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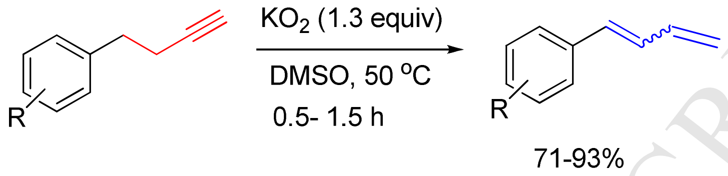

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Superoxide mediated isomerization of 4-aryl-but-1-ynes to 1-aryl-1,3-butadienes

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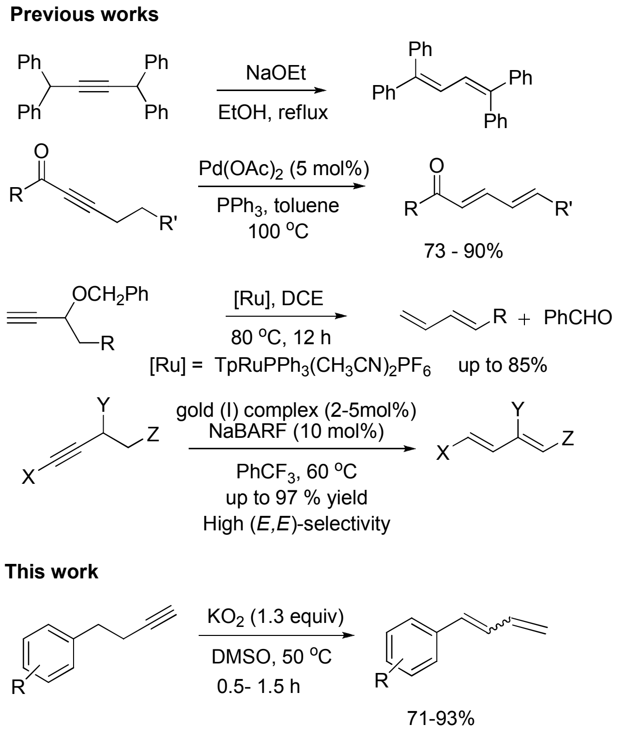
ABSTRACT

A new role of superoxide ion in the isomerization of homobenzylic acetylenes leading to 1-aryl-1,3-butadienes is reported. The unconventional reagent KO_2 is found to be superior in performing this kind of isomerization over other the commonly used bases. For substrates containing arene moiety and triple bond connected through more than two methylene groups, and for propargylcyclohexanol the reagent selectively effected migration of the triple bond. Reactivity of KO_2 towards the substrates having disubstitution at benzylic position varied depending on the nature of the substitution, alkyl-substitution lead to isomerization to give mixture of allene (an intermediate in the isomerization of acetylene to 1,3-butadiene) and triple bond migration product; whereas phenyl-substituted compound gave 1,3-diene. The utility of the methodology was demonstrated through a Diels-Alder reaction of one of the dienes obtained by the isomerization with suitable dienophiles.

1. Introduction

Base-catalyzed acetylenic bond migration along the alkyl chain has been extensively studied over the past century.[1] Mechanism of this processes involved an allene intermediate[2] but the kinetically unfavored conjugated dienes were not detected.[1a,2c,3] Formation of the conjugated dienes by isomerization of acetylenes catalyzed by base is only practicable either under extreme conditions[2c] or in the special cases where the formed diene must act as a junction completing a more extended conjugated system[3a] (Scheme 1). Although numerous methods have been developed for the synthesis of 1,3-butadiene[4] but the isomerization of acetylenes to conjugate dienes can be a useful synthetic protocol due to the ready accessibility of alkynes.[5] Isomerization of alkynones to dienones catalyzed by transition metals like Pd,[5] Ru,[6] Ir[6c] (Scheme 1) has been reported in the presence of phosphine ligands and triphenylphosphine[7] itself acted as a catalyst in the successful isomerization. More recently, isomerization of some of the acetylenes and allenes to 1,3-butadienes is also reported using mainly gold catalyst.[8] Conjugated dienes are valuable building blocks for the construction of more complex targets,[4c] for instance, they serve as substrates in cycloaddition reactions.[9] The terminal 1,3-dienes were used in the synthesis of highly functionalized alkenes via Pd-catalyzed 1,2-hydrovinylation.[10]



Scheme 1: Isomerization of acetylenes.

Over the past few decades the study of reactivity of superoxide ion with organic substrates has attracted much attention because of its ubiquitous generation in aerobic organisms. Such studies facilitate understanding the role of superoxide ion in metabolic processes.[11] The unconventional base, potassium superoxide, has propensity to abstract the labile protons such as in cyclopentadiene, diethylmalonate,

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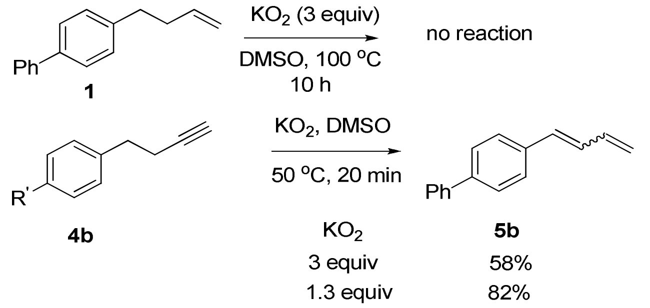
dibenzoylmethane and 1,3-cyclohexanedione.[12] The reaction of superoxide ion with pentachloro aryl-substituted bicyclo[2.2.1]hept-2-ene systems where dehydrohalogenation and an unexpected concomitant reactivity of superoxide in which abstraction of benzylic proton followed by rearrangement leading to methylenenortricyclenes was reported by us recently.[13]

2. Results and discussion

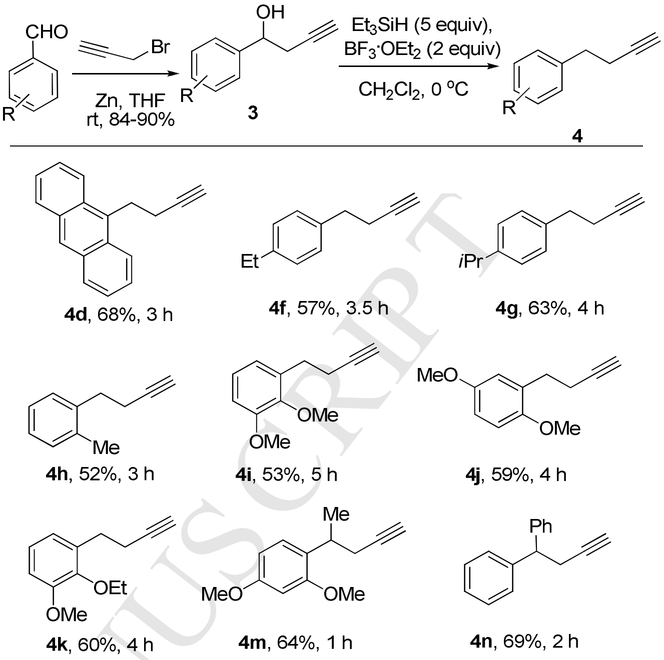
During our efforts to generalize and to further explore the synthetic role of superoxide ion, we observed an interesting isomerization of acetylenes to 1,3-butadienes. To the best of our knowledge a base mediated synthesis of 1,3-butadienes by isomerization of acetylenes is not reported so far. Here, in this paper we report our endeavors in developing a mild and an efficient method for isomerization of homobenzylic acetylenes leading to 1-aryl-1,3-butadienes mediated by superoxide ion.



Scheme 2: Optimization reactions.

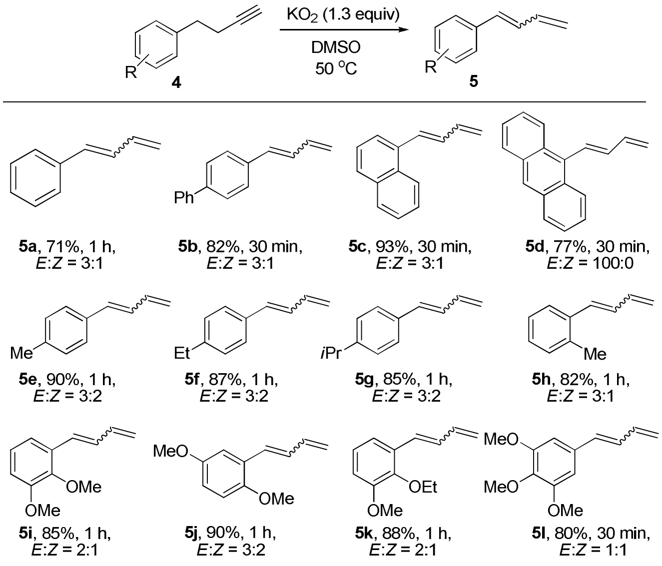
Prompted by the unexpected outcome of the reaction of superoxide with pentachloro-7-methyl-5-aryl substituted norbornenes,[13] we thought of extending the reaction to simple 4-aryl-but-1-ene. In this endeavor, 4-biphenylbut-1-ene **1**[14] was treated with superoxide under similar conditions. Unfortunately **1** was completely unreactive even up to 100 °C (Scheme 2). Then we replaced the double bond with a triple bond as in **4**. To our pleasant surprise, reaction of **4** with KO_2 lead to the smooth isomerization of terminal acetylenes to 1,3-butdienes (Scheme 2). When compound **4b** was initially treated with KO_2 (3 equiv) in DMSO at room temperature, no progress was recorded. However, heating the reaction mixture to 50 °C resulted in the complete conversion of starting material in 20 min (as indicated by TLC) to afford a separable mixture of two compounds. On the basis of ^{1}H NMR spectra, structures of the two products were assigned to *E*/*Z* (3:1) isomers (a dd at δ 6.85, J = 15.7, 10.8 Hz and a doublet at δ 6.62, J = 15.7 Hz for *E*-isomer, and a doublet at δ 6.50, J = 11.5 Hz and a triplet at δ 6.31, J = 11.3 Hz for *Z*-isomer) of 4-(buta-1,3-dienyl)biphenyl **5b** with *Z*-isomer being the minor as anticipated due to steric reasons. Optimization efforts to improve the initially obtained moderate yield (58%) by varying the amount of potassium superoxide used revealed that 1.3 equiv of the reagent furnished best results (82% in 0.5 h, Scheme 2). The reaction was sluggish when the quantity of the $KO_2$was reduced further.

Our synthetic endeavor was started with the preparation of homopropargyl alcohols (**3**) from aromatic aldehydes (**2**) and propargyl bromide. Treatment of aldehydes (**2**) and propargyl bromide with zinc dust (5 equiv) in THF furnished the benzyl alcohols (**3**) in excellent yields. Known protocols were applied for the preparation of other benzyl alcohols.[15] Having obtained benzyl alcohols, our next task was to convert them to but-3-ynylbenzenes (**4**). Deoxygenation of benzyl alcohols was carried out using the $BF_3\cdot OEt_2$ (2 equiv) and triethylsilane (5 equiv) in dichloromethane at 0 °C to obtain but-3-ynylbenzenes **4** in moderate to good yields (Scheme 3). Benzyl alcohols containing halogen substitution on phenyl group did not react under this reaction condition.



Scheme 3: Preparation of starting materials, 4-aryl-but-1-ynes. Reagents and condition: (a) Et_3SiH (5 equiv), $BF_3\cdot OEt_2$ (2 equiv), CH_2Cl_2, 0 °C. Some of the starting materials **4** were prepared using known protocols.[16]

With the encouraging result of the formation of **5b** (Scheme 2) we next extended this reaction to the other substrates (Scheme 4).The treatment of unsubstituted compound **4a** under optimal reaction condition delivered product **5a** in 3:1 (*E*/*Z*). Similarly 1-(but-3-ynyl)naphthalene **2c** afforded 1,3-butadiene **5c** in excellent yield (Scheme 4). Treatment of anthracene tethered substrate **4d** with KO_2 delivered desired compound **5d** in good yield as a single *E*-isomer. The other substrates, bearing alkyl substitution on phenyl ring, **4e-g** underwent smooth transformation to give the corresponding 1,3-butadienes in excellent yields with moderate diastereoselectivity (*E*/*Z* = 3:2).

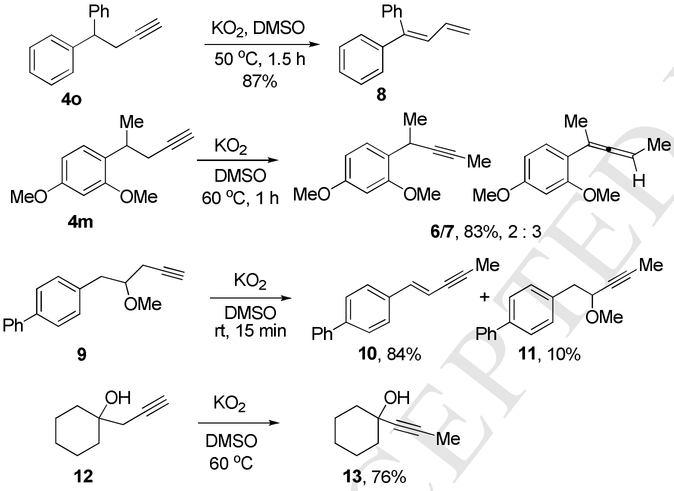


Scheme 4: Isomerization of acetylenes to 1,3-butadienes. Reaction conditions: KO_2 (1.3 equiv)/DMSO at 50 °C. The approximate *E*/*Z* ratio was calculated from the ^{1}H NMR.

The KO_2 reaction with the substrates containing electron donating groups, for instance, alkoxy substitution on phenyl was initiated at room temperature but sluggish. Upon heating at 50 °C, complete conversion of **4i** occurred in 1 h to give 1,3-butadiene **5i**. The other alkoxy substituted compounds **4j-l** also gave corresponding 1,3-butadienes **5i-l** in good to excellent yields with moderate diastereoselectivity (Scheme 4).

Next, we examined the scope of this reaction by varying the substitutions at benzylic position (Scheme 5). The methyl substituted substrate **4m** gave an inseparable mixture of two products, as shown by ^{1}H NMR. The two were identified as the triple bond migration product (**6**) and the allene **7** in 2:3 ratio. Allene **7** was ascertain by ^{1}H NMR (dd at δ 5.19 with J = 2.9, 6.8 Hz, for one proton) and ^{13}C NMR (δ 205.5). When a phenyl group was placed at the benzylic position as in substrate **2o**, 1,3-butadiene **8** was formed. We were curious to know what will be the result if we increase the alkyl chain by inserting an additional methylene group. Accordingly, the reaction of the compound **9** resulted in isolation of mixture of products formed by internal migration of triple bond yielding **11** (10%), and enyne **10** (84%) resulting from concomitant loss of MeOH.

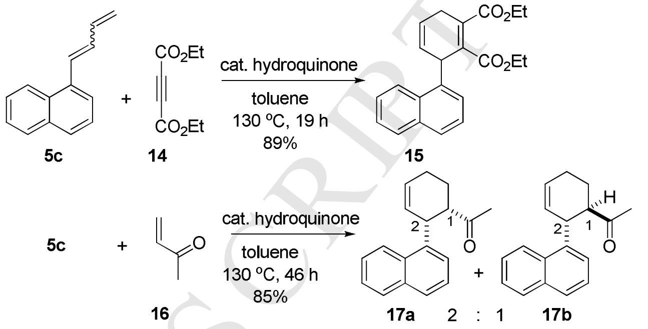
The cyclohexanol derivative **12**[17] was tested towards the reactivity of superoxide and it was found that the terminal triple bond migrated in this case to give exclusively propargyl alcohol **13** in good yield (Scheme 5). To the best of our knowledge, such isomerization of homopropargyl alcohols is not reported in the literature and this could perhaps be a better choice for the preparation of *tert*-propargylic alcohols rather than the addition of metal acetylides to ketones.



Scheme 5: Isomerization/ migration of acetylenes. Reaction conditions: KO_2 (1.3 equiv)/DMSO.

To examine the outcome of this reaction with commonly employed bases, we subjected acetylene derivative **4c** to KOH in EtOH at up to reflux temperature. The reaction did not proceed under these conditions as revealed from TLC monitoring. Also, as the anion basicity increases dramatically in an aprotic solvent,[18] compound **4f** was treated with KOH/DMSO and KO^{t}Bu/DMSO at up to 100 °C. Again, it was observed that the desired product was not formed (near quantitative amount of **4f** was recovered). These experiments suggest that there is a unique and exceptional degree of reactivity of superoxide ion which triggered this kind of isomerization under milder conditions.

The mechanism of base-catalyzed isomerization of acetylenes has been discussed in detail,[2] which probably involves the acetylene-allene-acetylene route for the migration of triple bond and for the isomerization to conjugate dienes acetylene-allene-1,3-diene path is favored. So, it is proposed that the allene would be formed initially by the abstraction of propargylic proton/hydrogen in **4a** by superoxide ion. As the benzylic (allylic) protons in allene are more acidic than the allenic ones, the isomerization would lead to diene **5a**. Since only 1.3 equiv of KO_2 is used in the reaction, involvement of hydroxide ion for the abstraction of the second proton or a [1,3]-hydrogen sigmatropic rearrangement[19] appears to be responsible for the formation of 1,3-diene.



Scheme 6: Diels-Alder reaction of **5c**.

In order to demonstrate a synthetic utility for the current methodology, a Diels-Alder reaction of diene **5c** was carried out using diethyl but-2-ynedioate **14** and methylvinyl ketone **16** in toluene at 130 °C in the presence of catalytic amount of hydroquinone. The corresponding adducts **15** and **17** respectively were obtained in excellent yields (Scheme 6). Endo/exo diastereomers **17a** and **17b** (enriched) were obtained in 2:1 ratio and are assigned by comparing the coupling constants (**17a**, C-1, δ 3.03, (AB) q, J = 5.9 Hz and for **17b**, C-1, δ 3.21, ddd, J = 3.4, 6.6, 10.5 Hz) with those of the related compounds reported in the literature.[9b]

3. Conclusion

In conclusion, we have demonstrated superoxide mediated isomerization of 4-aryl-1-butynes to buta-1,3-dienylbenzenes. This method could offer an attractive alternative for the isomerization of homobenzylic acetylenes to 1-aryl-1,3-butadienes. Propargylcyclohexanol and the substrates containing arene and triple bond separated by more than two methylene groups underwent migration of terminal triple bond to internal one indicating the necessity of presence of acidic benzylic protons in the substrates to give 1,3-butadienes. The Diels-Alder reaction of diene with alkyne as well as alkene dienophiles gave the corresponding adducts in excellent yields.

4. Experimental section

4.1. General

Unless otherwise specified, all reactions were carried out in oven dried glassware, under argon atmosphere. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. THF was dried by refluxing over sodium metal. Dimethyl sulfoxide (DMSO) was distilled from anhydrous $CaSO_4$/calcium hydride. Boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) was purchased from commercial source (Avra Synthesis Pvt Ltd) and purified immediately before use. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature with $CDCl_3$ as the solvent unless otherwise stated. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer (with complete proton decoupling) at ambient temperature. Chemical shifts are reported in parts per million relative to chloroform (^{1}H, δ 7.27; ^{13}C, δ 77.0). Data for ^{1}H NMR are reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, dd = double−doublet, dq = double quartet, ddd = double double doublet, sept = septet, m = multiplet, br = broad. The powdered potassium superoxide was purchased from Alfa Aesar and used as such. 'Caution should be taken when using KO_2, since it is explosive'.

4.2 General procedure for Preparation of homopropargyl alcohols

1-(2-Ethoxy-3-methoxyphenyl)but-3-yn-1-ol **3a**: To a stirred solution of 2-ethoxy-3-methoxybenzaldehyde (500 mg, 2.77 mmol) in THF (5 mL) were added propargyl bromide (494 mg, 4.15 mmol) and then zinc dust (540 mg, 8.31 mmol) at room temperature. After being stirred for 1 h, reaction mixture was filtered, washed with EtOAc (100 mL). The filtrate was washed with NH_4Cl solution (40 mL), water (50 mL), brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude was purified over silica gel column chromatography (15% EtOAc in Hexane) furnished compound **3a** (513 mg, 84%) as a colorless liquid. R_f = 0.5 (15% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.99 (m, 2H), 6.84 (m, 1H), 5.19-5.07 (m, 1H), 4.18-3.99 (m, 2H), 3.83 (d, *J* = 2.0 Hz, 3H), 3.09-2.97 (m, 1H), 2.76-2.53 (m, 2H), 2.04 (d, *J* = 2.0 Hz, 1H), 1.38 (td, *J* = 6.9, 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 145.1, 136.1, 123.9, 118.4, 111.8, 81.2, 70.5, 69.0, 68.1, 55.7, 28.2, 15.8; IR (neat) 3440, 3295, 2976, 2935, 2838, 1586, 1473, 1387, 1264, 1209, 1082, 1025 cm^{-1}; HRMS (ESI): *m/z*calcd for $C_{13}H_{17}O_3$ $[M + H]^+$ 221.1178; found: 221.1174.

1-(2,5-Dimethoxyphenyl)but-3-yn-1-ol **3b**: colorless liquid; Yield: 88%; R_f = 0.5 (15% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 2.9 Hz, 1H), 6.80-6.77 (m, 2H), 5.09-5.00 (m, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 2.99 (d, *J* = 5.9 Hz, 1H), 2.80-2.70 (m, 1H), 2.65-2.54 (m, 1H), 2.05 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 150.3, 131.5, 113.1, 113.0,111.3, 81.3, 70.5, 68.7, 55.7 (2C), 27.5; IR (neat) 3442, 3291, 2944, 2835, 2117, 1595, 1495, 1461, 1425, 1271, 1214, 1180, 1154, 1041, 873 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{12}O_2$ $[M – H_2O]^+$ 188.0837; found: 1.88.0830.

1-(2,3-Dimethoxyphenyl)but-3-yn-1-ol **3c**: colorless liquid; Yield: 90%; R_f = 0.5 (15% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.01 (m, 2H), 6.88 (dd, *J* = 2.2, 7.6 Hz, 1H), 5.13 (td, *J* = 4.8, 7.9 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.83 (d, *J* = 4.9 Hz, 1H), 2.77-2.69 (m, 1H), 2.68-2.58 (m, 1H), 2.07 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 146.0, 135.8, 124.1, 118.4, 112.0, 81.1, 70.7, 68.1, 61.0, 55.8, 28.3; IR (neat) 3445, 3293, 2971, 2929, 2854, 1582, 1472, 1387, 1264, 1209, 1082, 1044, 869 cm^{-1}; HRMS (ESI): *m/z*calcd for $C_{12}H_{14}O_3Na$ $[M + Na]^+$ 229.0841; found: 229.0838.

2-(2,4-Dimethoxyphenyl)pent-4-yn-2-ol **3d**: colorless liquid; Yield: 84%; R_f = 0.5 (15% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 1H), 6.51-6.46 (m, 2H), 3.93 (s, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 2.84 (dd, *J* = 2.7, 5.6 Hz, 2H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 157.4, 127.5, 105.0, 99.4, 81.5, 73.4, 70.6, 55.4, 55.3, 32.6, 36.7; IR (neat) 3439, 3295, 2926, 2843, 2119, 1592, 1492, 1473, 1422, 1256, 1214, 1154, 1020 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O_3$ $[M + H]^+$ 221.1178; found: 221.1171.

4.3. General procedure for the deoxygenation reaction:

1-(But-3-ynyl)-4-ethylbenzene **4f**: To a stirred solution of 1-(4-ethylphenyl)but-3-yn-1-ol (400 mg, 2.3 mmol) in CH_2Cl_2 (5 mL) was added triethylsilane (802 mg, 5.75 mmol) at room temperature and then reaction mixture was cooled to 0 °C before addition of $BF_3{\cdot}OEt_2$ (653 mg, 4.6 mmol). After being stirred for 1 h at same temperature (0 °C), aqueous $NaHCO_3$ (2 mL) was added diluted with CH_2Cl_2 (30 mL). The organic phase was separated and aqueous phase was extracted with CH_2Cl_2 (30 mL x 3) combined organic phase was washed with water (40 mL), brine (20 mL) dried over Na_2SO_4 and evaporated under reduced pressure. The resulting crude was purified over silica gel column chromatography (2% EtOAc in hexane) to afford **4f** (206 mg, 57%) as a colorless liquid; yield: 57% R_f = 0.5 (2% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.07 (m, 4H), 2.81 (t, *J* = 7.8 Hz, 2H), 2.61 (q, *J* = 7.8 Hz, 2H), 2.45 (td, *J* = 7.3, 2.4, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.24-1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.4, 128.4 (2C), 127.9 (2C), 84.0, 68.9, 34.5, 28.5, 20.7, 15.7; IR (neat) 2963, 2939, 2865, 2118, 1680, 1602, 1508, 1470, 1409,1365, 1051, 1020 cm^{-1}; HRMS (ESI): m/z calcd for $C_{12}H_{15}$ [M + H]+ 159.1174; found: 159.1159.

9-(But-3-ynyl)anthracene **4d**: pale yellow liquid; yield: 68% R_f = 0.5 (3% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.32 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.60-7.53 (m, 2H), 7.53-7.46 (m, 2H), 3.97-3.89 (m, 2H), 2.75-2.65 (m, 2H), 2.12 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4, 131.6 (2C), 129.6, 129.3 (2C), 126.5 (2C), 125.9 (2C), 124.9 (2C), 124.1 (2C), 83.9, 69.4, 27.3, 20.0; IR (neat) 3287, 3048, 2968, 2915, 2839, 2112, 1620, 1518, 1439, 1348, 1273, 1157, 994 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{15}$ $[M + H]^+$ 231.1174; found: 231.1170.

1-(But-3-ynyl)-4-isopropylbenzene **4g**: colorless liquid; yield: 63%; R_f = 0.5 (2% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 4H), 2.88 (td, *J* = 6.9, 14.1 Hz, 1H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.46 (dt, *J* = 2.7, 7.7 Hz, 2H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.23 (d, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 137.8, 128.3 (2C), 126.5 (2C), 84.1, 68.8, 34.5, 33.8, 24..1, 20.6; IR (neat) 2959, 2927, 2872, 2118, 1682, 1608, 1510, 1460, 1417,1361, 1173, 1051, 1014 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{20}N[M + NH_4]^+$ 190.1596; found: 190.1577.

1-(But-3-ynyl)-2-methylbenzene **4h**: colorless liquid; yield: 52%; R_f = 0.5 (1% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.34-7.27 (m, 3H), 3.06 (q, *J* = 7.3 Hz, 1H), 2.52 (qd, *J* = 7.2, 2.9 Hz, 2H), 2.04 (t, *J* = 2.7 Hz, 1H), 1.45 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 128.7 (2C), 126.9 (2C), 126.5, 83.1, 69.6, 38.9, 27.6, 20.8; IR (neat) 2961, 2933, 2859, 2117, 1681, 1606, 1503, 1450, 1413,1351, 1173, 1019 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{11}H_{13}$ $[M + H]^+$ 145.1017; found: 145.1013.

1-(But-3-ynyl)-2,3-dimethoxybenzene **4i**: colorless liquid; yield: 53%; R_f = 0.5 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-6.97 (m, 1H), 6.88-6.77 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.50 (dt, *J* = 2.7, 7.7 Hz, 2H), 1.99 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 147.2, 134.2, 123.8, 121.9, 110.8, 84.2, 68.7, 60.7, 55.7, 29.3, 19.6; IR (neat) 3290, 2983, 2946, 2844, 2117, 1590, 1498, 1464, 1283, 1221, 1180, 11529, 1120 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{18}O_2N[M + NH_4]^+$ 208.1338; found: 208.1340.

2-(But-3-ynyl)-1,4-dimethoxybenzene **4j**: colorless liquid; yield: 59%; R_f = 0.5 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82-6.69 (m, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 2.84 (d, *J* = 7.8 Hz, 2H), 2.48 (dt, *J* = 2.4, 7.6 Hz, 2H), 1.98 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 151.7, 129.9, 116.6, 111.5, 111.1, 84.4, 68.5, 55.8, 55.7, 29.9, 18.8; IR (neat) 3291, 2997, 2939, 2834, 2115, 1591, 1497, 1459, 1276, 1219, 1181, 1157, 1122, 1046 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O_2$ [M + H]$^+$ 191.1072; found: 191.1070.

1-(But-3-ynyl)-2-ethoxy-3-methoxybenzene **4k**: colorless liquid; yield: 60%; R_f = 0.5 (6% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-6.94 (m, 1H), 6.88-6.75 (m, 2H), 4.05 (q, *J* = 7.0, 2H), 3.85 (s, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.49 (dt, *J* = 2.7, 7.7 Hz, 2H), 1.98 (t, *J* = 2.5 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 146.3, 134.4, 123.6, 121.8, 110.7, 84.3, 68.7, 68.5, 55.7, 29.5, 19.5, 15.8; IR (neat) 3284, 3005, 2929, 2846, 2117, 1590, 1506, 1450, 1272, 1220, 1179, 1160, 1126, 1019 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{20}O_2N$ [M + NH_4]$^+$ 222.1494; found: 222.1492.

2,4-Dimethoxy-1-(pent-4-yn-2-yl)benzene **4m**: colorless liquid; yield: 64%; R_f = 0.5 (8% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 1H), 6.50- 645 (m, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.34 (dt, *J* = 5.4, 7.3 Hz, 1H), 2.58-2.47 (m, 1H), 2.41-2.31 (m, 1H), 1.96 (t, *J* = 2.7 Hz, 1 H), 1.35 (d,*J* =6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.8, 127.2, 126.1, 103.8, 98.6, 83.7, 69.0, 55.3, 31.4, 26.0, 19.2; IR (neat) 3290, 2993, 2940, 2844, 2117, 1579, 1508,1464, 1423, 1329, 1259, 1232, 1127, 1013 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O_2$ [M + H]$^+$ 205.1229; found: 205.1224.

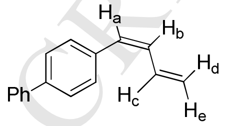
But-3-yne-1,1-diyldibenzene **4o**: yellow liquid; yield: 69%; R_f = 0.5 (1% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.40-7.30 (m, 8H), 7.30-7.25 (m, 2H), 4.30 (t, *J* = 7.7 Hz, 1H), 2.97 (dd, *J* = 7.7, 2.6 Hz, 2H), 1.99 (t, *J* = 2.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3(2c), 128.5 (4C), 127.9 (4C), 126.6 (2C), 82.8, 70.1, 50.0, 25.4; IR (neat) 3298, 3052, 2980, 2930, 2844, 2117, 1580, 1453, 1429, 1369, 1300, 1259, 1177, 1106, 1004, 955 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}$ [M + H]$^+$ 207.1174; found: 207.1163.

4.4 General procedure for the synthesis of 1-aryl-1,3-butadienes[20]

(*E*)-1-(Buta-1,3-dienyl)naphthalene and (Z)-1-(Buta-1,3-dienyl)naphthalene **5c**: To a stirred solution of **4c** (1.3 g, 7.30 mmol) DMSO (20 mL) was added potassium superoxide (675 mg, 9.49 mmol) at room temperature and heated at 50 °C. After being stirred for 0.5 h, water (5 mL) was added slowly drop wise, diluted with EtOAc (60 mL), organic phase was separated aqueous phase was extracted with EtOAc (60 mL x 3) combined organic phase was washed with water (50 mL x 2), brine (40 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The resulting crude was purified over silica gel column chromatography (hexane) to afford **5c** (1.21 g, 93%) as a colorless liquid in 3:1= *E:Z* ratio; R_f = 0.6 (hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.16 (m, 1H), 7.92-7.88 (m, 1H), 7.84-7.81 (m, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.58-7.53 (m, 2H), 7.53-7.47 (m, 1H), 7.41 (d, *J* = 15.3 Hz, 1H), 6.92 (dd, *J* = 15.2, 10.8 Hz, 1H), 6.74 (dd, *J* = 16.3, 10.3 1H), 5.45 (d, *J* = 16.6 Hz, 1H), 5.30 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.5, 133.8, 131.2, 129.7, 128.7, 128.1, 126.1, 125.8, 125.7, 123.7, 123.5, 118.0; NMR data for *Z*- isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.01 (m, 1H), 7.92-7.88 (m, 1H), 7.84-7.81 (m, 1H), 7.58-7.47 (m, 4H), 7.02 (d, *J* = 11.1 Hz, 1H), 6.78-6.69 (m, 1H), 6.58 (t, *J* = 11.1 Hz, 1H), 5.45 (d, *J* = 16.6 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 134.3, 133.6, 133.5, 131.8, 128.7, 128.3, 127.7, 127.2, 125.9, 125.8, 125.2, 124.9, 119.2; IR (neat) 3045, 2958, 1626, 1590, 1507, 1435, 1390, 1241, 1158, 1000, 900 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{12}Na$[M + Na]$^+$ 203.0837; found: 203.0834.

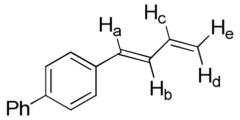
(*E*)-Buta-1,3-dienylbenzene and (*Z*)-Buta-1,3-dienylbenzene **5a**: colorless liquid; *E:Z* = 3:1; yield: 71%; R_f = 0.65 (hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.35-7.30 (m, 3H), 6.83-6.75 (m, 1H), 6.56-6.44 (m, 2H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.18 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 132.8, 129.6, 129.0, 128.6 (2C), 127.6, 126.4 (2C), 117.6; NMR data for *Z*- isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.35-7.30 (m, 3H), 6.89 (d, *J* = 16.6 Hz, 1 H), 6.56-6.44 (m, 1H), 6.26 (t, *J* = 11.4 Hz, 1H), 5.40 (d, *J* = 2.0 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 133.2, 130.8, 130.4, 128.5 (2C), 127.0, 126.7 (2C), 119.6; IR (neat) 2964, 2928, 2873, 1680, 1629, 1606, 1512, 1456, 1418, 1367, 1311, 1266, 1207, 1175, 1120, 1052, 1014, 969 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{10}H_{11}$ [M + H]$^+$ 131.0861, found: 131.0854.

(*E*)-4-(Buta-1,3-dienyl)biphenyl and (*Z*)-4-(Buta-1,3-dienyl)biphenyl **5b**:



5ba

NMR data for *Z*- isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.57 (m, 4H), 7.49-7.39 (m, 4H), 7.39-7.33 (m, 1H), 6.97 (dtd, *J* = 16.9, 10.8, 0.8 Hz, 1H, H_c), 6.50 (d, *J* = 11.5 Hz, 1H, H_a), 6.31 (t, *J* = 11.3 Hz, 1H, H_b), 5.42 (dd, *J* = 17.1, 0.9 Hz, 1H, H_d), 5.27 (d, *J* = 11.1 Hz, 1H, H_e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.8, 136.4, 133.2, 13.9, 129.9 (2C), 129.4, 128.8 (2C), 127.3 (2C), 127.0, 126.9 (2C), 119.8; IR (neat) 3030, 2959, 2879, 2824, 1675, 1602, 1485, 1441, 1405, 1248, 1279, 1120, 1075, 1004, 971, 909 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}$ [M + H]$^+$ 207.1174; found: 207.1168.



5bb

colorless liquid; *E:Z* = 3:1; yield: 82%; R_f = 0.65 (hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.55 (m, 4H), 7.53-7.42 (m, 4H), 7.39-7.32 (m, 1H), 6.85 (dd, *J* = 15.7, 10.8 Hz, 1H, H_b), 6.62 (d, *J* = 15.7 Hz, 1H, H_a), 6.53 (dt, *J* =16.8, 10.4 Hz, 1H, H_c), 5.37 (d, *J* = 16.6 Hz, 1H, H_d), 5.21 (d, *J* = 10.5 Hz, 1H, H_e); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.3, 137.2, 136.2, 132.4, 129.7, 128.8 (2C), 127.3, 127.3 (2C), 126.9 (2C), 126.8 (2C), 117.7; IR (neat): 3030, 2959, 2879, 2824, 1674, 1601, 1486, 1409, 1265, 1120, 1004, 975; HRMS (ESI): *m/z* calcd for $C_{16}H_{15}$ [M + H]$^+$ 207.1174; found: 207.1177.

(*E*)-9-(Buta-1,3-dienyl)anthracene **5d**: Pale yellow colored liquid; yield: 77% R_f = 0.8 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.34-8.26 (m, 2H), 8.07-7.98 (m, 2H), 7.56-7.46 (m, 4H), 7.41 (d, *J* = 16.1 Hz, 1H), 6.84 (td, *J* = 16.9,10.3 Hz, 1H), 6.65 (dd, *J* = 15.9, 10.5 Hz, 1H), 5.40 (dd, *J* = 16.2, 0.7 Hz, 1H), 5.34 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.2, 132.4, 131.4, 129.5, 128.9 (2C), 128.7 (2C), 126.5 (2C), 125.9 (2C), 125.5 (2C), 125.2 (2C), 118.2; IR (neat) 3044, 2960, 1610, 1586, 1503, 1432, 1393, 1240, 1153, 1013, 951 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}$ [M]$^+$ 230.1096; found: 230.1086.

(*E*)-1-(Buta-1,3-dienyl)-4-methylbenzene and (*Z*)-1-(Buta-1,3-dienyl)-4-methylbenzene **5e**: colorless liquid; *E:Z* = 3:2; yield: 90%; R_f = 0.7 (hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 9.1 Hz, 1H), 7.16-7.09 (m, 2H), 6.73 (dd, *J* = 15.5, 10.3 Hz, 1H), 6.53 (d, J = 15.6 Hz, 1H), 6.53-6.40 (m, 1H), 5.39-5.25 (m, 1H), 5.13 (d, J = 9.8 Hz, 1H), 2.3 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.5, 137.3, 134.8, 132.8, 130.4, 129.0 (2C), 126.7, 126.4, 117.0, 23.9; NMR data for *Z*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, J = 8.1 Hz, 1H), 7.21 (d, J = 9.1 Hz, 1H), 7.16-7.09 (m, 2H), 6.95-6.83 (m, 1H), 6.54-6.46 (m, 1H), 6.22 (t, J = 11.3 Hz, 1H), 5.37 (d, J = 2.0 Hz, 1H), 5.20 (d, J = 10.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.8, 134.9, 134.8, 133.4, 130.1, 128.8 (2C), 126.3 (2C), 119.2, 23.9; IR(neat) 3293, 3010, 2944, 2170, 160, 1498, 1488, 1259, 1102, 950 cm^{-1}; HRMS (ESI): *m/z*calcd for $C_{11}H_{13}$ [M + H]$^+$ 145.1017; found: 145.1013.

(*E*)-1-(Buta-1,3-dienyl)-4-ethylbenzene and (*Z*)-1-(Buta-1,3-dienyl)-4-ethylbenzene **5f**: colorless liquid; *E:Z* = 3:2; yield: 87% R$_f$ = 0.7 (hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, J = 8.1 Hz, 1H), 7.26 (s, 1H), 7.21-7.14 (m, 2H), 6.77 (dd, J = 15.6, 10.5 Hz, 1H), 6.54 (d, J = 15.7 Hz, 1H), 6.45 (dt, J = 16.8, 10.3 Hz, 1H), 5.32 (d, J = 17.2 Hz 1H), 5.15 (d, J = 10.3 Hz, 1H), 2.71-2.61 (m, 2H), 1.29-1.22 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.9, 137.3, 134.2, 132.8, 130.4, 128.1 (2C), 126.4 (2C), 117.1, 28.63, 15.56; NMR data for *Z*-isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, J = 8.1 Hz, 1H), 7.26 (s, 1H), 7.21-7.14 (m, 2H), 6.98-6.86 (m, 1H), 6.56-6.50 (m, 1H), 6.23 (t, J = 11.3 Hz, 1H), 5.41-5.34 (m, 1H), 5.22 (d, J = 9.8 Hz, 1H), 2.71-2.61 (m, 2H), 1.29-1.22 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.2, 134.8, 134.6, 133.4, 130.2, 128.8 (2C), 127.8 (2C), 119.2, 28.65, 15.54; IR (neat): 3295, 3009, 2945, 2173, 1609, 1499, 1452, 1430, 1252, 1100, 1039 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}$ [M + H]$^+$ 159.1174; found: 159.1161.

(*E*)-1-(Buta-1,3-dienyl)-4-isopropylbenzene and (*Z*)-1-(Buta-1,3-dienyl)-4-isopropylbenzene **5g**: colorless liquid; *E:Z* = 3:2; yield: 85%; R$_f$ = 0.65 (hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, J = 8.1 Hz, 1H), 7.26-7.23 (m, 1H), 7.22-7.15 (m, 2H), 6.75 (dd, J = 15.5, 10.3 Hz, 1H), 6.58-6.51 (m, 1H), 6.45-6.40 (m, 1H), 5.34-5.27 (m, 1H), 5.14 (d, J = 10.3 Hz, 1H), 2.95-2.84 (m, 1H), 1.28-1.21 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.5, 137.3, 132.8, 130.4, 129.0, 126.7 (2C), 126.4 (2C), 117.0, 33.9, 23.95 (2C); NMR data for *Z*-isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, J = 8.1 Hz, 1H), 7.26-7.23 (m, 1H), 7.22-7.15 (m, 2H), 6.91 (d, J = 16.6 Hz, 1H), 6.55-6.48 (m, 1H), 6.22 (t, J = 11.3 Hz, 1H), 5.39-5.32 (m, 1H), 5.20 (d, J = 9.8 Hz, 1H), 2.95-2.84 (m, 1H), 1.28-1.21 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.8, 134.9, 134.8, 133.4, 130.2, 128.8 (2C), 126.3 (2C), 119.2, 33.88, 23.91 (2C); IR(neat): 3296, 3019, 2178, 1601, 1495, 1457, 1433, 1250, 1102 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{20}N$ [M + NH$_4$]$^+$ 190.1596; found: 190.1564.

(*E*)-1-(Buta-1,3-dienyl)-2-methylbenzene and (*Z*)-1-(Buta-1,3-dienyl)-2-methylbenzene **5h**: colorless liquid; *E:Z* = 3:1; yield: 82%; R$_f$ = 0.7 (hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55-7.47 (m, 1H), 7.22-7.14 (m, 3H), 6.85-6.78 (m, 1H), 6.76-6.66 (m, 1H), 6.61-6.50 (m, 1H), 5.35 (d, J = 16.6 Hz, 1H), 5.18 (d, J = 10.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.5, 133.5, 130.8, 130.5, 130.4, 129.6, 127.5, 126.1, 125.2, 117.5, 19.8; NMR data for *Z*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55-7.47 (m, 1H), 7.22-7.14 (m, 3H), 6.71-6.63 (m, 1H), 6.57-6.50 (m, 1H), 6.32 (t, J = 11.3 Hz, 1H), 5.36 (d, J = 17.1 Hz, 1H), 5.17 (d, J = 9.8 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.4, 136.0, 135.6, 130.9, 130.2, 129.9, 129.8, 127.3, 125.2, 119.0, 19.8; IR (neat): 3293, 3019, 2949, 2171, 1604, 1492, 1458, 1431, 1255, 1109, 1050 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{11}H_{12}$ [M]$^+$ 144.0939; found: 144.0885.

(*E*)-1-(Buta-1,3-dienyl)-2,3-dimethoxybenzene and (*Z*)-1-(Buta-1,3-dienyl)-2,3-dimethoxybenzene **5i**: colorless liquid; *E:Z* = 2:1; yield: 85%; R$_f$ = 0.6 (5% EtOAc in hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.14 (dd, J = 1.2, 8.1 Hz, 1H), 7.05-6.99 (m, 1H), 6.97-6.92 (m, 1H), 6.91-6.86 (m, 1H), 6.86-6.78 (m, 1H), 6.64-6.54 (m, 1H), 5.33 (d, J = 10.7 Hz, 1H), 5.19 (d, J = 10.3 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.1, 146.8, 137.7, 131.4, 130.9, 127.1, 124.0, 117.9, 117.6, 111.4, 61.0, 55.83; NMR data for *Z*-isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.03-6.99 (m, 1H), 6.87 (d, J = 1.5 Hz, 1H), 6.81-6.77 (m, 1H), 6.62-6.58 (m, 1H), 6.57 (d, J = 3.4 Hz, 1H), 6.32 (t, J = 11.3 Hz, 1H), 5.36 (dd, J = 17.1, 1.9 Hz, 1H), 5.20 (d, J = 10.3 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.8, 147.1, 133.5, 131.6, 131.3, 125.9, 123.5, 122.7, 119.3, 111.6, 60.7, 55.8; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O_2$[M + H]$^+$ 191.1078; found: 191.1063.

(*E*)-2-(Buta-1,3-dienyl)-1,4-dimethoxybenzene and (*Z*)-2-(Buta-1,3-dienyl)-1,4-dimethoxybenzene **5j**: colorless liquid; *E:Z* = 3:2; yield: 90%; R$_f$ = 0.55 (5% EtOAc in hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.05 (d, J = 2.9 Hz, 1H), 6.91 (d, J = 2.9 Hz, 1H), 6.85-6.77 (m, 3H), 6.58 (d, J = 11.5 Hz, 1H), 6.52 (dt, J =16.9, 11.0 Hz, 1H), 5.36 (d, J = 16.6 Hz, 1H), 5.18 (d, J = 10.2 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.7, 151.4, 137.8, 130.4, 127.4, 127.1, 117.3, 113.8, 112.3, 111.6, 56.2, 55.7; NMR data for *Z*-isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.94-6.88 (m, 1H), 6.86-6.76 (m, 2H), 6.55-6.50 (m, 1H), 6.37-6.29 (m, 1H), 6.32 (t, J = 11.3 Hz, 1H), 5.41-5.31 (m, 1H), 5.21 (d, J = 10.3 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.1, 151.5, 133.4, 130.9, 126.9, 126.0, 119.3, 116.6, 113.0, 111.0, 56.1, 55.8; IR (neat) 2924, 2838, 1733, 1674, 1610, 1584, 1495, 1460, 1426, 1281, 1218, 1173, 1124, 1044 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O_2$[M + H]$^+$ 191.1072; found: 191.1063.

(*E*)-1-(Buta-1,3-dienyl)-2-ethoxy-3-methoxybenzene and (*Z*)-1-(Buta-1,3-dienyl)-2-ethoxy-3-methoxybenzene **5k**: colorless liquid; *E:Z* = 2:1; yield: 88%; R$_f$ = 0.55 (5% EtOAc in hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 (dd, J = 1.2, 8.6 Hz, 1H), 7.05-7.01 (m, 1H), 6.97-6.91 (m, 1H), 6.87-6.78 (m, 2H), 6.67-6.56 (m, 1H), 5.33 (d, J = 17.1 Hz, 1H), 5.18 (d, J = 10.3 Hz, 1H), 4.07-3.98 (m, 2H), 3.86 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.2, 145.9, 137.7, 132.0, 131.6, 126.4, 123.3, 122.6, 119.1, 111.5, 69.0, 55.80, 15.62; NMR data for *Z*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.05-6.99 (m, 1H), 6.96-6.94 (m, 1H), 6.88-6.78 (m, 2H), 6.58-6.52 (m, 1H), 6.32 (t, J = 11.4 Hz, 1H), 5.36 (dd, J = 17.1, 2.4 Hz, 1H), 5.20 (d, J = 10.3 Hz, 1H), 4.07-3.96 (m, 2H), 3.86 (s, 3H), 1.35 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.0, 146.2, 133.7, 132.0, 131.6, 126.4, 123.3, 122.6, 119.1, 111.5, 69.0, 55.82, 15.65; IR (neat): 2975, 2930, 1678, 1578, 1475, 1459, 1441, 1386, 1263, 1211, 1180, 1069, 1029 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O_2$ [M + H]$^+$ 205.1129; found: 205.1223.

(*E*)-5-(Buta-1,3-dienyl)-1,2,3-trimethoxybenzene and (*Z*)-5-(Buta-1,3-dienyl)-1,2,3-trimethoxybenzene **5l**: colorless liquid; *E:Z* = 1:1; yield: 80%; R$_f$ = 0.65 (10% EtOAc in hexane); NMR data for *E*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.96-6.84 (m, 1H), 6.64 (s, 2H), 6.50-6.37 (m, 2H), 5.35 (d, J= 17.1 Hz, 1H), 5.16 (dd, J = 9.6, 1.5 Hz, 1H), 3.87 (s, 6H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.3 (2C), 137.0, 133.1, 132.8, 130.5, 129.1, 117.5, 103.4 (2C), 60.95, 56.12 (2C); NMR data for *Z*- isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.73-6.66 (m, 1H), 6.54 (s, 2H), 6.51-6.46 (m, 1H), 6.23 (t, J = 11.3, 1H), 5.43-5.30 (m, 1H), 5.23 (d, J = 10.2 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 6H), ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.0 (2C), 137.9, 137.3, 133.0, 132.8, 130.3, 119.8, 106.2 (2C), 60.93, 56.1 (2C); IR (neat): 2973, 2932, 1673, 1560, 1476, 1462, 1444, 1387, 1261, 1211, 1061, 1020 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O_3$[M + H]$^+$ 221.1178; found: 221.1178.

Buta-1,3-diene-1,1-diyldibenzene **8**: colorless liquid; yield: 87%; R_f = 0.4 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 3H), 7.23-7.10 (m, 7H), 6.64 (d, *J* = 11.2 Hz, 1H), 6.37 (td, *J* = 10.4, 16.9 Hz, 1H), 5.31 (dd, *J* = 2.0, 16.6 Hz, 1H), 5.05 (dd, *J* = 2.2, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.1, 139.7, 135.0 (2C), 130.4 (2C), 128.5, 128.2 (2C), 128.18 (2C), 127.6, 127.5, 127.4, 118.6; IR (neat): 2967, 2923, 1573, 1470, 1456, 1446, 1380, 1269, 1215, 1183, 1061, 1023 cm^{-1}; NMR data matching with reported one.[4b]

4-(2-Methoxypent-4-ynyl)biphenyl **9**: To a stirred solution of 2-(biphenyl-4-yl)acetaldehyde[21] (80 mg, 0.38 mmol) in THF (2.5 mL) were added propargyl bromide (90 mg, 0.76 mmol) and then zinc dust (124 mg, 1.9 mmol) at room temperature. After being stirred for 30 min, reaction mixture was filtered, washed with EtOAc (50 mL). The filtrate was washed with NH_4Cl solution (20 mL), water (30 mL), brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude (83 mg) was dissolved in DMF (2 mL) to this solution were added MeI (169 mg, 1.33 mmol) and then NaH (26 mg, 0.66 mmol; 60% in mineral oil) at 0 °C. After being stirred for 1 h, (reaction monitored by TLC) 2 mL of water was added, diluted with 1:1 EtOAc:Hexane (30 mL) organic phase was separated, aqueous phase was extracted with 1:1 EtOAc:Hexane (30 mLx2) combined organic phase was washed with water (25 mL), brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude was purified over silica gel column chromatography (5% EtOAc in Hexane) furnished compound **9** (84 mg, 83% for two steps) as a colorless liquid; R_f = 0.55 (7% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 2H), 7.59-7.53 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39-7.33 (m, 3H), 3.65-3.56 (m, 1H), 3.44 (s, 3H), 3.01 (d, *J* = 6.4 Hz, 2H), 2.44 (dt, *J* = 2.7, 5.0 Hz, 2H), 2.12 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 139.3, 137.3, 129.9 (2C), 128.8 (2C), 127.2, 127.1 (2C), 127.1 (2C), 80.9, 80.3, 70.5, 57.3, 39.1, 22.7; IR (neat) 3292, 3028, 2982, 2927, 2826, 2178, 1604, 1486, 1449, 1358, 1190, 1102, 1008 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{18}ONa$ [M + Na]$^+$ 273.1255; found: 273.1262.

(*E*)-4-(Pent-1-en-3-ynyl)biphenyl **10**: colorless liquid; yield: 84%; R_f = 0.6 (3% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.45 (m, 4H), 7.40-7.32 (m, 4H), 7.31-7.23 (m, 1H), 6.83 (d, *J* = 16.6 Hz, 1H), 6.11 (dq, *J* = 16.2, 2.3 Hz, 1H), 1.95 (d, *J* = 2.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.5, 139.6, 135.6, 128.82 (2C), 128.8, 127.4, 127.3 (2C), 126.9 (2C), 126.5, 108.8, 88.6, 79.1, 4.6; HRMS (ESI): *m/z* calcd for $C_{17}H_{15}$[M + H]$^+$ 219.117; found: 219.1174.

4-(2-Methoxypent-3-ynyl)biphenyl **11**: colorless liquid; yield: 10%; R_f = 0.5 (3% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 2H), 7.57-7.51 (m, 2H), 7.47-7.40 (m, 2H), 7.38-7.33 (m, 3H), 4.19-4.10 (m, 1H), 3.42 (s, 3H), 3.11-2.94 (m, 2H), 1.87 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 139.4, 136.7, 130.0 (2C), 128.7 (2C), 127.1, 127.04 (2C), 126.9 (2C), 97.3, 82.8, 72.3, 56.4, 42.1, 3.6; IR (neat): 3025, 2952, 2912, 2849, 2213, 1709, 1601, 1518, 1484, 1409, 1268, 1220, 1107, 1010, 954 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{18}ONa$ [M + Na]$^+$ 273.1255; found: 273.1257.

1-(Prop-1-ynyl)cyclohexanol **13**: colorless liquid; yield: 76% R_f = 0.4 (8% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 1 H), 1.93-1.76 (m, 1H), 1.83 (s, 3H), 1.73-1.58 (m, 3H), 1.58-1.41 (m, 5H), 1.29-1.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.1, 79.9, 68.7, 40.2 (2C), 25.2, 23.3 (2C), 3.5; IR (neat) 3445, 2925, 2855, 2173, 1598, 1520, 1426, 1390, 1338, 1222, 1190, 1171 cm^{-1}; HRMS (ESI): *m/z* calcd for C_9H_{13} [M + H – H_2O]$^+$ 121.1017; found: 121.1009.

2,4-Dimethoxy-1-(pent-3-yn-2-yl)benzene and compound **6**/**7**: colorless liquid; ratio of **6:7** = 2:3; yield: 83%; R_f = 0.5 (4% EtOAc in hexane);); NMR data for **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 1H), 6.63-6.37 (m, 2H), 4.16-4.03 (m, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 1.89 (d, *J* = 2.4 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 156.9, 124.8, 121.0, 104.2, 97.3, 82.7, 76.5, 55.3 (2C), 24.9, 23.3, 3.6; NMR data for **7** isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 9.1 Hz, 1H), 6.56-6.44 (m, 2H), 5.19 (dd, *J* = 2.9, 6.8 Hz, 1 H), 3.84 (s, 3H), 3.82 (s, 3H), 2.09 (d, *J* = 2.9 Hz, 3H), 1. (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 159.8, 156.9, 129.6, 128.2, 104.3, 99.2, 98.4, 84.0, 55.6, 55.3, 19.8, 14.6; IR (neat) 3050, 3959, 2848, 1758, 1606, 1586, 1500, 1459, 1414, 1292, 1261, 1205, 1111, 1032 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}O_2$[M + H]$^+$ 205.1229; found: 205.1222.

4.5 General procedure for the synthesis of Diels-Alder Adducts.

Mixture of **5c** (50 mg, 0.28 mmol), methylvinyl ketone **16** (78 mg, 1.12 mmol), hydroquinone (4 mg) and toluene (0.5 mL) was heated in a sealed tube at 130–140 °C. After being heated for 46 h, reaction mixture was concentrated the resulting residue was purified over silica gel column chromatography (4% EtOAc in hexane) to give a separable mixture of **17a**, **17b** (39 mg, 57%; 19 mg, 28% yield respectively) as colorless solids.

1-(2-(Naphthalen-1-yl)cyclohex-3-enyl)ethanone **17a**: mp: 56-58 °C; R_f = 0.55 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.89-7.85 (m, 1H), 7.75 (dd, *J* = 2.0, 7.3 Hz, 1H), 7.55-7.46 (m, 2H), 7.46-7.38 (m, 2H), 5.96 (qd, *J* = 3.3, 10.2 Hz, 1H), 5.79 (dd, *J* = 2.7, 10.0 Hz, 1H), 4.60 (brs, 1H), 3.03 (q, *J* = 5.9 Hz, 1H), 2.33-2.22 (m, 1H), 2.22-2.10 (m, 1H), 1.98 (s, 3H), 1.95 (q, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 139.8, 134.2, 131.3, 129.7, 129.0, 127.3, 126.8, 126.2, 126.1, 125.5, 125.4, 123.5, 53.5, 38.9, 29.1, 23.66, 23.62; IR (neat) 3024, 2925, 2838, 1706, 1595, 1509, 1428, 1355, 1159, 1038 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{22}ON$ [M +NH_4]$^+$ 273.1255; found: 273.1250.

1-(5-(Naphthalen-1-yl)cyclohex-3-enyl)ethanone**17b**: mp: 58-60 °C; R_f = 0.5 (5% EtOAc in hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 1H), 7.87-7.83 (m, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.54-7.45 (m, 4H), 6.05-5.99 (m, 1H), 5.87-5.81 (m, 1H), 4.76 (brs, 1H), 3.21 (ddd, *J* = 3.4, 6.6, 10.5 Hz, 1H), 2.46 - 2.35 (m, 1H), 2.23 (ddd, *J* = 2.9, 6.1, 9.0 Hz, 1H), 2.12-2.03 (m, 1H), 1.93-1.85 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 136.7, 133.9, 131.8, 128.9, 128.8, 127.7, 127.6, 127.2, 126.1, 125.5, 125.2, 123.2, 52.0, 36.6, 28.8, 24.1, 21.1; IR (neat) 3022, 2923, 1703, 1595, 1510, 1429, 1392, 1352, 1220, 1159, cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{18}ONa$ [M + Na]$^+$ 273.1255; found: 273.1251.

Diethyl 3-(naphthalen-1-yl)cyclohexa-1,4-diene-1,2-dicarboxylate **15**: Colorless liquid; yield: 89%; R_f = 0.55 (5% EtOAc in hexane); ^{1}H NMR (400MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.88-7.85 (m, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.59 - 7.48 (m, 2H), 7.45 - 7.35 (m, 2H), 5.89-5.79 (m, 2H), 5.28 (br. s., 1H), 4.27 (q, *J* = 7.3 Hz, 2H), 3.86-3.73 (m, 2H), 3.40-3.28 (m, 1H), 3.17-3.03 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.73-0.64 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6 (2C), 134.8, 133.9, 131.2, 128.8, 127.6, 127.3, 126.7, 126.2, 126.0, 125.6, 125.5, 124.7, 123.1, 121.0, 61.3, 60.7, 39.9, 27.5, 14.0, 13.3; IR (neat) 2981, 1717, 1641, 1588, 1449, 1391, 1367, 1251, 1174, 1150, 1104, 1061, 1020 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{22}O_4Na$ [M + Na]$^+$ 373.1416; found: 373.1395.

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Supplementary Material

Supplementary data related to this article can be found at.

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Supporting Information

for

Superoxide mediated isomerization of 4-aryl-but-1-ynes to 1-aryl-1,3-butadienes

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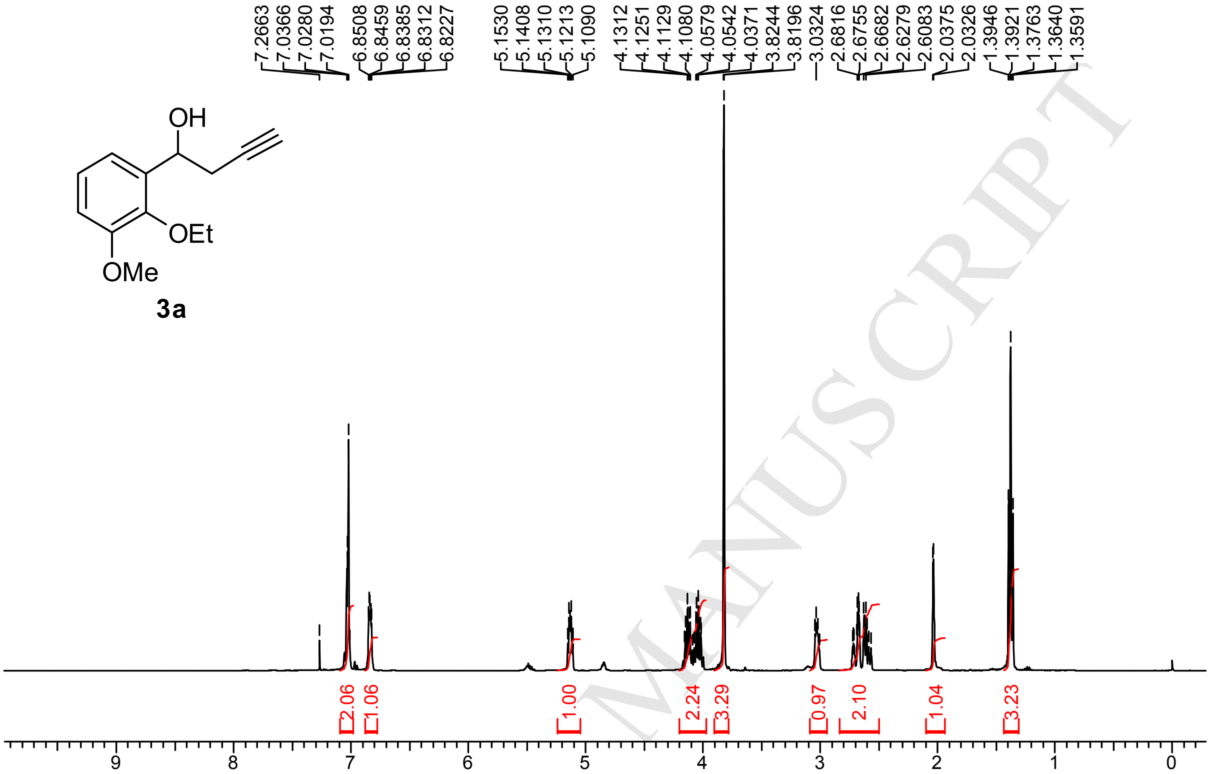
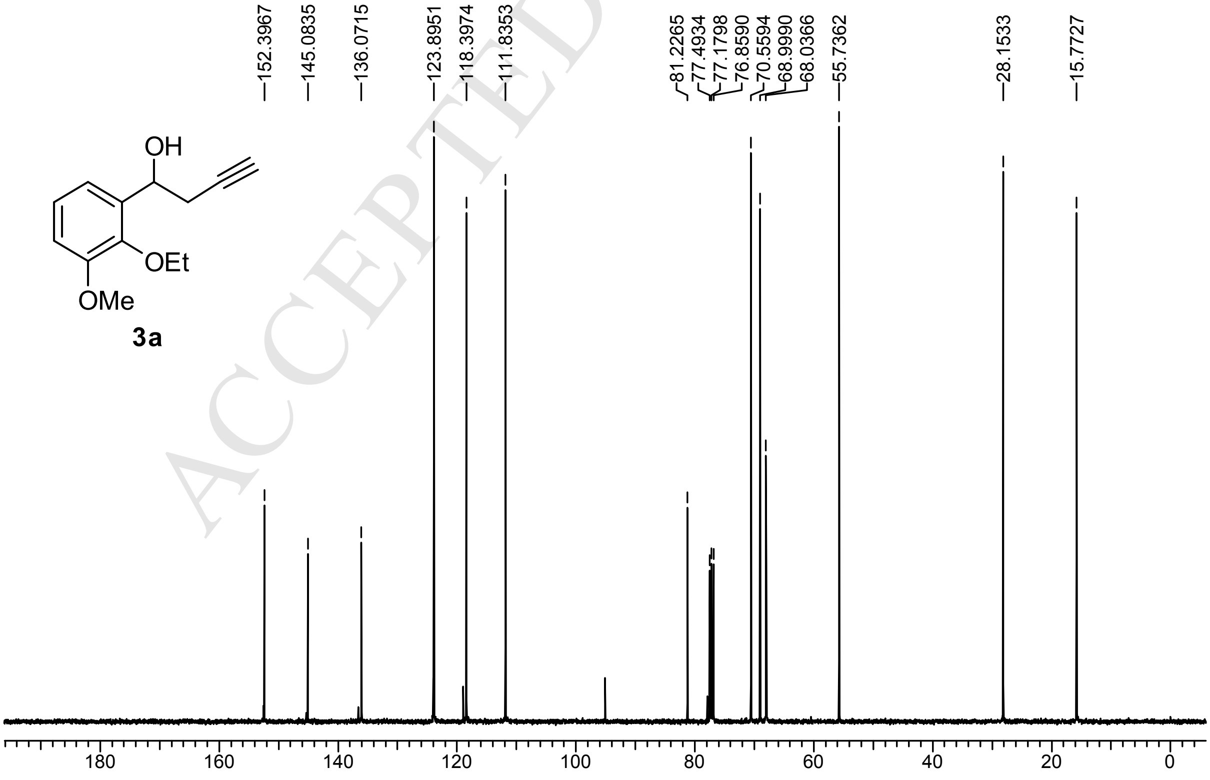
Table of content

NMR Spectra

Copies of ^{1}H and ^{13}C NMR spectra of propargylation products 3:

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **3a** in $CDCl_3$





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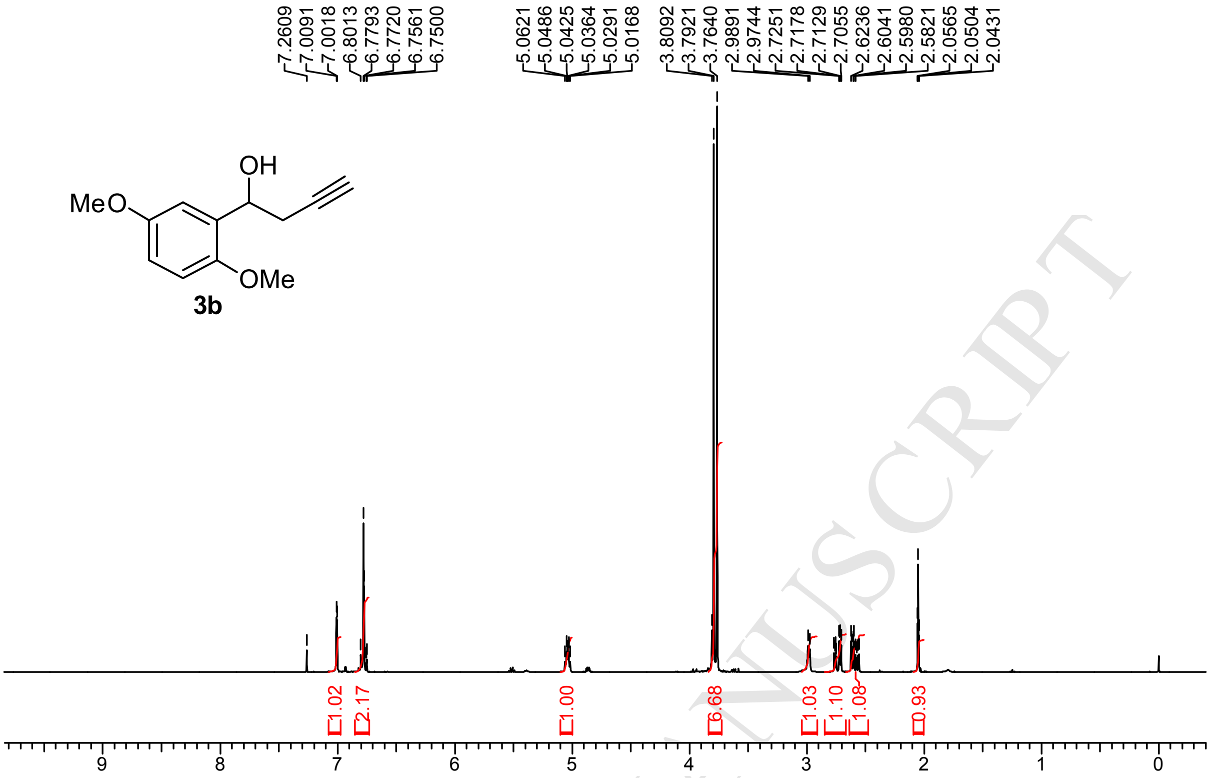

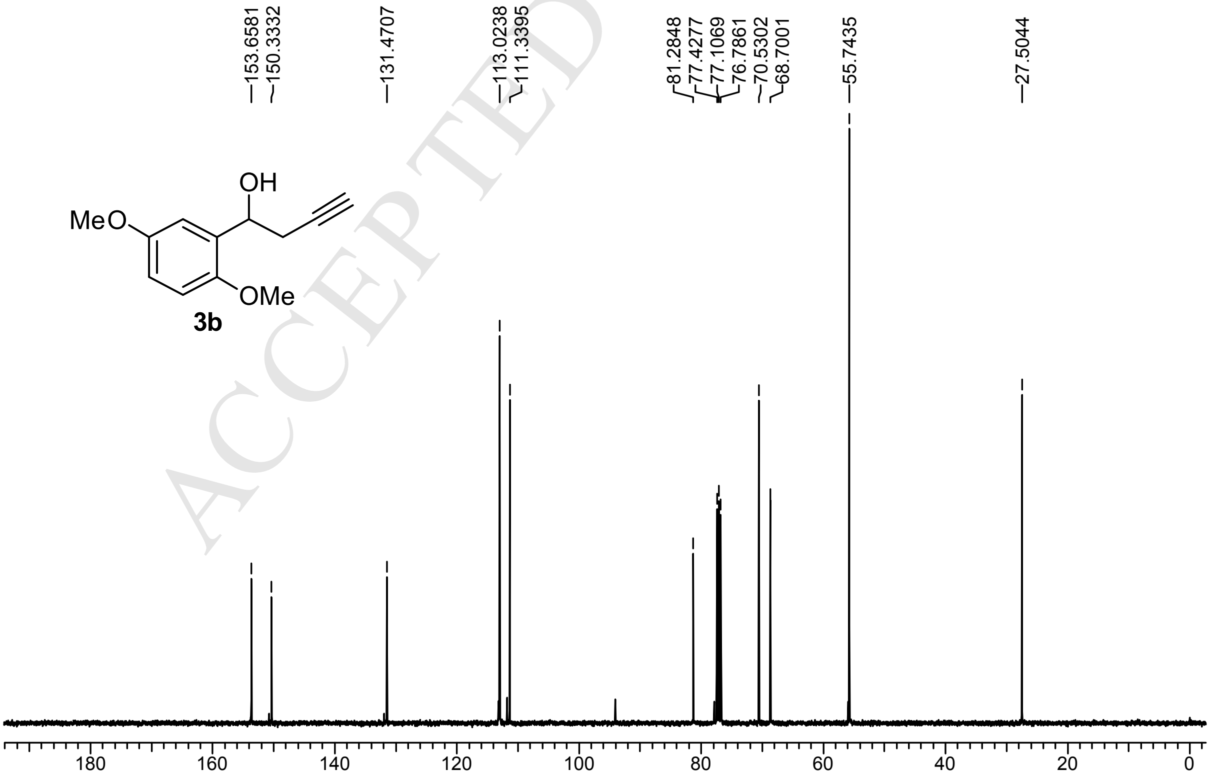

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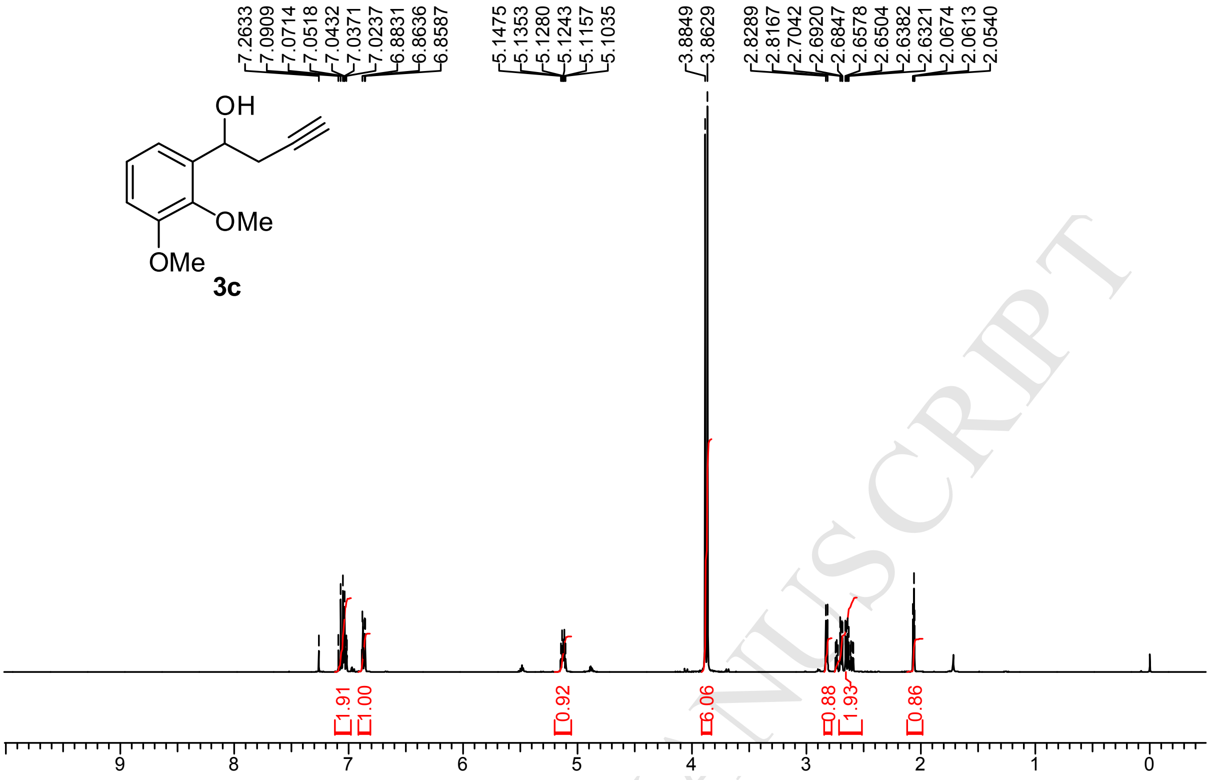

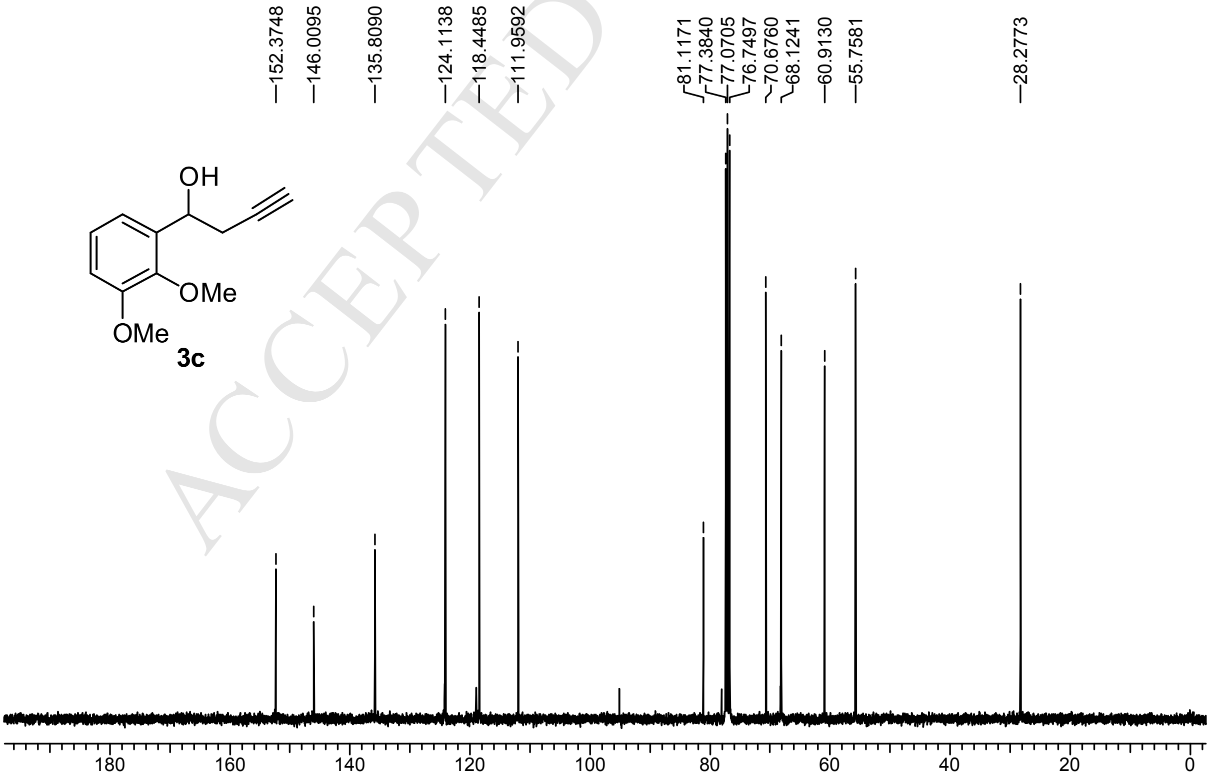

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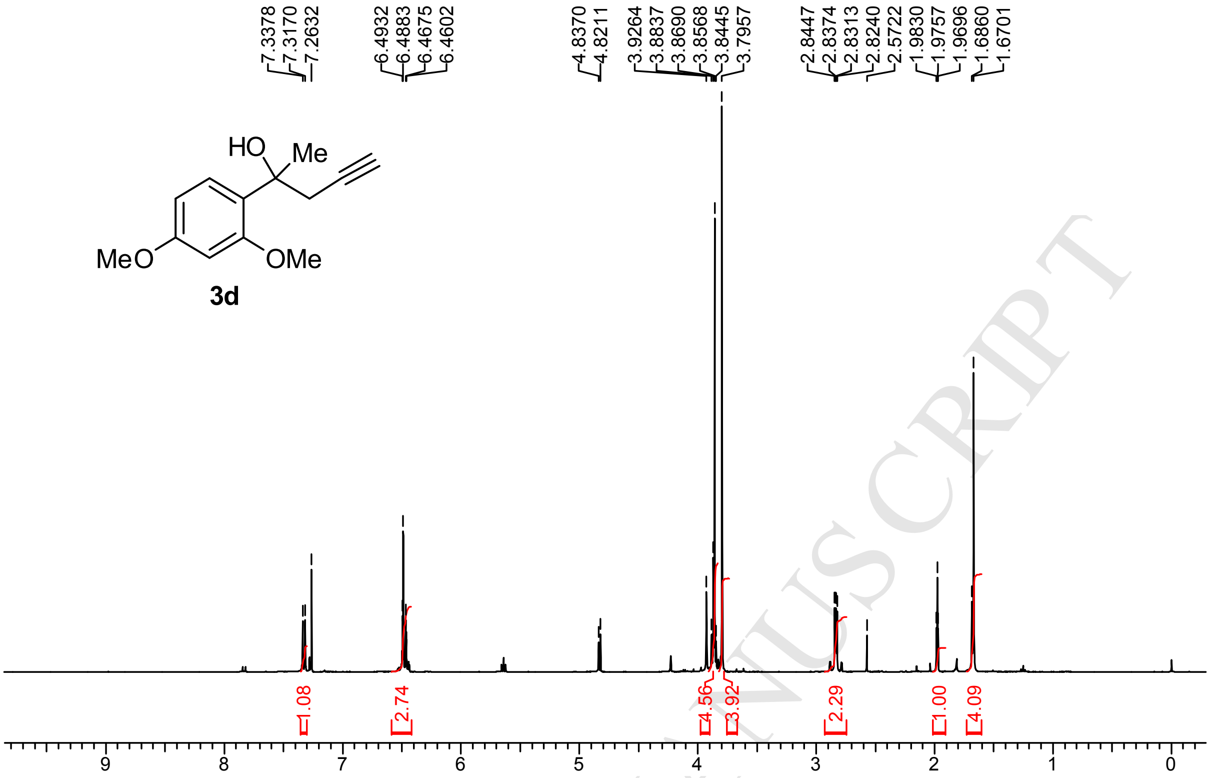
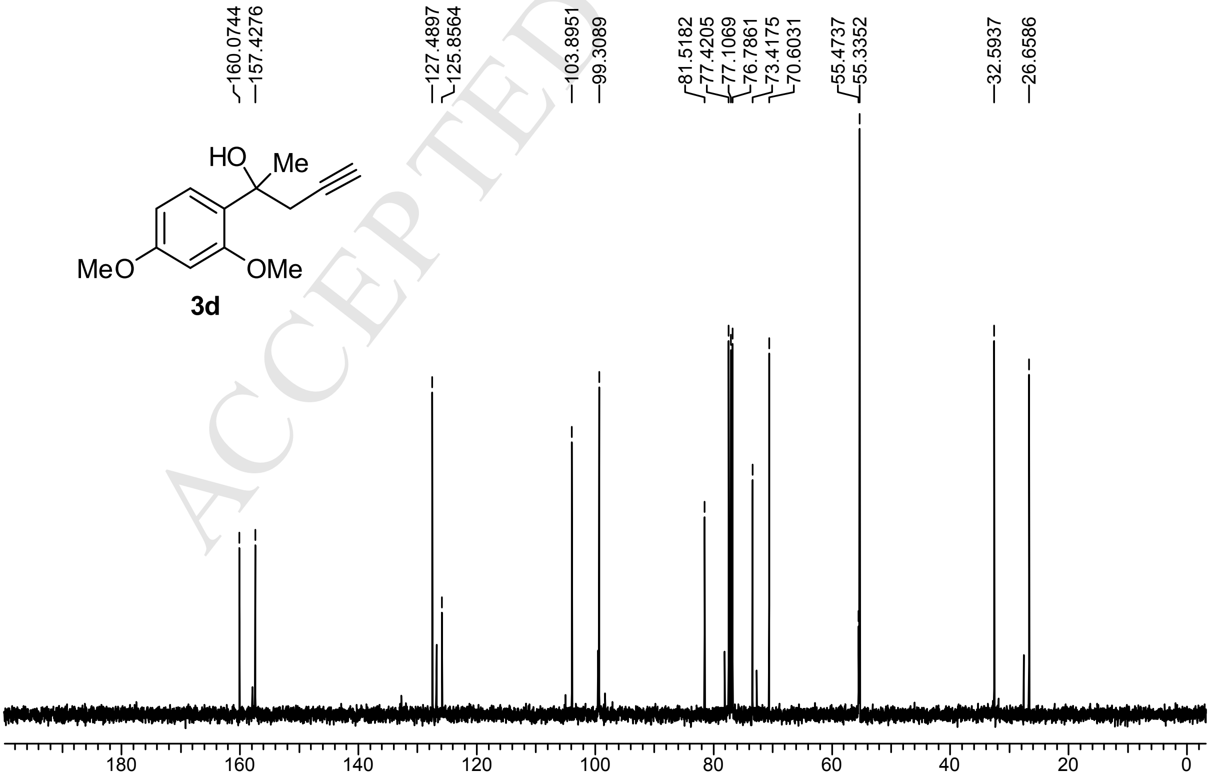
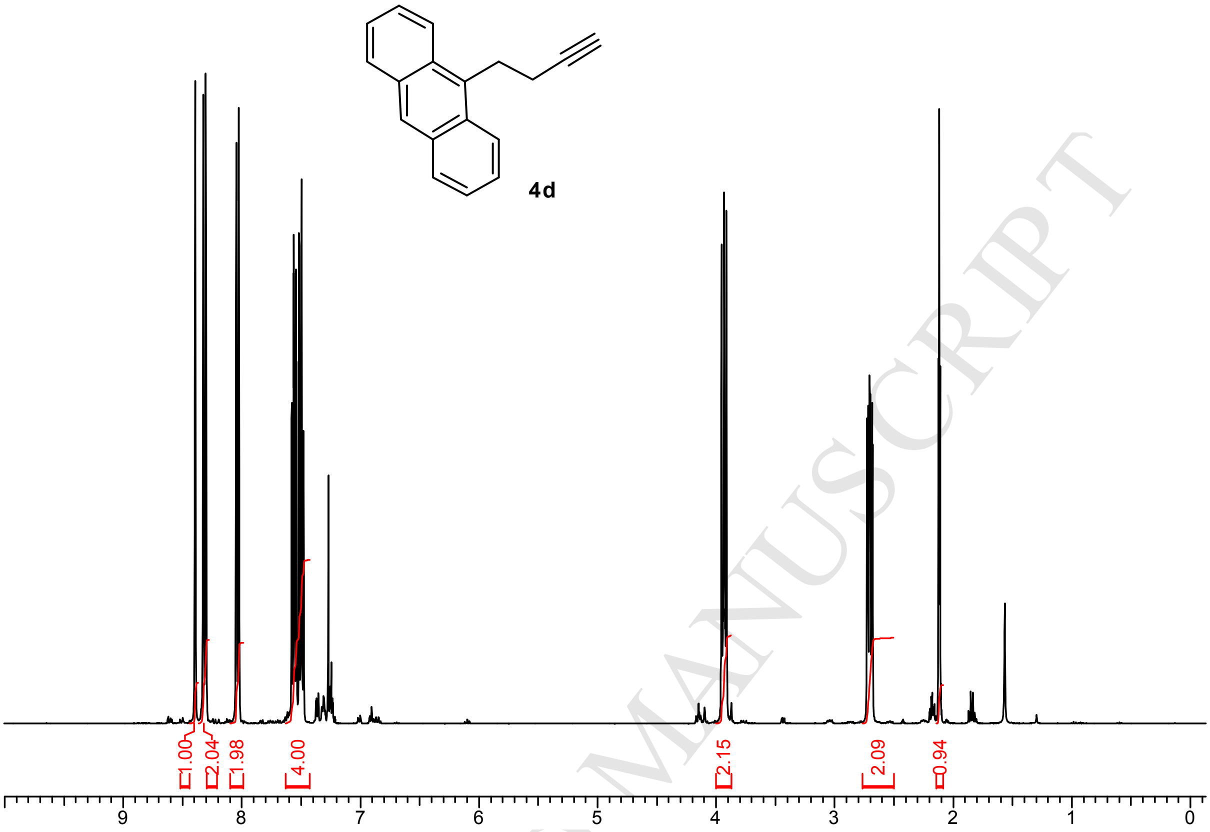
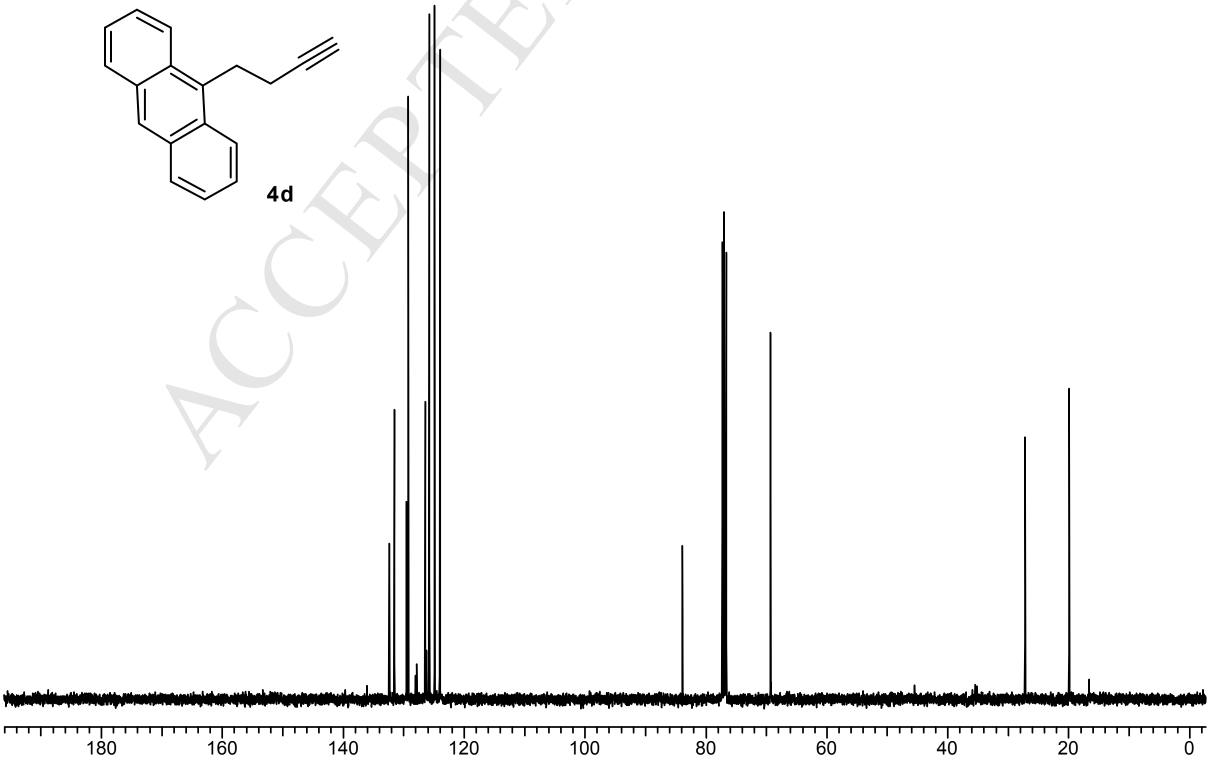




Copies of ^{1}H and ^{13}C NMR spectra of deoxygenation products 4:

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **4d** in $CDCl_3$





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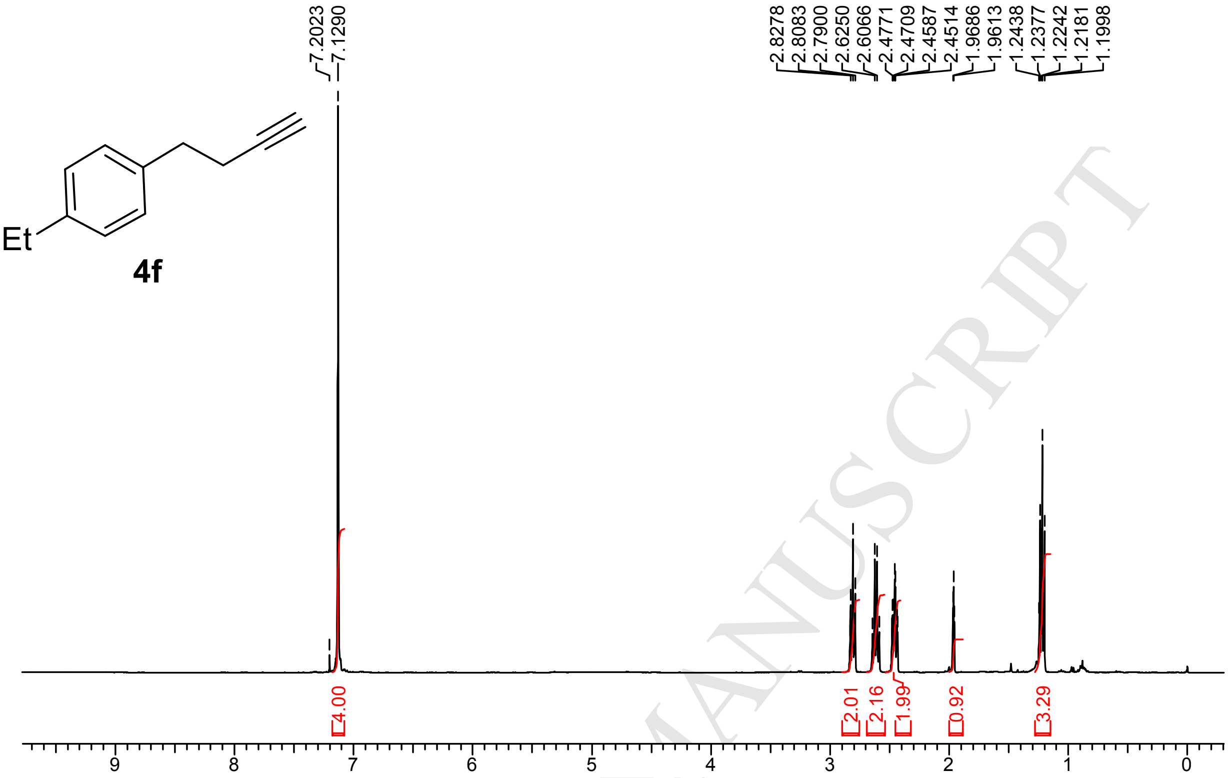

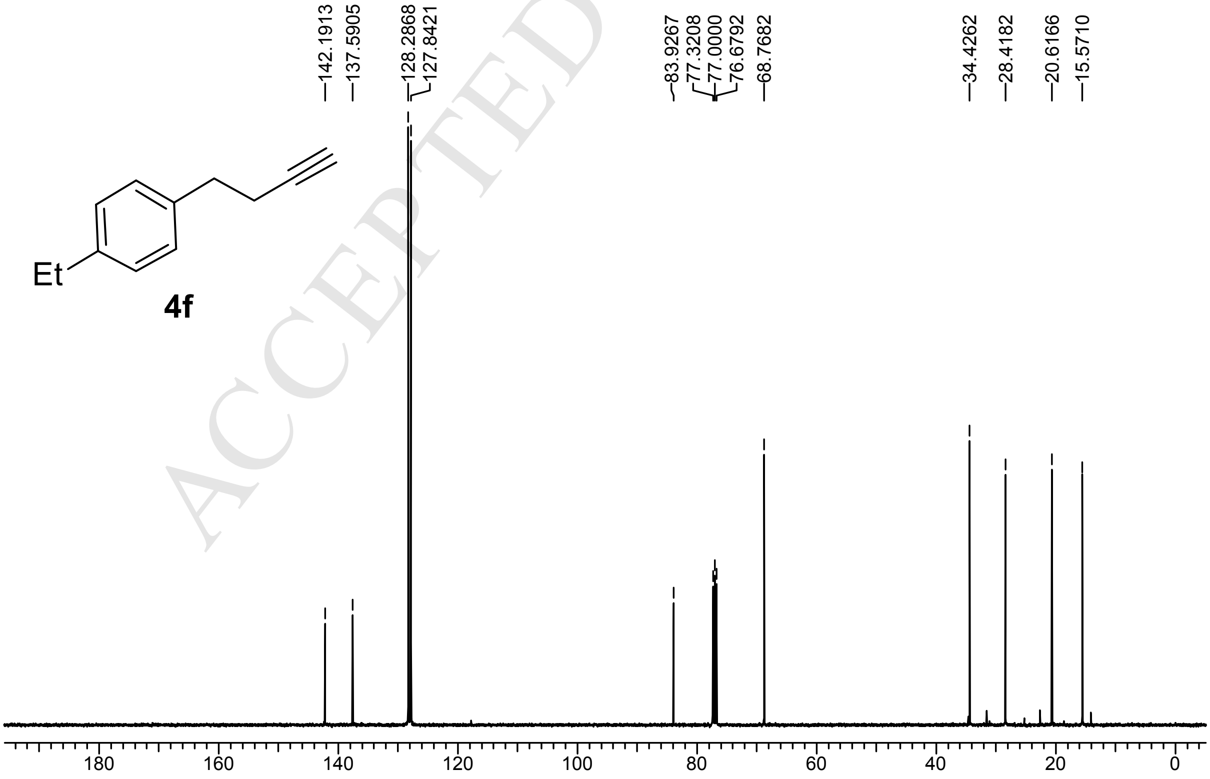

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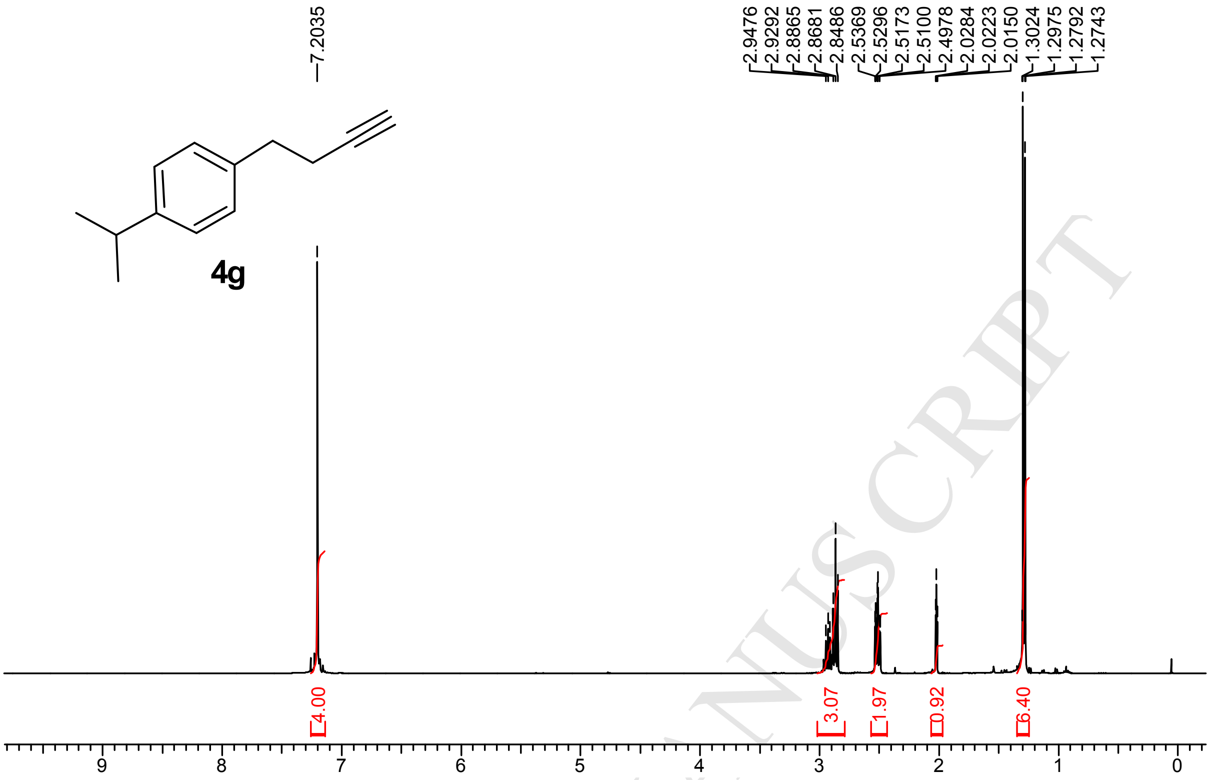

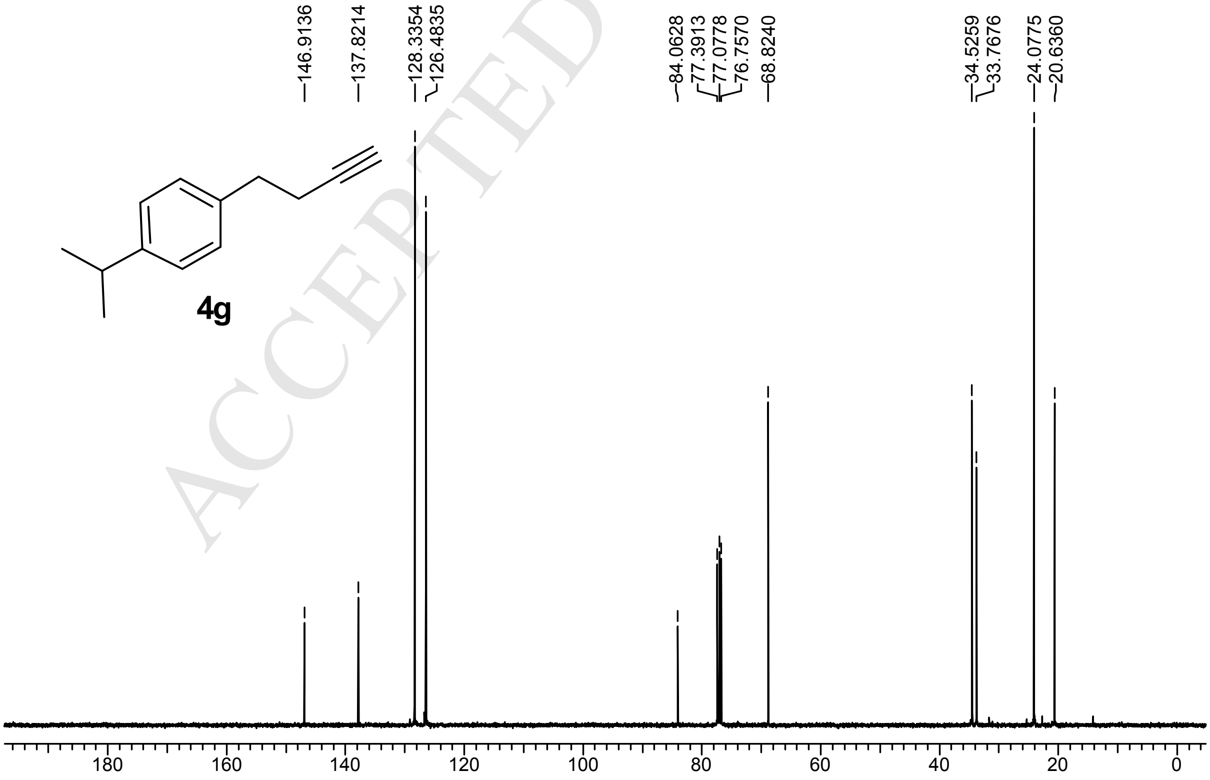

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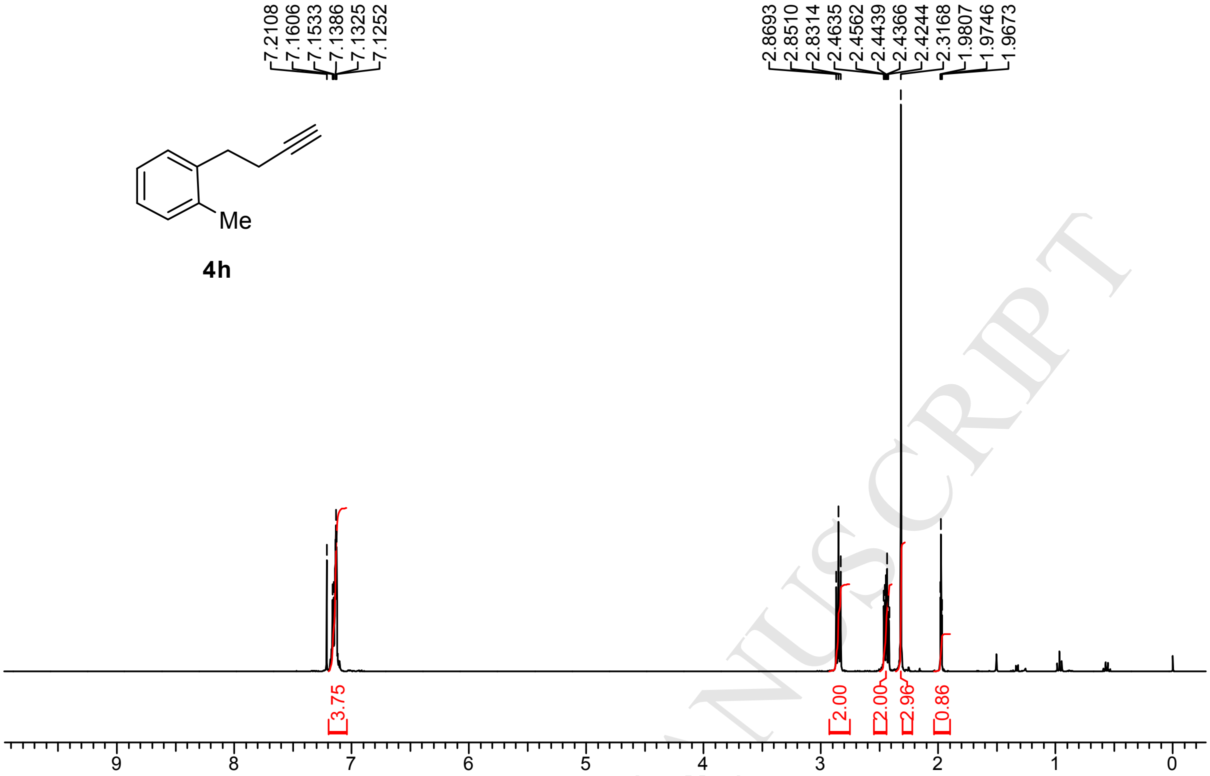

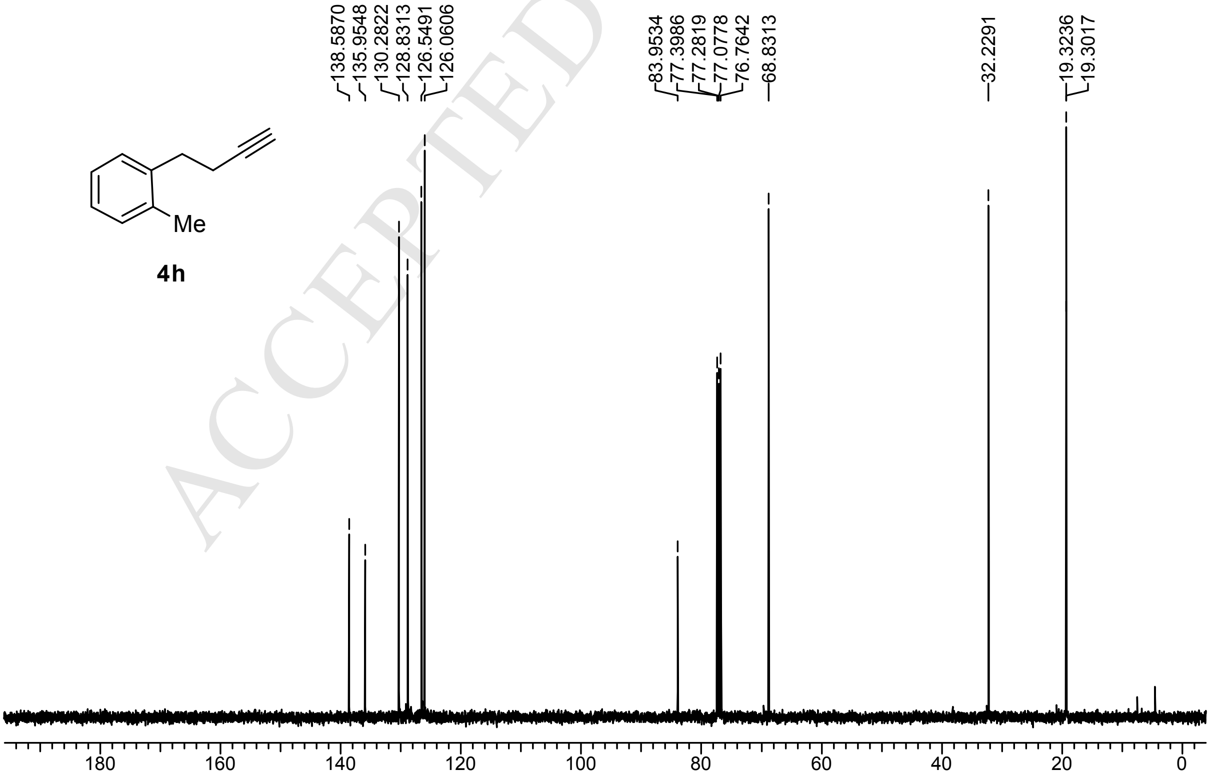

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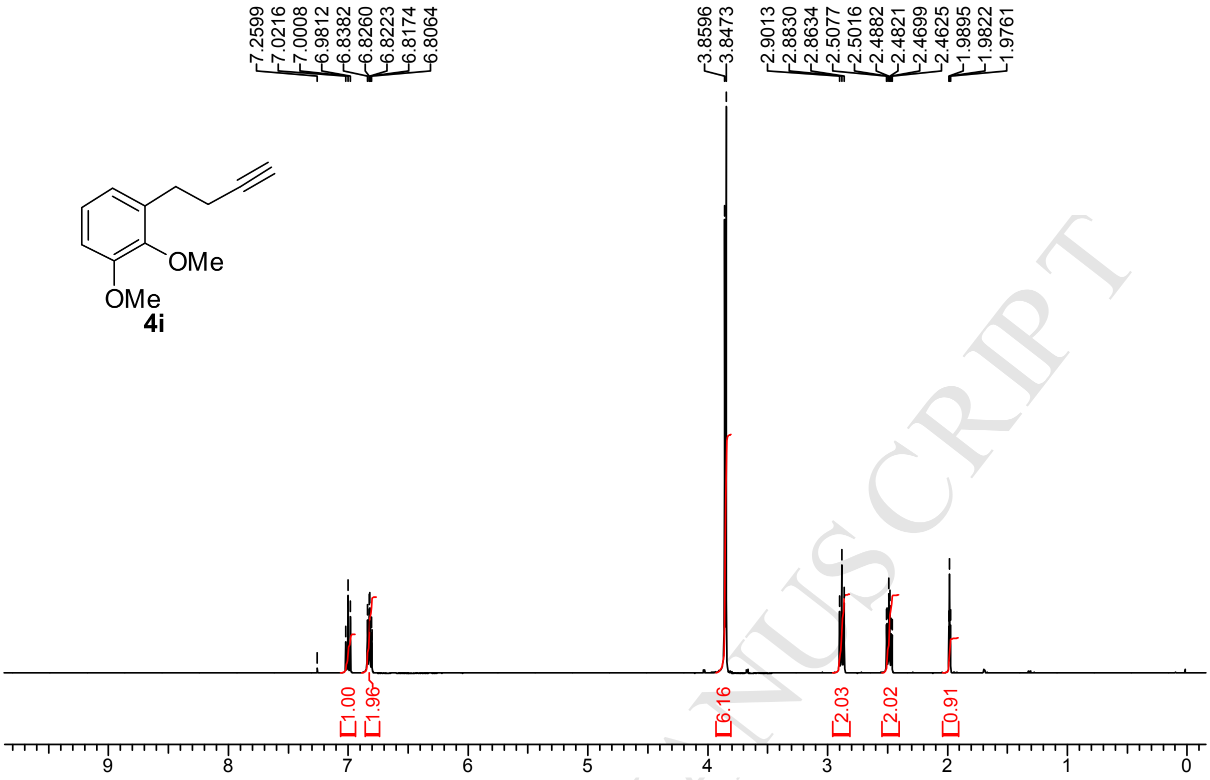
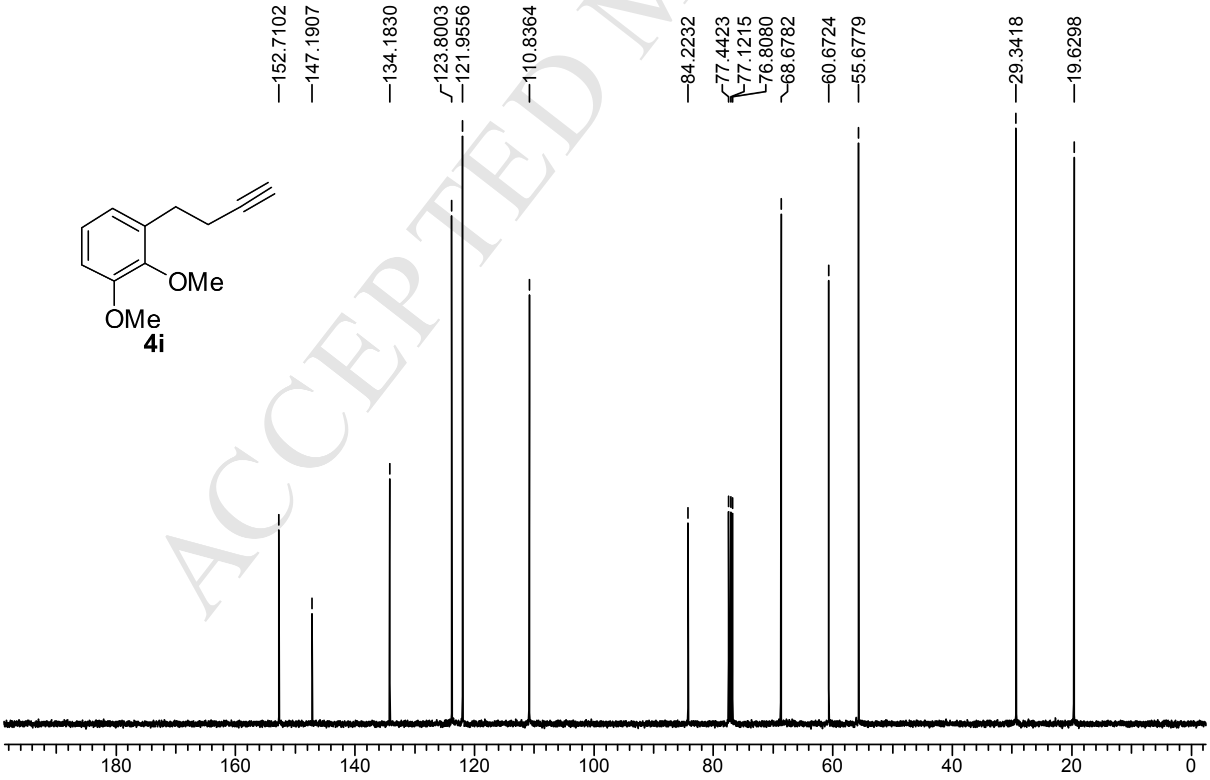
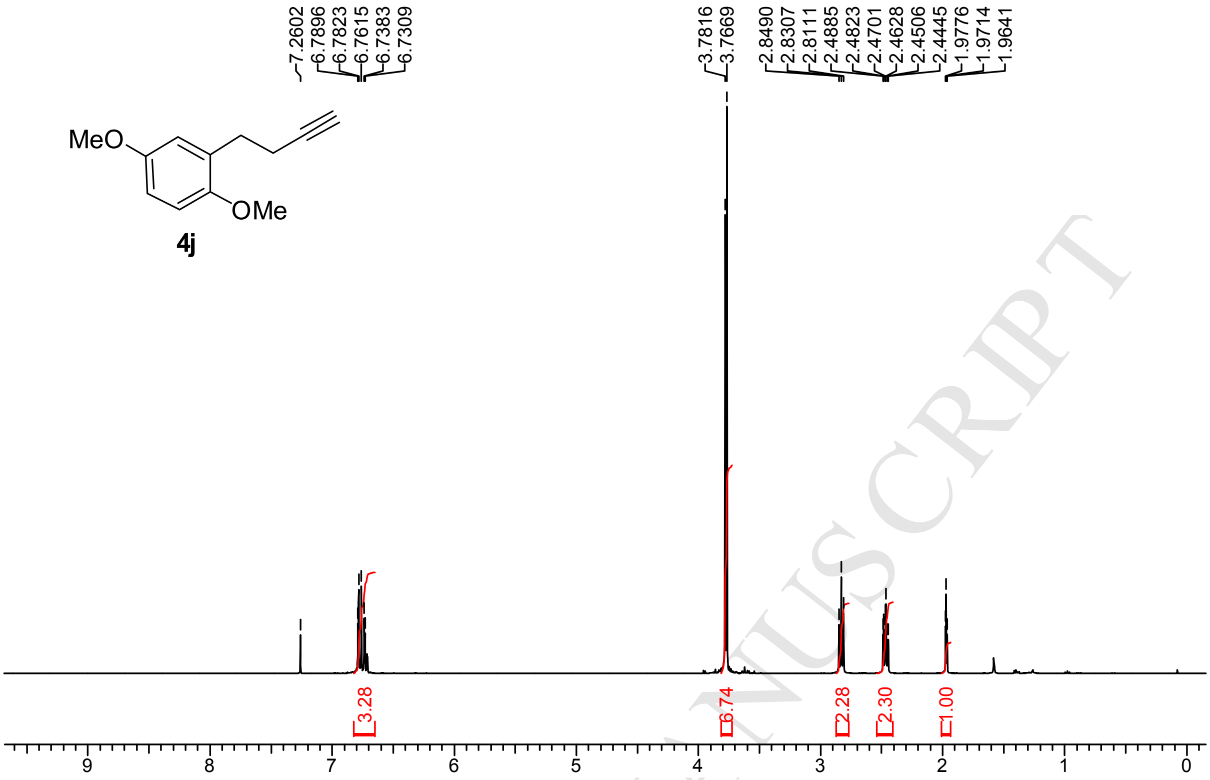
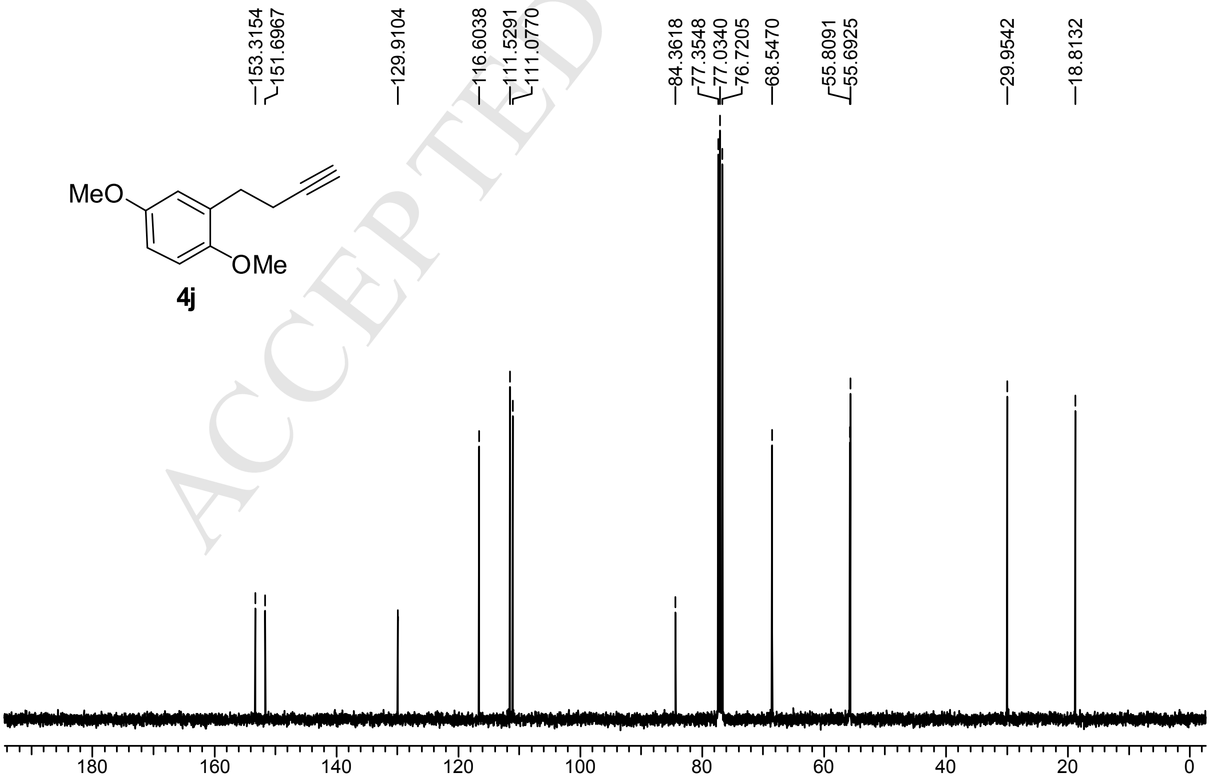


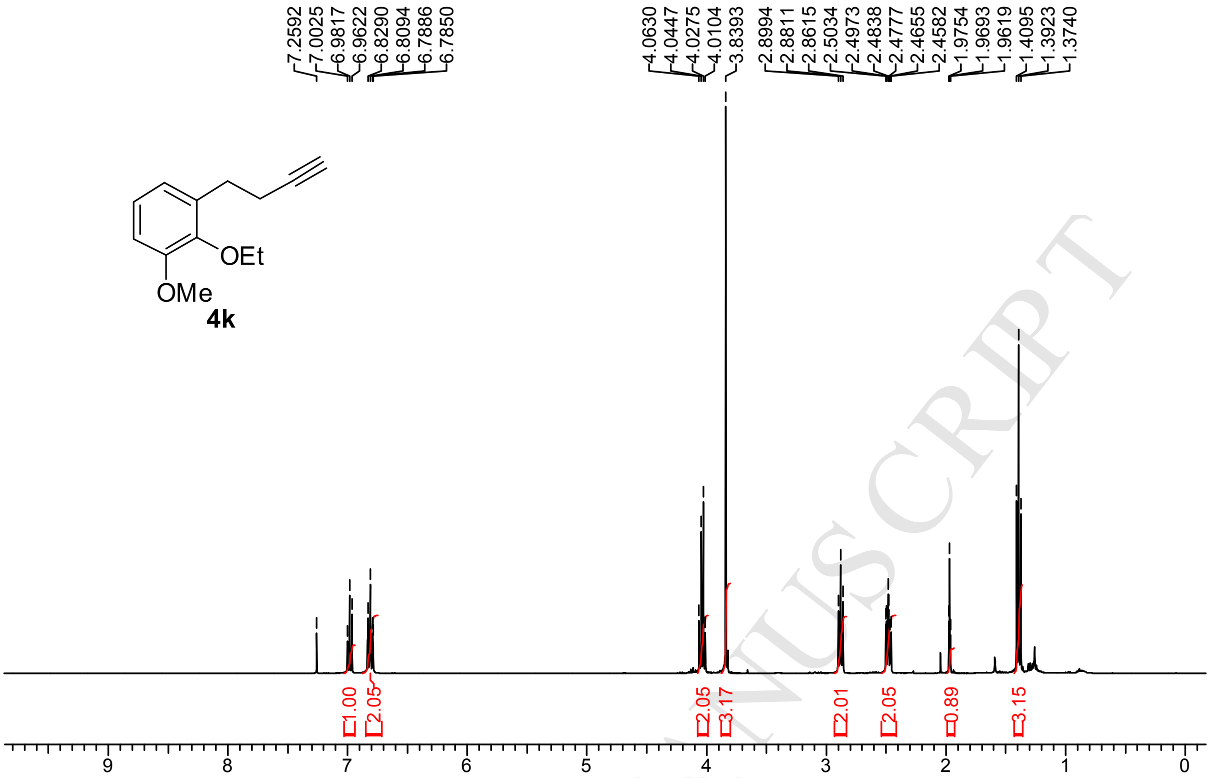


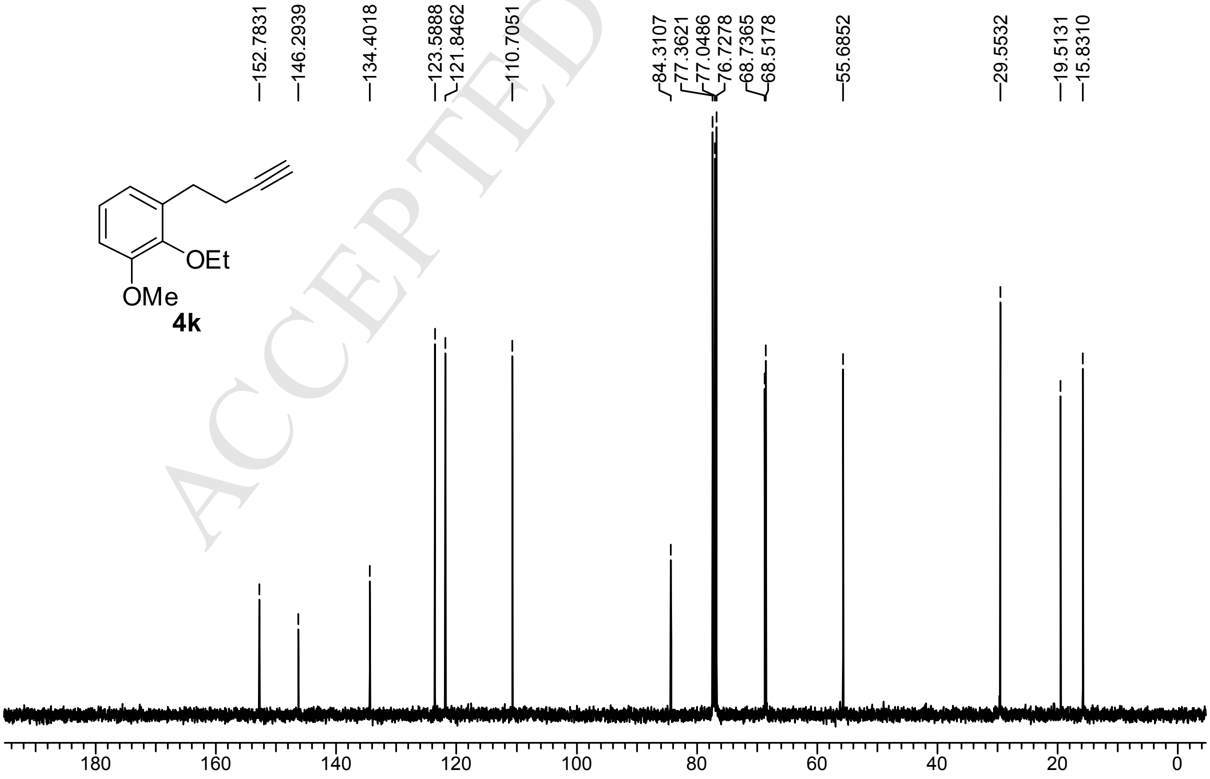
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **4j** in $CDCl_3$



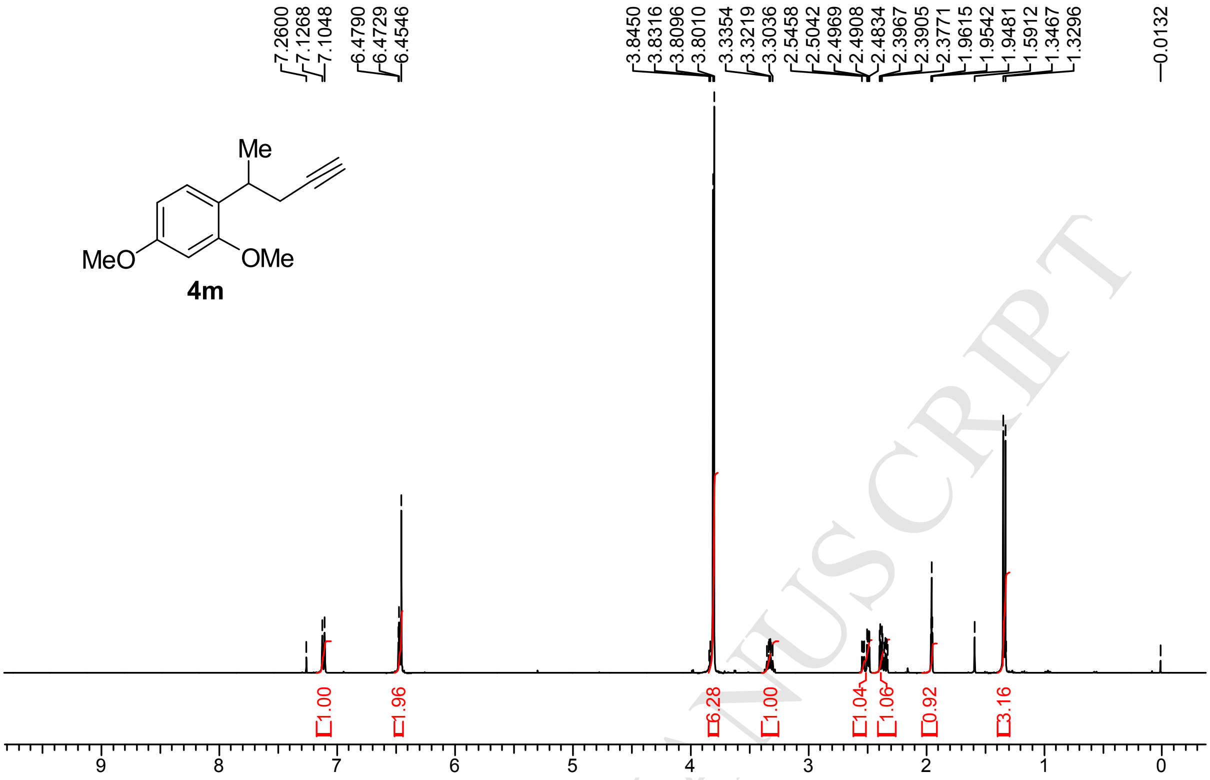


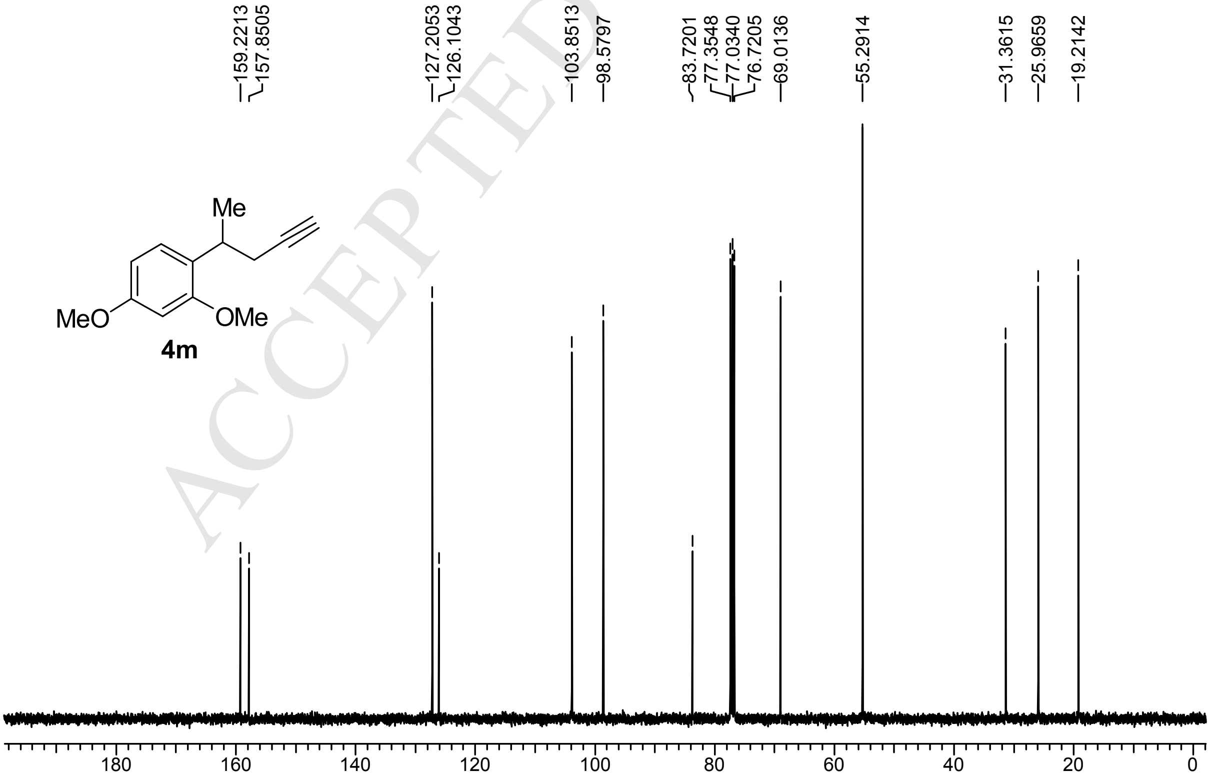
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **4k** in $CDCl_3$





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **4m** in $CDCl_3$





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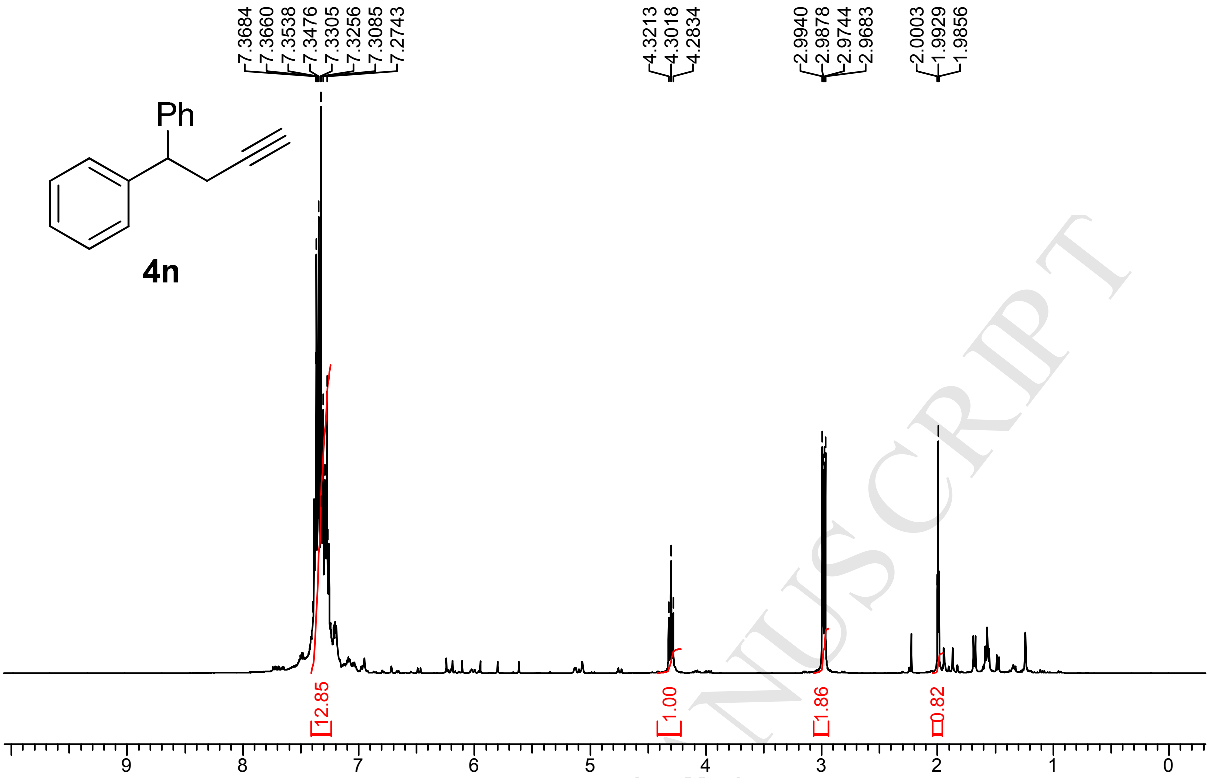
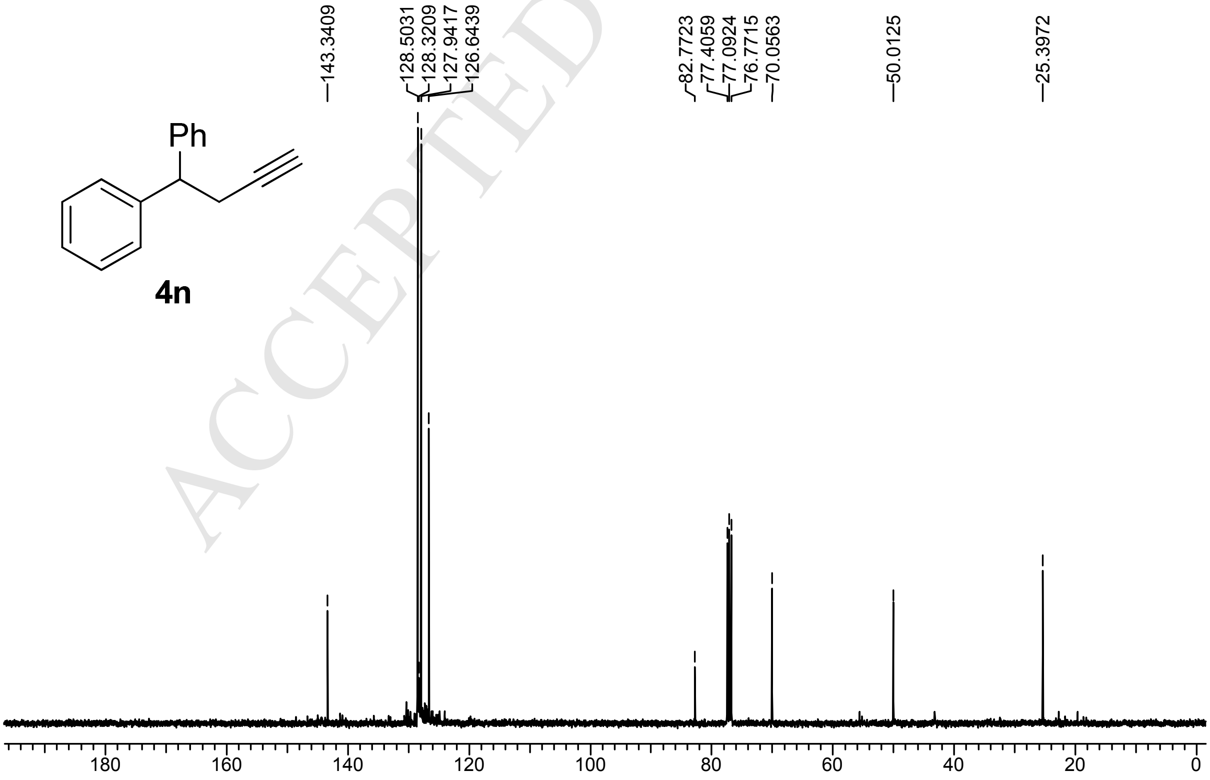
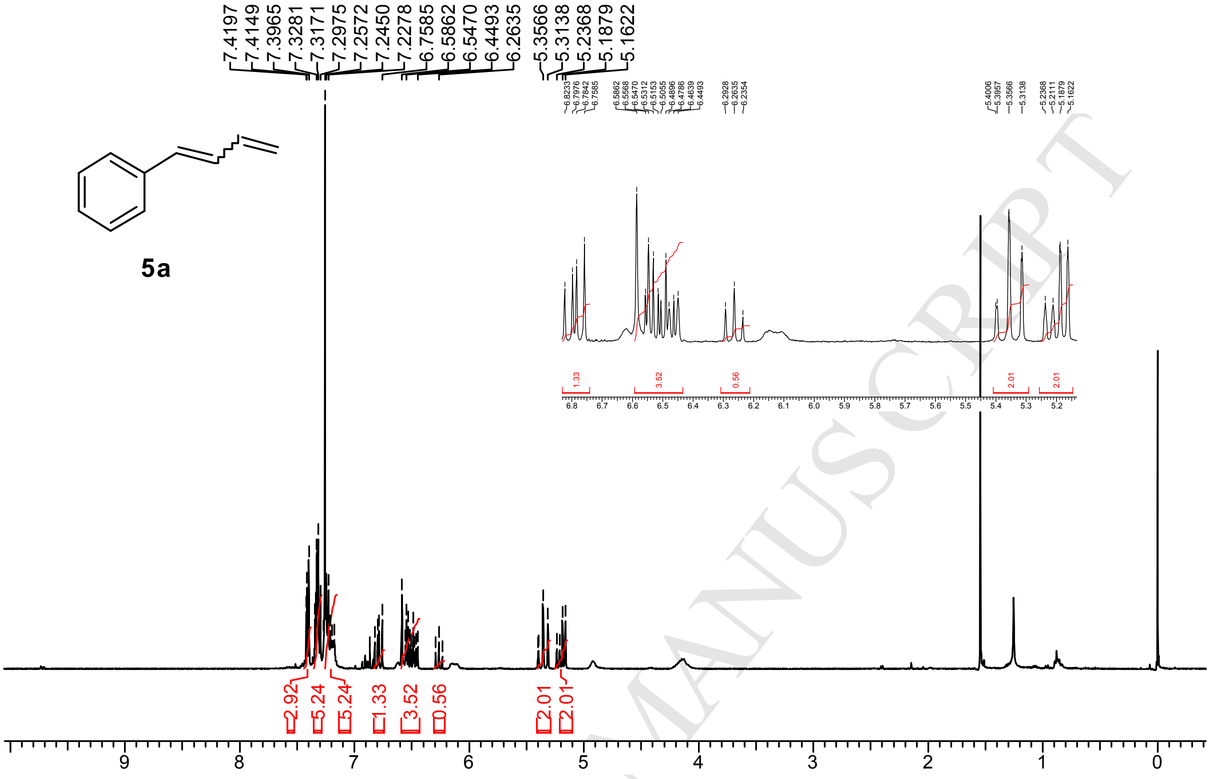
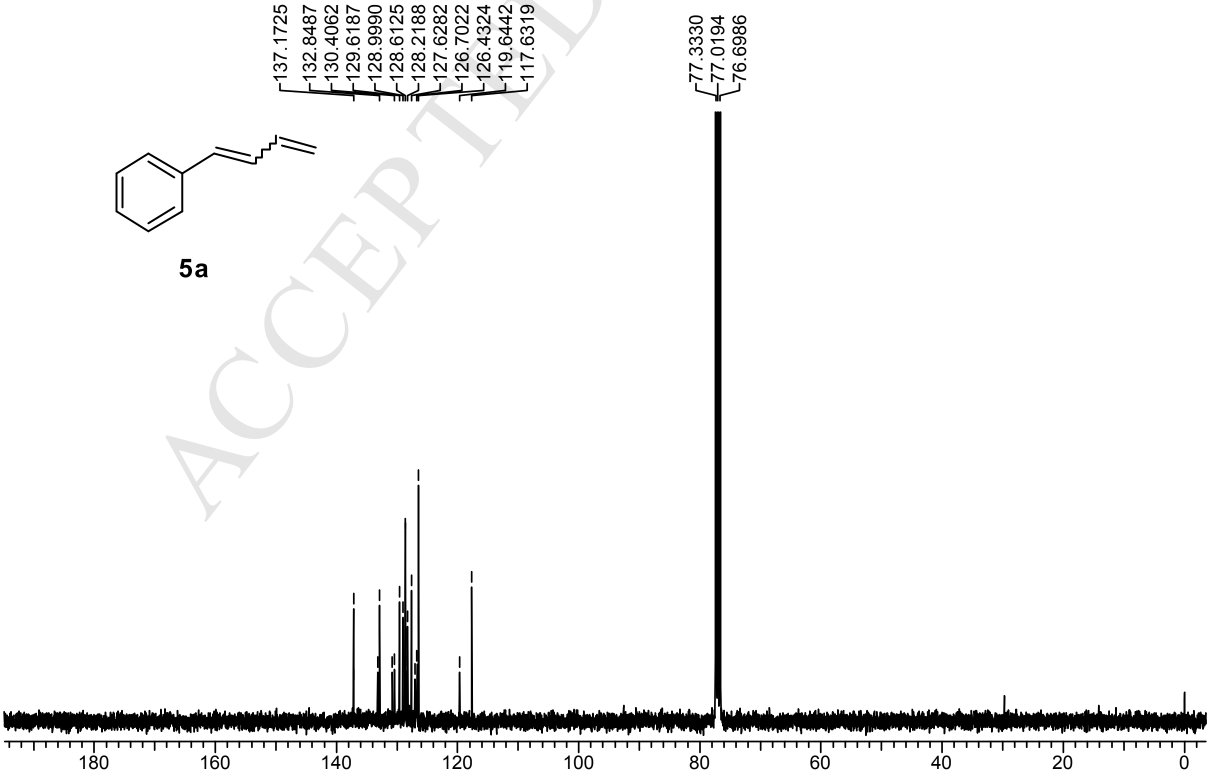




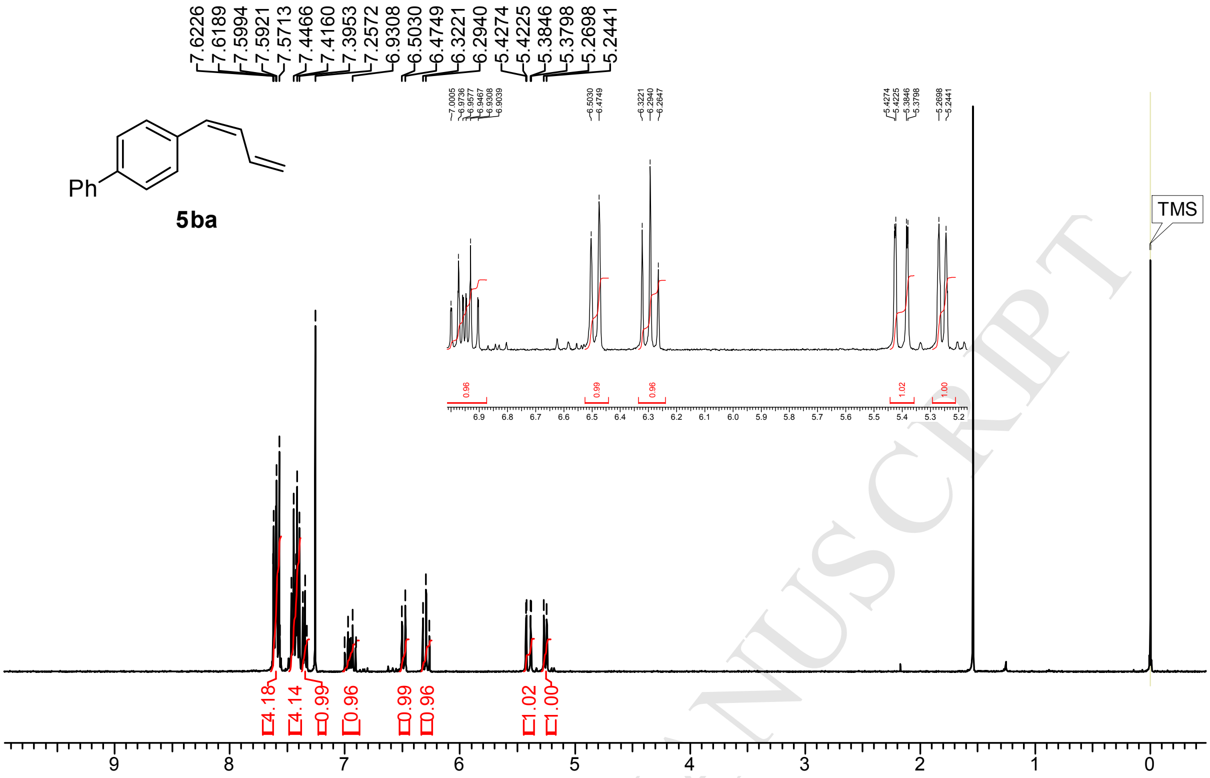
Copies of ^{1}H and ^{13}C NMR of 1-Aryl-1,3-butadienes 5:

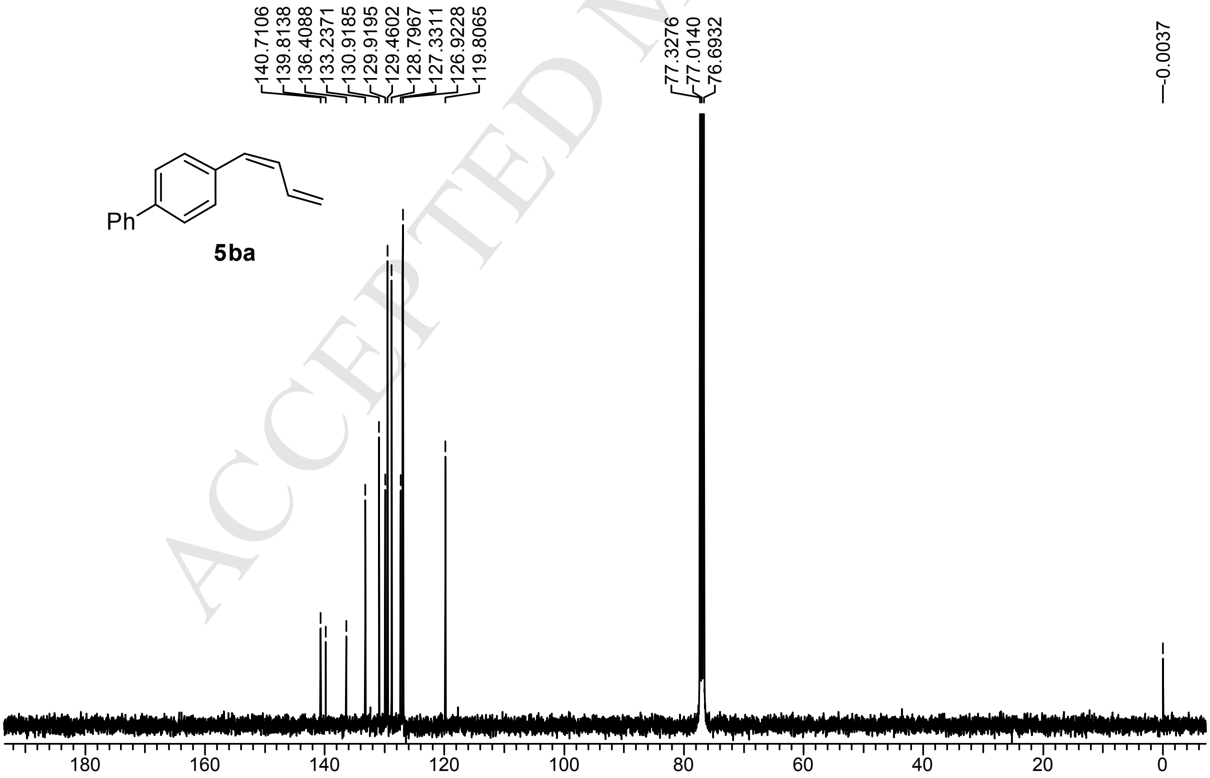
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5a** in $CDCl_3$





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5ba** in CDCl$_3$





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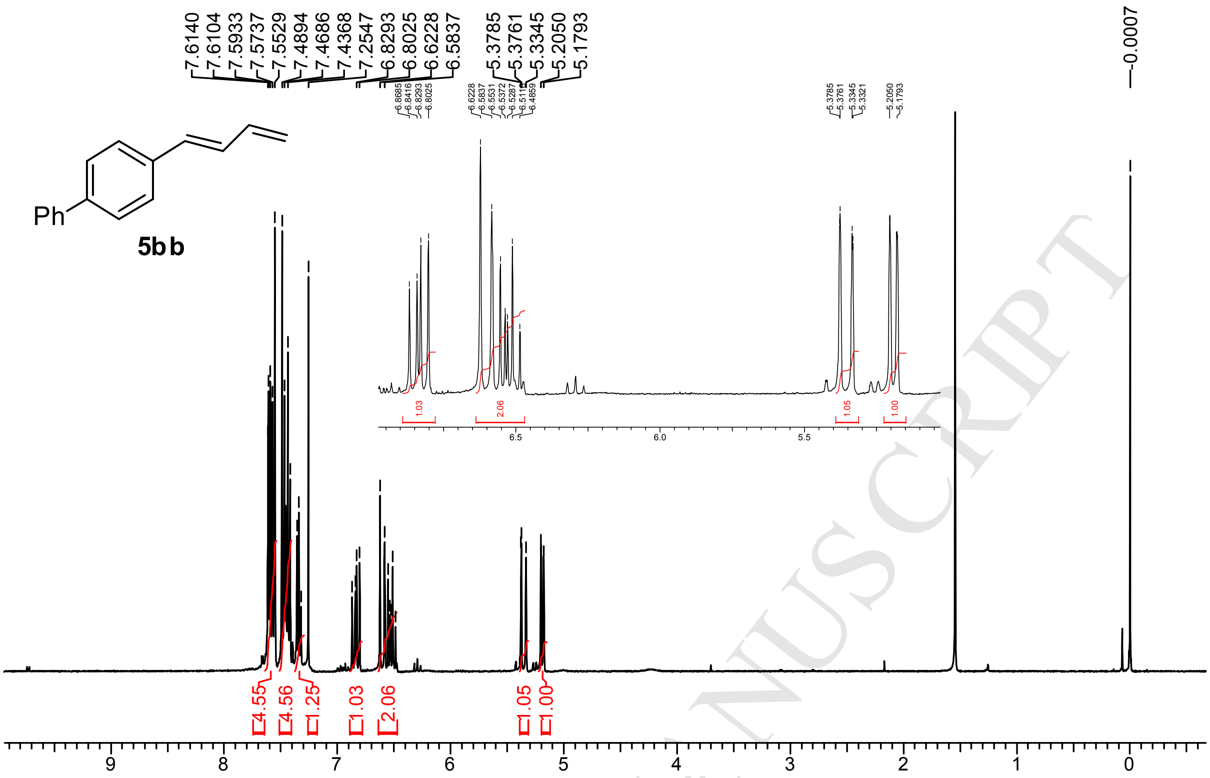
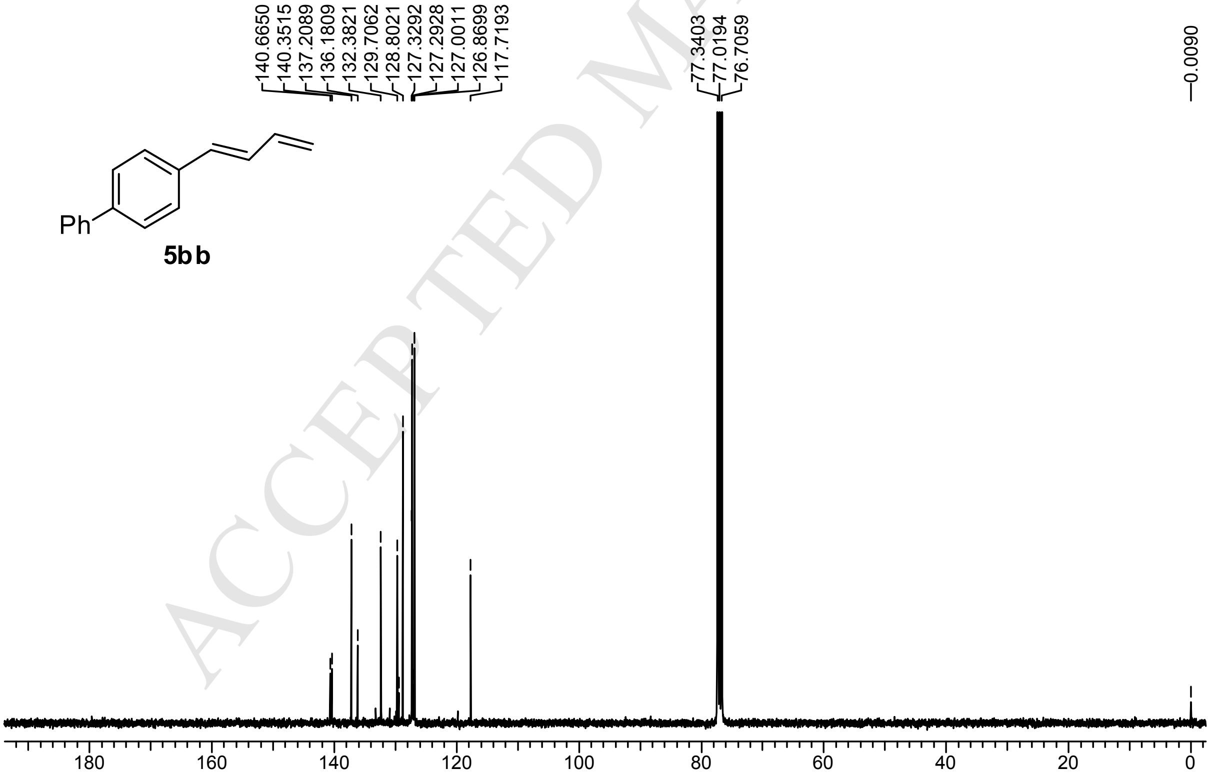
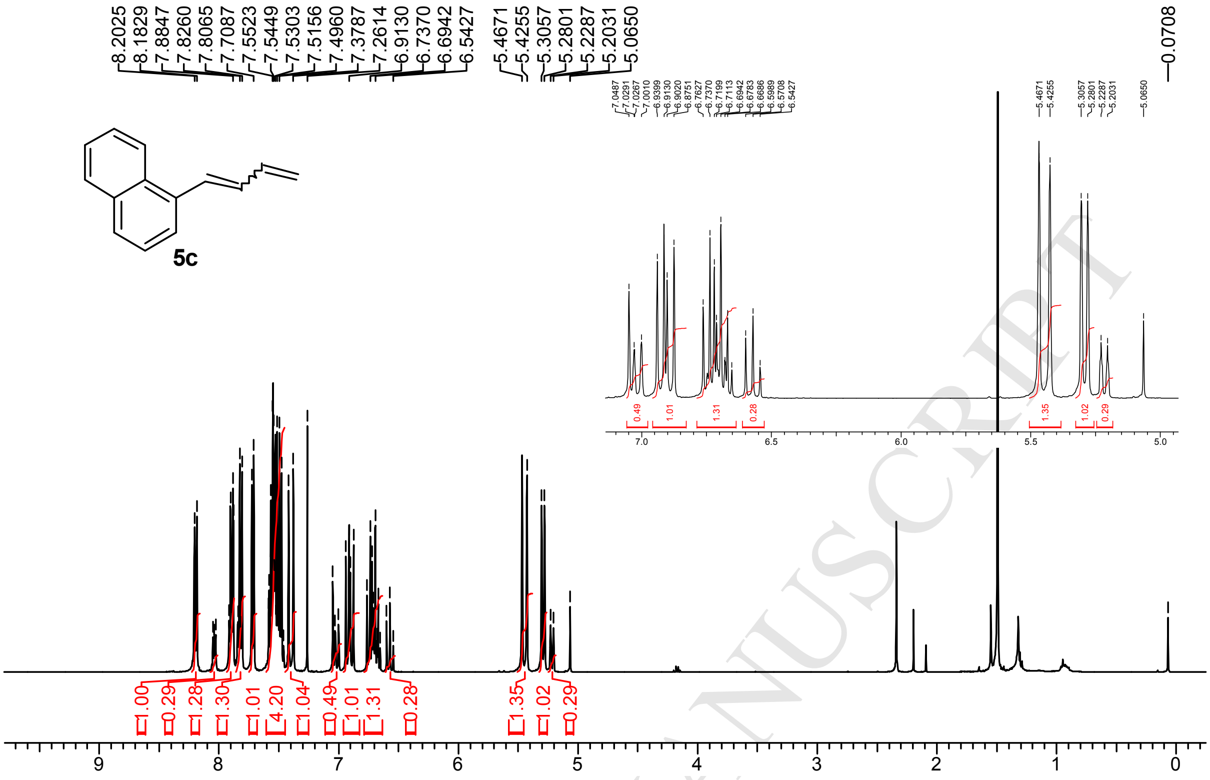
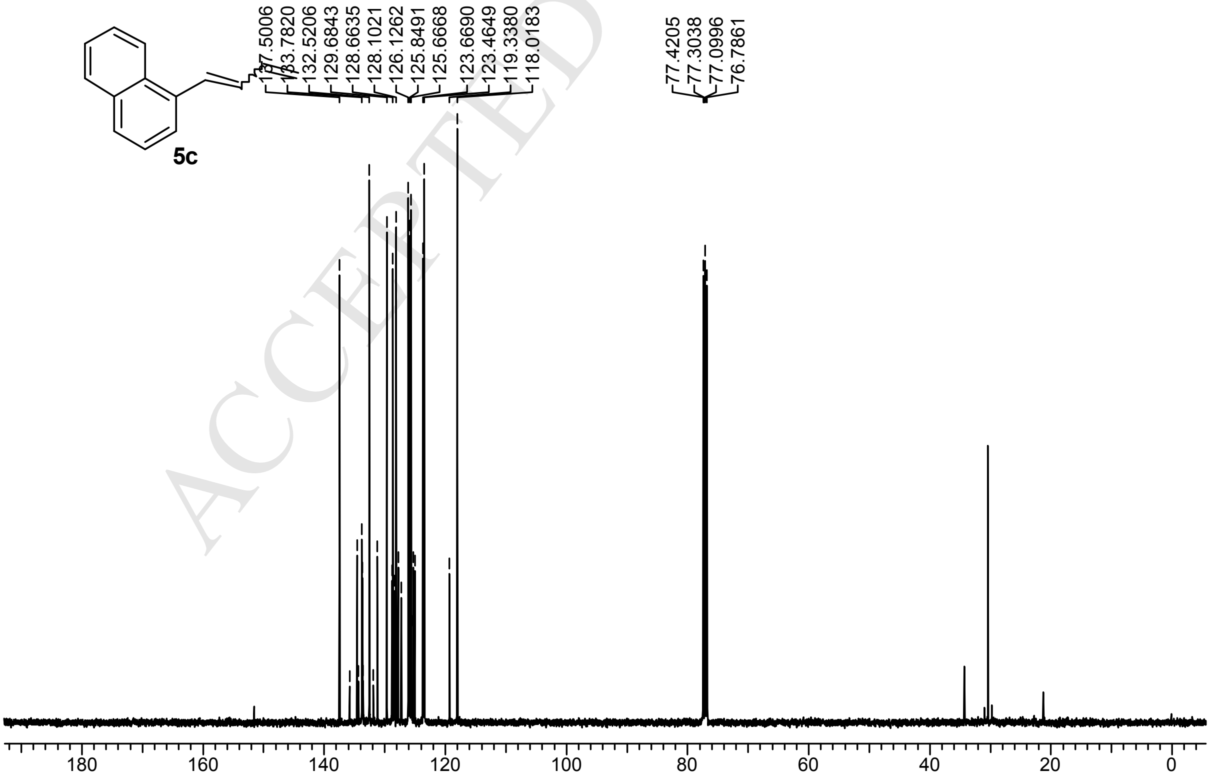


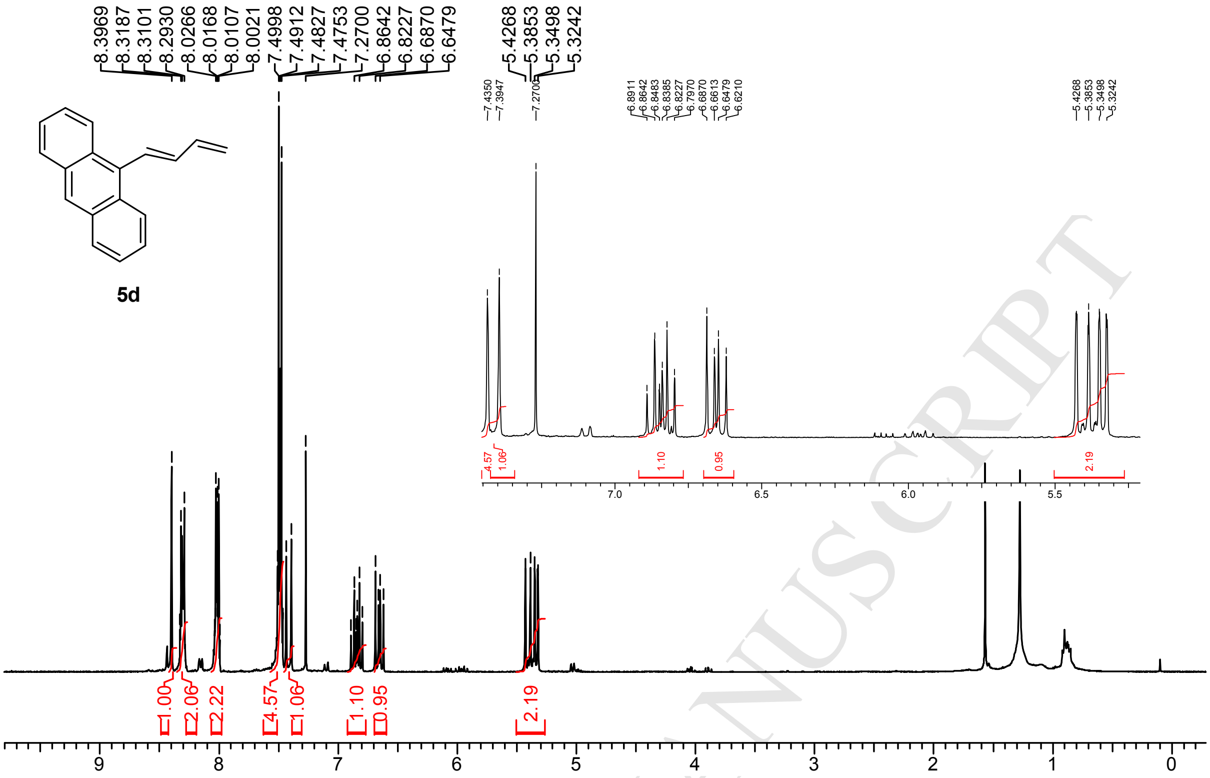


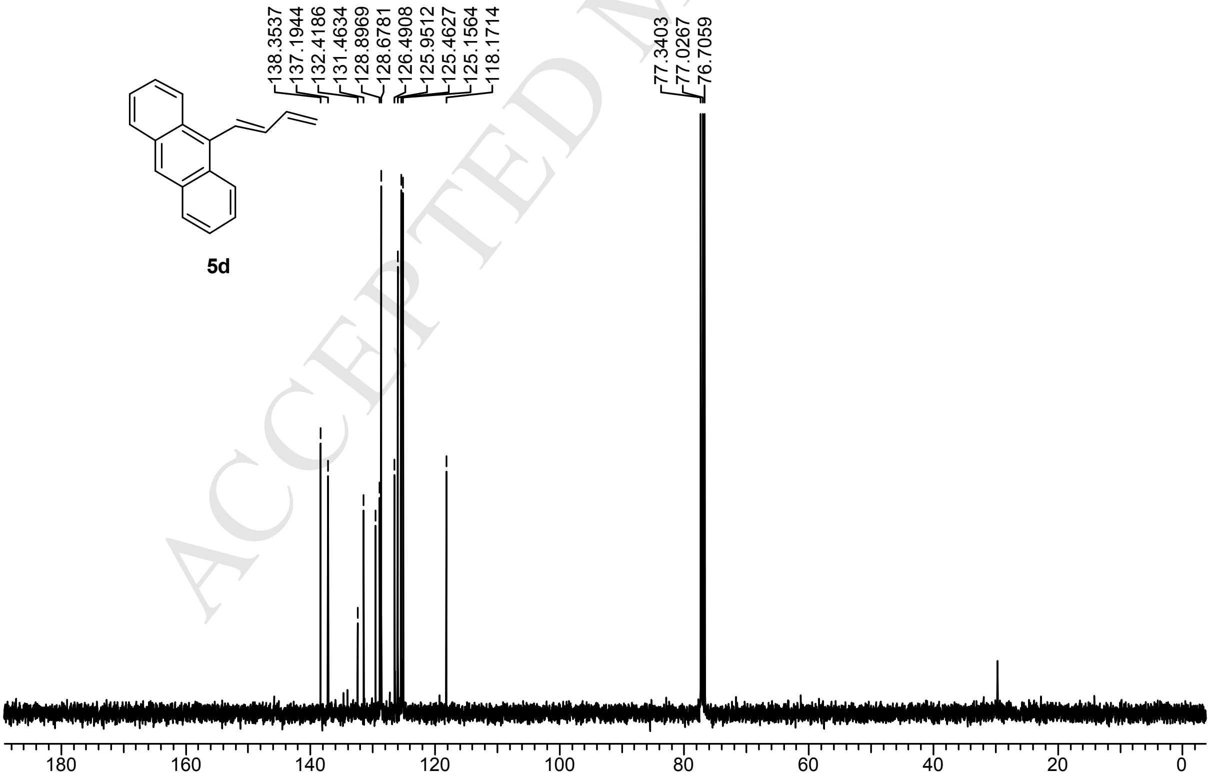
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5c** in $CDCl_3$



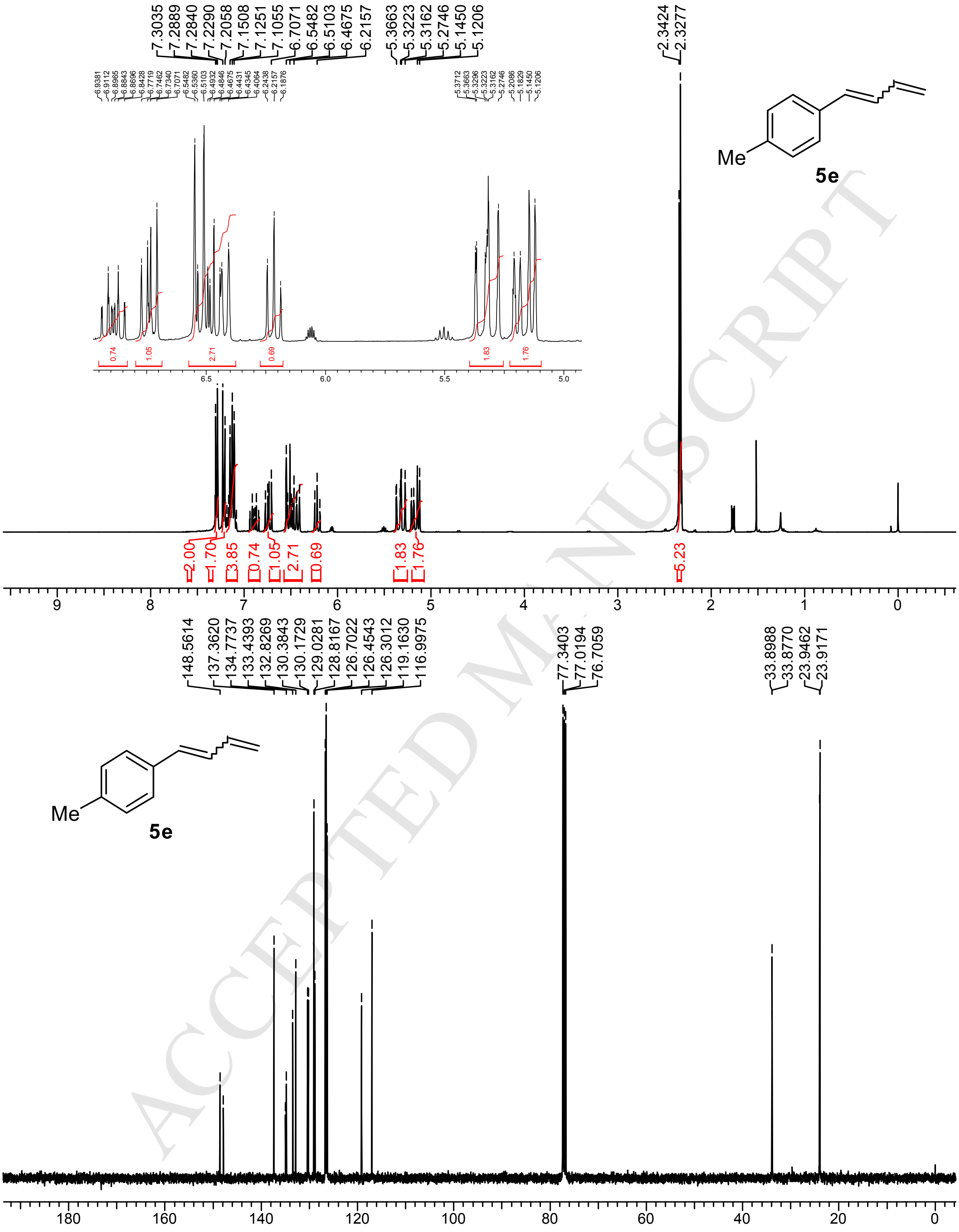


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5d** in $CDCl_3$

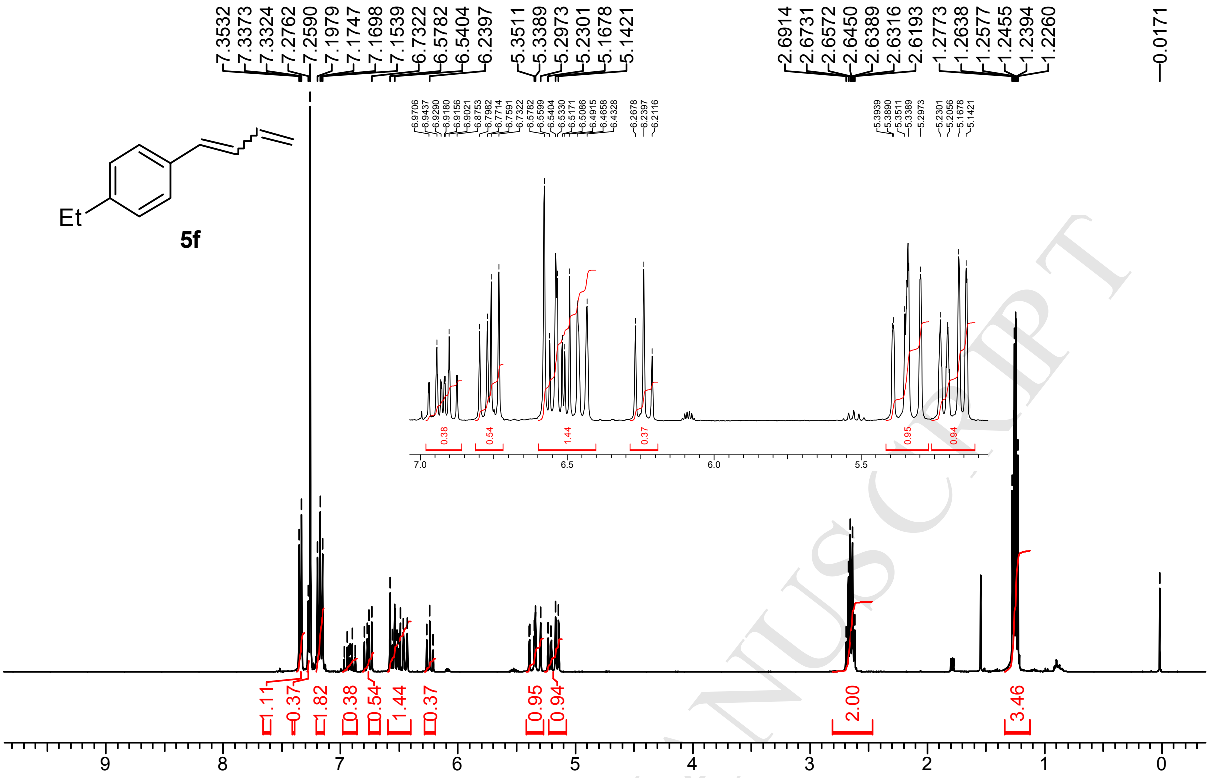


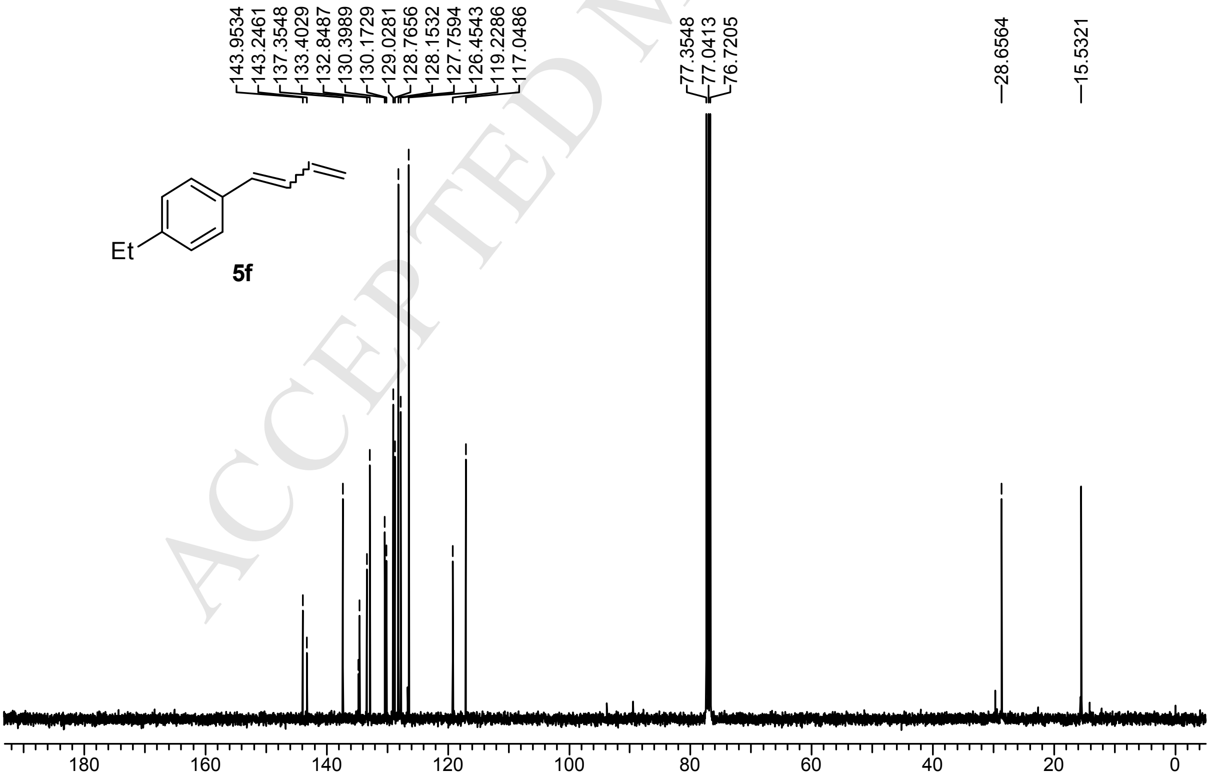


^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5e** in CDCl$_3$

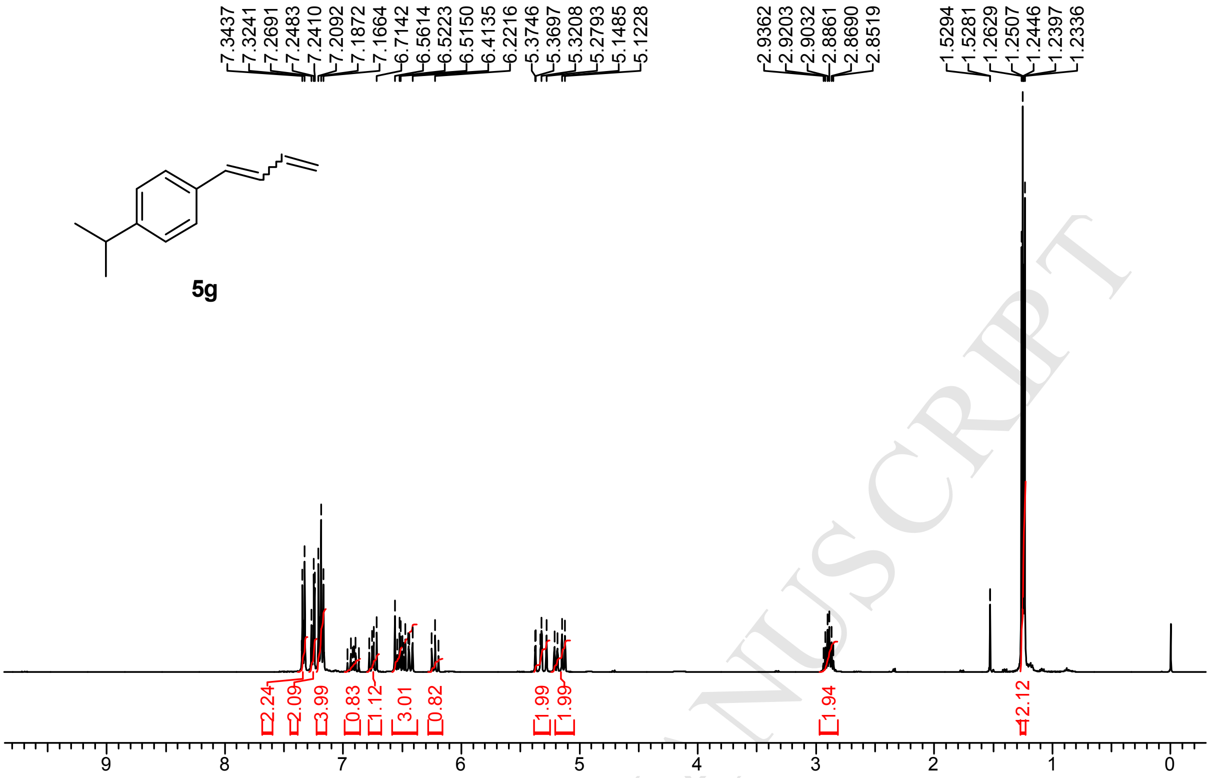


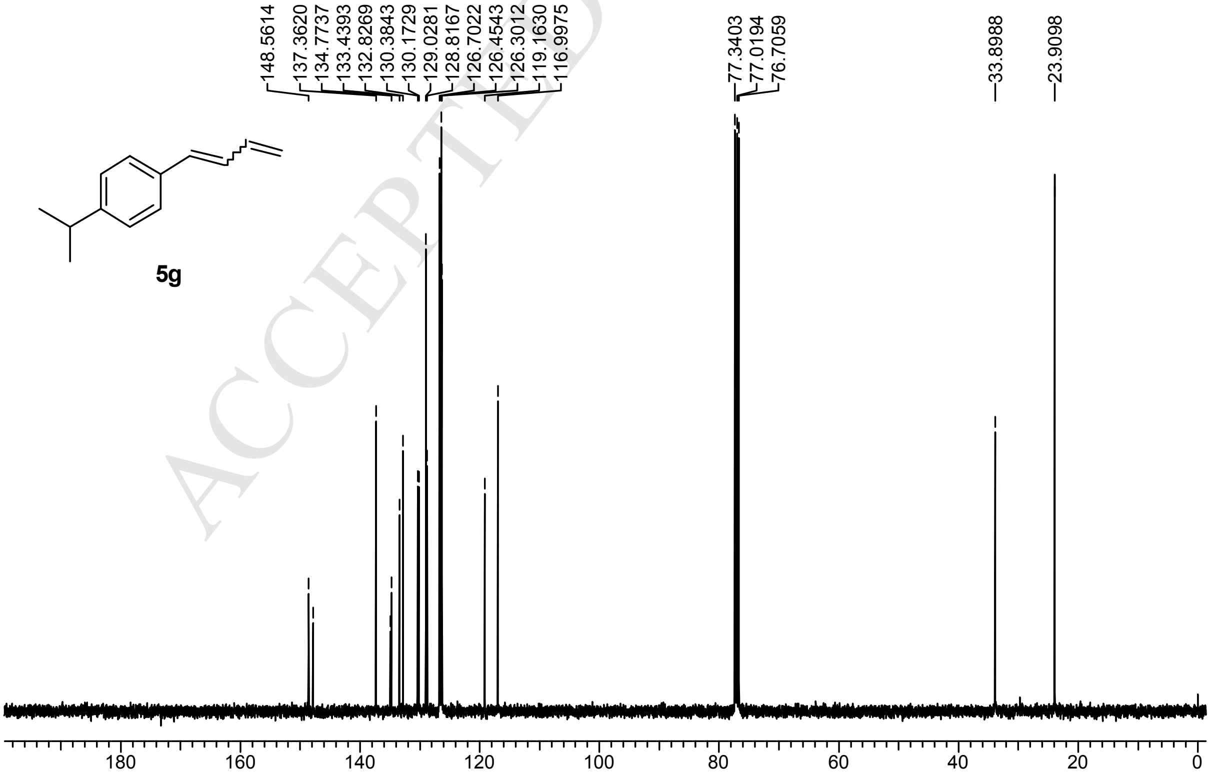
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5f** in $CDCl_3$





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5g** in $CDCl_3$





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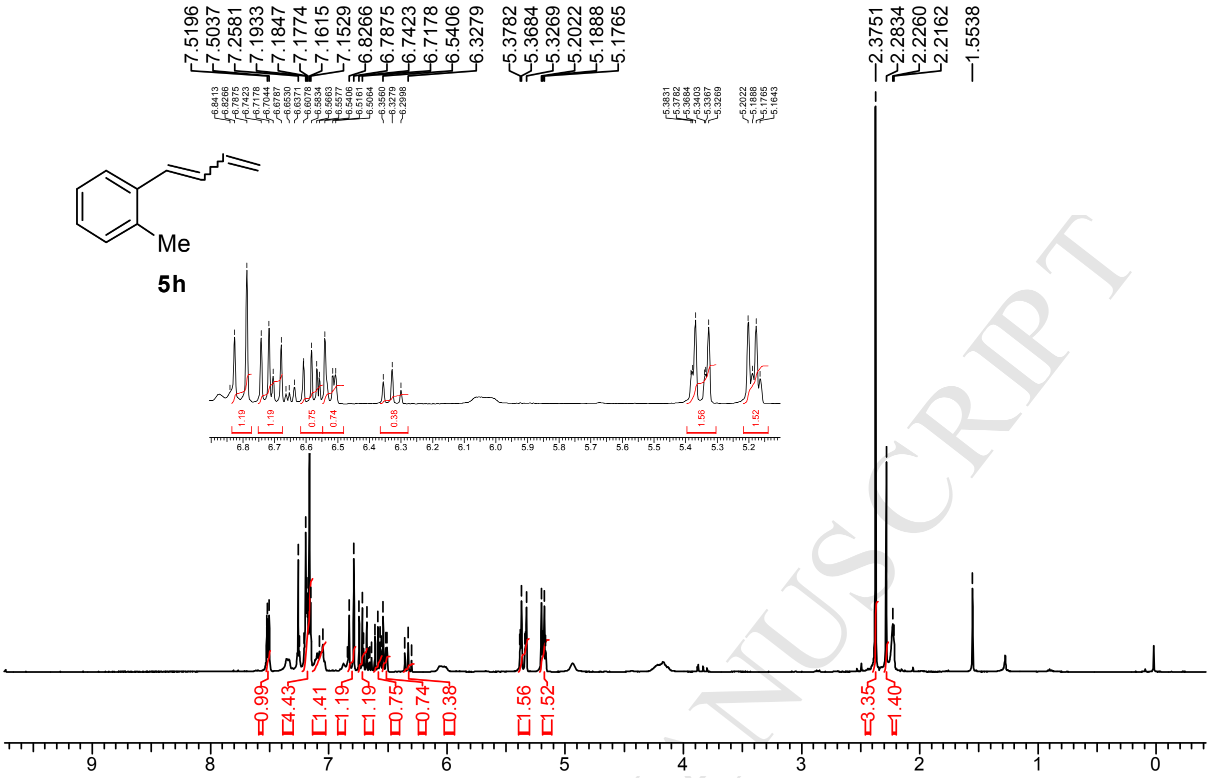

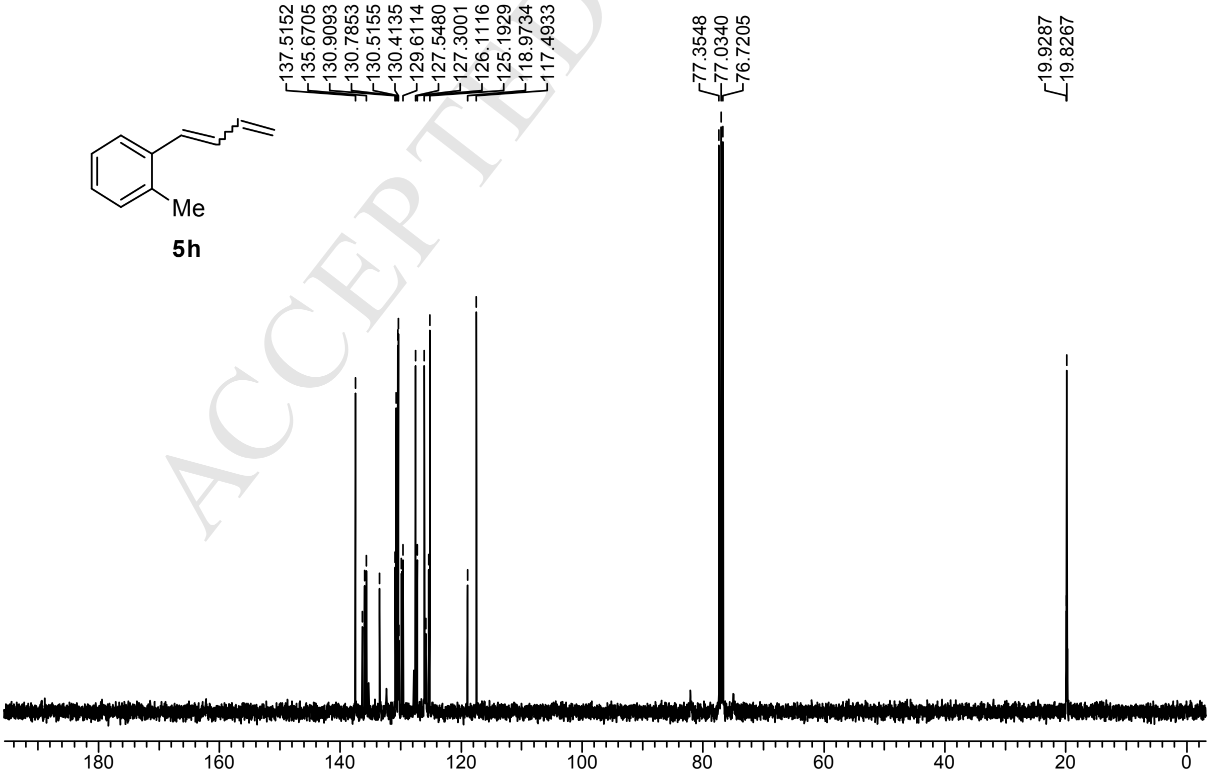

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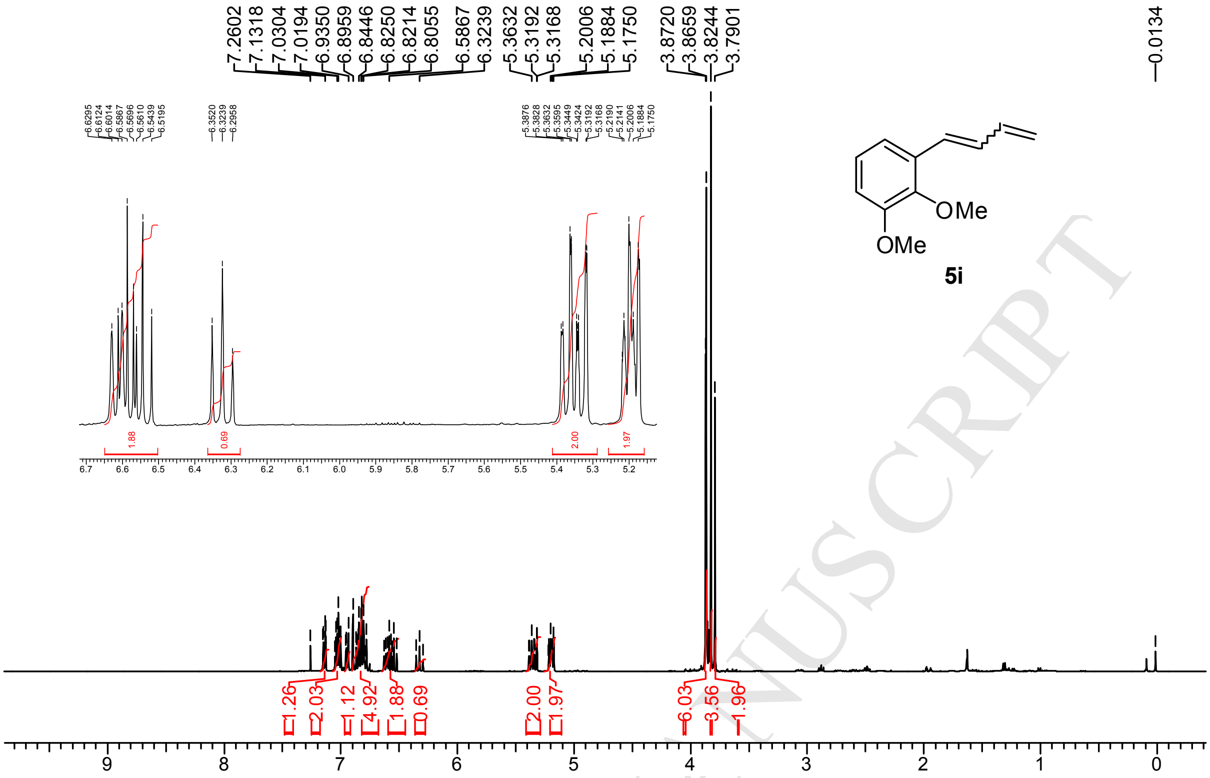

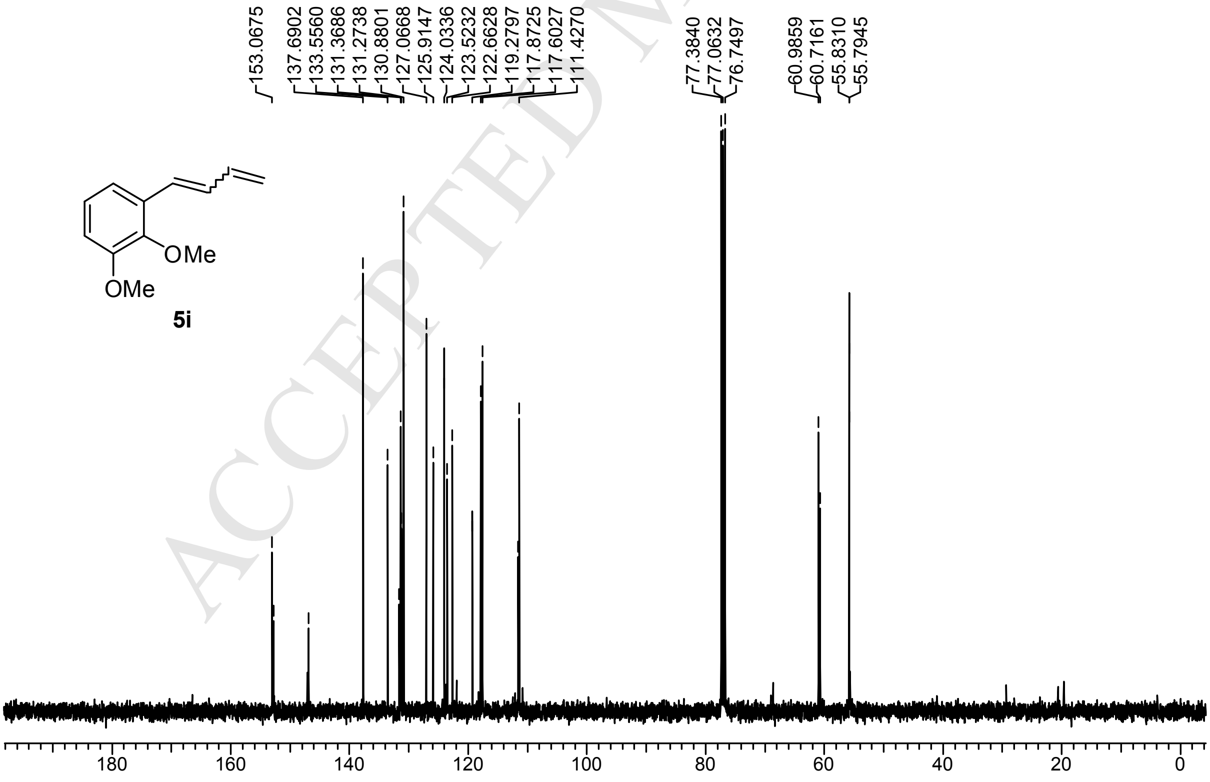

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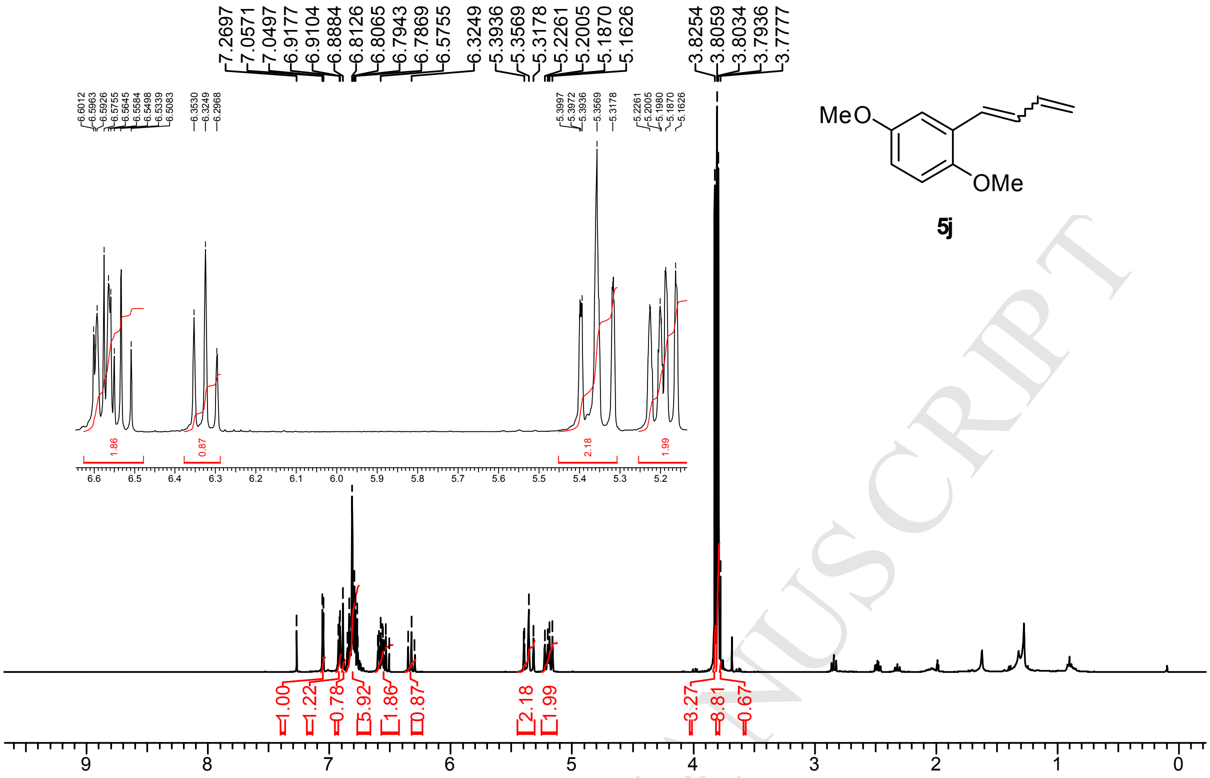
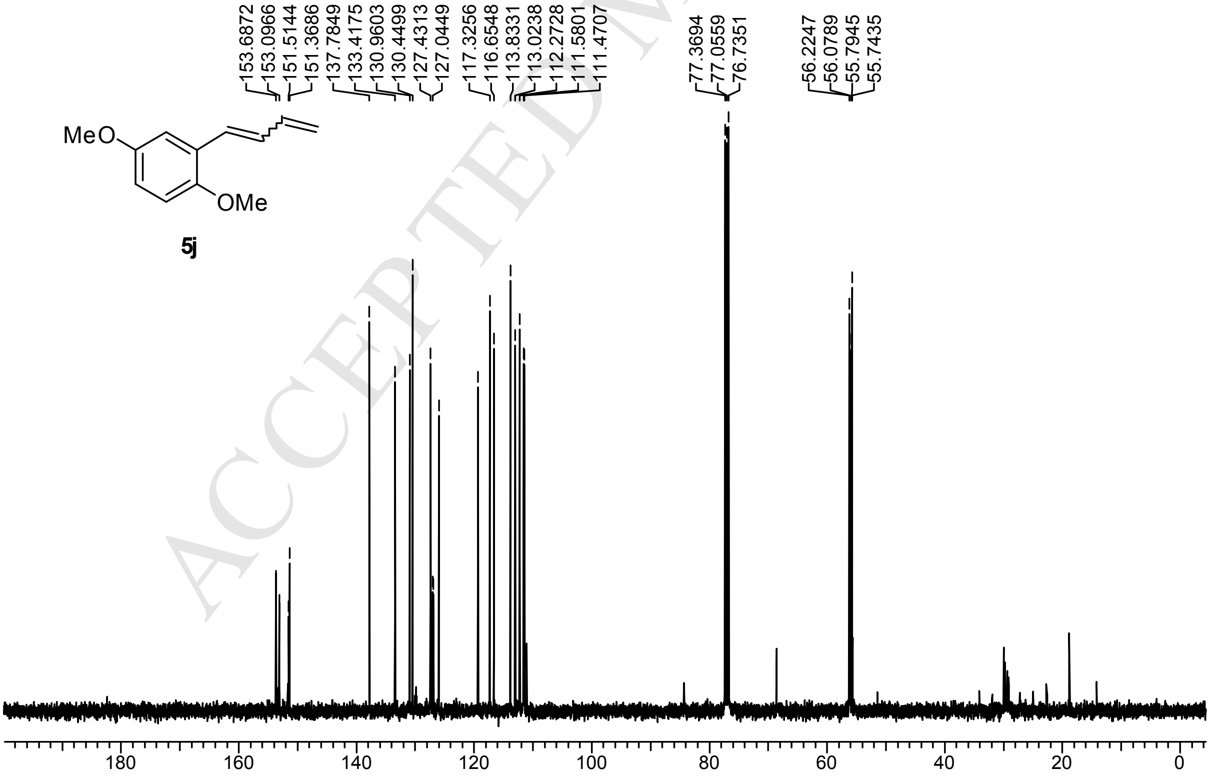
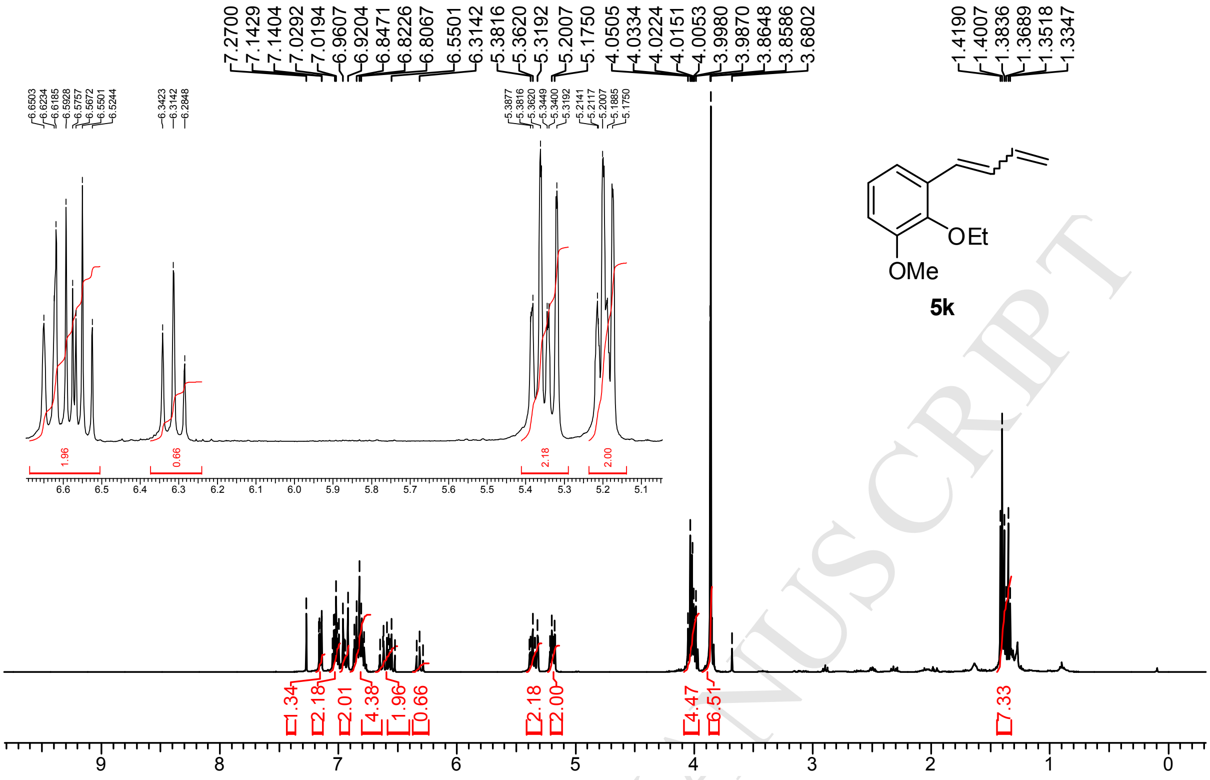
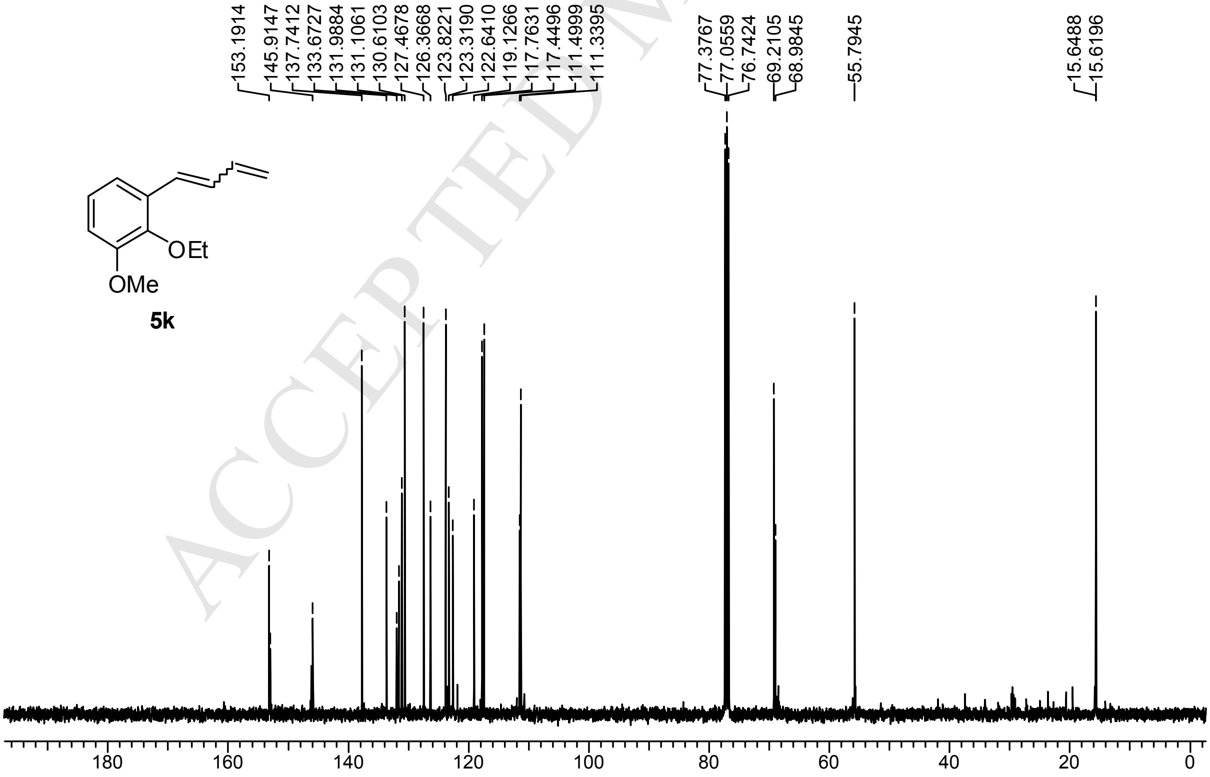


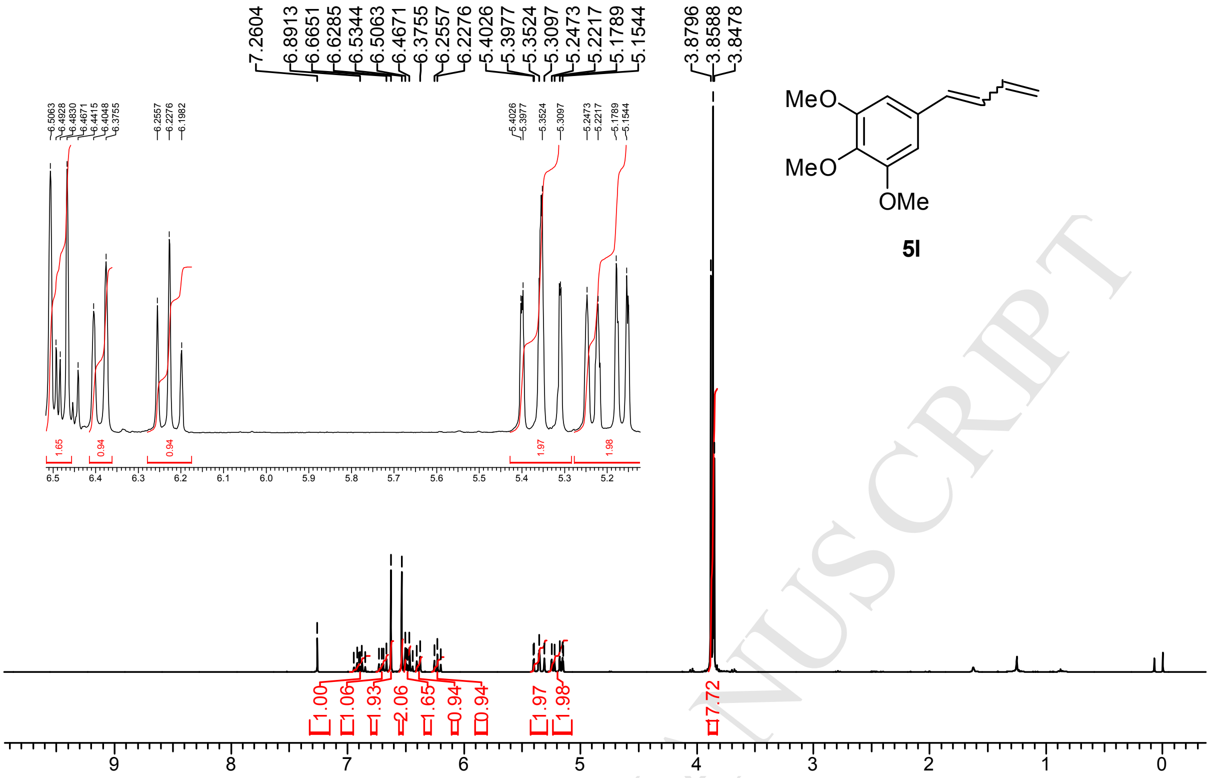


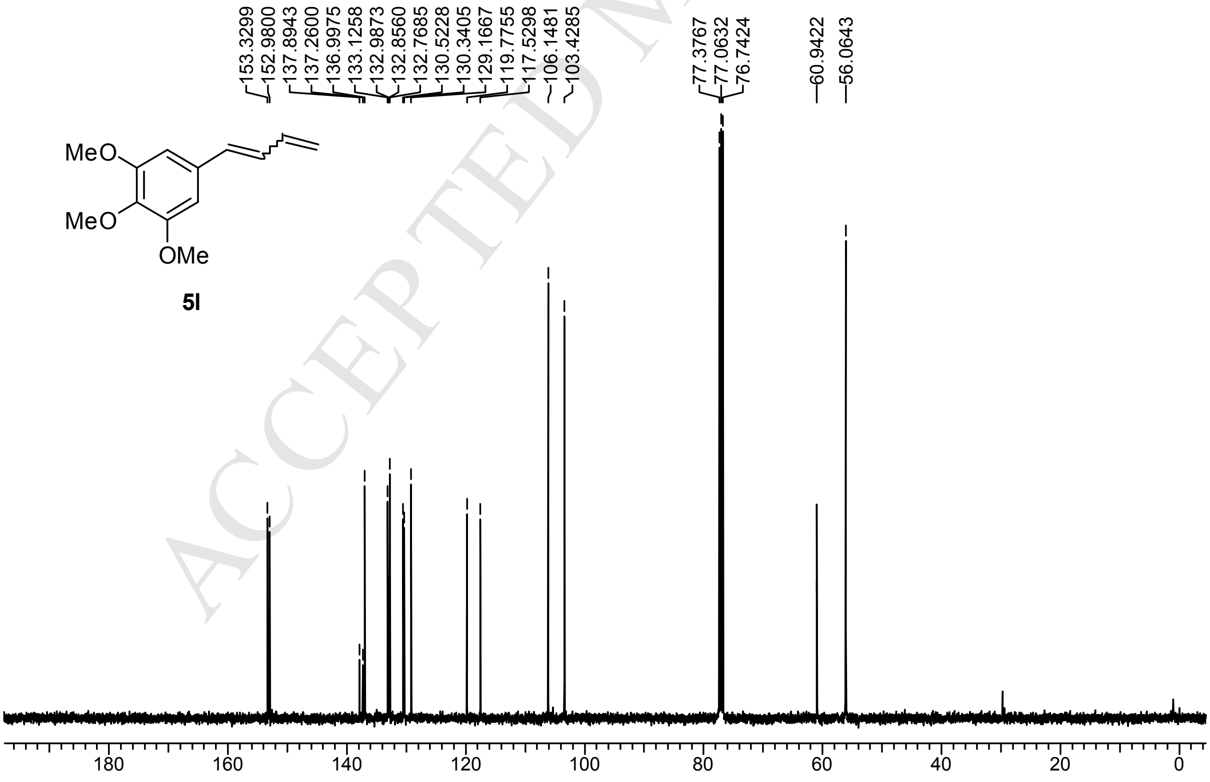
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5k** in $CDCl_3$



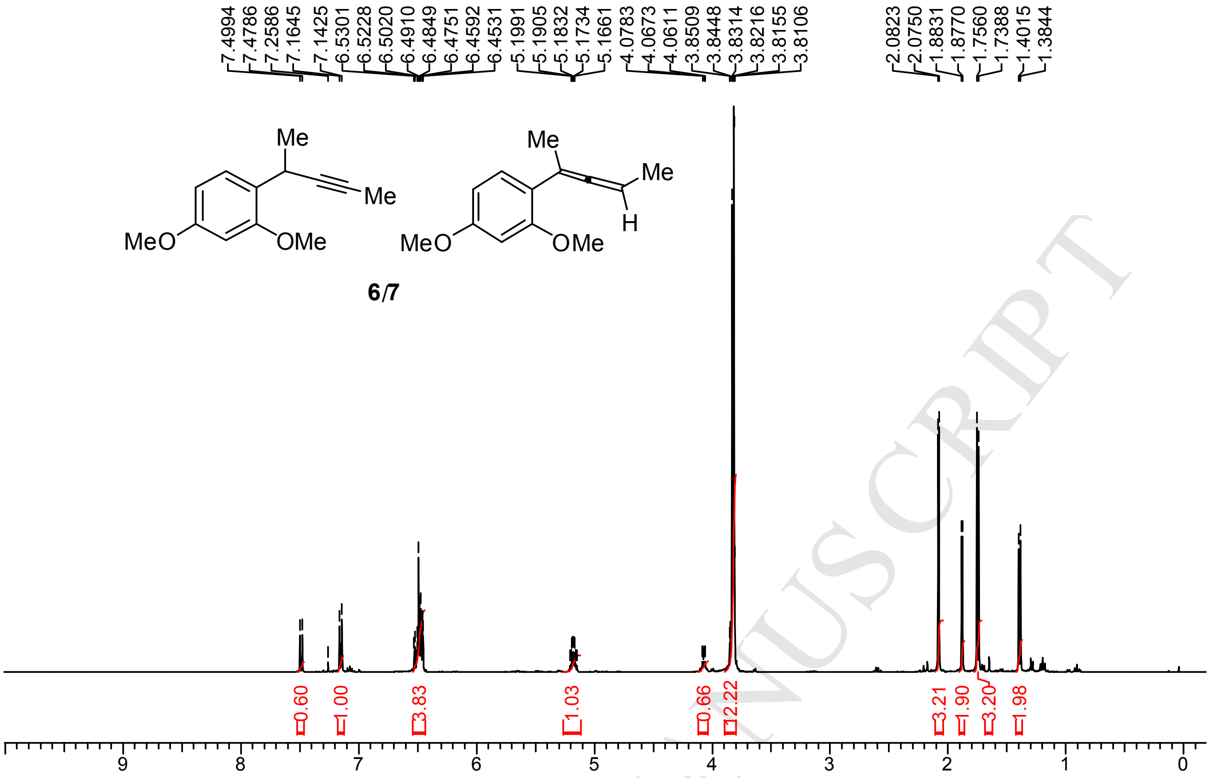


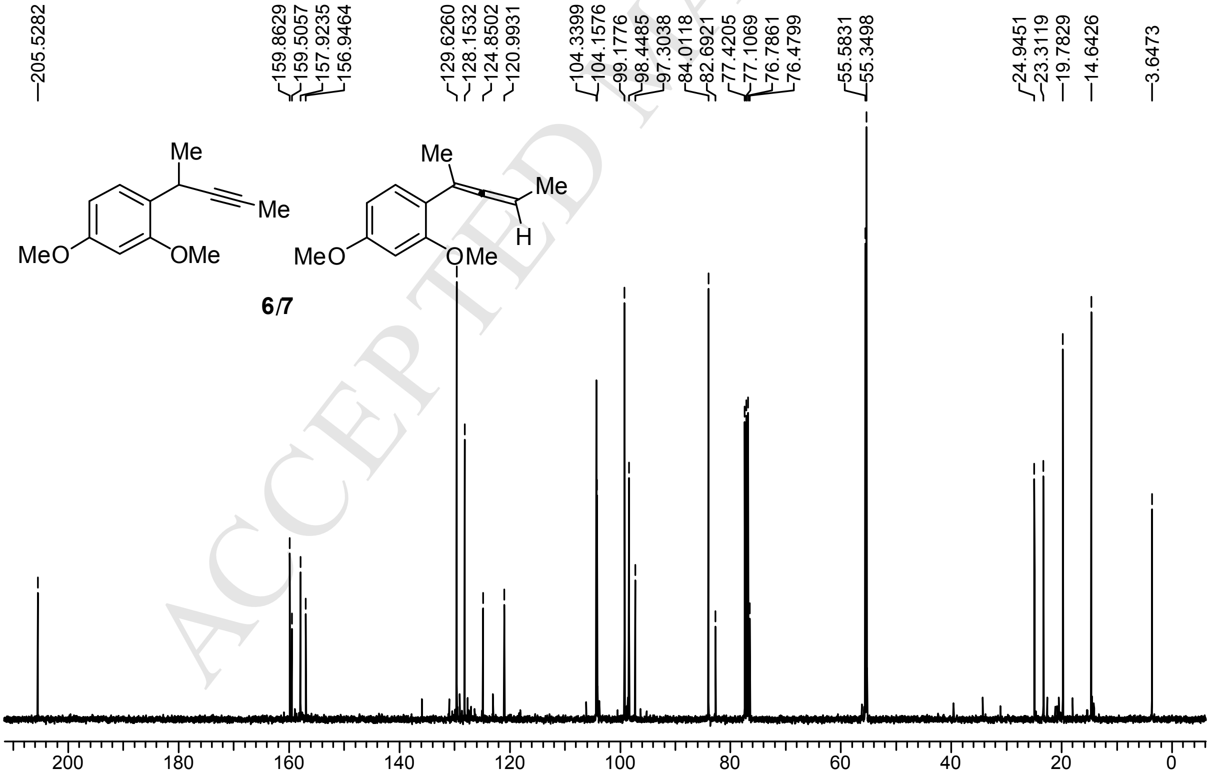
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **5l** in $CDCl_3$



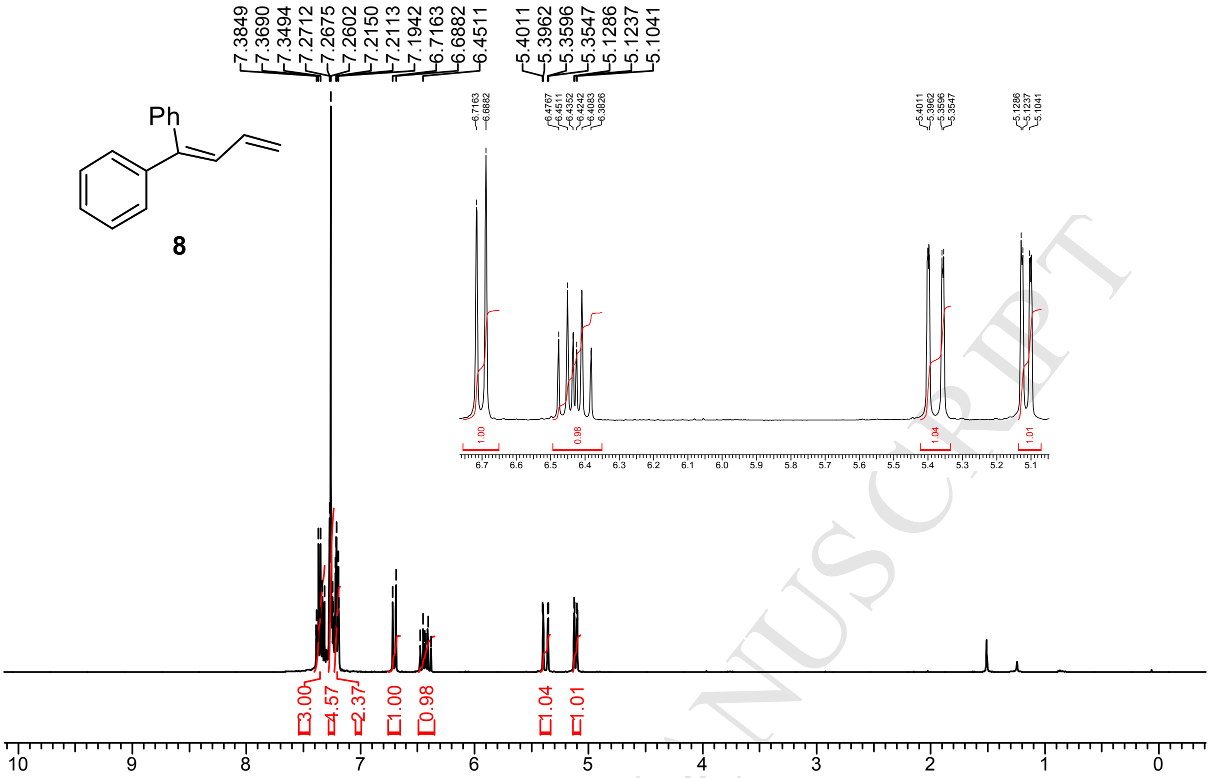


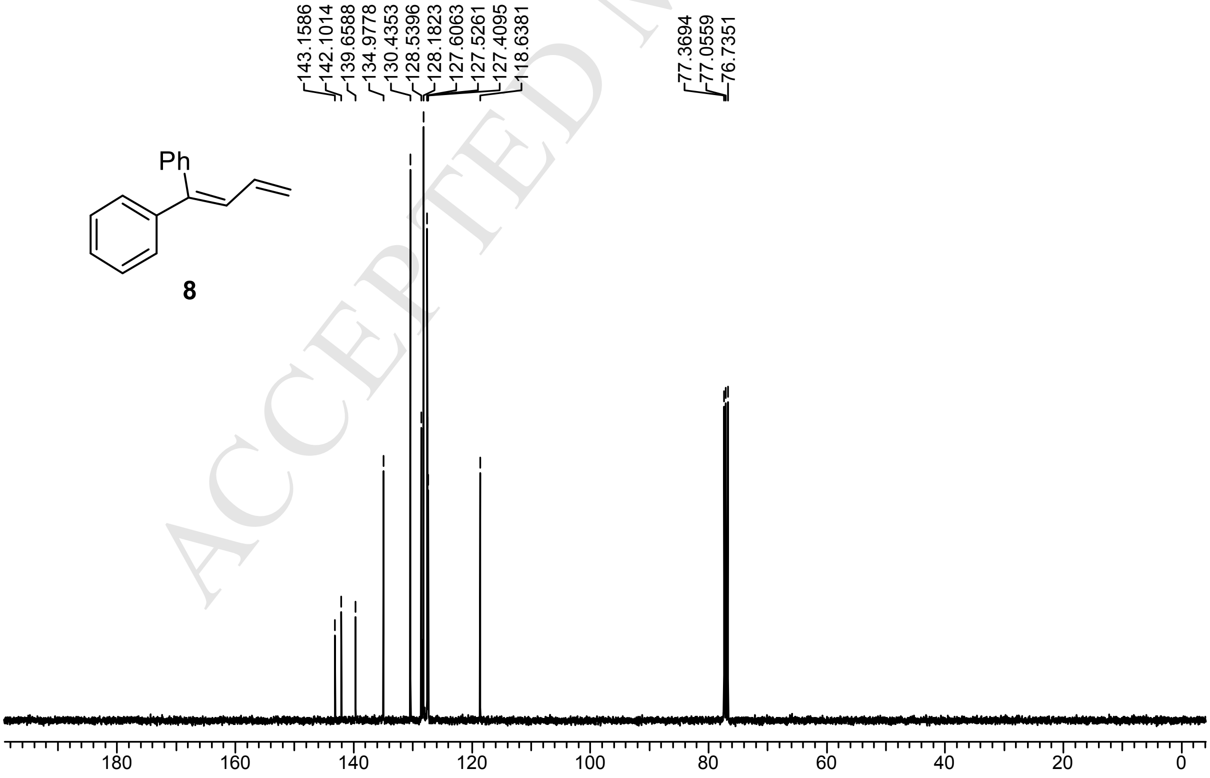
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **6**/**7** in $CDCl_3$



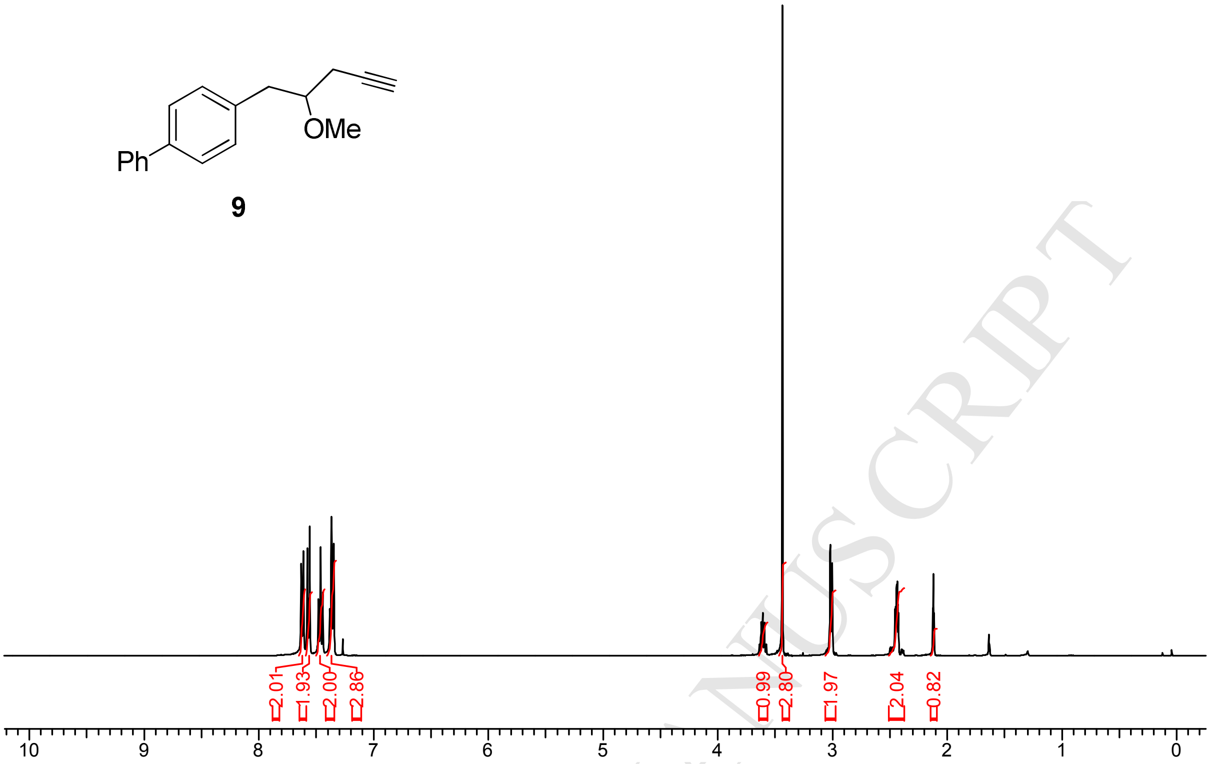


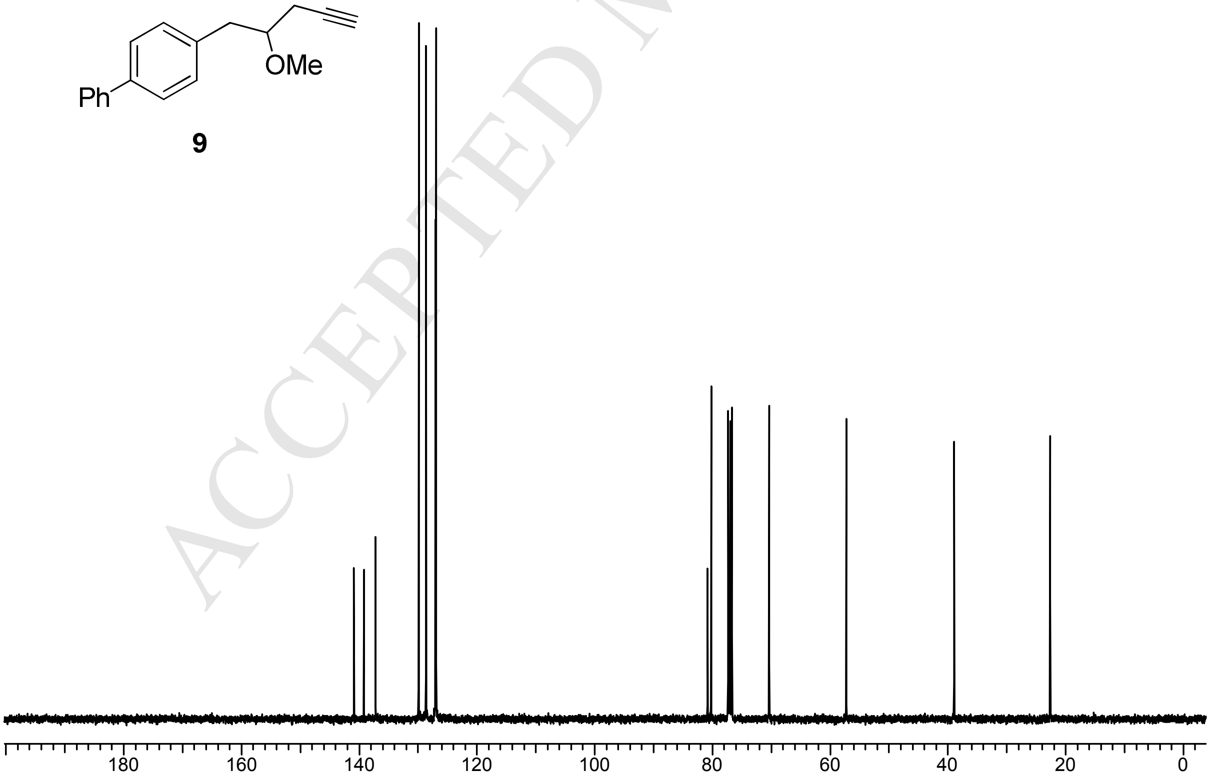
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **8** in $CDCl_3$



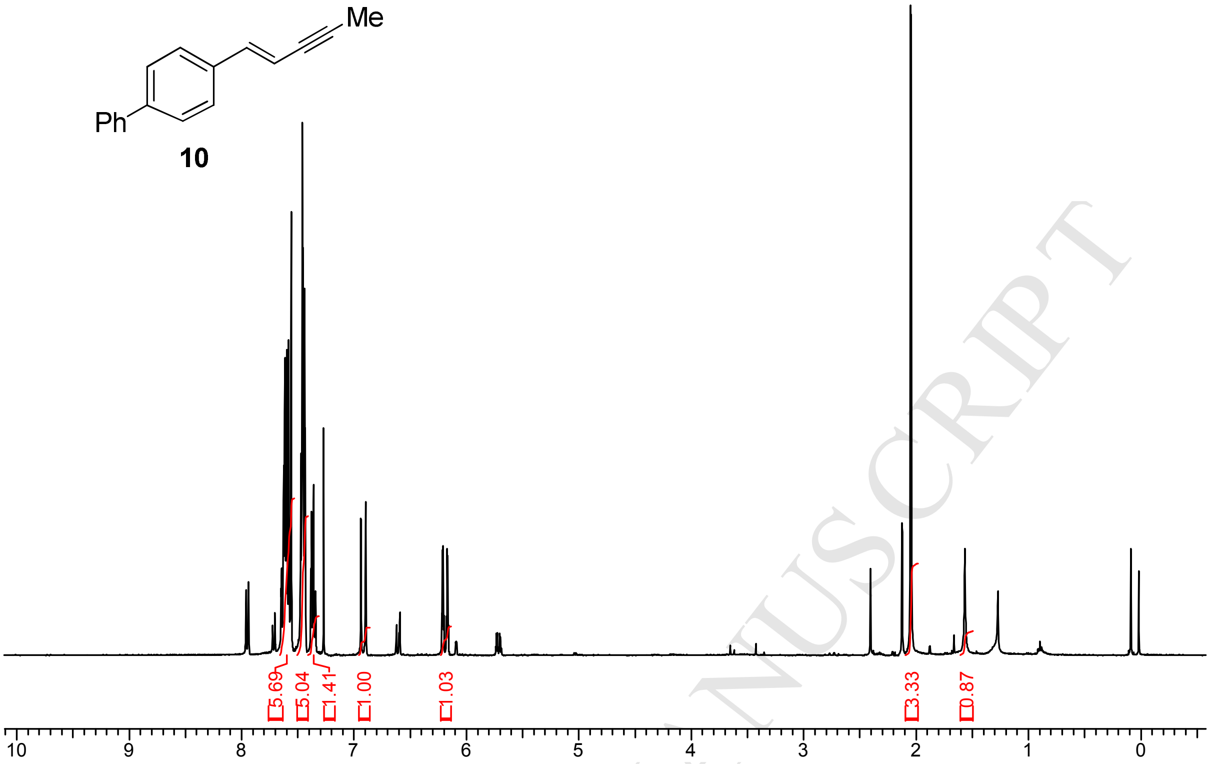


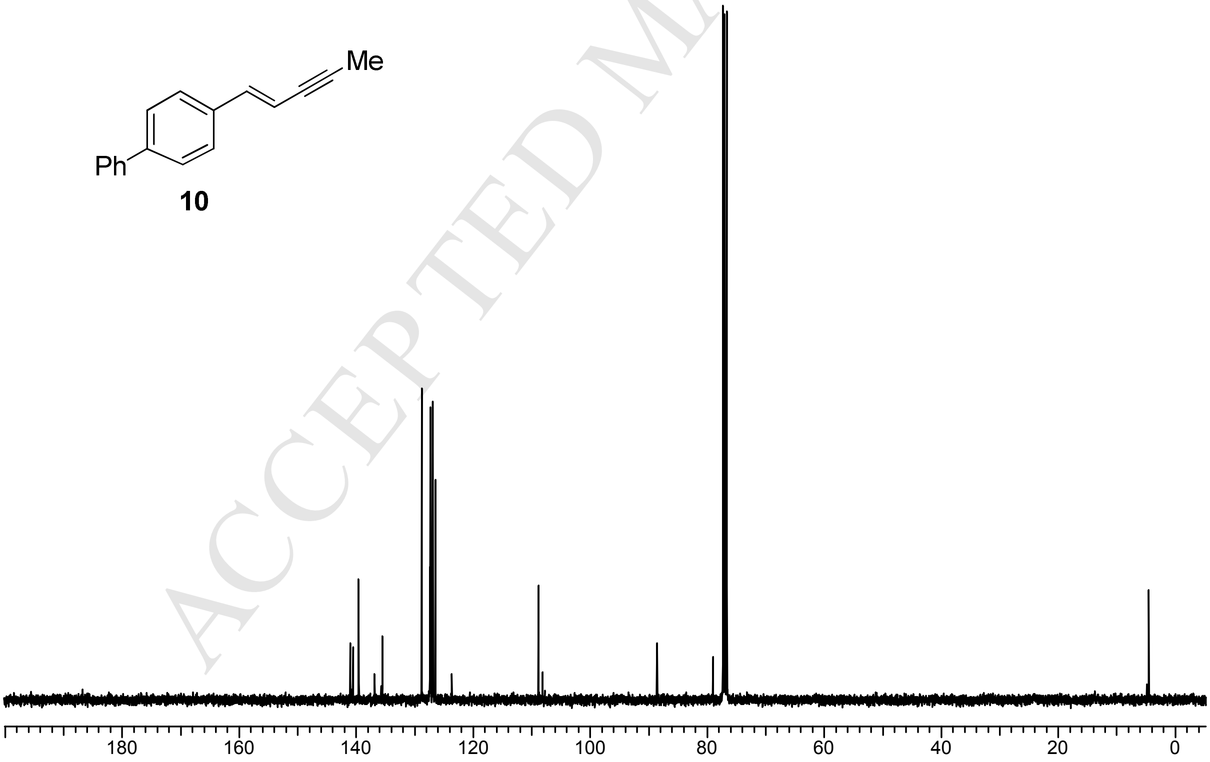
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **9** in $CDCl_3$



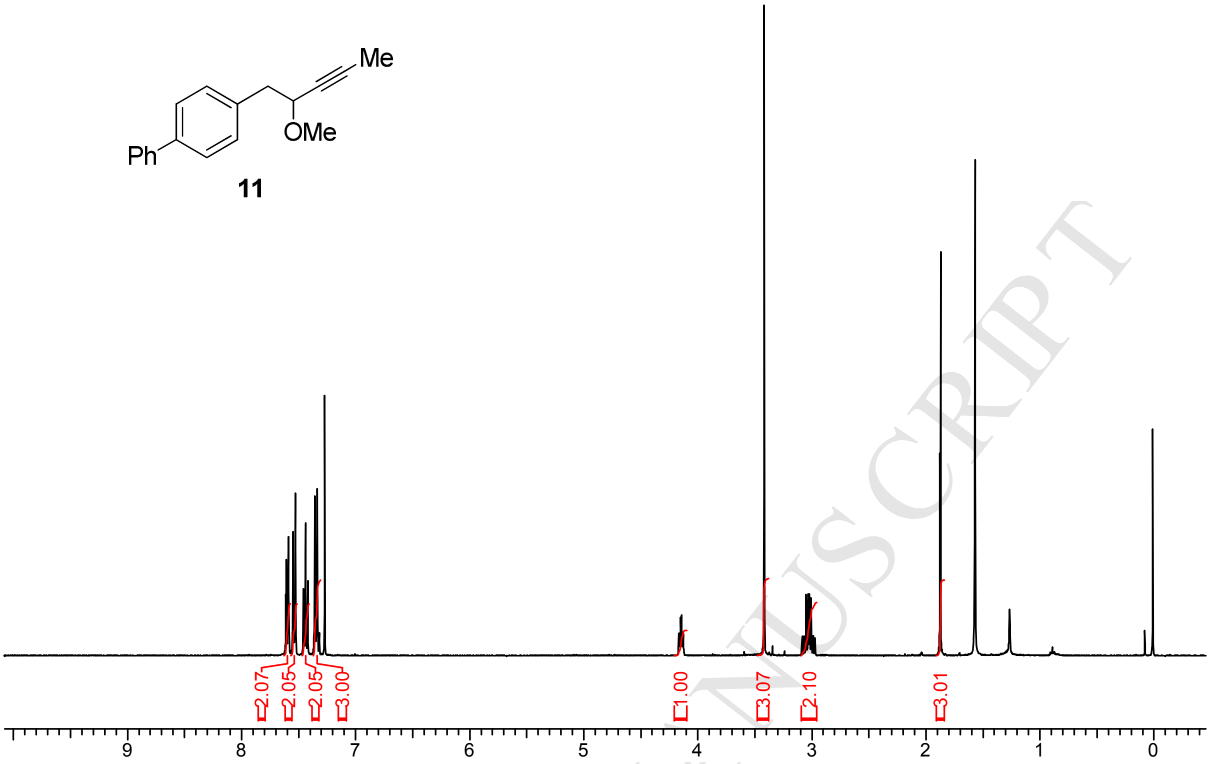


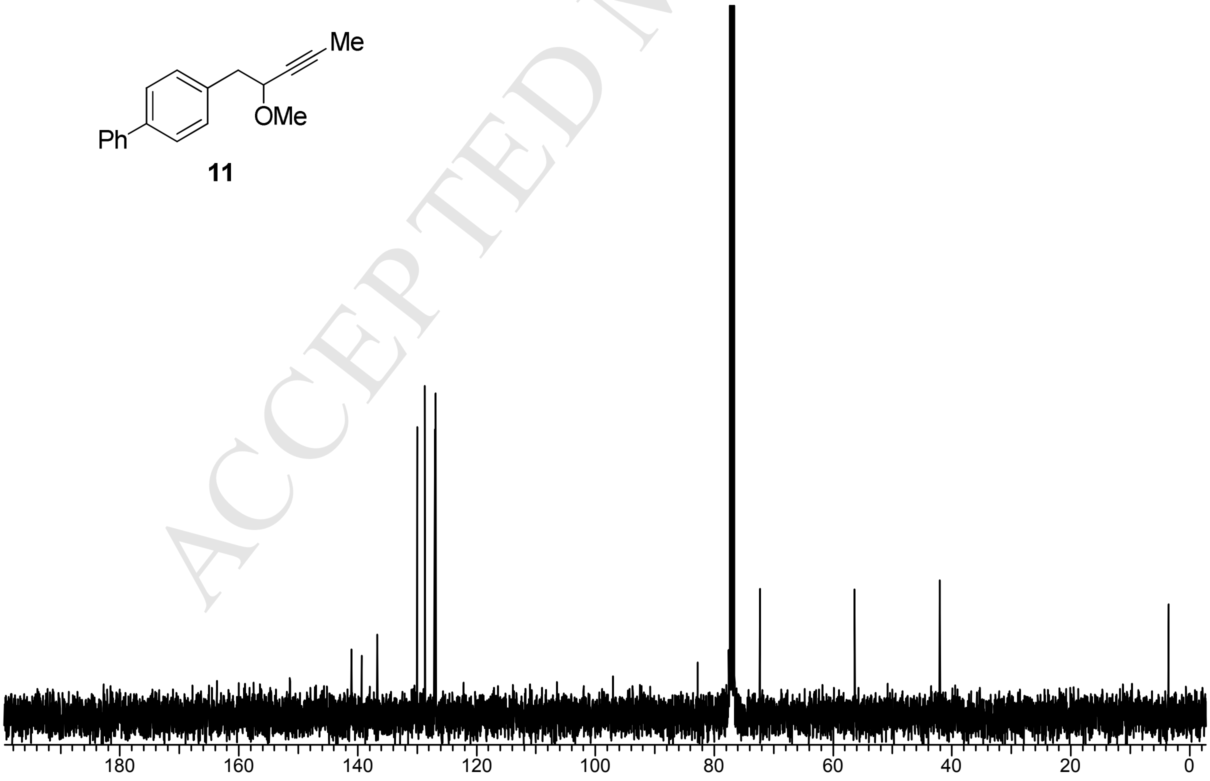
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **10** in $CDCl_3$



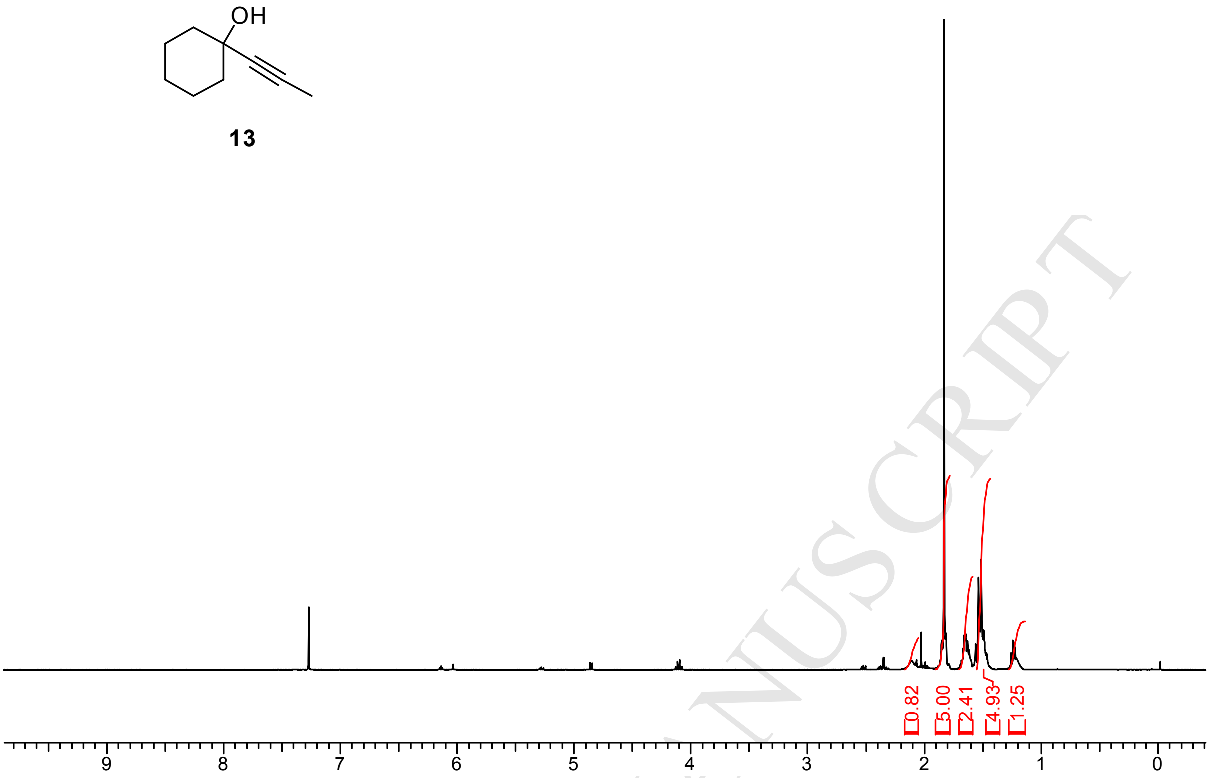


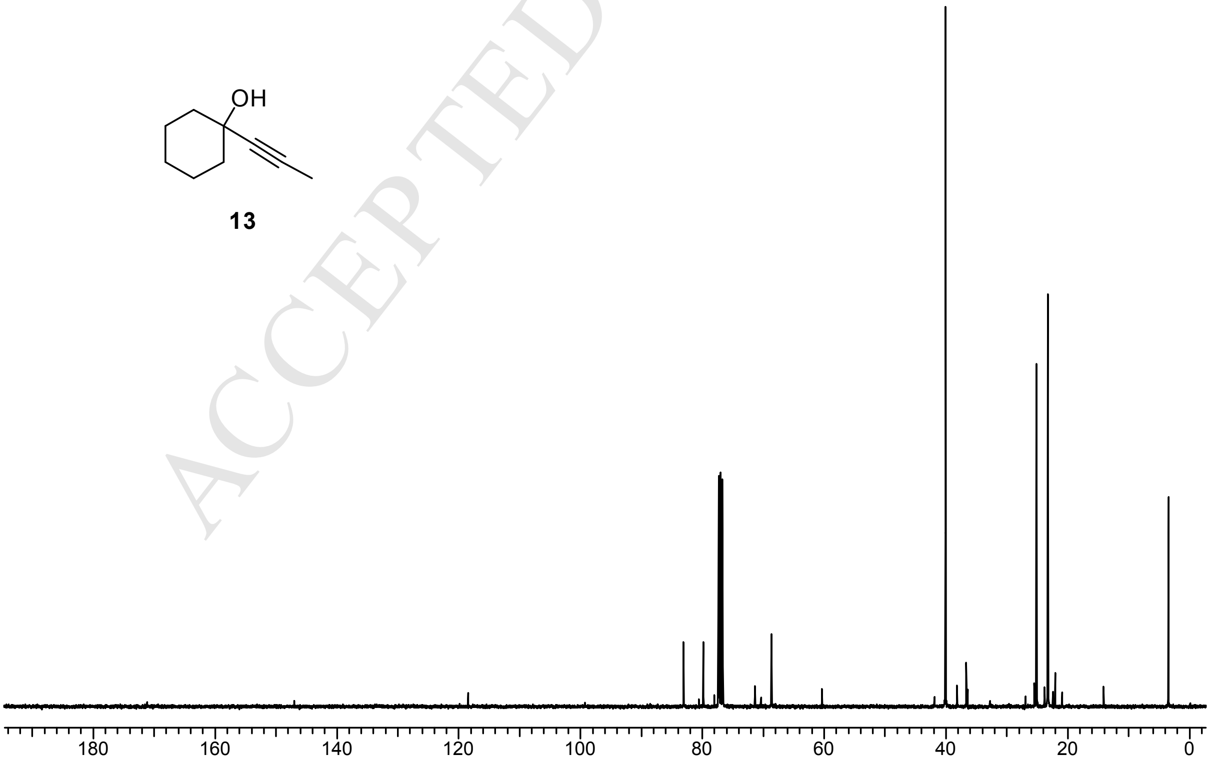
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **11** in $CDCl_3$



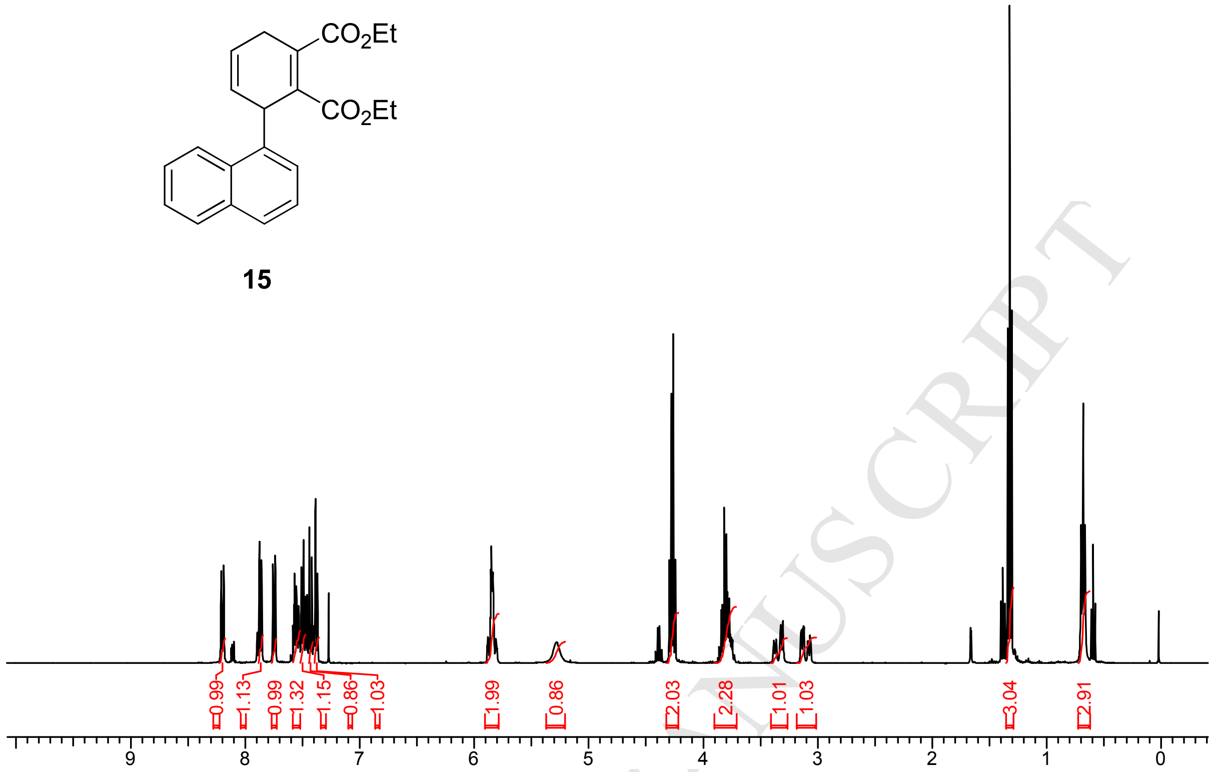


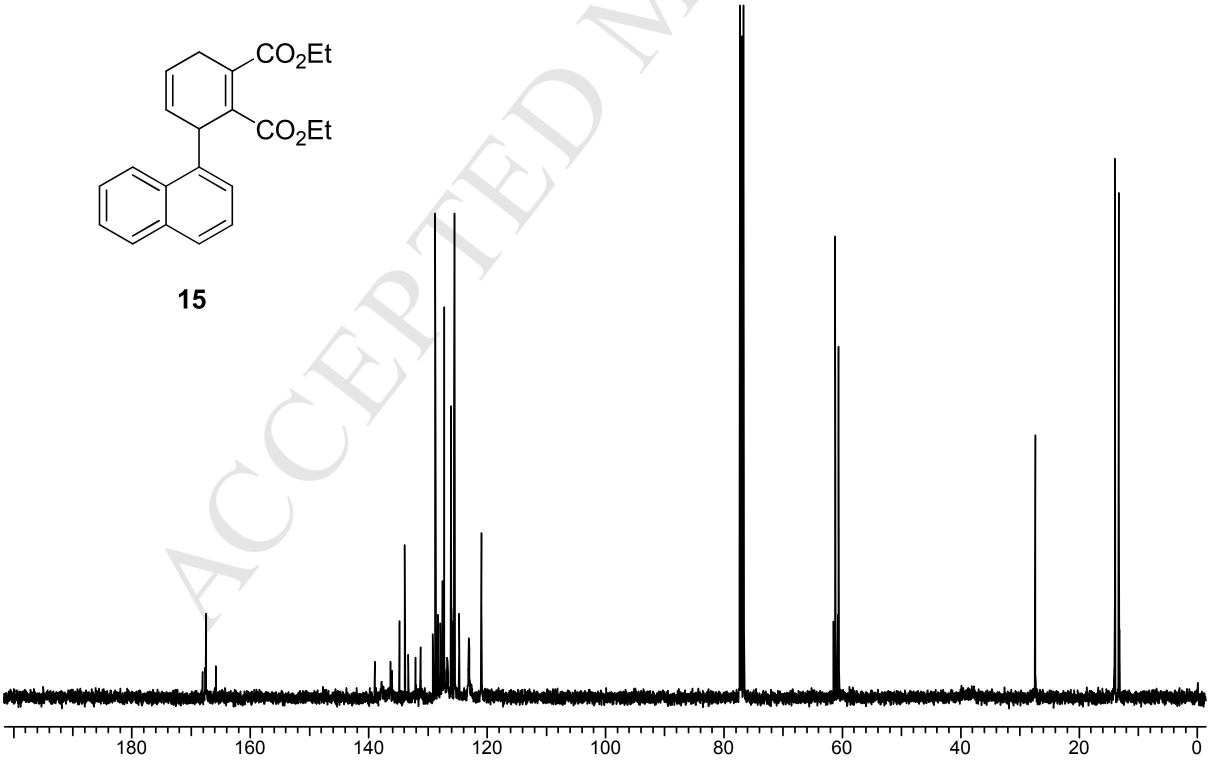
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **13** in $CDCl_3$


13

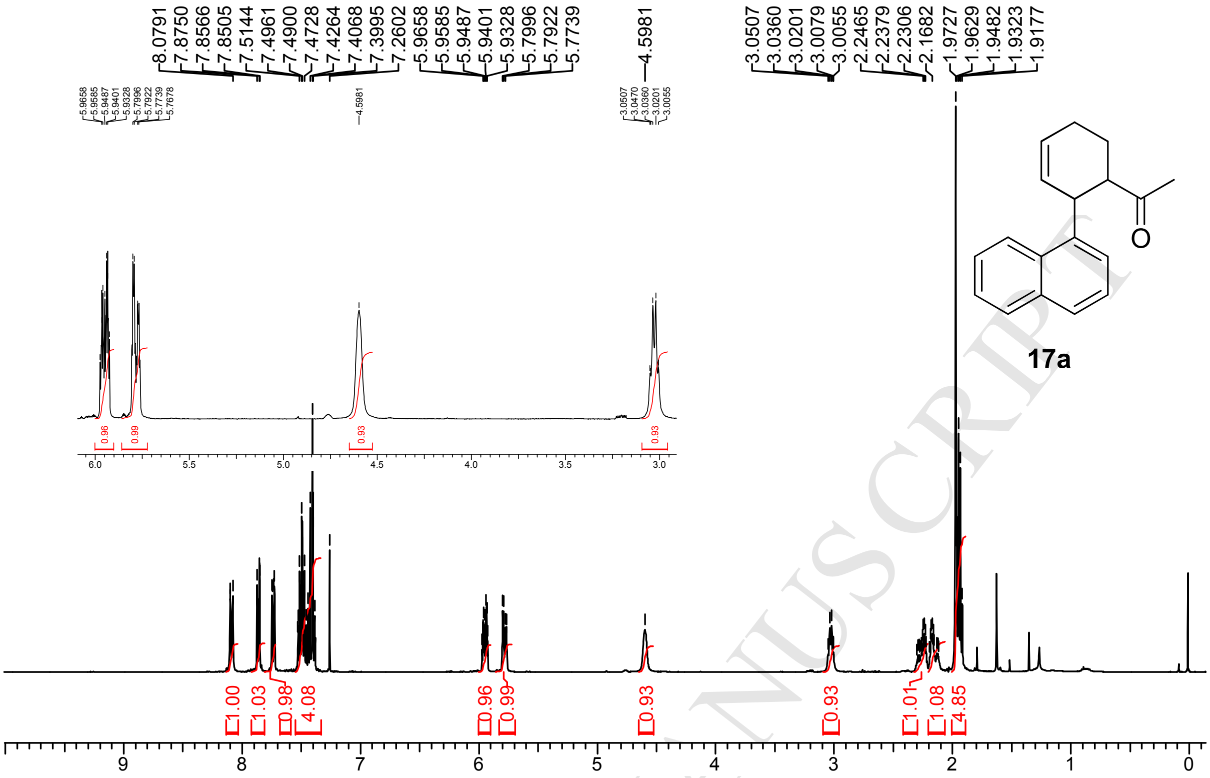

13

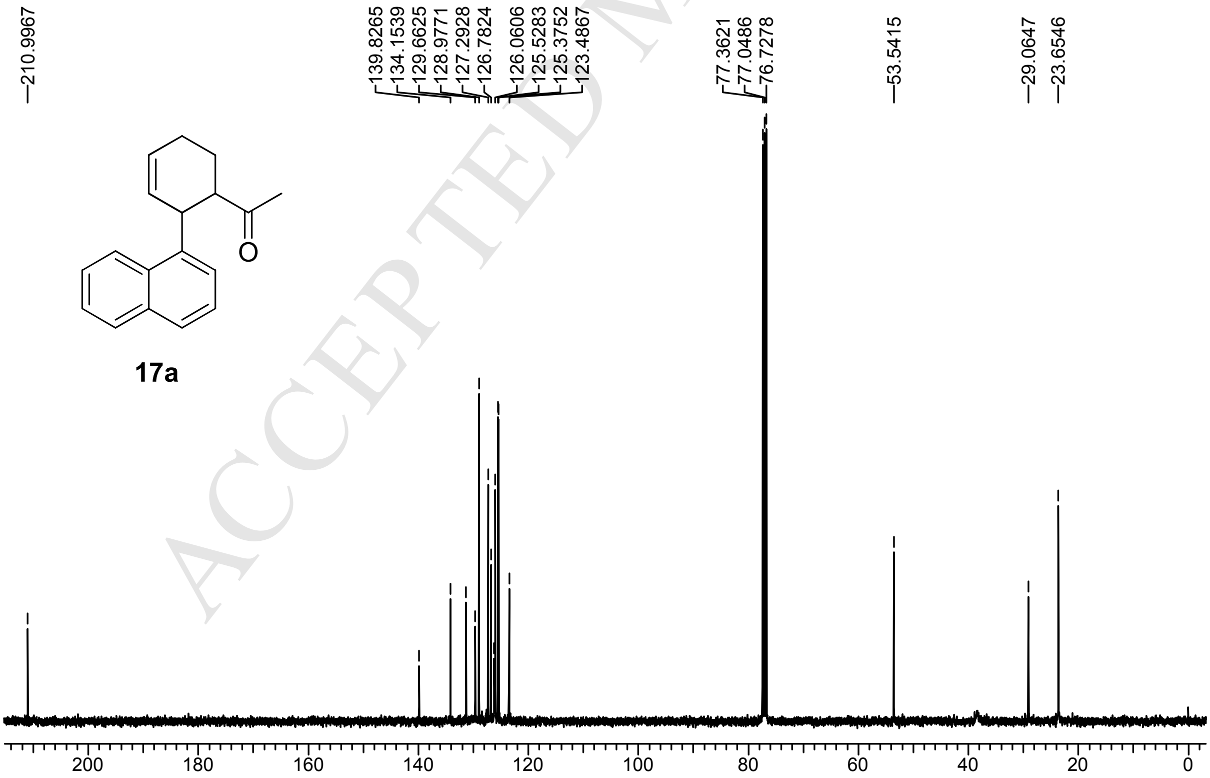
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **15** in CDCl$_3$





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **17a** in $CDCl_3$





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of **17b** in $CDCl_3$