Palladium-Catalyzed [1,3]-O-to-C Rearrangement of Pyrans Towards Functionalized Cyclohexanones

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Supplementary Data

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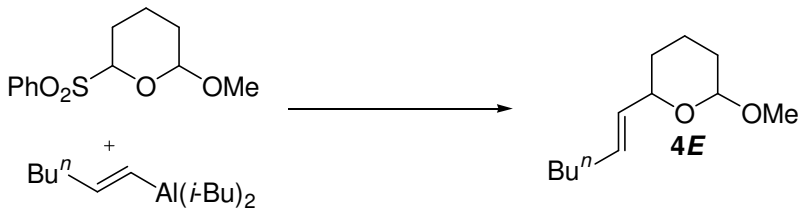
1. General Information

All reactions were conducted in oven or flame-dried glassware under an inert atmosphere of dry nitrogen. Flash chromatography was performed on silica gel (BDH Silica Gel 60 43-60, or Fluorochem Davisil silica gel 43-60). The solvent system used was a gradient of petroleum ether/ ethyl acetate (90-10), increasing in polarity to ethyl acetate. Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with silica (0.2 mm, Merck DC-alufolien Kieselgel 60 F254), which were developed using standard visualizing agents: Ultraviolet light or potassium permanganate. $^{1}H/^{13}C$ NMR spectra were recorded on Bruker AC-250 or AV1-250 instruments or AMX-400 or AV1-400 instruments. ^{1}H: Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$:δ7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet), integration, coupling constants (*J*) in Hz, and assignment. ^{13}C NMR spectra were with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0 ppm). Infrared (FTIR) spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, υ_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m) and weak (w). Samples were recorded as thin films using sodium chloride plates, as a DCM solution or as a KBr disc. Low resolution mass spectra were recorded on Micromass Autospec, operating in E.I., C.I. or FAB mode; or a Perkin-Elmer Turbomass Bench top GC-MS operating in either E.I. or C.I mode. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a MicroMass LCT operating in Electrospray mode (TOF ES+) or a MicroMass Prospec operating in either FAB (FAB+), EI (EI+) or CI (CI+) mode. Melting points were performed on recrystallised solids and recorded on a Gallenkamp melting point apparatus and are uncorrected. All solvents and reagents were purified using standard, laboratory techniques according to methods published in "Purification of Laboratory Chemicals" by Perrin, Armarego, and Perrin (Pergamon Press, 1966). ^{13}C spectra of phosphonium salts **7-9** were complex and are not included in the experimental section but are instead included in the NMR spectra appendix of the Supporting Information.

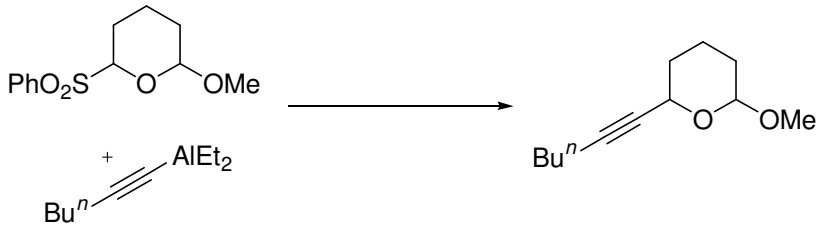
2. Experimental Procedures

Preparation of (*E*)-2-(hex-1-enyl)-6-methoxytetrahydro-2H-pyran (4*E*)



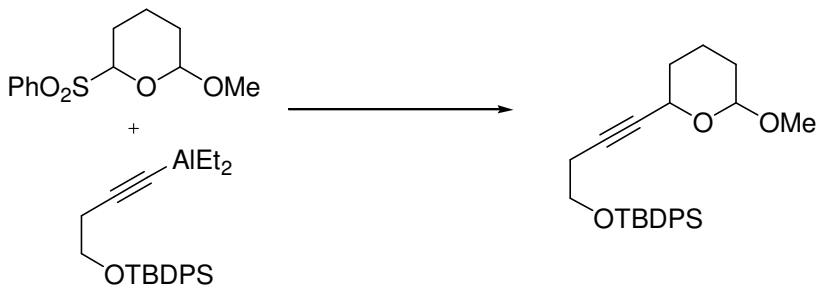
To a solution of DIBAL (1 M in toluene, 52.5 mL, 52.5 mmol) in anhydrous toluene (50 mL) was added dropwise at 0 °C neat 1-hexyne (5.7 mL, 50.6 mmol). The reaction was stirred at 40 °C for 2 h. After this time, the reaction was cooled to -78 °C and a solution of 2-(benzenesulphonyl)tetrahydro-6-methoxy-2*H*-pyran[1] (10 g, 39.0 mmol) in anhydrous DCM (15 mL) was added *via* cannula at -78 °C to the vinylaluminum reagent. The reaction was stirred at -78 °C for 2 h, then the cold bath was removed and the reaction stirred for a further 4 h. After this time, the reaction was quenched with H_2O (50 mL), and the mixture filtered through a pad of celite. The filtrate was extracted with EtOAc, and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel (92 : 2 / petroleum ether : EtOAc) to give **4*E*** as a yellow oil (6.3 g, 81%) containing an inseparable 4 : 1 / *trans* : *cis* mixture of diastereoisomers; (***trans***, ***cis***) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (1H, dtd, *J* = 15.0, 6.5, 1.0 Hz, ***trans***, ***cis*** CH_2-alkene-*H*), 5.54-5.4 (0.8H, ddt, 1H, *J* = 15.0, 7.0, 1.5 Hz, ***trans*** CH-alkene-*H* and 0.2H, m, ***cis*** CH-alkene-*H*), 4.73 (0.8H, br, ***trans*** OC*H*OMe), 4.34 (0.2H, dd, *J* = 9.0, 2.0 Hz, ***cis*** OC*H*OMe), 4.17-4.08 (0.8H, m, ***trans*** pyran-OC*H*), 3.88-3.82 (0.2H, m, ***cis*** pyran-OC*H*), 3.49 (0.6H, s, ***cis*** OCH_3), 3.37 (2.4H, s, ***trans*** OCH_3), 2.08-1.97 (2H, m, ***trans***, ***cis*** CH_2), 1.91-1.24 (10H, m, ***trans***, ***cis*** CH_2), 0.88 (3H, t, *J* = 7.0 Hz, ***trans***, ***cis*** CH_2CH_3); (***trans***) ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 132.5, 130.9, 98.6, 69.4, 54.5, 32.0, 31.4, 31.2, 29.4, 22.3, 18.0, 14.0; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 2933 (s), 2873 (s), 1458 (m), 1439 (m), 1195 (m), 1125 (s), 1062 (s), 1022 (s), 968 (m), 948 (s); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{12}H_{22}O_2$ 198.1620, found 198.1624.

General procedure for the alkynylation of 2-(benzenesulphonyl)tetrahydro-6-methoxy-2*H*-pyran. Preparation of 2-(hex-1-ynyl)-6-methoxytetrahydro-2*H*-pyran[2]



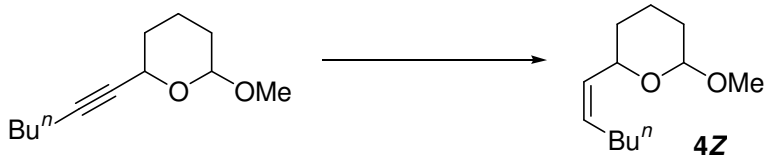
To solution of 1-hexyne (1.05 mL, 9.4 mmol) in anhydrous toluene (47 mL) at -78 ^{o}C was added *n*-BuLi (2.2 M, 4.25 mL, 9.4 mmol) dropwise. After 10 min the reaction was warmed to 0 ^{o}C and stirred for a further 15 min. Et_2AlCl (1 M in hexane, 9.4 mL, 9.4 mmol) was added to the reaction mixture. After 30 min at 0 ^{o}C the reaction was cooled to -78 ^{o}C and a solution of 2-(benzenesulphonyl)tetrahydro-6-methoxy-2*H*-pyran (2.0 g, 7.8 mmol) in anhydrous DCM (3.0 mL) was added dropwise *via* cannula. The reaction was slowly warmed to room temperature, stirred for 16 h and quenched at room temperature with H_2O (50 mL). The mixture was filtered through a pad of celite and the filtrate was extracted three times with EtOAc. The combined organic layers were washed with saturated aqueous K_2CO_3 solution, brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel (95 : 5 / petroleum ether : EtOAc) to give the desired product as an oil (1.33 g, 72%) containing an inseparable 3.5 : 1 / *trans* : *cis* mixture of diastereoisomers. The compound showed satisfactory NMR spectroscopic data.[2]

Preparation of *tert*-butyl(4-(6-methoxytetrahydro-2*H*-pyran-2-yl)but-3-ynyloxy)diphenylsilane



Following the general procedure, the alkynylaluminium reagent prepared from (but-3-ynyloxy)(*tert*-butyl)diphenylsilane (5.7 g, 18.5 mmol), *n*-BuLi (2.2 M, 8.4 mL, 18.5 mmol) and Et_2AlCl (1 M in hexane, 18.5 mL, 18.5 mmol) in toluene (90 mL), was treated with a solution of 2-(benzenesulphonyl)tetrahydro-6-methoxy-2*H*-pyran (3.94 g, 15.4 mmol) in DCM (6 mL). The crude residue was purified by flash chromatography on silica gel (90:10 / petroleum ether : EtOAc) to provide the desired product as an oil (5.0 g, 76%) containing an inseparable 5.8 : 1 / *trans* : *cis* mixture of diastereoisomers; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.65 (4H, m, ***trans***, ***cis*** Ar-*H*), 7.48-7.33 (6H, m, ***trans***, ***cis*** Ar-*H*), 4.75 (0.85H, br, ***trans*** OC*H*OMe), 4.55-4.46 (0.85H, m, ***trans*** alkyne-C*H*O), 4.33-4.27 (0.15H, m, ***cis*** OC*H*OMe), 4.19-4.12 (0.15H, m, ***cis*** alkyne-C*H*O), 3.78 (2H, t, *J* = 7.0 Hz, ***trans***, ***cis*** CH_2OSi), 3.48 (0.45H, s, ***cis*** OCH_3), 3.39 (2.55H, s, ***trans*** OCH_3), 2.52 (2H, dt, *J* = 7.0, 2.0 Hz, ***trans***, ***cis*** alkyne-CH_2), 1.90-1.41 (6H, m, ***trans***, ***cis*** CH_2), 1.06 (9H, s, ***trans***, ***cis*** $C(CH_3)_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) ***trans isomer***: δ 135.7, 133.8, 129.8, 127.8, 98.8, 81.9, 80.8, 62.5, 60.5, 55.1, 32.2, 29.5, 26.9, 23.0, 19.3, 18.0; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3043 (w), 3071 (m), 2932 (s), 2858 (s), 1472 (m), 1428 (m), 1197 (m), 1111 (s), 1060 (m), 1022 (s), 949 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{26}H_{34}O_3NaSi$ 445.2175, found 445.2181.

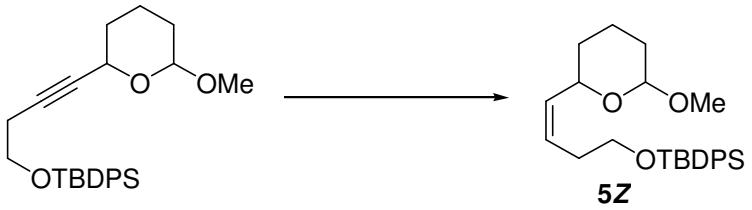
Preparation of (*Z*)-2-(hex-1-enyl)-6-methoxytetrahydro-2*H*-pyran (4*Z*)



To a solution of 2-(hex-1-ynyl)-6-methoxytetrahydro-2*H*-pyran (400 mg, 2.02 mmol) in MeOH (20 mL) was added palladium on carbon (80 mg, 20 wt%) and quinoline (280 μL, 2.36 mmol). The reaction mixture was stirred at RT under an atmosphere of hydrogen for 12 h. The reaction was filtered through celite and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel (90 : 10 / PE : EtOAc) to give pyranyl ether **4*Z*** as an oil (395 mg, 98%) containing an inseparable 3.5 : 1 / *trans* : *cis* mixture of diastereoisomers; ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.56-5.29 (2H, m, ***trans***, ***cis*** alkene-*H*), 4.72 (0.78H, br, ***trans*** OC*H*OMe), 4.53 (0.78H, app ddd, *J* = 11.0, 8.0, 2.5 Hz, ***trans*** pyran-C*H*O), 4.34 (0.22H, dd, *J* =

9.5, 2.0 Hz, ***cis*** OC*H*OMe), 4.24-4.14 (0.22H, m, ***cis*** pyran-C*H*O), 3.47 (0.66H, s, ***cis*** OCH_3), 3.38 (2.34H, s, ***trans*** OCH_3), 2.25-1.99 (2H, m, ***trans***, ***cis*** CH_2), 1.93-1.20 (10H, m, ***trans***, ***cis*** CH_2), 0.89 (3H, t, J = 7.0 Hz, CH_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) ***trans isomer***: δ 132.7, 130.8, 98.7, 64.9, 54.8, 32.0, 31.6, 29.5, 27.8, 22.4, 18.0, 14.1; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 2934 (s), 2872 (s), 1458 (m), 1440 (m), 1371 (m), 1194 (m), 1125 (s), 1062 (s), 1023 (s), 952 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{12}H_{22}O_2$ 198.1620, found 198.1621.

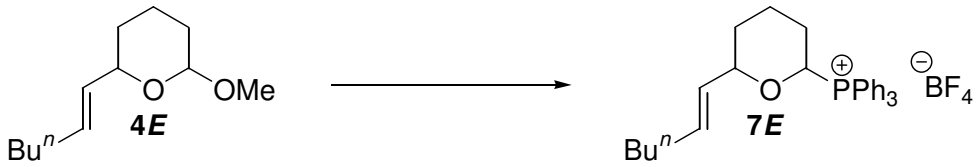
Preparation of (*Z*)-*tert*-butyl(4-(6-methoxytetrahydro-2*H*-pyran-2-yl)but-3 enyloxy)diphenylsilane (5*Z*)



To a solution of *tert*-butyl(4-(6-methoxytetrahydro-2*H*-pyran-2-yl)but-3-ynyloxy)diphenylsilane (2.0 g, 4.73 mmol) in hexane (95 mL) was added palladium on carbon (200 mg, 20 wt%) and quinoline (280 μL, 2.36 mmol). The reaction mixture was stirred at RT under an atmosphere of hydrogen for 24 h. The reaction was filtered through celite and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel (90 : 10 / petroleum ether : EtOAc) to give pyranyl ether **5*Z*** as an oil (1.7 g, 85%) containing an inseparable 9 : 1 / *trans* : *cis* mixture of diastereoisomers: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.64 (4H, m, ***trans***, ***cis*** Ar-*H*), 7.46-7.34 (6H, m, ***trans***, ***cis*** Ar-*H*), 5.75-5.40 (2H, m, ***trans***, ***cis***, alkene-*H*), 4.72 (0.9H, br, ***trans*** OC*H*OMe), 4.54-4.47 (0.9H, m, ***trans*** pyran-OC*H*), 4.21-4.26 (0.1H, m, ***cis*** OC*H*OMe), 4.17-4.09 (0.1H, m, ***cis*** pyran-OC*H*), 3.74-3.62 (2H, m, ***trans***, ***cis*** CH_2OSi), 3.36 (0.3H, s, ***cis*** OCH_3), 3.35 (2.70H, s, ***trans*** OCH_3), 2.47-2.28 (2H, m, ***trans***, ***cis*** CH_2), 1.92-1.78 (1H, m, ***trans***, ***cis*** CH_2), 1.72-1.24 (5H, m, ***trans***, ***cis*** CH_2), 1.05 (9H, s, ***trans***, ***cis*** C(CH_3)$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) ***trans isomer***: δ 135.7, 134.0, 132.6, 129.7, 128.5, 127.8, 98.7, 65.0, 63.7, 54.8, 31.5 (2C), 29.4, 27.0, 19.3, 17.9; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3071 (w), 3050 (w), 3016

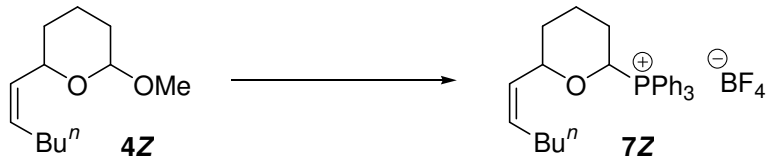
(w), 2934 (s), 2858 (s), 1472 (w), 1428 (m), 1194 (w), 1112 (s), 1069 (m), 1022 (s), 949 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{26}H_{36}O_3NaSi$ 447.2331, found 447.2349.

Representative Procedure for Wittig salts preparation. Preparation of (*E*)-(6-(hex-1-enyl)tetrahydro-2*H*-pyran-2-yl)triphenylphosphonium tetrafluoroborate (7*E*)



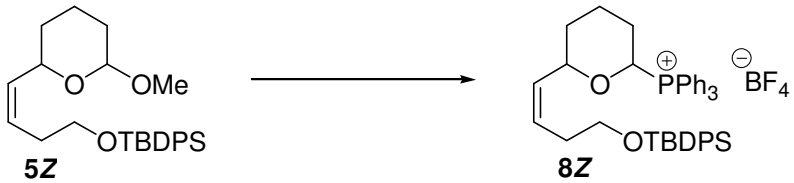
A round bottom flask fitted with a water-jacketed reflux condenser was charged with activated 4 Å molecular sieves (20 g) and a solution of $HPPh_3BF_4$ (22.2 g, 63.4 mmol) in MeCN (80 mL). A solution of pyranyl ether **4*E*** (6.3 g, 31.8 mmol) in MeCN (80 mL) was added and the reaction was heated at reflux for 20 h. After this time, the reaction was cooled to room temperature, diluted with DCM and filtered through celite. Concentration of the filtrate *in vacuo* afforded a crude residue, which was dissolved in DCM, re-filtered through celite and concentrated. To the filtrate was then added 2 mL of DCM followed by a 1 : 1 / Et_2O : petroleum ether mixture (100 mL). The mixture was subjected to vigorous stirring until the cloudy suspension became clear (10 - 15 min). The suspension was decanted and the solvent was carefully removed to leave a gummy residue. Trituration from DCM and 1 : 1 / Et_2O : PE mixture was repeated three times. After removal of the solvent, the Wittig salt **7*E*** was obtained (15.97 g, 97%) as a white solid containing an inseparable 5 : 1 mixture of diastereoisomers; M.p. = 80-81 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.88-7.56 (15H, m, **maj, min** Ar-*H*), 5.99-5.45 (2H, m, **maj, min** C*H*P, CH_2-alkene-*H*), 5.39-5.20 (1H, m, **maj, min** CH-alkene-*H*), 4.57-4.46 (0.2H, m, **min** pyran-OC*H*), 4.38-4.15 (0.8H, m, **maj** pyran-OC*H*), 2.24-1.49 (7H, m, **maj, min** CH_2), 1.44-1.09 (5H, m, **maj, min** CH_2), 0.87 (3H, t, J = 7.0 Hz, **maj, min** CH_3); ^{31}P NMR (250 MHz, $CDCl_3$): δ 19.9; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3646 (w), 3554 (w), 3065 (w), 2955 (s), 2930 (s), 2871 (m), 1588 (w), 1485 (w), 1440 (s), 1271 (w), 1193 (w), 1058 (s); HRMS (TOF MS ES) *m/z* $[M-BF_4]^+$ calcd for $C_{29}H_{34}OP$ 429.2347, found 429.2331.

Preparation of (*Z*)-(6-(hex-1-enyl)tetrahydro-2*H*-pyran-2-yl)triphenylphosphonium tetrafluoroborate (7*Z*)



Following the representative procedure, the Wittig salt **7Z** was prepared from pyranyl ether **4Z** (360 mg, 1.81 mmol), $HPPh_3BF_4$ (1.27 g, 3.63 mmol), 4 Å molecular sieves (1.2 g), and MeCN (19 mL). The desired product **7Z** was obtained (822 mg, 85%) as a white solid; M.p. = 148-150 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.86-7.58 (15H, m, Ar-*H*), 5.76 (1H, ddd, *J* = 12.0, 4.0, 2.0 Hz, C*H*P), 5.46 (1H, app dtd, *J* = 11.0, 7.5, 1.0 Hz, CH_2-alkene-*H*), 5.22 (1H, app ddt, *J* = 11.0, 8.0, 1.5 Hz, CH-alkene-*H*), 4.66 (1H, t, *J* = 9.0 Hz, pyran-OC*H*), 2.19-1.84 (5H, m, CH_2), 1.77-1.55 (2H, m, CH_2), 1.49-1.16 (5H, m, CH_2), 0.87 (3H, t, *J* = 7.0 Hz, CH_3); ^{31}P NMR (250 MHz, $CDCl_3$): δ 20.0; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3646 (w), 3551 (w), 3068 (w), 2955 (m), 2928 (m), 2870 (m), 1588 (w), 1486 (w), 1440 (s), 1193 (w), 1058 (s), 902 (w); HRMS (TOF MS ES) *m/z* $[M-BF_4]^+$ calcd for $C_{29}H_{34}OP$ 429.2347, found 429.2356.

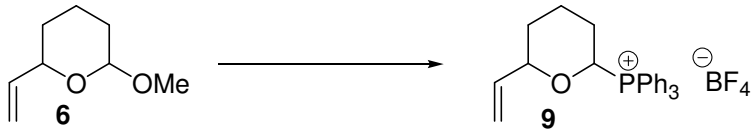
Preparation of (*Z*)-(6-(4-(*tert*-butyldiphenylsilyloxy)but-1-enyl)tetrahydro-2*H*-pyran-2-yl)triphenylphosphonium tetrafluoroborate (8*Z*)



Following the representative procedure, the Wittig salt **8Z** was prepared from pyranyl ether **5Z** (1.7 g, 4.01 mmol), $HPPh_3BF_4$ (2.8 g, 8.02 mmol), 4 Å molecular sieves (2.6 g), and MeCN (40 mL). The desired product **8Z** was obtained (2.83 g, 94%) as a pale yellow solid containing an inseparable 4 : 1 mixture of diastereoisomers; M.p. = 103-104 °C, ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.84-7.56 (19H, m, **maj, min** Ar-*H*, Si*Ph$_2$t*-Bu), 5.46-5.31 (6H, m, **maj, min** Si*Ph$_2$t*-Bu), 5.95-5.22 (3H, m, **maj, min** C*H*P, alkene-*H*), 4.92-4.75 (0.2H, m, **min** pyran-OC*H*), 4.61-

4.47 (0.8H, m, **maj-281** pyran-OC*H*), 3.69-3.42 (2H, m, **maj, min** CH_2OSi), 2.45-1.11 (8H, m, **maj, min** CH_2), 1.03 (9H, br, **maj, min** CH_3); ^{31}P NMR (250 MHz, $CDCl_3$): δ 20.2; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3657 (w), 3541 (w), 3070 (m), 2931 (m), 2868 (m), 1588 (w), 1485 (w), 1472 (w), 1440 (s), 1193 (w), 1111 (s), 1057 (s), 912 (m); HRMS (TOF MS ES) *m/z* [M-BF_4]$^+$ calcd for $C_{43}H_{48}O_2SiP$ 655.3161, found 655.3154.

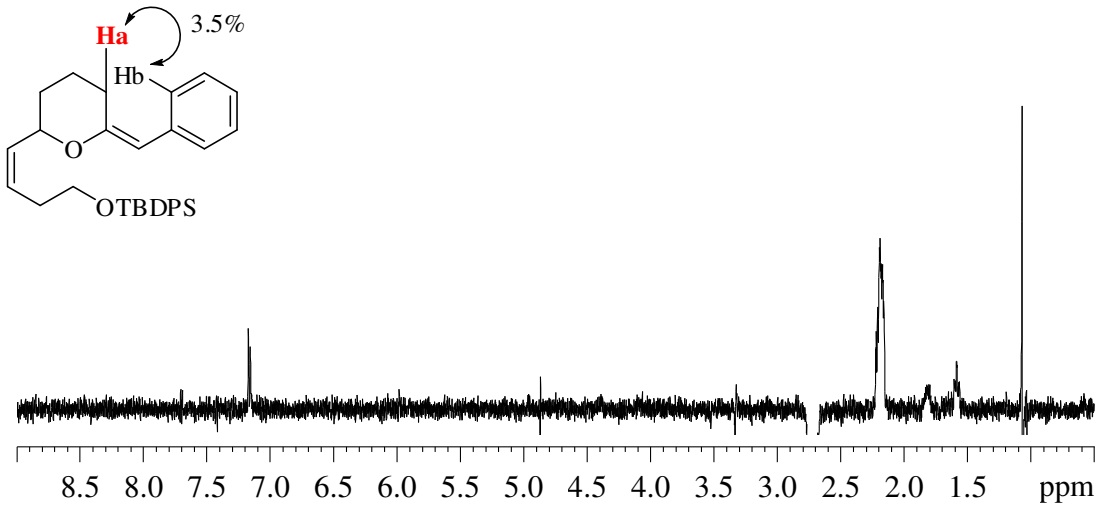
Preparation of triphenyl(6-vinyltetrahydro-2*H*-pyran-2-yl)phosphonium tetrafluoroborate (9)

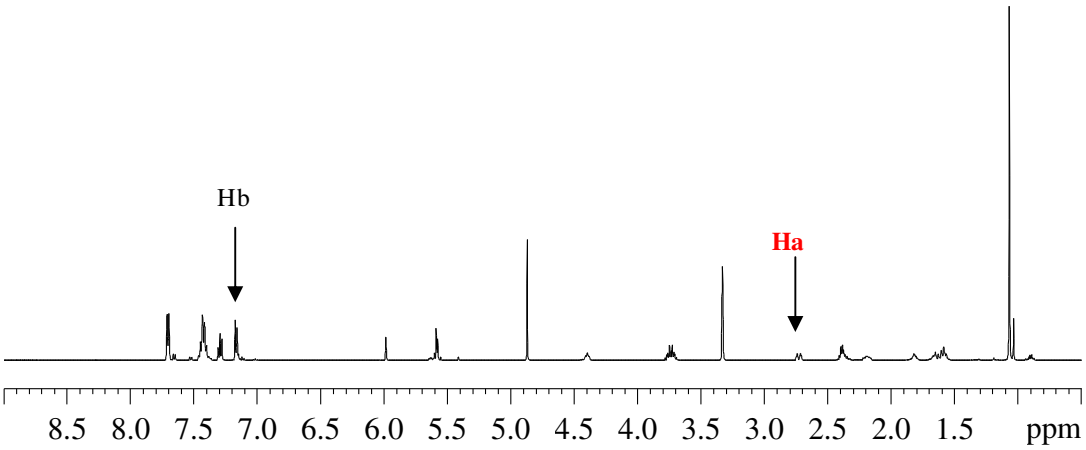


Following the representative procedure, the Wittig salt **9** was prepared from pyranyl ether **6**[3] (1.0 g, 7.0 mmol), $HPPh_3BF_4$ (4.9 g, 14.0 mmol), 4 Å molecular sieves (4.5 g), and MeCN (70 mL). The desired product **9** was obtained as a pale yellow solid (3.0 g, 93%); M.p. = 84-85 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.87-7.59 (15H, m, Ar-*H*), 5.91-5.57 (2H, m, C*H*P, alkene-*H*), 5.16-4.93 (2H, m, alkene-H_2), 4.39 (1H, br, pyran-OC*H*), 2.19-1.52 (5H, m, CH_2), 1.45-1.21 (1H, m CH_2); ^{31}P NMR (250 MHz, $CDCl_3$): δ 20.5; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3646 (w), 3556 (w), 3067 (m), 2947 (m), 2869 (m), 1588 (m), 1485 (m), 1440 (s), 1194 (m), 1057 (s), 912 (m); HRMS (TOF MS ES) *m/z* [M-BF_4]$^+$ calcd for $C_{25}H_{26}OP$ 373.1721, found 373.1709.

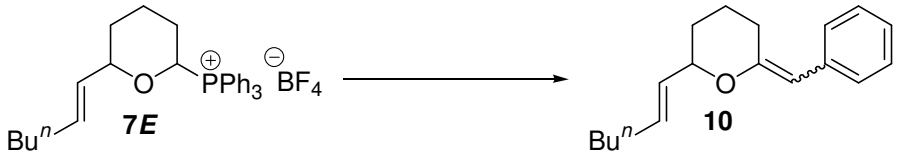
Stereochemical Assignment of Enol Ether Products 10-17

The chemical shift of the enol ether protons of compounds **10-17** were used as a basis to assign the *E*/*Z* stereochemistry, and is based on increment calculations performed on related enol ethers.[4] Specifically, the *E*-isomers are shifted 0.3-0.7 ppm to a lower field than the corresponding *Z*-isomers, and the general trends are followed for a large range of 6-membered ring based analogs, including work by Lieberknecht and Bravo (assignments based on NMR and X-ray),[5] Taylor (NMR)[6] and us (nOe)[7]. Moreover, we confirmed this assignment in the case of compound **15** by nOe spectroscopic analysis.





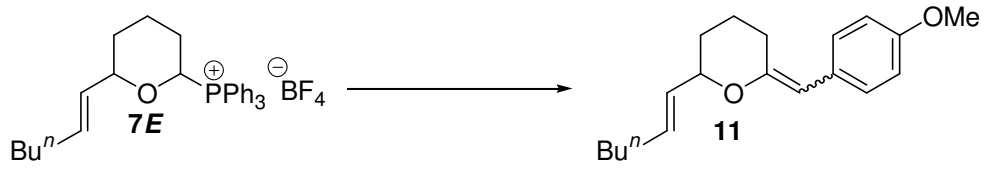
Representative Procedure for the Wittig reaction with Aromatic Aldehydes. Preparation of (*E*/*Z*)-2-Benzylidene-6-((*E*)-pent-1-enyl)tetrahydro-2*H*-pyran (10)



To a solution of Wittig salt **7*E*** (380 mg, 0.736 mmol) in anhydrous THF (8 mL) was added KHMDS dropwise at -78 °C (0.68 M, 1.14 mL, 0.773 mmol). The colour changed from colourless to deep red. The reaction was stirred for 5-10 min and freshly distilled benzaldehyde (93 µL, 0.883 mmol) was added to the reaction mixture. The colour changed to deep red to yellow. The reaction was stirred at -78 °C for 45 min, then the cold bath was removed and the reaction stirred for a further 1.5 h allowing the temperature to reach RT. The reaction was then quenched at 0 °C with H_2O (8 mL) and the aqueous layer was extracted with Et_2O (50 mL). The organic layer was washed three times with 20 mL of a mixture 3 : 3 : 1 / brine : H_2O : MeOH and dried over Na_2SO_4. After filtration through cotton wool, volatiles were removed *in vacuo* and the residue was dried under high *vacuum* for 30 min. The crude mixture was triturated with 1 - 2 mL of petroleum ether. The supernatant was carefully separated from triphenylphosphine oxide and placed in another flask. The previous operation was repeated five times, then the volume of petroleum ether was reduced *in vacuo* to around 1 mL and purified by chromatography on florisil (25 g, 2 mL fractions; 99 : 1 / petroleum ether : EtOAc) to give enol ether **10** as colourless oil (132 mg, 70%) containing an inseparable 5 : 1 / *E* : *Z* mixture of diastereoisomers; ^{1}H NMR (250 MHz, MeOD): δ 7.32-7.01 (5H, m, ***E***, ***Z*** Ar-*H*), 6.02 (0.85H, br, ***E*** O-alkene-*H*), 5.85-5.68 (1H, m, ***E***, ***Z*** CH_2-alkene-*H*), 5.65-5.46 (1H, m, alkene-*H*), 5.38 (0.15H, br, ***Z*** O-alkene-*H*), 4.31-4.21 (0.15H, m, ***Z***, pyran-OC*H*), 4.19-4.08 (0.85H, m, ***E*** pyran-OC*H*), 2.80-2.64 (1H, m, ***E***, ***Z*** CH_2), 2.37-1.99 (3H, m, ***E***, ***Z*** CH_2), 1.92-1.49 (4H, m, ***E***, ***Z*** CH_2), 1.47-1.25 (4H, m, ***E***, ***Z*** CH_2), 1.01-0.82 (3H, m, ***E***, ***Z*** CH_3); ^{13}C NMR ***E* isomer**: (100.6 MHz, MeOD): δ 156.7, 137.9, 133.6, 131.7, 129.8, 129.1, 126.7, 110.8, 81.3, 33.0, 32.5, 32.4, 26.0, 23.2, 23.1, 14.3; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3086 (w), 3063 (w), 3029 (m), 2828 (s), 2857 (s), 1714 (s), 1674

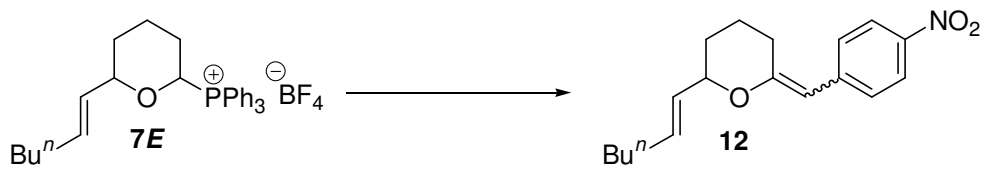
(m), 1496 (m), 1454 (m), 969 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{24}O_1$ 256.1827, found 256.1832.

Preparation of (*E*/*Z*)-2-((*E*)-hex-1-enyl)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran (11)



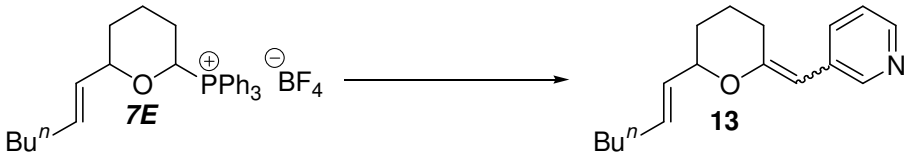
Following the representative procedure, a solution of Wittig salt **7*E*** (250 mg, 0.485 mmol) in THF (5 mL) at -78 °C was treated with KHMDS (0.68 M, 750 µL, 0.51 mmol) and freshly distilled *para*-methoxybenzaldehyde (70 µL, 0.58 mmol). The crude residue was purified by chromatography on florisil (98 : 2 / petroleum ether: EtOAc) to give enol ether **11** as yellow oil (115 mg, 80%) containing an inseparable 4 : 1 / *E* : *Z* mixture of diastereoisomers; ^{1}H NMR (400 MHz, MeOD): δ 7.57-7.49 (0.4H, m, ***Z*** Ar-*H*), 7.10-7.04 (1.6H, m, ***E*** Ar-*H*), 6.87-6.80 (1.6H, m, ***E*** Ar-*H*), 6.82-6.73 (0.4H, m, ***Z*** Ar-*H*), 5.99 (0.8H, br, ***E*** O-alkene-*H*), 5.83-572 (0.2H, m, ***Z*** CH_2-alkene-*H*), 5.77 (0.8H, dtd, *J* = 15.5, 8.0, 1.0 Hz, ***E*** CH_2-alkene-*H*), 5.66-5.58 (0.2H, m, ***Z*** CH-alkene-*H*), 5.56 (0.8H, ddt, *J* = 15.5, 6.5, 1.5 Hz, ***E*** CH-alkene-*H*), 5.36 (0.2H, br, ***Z*** O-alkene-*H*), 4.21-4.14 (0.2H, m, ***Z*** pyran-OC*H*), 4.11-4.04 (0.8H, m, ***E*** pyran-OC*H*), 3.79 (2.4H, s, ***E*** OCH_3), 3.78 (0.6H, s, ***Z*** OCH_3), 2.72-2.65 (1H, m, ***E*, *Z*** CH_2), 2.32-2.03 (3H, m, ***E*, *Z*** CH_2), 1.93-1.21 (8H, m, ***E*, *Z*** CH_2), 0.97-0.89 (3H, m, ***E*, *Z*** CH_3); ^{13}C NMR ***E* isomer**: (100.6 MHz, MeOD): δ 159.3, 155.6, 133.6, 131.8, 130.8, 130.2, 114.6, 110.5, 81.5, 55.6, 33.0, 32.5, 26.0, 23.8, 23.3, 23.2, 14.3; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3032 (m), 2997 (m), 2931 (s), 2860 (s), 1652 (s), 1608 (s), 1511 (m), 1464 (m), 1440 (m), 1292 (m), 1246 (m), 1034 (m), 969 (w); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{19}H_{26}O_2$ 286.1933, found 286.1946.

Preparation of (*E*/*Z*)-2-((*E*)-hex-1-enyl)-6-(4-nitrobenzylidene)tetrahydro-2*H*-pyran (12)



Following the representative procedure, a solution of Wittig salt **7*E*** (250 mg, 0.485 mmol) in THF (5 mL) at -78 °C was treated with KHMDS (0.68 M, 750 µL, 0.51 mmol) and a solution of freshly recrystallized *p*-nitrobenzaldehyde (88 mg, 0.58 mmol) in THF (1 mL). The crude residue was purified by chromatography on florisil (98 : 2 / petroleum ether : EtOAc) to give enol ether **12** as yellow oil (114 mg, 78%) containing an inseparable 1 : 1 / *E* : *Z* mixture of diastereoisomers; ^{1}H NMR (400 MHz, MeOD): δ 8.19-8.13 (1H, m, ***E***, ***Z*** Ar-*H*), 8.11-8.06 (1H, m, ***E***, ***Z*** Ar-*H*), 7.80-7.74 (1H, m, ***E***, ***Z*** Ar-*H*), 7.42-7.36 (1H, m, ***E***, ***Z***Ar-*H*), 6.08 (0.5H, br, ***E*** O-alkene-*H*), 5.90-5.74 (1H, m, ***E***, ***Z*** alkene-*H*), 5.66 (0.5H, ddt, *J* = 15.5, 6.5, 1.5 Hz, ***Z*** alkene-*H*), 5.60 (0.5H, ddt, *J* = 15.5, 6.5, 1.5 Hz, ***E*** CH-alkene-*H*), 5.52 (0.5H, br, ***Z*** O-alkene-*H*), 4.47-4.40 (0.5H, m, ***Z*** pyran-OC*H*), 4.29-4.20 (0.5H, m, ***E*** pyran-OC*H*), 2.82-2.74 (0.5H, m, ***E*** CH_2), 2.54-2.32 (1.5H, m, ***E***, ***Z*** CH_2), 2.17-2.07 (2H, m, ***E***, ***Z*** CH_2), 1.96-1.56 (4H, m, ***E***, ***Z*** CH_2), 1.57-1.23 (3H, m, ***E***, ***Z***CH_2), 1.03-0.91 (4H, m, ***E***, ***Z*** CH_2, CH_3); ^{13}C NMR ***E/Z* isomers**: (100.6 MHz, MeOD): δ 161.0, 160.6, 146.5, 145.8 (2C), 145.5, 134.6, 133.9, 131.4, 131.0, 130.1, 129.2, 124.5, 124.3, 108.7, 105.3, 81.0, 80.5, 33.0, 32.9, 32.5, 32.4, 31.8, 31.4, 30.7, 26.3, 23.2, 23.1, 22.2, 22.0, 14.3 (2C); FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 2955 (s), 2871 (s), 1651 (s), 1643 (s), 1591 (s), 1511 (s), 1337 (s), 1033 (m), 970 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{23}NO_3$ 301.1678, found 301.1686.

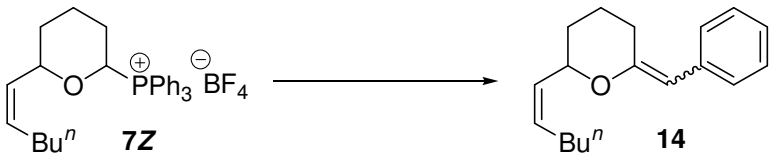
Preparation of (*E*/*Z*)-3-((6-((*E*)-hex-1-enyl)tetrahydro-2*H*-pyran-2-ylidene)methyl pyridine (13)



Following the representative procedure, a solution of Wittig salt **7*E*** (250 mg, 0.483 mmol) in THF (5 mL) at -78 °C was treated with KHMDS (0.68 M, 800 µL, 0.544 mmol) and freshly distilled 3-pyridinecarboxaldehyde (70 µL, 0.581 mmol). The

crude residue was purified by chromatography on florisil (3 : 1 / petroleum ether : EtOAc) to give enol ether **13** as a colourless oil (95 mg, 76%) containing an inseparable 9 : 1 / *E* : *Z* mixture of diastereoisomers. ^{1}H NMR (250 MHz, CD_3OD): δ 8.40-8.11 (2H, m, Ar-*H*), 7.64-7.53 (1H, m, Ar-*H*), 7.34-7.25 (1H, m, Ar-*H*), 5.92 (0.9H, s, ***E***-C*H*), 5.78-5.63 (1H, m, CH_2-alkene-*H*), 5.57-5.42 (1H, m, CH-alkene-*H*), 5.34 (0.1H, s, ***Z***-C*H*), 4.33-4.23 (0.1H, m, pyran-OC*H*), 4.18-4.06 (0.9H, m, pyran-OC*H*), 2.67-2.53 (1H, m, CH_2), 2.31-1.91 (3H, m, CH_2), 1.87-1.46 (4H, m, CH_2), 1.39-1.24 (4H, m, CH_2), 0.94-0.80 (3H, m, CH_3); ^{13}C NMR ***E* isomer**: (63 MHz, CD_3OD): δ 178.8, 159.2, 149.9, 146.7, 137.8, 133.8, 131.5, 124.9, 106.1, 81.2, 33.1, 32.5, 32.0, 25.9, 23.3, 22.6, 14.3; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3086 (w), 3063 (w), 3029 (m), 2828 (s), 2857 (s), 1714 (s), 1674 (m), 1496 (m), 1454 (m), 969 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{17}H_{24}NO$ 258.1858, found 258.1852.

Preparation of (*E*)-2-benzylidene-6-((*Z*)-hex-1-enyl)tetrahydro-2*H*-pyran (14)

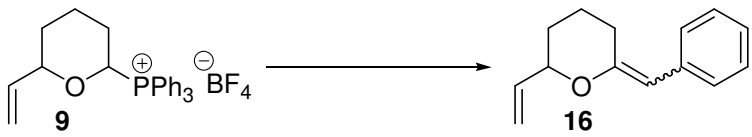


Following the representative procedure, a solution of Wittig salt **7Z** (300 mg, 0.58 mmol) in THF (6 mL) at -78 °C was treated with KHMDS (0.68 M, 900 µL 0.61 mmol), and freshly distilled benzaldehyde (73 µL, 0.69 mmol). The crude residue was purified by chromatography on florisil (99 : 1 / petroleum ether : EtOAc) to give enol ether **14** as colourless oil (114 mg, 76%) containing an inseparable 9 : 1 / *E* : *Z* mixture of diastereoisomers; ^{1}H NMR (400 MHz, MeOD): δ 7.37-7.02 (5H, m, ***E***, ***Z*** Ar-*H*), 6.01 (0.9H, br, ***E*** O-alkene-*H*), 5.61-5.42 (2H, m, ***E***, ***Z*** alkene-*H*), 5.40 (0.1H, br, ***Z*** O-alkene-*H*), 4.61-4.39 (1H, m, ***E***, ***Z*** pyran-OC*H*), 2.79-2.64 (1H, m, ***E***, ***Z*** CH_2), 2.35-1.97 (3H, m, ***E***, ***Z*** CH_2), 1.93-1.51 (4H, m, ***E***, ***Z*** CH_2), 1.47-1.20 (4H, m, ***E***, ***Z***), 1.02-0.76 (3H, m, ***E***, ***Z*** CH_3); ^{13}C NMR ***E* isomer**: (100.6 MHz, MeOD): δ 156.6, 137.9, 133.7, 131.1, 129.8, 129.2, 126.7, 110.9, 77.1, 32.9, 32.3, 28.5, 25.9, 23.3, 23.2, 14.3; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3080 (w), 3055 (w), 3021 (m), 2933 (s), 2871 (s), 1651 (s), 1456 (m), 1233 (m), 1136 (m), 1035 (m), 922 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{24}O$ 256.1827, found 256.1823.

((*Z*)-4-((*E*/*Z*)-6-benzylidenetetrahydro-2*H*-pyran-2-yl)but-3-enyloxy)(*tert*-butyl)diphenylsilane (15)

Following the representative procedure, a solution of Wittig salt **8Z** (500 mg, 0.67 mmol) in THF (7 mL) at -78 °C was treated with KHMDS (0.68 M, 1.03 mL, 0.70 mmol) and freshly distilled benzaldehyde (85 µL, 0.80 mmol). The crude residue was purified by chromatography on florisil (99 : 1 / petroleum ether : EtOAc) to give enol ether **15** as colourless oil (180 mg, 55%) containing an inseparable 9 : 1 / *E* : *Z* mixture of diastereoisomers; ^{1}H (500 MHz, MeOD): δ 7.73-7.63 (4H, m, ***E***, ***Z*** Si*Ph*$_2$*t*-Bu), 7.54-7.36 (6H, m, ***E***, ***Z*** Si*Ph*$_2$*t*-Bu), 7.33-7.26 (2H, m, ***E***, ***Z*** Ar-*H*), 7.20-7.00 (3H, m, ***E***, ***Z*** Ar-*H*), 5.99 (0.9H, br, ***E*** O-alkene-*H*), 5.64-5.51 (2H, m, ***E***, ***Z*** alkene-*H*), 5.42 (0.1H, br, ***Z*** O-alkene-*H*), 4.47-4.35 (1H, m, ***E***, ***Z*** pyran-OC*H*), 3.80-3.67 (2H, m, ***E***, ***Z*** C*H*$_2$OSi), 2.77-2.70 (0.9H, m, ***E*** C*H*$_2$), 2.45-2.14 (3.1H, m, ***E***, ***Z*** C*H*$_2$), 1.91-1.77 (1H, m, ***E***, ***Z*** C*H*$_2$), 1.73-1.53 (3H, m, ***E***, ***Z*** C*H*$_2$), 1.07 (8.1H, s, ***E*** C(C*H*$_3$)$_3$), 1.04 (0.9H, s, ***Z*** C(C*H*$_3$)$_3$); ^{13}C NMR ***E* isomer**: (125.7 MHz, MeOD): δ 156.5, 137.9, 136.7, 134.9, 133.1, 130.9, 129.8, 129.2, 128.8 (2C), 126.7, 111.1, 77.1, 64.7, 32.4, 32.3, 27.4, 25.9, 23.2, 20.2; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3071 (w), 3050 (w), 3021 (w), 2933 (s), 2859 (s), 1652 (s), 1472 (w), 1428 (m), 1233 (m), 1111 (m), 922 (w); HRMS (EI) *m/z* [M]$^+$ calcd for $C_{32}H_{38}O_2Si$ 482.2641, found 482.2638.

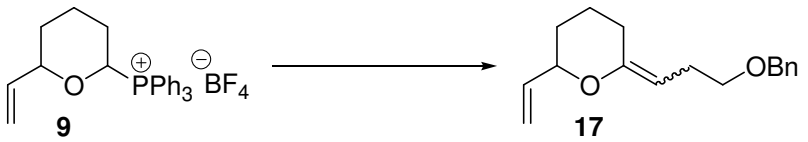
Preparation of 2-benzylidene-6-vinyltetrahydro-2*H*-pyran (16)



Following the representative procedure above, a solution of Wittig salt **9** (250 mg, 0.543 mmol) in THF (6 mL) at -78 °C was treated with KHMDS (0.68 M, 840 µL 0.570 mmol), and freshly distilled benzaldehyde (70 µL, 0.65 mmol). The crude residue was purified by chromatography on florisil (99 : 1 / petroleum ether : EtOAc) to give enol ether **16** as colourless oil (76 mg, 70%) containing an

inseparable 9 : 1 / *E* : *Z* mixture of diastereoisomers; ^{1}H NMR (400 MHz, MeOD): δ 7.31-7.11 (5H, m, ***E***, ***Z*** Ar-*H*), 6.05 (0.9H, br, ***E*** O-alkene-*H*), 6.04-5.90 (0.1H, m, ***Z*** alkene-*H*), 5.95 (0.9H, ddd, *J* = 17.0, 10.5, 5.5 Hz, ***E*** alkene-*H*) 5.42 (0.1H, br, ***Z*** O-alkene-*H*), 5.39-5.35 (0.1H, m, ***Z*** alkene-H_2), 5.33 (0.9H, dt, *J* = 17.0, 1.5 Hz ***E*** alkene-H_2), 5.21-5.13 (1H, m, ***E***, ***Z*** alkene-H_2), 4.33-4.27 (0.1H, m, ***Z*** pyran-OC*H*), 4.21-4.14 (0.9H, m, ***E*** pyran-OC*H*), 2.78-2.70 (1H, m, ***E***, ***Z*** CH_2), 2.41-2.16 (1H, m, ***E***, ***Z*** CH_2), 1.96-1.54 (4H, m, ***E***, ***Z*** CH_2); ^{13}C NMR ***E* isomer**: (100.6 MHz, MeOD): δ 156.5, 140.0, 137.9, 129.8, 129.2, 126.7, 115.5, 110.9, 81.2, 32.0, 26.0, 23.1; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3080 (m), 3021 (m), 2941 (s), 2865 (m), 1651 (s), 1598(m), 1445 (m), 1260 (s), 1235 (s), 1134 (s), 1038 (s), 923 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{14}H_{16}O$ 200.1201, found 200.1208.

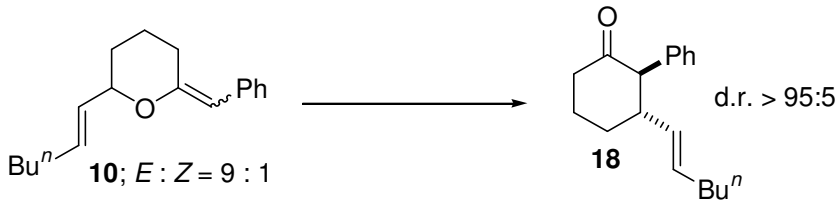
Preparation of 2-(3-(benzyloxy)propylidene)-6-vinyltetrahydro-2*H*-pyran (17)



To a solution of of Wittig salt **9** (260 mg, 0.565 mmol) in THF (6 mL) at -78 °C was added KHMDS (0.68 M, 885 µL, 0.593 mmol) dropwise. The colour changed from colourless to deep red. The reaction was stirred for 5-10 min and 3-(benzyloxy)propanal (111 mg, 0.678 mmol) was added to the reaction mixture. The colour changed to deep red to yellow. The reaction was stirred at -78 °C for 45 min, then the cold bath was removed and the reaction stirred for a further 1.5 h allowing the temperature to reach RT. The reaction was then quenched at 0 °C with H_2O (8 mL). The aqueous layer was extracted with Et_2O (50 mL). The organic layer was washed three times with 20 mL of a mixture 3:3:1 brine : H_2O : MeOH and dried over Na_2SO_4. After filtration through cotton wool, volatiles were removed *in vacuo* and the residue was dried under high *vacuum* for 30 min. The crude residue was purified by flash chromatography on florisil (98 : 2 / petroleum ether : EtOAc) to give enol ether **17** as an oil (113 mg, 78%) containing an inseparable 9 : 1 / *E* : *Z* mixture of diastereoisomers; ^{1}H NMR (400 MHz, MeOD): δ 7.38-7.26 (5H, m, ***E***, ***Z*** Ar-*H*), 5.96-5.84 (0.1H, m, ***Z*** alkene-*H*), 5.90 (0.9H, ddd, *J* = 17.0, 10.5, 5.5 Hz, ***E*** alkene-*H*), 5.30-5.23 (0.1H, m, ***Z*** alkene-H_2), 5.27 (0.9H, dt, *J* = 17.0, 1.5 Hz, ***E***

alkene-H_2), 5.15-5.12 (0.1H, m, ***Z*** alkene-H_2), 5.12 (0.9H, dt, J = 17.0, 1.5 Hz, ***E*** alkene-H_2), 4.95 (0.9H, td, J = 8.0, 1.5 Hz, ***E*** O-alkene-*H*), 4.57 (0.1H, td, J = 7.0, 1.5 Hz, ***Z*** O-alkene-*H*), 4.52 (1.8H, s, ***E*** OCH_2Ph), 4.51 (0.2H, s, ***Z*** OCH_2Ph), 4.05-3.99 (1H, m, ***E***, ***Z*** pyran-OCH), 3.51 (0.2H, t, J = 6.5 Hz, ***Z*** CH_2OBn), 3.47 (1.8H, t, J = 7.0 Hz, ***E*** CH_2OBn), 2.53-2.46 (0.9H, m, ***E*** CH_2), 2.46-2.03 (2.1H, m, ***E, Z*** CH_2), 2.01-1.67 (3H, m, ***E, Z*** CH_2), 1.65-1.47 (2H, m, ***E, Z*** CH_2); ^{13}C NMR ***E* isomer**: (100.6 MHz, MeOD): δ 155.3, 140.0, 139.8, 129.3, 128.8, 128.6, 115.3, 105.5, 81.4, 73.8, 71.5, 32.4, 27.5, 25.1, 23.6; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3030 (m), 2938 (s), 2859 (s), 1681 (s), 1454 (m), 1361 (m), 1100 (s), 911 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{17}H_{22}O_2$ 258.1619, found 258.1625.

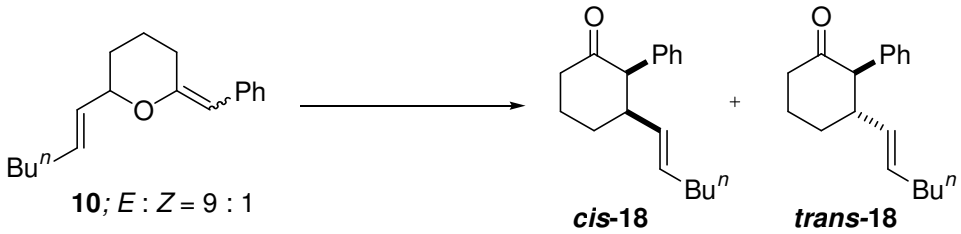
General procedure for the Pd-Catalysed O-to C-Rearrangement of Aryl Pyranyl Ethers. Preparation of (2*R, 3*S**)-3-((*E*)-hex-1-enyl)-2-phenylcyclohexanone (18)**



To a solution of $Pd(OAc)_2$ (10 mg, 10 mol%) in anhydrous MeCN (4 mL) was added PBu^n_3 (75 μL, 0.28 mmol). The solution was heated at reflux for 20 min during which time the colour changed from clear to yellow. After this time the reaction was cooled to 55 °C and a solution of enol ether **10** (119 mg, 0.46 mmol) in MeCN (4.5 mL) was added to the reaction mixture. After 24 h at 55 °C, the reaction was cooled to RT and diluted with Et_2O. The reaction mixture was filtered through a pad of celite and the volatiles were removed *in vacuo*. The crude residue was purified by flash chromatography on silica gel (BDH) (95 : 5 / petroleum ether : EtOAc) to give cyclohexanone **18** (98 mg, 82%) as a white solid; M.p. = 40-41 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.20 (3H, m, Ar-*H*), 7.05-6.98 (2H, m, Ar-*H*), 5.18 (1H, dt, J = 15.5, 6.0 Hz, CH_2-alkene-*H*), 5.11 (1H, dd, J = 15.5, 7.0 Hz, CH-alkene-*H*), 3.36 (1H, d, J = 11.5 Hz, (CO)C*H*), 2.70-2.60 (1H, m, alkene-C*H*), 2.58-2.40 (2H, m, CH_2), 2.20-2.11 (1H, m, CH_2), 2.07-1.98 (1H, m, CH_2), 1.91-1.67 (4H, m, CH_2), 1.14-0.92 (4H, m, CH_2), 0.77 (3H, t, J = 7.0 Hz, CH_3) ; ^{13}C NMR (62.9 MHz,

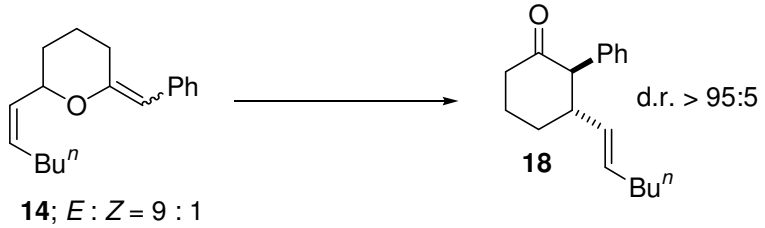
$CDCl_3$): δ 209.7, 137.3, 132.1, 131.5, 129.6, 128.1, 126.7, 63.4, 49.1, 42.0, 32.7, 32.0, 31.4, 25.9, 21.7, 13.9; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3064 (w), 3030 (w), 2931 (s), 2860 (s), 1715 (s), 1605 (w), 1498 (m), 1454 (m), 1356 (w), 1316 (w), 1279 (w), 1168 (m), 966 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{24}O$ 256.1827, found 256.1821.

Preparation of (2*R, 3*R**)-3-((*E*)-hex-1-enyl)-2-phenylcyclohexanone (*cis*-18)**



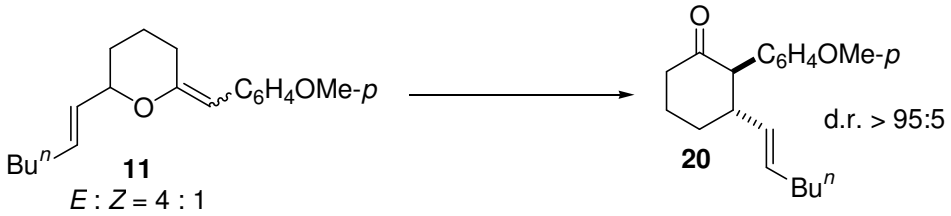
Following the representative procedure, a solution of $Pd(PPh_3)_4$ (58.6 mg, 10 mol%) in MeCN (4.1 mL) was treated with a solution of enol ether **10** (130 mg, 0.51 mmol) in MeCN (6.1 mL) at 55 °C for 48 h. The crude residue was purified by flash chromatography on silica gel (BDH) (95 : 5 / petroleum ether : EtOAc) to give ***trans*-18** (60 mg, 46%) and ***cis*-18** (30 mg, 23%) as an oil; (***cis*-18**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.28 (2H, m, Ar-*H*), 7.27-7.23 (3H, m, Ar-*H*), 5.45 (1H, ddt, *J* = 15.0, 9.0, 1.5 Hz, CH-alkene-*H*), 5.28 (1H, dtd, *J* = 15.0, 6.5, 1.0 Hz, CH_2-alkene-*H*), 3.90 (1H, d, *J* = 4.0 Hz, (CO)C*H*), 3.04-2.95 (1H, m, alkene-C*H*), 2.64-2.47 (2H, m, CH_2), 2.23-2.08 (2H, m, CH_2), 2.07-1.92 (4H, m, CH_2), 1.34-1.19 (4H, m, CH_2), 0.89 (3H, t, *J* = 7.0 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 210.0, 137.0, 133.7, 130.2, 128.5, 127.8, 126.8, 61.2, 48.0, 41.8, 32.3, 32.0, 31.5, 23.6, 22.2, 14.0; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3062 (w), 3029 (w), 2956 (s), 2931 (s), 2871 (s), 1714 (s), 1682 (m), 1496 (w), 1448 (w), 969 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{24}O$ 256.1827, found 256.1824.

Preparation of (2*R, 3*S**)-3-((*E*)-hex-1-enyl)-2-phenylcyclohexanone (18) from compound (14)**



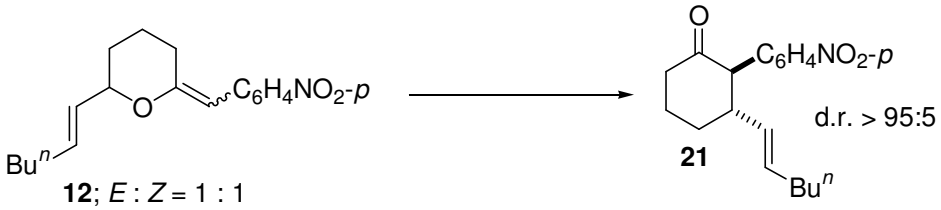
Following the representative procedure, a solution of $Pd(OAc)_2$ (7.9 mg, 10 mol%) and $P(n\text{-}Bu)_3$ (58 μL, 0.23 mmol) in anhydrous MeCN (3 mL) was treated with a solution of enol ether **14** (90 mg, 0.35 mmol) in MeCN (4.5 mL) at 55 °C for 24 h. The crude residue was purified by chromatography on silica gel (BDH) (95 : 5 / PE : EtOAc) to give cyclohexanone **18** (76 mg, 84%) as a white solid. The compound isolated showed identical spectroscopic data to that outlined earlier.

Preparation of (2R*, 3S*)-3-((*E*)-hex-1-enyl)-2-(4-methoxyphenyl)cyclohexanone (20)



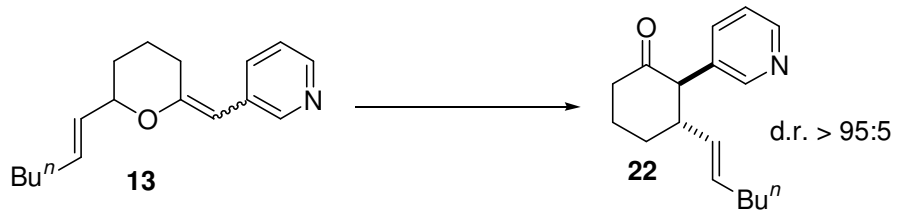
Following the representative procedure, a solution of $Pd(OAc)_2$ (12 mg, 10 mol%) and PBu^n_3 (85 μL, 0.22 mmol) in anhydrous MeCN (4.0 mL) was treated with a solution of enol ether **11** (150 mg, 0.52 mmol) in MeCN (6.5 mL) at 55 °C for 24 h. The crude residue was purified by flash chromatography on silica gel (BDH) (90 : 10 / petroleum ether : EtOAc) to give **20** (100 mg, 66%) as a pale yellow solid; M.p. = 58-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00-6.94 (2H, m, Ar-*H*), 6.89-6.63 (2H, m, Ar-*H*), 5.19 (1H, dt, *J* = 15.0 , 6.5 Hz, CH_2-alkene-*H*), 5.11 (1H, dd, *J* = 15.0, 7.0 Hz, CH-alkene-*H*), 3.81 (3H, s, OCH_3), 3.35 (1H, d, *J* = 11.5 Hz, (CO)C*H*), 2.64-2.39 (3H, m, alkene-C*H*, CH_2), 2.19-2.10 (1H, m, CH_2), 2.05-1.98 (1H, m, CH_2), 1.88-1.67 (4H, m, CH_2), 1.14-0.90 (4H, m, CH_2), 0.78 (3H, t, *J* = 7.0 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 210.1, 158.4, 132.3, 131.4, 130.6, 129.5, 113.7, 62.6, 55.3, 49.2, 42.0, 32.8, 32.1, 31.5, 26.0, 21.8, 14.0; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 2956 (s), 2930 (s), 2860 (s), 1714 (s), 1614 (m), 1514 (s), 1247 (m), 1037 (m), 966 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{19}H_{26}O_2$ 286.1932, found 286.1931.

Preparation of (2R*, 3S*)-3-((*E*)-hex-1-enyl)-2-(4-nitrophenyl)cyclohexanone (21)



Following the representative procedure, a solution of $Pd(OAc)_2$ (8 mg, 10 mol%) and PBu^n_3 (60 μL, 0.22 mmol) in anhydrous MeCN (3.0 mL) was treated with a solution of pyranyl ether **12** (112 mg, 0.37 mmol) in MeCN (4.0 mL) at 55 °C for 24h. The crude residue was purified by flash chromatography on silica gel (BDH) (90 : 10 / petroleum ether : EtOAc) to give cyclohexanone **21** (82 mg, 73%) as a white solid; M.p. = 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.10 (2H, m, Ar-*H*), 7.22-7.16 (2H, m, Ar-*H*), 5.13 (1H, dtd, *J* = 15.0, 7.0, 1.0 Hz, CH_2-alkene-*H*), 5.04 (1H, dd, *J* = 15.0, 8.0 Hz, CH-alkene-*H*), 3.51 (1H, d, *J* = 12.0 Hz, (CO)C*H*), 2.72-2.46 (3H, m, alkene-C*H*, CH_2), 2.28-2.18 (1H, m, CH_2), 2.12-2.03 (1H, m, CH_2), 2.01-1.68 (4H, m, CH_2), 1.12-0.85 (4H, m, CH_2), 0.73 (3H, t, *J* = 7.0 Hz, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 208.1, 146.9, 145.4, 132.6, 131.2, 130.7, 123.3, 63.2, 49.7, 41.9, 32.8, 31.8, 31.3, 25.9, 21.7, 13.8; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 2956 (m), 2930 (m), 2870 (m), 1712 (s), 1605 (w), 1519 (s), 1346 (s), 1170 (w), 970 (w);HRMS (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{23}NO_3$ 301.1678, found 301.1689.

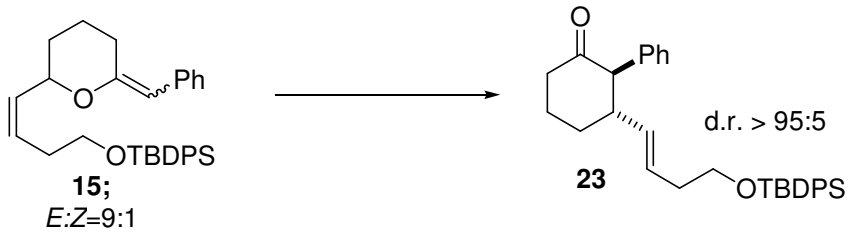
Preparation of (2*R, 3*S**)-3-((*E*)-hex-1-enyl)-2-(pyridin-3-yl)cyclohexanone (22)**



Following the representative procedure, a solution of $Pd(OAc)_2$ (3.4 mg, 10 mol%) and PBu^n_3 (38 μL, 0.15 mmol) in anhydrous MeCN (1.0 mL) was treated with a solution of enol ether **13** (39 mg, 0.15 mmol) in MeCN (1.5 mL) at 55 °C for 36 h. The crude residue was purified by flash chromatography on silica gel (BDH) (1 : 1 / petroleum ether : EtOAc) to give **22** (29 mg, 73%) as a colourless oil. ^{1}H NMR (250

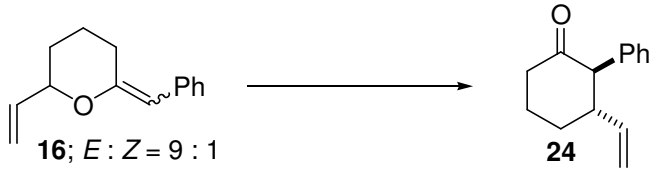
MHz, $CDCl_3$): δ 8.46 (1H, s, Ar-*H*), 8.25 (1H, s, Ar-*H*), 7.43-34 (1H, m, Ar-*H*), 7.29-7.17 (1H, m, Ar-*H*), 5.20-4.99 (2H, m, alkene-*H*), 3.41 (1H, d, *J* = 12.0 Hz, (CO)C*H*), 2.67-2.42 (3H, m, alkene-C*H*, CH_2), 2.26-1.60 (6H, m, CH_2), 1.13-0.82 (4H, m, CH_2), 0.74 (3H, t, *J* = 6.5 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.4, 150.6, 147.7, 137.4, 133.1, 132.5, 131.3, 123.1, 60.7, 49.6, 41.8, 32.8, 31.8, 31.2, 25.9, 21.6, 13.8; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3026 (w), 2946 (s), 2922 (s), 2858 (m), 1711 (s), 1575 (w), 1458 (w), 1422 (m), 1166 (m), 1021 (w), 965 (m), 797 (w); HRMS (EI) *m/z* $[MH]^+$ calcd for $C_{17}H_{24}NO$ 258.1858, found 258.1848.

Preparation of (2R*, 3S*)-3-((*Z*)-4-(*tert*-butyldiphenylsilyloxy)but-1-enyl)-2-phenylcyclohexanone (23)



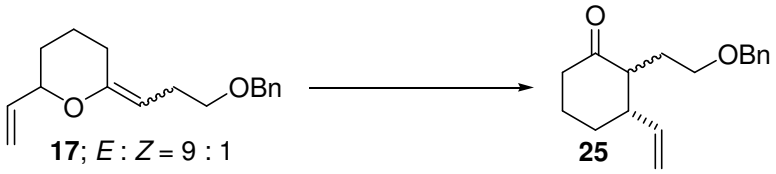
Following the representative procedure, a solution of $Pd(OAc)_2$ (8 mg, 10 mol%) and PBu^n_3 (50 μL, 0.20 mmol) in anhydrous MeCN (3.0 mL) was treated with a solution of enol ether **15** (165 mg, 0.34 mmol) in MeCN (4.0 mL) at 55 °C for 24 h. The crude residue was purified by chromatography on silica gel (BDH) (90 : 10 / PE : EtOAc) to give **23** (143 mg, 87%) as a viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.65 (4H, m, Si*Ph*$_2$*t*-Bu), 7.52-7.40 (6H, m, Si*Ph*$_2$*t*-Bu), 7.32-7.18 (3H, m, Ar-*H*), 7.07-7.01 (2H, m, Ar-*H*), 5.29-5.17 (2H, m, alkene-*H*), 3.45 (2H, td, *J* = 6.5, 1.5 Hz, CH_2OTBDPS), 3.38 (1H, d, *J* = 12.0 Hz, (CO)C*H*), 2.75-2.64 (1H, m, alkene-C*H*), 2.63-2.56 (1H, m, CH_2), 2.55-2.46 (1H, m, CH_2), 2.26-2.02 (4H, m, CH_2), 1.96-1.72 (2H, m, CH_2), 1.09 (9H, s, C(CH_3)$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 209.5, 137.2, 135.6, 134.1 (2C), 129.6, 129.5, 128.1, 127.7, 127.4, 126.7, 63.8, 63.2, 48.9, 41.9, 35.8, 32.3, 26.9, 25.8, 19.3; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3070 (m), 3030 (m), 2931 (s), 1715 (s), 1472 (m), 1428 (m), 1111 (m), 911 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{32}H_{38}O_2Si$ 482.2641, found 482.2619.

Preparation of (2R*, 3S*)-2-phenyl-3-vinylcyclohexanone (24)



Following the representative procedure, a solution of $Pd(OAc)_2$ (5.6 mg, 10 mol%) and PBu^n_3 (40 µL, 0.15 mmol) in anhydrous MeCN (2.0 mL) was treated at 55 °C with a solution of enol ether **16** (50 mg, 0.25 mmol) in MeCN (3.0 mL). The crude residue was purified by flash chromatography on silica gel (BDH) (95 : 5 / petroleum ether : EtOAc) to give cyclohexanone **24** (42 mg, 84%) as a white solid; Mp = 74-75 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.24 (3H, m, Ar-*H*), 7.11-7.06 (2H, m, Ar-*H*), 5.56 (1H, ddd, *J* = 17.5, 10.0, 7.5 Hz, alkene-*H*), 4.90-4.82 (2H, m, alkene-H_2), 3.43 (1H, d, *J* = 11.5 Hz, (CO)C*H*), 2.82-2.71 (1H, m, alkene-*CH*), 2.63-2.44 (2H, m, CH_2), 2.27-2.17 (1H, m, CH_2), 2.14-2.05 (1H, m, CH_2), 1.97-1.75 (2H, m, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 209.3, 140.4, 137.1, 129.6, 128.3, 127.0, 115.1, 62.9, 49.5, 41.9, 31.9, 25.8; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3077 (w), 3033 (w), 2954 (s), 2939 (s), 2860 (s), 1710 (s), 1643 (m), 1496 (w), 1311 (w), 1173 (w), 914 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{14}H_{16}O$ 200.1201, found 200.1198.

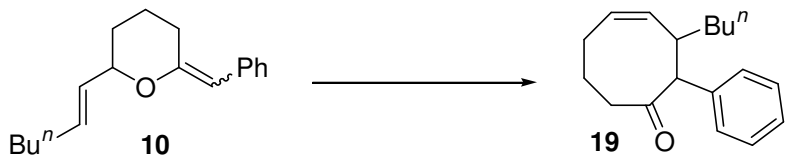
Preparation of 2-(2-(benzyloxy)ethyl)-3-vinylcyclohexanone (27)



A solution of $Pd(OAc)_2$ (5.6 mg, 10 mol%) and DavePhos (39.5 mg, 0.1 mmol) in anhydrous toluene (2 mL) was heated at reflux for 15 min. The colour change of clear to orange was observed. The reaction was cooled to RT and a solution of enol ether **17** (65 mg, 0.25 mmol) in anhydrous toluene (3 mL) was added to the reaction mixture followed by Et_2AlCl (0.1 M in hexane, 125 µL, 0.125 mmol). The reaction was heated 55 °C for 24 h. After this time, the reaction was cooled to RT, diluted with Et_2O, filtered through a pad of celite and all volatiles were removed *in vacuo*. The crude residue was purified by flash chromatography on silica gel (BDH) (95 : 5 / petroleum ether : EtOAc) to give cyclohexanone **25** (42 mg, 64%) as an oil

containing an inseparable 2.5 : 1 / *trans* : *cis* mixture of diastereoisomers; (***trans***, ***cis***) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.23 (5H, m, ***trans***, ***cis*** Ar-*H*), 5.68 (0.28H, ddd, *J* =16.5, 10.5, 8.5 Hz, ***cis*** alkene-*H*), 5.61 (0.72H, ddd, *J* = 16.5, 10.5, 9.0 Hz, ***trans*** alkene-*H*), 5.08-4.98 (2H, m, ***trans***, ***cis*** alkene-H_2), 4.51-4.39 (2H, m, ***trans***, ***cis*** OCH_2Ph), 3.54 (0.28H, ddd, *J* = 9.0, 7.0, 5.0 Hz, ***cis*** CH_2OBn), 3.49-3.40 (1.72H, m, ***trans***, ***cis*** CH_2OBn), 2.82-2.75 (0.72H, m, ***trans*** alkene-C*H*), 2.75-2.68 (0.72H, m, ***trans*** (CO)C*H*), 2.45-2.27 (2.28H, m, ***trans***, ***cis*** CH_2, ***cis*** alkene-C*H*, ***cis*** (CO)CH), 2.21-2.11 (0.28H, ***cis*** CH_2), 2.09-1.54 (7.28H, m, ***trans***, ***cis*** CH_2), 1.51-1.42 (0.72H, m, ***trans*** CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 212.9, 211.9, 141.1, 138.8, 138.6, 137.2, 128.5 (2C), 127.8, 127.7 (2C), 127.6, 117.1, 115.6, 73.0, 72.8, 68.7, 68.0, 51.3, 50.5, 50.2, 46.7, 42.1, 41.6, 32.5, 30.6, 27.3, 27.1, 26.3, 23.9; FTIR (CH_2Cl_2, ν_{max} cm^{-1}): 3066 (w), 3030 (w), 2934 (s), 2860 (s), 1714 (s), 1454 (m), 1429 (w), 1362 (m), 1101 (s), 996 (m), 919 (m); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{17}H_{22}O_1$ 258.1619, found 258.1611.

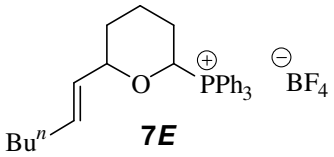
Representative Procedure for Claisen Rearrangement of Pyranyl Ethers. Preparation of (*Z*)-3-butyl-2-phenylcyclooct-4-enone (19) [8]



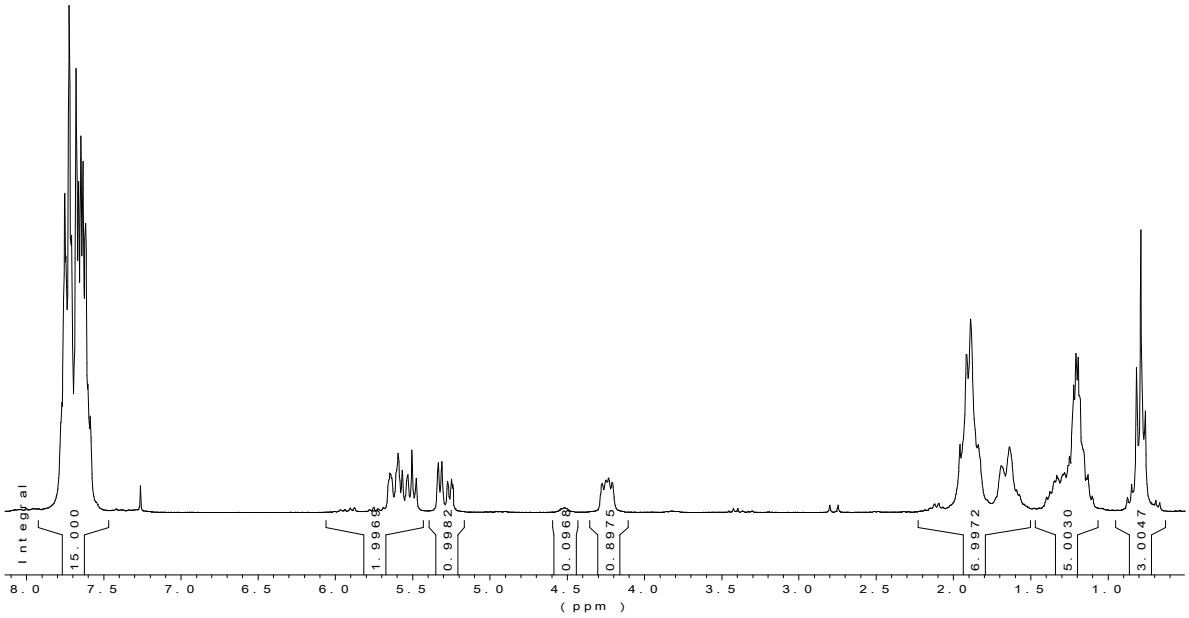
A solution of enol ether **10** (30 mg, 0.117 mmol) in nitrobenzene (1.5 ml) was heated at 185 °C for 1 h. After cooling to RT, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether, then 95 : 5 / petroleum ether : EtOAc) to give the cyclooctanone **20** as white solid (24 mg, 80%); M.p. = 67-68 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.32 (4H, m, Ar-*H*), 7.30-7.25 (1H, m, Ar-*H*), 5.78 (1H, dt, *J* = 10.5, 8.5 Hz, alkene-*H*), 5.44 (1H, ddd, *J* = 10.5, 8.5, 1.5 Hz, alkene-*H*), 3.44 (1H, d, *J* = 12.0 Hz, (CO)C*H*), 3.42-3.32 (1H, m, alkene-C*H*), 2.84 (1H, td, *J* = 12.0, 2.5 Hz, (CO)CH_2), 2.41-2.29 (1H, m, CH_2), 2.23-2.12 (1H, m, CH_2), 1.90 (1H, ddd, *J* = 12.0, 6.0, 2.5 Hz, (CO)CH_2), 1.85-1.76 (1H, m, CH_2), 1.68-1.54 (1H, m, CH_2), 1.53-1.41 (1H, m, CH_2), 1.39-1.15 (4H, m, CH_2), 1.13-1.01 (1H, m, CH_2), 0.84 (3H, t, *J* = 7.0 Hz, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 212.1, 136.0, 135.9, 131.1, 129.0, 128.6, 127.6, 69.6, 38.3, 35.7, 31.6, 29.9, 28.1, 27.2, 22.6,

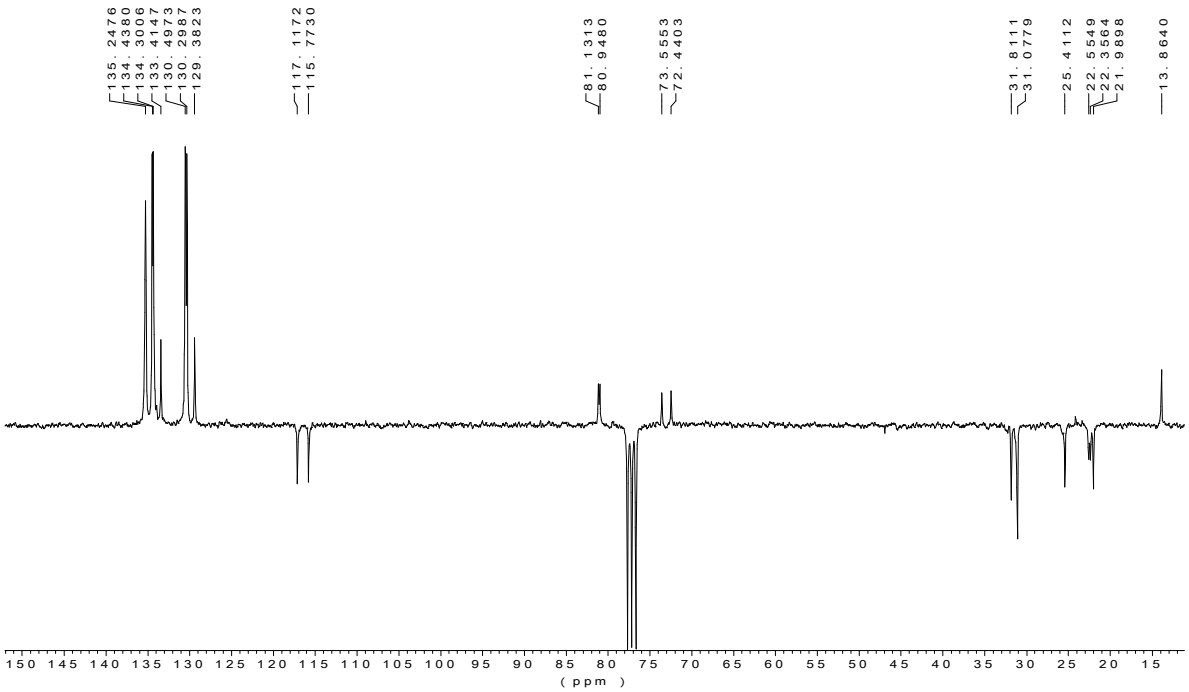
14.2; FTIR (CH_2Cl_2, ν_{max} cm^{-1}) 3009 (w), 2930 (s), 2860 (m), 1704 (s), 1598 (w), 1495 (w), 1451 (m), 1330 (w), 1203 (w), 1106 (w); HRMS (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{24}O_1$ 256.1827, found 256.1835.

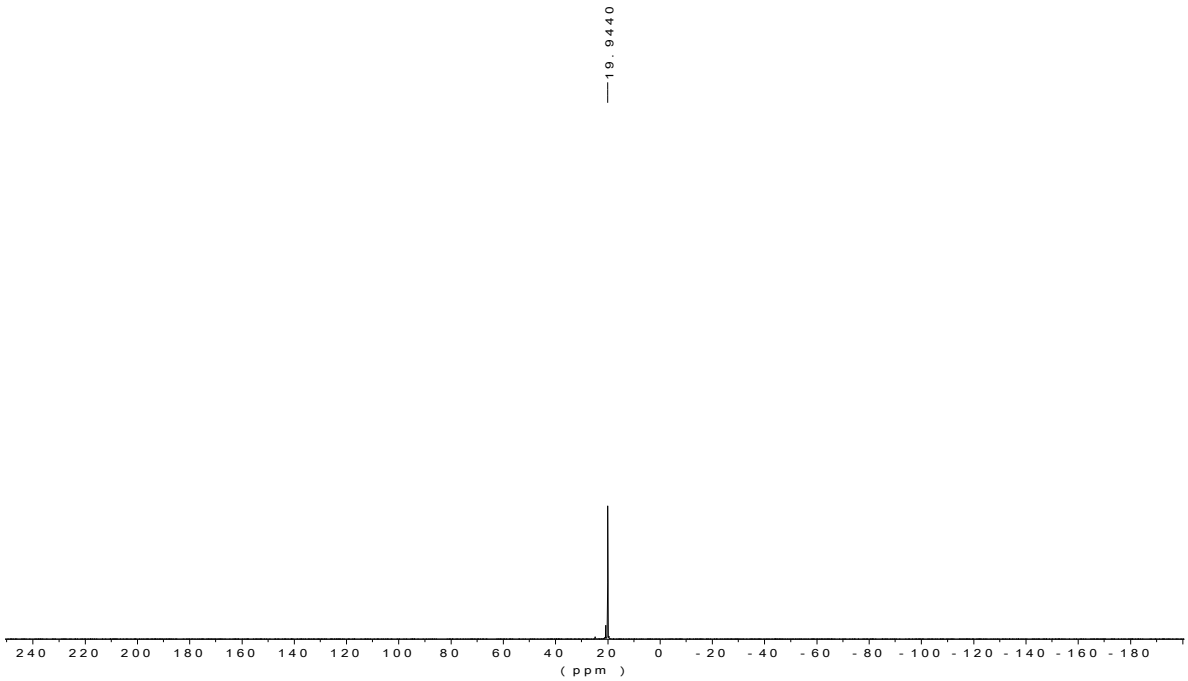
3. NMR Spectra

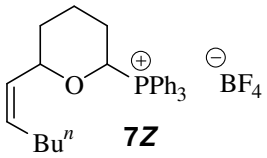


7E

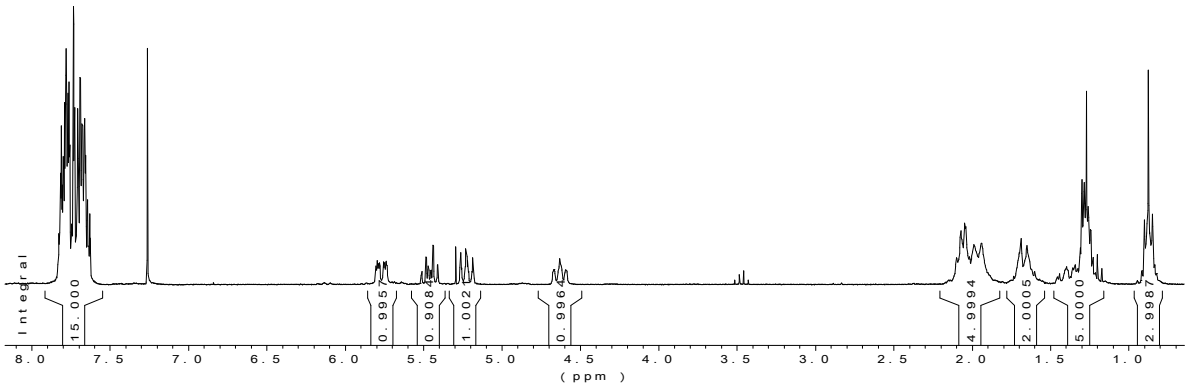


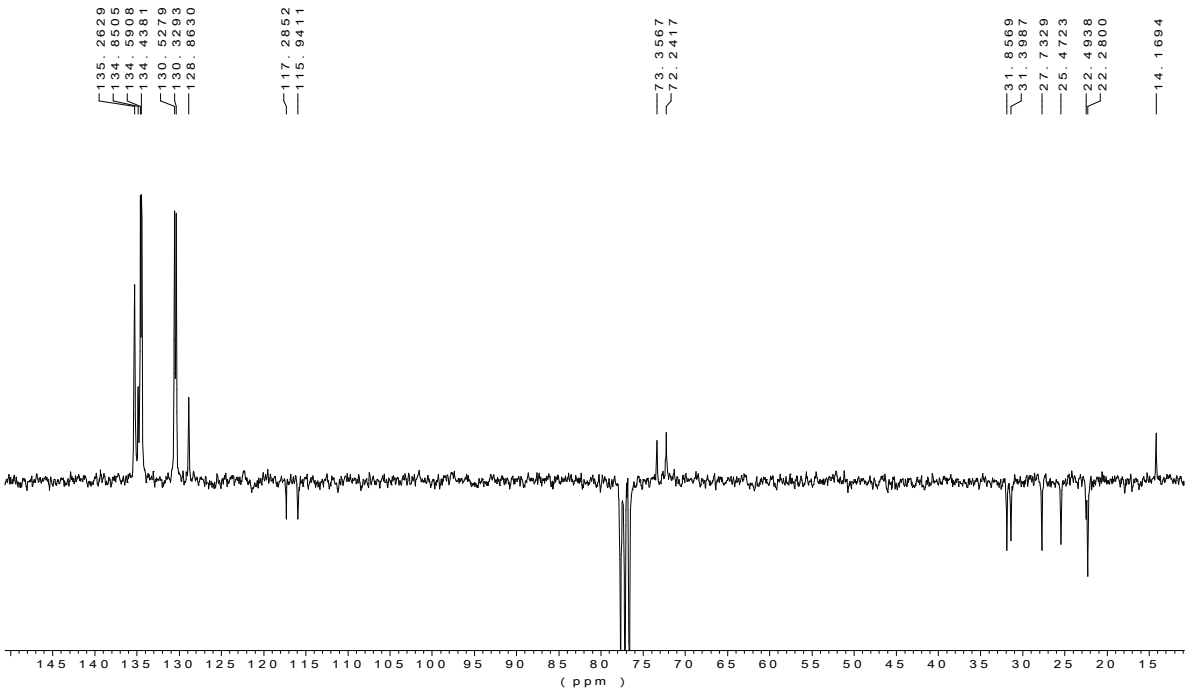


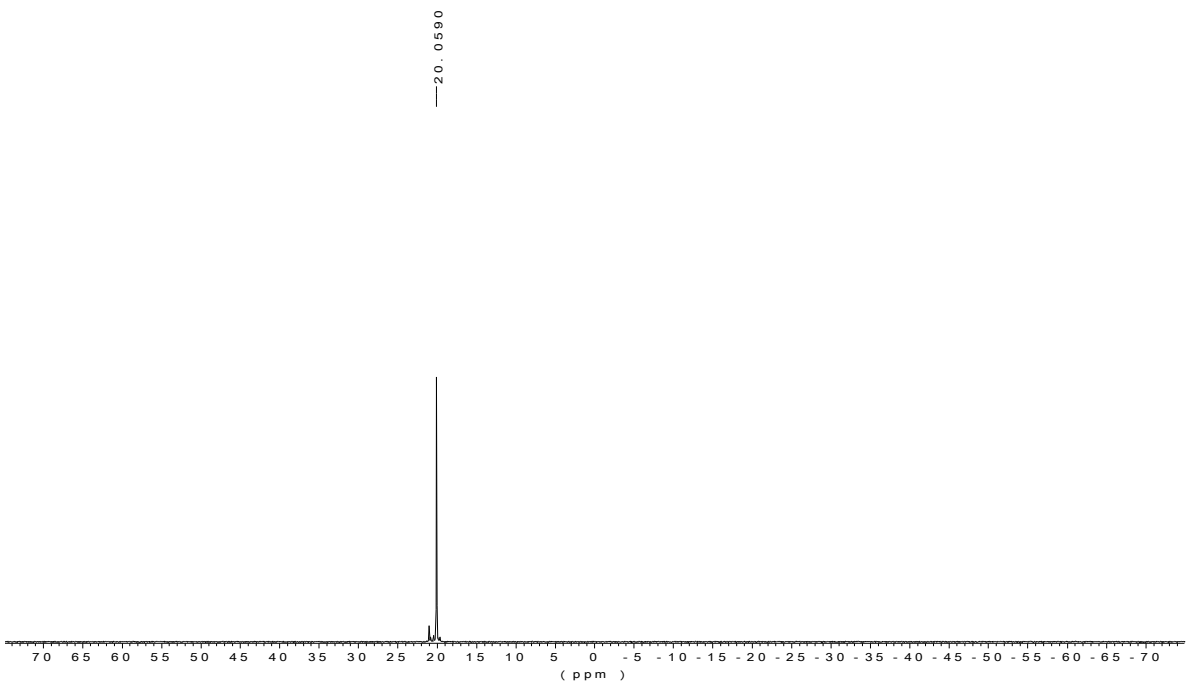

19.9440
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
(ppm)

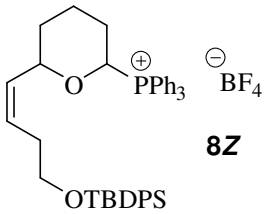

O
PPh3
BF4
Bun

7Z

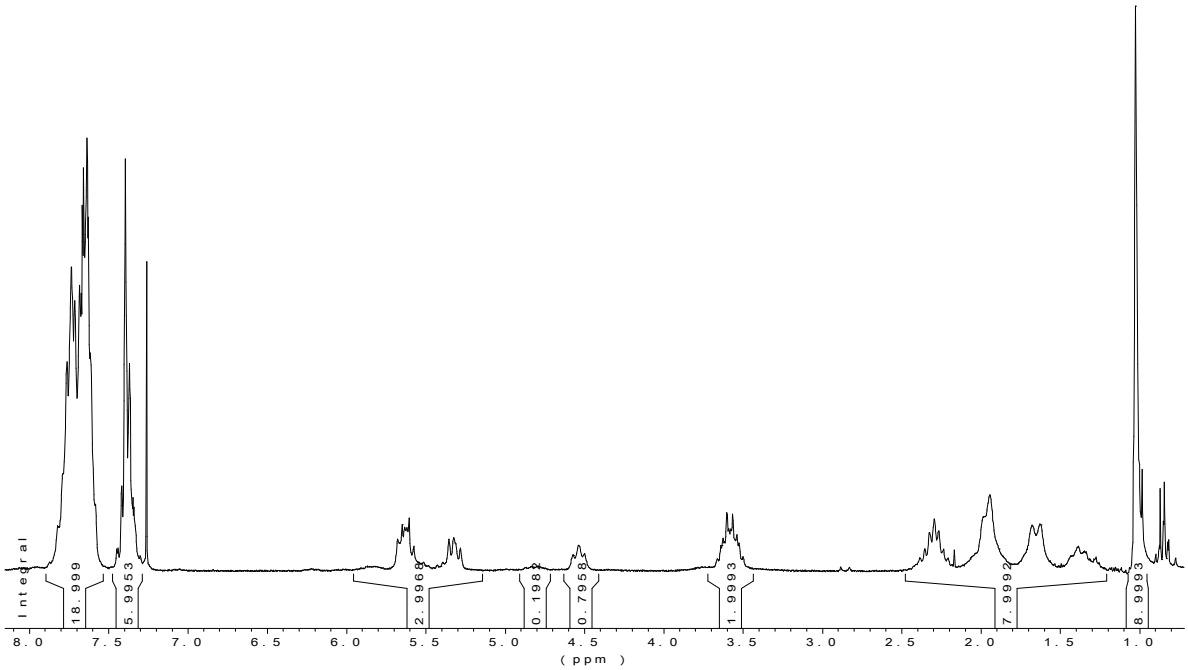

Integral
15.000
0.995
0.908
1.002
0.996
4.9994
2.0005
5.0000
2.9987
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

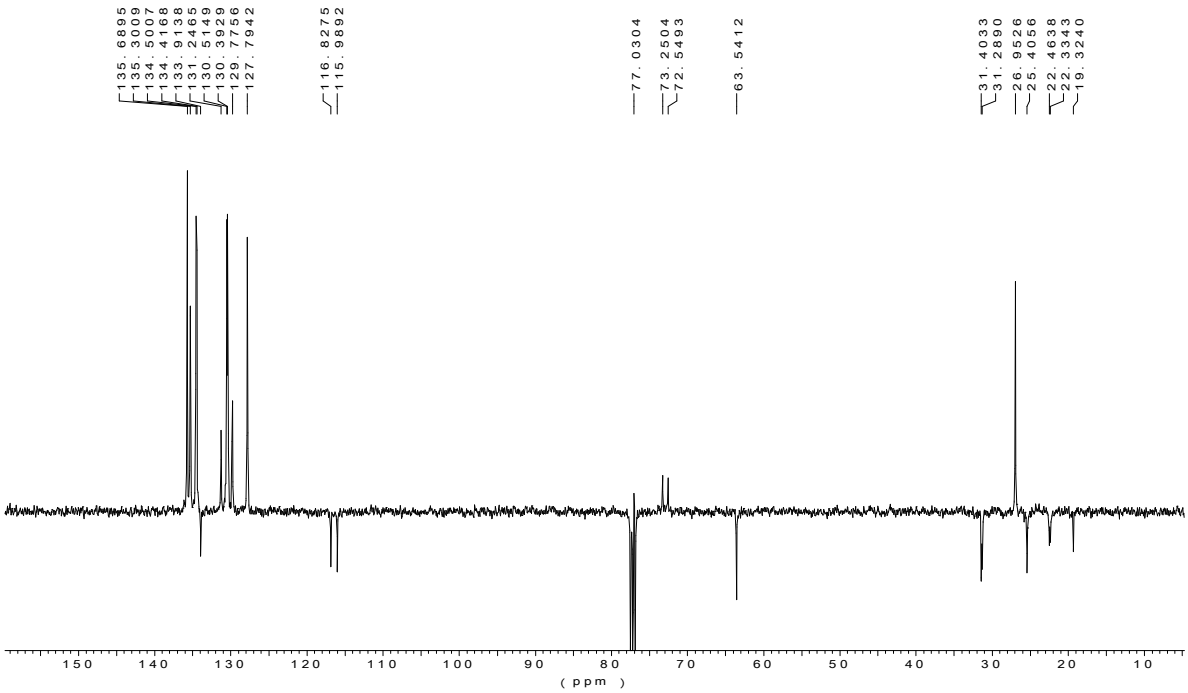

135.2629
134.8505
134.5908
134.4381
130.5279
130.3293
128.8630
117.2852
115.9411
73.3567
72.2417
31.8569
31.3987
27.7329
25.4723
22.4938
22.2800
14.1694
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
(ppm)

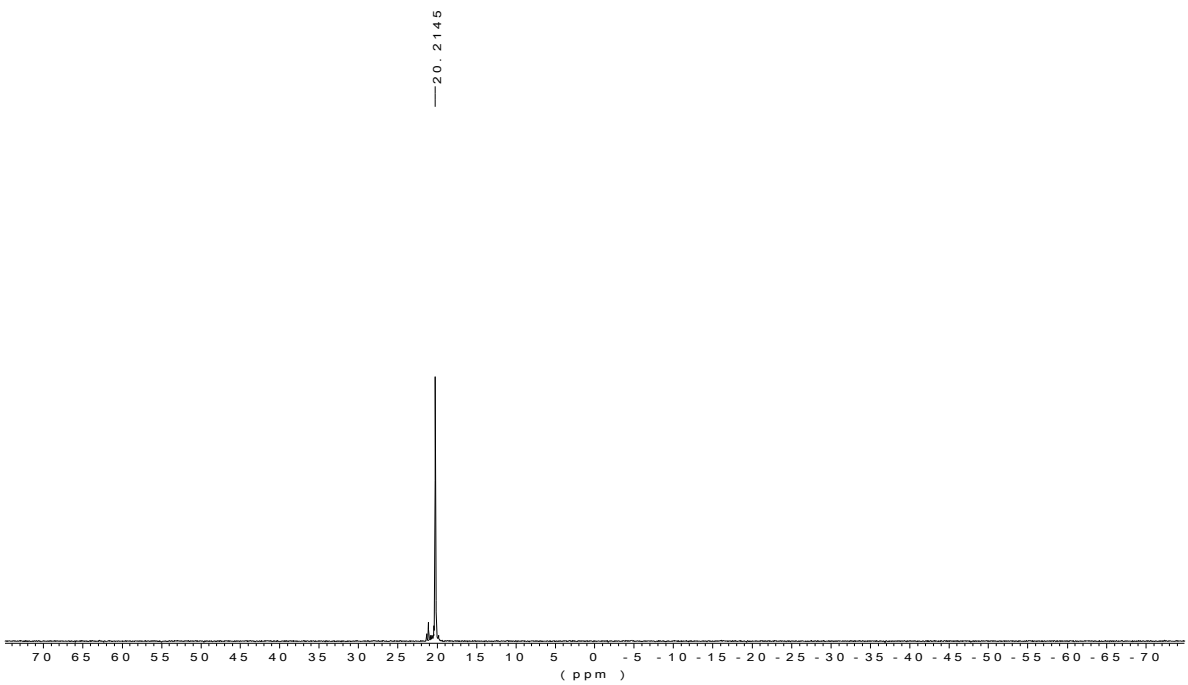

20.0590
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
(ppm)

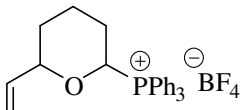

O
PPh3
BF4
OTBDPS

8*Z*

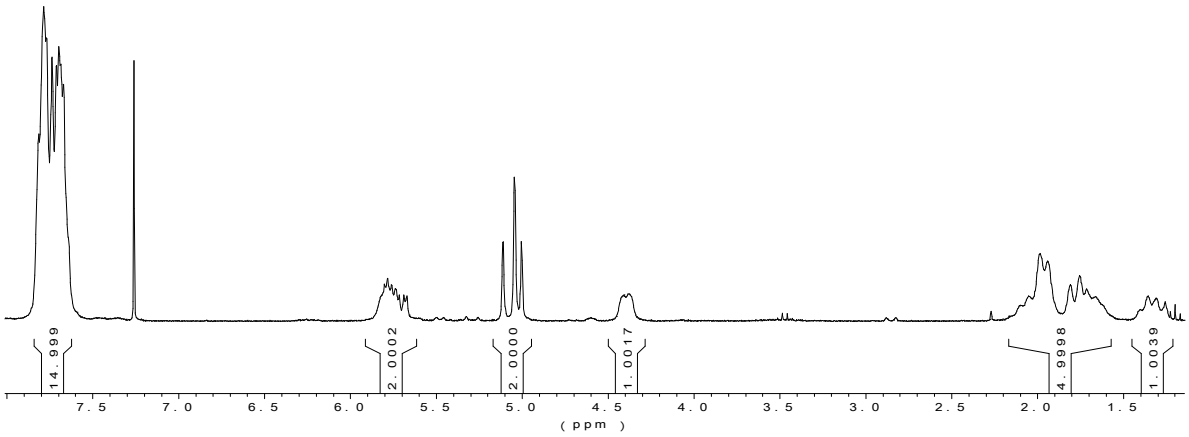

Integral
18.999
5.9953
2.9968
0.1988
0.7958
1.9993
7.9992
8.9993
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

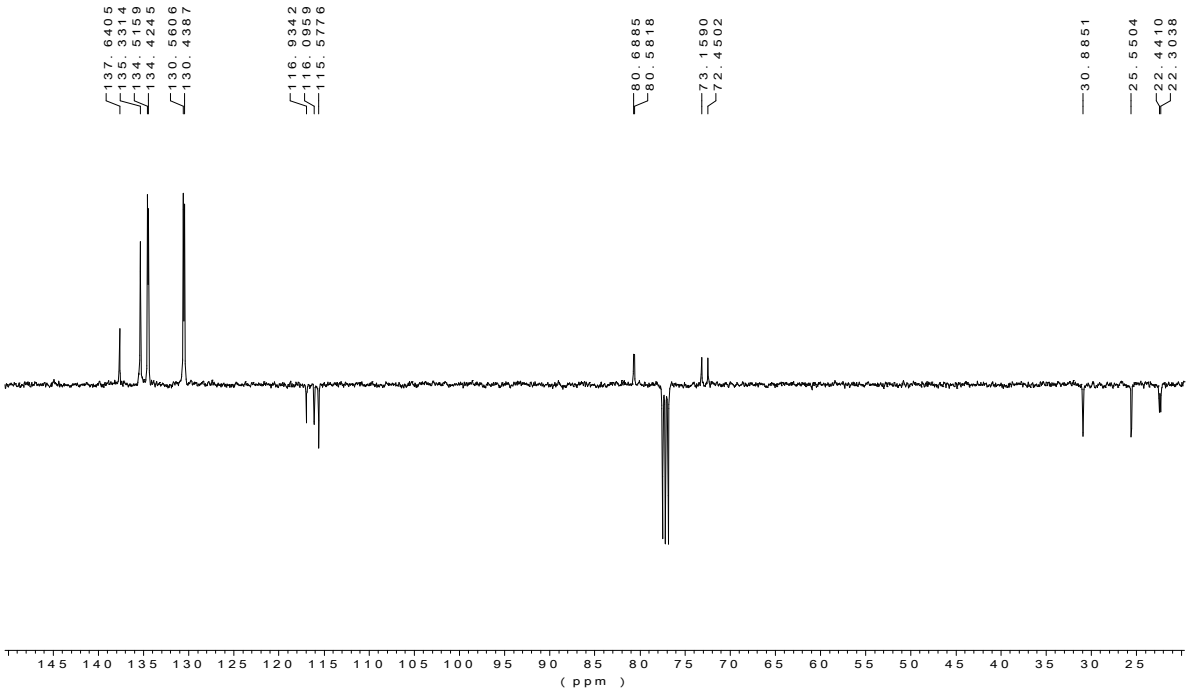

135.6895
135.3009
134.3007
134.4168
133.9138
131.2465
130.5149
130.3929
129.7756
127.7942
116.8275
115.9892
77.0304
73.2504
72.5493
63.5412
31.4033
31.2890
26.9526
25.4056
22.4638
22.3343
19.3240
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

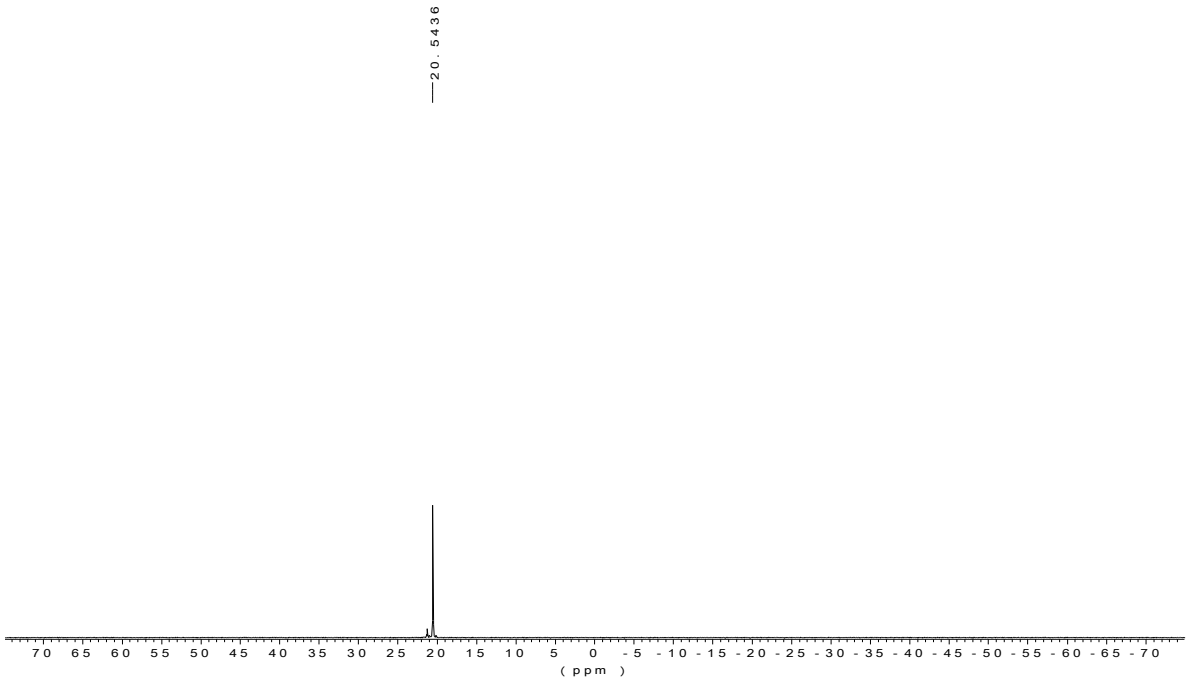

20.2145
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
(ppm)


O
PPh3
BF4

9


14.999
2.0002
2.0000
1.0017
4.9998
1.0039
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
(ppm)


137.6405
135.3314
134.5559
134.4245
130.5606
130.4387
116.9342
116.0959
115.5776
80.6885
80.5818
73.1590
72.4502
30.8851
25.5504
22.4410
22.3038
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
(ppm)


20.5436
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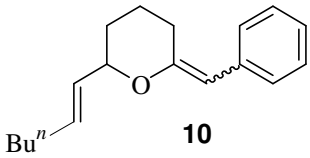
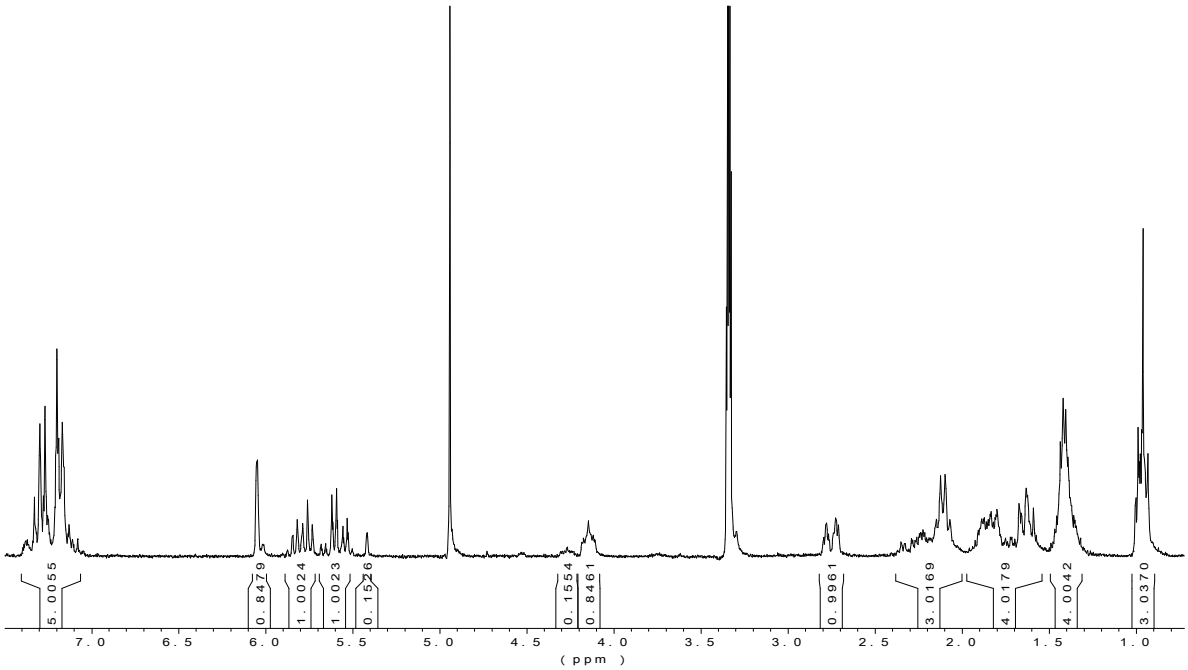
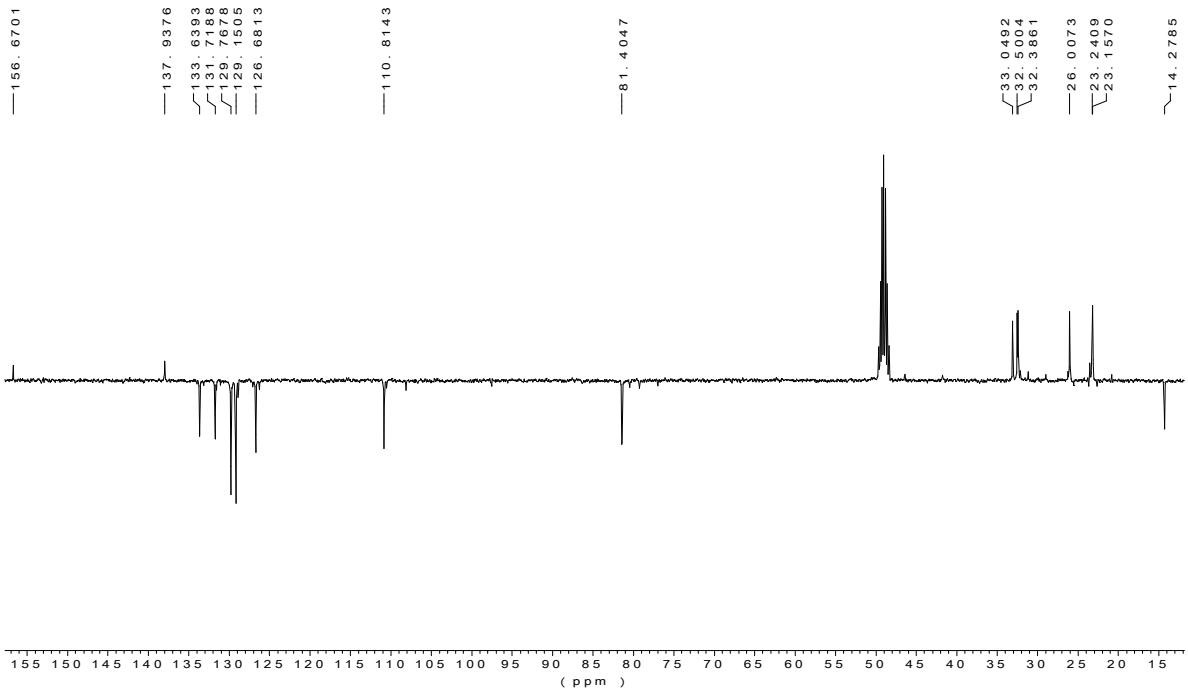
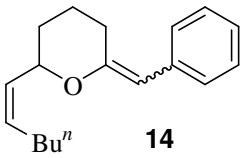
(ppm)


O
Bu^n

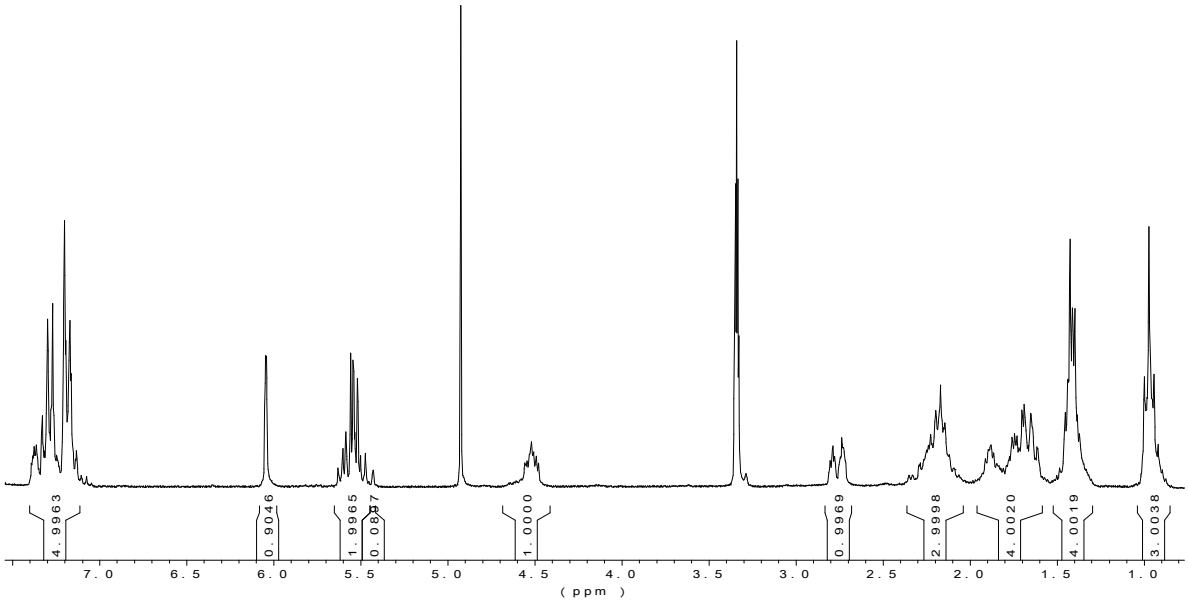
10

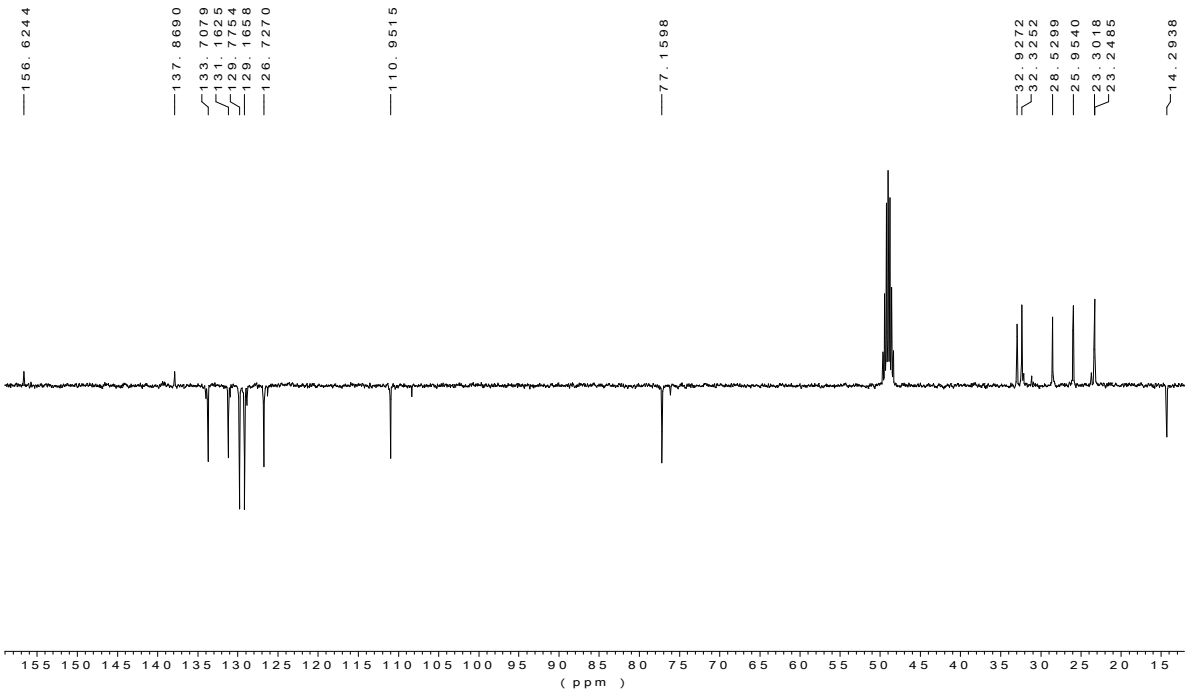

5.0055
0.8479
1.0024
1.0023
0.1526
0.1554
0.8461
0.9961
3.0169
4.0179
4.0042
3.0370
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

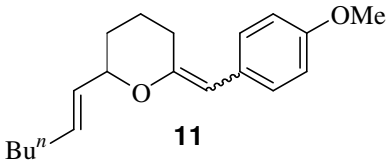

156.6701
137.9376
133.6393
131.7188
129.7678
129.1505
126.6813
110.8143
81.4047
33.0492
32.5004
32.3861
26.0073
23.2409
23.1570
14.2785
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
(ppm)


O
Bu^n

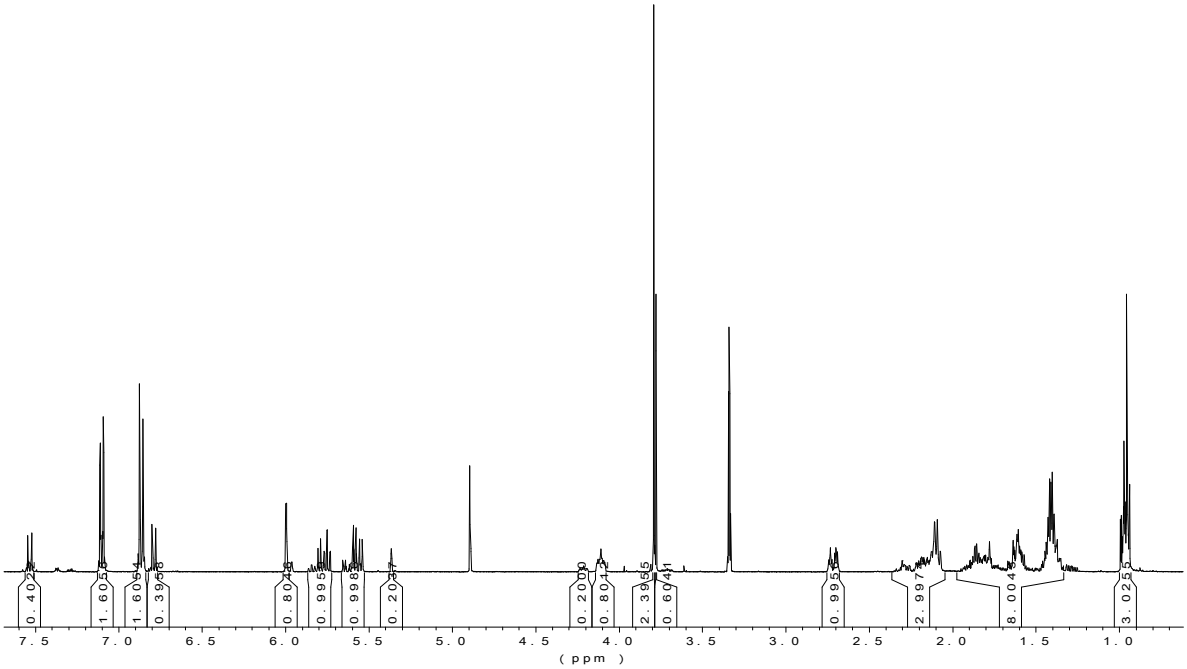
14

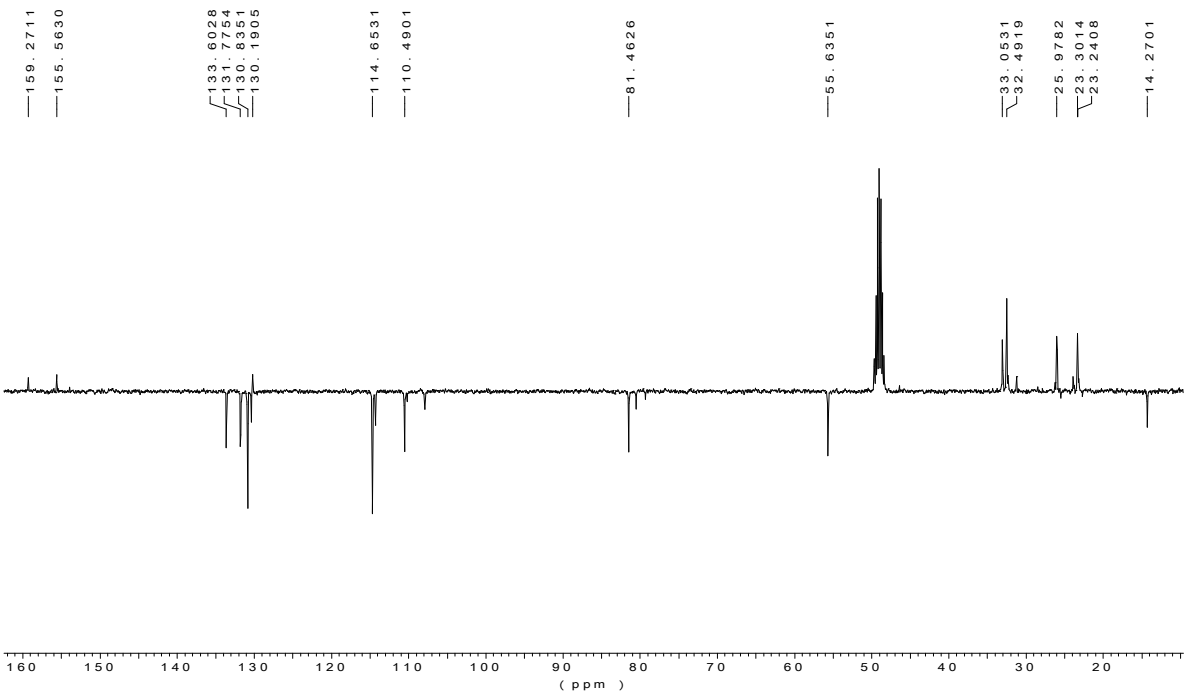

4.9963
0.9046
1.9965
0.0877
1.0000
0.9969
2.9998
4.0020
4.0019
3.0038
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

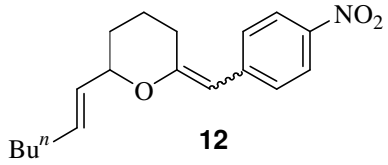

156.6244
137.8690
133.7079
131.1625
129.7754
129.1658
126.7270
110.9515
77.1598
32.9772
32.3252
28.5299
25.9540
23.3018
23.2485
14.2938
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
(ppm)


OMe
O
Bu^n

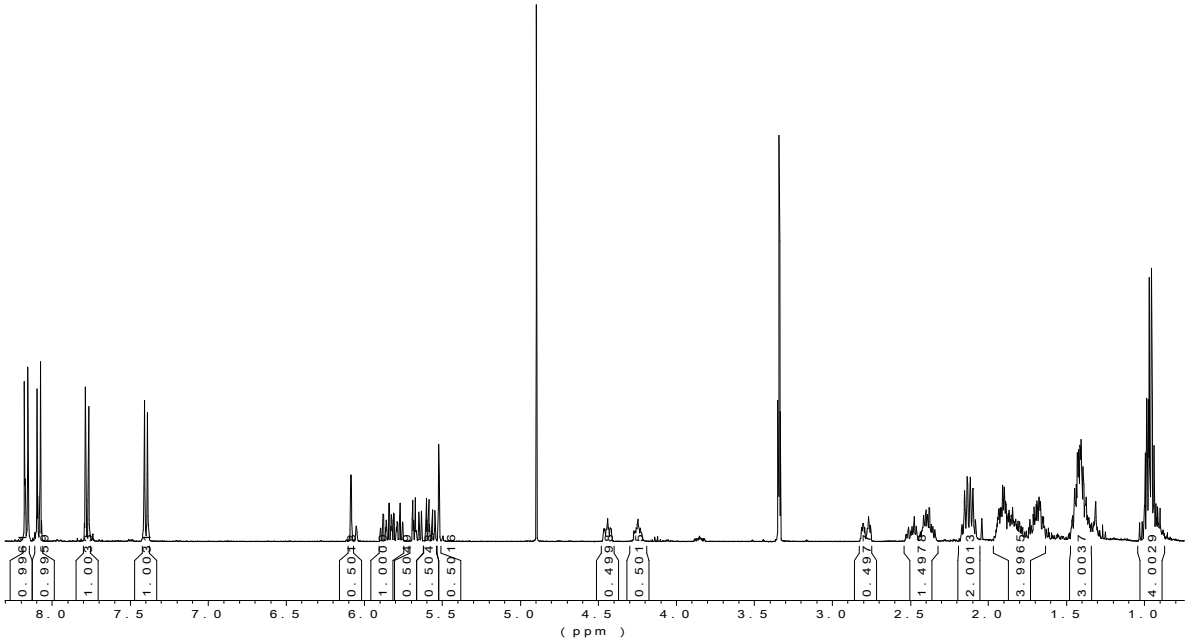
11

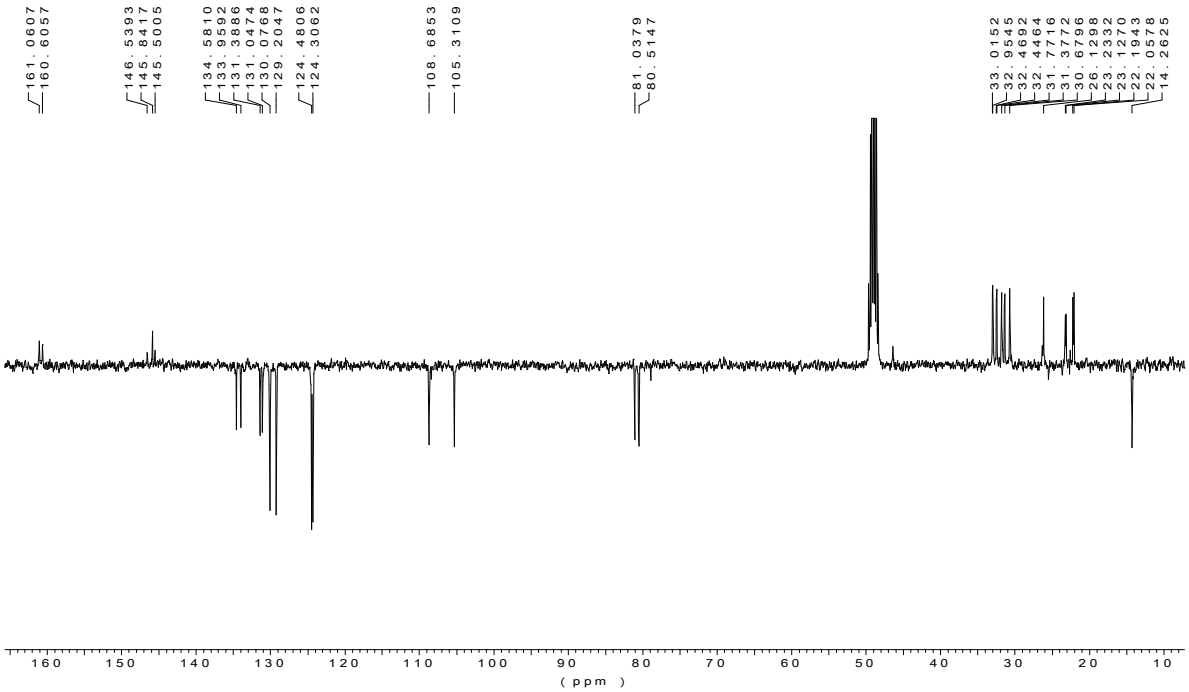

0.40
1.60
1.60
0.39
0.80
0.99
0.99
0.20
0.20
0.80
2.39
0.60
0.99
2.99
8.00
3.02
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

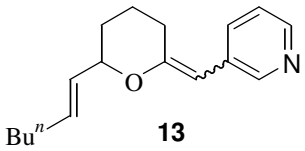

159.2711
155.5630
133.6028
131.7754
130.8351
130.1905
114.6531
110.4901
81.4626
55.6351
33.0531
32.4919
25.9782
23.3014
23.2408
14.2701
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
(ppm)


NO2
O
Bu^n

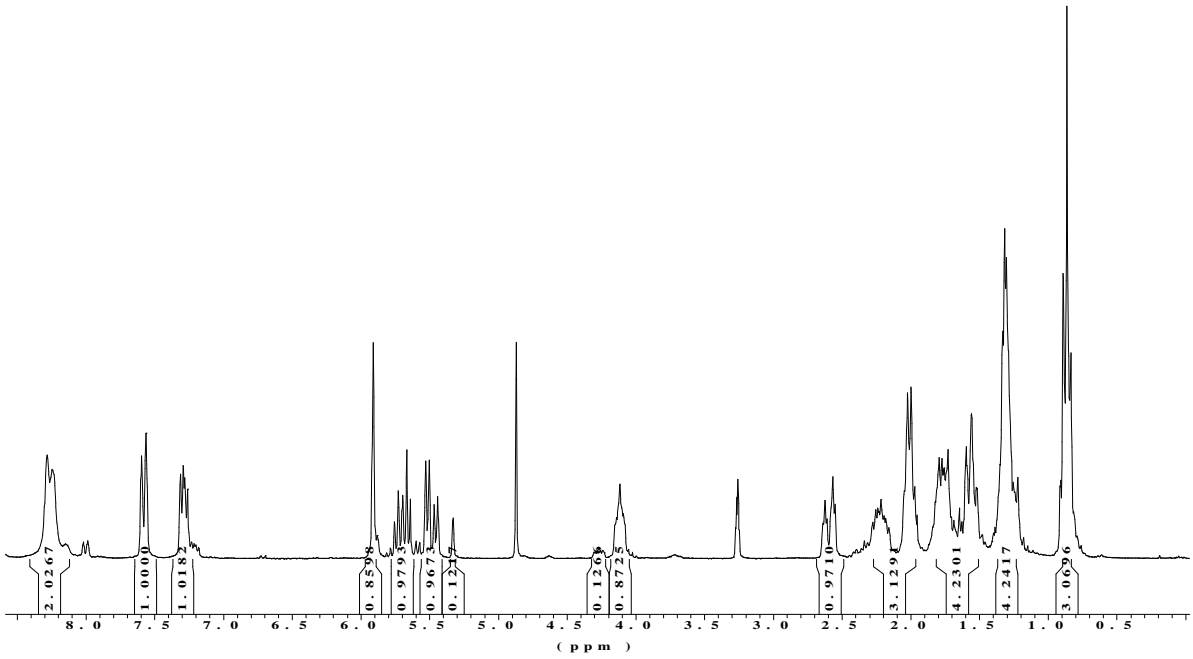
12

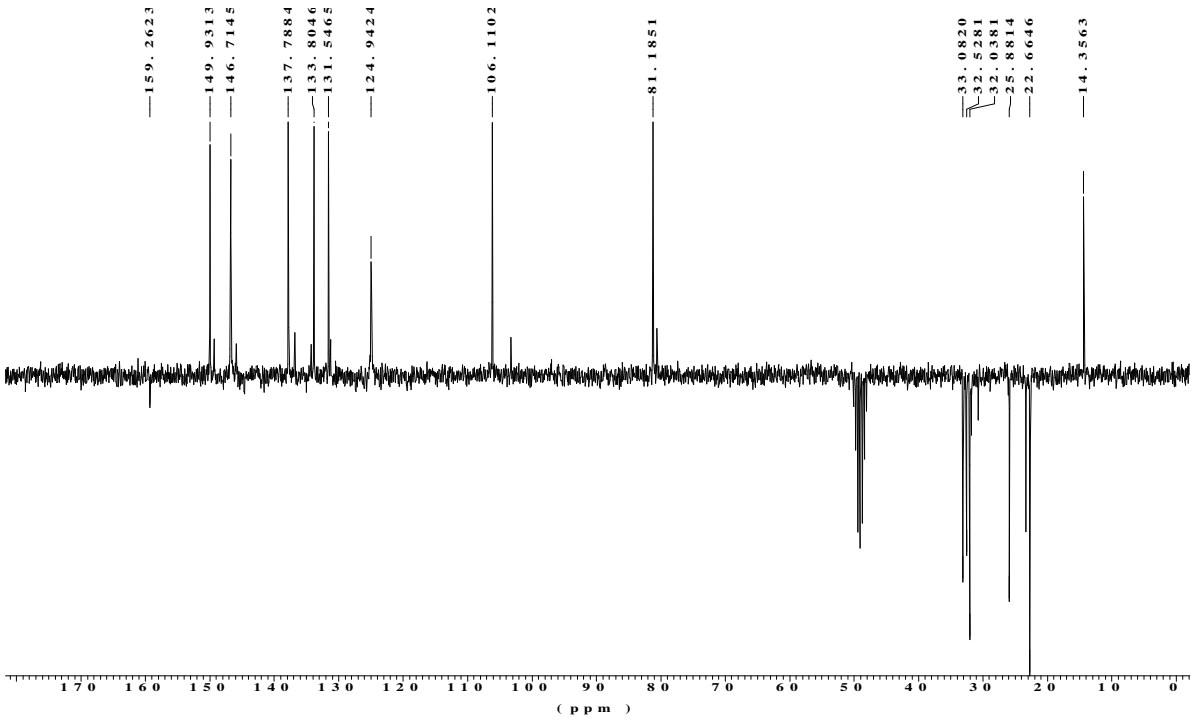

0.996
0.995
1.003
1.003
0.501
1.000
0.504
0.507
0.516
0.499
0.501
0.497
1.497
2.001
3.996
3.003
4.002
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)


161.0607
160.6057
146.5393
145.8417
145.5005
134.5810
133.9592
131.3886
131.0474
130.0768
129.2047
124.4806
124.3062
108.6853
105.3109
81.0379
80.5147
33.0152
32.9545
32.4692
32.4464
31.7716
31.3772
30.6796
26.1298
23.2332
23.1270
22.1943
22.0578
14.2625
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


N
O
Bu^n

13


2.0267
1.0000
1.0187
0.8598
0.9793
0.9675
0.1217
0.1269
0.8725
0.9710
3.1291
4.2301
4.2417
3.0696
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)


159.2623
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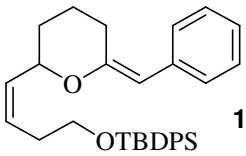
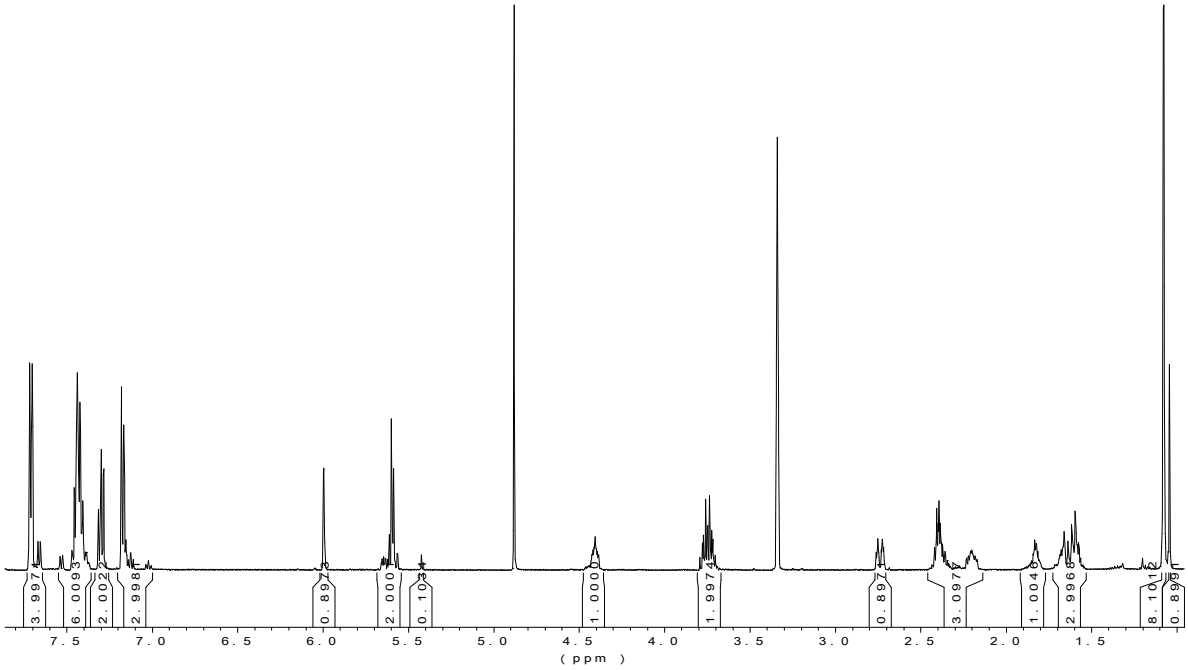
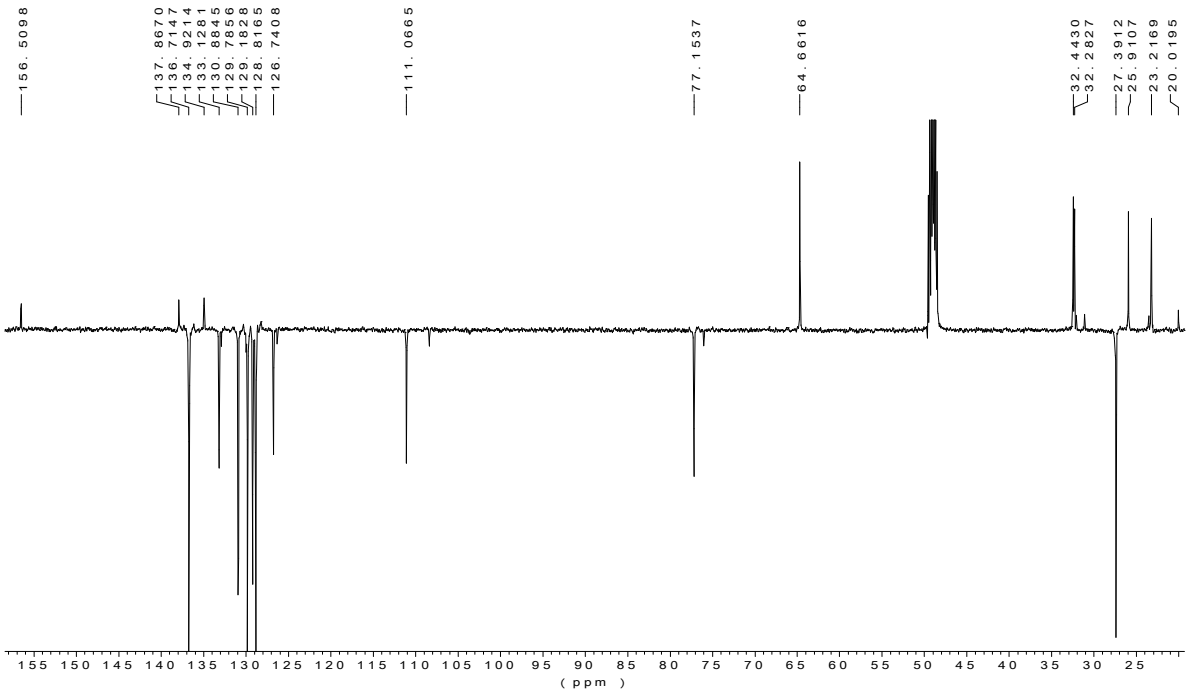
146.7145
137.7884
133.8046
131.5465
124.9424
106.1102
81.1851
33.0820
32.5281
32.0381
25.8814
22.6646
14.3563
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


O
OTBDPS

15


3.997
6.009
2.002
2.998
0.897
2.000
0.103
1.000
1.997
0.897
3.097
1.004
2.996
8.101
0.899
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
(ppm)


156.5098
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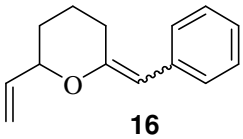
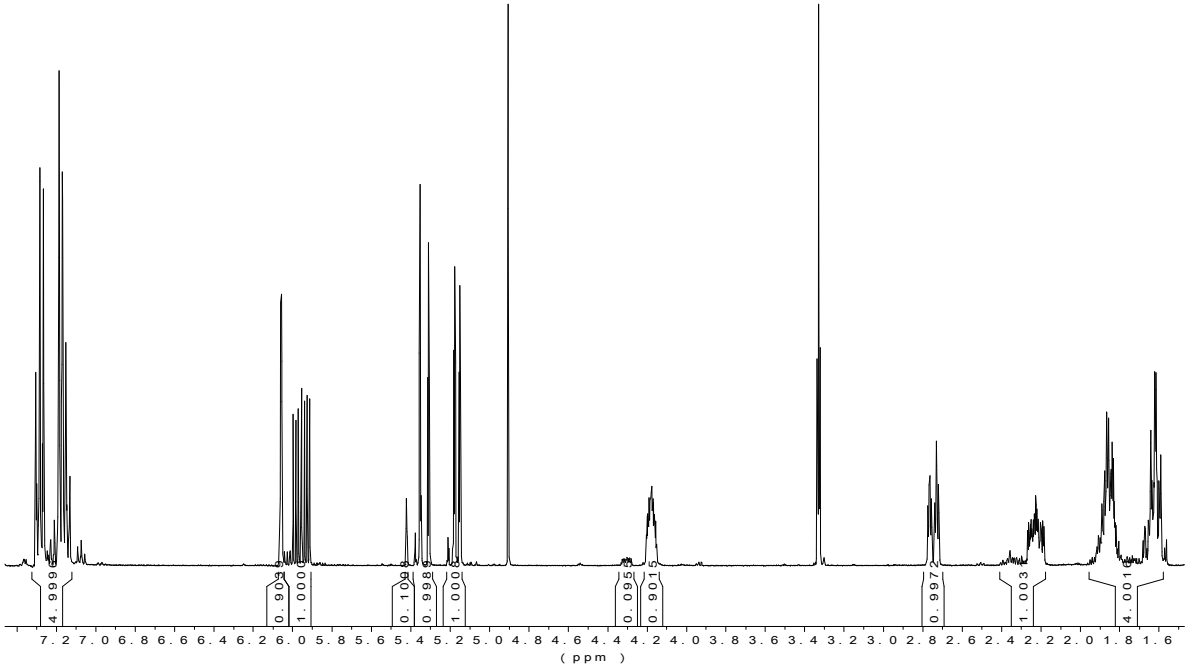
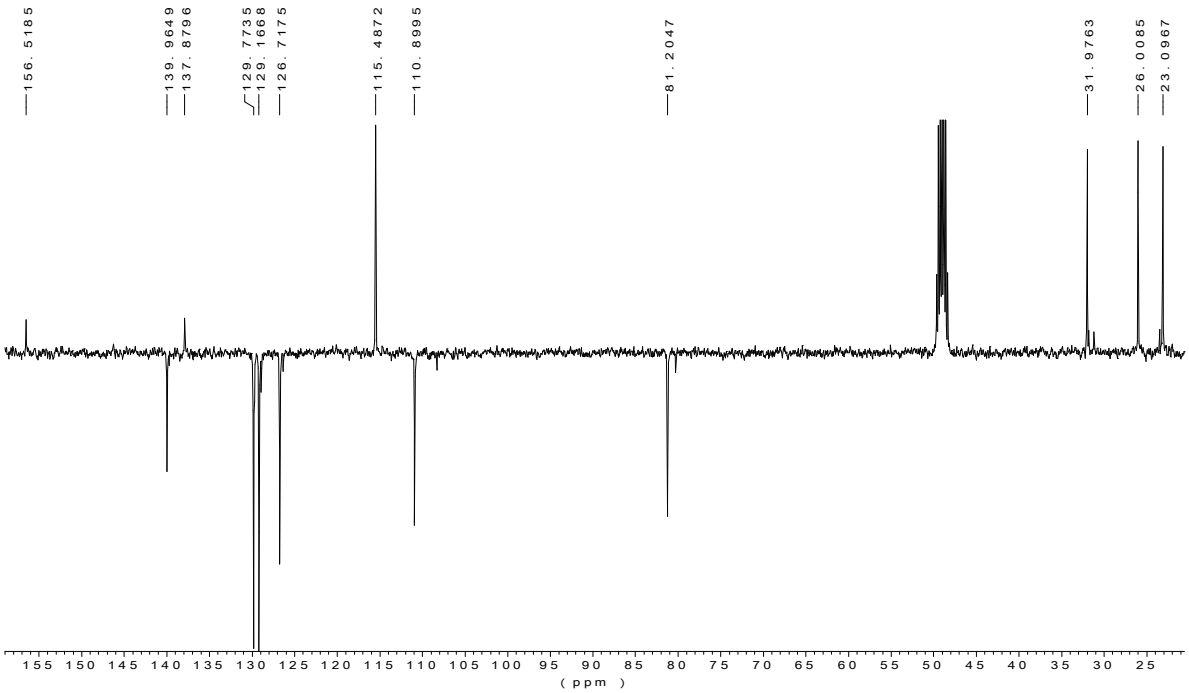
136.7147
134.9214
133.1281
130.8845
129.7856
129.1828
128.8165
126.7408
111.0665
77.1537
64.6616
32.4430
32.2827
27.3912
25.9107
23.2169
20.0195
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
(ppm)



16


4.999
0.904
1.000
0.109
0.998
1.000
0.095
0.901
0.997
1.003
4.001
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
(ppm)


156.5185
139.9649
137.8796
129.7735
129.1668
126.7175
115.4872
110.8995
81.2047
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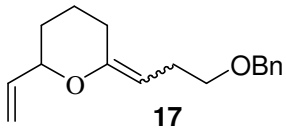
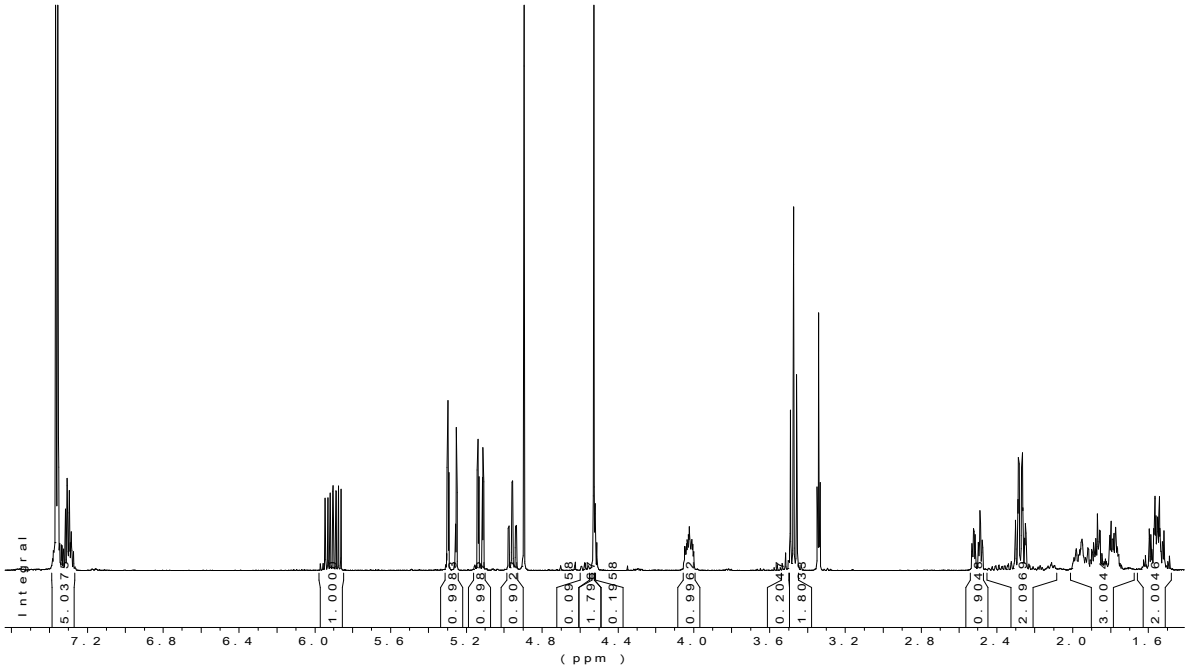
26.0085
23.0967
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
(ppm)


OBn
O

17


Integral
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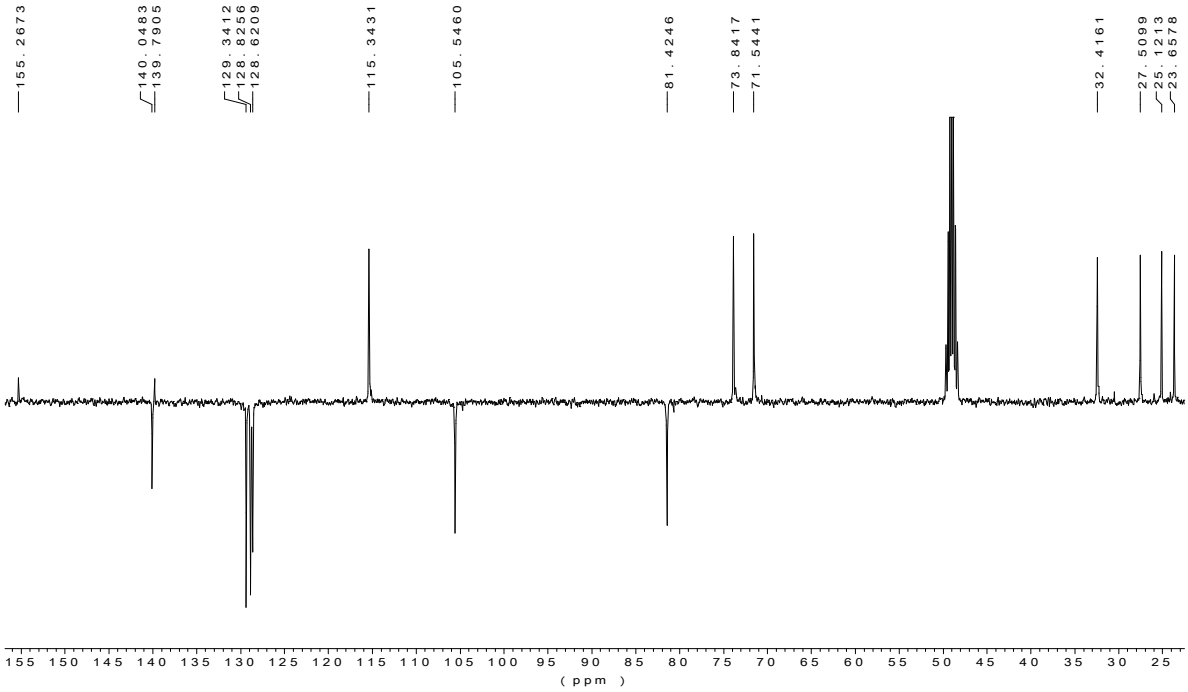
1.000
0.998
0.998
0.902
0.0458
1.798
0.1958
0.9962
0.2041
1.8035
0.9046
2.0969
3.004
2.004
7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6
(ppm)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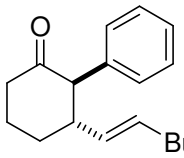
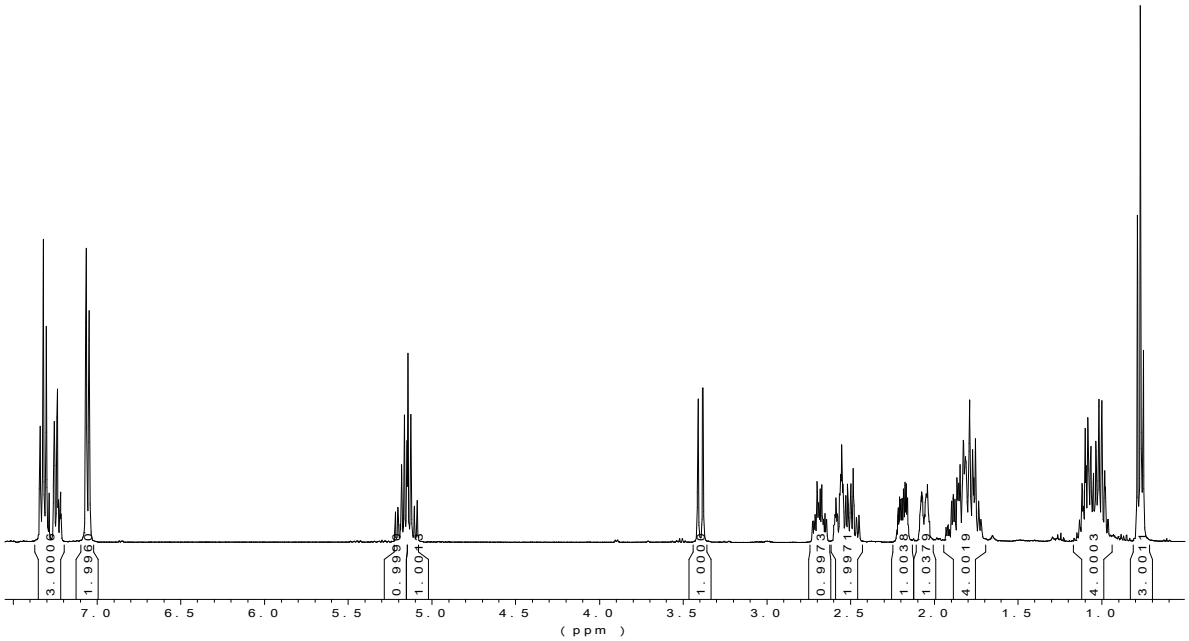
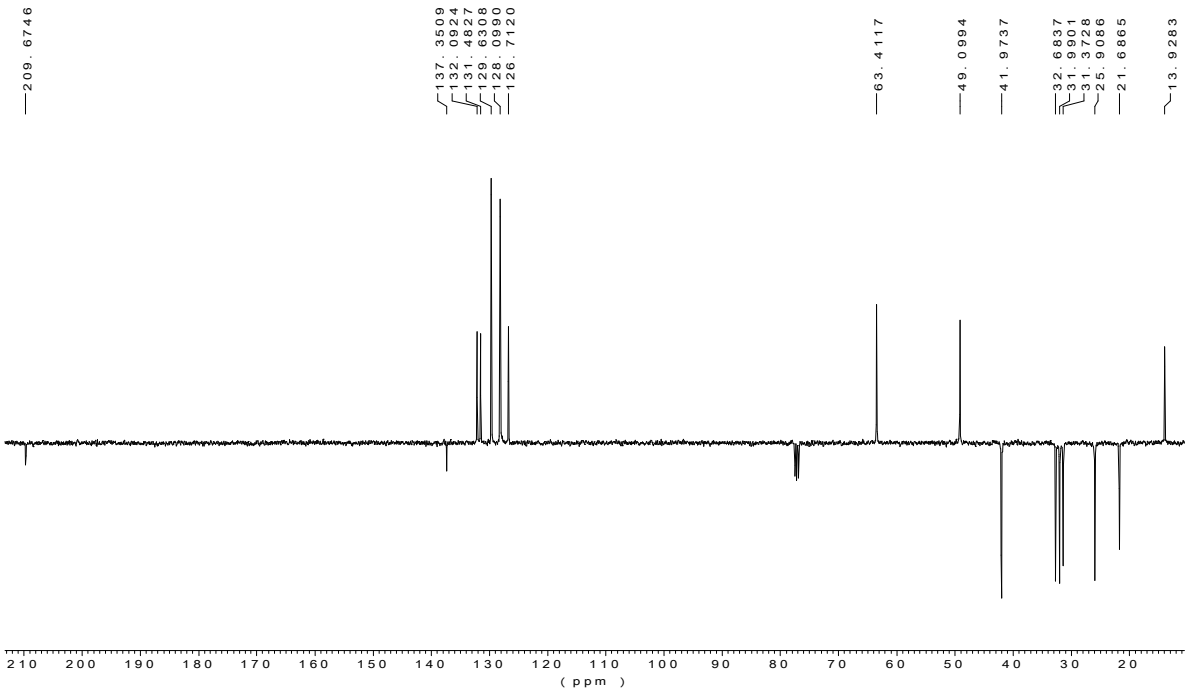
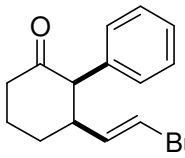
140.0483
139.7905
129.3412
128.8256
128.6209
115.3431
105.5460
81.4246
73.8417
71.5441
32.4161
27.5099
25.1213
23.6578
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
(ppm)


O
Bu^n

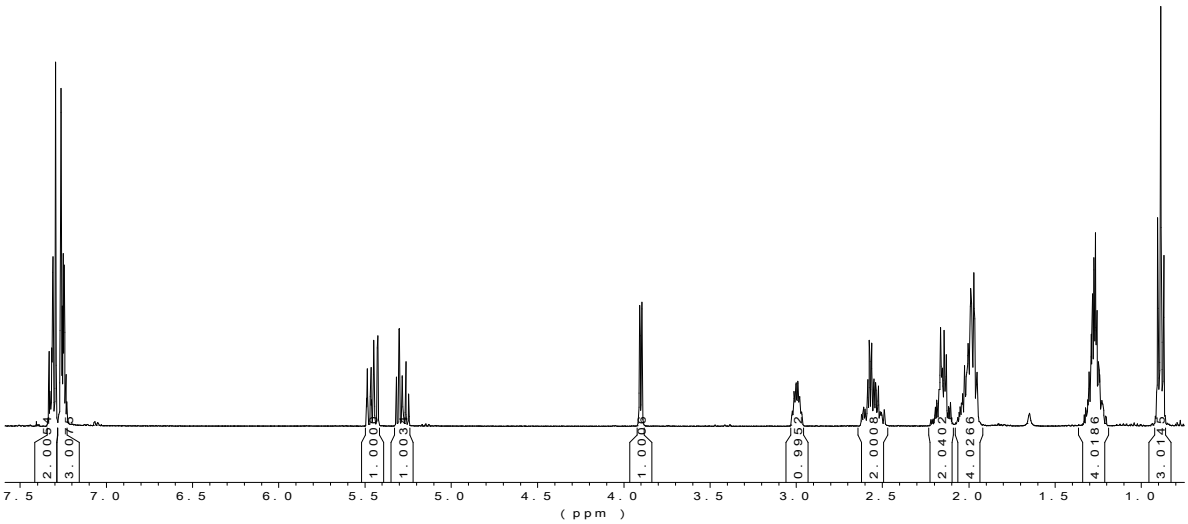
18

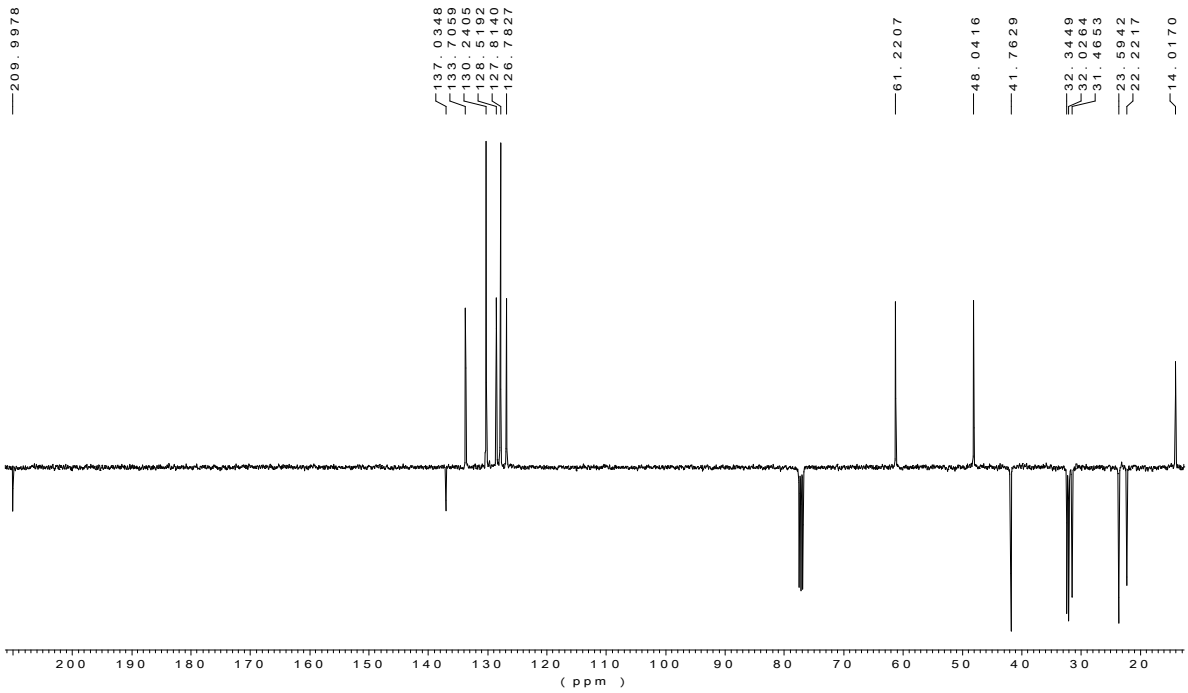

3.0006
1.996
0.9999
1.0040
1.0000
0.9973
1.9971
1.0038
1.0379
4.0019
4.0003
3.0011
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

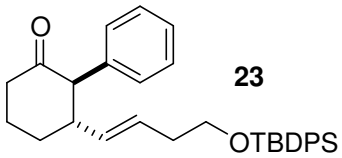

209.6746
137.3509
132.0924
131.4827
129.6308
128.0990
126.7120
63.4117
49.0994
41.9737
32.6837
31.9901
31.3728
25.9086
21.6865
13.9283
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
(ppm)


O
Bu^n

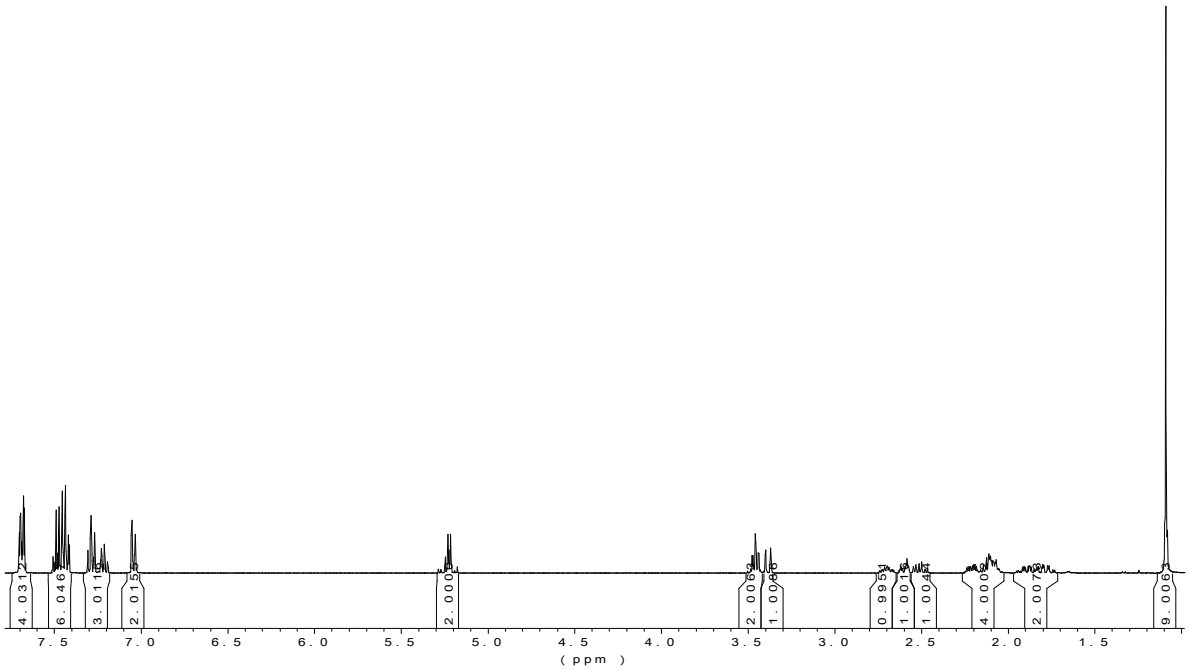
***cis*-18**

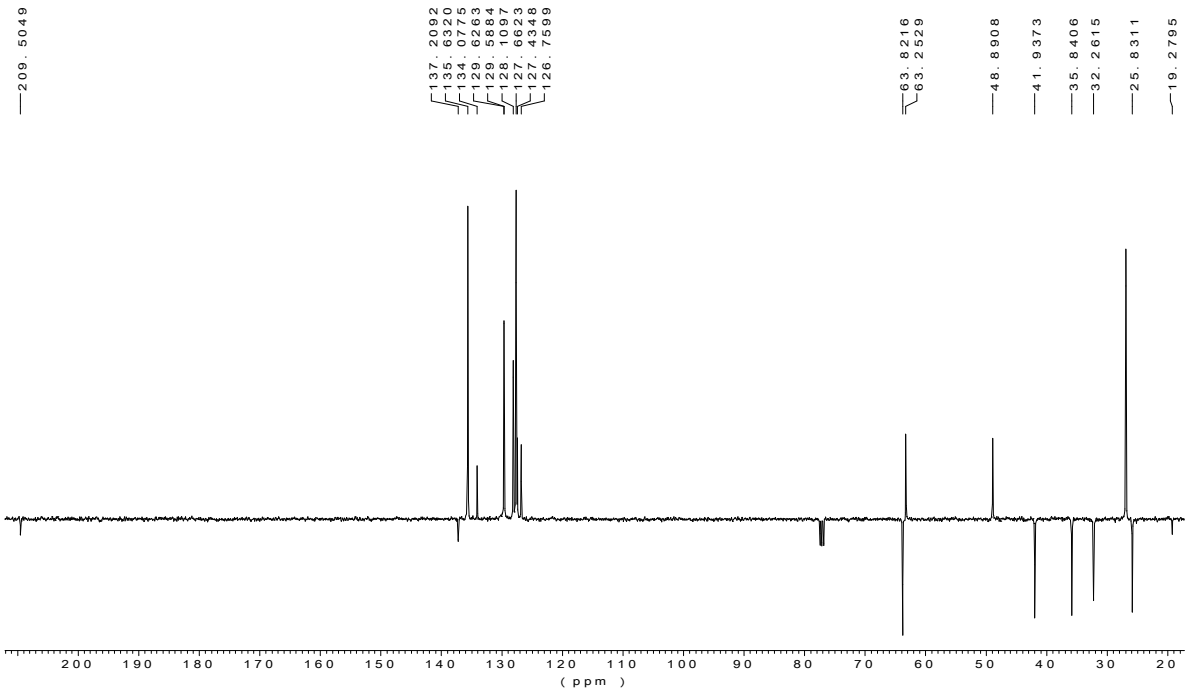

2.0054
3.0070
1.0000
1.0030
1.0000
0.9952
2.0008
2.0402
4.0266
4.0186
3.0145
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

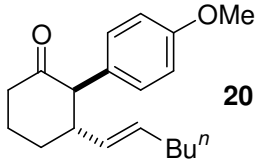

209.9978
137.0348
133.7059
130.2405
128.5192
127.8140
126.7827
61.2207
48.0416
41.7629
32.3449
32.0264
31.4653
23.5942
22.2217
14.0170
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
(ppm)


O
OTBDPS

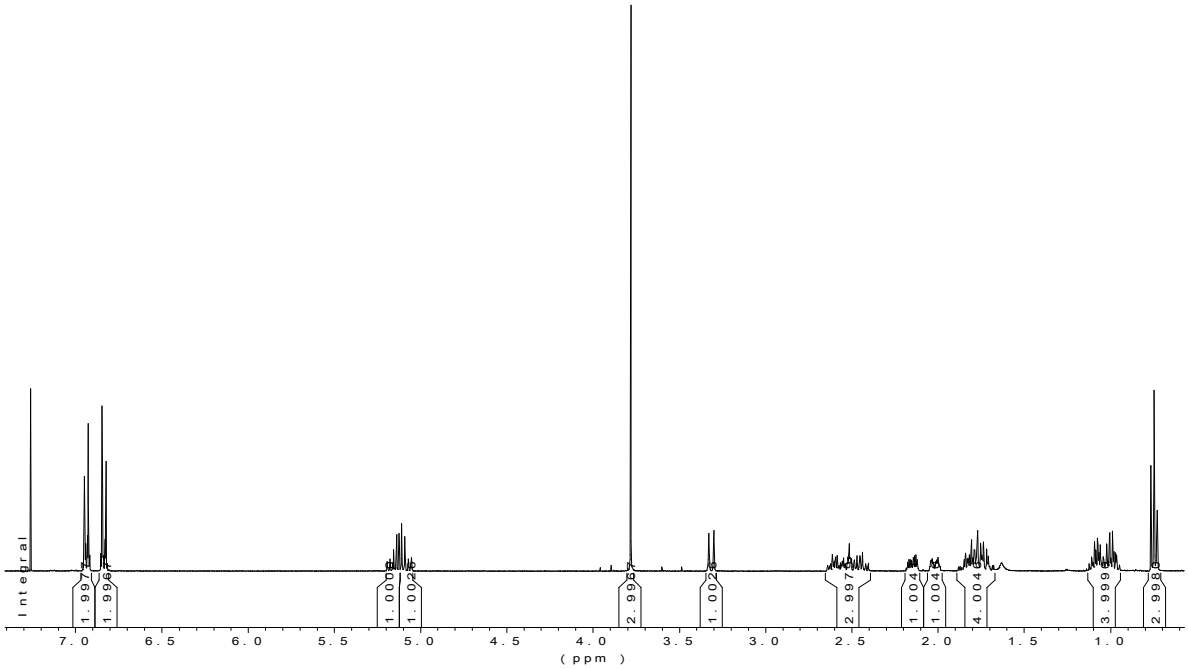
23

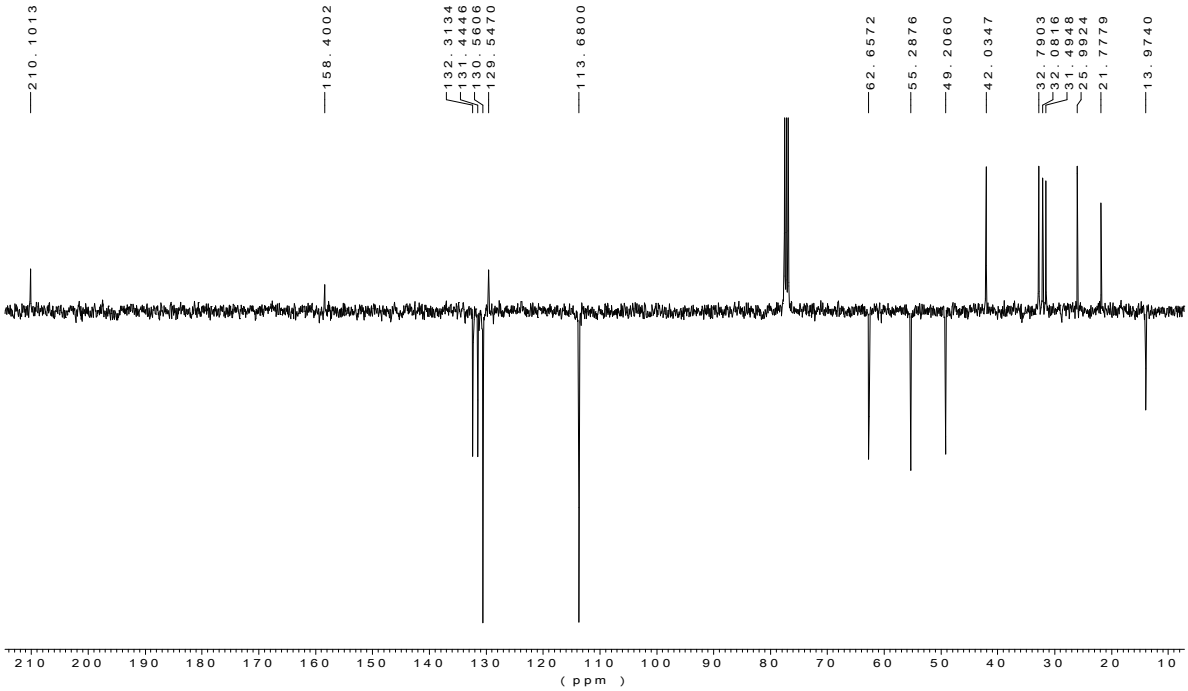

4.031
6.046
3.011
2.015
2.000
2.005
1.000
0.995
1.001
1.004
4.000
2.007
9.006
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
(ppm)

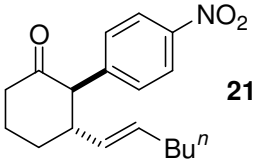

209.5049
137.2092
135.6320
134.0775
129.6263
129.5884
128.1097
127.6623
127.4348
126.7599
63.8216
63.2529
48.8908
41.9373
35.8406
32.2615
25.8311
19.2795
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
(ppm)


OMe
O
Bu^n

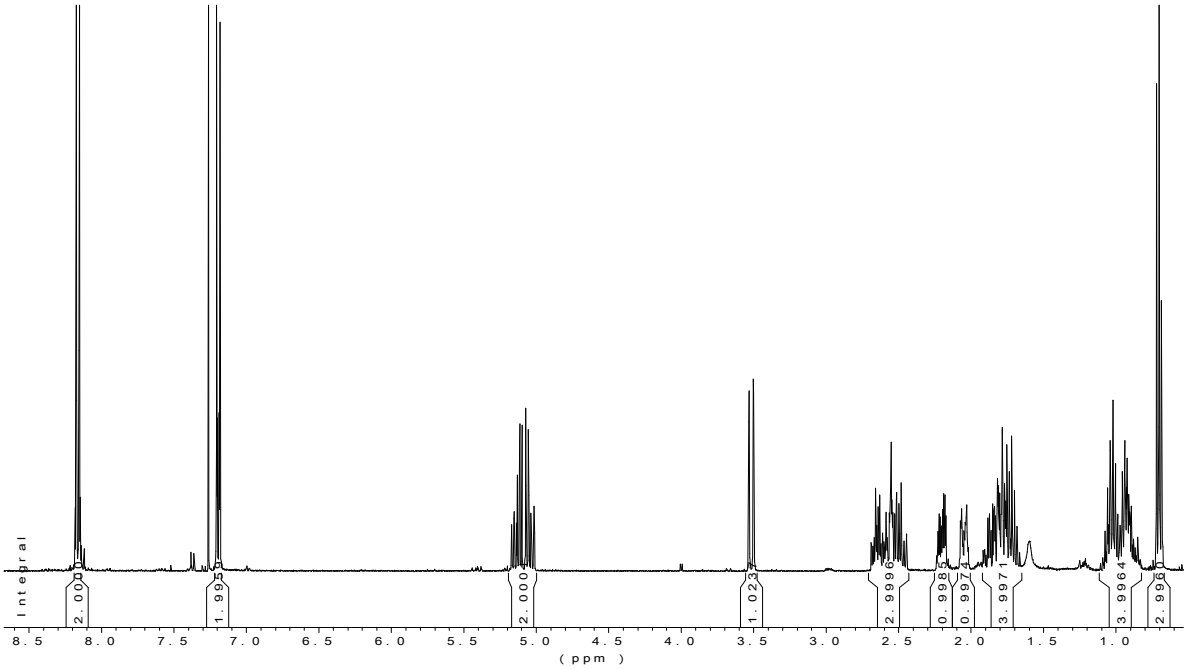
20

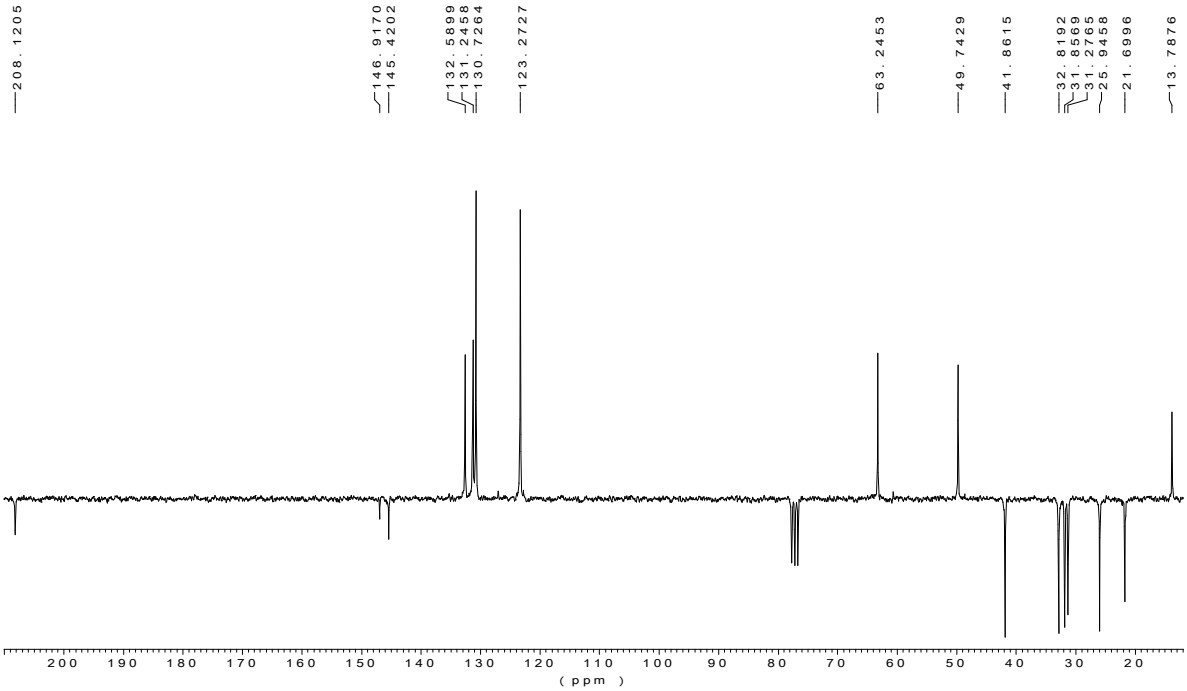

Integral
1.997
1.998
1.000
1.002
2.995
1.002
2.997
1.004
1.004
4.004
3.999
2.998
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

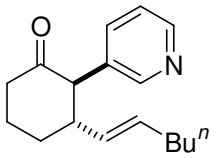

210.1013
158.4002
132.3134
131.4446
130.5606
129.5470
113.6800
62.6572
55.2876
49.2060
42.0347
32.7903
32.0816
31.4948
25.9924
21.7779
13.9740
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)


O
NO2
Bu^n

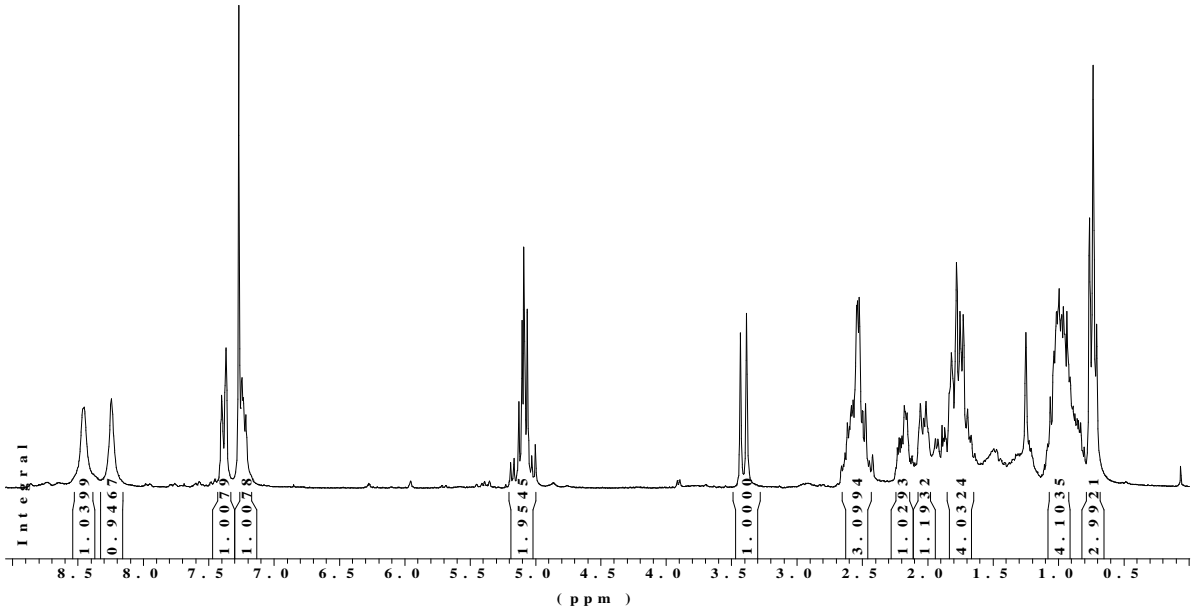
21

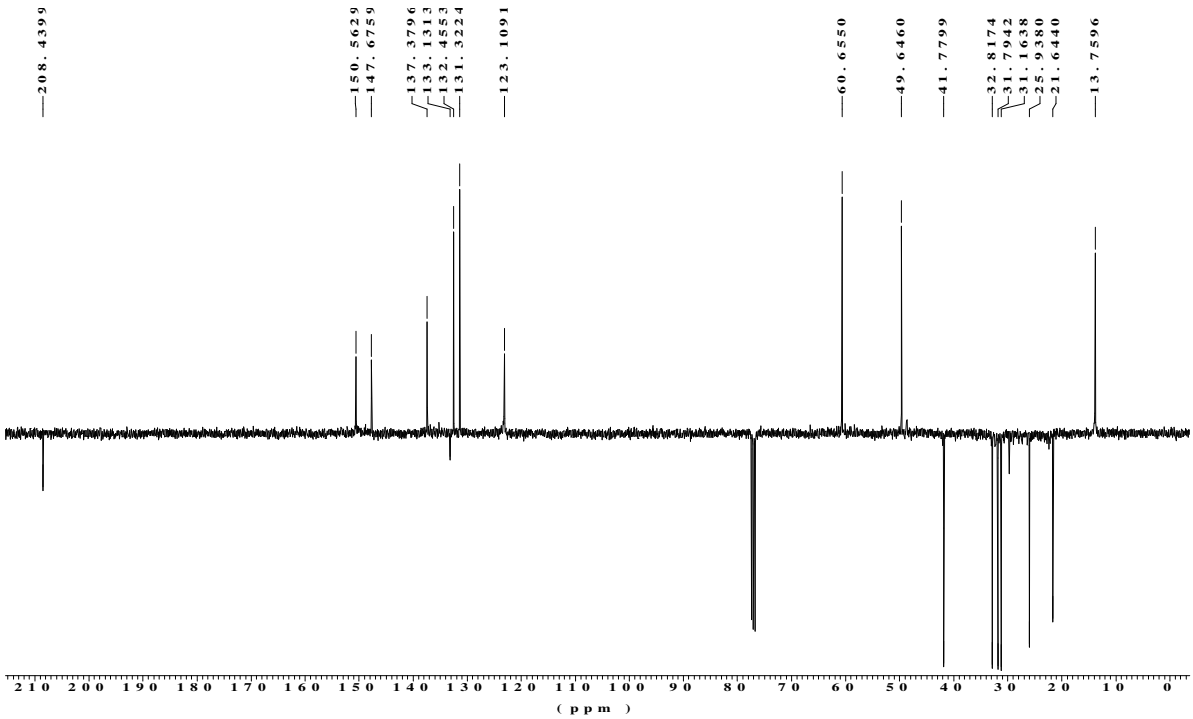

Integral
2.000
1.995
2.000
1.023
2.999
0.998
0.997
3.997
3.964
2.996
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)

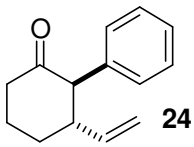

208.1205
146.9170
145.4202
132.5899
131.2458
130.7264
123.2727
63.2453
49.7429
41.8615
32.8192
31.8569
31.2765
25.9458
21.6996
13.7876
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
(ppm)



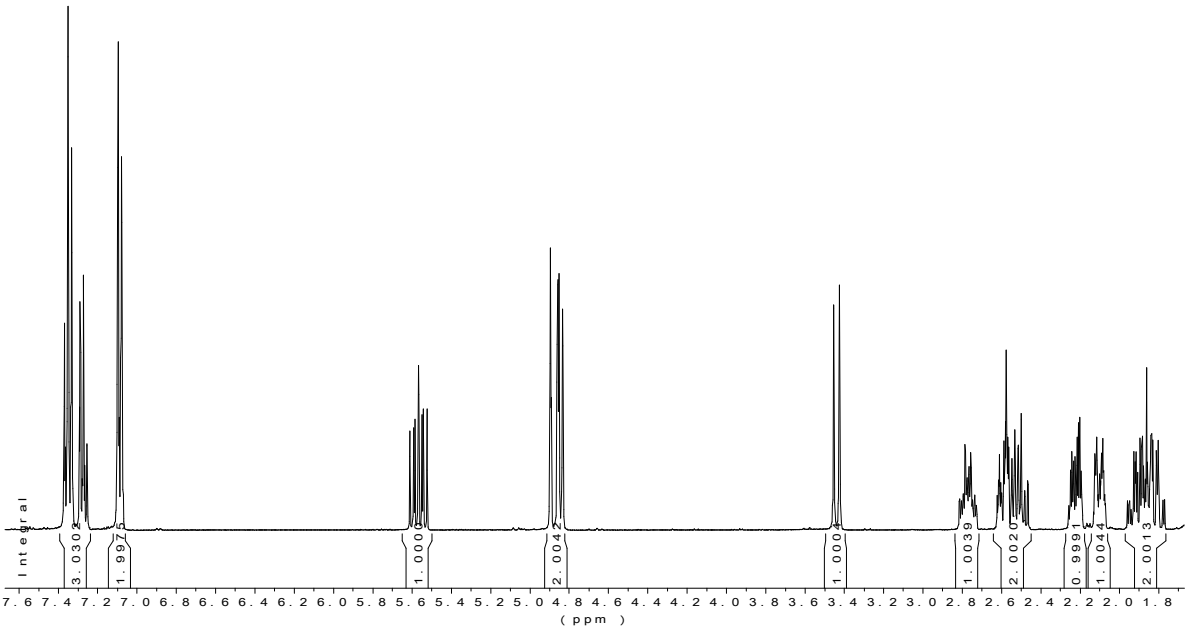
22

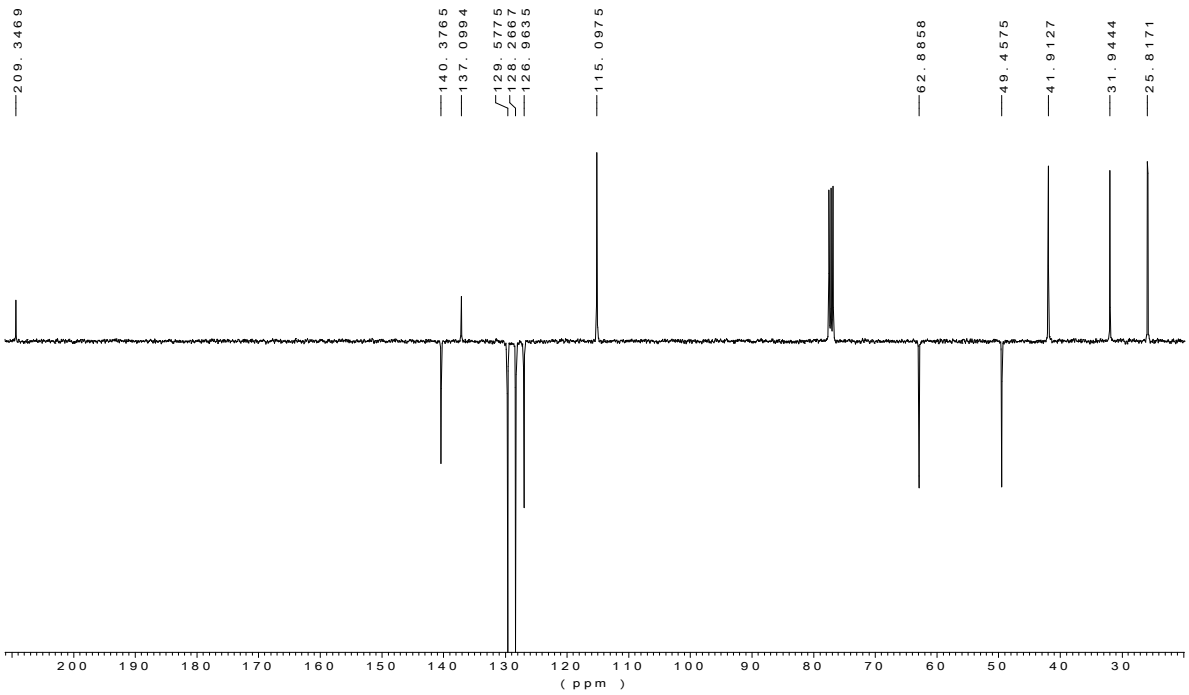

Integral
1.0399
0.9467
1.0079
1.0078
1.9545
1.0000
3.0994
1.0293
1.1932
4.0324
4.1035
2.9921
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

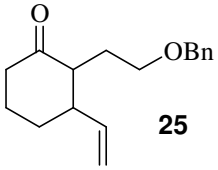

208.4399
150.5629
147.6759
137.3796
133.1313
132.4553
131.3224
123.1091
60.6550
49.6460
41.7799
32.8174
31.7942
31.1638
25.9380
21.6440
13.7596
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)



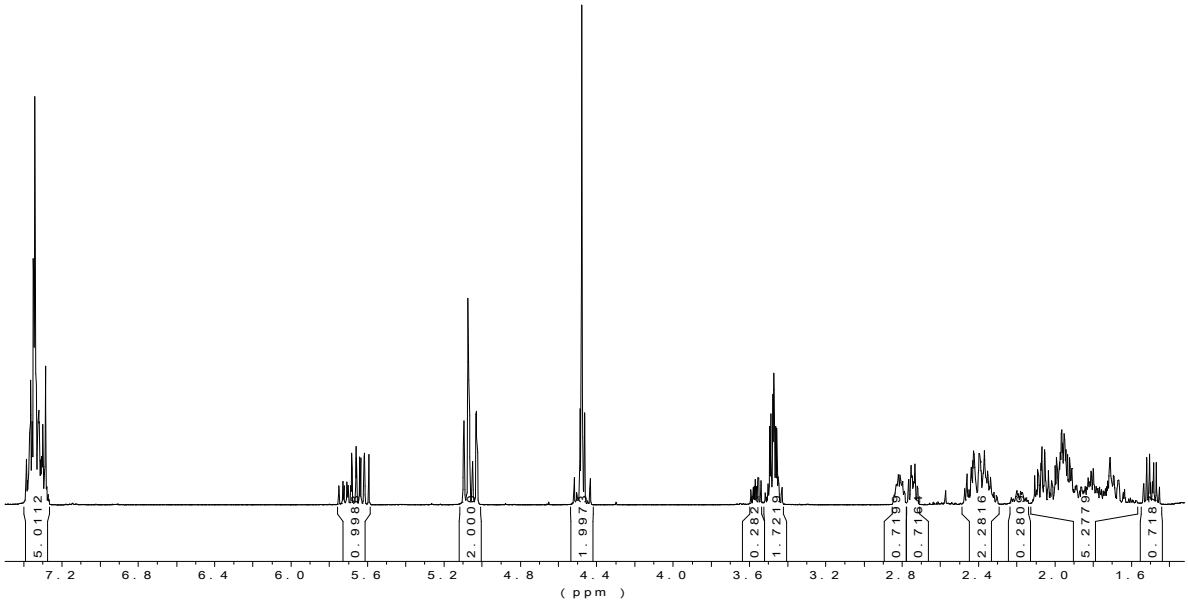
24

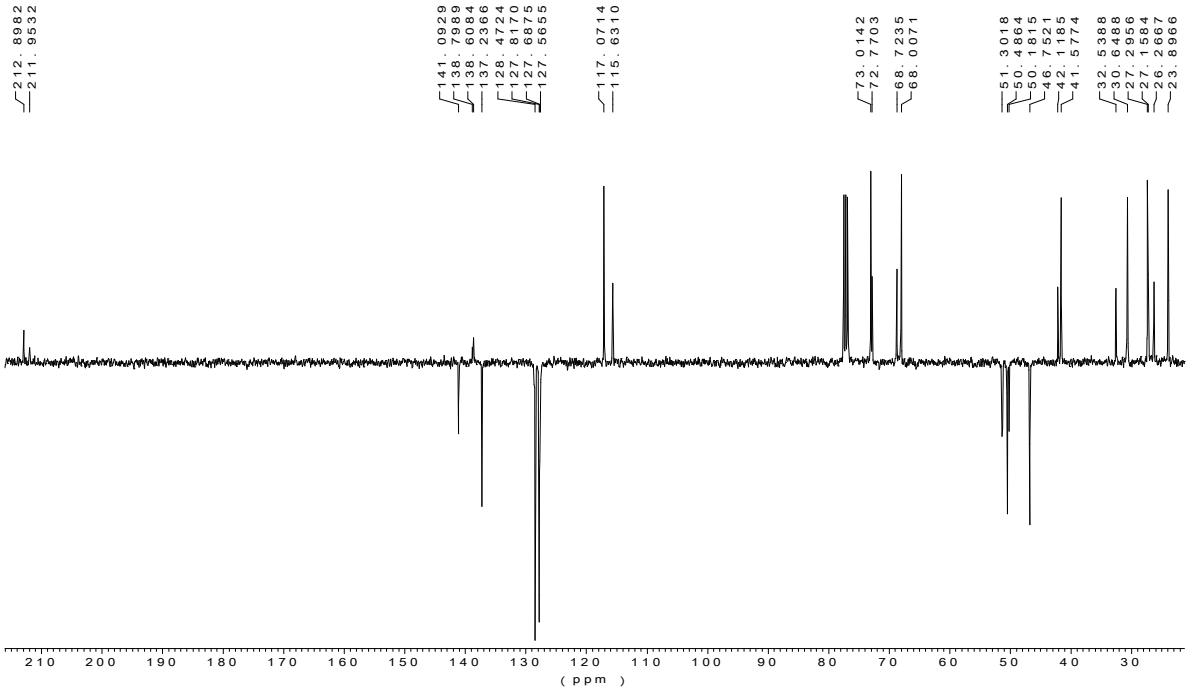

Integral
3.030
1.997
1.000
2.004
1.000
1.0039
2.0020
0.9991
1.004
2.0013
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
(ppm)

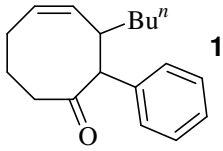

209.3469
140.3765
137.0994
129.5775
128.2667
126.9635
115.0975
62.8858
49.4575
41.9127
31.9444
25.8171
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
(ppm)


O
OBn

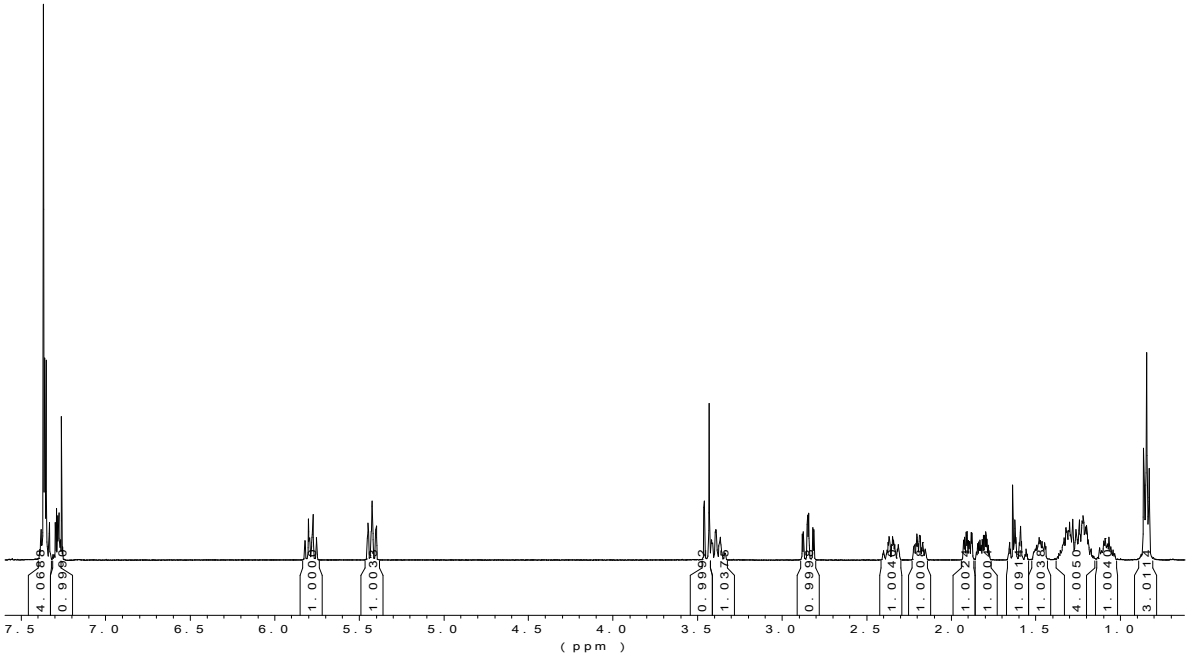
25

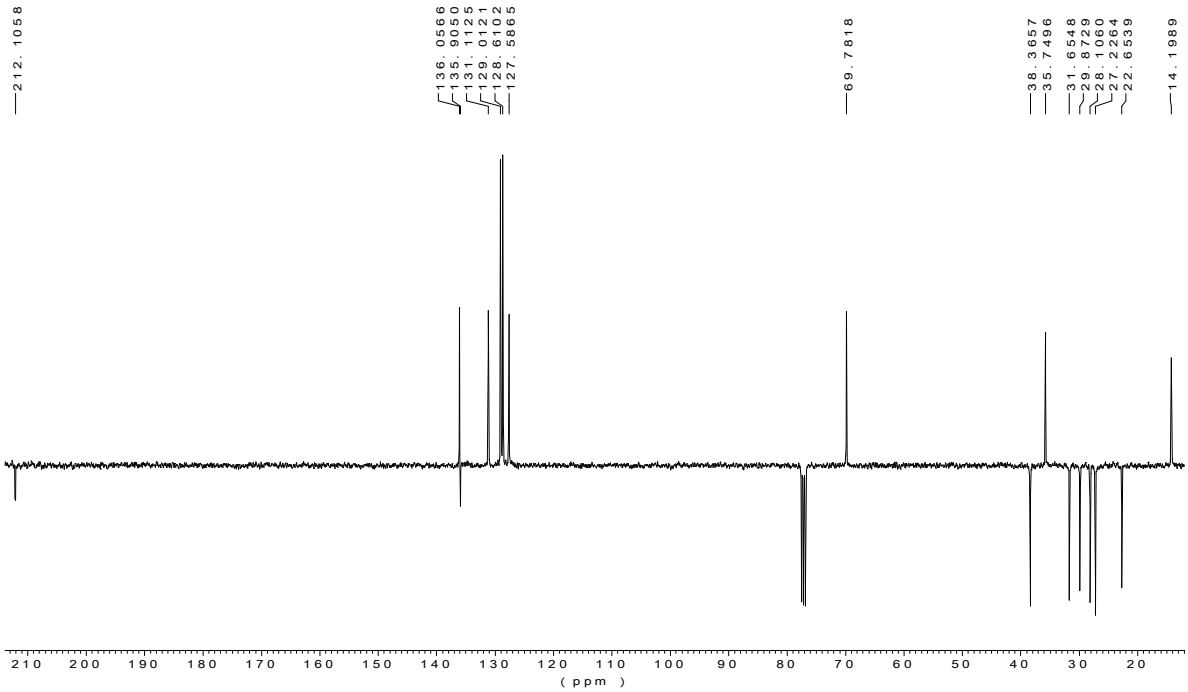

5.0112
0.998
2.000
1.997
0.282
1.7219
0.7199
0.716
2.2816
0.280
5.2779
0.718
7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6
(ppm)


212.8982
211.9532
141.0929
138.7989
138.6084
137.2366
128.4724
127.8170
127.6875
127.5655
117.0714
115.6310
73.0142
72.7703
68.7235
68.0071
51.3018
50.4864
50.1815
46.7521
42.1185
41.5774
32.5388
30.6488
27.2956
27.1584
26.2667
23.8966
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
(ppm)


Bu^n
O

19


4.0689
0.9993
1.0003
1.0033
0.9990
1.0376
0.9993
1.0042
1.0000
1.0021
1.0000
1.0911
1.0033
4.0050
1.0041
3.0111
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)


212.1058
136.0566
135.9050
131.1125
129.0121
128.6102
127.5865
69.7818
38.3657
35.7496
31.6548
29.8729
28.1060
27.2264
22.6539
14.1989
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
(ppm)

4. References

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[2] a) Meek, S. J.; Pradaux, F.; Demont, E.H.; Harrity, J.P.A. *J. Org. Chem.* **2007**, *72*, 3467; b) Meek, S. J.; Pradaux, F.; Carbery, D.R.; Demont, E.H.; Harrity, J.P.A. *J. Org. Chem.* **2005**, *70*, 10046.
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[5] (a) Lieberknecht, A.; Griesser, H.; Kramer, B.; Bravo, R.D.; Colinas, P.A.; Grigera, R.J. *Tetrahedron*, **1999**, *55*, 6475. (b) Colinas, P.A.; Jäger, V.; Lieberknecht, A.; Bravo, R.D. *Tetrahedron Lett.* **2003**, *44*, 1071.
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