Chapter III

Regioselective and oxidative [3+3] benzannulation reactions for the synthesis of highly substituted benzophenone derivatives

3.1. Introduction

Benzophenone is a privileged structural motif that is found in a variety of biologically active natural products and pharmaceuticals.[1] A number of benzophenone containing naturally occurring molecules exhibits a wide range of biological effects such as anti-inflammatory,[2] anti-microbial,[3] antioxidant,[4] anti-viral[5] and antiparasitic activities.[6] For example, cariphenone A, exhibits antioxidant activity and pestalone shows potent antibiotic activity against methicillin-resistant Staphylococcus aureus (MRSA) and vancomycin-resistant Enterococcus faecium (VREF). Additionally, cytotoxicity and anti-proliferative activity against cancer cells is commonly reported biological activity of a number of benzophenones.[7] Some important naturally occurring biologically active benzophenones are depicted in figure 1.

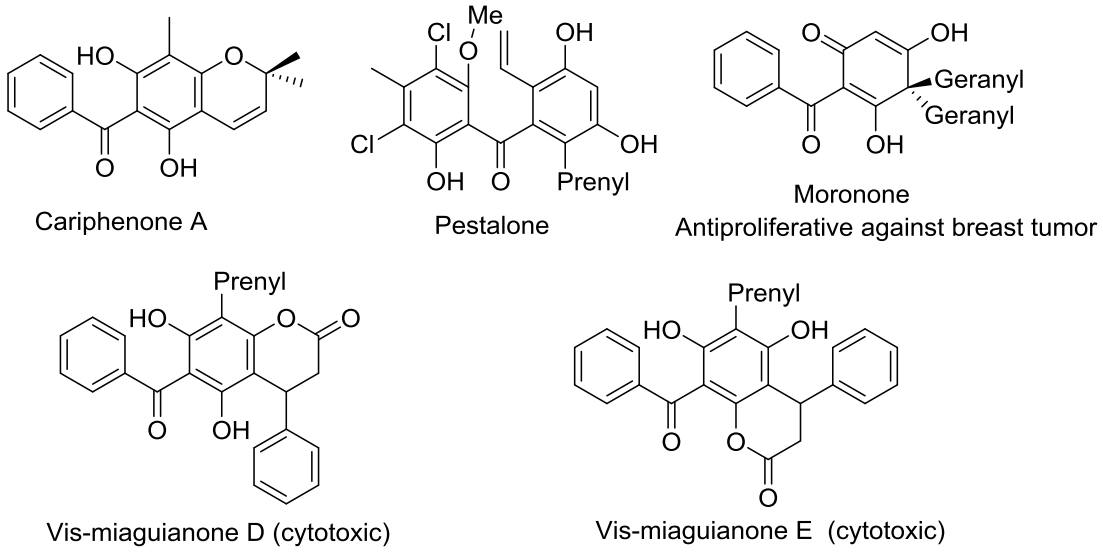


Figure 1: Some important naturally occurring biological active benzophenones

In addition to these biological activities, benzophenone represents one of the important classes of compounds in photochemical applications. Benzophenones show a significant absorption of ultra-violet (UV) light. Owing to their remarkable photochemistry they also find applications as photosenitizer,[8] photoredox catalysts[9] and active ingredients in sunscreens such as oxybenzone (Figure 2).[10] Additionally, a number of synthetic benzophenone derivatives are marketed as successful drugs. Tolcapone, a catechol-O-methyltranferase (COMT) inhibitor for the treatment of Parkinson's disease,[11] fenofibrate, a blood cholesterol reducing agent[12] and ketoprofen an antinflammatory drug, are three notable examples among these (Figure 2).

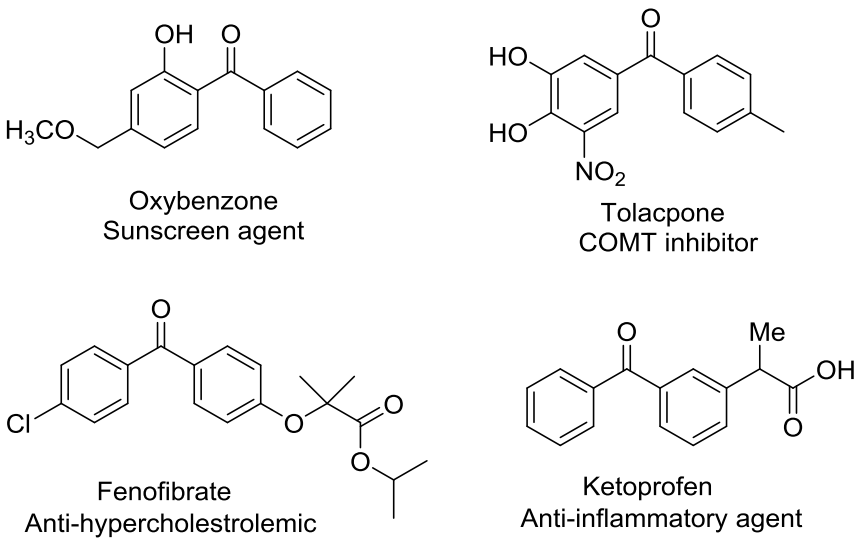


Figure 2: Selected examples of synthetic benzophenone-based drugs/cosmetics

Owing to their importance as building blocks in synthesis of many pharmacological compounds and photochemical properties, a number of synthetic methods for the construction of benzophenones have been developed. The most common among such methods is Friedel-Crafts benzoylation reactions.[14] The regiochemical outcome in these

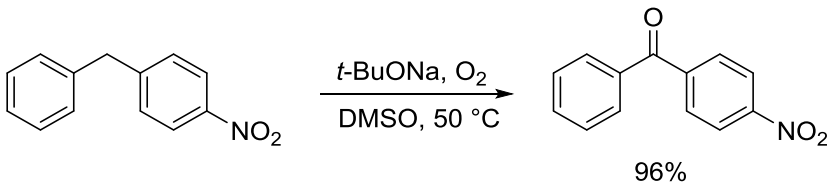
reactions is determined by the directing effect of the existing substituents on aryl ring. This feature may or may not lead to the selective formation of a desired regioisomer when the construction of poly-substituted benzophenone is attempted. Steric hinderence and deactivating effects of electron withdrawing groups also pose challenges in the synthesis of poly-substituted benzophenones.

To overcome these challenges, alternate methods such as oxidation of biarylmethanes,[15] oxidation of secondary alcohols,[16] metal-catalyzed coupling reactions,[17] oxidative cleavage of C-C double bonds[18] and direct addition of Grignard reagents to acyl chlorides[19] have been developed for their synthesis. Yet another alternative method is benzannulation reaction, wherein two acyclic precursors are combined together to form a benzene ring. The advantages of benzannulation reaction have been discussed in detail in chapter II. A brief overview of some of above-mentioned methods is described in following section.

3.2. Methods for the synthesis of benzophenone derivatives

3.2.1. Oxidation of biarylmethanes

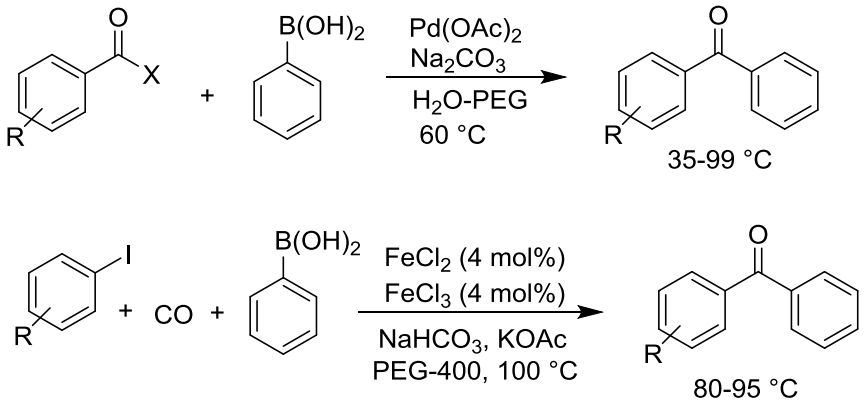
Li and co-workers developed a transition metal-free oxidation of benzylic sp^3 C-H bonds of biarylmethanes by O_2 and *t*-BuONa to generate the corresponding benzophenones (Scheme 1).[15a]



Scheme 1: Base and oxygen-mediated oxidation of biarymethanes to benzophenones

3.2.2. Transition metal-catalyzed coupling reactions

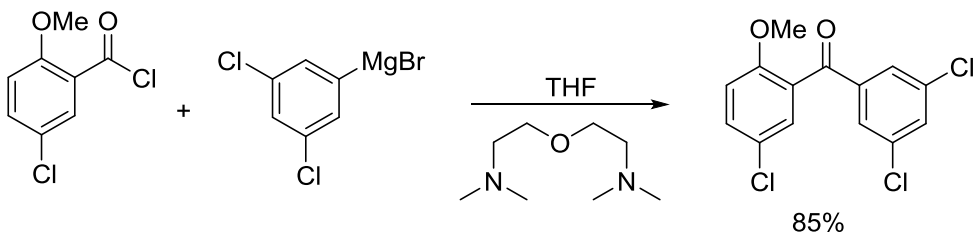
A variety of cross-coupling reactions for the synthesis of biaryl ketones are reported. Palladium-catalyzed cross coupling reactions of arylboronic acids with acyl halides, anhydrides or carboxylic acids is one among them.[17b] In addition, carbonylative coupling reaction is a widely used method for the construction of symmetrical and unsymmetrical benzophenones (Scheme 2).[17c]



Scheme 2: Synthesis of benzophenones via transition metal-catalyzed coupling reactions

3.2.3. Direct addition of Grignard reagents to acid chlorides

The addition of arylmagnesium halides to acid chlorides was reported by Wang and co-workers. The reaction afforded various aryl ketones in good yield when carried out in the presence of a simple tridentate ligand, *bis*-[2(N,N-dimethylamino)ethyl]ether (Scheme 3).[19]

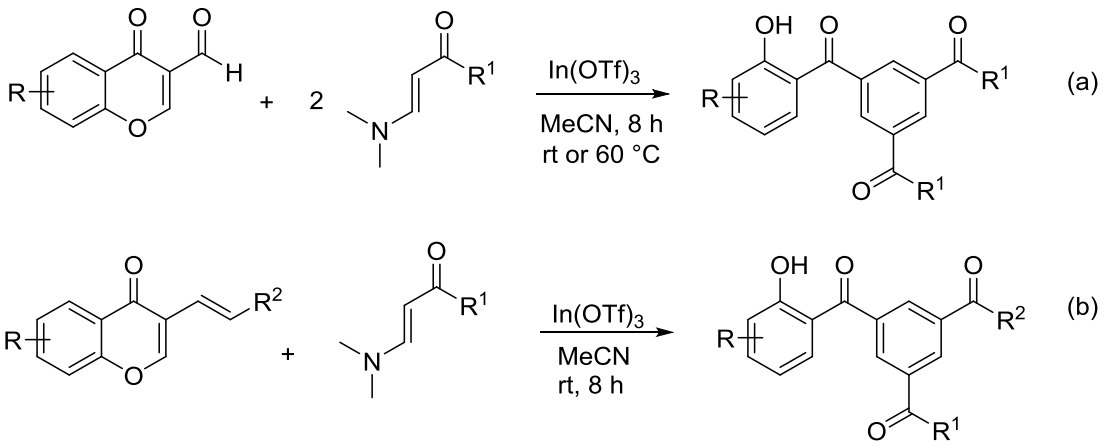


Scheme 3: Addition of arylmagnesium bromide to an acid chloride

It may be noted that the above discussed methods utilize precursors having pre-existing arene rings and conveniently provide access to a number of simple benzophenone derivatives. However, their scopes are limited when poly-functional benzophenones are required as the necessary building blocks would not be readily available. As stated above, benzannulation reactions, offer a number of advantages in such situations. Benzannulation reactions are superior to conventional methods in terms of variety of available reaction components, scope of catalysis and versatility of reaction conditions. A selection of benzannulation-based synthesis of benzophenone derivatives are described below to illustrate these virtues.

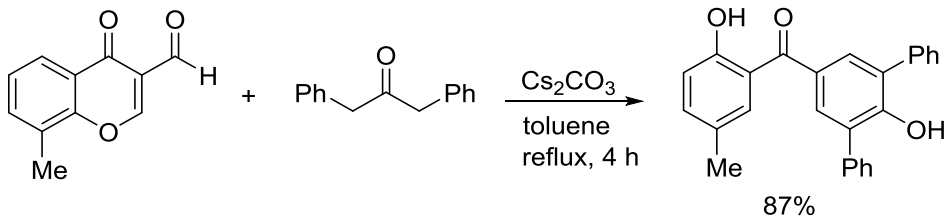
3.2.4. Benzannulation-based methods for synthesis of benzophenone derivatives

Lee and co-workers reported the construction of 2-hydroxybenzophenone derivatives *via* Indium(III)-catalyzed [2+2+2] benzannulation reaction of 3-formylchromones with β-enamino ketones or esters (Scheme 4a). In addition, they developed a [4+2] benzannulation reaction of 3-substituted chromen-4-ones with β-enamino ketones or esters that lead to the same class of products (Scheme 4b).[20]



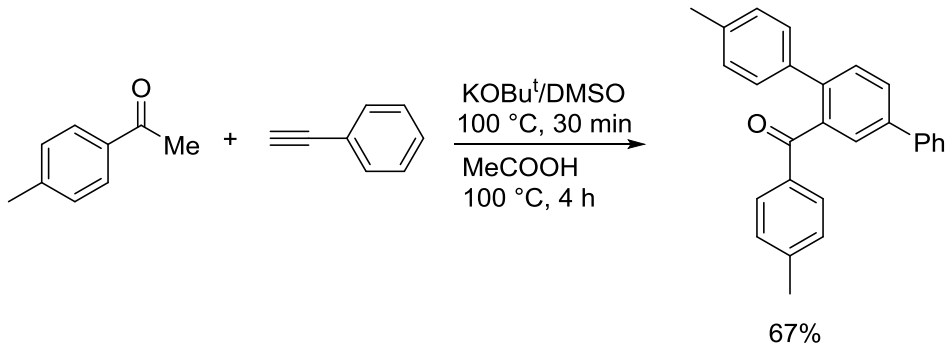
Scheme 4: Construction of 2-hydroxybenzophenone derivatives *via* [2+2+2] and [4+2] benzannulation reactions

A Cs_2CO_3-promoted benzannulation of 3-formyl chromones amd 1,3-diphenyl-2-propanone was also developed by Lee and co-workers. The reaction proceeds through an initial Knoevenagel condensation which is followed by an intramolecular Michael addition to generate substituted benzophenone derivatives (Scheme 5).[21]



Scheme 5: Synthesis of benzophenone derivatives from 3-formyl chromones and 1,3-diphenyl-2-propanone

A base-promoted reaction of acetylarenes with arylacetylenes furnished benzophenone derivatives. The reaction proceeds by the addition of enolate derived from acetylarene to arylacetylene to afford β,γ-unsaturated ketones. Subsequent [3+3] annulation reaction of the newly generated ketone with another molecule of β,γ-unsaturated ketone leads to the formation of benzophenone derivative (Scheme 6).[22]



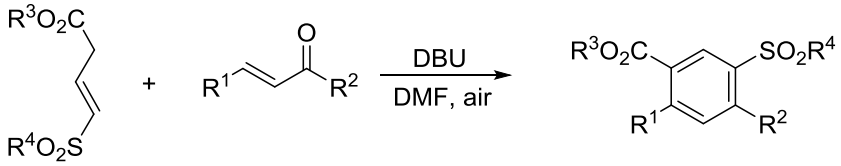
Scheme 6: Base-mediated synthesis of benzophenones from acetylarenes and arylacetylenes

3.3. Background to the present work

In view of the above-mentioned importance of benzophenone derivatives as well as the advantages of benzannulation reactions, we became interested in developing a convenient

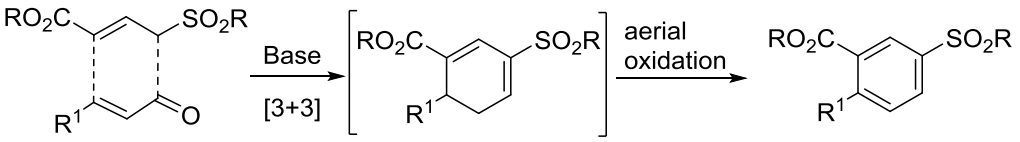
benzannulation-based route to benzophenones. The successful development of aerobic oxidative [3+3] benzannulation reaction of α,β-unsaturated carbonyl compounds with 4-sulfonyl crotonates to afford poly-substituted arenes (Scheme 7a)[23] and a related report[24] encouraged us to undertake this exploration. Mechanistically, our method involved a cyclocondensation of a bis-nucleophile and a bis-electrophile to generate a cyclohexadiene intermediate which underwent in situ aerial oxidation to the arene product (Scheme 7b). The bis-nucleophile (4-sulfonyl crotonate) may be viewed as a propene substituted with two electron withdrawing groups (ester and sulfonyl) at both ends. It was of interest to explore whether the ester group can be replaced with a ketone functionality (compound **1**). A parallel mechanistic scenario can be contemplated lading to the formation of a benzophenone product from **1** and enal **2** in the case of aroyl ketone (Scheme 7c).

Our previous work:



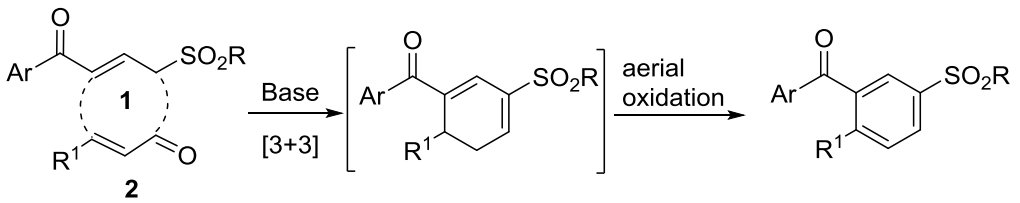
(a)

Simplified mechanistic overview:



(b)

Proposed benzannulation reaction:



(c)

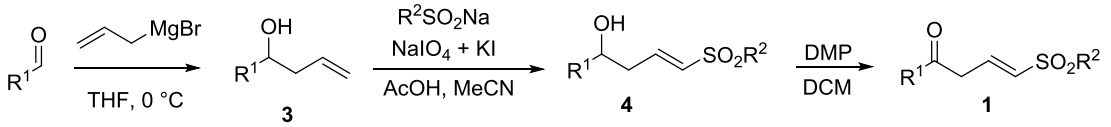
Scheme 7: [3+3] benzannulation reaction of α,β-unsaturated carbonyl compounds (a) with 4-sulfonyl crotonates (b) simplified mechanistic overview (c) Proposed benzannulation reaction

The implementation of the plan, however, posed two serious challenges: (i) ready availability of the 3-carbon nucleophilic component and (ii) the steric demands of a arylketo group would only be slightly different from that of the sulfonyl group thereby making steric differentiation of both ends of the propene unit by the bis-electrophile more challenging (the ester unit in the previous study is considerably smaller than the arylsulfonyl groups). This might lead to non-regioselective outcomes. However, in view of the importance of the product class and previous success we undertook the studies.

Our efforts towards this end, resulted in the discovery of a base-mediated, aerial oxidative [3+3] benzannulation reaction that afforded benzophenone/arene derivatives in excellent regioselectivity. The results of this study are presented in the following passages.

3.4. Results and discussion

In order to test our hypothesis, a convenient access to the required 1,3-bis-nucleophile **1** (1,3-disubstituted propene) was necessary and a three-step preparation from aldehydes was developed. The homoallylic alcohols **3** formed *via* allylation of aldehydes were treated with sodium arylsulfinates, $NaIO_4$ and KI to furnish the vinyl sulfones **4**.[25] This reaction proceeds via the iodosulfonylation of the terminal alkene and subsequent dehydroiodination. Oxidation of the secondary alcohol **4** using Dess-Martin periodinane (DMP) afforded the desired keto-sulfone **1** (Scheme 8).



Scheme 8: Preparation of the nucleophilic three-carbon building block **1** for the proposed benzannulation

Pleasingly this reaction was applicable to a number of aldehydes and a number of 1,3-bis-nucleophiles **(1a-1h)** were synthesized in good yields. A summary is depicted table 1. Substituted aryl ketones (**1a-f**, entries 1-6) were readily prepared from corresponding araldehydes, an alkyl derivative (**1g**, entry 7) was made from isovaleraldehyde and a heterocyclic analogue (**1h**, entry 8) from 2-formyl thiophene.

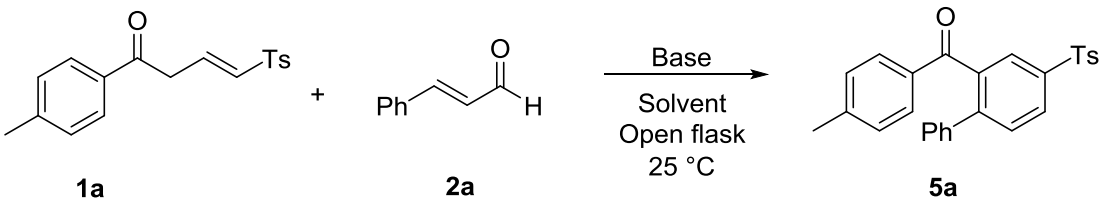
Table 1: Substrate scope for the preparation of 1,3-bis-nucleophile component 1

Entry	R^1	R^2	Isolated yield of **4** (%)	Isolated yield of **1** (%)
1	*p*-tolyl	*p*-tolyl	**4a**, 76	**1a**, 89
2	*p*-tolyl	Ph	**4b**, 74	**1b**, 87
3	phenyl	*p*-tolyl	**4c**, 75	**1c**, 89
4	4-bromophenyl	*p*-tolyl	**4d**, 81	**1d**, 91
5	2,3,4-trimethoxyphenyl	*p*-tolyl	**4e**, 78	**1e**, 89
6	4-isopropylphenyl	*p*-tolyl	**4f**, 73	**1f**, 84
7	isobutyl	*p*-tolyl	**4g**, 71	**1g**, 82
8	thiophene-2-yl	*p*-tolyl	**4h**, 68	**1h**, 78

Following the synthesis of precursors, we started our investigations with the benzannulation reaction of **1a** with a simple electrophilic partner cinnamaldehyde **2a**. Initially, these two reactants were treated under the optimized conditions for previously developed benzannulation reaction of sulfonyl crotonates (entry 1, Table 2). Reaction was carried out in open flask to promote aromatization via aerial oxidation. Pleasingly, a crystalline product was isolated after standard work-up and column chromatography. The product was tentatively assigned the structure **5a** on the basis of spectroscopic analysis. In the ^{1}H NMR spectrum of **5a** two different singlets at δ 2.34 (3H) and δ 2.42 (3H) were visible, indicating the presence of two methyl groups on aryl rings in the

final product. In ^{13}C NMR spectrum, the signals at δ 21.8 and δ 21.7 confirmed the presence of these two methyl groups. The signal at δ 8.01 (d, J = 2.0Hz, 1H) was assigned to proton that is sandwiched between the carbonyl and sulfonyl group on the newly formed ring. The other hydrogens in aromatic region gave the expected resonance pattern. In ^{13}C NMR spectrum, the signal at δ 196.3 indicated the presence of ketone carbon in the product. An absorption band at 1741 cm^{-1} in IR spectrum also agreed with this assignment. Other spectroscopic features were also in agreement with the assigned structure. It may be noted that the depicted regiochemistry was tentatively assigned at this stage for the compound **5a**.

Table 2: Optimization of reaction conditions for benzannulation reaction of 1,3-bis nucleophile 1a and cinnamaldehyde 2a[a]



1a **2a** **5a**

Entry	Base (mmol)	Solvent	Time (h)	Product (yield %)[b]
1	DBU (1.1)	DMF	2	54
2	DBU (1.1)	CH_3CN	2	43
3	DBU (1.1)	THF	2	49
4	DBU (1.1)	DMSO	2	42
5	DBU (1.1)	1,4-dioxane	2	29
6	DBU (1.1)	CH_2Cl_2	2	36
7	**DBU (2)**	**DMF**	**1**	**74**
8	Cs_2CO_3 (2)	DMF	1	41
9	Pyridine (2)	DMF	1	32
10	t-BuOK (2)	DMF	1	40
11[c]	DBU (2)	DMF	1	72

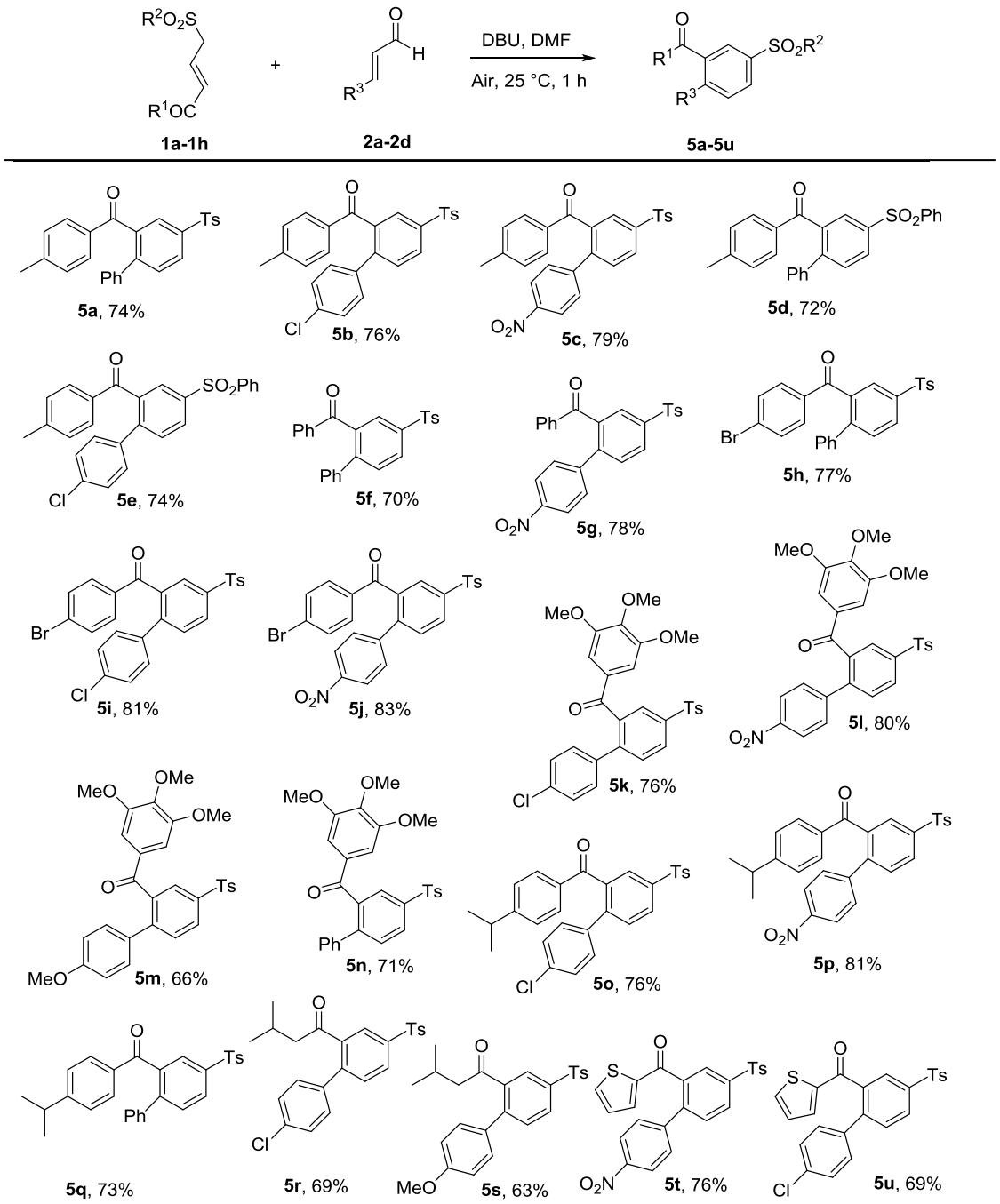
[a]Reaction conditions: **1a** (0.11 mmol), **2a** (0.1mmol), DMF (1 ml), 25 °C. [b]Yield of isolated product. [c]under oxygen atmosphere.

Although the product **5a** could be isolated and identified, the yield (54%) was less than satisfactory. Therefore, a number of reaction conditions were investigated by varying the nature and amount of base in various solvents. The same product **5a** was obtained in all cases in varying yields. The best result was obtained when the reactants were exposed to two molar equivalent of DBU in DMF for 1h (entry 7, table 2). Other bases such as cesium carbonate (entry 8), pyridine (entry 9), potassium tert-butoxide (entry 10) and solvents (entry 2-6) were less effective in promoting the benzannulation reaction. There was no significant change in yield when the reaction was carried out under an oxygen atmosphere (entry 11, table 2).

The pleasing outcome encouraged us to explore the substrate scope and generality for this benzannulation reaction. The various 1,3-bis-nucleophiles **1a-h** and α,β-unsaturated aldehydes were subjected to the optimized benzannulation conditions. Delightfully, the corresponding benzophenone derivatives isolated in all the cases. The results are summarized in Table 3.

All the 1,3-bis nucleophiles **1a-h** reacted smoothly with different α, β- unsaturated aldehydes and afforded a wide variety of highly substituted sulfone-bearing benzophenone and arene derivatives. Both electron withdrawing groups such as nitro **(5g, 5l, 5p, 5t)** and electron donating group such as methoxy **(5m, 5s)** are tolerated in benzannulation reaction. A heterocyclic residue such as thiophene can also be easily incorporated into final product by using the corresponding 1,3-bis-nucleophile **1h**.It is important to note that the reaction is not limited to aryl 1,3-bis-nucleophile. The alkyl ketone **1g** reacted smoothly with various enals in the benzannulation reaction to afford the corresponding substituted isobutyl aryl ketones **(5r, 5s)**.

Table 3: Generality and scope of the benzannulation reaction[a]



[a]Reaction conditions: **2a** (0.3mmol), 1,3-bis-nucleophile **1a-h** (0.33 mmol), DBU (0.45 mmol) DMF (4 ml), 25 °C, 1h. Yield of isolated products given.

Single crystal X-ray analysis of a representative product **5h** was also obtained at this stage (Figure 4). Thus the structure and regiochemistry assignment of the products **5a-u** were unambiguously established.

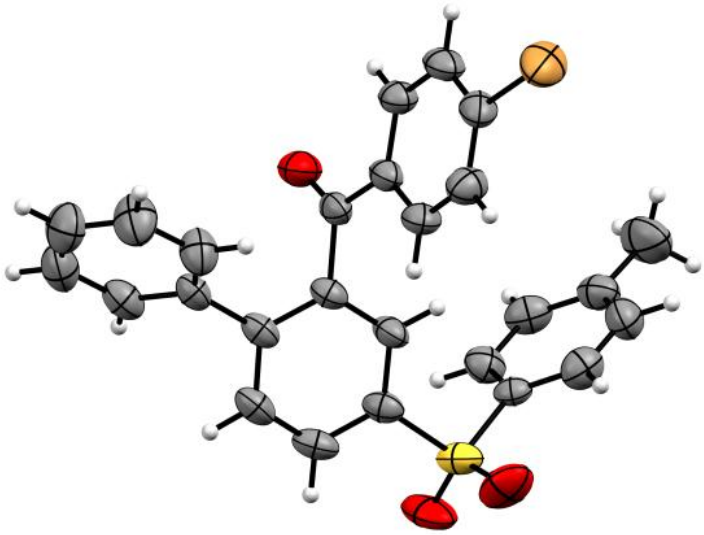
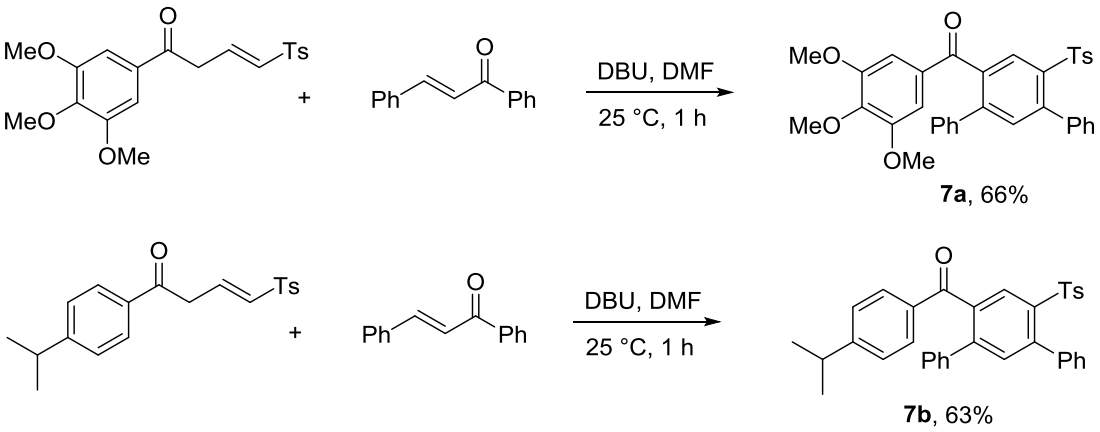


Figure 4: ORTEP diagram of **5h**

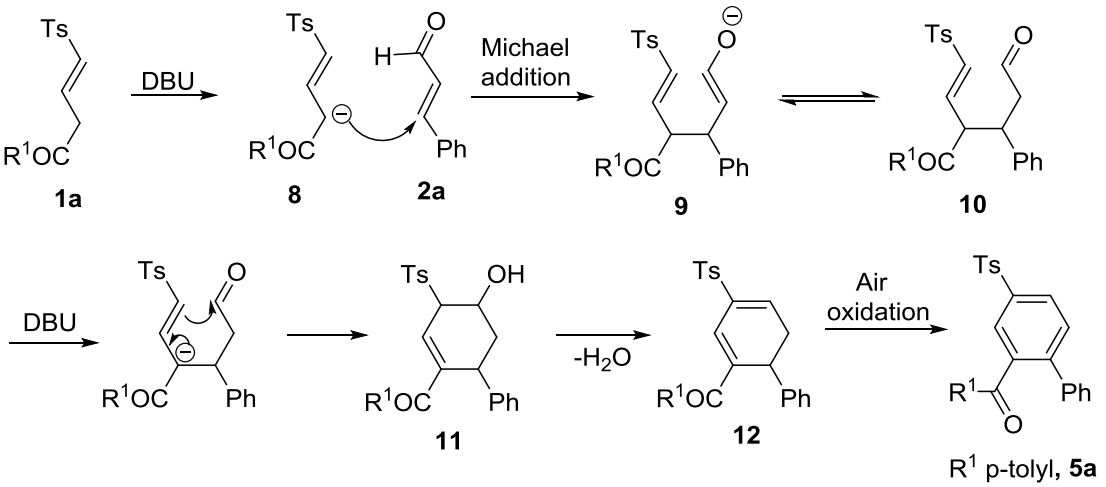
The promising results of benzannulation reaction with α, β- unsaturated aldehydes prompted us to explore its applicability to enones. Readily prepared chalcone **6** was chosen as a representative unsaturated ketone for this purpose. Smooth conversions of **6** to the highly substituted benzophenone derivatives **7a-b** were observed when the former was reacted with trimethoxyphenyl (**1e**) as well as isopropyl (**1f**) keto-sulfones, albeit in slightly reduced yields (Scheme 9). It may be noted that the newly installed benzene ring is endowed with four rather bulky substituents at well defined positions.



Scheme 9: Benzannulation reaction of trans-chalcone **6** and enals

3.5. Plausible mechanism of the benzannulation reaction

A simplified plausible mechanism for the benzannulation reaction is depicted in Scheme 10. It is likely that reaction is initiated by deprotonation of 1,3-substituted propene **1a** by DBU to generate the stabilized carbanion **8**. The latter may undergo an intermolecular Michael addition with enals/enones **2**. It may be noted that carbanion may react via either of its terminal carbons. It is presumable that the carboanion **8** reacts via the sterically less hindered α-carbonyl end with enal **2**, which results in the formation of enolate **9**. Further, deprotonation and intramolecular nucleophilic addition of the resulting carbanion to the aldehyde affords the cyclohexenol derivative **11**. The dehydydaration of **11** generates cyclohexadiene **12**. The final aromatic product **5a** is then formed via oxidation of **12** by atmospheric oxygen.



Scheme 10: Plausible mechanism for benzannulation reaction

It is worth to note that the cyclohexadiene moiety **12** can also undergo aromatization by eliminating tosyl moiety via base promoted H-shift and then β-elimination. This is presumably slower than the aerial oxidation and the sulfonyl moiety is retained in the final product.

3.6. Conclusion

In conclusion, a base promoted regioselective synthesis of substituted benzophenone/ arenes via aerobic oxidative [3+3] benzannulation reaction of α,β-unsaturated carbonyl compounds and 1,3-bisnucleophile (1,3-disubstituted propene) was developed. In this reaction two acyclic precursors were assembled to afford arylsulfonyl bearing benzophenone. The reaction described here proceeds at room temperature in an open flask, in presence of DBU under mild conditions. Additionally, the reaction uses no metals and utilizes atmospheric oxygen for oxidation. The benzannulation method is notable for its efficiency, scope and generality. The reaction afforded highly substituted sulfonyl containing benzophenone derivatives which are difficult to synthesize via conventional methods. It is presumable that the method may find applications in the targeted synthesis of designer benzophenone derivatives of importance.

3.7. 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 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 the reagents and solvents were used without further purification unless specified otherwise. Technical grade ethyl acetate and petroleum ether 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 commercially prepared 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.

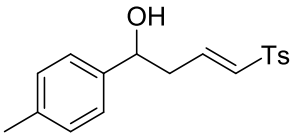
Synthesis of Alkene 3: General Procedure[25]

A solution of allyl magnesium bromide (1M in diethyl ether, 1.5 equiv) was added dropwise to a solution of aldehyde (1 equiv) in anhydrous diethyl ether at 0 ˚C. The reaction mixture was allowed to warm to room temperature and stirred for overnight. After completion of reaction an aqueous solution of NH_4Cl was added at 0 ˚C. The organic layer was extracted ether. The combined organic layer was dried over sodium sulfate and solvent was evaporated on rotavapour. The crude material was purified by Column chromatography on silica gel using ethyl acetate-petroleum ether as eluent to afford pure homoallylic alcohols **3**.

Synthesis of Vinyl Sulfones: General Procedure[26]

To a stirred solution of alkene **3** (2.0 mmol) and $ArSO_2Na$ (2 equiv) in MeCN (20 mL), $NaIO_4$ (10mol %), KI (10 mol %) and 2-3 drops of AcOH were added. The reaction mixture was stirred at room temperature for 24h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was quenched by adding sat. aq $Na_2S_2O_3$ (5 mL) and extracted with EtOAc (3 × 10 mL). The extract was dried with anhydrous sodium sulfate and solvent was evaporated on a rotavapor. Column chromatography of the resulting residue on silica gel using ethyl acetate-petroleum ether as eluent afforded analytically pure samples of the vinyl sulfones **4a-h**.

Spectroscopic data for vinyl sulfones



4a, (E)-1-(p-tolyl)-4-tosylbut-3-en-1-ol

White solid, 480 mg, 76%

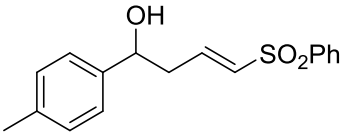
Melting point: 102-104˚C

IR (KBr) υ_{max}: 3508, 3041, 2922, 2883, 1635, 1595, 1440, 1267, 1138, 1031, 813, 522

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3Hz, 2H), 7.30 (d, J = 8.0Hz, 2H), 7.17 (d, J = 8.3Hz, 2H), 7.11 (d, J = 8.0Hz, 2H), 6.98–6.88(m, 1H), 6.32 (d,t, J = 15.2, 1.4Hz, 1H), 4.79 (d,d, J = 7.0, 5.8Hz, 1H), 2.71–2.53 (m, 2H), 2.43 (s, 3H), 2.32(s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.4, 140.1, 137.8, 137.5, 132.9, 129.9, 129.4, 127.7, 125.7, 72.6, 40.8, 21.7, 21.2

HRMS calcd for $C_{18}H_{22}O_4S$ (M+H_2O) 334.1239 ; found 334.1437



4b, (E)-4-(phenylsulfonyl)-1-(p-tolyl)but-3-en-1-ol

White solid, 447 mg, 74%

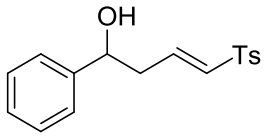
Melting point: 106-107˚C

IR (KBr) υ_{max}: 3535, 2889, 1629, 1583, 1444, 1419, 1300, 1138, 1047, 748, 580

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1Hz, 2H), 7.61(t, J = 7.4Hz, 1H), 7.51(t, J = 7.7Hz, 2H), 7.18 (d, J = 8.1Hz, 2H), 7.12 (d, J = 8.1Hz, 2H), 7.03–6.94 (m, 1H), 6.35 (dt, J = 15.1, 1.2Hz, 1H), 4.84–4.79 (m, 1H), 2.74-2.57 (m, 2H), 2.32 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.5, 140.0, 137.9, 133.3, 132.7, 129.4, 129.2, 127.6, 125.6, 72.6, 40.8, 21.1

HRMS calcd for $C_{17}H_{20}O_4S$ ($M+H_2O$) 320.1082 ; found 320.1283



4c, (E)-1-phenyl-4-tosylbut-3-en-1-ol

White solid, 453 mg, 75%

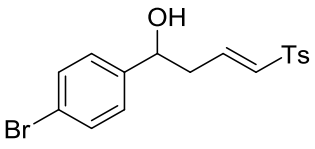
Melting point: 109-110˚C

IR (KBr) υ_{max}: 3491, 3064, 2926, 2870, 1624, 1593, 1450, 1398, 1284, 1139, 1078, 756, 673

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3Hz, 2H), 7.37–7.21 (m, 7H), 6.97-6.90 (m, 1H), 6.33 (d,t, J = 14.3, 1.2Hz, 1H), 4.82 (dd, J = 7.5, 5.2Hz, 1H), 2.71–2.54 (m, 2H), 2.42 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.1, 142.3, 137.4, 133.0, 129.9, 128.7, 128.1, 127.7, 125.7, 72.7, 40.8, 21.7

HRMS calcd for $C_{17}H_{20}O_4S$ ($M+H_2O$) 320.1082 ; found 320.1281



4d, (E)-1-(4-bromophenyl)-4-tosylbut-3-en-1-ol

Yellow solid, 617 mg, 81%

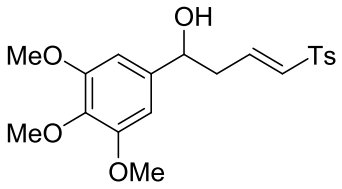
Melting point: 107-108˚C

IR (KBr) υ_{max}: 3510, 3047, 2879, 1635, 1593, 1483, 1309, 1280, 1141, 1041, 813, 657, 524

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0Hz, 2H), 7.41 (d, *J* = 8.4Hz, 2H), 7.31 (d, *J* = 8.0Hz, 2H), 7.15 (d, *J* = 8.4Hz, 2H), 6.94–6.87 (m, 1H), 6.30 (dt, *J* = 15.1, 1.3Hz, 1H), 4.83 (dd, *J* = 7.0, 5.5Hz, 1H), 2.68–2.54 9m, 2H), 2.44 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 142.0, 141.6, 137.3, 133.4, 131.8, 129.9, 127.6, 127.4, 121.8, 72.0, 40.8, 21.7

HRMS calcd for $C_{17}H_{19}BrO_4S$ (M+ H_2O) 398.0187; found 398.0406



4e, (E)-4-tosyl-1-(3,4,5-trimethoxyphenyl)but-3-en-1-ol

White solid, 612 mg, 78%

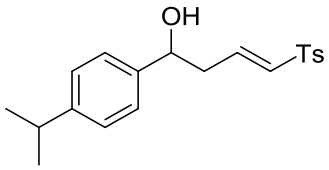
Melting point: 140-142˚C

IR (KBr) υ_{max}: 3512, 2935, 1589, 1485, 1419, 1305, 1235, 1122, 1082, 655, 534

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4Hz, 2H), 7.28 (d, *J* = 8.4Hz, 2H), 6.98–6.91 (m, 1H), 6.49 (s, 2H), 6.34 (dt, *J* = 15.2, 1.2Hz, 1H), 4.74 (dd, *J* = 7.3-5.2Hz, 1H), 3.80 (s, 6H), 3.78 (s, 3H), 2.62-2.56 (m, 2H), 2.39 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.38, 153.36, 144.4, 142.4, 139.0, 137.4, 132.8, 129.9, 127.6, 102.5, 72.8, 60.8, 56.1, 40.9, 21.6

HRMS calcd for $C_{20}H_{26}O_7S$ (M+H_2O) 410.1399 ; found 410.1643



4f, (E)-1-(4-isopropylphenyl)-4-tosylbut-3-en-1-ol

White solid, 502 mg, 73%

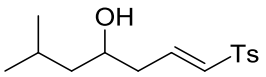
Melting point: 107-109˚C

IR (KBr) υ_{max}: 3566, 3047, 2958, 1629, 1593, 1458, 1415, 1300, 1139, 1082, 812, 661, 528

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2Hz, 2H), 7.30 (d, J = 8.4Hz, 2H), 7.21-7.15 (m, 4H), 6.99–6.94 (m, 1H), 6.34 (dt, J = 14.9, 1.2Hz, 1H), 2.90-2.83 (m, 1H), 2.68-2.59 (m, 2H), 2.40 (m, 3H), 1.22 (s, 3H), 1.21 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 144.3, 142.4, 140.4, 137.5, 133.0, 129.9, 127.7, 126.8, 125.7, 72.7, 40.7, 33.9, 24.03, 24.02, 21.6

HRMS calcd for $C_{20}H_{26}O_4S$ (M+H_2O) 362.1552 ; found 362.1793



4g, (E)-6-methyl-1-tosylhept-1-en-4-ol

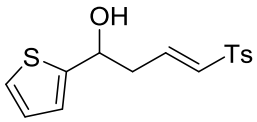
Yellow viscous liquid, 401 mg, 71%

IR (KBr) υ_{max}: 3506, 3047, 2954, 1631, 1597, 1462, 1402, 1288, 1139, 1085, 810, 661

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0Hz, 2H), 7.29 (d, J = 8.0Hz, 2H), 7.00-6.93 (m, 1H), 6.37 (d, J = 15.1Hz, 1H), 3.82–3.77 (m, 1H), 2.39 (s, 3H), 2.32–2.26 (m, 2H), 1.74–1.67 (m, 1H), 1.41-1.34 (m, 1H), 1.20–1.14 (m, 1H), 0.86 (t, J = 7.1Hz)

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 143.2, 137.5, 132.6, 129.9, 127.7, 68.2, 46.3, 39.8, 24.5, 23.3, 21.9, 21.6

HRMS calcd for $C_{15}H_{24}O_4S$ (M+H) 300.1395 ; found 300.1636



4h, (E)-1-(thiophen-2-yl)-4-tosylbut-3-en-1-ol

Reddish Solid, 419 mg, 68%

Melting point: 104-105˚C

IR (KBr) υ_{max}: 3483, 3049, 1631, 1597, 1492, 1402, 1286, 1139, 1082, 810, 659

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1Hz, 2H), 7.28 (d, J = 7.8Hz, 2H), 7.19 (dd, J = 5.6, 2.9Hz, 1H), 6.94–6.88 (m, 3H), 6.34 (d, J = 15.0Hz, 1H), 5.03 (s, 1H), 2.76-2.63 (m, 2H), 2.40 (s, 3H)

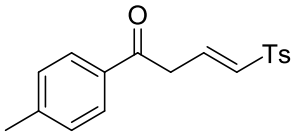
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 144.4, 141.9, 137.2, 133.1, 129.9, 127.7, 126.8, 125.0, 124.1, 68.5, 41.0, 21.7

HRMS calcd for $C_{15}H_{18}O_4S_2$ (M+H) 326.0647 ; found 326.0878

Synthesis of 1, 3-bisnucleophile: General procedure

To a solution of Dess-Martin Periodinane (2.0 mmol) in CH_2Cl_2 (10 ml) at room temperature was added a solution of vinyl sulfone (1.0 mmol) in CH_2Cl_2 (10 ml). After 1 h of stirring (reaction was monitored by TLC), the mixture was diluted with diethyl ether (20 mL) and quenched with 1/1 10% $Na_2S_2O_3$/saturated aqueous $NaHCO_3$ solution followed by brine. The extract was dried over anhydrous sodium sulfate and concentrated on a rotavapor. Column chromatography of the resulting residue on silica gel using ethyl acetate-petroleum ether as eluent afforded analytically pure samples of 1, 3-bisnucleophile **1a-h**.

Spectroscopic data of 1, 3-bisnucleophile



1a, (E)-1-(p-tolyl)-4-tosylbut-3-en-1-one

White solid, 279 mg, 89%

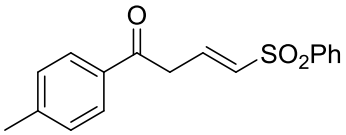
Melting point: 111-113˚C

IR (KBr) υ_{max}: 2980, 2929, 1664, 1624, 1598, 1450, 1409, 1319, 1288, 1143, 821

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.70 (m, 4H), 7.33 (d, *J* = 8.0Hz, 2H), 7.23 (d, *J* = 8.4Hz, 2H), 6.89 (d, *J* = 15.4Hz, 1H), 6.76–6.68 (m, 1H), 4.00 (dd, *J* = 7.7, 1.0Hz), 2.42 (s, 3H), 2.39(s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.75, 145.3, 144.4, 135.3, 134.3, 133.5, 132.0, 130.0, 129.4, 128.8, 128.5, 59.7, 21.7

HRMS calcd for $C_{18}H_{18}O_3S$ (M+H) 315.1056 ; found 315.1061



1b, (E)-4-(phenylsulfonyl)-1-(p-tolyl)but-3-en-1-one

White solid, 261 mg, 87%

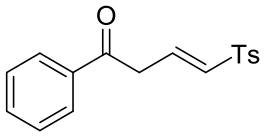
Melting point: 108-109˚C

IR (KBr) υ_{max}: 2974, 2918, 1664, 1608, 1448, 1408, 1292, 1145, 979, 727, 584

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.4, 1.2Hz, 2H), 7.72 (d, *J* = 8.0Hz, 2H), 7.69–7.64 (m, 1H), 7.56 (t, *J* = 7.7Hz, 2H), 7.24 (d, *J* = 8.0Hz, 2H), 6.90 (dt, *J* = 15.4, 1.0Hz, 1H), 6.77-6.70 (m, 1H), 4.03 (dd, 8.0, 1.0Hz, 2H), 2.4 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 144.5, 138.2, 134.3, 134.2, 133.6, 131.7, 129.5, 129.4, 128.8, 128.5, 59.6, 21.7

HRMS calcd for $C_{17}H_{16}O_3S$ (M+H) 301.0899 ; found 301.0901



1c, (E)-1-phenyl-4-tosylbut-3-en-1-on

White solid, 267 mg, 89%

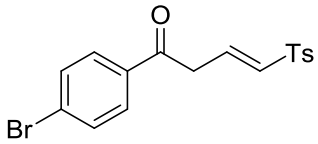
Melting point: 113-114˚C

IR (KBr) υ_{max}: 3082, 2978, 2918, 1658, 1624, 1446, 1409, 1317, 1292, 1139, 696, 516

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.0, 1.6Hz, 2H), 7.75 (d, *J* = 8.4Hz), 7.59-7.53 (m, 1H), 7.44 (t, *J* = 8.0Hz, 2H), 7.34 (d, *J* = 8.0Hz, 2H), 6.90 (dt, 15.4, 1.0Hz, 1H), 6.78–6.70 (m, 1H), 4.01 (dd, 7.6, 1.0Hz, 2H), 2.42(s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 145.3, 136.8, 135.3, 133.5, 133.4, 132.5, 130.1, 128.8, 128.7, 128.5, 59.7, 21.7

HRMS calcd for $C_{17}H_{16}O_3S$ (M+H) 301.0899 ; found 301.0904



1d, (E)-1-(4-bromophenyl)-4-tosylbut-3-en-1-one

Yellow solid, 345 mg, 91%

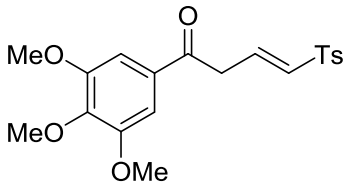
Melting point: 116-117˚C

IR (KBr) υ_{max}: 2924, 1668, 1622, 1581, 1487, 1444, 1286, 1134, 812, 513

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8Hz, 2H), 7.35 (d, J = 8.0Hz, 2H), 6.88 (d, J = 15.4Hz, 1H), 6.79-6.71 (m, 1H), 4.01 (dd, J = 7.6, 0.8Hz, 2H), 2.43 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 135.5, 135.3, 133.1, 132.9, 132.1, 130.2, 130.1, 128.7, 128.4, 59.6, 21.7

HRMS calcd for $C_{17}H_{15}BrO_3S$ (M+H) 379.0004 ; found 378.9996



1e, (E)-4-tosyl-1-(3,4,5-trimethoxyphenyl)but-3-en-1-one

White solid, 347 mg, 89%

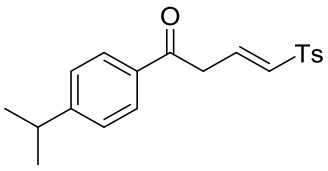
Melting point: 168-169˚C

IR (KBr) υ_{max}: 2951, 2839, 1668, 1625, 1583, 1460, 1413, 1307, 1116, 767, 516

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4Hz, 2H), 7.35 (d, J = 8.4Hz, 2H), 7.13 (s, 2H), 6.91 (d, J = 15.4Hz, 1H), 6.76–6.68 (m, 1H), 4.01 (dd, J = 7.6, 0.8Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 2.42 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 153.2, 145.4, 143.0, 135.4, 133.4, 132.1, 132.0, 130.1, 128.4, 106.4, 61.0, 59.6, 56.4, 21.7

HRMS calcd for $C_{20}H_{22}O_6S$ (M+H) 391.1216 ; found 391.1211



1f, (E)-1-(4-isopropylphenyl)-4-tosylbut-3-en-1-one

White solid, 288 mg, 84%

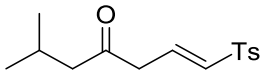
Melting point: 112-113˚C

IR (KBr) υ_{max}: 2969, 2927, 1659, 1598, 1463, 1409, 1292, 1139, 669, 518

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.75 (m , 4H), 7.35 (d, *J* = 8.0Hz, 2H), 7.31 (d, *J* = 8.0Hz, 2H), 6.90 (d, *J* = 15.4Hz, 1H), 6.77–6.69 (m, 1H), 4.02 (dd, *J* = 7.6, 0.8Hz, 2H), 3.00–2.93 (m, 1H), 2.44 (s, 3H), 1.27 (d, *J* = 6.8Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 155.1, 145.2, 135.3, 134.6, 133.6, 132.1, 130.0, 129.0, 128.5, 126.9, 59.7, 34.3, 23.7, 21.7

HRMS calcd for $C_{20}H_{22}O_3S$ (M+H) 343.1369 ; found 343.1363



1g, (E)-6-methyl-1-tosylhept-1-en-4-one

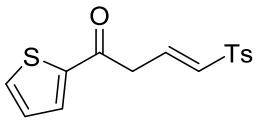
Yellow viscous liquid, 230 mg, 82%

IR (KBr) υ_{max}: 2958, 1707, 1670, 1597, 1429, 1404, 1292, 1141, 813, 516

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2Hz, 2H), 7.32 (d, *J* = 8.2Hz, 2H), 6.61–6.52 (m, 1H), 6.02 (dt, *J* = 16.0, 1.2Hz, 1H), 3.90 (dd, *J* = 7.6, 1.2Hz, 2H), 2.42 (s, 3H), 2.35 (d, 7.2Hz, 2H), 2.09–2.02 (m, 1H), 0.88 (d, *J* = 6.6Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 145.4, 137.3, 135.1, 130.8, 130.0, 128.4, 59.5, 49.4, 25.0, 22.6, 21.7

HRMS calcd for $C_{15}H_{20}O_3S$ (M+H) 281.1212 ; found 2811.1206



1h, (E)-1-(thiophen-2-yl)-4-tosylbut-3-en-1-one

Yellow solid, 239 mg, 78%

Melting point: 123-125˚C

IR (KBr) υ_{max}: 3039, 2972, 2906, 1649, 1616, 1512, 1408, 1290, 1139, 754, 518

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0Hz, 2H), 7.68–7.63 (m, 2H), 7.33 (d, *J* = 8.0Hz, 2H), 7.13 (t, *J* = 4.2 Hz, 1H), 6.83–6.74 (m, 2H), 4.01 (d, *J* = 4.8Hz, 2H), 2.42 (s, 3H)

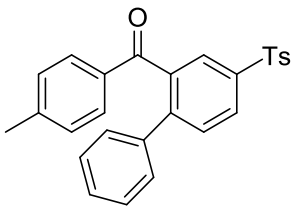
^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 145.4, 144.2, 135.3, 135.0, 132.9, 132.8, 131.9, 130.1, 128.5, 128.4, 59.5, 21.7

HRMS calcd for $C_{15}H_{14}O_3S_2$ (M+H) 307.0463; found 307.0458

DBU-mediated benzannulation reaction: General method

DBU (0.45 mmol) was added to a solution cinnamaldehyde **2** (0.3 mmol) and 1, 3-bis-nucleophile **1** (0.33 mmol) in DMF (4 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 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 analytically pure sample of the product.

Spectroscopic data for the products



5a, p-tolyl(4-tosyl-[1,1'-biphenyl]-2-yl)methanone

White solid, 95 mg, 74%

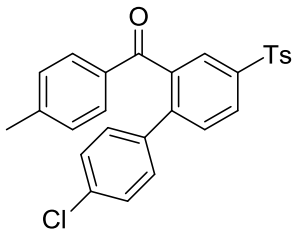
Melting point: 143-144˚C

IR (KBr) υ_{max}: 3022, 2970, 1741, 1660, 1598, 1369, 1153, 1097, 664, 532

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.0, 2.0Hz, 1H), 8.01 (d, *J* = 2.0Hz, 1H), 7.85 (d, *J* = 8.4Hz, 2H), 7.60 (d, *J* = 8.4Hz, 1H), 7.52 (d, *J* = 8.0Hz, 2H), 7.32 (d, *J* = 8.4Hz, 2H), 7.22 (s, 5H), 7.11 (d, *J* = 8.4Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 145.6, 144.7, 144.6, 140.8, 140.1, 138.5, 138.2, 133.9, 131.2, 130.2, 130.1, 129.2, 128.8, 128.6, 128.4, 127.9, 127.6, 21.8, 21.7

HRMS calcd for $C_{27}H_{22}O_3S$ (M+H) 427.1369 ; found 427.1390



5b, (4'-chloro-4-tosyl-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone

White solid, 105 mg, 76%

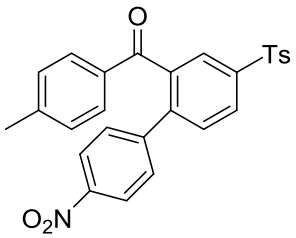
Melting point: 153-154˚C

IR (KBr) υ_{max}: 3010, 2982, 1746, 1621, 1570, 1388, 1190, 1060, 765, 540

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.4, 2.0Hz, 1H), 7.99 (d, *J* = 2.0Hz, 1H), 7.84–7.81 (m, 2H), 7.55 (d, *J* = 8.0Hz, 1H), 7.52 (d, *J* = 8.4Hz, 2H), 7.31 (dd, *J* = 8.4, 0.8Hz, 2H), 7.21–7.17 (m, 2H), 7.16–7.11(m, 4H), 2.40 (s, 3H), 2.35 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 145.0, 144.7, 144.3, 141.1, 140.0, 138.1, 136.9, 134.7, 133.7, 131.1, 130.25, 130.21, 130.1, 129.4, 128.9, 128.8, 127.9, 127.6, 21.8, 21.7

HRMS calcd for $C_{27}H_{21}ClO_3S$ (M+H) 461.0979 ; found 461.0959



5c, (4'-nitro-4-tosyl-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone

Yellow solid, 112 mg, 79%

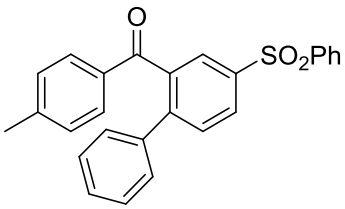
Melting point: 157-158˚C

IR (KBr) υ_{max}: 2924, 1660, 1597, 1512, 1448, 1408, 1340, 1249, 1157, 1157, 682, 596

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.09 (m, 3H), 8.04 (d, *J* = 1.2Hz, 1H), 7.84 (d, *J* = 8.4Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.0Hz, 2H), 7.39 (d, *J* = 8.4Hz, 2H), 7.33 (d, *J* = 8.0Hz 2H), 7.16 (d, *J* = 8.0Hz, 2H), 2.41 (s, 3H), 2.37 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 147.6, 145.5, 145.1, 144.9, 143.2, 142.2, 140.2, 137.8, 133.6, 131.1, 130.2, 129.7, 129.6, 129.1, 128.0, 127.8, 123.8, 21.8, 21.7

HRMS calcd for $C_{27}H_{21}NO_5S$ (M+H) 472.1219 ; found 472.1242



5d, (4-(phenylsulfonyl)-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone

White solid, 89 mg, 72%

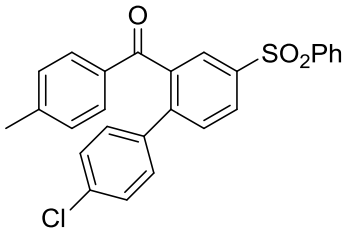
Melting point: 141-142˚C

IR (KBr) υ_{max}: 3017, 2951, 1744, 1634, 1568, 1440, 1370, 1110, 1012, 840, 548

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.4, 2.0Hz, 1H), 8.02 (d, *J* = 2.0Hz,1H), 7.97 (d, *J* = 7.6Hz, 2H), 7.59 (t, *J* = 7.6Hz, 2H), 7.52 (t, *J* = 8.0Hz, 4H), 7.21 (s, 5H), 7.10 (d, *J* = 8.4Hz, 2H), 2.33 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 145.8, 144.7, 141.2, 140.4, 140.2, 138.4, 133.9, 133.5, 131.2, 130.2, 129.5, 129.2, 129.0, 128.8, 128.6, 128.4, 127.8, 127.7, 21.8

HRMS calcd for $C_{26}H_{20}O_3S$ (M+H) 413.1209 ; found 413.1206



5e, (4'-chloro-4-(phenylsulfonyl)-[1,1'-biphenyl]-2-yl)(p-tolyl)methanone

White solid, 99 mg, 74%

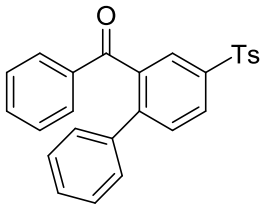
Melting point: 151-153˚C

IR (KBr) υ_{max}: 3045, 2981, 1745, 1654, 1520, 1448, 1358, 1138, 1028, 765, 535

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.0, 1.6Hz, 1H), 8.01 (d, J = 1.6Hz, 1H), 7.96 (d, J = 7.2Hz, 2H), 7.59–7.50 (m, 6H), 7.21-7.12 (m, 6H), 2.36 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 145.1, 144.5, 141.1, 140.7, 140.1, 136.9, 134.7, 133.7, 133.6, 131.2, 130.2, 130.1, 129.5, 129.4, 129.1, 128.9, 127.9, 127.7, 21.8

HRMS calcd for $C_{26}H_{19}ClO_3S$ (M+H) 447.0822 ; found 447.0842



5f, phenyl(4-tosyl-[1,1'-biphenyl]-2-yl)methanone

White solid, 86 mg, 70%

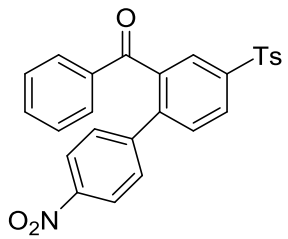
Melting point: 139-141˚C

IR (KBr) υ_{max}: 2922, 1666, 1591, 1446, 1400, 1315, 1248, 1149, 675, 548

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.0, 2.0Hz, 1H), 8.04 (d, J = 2.0Hz, 1H), 7.85 (d, J = 8.4Hz, 2H), 7.60–7.57 (m, 3H), 7.44 (t, J = 7.4Hz, 1H), 7.33–7.26 (m, 4H), 7.19 (s, 5H), 2.40 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 145.7, 144.6, 140.9, 139.9, 138.4, 138.2, 136.4, 133.5, 131.2, 130.2, 129.9, 129.0, 128.9, 128.6, 128.4, 127.9, 127.7, 21.7

HRMS calcd for $C_{26}H_{20}O_3S$ (M+H) 413.1212 ; found 413.1194



5g, (4'-nitro-4-tosyl-[1,1'-biphenyl]-2-yl)(phenyl)methanone

Yellow solid, 107 mg, 78%

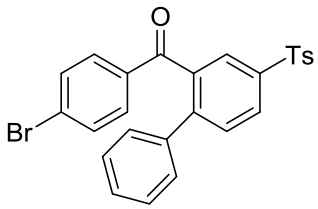
Melting point: 153-154˚C

IR (KBr) υ_{max}: 3022, 2970, 1739, 1589, 1367, 1224, 1037, 532

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 8.4, 2.0Hz, 1H), 8.12-8.08 (m, 3H), 7.86 (dt, J = 8.0, 2.0Hz, 2H), 7.64–7.59 (m, 3H), 7.55–7.51 (m, 1H), 7.40–7.33 (m, 6H), 2.42 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 147.6, 145.0, 143.4, 142.3, 139.9, 137.8, 136.1, 134.2, 131.2, 130.3, 130.0, 129.8, 128.8, 128.0, 127.9, 123.8, 21.7

HRMS calcd for $C_{26}H_{19}NO_5S$ (M+H) 458.1063 ; found 458.1038



5h, (4-bromophenyl)(4-tosyl-[1,1'-biphenyl]-2-yl)methanone

Yellow solid, 113 mg, 77%

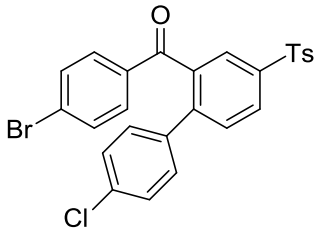
Melting point: 158-159˚C

IR (KBr) υ_{max}: 3012, 2967, 1735, 1665, 1570, 1443, 1361, 1047, 840, 546

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 2.0Hz, 1H), 8.02 (d, *J* = 2.0Hz, 1H), 7.85 (dt, *J* = 8.4, 1.6Hz, 2H), 7.59 (d, *J* = 8.0Hz, 1H), 7.42–7.38 (m, 4H), 7.32 (d, *J* = 8.0Hz, 2H), 7.22–7.16 (m, 5H), 2.41 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 145.6, 144.7, 141.2, 139.3, 138.2, 138.1, 135.2, 131.8, 131.28, 131.22, 130.2, 129.3, 128.9, 128.8, 128.7, 128.6, 127.9, 127.7, 21.7

HRMS calcd for $C_{26}H_{19}BrO_3S$ (M+H) 491.0317 ; found 491.0292



5i, (4-bromophenyl)(4'-chloro-4-tosyl-[1,1'-biphenyl]-2-yl)methanone

Yellow solid, 128 mg, 81%

R_f = 0.7 (20% ethyl acetate in hexanes)

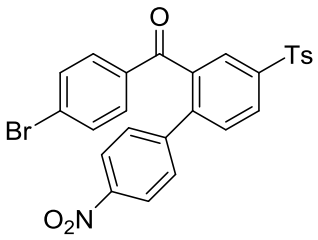
Melting point: 170-171˚C

IR (KBr) υ_{max}: 3064, 1668, 1581, 1494, 1469, 1292, 1147, 813, 648, 584

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.4, 2.0Hz, 1H), 8.00 (d, *J* = 2.0Hz, 1H), 7.84 (d, *J* = 8.4Hz, 2H), 7.56 (d, *J* = 8.4Hz, 1H), 7.47–7.42 (m, 4H), 7.32 (d, *J* = 8.4Hz), 7.21 (d, *J* = 8.5Hz, 2H), 7.12 (d, *J* = 8.5Hz, 2H), 2.41 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 144.8, 144.2, 141.5, 139.2, 139.2, 137.9, 136.6, 135.0, 132.0, 131.3, 131.2, 130.2, 130.0, 129.3, 129.0, 127.9, 127.7, 21.7

HRMS calcd for $C_{26}H_{18}BrClO_3S$ (M+H) 524.9928 ; found 524.9939



5j, (4-bromophenyl)(4'-nitro-4-tosyl-[1,1'-biphenyl]-2-yl)methanone

Yellow solid, 133 mg, 83%

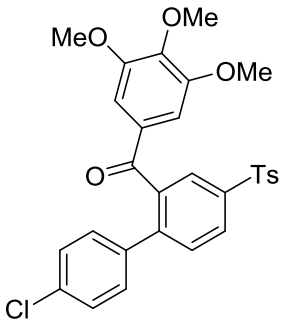
Melting point: 176-178˚C

IR (KBr) υ_{max}: 3057, 1668, 1585, 1517, 1396, 1344, 1151, 657, 584

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.0, 2.0Hz, 1H), 8.11 (d, *J* = 8.8Hz, 2H), 8.04 (d, *J* = 2.0Hz, 1H), 7.84 (d, *J* = 8.0Hz, 2H), 7.60 (d, *J* = 8.0Hz, 1H), 7.51-7.46 (m, 4H), 7.38–7.32 (m, 4H), 2.42 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 147.7, 145.1, 144.8, 143.2, 142.5, 139.3, 137.7, 134.8, 132.2, 131.3, 130.3, 129.7, 129.5, 128.0, 127.8, 123.9, 21.7

HRMS calcd for $C_{26}H_{18}BrNO_5S$ (M+H) 536.0168 ; found 536.0189



5k, (4'-chloro-4-tosyl-[1,1'-biphenyl]-2-yl)(3,4,5-trimethoxyphenyl)methanone

White solid, 121 mg, 76%

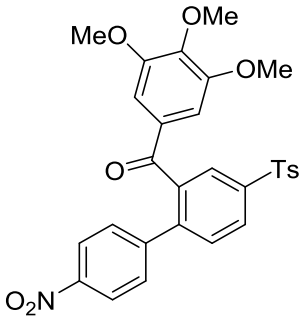
Melting point: 159-161˚C

IR (KBr) υ_{max}: 2931, 1743, 1662, 1583, 1498, 1460, 1409, 1321, 1120, 655, 584

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.0, 1.6Hz, 1H), 8.01 (d, *J* = 1.6Hz, 1H), 7.84 (d, *J* = 8.4Hz, 2H), 7.57 (d, *J* = 8.0Hz, 1H), 7.31 (d, *J* = 8.4Hz, 2H), 7.23 (d, *J* = 8.4Hz, 2H), 7.15 (d, *J* = 8.4Hz, 2H), 6.87 (s, 2H), 3.89 (s, 3H), 3.74 (s, 6H), 2.40 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 144.8, 144.5, 143.3, 141.1, 139.6, 138.0, 136.9, 134.8, 131.26, 131.21, 130.2, 130.0, 129.1, 129.0, 127.94, 127.90, 107.7, 61.0, 56.3, 21.7

HRMS calcd for $C_{29}H_{25}ClO_6S$ (M+H) 537.1139 ; found 537.1143



5l, (4'-nitro-4-tosyl-[1,1'-biphenyl]-2-yl)(3,4,5-trimethoxyphenyl)methanone

Yellow solid, 131 mg, 80%

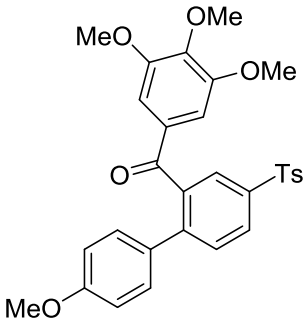
Melting point: 163-165 ˚C

IR (KBr) υ_{max}: 2973, 1758, 1648, 1582, 1469, 1454, 1413, 1308, 1164, 723, 567

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.11 (m , 3H), 8.05 (d, *J* = 2.0Hz, 1H), 7.84 (d, *J* = 8.4Hz, 2H), 7.61 (d, *J* = 8.0Hz, 1H), 7.40 (d, *J* = 8.8Hz, 2H), 7.32 (d, *J* = 8.4Hz, 2H), 6.90 (s, 2H), 3.90 (s, 3H), 3.75 (s, 6H), 2.40 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 153.1, 147.7, 145.1, 145.0, 143.7, 143.6, 142.1, 139.7, 137.8, 131.4, 130.9, 130.3, 129.7, 129.3, 128.0, 127.9, 123.9, 107.8, 61.1, 56.3, 21.7

HRMS calcd for $C_{29}H_{25}NO_8S$ (M+H) 548.1380 ; found 548.1353



5m, (4'-methoxy-4-tosyl-[1,1'-biphenyl]-2-yl)(3,4,5-trimethoxyphenyl)methanone

White solid, 105 mg, 66%

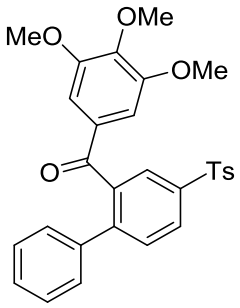
Melting point: 178-179˚C

IR (KBr) υ_{max}: 2933, 2837, 1664, 1583, 1508, 1458, 1409, 1321, 1153, 1006, 657, 567

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.0, 2.0Hz, 1H), 7.98 (d, *J* = 2.0Hz, 1H), 7.84 (d, *J* = 8.4Hz, 2H), 7.58 (d, *J* = 8.0Hz, 1H), 7.30 (d, *J* = 8.4Hz, 2H), 7.15 (d, *J* = 8.8Hz, 2H), 6.87 (s, 2H), 6.76 (d, *J* = 8.8Hz, 2H), 3.87 (s, 3H), 3.73 (s, 6H), 3.72(s, 3H), 2.39 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 159.9, 152.9, 145.3, 144.6, 143.0, 140.2, 139.4, 138.2, 131.3, 131.0, 130.8, 130.16, 130.10, 129.0, 127.8, 114.2, 107.7, 61.0, 56.3, 55.2, 21.6

HRMS calcd for $C_{30}H_{28}O_7S$ (M+H) 533.1635 ; found 533.1631



5n, (4-tosyl-[1,1'-biphenyl]-2-yl)(3,4,5-trimethoxyphenyl)methanone

White solid, 107 mg, 71%

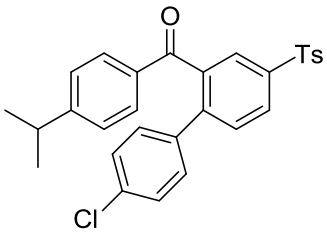
Melting point: 145-146˚C

IR (KBr) υ_{max}: 3053, 2933, 1664, 1583, 1498, 1454, 1323, 1226, 1118, 1004, 654, 574

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.4, 2.0Hz, 1H), 8.02 (d, J = 2.0Hz, 1H), 7.85 (d, J = 8.4Hz, 2H), 7.61 (d, J = 8.4Hz, 1H), 7.31 (d, J = 8.0Hz, 2H), 7.24–7.20 (m, 5H), 6.85 (s, 2H), 3.80 (s, 3H), 3.72 (s, 6H), 2.39 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 152.8, 145.7, 144.7, 143.0, 140.8, 139.7, 138.4, 138.2, 131.3, 131.2, 130.2, 129.0, 128.8, 128.7, 128.5, 127.93, 127.90, 107.7, 60.9, 56.3, 21.6

HRMS calcd for $C_{29}H_{26}O_6S$ (M+H) 503.1529 ; found 503.1524



5o, (4'-chloro-4-tosyl-[1,1'-biphenyl]-2-yl)(4-isopropylphenyl)methanone

White solid, 111 mg, 76%

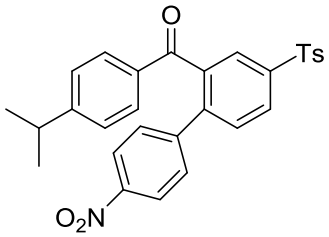
Melting point: 152-154˚C

IR (KBr) υ_{max}: 3057, 2960, 1664, 1598, 1465, 1411, 1292, 1151, 810, 665, 586

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.4, 2.0Hz, 1H), 8.00 (d, *J* = 2.0Hz, 1H), 7.83 (d, *J* = 8.4Hz, 2H), 7.56–7.53 (m, 3H), 7.31 (d, *J* = 8.0Hz, 2H), 7.20–7.12 (m, 6H), 2.94-2.87 (m, 1H), 2.40 (s, 3H), 1.23 (d, *J* = 7.2Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 155.6, 144.7, 144.5, 141.1, 140.1, 138.1, 137.0, 134.6, 134.0, 131.1, 130.4, 130.2, 130.1, 128.9, 128.8, 127.9, 127.7, 126.8, 34.3, 23.6, 21.9

HRMS calcd for $C_{29}H_{25}ClO_3S$ (M+H) 489.1292 ; found 489.1272



5p, (4-isopropylphenyl)(4'-nitro-4-tosyl-[1,1'-biphenyl]-2-yl)methanone

Yellow solid, 121 mg, 81%

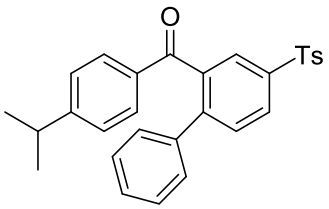
Melting point: 160-161˚C

IR (KBr) υ_{max}: 3061, 2962, 1662, 1598, 1517, 1462, 1413, 1344, 1286, 1153, 1101, 810, 586

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.10 (m, 3H), 8.05 (d, *J* = 2.0Hz, 1H), .84 (d, *J* = 8.4Hz, 2H), 7.59-7.56 (m, 3H), 7.31 (d, *J* = 8.8Hz, 2H), 7.33 (d, *J* = 8.0Hz, 2H), 7.22 (d, *J* = 8.4Hz, 2H), 2.95–2.89 (m, 1H), 2.41 (s, 3H), 1.23 (d, *J* = 6.8Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 156.1, 147.6, 145.1, 144.9, 143.4, 142.1, 140.2, 137.8, 134.0, 131.2, 130.5, 130.2, 129.8, 129.2, 128.0, 127.8, 127.0, 123.7, 34.4, 23.5, 21.7

HRMS calcd for $C_{29}H_{25}NO_5S$ (M+H) 500.1542 ; found 500.1538



5q, (4-isopropylphenyl)(4-tosyl-[1,1'-biphenyl]-2-yl)methanone

White solid, 99 mg, 73%

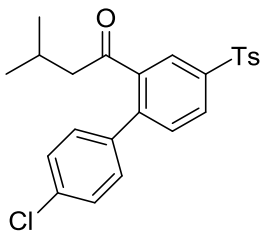
Melting point: 151-153˚C

IR (KBr) υ_{max}: 3057, 2964, 1666, 1597, 1465, 1413, 1315, 1151, 1101, 813, 578

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.4, 2.0Hz, 1H), 8.00 (d, *J* = 2.0Hz, 1H), 7.84 (d, *J* = 8.4Hz, 2H), 7.59 (d, *J* = 8.4Hz, 1H), 7.56 (d, *J* = 8.4Hz, 2H), 7.31 (d, *J* = 8.0Hz, 2H), 7.21 (s, 5H), 7.16 (d, *J* = 8.4Hz, 2H), 2.92–2.85 (m. 1H), 2.40 (s, 3H), 1.21 (d, *J* = 6.8Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 155.3, 145.8, 144.6, 140.7, 140.1, 138.5, 138.2, 134.3, 131.3, 130.4, 130.1128.8, 128.5, 128.3, 127.9, 127.6, 126.6, 34.3, 32.6, 21.6

HRMS calcd for $C_{29}H_{26}O_3S$ (M+H) 455.1682 ; found 455.1661



5r, 1-(4'-chloro-4-tosyl-[1,1'-biphenyl]-2-yl)-3-methylbutan-1-one

White solid, 88 mg, 69%

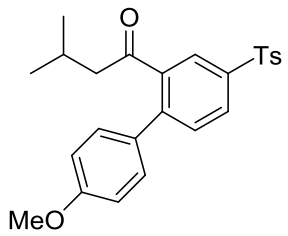
Melting point: 114-115˚C

IR (KBr) υ_{max}: 2958, 2927, 1689, 1591, 1496, 1463, 1317, 1296, 1151, 1089, 815, 659

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.97 (m, 2H), 7.84 (d, *J* = 8.4Hz, 2H), 7.44 (dd, *J* = 8.0, 0.4Hz, 1H), 7.38 (d, *J* = 8.8Hz, 2H), 7.31 (d, *J* = 8.0Hz, 2H), 7.19 (d, *J* = 8.8Hz, 2H), 2.39 (s, 3H), 2.19 (d, *J* = 6.8Hz, *J*, 2H), 2.00–1.90 (m, 1H), 0.74 (d, *J* = 6.4Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 144.7, 143.2, 142.0, 141.6, 138.0, 137.2, 135.1, 131.3, 130.2, 130.1, 129.1, 129.0, 127.9, 126.7, 51.7, 24.7, 22.4, 21.7

HRMS calcd for $C_{24}H_{23}ClO_3S$ (M+H) 427.1135 ; found 427.1122



5s, 1-(4'-methoxy-4-tosyl-[1,1'-biphenyl]-2-yl)-3-methylbutan-1-one

White solid, 80 mg, 63%

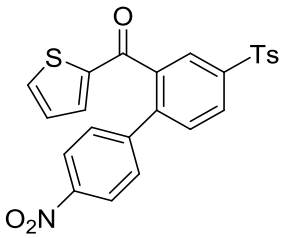
Melting point: 104-105˚C

IR (KBr) υ_{max}: 2964, 2927, 1691, 1606, 1516, 1463, 1392, 1247, 1147, 1095, 665, 536

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.2, 2.0Hz, 1H), 7.93 (d, *J* = 2.0, 1H), 7.84 (d, *J* = 8.4Hz, 2H), 7.46 (d, *J* = 8.2Hz, 1H), 7.30 (d, *J* = 8.4Hz, 2H), 7.19 (d, *J* = 8.8Hz, 2H), 6.93 (d, *J* = 8.8Hz, 2H), 3.82 (s, 3H), 2.39 (s, 3H), 2.12 (d, *J* = 6.8Hz, 2H), 1.95-1.88 (m, 1H), 0.71 (d, j = 6.8Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 160.2, 144.5, 144.1, 142.0, 140.8, 138.3, 131.1, 131.0, 130.16, 130.13, 128.8, 127.9, 126.7, 114.4, 55.4, 51.6, 24.9, 22.4, 21.6

HRMS calcd for $C_{25}H_{26}O_4S$ (M+H) 423.1631 ; found 423.1618



5t, (4'-nitro-4-tosyl-[1,1'-biphenyl]-2-yl)(thiophen-2-yl)methanone

Yellow solid, 106 mg, 76%

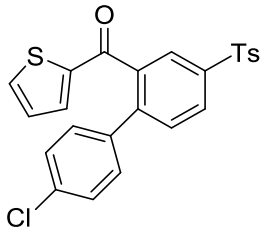
Melting point: 165-167˚C

IR (KBr) υ_{max}: 2967, 1649, 1584, 1487, 1458, 1309, 1137, 1058,819, 567

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.12 (m, 4H), 7.85 (d, *J* = 8.0Hz, 2H), 7.72 (dd, *J* = 4.8, 0.8Hz, 1H), 7.60 (d, *J* = 8.0Hz, 1H), 7.44 (d, *J* = 8.4Hz, 2H), 7.34–7.30 (m, 3H), 7.05 (dd, *J* = 4.8, 4.0Hz), 2.41 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 147.7, 145.0, 144.9, 143.4, 143.1, 142.3, 139.7, 137.7, 136.6, 136.1, 131.4, 130.3, 129.7, 129.5, 128.6, 128.0, 127.7, 123.9, 21.7

HRMS calcd for $C_{24}H_{17}NO_5S_2$ (M+H) 464.0627 ; found 464.0614



5u, (4'-chloro-4-tosyl-[1,1'-biphenyl]-2-yl)(thiophen-2-yl)methanone

Yellow solid, 94 mg, 69%

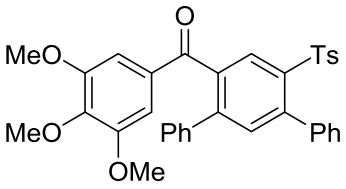
Melting point: 156-157˚C

IR (KBr) υ_{max}: 2924, 1656, 1591, 1496, 1441, 1318, 1143, 1081,829, 545

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 7.84 (d, *J* = 8.4Hz, 2H), 7.67 (dd, *J* = 4.8, 1.2Hz, 1H), 7.56 (d, *J* = 8.4Hz, 1H), 7.32 (d, *J* = 8.4Hz, 2H), 7.25–7.18 (m, 5H), 7.00 (dd, *J* = 4.8, 4.0Hz, 1H), 2.40 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 144.8, 144.1, 143.6, 141.2, 139.6, 138.0, 136.8, 136.0, 135.9, 134.8, 131.3, 130.2, 130.0, 129.2, 129.0, 128.4, 127.9, 127.5, 21.7

HRMS calcd for $C_{24}H_{17}ClO_3S_2$ (M+H) 453.0387 ; found 453.0380



7a, (6'-tosyl-[1,1':3',1''-terphenyl]-4'-yl)(3,4,5-trimethoxyphenyl)methanone

White solid, 114 mg, 66%

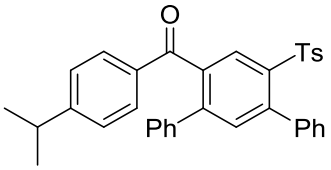
Melting point: 181-183˚C

IR (KBr) υ_{max}: 2926, 1658, 1583, 1498, 1454, 1325, 1122, 1001, 698, 578

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.35 (t, *J* = 7.2Hz, 2H), 7.28–7.22 (m, 7H), 7.15 (d, *J* = 8.4Hz, 2H), 7.08 (d, *J* = 8.4Hz, 2H), 7.01 (d, *J* = 7.6Hz, 4H), 3.89 (s, 3H), 3.82(s, 6H), 2.33 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 152.9, 143.9, 143.1, 138.8, 138.2, 137.9, 137.5, 137.4, 134.6, 131.6, 129.9, 129.3, 129.1, 128.4, 128.7, 128.6, 128.1, 128.0, 127.5, 107.9, 61.0, 56.4, 21.6

HRMS calcd for $C_{35}H_{30}O_6S$ (M+H) 579.1842 ; found 579.1823



7b, (4-isopropylphenyl)(6'-tosyl-[1,1':3',1''-terphenyl]-4'-yl)methanone

White solid, 100 mg, 63%

Melting point: 195-196˚C

IR (KBr) υ_{max}: 2958, 1664, 1600, 1537, 1492, 1448, 1290, 1143, 954, 700, 569

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.73 (d, *J* = 8.4Hz, 2H), 7.63–7.32 (m, 2H), 7.28–7.23 (m, 9H), 7.14 (d, *J* = 8.4Hz, 2H), 7.06 (d, *J* = 8.4Hz, 2H), 7.01 (d, *J* = 8.0Hz, 2H), 2.97-2.90 (m, 1H), 2.33 (s, 3H), 1.25 (d, *J* = 7.2Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 155.3, 145.6, 143.7, 143.6, 138.5, 138.36, 138.34, 137.6, 137.5, 134.7, 134.5, 130.6, 130.0, 129.1, 129.0, 128.8, 128.6, 128.3, 128.08, 128.04, 127.4, 126.7, 34.4, 23.6, 21.6

HRMS calcd for $C_{35}H_{30}O_3S$ (M+H) 531.1995 ; found 531.1983

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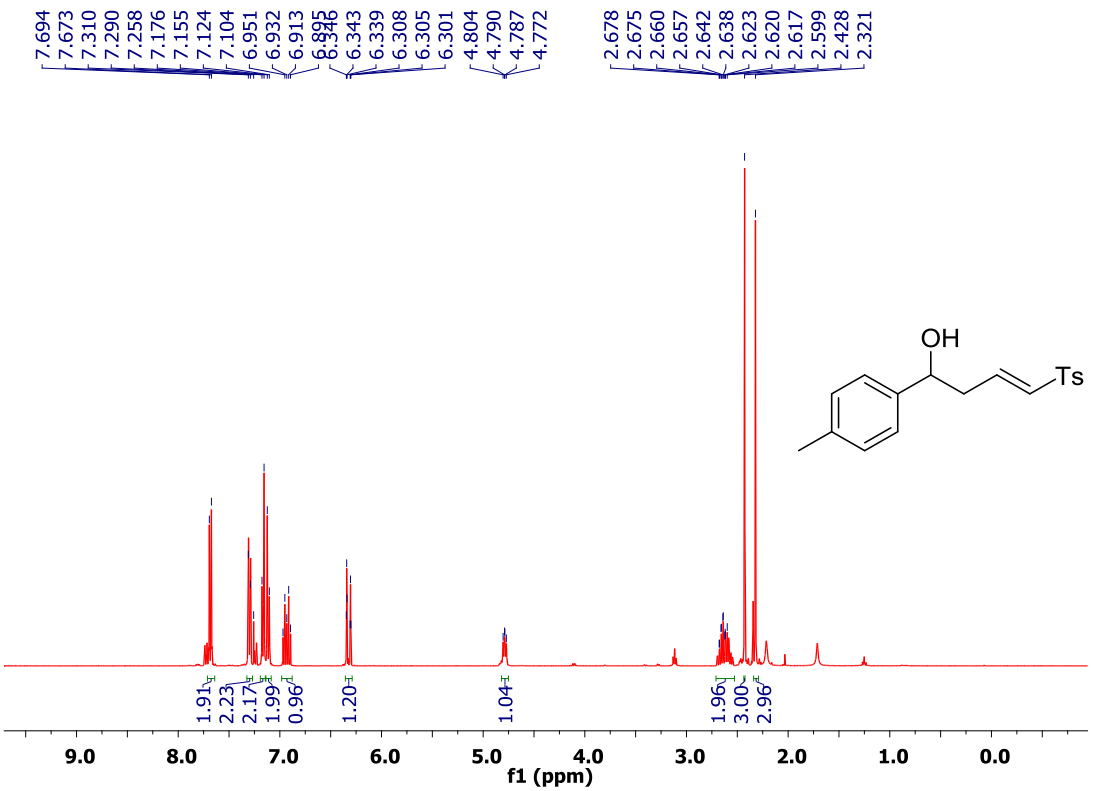
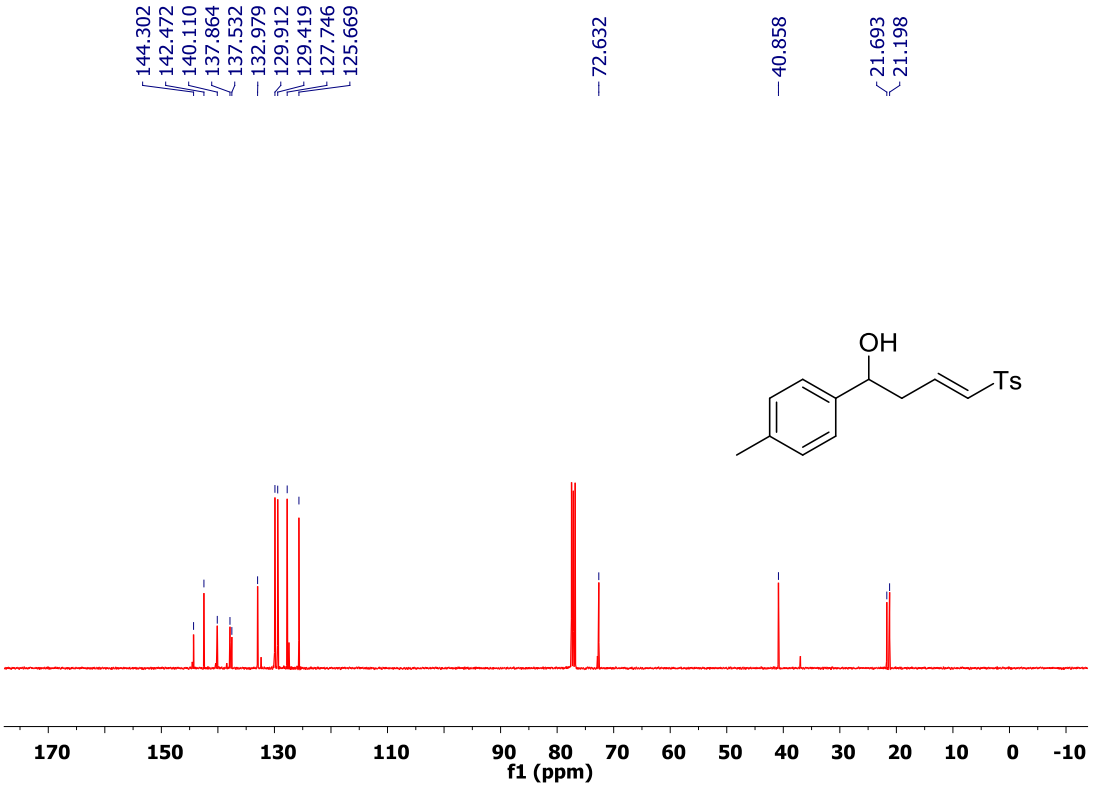
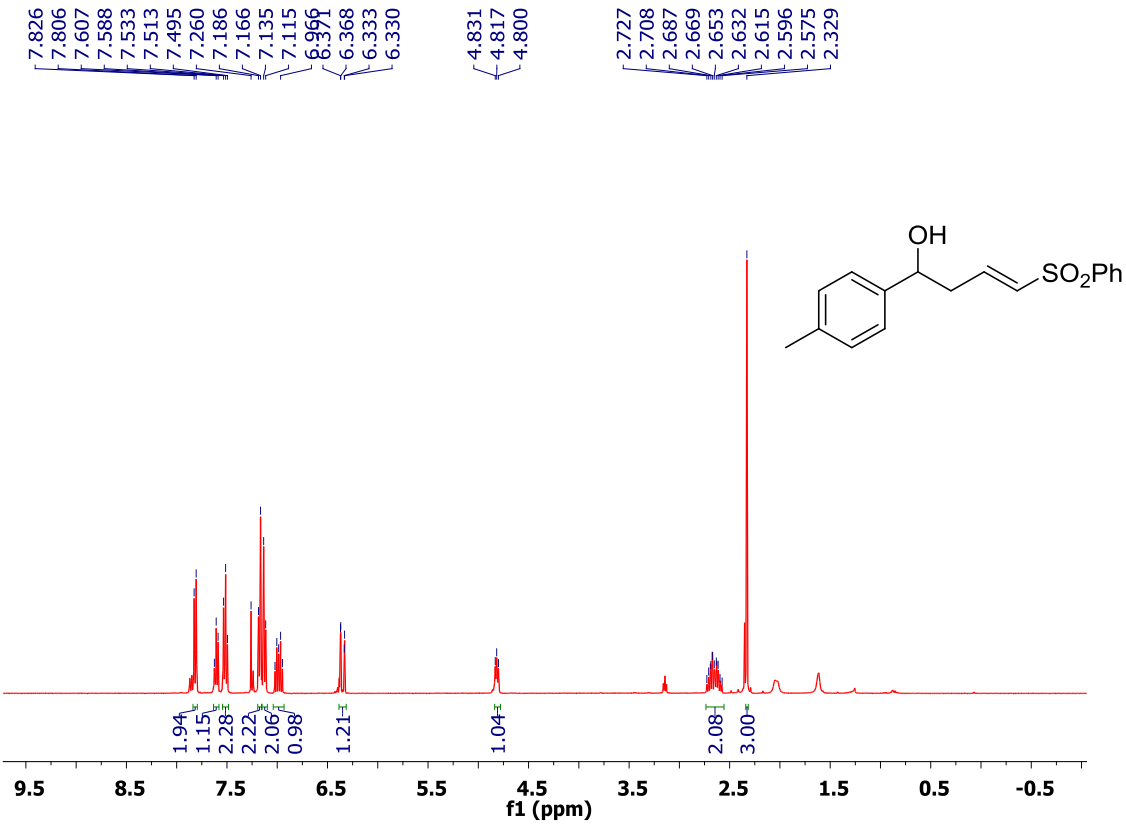
3.9. NMR spectra of new compounds [^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$)]



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2.575
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2.28
2.22
2.06
0.98
1.21
1.04
2.08
3.00
9.5
8.5
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6.5
5.5
4.5
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2.5
1.5
0.5
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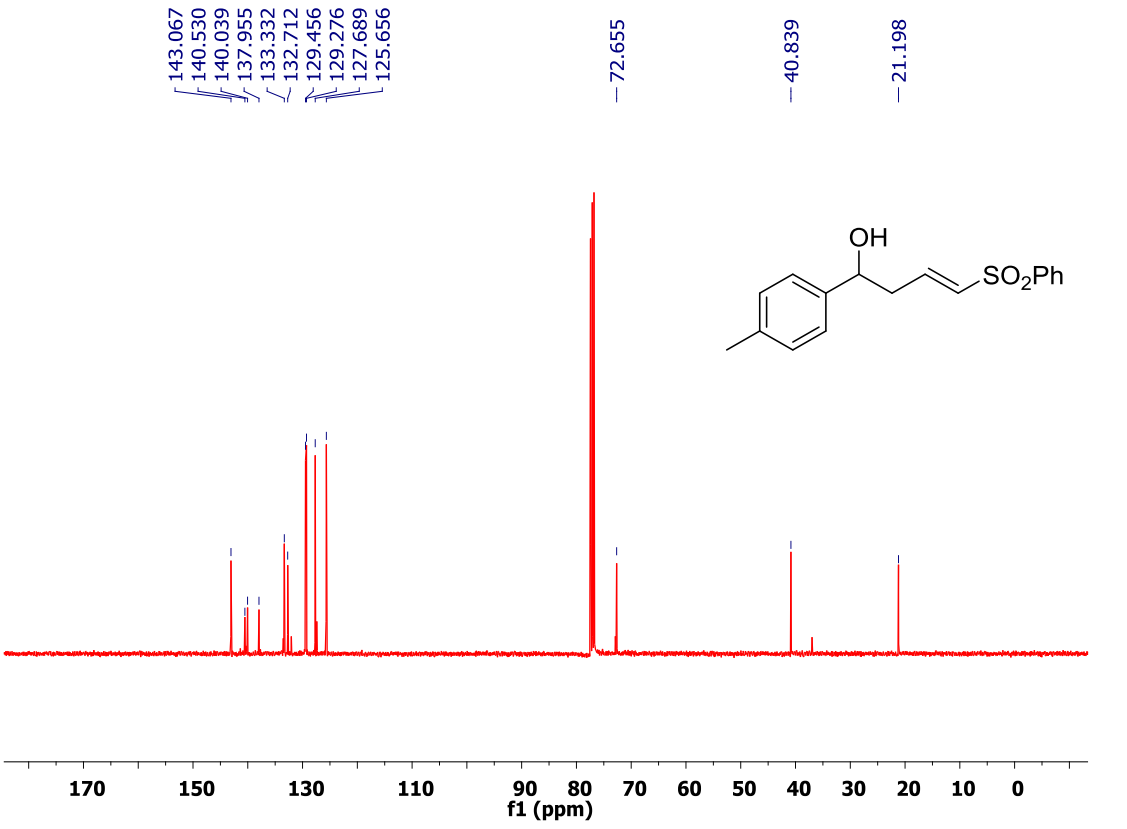
f1 (ppm)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50
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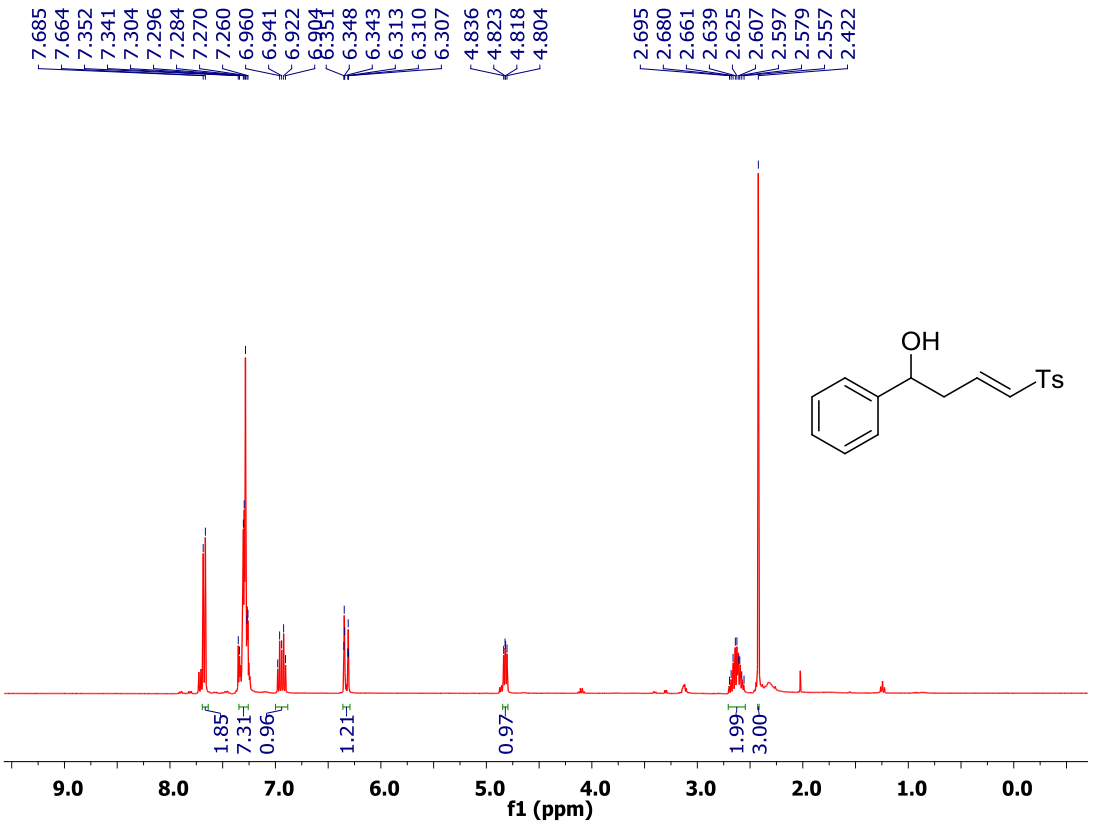
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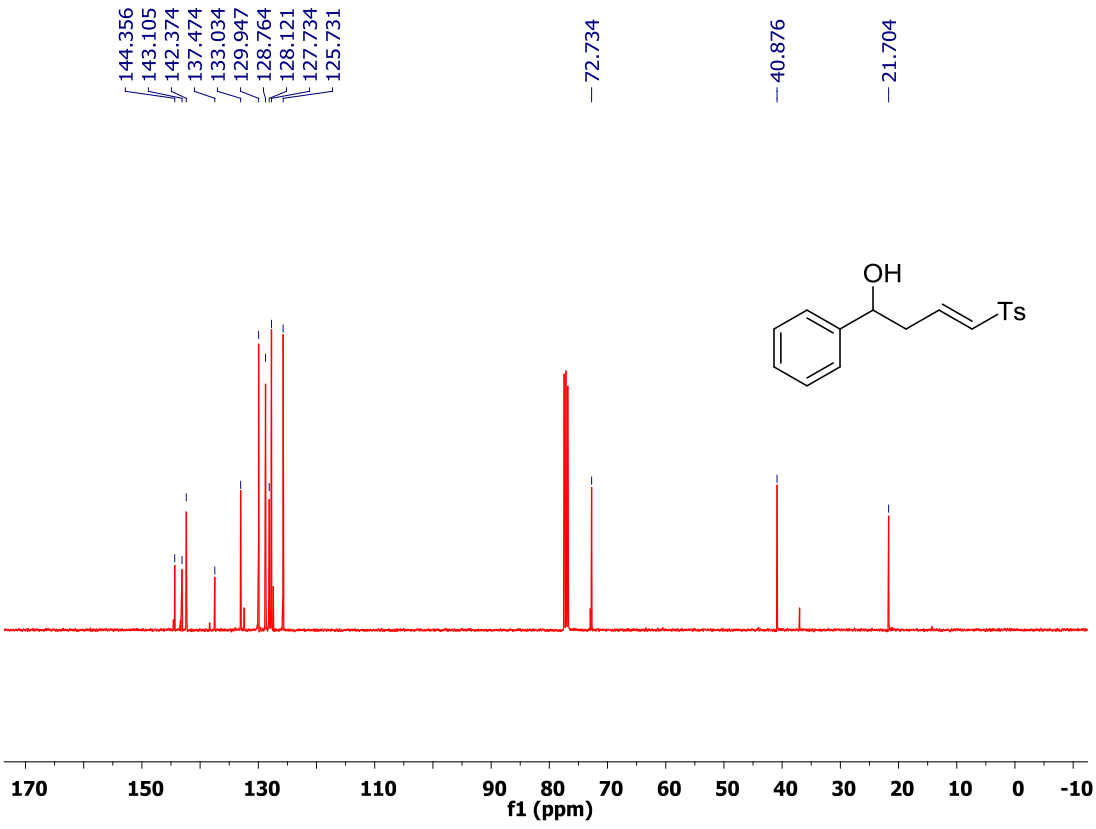
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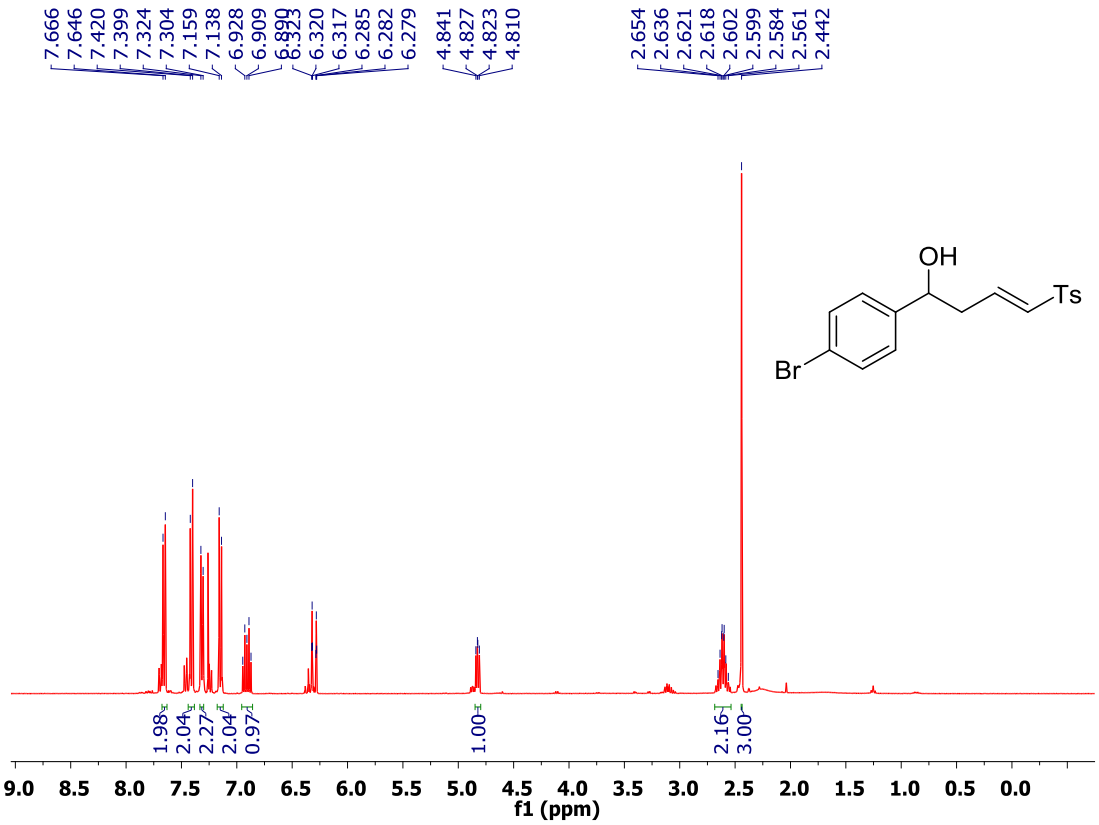
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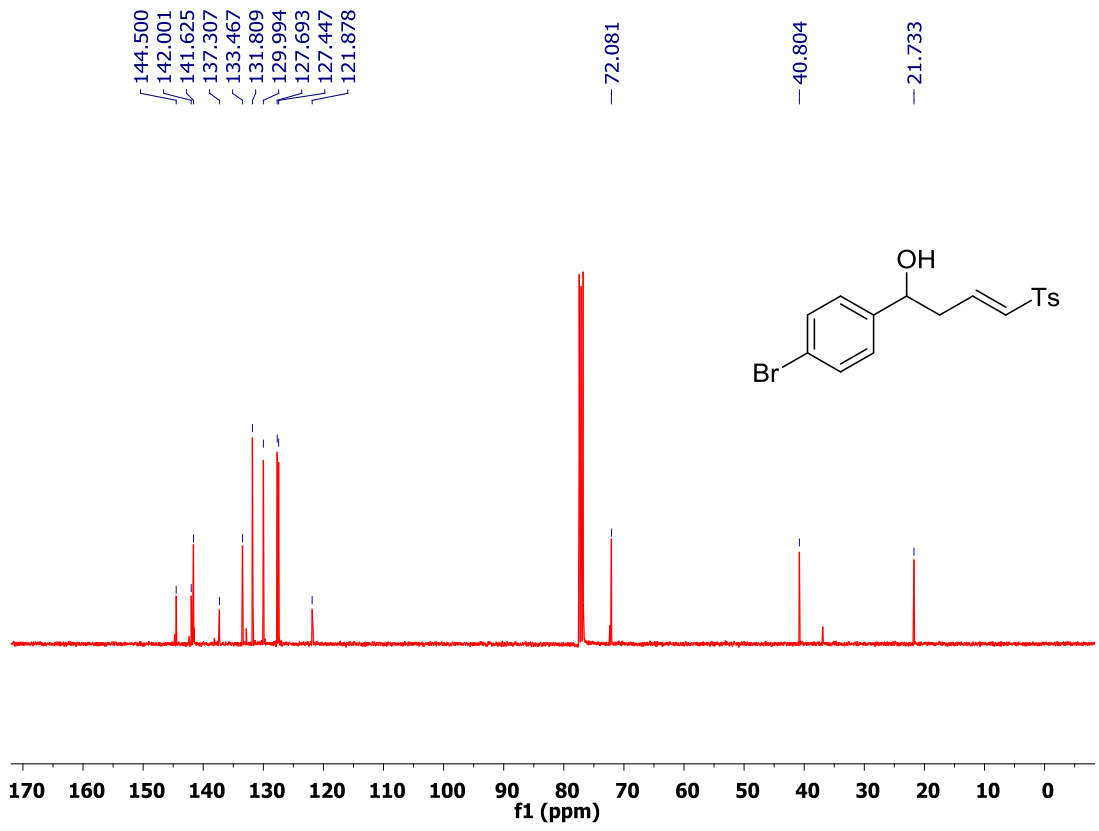
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Br
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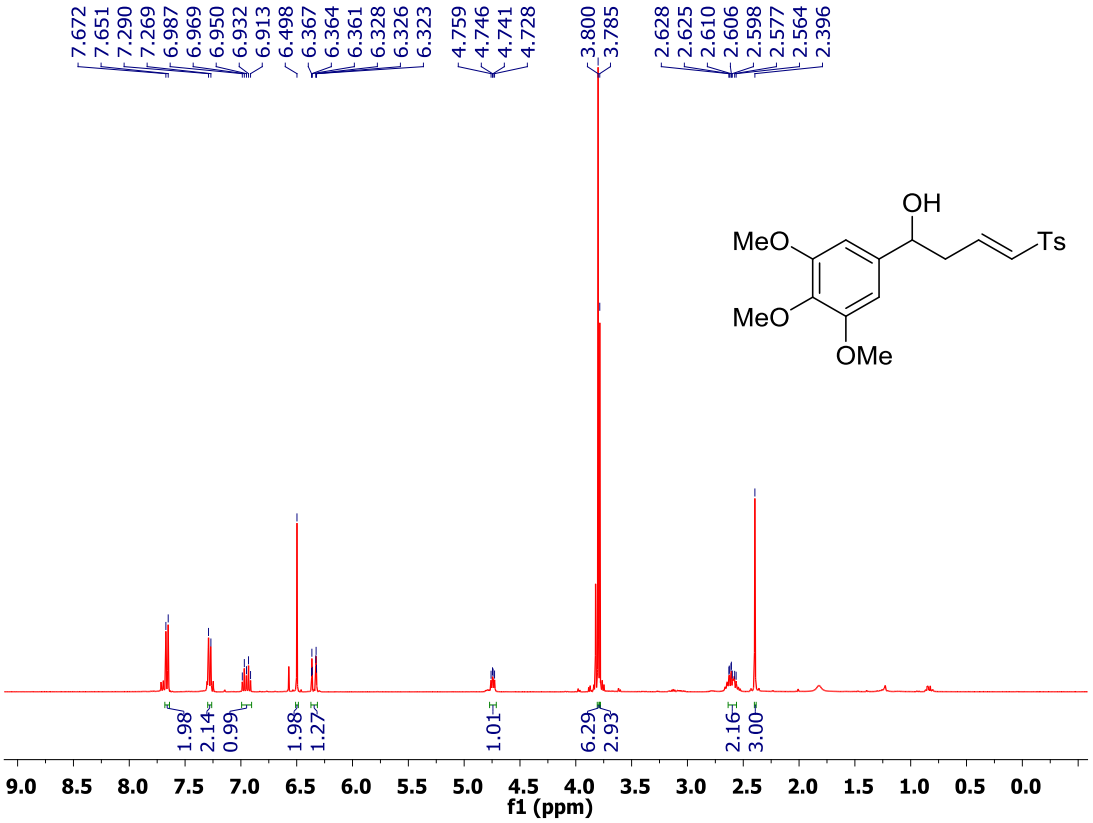
f1 (ppm)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MeO
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MeO
OMe
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0.99
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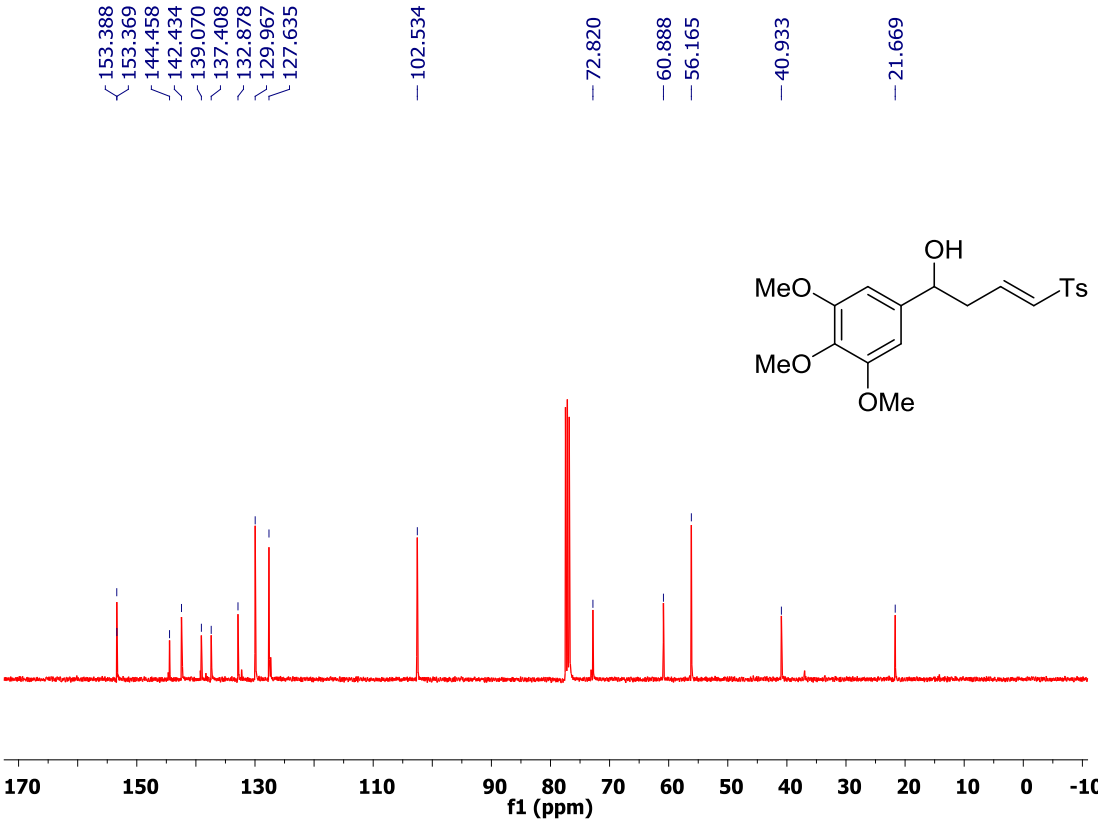
1.01
6.29
2.93
2.16
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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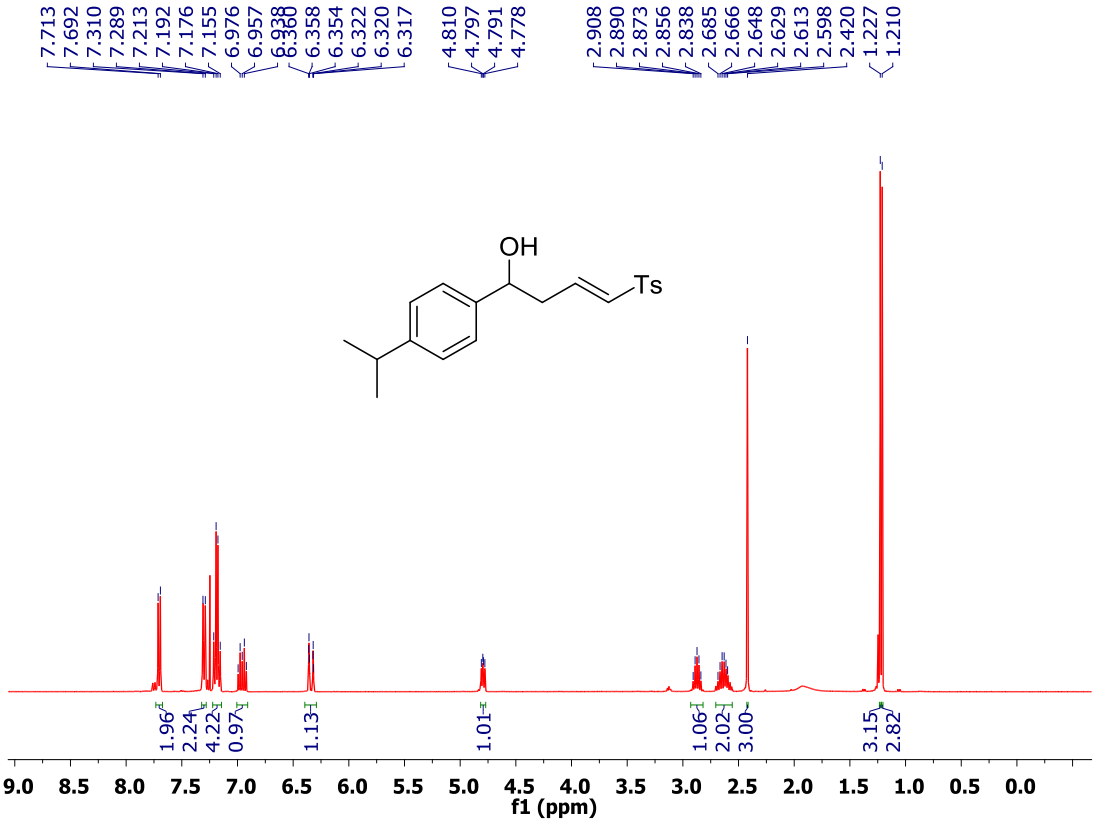
153.369
144.458
142.434
139.070
137.408
132.878
129.967
127.635
102.534
72.820
60.888
56.165
40.933
21.669
OH
MeO
Ts
MeO
OMe
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.692
7.310
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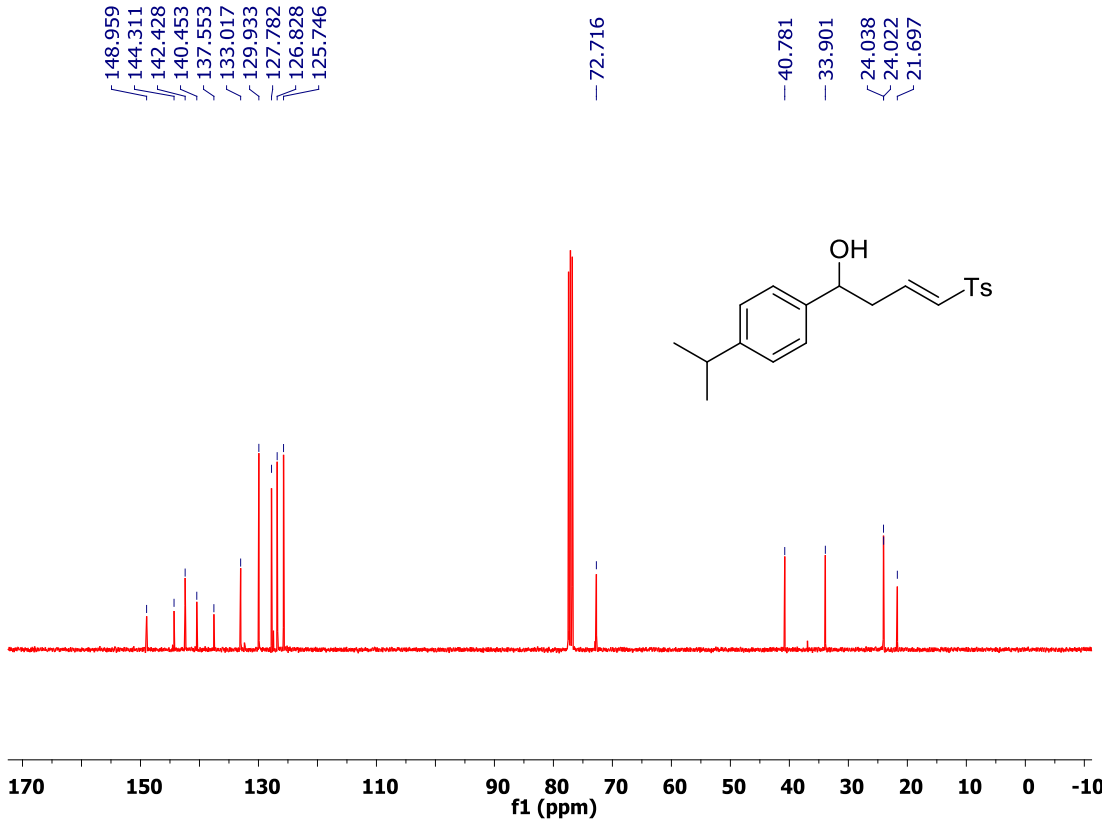
7.213
7.192
7.176
7.155
6.976
6.957
6.938
6.360
6.358
6.354
6.322
6.320
6.317
4.810
4.797
4.791
4.778
2.908
2.890
2.873
2.856
2.838
2.685
2.666
2.648
2.629
2.613
2.598
2.420
1.227
1.210
OH
Ts
1.96
2.24
4.22
0.97
1.13
1.01
1.06
2.02
3.00
3.15
2.82
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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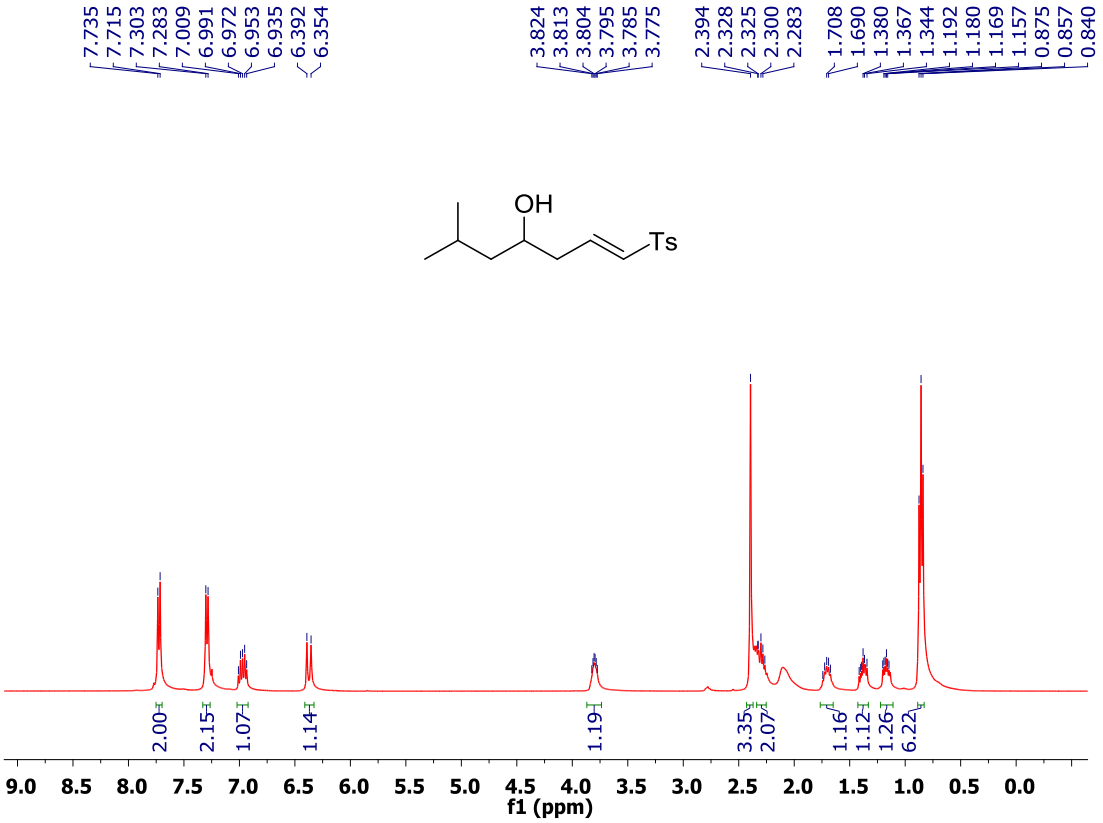
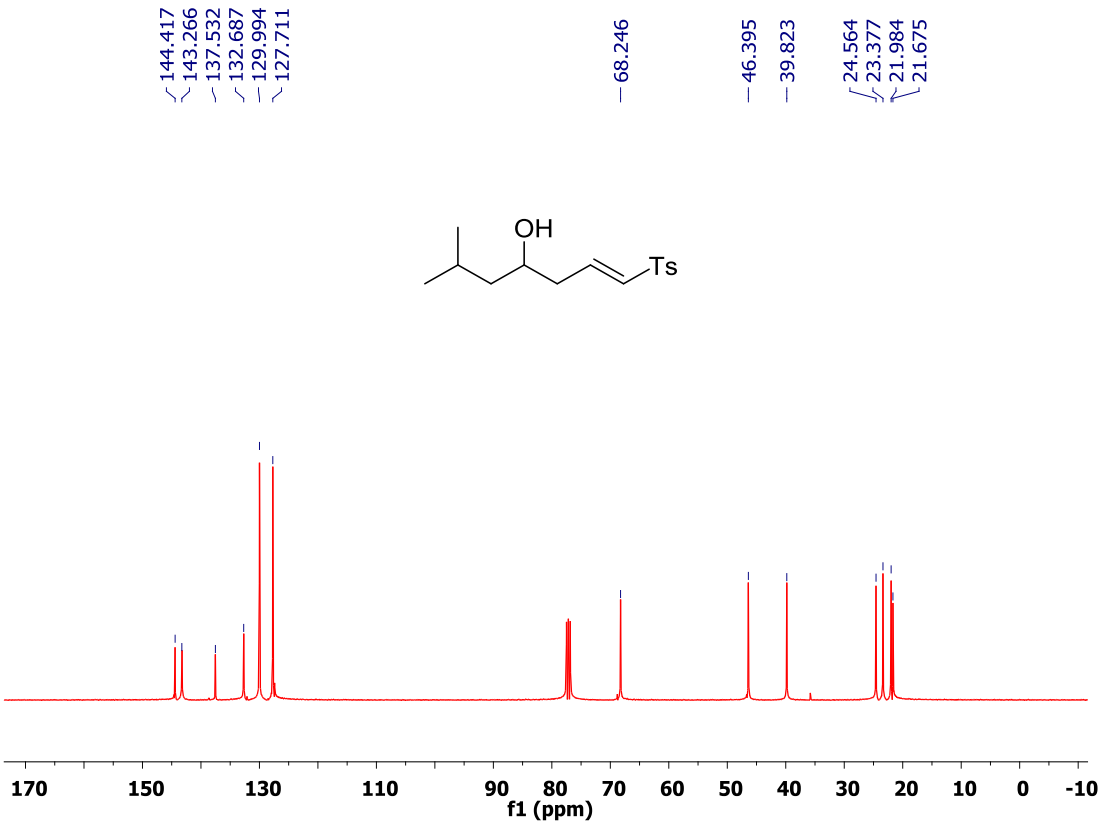
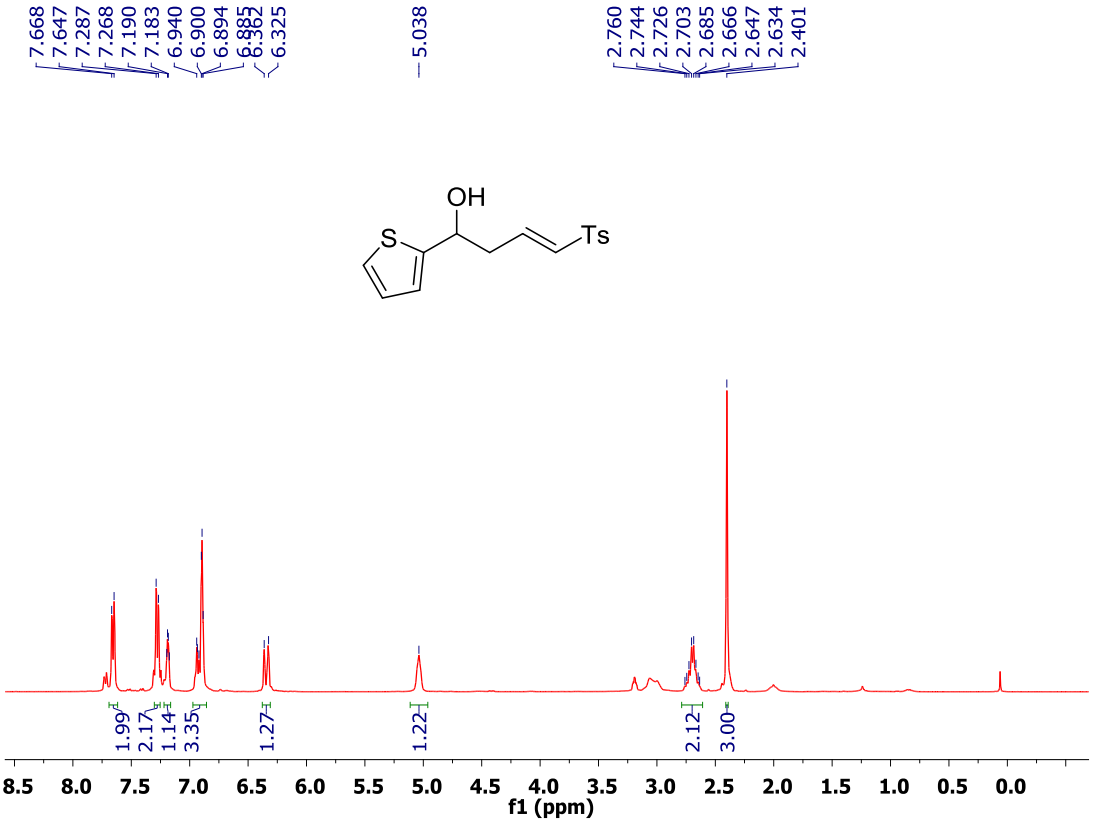
144.311
142.428
140.453
137.553
133.017
129.933
127.782
126.828
125.746
72.716
40.781
33.901
24.038
24.022
21.697
OH
Ts
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.735
7.715
7.303
7.283
7.009
6.991
6.972
6.953
6.935
6.392
6.354
3.824
3.813
3.804
3.795
3.785
3.775
2.394
2.328
2.325
2.300
2.283
1.708
1.690
1.380
1.367
1.344
1.192
1.180
1.169
1.157
0.875
0.857
0.840
OH
Ts
2.00
2.15
1.07
1.14
1.19
3.35
2.07
1.16
1.12
1.26
6.22
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)


144.417
143.266
137.532
132.687
129.994
127.711
68.246
46.395
39.823
24.564
23.377
21.984
21.675
OH
Ts
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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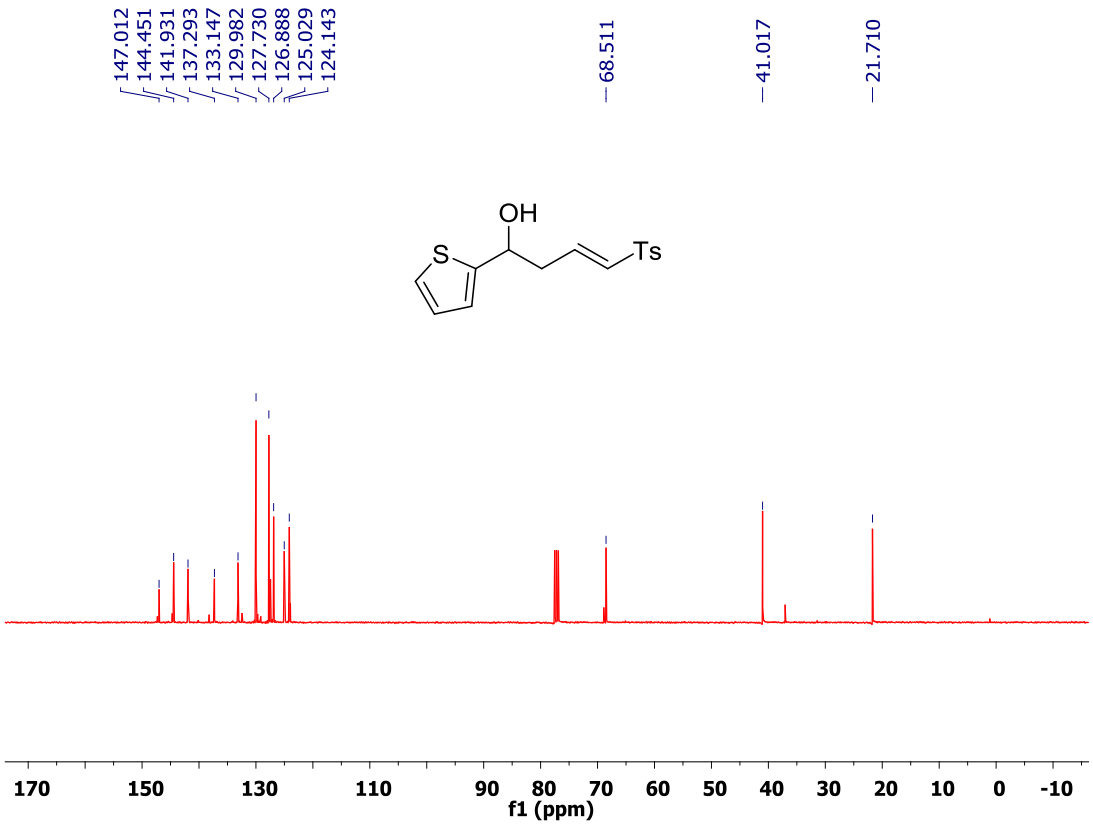
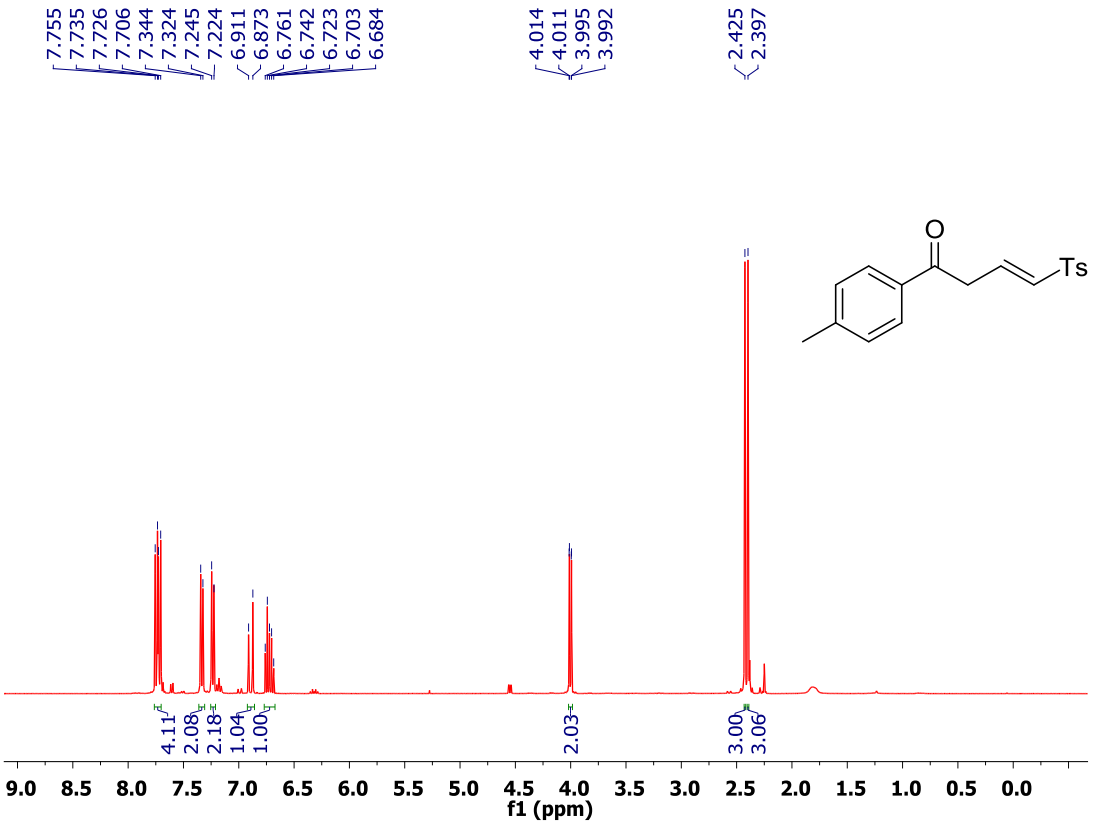
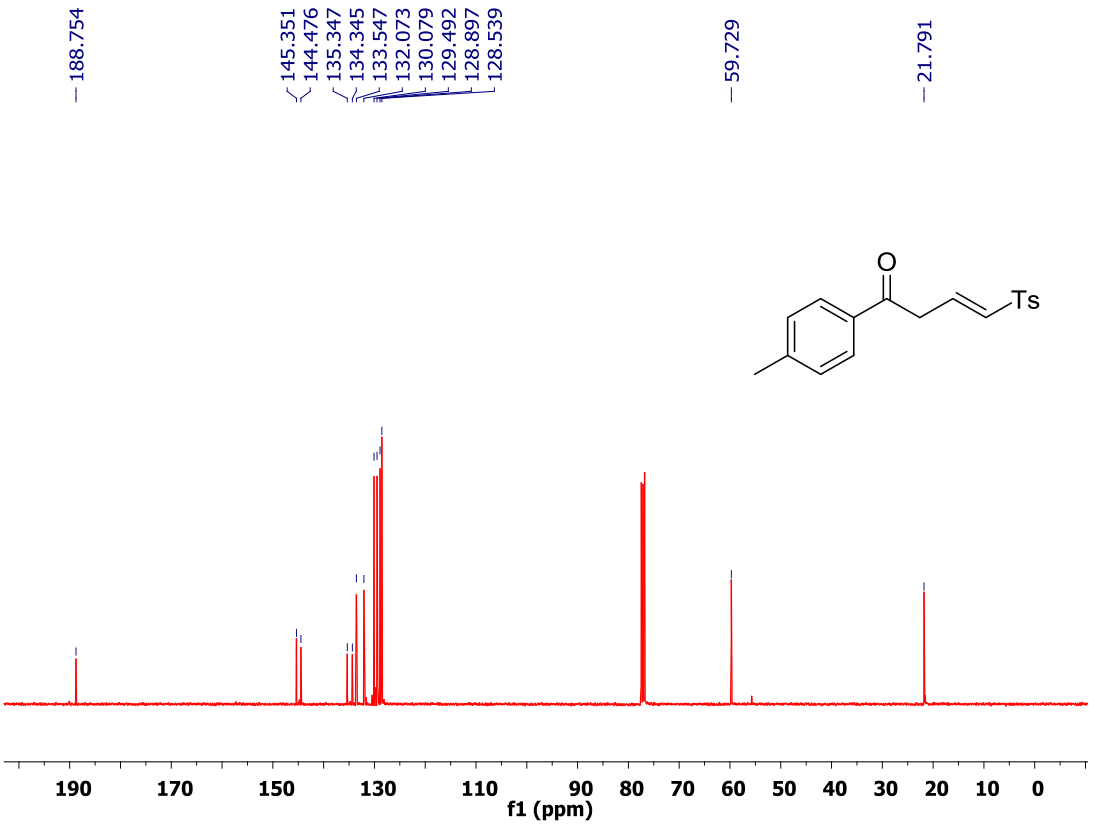
7.647
7.287
7.268
7.190
7.183
6.940
6.900
6.894
6.325
5.038
2.760
2.744
2.726
2.703
2.685
2.666
2.647
2.634
2.401
OH
S
Ts
1.99
2.17
1.14
3.35
1.27
1.22
2.12
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.012
144.451
141.931
137.293
133.147
129.982
127.730
126.888
125.029
124.143
68.511
41.017
21.710
OH
S
Ts
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.755
7.735
7.726
7.706
7.344
7.324
7.245
7.224
6.911
6.873
6.761
6.742
6.723
6.703
6.684
4.014
4.011
3.995
3.992
2.425
2.397
O
Ts
4.11
2.08
2.18
1.04
1.00
2.03
3.00
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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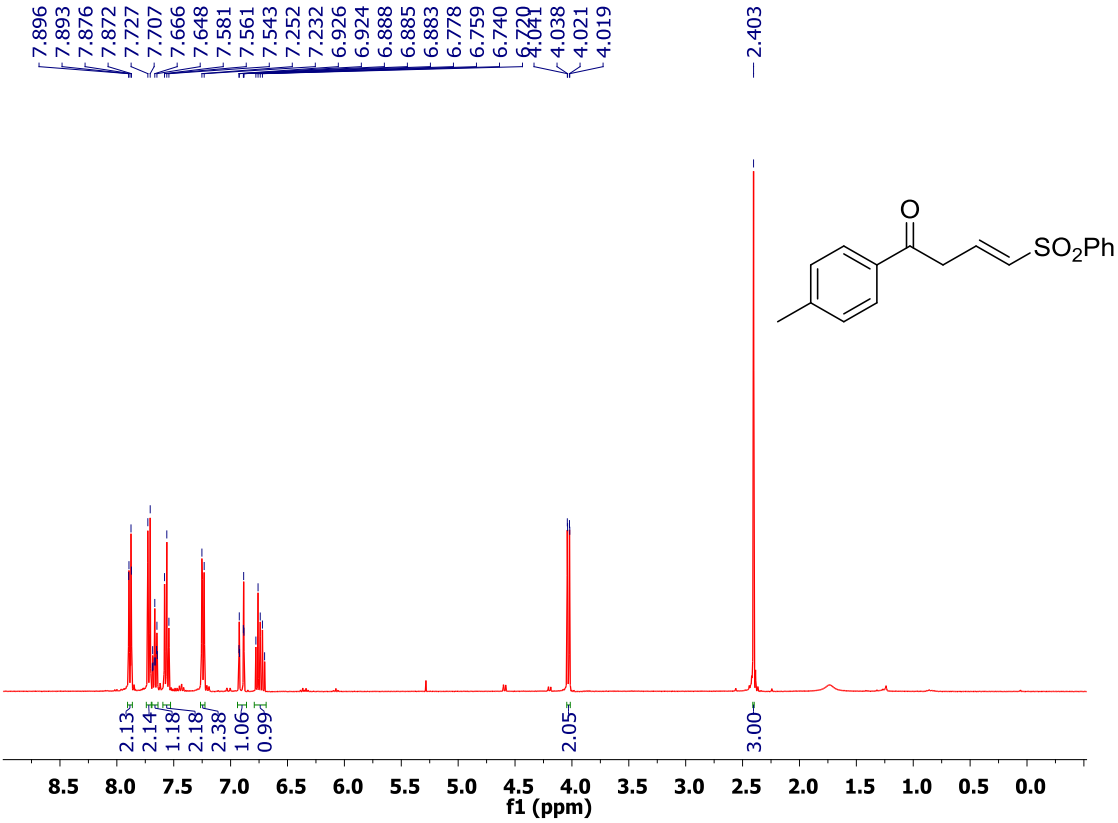
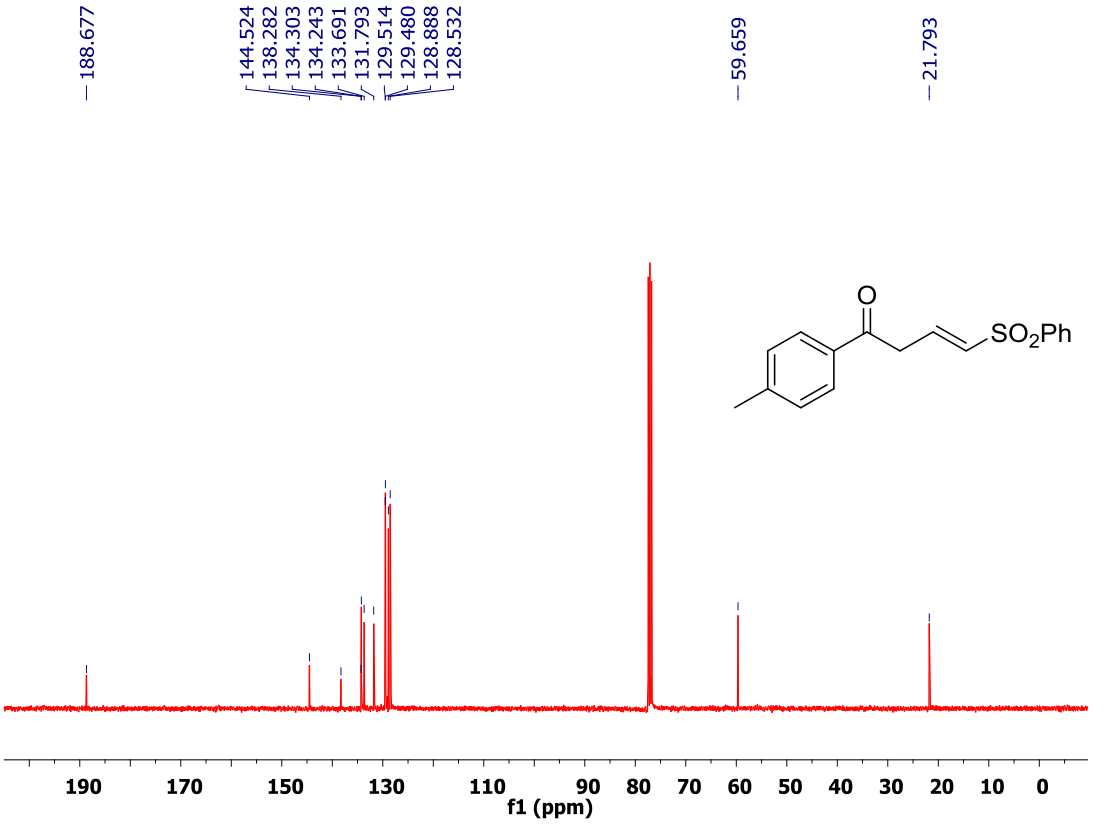
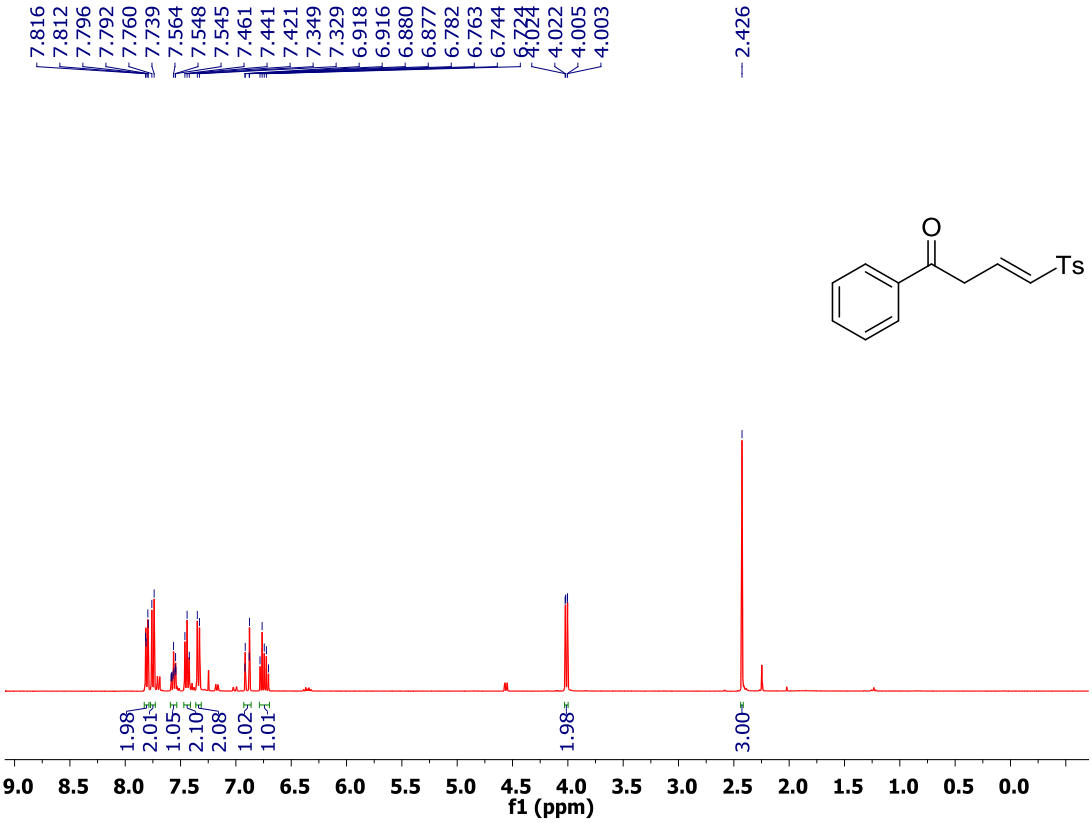
145.351
144.476
135.347
134.345
133.547
132.073
130.079
129.492
128.897
128.539
59.729
21.791
O
Ts
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.896
7.893
7.876
7.872
7.727
7.707
7.666
7.648
7.581
7.561
7.543
7.252
7.232
6.926
6.924
6.888
6.885
6.883
6.778
6.759
6.740
4.041
4.038
4.021
4.019
2.403
O
SO2Ph
2.13
2.14
1.18
2.18
2.38
1.06
0.99
2.05
3.00
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)


188.677
144.524
138.282
134.303
134.243
133.691
131.793
129.514
129.480
128.888
128.532
59.659
21.793
O
SO2Ph
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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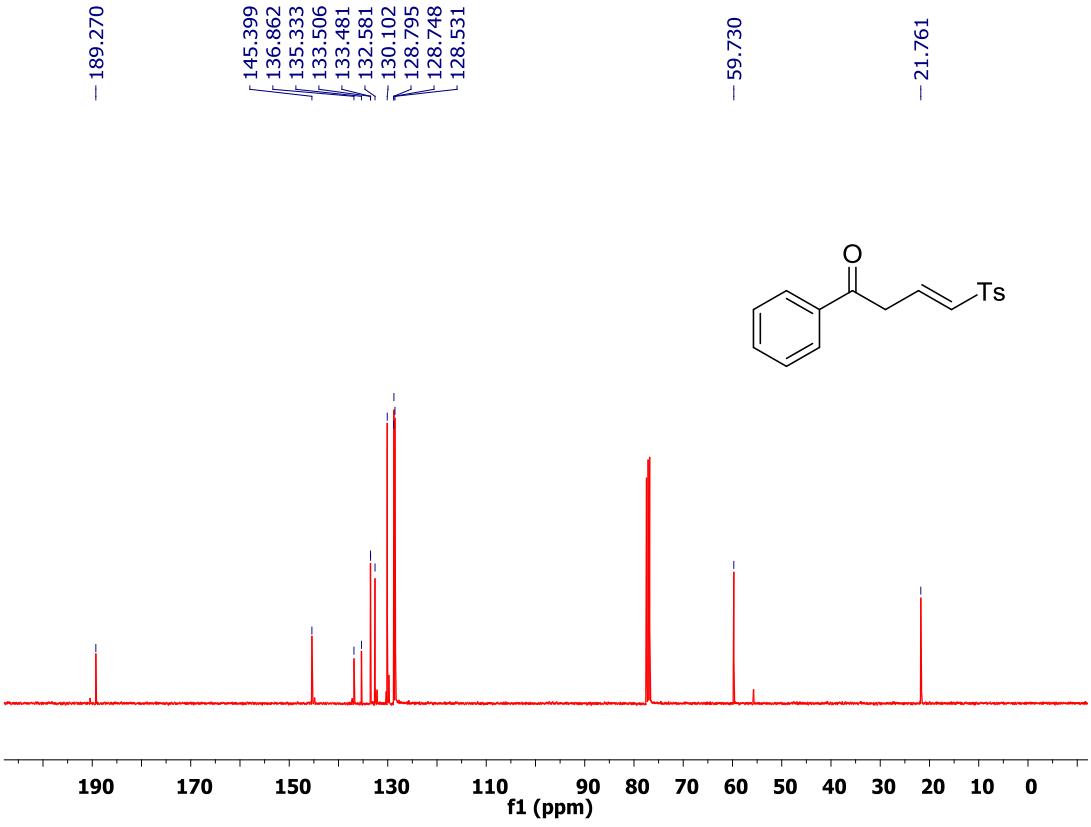
7.812
7.796
7.792
7.760
7.739
7.564
7.548
7.545
7.461
7.441
7.421
7.349
7.329
6.918
6.916
6.880
6.877
6.782
6.763
6.744
4.022
4.005
4.003
2.426
O
Ts
1.98
2.01
1.05
2.10
2.08
1.02
1.01
1.98
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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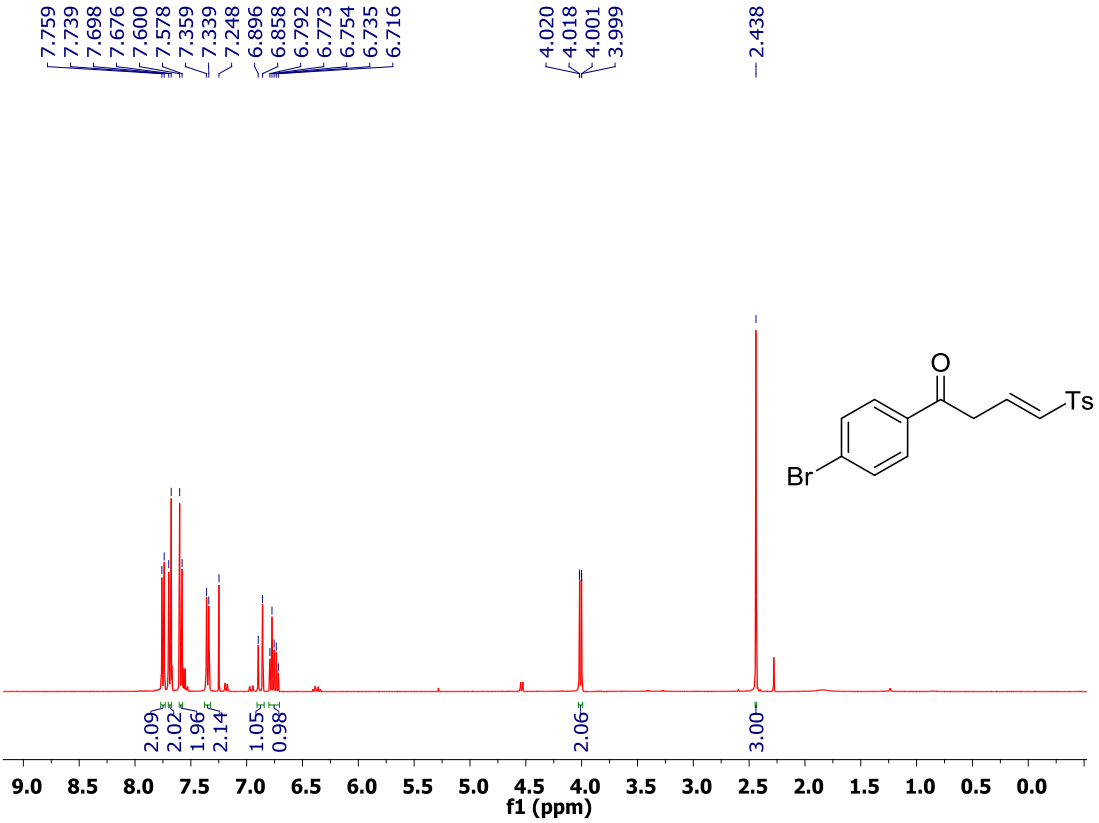
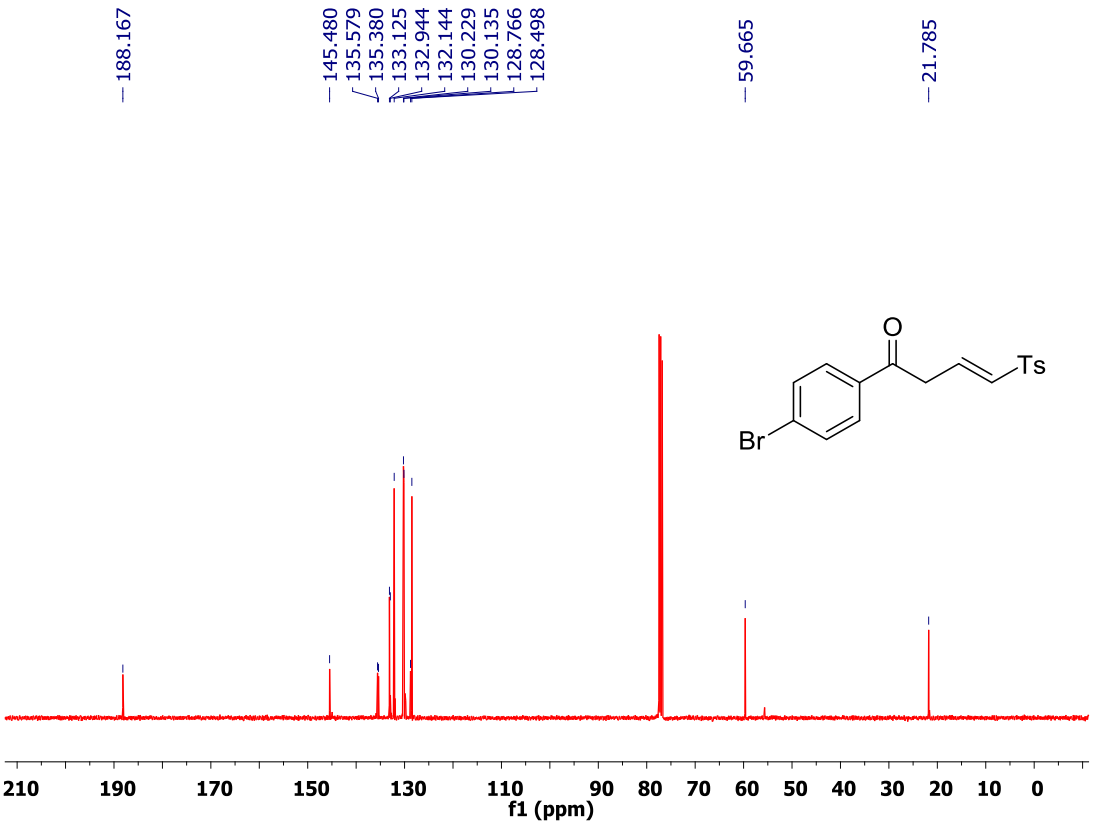
145.399
136.862
135.333
133.506
133.481
132.581
130.102
128.795
128.748
128.531
59.730
21.761
O
Ts
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.759
7.739
7.698
7.676
7.600
7.578
7.359
7.339
7.248
6.896
6.858
6.792
6.773
6.754
6.735
6.716
4.020
4.018
4.001
3.999
2.438
O
Ts
Br
2.09
2.02
1.96
2.14
1.05
0.98
2.06
3.00
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 0.0
f1 (ppm)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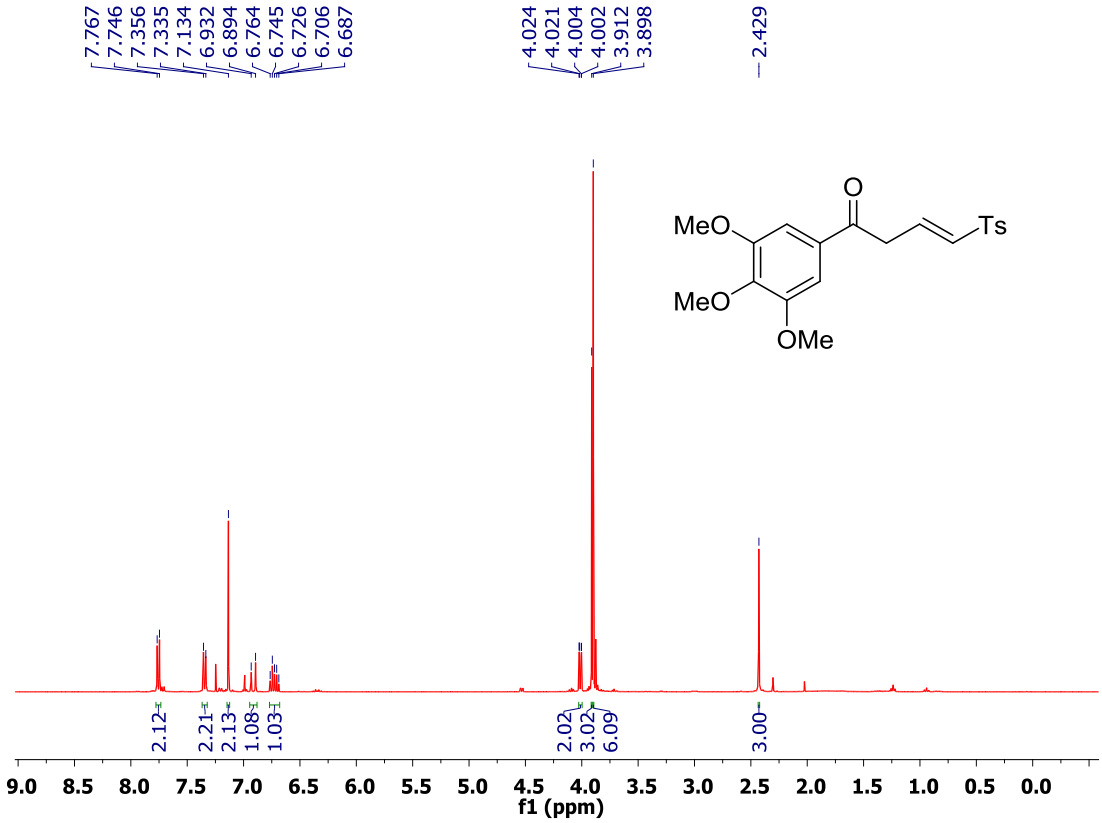
135.579
135.380
133.125
132.944
132.144
130.229
130.135
128.766
128.498
59.665
21.785
O
Ts
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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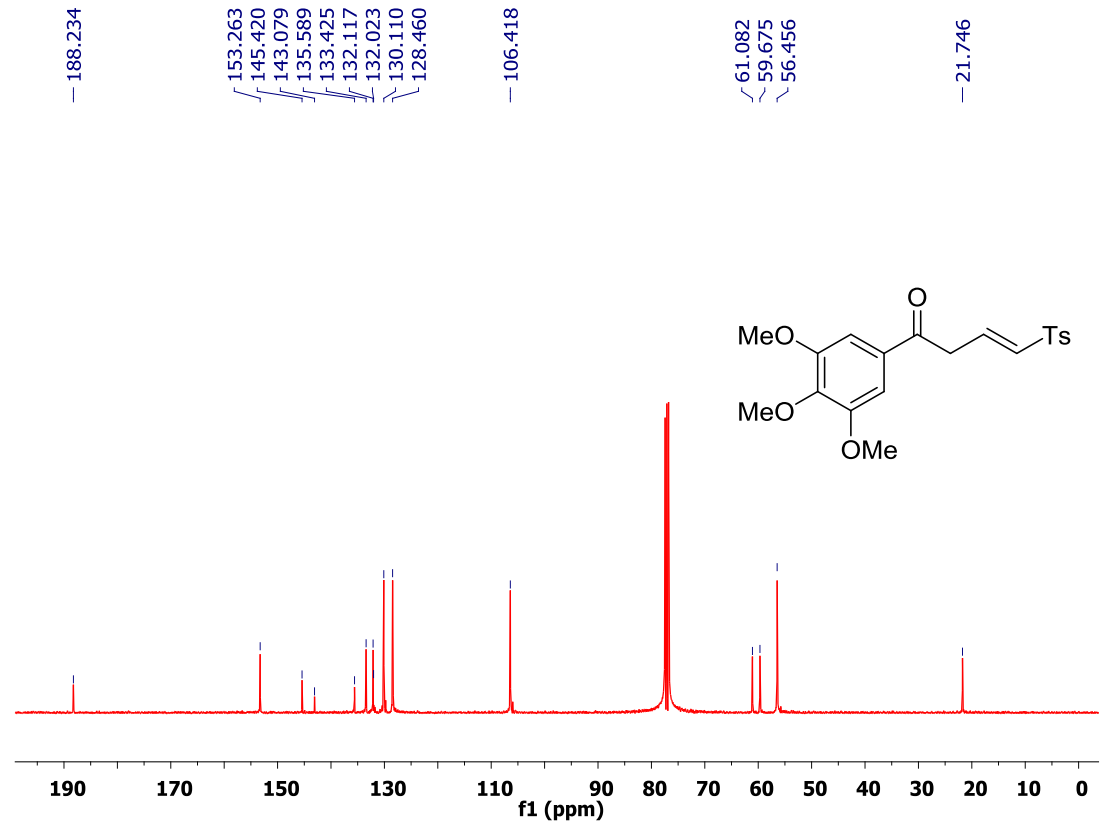
7.335
7.134
6.932
6.894
6.764
6.745
6.726
6.706
6.687
4.024
4.021
4.004
4.002
3.912
3.898
2.429
MeO
MeO
OMe
O
Ts
2.12
2.21
2.13
1.08
1.03
2.02
3.02
6.09
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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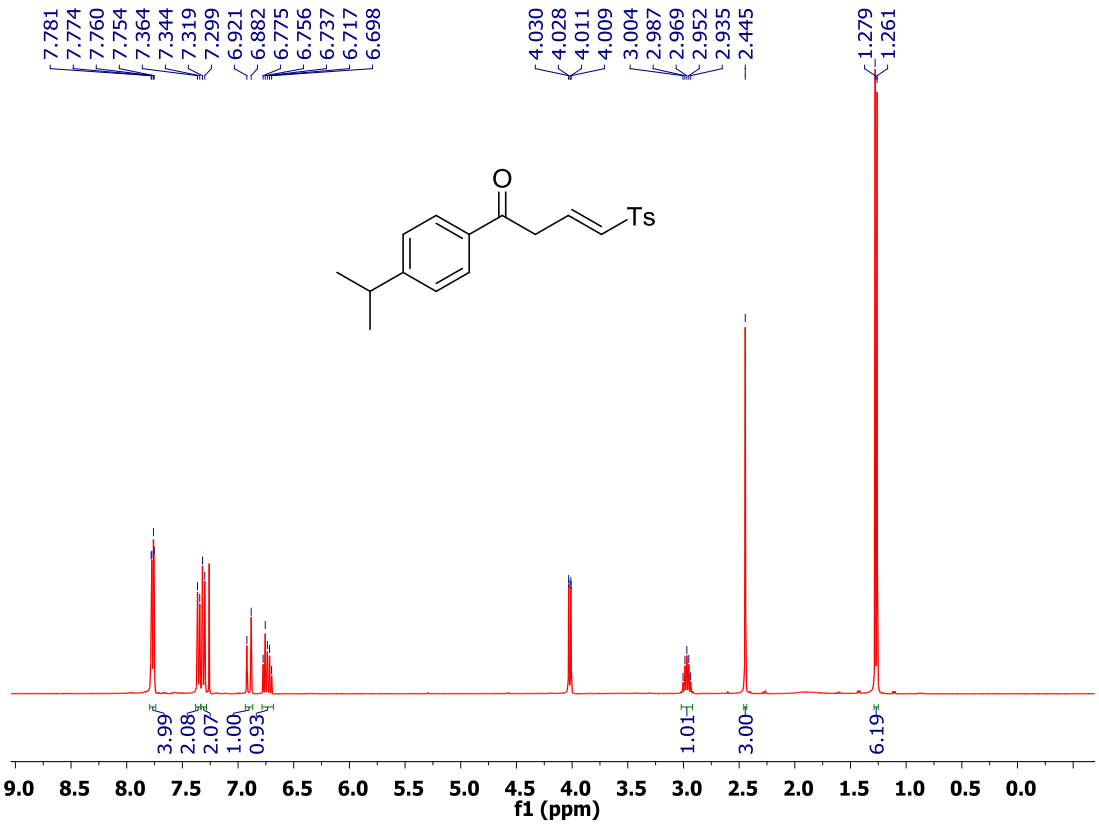
145.420
143.079
135.589
133.425
132.117
132.023
130.110
128.460
106.418
61.082
59.675
56.456
21.746
MeO
MeO
OMe
O
Ts
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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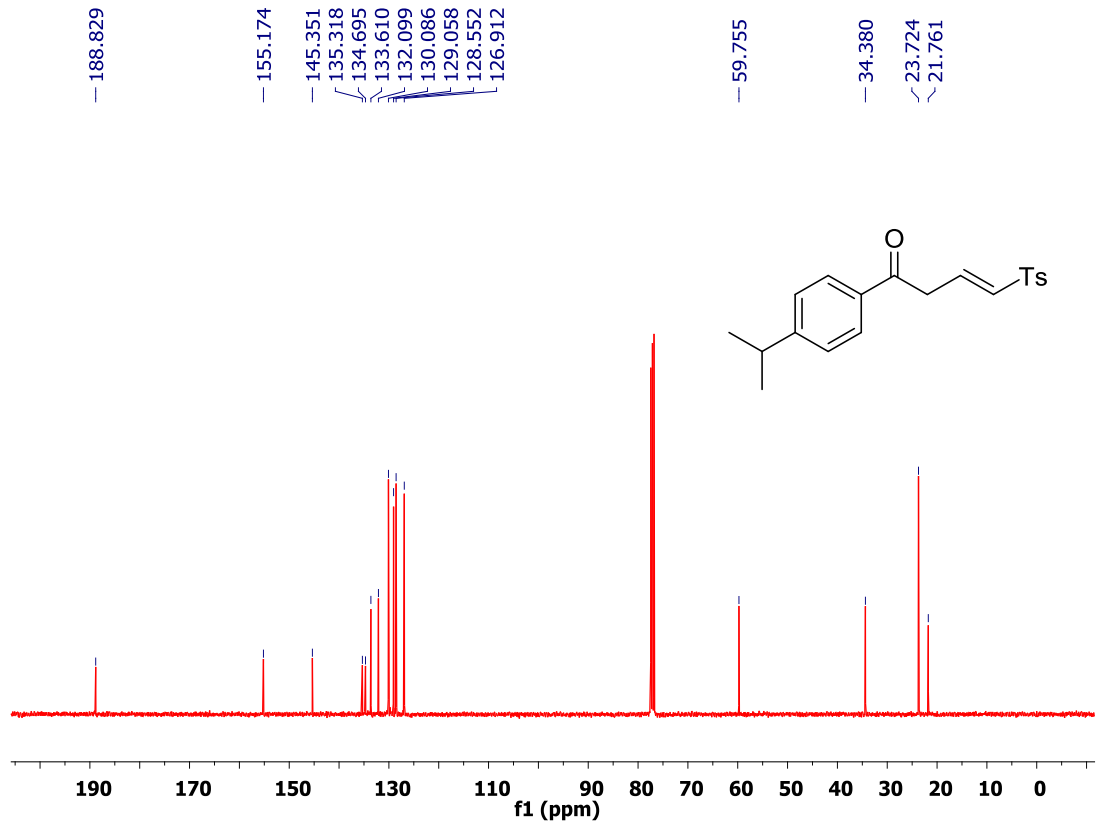
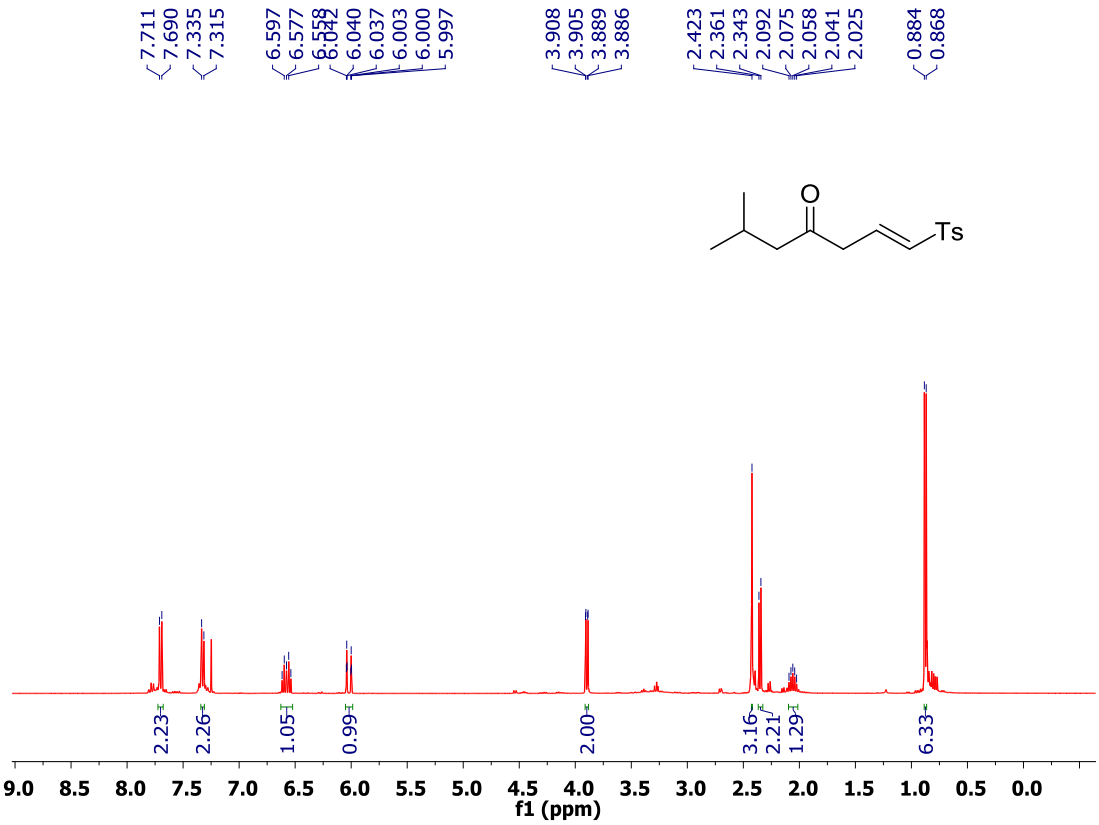
7.344
7.319
7.299
6.921
6.882
6.775
6.756
6.737
6.717
6.698
4.030
4.028
4.011
4.009
3.004
2.987
2.969
2.952
2.935
2.445
1.279
1.261
O
Ts
3.99
2.08
2.07
1.00
0.93
1.01
3.00
6.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


188.829
155.174
145.351
135.318
134.695
133.610
132.099
130.086
129.058
128.552
126.912
59.755
34.380
23.724
21.761
O
Ts
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.315
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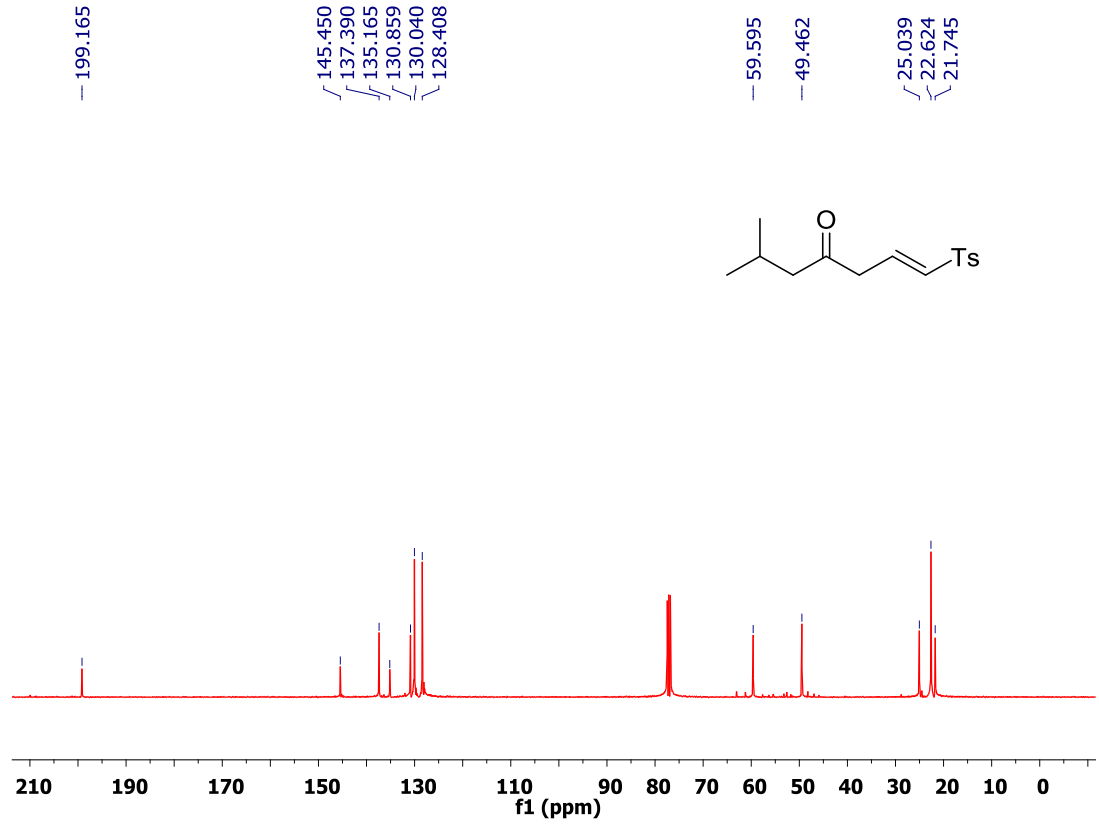
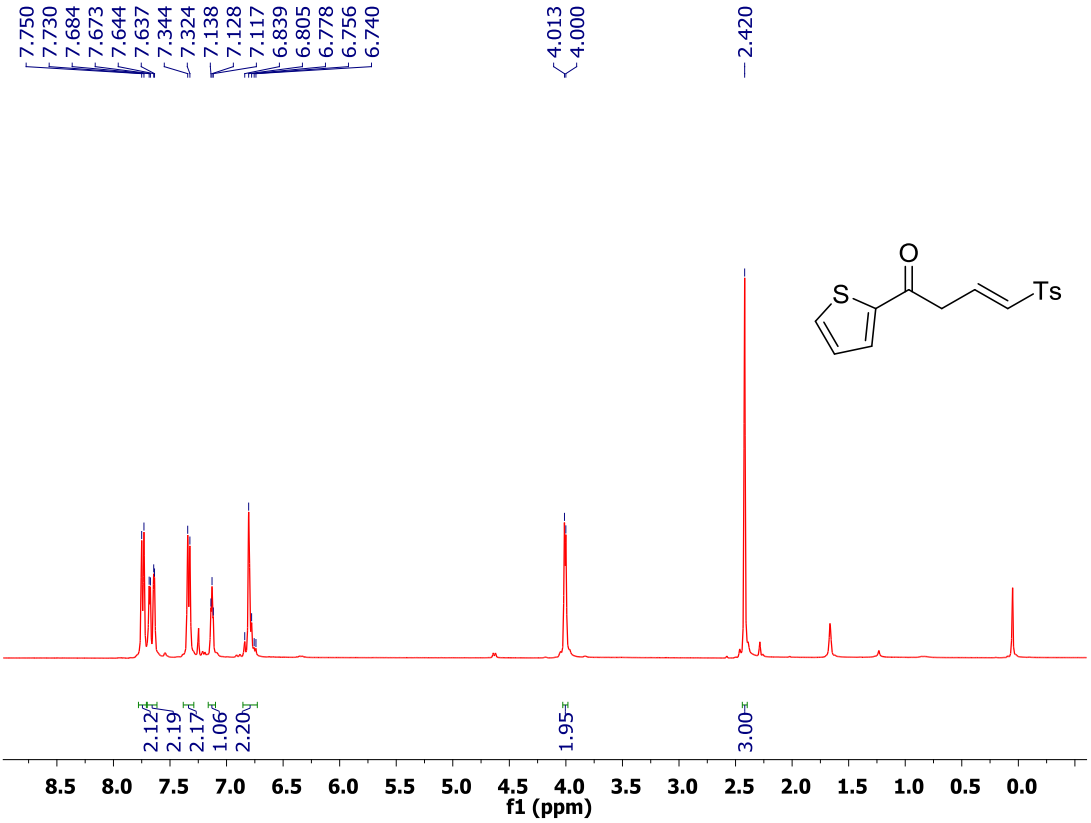
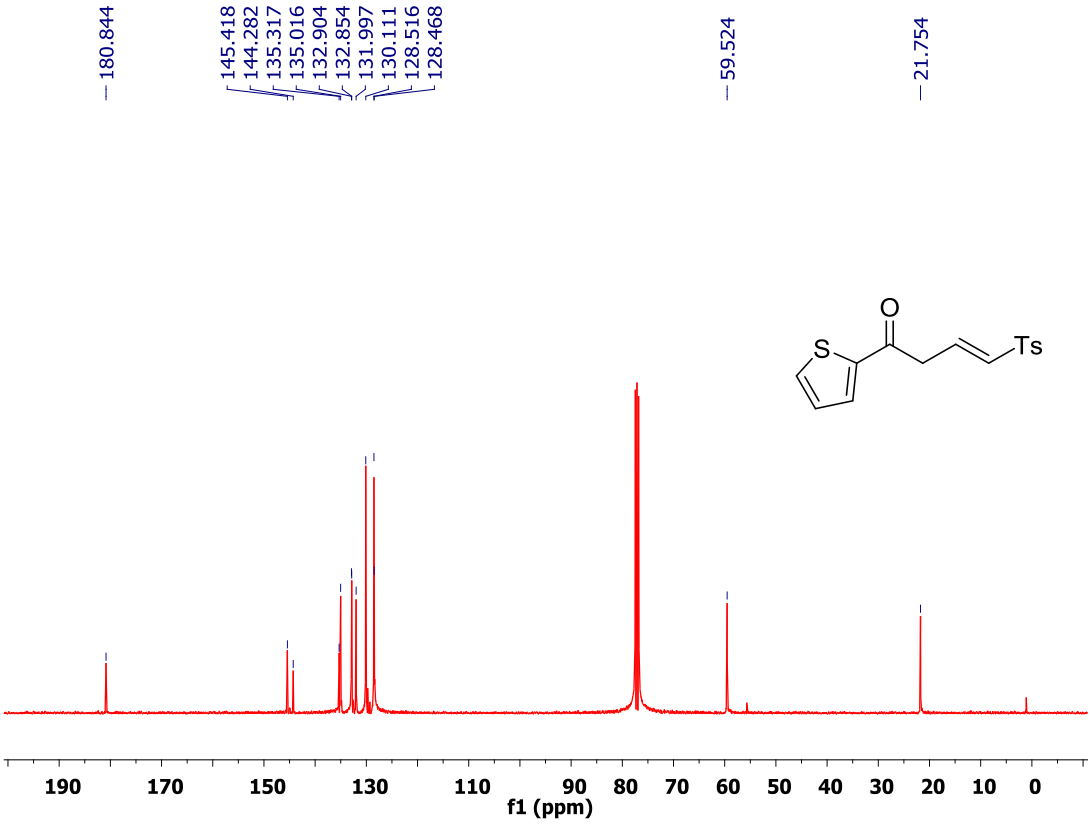
6.577
6.558
6.042
6.040
6.037
6.003
6.000
5.997
3.908
3.905
3.889
3.886
2.423
2.361
2.343
2.092
2.075
2.058
2.041
2.025
0.884
0.868
O
Ts
2.23
2.26
1.05
0.99
2.00
3.16
2.21
1.29
6.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


199.165
145.450
137.390
135.165
130.859
130.040
128.408
59.595
49.462
25.039
22.624
21.745
O
Ts
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.750
7.730
7.684
7.673
7.644
7.637
7.344
7.324
7.138
7.128
7.117
6.839
6.805
6.778
6.756
6.740
4.013
4.000
2.420
O
S
Ts
2.12
2.19
2.17
1.06
2.20
1.95
3.00
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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144.282
135.317
135.016
132.904
132.854
131.997
130.111
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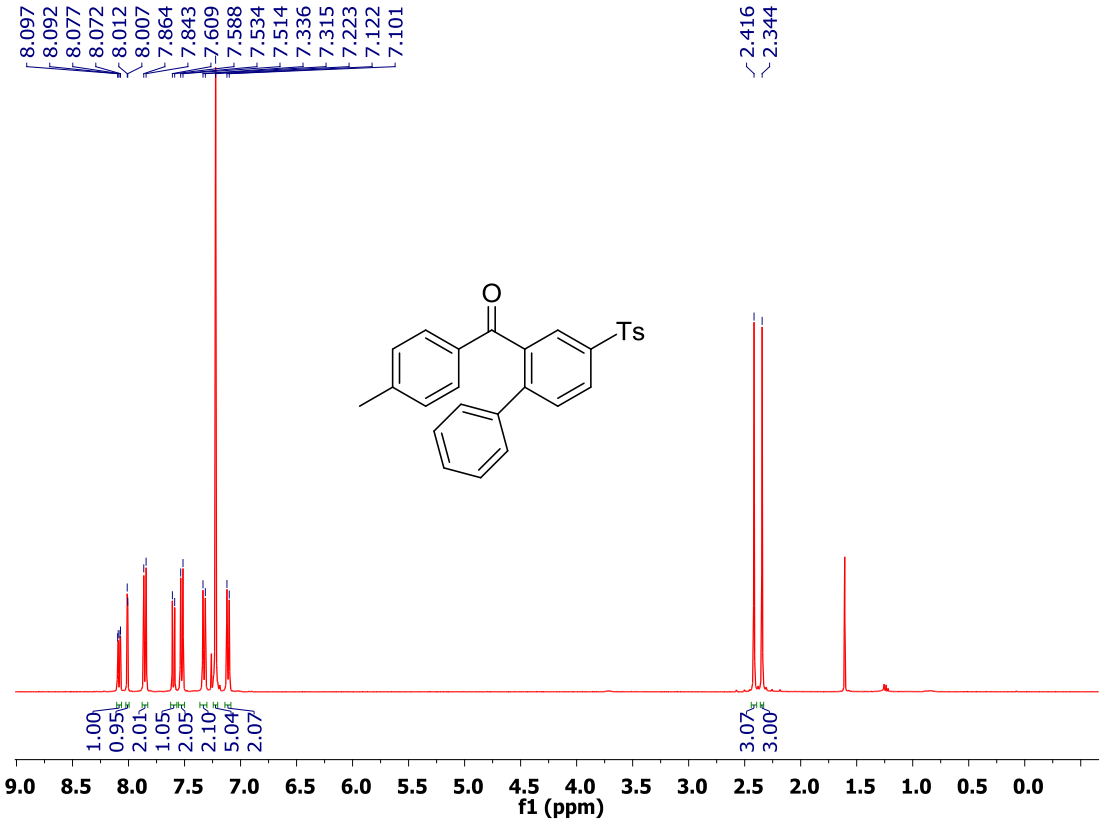
128.468
59.524
21.754
O
S
Ts
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.077
8.072
8.012
8.007
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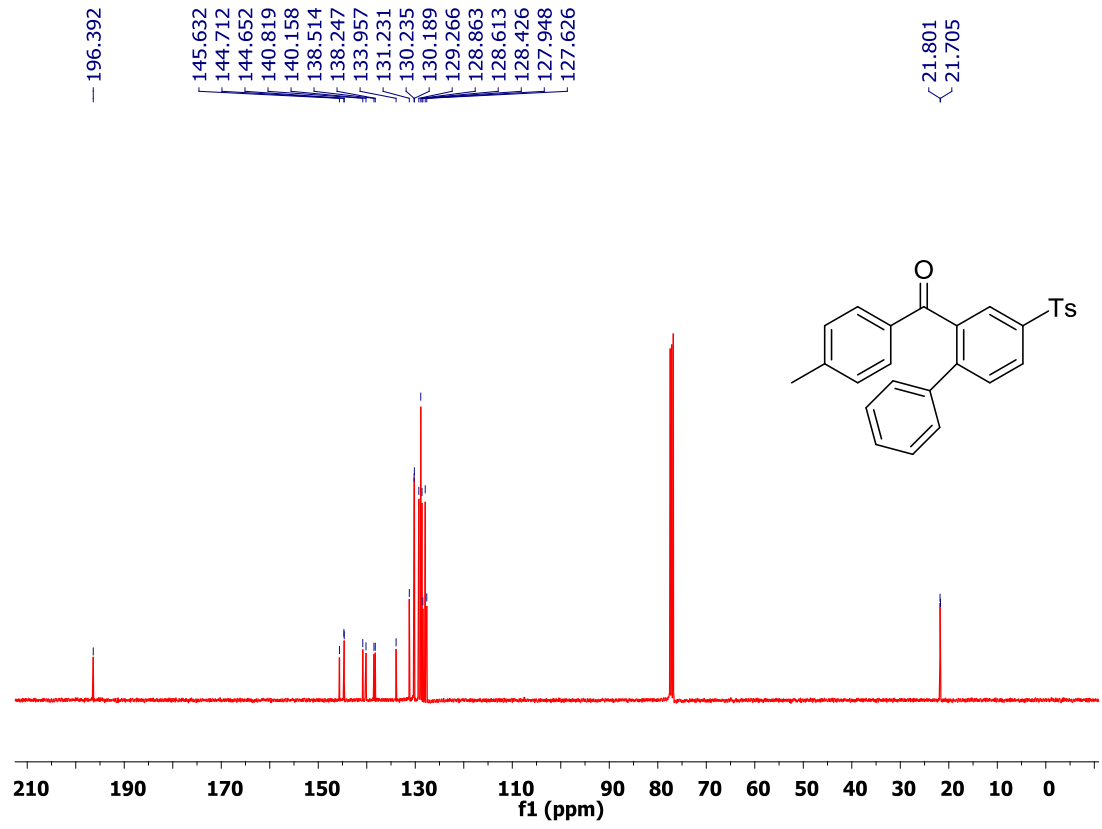
7.843
7.609
7.588
7.534
7.514
7.336
7.315
7.223
7.122
7.101
2.416
2.344
O
Ts
1.00
0.95
2.01
1.05
2.05
2.10
5.04
2.07
3.07
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.158
138.514
138.247
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131.231
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130.189
129.266
128.863
128.613
128.426
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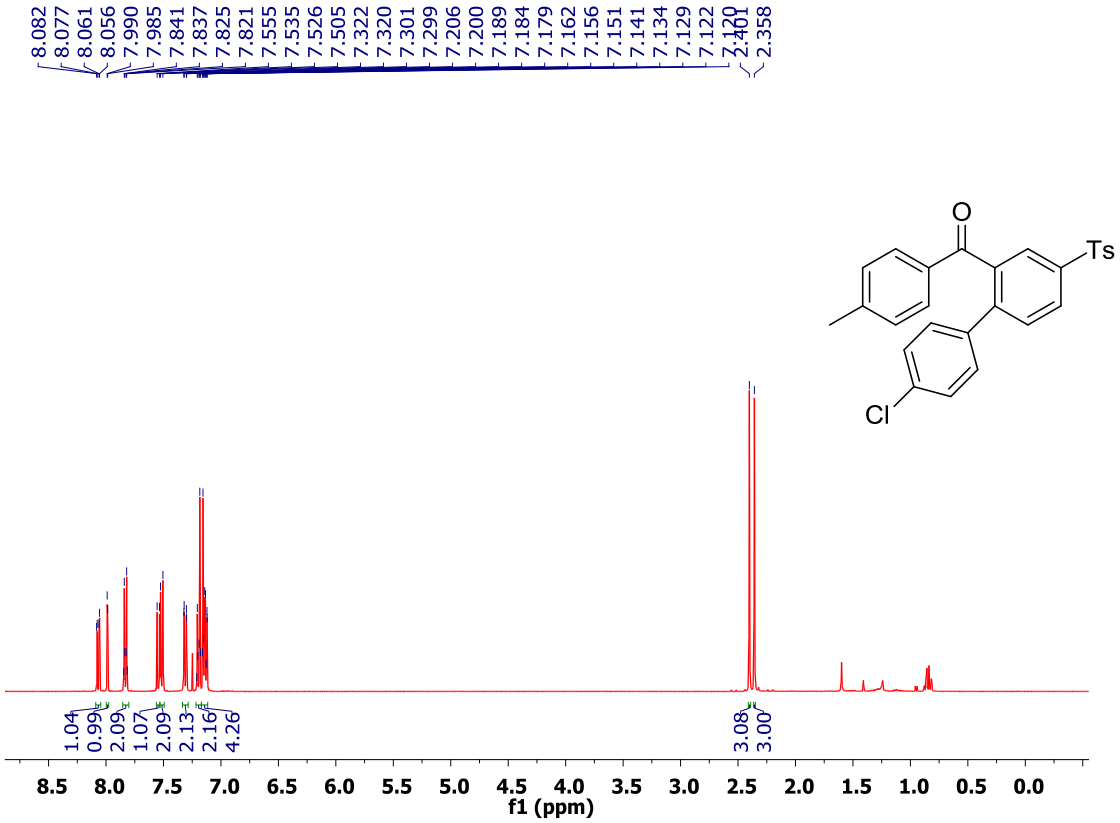
127.626
21.801
21.705
O
Ts
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.061
8.056
7.990
7.985
7.841
7.837
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7.821
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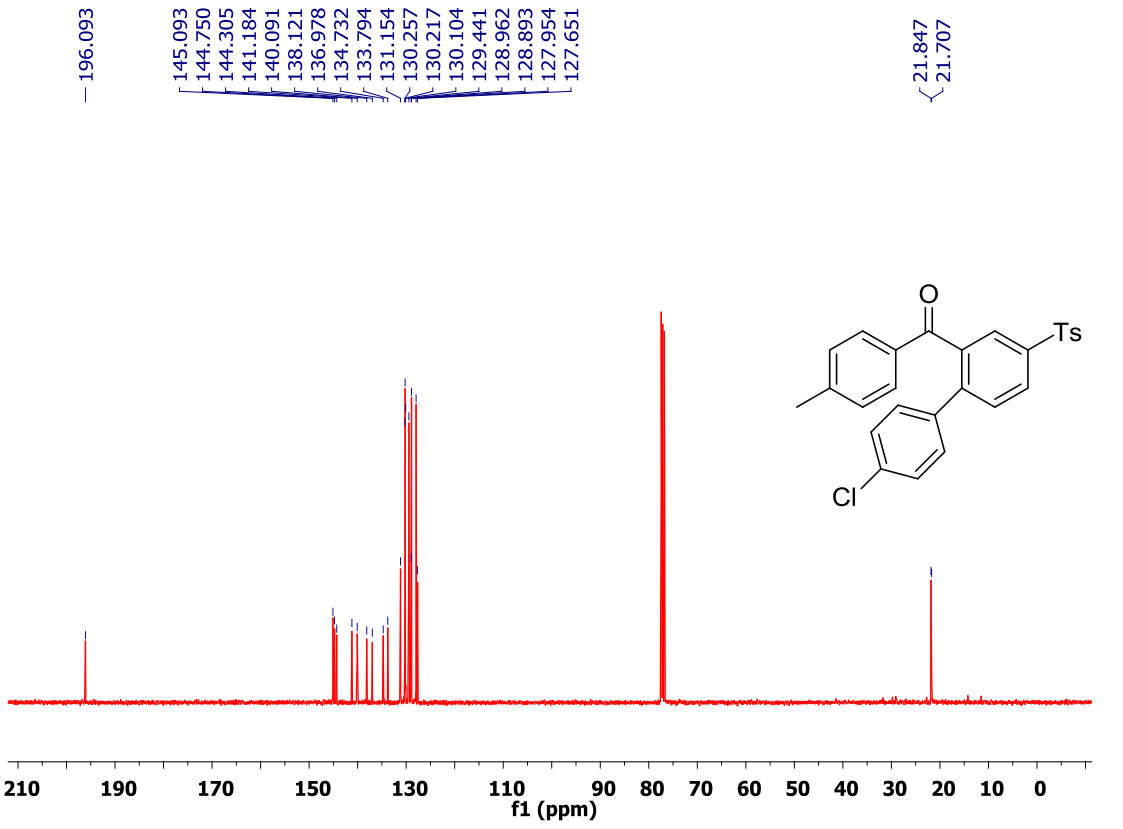
7.526
7.505
7.322
7.320
7.301
7.299
7.206
7.200
7.189
7.184
7.179
7.162
7.156
7.151
7.141
7.134
7.129
7.122
7.120
2.401
2.358
O
Ts
Cl
1.04
0.99
2.09
1.07
2.09
2.13
2.16
4.26
3.08
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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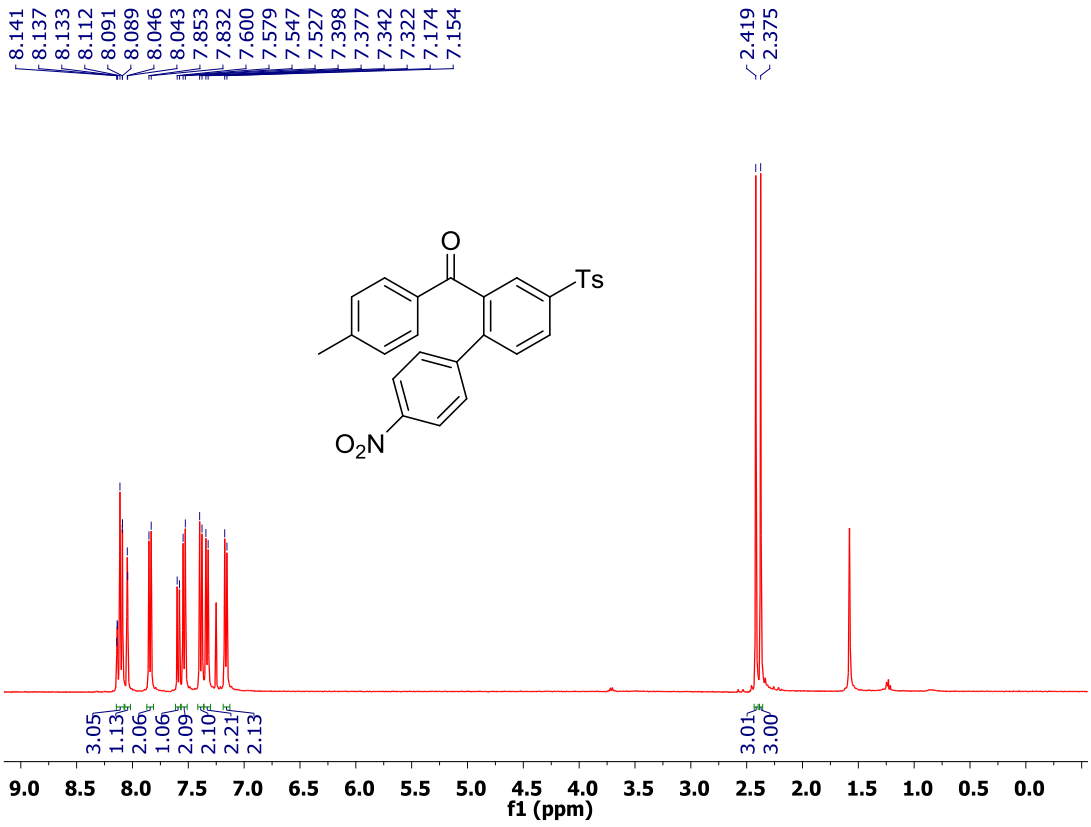
145.093
144.750
144.305
141.184
140.091
138.121
136.978
134.732
133.794
131.154
130.257
130.217
130.104
129.441
128.962
128.893
127.954
127.651
21.847
21.707
O
Ts
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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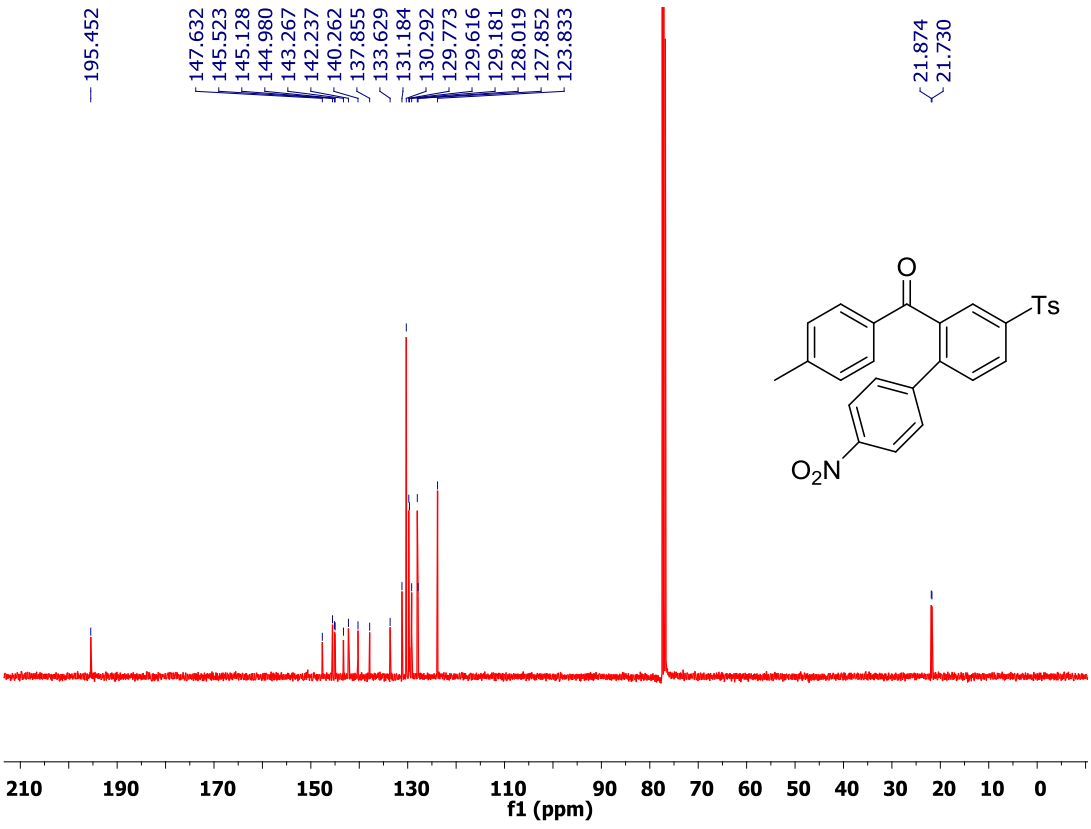
8.137
8.133
8.112
8.091
8.089
8.046
8.043
7.853
7.832
7.600
7.579
7.547
7.527
7.398
7.377
7.342
7.322
7.174
7.154
2.419
2.375
O
Ts
O2N
3.05
1.13
2.06
1.06
2.09
2.10
2.21
2.13
3.01
3.00
f1 (ppm)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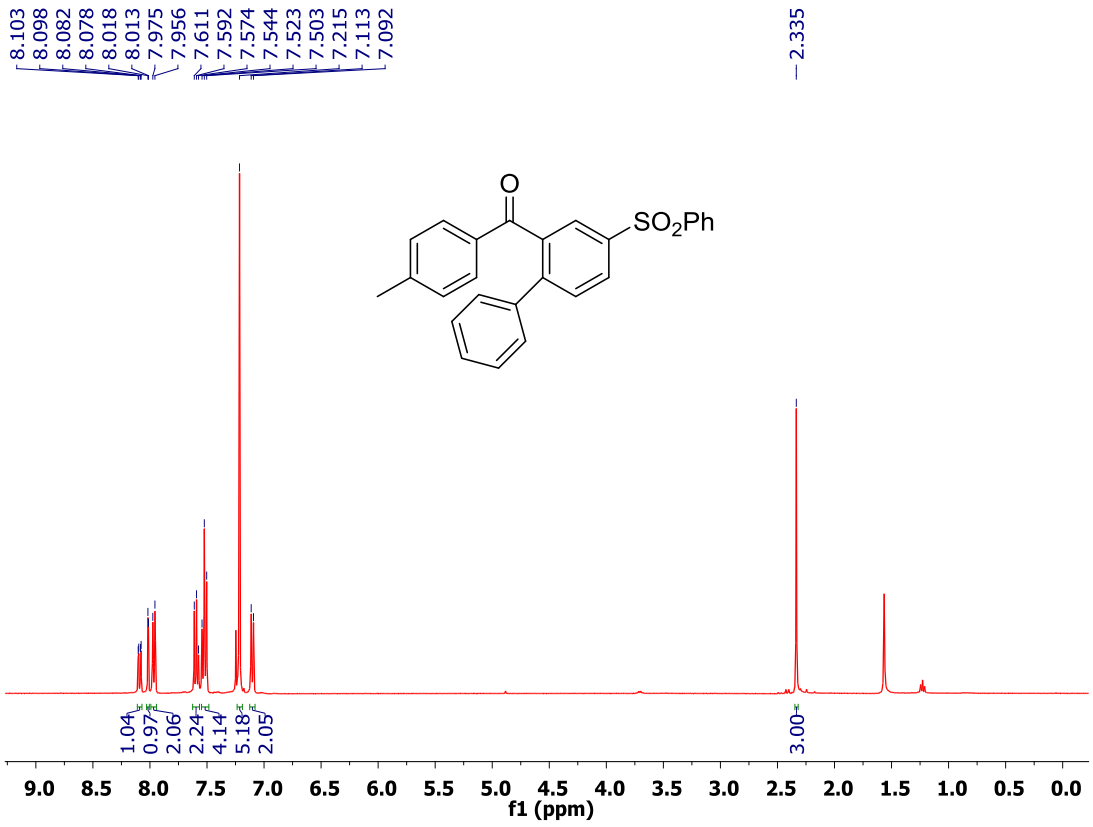
147.632
145.523
145.128
144.980
143.267
142.237
140.262
137.855
133.629
131.184
130.292
129.773
129.616
129.181
128.019
127.852
123.833
21.874
21.730
O
Ts
O2N
f1 (ppm)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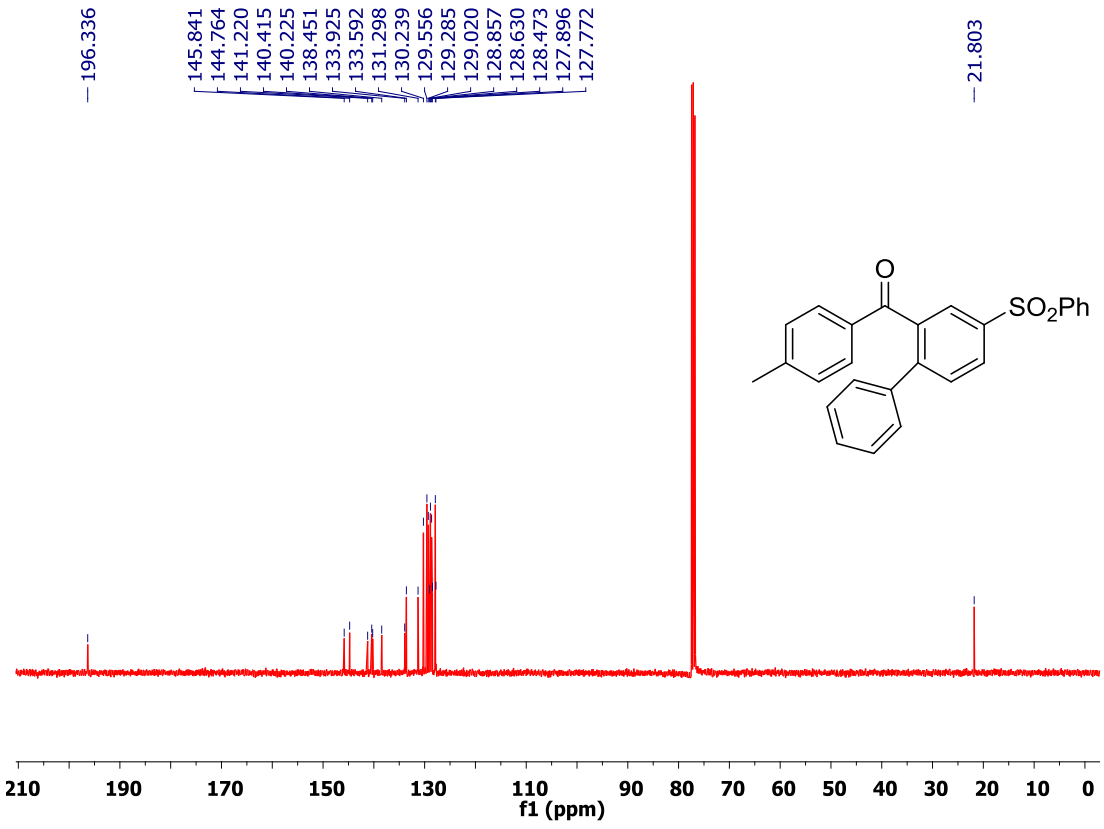
8.098
8.082
8.078
8.018
8.013
7.975
7.956
7.611
7.592
7.574
7.544
7.523
7.503
7.215
7.113
7.092
2.335
O
SO2Ph
1.04
0.97
2.06
2.24
4.14
5.18
2.05
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.225
138.451
133.925
133.592
131.298
130.239
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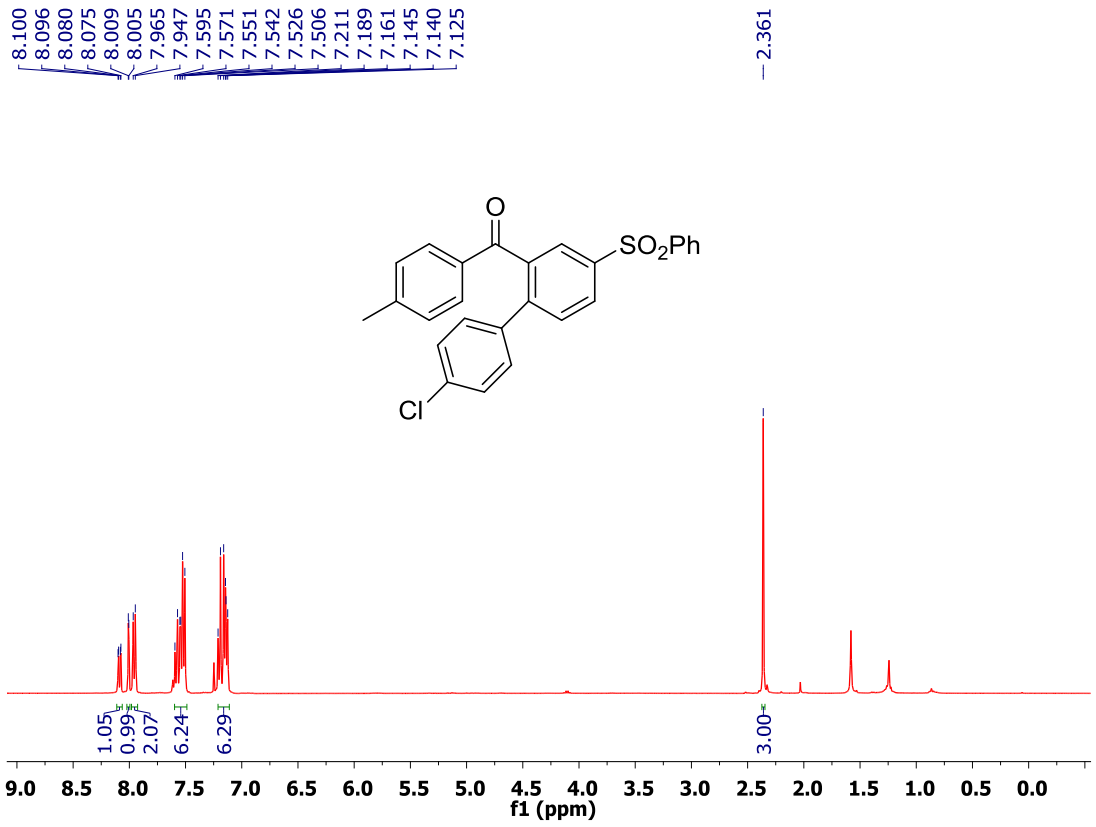
129.285
129.020
128.857
128.630
128.473
127.896
127.772
21.803
O
SO2Ph
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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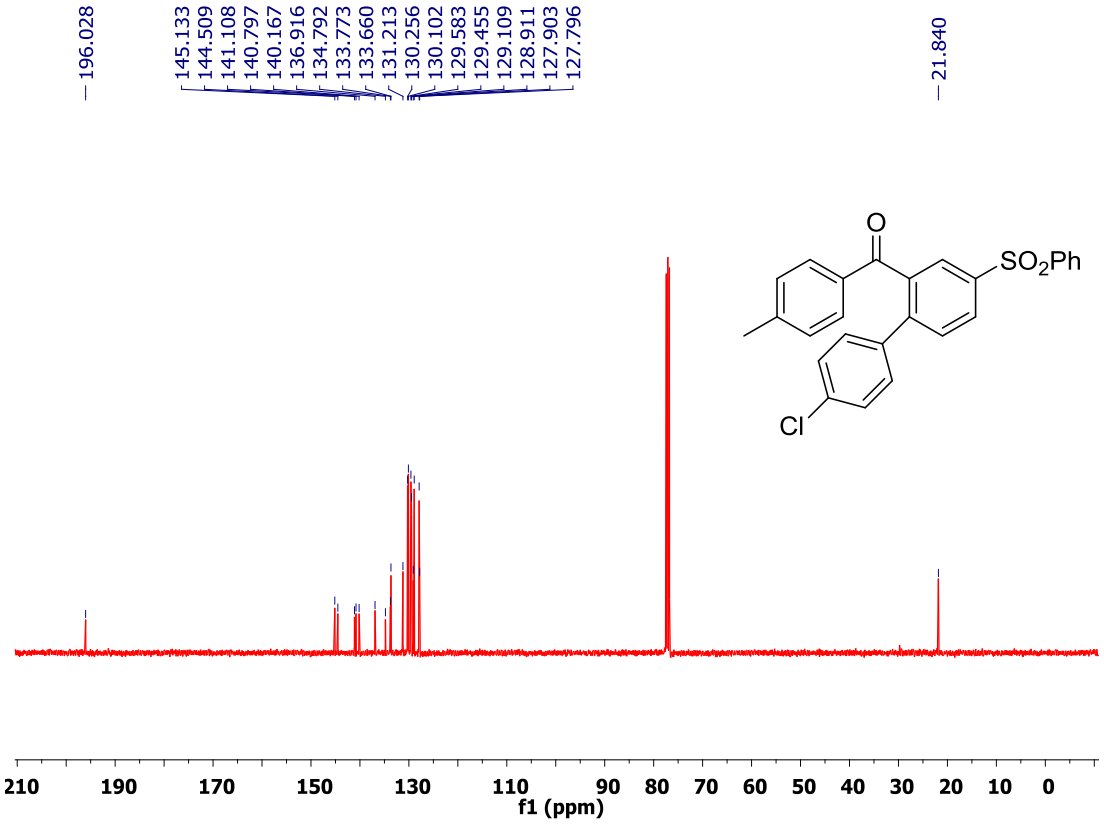
8.096
8.080
8.075
8.009
8.005
7.965
7.947
7.595
7.571
7.551
7.542
7.526
7.506
7.211
7.189
7.161
7.145
7.140
7.125
2.361
O
SO2Ph
Cl
1.05
0.99
2.07
6.24
6.29
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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144.509
141.108
140.797
140.167
136.916
134.792
133.773
133.660
131.213
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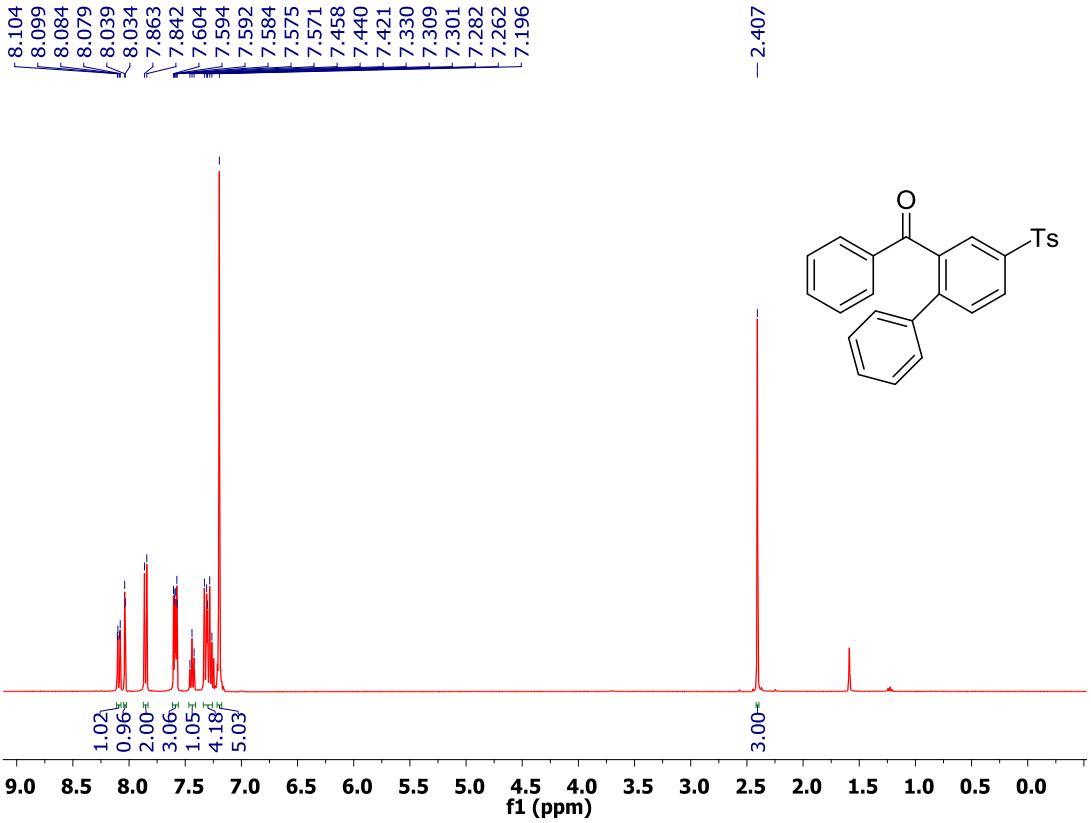
130.102
129.583
129.455
129.109
128.911
127.903
127.796
21.840
O
SO2Ph
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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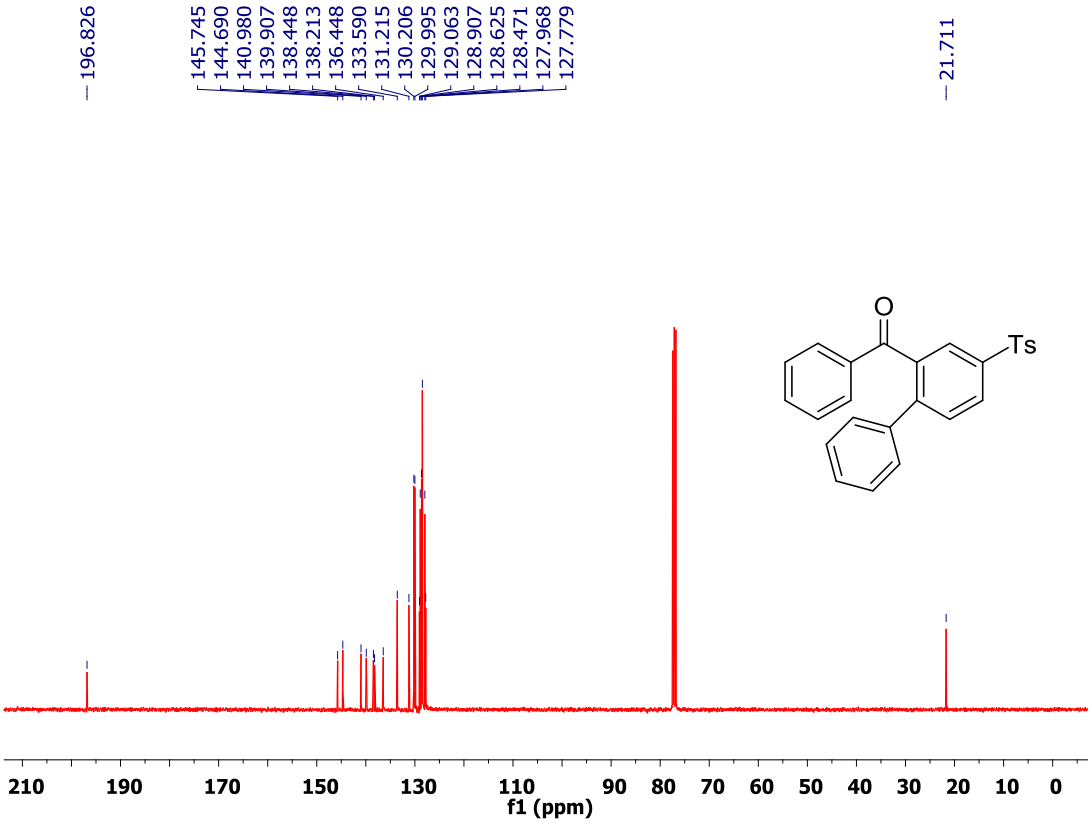
8.099
8.084
8.079
8.039
8.034
7.863
7.842
7.604
7.594
7.592
7.584
7.575
7.571
7.458
7.440
7.421
7.330
7.309
7.301
7.282
7.262
7.196
2.407
O
Ts
1.02
0.96
2.00
3.06
1.05
4.18
5.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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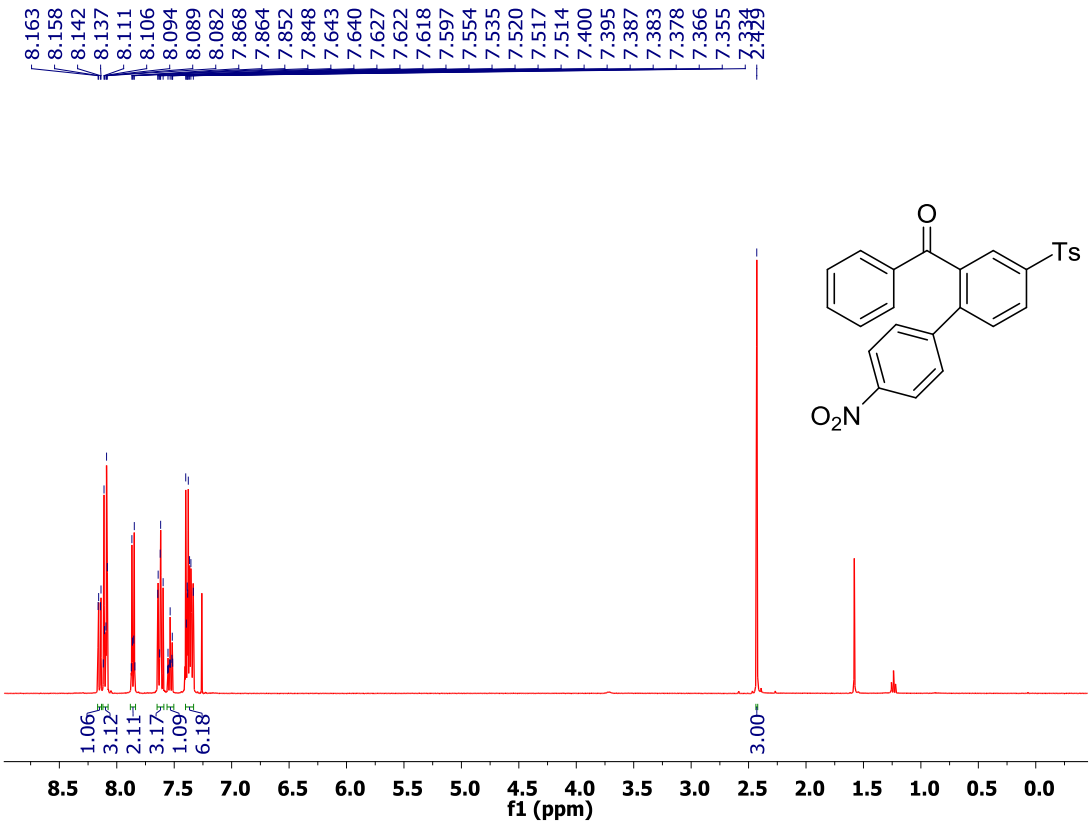
144.690
140.980
139.907
138.448
138.213
136.448
133.590
131.215
130.206
129.995
129.063
128.907
128.625
128.471
127.968
127.779
21.711
O
Ts
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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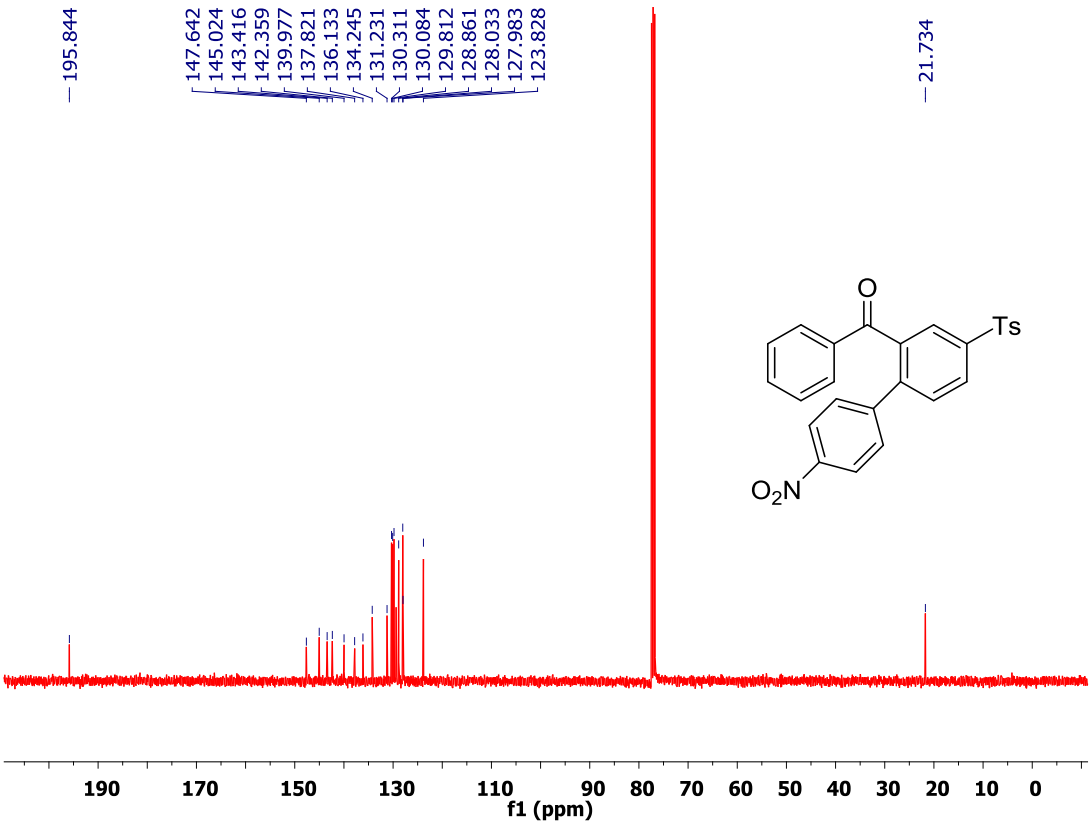
8.158
8.142
8.137
8.111
8.106
8.094
8.089
8.082
7.868
7.864
7.852
7.848
7.643
7.640
7.627
7.622
7.618
7.597
7.554
7.535
7.520
7.517
7.514
7.400
7.395
7.387
7.383
7.378
7.366
7.355
2.429
O
Ts
O2N
1.06
3.12
2.11
3.17
1.09
6.18
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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142.359
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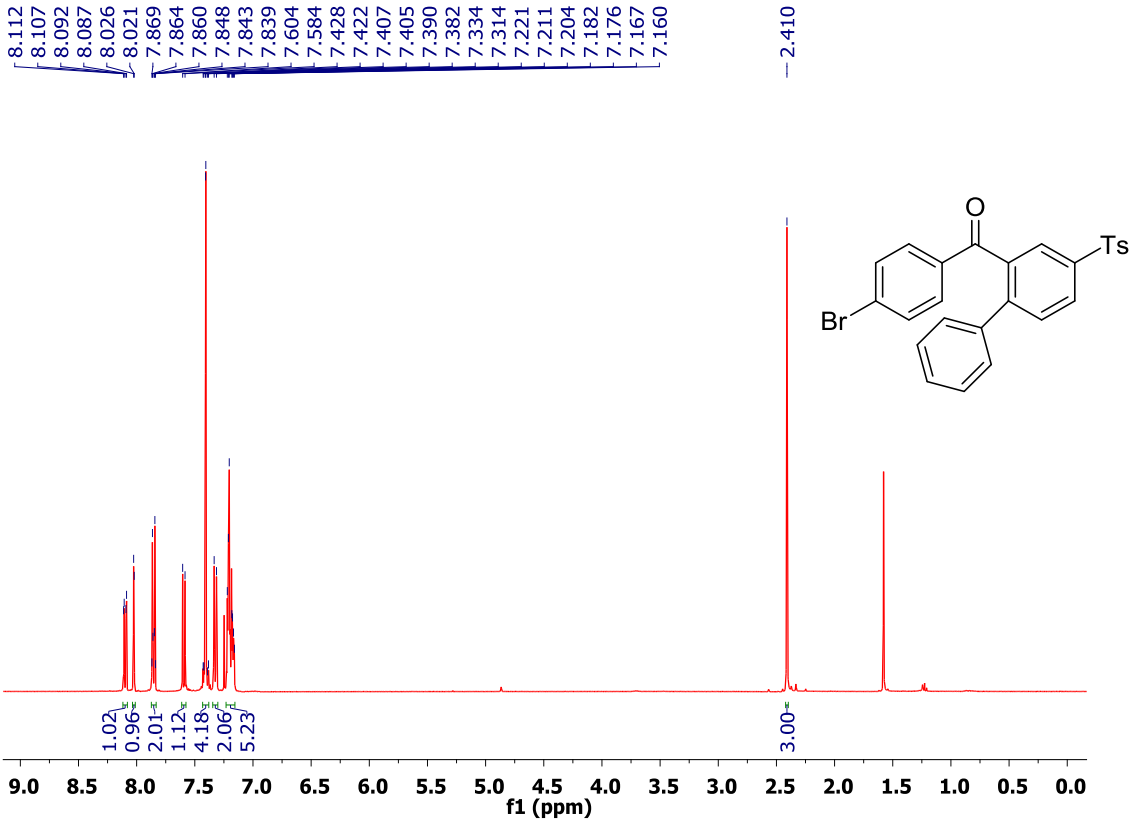
136.133
134.245
131.231
130.311
130.084
129.812
128.861
128.033
127.983
123.828
21.734
O
Ts
O2N
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.864
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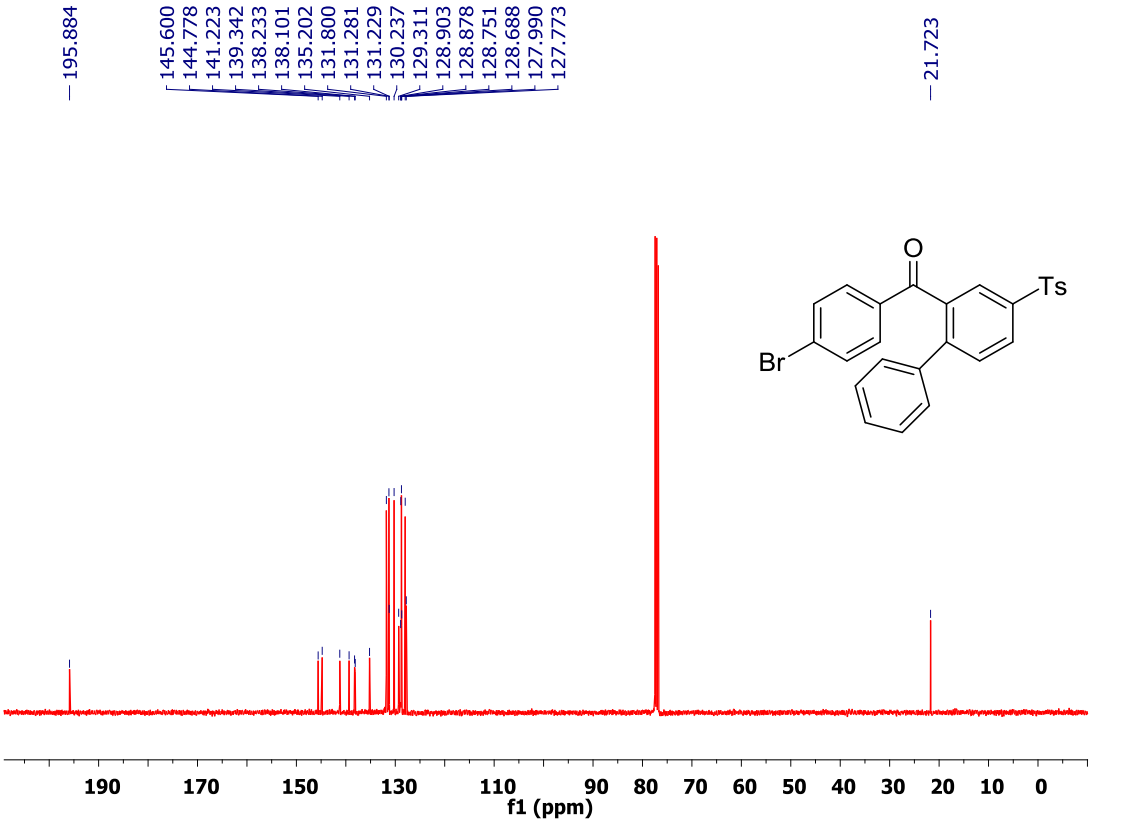
7.839
7.604
7.584
7.428
7.422
7.407
7.405
7.390
7.382
7.334
7.314
7.221
7.211
7.204
7.182
7.176
7.167
7.160
2.410
O
Ts
Br
1.02
0.96
2.01
1.12
4.18
2.06
5.23
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.101
135.202
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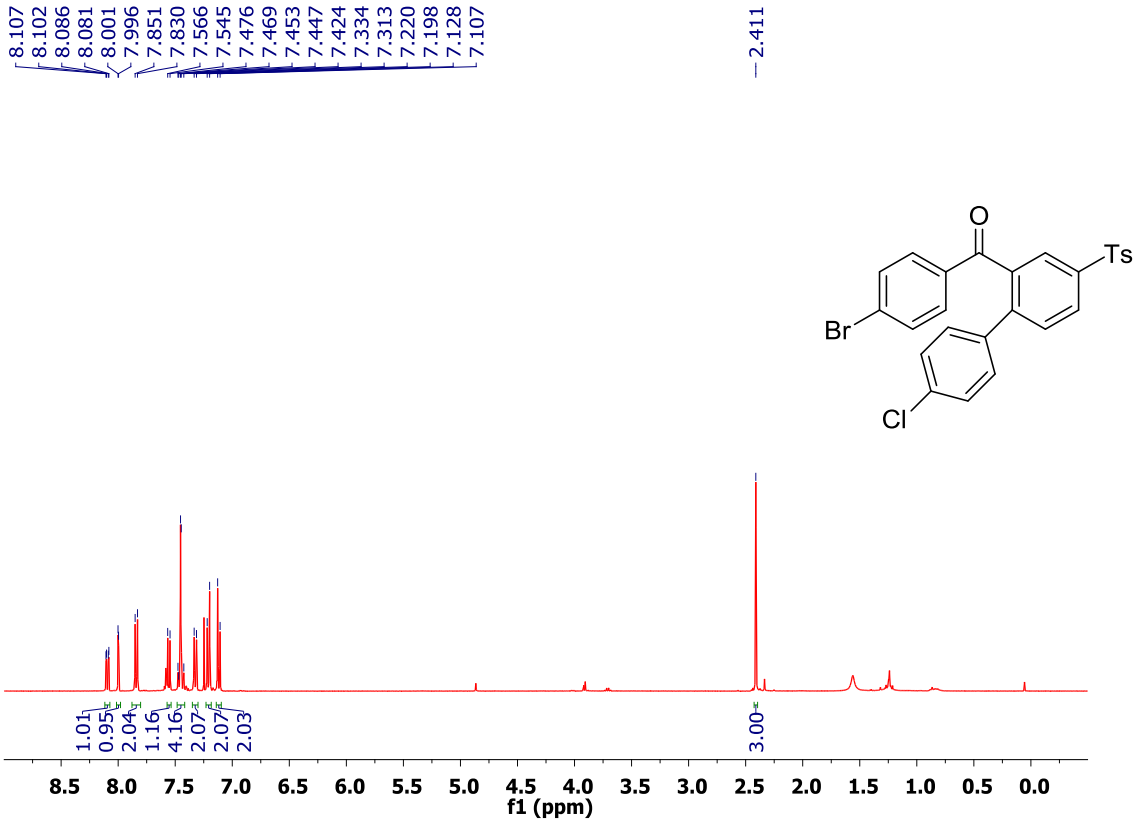
131.281
131.229
130.237
129.311
128.903
128.878
128.751
128.688
127.990
127.773
21.723
O
Ts
Br
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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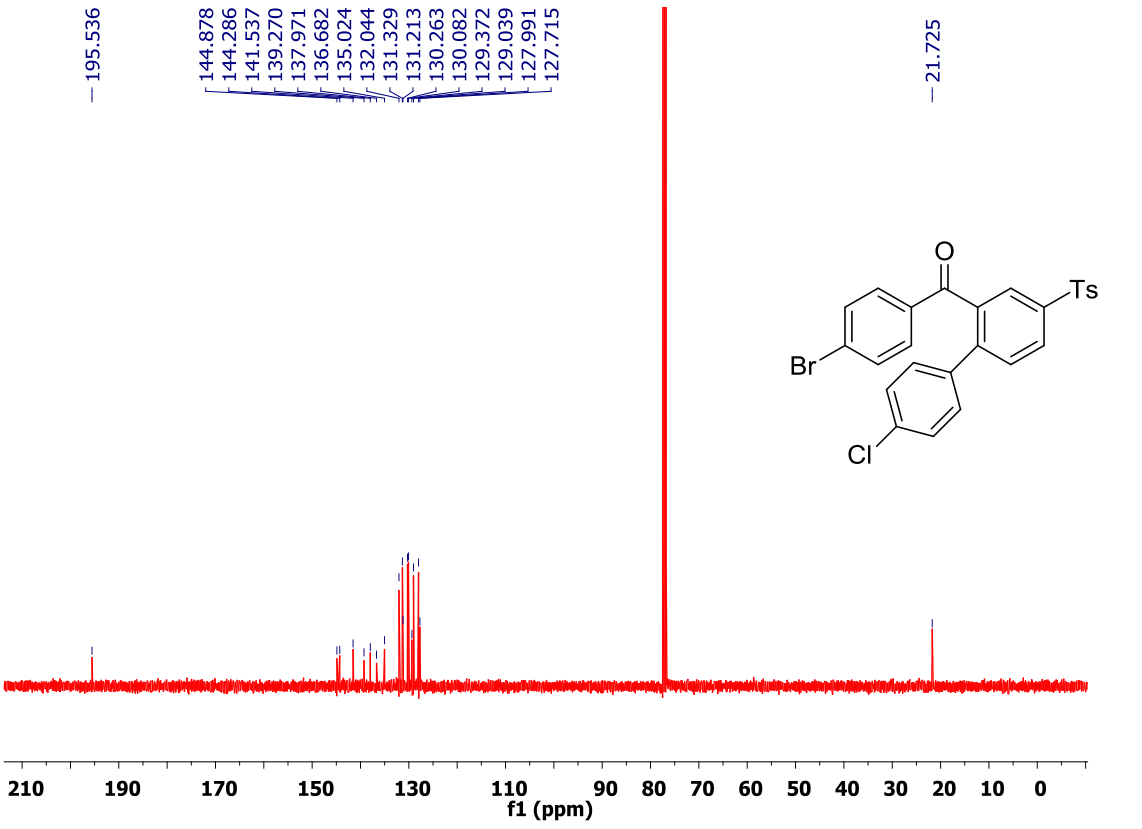
8.102
8.086
8.081
8.001
7.996
7.851
7.830
7.566
7.545
7.476
7.469
7.453
7.447
7.424
7.334
7.313
7.220
7.198
7.128
7.107
2.411
O
Ts
Br
Cl
1.01
0.95
2.04
1.16
4.16
2.07
2.07
2.03
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.537
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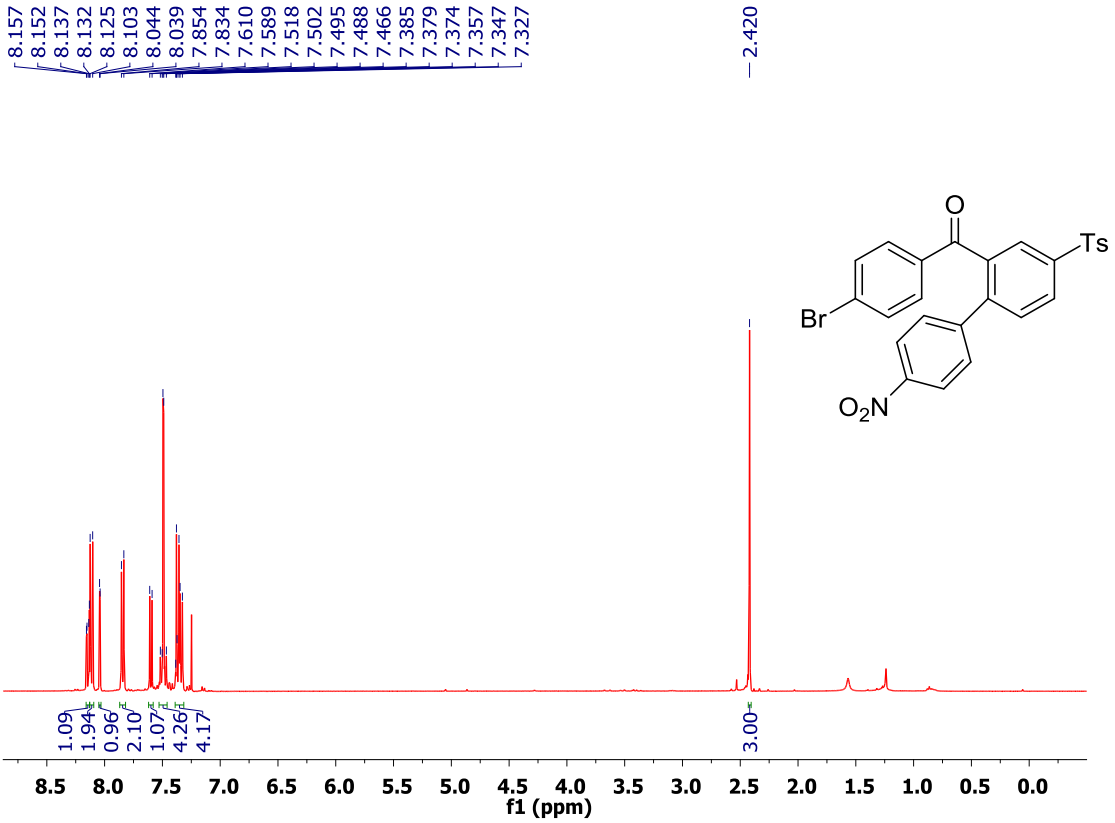
137.971
136.682
135.024
132.044
131.329
131.213
130.263
130.082
129.372
129.039
127.991
127.715
21.725
O
Ts
Br
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.044
8.039
7.854
7.834
7.610
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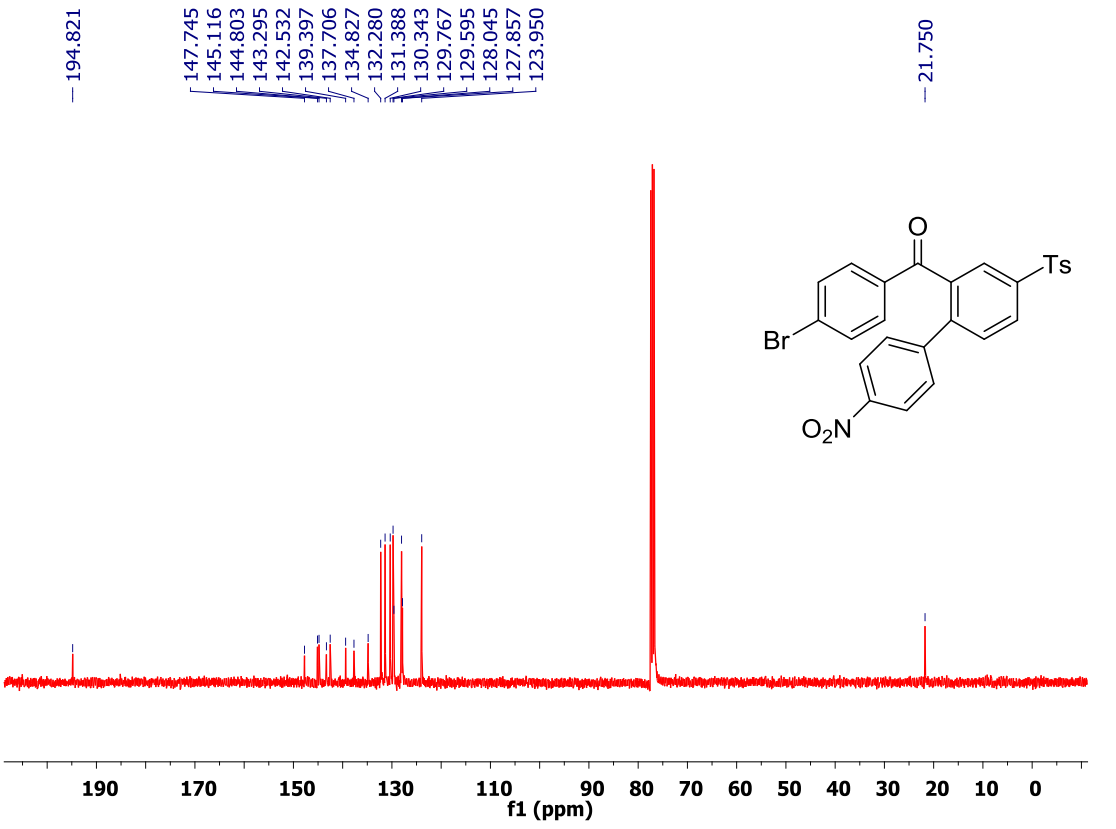
7.518
7.502
7.495
7.488
7.466
7.385
7.379
7.374
7.357
7.347
7.327
2.420
O
Ts
Br
O2N
1.09
1.94
0.96
2.10
1.07
4.26
4.17
3.00
f1 (ppm)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145.116
144.803
143.295
142.532
139.397
137.706
134.827
132.280
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130.343
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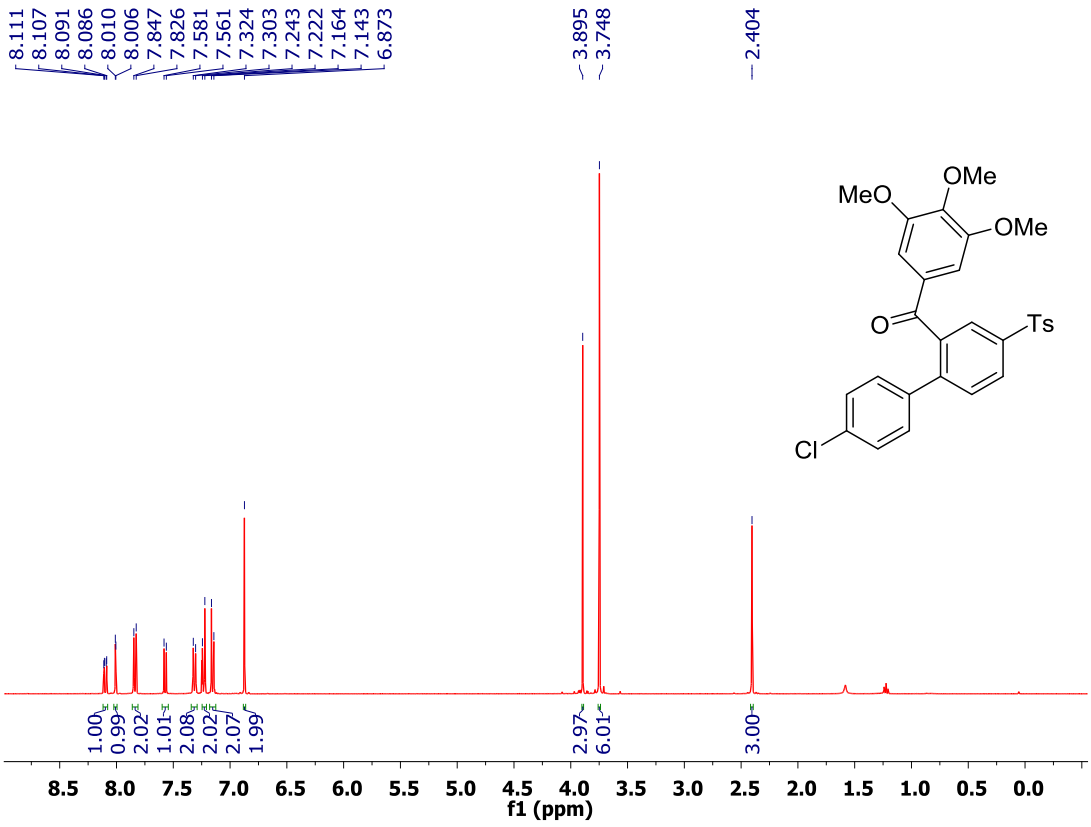
129.595
128.045
127.857
123.950
21.750
O
Ts
Br
O2N
f1 (ppm)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7.826
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7.561
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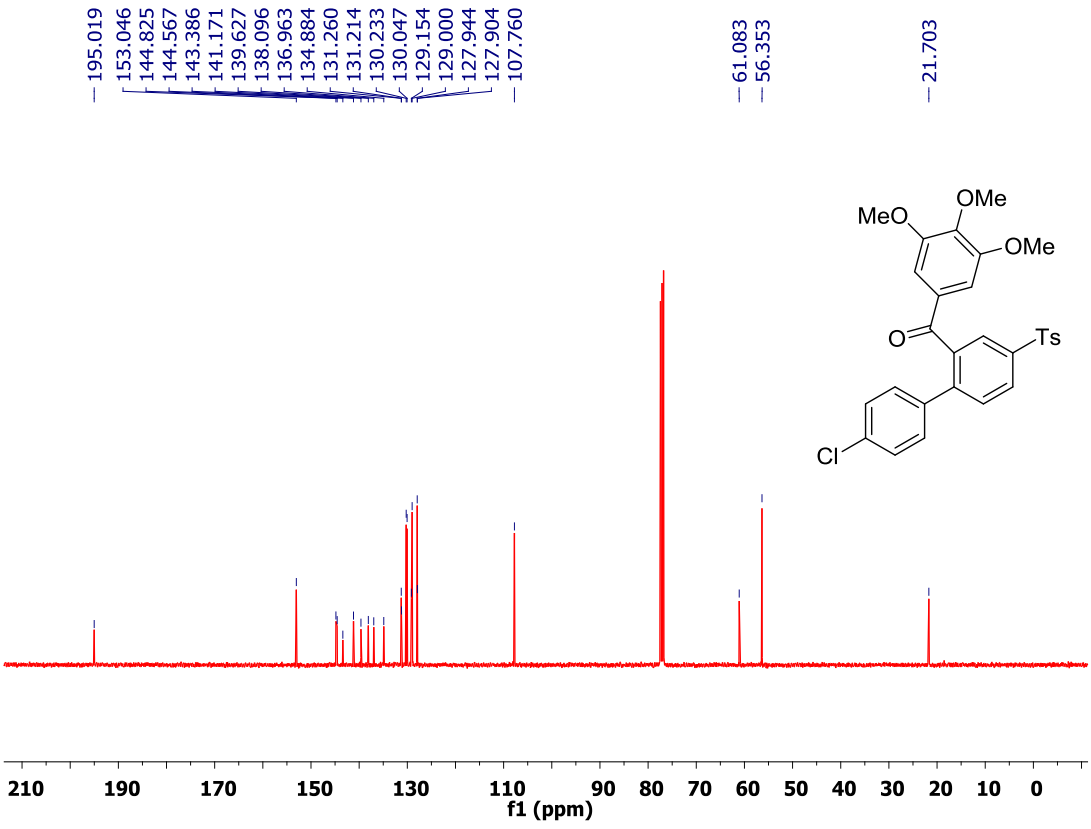
7.243
7.222
7.164
7.143
6.873
3.895
3.748
2.404
MeO
OMe
OMe
O
Ts
Cl
1.00
0.99
2.02
1.01
2.08
2.02
2.07
1.99
2.97
6.01
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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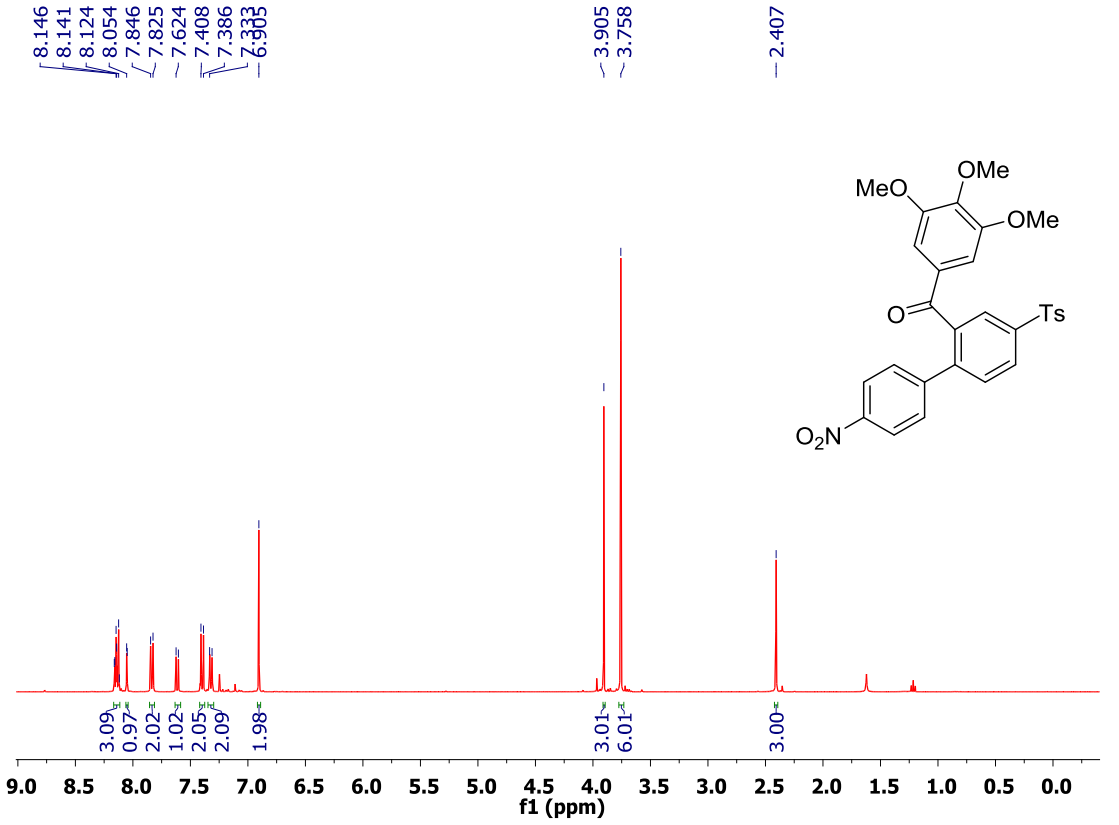
144.567
143.386
141.171
139.627
138.096
136.963
134.884
131.260
131.214
130.233
130.047
129.154
129.000
127.944
127.904
107.760
61.083
56.353
21.703
MeO
OMe
OMe
O
Ts
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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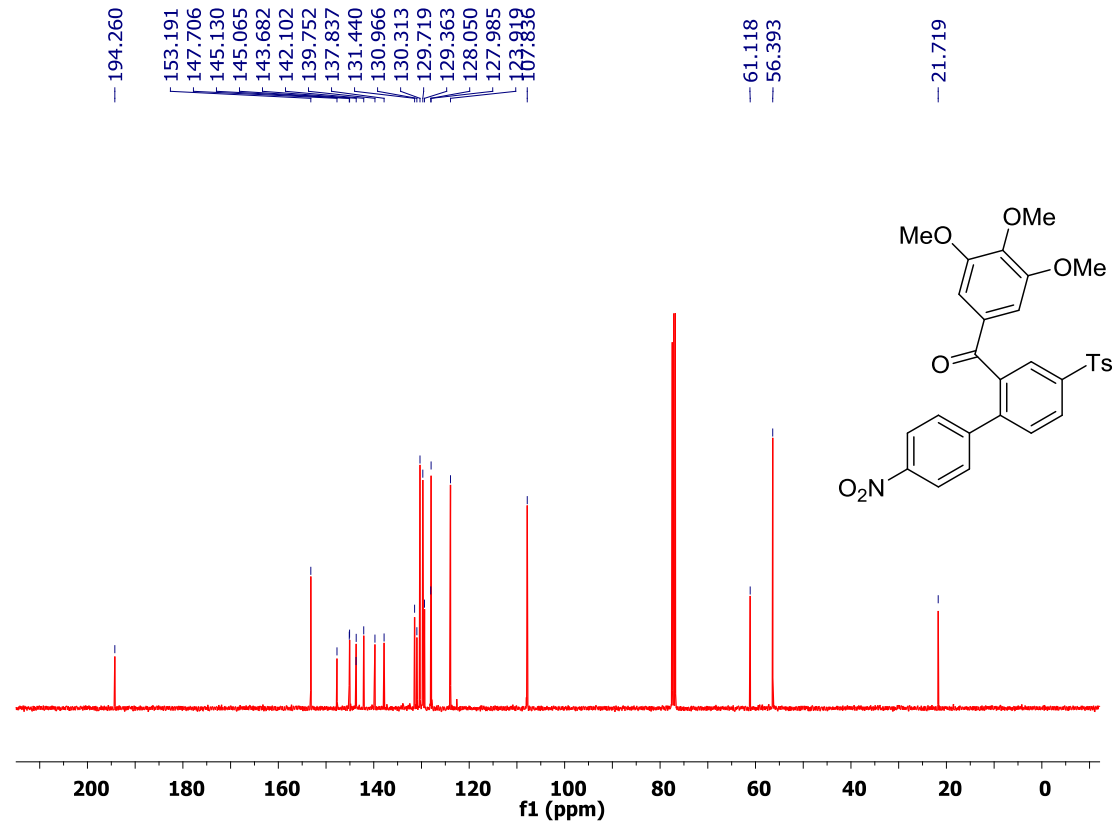
8.141
8.124
8.054
7.846
7.825
7.624
7.408
7.386
7.333
6.905
3.905
3.758
2.407
MeO
OMe
OMe
O
Ts
O2N
3.09
0.97
2.02
1.02
2.05
2.09
1.98
3.01
6.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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153.191
147.706
145.130
145.065
143.682
142.102
139.752
137.837
131.440
130.966
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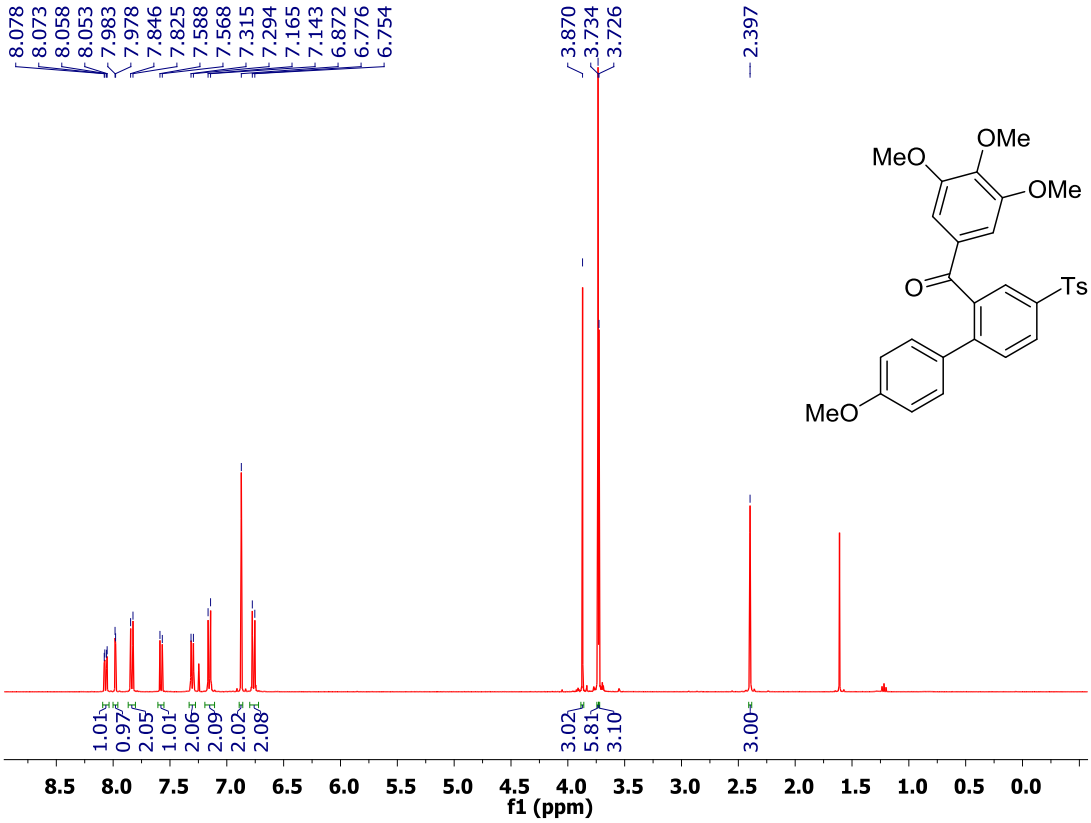
129.719
129.363
128.050
127.985
61.118
56.393
21.719
MeO
OMe
OMe
O
Ts
O2N
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)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8.053
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7.978
7.846
7.825
7.588
7.568
7.315
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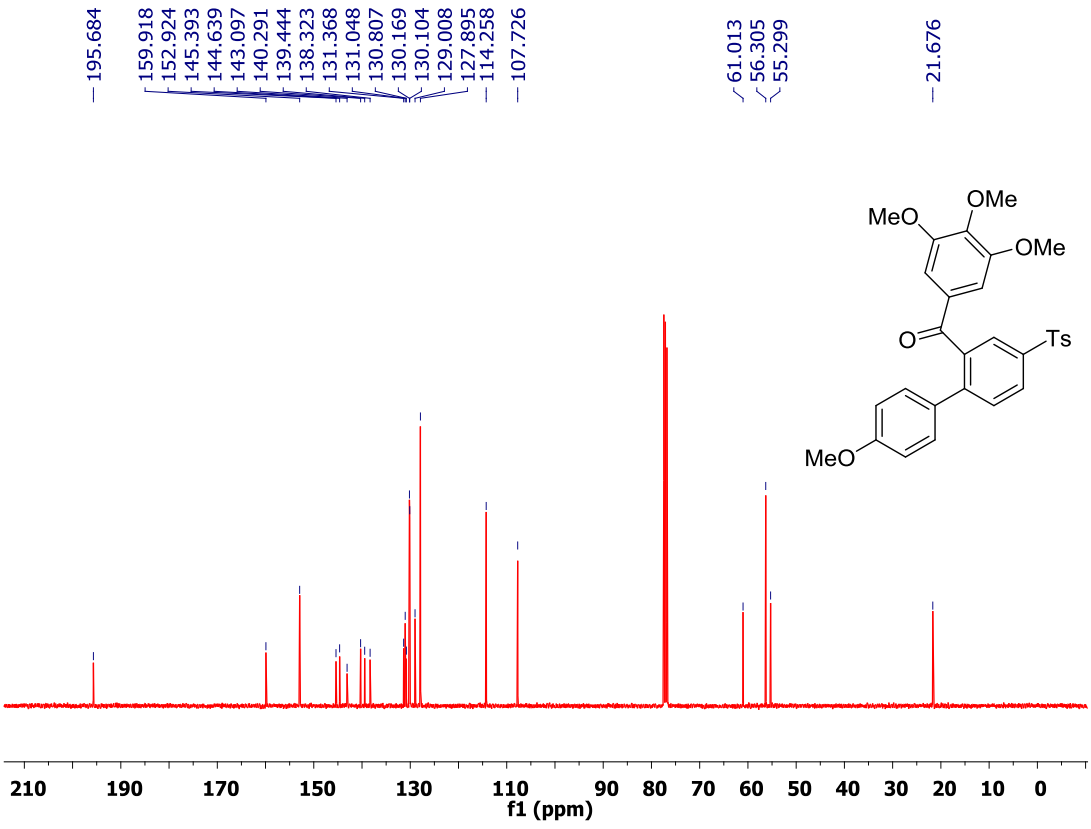
7.165
7.143
6.872
6.776
6.754
3.870
3.734
3.726
2.397
MeO
OMe
OMe
O
Ts
MeO
1.01
0.97
2.05
1.01
2.06
2.09
2.02
2.08
3.02
5.81
3.10
3.00
f1 (ppm)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140.291
139.444
138.323
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131.048
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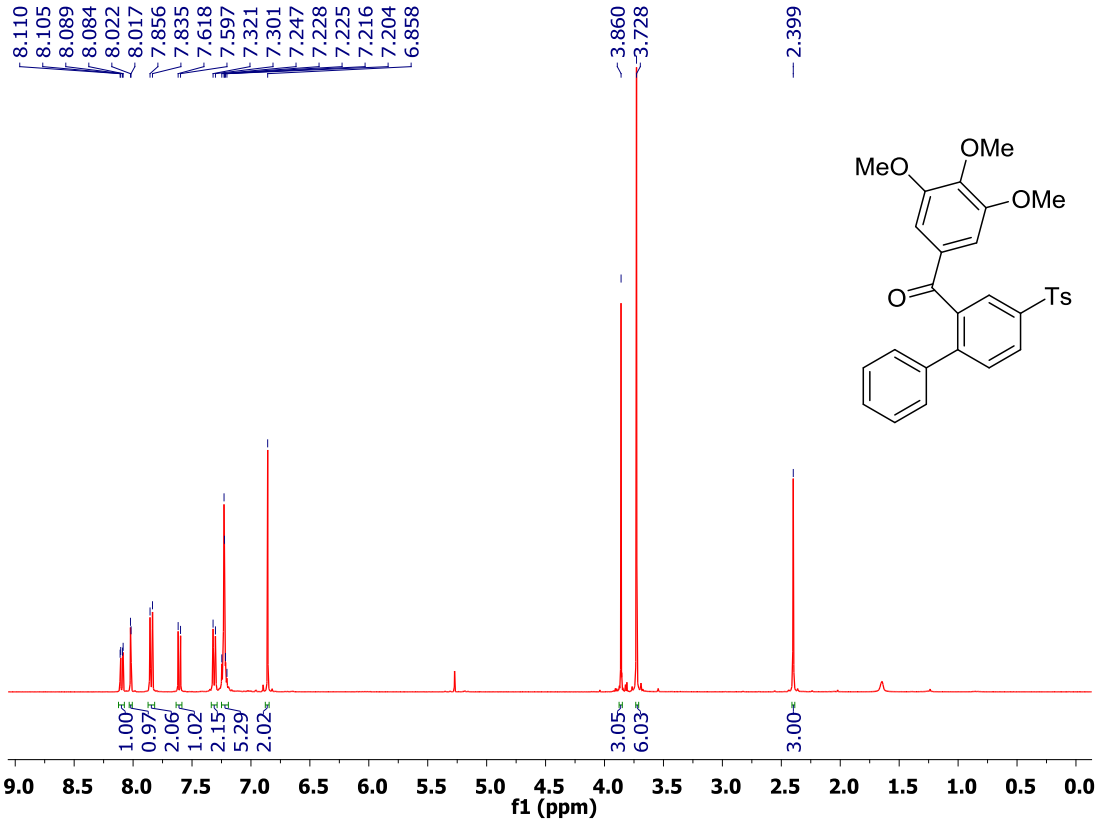
130.104
129.008
127.895
114.258
107.726
61.013
56.305
55.299
21.676
MeO
OMe
OMe
O
Ts
MeO
f1 (ppm)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8.022
8.017
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7.618
7.597
7.321
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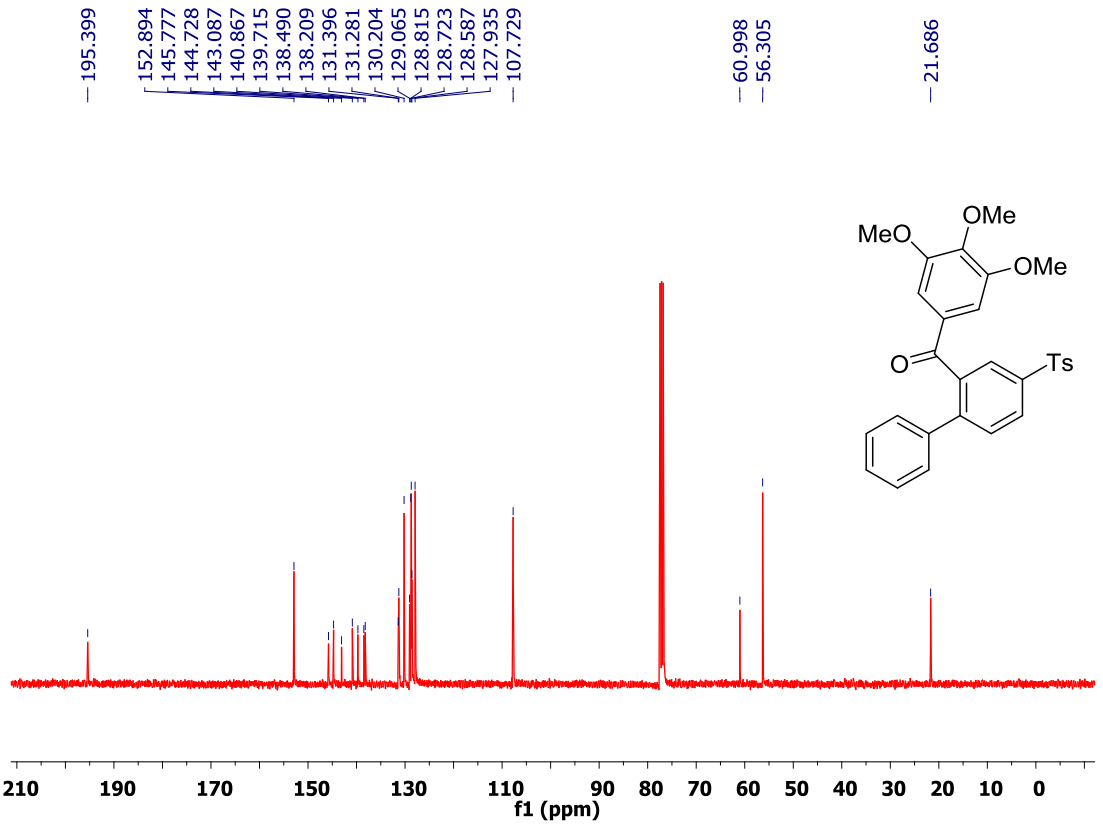
7.228
7.225
7.216
7.204
6.858
3.860
3.728
2.399
MeO
OMe
OMe
O
Ts
1.00
0.97
2.06
1.02
2.15
5.29
2.02
3.05
6.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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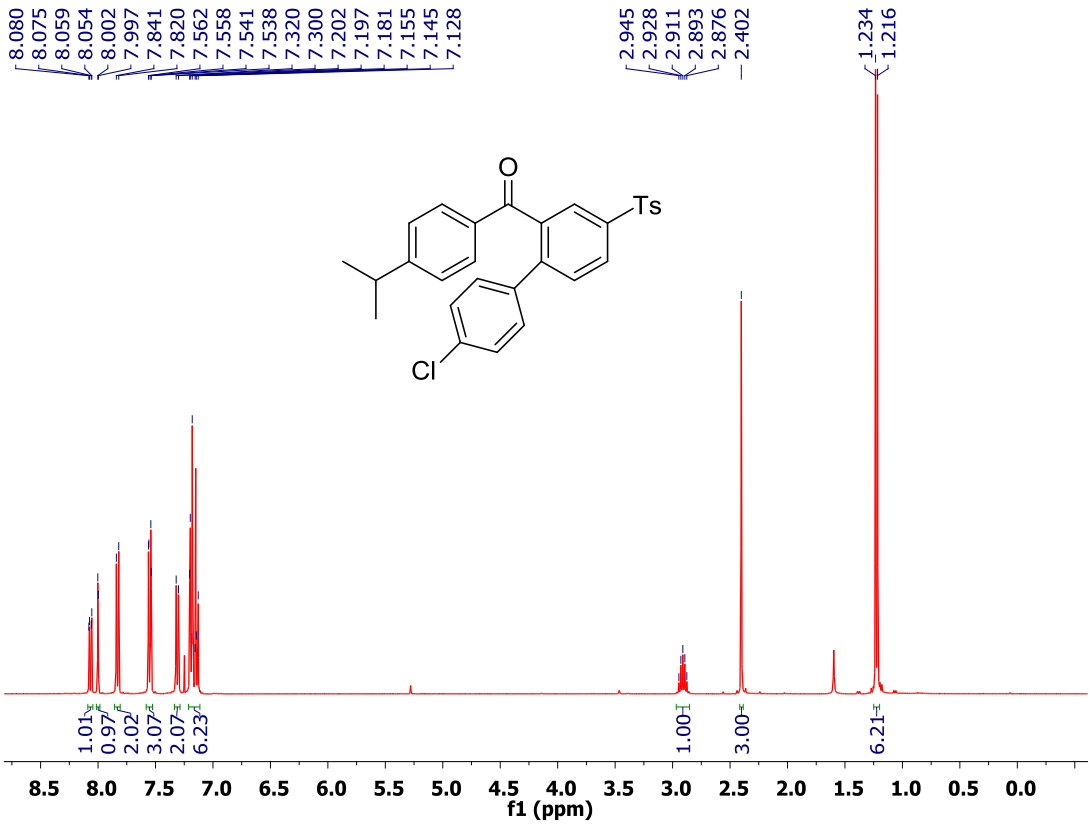
140.867
139.715
138.490
138.209
131.396
131.281
130.204
129.065
128.815
128.723
128.587
127.935
107.729
60.998
56.305
21.686
MeO
OMe
OMe
O
Ts
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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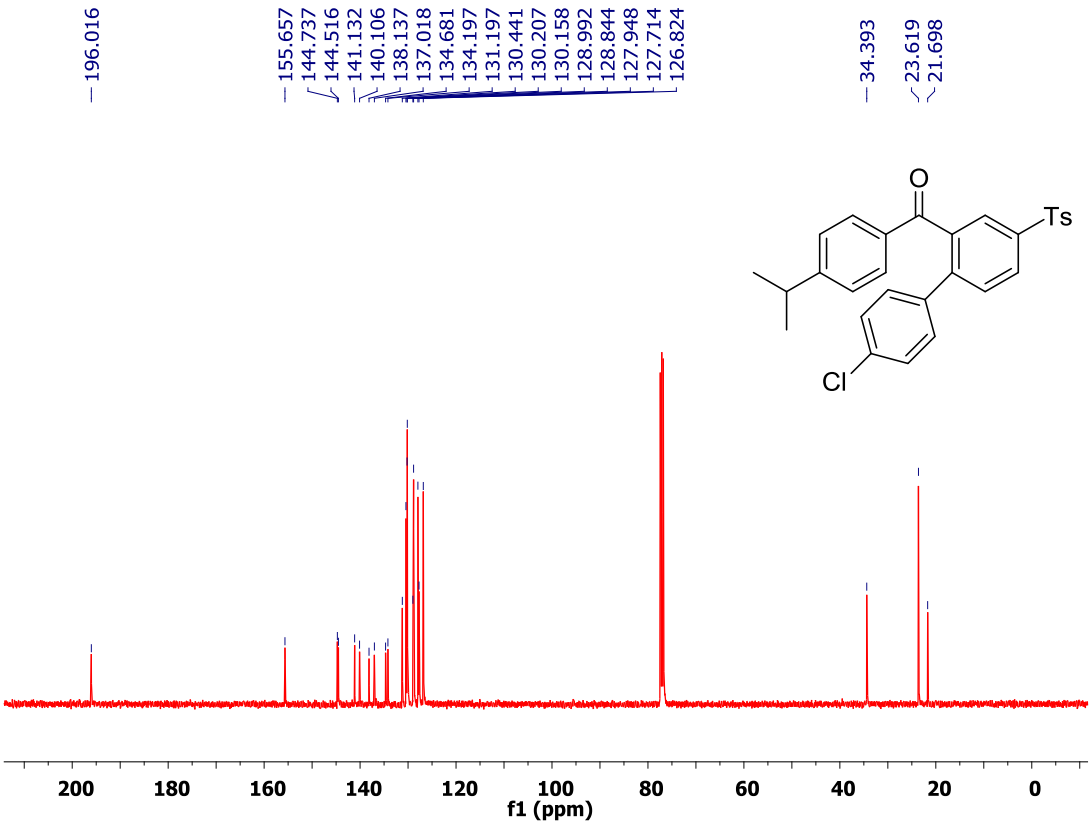
7.541
7.538
7.320
7.300
7.202
7.197
7.181
7.155
7.145
7.128
2.945
2.928
2.911
2.893
2.876
2.402
1.234
1.216
O
Ts
Cl
1.01
0.97
2.02
3.07
2.07
6.23
1.00
3.00
6.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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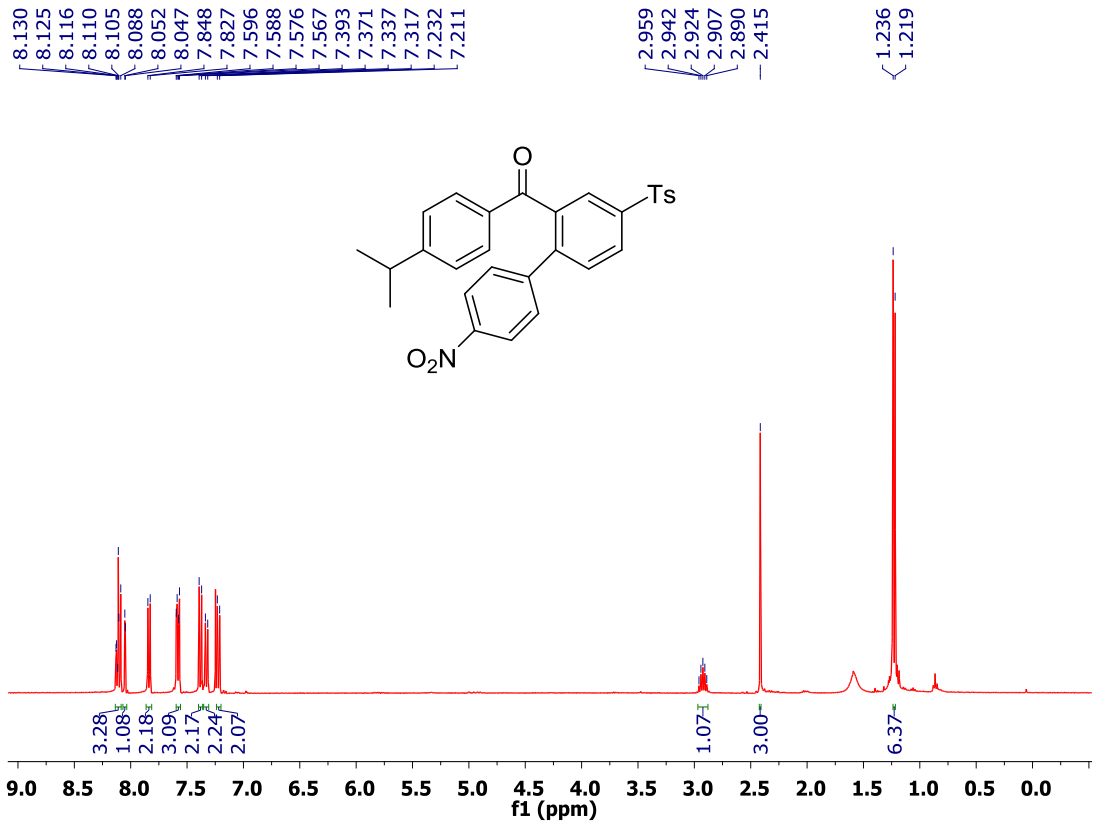
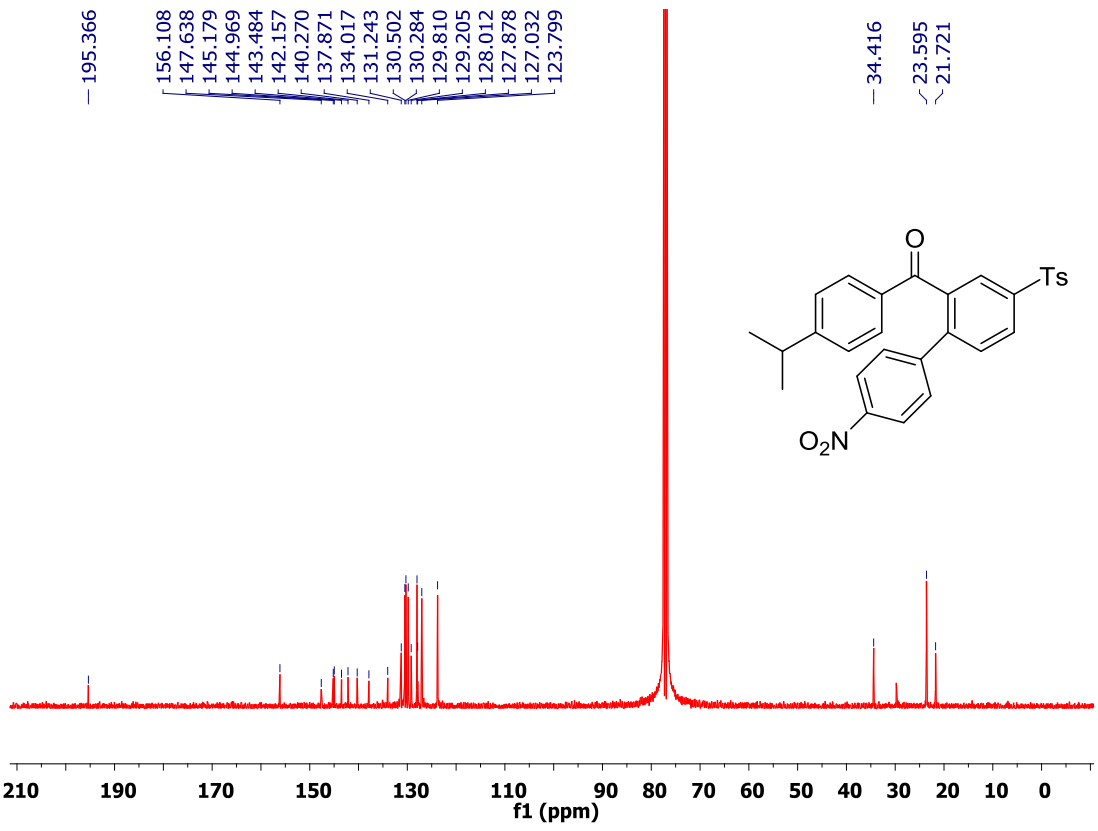
155.657
144.737
144.516
141.132
140.106
138.137
137.018
134.681
134.197
131.197
130.441
130.207
130.158
128.992
128.844
127.948
127.714
126.824
34.393
23.619
21.698
O
Ts
Cl
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


8.130
8.125
8.116
8.110
8.105
8.088
8.052
8.047
7.848
7.827
7.596
7.588
7.576
7.567
7.393
7.371
7.337
7.317
7.232
7.211
2.959
2.942
2.924
2.907
2.890
2.415
1.236
1.219
O
Ts
O2N
3.28
1.08
2.18
3.09
2.17
2.24
2.07
1.07
3.00
6.37
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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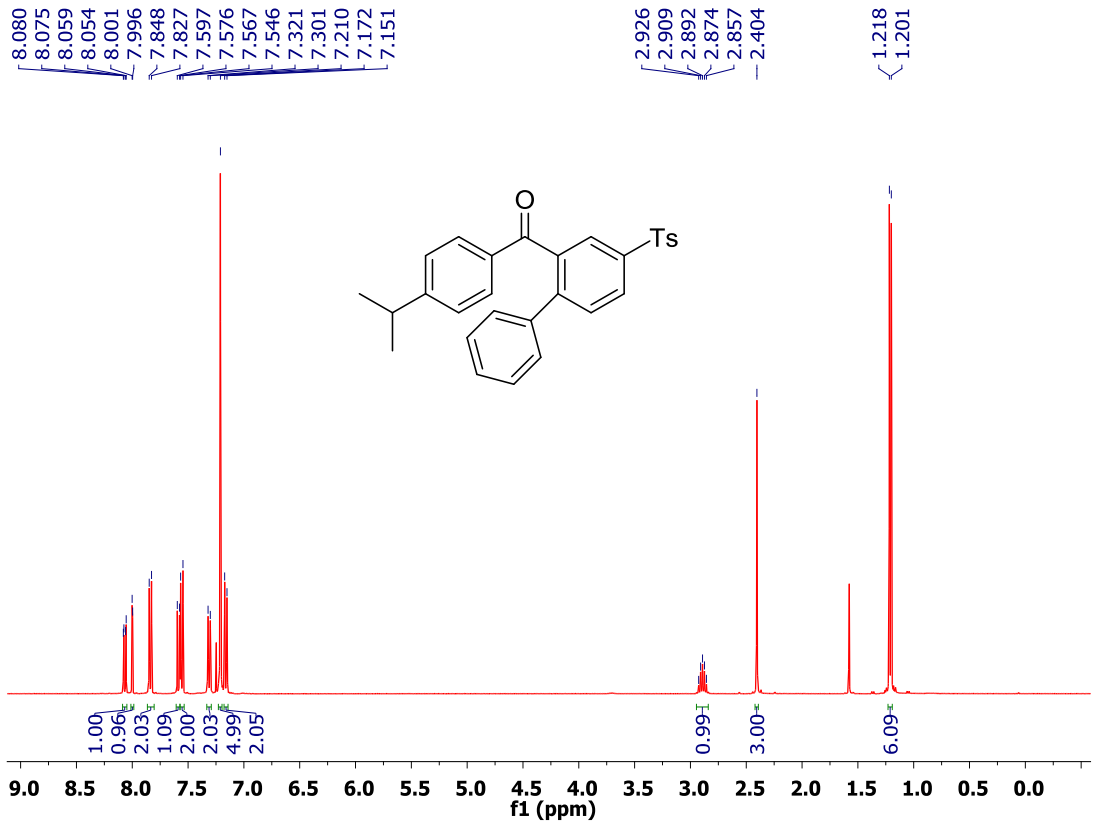
156.108
147.638
145.179
144.969
143.484
142.157
140.270
137.871
134.017
131.243
130.502
130.284
129.810
129.205
128.012
127.878
127.032
123.799
34.416
23.595
21.721
O
Ts
O2N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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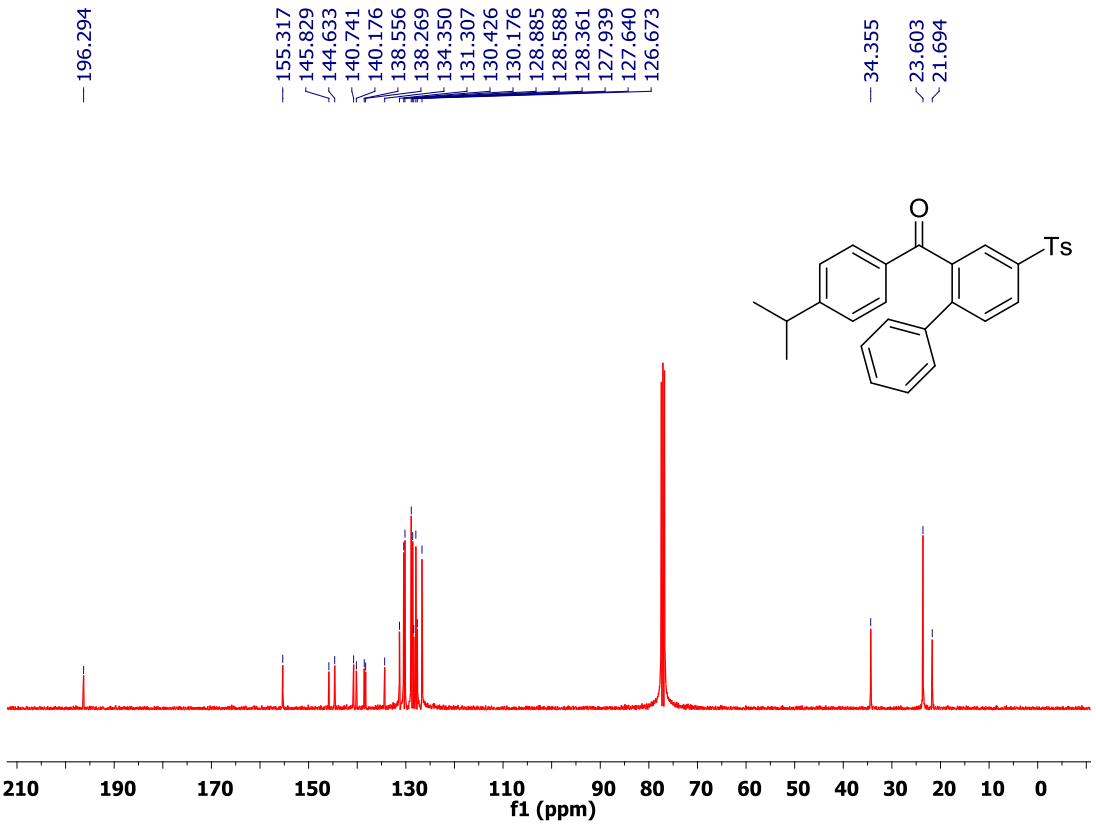
8.075
8.059
8.054
8.001
7.996
7.848
7.827
7.597
7.576
7.567
7.546
7.321
7.301
7.210
7.172
7.151
2.926
2.909
2.892
2.874
2.857
2.404
1.218
1.201
O
Ts
1.00
0.96
2.03
1.09
2.00
2.03
4.99
2.05
0.99
3.00
6.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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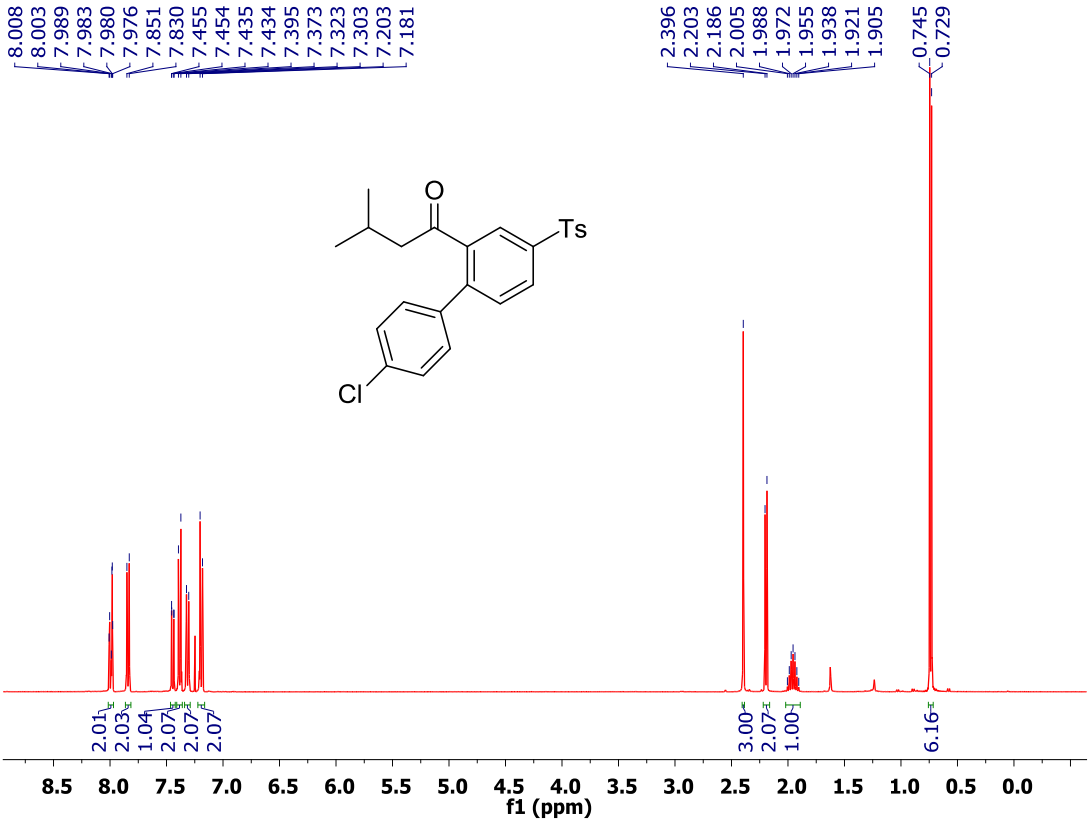
155.317
145.829
144.633
140.741
140.176
138.556
138.269
134.350
131.307
130.426
130.176
128.885
128.588
128.361
127.939
127.640
126.673
34.355
23.603
21.694
O
Ts
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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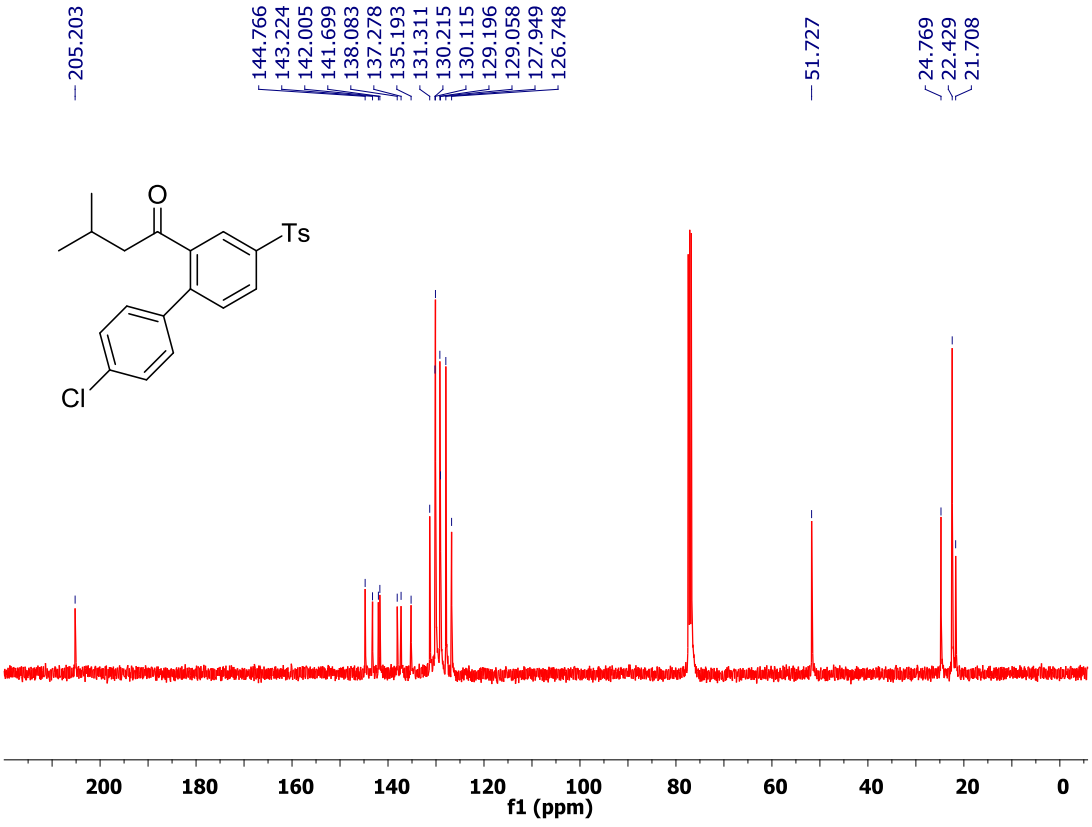
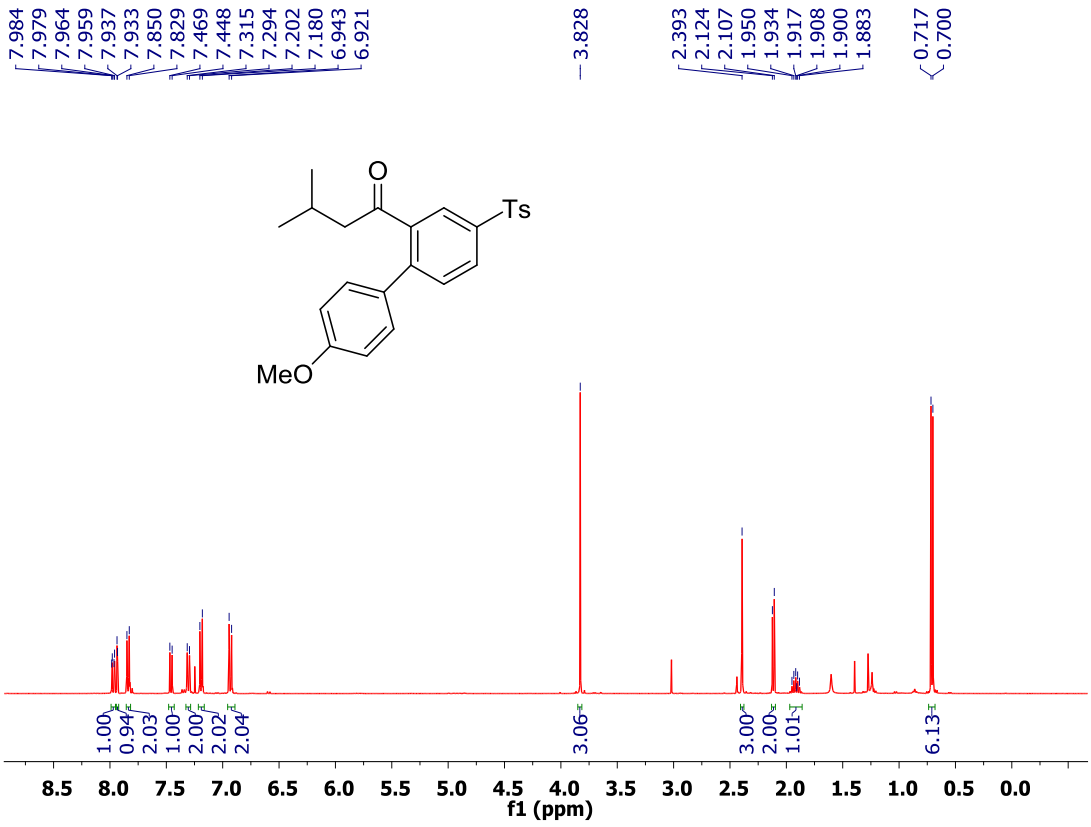
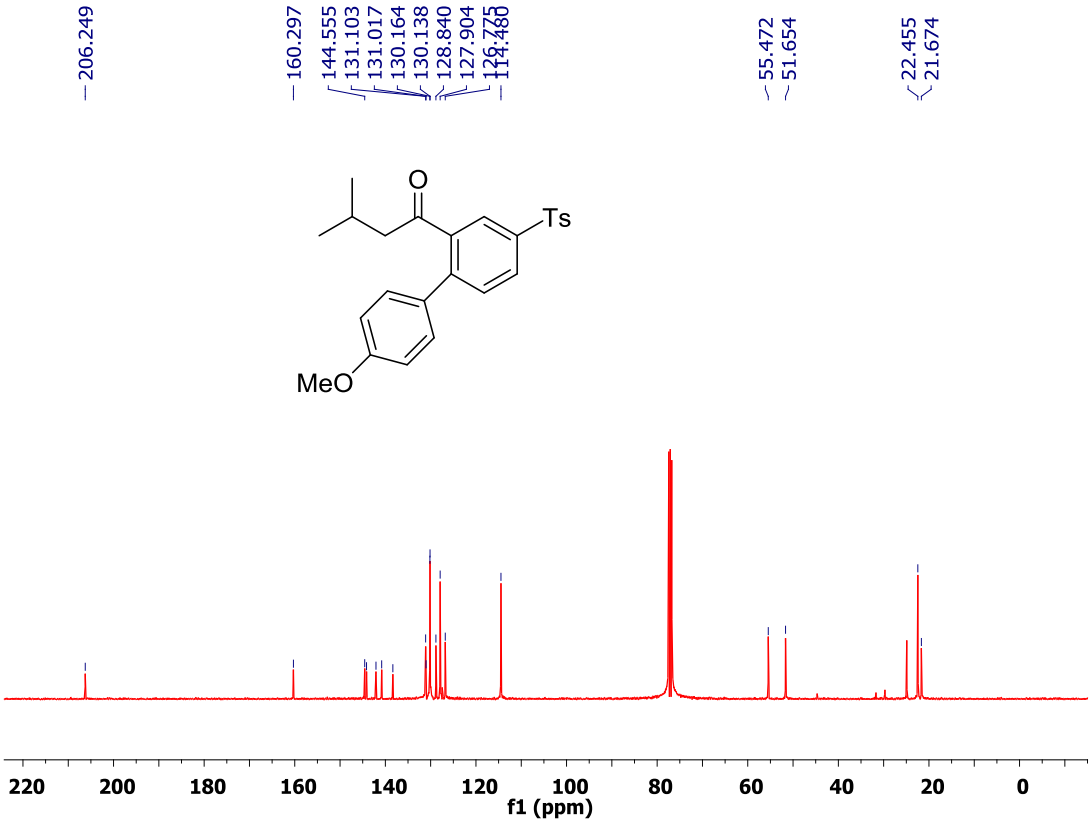
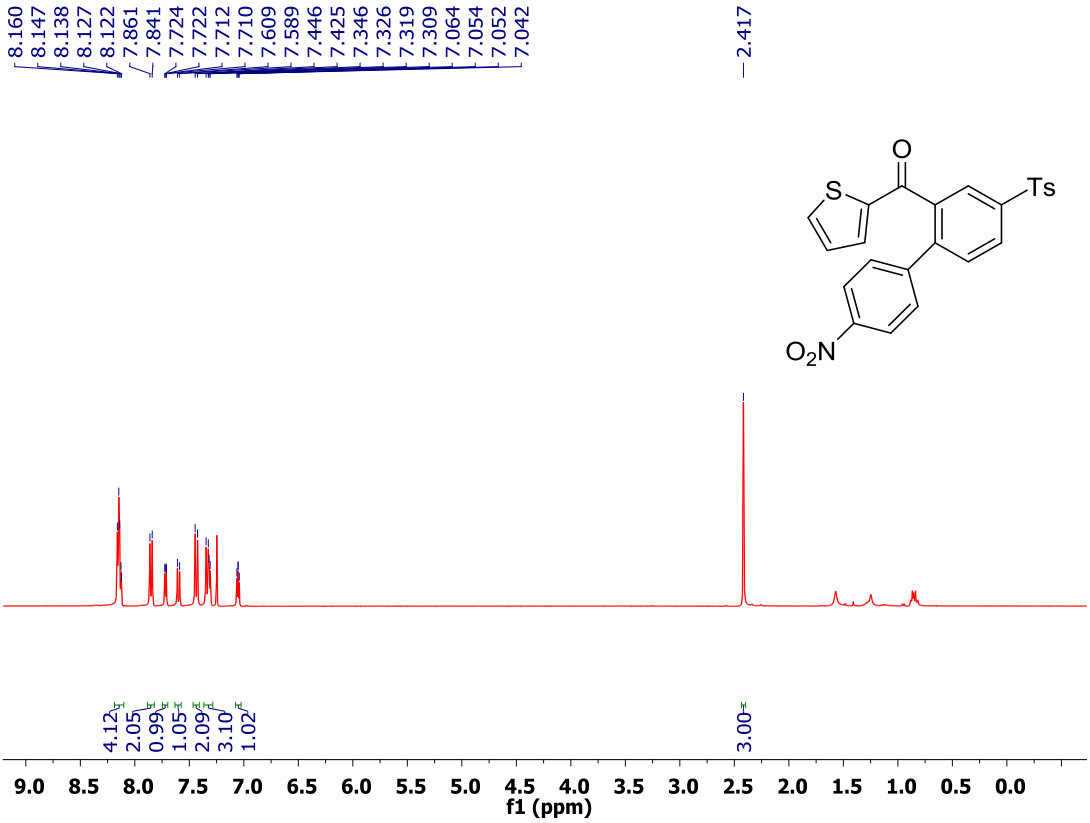
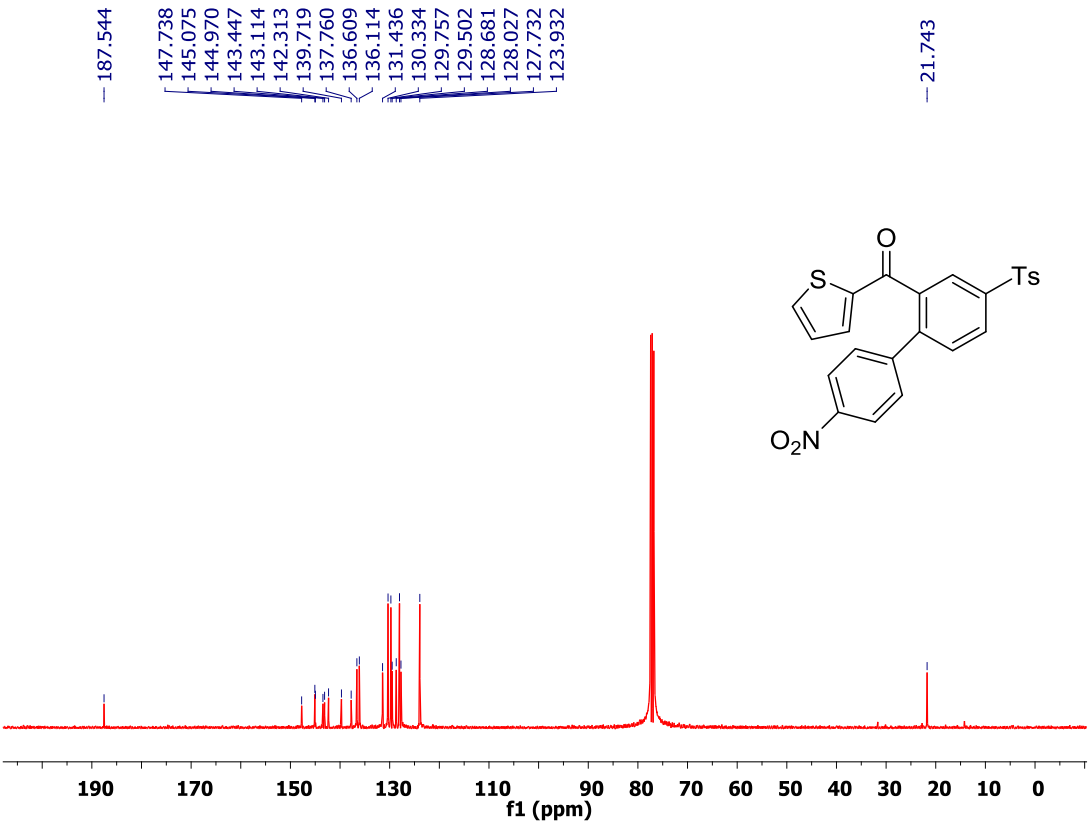
8.003
7.989
7.983
7.980
7.976
7.851
7.830
7.455
7.454
7.435
7.434
7.395
7.373
7.323
7.303
7.203
7.181
2.396
2.203
2.186
2.005
1.988
1.972
1.955
1.938
1.921
1.905
0.745
0.729
O
Ts
Cl
2.01
2.03
1.04
2.07
2.07
2.07
3.00
2.07
1.00
6.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

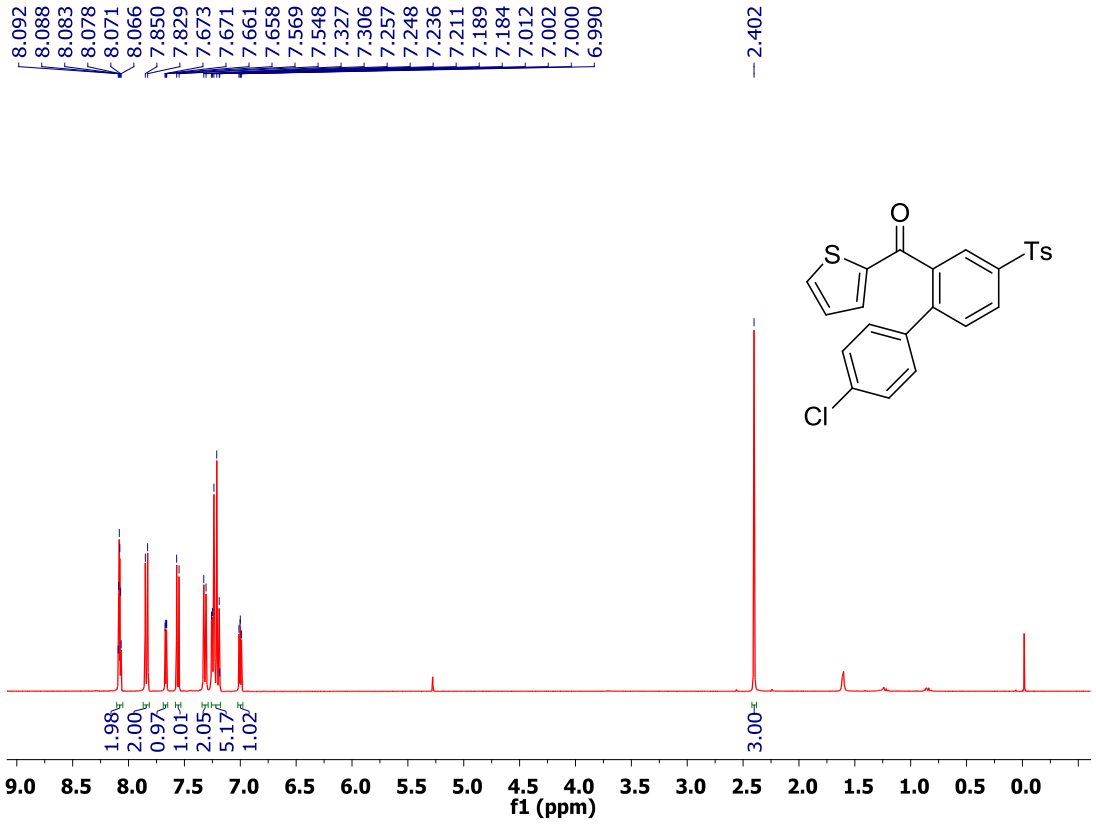

205.203
144.766
143.224
142.005
141.699
138.083
137.278
135.193
131.311
130.215
130.115
129.196
129.058
127.949
126.748
51.727
24.769
22.429
21.708
O
Ts
Cl
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


7.984
7.979
7.964
7.959
7.937
7.933
7.850
7.829
7.469
7.448
7.315
7.294
7.202
7.180
6.943
6.921
3.828
2.393
2.124
2.107
1.950
1.934
1.917
1.908
1.900
1.883
0.717
0.700
O
Ts
MeO
1.00
0.94
2.03
1.00
2.00
2.02
2.04
3.06
3.00
2.00
1.01
6.13
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)


206.249
160.297
144.555
131.103
131.017
130.164
130.138
128.840
127.904
126.775
114.480
55.472
51.654
22.455
21.674
O
Ts
MeO
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


8.160
8.147
8.138
8.127
8.122
7.861
7.841
7.724
7.722
7.712
7.710
7.609
7.589
7.446
7.425
7.346
7.326
7.319
7.309
7.064
7.054
7.052
7.042
2.417
O
S
Ts
O_2N
4.12
2.05
0.99
1.05
2.09
3.10
1.02
3.00
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 0.0
f1 (ppm)


187.544
147.738
145.075
144.970
143.447
143.114
142.313
139.719
137.760
136.609
136.114
131.436
130.334
129.757
129.502
128.681
128.027
127.732
123.932
21.743
O
S
Ts
O_2N
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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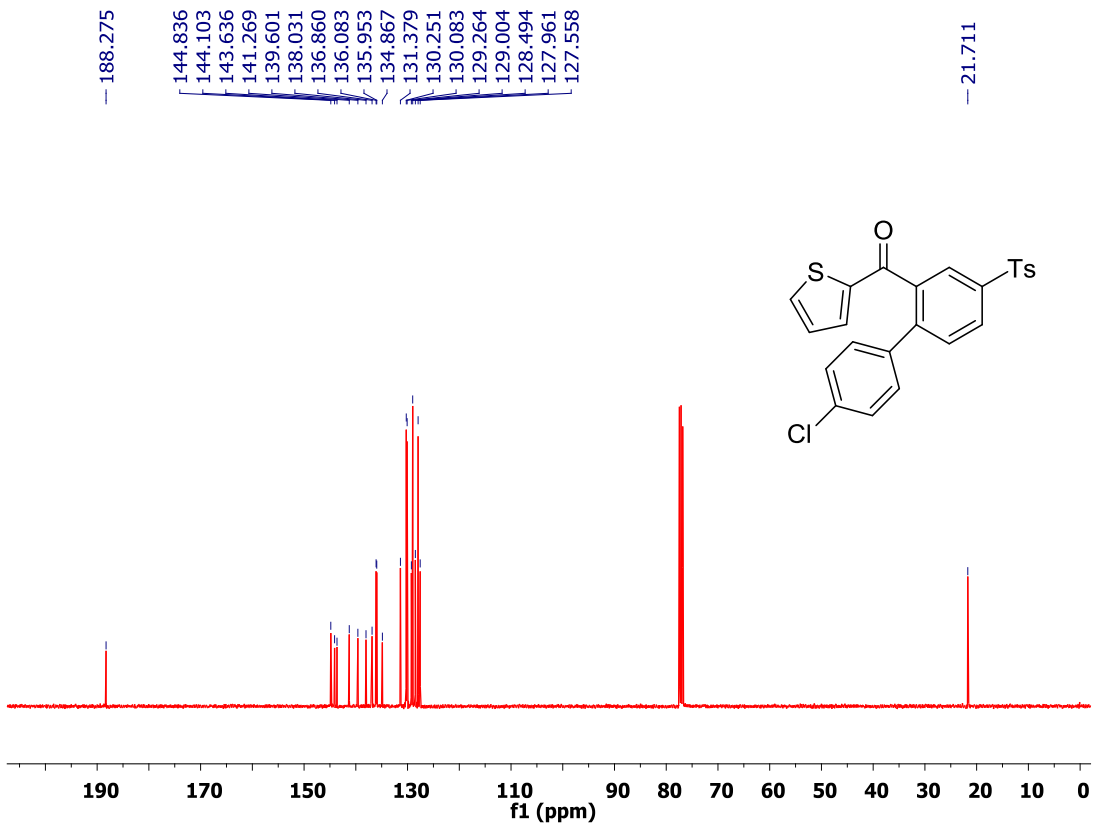
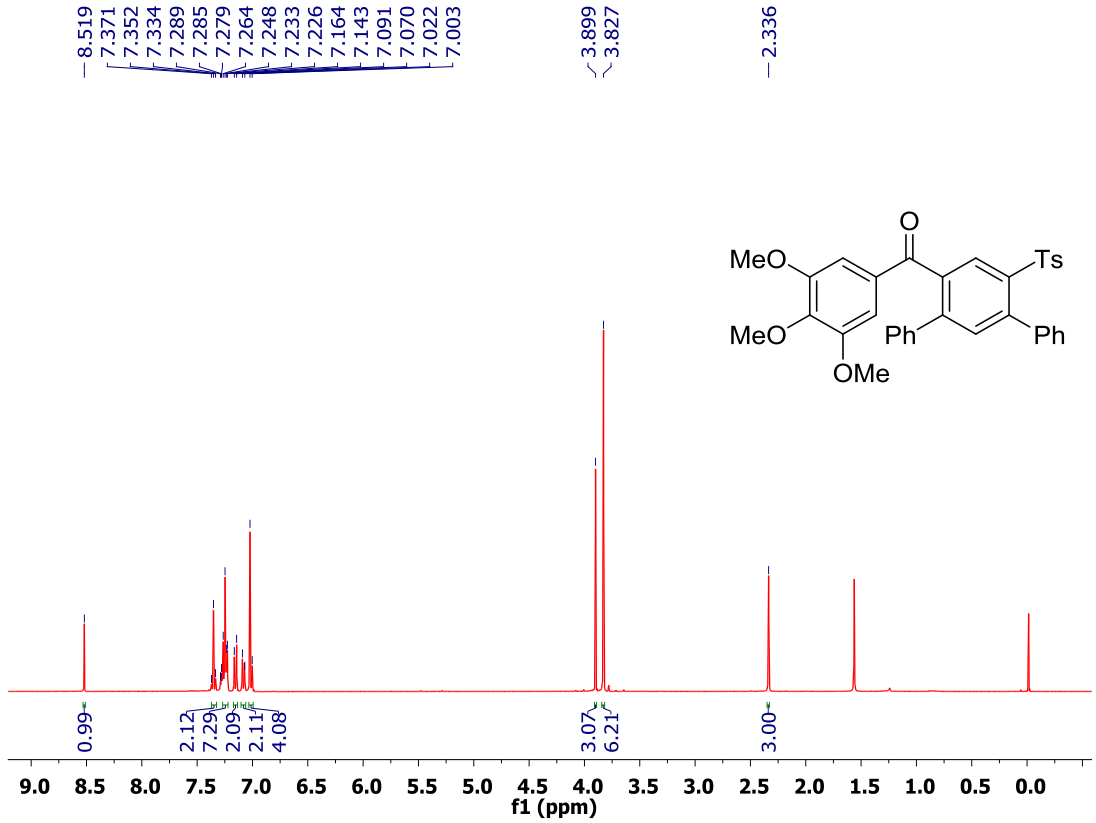
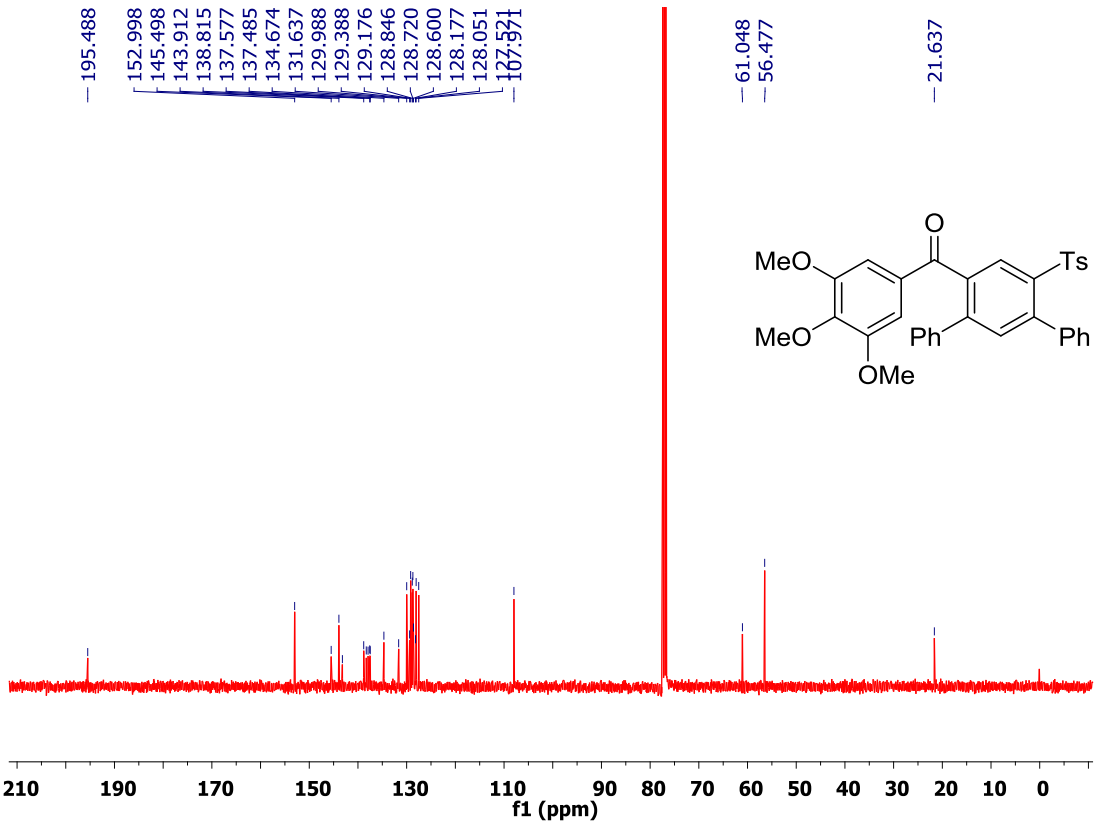
8.088
8.083
8.078
8.071
8.066
7.850
7.829
7.673
7.671
7.661
7.658
7.569
7.548
7.327
7.306
7.257
7.248
7.236
7.211
7.189
7.184
7.012
7.002
7.000
6.990
2.402
O
S
Ts
Cl
1.98
2.00
0.97
1.01
2.05
5.17
1.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


188.275
144.836
144.103
143.636
141.269
139.601
138.031
136.860
136.083
135.953
134.867
131.379
130.251
130.083
129.264
129.004
128.494
127.961
127.558
21.711
O
S
Ts
Cl
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.519
7.371
7.352
7.334
7.289
7.285
7.279
7.264
7.248
7.233
7.226
7.164
7.143
7.091
7.070
7.022
7.003
3.899
3.827
2.336
MeO
MeO
OMe
O
Ph
Ph
Ts
0.99
2.12
7.29
2.09
2.11
4.08
3.07
6.21
3.00
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 0.0
f1 (ppm)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145.498
143.912
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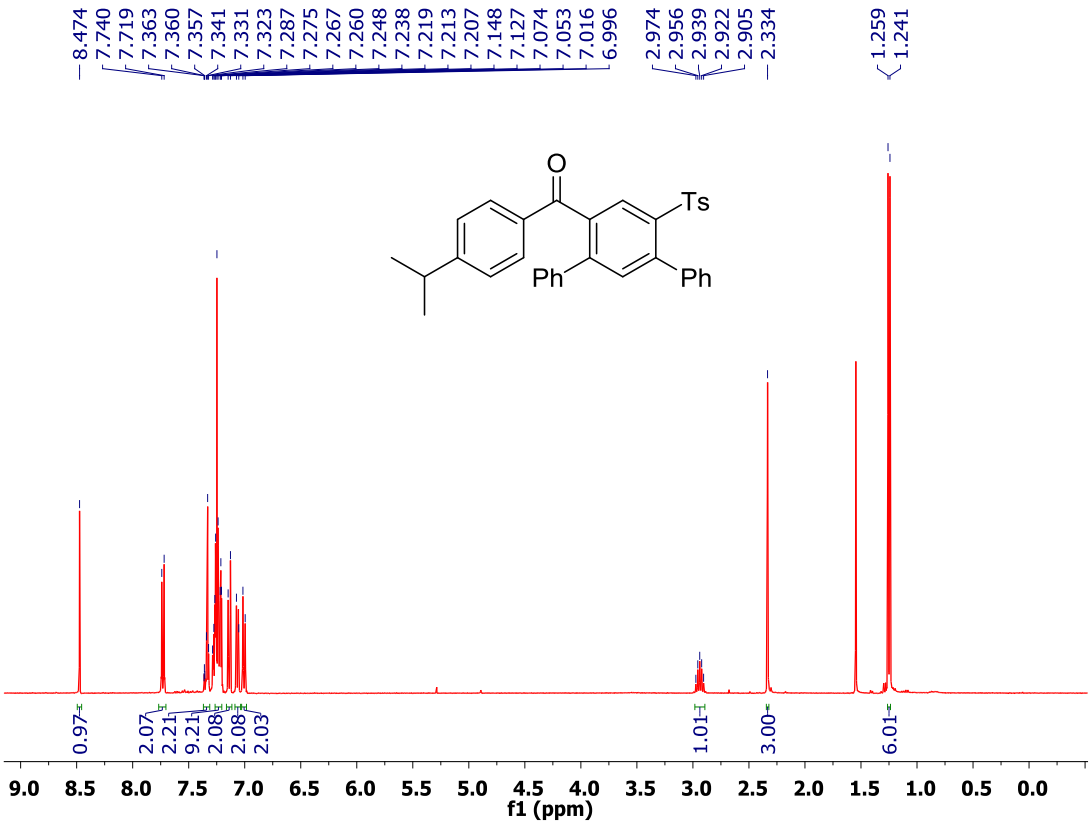
137.577
137.485
134.674
131.637
129.988
129.388
129.176
128.846
128.720
128.600
128.177
128.051
127.521
127.371
61.048
56.477
21.637
MeO
MeO
OMe
O
Ph
Ph
Ts
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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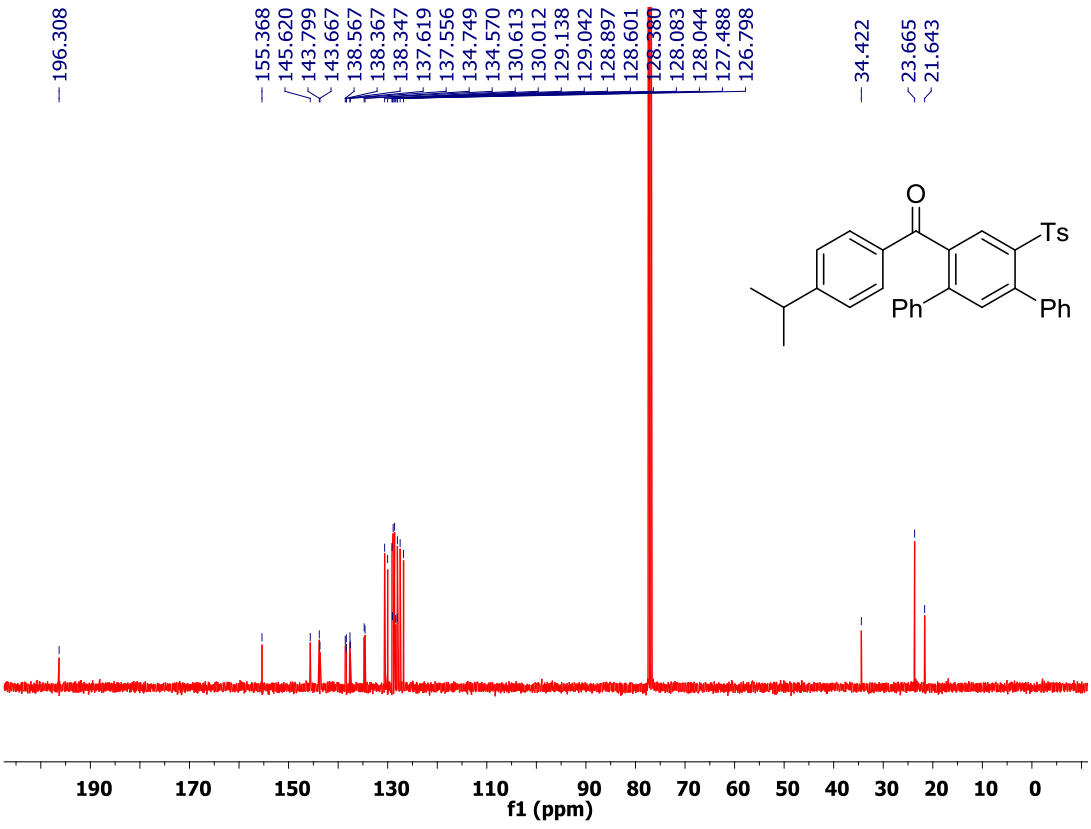
7.267
7.260
7.248
7.238
7.219
7.213
7.207
7.148
7.127
7.074
7.053
7.016
6.996
2.974
2.956
2.939
2.922
2.905
2.334
1.259
1.241
O
Ts
Ph
Ph
0.97
2.07
2.21
9.21
2.08
2.08
2.03
1.01
3.00
6.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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155.368
145.620
143.799
143.667
138.567
138.367
138.347
137.619
137.556
134.749
134.570
130.613
130.012
129.138
129.042
128.897
128.601
128.380
128.083
128.044
127.488
126.798
34.422
23.665
21.643
O
Ts
Ph
Ph
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)