) υ_{max}: 3066, 2920, 1595, 1492, 1435, 1404, 1303, 1143, 817, 711, 667 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 2.0, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4, 2H), 7.33–7.29 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4, 2H), 3.95 (s, 2H), 2.42 (s, 6H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (2), 143.1, 142.2, 142.1, 140.5, 137.8, 137.3, 136.3, 133.1, 132.7, 130.3, 130.0, 129.9, 129.0, 128.0, 127.9, 127.0, 39.0, 21.74, 16.3.

HRMS calcd for $C_{28}H_{26}ClO_4S_2$ (M+H) 525.0961; found 525.0978.



5bb, (5-(4-chlorobenzyl)-4-methyl-1, 3-phenylenedisulfonyl)dibenzene

White solid, 112 mg, 74%

R_f = 0.4 (20% ethyl acetate in hexanes)

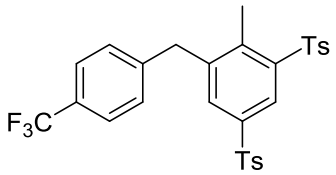
Melting point: 147-149 ˚C

IR (KBr) υ_{max}: 3082, 1581, 1489, 1442, 1315, 1149, 559 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 2.0 Hz, 1H), 7.92 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.64–7.59 (m, 2H), 7.55(d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.4Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.5, 141.8, 140.7, 140.2, 136.1, 133.8, 133.4, 132.8, 129.9, 129.7, 129.4, 129.1, 127.9, 127.3, 39.0, 16.4.

HRMS calcd for $C_{26}H_{22}ClO_4S_2$ (M+H) 497.0648; found 497.0631.



5ca, 4,4'-{4-methyl-5-[4-(trifluromethyl)benzyl]-1,3-phenylenedisulfonyl} bis(methylbenzene)

White solid, 110 mg, 66%

R_f = 0.6 (20% ethyl acetate in hexanes)

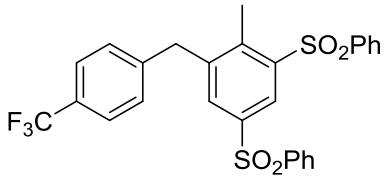
Melting point: 187-189 ˚C

IR (KBr) υ_{max}: 3082, 2925, 1593, 1419, 1323, 1149, 1112, 812, 709, 659 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 2.0, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4, 2H), 7.49 (d, *J* = 8.1, 2H), 7.33–7.28 (m, 4H), 7.05 (d, *J* = 8.1, 2H), 4.05 (s, 2H), 2.42 (s, 6H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 144.8, 142.4, 142.1 (2), 140.5, 137.6, 137.1, 133.1, 130.2, 129.9, 128.7, 127.9, 127.8, 127.1, 125.7(q, *J* = 3.8Hz), 39.3, 21.6 (2), 16.3

HRMS calcd for $C_{29}H_{26}F_3O_4S_2$ (M+H) 559.1225; found 559.1206.



5cb, {4-methyl-5-[4-(trifluromethyl)benzyl]-1,3-phenylenedisulfonyl}dibenzene

White solid, 110 mg, 69%

R_f = 0.5 (20% ethyl acetate in hexanes)

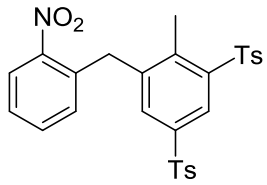
Melting point: 156-157 ˚C

IR (KBr) υ_{max}: 3066, 1583, 1448, 1325, 1298, 1142, 1112, 1070, 690, 549 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.63–7.54 (m, 2H), 7.53-7.49 (m, 6H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.07 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 142.4, 141.9, 141.7, 140.5, 140.2, 140.0, 133.8, 133.7, 133.4, 129.6, 129.3, 128.7, 127.8 (2), 127.3, 125.8 (q, *J* = 3.6 Hz), 39.3, 16.3

HRMS calcd for $C_{27}H_{22}F_3O_4S_2$ (M+H) 531.0912; found 531.0930.



5da, 4,4'-[4-methyl-5-(2-nitrobenzyl)-1,3-phenylenedisulfonyl]bis(methylbenzene)

White solid, 93 mg, 58%

R_f = 0.4 (20% ethyl acetate in hexanes)

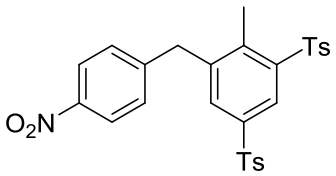
Melting point: 170-172 ˚C

IR (KBr) υ_{max}: 3059, 2922, 1593, 1523, 1435, 1348, 1315, 1143, 837, 659 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.6 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.73 (d, *J* = 8.4Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.53–7.40 (m, 2H), 7.32–7.28 (m ,4H), 6.92 (d, *J* = 7.6Hz, 1H), 4.28 (s, 2H), 2.41 (s, 6H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 144.9, 142.1(2), 141.8, 140.6, 137.7, 137.2, 133.8, 132.8, 132.3, 131.6, 130.2, 130.0, 128.5, 128.0, 127.9, 127.1, 125.5, 36.6, 21.8, 16.3.

HRMS calcd for $C_{28}H_{26}NO_6S_2$ (M+H) 536.1202; found 536.1243.



5ea, 4,4'-[4-methyl-5-(4-nitrobenzyl)-1,3-phenylenedisulfonyl]bis(methylbenzene)

White solid, 90 mg, 56%

R_f = 0.4 (20% ethyl acetate in hexanes)

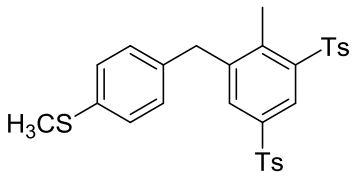
Melting point: 122-124 ˚C

IR (KBr) υ_{max}: 3072, 2924, 1597, 1519, 1492, 1438, 1348, 1309, 1145, 837, 812, 705, 661 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.33–7.29 (m, 4H), 7.10 (d, *J* = 8.5Hz, 2H), 4.10 (s, 2H), 2.42 (s, 6H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 145.5, 145.1(2), 142.4, 142.2, 141.8, 140.8, 137.6, 137.0, 133.2, 130.4, 130.1, 129.3, 128.0, 127.9, 127.4, 124.1, 39.5, 21.8, 16.4

HRMS calcd for $C_{28}H_{26}NO_6S_2$ (M+H) 536.1202; found 536.1225.



5fa, 4,4'-[4-methyl-5-(4-methylthiobenzyl)-1,3-phenylenedisulfonyl]bis(methylbenzene)

White solid, 126 mg, 78%

R_f = 0.5 (20% ethyl acetate in hexanes)

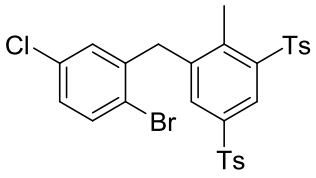
Melting point: 145-147 ˚C

IR (KBr) υ_{max}: 3062, 2924, 1593, 1492, 1436, 1319, 1147, 1085, 707, 671, 545 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.5 Hz, 1H), 7.86 (d, *J* = 1.5 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.32–7.28 (m, 4H), 7.12 (d, *J* = 8.2Hz, 2H), 6.85 (d, *J* = 8.2Hz, 2H), 3.94 (s, 2H), 2.45 (s, 3H), 2.42 (s, 6H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.4, 142.1, 141.8, 140.2, 137.7, 137.2, 136.8, 134.4, 133.0, 130.1, 129.9, 129.8, 128.9, 127.8, 126.9, 39.0, 21.6, 16.2, 15.8

HRMS calcd for $C_{29}H_{29}O_4S_3$ (M+H) 537.1228; found 537.1247.



5ga, 4,4'-[5-(2-bromo-5-chlorobenzyl)-4-methyl-1,3-phenylenedisulfonyl] bis(methylbenzene)

White solid, 121 mg, 67%

R_f = 0.5 (20% ethyl acetate in hexanes)

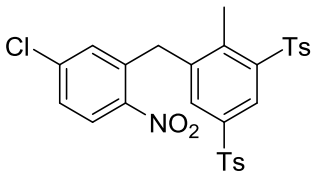
Melting point: 189-191 ˚C

IR (KBr) υ_{max}: 3062, 2924, 1593, 1448, 1317, 1143, 1087,812, 711, 549 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3Hz, 2H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.50(d, *J* = 8.5, 1H), 7.31 (d, *J* = 8.4 Hz, 4H), 7.11 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 4.00 (s, 2H), 2.42 (s, 6H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 142.2, 142.0, 141.5, 140.6, 139.0, 137.7, 137.2, 134.3, 134.2, 134.0, 132.7, 130.3(2), 130.1, 130.0, 129.0, 127.9, 127.1, 122.7, 39.7, 21.8, 21.73, 16.3.

HRMS calcd for $C_{28}H_{25}BrClO_4S_2$ (M+H) 603.0066; found 603.0076.



5ha, 4,4'-[5-(5-chloro-2-nitrobenzyl)-4-methyl-1,3-phenylenedisulfonyl] bis(methylbenzene)

White solid, 106 mg, 62%

R_f = 0.5 (20% ethyl acetate in hexanes)

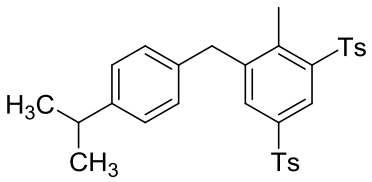
Melting point: 182-184 ˚C

IR (KBr) υ_{max}: 3067, 2927, 1525, 1440, 1313, 1296, 1145,813, 549 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 1.6, 1H), 7.42 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.32 (d, *J* = 8.0, 4H), 6.81 (d, *J* = 2.0, 1H), 4.28 (s, 2H), 2.42 (s, 6H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 145.0(2), 142.3, 142.0, 140.8(2), 140.3, 137.6, 137.2, 135.0, 132.3, 131.4, 130.3, 130.1, 128.7, 128.0, 127.9, 127.4, 127.0, 36.5, 21.7, 16.3.

HRMS calcd for $C_{28}H_{25}ClNO_6S_2$ (M+H) 570.0812; found 570.0832.



5ia, 4,4'-[5-(4-isopropylbenzyl)-4-methyl-1,3-phenylenedisulfonyl]bis(methylbenzene)

White solid, 120 mg, 75%

R_f = 0.7 (20% ethyl acetate in hexanes)

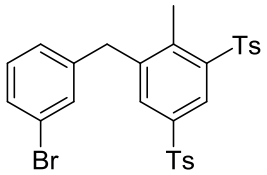
Melting point: 167-168 ˚C

IR (KBr) υ_{max}: 3078, 2964, 1593, 1425, 1319, 1139, 1083, 808, 705, 671, 565 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.8 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2Hz, 2H), 7.32-7.28 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 2H), 2.89-2.80 (m, 1H), 2.42 (s, 6H), 2.35 (s, 3H), 1.21 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 144.8(2), 144.0, 142.3, 141.8, 140.2, 138.0, 137.4, 135.0, 133.2, 130.2, 130.0, 128.4, 128.0, 127.9, 126.9, 126.8, 39.2, 33.7, 24.0, 21.74, 21.72, 16.4

HRMS calcd for $C_{31}H_{33}O_4S_2$ (M+H) 533.1820; found 533.1829.



5ja, 4,4'-[5-(3-bromobenzyl)-4-methyl-1,3-phenylenedisulfonyl]bis(methylbenzene)

White solid, 125 mg, 73%

R_f = 0.6 (20% ethyl acetate in hexanes)

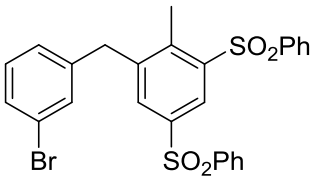
Melting point: 204-206 ˚C

IR (KBr) υ_{max}: 3072, 2924, 1591, 1566, 1446, 1294, 1141, 840, 812, 709, 661, 545 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 1.6Hz, 1H), 7.79 (d, *J* = 8.3Hz, 2H), 7.70 (d, *J* = 8.3Hz, 2H), 7.35-7.29 (m, 5H), 7.14–7.10 (m, 1H), 7.05 (s, 1H), 6.87 (d, *J* = 7.7Hz, 1H), 3.96 (s, 2H), 2.42 (s, 6H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 144.7, 142.6, 142.1, 141.9, 140.4, 139.9, 137.6, 137.1, 133.0, 131.4, 130.3, 130.2, 129.9, 127.8, 127.8, 127.1, 126.9, 122.8, 39.2, 21.6 (2), 16.2

HRMS calcd for $C_{28}H_{26}BrO_4S_2$ (M+H) 569.0456; found 569.0444.



5jb, [5-(3-bromobenzyl)-4-methyl-1,3-phenylenedisulfonyl]dibenzene

White solid, 124 mg, 76%

R_f = 0.5 (20% ethyl acetate in hexanes)

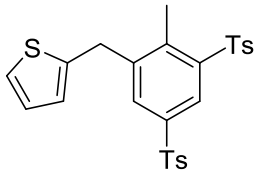
Melting point: 156-157 ˚C

IR (KBr) υ_{max}: 3064, 1568, 1446, 1309, 1143, 1978, 684, 567 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 1.6 Hz, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 1.6 Hz, 1H), 7.82 (d, J = 7.2 Hz, 2H), 7.62–7.60 (m, 2H), 7.56-7.50 (m, 4H), 7.34 (d, J = 7.4 Hz, 1H), 7.14-7.01 (m, 1H), 7.07 (s, 1H), 6.86 (d, J = 7.4 Hz, 1H), 3.97 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 142.6, 141.8, 140.7, 140.2, 139.9, 133.9, 133.8, 133.5, 131.5, 130.5, 130.2, 129.7, 129.5, 127.9, 127.3, 127.2, 123.0, 39.2, 16.4.

HRMS calcd for $C_{26}H_{22}BrO_4S_2$ (M+H) 541.0143; found 541.0122.



5ka, 2-(2-methyl-3,5ditosylbenzyl)thiophene

White solid, 107 mg, 72%

R_f = 0.6 (20% ethyl acetate in hexanes)

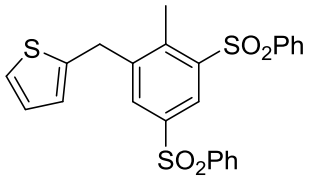
Melting point: 199-201 ˚C

IR (KBr) υ_{max}: 2924, 1591, 1498, 1436, 1315, 1294, 1143, 1083,812, 542 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 2.0 Hz, 1H), 7.95 (d, J = 2.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.32–7.29 (m, 4H), 7.14 (d, J = 5.1 Hz, 1H), 6.88 (dd, J = 5.1, 3.5 Hz, 1H), 6.58 (d, J = 3.5 Hz, 1H), 4.14 (s, 2H), 2.41 (s, 6H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.2, 142.0, 141.9, 140.5, 140.4, 137.9, 137.3, 132.8, 130.2, 130.0, 128.0, 127.9, 127.2, 125.9, 124.8, 124.7, 34.0, 21.8, 16.2.

HRMS calcd for $C_{26}H_{25}O_4S_3$ (M+H) 497.0915; found 497.0933.



5kb, 2-[2-methyl-3,5bis(phenylsulfonyl)benzyl]thiophene

White solid, 104 mg, 74%

R_f = 0.5 (20% ethyl acetate in hexanes)

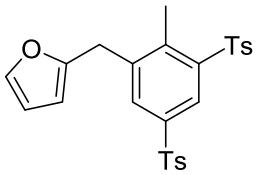
Melting point: 187-189 ˚C

IR (KBr) υ_{max}: 3082, 2362, 1581, 1444, 1311, 1147, 1089, 725, 686, 570 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.0 Hz, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.83 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.62–7.60 (m, 2H), 7.56 – 7.52 (m, 4H), 7.14 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.88 (dd, *J* = 5.2, 3.6Hz, 1H), 6.59 (dd, *J* = 3.6, 1.2Hz, 1H), 4.16 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.3, 141.7, 140.8, 140.3, 140.2(2), 133.8, 133.1, 129.7, 126.4, 127.9, 127.4, 127.2, 126.0, 124.8, 34.0, 16.2.

HRMS calcd for $C_{24}H_{21}O_4S_3$ (M+H) 469.0602; found 469.0590.



5la, 2-(2-methyl-3,5-ditosylbenzyl)furan

White solid, 100 mg, 70%

R_f = 0.5 (20% ethyl acetate in hexanes)

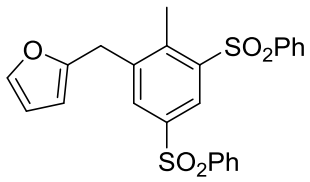
Melting point: 203-204 ˚C

IR (KBr) υ_{max}: 2926, 1593, 1498, 1440, 1315, 1294, 1143, 1083,810, 707, 553 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 8.3Hz, 2H), 7.71 (d, *J* = 8.3Hz, 2H), 7.32–7.30 (m, 4H), 7.28 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.25 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.87 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.95 (s, 2H), 2.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 144.8, 142.1, 142.0, 141.8, 141.2, 140.4, 137.9, 137.3, 133.0, 130.3, 130.0, 128.0, 127.9, 127.2, 110.6, 110.5, 107.5, 107.4, 32.5, 21.7, 16.1.

HRMS calcd for $C_{26}H_{25}O_5S_2$ (M+H) 481.1143; found 481.1166.



5lb, 2-[2-methyl-3,5bis(phenylsulfonyl)benzyl]furan

White solid, 97 mg, 71%

R_f = 0.5 (20% ethyl acetate in hexanes)

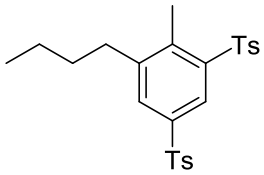
Melting point: 175-177 ˚C

IR (KBr) υ_{max}: 2922, 2855, 2306, 1585, 1444,1307, 1145, 725, 535 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 2.0 Hz, 1H), 7.97–7.88 (m, 3H), 7.83 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.64–7.56 (m, 2H), 7.56–7.48 (m, 4H), 7.28 (dd, *J* = 2.0, 0.8Hz, 1H), 6.26 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.88 (dd, *J* = 3.2, 0.8 Hz, 1H), 3.96 (s, 2H), 2.42 (s, 3H).).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 141.6, 141.4, 140.3, 140.1, 133.8, 133.3, 129.6, 129.4, 127.9, 110.6(2), 107.5(2), 32.5, 16.2.

HRMS calcd for $C_{24}H_{21}O_5S_2$ (M+H) 453.0830; found 453.0840.



5ma, 4, 4'-(5-butyl-4-methyl-1,3-phenylenedisulfonyl)bis(methylbenzene)

White solid, 99 mg, 72%

R_f = 0.7 (20% ethyl acetate in hexanes)

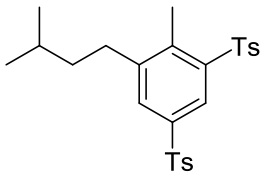
Melting point: 146-148 ˚C

IR (KBr) υ_{max}: 3068, 2953, 2924, 2864, 1593, 1442, 1309, 1296, 1145, 1085, 813, 565, 549 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 2.0Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.32-7.25 (m, 4H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 6H), 2.38 (s, 3H), 1.48-1.44 (m, 2H), 1.35-1.29 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 144.8, 144.7, 141.5, 141.4, 140.0, 138.1, 137.5, 132.2, 130.2, 130.0, 128.0, 127.9, 126.3, 33.5, 31.9, 22.6, 21.7, 15.8, 13.9.

HRMS calcd for $C_{25}H_{29}O_4S_2$ (M+H) 457.1507; found 457.1499.



5na, 4, 4'-(5-isopentyl-4-methyl-1,3-phenylenedisulfonyl)bis(methylbenzene)

White solid, 103 mg, 73%

R_f = 0.7 (20% ethyl acetate in hexanes)

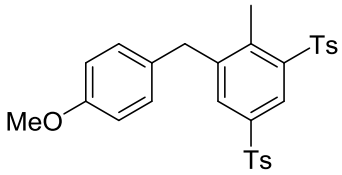
Melting point: 165-167 ˚C

IR (KBr) υ_{max}: 3072, 2958, 2908, 1593, 1442, 1313, 1296, 1145, 1083, 812, 549 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.33–7.26 (m, 4H), 2.60 (t, *J* = 8Hz, 2H), 2.42 (s, 6H),2.39 (s, 3H), 1.59–1.56 (m, 1H), 1.38-1.32 (m, 2H), 0.91 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 144.7(2), 141.5, 141.3, 140.1, 138.1, 137.5, 132.1, 130.2, 130.0, 128.0, 127.9, 126.3, 39.0, 31.7, 28.3, 22.4, 21.7, 15.7.

HRMS calcd for $C_{26}H_{31}O_4S_2$ (M+H) 471.1664; found 471.1657.



5oa, 4,4'-(5-(4-methoxybenzyl)-4-methyl-1,3-phenylenedisulfonyl)bis(methylbenzene)

White solid, 128 mg, 82%

R_f = 0.5 (20% ethyl acetate in hexanes)

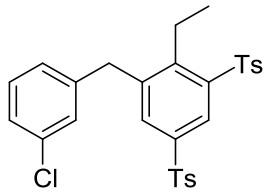
Melting point: 167-169 ˚C

IR (KBr) υ**max**: 2926, 1591, 1510, 1444, 1315, 1246, 1150, 567, 545 cm-1

1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.8 Hz, 1H), 7.84 (d, *J* = 1.8Hz, 1H), 7.78 (d, *J* = 8.2Hz, 2H), 7.69 (d, *J* = 8.2Hz, 2H), 7.29(dd, *J* = 7.9, 5.9Hz, 4H), 6.85 (d, *J* = 8.5Hz, 2H), 6.77 (d, *J* = 8.5Hz, 2H), 3.91 (s, 2H), 3.76 (s, 3H), 2.40(s, 6H), 2.34 (s, 3H).

13C NMR (100 MHz, $CDCl_3$) δ 158.4, 144.8, 144.7, 144.2, 142.2, 141.8, 140.2, 137.9, 137.4, 133.0, 130.2, 129.9.8, 129.6, 128.0, 127.9, 126.7, 114.3, 55.3, 38.8, 21.7, 16.2

HRMS calcd for $C_{29}H_{28}O_5S_2$ (M+H) 521.1457; found 521.1479.



5pa, 4,4'-(5-(3-chlorobenzyl)-4-ethyl-1,3-phenylenedisulfonyl)bis(methylbenzene)

White solid, 102 mg, 63 %

R_f = 0.6 (20% ethyl acetate in hexanes)

Melting point: 146-148 ˚C

IR (KBr) υ**max**: 2976, 1591, 1475, 1429, 1317, 1294, 1147, 669, 559 cm-1

1H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 1.6 Hz, 1H), 7.74–7.69 (m, 5H), 7.31 (dd, *J* = 8.4, 2.0Hz, 4H), 7.20-7.18 (m, 2H), 6.89(s, 1H), 6.84 (dd, *J* = 8.4, 1.6Hz, 1H), 3.99 (s, 2H), 2.89 (q, *J* = 7.4Hz 2H), 2.41(s, 6H), 0.88 (t, *J* = 7.4Hz, 3H).

13C NMR (100 MHz, $CDCl_3$) δ 147.7, 144.9, 144.8, 142.7, 141.9, 140.5, 140.4, 137.9, 137.7, 134.8, 133.7, 130.3, 130.2, 130.1, 128.7, 128.0, 127.9, 127.3, 127.2, 126.9, 37.6, 22.9, 21.7, 14.1.

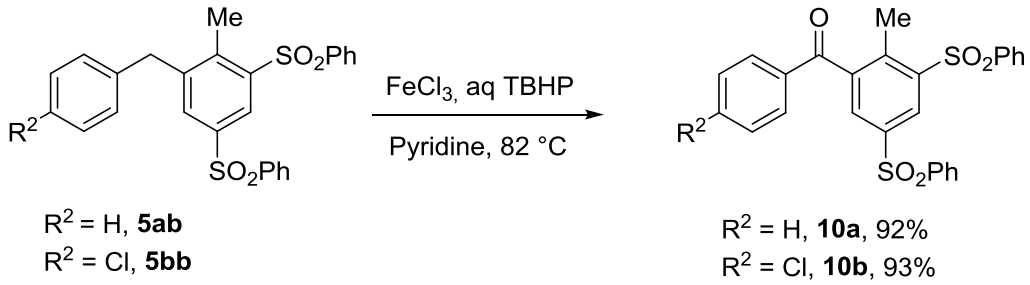
HRMS calcd for $C_{29}H_{27}ClO_4S_2$ (M+H) 539.1118; found 539.1121.

Procedure for gram scale benzannulation reaction

DBU (0.88ml, 5.88 mmol) was added to a solution of MBH bromide **4j** (1g, 3.92 mmol) and 1,3-bissulfonylpropene **3a-b** (1.51g, 4.31 mmol) in DMF (15 mL). The reaction mixture was stirred at 25 ˚C for 1h. After completion of the reaction, 50 mL deionized water was added and the solution was extracted with ethylacetate (3×30 mL). The combined organic layers were washed with brine, dried over sodium sulfate and the solvent was evaporated off on a rotavpor under reduced pressure. The residue was subjected to column charomatography on silica gel using petroleum ether-ethyl acetate

as eluent to afford analytically pure sample of the product. A white solid (1.58g, 71%) which was identical to the product **5ja** obtained in the low-scale reaction.

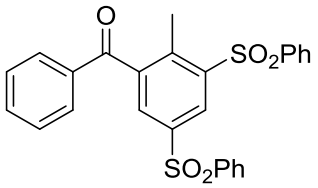
General procedure for $FeCl_3$-TBHP mediated benzylic oxidation



R^2 = H, **5ab**
R^2 = Cl, **5bb**

R^2 = H, **10a**, 92%
R^2 = Cl, **10b**, 93%

To a solution of $FeCl_3.6H_2O$ (2.2 mg, 0.008 mmol) in pyridine (0.5 mL), the bis-sulfonyl arene **5ab** or **5bb** (0.22 mmol) was added. To this, tert-butyl hydroperoxide (0.05 mL, 0.33 mmol) was added and the reation mixture heated at 82 ˚C for 24 h. Then the reaction mixture was poured into a separating funnel containing 10 mL 1N HCl. The solution was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried with anhydrous sodium sulphate, filtered and the solvent was evaporated off on a rotavapor under reduced pressure. The residue was subjected to column chromatography on silica gel using petroleum ether-ethyl acetate as eluent to afford the benzphenones **10a-b** in analytically pure form.



10a, [2-methyl-3,5-bis(phenylsulfonyl)phenyl](phenyl)methanone

White solid, 96 mg, 92%

R_f = 0.5 (20% ethyl acetate in hexanes)

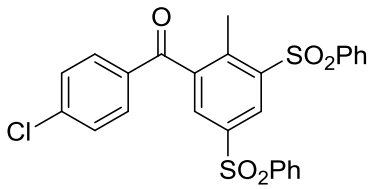
Melting point: 168-170 ˚C

IR (KBr) υ_{max}: 3066, 1664, 1583, 1442, 1296, 1145, 1078, 727, 684, 559 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 1.9 Hz, 1H), 8.03 (d, *J* = 1.9 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.67–7.63 (m, 5H), 7.58– 7.53 (m, 4H), 7.46 (t, *J* = 8.0 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 143.4, 142.3, 141.6, 140.5, 140.3, 139.6, 135.7, 134.8, 134.1, 130.8, 130.2, 129.8, 129.6, 129.1, 128.1, 128.0, 17.4.

HRMS calcd for $C_{26}H_{21}O_5S_2$ (M+H) 477.0830; found 477.0852.



10b, (4-chlorophenyl)[2-methyl-3,5-bis(phenylsulfonyl)phenyl]methanone

White solid, 102 mg, 91%

R_f = 0.6 (20% ethyl acetate in hexanes)

Melting point: 153-155 ˚C

IR (KBr) υ_{max}: 3068, 2974, 1672, 1585, 1444, 1317, 1143, 1085, 723, 688, 559 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 1.9 Hz, 1H), 8.00 (d, *J* = 1.9 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.6, 2H), 7.67–7.53(m, 8H), 7.43 (d, *J* = 8.5, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 142.8, 142.5, 141.6, 141.5, 140.7, 140.3, 139.6, 134.2, 134.1, 131.5, 130.7, 129.8, 129.6, 128.2, 128.0, 17.4.

HRMS calcd for $C_{26}H_{20}ClO_5S_2$ (M+H) 511.0441; found 511.0461.

2.11. References

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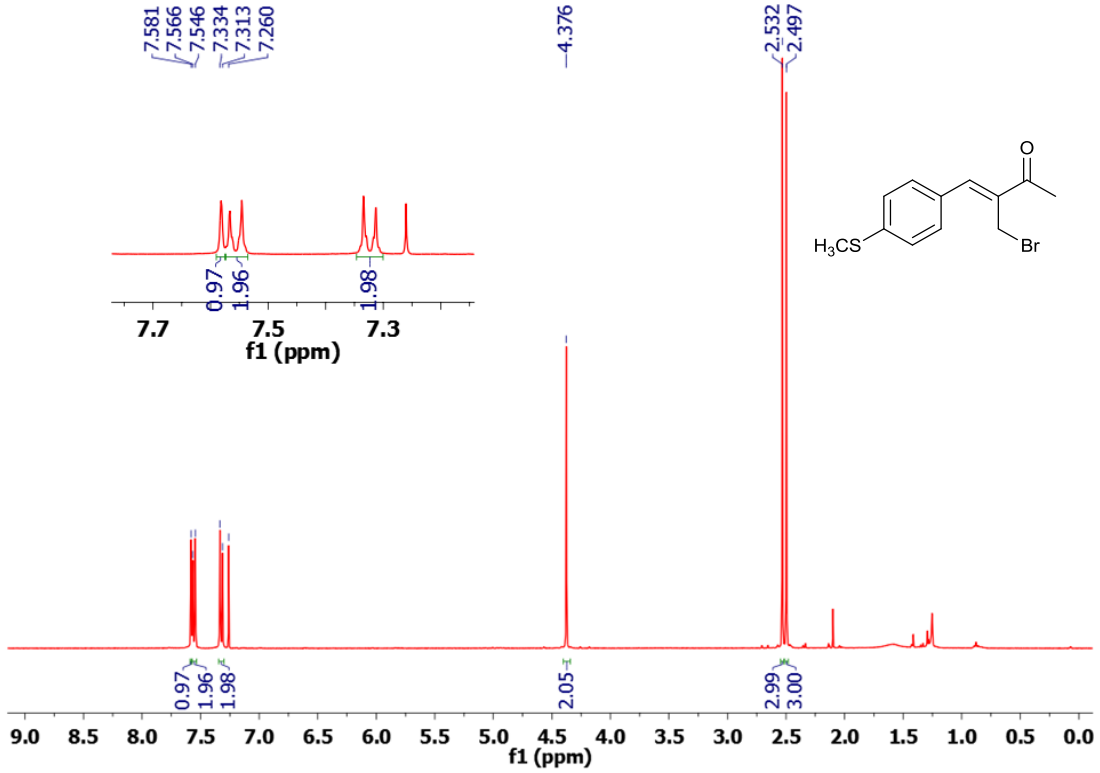
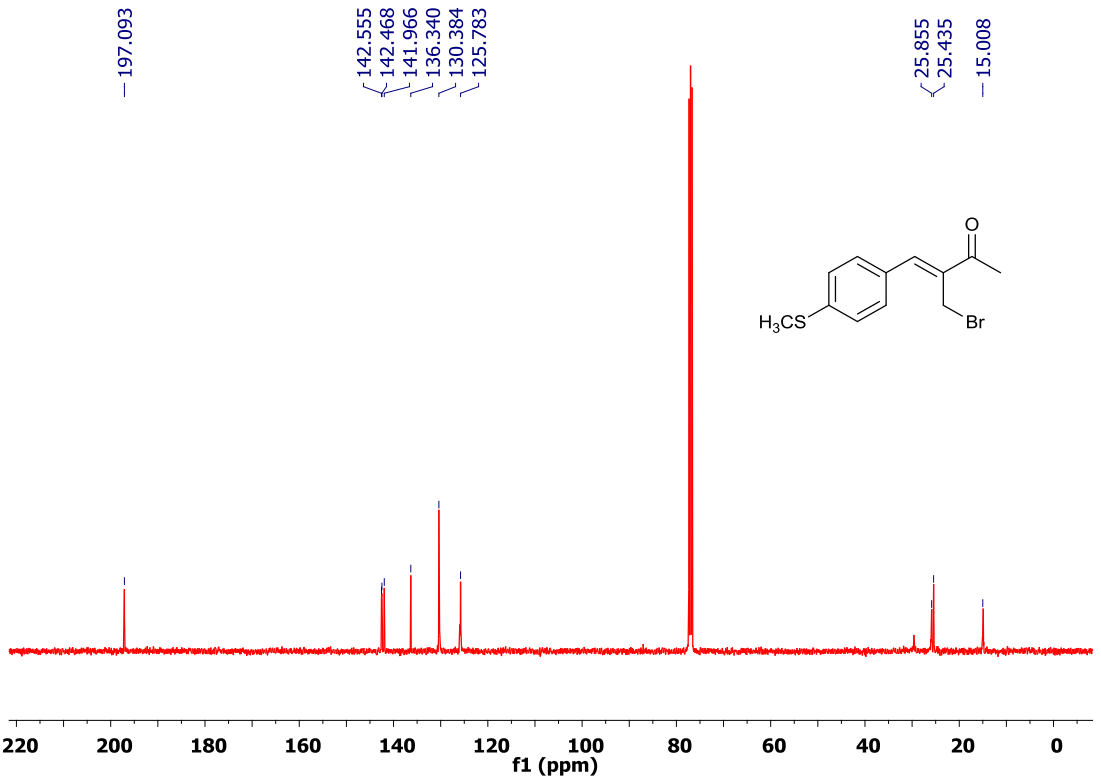
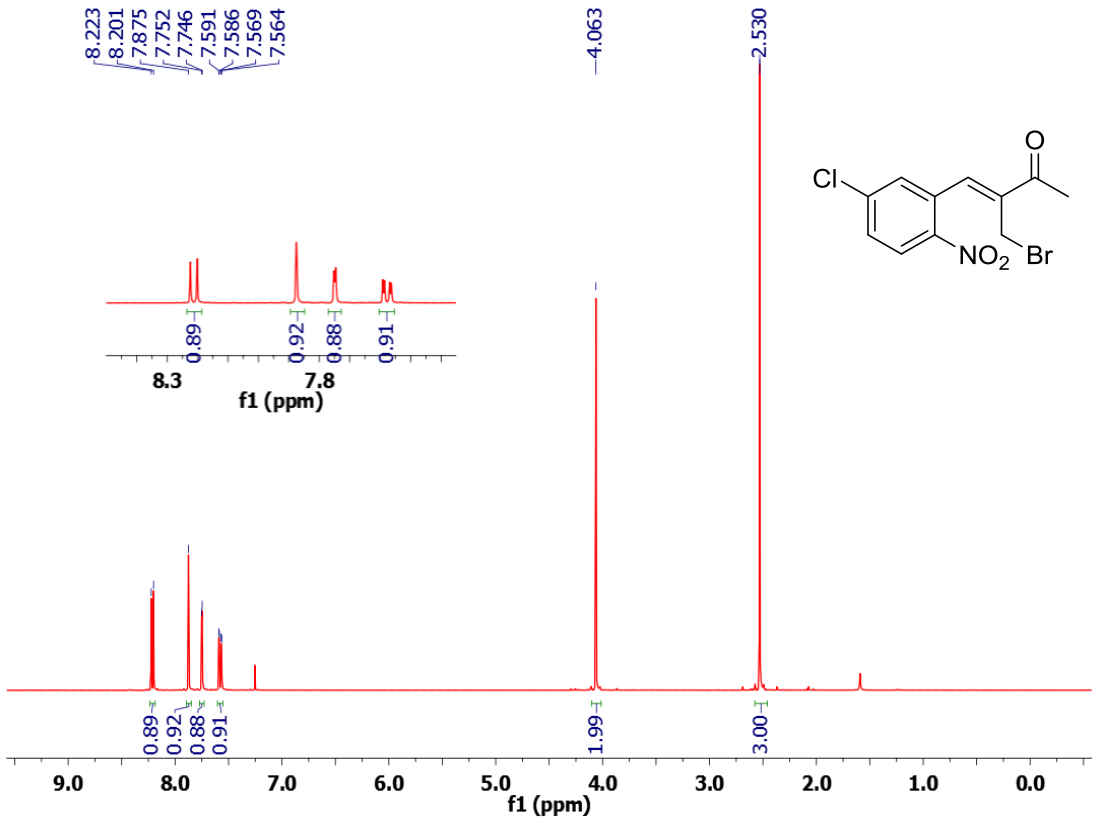
2.12. NMR spectra of new compounds [^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$)]



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7.586
7.569
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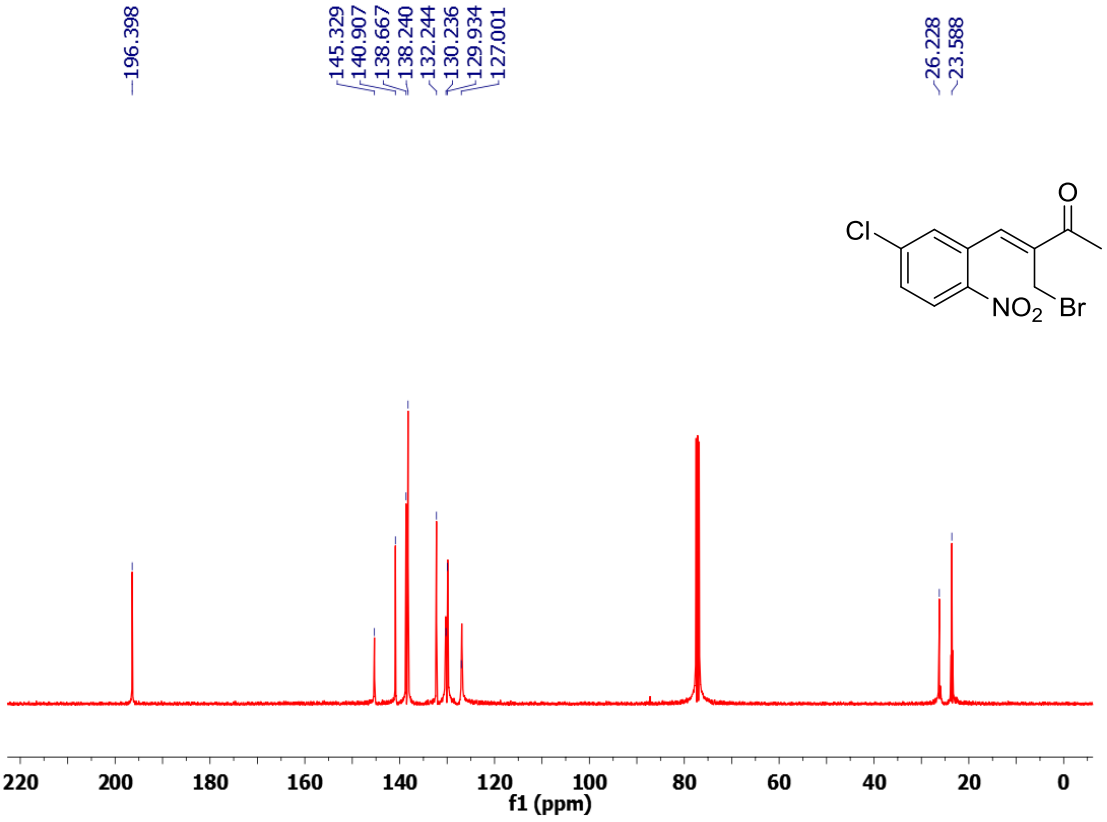
O
NO2
Br
0.89
0.92
0.88
0.91
8.3
7.8
f1 (ppm)
1.99
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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Cl
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NO2
Br
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200
180
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140
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80
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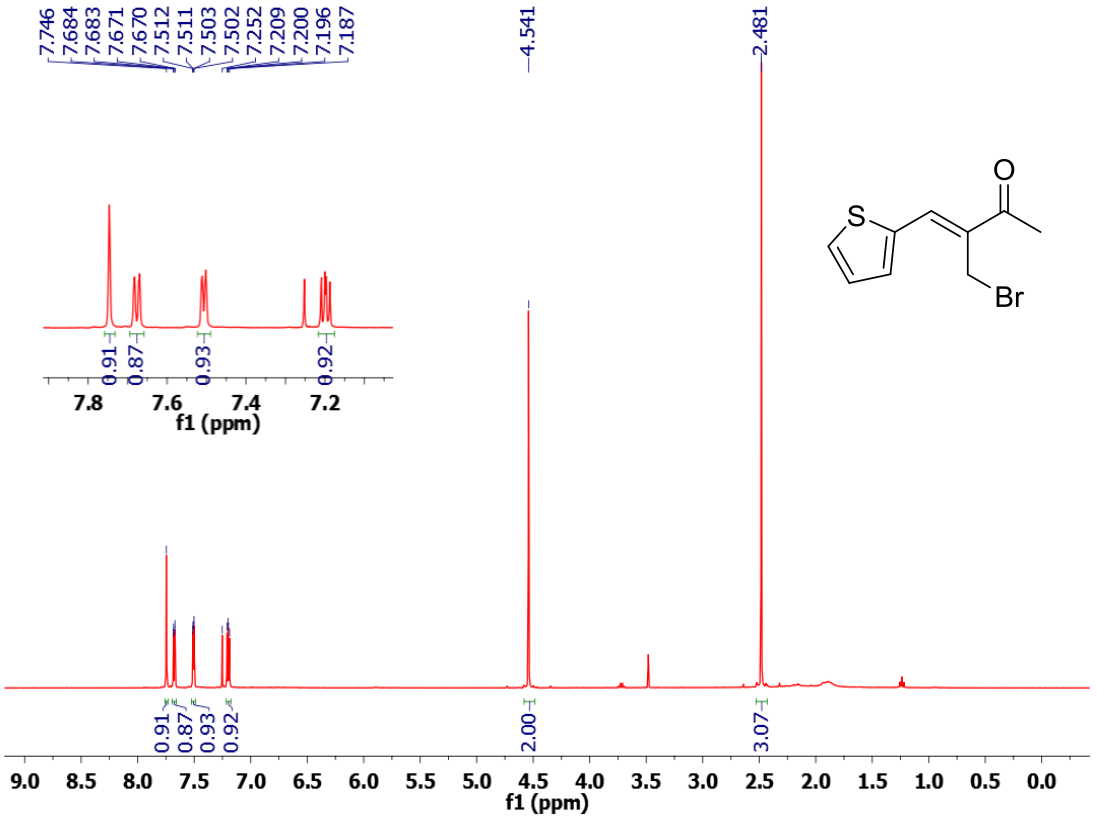
20
0
f1 (ppm)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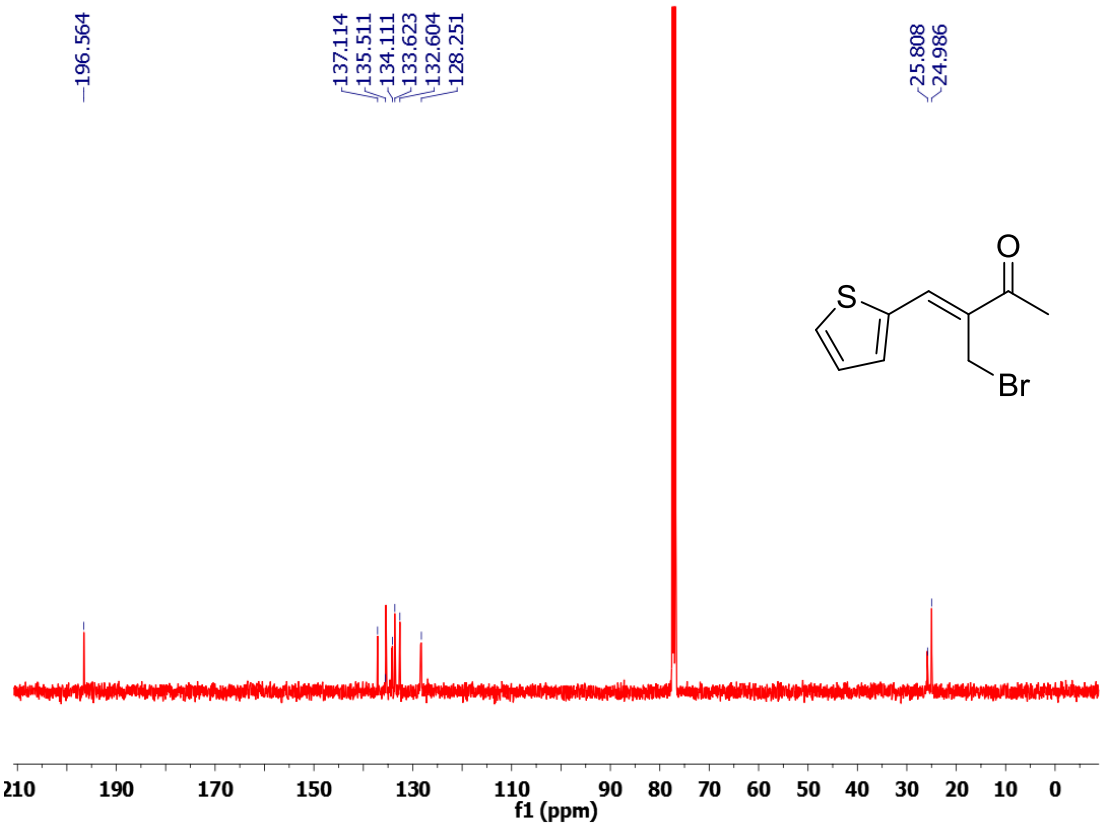
7.252
7.209
7.200
7.196
7.187
4.541
2.481
O
S
Br
0.91
0.87
0.93
0.92
7.8
7.6
7.4
7.2
f1 (ppm)
0.91
0.87
0.93
0.92
2.00
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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S
Br
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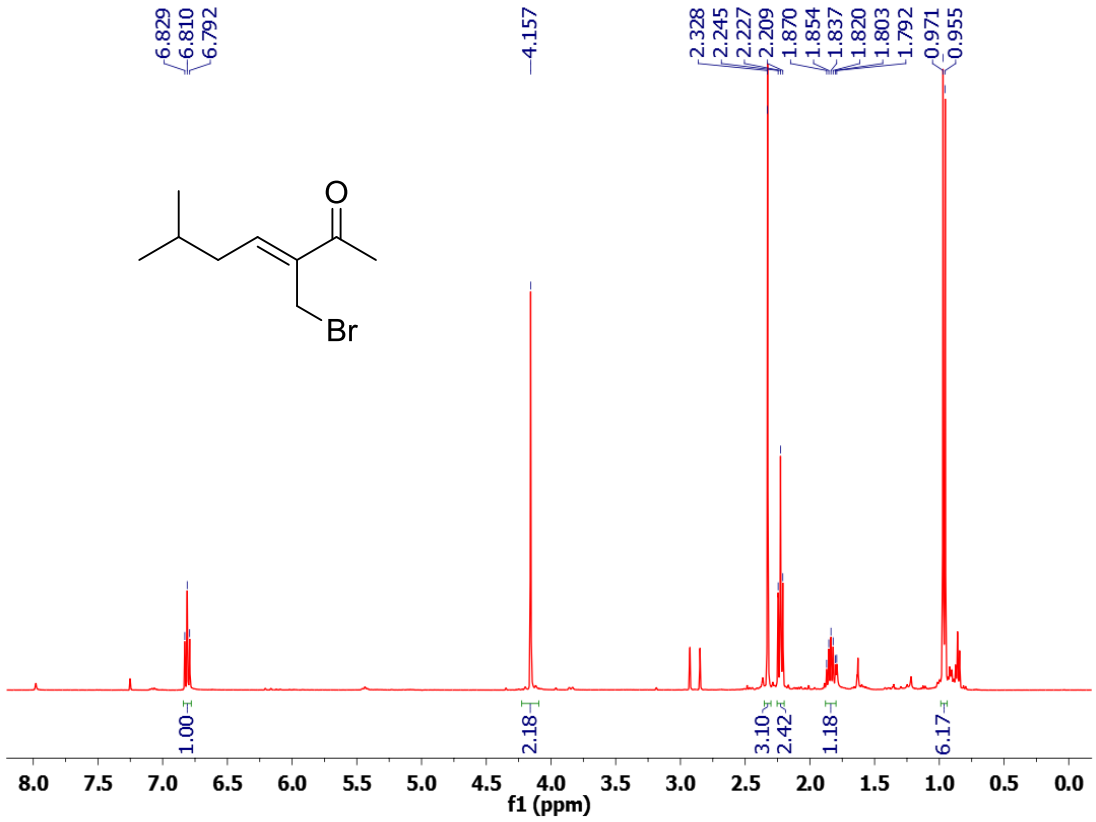
f1 (ppm)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1.803
1.792
0.971
0.955
O
Br
1.00
2.18
3.10
2.42
1.18
6.17
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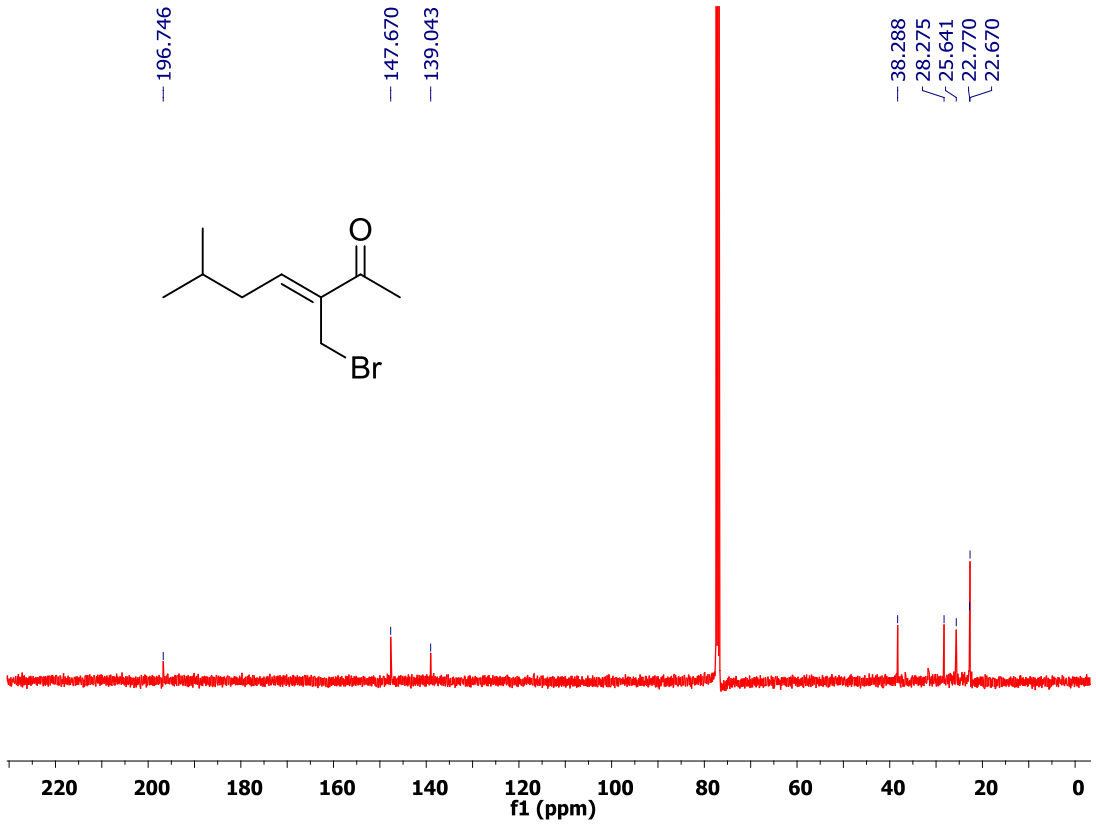
f1 (ppm)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O
Br
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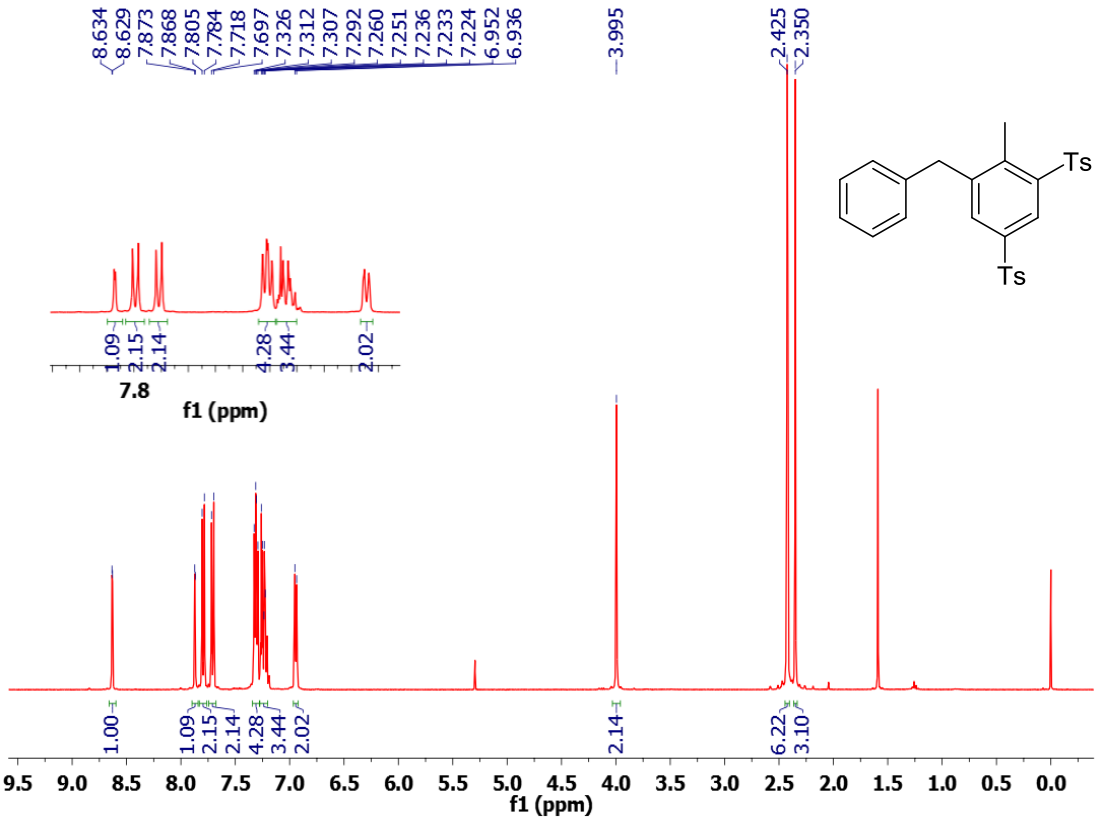
f1 (ppm)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7.292
7.260
7.251
7.236
7.233
7.224
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2.425
2.350
Ts
Ts
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2.15
2.14
4.28
3.44
2.02
7.8
f1 (ppm)
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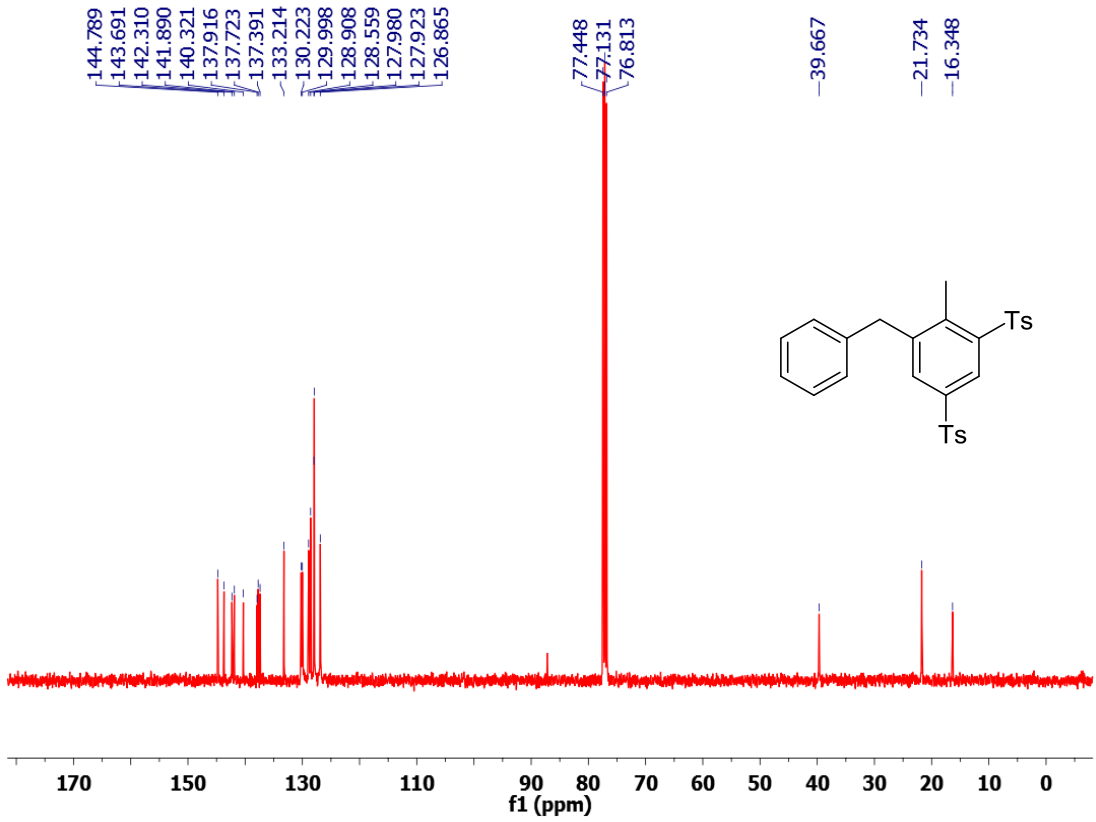
2.14
4.28
3.44
2.02
2.14
6.22
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.923
126.865
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Ts
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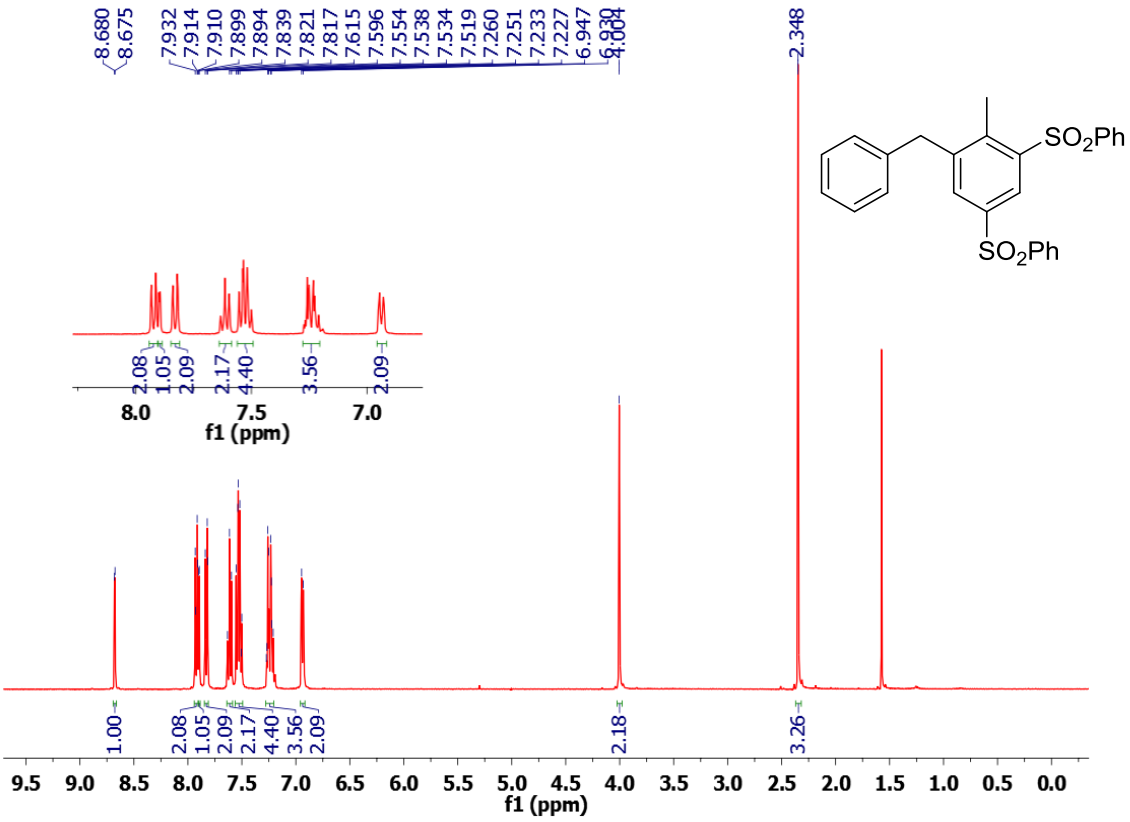
f1 (ppm)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7.538
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7.251
7.233
7.227
6.947
6.938
4.004
2.348
SO2Ph
SO2Ph
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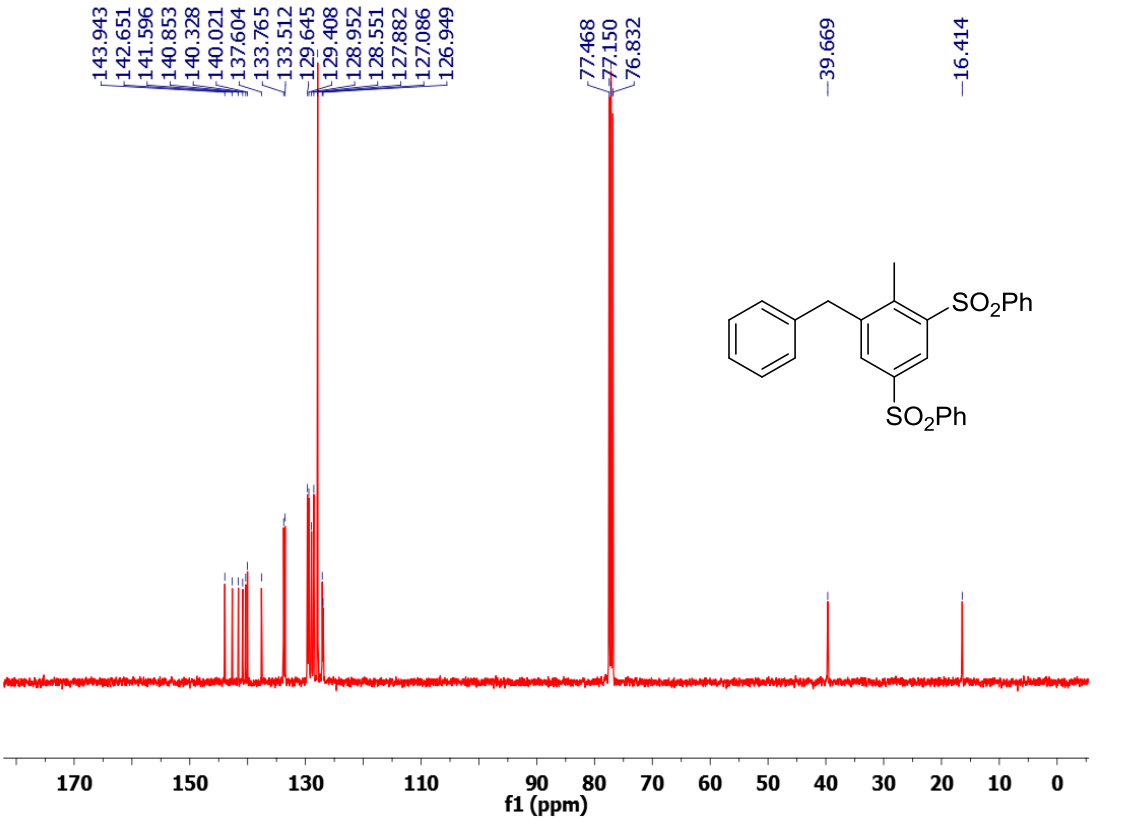
1.05
2.09
2.17
4.40
3.56
2.09
8.0
7.5
7.0
f1 (ppm)
1.00
2.08
1.05
2.09
2.17
4.40
3.56
2.09
2.18
3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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SO2Ph
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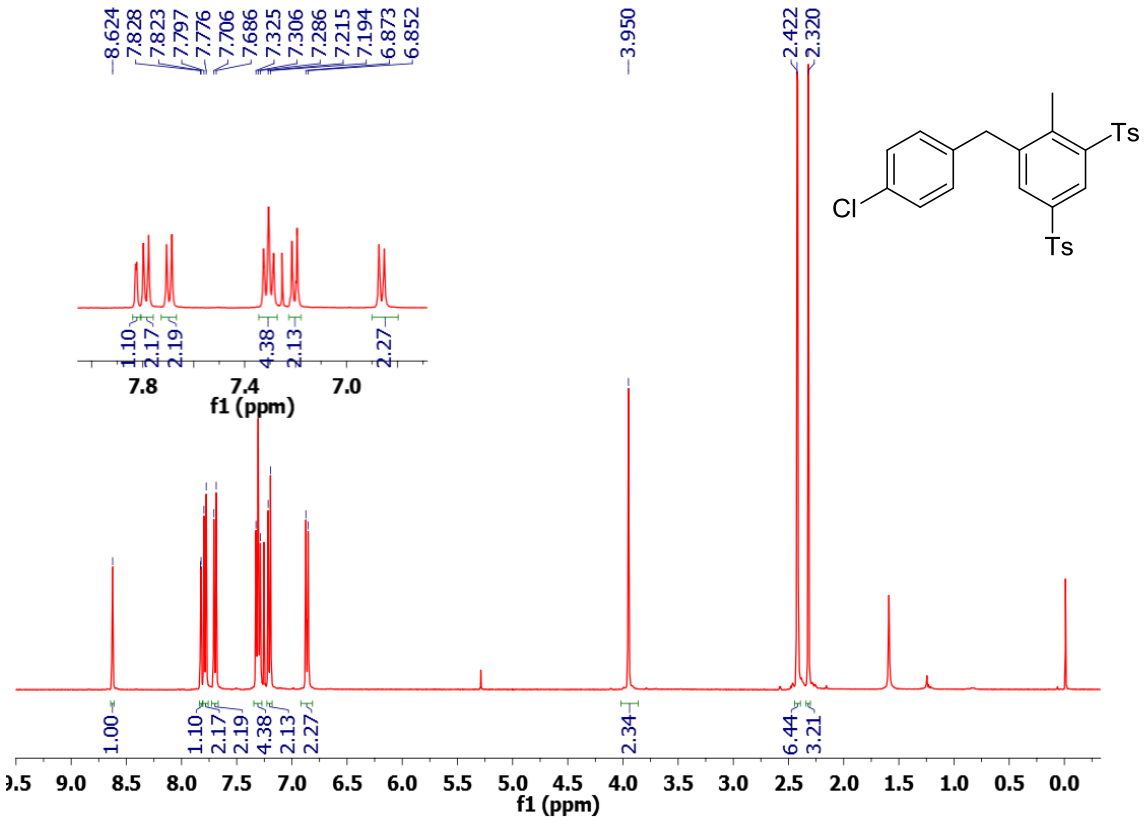
f1 (ppm)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2.422
2.320
Ts
Cl
Ts
1.10
2.17
2.19
4.38
2.13
2.27
7.8
7.4
7.0
f1 (ppm)
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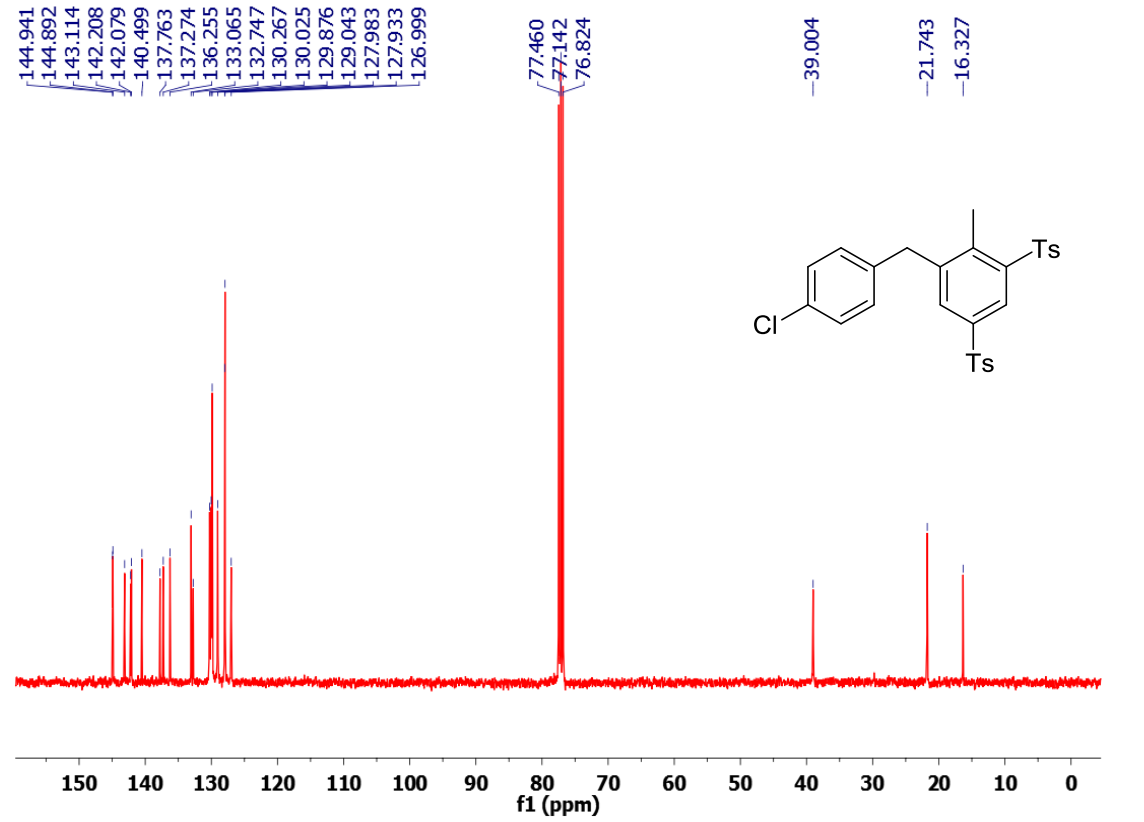
2.17
2.19
4.38
2.13
2.27
2.34
6.44
3.21
f1 (ppm)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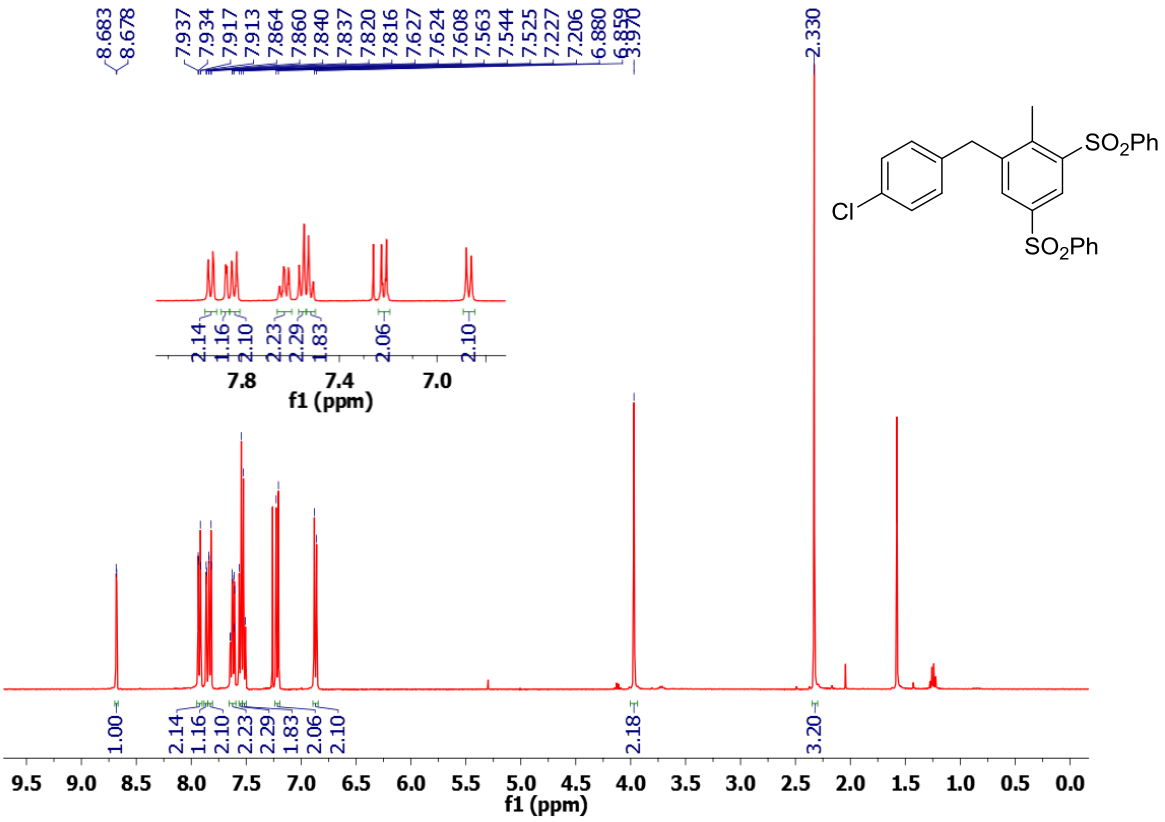
144.892
143.114
142.208
142.079
140.499
137.763
137.274
136.255
133.065
132.747
130.267
130.025
129.876
129.043
127.983
127.933
126.999
77.460
77.142
76.824
39.004
21.743
16.327
Ts
Cl
Ts
f1 (ppm)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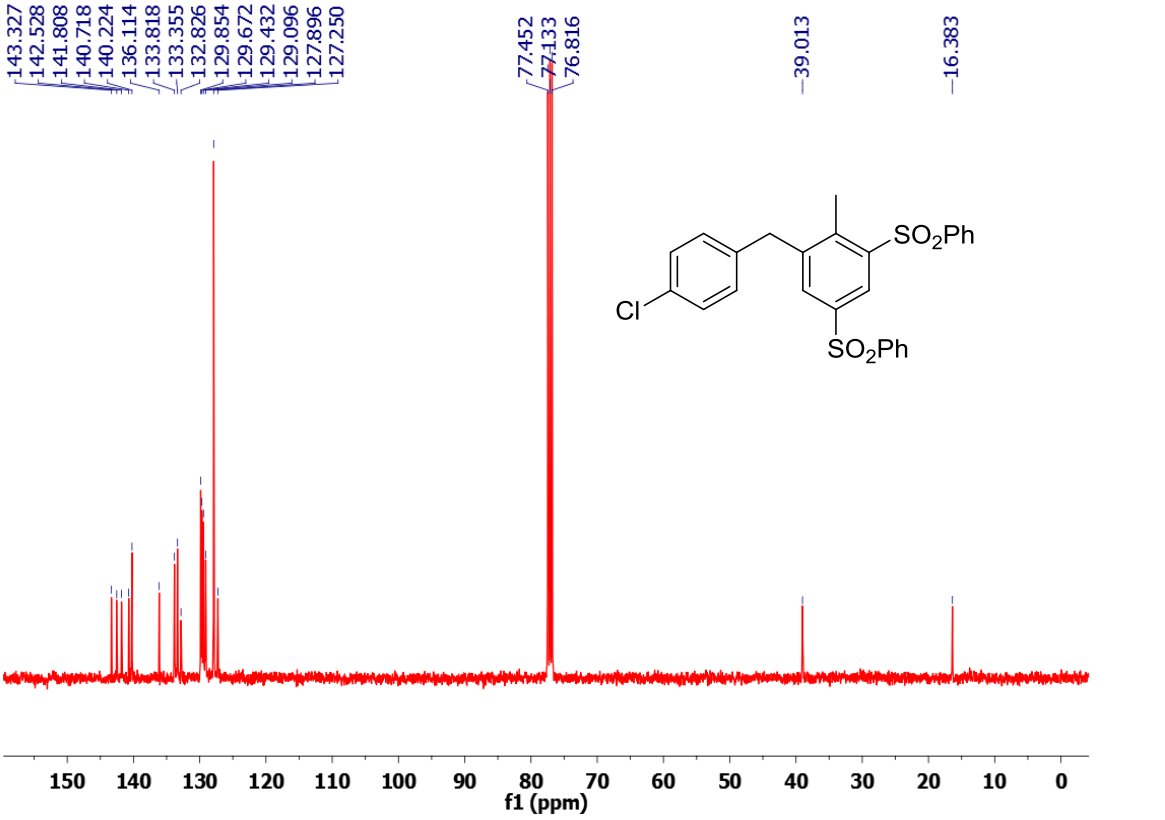
8.678
7.937
7.934
7.917
7.913
7.864
7.860
7.840
7.837
7.820
7.816
7.627
7.624
7.608
7.563
7.544
7.525
7.227
7.206
6.880
6.859
3.970
2.330
SO2Ph
Cl
SO2Ph
2.14
1.16
2.10
2.23
2.29
1.83
2.06
2.10
7.8
7.4
7.0
f1 (ppm)
1.00
2.14
1.16
2.10
2.23
2.29
1.83
2.06
2.10
2.18
3.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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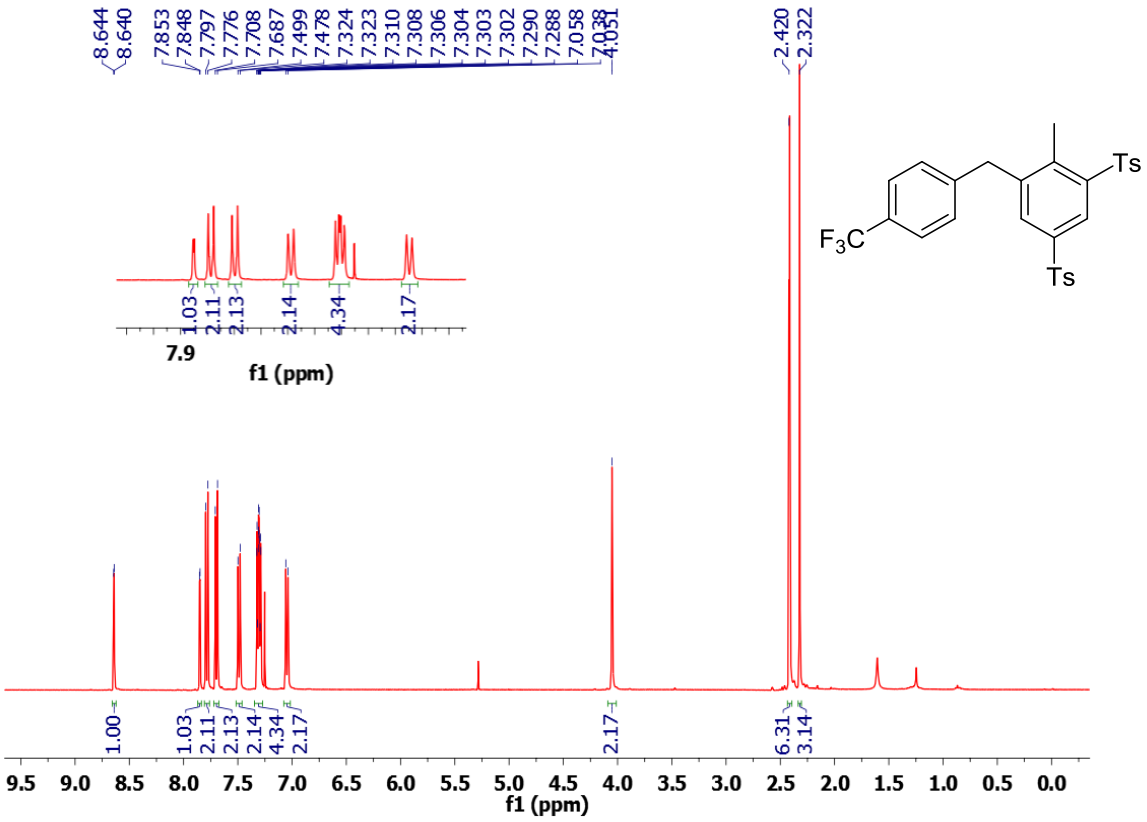
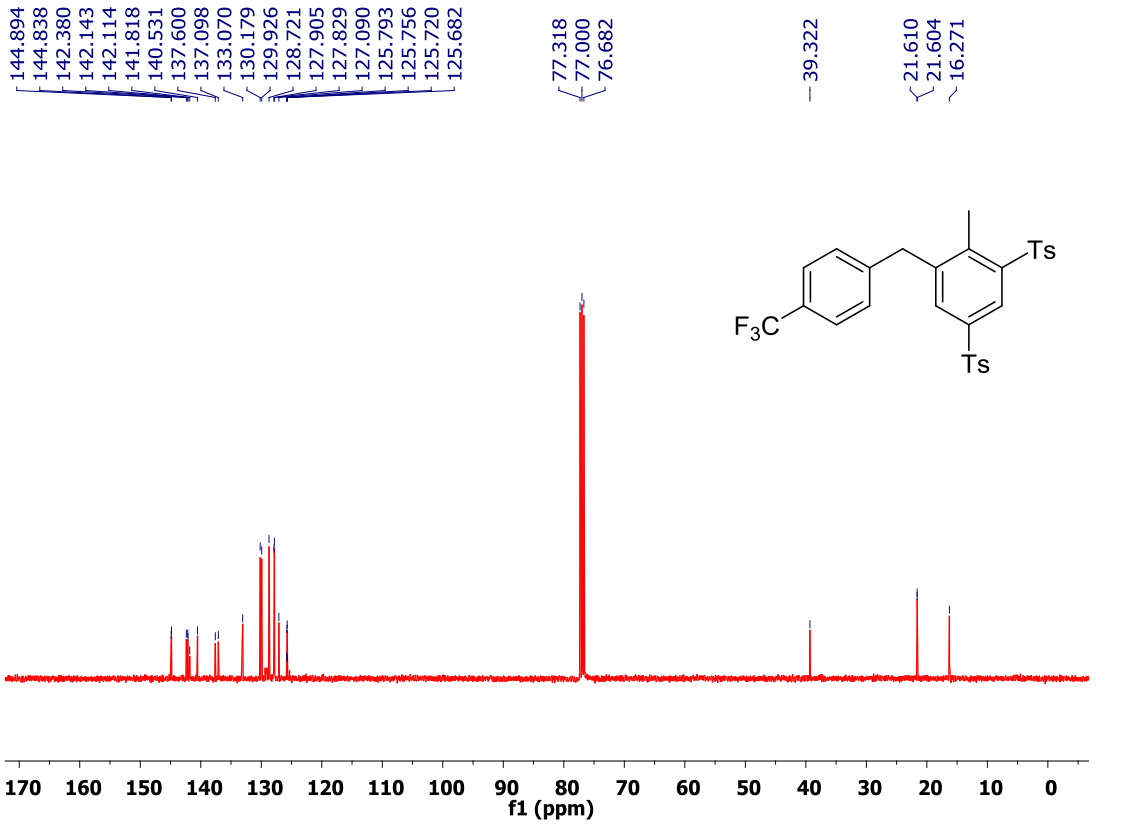
142.528
141.808
140.718
140.224
136.114
133.818
133.355
132.826
129.854
129.672
129.432
129.096
127.896
127.250
77.452
77.133
76.816
39.013
16.383
SO2Ph
Cl
SO2Ph
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.644
8.640
7.853
7.848
7.797
7.776
7.708
7.687
7.499
7.478
7.324
7.323
7.310
7.308
7.306
7.304
7.303
7.302
7.290
7.288
7.058
7.038
4.051
2.420
2.322
1.03
2.11
2.13
2.14
4.34
2.17
7.9
f1 (ppm)
Ts
F3C
Ts
1.00
1.03
2.11
2.13
2.14
4.34
2.17
2.17
6.31
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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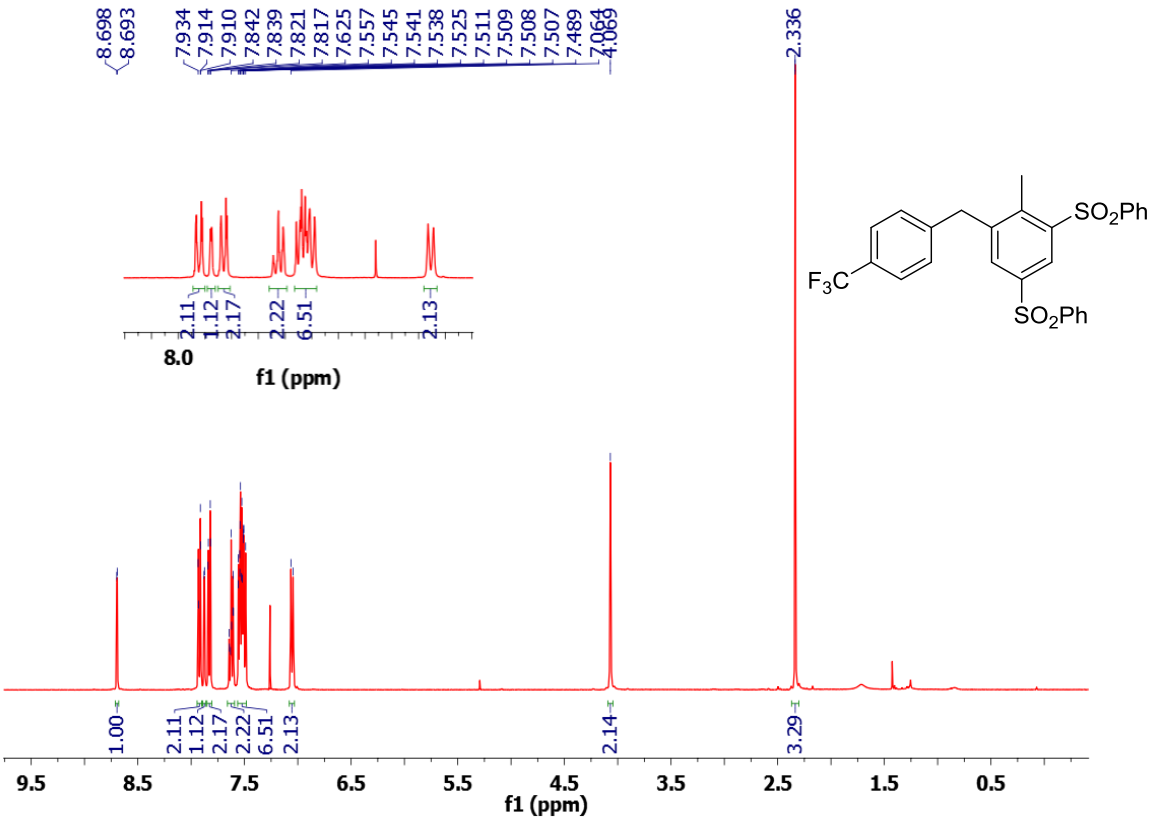
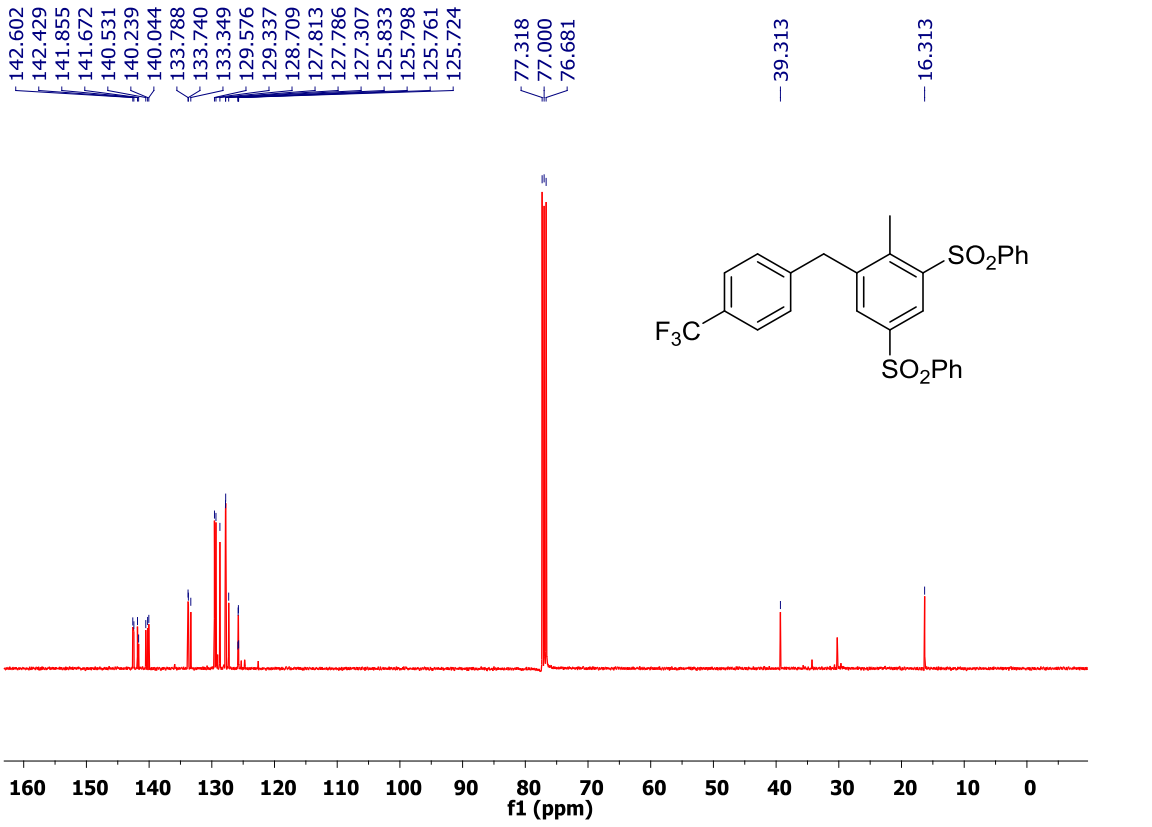
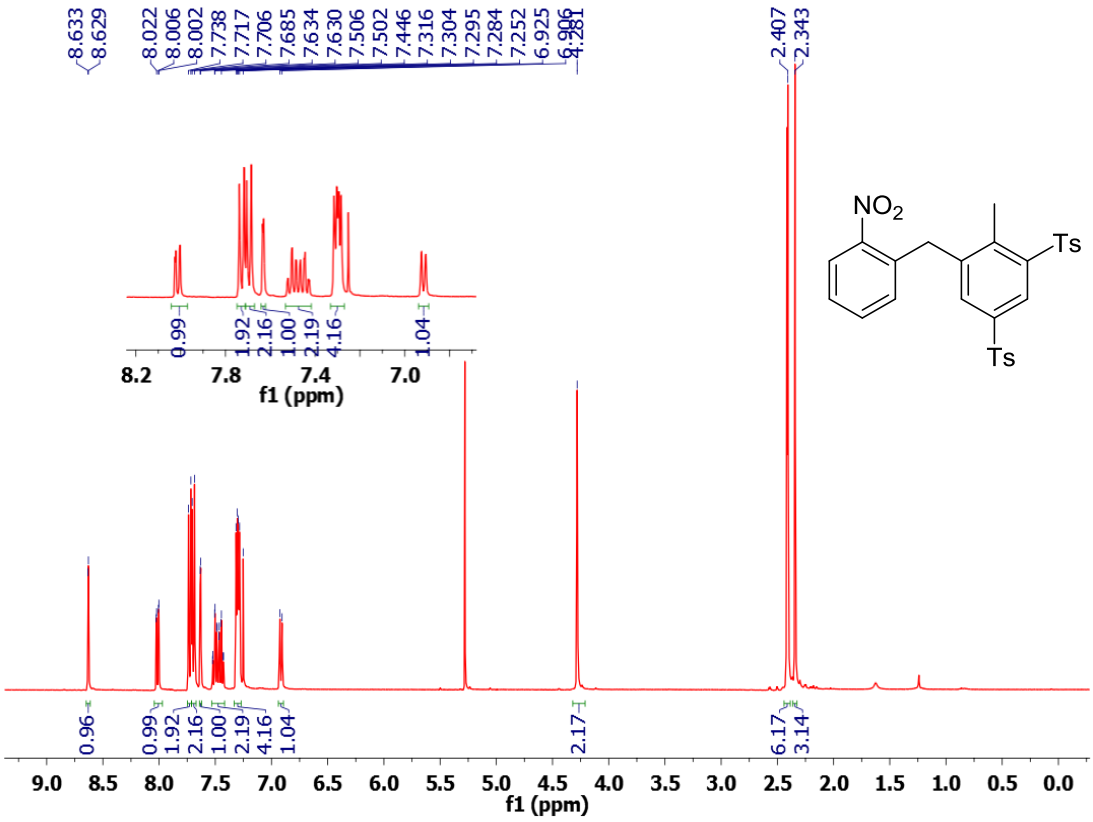
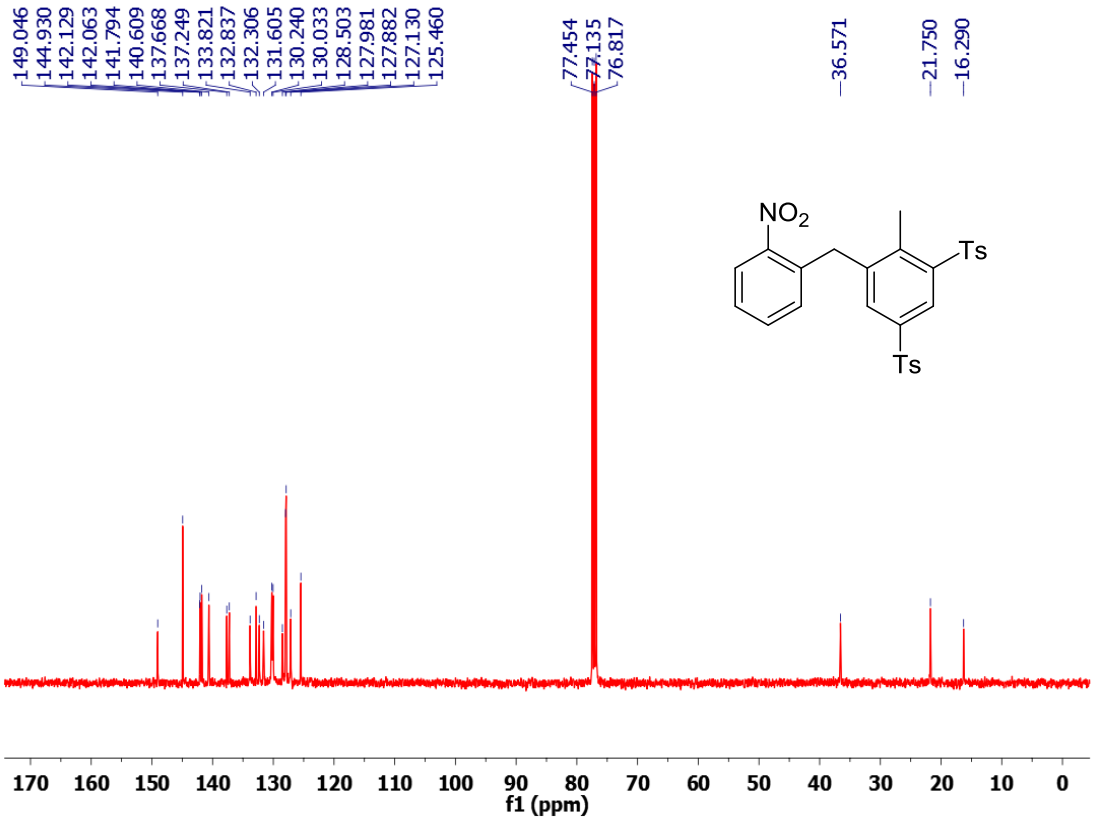
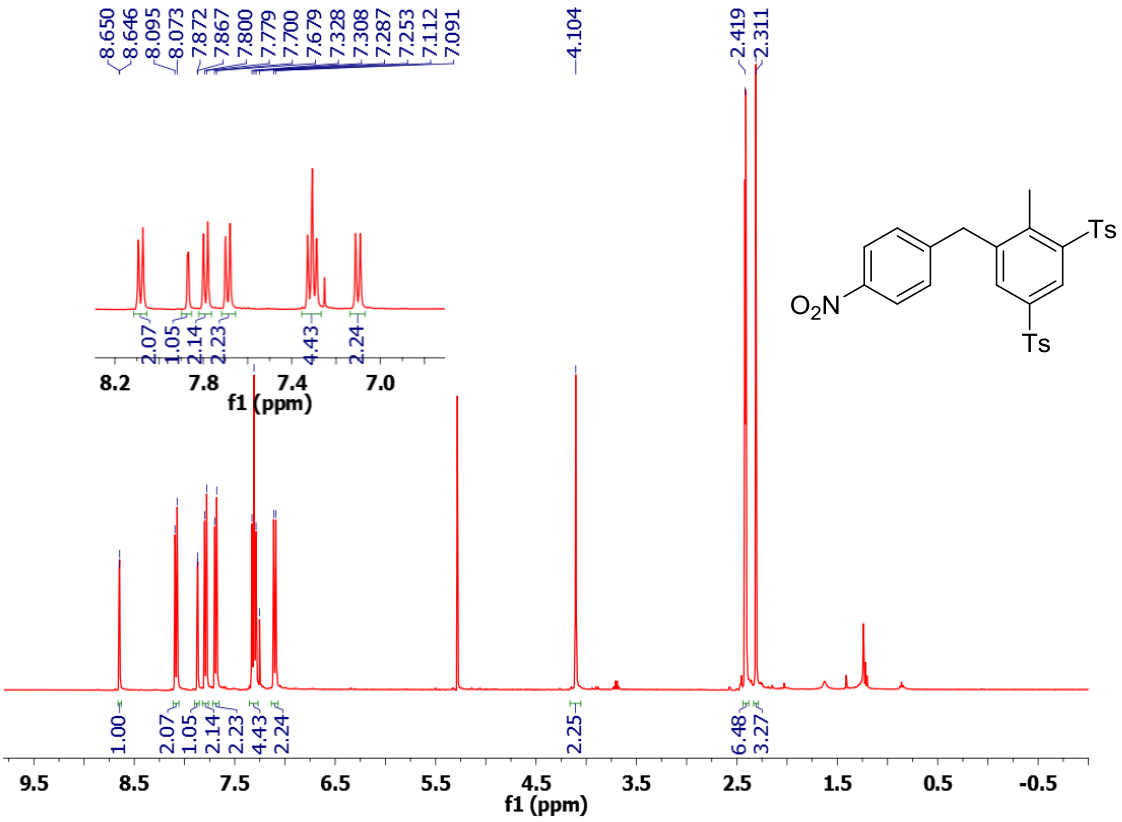
144.838
142.380
142.143
142.114
141.818
140.531
137.600
137.098
133.070
130.179
129.926
128.721
127.905
127.829
127.090
125.793
125.756
125.720
125.682
77.318
77.000
76.682
39.322
21.610
21.604
16.271
Ts
F3C
Ts
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

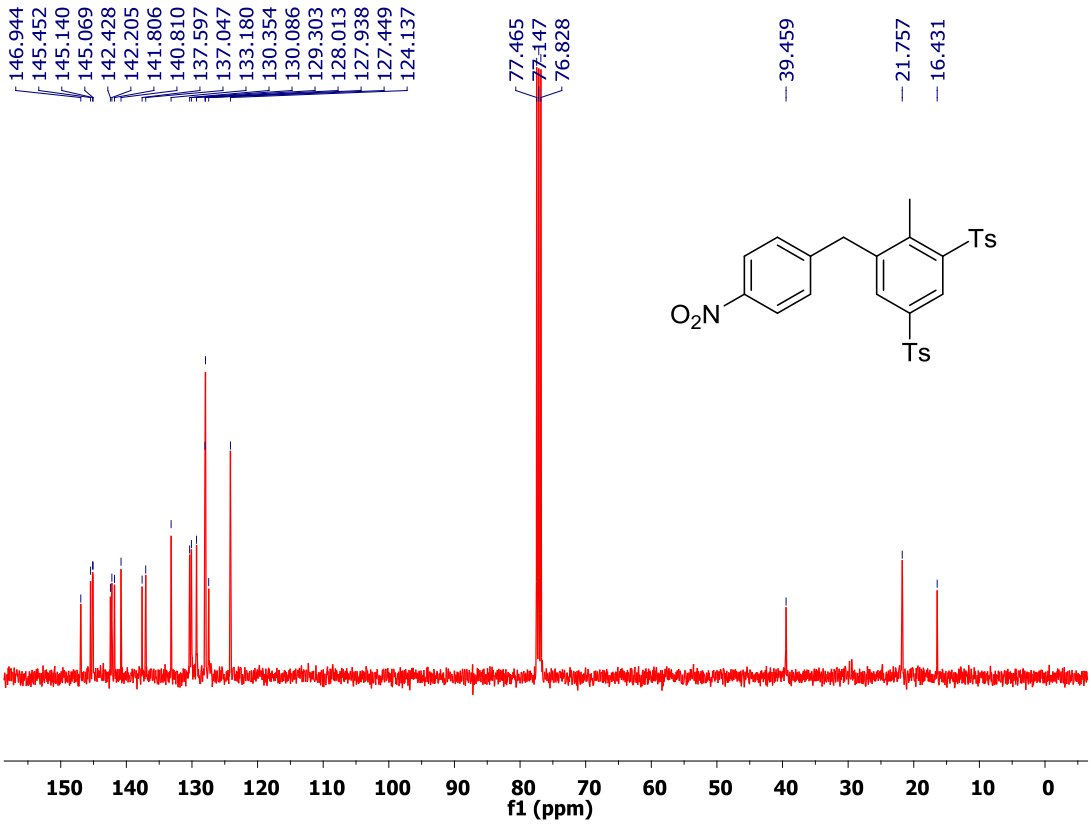

8.698
8.693
7.934
7.914
7.910
7.842
7.839
7.821
7.817
7.625
7.557
7.545
7.541
7.538
7.525
7.511
7.509
7.508
7.507
7.489
7.064
4.069
2.336
2.11
1.12
2.17
2.22
6.51
2.13
8.0
f1 (ppm)
SO2Ph
F3C
SO2Ph
1.00
2.11
1.12
2.17
2.22
6.51
2.13
2.14
3.29
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

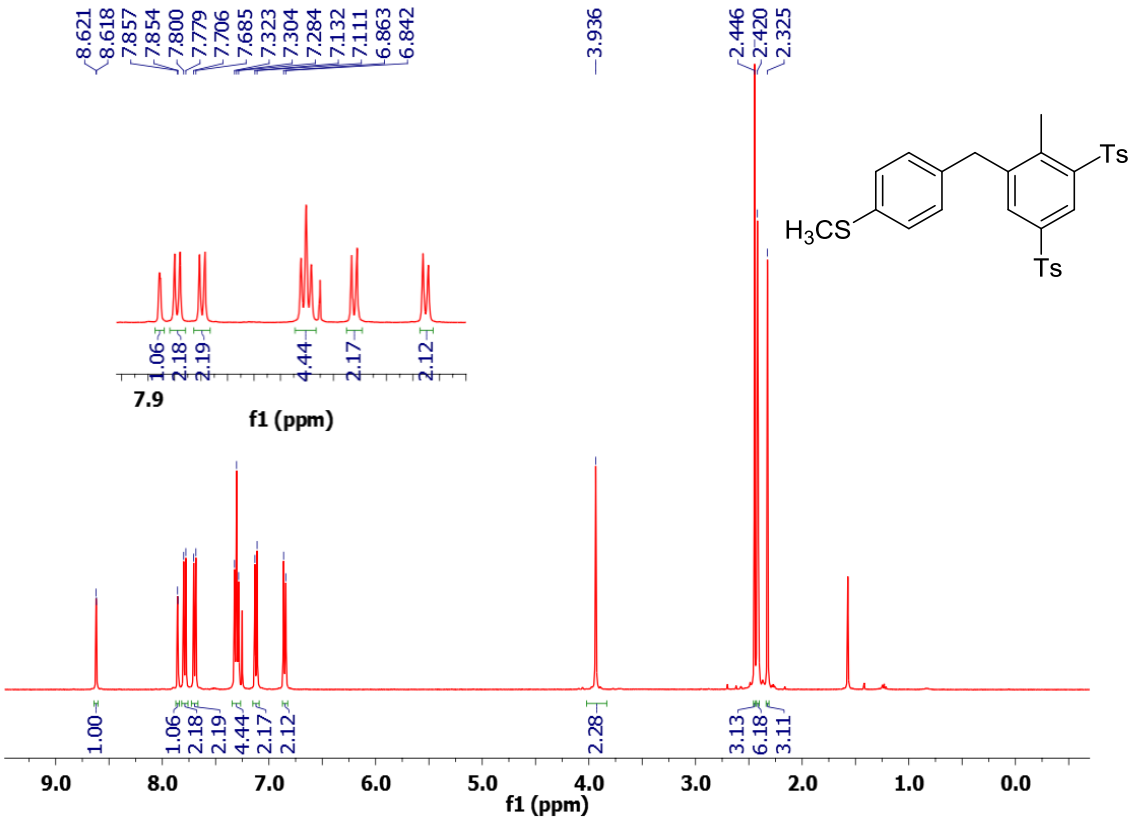

142.602
142.429
141.855
141.672
140.531
140.239
140.044
133.788
133.740
133.349
129.576
129.337
128.709
127.813
127.786
127.307
125.833
125.798
125.761
125.724
77.318
77.000
76.681
39.313
16.313
SO2Ph
F3C
SO2Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

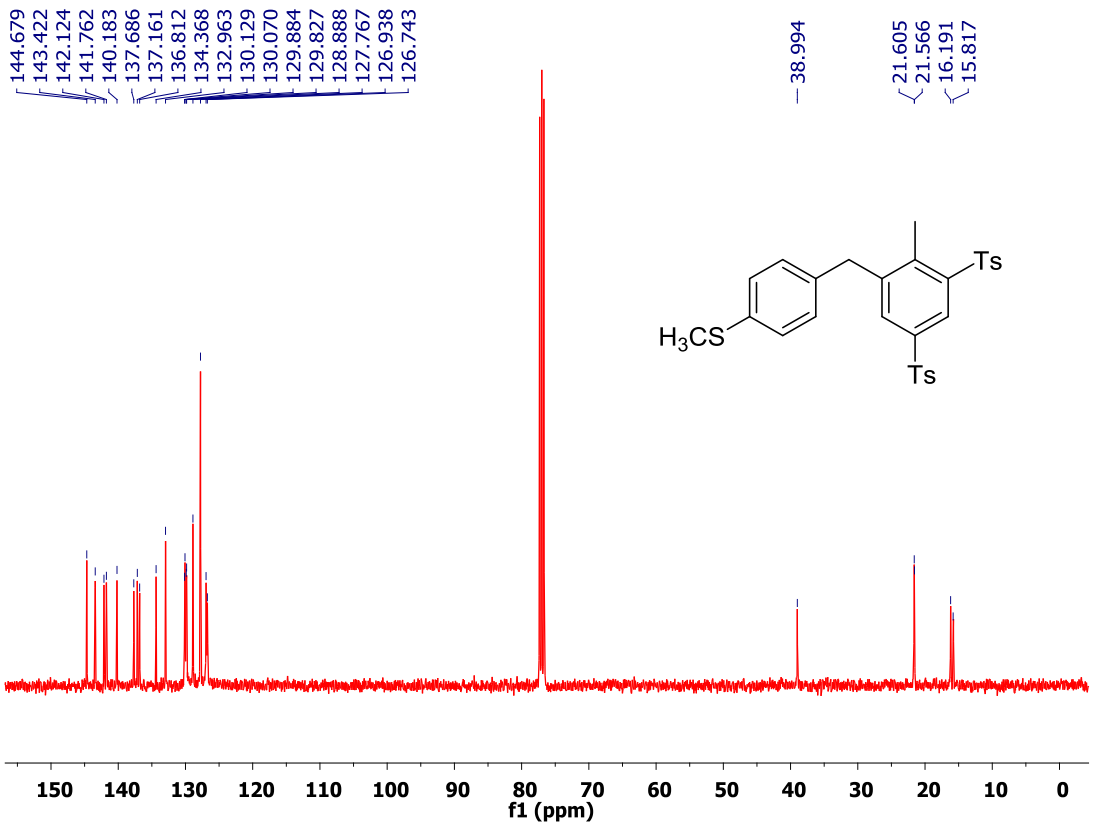

8.633
8.629
8.022
8.006
8.002
7.738
7.717
7.706
7.685
7.634
7.630
7.506
7.502
7.446
7.316
7.304
7.295
7.284
7.252
6.925
2.407
2.343
NO2
Ts
Ts
0.99
1.92
2.16
1.00
2.19
4.16
1.04
8.2
7.8
7.4
7.0
f1 (ppm)
0.96
0.99
1.92
2.16
1.00
2.19
4.16
1.04
2.17
6.17
3.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

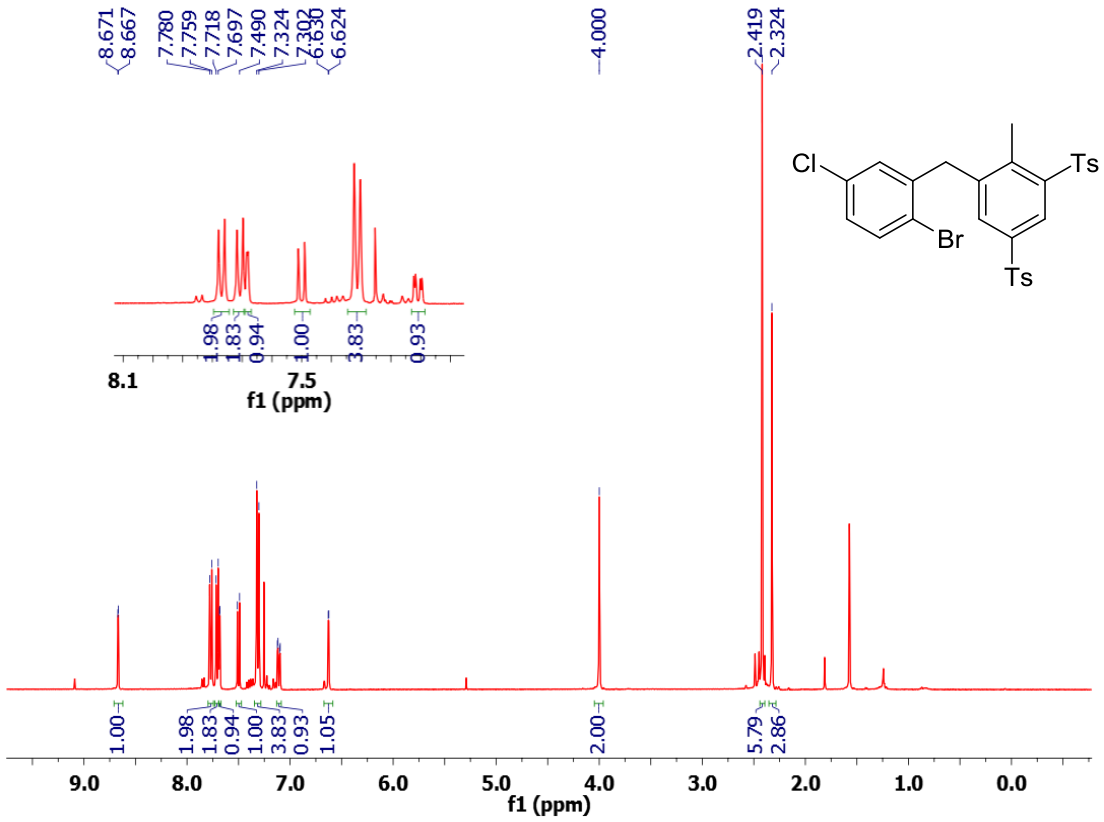

149.046
144.930
142.129
142.063
141.794
140.609
137.668
137.249
133.821
132.837
132.306
131.605
130.240
130.033
128.503
127.981
127.882
127.130
125.460
77.454
77.135
76.817
36.571
21.750
16.290
NO2
Ts
Ts
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.650
8.646
8.095
8.073
7.872
7.867
7.800
7.779
7.700
7.679
7.328
7.308
7.287
7.253
7.112
7.091
4.104
2.419
2.311
2.07
1.05
2.14
2.23
4.43
2.24
8.2
7.8
7.4
7.0
f1 (ppm)
Ts
O2N
Ts
1.00
2.07
1.05
2.14
2.23
4.43
2.24
2.25
6.48
3.27
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


146.944
145.452
145.140
145.069
142.428
142.205
141.806
140.810
137.597
137.047
133.180
130.354
130.086
129.303
128.013
127.938
127.449
124.137
77.465
77.147
76.828
39.459
21.757
16.431
Ts
O2N
Ts
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.621
8.618
7.857
7.854
7.800
7.779
7.706
7.685
7.323
7.304
7.284
7.132
7.111
6.863
6.842
3.936
2.446
2.420
2.325
Ts
H3CS
Ts
1.06
2.18
2.19
4.44
2.17
2.12
7.9
f1 (ppm)
1.00
1.06
2.18
2.19
4.44
2.17
2.12
2.28
3.13
6.18
3.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


144.679
143.422
142.124
141.762
140.183
137.686
137.161
136.812
134.368
132.963
130.129
130.070
129.884
129.827
128.888
127.767
126.938
126.743
38.994
21.605
21.566
16.191
15.817
Ts
H3CS
Ts
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.667
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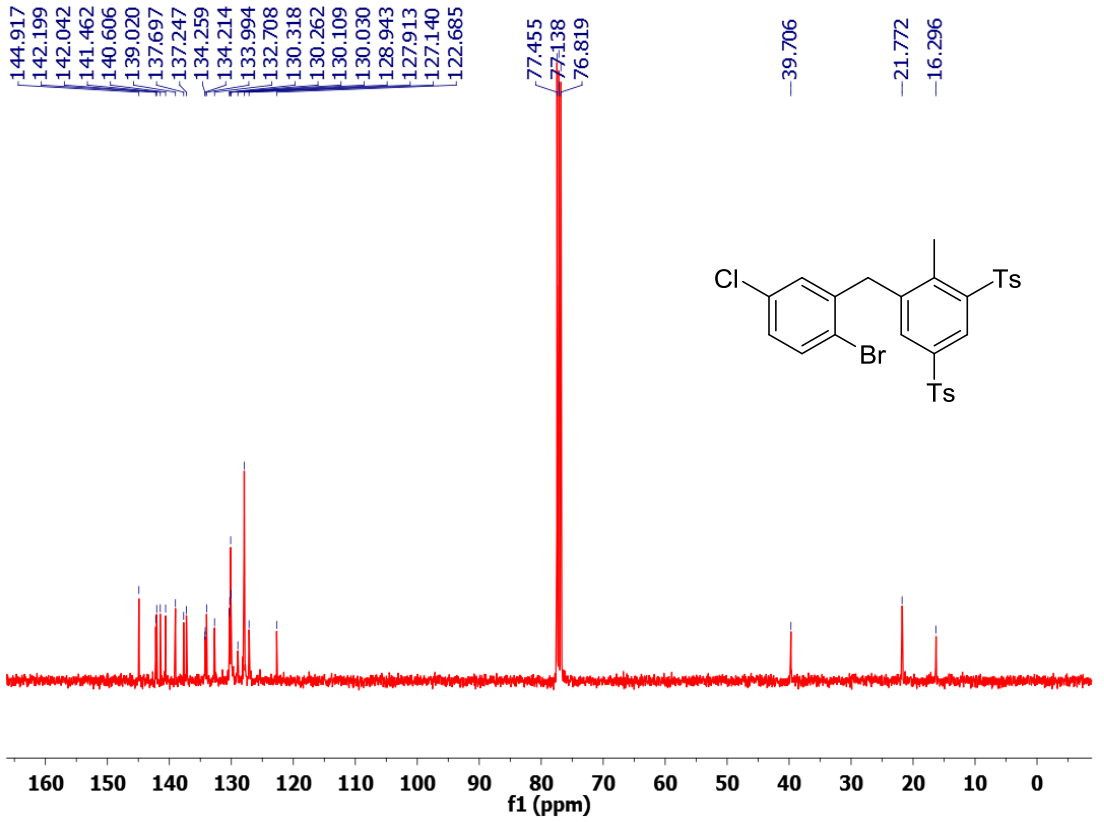
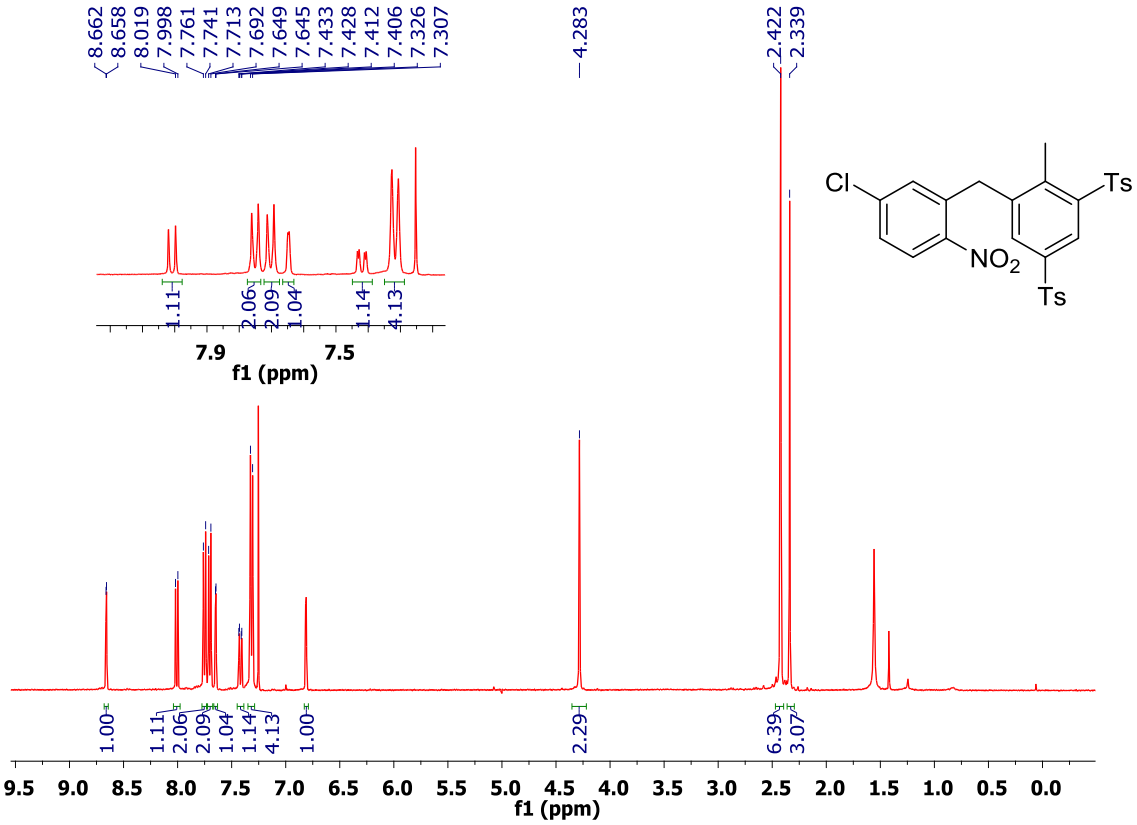
7.759
7.718
7.697
7.490
7.324
7.302
6.630
6.624
4.000
2.419
2.324
Cl
Ts
Br
Ts
1.98
1.83
0.94
1.00
3.83
0.93
8.1
7.5
f1 (ppm)
1.00
1.98
1.83
0.94
1.00
3.83
0.93
1.05
2.00
5.79
2.86
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


144.917
142.199
142.042
141.462
140.606
139.020
137.697
137.247
134.259
134.214
133.994
132.708
130.318
130.262
130.109
130.030
128.943
127.913
127.140
122.685
77.455
77.138
76.819
39.706
21.772
16.296
Cl
Ts
Br
Ts
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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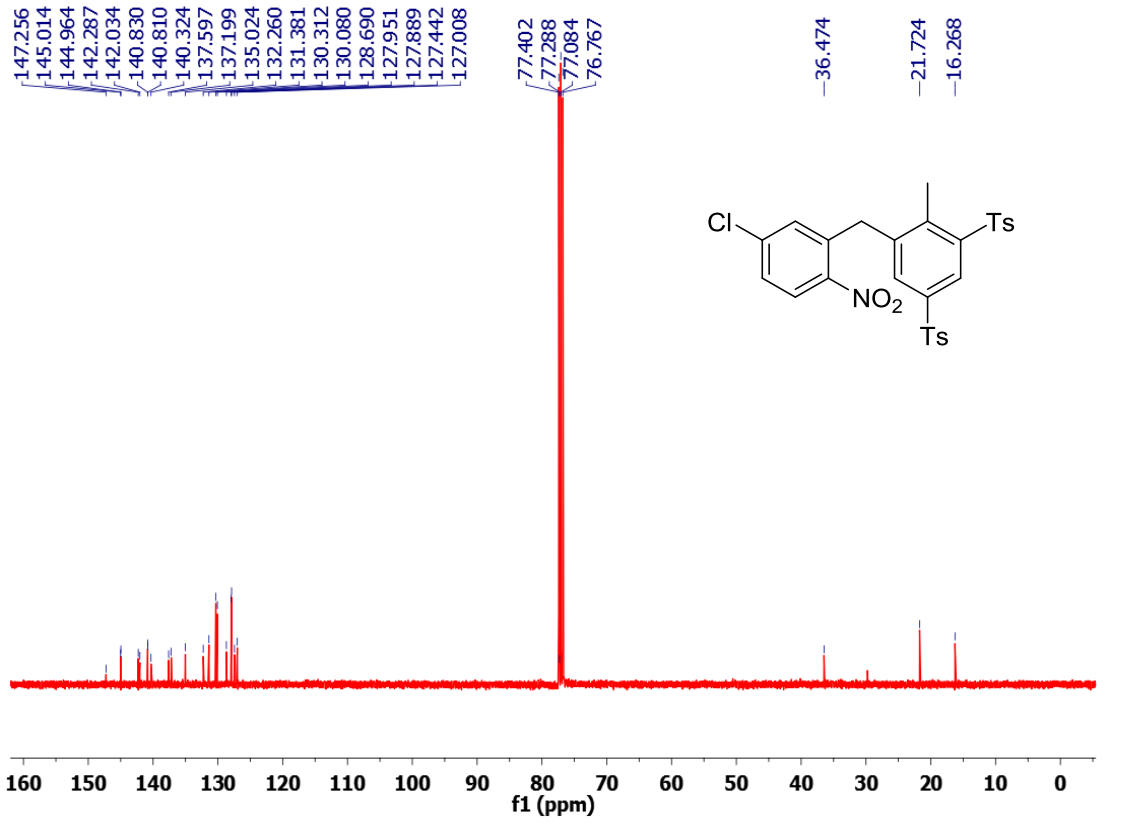
8.019
7.998
7.761
7.741
7.713
7.692
7.649
7.645
7.433
7.428
7.412
7.406
7.326
7.307
4.283
2.422
2.339
Cl
Ts
NO2
Ts
1.11
2.06
2.09
1.04
1.14
4.13
7.9
7.5
f1 (ppm)
1.00
1.11
2.06
2.09
1.04
1.14
4.13
1.00
2.29
6.39
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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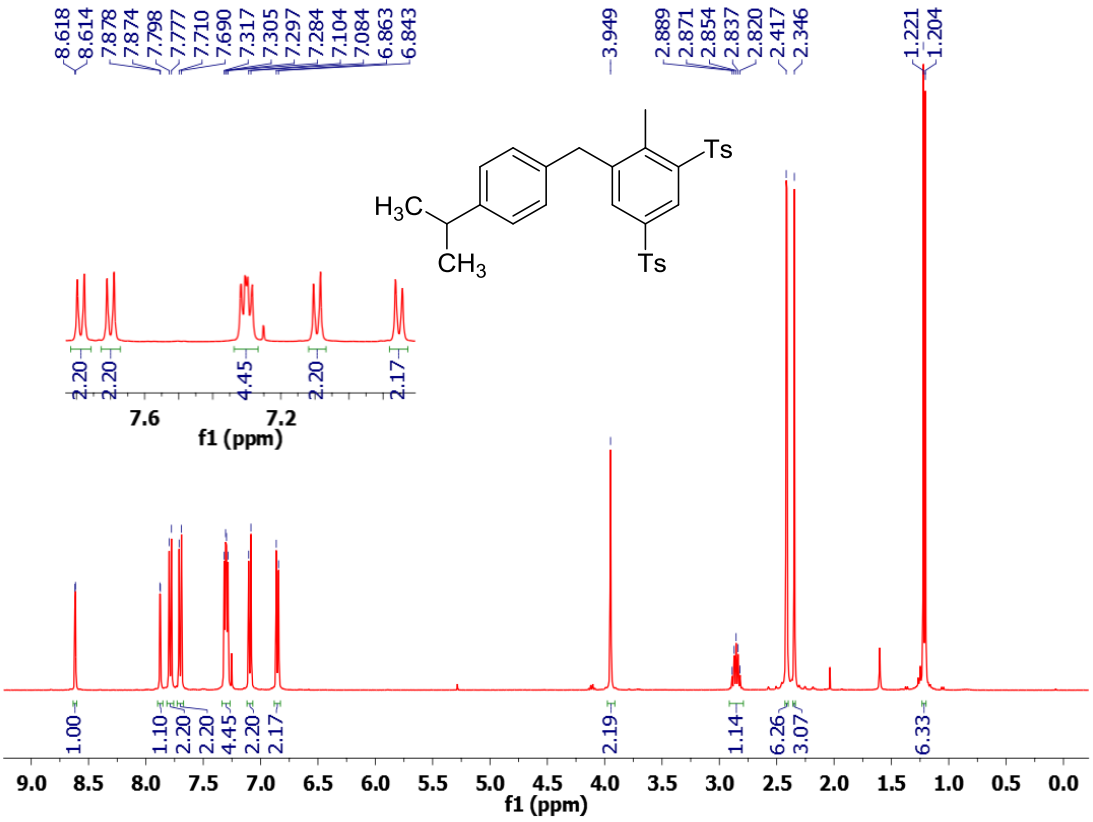
144.964
142.287
142.034
140.830
140.810
140.324
137.597
137.199
135.024
132.260
131.381
130.312
130.080
128.690
127.951
127.889
127.442
127.008
77.402
77.288
77.084
76.767
36.474
21.724
16.268
Cl
Ts
NO2
Ts
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.777
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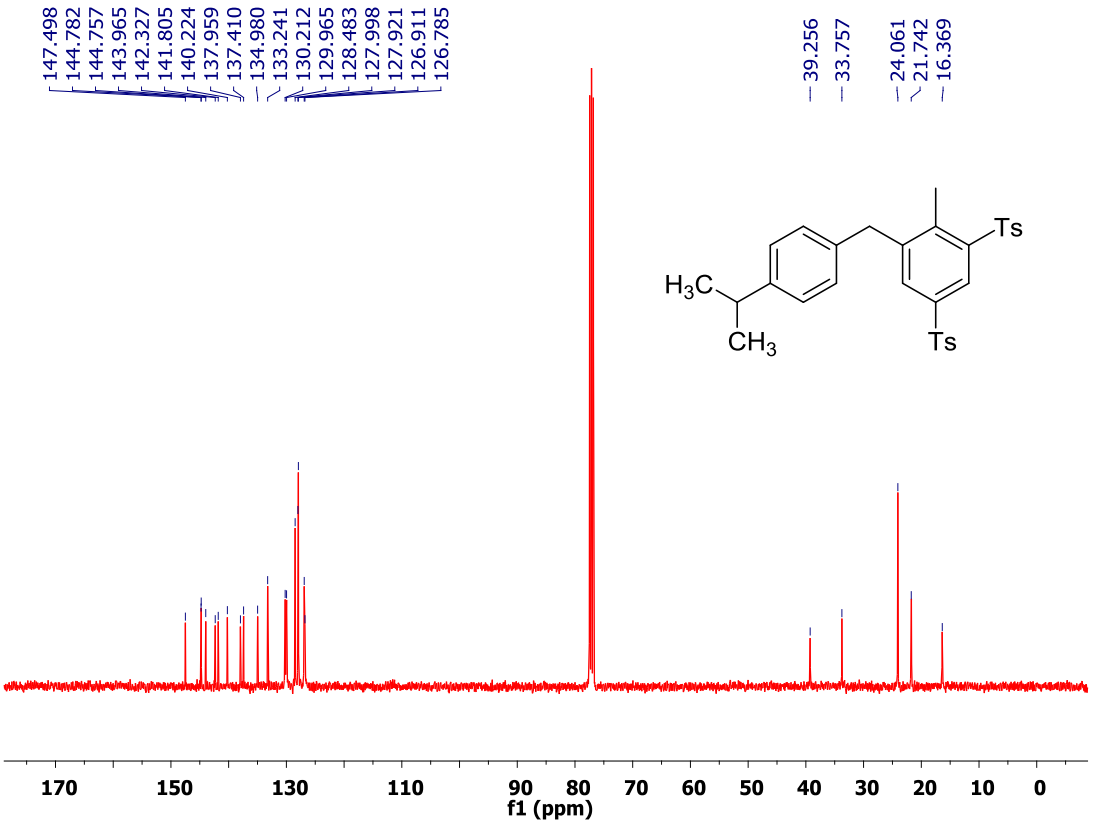
7.690
7.317
7.305
7.297
7.284
7.104
7.084
6.863
6.843
3.949
2.889
2.871
2.854
2.837
2.820
2.417
2.346
1.221
1.204
Ts
H3C
CH3
Ts
2.20
2.20
4.45
2.20
2.17
7.6
7.2
f1 (ppm)
1.00
1.10
2.20
2.20
4.45
2.20
2.17
2.19
1.14
6.26
3.07
6.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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144.757
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140.224
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137.410
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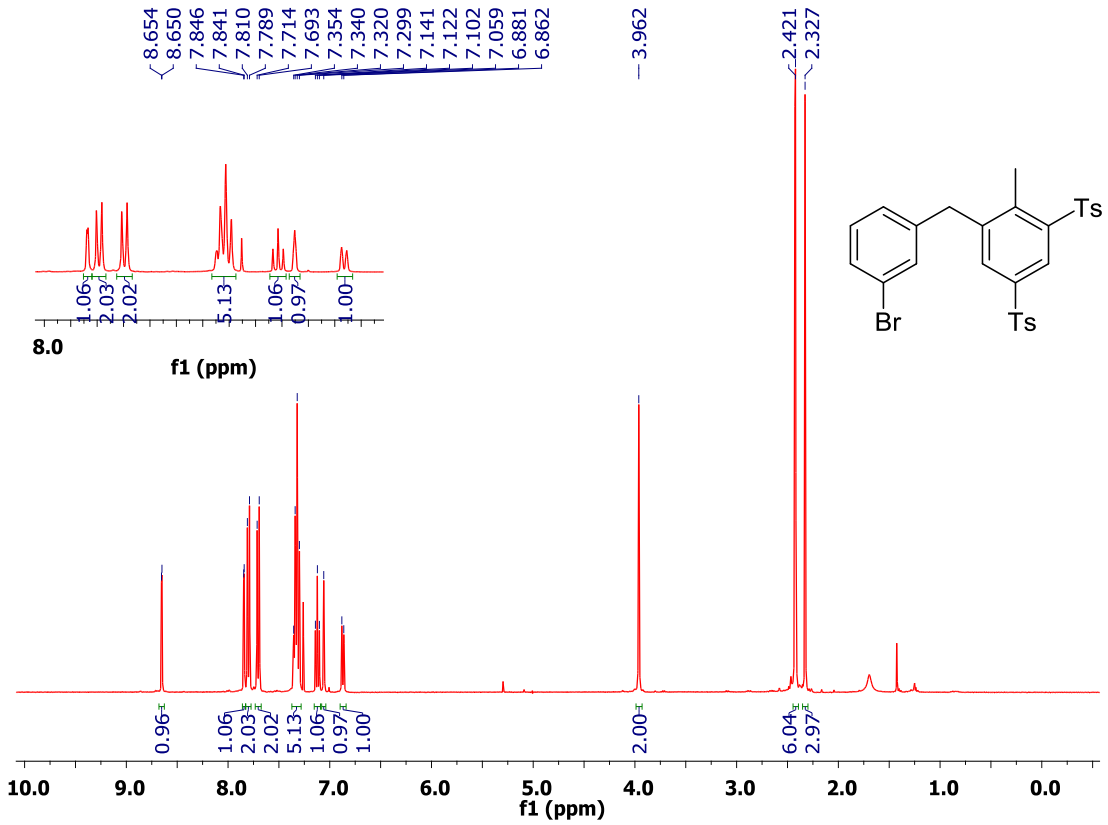
133.241
130.212
129.965
128.483
127.998
127.921
126.911
126.785
39.256
33.757
24.061
21.742
16.369
Ts
H3C
CH3
Ts
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.693
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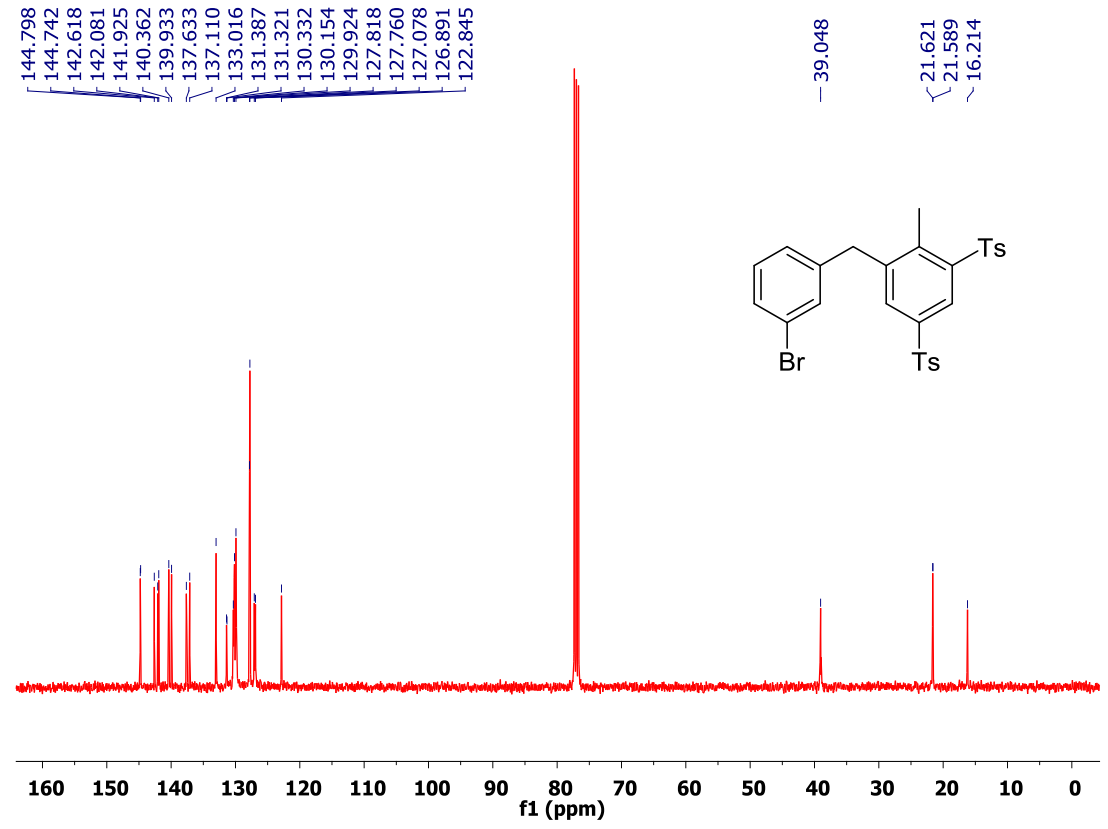
7.340
7.320
7.299
7.141
7.122
7.102
7.059
6.881
6.862
3.962
2.421
2.327
1.06
2.03
2.02
5.13
1.06
0.97
1.00
8.0
f1 (ppm)
Ts
Br
Ts
0.96
1.06
2.03
2.02
5.13
1.06
0.97
1.00
2.00
6.04
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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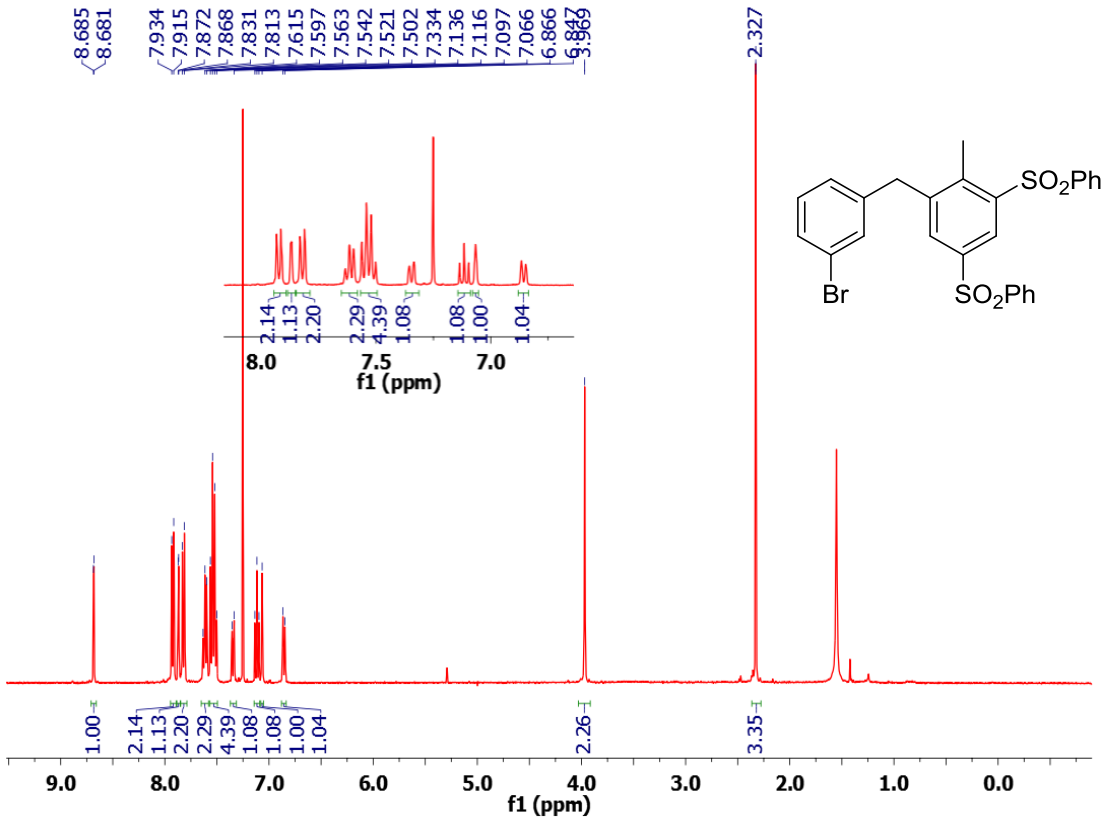
144.742
142.618
142.081
141.925
140.362
139.933
137.633
137.110
133.016
131.387
131.321
130.332
130.154
129.924
127.818
127.760
127.078
126.891
122.845
39.048
21.621
21.589
16.214
Ts
Br
Ts
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.685
8.681
7.934
7.915
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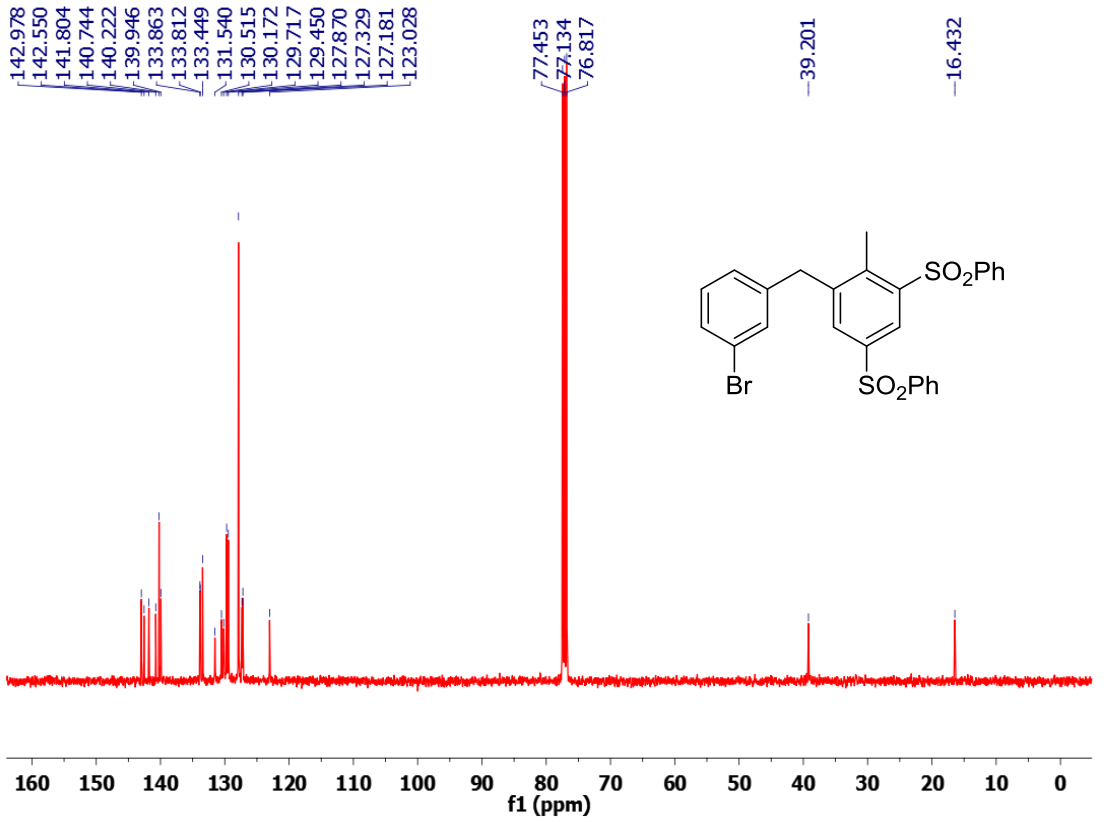
7.813
7.615
7.597
7.563
7.542
7.521
7.502
7.334
7.136
7.116
7.097
7.066
6.866
6.847
3.969
2.327
2.14
1.13
2.20
2.29
4.39
1.08
1.08
1.00
1.04
8.0
7.5
7.0
f1 (ppm)
SO2Ph
Br
SO2Ph
1.00
2.14
1.13
2.20
2.29
4.39
1.08
1.08
1.00
1.04
2.26
3.35
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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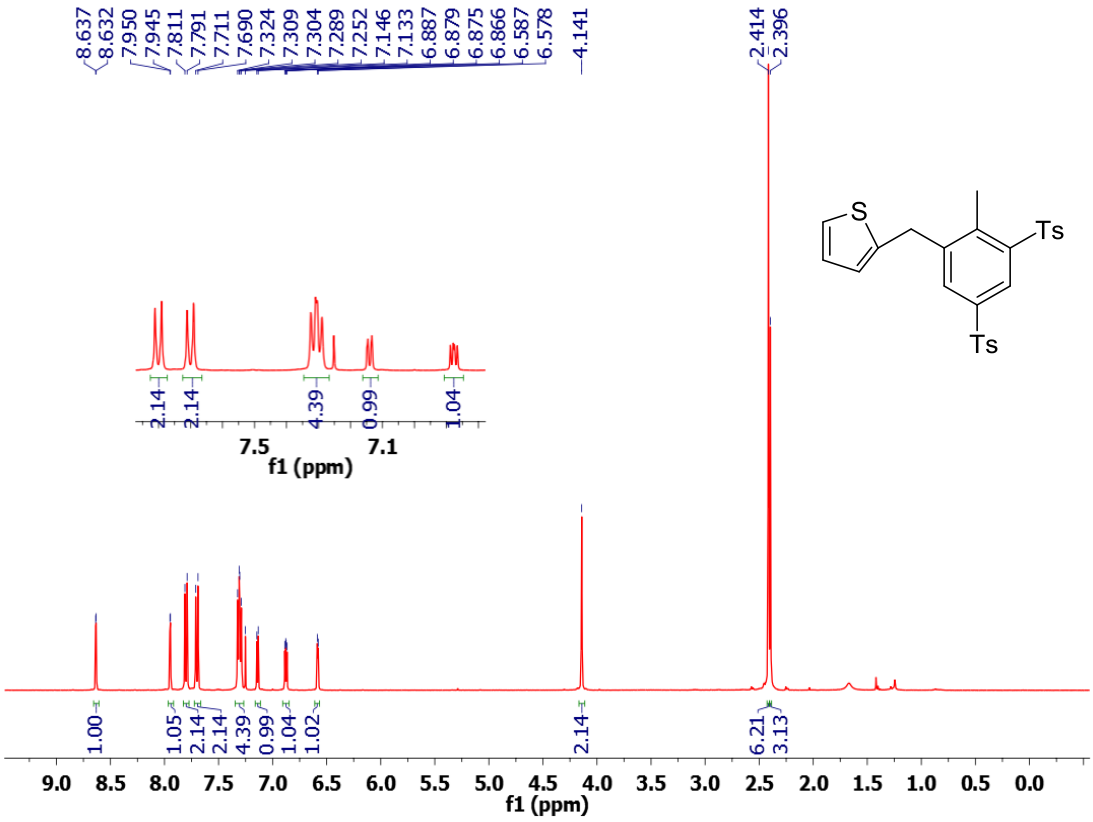
142.550
141.804
140.744
140.222
139.946
133.863
133.812
133.449
131.540
130.515
130.172
129.717
129.450
127.870
127.329
127.181
123.028
77.453
77.134
76.817
39.201
16.432
SO2Ph
Br
SO2Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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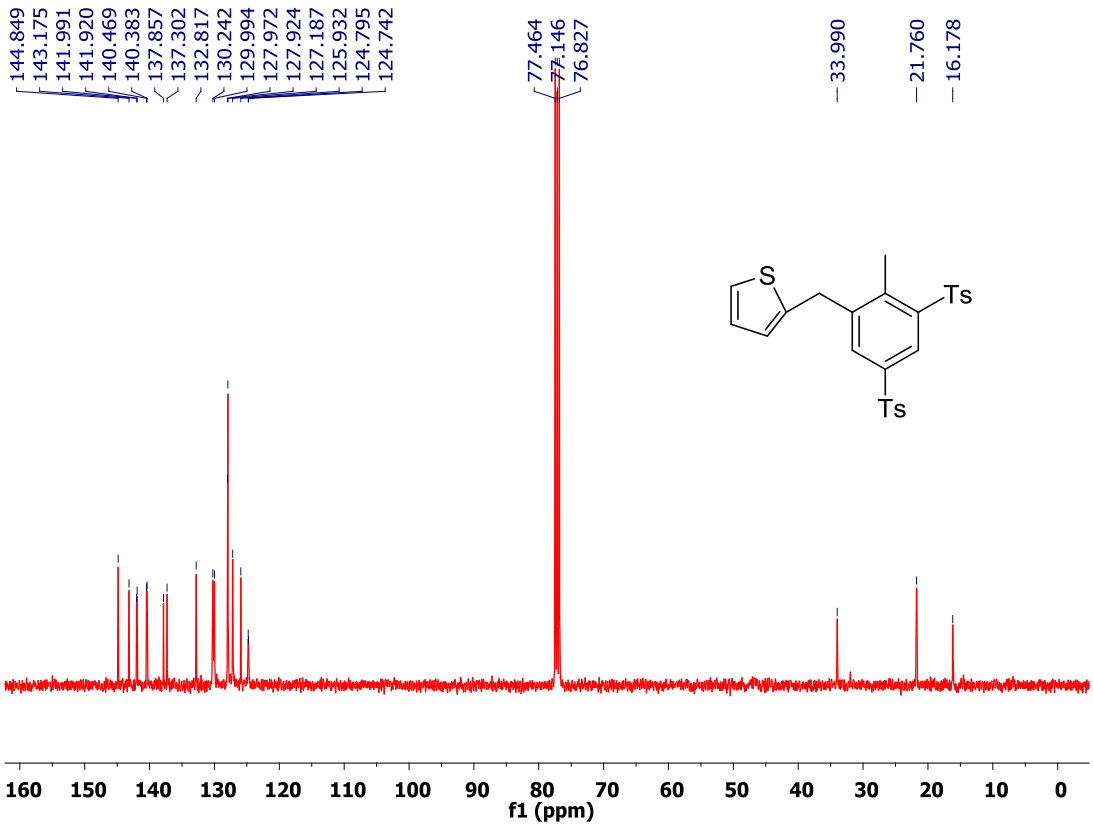
8.632
7.950
7.945
7.811
7.791
7.711
7.690
7.324
7.309
7.304
7.289
7.252
7.146
7.133
6.887
6.879
6.875
6.866
6.587
6.578
4.141
2.414
2.396
S
Ts
Ts
2.14
2.14
4.39
0.99
1.04
7.5
7.1
f1 (ppm)
1.00
1.05
2.14
2.14
4.39
0.99
1.04
1.02
2.14
6.21
3.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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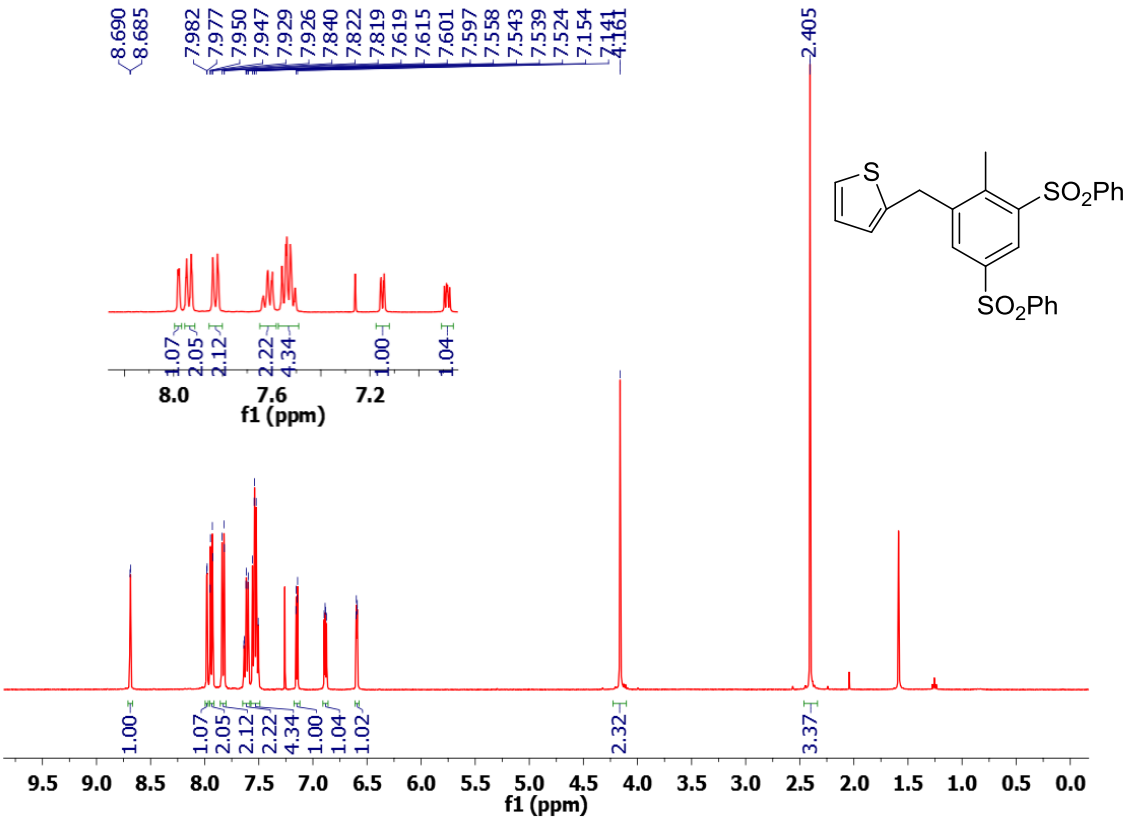
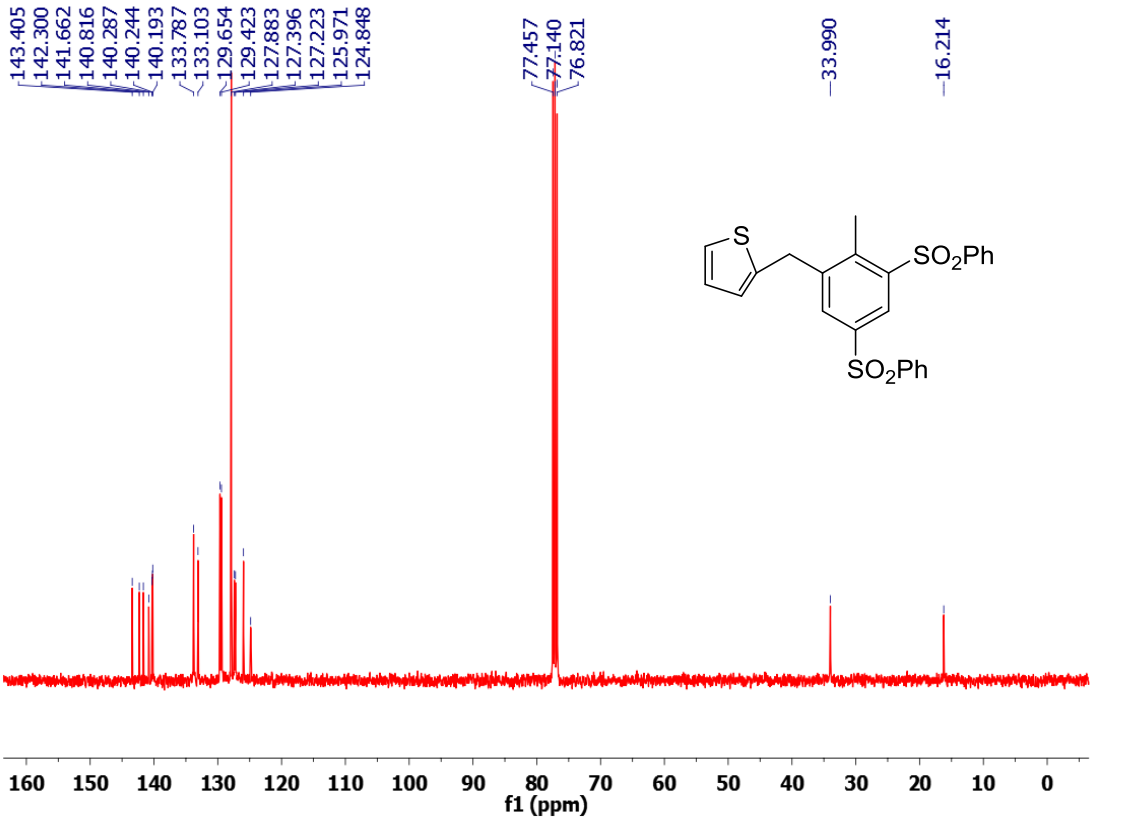
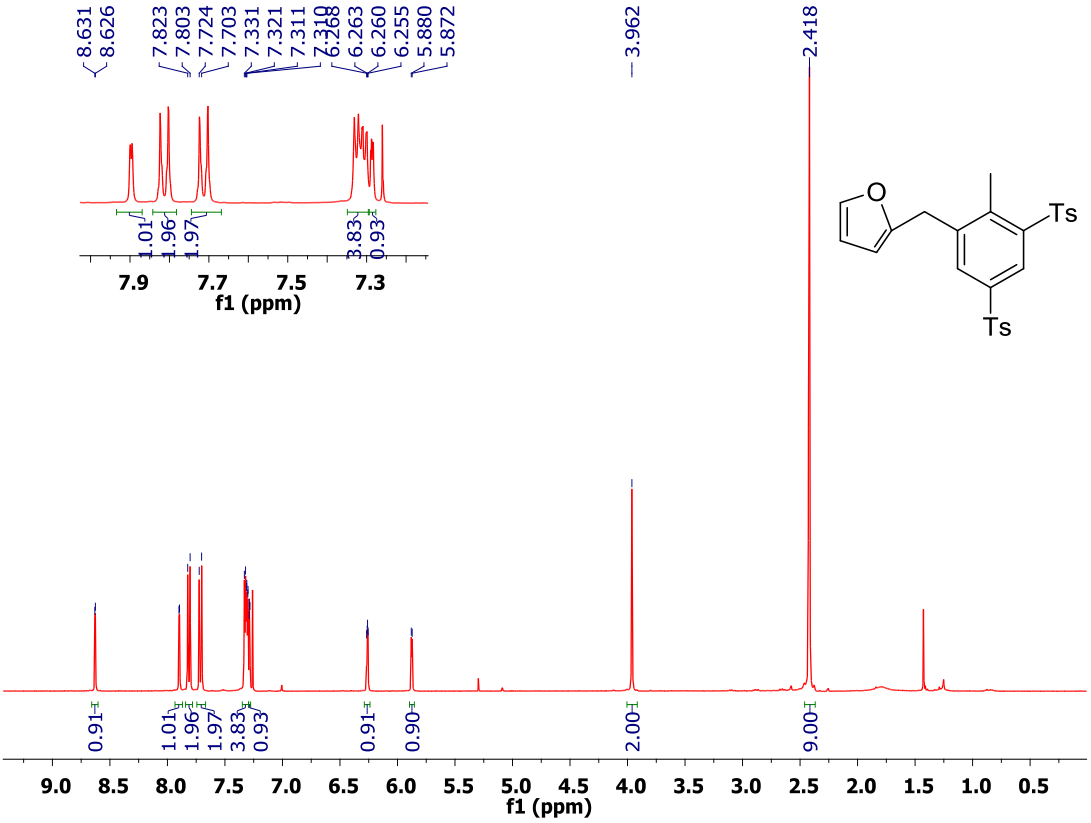
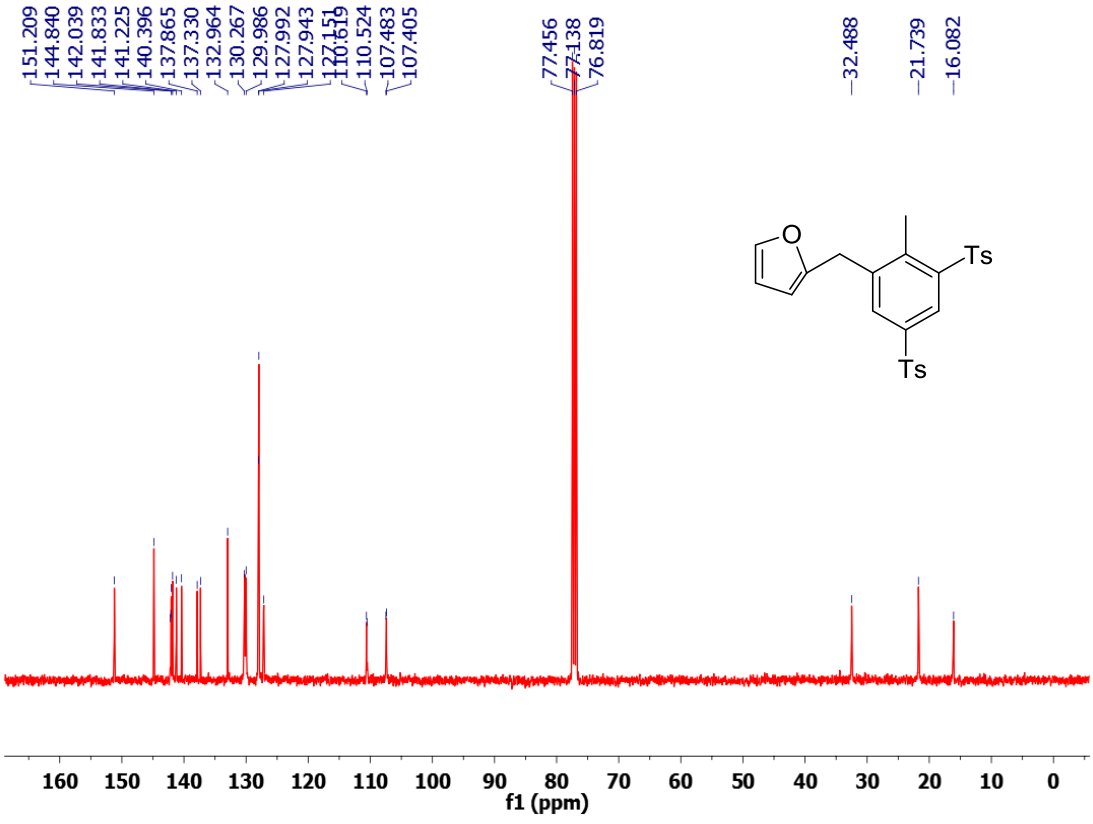
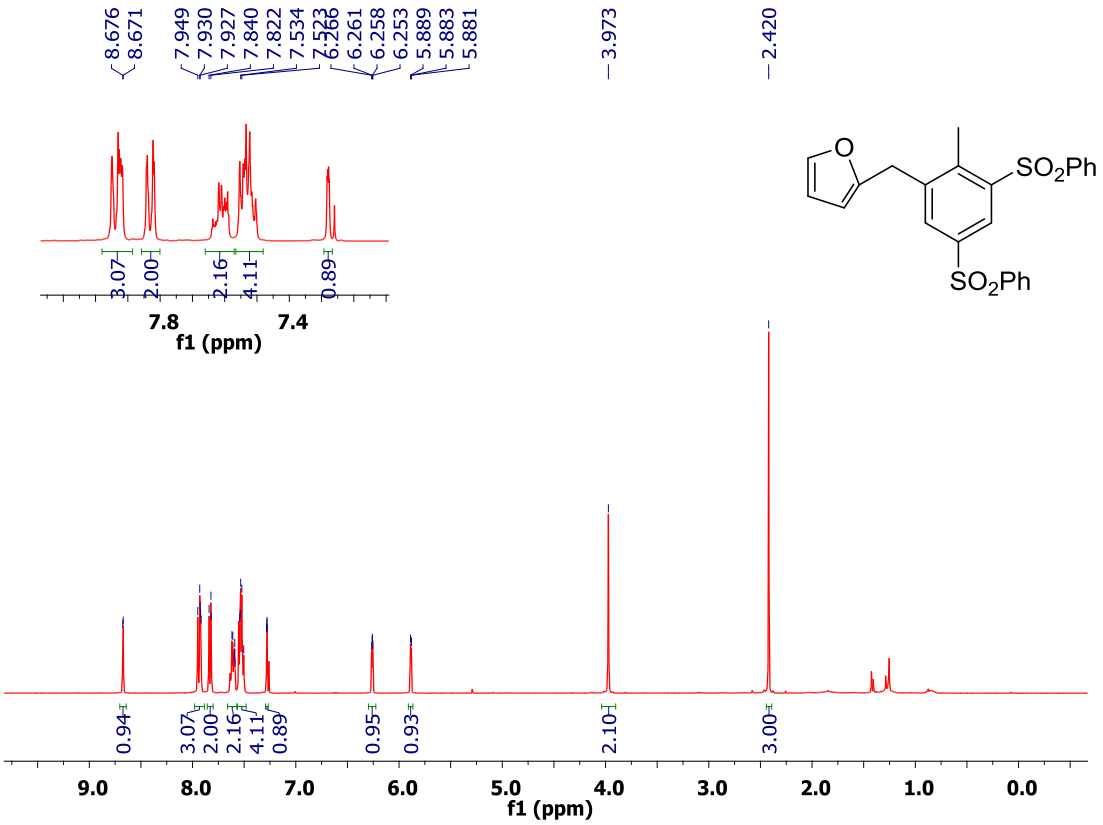
143.175
141.991
141.920
140.469
140.383
137.857
137.302
132.817
130.242
129.994
127.972
127.924
127.187
125.932
124.795
124.742
77.464
77.146
76.827
33.990
21.760
16.178
S
Ts
Ts
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

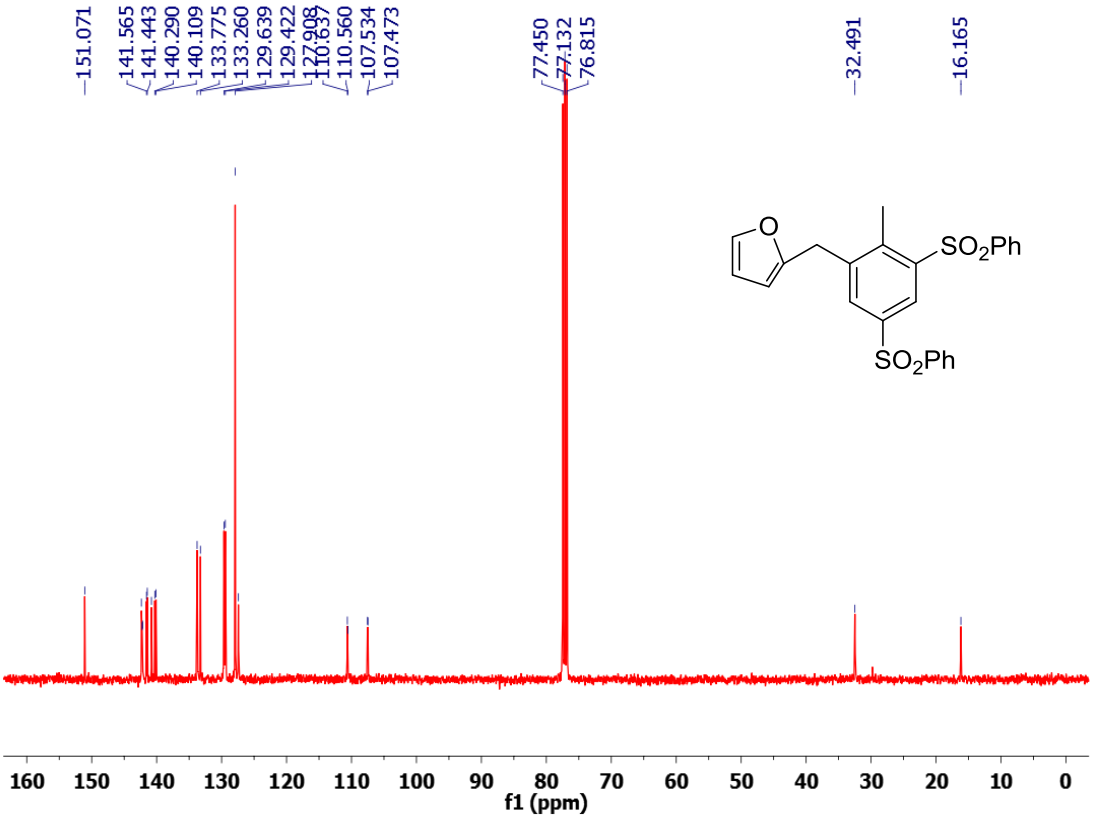

8.690
8.685
7.982
7.977
7.950
7.947
7.929
7.926
7.840
7.822
7.819
7.619
7.615
7.601
7.597
7.558
7.543
7.539
7.524
7.154
7.141
4.161
2.405
S
SO2Ph
SO2Ph
1.07
2.05
2.12
2.22
4.34
1.00
1.04
8.0
7.6
7.2
f1 (ppm)
1.00
1.07
2.05
2.12
2.22
4.34
1.00
1.04
1.02
2.32
3.37
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

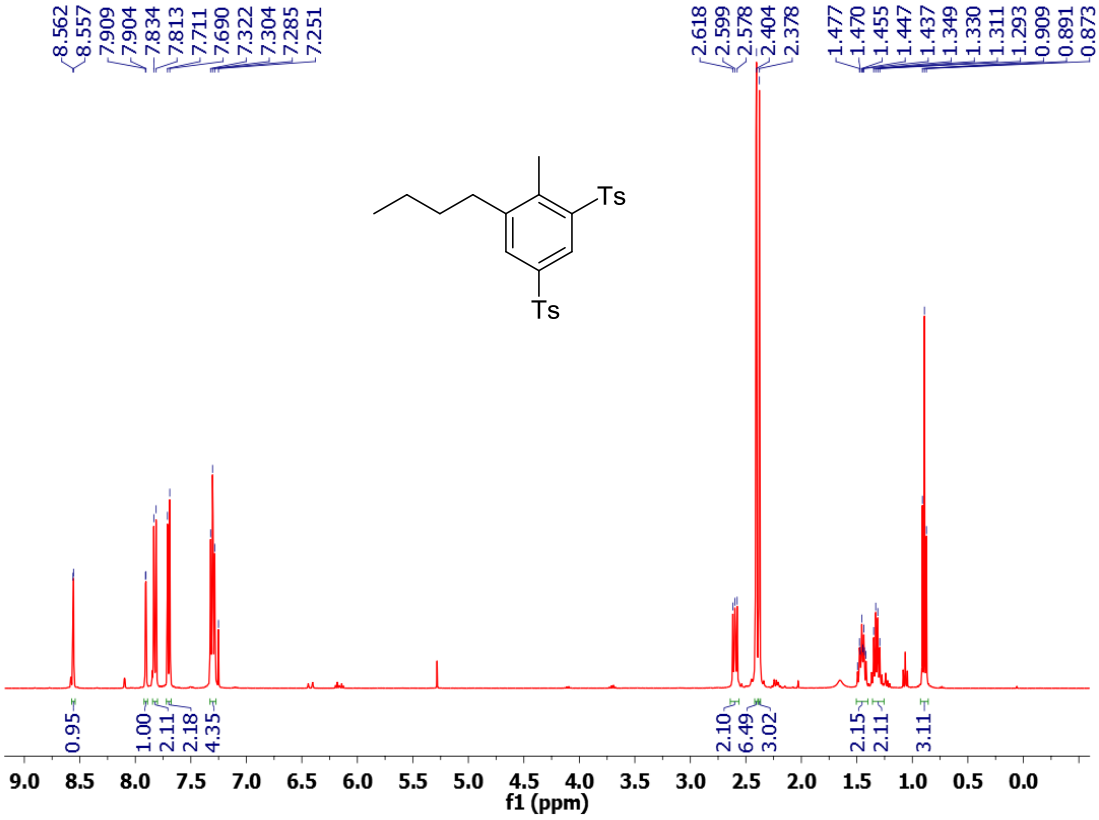

143.405
142.300
141.662
140.816
140.287
140.244
140.193
133.787
133.103
129.654
129.423
127.883
127.396
127.223
125.971
124.848
77.457
77.140
76.821
33.990
16.214
S
SO2Ph
SO2Ph
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

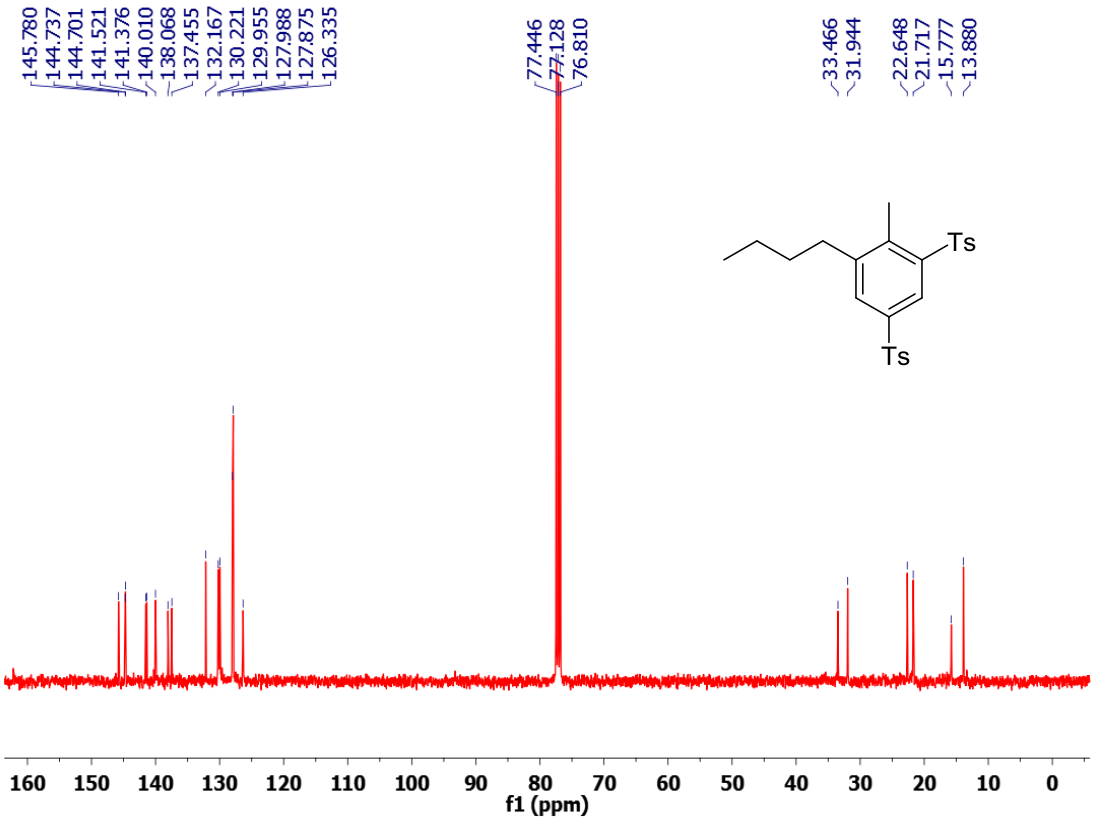

8.631
8.626
7.823
7.803
7.724
7.703
7.331
7.321
7.311
6.263
6.260
6.255
5.880
5.872
3.962
2.418
1.01
1.96
1.97
3.83
0.93
7.9
7.7
7.5
7.3
f1 (ppm)
O
Ts
Ts
0.91
1.01
1.96
1.97
3.83
0.93
0.91
0.90
2.00
9.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

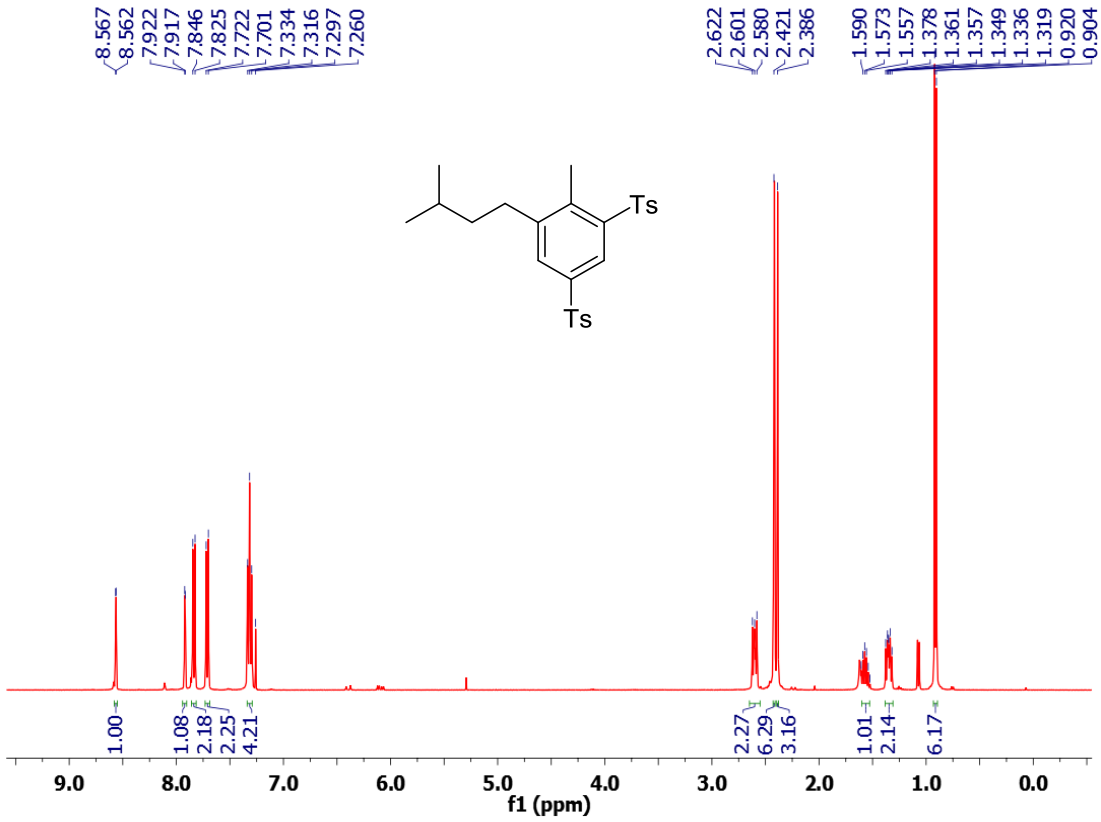

151.209
144.840
142.039
141.833
141.225
140.396
137.865
137.330
132.964
130.267
129.986
127.992
127.943
110.524
107.483
107.405
77.456
77.138
76.819
32.488
21.739
16.082
O
Ts
Ts
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

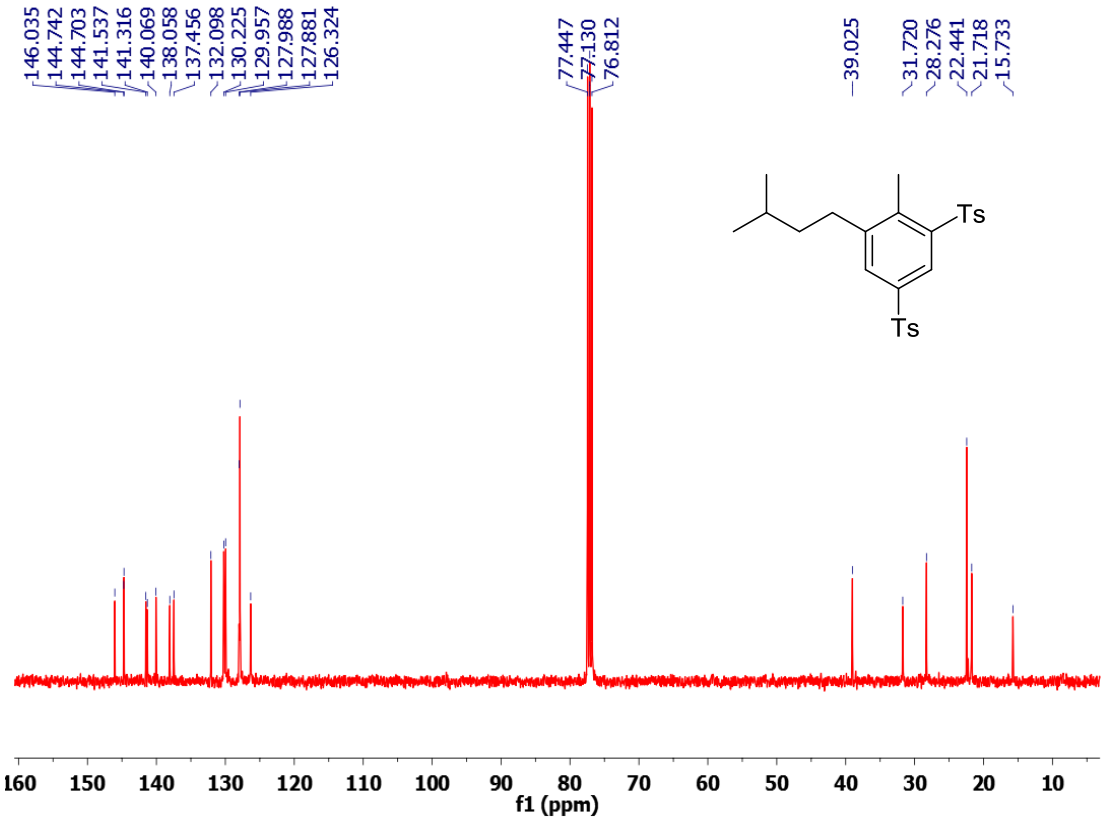

8.676
8.671
7.949
7.930
7.927
7.840
7.822
7.534
7.523
6.266
6.261
6.258
6.253
5.889
5.883
5.881
3.973
2.420
O
SO2Ph
SO2Ph
3.07
2.00
2.16
4.11
0.89
7.8
7.4
f1 (ppm)
0.94
3.07
2.00
2.16
4.11
0.89
0.95
0.93
2.10
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

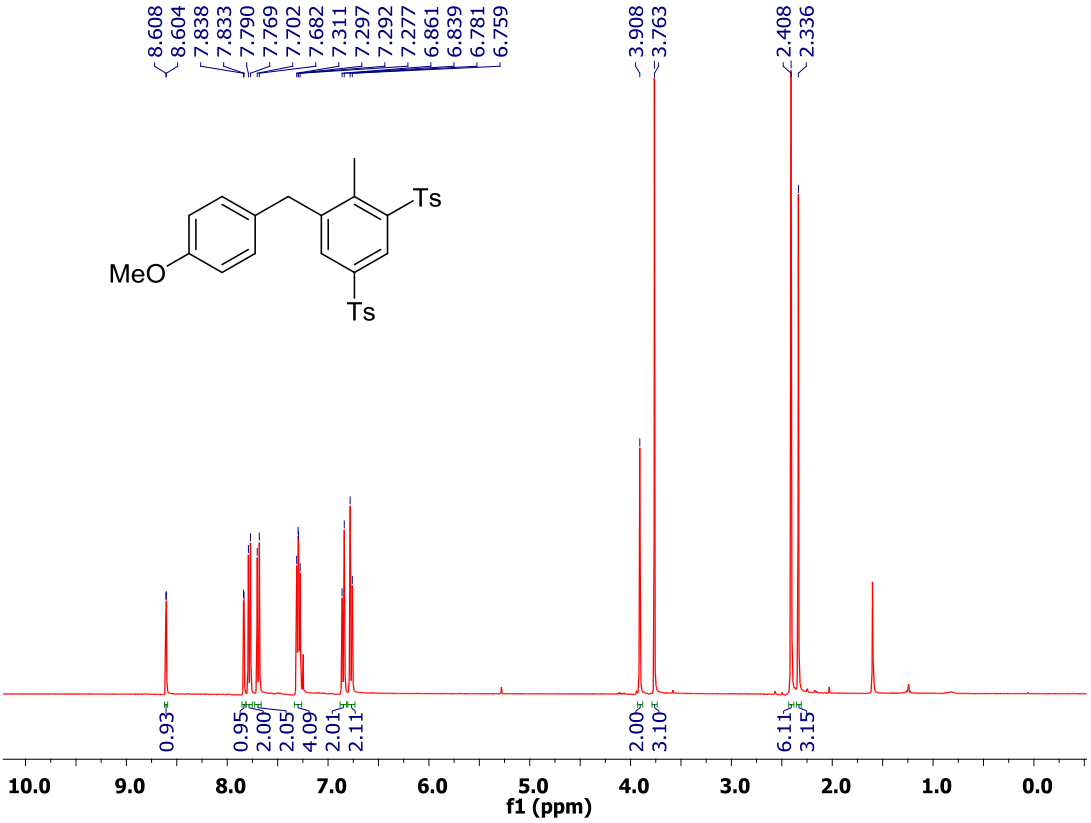

151.071
141.565
141.443
140.290
140.109
133.775
133.260
129.639
129.422
127.908
110.637
110.560
107.534
107.473
77.450
77.132
76.815
32.491
16.165
O
SO2Ph
SO2Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.562
8.557
7.909
7.904
7.834
7.813
7.711
7.690
7.322
7.304
7.285
7.251
2.618
2.599
2.578
2.404
2.378
1.477
1.470
1.455
1.447
1.437
1.349
1.330
1.311
1.293
0.909
0.891
0.873
Ts
Ts
0.95
1.00
2.11
2.18
4.35
2.10
6.49
3.02
2.15
2.11
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.780
144.737
144.701
141.521
141.376
140.010
138.068
137.455
132.167
130.221
129.955
127.988
127.875
126.335
77.446
77.128
76.810
33.466
31.944
22.648
21.717
15.777
13.880
Ts
Ts
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.567
8.562
7.922
7.917
7.846
7.825
7.722
7.701
7.334
7.316
7.297
7.260
2.622
2.601
2.580
2.421
2.386
1.590
1.573
1.557
1.378
1.361
1.357
1.349
1.336
1.319
0.920
0.904
Ts
Ts
1.00
1.08
2.18
2.25
4.21
2.27
6.29
3.16
1.01
2.14
6.17
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


146.035
144.742
144.703
141.537
141.316
140.069
138.058
137.456
132.098
130.225
129.957
127.988
127.881
126.324
77.447
77.130
76.812
39.025
31.720
28.276
22.441
21.718
15.733
Ts
Ts
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.608
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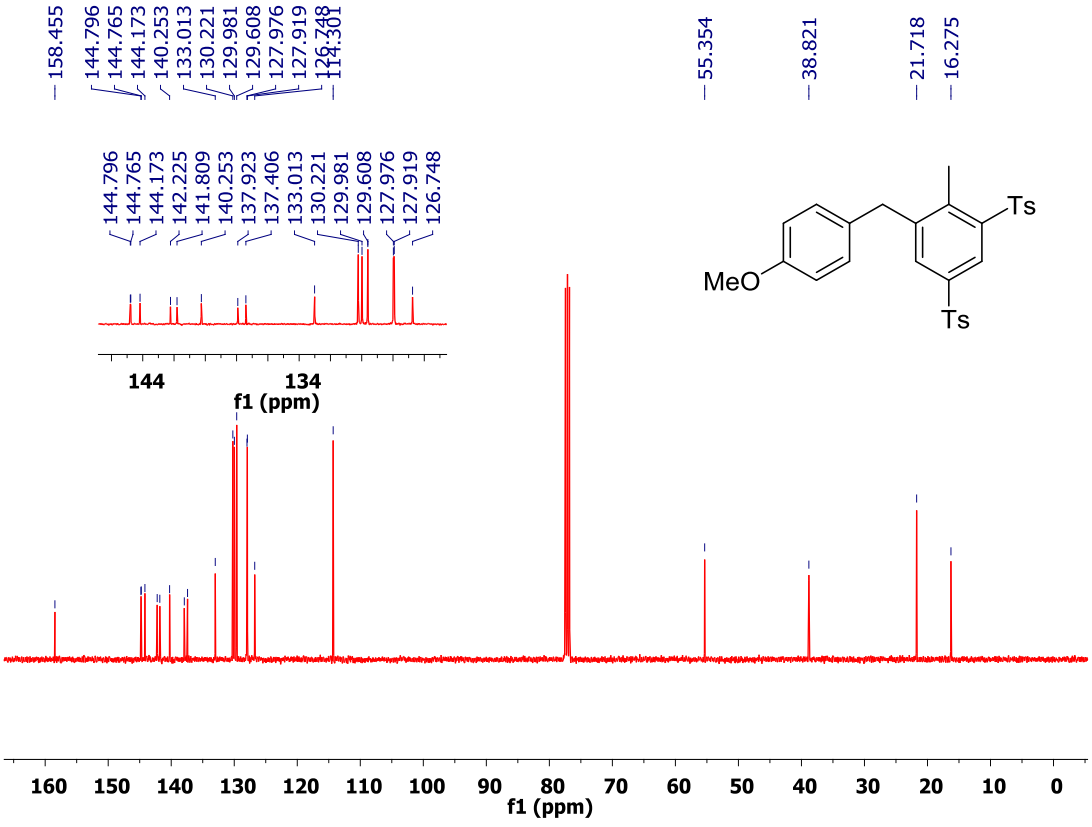
7.838
7.833
7.790
7.769
7.702
7.682
7.311
7.297
7.292
7.277
6.861
6.839
6.781
6.759
3.908
3.763
2.408
2.336
Ts
MeO
Ts
0.93
0.95
2.00
2.05
4.09
2.01
2.11
2.00
3.10
6.11
3.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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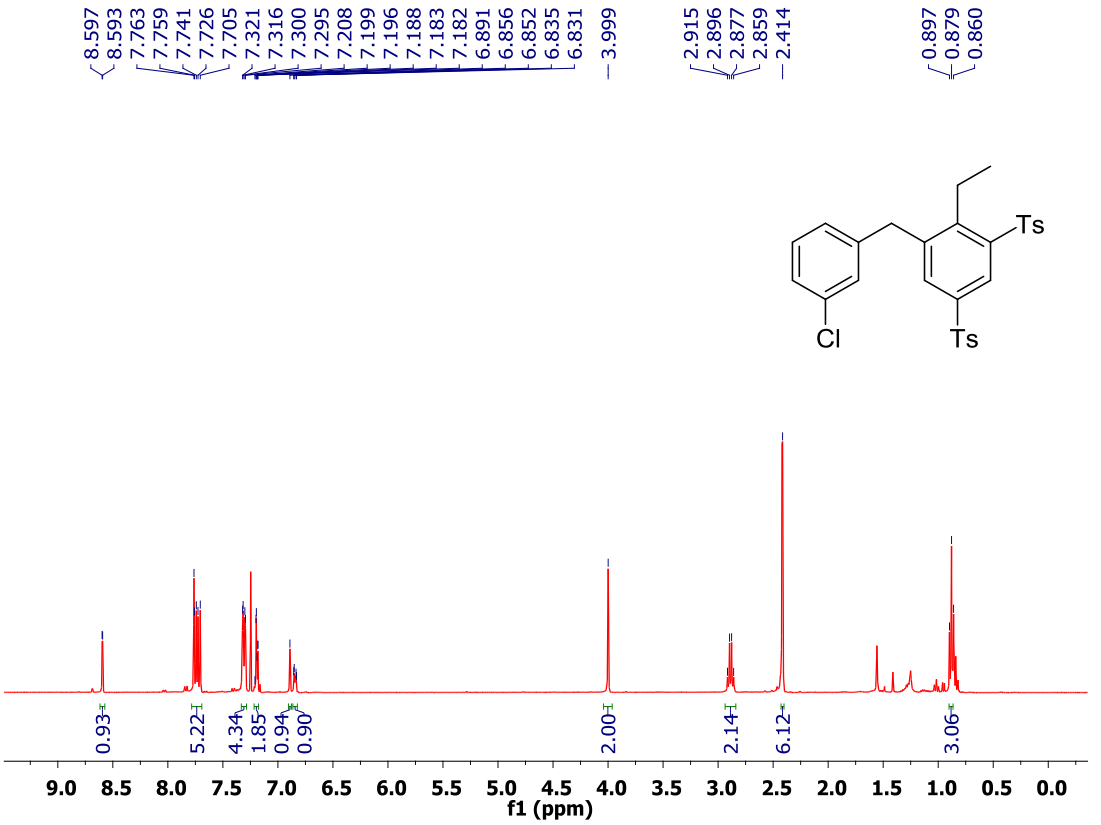
144.796
144.765
144.173
140.253
133.013
130.221
129.981
129.608
127.976
127.919
126.748
114.301
55.354
38.821
21.718
16.275
144.796
144.765
144.173
142.225
141.809
140.253
137.923
137.406
133.013
130.221
129.981
129.608
127.976
127.919
126.748
144
134
f1 (ppm)
Ts
MeO
Ts
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.763
7.759
7.741
7.726
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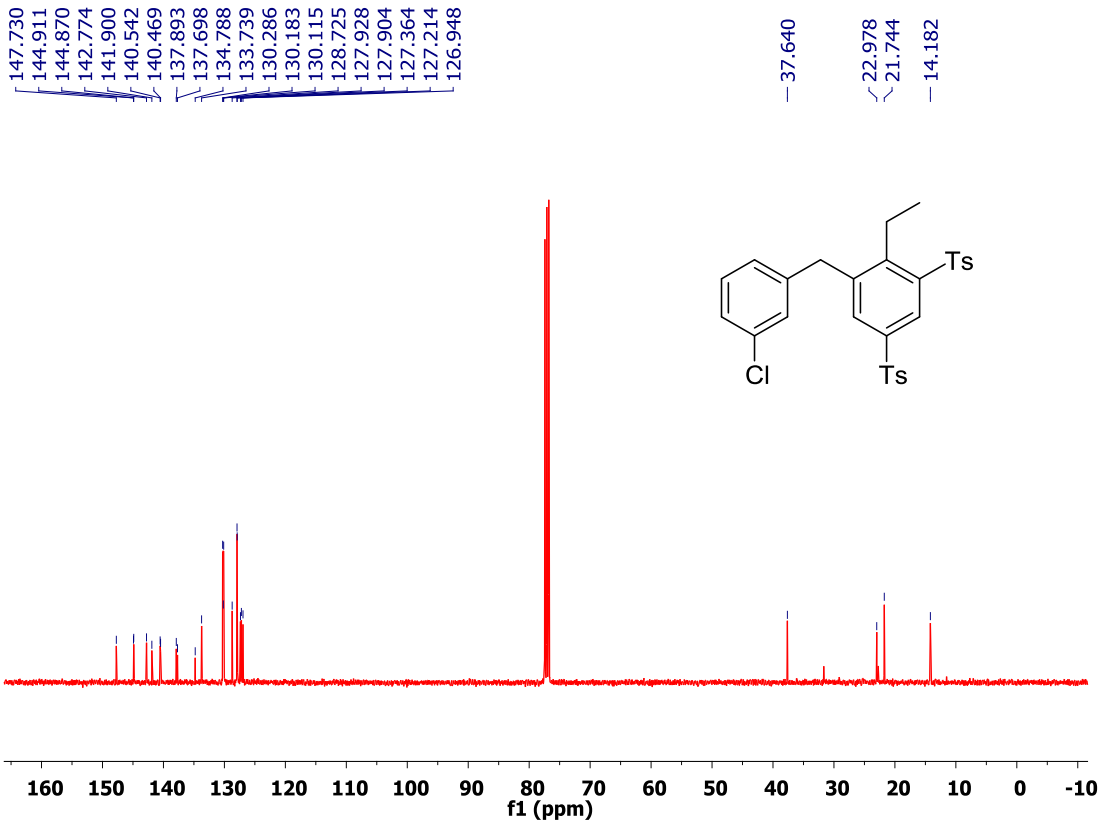
7.321
7.316
7.300
7.295
7.208
7.199
7.196
7.188
7.183
7.182
6.891
6.856
6.852
6.835
6.831
3.999
2.915
2.896
2.877
2.859
2.414
0.897
0.879
0.860
Ts
Cl
Ts
0.93
5.22
4.34
1.85
0.94
0.90
2.00
2.14
6.12
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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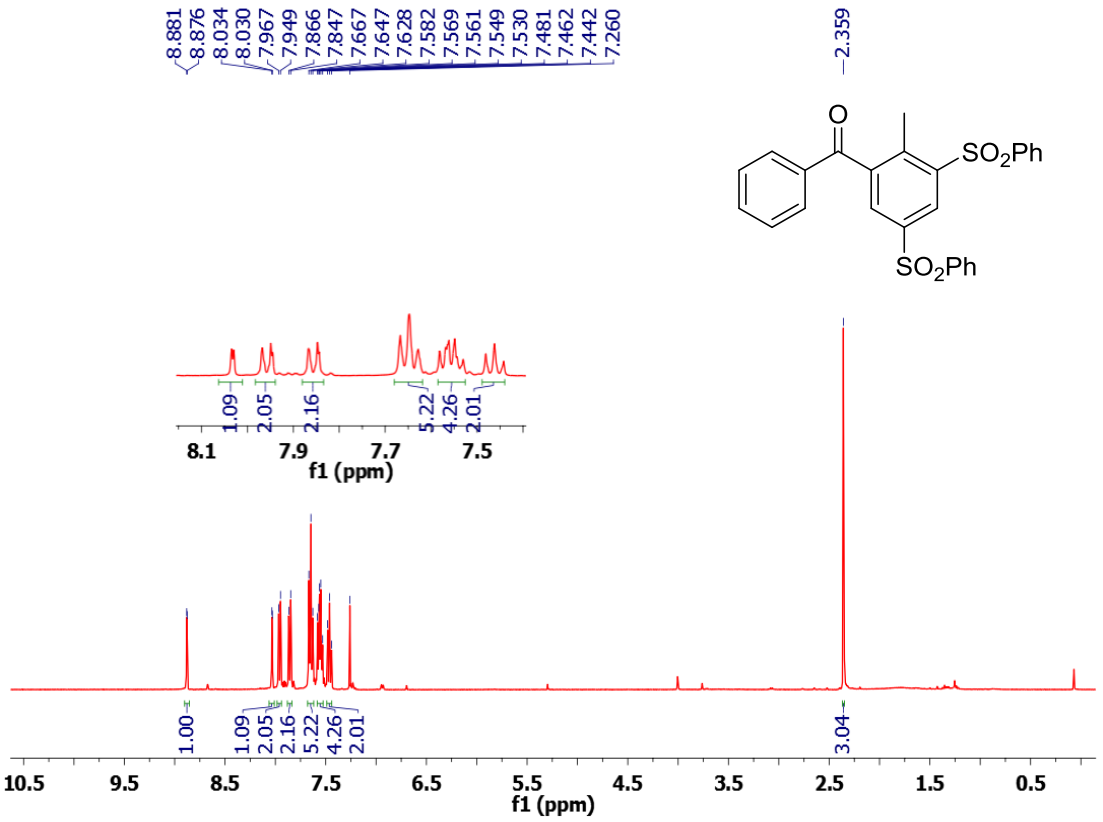
144.911
144.870
142.774
141.900
140.542
140.469
137.893
137.698
134.788
133.739
130.286
130.183
130.115
128.725
127.928
127.904
127.364
127.214
126.948
37.640
22.978
21.744
14.182
Ts
Cl
Ts
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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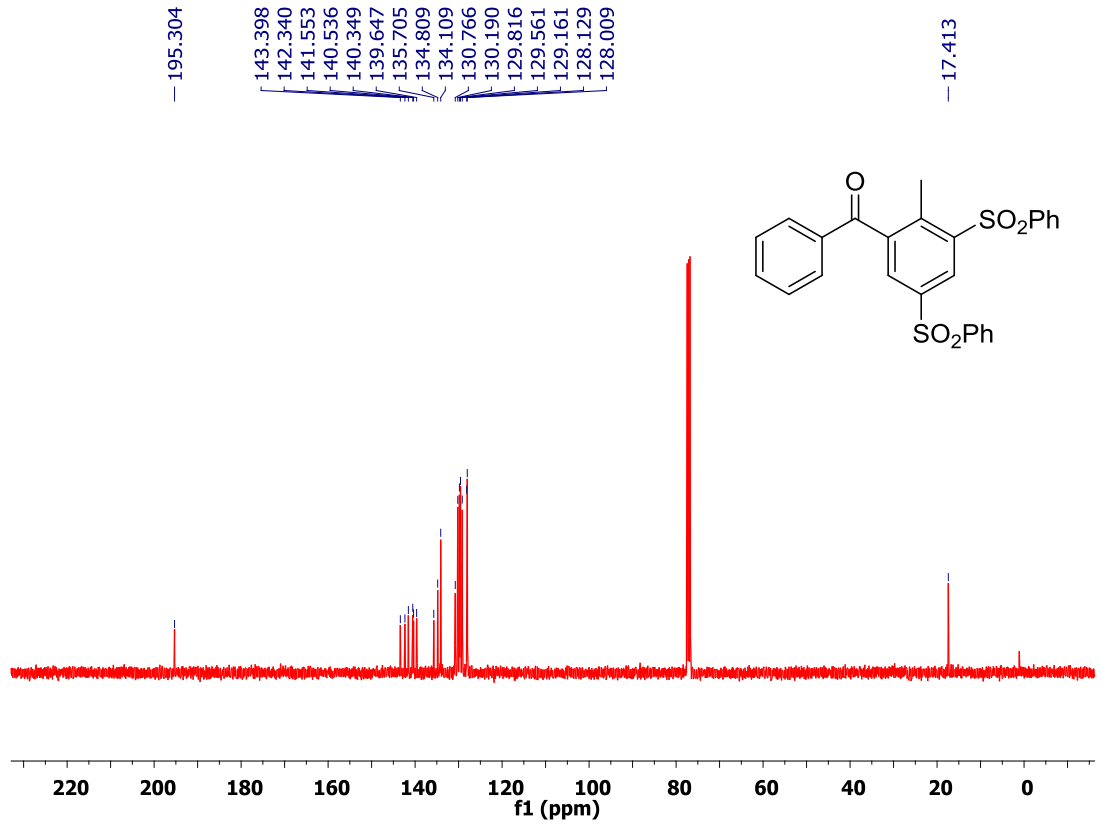
8.030
7.967
7.949
7.866
7.847
7.667
7.647
7.628
7.582
7.569
7.561
7.549
7.530
7.481
7.462
7.442
7.260
2.359
O
SO2Ph
SO2Ph
1.09
2.05
2.16
5.22
4.26
2.01
8.1
7.9
7.7
7.5
f1 (ppm)
1.00
1.09
2.05
2.16
5.22
4.26
2.01
3.04
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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142.340
141.553
140.536
140.349
139.647
135.705
134.809
134.109
130.766
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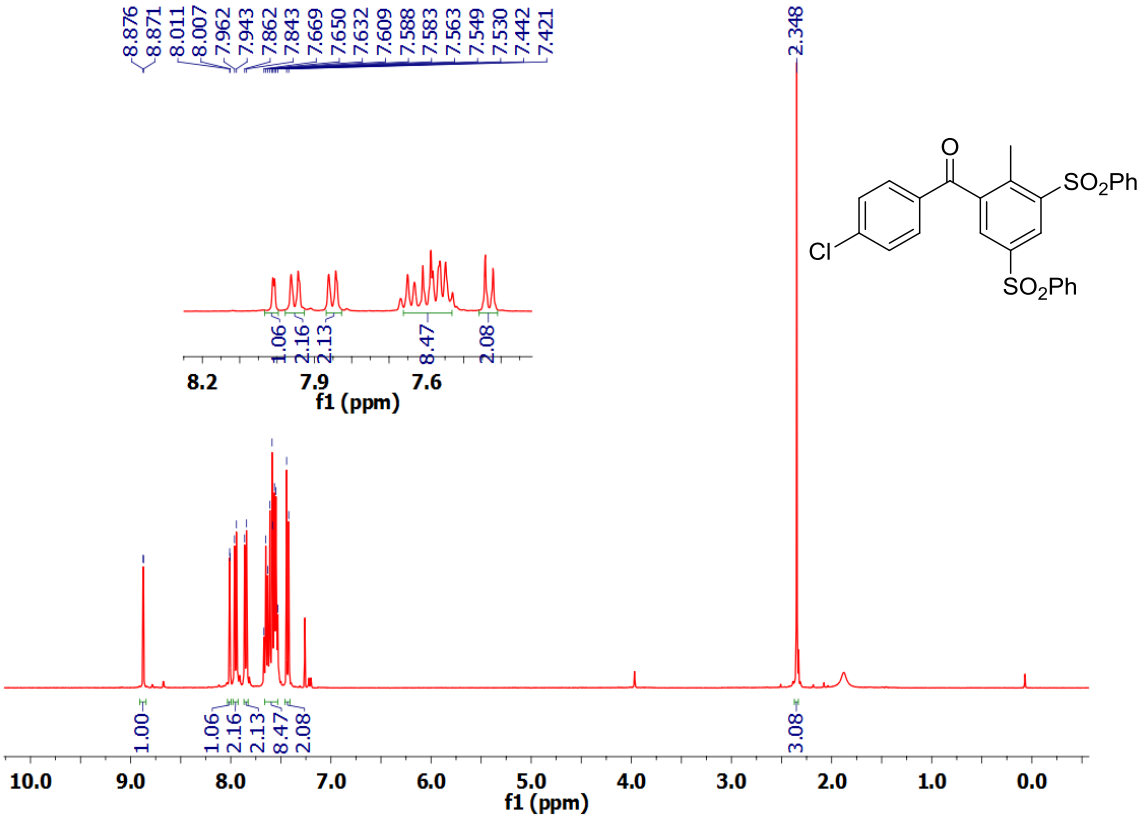
129.816
129.561
129.161
128.129
128.009
17.413
O
SO2Ph
SO2Ph
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.843
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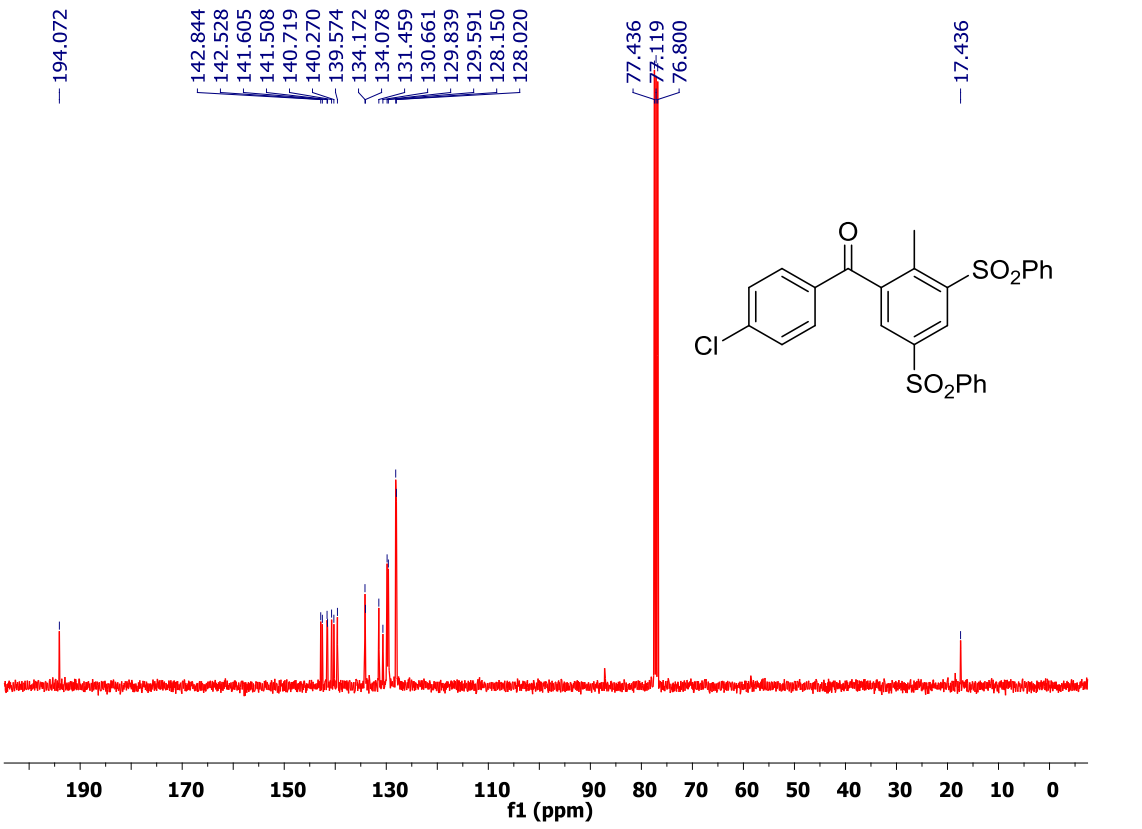
7.632
7.609
7.588
7.583
7.563
7.549
7.530
7.442
7.421
2.348
1.06
2.16
2.13
8.47
2.08
8.2
7.9
7.6
f1 (ppm)
1.00
1.06
2.16
2.13
8.47
2.08
3.08
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
O
SO2Ph
Cl
SO2Ph


194.072
142.844
142.528
141.605
141.508
140.719
140.270
139.574
134.172
134.078
131.459
130.661
129.839
129.591
128.150
128.020
77.436
77.119
76.800
17.436
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
SO2Ph
Cl
SO2Ph