CHEMISTRY
AN ASIAN JOURNAL

Supporting Information

Supporting Information for

Ring-Closing Olefin Metathesis for the Synthesis of Benzene Derivatives

Kazuhiro Yoshida,* Fumihiro Kawagoe, Noriyuki Iwadate, Hidetoshi Takahashi, and Tsuneo Imamoto*

[*] Assist. Prof. Dr. K. Yoshida, F. Kawagoe, N. Iwadate, H. Takahashi, Prof. Dr. T. Imamoto
Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522 (Japan)
Fax: (+81) 43-290-2791, E-mail: kyoshida@faculty.chiba-u.jp; imamoto@faculty.chiba-u.jp

[**] We appreciate the financial support from a Grant-in-Aid for Scientific Research, the Ministry of Education, Culture, Sports, Science and Technology, Japan.

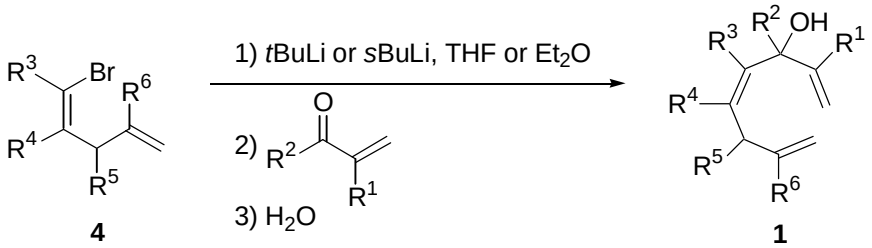
Supporting Data

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glove box techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H, 76.5 MHz for ^{2}H, and 125 MHz for ^{13}C) and LA-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR, chloroform-*d* (δ 7.26) for ^{2}H NMR, and chloroform-*d* (δ 77.0) for ^{13}C NMR.

Materials. THF was distilled from sodium benzophenone-ketyl under nitrogen prior to use. Et_2O was distilled from sodium benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Ruthenium complexes, $(PCy_3)_2Cl_2Ru{=}C(H)Ph$ (**6**)[1] and $(PCy_3)(Imes)Cl_2Ru{=}C(H)Ph$ (**7**)[2], were prepared according to the reported procedures. Bromodienes **5** were prepared by bromoallylation of alkynes according to the reported procedures.[3] 1,4,7-Trien-3-ols, **1a**, **1b**, **1c**, **1d**, **1f**, **1k**, **1l**, and **1m** were prepared by the reported procedures.[4] Phenylacrolein[5], 4-methoxy-1-phenylbut-1-yne[6], 2-iodo-2-propen-1-ol[7], 2-methyl-1-[(phenylsulfonyl)imino]-2-propene[8], and activated MnO_2[9] were prepared according to the reported procedures. 2-Chloroacrolein and 2-iodoacrolein were prepared by the oxidation of the corresponding allyl alcohols with Dess-Martin periodinane. Methacrolein, methyl vinyl ketone, MnI_2, 2-chloro-2-propen-1-ol, *p*-toluenesulfonic acid, *N*-*tert*-butylbenzenesulfinimidoyl chloride, and DBU were used as received.

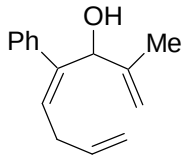
Preparation of 1,4,7-octatrien-3-ol 1. *t*BuLi (1.5 M solution in *n*-pentane, 10.0 mmol) or *s*BuLi (1.0 M solution in cyclohexane and *n*-hexane, 5.50 mmol) was added to a solution of

bromodiene **4** (5.00 mmol) in THF or Et_2O (12.5 mL) at –78 °C. After 5 min, α,β-unsaturated aldehyde or ketone (4.00-6.00 mmol) was added and the mixture was stirred for 30 min at the same temperature. The reaction mixture was then quenched by addition of water and extracted twice with EtOAc. The organic phases were dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by silica gel column chromatography to give trienol **1**.



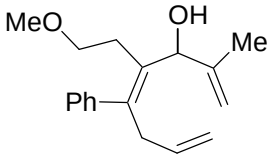
4 **1**

(*Z*)-2-Methyl-4-phenyl-1,4,7-octatrien-3-ol (1e); purified by PTLC (hexane/EtOAc = 10/1) (67% yield); ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3H), 1.88 (br s, 1H), 3.01-3.15 (m, 2H), 4.94 (sextet, *J* = 1.7 Hz, 1H), 5.06 (dq, *J* = 10.2, 1.5 Hz, 1H), 5.10-5.16 (m, 2H), 5.21 (br s, 1H), 5.79 (t, *J* = 7.6 Hz, 1H), 5.90 (ddt, *J* = 16.4, 10.3, 6.1 Hz, 1H), 7.22-7.30 (m, 3H), 7.35-7.39 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 19.82, 32.38, 72.97, 110.63, 115.53, 127.07, 127.91, 127.93, 130.51, 136.26, 140.36, 140.98, 145.35. HRMS (FAB) calcd for $C_{15}H_{18}O$ (M^+) 214.1358, found 214.1353.



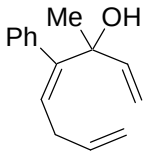
1e

(*E*)-4-(2-Methoxyethyl)-2-methyl-5-phenyl-1,4,7-octatrien-3-ol (1g); Manganese catalyzed allylmagnesation of 4-methoxy-1-phenylbut-1-yne with allylmagnesium bromide was employed.[10] ; purified by PTLC (CH_2Cl_2/EtOAc = 3/1) (64% yield); ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3H), 2.10 (ddd, *J* = 15.2, 10.8, 4.6 Hz, 1H), 2.21 (dt, *J* = 14.9, 3.7 Hz, 1H), 3.07 (ddd, *J* = 10.5, 8.8, 3.4 Hz, 1H), 3.14-3.22 (m, 2H), 3.28 (s, 3H), 3.34 (dd, *J* = 14.9, 7.1 Hz, 1H), 4.48 (d, *J* = 7.1 Hz, 1H), 4.94-5.05 (m, 4H), 5.23 (s, 1H), 5.73 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 7.08 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.23 (tt, *J* = 7.6, 1.5 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 19.86, 27.82, 39.41, 58.61, 72.47, 72.62, 110.35, 115.92, 126.47, 128.25, 134.68, 135.11, 140.17, 142.75, 146.54. HRMS (FAB) calcd for $C_{18}H_{23}O$ (M^+–OH) 255.1750, found 255.1750.



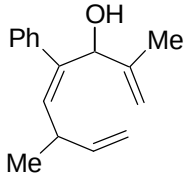
1g

(*Z*)-3-Methyl-4-phenyl-1,4,7-octatrien-3-ol (1h); Dry $CeCl_3$ was added before addition of methyl vinyl ketone[11]; purified by PTLC (hexane/EtOAc = 5/1) (11% yield); ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 3H), 1.74 (br s, 1H), 3.09-3.22 (m, 2H), 5.03 (d, *J* = 10.5 Hz, 1H), 5.09 (d, *J* = 17.0 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.45 (t, *J* = 8.0 Hz, 1H), 5.88 (ddt, *J* = 16.7, 10.5, 6.2 Hz, 1H), 6.12 (dd, *J* = 17.6, 10.8 Hz, 1H), 7.18-7.30 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 29.28, 33.70, 75.24, 112.22, 115.02, 126.60, 127.69, 128.82, 130.17, 137.05, 143.14, 144.16, 146.33. HRMS (FAB) calcd for $C_{15}H_{17}$ (M^+–OH) 197.1331, found 197.1325.



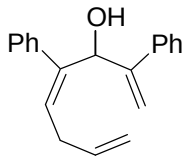
1h

(*Z*)-2,6-Dimethyl-4-phenyl-1,4,7-octatrien-3-ol (1i); mixture of diastereomers; purified by PTLC (hexane/EtOAc = 5/1) (66% yield); ^{1}H NMR ($CDCl_3$) δ 1.16-1.19 (m, 3H), 1.68-1.71 (m, 3H), 1.87-1.93 (br m, 1H), 3.41-3.53 (m, 1H), 4.91-5.12 (m, 4H), 5.19-5.22 (br m, 1H), 5.57-5.61 (m, 1H), 5.80-5.90 (m, 1H), 7.21-7.30 (m, 3H), 7.35-7.39 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 19.91, 19.96, 20.61, 20.87, 36.19, 36.42, 73.09, 73.40, 110.58, 110.76, 113.14, 113.19, 127.02, 127.85, 127.87, 127.93, 127.98, 136.88, 137.10, 139.16, 139.34, 140.30, 140.55, 142.33, 142.35, 145.15, 145.48. HRMS (FAB) calcd for $C_{16}H_{19}$ (M^+–OH) 211.1488, found 211.1489.



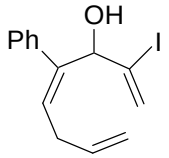
1i

(*Z*)-2,4-Diphenyl-1,4,7-octatrien-3-ol (1j); purified by PTLC (hexane/Et_2O = 1/1) (35% yield); ^{1}H NMR ($CDCl_3$) δ 1.97 (d, *J* = 4.6 Hz, 1H), 2.96 (dddt, *J* = 16.5, 7.7, 6.1, 1.5 Hz, 1H), 3.05 (dddt, *J* = 16.2, 7.7, 6.6, 1.5 Hz, 1H), 5.02 (dq, *J* = 10.1, 1.6 Hz, 1H), 5.06 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.32 (t, *J* = 1.2 Hz, 1H), 5.41 (t, *J* = 1.2 Hz, 1H), 5.70 (t, *J* = 7.6 Hz, 1H), 5.79 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.82 (d, *J* = 4.0 Hz, 1H), 7.22-7.29 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 32.49, 71.49, 113.98, 115.58, 126.93, 127.08, 127.54, 127.72, 128.12, 131.04, 131.10, 136.22, 139.84, 140.56, 140.93, 149.14. HRMS (FAB) calcd for $C_{20}H_{20}O$ (M^+) 276.1515, found 276.1507.



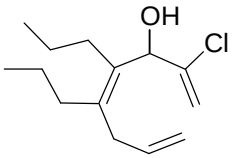
1j

(*Z*)-2-Iodo-4,5-phenyl-1,4,7-octatrien-3-ol (1n); purified by PTLC (hexane/EtOAc = 10/1) (29% yield); ^{1}H NMR ($CDCl_3$) δ 2.19 (d, *J* = 5.9 Hz, 1H), 3.07-3.13 (m, 2H), 5.09 (dq, *J* = 10.2, 1.5 Hz, 1H), 5.17 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.34 (dt, *J* = 5.9, 1.7 Hz, 1H), 5.85 (t, *J* = 7.6 Hz, 1H), 5.93 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.93 (t, *J* = 1.7 Hz, 1H), 6.47 (t, *J* = 2.0 Hz, 1H), 7.25-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 33.09, 76.58, 113.03, 116.23, 126.08, 127.69, 128.31, 128.65, 132.80, 136.13, 139.27, 139.72. HRMS (FAB) calcd for $C_{14}H_{14}I$ (M^+–OH) 309.0141, found 309.0142.



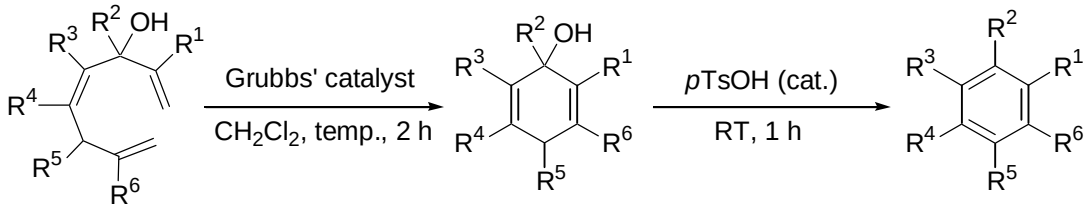
1n

(*Z*)-2-Chloro-4,5-dipropyl-1,4,7-octatrien-3-ol (1o); purified by PTLC (hexane/EtOAc = 10/1) (58% yield); ^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H), 1.37-1.51 (m, 4H), 1.84 (d, *J* = 3.7 Hz, 1H), 1.93-2.13 (m, 4H), 2.83 (ddt, *J* = 15.9, 5.9, 1.7 Hz, 1H), 2.98 (ddt, *J* = 15.9, 6.6, 1.7 Hz, 1H), 5.00-5.10 (m, 3H), 5.37 (t, *J* = 1.5 Hz, 1H), 5.61 (t, *J* = 1.5 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.33, 14.81, 21.57, 24.19, 30.03, 34.83, 35.65, 73.86, 111.78, 115.28, 132.96, 136.91, 138.40, 142.57. HRMS (FAB) calcd for $C_{14}H_{22}Cl$ (M^+–OH) 225.1412, found 225.1405.



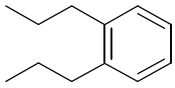
1o

General procedure of the tandem RCM/dehydration for the synthesis of benzene derivatives 3. To a solution of trienol **1** (0.200 mmol) in CH_2Cl_2 (20 mL, 0.01 M) was added 7.5 mol% catalyst **6** or **7** (0.015 mmol) in one portion under nitrogen at room temperature. After stirring for 2 h, the reaction mixture was treated with *p*-toluenesulfonic acid (0.020 mmol) and stirred for 1 h at room temperature. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography or PTLC on silica gel to give benzene **3**.



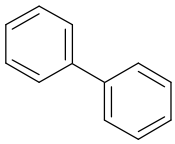
1 **2** **3**

1,2-Dipropylbenzene (3a); purified by PTLC (hexane) (>99% yield); ^{1}H NMR ($CDCl_3$) δ 0.98 (t, *J* = 7.3 Hz, 6H), 1.61 (sextet, *J* = 7.3 Hz, 4H), 2.58 (t, *J* = 7.9 Hz, 4H), 7.09-7.15 (m, 4H). This product was characterized by comparison of the spectroscopic data with those reported previously.[12]



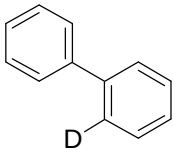
3a

Biphenyl (3b); purified by PTLC (hexane) (97% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.[13]



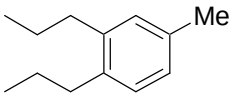
3b

2-Deuteriobiphenyl (3c); purified by PTLC (hexane) (96% yield); ^{2}H NMR ($CHCl_3$) δ 7.59.



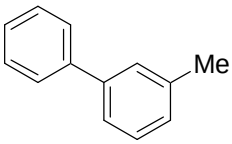
3c

4-Methyl-1,2-dipropylbenzene (3d); purified by PTLC (hexane) (>99% yield); ^{1}H NMR ($CDCl_3$) δ 0.98 (t, *J* = 7.3 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H), 1.55-1.62 (m, 4H), 2.29 (s, 3H), 2.53-2.56 (m, 4H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.96 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.67, 14.72, 21.38, 24.87, 24.88, 34.80, 35.19, 126.82, 129.48, 130.32, 135.41, 137.70, 140.63. HRMS (EI) calcd for $C_{13}H_{20}$ (M^+) 176.1566, found 176.1578.



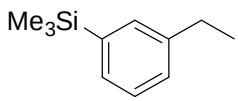
3d

3-Methylbiphenyl (3e); purified by PTLC (hexane) (>99% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.[14]



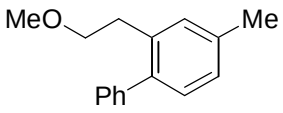
3e

1-Ethyl-3-(trimethylsilyl)benzene (3f); purified by PTLC (hexane) (94% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.[15]



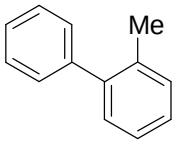
3f

2-(2-Methoxyethyl)-1,4-dimethylbenzene (3g); purified by PTLC (hexane/EtOAc = 5/1) (99% yield); ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 2.85 (t, *J* = 7.6 Hz, 2H), 3.23 (s, 3H), 3.43 (t, *J* = 7.6 Hz, 2H), 7.06-7.14 (m, 3H), 7.28-7.41 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 21.13, 33.07, 58.41, 73.21, 126.71, 126.96, 128.06, 129.32, 130.06, 130.40, 135.80, 136.98, 139.49, 141.62. HRMS (FAB) calcd for $C_{16}H_{18}O$ (M^+) 226.1358, found 226.1363.



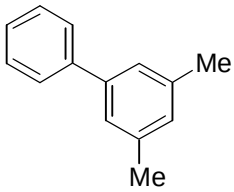
3g

2-Methylbiphenyl (3h); purified by PTLC (hexane/EtOAc = 20/1) (80% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.[16]



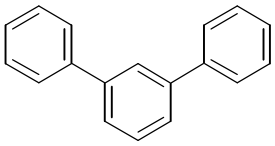
3h

3,5-Dimethylbiphenyl (3i); purified by PTLC (hexane/EtOAc = 20/1) (84% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.[13]



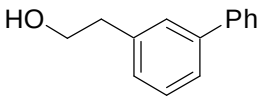
3i

1,3-Diphenylbenzene (3j); purified by PTLC (hexane/EtOAc = 7/1) (96% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.[17]



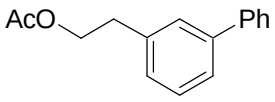
3j

3-(2-Hydroxyethyl)biphenyl (3k); purified by PTLC (CH_2Cl_2/EtOAc = 3/1) (84% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.[18]



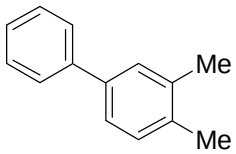
3k

3-(2-Acetoxyethyl)biphenyl (3l); purified by PTLC (hexane/EtOAc = 4/1) (>99% yield); ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3H), 3.00 (t, *J* = 7.4 Hz, 2H), 4.33 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.32-7.48 (m, 6H), 7.57-7.59 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 20.94, 35.10, 64.88, 125.43, 127.12, 127.28, 127.72, 127.74, 128.71, 128.89, 138.25, 141.01, 141.45, 171.02. HRMS (FAB) calcd for $C_{16}H_{16}O_2$ (M^+) 240.1151, found 240.1145.



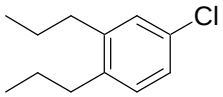
3l

3,4-Dimethylbiphenyl (3m); purified by PTLC (hexane/EtOAc = 20/1) (91% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.[19]



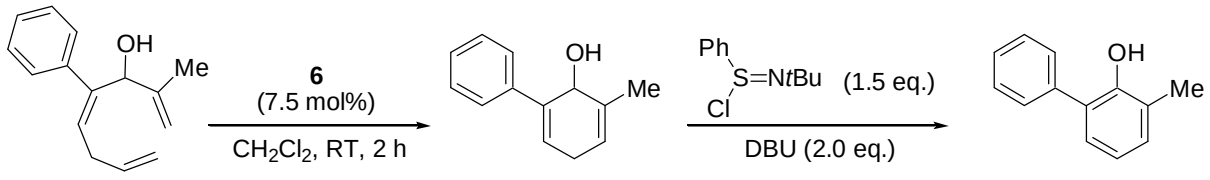
3m

4-Chloro-1,2-dipropylbenzene (3o); purified by PTLC (hexane/EtOAc = 4/1) (86% yield); ^{1}H NMR ($CDCl_3$) δ 0.97 (t, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H), 1.57 (sextet, *J* = 7.4 Hz, 2H), 1.59 (sextet, *J* = 7.4 Hz, 2H), 2.52-2.57 (m, 4H), 7.04-7.12 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 14.10, 14.12, 24.06, 24.20, 34.15, 34.53, 125.66, 128.88, 130.42, 131.10, 138.78, 142.27. HRMS (EI) calcd for $C_{12}H_{17}Cl$ (M^+) 196.1020, found 196.1021.



3o

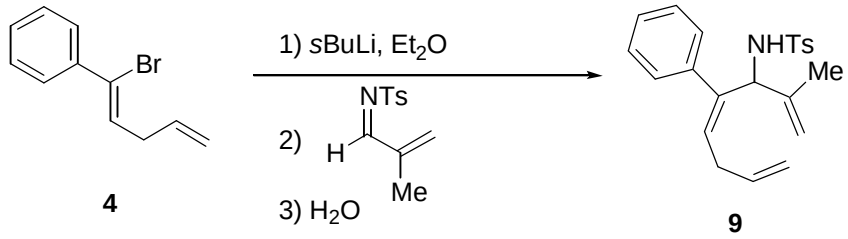
Preparation of 2-Methyl-6-phenylphenol (8e). To a solution of trienol **1e** (32.2mg, 0.150 mmol) in CH_2Cl_2 (15 mL, 0.01 M) was added 7.5 mol% catalyst **6** (9.3 mg, 0.0113 mmol) in one portion under nitrogen and the mixture was stirred for 2 h at room temperature. To the reaction mixture was added a solution of *N*-*tert*-butylbenzenesulfinimidoyl chloride (48.6 mg, 0.225 mmol) and DBU (45.8 mg, 0.300 mmol) in CH_2Cl_2 (2.0 mL) and stirred overnight at room temperature. The reaction mixture was then quenched by addition of sat. $NaHCO_3$ (aq.) and extracted twice with EtOAc. The organic phases were dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by silica gel column chromatography (hexane/EtOAc = 5/1) to give the desired product **8e** (7.0 mg, 0.038 mmol, 25% yield). This product was characterized by comparison of the spectroscopic data with those reported previously.[20]



1e **2e** **8e**

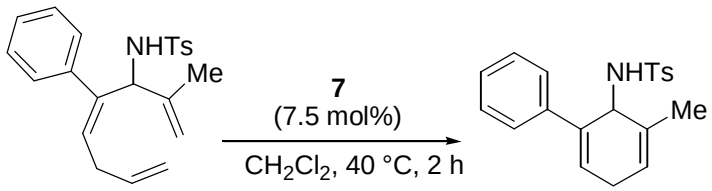
Preparation of (*Z*)-*N*-(1-isopropenyl-2-phenyl-2,5-hexadienyl)-4-methylbenzenesulfonamide (9). *s*BuLi (0.95 M solution in cyclohexane and *n*-hexane, 2.00 mmol) was added to a solution of bromodiene **4** (2.10 mmol) in Et_2O (3.0 mL) at –78 °C. After 5 min, a solution of 2-methyl-1-[(phenylsulfonyl)imino]-2-propene (1.05 mmol) in Et_2O (6.0 mL) was added. The

mixture was stirred for 10 min at –78 °C, then warmed to room temperature. After stirring for 30 min, the reaction mixture was quenched by addition of water and extracted twice with EtOAc. The organic phases were dried with Na_2SO_4 and concentrated under vacuum. The residue was purified by silica gel column chromatography (hexane/EtOAc = 5/1) to give **9** (235 mg, 61% yield); m.p. 114-117 °C; ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 3H), 2.44 (s, 3H), 2.76-2.89 (m, 2H), 4.65 (d, *J* = 9.8 Hz, 1H), 4.99 (d, *J* = 9.8 Hz, 1H), 5.01-5.06 (m, 2H), 5.06-5.07(m, 1H), 5.14-5.16 (m, 1H), 5.55 (t, *J* = 7.4 Hz, 1H), 5.73 (ddt, *J* = 17.4, 9.8, 6.4 Hz, 1H), 6.91 (dt, *J* = 6.8, 1.5 Hz, 2H), 7.17-7.23 (m, 5H), 7.53 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 20.69, 21.51, 32.64, 57.45, 113.12, 115.87, 127.12, 127.40, 127.49, 128.37, 129.32, 130.40, 135.35, 137.48, 137.60, 139.31, 143.13, 143.30. HRMS (FAB) calcd for $C_{22}H_{26}NO_2S$ (M^++H) 368.1686, found 368.1669.



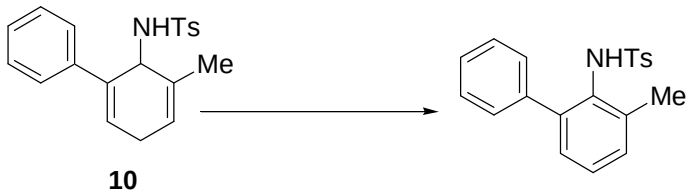
4 **9**

Preparation of *N*-(2-methyl-6-phenyl-2,5-cyclohexadienyl)-4-methylbenzenesulfonamide (10). A solution of trienamine **9** (38.6 mg, 0.105 mmol) in CH_2Cl_2 (10.5 mL, 0.01 M) was treated with 7.5 mol% catalyst **7** (6.7 mg, 0.00788 mmol, 7.5 mol%) in one portion under nitrogen and stirred for 2 h at 40 °C. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography (hexane/EtOAc = 4/1) to give **10** (35.3 mg, 0.104 mmol, 99% yield); m.p. 109-112 °C; ^{1}H NMR ($CDCl_3$) δ 1.96 (d, *J* = 3.1, 1.5 Hz, 3H), 2.31 (s, 3H), 2.73-2.87 (m, 2H), 4.31 (d, *J* = 8.9 Hz, 1H), 4.95 (dt, *J* = 9.2, 5.5 Hz, 1H), 5.71-5.74 (br m, 1H), 5.98 (dt, *J* = 3.5, 1.5 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 7.06-7.16 (m, 5H), 7.21 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.11, 21.34, 27.92, 53.72, 123.49, 126.36, 126.56, 126.76, 127.17, 128.16, 128.98, 132.76, 136.93, 138.65, 140.32, 142.09. HRMS (FAB) calcd for $C_{13}H_{13}$ (M^+–NHTs) 169.1018, found 169.1014.



9 **10**

Preparation of *N*-(3-methylbiphenyl-2-yl)-4-methylbenzenesulfonamide (11) by the tandem RCM/oxidation. A solution of **10** (28.5 mg, 0.0839 mmol) in CH_2Cl_2 (7.6 mL) was added MnO_2 (729 mg, 8.39 mmol) in one portion under air and stirred for 12 h at room temperature. The reaction mixture passed through celite and the residual solid was washed thoroughly with CH_2Cl_2. The filtrate was concentrated under reduced pressure. Purification by PTLC on silica gel (hexane/EtOAc = 2/1) gave the corresponding aniline **11** (21.7 mg, 0.0643 mmol, 77% yield); m.p. 135-138 °C; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 2.56 (s, 3H), 6.63 (br s, 1H), 6.77-6.80 (m, 2H), 6.94-6.98 (m, 3H), 7.08-7.23 (m, 6H), 7.28 (dd, *J* = 7.8, 0.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 19.86, 21.47, 126.75, 126.78, 127.49, 128.24, 128.31, 128.36, 129.27, 130.82, 130.92, 136.51, 138.87, 138.90, 140.50, 142.81. HRMS (FAB) calcd for $C_{20}H_{19}NO_2S$ (M^+) 337.1138, found 337.1133.



10 **11**

References

[1] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100-110.

[2] T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 2546-2558.

[3] a) K. Kaneda, T. Uchiyama, Y. Fujiwara, T. Imanaka, S. Teranishi, *J. Org. Chem.* **1979**, *44*, 55-63; b) A. Llebaria, F. Camps, J. M. Moreto, *Tetrahedron* **1993**, *49*, 1283-1296; c) A. N. Thadani, V. H. Rawal, *Org. Lett.* **2002**, *4*, 4317-4320.

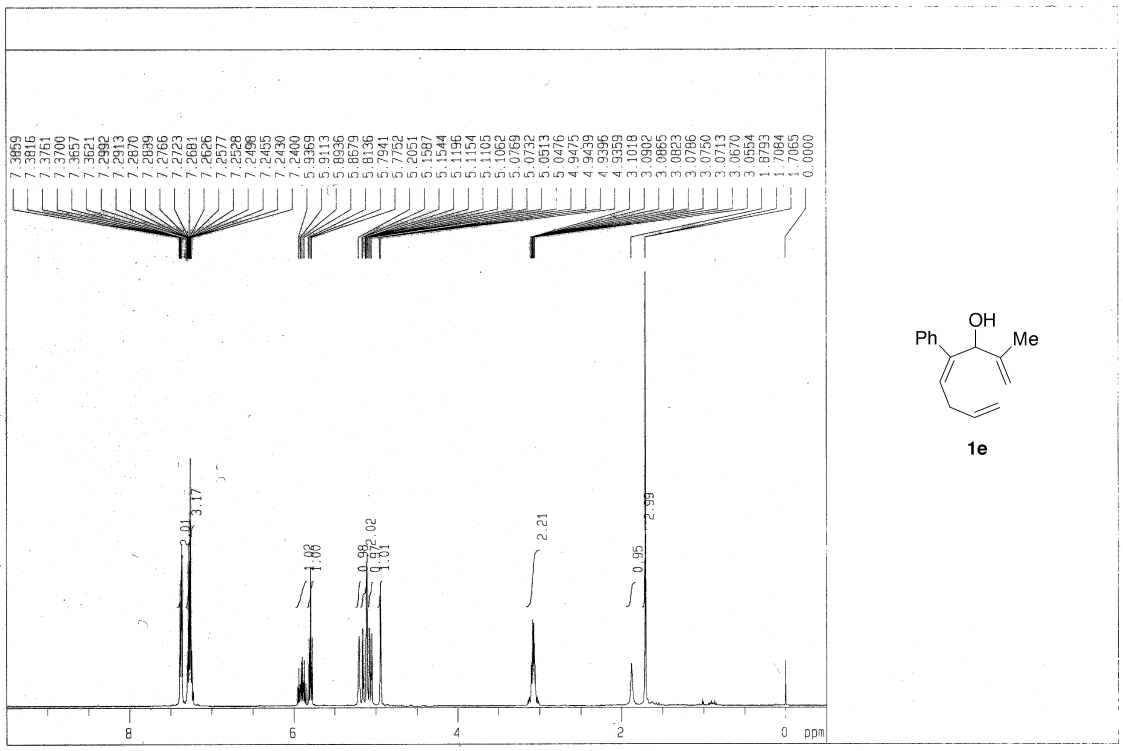
[4] K. Yoshida, T. Imamoto, *J. Am. Chem. Soc.* **2005**, *127*, 10470-10471.

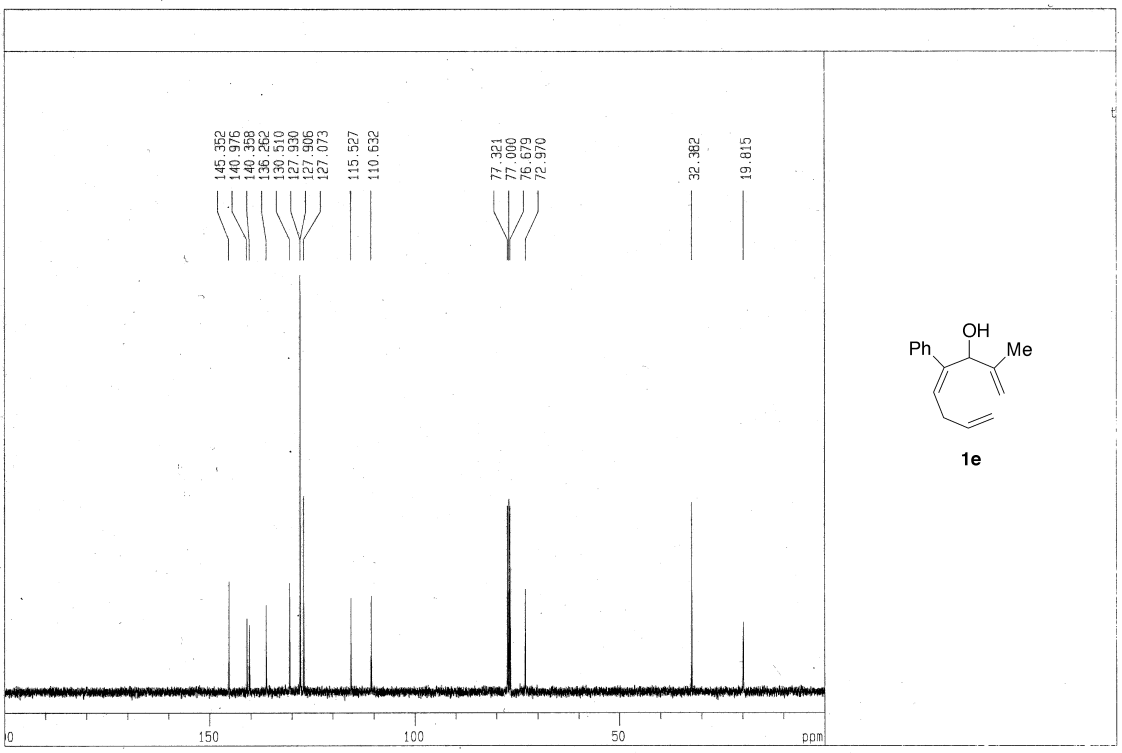
[5] R. H. Newman-Evans, R. J. Simon, B. K. Carpenter, *J. Org. Chem.* **1990**, *55*, 695-711.

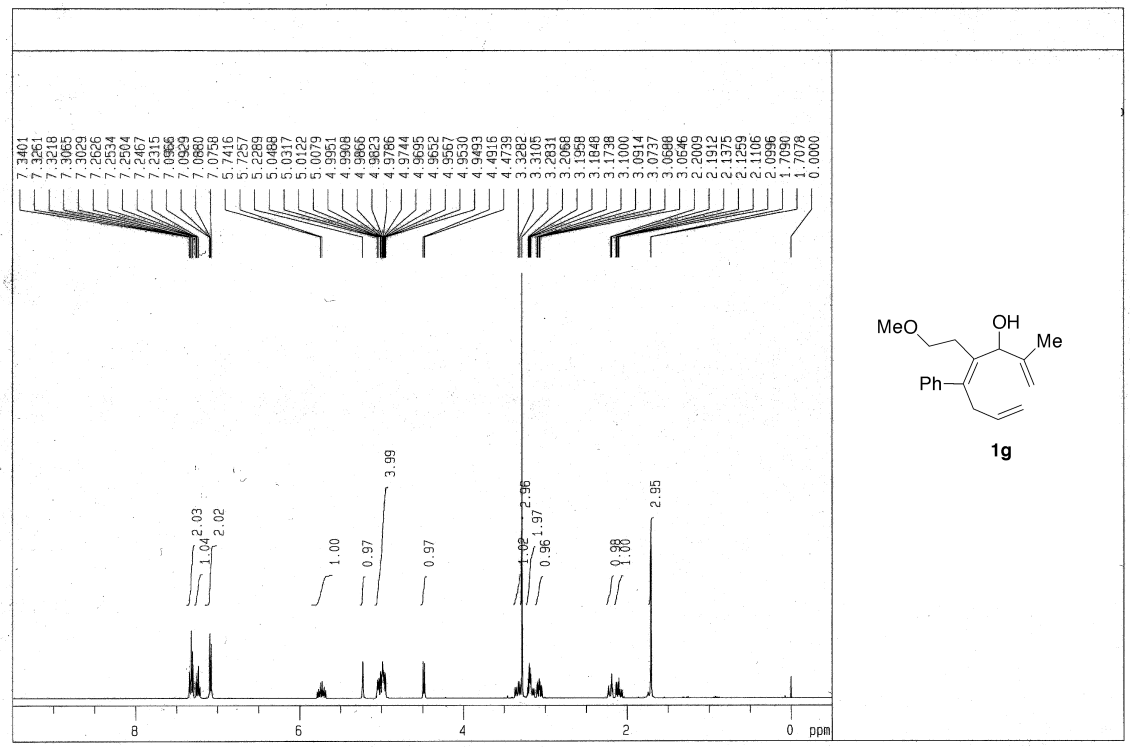
[6] W. R. Jackson, P. Perlmutter, A. J. Smallridge, *Aust. J. Chem.* **1988**, *41*, 251-261.

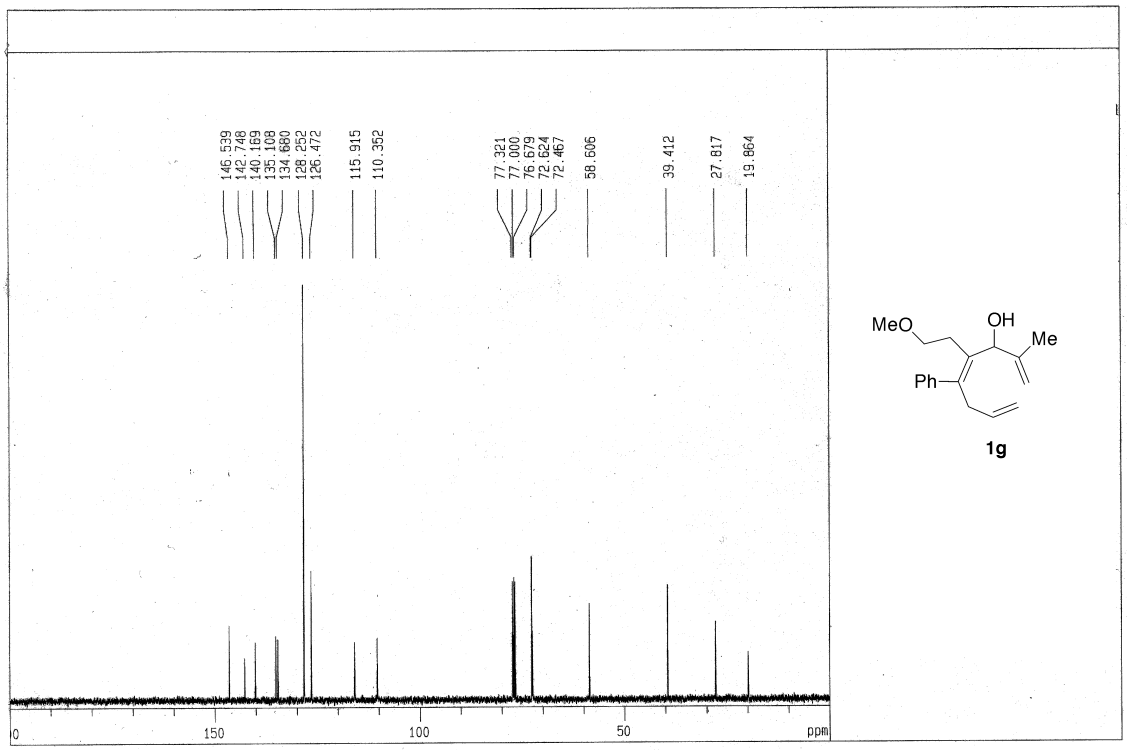
[7] S. Irifune, T. Kibayashi, Y. Ishii, M. Ogawa, *Synthesis* **1988**, 366-369.

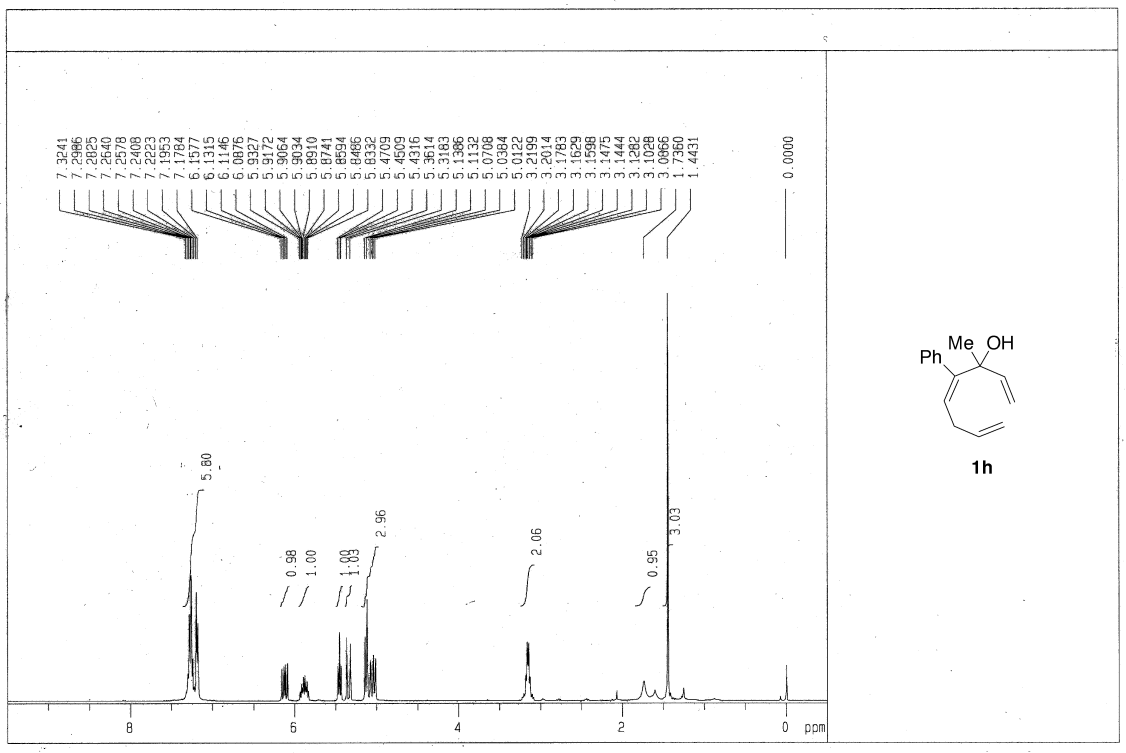
[8] D. L. Boger, W. L. Corbett, T. T. Curran, A. M. Kasper, *J. Am. Chem. Soc.* **1991**, *113*, 1713-1729.
[9] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, T. Walker, *J. Chem. Soc.* **1952**, 1094-1111.
[10] a) K. Okada, K. Oshima, K. Utimoto, *J. Am. Chem. Soc.* **1996**, *118*, 6076-6077; b) J. Tang, K. Okada, H. Shinokubo, K. Oshima, *Tetrahedron* **1997**, *53*, 5061-5072.
[11] T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, M. Yokoyama, *J. Org. Chem.* **1984**, *49*, 3904-3912.
[12] T. P. Lockhart, P. B. Comita, R. G. Bergman, *J. Am. Chem. Soc.* **1981**, *103*, 4082-4090.
[13] J.-H. Li, Y. Liang, D.-P. Wang, W.-J. Liu, Y.-X. Xie, D.-L. Yin, *J. Org. Chem.* **2005**, *70*, 2832-2834.
[14] M. B. Andrus, C. Song, *Org. Lett.* **2001**, *3*, 3761-3764.
[15] B. Bennetau, M. Krempp, J. Dunogues, *Tetrahedron* **1990**, *46*, 8131-8142.
[16] C. Song, Y. Ma, Q. Chai, C. Ma, W. Jiang, M. B. Andrus, *Tetrahedron* **2005**, *61*, 7438-7446.
[17] F. Berthiol, I. Kondolff, H. Doucet, M. Santelli, *J. Organomet. Chem.* **2004**, *689*, 2786-2798.
[18] T. A. Lyle, G. H. Daub, *J. Org. Chem.* **1979**, *44*, 4933-4938.
[19] F. Gavina, A. M. Costero, A. M. Gonzalez, *J. Org. Chem.* **1990**, *55*, 2060-2063.
[20] T. Keumi, C. Murata, Y. Sasaki, H. Kitajima, *Synthesis* **1980**, 634-635.

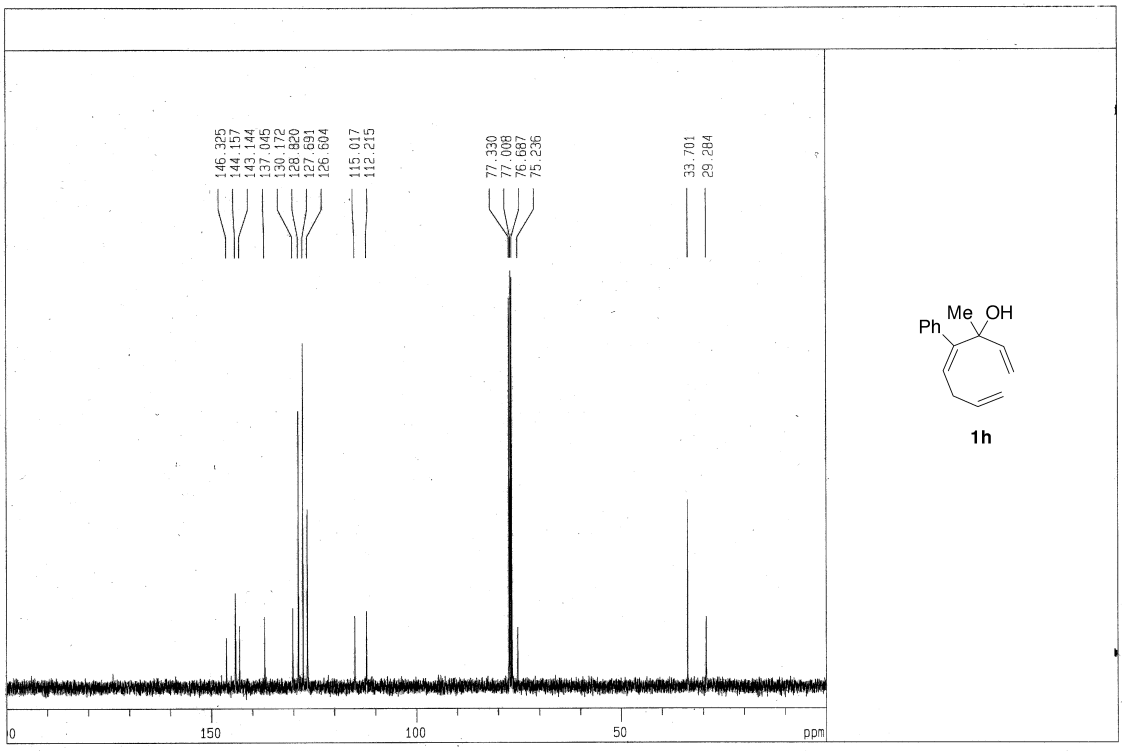

7.3859
7.3816
7.3761
7.3700
7.3657
7.3621
7.2992
7.2913
7.2870
7.2839
7.2766
7.2723
7.2681
7.2626
7.2577
7.2528
7.2498
7.2455
7.2430
7.2400
5.9369
5.9113
5.8936
5.8679
5.8136
5.7941
5.7752
5.2051
5.1587
5.1544
5.1196
5.1154
5.1105
5.1062
5.0769
5.0732
5.0513
5.0476
4.9475
4.9439
4.9396
4.9359
3.1018
3.0902
3.0865
3.0823
3.0786
3.0750
3.0713
3.0670
3.0554
1.8793
1.7084
1.7065
0.0000
2.01
3.17
1.00
0.98
0.97
1.01
2.02
2.21
0.95
2.99
8
6
4
2
0 ppm
Ph
OH
Me
1e

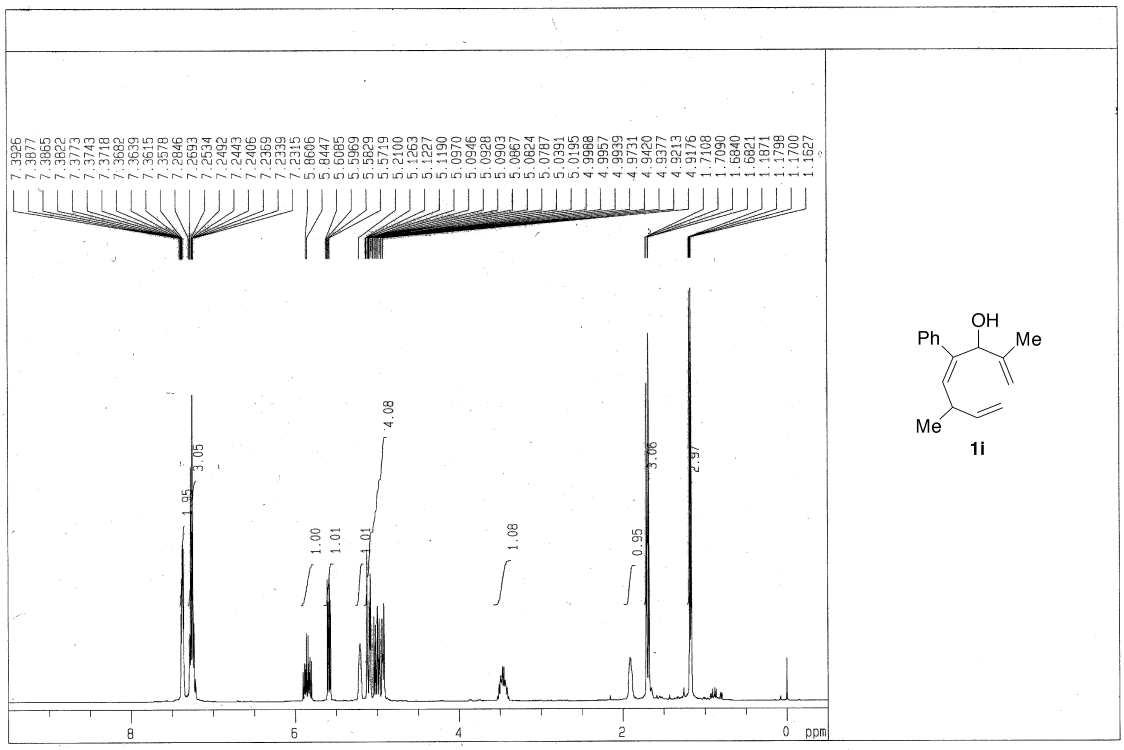

145.352
140.976
140.358
136.262
130.510
127.930
127.906
127.073
115.527
110.632
77.321
77.000
76.679
72.970
32.382
19.815
150
100
50
ppm
Ph
OH
Me
1e

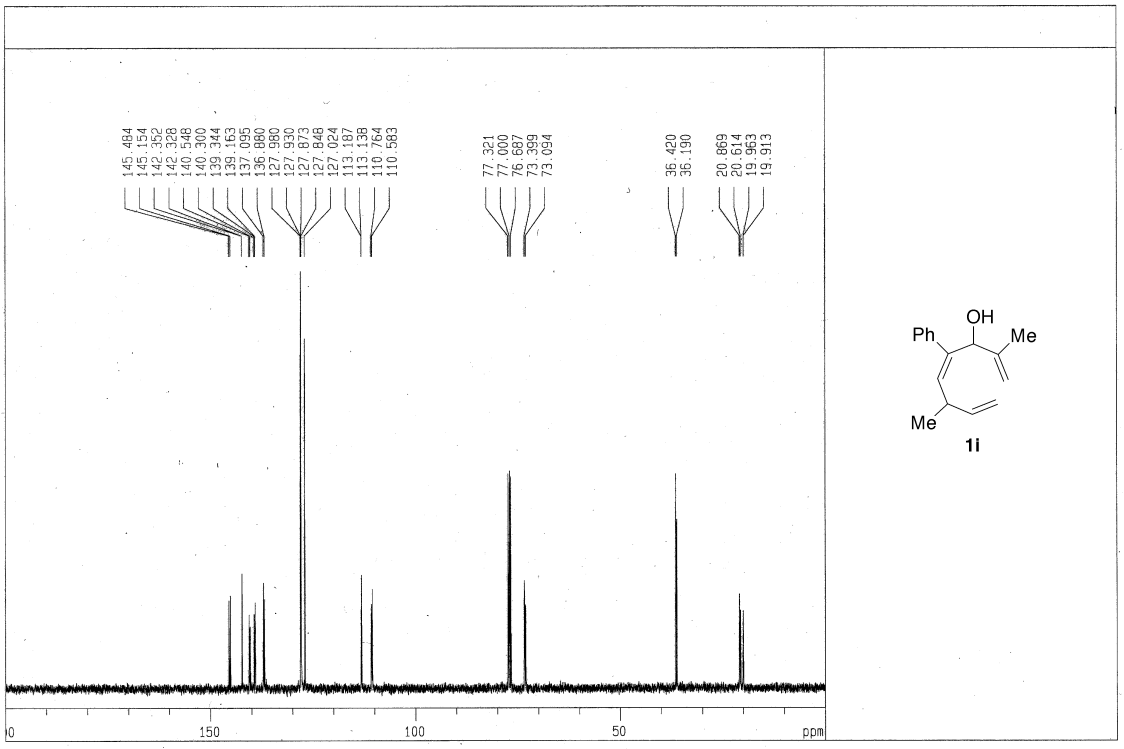

7.3401
7.3261
7.3218
7.3065
7.3029
7.2626
7.2534
7.2504
7.2467
7.2315
7.0929
7.0880
7.0758
5.7416
5.7257
5.2269
5.0488
5.0317
5.0122
5.0079
4.9951
4.9908
4.9866
4.9623
4.9786
4.9744
4.9695
4.9652
4.9567
4.9530
4.9493
4.4916
4.4739
3.3282
3.3105
3.2831
3.2068
3.1958
3.1848
3.1738
3.1000
3.0914
3.0737
3.0688
3.0546
2.2009
2.1912
2.1375
2.1259
2.1106
2.0996
1.7090
1.7078
0.0000
2.03
1.04
2.02
1.00
0.97
3.99
0.97
2.96
1.97
0.96
0.98
1.00
2.95
8
6
4
2
0 ppm
MeO
OH
Me
Ph
1g

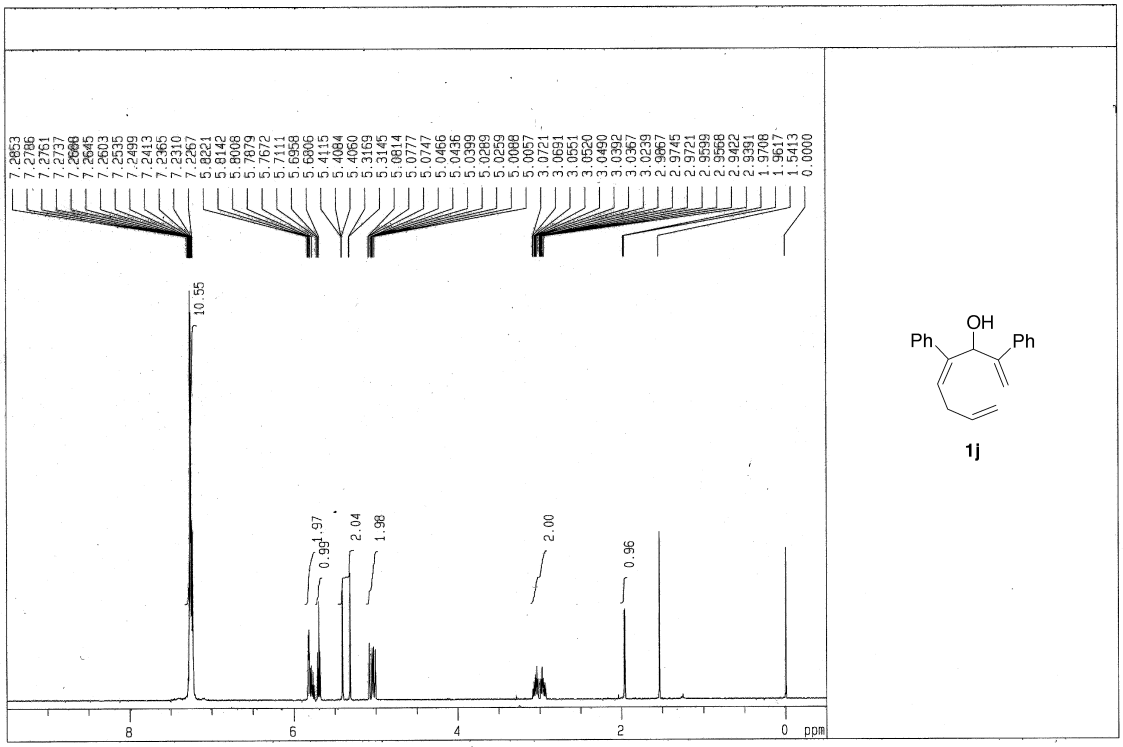

146.539
142.748
140.169
135.108
134.660
128.252
126.472
115.915
110.352
77.321
77.000
76.679
72.624
72.467
58.606
39.412
27.817
19.864
0
150
100
50
ppm
MeO
OH
Me
Ph
1g

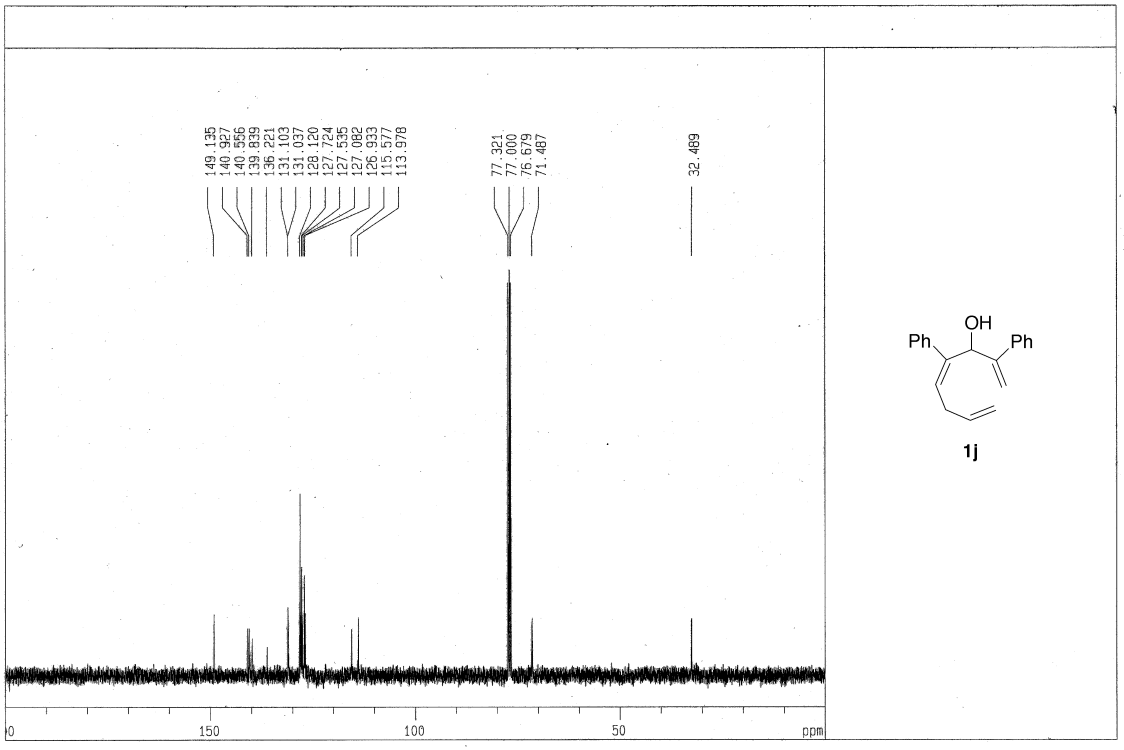

7.3241
7.2986
7.2825
7.2640
7.2378
7.2408
7.2223
7.1953
7.1764
6.1577
6.1315
6.1146
6.0876
5.9327
5.9172
5.9064
5.9034
5.8910
5.8741
5.8594
5.8486
5.8332
5.4709
5.4509
5.4316
5.3614
5.3163
5.1386
5.1132
5.0708
5.0384
5.0122
3.2199
3.2014
3.1783
3.1629
3.1598
3.1475
3.1444
3.1282
3.1028
3.0866
1.7360
1.4431
0.0000
5.80
0.98
1.00
1.00
1.03
2.96
2.06
0.95
3.03
8
6
4
2
0
ppm
Ph
Me
OH
1h

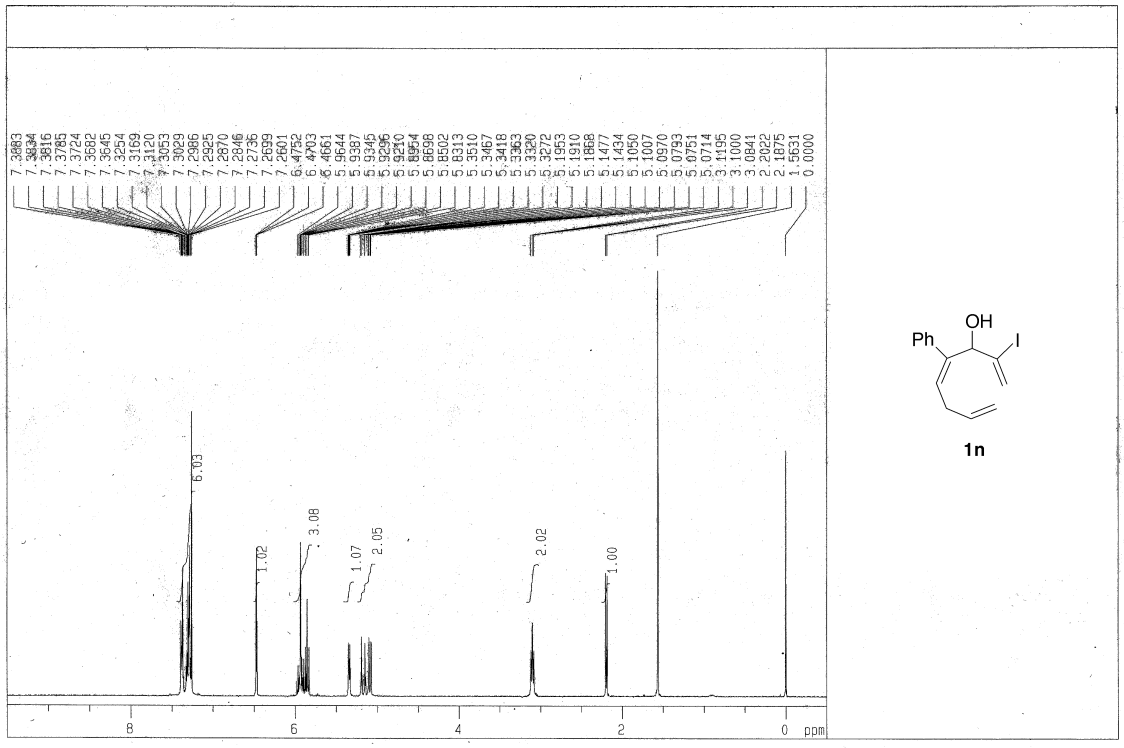

146.325
144.157
143.144
137.045
130.172
128.820
127.691
126.604
115.017
112.215
77.330
77.008
76.687
75.236
33.701
29.284
150
100
50
ppm
Ph
Me
OH
1h


7.3926
7.3877
7.3865
7.3822
7.3773
7.3743
7.3718
7.3682
7.3639
7.3615
7.3578
7.2946
7.2693
7.2534
7.2492
7.2443
7.2406
7.2369
7.2339
7.2315
5.8606
5.8447
5.6085
5.5969
5.5829
5.5719
5.5210
5.5100
5.1263
5.1227
5.1190
5.0970
5.0946
5.0928
5.0903
5.0867
5.0824
5.0787
5.0391
5.0195
4.9968
4.9957
4.9939
4.9731
4.9420
4.9377
4.9213
4.9176
1.7108
1.7090
1.6940
1.6821
1.1971
1.1798
1.1700
1.1627
1.95
3.05
1.00
1.01
1.01
4.08
1.08
0.95
3.06
2.97
8
6
4
2
0 ppm
OH
Ph
Me
Me
1i

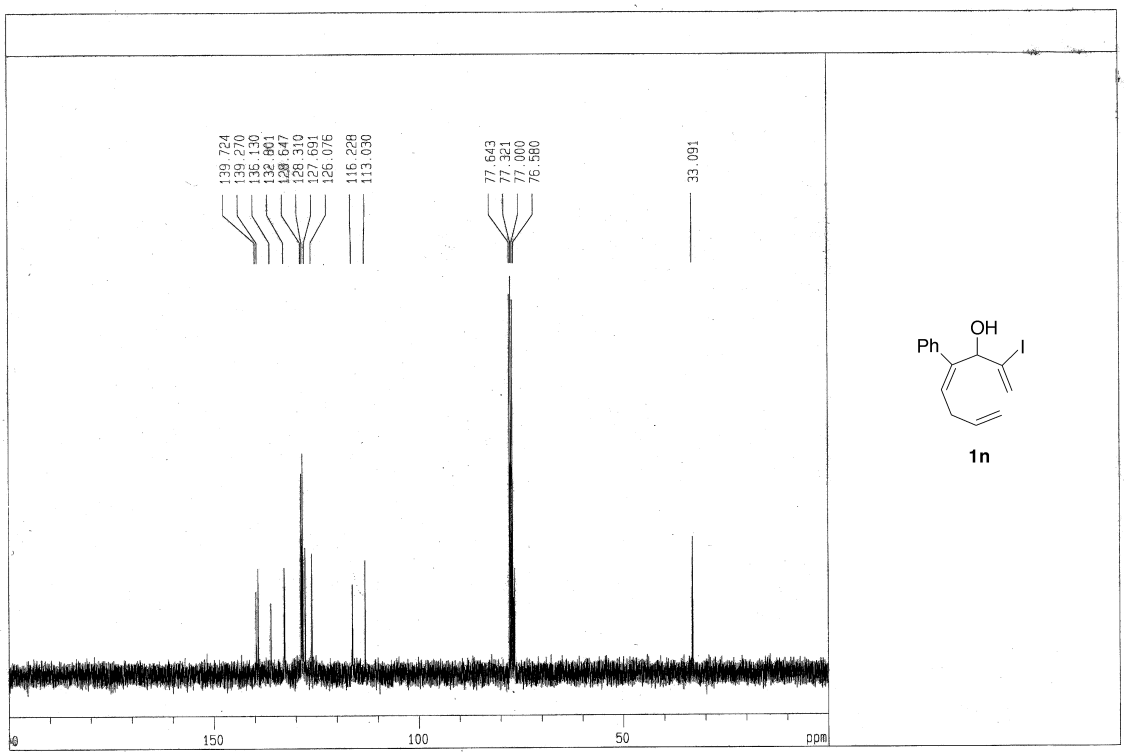

145.484
145.154
142.352
142.328
140.548
140.300
139.344
139.163
137.095
136.860
127.980
127.930
127.873
127.846
127.024
113.187
113.138
110.764
110.583
77.321
77.000
76.687
73.399
73.094
36.420
36.190
20.869
20.614
19.963
19.913
150
100
50
ppm
OH
Ph
Me
Me
1i


7.2853
7.2786
7.2761
7.2737
7.2645
7.2603
7.2535
7.2499
7.2413
7.2365
7.2310
7.2267
5.8221
5.8142
5.8008
5.7879
5.7672
5.7111
5.6958
5.6806
5.4115
5.4084
5.4050
5.3169
5.3145
5.0814
5.0777
5.0747
5.0466
5.0436
5.0399
5.0289
5.0259
5.0088
5.0057
3.0721
3.0691
3.0551
3.0520
3.0490
3.0392
3.0367
3.0239
2.9967
2.9745
2.9721
2.9599
2.9568
2.9422
2.9391
1.9708
1.9617
1.5413
0.0000
10.55
1.97
0.99
2.04
1.98
2.00
0.96
8
6
4
2
0 ppm
OH
Ph
Ph
1j

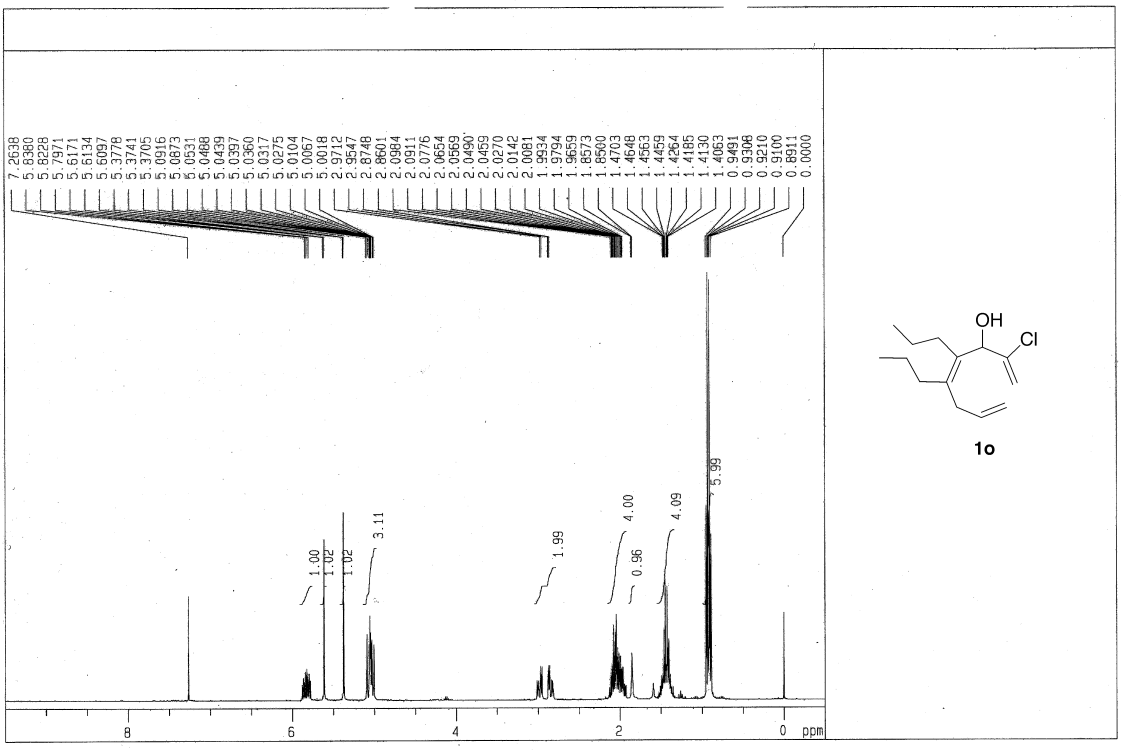

149.135
140.927
140.556
139.839
136.221
131.103
131.037
128.120
127.724
127.535
127.082
126.933
115.577
113.978
77.321
77.000
76.679
71.487
32.489
150
100
50
ppm
OH
Ph
Ph
1j


6.03
1.02
3.08
1.07
2.05
2.02
1.00
8
6
4
2
0
ppm
OH
Ph
I

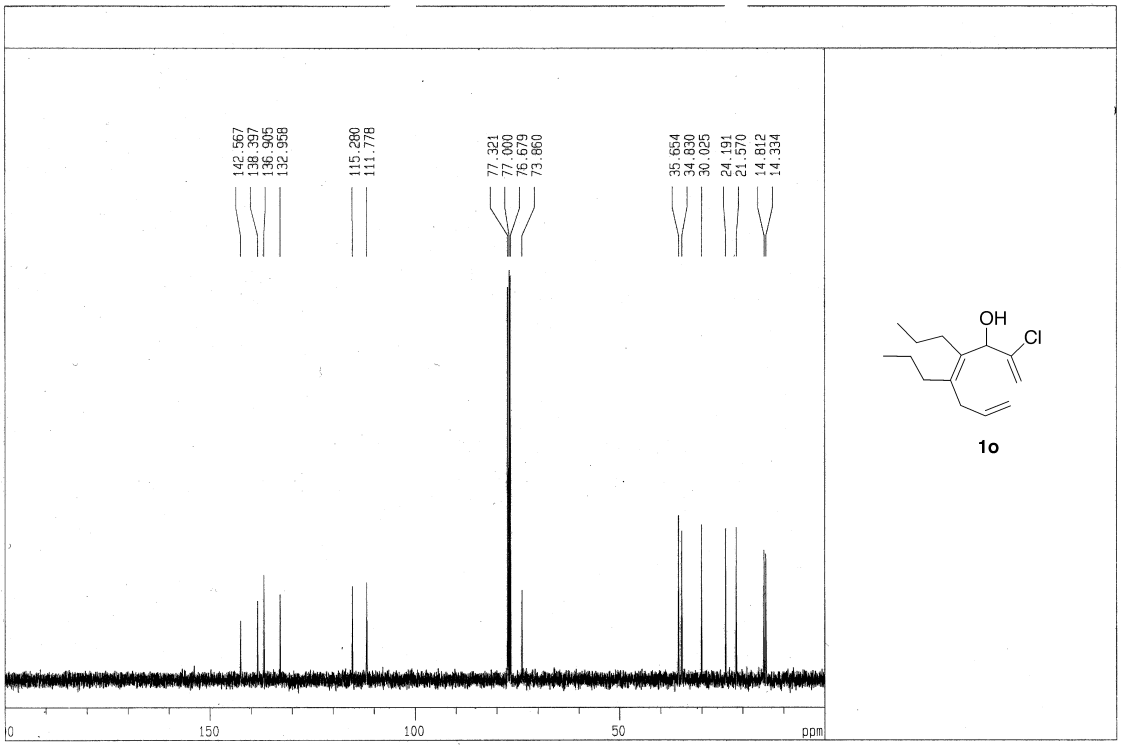
1n


139.724
139.270
136.130
116.228
113.030
77.643
77.321
77.000
76.580
33.091
150
100
50
ppm
OH
Ph
I

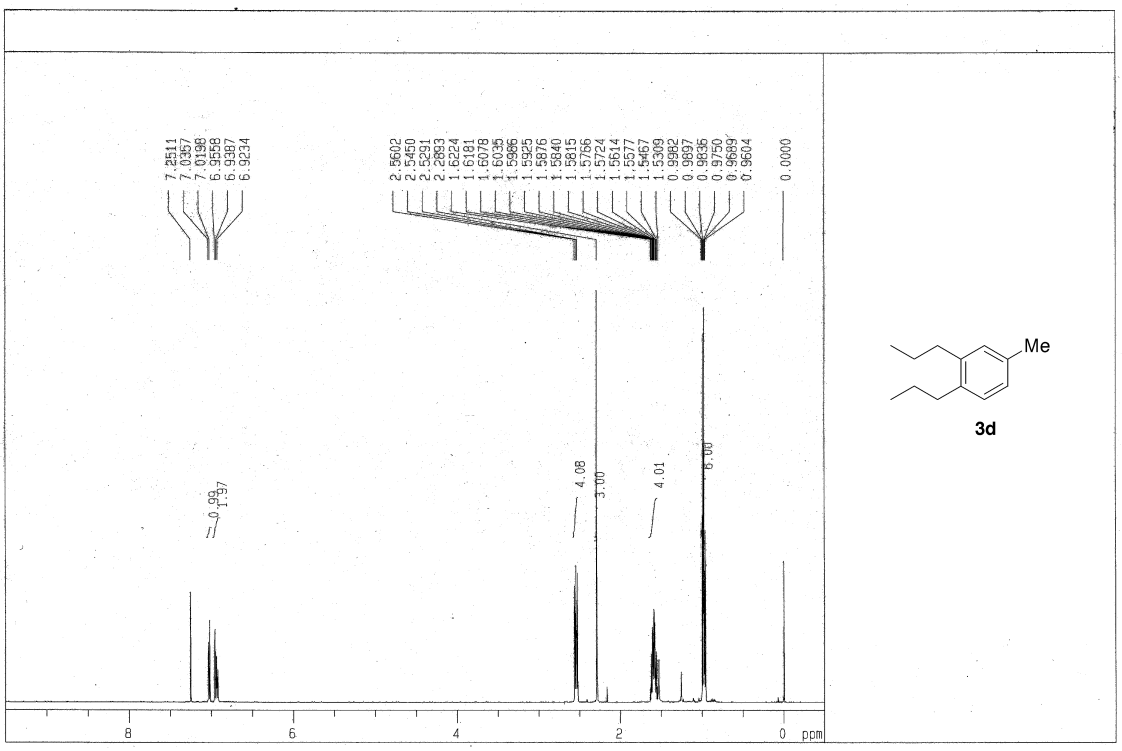
1n

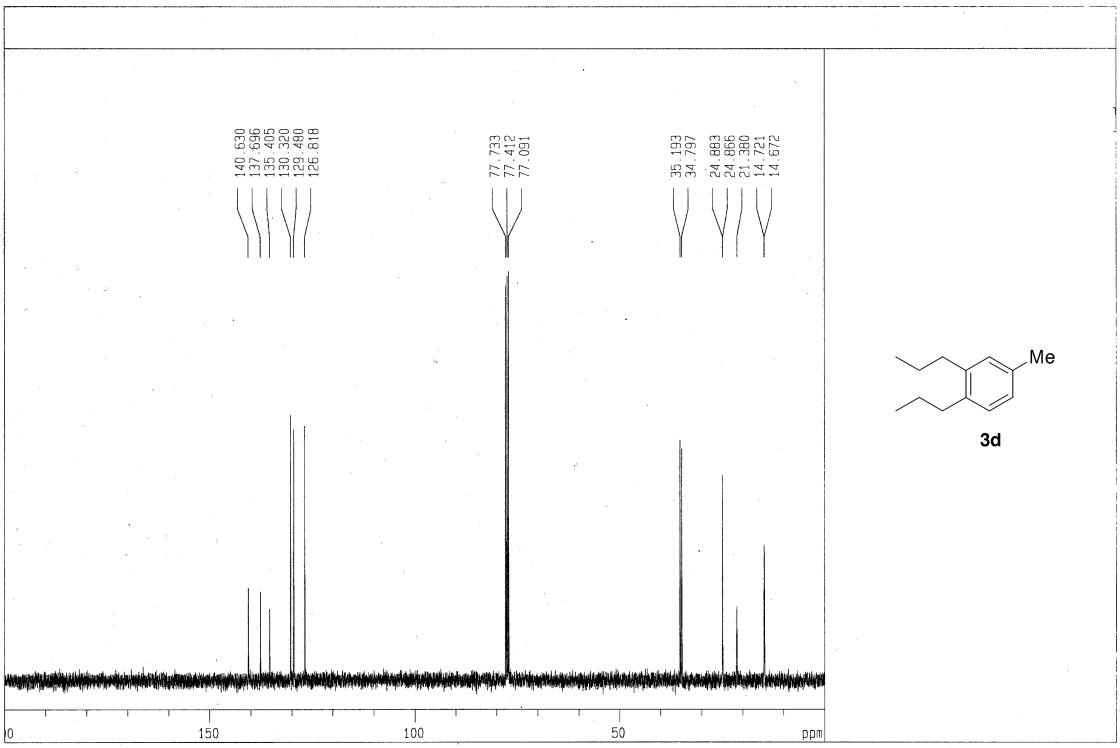

7.2638
5.8380
5.8228
5.7971
5.6171
5.6134
5.6097
5.3778
5.3741
5.3705
5.0916
5.0873
5.0531
5.0488
5.0439
5.0397
5.0360
5.0317
5.0275
5.0104
5.0067
5.0018
2.9712
2.9547
2.8748
2.8601
2.0984
2.0911
2.0776
2.0654
2.0569
2.0490
2.0459
2.0270
2.0142
2.0081
1.9934
1.9794
1.9659
1.8573
1.8500
1.4703
1.4648
1.4563
1.4459
1.4264
1.4185
1.4130
1.4063
0.9491
0.9306
0.9210
0.9100
0.8911
0.0000
1.00
1.02
1.02
3.11
1.99
4.00
0.96
4.09
5.99
8
6
4
2
0
ppm
OH
Cl

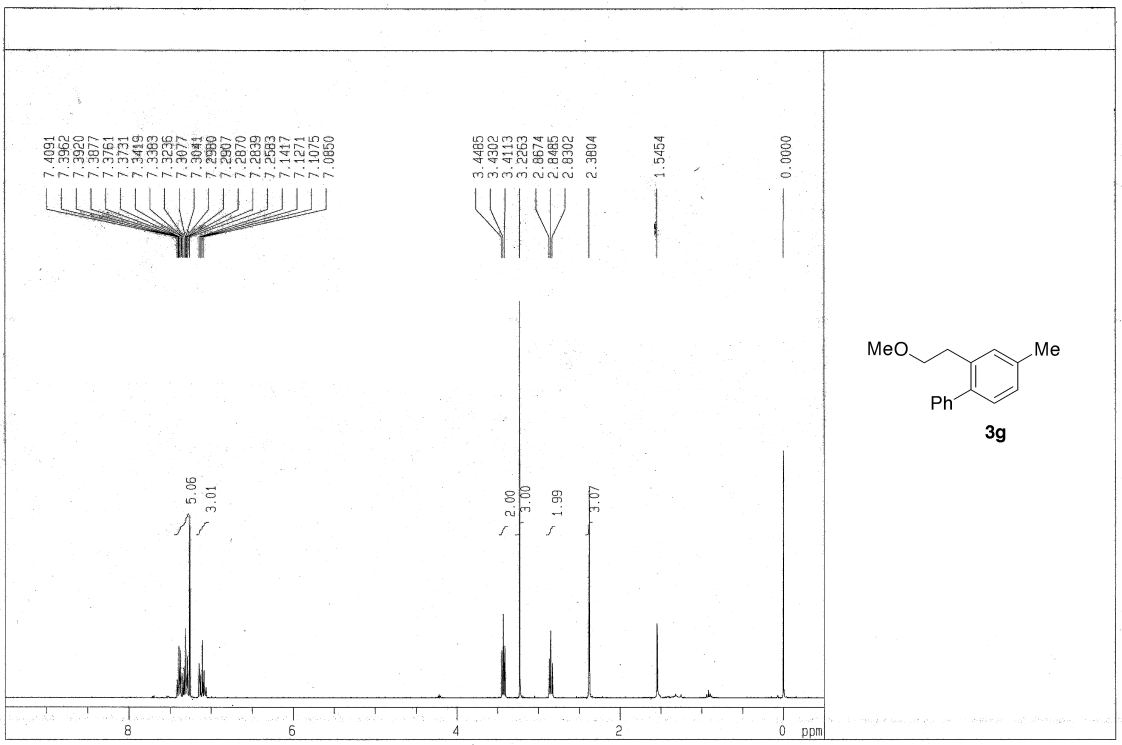
1o

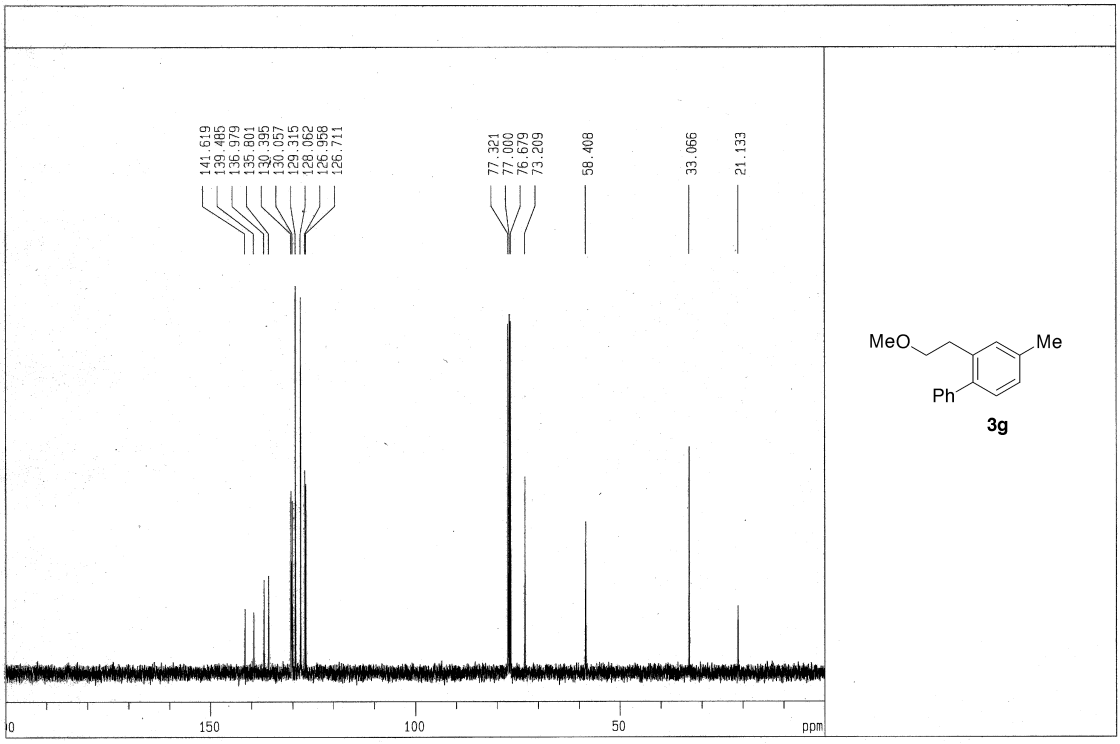

142.567
138.397
136.905
132.958
115.280
111.778
77.321
77.000
76.679
73.860
35.654
34.830
30.025
24.191
21.570
14.812
14.334
150
100
50
ppm
OH
Cl

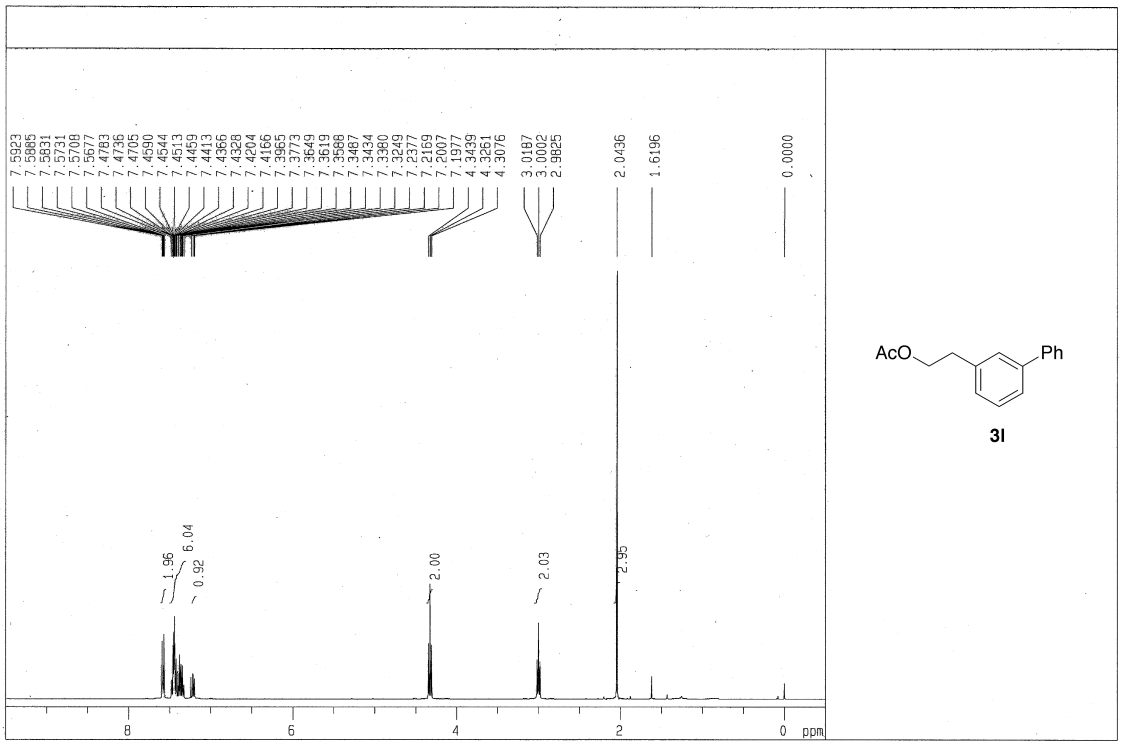
1o

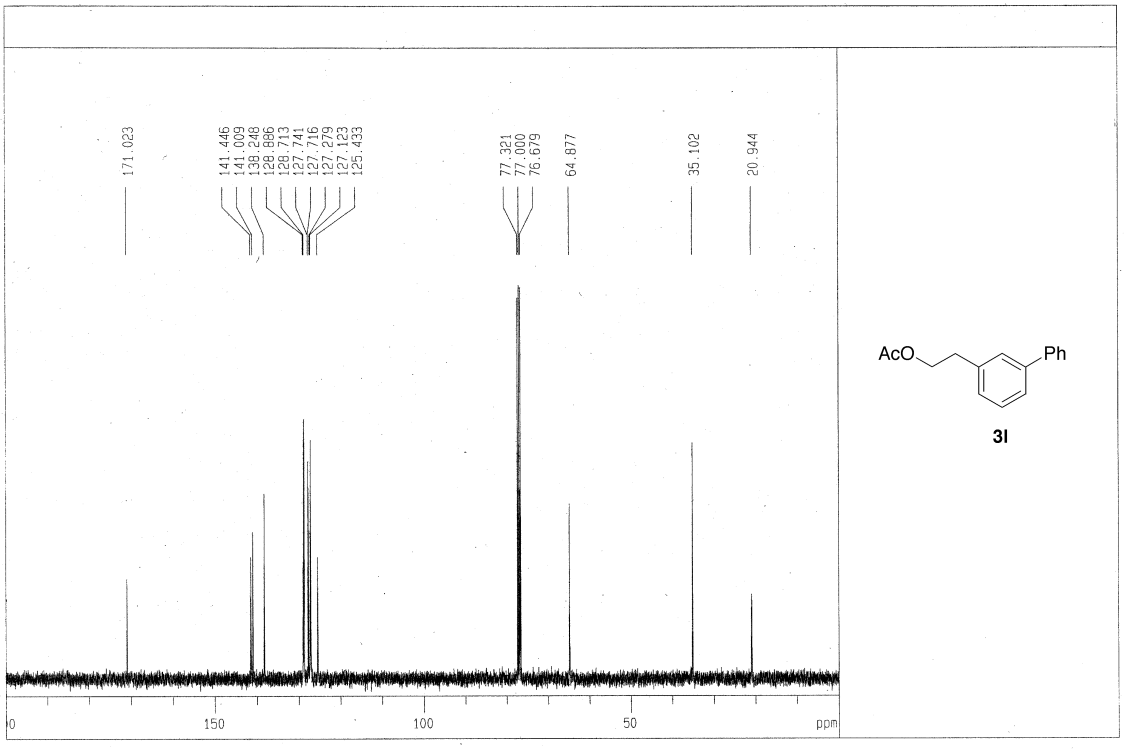

7.2511
7.0357
7.0198
6.9558
6.9387
6.9234
2.5602
2.5450
2.5291
2.2893
1.6224
1.6181
1.6078
1.6035
1.5986
1.5925
1.5876
1.5840
1.5815
1.5766
1.5724
1.5614
1.5577
1.5467
1.5309
0.9982
0.9897
0.9835
0.9750
0.9689
0.9604
0.0000
0.99
1.97
4.08
3.00
4.01
6.00
8
6
4
2
0
ppm
Me
3d

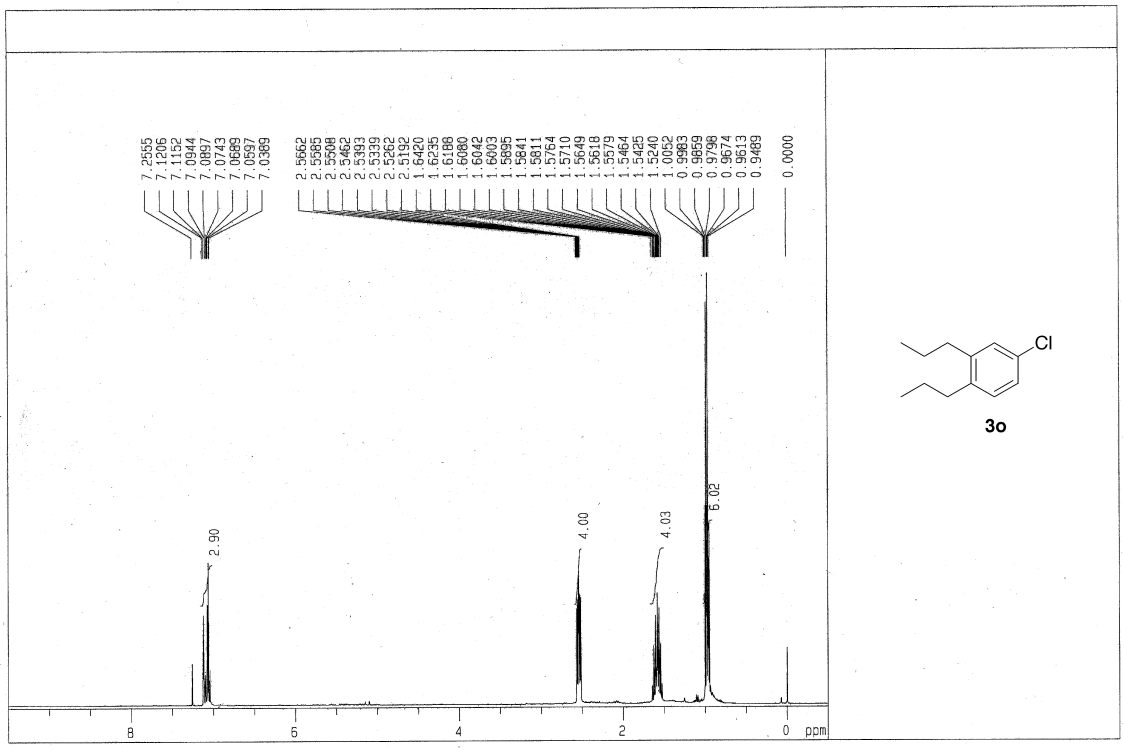

140.630
137.696
135.405
130.320
129.480
126.818
77.733
77.412
77.091
35.193
34.797
24.883
24.866
21.380
14.721
14.672
150
100
50
ppm
Me
3d

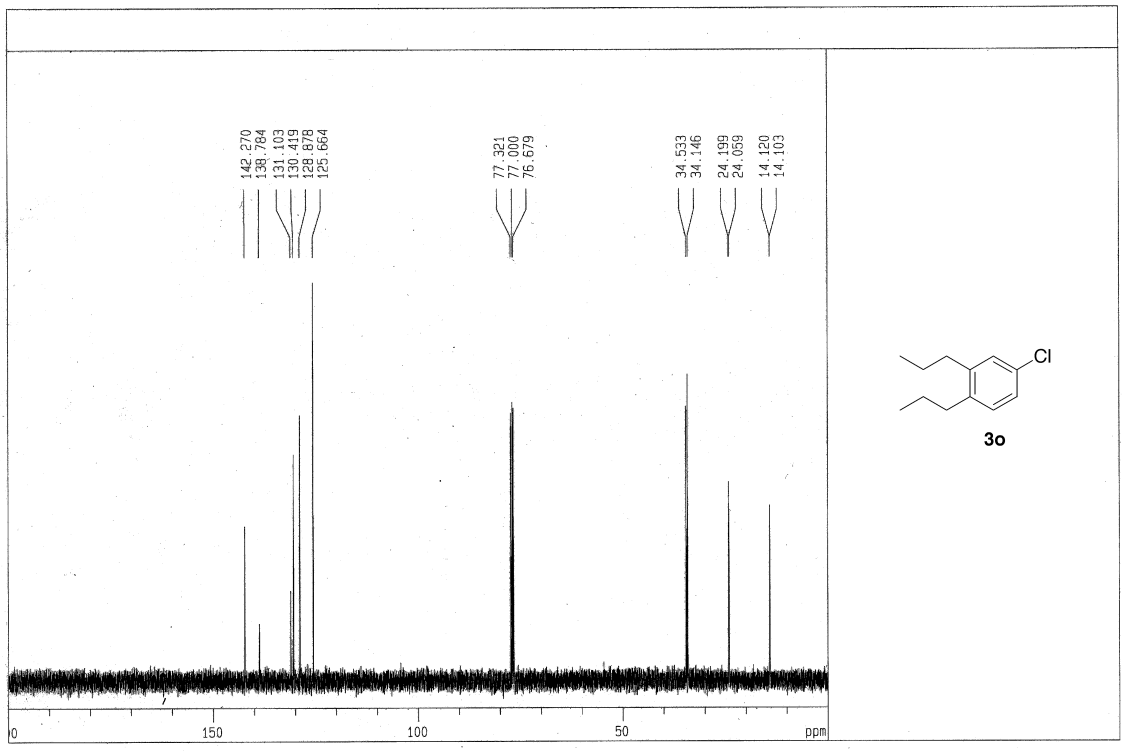

7.4091
7.3962
7.3920
7.3877
7.3761
7.3731
7.3419
7.3383
7.3236
7.3077
7.3041
7.2907
7.2870
7.2839
7.2583
7.1417
7.1271
7.1075
7.0850
3.4485
3.4302
3.4113
3.2653
2.8674
2.8485
2.8302
2.3804
1.5454
0.0000
5.06
3.01
2.00
3.00
1.99
3.07
8
6
4
2
0
ppm
MeO
Me
Ph
3g

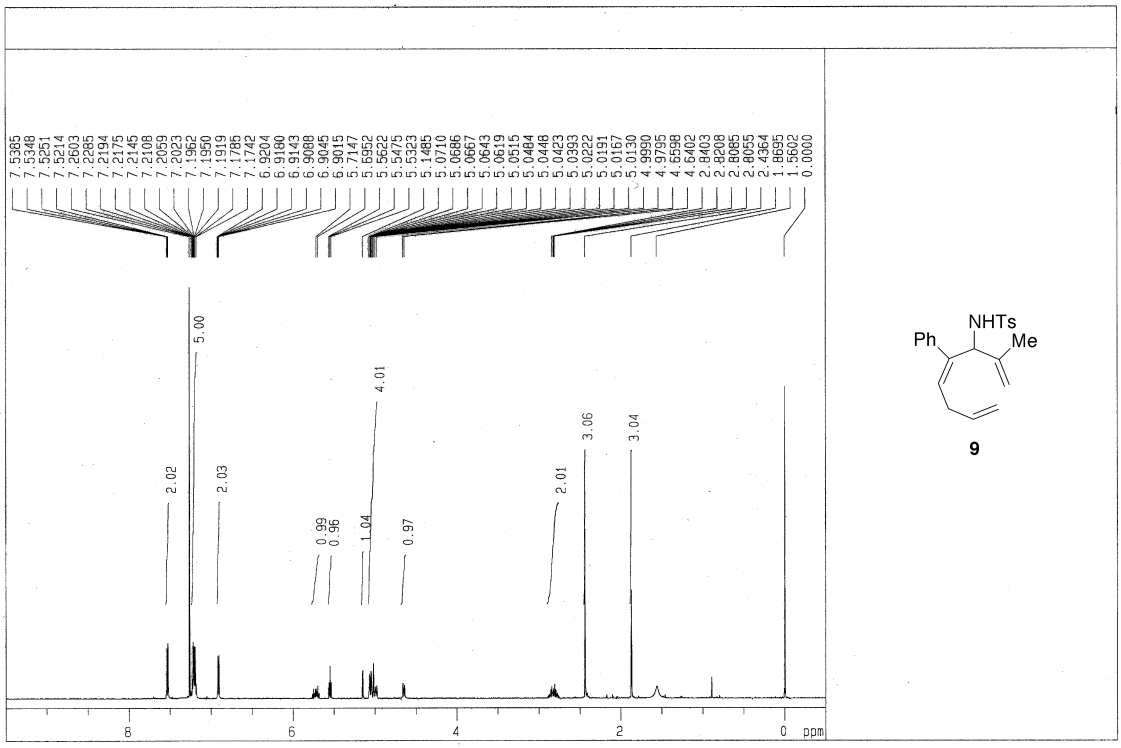

141.619
139.485
136.979
135.801
130.395
130.057
129.315
128.062
126.958
126.711
77.321
77.000
76.679
73.209
58.408
33.066
21.133
150
100
50
ppm
MeO
Me
Ph
3g

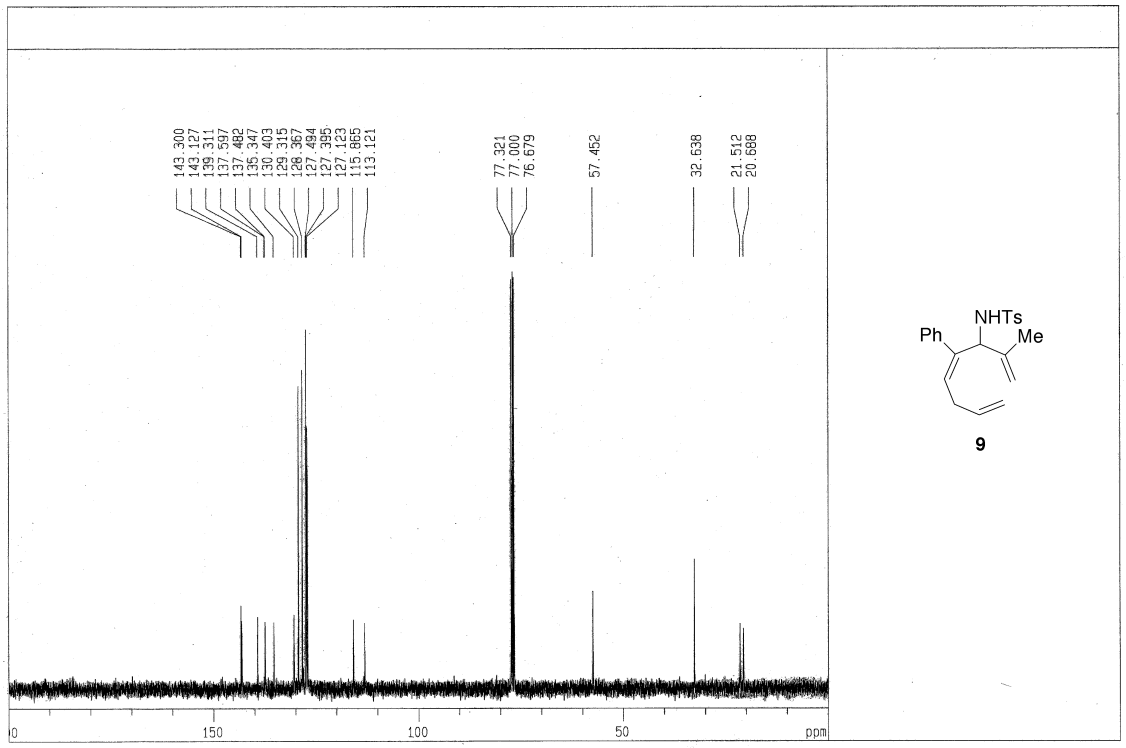

7.5923
7.5885
7.5831
7.5731
7.5708
7.5677
7.4783
7.4736
7.4705
7.4590
7.4544
7.4513
7.4459
7.4413
7.4366
7.4328
7.4294
7.4166
7.3965
7.3773
7.3649
7.3619
7.3588
7.3487
7.3434
7.3380
7.3249
7.2377
7.2169
7.2007
7.1977
4.3439
4.3251
4.3076
3.0187
3.0002
2.9825
2.0436
1.6196
0.0000
1.96
6.04
0.92
2.00
2.03
2.95
8
6
4
2
0 ppm
AcO
Ph
3l

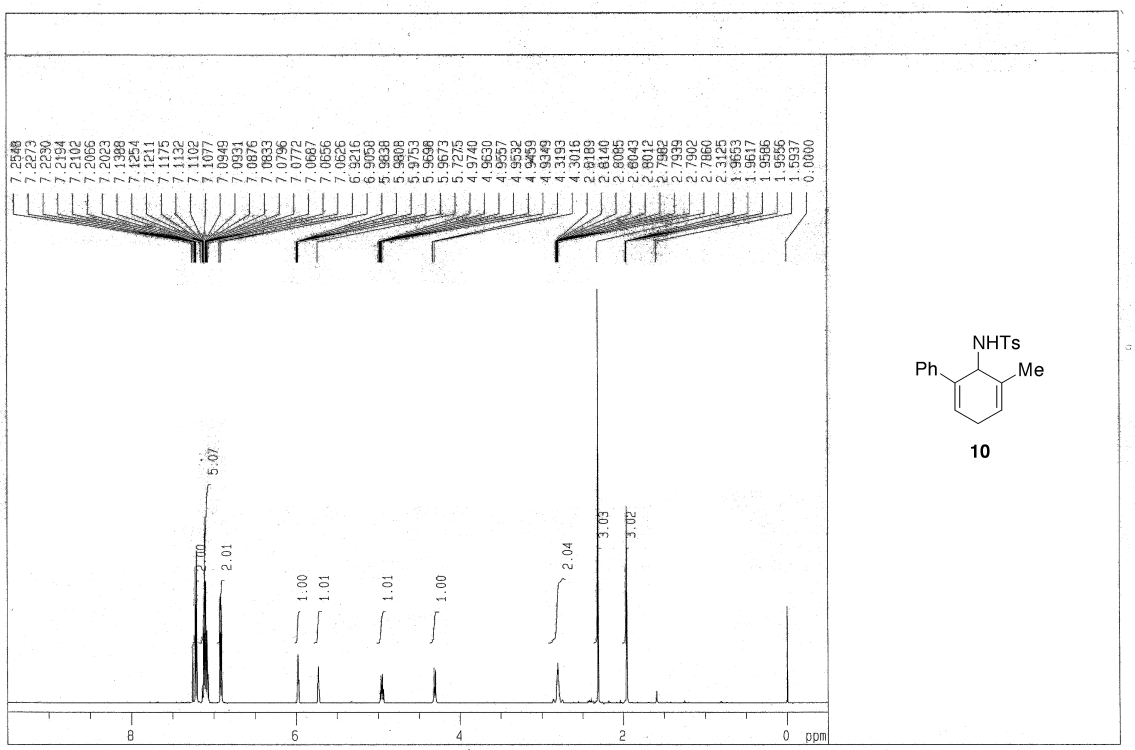

171.023
141.446
141.009
138.248
128.886
128.713
127.741
127.716
127.279
127.123
125.433
77.321
77.000
76.679
64.877
35.102
20.944
150
100
50
ppm
AcO
Ph
3l

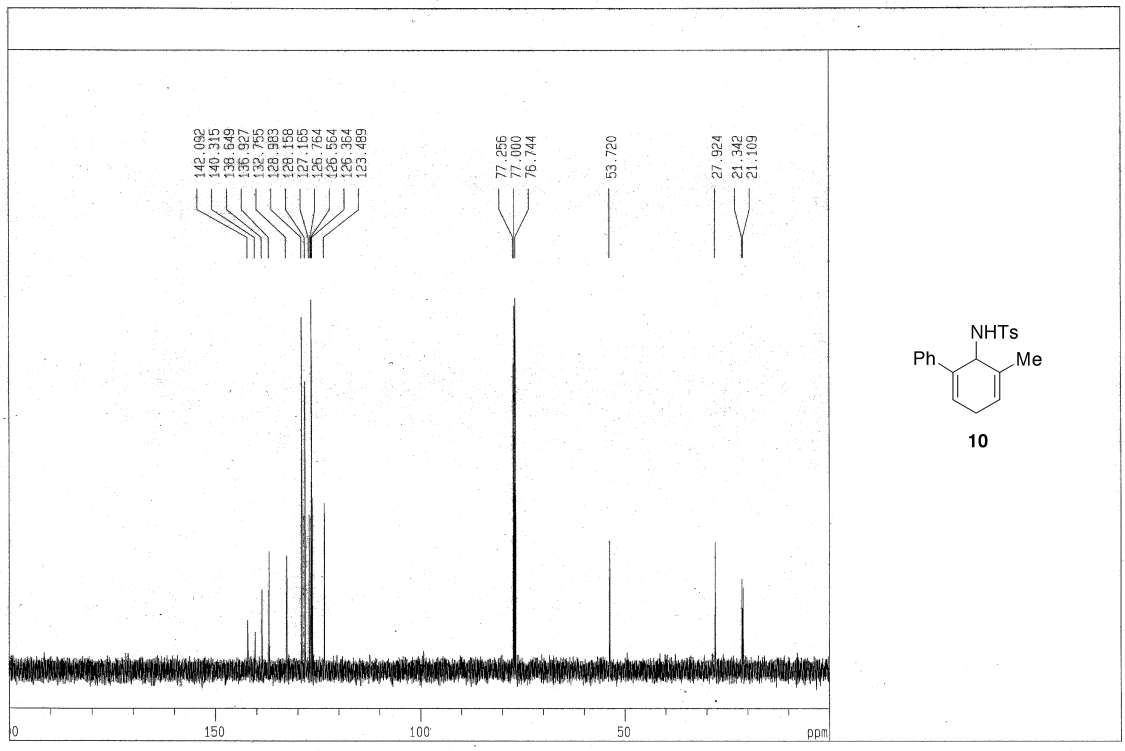

7.2555
7.1206
7.1152
7.0944
7.0897
7.0743
7.0689
7.0597
7.0389
2.5662
2.5585
2.5508
2.5462
2.5393
2.5339
2.5262
2.5192
1.6420
1.6235
1.6188
1.6080
1.6042
1.6003
1.5895
1.5841
1.5811
1.5764
1.5710
1.5649
1.5618
1.5579
1.5464
1.5425
1.5240
1.0052
0.9983
0.9859
0.9796
0.9674
0.9613
0.9489
0.0000
2.90
4.00
4.03
6.02
8
6
4
2
0
ppm
Cl
3o

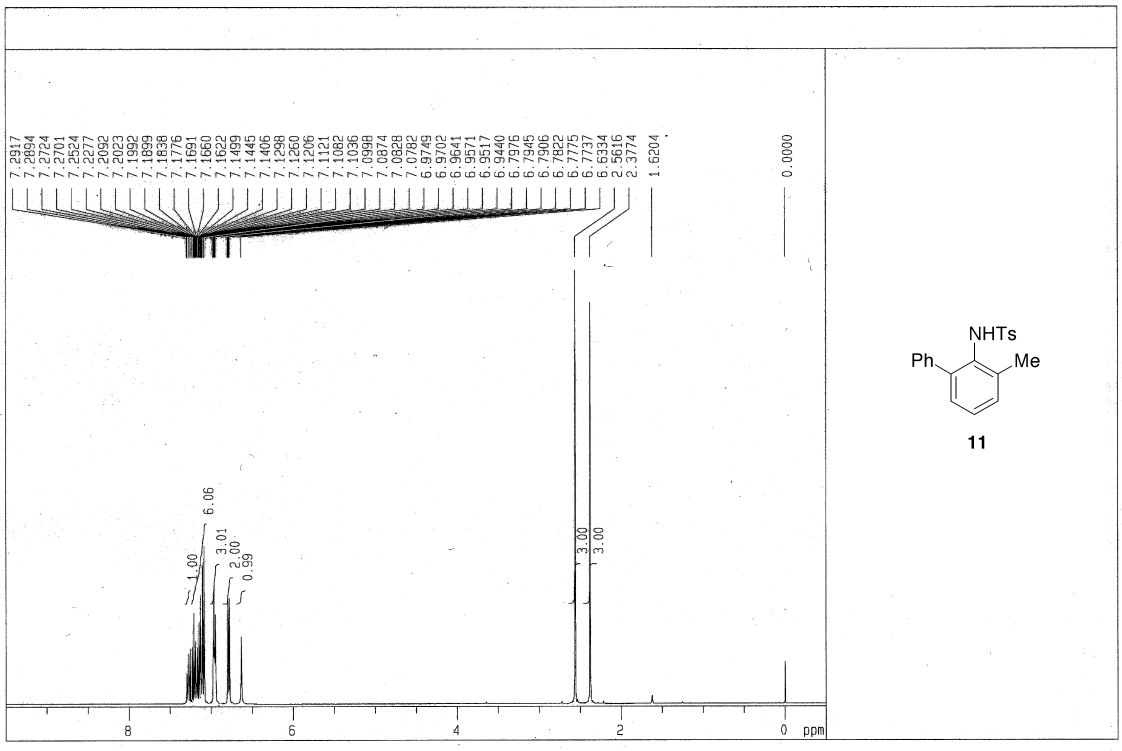

142.270
138.784
131.103
130.419
128.878
125.664
77.321
77.000
76.679
34.533
34.146
24.199
24.059
14.120
14.103
150
100
50
ppm
Cl
3o

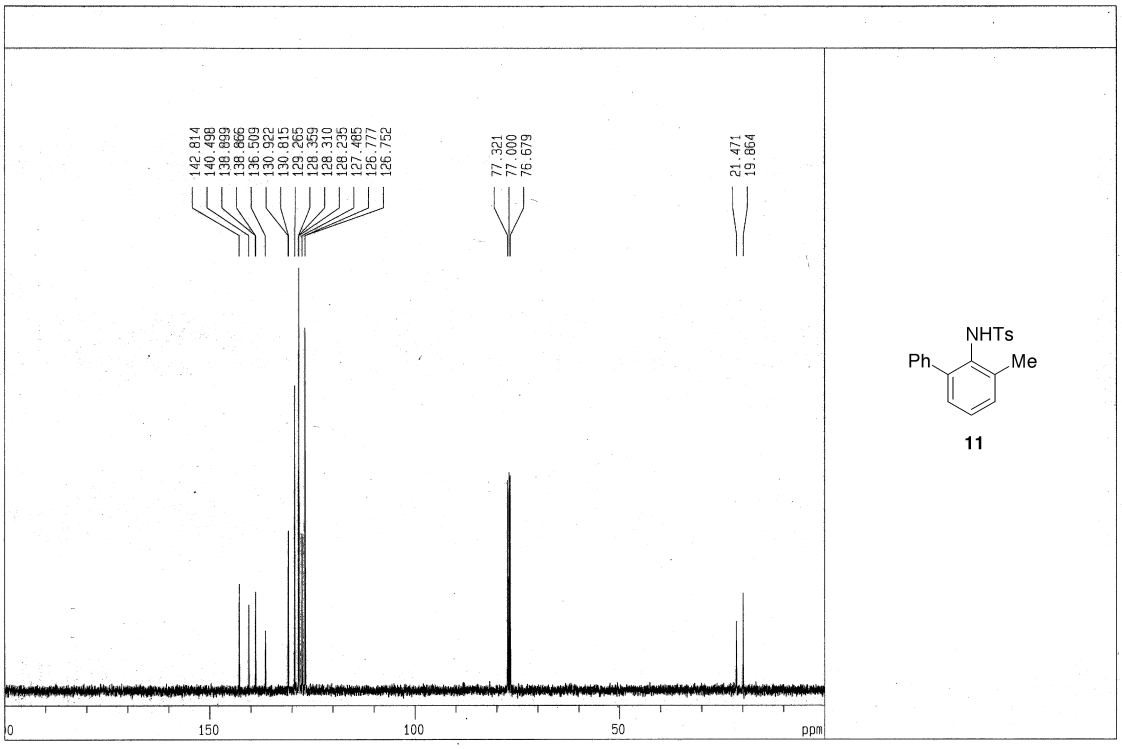

7.5365
7.5348
7.5251
7.5214
7.2603
7.2285
7.2194
7.2175
7.2145
7.2108
7.2059
7.2023
7.1962
7.1950
7.1919
7.1785
7.1742
6.9204
6.9180
6.9143
6.9088
6.9045
6.9015
5.7147
5.6952
5.5622
5.5475
5.5323
5.1485
5.0710
5.0686
5.0667
5.0643
5.0619
5.0515
5.0484
5.0448
5.0423
5.0393
5.0222
5.0191
5.0167
5.0130
4.9990
4.9795
4.6598
4.6402
2.8403
2.8208
2.8085
2.8055
2.4364
1.8695
1.5602
0.0000
5.00
4.01
3.06
3.04
2.02
2.03
2.01
0.99
0.96
1.04
0.97
8
6
4
2
0
ppm
NHTs
Ph
Me
9


143.300
143.127
139.311
137.597
137.482
135.347
130.403
129.315
128.367
127.494
127.395
127.123
115.865
113.121
77.321
77.000
76.679
57.452
32.638
21.512
20.888
150
100
50
ppm
NHTs
Ph
Me
9


NHTs
Ph
Me
10


NHTs
Ph
Me
10


7.2917
7.2894
7.2724
7.2701
7.2524
7.2277
7.2092
7.2023
7.1992
7.1899
7.1838
7.1776
7.1691
7.1660
7.1622
7.1499
7.1445
7.1406
7.1298
7.1260
7.1206
7.1121
7.1082
7.1036
7.0998
7.0874
7.0828
7.0782
6.9749
6.9702
6.9641
6.9571
6.9517
6.9440
6.7976
6.7945
6.7906
6.7822
6.7775
6.7737
6.6334
2.5616
2.3774
1.6204
0.0000
1.00
6.06
3.01
2.00
0.99
3.00
3.00
8
6
4
2
0
ppm
NHTs
Ph
Me
11


142.814
140.498
138.899
138.866
136.509
130.922
130.815
129.265
128.359
128.310
128.235
127.485
126.777
126.752
77.321
77.000
76.679
21.471
19.864
150
100
50
ppm
NHTs
Ph
Me
11