Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Pd-Catalyzed Kinetic Resolution of Cyclic Enol Ethers. An Enantioselective Route to Functionalized Pyrans.

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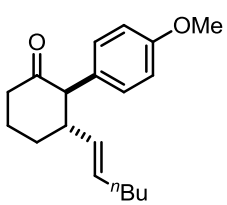
General Information

Unless otherwise stated, reactions were performed in flame-dried glassware under an inert atmosphere of argon or nitrogen using dry, deoxygenated solvents. Reaction progress was monitored by thin-layer chromatography (TLC) or ^{1}H NMR spectroscopy. 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). 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, MeOD: 3.34 ppm, DMSO-*d*: 2.54 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, MeOD: 49.9 ppm, DMSO-*d*: 40.4 ppm). Infrared (FTIR) spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, υmax 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 GCMS 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).

The following compounds were not numbered in the manuscript, but have been assigned numbers in the SI for convenience:



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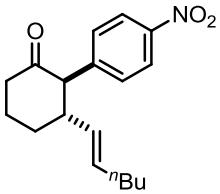

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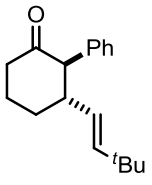

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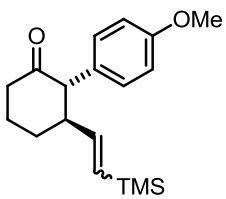

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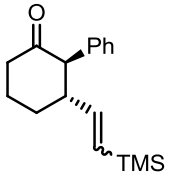

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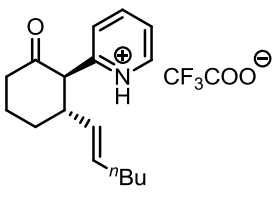

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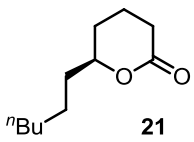

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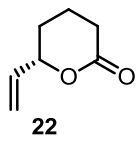

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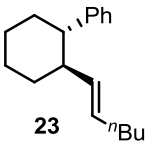

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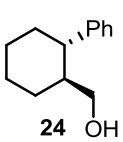

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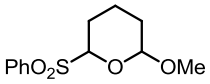
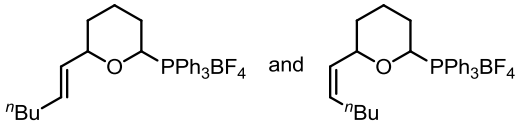
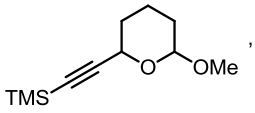
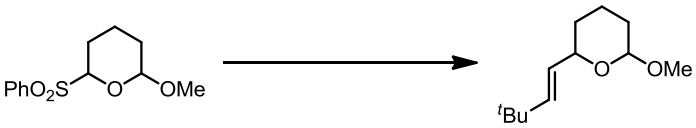
Synthesis of cyclic enol ethers

	Prepared according to literature methods.[1]
	Prepared according to literature methods.[2]
	Prepared according to literature methods.[3]

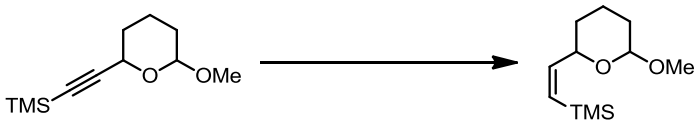
Preparation of (*E*)-2-(hex-1-enyl)-6-methoxytetrahydro-2*H*-pyran



To a solution of DIBAL (1 M in toluene, 71.0 mL, 71.0 mmol) was added dropwise at 0 °C neat 3,3-dimethyl-1-butyne (5.0 mL, 60.8 mmol). The reaction was stirred at 55 °C for 4 h. After this time, the reaction was cooled to -78 °C and a solution of 2-(benzenesulphonyl)tetrahydro-6-methoxy-2*H*-pyran (13 g, 50.7 mmol) in anhydrous DCM (25 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 as removed and the reaction stirred for overnight. The reaction mixture was then quenched slowly with H_2O and 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 (96 : 4 / petroleum ether : EtOAc) to give the desired pyran as a yellow oil (7.5 g, 75%) containing an inseparable 2.3 : 1 / *trans* : *cis* mixture of diastereoisomers; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.68 (1H, dd, *J* = 16.0, 1.0 Hz, C-alkene-*H*), 5.46-5.34 (0.7H, dd, *J* = 16.0, 6.5 Hz, *trans* CH-alkene-*H* and 0.3H, m, *cis* CH-alkene-*H*), 4.75 (0.7H, br, OC*H*OMe), 4.35 (0.3H, dd, *J* = 9.0, 2.0 Hz, *cis* OC*H*OMe), 4.16-4.11 (0.7H, m, *trans* pyran-OC*H*), 3.88-3.84 (0.3H, m, *cis* pyran-OC*H*), 3.51 (0.9H, s, *cis* OCH_3), 3.38 (2.1H, s, *trans* OCH_3), 1.89-1.78 (1H, m, CH_2), 1.67-1.57 (4H, m, CH_2), 1.47-1.37 (1H, m, CH_2), 1.02 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): Major isomer only: δ 143.7, 126.5, 103.8, 99.3, 70.3, 55.2, 32.1, 32.0, 30.2, 16.7; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2951 (s), 2867 (m), 2831 (w), 1712 (m), 1461 (m), 1363 (m), 1193 (m), 1126 (m), 1059 (m), 1016 (s), 946 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{12}H_{23}O_2$: 199.1699, found 199.1698.

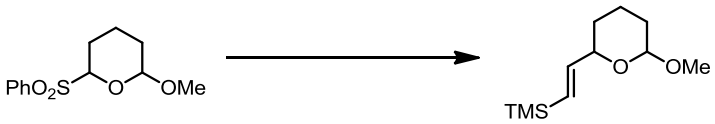
[1] D.S. Brown, M. Bruno, R.J. Davenport, S.V. Ley, *Tetrahedron* 1989, **45**, 4293.
[2] J. C. R., Brioche; T. A., Barker; D. J., Whatrup; M. D. Barker and J. P. A. Harrity, *Org. Lett*., 2010, **12**, 4832.
[3] S.J. Meek, F. Pradaux, D.R. Carbery, E.H. Demont and J.P.A. Harrity, *J. Org. Chem*., 2005, **70**, 10046.

Preparation of (*Z*)-(2-(6-methoxytetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



To a solution of ((6-methoxytetrahydro-2*H*-pyran-2-yl)ethynyl)trimethylsilane[1] (6.8 g, 32.1 mmol) in THF (42 mL) at 0 °C, DIBAL-H (1 M in hexane, 42.0 mL, 42.0 mmol) was added slowly. After 15 min the reaction was warmed to room temperature for 30 min then heated at 65°C for 38 h. The reaction mixture was then quenched slowly with H_2O (around 100 mL) at room temperature, and the mixture was 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 (98 : 2 / petroleum ether : EtOAc) to give the desired pyran as a yellow oil (4.9 g, 72%) containing *trans* isomer; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.25 (1H, dd, *J* = 14.5, 8.5 Hz, CH-alkene-*H*), 5.65 (1H, dd, *J* = 14.5, 1.0 Hz, TMS-alkene-*H*), 4.75 (1H, br, OC*H*OMe), 4.39 (1H, ddd, *J* = 11.0, 8.5, 2.5 pyran-OC*H*), 3.40 (3H, s, OCH_3), 1.91-1.82 (1H, m, CH_2), 1.70- 1.54 (4H, m, CH_2), 1.48- 1.38 (1H, m, CH_2), -0.16 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 148.2, 130.6, 69.7, 98.4, 54.8, 31.4, 29.3, 17.7, 0.42; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2949 (s), 1612 (m), 1373 (m), 1248 (m), 11125 (s) 1025 (s), 839 (s); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{11}H_{22}O_2Si$: 214.1389, found 214.1379.

Preparation of (*E*)-(2-(6-methoxytetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane

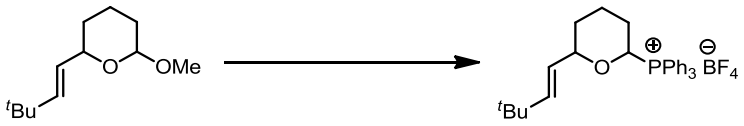


To a solution of (*E*)-(2-bromoethenyl)trimethylsilane (10 g, 55.8 mmol) in Et_2O (180 mL) at -78 °C, ^{t}BuLi (1.7 M in pentane, 79.0 mL, 133.9 mmol) was added dropwise. After 10 min the reaction was warmed to 0 °C and stirred for further 1 h. Neat Et_2AlCl (7.6 mL, 60.8 mmol) was added to the reaction at 0 °C. After 15 min, the reaction mixture was cooled to -78 °C and a solution of 2-(benzenesulphonyl)tetrahydro-6-methoxy-2*H*-pyran (13 g, 50.7 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 as removed and the reaction stirred for overnight. The reaction mixture was then quenched slowly with H_2O (around 100 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 (98 : 2 / petroleum ether : EtOAc) to give the desired pyran as a yellow oil (6.3 g, 58%) containing an inseparable 1 : 1.4 / *trans* : *cis* mixture of diastereoisomers; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.08 (0.4H, dd, *J* = 19.0, 4.5 Hz, *trans* CH-alkene-*H*), 6.02 (0.6H, dd, *J* =

19.0, 5.0 Hz, *cis* CH-alkene-*H*), 5.89 (0.6H, dd, *J* = 19.0, 1.5 Hz, *cis* TMS-alkene-*H*), 5.86 (0.4H, dd, *J* = 19.0, 1.0 Hz, *trans* TMS-alkene-*H*), 4.78 (0.4H, br, *trans* OC*H*OMe), 4.36 (0.6H, dd, *J* = 9.5, 2.0 Hz, *cis* OC*H*OMe), 4.20- 4.16 (0.4H, m, *trans* pyran-OC*H*), 3.92-3.87 (0.6H, m, *cis* pyran-OC*H*), 3.52 (1.8H, s, *cis* OCH_3), 3.37 (1.2H, s, *trans* OCH_3), 1.90-1.76 (2H, m, *trans*, *cis* CH_2), 1.70- 1.58 (2H, m, *trans*, *cis* CH_2), 1.43- 1.25 (2H, m, *trans*, *cis* CH_2), 0.07 (9H, s, *trans*, *cis* CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$) *trans* isomer: δ 146.5, 129.7, 98.5, 70.8, 54.5, 30.8, 29.4, 18.0, -1.4; *cis* isomer: δ 145.8, 129.1, 103.1, 77.8, 56.0, 30.9, 30.6, 22.0, -1.4; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2994 (s), 2830 (m), 1386 (m), 1249 (s), 1027 (s) 870 (s), 969 (m) 837 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{11}H_{22}O_2Si$: 214.1389, found 214.1398.

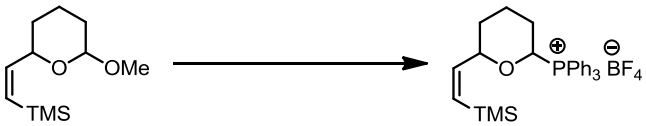
Representative Procedure for Wittig salts preparation

Preparation of (*E*)-(6-(3,3-dimethylbut-1-en-1-yl)tetrahydro-2*H*-pyran-2-yl)triphenylphosphonium tetrafluoroborate



To a solution of (*E*)-2-(3,3-dimethylbut-1-en-1-yl)-6-methoxytetrahydro-2*H*-pyran (6.7 g, 34 mmol, 1 eq.) and 4 Å molecular sieves (22 g) in MeCN (225 mL) was added $HPPh_3BF_4$ (24 g, 68 mmol, 2 eq.). The reaction mixture was refluxed overnight. The reaction mixture was then was filtered through a pad of 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 was obtained (16.5 g, 94%) as a white solid containing an inseparable 9 : 1 mixture of diastereoisomers; **M.p.** =149-151 °C; **^{1}H NMR** (400 MHz, CD_3OD): δ 7.81-7.66 (15H, m, Ar-*H*), 6.00-5.78 (1H, m, C*H*P), 5.61 (1H, d, *J* = 16.0 Hz, C-alkene-*H*), 5.23 (1H, dd, *J* = 16.0, 6.0 Hz, CH-alkene-*H*), 4.56-4.53 (0.1H, m, pyran-OC*H*), 4.34-4.30 (0.9H, m, pyran-OC*H*), 2.10-1.95 (3H, m, C*H*$_2$), 1.77-1.63 (2H, m, C*H*$_2$), 1.40-1.29 (1H, m, C*H*$_2$), 0.94 (9H, s, C*H*$_3$); **^{31}P NMR** (400 MHz, $CDCl_3$): δ 20.12; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2951 (s), 2867 (m), 1589 (m), 1440 (m), 1108 (m), 1052 (s), 691 (m); **HRMS** (EI) *m/z* $[M\text{-}BF_4]^+$ calcd for $C_{29}H_{34}OP$: 429.2347, found 429.2350.

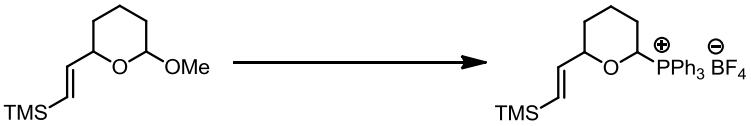
Preparation of (*Z*)-triphenyl(6-(2-(trimethylsilyl)vinyl)tetrahydro-2*H*-pyran-2-yl)phosphonium tetrafluoroborate



Following the representative procedure for Wittig salt preparation; to a solution of (*Z*)-(2-(6-methoxytetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane (1.4 g, 6.5 mmol) and 4 Å molecular sieves (2 g) in MeCN (55 mL) was added $HPPh_3BF_4$ (3.0 g, 7.8 mmol). The reaction mixture was stirred at 25 °C for overnight to give the desired Wittig salt (3.4 g, 99%) as a white solid containing an inseparable 1.3 : 1 mixture of diastereoisomers; **M.p.** = 63-64 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82-7.66 (15H, m, Ar-*H*), 7.16 (0.4H, dd, *J* = 14.0, 10.0 Hz, CH-alkene-*H*), 6.11-6.02 (1H, m, CH-alkene-*H* and TMS-alkene-*H*), 5.85-5.82 (0.4H, m, C*H*P); 5.72-5.66 (1.2H, m, TMS-alkene-*H*, C*H*P), 4.65-4.62 (0.4H, m, pyran-OC*H*), 4.44-4.40 (0.6H, m, pyran-OC*H*), 2.00-1.38 (6H, m, C*H*$_2$), 0.16 (5.4H, s, CH_3), 0.03 (3.6H, s, CH_3); **^{31}P NMR** (400

MHz, $CDCl_3$): δ 21.1, 20.1; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 3067 (m), 2953 (s), 1437 (s), 1249 (m), 1108 (s), 1057 (s), 839 (s), 688 (s); **HRMS** (EI) *m/z* $[M\text{-}BF_4]^+$ calcd for $C_{28}H_{34}OSiP$: 445.2117, found 445.2124.

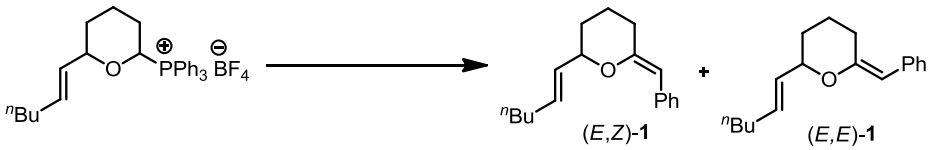
Preparation of (*E*)-triphenyl(6-(2-(trimethylsilyl)vinyl)tetrahydro-2*H*-pyran-2-yl)phosphonium tetrafluoroborate



Following the representative procedure for Wittig salt preparation; to a solution of (*E*)-(2-(6-methoxytetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane (4.5 g, 21.0 mmol) and 4 Å molecular sieves (4 g) in MeCN (200 mL) was added $HPPh_3BF_4$ (9.6 g, 27.4 mmol). The reaction mixture was stirred at 25°C for 4 h to give the desired Wittig salt (11.2 g, 100%) as a white salid containing an inseparable 1.2 : 1 mixture of diastereoisomers; **M.p.** = 42-44 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86-7.67 (15H, m, Ar-*H*), 6.32 (0.4H, dd, *J* = 19.0, 5.0 Hz, CH-alkene-*H*), 6.10-6.06 (0.6H, m, C*H*P), 5.99 (0.4H, dd, *J* = 19.0, 1.5Hz, TMS-alkene-*H*), 5.88 (0.6H, dd, *J* = 19.0, 4.5 Hz, CH-alkene-*H*), 5.68 (0.6H, dd, *J* = 19.0, 1.5 Hz, TMS-alkene-*H*), 5.57-5.54 (0.4H, m, C*H*P), 4.58 (0.4H, br, pyran-OC*H*), 4.46-4.30 (0.6H, m, pyran-OC*H*), 2.18-2.05 (1H, m, CH_2), 1.99- 1.80 (4H, m, CH_2), 1.73- 1.61 (1H, m, CH_2), 0.15 (4H, s, CH_3), 0.01 (5H, s, CH_3) ; **^{31}P NMR** (400 MHz, $CDCl_3$): δ 21.1, 20.5; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2951 (s), 2899 (m), 1484 (m), 1438 (s), 1249 (s), 1108 (s), 1056 (s), 840 (m), 722 (m); **HRMS** (EI) *m/z* $[M\text{-}BF_4]^+$ calcd for $C_{28}H_{34}OSiP$: 445.2117, found 445.2135.

Representative procedure for the Wittig reaction using LiHMDS

Preparation of (*Z*)-2-benzylidene-6-((*E*)-pent-1-enyl)tetrahydro-2*H*-pyran and (*E*)-2-benzylidene-6-((*E*)-pent-1-enyl)tetrahydro-2*H*-pyran.

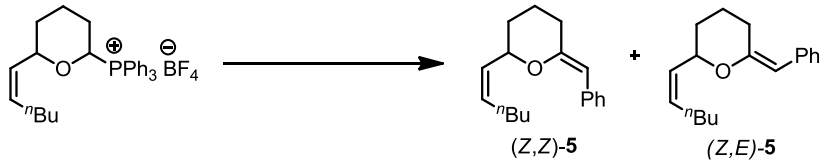


To a stirred solution of phosphonium salt (1 g, 1. 9 mmol) in THF (20 mL) at -78 ^{o}C was added dropwise LiHMDS (1.0 M in THF, 2.3 mL, 2.3 mmol, 1.2 eq). The resulting red solution was stirred at -78 ^{o}C for 5 min, then the dry-ice bath was removed and stirring continued for 10 min before allowing the mixture to reach room temperature. Benzaldehyde (250 mg, 2.3 mmol, 1.2 eq) was then added *via* syringe and the resulting yellow solution was stirred at room temperature overnight. Water (5 mL) then H_2O_2 (1 mL) were added and the mixture stirred at room temperature for 1 h. The reaction mixture was quenched with water and extracted with diethyl ether. The ether layer was washed with a 3: 3: 1 / brine: water: methanol mixture (3 x 25 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was purified *via* column chromatography on Florisil® (99: 1 / petroleum ether: EtOAc) to give a mixture of enol ethers as a colourless oil (357 mg, 72% yield) containing a 1: 1.8 / (*E*,*E*): (*E*,*Z*) mixture of diastereoisomers. Separation of the diasteroisomers was accomplished *via* preparative HPLC using an Alltech "Alltima HP C18 5u" column (150 mm x 22 mm) to give (*E*,*E*)-enol ether (134 mg, 27%) and (*E*,*Z*)-enol ether (178 mg, 36%); conditions: 15: 85 / water: MeOH/NH_3 (1%), 20.0 mL/min, 254 nm.

(*E*,*E*): **^{1}H NMR** (400 MHz, MeOD): δ 7.30-7.26 (2H, m, Ar-*H*), 7.18-7.13 (3H, m, Ar-*H*), 6.04 (1H, s, O-alkene-*H*), 5.80-5.73 (1H, m, CH_2-alkene-*H*), 5.59-5.53 (1H, m, CH-alkene-*H*), 4.14-4.11 (1H, m, pyran-OC*H*), 2.76-2.71 (1H, m, CH_2), 2.24-2.07 (3H, m, CH_2), 1.87-1.75 (2H, m, CH_2), 1.66-1.57 (2H, m, CH_2), 1.43-1.33 (4H, m, CH_2), 0.95 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, MeOD): δ 156.7, 137.9, 133.7, 131.7, 129.8, 128.9, 126.7, 110.8, 81.4, 33.1, 32.5, 32.4, 26.0, 23.2, 23.2, 14.3; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2956 (s), 2929 (s), 2860 (m), 1656 (m), 1363 (m), 1165 (m), 1028 (s) 967 (m) 922 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{25}O$: 257.1905, found 257.1906.

(*E*,*Z*): **^{1}H NMR** (400 MHz, MeOD): δ 7.59-7.57 (2H, m, Ar-*H*), 7.22-7.18 (2H, m, Ar-*H*), 7.09-7.05 (1H, m, Ar-*H*), 5.90-5.79 (1H, m, CH_2-alkene-*H*), 5.62 (1H, ddt, *J* = 15.5, 6.0, 1.5 Hz, CH-alkene-*H*), 5.40 (1H, s, O-alkene-*H*), 4.28-4.23 (1H, m, pyran-OC*H*), 2.39-2.25 (2H, m, CH_2), 2.14-2.09 (2H, m, CH_2), 1.94-1.58 (4H, m, CH_2), 1.44-1.34 (4H, m, CH_2), 0.95 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (63 MHz, MeOD): δ 155.8, 137.9, 133.7, 131.5, 129.2, 128.9, 126.2, 108.1, 80.4, 33.0, 32.5, 32.1, 31.1, 23.5, 23.1, 14.3; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2928 (s), 2859 (m), 1655 (m), 1496 (m), 1454 (m), 1166 (m), 1030 (s), 968 (m), 928 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{25}O$: 257.1905, found 257.1899.

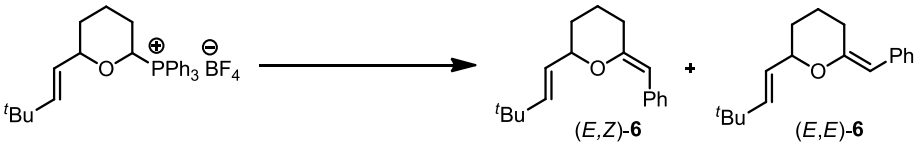
Preparation of (*Z*)-2-benzylidene-6-((*Z*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran and (*E*)-2-benzylidene-6-((*Z*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran



Following the representative procedure, a solution of Wittig salt (3.36 g, 6.5 mmol) in THF (50 mL) was treated with LiHMDS (1M, 7.8 mL, 7.8 mmol, 1.2 eq) and benzaldehyde (0.7 mL, 7.2 mL, 1.1 eq) over night. The crude residue was purified by flash chromatography on silica (500: 0.4: 0.2/ hexanes: Et_2O: Et_3N) to give (*Z*,*E*)-enol ether (533 mg, 32%) as a colorless oil and (*Z*,*Z*)-enol ether (483 mg, 29%) as colorless oil; **(*Z*,*E*)**: **^{1}H NMR** (400 MHz, MeOD): δ 7.31-7.27 (2H, m, Ar-*H*), 7.19-7.14 (3H, m, Ar-*H*), 6.05 (1H, br,O-alkene-*H*), 5.60-5.48 (2H, m, alkene-*H*), 4.54-4.49 (1H, m, pyran-OC*H*), 2.78-2.73 (1H, m, CH_2), 2.26-2.10 (3H, m, CH_2), 1.90-1.84 (1H, m, CH_2), 1.76-1.61 (3H, m, CH_2), 1.44-1.37 (4H, CH_2), 0.96 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (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, υ_{max} cm^{-1}): 3019 (m), 2933 (s), 2864 (m), 1649 (s), 1444 (m), 1231 (s), 1134 (m), 1032 (s), 917 (m), 744 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{25}O$: 257.1905, found 257.1903.

(*Z*,*Z*): **^{1}H NMR** (400 MHz, MeOD): δ 7.59-7.55 (2H, m, Ar-*H*), 7.21-7.17 (2H, m, Ar-*H*), 7.08-7.04 (1H, m, Ar-*H*), 5.62-5.54 (2H, m, alkene-*H*), 5.41 (1H, br, O-alkene-*H*), 4.61-4.57 (1H, m, pyran-OC*H*), 2.37-2.04 (4H, m, CH_2), 1.93-1.87 (1H, m, CH_2), 1.79-1.58 (3H, m, CH_2), 1.43-1.30 (4H, m, CH_2), 0.90 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 155.7, 137.8, 133.9, 130.9, 129.2, 128.9, 126.3, 108.3, 76.1, 32.9, 32.1, 31.1, 28.5, 23.6, 23.3, 14.3; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 3019 (m), 2936 (s), 2864 (m), 1653 (s), 1490 (m), 1303 (m), 1166 (m), 1025 (m), 924 (m), 751 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{25}O$: 257.1905, found 257.1897.

Preparation of (*Z*)-2-benzylidene-6-((*E*)-3,3-dimethylbut-1-en-1-yl)tetrahydro-2H-pyran and (*E*)-2-benzylidene-6-((*E*)-3,3-dimethylbut-1-en-1-yl)tetrahydro-2*H*-pyran

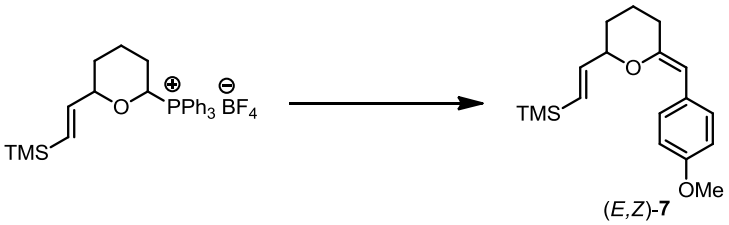


Following the representative procedure, a solution of Wittig salt (4 g, 7.8 mmol, 1 eq.) in THF (70 mL) was treated with LiHMDS (1M, 10.1 mL, 10.1 mmol, 1.3 eq) and benzaldehyde (1 mL, 1.1 eq). The crude residue was purified by flash chromatography on silica (500: 0.2: 0.1/ hexanes: Et_2O: Et_3N) to give (*E*,*E*)-enol ether (579 mg, 29%) as a colorless oil and (*E*,*Z*)-enol ether (679 mg, 34%) as colorless oil; **(*E*,*E*)**: **^{1}H NMR** (400 MHz, CD_3OD): δ 7.27-7.23 (2H, m, Ar-*H*) 7.16-7.11 (3H, m, Ar-*H*), 6.03 (1H, br, O-alkene-*H*), 5.78 (1H, dd, *J* = 16.0, 1.0 Hz, alkene-*H*), 5.48 (1H, dd, *J* = 16.0, 6.5 Hz, alkene-*H*), 4.13-4.08 (1H, m, pyran-OC*H*),

2.75-2.69 (1H, m, C*H*$_2$), 2.22-2.14 (1H, m, C*H*$_2$), 1.86-1.74 (2H, m, C*H*$_2$), 1.62-1.57 (2H, m, C*H*$_2$), 1.04 (9H, s, C*H*$_3$); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 157.6, 145.3, 138.8, 130.7, 130.0, 127.6, 111.7, 82.6, 33.4, 30.8, 26.9, 24.1; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 3022 (w), 2955 (s), 2863 (m), 1652 (s), 1444 (m), 1359 (m), 1232 (s), 1129 (m), 1027 (s), 974 (m), 917 (m), 702 (s); **HRMS** (EI) *m/z* [MH]$^+$ calcd for $C_{18}H_{25}O$: 257.1905, found 257.1899.

(*E,Z*): **^{1}H NMR** (400 MHz, CD_3OD): δ 7.57-7.55 (2H, m, Ar-*H*) 7.19-7.16 (1H, m, Ar-*H*), 7.07-7.03 (1H, m, Ar-*H*) 5.85 (1H, dd, *J* = 16.0, 1.0 Hz, alkene-*H*), 5.52 (1H, dd, *J* = 16.0, 6.0 Hz, alkene-*H*), 5.38 (1H, br, O-alkene-*H*), 4.25-4.20 (1H, m, pyran-OC*H*), 2.34-2.22 (2H, m, C*H*$_2$), 1.91-1.76 (2H, m, C*H*$_2$), 1.75-1.55 (2H, m, C*H*$_2$), 1.05 (9H, s, C*H*$_3$); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 155.7, 144.6, 137.9, 129.2, 128.8, 126.3, 126,2, 108.2, 80.6, 33.6, 32.1, 31.1, 29.9, 23.5; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}) 3022 (w), 2955 (s), 2866 (m), 1656 (s), 1489 (m), 1443 (m), 1161 (m), 1027 (s), 974 (m), 921 (m), 695 (s); **HRMS** (EI) *m/z* [MH]$^+$ calcd for $C_{18}H_{25}O$: 257.1905, found 257.1909.

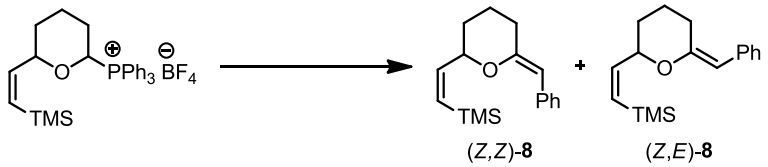
Preparation of ((E)-2-((Z)-6-(4-methoxybenzylidene)tetrahydro-2H-pyran-2-yl)vinyl)trimethylsilane



(*E,Z*)-**7**

Following the representative procedure, a solution of Wittig salt (4.5 g, 8.5 mmol, 1 eq.) in THF (70 mL) was treated with LiHMDS (1M, 12.0 mL, 1.3 mmol, 1.2 eq) and benzaldehyde (1.2 mL, 1.1 eq). The crude residue was purified by flash chromatography on silica (1000: 1.0: 0.1/ hexanes: Et_2O: Et_3N) gel to give (*E,Z*)-enol ether (613 mg, 24%) as colorless oil and (*E,E*)/(*E,*Z)-enol ether mixtures (1.05g, 41%); **(*E,Z*)**: **^{1}H NMR** (400 MHz, CD_3OD): δ 7.54-7.52 (2H, m, Ar-*H*), 6.80-6.78 (2H, m, Ar-*H*), 6.20 (1H, dd, *J* = 19.0, 4.5 Hz, CH-alkene-*H*), 6.05 (1H, dd, *J* = 19.0, 1.5 Hz, TMS-alkene-*H*), 5.38 (1H, br, O-alkene-*H*), 4.27-4.22 (1H, m, pyran-OC*H*), 3.77 (3H, s, C*H*$_3$), 2.34-2.23 (2H, m, C*H*$_2$), 1.93-1.85 (2H, m, C*H*$_2$), 1.77-1.66 (1H, m, C*H*$_2$), 1.63-1.53 (1H, m, C*H*$_2$), 0.12 (9H, s, C*H*$_3$); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 159.8, 154.6, 148.0, 131.6, 131.3, 115.2, 108.9, 82.5, 56.5, 32.6, 32.2, 24.6, -0.4; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2952 (s), 2835 (w), 1659 (w), 1607 (w), 1506 (s), 1245 (s), 1033 (m), 837 (s); **HRMS** (EI) *m/z* [MH]$^+$ calcd $C_{18}H_{27}O_2Si$: 303.1780, found 303.1778.

Preparation of ((*Z*)-2-((*Z*)-6-benzylidenetetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane and ((*Z*)-2-((*E*)-6-benzylidenetetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane

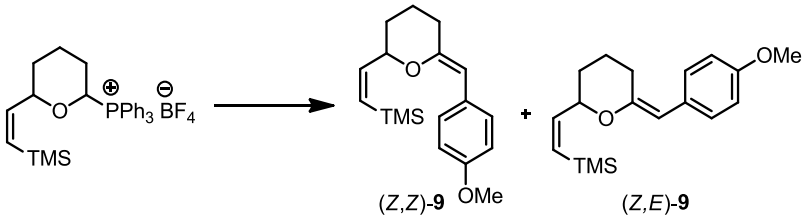


(*Z*,*Z*)-**8** (*Z*,*E*)-**8**

Following the representative procedure, a solution of Wittig salt (4 g, 7.5 mmol) in THF (70 mL) was treated with LiHMDS (1M, 9.7 mL, 9.7 mmol) and benzaldehyde (0.9 mL, 8.3 mmol). The crude residue was purified by flash chromatography on silica (500: 0.4: 0.1/ hexanes: Et_2O: Et_3N) to give (*Z*,*E*)-enol ether (612 mg, 30%) as a colorless oil and (*Z*,*Z*)-enol ether (673 mg, 33%) as a colorless oil; **(*Z*,*E*)**: **^{1}H NMR** (400 MHz, CD_3OD): δ 7.30-7.27 (2H, m, Ar-*H*) 7.18-7.14 (3H, m, Ar-*H*), 6.36 (1H, dd, *J* = 14.5, 8.0 Hz, CH-alkene-*H*), 6.06 (1H, br, O-alkene-*H*), 5.73 (1H, dd, *J* = 14.5, 0.5 Hz, TMS-alkene-*H*), 4.34-4.29 (1H, m, pyran-OC*H*), 2.79-2.74 (1H, m, CH_2), 2.25-2.16 (1H, m, CH_2), 1.92-1.86 (1H, m, CH_2), 1.80-1.75 (1H, m, CH_2), 1.70-1.59 (2H, m, CH_2), 1.19 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 153.5, 145.7, 134.9, 129.7, 126.9, 126.3, 123.9, 108.3, 78.3, 29.4, 23.0, 20.4, -2.4; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 3023 (w), 2952 (s), 2867 (w), 1654 (m), 1245 (m), 1131 (m), 1053 (m), 839 (m), 695 (s); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{25}O$: 273.1675, found 273.1683.

(*Z*,*Z*): **^{1}H NMR** (400 MHz, CD_3OD): δ 7.57-7.56 (2H, m, Ar-*H*), 7.21-7.17 (2H, m, Ar-*H*), 7.09-7.05 (1H, m, Ar-*H*), 6.43 (1H, dd, *J* = 14.0, 9.0 Hz, CH-alkene-*H*), 5.78 (1H, d, *J* = 14.0 Hz, TMS-alkene-*H*), 5.44 (1H, br, O-alkene-*H*), 4.44-4.38 (1H, m, pyran-OC*H*), 2.38-2.26 (2H, m, CH_2), 1.98-1.93 (1H, m, CH_2), 1.79-1.66 (3H, m, CH_2), 0.12 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 152.5, 145.5, 134.8, 130.0, 126.4, 126.0, 123.5, 105.7, 77.8, 29.2, 28.2, 20.8. -2.5; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 3023 (w), 2953 (s), 2897 (w), 1658 (m), 1252 (m), 1049 (m), 1027 (m), 839 (s), 695 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{17}H_{25}OSi$: 273.1675, found 273.1677.

Preparation of ((*Z*)-2-((*Z*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane and ((*Z*)-2-((*E*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



(*Z*,*Z*)-**9** (*Z*,*E*)-**9**

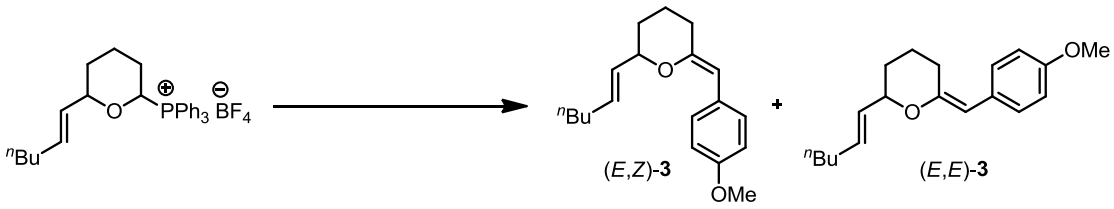
Following the representative procedure, a solution of Wittig salt (2 g, 3.7 mmol) in THF (34 mL) was treated with LiHMDS (1M, 4.5 mL, 4.5 mmol) and *para*-methoxybenzaldehyde (0.5 mL, 4.1 mmol). The crude residue was purified by flash chromatography on silica gel (500: 0.8: 0.1/ hexanes: Et_2O: Et_3N then 500:1.5:0.1 when (Z)-enol ether was eluted) to give (*E*)-enol ether (358 mg, 32%) as a colorless oil and (*Z*)-

enol ether (313 mg, 30%) as colorless oil; **(*Z,E*)**: **^{1}H NMR** (400 MHz, CD_3OD): δ 7.10-7.08 (2H, m, Ar-*H*) 6.87-6.85 (2H, m, Ar-*H*), 6.35 (1H, dd, *J* = 14.5, 8.0 Hz, CH-alkene-*H*), 6.01 (1H, br, O-alkene-*H*), 5.72 (1H, dd, *J* = 14.5, 1.0 Hz, TMS-alkene-*H*), 4.30-4.25 (1H, m, pyran-OC*H*), 3.78 (3H, s, CH_3), 2.77-2.72 (1H, m, CH_2), 2.20-2.12 (1H, m, CH_2), 1.91-1.86 (1H, m, CH_2), 1.75-1.73 (1H, m, CH_2), 1.64-1.59 (2H, m, CH_2), 1.18 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 157.9, 153.9, 147.3, 131.1, 129.5, 128.6, 113.3, 109.4, 80.0, 54.2, 31.0, 24.5, 22.1, -0.8; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2949 (s), 2834 (w), 1656 (w), 1608 (m), 1511 (s), 1133 (m), 1036 (m), 839 (s), 764 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{27}O_2Si$: 303.1780, found 303.1781.

(*Z,Z*): **^{1}H NMR** (400 MHz, CD_3OD): δ 7.52-7.50 (2H, m, Ar-*H*), 6.78-6.75 (2H, m, Ar-*H*), 6.42 (1H, dd, *J* = 14.0, 9.0 Hz, CH-alkene-*H*), 5.75 (1H, d, *J* = 14.0 Hz, TMS-alkene-*H*), 5.38 (1H, br, O-alkene-*H*), 4.38-4.33 (1H, m, pyran-OC*H*), 3.75 (3H, s, CH_3), 2.31-2.25 (2H, m, CH_2), 1.95-1.90 (1H, m, CH_2), 1.75-1.63 (3H, m, CH_2), 0.12 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 157.5, 152.0, 147.2, 131.3, 129.1, 112.9, 107.0, 79.3, 54.2, 30.8, 29.7, 22.6, -0.9; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2949 (s), 2834 (w), 1656 (w), 1604 (w), 1247 (s), 1032 (m), 839 (s), 764 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{27}O_2Si$: 303.1780, found 303.1769.

Procedures for the Wittig reaction using KHMDS

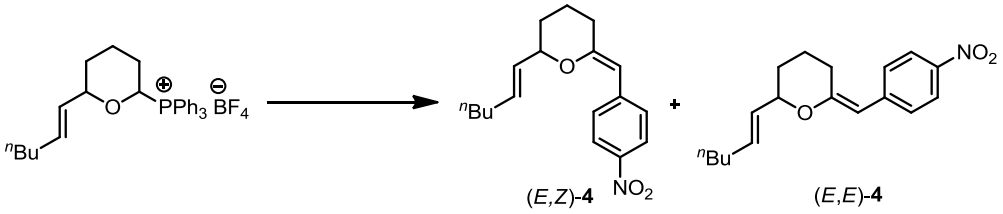
Preparation of (*E*)-2-((*E*)-hex-1-enyl)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran and (*Z*)-2-((*E*)-hex-1-enyl)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran



Following the representative procedure, a solution of Wittig salt (4 g, 7.7 mmol) in THF (77 mL) at -78 °C was treated with KHMDS (0.68 M, 14.8 mL, 10.1 mmol, 1.3 eq) and *para*-methoxybenzaldehyde (1.1 mL, 8.5 mmol, 1.1 eq). The crude residue was purified by chromatography on silica gel (500: 0.5: 0.2 mL / hexanes: Et_2O: Et_3N) to give the (*E*,*Z*)-enol ether as a yellow oil (329 mg, 15%). Further elution with the solvent mixture (500: 2: 0.2 mL / hexanes: Et_2O: Et_3N) gave the (*E*,*E*)-enol ether (1.32 g, 60%) as yellow oil; **(*E*,*E*)**: **^{1}HNMR** (400 MHz, CD_3OD): δ 7.11-7.09 (2H, m, Ar-*H*), 6.87-6.85 (2H, m, Ar-*H*), 5.96 (1H, br, O-alkene-*H*), 5.74 (1H, dtd, *J* =15.0, 7.0, 1.0 Hz, CH_2-alkene-*H*), 5.54 (1H, ddt, *J* = 15.0, 6.5, 1.5 Hz, CH-alkene-*H*), 4.10-4.06 (1H, m, pyran-OC*H*), 3.76 (3H, s, CH_3), 2.71-2.66 (1H, m, CH_2), 2.18-1.97 (3H, m, CH_2), 1.85-1.74 (2H, m, CH_2), 1.61-1.54 (2H, m, CH_2), 1.41-1.32 (4H, m, CH_2), 0.93 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 159.3, 155.6, 133.6, 131.8, 130.9, 130.2, 114.7, 110.5, 81.5, 55.7, 33.1, 32.5 (2), 26.0, 23.3 , 23.2, 14.3; **FITR** (CH_2Cl_2, υ_{max} cm^{-1}): 2955 (s), 2930 (s), 2870 (m), 1610 (w), 1461 (m), 1299 (m), 1175 (m), 1034(s), 822 (w); **HRMS** (ES) *m/z* $[M+H]^+$ calc'd for $C_{19}H_{27}O_2$: 287.2011, found 287.2005.

(*E*,*Z*): **^{1}HNMR** (400 MHz, CD_3OD): δ 7.54-7.52 (2H, m, Ar-*H*), 6.80-6.78 (2H, m, Ar-*H*), 5.82 (1H, dtd, *J* =15.5, 7.0, 1.0 Hz, CH_2-alkene-*H*), 5.62 (1H, ddt, *J* = 15.5, 6.5, 1.5 Hz, CH-alkene-*H*), 5.36 (1H, br, O-alkene-*H*), 4.23-4.19 (1H, m, pyran-OC*H*), 3.78 (3H, s, CH_3), 2.34-2.22 (3H, m, CH_2), 2.15-2.10 (2H, m, CH_2), 1.94-1.57 (2H, m, CH_2), 1.45-1.36 (2H, m, CH_2), 1.41-1.32 (3H, m, CH_2), 0.97 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 158.8, 153.9, 133.6, 131.6, 130.7, 130.3, 114.3, 107.9, 80.5, 55.6, 33.0, 32.5, 32.3, 31.2, 23.8, 23.1, 14.3; **FITR** (CH_2Cl_2, υ_{max} cm^{-1}): 2954 (s), 2929 (s), 2860 (m), 1656 (w), 1510 (s), 1246 (s), 1177 (m), 1031 (m), 845 (w); **HRMS** (ES) *m/z* $[M+H]^+$ calc'd for $C_{19}H_{27}O_2$: 287.2011, found 287.2011.

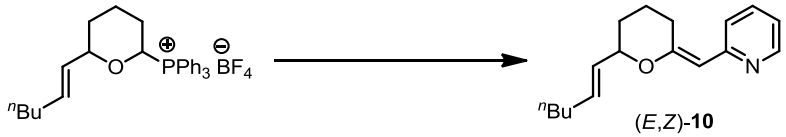
Preparation of (*Z*)-2-((*E*)-hex-1-enyl)-6-(4-nitrobenzylidene)tetrahydro-2*H*pyran and (*E*)-2-((*E*)-hex-1-enyl)-6-(4-nitrobenzylidene)tetrahydro-2*H*pyran



Following the representative procedure, a solution of Wittig salt (4 g, 7.7 mmol) in THF (77 mL) at -78 °C was treated with KHMDS (0.68 M, 14.8 mL, 10.1 mmol, 1.3 eq) and 4-nitrobenzaldehyde (1.3 g, 8.5 mmol, 1.1 eq). The crude residue was purified by chromatography on silica gel (500: 0.5: 0.2 mL / hexanes: Et_2O: Et_3N) to give the (*E,Z*)-enol ether as yellow oil (0.91 g, 39%). Further elution with the solvent mixture (500: 2: 0.2 mL / hexanes: Et_2O: Et_3N) gave the (*E,E*)-enol ether as yellow oil (0.97 g, 42%); **(*E,E*)**: **^{1}H NMR** (400 MHz, CD_3OD): δ 8.08 (2H, d, *J* = 9.0 Hz, Ar-*H*), 7.31 (2H, d, *J* = 9.0 Hz, Ar-*H*), 6.00 (1H, m, O-alkene-*H*), 5.74-5.66 (1H, m, CH_2-alkene-*H*), 5.51-5.45 (1H, m, CH_2-alkene-*H*), 4.18-4.14 (1H, m, pyran-OC*H*), 2.72-2.67 (1H, m, CH_2), 2.34-2.27 (1H, m, CH_2), 2.04-1.99 (2H, m, CH_2), 1.83-1.74 (2H, m, CH_2), 1.60-1.56 (2H, m, CH_2), 1.36-1.27 (4H, m, CH_2), 0.87 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 160.6, 146.6, 145.9, 134.0, 131.4, 130.1, 124.5, 108.7, 81.1, 33.1, 32.5, 31.8, 26.2, 23.3, 22.2, 14.3; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2931 (s), 2870 (m), 1638 (m), 1512 (s), 1106 (m), 1034 (s), 747 (m), 701 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{23}NO_3$: 301.1678, found 301.1673.

(*E,Z*): **^{1}H NMR** (400 MHz, CD_3OD): δ 7.99 (2H, d, *J* = 9.5 Hz, Ar-*H*), 7.68 (2H, d, *J* = 9.5 Hz, Ar-*H*), 5.80-5.73 (1H, m, CH_2-alkene-*H*), 5.59-5.54 (1H, m, CH_2-alkene-*H*), 5.42 (1H, m, O-alkene-*H*), 4.36-4.32 (1H, m, pyran-OC*H*), 2.42-2.25 (2H, m, CH_2), 2.08-2.03 (2H, m, CH_2), 1.86-1.56 (4H, m, CH_2), 1.40-1.26 (4H, m, CH_2), 0.88 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 161.1, 145.9, 145.5, 134.6, 131.1, 129.2, 124.3, 105.3, 80.6, 33.0, 32.5, 31.4, 30.7, 23.2, 22.1, 14.3; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 2927 (s), 2867 (m), 1642 (m), 1509 (s), 1109 (m), 1031 (s), 749 (m), 695 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{23}NO_3$: 301.1678, found 301.1666.

Preparation of 2-((*E*)-(6-((*E*)-hex-1-en-1-yl)tetrahydro-2H-pyran-2-ylidene)methyl)pyridine



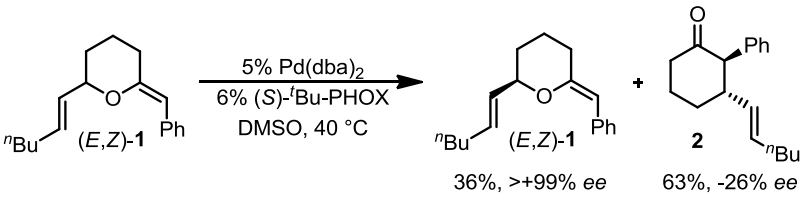
Following the representative procedure, a solution of Wittig salt (4 g, 7.7 mmol) in THF (80 mL) at -78 °C was treated with KHMDS (0.68 M, 14.8 mL, 10.1 mmol, 1.3 eq) and 2-pyridinecarboxyaldehyde (810 µL, 8.5 mmol, 1.1 eq). The crude residue was purified by chromatography on silica gel (500: 30: 0.2 mL / hexanes: Et_2O: Et_3N) to give the enol ether as a yellow oil (1.34 g, 67%) containing only the (*E,E*)-

diastereoisomer; **^{1}H NMR** (400 MHz, CD_3OD): δ 8.38-8.36 (1H, m, Ar-*H*), 7.63 (1H, ddd, *J* = 7.5, 7.5, 2.0 Hz, Ar-*H*), 7.16-7.14 (1H, m, Ar-H), 7.06 (1H, ddd, *J* =7.5, 5.0, 1.0 Hz, Ar-H), 5.98 (1H, br, O-alkene-*H*), 5.70 (1H, dtd, *J* =15.5, 7.0, 1.0 Hz, CH_2-alkene-*H*), 5.50 (1H, ddt, *J* = 15.5, 6.5, 1.5 Hz, CH-alkene-*H*), 4.20-4.16 (1H, m, pyran-OC*H*), 3.00-2.96 (1H, m, CH_2), 2.42-2.35 (1H, m, CH_2), 2.05-2.00 (2H, m, CH_2), 1.81-1.75 (2H, m, CH_2), 1.60-1.57 (2H, m, CH_2), 1.37-1.28 (4H, m, CH_2), 0.88 (3H, t, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, CD_3OD): δ 161.6, 157.7, 149.6, 137.9, 133.8, 131.5, 125.1, 121.3, 80.9, 33.0, 32.5, 32.0, 31.8, 26.3, 23.3, 22.1, 14.3; **FITR** (CH_2Cl_2, υ_{max} cm^{-1}): 2954 (s), 2930 (s), 2871 (m), 1737 (s), 1649 (m), 1588 (m), 1234 (m), 1132 (m), 1035 (s), 745 (w); **HRMS** (ES) *m/z* $[M+H]^+$ calc'd for $C_{17}H_{24}NO$ 258.1858, found 258.1867.

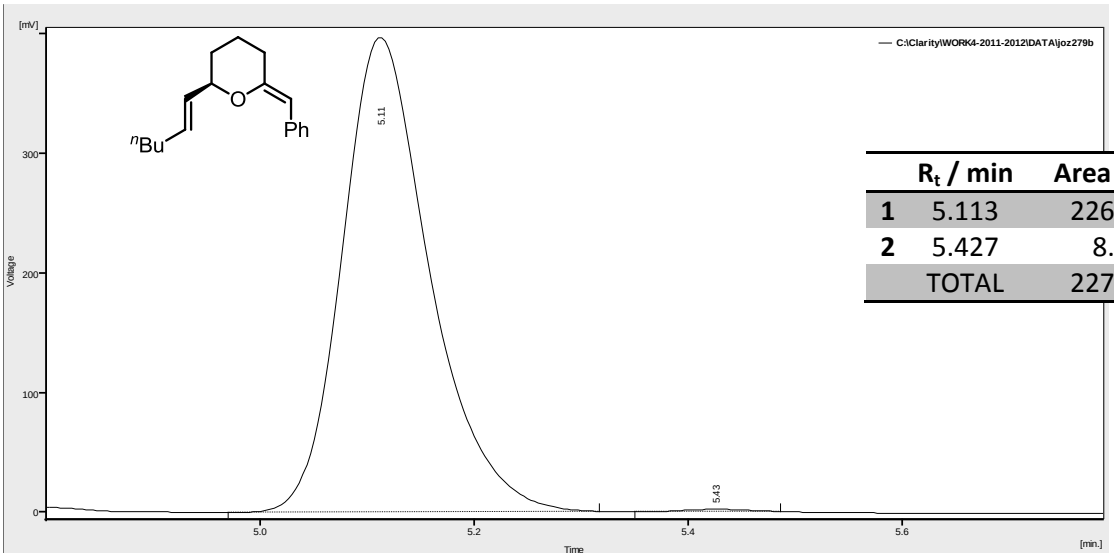
General procedure for the kinetic resolution of racemic enol ethers

To a Schlenk tube containing a magnetic stir bar was added racemic enol ether (1 eq.), $Pd(dba)_2$ (5 mol%) and ^{t}Bu-Phox (6 mol%). The tube was sealed, evacuated under reduced pressure and back filled with argon. DMSO (to make up a 0.4 M solution) was added under argon, and the tube evacuated for *ca.* 2 minutes. The tube was back filled with argon and the new mixture was stirred in a preheated heating block at the stated temperature for the stated time. The reaction mixture was cooled to room temperature, and directly purified *via* column chromatography to give enantioenriched enol ethers and enantioenriched cyclic ketones.

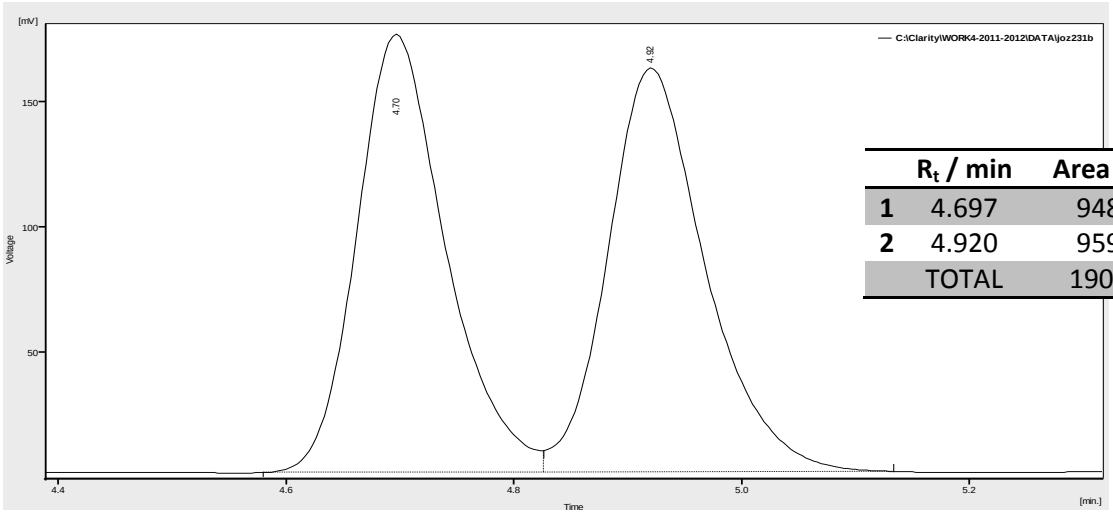
Preparation of (*R*,*Z*)-2-benzylidene-6-((*E*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran



Prepared using (*E*,*Z*)-enol ether (203 mg, 0.8 mmol), $Pd(dba)_2$ (23 mg, 0.04 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (18.5 mg, 0.05 mmol, 6 mol%) at 40 °C for 6.5 h to give enantioenriched (*R*)-(*E*,*Z*)-enol ether (73.1 mg, 36% yield; >+99% *ee*), $[\alpha]_D^{23}$= -20.0 (*c* 1.0, MeOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane (100%), flow rate = 1.0 mL/min, detection at 254 nm and enantioenriched (2*S*,3*R*)-*trans*-cyclic ketone (127.8 mg, 63% yield, -26% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95:5; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 16.8.

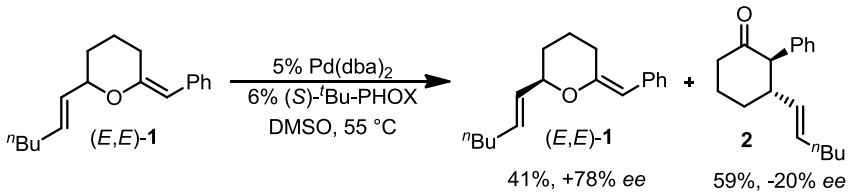


	R_t / min	Area / mV.s	Area / %
1	5.113	2265.088	99.6
2	5.427	8.623	0.4
	TOTAL	2273.712	100.0

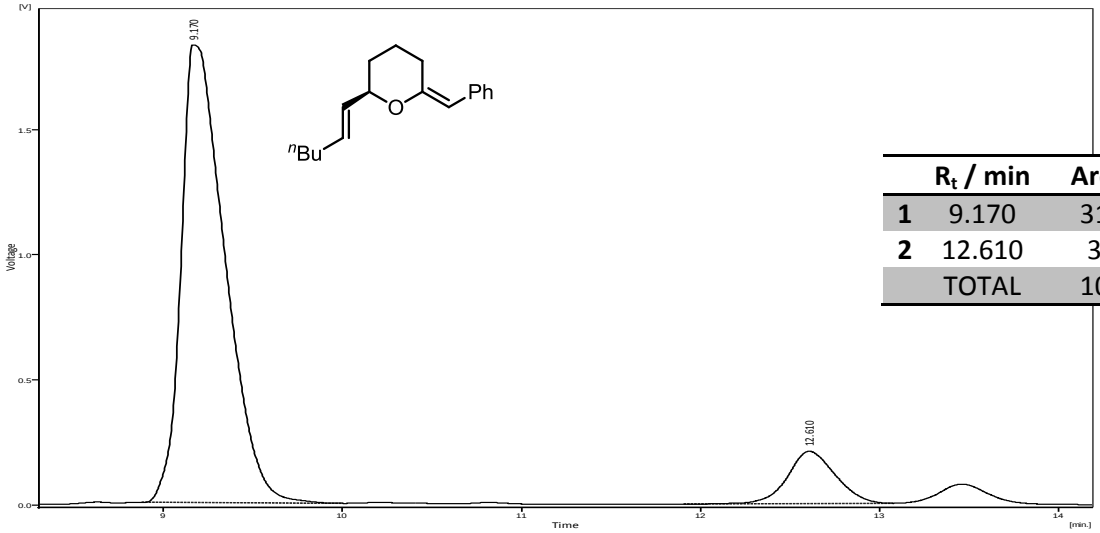


	R_t / min	Area / mV.s	Area / %
1	4.697	948.779	49.7
2	4.920	959.377	50.3
	TOTAL	1908.155	100.0

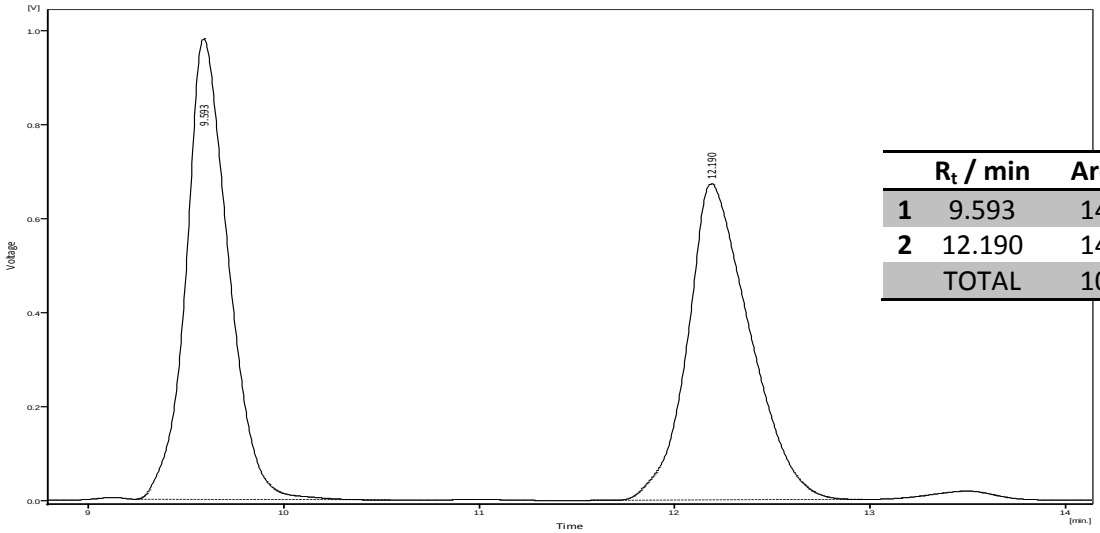
Preparation of (+)-(*E*)-2-Benzylidene-6-((pent-1-enyltetrahedro-2*H*-pyran



Prepared using (*E*,*E*)-enol ether (100 mg, 0.4 mmol), $Pd(dba)_2$ (11.2 mg, 0.02 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (9.1 mg, 0.02 mmol, 6 mol%) at 55 °C for 9.5 h to give enantioenriched (*R*)-(*E*,*E*)-enol ether (41 mg, 0.2 mmol, 41% yield, +78% *ee*), $[\alpha]_D^{22}$= -50.0 (*c* 1.0, MeOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane (100%), flow rate = 1.0 mL/min, detection at 254 nm and enantioenriched (2*S*,3*R*)-*trans*-cyclic ketone (59 mg, 59% yield, -20% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95:5; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 7.6

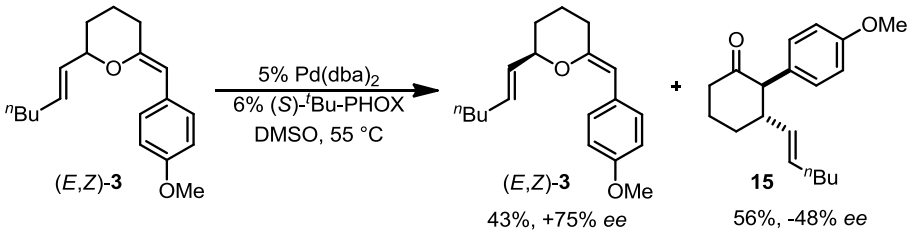


	R_t / min	Area / mV.s	Area / %
1	9.170	31172.761	88.8
2	12.610	3928.753	11.2
	TOTAL	10066.398	100.0

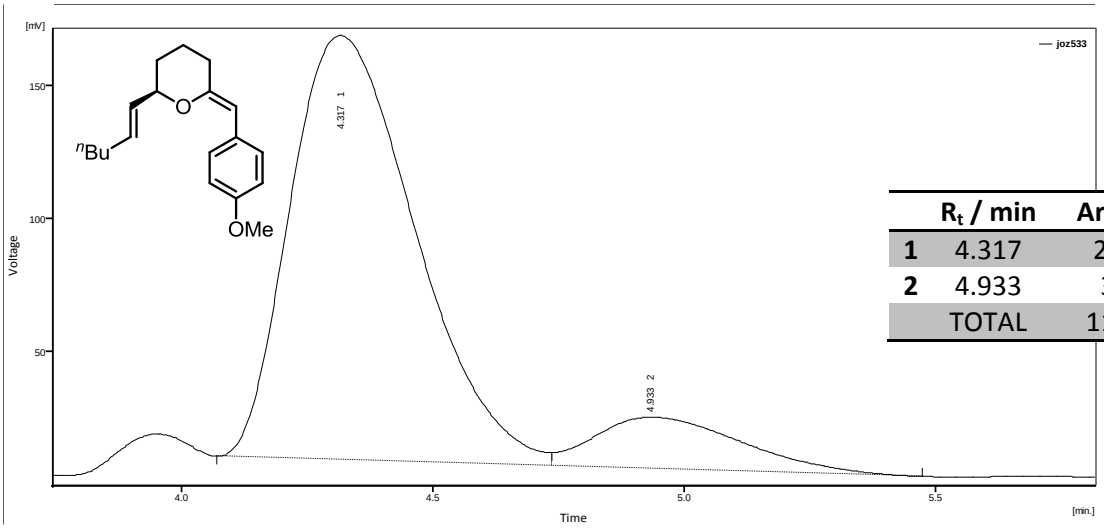


	R_t / min	Area / mV.s	Area / %
1	9.593	14784.545	49.8
2	12.190	14928.092	50.2
	TOTAL	10066.398	100.0

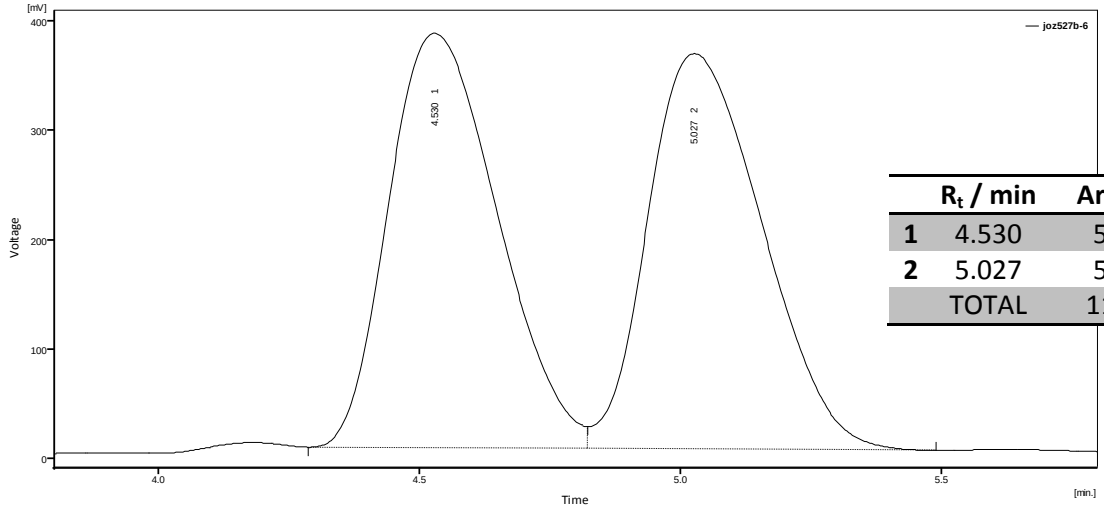
Preparation of (+)-(*Z*)-2-((*E*)-hex-1-en-1-yl)-6-(4-methoxybenzylidene)tetrahydro-2H-pyran



Following the general procedure for the kinetic resolution, (*E*,*Z*)-enol ether (54 mg, 0.19 mmol), $Pd(dba)_2$ (5 mg, 0.009 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (4 mg, 0.011 mmol, 6 mol%) were reacted at 55 ^{o}C for 10 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1.5: 0.2 mL / hexane: Et_2O: Et_3N then 100: 5 / PE: EtOAc when enol ether is eluted) to give enantioenriched (*R*)-(*E*,*Z*)-enol ether (23.3 mg, 43% yield, +75% *ee*), $[\alpha]_D^{23}$= -14.0 (*c* 1.0, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99:1; flow rate = 1.0 mL/min; detection at 254 nm and enantioenriched *trans*-cyclic ketone (30.1 mg, 56% yield, +48% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95:5; flow rate = 1.0 mL/min; detection at 230 nm. **Calculated S-factor** = 7.8

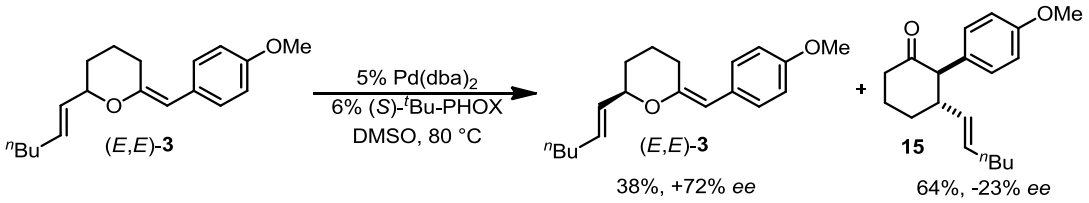


	R_t / min	Area / mV.s	Area / %
1	4.317	2763.591	87.4
2	4.933	399.244	12.6
	TOTAL	11025.990	100.0

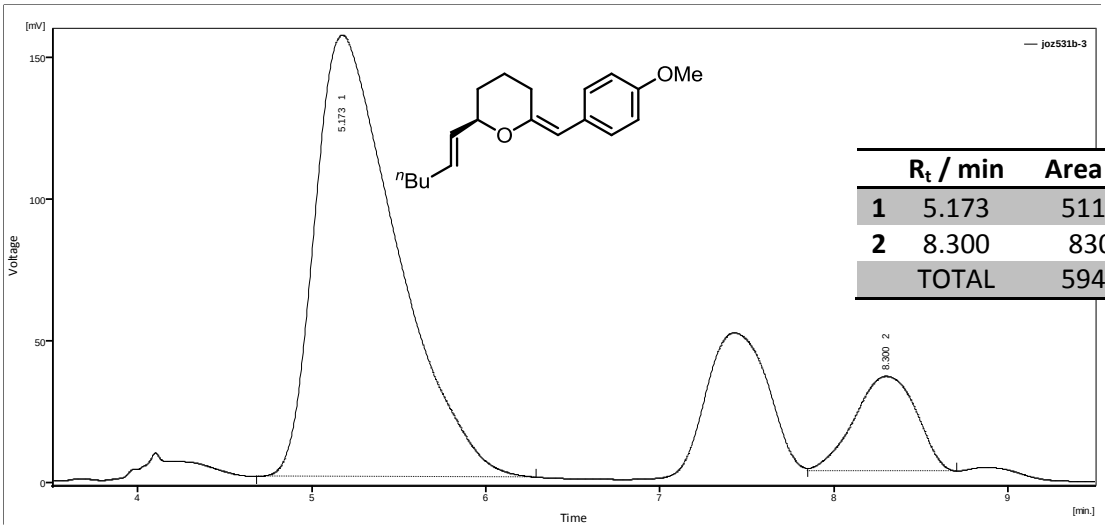


	R_t / min	Area / mV.s	Area / %
1	4.530	5512.563	50.0
2	5.027	5513.427	50.0
	TOTAL	11025.990	100.0

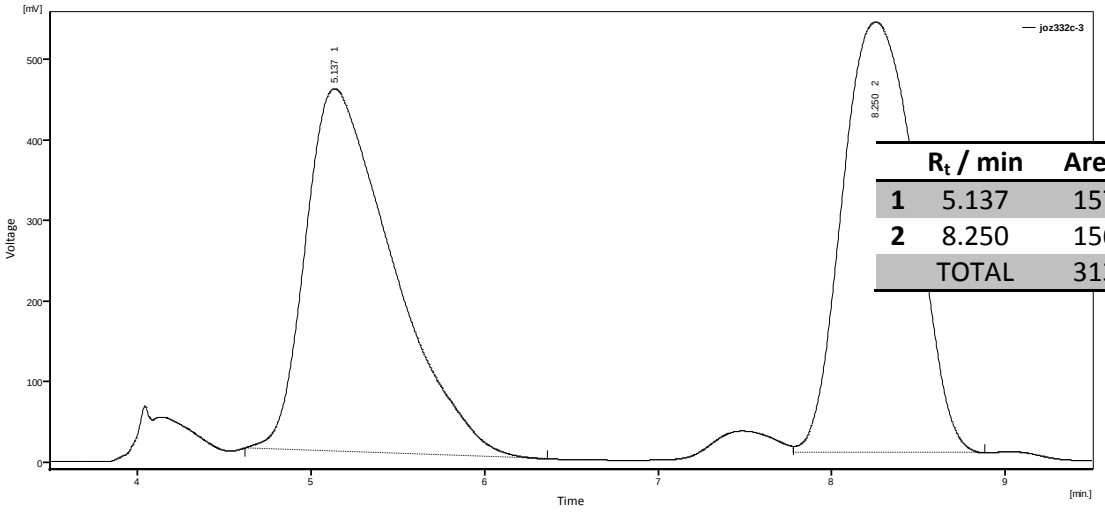
Preparation of (+)-(*E*)-2-((*E*)-hex-1-enyl)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran



Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (54 mg, 0.19 mmol), $Pd(dba)_2$ (5 mg, 0.009 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (4 mg, 0.011 mmol, 6 mol%) were reacted at 80 ^{o}C for 3.25 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1.5: 0.2 mL then 500: 50: 0 / hexane: Et_2O: Et_3N when enol ether is eluted) to give enantioenriched (*R*)-(*E*,*E*)-enol ether (20.6 mg, 38% yield, +72% *ee*), $[\alpha]_D^{23}$= -87.5 (*c* 0.4, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99:1; flow rate = 1.0 mL/min; detection at 254 nm and enantioenriched *trans*-cyclic ketone (34.6 mg, 64% yield, -23% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95:5; flow rate = 1.0 mL/min; detection at 230 nm. **Calculated S-factor** = 5.3

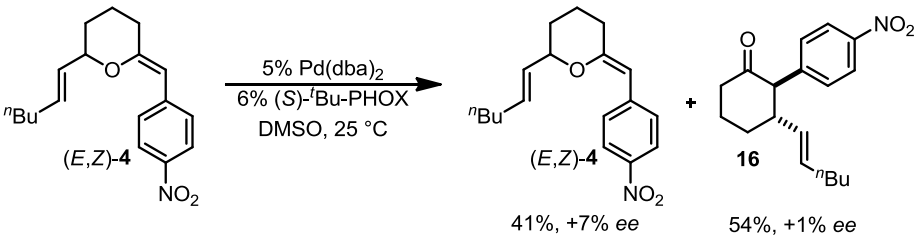


	R_t / min	Area / mV.s	Area / %
1	5.173	5110.840	86.0
2	8.300	830.336	14.0
	TOTAL	5941.176	100.0

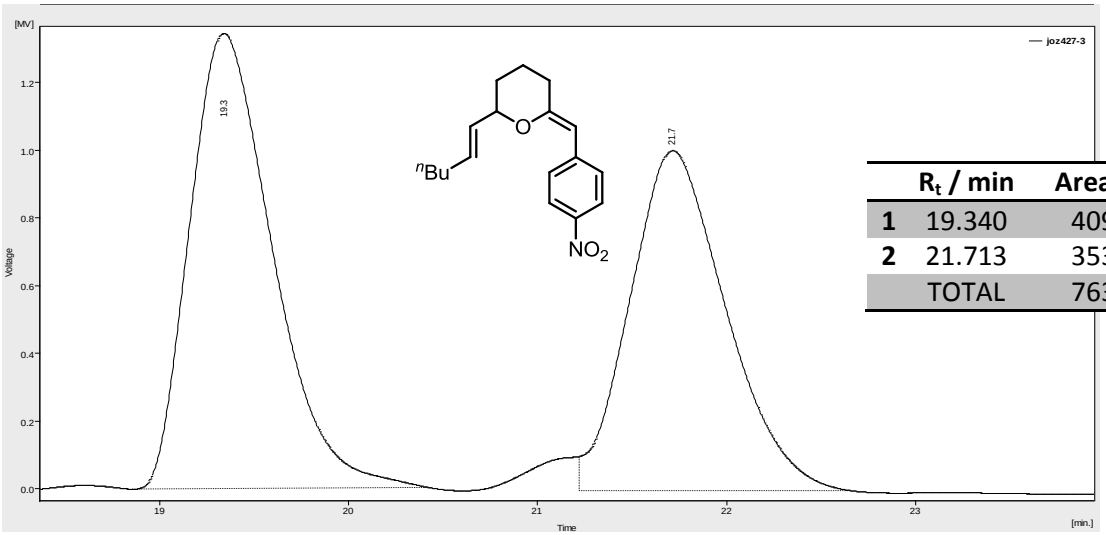


	R_t / min	Area / mV.s	Area / %
1	5.137	15720.806	50.1
2	8.250	15652.482	49.9
	TOTAL	31373.288	100.0

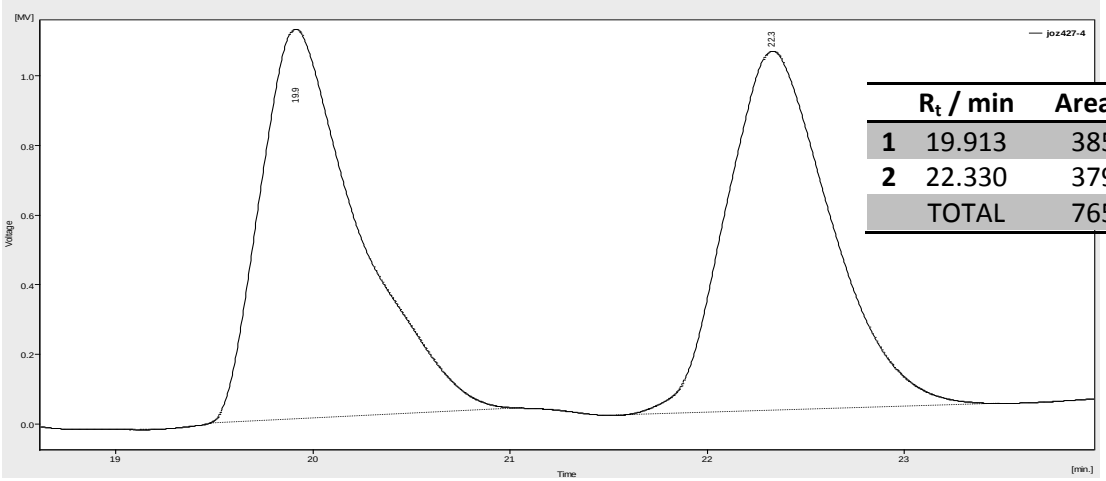
Preparation of (+)-(*Z*)-2-((*E*)-hex-1-enyl)-6-(4-nitrobenzylidene)tetrahydro-2*H*-pyran



Following the general procedure for the kinetic resolution, (*E*,Z)-enol ether (91 mg, 0.3 mmol), $Pd(dba)_2$ (8.7 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (7.1 mg, 0.02 mmol, 6 mol%) were reacted at 25 °C for 10 minutes. The reaction mixture was purified *via* column chromatography on silica gel (500: 2: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 5 mL/ PE: EtOAc when enol ether is eluted) to give enantioenriched (*E*,Z)-enol ether (37 mg, 41% yield, +7% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane (100%); flow rate = 0.9 mL/min; detection at 254 nm and enantioenriched *trans*-cyclic ketone (49 mg, 54% yield, +1% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95:5; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 1.2

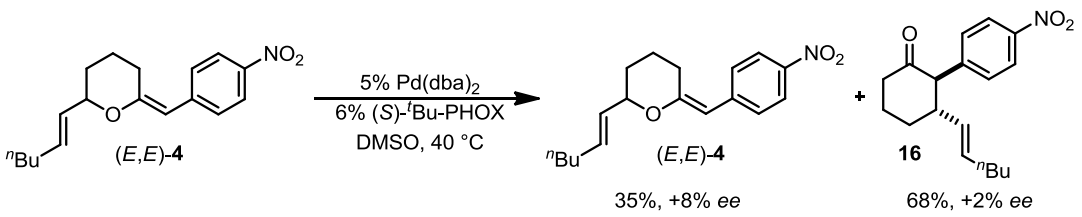


	R_t / min	Area / mV.s	Area / %
1	19.340	4095.709	53.6
2	21.713	3538.905	46.4
	TOTAL	7634.614	100.0

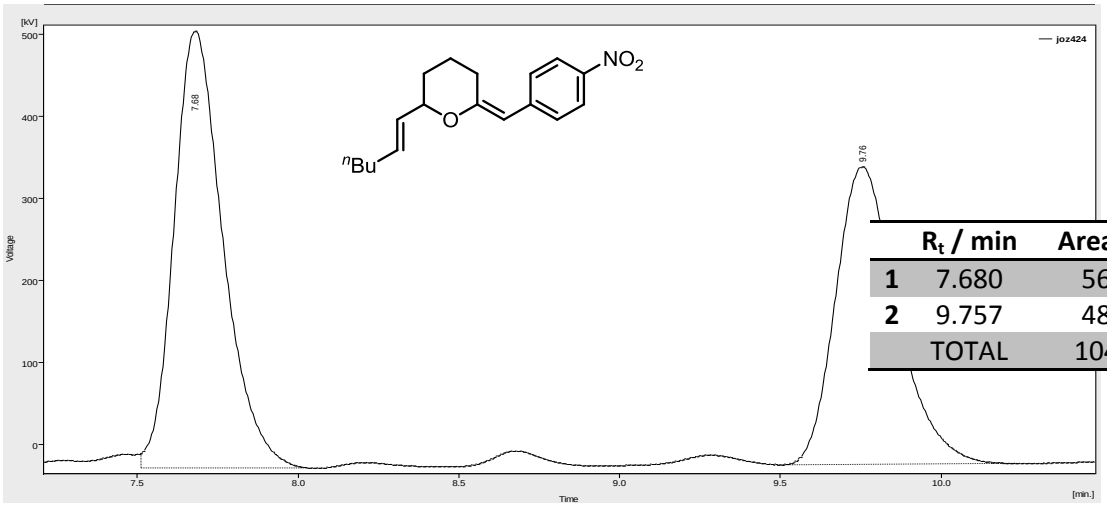


	R_t / min	Area / mV.s	Area / %
1	19.913	3855.334	50.4
2	22.330	3796.099	49.6
	TOTAL	7651.433	100.0

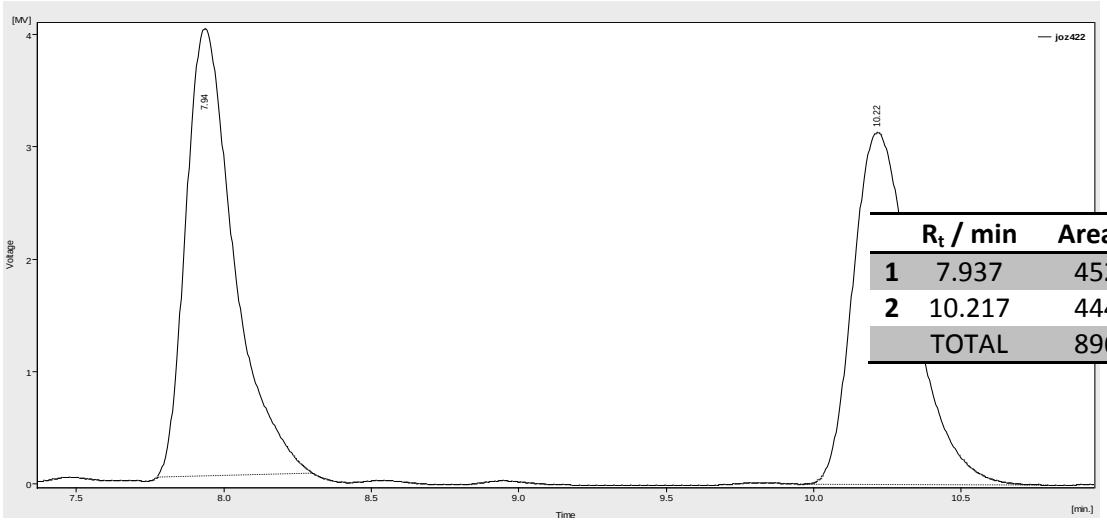
Preparation of (+)-(*E*)-2-((*E*)-hex-1-enyl)-6-(4-nitrobenzylidene)tetrahydro-2*H*-pyran



Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (45 mg, 0.15 mmol), $Pd(dba)_2$ (4.3 mg, 0.07 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (3.5 mg, 0.01 mmol, 6 mol%) were reacted at 25 °C for 1 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 5 mL/ PE: EtOAc when enol ether is eluted) to give enantioenriched (*E*,*E*)-enol ether (16 mg, 35% yield, +8% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 99:1; flow rate = 1.0 mL/min; detection at 254 nm and enantioenriched *trans*-cyclic ketone (31 mg, 68% yield, +2% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95:5; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 1.2

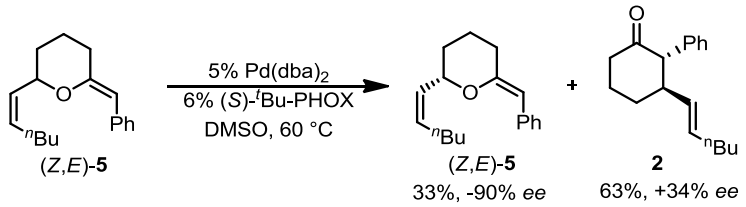


	R_t / min	Area / mV.s	Area / %
1	7.680	567.052	54.1
2	9.757	480.831	45.9
	TOTAL	1047.883	100.0

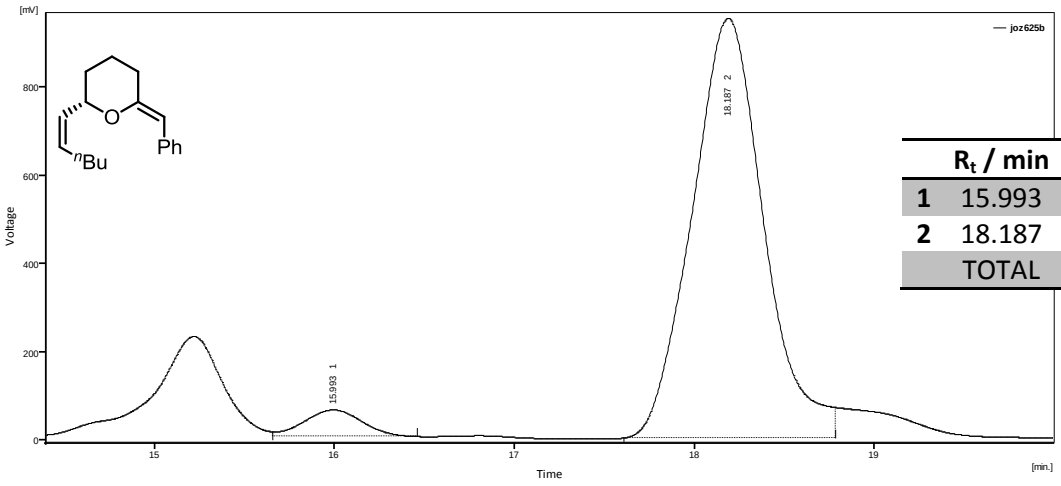


	R_t / min	Area / mV.s	Area / %
1	7.937	4524.079	50.4
2	10.217	4443.553	49.6
	TOTAL	8967.632	100.0

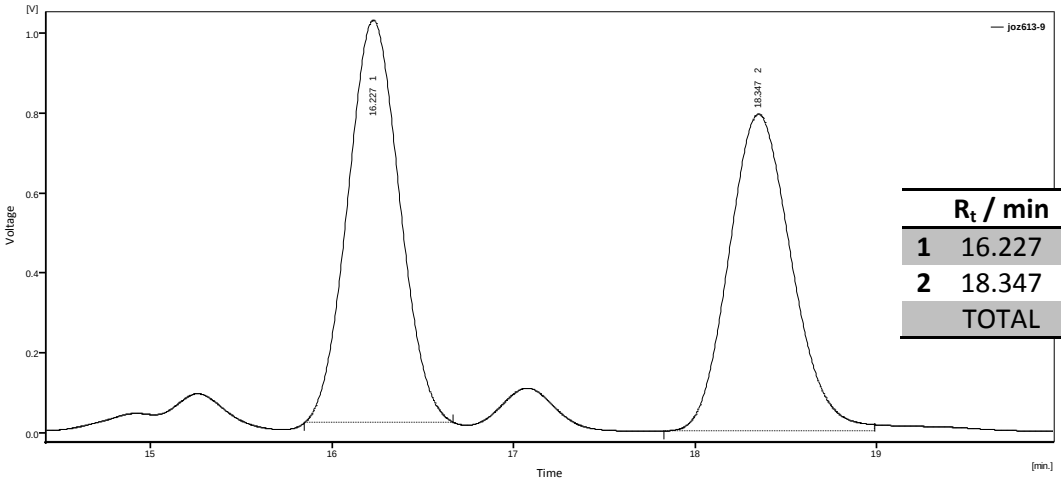
Preparation of (-)-(*Z*)-2-benzylidene-6-((*Z*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran



Following the general procedure for the kinetic resolution, (*Z*,*Z*)-enol ether (154 mg, 0.60 mmol), $Pd(dba)_2$ (18 mg, 0.02 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (12 mg, 0.04 mmol, 6 mol%) at 60 °C for 1.75 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 2: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 5 mL/ PE: EtOAc when enol ether was eluted) to give enantioenriched (*S*)-(*Z*,*Z*)-enol ether (51.1 mg, 33% yield, -90% *ee*), $[\alpha]_D^{22}$= +186.0 (*c* 0.5, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane (100%); flow rate = 0.3 mL/min; detection at 254 nm and enantioenriched (2*R*,3*S*)-*trans*-cyclic ketone (97.0 mg, 63% yield, +34% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95: 5; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 7.7

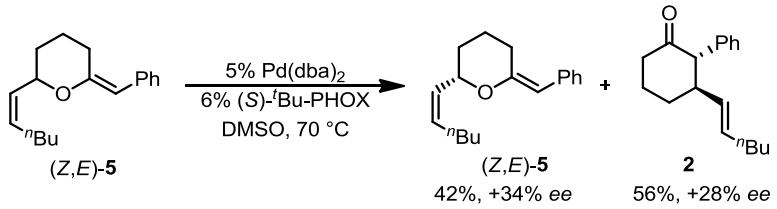


	R_t / min	Area / mV.s	Area / %
1	15.993	1360.922	4.9
2	18.187	26204.276	95.1
	TOTAL	27565.198	100.0

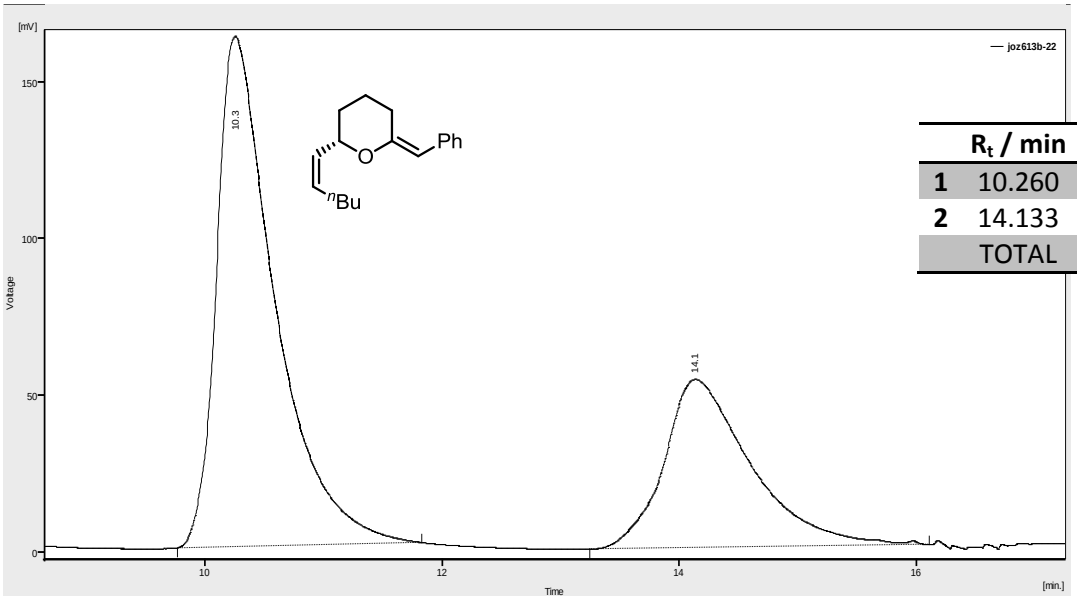


	R_t / min	Area / mV.s	Area / %
1	16.227	19969.657	51.2
2	18.347	19001.366	48.8
	TOTAL	38971.022	100.0

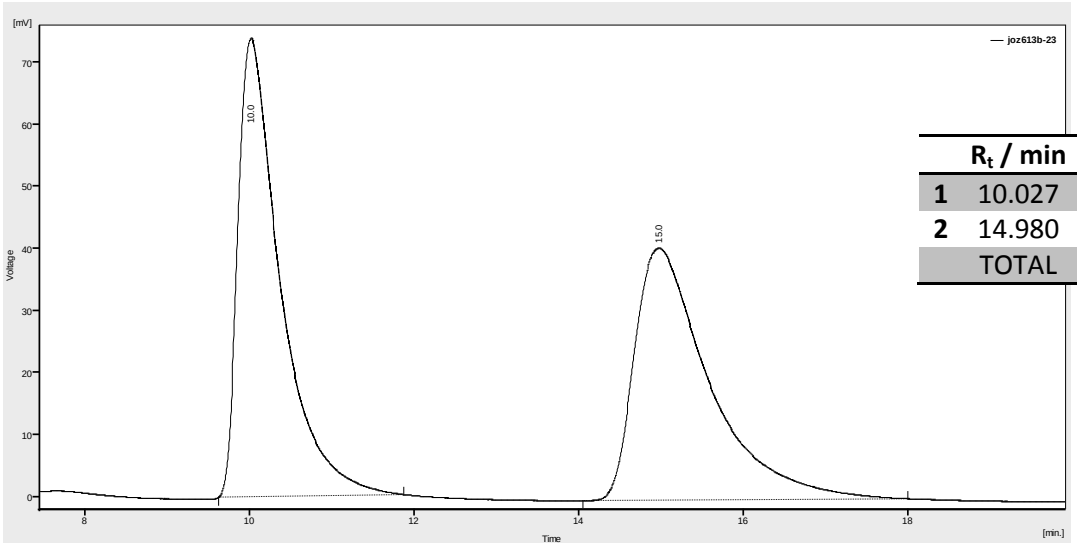
Preparation of (-)-(*E*)-2-benzylidene-6-((*Z*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran



Following the general procedure for the kinetic resolution, (*Z*,*E*)-enol ether (76 mg, 0.30 mmol), $Pd(dba)_2$ (9 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (6 mg, 0.02 mmol, 6 mol%) at 70 °C for 7.25 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 2: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 5 mL/ PE: EtOAc when enol ether was eluted) to give enantioenriched (*S*)-(*Z*,*E*)-enol ether (32 mg, 42% yield, +34% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Amylose-2 column; ^{n}hexane (100%); flow rate = 1.4 mL/min; detection at 254 nm and enantioenriched (2*R*,3*S*)-*trans*-cyclic ketone (43 mg, 56% yield, +28% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95: 5; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** =2.2

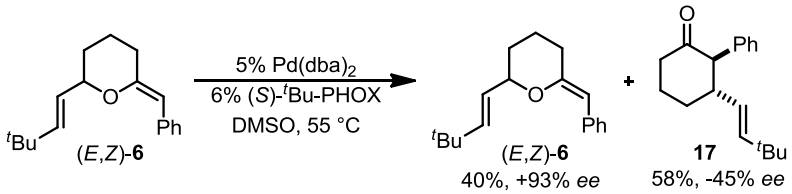


	R_t / min	Area / mV.s	Area / %
1	10.260	5572.219	67.0
2	14.133	2744.858	33.0
	TOTAL	8317.077	100.0

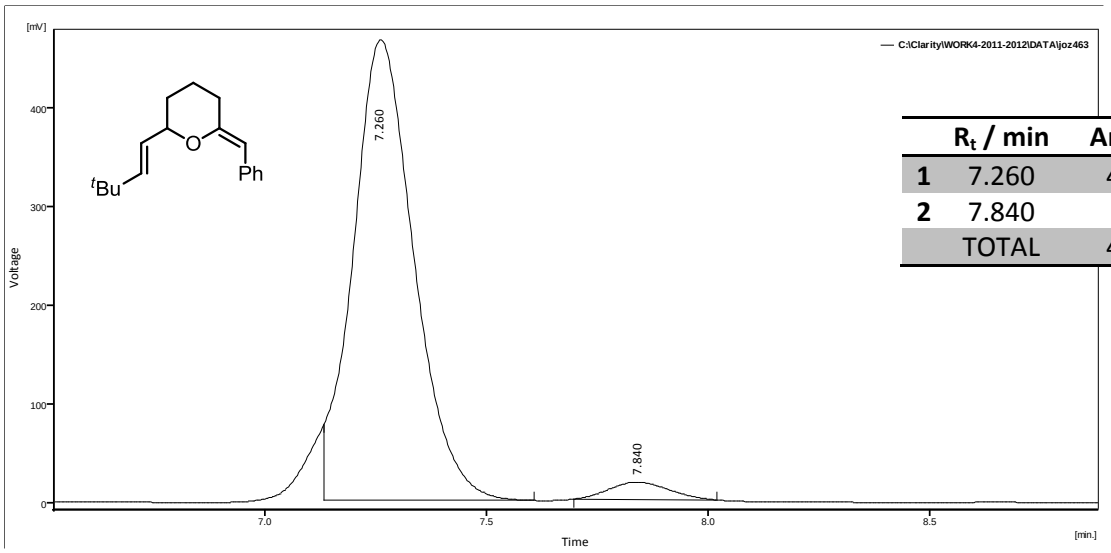


	R_t / min	Area / mV.s	Area / %
1	10.027	2633.453	50.7
2	14.980	2561.594	49.3
	TOTAL	5195.047	100.0

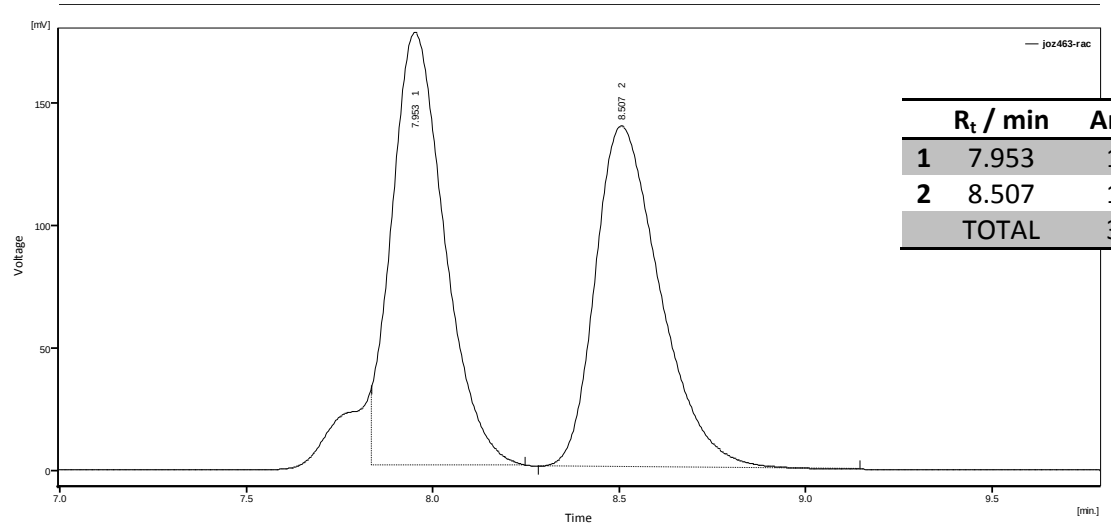
Preparation of (+)-(*Z*)-2-benzylidene-6-((*E*)-3,3-dimethylbut-1-en-1-yl)tetrahydro-2*H*-pyran



Following the general procedure for the kinetic resolution, (*E*,*Z*)-enol ether (77 mg, 0.3 mmol), $Pd(dba)_2$ (9 mg, 0.015 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (7 mg, 0.016 mmol, 6 mol%) were reacted at 55 °C for 6.5 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 5 mL/ PE: EtOAc when enol ether is eluted) to give enantioenriched (*E*,*Z*)-enol ether (30.8 mg, 40% yield, +93% *ee*); $[\alpha]_D^{23}$= -17.1 (*c* 1.7, Et_2O); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane (100%); flow rate = 1 mL/min; detection at 254 nm and enantioenriched *trans*-cyclic ketone (44.7 mg, 58% yield, -45% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 97:3; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 13.8

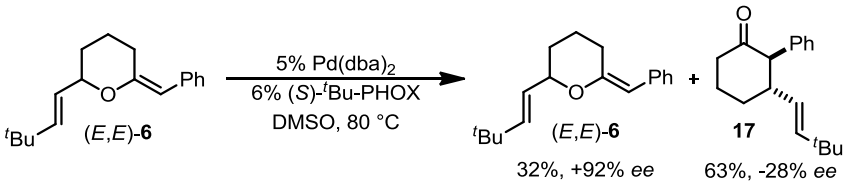


	R_t / min	Area / mV.s	Area / %
1	7.260	4461.151	96.4
2	7.840	165.564	3.6
	TOTAL	4626.715	100.0

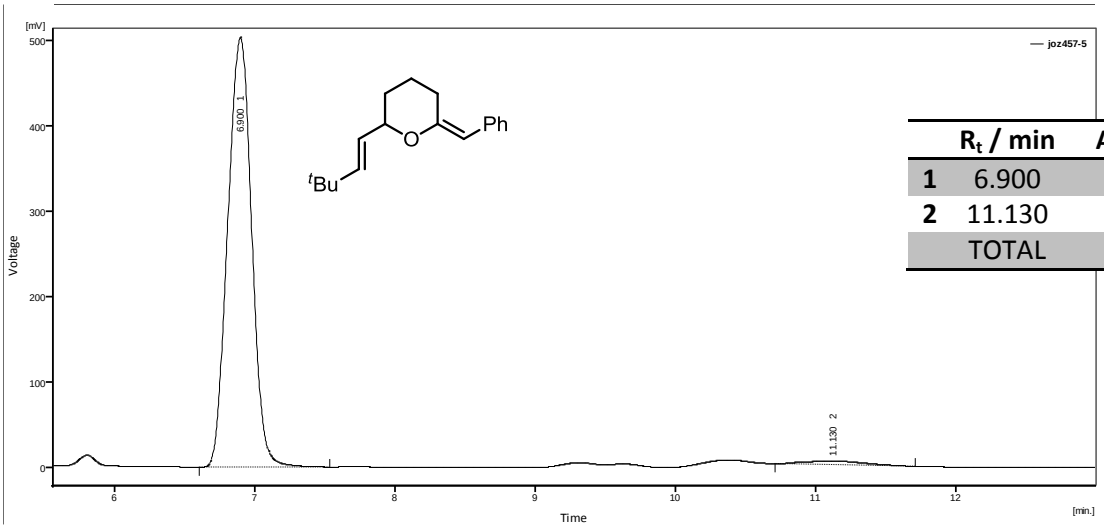


	R_t / min	Area / mV.s	Area / %
1	7.953	1741.576	50.8
2	8.507	1684.164	49.2
	TOTAL	3425.740	100.0

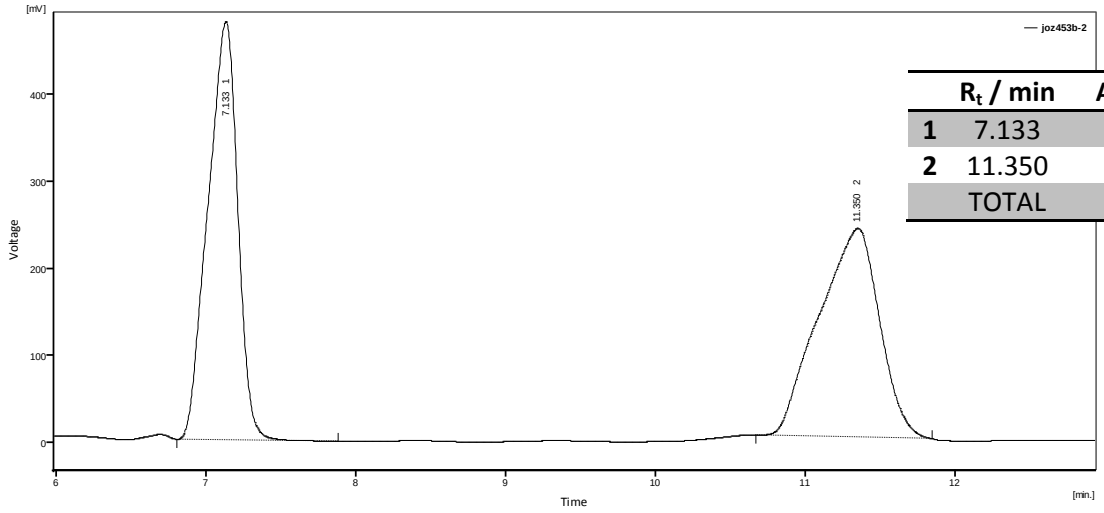
Preparation of (+)-(*E*)-2-benzylidene-6-((*E*)-3,3-dimethylbut-1-en-1-yl)tetrahydro-2*H*-pyran



Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (62 mg, 0.24 mmol), $Pd(dba)_2$ (7 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (6 mg, 0.01 mmol, 6 mol%) were reacted at 80 °C for 4 h 45 min. The reaction mixture was purified *via* column chromatography on silica gel (500: 1: 0.1 mL/ hexane: Et_2O: Et_3N then 100: 5 mL/ PE: EtOAc when enol ether is eluted) to give enantioenriched (*E*,*E*)-enol ether (19.8 mg, 32% yield, +92% *ee*); $[\alpha]_D^{23}$= -76.2 (*c* 1.0, Et_2O); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane (100%); flow rate = 1 mL/min; detection at 254 nm and enantioenriched *trans*-cyclic ketone (39.1 mg, 63% yield, -28% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 97:3; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 7.5

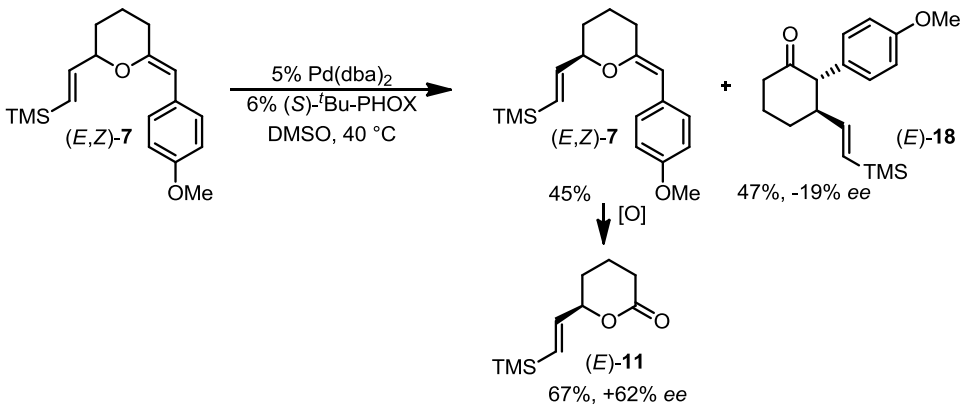


	R_t / min	Area / mV.s	Area / %
1	6.900	5963.680	96.2
2	11.130	233.110	3.8
	TOTAL	6196.790	100.0

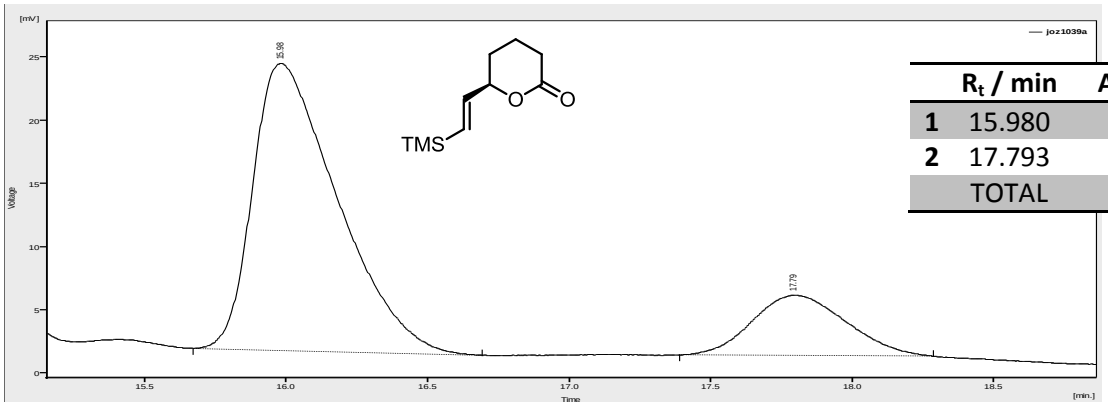


	R_t / min	Area / mV.s	Area / %
1	7.133	6671.326	49.8
2	11.350	6737.628	50.2
	TOTAL	13408.953	100.0

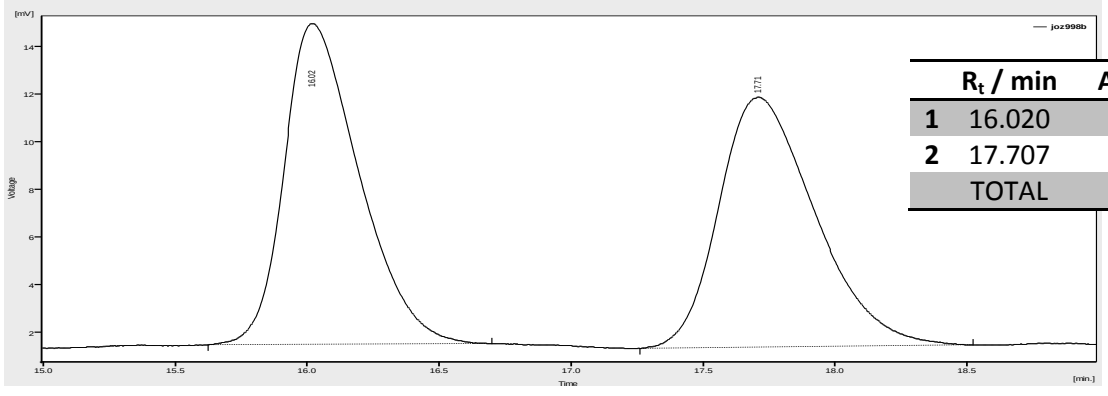
Preparation of ((*Z*)-2-((*S*,*Z*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



Following the general procedure for the kinetic resolution, (*E*,*Z*)-enol ether (91 mg, 0.3 mmol), $Pd(dba)_2$ (7 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (9 mg, 0.01 mmol, 6 mol%) were reacted at 40 °C for 1 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 2: 0.1 mL/ hexane: Et_2O: Et_3N then 100: 3 mL/ PE: EtOAc when enol ether was eluted) to give enantioenriched (*R*)-(*E*,*Z*)-enol ether (41 mg, 45% yield), $[\alpha]_D^{24}$= +8.8 (*c* 9.0, ^{i}PrOH); and enantioenriched *trans*-cyclic ketone (43 mg, 47% yield, -19% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Amylose-2 column; ^{n}hexane: isopropanol/ 96: 4; flow rate = 1.0 mL/min; detection at 220 nm. The enantioriched (*R*)-(*E*,*Z*)-enol ether (30 mg, 0.1 mmol) was reacted with $RuCl_3$ stock solution (0.4 mg, 2.0 µmol, 2 mol%), Oxone® (92 mg, 0.15 mmol) and $NaHCO_3$ (34 mg, 0.4 mmol) in CH_3CN (10 mL) and H_2O (3 mL) to afford the corresponding lactone (67% yield, +62% *ee*) (for the procedure, see above the representative procedure for ruthenium-catalyzed oxidative cleavage of enol ethers); $[\alpha]_D^{24}$= -3.3 (*c* 3.0, $CHCl_3$); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99: 1; flow rate = 1.0 mL/min; detection at 245 nm; **Calculated S-factor** = 5.6

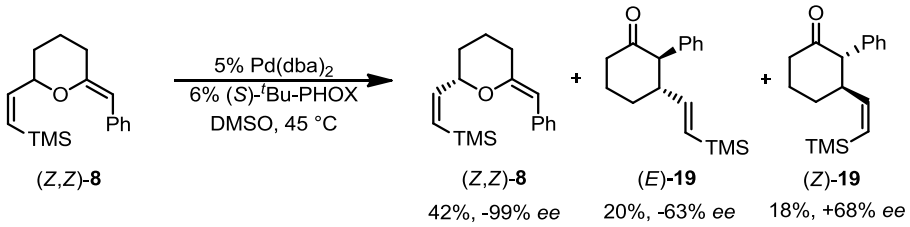


	R_t / min	Area / mV.s	Area / %
1	15.980	473.325	81.2
2	17.793	109.765	18.8
	TOTAL	583.090	100.0

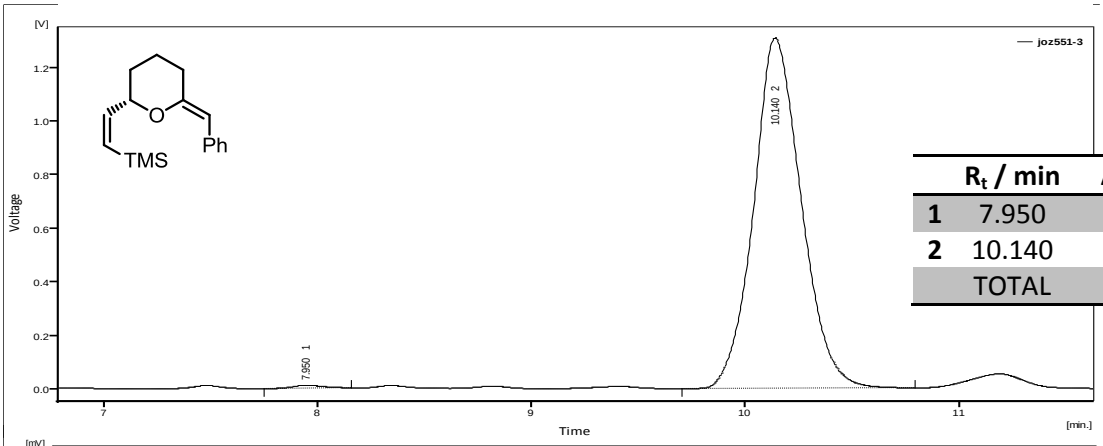


	R_t / min	Area / mV.s	Area / %
1	16.020	268.681	50.2
2	17.707	266.854	49.8
	TOTAL	535.535	100.0

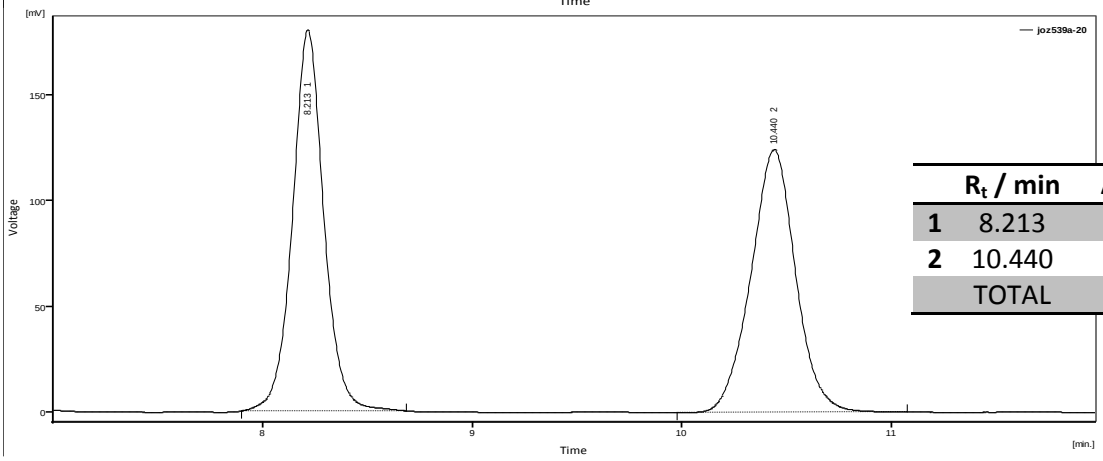
Preparation of ((*Z*)-2-((*S*,*Z*)-6-benzylidenetetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



Following the general procedure for the kinetic resolution, (*Z*,*Z*)-enol ether (83 mg, 0.30 mmol), $Pd(dba)_2$ (9 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (7 mg, 0.02 mmol, 6 mol%) were reacted at 45 °C for 3.5 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 3 mL/ PE: EtOAc when enol ether is eluted) to give enantioenriched (*S*)-(*Z*,*Z*)-enol ether (35 mg, 42% yield, -99% *ee*), $[\alpha]_D^{25}$= +275.8 (*c* 0.1, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane (100%); flow rate = 0.7 mL/min; detection at 254 nm and enantioenriched (*E*)/(*Z*)-*trans*-cyclic ketone (40 mg, 48% yield; (*E*)/(*Z*): 1.0/1.4); then the separation of the diasteroisomers was accomplished *via* preparative HPLC using Waters Xbridge C18 5 µm OBD™ (19 × 250 mm) column to give (*E*)-*trans*-cyclohexanone (19.1 mg, 20% yield, -63% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99.5: 0.5; flow rate = 1.0 mL/min; detection at 220 nm and (*Z*)-*trans*-cyclohexanone (12.4 mg, 18% yield, +68% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99: 1; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 30.5

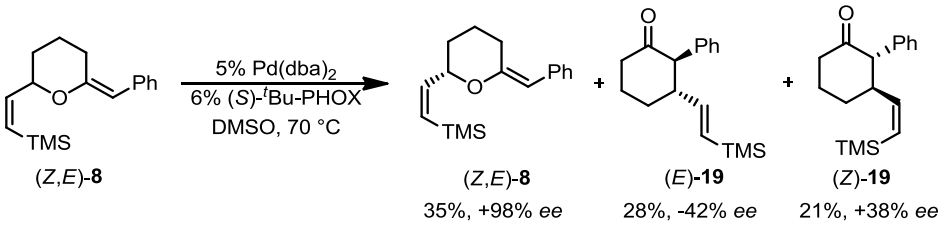


	R_t / min	Area / mV.s	Area / %
1	7.950	123.464	0.6
2	10.140	20288.469	99.4
	TOTAL	20411.933	100.0



	R_t / min	Area / mV.s	Area / %
1	8.213	1873.904	50.4
2	10.440	1846.671	49.6
	TOTAL	3720.574	100.0

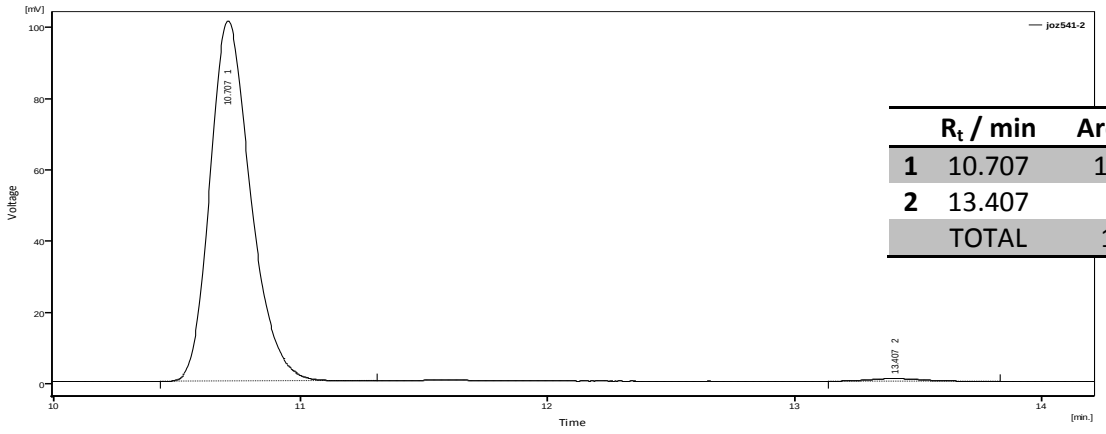
Preparation of ((*Z*)-2-((*S*,*E*)-6-benzylidenetetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



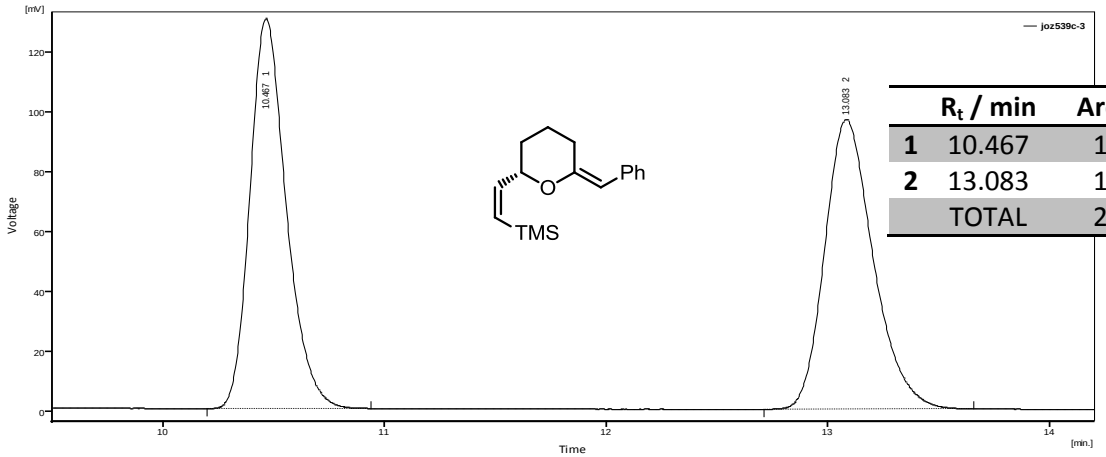
(*Z*,*E*)-**8** (*Z*,*E*)-**8** (*E*)-**19** (*Z*)-**19**

35%, +98% *ee* 28%, -42% *ee* 21%, +38% *ee*

Following the general procedure for the kinetic resolution, (*Z*,*E*)-enol ether (55 mg, 0.19 mmol), $Pd(dba)_2$ (6 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (5 mg, 0.01 mmol, 6 mol%) were reacted at 70 °C for 2 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 3 mL/ PE: EtOAc when enol ether is eluted) to give enantioenriched (*S*)-(*Z*,*E*)-enol ether (19.2 mg, 35% yield, +98% *ee*), $[\alpha]_D^{23}$= +285.7 (*c* 0.1, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane (100%); flow rate = 0.6 mL/min; detection at 254 nm and enantioenriched (*E*)/(*Z*)-*trans*-cyclic ketone (33.5 mg, 61% yield, (*E*)/(*Z*): 1.0/1.6); then the separation of the diasteroisomers was accomplished *via* preparative HPLC using Waters Xbridge C18 5 µm OBD™ (19 × 250 mm) column to give (*E*)-*trans*-cyclohexanone (15.4 mg, 38% yield, -42% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99.5: 0.5; flow rate = 1.0 mL/min; detection at 220 nm and (*Z*)-*trans*-cyclohexanone (11.5 mg, 21% yield, +38% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99: 1; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 13.5

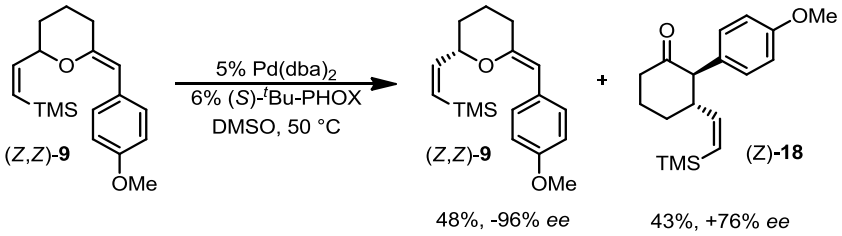


	R_t / min	Area / mV.s	Area / %
1	10.707	1159.745	99.0
2	13.407	0.767	1.0
	TOTAL	101.930	100.0

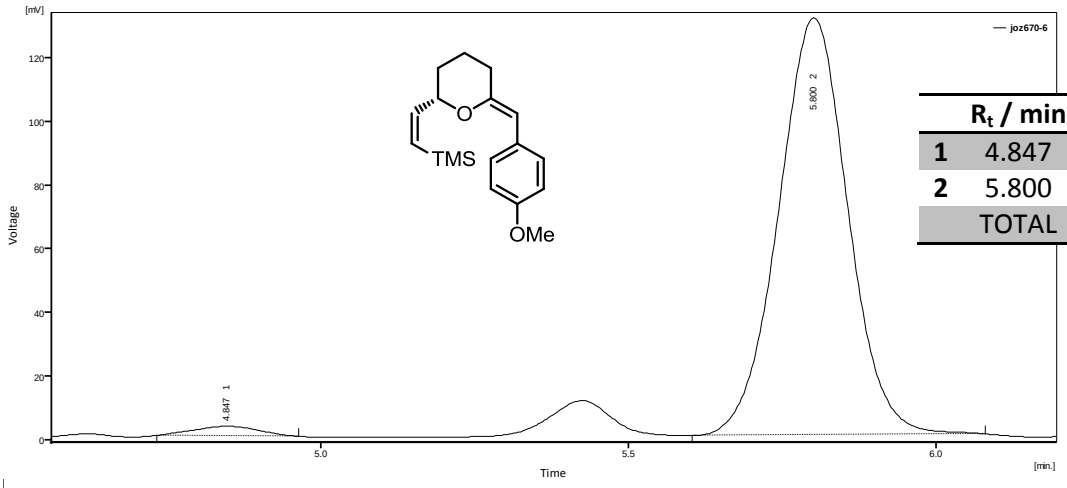


	R_t / min	Area / mV.s	Area / %
1	10.467	1485.917	50.2
2	13.083	1973.217	49.8
	TOTAL	2959.135	100.0

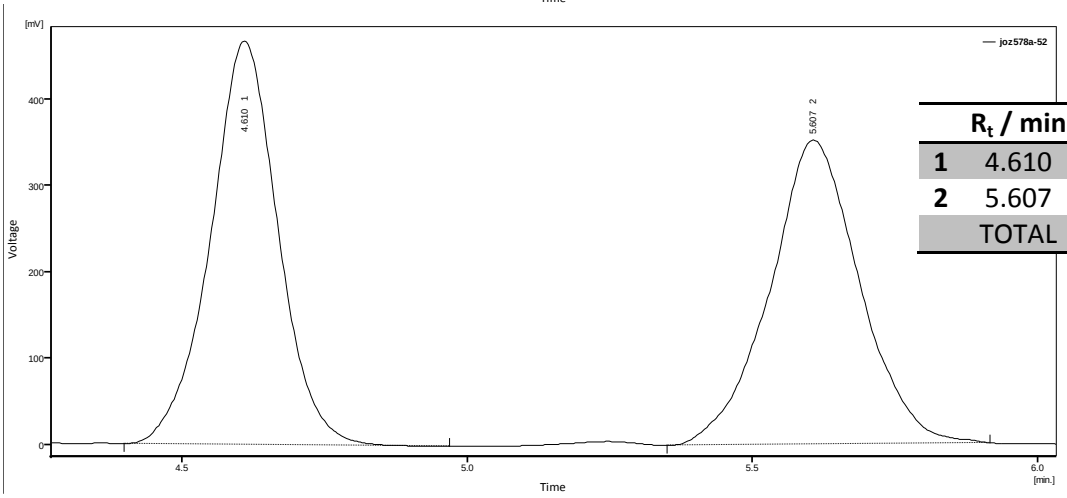
Preparation of ((*Z*)-2-((*S*,*Z*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



Following the general procedure for the kinetic resolution, (*Z*,*Z*)-enol ether (76 mg, 0.25 mmol), $Pd(dba)_2$ (7 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (6 mg, 0.01 mmol, 6 mol%) were reacted at 50 °C for 2 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 5: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 5 mL/ PE: EtOAc when enol ether was eluted) to give enantioenriched (*S*)-(Z,*Z*)-enol ether (36.5 mg, 48% yield, -96% *ee*), $[\alpha]_D^{24}$= +145.8 (*c* 1.2, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99.8: 0.2; flow rate = 1.0 mL/min; detection at 254 nm, and enantioenriched *trans*-cyclic ketone (32.7 mg, 43% yield, +76% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 97: 3; flow rate = 1.0 mL/min; detection at 220 nm. **Calculated S-factor** = 64.7

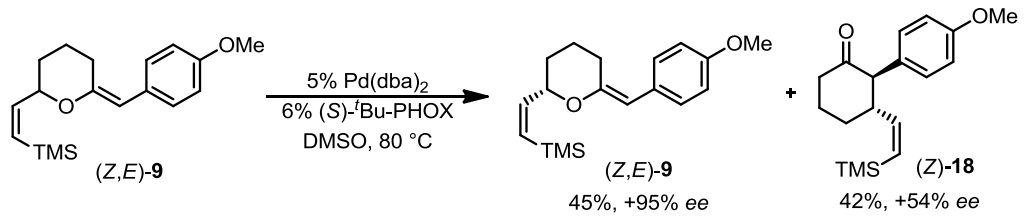


	R_t / min	Area / mV.s	Area / %
1	4.847	22.106	2.1
2	5.800	1025.089	97.9
	TOTAL	1047.195	100.0

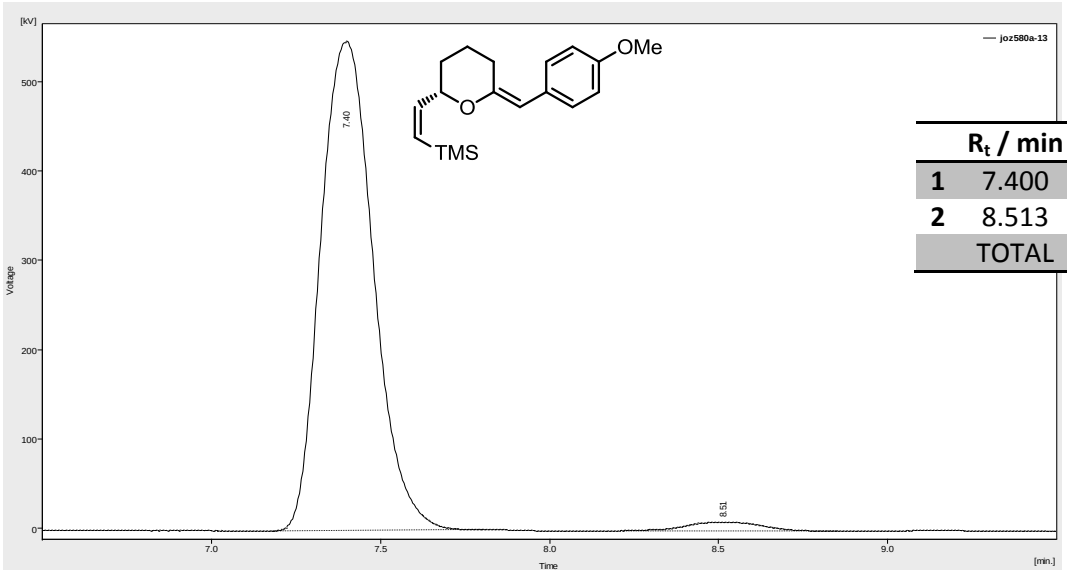


	R_t / min	Area / mV.s	Area / %
1	4.610	3847.233	50.0
2	5.607	3850.357	50.0
	TOTAL	7697.590	100.0

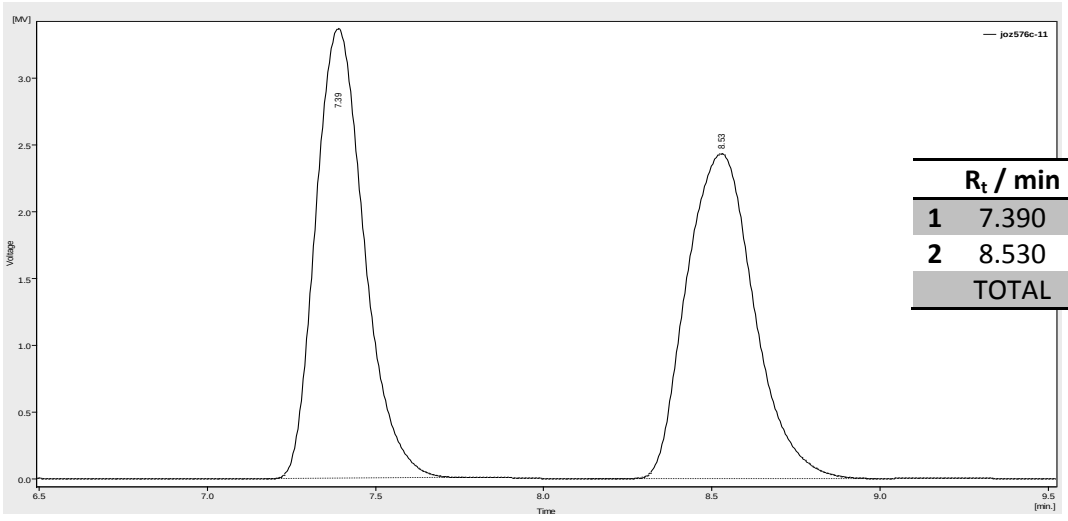
Preparation of ((*Z*)-2-((*S*,*E*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



Following the general procedure for the kinetic resolution, (*Z*,*E*)-enol ether (91 mg, 0.30 mmol), $Pd(dba)_2$ (9 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (7 mg, 0.02 mmol, 6 mol%) were reacted at 80 °C for 4 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 10: 0.2 mL/ hexane: Et_2O: Et_3N then 100: 10 mL/ PE: EtOAc when enol ether was eluted) to give enantioenriched (*S*)-(*Z*,*E*)-enol ether (41 mg, 45% yield, +95% *ee*), $\mathbf{[\alpha]_D^{24}}$= +133.3 (*c* 0.7, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 99.8: 0.2; flow rate = 1 mL/min; detection at 254 nm and enantioenriched *trans*-cyclic ketone (38 mg, 42% yield, +54% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 99: 1; flow rate = 1.0 mL/min; detection at 254 nm. **Calculated S-factor** = 29.0

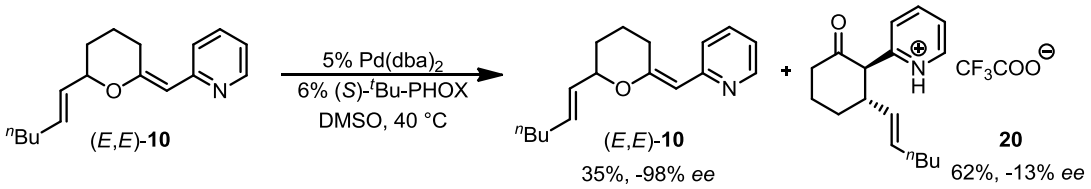


	R_t / min	Area / mV.s	Area / %
1	7.400	594.039	97.4
2	8.513	15.836	2.6
	TOTAL	609.875	100.0

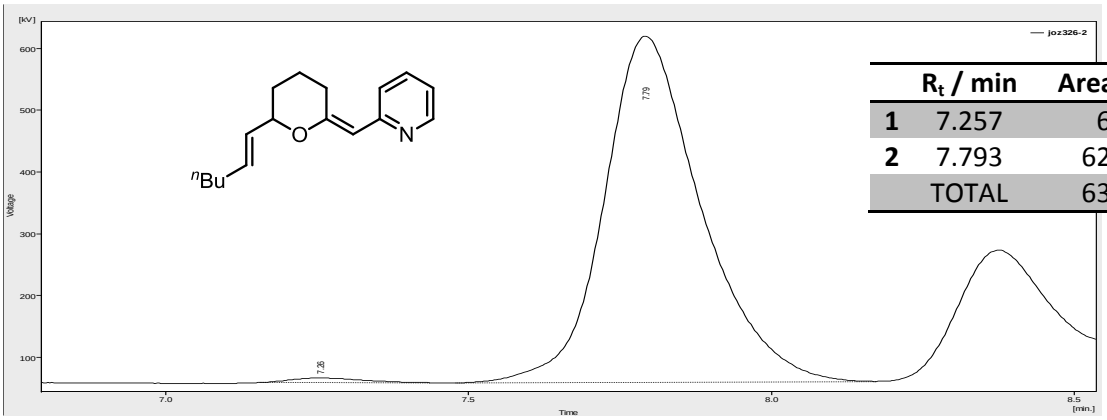


	R_t / min	Area / mV.s	Area / %
1	7.390	335.653	49.9
2	8.530	243.224	50.1
	TOTAL	579.877	100.0

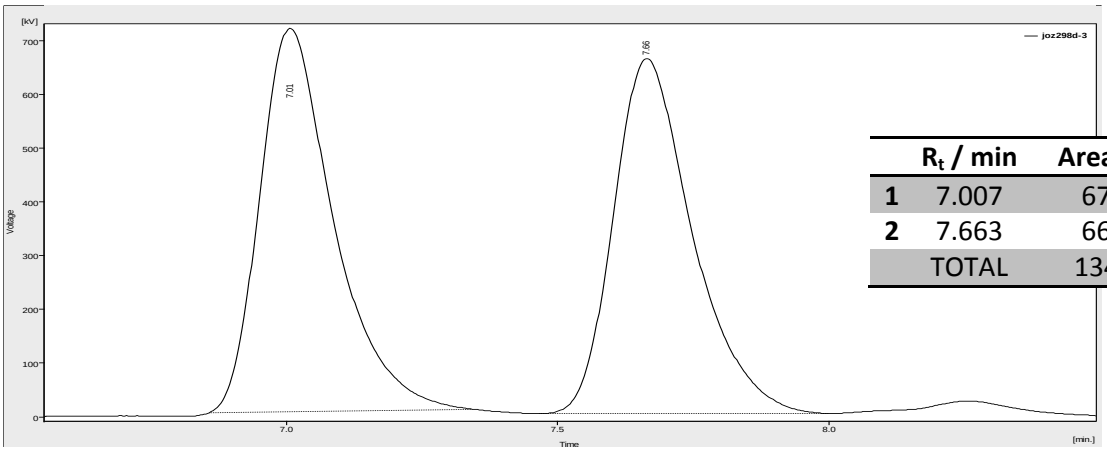
Preparation of (-)-2-((*E*)-(6-((*E*)-hex-1-en-1-yl)tetrahydro-2H-pyran-2-ylidene)methyl)pyridine



Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (156 mg, 0.6 mmol), $Pd(dba)_2$ (17.4 mg, 0.03 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (14.1 mg, 0.03 mmol, 6 mol%) were reacted at 40 °C for 6.0 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 2: 0.2 mL to 500: 50: 0 / hexane: Et_2O: Et_3N when enol ether is eluted) to give enantioenriched (*E*,*E*)-enol ether (54.6 mg, 35% yield, -98% *ee*), $[\alpha]_D^{23}$= -30.0 (*c* 1.0, MeOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 95:5; flow rate = 1.0 mL/min; detection at 254 nm and a mixture of enantioenriched *trans*-cyclic ketone with its tautomeric form 1:0.54 (97 mg, 0.39 mmol, 62% yield). To this mixture in EtOAc (1.5 mL) was added trifluoroacetatic acid (0.09 mL, 1.16 mmol, 3eq.). Reaction mixture was stirred at room temperature for 10 minutes. The reaction was quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography on silica gel (50: 50/ petroleum ether: EtOAc) to give the *trans*-cyclic ketone trifluoroacetate salt as a yellow oil (145 mg, 100%, -13% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 80:20; flow rate = 1.0 mL/min; detection at 254 nm. **Calculated S-factor** = 13.5



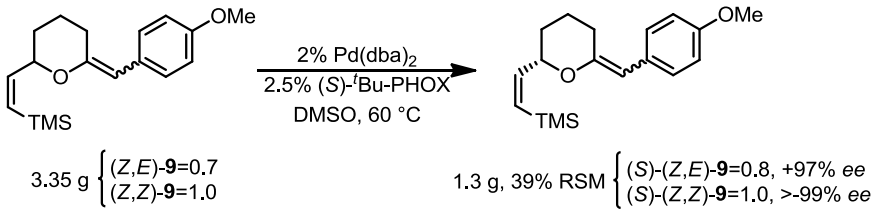
	R_t / min	Area / mV.s	Area / %
1	7.257	6.248	1.0
2	7.793	624.656	99.0
	TOTAL	630.904	100.0



	R_t / min	Area / mV.s	Area / %
1	7.007	674.336	50.3
2	7.663	665.876	49.7
	TOTAL	1340.211	100.0

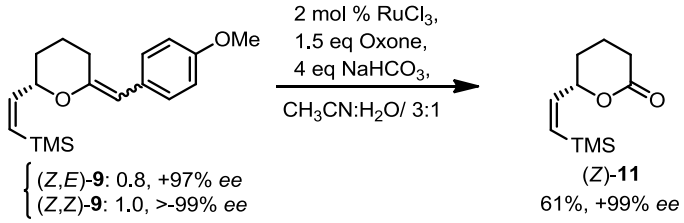
Kinetic resolution of (*E*,*E*)/(*E*,*Z*)-enol ether isomer mixtures

Preparation of ((1*Z*)-2-((*S*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



Following the general procedure for the kinetic resolution, a mixture of (*Z*,*E*)/(*Z*,*Z*)-enol ether (3.35 g, *E*: 0.7/ *Z*: 1.0, 11.1 mmol), $Pd(dba)_2$ (127 mg, 0.22 mmol, 2 mol%) and (*S*)-^{t}Bu-Phox (108 mg, 0.28 mmol, 2.5 mol%) was heated at 60 °C for 2.3 h. The reaction mixture was then purified *via* column chromatography on silica gel (500 : 10 : 0.2 mL/ hexane : Et_2O : Et_3N) to give enantioenriched (*S*)-(*Z*,*E*)/(*S*)-(*Z*,*Z*)-enol ether mixture (1.3 g, 39% yield, (*S*)-(*Z*,*E*): 0.8, +97% *ee*/ (*S*)-(*Z*,*Z*): 1.0; >-99% *ee*). A sample of 14 mg was purified by HPLC preparative using an Alltech "Alltima HP C18 5u" column (150 mm x 22 mm) for chiral HPLC analysis; **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane: isopropanol/ 99.8 : 0.2; flow rate = 1 mL/min; detection at 254 nm for (*S*)-(*Z*,*E*)-enol ether and phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99.8 : 0.2; flow rate = 1 mL/min; detection at 254 nm for (*S*)-(*Z*,*Z*)-enol ether. These enol ethers showed satisfactory HPLC traces.

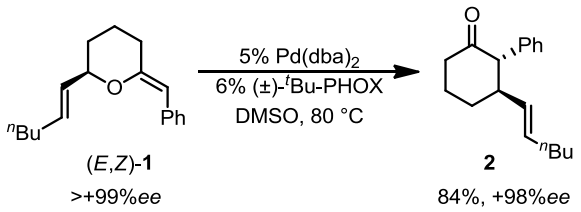
Preparation of (*S*,*Z*)-6-(2-(trimethylsilyl)vinyl)tetrahydro-2*H*-pyran-2-one



Following the representative procedure, a solution of enantioenriched (*S*)-(*Z*,*E*)/(*S*)-(*Z*,*Z*)-enol ether mixture (1.3 g, 4.30 mmol, *E*: 0.8; +97% *ee*/ *Z*: 1.0; -99% *ee*), $RuCl_3.xH_2O$ (18 mg, 0.09 mmol, 2 mol%), Oxone® (3.9 g, 6.45 mmol, 1.5 eq) and $NaHCO_3$ (1.5 g, 17.2 mmol, 4 eq) were used in CH_3CN (360 mL) and distilled water (120 mL). After completion in 1 h; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*S*)-lactone as white solid (520 mg, 61% yield, +99% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Amylose-2 column; ^{n}hexane: isopropanol/ 96: 4; flow rate = 1.0 mL/min; detection at 220 nm. This lactone showed satisfactory HPLC trace.

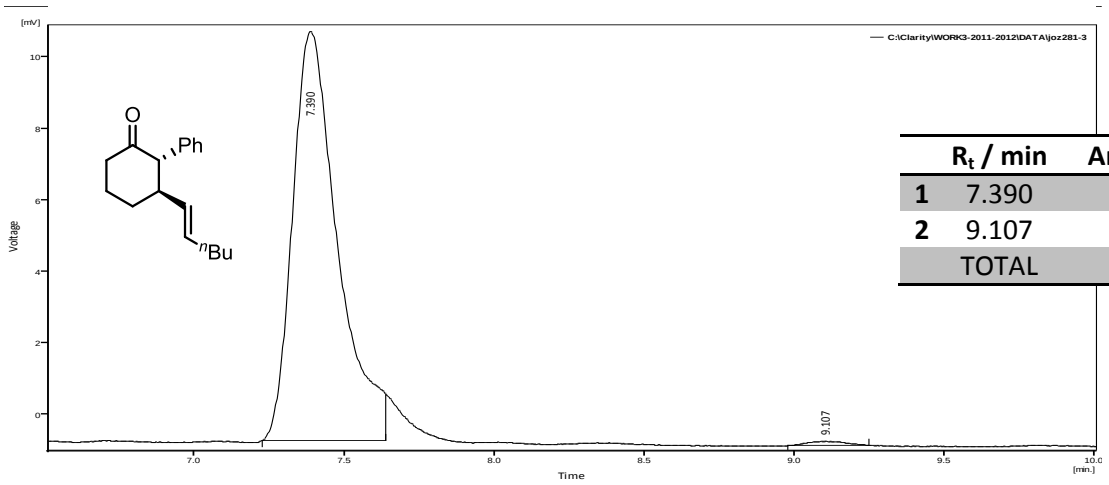
Enantioenriched enol ethers transformations

Preparation of (2*R*,3*S*)-3-((*E*)-hex-1-en-1-yl)-2-phenylcyclohexanone

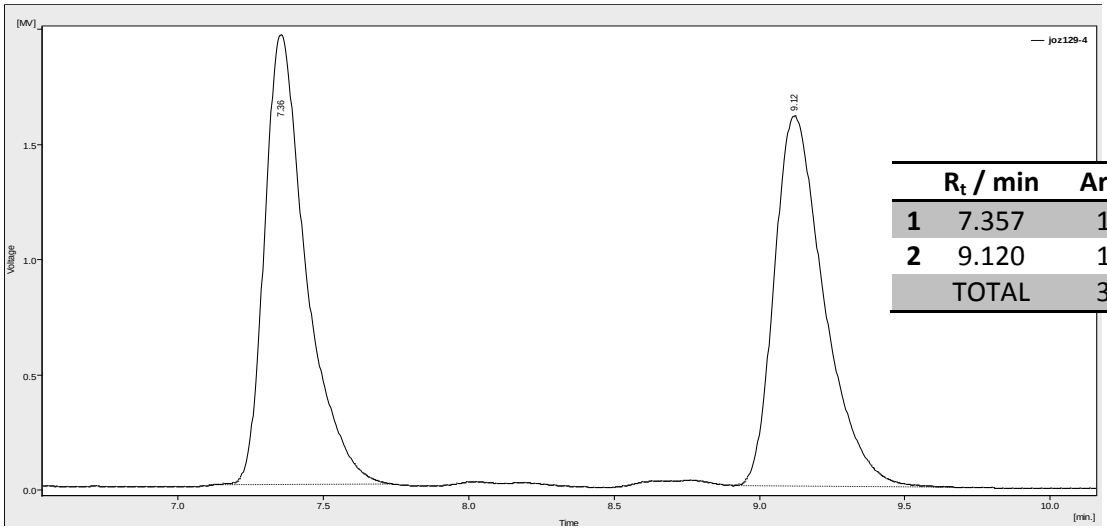


(*E*,*Z*)-**1** >+99%*ee* — **2** 84%, +98%*ee*

To a reaction vial was added (*R*)-(*E*,*Z*)-enol ether (43 mg, 0.17 mmol, >+99% *ee*), $Pd(dba)_2$ (5 mg, 0.01 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (4 mg, 0.01 mmol, 6 mol%). The vial was sealed with a rubber septum, evacuated under reduced pressure and back filled with argon. DMSO (0.3 mL, 0.4 N) was added under argon, and the vial evacuated for *ca.* 2 min. The vial was back filled with argon and stirred in a preheated heating block at 80 °C for 3 h. The reaction vial was cooled to room temperature and directly purified by flash chromatography on silica gel (95:5/ petroleum ether : EtOAc) to give enantioenriched (2*R*,3*S*)-*trans*-cyclic ketone (36 mg, 84% yield, +98% *ee*), $[\alpha]_D^{22}$= -30.0 (*c* 1.0, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane : isopropanol/ 95 : 5; flow rate = 1.0 mL/min; detection at 220 nm.

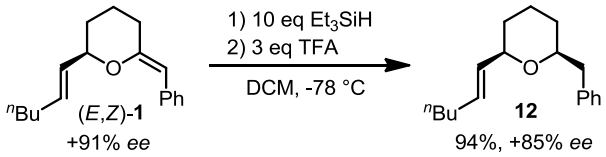


	R_t / min	Area / mV.s	Area / %
1	7.390	118.689	99.2
2	9.107	1.012	0.8
	TOTAL	119.701	100.0

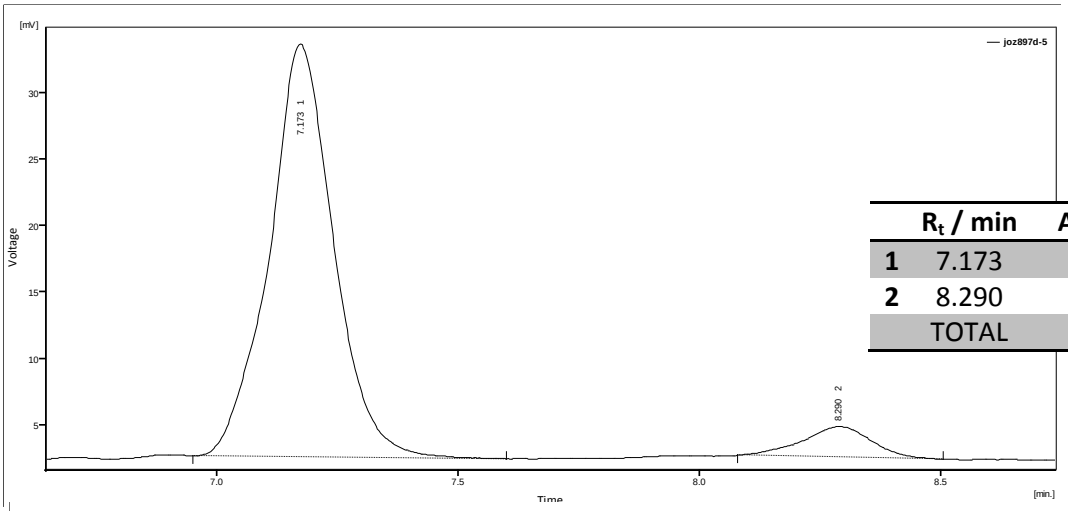


	R_t / min	Area / mV.s	Area / %
1	7.357	1927.869	50.2
2	9.120	1916.043	49.8
	TOTAL	3857.770	100.0

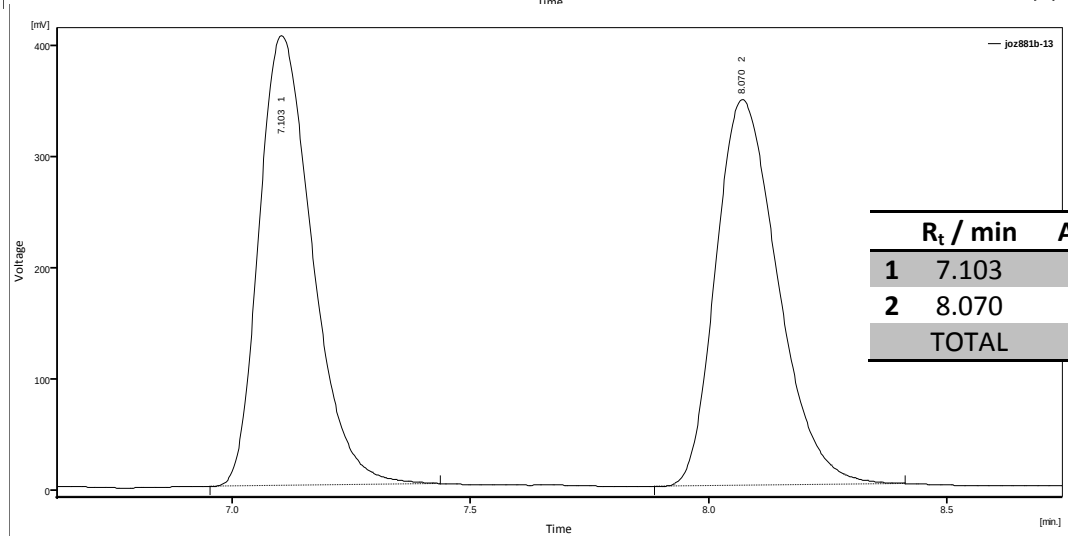
Preparation of (2*S*,6*R*)-2-benzyl-6-((*E*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran



To a cooled (-78°C) solution of (+)-(*Z*)-enol ether (60 mg, 0.23 mmol, +91% *ee*) and triethylsilane (0.4 mL, 2.3 mmol, 10 eq.) in DCM (2 mL) was added dropwise during 2 min a solution of TFA (55 µL, 0.7 mmol, 3 eq.) in DCM (1mL). The solution was stirred at –78°C for 45 min. The reaction mixture was then quenched with water, allowed to warm at room temperature and diluted with DCM. The organic layer was washed with brine, dried over $MgSO_4$, concentrated, and the residue was purified by column chromatography on silica gel (99.5: 0.5/ petroleum ether: EtOAc) to give the (+)-pyran as white oil (55 mg, 94% yield, +85% *ee*); $[\alpha]_D^{22}$= +12.0 (*c* 1.0, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 100: 0; flow rate = 0.7 mL/min; detection at 220 nm

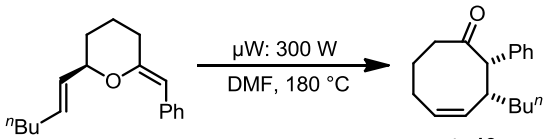


	R_t / min	Area / mV.s	Area / %
1	7.173	288.526	92.5
2	8.290	23.269	7.5
	TOTAL	311.796	100.0



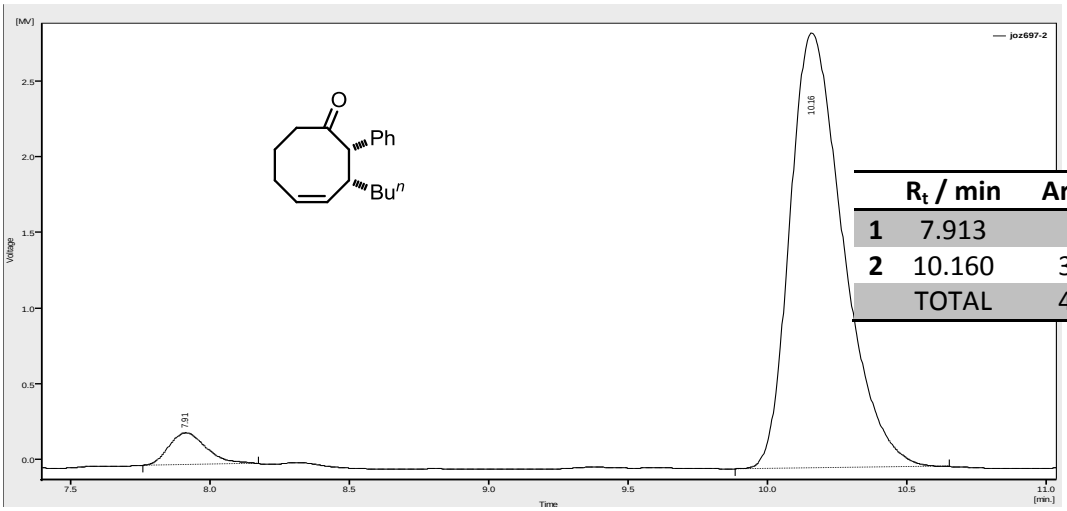
	R_t / min	Area / mV.s	Area / %
1	7.103	3148.454	50.0
2	8.070	3148.909	50.0
	TOTAL	6297.363	100.0

Preparation of (2*S*,3*R*,*Z*)-3-butyl-2-phenylcyclooct-4-enone

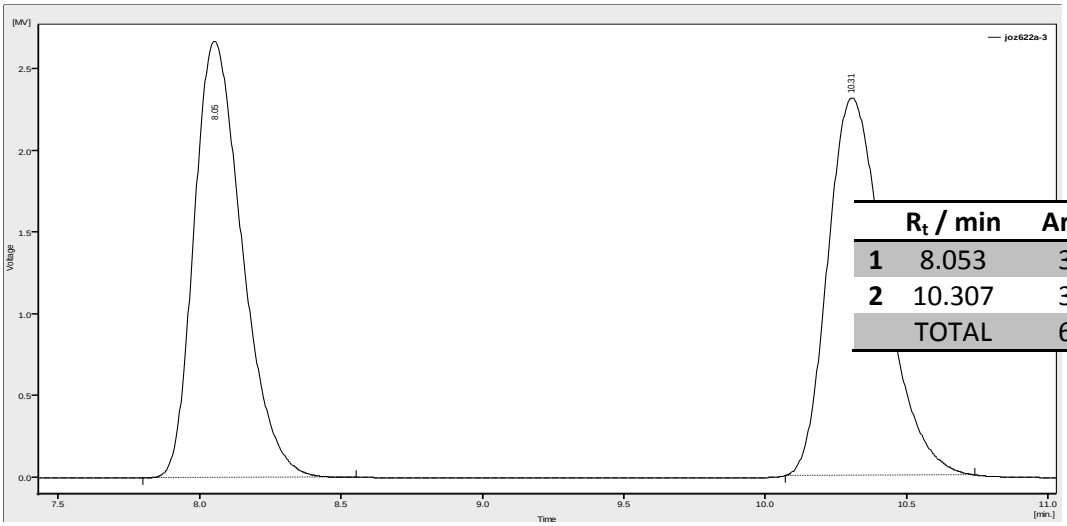


(*E*,*Z*)-**1** +90% *ee* → *cis*-**13** 90%, -90% *ee*

To a 10 mL glass pressure microwave tube equipped with a magnetic stirrer bar was added enantioenriched enol ether (+)-(*Z*)-enol ether (52 mg, 0.2 mmol, +90% *ee*) and DMF (0.5 N). The tube was closed with a silicon septum. The reaction mixture was subjected to microwave irradiation (power: 300 W) at 180 °C for 20 min. The reaction vial was cooled to room temperature and directly purified by flash chromatography on silica gel (98 : 2 / petroleum ether : EtOAc) to give enantioenriched (-)-*cis*-cyclic ketone as colorless oil (47 mg, 90% yield, -90% *ee*), $[\alpha]_D^{23}$= -71.1 (*c* 0.5, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane:isopropanol/ 98:2; flow rate = 1.0 mL/min; detection at 220 nm.



	R_t / min	Area / mV.s	Area / %
1	7.913	198.053	4.9
2	10.160	3815.840	95.1
	TOTAL	4013.893	100.0



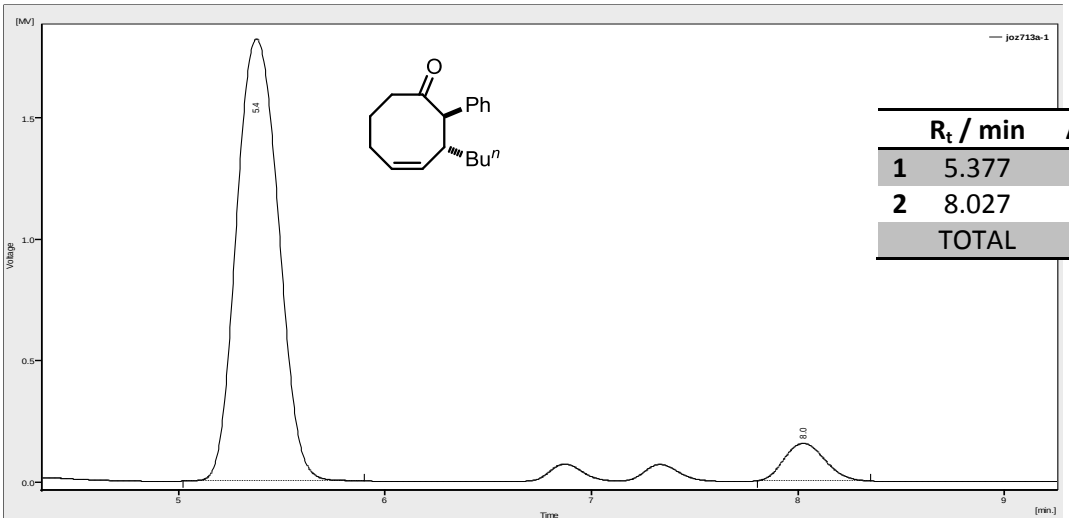
	R_t / min	Area / mV.s	Area / %
1	8.053	3165.036	49.4
2	10.307	3238.205	50.6
	TOTAL	6403.241	100.0

Preparation of (2*R*,3*R*,*Z*)-3-butyl-2-phenylcyclooct-4-enone

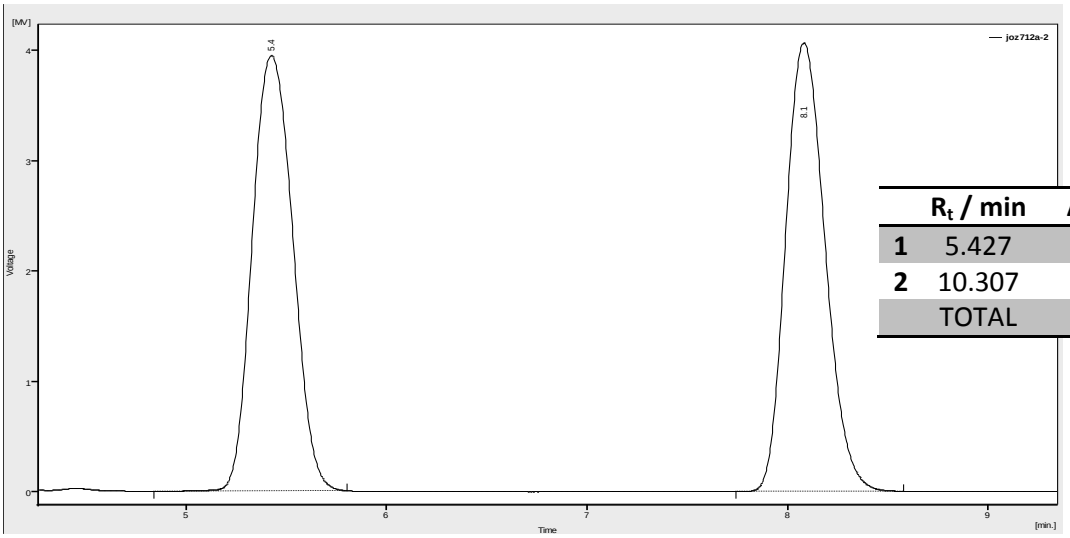
(*E*,*E*)-**1**
+87% *ee*

trans-**13**
86%, +85% *ee*

To a 10 mL glass pressure microwave tube equipped with a magnetic stirrer bar was added enantioenriched enol ether (+)-(*E*)-enol ether (49 mg, 0.2 mmol, +90% *ee*) and DMF (0.5 N). The tube was closed with a silicon septum. The reaction mixture was subjected to microwave irradiation (power: 300 W) at 180 °C for 20 min. The reaction vial was cooled to room temperature and directly purified by flash chromatography on silica gel (99: 1 / petroleum ether: EtOAc) to give enantioenriched (+)-*trans*-cyclic ketone as white solid (42 mg, 86% yield, +85% *ee*), $[\alpha]_D^{23}$= +164.0 (*c* 0.3, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-1 column; ^{n}hexane:isopropanol/ 99:1; flow rate = 1.0 mL/min; detection at 220 nm.



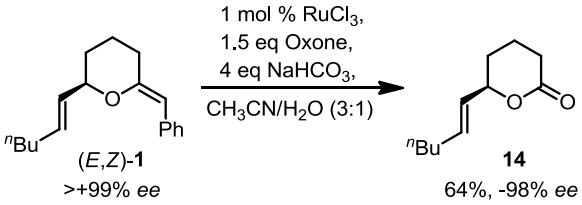
	R_t / min	Area / mV.s	Area / %
1	5.377	2572.218	92.4
2	8.027	211.441	7.6
	TOTAL	2783.659	100.0



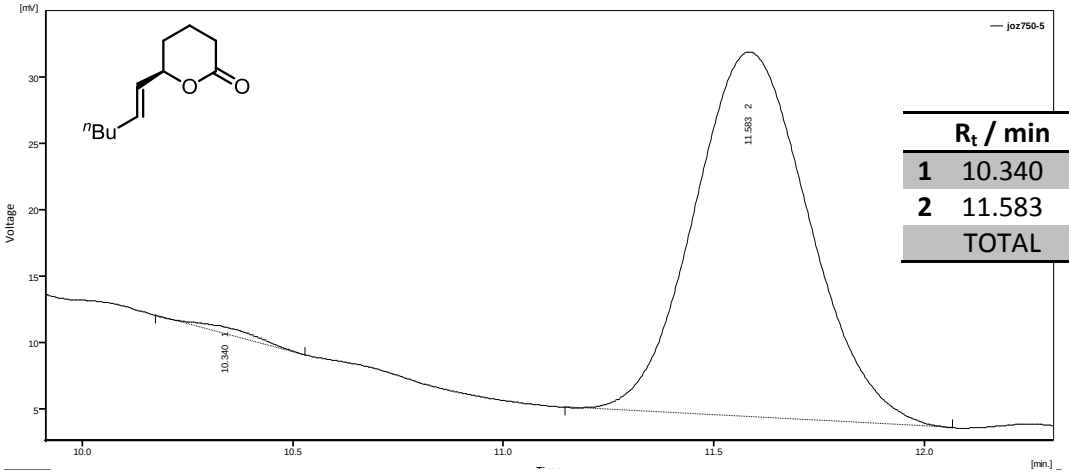
	R_t / min	Area / mV.s	Area / %
1	5.427	5549.075	50.0
2	10.307	5555.078	50.0
	TOTAL	11104.153	100.0

Representative procedure for ruthenium-catalyzed oxidative cleavage of enol ethers to lactones

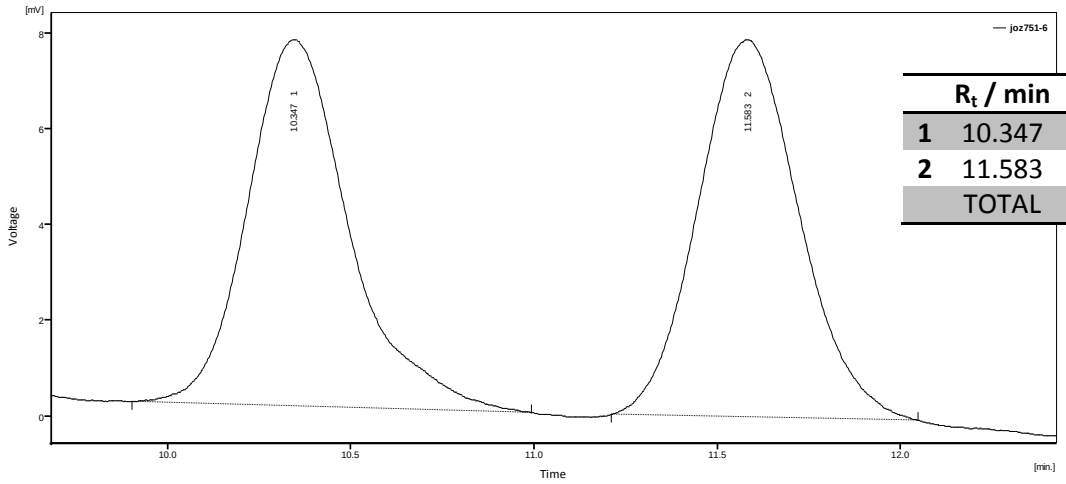
Preparation of (*R*,*E*)-6-(hex-1-en-1-yl)tetrahydro-2*H*-pyran-2-one



To a stirred mixture of enantioenriched (*R*)-(*E*,*Z*)-enol ether (64 mg, 0.25 mmol, >+99% *ee*) and $RuCl_3$ stock solution (0.5 mg, 2.5 µmol, 1 mol% equiv) in CH_3CN (12 mL) and distilled water (4 mL) was added in portions a mixture of Oxone® (230 mg, 0.38 mmol) and $NaHCO_3$ (84 mg, 1 mmol) over a period of 4 min at room temperature. The solution turned from black to yellow colour in 5 min. The reaction was monitored by TLC. After completion in 18 min, the reaction was quenched with saturated aqueous solution of NaS_2O_3 and then extracted with DCM twice. The combined organic layer was washed with water and brine, respectively, dried over anhydrous $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography on silica gel (90 : 10/ petroleum ether : EtOAc) to give the (*R*)-lactone as colourless oil (29 mg, 64% yield, -98% *ee*); $[\alpha]_D^{23}$= -24.4 (*c* 0.5, ^{i}PrOH); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99: 1; flow rate = 1.0 mL/min; detection at 245 nm



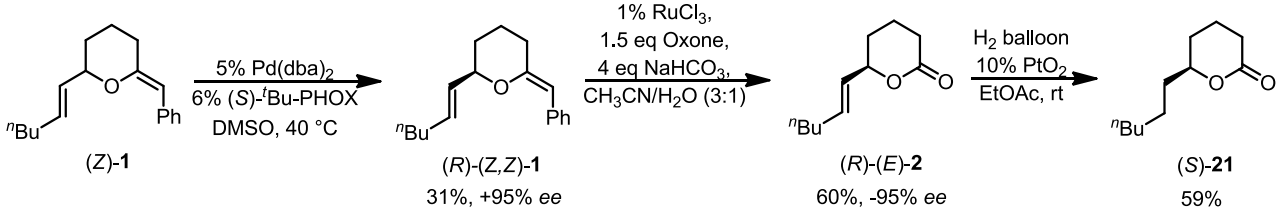
	R_t / min	Area / mV.s	Area / %
1	10.340	5.804	1.1
2	11.583	522.698	98.9
	TOTAL	528.502	100.0



	R_t / min	Area / mV.s	Area / %
1	10.347	148.025	49.4
2	11.583	151.374	50.6
	TOTAL	299.398	100.0

Stereochemistry proofs: Schemes and HPLC data

Stereochemistry proofs of (*R,Z*)-2-benzylidene-6-((*E*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran and (*R,E*)-6-(hex-1-en-1-yl)tetrahydro-2*H*-pyran-2-one



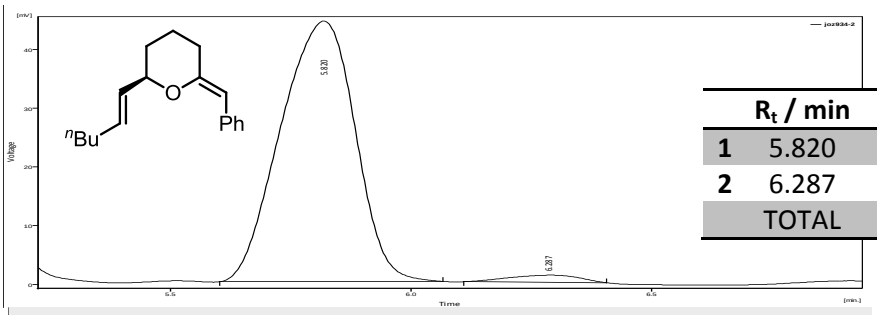
(*Z*)-**1**

(*R*)-(*Z,Z*)-**1**
31%, +95% *ee*

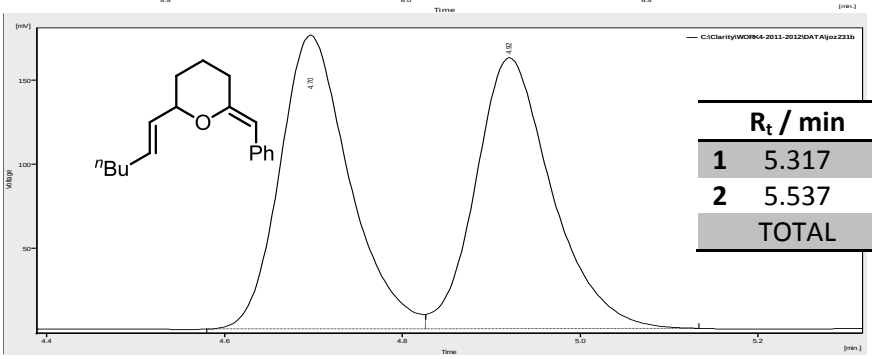
(*R*)-(*E*)-**2**
60%, -95% *ee*

(*S*)-**21**
59%
$[\alpha]_D^{23}$= -31.2 (*c* 0.45 $CHCl_3$)
(lit.[4] for the (*R*)-enantiomer
$[\alpha]_D^{20}$= +46.1 (c 0.61 $CHCl_3$))

Chiral HPLC:
Phenomenex® Lux 3u
Cellulose-2 column;
*n*hexane (100%);
1.0 mL/min;
254 nm

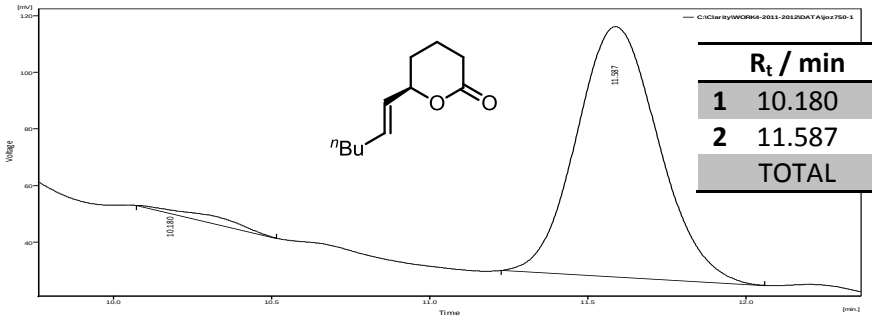


	R_t / min	Area / mV.s	Area / %
1	5.820	476.867	97.5
2	6.287	12.423	2.5
	TOTAL	489.290	100.0

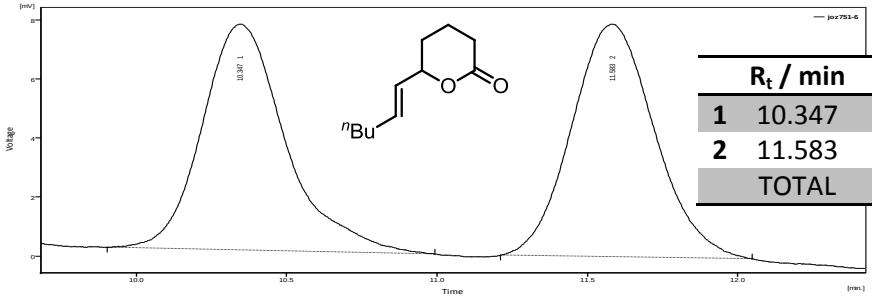


	R_t / min	Area / mV.s	Area / %
1	5.317	1006.000	49.3
2	5.537	1033.548	50.7
	TOTAL	2039.548	100.0

Chiral HPLC:
Phenomenex® Lux 3u
Cellulose-2 column;
*n*hexane: isopropanol/
99:1;
1.0 mL/min;
245 nm



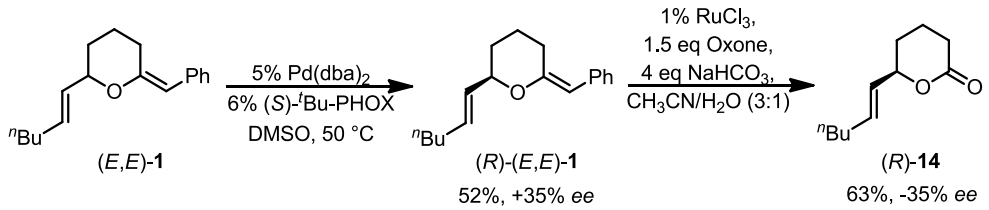
	R_t / min	Area / mV.s	Area / %
1	10.180	38.177	2.3
2	11.587	1597.208	97.7
	TOTAL	1635.385	100.0



	R_t / min	Area / mV.s	Area / %
1	10.347	148.025	49.4
2	11.583	151.374	50.6
	TOTAL	299.398	100.0

[4] U. Goergens, U. and M. P. Schneider, *Tertrahedron: Asymmetry* 1992, **3**, 831

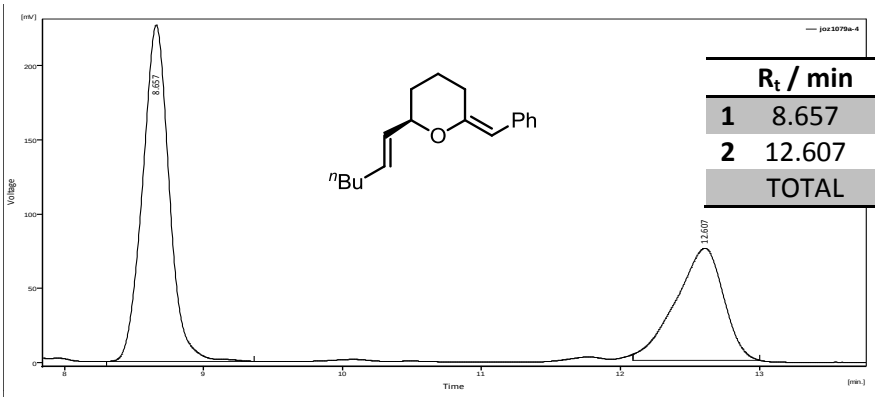
Stereochemistry proofs of (*R*,*E*)-2-benzylidene-6-((*E*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran



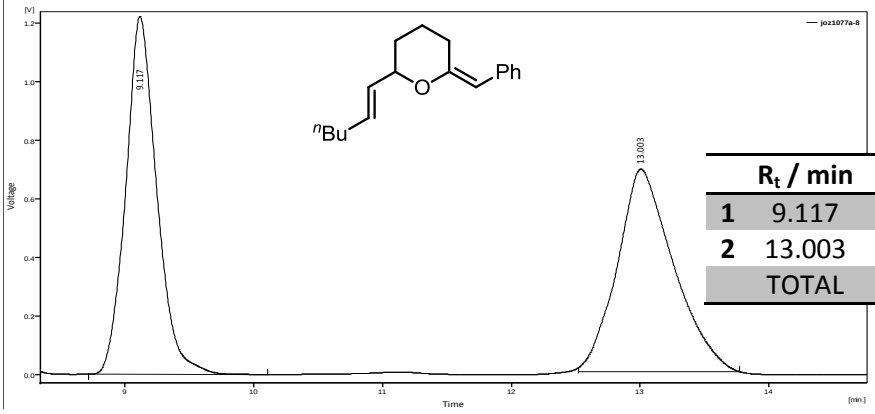
(*E*,*E*)-**1** → (*R*)-(*E*,*E*)-**1** 52%, +35% *ee* → (*R*)-**14** 63%, -35% *ee*

Chiral HPLC:

Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane (100%); 1.0 mL/min; 254 nm



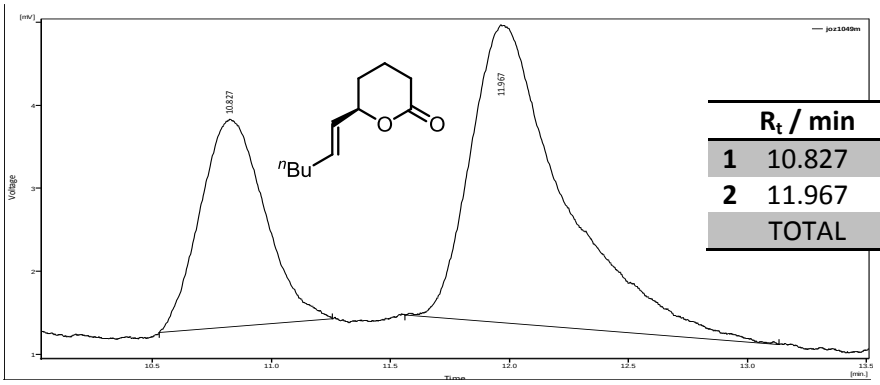
	R_t / min	Area / mV.s	Area / %
1	8.657	3021.091	62.5
2	12.607	1813.141	37.5
	TOTAL	12012.425	100.0



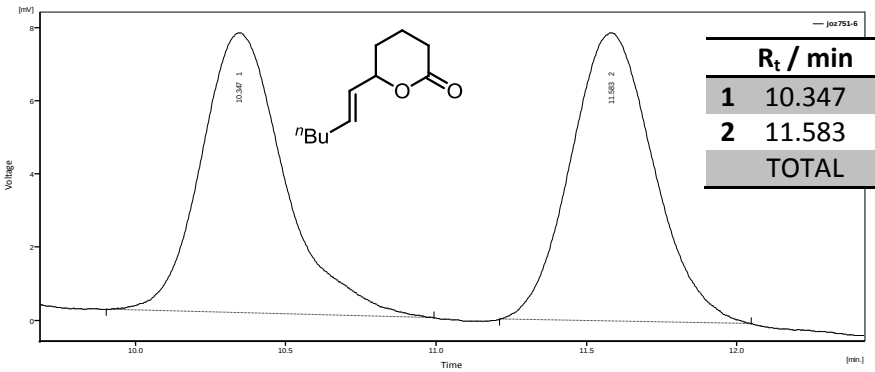
	R_t / min	Area / mV.s	Area / %
1	9.117	20472.232	49.4
2	13.003	21009.043	50.6
	TOTAL	12012.425	100.0

Chiral HPLC:

Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99:1; 1.0 mL/min; 245 nm

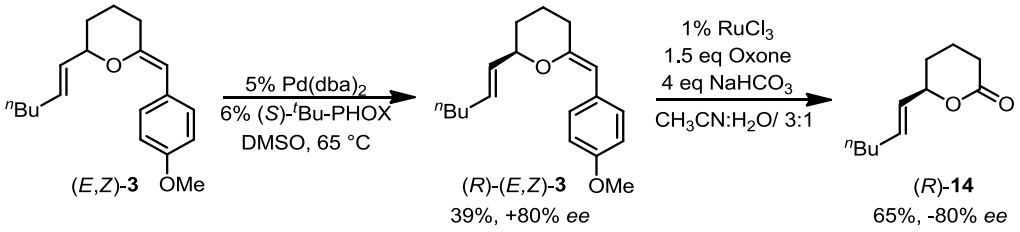


	R_t / min	Area / mV.s	Area / %
1	10.827	47.162	32.6
2	11.967	97.516	67.4
	TOTAL	144.678	100.0



	R_t / min	Area / mV.s	Area / %
1	10.347	148.025	49.4
2	11.583	151.374	50.6
	TOTAL	258.480	100.0

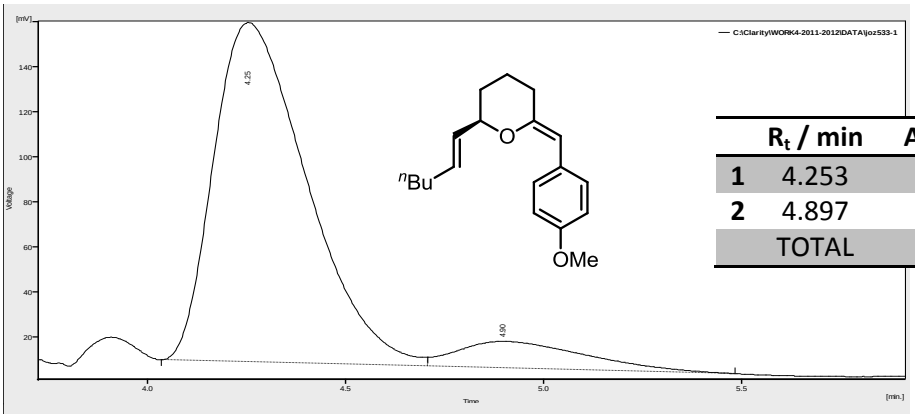
Stereochemistry proofs of (*R*,*Z*)-2-((*E*)-hex-1-en-1-yl)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran



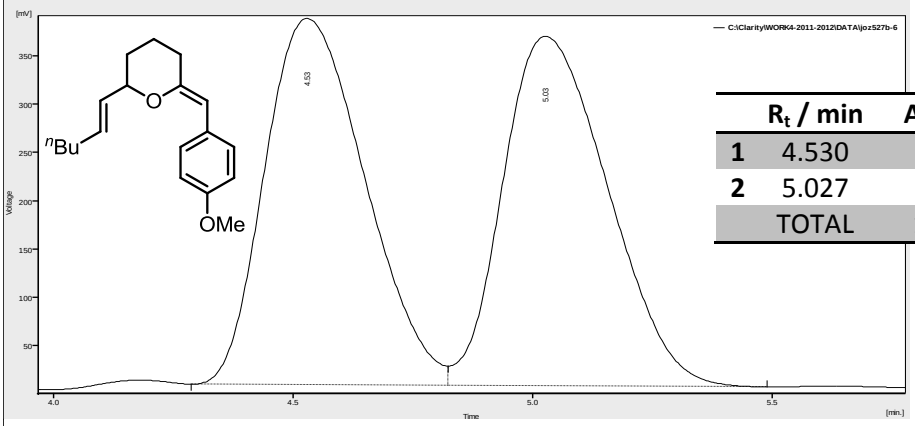
(*E*,*Z*)-**3** | (*R*)-(*E*,*Z*)-**3**, 39%, +80% *ee* | (*R*)-**14**, 65%, -80% *ee*

Chiral HPLC:

Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99:1; 1.0 mL/min; 254 nm



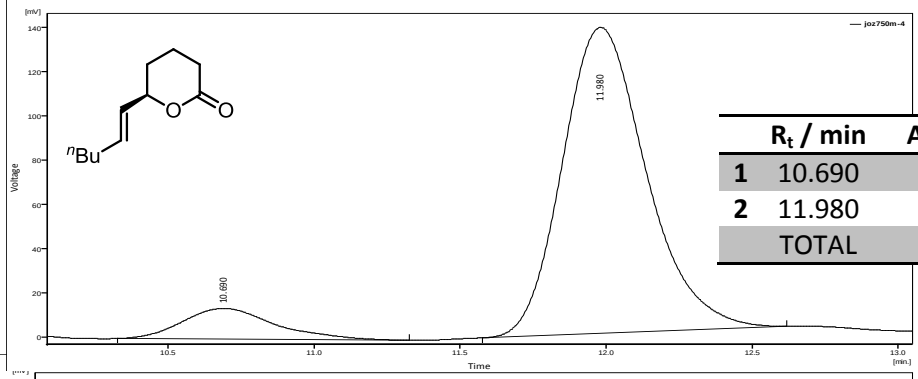
	R_t / min	Area / mV.s	Area / %
1	4.253	2475.413	90.1
2	4.897	273.112	9.9
	TOTAL	2748.525	100.0



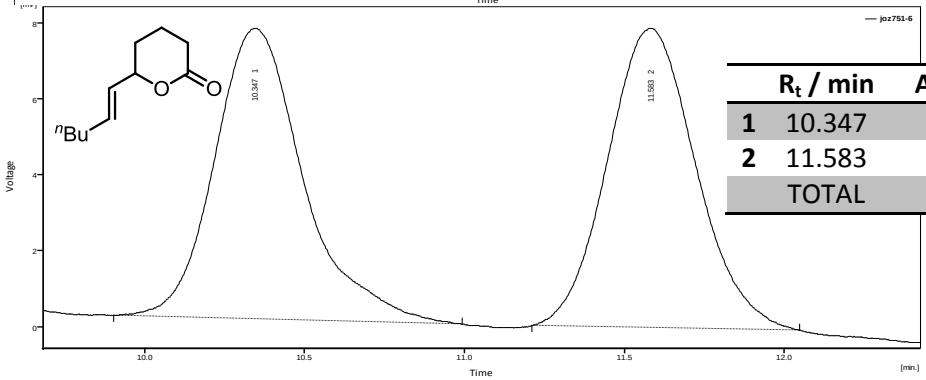
	R_t / min	Area / mV.s	Area / %
1	4.530	5512.563	50.0
2	5.027	5513.427	50.0
	TOTAL	11025.990	100.0

Chiral HPLC:

Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99:1; 1.0 mL/min; 245 nm

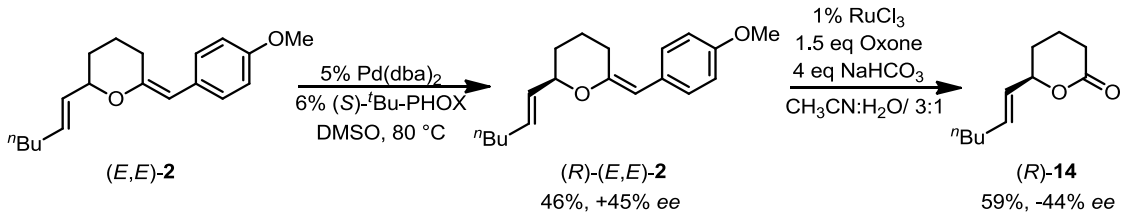


	R_t / min	Area / mV.s	Area / %
1	10.690	307.334	10.0
2	11.980	2757.803	90.0
	TOTAL	3065.136	100.0



	R_t / min	Area / mV.s	Area / %
1	10.347	148.025	49.4
2	11.583	151.374	50.6
	TOTAL	299.398	100.0

Stereochemistry proofs of (*R*,*E*)-2-((*E*)-hex-1-en-1-yl)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran

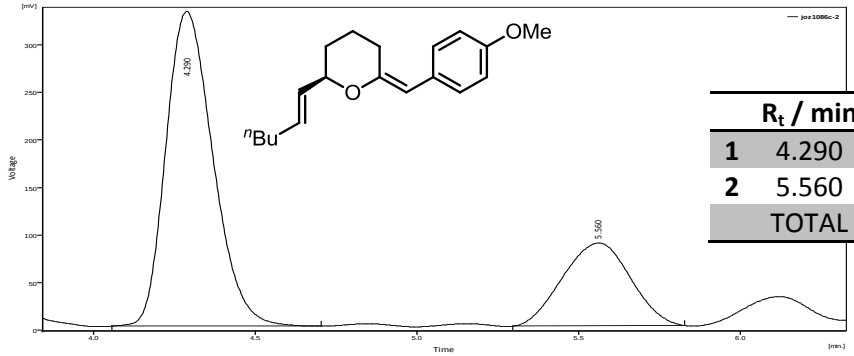


(*E*,*E*)-**2**

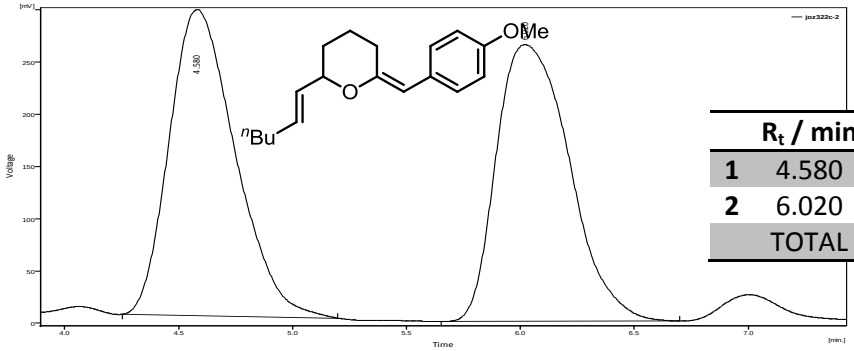
(*R*)-(*E*,*E*)-**2**
46%, +45% *ee*

(*R*)-**14**
59%, -44% *ee*

Chiral HPLC:
Phenomenex® Lux 3u
Cellulose-2 column;
^{n}hexane: isopropanol/
99:1;
1.0 mL/min;
254 nm

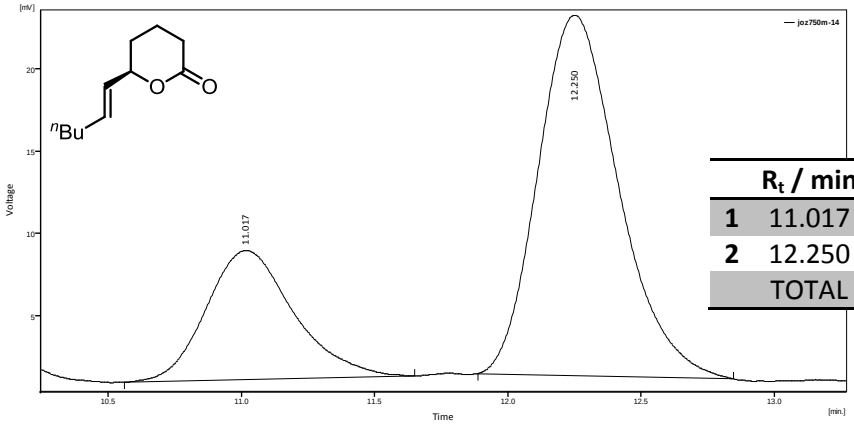


	R_t / min	Area / mV.s	Area / %
1	4.290	3351.099	72.4
2	5.560	1274.545	27.6
	TOTAL	4625.645	100.0

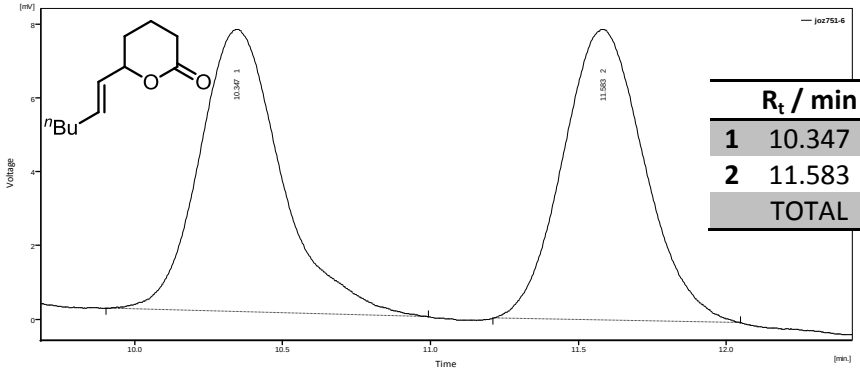


	R_t / min	Area / mV.s	Area / %
1	4.580	5910.652	50.0
2	6.020	5906.634	50.0
	TOTAL	11817.286	100.0

Chiral HPLC:
Phenomenex® Lux 3u
Cellulose-2 column;
^{n}hexane: isopropanol/
99:1;
1.0 mL/min;
245 nm

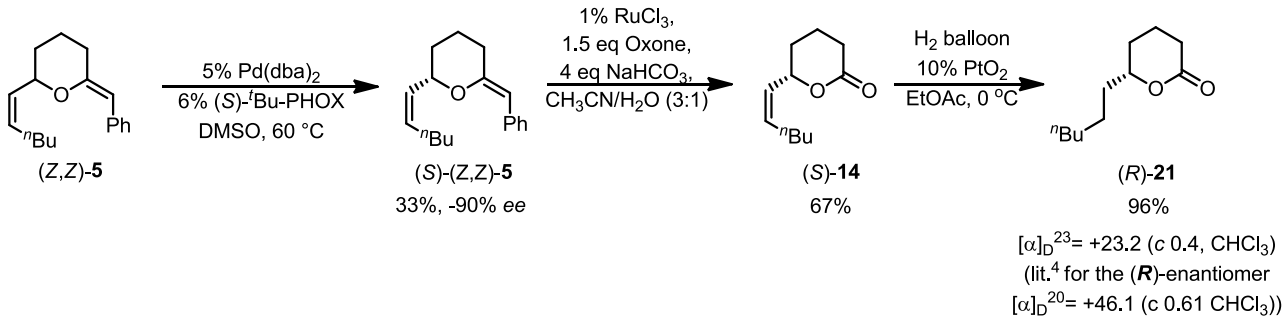


	R_t / min	Area / mV.s	Area / %
1	11.017	179.303	28.0
2	12.250	460.828	72.0
	TOTAL	640.131	100.0



	R_t / min	Area / mV.s	Area / %
1	10.347	148.025	49.4
2	11.583	151.374	50.6
	TOTAL	299.398	100.0

Stereochemistry proofs of (*R*,*Z*)-2-benzylidene-6-((*Z*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran



(*Z*,*Z*)-**5**

(*S*)-(Z,Z)-**5**
33%, -90% *ee*

(*S*)-**14**
67%

(*R*)-**21**
96%

$[\alpha]_D^{23}$= +23.2 (*c* 0.4, $CHCl_3$)
(lit.[4] for the (***R***)-enantiomer
$[\alpha]_D^{20}$= +46.1 (c 0.61 $CHCl_3$))

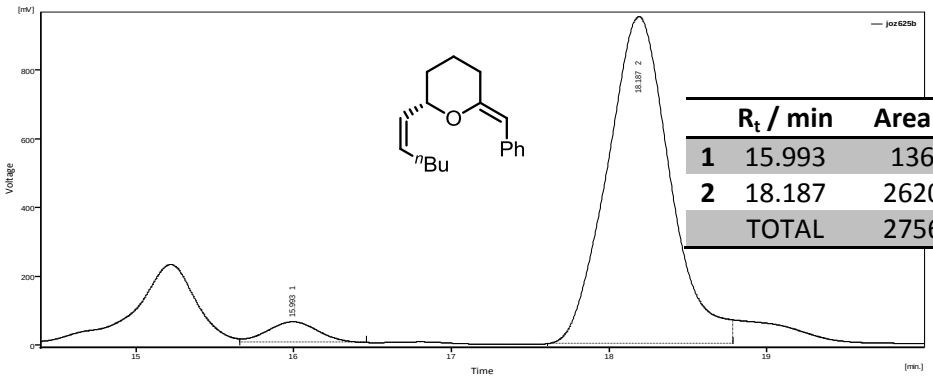
Chiral HPLC:

Phenomenex® Lux 3u Cellulose-2 column;

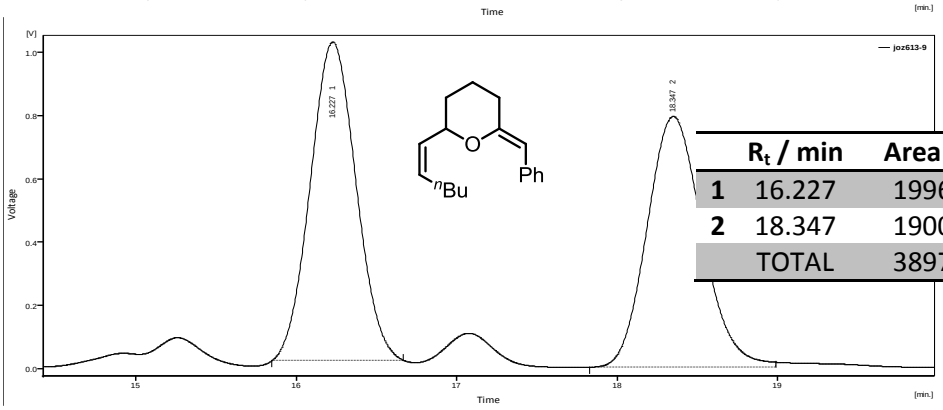
^{n}hexane (100%);

0.3 mL/min;

254 nm.

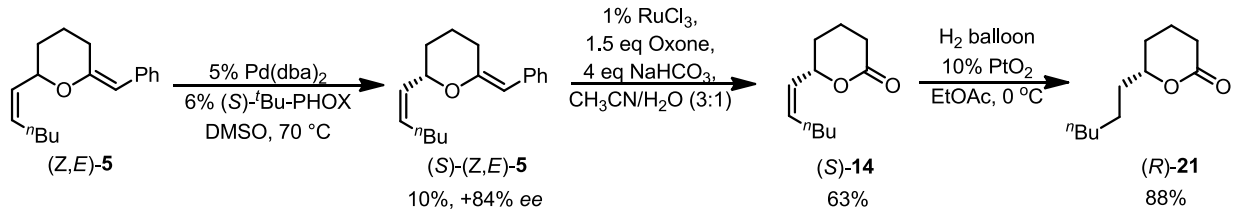


	R_t / min	Area / mV.s	Area / %
1	15.993	1360.922	4.9
2	18.187	26204.276	95.1
	TOTAL	27565.198	100.0



	R_t / min	Area / mV.s	Area / %
1	16.227	19969.657	51.2
2	18.347	19001.366	48.8
	TOTAL	38971.022	100.0

Stereochemistry proofs of (*R*,*E*)-2-benzylidene-6-((*Z*)-hex-1-en-1-yl)tetrahydro-2*H*-pyran



$[\alpha]_D^{22}$= +21.6 (*c* 1.1, $CHCl_3$)
(lit.[4] for the (***R***)-enantiomer
$[\alpha]_D^{20}$= +46.1 (c 0.61 $CHCl_3$))

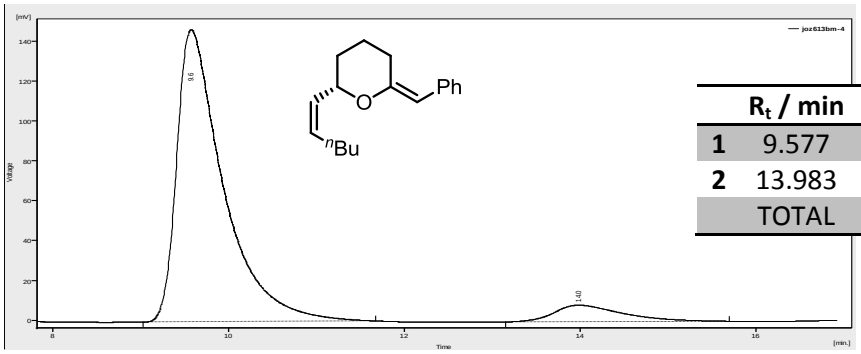
Chiral HPLC:

Phenomenex® Lux 3u Amylose-2 column;

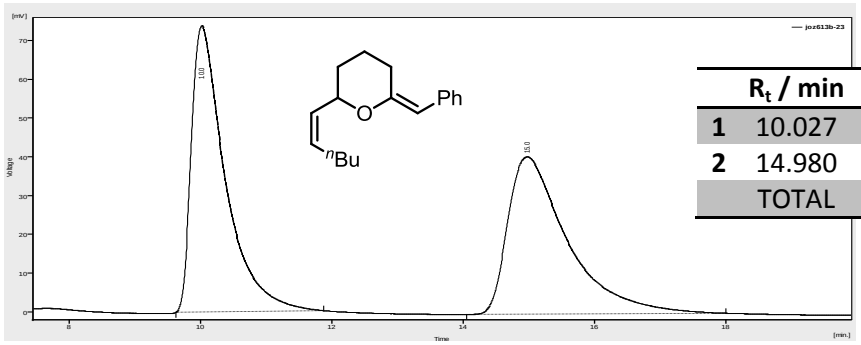
*n*hexane (100%);

1.4 mL/min;

254 nm.

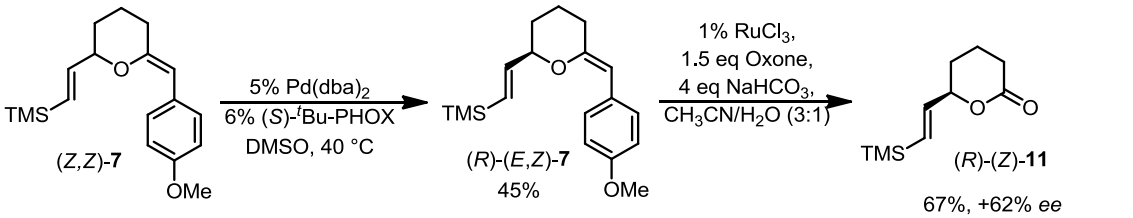


	R_t / min	Area / mV.s	Area / %
1	9.577	5386.505	92.2
2	13.983	453.449	7.8
	TOTAL	5839.954	100.0



	R_t / min	Area / mV.s	Area / %
1	10.027	2633.453	50.7
2	14.980	2561.594	49.3
	TOTAL	5195.047	100.0

Preparation of ((*Z*)-2-((*S*,*Z*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



67%, +62% *ee*

$[\alpha]_D^{24}$= -3.3 (*c* 3.1, $CHCl_3$)

(lit.[5] for the (***S***)-enantiomer

$[\alpha]_D^{20}$= +22.0 (*c* 1.1, $CDCl_3$)) [5]

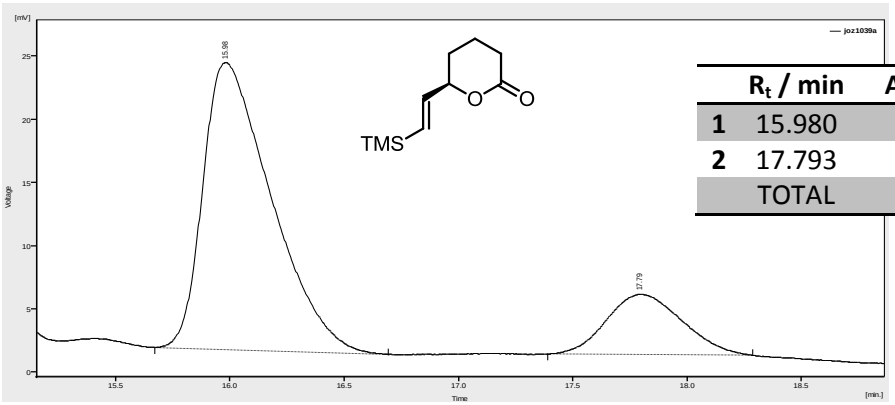
Chiral HPLC:

Phenomenex® Lux 3u Cellulose-2 column;

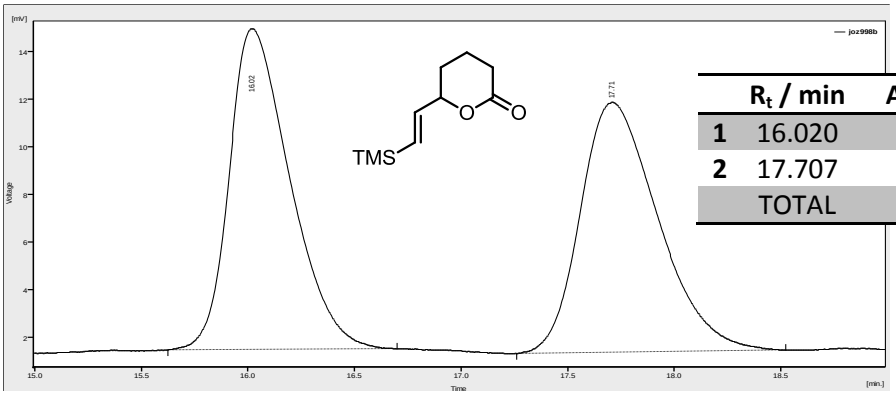
*n*hexane: isopropanol/ 99: 1;

1.0 mL/min;

245 nm



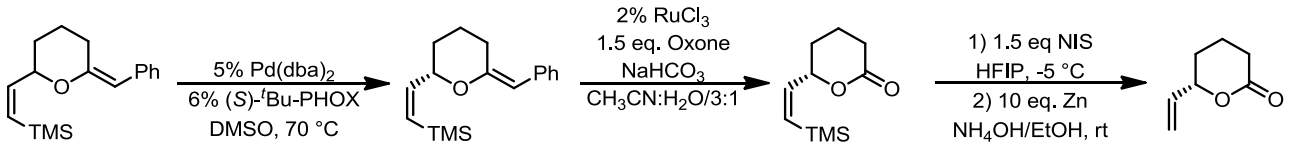
	R_t / min	Area / mV.s	Area / %
1	15.980	473.325	81.2
2	17.793	109.765	18.8
	TOTAL	583.090	100.0



	R_t / min	Area / mV.s	Area / %
1	16.020	268.681	50.2
2	17.707	266.854	49.8
	TOTAL	535.535	100.0

[5] E. J. Corey, A. Guzman-Perez and S. E. Lazerweith, *J. Am. Chem. Soc.*, 1997, **119**, 11769

Stereochemistry proofs of ((*Z*)-2-((*S*,*E*)-6-benzylidenetetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



(*Z*,*E*)-**8**

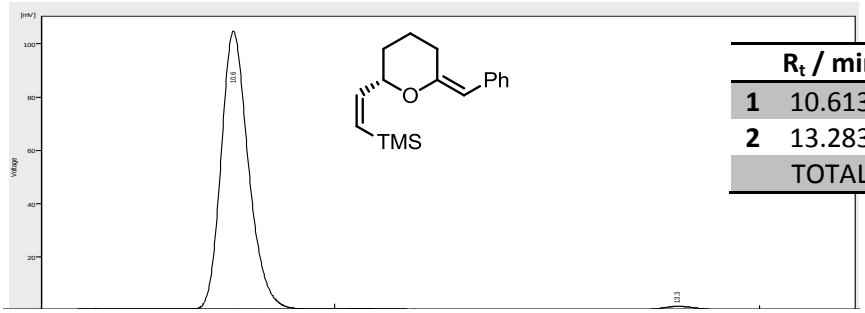
(*S*)-(*Z*,*E*)-**8**
40%, +96% *ee*

(*S*)-**11**
55%, +95% *ee*

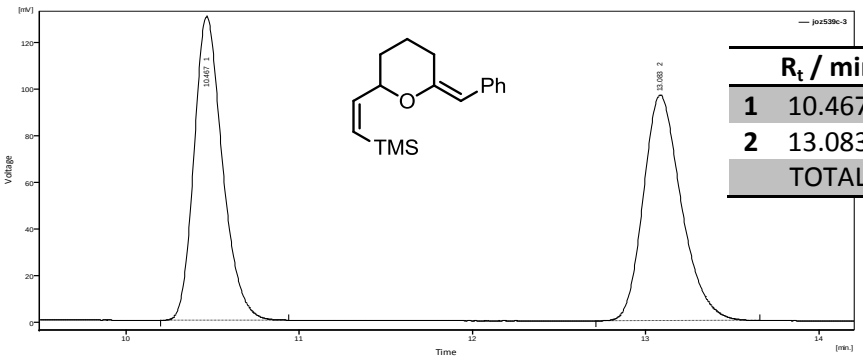
(*S*)-**22**
71%, -89% *ee*

$[\alpha]_D^{22}$= +15.3 (*c* 1.3, DCM);
(lit.[5] for the (*R*)-enantiomer
$[\alpha]_D^{23}$= -61.3 (*c* 1.6, DCM))

Chiral HPLC:
Phenomenex® Lux 3u
Cellulose-2 column;
*n*hexane (100%);
0.6 mL/min;
254 nm

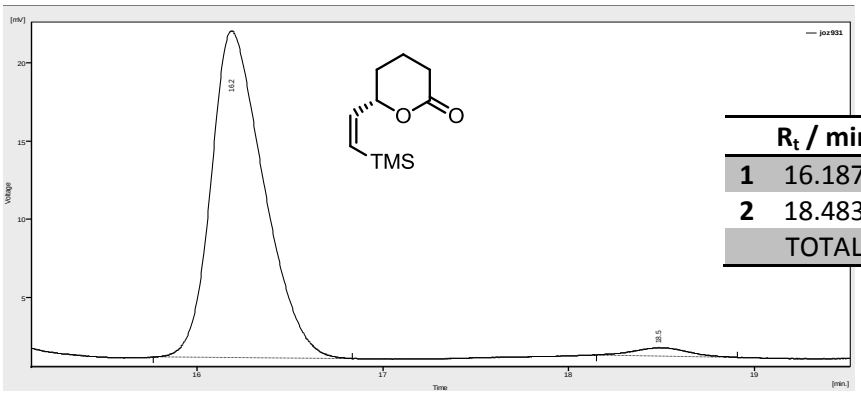


	R_t / min	Area / mV.s	Area / %
1	10.613	1189.670	98.1
2	13.283	23.114	1.9
	TOTAL	1212.784	100.0

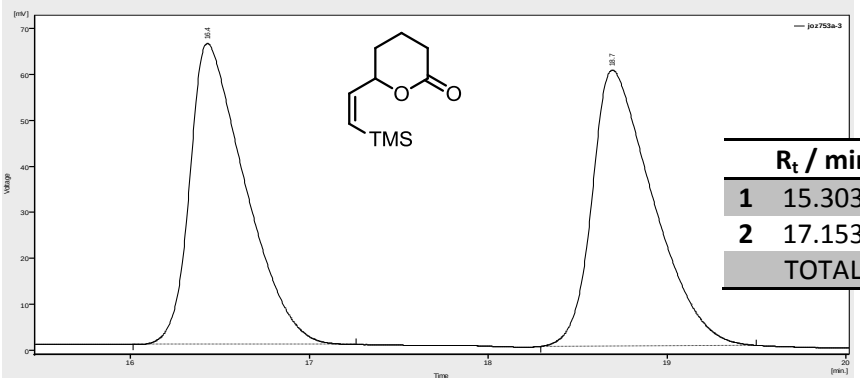


	R_t / min	Area / mV.s	Area / %
1	10.467	1485.917	50.2
2	13.083	1973.217	49.8
	TOTAL	2959.135	100.0

Chiral HPLC:
Phenomenex® Lux 3u
Amylose-2 column;
*n*hexane: isopropanol/
96: 4;
1.0 mL/min;
220 nm.

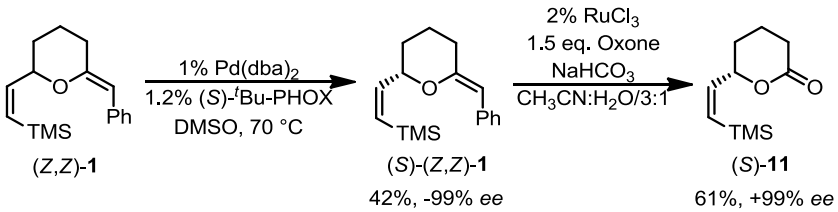


	R_t / min	Area / mV.s	Area / %
1	16.187	411.654	97.4
2	18.483	10.868	2.6
	TOTAL	422.522	100.0



	R_t / min	Area / mV.s	Area / %
1	15.303	4519.438	50.0
2	17.153	4516.804	50.0
	TOTAL	9036.242	100.0

Stereochemistry proofs of ((*Z*)-2-((*S*,*Z*)-6-benzylidenetetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



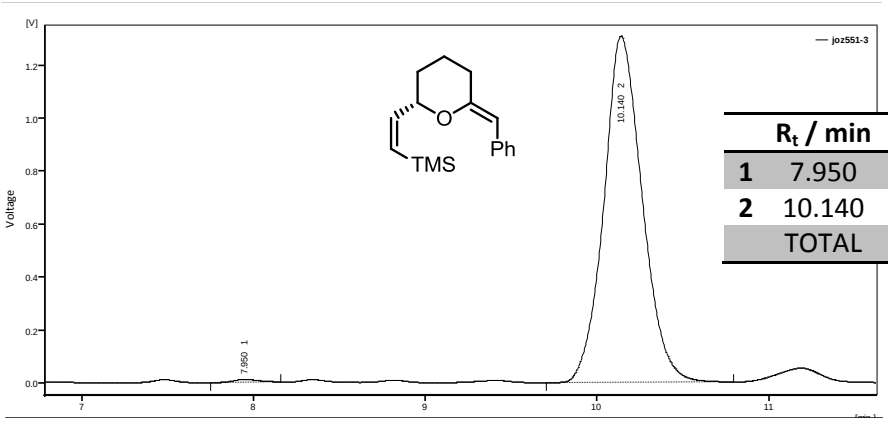
Chiral HPLC:

Phenomenex® Lux 3u Cellulose-2 column;

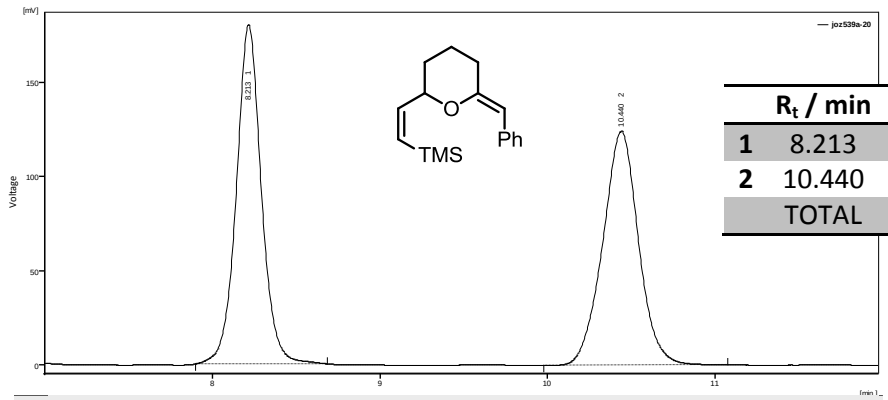
*n*hexane (100%);

0.7 mL/min;

254 nm



	R_t / min	Area / mV.s	Area / %
1	7.950	123.464	0.6
2	10.140	20288.469	99.4
	TOTAL	20411.933	100.0



	R_t / min	Area / mV.s	Area / %
1	8.213	1873.904	50.4
2	10.440	1846.671	49.6
	TOTAL	3720.574	100.0

Chiral HPLC:

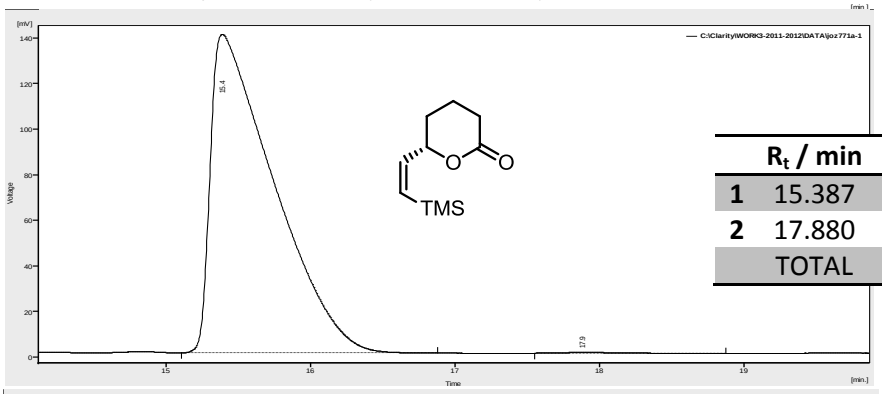
Phenomenex® Lux 3u Amylose-2 column;

*n*hexane: isopropanol/

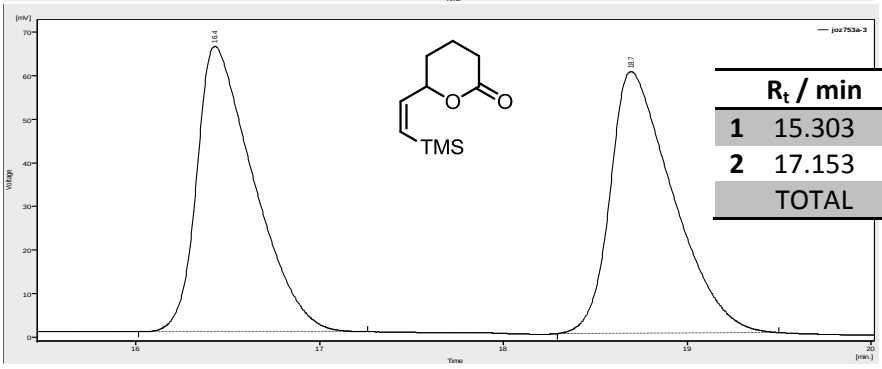
96: 4;

1.0 mL/min;

220 nm.

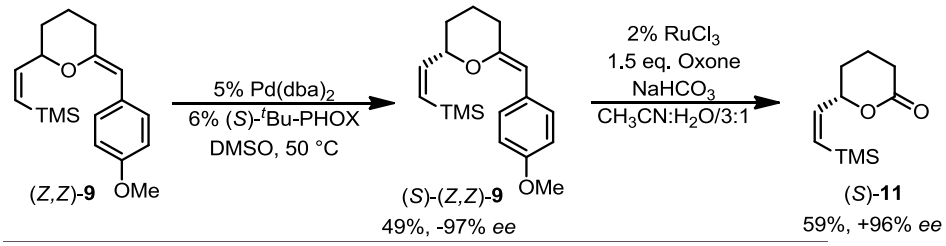


	R_t / min	Area / mV.s	Area / %
1	15.387	4258.862	99.6
2	17.880	15.692	0.4
	TOTAL	4274.554	100.0



	R_t / min	Area / mV.s	Area / %
1	15.303	4519.438	50.0
2	17.153	4516.804	50.0
	TOTAL	9036.242	100.0

Stereochemistry proofs of ((*Z*)-2-((*S*,*E*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane



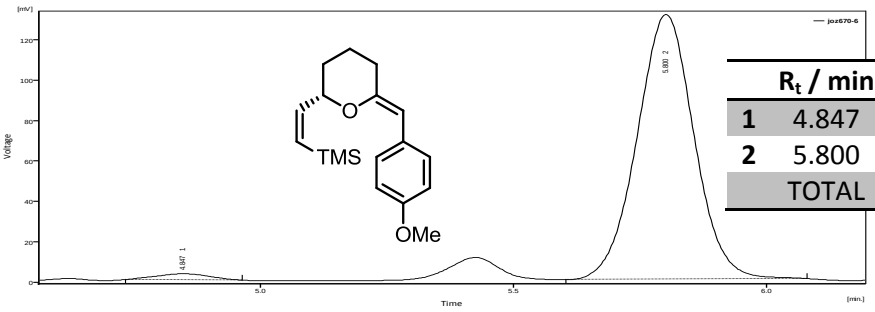
Chiral HPLC:

Phenomenex® Lux 3u Cellulose-2 column;

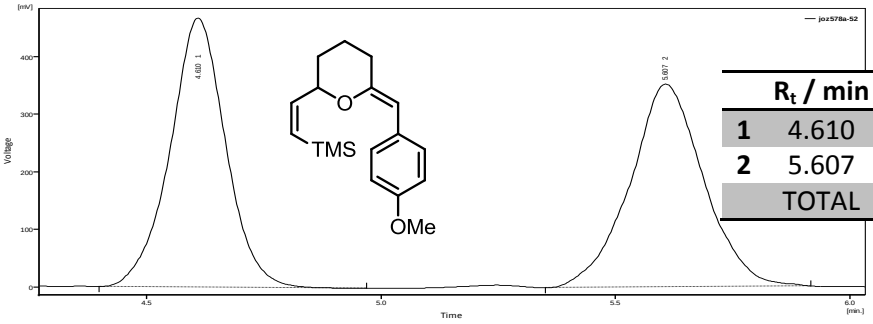
^{n}hexane: isopropanol/ 99.8: 0.2;

1.0 mL/min;

254 nm.



	R_t / min	Area / mV.s	Area / %
1	4.847	17.157	1.6
2	5.800	1029.618	98.4
	TOTAL	1046.775	100.0



	R_t / min	Area / mV.s	Area / %
1	4.610	3847.233	50.0
2	5.607	3850.357	50.0
	TOTAL	7697.590	100.0

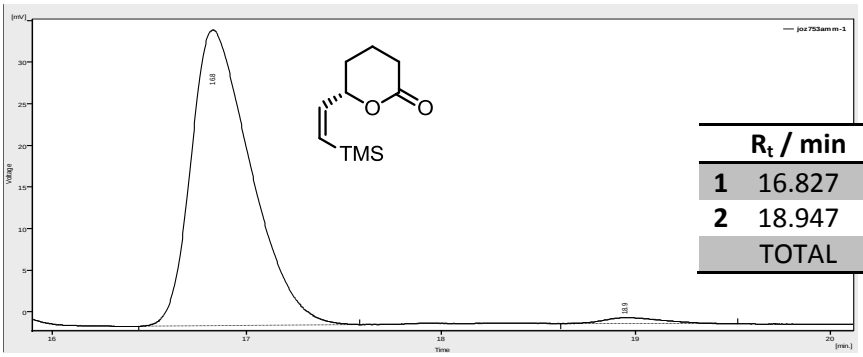
Chiral HPLC:

Phenomenex® Lux 3u Amylose-2 column;

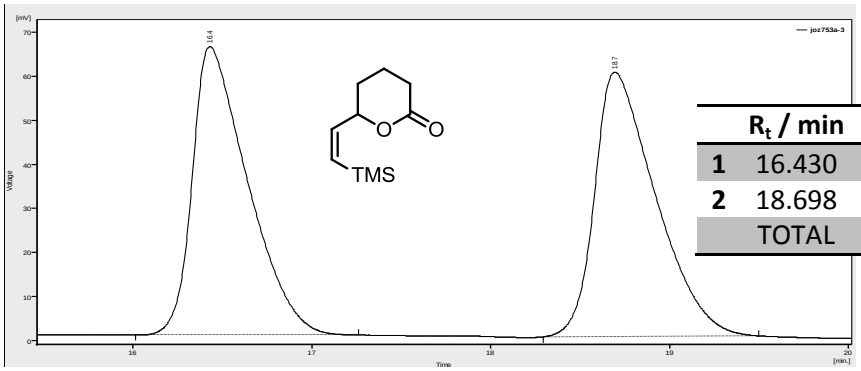
^{n}hexane: isopropanol/ 96: 4;

1.0 mL/min;

220 nm.

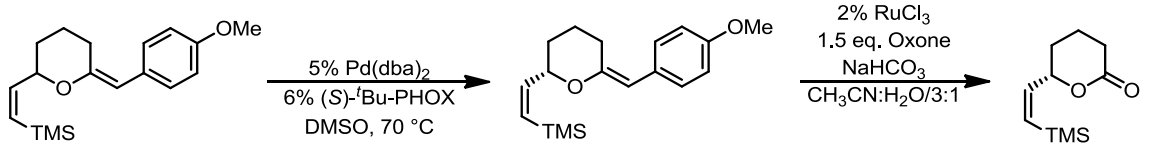


	R_t / min	Area / mV.s	Area / %
1	16.827	758.741	97.9
2	18.947	16.094	2.1
	TOTAL	744.835	100.0



	R_t / min	Area / mV.s	Area / %
1	16.430	1411.357	49.8
2	18.698	1422.695	50.2
	TOTAL	2834.052	100.0

Stereochemistry proofs of ((*Z*)-2-((*S*,*E*)-6-(4-methoxybenzylidene)tetrahydro-2*H*-pyran-2-yl)vinyl)trimethylsilane

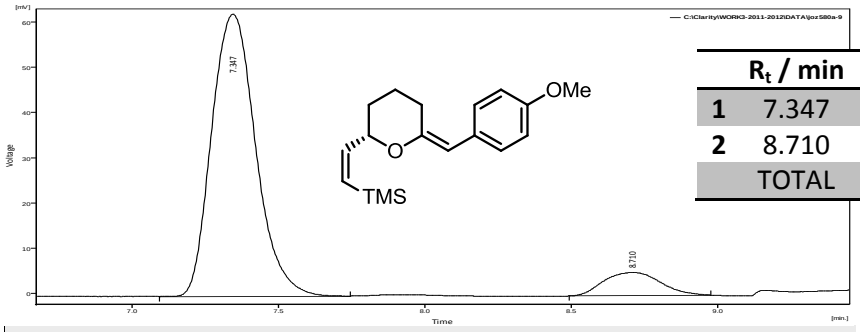


(*Z*,*E*)-**9**

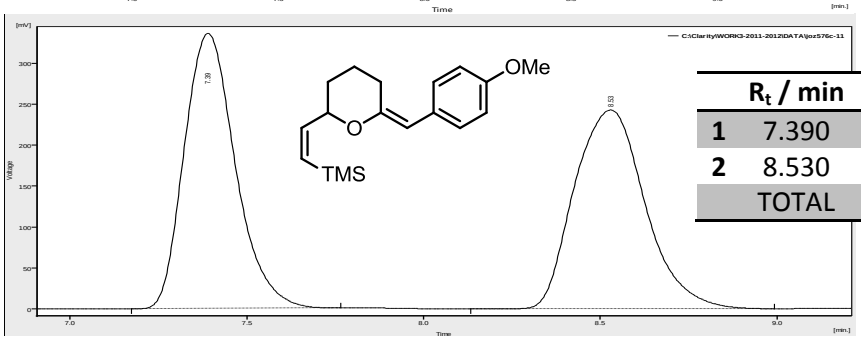
(*S*)-(*Z*,*E*)-**9**
49%, +81% *ee*

(*S*)-**11**
53%, +81% *ee*

Chiral HPLC:
Phenomenex® Lux 3u
Cellulose-1 column;
^{n}hexane: isopropanol/
99.8: 0.2;
1 mL/min;
254 nm

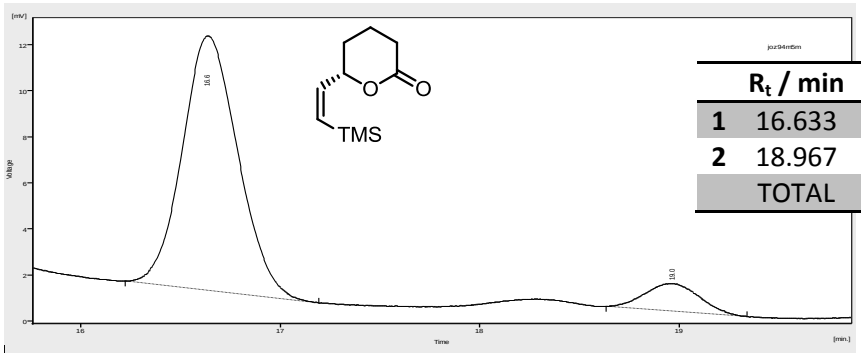


	R_t / min	Area / mV.s	Area / %
1	7.347	651.244	90.4
2	8.710	68.909	9.6
	TOTAL	720.194	100.0

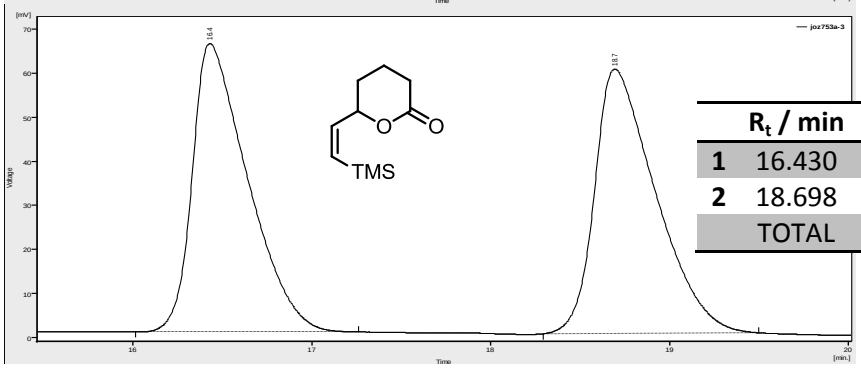


	R_t / min	Area / mV.s	Area / %
1	7.390	3377.656	49.9
2	8.530	3388.786	50.1
	TOTAL	6766.442	100.0

Chiral HPLC:
Phenomenex® Lux 3u
Amylose-2 column;
^{n}hexane: isopropanol/
96: 4;
1.0 mL/min;
220 nm.

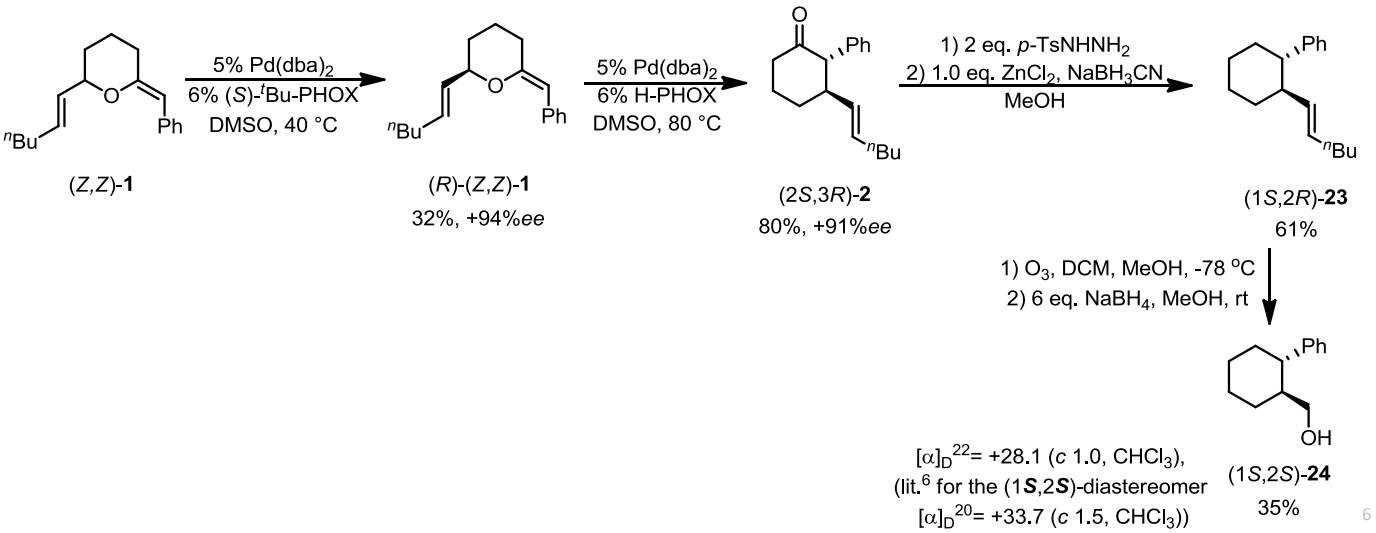


	R_t / min	Area / mV.s	Area / %
1	16.633	215.136	90.5
2	18.967	22.560	9.5
	TOTAL	237.696	100.0



	R_t / min	Area / mV.s	Area / %
1	16.430	1411.357	49.8
2	18.698	1422.695	50.2
	TOTAL	2834.052	100.0

Stereochemistry proofs of (2*S*,3*R*)-3-((*E*)-hex-1-en-1-yl)-2-phenylcyclohexanone



(*Z*,*Z*)-**1**

(*R*)-(*Z*,*Z*)-**1**
32%, +94%*ee*

(2*S*,3*R*)-**2**
80%, +91%*ee*

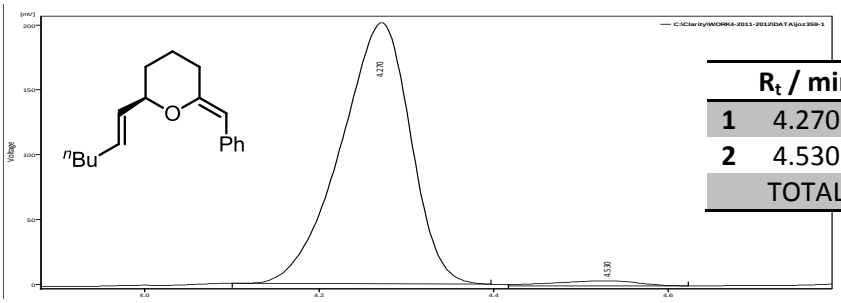
(1*S*,2*R*)-**23**
61%

(1*S*,2*S*)-**24**
35%

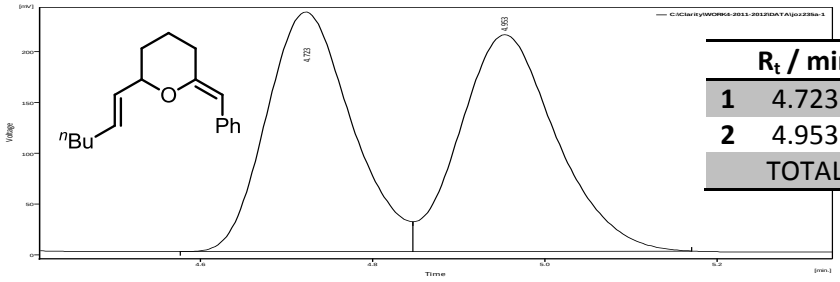
$[\alpha]_D^{22}$= +28.1 (*c* 1.0, $CHCl_3$),
(lit.[6] for the (1***S***,2***S***)-diastereomer
$[\alpha]_D^{20}$= +33.7 (*c* 1.5, $CHCl_3$))

6

Chiral HPLC:
Phenomenex® Lux 3u
Cellulose-2 column;
*n*hexane (100%);
1.0 mL/min;
254 nm

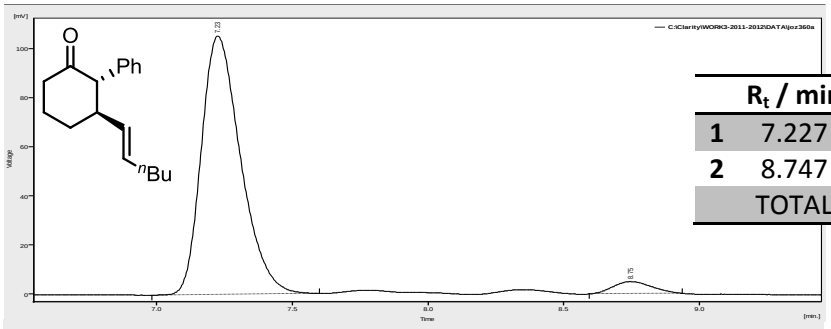


	R_t / min	Area / mV.s	Area / %
1	4.270	1119.948	97.7
2	4.530	37.314	3.3
	TOTAL	1157.262	100.0

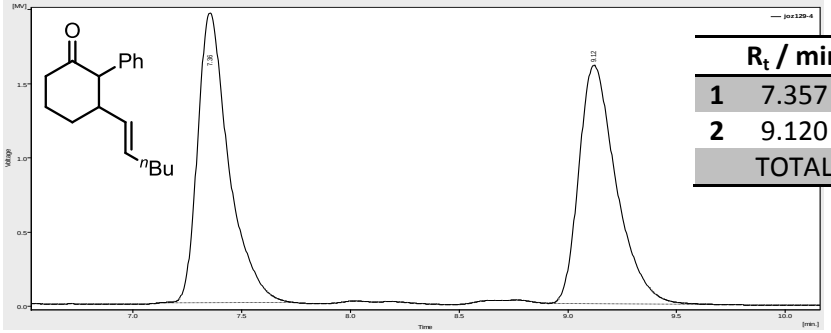


	R_t / min	Area / mV.s	Area / %
1	4.723	1615.441	49.4
2	4.953	1657.506	50.6
	TOTAL	3272.947	100.0

Chiral HPLC:
Phenomenex® Lux 3u
Cellulose-2 column;
*n*hexane: isopropanol/
95:5;
1.0 mL/min;
220 nm



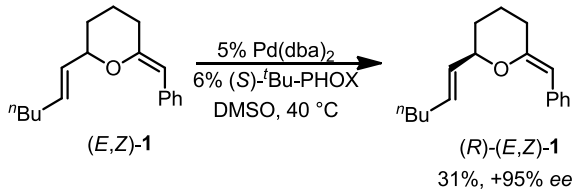
	R_t / min	Area / mV.s	Area / %
1	7.227	1059.135	95.6
2	8.747	49.092	4.4
	TOTAL	1108.227	100.0



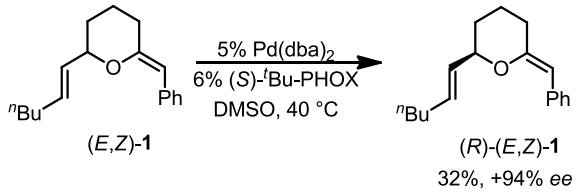
	R_t / min	Area / mV.s	Area / %
1	7.357	1927.869	50.2
2	9.120	1916.043	49.8
	TOTAL	3857.770	100.0

[6] B. -C. Hong, R. Y. Nimje, A. A. Sadani and J. -H. Liao, *Org. Lett.* 2008, **10**, 2345

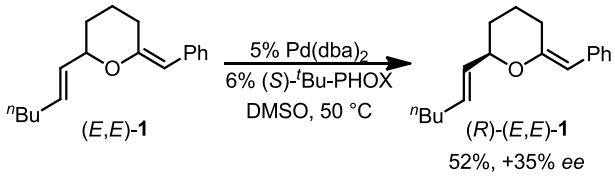
Stereochemistry proofs: Experimental procedures



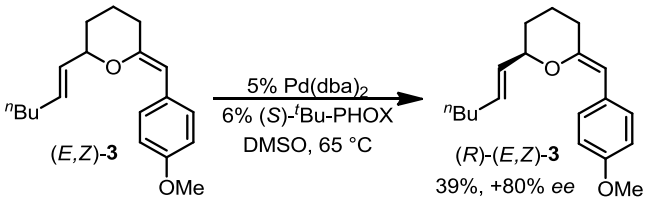
Following the general procedure for the kinetic resolution, (*E*,*Z*)-enol ether (190 mg, 0.74 mmol), $Pd(dba)_2$ (21 mg, 0.037 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (17 mg, 0.04 mmol, 6 mol%) were reacted at 40 ^{o}C for 6.5 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1.5: 0.2 mL / hexane: Et_2O: Et_3N) to give enantioenriched (*R*)-(*E*,*Z*)-enol ether (58.9 mg, 31% yield, +95% *ee*).



Following the general procedure for the kinetic resolution, (*E*,*Z*)-enol ether (310 mg, 1.21 mmol), $Pd(dba)_2$ (35 mg, 0.060 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (28 mg, 0.073 mmol, 6 mol%) were reacted at 40 ^{o}C for 6.3 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1.5: 0.2 mL / hexane: Et_2O: Et_3N) to give enantioenriched (*R*)-(*E*,*Z*)-enol ether (99.1 mg, 32% yield, +94% *ee*).

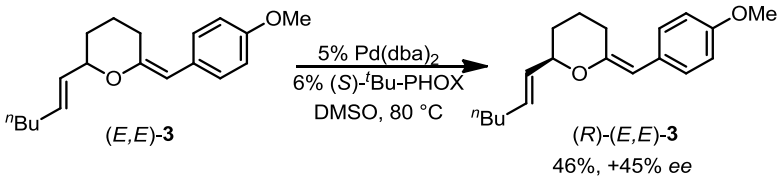


Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (108 mg, 0.42 mmol), $Pd(dba)_2$ (12 mg, 0.021 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (10 mg, 0.03 mmol, 6 mol%) were reacted at 50 ^{o}C for 12 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1.5: 0.2 mL / hexane: Et_2O: Et_3N) to give enantioenriched (*R*)-(*E*,*E*)-enol ether (56.2 mg, 35% yield, +35% *ee*).

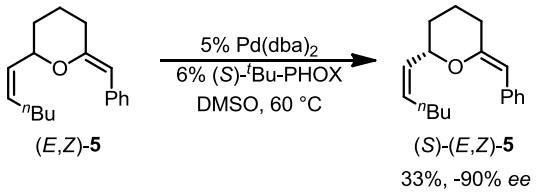


Following the general procedure for the kinetic resolution, (*E*,*Z*)-enol ether (108 mg, 0.38 mmol), $Pd(dba)_2$ (11 mg, 0.019 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (9 mg, 0.023 mmol, 6 mol%) were reacted at 65 ^{o}C for 6.5

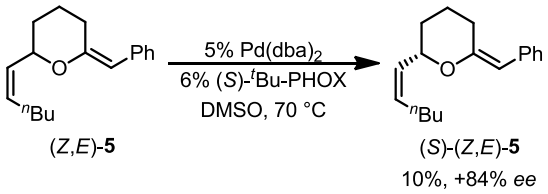
h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1.5: 0.2 mL/ hexane: Et_2O: Et_3N) to give enantioenriched (*R*)-(*E*,*Z*)-enol ether (42.1 mg, 39% yield, +45% *ee*).



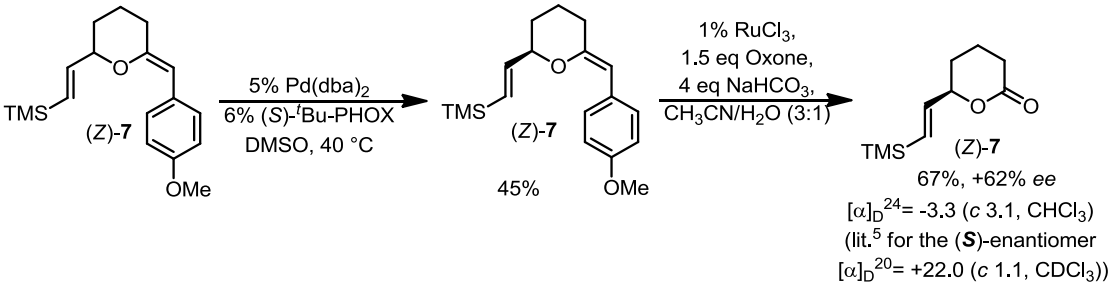
Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (72 mg, 0.25 mmol), $Pd(dba)_2$ (7.2 mg, 0.012 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (6 mg, 0.015 mmol, 6 mol%) were reacted at 80 ^{o}C for 2.75 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1.5: 0.2 mL/ hexane: Et_2O: Et_3N) to give enantioenriched (*R*)-(*E*,*E*)-enol ether (33.1 mg, 46% yield, +45% *ee*).



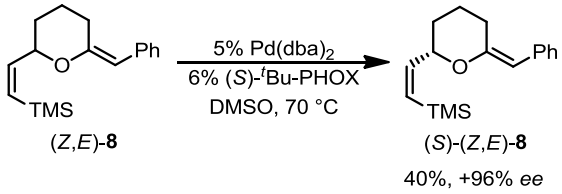
See the above general procedure for the kinetic resolution.



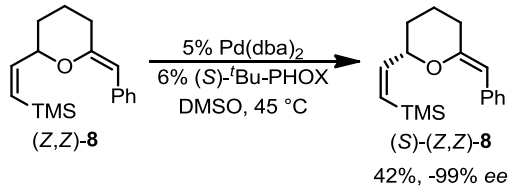
Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (273 mg, 1.06 mmol), $Pd(dba)_2$ (30 mg, 0.053 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (24 mg, 0.064 mmol, 6 mol%) were reacted at 70 ^{o}C for 9 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 2: 0.2 mL/ hexane: Et_2O: Et_3N) to give enantioenriched (*S*)-(*E*,*E*)-enol ether (27.2 mg, 10% yield, +84% *ee*).



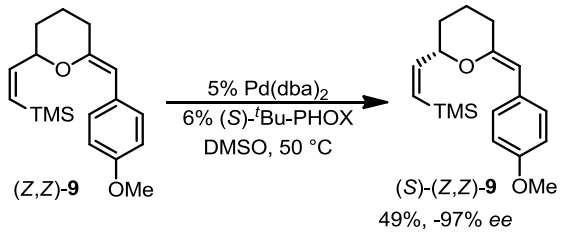
See the above general procedure for the kinetic resolution.



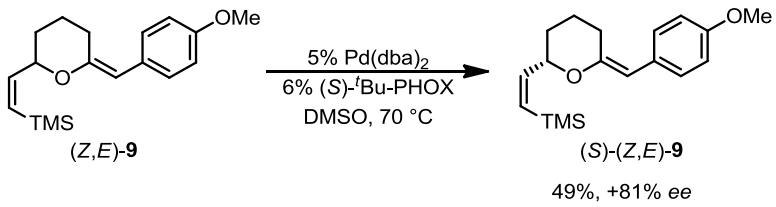
Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (165 mg, 0.60 mmol), $Pd(dba)_2$ (17 mg, 0.030 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (14 mg, 0.036 mmol, 6 mol%) were reacted at 70 ^{o}C for 1.75 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 1: 0.2 mL/ hexane: Et_2O: Et_3N) to give enantioenriched (*S*)-(*E*,*E*)-enol ether (66.0 mg, 40% yield, +96% *ee*).



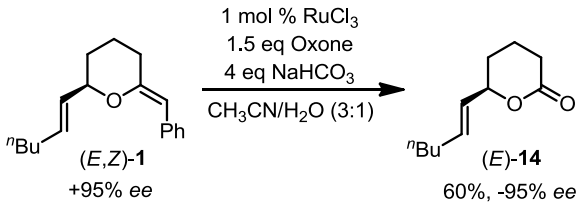
See the above general procedure for the kinetic resolution.



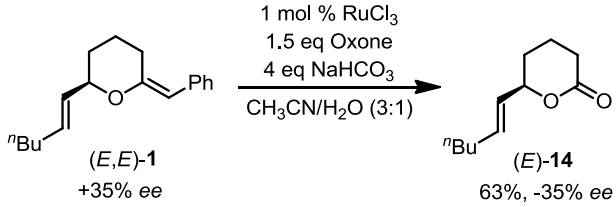
See the above general procedure for the kinetic resolution.



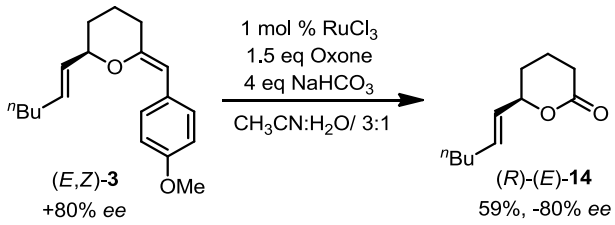
Following the general procedure for the kinetic resolution, (*E*,*E*)-enol ether (30 mg, 0.10 mmol), $Pd(dba)_2$ (3 mg, 0.005 mmol, 5 mol%) and (*S*)-^{t}Bu-Phox (2 mg, 0.006 mmol, 6 mol%) were reacted at 70 ^{o}C for 4 h. The reaction mixture was purified *via* column chromatography on silica gel (500: 10: 0.2 mL/ hexane: Et_2O: Et_3N) to give enantioenriched (*S*)-(*E*,*E*)-enol ether (14.7 mg, 49% yield, +81% *ee*).



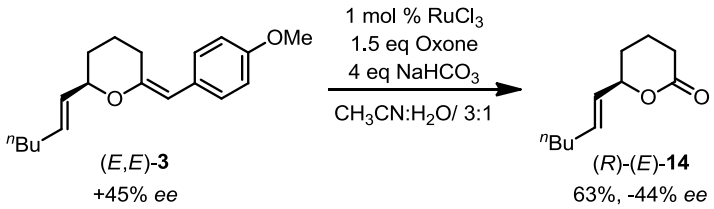
Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*R*)-(*E*,*Z*)-enol ether (52 mg, 0.20 mmol, +95% *ee*), $RuCl_3.xH_2O$ (0.4 mg, 0.002 mmol, 1 mol%), Oxone® (187 mg, 0.30 mmol, 1.5 eq) and $NaHCO_3$ (68 mg, 0.81 mmol, 4 eq) were used in CH_3CN (25 mL) and distilled water (8 mL). After completion in 38 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*R*)-lactone as colourless oil (22.2 mg, 60%, -95% *ee*); $[\alpha]_D^{22}$= +46.1 (*c* 0.6, ^{i}PrOH).



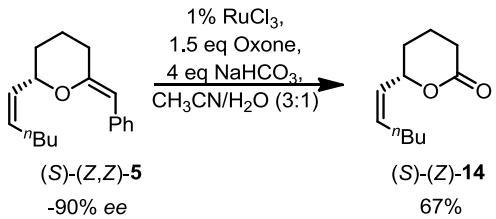
Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*R*)-(*E*,*E*)-enol ether (41 mg, 0.16 mmol, +35% *ee*), $RuCl_3.xH_2O$ (0.3 mg, 0.002 mmol, 1 mol%), Oxone® (148 mg, 0.24 mmol, 1.5 eq) and $NaHCO_3$ (54 mg, 0.64 mmol, 4 eq) were used in CH_3CN (14 mL) and distilled water (5 mL). After completion in 35 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*R*)-lactone as colourless oil (15 mg, 63%, -35% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99:1; flow rate = 1.0 mL/min; detection at 245 nm.



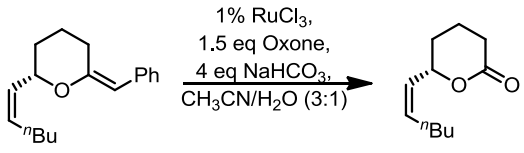
Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*R*)-(*E,Z*)-enol ether (40 mg, 0.14 mmol, +80% *ee*), $RuCl_3.xH_2O$ (0.2 mg, 0.001 mmol, 1 mol%), Oxone® (129 mg, 0.21 mmol, 1.5 eq) and $NaHCO_3$ (47 mg, 0.56 mmol, 4 eq) were used in CH_3CN (20 mL) and distilled water (7 mL). After completion in 45 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*R*)-lactone as colourless oil (15 mg, 59%, -80% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99:1; flow rate = 1.0 mL/min; detection at 245 nm.



Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*R*)-(*E,E*)-enol ether (23 mg, 0.08 mmol, +45% *ee*), $RuCl_3.xH_2O$ (0.1 mg, 0.001 mmol, 1 mol%), Oxone® (74 mg, 0.12 mmol, 1.5 eq) and $NaHCO_3$ (27 mg, 0.32 mmol, 4 eq) were used in CH_3CN (12 mL) and distilled water (4 mL). After completion in 55 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*R*)-lactone as colourless oil (9.2 mg, 63%, -44% *ee*); **Chiral HPLC:** Phenomenex® Lux 3u Cellulose-2 column; ^{n}hexane: isopropanol/ 99:1; flow rate = 1.0 mL/min; detection at 245 nm.



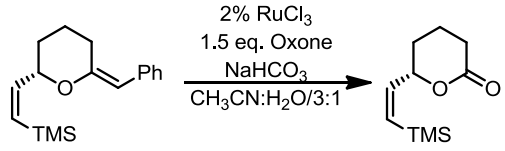
Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*S*)-(*Z,Z*)-enol ether (49 mg, 0.19 mmol, -90% *ee*), $RuCl_3.xH_2O$ (0.4 mg, 0.002 mmol, 1 mol%), Oxone® (176 mg, 0.29 mmol, 1.5 eq) and $NaHCO_3$ (64 mg, 0.77 mmol, 4 eq) were used in CH_3CN (45 mL) and distilled water (20 mL). After completion in 40 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*S*)-lactone as colourless oil (23.2 mg, 67%).



(*S*)-(*Z*,*E*)-**5**
+84% *ee*

(*S*)-(Z)-**14**
63%

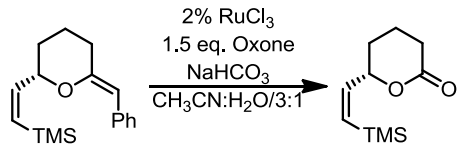
Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*S*)-(*Z*,*E*)-enol ether (30 mg, 0.12 mmol, +84% *ee*), $RuCl_3.xH_2O$ (0.3 mg, 0.001 mmol, 1 mol%), Oxone® (110 mg, 0.18 mmol, 1.5 eq) and $NaHCO_3$ (40 mg, 0.48 mmol, 4 eq) were used in CH_3CN (20 mL) and distilled water (8 mL). After completion in 35 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*S*)-lactone as colourless oil (13.7 mg, 63%).



(*S*)-(Z,*E*)-**8**
+96% *ee*

(*S*)-**11**
55%, +95% *ee*

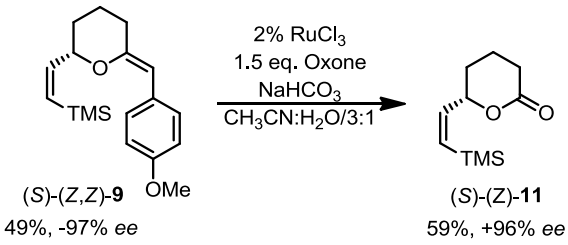
Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*S*)-(*Z*,*E*)-enol ether (55 mg, 0.20 mmol, +96% *ee*), $RuCl_3.xH_2O$ (0.8 mg, 0.004 mmol, 2 mol%), Oxone® (184 mg, 0.30 mmol, 1.5 eq) and $NaHCO_3$ (67 mg, 0.80 mmol, 4 eq) were used in CH_3CN (60 mL) and distilled water (15 mL). After completion in 40 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*S*)-lactone as colourless oil (21.8 mg, 55%, +95% *ee*).



(*S*)-(*Z*,*Z*)-**1**
42%, -99% *ee*

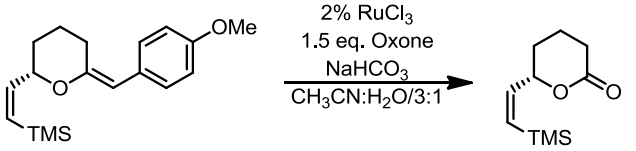
(*S*)-(Z)-**11**
61%, +99% *ee*

Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*S*)-(*Z*,*Z*)-enol ether (29 mg, 0.11 mmol, -99% *ee*), $RuCl_3.xH_2O$ (0.4 mg, 0.002 mmol, 2 mol%), Oxone® (97 mg, 0.16 mmol, 1.5 eq) and $NaHCO_3$ (37 mg, 0.44 mmol, 4 eq) were used in CH_3CN (20 mL) and distilled water (8 mL). After completion in 45 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*S*)-lactone as colourless oil (12.7 mg, 61%, +99% *ee*).



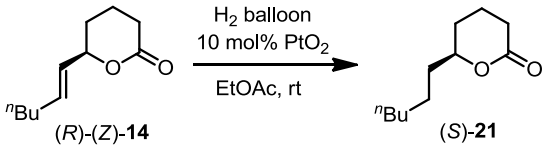
(*S*)-(*Z*,*Z*)-**9** (*S*)-(Z)-**11**
49%, -97% *ee* 59%, +96% *ee*

Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*S*)-(*Z*,*Z*)-enol ether (30.1 mg, 0.10 mmol, -97% *ee*), $RuCl_3.xH_2O$ (0.4 mg, 0.002 mmol, 2 mol%), Oxone® (92 mg, 0.15 mmol, 1.5 eq) and $NaHCO_3$ (34 mg, 0.40 mmol, 4 eq) were used in CH_3CN (32 mL) and distilled water (9 mL). After completion in 35 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*S*)-lactone as colourless oil (11.7 mg, 59%, +96% *ee*).



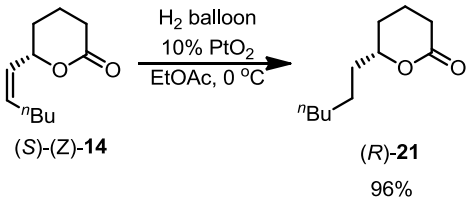
(*S*)-(*Z*,*E*)-**9** (*S*)-(Z)-**11**
+81% *ee* 53%, +81% *ee*

Following the representative procedure for ruthenium-catalyzed oxidative cleavage, a solution of enantioenriched (*S*)-(*Z*,*E*)-enol ether (14.7 mg, 0.048 mmol, +81% *ee*), $RuCl_3.xH_2O$ (0.2 mg, 0.001 mmol, 2 mol%), Oxone® (44 mg, 0.072 mmol, 1.5 eq) and $NaHCO_3$ (16 mg, 0.19 mmol, 4 eq) were used in CH_3CN (15 mL) and distilled water (5 mL). After completion in 40 min; the crude residue was purified by flash chromatography on silica gel (90: 10/ petroleum ether: EtOAc) to give the (*S*)-lactone as colourless oil (5.1 mg, 53%, +81% *ee*).



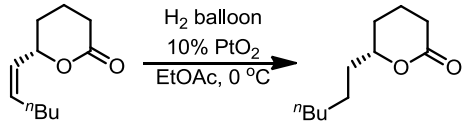
(*R*)-(*Z*)-**14** (*S*)-**21**
59%

A solution of enantioenriched (*R*)-lactone (20.5 mg, 0.11 mmol, -95% *ee*) and platinum (IV) oxide (Adam's catalyst, 2.1 mg, 10% w/w) in EtOAc (7 mL) was stired at room temperature under an atmosphere of hydrogen (balloon) for 5.5 h. Upon completion, the atmosphere was replaced with nitrogen, and the dark solution filtered through Celite®, washed with EtOAc and concentrated *in vacuo*. The crude mixture was purified *via* column chromatography on silica gel (80: 20/ petroleum ether: EtOAc) to give the (*S*)-lactone as colourless oil (12.0 mg, 59%); $[\alpha]_D^{23}$= -31.2 (*c* 0.45 $CHCl_3$); (lit.[4] for the (*R*)-enantiomer $[\alpha]_D^{20}$= +46.1 (*c* 0.61 $CHCl_3$)).



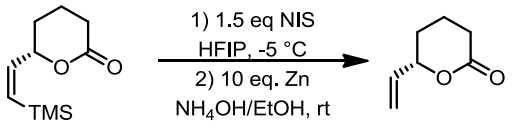
(*S*)-(Z)-**14** (*R*)-**21** 96%

A solution of enantioenriched (*S*)-lactone (23 mg, 0.13 mmol) and platinum (IV) oxide (Adam's catalyst, 2.5 mg, 10% w/w) in EtOAc (15 mL) was stired at 0°C under an atmosphere of hydrogen (balloon) for 0.5 h and was left to warm at room temperature for 4 h. The dark solution was then filtered through Celite®, washed with EtOAc and concentrated *in vacuo*. The crude mixture was purified *via* column chromatography on silica gel (80: 20/ petroleum ether: EtOAc) to give the (*R*)-lactone as colourless oil (15.9 mg, 96%); $[\alpha]_D^{23}$= +23.2 (c 0.4, $CHCl_3$); (lit.[4] for the (*R*)-enantiomer $[\alpha]_D^{20}$= +46.1 (*c* 0.61 $CHCl_3$)).



(*S*)-(Z)-**14** (*R*)-**21** 88%

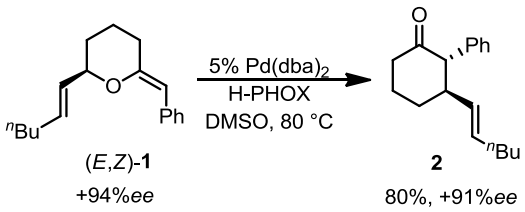
A solution of enantioenriched (*S*)-lactone (12 mg, 0.07 mmol) and platinum (IV) oxide (Adam's catalyst, 1.2 mg, 10% w/w) in EtOAc (10 mL) was stired at 0°C under an atmosphere of hydrogen (balloon) for 0.5 h and was left to warm at room temperature for 4 h. The dark solution was then filtered through Celite®, washed with EtOAc and concentrated *in vacuo*. The crude mixture was purified *via* column chromatography on silica gel (80: 20/ petroleum ether: EtOAc) to give the (*R*)-lactone as colourless oil (10.7 mg, 88%); $[\alpha]_D^{23}$= +21.6 (c 1.1, $CHCl_3$); (lit.[4] for the (*R*)-enantiomer $[\alpha]_D^{20}$= +46.1 (*c* 0.61 $CHCl_3$)).



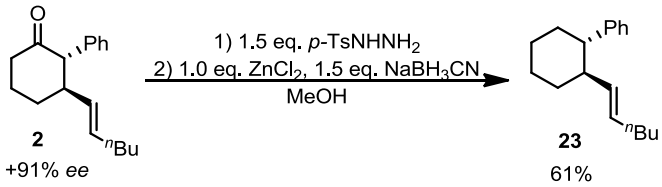
(*S*)-(*Z*)-**11** +95% *ee* (*S*)-**22** 71%, -89% *ee*

In the reaction vessel wrapped with aluminium foil; N-iodosuccinimide (37.1 mg, 0.16 mmol, 1.5 eq) dissolved in hexafluoroisopropanol (0.5 mL) was added to a solution of enantioenriched (*S*)-lactone (21.8 mg, 0.11 mmol, +95% *ee*) and hexafluoroisopropanol (8 ml) at room temperature. After 40 min, the reaction mixture was quenched with saturated aqueous solution of NaS_2O_3 and then extracted with DCM tree times. The organic layer was washed with saturated aqueous sodium bicarbonate, dried over sodium sulfate, concentrated, and the residue was purified by column chromatography on silica gel (85: 15/ petroleum ether: EtOAc) to give the enantioenriched lactone as colorless oil (24.9 mg, 0.10 mmol, 90%). To a solution of this compound in EtOH (3 mL) and aqueous saturated NH_4Cl (3 mL) in the reaction vessel wrapped with aluminium foil; zinc dust (65 mg, 1.00 mmol) in pouder was added. The mixture was allowed to stir at room

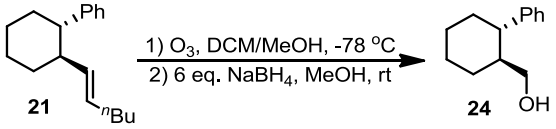
temperature for overnight. The reaction mixture was then diluted with water and zinc dust was filtered off and the filtrate was extracted with DCM. The organic layer was washed with brine, dried over $MgSO_4$, concentrated, and the residue was purified by column chromatography on silica gel (85: 15/ petroleum ether: EtOAc) to give the enantioenriched lactone as colorless oil (9.9 mg, 79%, -89% *ee*); $[\alpha]_D^{23}$= +25.3 (*c* 1.0, DCM), (lit[5] for the (*R*)-enantiomer $[\alpha]_D^{23}$= -61.3 (*c* 1.65, DCM)); **Chiral HPLC:** Phenomenex® Lux 3u Amylose-2 column; ^{n}hexane: isopropanol/ 80: 20; flow rate = 1 mL/min; detection at 210 nm.



To a reaction vial was added (*R*)-(*E*,*Z*)-enol ether (99.1 mg 0.39 mmol, 94% *ee*), $Pd(dba)_2$ (11 mg, 0.02 mmol, 5 mol%) and H-Phox (8 mg, 0.02 mmol, 6 mol%). The vial was sealed with a rubber septum, evacuated under reduced pressure and back filled with argon. DMSO (0.3 mL, 0.4 N) was added under argon, and the vial evacuated for *ca.* 2 min. The vial was back filled with argon and stirred in a preheated heating block at 80 °C for 5 h. The reaction vial was cooled to room temperature and directly purified by flash chromatography on silica gel (95:5/ petroleum ether : EtOAc) to give enantioenriched (2*R*,3*S*)-*trans*-cyclic ketone (79.3 mg, 80% yield, +91% *ee*).



A solution of enantioriched (2*S*,3*R*)-*trans*-cyclic ketone (73 mg, 0.285 mmol, +91% *ee*) and p-toluenesulfonyl hydrazine (80 mg, 0.428 mmol) in MeOH (1.5 mL) was stirred at rt for 2 h. To this was added a solution of $ZnCl_2$ (27 mg, 0,199 mmol) and $NaBH_3CN$ (27 mg, 0.428 mmol) in MeOH (0.75 mL) *via* cannula. The reaction mixture was then heated at 65 ^oC for o/n. The reaction mixture was cooled to rt and diluated with EtOAc, washed with 1M HCl, $NaHCO_3$, brine, dried over Na_2SO_4 and concetrated. The crude mixture was subjected to flash column chromatography on silica gel (100% petroleum ether) to give enantioenriched *trans*-cyclohexane as colourless oil (42.1 mg, 61% yield).

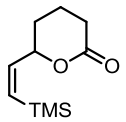


A stirred solution of enantioenriched *trans*-cyclohexane (30 mg, 0.124 mmol) MeOH /DCM (1 : 1, 5.0 mL) containg a small amount of $NaHCO_3$ at -78 ^oC was bubbled through the solution until a blue colour persisted. At this point, N_2 was bubbled through the solution until disappearance of the blue colour. $NaBH_4$ (28 mg, 0.744 mmol) was added and the reaction mixture stirred at rt for 1 h. The reaction mixture was quenched with EtOAc, washed with H_2O, brine, dried over Na_2SO_4 and concentrated. The crude mixture was subjected to flash column chromatography on silica gel (100% petroleum ether) to give enantioenriched (1*S*,2*S*)-*trans*-cyclohexanemethol as colourless oil (8.2 mg, 35% yield); $\mathbf{[\alpha]_D^{22}}$= +28.1 (*c* 1.0, $CHCl_3$), (lit.[6] for the (1*S*,2*S*)-*trans*-cyclohexanemethanol $\mathbf{[\alpha]_D^{22}}$= +33.7 (*c* 1.5, $CHCl_3$).

NMR spectral data for all new products

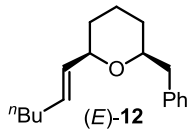
The compound **2**,[2] **15**,[2] **16**,[2] **21**,[4] **22**[5] and **24**[6] showed satisfactory NMR spectroscopic data.

Purification by flash chromatography failed to give clean (*E*,Z)-**7** enol ether. Only ^{1}HNMR and ^{13}CNMR spectra of this enol ether are provided.



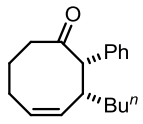
(*Z*)-**11**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (1H, dd, *J* = 14.5, 8.5 Hz, CH-alkene-*H*), 5.80 (1H, dd, *J* = 14.5, 0.5 Hz, TMS-alkene-*H*), 4.93-4.88 (1H, m, pyran-OC*H*), 2.66-2.58 (1H, m, *CH*$_2$), 2.52-2.44 (1H, m, *CH*$_2$), 2.00-1.86 (3H, m, C*H*$_2$), 1.72-1.64 (1H, m, C*H*$_2$), 0.16 (9H, s, C*H*$_3$); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 171.0, 144.5, 133.9, 80.3, 29.5, 28.7, 18.6, 0.2; **FTIR** (CH_2Cl_2, ν_{max} cm^{-1}): 2954 (s), 2898 (m), 1736 (s), 1340 (m), 1247 (s), 1042 (s), 839 (s), 765 (s); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{10}H_{19}O_2Si$ 199.1154, found 199.1152.



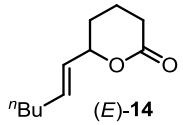
(*E*)-**12**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.21 (5H, m, Ar-*H*), 5.72-5.66 (1H, m, CH_2-alkene-*H*), 5.51 (1H, dd, *J* = 15.5, 6.0 Hz, CH-alkene-*H*), 3.83-3.79 (1H, m, pyran-OC*H*), 3.57-3.54 (1H, m, pyran-OC*H*), 3.03 (1H, dd, *J* = 13.5, 5.5 Hz, PhC*H*), 2.65 (1H, dd, *J* = 13.5, 8.0 Hz, PhC*H*), 2.08-2.02 (2H, m, C*H*$_2$), 1.83-1.80 (1H, m, C*H*$_2$), 1.62-1.18 (9H, m, C*H*$_2$), 0.91 (3H, t, *J* = 7.0 Hz, C*H*$_3$); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 138.8, 131.6, 131.2, 129.5, 128.1, 126.0, 78.7, 78.3, 43.2, 32.0, 31.8, 31.2, 30.4, 23.4, 22.2, 13.9; **FTIR** (CH_2Cl_2, υ_{max} cm^{-1}): 3027 (w), 2933 (s), 2856 (m), 1454 (m), 1078 (m), 1050 (m), 966 (m), 750 (m), 998 (m); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{18}H_{27}O$: 259.2062, found 259.2072.



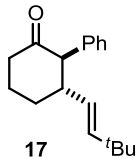
cis-**13**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.26 (3H, m, Ar-*H*), 7.17-7.15 (2H, m, Ar-*H*), 5.84 (1H, dtd, *J* = 10.5, 8.0, 1.0 Hz, alkene-*H*), 5.55 (1H, dd, *J* = 10.5, 1.5 Hz, alkene-*H*), 3.92 (1H, d, *J* = 5.0 Hz, (CO)C*H*), 3.56-3.51 (1H, m, alkene-C*H*), 2.86 (1H, td, *J* = 12.0, 3.0 Hz, (CO)C*H2*), 2.46-2.34 (2H, m, C*H2*), 2.25-2.17 (1H, m, C*H2*), 1.93-1.71 (2H, m, (CO)C*H2*, C*H2*), 1.26-1.18 (5H, m, C*H2*), 0.88-0.92 (1H, m, C*H2*), 0.84 (3H, t, *J* = 7.0 Hz, C*H3*); **^{13}C NMR** (100.6 MHz, CD_2Cl_2): δ 211.1, 135.4, 135.3, 130.9, 130.5, 127.7, 126.9, 67.7, 41.2, 37.2, 32.8, 30.0, 27.7, 26.5, 22.5, 14.0; **FTIR** (CH_2Cl_2, νmax cm^{-1}): 3013 (w), 2925 (s), 2856 (m), 1709 (s), 1499 (w), 1453 (m), 1086 (w); **HRMS** (EI) *m/z* [MH]+ calcd for $C_{18}H_{25}O$ 257.1905, found 257.1907.



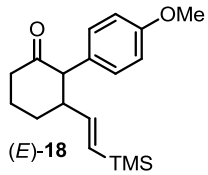
(*E*)-**14**

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (1H, dtd, *J* = 15.5, 7.0, 1.0 Hz, CH_2-alkene-*H*), 5.48 (1H, ddt, *J* = 15.5, 6.5, 1.5 Hz, CH-alkene-*H*), 5.78-5.71 (1H, m, OC*H*), 2.61-2.52 (1H, m, C(O)C*H*), 2.50-2.40 (1H, m, C(O)C*H*), 2.08-2.00 (2H, m, CH_2), 1.98-1.82 (2H, m, CH_2), 1.67-1.59 (1H, m, C*H*), 1.40-1.26 (5H, m, CH_2), 0.88 (3H, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 171.4, 134.6, 127.9, 80.7, 31.8, 31.0, 29,5, 28,4, 22.1, 18.2, 13.9; **FTIR** (CH_2Cl_2, ν_{max} cm^{-1}): 2956 (m), 2828 (m), 2876 (w), 1735 (s), 1237 (m), 1037 (m), 970 (w); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{11}H_{19}O_2$ 183.1385, found 183.1392.



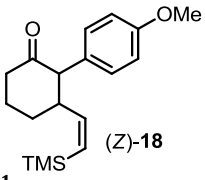
17

M.p. = 62-63 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30-7.26 (2H, m, Ar-*H*), 7.21-7.17 (1H, m, Ar-*H*), 7.02-7.00 (2H, m, Ar-*H*), 5.09 (1H, d, *J* = 15.5 Hz, C-alkene-*H*), 4.96 (1H, dd, *J* = 15.5, 8.0 Hz, CH-alkene-*H*), 3.36 (1H, d, *J* = 11.5 Hz, (CO)C*H*), 2.62-2.43 (3H, m, CH_2), 2.21-2.15 (1H, m, CH_2), 2.05-2.00 (1H, m, CH_2), 1.91-1.70 (2H, m, CH_2), 0.72 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 209.5, 142.6, 137.2, 129.6, 127.9, 126.5, 126.3, 63.6, 49.6, 41.9, 32.6, 29.2, 25.9; **FITR** (CH_2Cl_2, υ_{max} cm^{-1}): 3034 (w), 2960 (m), 2945 (m), 2863 (m), 1705 (s), 1447 (w), 1362 (w), 972 (w), 700 (m); **HRMS** (ES) *m/z* $[M+H]^+$ calcd for $C_{18}H_{25}O$ 257.1905, found 257.1894.



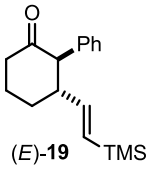
(*E*)-**18**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95-6.93 (2H, m, Ar-*H*), 6.85-6.82 (2H, m, Ar-*H*), 5.66 (1H, dd, *J* = 18.5, 7.0 Hz, CH-alkene-*H*), 5.39 (1H, dd, *J* = 18.5, 1.0 Hz, TMS-alkene-*H*), 3.79 (3H, s, OCH_3), 3.35 (1H, d, *J* = 11.5 Hz, (CO)C*H*), 2.68-2.42 (3H, m, alkene-C*H*, CH_2), 2.21-2.15 (1H, m, CH_2), 2.07-2.03 (1H, m, CH_2), 1.88-1.75 (2H, m, CH_2), -0.12 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 209.7, 158.3, 147.7, 130.6, 130.4, 129.1, 113.5, 61.9, 55.2, 52.4, 41.9, 31.5, 25.7, -1.5; **FTIR** (CH_2Cl_2, ν_{max} cm^{-1}): 2952 (s), 2934 (m), 1714 (s), 1614 (m), 1514 (s), 1248 (m), 1036 (m), 836 (s); **HRMS** (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{27}O_2Si$ 303.1780, found 303.1772.



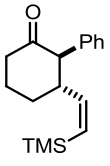
(*Z*)-**18**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99-6.95 (2H, m, Ar-*H*), 6.86-6.83 (2H, m, Ar-*H*), 6.02 (1H, dd, *J* = 14.5, 9.5 Hz, CH-alkene-*H*), 5.28 (1H, d, *J* = 14.5 Hz, TMS-alkene-*H*), 3.79 (3H, s, OCH_3), 3.40 (1H, d, *J* = 11.5 Hz, (CO)C*H*), 2.88-2.80 (1H, m, alkene-C*H*), 2.58-2.43 (2H, m, CH_2), 2.20-2.16 (1H, m, CH_2), 1.95-1.72 (3H, m, CH_2), 0.02 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 209.4, 158.4, 150.1, 130.5, 129.0, 113.6, 62.1, 55.1, 49.8, 41.7, 33.4, 25.9, 0.2; **FTIR** (CH_2Cl_2, ν_{max} cm^{-1}): 2953 (m), 2860 (s), 1713 (m), 1614 (w), 1249 (s), 1034 (w), 839 (s); **HRMS** (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{27}O_2Si$ 303.1780, found 303.1772.



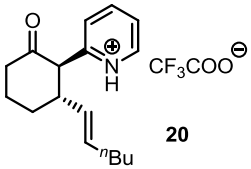
(*E*)-**19**

M.p. = 38-40 ^{0}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31-7.27 (2H, m, Ar-*H*), 7.22-7.19 (1H, m, Ar-*H*), 7.04-7.01 (2H, m, Ar-*H*), 5.65 (1H, dd, *J* = 18.5, 7.5 Hz, CH-alkene-*H*), 5.37 (1H, dd, *J* = 18.5, 0.5 Hz, TMS-alkene-*H*), 3.40 (1H, d, *J* = 11.5 Hz, (CO)C*H*), 2.73-2.65 (1H, m, C*H*), 2.59-2.44 (2H, m, CH_2), 2.22-2.16 (1H, m, CH_2), 2.08-2.04 (1H, m, CH_2), 1.92-1.73 (2H, m, CH_2), -0.14 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 209.2, 147.5, 137.0, 130.7, 129.5, 127.9, 126.6, 62.7, 52.3, 41.8, 31.5, 25.7, 1.6; **FITR** (CH_2Cl_2, υ_{max} cm^{-1}): 2956 (m), 2929 (m), 2857(w), 1715 (s), 1249 (m), 855 (m), 835 (s), 695 (m); **HRMS** (ES) *m/z* $[M+H]^+$ calcd for $C_{17}H_{25}OSi$ 273.1675, found 273.1686.



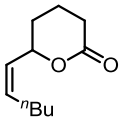
(*Z*)-**19**

M.p. = 81-83 ^{0}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.33 (3H, m, Ar-*H*), 7.08-7.06 (2H, m, Ar-*H*), 6.04 (1H, dd, *J* = 14.0, 9.5 Hz, CH-alkene-*H*), 5.29 (1H, dd, *J* = 14.0 Hz, TMS-alkene-*H*), 3.45 (1H, d, *J* = 11.5 Hz, (CO)C*H*), 2.94-2.85 (1H, m, C*H*), 2.61-2.46 (2H, m, CH_2), 2.24-2.17 (1H, m, CH_2), 1.97-1.73 (3H, m, CH_2), 0.02 (9H, s, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 209.0, 149.9, 136.9, 129.6, 129.1, 128.0, 126.9, 62.9, 49.8, 41.7, 33.3, 25.9, -0.2; **FITR** (CH_2Cl_2, υ_{max} cm^{-1}): 2953 (m), 2912 (w), 2864 (w), 1704 (s), 1245 (m), 838 (s), 749 (m), 697 (s); **HRMS** (ES) *m/z* $[M+H]^+$ calcd for $C_{17}H_{25}OSi$ 273.1675, found 273.1676.



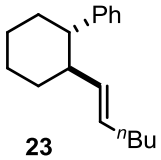
20

^{1}H NMR (400 MHz, $CDCl_3$): δ 14.65 (1H, br, N-*H*), 8.82-8.77 (1H, m, Ar-*H*), 8.19 (1H, td, *J* = 7.9, 1.4 Hz, Ar-*H*), 7.66-7.60 (1H, m, Ar-*H*), 7.56 (1H, d, *J* = 8.0 Hz, Ar-*H*), 5.28-5.11 (2H, m, CH-alkene-*H*), 4.43 (1H, d, *J* = 12.0 Hz, (CO)C*H*), 2.85-2.71 (1H, m, alkene-C*H*), 2.68-2.52 (2H, m, CH_2), 2.28-2.15 (1H, m, CH_2), 2.09-1.98 (1H, m, CH_2), 1.96-1.85 (2H, m, CH_2), 1.85-1.66 (2H, m, CH_2), 1.10-0.92 (4H, m, CH_2), 0.79-0.69 (3H, m, CH_3); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ 205.9, 162.1 (q, *J* = 145.5 Hz, CF_3C(O)O), 154.9, 142.7, 142.3, 133.5, 130.1, 127.5, 124.0, 116.5 (q, *J* = 1158.0 Hz, CF_3C(O)O), 60.4, 49.6, 41.1, 32.3, 31.5, 31.0, 25.5, 21.6, 13.6; **FITR** (CH_2Cl_2, υ_{max} cm^{-1}) 3064 (w), 2959 (s), 2933 (s), 2873 (m), 2858 (m), 1716 (s), 1675 (s), 1630 (m), 1596 (w), 1192 (s), 1135 (s), 971 (m), 799 (m); **HRMS** (ES) *m/z* $[M+H]^+$ calc'd for $C_{17}H_{24}NO$ 258.1858, found 258.1852.



(*Z*)-**14**

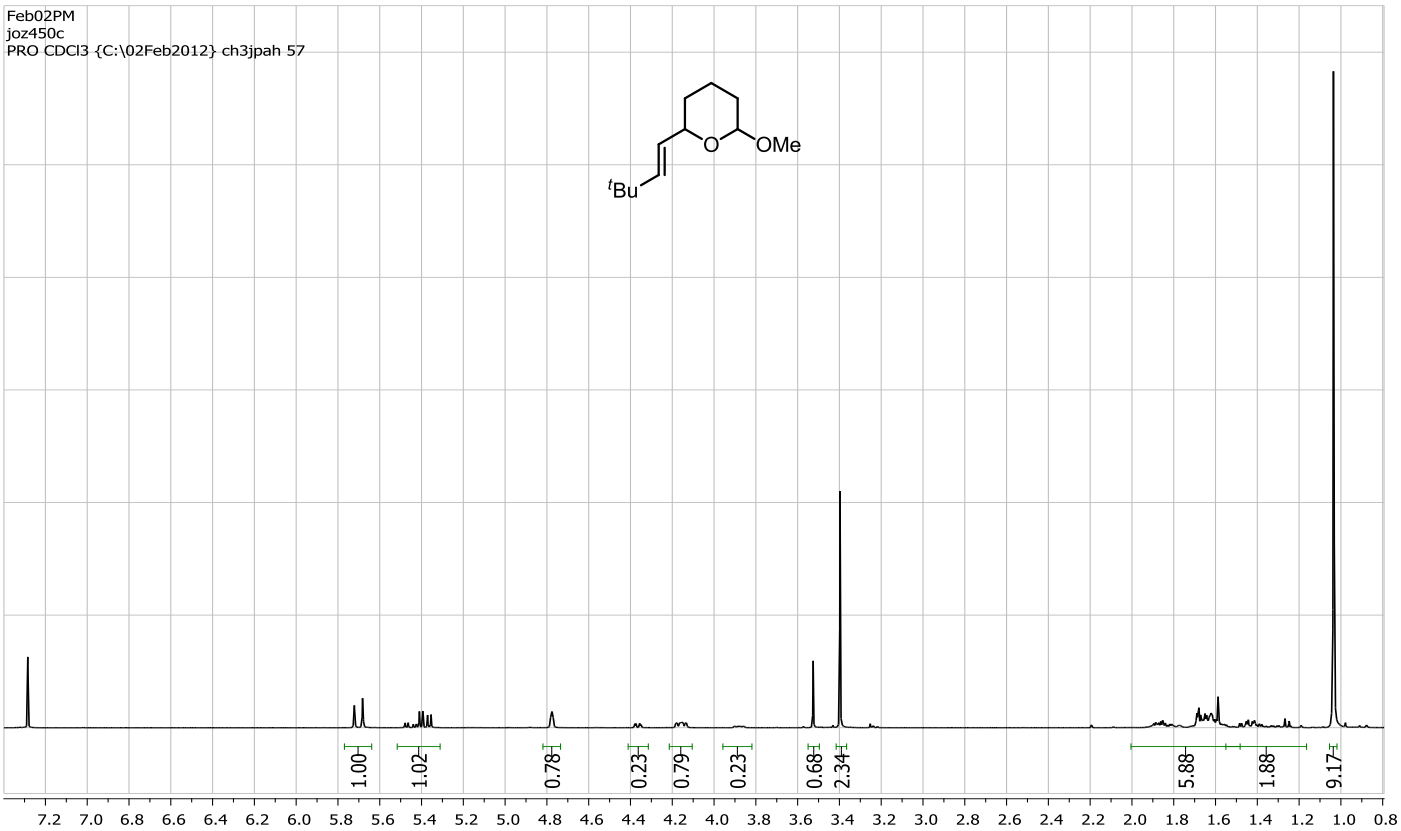
M.p. = 42-44 ^{0}C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.60 (1H, dtd, *J* = 11.0, 7.5, 1.0 Hz, CH_2-alkene-*H*), 5.48-5.43 (1H, m, alkene-*H*), 5.13-5.08 (1H, m, OC*H*), 2.66-2.58 (1H, m, C(O)C*H*), 2.52-2.44 (1H, m, C(O)C*H*), 2.14-2.04 (2H, m, *CH*$_2$), 1.98-1.86 (3H, m, CH_2), 1.70-1.61 (1H, m, C*H*), 1.40-1.30 (4H, m, CH_2), 0.91 (3H, *J* = 7.0 Hz, CH_3); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 171.5, 134.5, 127.6, 76.4, 31.6, 29.4, 28.6, 27.5, 22.3, 18.6, 13.9; **FTIR** (CH_2Cl_2, ν_{max} cm^{-1}): 2956 (m), 2929 (m), 2874 (w), 1735 (s), 1237 (m), 1038 (m), 924 (w); **HRMS** (EI) *m/z* $[MH]^+$ calcd for $C_{11}H_{19}O_2$ 183.1385, found 183.1387.

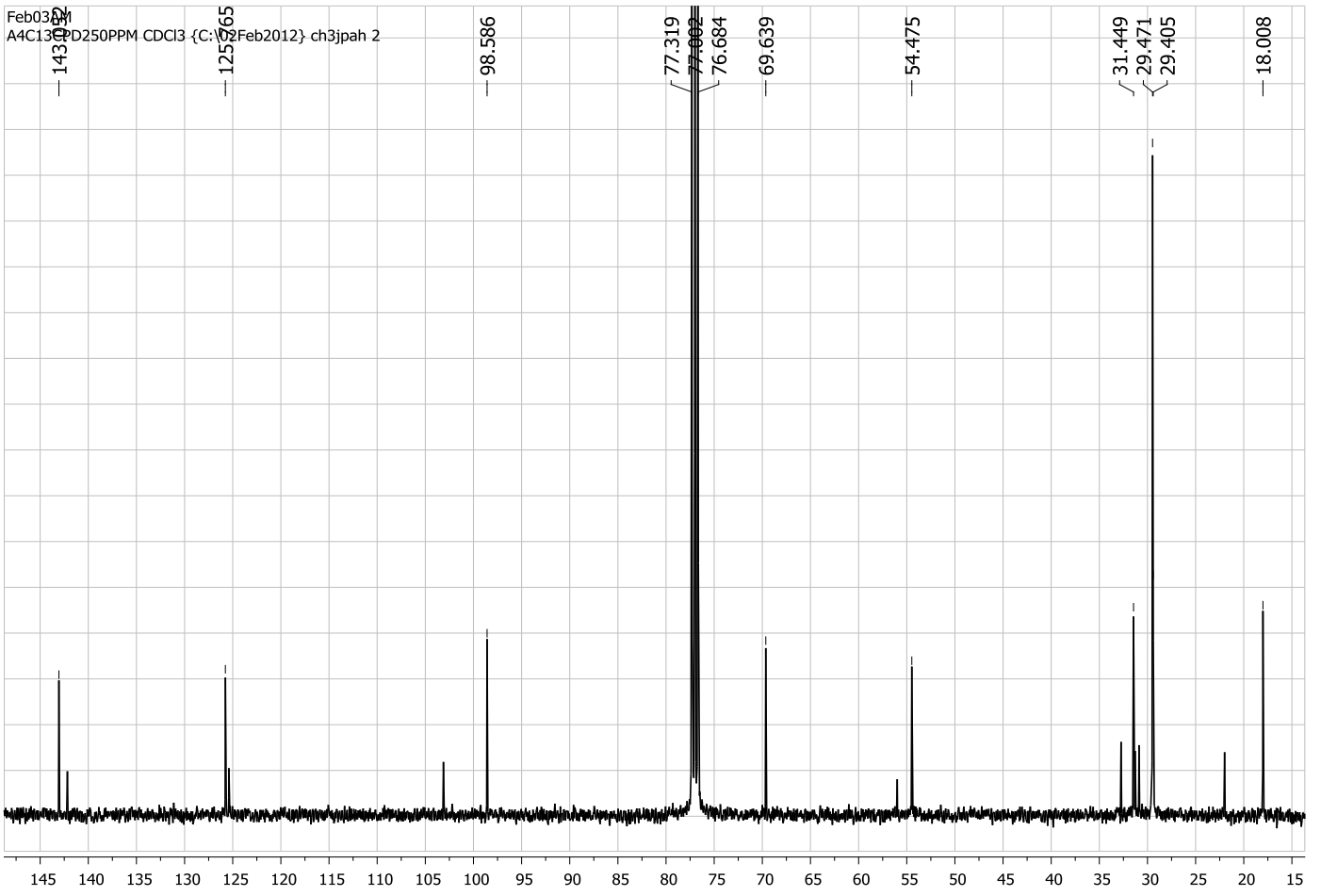


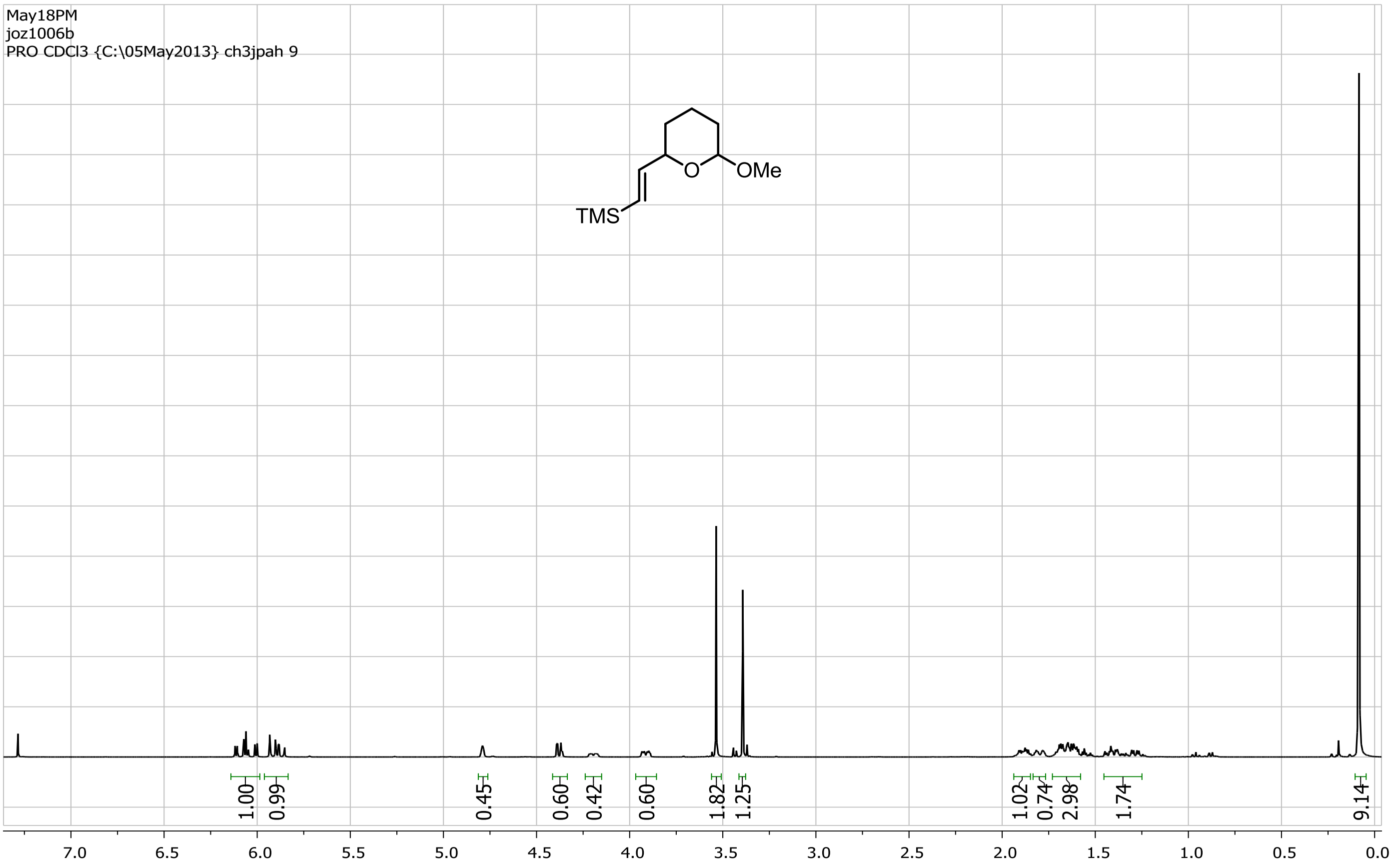
23

^{1}H NMR (250 MHz, $CDCl_3$): δ 7.30-7.19 (2H, m, Ar-*H*), 7.18-7.07 (3H, m, Ar-*H*), 5.18-4.93 (2H, m, alkene-*H*), 2.33-2.06 (2H, m, CH_2), 1.92-1.64 (6H, m, CH_2), 1.49-1.22 (4H, m, CH_2), 1.13-0.94 (4H, m, CH_2), 0.74 (3H, t, J = 7.0 Hz, CH_3); **^{13}C NMR** (63 MHz, $CDCl_3$): δ 146.5, 134.3, 129.7, 128.0, 127.8, 125.6, 50.7, 46.4, 35.4, 33.7, 32.1, 31.6, 26.8, 26.2, 21.7, 13.8; **FTIR** (CH_2Cl_2, ν_{max} cm^{-1}): 2956 (s), 2924 (s), 2852 (s), 1446 (w), 965 (w), 754 (w), 698 (w); **HRMS** (EI) m/z [M] calcd for $C_{18}H_{26}$: 242.2034, found 242.2024.

$^{1}H/^{13}C$ NMR spectra



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1.82
1.25
1.02
0.74
2.98
1.74
9.14
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6.5
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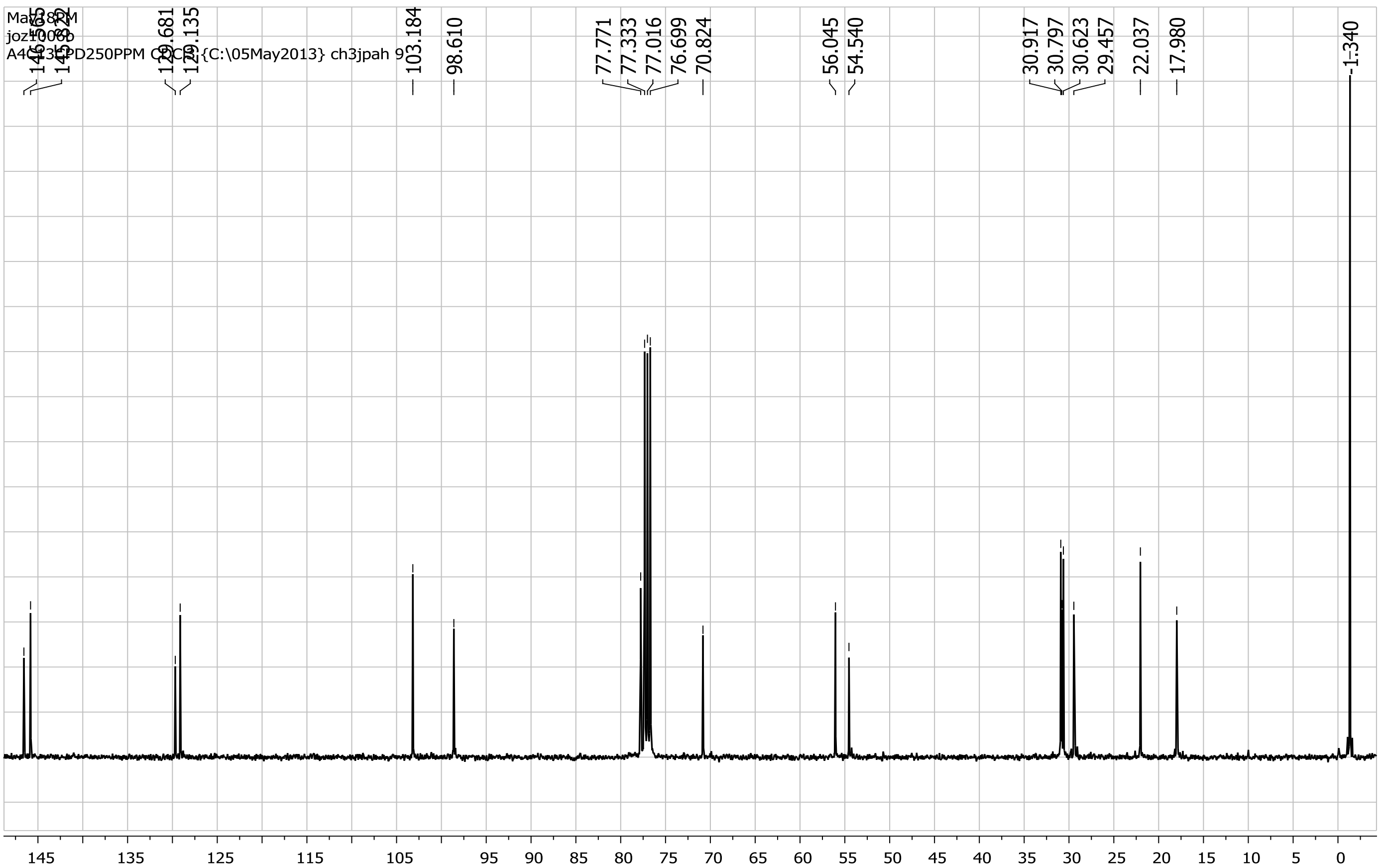
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30.623
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22.037
17.980
-1.340
145
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125
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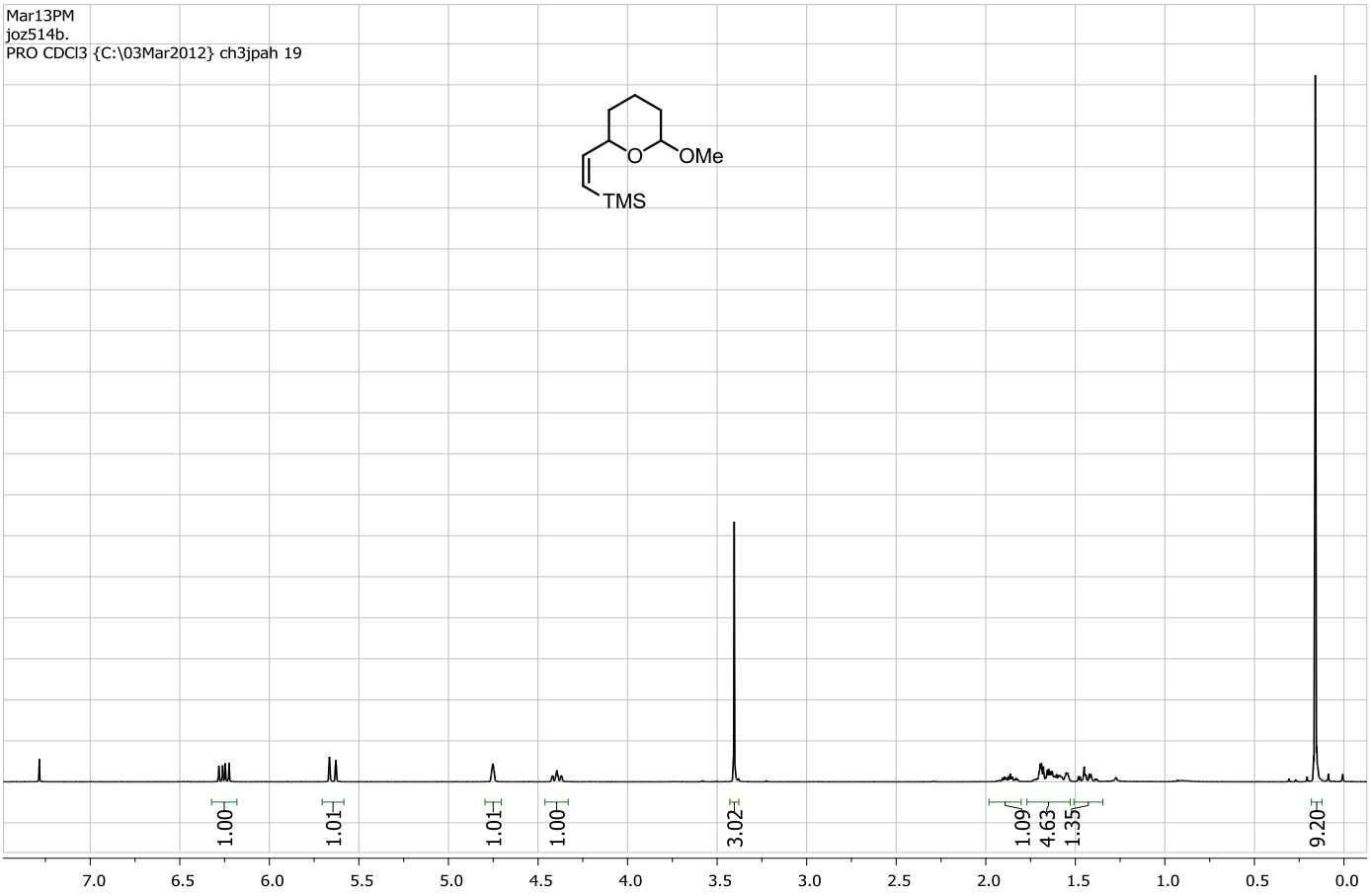
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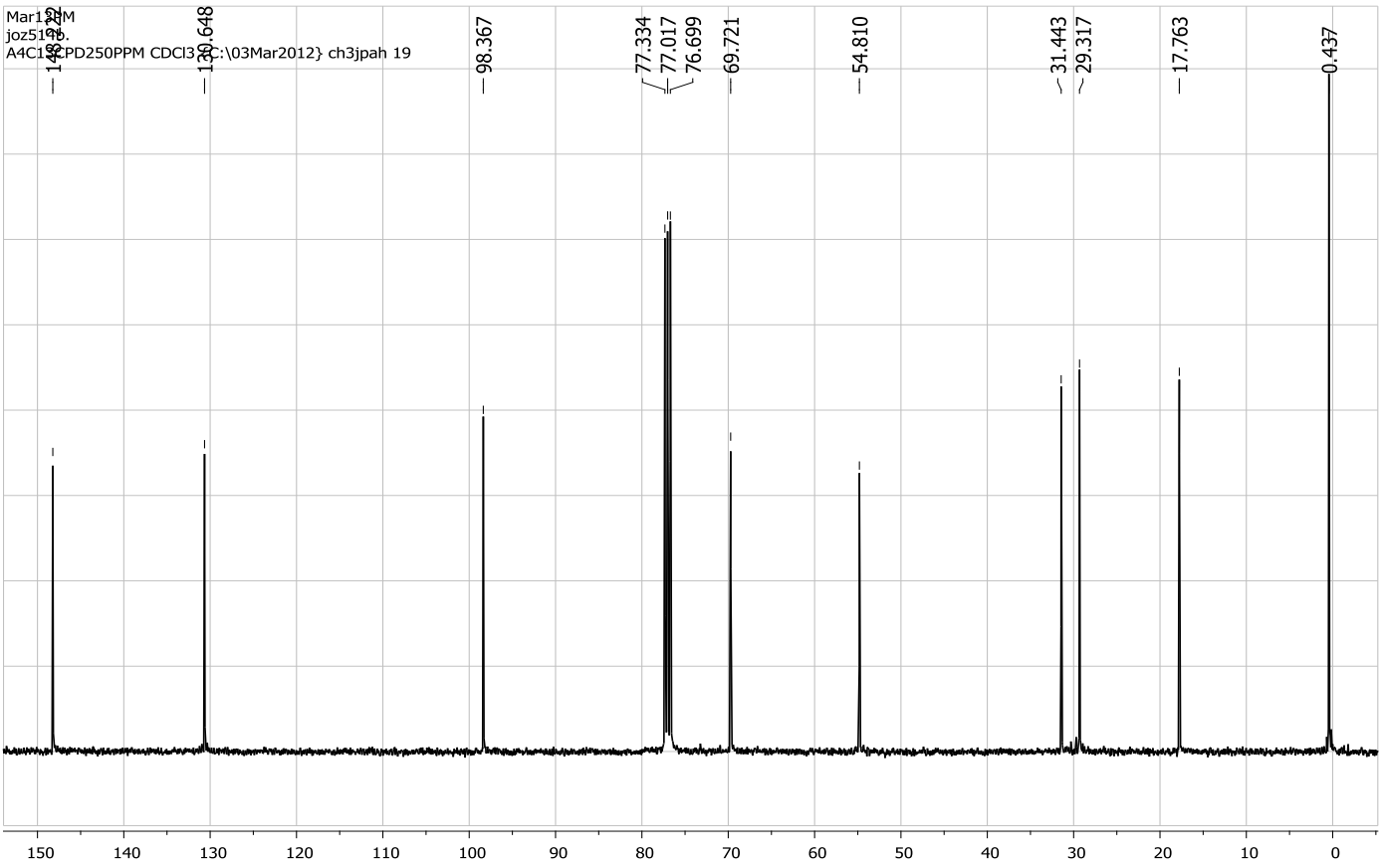
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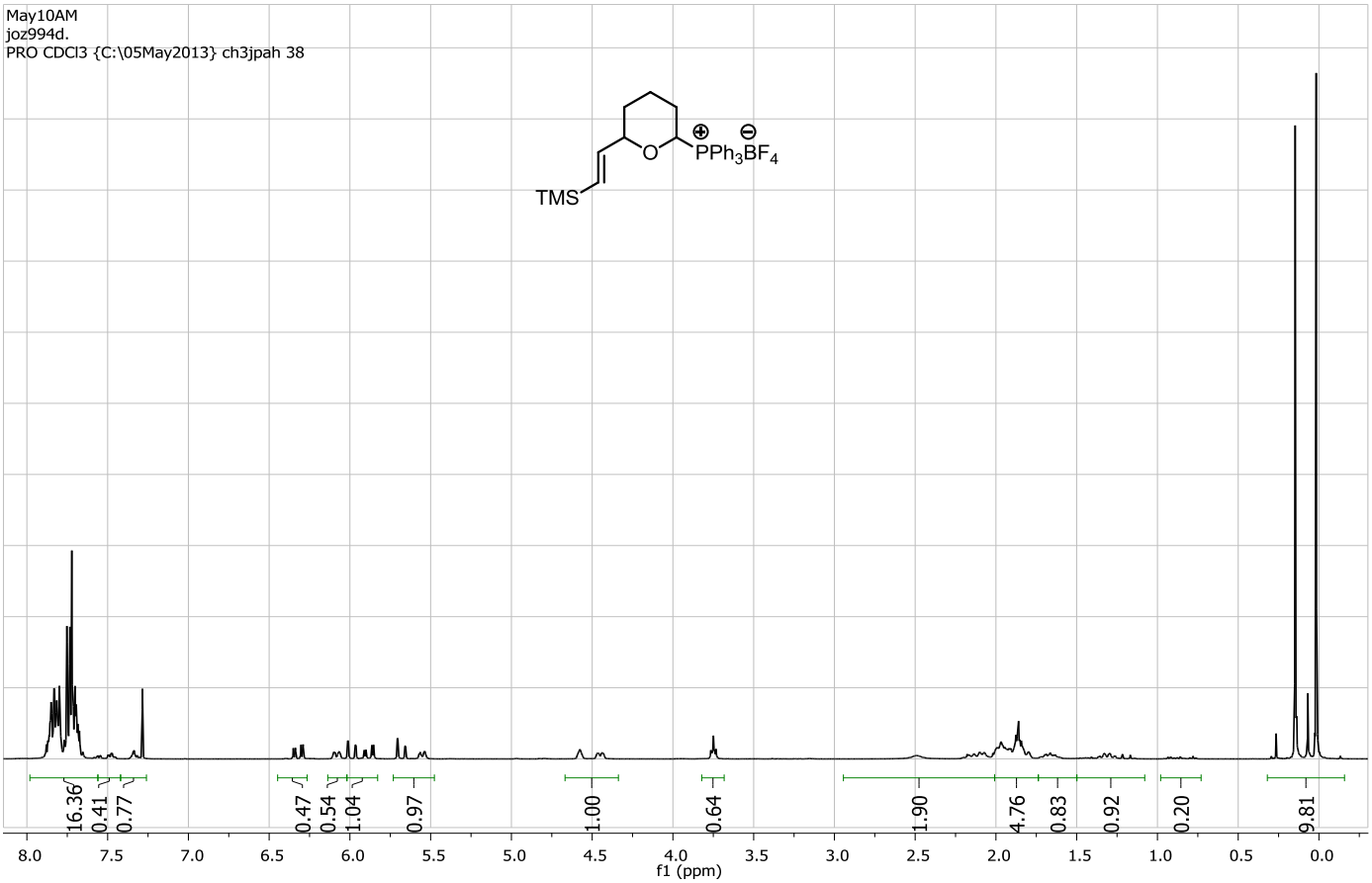
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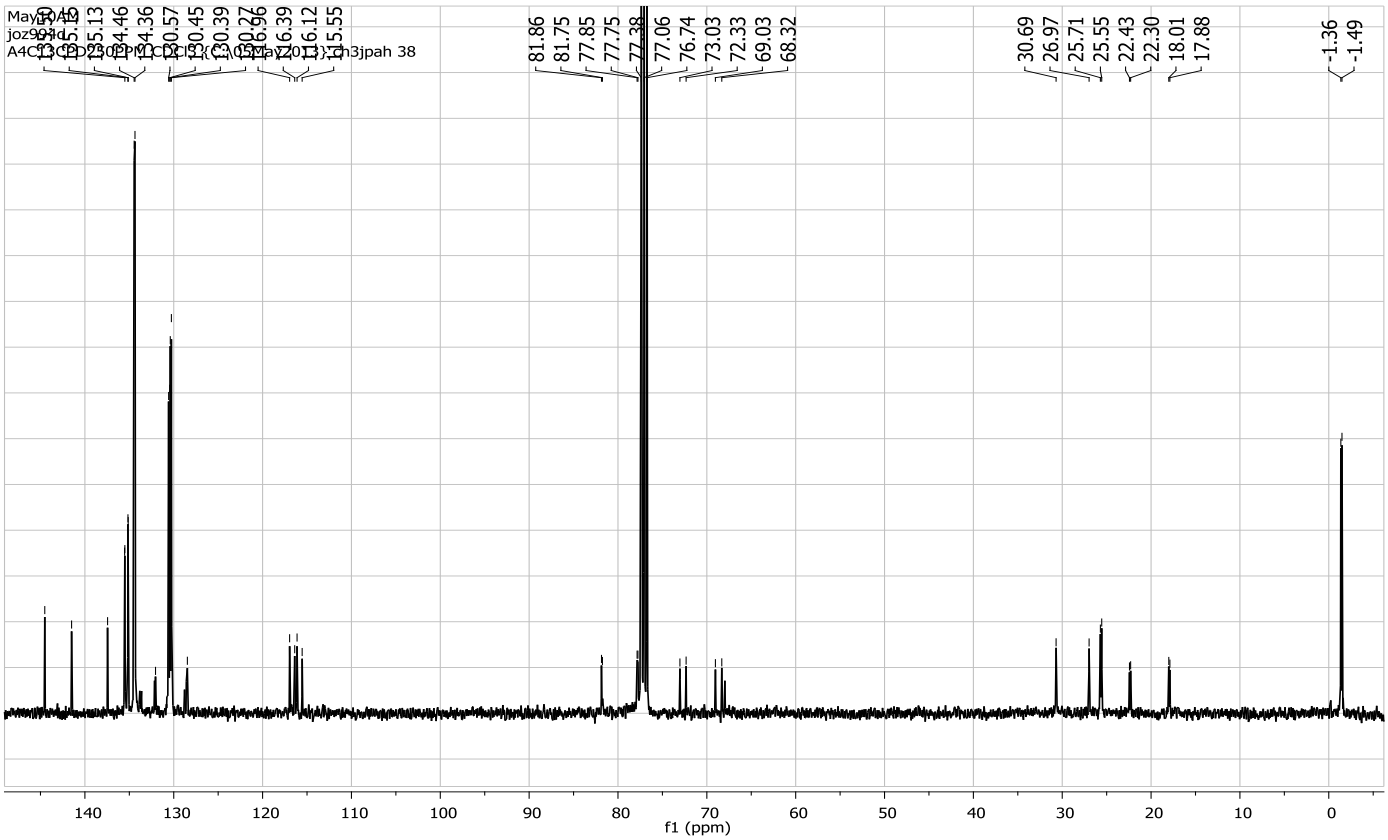
0.92
0.20
9.81
f1 (ppm)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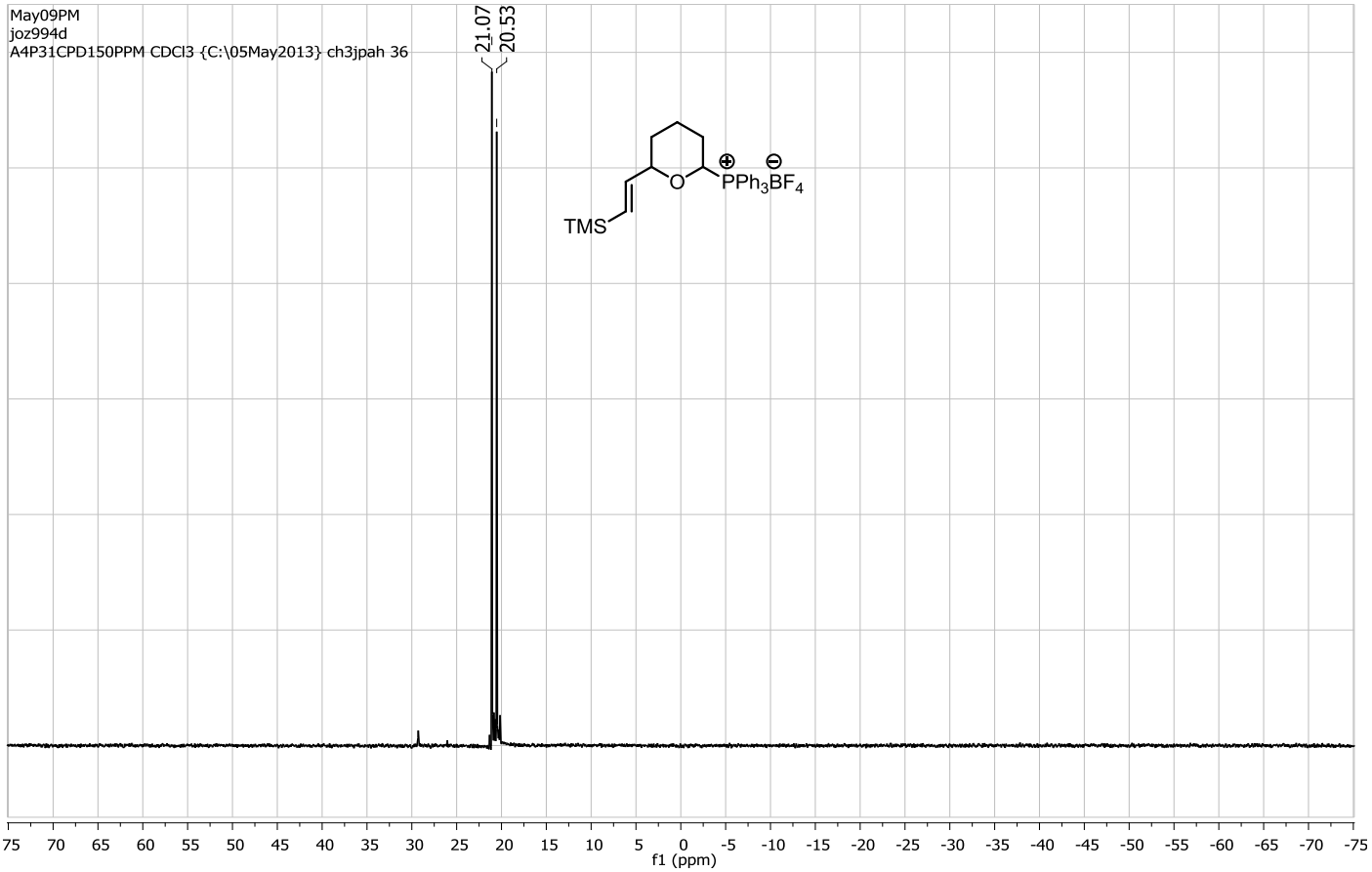
-1.49
f1 (ppm)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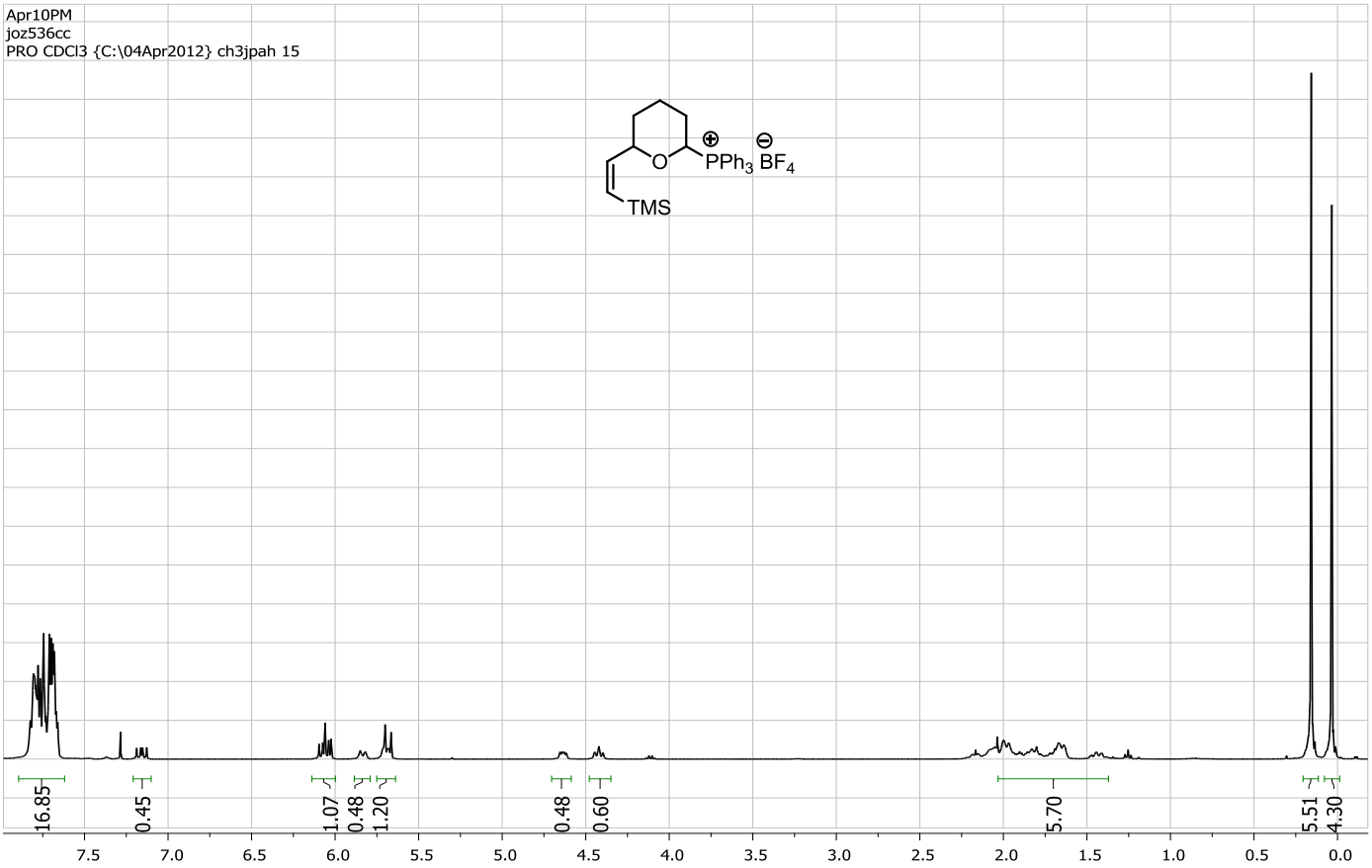
f1 (ppm)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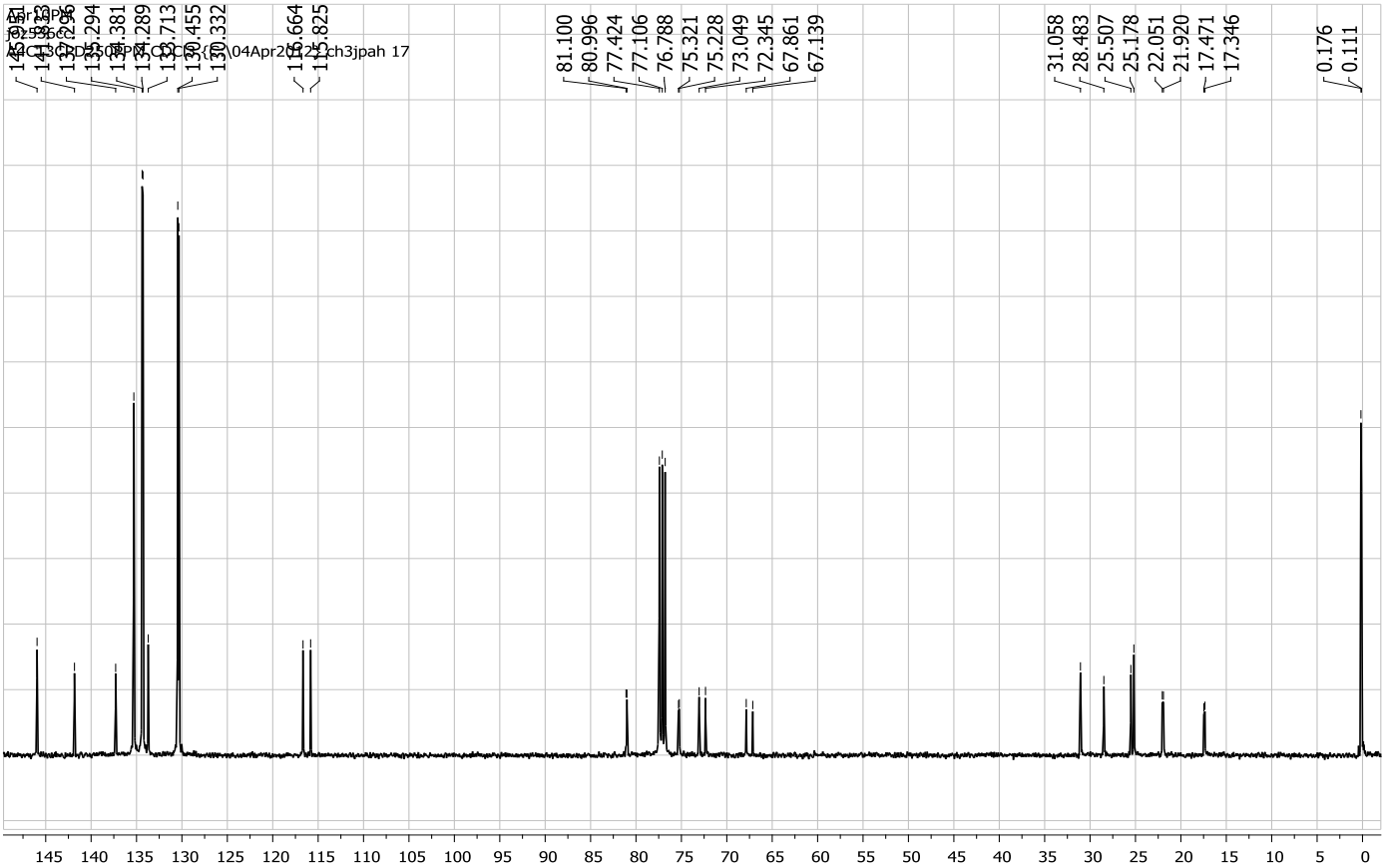
5.51
4.30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21.920
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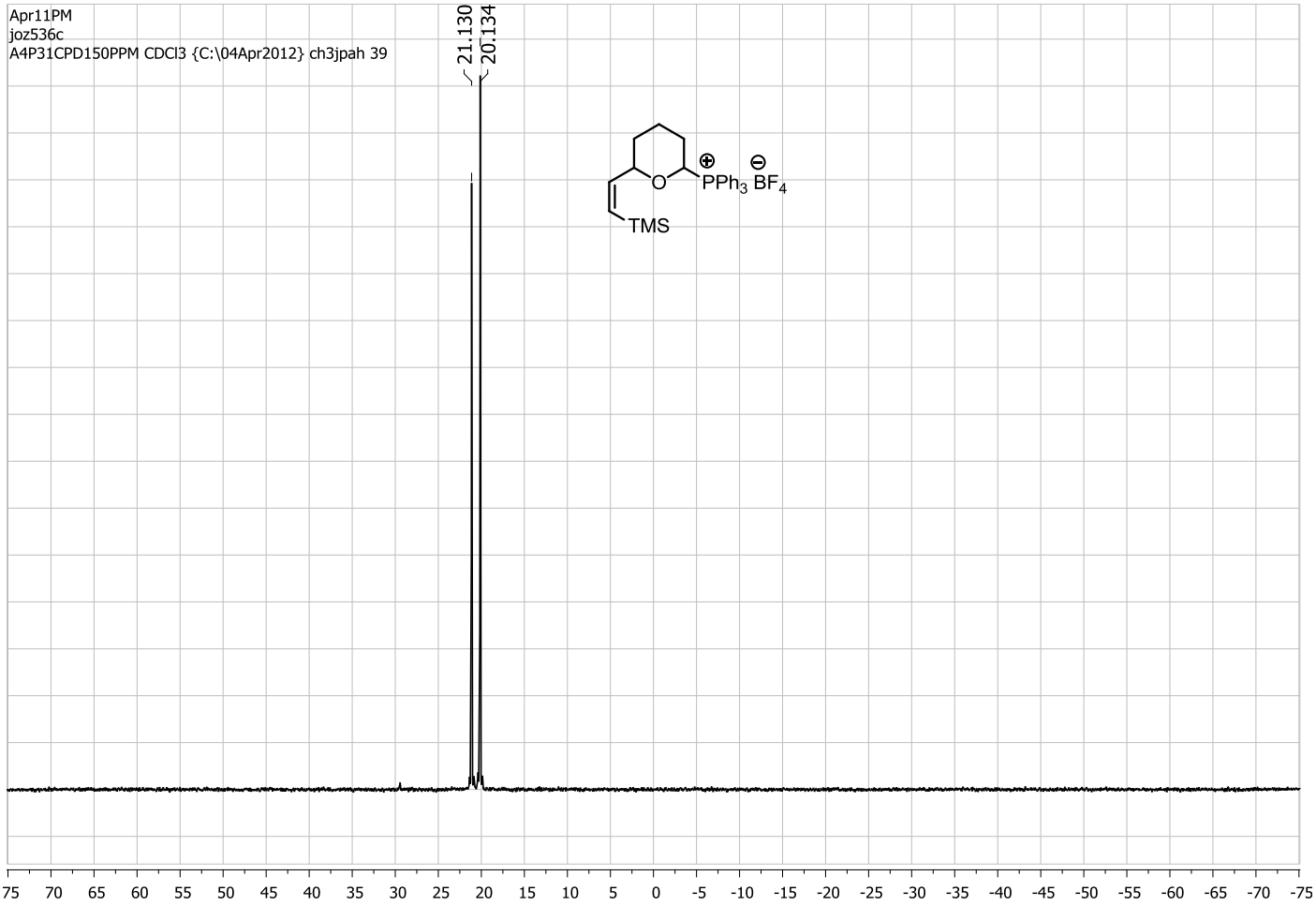
0.111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20.134
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PPh3 BF4
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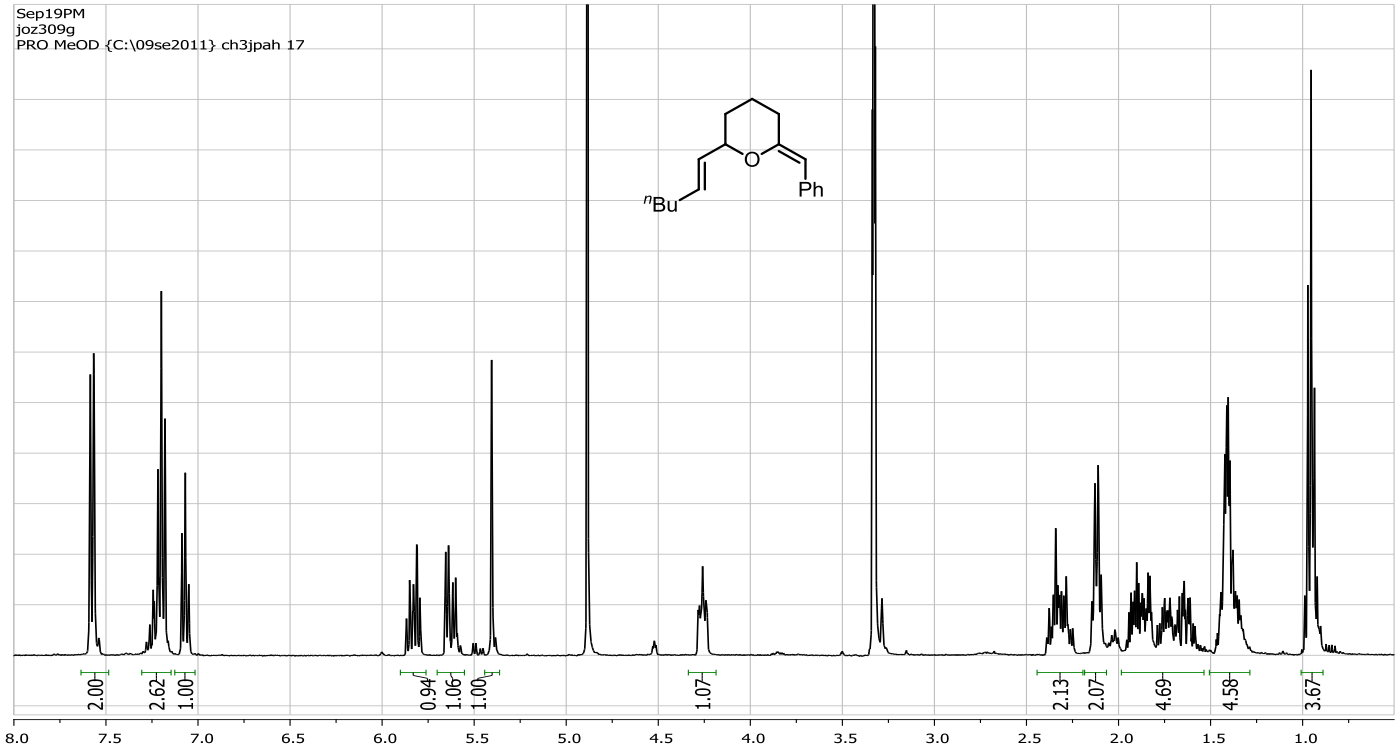
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1.07
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3.67
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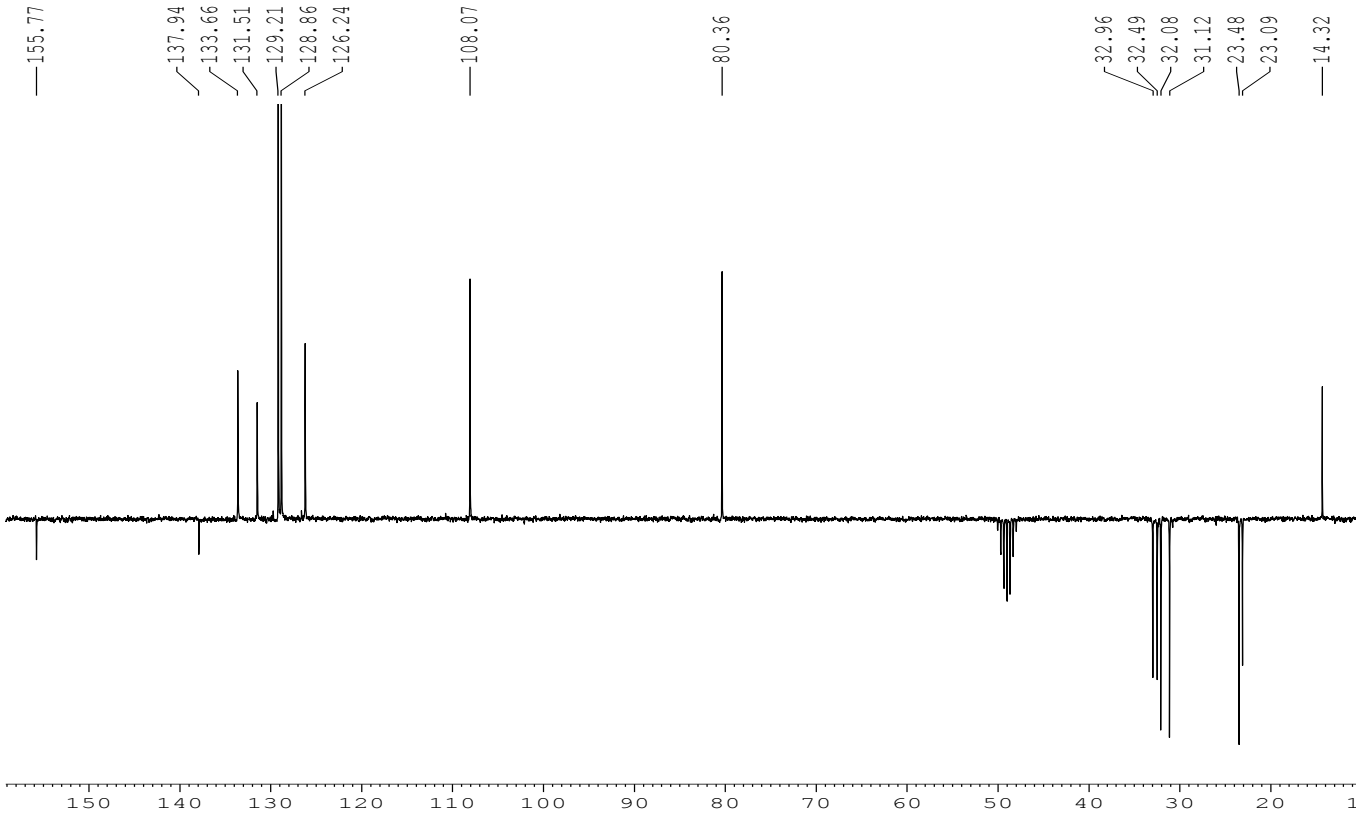
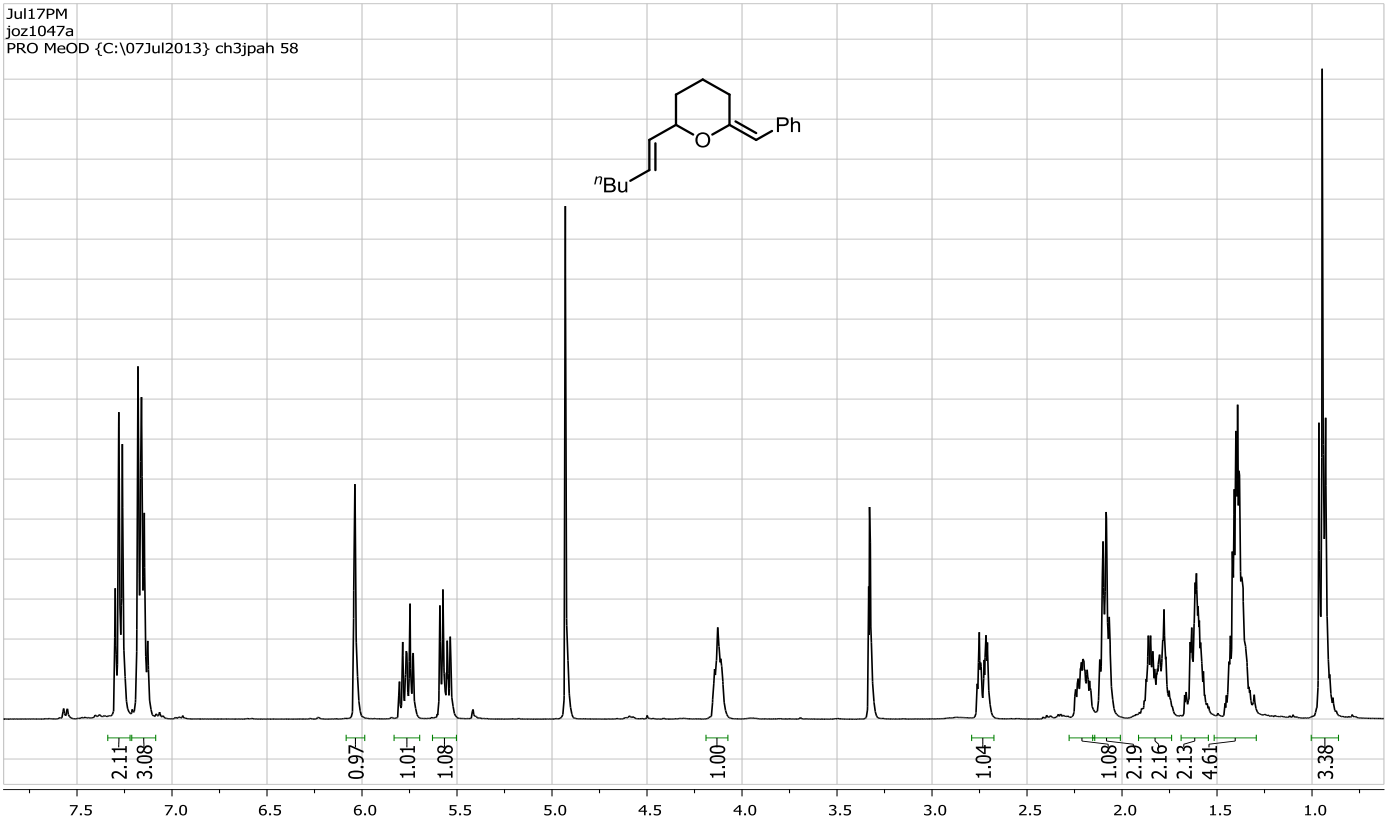
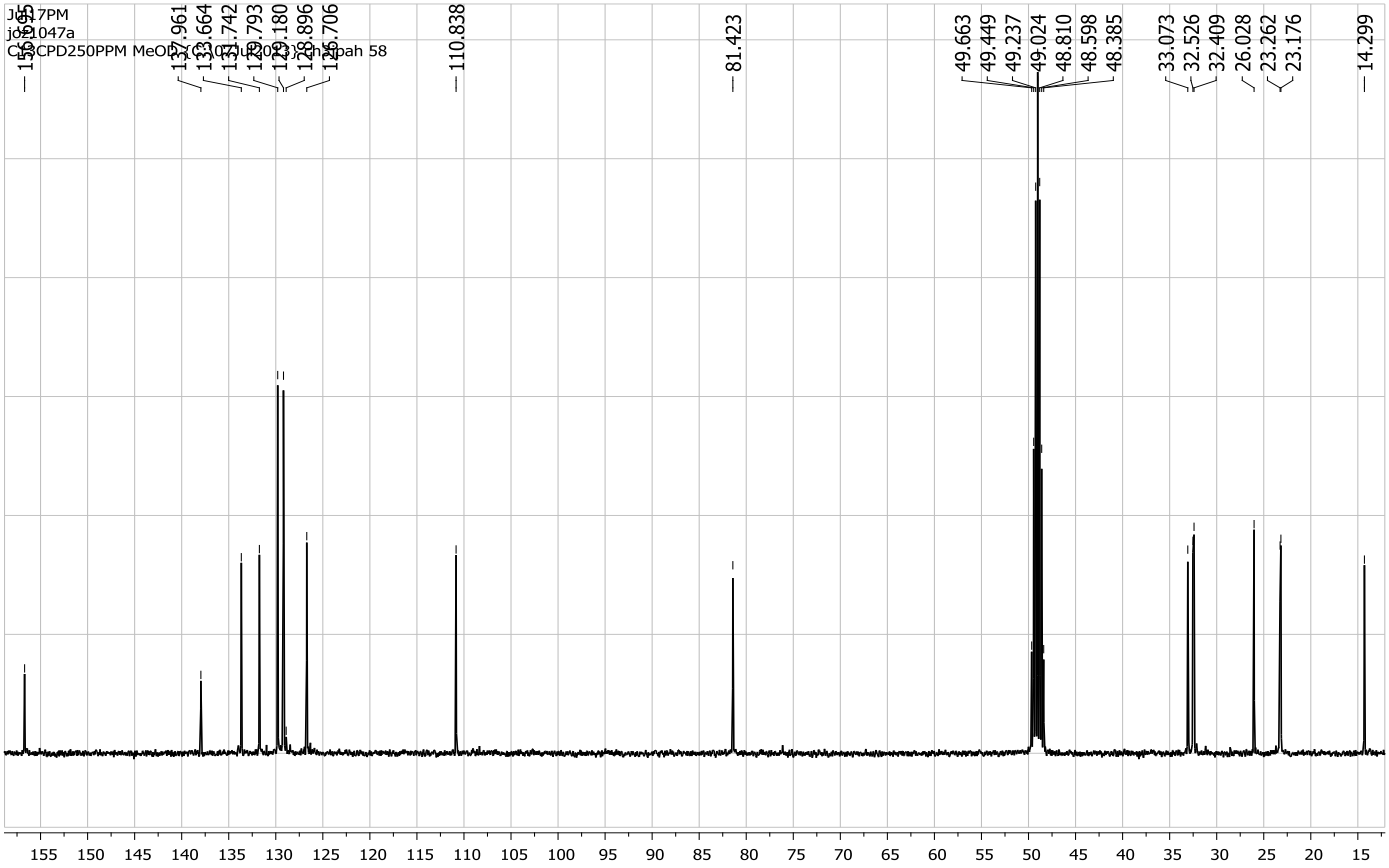
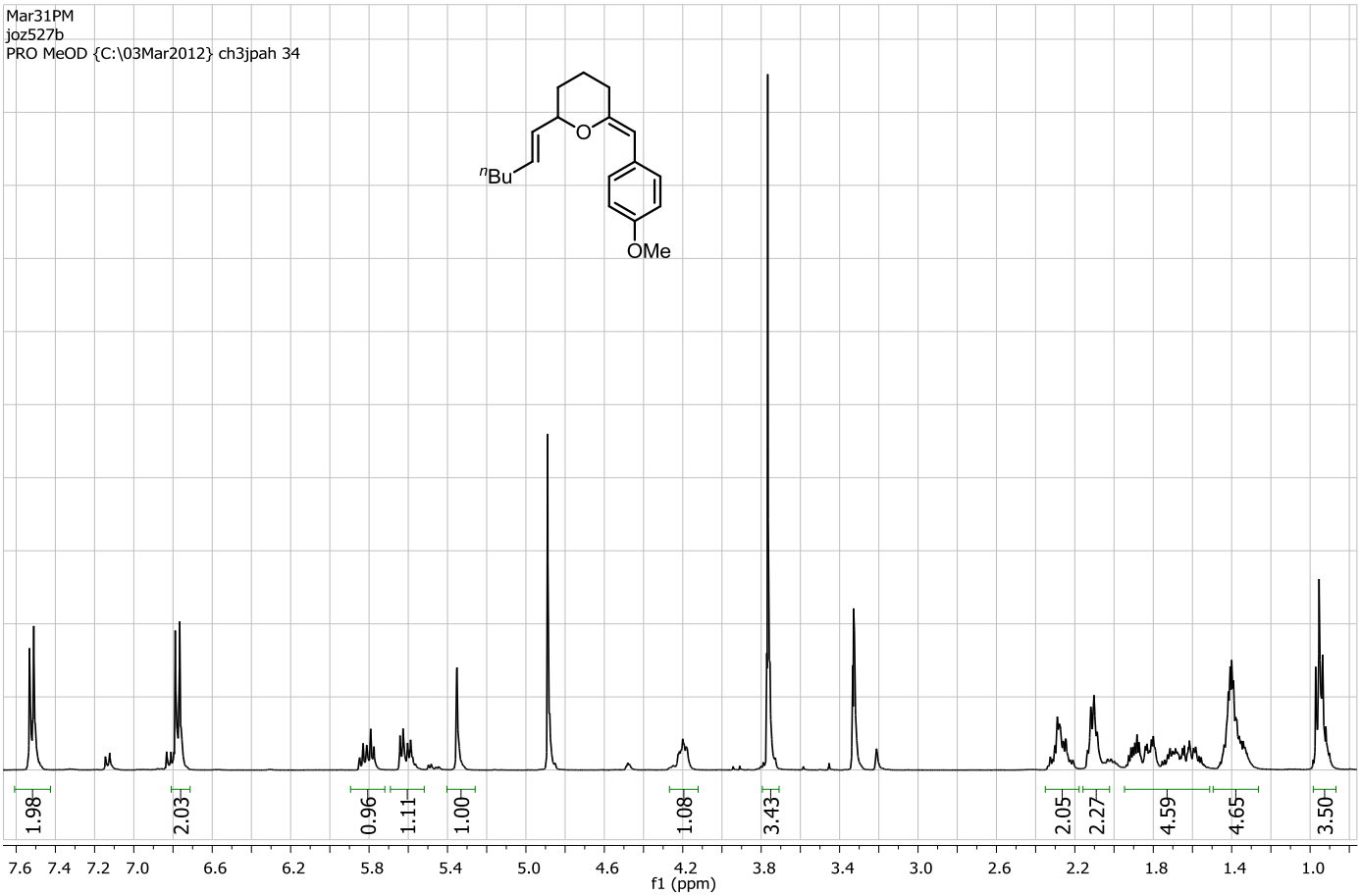
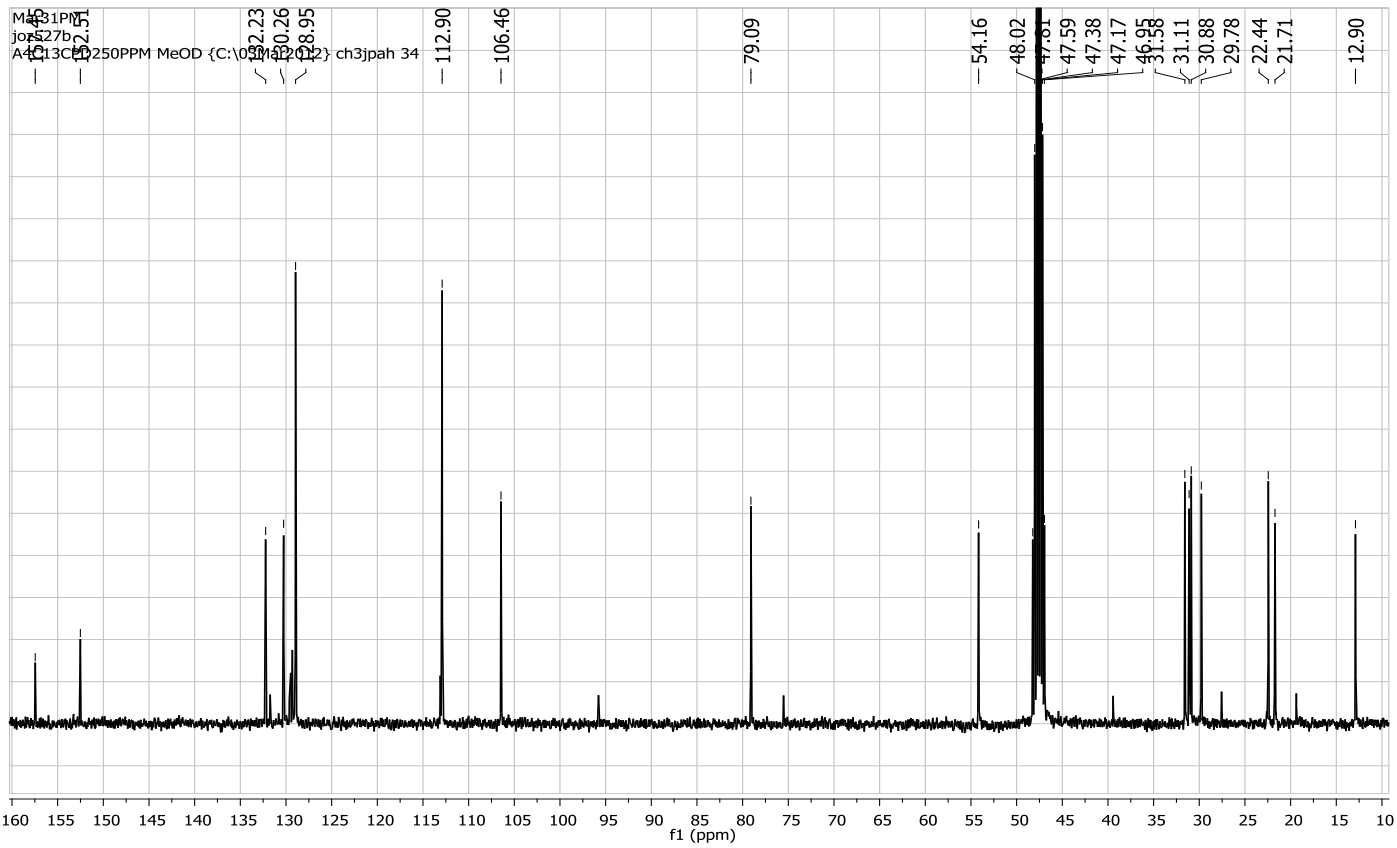
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

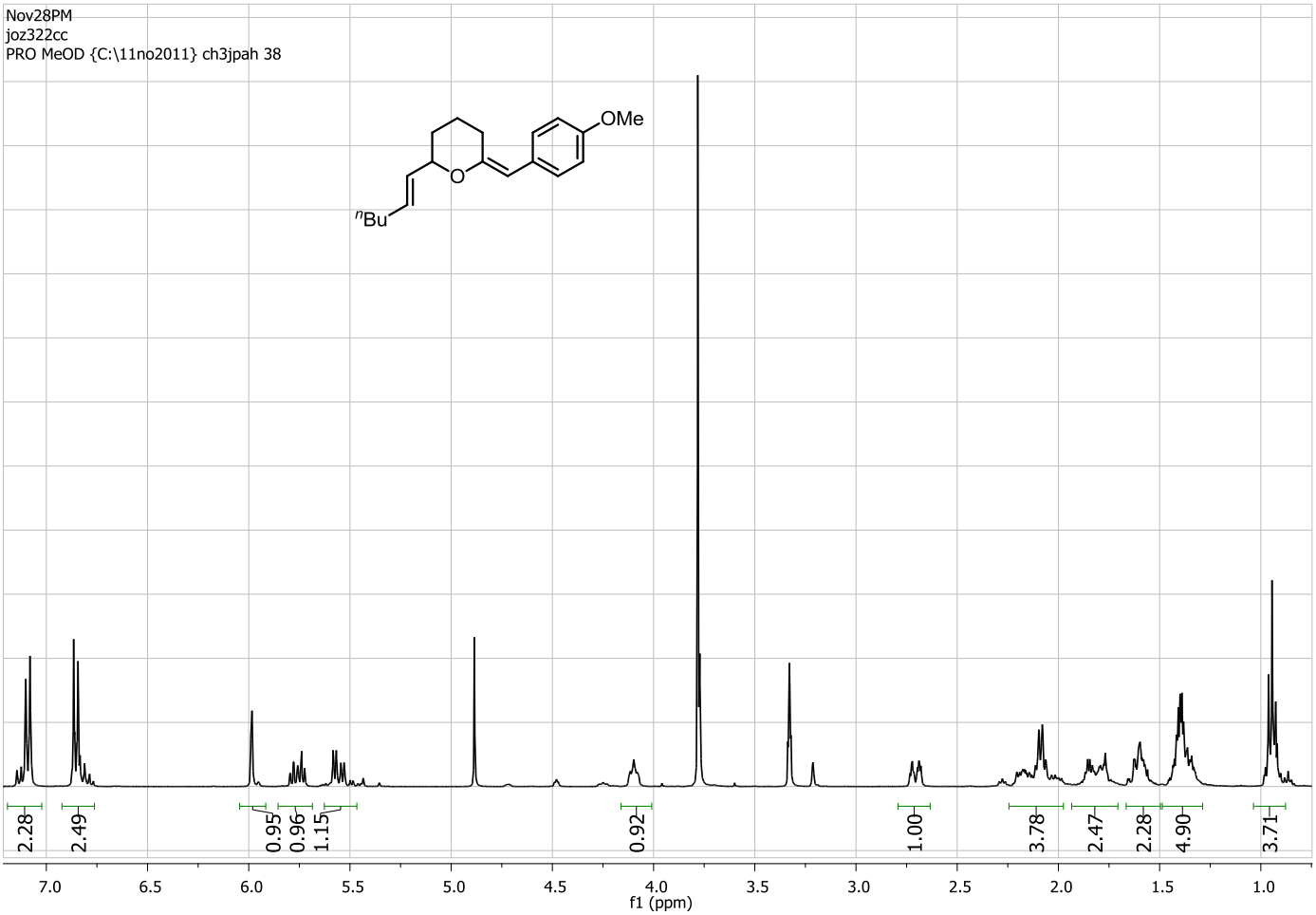

155.77
137.94
133.66
131.51
129.21
128.86
126.24
108.07
80.36
32.96
32.49
32.08
31.12
23.48
23.09
14.32
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1

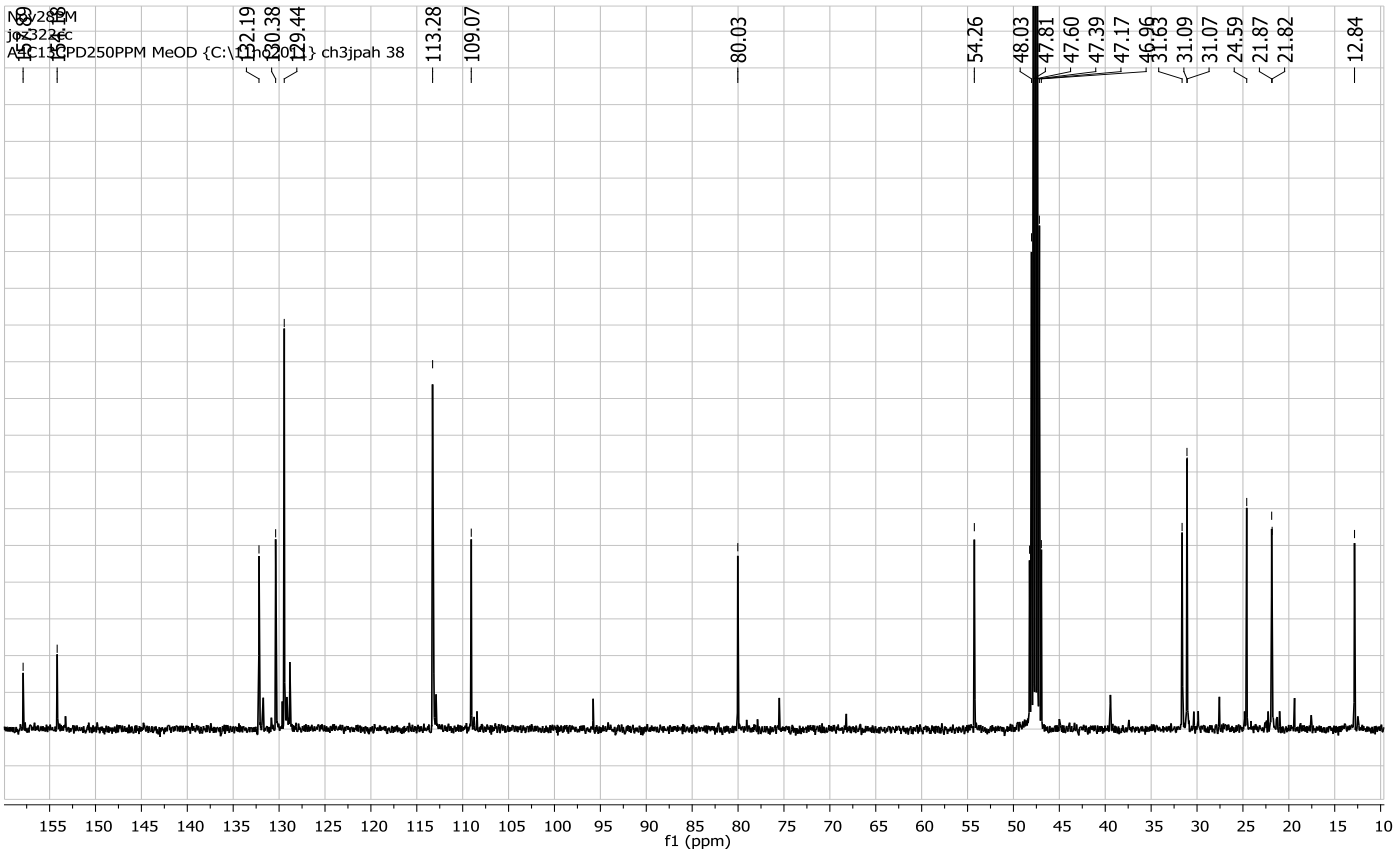

Jul17PM
joz1047a
PRO MeOD {C:\07Jul2013} ch3jpah 58
Ph
nBu
2.11
3.08
0.97
1.01
1.08
1.00
1.04
1.08
2.19
2.16
2.13
4.61
3.38

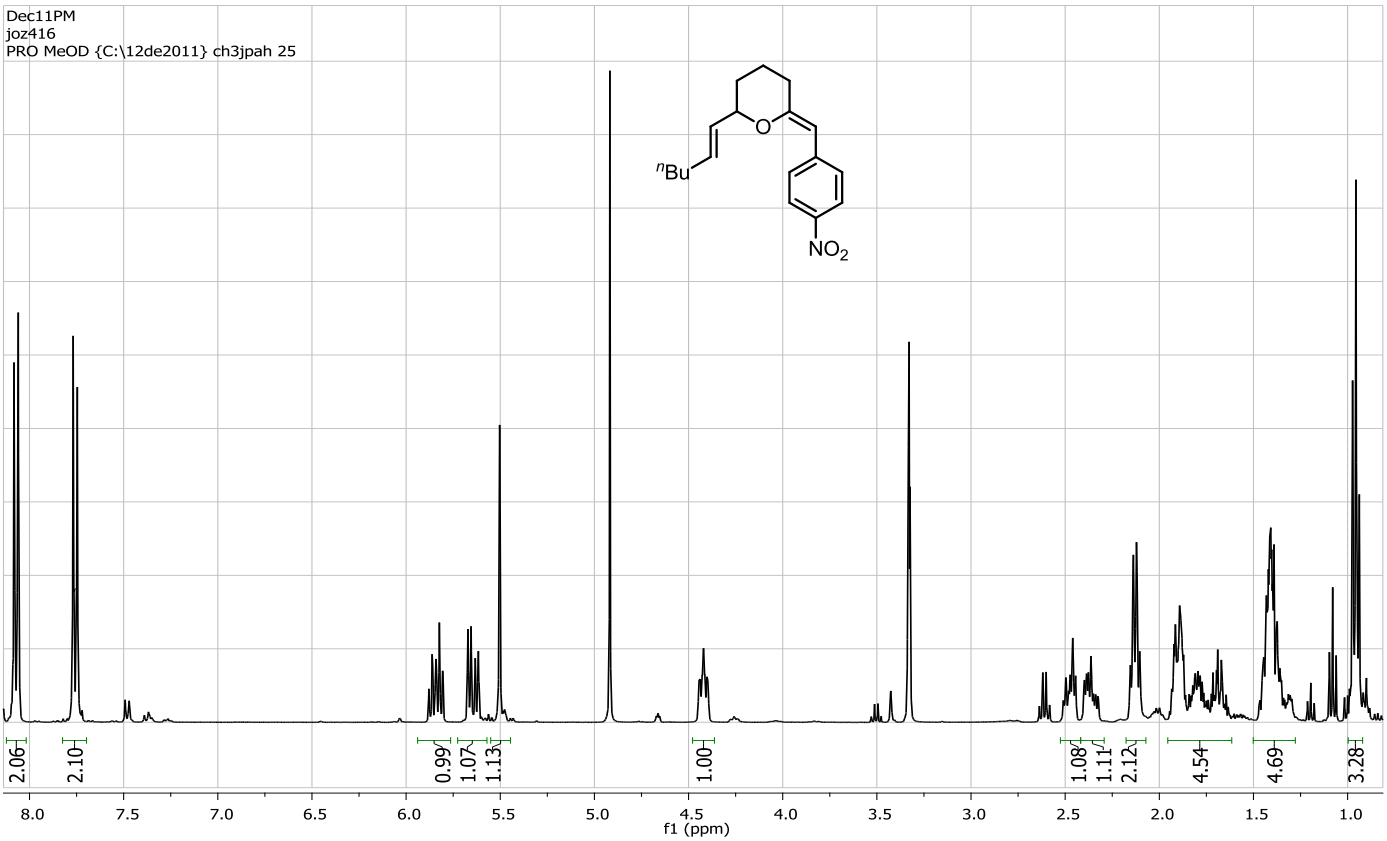

Jul17PM
joz1047a
C13CPD250PPM MeOD {C:\07Jul2013} ch3jpah 58
137.961
133.664
131.742
129.793
129.180
128.896
126.706
110.838
81.423
49.663
49.449
49.237
49.024
48.810
48.598
48.385
33.073
32.526
32.409
26.028
23.262
23.176
14.299

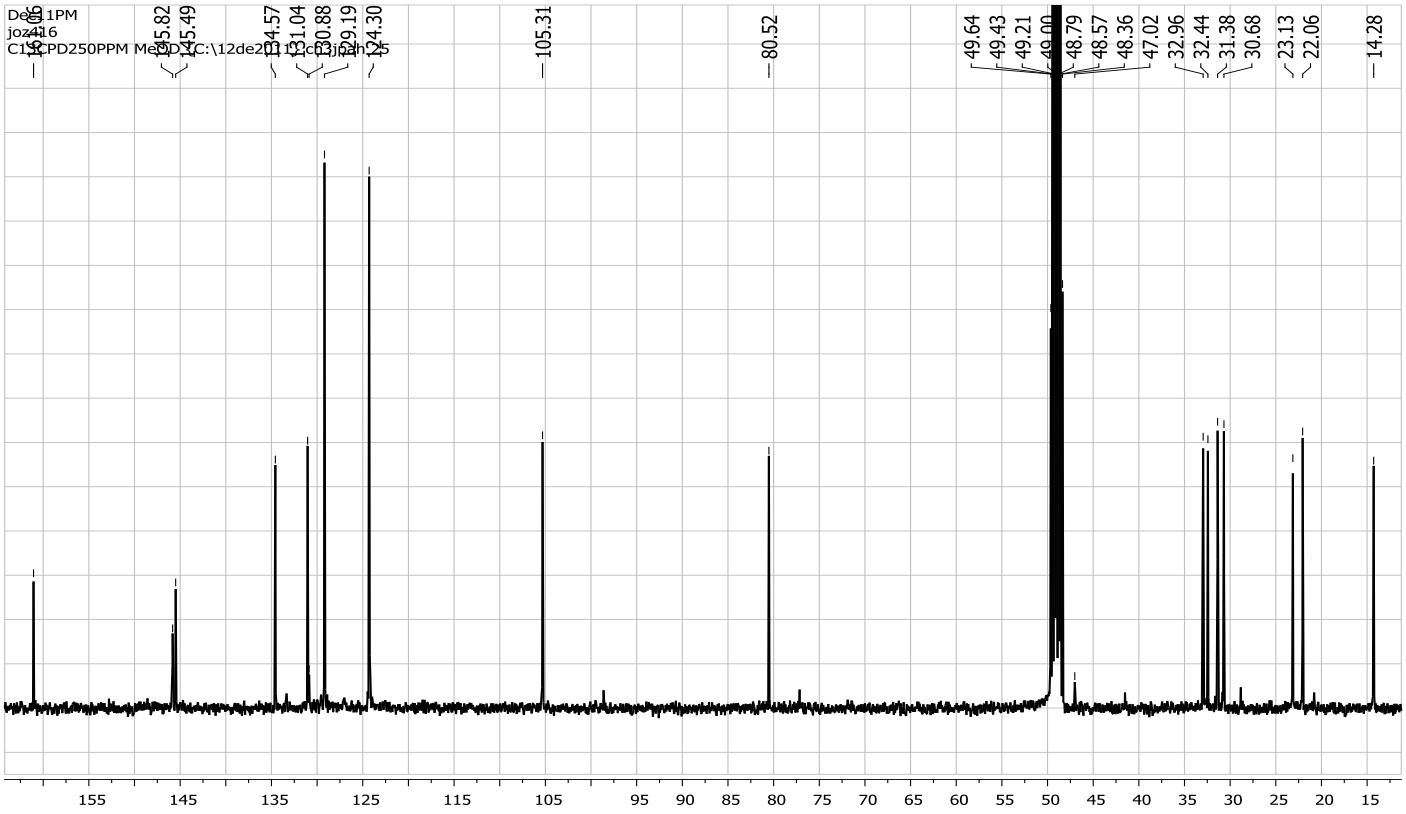

Mar31PM
joz527b
PRO MeOD {C:\03Mar2012} ch3jpah 34
nBu
O
OMe
1.98
2.03
0.96
1.11
1.00
1.08
3.43
2.05
2.27
4.59
4.65
3.50
f1 (ppm)

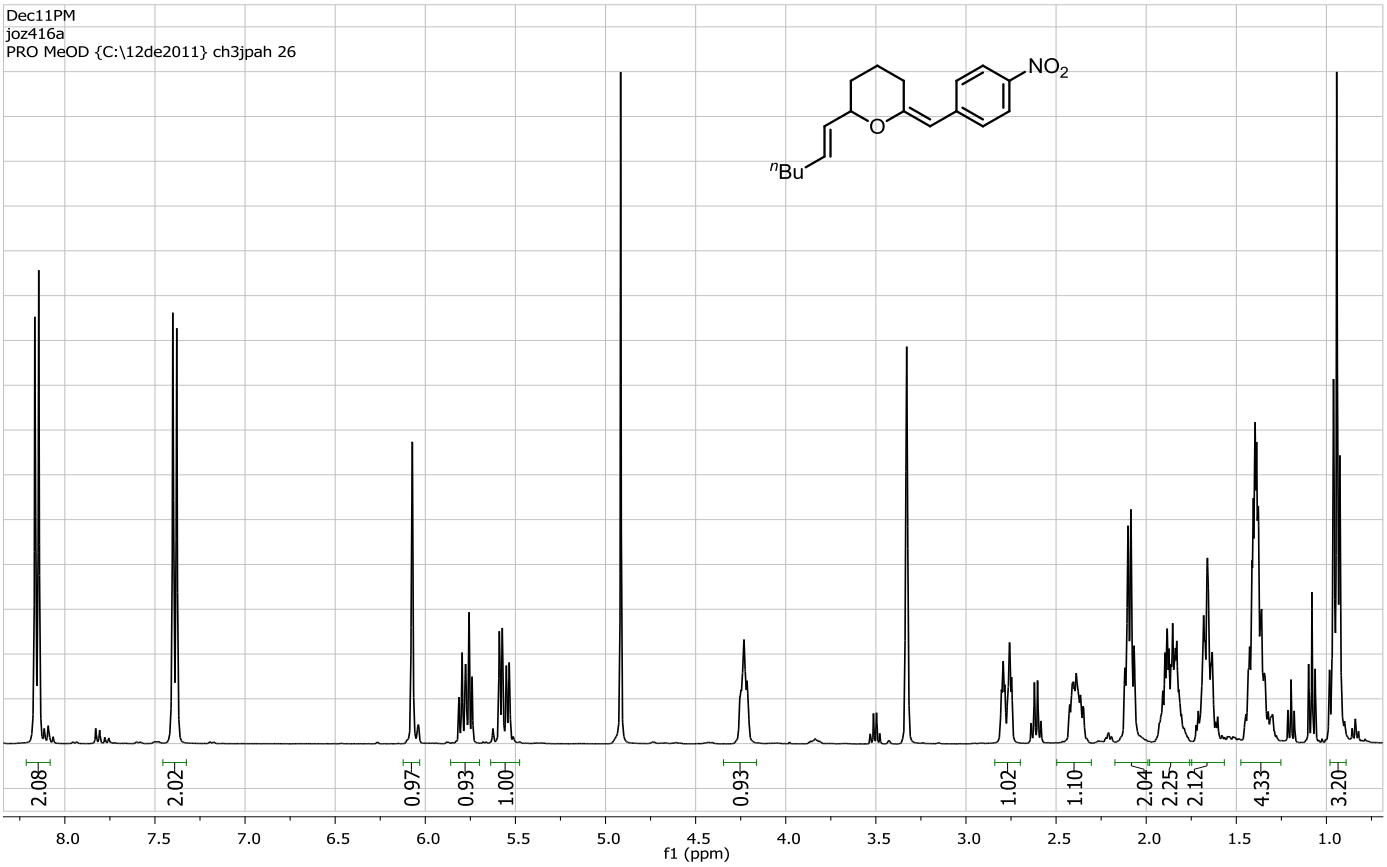

Mar31PM
joz527b
A4 13CCPD250PPM MeOD {C:\03Mar2012} ch3jpah 34
152.51
132.23
130.26
128.95
112.90
106.46
79.09
54.16
48.02
47.81
47.59
47.38
47.17
46.95
31.58
31.11
30.88
29.78
22.44
21.71
12.90
f1 (ppm)

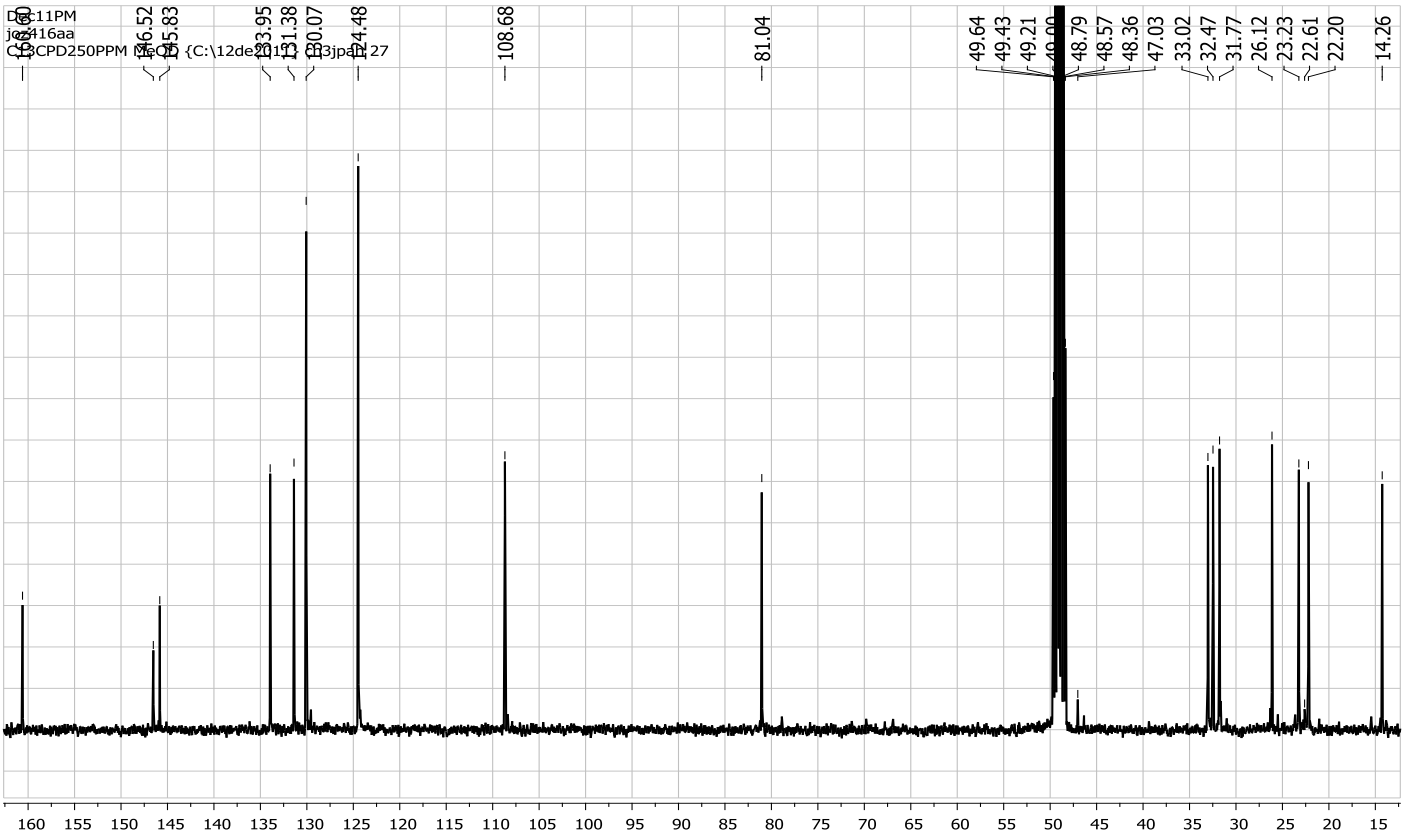

Nov28PM
joz322cc
PRO MeOD {C:\11no2011} ch3jpah 38
OMe
O
nBu
2.28
2.49
0.95
0.96
1.15
0.92
1.00
3.78
2.47
2.28
4.90
3.71
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

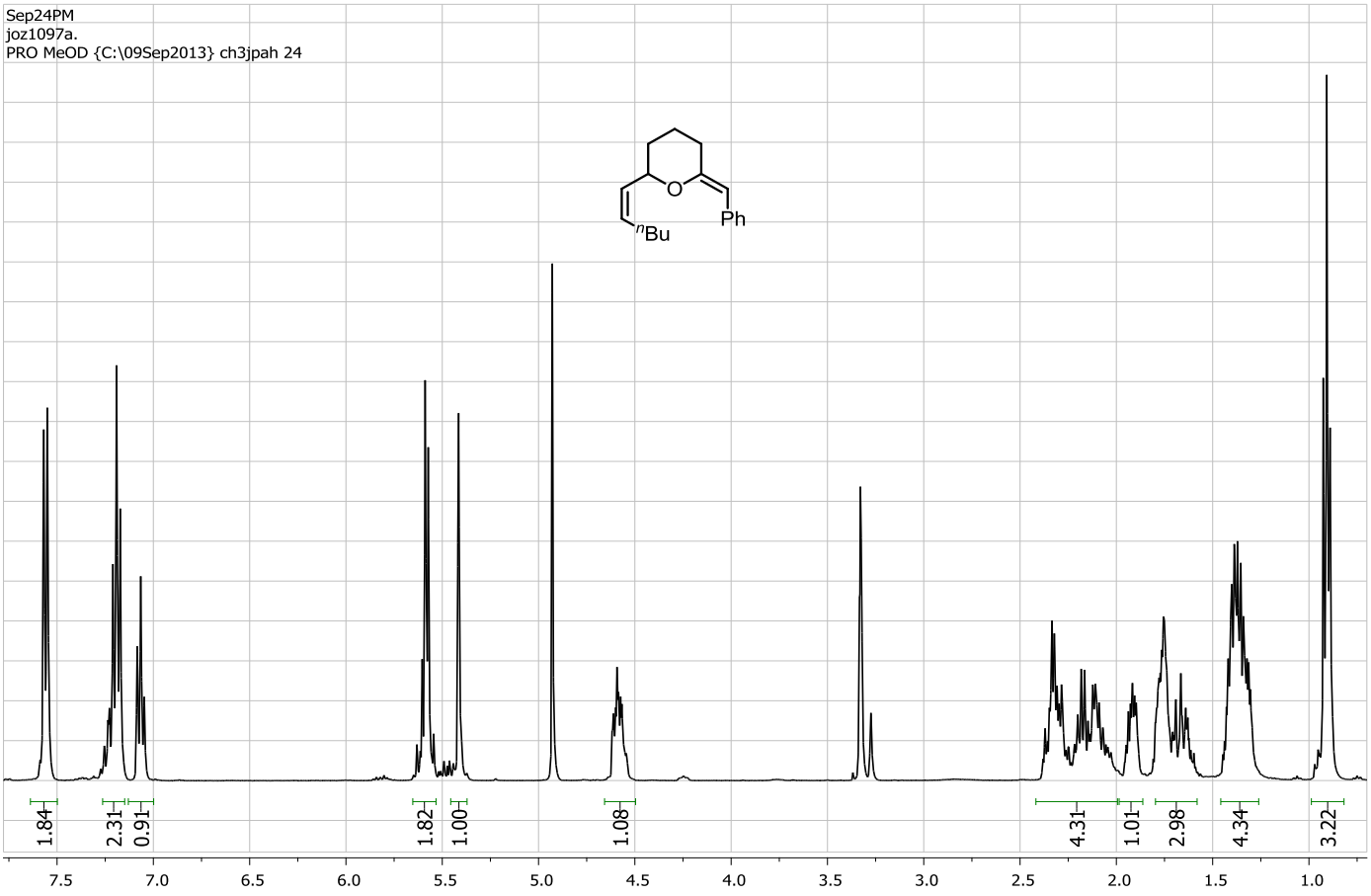

132.19
130.38
129.44
113.28
109.07
80.03
54.26
48.03
47.81
47.60
47.39
47.17
46.96
31.63
31.09
31.07
24.59
21.87
21.82
12.84
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

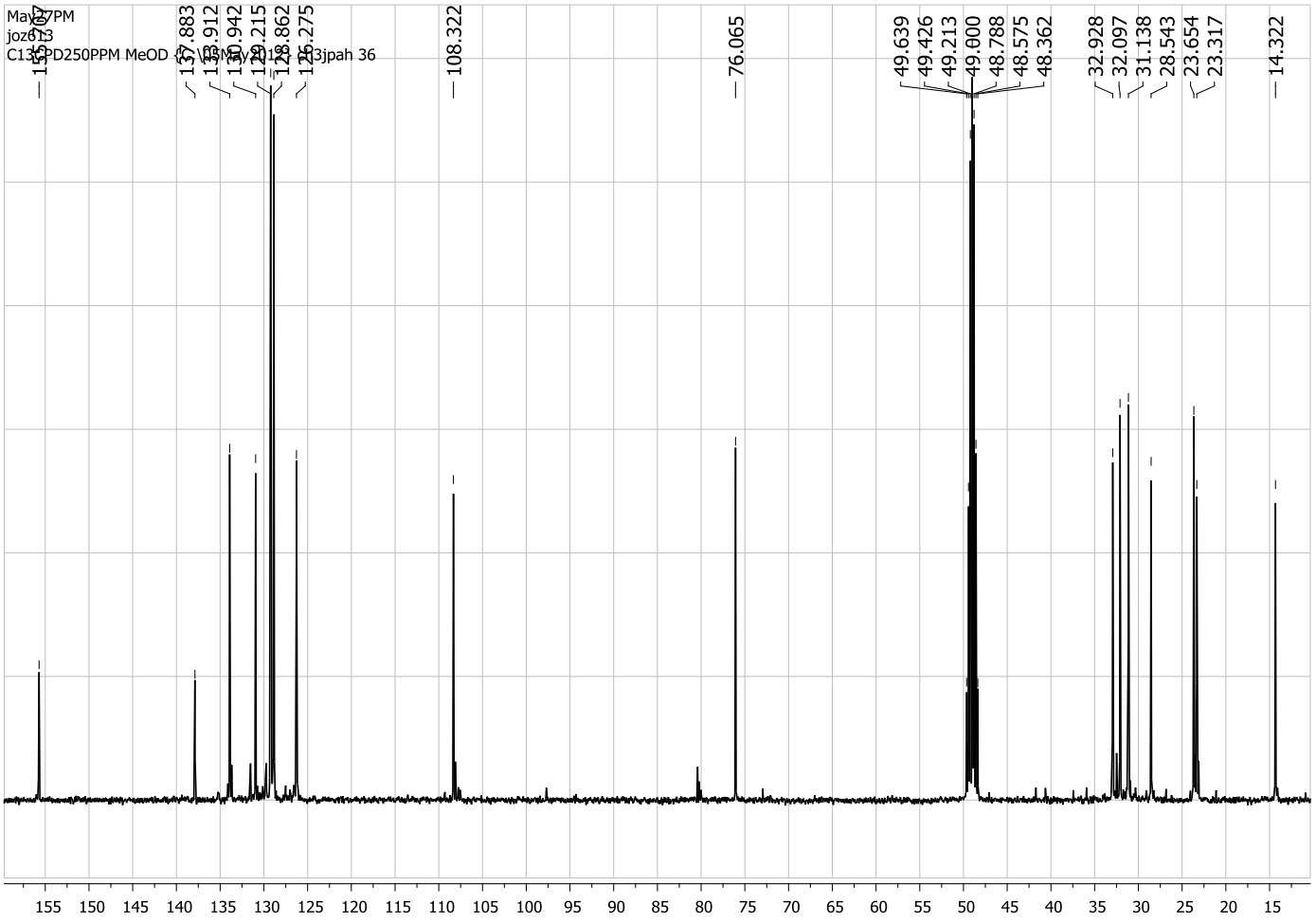

Dec11PM
joz416
PRO MeOD {C:\12de2011} ch3jpah 25
O
nBu
NO2
2.06
2.10
0.99
1.07
1.13
1.00
1.08
1.11
2.12
4.54
4.69
3.28
f1 (ppm)

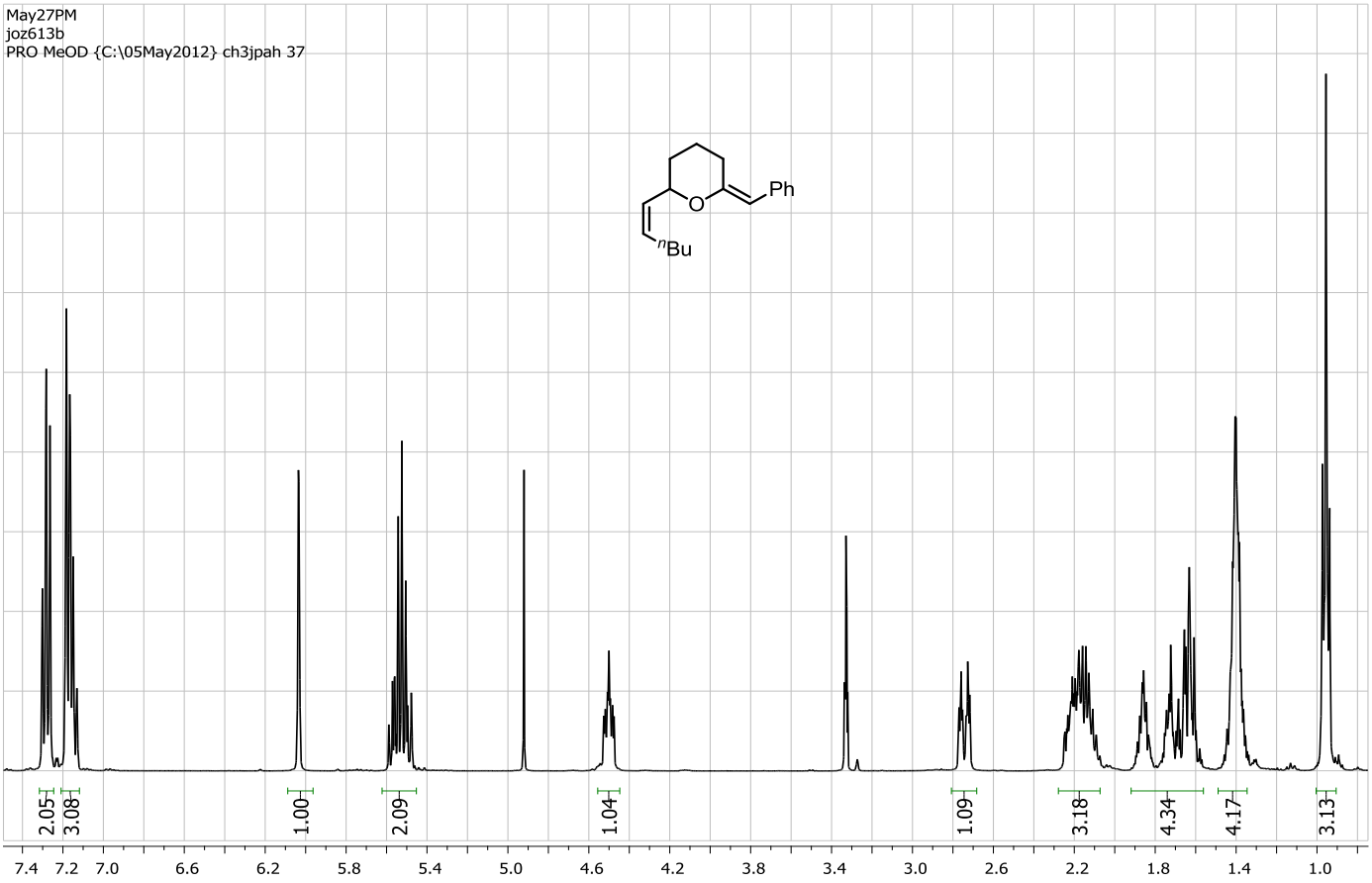

joz416
145.82
145.49
134.57
131.04
130.88
129.19
124.30
105.31
80.52
49.64
49.43
49.21
48.79
48.57
48.36
47.02
32.96
32.44
31.38
30.68
23.13
22.06
14.28

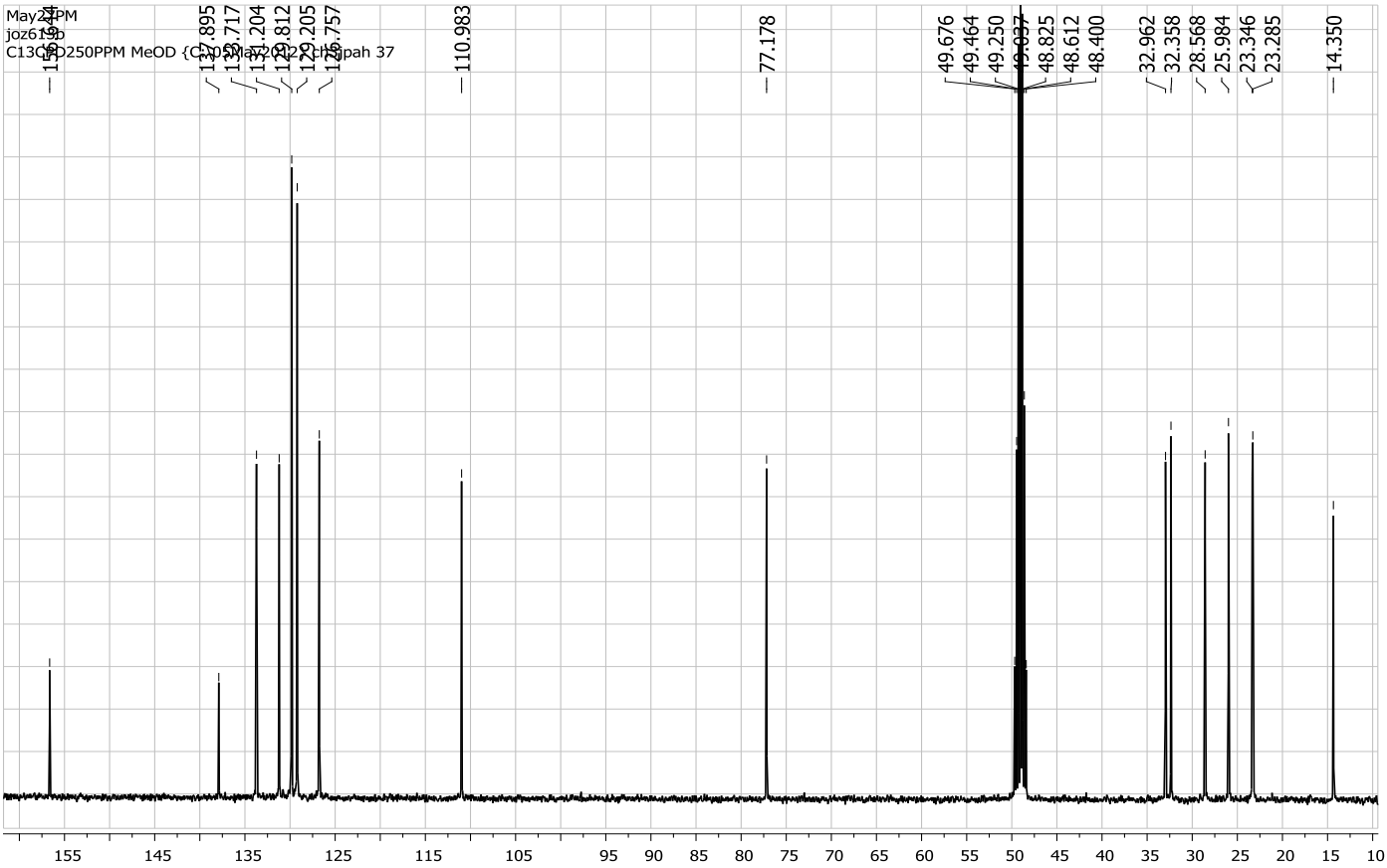

Dec11PM
joz416a
PRO MeOD {C:\12de2011} ch3jpah 26
NO2
O
nBu
2.08
2.02
0.97
0.93
1.00
0.93
1.02
1.10
2.04
2.25
2.12
4.33
3.20
f1 (ppm)

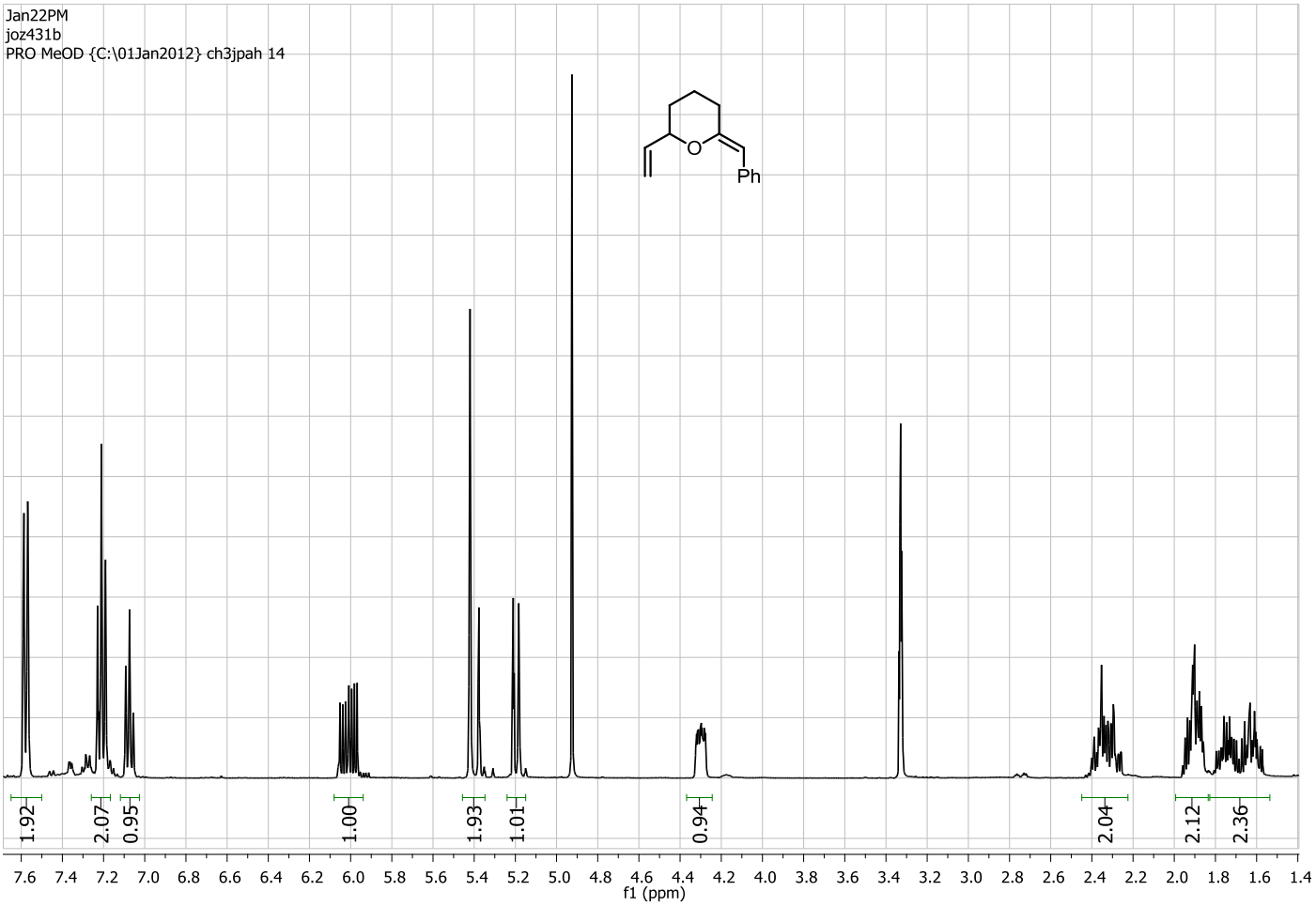

Dec11PM
joz416aa
CDCl3CPD250PPM MeOD {C:\12de2011} ch3jpah 27
146.52
135.83
123.95
131.38
130.07
124.48
108.68
81.04
49.64
49.43
49.21
49.00
48.79
48.57
48.36
47.03
33.02
32.47
31.77
26.12
23.23
22.61
22.20
14.26

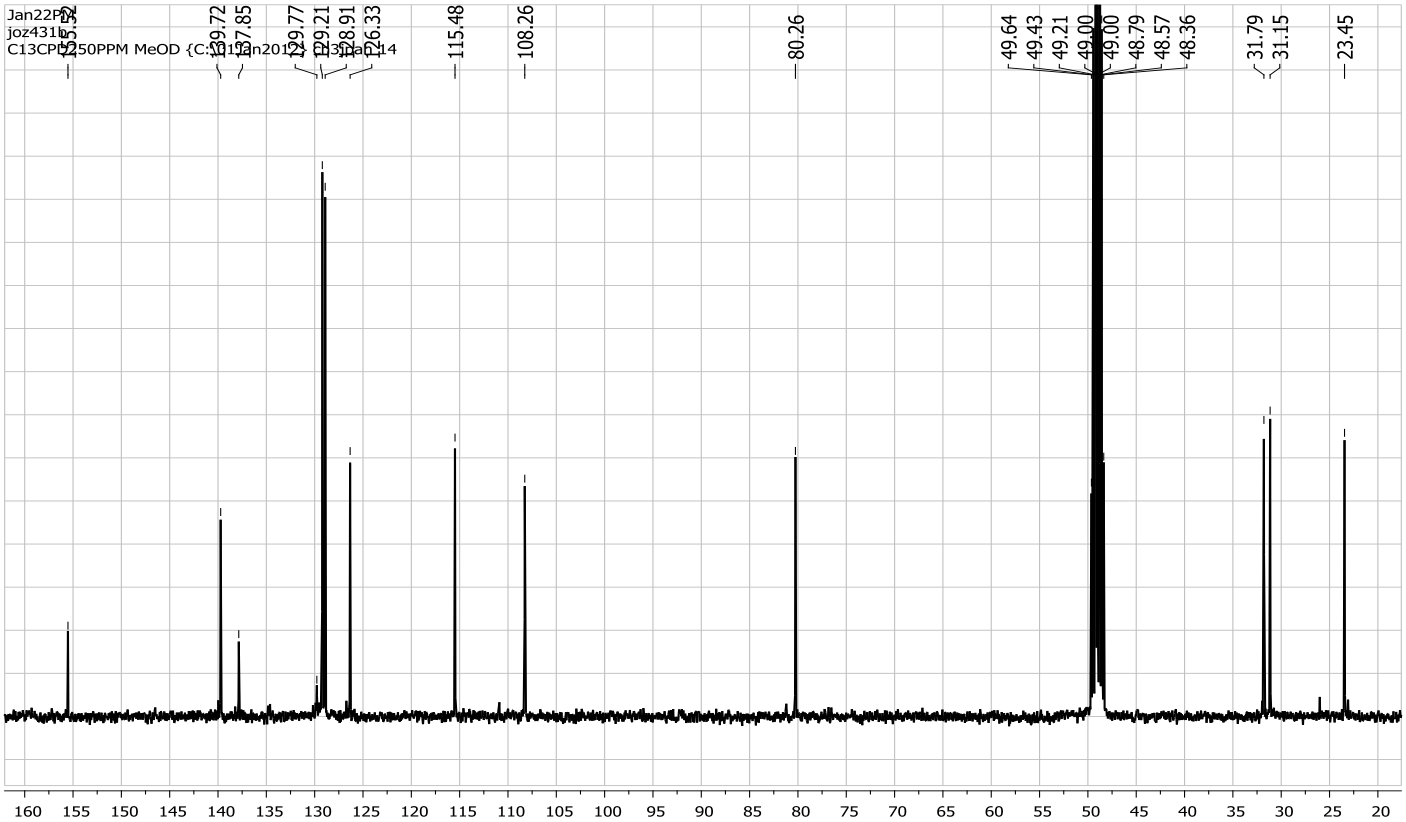

Sep24PM
joz1097a.
PRO MeOD {C:\09Sep2013} ch3jpah 24
O
Ph
nBu
1.84
2.31
0.91
1.82
1.00
1.08
4.31
1.01
2.98
4.34
3.22
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

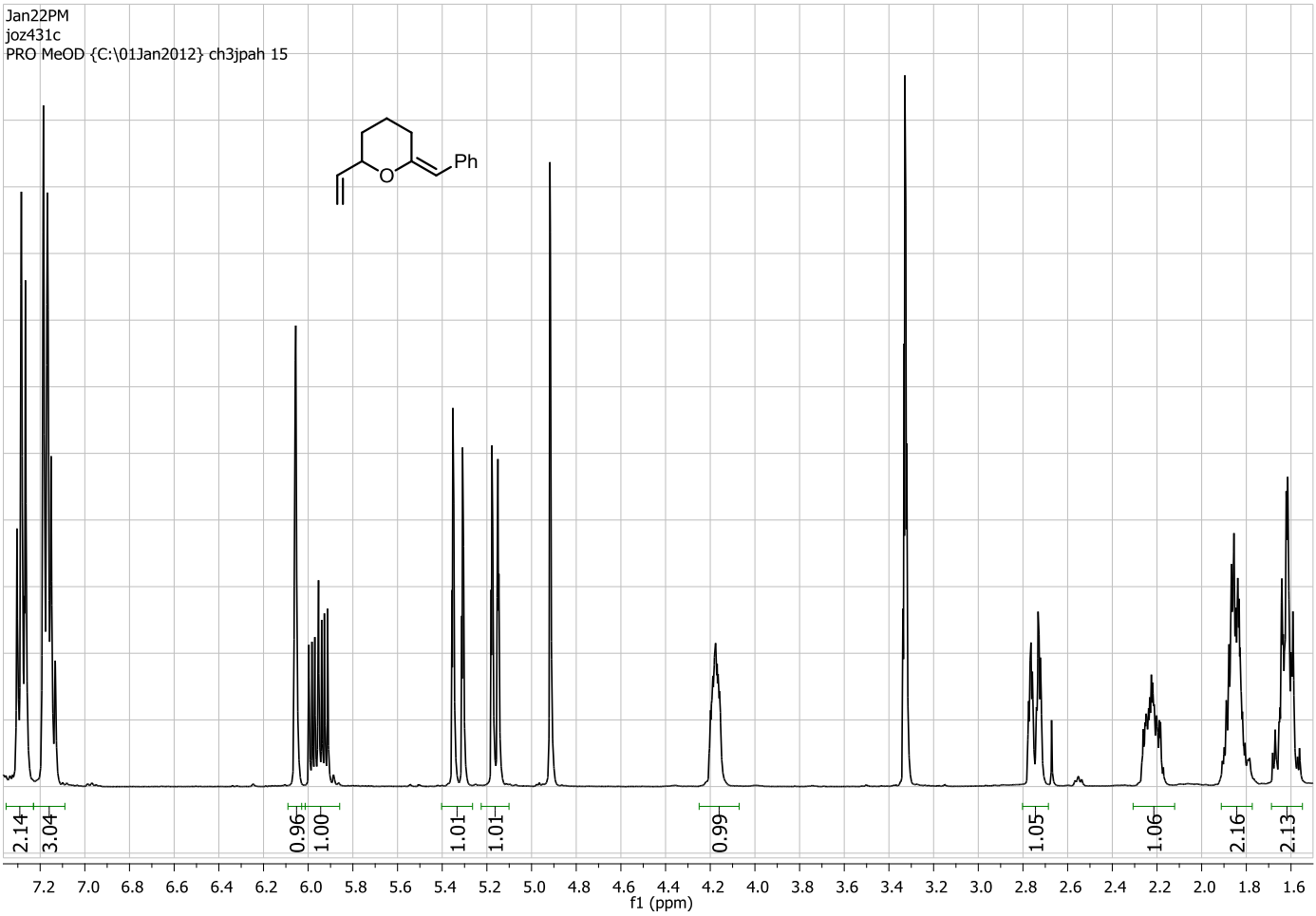

May27PM
joz613
137.883
135.912
135.942
129.215
128.862
126.275
108.322
76.065
49.639
49.426
49.213
49.000
48.788
48.575
48.362
32.928
32.097
31.138
28.543
23.654
23.317
14.322
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15

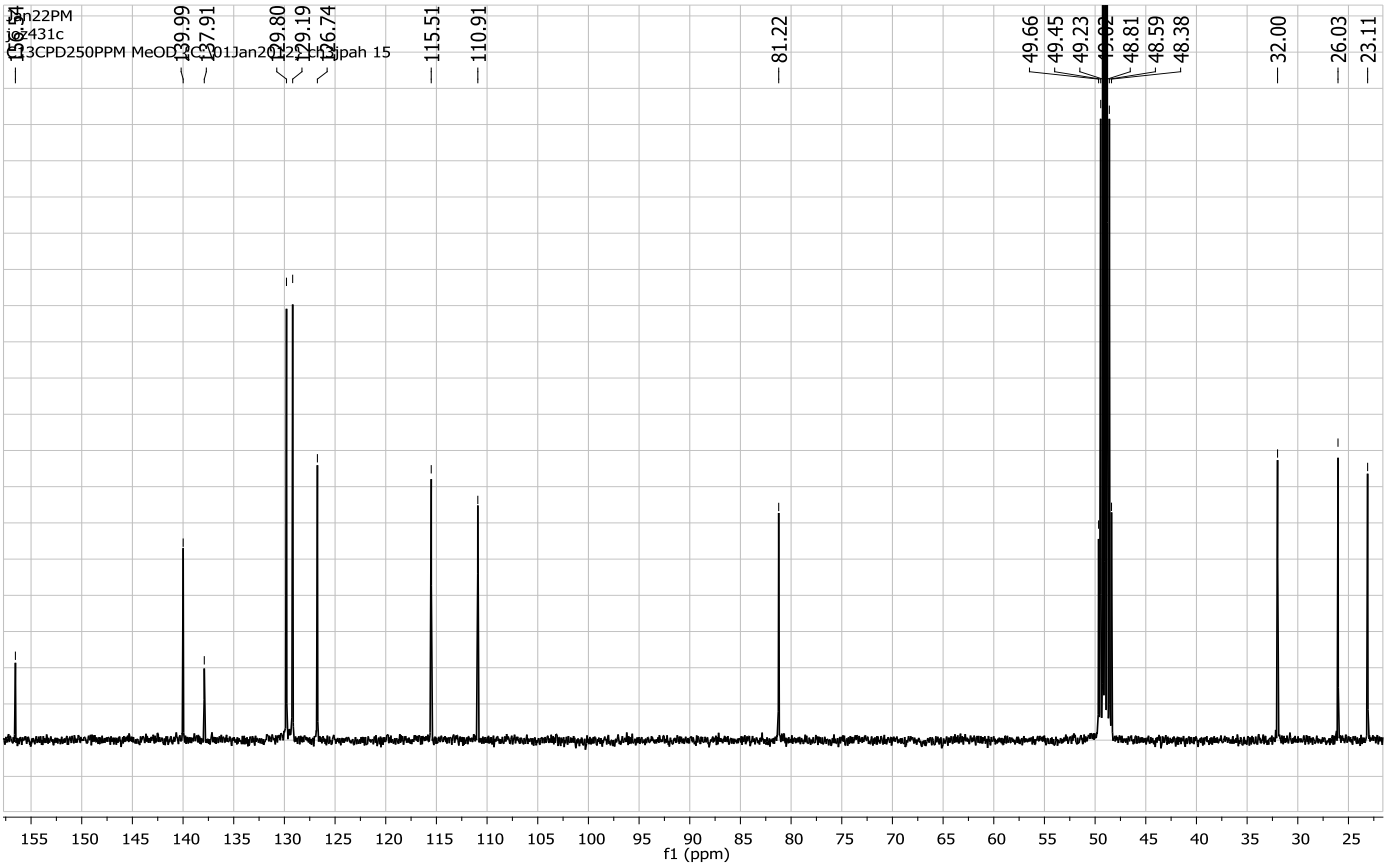

May27PM
joz613b
PRO MeOD {C:\05May2012} ch3jpah 37
Ph
O
nBu
2.05
3.08
1.00
2.09
1.04
1.09
3.18
4.34
4.17
3.13
7.4
7.2
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0

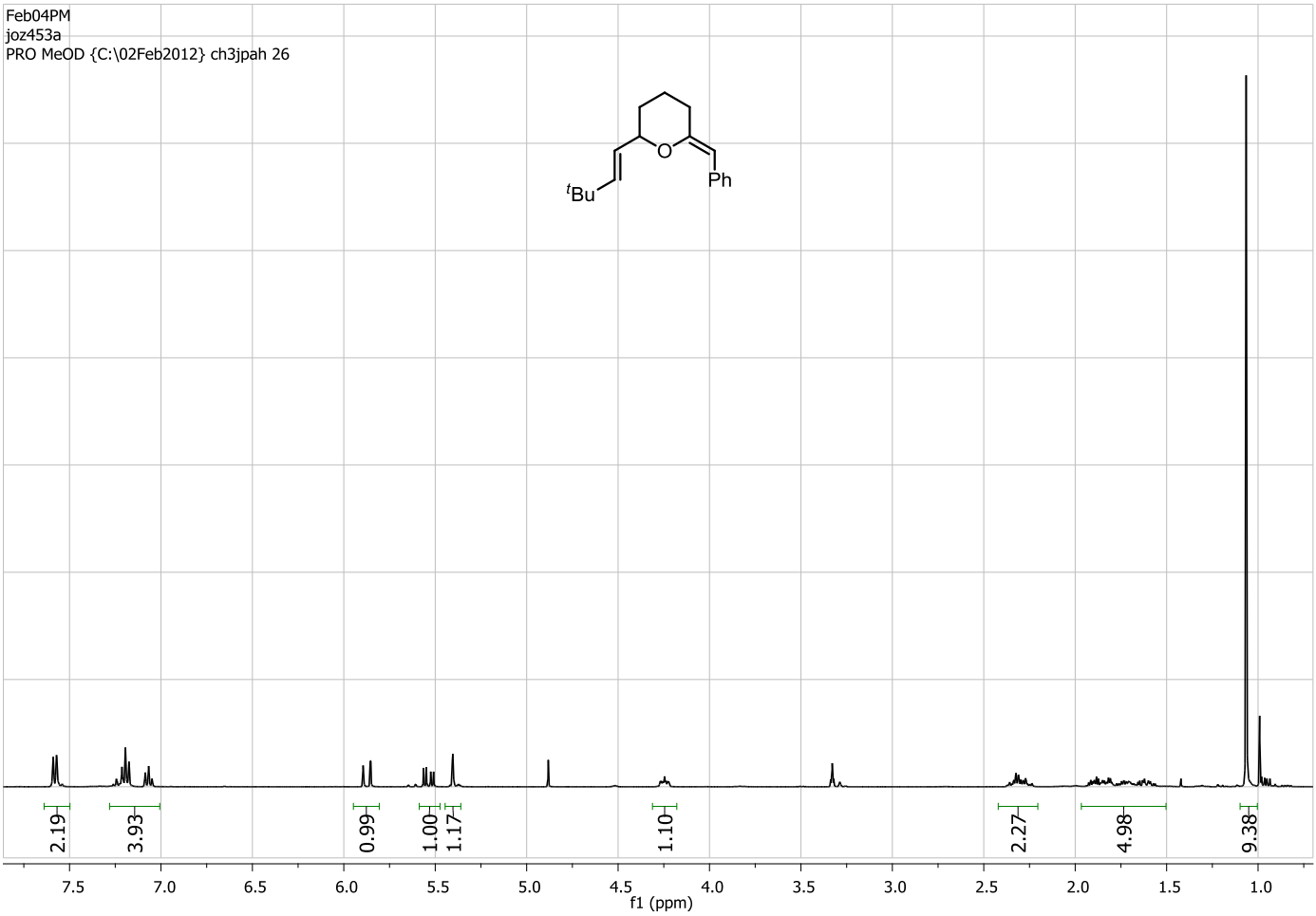

May24PM
joz613b
C13CPD250PPM MeOD {C:\05May2012} ch3jpah 37
139.895
139.717
131.204
129.812
129.205
126.757
110.983
77.178
49.676
49.464
49.250
49.037
48.825
48.612
48.400
32.962
32.358
28.568
25.984
23.346
23.285
14.350
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10

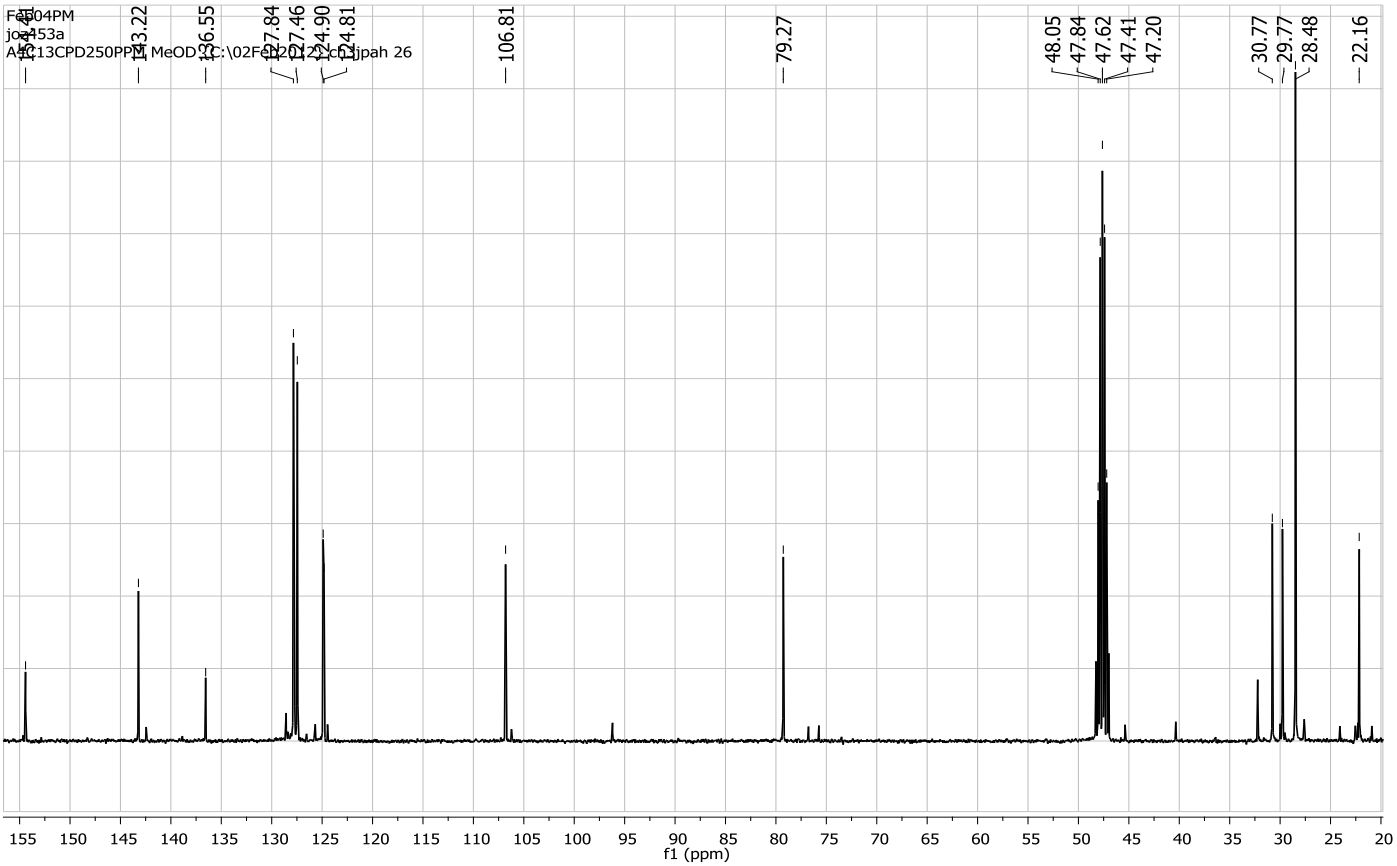

Jan22PM
joz431b
PRO MeOD {C:\01Jan2012} ch3jpah 14
O
Ph
1.92
2.07
0.95
1.00
1.93
1.01
0.94
2.04
2.12
2.36
f1 (ppm)

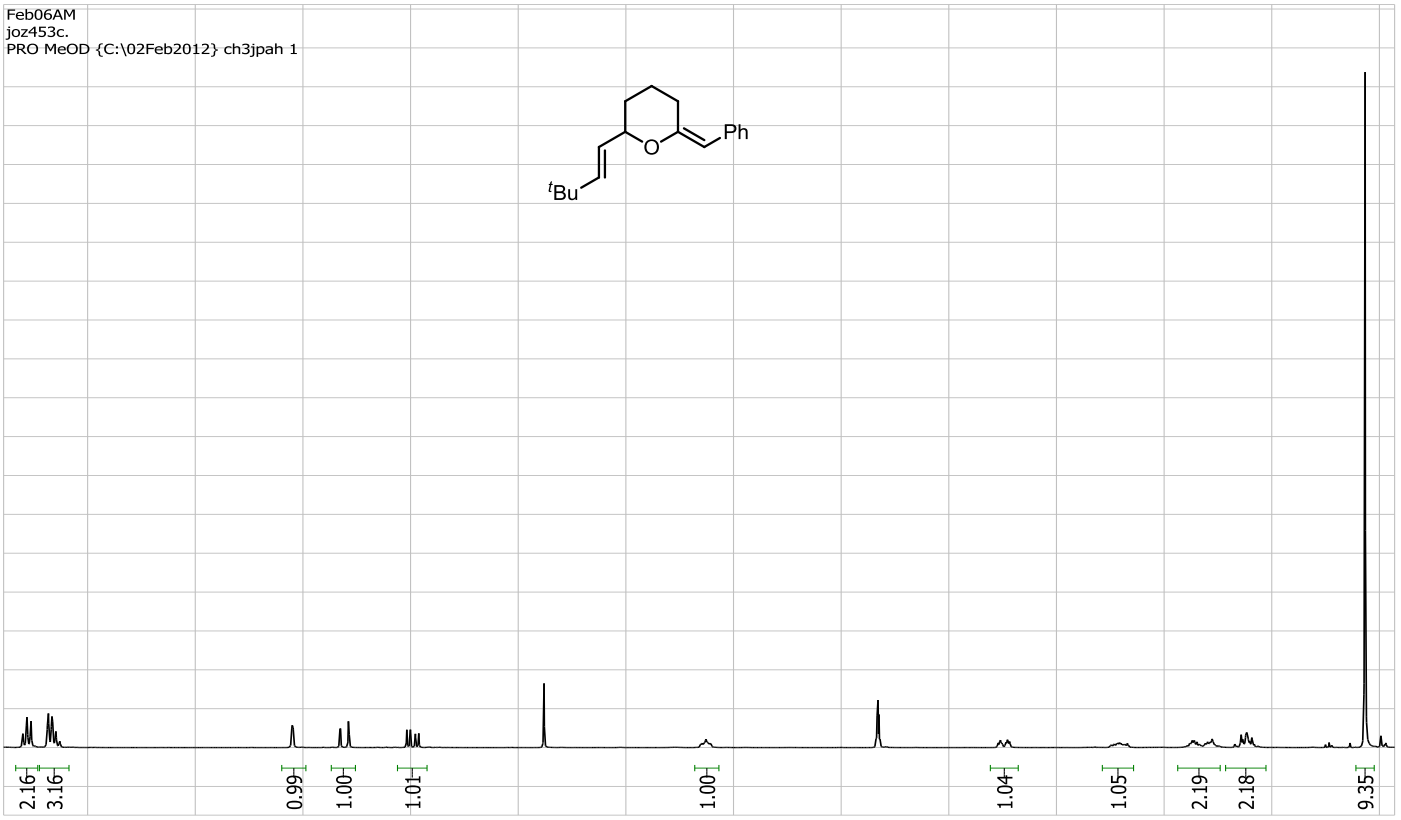

Jan22PM
joz431b
C13CPD 250PPM MeOD {C:\01Jan2012} ch3jpah 14
139.72
137.85
129.77
129.21
128.91
126.33
115.48
108.26
80.26
49.64
49.43
49.21
49.00
49.00
48.79
48.57
48.36
31.79
31.15
23.45

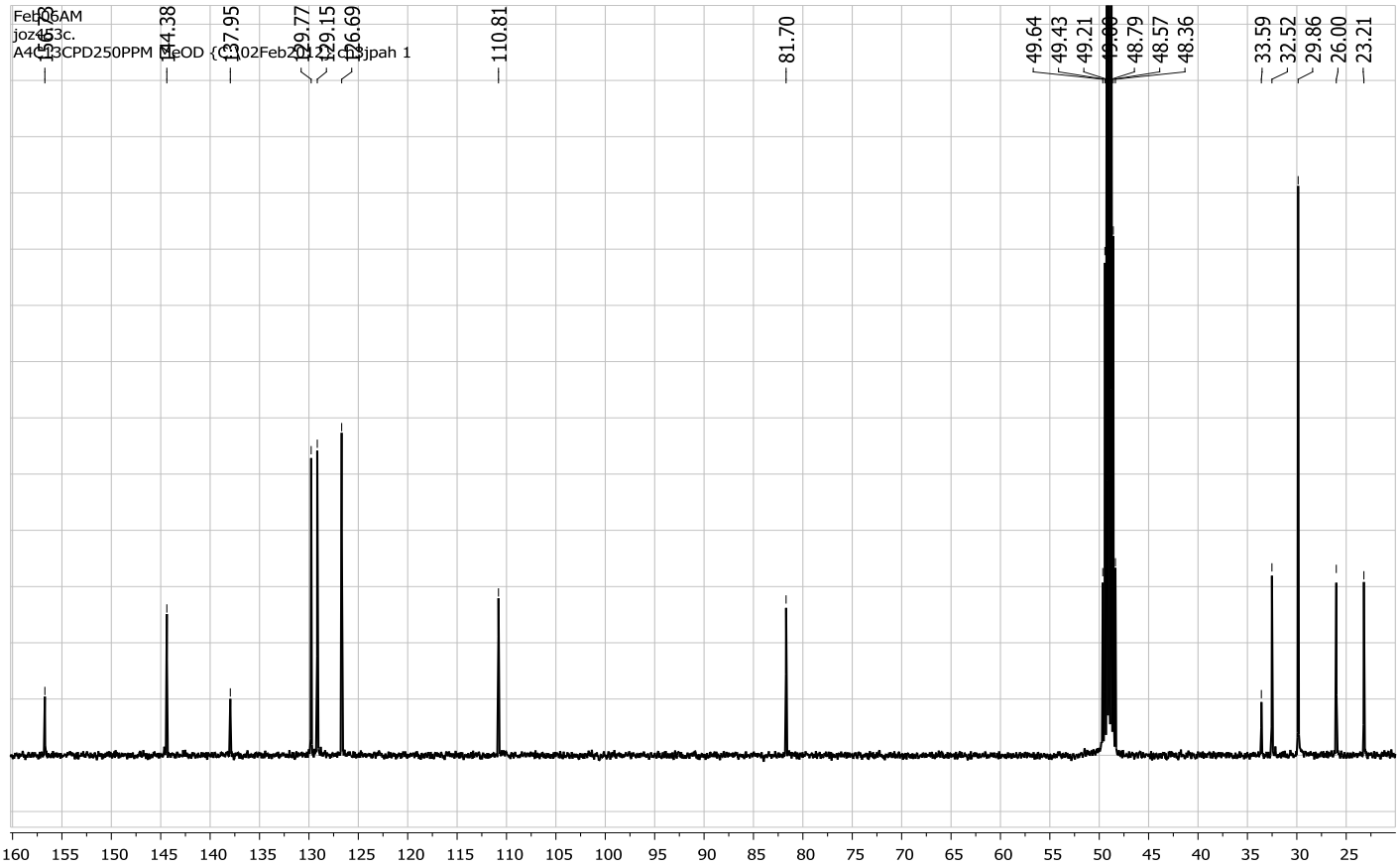

Jan22PM
joz431c
PRO MeOD {C:\01Jan2012} ch3jpah 15
Ph
O
2.14
3.04
0.96
1.00
1.01
1.01
0.99
1.05
1.06
2.16
2.13
f1 (ppm)

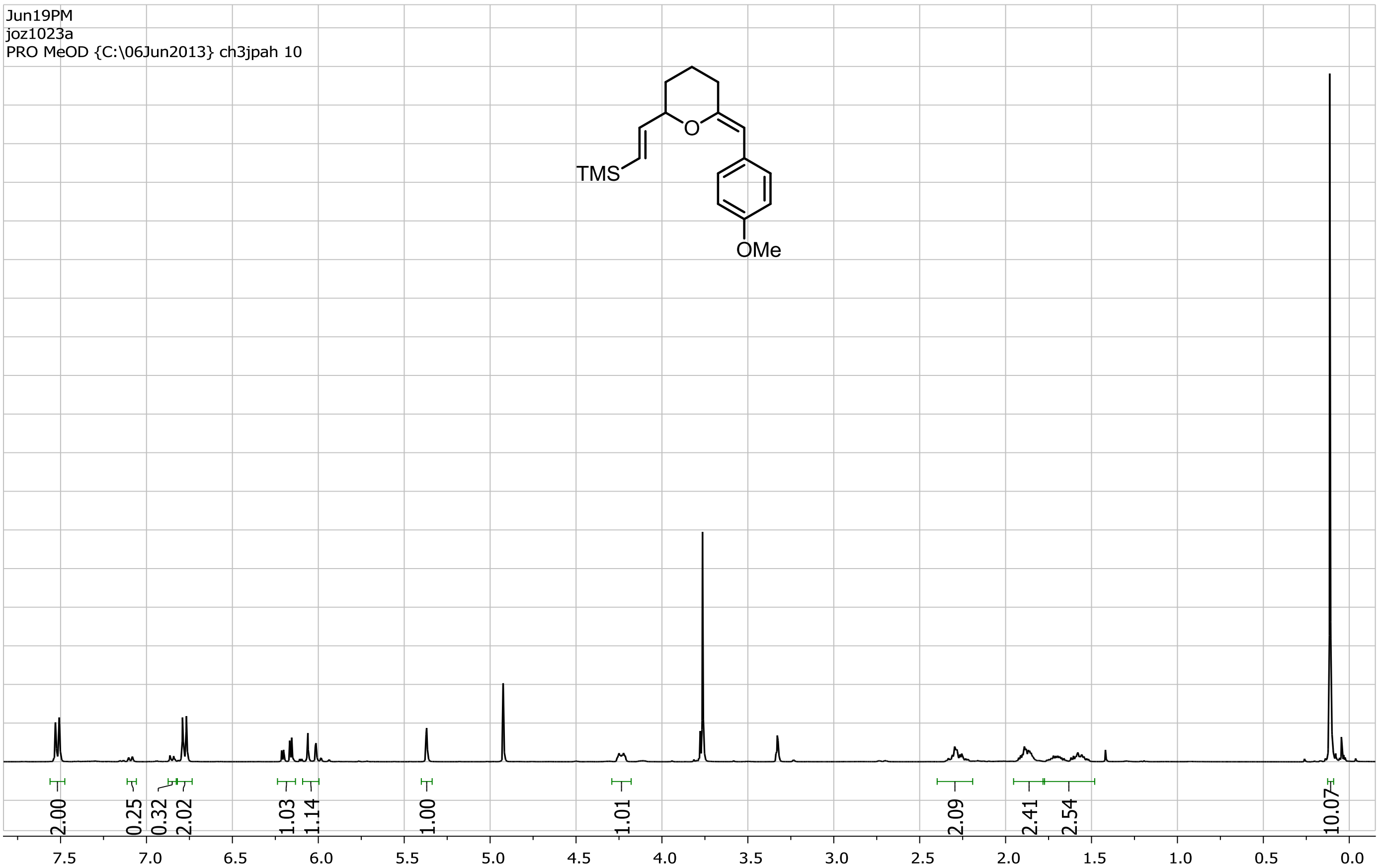

Jan22PM
joz431c
13CPD250PPM MeOD {C:\01Jan2012} ch3jpah 15
139.99
127.91
129.80
129.19
126.74
115.51
110.91
81.22
49.66
49.45
49.23
48.81
48.59
48.38
32.00
26.03
23.11
f1 (ppm)

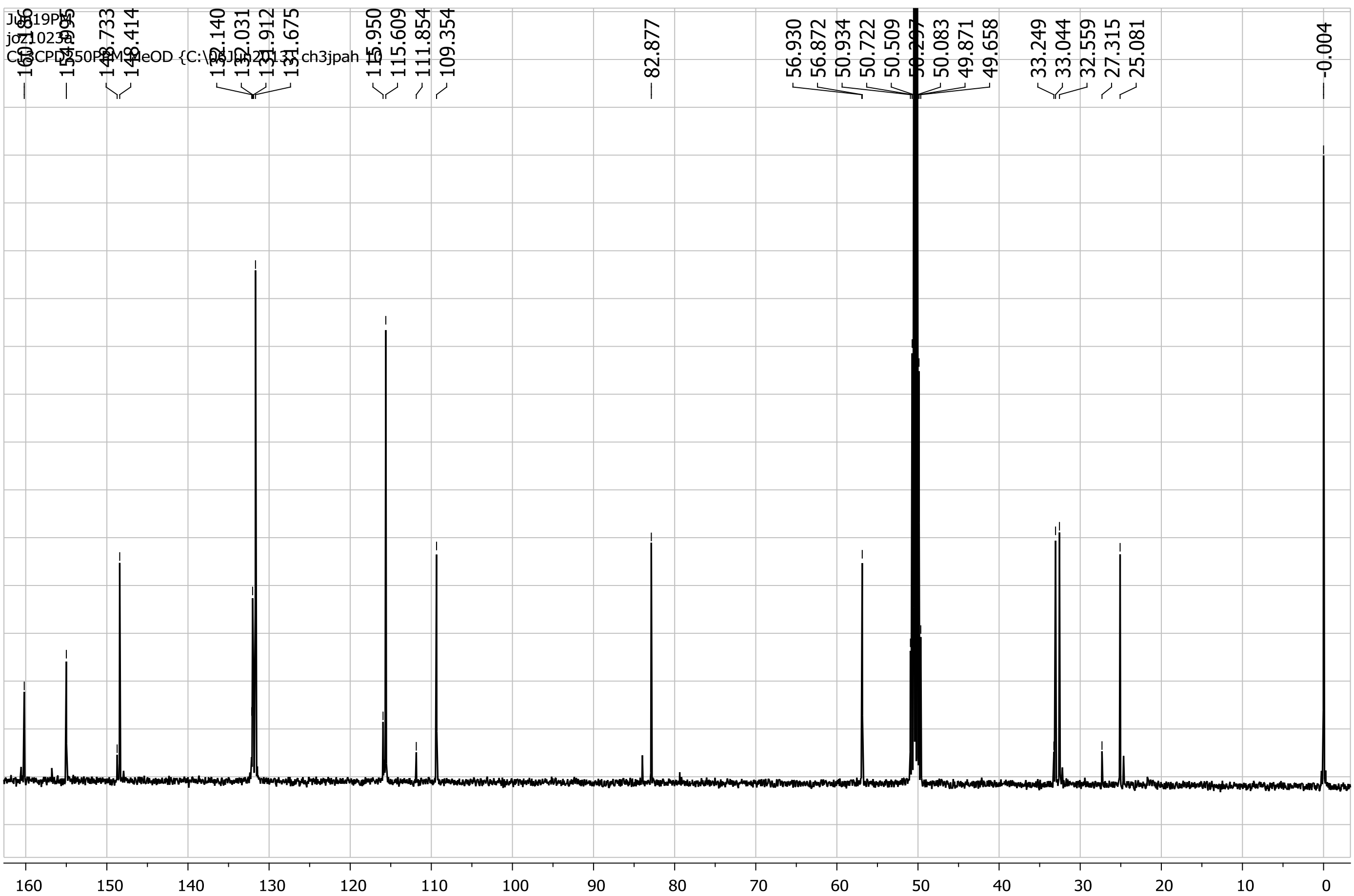

Feb04PM
joz453a
PRO MeOD {C:\02Feb2012} ch3jpah 26
O
tBu
Ph
2.19
3.93
0.99
1.00
1.17
1.10
2.27
4.98
9.38
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

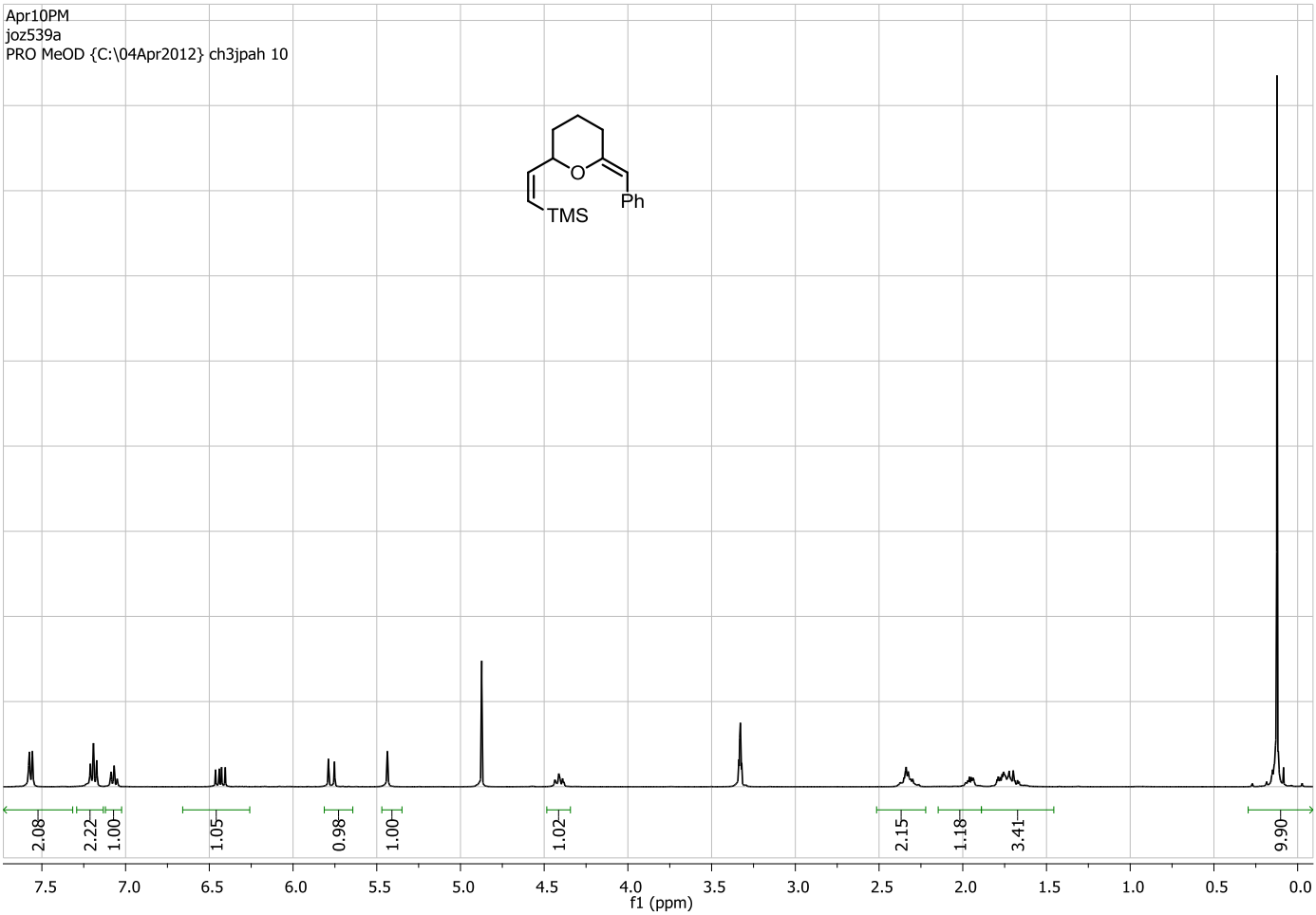

Feb04PM
joz453a
106.81
79.27
48.05
47.84
47.62
47.41
47.20
30.77
29.77
28.48
22.16
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

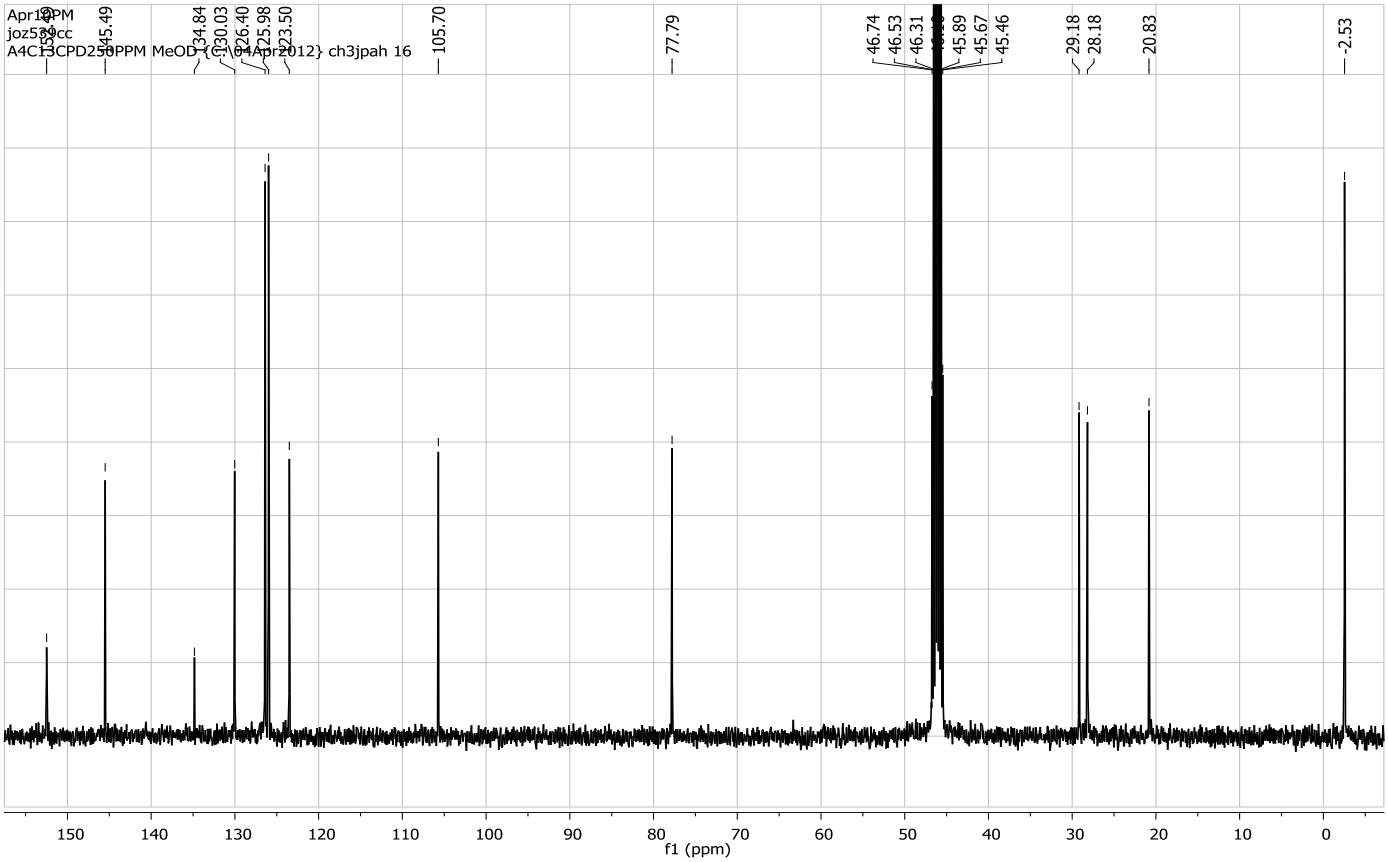

Feb06AM
joz453c.
PRO MeOD {C:\02Feb2012} ch3jpah 1
Ph
O
tBu
2.16
3.16
0.99
1.00
1.01
1.00
1.04
1.05
2.19
2.18
9.35

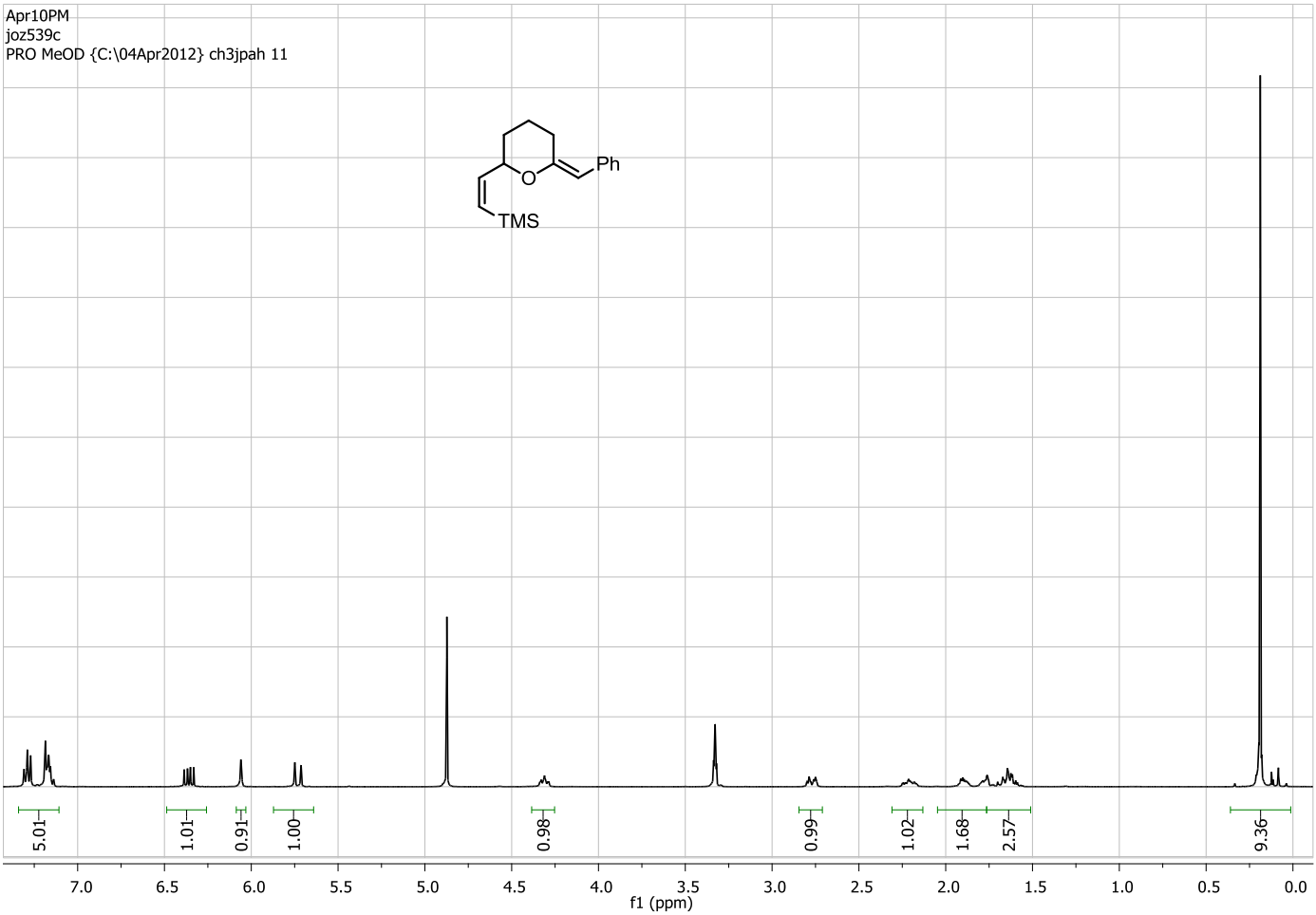

Feb06AM
joz453c.
144.38
137.95
129.77
129.15
126.69
110.81
81.70
49.64
49.43
49.21
48.79
48.57
48.36
33.59
32.52
29.86
26.00
23.21
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25

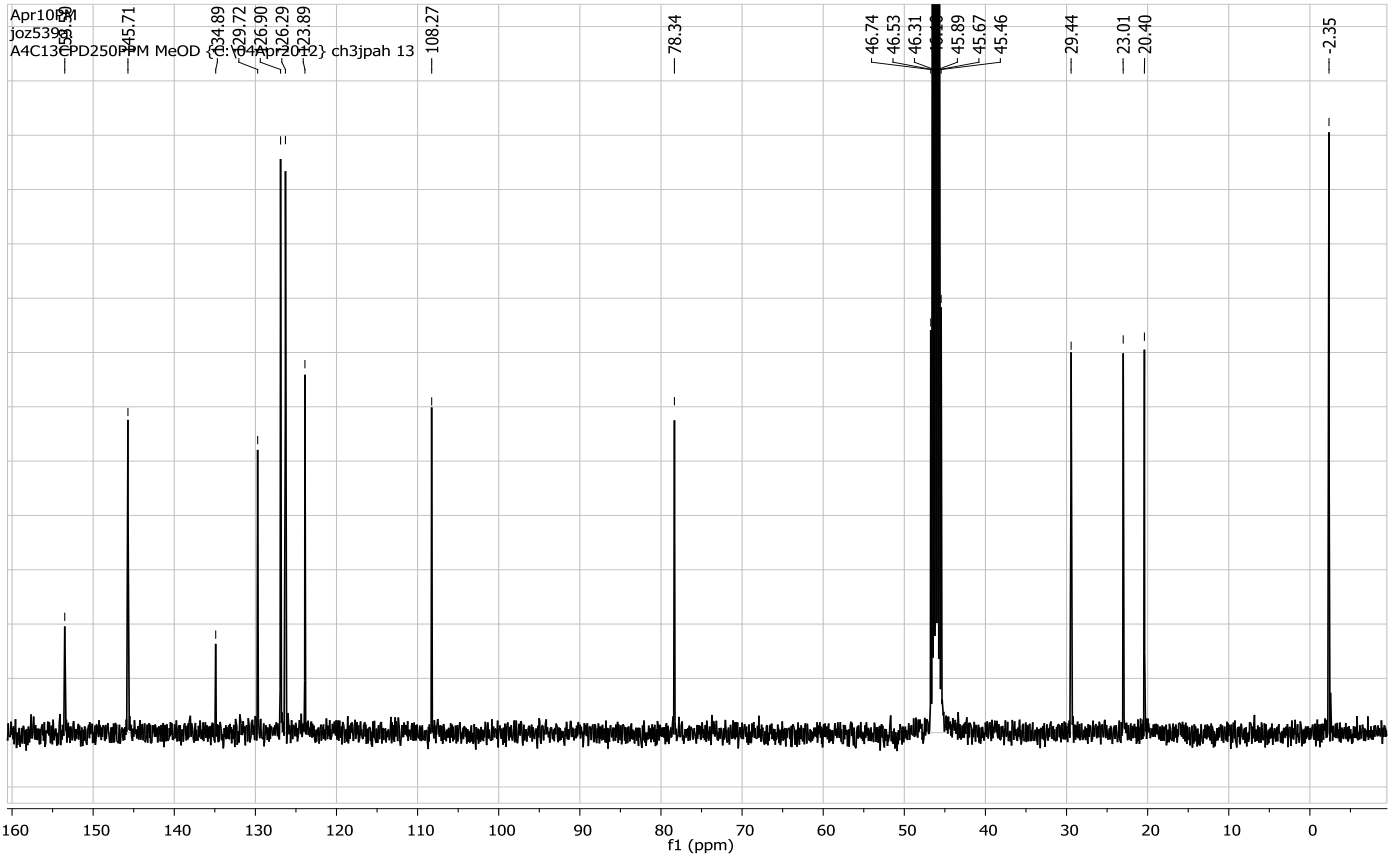

Jun19PM
joz1023a
PRO MeOD {C:\06Jun2013} ch3jpah 10
TMS
O
OMe
2.00
0.25
0.32
2.02
1.03
1.14
1.00
1.01
2.09
2.41
2.54
10.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

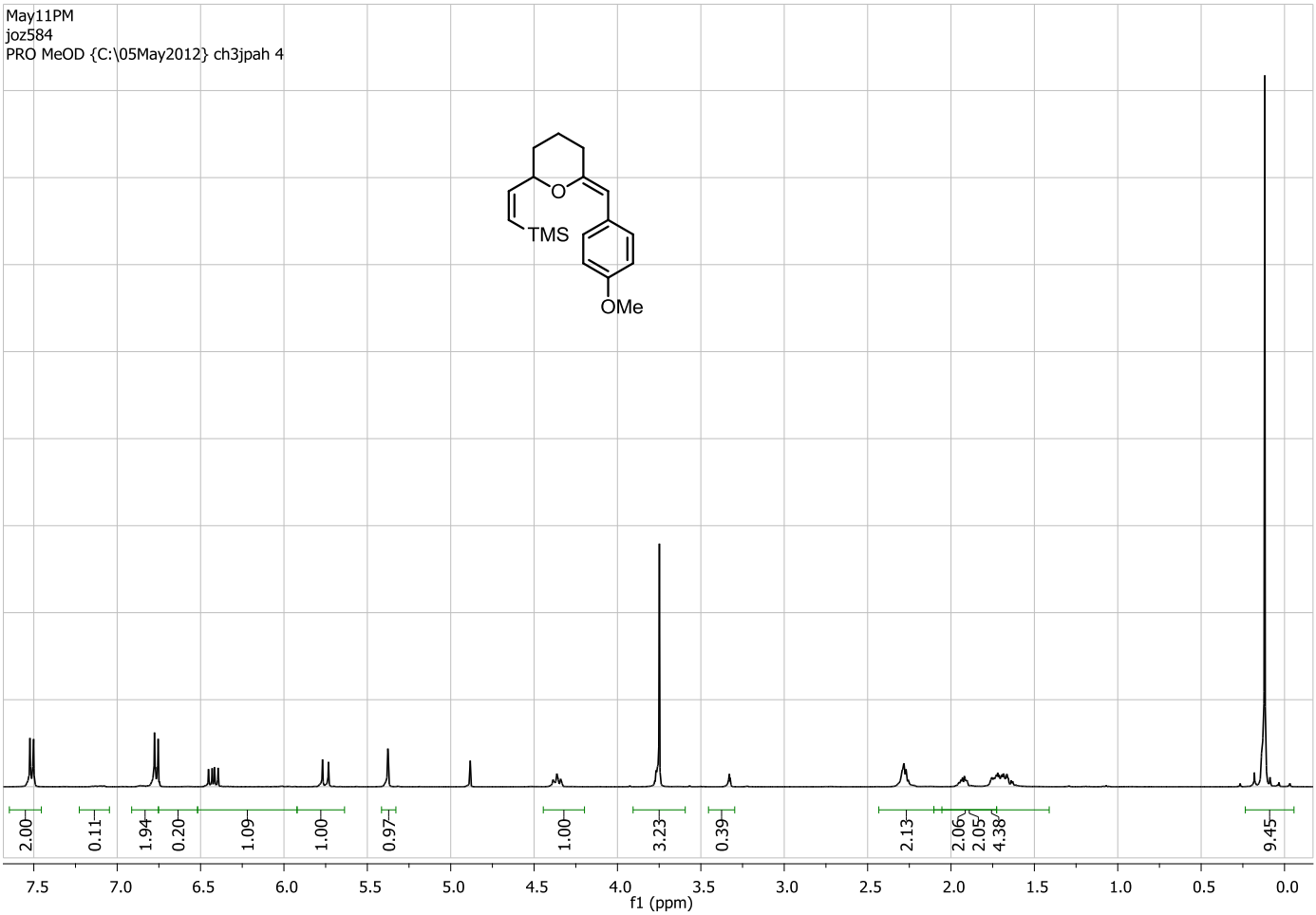

Jun19PM
joz1023a
C13CPD250PPM MeOD {C:\06Jun2013} ch3jpah 10
148.733
148.414
132.140
132.031
131.912
131.675
115.950
115.609
111.854
109.354
82.877
56.930
56.872
50.934
50.722
50.509
50.083
49.871
49.658
33.249
33.044
32.559
27.315
25.081
-0.004
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

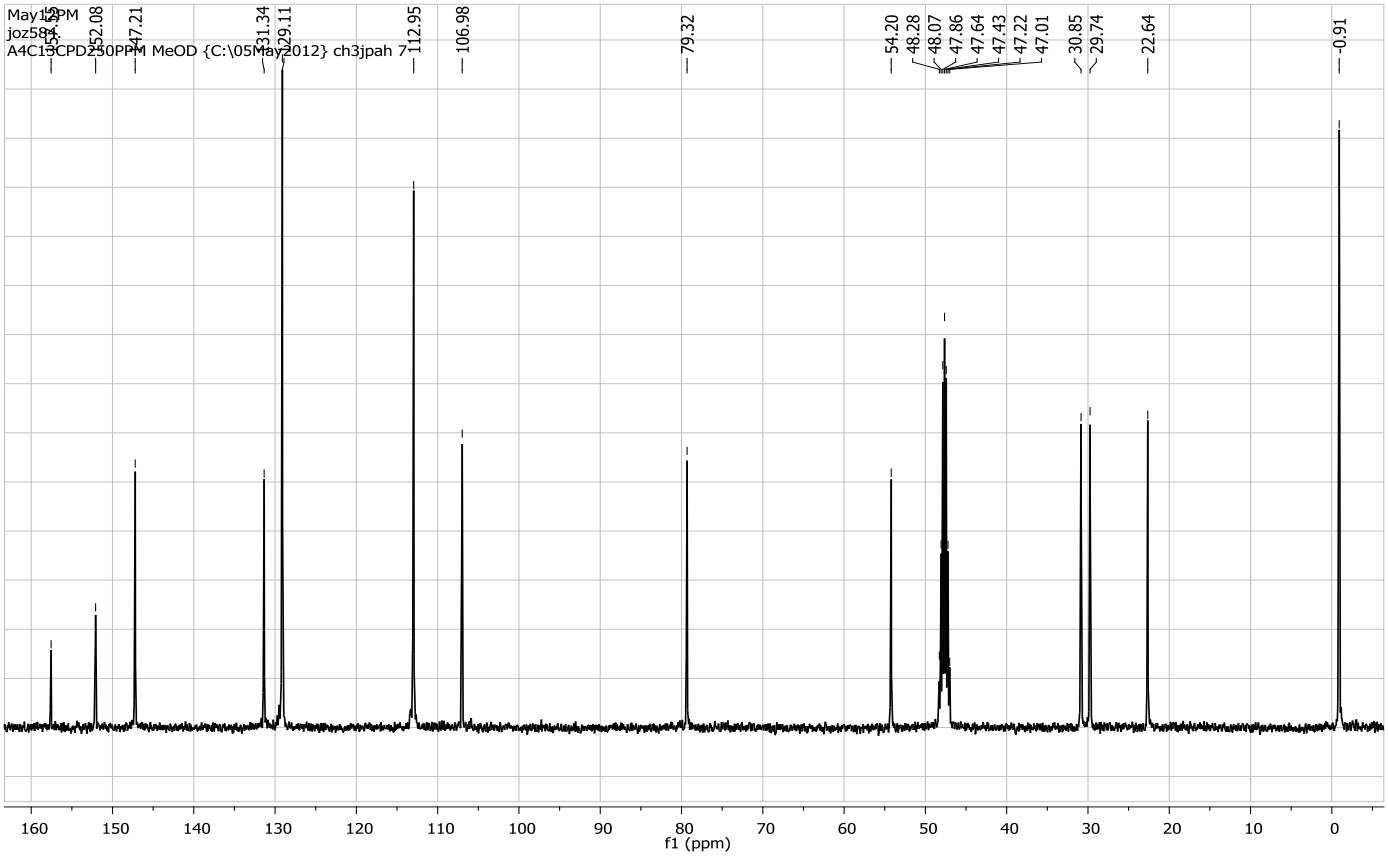

Apr10PM
joz539a
PRO MeOD {C:\04Apr2012} ch3jpah 10
O
TMS
Ph
2.08
2.22
1.00
1.05
0.98
1.00
1.02
2.15
1.18
3.41
9.90
f1 (ppm)

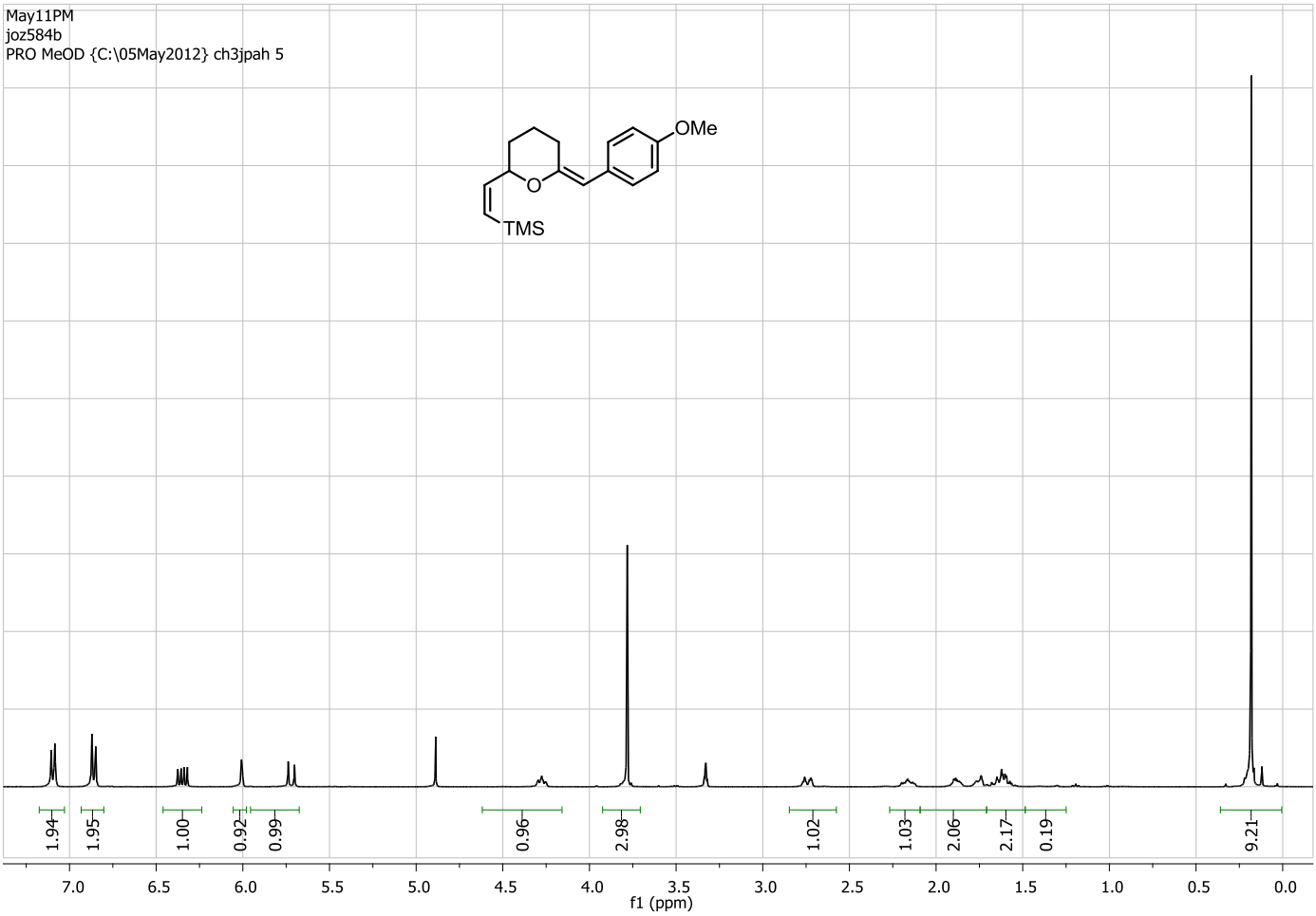

joz539cc
A4C13CPD250PPM MeOD {C:\04Apr2012} ch3jpah 16
145.49
134.84
130.03
126.40
125.98
123.50
105.70
77.79
46.74
46.53
46.31
45.89
45.67
45.46
29.18
28.18
20.83
-2.53
f1 (ppm)

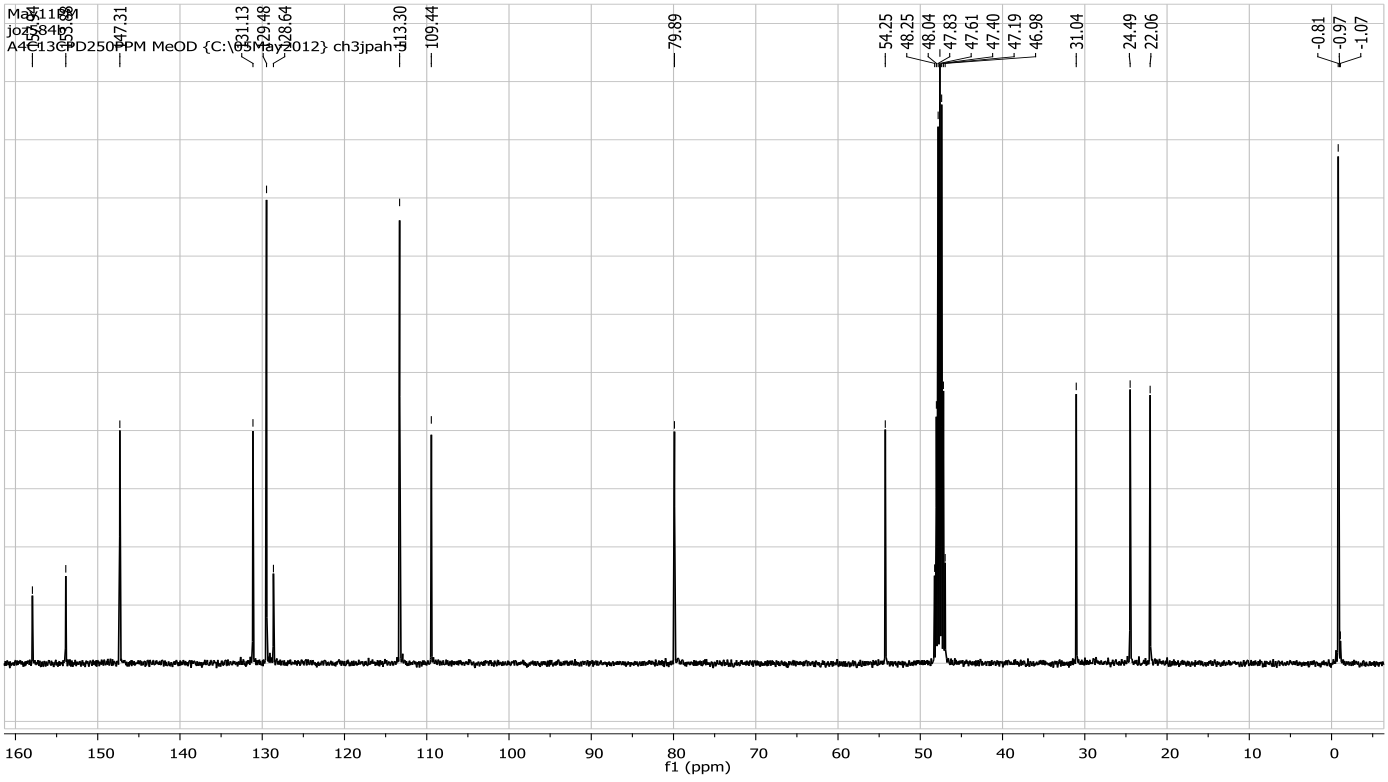

Apr10PM
joz539c
PRO MeOD {C:\04Apr2012} ch3jpah 11
Ph
O
TMS
5.01
1.01
0.91
1.00
0.98
0.99
1.02
1.68
2.57
9.36
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Apr10PM
joz539c
A4C13CPD250PPM MeOD {C:\04Apr2012} ch3jpah 13
145.71
134.89
129.72
126.90
126.29
123.89
108.27
78.34
46.74
46.53
46.31
45.89
45.67
45.46
29.44
23.01
20.40
-2.35
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


May11PM
joz584
PRO MeOD {C:\05May2012} ch3jpah 4
O
TMS
OMe
2.00
0.11
1.94
0.20
1.09
1.00
0.97
1.00
3.23
0.39
2.13
2.06
2.05
4.38
9.45
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
0.0
f1 (ppm)


May12PM
joz584
A4C13CPD250PPM MeOD {C:\05May2012} ch3jpah 7
152.08
147.21
131.34
129.11
112.95
106.98
79.32
54.20
48.28
48.07
47.86
47.64
47.43
47.22
47.01
30.85
29.74
22.64
-0.91
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


May11PM
joz584b
PRO MeOD {C:\05May2012} ch3jpah 5
OMe
O
TMS
1.94
1.95
1.00
0.92
0.99
0.96
2.98
1.02
1.03
2.06
2.17
0.19
9.21
f1 (ppm)


joz584b
A4EC13GPD250PPM MeOD {C:\05May2012} ch3jpah 1
147.31
131.13
129.48
128.64
113.30
109.44
79.89
54.25
48.25
48.04
47.83
47.61
47.40
47.19
46.98
31.04
24.49
22.06
-0.81
-0.97
-1.07
f1 (ppm)

Electronic Supplementary Material (ESI) for Chemical Communications
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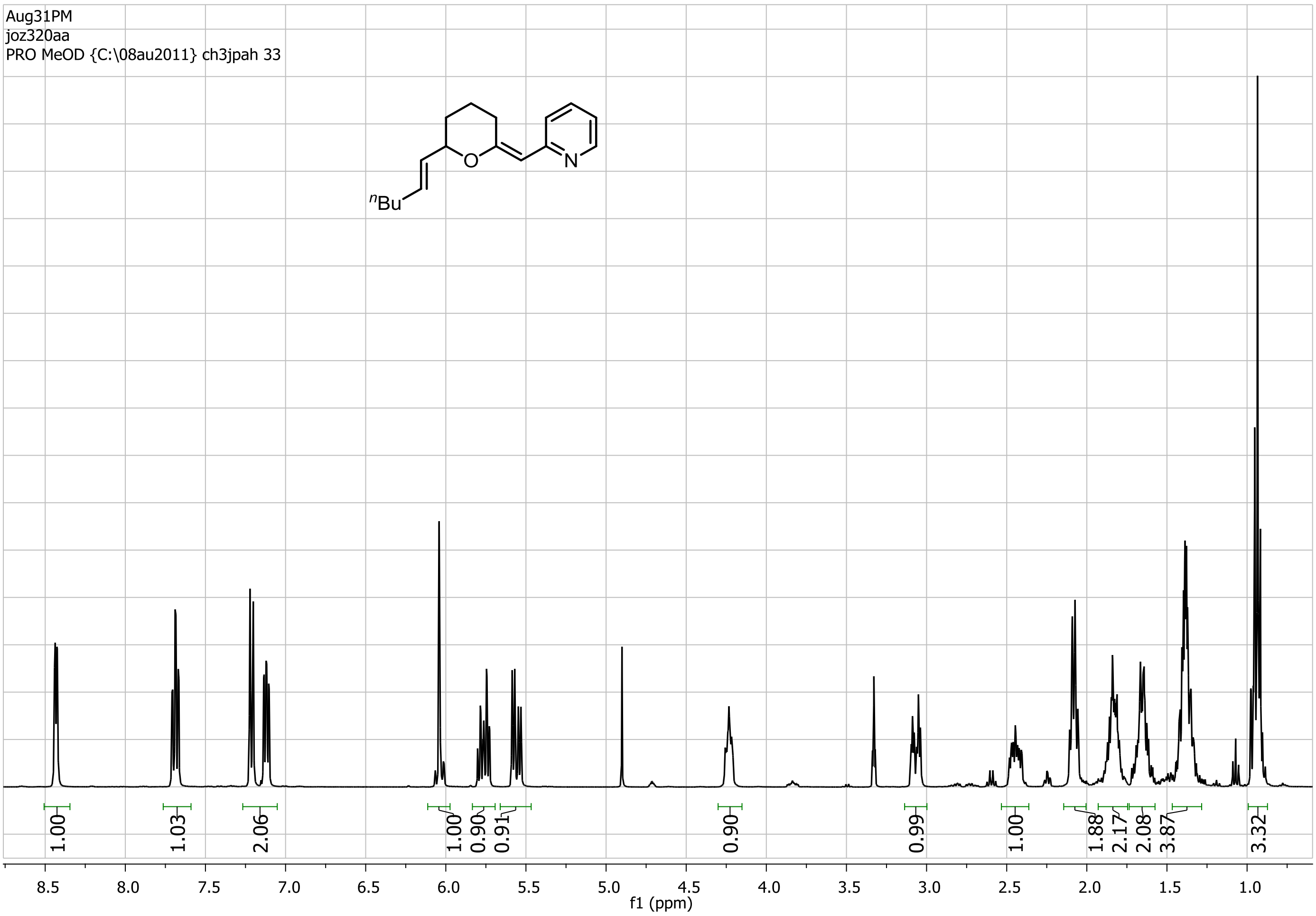
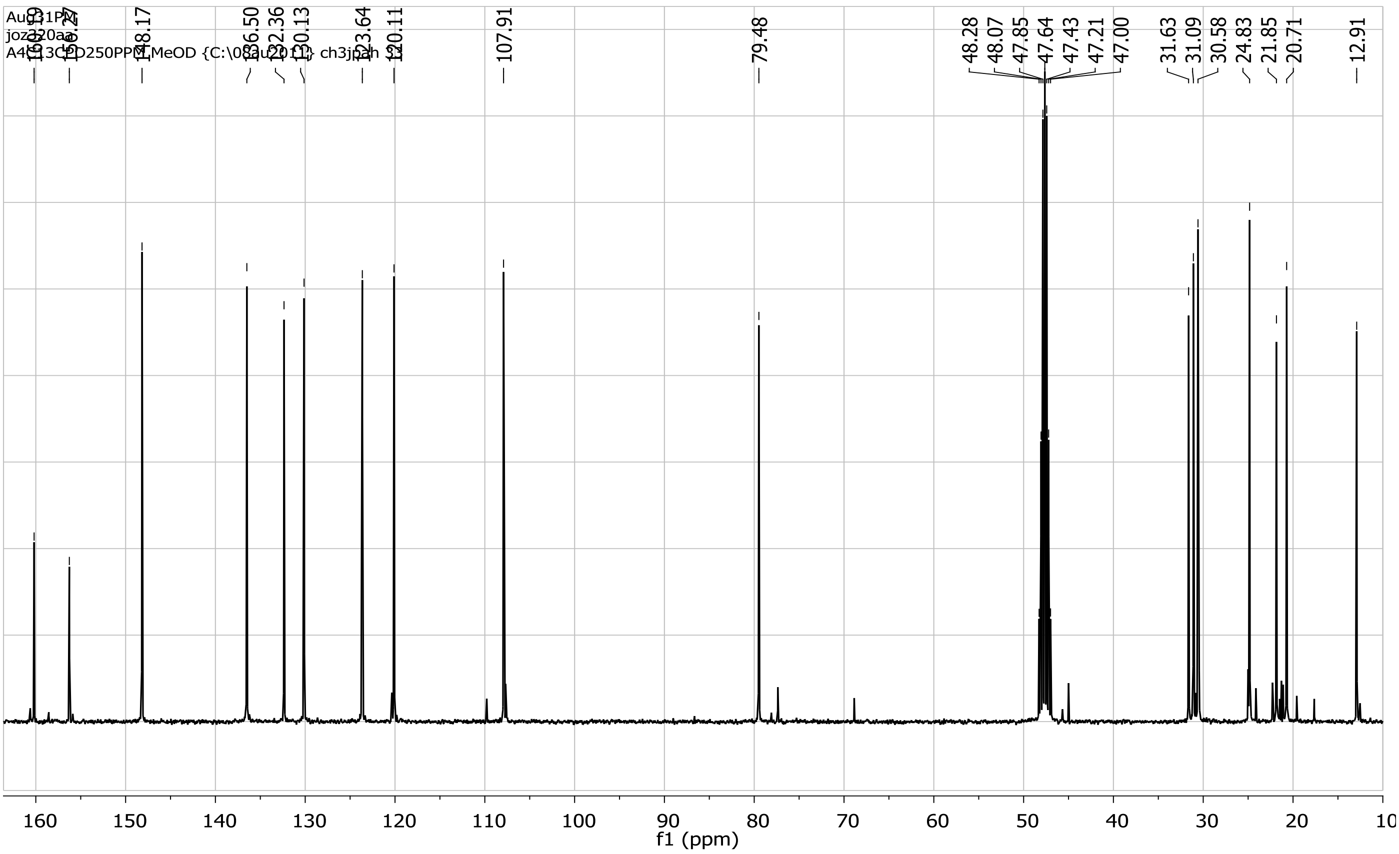
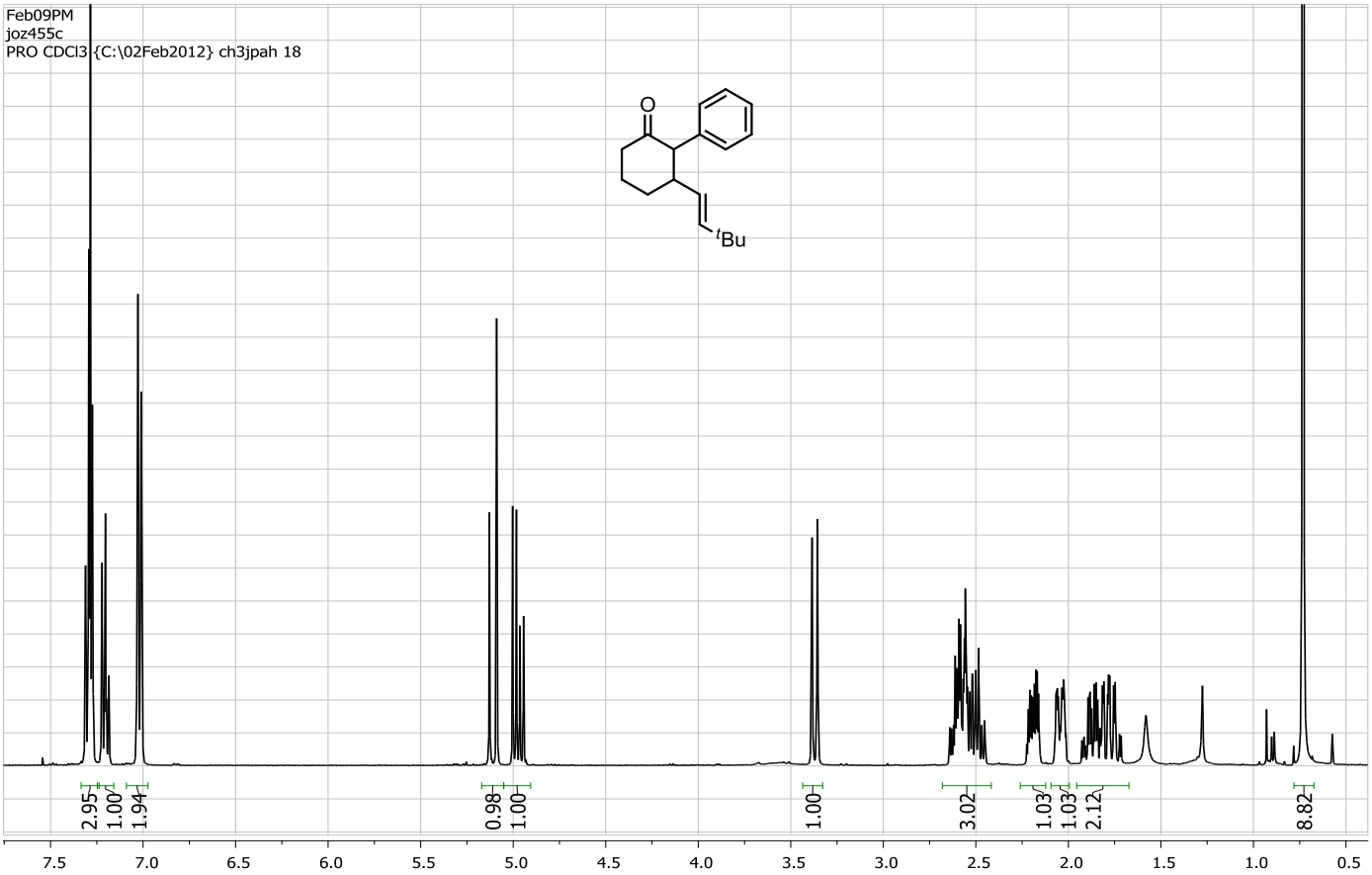
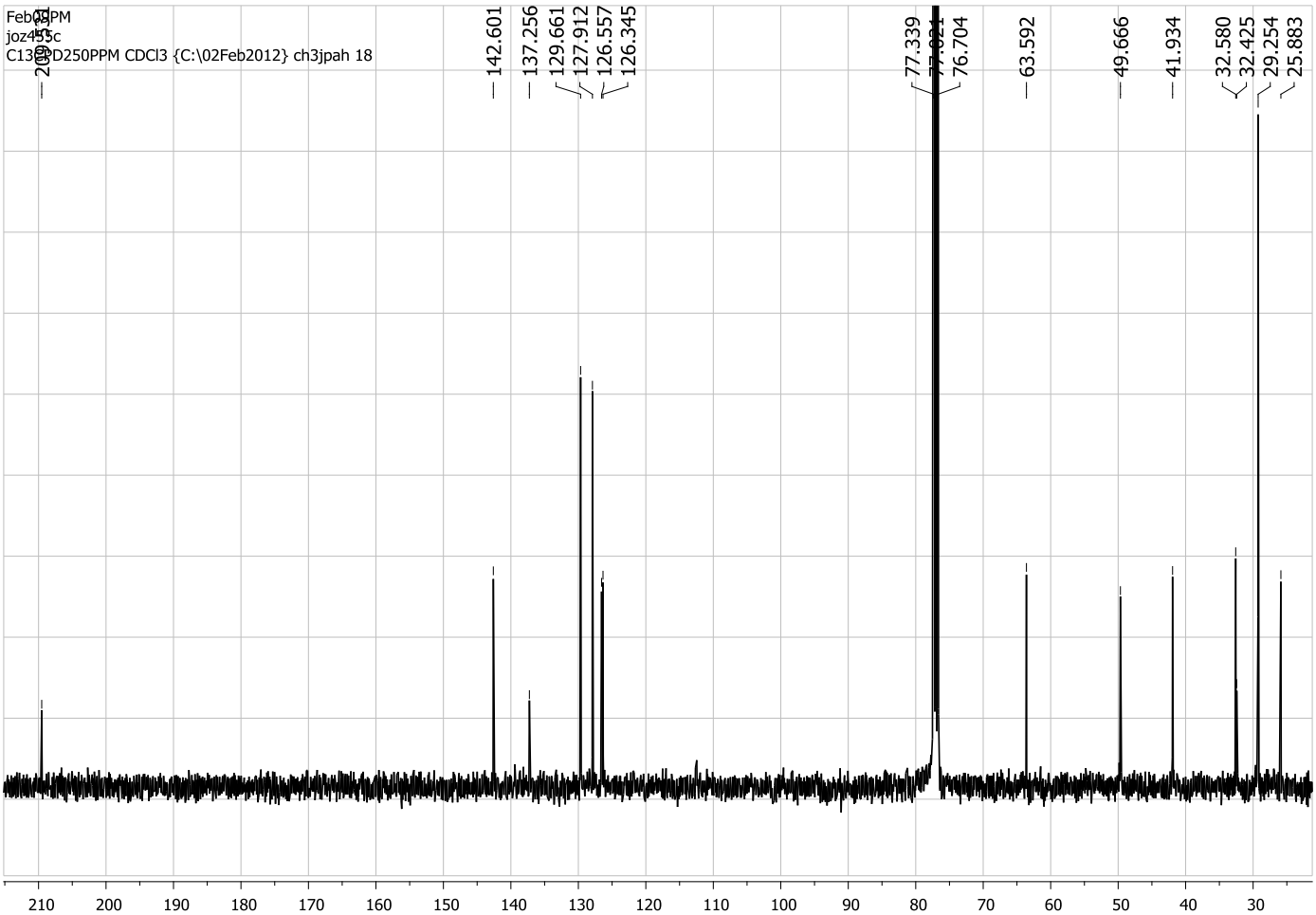
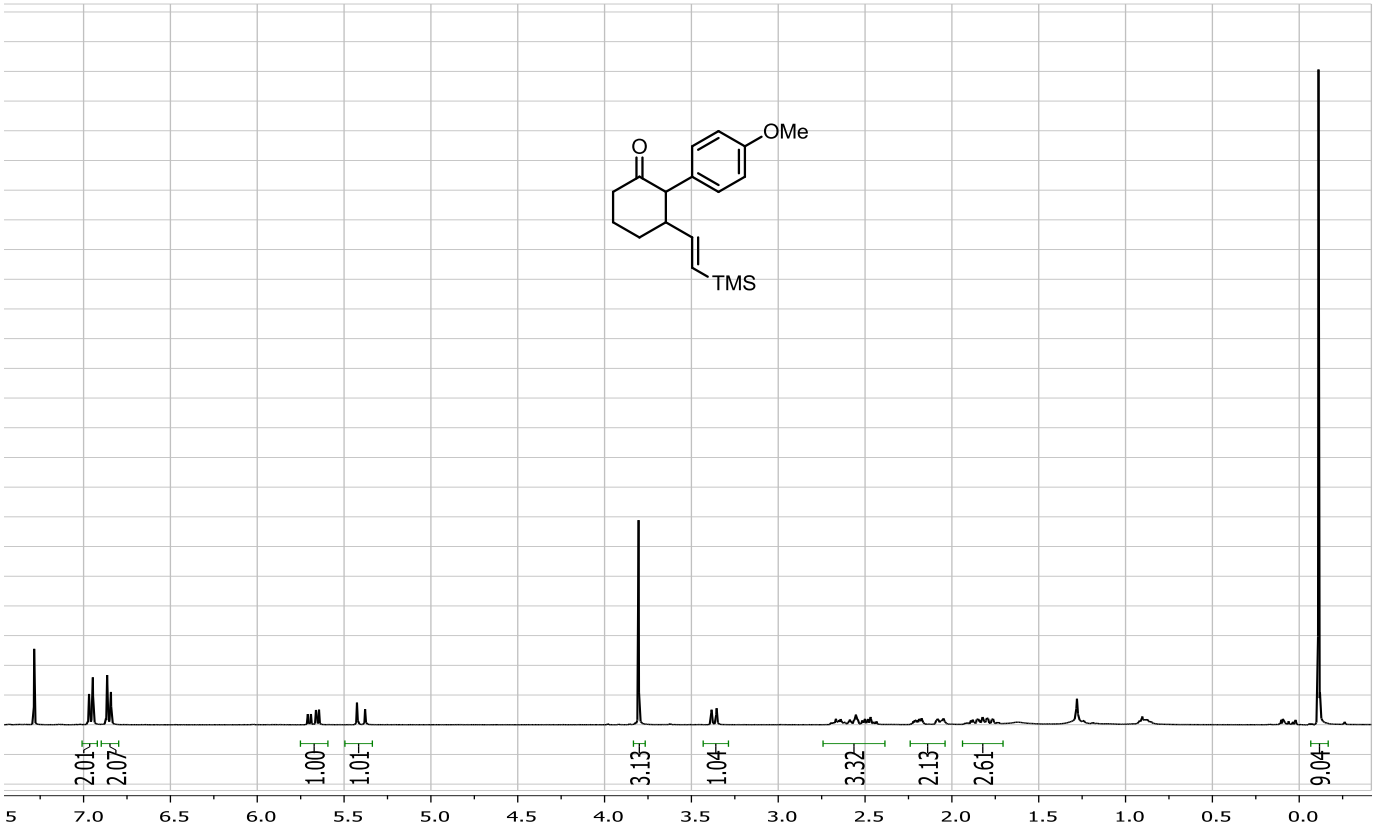
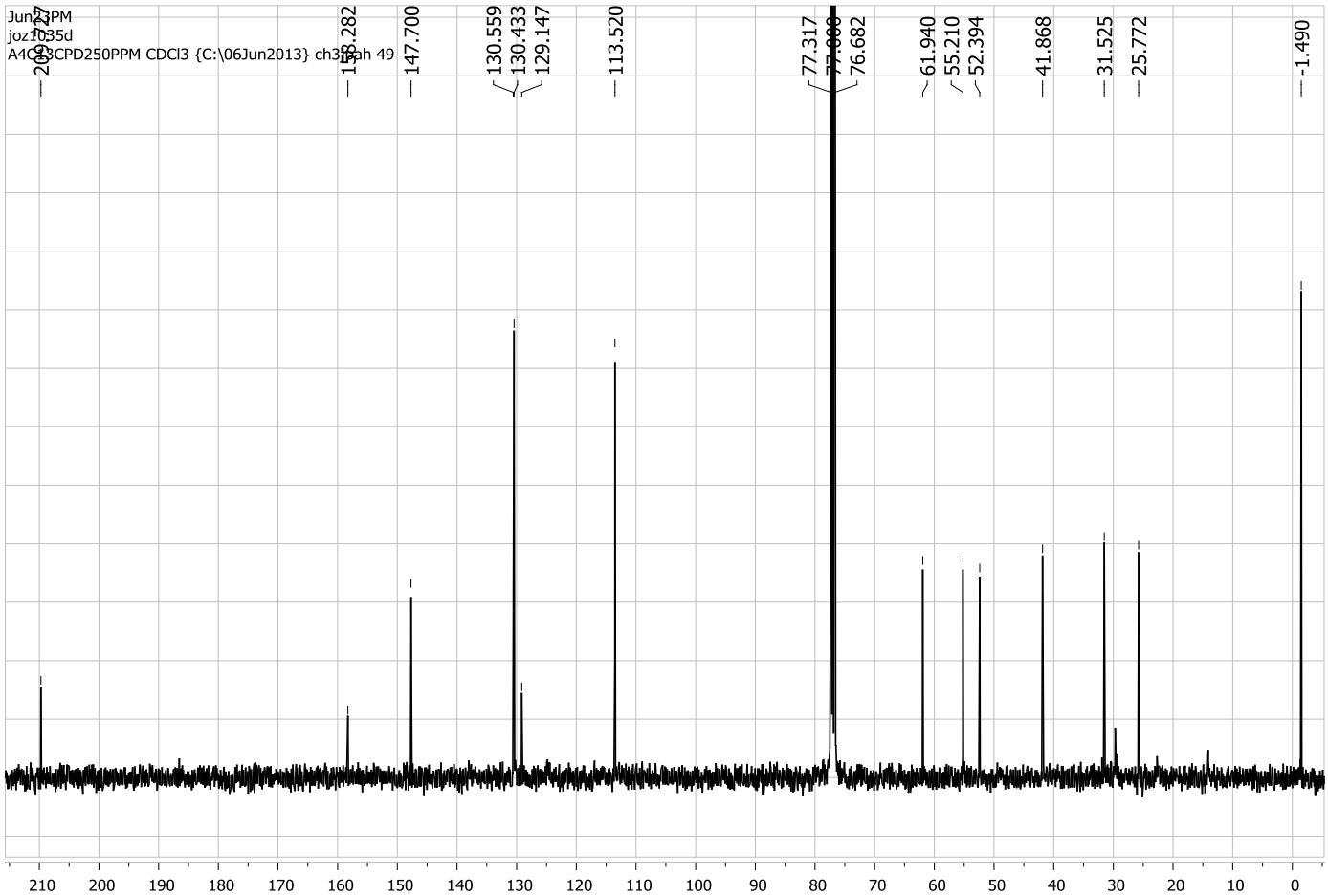


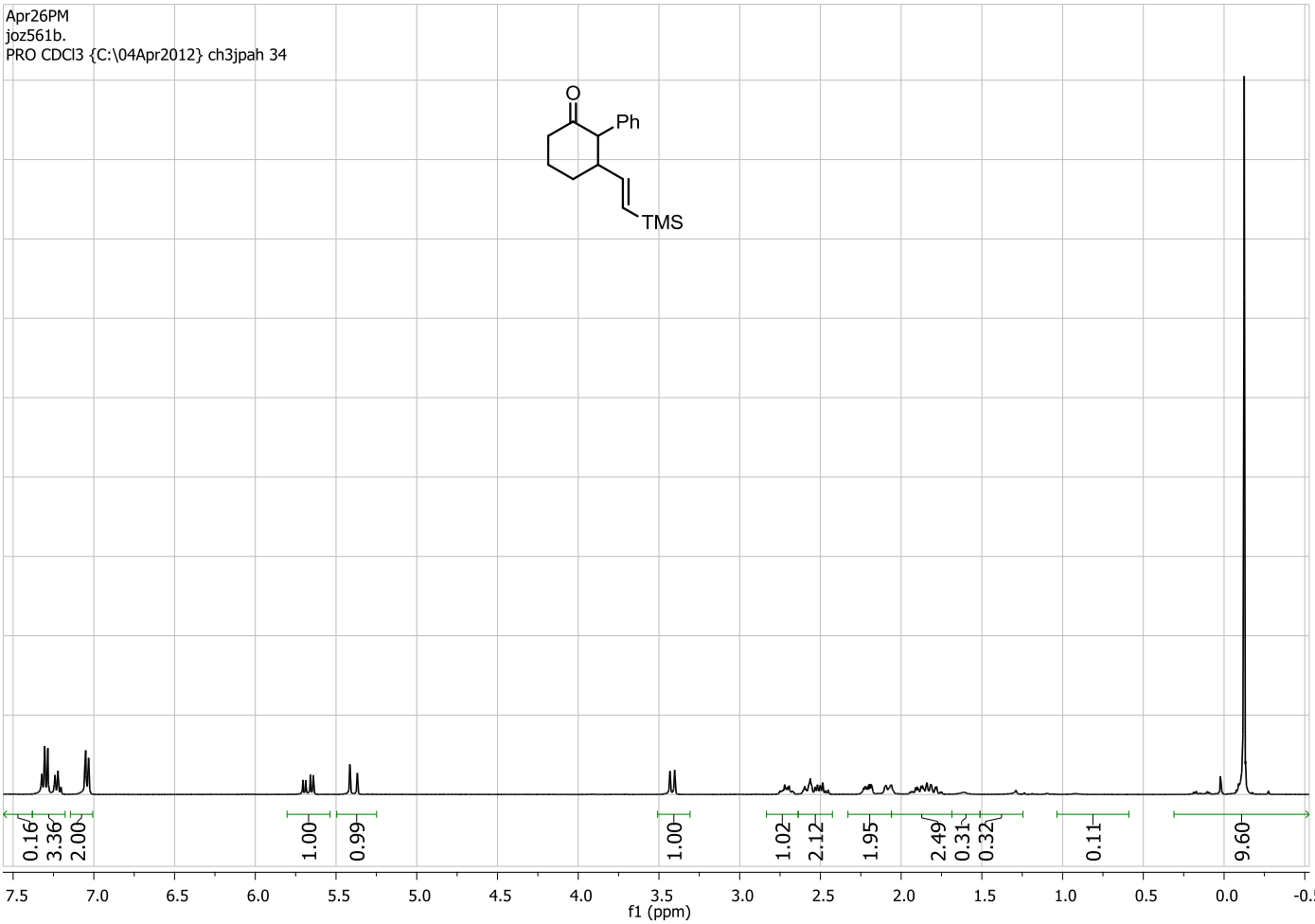


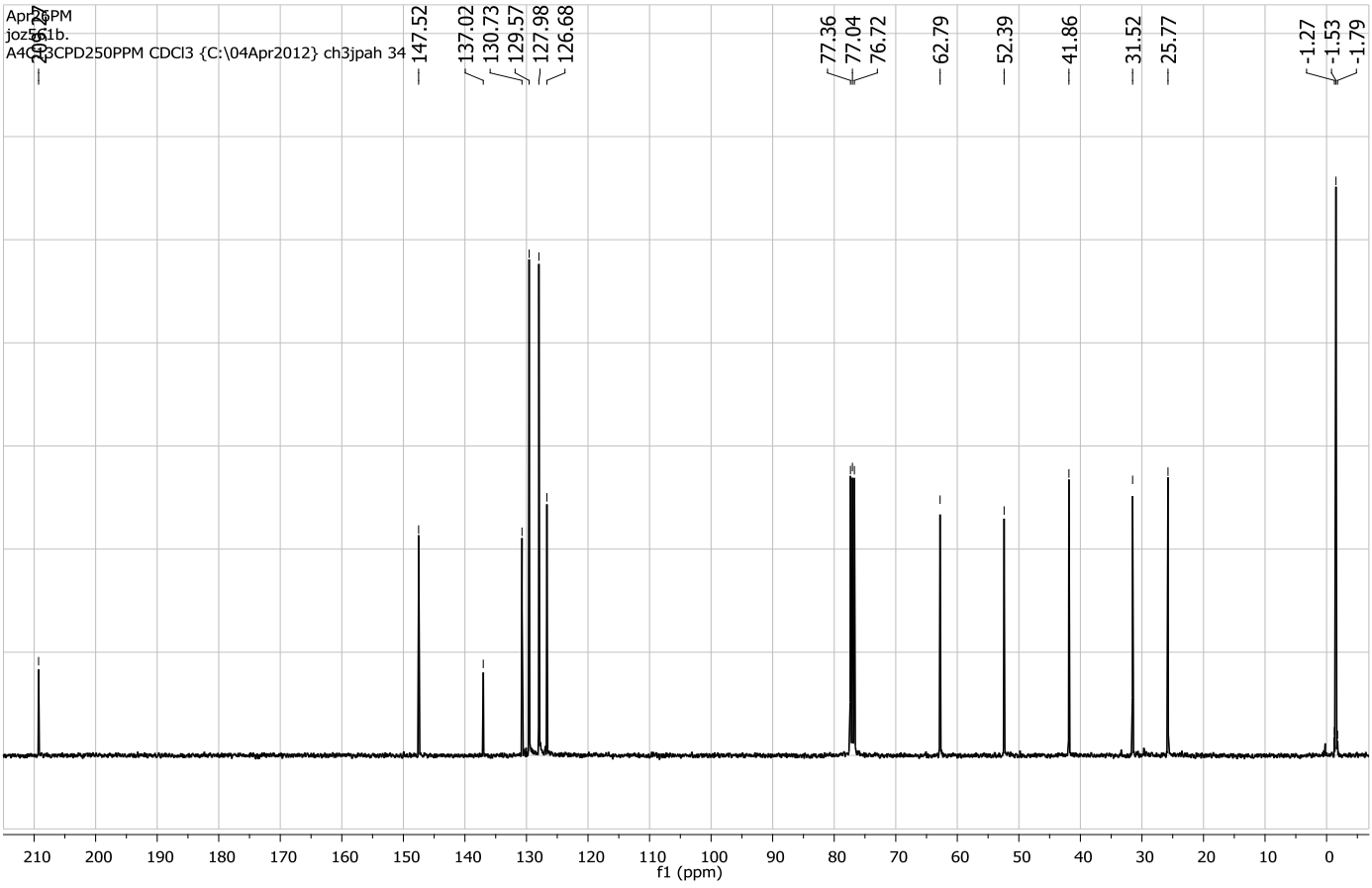

Feb09PM
joz455c
PRO CDCl3 {C:\02Feb2012} ch3jpah 18
O
tBu
2.95
1.00
1.94
0.98
1.00
1.00
3.02
1.03
1.03
2.12
8.82
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

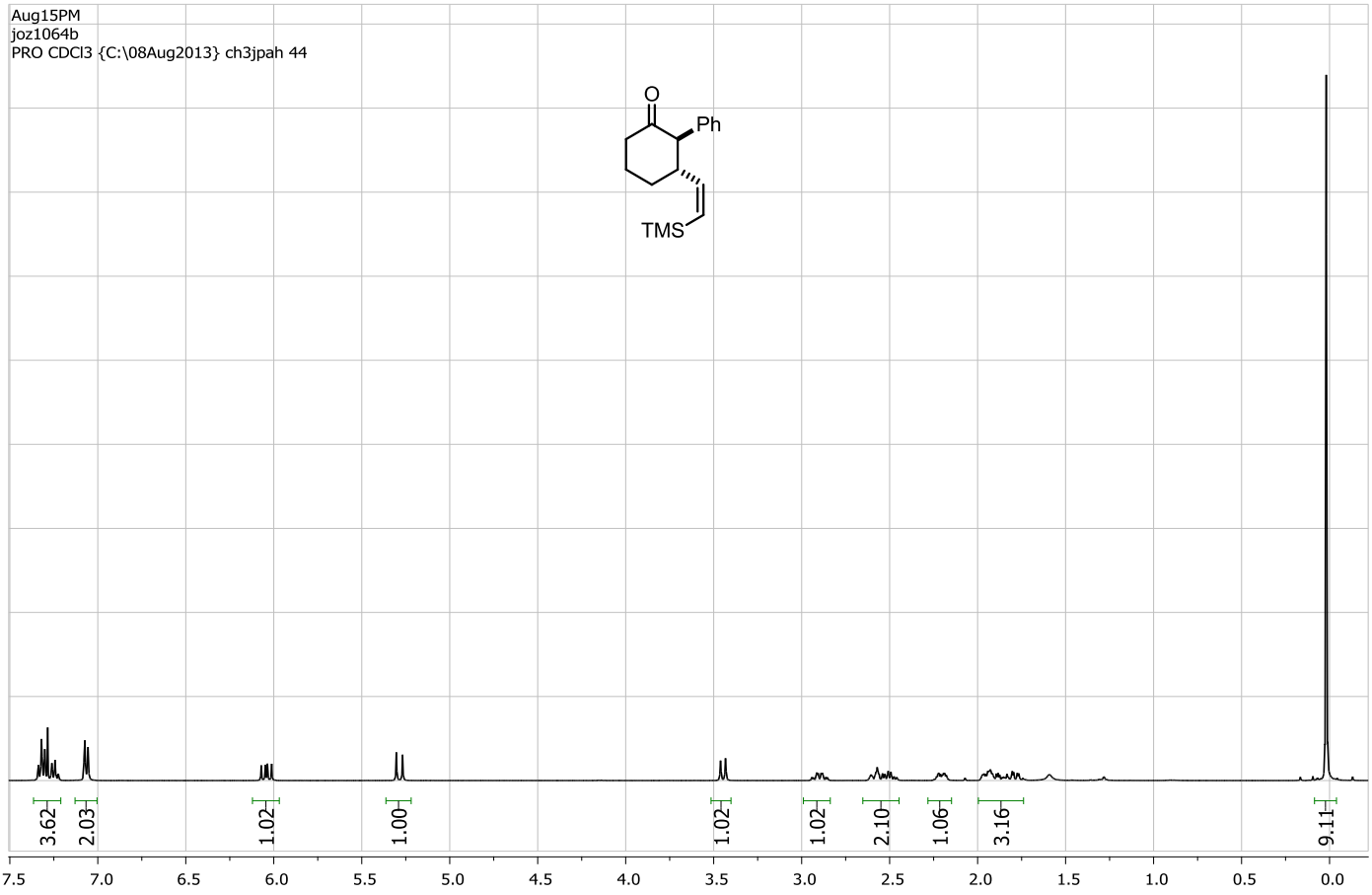

Feb09PM
joz455c
C13CPD250PPM CDCl3 {C:\02Feb2012} ch3jpah 18
142.601
137.256
129.661
127.912
126.557
126.345
77.339
77.021
76.704
63.592
49.666
41.934
32.580
32.425
29.254
25.883
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30

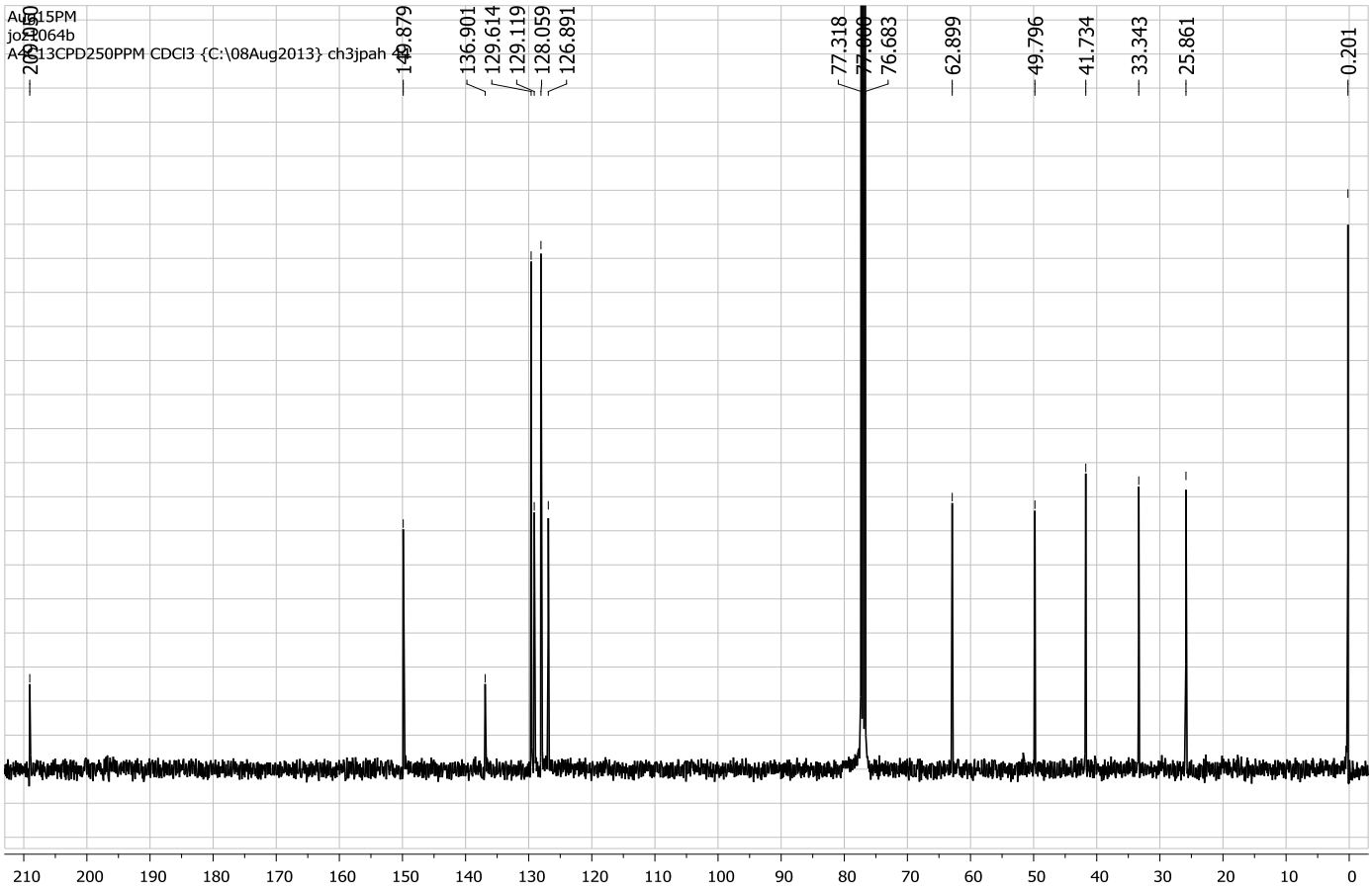

OMe
O
TMS
2.01
2.07
1.00
1.01
3.13
1.04
3.32
2.13
2.61
9.04
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

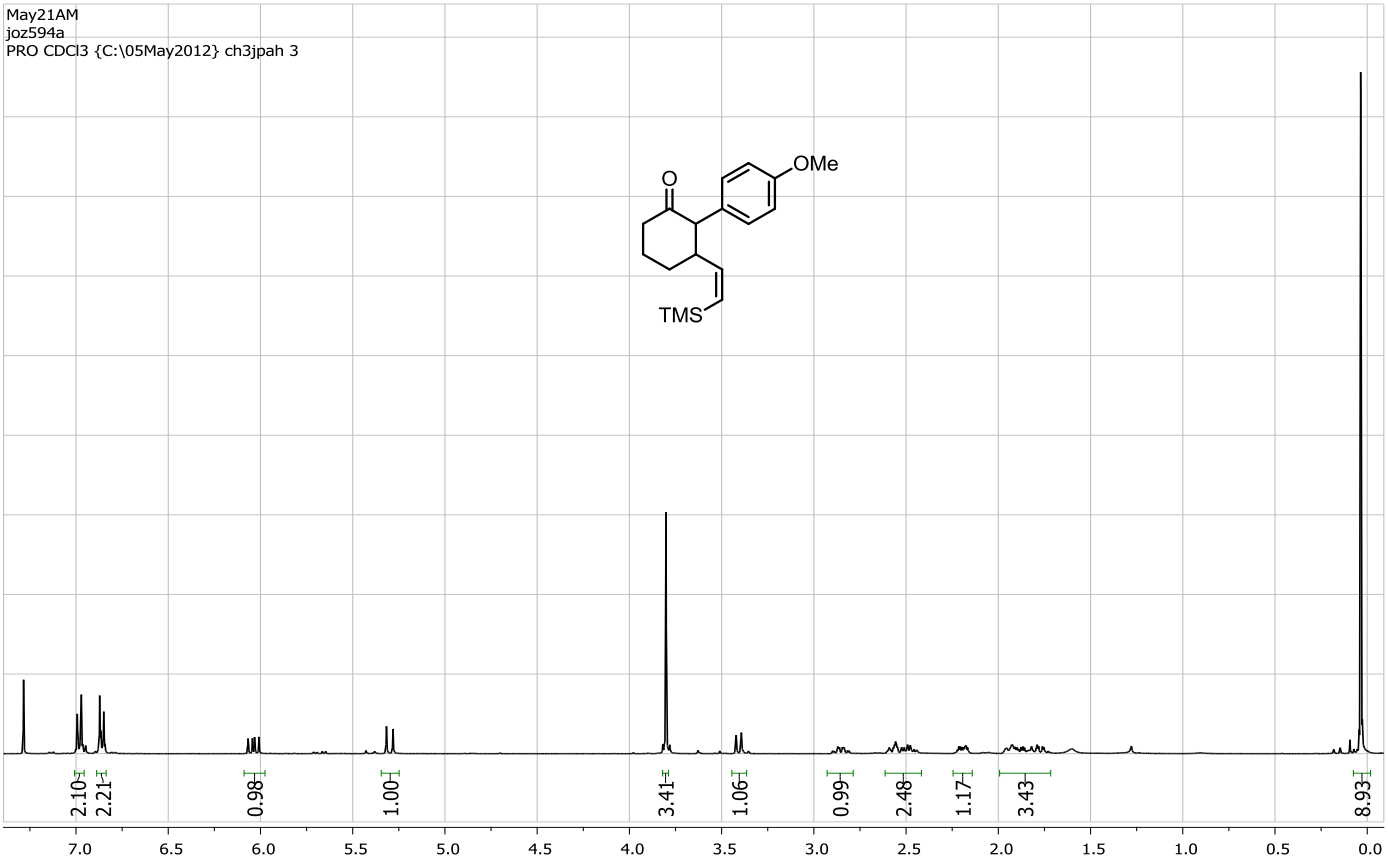

Jun23PM
joz1035d
A4CDCPD250PPM CDCl3 {C:\06Jun2013} ch3 pah 49
198.282
147.700
130.559
130.433
129.147
113.520
77.317
77.000
76.682
61.940
55.210
52.394
41.868
31.525
25.772
-1.490
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

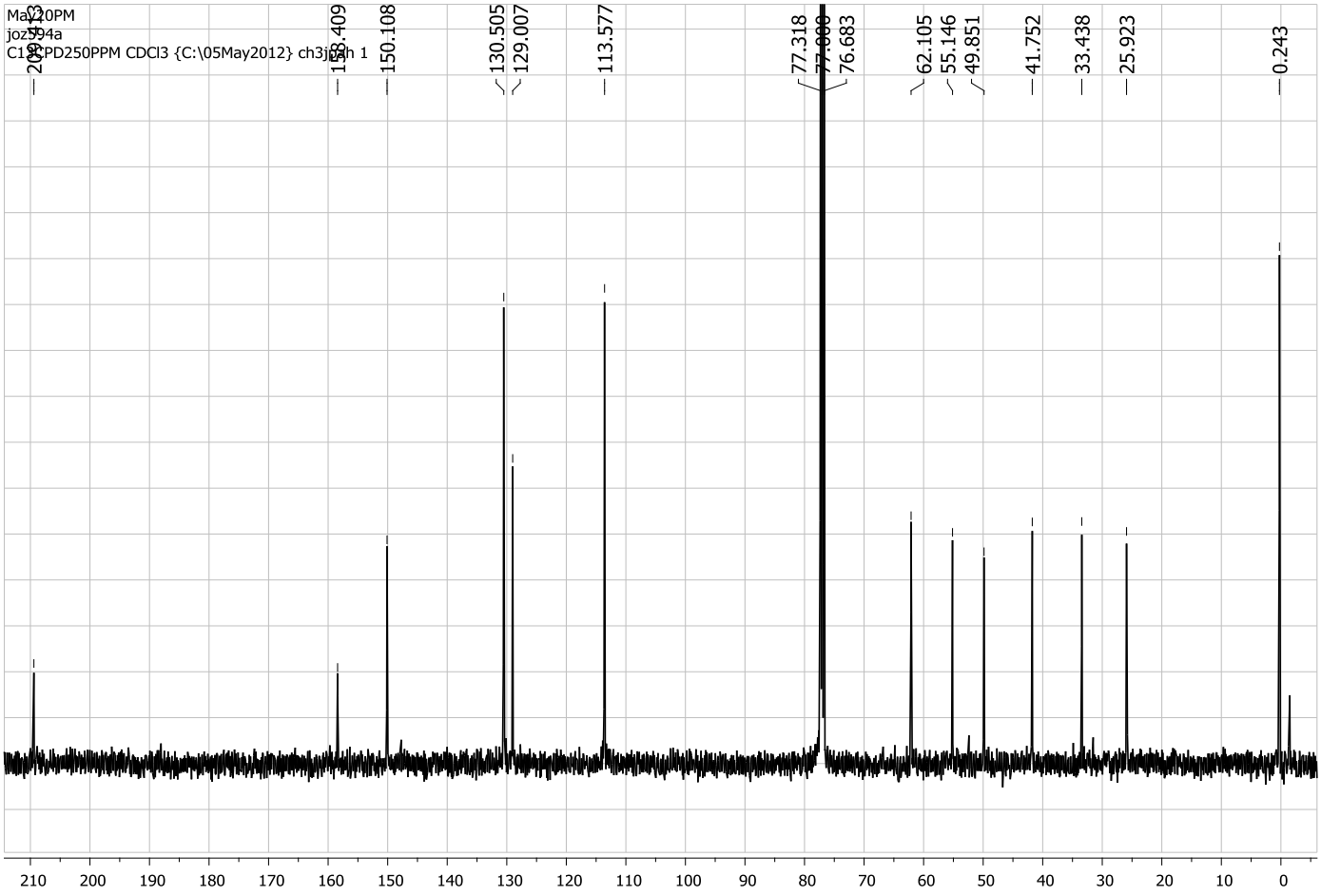

Apr26PM
joz561b.
PRO CDCl3 {C:\04Apr2012} ch3jpah 34
O
Ph
TMS
0.16
3.36
2.00
1.00
0.99
1.00
1.02
2.12
1.95
2.49
0.31
0.32
0.11
9.60
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

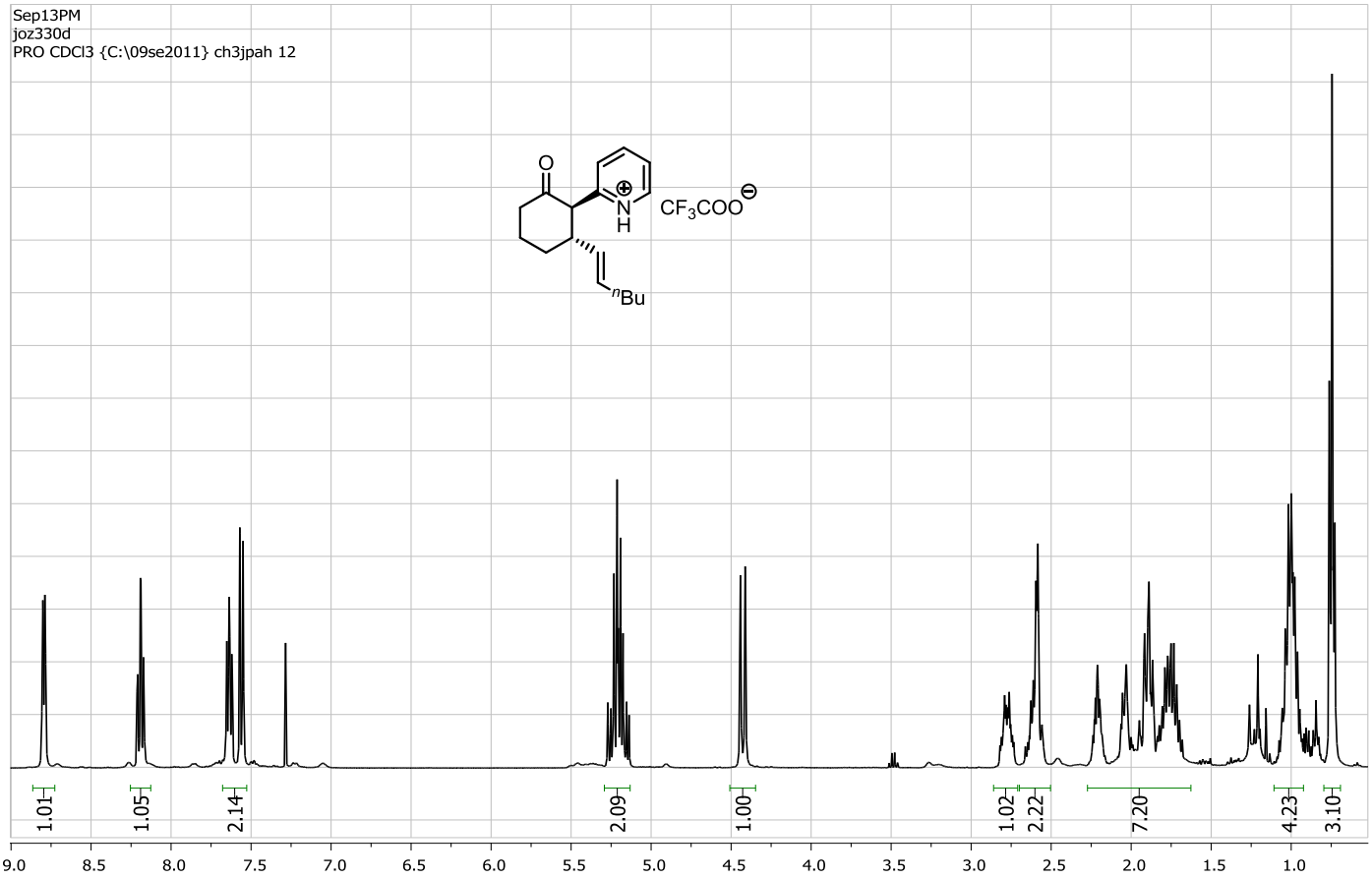

Apr26PM
joz561b.
A4CD3CPD250PPM CDCl3 {C:\04Apr2012} ch3jpah 34
147.52
137.02
130.73
129.57
127.98
126.68
77.36
77.04
76.72
62.79
52.39
41.86
31.52
25.77
-1.27
-1.53
-1.79
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

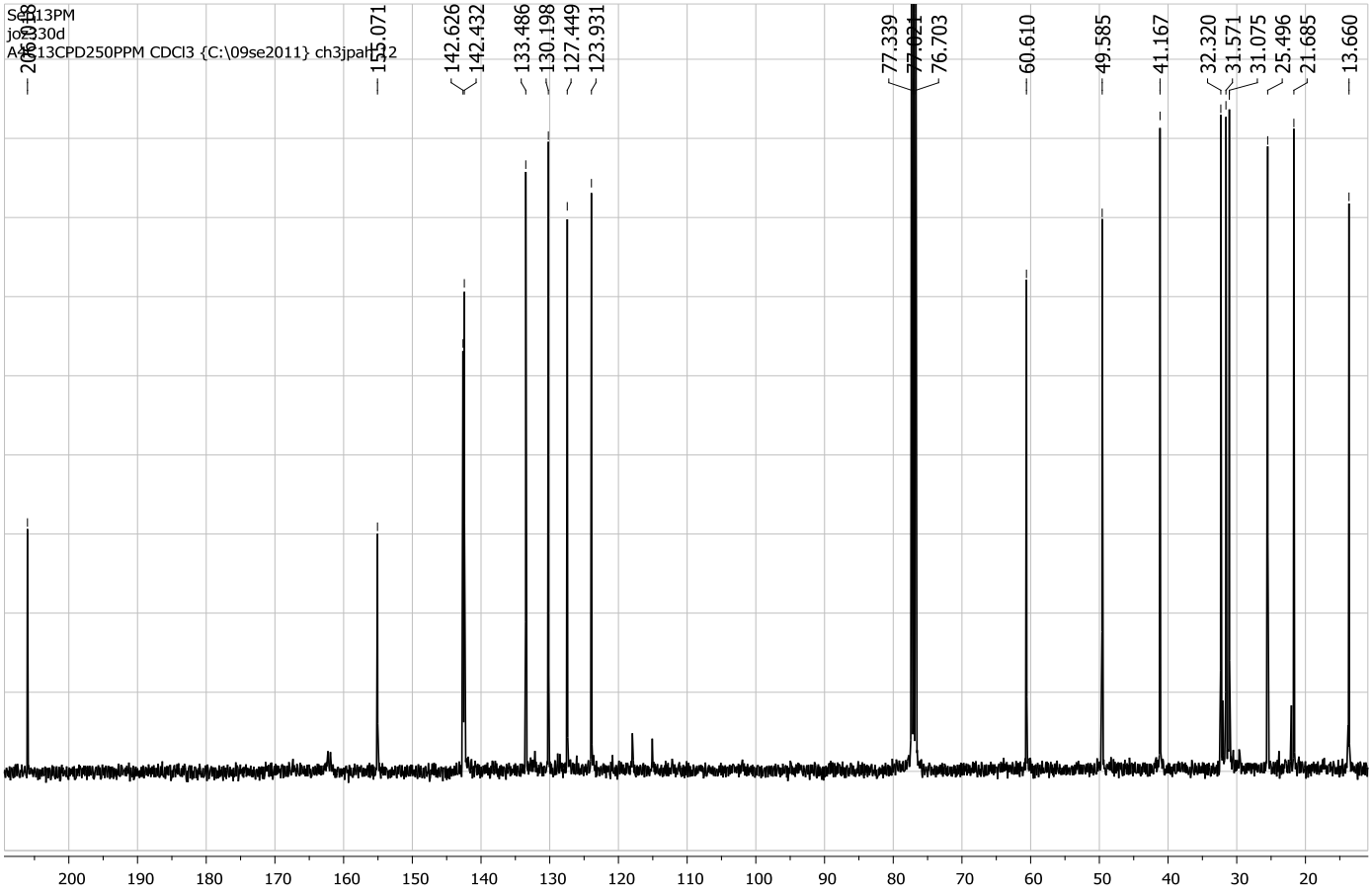

Aug15PM
joz1064b
PRO CDCl3 {C:\08Aug2013} ch3jpah 44
O
Ph
TMS
3.62
2.03
1.02
1.00
1.02
1.02
2.10
1.06
3.16
9.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

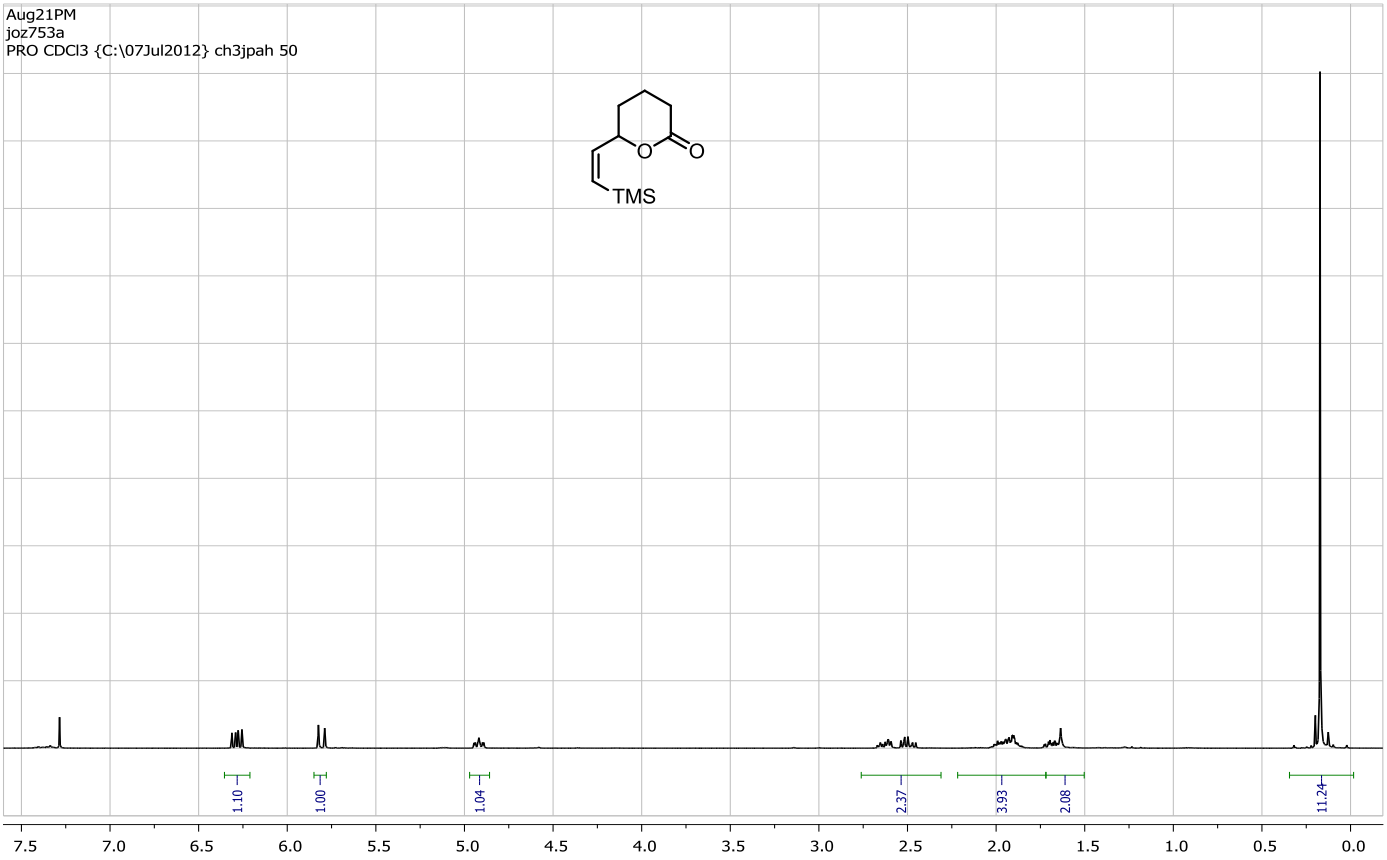

Aug15PM
joz1064b
A4C13CPD250PPM CDCl3 {C:\08Aug2013} ch3jpah 44
149.879
136.901
129.614
129.119
128.059
126.891
77.318
77.000
76.683
62.899
49.796
41.734
33.343
25.861
0.201
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

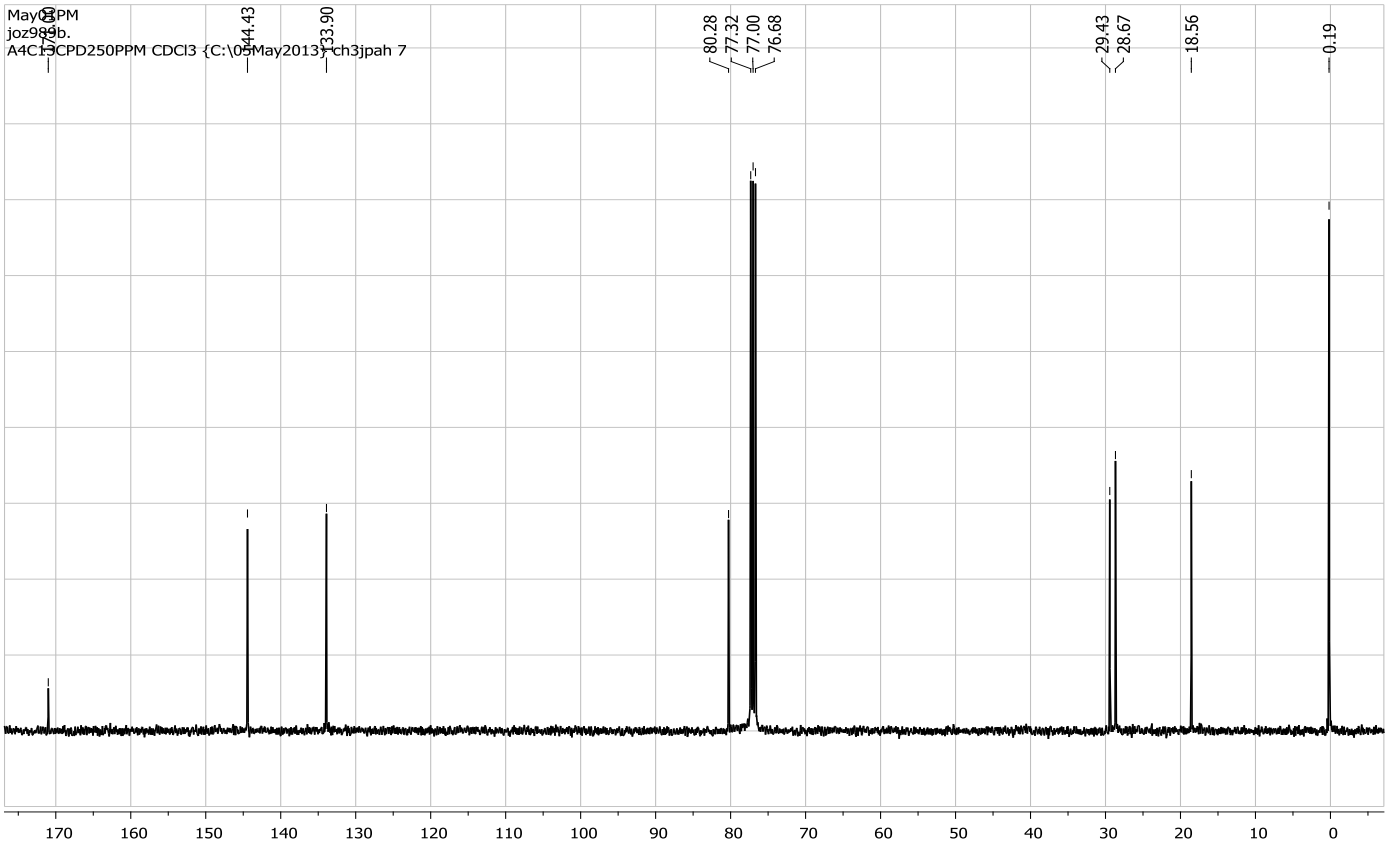

May21AM
joz594a
PRO CDCl3 {C:\05May2012} ch3jpah 3
O
OMe
TMS
2.10
2.21
0.98
1.00
3.41
1.06
0.99
2.48
1.17
3.43
8.93
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

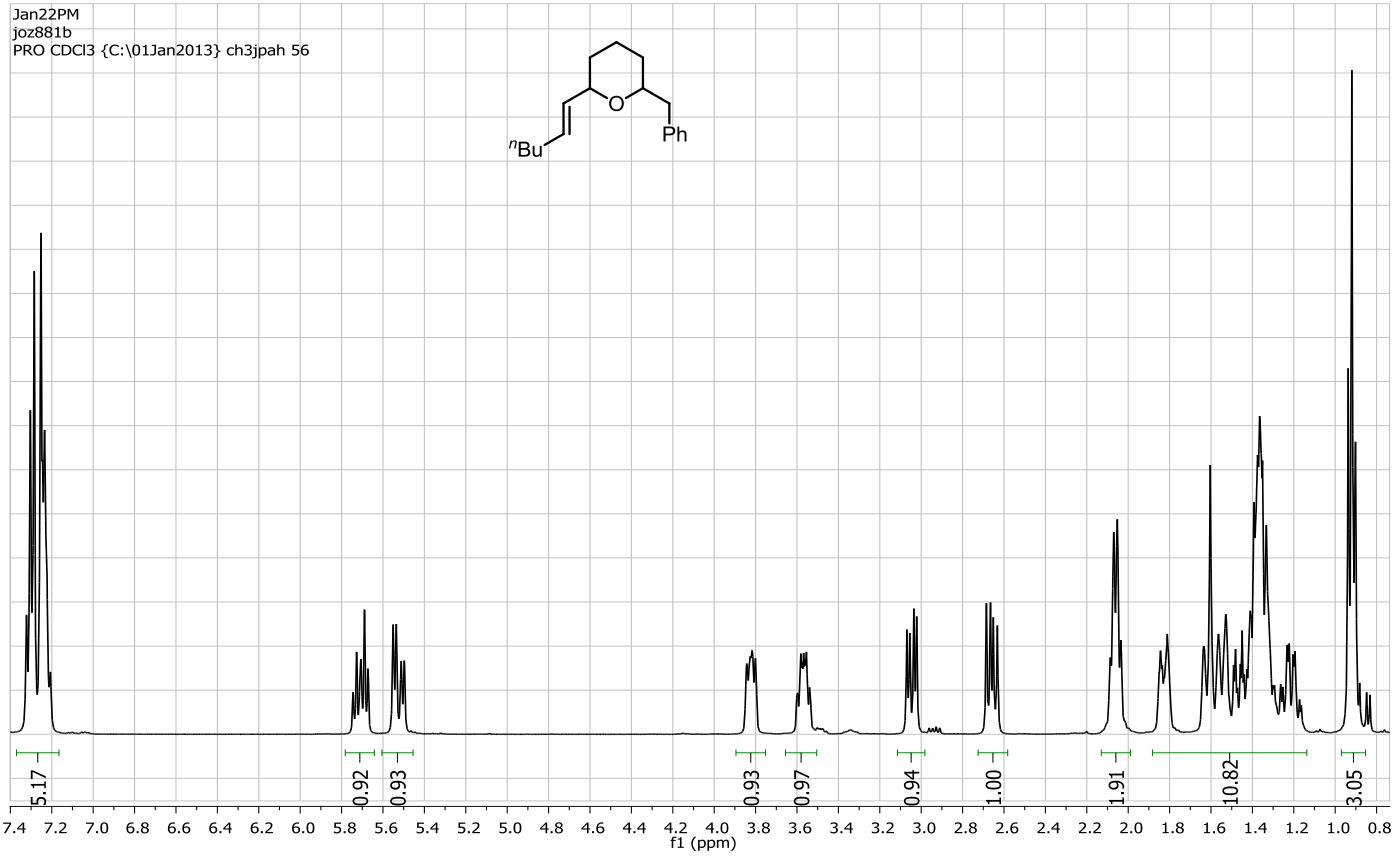

May20PM
joz594a
C13CPD250PPM CDCl3 {C:\05May2012} ch3jpah 1
161.409
150.108
130.505
129.007
113.577
77.318
77.000
76.683
62.105
55.146
49.851
41.752
33.438
25.923
0.243
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

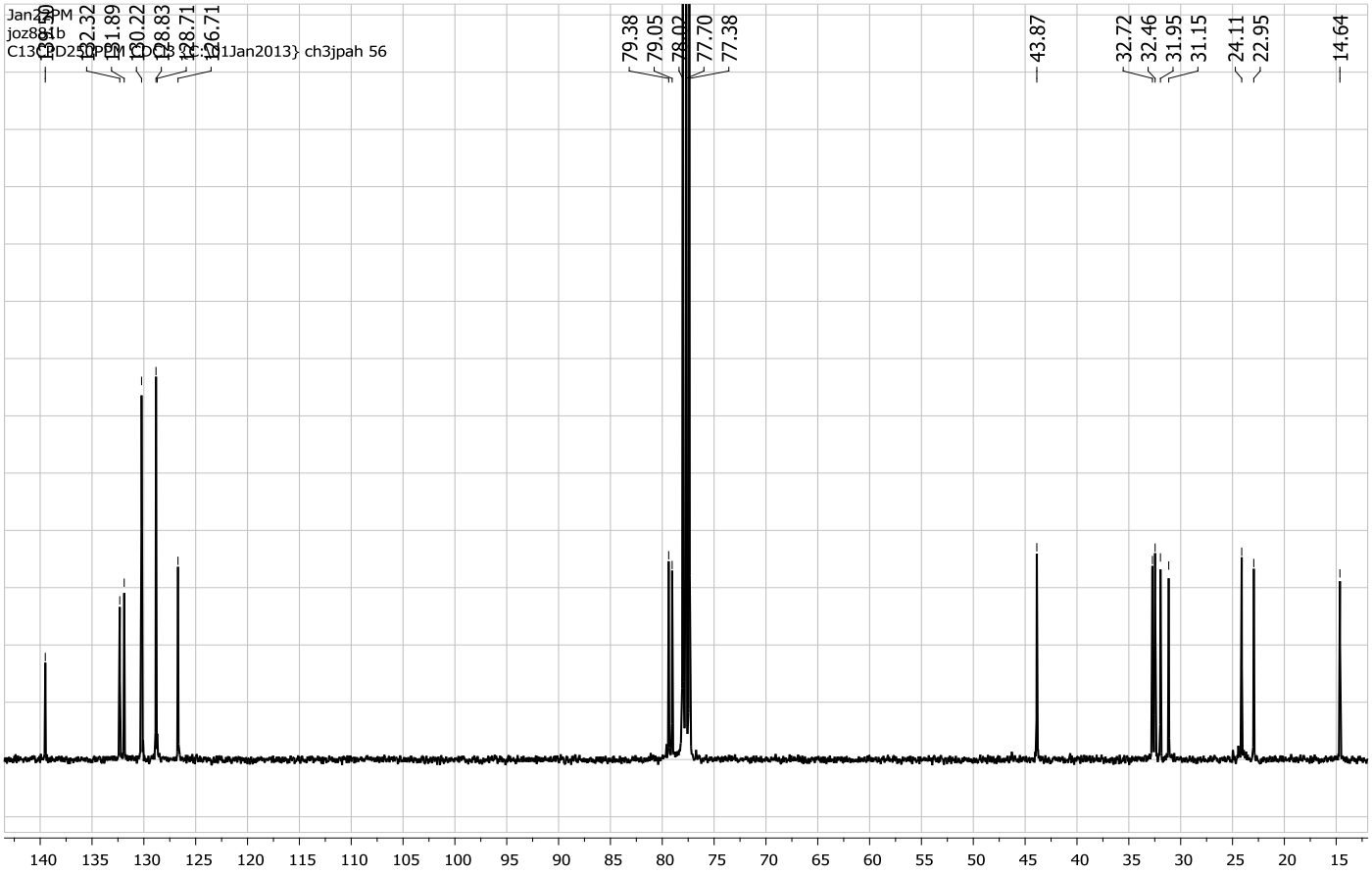

Sep13PM
joz330d
PRO CDCl3 {C:\09se2011} ch3jpah 12
O
N
H
CF3COO
nBu
1.01
1.05
2.14
2.09
1.00
1.02
2.22
7.20
4.23
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

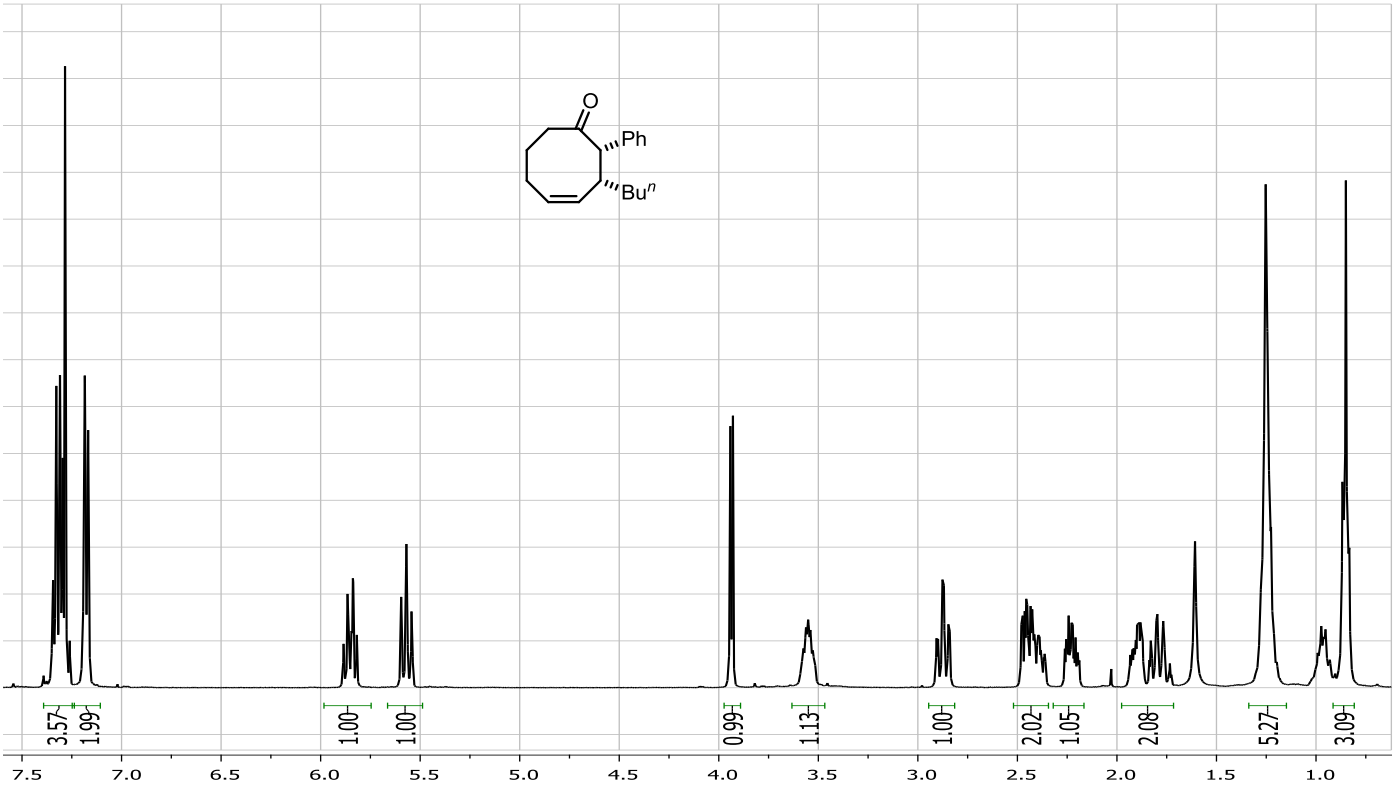

Sep13PM
joz330d
A 13CPD250PPM CDCl3 {C:\09se2011} ch3jpah 12
155.071
142.626
142.432
133.486
130.198
127.449
123.931
77.339
77.021
76.703
60.610
49.585
41.167
32.320
31.571
31.075
25.496
21.685
13.660
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

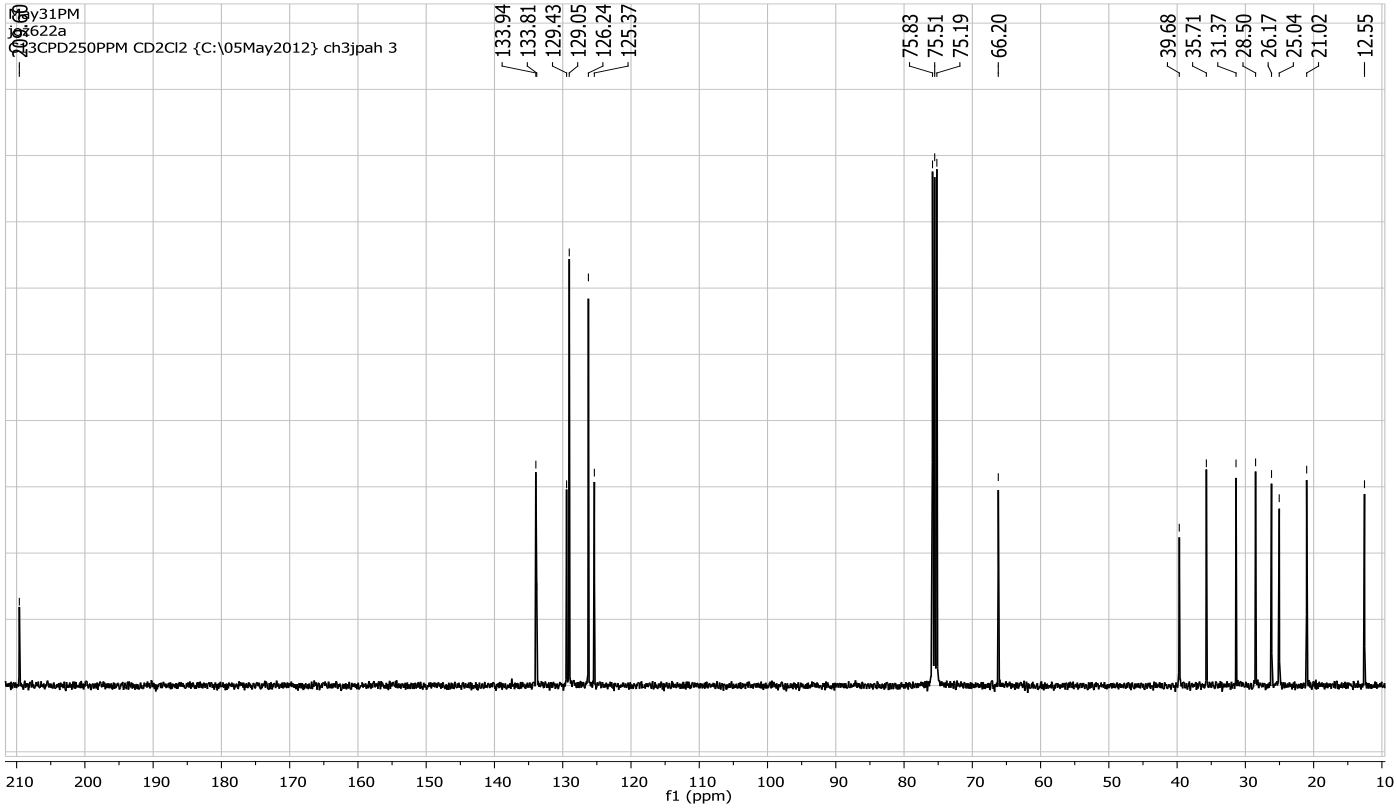


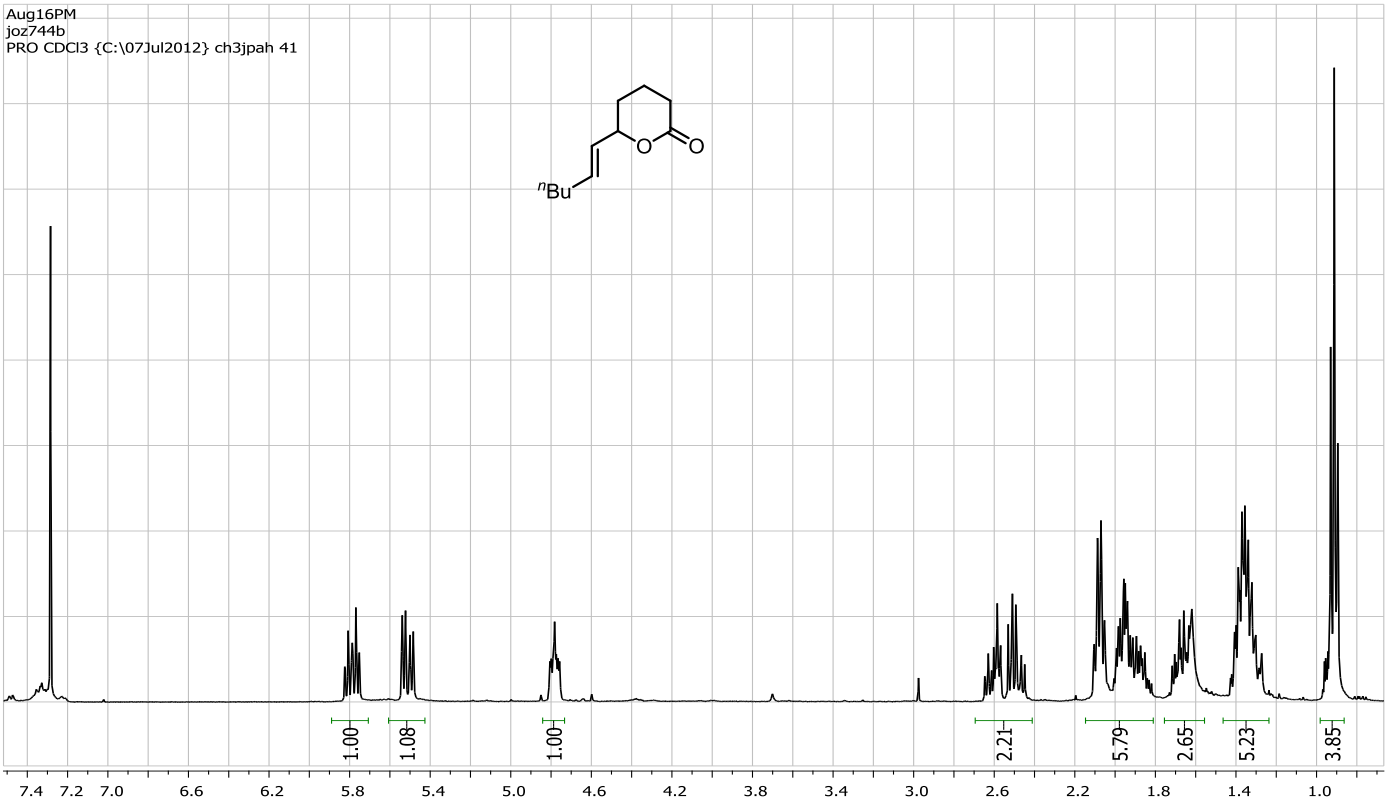


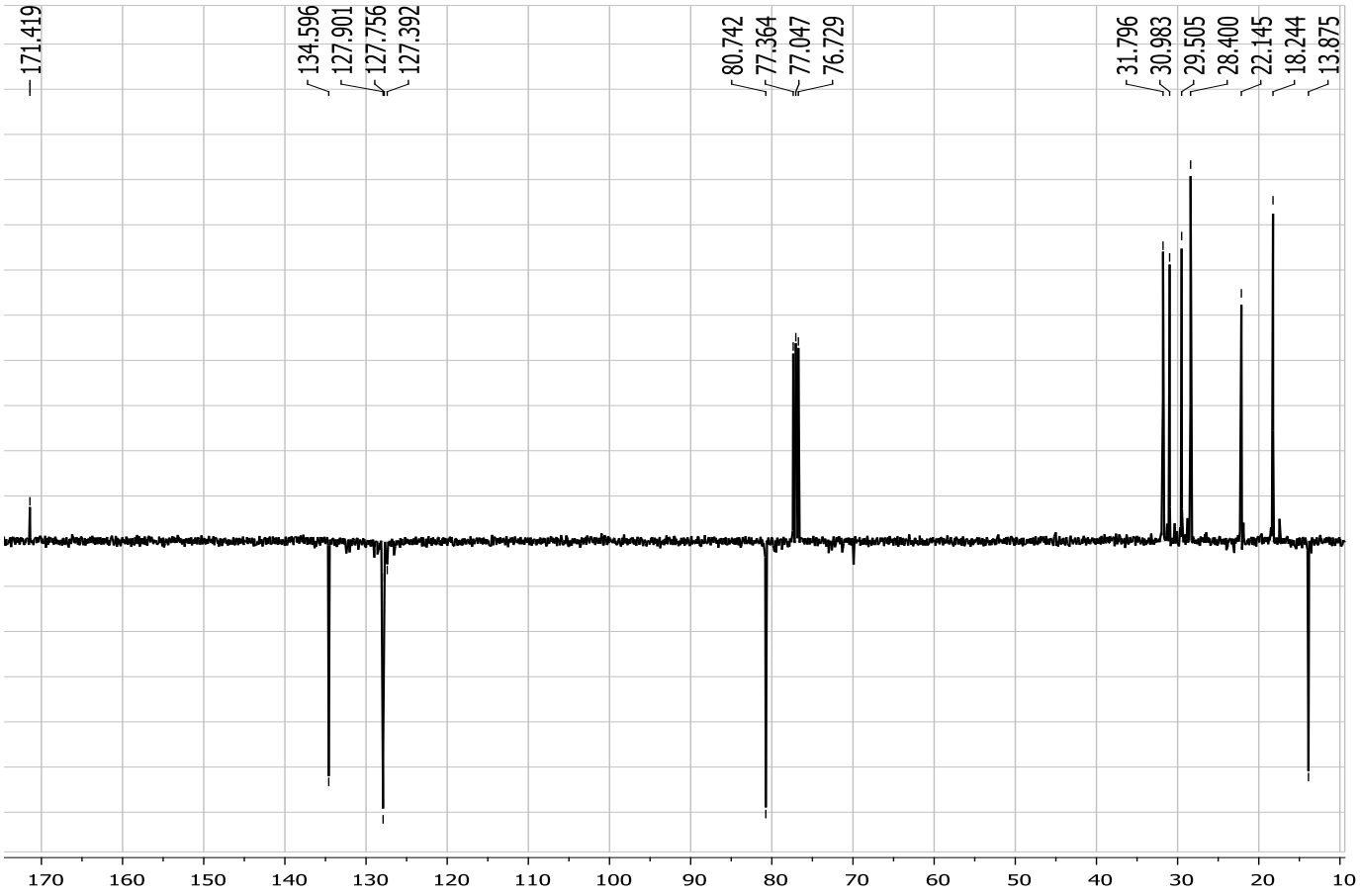

Jan22PM
joz881b
PRO CDCl3 {C:\01Jan2013} ch3jpah 56
O
nBu
Ph
5.17
0.92
0.93
0.93
0.97
0.94
1.00
1.91
10.82
3.05
f1 (ppm)

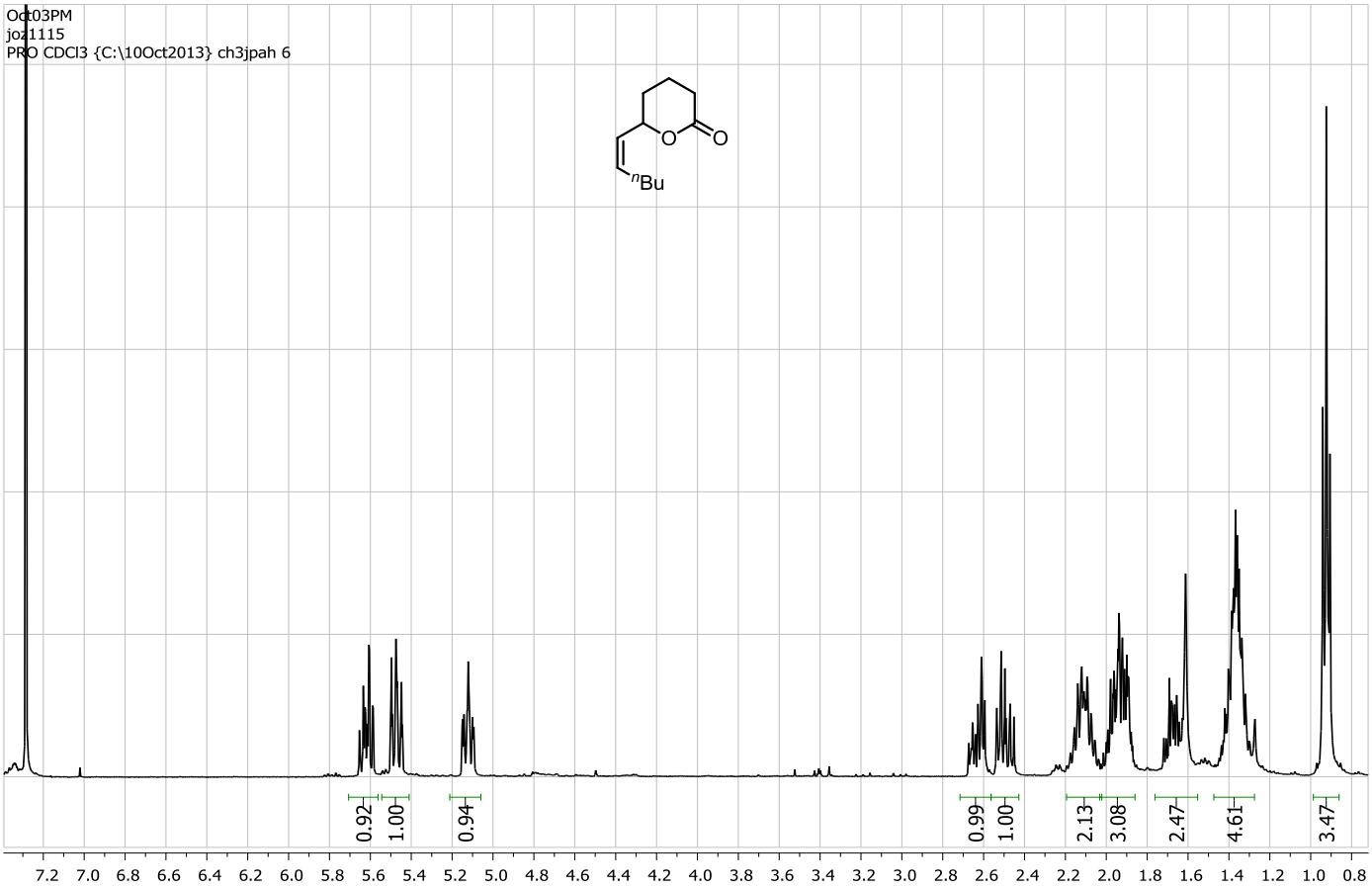

Jan22PM
joz881b
C13CPD25DEPT {C:\01Jan2013} ch3jpah 56
132.32
131.89
130.22
128.83
128.71
126.71
79.38
79.05
78.02
77.70
77.38
43.87
32.72
32.46
31.95
31.15
24.11
22.95
14.64

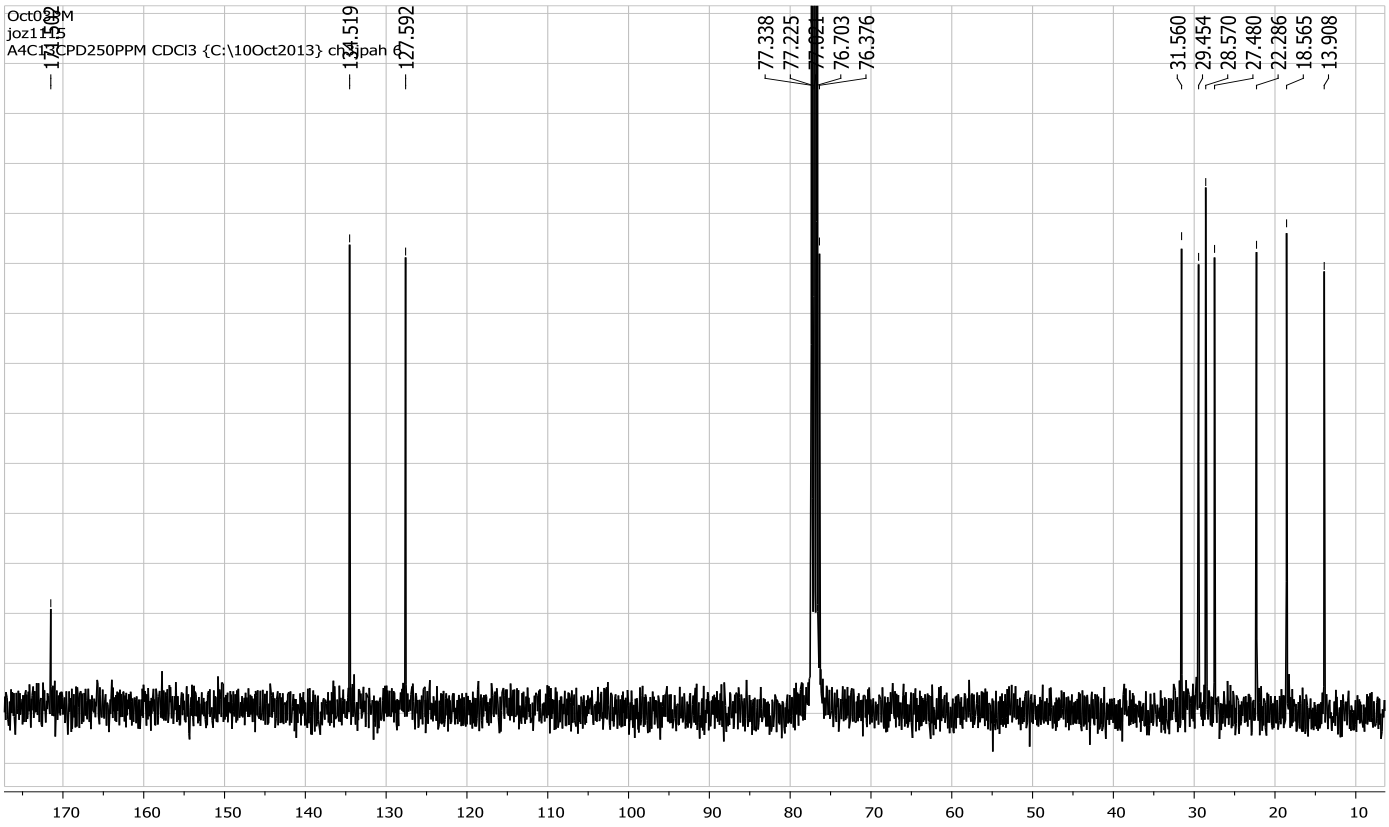

O
Ph
Bu^n
3.57
1.99
1.00
1.00
0.99
1.13
1.00
2.02
1.05
2.08
5.27
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

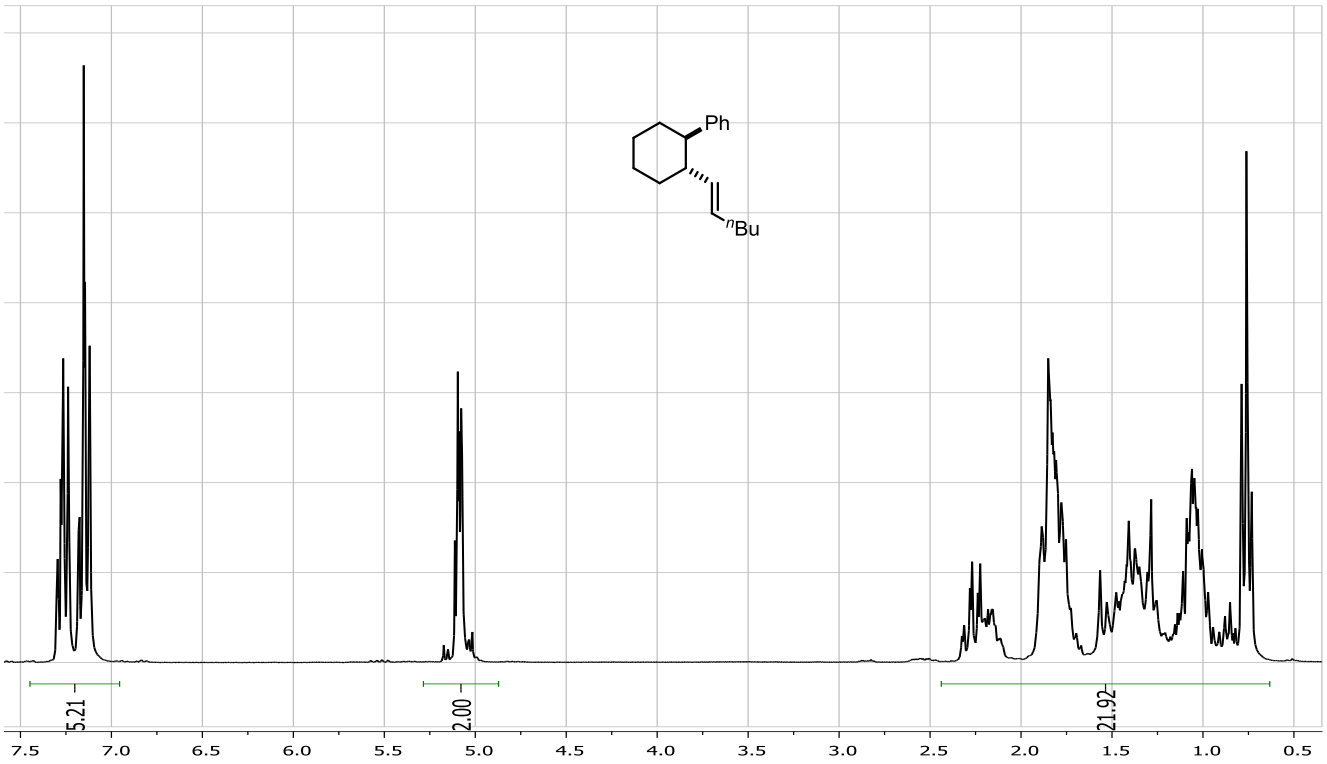

May31PM
jc2622a
13CPD250PPM CD2Cl2 {C:\05May2012} ch3jpah 3
133.94
133.81
129.43
129.05
126.24
125.37
75.83
75.51
75.19
66.20
39.68
35.71
31.37
28.50
26.17
25.04
21.02
12.55
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

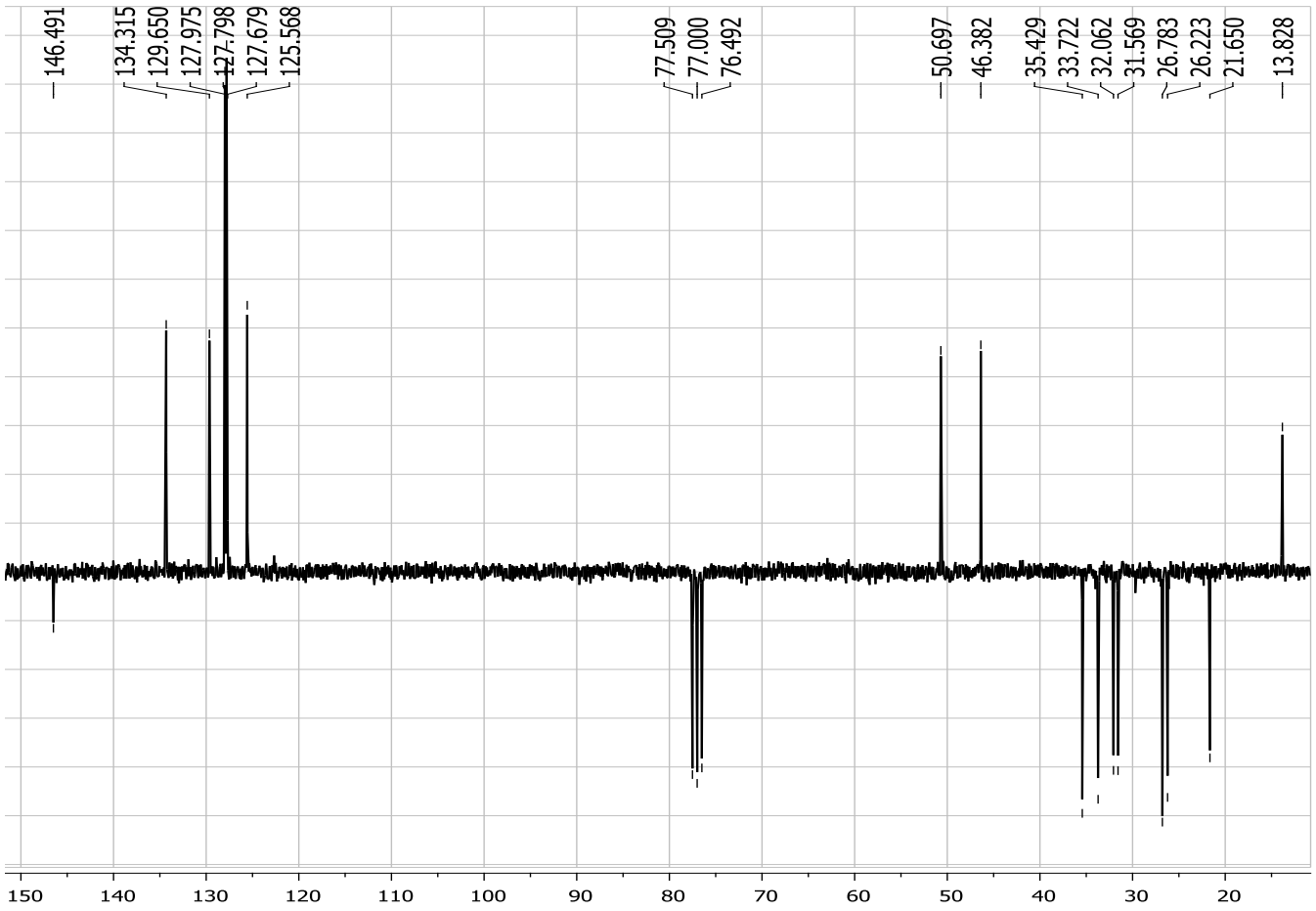

Aug16PM
joz744b
PRO CDCl3 {C:\07Jul2012} ch3jpah 41
nBu
O
O
1.00
1.08
1.00
2.21
5.79
2.65
5.23
3.85
7.4 7.2 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4 1.0


171.419
134.596
127.901
127.756
127.392
80.742
77.364
77.047
76.729
31.796
30.983
29.505
28.400
22.145
18.244
13.875
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


Oct03PM
joz1115
PRO CDCl3 {C:\10Oct2013} ch3jpah 6
O
O
nBu
0.92
1.00
0.94
0.99
1.00
2.13
3.08
2.47
4.61
3.47
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 1.4 1.2 1.0 0.8


Oct03PM
joz1115
A4C13CPD250PPM CDCl3 {C:\10Oct2013} ch3jpah 2
134.519
127.592
77.338
77.225
77.021
76.703
76.376
31.560
29.454
28.570
27.480
22.286
18.565
13.908
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


Ph
nBu
5.21
2.00
21.92
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


146.491
134.315
129.650
127.975
127.798
127.679
125.568
77.509
77.000
76.492
50.697
46.382
35.429
33.722
32.062
31.569
26.783
26.223
21.650
13.828
150
140
130
120
110
100
90
80
70
60
50
40
30
20

X-Ray Crystal Structure Data for *trans*-13

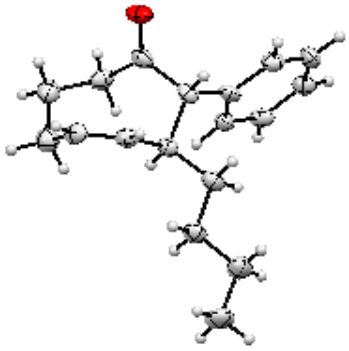


Table 1. Crystal data and structure refinement for ohj243_0m.

Identification code	ohj243_0m	
Empirical formula	C18 H24 O	
Formula weight	256.37	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P12(1)/c1	
Unit cell dimensions	a = 5.6803(17) Å	α= 90°.
	b = 32.719(9) Å	β= 98.393(17)°
	c = 16.563(5) Å	γ = 90°.
Volume	3045.3(15) $Å^3$	
Z	8	
Density (calculated)	1.118 Mg/m^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	1120	
Crystal size	0.32 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.24 to 27.61°	
Index ranges	-7<=h<=7, -41<=k<=42, -21<=l<=21	
Reflections collected	25713	
Independent reflections	6940 [R(int) = 0.2104]	
Completeness to theta = 27.61°	98.1 %	
Absorption correction	None	
Max. and min. transmission	0.9967 and 0.9789	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6940 / 0 / 346	
Goodness-of-fit on F^2	0.908	
Final R indices [I>2sigma(I)]	R1 = 0.1003, wR2 = 0.1670	
R indices (all data)	R1 = 0.3016, wR2 = 0.2370	
Extinction coefficient	0.0212(17)	
Largest diff. peak and hole	0.272 and -0.261 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ohj243_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1374(5)	4400(1)	-1629(2)	42(1)
O(2)	-2004(5)	3188(1)	2222(2)	39(1)
C(1)	5959(8)	3159(2)	249(3)	36(1)
C(2)	7556(8)	3422(2)	-25(3)	35(1)
C(3)	6941(8)	3639(1)	-732(3)	32(1)
C(4)	4674(8)	3605(1)	-1188(3)	30(1)
C(5)	3880(7)	3858(1)	-1949(3)	31(1)
C(6)	5511(8)	3842(1)	-2616(3)	31(1)
C(7)	5776(8)	3403(1)	-2891(3)	32(1)
C(8)	7416(8)	3354(2)	-3538(3)	33(1)
C(9)	7319(8)	2931(2)	-3923(3)	35(1)
C(10)	8959(9)	2891(2)	-4560(3)	48(2)
C(11)	3400(9)	4294(2)	-1695(3)	37(1)
C(12)	5419(8)	4596(1)	-1489(3)	36(1)
C(13)	5551(8)	4923(2)	-2138(3)	40(1)
C(14)	6547(8)	4760(2)	-2889(3)	37(1)
C(15)	4811(8)	4495(2)	-3432(3)	36(1)
C(16)	4422(8)	4106(2)	-3306(3)	35(1)
C(17)	3076(8)	3339(1)	-913(3)	33(1)
C(18)	3715(8)	3114(2)	-200(3)	36(1)
C(19)	9287(8)	4431(2)	5190(3)	50(2)
C(20)	7205(9)	4468(2)	4489(3)	45(2)
C(21)	6255(8)	4054(2)	4201(3)	35(1)
C(22)	4119(8)	4077(1)	3524(3)	34(1)
C(23)	3277(7)	3656(1)	3193(3)	28(1)
C(24)	980(7)	3695(1)	2561(3)	29(1)
C(25)	1166(7)	3964(1)	1824(3)	29(1)
C(26)	2988(8)	3934(1)	1358(3)	29(1)
C(27)	2988(8)	4165(2)	661(3)	33(1)
C(28)	1139(8)	4433(2)	410(3)	35(1)
C(29)	2701(7)	3377(2)	3859(3)	33(1)
C(30)	3041(8)	2976(2)	3907(3)	35(1)
C(31)	4189(8)	2722(2)	3312(3)	41(1)
C(32)	2453(8)	2612(2)	2550(3)	39(1)
C(33)	1790(8)	2968(2)	1959(3)	36(1)

C(34)	103(8)	3273(2)	2244(3)	32(1)
C(35)	-647(8)	4477(2)	882(3)	37(1)
C(36)	-618(8)	4243(1)	1569(3)	33(1)

Table 3. Bond lengths [Å] and angles [°] for ohj243_0m.

O(1)-C(11)	1.222(5)
O(2)-C(34)	1.224(5)
C(1)-C(2)	1.376(6)
C(1)-C(18)	1.387(6)
C(1)-H(1)	0.9300
C(2)-C(3)	1.369(6)
C(2)-H(2)	0.9300
C(3)-C(4)	1.400(6)
C(3)-H(3)	0.9300
C(4)-C(17)	1.382(6)
C(4)-C(5)	1.520(6)
C(5)-C(11)	1.523(6)
C(5)-C(6)	1.543(6)
C(5)-H(5)	0.9800
C(6)-C(16)	1.492(6)
C(6)-C(7)	1.521(6)
C(6)-H(6)	0.9800
C(7)-C(8)	1.528(6)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.520(6)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.511(7)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(12)	1.514(6)
C(12)-C(13)	1.527(6)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700

C(13)-C(14)	1.535(7)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-C(15)	1.508(6)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(16)	1.315(6)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(18)	1.395(6)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-C(20)	1.537(6)
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-C(21)	1.509(6)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(22)	1.529(5)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(23)	1.531(6)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-C(29)	1.505(6)
C(23)-C(24)	1.555(6)
C(23)-H(23)	0.9800
C(24)-C(25)	1.521(6)
C(24)-C(34)	1.535(6)
C(24)-H(24)	0.9800
C(25)-C(26)	1.381(6)
C(25)-C(36)	1.384(6)
C(26)-C(27)	1.380(6)
C(26)-H(26)	0.9300
C(27)-C(28)	1.385(6)
C(27)-H(27)	0.9300
C(28)-C(35)	1.375(6)
C(28)-H(28)	0.9300
C(29)-C(30)	1.326(6)

C(29)-H(29)	0.9300
C(30)-C(31)	1.509(7)
C(30)-H(30)	0.9300
C(31)-C(32)	1.527(6)
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-C(33)	1.533(6)
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-C(34)	1.506(6)
C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700
C(35)-C(36)	1.369(6)
C(35)-H(35)	0.9300
C(36)-H(36)	0.9300

C(2)-C(1)-C(18)	119.2(4)
C(2)-C(1)-H(1)	120.4
C(18)-C(1)-H(1)	120.4
C(3)-C(2)-C(1)	120.6(4)
C(3)-C(2)-H(2)	119.7
C(1)-C(2)-H(2)	119.7
C(2)-C(3)-C(4)	121.3(5)
C(2)-C(3)-H(3)	119.3
C(4)-C(3)-H(3)	119.3
C(17)-C(4)-C(3)	118.0(4)
C(17)-C(4)-C(5)	119.1(4)
C(3)-C(4)-C(5)	122.9(4)
C(4)-C(5)-C(11)	108.9(4)
C(4)-C(5)-C(6)	116.0(4)
C(11)-C(5)-C(6)	112.3(4)
C(4)-C(5)-H(5)	106.3
C(11)-C(5)-H(5)	106.3
C(6)-C(5)-H(5)	106.3
C(16)-C(6)-C(7)	111.4(4)
C(16)-C(6)-C(5)	107.7(4)
C(7)-C(6)-C(5)	110.0(4)
C(16)-C(6)-H(6)	109.2
C(7)-C(6)-H(6)	109.2
C(5)-C(6)-H(6)	109.2

C(6)-C(7)-C(8)	114.0(4)
C(6)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7A)	108.8
C(6)-C(7)-H(7B)	108.8
C(8)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7
C(9)-C(8)-C(7)	113.7(4)
C(9)-C(8)-H(8A)	108.8
C(7)-C(8)-H(8A)	108.8
C(9)-C(8)-H(8B)	108.8
C(7)-C(8)-H(8B)	108.8
H(8A)-C(8)-H(8B)	107.7
C(10)-C(9)-C(8)	112.6(4)
C(10)-C(9)-H(9A)	109.1
C(8)-C(9)-H(9A)	109.1
C(10)-C(9)-H(9B)	109.1
C(8)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.8
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(1)-C(11)-C(12)	119.1(5)
O(1)-C(11)-C(5)	119.9(4)
C(12)-C(11)-C(5)	120.9(4)
C(11)-C(12)-C(13)	114.4(4)
C(11)-C(12)-H(12A)	108.7
C(13)-C(12)-H(12A)	108.7
C(11)-C(12)-H(12B)	108.7
C(13)-C(12)-H(12B)	108.7
H(12A)-C(12)-H(12B)	107.6
C(12)-C(13)-C(14)	112.8(4)
C(12)-C(13)-H(13A)	109.0
C(14)-C(13)-H(13A)	109.0
C(12)-C(13)-H(13B)	109.0
C(14)-C(13)-H(13B)	109.0
H(13A)-C(13)-H(13B)	107.8
C(15)-C(14)-C(13)	113.4(4)

C(15)-C(14)-H(14A)	108.9
C(13)-C(14)-H(14A)	108.9
C(15)-C(14)-H(14B)	108.9
C(13)-C(14)-H(14B)	108.9
H(14A)-C(14)-H(14B)	107.7
C(16)-C(15)-C(14)	125.0(4)
C(16)-C(15)-H(15)	117.5
C(14)-C(15)-H(15)	117.5
C(15)-C(16)-C(6)	128.4(4)
C(15)-C(16)-H(16)	115.8
C(6)-C(16)-H(16)	115.8
C(4)-C(17)-C(18)	120.7(4)
C(4)-C(17)-H(17)	119.7
C(18)-C(17)-H(17)	119.7
C(1)-C(18)-C(17)	120.2(5)
C(1)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(20)-C(19)-H(19A)	109.5
C(20)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(20)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-C(19)	111.7(4)
C(21)-C(20)-H(20A)	109.3
C(19)-C(20)-H(20A)	109.3
C(21)-C(20)-H(20B)	109.3
C(19)-C(20)-H(20B)	109.3
H(20A)-C(20)-H(20B)	107.9
C(20)-C(21)-C(22)	113.4(4)
C(20)-C(21)-H(21A)	108.9
C(22)-C(21)-H(21A)	108.9
C(20)-C(21)-H(21B)	108.9
C(22)-C(21)-H(21B)	108.9
H(21A)-C(21)-H(21B)	107.7
C(21)-C(22)-C(23)	113.0(4)
C(21)-C(22)-H(22A)	109.0
C(23)-C(22)-H(22A)	109.0
C(21)-C(22)-H(22B)	109.0
C(23)-C(22)-H(22B)	109.0

H(22A)-C(22)-H(22B)	107.8
C(29)-C(23)-C(22)	111.9(4)
C(29)-C(23)-C(24)	107.0(4)
C(22)-C(23)-C(24)	110.8(4)
C(29)-C(23)-H(23)	109.0
C(22)-C(23)-H(23)	109.0
C(24)-C(23)-H(23)	109.0
C(25)-C(24)-C(34)	107.6(4)
C(25)-C(24)-C(23)	116.0(4)
C(34)-C(24)-C(23)	110.8(4)
C(25)-C(24)-H(24)	107.3
C(34)-C(24)-H(24)	107.4
C(23)-C(24)-H(24)	107.3
C(26)-C(25)-C(36)	116.8(5)
C(26)-C(25)-C(24)	123.6(4)
C(36)-C(25)-C(24)	119.5(4)
C(27)-C(26)-C(25)	121.3(4)
C(27)-C(26)-H(26)	119.3
C(25)-C(26)-H(26)	119.3
C(26)-C(27)-C(28)	120.3(5)
C(26)-C(27)-H(27)	119.8
C(28)-C(27)-H(27)	119.8
C(35)-C(28)-C(27)	119.1(5)
C(35)-C(28)-H(28)	120.4
C(27)-C(28)-H(28)	120.4
C(30)-C(29)-C(23)	126.8(5)
C(30)-C(29)-H(29)	116.6
C(23)-C(29)-H(29)	116.6
C(29)-C(30)-C(31)	125.4(5)
C(29)-C(30)-H(30)	117.3
C(31)-C(30)-H(30)	117.3
C(30)-C(31)-C(32)	112.4(4)
C(30)-C(31)-H(31A)	109.1
C(32)-C(31)-H(31A)	109.1
C(30)-C(31)-H(31B)	109.1
C(32)-C(31)-H(31B)	109.1
H(31A)-C(31)-H(31B)	107.8
C(31)-C(32)-C(33)	114.7(4)
C(31)-C(32)-H(32A)	108.6
C(33)-C(32)-H(32A)	108.6

C(31)-C(32)-H(32B)	108.6
C(33)-C(32)-H(32B)	108.6
H(32A)-C(32)-H(32B)	107.6
C(34)-C(33)-C(32)	114.3(4)
C(34)-C(33)-H(33A)	108.7
C(32)-C(33)-H(33A)	108.7
C(34)-C(33)-H(33B)	108.7
C(32)-C(33)-H(33B)	108.7
H(33A)-C(33)-H(33B)	107.6
O(2)-C(34)-C(33)	120.3(4)
O(2)-C(34)-C(24)	118.8(4)
C(33)-C(34)-C(24)	120.9(4)
C(36)-C(35)-C(28)	119.6(5)
C(36)-C(35)-H(35)	120.2
C(28)-C(35)-H(35)	120.2
C(35)-C(36)-C(25)	122.8(5)
C(35)-C(36)-H(36)	118.6
C(25)-C(36)-H(36)	118.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ohj243_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	31(2)	53(2)	44(2)	5(2)	7(2)	10(2)
O(2)	24(2)	53(2)	40(2)	2(2)	4(2)	-4(2)
C(1)	40(3)	43(4)	24(3)	-1(3)	4(3)	12(3)
C(2)	28(3)	41(4)	34(3)	2(3)	0(2)	3(2)
C(3)	27(3)	41(3)	29(3)	-3(3)	6(2)	-1(2)
C(4)	24(2)	35(3)	28(3)	-5(2)	-3(2)	-2(2)
C(5)	22(2)	36(3)	34(3)	-3(3)	-1(2)	-4(2)
C(6)	21(2)	39(3)	33(3)	1(3)	5(2)	-1(2)
C(7)	27(2)	40(3)	29(3)	-1(2)	2(2)	0(2)
C(8)	31(3)	38(3)	31(3)	-1(3)	6(2)	-1(2)
C(9)	28(3)	41(4)	36(3)	-2(3)	9(2)	6(2)
C(10)	46(3)	54(4)	45(4)	-5(3)	12(3)	5(3)
C(11)	32(3)	50(4)	28(3)	6(3)	1(2)	4(3)
C(12)	31(3)	36(3)	37(3)	-8(3)	-1(2)	4(2)
C(13)	34(3)	35(3)	48(4)	1(3)	1(3)	4(2)
C(14)	32(3)	40(4)	36(3)	2(3)	-4(3)	3(2)
C(15)	33(3)	40(4)	33(3)	5(3)	-8(2)	6(2)
C(16)	31(3)	42(4)	30(3)	-1(3)	-3(2)	0(2)
C(17)	24(2)	36(3)	38(3)	-7(3)	1(2)	-1(2)
C(18)	36(3)	40(4)	33(3)	-3(3)	11(3)	2(2)
C(19)	44(3)	60(4)	40(3)	-4(3)	-12(3)	-12(3)
C(20)	47(3)	44(4)	38(3)	3(3)	-9(3)	-7(3)
C(21)	34(3)	41(4)	28(3)	-4(2)	-2(2)	2(2)
C(22)	33(3)	40(4)	28(3)	0(2)	0(2)	3(2)
C(23)	26(2)	35(3)	23(3)	1(2)	2(2)	2(2)
C(24)	26(2)	35(3)	28(3)	0(2)	7(2)	8(2)
C(25)	21(2)	38(3)	27(3)	-1(2)	-3(2)	2(2)
C(26)	25(3)	30(3)	30(3)	-1(2)	0(2)	3(2)
C(27)	27(3)	45(4)	25(3)	-3(3)	2(2)	-5(2)
C(28)	34(3)	41(3)	29(3)	-1(3)	1(3)	-1(3)
C(29)	30(3)	42(4)	27(3)	1(3)	3(2)	-5(2)
C(30)	34(3)	41(4)	29(3)	9(3)	2(2)	-8(3)
C(31)	41(3)	41(4)	40(3)	4(3)	5(3)	1(2)
C(32)	37(3)	38(4)	46(4)	-1(3)	13(3)	1(2)
C(33)	35(3)	37(4)	34(3)	-8(3)	6(3)	-4(2)

C(34)	28(3)	39(4)	27(3)	7(3)	0(2)	3(2)
C(35)	30(3)	35(3)	42(3)	8(3)	-3(3)	3(2)
C(36)	26(3)	37(3)	38(3)	-2(3)	6(2)	-1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for ohj243_0m.

	x	y	z	U(eq)
H(1)	6381	3012	729	43
H(2)	9066	3454	272	42
H(3)	8053	3813	-912	39
H(5)	2342	3746	-2196	37
H(6)	7081	3951	-2395	37
H(7A)	4215	3297	-3107	39
H(7B)	6393	3239	-2420	39
H(8A)	6982	3555	-3964	40
H(8B)	9038	3410	-3291	40
H(9A)	7755	2729	-3499	42
H(9B)	5700	2875	-4174	42
H(10A)	8516	3086	-4987	71
H(10B)	8834	2620	-4784	71
H(10C)	10570	2940	-4312	71
H(12A)	6910	4447	-1407	43
H(12B)	5245	4729	-978	43
H(13A)	6552	5145	-1900	48
H(13B)	3970	5033	-2309	48
H(14A)	6994	4990	-3204	44
H(14B)	7974	4603	-2707	44
H(15)	3951	4616	-3890	44
H(16)	3326	3978	-3698	42
H(17)	1560	3310	-1207	40
H(18)	2632	2933	-25	43
H(19A)	8789	4277	5629	75
H(19B)	9780	4699	5382	75
H(19C)	10594	4294	4999	75
H(20A)	5938	4626	4671	53
H(20B)	7734	4612	4037	53

H(21A)	5795	3906	4661	42
H(21B)	7516	3901	4003	42
H(22A)	4542	4241	3080	41
H(22B)	2816	4213	3734	41
H(23)	4533	3531	2928	34
H(24)	-257	3813	2846	35
H(26)	4239	3755	1518	35
H(27)	4236	4140	358	39
H(28)	1106	4581	-70	42
H(29)	2037	3498	4281	40
H(30)	2531	2841	4344	42
H(31A)	4809	2473	3580	49
H(31B)	5517	2872	3151	49
H(32A)	1008	2505	2719	47
H(32B)	3149	2396	2261	47
H(33A)	3235	3109	1875	43
H(33B)	1071	2858	1437	43
H(35)	-1867	4664	734	44
H(36)	-1849	4274	1878	40