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Supporting Information

New Synthetic Approach for the Construction of Multi-Substituted 2-Acyl Furans via IBX-Mediated Cascade Oxidation/Cyclization of *cis*-2-En-4-yn-1-ols

Xiangwei Du, Haoyi Chen and Yuanhong Liu*

State Key Laboratory of Organometallic Chemistry

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,

354 Fenglin Lu, Shanghai 200032, People's Republic of China

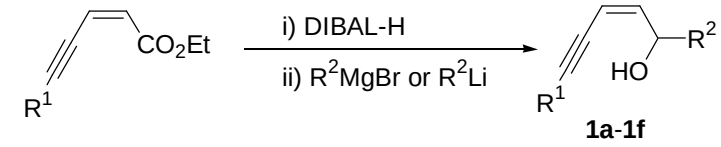
Contents:

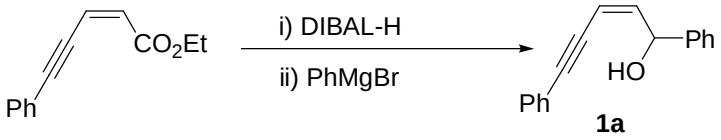
Experimental section

All reactions were carried out under nitrogen. DMSO was distilled from CaH_2. Unless noted, all commercial reagents were used without further purification. *cis*-Enynols **1a-q** were synthesized through multistep transformations by the modified procedures according to the published reports[1]. (*Z*)-Enynol **1r** was prepared by the published procedure.[2] IBX was prepared by the published reports.[3] IBA and DMP were purchased from Aldrich chemical company.

^1H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, and in $CDCl_3$ (containing 0.03% TMS) solutions. ^1H NMR spectra was recorded with tetramethylsilane (d= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (d = 77.00 ppm) as internal reference. Melting points were uncorrected. NMR yields were determined using dibromomethane as an internal standard. High-resolution mass spectra was obtained by using Waters Micromass GCT mass spectrometer. Single crystal X-ray diffraction data was collected in Bruker SMART APEX diffractiometers with molybdenum cathodes. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer.

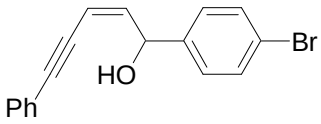
A typical procedure for the synthesis of (*Z*)-enynols 1a-1f and 6.[1a,b]



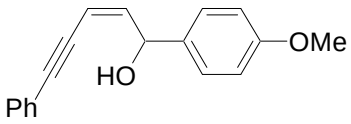


Synthesis of **1a.** To a solution of 5-phenyl-pent-2-en-4-ynoic acid ethyl ester (8.02 g, 40.0 mmol) in dry dichloromethane (200 mL) at -78 ^oC (internal temperature) was added dropwise of DIBAL (42 mL, 42 mmol, 1.0 M solution in toluene). The solution was stirred at -78 ^oC for 1.5 h, then quenched with 25 mL of 1 M HCl. The solution was diluted with 40 mL of ether and allowed to warm up to room temperature. The aqueous layer was extracted three times with ether. The combined organic layers were

washed successively with 1M HCl, water, and saturated sodium chloride solution, and then dried over sodium sulfate. Purification by chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 10:1) afforded the crude aldehyde, which was used directly for the next step without further purification. To a solution containing above aldehyde in THF at 0 ^{o}C was added 2.0 equiv phenylmagnesium bromide (prepared from 2 equiv of phenylbromide and magnesium turning). The mixture was stirred at room temperature until the reaction was complete as monitored by TLC. The reaction was quenched by saturated NH_4Cl solution and extracted with ether. The aqueous layer was extracted three times with ether. The combined organic layers were dried over Na_2SO_4. Purification by column chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 7:1) afforded **1a** in 54% yield (5.03 g) as a yellow solid. M.p. 43-45 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 3.00 (s, 1H), 5.74 (d, *J*= 10.5 Hz, 1H), 5.85 (d, *J*= 8.4 Hz, 1H), 6.06 (dd, *J*= 10.5 Hz, 8.4 Hz, 1H), 7.19-7.30 (m, 6H), 7.41-7.45 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 71.89, 85.36, 94.97, 109.59, 122.83, 125.74, 127.54, 128.28, 128.37, 128.43, 131.39, 142.31, 144.11; IR (neat) 3389, 3060, 2187, 1489, 1027, 754 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{14}O$ 234.1045, found 234.1043.

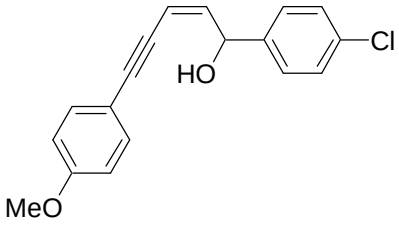


(*Z*)-1-(4-bromophenyl)-5-phenyl-pent-2-en-4-yn-1-ol (**1b**). Isolated yield: 34%. White solid. M.p. 89-90 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.49 (s, 1H), 5.82 (d, *J*= 10.8 Hz, 1H), 5.85 (d, *J*= 7.5 Hz, 1H), 6.05 (dd, *J*= 10.7 Hz, 8.6 Hz, 1H), 7.32-7.34 (m, 5H), 7.43-7.48 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 71.41, 85.04, 95.42, 110.35, 121.51, 122.68, 127.51, 128.41, 128.62, 131.47, 131.58, 141.24, 143.44; IR (neat) 3345, 3062, 2888, 1488, 1032, 825, 690 cm^{-1}; Anal. Calcd for $C_{17}H_{13}OBr$: C, 65.19, H, 4.18, Br, 25.51; Found C, 65.26, H, 4.27, Br, 25.85.

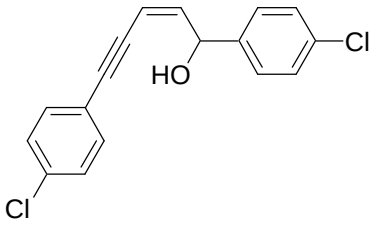


(*Z*)-1-(4-Methoxyphenyl)-5-phenyl-pent-2-en-4-yn-1-ol (**1c**). Isolated yield: 42%.

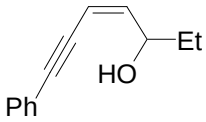
White solid. M.p. 69-70 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.17 (s, 1H), 3.80 (s, 3H), 5.80 (d, *J*= 11.4 Hz, 1H), 5.86 (dd, *J*= 8.7, 3.0 Hz, 1H), 6.15 (dd, *J*= 10.8, 8.4 Hz, 1H), 6.90 (d, *J*= 8.7 Hz, 2H), 7.33-7.48 (m, 7H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 55.13, 71.60, 85.35, 94.93, 109.26, 113.86, 122.89, 127.05, 128.30, 128.38, 131.40, 134.65, 144.39, 158.98; IR (neat) 3383, 2189, 1611, 1513, 1243, 1027, 836 cm^{-1}; Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79, H, 12.11; Found C, 81.56, H, 6.03.



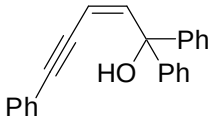
(*Z*)-1-(4-Chlorophenyl)-5-(4-methoxy-phenyl)-pent-2-en-4-yn-1-ol (**1d**). Isolated yield: 65%. Yellow solid. M.p. 68 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.50 (s, 1H), 3.81 (s, 3H), 5.81 (d, *J*= 10.5 Hz, 1H), 5.85 (dd, *J*= 8.9 Hz, 2.1 Hz, 1H), 6.02 (dd, *J*= 10.8 Hz, 8.4 Hz, 1H), 6.86 (d, *J*= 9.0 Hz, 2H), 7.29-7.41 (m, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 55.27, 71.37, 83.91, 95.52, 110.60, 114.06, 114.81, 127.18, 128.62, 132.98, 133.27, 140.90, 142.74, 159.82; IR (neat) 3190, 2189, 1598, 1508, 1293, 1033, 831 cm^{-1}; Anal. Calcd for $C_{18}H_{15}O_2Cl$: C, 72.36, H, 5.06, Cl, 11.87; Found C, 72.31, H, 5.19, Cl, 11.76.



(*Z*)-1,5-Bis(4-chlorophenyl)-pent-2-en-4-yn-1-ol (**1e**). Isolated yield: 66%. Yellow solid. M.p. 58 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.45 (d, *J*= 3.0 Hz, 1H), 5.81 (d, *J*= 10.2 Hz, 1H), 5.83 (dd, *J*= 7.7 Hz, 2.4 Hz, 1H), 6.08 (dd, *J*= 11.0 Hz, 8.6 Hz, 1H), 7.28-7.40 (m, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 71.39, 85.94, 94.20, 110.10, 121.16, 127.15, 128.69, 128.77, 132.67, 133.44, 134.67, 140.59, 143.89 ; IR (neat) 3193, 2195, 1587, 1487, 1090, 825 cm^{-1}; Anal. Calcd for $C_{17}H_{12}OCl_2$: C, 67.35, H, 3.99, Cl, 23.39; Found C, 67.21, H, 4.35, Cl, 23.00.

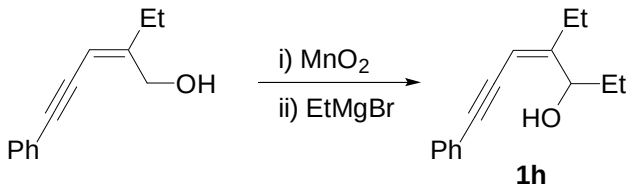


(Z)-7-Phenyl-hept-4-en-6-yn-3-ol (**1f**). This compound was prepared by Sonogashira coupling of corresponding 1*Z*-1-iodo-pent-1-en-3-ol with terminal alkyne. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.98 (t, *J*= 7.5 Hz, 3H), 1.55-1.76 (m, 2H), 2.25 (s, 1H), 4.69 (q, *J*= 7.5 Hz, 1H), 5.77 (d, *J*= 10.5 Hz, 1H), 5.94 (dd, *J*= 10.8 Hz, 8.1 Hz, 1H), 7.29-7.33 (m, 3H), 7.40-7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 9.51, 29.58, 71.48, 85.30, 94.59, 109.97, 122.97, 128.29, 128.33, 131.34, 145.06; IR (neat) 3446, 3061, 2969, 2195, 1649, 1490, 694 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{14}O$ 186.1045, found 186.1050.



(*Z*)-1,1,5-Triphenyl-pent-2-en-4-yn-1-ol (**6**). Isolated yield: 62%. Brown solid, M.p. 64 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 4.09 (s, 1H), 6.00 (d, *J*= 11.4 Hz, 1H), 6.63 (d, *J*= 11.7 Hz, 1H), 7.24-7.48 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 80.03, 85.23, 98.34, 108.76, 122.34, 126.69, 127.25, 128.18, 128.24, 128.66, 131.38, 146.11, 148.18; IR (neat) 3575, 3051, 2193, 1596, 1489, 999, 759 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{18}O$: 310.1358, found 310.1353.

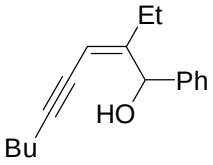
A typical procedure for the synthesis of (*Z*)-enynols 1g-1k.[1b]



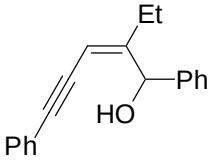
1h

Synthesis of 1h. To a solution of (*Z*)-2-ethyl-5-phenyl-pent-2-en-4-yn-1-ol (86.5 mg, 0.45 mmol) in dichloromethane was added MnO_2 (885 mg, 9 mmol, or 40~50 equiv MnO_2). After stirring at room temperature for 10 h, the solution was filtered and

concentrated. Then 2 mL THF was added at 0 ^{o}C followed by adding 2.0 equiv ethylmagnesium bromide. The mixture was stirred at room temperature until the reaction was complete as monitored by TLC. Purification by column chromatography on silica gel afforded **1h** as a yellow oil in 61% overall yield (60.3 mg). **(*Z*)-4-Ethyl-7-phenyl-hept-4-en-6-yn-3-ol** (**1h**). ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.98 (t, *J* = 7.4 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H), 1.61-1.77 (m, 2H), 2.09 (bs, 1H), 2.11-2.32 (m, 2H), 4.84 (t, *J*= 7.1 Hz, 1H), 5.58 (s, 1H), 7.29-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 10.26, 12.33, 23.14, 28.43, 74.34, 86.23, 94.11, 104.33, 123.53, 127.94, 128.27, 131.14, 158.64; IR (neat) 3418, 3092, 2965, 2195, 1489, 1490, 1012, 755 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{18}O$ 214.1358, found 214.1351.

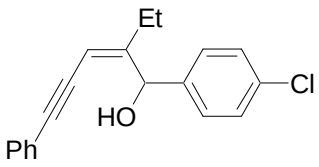


(Z)-2-Ethyl-1-phenyl-non-2-en-4-yn-1-ol (**1g**). Isolated yield: 60%. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.89-0.98 (m, 6H), 1.39-1.59 (m, 4H), 1.85-1.94 (m, 1H), 2.14-2.23 (m, 1H), 2.34-2.40 (m, 3H), 5.43-5.46 (m, 1H), 6.06 (d, *J*= 4.2 Hz, 1H), 7.22-7.36 (m, 3H), 7.44-7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 12.15, 13.56, 19.25, 21.98, 22.56, 30.84, 73.64, 95.08, 105.57, 125.41, 127.04, 128.12, 142.20, 155.83; IR (neat) 3476, 3061, 2961, 2191, 1602, 1450, 1025, 700 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{22}O$ 242.1671, found 242.1667.

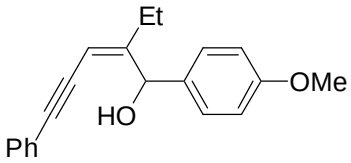


(*Z*)-2-Ethyl-1,5-diphenyl-pent-2-en-4-yn-1-ol (**1i**). Isolated yield: 68%. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.96 (t, *J*= 7.5 Hz, 3H), 1.92-2.01 (m, 1H), 2.24-2.32 (m, 1H), 2.50 (s, 1H), 5.66 (s, 1H), 6.21 (s, 1H), 7.21-7.34 (m, 6H), 7.40-7.51 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 12.05, 22.44, 73.58, 86.55, 93.82, 105.02, 123.35, 125.35, 127.13, 128.05, 128.19, 128.28, 131.28, 141.97, 157.88; IR (neat) 3444, 3060, 2966, 1595,

1490, 1037, 755 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{18}O$: 262.1358, found 262.1364.

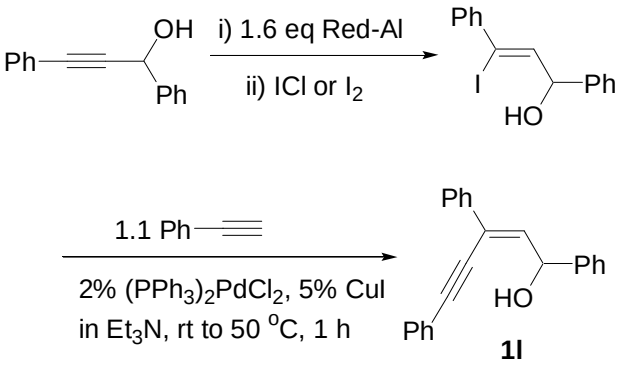


(*Z*)-1-(4-Chlorophenyl)-2-ethyl-5-phenyl-pent-2-en-4-yn-1-ol (**1j).** Isolated yield: 72%. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.98 (t, *J*= 7.2 Hz, 3H), 1.90-1.99 (m, 1H), 2.21-2.23 (m, 1H), 2.32 (d, *J*= 3.9 Hz, 1H), 5.68 (t, *J*= 1.5 Hz, 1H), 6.18 (d, *J*= 3.9 Hz, 1H), 7.28-7.36 (m, 5H), 7.42-7.45 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 12.11, 22.41, 73.04, 86.24, 94.11, 105.50, 123.18, 126.81, 128.24, 128.38, 131.31, 132.88, 140.38, 157.34; IR (neat) 3449, 3080, 2967, 2195, 1489, 1091, 755 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{17}OCl$: 296.0968, found 296.0970.



(*Z*)-2-Ethyl-1-(4-methoxyphenyl)-5-phenyl-pent-2-en-4-yn-1-ol (**1k**). Isolated yield: 73%. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.99 (t, *J*= 7.5 Hz, 3H), 1.96-2.05 (m, 1H), 2.25-2.33 (m, 1H), 2.30 (d, *J*= 3.9 Hz, 1H), 3.79 (s, 3H), 5.65 (t, *J*= 1.5 Hz, 1H), 6.14 (d, *J*= 3.9 Hz, 1H), 6.86-6.89 (m, 2H), 7.29-7.33 (m, 3H), 7.39-7.45 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 12.17, 22.62, 55.21, 73.45, 86.57, 93.91, 104.73, 113.62, 123.43, 126.63, 128.07, 128.33, 131.30, 134.20, 158.20, 158.76; IR (neat) 3467, 3031, 2965, 2187, 1610, 1509, 1034, 756 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{20}O_2$: 292.1463, found 292.1473.

A typical procedure for the synthesis of enynols 1l-1q.[1c-e]



1l

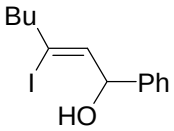
1) Synthesis of (*Z*)-3-iodo-1,3-diphenylprop-2-en-1-ol

Under a nitrogen atmosphere, to a solution of 1,3-diphenylprop-2-yn-1-ol (3.12 g, 15 mmol) in dry THF (40 ml) was add Red-Al (7.2 ml, 24 mmol, 65% w/w in toluene) at 0 ^{o}C, then the mixture was warmed to room temperature and stirred for 3 h. A solution of ICl in THF (30 ml, 30 mmol, 1.0 M in THF) was added dropwise at -78 ^{o}C. Then the mixture was warmed up to room temperature and stirred for 1 h and then 50 ^{o}C for additional 1h. The mixture was treated with an aqueous solution of potassium sodium tartrate (10 g in 100 ml H_2O), and extracted with ethyl acetate (3 x 40 ml). The extract was washed with saturated $Na_2S_2O_3$, brine, dried over anhydrous $MgSO_4$ and evaporated. Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded **(Z)-3-iodo-1,3-diphenylprop-2-en-1-ol** in 67% yield (3.38 g). ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.36 (d, *J*= 2.1 Hz, 1H), 5.60 (dd, *J*= 7.7, 3.2 Hz, 1H), 6.19 (d, *J*= 8.1 Hz, 1H), 7.24-7.53 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 78.78, 105.54, 126.08, 127.74, 128.06, 128.48, 128.52, 128.56, 139.43, 141.57, 141.98; HRMS (EI) calcd for $C_{15}H_{13}OI$: 336.0011, found 336.0025.

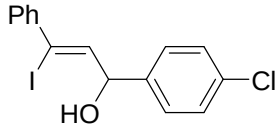
2) Synthesis of compound (*Z*)-1,3,5-triphenylpent-2-en-4-yn-1-ol

To a solution of (*Z*)-3-iodo-1,3-diphenylprop-2-en-1-ol (168 mg, 0.5 mmol) in Et_3N (5 ml) was added ethynylbenzene (60.3 uL, 0.55 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol) and CuI (4.8 mg, 0.025 mmol) at room temperature. Then the mixture was warmed up to 50 ^{o}C and stirred for 1 h. The mixture was filtrated, and the filtrate was evaporated to remove Et_3N under reduce pressure. The residue was extracted with ethyl acetate (3 x 40 ml), washed with brine, dried over anhydrous $MgSO_4$ and

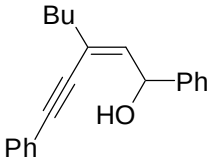
evaporated. Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded (*Z*)-1,3,5-triphenylpent-2-en-4-yn-1-ol in 97% yield (150 mg) as a liquid. **(Z)-1,3,5-Triphenyl-pent-2-en-4-yn-1-ol** (**1l**). ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.24 (d, *J*= 3.6 Hz, 1H), 6.10 (dd, *J*= 8.7, 3.0 Hz, 1H), 6.59 (d, *J*= 8.7 Hz, 1H), 7.27-7.41 (m, 9H), 7.54-7.58 (m, 4H), 7.68-7.71 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 72.92, 85.89, 96.44, 122.72, 123.93, 125.85, 126.24, 127.59, 128.18, 128.33, 128.37, 128.51, 128.58, 131.53, 136.91, 138.24, 142.49. The spectroscopic data is in agreement with that previously reported.[1f]



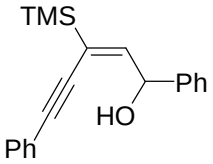
3-Iodo-1-phenyl-hept-2-en-1-ol. Isolated yield: 77%. The structure was further comfirmed by HMBC and NOESY spectra. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.89 (t, *J*= 7.1 Hz, 3H), 1.22-1.34 (m, 2H), 1.45-1.55 (m, 2H), 2.48 (t, *J*= 7.5 Hz, 2H), 2.57 (bs, 1H), 5.41 (d, *J*= 7.8 Hz, 1H), 5.76 (d, *J*= 7.2 Hz, 1H), 7.22-7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 13.81, 21.32, 31.21, 45.03, 78.24, 110.86, 125.88, 127.64, 128.45, 136.35, 142.03; HRMS (EI) calcd for $C_{13}H_{17}OI$: 316.0324, found 316.0327.



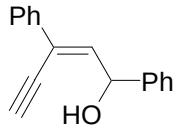
(Z)-1-(4-chlorophenyl)-3-iodo-3-phenylprop-2-en-1-ol. Isolated yield: 73%. ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.69 (d, *J*= 3.3 Hz, 1H), 5.55 (dd, *J*= 8.0, 3.5 Hz, 1H), 6.11 (d, *J*= 8.1 Hz, 1H), 7.23-7.33 (m, 5H), 7.41-7.44 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 78.35, 106.28, 127.51, 128.27, 128.56, 128.77, 128.91, 133.64, 139.05, 140.04, 141.97; IR (neat) 3381, 3038, 2896, 1595, 1489, 1013, 758 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{12}OClI$: 369.9621, found 369.9626.



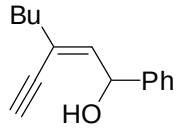
(*Z*)-3-Butyl-1,5-diphenyl-pent-2-en-4-yn-1-ol (**1m**). Isolated yield: 80%. Yellow solid. M.p. 49-50 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.91 (t, *J*= 7.2 Hz, 3H), 1.30-1.38 (m, 2H), 1.53-1.63 (m, 2H), 2.23 (t, *J*= 7.7 Hz, 2H), 2.35 (bs, 1H), 5.86 (d, *J*= 8.7 Hz, 1H), 5.90 (d, *J*= 8.7 Hz, 1H), 7.21-7.38 (m, 6H), 7.46-7.48 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 13.88, 22.03, 30.31, 36.67, 72.57, 87.18, 94.72, 123.07, 124.95, 125.70, 127.40, 128.31, 128.43, 131.50, 138.31, 143.01; IR (neat) 3286, 3032, 2952, 1489, 1018, 760 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{22}O$: 290.1671, found 290.1670.



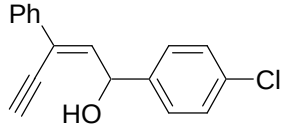
(*E*)-1,5-Diphenyl-3-(trimethylsilyl)pent-2-en-4-yn-1-ol (**1n**). Isolated yield: 51%. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.20 (s, 9H), 2.46 (d, *J*= 1.8 Hz, 1H), 5.92 (dd, *J*= 8.0, 2.0 Hz, 1H), 6.27 (d, *J*= 7.8 Hz, 1H), 7.28-7.37 (m, 6H), 7.42-7.49 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) d -2.11, 73.46, 87.75, 99.09, 123.74, 125.77, 125.87, 127.49, 128.06, 128.29, 128.48, 131.38, 142.54, 150.04; IR (neat) 3394, 3062, 2957, 1489, 1249, 1037, 842 , 698 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{22}OSi$: 306.1440, found 306.1453.



(*E*)-1,3-Diphenyl-pent-2-en-4-yn-1-ol (**1o**). Isolated yield: 54% (two steps of Sonagashira coupling/desilylation). ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.71 (d, *J*= 3.0 Hz, 1H), 3.39 (s, 1H), 5.96 (dd, *J*= 8.7, 2.7 Hz, 1H), 6.55 (d, *J*= 9.0 Hz, 1H), 7.22-7.35 (m, 6H), 7.45-7.48 (d, *J*= 7.5 Hz, 2H), 7.56-7.59 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 72.63, 80.08, 84.56, 123.06, 125.81, 126.18, 127.68, 128.30, 128.35, 128.53, 136.41, 139.81, 142.31; IR (neat) 3289, 3030, 2098, 1493, 1020, 697 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{14}O$: 234.1045, found 234.1050.



(*Z*)- 3-Butyl-1-phenyl-pent-2-en-4-yn-1-ol (**1p**). Isolated yield: 50% (two steps of Sonagashira coupling/desilylation). ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.86 (t, *J*= 7.2 Hz, 3H), 1.23-1.35 (m, 2H), 1.45-1.55 (m, 2H), 2.13 (t, *J*= 7.5 Hz, 2H), 2.54 (d, *J*= 3.3 Hz, 1H), 3.19 (s, 1H), 5.74 (dd, *J*= 9.0, 2.7Hz, 1H), 5.88 (d, *J*= 8.7 Hz, 1H), 7.19-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 13.79, 21.94, 30.01, 36.44, 72.19, 81.48, 82.56, 123.82, 125.63, 127.40, 128.37, 139.91, 142.80; IR (neat) 3293, 3030, 2930, 2093, 1602, 1451, 1014, 759 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{18}O$: 214.1358, found 214.1361.

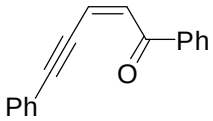


(*E*)-1-(4-Chlorophenyl)-3-phenyl-pent-2-en-4-yn-1-ol (**1q**). Isolated yield: 66% (two steps of Sonagashira coupling/desilylation). Brown solid, M.p. 64-66 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.68 (d, *J*= 7.2 Hz, 1H), 3.43 (d, *J*= 0.6 Hz, 1H), 5.94 (d, *J*= 8.7 Hz, 1H), 6.50 (d, *J*= 9.0 Hz, 1H), 7.28-7.42 (m, 7H), 7.56-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 72.03, 79.91, 84.84, 123.49, 126.17, 127.18, 128.43, 128.51, 128.66, 133.37, 136.18, 139.19, 140.68; IR (neat) 3279, 1594, 1494, 1088, 1012, 825, 649 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{13}OCl$: 268.0655, found 268.0666.

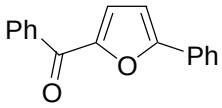
A typical procedure for IBX-mediated oxidation of (*Z*)-1,5-Diphenyl-pent-2-en-4-yn-1-ol (**1a**): To a solution of (Z)-enynol **1a** (150 mg, 0.64 mmol) in 1.83 mL DMSO was added 2.0 equiv IBX (358 mg, 1.28 mmol). The resulting solution was stirred at room temperature for 45 minutes. After the reaction, the precipitate of IBA was removed by filtration and the filtrate was extracted with ether and washed with water. The aqueous phase was extracted with ether for three times. The combined organic layers were dried over anhydrous Na_2SO_4, and

concentrated in vacuo. The crude product was purified by chromatography on silica gel to afford the **(*Z*)-1,5-diphenyl-pent-2-en-4-yn-1-one 2a** in 81% yield.

A typical procedure for IBX-mediated cyclization of (*Z*)-3-butyl-1,5-diphenyl-pent-2-en-4-yn-1-ol (**1m**): To a solution of (Z)-enynol **1m** (102 mg, 0.35 mmol) in 1.0 mL DMSO was added 3.0 equiv IBX (296 mg, 1.05 mmol). The resulting solution was stirred at 90 ^{o}C until the reaction was complete as monitored by thin-layer chromatography. After the reaction, the precipitate of IBA was removed by filtration and the filtrate was extracted with ether and washed with water. The aqueous phase was extracted with ether for three times. The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by chromatography on silica gel to afford the 2-acyl furan derivative **(3-butyl-5-phenyl-furan-2-yl)-phenyl-methanone (3m)** in 70% yield.

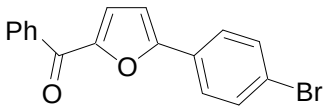


(*Z*)-1,5-Diphenyl-pent-2-en-4-yn-1-one (**2a**). Column chromatography on silica gel (petroleum ether / ethyl acetate =18:1) afforded the title product in 81% isolated yield as a pale yellow solid. M.p. 57-60 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 6.44 (d, *J*= 12.0 Hz, 1H), 7.07 (d, *J*= 12.0 Hz, 1H), 7.29-7.56 (m, 8H), 7.96-7.99 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 87.58, 100.73, 121.38, 122.44, 128.22, 128.52, 128.55, 129.12, 132.12, 132.64, 132.91, 137.66, 189.81; IR (neat) 3062, 2186, 1658, 1229, 968, 753 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{12}O$: 232.0888, found 232.0898.

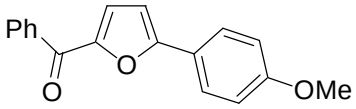


Phenyl(5-phenyl-furan-2-yl)methanone (**3a**). Column chromatography on silica gel (petroleum ether / ethyl acetate =18:1) afforded the title product in 79% isolated yield as a yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 6.83 (d, *J*= 4.2 Hz, 1H), 7.31 (d, *J*= 3.6 Hz, 1H), 7.37-7.60 (m, 6H), 7.80-7.84 (m, 2H), 7.99-8.02 (m, 2H); ^{13}C NMR ($CDCl_3$,

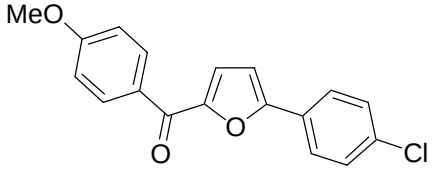
Me_4Si) d 107.36, 122.82, 124.97, 128.29, 128.78, 129.12, 129.18, 132.28, 137.44, 151.25, 158.26, 181.97. The spectroscopic data is in agreement with that previously reported.[5]



(5-(4-Bromophenyl)furan-2-yl)(phenyl)methanone (**3b**). Column chromatography on silica gel (petroleum ether / ethyl acetate =7:1) afforded the title product in 64% isolated yield as a yellow solid. M.p. 119-121 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 6.82 (d, *J*= 3.6 Hz, 1H), 7.28 (d, *J*= 3.6 Hz, 1H), 7.48-7.68 (m, 7H), 7.97 (d, *J*= 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 107.80, 122.81, 123.36, 126.43, 128.09, 128.39, 129.12, 132.04, 132.44, 137.34, 151.39, 157.12, 182.05; IR (neat) 1634, 1468, 1321, 1072, 985, 697 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{11}O_2Br$: 325.9942, found 325.9928.

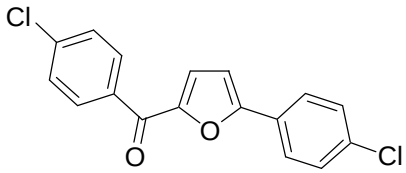


(5-(4-Methoxyphenyl)-furan-2-yl)(phenyl)methanone (**3c**). Column chromatography on silica gel (petroleum ether / ethyl acetate =6:1) afforded the title product in 72% isolated yield as a yellow solid. M.p. 85-86 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 3.83 (s, 3H), 6.69 (d, *J*= 3.9 Hz, 1H), 6.95 (d, *J*= 8.7 Hz, 2H), 7.27 (d, *J*= 3.9 Hz, 1H), 7.47-7.61 (m, 3H), 7.75 (d, *J*= 8.7 Hz, 2H), 7.97 (d, *J*= 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 55.24, 105.99, 114.20, 121.94, 123.49, 126.62, 128.27, 129.04, 132.15, 137.61, 150.66, 158.68, 160.39, 181.88; IR (neat) 3068, 2966, 1599, 1477, 1255, 837 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{14}O_3$: 278.0943, found 278.0940.

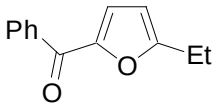


[5-(4-Chloro-phenyl)-furan-2-yl]-(4-methoxy-phenyl)-methanone (**3d**). Column

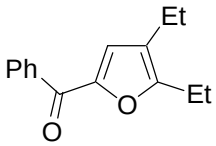
chromatography on silica gel (petroleum ether / ethyl acetate =7:1) afforded the title product in 67% isolated yield as a pale yellow solid. M.p. 123 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 3.89 (s, 3H), 6.80 (d, *J*= 3.6 Hz, 1H), 7.00 (d, *J*= 9.0 Hz, 2H), 7.28 (d, *J*= 3.6 Hz, 1H), 7.39 (d, *J*= 8.7 Hz, 2H), 7.72 (d, *J*= 8.7 Hz, 2H), 8.04 (d, *J*= 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 55.41, 107.61, 113.66, 121.86, 126.10, 127.83, 129.07, 129.87, 131.54, 134.85, 151.75, 156.53, 163.15, 180.63; IR (neat) 1633, 1473, 1309, 1039, 987, 802 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{13}O_3Cl$: 312.0553, found 312.0560.



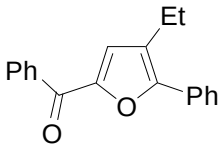
(4-Chloro-phenyl)-[5-(4-chloro-phenyl)-furan-2-yl]-methanone (**3e**). Column chromatography on silica gel (petroleum ether / ethyl acetate =12:1) afforded the title product in 86% isolated yield as a pale yellow solid. M.p. 160 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 6.84 (d, *J*= 3.9 Hz, 1H), 7.33 (d, *J*= 4.2 Hz, 1H), 7.43 (d, *J*= 8.7 Hz, 2H), 7.51 (d, *J*= 8.4 Hz, 2H), 7.74 (d, *J*= 8.4 Hz, 2H), 7.97 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 107.83, 122.76, 126.21, 127.55, 128.71, 129.16, 130.58, 135.22, 135.54, 138.84, 151.21, 157.25, 180.52; IR (neat) 1638, 1470, 1312, 1097, 987, 803 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{10}O_2Cl_2$: 316.0058, found 316.0064.



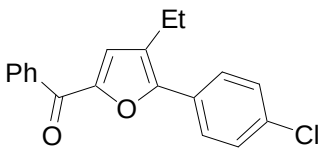
(5-Ethyl-furan-2-yl)(phenyl)methanone (**3f**). Column chromatography on silica gel (petroleum ether / ethyl acetate =12:1) afforded the title product in 60% isolated yield as a brown liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 1.31 (t, *J*= 7.5 Hz, 3H), 2.79 (q, *J*= 7.5 Hz, 2H), 6.22 (d, *J*= 3.6 Hz, 1H), 7.12 (d, *J*= 3.3 Hz, 1H), 7.44-7.56 (m, 3H), 7.90-7.92 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 11.62, 21.66, 107.36, 122.67, 128.18, 128.92, 132.05, 137.57, 150.57, 164.02, 182.12; IR (neat) 3064, 2977, 1779, 1642, 1509, 1321, 881 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}O_2$: 200.0837, found 200.0831.



(4,5-Diethyl-furan-2-yl)(phenyl)methanone (**3h**). Column chromatography on silica gel (petroleum ether / ethyl acetate =10:1) afforded the title product in 41% isolated yield as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 1.17 (t, *J*= 7.7 Hz, 3H), 1.29 (t, *J*= 7.5 Hz, 3H), 2.42 (q, *J*= 7.7 Hz, 2H), 2.73 (q, *J*= 7.5 Hz, 2H), 7.06 (s, 1H), 7.45-7.56 (m, 3H), 7.90-7.93 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 12.71, 14.86, 17.65, 19.89, 123.45, 123.72, 128.24, 129.04, 131.96, 137.90, 149.72, 159.05, 182.06; IR (neat) 3062, 2972, 1768, 1510, 884, 714 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}O_2$: 228.1150, found 228.1154.

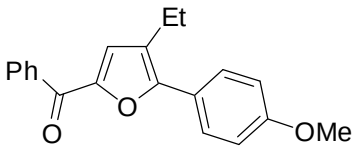


(4-Ethyl-5-phenyl-furan-2-yl)(phenyl)methanone (**3i**). Column chromatography on silica gel (petroleum ether / ethyl acetate =15:1) afforded the title product in 68% isolated yield as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 1.29 (t, *J*= 7.5 Hz, 3H), 2.75 (q, *J*= 7.5 Hz, 2H), 7.26 (s, 1H), 7.34-7.60 (m, 6H), 7.73-7.76 (m, 2H), 8.00-8.04 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 14.11, 19.04, 123.75, 125.71, 126.51, 128.30, 128.54, 128.67, 129.20, 130.21, 132.21, 137.57, 150.08, 153.02, 182.05; IR (neat) 3062, 2970, 1782, 1481, 1209, 693 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{16}O_2$: 276.1150, found 276.1157.

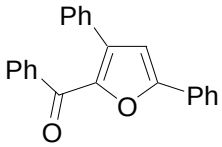


(5-(4-Chlorophenyl)-4-ethyl-furan-2-yl)(phenyl)methanone (**3j**). Column chromatography on silica gel (petroleum ether / ethyl acetate =12:1) afforded the title product in 85% isolated yield as a yellow solid. M.p. 75 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d

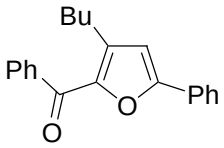
1.28 (t, *J*= 7.4 Hz, 3H), 2.71 (q, *J*= 7.5 Hz, 2H), 7.22 (s, 1H), 7.38-7.68 (m, 7H), 7.96-7.80 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 13.92, 19.02, 123.65, 125.97, 127.57, 128.28, 128.60, 128.86, 129.09, 132.26, 134.34, 137.39, 150.01, 151.71, 181.93; IR (neat) 2967, 1638, 1476, 1323, 892, 732 cm^{-1}; Anal. Calcd for $C_{19}H_{15}O_2Cl$: C, 73.43, H, 4.86, Cl, 11.41; Found C, 73.30, H, 5.11, Cl, 11.16.



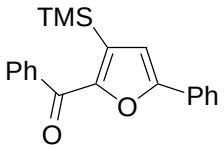
[4-Ethyl-5-(4-methoxy-phenyl)-furan-2-yl]-phenyl-methanone (**3k**). Column chromatography on silica gel (petroleum ether / ethyl acetate =9:1) afforded the title product in 81% isolated yield as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 1.27 (t, *J*= 7.4 Hz, 3H), 2.70 (q, *J*= 7.4 Hz, 2H), 3.82 (s, 3H), 6.95 (d, *J* = 9.0 Hz, 2H), 7.23 (s, 1H), 7.46-7.59 (m, 3H), 7.68 (d, *J*= 8.7 Hz, 2H), 7.97-8.00 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 14.04, 18.97, 55.17, 114.06, 122.87, 124.11, 124.33, 127.96, 128.22, 129.06, 132.02, 137.70, 149.50, 153.35, 159.76, 181.79; IR (neat) 3061, 2967, 1637, 1484, 1254, 834 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{18}O_3$: 306.1256, found 306.1270.



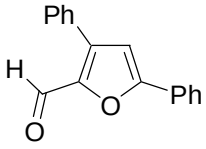
(3,5-Diphenyl-furan-2-yl)-phenyl-methanone (**3l**). Column chromatography on silica gel (petroleum ether / ethyl acetate =20:1) afforded the title product in 50% isolated yield as a yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 6.96 (s, 1H), 7.31-7.54 (m, 9H), 7.58-7.63 (m, 2H), 7.75-7.78 (m, 2H), 7.93-7.98 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 109.76, 124.91, 128.00, 128.09, 128.34, 128.91, 129.14, 129.20, 129.66, 129.83, 132.12, 134.83, 137.60, 137.95, 145.82, 155.91, 183.36. The spectroscopic data is in agreement with that previously reported.[6]



(3-Butyl-5-phenyl-furan-2-yl)-phenyl-methanone (**3m**). Column chromatography on silica gel (petroleum ether / ethyl acetate =18:1) afforded the title product in 70% isolated yield as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.96 (t, *J*= 7.4 Hz, 3H), 1.41-1.48 (m, 2H), 1.63-1.71 (m, 2H), 2.96 (t, *J*= 7.7 Hz, 2H), 6.77 (s, 1H), 7.32-7.42 (m, 3H), 7.47-7.56 (m, 3H), 7.69-7.72 (m, 2H), 8.06-8.09 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 13.90, 22.51, 26.08, 31.59, 109.73, 124.76, 128.09, 128.81, 128.92, 129.41, 129.48, 131.89, 138.24, 140.50, 147.18, 155.54, 183.21; IR (neat) 3064, 2957, 1637, 1476, 1291, 907, 691 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{20}O_2$: 304.1463, found 304.1459.

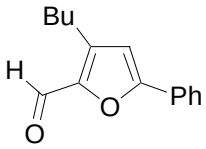


Phenyl-(5-phenyl-3-trimethylsilyl-furan-2-yl)-methanone (**3n**). Column chromatography on silica gel (petroleum ether / ethyl acetate =30:1) afforded title product in 70% isolated yield as a yellow solid. M.p. 79-81 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.40 (s, 9H), 6.88 (s, 1H), 7.31-7.42 (m, 3H), 7.51-7.56 (m, 3H), 7.71-7.74 (m, 2H), 8.14-8.17 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d -1.40, 0.86, 113.38, 124.82, 128.19, 128.80, 128.86, 129.47, 129.80, 132.19, 134.15, 137.51, 155.67, 156.46, 182.47; IR (neat) 3067, 2959, 1635, 1468, 1267, 1060, 842 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{20}O_2Si$: 320.1233, found 320.1234.

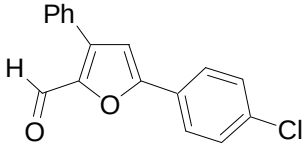


3,5-Diphenyl-furan-2-carbaldehyde (**3o**). Column chromatography on silica gel (petroleum ether / ethyl acetate =8:1) afforded the title product in 78% isolated yield as a yellow solid. M.p. 100-101 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 6.93 (s, 1H), 7.38-7.59 (m, 8H), 7.82-7.86 (m, 2H), 9.70 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 108.44, 125.30,

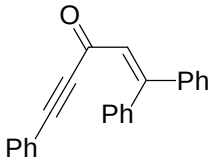
128.55, 128.81, 128.84, 129.13, 129.74, 130.44, 140.90, 146.55, 158.25, 177.09; IR (neat) 2836, 1667, 1450, 1252, 928, 763 cm^{-1}; Anal. calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87; Found C, 82.39, H, 5.07.



3-Butyl-5-phenyl-furan-2-carbaldehyde (**3p**). Column chromatography on silica gel (petroleum ether / ethyl acetate =20:1) afforded the title product in 76% isolated yield as a red liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.95 (t, *J*= 7.2 Hz, 3H), 1.34-1.47 (m, 2H), 1.60-1.70 (m, 2H), 2.81 (t, *J*= 7.7 Hz, 2H), 6.72 (s, 1H), 7.34-7.45 (m, 3H), 7.76-7.81 (m, 2H), 9.75 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 13.71, 22.18, 24.43, 32.00, 109.19, 125.10, 128.76, 128.91, 129.42, 141.19 (br), 147.57, 158.13, 176.88 (br); IR (neat) 2957, 1672, 1452, 1259, 931, 765 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}O_2$: 228.1150, found 228.1145.

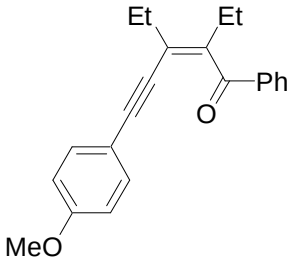


5-(4-Chloro-phenyl)-3-phenyl-furan-2-carbaldehyde (**3q**). Column chromatography on silica gel (petroleum ether / ethyl acetate =10:1) afforded the title product in 40% isolated yield as a yellow solid. M.p. 103-105 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 6.93 (s, 1H), 7.40-7.60 (m, 7H), 7.78 (d, *J*= 8.7 Hz, 2H), 9.71 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 108.79, 126.58, 127.13, 128.88, 128.94, 129.19, 129.31, 130.30, 135.76, 140.92, 146.73, 157.11, 177.17; IR (neat) 2835, 1659, 1477, 1091, 927, 827 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{11}O_2Cl$: 282.0448, found 282.0455.

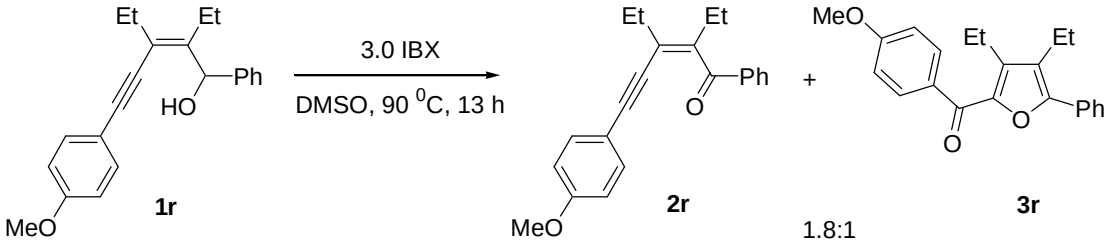


1,1,5-Triphenylpent-1-en-4-yn-3-one (**7**). Column chromatography on silica gel

(petroleum ether / ethyl acetate =8:1) afforded the title product in 23% isolated yield as a pale yellow solid. M.p. 134-137 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 6.75 (s, 1H), 7.14 (d, *J*= 7.5 Hz, 2H), 7.24 (t, *J*= 7.5 Hz, 2H), 7.32-7.42 (m, 11H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 88.73, 92.29, 120.19, 127.70, 128.10, 128.19, 128.48, 128.82, 129.34, 130.06, 130.12, 130.77, 133.04, 138.21, 140.69, 157.79, 177.69; IR (neat) 2200, 1602, 1488, 1301, 1185, 759 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{16}O$: 308.1201, found 308.1188.



(*Z*)-2,3-Diethyl-5-(4-methoxyphenyl)-1-phenylpent-2-en-4-yn-1-one (2r). The title compound was prepared by the reaction with 2 equiv. IBX in DMSO at room temperature for 1 h. Column chromatography on silica gel (petroleum ether / ethyl acetate =30:1) afforded the title product in 87% isolated yield as a pale yellow solid. M.p. 60-62 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 1.09 (t, *J*= 7.7 Hz, 3H), 1.25 (t, *J*= 7.5 Hz, 3H), 2.41 (q, *J*= 7.6 Hz, 2H), 2.54 (q, *J*= 7.5 Hz, 2H), 3.71 (s, 3H), 6.64 (d, *J*= 9.0 Hz, 2H), 6.76 (d, *J*= 8.7 Hz, 2H), 7.43-7.56 (m, 3H), 7.98 (d, *J*= 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 13.18, 23.68, 25.42, 55.09, 87.64, 96.49, 113.50, 114.98, 125.64, 128.34, 129.56, 132.53, 132.73, 137.55, 145.76, 159.32, 199.83; HRMS (EI) calcd for $C_{22}H_{22}O_2$: 318.1620, found 318.1634.



(3,4-Diethyl-5-phenylfuran-2-yl)(4-methoxyphenyl)methanone (3r). Column chromatography on silica gel (petroleum ether / ethyl acetate =20:1) afforded the products as a mixture of **2r** and **3r** in a ratio of 1.8:1 in 72% combined yield as a pale

yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) for **3r**: d 1.28 (m, 6H), 2.71 (q, *J*= 7.6 Hz, 2H), 2.54 (q, *J*= 7.5 Hz, 2H), 3.86 (s, 3H), 6.98 (d, *J*= 8.7 Hz, 2H), 7.31-7.36 (m, 1H), 7.44 (d, *J*= 7.5 Hz, 2H), 7.68-7.71 (m, 2H), 8.13-8.17 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) for **3r**: d 14.47, 14.73, 16.83, 17.84, 55.29, 113.34, 125.69, 126.17, 128.18, 128.74, 130.69, 130.97, 131.87, 140.54, 146.74, 150.68, 162.61, 181.64; HRMS (EI) calcd for $C_{22}H_{22}O_3$: 334.1569, found 334.1577.

Reference:

[1] a) R. Takeuchi, K. Tanabe, S. Tanaka, *J. Org. Chem.* **2000**, *65*, 1558; b) Y. Zhang, J. W. Herndon, *Org. Lett.* **2003**, *5*, 2043; c) J. A. Marshall, B. A. Dehoff, *J. Org. Chem.* **1986**, *51*, 863; d) K. D. Kim, P. A. Magriotis, *Tetrahedron Lett.* **1990**, *43*, 6137; e) D. L. Romero, E. L. Fritzen, *Tetrahedron Lett.* **1997**, *38*, 8659; f) S. Wang, Y. Tu, P. Chen, X. Hu, F. Zhang, A. Wang, *J. Org. Chem.* **2006**, *71*, 4343.

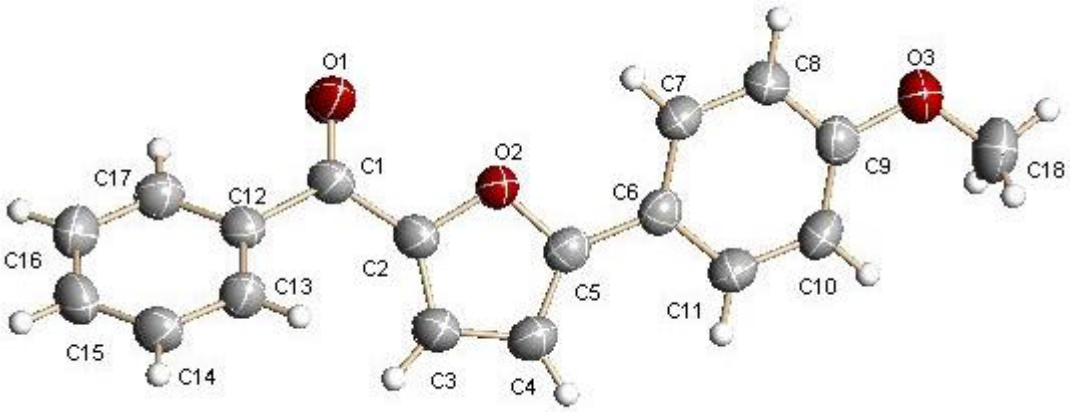
[2] S. Guo, H. Zhang, F. Song and Y. Liu, *Tetrahedron* **2007**, *63*, 2009.

[3] a) M. Frigerio, M. Santagostino, S. Sputore, *J. Org. Chem.* **1999**, *64*, 4537; b) D. B. Dess, J. C. Martin, *J. Org. Chem.* **1983**, *48*, 4155.

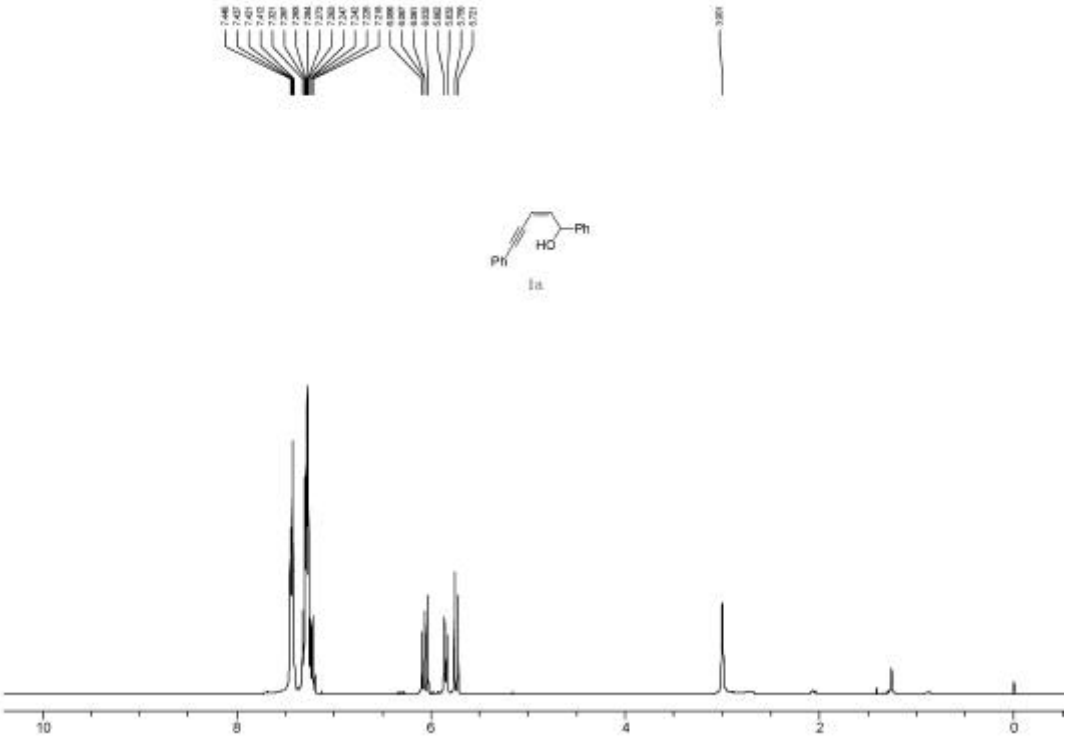
[4] S. Wang, Y. Tu, P. Chen, X. Hu, F. Zhang, A. Wang, *J. Org. Chem.* **2006**, *71*, 4343.

[5] J. Guillard, C. Lamazzi, O. Meth-Cohn, C. W. Rees, A. J. P. White, D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 1304.

[6] I. Francesconi, A. Patel, D. W. Boykin, *Synthesis* **1999**, 61.



X-ray single-crystal structure of **3c**.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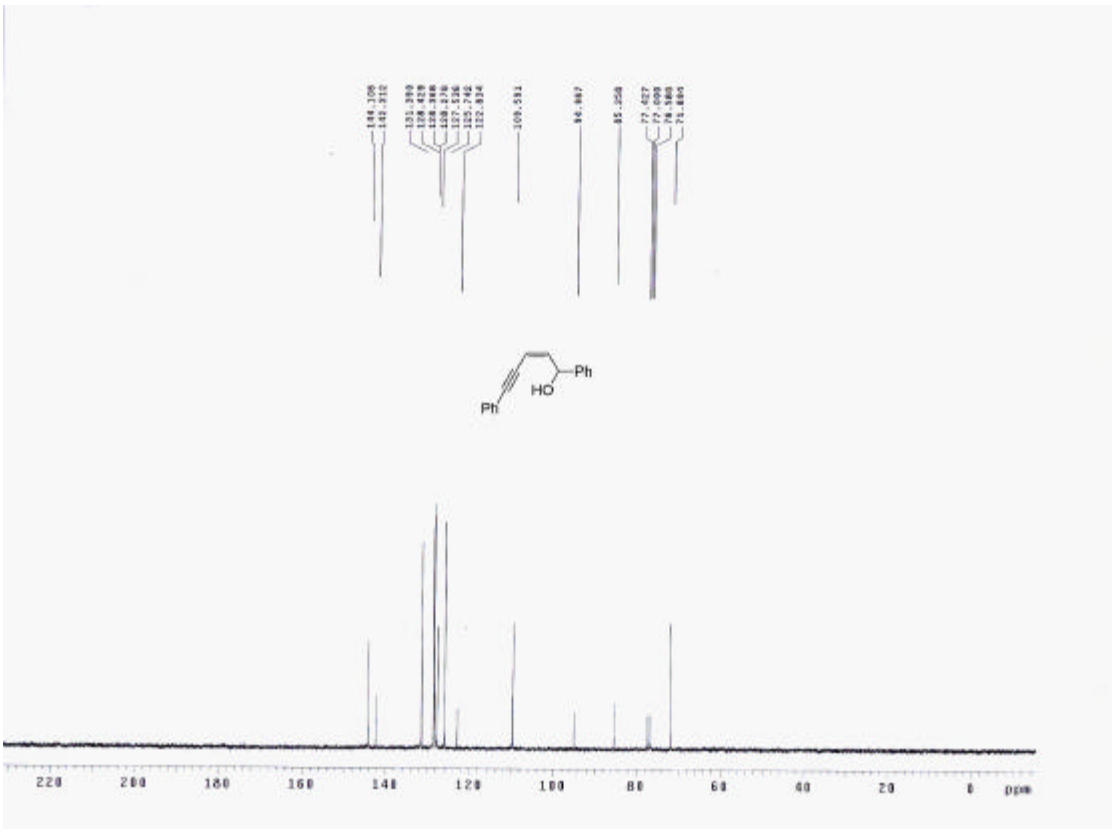
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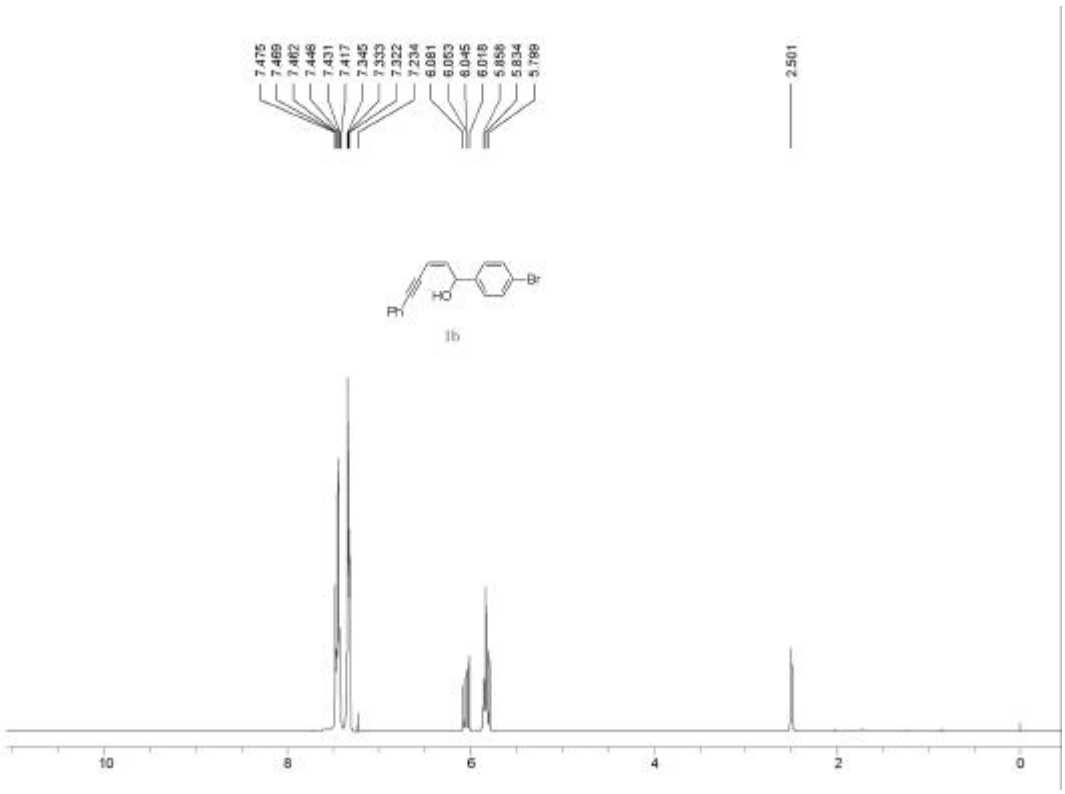
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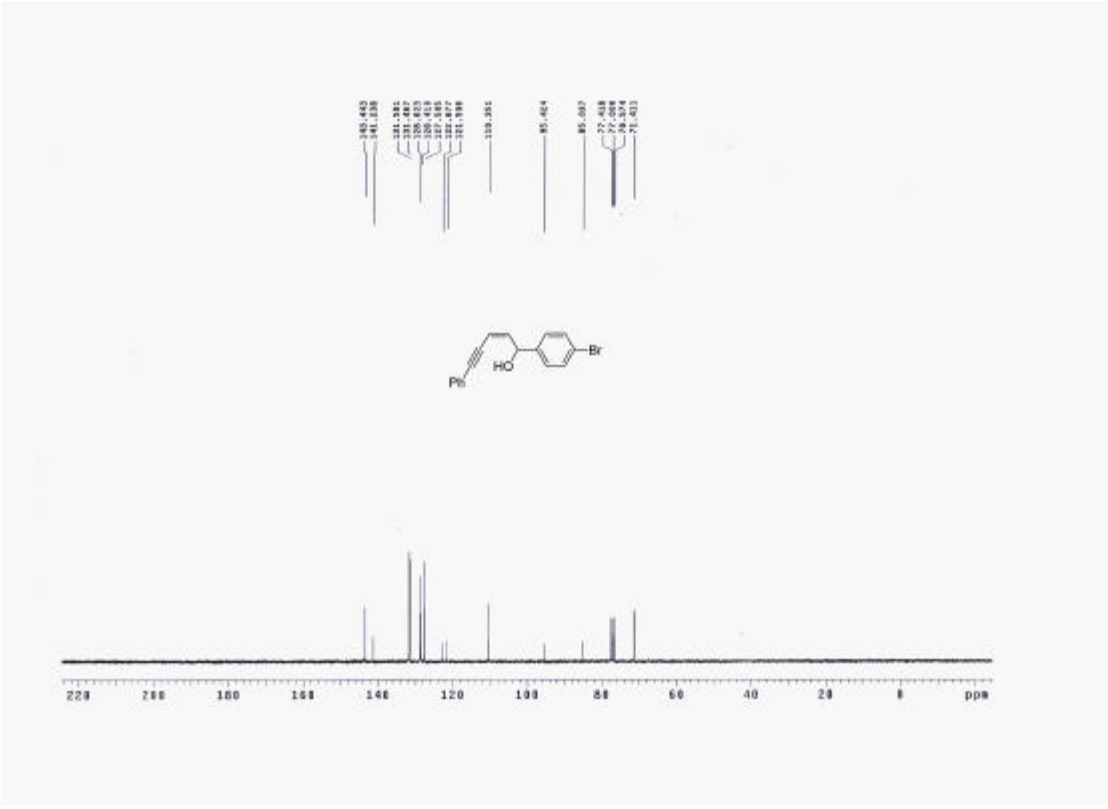
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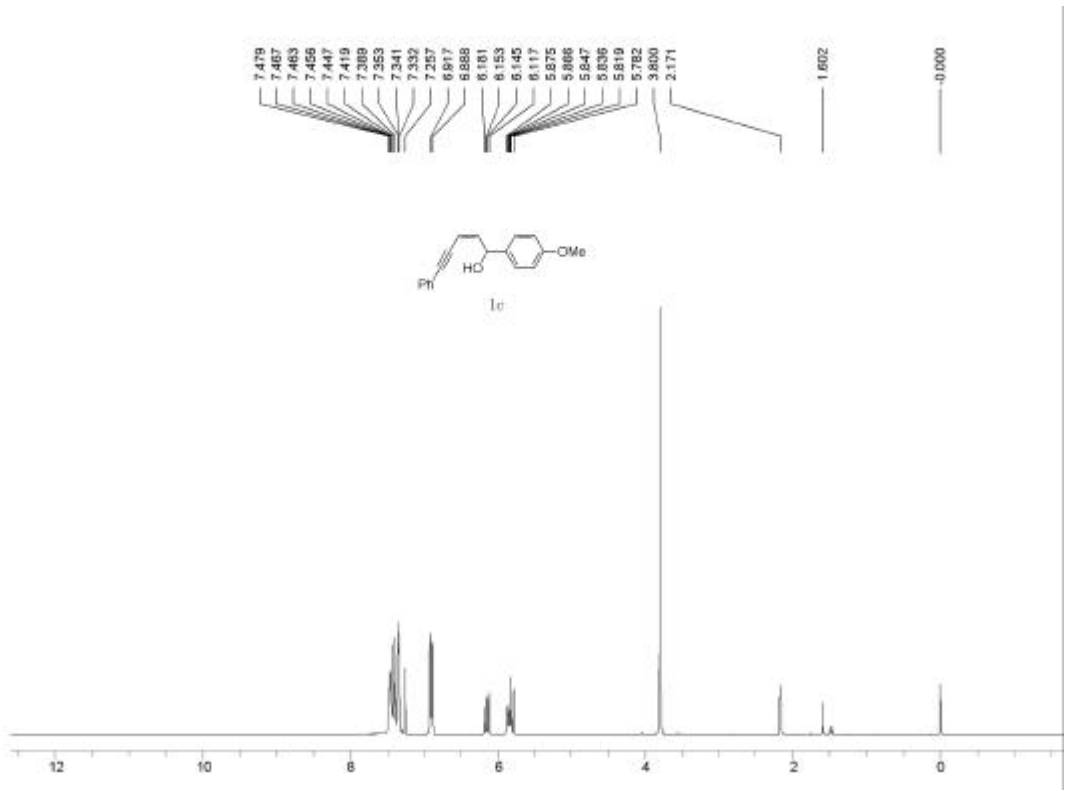
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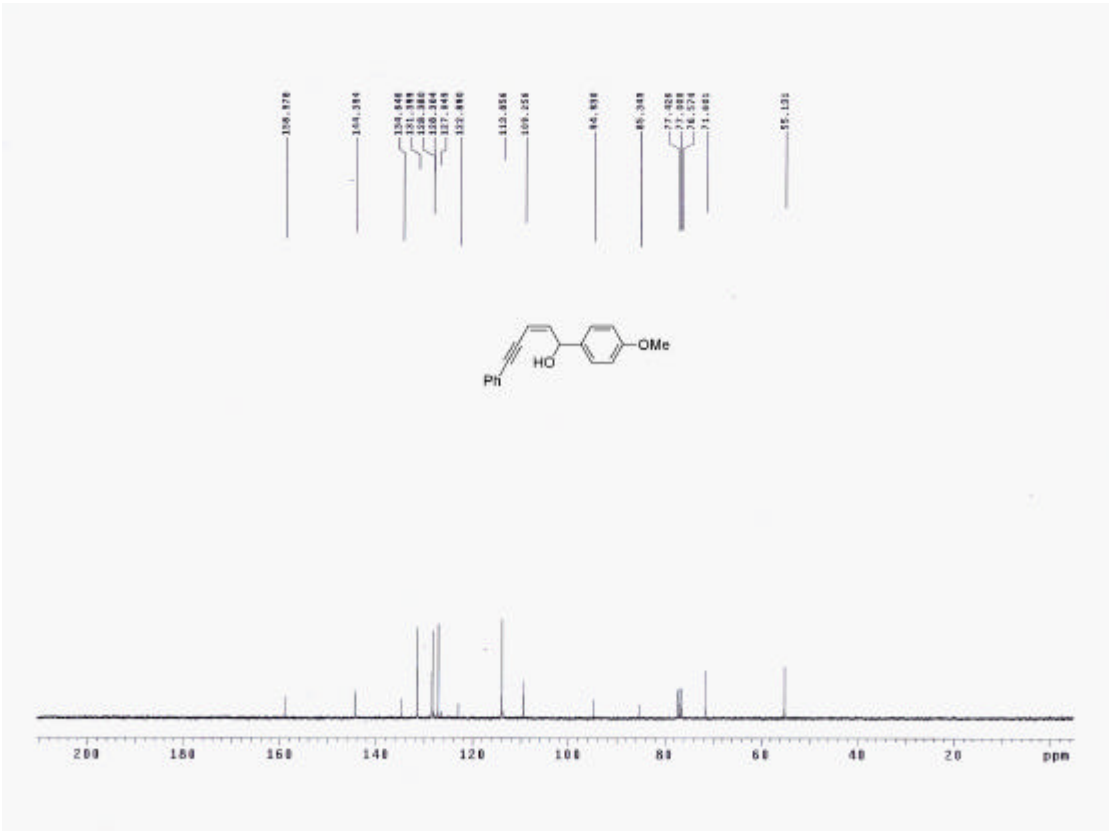
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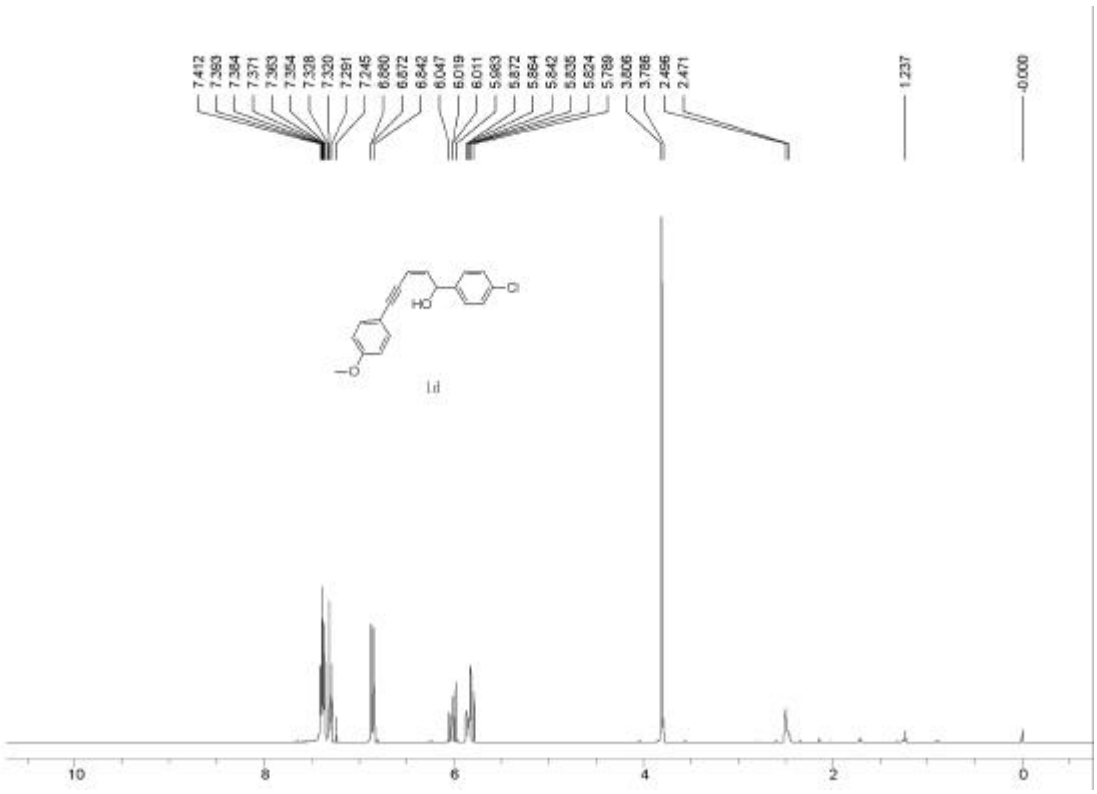
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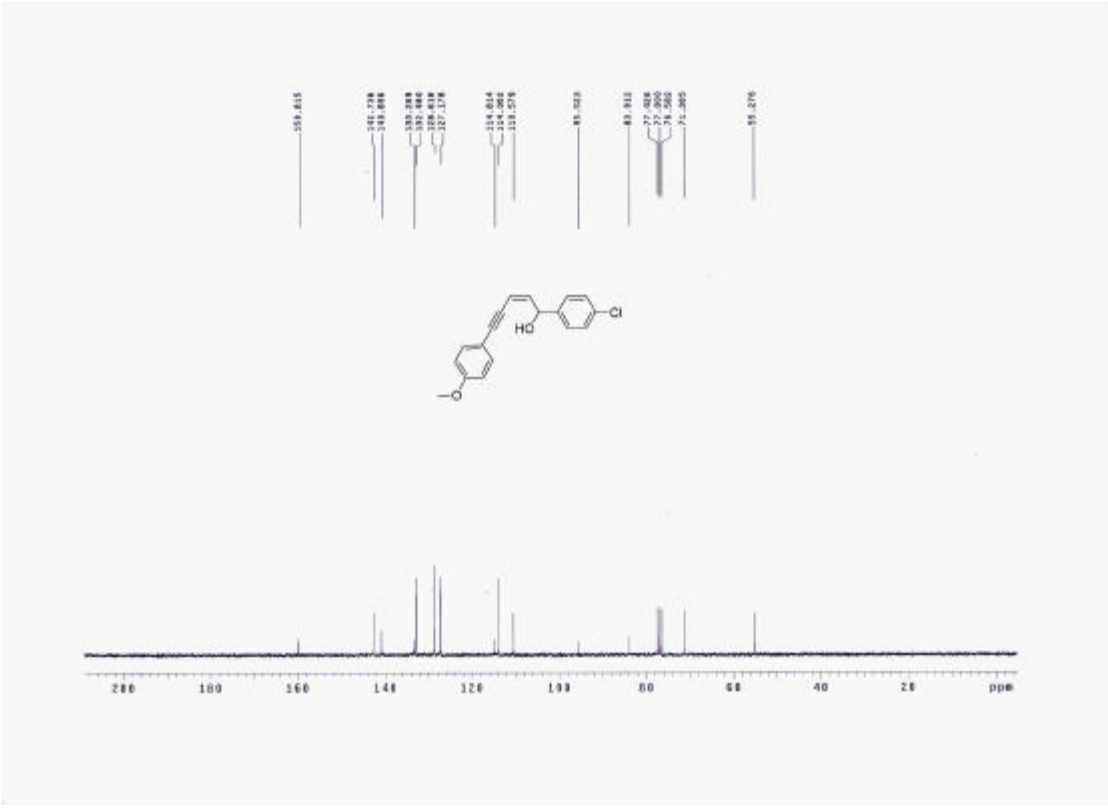
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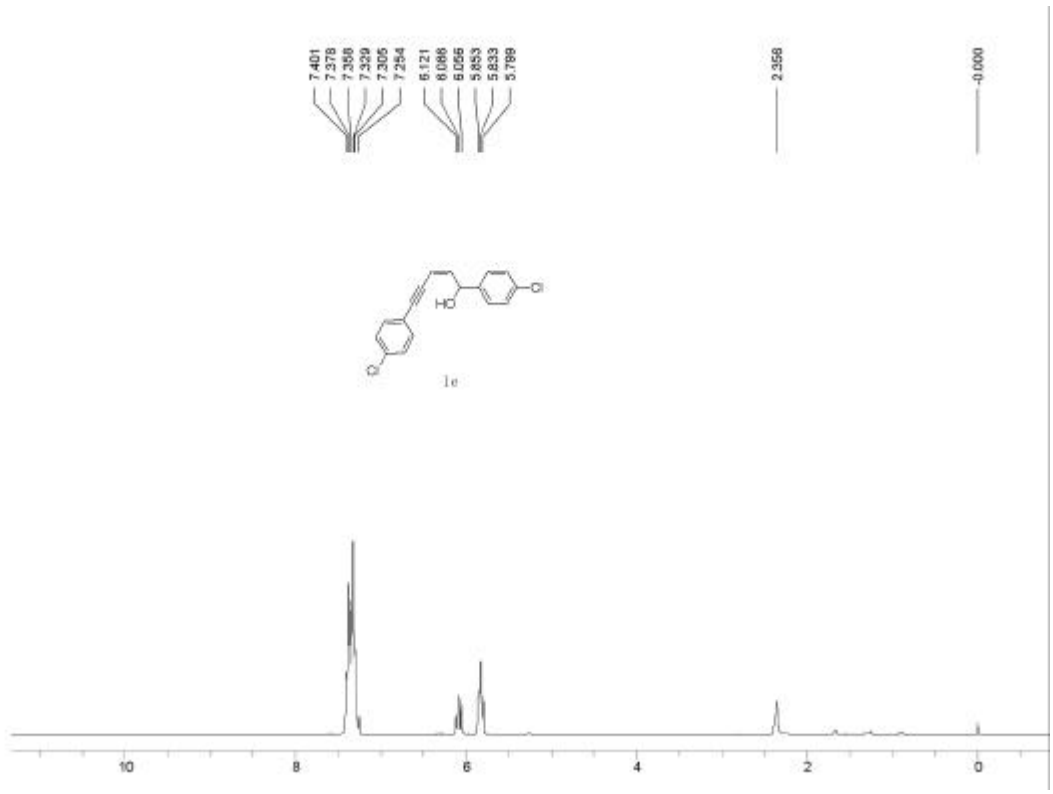
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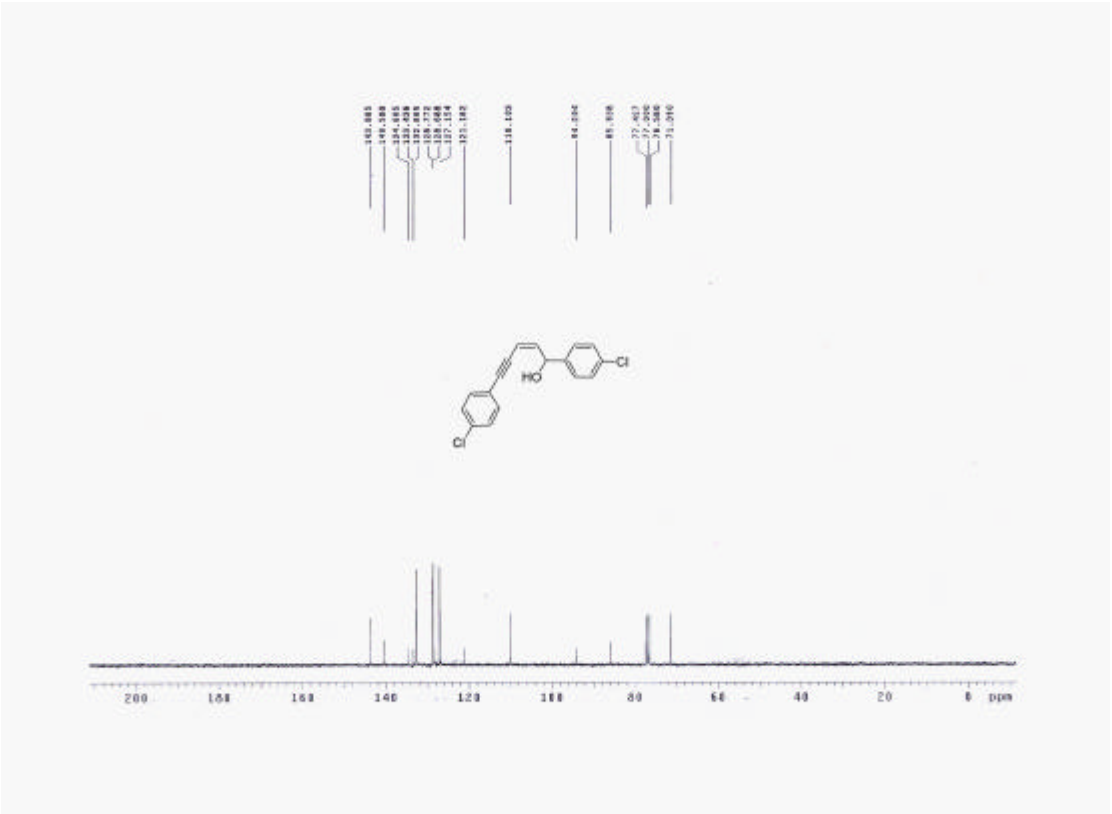
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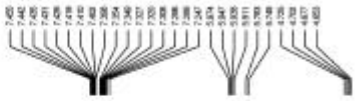

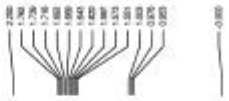

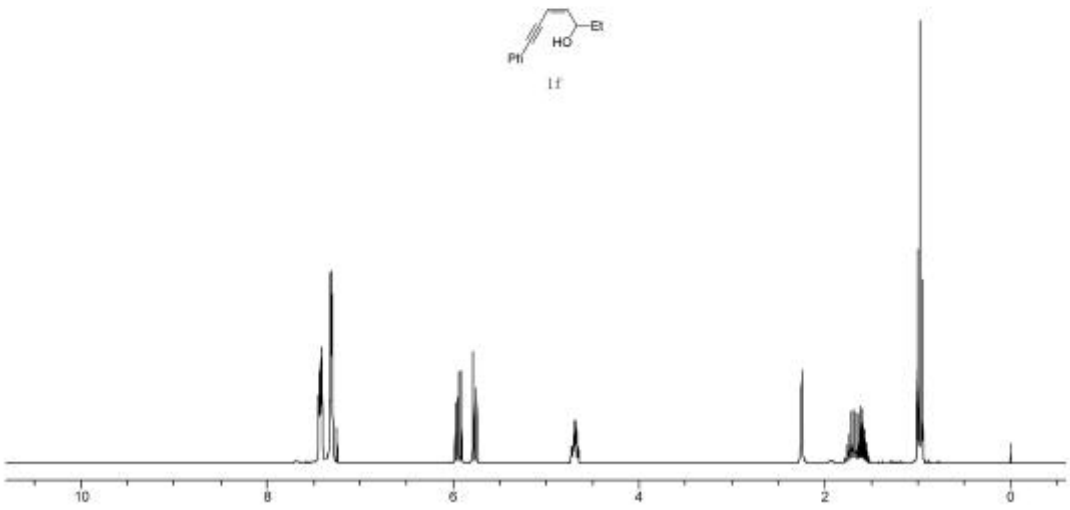
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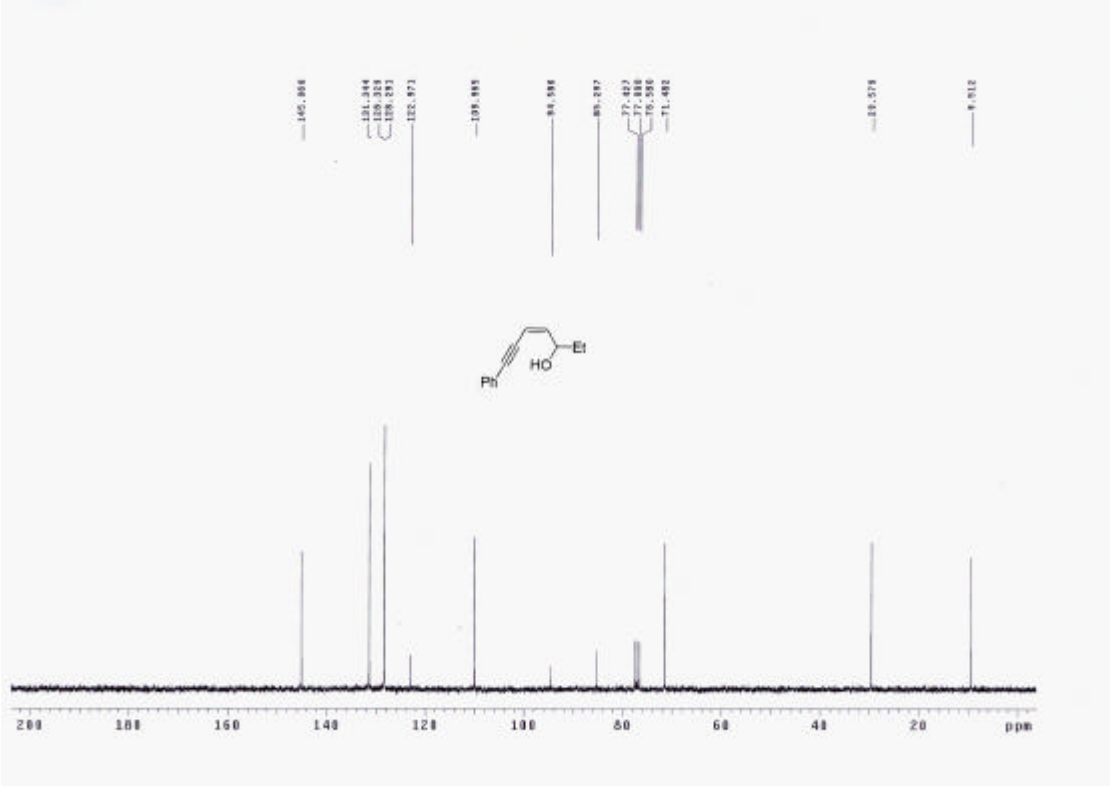
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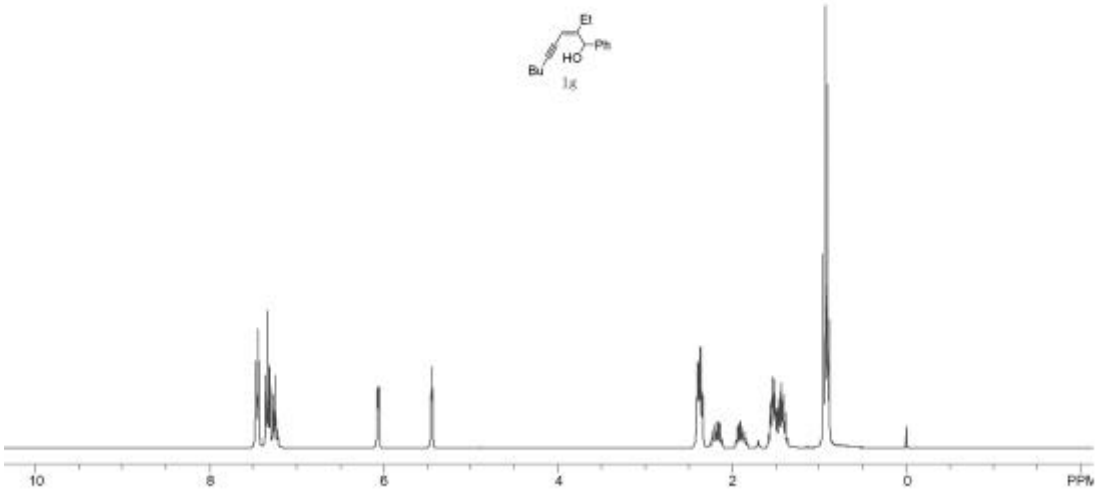
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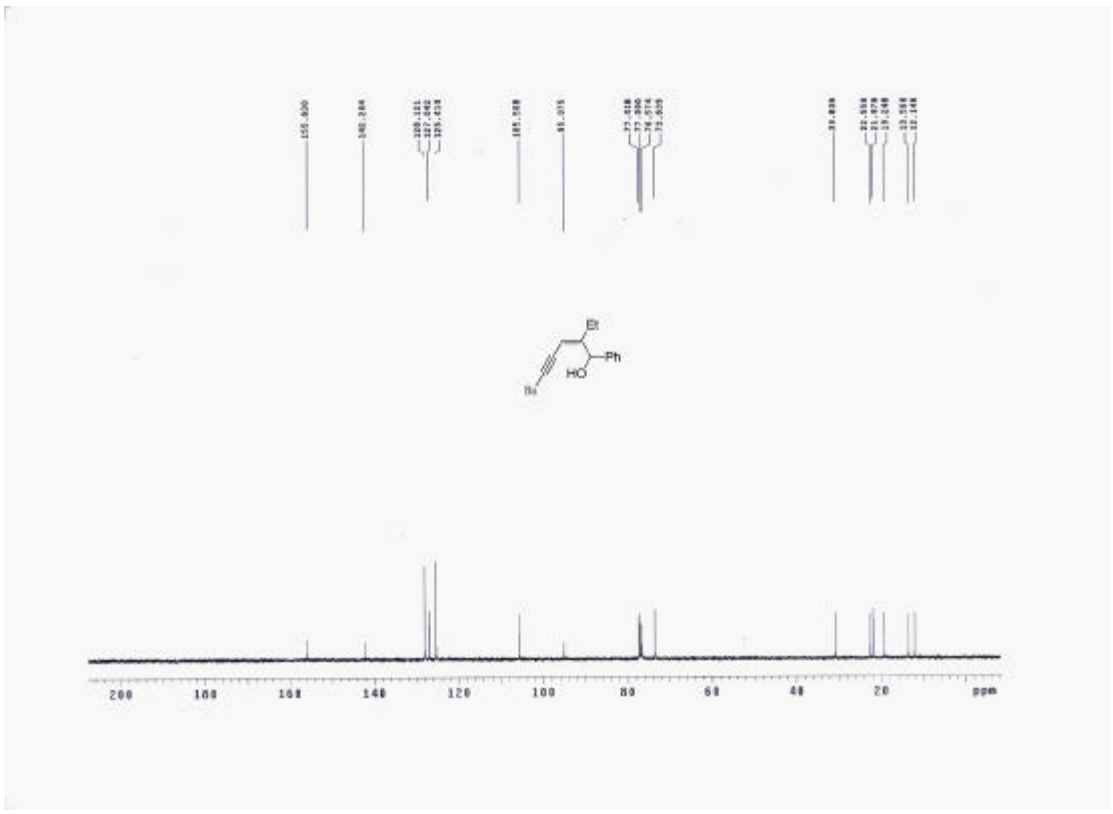
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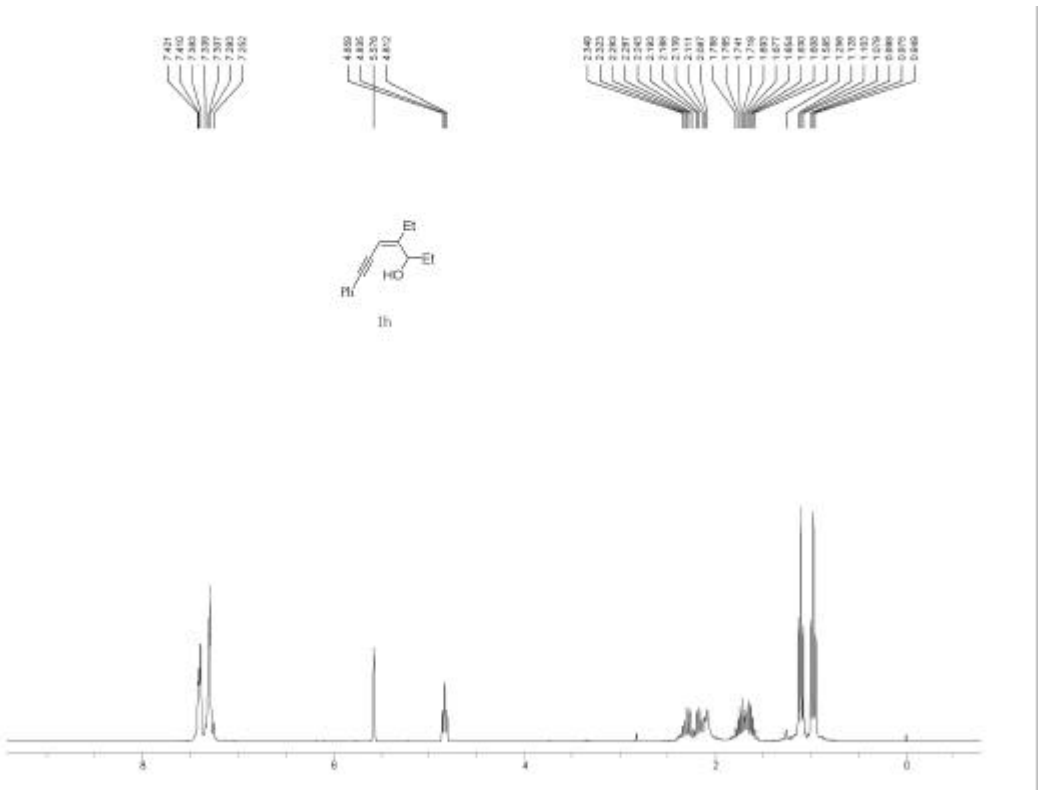
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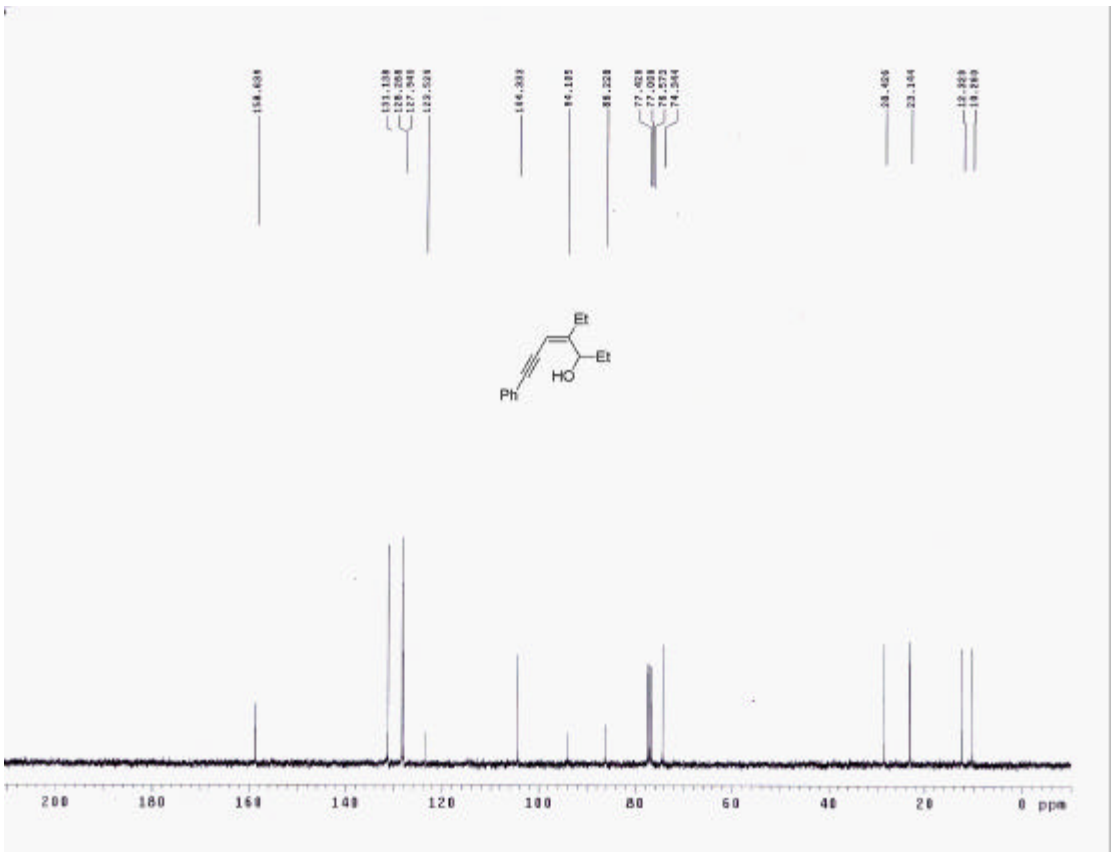
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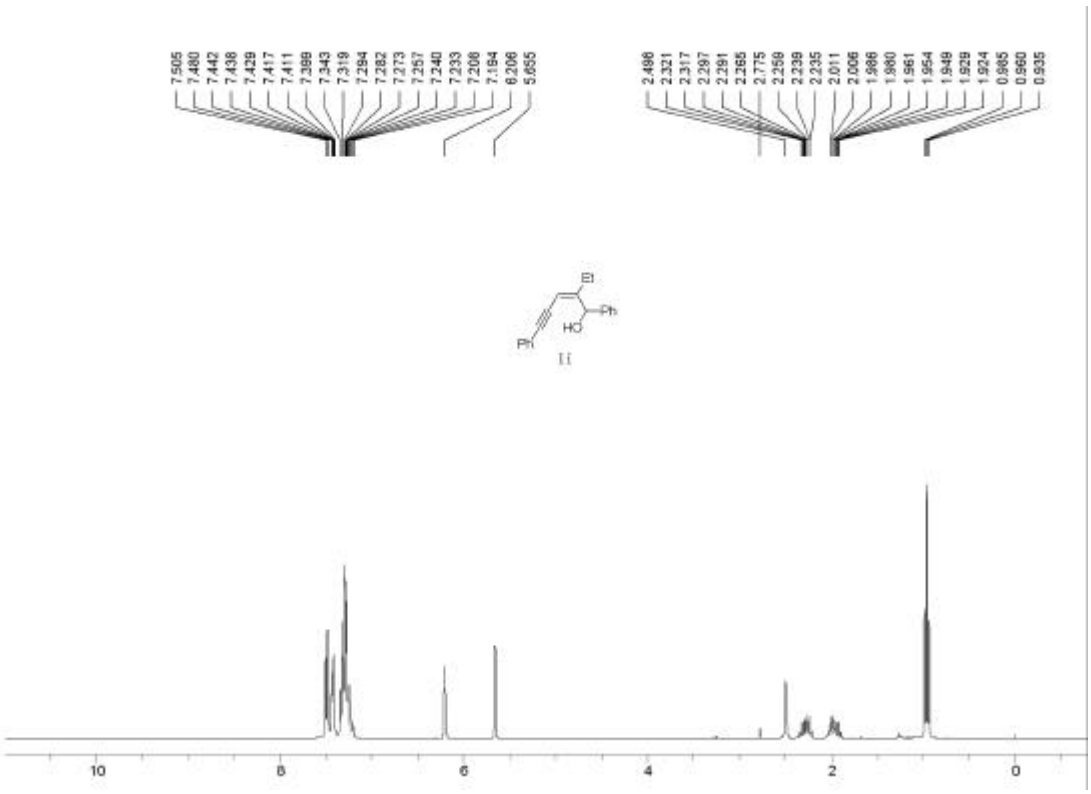
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2.317
2.297
2.291
2.265
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2.259
2.239
2.235
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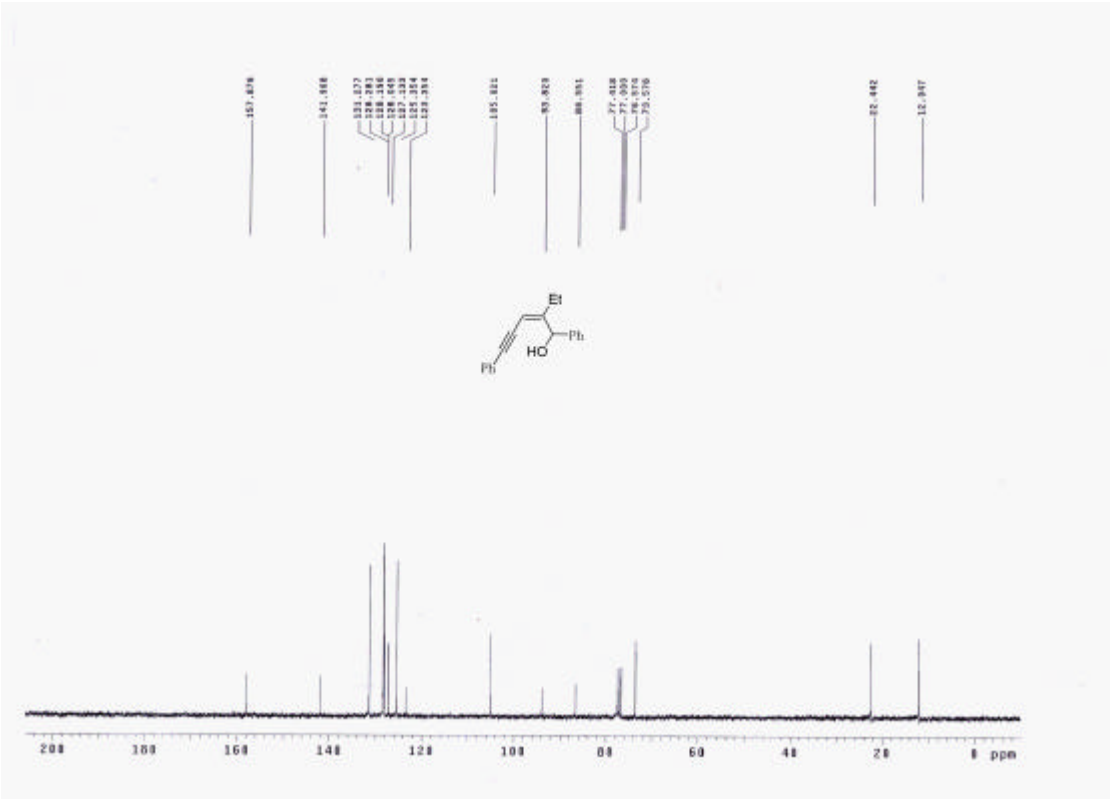
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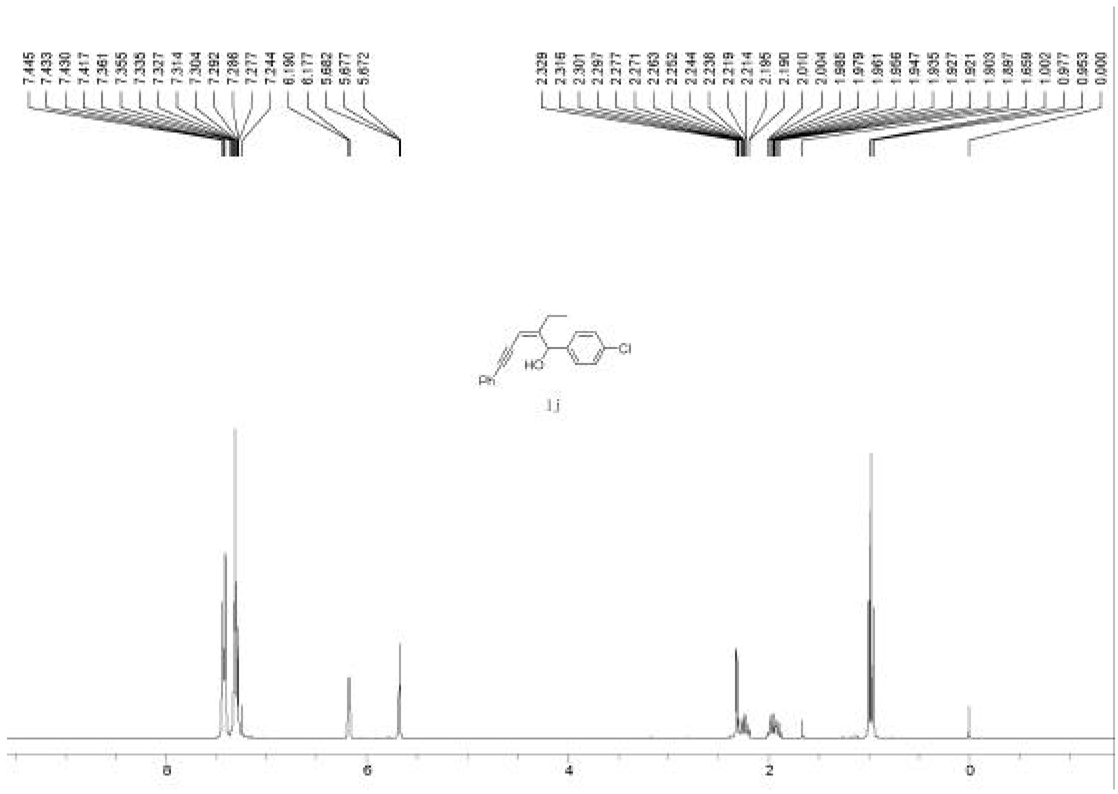
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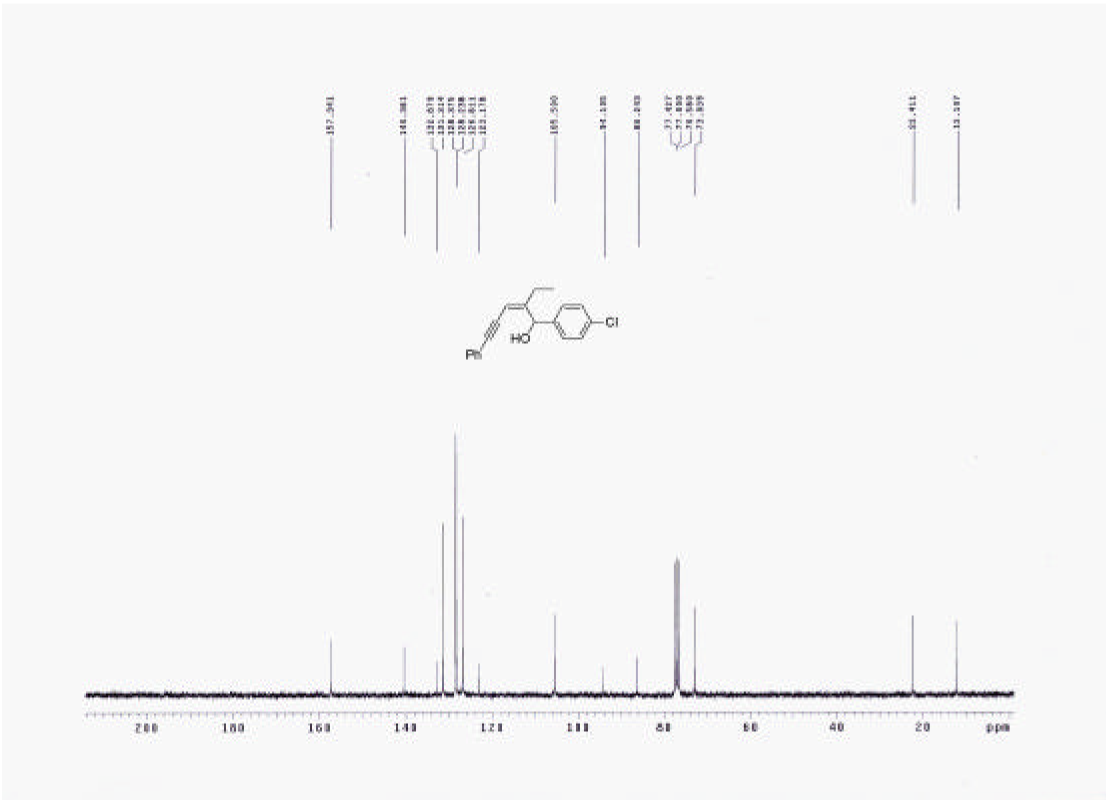
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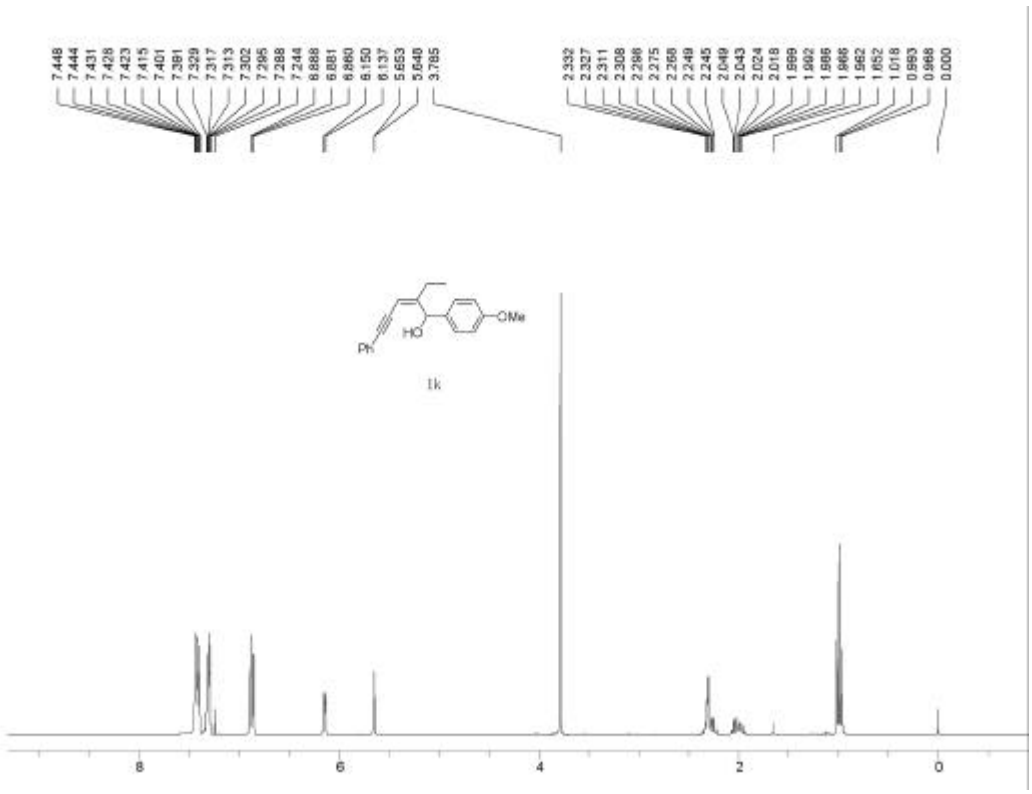
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7.295
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7.244
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6.150
6.137
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2.308
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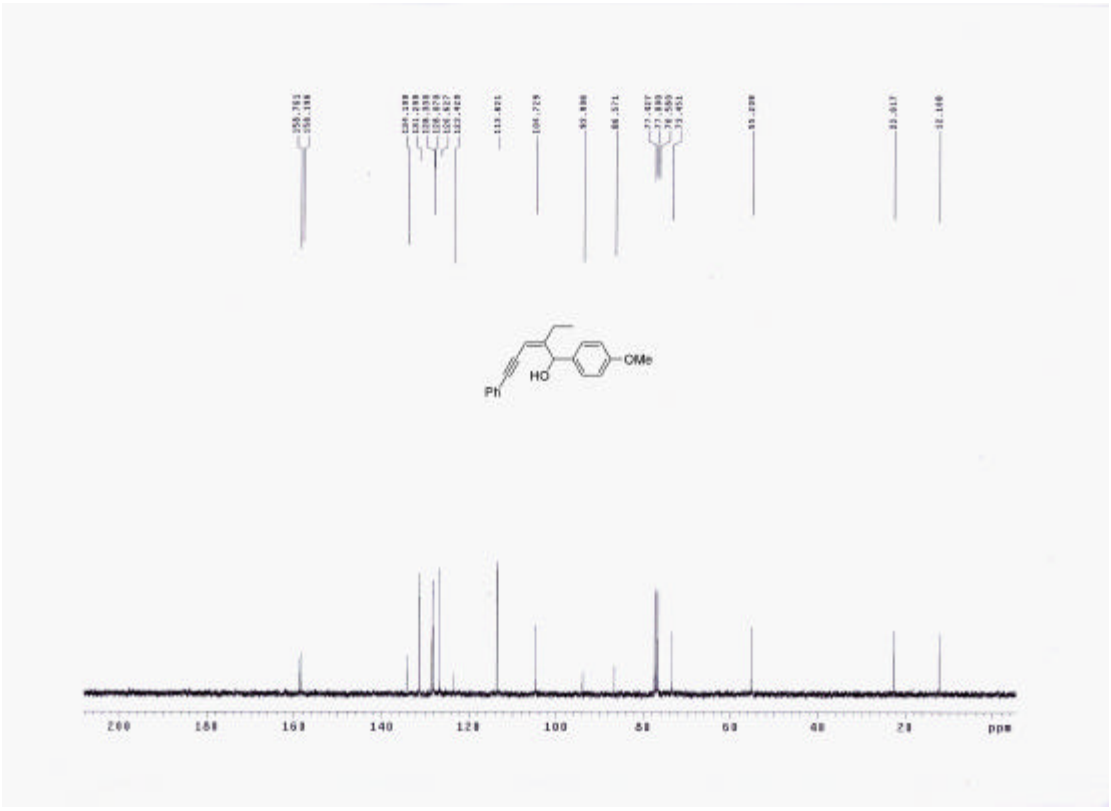
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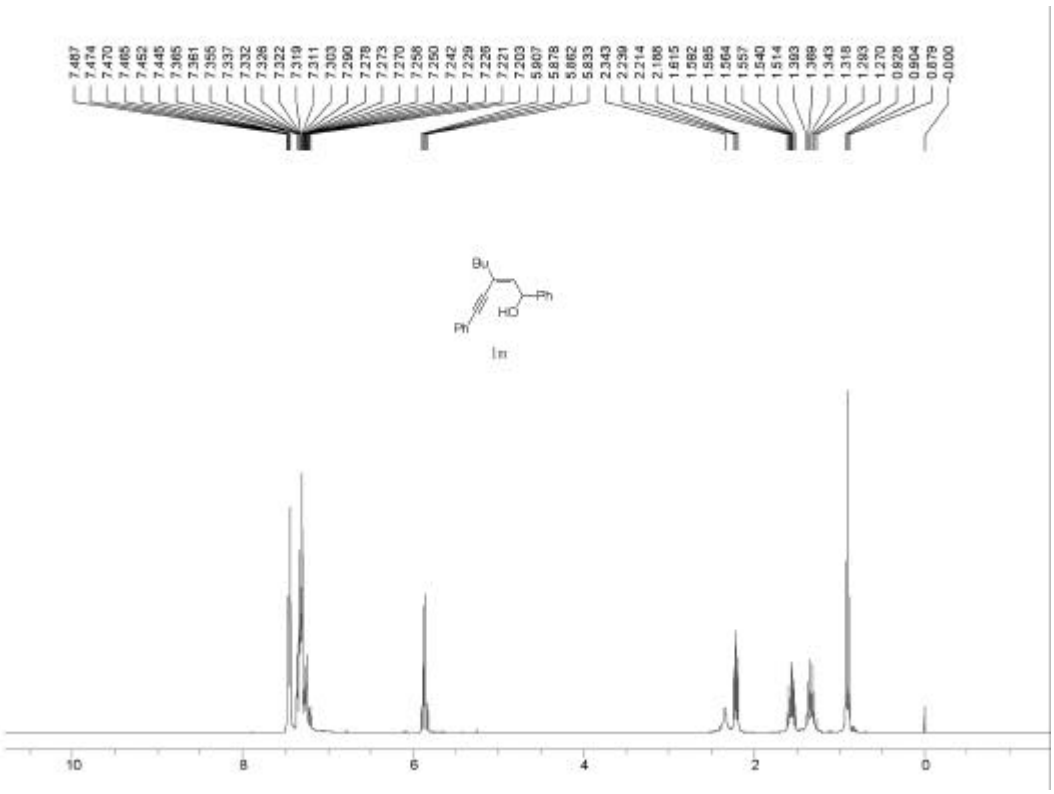
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7.319
7.311
7.303
7.290
7.278
7.273
7.270
7.258
7.250
7.242
7.229
7.226
7.221
7.203
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5.862
5.833
2.343
2.239
2.214
2.186
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1.582
1.585
1.564
1.557
1.540
1.514
1.393
1.369
1.343
1.318
1.293
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Ph
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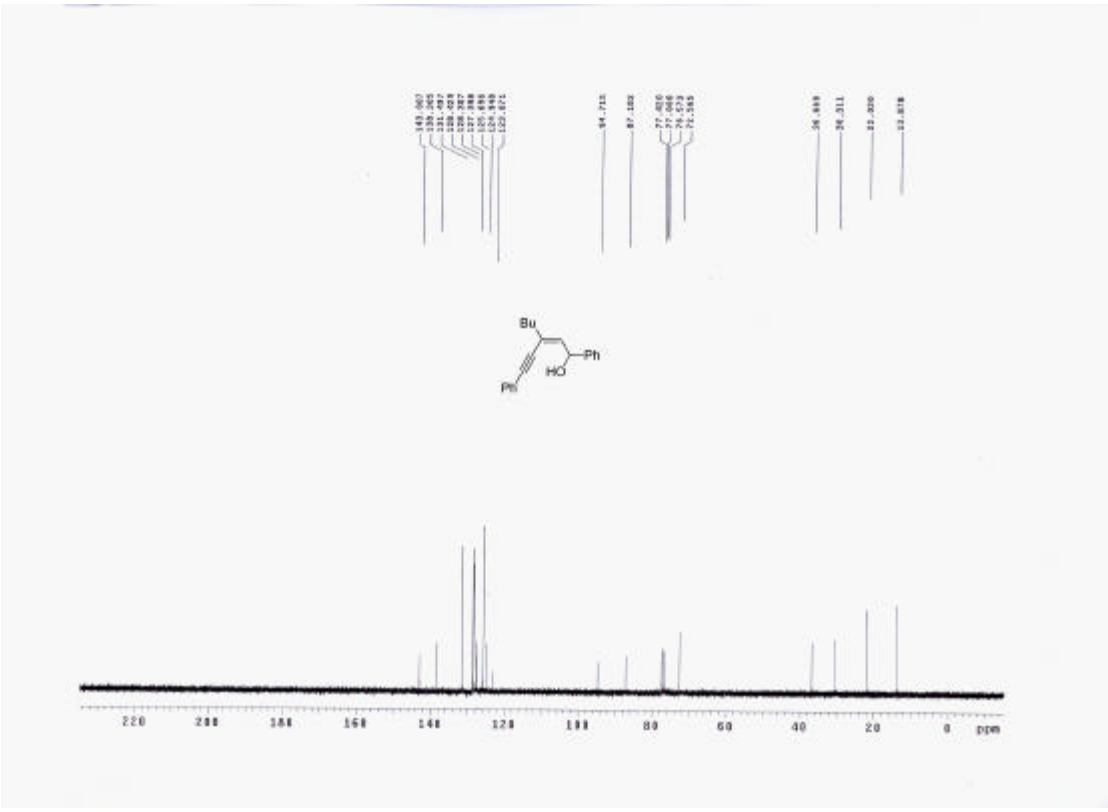
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HO
Ph
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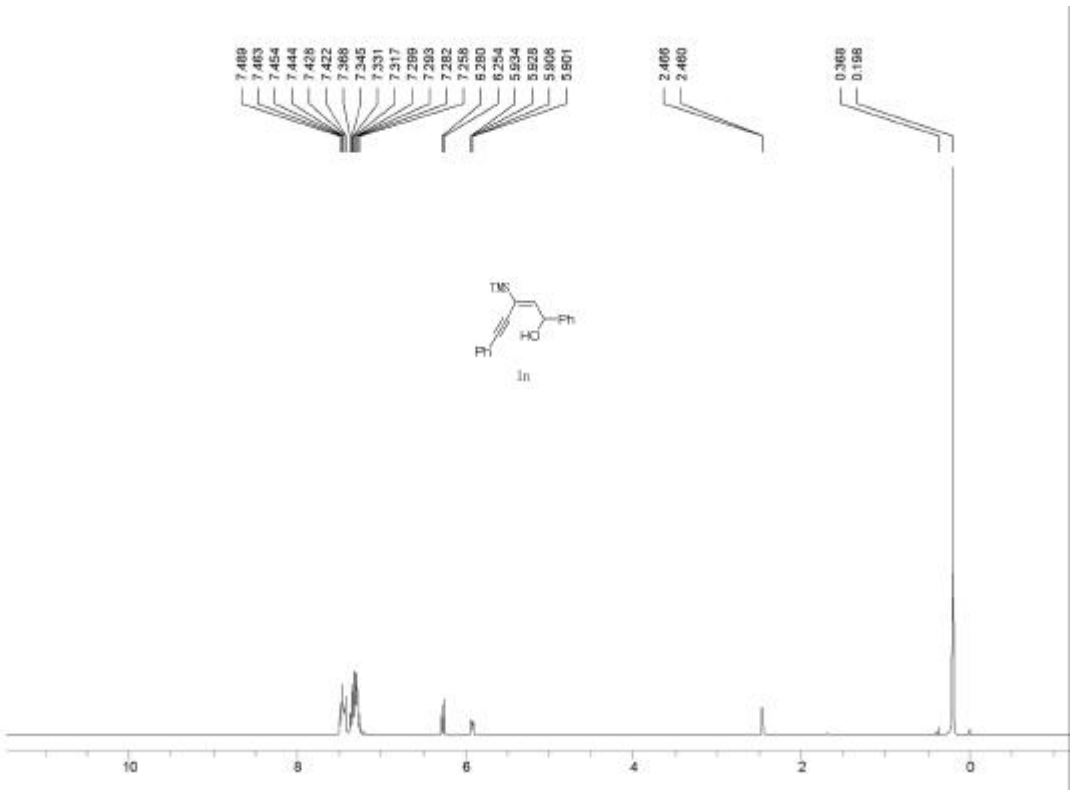
0
ppm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7.282
7.256
6.280
6.254
5.934
5.928
5.906
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Ph
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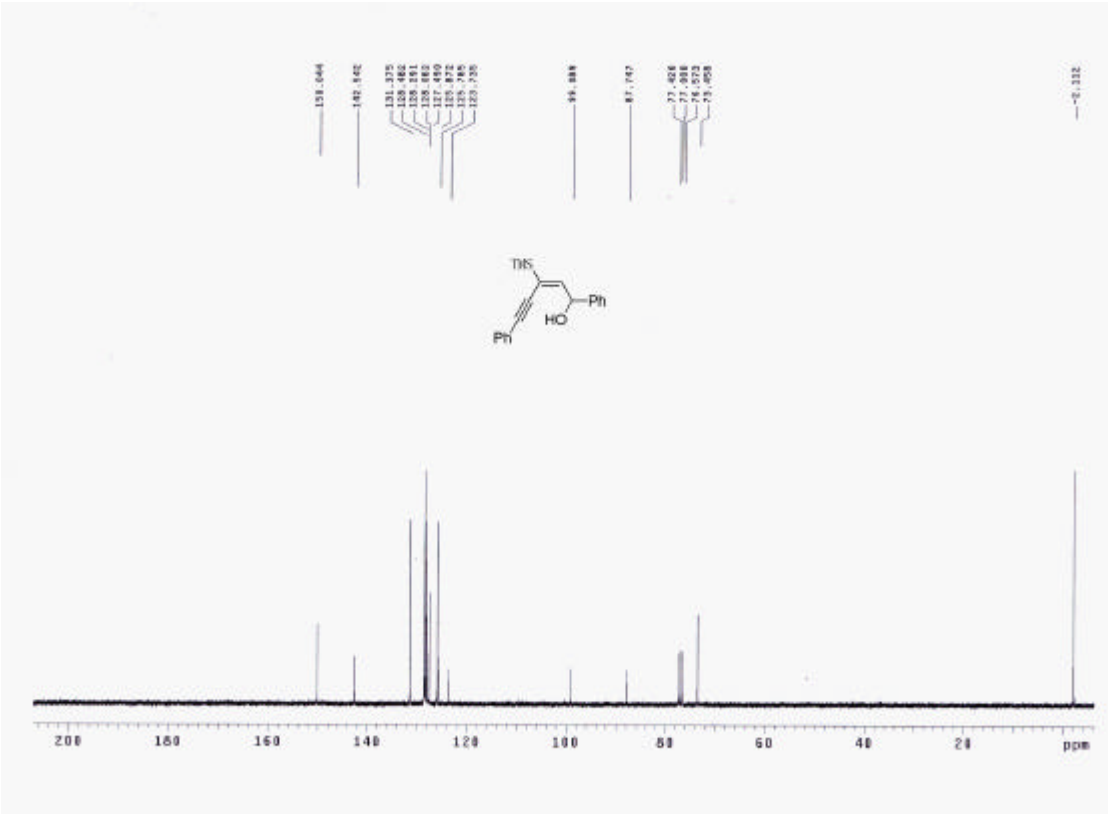
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Ph
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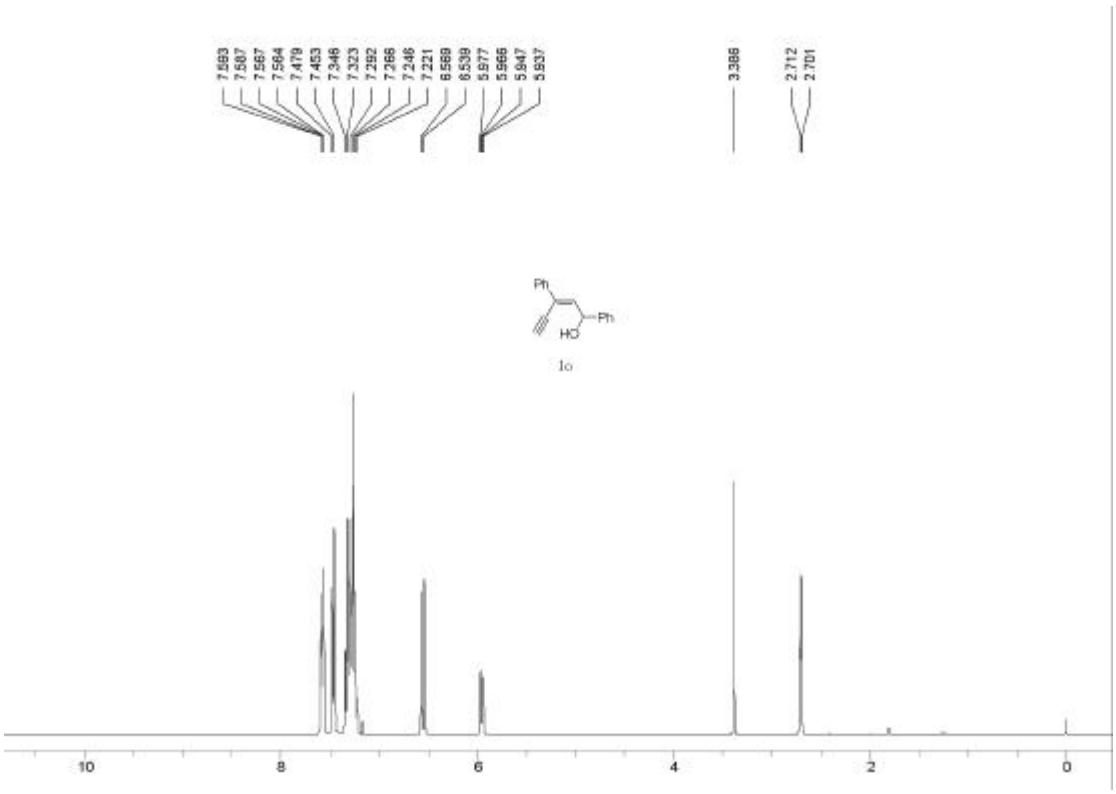
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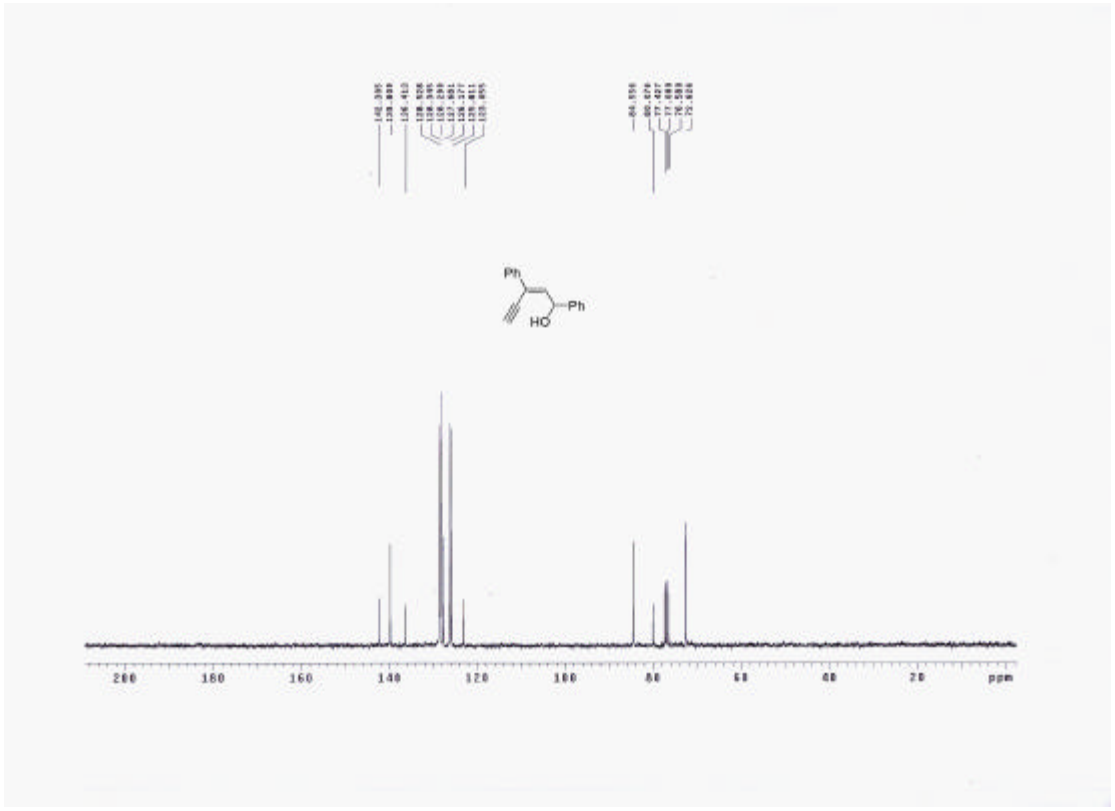
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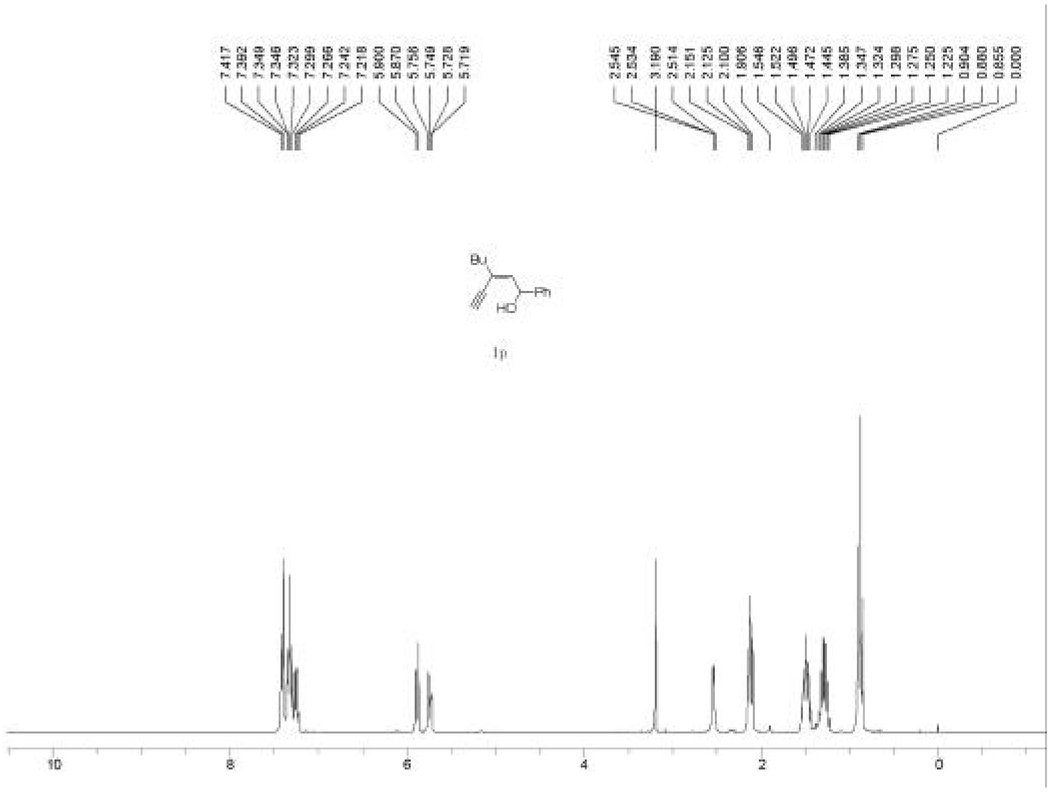
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5.728
5.719
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2.534
3.190
2.514
2.151
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2.100
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1.275
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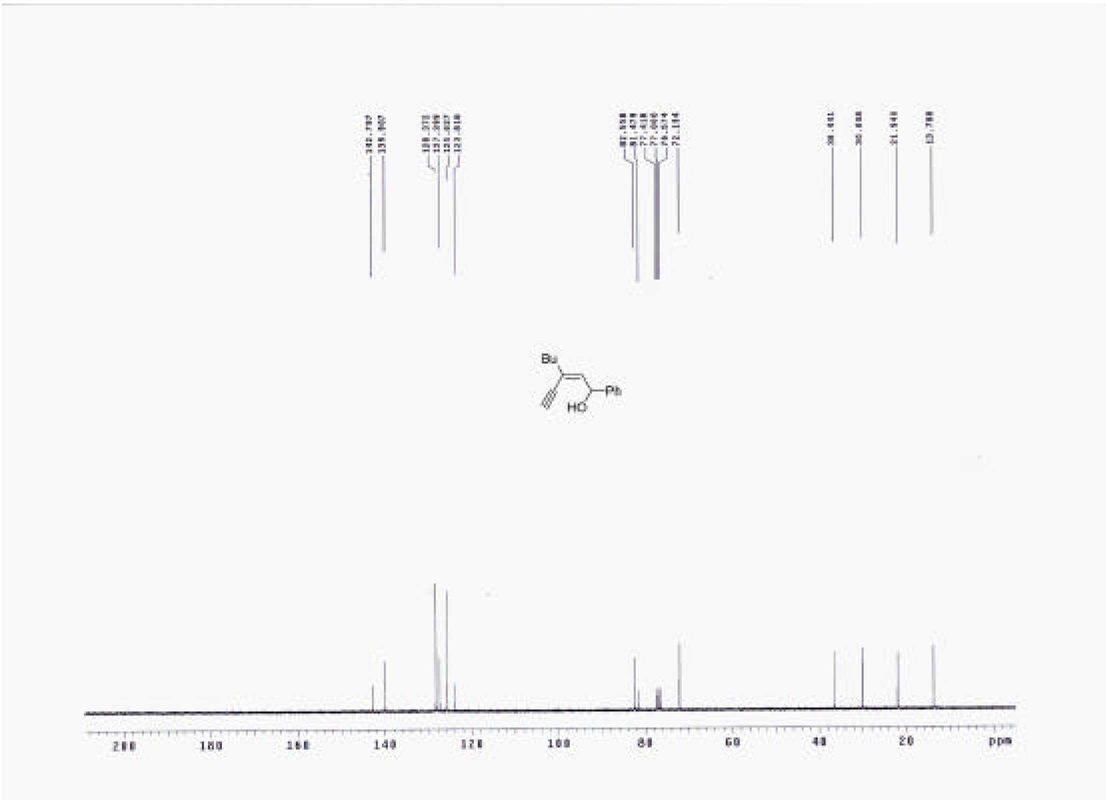
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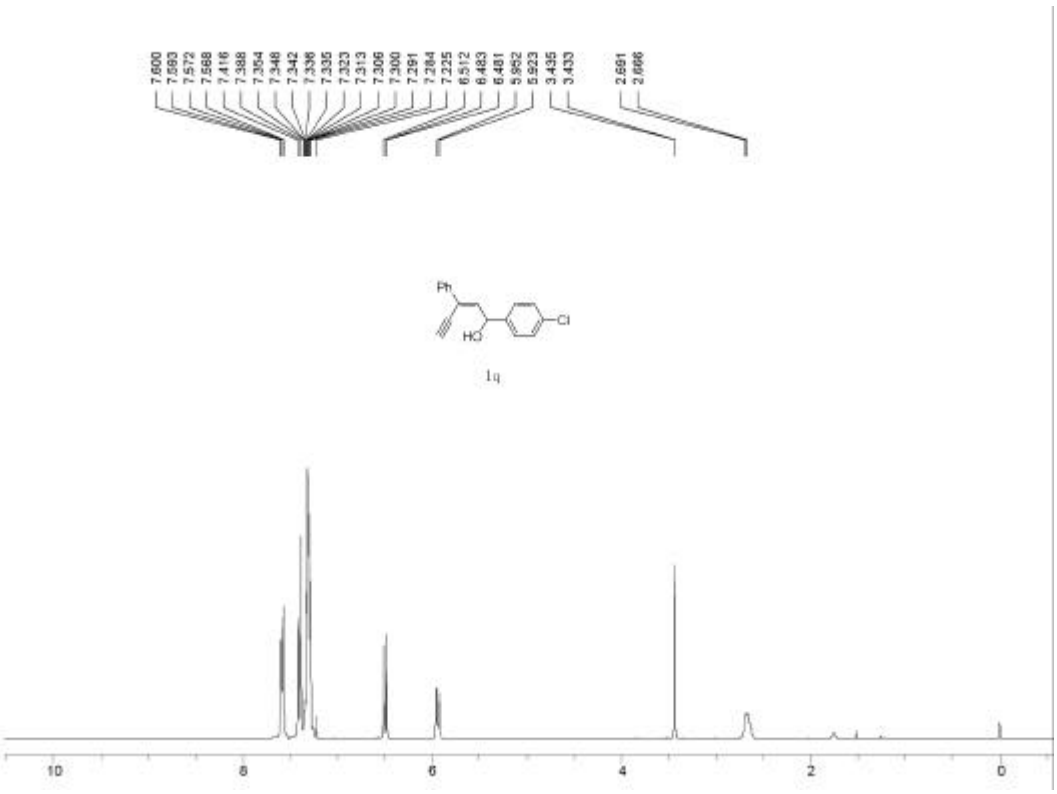
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7.335
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7.313
7.306
7.300
7.291
7.264
7.225
6.512
6.483
6.481
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3.433
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Cl
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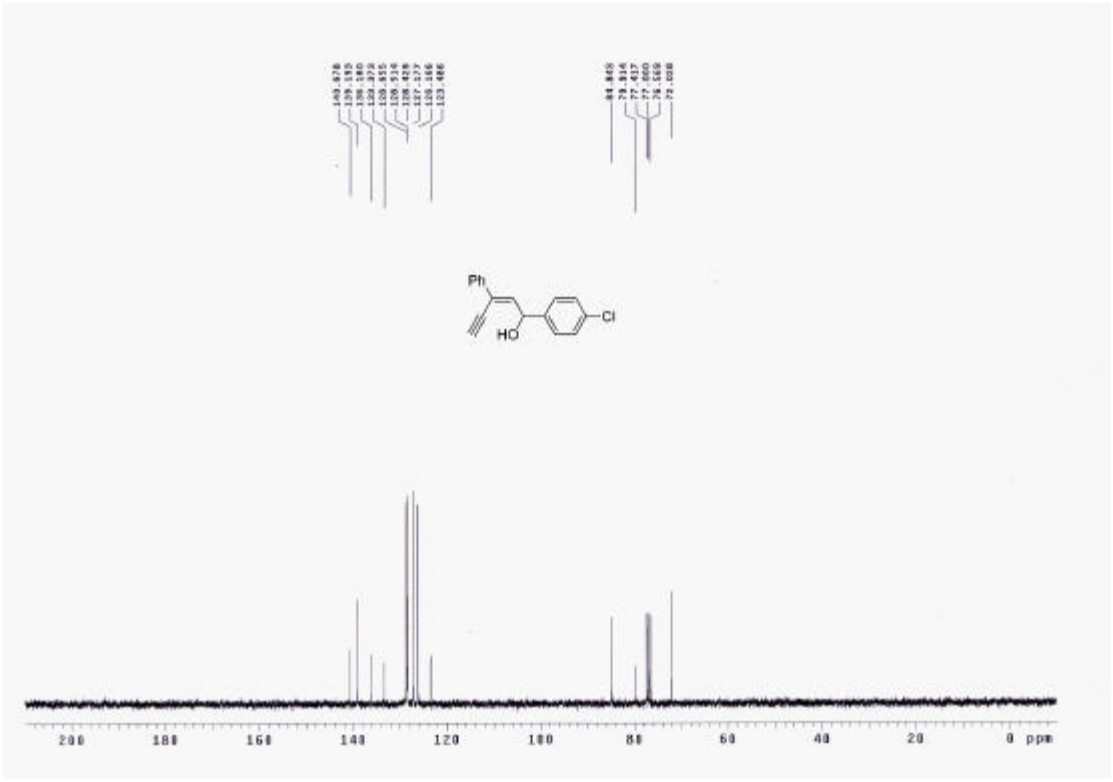
4
2
0

1q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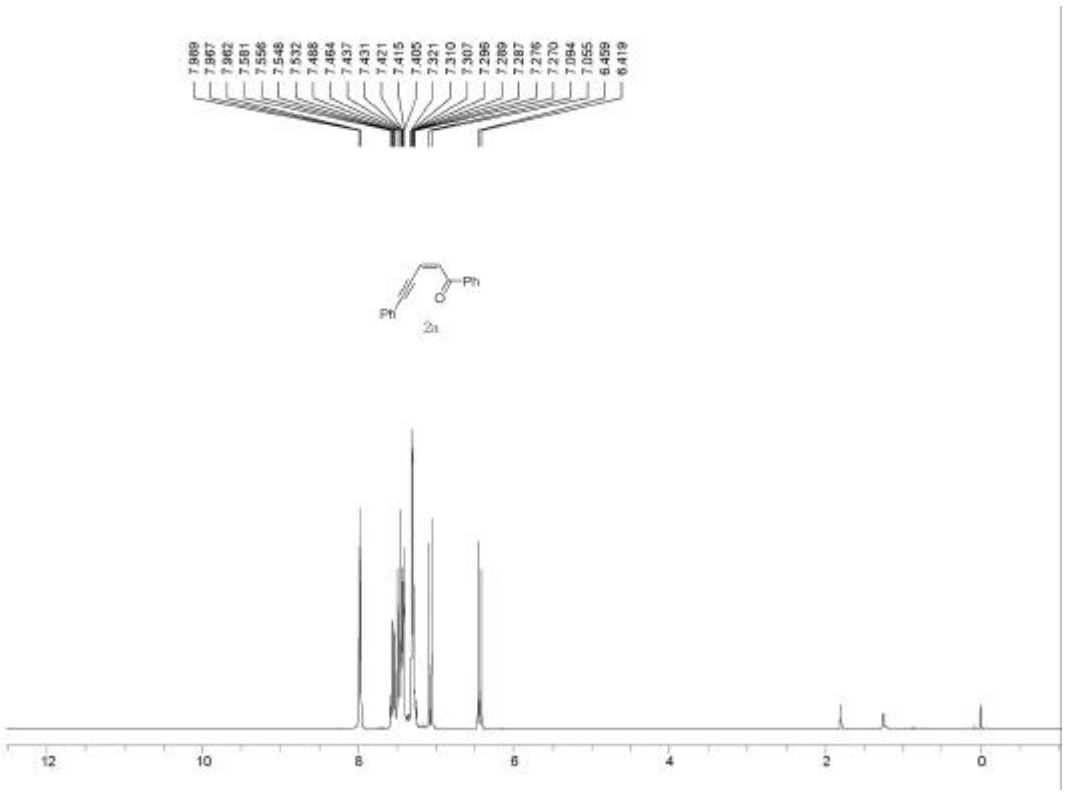
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7.415
7.405
7.321
7.310
7.307
7.296
7.289
7.287
7.276
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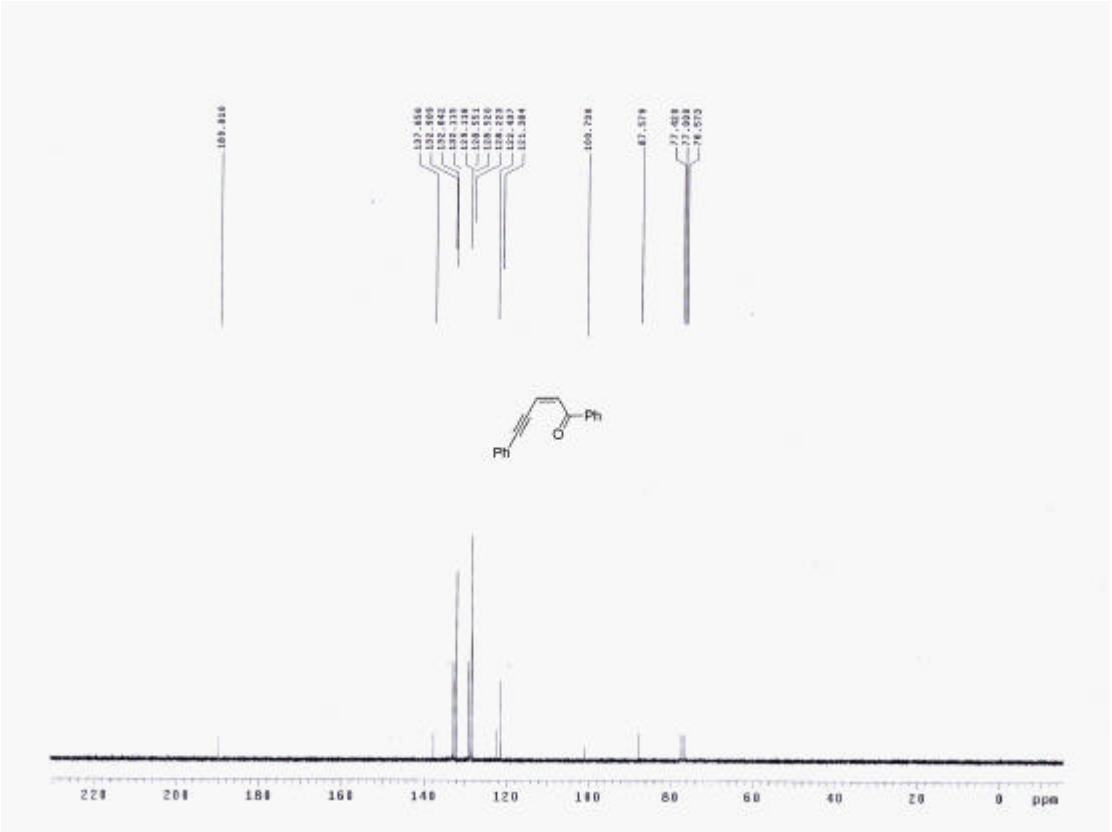
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Ph
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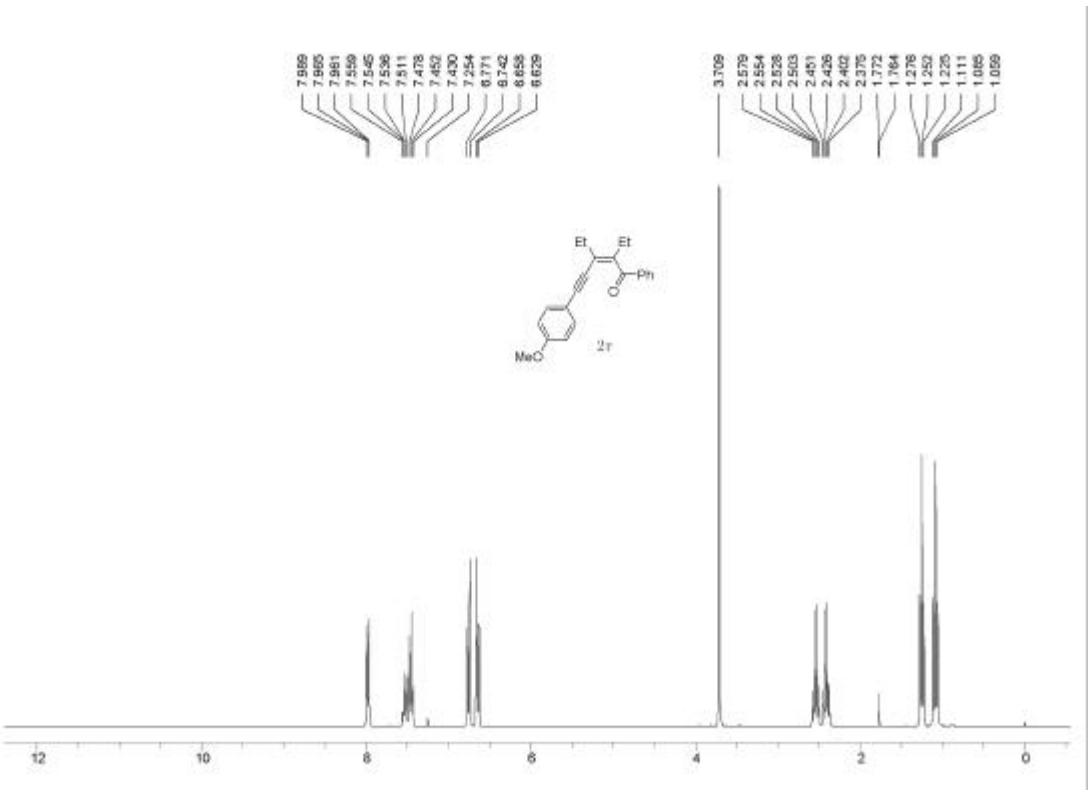
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6.629
3.709
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2.554
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2.402
2.375
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1.764
1.276
1.252
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Et
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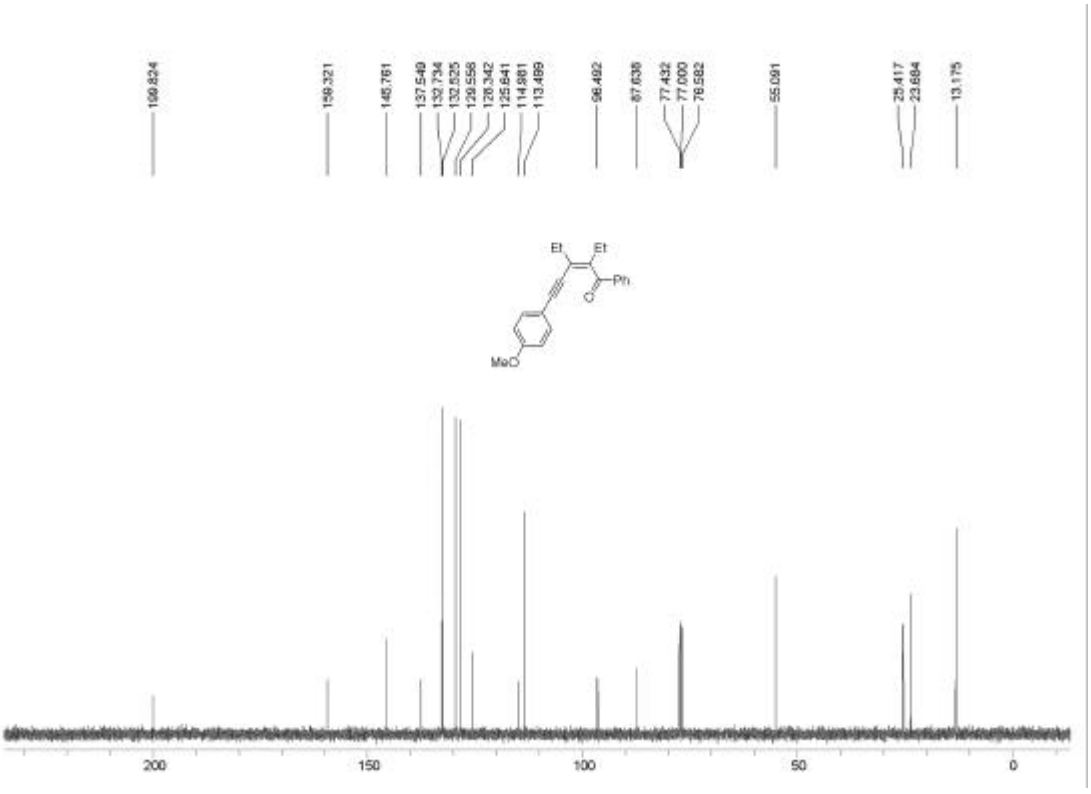
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96.492
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77.432
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MeO
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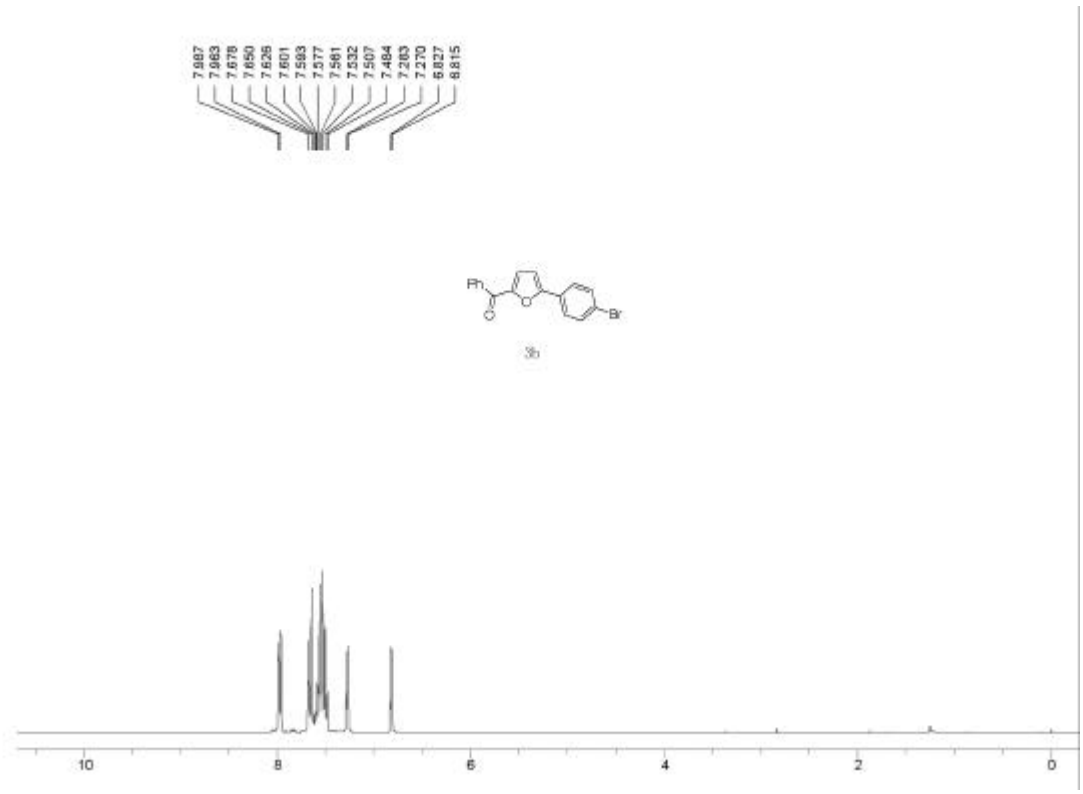
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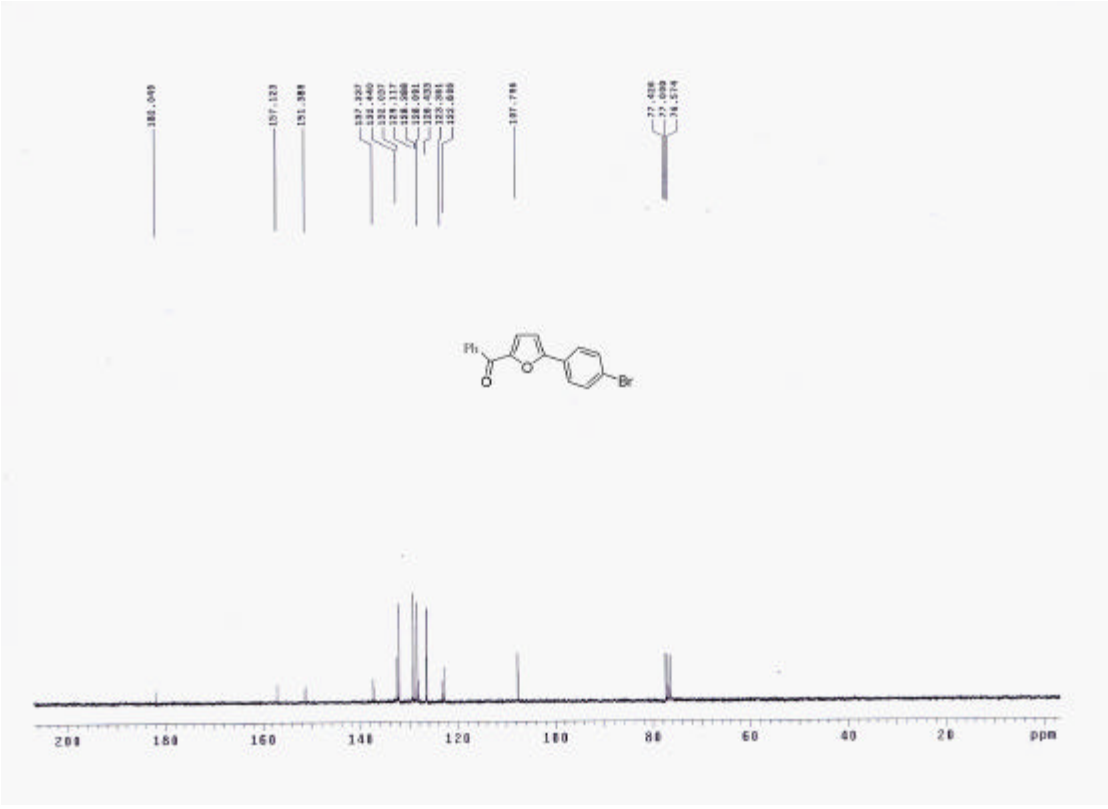
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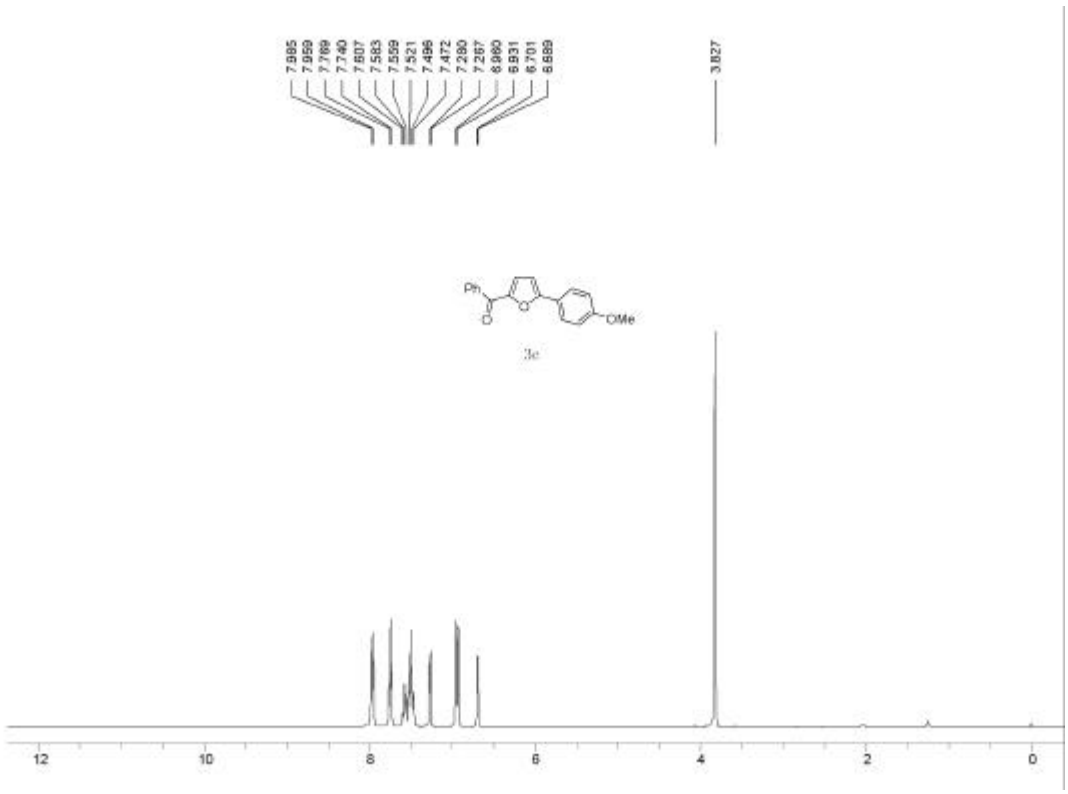
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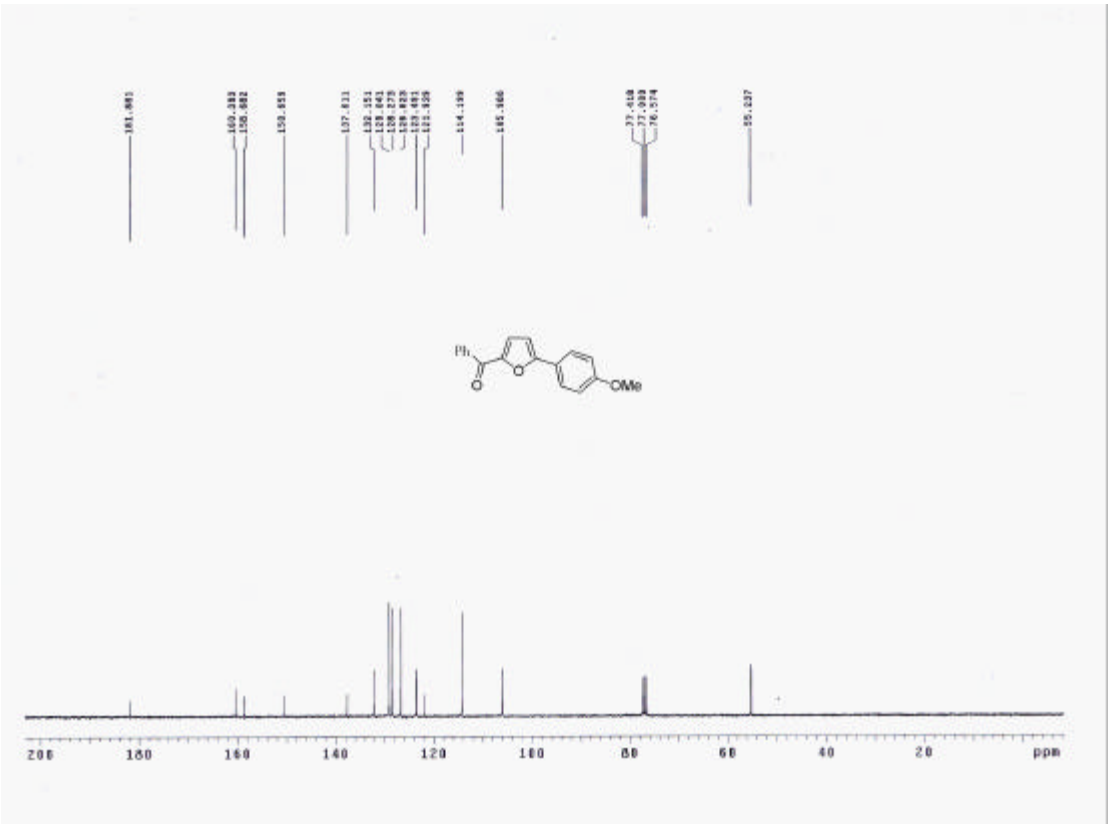
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OMe
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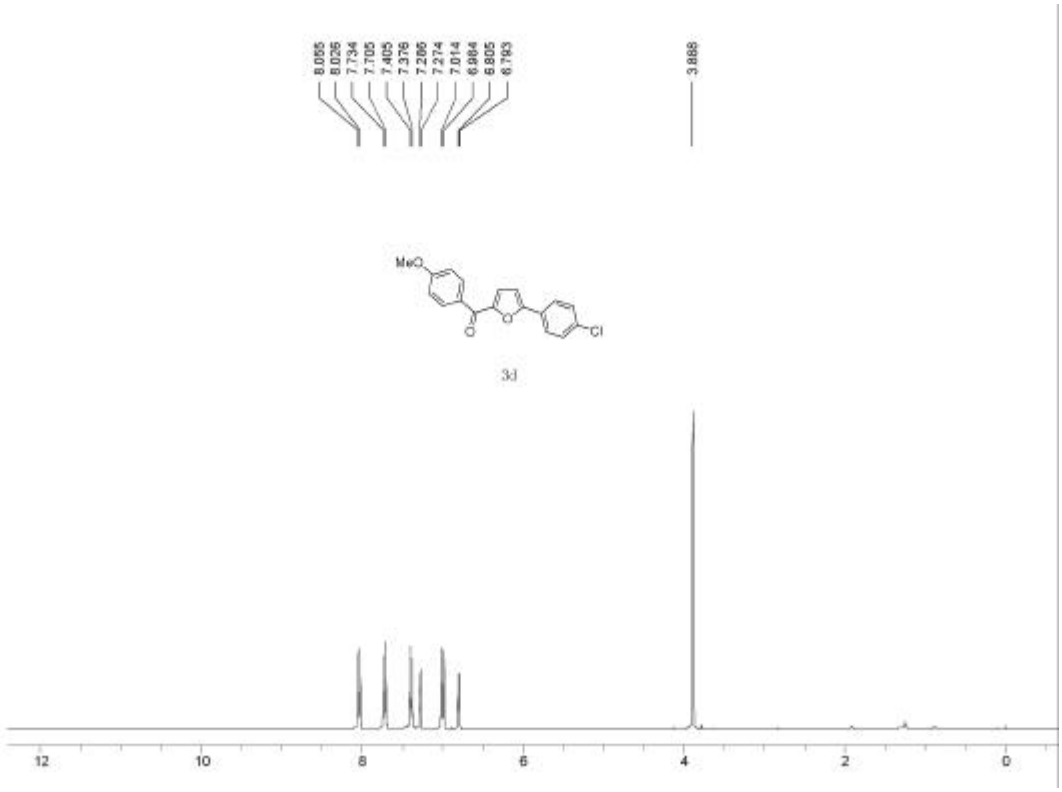
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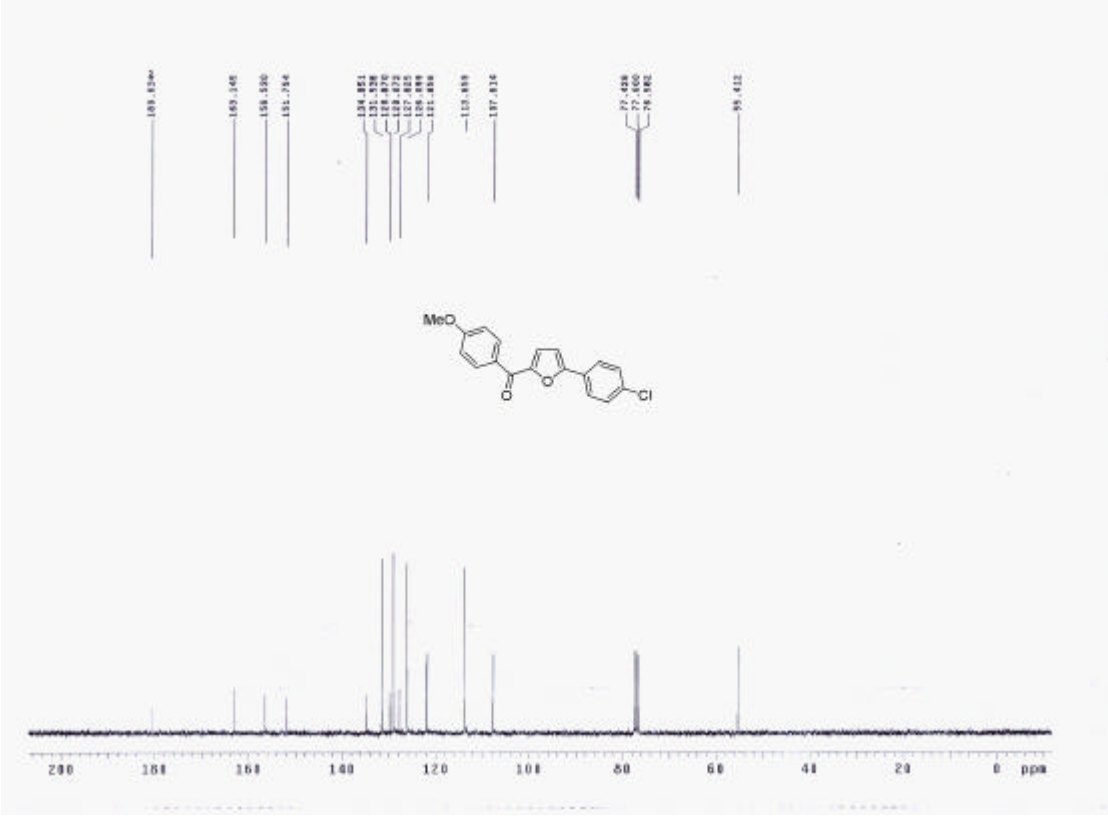
3j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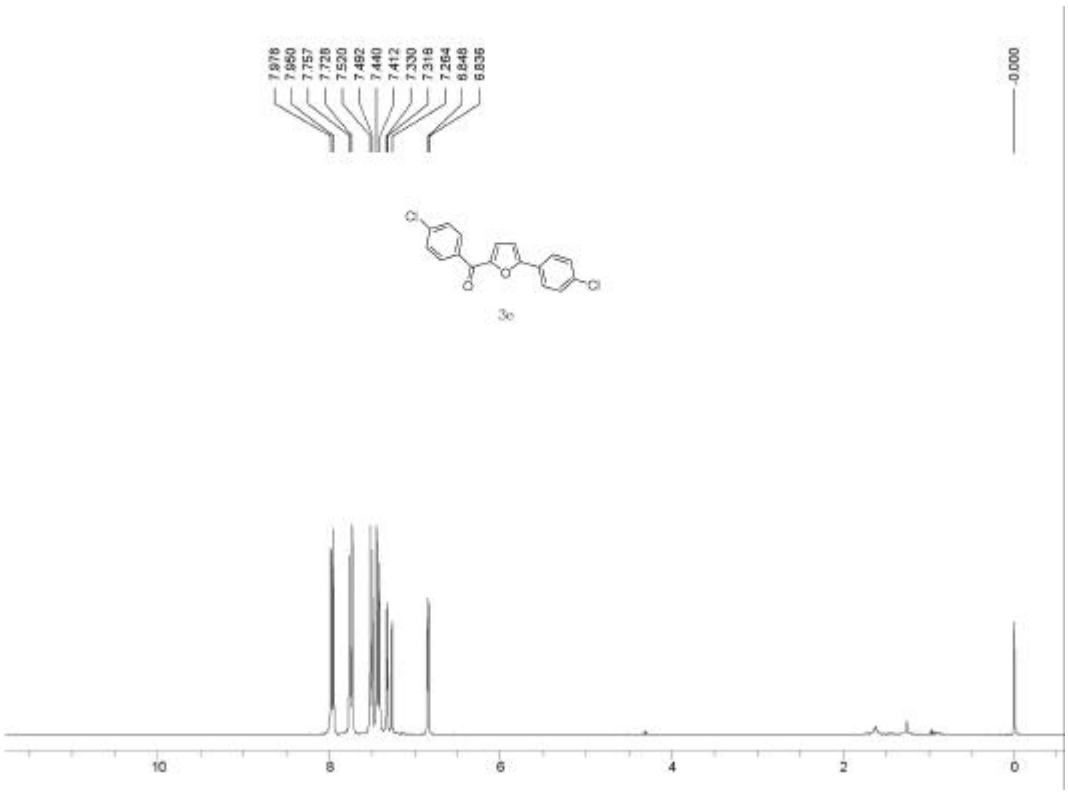
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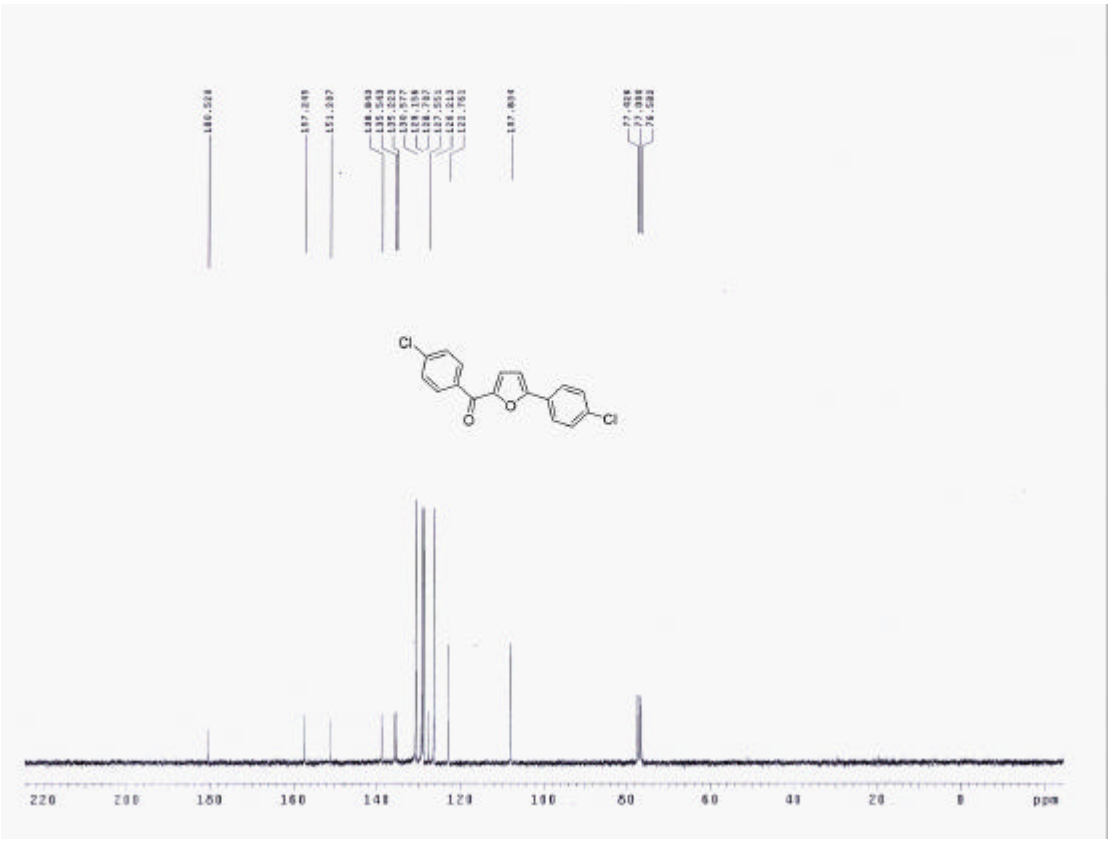
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Cl
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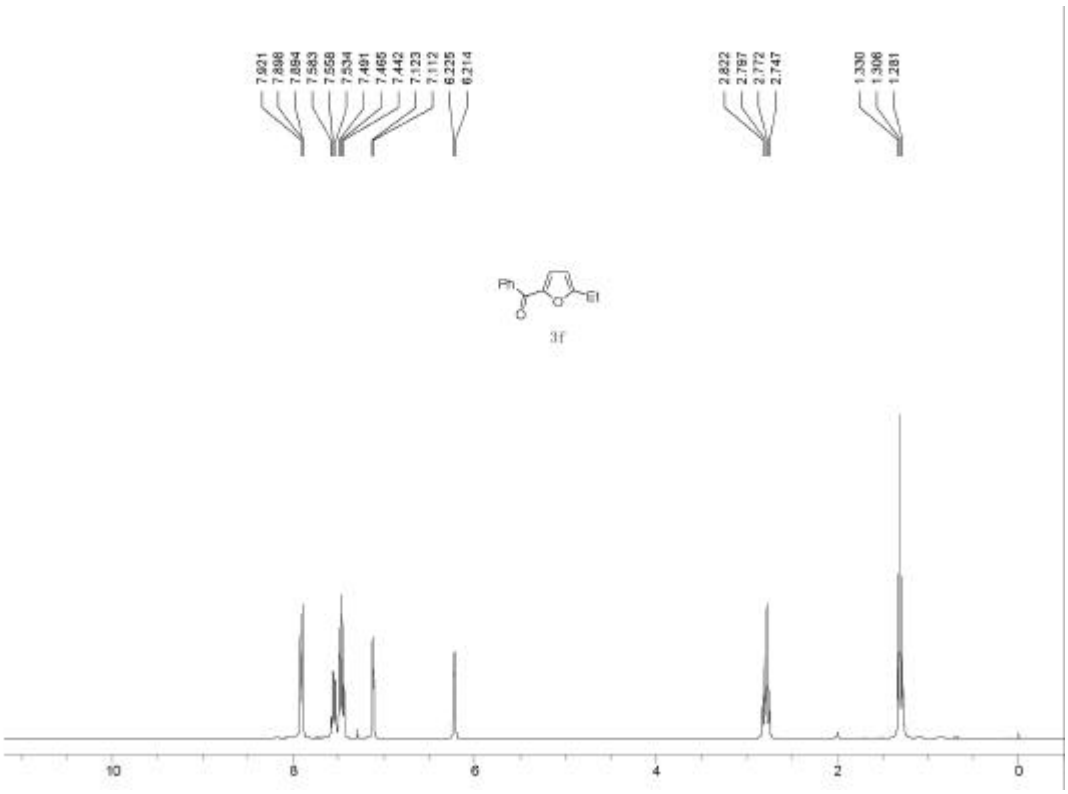
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6.214
2.822
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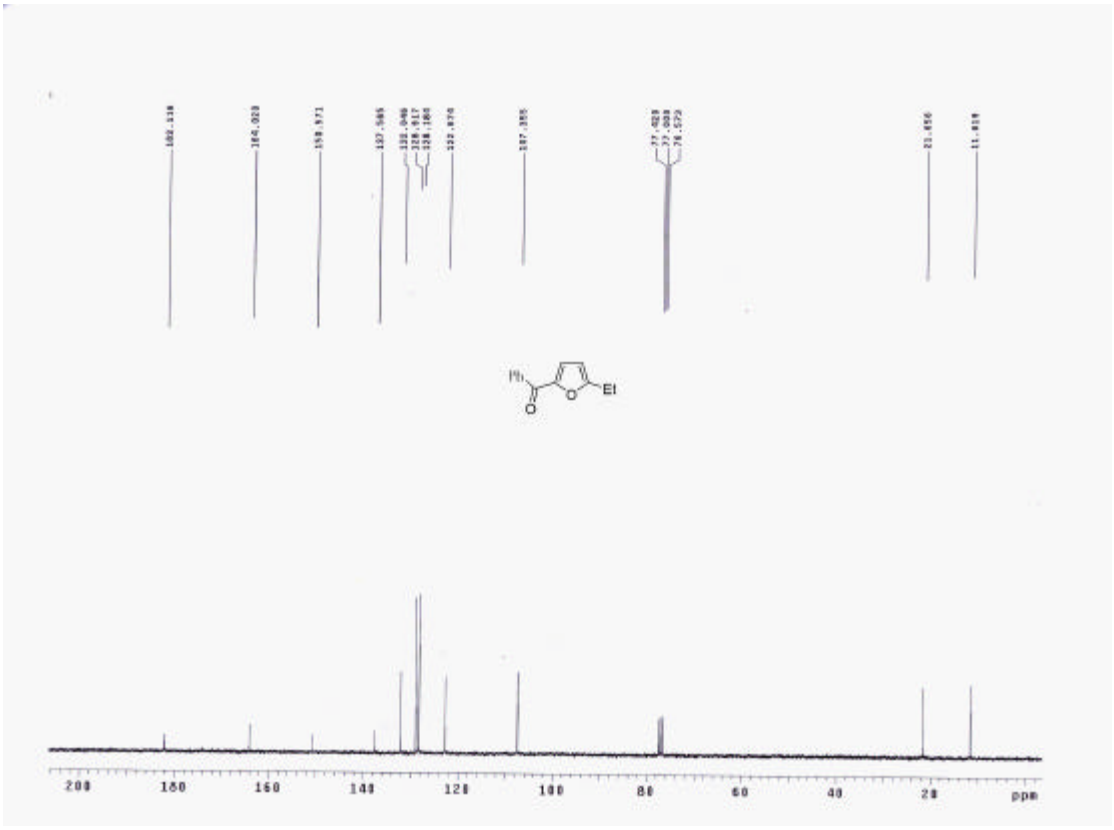
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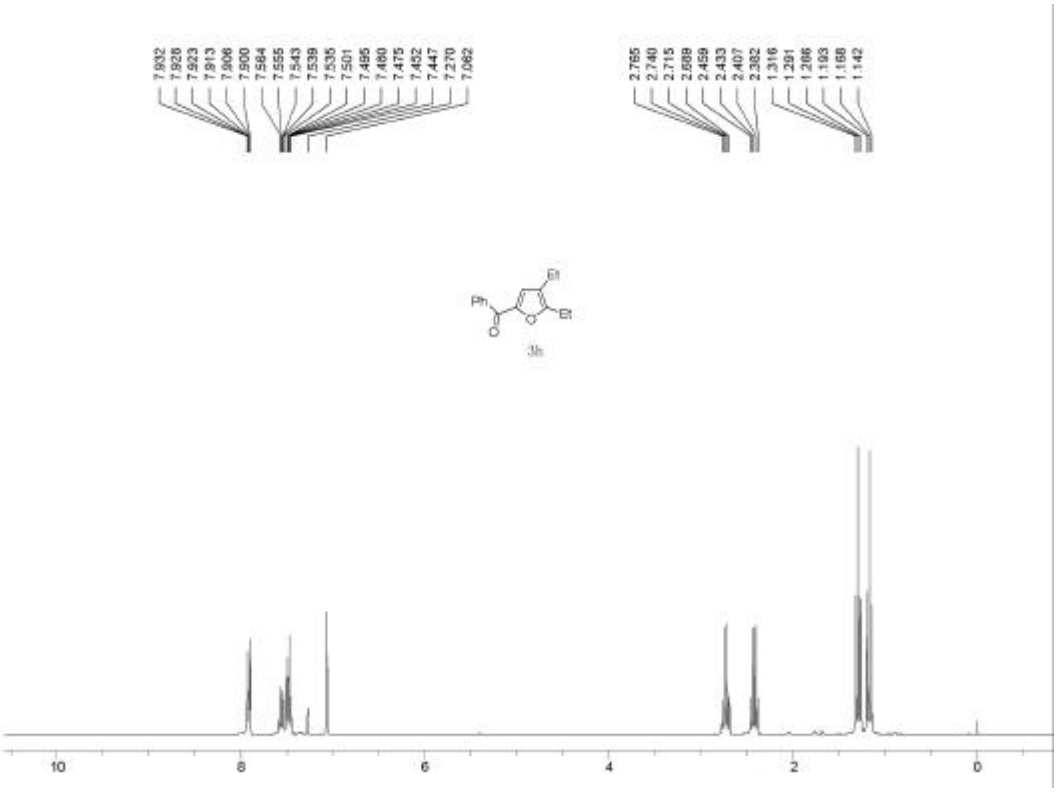
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1.291
1.266
1.193
1.168
1.142
Ph
Et
Et
O
3h
10
8
6
4
2
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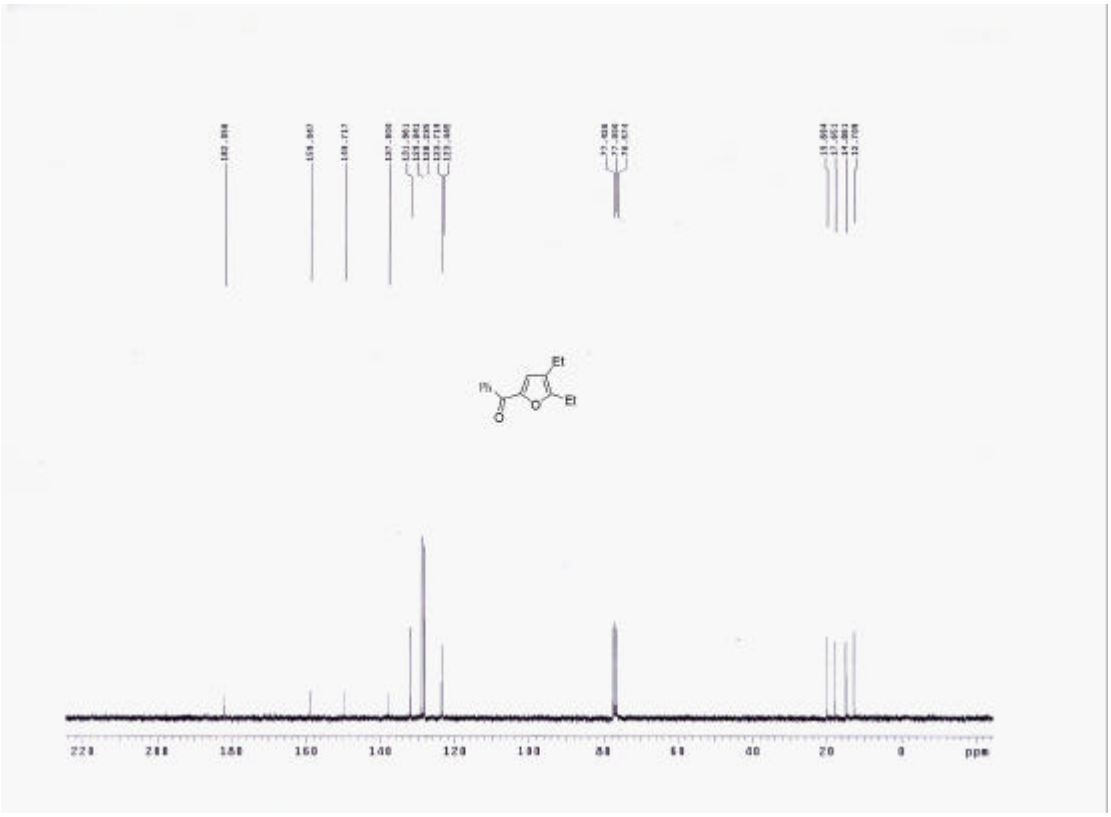
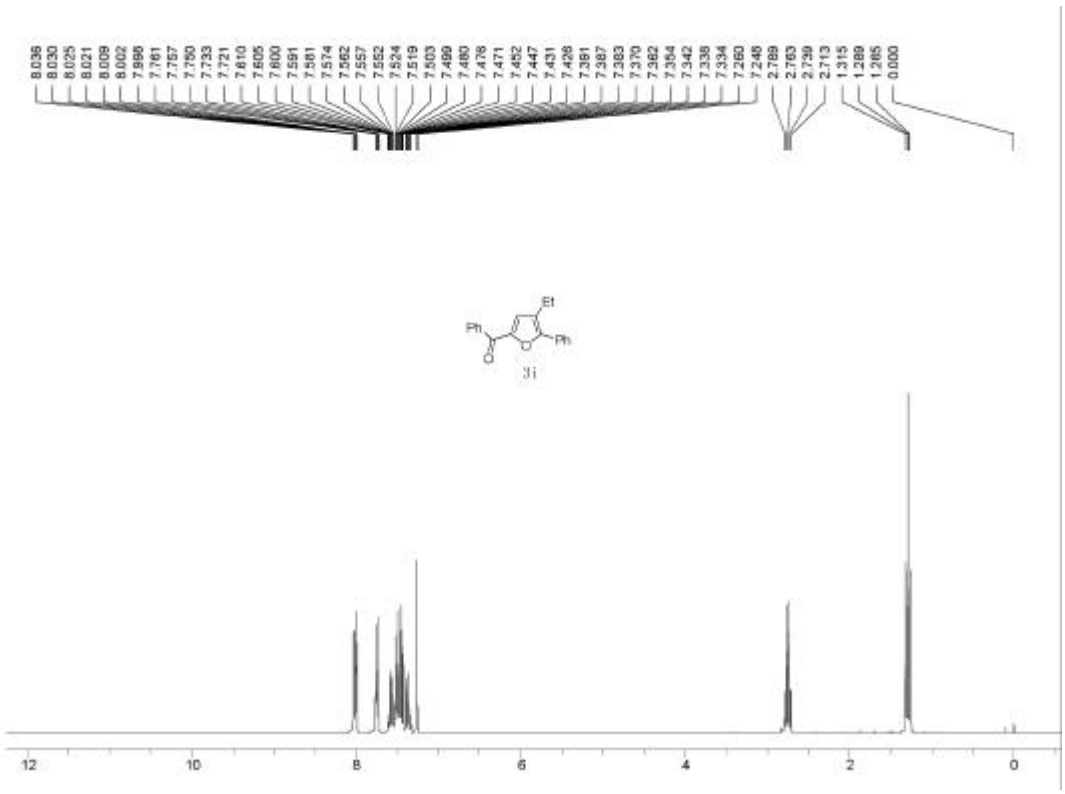

Ph
Et
Et
O
ppm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8.002
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7.761
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7.750
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7.721
7.610
7.605
7.600
7.591
7.581
7.574
7.562
7.557
7.552
7.524
7.519
7.503
7.499
7.480
7.476
7.471
7.452
7.447
7.431
7.428
7.391
7.387
7.383
7.370
7.362
7.354
7.342
7.336
7.334
7.260
7.246
2.789
2.763
2.739
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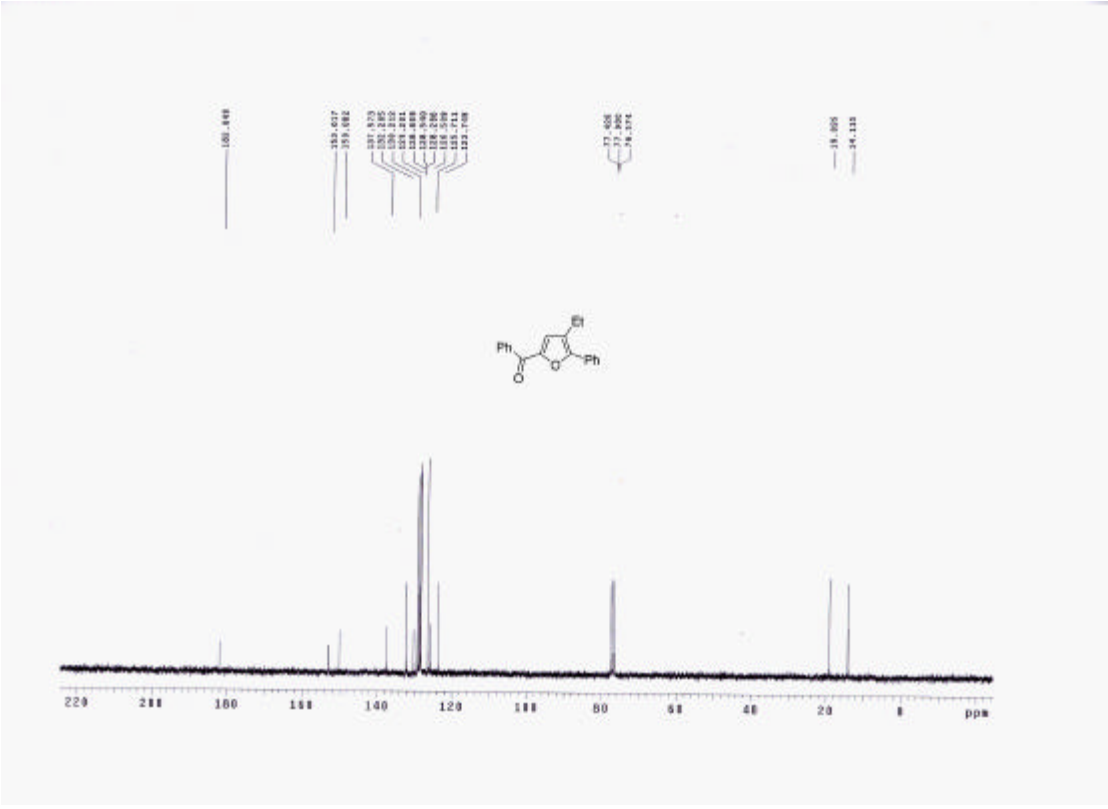
1.265
0.000
Et
Ph
Ph
O
3i
12
10
8
6
4
2
0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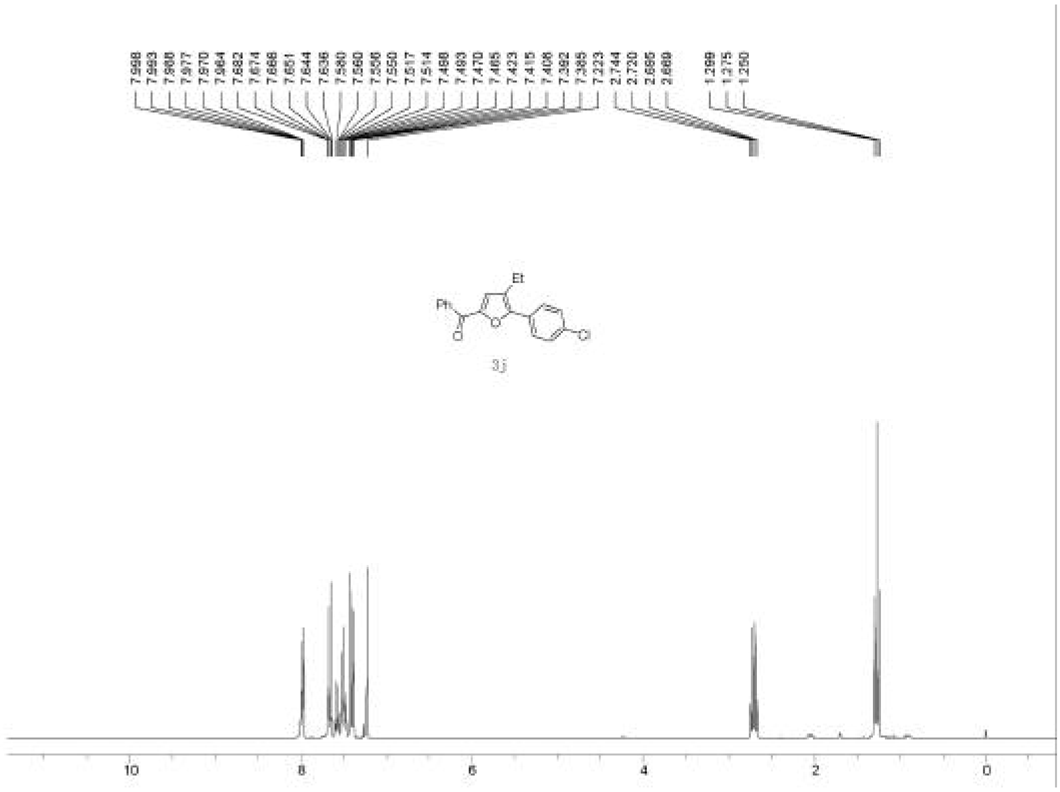
Ph
Ph
O
ppm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7.993
7.988
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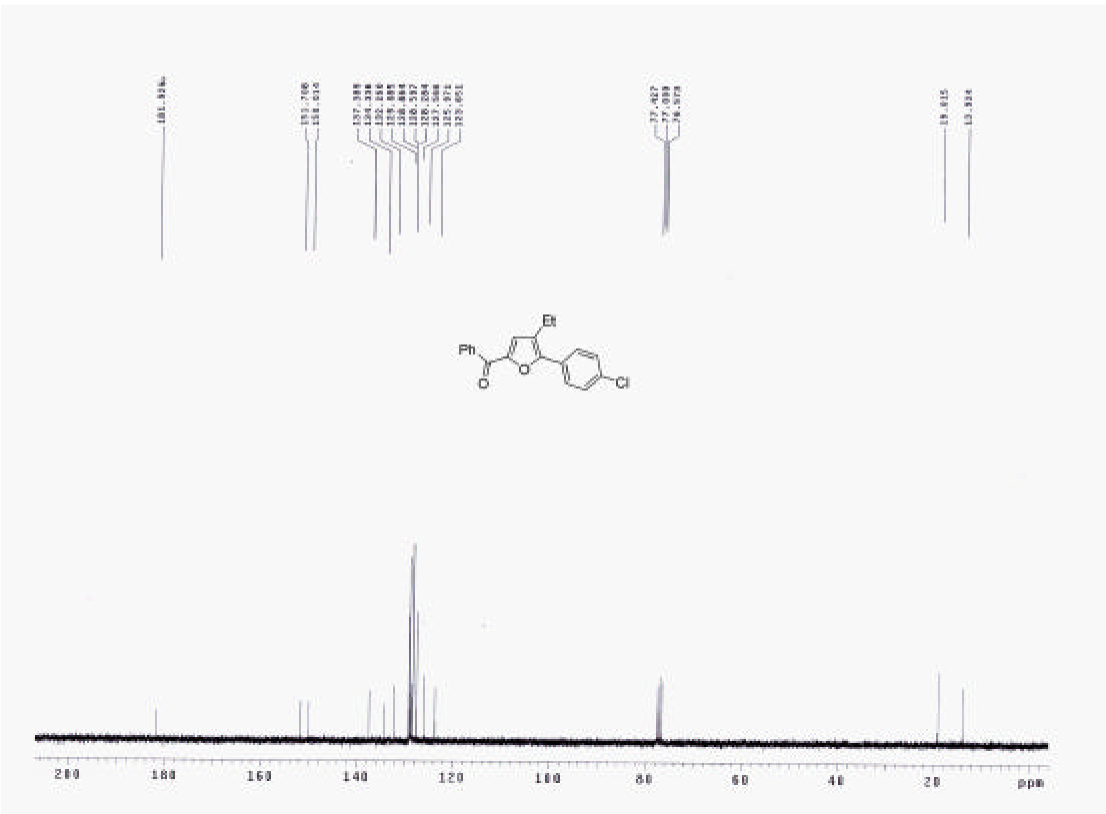
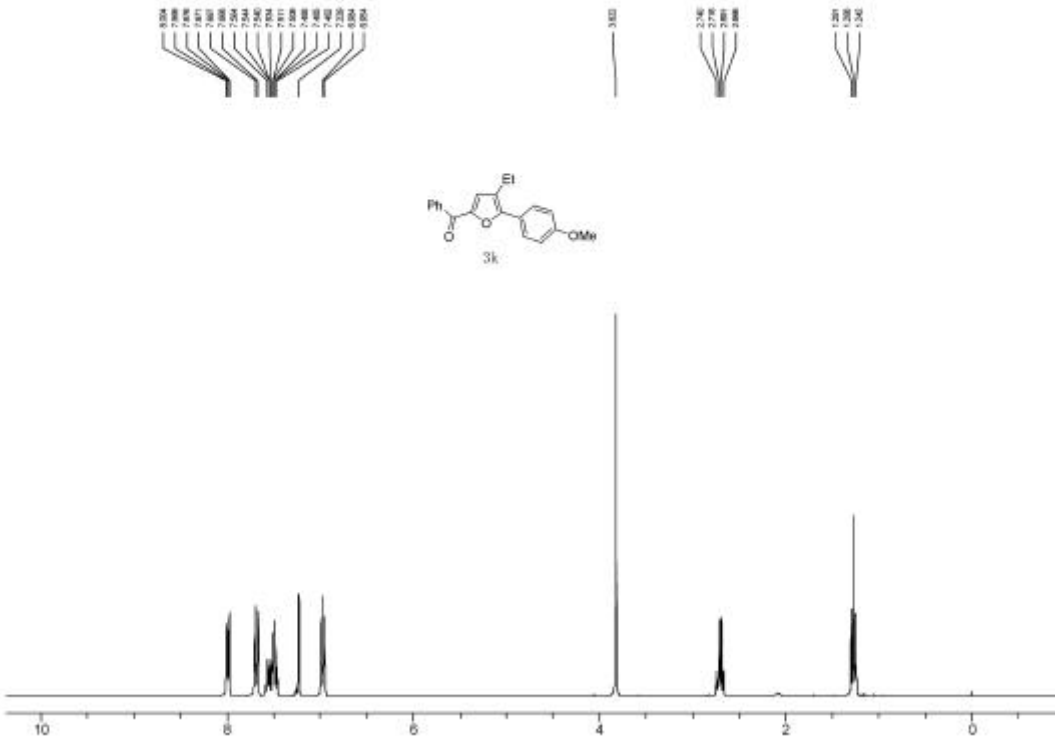
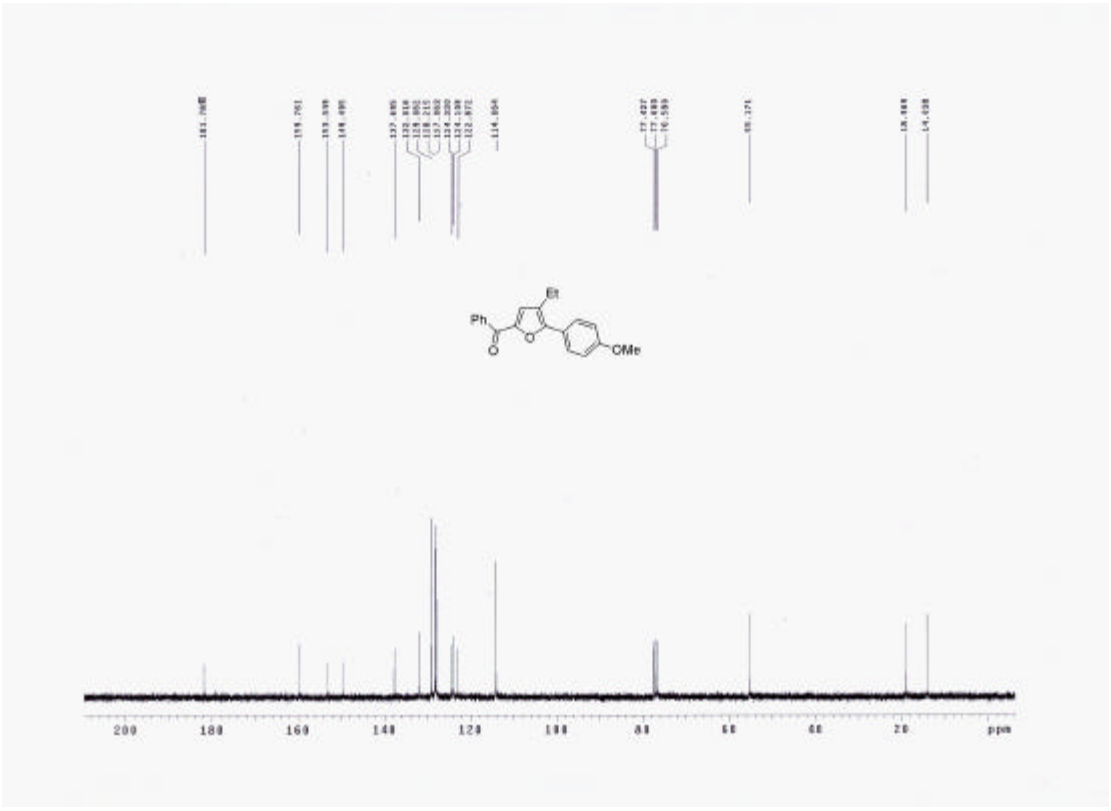
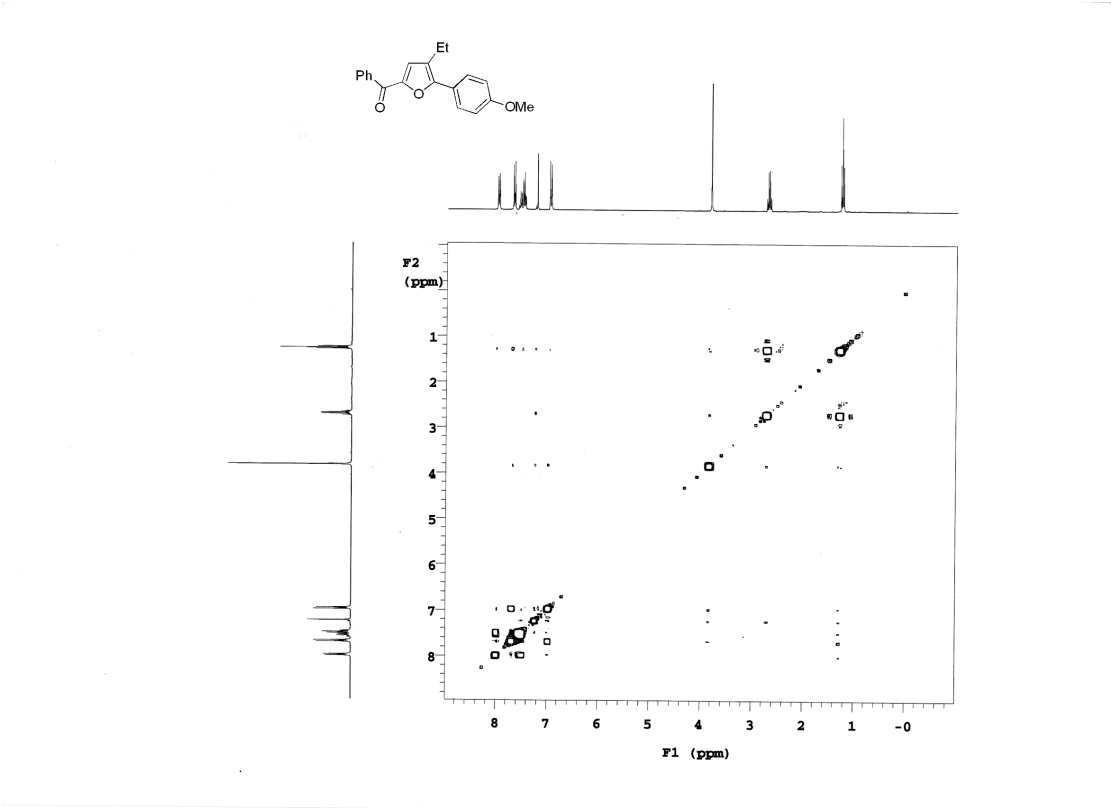
7.964
7.682
7.674
7.668
7.651
7.644
7.636
7.580
7.560
7.556
7.550
7.517
7.514
7.488
7.483
7.470
7.465
7.423
7.415
7.408
7.392
7.385
7.223
2.744
2.720
2.695
2.669
1.299
1.275
1.250
Et
Ph
O
O
Cl
10
8
6
4
2
0

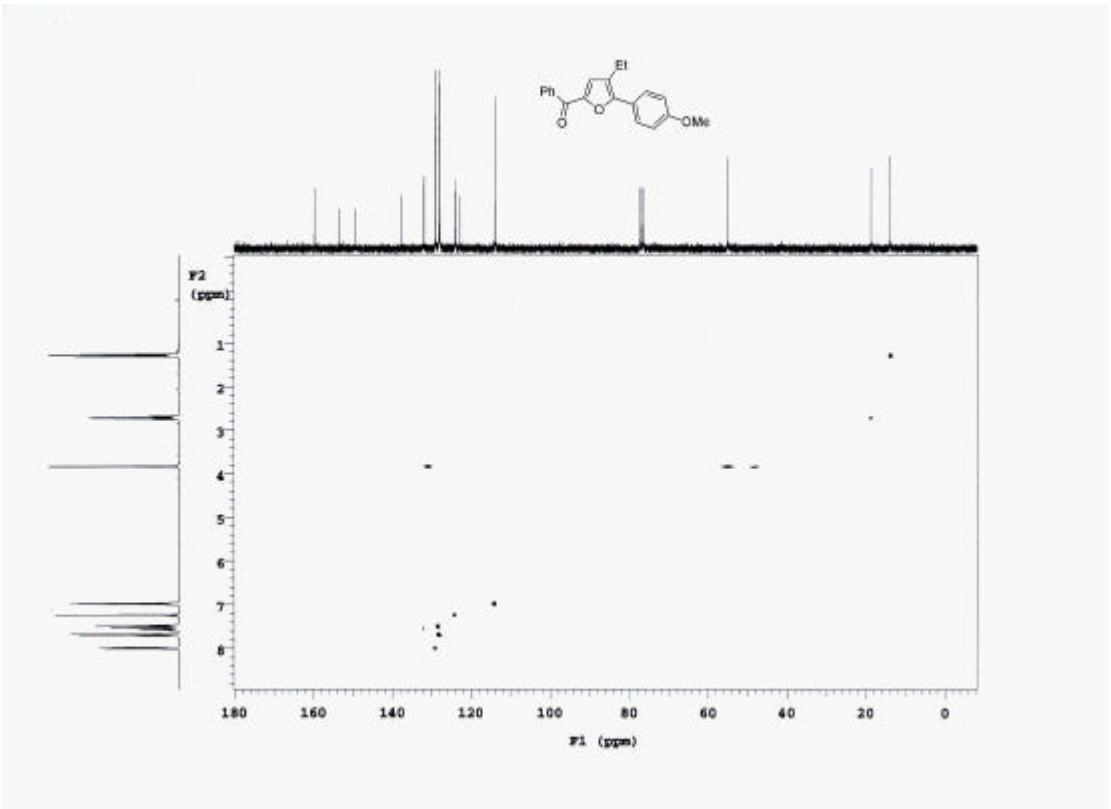
3j

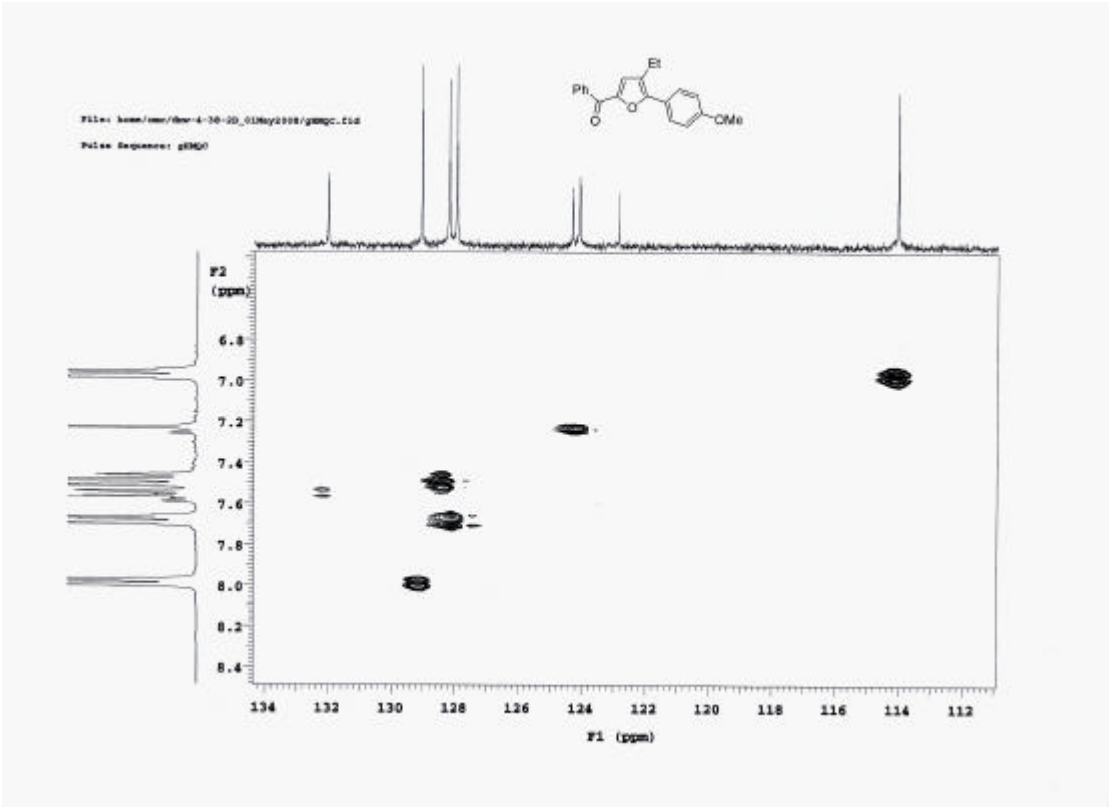

Et
Ph
O
O
Cl
200
180
160
140
120
100
80
60
40
20
ppm

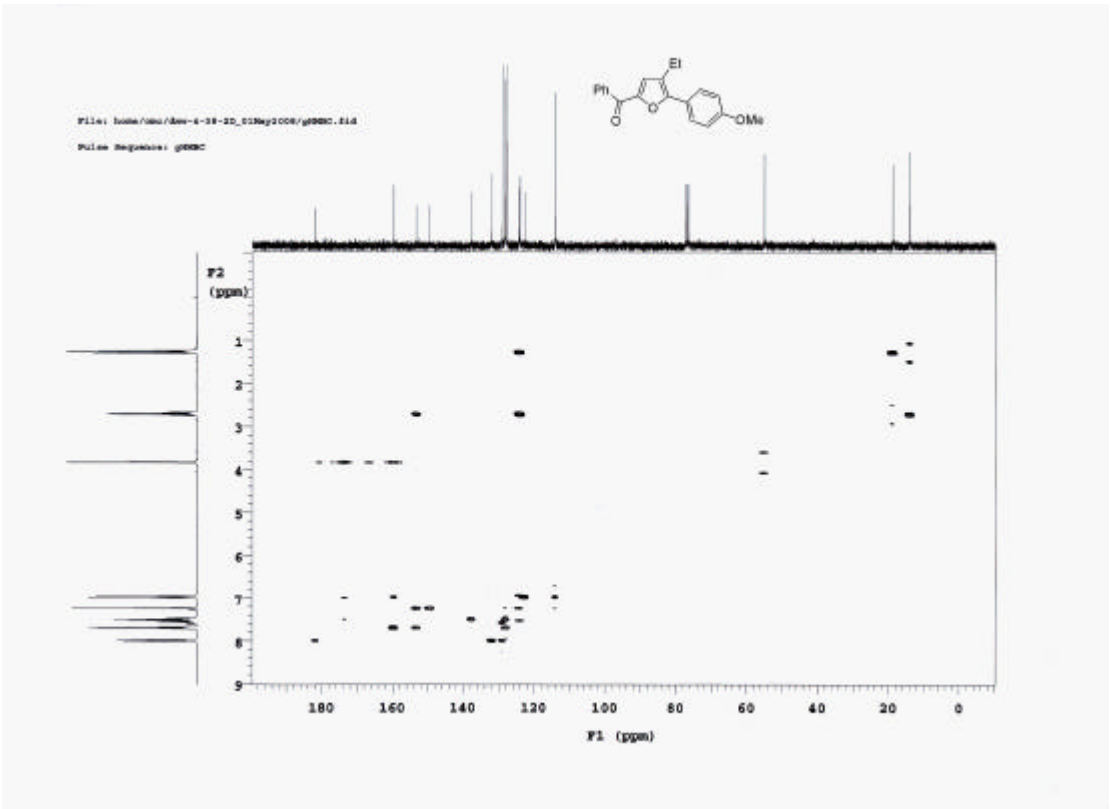

Et
Ph
O
OMe
3k
10
8
6
4
2
0

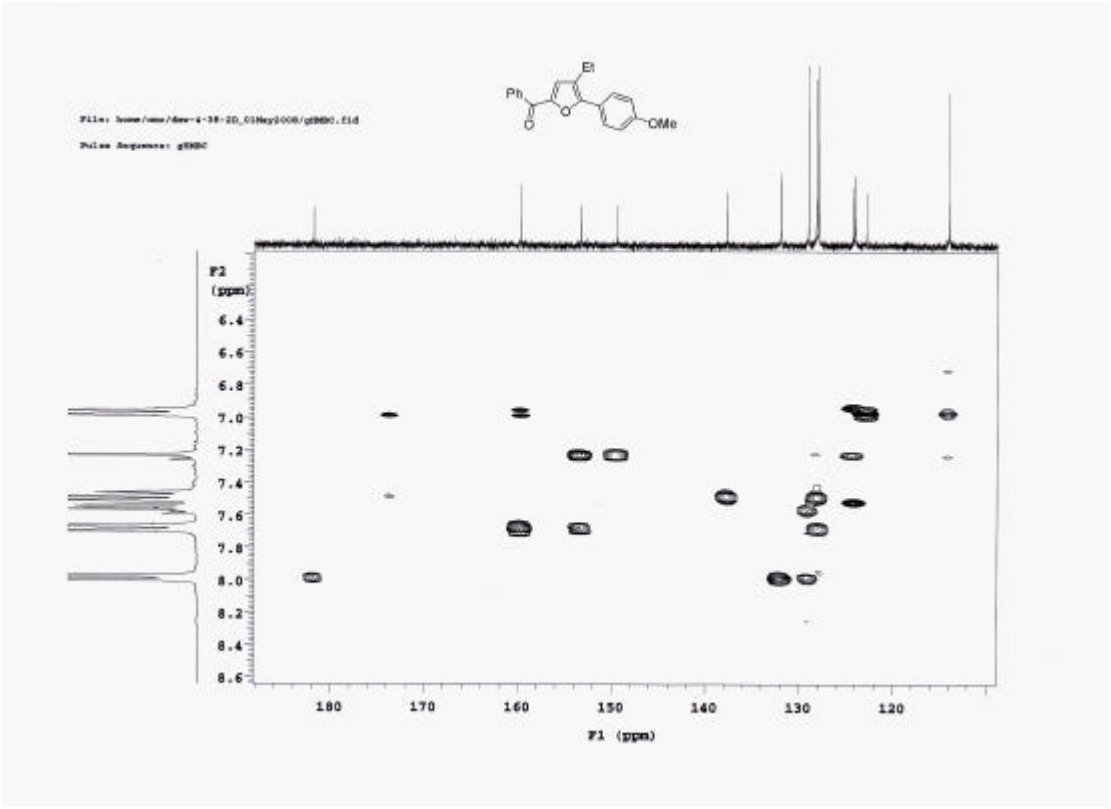

Et
Ph
O
OMe
200
180
160
140
120
100
80
60
40
20
ppm

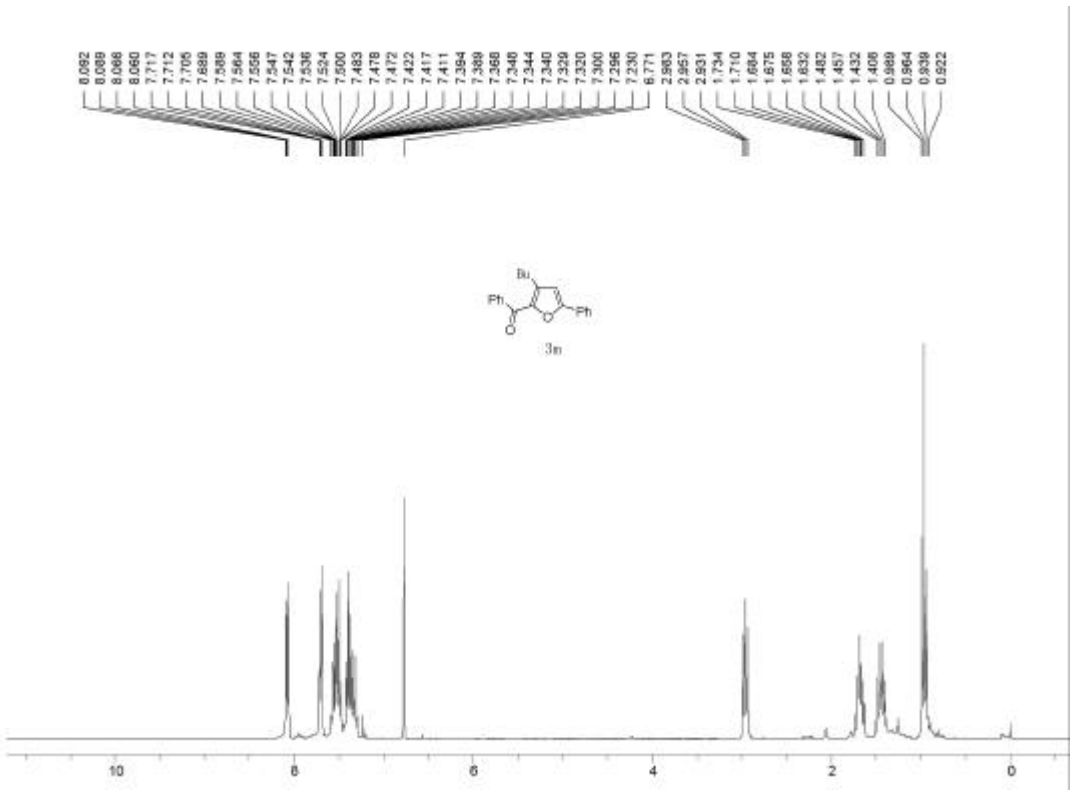

Et
Ph
O
OMe
F2
(ppm)
F1 (ppm)


Et
Ph
O
OMe
F2
(ppm)
F1 (ppm)


Et
Ph
O
OMe
F2 (ppm)
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
134
132
130
128
126
124
122
120
118
116
114
112
F1 (ppm)


Et
Ph
O
OMe
F2 (ppm)
1
2
3
4
5
6
7
8
9
180
160
140
120
100
80
60
40
20
0
F1 (ppm)


Et
Ph
O
OMe
F2
(ppm)
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
180
170
160
150
140
130
120
F1 (ppm)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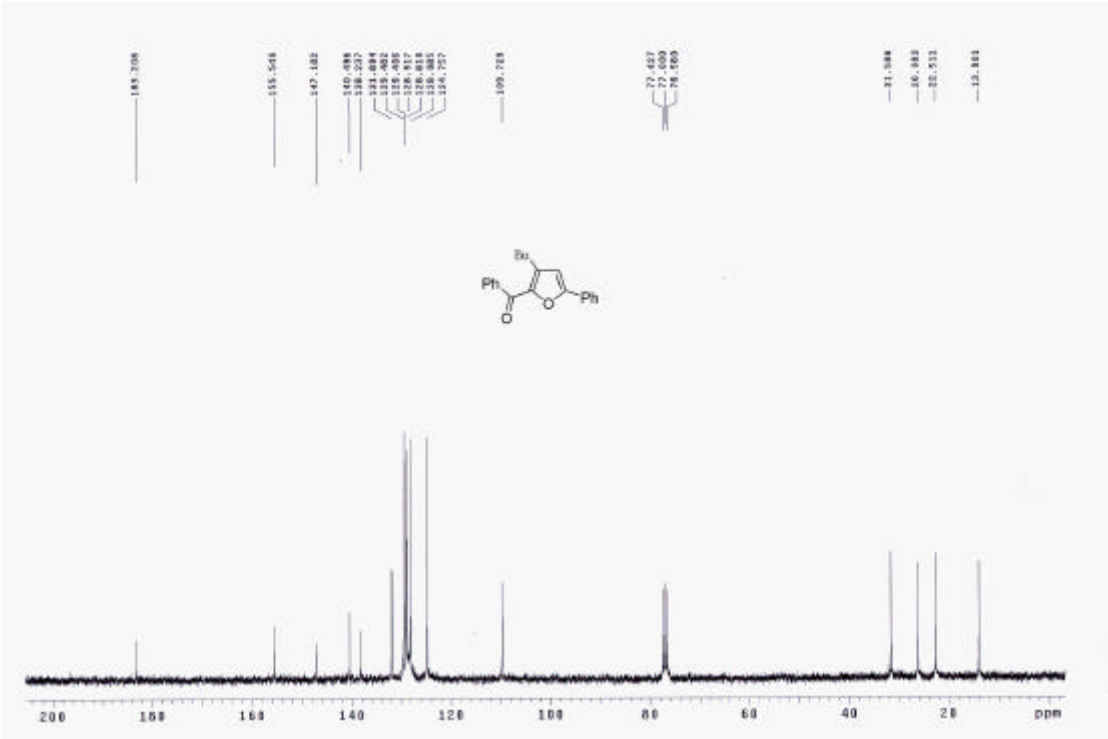
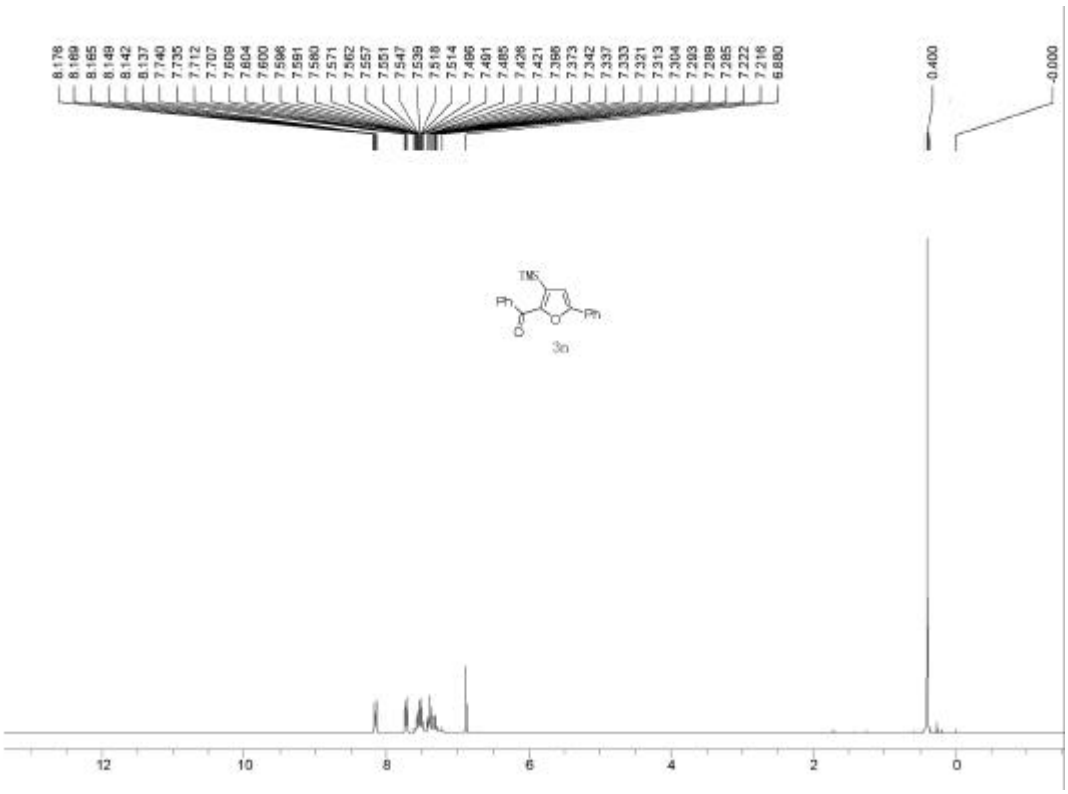
8.088
8.068
8.060
7.717
7.712
7.705
7.689
7.569
7.564
7.556
7.547
7.542
7.536
7.524
7.500
7.483
7.478
7.472
7.422
7.417
7.411
7.394
7.369
7.368
7.346
7.344
7.340
7.329
7.320
7.300
7.296
7.230
6.771
2.963
2.957
2.931
1.734
1.710
1.684
1.675
1.658
1.632
1.482
1.457
1.432
1.406
0.969
0.964
0.939
0.922
Bu
Ph
Ph
O
3m
10
8
6
4
2
0


185.209
155.549
147.183
140.488
138.227
131.684
129.482
128.486
126.617
126.558
126.085
124.757
109.728
77.427
77.000
76.569
31.588
30.883
22.533
13.861
Bu
Ph
Ph
O
200
160
160
140
120
100
80
60
40
20
ppm


8.176
8.169
8.165
8.149
8.142
8.137
7.740
7.735
7.712
7.707
7.609
7.604
7.600
7.586
7.591
7.580
7.571
7.562
7.557
7.551
7.547
7.539
7.518
7.514
7.496
7.491
7.485
7.426
7.421
7.398
7.373
7.342
7.337
7.333
7.321
7.313
7.304
7.293
7.289
7.285
7.222
7.216
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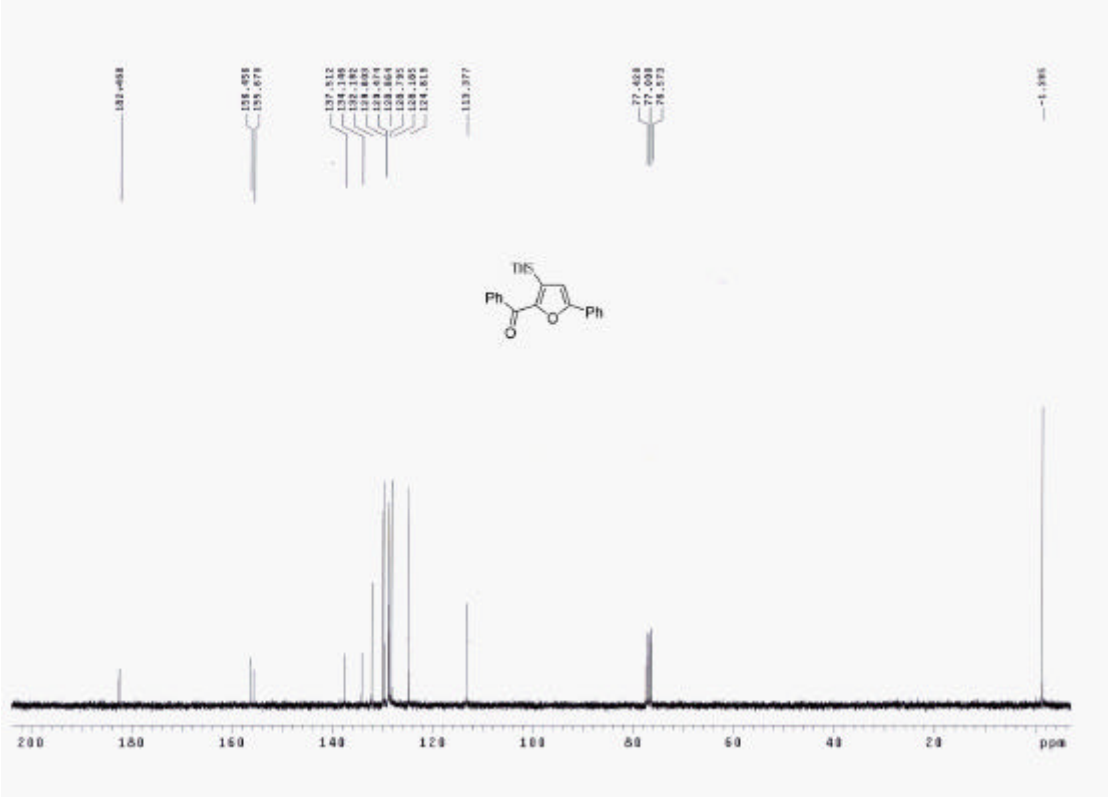
0.400
0.000
TMS
Ph
Ph
O
3o
12
10
8
6
4
2
0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155.079
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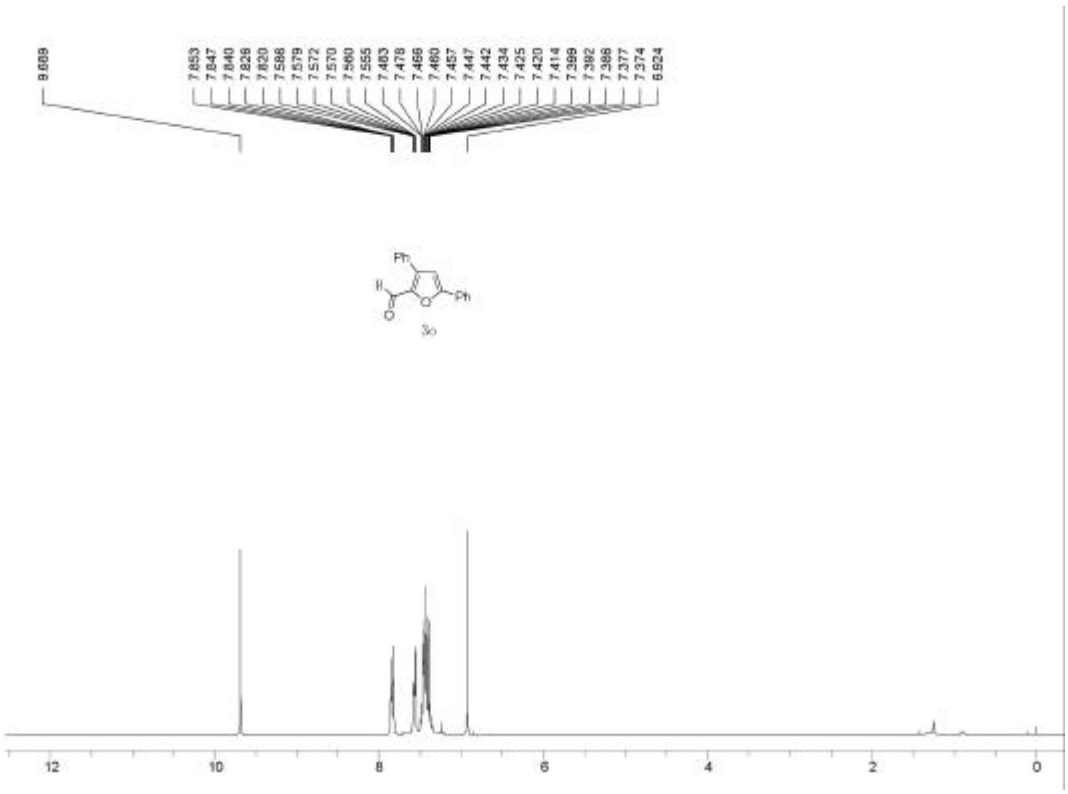
134.196
132.182
129.669
129.474
128.864
128.795
128.185
124.819
133.377
77.424
77.099
76.573
-1.395
TMS
Ph
Ph
O
200
180
160
140
120
100
80
60
40
20
ppm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7.847
7.840
7.826
7.820
7.586
7.579
7.572
7.570
7.560
7.555
7.483
7.478
7.466
7.460
7.457
7.447
7.442
7.434
7.425
7.420
7.414
7.389
7.382
7.377
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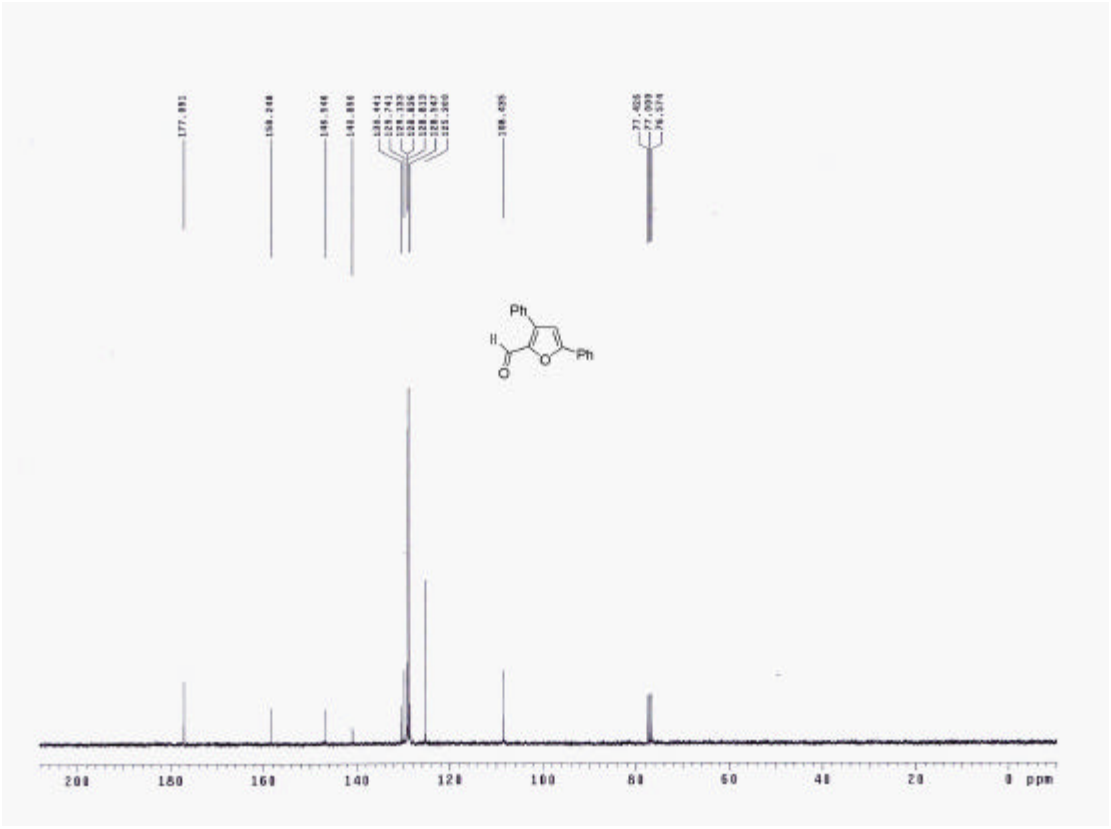
O
3o
12
10
8
6
4
2
0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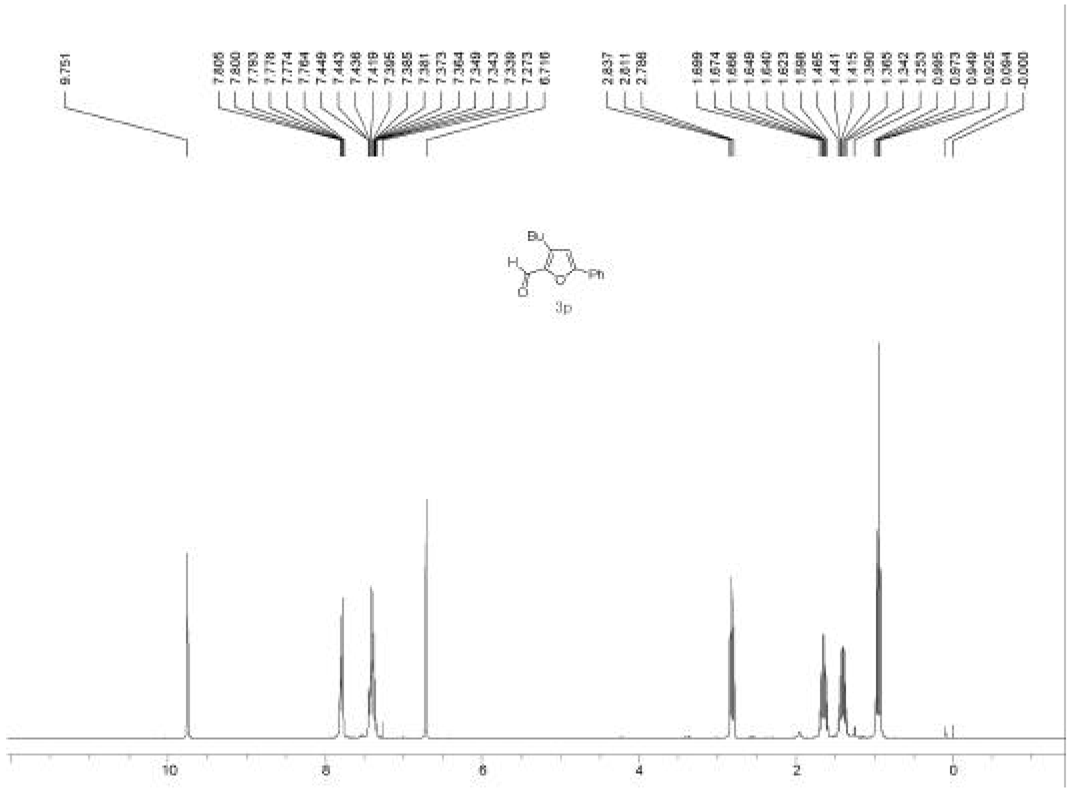
150.248
140.544
140.886
Ph
Ph
O
200
180
160
140
120
100
80
60
40
20
0 ppm



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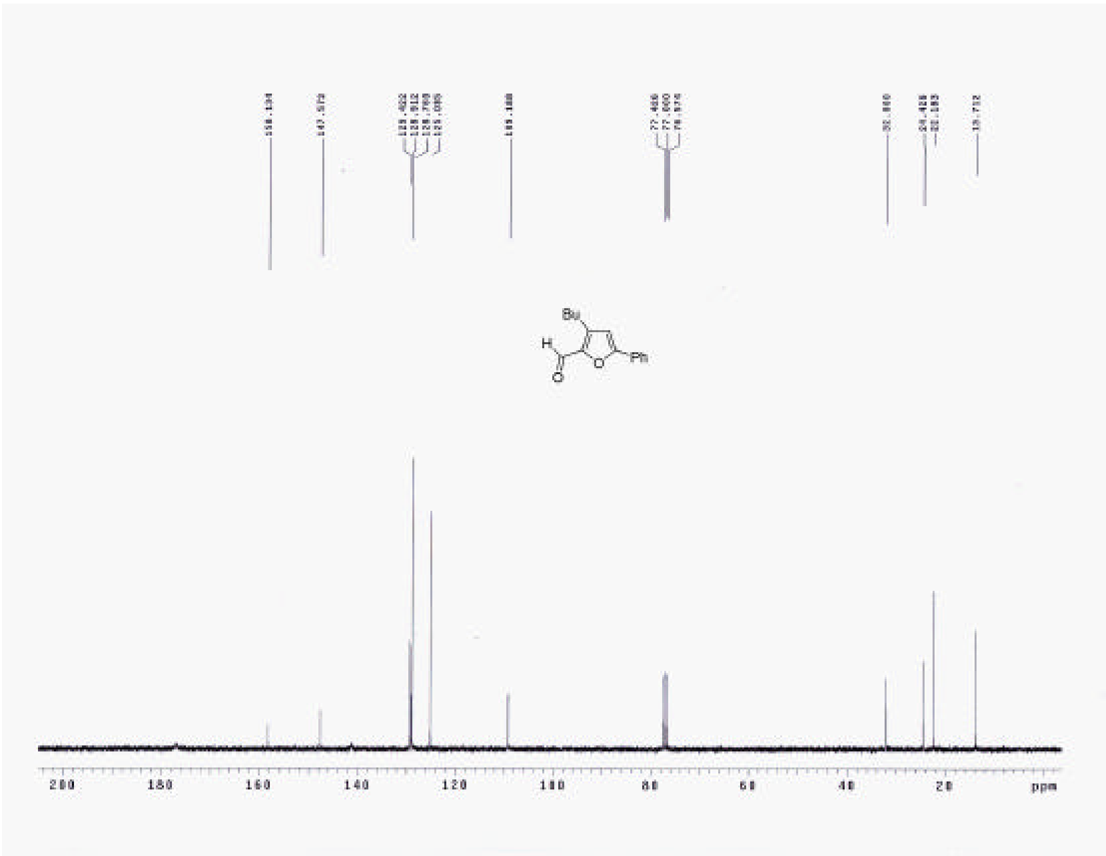
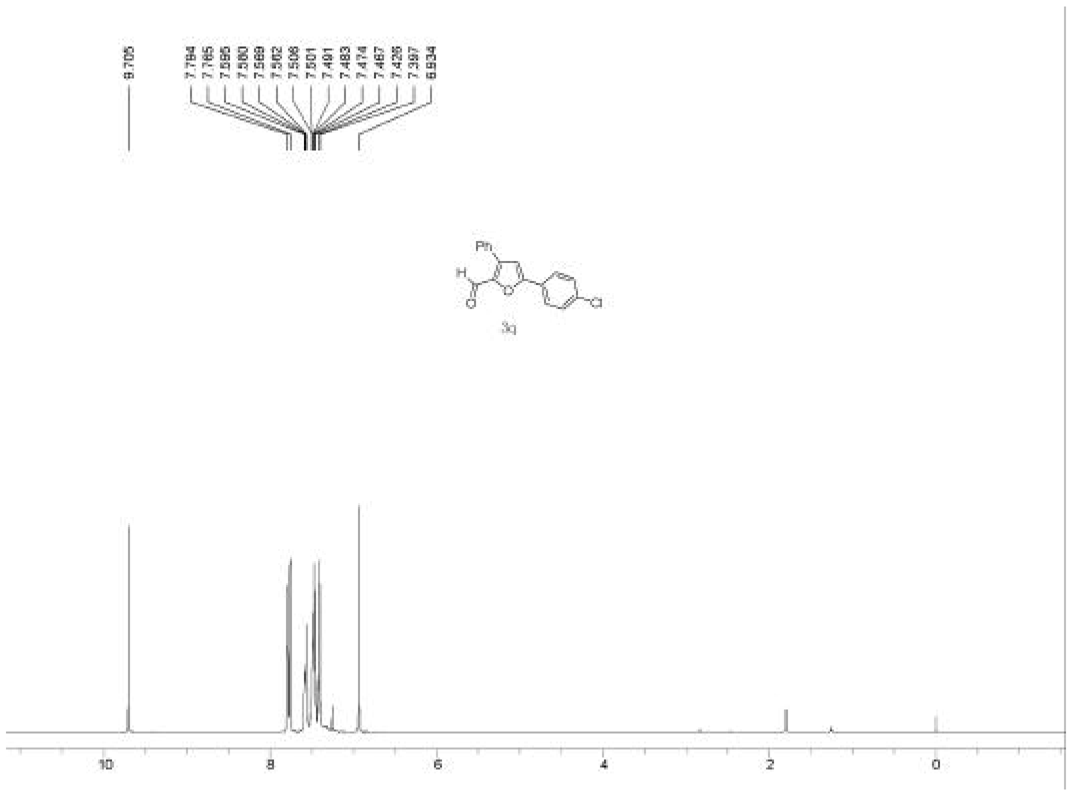
7.800
7.783
7.778
7.774
7.764
7.449
7.443
7.436
7.419
7.395
7.385
7.381
7.373
7.364
7.349
7.343
7.338
7.273
6.716
2.837
2.811
2.788
1.699
1.674
1.666
1.649
1.640
1.623
1.598
1.465
1.441
1.415
1.390
1.365
1.342
1.253
0.985
0.973
0.949
0.925
0.084
0.000
Bu
H
O
Ph
3p
10
8
6
4
2
0



Bu
H
O
Ph
200
180
160
140
120
100
80
60
40
20
ppm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7.569
7.562
7.506
7.501
7.491
7.483
7.474
7.467
7.426
7.397
6.934
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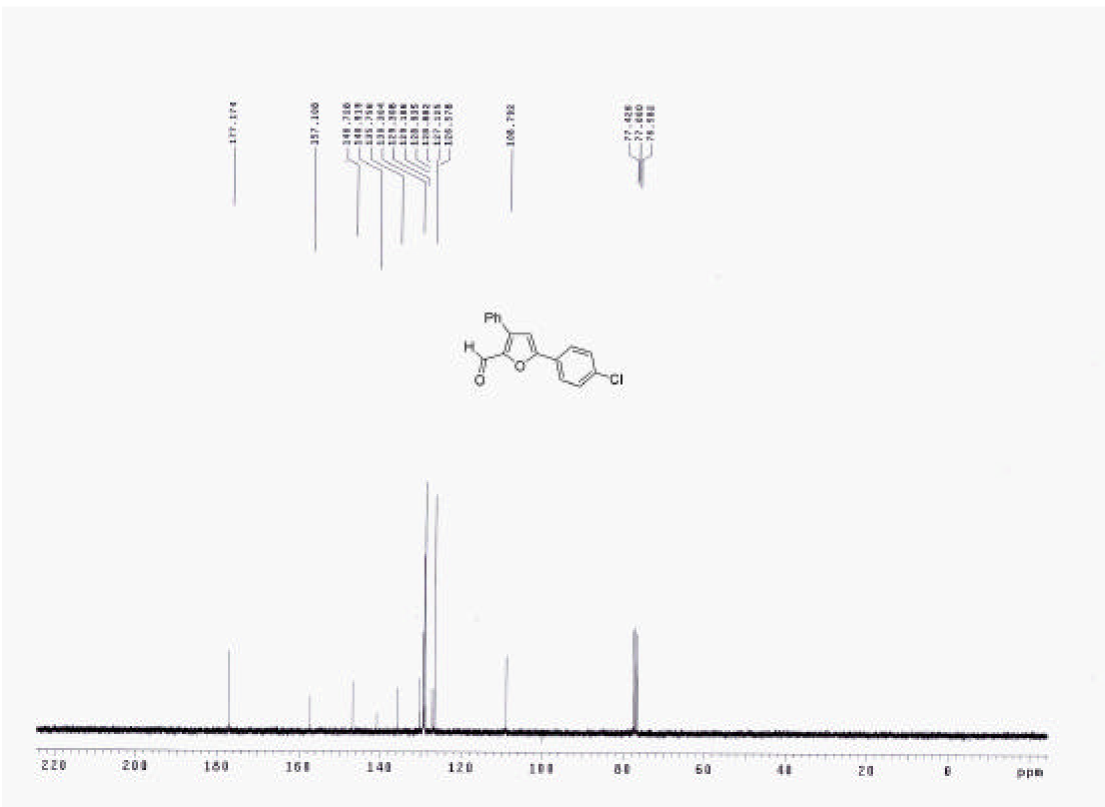
H
O
Cl
3q
10
8
6
4
2
0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H
O
Cl
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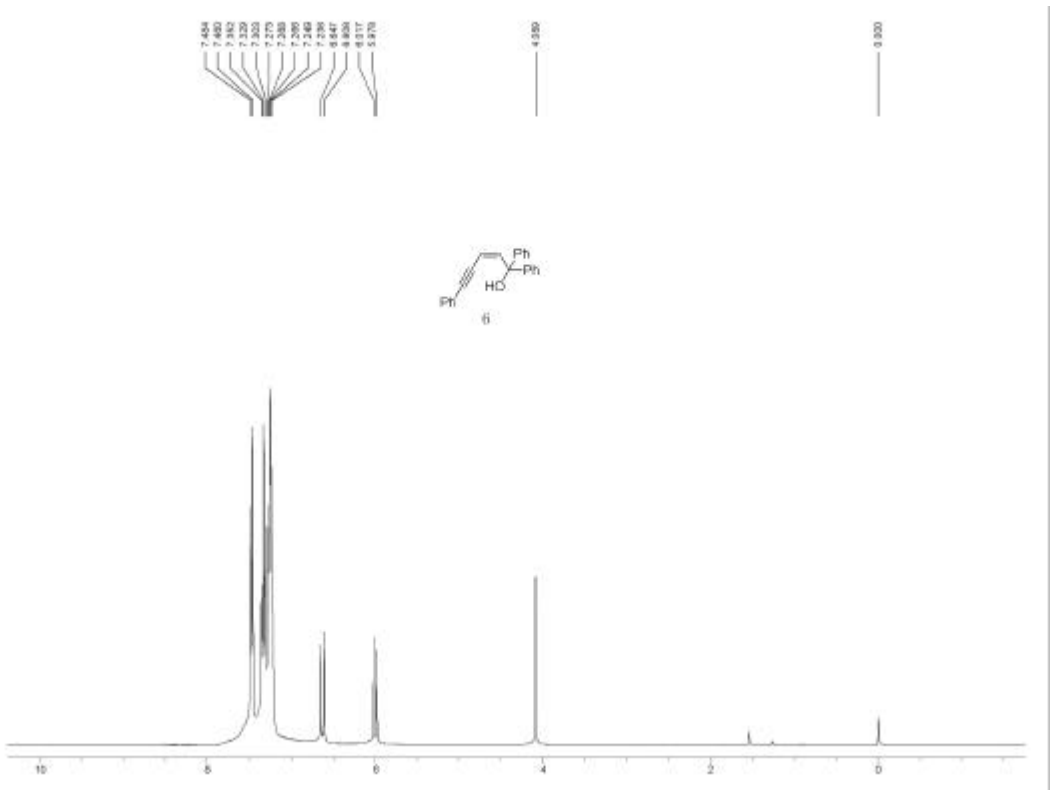
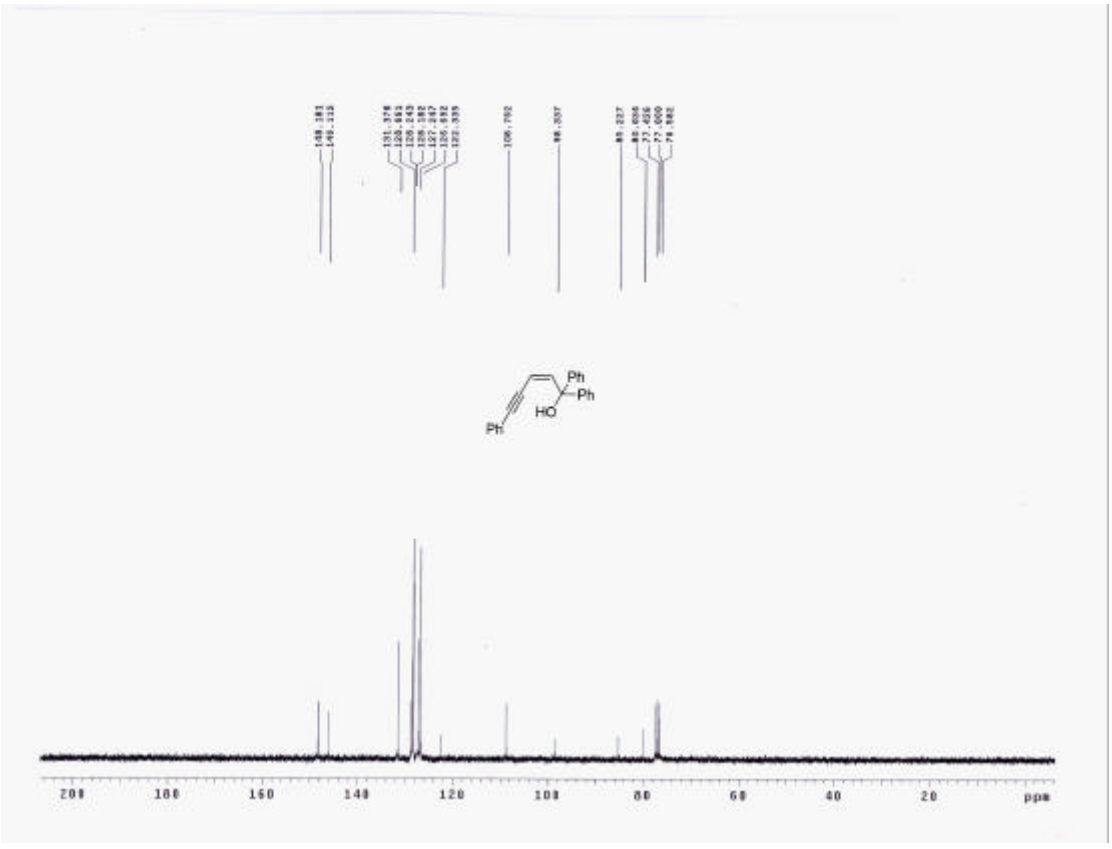
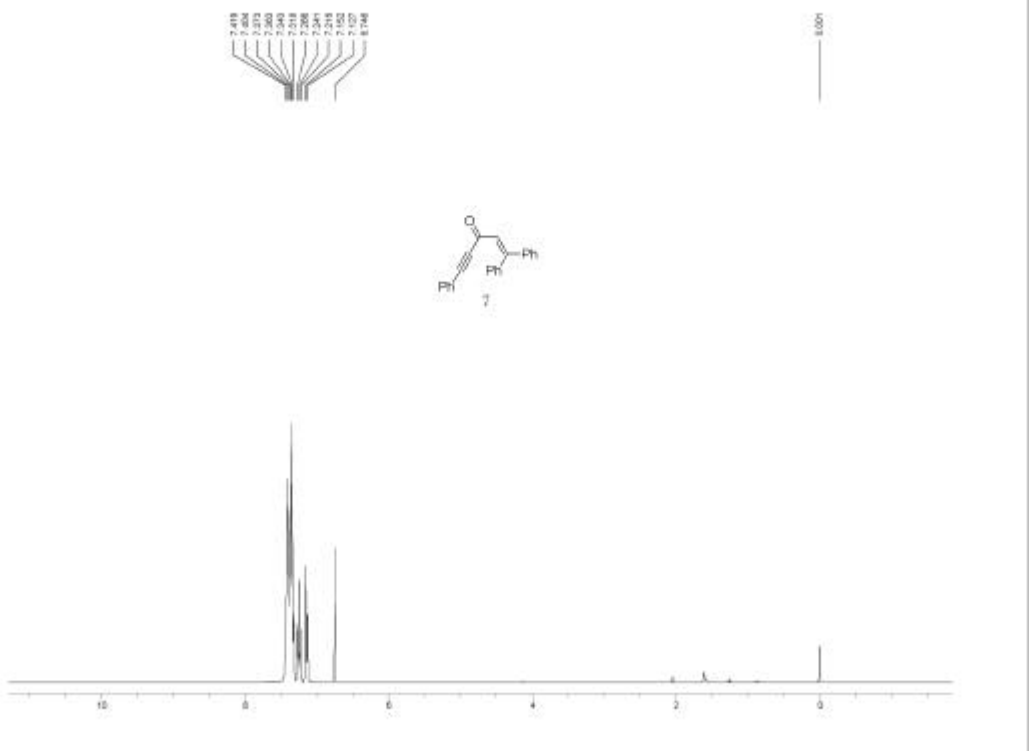
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
Ph
HO
Ph
6


Ph
Ph
HO
Ph
ppm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7.318
7.308
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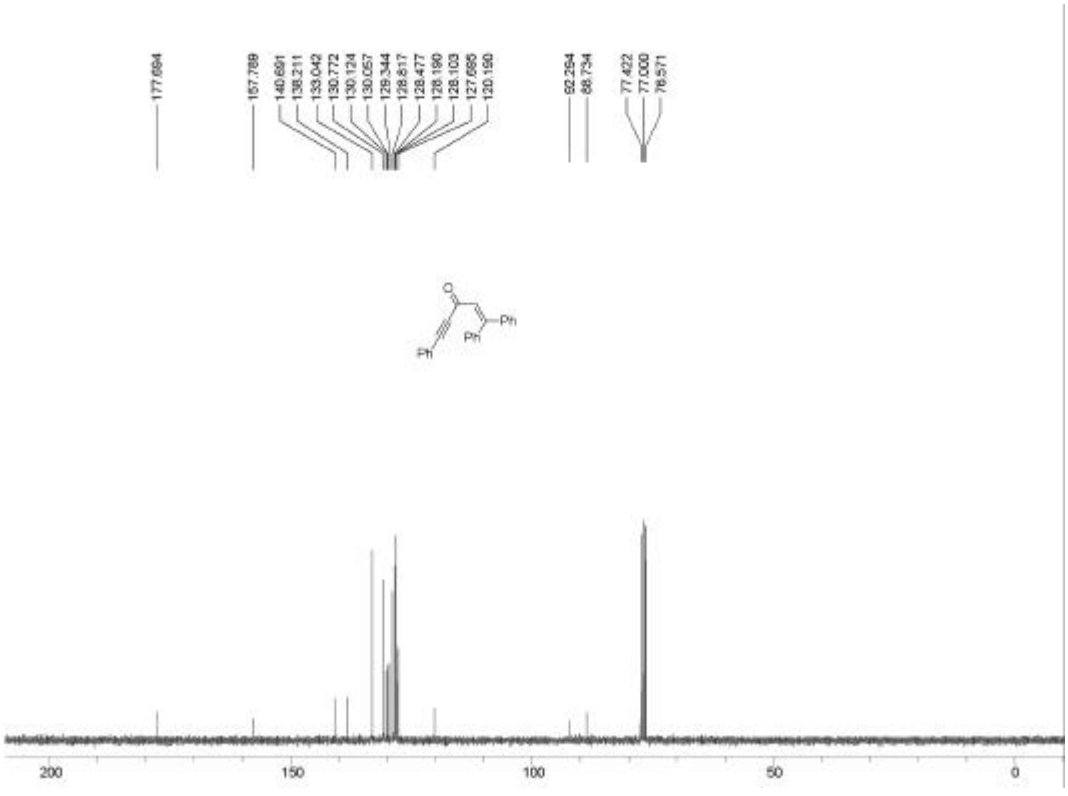
7.215
7.153
7.137
6.744
0.000
O
Ph
Ph
Ph
7
10
8
6
4
2
0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157.789
140.691
136.211
133.042
130.772
130.124
130.057
129.344
128.617
128.477
128.190
128.103
127.686
120.190
92.264
88.734
77.422
77.000
76.571
O
Ph
Ph
Ph
200
150
100
50
0