

Weakening C-O Bonds: Ti(III), a New Reagent for Alcohol Deoxygenation and Carbonyl Coupling Olefination

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Supporting Information

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General Details

IR spectra were recorded on a Mattson Satellite FTIR spectrometer. NMR spectra were performed with a Varian Direct-Drive 600 (^1H 600 MHz/ ^{13}C 150 MHz), 500 (^1H 500 MHz/ ^{13}C 125 MHz), Bruker ARX 400 (^1H 400 MHz/ ^{13}C 100 MHz) and Varian Inova Unity 300 (^1H 300 MHz/ ^{13}C 75 MHz) spectrometers. The accurate mass determination was carried out with a AutoSpec-Q mass spectrometer arranged in a EBE geometry (Micromass Instrument, Manchester, UK) and equipped with a FAB (LSIMS) source. The instrument was operated at 8 KV of accelerating voltage and Cs^+ were used as primary ions. Optical rotations were measured on a Perkin-Elmer 141 polarimeter, using CHCl_3 as the solvent. Silica gel SDS 60 (35-70 μm) was used for flash column chromatography. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as the visualizing agent and a solution of phosphomolybdic acid in ethanol and heat as developing agent. GC-MS analyses were carried out in a Hewlett Packard 6890 chromatograph connected to a Hewlett-Packard 5988A mass spectrometer using an ionization voltage of 70 eV. The GC conditions were: HP-1 methylsilicone capillary column (25 m x 0.2 mm); He 1.9 mL/min; the injection and detector heater temperature was 250°C; temperature program from 50°-300°C at 10°C/min. Quantitative chromatographic analysis were carried out on Hewlett Packard 6890 chromatograph equipped with a flame ionization detector (FID) and coupled to an integrator HP-3390A. The column and experimental conditions were the same as those described above, except that the detector heater temperature was 300°C and the inlet head was 20 psi. The percentage compositions were computed from the GC peak areas without correction factors. HPLC with UV and RI detection was used. Semi-preparative HPLC separations were carried out on a column (5 μm Silica, 10 x 250 mm) at a flow rate of 2.0 mL/min in an Agilent Serie 1100 instrument. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as the visualizing agent and a solution of phosphomolybdic acid in ethanol and heat as developing agent. All air- and water-sensitive reactions were performed in flasks flame-dried under a positive flow of argon and conducted under an argon atmosphere. The solvents used were purified according to standard

literature techniques and stored under argon. THF and toluene were freshly distilled immediately prior to use from sodium/benzophenone and strictly deoxygenated for 30 min under argon for each of the $\text{Cp}_2\text{TiCl}_2/\text{Mn}$ or Zn reactions. Reagents were purchased at the higher commercial quality and used without further purification, unless otherwise stated.

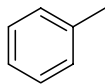
General procedure for stoichiometric deoxygenation-reduction reactions (Procedure A): toluene, 8, 10, 12, 14, 16, 18, 20, 23, 25, 27, 29, 31, 33, 35, 37, 38.

A mixture of Cp_2TiCl_2 (998 mg, 3.88 mmol) and Mn dust (154 mg, 2.77 mmol) in strictly deoxygenated THF (7 mL) was heated at reflux under stirring until the red solution turned green. Then, to this mixture was added a solution of the corresponding alcohol (1.85 mmol) in strictly deoxygenated THF (4 mL). The reaction mixture was heated at reflux under stirring until starting material disappearance (TLC monitoring), quenched with 1N HCl and extracted with *t*-BuOMe. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo yielding a. crude which was analyzed by CG-MS, purified by column chromatography over silica gel column and/or subjected to HPLC.

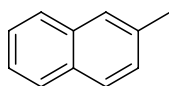
General procedure for catalytic deoxygenation- homocoupling carbonyl reactions (Procedure B): 20, 27, 31.

A mixture of Cp_2TiCl_2 (160 mg, 0.639 mmol) and Mn dust (935 mg, 17.04 mmol) in thoroughly deoxygenated THF (8 mL) and under Ar atmosphere was stirred until the red solution turned green. This mixture was then heated at reflux and the corresponding TMSCl (1.07 mL, 8.52 mmol) was added, finally the allylic aldehyde (1.92 mmol) in strictly deoxygenated THF (2 mL) was then added. The reaction mixture was stirred until starting material disappearance (TLC monitoring). It was then quenched with *t*-BuOMe, washed with 1 N HCl, brine, dried over anhydrous Na_2SO_4 and concentrated

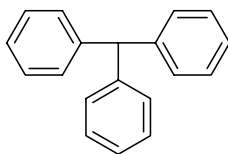
under reduced pressure. The resulting crude was purified by column chromatography on silica gel to afford the corresponding coupling products.



Toluene: According to the procedure A, the mixture containing benzyl alcohol (**1**) was heated for 45 min. The resulting crude was analyzed by GC-MS. **Toluene** (93 %, R_t = 4.42 min) was identified by the standard use.

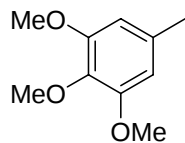


2-Methylnaphthalene (8): According to the procedure A described for deoxygenation-reduction, the mixture containing 2-naphtylmethanol (**7**) was heated for 60 min. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 6:1) on silica gel to afford **8** (79%). ^1H NMR (CD_3Cl , 300 MHz): δ 2.56 (s, 3H), 7.37 (d, J = 8.5 Hz, 1H), 7.47 (quintet, J = 6.4 Hz, 2H), 7.66 (bs, 1H), 7.78-7.86 (m, 3H); ^{13}C NMR (CD_3Cl , 75 MHz): δ 21.8, 125.0, 125.9, 126.9, 127.3, 127.7, 127.8, 128.2, 131.8, 133.7, 135.5. ^1H NMR spectroscopic data of this compound were identical to that of a standard.

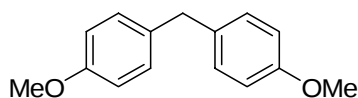


Triphenylmethane (10): According to the procedure A described for deoxygenation-reduction, the mixture containing triphenylmethanol (**9**) was heated for 60 min. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 6:1) on silica gel to afford **10** (91%). ^1H NMR (CD_3Cl , 300

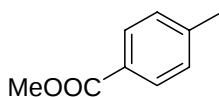
MHz): δ 7.38 (br s, 15H); ^{13}C NMR (CD_3Cl , 75 MHz): δ 82.1, 127.3, 128.0, 146.9. ^1H NMR spectroscopic data of this compound were identical to that of a standard.



1,2,3-Trimethoxy-5-methylbenzene (12): According to the procedure A described for deoxygenation-reduction, the mixture containing (3,4,5-trimethoxyphenyl)methanol (**11**) was heated for 50 min. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 4:1) on silica gel to afford **12** (90%). ^1H NMR (CD_3Cl , 300 MHz): δ 2.32 (s, 3H), 3.83 (s, 3H), 3.85 (s, 6H), 6.41 (s, 2H); ^{13}C NMR (CD_3Cl , 300 MHz): δ 21.7, 55.9, 60.8, 105.9, 133.5, 135.7, 152.9. ^1H NMR spectroscopic data of this compound were identical to that of a standard.

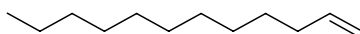


Bis(4-methoxyphenyl)methane (14): According to the procedure A described for deoxygenation-reduction, the mixture containing bis(4-methoxyphenyl)methanol (**13**) was heated for 90 min. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 6:1) on silica gel to afford **14** (60%). ^1H NMR (CD_3Cl , 300 MHz): δ 3.82 (s, 6H), 3.90 (s, 2H), 6.86 (d, J = 8.5 Hz, 4H), 7.12 (d, J = 8.5 Hz, 4H); ^{13}C NMR (CD_3Cl , 75 MHz): δ 40.2, 55.3, 113.9, 129.8, 133.8, 158.0. ^1H NMR spectroscopic data of this compound were identical to that of a standard.

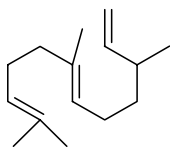


Methyl p-toluate (16): According to the procedure A described for the deoxygenation-reduction, the mixture containing methyl 4-formolbenzoate **15** was heated at reflux for 55 min. The resulting crude

was purified by column chromatography using hexane as eluent on silica gel to afford **16** (83 %) as brown prisms. IR (film): 2952, 2925, 2855, 1725, 1614, 1435, 1310, 1108, 1021, 840, 754, 691 cm^{-1} . ^1H NMR (400 MHz; CDCl_3) δ 2.31 (s, 3H) , 3.81 (s, 3H) , 7.14 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz; CDCl_3) δ 21.6, 51.9, 127.5, 129.1 (2C), 129.6 (2C), 143.5, 167.1. HREIMS (m/z): $[\text{M}]^+$ calcd. for $\text{C}_9\text{H}_{10}\text{O}_2$ 150.0681 found 150.0675.



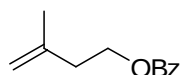
1-Dodecene (18): According to the procedure A described for deoxygenation-reduction, the mixture containing (*E*)-2-dodecen-1-ol (**17**) was heated for 50 min. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 9:1) on silica gel to afford **18** (91%). ^1H NMR (CD_3Cl , 500 MHz): δ 0.88 (t, J = 6.8 Hz, 3H), 1.21-1.41 (m, 16H), 2.04 (q, J = 6.8 Hz, 2H), 4.92 (br d, J = 10.0 Hz, 1H), 4.99 (br d, J = 17.0 Hz, 1H), 5.81 (ddt, J = 6.8 Hz, 10.0 Hz, 17.0 Hz, 1H); ^{13}C NMR (CD_3Cl , 125 MHz): δ 14.1, 22.6, 28.9, 29.1, 29.3, 29.4, 29.6, 31.9, 33.8, 114.0, 139.2. ^1H NMR spectroscopic data of this compound were identical to that of a standard.



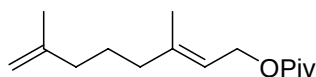
(*E*)-3,7,11-Trimethyldodeca-1,6,10-triene (20): According to the procedure A described for deoxygenation-reduction, the mixture containing *trans-trans*-farnesol (**19**) was heated for 60 min. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 8:1) on silica gel to afford a mixture of **20**² (80%).

According to the procedure B described for catalytic deoxygenation-reduction, the mixture containing *trans-trans*-farnesol (**19**) was heated for 55 min. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 8:1) on silica gel to afford a mixture of **20**² (92%). ^1H NMR (CD_3Cl , 500 MHz): δ 0.99 (d, J = 7.0 Hz, 3H), 1.30-1.36 (m, 2H), 1.59 (s, 3H), 1.61 (s, 3H), 1.69 (s,

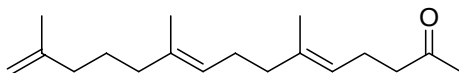
3H), 1.96-2.01 (m, 2H), 2.05-2.10 (m, 4H), 2.13 (sept, $J = 7.2$ Hz, 1H), 4.92 (br d, $J = 10.0$ Hz, 1H), 4.96 (br d, $J = 17.4$ Hz, 1H), 5.08-5.14 (m, 2H), 5.70 (ddd, $J = 7.2$ Hz, 10.0 Hz, 17.4 Hz, 1H); ^{13}C NMR (CD_3Cl , 125 MHz): δ 15.9, 17.6, 20.1, 25.6, 25.7, 26.6, 36.7, 37.3, 39.7, 112.4, 124.4, 124.5, 131.2, 134.8, 144.7.



3-Methyl-3-butenyl benzoate (23): According to the procedure A described for deoxygenation-reduction, the mixture containing (*E*)-4-hydroxy-3-methyl-2-butenyl benzoate (**22**) was heated for 60 min. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 5:1) on silica gel to afford **23**¹ (70%). ^1H NMR (CD_3Cl , 500 MHz): δ 1.82 (s, 3H), 2.49 (t, $J = 6.8$ Hz, 2H), 4.44 (t, $J = 6.8$ Hz, 2H), 4.81 (br s, 1H), 4.84 (br s, 1H), 7.43 (br t, $J = 7.9$ Hz, 2H), 7.55 (tt, $J = 1.1$ Hz, 7.9 Hz, 1H), 8.03 (dd, $J = 1.1$ Hz, 7.9 Hz, 1H); ^{13}C NMR (CD_3Cl , 300 MHz): δ 14.1, 29.6, 63.1, 112.4, 128.3, 129.5, 132.8, 141.7, 166.5.

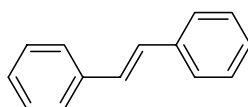


(2E)-3,7-Dimethylocta-2,7-dienyl pivalate (25): According to the procedure A described for the deoxygenation-reduction, the mixture containing (3*E*,7*E*)-8-hydroxy-3,7-dimethylocta-2,6-dienyl pivalate **24** was heated at reflux for 2 h. The resulting crude was purified by column chromatography using hexane as eluent on silica gel to afford **25** as colorless oil. IR (film): 2971, 2935, 1729, 1480, 1459, 1397, 1282, 1151, 1032, 955, 887 cm^{-1} . ^1H NMR (400 MHz; CDCl_3) δ 5.32 (t, $J = 7.0$ Hz, 1H), 4.70 (s, 1H), 4.66 (s, 1H), 4.56 (d, $J = 7.0$ Hz, 2H), 2.01 (m, 4H), 1.71 (s, 3H), 1.69 (s, 3H), 1.55 (qt, $J = 8.0$ Hz, 2H), 1.18 (s, 9H). ^{13}C NMR (100 MHz; CDCl_3) δ 16.3, 22.3, 25.4, 27.2 (3C), 37.2, 38.8, 38.9, 61.3, 109.9, 118.8, 141.7, 145.7, 178.5. HRCIMS (m/z): $[\text{M}-\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{26}\text{O}_2$ 238.1933 found 237.1859.

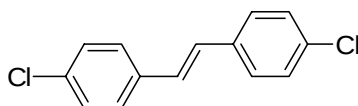


(5E,9E)-6,10,14-Trimethylpentadeca-5,9,14-trien-2-one (27): According to the procedure A described for the deoxygenation-reduction, (5E,9E,13Z)-15-hydroxy-6,10,14-trimethylpentadeca-5,9,13-trien-2-one **26** was heated at reflux for 2 h. The resulting crude was purified by column chromatography using (4:1) hexanes: *t*-BuOMe as eluent on silica gel to afford **27**(38 %) as a colorless oil.

According to the procedure B described for the catalytic deoxygenation-reduction, the compound **26** was heated at reflux for 4 h. The resulting crude was purified by column chromatography (hexane/*t*-BuOMe 4:1) as eluent on silica gel to afford **27**(85 %). IR (film): 3073, 2933, 1719, 1649, 1441, 1358, 1158, 885 cm^{-1} . ^1H NMR (400 MHz; CDCl_3) δ 1.39 (quintuplet, $J = 7.4$ Hz, 2H), 1.47 (s, 3H), 1.49 (s, 3H), 1.59 (s, 3H), 1.85 (m, 6H), 1.95 (t, $J = 7.4$ Hz, 2H), 2.01 (s, 3H), 2.15 (t, $J = 7.4$ Hz, 2H), 2.33 (t, $J = 7.4$ Hz, 2H), 4.54 (s, 1H), 4.58 (s, 1H), 4.96 (m, 2H). ^{13}C NMR (100 MHz; CDCl_3) δ 15.8, 15.9, 22.3, 22.4, 25.9, 26.4, 29.8, 37.3, 39.2, 39.6, 43.7, 109.7, 122.5, 124.1, 134.9, 136.2, 145.9, 208.7. HRFABMS (m/z): $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{30}\text{ONa}$ 285.2194 found 285.2197.

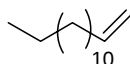


trans-Stilbene (29): According to the procedure A described for deoxygenation-reduction, the mixture containing 1,2-diphenylethane-1,2-diol (**28**) was heated for 65 min, the resulting crude was purified by column chromatography (hexane/*t*-BuOMe, 6:1) on silica gel to afford **29**³ (94 %). ^1H NMR (CD_3Cl , 300 MHz): δ 7.22 (s, 2H), 7.37 (t, $J = 7.3$ Hz, 2H), 7.47 (t, $J = 7.3$ Hz, 4H), 7.62 (d, $J = 7.3$ Hz, 4H); ^{13}C NMR (CD_3Cl , 75 MHz): δ 126.6, 127.7, 128.7, 128.8, 137.4.

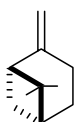


(E)-4,4'-Dichlorostilbene (31): According to the procedure A described for the deoxygenation-reduction, the mixture containing 1,2-bis(4-chlorophenyl)ethane-1,2-diol **30** was heated at reflux for 1 h. The resulting crude was purified by column chromatography using (hexane/*t*-BuOMe 1:1) as eluent on silica gel to afford **31** (79 %) as a white powder.

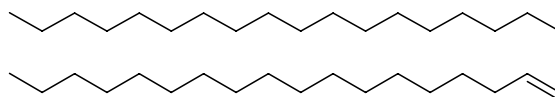
According to the procedure B described for the catalytic deoxygenation-reduction, the mixture containing 1,2-bis(4-chlorophenyl)ethane-1,2-diol **30** was heated at reflux for 1.5 h. The resulting crude was purified by column chromatography using (hexane/*t*-BuOMe 1:1) as eluent on silica gel to afford **31** (86 %). IR (film): 3040, 3010, 2938, 1701, 1600, 1497, 1405, 1102 cm^{-1} . ^1H NMR (400 MHz; CDCl_3) δ 7.02 (s, 2H), 7.33 (d, $J = 8.2$ Hz, 4H), 7.43 (d, $J = 8.2$ Hz, 4H). ^{13}C NMR (100 MHz; CDCl_3) δ 135.5, 133.4, 128.9, 127.9, 127.6. HREIMS (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{14}\text{H}_{10}\text{Cl}_2$ 248.0160 found 248.0150.



1-Tetradecene (33): According to the procedure A described for deoxygenation-reduction, the mixture containing tetradecane-1,2-diol (**32**) was heated for 90 min. The resulting crude was purified by column chromatography on silica gel to afford **33** (68 %). ^1H NMR (CD_3Cl , 500 MHz): δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.22-1.42 (m, 20H), 2.04 (q, $J = 6.8$ Hz, 2H), 4.93 (br d, $J = 10.2$ Hz, 1H), 4.99 (br d, $J = 17.1$ Hz, 1H), 5.81 (ddt, $J = 6.8$ Hz, 10.2 Hz, 17.1 Hz, 1H); ^{13}C NMR (CD_3Cl , 125 MHz): δ 14.2, 22.8, 29.0, 29.3, 29.4, 29.6, 29.7, 29.8, 32.0, 33.9, 114.1, 139.3. ^1H NMR spectroscopic data of this compound were identical to that of a standard.



β -Pinene (35): According to the procedure A described for deoxygenation-reduction, the mixture containing pinane-2 α ,10-diol (**34**) was heated for 90 min. The resulting crude was analyzed by GC-MS. **35** (92%, RT = 6.32 min) was identified by the standard use.



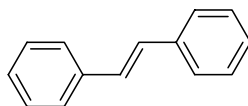
Octadecane (37) and 1-octadecene (38): A mixture of Cp_2TiCl_2 (200 mg, 0.77 mmol) and Zn dust (36.72 mg, 0.55 mmol) in strictly deoxygenated toluene (2 mL) was heated at reflux under stirring until the red solution turned green. Then, to this mixture was added a solution of octadecan-1-ol (**36**) (100 mg, 0.37 mmol) in strictly deoxygenated toluene (1 mL). The reaction mixture was heated at reflux under stirring for 120 min. It was then quenched with 1N HCl and extracted with *t*-BuOMe. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo yielding a. crude was purified by column chromatography (hexane/*t*-BuOMe, 9:1) on silica gel to afford a mixture (90%) that was analyzed by GC-MS. This mixture was constituted for **37** (RT = 17.21 min) and **38** (RT = 17.10 min) at a ratio 1:1. These compounds were identified by the standard use.

When the procedure A described for deoxygenation-reduction was followed, starting compound **36** was recovered.

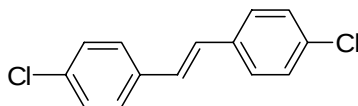
General procedure for stoichiometric homocoupling carbonyl reactions (Procedure C): 29, 31, 41, 43, 45, 48, 50, 52, 54, 56, 58.

A mixture of Cp_2TiCl_2 (392 mg, 1.57 mmol) and Mn dust (172 mg, 3.15 mmol) or Zn dust (206 mg, 3.15 mmol) in thoroughly deoxygenated THF (6.5 mL) and under Ar atmosphere was stirred until the red solution turned green. This mixture was then heated at reflux and the corresponding allylic aldehyde (1.31 mmol) in strictly deoxygenated THF (2 mL) was then added. The reaction mixture was stirred until starting material disappearance (TLC monitoring). It was then quenched with *t*-BuOMe, washed

with 1 N HCl, brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude was purified by column chromatography on silica gel to afford the corresponding coupling products.

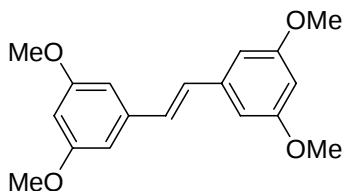


***trans*-Stilbene (29):** According to the procedure C described for the carbonyl homocoupling, the mixture containing benzaldehyde (**39**) was heated at reflux for 1 h. The resulting crude was purified by column chromatography (hexane) on silica gel to afford **29** (93%).



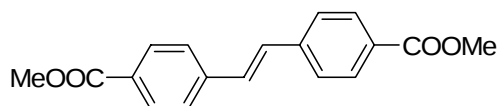
***(E)*-4,4'-Dichlorostilbene (31):** According to the procedure C described for the carbonyl homocoupling, the mixture containing 4-chlorobenzaldehyde **46** was heated at reflux for 1.5 h. The resulting crude was purified by column chromatography using (hexane/*t*-BuOMe 1:1) as eluent on silica gel to afford **31** (74 %) as a white powder.

According to the procedure B described for the catalytic carbonyl homocoupling, the mixture containing 4-chlorobenzaldehyde **46** was heated at reflux for 2 h. The resulting crude was purified by column chromatography using (hexane/*t*-BuOMe 1:1) as eluent on silica gel to afford **31** (95 %).

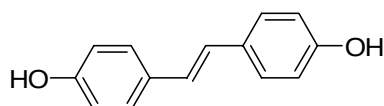


***(E)*-3,3',5,5'-Tetramethoxystilbene (41):** According to the procedure C described for the carbonyl homocoupling, the mixture containing 3,5-dimethoxybenzaldehyde (**40**) was heated at reflux for 1 h.

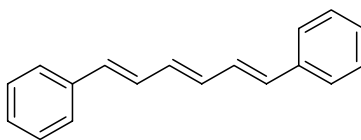
The resulting crude was purified by column chromatography (hexane) on silica gel to afford **41**⁴ (87%). ¹H NMR (300 MHz; CDCl₃): δ 3.75 (s, 12H), 6.33 (t, *J* = 2.3 Hz, 2H), 6.60 (d, *J* = 2.3 Hz, 4H), 6.94 (s, 2H); ¹³C NMR (75 MHz; CDCl₃): δ 55.5, 100.3, 104.8, 129.3, 139.3, 161.1.



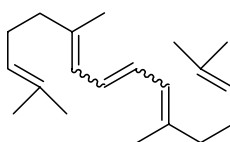
Dimethyl (E)-4,4'-stilbenedicarboxylate (43): According to the procedure C described for the carbonyl homocoupling, the mixture containing methyl 4-formylbenzoate **42** was heated at reflux for 2 h. The resulting crude was purified by column chromatography using EtOAc as eluent on silica gel to afford **43** (94%) as a white powder. IR (film): 1721, 1284, 1108, 965, 858, 774 cm⁻¹. ¹H NMR (400 MHz; CDCl₃) δ 3.93 (s, 6H), 7.25 (s, 2H), 7.59 (d, *J* = 8.6 Hz, 4H), 8.04(d, *J* = 8.6 Hz, 4H). ¹³C NMR (100 MHz; CDCl₃) δ 26.9, 52.1, 86.6, 126.6, 130.1, 141.2, 166.7. HREIMS (*m/z*): [*M*]⁺ calcd. for C₁₈H₁₆O₄ 296.1049 found 296.1048.



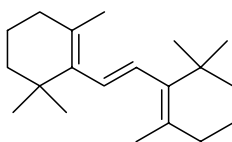
(E)-4,4'-Dihydroxystilbene(45): According to the procedure C described for the carbonyl homocoupling, the mixture containing 4-Hydroxybenzaldehyde **44** was heated at reflux for 4 h. The resulting crude was purified by column chromatography using *t*-BuOMe as eluent on silica gel to afford **45** (93 %) as a white powder. IR (film): 3333, 2926, 1510, 1439, 1270, 825 cm⁻¹. ¹H NMR (500 MHz; CDCl₃) δ 6.82 (d, *J* = 8.7 Hz, 4H), 6.96 (s, 2H), 7.39 (d, *J* = 8.7 Hz, 4H), 8.37 (s, 2H). ¹³C NMR (125 MHz; CDCl₃) δ 116.3, 126.5 128.3, 130.5, 157.7 ppm. HREIMS (*m/z*): [*M*]⁺ calcd. for C₁₄H₁₂O₂ 212.0837 found 212.0841.



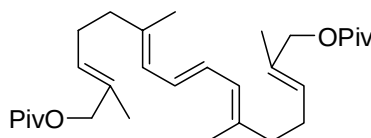
(1E,3E,5E)-1,6-Diphenylhexa-1,3,5-triene (48): According to the procedure C described for the carbonyl homocoupling, the mixture including *E*-cinnamaldehyde (**47**) was heated at reflux for 2 h. The resulting crude was purified by column chromatography (hexane) on silica gel to afford **48**⁵ (65%). ¹H NMR (CDCl₃, 500 MHz): δ 6.53 (dd, J = 7.0, 2.9 Hz, 2H), 6.61 (d, J = 15.5 Hz, 2H), 6.90 (ddd, J = 15.5, 7.0, 3.0 Hz, 2H), 7.24 (t, J = 7.3 Hz, 2H), 7.33 (t, J = 7.4 Hz, 4H), 7.43 (d, J = 7.5 Hz, 4H); ¹³C NMR (CDCl₃, 125 MHz): δ 126.4, 127.5, 128.6, 129.1, 132.7, 133.6, 137.4.



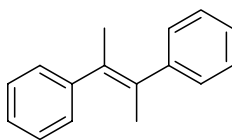
(6E,8E,10E)- and (6E,8Z,10E)-2,6,11,15-Tetramethylhexadeca-2,6,8,10,14-pentaene (50): According to the procedure C described for the carbonyl homocoupling, the mixture including citral (**49**) was heated at reflux for 1 h. The resulting crude was purified by column chromatography (hexane) on silica gel to afford **50**⁶ (76%) as a mixture of (6E,8E,10E) and (6E,8Z,10E) isomers at a 6:1 ratio. (6E,8E,10E) isomer: ¹H NMR (CDCl₃, 500 MHz): δ 1.59 (s, 6H), 1.67 (s, 6H), 1.76 (s, 6H), 2.07 (m, 8H), 5.09 (bt, J = 6.7 Hz, 2H), 5.90 (bd, J = 7.5 Hz, 1H), 6.33 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz): δ 16.7, 17.7, 25.7, 26.7, 40.1, 124.1, 125.4, 127.2, 131.6, 138.1. (6E,8Z,10E) isomer: ¹H NMR (CDCl₃, 500 MHz): δ 1.59 (s, 3H), 1.67 (s, 3H), 1.76 (s, 3H), 2.07 (m, 4H), 5.09 (bt, J = 6.7 Hz, 1H), 6.10 (m, 1H), 6.33 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz): δ 16.5, 17.7, 25.7, 26.7, 40.4, 120.3, 123.4, 124.0, 131.6, 139.3.



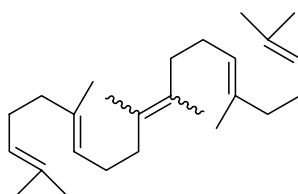
Mini-3-β-carotene (52): According to the procedure C described for the carbonyl homocoupling, the mixture including β-cyclocitral (**51**) was heated at reflux for 2 h 30 min. The resulting crude was purified by column chromatography (hexane) on silica gel to afford **52** (74%). IR (film) 2960, 2923, 2849, 2823, 1652, 1452, 1378, 1357, 1032, 971, 740 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz): δ 1.03 (s, 12H), 1.45-1.48 (m, 4H), 1.59-1.64 (m, 4H), 1.76 (s, 6H), 2.01 (t, $J = 6.3$ Hz, 4H), 5.81 (s, 2H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 19.5, 22.0, 29.0, 29.9, 33.0, 34.4, 39.7, 128.4, 132.3, 139.3; HRFABMS (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{32}\text{Na}$ 295.2402, found 295.2403.



(2E,6E,10E)-2,6,11,15-Tetramethylhexadeca-2,6,8,10,14-pentaene-1,16-pivaloate (54): According to the procedure C described for the carbonyl homocoupling, the mixture containing the corresponding aldehyde **53** was heated at reflux for 1.15 h. The resulting crude was purified by column chromatography using hexane as eluent on silica gel to afford **54** (73 %) as a colorless oil. IR (film): 2969, 2931, 2872, 1726, 1281, 1151, 955 cm^{-1} . ^1H NMR (600 MHz; CDCl_3) δ 1.19 (s, 18H), 1.71 (s, 6H), 1.76 (s, 6H), 2.10 (t, $J = 7.7$ Hz, 4H), 2.28 (q, $J = 7.1$ Hz, 4H), 4.57 (d, $J = 6.9$ Hz, 4H), 5.33 (d, $J = 6.9$, 2H), 5.34 (d, $J = 6.9$ Hz, 2H), 5.45 (t, $J = 7.2$ Hz, 2H). ^{13}C NMR (150 MHz; CDCl_3) δ 12.4, 16.4, 26.6, 27.2 (3C), 38.7, 39.2, 61.2, 119.1, 130.9, 131.2, 134.2, 141.2, 178.6 ppm. . HRFABMS (m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{30}\text{H}_{48}\text{O}_4\text{Na}$ 495.3450 found 495.3448.

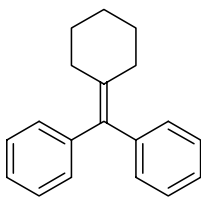


(*E*)- α,β -Dimethylstilbene (56): According to the procedure C described for the carbonyl homocoupling, the mixture including acetophenone (**55**) was heated at reflux for 4 h. The resulting crude was purified by column chromatography (hexane) on silica gel to afford **56**⁷ (71%). ¹H NMR (CDCl₃, 500 MHz): δ 1.89 (s, 6H), 7.27 (m, 6H), 7.37 (t, J = 7.6 Hz, 4H); ¹³C NMR (CDCl₃, 125 MHz): δ 22.5, 126.3, 128.2, 128.3, 133.1, 144.6.

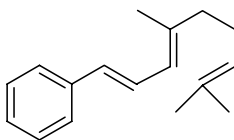


(6*E*,14*E*)-2,6,10,11,15,19-hexamethylicos-2,6,10,14,18-pentaene (58): According to the procedure C described for the carbonyl homocoupling, the mixture including geranylacetone (**57**) was heated at reflux for 4 h. The resulting crude was purified by column chromatography (hexane) on silica gel to afford **58** (62%). IR (film) 2964, 2923, 2855, 1705, 1630, 1448, 1375, 1260, 1105, 1079, 979, 894, 746 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ 1.60 (bs, 15H), 1.68 (bs, 9H), 1.91-2.08 (m, 16H), 5.02-5.08 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz): δ 16.1, 17.8, 25.8, 26.8, 27.1, 39.8, 124.5, 124.6, 124.7, 131.4, 135.1, 135.2. HRFABMS (m/z): $[M + Na]^+$ calcd for C₂₆H₄₄Na 379.3341, found 379.3358.

General procedure for heterocoupling carbonyl reactions: 61, 62.



Diphenylmethylenecyclohexane (61). A mixture of Cp_2TiCl_2 (845 mg, 3.29 mmol) and Mn dust (487 mg, 8.78 mmol) or Zn dust (573 mg, 8.78 mmol) in thoroughly deoxygenated THF (4 mL) and under Ar atmosphere was stirred until the red solution turned green. This mixture was then heated at reflux and the corresponding mixture of benzophenone (**60**) (200 mg, 1.10 mmol) and cyclohexanone (**59**) (431 mg, 4.40 mmol) in strictly deoxygenated THF (2 mL) were then added. The reaction mixture was stirred until starting material disappearance (TLC monitoring). It was then quenched with *t*-BuOMe, washed twice with 1N HCl, brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude was purified by column chromatography (hexane) on silica gel to afford **61**⁸ (65%). ^1H NMR (CDCl_3 , 500 MHz): δ 1.56–1.60 (m, 6H), 2.23–2.25 (m, 4H), 7.10–7.29 (m, 10H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 26.8, 28.7, 32.4, 126.0, 127.8, 129.8, 134.5, 139.1, 143.1.



(1E,3E)-4,8-Dimethyl-1-phenyl-1,3,7-nonatriene (62). A mixture of Cp_2TiCl_2 (2.45 g, 9.85 mmol) and Mn dust (1.44 g, 26.28 mmol) or Zn dust (1.71 g, 26.28 mmol) in thoroughly deoxygenated THF (140 mL) and under Ar atmosphere was stirred until the red solution turned green. This mixture was then heated at reflux and the corresponding mixture of citral (**49**) (500 mg, 3.28 mmol) and benzaldehyde (**39**) (1.743 g, 16.42 mmol) in strictly deoxygenated THF (23 mL) were then added. The reaction mixture was stirred until starting material disappearance (TLC monitoring). It was then quenched with *t*-BuOMe, washed twice with 1N HCl, brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude was purified, by column chromatography (hexane) on silica gel to afford **62**⁹ (77%). ^1H NMR (CDCl_3 , 500 MHz): δ 1.62 (s, 3 H) , 1.69 (s, 3 H) ,

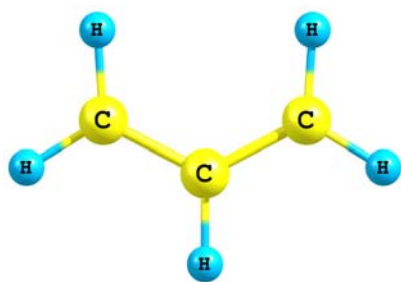
1.85 (s, 3 H) , 2.13 (m, 4 H) , 5.12 (bs, 1 H) , 6.00 (d, $J = 11.0$ Hz, 1 H) , 6.44 (d, $J = 15.4$ Hz, 1 H) , 7.02 (dd, $J = 15.4, 11.0$ Hz, 1 H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.29 (t, $J = 7.3$ Hz, 2H), 7.39 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 16.9, 17.7, 25.7, 26.6, 40.1, 123.9, 125.1, 125.7, 126.1, 126.9, 128.5, 129.9, 131.8, 138.1, 140.2.

Computational Details

Calculations based on density functional theory (DFT) were performed with Gaussian 03 package. We have used the M05 functional from the Truhlar group together with the “Ahlrichs VDZ” basis set, for the geometry optimization and for the calculation of the Gibbs free energy of activation and free energy of reactions. The local stability of all structures was checked through the eigenvalues of the matrix of second derivatives (Hessian); all energetic minima presented no imaginary frequencies, while transition states (TS) presented a single imaginary frequency. Unrestricted calculations (UM05) were carried out for all the structures, being the electronic state doublet for the reactives, TS's and products and singlet for the Cp_2TiClOH compound.

DFT energies (a.u.), first frequency value (cm^{-1}) in parentheses, zero point vibrational energy (ZPVE a.u.), and cartesian coordinates (Å) of the optimized structures discussed:

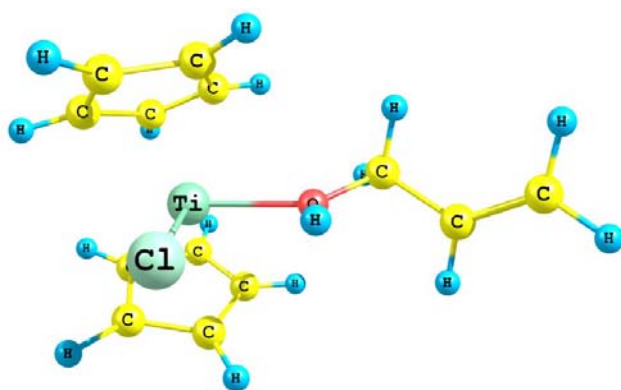
1prod. $E(\text{UM05/Ahlrichs-VDZ}) = -117.036600505$ a.u. / (441 cm^{-1}) / $\text{ZPVE} = 0.066701$ a.u.



C	1.238023000	-0.196776000	0.000000000
C	0.000000000	0.443327000	0.000000000
C	-1.238021000	-0.196742000	0.000000000

H	0.000013000	1.540943000	0.000000000
H	-2.173762000	0.371126000	0.000000000
H	-1.311224000	-1.290980000	0.000000000
H	2.173772000	0.371073000	0.000000000
H	1.311191000	-1.291017000	0.000000000

1react. E(UM05/Ahlrichs-VDZ) = -1888.72168194 a.u. / (11 cm⁻¹) / ZPVE = 0.259089 a.u.

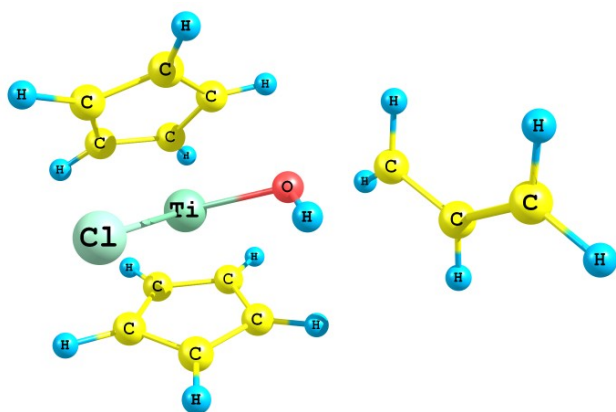


Ti	0.649184000	0.010637000	0.032543000
Cl	-0.014115000	-0.145174000	2.459283000
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C	-2.606385000	-0.321118000	-0.829773000
H	-1.721399000	-0.148357000	1.056265000
H	-2.235934000	0.009241000	-1.814073000
H	-2.790019000	-1.410291000	-0.880053000
C	1.347401000	1.688622000	-1.554236000
C	0.146336000	2.137068000	-0.945021000

C	0.391322000	2.290983000	0.450018000
C	1.762330000	1.970245000	0.700226000
C	2.349126000	1.596113000	-0.538045000
H	1.485575000	1.471105000	-2.611491000
H	-0.803823000	2.302853000	-1.449659000
H	-0.335461000	2.576748000	1.205277000
H	2.249034000	1.984474000	1.672562000
H	3.381826000	1.288591000	-0.689086000
C	1.915240000	-1.305879000	-1.464273000
C	0.566725000	-1.764998000	-1.483537000
C	0.285927000	-2.313635000	-0.191042000
C	1.454383000	-2.201556000	0.608282000
C	2.455414000	-1.555596000	-0.164401000
H	2.448547000	-0.856169000	-2.298168000
H	-0.106550000	-1.744084000	-2.339026000
H	-0.659966000	-2.739524000	0.137015000
H	1.535134000	-2.483347000	1.654469000
H	3.463455000	-1.317286000	0.169116000
C	-3.847971000	0.421694000	-0.444087000

C	-5.038598000	-0.155831000	-0.218035000
H	-3.735597000	1.509349000	-0.349071000
H	-5.920273000	0.435192000	0.050917000
H	-5.179041000	-1.241456000	-0.297532000

1ts. E(UM05/Ahlrichs-VDZ) = -1888.6706425 a.u. / (731i cm⁻¹) / ZPVE = 0.254425 a.u.

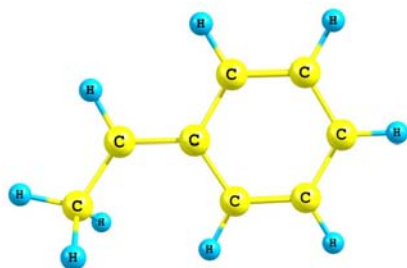


Ti	0.557818000	0.015559000	0.039625000
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C	-2.815941000	-0.757425000	-0.965625000
H	-1.803878000	-0.070736000	1.031429000
H	-2.278676000	-0.457593000	-1.869539000
H	-2.839945000	-1.832977000	-0.764384000
C	0.437997000	1.594576000	-1.719198000
C	-0.499495000	2.067211000	-0.753010000

C	0.204883000	2.377971000	0.430601000
C	1.599881000	2.151483000	0.192365000
C	1.745326000	1.709067000	-1.146316000
H	0.210277000	1.291298000	-2.739527000
H	-1.578924000	2.106607000	-0.880237000
H	-0.224890000	2.692699000	1.377071000
H	2.394130000	2.295705000	0.921034000
H	2.681305000	1.476840000	-1.647528000
C	1.662729000	-1.292814000	-1.635938000
C	0.552692000	-2.033889000	-1.146205000
C	0.791459000	-2.328295000	0.227608000
C	2.062078000	-1.789070000	0.579361000
C	2.596893000	-1.141038000	-0.564939000
H	1.787398000	-0.921996000	-2.651064000
H	-0.336237000	-2.305807000	-1.711667000
H	0.106586000	-2.830331000	0.904837000
H	2.508847000	-1.816649000	1.568916000
H	3.554184000	-0.626756000	-0.614631000
C	-3.893259000	0.058268000	-0.493665000

C	-4.779008000	-0.321162000	0.480043000
H	-3.970660000	1.073368000	-0.903040000
H	-5.559338000	0.357513000	0.838984000
H	-4.746242000	-1.323498000	0.925338000

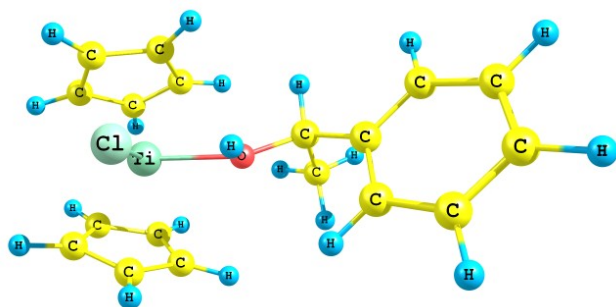
2prod. E(UM05/Ahlrichs-VDZ) = -309.667408309 a.u. / (49 cm⁻¹) / ZPVE = 0.144905 a.u.



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C	0.540858000	-1.315242000	-0.000025000
H	0.227341000	-2.363152000	-0.000014000
C	1.896422000	-0.994940000	0.000070000
H	2.642376000	-1.793865000	0.000158000
C	2.310573000	0.350757000	0.000078000
C	1.342390000	1.371242000	0.000004000
H	1.656972000	2.418164000	0.000048000
C	-0.017373000	1.060673000	-0.000122000
H	-0.752066000	1.869145000	-0.000040000
C	-1.842702000	-0.646714000	-0.000351000

C	-2.969845000	0.333075000	0.000111000
H	-2.085270000	-1.715757000	0.000777000
H	3.374329000	0.599908000	0.000147000
H	-2.940947000	1.002399000	-0.882677000
H	-2.947691000	0.993555000	0.889873000
H	-3.945995000	-0.176632000	-0.005985000

2react. E(UM05/Ahlrichs-VDZ) = -2081.3576433 a.u. / (16 cm⁻¹) / ZPVE = 0.337207 a.u.

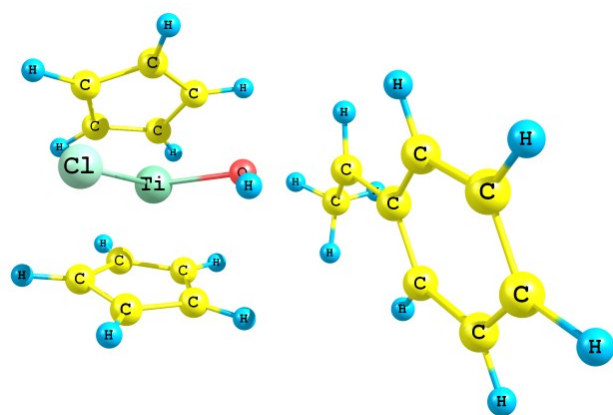


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Cl	-0.678348000	-0.609397000	2.382781000
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C	1.609737000	0.660749000	-0.857276000
H	0.818779000	-0.192731000	0.868349000
H	1.463969000	1.747428000	-0.717014000
C	-2.299964000	-1.207148000	-1.852766000
C	-1.243570000	-1.975486000	-1.290715000

C	-1.638711000	-2.398238000	0.003576000
C	-2.967059000	-1.921922000	0.243903000
C	-3.379333000	-1.203539000	-0.914054000
H	-2.305253000	-0.745551000	-2.838802000
H	-0.273248000	-2.154927000	-1.746985000
H	-1.030762000	-2.951869000	0.713142000
H	-3.550770000	-2.094944000	1.145455000
H	-4.349368000	-0.735495000	-1.062657000
C	-2.868672000	1.761663000	-0.843349000
C	-1.514500000	2.173894000	-0.712619000
C	-1.208207000	2.205663000	0.685221000
C	-2.381361000	1.846308000	1.408066000
C	-3.400016000	1.550392000	0.467563000
H	-3.409655000	1.637243000	-1.778937000
H	-0.847232000	2.443292000	-1.529291000
H	-0.251671000	2.465307000	1.133724000
H	-2.450947000	1.742884000	2.487471000
H	-4.411672000	1.227056000	0.704626000
C	2.986927000	0.290931000	-0.344486000

C	3.286863000	-1.030727000	0.032295000
C	3.999151000	1.263354000	-0.280216000
C	4.574446000	-1.370064000	0.466317000
H	2.505105000	-1.794173000	-0.000358000
C	5.289685000	0.923144000	0.145692000
H	3.775690000	2.297516000	-0.559615000
C	5.580145000	-0.395335000	0.520724000
H	4.791350000	-2.398490000	0.764746000
H	6.065847000	1.690706000	0.193273000
H	6.584035000	-0.660917000	0.860341000
C	1.416997000	0.318157000	-2.328884000
H	0.388816000	0.550638000	-2.652346000
H	2.120110000	0.901336000	-2.945715000
H	1.608010000	-0.752441000	-2.507696000

2ts. E(UM05/Ahlrichs-VDZ) = -2081.30718572 a.u. / (623i cm⁻¹) / ZPVE = 0.332613 a.u.

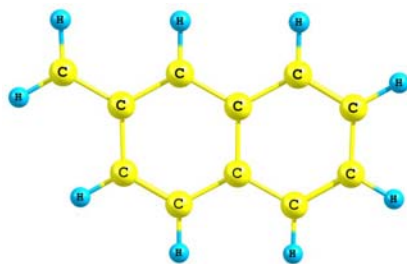


Ti	1.464306000	0.011666000	0.135544000
Cl	1.122356000	-0.855594000	2.419190000
O	-0.381142000	-0.508028000	-0.109648000
C	-1.832388000	-0.528648000	-1.540603000
H	-0.952869000	-0.549463000	0.683153000
H	-1.595297000	-1.576470000	-1.745273000
C	1.366863000	2.165856000	-0.830590000
C	0.386261000	2.199253000	0.209252000
C	1.046718000	2.025641000	1.443339000
C	2.451559000	1.911268000	1.187106000
C	2.649873000	2.053034000	-0.211274000
H	1.180782000	2.296874000	-1.894681000
H	-0.690574000	2.265873000	0.071602000
H	0.577150000	1.929574000	2.417559000

H	3.220229000	1.761617000	1.942290000
H	3.605581000	2.054588000	-0.728327000
C	2.820925000	-0.598103000	-1.746688000
C	1.776577000	-1.558116000	-1.639462000
C	1.934428000	-2.245935000	-0.406381000
C	3.110824000	-1.745841000	0.230723000
C	3.659587000	-0.734023000	-0.595206000
H	2.978724000	0.088633000	-2.576236000
H	0.968494000	-1.709847000	-2.351348000
H	1.259676000	-2.989821000	0.007336000
H	3.481594000	-2.056285000	1.203492000
H	4.557205000	-0.157883000	-0.382731000
C	-3.009788000	-0.314935000	-0.723739000
C	-3.664826000	0.940555000	-0.617666000
C	-3.508549000	-1.389574000	0.062240000
C	-4.767244000	1.104989000	0.224307000
H	-3.316170000	1.791457000	-1.206888000
C	-4.606764000	-1.218012000	0.906793000
H	-3.018085000	-2.365328000	-0.000281000

C	-5.244297000	0.030270000	0.992240000
H	-5.259801000	2.078614000	0.284543000
H	-4.970076000	-2.059509000	1.501459000
H	-6.104889000	0.164673000	1.651447000
C	-1.332766000	0.449123000	-2.547760000
H	-0.267804000	0.269515000	-2.766595000
H	-1.886884000	0.340208000	-3.500958000
H	-1.434600000	1.494851000	-2.220358000

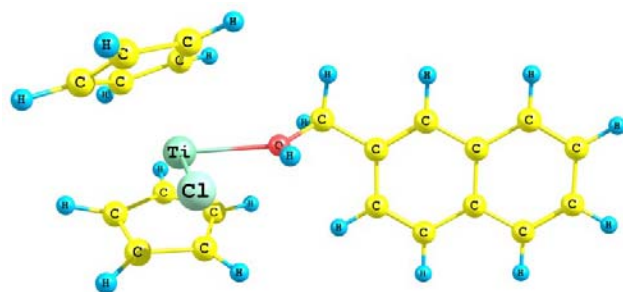
3prod. E(UM05/Ahlrichs-VDZ) = -423.800904062 a.u. / (116 cm⁻¹) / ZPVE = 0.164236 a.u.



C	2.184542000	-0.231630000	-0.000088000
C	1.067675000	-1.108160000	-0.000383000
C	-0.266904000	-0.629665000	-0.000325000
C	-0.504838000	0.789604000	-0.000238000
C	0.626798000	1.672435000	-0.000458000
C	1.911242000	1.190226000	-0.000325000
H	2.757567000	1.882287000	-0.000312000

H	1.240244000	-2.188371000	-0.000473000
C	3.505235000	-0.714562000	0.000581000
H	4.357649000	-0.027765000	0.001011000
H	3.714063000	-1.789138000	0.000698000
H	0.445021000	2.750711000	-0.000599000
C	-1.389785000	-1.510688000	-0.000161000
C	-1.839766000	1.266087000	0.000166000
C	-2.913484000	0.383839000	0.000558000
C	-2.683990000	-1.015273000	0.000354000
H	-1.210882000	-2.589425000	-0.000336000
H	-2.014259000	2.345645000	0.000267000
H	-3.936981000	0.766207000	0.001024000
H	-3.532778000	-1.703438000	0.000632000

3react. E(UM05/Ahlrichs-VDZ) = -2195.49075667 a.u. / (6 cm⁻¹) / ZPVE = 0.356129 a.u.



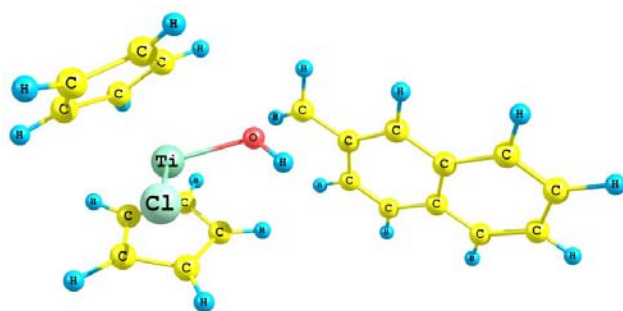
Ti	2.519859000	0.015508000	0.050504000
Cl	1.809173000	-0.036722000	2.464242000

C	3.136049000	1.645417000	-1.614825000
C	1.807474000	1.911612000	-1.191089000
C	1.849704000	2.238315000	0.197786000
C	3.213262000	2.206351000	0.622410000
C	4.004578000	1.829936000	-0.493994000
H	3.439980000	1.362785000	-2.620646000
H	0.915840000	1.860702000	-1.814038000
H	0.998249000	2.453530000	0.838282000
H	3.564051000	2.388769000	1.635238000
H	5.085146000	1.699434000	-0.496484000
C	4.099301000	-1.174862000	-1.214087000
C	2.830928000	-1.805801000	-1.381789000
C	2.465864000	-2.365082000	-0.115746000
C	3.493488000	-2.077718000	0.817541000
C	4.493882000	-1.316089000	0.152578000
H	4.677506000	-0.686474000	-1.994100000
H	2.275949000	-1.895873000	-2.314326000
H	1.550296000	-2.909978000	0.105555000
H	3.475818000	-2.322070000	1.875912000

H	5.412739000	-0.941577000	0.599713000
C	-4.403407000	-0.661644000	-0.207080000
C	-3.092544000	-1.161116000	-0.459916000
C	-1.998082000	-0.316043000	-0.545506000
C	-2.186480000	1.085929000	-0.357617000
C	-3.441728000	1.600294000	-0.103227000
C	-4.584026000	0.749965000	-0.025111000
C	-5.539367000	-1.518237000	-0.125326000
C	-5.893123000	1.251578000	0.228272000
C	-6.798972000	-1.001787000	0.120797000
C	-6.977745000	0.395959000	0.298439000
H	-2.963101000	-2.240242000	-0.589304000
H	-1.321190000	1.752233000	-0.407175000
H	-3.575551000	2.675430000	0.041856000
C	-0.625528000	-0.852941000	-0.853444000
H	-0.629453000	-1.957589000	-0.849976000
H	-0.282965000	-0.518897000	-1.846664000
O	0.371321000	-0.357883000	0.065789000
H	0.157993000	-0.416268000	1.034969000

H	-5.399508000	-2.594014000	-0.261505000
H	-6.026823000	2.327732000	0.366674000
H	-7.662408000	-1.668428000	0.179976000
H	-7.977146000	0.792745000	0.492128000

3ts. E(UM05/Ahlrichs-VDZ) = -2195.43925331 a.u. / (697i cm⁻¹) / ZPVE = 0.351863 a.u.

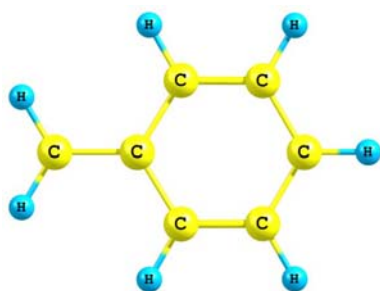


Ti	2.314759000	-0.020170000	0.152395000
Cl	1.992751000	-1.104928000	2.320626000
C	2.060915000	2.179737000	-0.642052000
C	1.033979000	2.045774000	0.343178000
C	1.649029000	1.829227000	1.594214000
C	3.068536000	1.861229000	1.406693000
C	3.319391000	2.130348000	0.035969000
H	1.912975000	2.376305000	-1.702806000
H	-0.036669000	2.039763000	0.151494000
H	1.145205000	1.616868000	2.532422000

H	3.811234000	1.717442000	2.188483000
H	4.295541000	2.256101000	-0.424670000
C	3.808273000	-0.289260000	-1.703191000
C	2.804767000	-1.290944000	-1.797351000
C	2.930328000	-2.148872000	-0.668114000
C	4.039966000	-1.698324000	0.106195000
C	4.577789000	-0.547831000	-0.525456000
H	3.977008000	0.516425000	-2.414743000
H	2.047368000	-1.366192000	-2.574272000
H	2.271845000	-2.973624000	-0.411041000
H	4.369720000	-2.128254000	1.047464000
H	5.428077000	0.032213000	-0.173296000
C	-4.079015000	-0.685915000	-0.212419000
C	-2.831570000	-1.054981000	-0.779235000
C	-1.956907000	-0.103237000	-1.334361000
C	-2.359784000	1.277963000	-1.313386000
C	-3.566375000	1.660243000	-0.774103000
C	-4.462706000	0.700284000	-0.205281000
C	-4.970993000	-1.647005000	0.351231000

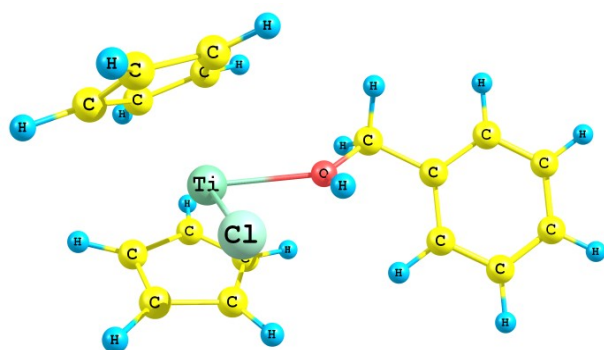
C	-5.712421000	1.068329000	0.360198000
C	-6.182148000	-1.257174000	0.895751000
C	-6.557885000	0.111433000	0.901278000
H	-2.550178000	-2.112578000	-0.784650000
H	-1.695031000	2.028247000	-1.751286000
H	-3.860636000	2.713217000	-0.776395000
C	-0.673917000	-0.490667000	-1.846080000
H	-0.510866000	-1.533288000	-2.128402000
H	-0.075855000	0.250951000	-2.383722000
O	0.528184000	-0.657715000	-0.271249000
H	-0.142898000	-0.673433000	0.440997000
H	-4.679615000	-2.700760000	0.347248000
H	-5.999319000	2.123439000	0.362942000
H	-6.854277000	-2.004061000	1.324848000
H	-7.516093000	0.408325000	1.333974000

4prod. E(UM05/Ahlrichs-VDZ) = -270.423582107 a.u. / (205 cm⁻¹) / ZPVE = 0.116375 a.u.



C	2.411443000	-0.000001000	0.000132000
H	2.975914000	0.938025000	0.000313000
H	2.975900000	-0.938029000	0.000026000
C	1.000402000	0.000003000	-0.000130000
C	0.253896000	1.222665000	-0.000364000
C	0.253902000	-1.222659000	-0.000049000
C	-1.138960000	1.216910000	-0.000200000
H	0.797780000	2.171325000	-0.000641000
C	-1.138955000	-1.216912000	0.000272000
H	0.797789000	-2.171317000	-0.000134000
C	-1.847926000	-0.000004000	0.000284000
H	-1.684881000	2.163754000	-0.000369000
H	-1.684869000	-2.163761000	0.000537000
H	-2.940443000	-0.000009000	0.000595000

4reac. E(UM05/Ahlrichs-VDZ) = -2042.11502756 a.u. / (4 cm⁻¹) / ZPVE = 0.308330 a.u.

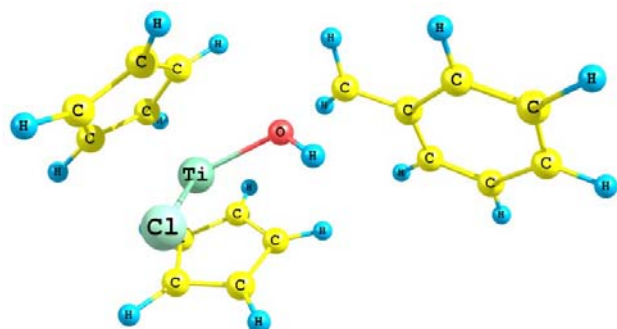


Ti	1.524408000	0.044127000	0.022064000
Cl	0.902565000	0.173228000	2.460574000
C	1.902816000	1.540333000	-1.830023000
C	0.654859000	1.881699000	-1.246120000
C	0.895002000	2.290738000	0.096897000
C	2.304158000	2.237400000	0.335149000
C	2.923246000	1.772285000	-0.855642000
H	2.056793000	1.182750000	-2.846199000
H	-0.318255000	1.810571000	-1.729030000
H	0.145810000	2.573940000	0.831210000
H	2.798138000	2.482278000	1.272331000
H	3.989759000	1.615013000	-1.001806000
C	3.001748000	-1.259253000	-1.274281000
C	1.751154000	-1.936888000	-1.194820000
C	1.559525000	-2.315880000	0.172509000

C	2.686326000	-1.884775000	0.920932000
C	3.567688000	-1.207089000	0.037551000
H	3.455990000	-0.862513000	-2.178791000
H	1.089905000	-2.164479000	-2.029308000
H	0.698328000	-2.839956000	0.581540000
H	2.806358000	-1.981865000	1.996268000
H	4.518334000	-0.752849000	0.309497000
C	-5.405947000	-0.888141000	-0.252159000
C	-4.104477000	-1.342909000	-0.501186000
C	-3.006518000	-0.474387000	-0.375663000
C	-3.232698000	0.857443000	0.016041000
C	-4.532533000	1.310612000	0.273446000
C	-5.622931000	0.440533000	0.136357000
H	-3.941231000	-2.385180000	-0.791425000
H	-2.384463000	1.537254000	0.131655000
H	-4.693563000	2.346033000	0.582686000
C	-1.615404000	-0.962603000	-0.694122000
H	-1.566197000	-2.064638000	-0.621559000
H	-1.324949000	-0.683201000	-1.721274000

O	-0.612124000	-0.366796000	0.149491000
H	-0.784162000	-0.368686000	1.128546000
H	-6.249595000	-1.575184000	-0.352451000
H	-6.636660000	0.794706000	0.337825000

4ts. E(UM05/Ahlrichs-VDZ) = -2042.0624215 a.u. / (683i cm⁻¹) / ZPVE = 0.304015 a.u.

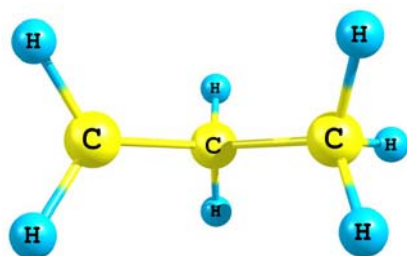


Ti	1.415291000	0.036074000	0.069476000
Cl	1.379701000	-0.321414000	2.492030000
C	1.055606000	1.888979000	-1.341623000
C	0.097586000	2.055179000	-0.295301000
C	0.795859000	2.226797000	0.918848000
C	2.199765000	2.212963000	0.633414000
C	2.356199000	2.053222000	-0.767202000
H	0.835733000	1.753831000	-2.399355000
H	-0.982533000	1.983867000	-0.401981000
H	0.358983000	2.304153000	1.909953000

H	2.993552000	2.314682000	1.370172000
H	3.297661000	2.036901000	-1.309765000
C	2.721257000	-0.779320000	-1.770400000
C	1.726589000	-1.747503000	-1.465468000
C	1.982973000	-2.245575000	-0.155685000
C	3.157777000	-1.605965000	0.336530000
C	3.609618000	-0.695045000	-0.653226000
H	2.804010000	-0.217029000	-2.698169000
H	0.895648000	-2.034248000	-2.106212000
H	1.367552000	-2.950961000	0.395157000
H	3.588639000	-1.748031000	1.323309000
H	4.481814000	-0.049848000	-0.572690000
C	-4.883968000	-0.970815000	0.815067000
C	-3.712922000	-1.406236000	0.192384000
C	-3.015695000	-0.567474000	-0.720696000
C	-3.549134000	0.726211000	-0.975970000
C	-4.723449000	1.153271000	-0.354230000
C	-5.396637000	0.309627000	0.546406000
H	-3.320594000	-2.405037000	0.404210000

H	-3.036586000	1.385561000	-1.682834000
H	-5.121162000	2.147784000	-0.570724000
C	-1.777344000	-1.000479000	-1.309198000
H	-1.558598000	-2.069886000	-1.350710000
H	-1.321720000	-0.385283000	-2.090963000
O	-0.382223000	-0.696604000	0.086536000
H	-0.961754000	-0.486600000	0.846772000
H	-5.404468000	-1.630953000	1.513108000
H	-6.314205000	0.647313000	1.033551000

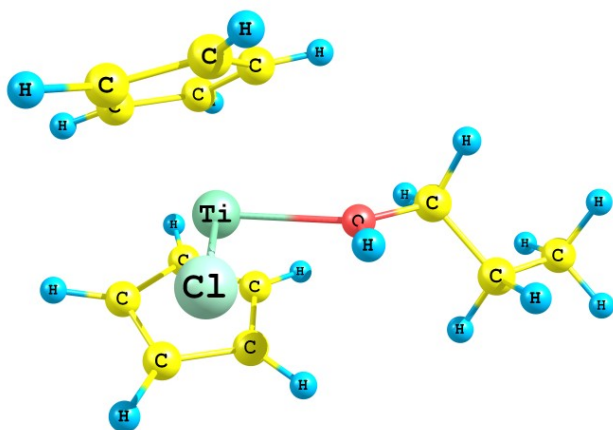
5prod. E(UM05/Ahlrichs-VDZ) = -118.235153895 a.u. / (38 cm⁻¹) / ZPVE = 0.089354 a.u.



C	-1.323463000	-0.240423000	0.002960000
H	-1.807268000	-0.515427000	0.948273000
H	-1.715466000	-0.693438000	-0.916433000
C	-0.069045000	0.566698000	-0.017570000
C	1.220016000	-0.283783000	0.012727000
H	-0.051446000	1.259068000	0.844248000

H	-0.043343000	1.199431000	-0.925339000
H	2.116048000	0.361794000	-0.010481000
H	1.268299000	-0.901783000	0.926309000
H	1.268124000	-0.964595000	-0.855275000

5reac. E(UM05/Ahlrichs-VDZ) = -1889.95058967 a.u. / (4 cm⁻¹) / ZPVE = 0.283029 a.u.

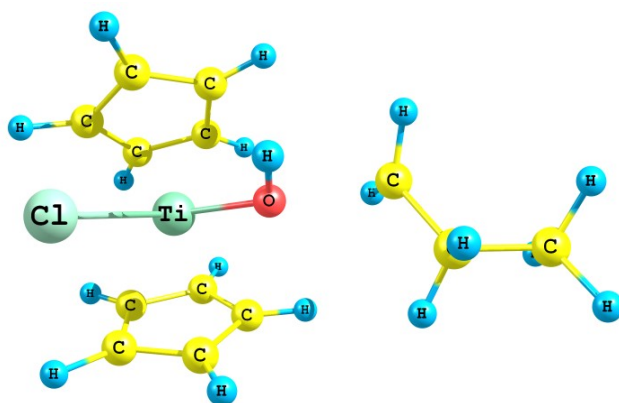


Ti	0.706423000	0.029978000	0.007984000
Cl	0.422952000	-0.073488000	2.514848000
O	-1.378467000	-0.424808000	0.384636000
C	-2.584877000	-0.702903000	-0.352364000
H	-1.425035000	-0.470891000	1.375556000
H	-2.352808000	-0.462338000	-1.402043000
H	-2.810385000	-1.785196000	-0.294772000
C	-0.048765000	1.806322000	-1.308730000
C	-0.179025000	2.211570000	0.057861000

C	1.122025000	2.334328000	0.615938000
C	2.064028000	1.976967000	-0.384247000
C	1.343084000	1.667971000	-1.579123000
H	-0.859423000	1.668442000	-2.023019000
H	-1.110374000	2.381584000	0.593074000
H	1.346087000	2.578291000	1.650915000
H	3.145512000	1.960784000	-0.264682000
H	1.784193000	1.390611000	-2.533525000
C	1.509149000	-1.384307000	-1.774516000
C	0.568151000	-2.133924000	-1.020664000
C	1.068392000	-2.261301000	0.306588000
C	2.344390000	-1.617811000	0.366283000
C	2.613578000	-1.077442000	-0.919393000
H	1.416214000	-1.111815000	-2.823733000
H	-0.382177000	-2.518737000	-1.386954000
H	0.568178000	-2.741541000	1.143480000
H	2.971990000	-1.537347000	1.250634000
H	3.504265000	-0.522630000	-1.206027000
C	-3.762377000	0.122228000	0.147792000

C	-5.045479000	-0.152960000	-0.634292000
H	-3.497920000	1.192817000	0.084301000
H	-3.923454000	-0.096643000	1.220086000
H	-5.882038000	0.451025000	-0.245286000
H	-4.927403000	0.094032000	-1.704398000
H	-5.342829000	-1.214630000	-0.565559000

5ts. E(UM05/Ahlrichs-VDZ) = -1889.88014427 a.u. / (505i cm⁻¹) / ZPVE = 0.277385 a.u.

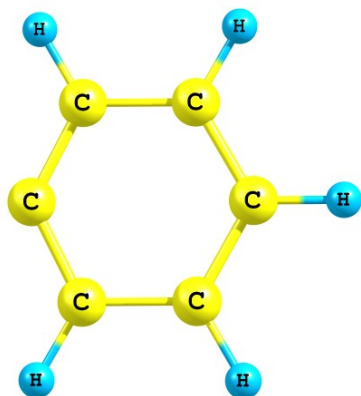


Ti	0.665763000	0.032436000	0.028526000
Cl	1.374527000	0.157879000	2.368671000
O	-1.095468000	-0.358852000	0.696472000
C	-2.896194000	-0.912696000	-0.247038000
H	-1.171352000	-0.951849000	1.469610000
H	-2.554217000	-0.721005000	-1.270981000
H	-2.925319000	-1.972786000	0.041940000

C	-0.542806000	1.767949000	-1.047883000
C	-0.140663000	2.246786000	0.231825000
C	1.280002000	2.354335000	0.234801000
C	1.756963000	1.916605000	-1.028576000
C	0.627551000	1.551435000	-1.825095000
H	-1.565373000	1.569142000	-1.360223000
H	-0.794325000	2.444261000	1.076495000
H	1.890110000	2.656572000	1.080835000
H	2.800053000	1.875569000	-1.334393000
H	0.657875000	1.191675000	-2.851328000
C	0.875208000	-1.565542000	-1.700653000
C	0.489455000	-2.325632000	-0.556407000
C	1.505650000	-2.204735000	0.416492000
C	2.561555000	-1.409170000	-0.137887000
C	2.189618000	-1.052086000	-1.457228000
H	0.310215000	-1.470604000	-2.625990000
H	-0.458772000	-2.843733000	-0.432390000
H	1.489813000	-2.604404000	1.426490000
H	3.476956000	-1.131208000	0.379092000

H	2.784278000	-0.470621000	-2.156896000
C	-3.859044000	0.032755000	0.389794000
C	-5.309413000	-0.148813000	-0.095010000
H	-3.534013000	1.070271000	0.195503000
H	-3.826676000	-0.095598000	1.487252000
H	-5.979548000	0.570702000	0.407299000
H	-5.394039000	0.014879000	-1.183752000
H	-5.682952000	-1.165127000	0.121887000

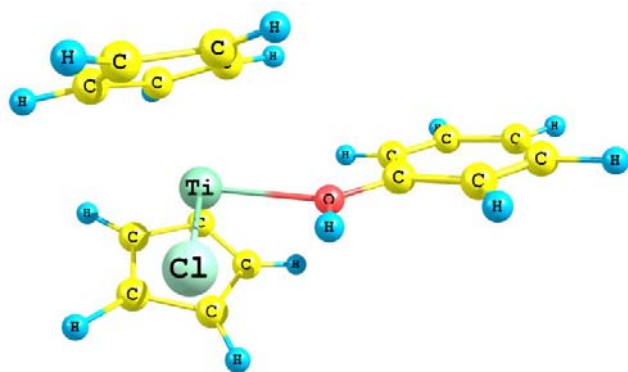
6prod. E(UM05/Ahlrichs-VDZ) = -231.141931752 a.u. / (408 cm⁻¹) / ZPVE = 0.088812 a.u.



C	0.000000000	0.000000000	1.410155000
C	0.000000000	1.231036000	0.774398000
C	0.000000000	-1.231036000	0.774398000
C	0.000000000	1.219876000	-0.635751000
H	0.000000000	2.174527000	1.327045000

C	0.000000000	-1.219876000	-0.635751000
H	0.000000000	-2.174527000	1.327045000
C	0.000000000	0.000000000	-1.330905000
H	0.000000000	2.165569000	-1.184873000
H	0.000000000	-2.165569000	-1.184873000
H	0.000000000	0.000000000	-2.423611000

6reac. E(UM05/Ahlrichs-VDZ) = -2002.8814114 a.u. / (6 cm⁻¹) / ZPVE = 0.279397 a.u.

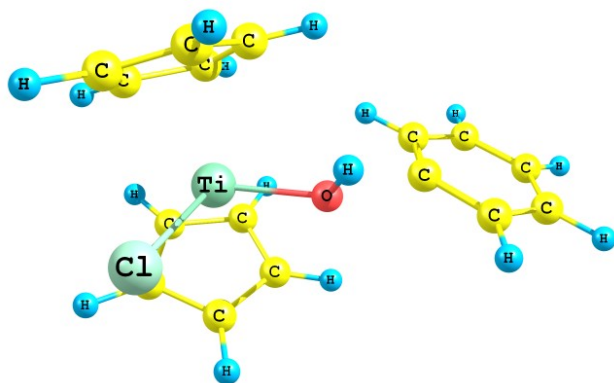


Ti	-1.155932000	-0.006428000	0.010506000
Cl	-1.161216000	-2.034510000	-1.520662000
C	-2.666498000	-0.590432000	1.772375000
C	-1.793914000	0.443884000	2.236173000
C	-0.463419000	-0.062940000	2.239558000
C	-0.521586000	-1.417095000	1.778803000
C	-1.880181000	-1.744679000	1.518717000
H	-2.098827000	1.440191000	2.547745000

H	0.429342000	0.465246000	2.568707000
H	0.325755000	-2.086882000	1.649621000
H	-2.237562000	-2.687363000	1.113388000
H	-3.745624000	-0.515457000	1.653513000
C	-2.640071000	0.914855000	-1.548111000
C	-2.750893000	1.711530000	-0.376837000
C	-1.496469000	2.363231000	-0.157952000
C	-0.620096000	1.987546000	-1.209967000
C	-1.312200000	1.076066000	-2.055648000
H	-3.636331000	1.810840000	0.247112000
H	-1.262981000	3.044782000	0.657741000
H	0.412591000	2.309026000	-1.330264000
H	-0.906207000	0.570285000	-2.927029000
H	-3.409731000	0.277278000	-1.976500000
C	4.933482000	0.460054000	0.340197000
C	4.624103000	-0.697951000	-0.386517000
C	3.294340000	-1.010374000	-0.694399000
C	2.269852000	-0.152174000	-0.269936000
C	2.564146000	1.010076000	0.454917000

C	3.898595000	1.308820000	0.757253000
H	5.971809000	0.699000000	0.578825000
H	4.128632000	2.214990000	1.322573000
H	1.754983000	1.667960000	0.773654000
H	3.051421000	-1.913635000	-1.259876000
H	5.420945000	-1.367672000	-0.717982000
O	0.946672000	-0.444015000	-0.567448000
H	0.764422000	-1.250889000	-1.133293000

6ts. E(UM05/Ahlrichs-VDZ) = -2002.79311832 a.u. / (437*i* cm⁻¹) / ZPVE = 0.274919 a.u.

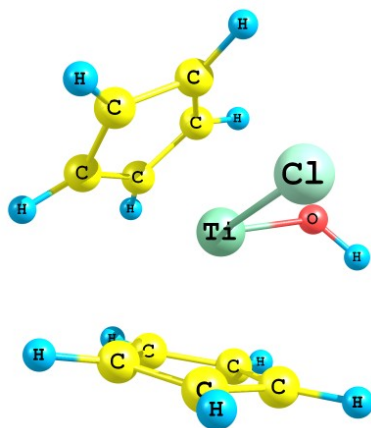


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Cl	2.352271000	-0.997982000	-1.908009000
C	2.493317000	1.744780000	0.854463000
C	1.115190000	2.090850000	1.049310000
C	0.530624000	2.285067000	-0.231184000
C	1.512860000	1.985057000	-1.212529000

C	2.736377000	1.682094000	-0.537548000
H	0.623990000	2.239245000	2.008633000
H	-0.508766000	2.543374000	-0.423410000
H	1.381363000	1.995012000	-2.291897000
H	3.667437000	1.397678000	-1.018667000
H	3.229059000	1.578165000	1.636441000
C	2.212627000	-1.801239000	1.153131000
C	1.786541000	-0.853314000	2.118411000
C	0.356392000	-0.795910000	2.078580000
C	-0.092139000	-1.777064000	1.148321000
C	1.043750000	-2.368481000	0.550030000
H	2.428361000	-0.274268000	2.776433000
H	-0.278712000	-0.178417000	2.710442000
H	-1.125325000	-1.959445000	0.865847000
H	1.040873000	-3.089135000	-0.262391000
H	3.239398000	-2.048826000	0.894466000
C	-5.100767000	0.135662000	0.213219000
C	-4.712412000	-0.582277000	-0.929831000
C	-3.357023000	-0.627618000	-1.308204000

C	-2.449804000	0.066622000	-0.521884000
C	-2.785891000	0.775696000	0.620871000
C	-4.145074000	0.810581000	0.989318000
H	-6.153513000	0.164289000	0.503935000
H	-4.454358000	1.363680000	1.880815000
H	-2.027819000	1.290070000	1.219832000
H	-3.032745000	-1.196174000	-2.184441000
H	-5.461514000	-1.111657000	-1.525286000
O	-0.500856000	-0.219808000	-1.015240000
H	-0.550608000	0.193494000	-1.900111000

(TiCp₂ClOH). E(UM05/Ahlrichs-VDZ) = -1771.6588927 a.u. / (38 cm⁻¹) / ZPVE = 0.185620 a.u.



Ti	-0.002442000	0.035201000	0.228339000
Cl	-0.012950000	2.386425000	-0.280607000
O	0.043503000	0.227126000	2.060855000

H	-0.712286000	0.406188000	2.648226000
C	-1.436079000	-1.758281000	-0.370822000
C	-1.974955000	-1.172128000	0.803142000
C	-2.361133000	0.163953000	0.488413000
C	-2.124608000	0.377205000	-0.899343000
C	-1.525781000	-0.792371000	-1.427154000
H	-1.057071000	-2.772916000	-0.463137000
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H	-2.778823000	0.899208000	1.172811000
H	-2.296001000	1.305869000	-1.434527000
H	-1.223771000	-0.940784000	-2.460777000
C	1.579995000	-1.717793000	0.089583000
C	2.216277000	-0.729248000	0.891125000
C	2.370838000	0.435900000	0.107692000
C	1.908494000	0.147111000	-1.219374000
C	1.447963000	-1.189443000	-1.238474000
H	1.323483000	-2.726176000	0.406995000
H	2.403387000	-0.802904000	1.958097000
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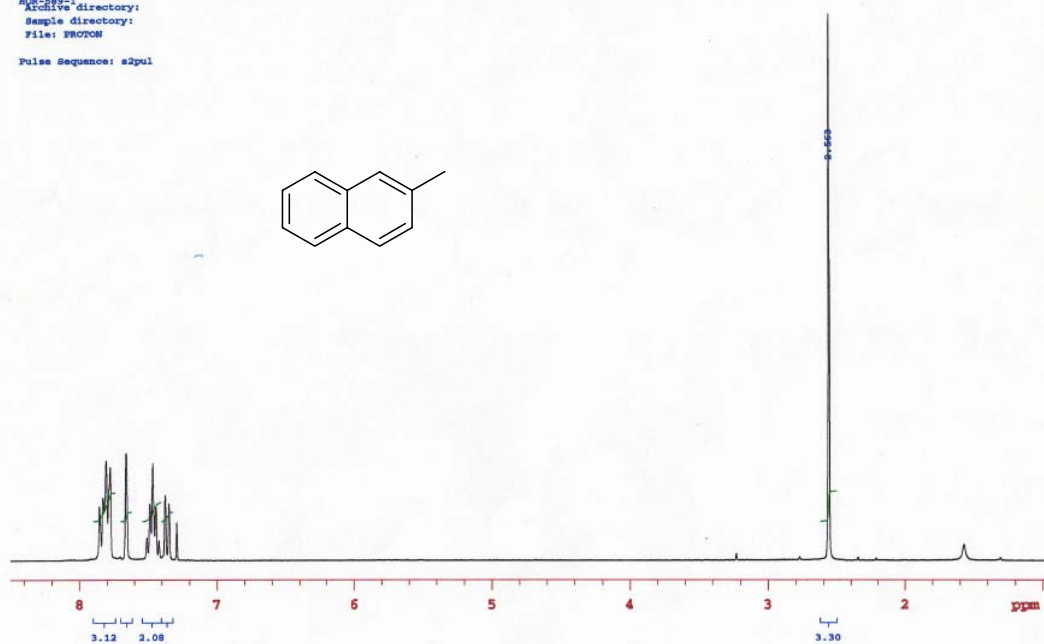
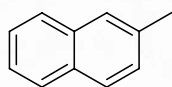
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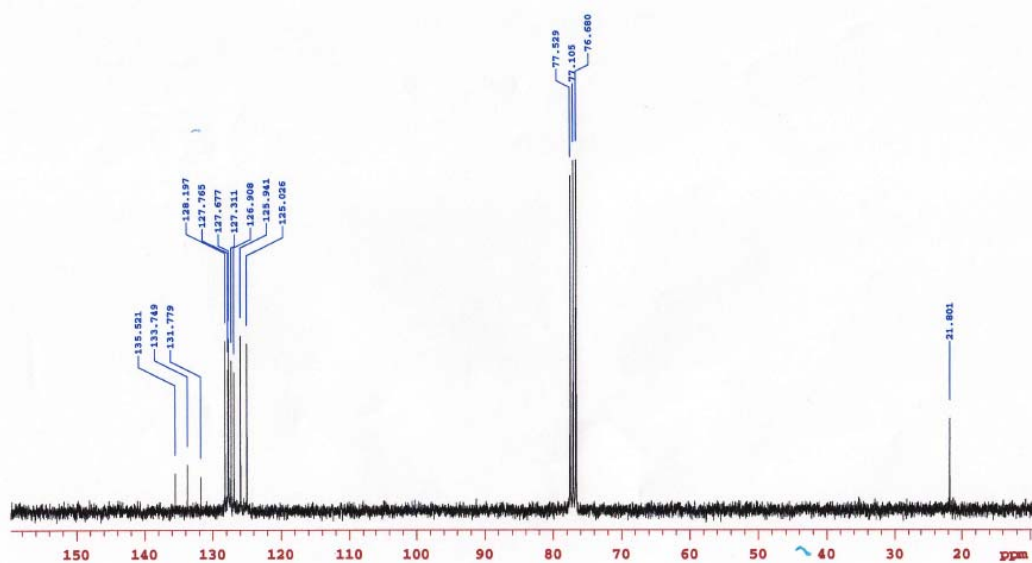
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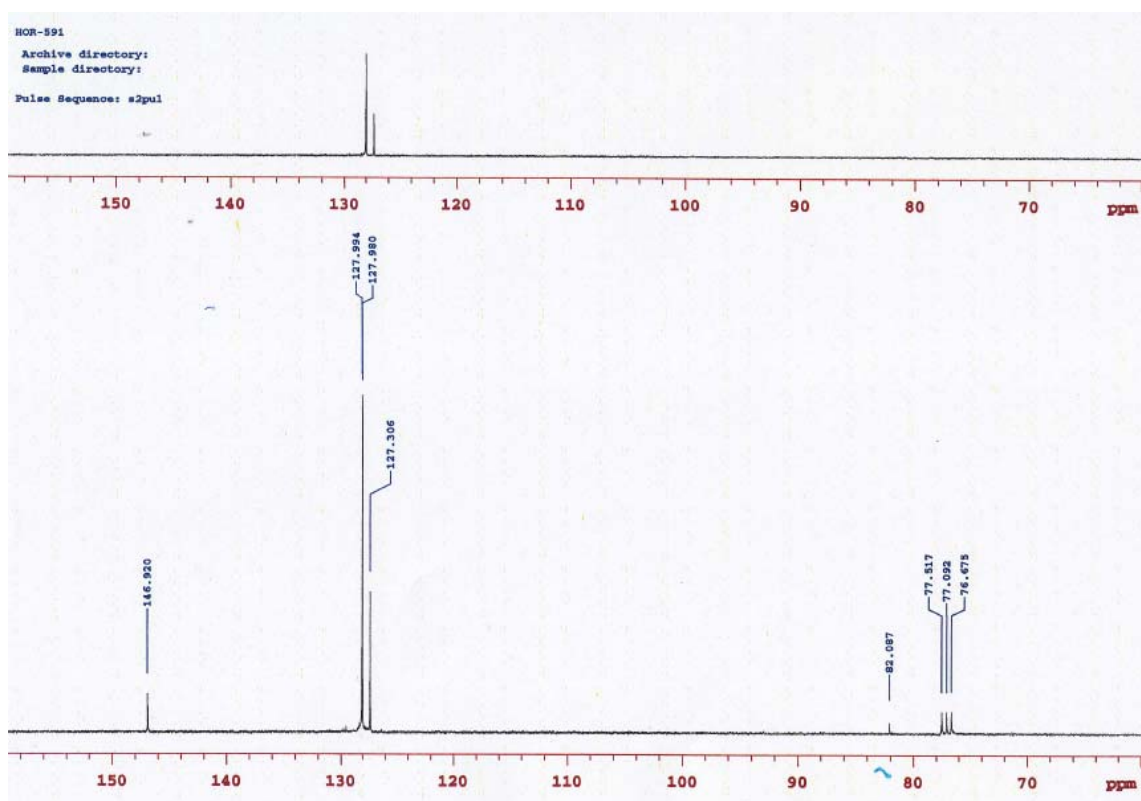
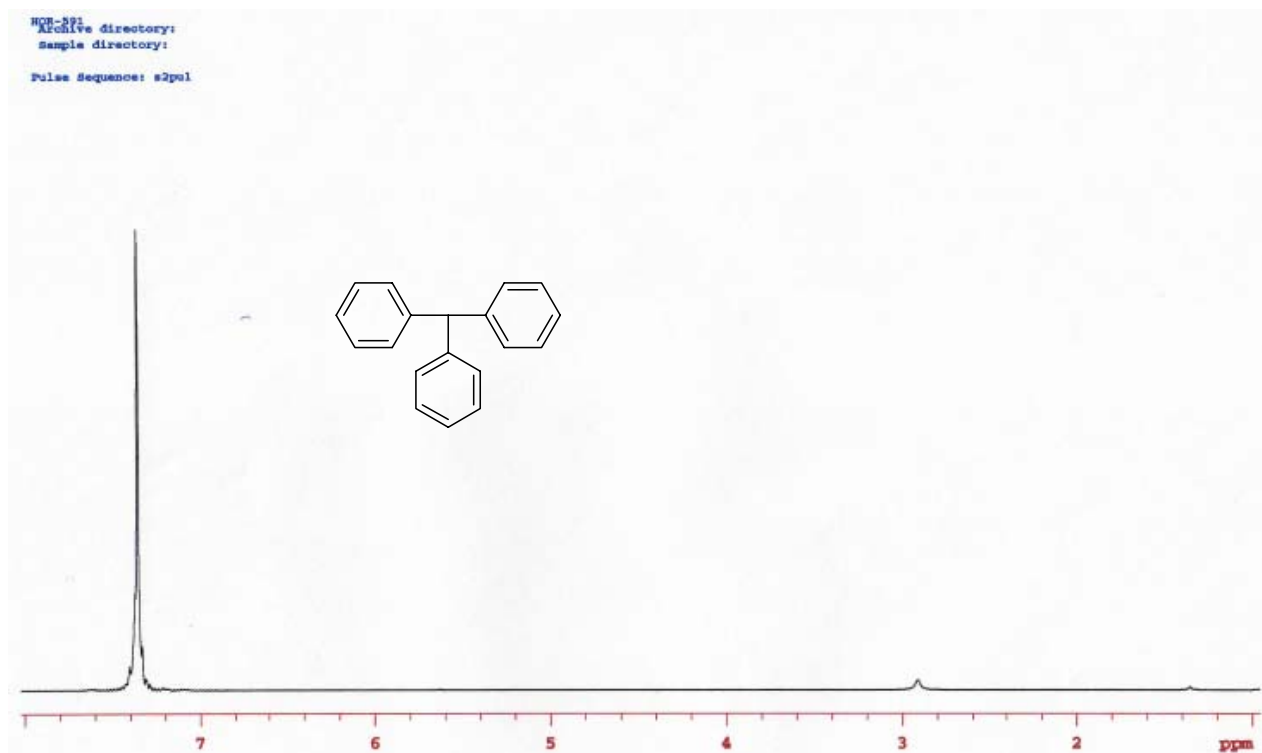
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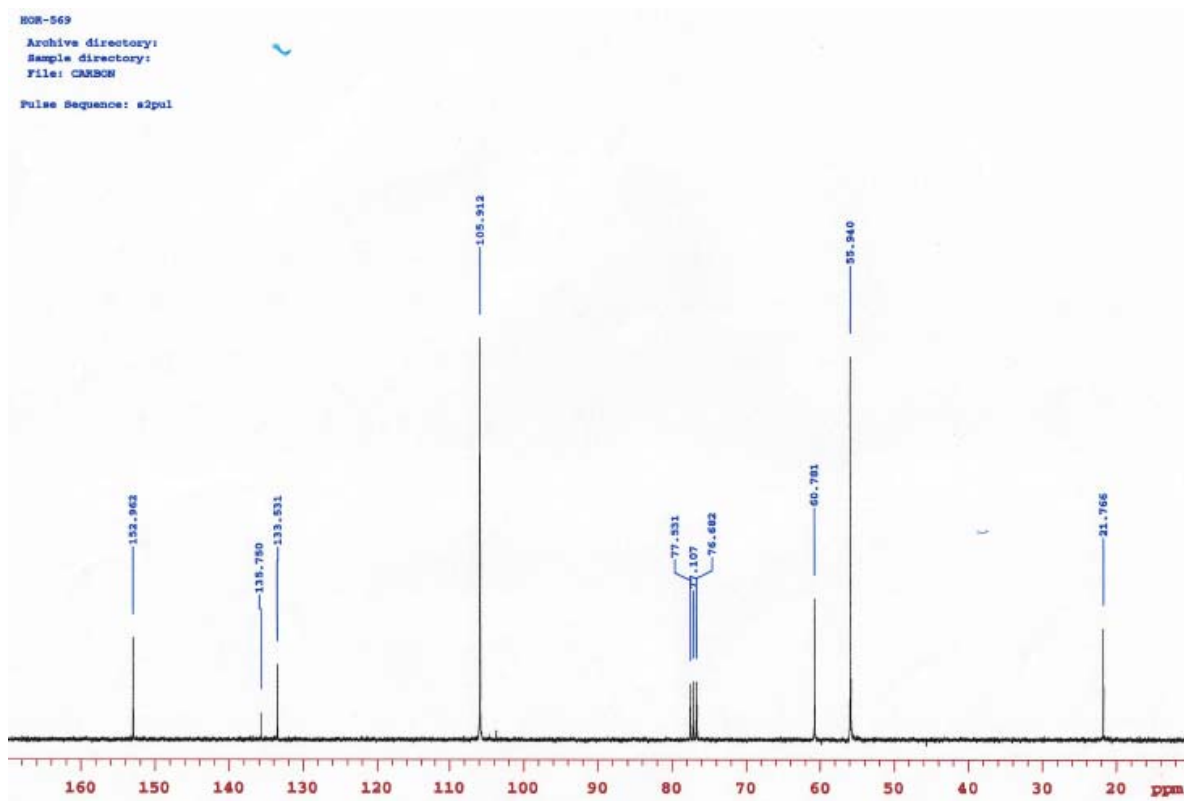
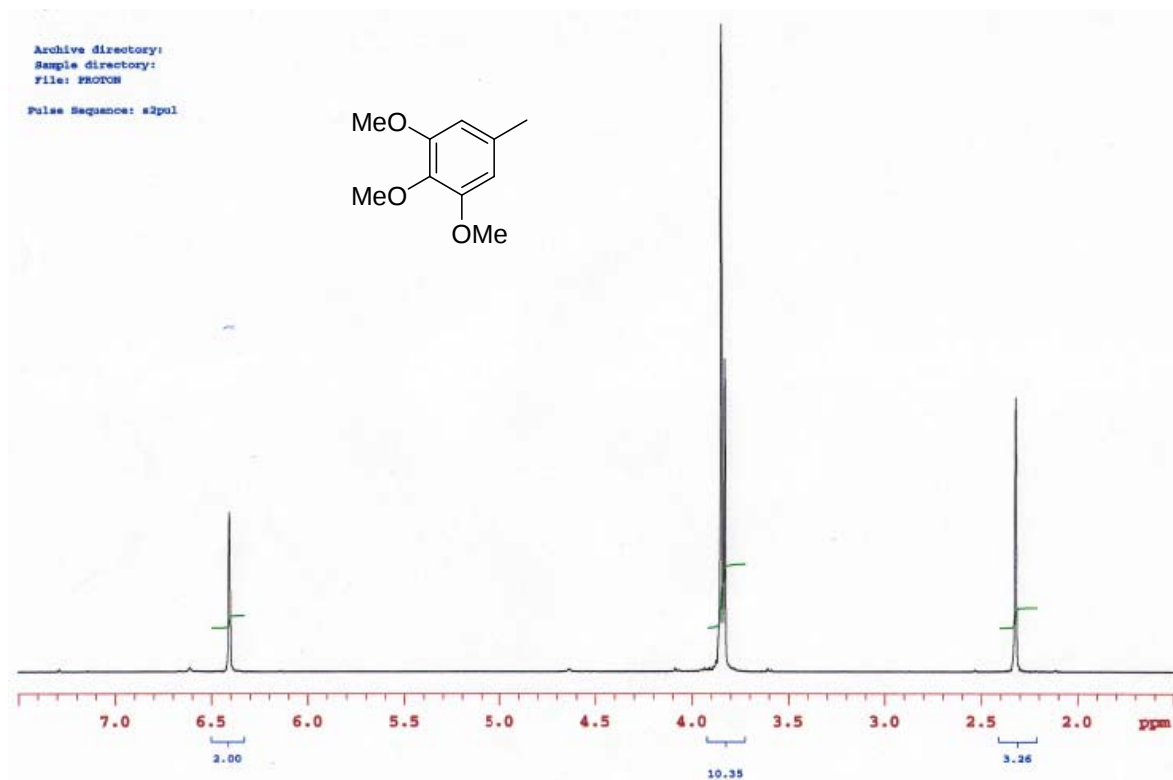
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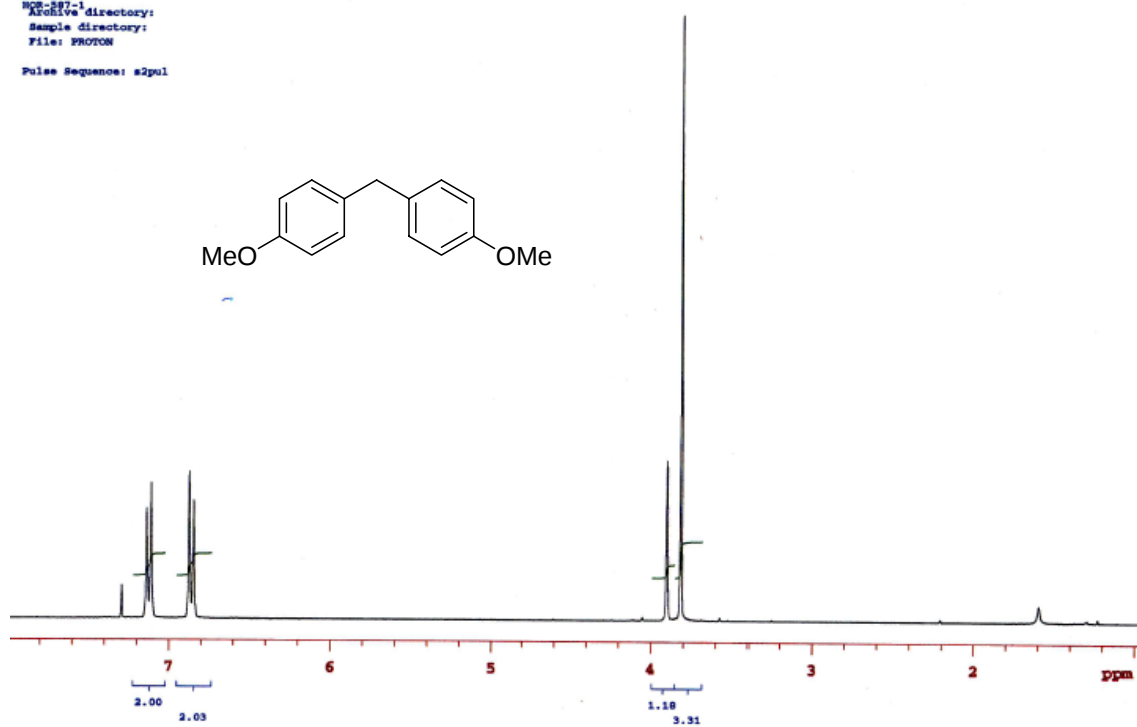
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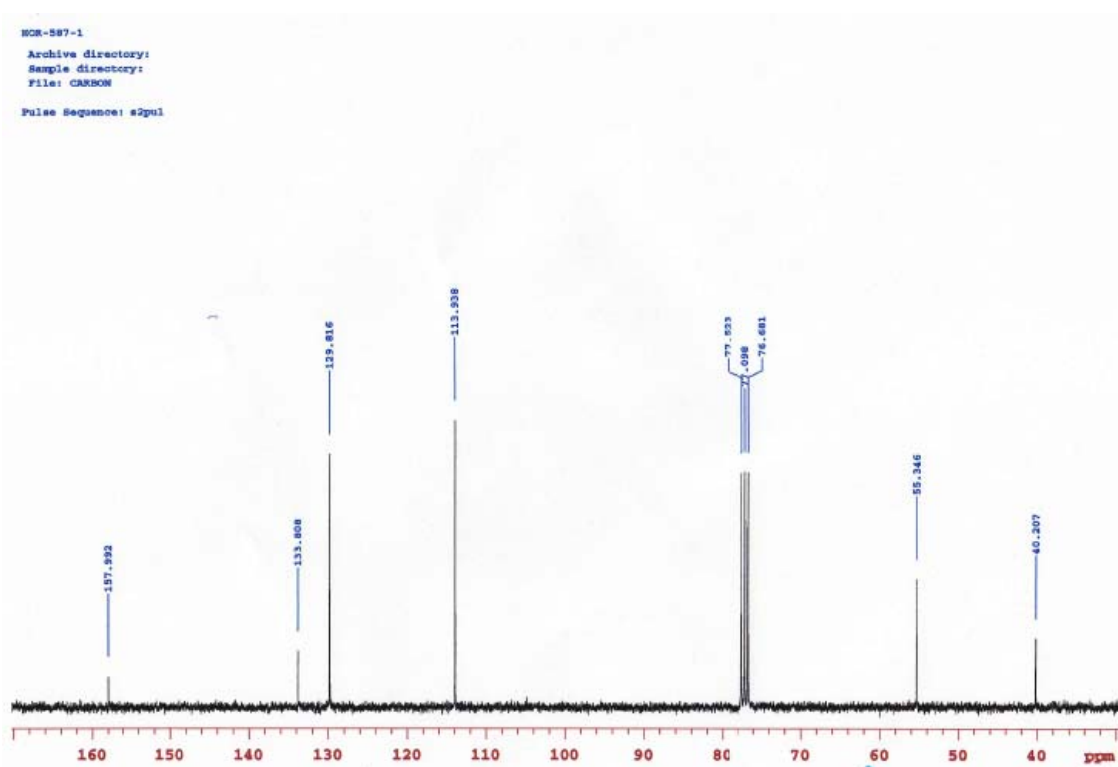




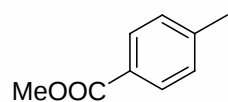
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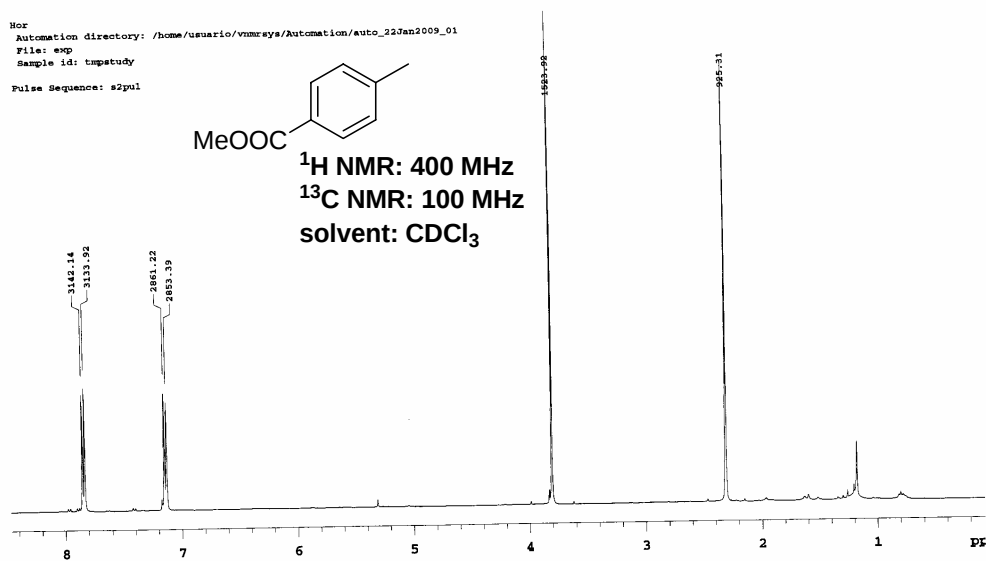
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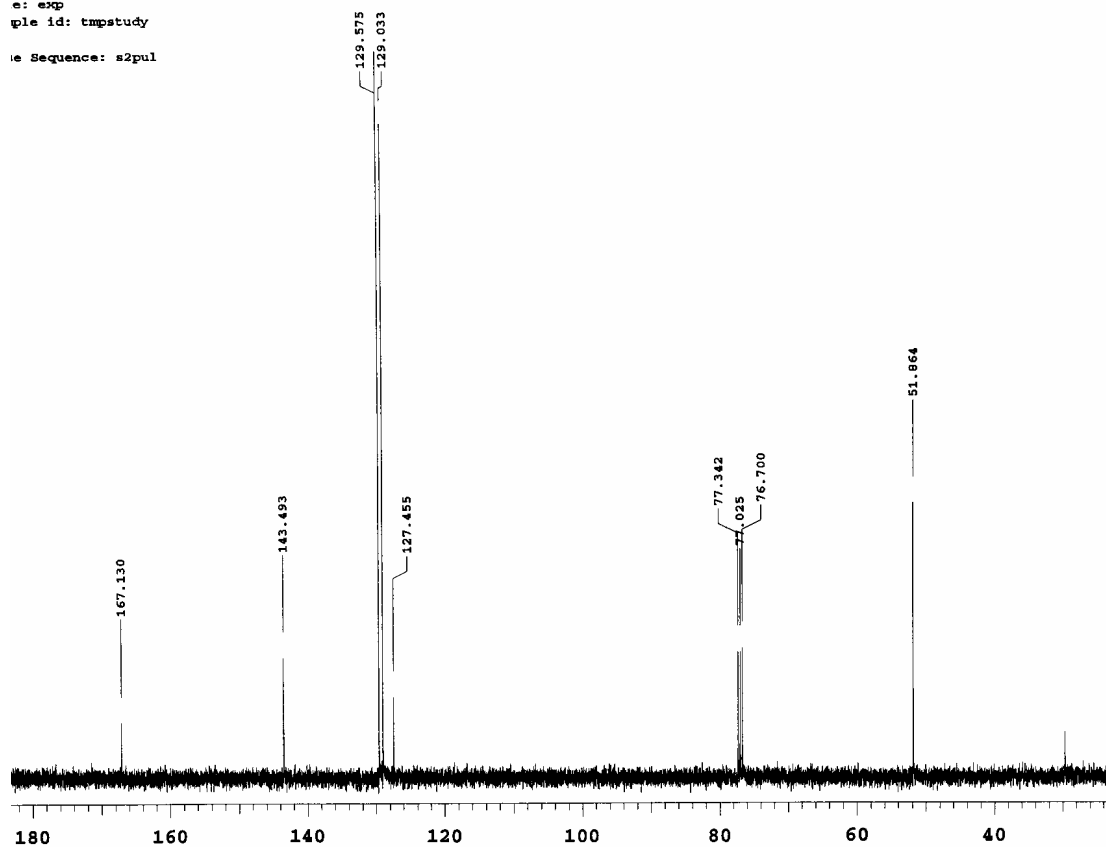
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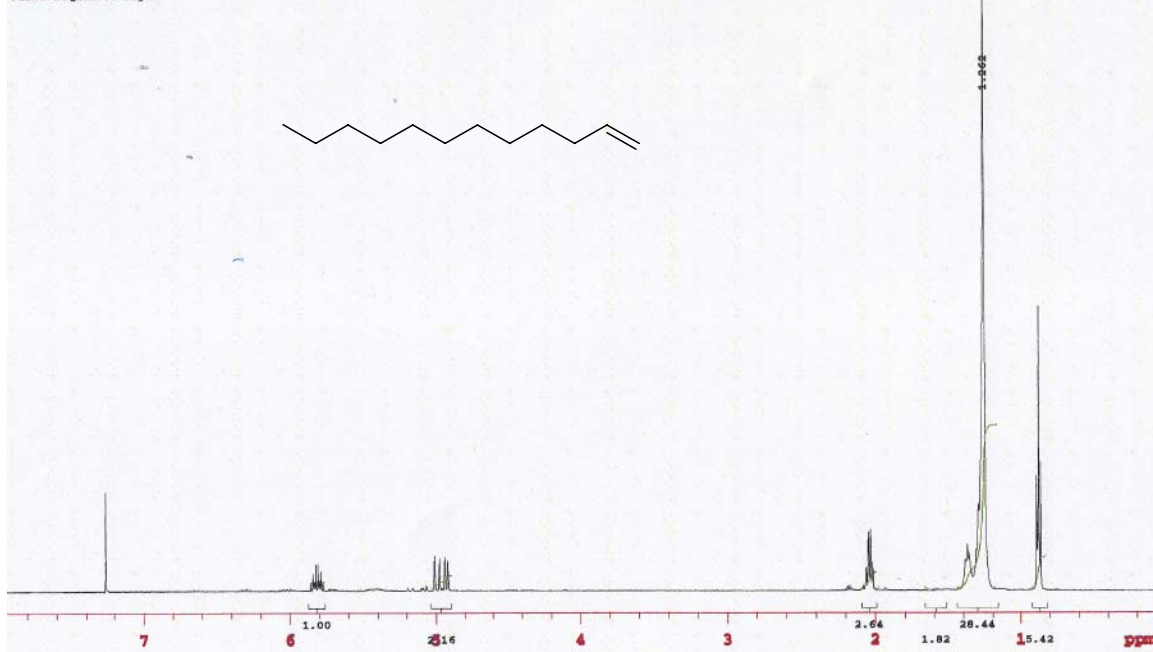
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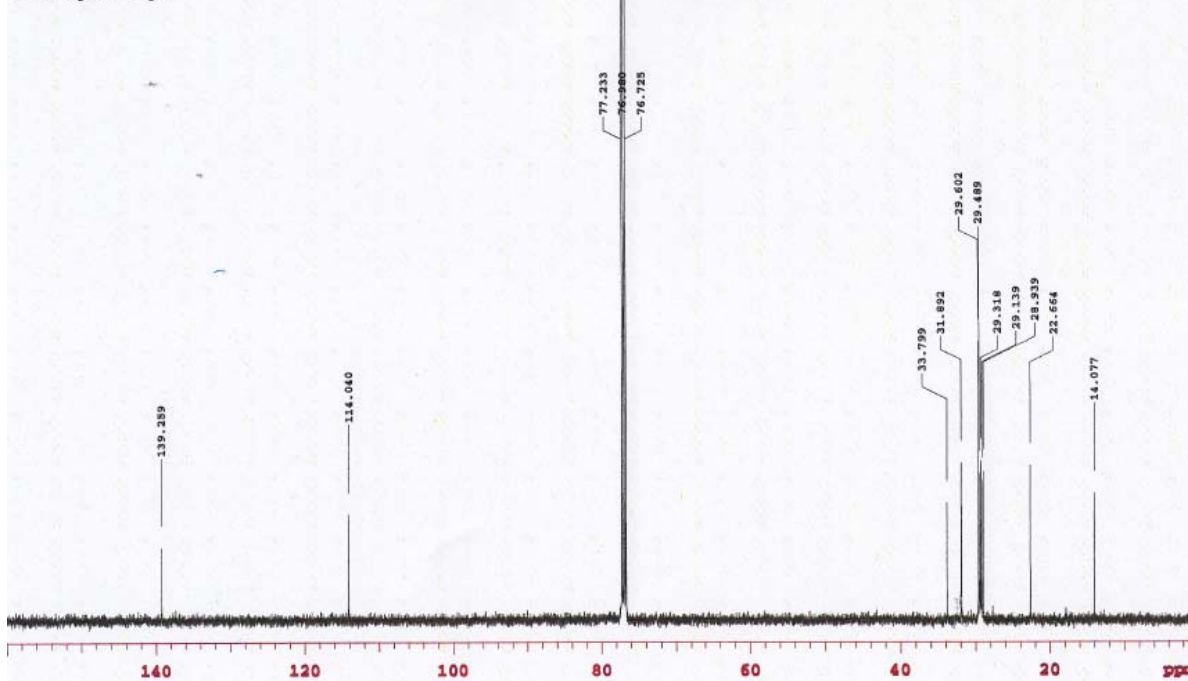
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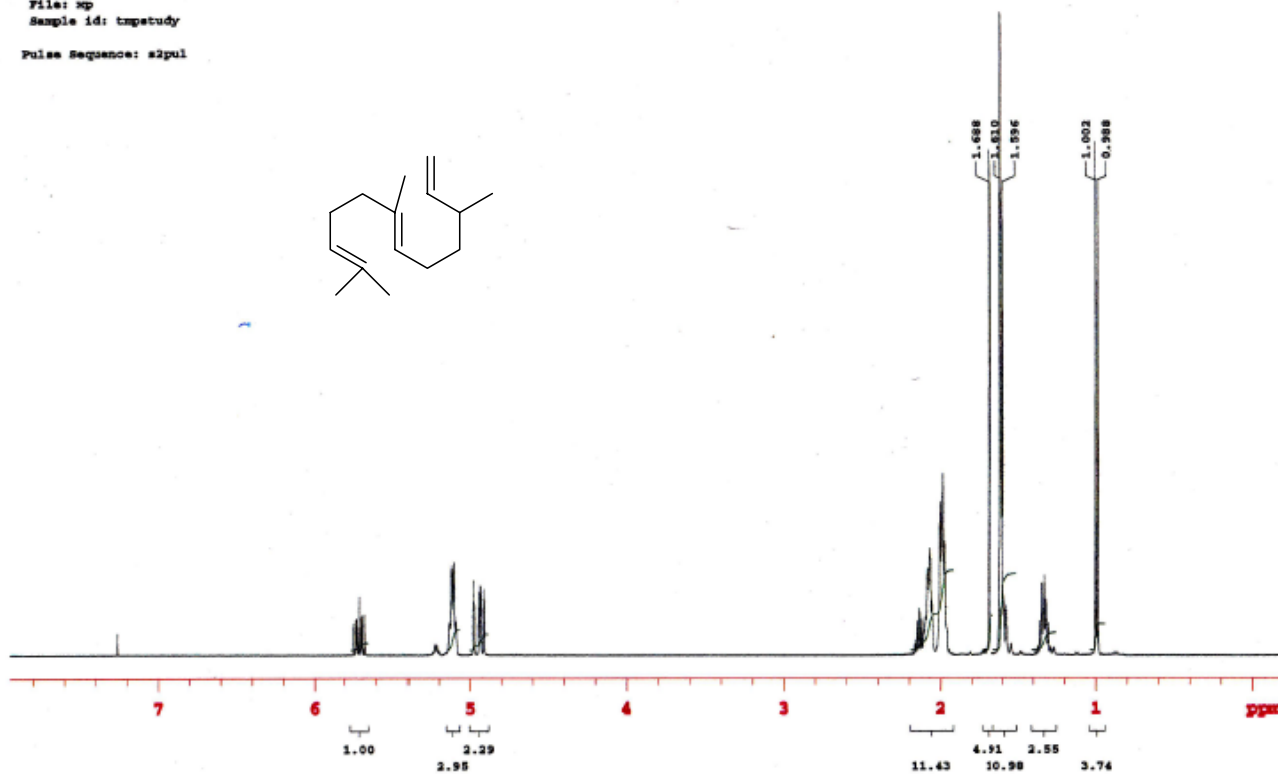
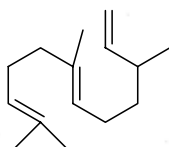
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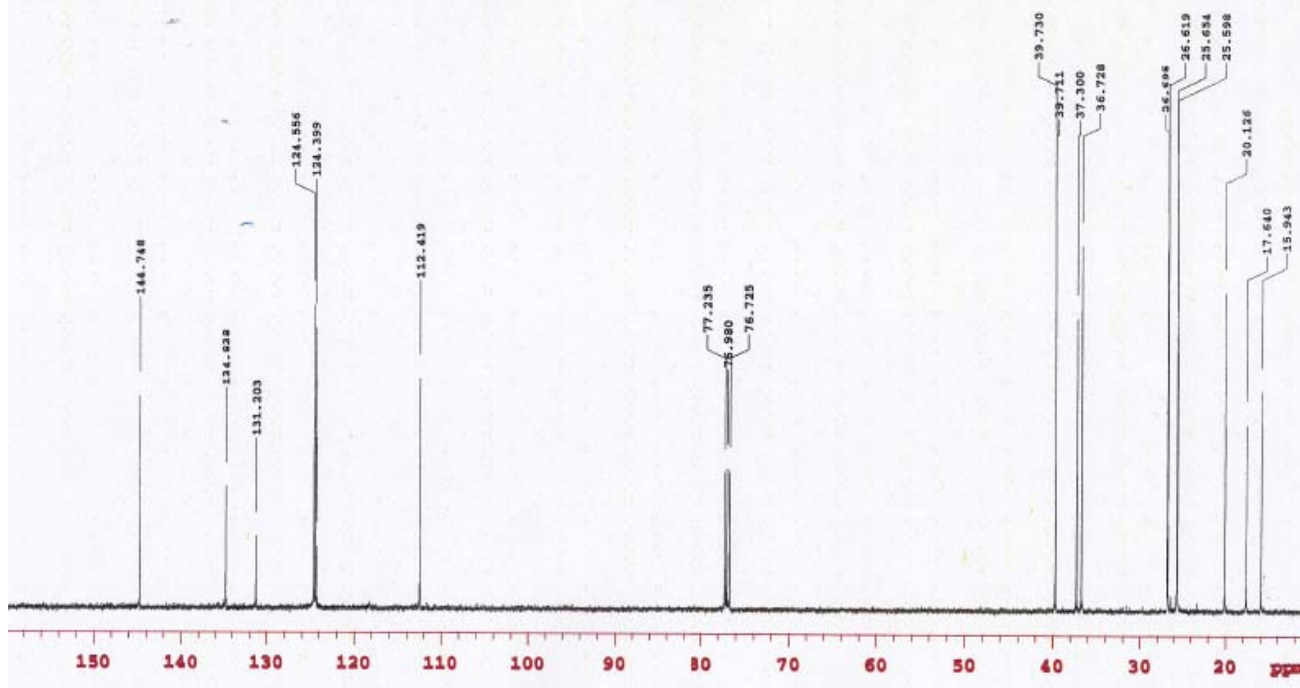
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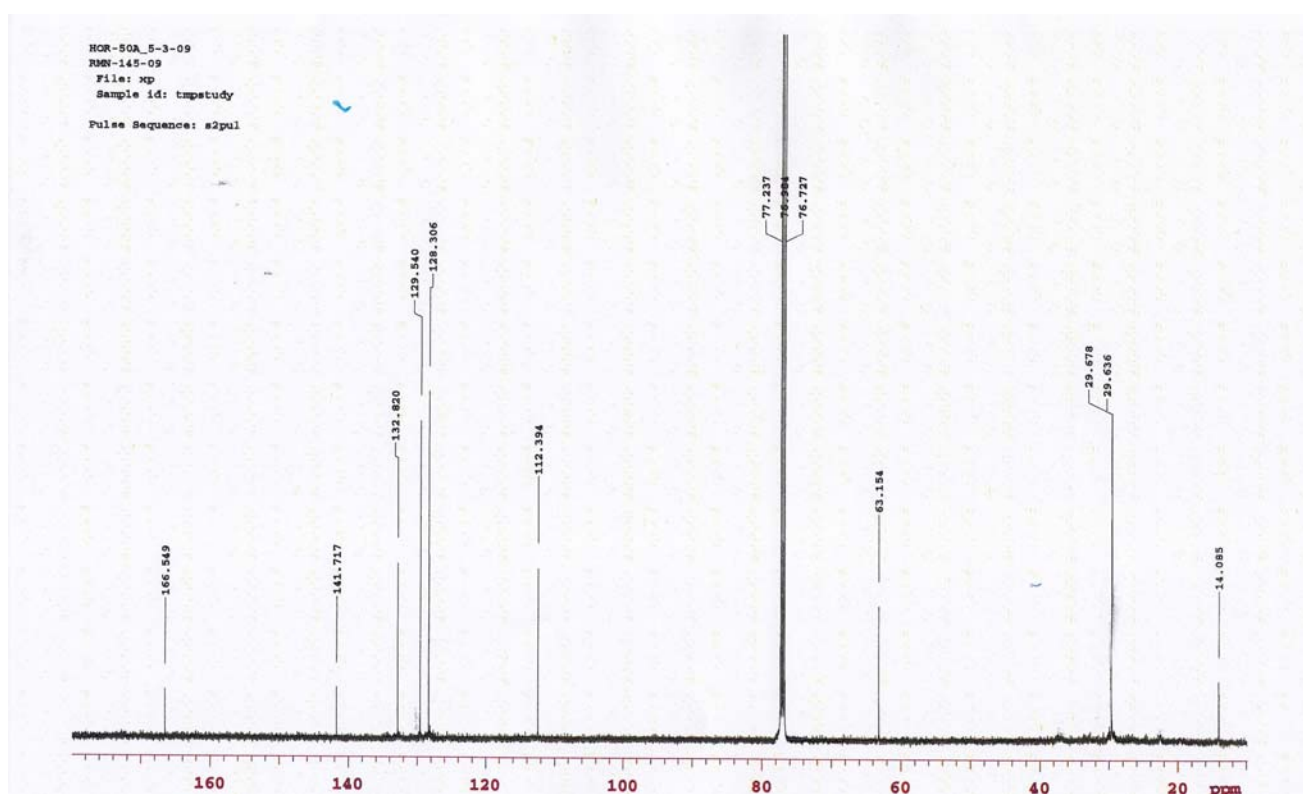
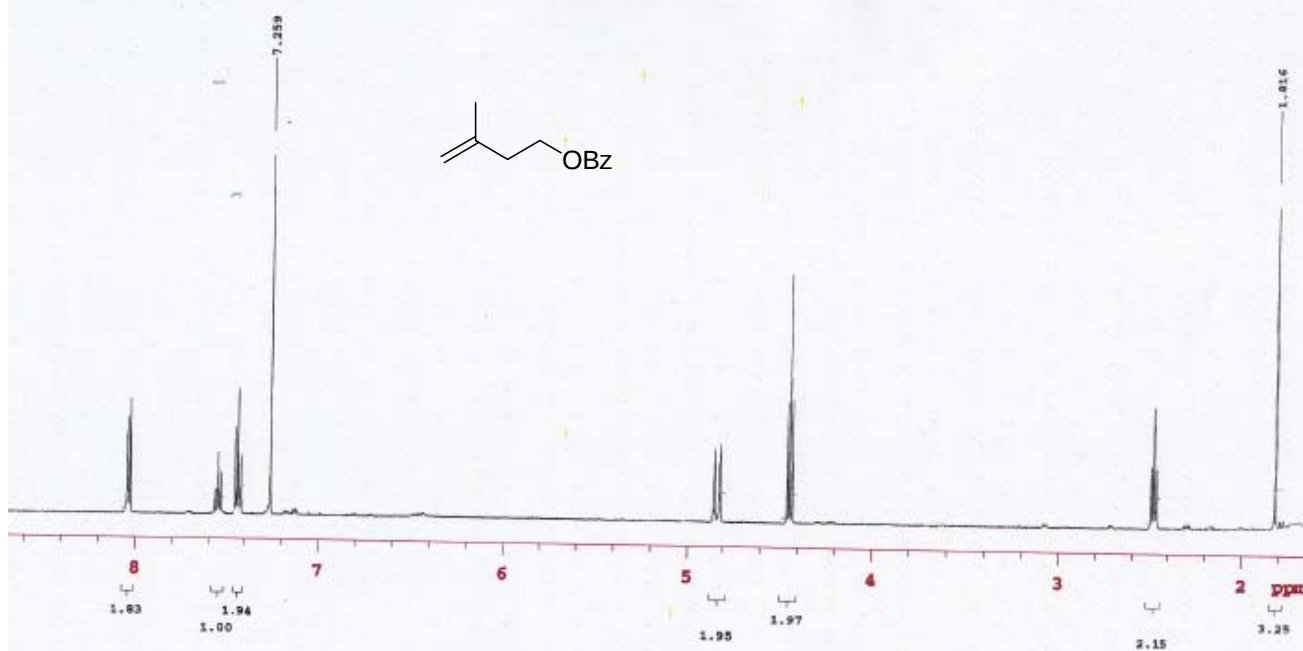
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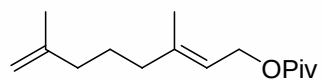
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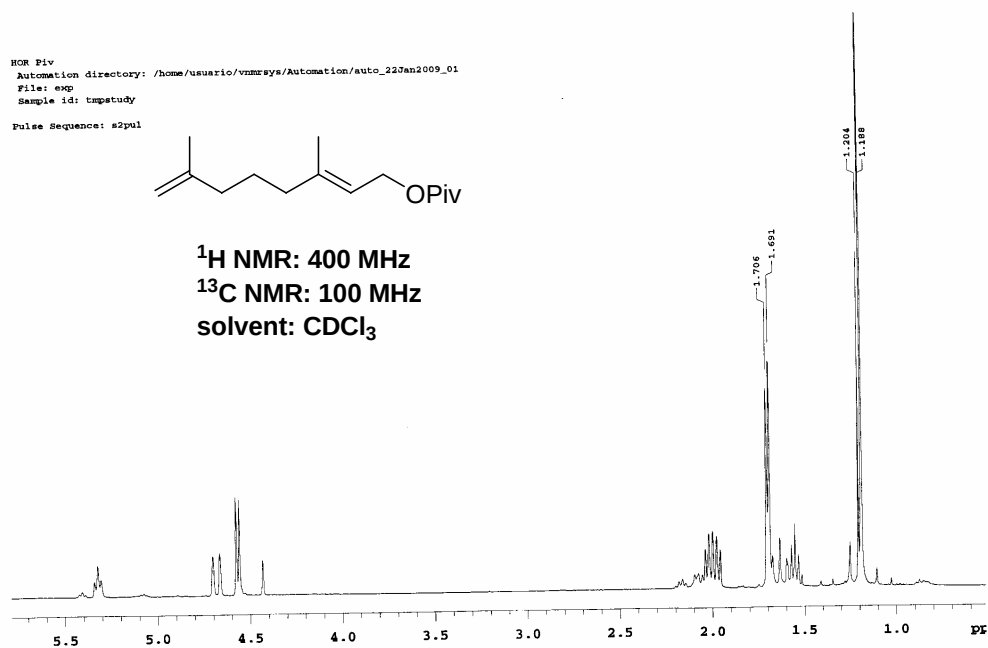
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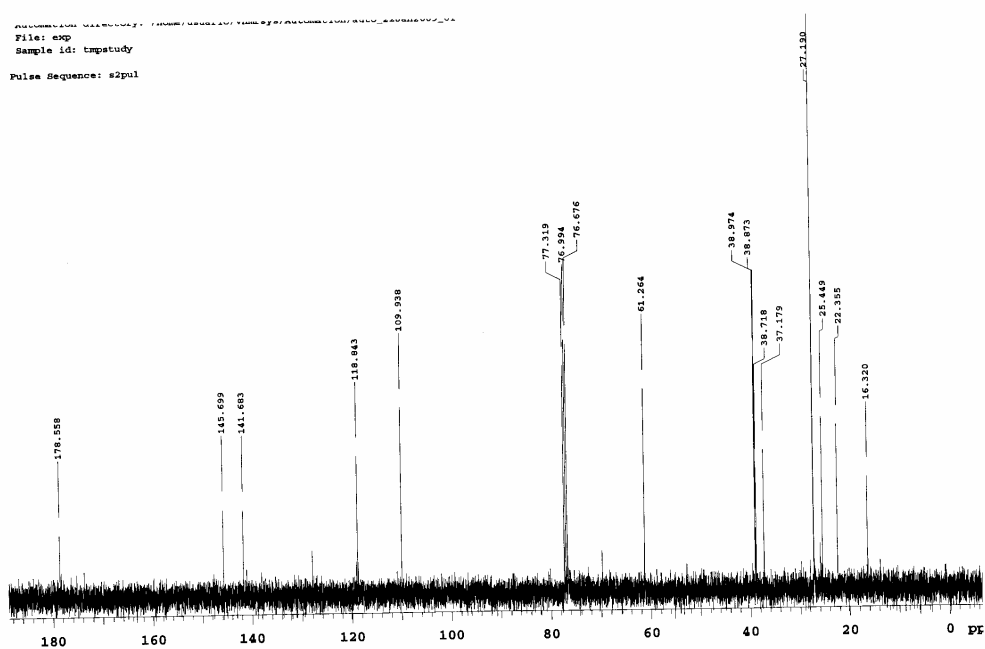
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¹³C NMR: 100 MHz

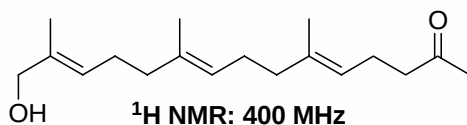
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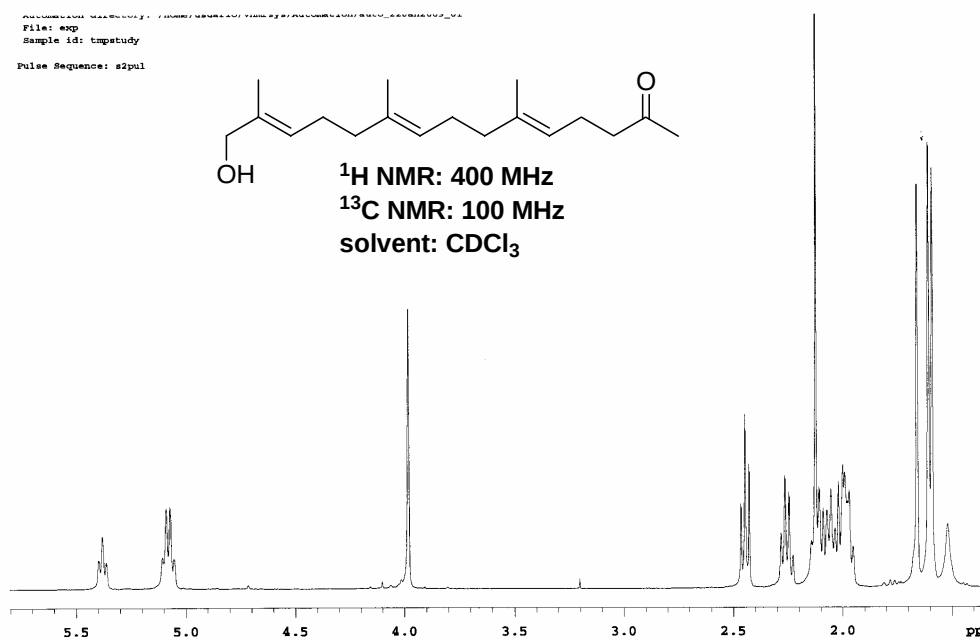
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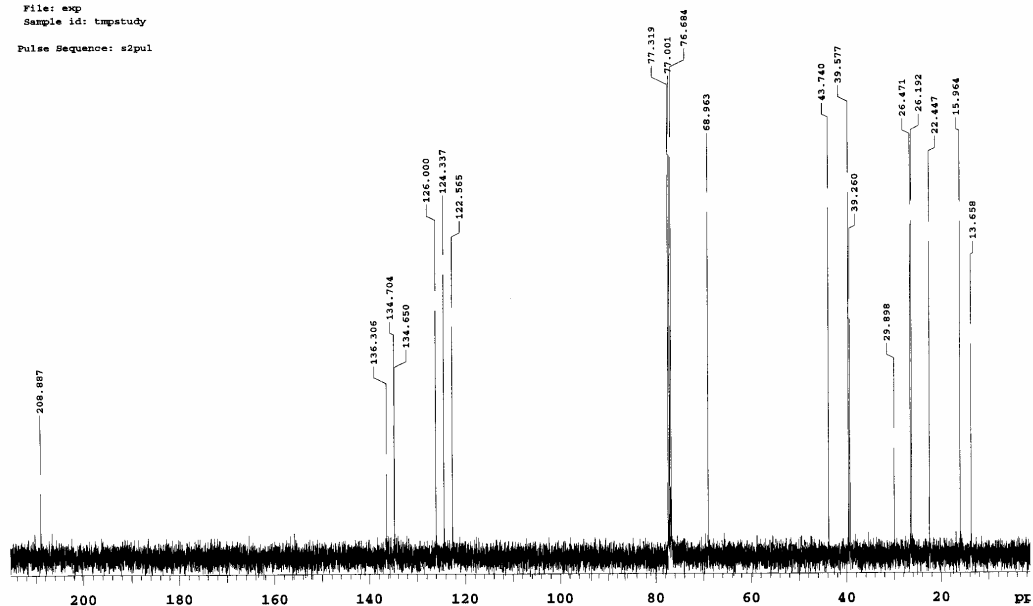
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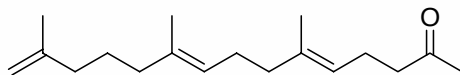
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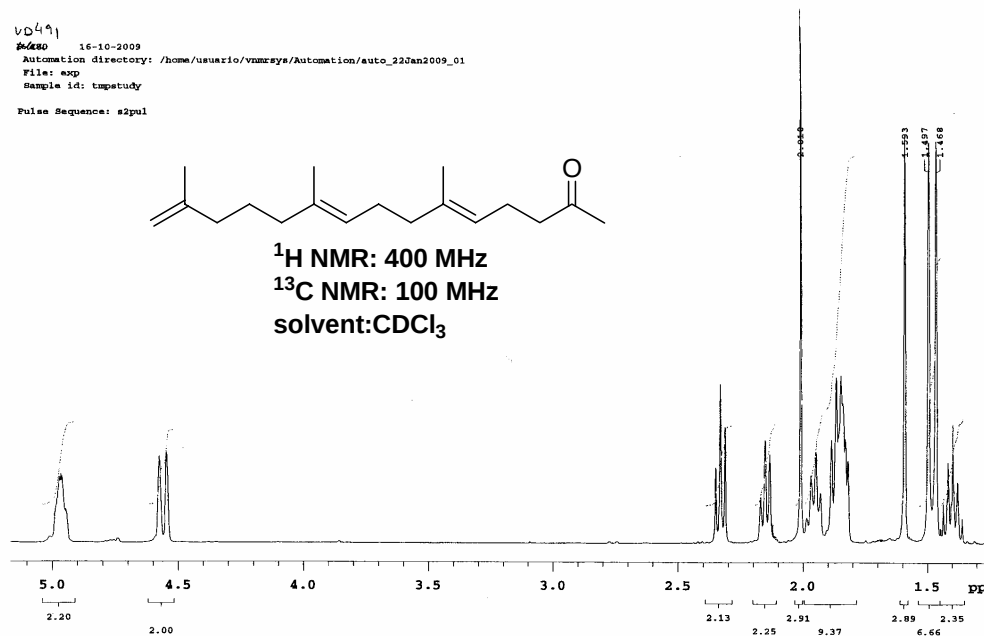
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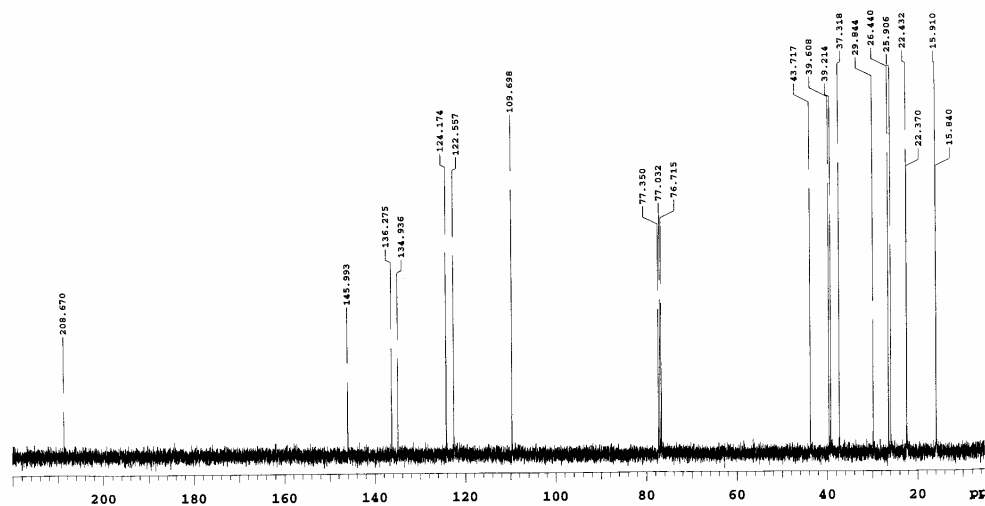
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 Sample id: tmpstudy
 Pulse Sequence: s2pul



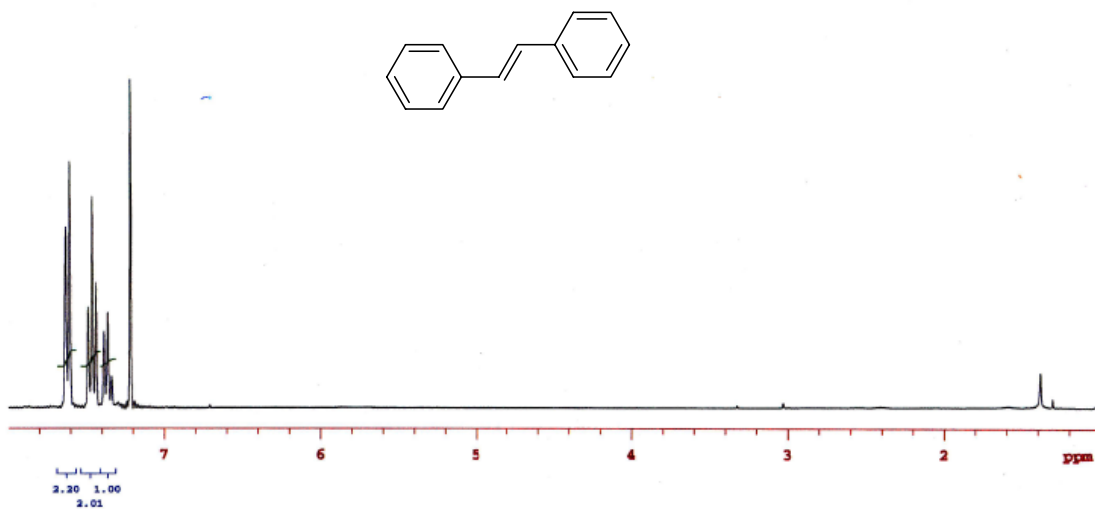
¹H NMR: 400 MHz
¹³C NMR: 100 MHz
 solvent: CDCl₃



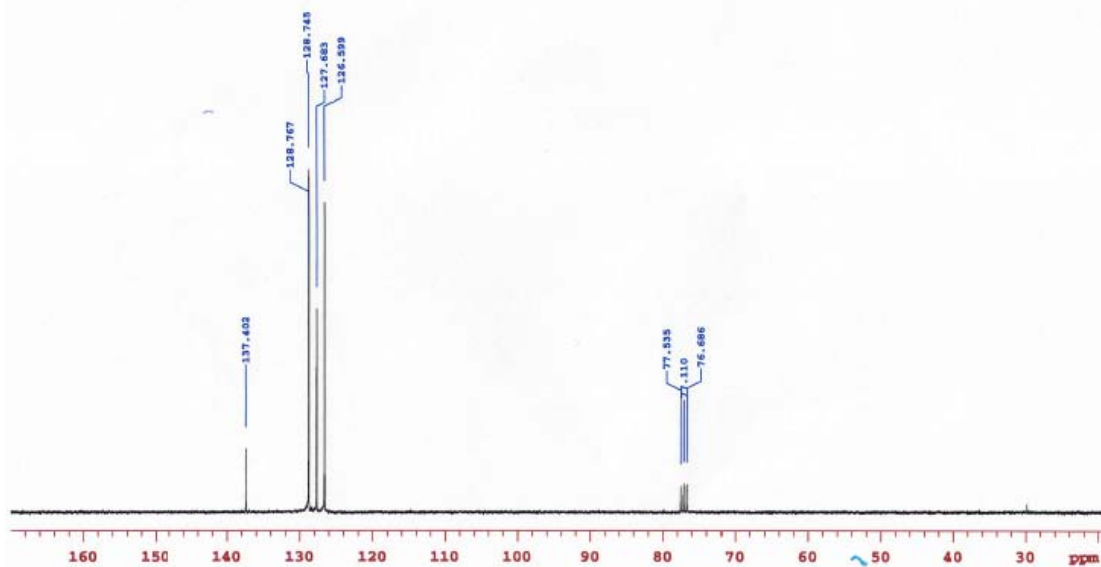
File: exp
 Sample id: tmpstudy
 Pulse Sequence: s2pul



NOR-665
 Archive directory:
 Sample directory:
 File: PROTON
 Pulse Sequence: s2pul

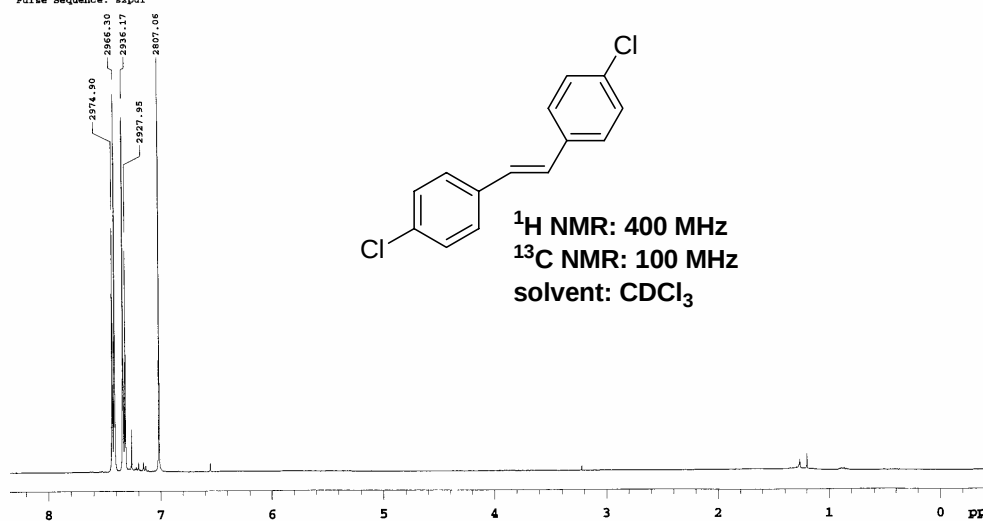


NOR-665
 Archive directory:
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pul

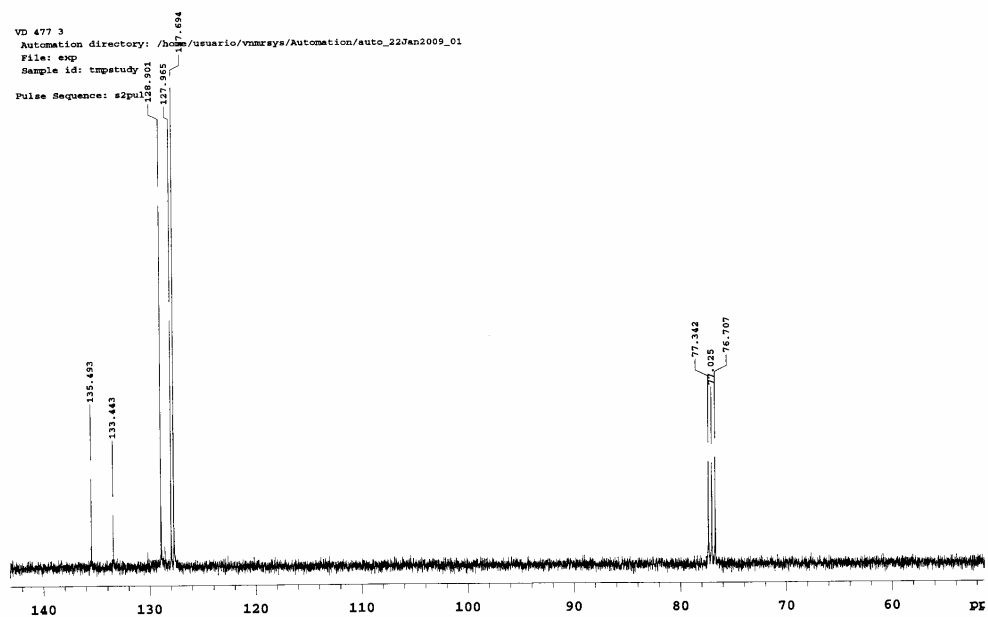


VD 477 5
Automation directory: /home/usuario/vnmrsys/Automation/auto_22Jan2009_01
File: /home/usuario/vnmrsys/data/Barrero/VD477-5-H.fid
Sample id: tmpstudy

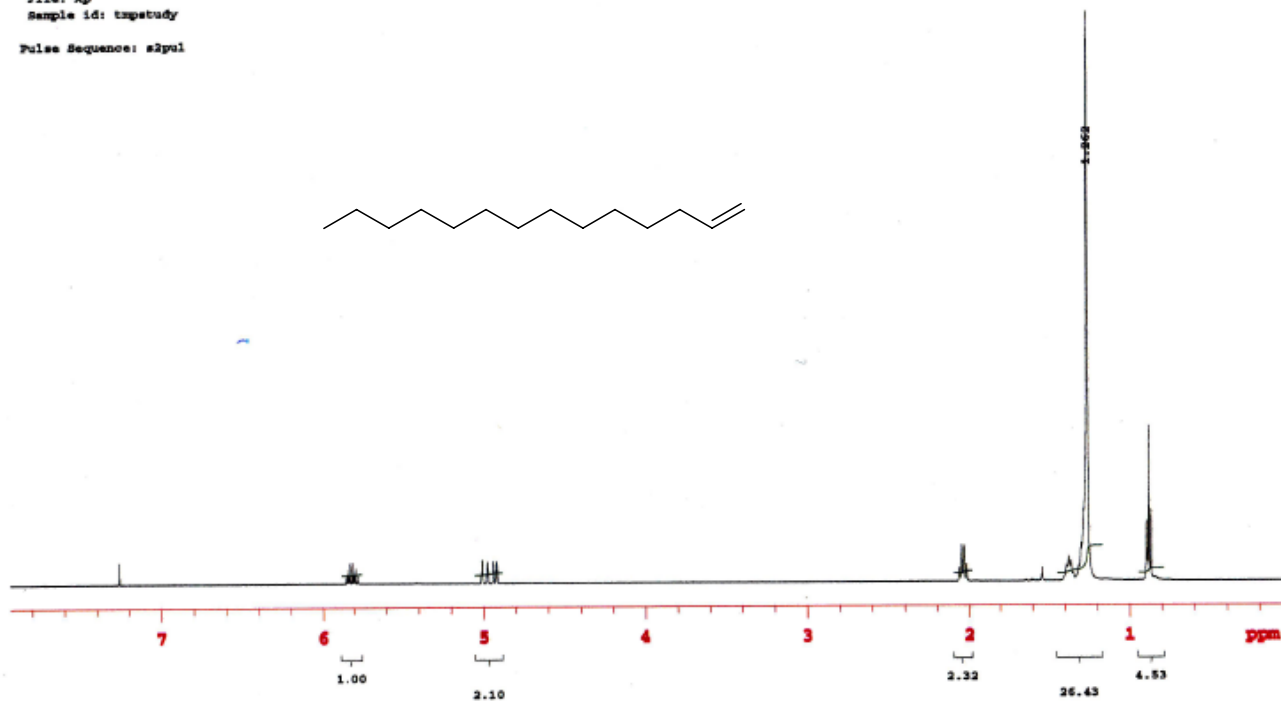
Pulse Sequence: s2pul



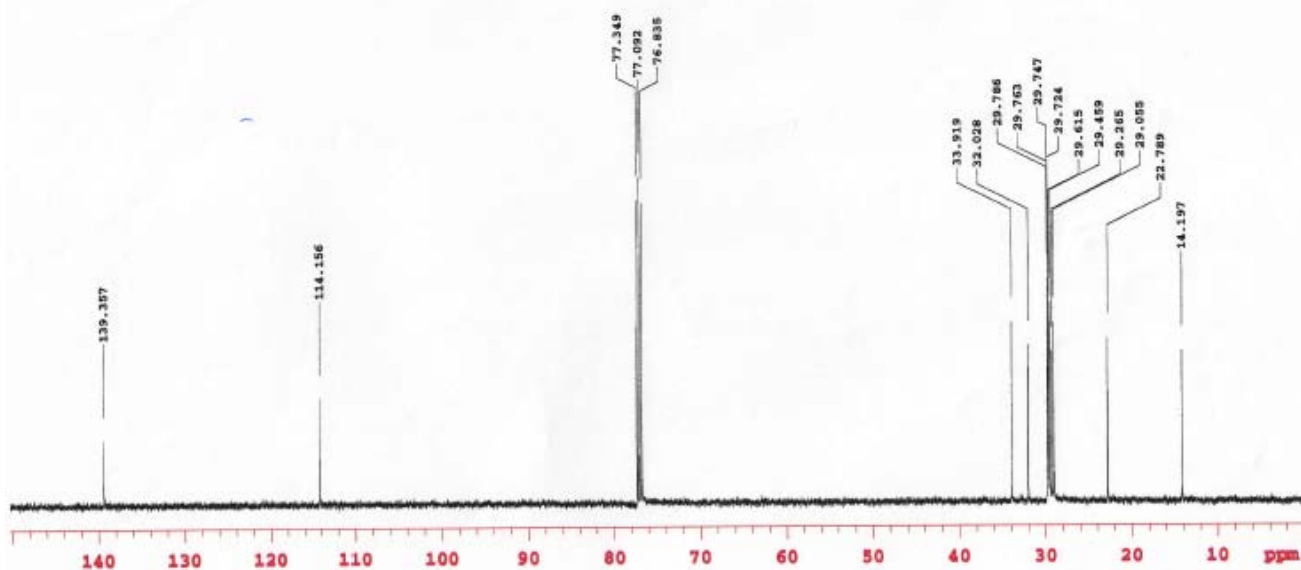
VD 477 3
Automation directory: /home/usuario/vnmrsys/Automation/auto_22Jan2009_01
File: exp
Sample id: tmpstudy
Pulse Sequence: s2pul

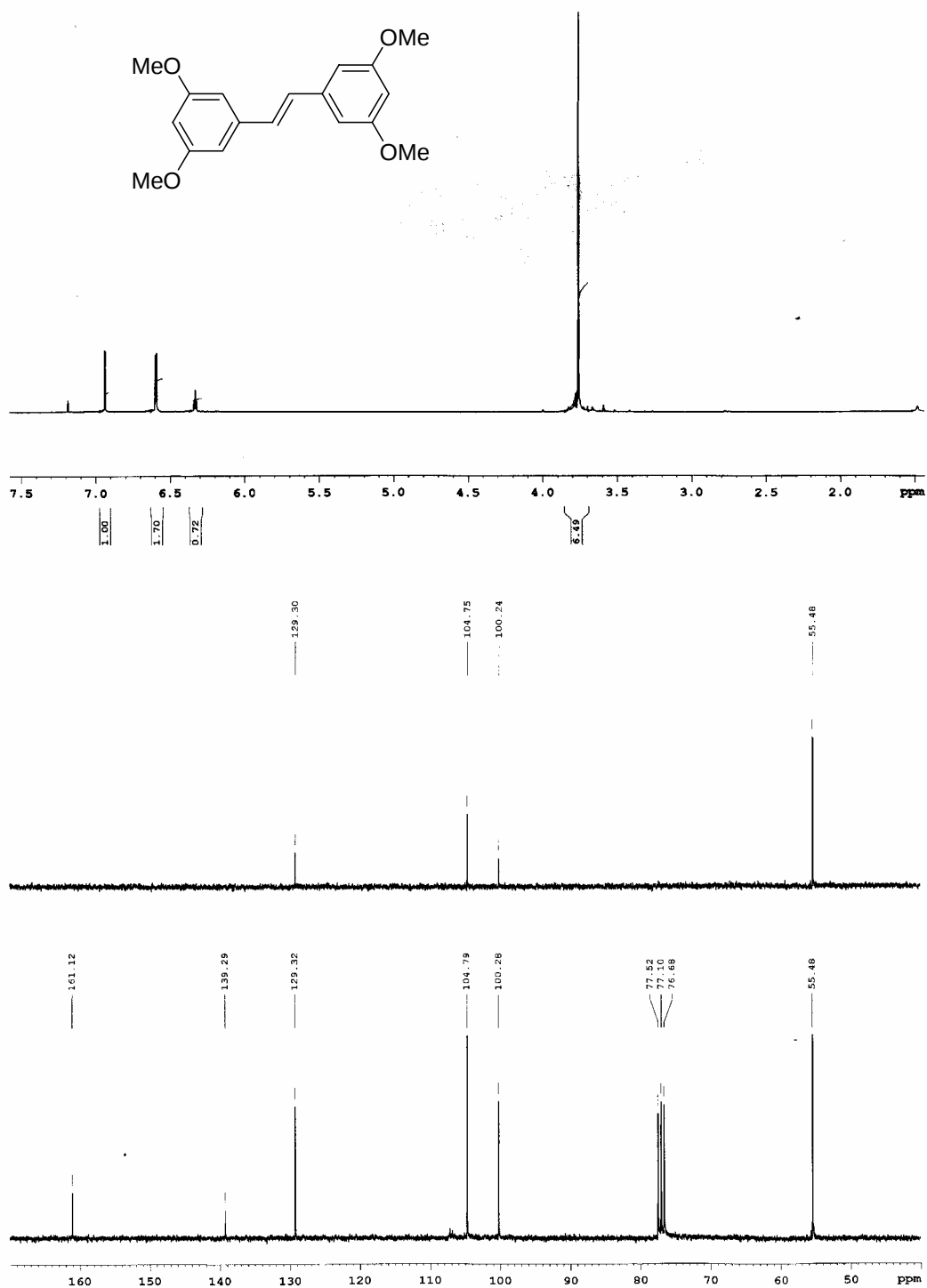


HMR-607_9-9-08
 File: mp
 Sample id: tmpstudy
 Pulse Sequence: s2pul

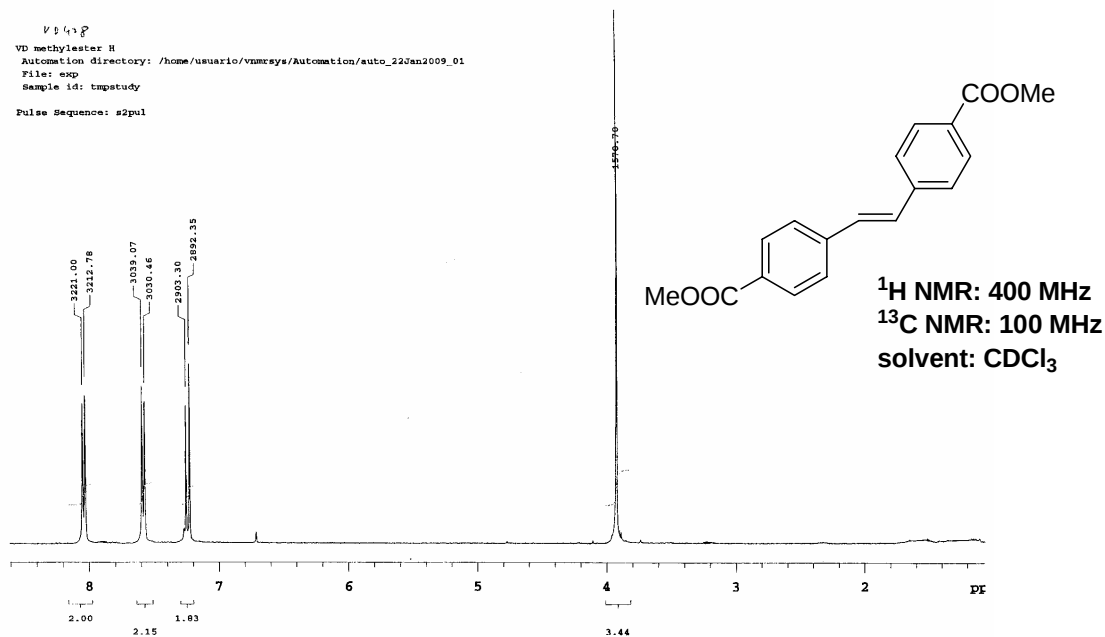


HMR-607_9-9-08
 File: mp
 Sample id: tmpstudy
 Pulse Sequence: s2pul

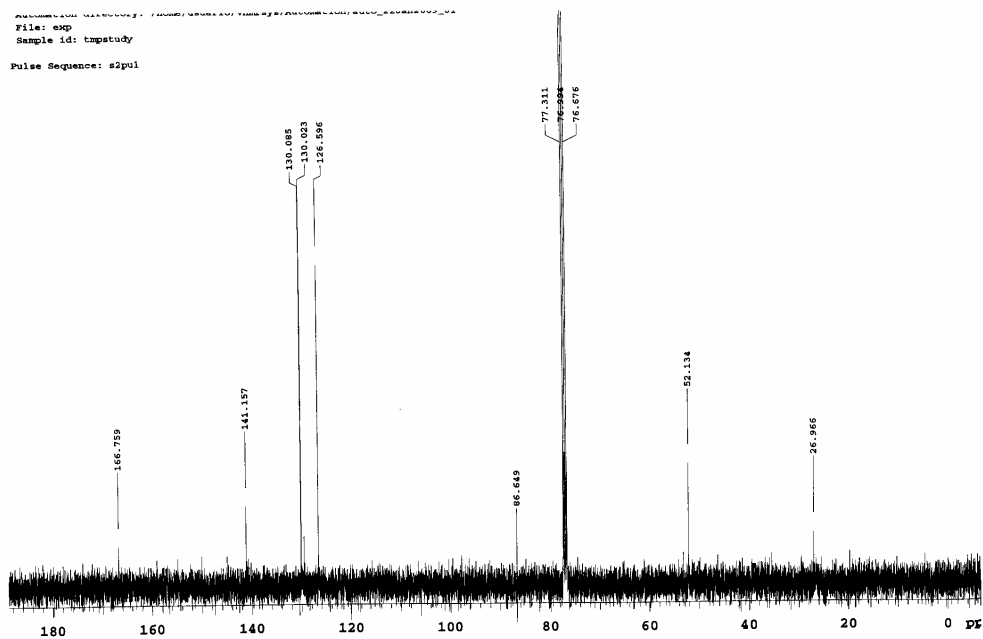




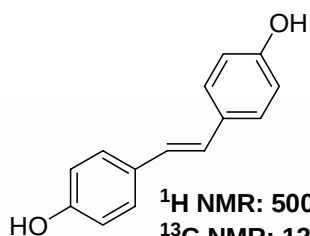
VB43P
 VD methyl ester H
 Automation directory: /home/usuario/vnmr/automation/auto_22Jan2009_01
 File: exp
 Sample id: tmpstudy
 Pulse Sequence: s2pul



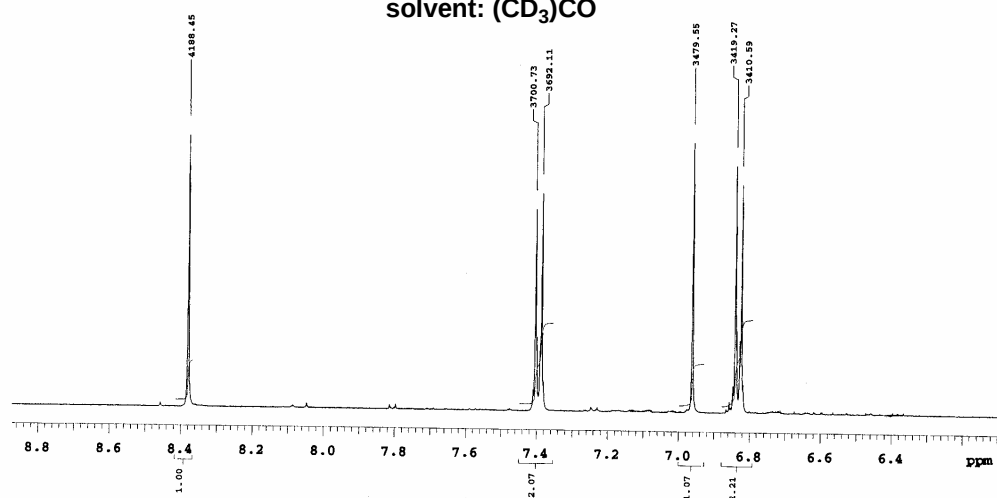
VB43P
 VD methyl ester H
 Automation directory: /home/usuario/vnmr/automation/auto_22Jan2009_01
 File: exp
 Sample id: tmpstudy
 Pulse Sequence: s2pul



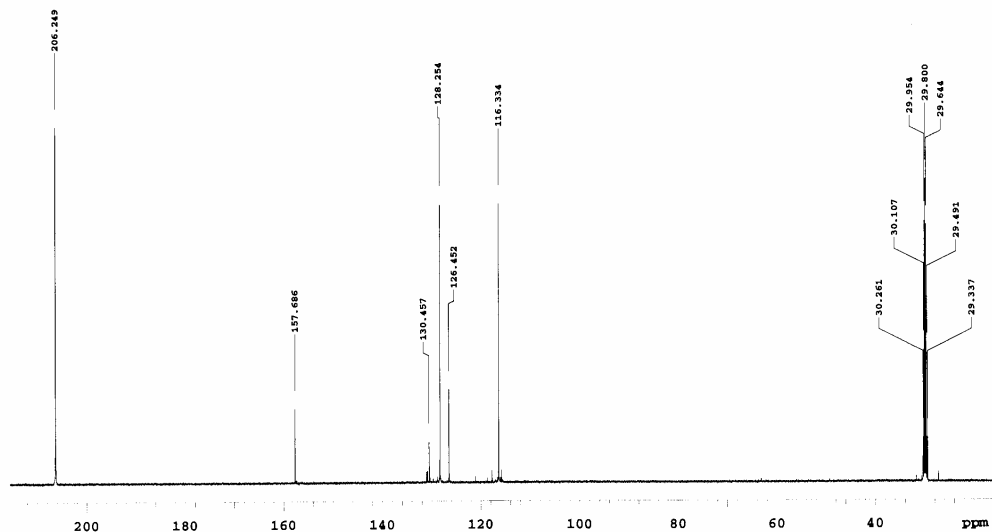
VD-484
NMN-548-09
File: xp
Sample id: tmpstudy
Pulse Sequence: s2pul



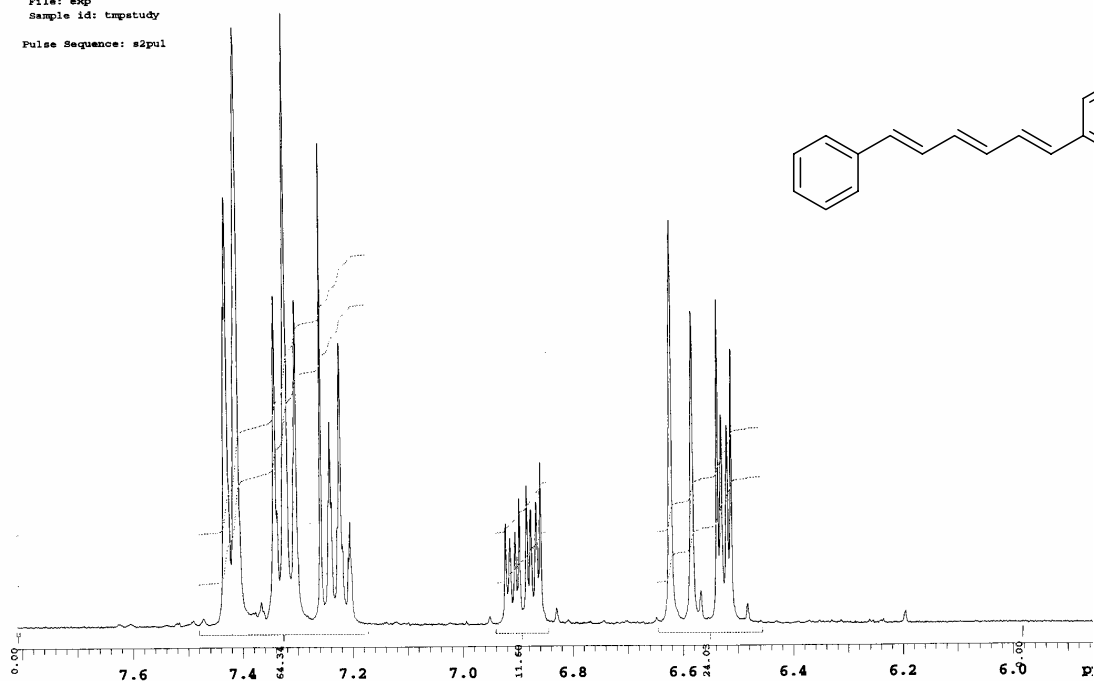
¹H NMR: 500 MHz
¹³C NMR: 125 MHz
solvent: (CD₃)CO



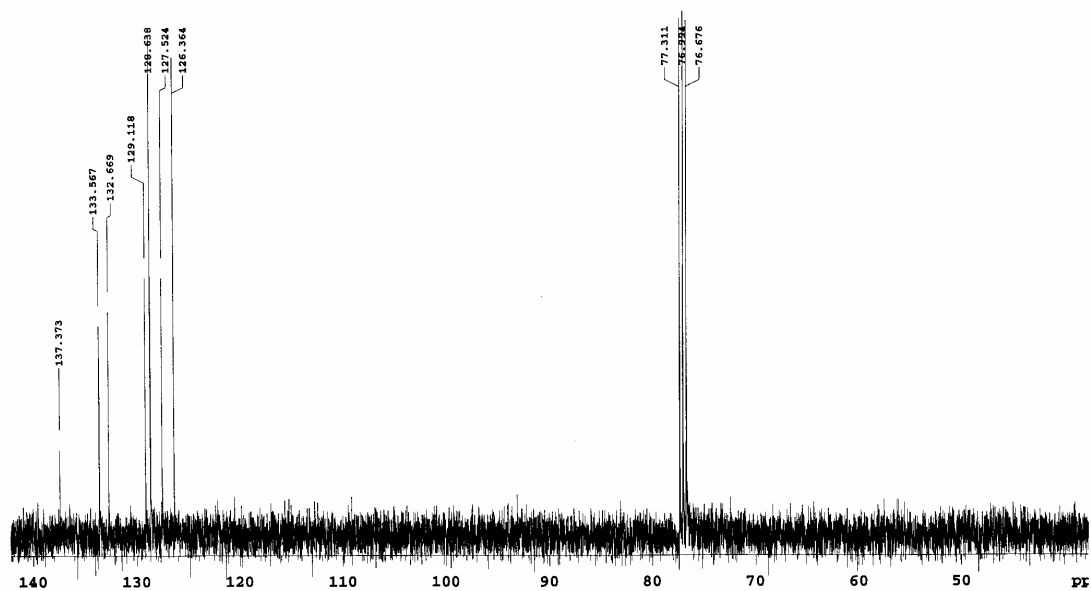
VD-484
NMN-548-09
File: xp
Sample id: tmpstudy
Pulse Sequence: s2pul



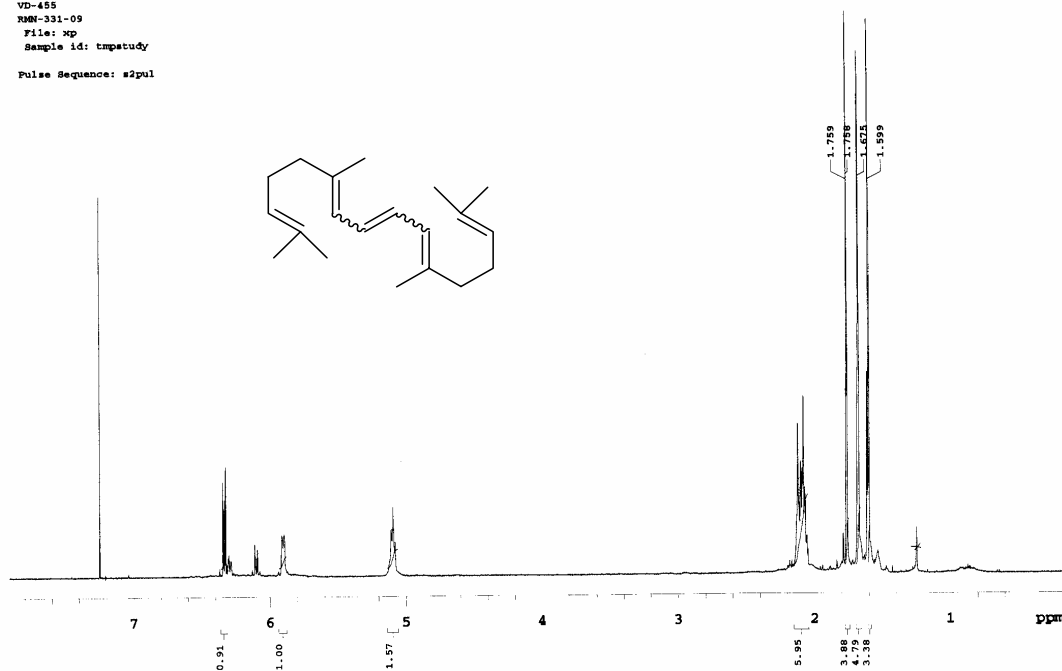
File: exp
Sample id: tmpstudy
Pulse Sequence: s2pul



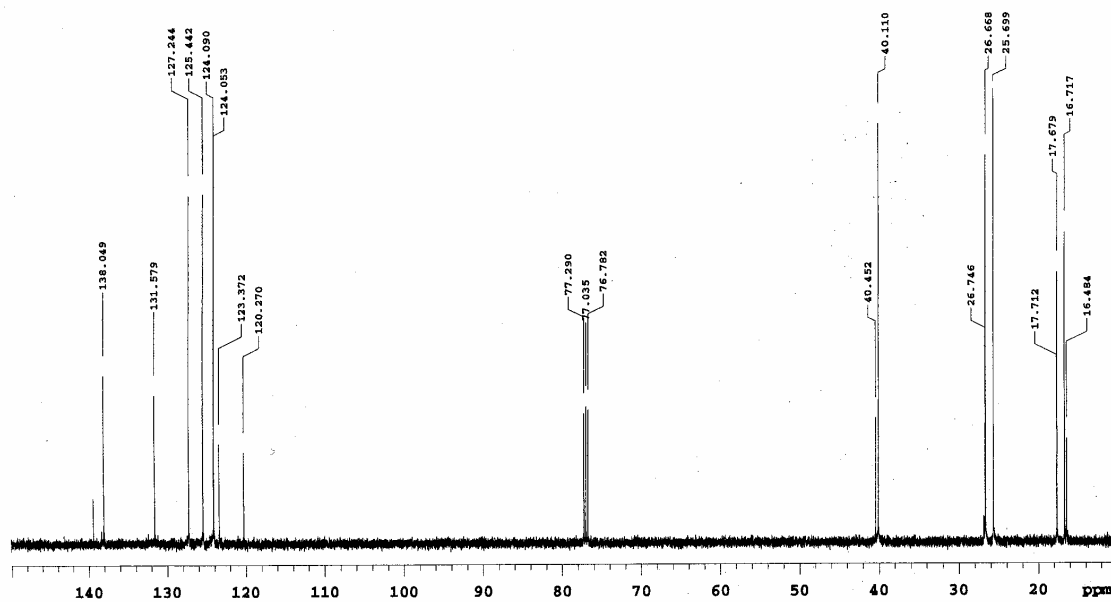
File: exp
Sample id: tmpstudy
Pulse Sequence: s2pul

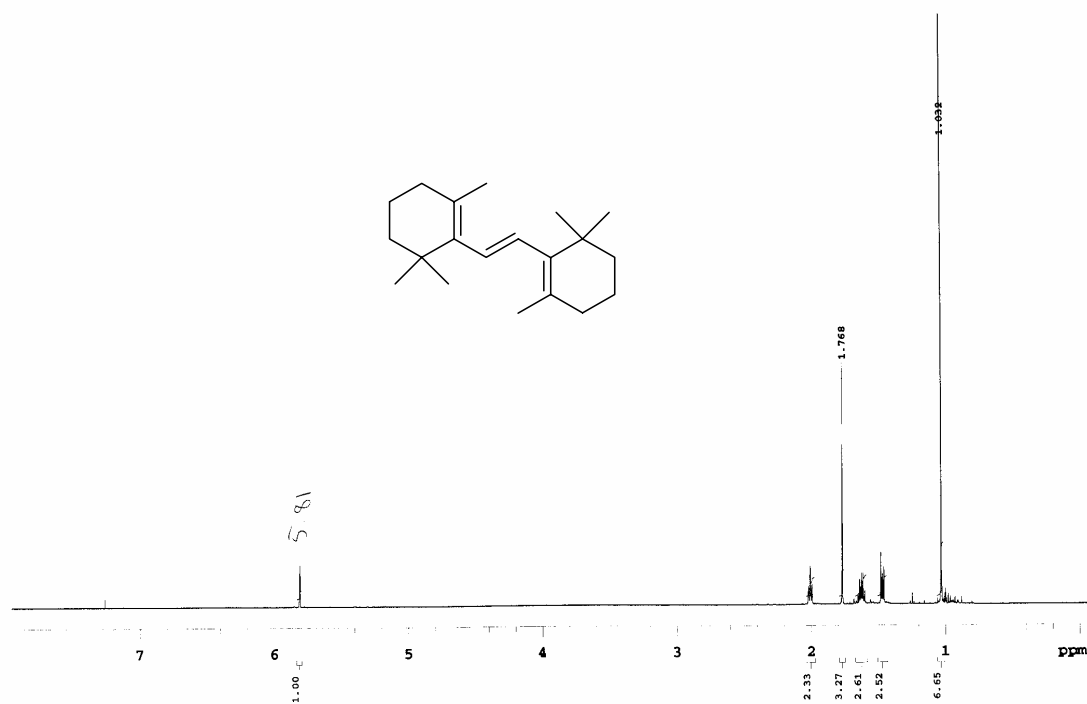


VD-455
 RMN-331-09
 File: xp
 Sample id: tmpstudy
 Pulse Sequence: s2pul



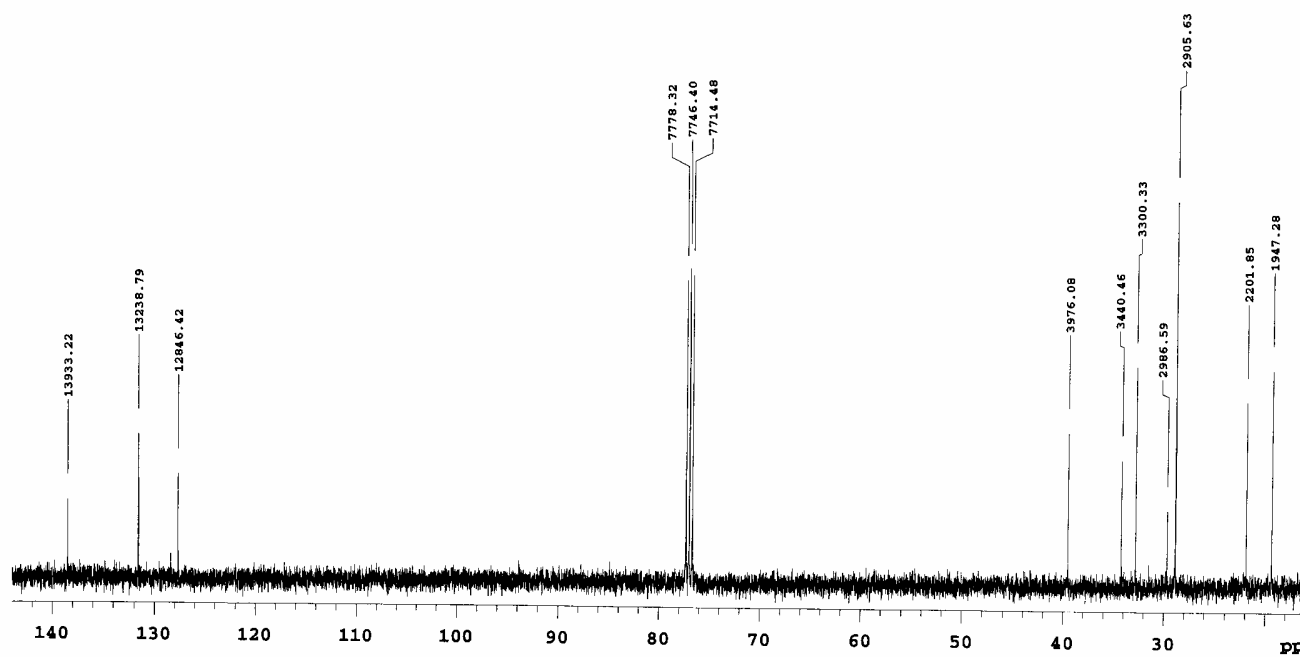
VD-455
 RMN-331-09
 File: xp
 Sample id: tmpstudy
 Pulse Sequence: s2pul



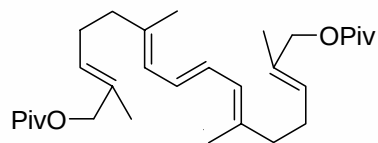


sample id: tmpstudy

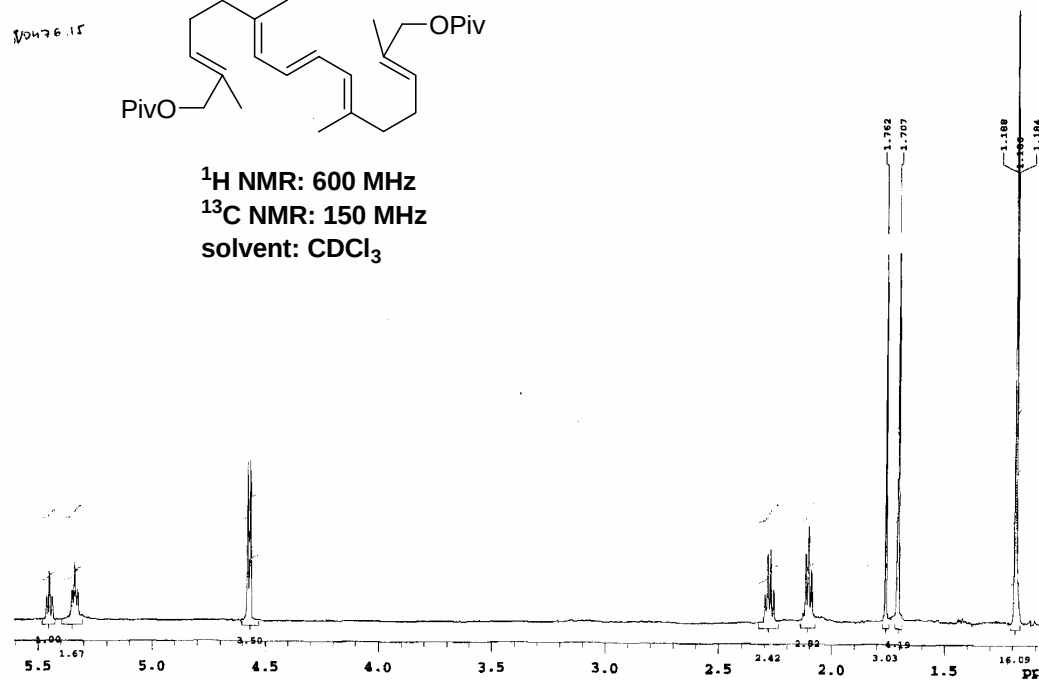
Pulse Sequence: s2pul



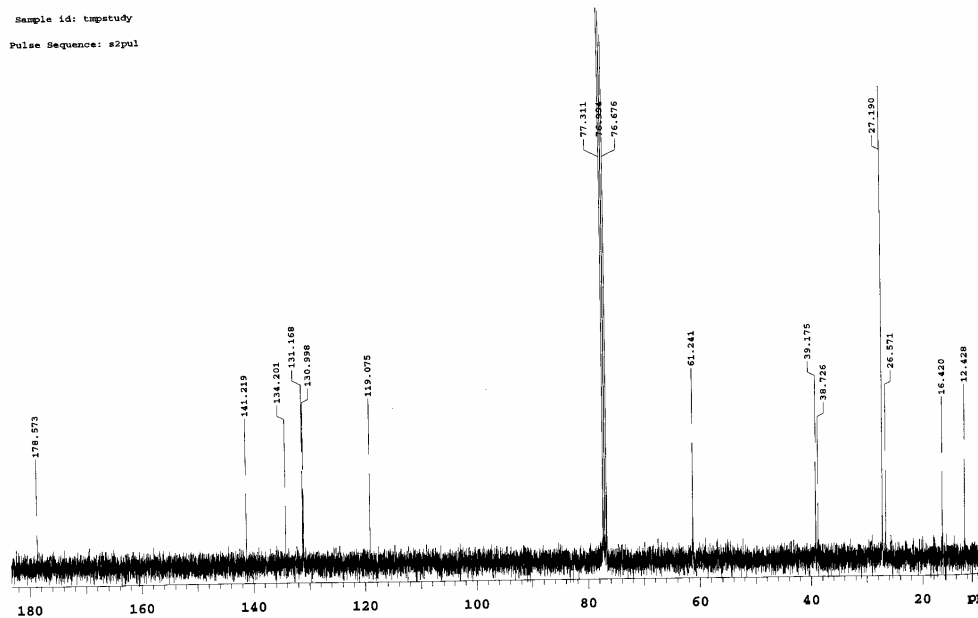
2026.15



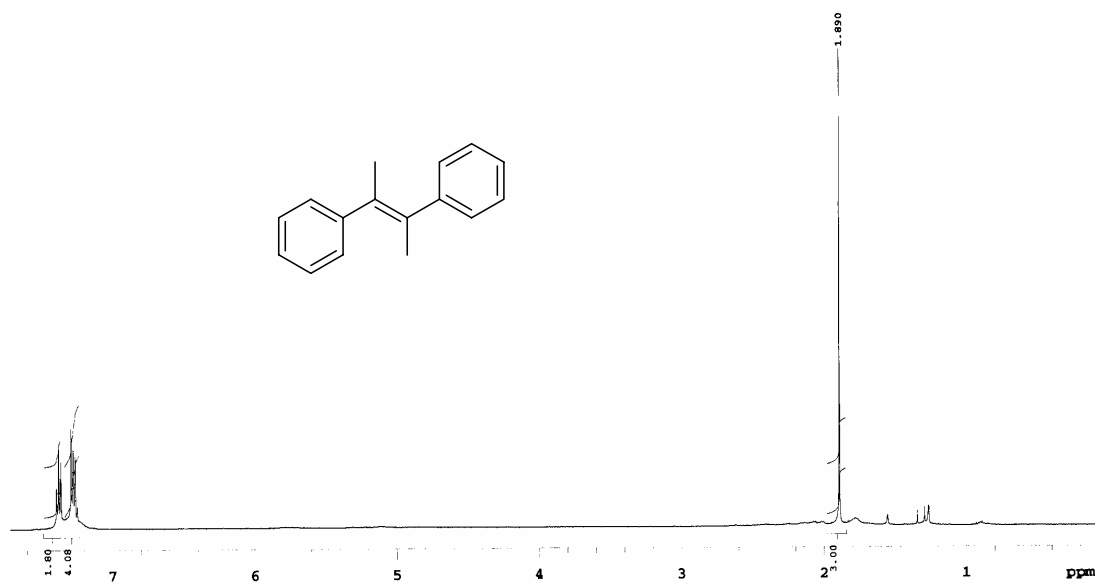
^1H NMR: 600 MHz
 ^{13}C NMR: 150 MHz
 solvent: CDCl_3



Sample id: tmpstudy
 Pulse Sequence: s2pul

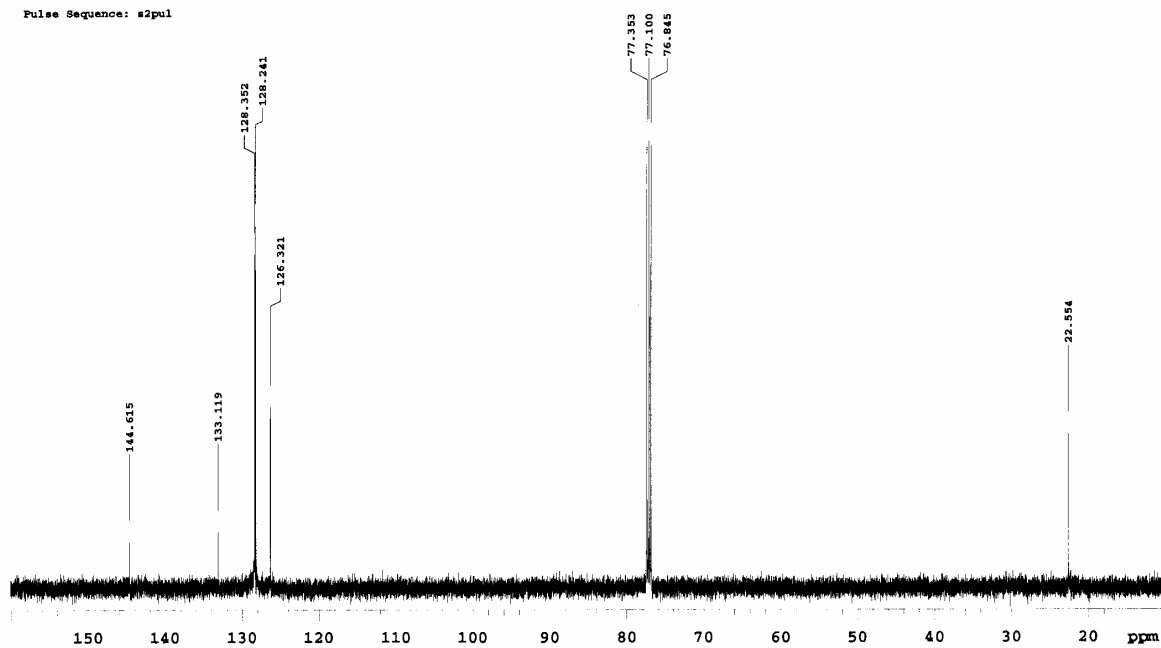


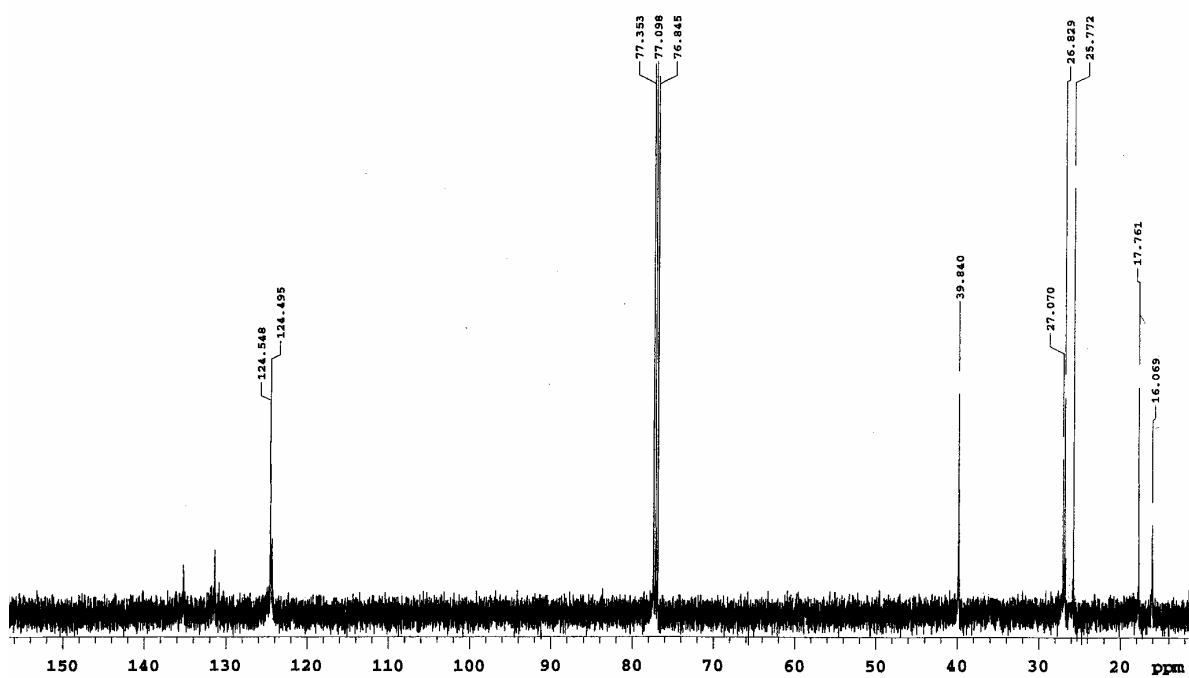
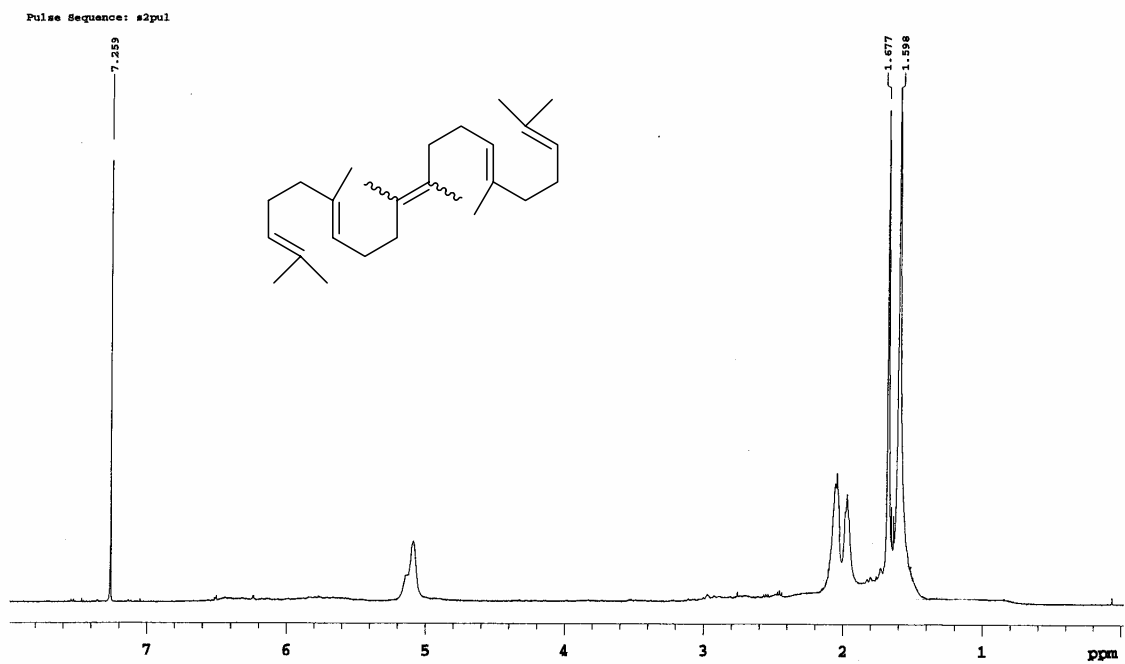
Pulse Sequence: s2pul

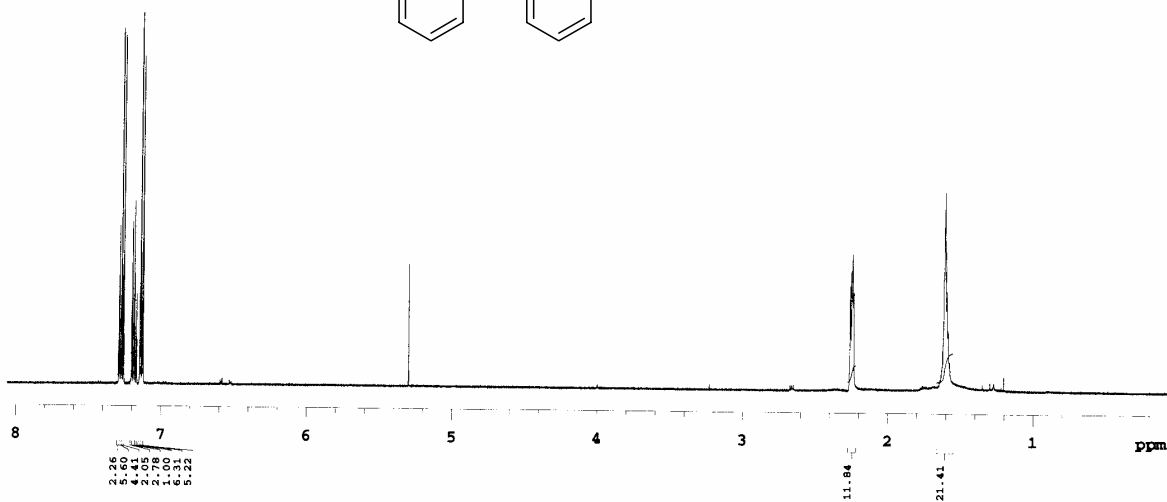


Sample id: tmpstudy

Pulse Sequence: s2pul



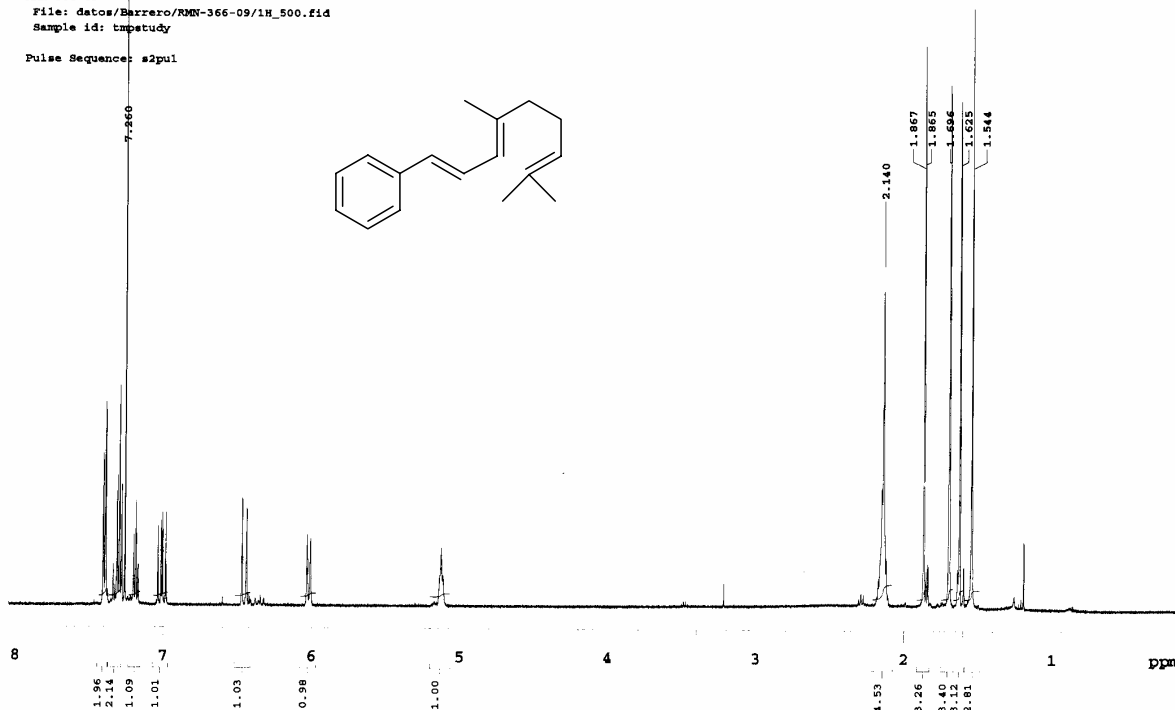




File: xp
Sample id: tmpstudy
Pulse Sequence: s2pul

The image displays a ¹³C NMR spectrum with the following peak labels (ppm): 143.127, 139.158, 134.833, 129.783, 127.857, 126.004, 77.262, 77.008, 76.753, 32.400, 28.668, and 26.802. The x-axis is labeled 'ppm' and ranges from 150 to 30.

VD-464 500MHz
 RMN-366-09
 File: datos/Barrero/RMN-366-09/1H_500.fid
 Sample id: tmpstudy
 Pulse Sequence: s2pul



VD-464
 RMN-366-09
 File: datos/Barrero/RMN-366-09/carbano.fid
 Sample id: tmpstudy
 Sample: Indanona
 Pulse Sequence: s2pul

