Pd-Catalyzed Three-Component Coupling of *N*-Tosylhydrazone, Terminal Alkyne and Aryl Halide

Lei Zhou, Fei Ye, Yan Zhang and Jianbo Wang*

Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China,

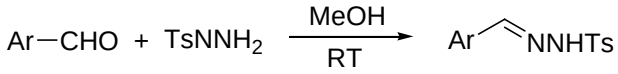
E-mail: wangjb@pku.edu.cn

CONTENTS

General All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. Toluene was dried over Na before use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR and ^{13}CNMR spectra were recorded on Varian 300 or Bruker ARX 400 spectrometer in $CDCl_3$ solution and the chemical shifts were reported in parts per million (d) relative to internal standard TMS (0 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

The synthesis of N-tosylhydrazones

N-Tosylhydrazones was prepared by literature procedure.[1]



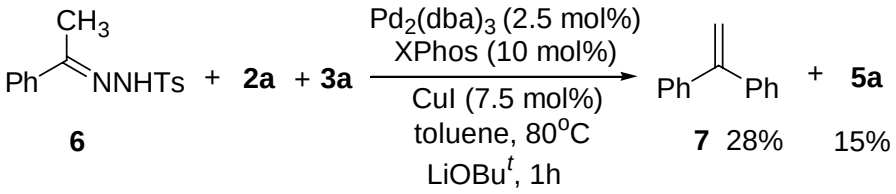
General procedure. A solution of pure $TsNHNH_2$ (5 mmol) in methanol (5 mL) was stirred and heated to 60 ^{o}C until the $TsNHNH_2$ was completely dissolved. The mixture was cooled to room temperature, and then carbonyl compounds were dropped to the mixture slowly. After approximately 5 min the crude products could be obtained as precipitates. The precipitates were washed by petroleum ether then removed *in vacuo* to afford the pure products. The reaction provides the *N*-tosylhydrazones in about 80% yield.

Representative experimental procedure for the three-component coupling of N-tosylhydrazone, terminal alkyne and aryl halide: $Pd_2(dba)_3$ (2.5 mol%, 4.5 mg), 2-(dicyclohexylphosphino)-2',4',6'-triisopropylbiphenyl (Xphos, 10 mol%, 9.5 mg), CuI (7.5 mol%, 3 mg), *t*-BuOLi (0.7 mmol, 56 mg) and *N*-tosylhydrazone **1a** (0.2 mmol, 55 mg) were suspended in toluene (0.8 mL) in a 5 mL Schlenk tube under nitrogen. Then bromobenzene **2** (X = Br) (34.3 mg, 0.22 mmol) and phenylacetylene (22.5 mg, 0.22 mmol) were added. The resulting solution was stirred at 90 ^{o}C for 1 h. After cooling to room temperature, the resulting mixture was filtered through a short path of silica gel, eluting with hexane and CH_2Cl_2. The volatile compounds were

removed *in vacuo* and the crude residue was purified by column chromatography (SiO_2, hexane) to give **4a** as a white solid (43 mg, 81%).

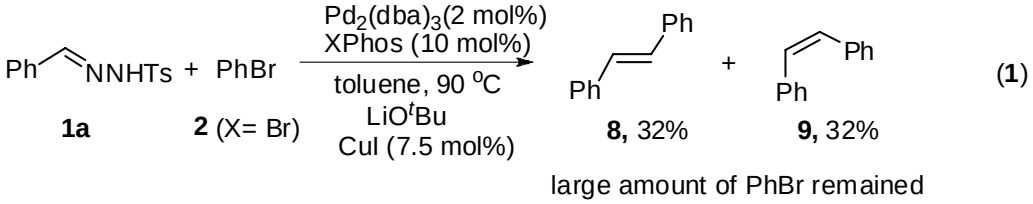
Control Experiments and Mechanistic Rationale

First, we examined the reaction of *N*-tosylhydrazones **6** with bromobenzene **2a** and phenylacetylene **3a**. Since in this case *β*-H is available, it is thus intriguing to see if the three-component is still possible. However, the results show that instead of the expected three-component product, olefin **7** was isolated in 28 % yield, along with direct Sonogashira coupling product **5a** (15 %).



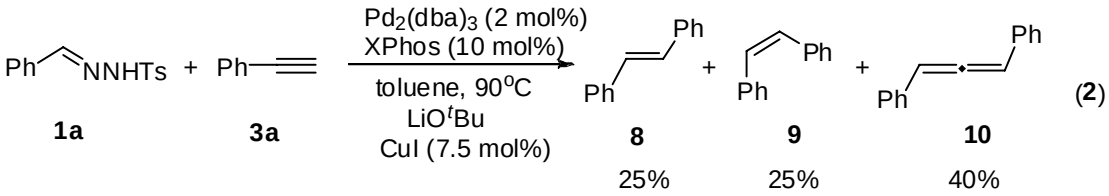
To gain further insight into the reaction mechanism, we carried out some control experiments (eqs 1-3). The reaction of **1a** and bromobenzene **2** (X = Br) in the absence of phenylacetylene afforded *cis*-stilbene and *trans*-stilbene in same yields of 32%, which were formed from the homo-coupling of **1a**. Most bromobenzene was remained unchanged (eq 1). When the reaction was carried out in the absence of halide, except stilbene **8** and **9**, allene **10** was also isolated in 40% yield. Lastly, under the standard reaction conditions the Sonogashira coupling of bromobenzene and phenylacetylene afforded the diphenylacetylene **5a** in 57% yield.

Reaction in the absence of alkyne

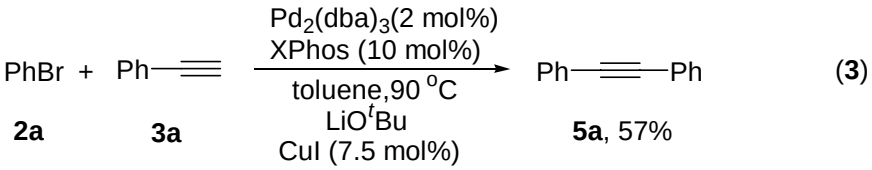


(**1**)

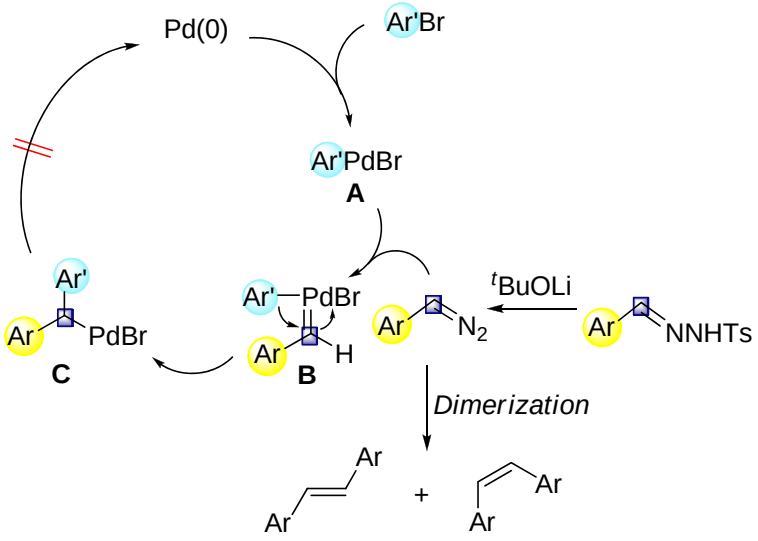
Reaction in the absence of halide



Reaction in the absence of N-tosylhydrazone

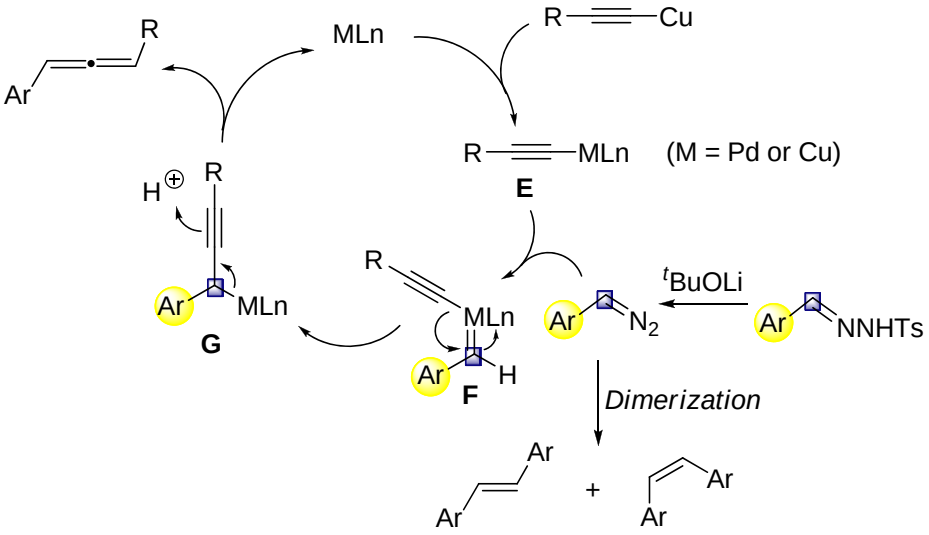


The control experiment results are in accordance with the reaction mechanism proposed in Scheme 2. In the absence of terminal alkyne (eq 1), the arylpalladium species **A** will decompose the diazo substrate to form Pd carbene **B**, from which migratory insertion occurs. Since transmetallation with copper acetylide is not possible due to the absence of terminal alkyne, the catalytic cycle will not complete and Pd(0) species will not regenerate. Thus, most aryl bromide remains intact. On the other hand, the diazo substrate will dimerize under the reaction conditions.



When aryl halide is not presence in the reaction, except the dimerization products,

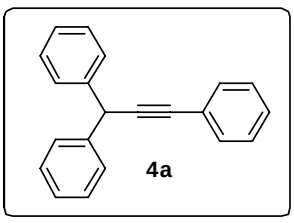
allene **10** was also obtained. The formation of allene can be rationalized by the formation of alkynyl palladium or copper species **E**, which decompose diazo substrate to form corresponding metal carbene intermediate **F**. Migratory insertion of alkynyl group to the carbenic carbon to generate **G**, which is followed by protonation to afford the allene product.



In the absence of *N*-tosylhydrazone, the Sonogashira coupling product was obtained in moderate yields, which are in accordance with the reaction mechanism proposed in Scheme 2.

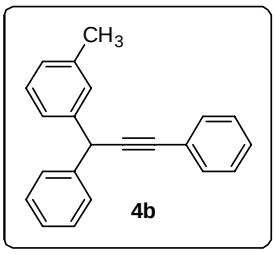
Spectral data for the products

1, 3, 3-Triphenyl-1-propyne (4a)[2]



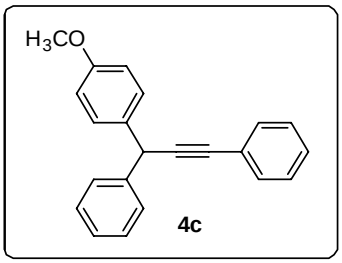
IR: ν_{max} 1596, 1489, 756, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 6 H), 7.33-7.20 (m, 9H), 5.20 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 131.8, 128.8, 128.4, 128.1, 128.0, 127.0, 123.7, 90.4, 85.1, 43.9; MS (70 eV) *m*/*z* (%) 268 (100) [M^+].

1-Phenyl-3-phenyl-3-(3-methylphenyl)-1-propyne (4b)[2]



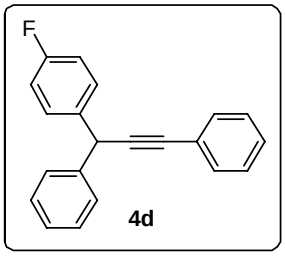
IR: ν_{max} 3339, 2925, 1598, 1490, 1048, 756, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 4H), 7.35-7.30 (m,5 H), 7.30-7.20 (m, 4H), 7.06-7.05 (m, 1 H), 5.18 (s. 1H), 2.34 (s 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 141.6, 138.2, 131.6, 128.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.6, 126.8, 124.9, 123.5, 90.3, 84.7, 43.7, 21.5; MS (70 eV) *m/z* (%) 282 (100) $[M^+]$.

1-Phenyl-3-phenyl-3-(4-methoxyphenyl)-1-propyne (4c)[2]



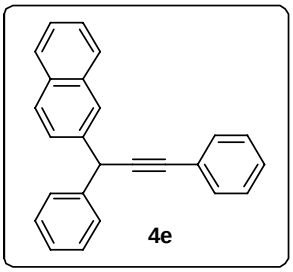
IR: ν_{max} 2925, 1607, 1491, 756, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 4H), 7.36-7.29 (m, 7H), 7.25-7.23 (m, 1H), 6.87-6.85 (m, 2 H), 5.17 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.0, 133.9, 131.6, 128.9, 128.6, 128.2, 127.9, 127.8, 126.8, 123.5, 114.0, 90.5, 84.7, 55.3, 42.9; MS (70 eV) *m/z* (%) 298 (100) $[M^+]$.

1-Phenyl-3-phenyl-3-(4-fluorophenyl)-1-propyne (4d)



IR: ν_{max} 3029, 1505, 1491, 755, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2 H), 7.43-7.38 (m, 4H), 7.35-7.30 (m, 5H), 7.27-7.23 (m, 1H), 7.03-7.00 (m, 2H), 5.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J = 244 Hz), 141.5, 137.5 (d, J = 3 Hz), 131.6, 129.4 (d, J = 8.1 Hz), 128.6, 128.2, 128.0, 127.8, 127.0, 123.3, 115.4 (d, J = 21 Hz), 89.9, 85.0, 43.0; MS (70 eV) *m/z* (%) 286 (100) $[M^+]$; HRMS (ESI) calcd. for $C_{21}H_{16}F$ $[(M+H)^+]$ 287.1230, found: 287.1236.

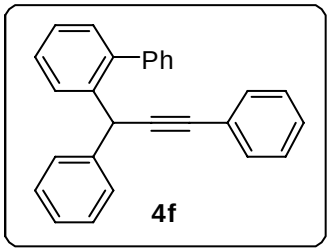
1-Phenyl-3-phenyl-3-(2-naphthyl)-1-propyne (4e)



IR: ν_{max} 3339, 1598, 1490, 754, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.86-7.80 (m, 3H), 7.54-7.46 (m, 7H), 7.37-7.33 (m, 5H), 7.33-7.25 (m, 1H), 5.40, (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 139.1, 133.4, 132.5,

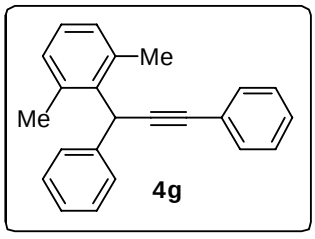
131.7, 128.7, 128.4, 128.2, 128.0, 127.9, 127.6, 127.0, 126.3, 126.2, 126.1, 125.8, 123.5, 90.1, 85.3, 43.9; MS (70 eV) *m/z* (%) 318 (100) [M^+]; HRMS (ESI) calcd. for $C_{25}H_{19}$ [$(M+H)^+$] 319.1481, found: 319.1486.

1-Phenyl-3-phenyl-3-(4-biphenyl)-1-propyne (4f)



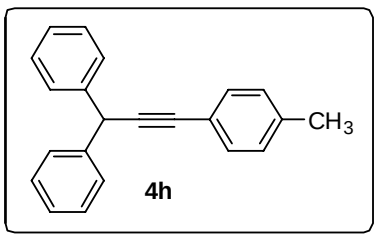
IR: ν_{max} 3330, 1597, 1490, 753, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 1H), 7.50-7.47 (m, 2H), 7.46-7.42 (m, 2 H), 7.40-7.35 (m, 4H), 7.33-7.27 (m, 5H), 7.25-7.18 (m, 5H), 5.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 141.3, 141.0, 139.6, 131.6, 130.0, 129.4, 129.2, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.2, 126.8, 126.5, 123.6, 91.0, 84.5, 39.8; MS (70 eV) *m/z* (%) 344 (96) [M^+]; HRMS (ESI) calcd. for $C_{27}H_{21}$ [$(M+H)^+$] 345.1637, found: 345.1639.

1-Phenyl-3-phenyl-3-(2,6-dimethylphenyl)-1-propyne (4g)



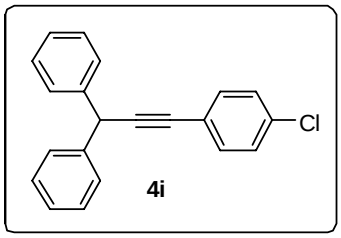
IR: ν_{max} 3024, 1598, 1490, 1029, 755, 700, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.47 (m, 2 H), 7.38-7.20 (m, 8H), 7.13-7.04 (m, 3H), 5.77 (s, 1H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 137.8, 137.3, 131.8, 129.3, 128.5, 128.4, 128.0, 127.3, 127.1, 126.5, 123.9, 89.1, 84.4, 37.4, 21.1; MS (70 eV) *m/z* (%) 296 (100) [M^+]; HRMS (ESI) calcd. for $C_{23}H_{21}$ [$(M+H)^+$] 297.1637, found: 297.1643.

1-(4-Methylphenyl)-3,3-diphenyl-1-propyne (4h)[2]



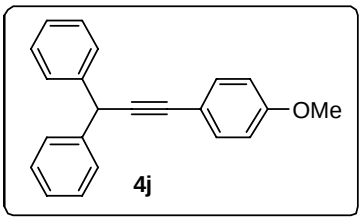
IR: ν_{max} 3207, 1598, 1492, 906, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.08 (m, 14H), 5.19 (s, 1 H), 2.32, (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 138.2, 131.7, 129.1, 128.7, 128.1, 127.0, 120.6, 89.6, 85.1, 43.9, 21.6; MS (70 eV) *m/z* (%) 282 (100) [M^+].

1-(4-Chlorophenyl)-3,3-diphenyl-1-propyne (4i):



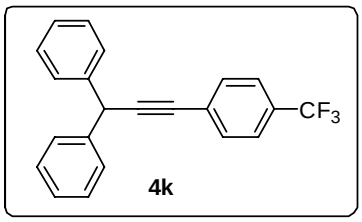
IR: ν_{max} 3328, 2973, 1596, 1489, 1089, 1048, 907, 698, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.37 (m, 6H), 7.33-7.30 (m, 4H), 7.27-7.21 (m, 4H), 5.19 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 133.1, 130.2, 128.8, 128.7, 128.0, 127.1, 122.1, 91.4, 83.9, 43.9; MS (70 eV): *m/z* (%) 302 (86) [M^+], 304 (29) MS (70 eV) *m/z* (%) 296 (100) [$(M+2)^+$]; HRMS (ESI) calcd. for $C_{21}H_{15}Cl$ [$(M+H)^+$] 303.0935, found: 303.0935.

1-(4-Methoxylphenyl)-3,3-diphenyl-1-propyne (4j)



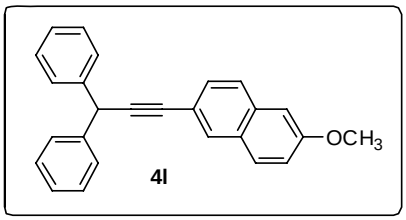
IR: ν_{max} 3027, 1605, 1508, 1492,1030, 831, 699, 757cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.39 (m, 7H), 7.32-7.29 (m, 5 H),7.23-7.20 (m, 2H), 6.83 (s, 1 H), 6.81 (s, 1H), 5.19 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 142.1, 133.2, 128.7, 128.1, 127.0, 115.8, 114.0, 88.8, 84.8, 55.4, 43.9; MS (70 eV) *m/z* (%) 298 (100) [M^+]; HRMS (ESI) calcd. for $C_{22}H_{19}O$ [$(M+H)^+$] 299.1430, found: 299.1433.

1-(4-Trifluoromethyl)-3,3-diphenyl-1-propyne (4k)



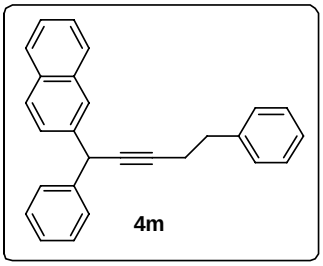
IR: ν_{max} 1614, 1493, 1047, 907, 841, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 4H), 7.43-7.41 (m, 4 H), 7.35-7.31 (m, 4H), 7.27-7.25 (m, 2H), 5.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 132.1, 130.2, 129.9 (d, *J* = 32.0 Hz), 128.9, 128.0, 127.5, 127.2, 125.2 (q, *J* = 3.6 Hz), 93.1, 83.8, 43.9; MS (70 eV) *m/z* (%) 336 (74) [M^+]; HRMS (ESI) calcd. for $C_{22}H_{16}F_3$ [$(M+H)^+$] 337.1198, found: 337.1209.

1-(6-methoxy-2-naphthyl)-3,3-diphenyl-1-propyne (4l)



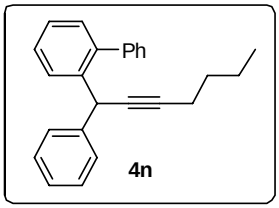
IR: ν_{max} 3207, 1600, 1493, 1260, 1030, 806, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.68-7.09 (m, 15H), 5.25 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 142.0, 134.1, 131.3, 129.4, 129.3, 128.8, 128.6, 128.1, 127.0, 126.8, 119.5, 118.6, 106.0, 89.9, 85.5, 55.5, 44.0; MS (70 eV) *m*/*z* (%) 348 (47) $[M^+]$; HRMS (ESI) calcd. for $C_{26}H_{21}O$ $[(M+H)^+]$ 349.1586, found: 349.1593.

2-(1,5-diphenylpent-2-ynyl)naphthalene (4m)



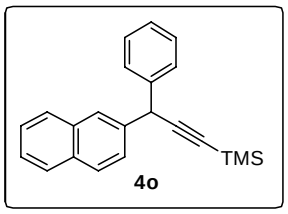
IR: ν_{max} 3339, 2973, 1600, 1492, 1048, 907, 730, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 4H), 7.49-7.45 (m, 2 H), 7.46-7.42 (m, 2 H), 7.37-7.31 (m, 2H), 7.30-7.23 (m, 9H), 5.13 (s, 1 H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.65 (dt, *J* = 7.2, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 141.3, 141.0, 139.6, 131.6, 130.0, 129.4, 129.2, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.2, 126.8, 126.5, 123.6, 91.0, 84.5, 39.8; MS (70 eV) *m*/*z* (%) 346 (100) $[M^+]$; HRMS (ESI) calcd. for $C_{27}H_{23}$ $[(M+H)^+]$ 347.1794, found: 347.1796.

Hept-2-yne-1,1-diyldibenzene (4n)



IR: ν_{max} 3059, 2927, 1597, 1492, 908, 753, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 1H), 7.43-7.26 (m, 8H), 7.22-7.14 (m, 5H), 5.19 (s, 1H), 2.30 (dt, *J* = 6.8, 2.4 Hz, 2H), 1.59-1.42 (m, 4H), 0.96 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.19, 141.17, 140.3, 129.9, 129.4, 129.0, 128.16, 128.10, 127.8, 127.7, 127.0, 126.5, 126.2, 84.7, 81.3, 39.2, 31.1, 22.0, 18.7, 13.6; MS (70 eV): *m*/*z* (%) 324 (20) $[M^+]$, 267 (100); HRMS (ESI) calcd. for $C_{27}H_{23}$ $[(M+H)^+]$ 325.1950, Found: 325.1958.

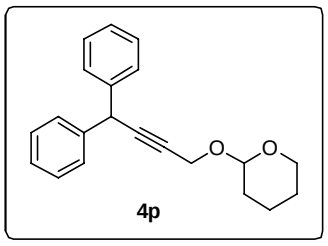
trimethyl(3-(naphthalen-2-yl)-3-phenylprop-1-ynyl)silane (**4o**)



4o

IR: ν_{max} 3027, 1598, 1493, 906, 697cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.86-7.79 (m, 3H), 7.51-7.46 (m, 5H), 7.37-7.26 (m, 3H), 5.23 (s, 1H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 139.0, 133.5, 132.5, 128.7, 128.5, 128.1, 128.0, 127.7, 127.0, 126.4, 126.2, 125.9, 106.7, 89.7, 44.4, 0.29; MS (70 eV): *m*/*z* (%): 314 (64) [M^{+}] 239 (28), 73 (100); HRMS (ESI): Calcd. for $C_{22}H_{22}Si$ [(M+H)$^{+}$] 315.1563, Found: 315.1564.

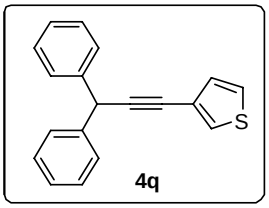
2-(4,4-Diphenylbut-2-ynyloxy)tetrahydro-2H-pyran (4p)



4p

IR: ν_{max} 3327, 2924, 1600, 1043, 754, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.25 (m, 10H), 5.80 (t, J = 6.4 Hz, 1H), 4.69 (t, J = 3.6 Hz, 1H), 4.41-4.23 (m, 2H), 3.89-3.83 (m, 1H), 3.46-3.41 (m, 1H), 1.83-1.66 (m, 2H), 1.59-1.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 136.5, 128.7, 128.6, 128.5, 128.0, 127.48, 127.47, 111.1, 97.8, 92.1, 64.8, 62.5, 43.4, 30.7, 25.5, 19.6; MS (70 eV): *m*/*z* (%): 324 (8) [M^{+}], 222 (45), 205 (100), 191 (53); HRMS (ESI): Calcd. for $C_{11}H_{22}O_2$ [(M+H)$^{+}$] 307.0643, Found: 307.0632.

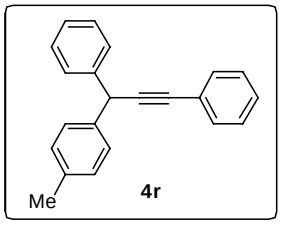
1-thienyl-3,3-diphenyl-1-propyne (4q)



4q

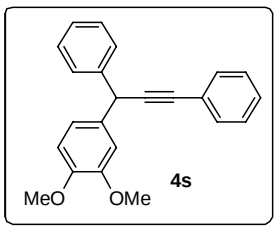
IR: ν_{max} 3026, 1492, 907, 755, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 5H), 7.32-7.28 (m, 4H), 7.23-7.20 (m, 3H), 7.12-7.11 (m, 1H), 5.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 130.2, 128.8, 128.4, 128.0, 127.0, 125.2, 122.6, 89.8, 80.1, 43.9; MS (70 eV) *m*/*z* (%) 274 (100) [M^{+}]; HRMS (ESI) calcd. for $C_{19}H_{15}S$ [(M+H)$^{+}$] 275.0889, found: 275.0890.

1-Phenyl-3-phenyl-3-(4-methylphenyl)-1-propyne (4r)[2]



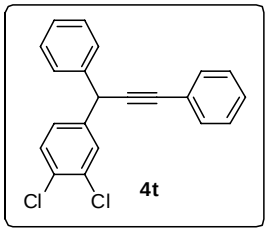
IR: ν_{max} 3026, 1598, 1490, 908, 755, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 1H), 7.45-7.44 (m, 2H), 7.38-7.36 (m, 2H), 7.32-7.27 (m, 5H), 7.23-7.14 (m, 4H), 5.38 (s, 1H), 2.32 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.6, 136.1, 131.8, 130.9, 129.0, 128.6, 128.3, 128.2, 128.1, 127.3, 126.9, 126.5, 123.7, 90.4, 84.9, 41.0, 19.9; MS (70 eV) *m/z* (%) 282 (100) [M^+].

1-Phenyl-3-phenyl-3-(3,4-dimethoxylphenyl)-1-propyne (4s)



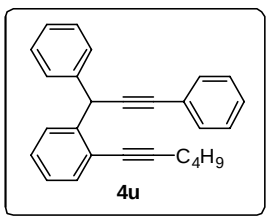
IR: ν_{max} 2930, 1594, 1490, 1028, 757, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 4H), 7.34-7.24 (m, 6 H), 6.98-6.96 (m, 2H), 6.83-6.81 (m, 1H), 5.17 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 148.2, 142.0, 134.4, 131.8, 128.7, 128.4, 128.1, 127.9, 127.0, 123.7, 120.2, 111.4, 111.3, 90.6, 84.9, 56.1, 56.0, 43.4; MS (70 eV) *m/z* (%) 328 (100) [M^+]; HRMS (ESI): calcd. for $C_{23}H_{21}O_2$ [$(M+H)^+$] 329.1536, found: 329.1541.

1-Phenyl-3-phenyl-3-(3,4-dichlorophenyl)-1-propyne (4t)



IR: ν_{max} 3029, 1598, 1490, 1031, 907, 756, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.52 (m, 1H), 7.49-7.46 (m, 2H), 7.42-7.25 (m, 10H), 5.16 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 142.0, 140.6, 132.6, 131.0, 130.5, 129.8, 128.8, 128.3, 127.8, 127.3, 127.2, 123.0, 88.8, 85.6, 42.9; MS (70 eV) *m/z* (%) 336 (70) [M^+], 301(100); HRMS (ESI) calcd. for $C_{23}H_{15}Cl_2$ [$(M+H)^+$] 337.0545, found: 337.0549.

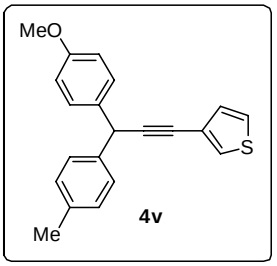
(3-(2-(Hex-1-ynyl)phenyl)prop-1-yne-1,3-diyl)dibenzene (4u)



IR: ν_{max} 1597, 1490, 754, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59-7.34 (m, 5H), 7.32-7.14 (m, 9 H), 5.84 (s, 1H), 2.48-2.44 (t, *J* = 10.8 Hz, 2H), 1.63-1.53 (m, 2H), 1.51-1.44

(m, 2H), 0.94-0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.6, 132.4, 131.9, 131.4, 128.4, 128.3, 128.1, 127.9, 126.9, 126.8, 123.8, 123.2, 95.6, 90.1, 84.4, 79.2, 41.3, 31.0, 22.2, 19.5, 13.8; MS (70 eV) *m*/*z* (%) 348 (62) [M^+] HRMS (ESI) calcd. for $C_{27}H_{25}$ [$(M+H)^+$] 349.1950, found: 349.1956.

1-thienyl-3-(4-methoxylphenyl)-3-(4-methylphenyl)-1-propyne (4v)

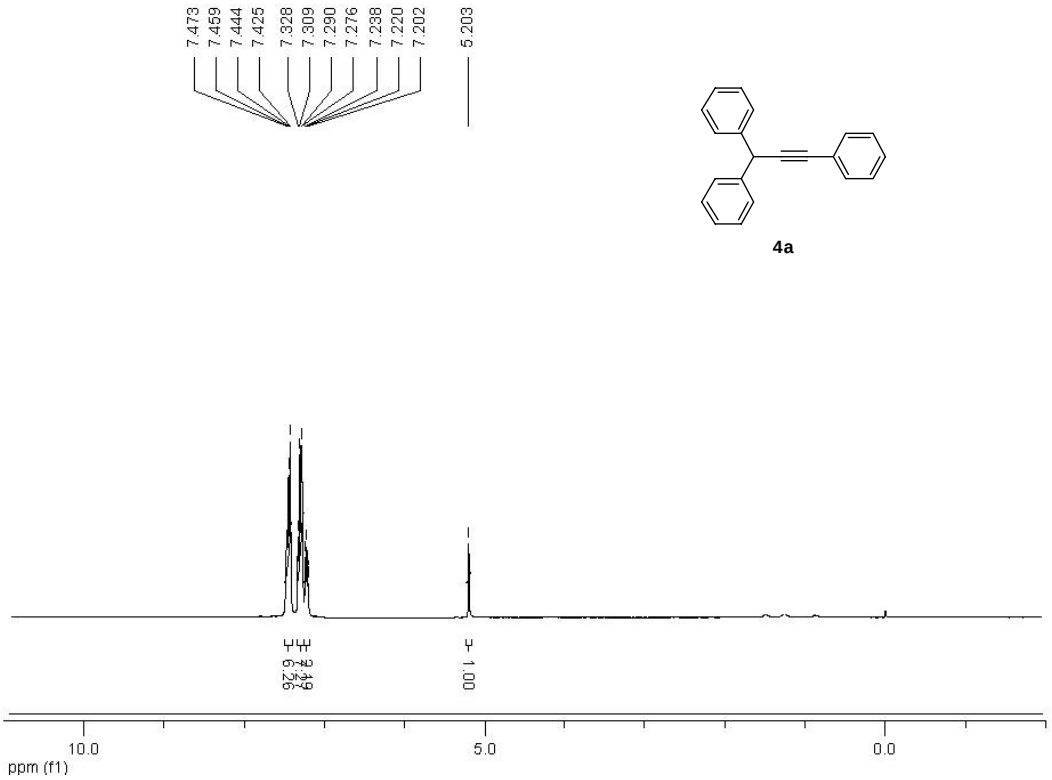


IR: ν_{max} 3004，2676，1156，1540，908，732，653 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 2.8 Hz, 1 H), 7.33-7.35 (m, 2 H), 7.16-7.28 (m, 5 H), 6.91 (d, J = 8.8 Hz, 2H), 5.39 (s, 1 H), 3.83 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 139.7, 135.9, 132.8, 130.8, 130.0, 129.0, 128.7, 128.1, 127.1, 126.3, 125.1, 122.6, 113.9, 90.0, 79.5, 55.3, 40.1, 19.7; MS (70 eV) *m*/*z* (%) 318 (100) [M^+]; HRMS (ESI) calcd. for $C_{21}H_{18}OS$ [$(M+H)^+$] 319.1151, found: 319.1148.

Reference

(1) Fulton, J. R.; Aggarwal,V. K.; de Vicente, J. *Eur. J. Org. Chem.* **2005**, 1479.

(2) Xiang, S. -K.; Zhang, L. -H.; Jiao, N. *Chem. Commun.* **2009**, 6487.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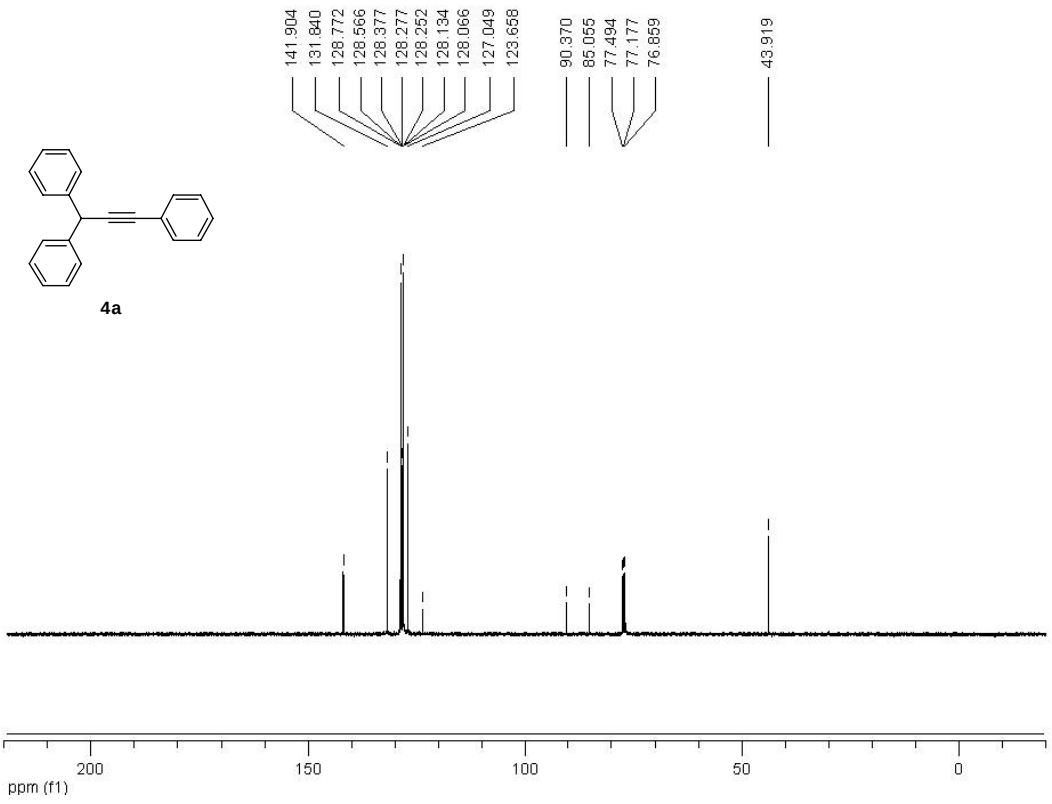
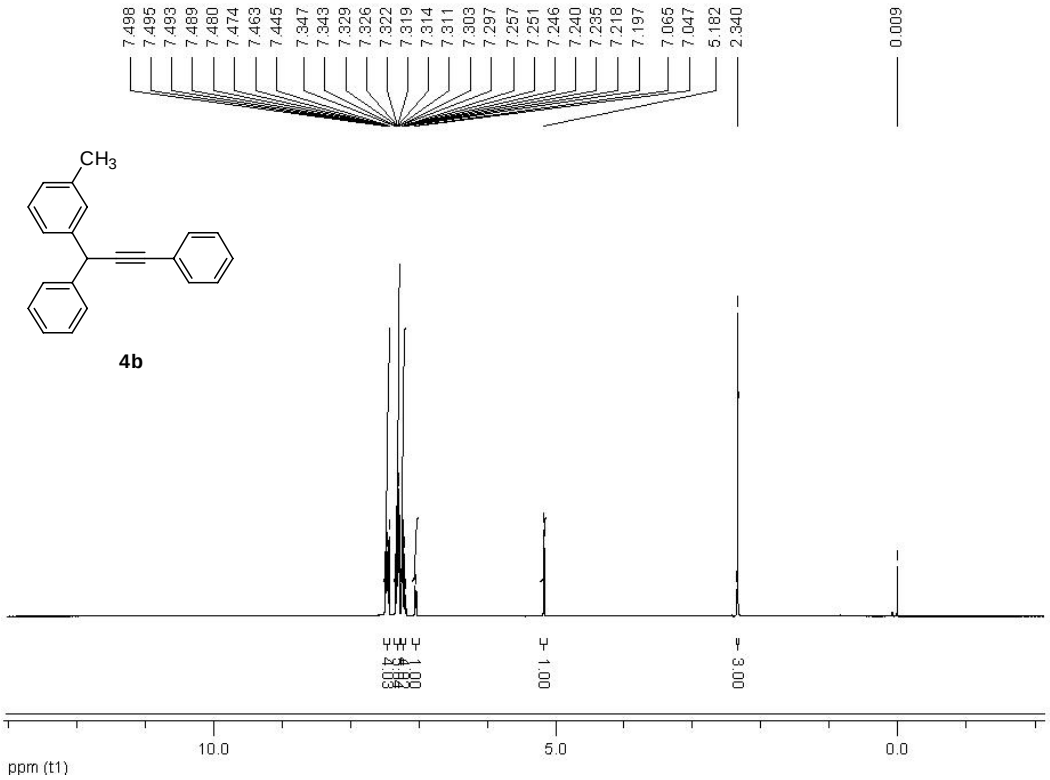
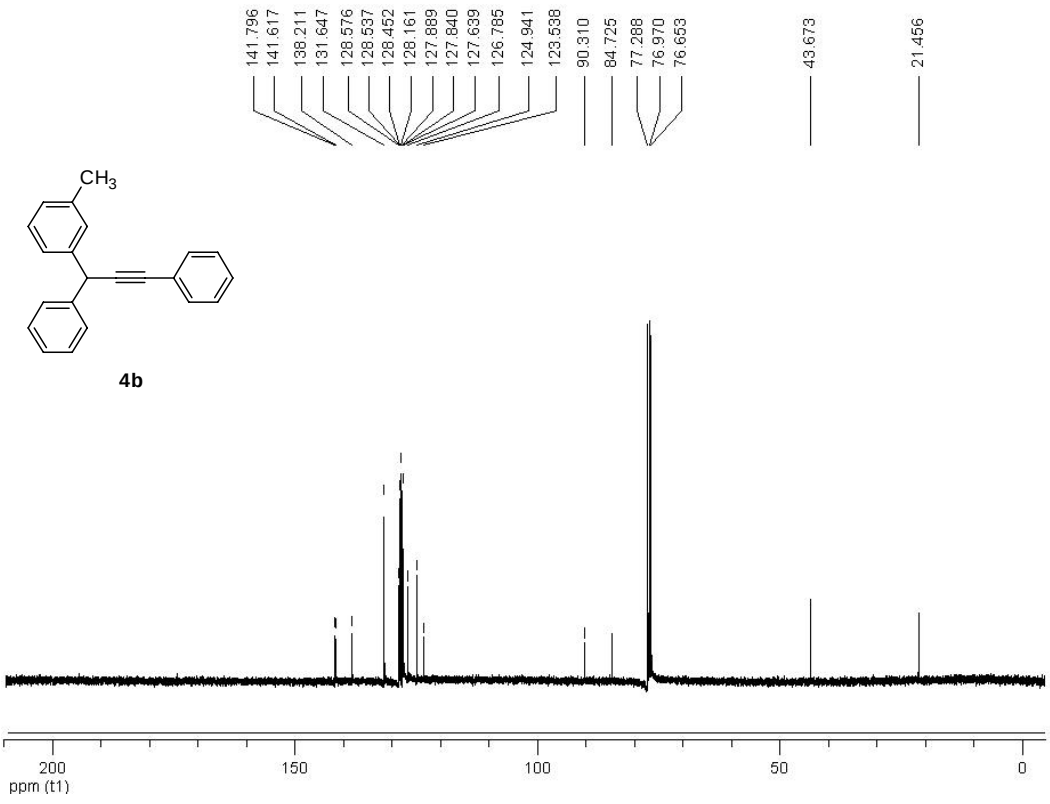
7.444
7.425
7.328
7.309
7.290
7.276
7.238
7.220
7.202
5.203
4a
10.0
5.0
0.0
ppm (f1)


141.904
131.840
128.772
128.566
128.377
128.277
128.252
128.134
128.066
127.049
123.658
90.370
85.055
77.494
77.177
76.859
43.919
4a
200
150
100
50
0
ppm (f1)


7.498
7.495
7.493
7.489
7.480
7.474
7.463
7.445
7.347
7.343
7.329
7.326
7.322
7.319
7.314
7.311
7.303
7.297
7.257
7.251
7.246
7.240
7.235
7.218
7.197
7.065
7.047
5.182
2.340
0.009
CH3
4b
3.00
1.00
10.0
5.0
0.0
ppm (t1)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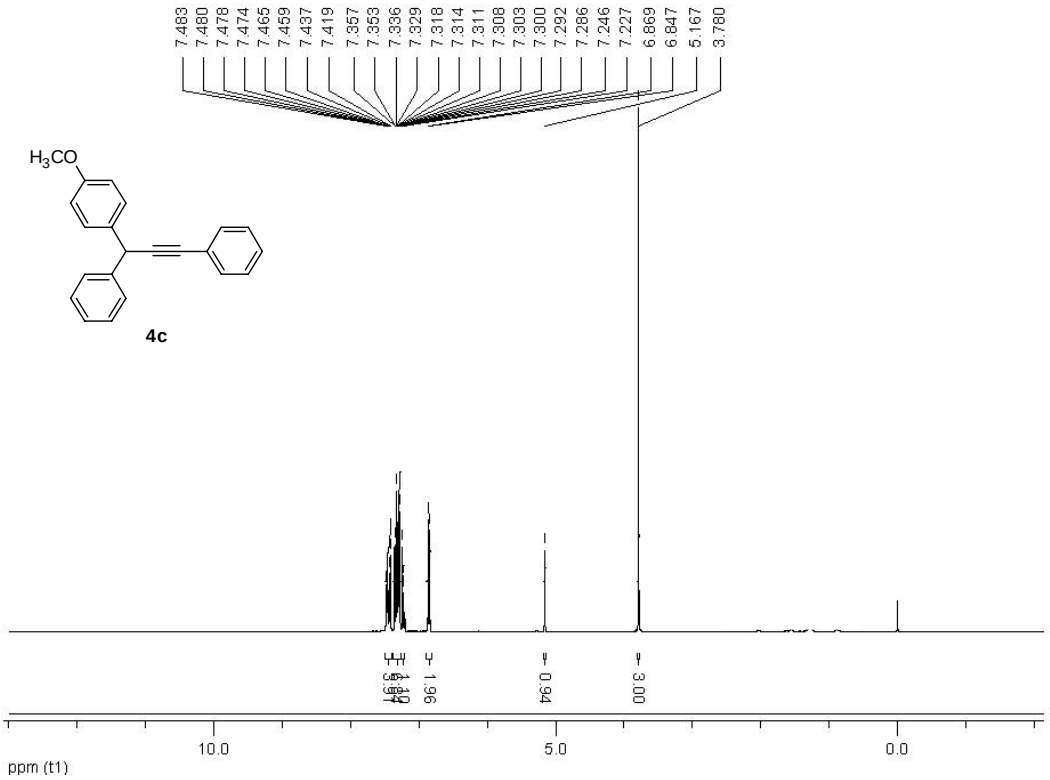
141.617
138.211
131.647
128.576
128.537
128.452
128.161
127.889
127.840
127.639
126.785
124.941
123.538
90.310
84.725
77.288
76.970
76.653
43.673
21.456
CH3
4b
200
150
100
50
0
ppm (t1)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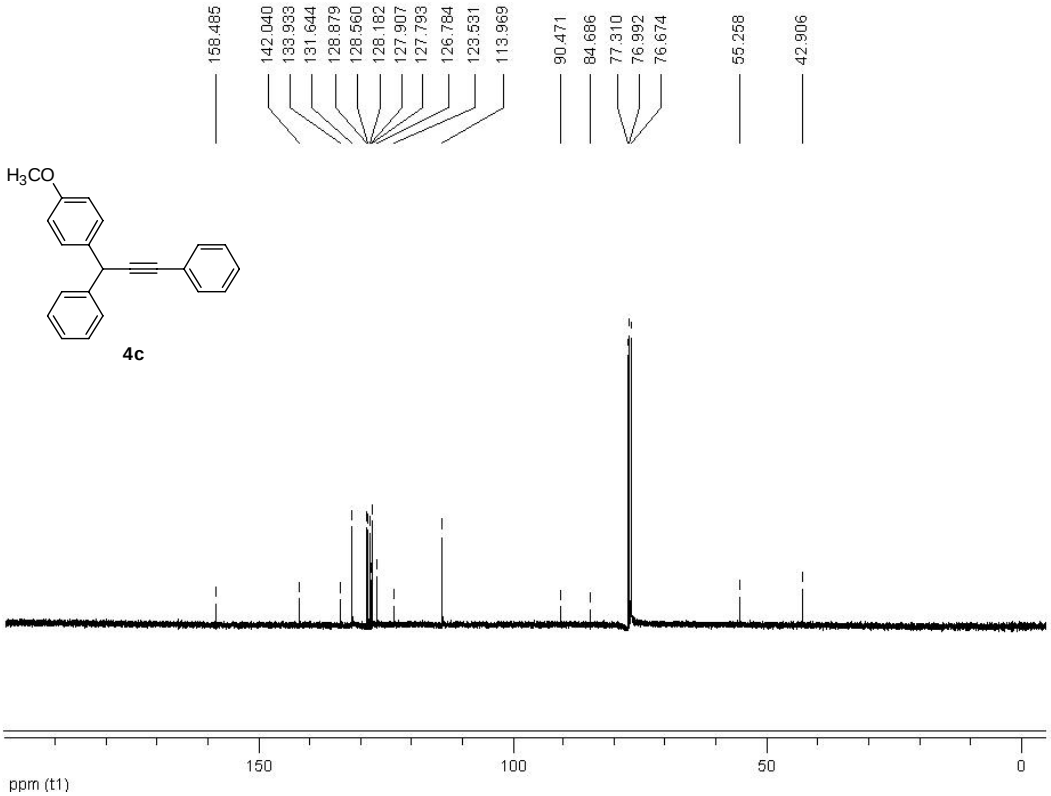
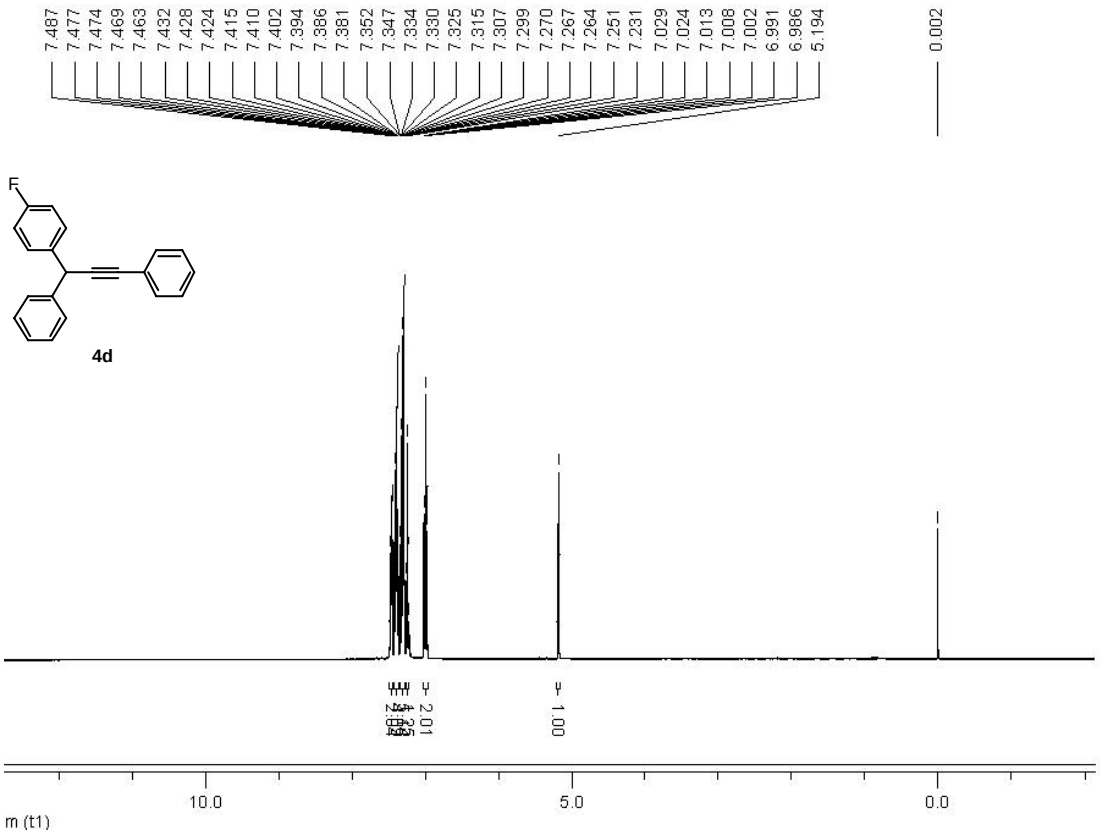
7.480
7.478
7.474
7.465
7.459
7.437
7.419
7.357
7.353
7.336
7.329
7.318
7.314
7.311
7.308
7.303
7.300
7.292
7.286
7.246
7.227
6.869
6.847
5.167
3.780
H3CO
4c
3.00
0.94
1.96
10.0
5.0
0.0
ppm (t1)


158.485
142.040
133.933
131.644
128.879
128.560
128.182
127.907
127.793
126.784
123.531
113.969
90.471
84.686
77.310
76.992
76.674
55.258
42.906
H3CO
4c
150
100
50
0
ppm (t1)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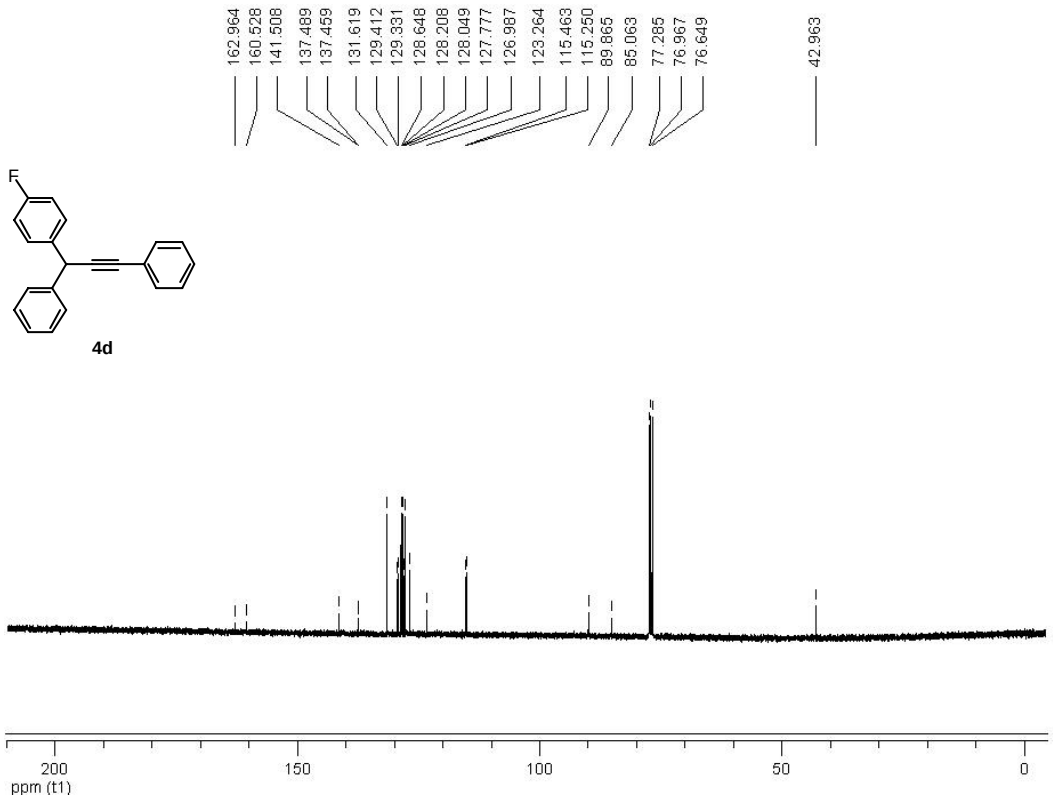
7.477
7.474
7.469
7.463
7.432
7.428
7.424
7.415
7.410
7.402
7.394
7.386
7.381
7.352
7.347
7.334
7.330
7.325
7.315
7.307
7.299
7.270
7.267
7.264
7.251
7.231
7.029
7.024
7.013
7.008
7.002
6.991
6.986
5.194
0.002
F
4d
2.01
1.00
10.0
5.0
0.0
m (t1)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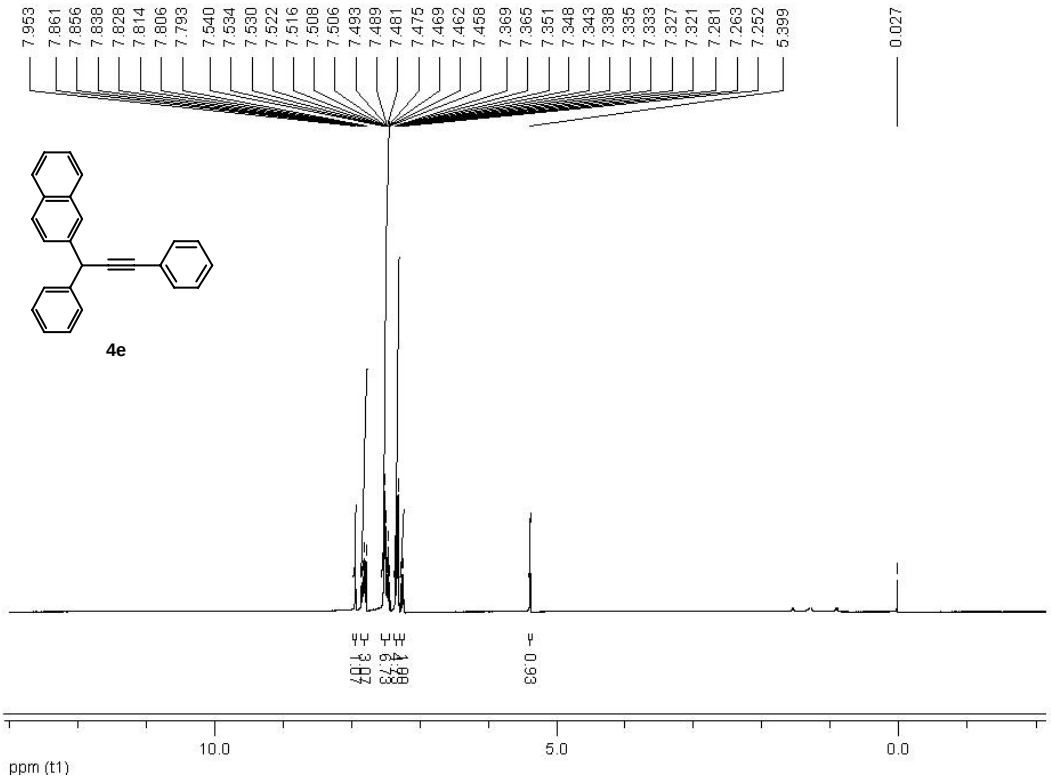
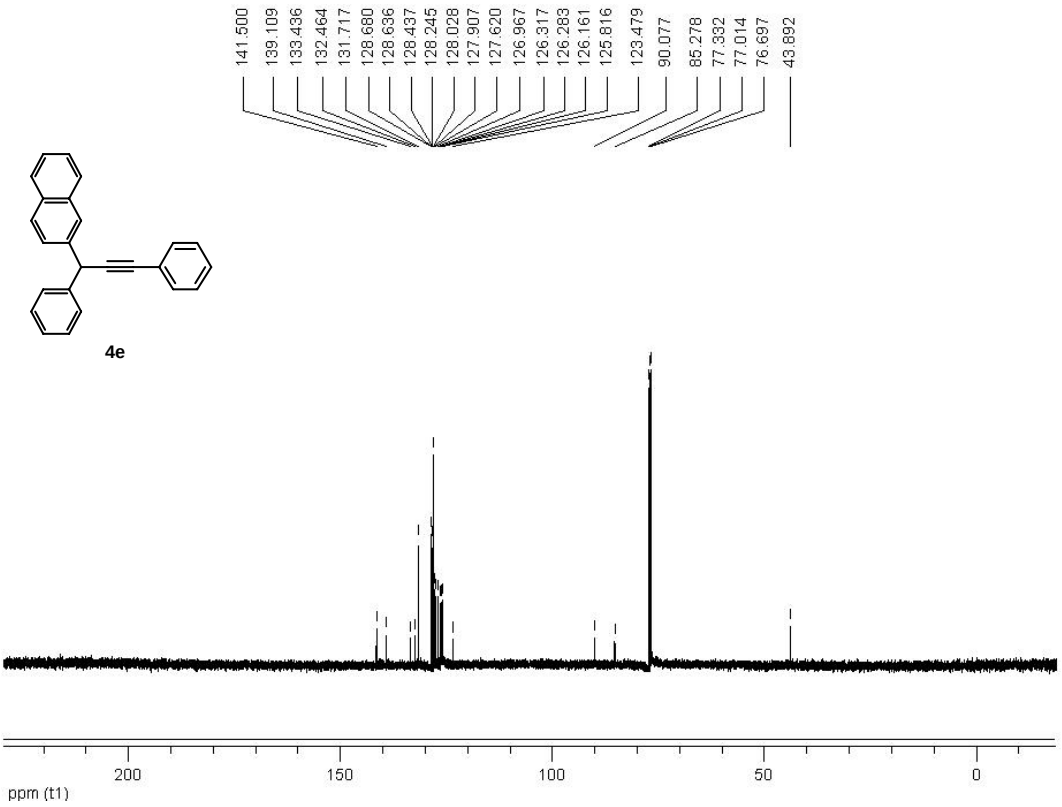
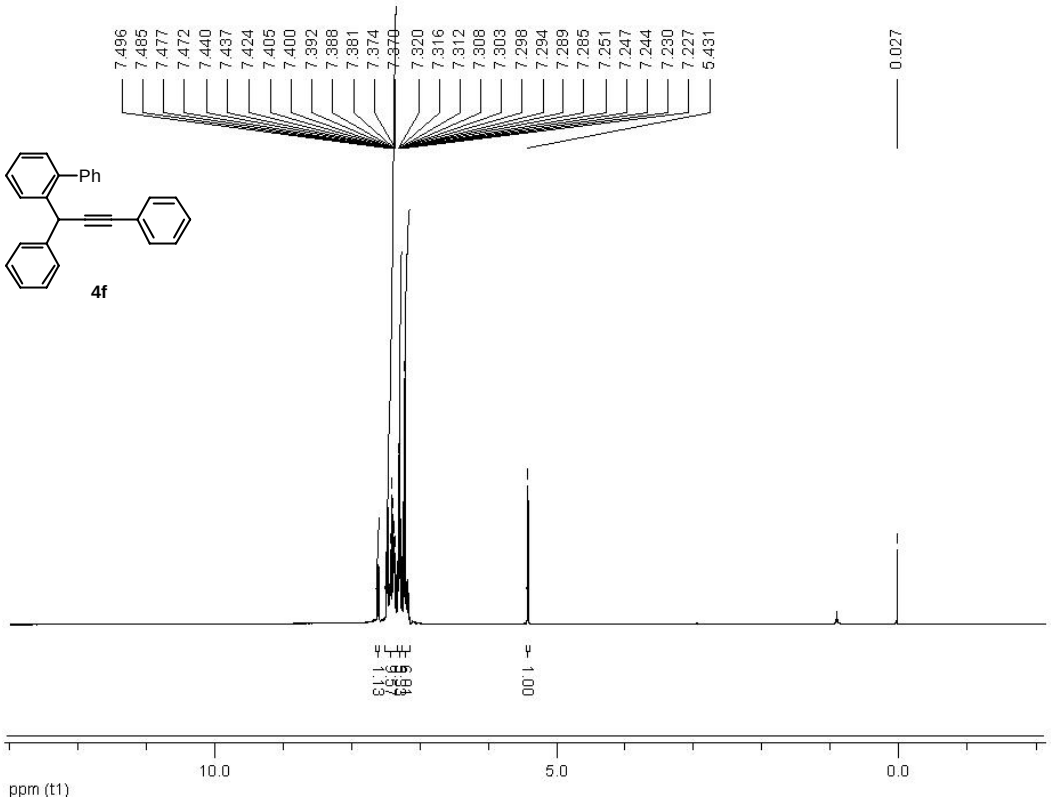
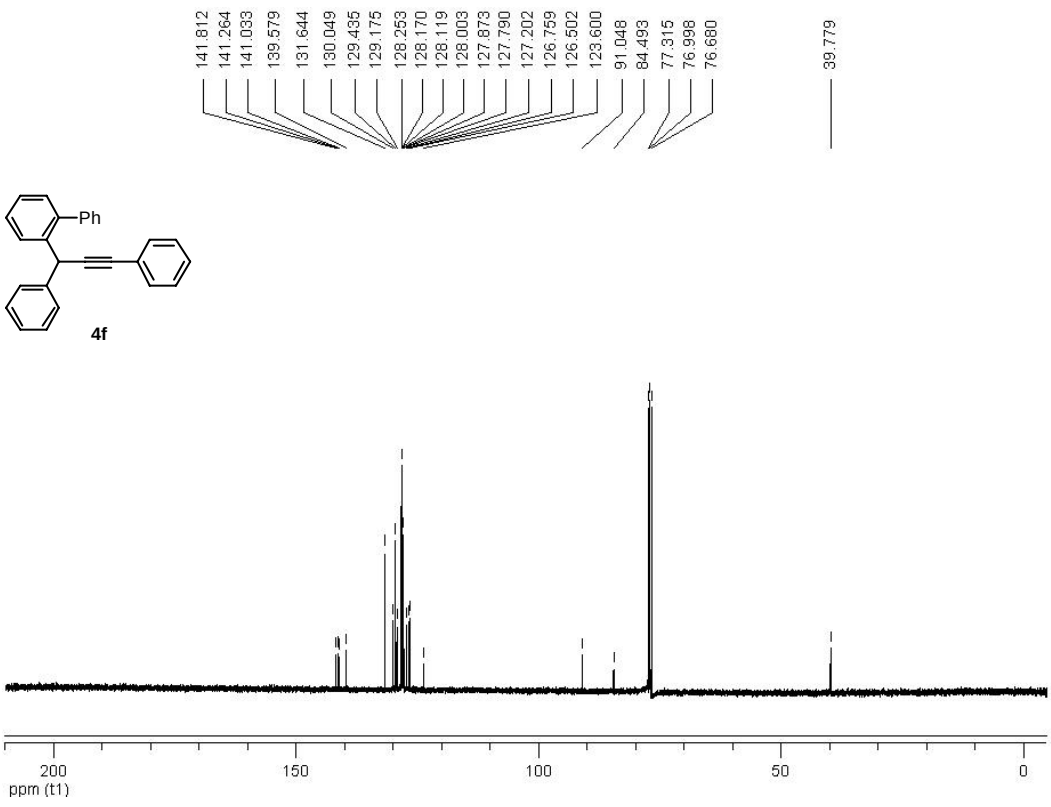
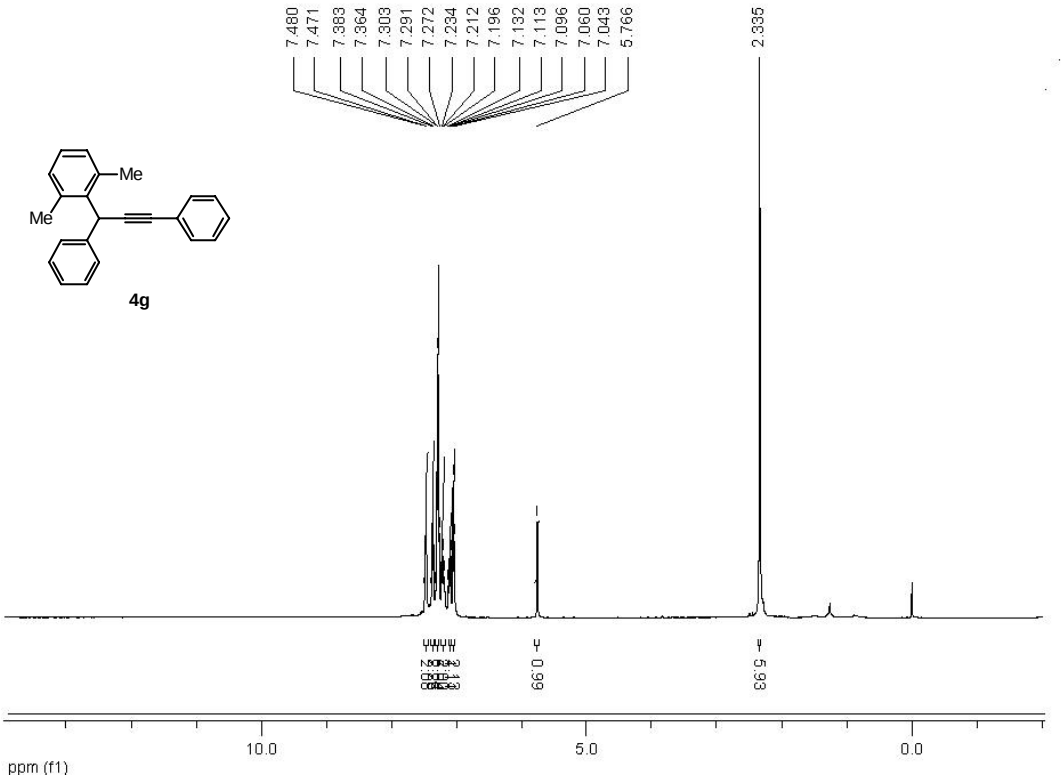
160.528
141.508
137.489
137.459
131.619
129.412
129.331
128.648
128.208
128.049
127.777
126.987
123.264
115.463
115.250
89.865
85.063
77.285
76.967
76.649
42.963
F
4d
200
150
100
50
0
ppm (t1)

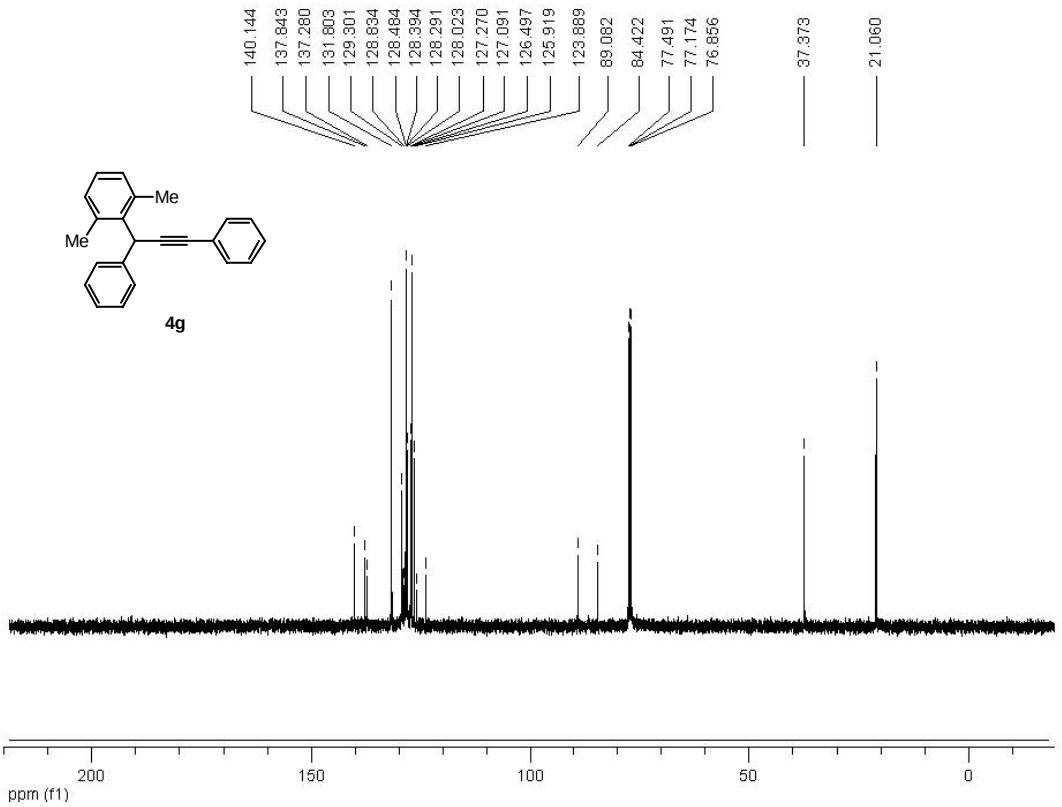

7.953
7.861
7.856
7.838
7.828
7.814
7.806
7.793
7.540
7.534
7.530
7.522
7.516
7.508
7.506
7.493
7.489
7.481
7.475
7.469
7.462
7.458
7.369
7.365
7.351
7.348
7.343
7.338
7.335
7.333
7.327
7.321
7.281
7.263
7.252
5.399
0.027
4e
3.07
4.99
6.73
0.93
10.0
5.0
0.0
ppm (t1)

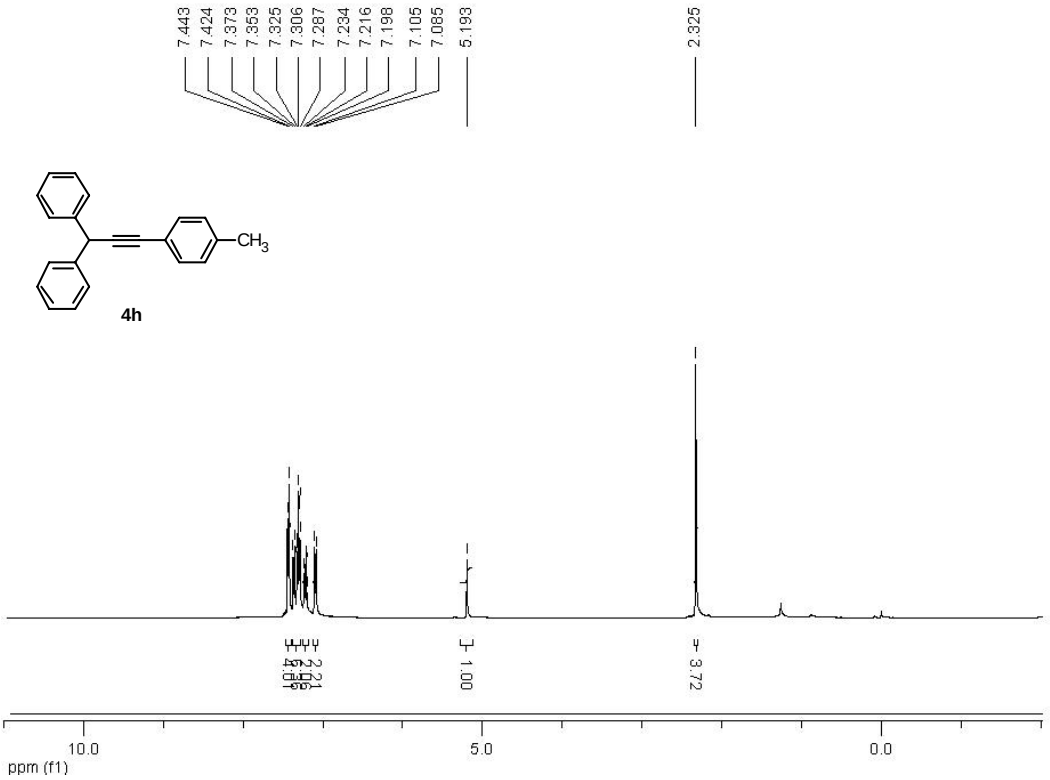

141.500
139.109
133.436
132.464
131.717
128.680
128.636
128.437
128.245
128.028
127.907
127.620
126.967
126.317
126.283
126.161
125.816
123.479
90.077
85.278
77.332
77.014
76.697
43.892
4e
200
150
100
50
0
ppm (t1)


7.496
7.485
7.477
7.472
7.440
7.437
7.424
7.405
7.400
7.392
7.388
7.381
7.374
7.370
7.320
7.316
7.312
7.308
7.303
7.298
7.294
7.289
7.285
7.251
7.247
7.244
7.230
7.227
5.431
0.027
Ph
4f
13.13
1.00
10.0
5.0
0.0
ppm (t1)


141.812
141.264
141.033
139.579
131.644
130.049
129.435
129.175
128.253
128.170
128.119
128.003
127.873
127.790
127.202
126.759
126.502
123.600
91.048
84.493
77.315
76.998
76.680
39.779
Ph
4f
200
150
100
50
0
ppm (t1)


7.480
7.471
7.383
7.364
7.303
7.291
7.272
7.234
7.212
7.196
7.132
7.113
7.096
7.060
7.043
5.766
2.335
Me
Me
4g
6.00
6.99
10.0
5.0
0.0
ppm (f1)


140.144
137.843
137.280
131.803
129.301
128.834
128.484
128.394
128.291
128.023
127.270
127.091
126.497
125.919
123.889
89.082
84.422
77.491
77.174
76.856
37.373
21.060
Me
Me
4g
200
150
100
50
0
ppm (f1)


7.443
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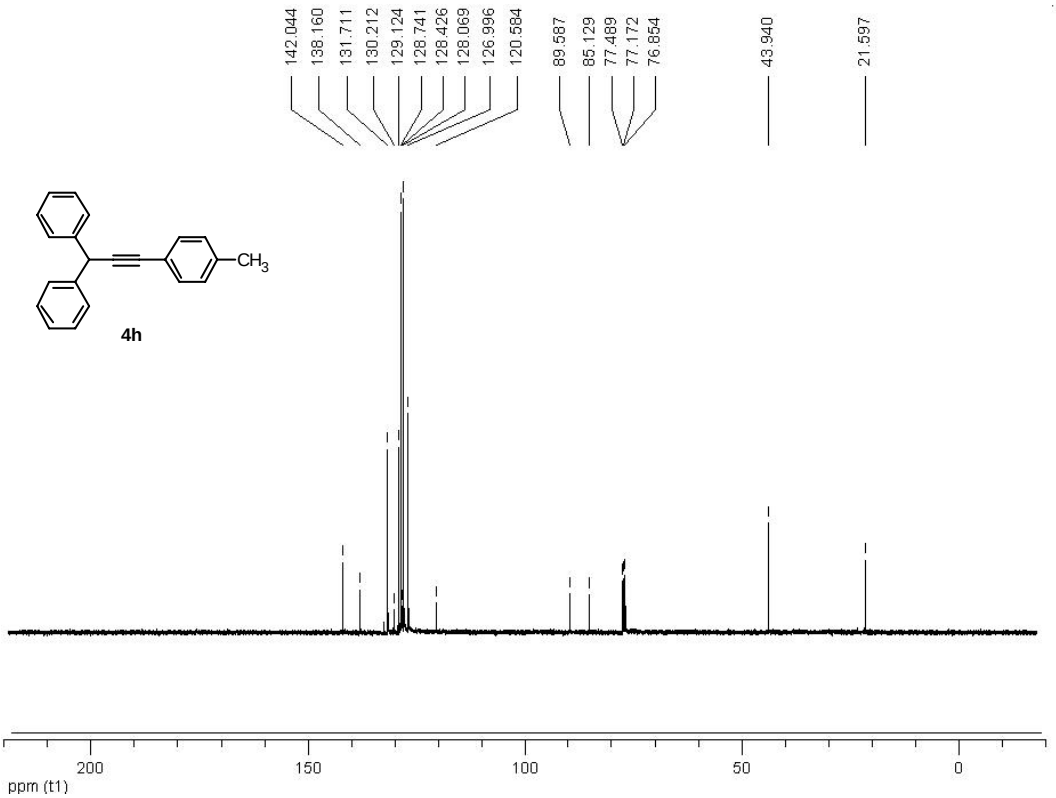
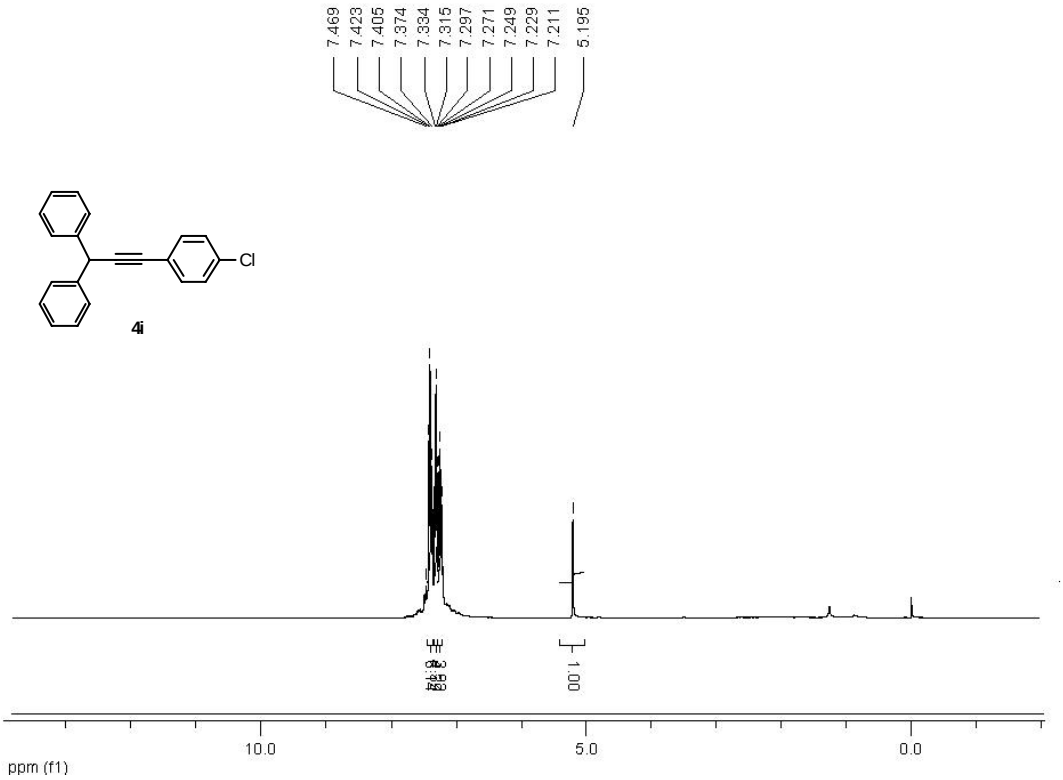
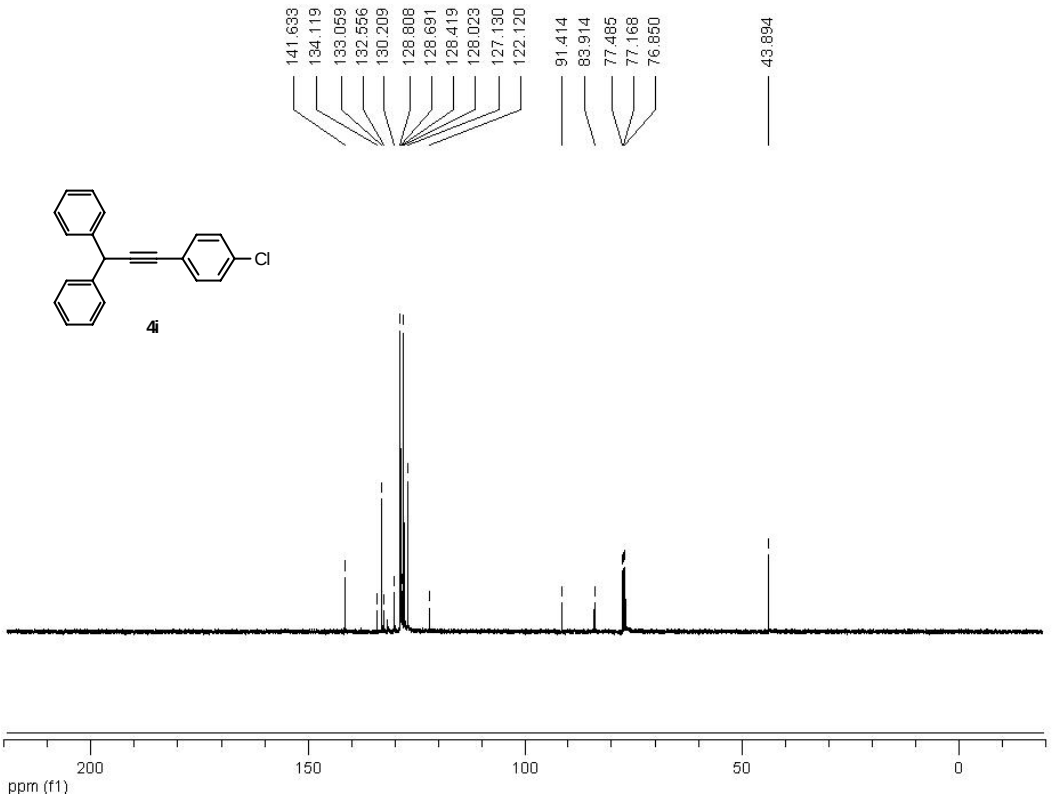
7.373
7.353
7.325
7.306
7.287
7.234
7.216
7.198
7.105
7.085
5.193
2.325
CH3
4h
1.00
3.72
10.0
5.0
0.0
ppm (f1)


142.044
138.160
131.711
130.212
129.124
128.741
128.426
128.069
126.996
120.584
89.587
85.129
77.489
77.172
76.854
43.940
21.597
CH3
4h
200
150
100
50
0
ppm (t1)


7.469
7.423
7.405
7.374
7.334
7.315
7.297
7.271
7.249
7.229
7.211
5.195
Cl
4i
8.19
1.00
10.0
5.0
0.0
ppm (f1)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133.059
132.556
130.209
128.808
128.691
128.419
128.023
127.130
122.120
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77.485
77.168
76.850
43.894
Cl
4i
200
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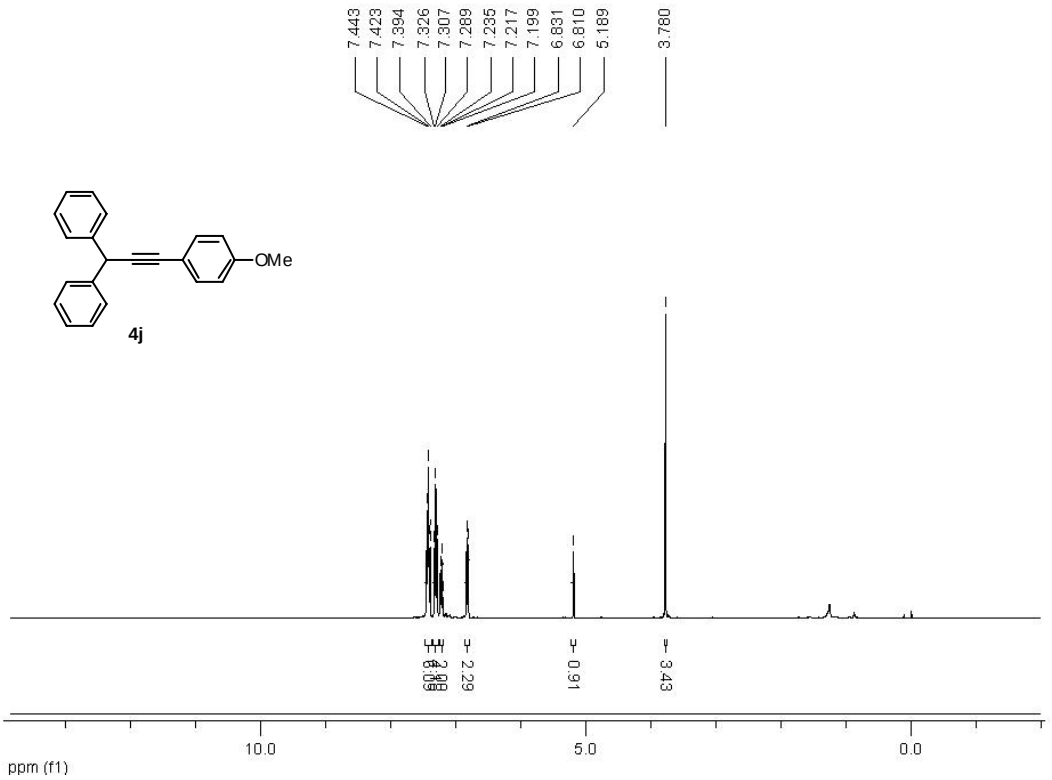
50
0
ppm (f1)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7.423
7.394
7.326
7.307
7.289
7.235
7.217
7.199
6.831
6.810
5.189
3.780
OMe
4j
2.29
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3.43
10.0
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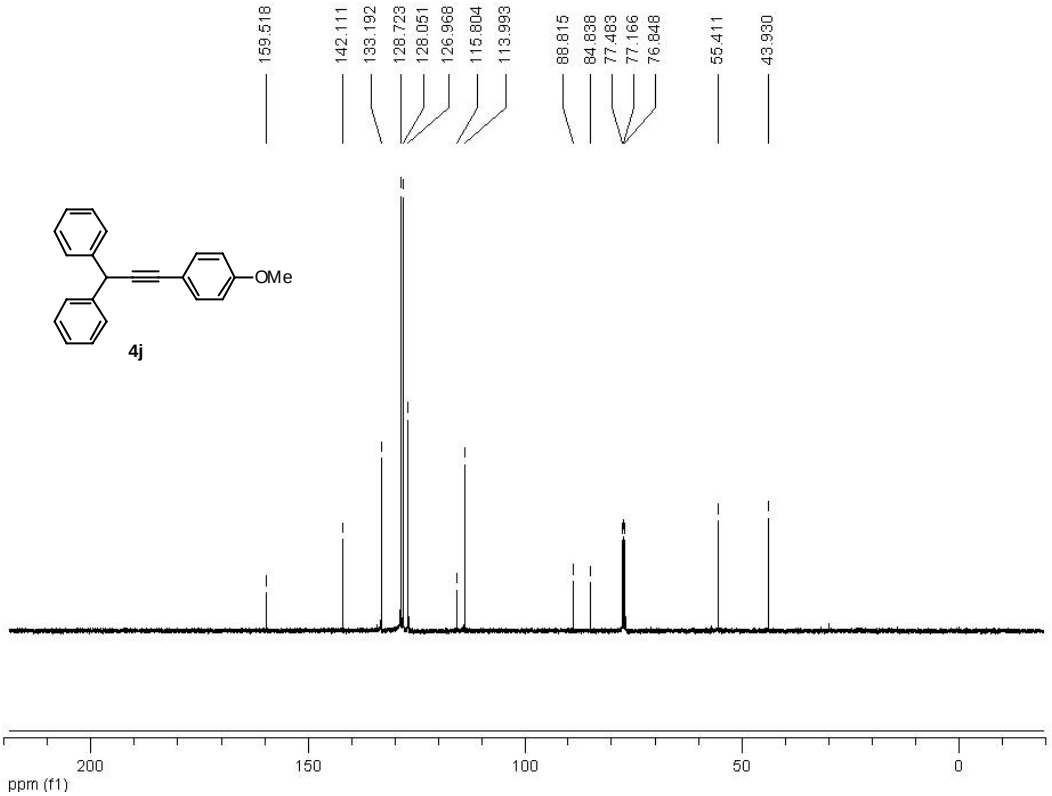
ppm (f1)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115.804
113.993
88.815
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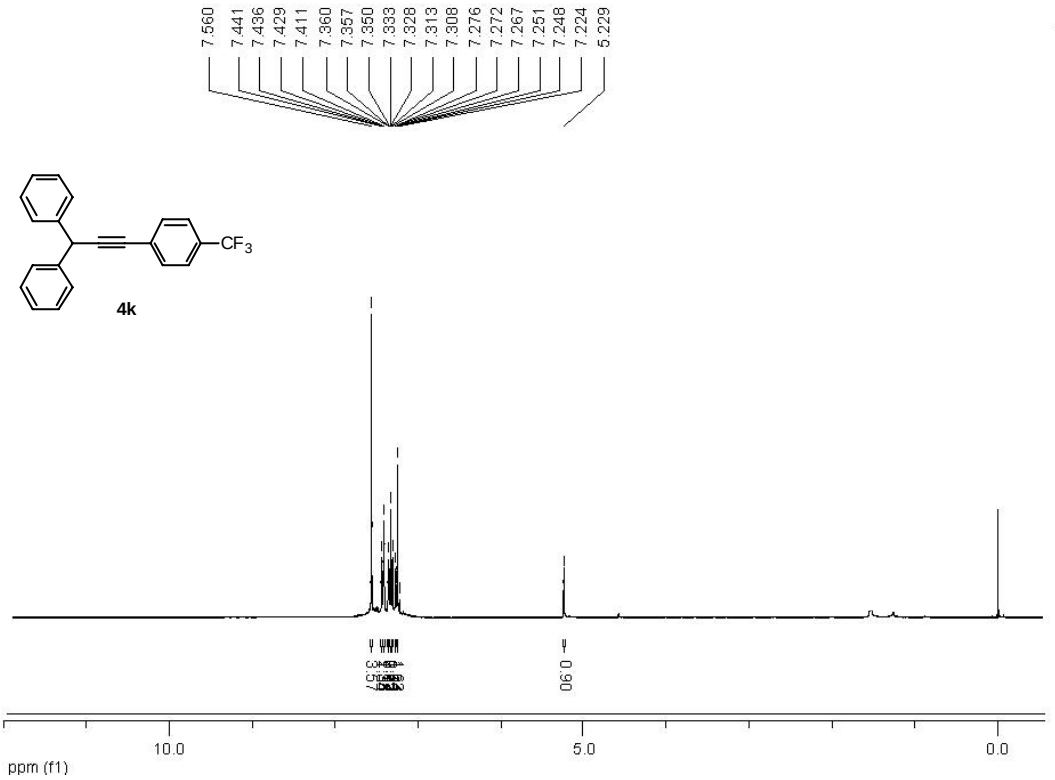
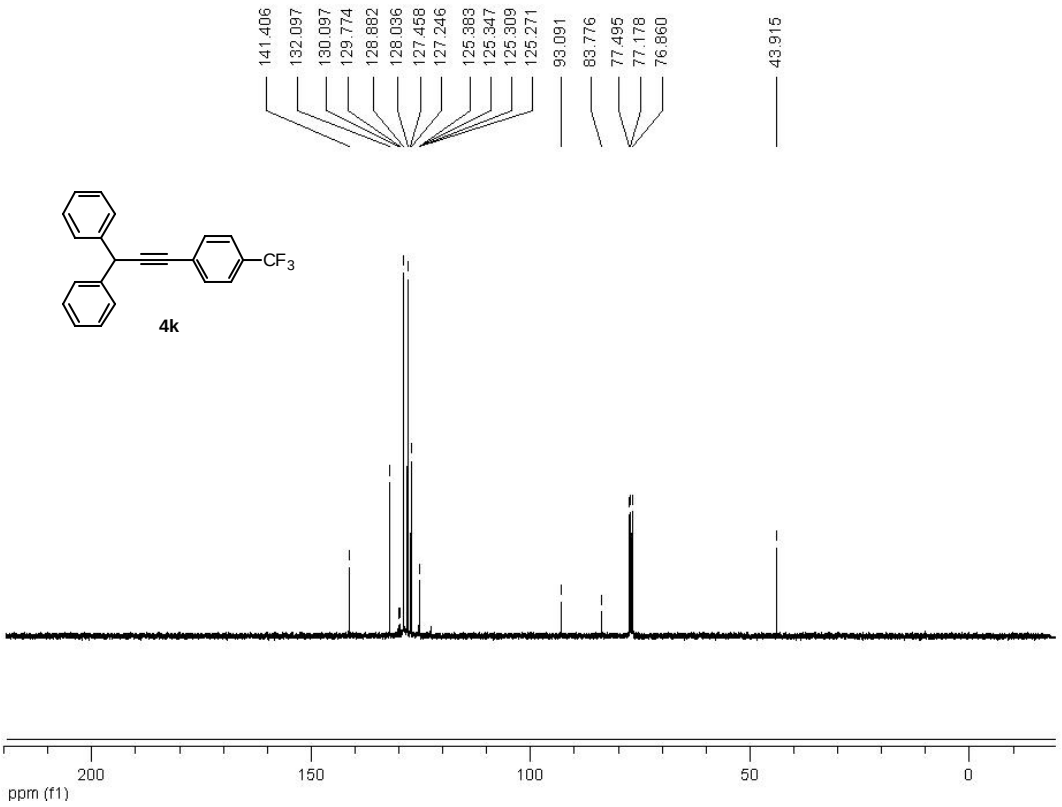
76.848
55.411
43.930
OMe
4j
200
150
100
50
0
ppm (f1)


7.560
7.441
7.436
7.429
7.411
7.360
7.357
7.350
7.333
7.328
7.313
7.308
7.276
7.272
7.267
7.251
7.248
7.224
5.229
CF3
4k
6.00
10.0
5.0
0.0
ppm (f1)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130.097
129.774
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128.036
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127.246
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125.347
125.309
125.271
93.091
83.776
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77.178
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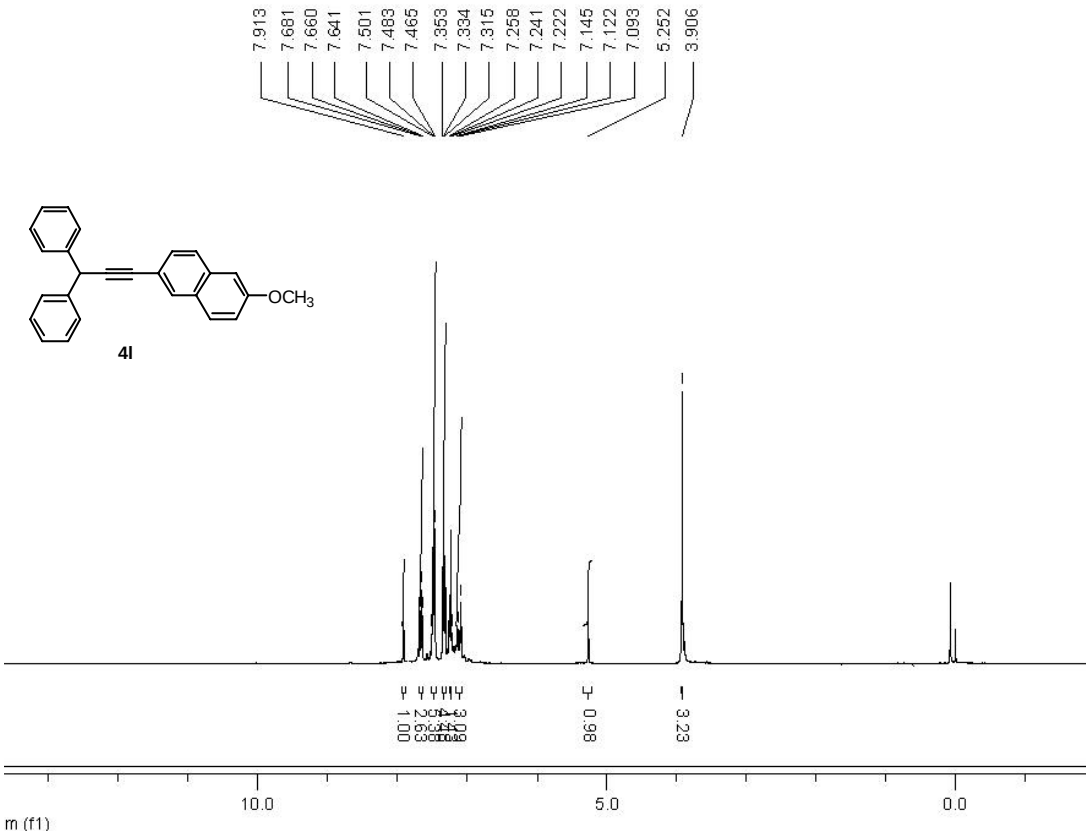
CF3
4k
200
150
100
50
0
ppm (f1)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7.660
7.641
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7.465
7.353
7.334
7.315
7.258
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7.222
7.145
7.122
7.093
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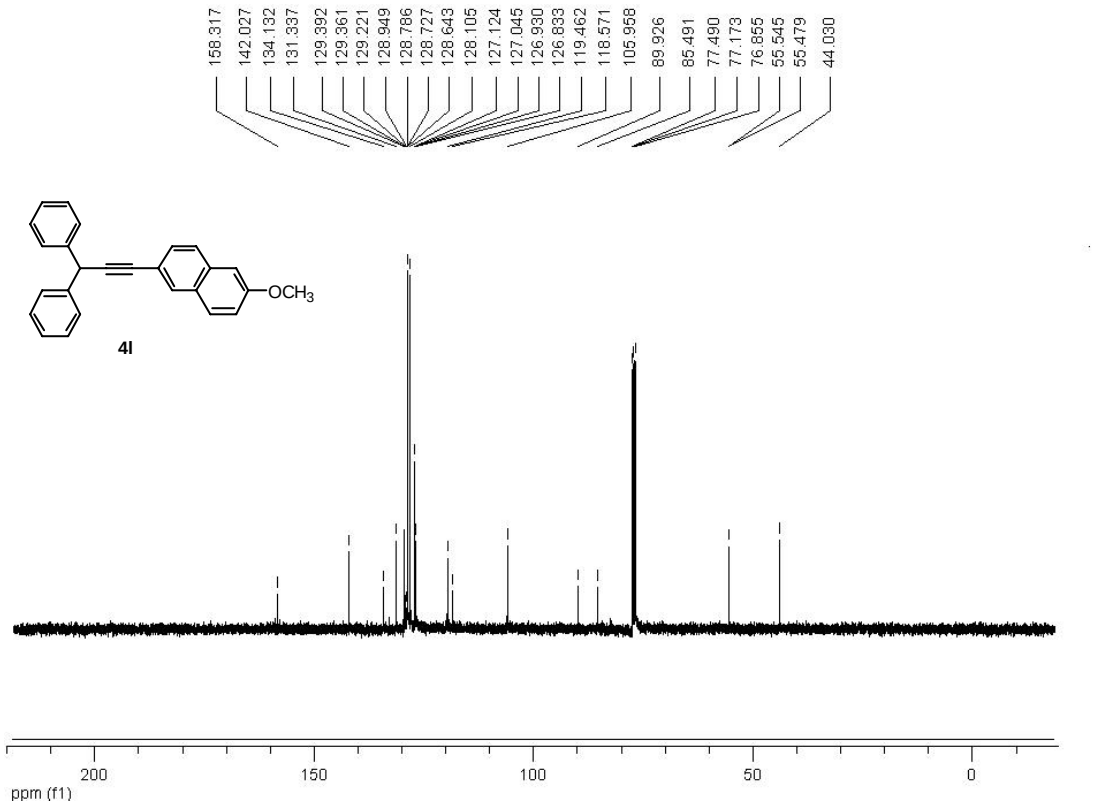
OCH3
4l
1.00
0.98
3.23
10.0
5.0
0.0
m (f1)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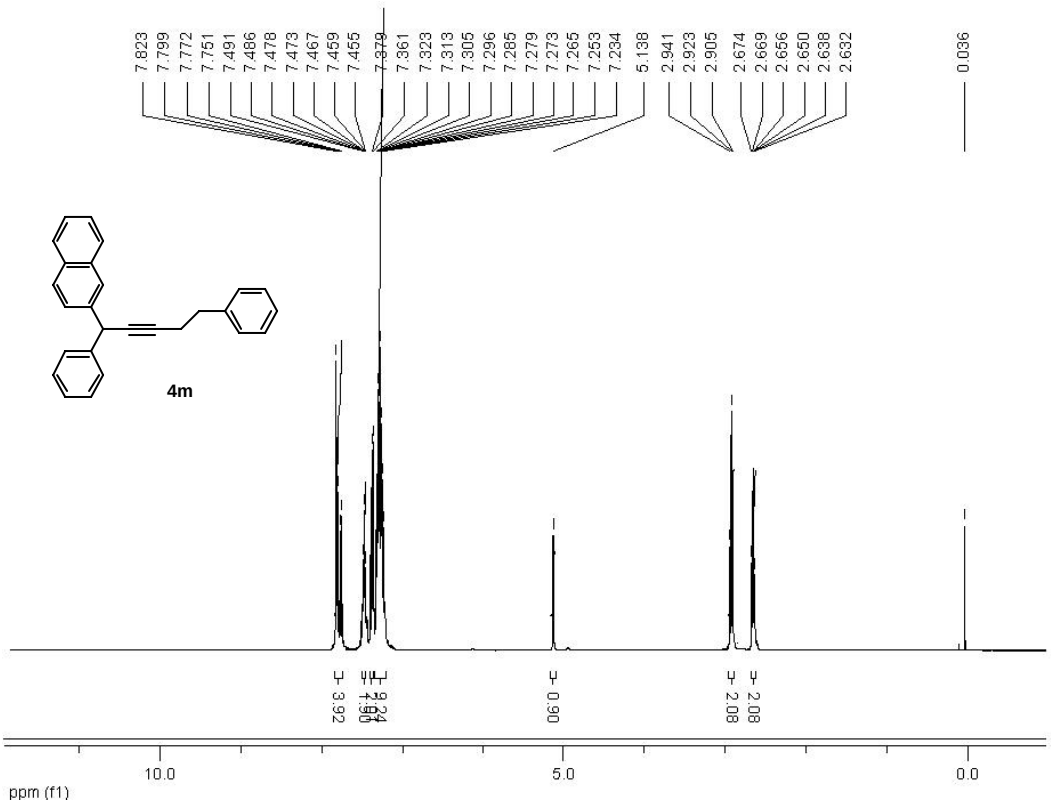
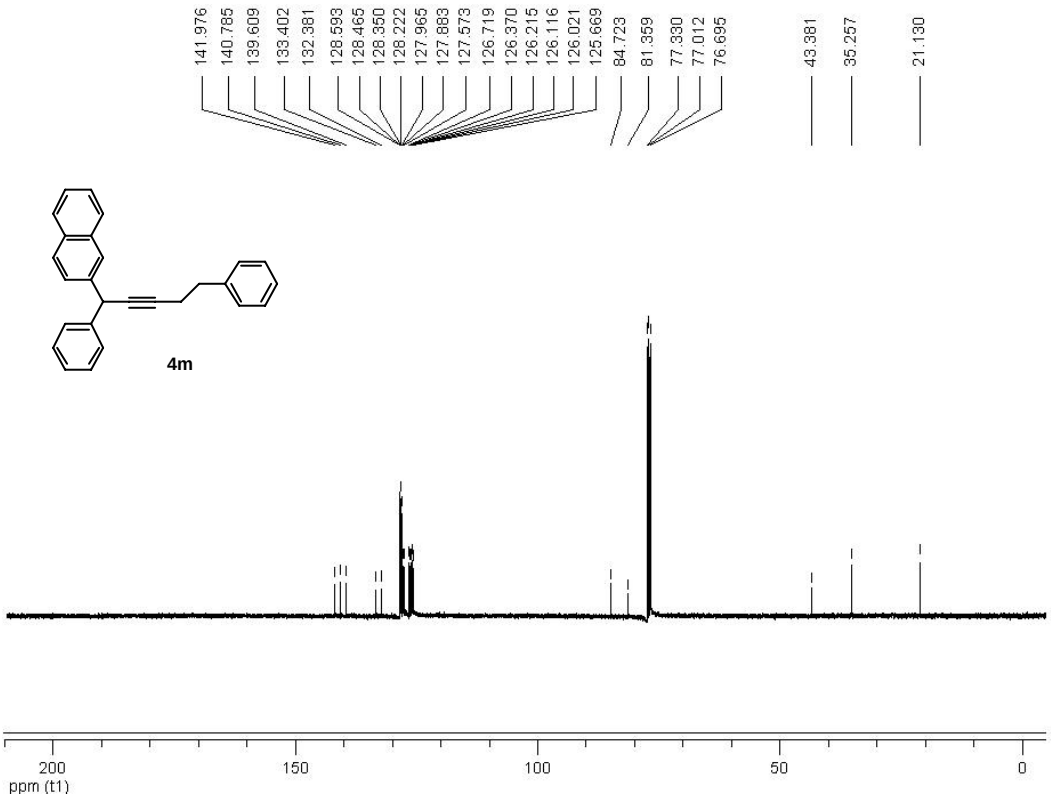
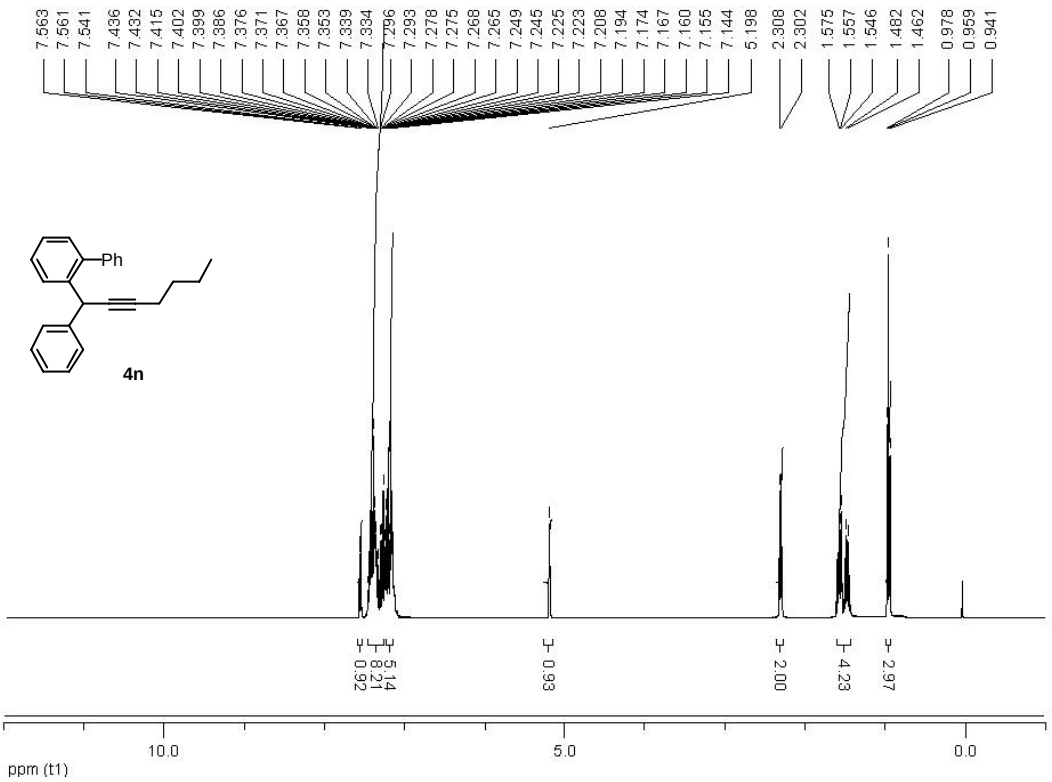
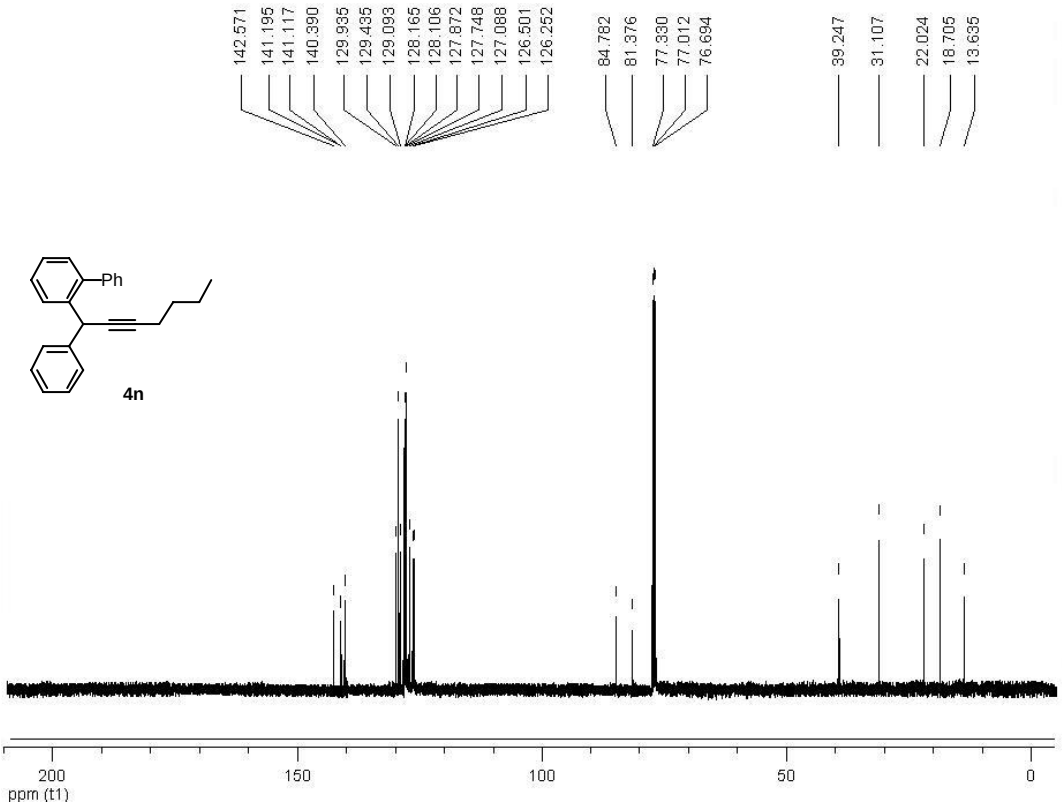
134.132
131.337
129.392
129.361
129.221
128.949
128.786
128.727
128.643
128.105
127.124
127.045
126.930
126.833
119.462
118.571
105.958
89.926
85.491
77.490
77.173
76.855
55.545
55.479
44.030
OCH3
4l
200
150
100
50
0
ppm (f1)


7.823
7.799
7.772
7.751
7.491
7.486
7.478
7.473
7.467
7.459
7.455
7.379
7.361
7.323
7.313
7.305
7.296
7.285
7.279
7.273
7.265
7.253
7.234
5.138
2.941
2.923
2.905
2.674
2.669
2.656
2.650
2.638
2.632
0.036
4m
3.92
2.08
0.90
2.08
10.0
5.0
0.0
ppm (f1)


141.976
140.785
139.609
133.402
132.381
128.593
128.465
128.350
128.222
127.965
127.883
127.573
126.719
126.370
126.215
126.116
126.021
125.669
84.723
81.359
77.330
77.012
76.695
43.381
35.257
21.130
4m
200
150
100
50
0
ppm (t1)


7.563
7.561
7.541
7.436
7.432
7.415
7.402
7.399
7.386
7.376
7.371
7.367
7.358
7.353
7.339
7.334
7.296
7.293
7.278
7.275
7.268
7.265
7.249
7.245
7.225
7.223
7.208
7.194
7.174
7.167
7.160
7.155
7.144
5.198
2.308
2.302
1.575
1.557
1.546
1.482
1.462
0.978
0.959
0.941
Ph
4n
0.92
2.11
5.14
0.93
2.00
4.23
2.97
10.0
5.0
0.0
ppm (t1)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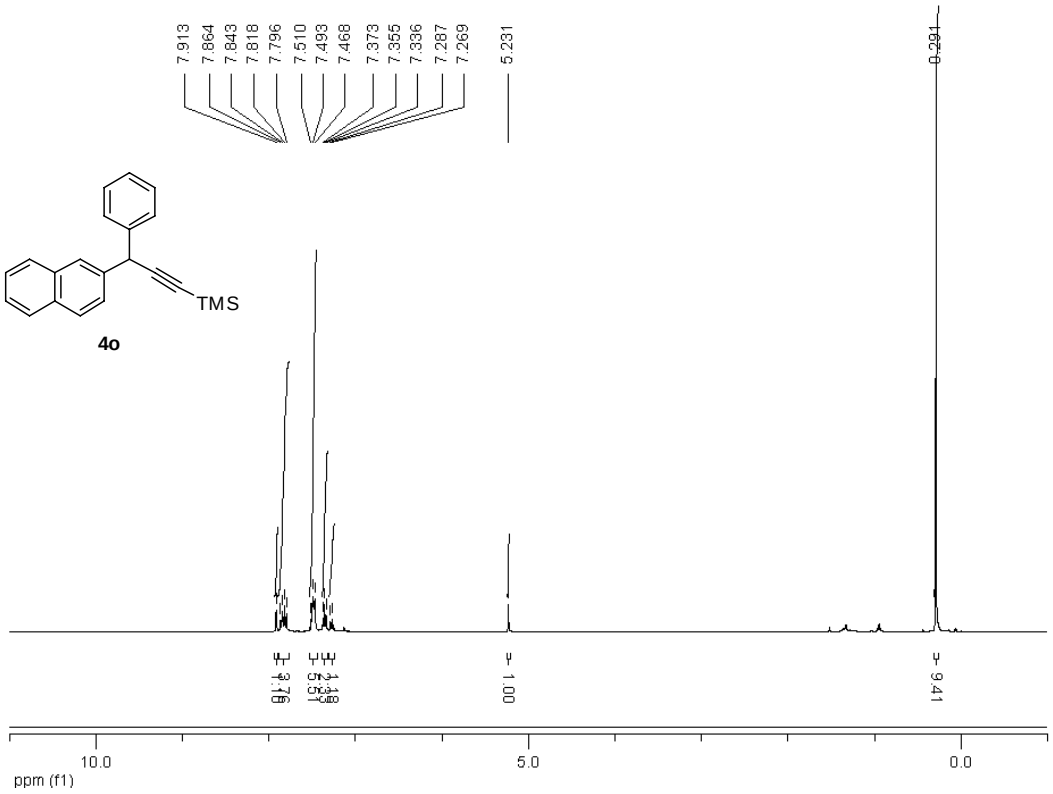
129.093
128.165
128.106
127.872
127.748
127.088
126.501
126.252
84.782
81.376
77.330
77.012
76.694
39.247
31.107
22.024
18.705
13.635
Ph
4n
200
150
100
50
0
ppm (t1)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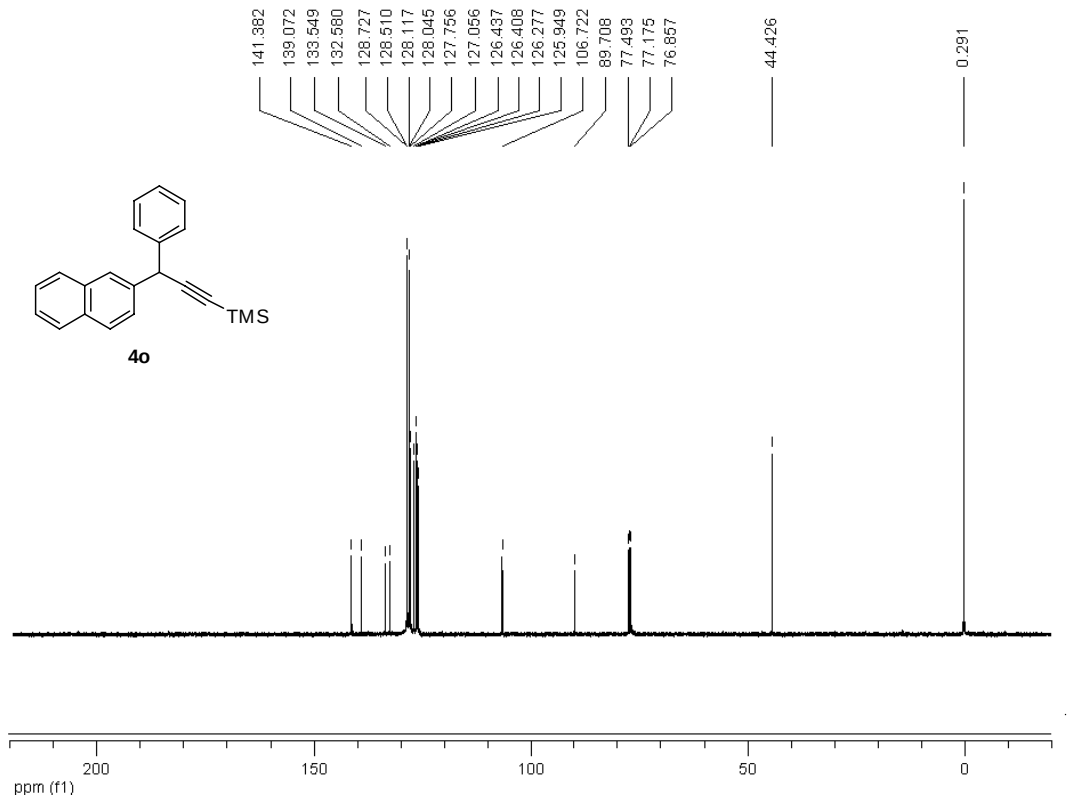
7.864
7.843
7.818
7.796
7.510
7.493
7.468
7.373
7.355
7.336
7.287
7.269
5.231
0.291
TMS
4o
3.16
3.00
1.00
9.41
10.0
5.0
0.0
ppm (f1)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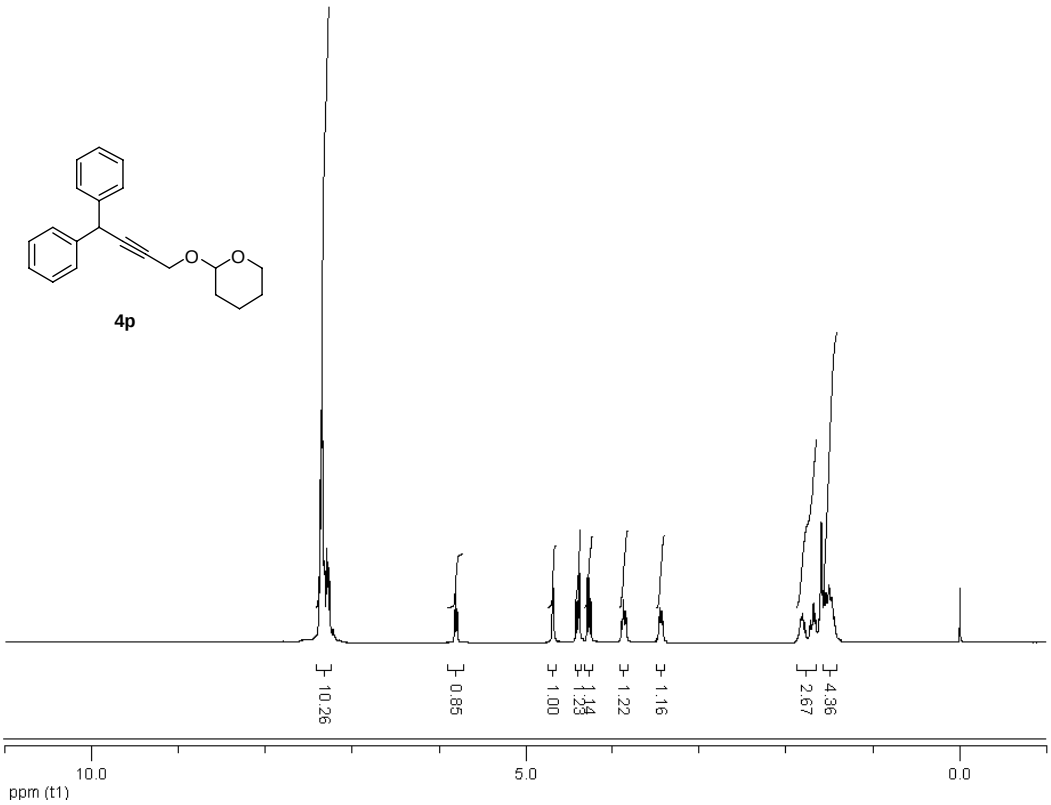
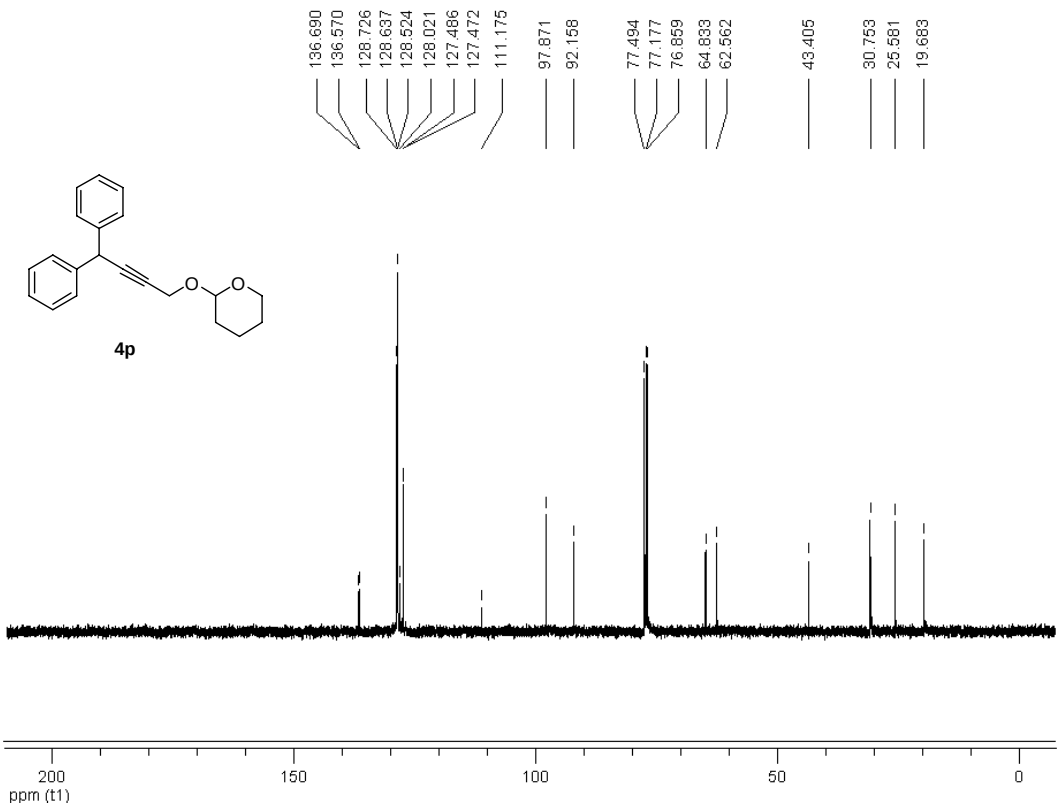
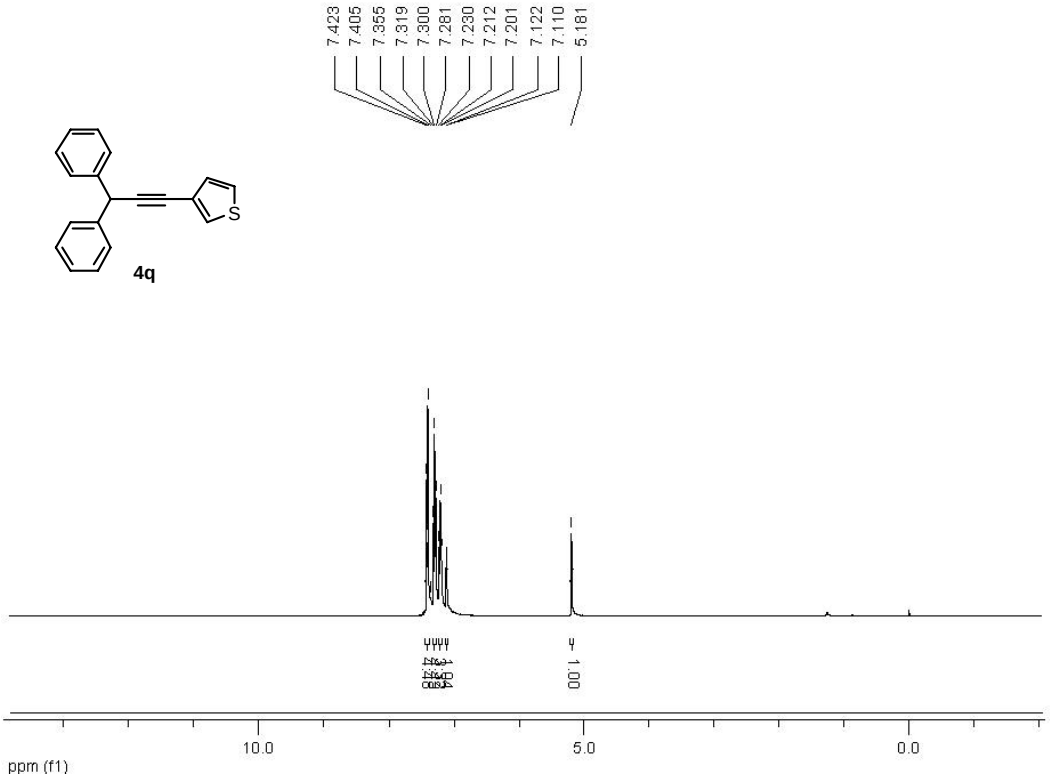
128.727
128.510
128.117
128.045
127.756
127.056
126.437
126.408
126.277
125.949
106.722
89.708
77.493
77.175
76.857
44.426
0.291
TMS
4o
200
150
100
50
0
ppm (f1)


4p
10.29
0.85
1.00
1.23
1.14
1.22
1.16
2.67
4.36
10.0
5.0
0.0
ppm (t1)


136.690
136.570
128.726
128.637
128.524
128.021
127.486
127.472
111.175
97.871
92.158
77.494
77.177
76.859
64.833
62.562
43.405
30.753
25.581
19.683
4p
200
150
100
50
0
ppm (t1)


7.423
7.405
7.355
7.319
7.300
7.281
7.230
7.212
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7.122
7.110
5.181
S
4q
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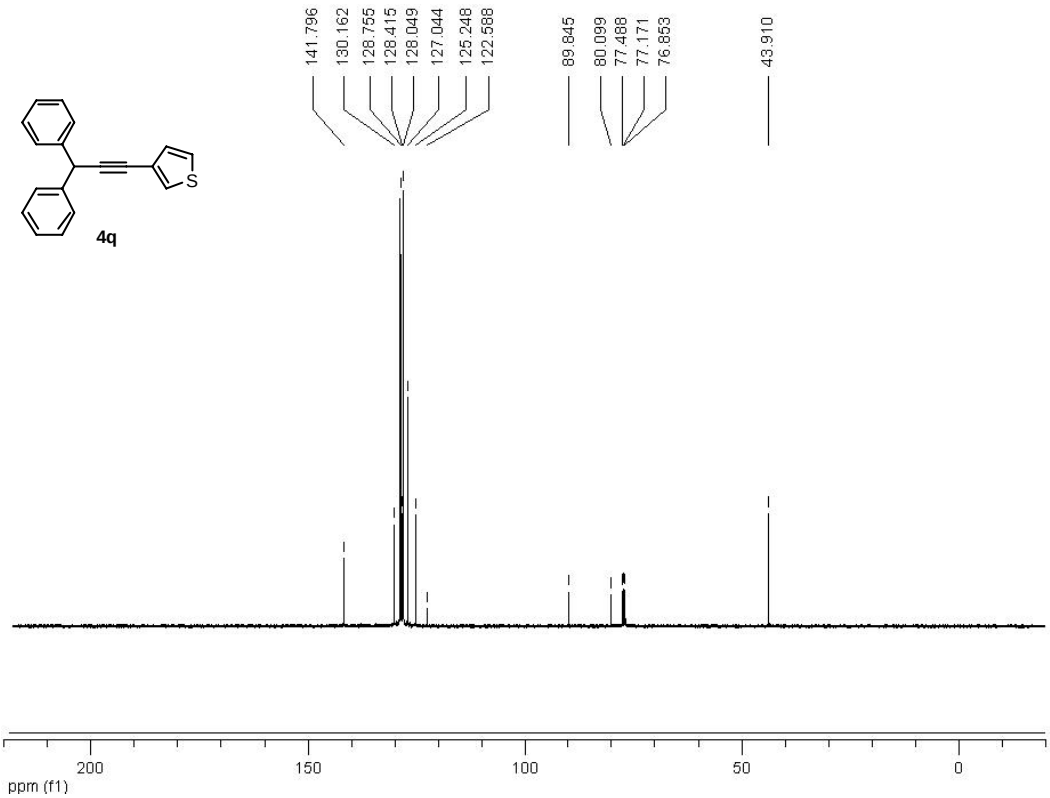
10.0
5.0
0.0
ppm (f1)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128.049
127.044
125.248
122.588
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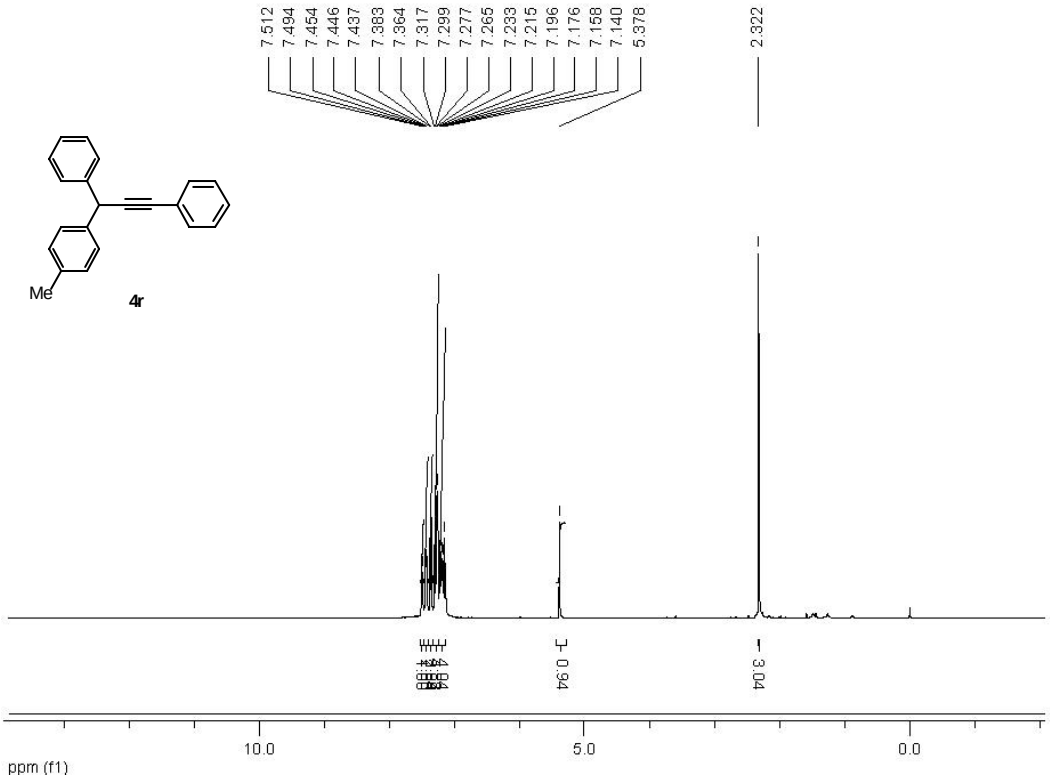
77.488
77.171
76.853
43.910
S
4q
200
150
100
50
0
ppm (f1)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7.494
7.454
7.446
7.437
7.383
7.364
7.317
7.299
7.277
7.265
7.233
7.215
7.196
7.176
7.158
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2.322
Me
4r
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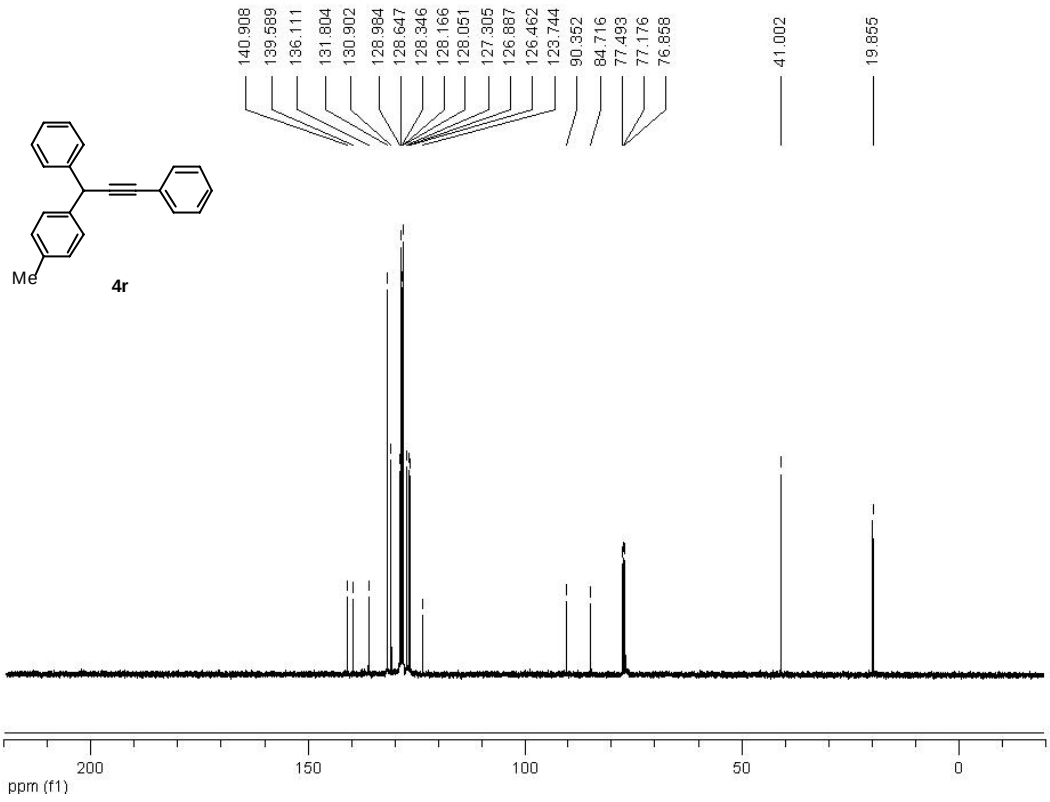
ppm (f1)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128.647
128.346
128.166
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126.887
126.462
123.744
90.352
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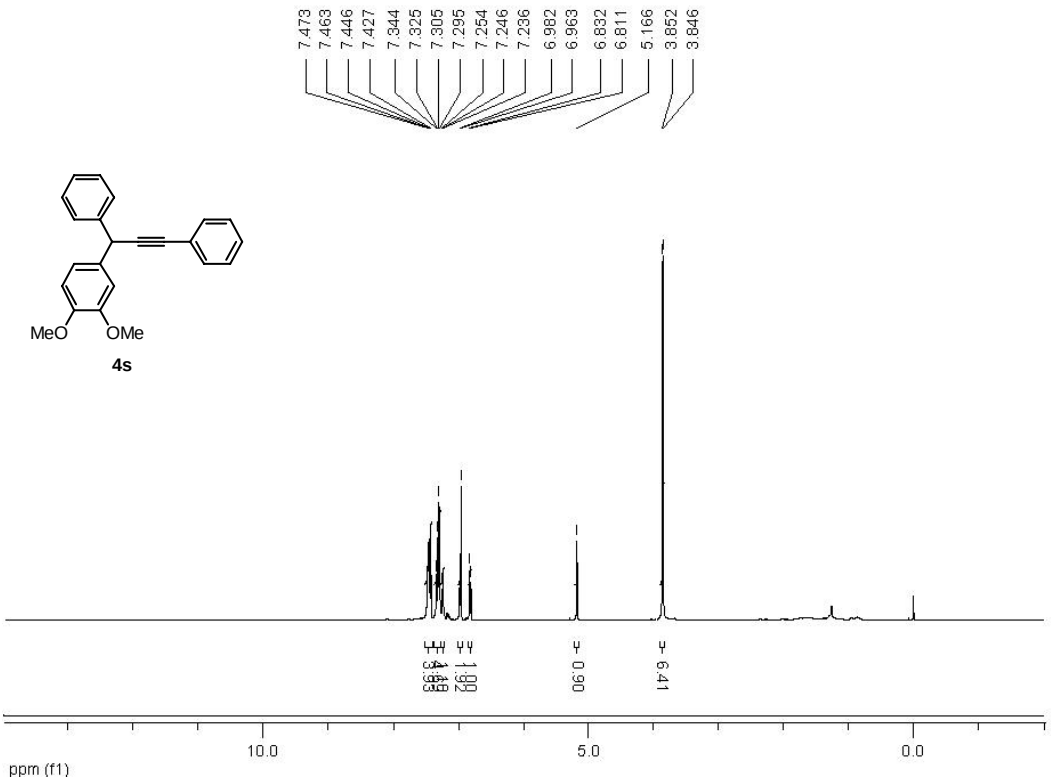
77.176
76.858
41.002
19.855
Me
4r
200
150
100
50
0
ppm (f1)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7.295
7.254
7.246
7.236
6.982
6.963
6.832
6.811
5.166
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MeO
OMe
4s
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10.0
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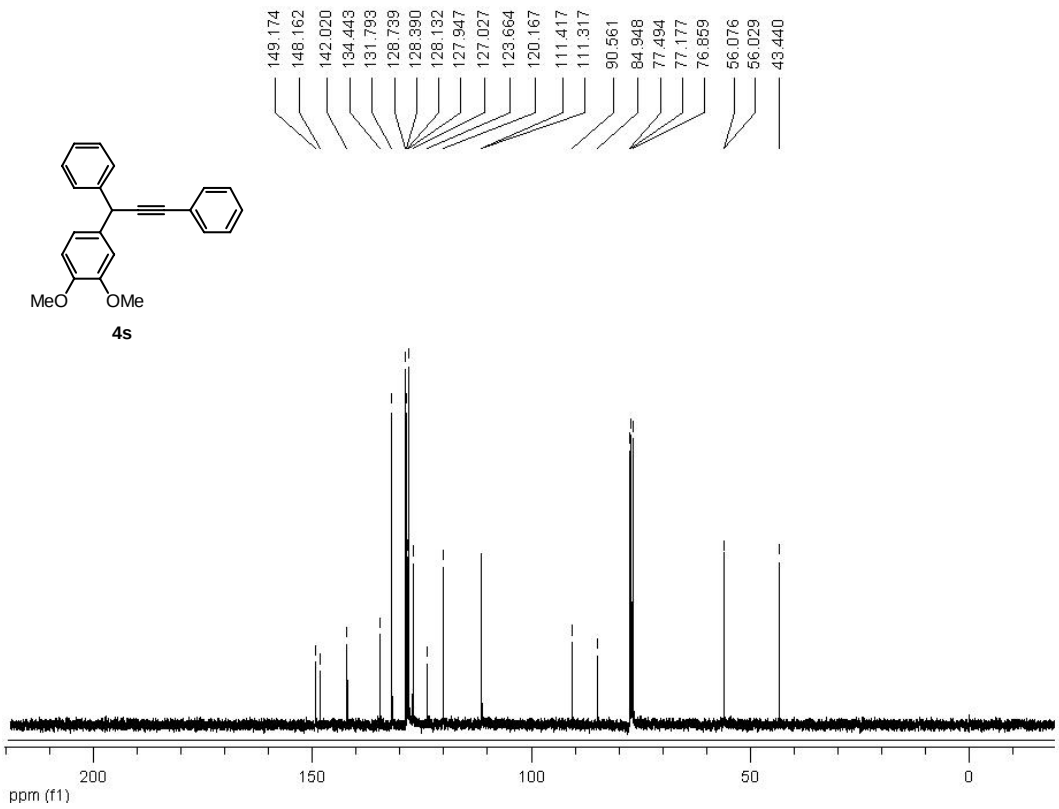
ppm (f1)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128.132
127.947
127.027
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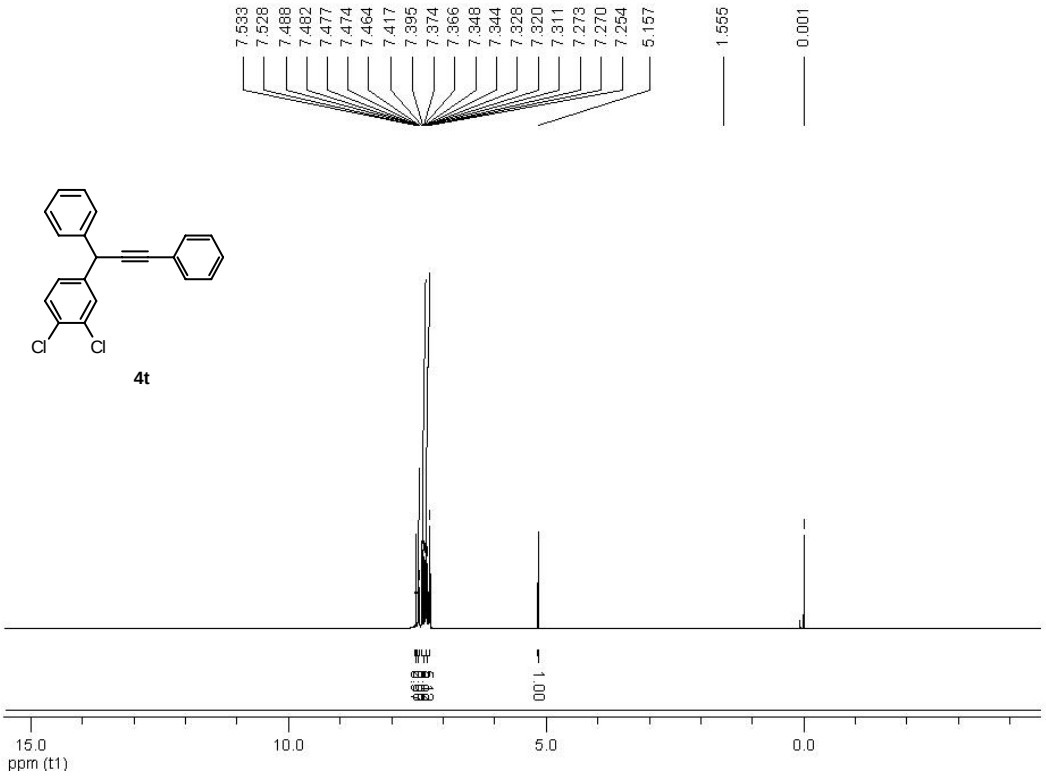
120.167
111.417
111.317
90.561
84.948
77.494
77.177
76.859
56.076
56.029
43.440
MeO
OMe
4s
200
150
100
50
0
ppm (f1)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7.474
7.464
7.417
7.395
7.374
7.366
7.348
7.344
7.328
7.320
7.311
7.273
7.270
7.254
5.157
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0.001
Cl
Cl
4t
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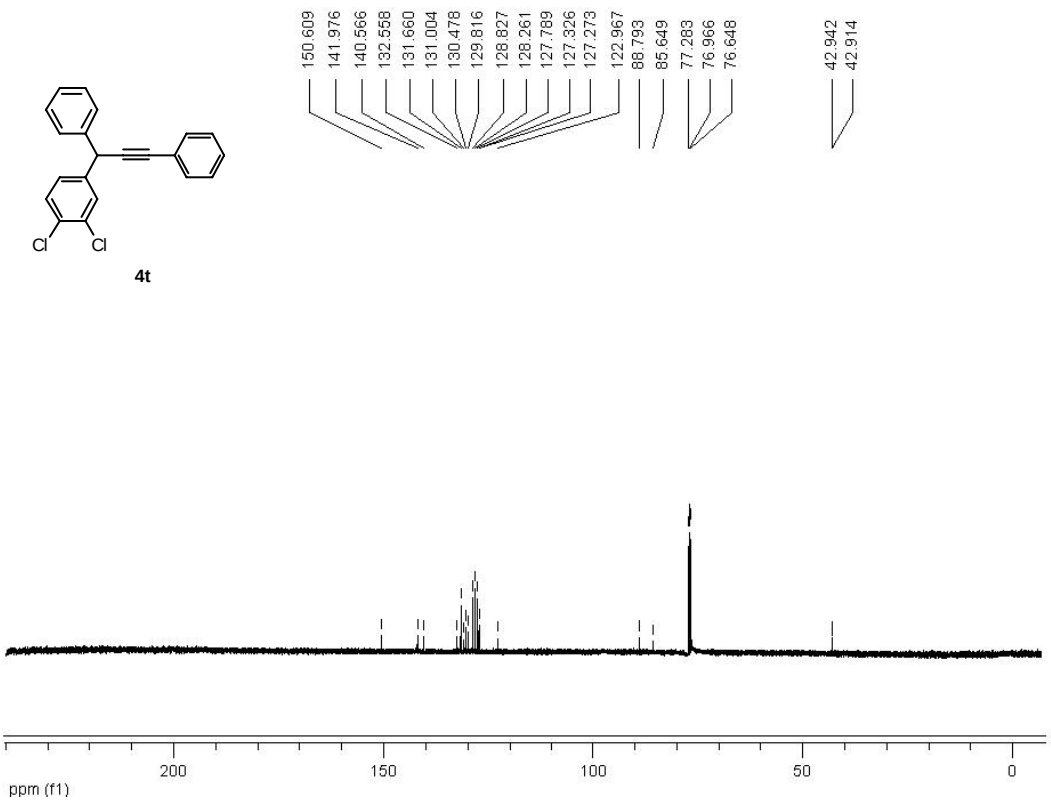
10.0
5.0
0.0
ppm (t1)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127.326
127.273
122.967
88.793
85.649
77.283
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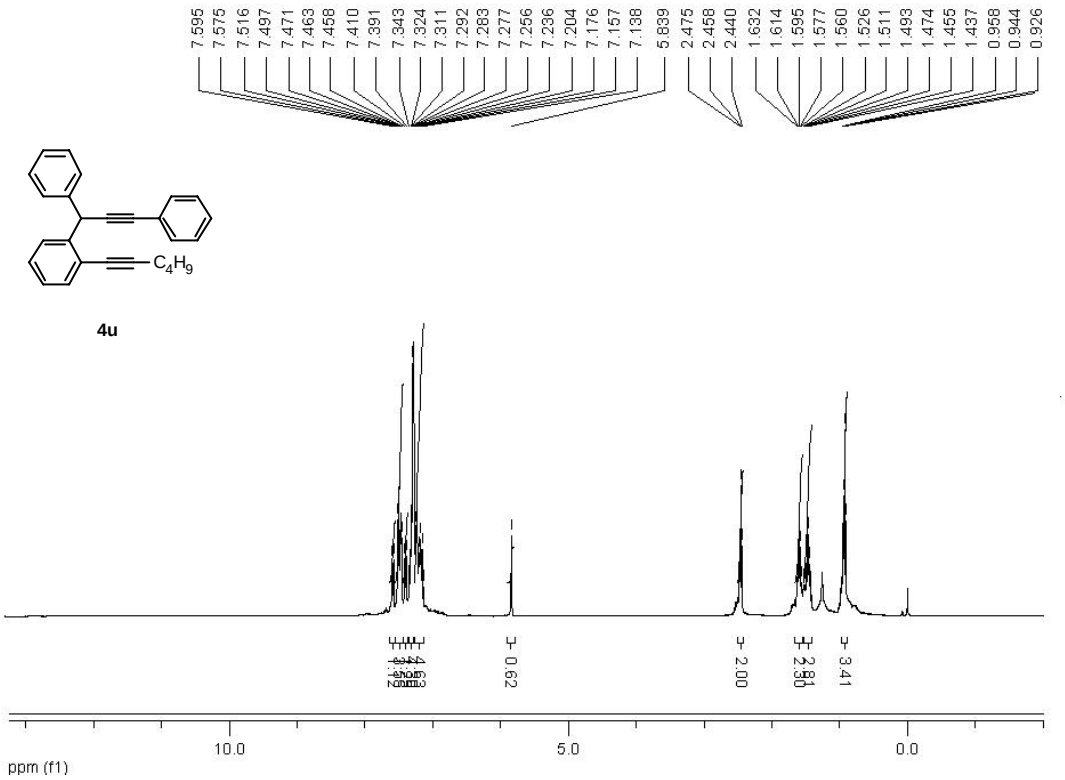
76.648
42.942
42.914
Cl
Cl
4t
200
150
100
50
0
ppm (f1)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7.324
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7.292
7.283
7.277
7.256
7.236
7.204
7.176
7.157
7.138
5.839
2.475
2.458
2.440
1.632
1.614
1.595
1.577
1.560
1.526
1.511
1.493
1.474
1.455
1.437
0.958
0.944
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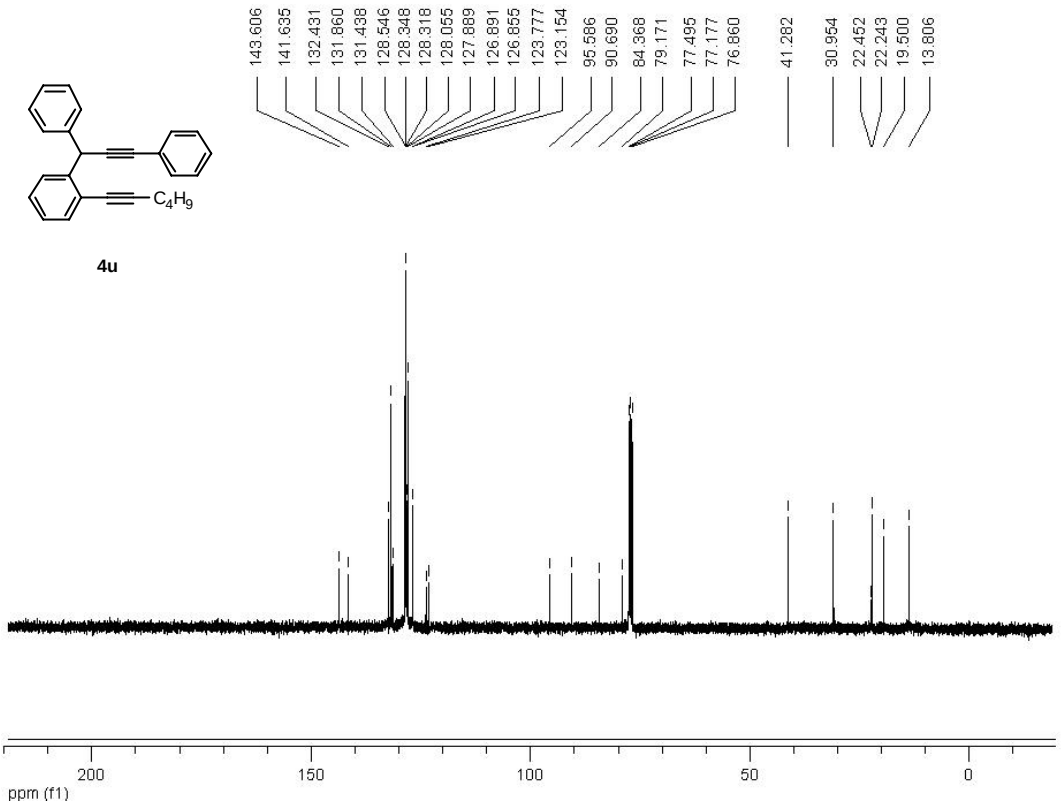
ppm (f1)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141.635
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131.860
131.438
128.546
128.348
128.318
128.055
127.889
126.891
126.855
123.777
123.154
95.586
90.690
84.368
79.171
77.495
77.177
76.860
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30.954
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22.243
19.500
13.806
C4H9
4u
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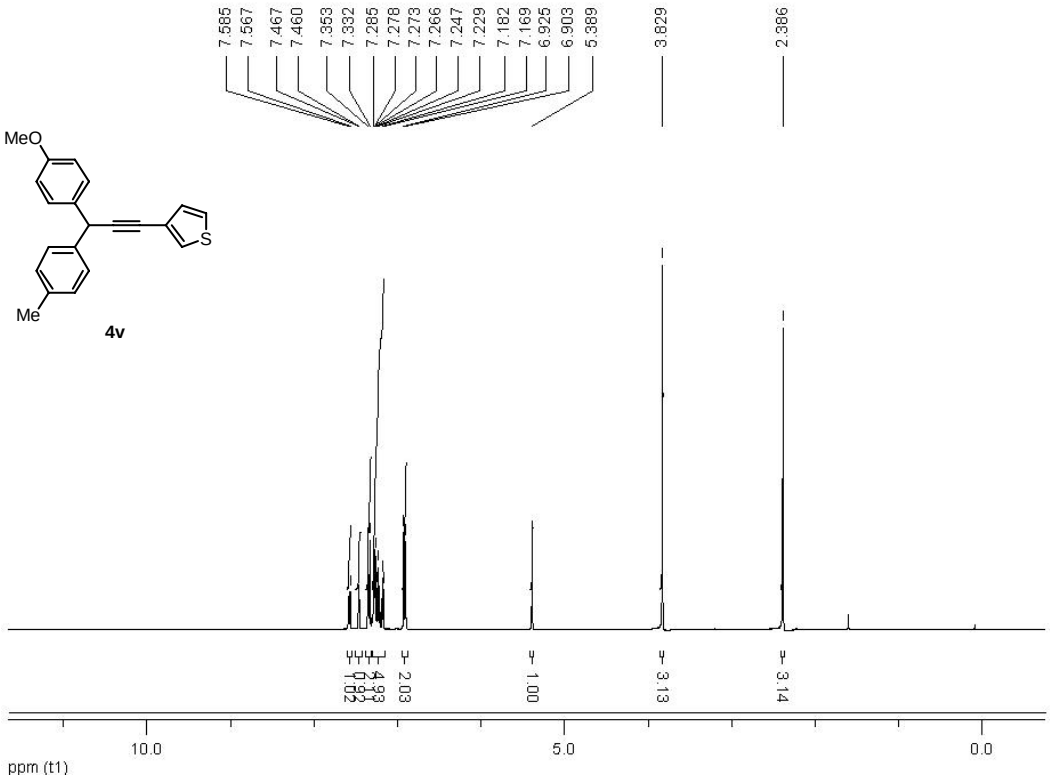
100
50
0
ppm (f1)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7.278
7.273
7.266
7.247
7.229
7.182
7.169
6.925
6.903
5.389
3.829
2.386
MeO
S
Me
4v
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5.0
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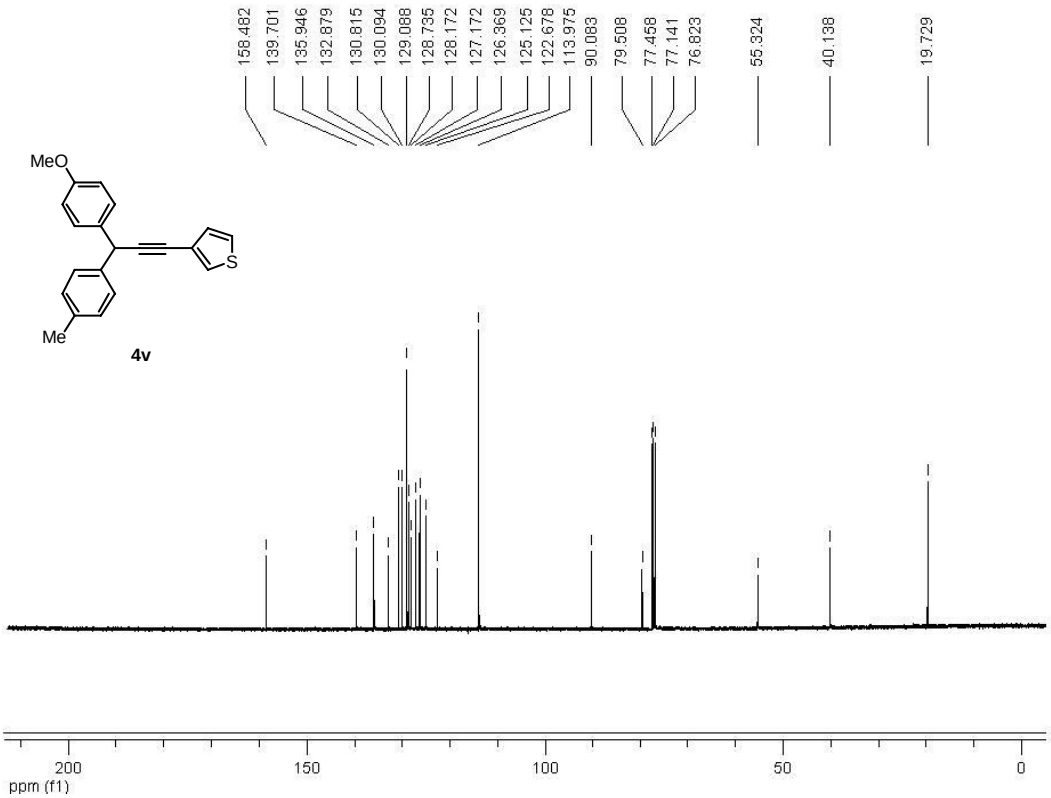
ppm (t1)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122.678
113.975
90.083
79.508
77.458
77.141
76.823
55.324
40.138
19.729
MeO
S
Me
4v
200
150
100
50
0
ppm (f1)