Supplementry Material (ESI) for Chemical Communications

Thermodynamic- and Kinetic-Controlled Friedel-Crafts Alkenylation of Arenes with Alkynes using an Acidic Fluoroantimonate(V) Ionic Liquid as Catalyst

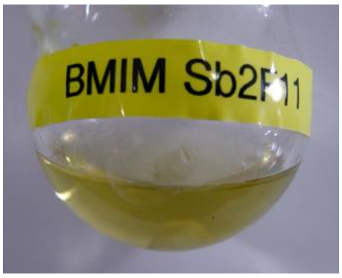
*Doo Seong Choi, Jin Hong Kim, Ueon Sang Shin, Ravindra R. Deshmukh, Choong Eui Song**
Department of Chemistry, Institute of Basic Science, Sungkyunkwan University, Suwon 440-746 Korea

PART 1: Experimental Procedures and Spectroscopic Data

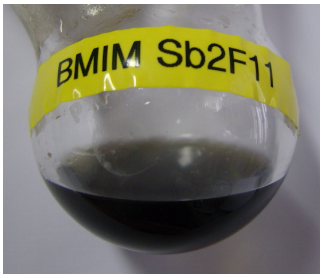
General Remarks. All reactions were performed in argon atmosphere using standard Schlenk techniques. Chromatographic purification of products was carried out by flash chromatography using Merck silica gel 60 (230-400 mesh). Thin layer chromatography was carried out on Merck silica gel 60F plates. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) and ^{19}F NMR (282 MHz) were recorded on Varian 300 spectrometers using TMS as an internal standard for ^{1}H and ^{13}C NMR or using $CFCl_3$ as an external standard for ^{19}F NMR. GC-MS analysis was performed using GC/MSD; Varian 4000. Ionic liquid, [bmim][SbF_6], was purchased from C-Tri Co., Ltd., Korea, www.c-tri.co.kr and used without further purification. It was nearly chloride-free (<10 ppm) and its water content was <50 ppm (determined by Karl-Fisher titration). Other organic solvents were dried (CaH_2 or Na) and distilled under argon atmosphere prior to use. All other chemicals were obtained from commercial sources and used without further purification. The stereochemistry of all adducts were assigned by comparison with literature NMR spectroscopic data.[a) C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura and Y. Fujiwara *Science*, 2000**, 287**, 1992-1995; b) C. Jia, W. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie and Y. Fujiwara, *J. Am. Chem. Soc.*, 2000, **122**, 7252-7263; c) C. Jia, T. Kitamura and Y. Fujiwara, *Acc. Chem. Res.*, 2001, **34**, 633-639; d) M.T. Reetz and K. Sommer, *Eur. J. Org. Chem.*, 2003**,** 3485-3496; e) Z. Shi and C. He, *J. Org. Chem.*, 2004**, 69**, 3669-3671; f) M. S. Viciu, E. D. Stevens, J. L. Petersen and S. P. Nolan, *Organometallics*, 2004, **23**, 3752] In case of new and uncharacterized compounds, E/Z-configuration was established on the basis of 1D differential NOE experiments.

Typical Procedure for the Preparation of 1

The superacidic fluoroantimonate ionic liquid (IL), [bmim][Sb_2F_{11}] (**1**), was prepared by mixing [bmim][SbF_6] (16.3 g, 46.3 mmol) and SbF_5 (10 g, 46.3 mmol) under an Ar atmosphere. SbF_5 was transferred to the dried [bmim][SbF_6] under Ar atmosphere over 10 min at 0 ^{o}C, affording the pale-yellow liquid **1**. However, the color of **1** changes from pale-yellow to violet with time. Thus, the direct use of freshly prepared **1** is advisable.



Freshly prepared 1



After 3 weeks

The resulting superacidic fluoroantimonate IL **1** was verified by different spectroscopic methods such as ^{1}H-, ^{13}C- and ^{19}F-NMR and FAB-MS (Note: During NMR experiment**,** the d_8-THF solvent used was fast polymerized due to the strong acidity of the catalyst**.** Therefore, quick NMR experiment was performed (within 10 min)). FAB-MS analysis showed that mainly SbF_6^- and $Sb_2F_{11}^-$ anions exist in the acidic IL **1**. The $Sb_3F_{16}^-$ anion was observed in a trace of amount.

^{1}H NMR (300 MHz, d_8-THF) δ 1.99 1.12 (t, J = 6.0 Hz, 3H), 1.53 (m, J = 6.0 Hz, 2H), 2.03 (m, J = 6.0 Hz, 2H), 4.07 (s, 3H), 4.36 (t, J = 6.0 Hz, 2H), 7.67 (s, 1H), 7.71 (s, 1H), 8.85 (s, 1H); ^{13}C NMR (75 MHz, d_8-THF) δ 14.09, 20.47, 33.06, 36.65, 50.57, 123.46, 124.86, 137.55; ^{19}F NMR (282 MHz, d_8-THF, $CFCl_3$ as external standard) δ -122.4 ppm (sextet, $J_{(F\text{-}Sb(I=5/2)}$ = 1954 Hz, octet, $J_{(F\text{-}Sb(I=7/2)}$ = 1039 Hz)

FAB-MS (the analysis was proceeded for anionic species without using any external matrix): m/z = 234.8 (100 %) and 236.8 (74 %) for $[SbF_6]^-$ anion; 428.8 (67 %), 430.7 (100 %) and 432.8 (37 %) for $[Sb_2F_9O]^-$ which might be formed due to the non-anhydrous analysis condition; 450.8 (67 %), 452.8 (100 %) and 454.8 (37 %) for $[Sb_2F_{11}]^-$ anion.

Typical Procedure for Thermodynamically Controlled Hydroarylations of Alkynes (Table 2)

Liquid Arenes (entry 5): Under an Ar atmosphere, 1-phenyl-1-propyne (116 mg, 1 mmol) was added to a mixture of *p*-xylene (6 mL) and [bmim][Sb_2F_{11}] (29 mg, 0.05 mmol). The mixture was stirred at 90 °C until the disappearance of alkyne, as monitored by TLC or GC. After cooling to RT, the reaction mixture was poured into a saturated NaCl aqueous solution and extracted with ethyl acetate. The organic layer was washed with saturated NaCl aqueous solution, and dried over anhydrous $MgSO_4$. The solvent was removed in a vacuum, and the residue was purified by flash column chromatography on silica (hexane) to give 198 mg (89 %) of pure 1-phenyl-1-(*p*-xylyl)-1-propene in *E*/*Z* ratio of 7/93 as a white solid.

Solid Arenes (entry 13): Under an Ar atmosphere, 3-butyn-2-one (68 mg, 1 mmol) was added to a mixture of pentamethylbenzene (148 mg, 1 mmol) in dichloroethane (4 mL) and [bmim][Sb_2F_{11}] (29 mg, 0.05 mmol). The reaction mixture was stirred until the disappearance of alkyne, as monitored by TLC or GC. After cooling to RT, the reaction mixture was poured into a saturated NaCl aqueous solution and extracted with ethyl acetate. The organic layer was washed with saturated NaCl aqueous solution, and dried over anhydrous $MgSO_4$. The solvent was removed in a vacuum, and the residue was purified by flash column chromatography on silica (hexane) to give 141 mg (65 %) of pure 4-(pentamethylphenyl)-3-buten-2-one in *E*/*Z* ratio of 94/6.

Typical Procedure for Kinetically Controlled Hydroarylations of Alkynes (Table 3)

Entry 5: Under an Ar atmosphere, 1,2-diphenylacetylene (178.2 mg, 1 mmol) was added to a mixture of pentamethylbenzene (296 mg, 2 mmol.) and [bmim][Sb_2F_{11}] (118 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) at -25 °C. The mixture was stirred at -25 °C until the disappearance of alkyne, as monitored by TLC or GC. A mixture of saturated NaCl aqueous solution and pyridine was poured into the reaction mixture and the organic phase was extracted with ethyl acetate. The organic layer was again washed with saturated NaCl aqueous solution, and dried over anhydrous $MgSO_4$. The solvent was removed in a vacuum, and the residue was purified by flash column chromatography on silica (hexane) to give 284 mg (87 %) of pure (*E*)-1,2-diphenyl-1-pentamethylphenylethane in E/Z ratio of 91/9.

[a]Detailed experimental conditions in Table 3

The kinetically controlled hydroarylation reactions for entry 1-3 were carried out with an alkyne (1 mmol), an arene (3.6 mmol), and **1** (20 mol %). 1 mmol and 2 mmol arene was used for entry 4 and 5, respectively. For all the kinetically controlled hydroarylation reactions, CH_2Cl_2 as a cosolvent was used. For example, 2 mL CH_2Cl_2 was used for entries 1, 4 and 5, and 0.2 mL for entry 2 and 0.5 ml for entry 3.

Spectroscopic Data for the Products in Table 1

1-(*p*-Chlorophenyl)-1-(*p*-xylyl)ethene (entry 5): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 3H), 2.33 (s, 3H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.71 (d, *J* = 1.2 Hz, 1H), 7.01 – 7.25 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.99, 21.31, 115.52, 128.22, 128.83, 128.88, 130.50, 131.02, 133.25, 133.78, 135.62, 139.60, 141.35, 148.94.

1-(*p*-Trifluoromethylphenyl)-1-(*p*-xylyl)ethane (entry 9): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.34, (s, 3H), 5.38 (d, *J*= 1.1 Hz, 1H), 5.80 (d, *J* = 1.1 Hz, 1H), 7.02 – 7.58 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.10, 21.38, 116.82, 123.50 (q, ^3J(C-C-C-F) = 3.8 Hz), 124.65 (q, ^1J(C-F) = 272.4 Hz), 124.67 (q, ^3J(C-C-C-F) = 3.8 Hz), 129.12, 129.28, 130.39, 130.69, 131.16, 131.31 (q, ^2J(C-C-F) = 32.0 Hz), 133.26, 135.83, 140.96, 142.05, 149.00.

Spectroscopic Data for the Products in Table 2

1,1-Diphenylethene (entry 1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45 (s, 2H), 7.29-7.35 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 114.76, 128.16, 128.61, 128.72, 141.92, 150.48.

1-(*p*-Chlorophenyl)-1-phenylethene (entry 2): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.44 (d, *J* = 0.9 Hz, 1H), 5.46 (d, *J* = 0.9 Hz, 1H), 7.20-7.42 (m, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 114.93, 128.15, 128.41, 128.49, 128.57, 129.78, 133.80, 140.16, 141.23, 149.19.

1-Phenyl-1-(*p*-Trifluoromethylphenyl)ethene (entry 3): ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.51 (d, *J* = 0.9 Hz, 1H), 5.56 (d, *J* = 0.9 Hz, 1H), 7.27-7.64 (m, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 116.2, 124.4, 125.4 (q, ^{3}*J*(C-C-C-F) = 3.8 Hz), 128.33, 128.39, 128.61, 128.79, 129.9(q, ^{2}*J*(C-C-F) = 32.2 Hz), 140.8, 145.3(q, ^{4}*J*(C-C-C-C-F) = 1.2 Hz), 149.1 (q, ^{1}*J*(C-F) = 271.0 Hz).

1-Phenyl-1-(*p*-xylyl)ethene (entry 4): ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.99 (s, 3H), 2.30 (s, 3H), 5.16 (d, *J* = 1.4 Hz, 1H), 5.73 (d, *J* = 1.4 Hz, 1H), 7.04-7.28 (m, 8H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 20.12, 21.42, 115.13, 127.00, 128.01, 128.71, 128.81, 130.49, 131.17, 133.43, 135.53, 141.16, 141.97, 150.09.

(*Z*)-1-Phenyl-1-(*p*-xylyl)-1-propene (entry 5): ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.59 (d, *J* = 9.0 Hz, 3H), 2.03 (s, 3H), 2.30 (s, 3H), 6.27 (q, *J* = 9.0 Hz ,1H), 6.82-7.35(m, 7H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 15.78, 19.36, 21.32, 123.92, 126.40, 126.89, 128.14, 128.51, 129.76, 130.21, 130.92, 133.70, 135.36, 139.41, 141.83.

(*Z*)-1,2-Diphenyl-1-(*p*-xylyl)ethene (entry 6): ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.99 (s, 3H), 2.27 (s, 3H), 6.94-7.32 (m, 14H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 19.43, 21.31, 126.91, 127.16, 127.61, 128.28, 128.40, 128.63, 128.68, 129.28, 130.68, 130.77, 133.57, 136.07, 137.65, 139.76, 141.65, 142.74.

1-Mesityl-1-phenylethene (entry 7): ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.11 (s, 6H), 2.31 (s, 3H), 5.09 (d, *J* = 1.4 Hz, 1H), 5.95 (d, *J* = 1.4 Hz, 1H), 6.90 (s, 2H), 7.19 – 7.28 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 20.1, 21.1, 114.5, 125.8, 127.5, 128.1, 128.4, 136.1, 136.4, 138.2, 139.6, 146.9.

1-(*p*-Chlorophenyl)-1-mesitylethene (entry 8): ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.09 (s, 6H), 2.31 (s, 3H), 5.10 (d, *J* = 1.2 Hz, 1H), 5.93 (d, *J* = 1.2 Hz, 1H), 6.90 (s, 2H), 7.17 – 7.24 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 20.0, 21.0, 115.0, 127.1, 128.2, 128.6, 133.4, 136.0, 136.7, 137.6, 138.0, 145.8.

1-Mesityl-1-(*p*-trifluoromethylphenyl)ethene (entry 9) ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.09 (s, 6H), 2.31 (s, 3H), 5.21 (d, *J* = 1.2 Hz, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 6.92 (s, 2H), 7.32 – 7.54 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 20.39, 21.52, 117.1, 124.5 (q, ^{1}*J*(C-F) = 271.0 Hz), 125.7 (q, ^{3}*J*(C-C-C-F) = 3.8 Hz), 126.3, 128.6, 129.75 (q, ^{2}*J*(C-C-F) = 32.2 Hz), 136.3, 137.2, 137.5, 143.3 (q, ^{4}*J*(C-C-C-C-F) = 1.2 Hz), 146.0.

(*E*)-4-Mesityl-3-buten-2-one (entry 10): ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.29 (s, 3H, CH$_3$), 2.33 (s, 6H, 2CH$_3$), 2.38 (s, 3H, CH$_3$), 6.33 (d, *J*=16.5 Hz, 1H), 6.90(s, 2H), 7.67(d, *J* =16.5 Hz, 1H); ^{13}C NMR (75MHz, CDCl$_3$) δ 21.31, 21.35, 27.70, 129.49, 131.09, 132.62, 137.04, 138.79, 142.26, 198.80.

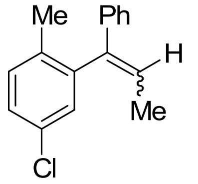
(*Z*)-1-Mesityl -1-phenyl-1-propene (entry 11): ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.53 (d, *J* = 6.0 Hz, 3H), 2.04 (s, 6H), 2.32 (s, 3H), 6.36 (q, *J* = 6.0 Hz, 1H), 6.91 (s, 2H), 7.11 – 7.32 (m, 5H); ^{13}C NMR (75 MHz) δ 15.35, 20.05, 21.44, 123.67, 125.85, 126.91, 128.46, 128.64, 135.90, 136.54, 136.57, 140.16, 140.77.

(*Z*)-1,2-Diphenyl-1-mesitylethene (entry 12): ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.00 (s, 6H), 2.34 (s, 3H), 6.87 – 7.34 (m, 13H); ^{13}C NMR (75MHz, CDCl$_3$) δ 20.05, 21.45, 126.24, 127.19, 127.51, 128.30, 128.46, 128.66, 128.69, 128.95, 136.13, 136.27, 137.11, 137.71, 140.03, 141.75.

(*E*)-4-(Pentamethylphenyl)-3-buten-2-one (entry 13): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22-2.23 (s, 12H), 2.26 (s, 3H), 2.39 (s, 3H), 6.15 (d, *J*=16.5 Hz, 1H), 7.73(d, *J*=16.5 Hz, 1H); ^{13}C NMR (75MHz, CDCl3) δ 16.43, 16.85, 17.88, 27.33, 131.03, 132.57, 132.79, 133.80, 135.27, 145.05, 198.25.

1-(*p*-Chlorotoluyl)-1-phenylpropene (entry 14): The reaction gave two sets of total 4 isomers where, the top spot contain the mixture of two inseparable *ortho* (to methyl group*)-Z* and *o-E* isomers and the bottom spot contain the mixture of two inseparable *meta* (to methyl group*)-Z* and *m-E* isomers. The isomers were identified by NOE experiment and the ratio was determined by ^{1}H NMR analysis.

Top spot: *E/Z*-mixture of *ortho*-isomers to the methyl group of *p*-chlorotoluene (Rf value on TLC in Hexane = 0.35).

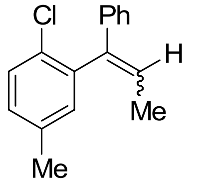


(*Z*)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (d, *J* = 9.0 Hz, 3H), 2.06 (s, 3H), 6.33 (q, *J* = 9.0 Hz, 1H), 7.08-7.30 (m, 8H).

(*E*)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93 (d, *J* = 6.0 Hz, 3H), 1.98 (s, 3H), 5.81(q, *J* = 6.0 Hz, 1H), 7.08-7.30 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) of the top spot: δ 15.70, 19.20, 124.74, 126.26, 127.13, 127.42, 128.24, 128.57, 129.63, 130.05, 131.50, 131.62, 135.46, 140.61, 140.93, 141.24.

Bottom spot: *E/Z*-mixture of *meta*-isomers to the methyl group of *p*-chlorotoluene (Rf value on TLC in Hexane = 0.33).



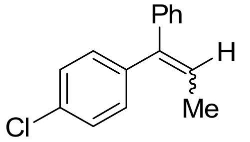
(*Z*)-1-(2-chloro-5-methylphenyl)-1-phenylpropene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (d, *J* = 6.0 Hz, 3H), 2.31 (s, 3H), 6.32 (q, *J* = 6.0 Hz, 1H), 6.98-7.33 (m, 8H).

(*E*)-1-(2-chloro-5-methylphenyl)-1-phenylpropene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89 (d, *J* = 9.0 Hz, 3H), 2.30 (s, 3H), 5.85 (q, *J* = 9.0 Hz, 1H), 6.98-7.33 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) of the bottom spot: δ 15.77, 21.12, 125.62, 126.31, 126.37, 127.04, 128.07, 128.48, 128.60, 129.535, 129.544, 129.72, 131.11, 132.41, 136.82, 138.49, 139.83, 141.10.

1-(Chlorophenyl)-1-phenylpropene (entry 15): The reaction gave two sets of total 4 isomers where, the top spot contain the mixture of two inseparable *p-Z* and *p-E* isomers and the bottom spot contain the mixture of two inseparable *o-Z* and *o-E* isomers. The *o*- and *p*-isomers were identified by comparing with standard samples prepared by literature method [Ref. *Org. Lett.* 2003, Vol.5, No. 20, 3641. *J. Org. Chem.* 1962, 2377] and their stereoisomer was identified by differential NOE experiments.

Top spot: E/Z-mixture of *p*ara-isomers (Rf value on TLC in Hexane = 0.3)

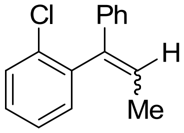


(*Z*)-1-(*p*-Chlorophenyl)-1-phenylpropene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (*d*, *J* = 9.0 Hz, 3H), 6.15 (q, *J* = 9.0 Hz, 1H), 7.1-7.40 (m, 9H).

(*E*)-1-(*p*-Chlorophenyl)-1-phenylpropene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (*d*, *J* = 9.0 Hz, 3H), 6.18 (q, *J* = 9.0 Hz, 1H), 7.1-7.40 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) of the top spot: δ 15.97, 15.99, 124.94, 124.97, 127.18, 127.29, 127.41, 128.40, 128.42, 128.50, 128.64, 128.70, 130.21, 131.69, 132.74, 132.94, 138.66, 139.74, 141.57, 141.63, 141.68, 142.76.

Bottom spot: E/Z-mixture of *ortho*-isomers (Rf value on TLC in Hexane = 0.27)



(*Z*)-1-(*o*-Chlorophenyl)-1-phenylpropene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92, (*d*, *J* = 6.9 Hz, 3H), 6.33 (q, *J* = 6.9 Hz, 1H), 7.1-7.40 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.71, 125.76, 126.31, 126.98, 127.06, 128.47, 128.75, 129.88, 131.97, 134.22, 138.82, 139.77, 140.94.

(*E*)-1-(*o*-Chlorophenyl)-1-phenylpropene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92, (*d*, *J* = 7.2 Hz, 3H), 5.87(q, *J* = 7.2 Hz, 1H), 7.1-7.40 (m, 9H).

Spectroscopic Data for the Products in Table 3

(*E*)-1,2-Diphenyl-1-(*p*-xylyl)ethene (entry 1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.34 (s, 3H), 6.62 (s, 1H), 7.05-7.27 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.28, 21.19, 126.95, 127.31, 128.24, 128.36, 128.41, 129.66, 130.13, 130.16, 130.60, 131.10, 133.34, 135.24, 137.68, 140.52, 143.30, 144.07.

(*E*)-1-Mesityl -1-phenyl-1-propene (entry 2): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (d, *J* = 9.0 Hz, 3H), 2.15 (s, 6H), 2.27 (s, 3H), 5.63 (q, *J* = 9.0 Hz, 1H), 6.86 (s, 2H), 7.14 – 7.30 (m, 5H); ^{13}C NMR (75 MHz) δ 15.71, 20.76, 21.30, 126.53, 126.63, 128.09, 128.45, 129.41, 136.30, 136.61, 139.68, 139.74, 141.21.

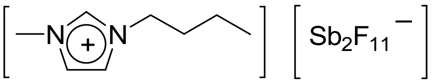
(*E*)-1,2-Diphenyl-1-mesitylethene (entry 3): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (s, 6H), 2.30 (s, 3H), 6.51 (s, 1H), 6.90 (s, 2H), 7.10–7.23 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.75, 21.36, 127.03, 127.28, 128.27, 128.40, 128.64, 129.56, 129.92, 130.59, 136.56, 136.82, 137.91, 139.51, 141.00, 141.03.

(*E*)-1-Pentamethylphenyl-1-phenyl-1-propene (entry 4): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99(d, *J* = 7.2 Hz, 3H) 2.16 (s, 6H), 2.20 (s, 6H), 2.25 (s, 3H), 5.60 (q, *J*=7.2 Hz, 1H), 7.15-7.31(m, 5H); ^{13}C NMR (75MHz, $CDCl_3$) δ 15.81, 16.95, 17.10, 18.43, 126.22, 126.53, 128.08, 129.44, 132.11, 132.59, 133.70, 140.12, 141.49, 141.85.

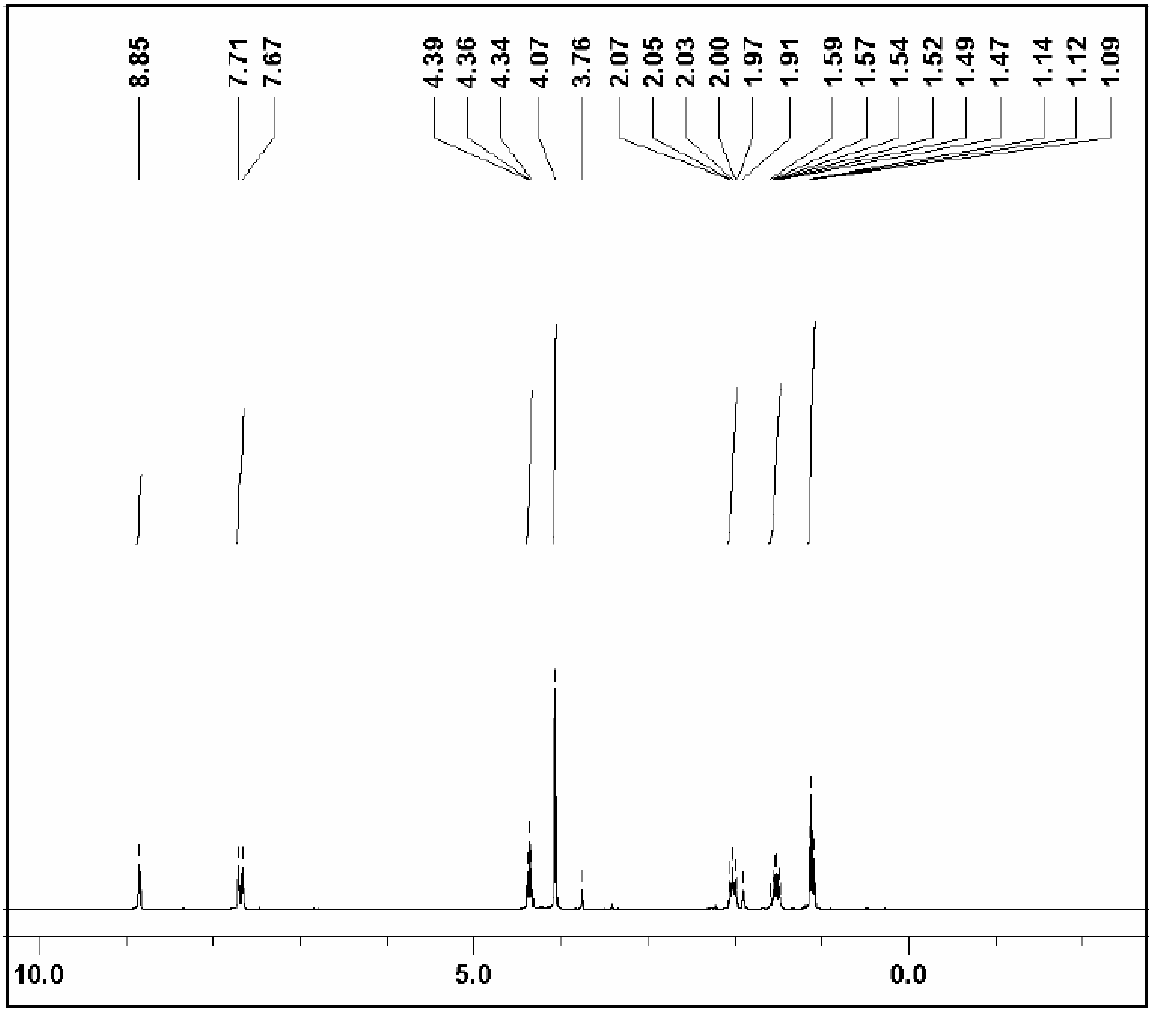
(*E*)-1,2-Diphenyl-1-pentamethylphenylethene (entry 5): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23(s, 6H), 2.27(m, 9H), 6.49(s, 1H), 7.10-7.25(m, 10H); ^{13}C NMR (75MHz, $CDCl_3$) δ 16.90, 17.11, 18.38, 126.90, 127.15, 128.21, 128.36, 129.47, 129.92, 130.26, 131.88, 132.80, 134.14, 138.08, 139.89, 141.60, 142.79.

Part II: NMR and MS Spectra of Compounds and E/Z-Caculation by GC-MS

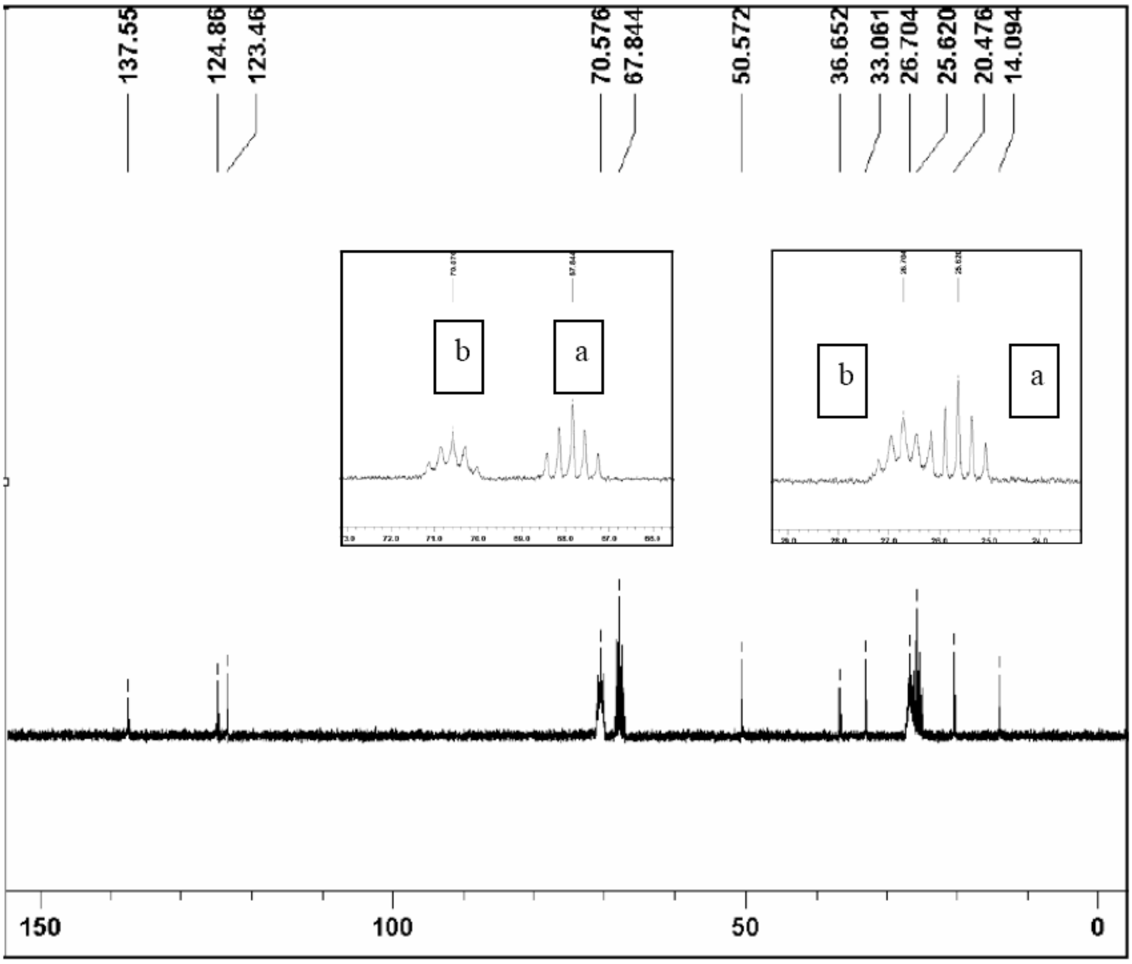
1. ^{1}H, ^{13}C, and ^{19}F NMR and FAB-MS spectra of 1



^{1}H NMR Spectrum of 1 (300 MHz, d_8-THF)

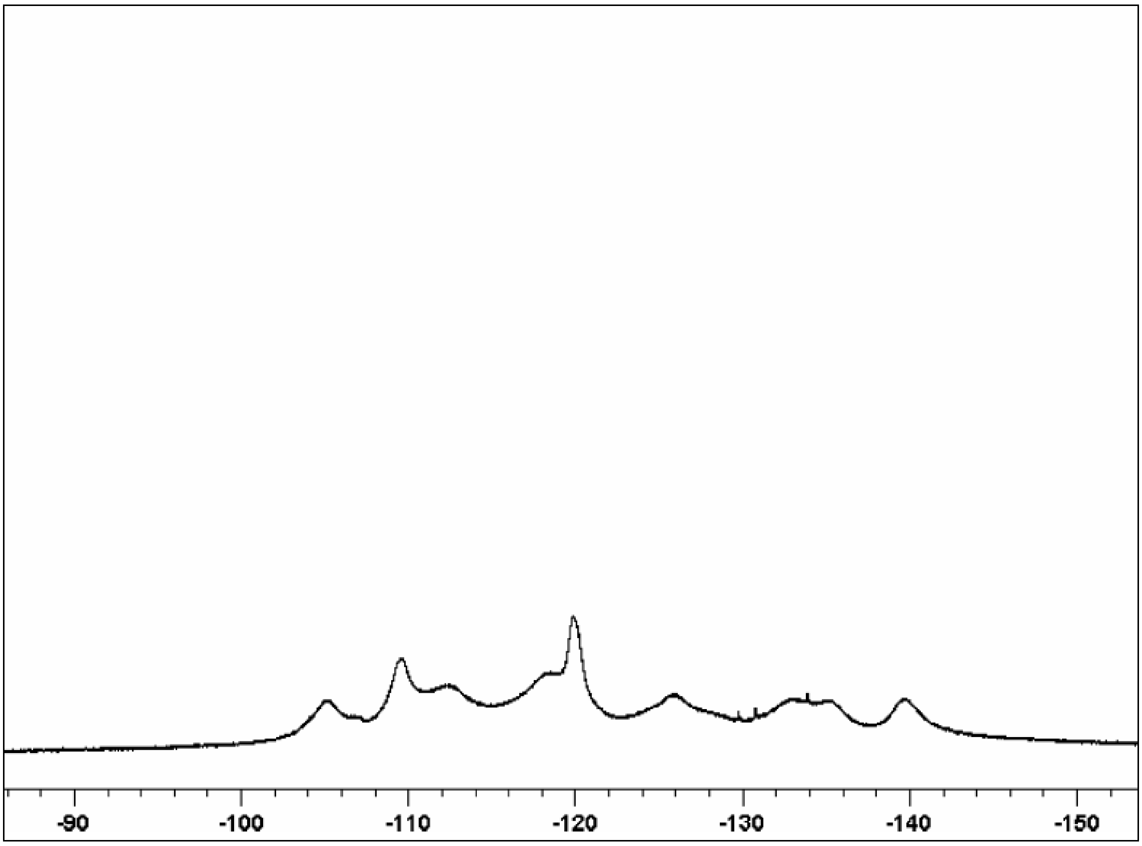


^{13}C NMR Spectrum of 1 (300 MHz, d_8-THF)

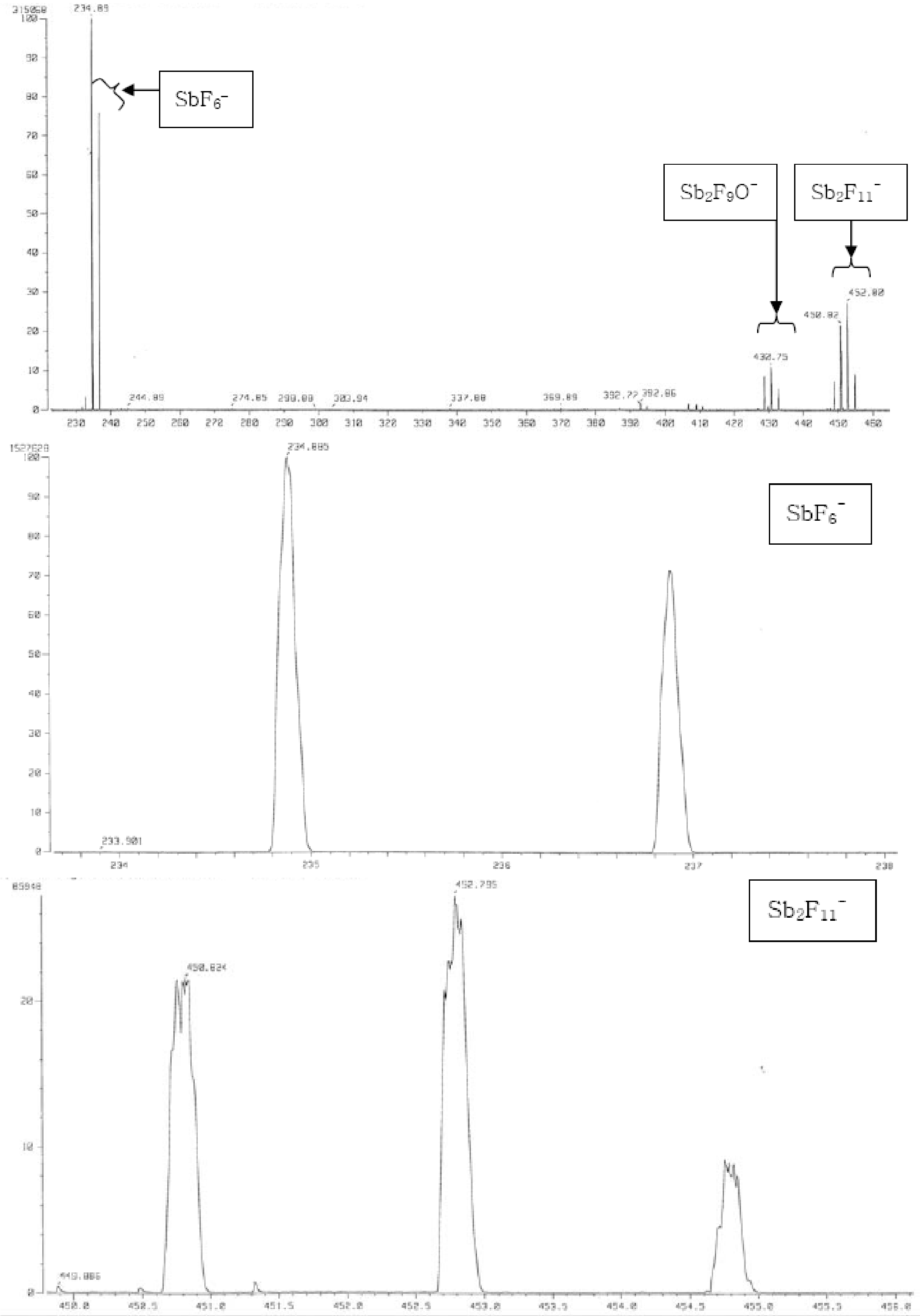


During NMR analysis, the d_8-THF solvent was very fast polymerized because of very strong acidity of the catalyst [bmim]Sb_nF_{5n+1} (n > 2) and we observed two type of THF peaks; **a**: carbon peaks of d_8-THF monomer as a NMR solvent, **b**; carbon peaks of d_8-THF polymerized by the strong acidity of **1**.

^{19}F NMR Spectrum of 1 (288 MHz, d_8-THF)

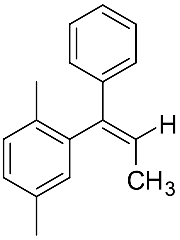


FAB-MS Spectrum of 1



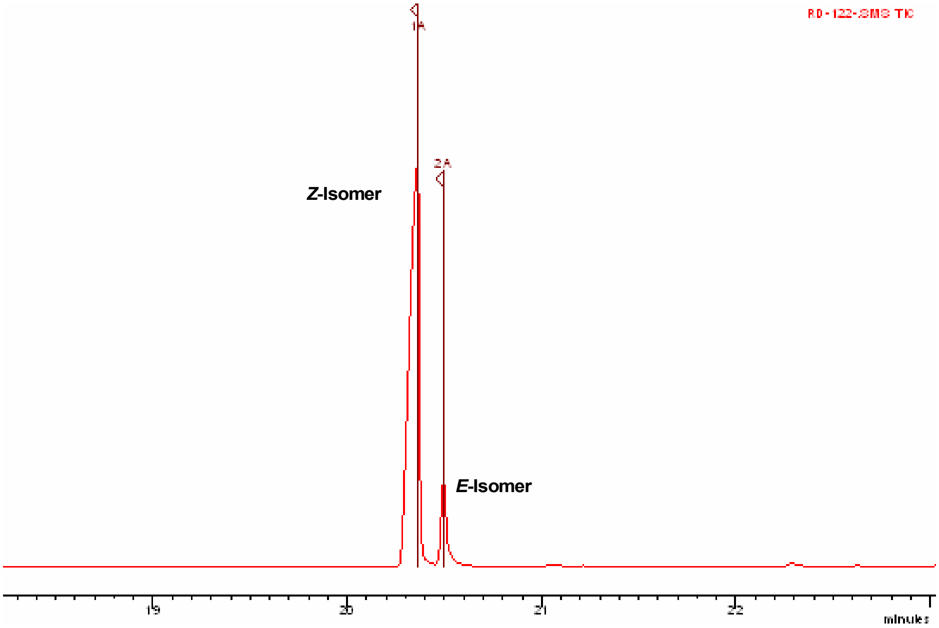
2. GC-MS, ^{1}H, ^{13}C NMR and differential NOE spectra for Table 2.

Entry 5 in Table 2

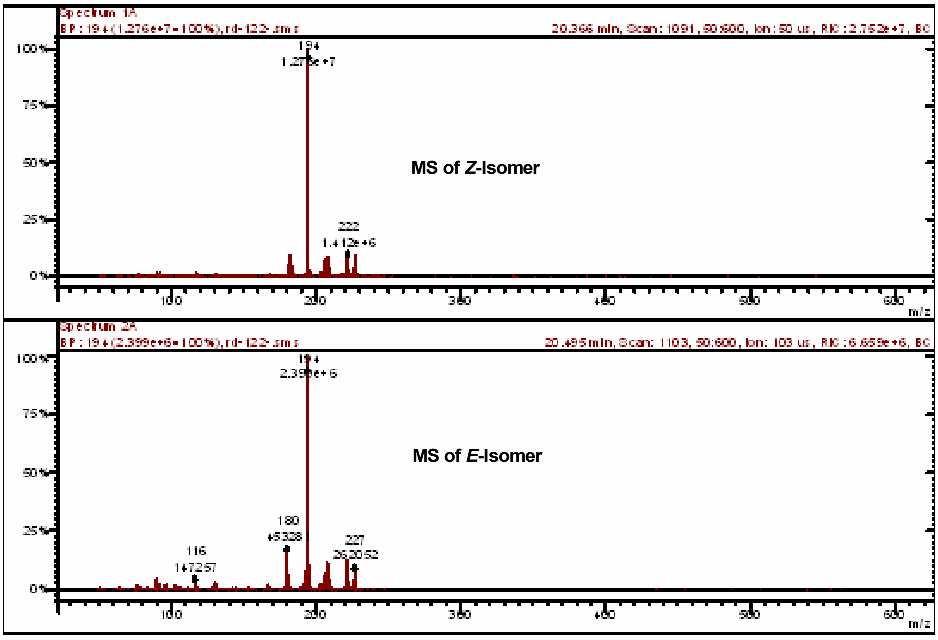


(*Z*)-1-Phenyl-1-(*p*-xylyl)propene

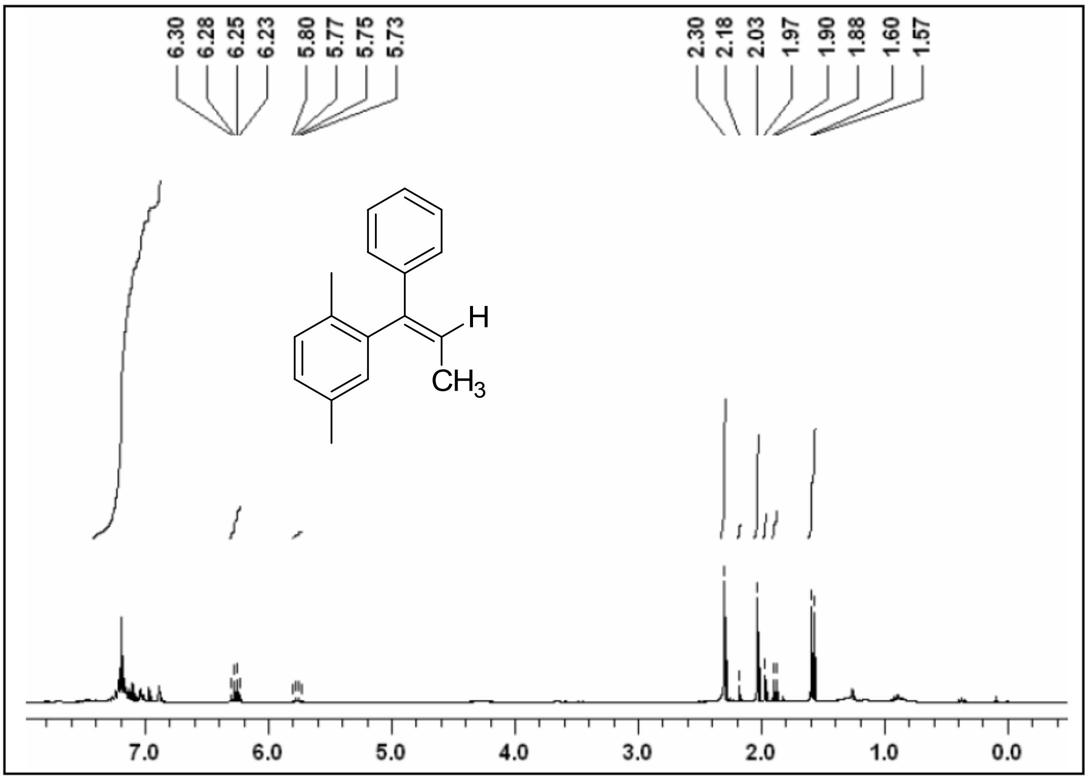
GC-MS Spectrum of 1-phenyl-1-(*p*-xylyl)propene



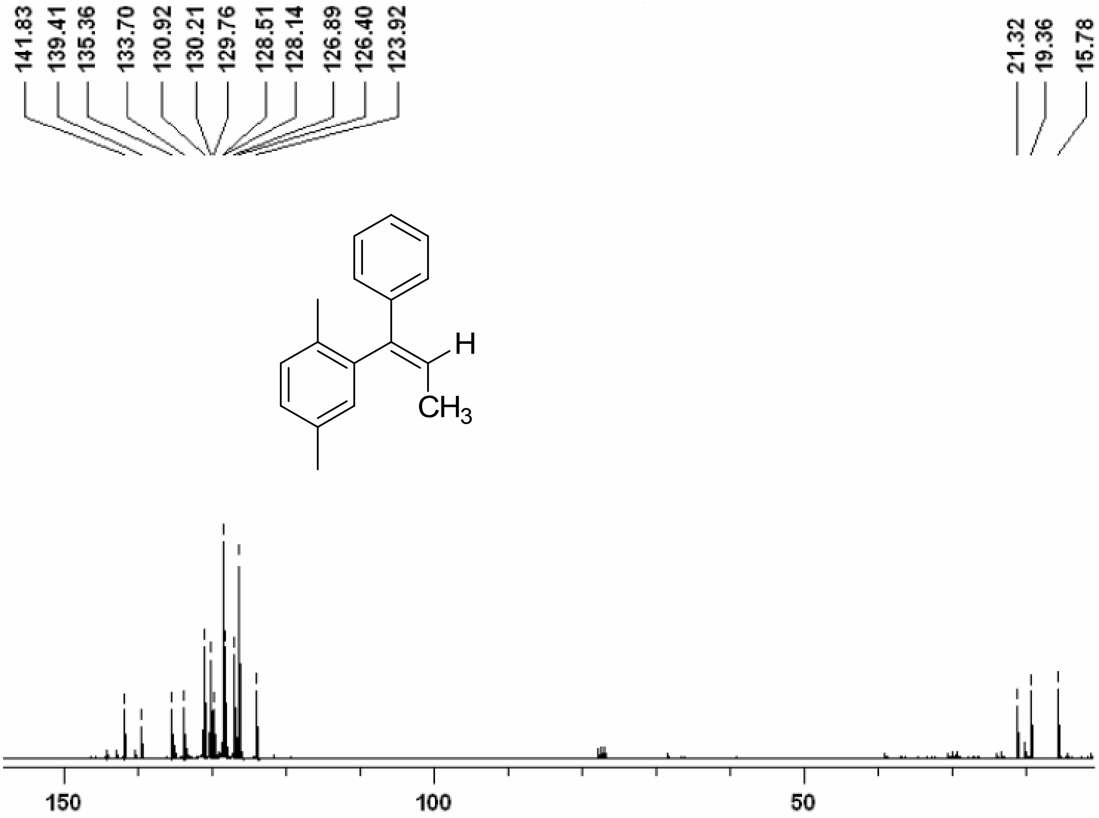
RT	Quan Ions	Area	Area %	Height
20.291	RIC	1.601E8	92.78	5.326E7
20.463	RIC	1.245E7	7.22	3.844E6



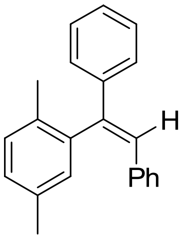
^{1}H Spectrum of 1-phenyl-1-(*p*-xylyl)propene



^{13}C Spectrum of 1-phenyl-1-(*p*-xylyl)propene

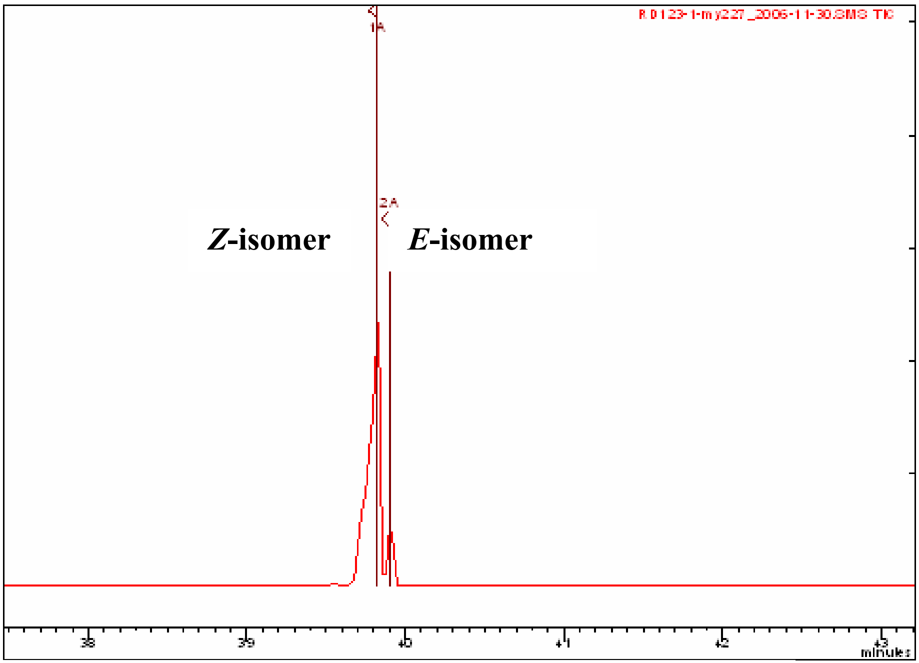


Entry 6 in Table 2

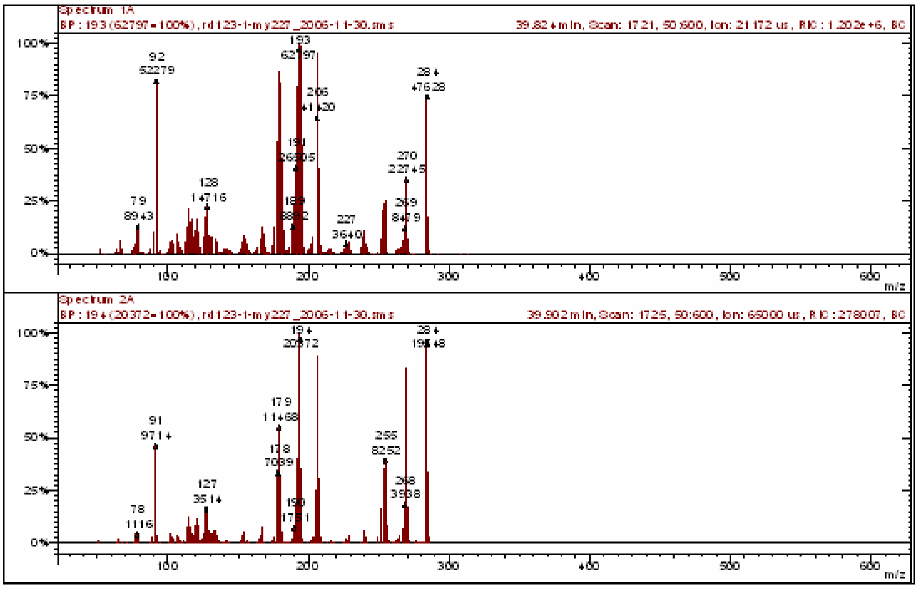


(*Z*)-1,2-Diphenyl-1-(*p*-xylyl)ethane

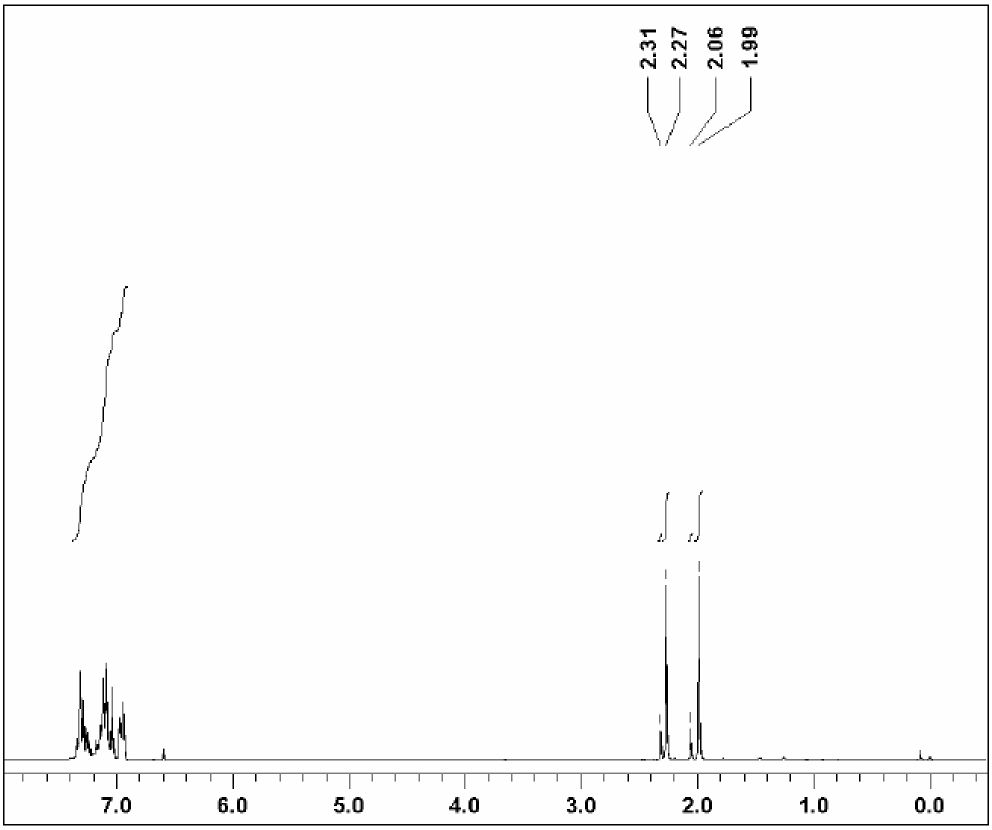
GC-MS Spectrum of 1,2-diphenyl-1-(*p*-xylyl)ethane



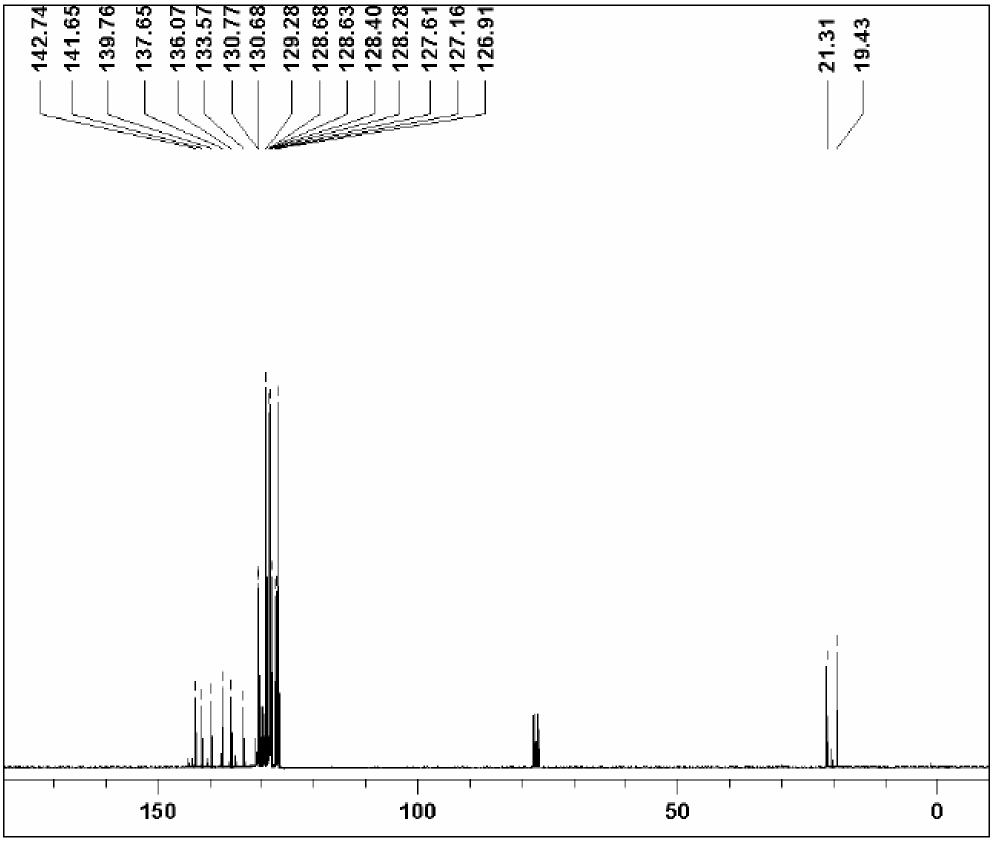
RT	Quan Ions	Area	Area %	Height
39.818	RIC	6.017 E6	90.59	1.020 E6
39.907	RIC	624788	9.41	164264



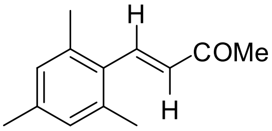
^{1}H NMR Spectrum of 1,2-diphenyl-1-(*p*-xylyl)ethane



^{13}C NMR Spectrum of 1,2-diphenyl-1-(*p*-xylyl)ethane

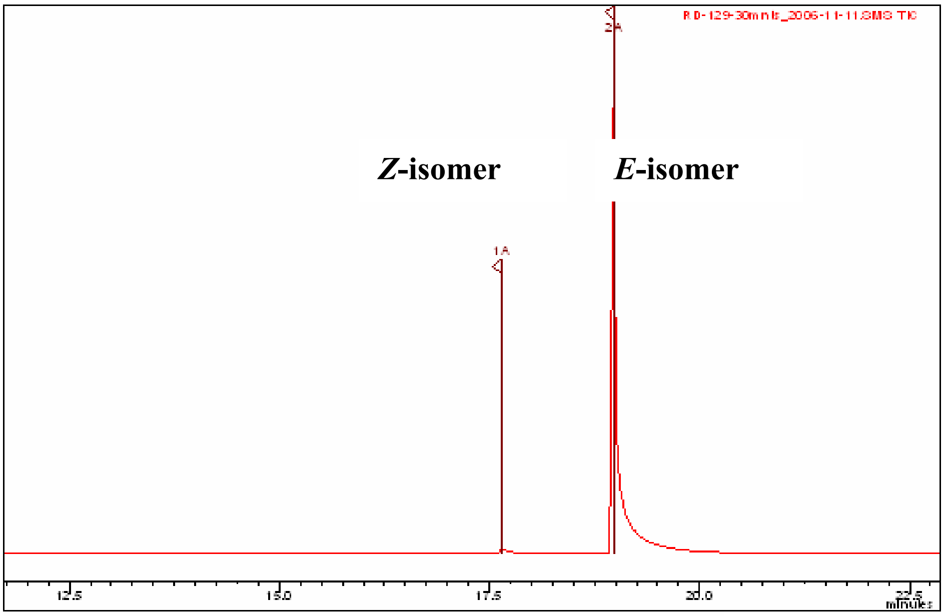


Entry 10 in Table 2

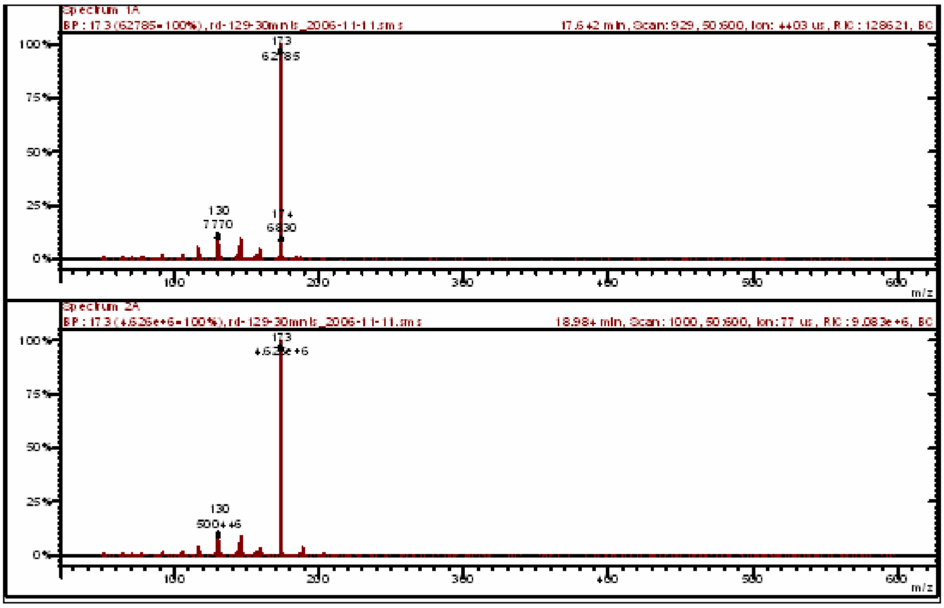


(*E*)-4-Mesityl-3-buten-2-one `

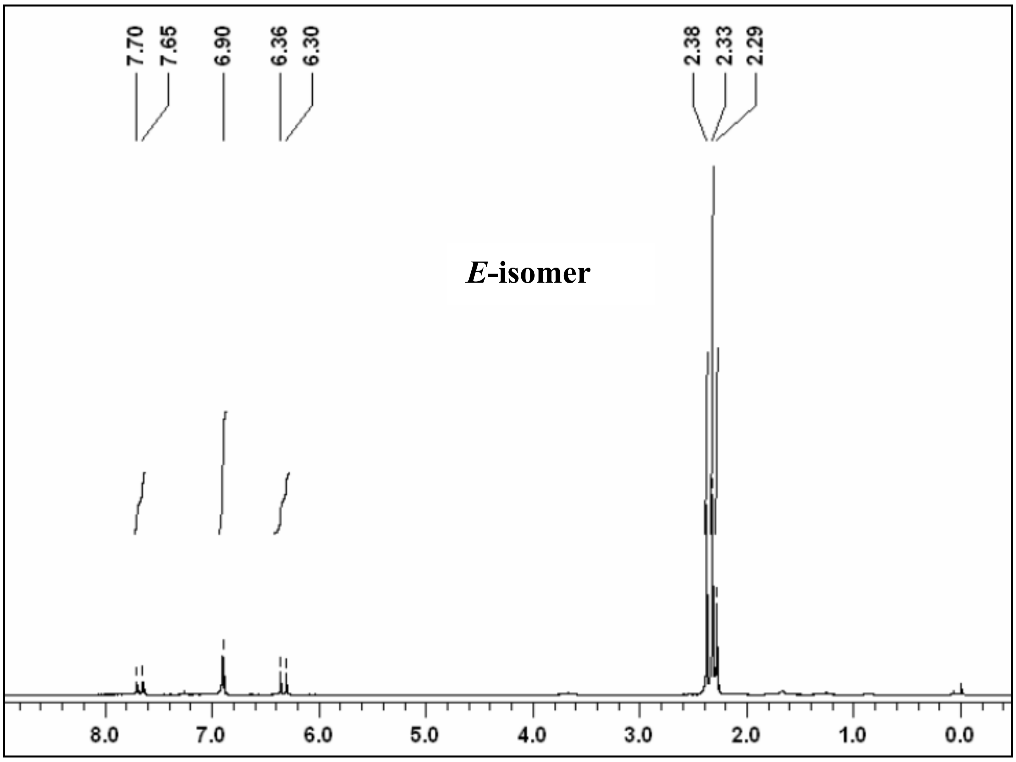
GC-MS Spectrum of 4-mesityl-3-buten-2-one



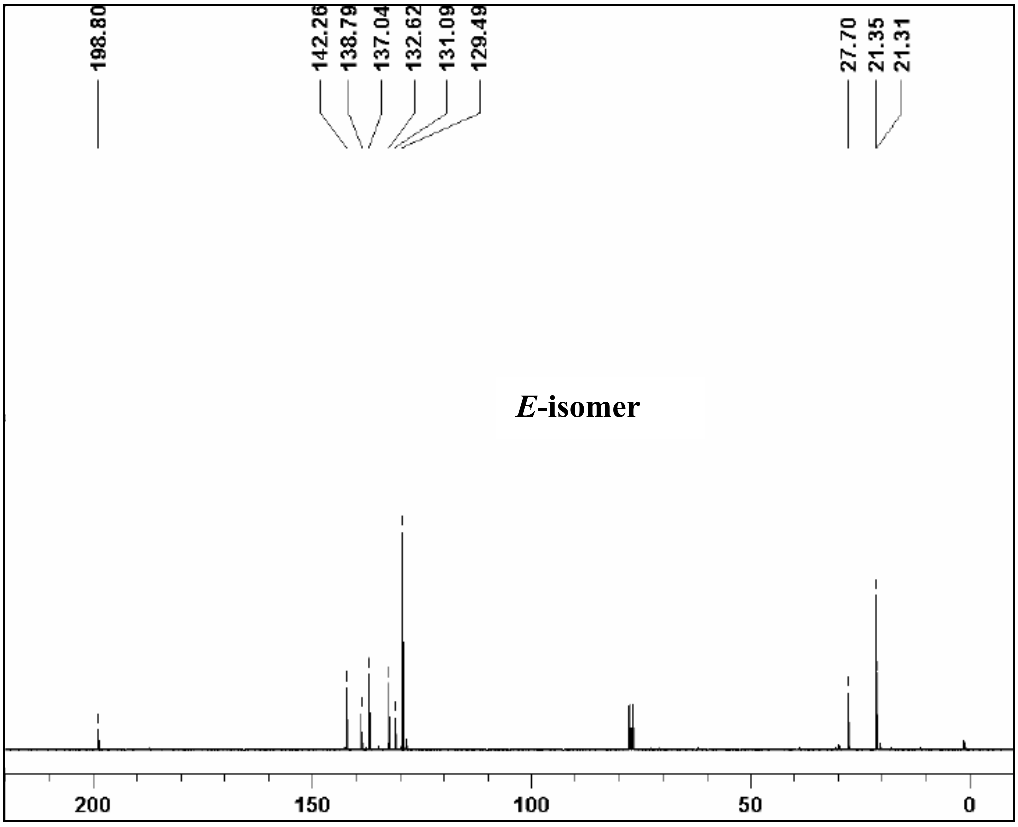
RT	Quan Ions	Area	Area %	Height
17.645	RIC	776130	1.92	124440
18.980	RIC	3.967 E7	98.08	9.070 E6



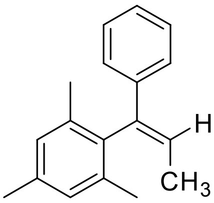
^{1}H NMR Spectrum of 4-mesityl-3-buten-2-one



^{13}C NMR Spectrum of 4-mesityl-3-buten-2-one

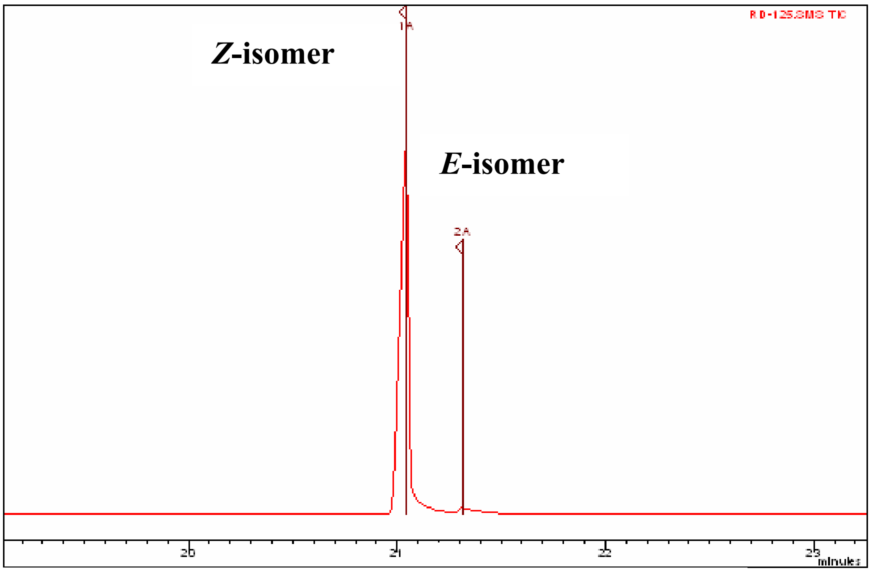


Entry 11 in Table 2

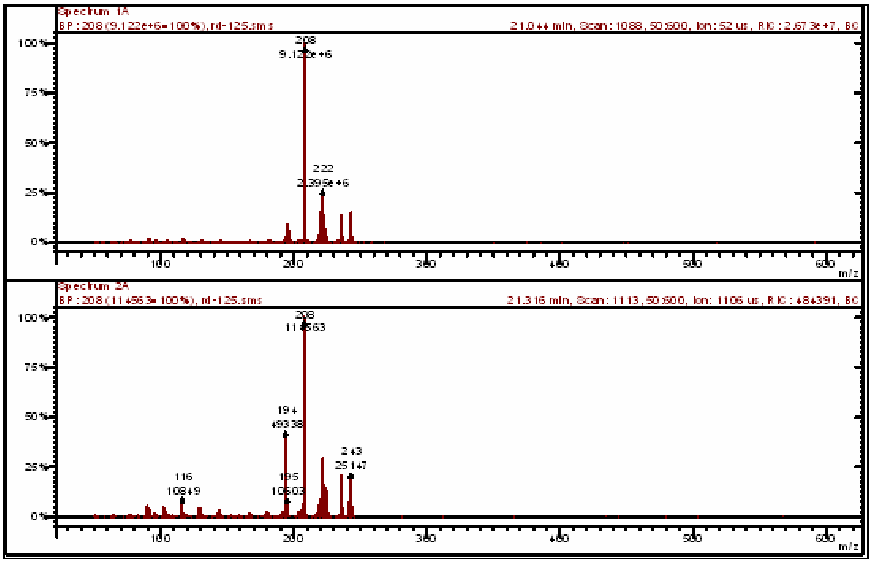


(*Z*)-1-Mesityl -1-phenylpropene

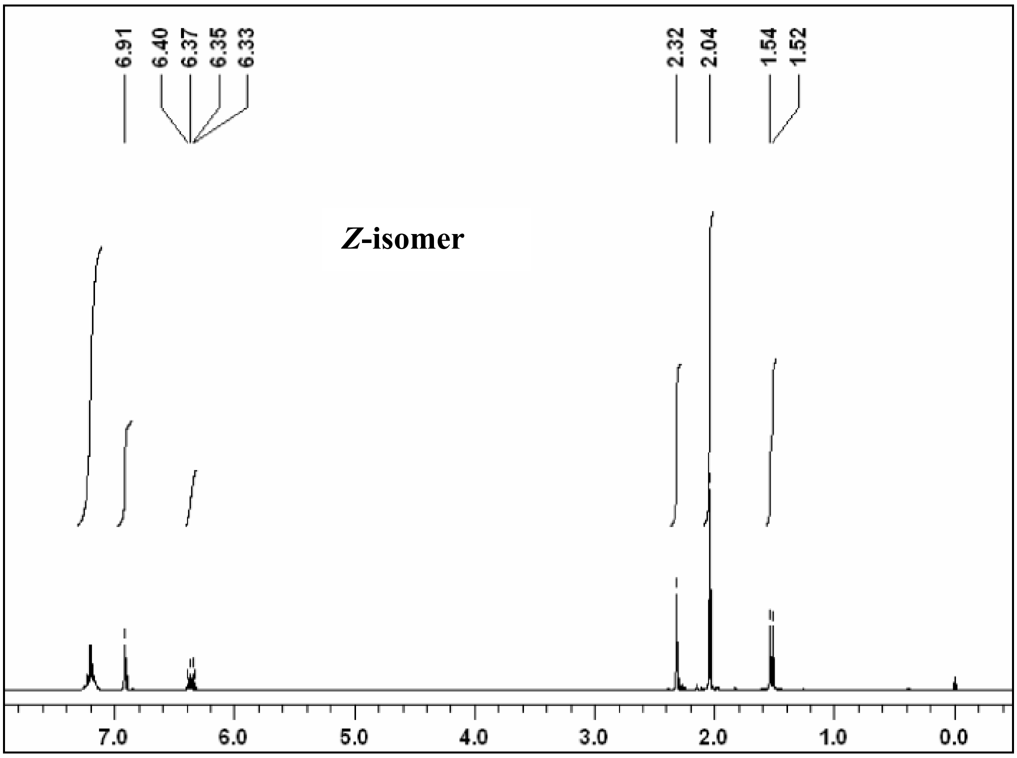
GC-MS Spectrum of 1-mesityl -1-phenylpropene



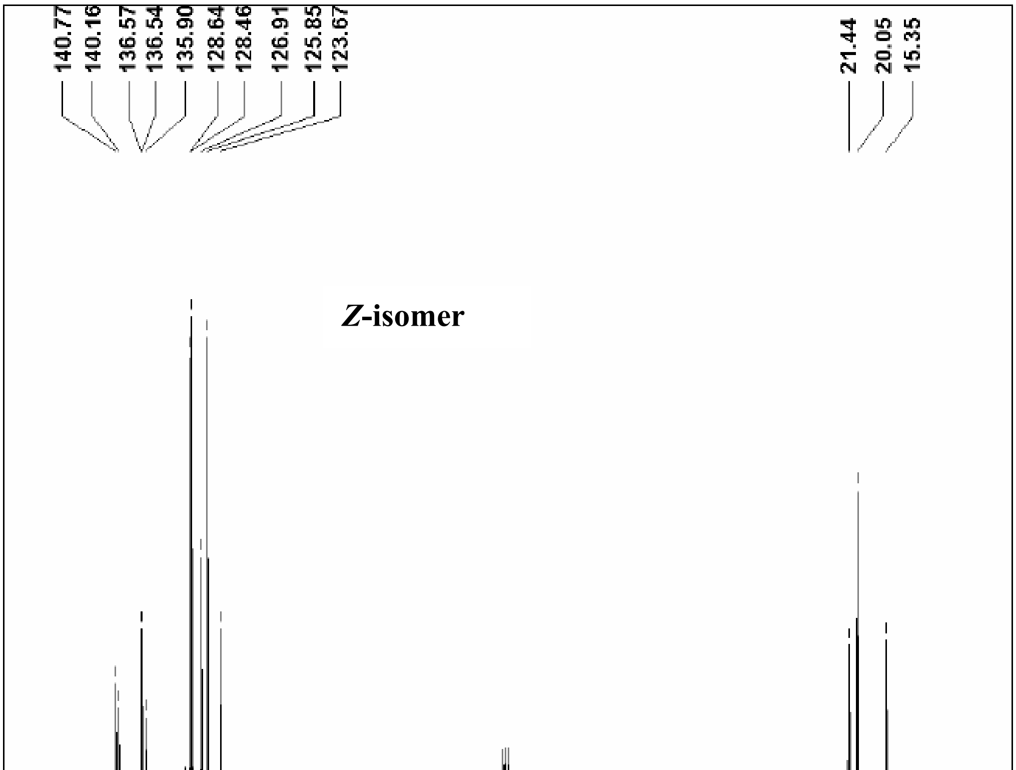
RT	Quan Ions	Area	Area %	Height
21.041	RIC	8.236E7	98.51	2.672E7
21.311	RIC	1.242E6	1.49	319841



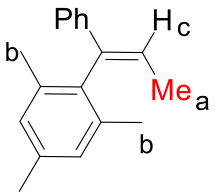
^{1}H NMR Spectrum of 1-mesityl -1-phenylpropene

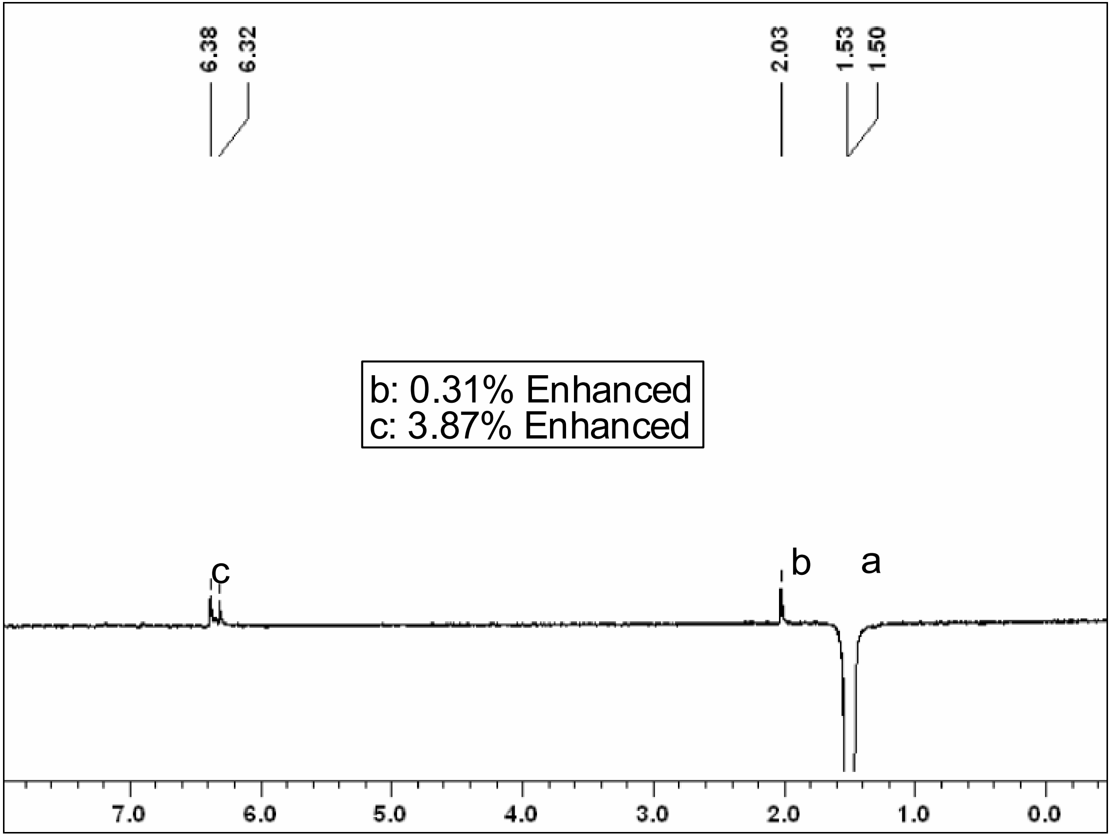


^{13}C NMR Spectrum of 1-mesityl -1-phenylpropene

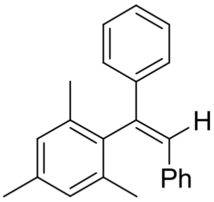


Differential NOE spectrum of (*Z*)-1-Mesityl -1-phenylpropene



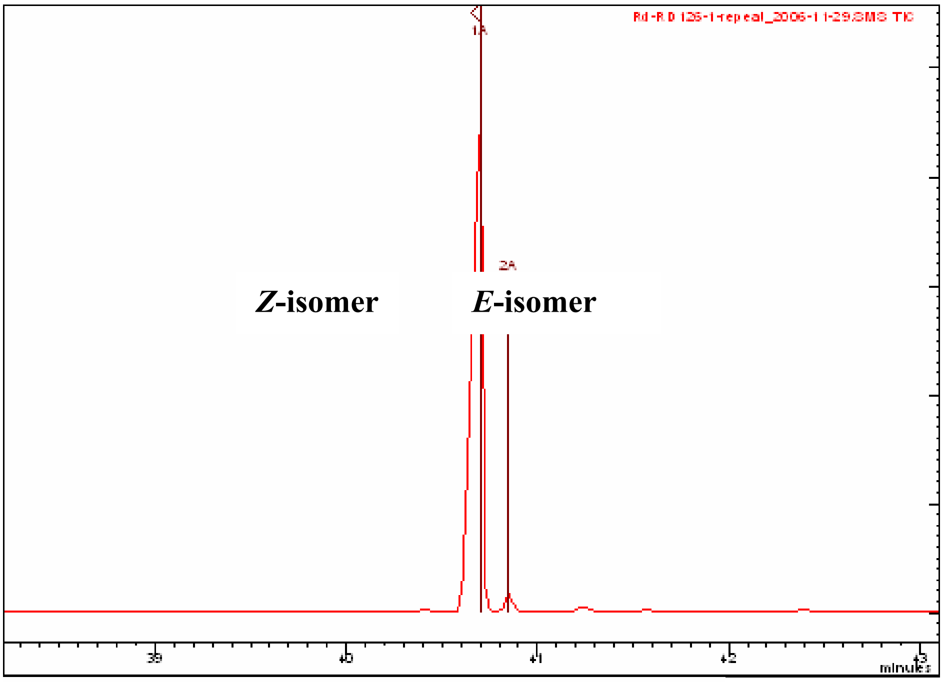


Entry 12 in table 2

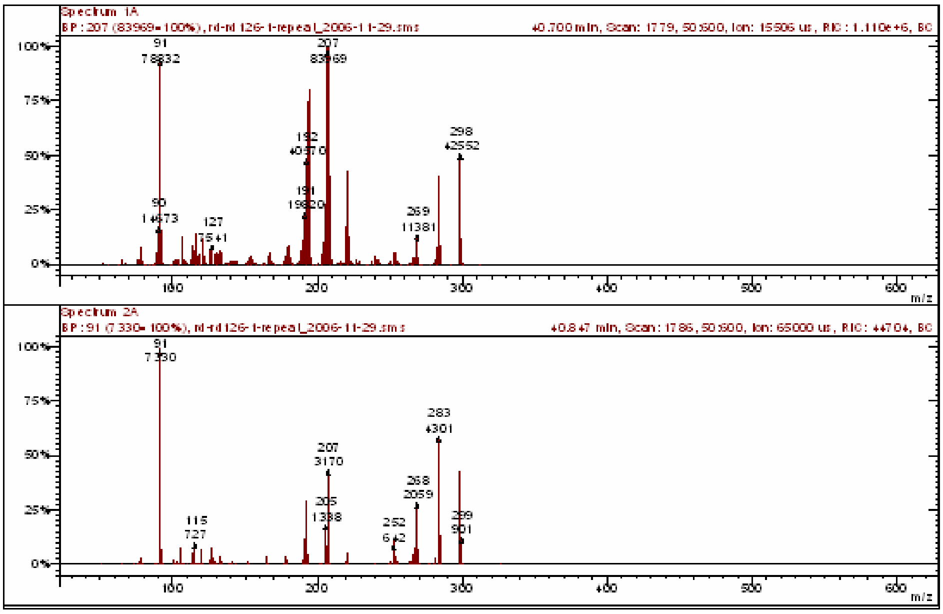


(*Z*)-1,2-Diphenyl-1-mesitylethene

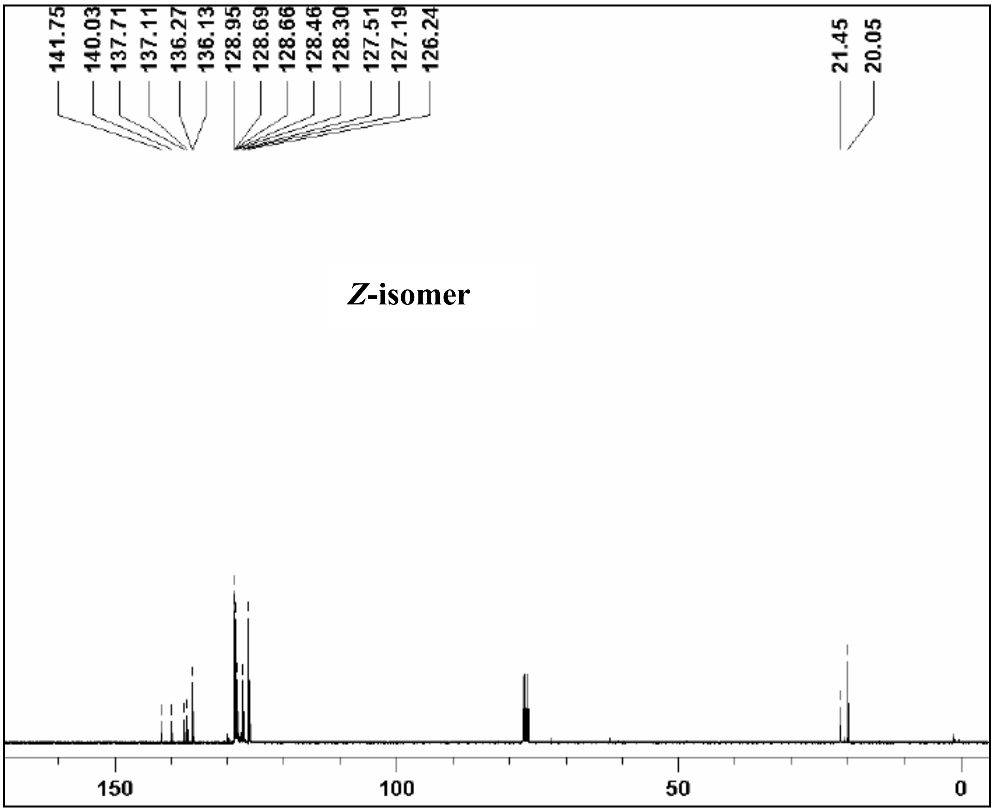
GC-MS Spectrum of 1,2-diphenyl-1-mesitylethene



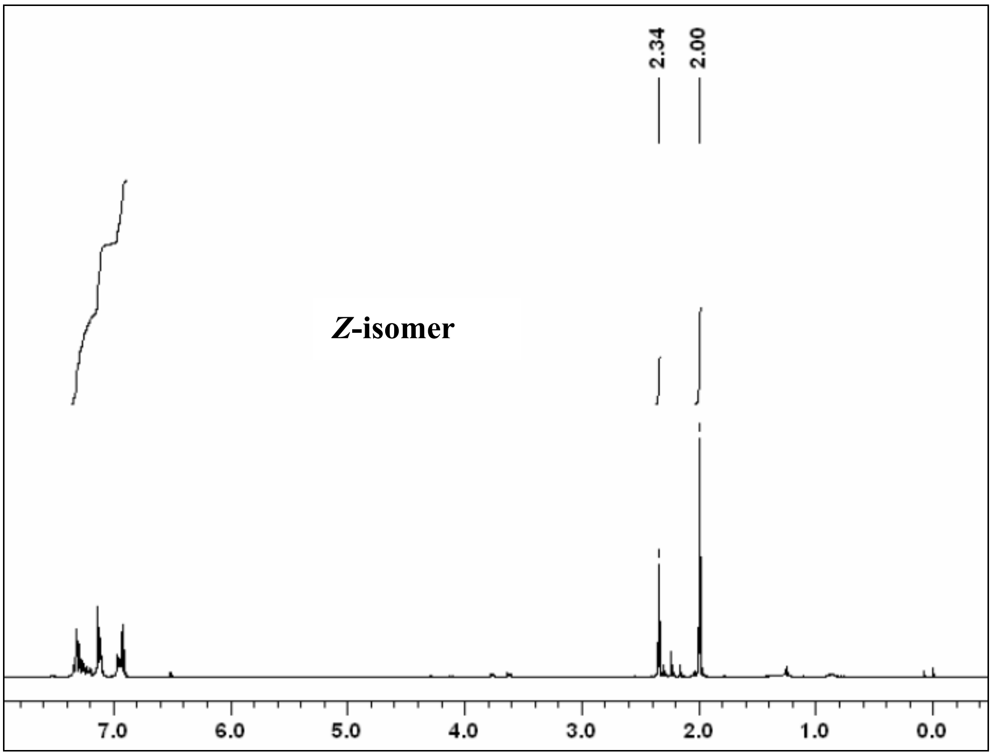
RT	Quan Ions	Area	Area %	Height
40.696	RIC	4.509E6	97.70	1.109E6
40.849	RIC	106277	2.30	43095



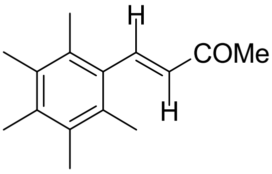
^{1}H NMR Spectrum of 1,2-diphenyl-1-mesitylethene



^{13}C NMR Spectrum of 1,2-diphenyl-1-mesitylethene

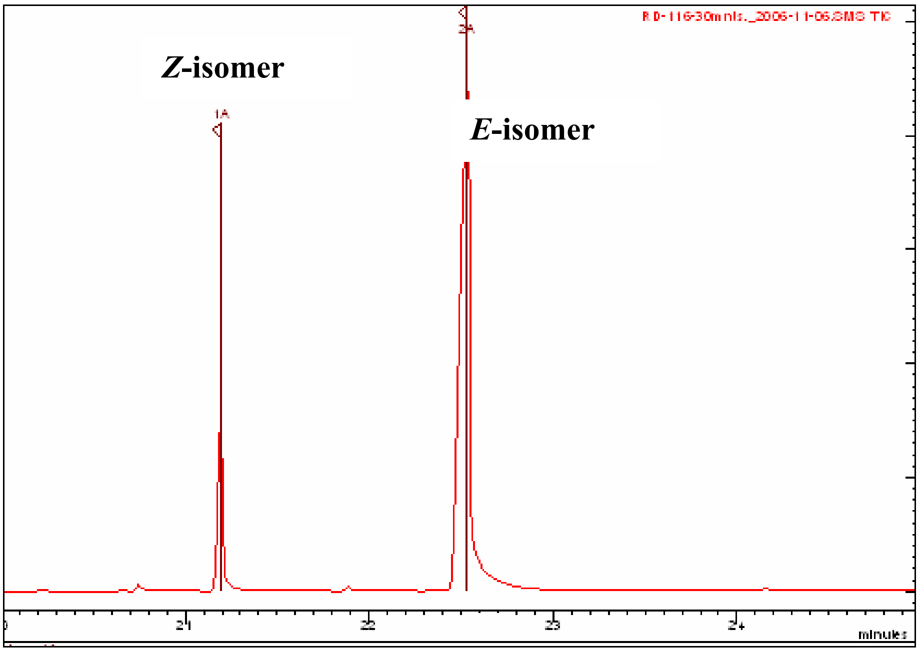


Entry 13 in Table 2

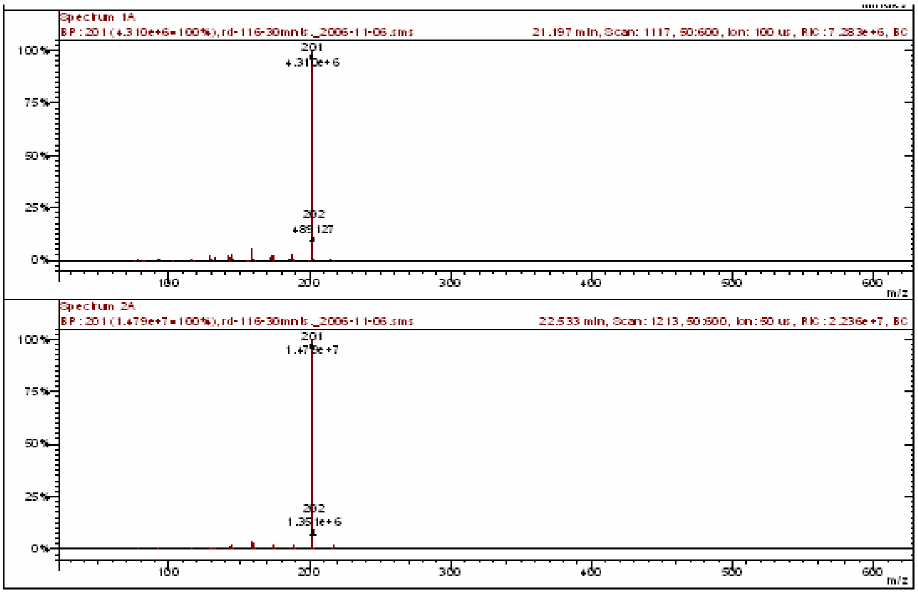


(*E*)-4-(Pentamethylphenyl)-3-buten-2-one

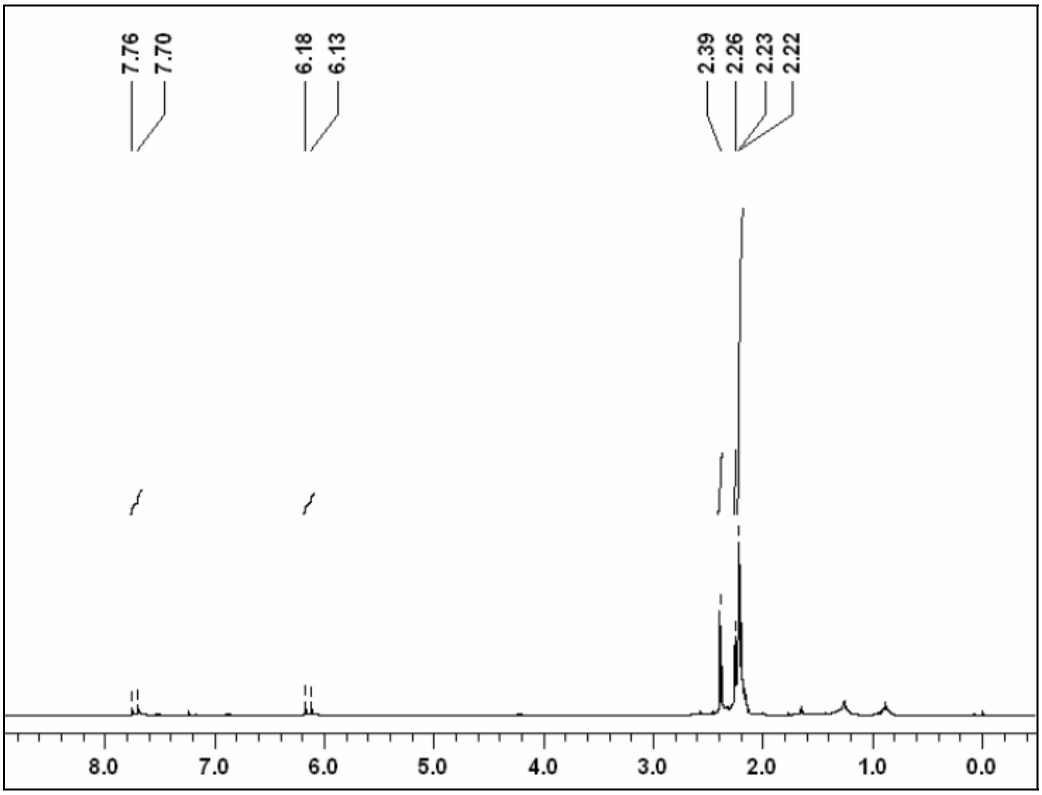
GC-MS Spectrum of 4-(pentamethylphenyl)-3-buten-2-one



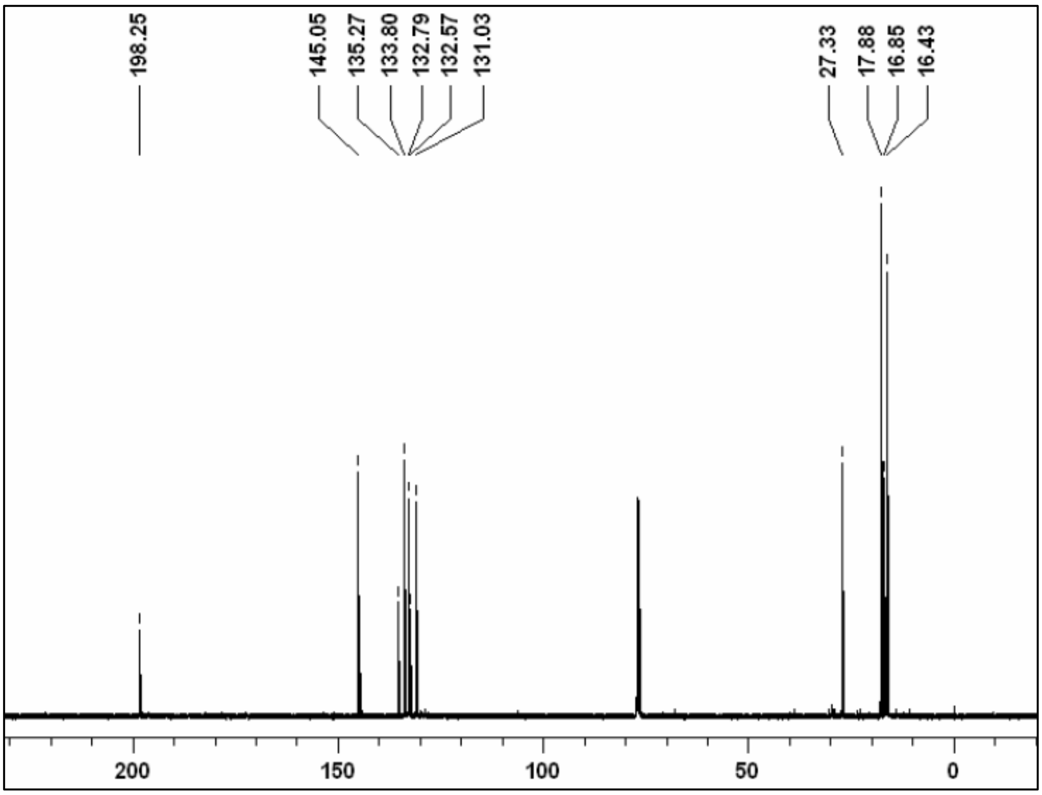
RT	Quan Ions	Area	Area %	Height
21.221	RIC	1.375E6	5.98	455977
22.504	RIC	2.164E7	94.02	4.081E6



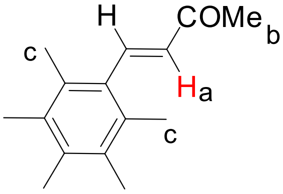
^{1}H NMR Spectrum of 4-(pentamethylphenyl)-3-buten-2-one

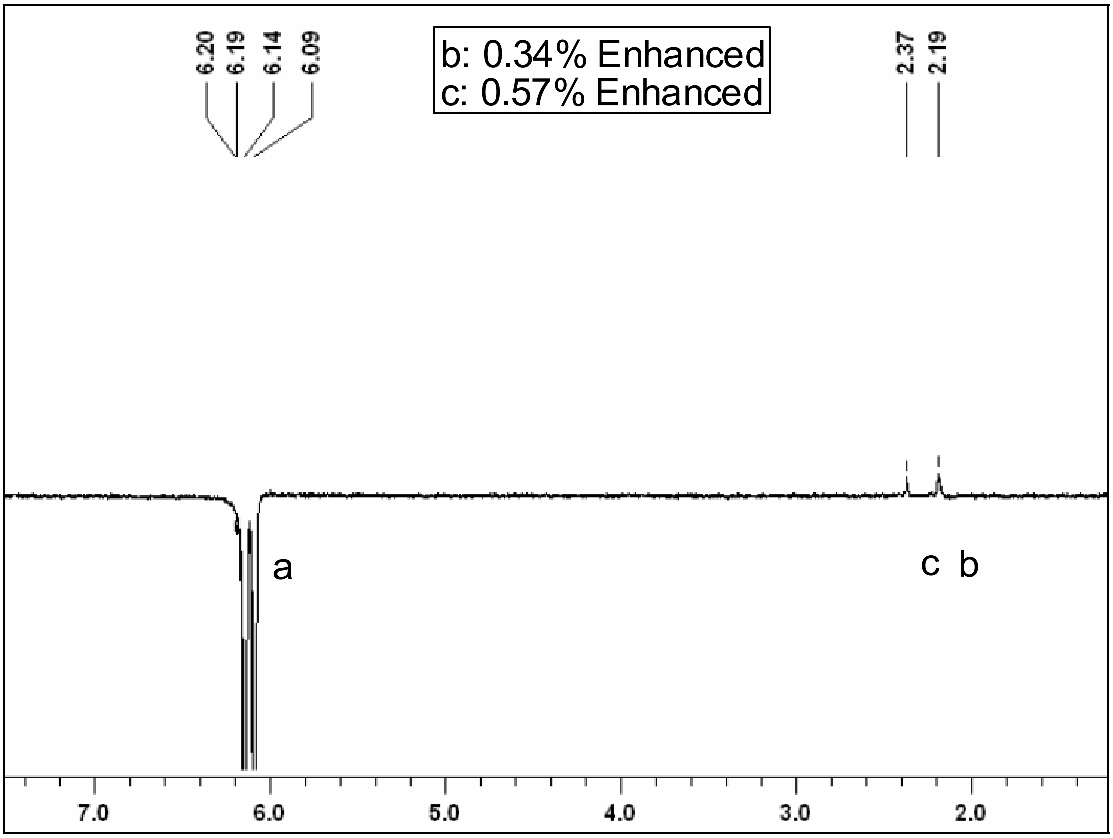


^{13}C NMR Spectrum of 4-(pentamethylphenyl)-3-buten-2-one



Differential NOE spectrum of (*E*)-4-(Pentamethylphenyl)-3-buten-2-one

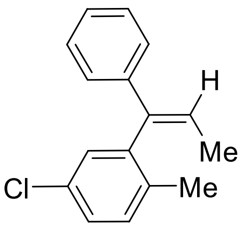




Entry 14 in Table 2

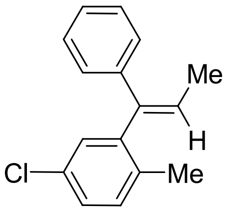
The reaction gave two separable mixtures including *ortho*- and *meta*-regioisomers to the methyl group of *p*-chlorotoluene and the corresponding *E*/*Z* isomers. Each isomers were identified by NOE experiment and the ratio was determined by ^{1}H NMR analysis.

- The first mixture: Rf value on TLC (Hexane) = 0.35



$C_{16}H_{15}Cl$
Exact Mass: 242.1
m/e: 242.1 (100.0%), 244.1 (33.5%), 243.1 (18.0%), 245.1 (5.8%)

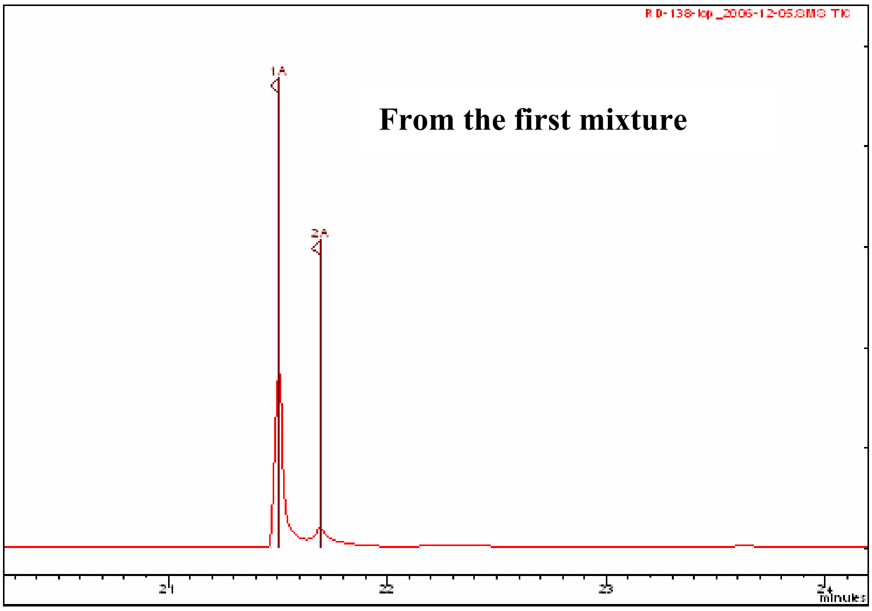
(*Z*)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene

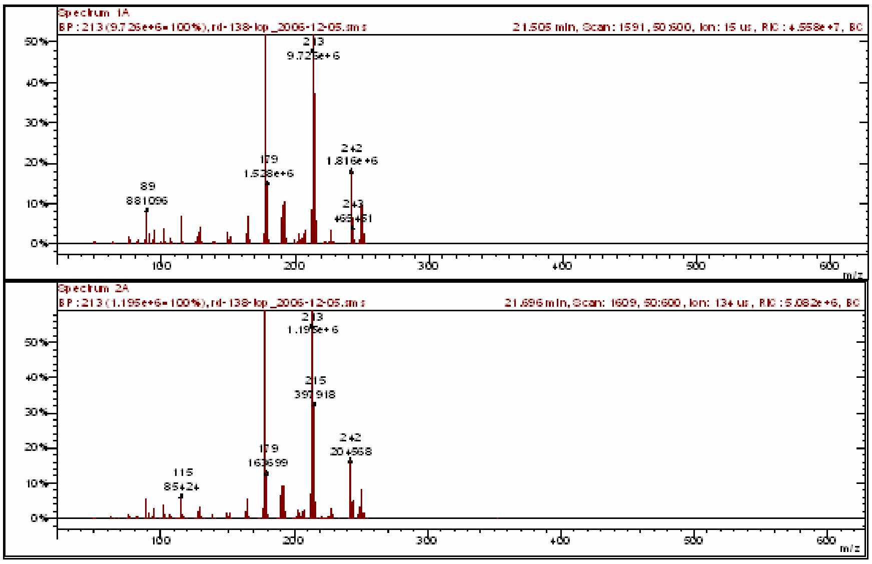


$C_{16}H_{15}Cl$
Exact Mass: 242.1
m/e: 242.1 (100.0%), 244.1 (33.5%), 243.1 (18.0%), 245.1 (5.8%)

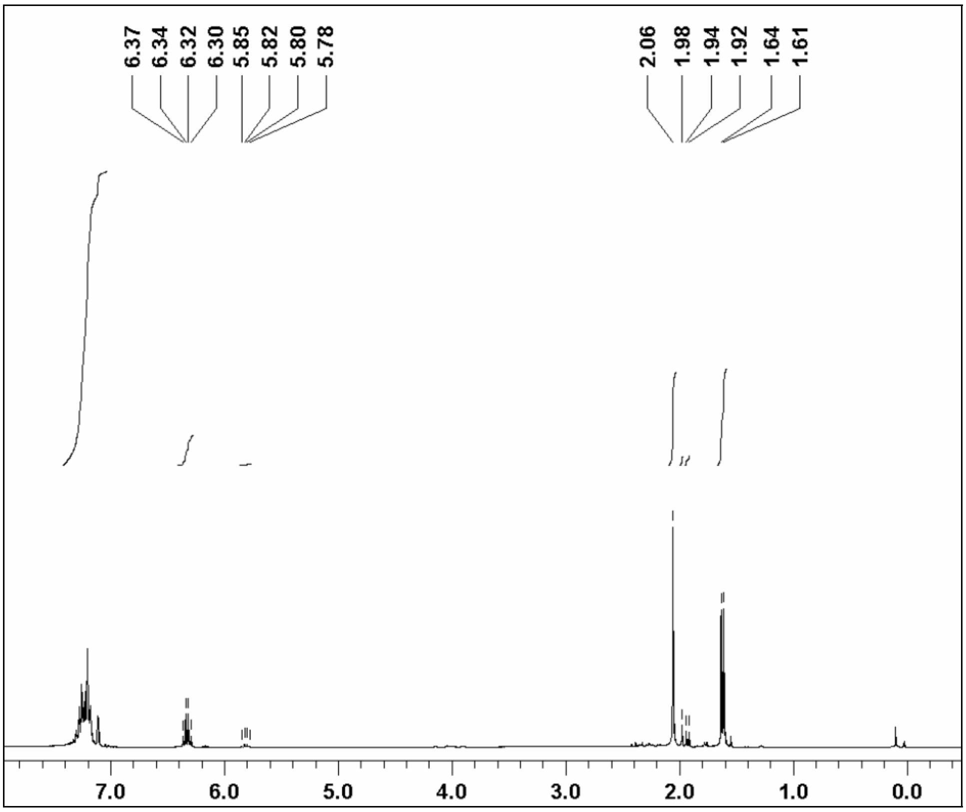
(*E*)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene

GC-MS Spectrum of 1-(2-methyl-5-chlorophenyl)-1-phenylpropene

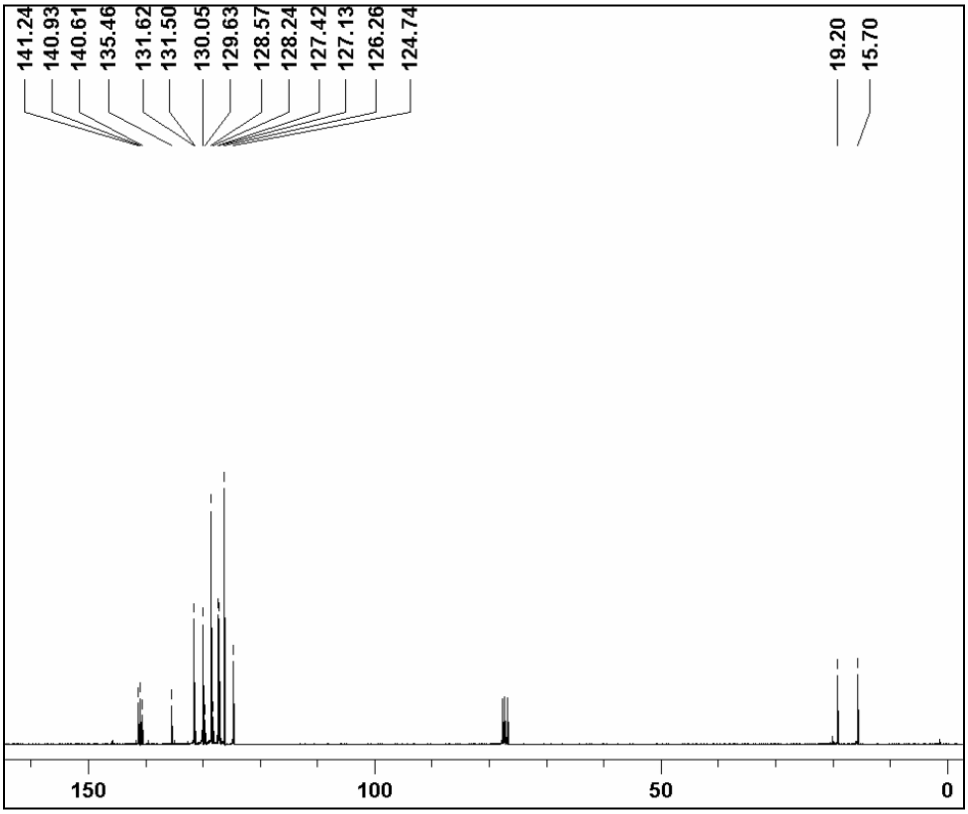




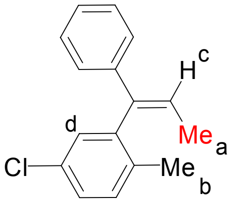
^{1}H NMR Spectrum of 1-(2-methyl-5-chlorophenyl)-1-phenylpropene

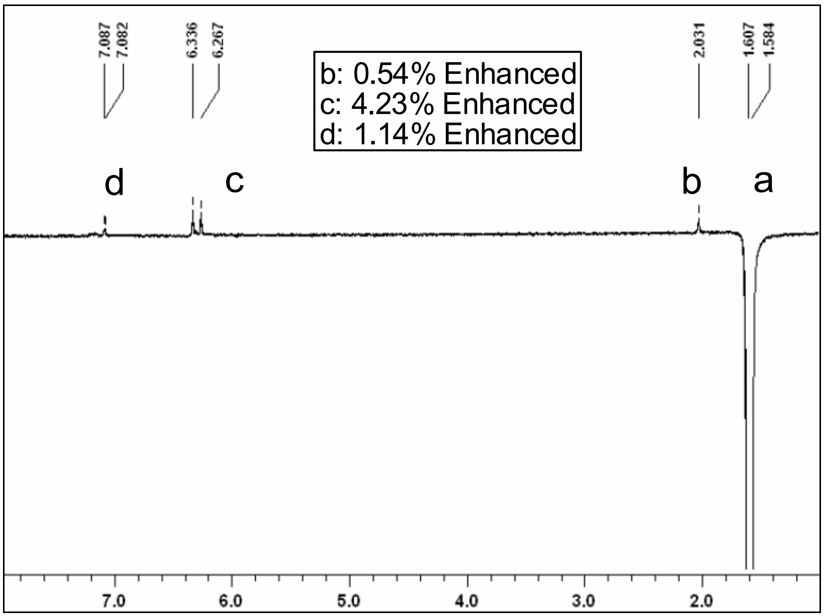


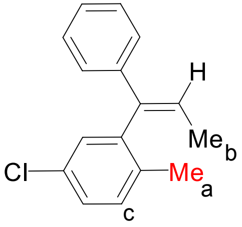
^{13}C NMR Spectrum of 1-(2-methyl-5-chlorophenyl)-1-phenylpropene

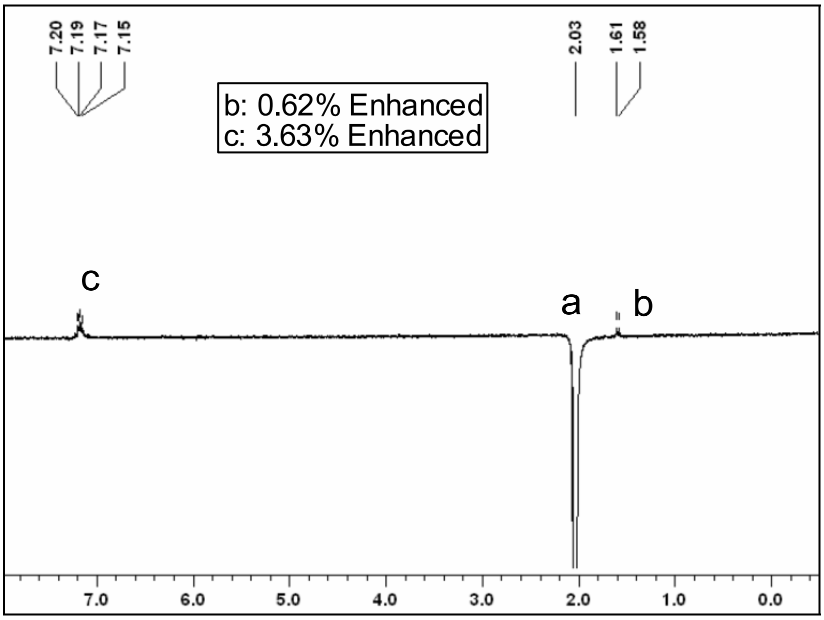


Differential NOE Spectrum of (*Z*)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene

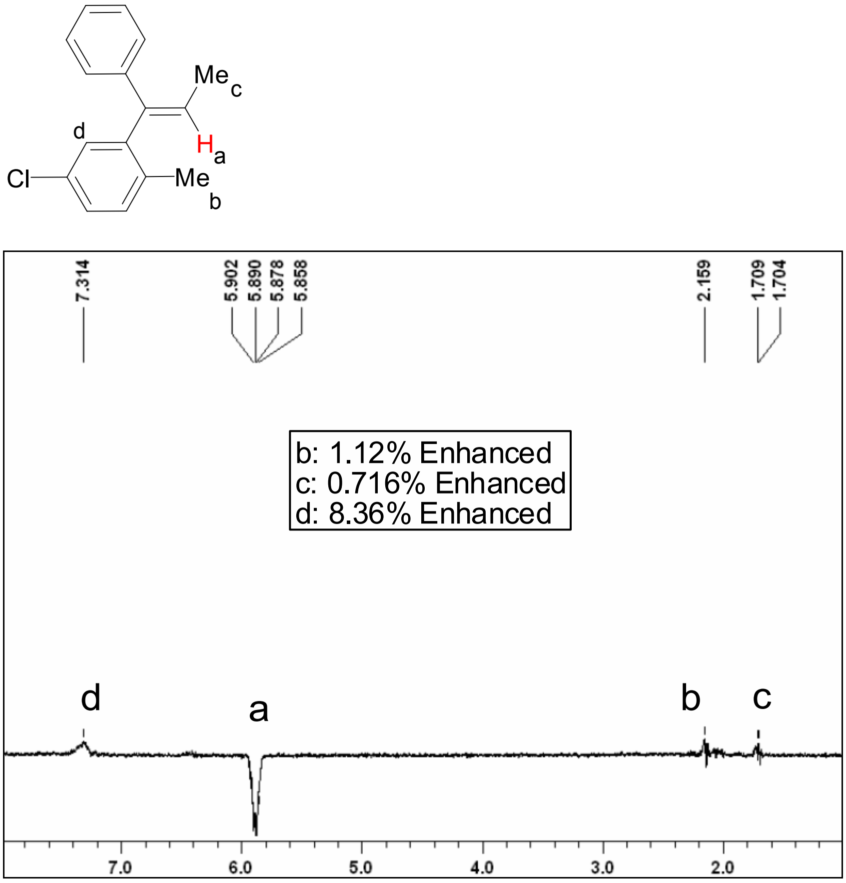


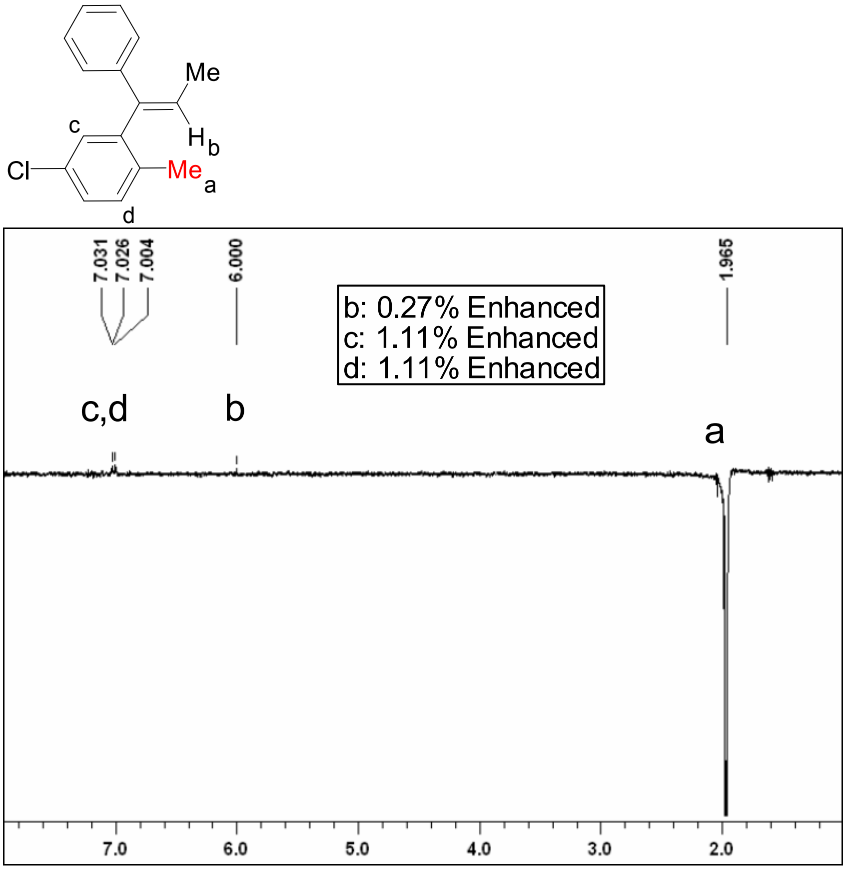




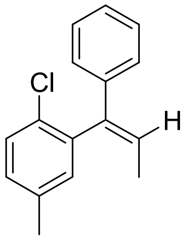


Differential NOE Spectrum of (*E*)-1-(2-methyl-5-chlorophenyl)-1-phenylpropene

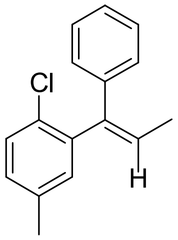




- The second mixture: Rf value on TLC (Hexane) = 0.33

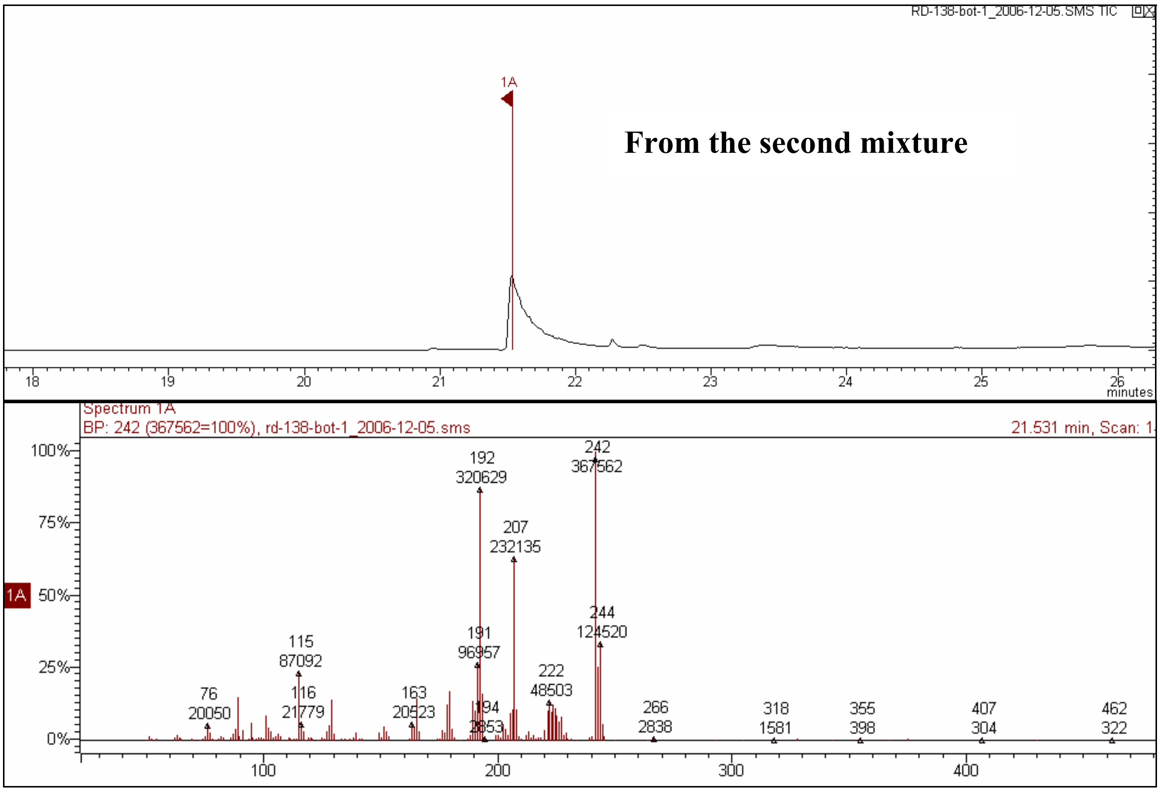


$C_{16}H_{15}Cl$
Exact Mass: 242.1
m/e: 242.1 (100.0%), 244.1 (33.5%), 243.1 (18.0%), 245.1 (5.8%)
(*Z*)-1-(2-chloro-5-methylphenyl)-1-phenylpropene

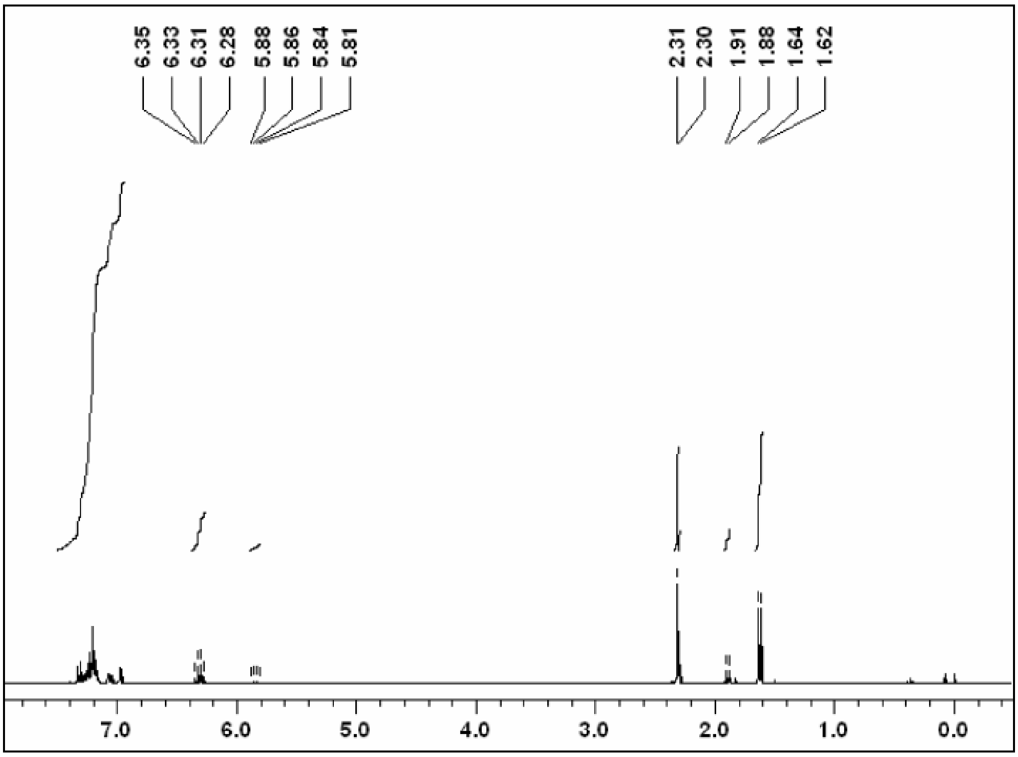


$C_{16}H_{15}Cl$
Exact Mass: 242.1
m/e: 242.1 (100.0%), 244.1 (33.5%), 243.1 (18.0%), 245.1 (5.8%)
(*E*)-1-(2-chloro-5-methylphenyl)-1-phenylpropene

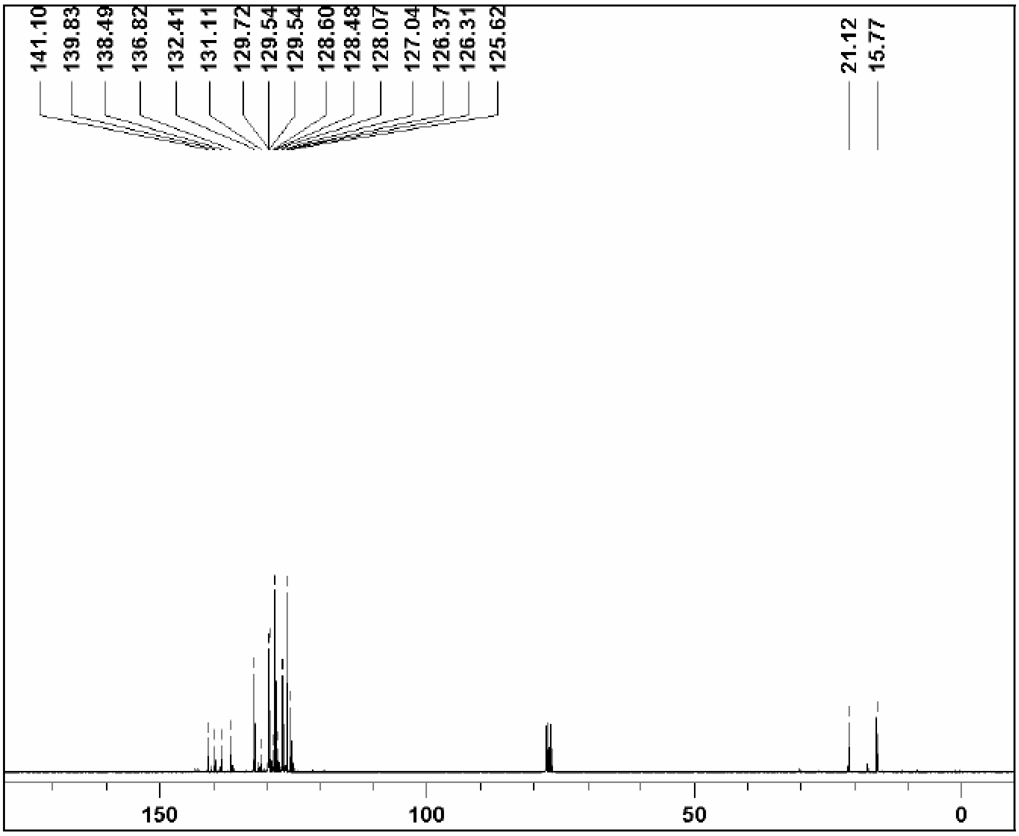
GC-Spectrum of 1-(2-chloro-5-methylphenyl)-1-phenylpropene


From the second mixture

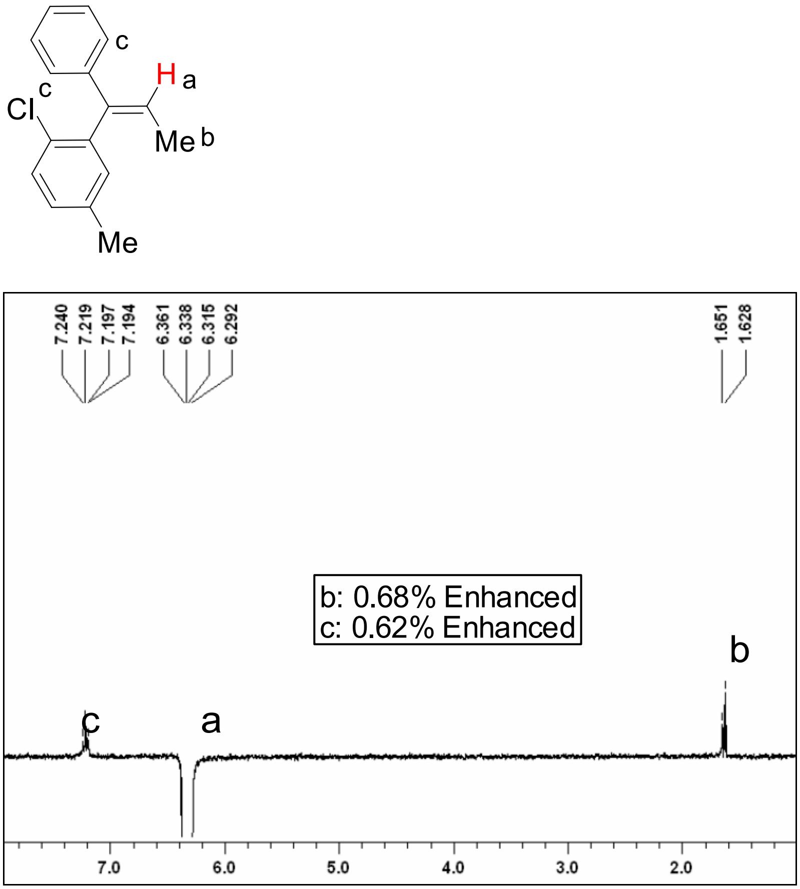
^{1}H NMR Spectrum of 1-(2-chloro-5-methylphenyl)-1-phenylpropene

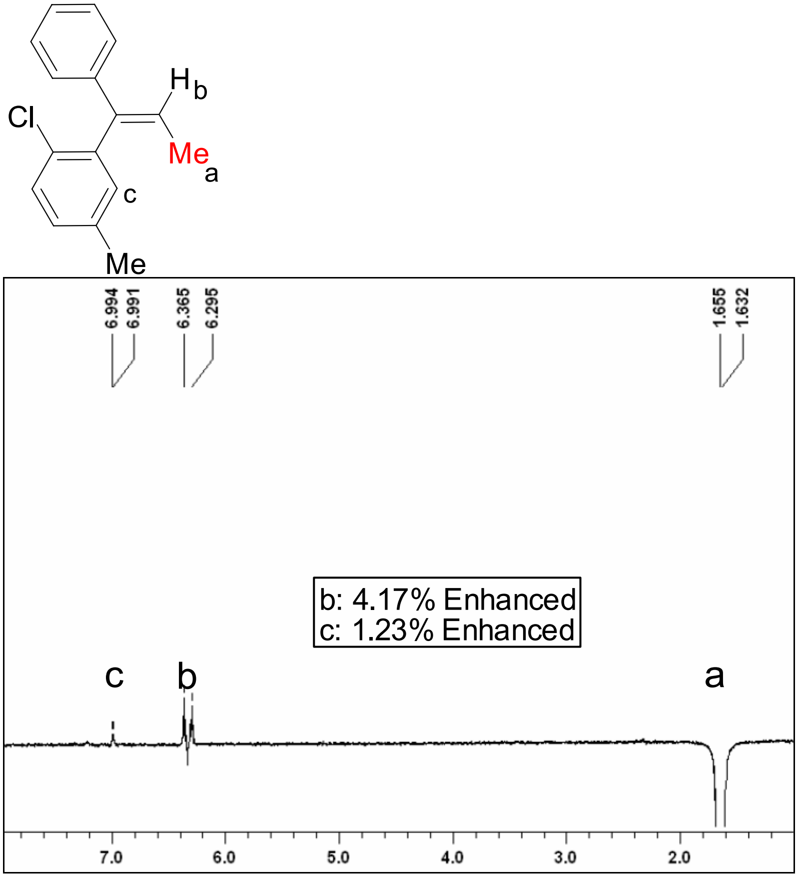


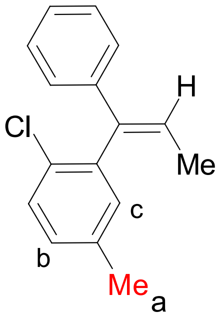
^{13}C NMR Spectrum of 1-(2-chloro-5-methylphenyl)-1-phenylpropene

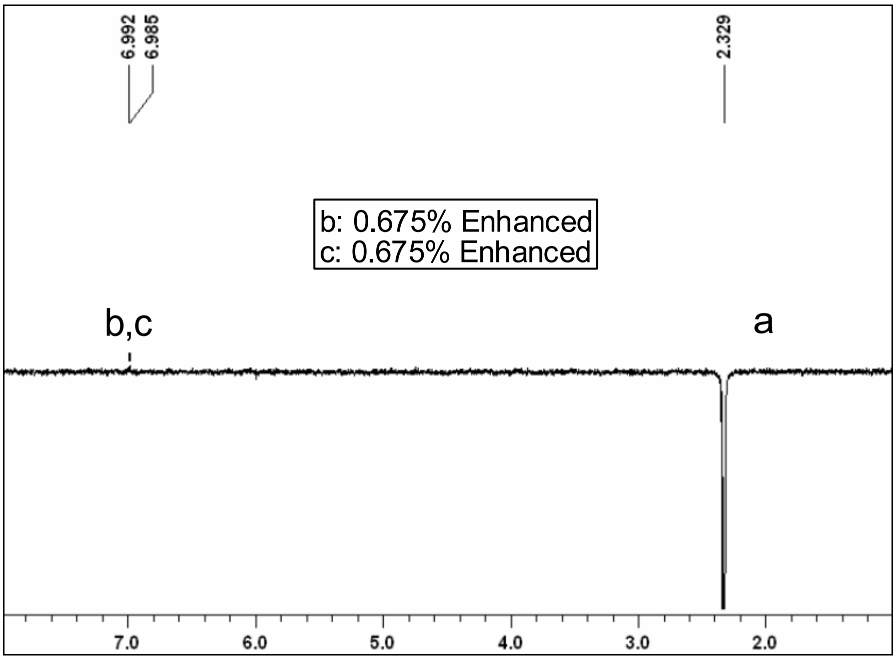


Differential NOE Spectrum of (*Z*)-1-(2-chloro-5-methylphenyl)-1-phenylpropene





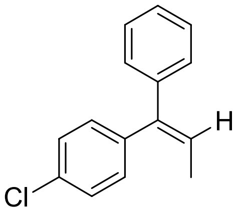

H
Cl
Me
c
b
Me
a


6.992
6.985
2.329
b: 0.675% Enhanced
c: 0.675% Enhanced
b,c
a
7.0
6.0
5.0
4.0
3.0
2.0

Entry 15 in Table 2

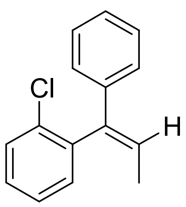
The reaction gave two separable mixtures including *ortho*- and *para*-regioisomers and the corresponding *E*/*Z* isomers. The isomers were identified by NOE experiment and the ratio was determined by ^{1}H NMR analysis.

- The first mixture: Rf value on TLC (Hexane) = 0.30



$C_{15}H_{13}Cl$
Exact Mass: 228.1
m/e: 228.1 (100.0%), 230.1 (33.3%), 229.1 (16.9%), 231.1 (5.5%)

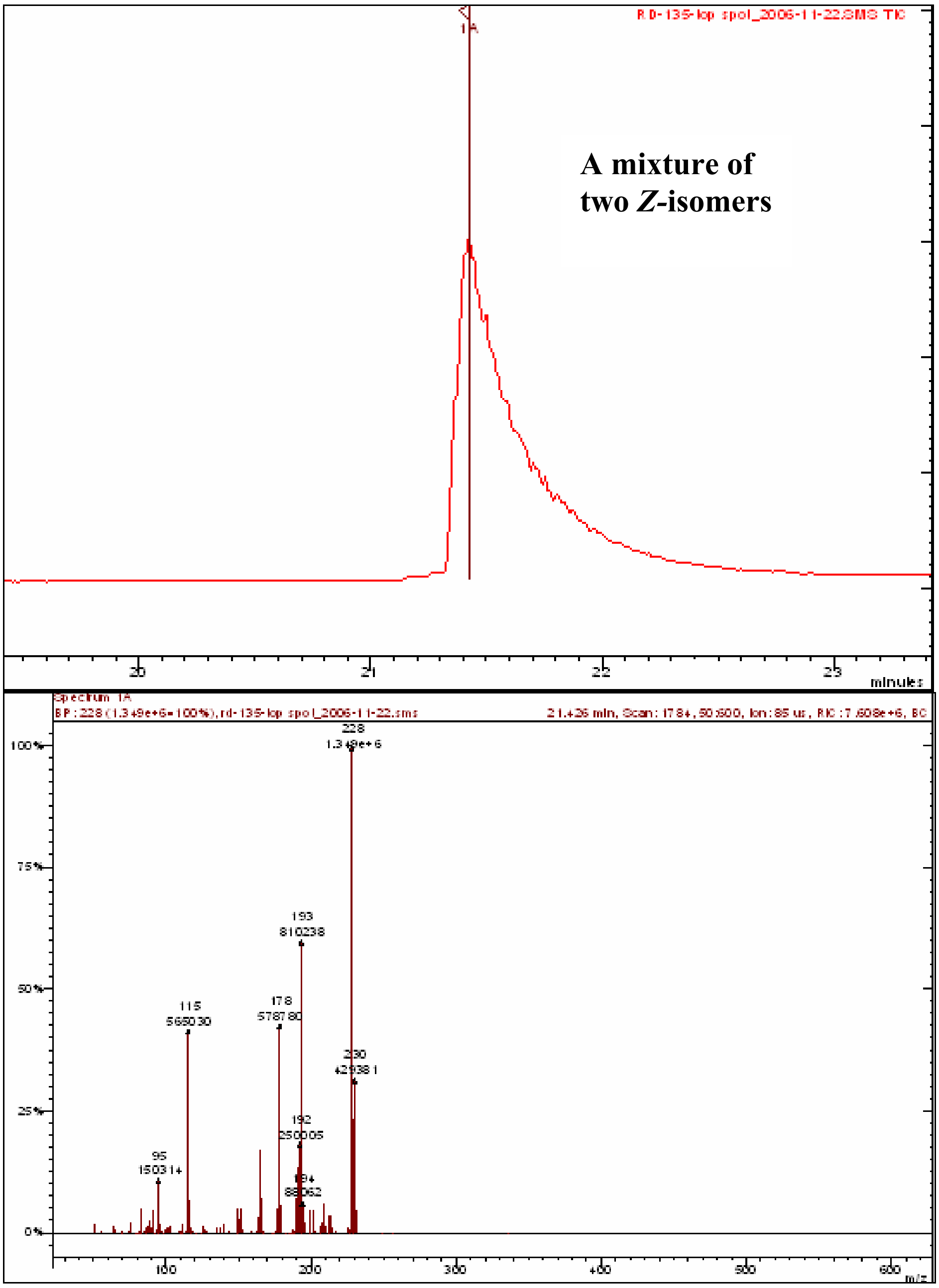
(*Z*)-1-(*p*-Chlorophenyl)-1-phenylpropene



$C_{15}H_{13}Cl$
Exact Mass: 228.1
m/e: 228.1 (100.0%), 230.1 (33.3%), 229.1 (16.9%), 231.1 (5.5%)

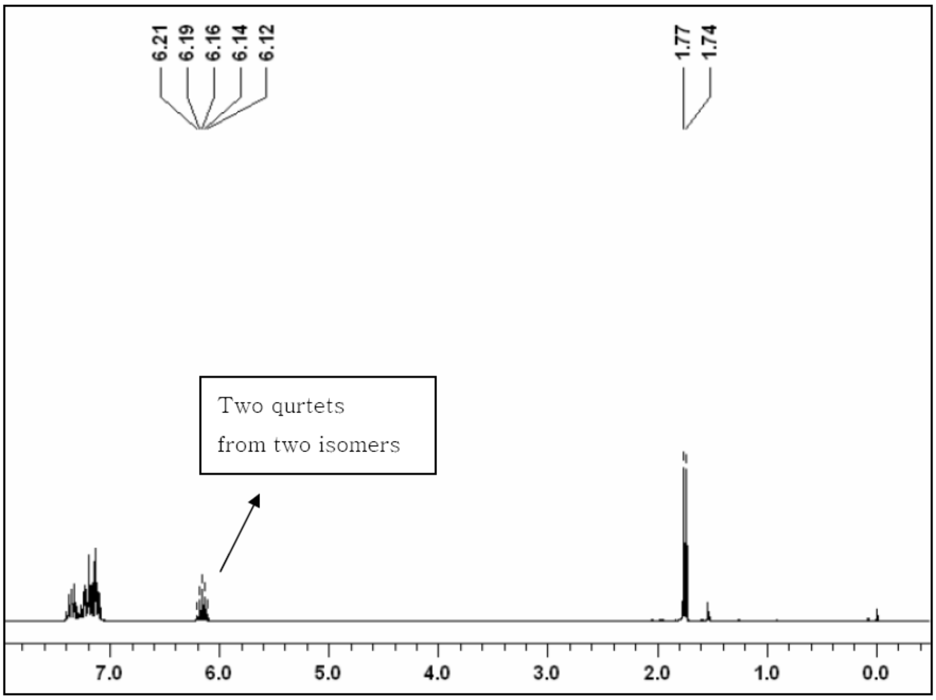
(*Z*)-1-(*o*-Chlorophenyl)-1-phenylpropene

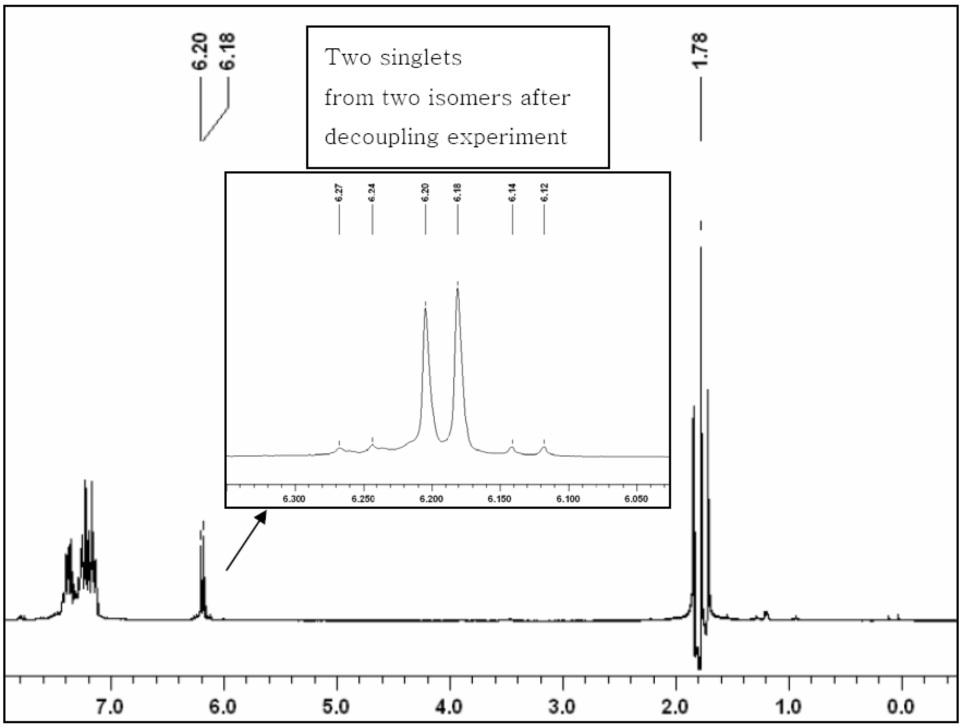
GC-MS Spectrum of 1-(*o*-chlorophenyl)-1-phenylpropene



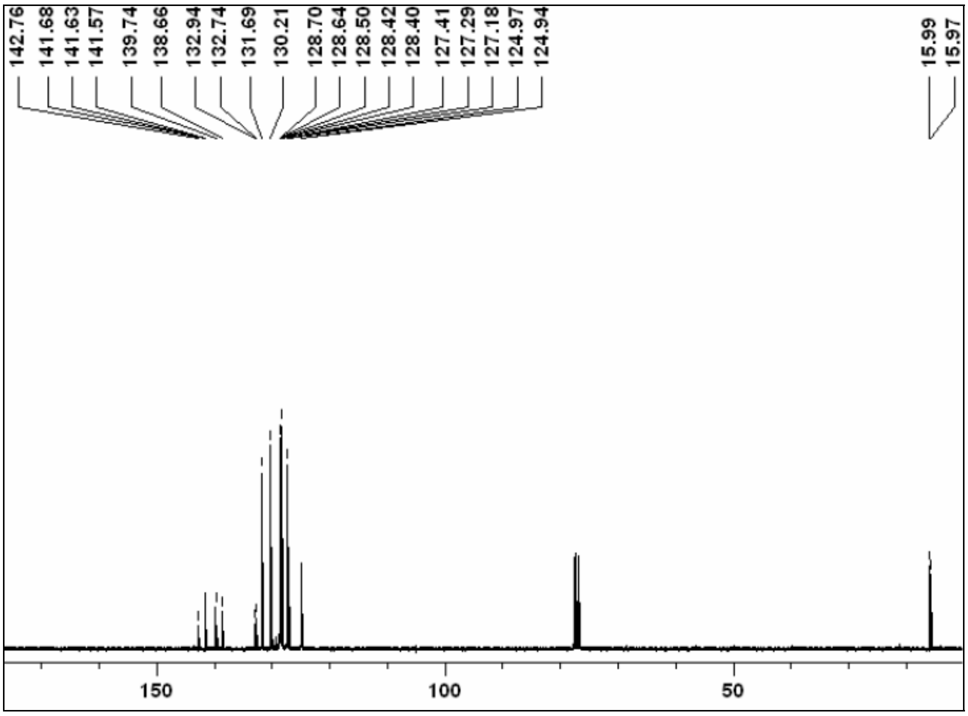
A mixture of two *Z*-isomers

^{1}H NMR Spectrum of 1-(*o*-chlorophenyl)-1-phenylpropene

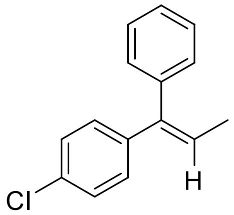




^{13}C NMR Spectrum of 1-(*o*-chlorophenyl)-1-phenylpropene

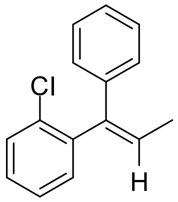


- **The second mixture: Rf value on TLC (Hexane) = 0.27**



$C_{15}H_{13}Cl$
Exact Mass: 228.1
m/e: 228.1 (100.0%), 230.1 (33.3%), 229.1 (16.9%), 231.1 (5.5%)

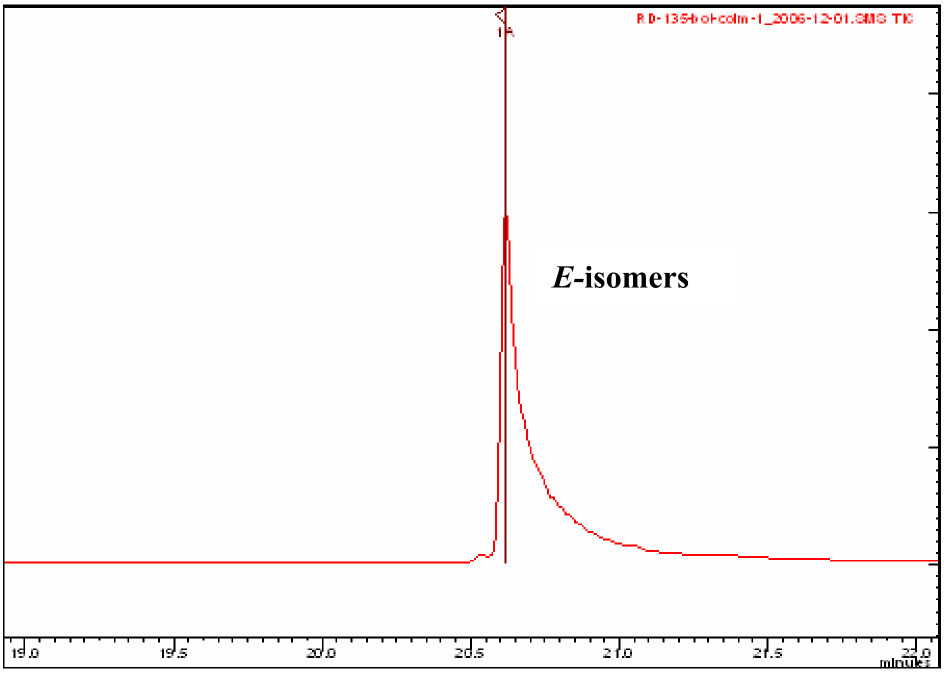
(*E*)-1-(*p*-chlorophenyl)-1-phenylpropene

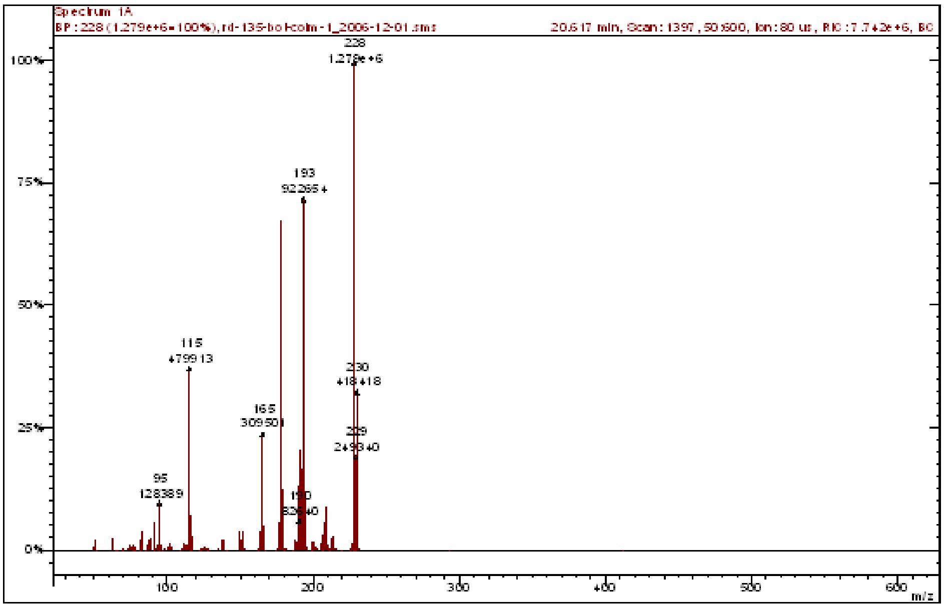


$C_{15}H_{13}Cl$
Exact Mass: 228.1
m/e: 228.1 (100.0%), 230.1 (33.3%), 229.1 (16.9%), 231.1 (5.5%)

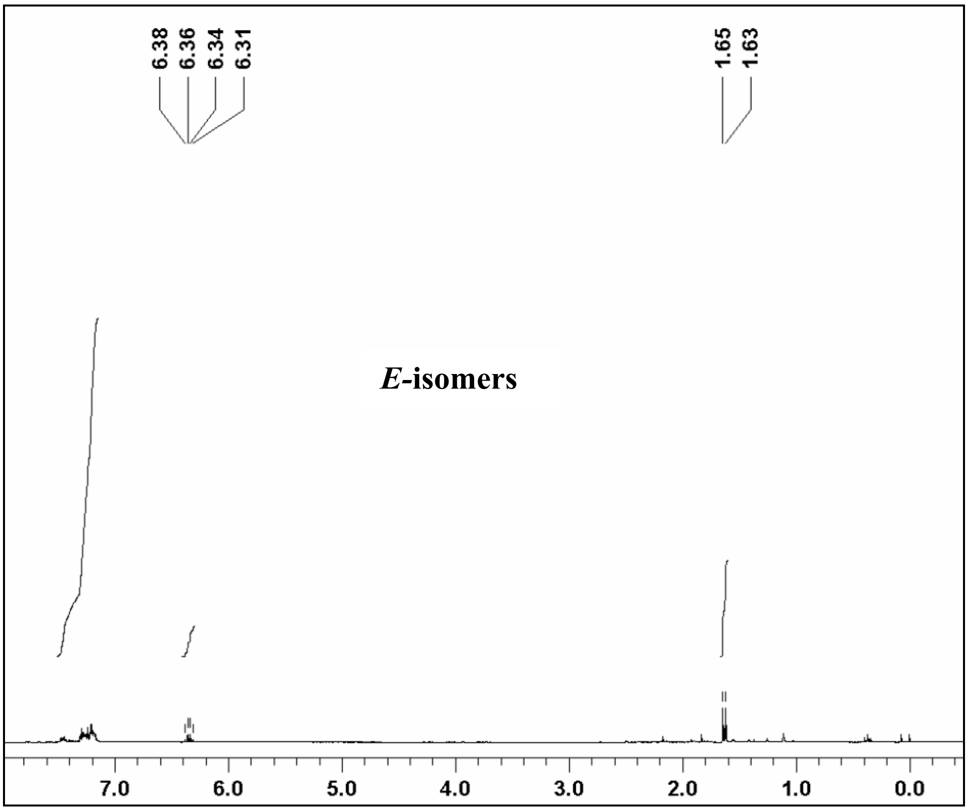
(*E*)-1-(*o*-chlorophenyl)-1-phenylpropene

GC-MS Spectrum of 1-(*p*-chlorophenyl)-1-phenylpropene

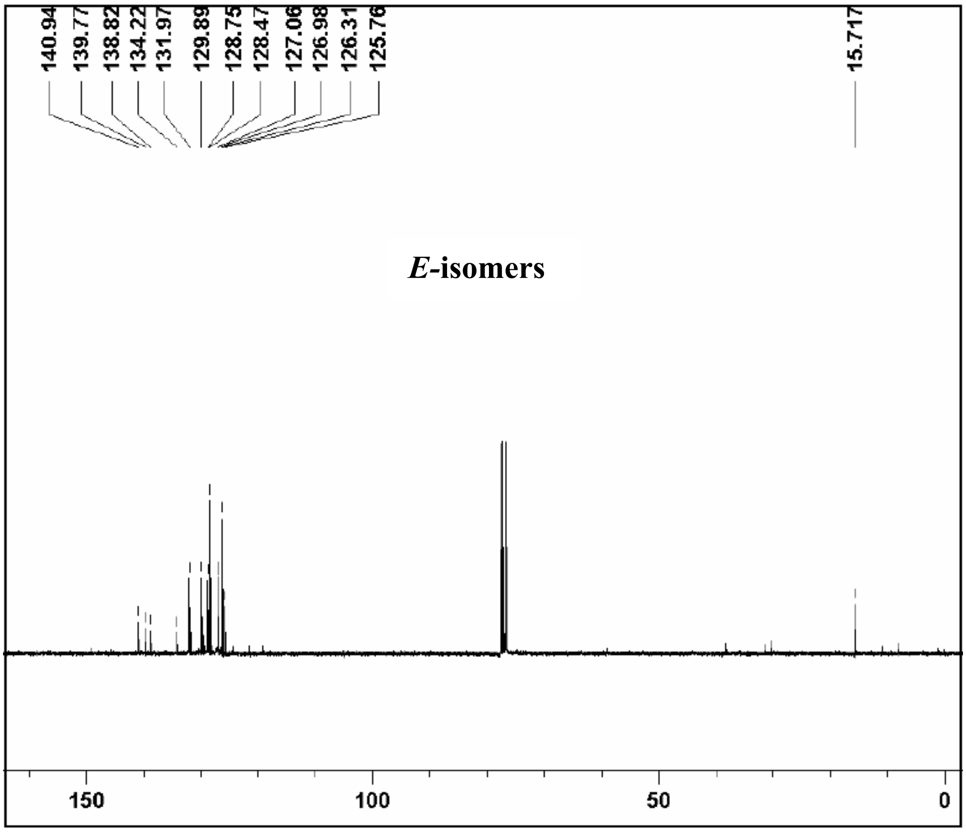




^{1}H NMR Spectrum of 1-(*p*-chlorophenyl)-1-phenylpropene

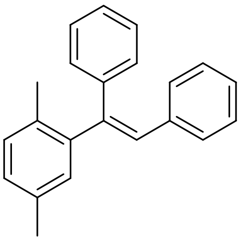


^{13}C NMR Spectrum of 1-(*p*-chlorophenyl)-1-phenylpropene



3. GC-MS, ^{1}H, ^{13}C NMR and differential NOE spectra for Table 3.

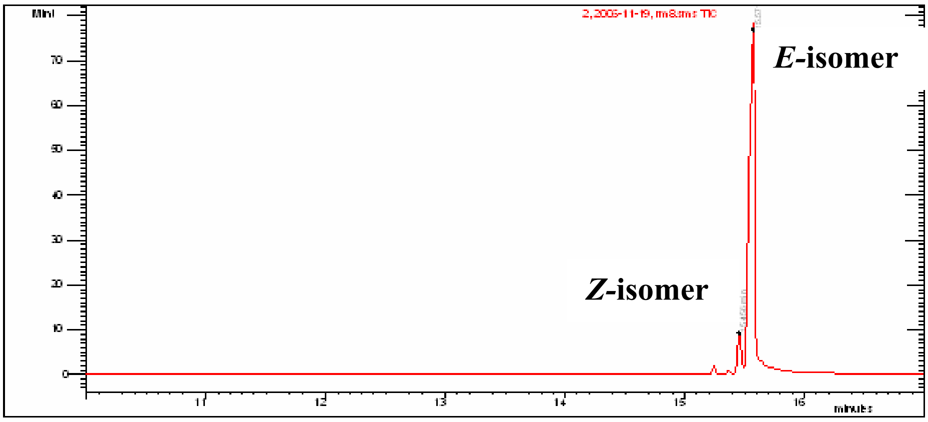
Entry 1 in Table 3



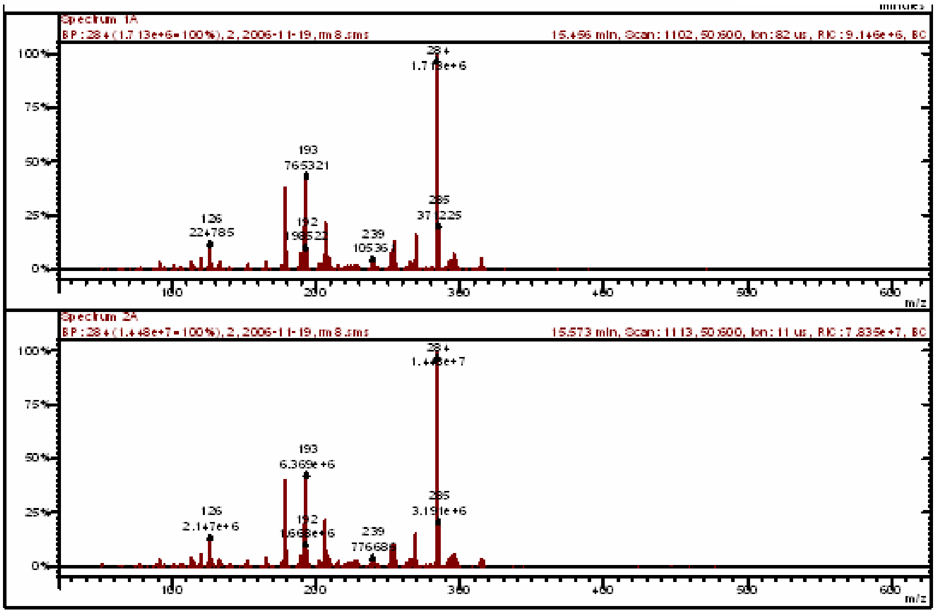
$C_{22}H_{20}$
Exact Mass: 284.2
m/e: 284.2 (100.0%), 285.2 (24.8%), 286.2 (2.9%)

(*E*)-1,2-Diphenyl-1-(*p*-xylyl)ethane

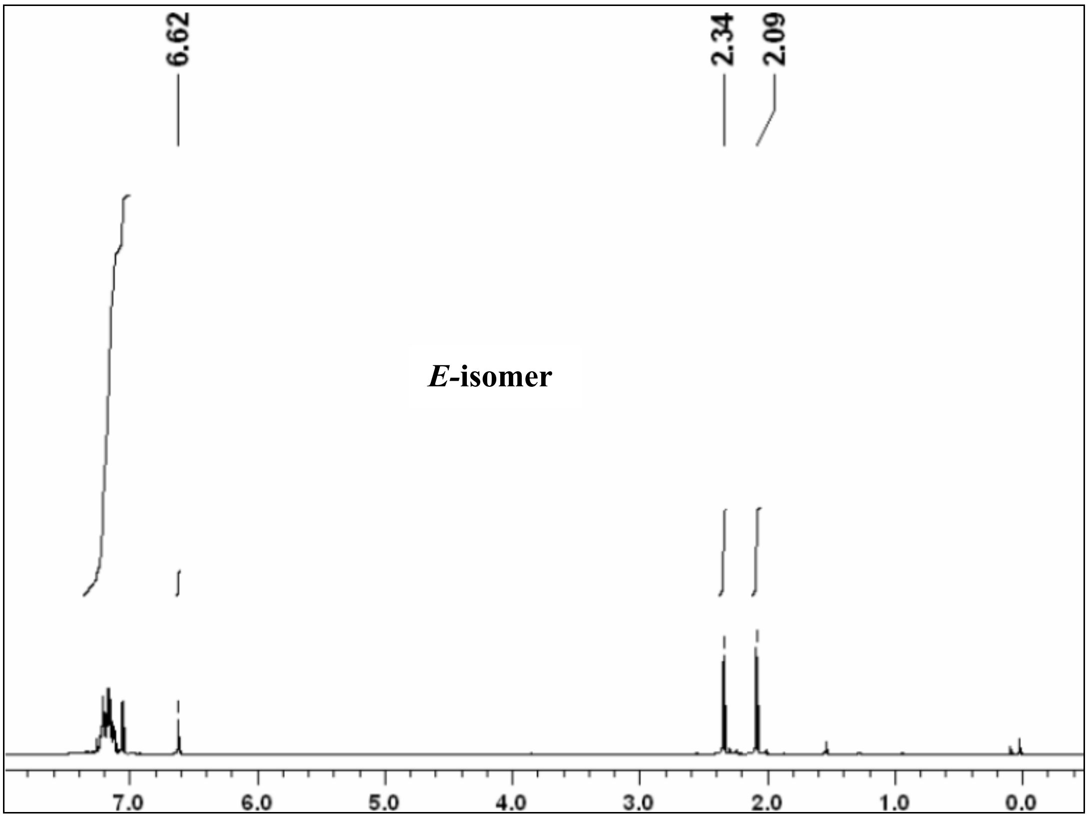
GC-MS Spectrum of (*E*)-1,2-diphenyl-1-(*p*-xylyl)ethane



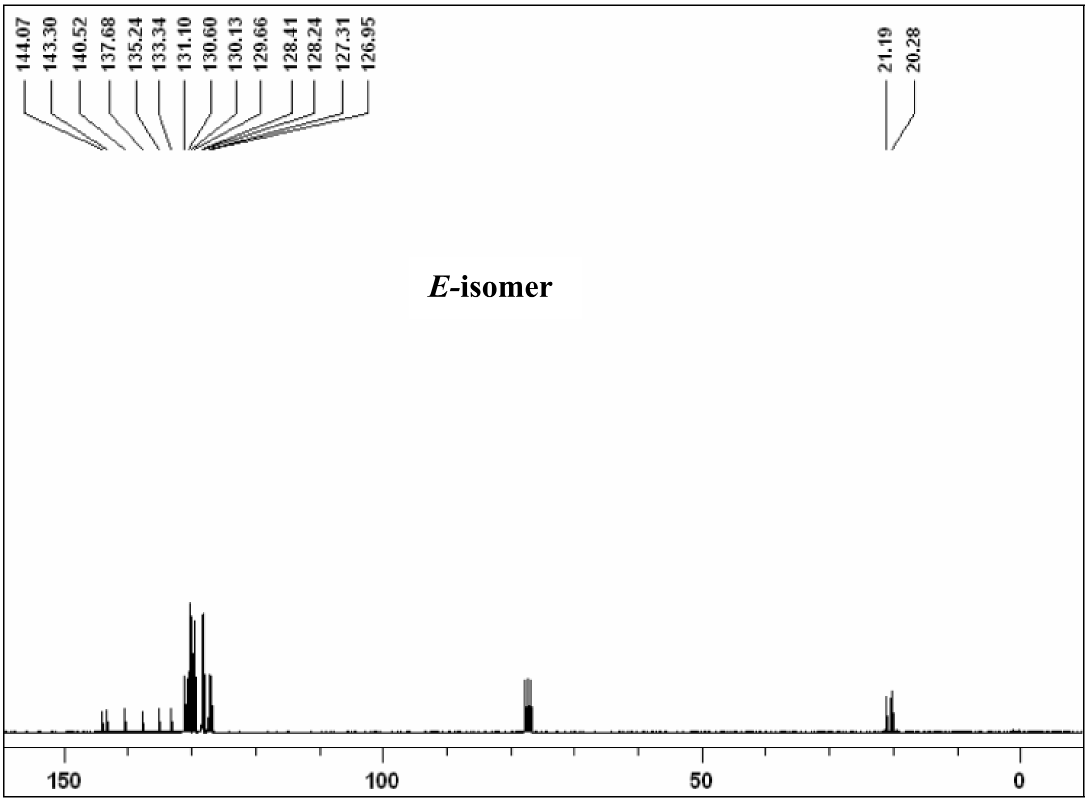
RT	Quan Ions	Area	Area %	Height
15.456	RIC	1.878E7	6.73	9.070E6
15.571	RIC	2.602E8	93.27	7.814E7



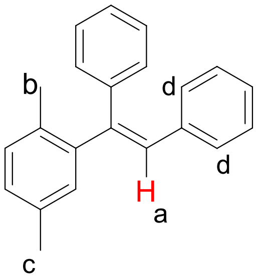
^{1}H NMR Spectrum of (*E*)-1,2-diphenyl-1-(*p*-xylyl)ethane

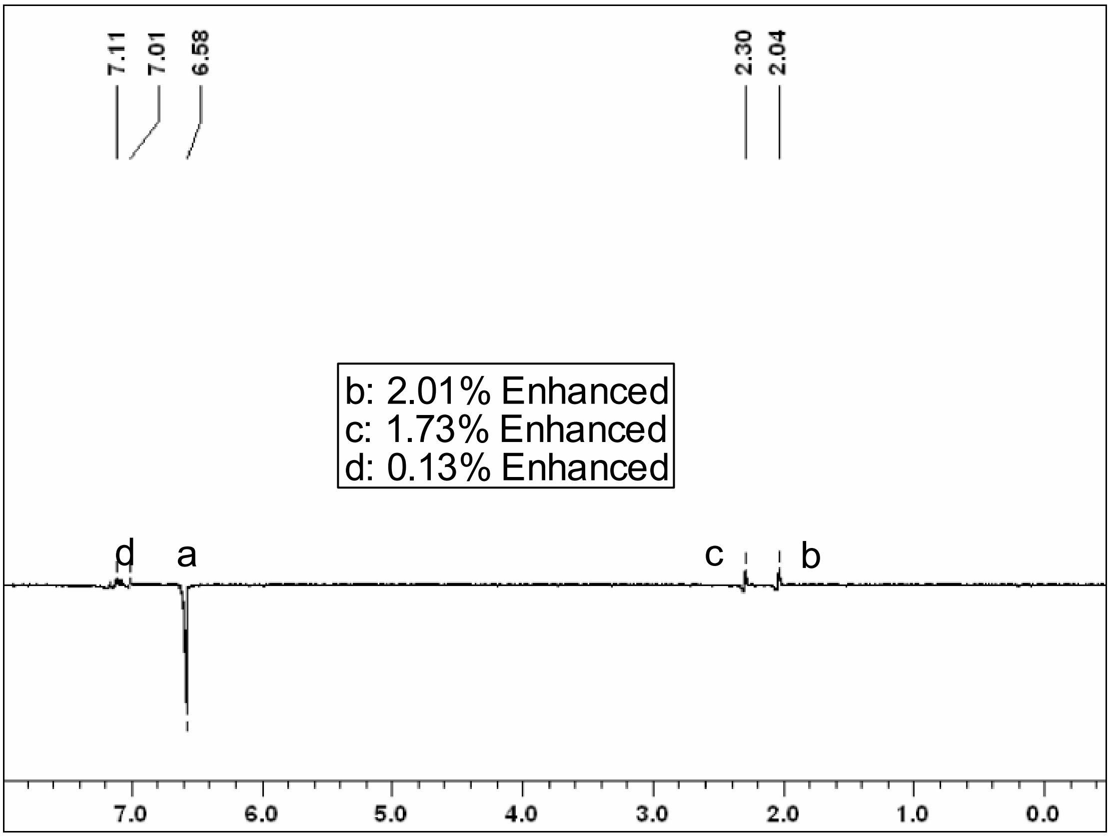


^{13}C NMR Spectrum of (*E*)-1,2-diphenyl-1-(*p*-xylyl)ethane

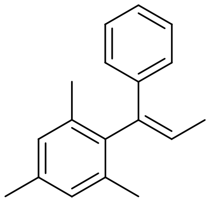


Differential NOE Spectrum of (*E*)-1,2-Diphenyl-1-(*p*-xylyl)ethane





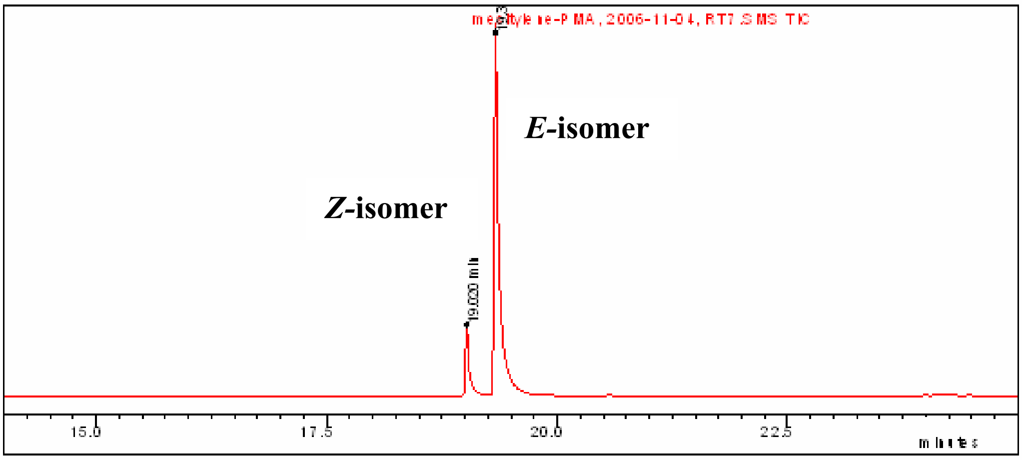
Entry 2 in Table 3



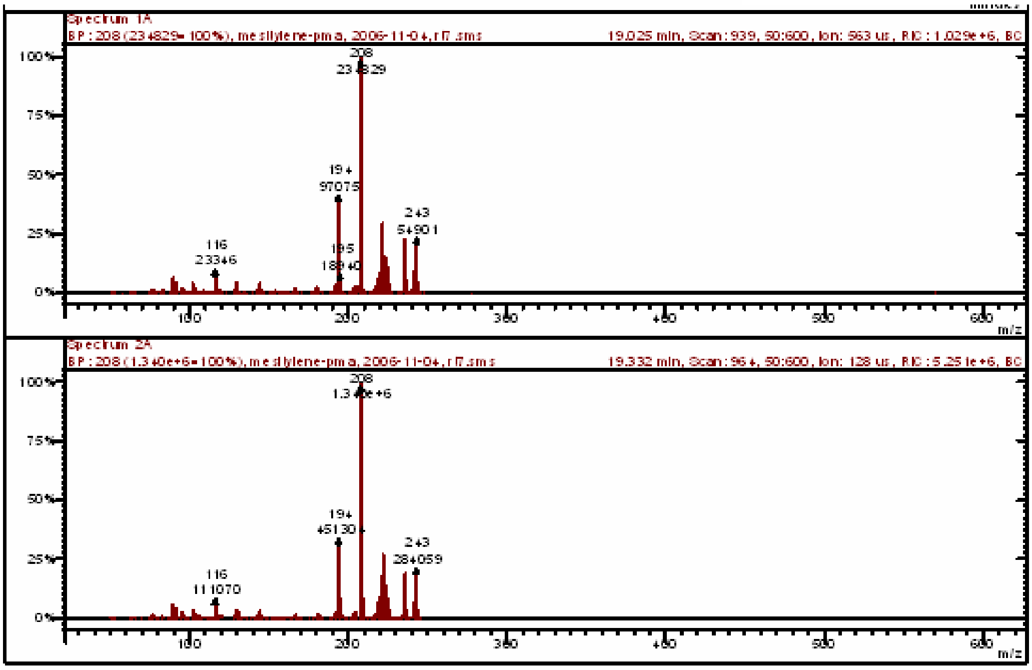
$C_{18}H_{20}$
Exact Mass: 236.2
m/e: 236.2 (100.0%), 237.2 (20.3%), 238.2 (2.0%)

(*E*)-1-Mesityl -1-phenylpropene

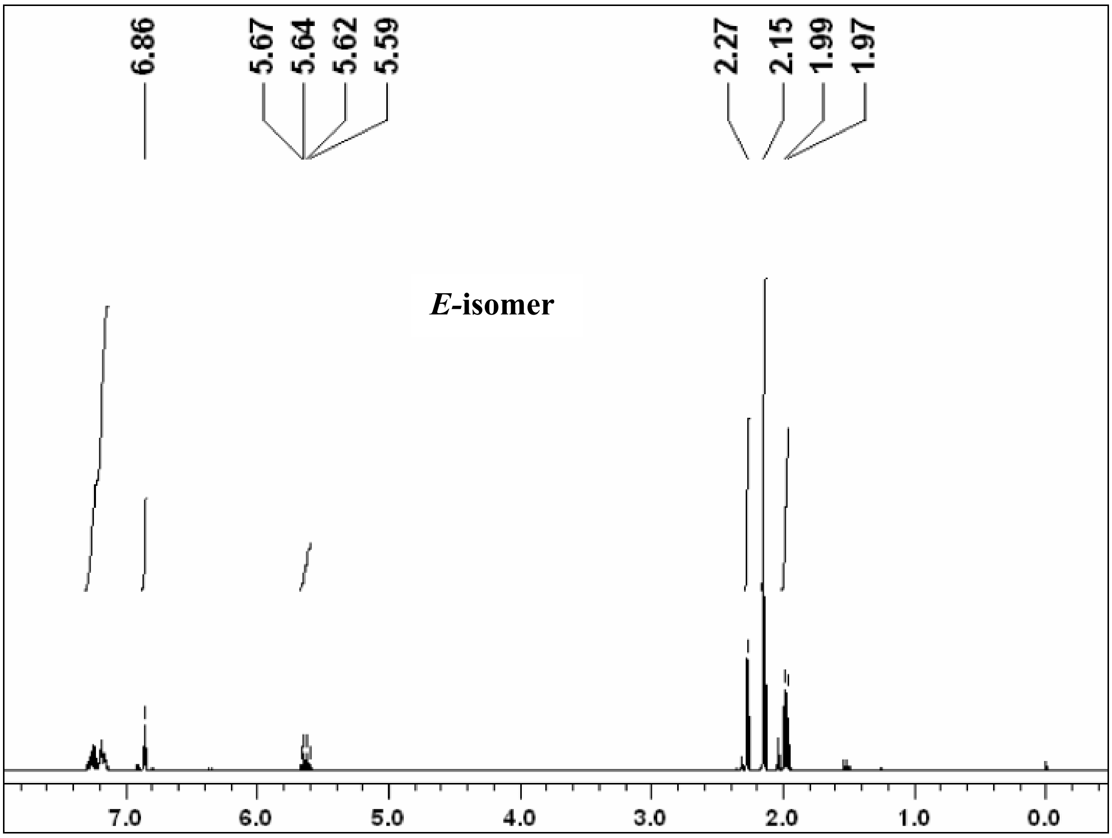
GC-MS Spectrum of 1-mesityl -1-phenylpropene



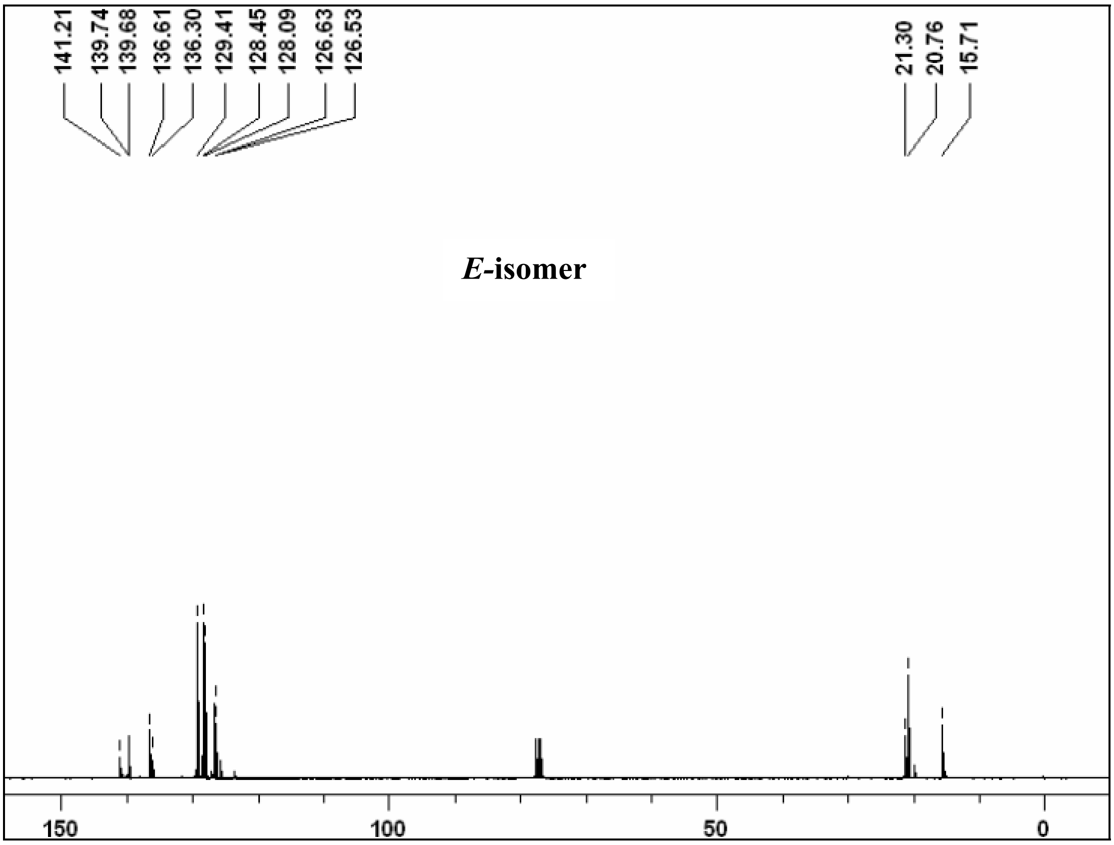
RT	Quan Ions	Area	Area %	Height
19.020	RIC	3.123E6	13.71	1.025E6
19.333	RIC	1.966E7	86.29	5.244E6



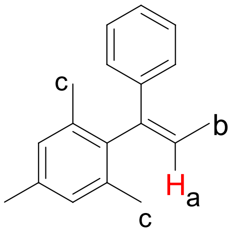
^{1}H NMR Spectrum of 1-mesityl -1-phenylpropene

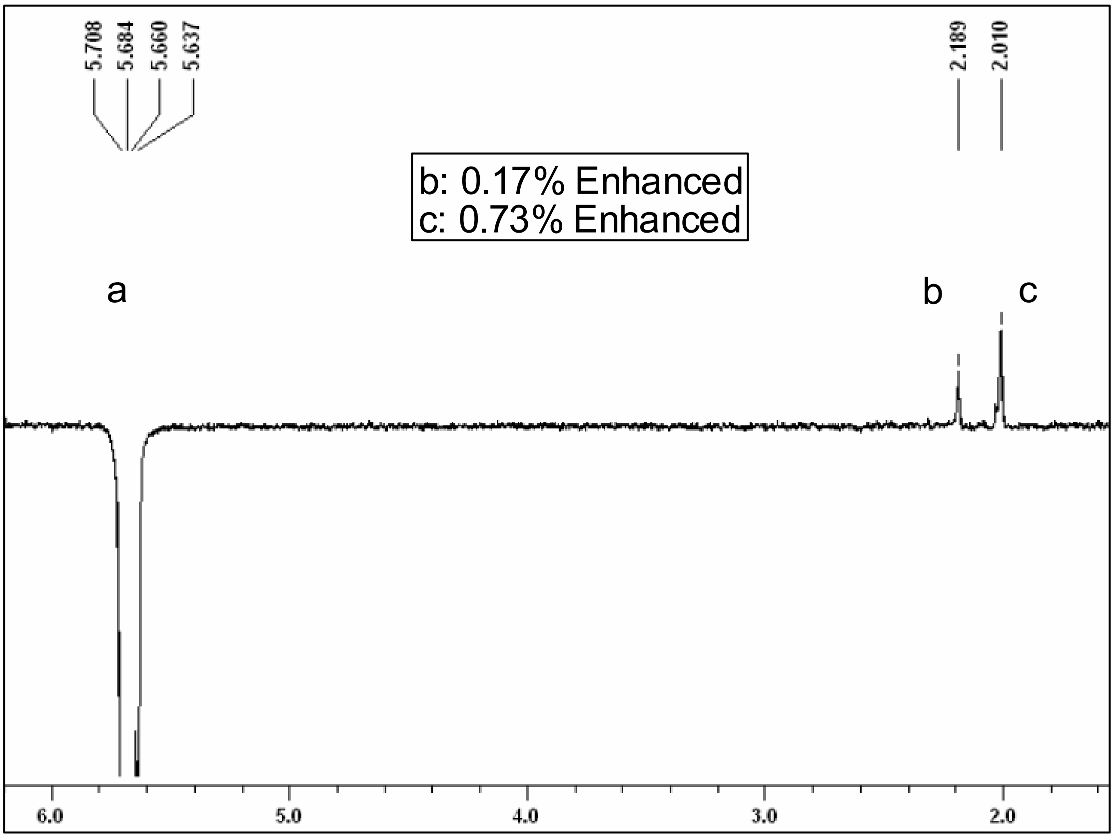


^{13}C NMR Spectrum of 1-mesityl -1-phenylpropene

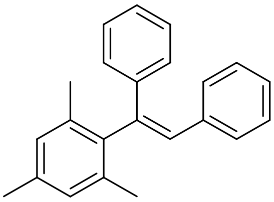


Differential NOE Spectrum of (*E*)-1-Mesityl-1-phenylpropene





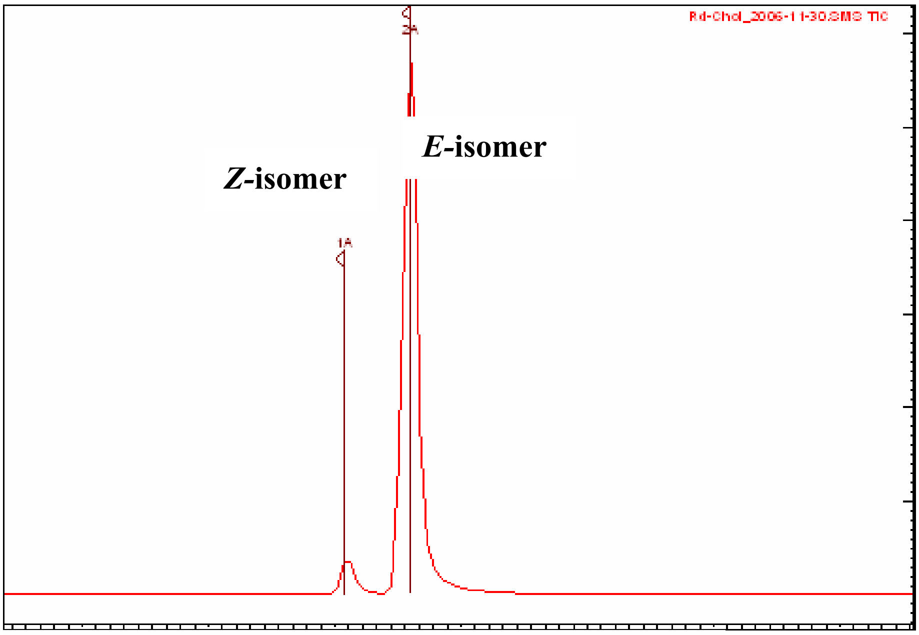
Entry 3 in Table 3



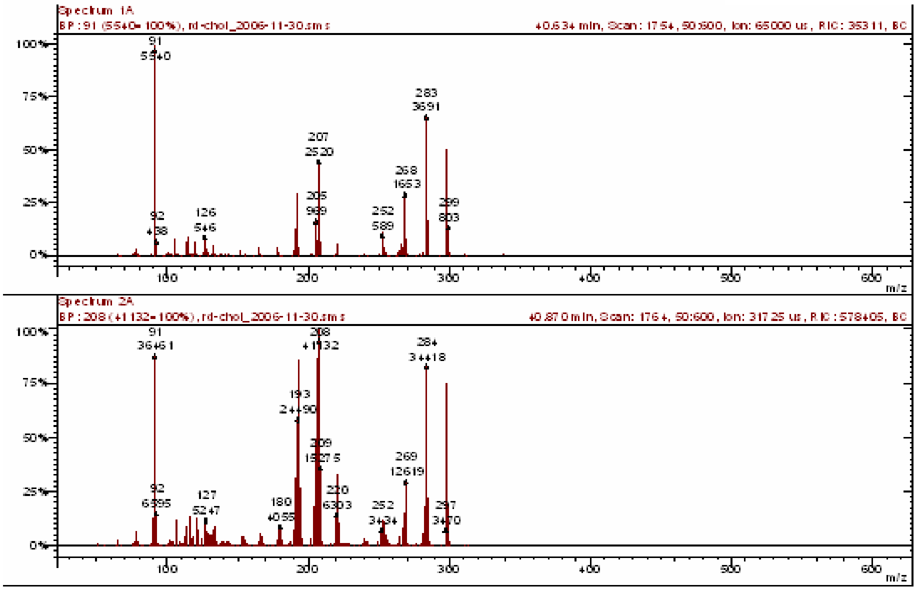
$C_{23}H_{22}$
Exact Mass: 298.2
m/e: 298.2 (100.0%), 299.2 (25.9%), 300.2 (3.2%)

(*E*)-1,2-Diphenyl-1-mesitylethene

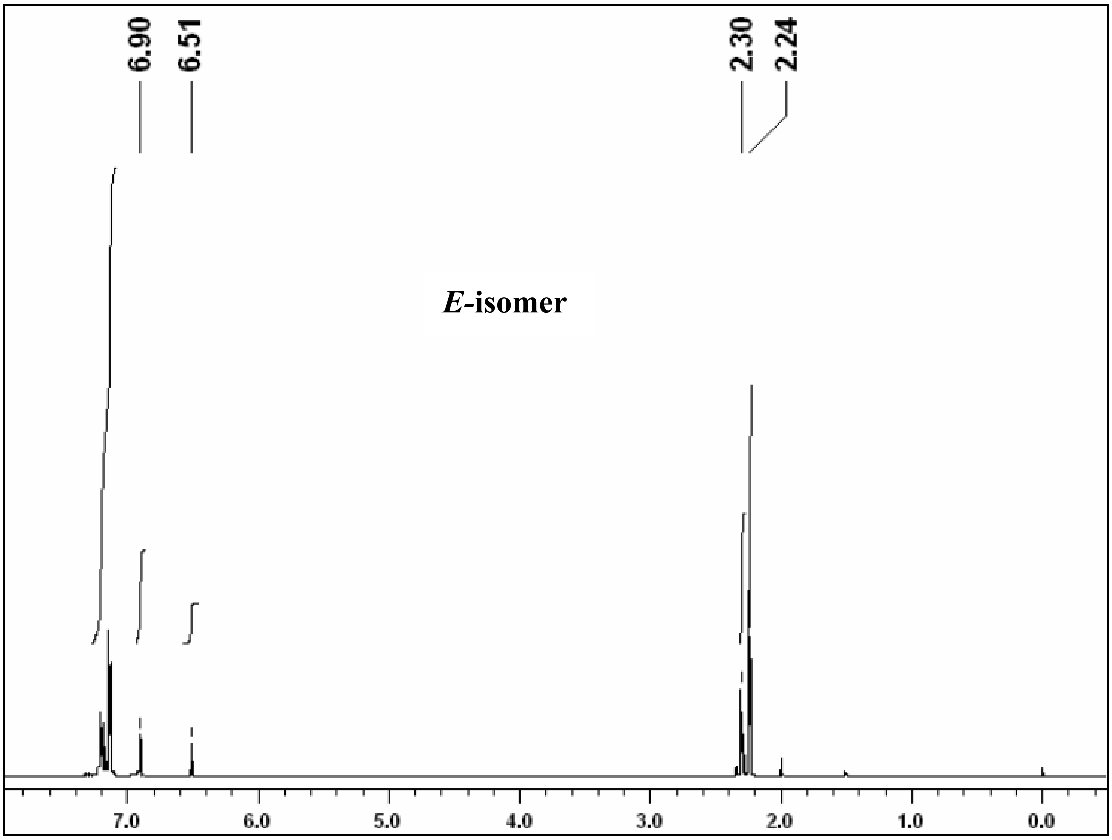
GC-MS Spectrum of 1,2-diphenyl-1-mesitylethene



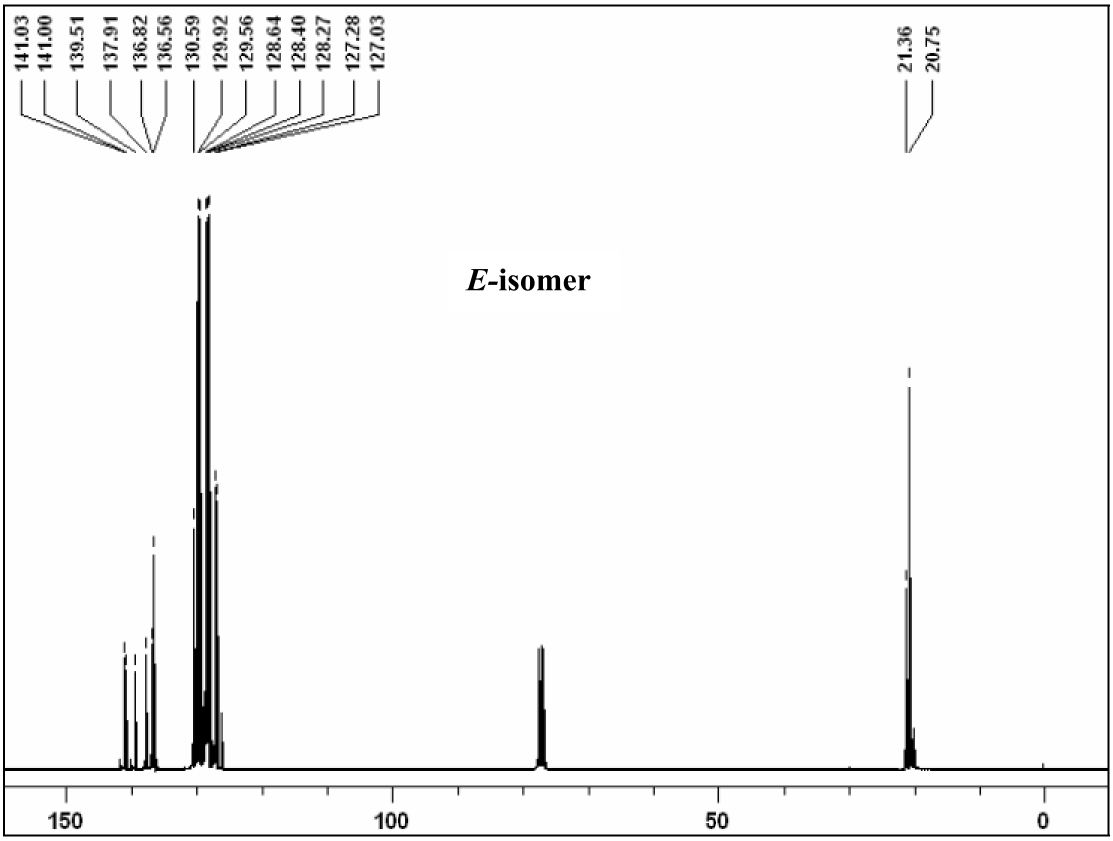
RT	Quan Ions	Area	Area %	Height
40.644	RIC	134793	5.91	35962
40.871	RIC	2.144E6	94.09	572300



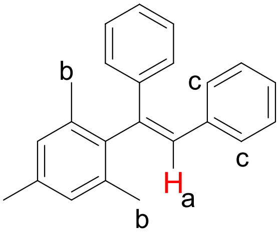
^{1}H NMR Spectrum of 1,2-diphenyl-1-mesitylethene

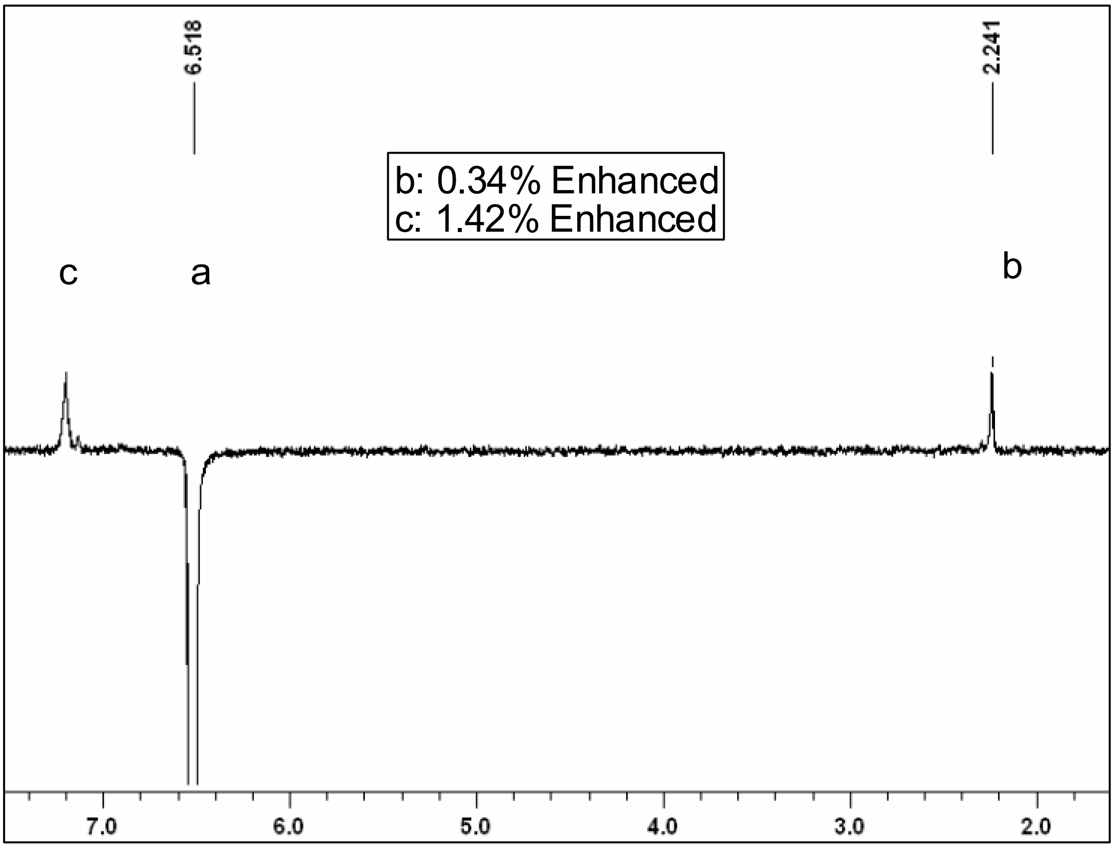


^{13}C NMR Spectrum of 1,2-diphenyl-1-mesitylethene

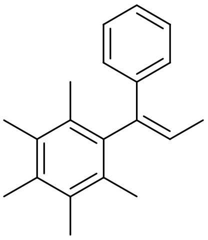


Differential NOE Spectrum of (*E*)-1,2-Diphenyl-1-mesitylethene





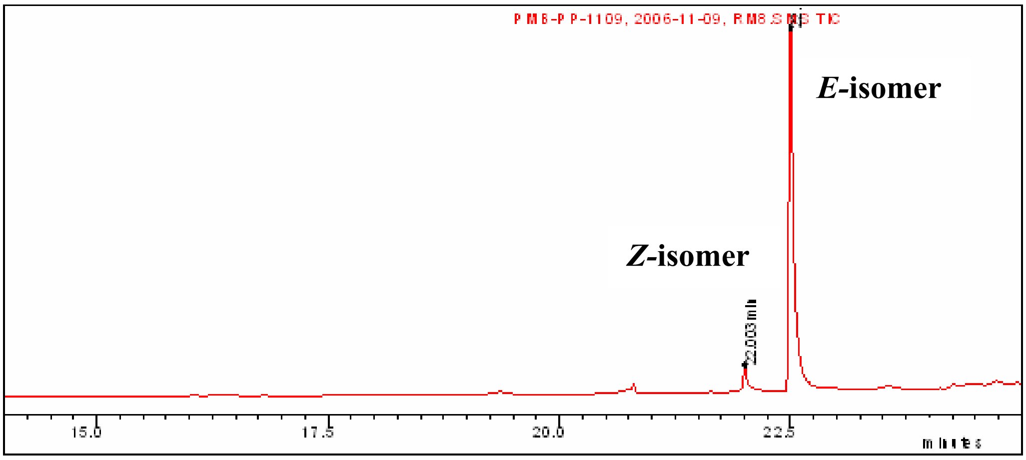
Entry 4 in Table 3



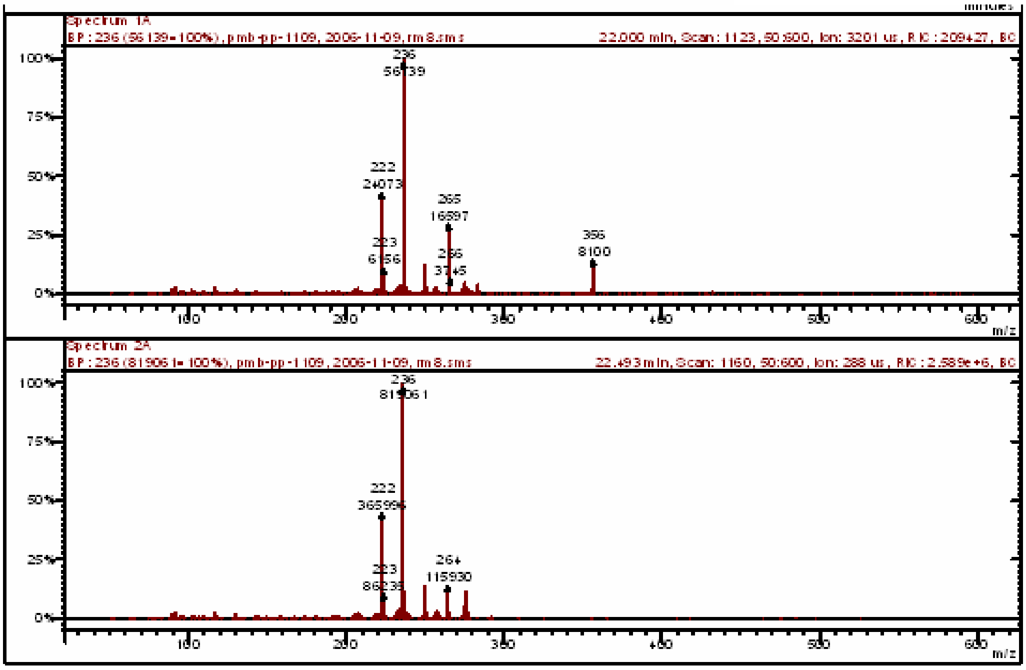
$C_{20}H_{24}$
Exact Mass: 264.2
m/e: 264.2 (100.0%), 265.2 (22.6%), 266.2 (2.4%)

(*E*)-1-Pentamethylphenyl-1-phenylpropene

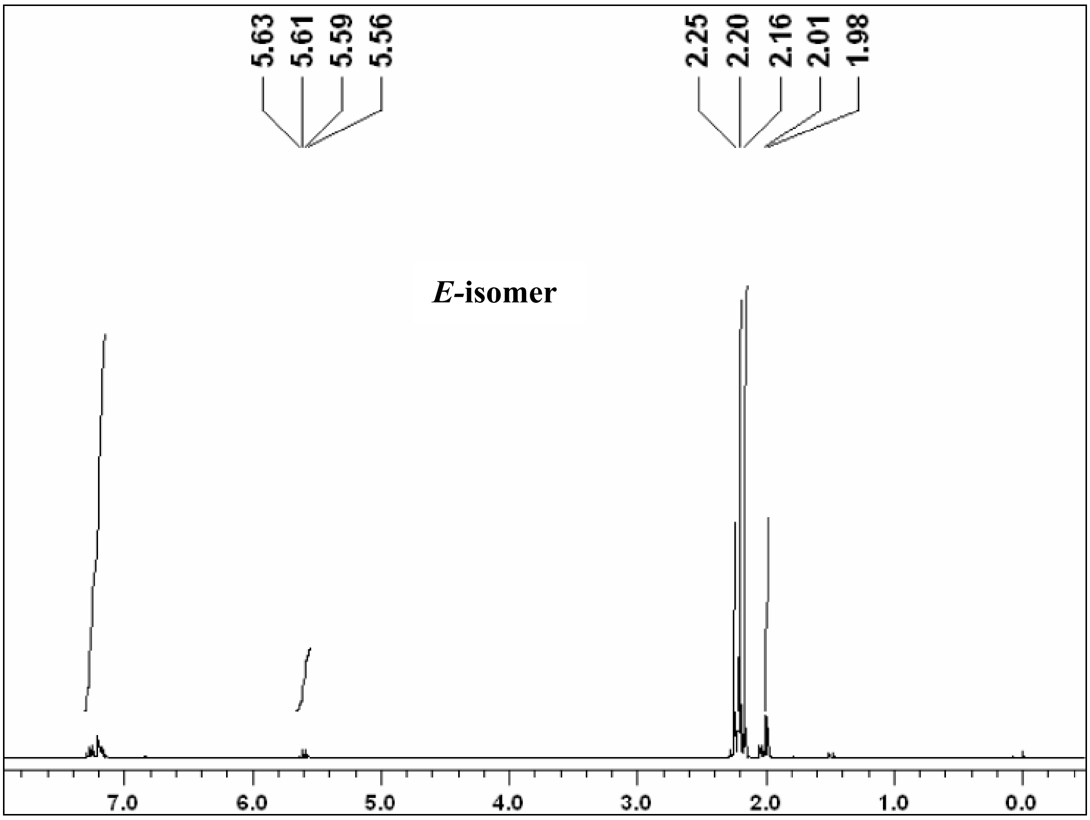
GC-MS Spectrum of 1-pentamethylphenyl-1-phenylpropene



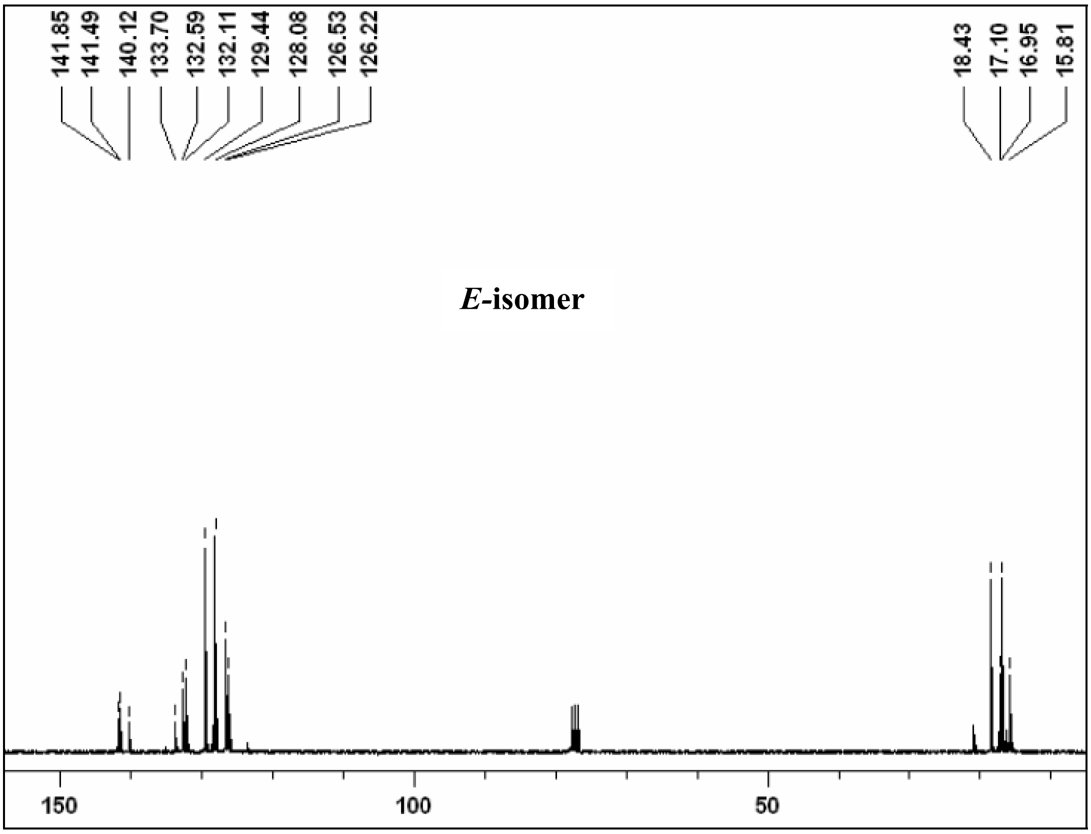
RT	Quan Ions	Area	Area %	Height
22.003	RIC	436308	4.40	173963
22.498	RIC	9.481E6	95.60	2.551E6



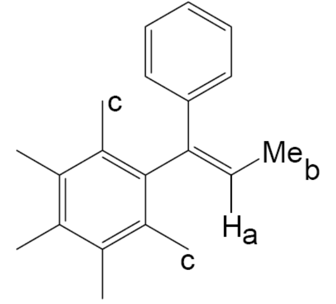
^{1}H NMR Spectrum of 1-pentamethylphenyl-1-phenylpropene

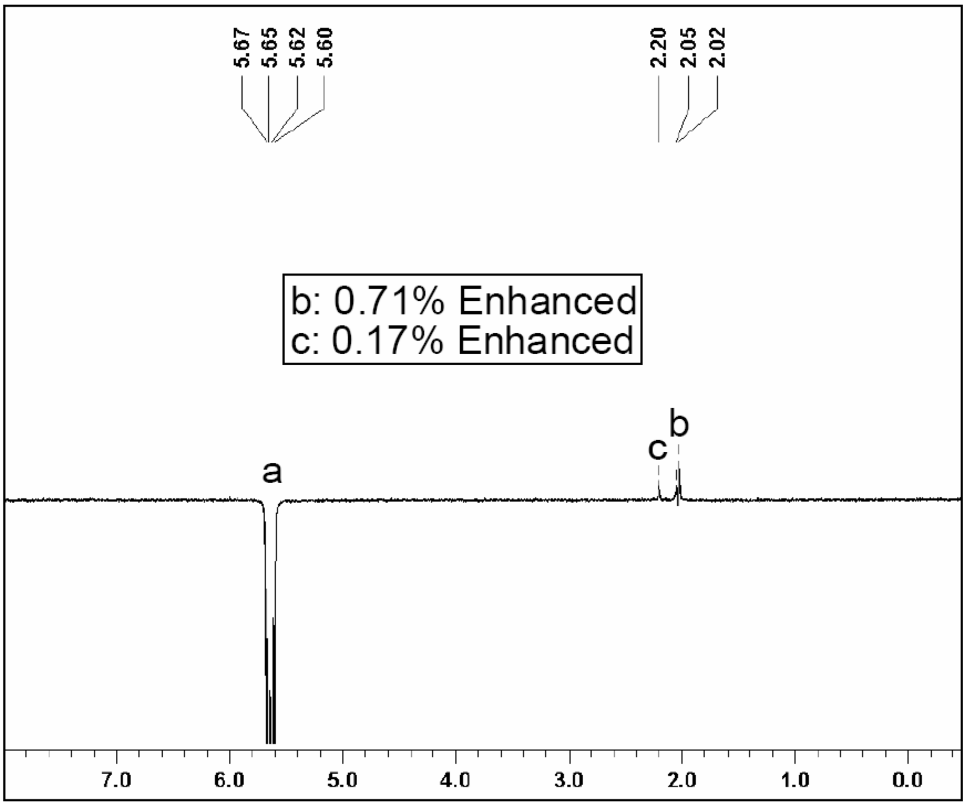


^{13}C NMR Spectrum of 1-pentamethylphenyl-1-phenylpropene

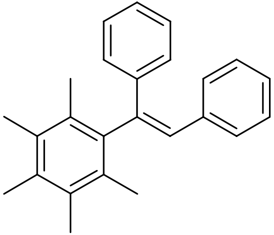


Differential NOE Spectrum of (*E*)-1-Pentamethylphenyl-1-phenylpropene





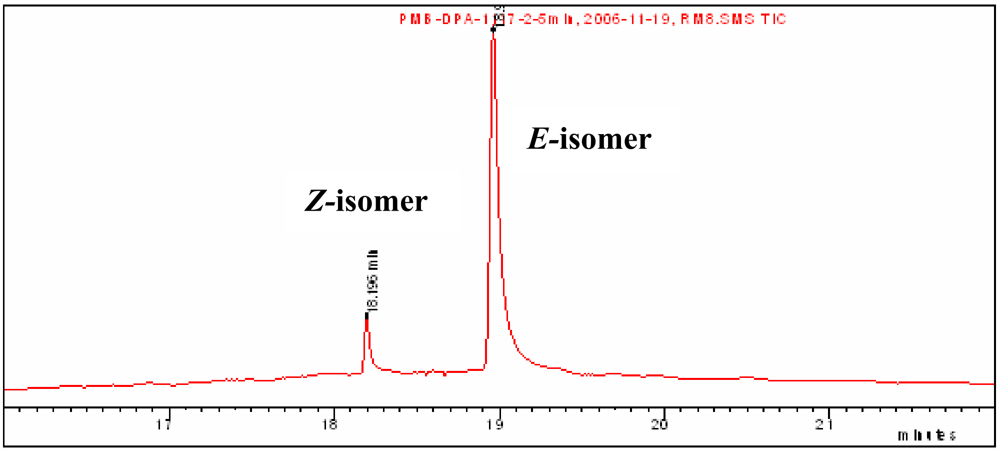
Entry 5 in Table 3



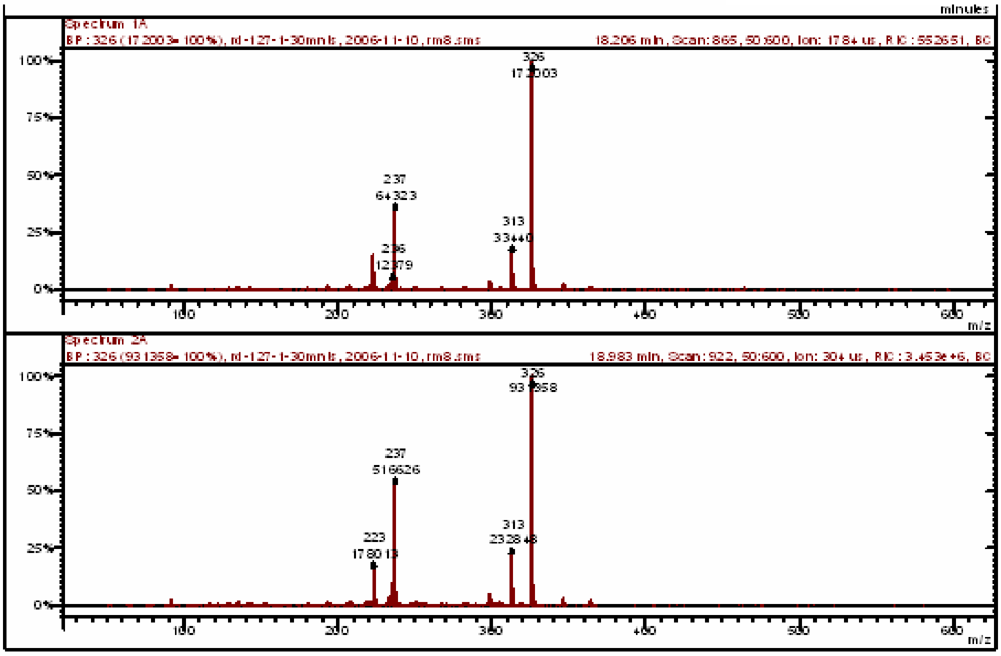
$C_{25}H_{26}$
Exact Mass: 326.2
m/e: 326.2 (100.0%), 327.2 (28.2%), 328.2 (3.8%)

(*E*)-1,2-Diphenyl-1-(pentamethylphenyl)ethane

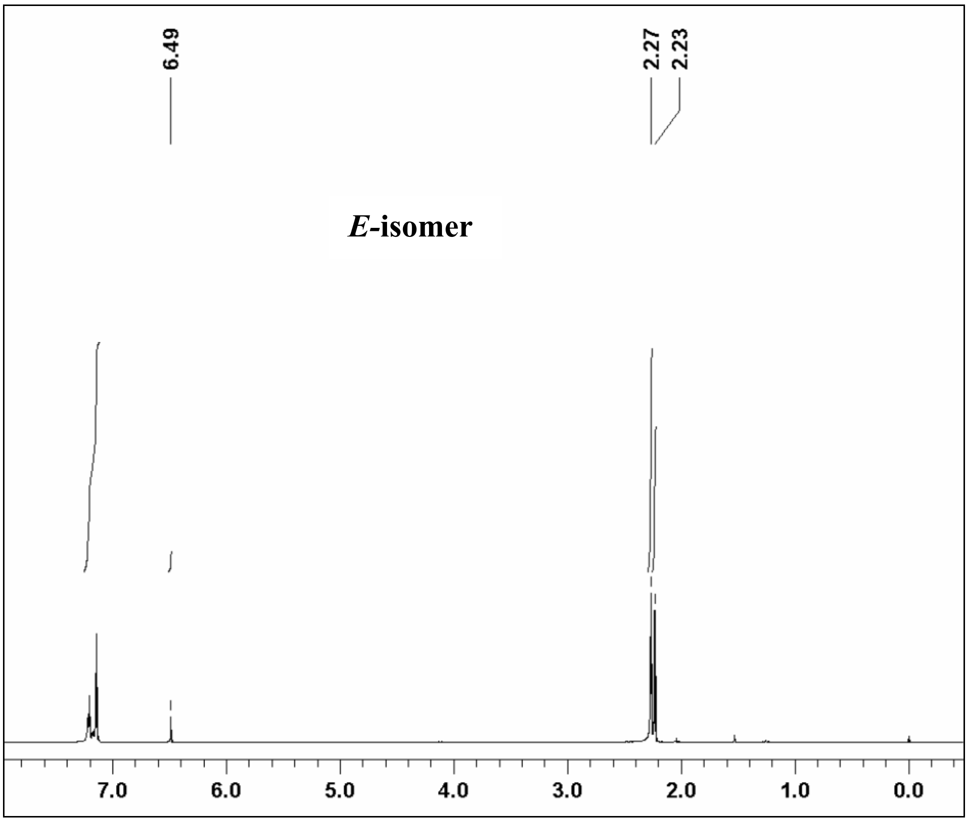
GC-MS Spectrum of 1,2-diphenyl-1-(pentamethylphenyl)ethane



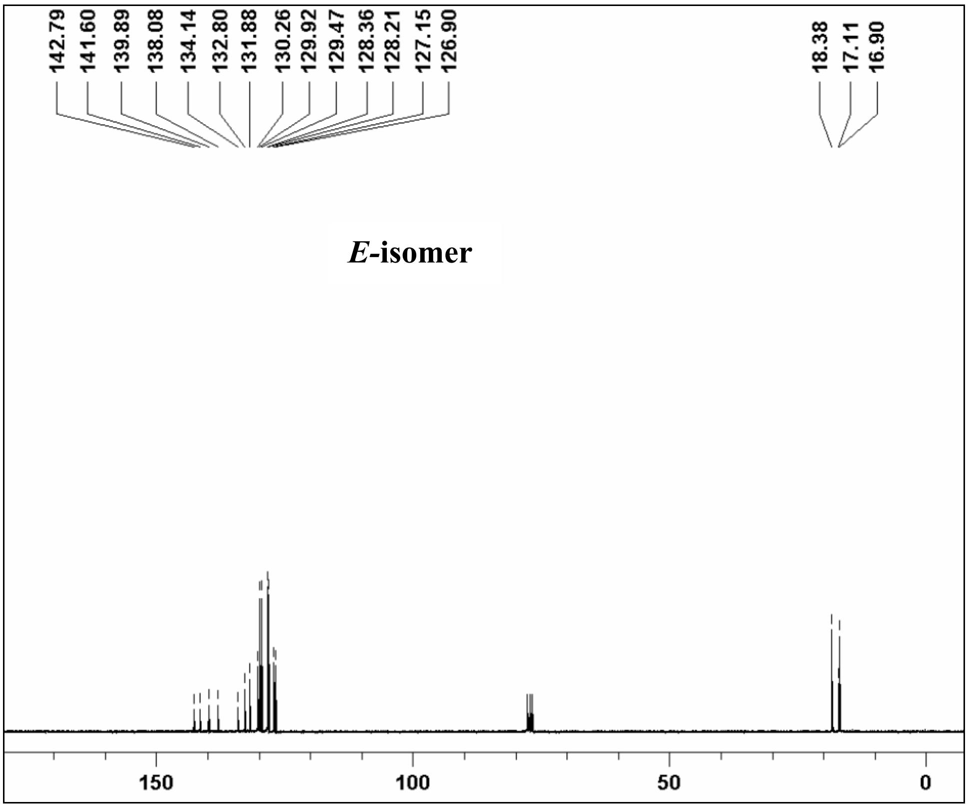
RT	Quan Ions	Area	Area %	Height
18.196	RIC	5.123E6	8.60	2.014E6
18.962	RIC	5.445E7	91.40	1.187E7



^{1}H NMR Spectrum of 1,2-diphenyl-1-(pentamethylphenyl)ethane



^{13}C NMR Spectrum of 1,2-diphenyl-1-(pentamethylphenyl)ethane



Differential NOE Spectrum of (*E*)-1,2-Diphenyl-1-(pentamethylphenyl)ethane