Supporting Information

Catalytic Asymmetric [4+2]-Cycloaddition of Dienes with Aldehydes

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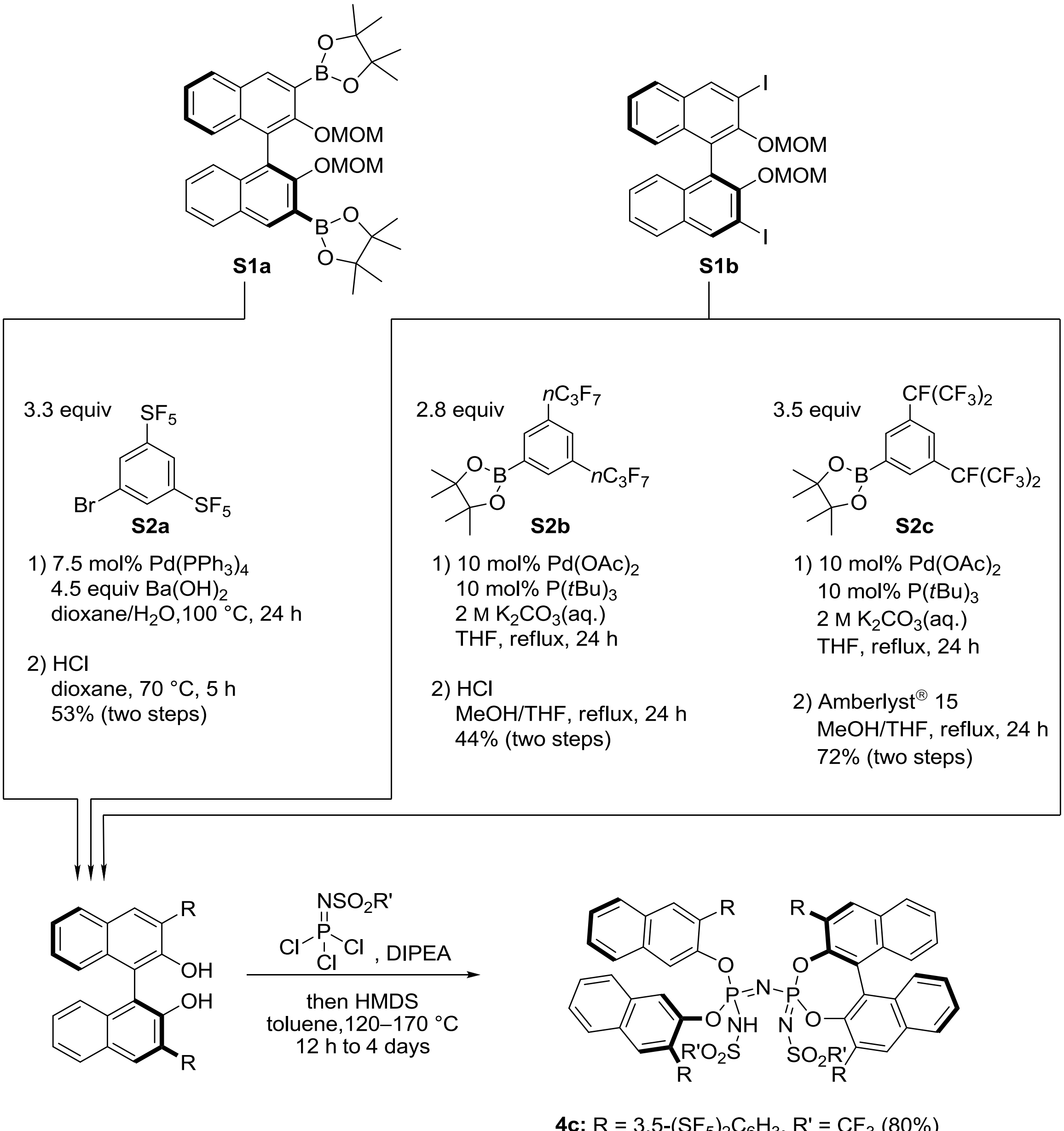
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Aldehydes were distilled and stored under argon prior to use. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin layer chromatography (TLC) on silica gel pre-coated plastic sheets (0.2 mm, Macherey-Nagel) or glass plates (SIL G-25 UV_{254}, 0.25 mm, (Macherey-Nagel). Visualization was accomplished by irradiation with UV light at 254 nm and/or phosphomolybdic acid (PMA) stain. PMA stain: PMA (10 g) in EtOH (100 mL). Column chromatography was performed on Merck silica gel (60, particle size 0.040–0.063 mm). NMR spectra were recorded on Bruker AV-500, Bruker AV-400 or Bruker AV-300 spectrometer in deuterated solvents. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ δ 7.26 ppm; CD_2Cl_2 δ 5.32 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext = sextet, h = heptet, m = multiplet, br = broad), coupling constants (Hz) and integration. ^{13}C chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.16 ppm; CD_2Cl_2 δ 53.84 ppm). ^{19}F, ^{31}P NMR spectra were referenced in ppm from CCl_3F and H_3PO_4, respectively. High resolution mass spectra were determined on a Bruker APEX III FTMS (7 T magnet). All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds. Optical rotations were determined with Autopol IV polarimeter (Rudolph Research Analytical) at 589 nm and 20 or 25 °C. Data are reported as follows: $[\alpha]_{\lambda}^{temp}$, concentration (*c*; g/100 mL), and solvents. Enantiomeric ratios (e.r.) were determined by GC or HPLC analysis employing a chiral stationary phase column specified in the individual experiment, by comparing the samples with the appropriate racemic mixtures. Diastereomeric ratios (d.r.) were determined by ^{1}H NMR spectra of the crude reaction mixtures, GC or HPLC analysis employing a chiral stationary phase. The crystals were measured and analyzed in the department of Chemical Crystallography and Electron Microscopy at Max-Planck-Institut für Kohlenforschung. Data were face-indexed absorption corrected and scaled using the program SADABS (Bruker AXS, 2014). The structure was solved and refined using the programs SHELXS and SHELXL, both programs from G. M. Sheldrick (Göttingen, 2014).

Synthesis and Characterization of Chiral Imidodiphosphorimidates (IDPis)

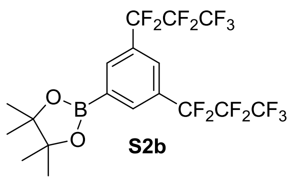


S3a: R = 3,5-$(SF_5)_2C_6H_3$
S3b: R = 3,5-$(nC_3F_7)_2C_6H_3$
S3c: R = 3,5-$(CF(CF_3)_2)_2C_6H_3$

4c: R = 3,5-$(SF_5)_2C_6H_3$, R' = CF_3 (80%)
4d: R = 3,5-$(nC_3F_7)_2C_6H_3$, R' = CF_3 (90%)
4e: R = 3,5-$(SF_5)_2C_6H_3$, R' = C_2F_5 (71%)
4f: R = 3,5-$(CF(CF_3)_2)_2C_6H_3$, R' = CF_3 (53%)

Figure S1. Synthesis of IDPis **4c–4f**.

2-(3,5-Bis(perfluoropropyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborol (S2b)



S2b

To a flame-dried Schlenk flask charged with activated copper powder (13 g, 0.20 mol, 8.0 equiv) were added degassed dry DMF (65 mL), 1,3-dibromobenzene (6.0 g, 25 mmol, 1.0 equiv), and perfluoropropyl iodide (20 g, 69 mmol, 2.8 equiv) under argon at room temperature. The mixture was then heated to 100 °C for 2 days. Upon completion of the reaction, the reaction mixture was cooled to room temperature, diluted with water (65 mL), filtered through celite, and washed with Et_2O (150 mL). The filtrate was washed with HCl (1.0 M, aq., 100 mL) and extracted with Et_2O (2×150 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Filtration through a short pad of silica gel using pentane as an eluent afforded 1,3-bis(perfluoropropyl)benzene (7.5 g, 18 mmol, 68%) as a colorless liquid which was then used for the next step without further purification.

To a flame-dried Schlenk flask charged with bis(1,5-cyclooctadiene)di-μ-methoxydiiridium(I) (0.31 g, 0.46 mmol, 0.05 equiv), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.25 g, 0.92 mmol, 0.10 equiv), bis(pinacolato)diboron (3.5 g, 14 mmol, 1.5 equiv), and 1,3-bis(perfluoropropyl)benzene (3.8 g, 9.2 mmol, 1.0 equiv) was added dry THF (54 mL) under argon at room temperature. The mixture was then heated to 80 °C for 16 h. Upon completion of the reaction monitored by TLC, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. Filtration through a short pad of silica gel using hexanes as an eluent afforded 2-(3,5-bis(perfluoropropyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S2b**, 4.7 g, 93%) as a colorless solid which was then used for the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 1.7 Hz, 2H), 7.85 (s, 1H), 1.37 (s, 12H).

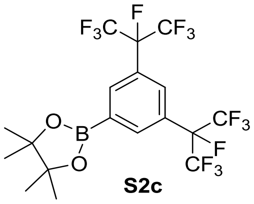
^{11}B NMR (160 MHz, $CDCl_3$): δ 30.22.

^{13}C NMR (126 MHz, $CDCl_3$): 136.5 (t, *J* = 6.0 Hz, 2C), 131.4 (br, 1C), 129.3 (t, *J* = 24.7 Hz, 2C), 127.8 (q, *J* = 6.6 Hz, 1C), 118.1 (qt, *J* = 288, 34 Hz, 2C), 114.9 (tt, *J* = 256, 31 Hz, 2C), 108.7 (tq, *J* = 264, 38 Hz, 2C), 85.03 (s, 2C), 25.0 (s, 4C).

^{19}F NMR (470 MHz, $CDCl_3$): δ –126.2 (s, 4F), –112.1 (q, *J* = 9.8 Hz, 4F), –80 (t, *J* = 9.8 Hz, 6F).

HRMS (EI) (*m*/*z*): calculated for $C_{18}H_{15}O_2B_1F_{14}$ [M]: 540.0940; found: 540.0942.

2-(3,5-Bis(perfluoropropan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S2c)



S2c

To a flame-dried Schlenk flask charged with activated copper powder (13 g, 0.20 mol, 8.0 equiv) were added degassed dry DMF (70 mL), 1,3-dibromobenzene (6.0 g, 25 mmol, 1.0 equiv), and heptafluoro-2-iodopropane (26 g, 87 mmol, 3.5 equiv) under argon at room temperature. The mixture was then heated to 100 °C for 2 d. Upon completion of the reaction, the reaction mixture was cooled to room temperature, diluted with water (70 mL), filtered through celite, and washed with Et_2O (150 mL). The filtrate was washed with HCl (1.0 M, aq., 100 mL) and extracted with Et_2O (2×150 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Filtration through a short pad of silica gel using pentane as an eluent afforded 1,3-bis(perfluoropropan-2-yl)benzene (5.1 g, 12 mmol, 50%) as a colorless liquid which was then used for the next step without further purification.

To a flame-dried Schlenk flask charged with bis(1,5-cyclooctadiene)di-μ-methoxydiiridium(I) (0.18 g, 0.27 mmol, 0.04 equiv), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.14 g, 0.53 mmol, 0.08 equiv), bis(pinacolato)diboron (2.5 g, 10 mmol, 1.5 equiv), and 1,3-bis(perfluoropropan-2-yl)benzene (2.8 g, 6.7 mmol, 1.0 equiv) was added dry THF (30 mL) under argon at room temperature. The mixture was then heated to 80 °C for 16 h. Upon completion of the reaction monitored by TLC, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. Filtration through a short pad of silica gel using hexanes as an eluent afforded 2-(3,5-bis(perfluoropropan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S2c**, 3.1 g, 5.8 mmol, 86%) as a colorless solid which was then used for the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, *J* = 1.8 Hz, 2H), 7.90 (s, 1H), 1.37 (s, 12H).

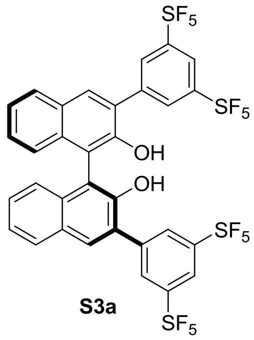
^{13}C NMR (126 MHz, $CDCl_3$): δ 134.3 (d, *J* = 10.1 Hz), 127.4 (dd, *J* = 20.8, 2.5 Hz), 125.4 (t, *J* = 11.5 Hz), 120.3 (qd, *J* = 286.7, 27.9 Hz), 91.1 (dp, *J* = 203.6, 33.2 Hz), 84.8, 24.8.

^{11}B NMR (160 MHz, $CDCl_3$): δ 30.37.

^{19}F NMR (470 MHz, $CDCl_3$): δ –75.62 (d, *J* = 7.3 Hz, 12F), –182.48 (hept, *J* = 7.3 Hz, 2F).

HRMS (EI) (*m*/*z*): calculated for $C_{18}H_{15}O_2B_1F_{14}$ [M]: 540.0940; found: 540.0942.

(*S*)-3,3'-Bis(3,5-bis(pentafluoro-λ^6-sulfanyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (S3a)



S3a

To a three-necked round bottom flask with a condenser were added barium hydroxide octahydrate (2.3 g, 7.2 mmol, 4.5 equiv), a 1,4-dioxane/H_2O solution (3:1, 30 mL), (*S*)-2,2'-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthyl]-3,3'-diyl)bis(4,4,-5,5-tetramethyl-1,3,2-dioxaborolane)[25] (**S1a**, 1.0 g, 1.6 mmol, 1.0 equiv), and 2,4-bis(pentafluorosulfanyl)bromobenzene (**S2a**, 2.17 g, 5.3 mmol, 3.3 equiv). After degassing the reaction mixture with argon for 20 min, tetrakis(triphenylphosphine)palladium (0.14 g, 0.12 mmol, 0.075 equiv) was added. The mixture was refluxed for 24 h, then cooled to room temperature, and quenched with HCl (10 mL, 1.0 M, aq.). After extraction with CH_2Cl_2 (3×30 mL), the combined organic layers were successively washed with HCl (60 mL, 1.0 M, aq.), $NaHCO_3$ (60 mL, sat., aq.), and brine (60 mL). The organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. 1,4-dioxane (90 mL) and HCl (30 mL, conc. aq.) were added to the residue and the reaction mixture was stirred at 70 °C for 5 h in a round bottom flask equipped with a condenser. After cooling to room temperature, the reaction solution was extracted with CH_2Cl_2 (3×100 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using 5–10% ethyl acetate/hexanes to give (*S*)-3,3'-Bis(3,5-bis(pentafluoro-λ^6-sulfanyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol[26] (**S3a,** 1.0 g, 1.06 mmol, 66%) as a colorless solid.

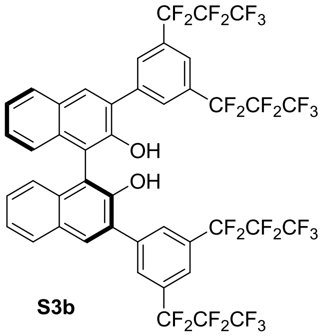
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, *J* = 1.9 Hz, 4H), 8.17 (t, *J* = 1.9 Hz, 2H), 8.10 (s, 2H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.50 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 2H), 7.44 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.39 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.9, 153.7, 153.6, 153.4, 153.3, 149.8, 139.6, 133.5, 132.7, 130.4, 129.6, 129.1, 127.1, 125.6, 124.1, 123.1, 111.9; δ 153.6 (p, *J* = 18.8 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ 81.94 (p, *J* = 150.5 Hz), 63.09 (d, *J* = 150.5 Hz).

HRMS (ESI–) (*m*/*z*): calculated for $C_{32}H_{17}O_2F_{20}S_4$ $[M–H]^-$: 940.9798; found: 940.9803.

(*S*)-3,3'-Bis(3,5-bis(perfluoropropyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (S3b)



S3b

To a flame-dried two-necked round-bottom flask charged with (*S*)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene[27] (**S1b**, 1.9 g, 3.0 mmol, 1.0 equiv), 2-(3,5-bis(perfluoropropyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S2b**, 4.6 g, 8.5 mmol, 2.8 equiv), and palladium(II)-acetate (68 mg, 0.30 mmol, 0.10 equiv) in THF (160 mL) was added K_2CO_3 (2.0 M, aq., 18 mL) at room temperature. After degassing the reaction mixture with argon for 5 min, tri-*tert*-butylphosphine (1.0 M in toluene, 0.30 mmol, 0.10 equiv) was added to the mixture. The reaction mixture was then heated to 85 ºC for 24 h. After cooling down to room temperature, HCl (10%, aq., 20 mL) was added and the reaction mixture was extracted three times with CH_2Cl_2 (3×150 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.32, hexanes/CH_2Cl_2, 10:1) to give (*S*)-3,3'-bis(3,5-bis(perfluoropropyl)phenyl)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (2.7 g, 2.3 mmol, 74%) as a colorless solid (HRMS (ESI+) (*m*/*z*): calculated for $C_{48}H_{26}O_4F_{28}Na_1$ $[M+Na]^+$: 1221.1276; found 1221.1274).

To a round-bottom flask charged with (*S*)-3,3'-bis(3,5-bis(perfluoropropyl)phenyl)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (2.7 g, 2.3 mmol) in MeOH (100 ml) and THF (20 mL) was added HCl (6.0 M. aq., 15 mL) at room temperature. The reaction mixture was then refluxed to 80 ºC for 24 h and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.52, hexanes/CH_2Cl_2, 10:1) to give (*S*)-3,3'-bis(3,5-bis(perfluoropropyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (**S3b**) as a colorless solid which was then recrystallized from a hot solution of hexanes and EtOAc (10:1) to provide the product as a colorless crystalline solid (1.5 g, 1.4 mmol, 60%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23 (d, *J* = 1.7 Hz, 4H), 8.11 (s, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.84–7.81 (m, 2H), 7.49 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.43 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.38 (d, *J* = 0.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 150.0, 139.4, 133.5, 132.6, 131.7, 130.1, 130.0, 129.8, 129.6, 129.1, 128.9, 127.7, 125.4, 124.4, 124.2, 120.9, 119.2, 119.0, 118.8, 117.3, 117.1, 116.9, 116.8, 116.6, 116.4, 115.1, 114.9, 114.7, 113.4, 113.2, 113.0, 111.9, 110.7, 110.4, 109.1, 108.9, 108.6, 108.4, 107.1, 106.9; δ 131.7 (t, *J* = 6.0 Hz), 130.0 (t, *J* = 25.0 Hz), 124.4 (p, *J* =

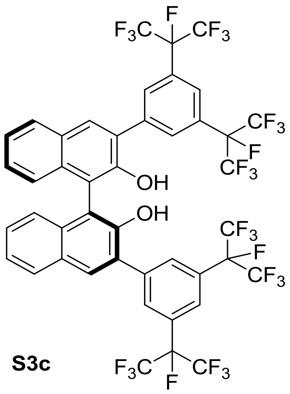
6.5 Hz), 118.1 (qt, J = 288.0, 34.0 Hz), 115.1 (tt, J = 256.0, 32.5 Hz), 108.8 (th, J = 265.0, 38.0 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ –79.92 (t, J = 9.8 Hz), –111.91 (q, J = 9.8 Hz), –126.16 (br s).

HRMS (ESI–) (m/z): calculated for $C_{44}H_{17}O_2F_{28}$ $[M–H]^-$: 1109.0787; found: 1109.0790.

$[\alpha]_D^{25}$: –20.6 (c = 0.36, CH_2Cl_2).

(*S*)-3,3'-Bis(3,5-bis(perfluoropropan-2-yl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (S3c)



S3c

To a flame-dried two-necked round-bottom flask charged with (*S*)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene[27] (**S1b**, 0.25 g, 0.4 mmol, 1.0 equiv), 2-(3,5-bis(perfluoropropan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S2c**, 0.76 g, 1.4 mmol, 3.5 equiv), and palladium(II)-acetate (9.0 mg, 0.04 mmol, 0.10 equiv) in THF (21 mL) was added K_2CO_3 (2.0 M, aq., 2.4 mL) at room temperature. After degassing the reaction mixture with argon for 5 min, tri-*tert*-butylphosphine (1.0 M in toluene, 0.04 mmol, 0.10 equiv) was added to the mixture. The reaction mixture was then heated to 85 ºC for 24 h. After cooling down to room temperature, HCl (10%, aq., 2.5 mL) was added and the reaction mixture was extracted three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.56, hexanes/EtOAc, 20:1) to give (*S*)-3,3'-bis(3,5-bis(perfluoropropan-2-yl)phenyl)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (0.37 g, 0.31 mmol, 77%) as a colorless solid (HRMS (ESI+) (m/z): calculated or $C_{48}H_{26}O_4F_{28}Na_1$ $[M+Na]^+$: 1221.1276; found 1221.1285).

To a round-bottom flask charged with (*S*)-3,3'-bis(3,5-bis(perfluoropropan-2-yl)phenyl)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (0.35 g, 0.29 mmol) in MeOH (6 mL) and THF (6 mL) was added Amberlyst® 15 ion-exchange resin (0.70 g) at room temperature. The reaction mixture was then refluxed at 80 ºC for 24 h. The residue was purified by column chromatography on silica gel (R_f 0.42, hexanes/CH_2Cl_2, 20:1) to give (*S*)-3,3'-Bis(3,5-bis(perfluoropropan-2-yl)phenyl)-[1,1'-binaphthalene]-2,2'-diol (**S3c,** 0.30 g, 0.27 mmol, 93%) as a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (d, *J* = 1.7 Hz, 4H), 8.10 (s, 2H), 8.04–7.99 (m, 2H), 7.87 (s, 2H), 7.49 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.43 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2H), 7.24 (ddt, *J* = 8.4, 1.4, 0.7 Hz, 2H), 5.38 (d, *J* = 0.7 Hz, 2H).

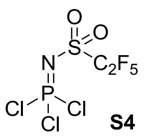
^{13}C NMR (151 MHz, $CDCl_3$): δ 150.0, 139.74, 139.72, 139.70, 133.4, 132.6, 129.9, 129.8, 129.6, 129.1, 128.8, 128.3, 128.2, 128.12, 128.10, 128.0, 125.4, 124.2, 123.5, 123.3, 122.3, 122.23, 122.15, 121.6, 121.4, 119.7, 119.5, 117.8, 117.6, 112.0, 92.5, 92.3, 92.0, 91.8, 91.6, 91.1, 90.9, 90.7, 90.5, 90.2; δ 139.72 (t, *J* = 2.3 Hz), 129.87 (d, *J* = 10.2 Hz), 128.18 (dd, *J* = 20.7, 2.3 Hz), 122.23 (t, *J* = 12.0 Hz), 120.73 (qd, *J* = 287.0, 28.0 Hz), 91.36 (dhept, *J* = 204.0, 33.0 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ –75.43, –75.44, –181.96, –181.97, –181.99, –182.00, –182.02, –182.04, –182.05.

HRMS (ESI–) (*m/z*): calculated for $C_{44}H_{17}O_2F_{28}$ $[M–H]^-$: 1109.0787; found: 1109.0790.

$[\alpha]_D^{25}$: –27.8 (*c* = 0.26, CH_2Cl_2).

((Perfluoroethyl)sulfonyl)phosphorimidoyl trichloride (S4)



S4

In a flame-dried flask under argon equipped with a magnetic stirring bar, which was connected to a gas wash bottle containing a NaOH solution (10 wt%, aq.), a cooling trap, and a vacuum pump in sequence, a mixture of 1,1,2,2,2-pentafluoroethane-1-sulfonamide (10.1 g, 51.0 mmol, 1.0 equiv) and PCl_5 (11.2 g, 54.0 mmol, 1.06 equiv) was heated to 100 ºC under air pressure for 1 h. The reaction was monitored by ^{1}H, ^{19}F, and ^{31}P NMR to ensure full consumption of sulfonamide. Pumping off the excess amount of PCl_5 under reduced pressure to give the title compound **S4** (15.2 g, 45.5 mmol, 90%) as colorless oil.

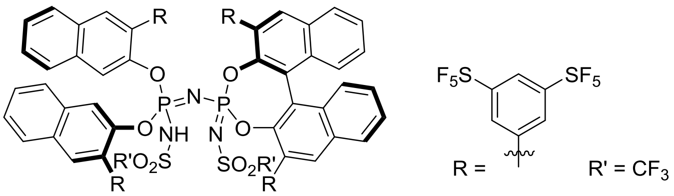
^{13}C NMR (126 MHz, $CDCl_3$): δ 121.2, 121.0, 120.8, 119.0, 118.7, 118.4, 116.7, 116.44, 116.42, 116.2, 114.4, 114.1, 113.9, 113.5, 112.1, 111.8, 111.5, 111.2, 109.8, 109.5, 109.2, 108.8.

^{19}F NMR (470 MHz, $CDCl_3$): δ –78.8 (d, *J* = 13.5 Hz, 3F), –116.6 (d, *J* = 14.3 Hz, 2F).

^{31}P NMR (203 MHz, $CDCl_3$): δ 15.7.

HRMS (ESI+) (*m/z*): calculated for $C_2H_1N_1O_2Cl_3F_5P_1S_1$ $[M+H]^+$: 333.8451; found: 333.8452.

_N_,_N'_-((11b_S_,11b'_S_)-Azanediylbis(2,6-bis(3,5-bis(pentafluoro-λ^6-sulfanyl)phenyl)-4λ^5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(1,1,1-trifluoromethanesulfonamide) (4c)



4c

In a flame-dried flask under argon, diol **S3a** (0.1 g, 0.1 mmol, 2.1 equiv) was dissolved in toluene (1.4 mL). Subsequently, _N_,_N_-diisopropylethylamine (DIPEA, 0.14 mL, 0.80 mmol, 16.0 equiv), followed by trifluoromethylsulfonyl trichlorophosphazene ($P(NTf)Cl_3$, 30.4 mg, 0.1 mmol, 2.1 equiv) were added and the solution was stirred at room temperature for 5 min. 1,1,1,3,3,3-hexamethyldisilazane (HMDS, 10.4 mg, 0.05 mmol, 1.0 equiv) was added to the reaction mixture, which was stirred at stirred at 120 °C for 12 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using 20–40% ethyl acetate/hexanes as the eluent affording a colorless solid. The solid was dissolved in CH_2Cl_2 (25 mL) and stirred with HCl (6.0 M, aq., 25 mL) for 30 min. The organic layer was separated, washed with HCl (6.0 M, aq., 25 mL), and concentrated under reduced pressure to provide compound **4c** as a colorless solid (90 mg, 0.04 mmol, 80%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.20 (br s, 2H), 8.18 (t, _J_ = 1.75 Hz, 2H), 8.16–8.15 (m, 2H), 8.13 (br s, 2H), 7.97–7.94 (m, 2H), 7.92–7.91 (m, 2H), 7.87 (d, _J_ = 1.60 Hz, 4H), 7.80–7.75 (m, 4H), 7.66 (t, _J_ = 7.30 Hz, 2H), 7.48 (br s, 4H), 7.40–7.37 (m, 2H), 7.36 (s, 2H), 7.07 (d, _J_ = 8.60 Hz, 2H), 6.58 (s, 2H), 4.93 (br s, 2H).

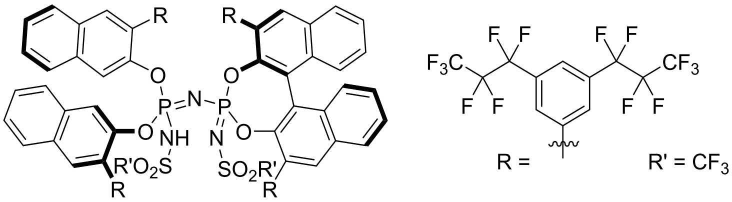
^{13}C NMR (126 MHz, CD_2Cl_2): δ 154.0, 153.9, 153.8, 153.6, 144.0, 141.4, 138.6, 138.2, 134.0, 133.0, 132.6, 132.4, 132.3, 131.5, 130.84, 130.78, 130.1, 129.9, 129.61, 129,56, 128.7, 128.6, 127.9, 127.8, 127.14, 127.11, 124.5, 124.1, 123.9, 121.7, 120.3, 117.7.

^{19}F NMR (470 MHz, CD_2Cl_2): δ 80.8 (sext, _J_ = 152.0 Hz, 8F), 63.1 (d, _J_ = 150.6 Hz, 16F), 62.3 (d, _J_ = 150.0 Hz, 16F), –79.5 (s, 6F).

^{31}P NMR (202 MHz, CD_2Cl_2): δ –15.3.

HRMS (ESI–) (_m/z_): calculated for $C_{66}H_{32}N_3O_8F_{46}P_2S_{10}$ $[M-H]^-$: 2249.8143; found: 2249.8128.

***N*,*N*'-((11b*S*,11b'*S*)-Azanediylbis(2,6-bis(3,5-bis(perfluoropropyl)phenyl)-4λ⁵-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(1,1,1-trifluoromethanesulfonamide) (4d)**



4d

In a flame-dried flask under argon, diol **S3b** (0.60 g, 0.54 mmol, 2.1 equiv) was dissolved in toluene (5.0 mL, 0.1 M). Subsequently, $P(NTf)Cl_3$ (0.15 g, 0.54 mmol, 2.1 equiv), followed by DIPEA (0.53 g, 4.1 mmol, 16.0 equiv) were added and the solution was stirred at room temperature for 15 min. HMDS (42 mg, 0.26 mmol, 1.0 equiv) was added to the reaction mixture, which was stirred at room temperature for 10 min, and heated to 130 °C for 3 days. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (5 mL), and stirred with HCl (6.0 M, aq., 3 mL) for 30 min. The organic phase was then separated, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.58, hexanes/EtOAc, 5:1) to afford a colorless solid, which was then acidified in CH_2Cl_2 (6 mL) with HCl (6.0 M, aq., 6 mL) by stirring at room temperature for 30 min. The organic layer was diluted with CH_2Cl_2 (14 mL), washed with HCl (6.0 M, aq., 2×20 mL), followed by drying under reduced pressure to provide compound **4d** as a colorless solid (0.60 g, 0.23 mmol, 90%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12–8.05 (m, 4H), 7.93–7.86 (m, 4H), 7.77–7.64 (m, 13H), 7.61 (t, J = 7.6 Hz, 2H), 7.40–7.35 (m, 2H), 7.32 (s, 4H), 7.13 (d, J = 8.6 Hz, 2H), 6.57 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.0, 141.8, 138.2, 138.0, 133.7, 132.3, 132.0, 132.0, 131.9, 131.6, 131.2, 130.9, 130.7, 130.4, 130.21, 130.15, 130.11, 130.0, 129.9, 129.7, 129.2, 128.7, 128.0, 127.2, 127.1, 126.8, 125.3, 123.67, 123.66, 123.65, 122.73, 121.72, 121.52, 121.45, 121.42, 121.24, 121.18, 120.9, 120.2, 119.4, 119.22, 119.17, 119.0, 118.9, 118.7, 117.6, 117.2, 116.94, 116.88, 116.8, 116.71, 116.67, 116.61, 116.55, 116.47, 116.4, 116.31, 116.30, 116.2, 115.1, 114.9, 114.8, 114.67, 114.66, 114.6, 114.5, 114.42, 114.39, 114.33, 114.26, 114.2, 114.1, 112.7, 112.6, 112.5, 112.4, 112.2, 112.1, 111.6, 111.30, 111.29, 110.99, 110.98, 110.68, 110.68, 110.39, 110.38, 110.07, 110.07, 109.8, 109.5, 109.19, 109.18, 108.89, 108.88, 108.58, 108.58, 108.28, 108.27, 107.97, 107.96, 107.7, 107.4, 107.09, 107.08, 106.78, 106.78, 106.48, 106.47, 106.17, 106.16, 105.86, 105.86, 105.58; δ 130.15 (t, J = 25.0 Hz), 129.90 (t, J = 25.0 Hz), 118.91 (q, J = 319.9 Hz), 118.02 (qt, J = 287.0, 34.0 Hz), 117.82 (qt, J = 287.0, 34.0 Hz), 114.51 (tt, J = 256.9, 30.9 Hz), 114.42 (tt, J = 256.6, 30.8 Hz), 108.73 (th, J = 264.2, 38.0 Hz), 108.43 (th, J = 264.2, 38.0 Hz).

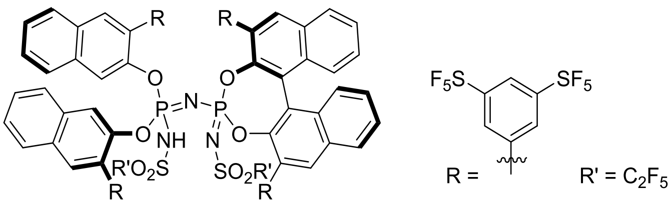
^{19}F NMR (470 MHz, $CDCl_3$): δ –78.94 (s), –80.04 (t, J = 9.3 Hz), –80.20 (t, J = 9.6 Hz), –112.20 (d, J = 276.8 Hz), –112.55 (s), –113.78 (d, J = 276.8 Hz), –126.05 (d, J = 291.0 Hz), –126.11 (s), –126.47 (d, J = 291.0 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ –13.92.

HRMS (ESI–) (m/z): calculated for $C_{90}H_{32}N_3O_8F_{62}P_2S_2$ $[M–H]^-$: 2586.0122; found: 2586.0086.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +208.4 ($c$ = 0.50, $CHCl_3$).

***N*,*N*'-((11b*S*,11b'*S*)-Azanediylbis(2,6-bis(3,5-bis(pentafluoro-λ^6-sulfanyl)phenyl)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(1,1,2,2,2-pentafluoroethane-1-sulfonamide) (4e)**



4e

In a flame-dried flask under argon, diol **S3a** (0.11 g, 0.12 mmol, 2.1 equiv) was dissolved in toluene (1.0 mL, 0.12 M). Subsequently, ((perfluoroethyl)-sulfonyl)phosphorimidoyl trichloride, $P(NSO_2C_2F_5)Cl_3$ (**S4**, 39 mg, 0.12 mmol, 2.1 equiv), followed by DIPEA (0.11 g, 0.89 mmol, 16.0 equiv) were added and the solution was stirred at room temperature for 15 min. HMDS (9.0 mg, 0.06 mmol, 1.0 equiv) was added to the reaction mixture, which was stirred at room temperature for 10 min, and heated to 130 °C for 3 days. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (3 mL), and stirred with HCl (6.0 M, aq., 1 mL) for 30 min. The organic phase was then separated, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.28, hexanes/EtOAc, 2:1) to give a colorless solid, which was then acidified in CH_2Cl_2 (2 mL) with HCl (6.0 M, aq., 2 mL) by stirring at room temperature for 30 min. The organic layer was diluted with CH_2Cl_2 (8 mL), washed with HCl (6.0 M, aq., 2×10 mL), followed by drying under reduced pressure to provide compound **4e** as a colorless solid (93 mg, 0.04 mmol, 71%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17–8.07 (m, 8H), 7.93–7.85 (m, 4H), 7.83 (s, 4H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.72 (ddd, *J* = 8.2, 6.3, 1.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.47–7.35 (m, 6H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.52 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.8, 141.5, 138.4, 137.7, 133.8, 132.5, 132.3, 132.1, 131.9, 131.0, 130.4, 130.23, 130.15, 129.4, 129.0, 128.3, 127.4, 127.3, 127.2, 126.7, 124.2, 123.9, 121.5.

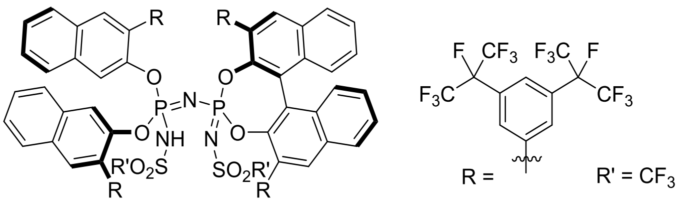
^{19}F NMR (470 MHz, $CDCl_3$): δ 81.14 (p, *J* = 151.0 Hz), 80.97 (p, *J* = 151.0 Hz), 63.32 (d, *J* = 151.0 Hz), 62.51 (d, *J* = 151.0 Hz), –79.01, –117.08.

^{31}P NMR (202 MHz, $CDCl_3$): δ –14.39.

HRMS (ESI–) (*m*/*z*): calculated for $C_{68}H_{32}N_3O_8F_{50}P_2S_{10}$ $[M–H]^-$: 2349.8079; found: 2349.8069.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +201.3 (*c* = 0.15, CH_2Cl_2).

N,N'-((11bS,11b'S)-Azanediylbis(2,6-bis(3,5-bis(perfluoropropan-2-yl)phenyl)-4λ^5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(1,1,1-trifluoromethanesulfonamide) (4f)



4f

In a flame-dried flask under argon, diol **S3c** (0.15 g, 0.14 mmol, 2.1 equiv) was dissolved in toluene (1.0 mL, 0.14 M). Subsequently, $P(NTf)Cl_3$ (38 mg, 0.14 mmol, 2.1 equiv), followed by DIPEA (0.13 g, 0.98 mmol, 16.0 equiv) were added and the solution was stirred at room temperature for 15 min. HMDS (10 mg, 0.06 mmol, 1.0 equiv) was added to the reaction mixture, which was stirred at room temperature for 10 min, and heated to 170 °C for 4 d. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (3 mL), and stirred with HCl (6.0 M, aq., 1 mL) for 30 min. The organic phase was then separated, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (R_f 0.20, hexanes/EtOAc, 4:1) to give a colorless solid, which was then acidified in CH_2Cl_2 (2 mL) with HCl (6.0 M, aq., 2 mL) by stirring at room temperature for 30 min. The organic layer was diluted with CH_2Cl_2 (8 mL), washed with HCl

(6.0 M, aq., 2×10 mL), followed by drying under reduced pressure to provide compound **4f** as a colorless solid (84 mg, 0.03 mmol, 53%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.2 Hz, 2H), 8.01 (s, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.87 (dd, *J* = 8.0, 6.9 Hz, 2H), 7.82 (s, 4H), 7.77 (s, 2H), 7.72 (s, 2H), 7.65 (dd, *J* = 8.7, 6.9 Hz, 3H), 7.63 (d, *J* = 8.7 Hz, 3H), 7.58 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.42 (s, 4H), 7.29 (dd, *J* = 8.7, 6.9 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.63 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 144.3, 141.7, 138.8, 138.7, 134.7, 132.9, 132.3, 132.2, 131.9, 131.04, 130.98, 130.4, 130.2, 130.1, 129.7, 129.30, 129.25, 129.0, 128.6, 128.5, 128.3, 127.9, 127.5, 127.11, 127.06, 126.8, 123.7, 123.35, 123.29, 123.2, 123.11, 123.08, 122.9, 122.8, 121.8, 121.6, 121.45, 121.39, 121.3, 121.20, 121.19, 121.0, 119.7, 119.55, 119.50, 119.4, 119.31, 119.29, 119.1, 117.9, 117.7, 117.62, 117.61, 117.5, 117.42, 117.40, 117.2, 115.5, 92.3, 92.1, 91.8, 91.6, 91.4, 90.9, 90.7, 90.5, 90.3, 90.0; δ 120.41 (qd, *J* = 287.0, 27.0 Hz), 120.35 (qd, *J* = 287.0, 27.0 Hz), 120.15 (qd, *J* = 287.0, 28.0 Hz), 118.67 (q, *J* = 318.0 Hz), 91.16 (dhept, *J* = 205.0, 33.0 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ –74.79, –75.30, –75.92, –76.11, –79.29, –181.21, –182.75.

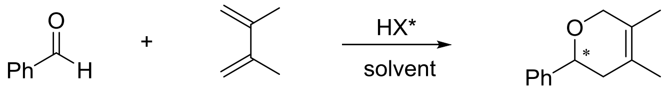
^{31}P NMR (202 MHz, $CDCl_3$): δ –14.31.

HRMS (ESI–) (*m*/*z*): calculated for $C_{90}H_{32}N_3O_8F_{62}P_2S_2$ $[M–H]^-$: 2586.0122; found: 2586.0108.

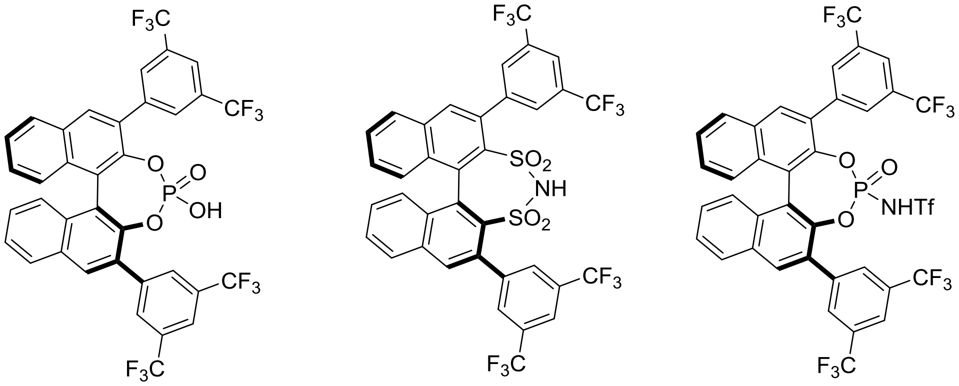
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +235.8 (*c* = 0.44, CH_2Cl_2).

Optimization of Reaction Conditions

Table S1. Comparison of different chiral Brønsted acids[a].



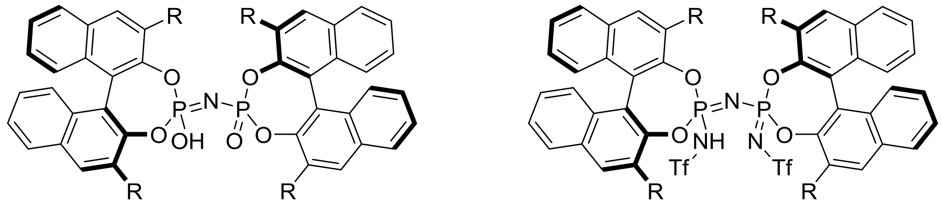
1a **2a** **3a**



phosphoric acid
S5

disulfonimide
S6

N-triflylphosphoramide
S7



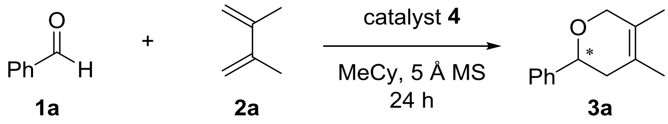
imidodiphosphate (**IDP**)
S8: R = 3,5-$(CF_3)_2C_6H_3$

imidodiphosphorimidate (**IDPi**)
4a: R = C_6H_5
4b: R = 3,5-$(CF_3)_2C_6H_3$

entry	catalyst[b]	HX* (mol%)	T (°C)	t (h)	solvent	conv. (%)[c]	e.r.[d]
1	**S5**	5	22	24	CyH	n.r.	-
2	**S6**	5	22	24	CyH	n.r.	-
3	**S7**	5	22	24	CyH	11	64:36
4	**S8**	5	22	24	CyH	n.r.	-
5	**4a**	5	22	24	CyH	<10	59:41
6	**4b**	5	22	24	CyH	>95	79:21

[a] Unless otherwise indicated, reactions were performed with benzaldehyde (**1a**, 0.02 mmol), 2,3-dimethyl-1,3-butadiene (**2a**, 0.1 mmol), and a catalyst (5 mol%) in cyclohexane (CyH, 0.2 mL) at room temperature for 24 h and no side product was observed. [b] Catalysts were prepared according to the known procedures: **S5**[15], **S6**[16], **S7**[18], **S8**[28], **4a** and **4b**[19]. [c] Conversion ratios were determined by ^{1}H NMR analysis by comparison to 1,2,4,5-tetramethylbenzene as an internal standard after addition of TEA. [d] The enantiomeric ratio was measured by HPLC analysis on a chiral stationary phase.

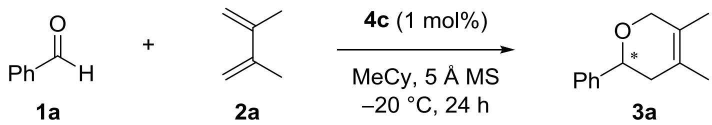
Table S2. Screening IDPis **4b-4c** and optimization[a].



entry	catalyst	HX* (mol%)	MeCy (μL)	T (°C)	conv. (%)[b]	e.r.[c]
1	**4c**	5	200	22	>95	90:10
2	**4b**	5	200	–20	<10	85:15
3	**4c**	1	200	–20	>95	98:2
4[d]	**4c**	1	67	–20	>95	98:2
5	**4c**	0.2	67	–20	>95	98:2

[a] Unless otherwise indicated, reactions were performed with aldehyde **1a** (0.02 mmol), diene **2a** (0.1 mmol), a catalyst, and 5 Å molecular sieves (70 mg/mL) in methylcyclohexane (MeCy) for 24 h and no side product was observed. [b] Conversion ratios were determined by ^{1}H NMR analysis by comparison to 1,2,4,5-tetramethylbenzene as an internal standard after quenching reactions by addition of TEA. [c] The enantiomeric ratio was measured by HPLC analysis on a chiral stationary phase. [d] The reaction was completed within 4 h.

Table S3. Optimization of the ratio of substrates[a].



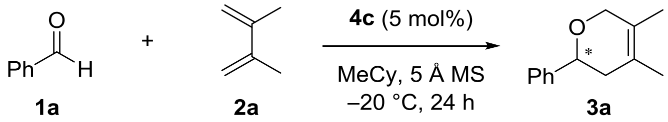
entry	**1a** (mmol)	**2a** (mmol)	conv. (%)[b]	e.r.[c]
1	0.1	0.5	>95	98:2
2	0.1	0.2	>95	98:2
3	0.1	0.12	>95	98:2
4	0.12	0.1	>95	98:2

[a] Unless otherwise indicated, reactions were performed with aldehyde **1a**, diene **2a**, catalyst **4c**, and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –20 °C for 24 h and no side product was observed. [b] Conversion ratios were determined by ^{1}H NMR analysis by comparison to 1,2,4,5-tetramethylbenzene as an internal standard after quenching reactions by addition of TEA. [c] The enantiomeric ratio was measured by HPLC analysis on a chiral stationary phase.

The role of molecular sieves

In the absence of 5 Å molecular sieves, the reaction proceeded slightly slower (Table S4, entry 2). However, the enantioselectivity remained essential the same, suggesting a pure Brønsted acid-catalysis, not a Lewis acid catalysis potentially introduced by the metal species in 5 Å molecular sieves with a formula of $0.7CaO•0.30Na_2O•Al_2O_3•2.0SiO_2•4.5H_2O$.

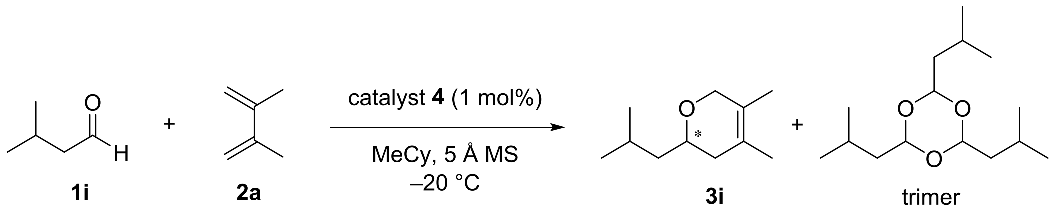
Table S4. Effect of molecular sieves[a].



entry	5 Å MS	conv. (%)[b]	e.r.[c]
1	21 mg	>95	98:2
2	_	92	97.5:2.5

[a] Unless otherwise indicated, reactions were performed with aldehyde **1a** (0.1 mmol), diene **2a** (0.5 mmol), catalyst **4c** (5 mol%), and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –20 °C for 24 h and no side product was observed. [b] Conversion ratios were determined by ^1H NMR analysis by comparison to 1,2,4,5-tetramethylbenzene as an internal standard after quenching reactions by addition of TEA. [c] The enantiomeric ratio was measured by HPLC analysis on a chiral stationary phase.

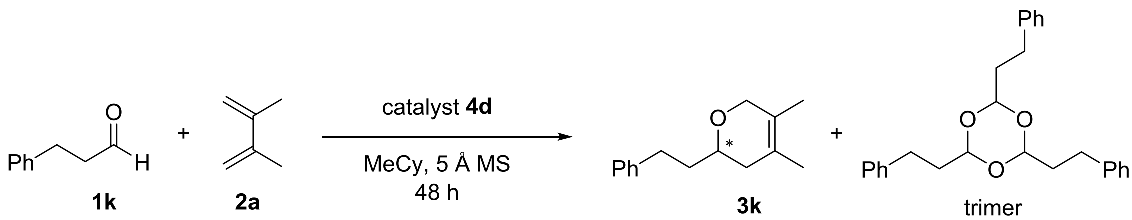
Table S5. Optimization of the reaction between aldehyde **1i** and diene **2a**[a].



entry	catalyst	**2a** (equiv)	t (d)	conv. (%)[b]	**3i** (%)[b]	trimer (%)[b]	e.r.[c]
1	**4b**	5	7	87	7	80	89:11
2	**4c**	5	7	98	55	43	91:9
3	**4c**	10	7	100	99	0	92:8
4	**4d**	10	3	96	96	0	94:6

[a] Reactions were performed on a 0.03 mmol scale of aldehyde **1i** in MeCy (0.1 mL). [b] Yields and conversion ratios were determined by ^{1}H NMR analysis by comparison to triphenylmethane as an internal standard after addition of TEA. [c] The enantiomeric ratio was measured by GC analysis on a chiral stationary phase.

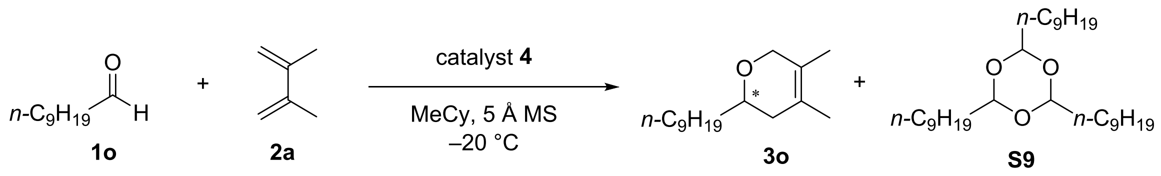
Table S6. Optimization of the reaction between aldehyde **1k** and diene **2a**[a].



entry	HX* (mol%)	**2a** (equiv)	T (°C)	conv. (%)[b]	**3k** (%)[b]	trimer (%)[b]	e.r.[c]
1	1	10	–20	99	7	92	97:3
2	1	20	–20	100	20	80	96:4
3	2	10	–20	99	25	74	95:5
4	1	10	–10	100	76	0	95.5:4.5
5	1	10	–5	97	65	0	94:6
6	1	10	23	100	55	0	92:8

[a] Reactions were performed on a 0.03 mmol scale of aldehyde **1k** in MeCy (0.1 mL). [b] Yields and conversion ratios were determined by ^{1}H NMR analysis by comparison to triphenylmethane as an internal standard after addition of TEA. [c] The enantiomeric ratio was measured by GC analysis on a chiral stationary phase.

Table S7. Optimization of the reaction between aldehyde **1o** and diene **2a**[a].



entry	catalyst	HX* (mol%)	**2a** (equiv)	t (h)	conv. (%)[b]	**3o** (%)[b]	**S9** (%)[b]	e.r.[c]
1	**4c**	1	10	20	94	4.5	89	-
2	**4c**	1	10	57	97	17	79.5	-
3	**4d**	1	10	12	97	34	63	97:3
4	**4d**	1	10	24	97	57	40	97:3
5	**4d**	1	10	48	100	94	trace	97:3
6	**4d**	0.5	10	48	100	94	trace	97:3
7	**4d**	1	5	48	99	54	45	97:3
8	**4d**	3	10	12	95	30.5	65	97:3
9	**4d**	5	10	12	96.5	31	66	97:3

[a] Reactions were performed on a 0.03 mmol scale of aldehyde **1o** in MeCy (0.1 mL). [b] Yields and conversion ratios were determined by ^{1}H NMR analysis by comparison to triphenylmethane as an internal standard after addition of TEA. [c] The enantiomeric ratio was measured by GC analysis on a chiral stationary phase.

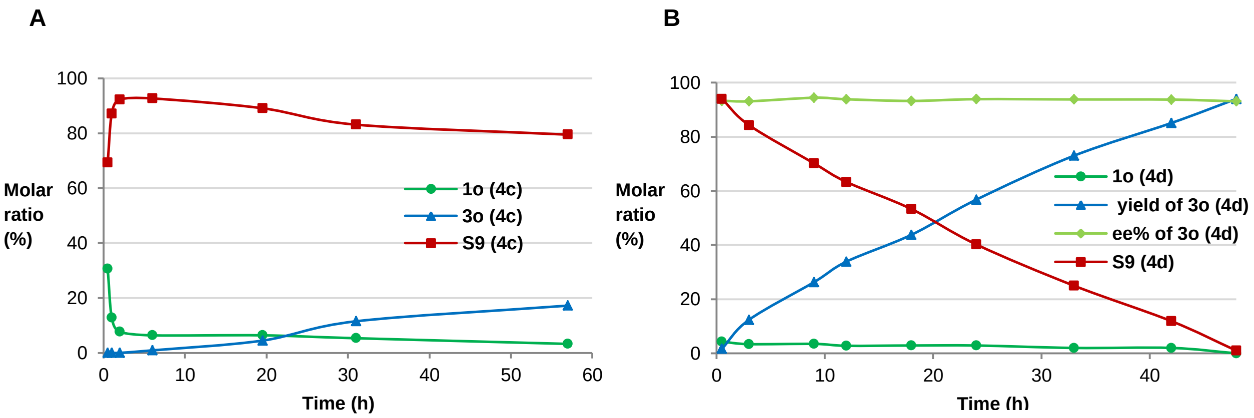
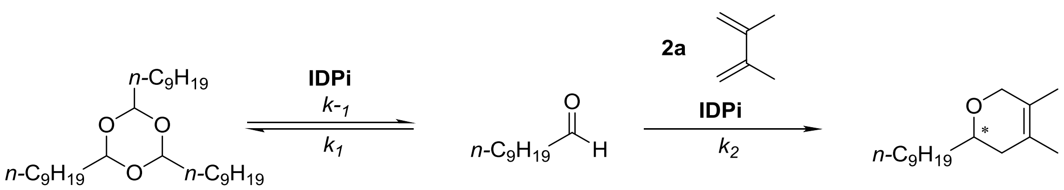


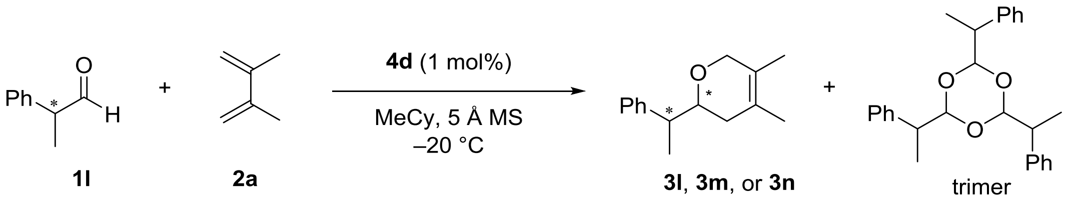
Figure S2. Kinetic experiments of the HDA reaction of aldehyde **1o** and diene **2a**[a].

[a] Reactions were performed with aldehyde **1o** (0.15 mmol), diene **2a** (1.5 mmol), and 1 mol% of catalyst **4c** (**A**) or **4d** (**B**) in MeCy (0.5 mL) at –20 °C. Yields were determined by ^{1}H NMR analysis and the enantiomeric ratio was measured by GC analysis on a chiral stationary phase.

The hetero-Diels–Alder reaction of **1o** and **2a** was investigated using **4c** and **4d** as the catalyst (Fig. S2). In the case of **4c** as the catalyst, the rate of trimerization exceeded the rate of cycloaddition (Fig. S2, A). In contrast, in the presence of catalyst **4d**, the rapidly generated trimer (**S9**) was constantly consumed, furnishing the cycloadduct (**3o**) over time (Fig. S2, B). Trimer **S9** was not afforded in the absence of the catalyst. It was also possible to use trimer **S9** as the starting material for the cycloaddition, producing **3o** in 96% yield with 96:4 e.r. (1 mol% **4d**, –20 °C, 48 h). In all cases, the monomer aldehyde (**1o**) was detected by ^{1}H NMR spectroscopy throughout the reaction, indicating a dynamic equilibrium between aldehyde **1o** and trimer **S9.**



S9 $k_1 > k_{-1}$ **1o** $k_{-1} > k_2$ **3o**



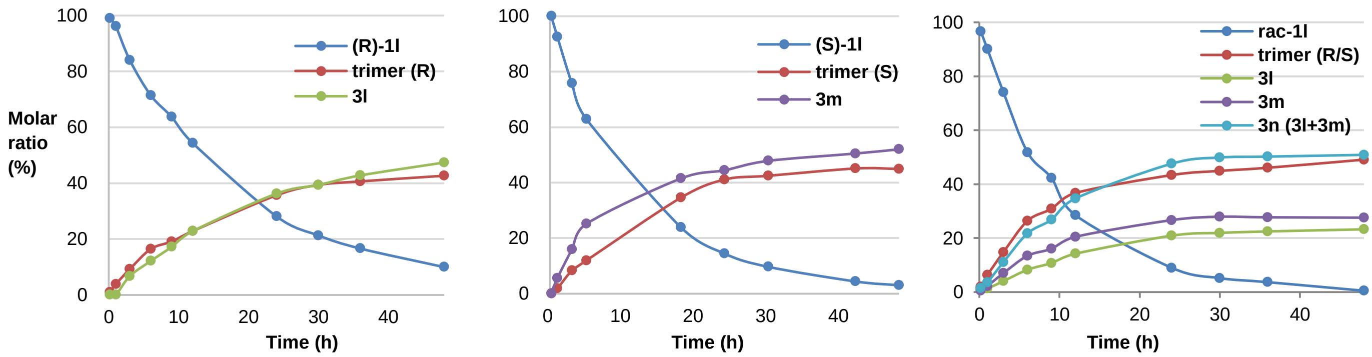


Figure S3. Kinetic experiments of hetero-Diels–Alder reaction of aldehyde **1l** and diene **2a**[a].

[a] Reactions were performed with aldehyde **1l** (0.15 mmol), diene **2a** (1.5 mmol), and 1 mol% of catalyst **4d** in MeCy (0.5 mL) at –20 °C. Yields were determined by ^{1}H NMR analysis.

Despite the improved efficiency of the cycloaddition reaction using catalyst **4d** for most aliphatic aldehydes, the acid catalyzed trimerization of the alpha-branched aldehyde (**1l**) was found to be irreversible and a competitive process to the desired cycloaddition. Consequently, low yields of cycloadducts **3l**, **3m**, and **3n** were observed (Fig. S3).

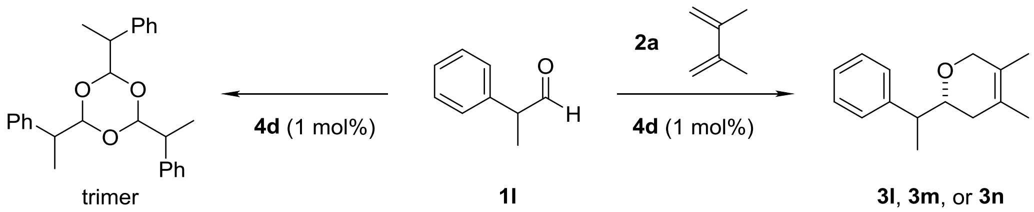
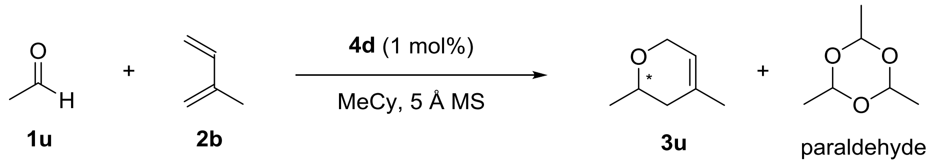


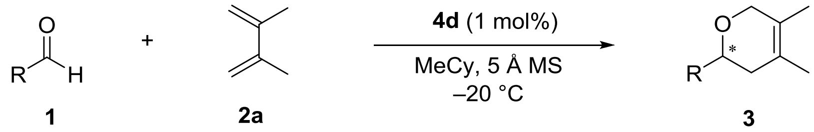
Table S8. Optimization of the reaction between aldehyde **1u** and diene **2b**[a].

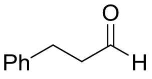
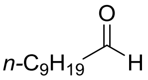
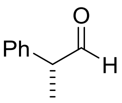
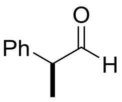


entry	starting material	catalyst	HX* (mol%)	additive	t (d)	**3u** (%)[b]	e.r.[c]
1	**1u** (non-distilled)	**4d**	1	-	2	45	90.5:9.5
2	**1u** (non-distilled)	**4d**	1	-	5	33	90:10
3	**1u** (distilled)	**4d**	1	-	4	1	nd
4[d]	**1u** (distilled)	**4d**	1	-	5	3	nd
5	**1u** (distilled)	**4d**	1	10 mol% acetic acid	2	22	90:10
6	**1u** (distilled)	**4d**	1	15 mol% acetic acid	2	29	91:9
7	**1u** (distilled)	**4d**	1	30 mol% acetic acid	2	27	91:9
8	**1u** (distilled)	**4d**	1	50 mol% acetic acid	2	31	90:10
9	**1u** (distilled)	**4d**	1	100 mol% acetic acid	2	13	86:14
10	**1u** (distilled)	**4d**	1	200 mol% acetic acid	2	12	86.5:13.5
11	**1u** (distilled)	**4d**	1	400 mol% acetic acid	2	10	86.5:13.5
12	**1u** (distilled)	**4c**	1	15 mol% acetic acid	2	39	85:15
13	**1u** (distilled)	**4e**	1	15 mol% acetic acid	2	41	87:13
14	**1u** (distilled)	**4f**	1	15 mol% acetic acid	2	2	74:26
15	**1u** (distilled)	**4d**	2	50 mol% acetic acid	3	45	90:10
16	**1u** (distilled)	**4d**	3	50 mol% acetic acid	2.5	50	89:11
17[e]	**1u** (distilled)	**4d**	1	50 mol% acetic acid	2.5	22	85:15
18	paraldehyde (non-distilled)	**4d**	1	-	5	33	86:14
19	paraldehyde (distilled)	**4d**	1	-	5	9	89:11
20	paraldehyde (distilled)	**4d**	2	50 mol% acetic acid	3	45	90:10

[a] Reactions were performed on a 0.10 mmol scale of aldehyde **1u** (or 33 μmol of paraldehyde) and 1.5 mmol of diene **2b** in MeCy (0.33 mL). [b] Yields and conversion ratios were determined by ^{1}H NMR analysis by comparison to triphenylmethane as an internal standard after addition of TEA. [c] The enantiomeric ratio was measured by GC analysis on a chiral stationary phase. [d] The reaction was performed for 4 d at –20 °C followed by 1 d at room temperature. [e] 0.16 mL of MeCy was used.

Table S9. Effects of acetic acid[a].



entry	1	additive	t (h)	conv. (%)[b]	**3** (%)[b]	trimer (%)[b]	e.r.[c]
1		15 mol% acetic acid	48	99	13	85	96:4
2	**1k**	–	48	99	7	91	96:4
3		15 mol% acetic acid	48	96	10	86	97:3
4	**1o**	–	48	100	94	trace	97:3
5		15 mol% acetic acid	24	20	6	14	*syn*:*anti* >20:1 e.r.$_{syn}$ >99.5:0.5
6	(*R*)-**1l**	–	24	72	36	36	*syn*:*anti* >20:1 e.r.$_{syn}$ >99.5:0.5
7		15 mol% acetic acid	24	44	22	21	*anti*:*syn* >20:1 e.r.$_{anti}$ >99.5:0.5
8	(*S*)-**1l**	–	24	85	44	41	*anti*:*syn* >20:1 e.r.$_{anti}$ >99.5:0.5

[a] Reactions were performed on a 0.03 mmol scale of aldehydes and 0.3 mmol of diene **2a** in MeCy (0.1 mL). [b] Yields and conversion ratios were determined by ^{1}H NMR analysis by comparison to triphenylmethane as an internal standard after addition of TEA. [c] The enantiomeric ratio was measured by GC analysis on a chiral stationary phase.

The hetero-Diels–Alder reaction of acetaldehyde **1u** and diene **2a** was investigated (Table S8). Initially, it was found that reactions using different commercial batches of acetaldehyde, which contained varying amounts of acetaldehyde, acetic acid, and paraldehyde, irreproducibly generated cycloadduct **3u** (Table S8, entries 1 and 2). However, reactions using distilled acetaldehyde (prepared as a stock solution in MeCy) or paraldehyde proved to be inactive under the reaction conditions, even at elevated temperature (entries 3, 4, and 19). Interestingly, the addition of acetic acid indeed triggered the cycloaddition reaction, and the catalytic amount of acetic acid could improve the yield without diminishing the enantioselectivity (Table S8, entries 5–8 vs. 9–11). Other IDPis (**4c**, **4e**, and **4f**) proved to be less reactive and/or less stereoselective (Table S8, entries 6 vs. 12–14). Higher loadings of catalyst **4d** and prolonged reaction times increased the yield while a higher concentration decreased the yield and enantioselectivity (Table S8, entries 15–17). In contrast, the assistive effect of acetic acid was not effective for other aliphatic aldehydes (Table S9). In most cases, the desired cycloaddition reactions showed a reduced rate of the conversion and/or yield, plausibly caused by the predominant generation of their corresponding trimers.

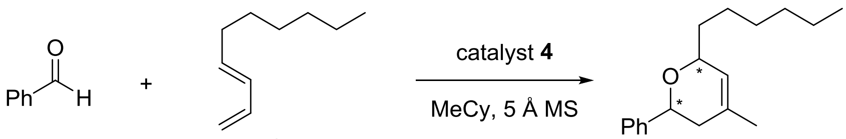
Table S10. Optimization of the reaction for aldehyde **1i** and diene **2b**[a].

1i **2b** **3v** trimer

entry	HX* (mol%)	**2b** (equiv)	conv. (%)[b]	**3v** (%)[b]	trimer (%)[b]	e.r.[c]
1	0.5	10	88	39	48	93:7
2	1	10	96	20	76	89:11
3	1	15	100	87	0	94:6
4	1	20	93	76	17	93:7

[a] Reactions were performed on a 0.03 mmol scale of aldehyde **1i** in MeCy (0.1 mL). [b] Yields and conversion ratios were determined by ^{1}H NMR analysis by comparison to triphenylmethane as an internal standard after addition of TEA. [c] The enantiomeric ratio was measured by GC analysis on a chiral stationary phase.

Table S11. Optimization of the reaction for aldehyde **1a** and diene **2f** [a].

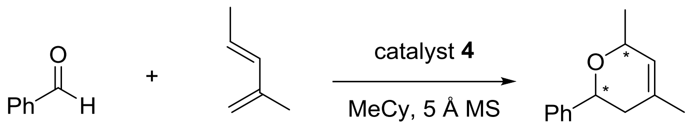


1a 2f 3aa

entry	catalyst	HX* (mol%)	T (°C)	t (d)	conv. (%)[b]	*trans*:*cis*[b]	e.r.$_{trans}$[c]
1	**4d**	2	–30	3	18	10:1	98:2
2	**4e**	2	–30	3	>95	12:1	>99.5:0.5
3	**4e**	0.5	–30	3	>95	32:1	>99.5:0.5

[a] Unless otherwise indicated, reactions were performed with aldehyde **1a** (0.03 mmol), diene **2f** (0.3 mmol), a catalyst, and 5 Å molecular sieves (7 mg) in MeCy (0.1 mL). [b] Conversion ratios were determined by ^{1}H NMR analysis by comparison to 1,2,4,5-tetramethylbenzene as an internal standard after quenching reactions by addition of TEA. [c] The enantiomeric ratio was measured by HPLC analysis on a chiral stationary phase.

Table S12. Optimization of the reaction for aldehyde **1a** and diene **2h**[a].

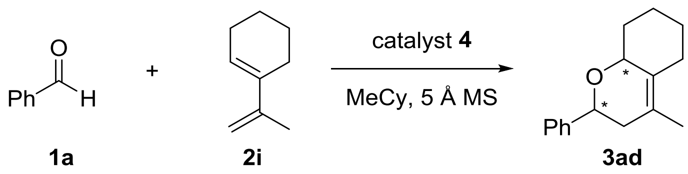


1a 2h 3ac

entry	catalyst	HX* (mol%)	T (°C)	t (h)	conv. (%)[b]	*cis*:*trans*[b]	e.r.$_{cis}$[c]
1	**4c**	1	–60	24	>95	1.4:1	N.D.
2	**4d**	1	–60	24	>95	7:1	95:5
3	**4f**	1	–60	24	<10	10:1	90:10

[a] Unless otherwise indicated, reactions were performed with aldehyde **1a** (0.02 mmol), diene **2h** (0.1 mmol), a catalyst, and 5 Å molecular sieves (14 mg) in MeCy (0.2 mL). [b] Conversion ratios were determined by ^{1}H NMR analysis by comparison to 1,2,4,5-tetramethylbenzene as an internal standard after quenching reactions by addition of TEA. [c] The enantiomeric ratio was measured by HPLC analysis on a chiral stationary phase.

Table S13. Optimization of the reaction for aldehyde **1a** and diene **2i**[a].



entry	catalyst	HX* (mol%)	T (°C)	t (h)	conv. (%)[b]	*cis*:*trans*[b]	e.r.$_{cis}$ [c]
1	**4d**	1	–60	48	>95	2.5:1	97.5:2.5
2	**4d**	1	–30	24	>95	3:1	96:2
3	**4f**	1	–30	24	>95	10:1	94.2:5.8

[a] Unless otherwise indicated, reactions were performed with aldehyde **1a** (0.03 mmol), diene **2i** (0.15 mmol), a catalyst, and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL). [b] Conversion ratios were determined by ^{1}H NMR analysis by comparison to 1,2,4,5-tetramethylbenzene as an internal standard after quenching reactions by addition of TEA. [c] The enantiomeric ratio was measured by HPLC analysis on a chiral stationary phase.

Substrate Synthesis and Characterization

Substrates (*R*)-**1l**, (*S*)-**1l**, **1p**, **1q**, **2f**, **2g**, and **2i** have been previously reported[19, 29–32]. Aldehydes (*R*)-**1l** and (*S*)-**1l** were synthesized from the corresponding alcohols via a Dess-Martin oxidation and the optical purities of products were determined using reported methods[19, 29]. Aldehydes **1p** and **1q** were prepared from the corresponding alcohols via a Jones oxidation[30]. Dienes **2f** and **2g** were prepared from the corresponding aldehydes via a Wittig reaction[31]. Diene **2i** was prepared from the corresponding ketone via Wittig reaction[32].

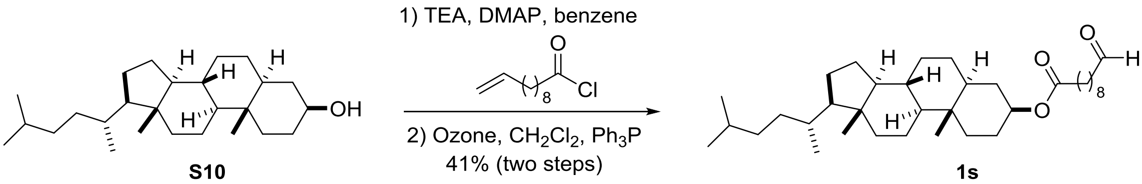
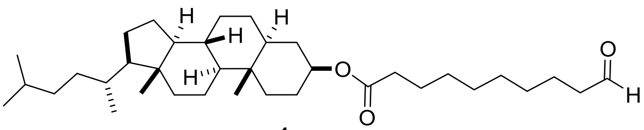


Figure S4. Synthesis of dihydrocholesterol-derivatized aldehyde **1s**.

(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-5-methylhexan-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 10-oxodecanoate (1s)



To a round-bottom flask were added dihydrocholesterol (**S10**, 1.2 g, 3.0 mmol, 1.0 equiv), 4-(dimethylamino)-pyridine (DMAP, 18.3 mg, 0.15 mmol, 0.05 equiv), benzene (18.0 mL), trimethylamine (TEA, 0.46 mL, 3.3 mmol, 1.1 equiv), and followed by the addition of 10-undecenoyl chloride (1.0 mL, 4.5 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using 5–10% ethyl acetate/hexanes as the eluent giving the corresponding alkene as a colorless solid (0.98 g, 1.8 mmol, 59%). To a round bottom flask were added the obtained alkene (0.55 g, 1.0 mmol, 1.0 equiv), triphenylphosphine (Ph_3P, 0.80 g, 3.0 mmol, 3.0 equiv), and CH_2Cl_2 (10 mL), followed by the bubbling of the ozone at –40 °C until the starting material was fully consumed. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using 5–10% ethyl acetate/hexanes as eluents to give **1s** as a colorless solid (0.38 g, 0.69 mmol, 69%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.72 (s, 1H), 4.66 (hept, J = 4.6 Hz, 1H), 2.39 (dt, J = 7.4, 1.6 Hz, 2H), 2.23 (t, J = 7.5 Hz, 2H), 1.97 (td, J = 12.6, 3.2 Hz, 1H), 1.85–1.71 (m, 3H), 1.67–1.43 (m, 10.6H), 1.38–0.95 (m, 28H), 0.91 (d, J = 6.5 Hz, 3H), 0.86 (dd, J = 6.6, 1.9 Hz, 6H), 0.82 (s, 3H), 0.69–0.63 (m, 4H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 203.1, 173.5, 73.7, 56.9, 56.7, 54.7, 45.1, 44.3, 43.0, 40.5, 39.9, 37.2, 36.6, 36.3, 35.92, 35.87, 35.0, 34.5, 32.5, 29.6, 29.50, 29.48, 29.4, 29.1, 28.6, 28.4, 28.0, 25.4, 24.6, 24.2, 23.0, 22.7, 22.5, 21.6, 18.9, 12.4, 12.2.

HRMS (ESI+) (*m/z*): calculated for $C_{37}H_{64}O_3Na_1$ $[M+Na]^+$: 579.4748; found: 579.4756.

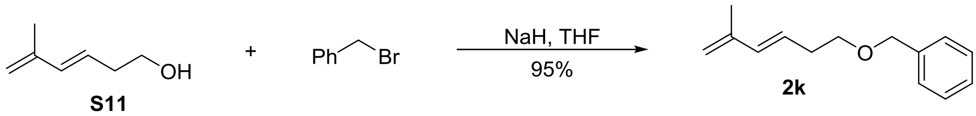
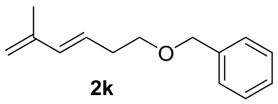


Figure S5. Synthesis of diene **2k**.

(*E*)-(((5-methylhexa-3,5-dien-1-yl)oxy)methyl)benzene (2k)



To a round-bottom flask were added the starting alcohol (**S11**, 300 mg, 2.67 mmol), Benzyl bromide (0.64 mL, 5.35 mmol), and THF (2 mL), followed by the addition of NaH (60% dispersion in Mineral oil, 214 mg, 5.35 mmol). The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was then quenched with 20 mL saturated aqueous NH_4Cl solution, and the aqueous phase was extracted with Et_2O (3×30 mL). The combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using 1–3% ethyl acetate/hexanes as the eluent to give **2k** as a colorless oil (514 mg, 2.54 mmol, 95%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.34 (m, 4H), 7.31–7.28 (m, 1H), 6.22 (d, J = 15.7 Hz, 1H), 5.68 (td, J = 15.7, 7.0 Hz, 1H), 4.89 (br s, 2H), 4.53 (br s, 2H), 3.54 (t, J = 6.8 Hz, 2H), 2.44 (q, J = 6.9 Hz, 2H), 1.84 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 142.1, 138.6, 134.7, 128.6, 128.5, 127.9, 127.83, 127.78, 127.71, 126.9, 115.0, 73.1, 70.0, 33.4, 18.8.

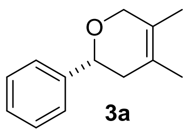
HRMS (ESI+) (*m/z*): calculated for $C_{14}H_{18}O_1Na_1$ $[M+Na]^+$: 225.1250; found: 225.1249.

General Procedure for the Asymmetric [4+2]-Cycloaddition

Unless specified otherwise, in a flame-dried flask under argon, catalyst **4** (0.2–3 mol%) and 5 Å molecular sieves (70 mg/mL) were dissolved in MeCy (0.3–10.0 mL). Subsequently, aldehyde **1** (0.1–0.3 mmol) and diene **2** (0.2–3.0 mmol) were added. Purification was performed by column chromatography or preparative thin layer chromatography on silica gel using 2–6% diethyl ether/pentane as the eluent. The corresponding racemic samples were prepared according to the reported method.[13a]

Characterization of Cycloadducts

(*R*)-4,5-dimethyl-2-phenyl-3,6-dihydro-2*H*-pyran (3a)



3a

Aldehyde **1a** (10.6 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (16.4 mg, 0.2 mmol, 2.0 equiv) were added to a mixture of catalyst **4c** (1 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 24 h. **3a** was obtained as a colorless oil (18.2 mg, 0.097 mmol, 97%).

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.39–7.34 (m, 4H), 7.28 (tt, *J* = 7.1, 1.6 Hz, 1H), 4.54 (dd, *J* = 10.6, 3.5 Hz, 1H), 4.21 (pd, *J* = 15.5, 1.0 Hz, 1H), 4.09 (d, *J* = 15.5 Hz, 1H), 2.30–2.24 (m, 1H), 2.10 (dd, *J* = 16.7, 0.6 Hz, 1H), 1.72 (br s, 3H), 1.62–1.616 (m, 3H).

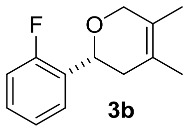
^{13}C NMR (151 MHz, CD_2Cl_2): δ 143.5, 128.6, 127.6, 126.2, 125.0, 124.2, 76.5, 70.6, 39.0, 18.5, 14.0.

HRMS (ESI+) (*m/z*): calculated for $C_{13}H_{16}O_1Na_1$ $[M+Na]^+$: 211.1093; found: 211.1092.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +224.0 (*c* = 0.50, $CHCl_3$).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Hydrodex-gamma-TBDAc column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 100 °C (108 min, iso); Gas: H_2 (0.50 bar); t_R = 88.43 min (major) and t_R= 92.67 min (minor), e.r. = 98:2.

(*R*)-2-(2-fluorophenyl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3b)



3b

Aldehyde **1b** (12.4 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (16.4 mg, 0.2 mmol, 2.0 equiv) were added to a mixture of catalyst **4c** (1 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –10 °C for 72 h. **3b** was obtained as a colorless oil (16.6 mg, 0.081 mmol, 81%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.25–7.22 (m, 1H), 7.15 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.01 (ddd, *J* = 10.2, 8.2, 0.8 Hz, 1H), 4.86 (dd, *J* = 10.6, 3.6 Hz, 1H), 4.24 (d, *J* = 15.5 Hz, 1H), 4.12 (d, *J* = 15.5 Hz, 1H), 2.28–2.22 (m, 1H), 2.14 (d, *J* = 16.6 Hz, 1H), 1.69 (br s, 3 H), 1.60 (br s, 3 H).

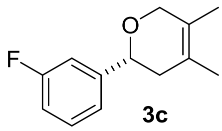
^{13}C NMR (126 MHz, $CDCl_3$): δ 160.7, 158.7, 130.0, 129.9, 129.6, 128.8, 128.7, 128.4, 127.24, 127.20, 126.4, 124.48, 124.45, 124.0, 115.3, 115.1, 70.4, 70.35, 70.33, 37.7, 18.4, 14.0.

HRMS (ESI+) (*m/z*): calculated for $C_{13}H_{15}O_1F_1Na_1$ $[M+Na]^+$: 229.0999; found: 229.1000.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +178.4 (*c* = 0.50, $CHCl_3$).

HPLC: The enantiomeric ratio was measured by HPLC analysis using Chiralpak IA-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 99.5:0.5, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 4.10 min (major) and t_R= 4.50 min (minor), e.r. = 92:8.

(*R*)-2-(3-fluorophenyl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3c)



3c

Aldehyde **1c** (12.4 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (16.4 mg, 0.2 mmol, 2.0 equiv) were added to a mixture of catalyst **4c** (1 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 24 h. **3c** was obtained as a colorless oil (19.5 mg, 0.0945 mmol, 94.5%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.14–7.09 (m, 2H), 6.95 (ddt, *J* = 8.9, 2.5, 0.5 Hz, 1H), 4.54 (dd, *J* = 10.6, 3.8 Hz, 1H), 4.20 (td, *J* = 15.6, 1.1 Hz, 1H), 4.10 (d,

J = 15.5 Hz, 1H), 2.29–2.22 (m, 1H), 2.09 (d, J = 16.6 Hz, 1H), 1.69 (br s, 3H), 1.59 (br s, 3H).

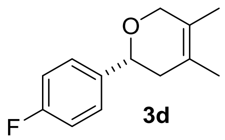
^{13}C NMR (126 MHz, $CDCl_3$): δ 164.0, 162.1, 145.54, 145.49, 129.96, 129.90, 124.7, 123.7, 121.46, 121.45, 114.4, 114.2, 113.0, 112.8, 75.71, 75.70, 70.4, 38.6, 18.5, 14.0.

HRMS (ESI+) (*m/z*): calculated for $C_{13}H_{15}O_1F_1Na_1$ $[M+Na]^+$: 229.0999; found: 229.1001.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +184.0 ($c$ = 0.50, $CHCl_3$).

HPLC: The enantiomeric ratio was measured by HPLC analysis using Chiralpak IA-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 99.5:0.5, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 4.52 min (major) and t_R= 4.92 min (minor), e.r. = 98:2.

(*R*)-2-(4-fluorophenyl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3d)



3d

Aldehyde **1d** (12.4 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (16.4 mg, 0.2 mmol, 2.0 equiv) were added to a mixture of catalyst **4c** (1 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 24 h. **3d** was obtained as a colorless oil (16 mg, 0.089 mmol, 89%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dt, J = 5.6, 2.0 Hz, 2H), 7.02 (tt, J = 6.8, 2.9 Hz, 2H), 4.52 (dd, J = 10.6, 3.5 Hz, 1H), 4.20 (td, J = 15.5, 1.1 Hz, 1H), 4.10 (d, J = 15.5 Hz, 1H), 2.30–2.24 (m, 1H), 2.07 (d, J = 16.7 Hz, 1H), 1.69 (br s, 3H), 1.59 (br s, 3H).

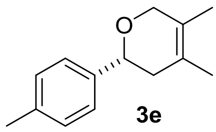
^{13}C NMR (126 MHz, $CDCl_3$): δ 163.2, 161.3, 138.63, 138.60, 127.7, 127.6, 124.7, 123.8, 115.4, 115.2, 75.8, 70.4, 38.7, 18.5, 14.0.

HRMS (ESI+) (*m/z*): calculated for $C_{13}H_{15}O_1F_1Na_1$ $[M+Na]^+$: 229.0999; found: 229.1001.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +164.0 ($c$ = 0.50, $CHCl_3$).

HPLC: The enantiomeric ratio was measured by HPLC analysis using Chiralpak IA-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 99.5:0.5, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 4.95 min (major) and t_R= 5.46 min (minor), e.r. = 97:3.

(*R*)-4,5-dimethyl-2-(*p*-tolyl)-3,6-dihydro-2*H*-pyran (3e)



3e

Aldehyde **1e** (12.0 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (41 mg, 0.5 mmol, 5.0 equiv) were added to a mixture of catalyst **4c** (3 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –60 °C for 6 days. **3e** was obtained as a colorless oil (18.9 mg, 0.093 mmol, 93%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.23 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.48 (dd, J = 10.6, 3.5 Hz, 1H), 4.17 (d, J = 15.5 Hz, 1H), 4.05 (d, J = 15.5 Hz, 1H), 2.33 (s, 3H), 2.26–2.21 (m, 1H), 2.06 (d, J = 16.7 Hz, 1H), 1.69 (br s, 3H), 1.59 (br s, 3H).

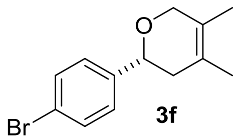
^{13}C NMR (126 MHz, CD_2Cl_2): δ 140.4, 137.3, 129.2, 126.1, 124.9, 124.2, 76.4, 70.6, 38.9, 21.2, 18.5, 13.9.

HRMS (ESI+) (*m/z*): calculated for $C_{14}H_{18}O_1Na_1$ $[M+Na]^+$: 225.1250; found: 225.1250.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +184.0 ($c$ = 0.50, $CHCl_3$).

HPLC: The enantiomeric ratio was measured by HPLC analysis using Chiralpak IA-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 99.5:0.5, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 5.37 min (major) and t_R= 6.16 min (minor), e.r. = 95:5.

(*R*)-2-(4-bromophenyl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3f)



3f

Aldehyde **1f** (18.5 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (82 mg, 1.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4c** (3 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –60 °C for 6 days. **3f** was obtained as a colorless oil (9.6 mg, 0.036 mmol, 36%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (dt, J = 8.5, 2.4 Hz, 2H), 7.25 (dt, J = 8.4, 1.5 Hz, 2H), 4.50 (dd, J = 10.6, 3.5 Hz, 1H), 4.19 (td, J = 15.6, 1.1 Hz, 1H), 4.09 (d, J = 15.6 Hz, 1H), 2.26–2.20 (m, 1H), 2.07 (d, J = 16.7 Hz, 1H), 1.68 (br s, 3H), 1.59 (br s, 3H).

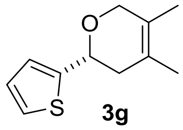
^{13}C NMR (126 MHz, $CDCl_3$): δ 141.9, 131.6, 127.7, 124.7, 123.7, 121.2, 75.7, 70.4, 38.6, 18.5, 14.0.

HRMS (ESI+) (*m/z*): calculated for $C_{13}H_{16}O_1Br_1$ $[M+H]^+$: 267.0379; found: 267.0380.

$[\alpha]_D^{20}$: +154.0 (c = 0.50, $CHCl_3$).

HPLC: The enantiomeric ratio was measured by HPLC analysis using Chiralpak IA-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 99.5:0.5, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 5.57 min (major) and t_R= 6.17 min (minor), e.r. = 95:5.

(*R*)-4,5-dimethyl-2-(thiophen-2-yl)-3,6-dihydro-2*H*-pyran (3g)



3g

Aldehyde **1g** (11.2 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (16..4 mg, 0.2 mmol, 2.0 equiv) were added to a mixture of catalyst **4c** (1 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –10 °C for 72 h. **3g** was obtained as a colorless oil (9.3 mg, 0.048 mmol, 48%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.25 (dd, *J* = 4.5, 1. Hz, 1H), 6.98–6.96 (m, 2H), 4.49 (dd, *J* = 10.0, 3.7 Hz, 1H), 4.17 (d, *J* = 15.6 Hz, 1H), 4.02 (d, *J* = 15.5 Hz, 1H), 2.42–2.36 (m, 1H), 2.21 (d, *J* = 16.6 Hz, 1H), 1.70 (br s, 3H), 1.57 (br s, 3H).

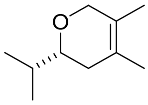
^{13}C NMR (126 MHz, CD_2Cl_2): δ 146.6, 126.8, 124.9, 124.8, 124.0, 123.6, 72.4, 70.2, 38.6, 18.4, 13.9.

HRMS (ESI+) (*m/z*): calculated for $C_{11}H_{14}O_1S_1Na_1$ $[M+Na]^+$: 217.0658; found: 217.0659.

$[\alpha]_D^{20}$: +64.0 (c = 0.50, $CHCl_3$).

HPLC: The enantiomeric ratio was measured by HPLC analysis using Chiralpak IA-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 99.5:0.5, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 5.52 min (major) and t_R= 5.96 min (minor), e.r. = 99.7:0.3.

(*R*)-2-isopropyl-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3h)



3h

Aldehyde **1h** (22 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –10 °C for 70 h. **3h** was obtained as a colorless oil (38 mg, 0.25 mmol, 83%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.92–3.77 (m, 2H), 3.03 (ddd, *J* = 10.4, 6.8, 3.4 Hz, 1H), 1.90–1.82 (m, 1H), 1.69 (d, *J* = 16.5 Hz, 1H), 1.61–1.52 (m, 4H), 1.44 (dt, *J* = 2.3, 1.2 Hz, 3H), 0.83 (dd, *J* = 26.5, 6.8 Hz, 6H).

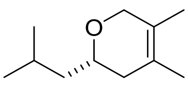
^{13}C NMR (126 MHz, CD_2Cl_2): δ 124.4, 123.5, 79.3, 70.0, 33.7, 32.9, 18.4, 18.1, 17.9, 13.5.

HRMS (ESI+) (*m*/*z*): calculated for $C_{10}H_{19}O_1$ $[M+H]^+$: 155.1430; found: 155.1432.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +163.2 (*c* = 0.32, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Hydrodex-gamma-TBDAc column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 65 °C (25 min, iso) to 220 °C (8 °C/min, 5 min iso); Gas: H_2 (0.50 bar); t_R = 21.81 min (minor) and t_R = 23.46 min (major), e.r. = 97:3.

(*S*)-2-isobutyl-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3i)



3i

Aldehyde **1i** (26 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 70 h. **3i** was obtained as a colorless oil (46 mg, 0.27 mmol, 91%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.91–3.75 (m, 2H), 3.42 (dddd, *J* = 10.1, 8.2, 4.8, 3.6 Hz, 1H), 1.84–1.76 (m, 1H), 1.73–1.66 (m, 2H), 1.54 (s, 3H), 1.44 (s, 3H), 1.37 (ddd, *J* = 14.1, 8.2, 6.2 Hz, 1H), 1.14 (ddd, *J* = 13.7, 7.9, 4.8 Hz, 1H), 0.82 (dd, *J* = 6.7, 2.0 Hz, 6H).

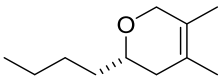
^{13}C NMR (126 MHz, CD_2Cl_2): δ 124.6, 123.7, 72.5, 69.7, 45.2, 37.3, 24.6, 23.1, 22.4, 18.2, 13.7.

HRMS (EI) (*m*/*z*): calculated for $C_{11}H_{20}O_1$ [M]: 168.1509; found: 168.1510.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +64.4 (*c* = 0.30, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 75 °C (iso); Gas: H_2 (0.40 bar); t_R = 20.68 min (minor) and t_R = 21.55 min (major), e.r. = 94:6.

(*S*)-2-butyl-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3j)


3j

Aldehyde **1j** (26 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 48 h. **3j** was obtained as a colorless oil (44 mg, 0.26 mmol, 87%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.91–3.76 (m, 2H), 3.33 (dddd, *J* = 10.4, 7.4, 5.0, 3.6 Hz, 1H), 1.86–1.76 (m, 1H), 1.71 (d, *J* = 16.5 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.38–1.17 (m, 6H), 0.82 (t, *J* = 7.1 Hz, 3H).

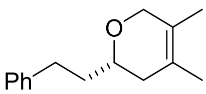
^{13}C NMR (126 MHz, CD_2Cl_2): δ 124.4, 123.4, 74.2, 69.6, 36.7, 35.6, 27.7, 22.8, 18.0, 13.8, 13.5.

HRMS (EI) (*m*/*z*): calculated for $C_{11}H_{20}O_1$ [M]: 168.1509; found: 168.1508.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +66.1 (*c* = 0.36, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 230 °C (injector), 350 °C (detector), 115 °C (10 min, iso) to 170 °C (8 °C/min, 3 min iso); Gas: H_2 (0.50 bar); t_R = 4.21 min (minor) and t_R = 4.35 min (major), e.r. = 97:3.

(*S*)-4,5-dimethyl-2-phenethyl-3,6-dihydro-2*H*-pyran (3k)


3k

Aldehyde **1k** (40 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –10 °C for 48 h. **3k** was obtained as a colorless oil (47 mg, 0.22 mmol, 73%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.23–7.03 (m, 5H), 3.94–3.77 (m, 2H), 3.34 (dddd, *J* = 10.3, 8.0, 4.6, 3.5 Hz, 1H), 2.68 (ddd, *J* = 13.7, 9.8, 5.5 Hz, 1H), 2.58 (ddd, *J* = 13.7, 9.6, 6.9 Hz, 1H), 1.91–1.83 (m, 1H), 1.77–1.61 (m, 3H), 1.54 (s, 3H), 1.44 (s, 3H).

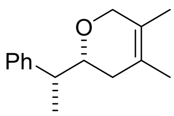
^{13}C NMR (126 MHz, CD_2Cl_2): δ 142.5, 128.4, 128.2, 125.6, 124.4, 123.4, 73.2, 69.6, 37.5, 36.6, 31.7, 18.0, 13.5.

HRMS (EI) (*m*/*z*): calculated for $C_{15}H_{20}O_1$ [M]: 216.1509; found: 216.1511.

$[\alpha]_D^{25}$: +80.2 (c = 0.34, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 230 °C (injector), 350 °C (detector), 125 °C (45 min, iso) to 170 °C (8 °C/min, 3 min iso); Gas: H_2 (0.60 bar); t_R = 37.79 min (minor) and t_R = 38.98 min (major), e.r. = 96:4.

(*R*)-4,5-dimethyl-2-((*R*)-1-phenylethyl)-3,6-dihydro-2*H*-pyran (3l)



3l

Aldehyde (*R*)-**1l** (13 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (82 mg, 1.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (23 mg) in MeCy (0.33 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 48 h. **3l** was obtained as a colorless oil (9 mg, 43 μmol, 43%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.32–7.25 (m, 2H, *H10*), 7.23–7.16 (m, 3H, *H11*, *H9*), 4.02 (br d, *J* = 15.4 Hz, 1H, *H5eq*), 3.95 (d, *J* = 15.1 Hz, 1H, *H5ax*), 3.51 (ddd, *J* = 10.5, 8.1, 3.3 Hz, 1H, *H1*), 2.72 (p, *J* = 8.1, 7.0 Hz, 1H, *H6*), 1.84 (dd, *J* = 17.5, 10.5 Hz, 1H, *H2ax*), 1.54–1.50 (m, 6H, *H12*, *H13*), 1.45 (d, *J* = 17.5 Hz, 1H, *H2eq*), 1.33 (d, *J* = 6.9 Hz, 3H, *H7*).

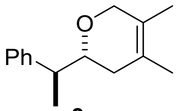
^{13}C NMR (126 MHz, CD_2Cl_2): δ 145.0 (*C8*), 128.6 (*C10*), 128.3 (*C9*), 126.6 (*C11*), 124.6 (*C3*), 124.0 (*C4*), 79.1 (*C1*), 70.4 (*C5*), 45.8 (*C6*), 35.3 (*C2*), 18.5 (*C7*), 18.4 (*C12*), 13.9 (*C13*).

HRMS (EI) (*m*/*z*): calculated for $C_{15}H_{20}O_1$ [M]: 216.1509; found: 216.1509.

$[\alpha]_D^{25}$: +46.6 (c = 0.10, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (BGB 176 column: 30.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 220 °C (detector), 150 °C (10 min, iso) to 220 °C (4 °C/min, 3 min iso); Gas: H_2 (1.00 bar); t_R = 12.54 min (major), 13.81 min (minor), d.r.$_{syn:anti}$ = 29:1, e.r.$_{syn}$ = >99.5:0.5.

(*R*)-4,5-dimethyl-2-((*S*)-1-phenylethyl)-3,6-dihydro-2*H*-pyran (3m)



3m

Aldehyde (*S*)-**1l** (13 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (82 mg, 1.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (23 mg) in MeCy (0.33 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 48 h. **3m** was obtained as a colorless oil (10 mg, 48 μmol, 48%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.30–7.25 (m, 2H, *H10*), 7.25–7.21 (m, 2H, *H9*), 7.21–7.16 (m, 1H, *H11*), 3.89 (dm, J = 15.5, 2.3, 1.1 Hz, 1H, *H5ax)*, 3.82 (d, J = 15.4 Hz, 1H, *H5eq*), 3.61 (ddd, J = 10.6, 7.3, 3.4 Hz, 1H, *H1*), 2.80 (p, J = 7.3 Hz, 1H, *H6*), 1.97 (t, J = 16.8, 10.6 Hz, 1H, *H2ax*), 1.84 (d, J = 16.8 Hz, 1H, *H2eq*), 1.62 (dh, J = 2.1, 0.9 Hz, 3H, *H12*), 1.50 (h, J = 2.3, 1.1 Hz, 3H, *H13*), 1.24 (d, J = 7.2 Hz, 3H, *H7*).

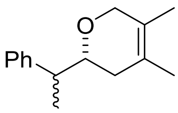
^{13}C NMR (126 MHz, CD_2Cl_2): δ 145.4 (*C8*), 128.42 (*C10*), 128.35 (*C9*), 126.4 (*C11*), 124.8 (*C3*), 123.8 (*C4*), 78.6 (*C1*), 70.4 (*C5*), 45.3 (*C6*), 34.7 (*C2*), 18.5 (*C7*), 18.0 (*C12*), 13.9 (*C13*).

HRMS (EI) (*m*/*z*): calculated for $C_{15}H_{20}O_1$ [M]: 216.1509; found: 216.1509.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +67.2 ($c$ = 0.13, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (BGB 176 column: 30.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 220 °C (detector), 150 °C (10 min, iso) to 220 °C (4 °C/min, 3 min iso); Gas: H_2 (1.00 bar); t_R = 12.54 min (minor1), 12.87 min (minor2) and t_R = 13.56 min (major), d.r.$_{syn:anti}$ = 1:31, e.r.$_{anti}$ = >99.5:0.5.

(2*R*)-4,5-dimethyl-2-(1-phenylethyl)-3,6-dihydro-2*H*-pyran (3n)



3n

Aldehyde *rac*-**1l** (40 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 48 h. **3n** was obtained as a colorless oil (29 mg, 0.14 mmol, 45%).

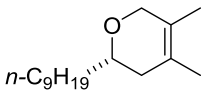
^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.23–7.07 (m, 10H), 3.97–3.71 (m, 4H), 3.52 (ddd, J = 10.6, 7.3, 3.4 Hz, 1H), 3.43 (ddd, J = 10.5, 8.1, 3.3 Hz, 1H), 2.76–2.60 (m, 2H), 1.99–1.83 (m, 2H), 1.80–1.71 (m, 2H), 1.54 (s, 3H), 1.44–1.33 (m, 10H), 1.24 (d, J = 7.0 Hz, 3H), 1.16 (d, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 145.0, 144.6, 128.2, 128.0, 127.94, 127.90, 126.2, 126.0, 124.4, 124.2, 123.5, 123.4, 78.7, 78.2, 70.0, 45.4, 44.9, 34.9, 34.2, 18.12, 18.10, 18.0, 17.9, 17.6, 13.5, 13.4.

HRMS (EI) (*m*/*z*): calculated for $C_{15}H_{20}O_1$ [M]: 216.1509; found: 216.1508.

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (BGB 176 column: 30.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 220 °C (detector), 150 °C (10 min, iso) to 220 °C (4 °C/min, 3 min iso); Gas: H_2 (1.00 bar); t_R = 12.54 min (major 1), 12.88 min (minor 1) and t_R = 13.56 min (major 2), 13.80 min (minor 2), d.r.$_{syn:anti}$ = 1:1.2, e.r.$_{syn}$ = 98:2, e.r.$_{anti}$ = 96:4.

(*S*)-4,5-dimethyl-2-nonyl-3,6-dihydro-2*H*-pyran (3o)



3o

Aldehyde **1o** (47 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 48 h. **3o** was obtained as a colorless oil (67 mg, 0.28 mmol, 94%).

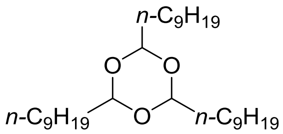
^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.91–3.75 (m, 2H), 3.33 (dddd, J = 10.4, 7.2, 4.9, 3.4 Hz, 1H), 1.86–1.76 (m, 1H), 1.71 (d, J = 16.5 Hz, 1H), 1.54 (s, 3H), 1.45–1.39 (m, 4H), 1.36–1.29 (m, 2H), 1.24–1.16 (m, 13H), 0.80 (t, J = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 126.3, 125.4, 76.1, 71.5, 38.6, 37.8, 33.8, 31.63, 31.55, 31.5, 31.2, 27.4, 24.6, 20.0, 15.8, 15.4.

HRMS (EI) (*m*/*z*): calculated for $C_{16}H_{30}O_1$ [M]: 238.2291; found: 238.2288.

$[\alpha]_D^{25}$: +118.0 (c = 0.36, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 130 °C (40 min, iso); Gas: H_2 (0.50 bar); t_R = 34.49 min (minor) and t_R = 35.43 min (major), e.r. = 97:3.



S9

2,4,6-trinonyl-1,3,5-trioxane (S9)

A colorless solid.

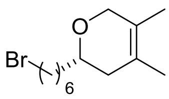
***R*$_f$** 0.40 (*n*-pentane/CH_2Cl_2, 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.83 (t, *J* = 5.3 Hz, 1H), 1.71–1.60 (m, 2H), 1.44–1.35 (m, 2H), 1.33–1.22 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 101.7, 34.4, 31.9, 29.52, 29.50, 29.4, 29.3, 23.6, 22.7, 14.1.

HRMS (ESI+) (*m*/*z*): calculated for $C_{30}H_{60}O_3Na_1$ $[M+Na]^+$: 491.4435; found: 491.4438.

(*S*)-2-(6-bromohexyl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3p)



3p

Aldehyde **1p** (58 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 48 h. **3p** was obtained as a colorless oil (66 mg, 0.24 mmol, 80%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.88 (d, *J* = 15.4 Hz, 1H), 3.79 (d, *J* = 16.6 Hz, 1H), 3.38–3.23 (m, 3H), 1.85–1.68 (m, 4H), 1.54 (s, 3H), 1.46–1.38 (m, 4H), 1.38–1.31 (m, 4H), 1.29–1.21 (m, 3H).

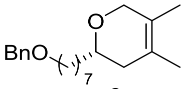
^{13}C NMR (126 MHz, CD_2Cl_2): δ 126.3, 125.3, 76.0, 71.6, 38.6, 37.6, 36.1, 34.7, 30.7, 30.0, 27.2, 20.0, 15.4.

HRMS (EI) (*m*/*z*): calculated for $C_{13}H_{23}O_1Br_1$ [M]: 274.0927; found: 274.0929.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +85.8 (*c* = 0.50, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 120 °C (120 min, iso); Gas: H_2 (0.50 bar); t_R = 102.41 min (minor) and t_R = 104.94 min (major), e.r. = 96:4.

(*S*)-2-(7-(benzyloxy)heptyl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3q)



3q

Aldehyde **1q** (70 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 48 h. **3q** was obtained as a colorless oil (79 mg, 0.25 mmol, 83%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.29–7.12 (m, 5H), 4.37 (s, 2H), 3.93–3.71 (m, 2H), 3.36 (t, *J* = 6.6 Hz, 2H), 3.31 (dddd, *J* = 10.5, 7.3, 3.6, 1.4 Hz, 1H), 1.85–1.74 (m, 1H), 1.73–1.66 (m, 1H), 1.53 (td, *J* = 2.0, 1.0 Hz, 3H), 1.50 (dt, *J* = 8.1, 6.4 Hz, 2H), 1.43 (dt, *J* = 2.5, 1.2 Hz, 4H), 1.33–1.17 (m, 9H).

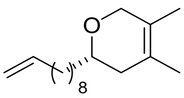
^{13}C NMR (126 MHz, CD_2Cl_2): δ 139.1, 128.2, 127.5, 127.3, 125.4, 124.4, 123.5, 74.2, 72.7, 70.5, 69.6, 36.7, 35.9, 30.1, 29.8, 29.7, 29.4, 26.2, 25.5, 18.0, 13.5.

HRMS (ESI+) (*m*/*z*): calculated for $C_{21}H_{32}O_2Na_1$ $[M+Na]^+$: 339.2294; found: 339.2296.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +69.9 (*c* = 0.50, CH_2Cl_2).

HPLC: The enantiomeric ratio was measured by HPLC analysis using Chiralpak IA-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 98:2, flow rate = 1.0 mL/min, λ = 210 nm, t_R = 4.86 min (minor) and t_R= 5.63 min (major). e.r. = 95:5.

(*S*)-2-(dec-9-en-1-yl)-4,5-dimethyl-3,6-dihydro-2*H*-pyran (3r)



3r

Aldehyde **1r** (52 mg, 0.3 mmol, 1.0 equiv) and diene **2a** (0.25 g, 3.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 48 h. **3r** was obtained as a colorless oil (68 mg, 0.27 mmol, 89%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 5.74 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 4.98–4.76 (m, 2H), 3.94–3.72 (m, 2H), 3.33 (dddd, *J* = 10.3, 7.2, 4.9, 3.5 Hz, 1H), 1.98–1.93 (m, 2H), 1.87–1.76 (m, 1H), 1.71 (d, *J* = 16.3 Hz, 1H), 1.58–1.50 (m, 3H), 1.44 (s, 4H), 1.36–1.25 (m, 4H), 1.25–1.16 (m, 9H).

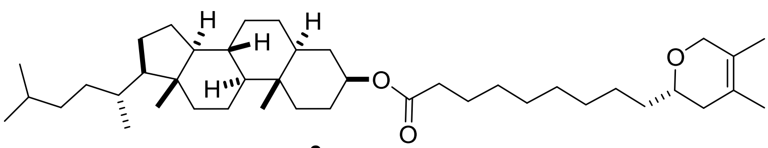
^{13}**C NMR** (126 MHz, CD_2Cl_2): δ 139.3, 124.4, 123.5, 113.8, 74.2, 69.6, 36.7, 35.9, 33.8, 29.7, 29.6, 29.4, 29.1, 29.0, 25.5, 18.0, 13.5.

HRMS (ESI+) (*m/z*): calculated for $C_{17}H_{31}O_1$ $[M+H]^+$: 251.2369; found: 251.2373.

$[\boldsymbol{\alpha}]_D^{25}$: +59.5 ($c$ = 0.26, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 130 °C (60 min, iso); Gas: H_2 (0.50 bar); t_R = 52.26 min (minor) and t_R = 53.72 min (major), e.r. = 97:3.

(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-5-methylhexan-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 9-((*S*)-4,5-dimethyl-3,6-dihydro-2*H*-pyran-2-yl)nonanoate (3s)



3s

Aldehyde **1s** (55.7 mg, 0.1 mmol, 1.0 equiv) and diene **2a** (82 mg, 1.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –10 °C for 72 h. **3s** was obtained as a colorless solid (52 mg, 0.081 mmol, 81%).

^{1}**H NMR** (500 MHz, CD_2Cl_2): δ 4.66 (hept, J = 5.0 Hz, 1H), 3.96 (td, J = 15.4, 0.9 Hz, 1H), 3.87 (d, J = 15.4 Hz, 1H), 3.43–3.38 (m, 1H), 2.23 (t, J = 7.4 Hz, 2H), 1.97 (td, J = 12.6, 3.3 Hz, 1H), 1.92–1.60 (m, 10H), 1.60–1.46 (m, 10.8H), 1.44–0.96 (m, 30.9H), 0.91 (d, J = 6.5 Hz, 3H), 0.86 (dd, J = 6.6, 2.0 Hz, 6H), 0.83 (s, 3H), 0.69–0.61 (m, 4H).

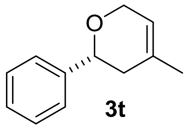
^{13}**C NMR** (126 MHz, CD_2Cl_2): δ 173.5, 124.8, 123.9, 74.6, 73.7, 70.1, 56.9, 56.8, 54.7, 45.1, 43.0, 40.5, 39.9, 37.21, 37.19, 36.6, 36.32, 36.26, 35.93, 35.88, 35.1, 34.5, 32.5, 30.1, 29.9, 29.7, 29.5, 29.1, 28.6, 28.5, 28.0, 25.9, 25.5, 24.6, 24.3, 23.0, 22.7, 21.6, 18.9, 18.5, 14.0, 12.4, 12.3.

HRMS (ESI+) (*m/z*): calculated for $C_{43}H_{74}O_3Na_1$ $[M+Na]^+$: 661.5530; found: 661.5540.

$[\boldsymbol{\alpha}]_D^{20}$: +32.0 ($c$ = 0.50, $CHCl_3$).

HPLC: The diastereomeric ratio was measured by Heart-Cut-HPLC analysis using Chiralpak OD-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 99:1, flow rate = 1.0 mL/min, λ = 204 nm, t_R = 3.96 min (major) and t_R= 4.66 min (minor), d.r. = 19:1.

(*R*)-4-methyl-2-phenyl-3,6-dihydro-2*H*-pyran (3t)



3t

Aldehyde **1a** (10.6 mg, 0.1 mmol, 1.0 equiv) and diene **2b** (13.6 mg, 0.2 mmol, 2.0 equiv) were added to a mixture of catalyst **4c** (1 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 24 h. **3t** was obtained as a colorless oil (17 mg, 0.097 mmol, 97%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38–7.33 (m, 4H), 7.27 (tt, *J* = 8.6, 1.8 Hz, 1H), 5.51 (br s, 1H), 4.51 (dd, *J* = 10.4, 3.5 Hz, 1H), 4.29–4.28 (m, 2H), 2.28–2.22 (m, 1H), 2.10 (d, *J* = 16.8 Hz, 1H), 1.75 (br s, 3H).

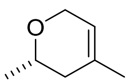
^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.4, 132.5, 128.6, 127.7, 126.2, 120.2, 76.1, 66.8, 38.1, 23.0.

HRMS (ESI+) (*m/z*): calculated for $C_{12}H_{14}O_1Na_1$ $[M+Na]^+$: 197.0937; found: 197.0937.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +161.0 (*c* = 0.50, $CHCl_3$).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Hydrodex-gamma-TBDAc column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 115 °C (35 min, iso); Gas: H_2 (0.53 bar); t_R = 18.86 min (major) and t_R= 19.87 min (minor), e.r. = 98:2.

(*S*)-2,4,5-trimethyl-3,6-dihydro-2*H*-pyran (3u)



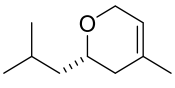
3u

Acetic acid (0.05 mmol, 0.2 M in MeCy), aldehyde **1u** (0.1 mmol, 1.3 M in MeCy), and diene **2b** (0.1 g, 1.5 mmol) were added to a mixture of catalyst **4d** (2 mol%) and 5 Å molecular sieves (23 mg) at –78 °C. The reaction mixture was stirred at –20 °C for 72 h. **3u** was obtained in 45% yield, determined by ^{1}H NMR analysis using internal standard because of the low boiling point of the compound[33].

HRMS (EI) (*m*/*z*): calculated for $C_7H_{12}O_1$ [M]: 112.0883; found: 112.0885.

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Ivadex-1 column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 220 °C (detector), 50 °C (20 min, iso); Gas: He (1.35 bar); t_R = 4.29 min (major) and t_R = 4.74 min (minor), e.r. = 90:10.

(*S*)-2-isobutyl-4-methyl-3,6-dihydro-2*H*-pyran (3v)



3v

Aldehyde **1i** (26 mg, 0.3 mmol, 1.0 equiv) and diene **2b** (0.31 g, 4.5 mmol, 15 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 70 h. **3v** was obtained as a colorless oil (37 mg, 0.24 mmol, 81%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 5.34–5.29 (m, 1H), 4.02–3.95 (m, 2H), 3.42 (dddd, *J* = 9.9, 8.3, 4.7, 3.7 Hz, 1H), 1.84–1.76 (m, 1H), 1.75–1.66 (m, 2H), 1.60 (s, 3H), 1.39 (ddd, *J* = 14.3, 8.3, 6.1 Hz, 1H), 1.15 (ddd, *J* = 13.7, 8.1, 4.8 Hz, 1H), 0.82 (dd, *J* = 6.7, 2.8 Hz, 6H).

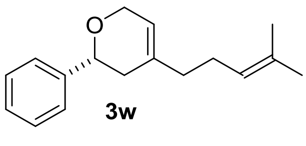
^{13}C NMR (126 MHz, CD_2Cl_2) δ 132.0, 119.7, 71.9, 65.7, 45.1, 36.3, 24.4, 22.9, 22.7, 22.2.

HRMS (EI) (*m*/*z*): calculated for $C_{10}H_{18}O_1$ [M]: 154.1352; found: 154.1351.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +31.3 (*c* = 0.33, CH_2Cl_2).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 230 °C (injector), 350 °C (detector), 90 °C (15 min, iso) to 170 °C (8 °C/min, 3 min iso); Gas: H_2 (0.40 bar); t_R = 6.06 min (minor) and t_R = 7.22 min (major), e.r. = 94:6.

(*R*)-4,6,6-trimethyl-2-phenyl-3,6-dihydro-2*H*-pyran (3w)



3w

Aldehyde **1a** (10.6 mg, 0.1 mmol, 1.0 equiv) and diene **2c** (41 mg, 0.3 mmol, 3.0 equiv) were added to a mixture of catalyst **4c** (2 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at –78 °C, then the reaction mixture was stirred at –40 °C for 4 days. **3w** was obtained as a colorless oil (8.7 mg, 0.036 mmol, 36%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38–7.32 (m, 4H), 7.27 (tt, *J* = 6.2, 1.8 Hz, 1H), 5.51 (q, *J* = 1.2 Hz, 1H), 5.13 (ddt, *J* = 8.2, 2.8, 1.4 Hz, 1H), 4.50 (dd, *J* = 10.4, 3.5 Hz, 1H), 4.31 (p, *J* = 1.7 Hz, 2H), 2.28–2.22 (m, 1H), 2.15–2.11 (m, 3H), 2.07–2.04 (m, 2H), 1.69 (d, *J* = 0.9 Hz, 3H), 1.62 (br s, 3H).

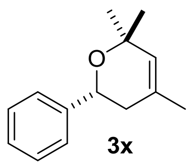
^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.5, 136.2, 132.1, 128.7, 128.6, 127.6, 126.2, 124.3, 119.9, 76.1, 66.8, 37.3, 36.7, 26.4, 25.8, 17.8.

HRMS (ESI+) (*m/z*): calculated for $C_{17}H_{22}O_1Na_1$ $[M+Na]^+$: 265.1563; found: 265.1562.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$: +36.0 (*c* = 0.45, $CHCl_3$).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Hydrodex-gamma-TBDAc column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 130 °C (140 min, iso); Gas: H_2 (0.50 bar); t_R = 114.52 min (major) and t_R= 117.41 min (minor), e.r. = 96:4.

(*R*)-4,6,6-trimethyl-2-phenyl-3,6-dihydro-2*H*-pyran (3x)



3x

Aldehyde **1a** (10.6 mg, 0.1 mmol, 1.0 equiv) and diene **2d** (48 mg, 0.5 mmol, 5.0 equiv) were added to a mixture of catalyst **4d** (2 mol%) and 5 Å molecular sieves (700 mg) in MeCy (10.0 mL) at –78 °C, then the reaction mixture was stirred at –45 °C for 48 h. **3x** was obtained as a colorless oil (16.5 mg, 0.082 mmol, 82%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.40–7.38 (m, 2H), 7.33 (dt, *J* = 7.4, 2.0 Hz, 2H), 7.26 (tt, *J* = 6.6, 1.4 Hz, 1H), 5.42 (t, *J* = 1.0 Hz, 1H), 4.69 (dd, *J* = 10.7, 3.3 Hz, 1H), 2.18–2.11 (m, 1H), 2.01 (dd, *J* = 16.7, 3.3 Hz, 1H), 1.72 (br s, 3H), 1.29 (d, *J* = 1.6 Hz, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.9, 130.6, 129.1, 128.6, 127.5, 126.5, 73.7, 71.1, 37.8, 30.1, 26.2, 23.1.

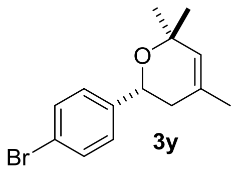
HRMS (ESI+) (*m/z*): calculated for $C_{14}H_{18}O_1Na_1$ $[M+Na]^+$: 225.1250; found: 225.1248.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$: +80.0 (*c* = 0.50, $CHCl_3$).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 90 °C

(60 min, iso); Gas: H_2 (0.50 bar); t_R = 41.98 min (minor) and t_R = 45.20 min (major), e.r. = 96:4.

(*R*)-2-(4-bromophenyl)-4,6,6-trimethyl-3,6-dihydro-2*H*-pyran (3y)



Aldehyde **1f** (18.5 mg, 0.1 mmol, 1.0 equiv) and diene **2d** (48 mg, 0.5 mmol, 5.0 equiv) were added to a mixture of catalyst **4d** (2 mol%) and 5 Å molecular sieves (700 mg) in MeCy (10.0 mL) at –78 °C, then the reaction mixture was stirred at –45 °C for 4 days. The titled compound **3y** was obtained as a colorless oil (23.4 mg, 0.083 mmol, 83%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.47 (td, *J* = 8.5, 2.5 Hz, 2H), 7.29 (td, *J* = 8.3, 2.2 Hz, 2H), 5.41 (p, *J* = 1.1 Hz, 1H), 4.66 (dd, *J* = 10.5, 3.6 Hz, 1H), 2.11–2.05 (m, 1H), 2.00 (dd, *J* = 16.7, 3.6 Hz, 1H), 1.71 (br s, 3H), 1.28 (d, *J* = 2.0 Hz, 6H).

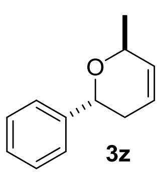
^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.1, 131.6, 130.3, 129.1, 128.3, 121.1, 73.9, 70.5, 37.8, 30.0, 26.2, 23.1.

HRMS (ESI+) (*m/z*): calculated for $C_{14}H_{17}O_1Br_1Na_1$ $[M+Na]^+$: 303.0355; found: 303.0356.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +79.0 (*c* = 0.90, $CHCl_3$).

GC: The enantiomeric ratio was measured by GC analysis analysis on a chiral column (BGB-176 column: 30.0 m); FID; Temperature: 230 °C (injector), 350 °C (detector), 160 °C (55 min, 8 min, iso); 220 °C (3 min, iso); Gas: H_2 (0.50 bar); t_R = 31.01 min (minor) and t_R = 31.97 min (major), e.r. = 95:5.

(2*R*,6*S*)-6-methyl-2-phenyl-3,6-dihydro-2*H*-pyran (3z)



Aldehyde **1a** (21.2 mg, 0.2 mmol, 1.0 equiv) and diene **2e** (136 mg, 2.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4d** (2 mol%) and 5 Å molecular sieves (42 mg) in MeCy (0.6 mL) at –78 °C, then the reaction mixture was stirred at –20 °C for 72 h. **3z** was obtained as a colorless oil (7.0 mg, 0.04 mmol, 20%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38–7.32 (m, 4H), 7.26 (tt, *J* = 7.2, 1.5 Hz, 1H), 5.93–5.88 (m, 1H), 5.78 (qd, *J* = 12.2, 2.0 Hz, 1H), 4.72 (t, *J* = 6.5 Hz, 1H), 4.46–4.41 (m, 1H), 2.26–2.23 (m, 2H), 1.30 (d, *J* = 6.8 Hz, 3H).

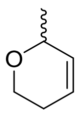
^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.4, 131.6, 128.6, 127.6, 126.6, 124.1, 69.9, 69.7, 32.6, 20.2.

HRMS (EI) (*m/z*): calculated for $C_{12}H_{14}O_1$ [M]: 174.1045; found: 174.1042.

$[\alpha]_D^{20}$: +124.0 (*c* = 0.15, $CHCl_3$).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Hydrodex-gamma-TBDAc column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 110 °C (30 min, iso); 230 °C (8 min); Gas: H_2 (0.50 bar); t_R = 22.14 min (minor) and t_R= 23.39 min (major), e.r. = 99:1.

6-methyl-3,6-dihydro-2*H*-pyran (S12)

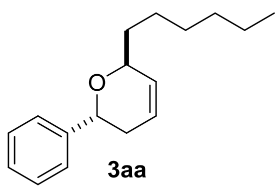

S12

Paraformaldehyde (3 mg, 0.1 mmol), and diene **2e** (68 mg, 1.0 mmol) were added to a mixture of catalyst **4c** (1 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.3 mL) at 22 °C. The reaction mixture was stirred at 22 °C for 48 h. **S12** was obtained in 18% yield, determined by ^{1}H NMR analysis using internal standard because of the low boiling point of the compound[34]. Preliminary characterization:

HRMS (EI) (*m*/*z*): calculated for $C_6H_{11}O_1$ $[M+H]^+$: 99.0804; found: 99.0805.

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Lipodex-A column: 30.0 m; i.D. 0.25mm); FID; Temperature: 200 °C (injector), 350 °C (detector), 35 °C (10 min, iso); Gas: H_2 (0.4 bar); t_R = 4.05 min (major) and t_R = 4.25 min (minor), e.r. = 50:50.

(2*R*,6*S*)-6-hexyl-2-phenyl-3,6-dihydro-2*H*-pyran (3aa)


3aa

Aldehyde **1a** (10.6 mg, 0.1 mmol, 1.0 equiv) and diene **2f** (138 mg, 1.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4e** (0.5 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.6 mL) at –78 °C, then the reaction mixture was stirred at –30 °C for 48 h. **3aa** was obtained as a colorless oil (17.5 mg, 0.0716 mmol, 72%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (tt, *J* = 7.3, 1.3 Hz, 1H), 5.93–5.89 (m, 1H), 5.81 (qd, *J* = 10.3, 2.0 Hz, 1H), 4.69 (t, *J* = 6.6 Hz, 1H), 4.23–4.20 (m, 1H), 2.28–2.25 (m, 2H), 1.76–1.69 (m, 1H), 1.57–1.44 (m, 3H), 1.39–1.29 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

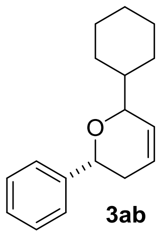
^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.5, 130.7, 128.6, 127.6, 126.6, 124.2, 74.0, 69.6, 34.4, 32.5, 32.2, 29.7, 26.5, 23.1, 14.3.

HRMS (ESI+) (*m/z*): calculated for $C_{17}H_{24}O_1Na_1$ $[M+Na]^+$: 267.1719; found: 267.1720.

$[\alpha]_D^{25}$: +142.0 (*c* = 0.71, CH_2Cl_2).

HPLC: The enantiomeric ratio was measured by HPLC analysis using 150 mm 3-AmyCoat RP, i.D. 4.6 mm. Acetonitrile/H_2O = 50:50, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 39.28 min (minor) and t_R= 47.05 min (major), e.r. = 99.8:0.2.

(*R*)-6-cyclohexyl-2-phenyl-3,6-dihydro-2*H*-pyran (3ab)



3ab

Aldehyde **1a** (10.6 mg, 0.1 mmol, 1.0 equiv) and diene **2g** (136 mg, 1.0 mmol, 10.0 equiv) were added to a mixture of catalyst **4e** (0.5 mol%) and 5 Å molecular sieves (21 mg) in MeCy (0.6 mL) at –78 °C, then the reaction mixture was stirred at –30 °C for 72 h. **3ab** was obtained as a colorless oil (*trans*-diastereomer: 13.1 mg, 0.0541 mmol, 54.1%; *cis*-diastereomer: 3.0 mg, 0.0124 mmol, 12.4%).

***trans*-diastereomer**:

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.39–7.37 (m, 2H), 7.33 (dt, *J* = 7.4, 2.0 Hz, 2H), 7.26 (tt, *J* = 6.6, 1.4 Hz, 1H), 5.97–5.91 (m, 2H), 4.70 (q, *J* = 4.3 Hz, 1H), 3.85 (dd, *J* = 8.1, 1.1 Hz, 1H), 2.33–2.21 (m, 2H), 2.01–1.94 (m, 1H), 1.78–1.63 (m, 6H), 1.30–0.97 (m, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.5, 129.1, 128.6, 127.5, 126.6, 124.7, 78.2, 70.4, 42.5, 32.3, 30.1, 29.8, 26.9, 26.6, 26.5.

HRMS (EI) (*m/z*): calculated for $C_{17}H_{22}O_1$ [M]: 242.1665; found: 242.1667.

$[\alpha]_D^{25}$: +161.0 (c = 0.49, CH_2Cl_2).

HPLC: The enantiomeric ratio was measured by HPLC analysis using 150 mm 3-AmyCoat RP, i.D. 4.6 mm. Acetonitrile/H_2O = 50:50, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 31.65 min (minor) and t_R= 33.78 min (major), e.r. = 99.8:0.2.

***cis*-diastereomer**:

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38–7.36 (m, 2H), 7.33 (dt, J = 7.4, 2.0 Hz, 2H), 7.25 (tt, J = 6.6, 1.4 Hz, 1H), 5.94–5.90 (m, 1H), 5.78–5.74 (m, 1H), 4.57 (q, J = 4.7 Hz, 1H), 4.14–4.10 (m, 1H), 2.26–2.12 (m, 2H), 1.82–1.75 (m, 4H), 1.69–1.66 (m, 1H), 1.32–1.14 (m, 6H).

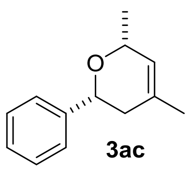
^{13}C NMR (126 MHz, CD_2Cl_2): δ 144.0, 129.5, 128.5, 127.5, 126.1, 125.5, 79.9, 75.7, 43.4, 33.9, 29.2, 28.3, 27.1, 26.87, 26.86.

HRMS (ESI+) (*m/z*): calculated for $C_{17}H_{22}O_1Na_1$ $[M+Na]^+$: 265.1563; found: 265.1565.

$[\alpha]_D^{25}$: +39.0 (c = 0.11, CH_2Cl_2).

HPLC: The enantiomeric ratio was measured by HPLC analysis using 150 mm 3-AmyCoat RP, i.D. 4.6 mm. Acetonitrile/H_2O = 50:50, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 40.46 min (minor) and t_R= 42.39 min (major), e.r. = 97:3.

(2*R*,6*R*)-4,6-dimethyl-2-phenyl-3,6-dihydro-2*H*-pyran (3ac)



3ac

Aldehyde **1a** (21.2 mg, 0.20 mmol, 1.0 equiv) and diene **2h** (82 mg, 1.0 mmol, 5.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (140 mg) in MeCy (2.0 mL) at –78 °C, then the reaction mixture was stirred at –60 °C for 24 h. **3ac** was obtained as a colorless oil (30.5 mg, 0.162 mmol, 81%)[21].

^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.40–7.23 (m, 5H), 5.42–5.40 (m, 1H), 4.56 (dd, J = 10.5, 3.7 Hz, 1H), 4.39–4.30 (m, 1H), 2.26–2.14 (m, 1H), 2.06 (td, J = 16.8, 2.7 Hz, 1H), 1.74–1.73 (m, 3H), 1.25 (d, J = 6.6 Hz, 3H).

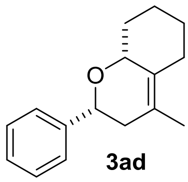
^{13}C NMR (75 MHz, CD_2Cl_2): δ 143.6, 132.5, 128.6, 127.6, 126.3, 125.6, 76.4, 72.0, 38.1, 22.9, 21.8.

HRMS (EI) (*m/z*): calculated for $C_{13}H_{16}O_1$ [M]: 188.1196; found: 188.1195.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +81.0 ($c$ = 0.39, $CHCl_3$).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Hydrodex-gamma-TBDAc column: 25.0 m); FID; Temperature: 230 °C (injector), 350 °C (detector), 100 °C (50 min, iso, 8 min); 220 °C (3 min); Gas: H_2 (0.60 bar); t_R = 38.19 min (minor) and t_R= 39.59 min (major), e.r. = 96:4.

(2*R*,8*aR*)-4-methyl-2-phenyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (3ad)



3ad

Aldehyde **1a** (10.6 mg, 0.10 mmol, 1.0 equiv) and diene **2i** (61 mg, 0.50 mmol, 5.0 equiv) were added to a mixture of catalyst **4f** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –60 °C for 24 h. **3ad** was obtained as a colorless oil (19.4 mg, 0.085 mmol, 85%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38–7.32 (m, 4H), 7.26 (tt, *J* = 7.2, 1.3 Hz, 1H), 4.50 (dd, *J* = 10.9, 3.8 Hz, 1H), 4.10 (d, *J* = 10.6 Hz, 1H), 2.77 (qd, *J* = 14.2, 2.5 Hz, 1H), 2.32–2.26 (m, 1H), 2.13–2.10 (m, 1H), 2.04 (qd, *J* = 16.6, 2.6 Hz, 1H), 1.83–1.78 (m, 1H), 1.76–1.73 (m, 1H), 1.70 (s, 3H), 1.65 (d, *J* = 14.1 Hz, 1H), 1.44 (tq, *J* = 13.3, 3.4 Hz, 1H), 1.32 (dq, *J* = 11.7, 3.6 Hz, 1H), 1.19 (tq, *J* = 13.0, 3.8 Hz, 1H).

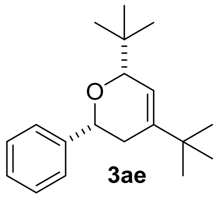
^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.7, 132.4, 128.6, 127.5, 126.3, 122.3, 77.2, 75.3, 39.7, 35.0, 27.4, 27.2, 25.0, 18.3.

HRMS (EI) (*m/z*): calculated for $C_{16}H_{20}O_1$ [M]: 228.1509; found: 228.1510.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +144.0 ($c$ = 0.86, CH_2Cl_2).

HPLC: The enantiomeric ratio was measured by HPLC analysis using 150 mm 3-AmyCoat RP, i.D. 4.6 mm. Acetonitrile/H_2O = 50:50, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 27.12 min (minor) and t_R= 29.22 min (major), e.r. = 95:5.

(2*R*,6*S*)-4,6-di-*tert*-butyl-2-phenyl-3,6-dihydro-2*H*-pyran (3ae)



3ae

Aldehyde **1a** (10.6 mg, 0.10 mmol, 1.0 equiv) and diene **2j** (83 mg, 0.50 mmol, 5.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –60 °C for 48 h. **3ae** was obtained as a colorless oil (20 mg, 0.0735 mmol, 73.5%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 5.56 (t, *J* = 2.0 Hz, 1H), 4.46 (dd, *J* = 10.7, 2.9 Hz, 1H), 3.94 (p, *J* = 2.3 Hz, 1H), 2.26 (td, *J* = 16.4, 2.7 Hz, 1H), 2.06 (ddt, *J* = 10.7, 2.8, 0.8 Hz, 1H), 1.07 (s, 9H), 0.98 (s, 9H).

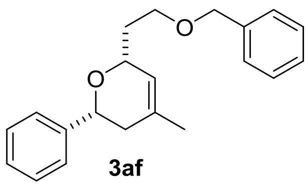
^{13}C NMR (126 MHz, CD_2Cl_2): δ 145.9, 144.6, 128.5, 127.4, 126.1, 117.8, 83.3, 75.9, 35.6, 35.4, 33.7, 28.8, 26.1.

HRMS (EI) (*m/z*): calculated for $C_{19}H_{28}O_1$ [M]: 272.2140; found: 272.2140.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +101.0 (*c* = 0.50, $CHCl_3$).

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Cyclodextrin-H column: 25.0 m; i.D. 0.25mm); FID; Temperature: 230 °C (injector), 350 °C (detector), 100 °C (135 min, iso, 8 min); 170 °C (3 min, iso); Gas: H_2 (0.50 bar); t_R = 113.99 min (minor) and t_R= 119.57 min (major), e.r. = 95:5.

(2*R*,6*R*)-6-(2-(benzyloxy)ethyl)-4-methyl-2-phenyl-3,6-dihydro-2*H*-pyran (3af)



3af

The aldehyde **1a** (10.6 mg, 0.10 mmol, 1.0 equiv) and diene **2k** (101 mg, 0.50 mmol, 5.0 equiv) were added to a mixture of catalyst **4d** (1 mol%) and 5 Å molecular sieves (70 mg) in MeCy (1.0 mL) at –78 °C, then the reaction mixture was stirred at –60 °C for 48 h. **3af** was obtained as a colorless solid (26 mg, 0.084 mmol, 84%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38–7.30 (m, 8H), 7.28–7.25 (m, 2H), 5.54 (br s, 1H), 4.57 (dd, *J* = 10.6, 3.6 Hz, 1H), 4.50 (s, 2H), 4.42–4.37 (m, 1H), 3.73–3.62 (m, 2H), 2.21–2.16 (m, 1H), 2.10 (td, *J* = 16.8, 3.0 Hz, 1H), 1.95–1.81 (m, 2H), 1.74 (br s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 143.6, 139.4, 133.0, 128.6, 127.9, 127.7, 127.6, 126.1, 124.3, 76.0, 73.2, 73.1, 67.4, 38.2, 36.5, 23.0.

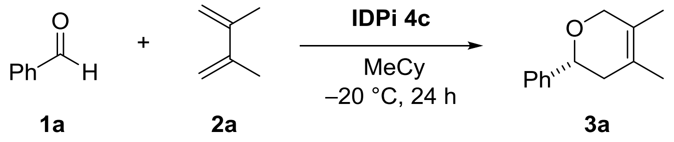
HRMS (ESI+) (*m/z*): calculated for $C_{21}H_{25}O_2$ $[M+H]^+$: 309.1849; found: 309.1849.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +62.4 ($c$ = 0.50, $CHCl_3$).

HPLC: The enantiomeric ratio was measured by HPLC analysis using Chiralpak OD-3, i.D. 4.6 mm. Heptane/^{i}PrOH = 99:1, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 5.56 min (minor) and t_R= 6.49 min (major), e.r. = 95:5.

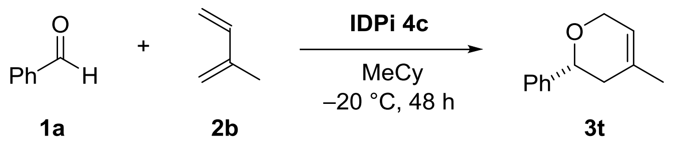
Gram Scale Reaction and Derivatization

Gram Scale Reaction

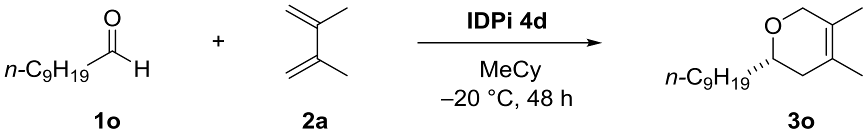


To a flame-dried Schlenk tube under argon were added 5 Å molecular sieves (700 mg), catalyst IDPi **4c** (45 mg, 0.02 mmol, 0.02 equiv), and MeCy (10.0 mL) at room temperature. Then aldehyde **1a** (1.06 g, 10.0 mmol, 1.0 equiv) and diene **2a** (986 mg, 12.0 mmol, 1.2 equiv) were added to the reaction mixture in sequence at –78 °C. The reaction was stirred at –20 °C for 24 h. Purification of product **3a** (1.83 g, 9.7 mmol, 97%, 98:2 e.r.) was performed by column chromatography on silica gel using 2% diethyl ether/pentane as the eluent. The catalyst IDPi **4c** could be recovered via the same column chromatography on silica gel using 50% hexanes/ethyl acetate as the eluent affording the salt state of IDPi **4c**. The salt was dissolved in CH_2Cl_2 (10 mL) and stirred with HCl (6 M, aq., 10.0 mL) for 30 min. The organic layer was separated, washed with HCl (6 M, aq., 10.0 mL), and concentrated under reduced pressure affording the recovered catalyst IDPi **4c** (43.7 mg, 97%).

The recovered IDPi **4c** was continually employed to catalyze the [4+2]-cycloaddition reaction of aldehyde **1a** and diene **2a** (Table S3, entry 3).

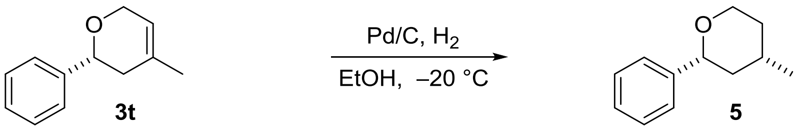


To a flame-dried Schlenk tube under argon were added 5 Å molecular sieves (700 mg), catalyst IDPi **4c** (45 mg, 0.02 mmol, 0.02 equiv), and MeCy (10.0 mL) at room temperature. Then aldehyde **1a** (1.06 g, 10.0 mmol, 1.0 equiv) and diene **2b** (817 mg, 12.0 mmol, 1.2 equiv) were added to the reaction mixture in sequence at –78 °C. The reaction was stirred at –20 °C for 48 h. Purification of product **3t** (1.51 g, 8.7 mmol, 87%, 98:2 e.r.) was performed by column chromatography on silica gel using 2% diethyl ether/pentane as the eluent. The catalyst IDPi **4c** was recovered via the same column chromatography.

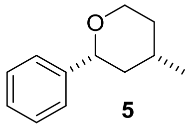


To a flame-dried Schlenk tube under argon were added 5 Å molecular sieves (1.05 g), catalyst IDPi **4d** (105 mg, 0.045 mmol, 0.01 equiv), and MeCy (15.0 mL) at room temperature. Then diene **2a** (3.70 g, 45.0 mmol, 10.0 equiv) and aldehyde **1o** (703 mg, 4.5 mmol, 1.0 equiv) were added to the reaction mixture in sequence at –20 °C. The reaction was stirred at –20 °C for 48 h. Purification of product **3o** (0.95 g, 4.0 mmol, 89%, 97:3 e.r.) was performed by column chromatography on silica gel using 2% diethyl ether/pentane as the eluent.

Derivatization



(2*R*,4*S*)-4-methyl-2-phenyltetrahydro-2*H*-pyran (5)



3t (31.5 mg, 0.18 mmol, 1.0 equiv) was dissolved in ethanol (1.0 mL) at room temperature, followed by the addition of palladium (10%) on charcoal (10.4 mg). An atmosphere of hydrogen was introduced and the resulting suspension was stirred at –20 °C for 2 h. The reaction mixture was warmed up to room temperature and stirred for 12 h. The reaction mixture was filtered over Celite and the residue was purified by column chromatography on silica gel using 5% diethyl ether/pentane as the eluent affording *Doremox* **5** as colorless oil. (31.0 mg, 0.18 mmol, 98%, *cis*:*trans* = 8.5:1, 98:2 e.r.$_{cis}$, 94.5:5.5 e.r.$_{trans}$).

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.34–7.30 (m, 4H), 7.25–7.22 (m, 1H), 4.64 (*trans* isomer, dd, J = 9.9, 3.0 Hz, 0. 12H), 4.29 (*cis* isomer, dd, J = 11.3, 2.2 Hz, 0.95H), 4.10 (*cis* isomer, ddd, J = 11.5, 4.7, 1.6 Hz, 0.97H), 3.81–3.79 (*trans* isomer, m, 0.24H), 3.57 (*cis* isomer, ddd, J = 12.4, 11.4, 2.2 Hz, 0.99H), 2.12–2.07 (*trans* isomer, m, 0.12H), 1.92–1.73 (m, 2.22H), 1.63-1.58 (m, 1.13H), 1.35–1.26 (m, 1.22H), 1.20–1.14 (m, 1.37H), 0.97 (d, J = 6.5 Hz, 3.0H), (spectra were complicated due to the presence of two diastereomers).

^{13}C NMR (151 MHz, CD_2Cl_2): δ 144.1 (*cis* isomer), 143.8 (*trans* isomer), 128.54 (*trans* isomer), 128.52 (*cis* isomer), 127.5 (*cis* isomer), 127.3 (*trans* isomer), 126.4 (*trans* isomer), 126.2 (*cis* isomer), 80.0 (*cis* isomer), 74.2 (*trans* isomer), 68.8 (*cis* isomer), 63.3 (*trans* isomer), 43.3 (*cis* isomer), 39.6 (*trans* isomer), 34.9 (*cis* isomer), 32.4 (*trans* isomer), 31.2 (*cis* isomer), 25.9 (*trans* isomer), 22.5 (*cis* isomer), 18.5 (*trans* isomer), (spectra were complicated due to the presence of two diastereomers).

HRMS (ESI+) (*m/z*) calculated for $C_{12}H_{16}O_1Na_1$ $[M+Na]^+$: 199.1093; found: 199.1094.

GC: The enantiomeric ratio was measured by GC analysis on a chiral column (Hydrodex-gamma-TBDAc column: 25.0 m; i.D. 0.25mm); FID; Temperature: 220 °C (injector), 350 °C (detector), 120 °C (30 min, iso); Gas: H_2 (0.50 bar); t_R (*cis*) = 17.04 min (minor) and t_R (*cis*) = 17.76 min (major), e.r. = 98:2; t_R (*trans*) = 19.45 min (major) and t_R (*trans*) = 21.17 min (minor), e.r. = 94.5:5.5.

Kinetic Isotope Effect (KIE) Studies

The relative ^{13}C compositions of **3a** at C3 and C4 were respectively assigned to be 1.000 in this intramolecular KIE measurement. The relative ^{13}C composition at C1 was calculated from the integration at C1 versus C4. The intramolecular KIE of C1 was the reciprocal of the average of relative ^{13}C compositions at C1. Similarly, the relative ^{13}C composition at C2 was calculated from the integration at C2 versus C3. The intramolecular KIE of C2 was the reciprocal of the average of relative ^{13}C compositions at C2. The standard deviations in the parentheses were calculated in a standard way[22,23].

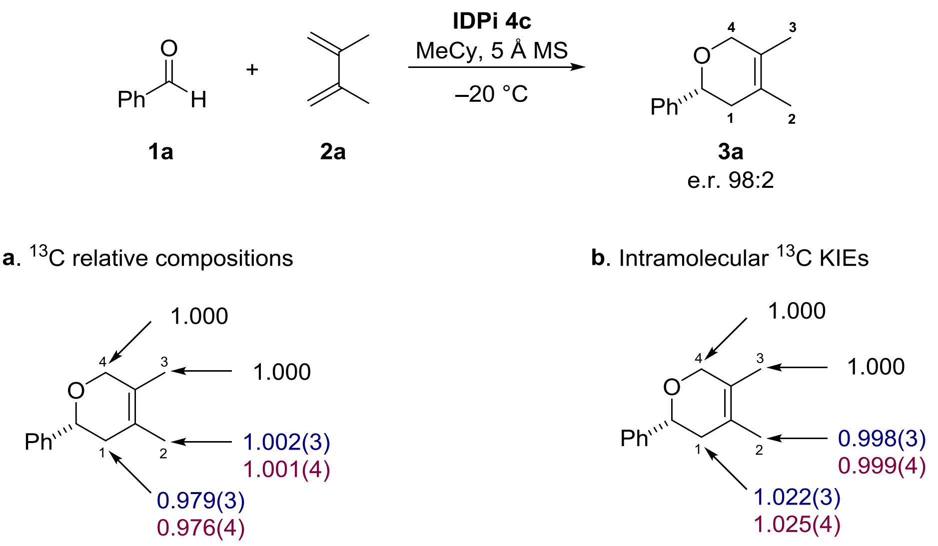


Figure S6. Intramolecular KIEs. (The values in blue were measured at 15 ± 0.6% completion of **2a** and the values in purple were measured at 16 ± 0.8% completion of **2a**.)

Excess amount of diene reaction:

In a flame-dried Schlenk tube under argon, catalyst **4c** (27 mg, 12 μmol, 0.05 equiv), 5 Å molecular sieves (210 mg), MeCy (3.0 mL) were added. Subsequently, benzaldehyde (**1a**) (250 mg, 2.36 mmol, 1.0 equiv), followed by 2,3-dimethyl-1,3-butadiene (**2a**) (800 mg, 9.74 mmol， 4.1 equiv) were added in at −78 °C. The reaction mixture was then stirred at −20 °C for 30 min and quenched by the addition of trimethylamine (1 drop). The solution was warmed to room temperature and 1,2,4,5-tetramethylbenzene (134 mg, 1.0 mmol) was added as an internal standard. Analysis of the crude reaction mixture by ^{1}H NMR showed that the reaction was quenched at 15 ± 0.6% completion of **2a** (relative to starting diene **2a**). Purification of **3a** was performed by column chromatography on silica gel using diethyl 2–6% ether/pentane as the eluent (198 mg, 1.05 mmol). Under argon, the obtained **3a** was transferred to a NMR tube (50 mg of **3a** in 0.5 mL CD_2Cl_2), and the NMR tube was then sealed by melting. Two samples were identically prepared for the following NMR analysis.

The reaction was carefully repeated and **3a** (210 mg, 1.12 mmol) was obtained at 16 ± 0.8% completion of **2a** (relative to starting diene **2a**). Another two identical NMR samples were prepared.

^{13}C spectra measurement:

The ^{13}C spectra were measured at 150.93 MHz on an Avance 600 MHz NMR spectrometer equipped with a cryogenically-cooled TXI (^{1}H/^{13}C/^{15}N) probe head, using a single pulse calibrated at 40° followed by inverse-gated decoupling. A 40-s delay was used between pulses, the longest T_1 for the ^{13}C of interest being about 6 s (C3). To obtain digital resolution of at least 5 points at the peak linewidth at half-height, an instrumental maximum of 128K points were collected over a sweep-width of 155 ppm centered at 46 ppm, followed by zero-filling to 256K points before Fourier transformation. Integrations were determined numerically using a ±7.5 Hz region for each peak. In general, an automatic polynomial baseline correction of order of at least 3 was applied. Integrals were simply calculated by summing the signal intensities over the peak regions.

Table S14. Values shown are raw ^{13}C integrals of **3a** at 15 ± 0.6% completion of **2a**.

Sample	C_1	C_2	C_3	C_4
1	85901	91898	91307	88351
1	85960	92516	91861	87659
1	86779	92491	92002	88020
1	86069	92518	93114	87888
1	95521	102349	101247	97308
1	95284	101747	101450	97669
1	95647	101314	101403	97199
1	86724	92809	93180	88907
2	350900	373893	373560	360129
2	355073	377562	376117	362694
2	354592	377015	377226	362330
2	355307	378537	378589	363559
2	356656	379971	379377	365966
2	358969	382854	381606	366213
2	357178	379629	380955	364419
2	357657	381297	380861	365602

Table S15. Values shown are raw ^{13}C integrals of **3a** at 16 ± 0.8% completion of **2a**.

Sample	C_1	C_2	C_3	C_4
1	88077	93934	94519	89963
1	88941	93702	94374	90204
1	88368	94464	95318	91427
1	88895	94891	94633	91014
1	85510	91436	90853	88089
1	85932	92064	91378	88353
1	86267	91589	91263	88107
1	85986	91887	91145	87680
2	86474	91458	91995	87824
2	86153	91650	91278	88730
2	86674	91770	92088	89318
2	87694	92747	92224	89682
2	86601	93065	92773	89684
2	87276	93685	93009	89642
2	87239	93314	92793	88873
2	87527	93076	93567	89466

Single-Crystal X-ray Diffraction Analysis

Determination of the absolute configuration of 3f by X-ray diffraction

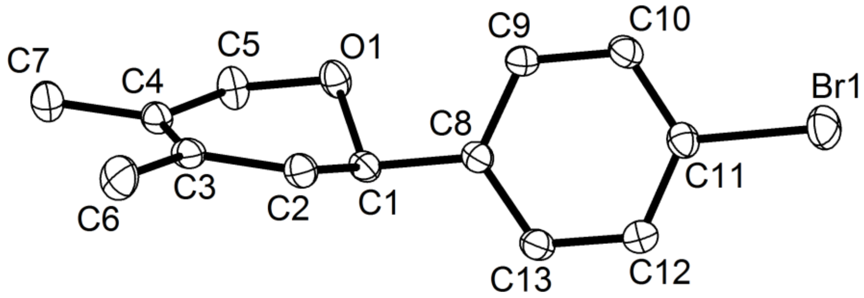


Figure S7. The molecular structure of **3f**. H atoms have been omitted for clarity.

Crystal data and structure refinement

Identification code	**3f** (10450)	
Empirical formula	$C_{13} H_{15} Br O$	
Color	colourless	
Formula weight	267.16 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P\ 2_1\ 2_1\ 2_1$, (no. 19)	
Unit cell dimensions	a = 6.836(2) Å	α= 90°.
	b = 11.5511(9) Å	β= 90°.
	c = 15.3107(9) Å	γ = 90°.
Volume	1208.9(4) $Å^3$	
Z	4	
Density (calculated)	1.468 $Mg \cdot m^{-3}$	
Absorption coefficient	3.372 mm^{-1}	
F(000)	544 e	
Crystal size	0.23 x 0.15 x 0.09 mm^3	
θ range for data collection	3.528 to 33.119°.	
Index ranges	$-10 \le h \le 10$, $-17 \le k \le 17$, $-23 \le l \le 23$	
Reflections collected	65284	
Independent reflections	4595 [R_{int} = 0.0406]	
Reflections with $I>2\sigma(I)$	4427	
Completeness to θ = 25.242°	99.1 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.75447 and 0.51719	

Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4595 / 0 / 138	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2σ(I)]	R_1 = 0.0203	wR^2= 0.0521
R indices (all data)	R_1 = 0.0220	wR^2 = 0.0530
Absolute structure parameter	-0.006(3)	
Extinction coefficient	0	
Largest diff. peak and hole	0.463 and -0.355 e·Å^{-3}	

Atomic coordinates and equivalent isotropic displacement parameters (Å^2).
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	0.2649(2)	0.3189(2)	0.5884(1)	0.018(1)
C(2)	0.0983(2)	0.3329(2)	0.6540(1)	0.020(1)
C(3)	0.0412(2)	0.4578(2)	0.6672(1)	0.021(1)
C(4)	0.1547(2)	0.5432(2)	0.6371(1)	0.021(1)
C(5)	0.3487(2)	0.5167(2)	0.5945(1)	0.023(1)
C(6)	-0.1475(3)	0.4750(2)	0.7163(2)	0.032(1)
C(7)	0.1107(3)	0.6705(2)	0.6422(1)	0.028(1)
C(8)	0.3544(2)	0.1997(1)	0.5929(1)	0.017(1)
C(9)	0.5089(2)	0.1772(2)	0.6500(1)	0.020(1)
C(10)	0.5871(2)	0.0659(2)	0.6570(1)	0.022(1)
C(11)	0.5082(2)	-0.0221(1)	0.6060(1)	0.020(1)
C(12)	0.3551(3)	-0.0018(1)	0.5486(1)	0.022(1)
C(13)	0.2789(2)	0.1097(2)	0.5422(1)	0.021(1)
Br(1)	0.6150(1)	-0.1736(1)	0.6157(1)	0.029(1)
O(1)	0.4148(2)	0.4013(1)	0.6078(1)	0.021(1)

Bond lengths [Å] and angles [°].

C(1)-O(1)	1.430(2)	C(1)-C(8)	1.508(2)
C(1)-C(2)	1.528(2)	C(2)-C(3)	1.507(2)
C(3)-C(4)	1.337(3)	C(3)-C(6)	1.506(2)
C(4)-C(7)	1.502(2)	C(4)-C(5)	1.509(2)
C(5)-O(1)	1.422(2)	C(8)-C(9)	1.396(2)
C(8)-C(13)	1.397(2)	C(9)-C(10)	1.397(2)

C(10)-C(11)	1.390(2)	C(11)-C(12)	1.387(2)
C(11)-Br(1)	1.9020(16)	C(12)-C(13)	1.393(2)
O(1)-C(1)-C(8)	107.89(12)	O(1)-C(1)-C(2)	109.09(13)
C(8)-C(1)-C(2)	111.72(13)	C(3)-C(2)-C(1)	112.47(14)
C(4)-C(3)-C(6)	124.83(17)	C(4)-C(3)-C(2)	120.68(14)
C(6)-C(3)-C(2)	114.48(16)	C(3)-C(4)-C(7)	126.01(15)
C(3)-C(4)-C(5)	120.57(15)	C(7)-C(4)-C(5)	113.41(15)
O(1)-C(5)-C(4)	114.07(14)	C(9)-C(8)-C(13)	119.29(15)
C(9)-C(8)-C(1)	120.38(14)	C(13)-C(8)-C(1)	120.29(14)
C(8)-C(9)-C(10)	120.58(15)	C(11)-C(10)-C(9)	118.82(14)
C(12)-C(11)-C(10)	121.68(15)	C(12)-C(11)-Br(1)	119.63(13)
C(10)-C(11)-Br(1)	118.70(12)	C(11)-C(12)-C(13)	118.89(15)
C(12)-C(13)-C(8)	120.74(15)	C(5)-O(1)-C(1)	111.52(12)

Anisotropic displacement parameters (Å^2).

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.016(1)	0.021(1)	0.016(1)	0.000(1)	0.000(1)	0.003(1)
C(2)	0.015(1)	0.024(1)	0.021(1)	-0.002(1)	0.003(1)	0.001(1)
C(3)	0.015(1)	0.027(1)	0.019(1)	-0.005(1)	0.000(1)	0.002(1)
C(4)	0.019(1)	0.024(1)	0.019(1)	-0.004(1)	-0.002(1)	0.005(1)
C(5)	0.023(1)	0.020(1)	0.027(1)	0.004(1)	0.006(1)	0.004(1)
C(6)	0.019(1)	0.036(1)	0.041(1)	-0.011(1)	0.008(1)	0.003(1)
C(7)	0.029(1)	0.025(1)	0.030(1)	-0.003(1)	-0.001(1)	0.008(1)
C(8)	0.016(1)	0.021(1)	0.015(1)	0.000(1)	0.001(1)	0.002(1)
C(9)	0.020(1)	0.022(1)	0.017(1)	-0.002(1)	-0.004(1)	0.002(1)
C(10)	0.022(1)	0.024(1)	0.019(1)	0.001(1)	-0.004(1)	0.004(1)
C(11)	0.022(1)	0.020(1)	0.018(1)	0.002(1)	0.001(1)	0.003(1)
C(12)	0.023(1)	0.022(1)	0.021(1)	-0.002(1)	-0.002(1)	0.000(1)
C(13)	0.019(1)	0.024(1)	0.019(1)	-0.001(1)	-0.003(1)	0.002(1)
Br(1)	0.037(1)	0.021(1)	0.029(1)	0.004(1)	-0.001(1)	0.007(1)
O(1)	0.015(1)	0.020(1)	0.027(1)	0.002(1)	0.003(1)	0.002(1)

Hydrogen coordinates and isotropic displacement parameters (Å^2).

	x	y	z	U_{eq}
H(1)	0.2141	0.3330	0.5281	0.021
H(2A)	-0.0170	0.2890	0.6333	0.024
H(2B)	0.1388	0.2996	0.7108	0.024
H(5A)	0.3372	0.5309	0.5309	0.028
H(5B)	0.4484	0.5707	0.6177	0.028
H(6A)	-0.1378	0.4383	0.7738	0.048
H(6B)	-0.2553	0.4399	0.6834	0.048
H(6C)	-0.1722	0.5580	0.7235	0.048
H(7A)	-0.0276	0.6816	0.6568	0.042
H(7B)	0.1386	0.7068	0.5857	0.042
H(7C)	0.1924	0.7061	0.6874	0.042
H(9)	0.5614	0.2382	0.6845	0.024
H(10)	0.6922	0.0506	0.6959	0.026
H(12)	0.3031	-0.0630	0.5142	0.026
H(13)	0.1743	0.1246	0.5029	0.025

The structure of **3f** was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0203 [$I > 2\sigma(I)$], wR_2 = 0.0530, 138 parameters. H atoms were refined using a riding model with C–H distances of 0.98 Å and $U_H = 1.5$ x U_C (CH_3), 0.99 Å and $U_H = 1.2 \times U_C$ (CH_2), 1.0 Å and $U_H = 1.2 \times U_C$ (CH) and 0.95 Å and $U_H = 1.2 \times U_C$ ($CH_{aromatic}$). S = 1.109, residual electron density 0.46 (1.09 Å from H5A)/ -0.36 (0.60 from Br1) e Å^{-3}. Three independent crystals from the sample **3f** were investigated and their absolute configurations determined. The respective Flack parameters (Parsons' method: Parsons, Flack and Wagner, *Acta Cryst*. B69 (2013) 249-259) are -0.006(3) [1850 quotients] (this crystal), -0.007(7) [1328 quotients] (crystal 2, Mo-K_α *X*-radiation, R_1 = 0.0364, S = 1.005, data completeness 99.7 %), and -0.011(9) [867 quotients] (crystal 3, Cu-K_α *X*-radiation, R_1 = 0.0258, S = 1.096, data completeness 98.4 %). **CCDC 1559570**.

Crystal structure analysis of the imidodiphosphorimidate (IDPI) 4c

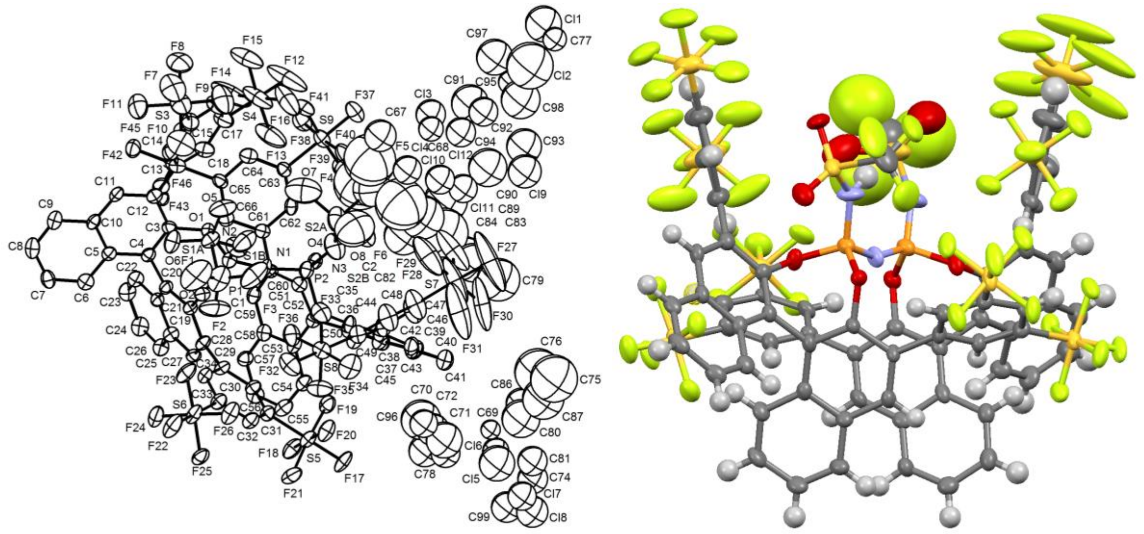


Figure S8. Left: The structure of the asymmetric unit in the crystal of **4c,** with crystal solvent (hexane and dichloromethane). H atoms have been omitted for clarity. Right: The molecular structure of **4c**, without crystal solvent.

Crystal data and structure refinement

Identification code	**4c** (10698)	
Empirical formula	$C_{83.20}\ H_{33}\ Cl_{3.80}\ F_{44.80}\ N_3\ O_{7.20}\ P_2\ S_{10}$	
Color	colourless	
Formula weight	2558.17 g·mol^{-1}	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	orthorhombic	
Space group	$P\ 2_1\ 2_1\ 2$, (no. 18)	
Unit cell dimensions	a = 18.7656(13) Å	α= 90°.
	b = 41.726(3) Å	β= 90°.
	c = 14.4668(10) Å	γ = 90°.
Volume	11327.8(14) Å^3	
Z	4	
Density (calculated)	1.500 Mg·m^{-3}	
Absorption coefficient	4.015 mm^{-1}	
F(000)	5074 e	
Crystal size	0.300 x 0.189 x 0.030 mm^3	
θ range for data collection	4.831 to 63.596°.	
Index ranges	$-21 \le h \le 21$, $-47 \le k \le 48$, $-14 \le l \le 16$	
Reflections collected	165258	

Independent reflections	18356 [R_{int} = 0.0717]	
Reflections with I>2σ(I)	16034	
Completeness to θ = 63.596°	99.1 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.90830 and 0.51138	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18356 / 46 / 1405	
Goodness-of-fit on F^2	1.513	
Final R indices [I>2σ(I)]	R_1 = 0.0674	wR^2 = 0.1847
R indices (all data)	R_1 = 0.0785	wR^2 = 0.1920
Absolute structure parameter	0.031(4)	
Extinction coefficient	0	
Largest diff. peak and hole	0.905 and -0.805 e·Å^{-3}	

Atomic coordinates and equivalent isotropic displacement parameters (Å^2).

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	-0.0927(7)	0.3431(4)	0.5747(8)	0.068(4)
C(2)	0.1322(13)	0.4636(6)	0.3201(18)	0.203(16)
C(3)	-0.1190(4)	0.3272(2)	0.2149(5)	0.027(2)
C(4)	-0.1132(4)	0.2951(2)	0.1997(4)	0.025(1)
C(5)	-0.1765(3)	0.2761(2)	0.1881(5)	0.026(2)
C(6)	-0.1755(4)	0.2426(2)	0.1802(5)	0.031(2)
C(7)	-0.2386(4)	0.2255(2)	0.1698(5)	0.033(2)
C(8)	-0.3053(4)	0.2416(2)	0.1692(5)	0.037(2)
C(9)	-0.3075(4)	0.2742(2)	0.1772(5)	0.030(2)
C(10)	-0.2437(3)	0.2927(2)	0.1873(5)	0.027(2)
C(11)	-0.2458(3)	0.3257(2)	0.1999(5)	0.028(2)
C(12)	-0.1853(4)	0.3440(2)	0.2145(5)	0.030(2)
C(13)	-0.1913(4)	0.3790(2)	0.2275(5)	0.031(2)
C(14)	-0.2424(4)	0.3916(2)	0.2894(6)	0.039(2)
C(15)	-0.2506(4)	0.4242(2)	0.2958(6)	0.043(2)
C(16)	-0.2105(5)	0.4456(2)	0.2446(7)	0.052(2)
C(17)	-0.1597(5)	0.4330(2)	0.1841(7)	0.048(2)
C(18)	-0.1497(4)	0.4002(2)	0.1766(6)	0.041(2)
C(19)	-0.0018(3)	0.2821(2)	0.2825(4)	0.024(1)

C(20)	-0.0423(3)	0.2793(2)	0.2040(5)	0.026(2)
C(21)	-0.0156(4)	0.2594(2)	0.1311(5)	0.027(2)
C(22)	-0.0490(4)	0.2573(2)	0.0444(5)	0.030(2)
C(23)	-0.0231(4)	0.2377(2)	-0.0240(5)	0.037(2)
C(24)	0.0378(4)	0.2190(2)	-0.0065(5)	0.037(2)
C(25)	0.0720(4)	0.2203(2)	0.0755(5)	0.032(2)
C(26)	0.0476(4)	0.2411(2)	0.1460(5)	0.028(2)
C(27)	0.0834(4)	0.2433(2)	0.2328(5)	0.028(2)
C(28)	0.0595(3)	0.2632(2)	0.3005(4)	0.025(1)
C(29)	0.0913(4)	0.2616(2)	0.3962(5)	0.029(2)
C(30)	0.1641(4)	0.2630(2)	0.4099(5)	0.029(2)
C(31)	0.1922(4)	0.2579(2)	0.4975(5)	0.029(2)
C(32)	0.1477(4)	0.2506(2)	0.5721(5)	0.033(2)
C(33)	0.0748(4)	0.2482(2)	0.5559(5)	0.031(2)
C(34)	0.0474(4)	0.2539(2)	0.4701(5)	0.028(2)
C(35)	0.2607(4)	0.3532(2)	0.3578(5)	0.030(2)
C(36)	0.2917(4)	0.3416(2)	0.2776(5)	0.030(2)
C(37)	0.3657(4)	0.3473(2)	0.2622(5)	0.036(2)
C(38)	0.3991(4)	0.3406(2)	0.1758(5)	0.036(2)
C(39)	0.4693(4)	0.3488(2)	0.1631(6)	0.043(2)
C(40)	0.5094(5)	0.3617(2)	0.2346(7)	0.050(2)
C(41)	0.4793(4)	0.3686(2)	0.3167(6)	0.043(2)
C(42)	0.4060(4)	0.3623(2)	0.3334(6)	0.036(2)
C(43)	0.3726(4)	0.3715(2)	0.4160(6)	0.039(2)
C(44)	0.2996(4)	0.3677(2)	0.4293(5)	0.034(2)
C(45)	0.2668(4)	0.3808(2)	0.5138(5)	0.036(2)
C(46)	0.2838(6)	0.4109(3)	0.5440(7)	0.063(3)
C(47)	0.2534(6)	0.4231(3)	0.6257(7)	0.068(3)
C(48)	0.2061(6)	0.4044(2)	0.6782(7)	0.061(3)
C(49)	0.1888(4)	0.3742(2)	0.6464(5)	0.038(2)
C(50)	0.2180(4)	0.3615(2)	0.5661(5)	0.034(2)
C(51)	0.1884(4)	0.3429(2)	0.1702(5)	0.029(2)
C(52)	0.2461(4)	0.3263(2)	0.2059(5)	0.029(2)
C(53)	0.2586(3)	0.2949(2)	0.1730(5)	0.029(2)
C(54)	0.3097(4)	0.2745(2)	0.2155(5)	0.033(2)
C(55)	0.3197(4)	0.2431(2)	0.1826(5)	0.039(2)
C(56)	0.2816(4)	0.2325(2)	0.1048(5)	0.036(2)
C(57)	0.2323(4)	0.2515(2)	0.0623(5)	0.031(2)
C(58)	0.2180(4)	0.2830(2)	0.0962(5)	0.029(2)

C(59)	0.1651(4)	0.3033(2)	0.0572(5)	0.032(2)
C(60)	0.1499(4)	0.3326(2)	0.0912(5)	0.026(2)
C(61)	0.0998(4)	0.3548(2)	0.0421(5)	0.028(2)
C(62)	0.1227(4)	0.3859(2)	0.0221(5)	0.031(2)
C(63)	0.0815(4)	0.4055(2)	-0.0332(5)	0.028(2)
C(64)	0.0164(4)	0.3957(2)	-0.0689(5)	0.035(2)
C(65)	-0.0058(4)	0.3648(2)	-0.0458(5)	0.031(2)
C(66)	0.0349(4)	0.3439(2)	0.0092(5)	0.032(2)
C(67)	-0.026(4)	0.5337(17)	0.623(5)	0.14(2)
C(68)	0.036(2)	0.5669(11)	0.660(3)	0.083(12)
C(69)	0.444(2)	0.3890(11)	0.913(3)	0.051(11)
C(70)	0.3138(9)	0.3638(4)	0.9426(12)	0.107(5)
C(71)	0.3838(17)	0.3577(7)	0.902(2)	0.178(11)
C(72)	0.3852(12)	0.3514(5)	0.8029(16)	0.144(7)
C(73)	0.4503(14)	0.3365(6)	0.7647(19)	0.117(7)
C(74)	0.6996(17)	0.3420(8)	0.559(2)	0.123(9)
C(75)	0.529(5)	0.447(2)	0.782(7)	0.31(4)
C(76)	0.534(5)	0.434(2)	0.662(6)	0.30(4)
C(77)	0.352(3)	0.6380(12)	0.000(3)	0.077(12)
C(78)	0.4494(12)	0.3193(5)	0.6588(16)	0.142(7)
C(79)	0.437(2)	0.4626(10)	0.398(3)	0.262(17)
C(80)	0.591(3)	0.3843(12)	0.596(4)	0.188(17)
C(81)	0.6619(17)	0.3586(8)	0.602(2)	0.121(9)
C(82)	0.3048(18)	0.4290(8)	0.151(2)	0.211(12)
C(83)	0.348(5)	0.4560(17)	0.217(5)	0.33(3)
C(84)	0.400(3)	0.4567(13)	0.322(5)	0.20(2)
C(85)	0.380(3)	0.4419(14)	0.161(4)	0.108(16)
C(86)	0.600(5)	0.389(3)	0.507(8)	0.13(3)
C(87)	0.566(8)	0.419(4)	0.691(10)	0.25(6)
C(88)	0.404(3)	0.4524(11)	0.234(4)	0.160(15)
C(89)	0.281(5)	0.4597(18)	0.243(6)	0.28(3)
C(90)	0.361(4)	0.4683(16)	0.056(5)	0.26(3)
C(91)	0.326(5)	0.541(2)	-0.091(7)	0.19(3)
C(92)	0.320(3)	0.5505(16)	0.019(4)	0.118(18)
C(93)	0.413(5)	0.549(2)	0.080(6)	0.18(3)
C(94)	0.324(3)	0.5206(16)	-0.022(5)	0.121(18)
C(95)	0.342(2)	0.5822(11)	-0.025(3)	0.079(11)
C(96)	0.399(3)	0.3417(14)	0.669(4)	0.21(2)
C(97)	0.308(5)	0.588(2)	-0.102(7)	0.18(3)

C(98)	0.359(7)	0.580(3)	0.044(9)	0.22(4)
C(99)	0.701(5)	0.306(3)	0.537(7)	0.13(3)
N(1)	0.0636(3)	0.3502(2)	0.3053(4)	0.036(2)
N(2A)	-0.0478(4)	0.3613(2)	0.4081(5)	0.048(2)
N(2B)	-0.0478(4)	0.3613(2)	0.4081(5)	0.048(2)
N(3A)	0.1359(5)	0.4043(2)	0.3498(6)	0.066(2)
N(3B)	0.1359(5)	0.4043(2)	0.3498(6)	0.066(2)
O(1)	-0.0571(2)	0.3453(1)	0.2326(4)	0.032(1)
O(2)	-0.0232(2)	0.3040(1)	0.3516(3)	0.028(1)
O(3)	0.1863(2)	0.3488(1)	0.3700(3)	0.035(1)
O(4)	0.1696(3)	0.3722(1)	0.2120(3)	0.031(1)
O(5)	-0.1466(5)	0.3905(2)	0.4826(6)	0.063(2)
O(6)	-0.1675(4)	0.3358(2)	0.4240(5)	0.048(2)
O(7)	0.0153(8)	0.4304(3)	0.3361(9)	0.119(4)
O(8)	0.1010(12)	0.4386(5)	0.4791(13)	0.186(7)
F(1)	-0.1516(5)	0.3389(3)	0.6237(5)	0.107(4)
F(2)	-0.0569(5)	0.3175(2)	0.5644(6)	0.090(3)
F(3)	-0.0526(4)	0.3662(2)	0.6167(5)	0.083(3)
F(4)	0.1332(19)	0.4545(8)	0.2377(19)	0.364(11)
F(5)	0.0871(19)	0.4855(6)	0.332(2)	0.364(11)
F(6)	0.1901(16)	0.4691(8)	0.353(2)	0.364(11)
F(7)	-0.3746(4)	0.4542(2)	0.4431(5)	0.084(2)
F(8)	-0.3467(3)	0.4643(1)	0.2980(5)	0.074(2)
F(9)	-0.2647(4)	0.4668(2)	0.4098(5)	0.080(2)
F(10)	-0.2924(4)	0.4173(2)	0.4545(4)	0.079(2)
F(11)	-0.3743(3)	0.4148(1)	0.3427(5)	0.069(2)
F(12)	-0.0636(5)	0.4838(2)	0.0563(7)	0.141(4)
F(13)	-0.0395(4)	0.4385(2)	0.1259(7)	0.112(3)
F(14)	-0.1259(6)	0.4420(2)	0.0260(5)	0.122(4)
F(15)	-0.1731(4)	0.4836(1)	0.1025(5)	0.093(2)
F(16)	-0.0849(4)	0.4798(2)	0.2040(6)	0.104(3)
F(17)	0.3697(2)	0.2610(1)	0.5347(3)	0.045(1)
F(18)	0.3022(2)	0.2373(1)	0.4315(3)	0.044(1)
F(19)	0.2957(2)	0.2900(1)	0.4535(3)	0.040(1)
F(20)	0.2773(2)	0.2823(1)	0.6041(3)	0.043(1)
F(21)	0.2848(2)	0.2296(1)	0.5828(3)	0.046(1)
F(22)	-0.0297(2)	0.2222(2)	0.7298(3)	0.058(2)
F(23)	-0.0408(2)	0.2600(1)	0.6255(3)	0.047(1)
F(24)	-0.0201(2)	0.2088(1)	0.5841(3)	0.047(1)

F(25)	0.0747(2)	0.2079(1)	0.6785(3)	0.041(1)
F(26)	0.0535(2)	0.2588(1)	0.7194(3)	0.045(1)
F(27)	0.2966(9)	0.4976(3)	0.6963(8)	0.234(9)
F(28)	0.1908(6)	0.4710(2)	0.6838(7)	0.133(4)
F(29)	0.2658(7)	0.4768(2)	0.5627(7)	0.144(5)
F(30)	0.3572(7)	0.4570(3)	0.6434(7)	0.170(6)
F(31)	0.2857(8)	0.4506(3)	0.7654(7)	0.193(7)
F(32)	0.0732(3)	0.3289(1)	0.7669(4)	0.059(1)
F(33)	0.0735(3)	0.3790(1)	0.7210(4)	0.050(1)
F(34)	0.1630(3)	0.3595(2)	0.8062(3)	0.064(2)
F(35)	0.1766(3)	0.3195(1)	0.7041(4)	0.058(1)
F(36)	0.0881(2)	0.3390(1)	0.6195(3)	0.047(1)
F(37)	0.1457(3)	0.4783(1)	-0.0944(4)	0.056(1)
F(38)	0.0959(3)	0.4390(1)	-0.1701(3)	0.047(1)
F(39)	0.1926(2)	0.4305(1)	-0.0841(4)	0.049(1)
F(40)	0.1370(3)	0.4524(1)	0.0370(3)	0.047(1)
F(41)	0.0406(3)	0.4607(1)	-0.0502(4)	0.047(1)
F(42)	-0.1634(2)	0.3399(1)	-0.1351(3)	0.049(1)
F(43)	-0.0573(2)	0.3176(1)	-0.1228(3)	0.043(1)
F(44)	-0.0710(3)	0.3654(1)	-0.1918(3)	0.049(1)
F(45)	-0.1280(2)	0.3835(1)	-0.0675(3)	0.047(1)
F(46)	-0.1138(2)	0.3362(1)	0.0016(3)	0.041(1)
P(1)	-0.0144(1)	0.3413(1)	0.3268(1)	0.029(1)
P(2)	0.1328(1)	0.3696(1)	0.3114(1)	0.032(1)
S(1A)	-0.1190(1)	0.3589(1)	0.4613(2)	0.036(1)
S(1B)	-0.0649(7)	0.3753(4)	0.4756(10)	0.069(4)
S(3)	-0.3172(1)	0.4402(1)	0.3746(2)	0.058(1)
S(2A)	0.0916(2)	0.4294(1)	0.3878(3)	0.068(1)
S(2B)	0.1563(11)	0.4310(4)	0.3799(12)	0.082(5)
S(4)	-0.1079(2)	0.4601(1)	0.1158(3)	0.087(1)
S(5)	0.2868(1)	0.2595(1)	0.5178(1)	0.033(1)
S(6)	0.0186(1)	0.2345(1)	0.6485(1)	0.039(1)
S(7)	0.2751(3)	0.4630(1)	0.6628(3)	0.145(2)
S(8)	0.1270(1)	0.3501(1)	0.7103(1)	0.040(1)
S(9)	0.1155(1)	0.4446(1)	-0.0650(1)	0.040(1)
S(10)	-0.0899(1)	0.3512(1)	-0.0941(1)	0.037(1)
Cl(1)	0.3225(15)	0.6421(7)	-0.026(2)	0.180(10)
Cl(2)	0.336(3)	0.6082(14)	0.027(3)	0.304(19)
Cl(3)	0.1011(8)	0.5567(4)	0.4146(11)	0.122(4)

Cl(4)	0.0986(12)	0.5123(5)	0.5210(15)	0.113(6)
Cl(5)	0.6299(6)	0.3380(3)	0.4771(8)	0.095(3)
Cl(6)	0.6318(11)	0.3333(5)	0.5244(15)	0.175(7)
Cl(7)	0.6658(7)	0.3332(3)	0.6724(9)	0.113(4)
Cl(8)	0.6984(12)	0.3277(5)	0.6874(14)	0.137(6)
Cl(9)	0.2268(11)	0.5852(5)	0.7243(15)	0.152(6)
Cl(10)	0.0796(9)	0.5422(4)	0.7731(12)	0.117(4)
Cl(11)	0.1244(9)	0.5479(4)	0.7886(11)	0.111(4)
Cl(12)	0.1749(16)	0.5665(7)	0.680(2)	0.202(10)

Bond lengths [Å] and angles [°].

C(1)-F(2)	1.273(17)	C(1)-F(1)	1.325(15)
C(1)-F(3)	1.365(17)	C(1)-S(1A)	1.836(13)
C(1)-S(1B)	2.03(2)	C(2)-F(6)	1.21(3)
C(2)-F(4)	1.25(3)	C(2)-F(5)	1.26(3)
C(2)-S(2B)	1.68(3)	C(2)-S(2A)	1.89(3)
C(3)-C(4)	1.359(10)	C(3)-O(1)	1.410(8)
C(3)-C(12)	1.430(10)	C(4)-C(5)	1.439(10)
C(4)-C(20)	1.488(10)	C(5)-C(6)	1.405(10)
C(5)-C(10)	1.437(10)	C(6)-C(7)	1.389(10)
C(7)-C(8)	1.422(11)	C(8)-C(9)	1.365(11)
C(9)-C(10)	1.433(10)	C(10)-C(11)	1.388(10)
C(11)-C(12)	1.386(10)	C(12)-C(13)	1.474(10)
C(13)-C(18)	1.390(11)	C(13)-C(14)	1.415(11)
C(14)-C(15)	1.370(12)	C(15)-C(16)	1.382(12)
C(15)-S(3)	1.817(8)	C(16)-C(17)	1.396(13)
C(17)-C(18)	1.387(12)	C(17)-S(4)	1.788(9)
C(19)-C(20)	1.372(9)	C(19)-O(2)	1.413(8)
C(19)-C(28)	1.418(9)	C(20)-C(21)	1.432(10)
C(21)-C(22)	1.405(10)	C(21)-C(26)	1.427(10)
C(22)-C(23)	1.372(10)	C(23)-C(24)	1.410(11)
C(24)-C(25)	1.350(11)	C(25)-C(26)	1.414(10)
C(26)-C(27)	1.427(10)	C(27)-C(28)	1.361(10)
C(28)-C(29)	1.509(9)	C(29)-C(30)	1.383(10)
C(29)-C(34)	1.388(10)	C(30)-C(31)	1.389(10)

C(31)-C(32)	1.397(10)	C(31)-S(5)	1.801(7)
C(32)-C(33)	1.390(10)	C(33)-C(34)	1.365(10)
C(33)-S(6)	1.798(7)	C(35)-C(36)	1.385(10)
C(35)-C(44)	1.403(10)	C(35)-O(3)	1.420(8)
C(36)-C(37)	1.425(10)	C(36)-C(52)	1.488(10)
C(37)-C(42)	1.424(11)	C(37)-C(38)	1.425(11)
C(38)-C(39)	1.375(11)	C(39)-C(40)	1.388(12)
C(40)-C(41)	1.348(12)	C(41)-C(42)	1.420(11)
C(42)-C(43)	1.404(12)	C(43)-C(44)	1.392(11)
C(44)-C(45)	1.473(11)	C(45)-C(46)	1.368(12)
C(45)-C(50)	1.432(11)	C(46)-C(47)	1.409(13)
C(47)-C(48)	1.406(14)	C(47)-S(7)	1.795(10)
C(48)-C(49)	1.377(12)	C(49)-C(50)	1.390(11)
C(49)-S(8)	1.793(8)	C(51)-C(52)	1.385(10)
C(51)-O(4)	1.408(9)	C(51)-C(60)	1.420(10)
C(52)-C(53)	1.414(11)	C(53)-C(54)	1.425(10)
C(53)-C(58)	1.435(10)	C(54)-C(55)	1.406(12)
C(55)-C(56)	1.404(11)	C(56)-C(57)	1.363(11)
C(57)-C(58)	1.431(10)	C(58)-C(59)	1.420(10)
C(59)-C(60)	1.350(10)	C(60)-C(61)	1.500(10)
C(61)-C(66)	1.385(10)	C(61)-C(62)	1.394(10)
C(62)-C(63)	1.381(10)	C(63)-C(64)	1.386(11)
C(63)-S(9)	1.813(7)	C(64)-C(65)	1.398(10)
C(65)-C(66)	1.406(10)	C(65)-S(10)	1.817(7)
C(67)-C(68)	1.89(8)	C(68)-Cl(10)	2.10(5)
C(69)-C(71)	1.74(5)	C(70)-C(71)	1.46(3)
C(71)-C(72)	1.46(3)	C(72)-C(73)	1.48(3)
C(72)-C(96)	2.00(6)	C(73)-C(78)	1.69(3)
C(73)-C(96)	1.70(6)	C(74)-C(81)	1.17(4)
C(74)-Cl(6)	1.42(3)	C(74)-C(99)	1.54(11)
C(74)-Cl(5)	1.78(3)	C(74)-Cl(7)	1.79(4)
C(74)-Cl(8)	1.95(4)	C(75)-C(76)	1.82(12)
C(75)-C(87)	1.89(16)	C(76)-C(87)	0.96(16)
C(77)-Cl(1)	0.68(5)	C(77)-Cl(2)	1.34(6)
C(78)-C(96)	1.34(5)	C(79)-C(84)	1.32(6)
C(80)-C(86)	1.32(10)	C(80)-C(81)	1.72(5)
C(81)-Cl(7)	1.47(3)	C(81)-Cl(6)	1.64(4)
C(81)-Cl(8)	1.91(4)	C(81)-Cl(5)	2.09(3)
C(82)-C(85)	1.52(7)	C(82)-C(83)	1.68(7)

C(82)-C(89)	1.90(9)	C(83)-C(88)	1.09(8)
C(83)-C(85)	1.17(9)	C(83)-C(89)	1.32(9)
C(83)-C(84)	1.81(9)	C(84)-C(88)	1.29(6)
C(85)-C(88)	1.23(7)	C(85)-C(90)	1.91(9)
C(86)-Cl(5)	2.26(10)	C(91)-C(94)	1.32(10)
C(91)-C(92)	1.64(11)	C(91)-C(97)	1.97(13)
C(91)-C(95)	1.97(11)	C(92)-C(94)	1.38(8)
C(92)-C(98)	1.47(13)	C(92)-C(95)	1.52(8)
C(92)-C(93)	1.95(11)	C(93)-C(98)	1.70(14)
C(95)-C(98)	1.06(12)	C(95)-C(97)	1.30(9)
C(95)-Cl(2)	1.33(6)	C(97)-Cl(2)	2.12(10)
C(98)-Cl(2)	1.28(13)	C(99)-Cl(6)	1.74(10)
C(99)-Cl(5)	2.08(10)	N(1)-P(2)	1.531(6)
N(1)-P(1)	1.543(6)	N(2A)-S(1A)	1.545(7)
N(2A)-P(1)	1.573(6)	N(2B)-S(1B)	1.183(15)
N(2B)-P(1)	1.573(6)	N(3A)-S(2A)	1.445(9)
N(3A)-P(2)	1.553(8)	N(3B)-S(2B)	1.256(17)
N(3B)-P(2)	1.553(8)	O(1)-P(1)	1.589(5)
O(2)-P(1)	1.604(5)	O(3)-P(2)	1.575(5)
O(4)-P(2)	1.600(5)	O(5)-S(1A)	1.447(8)
O(6)-S(1A)	1.434(7)	O(7)-S(2A)	1.615(16)
O(8)-S(2A)	1.386(18)	F(7)-S(3)	1.576(6)
F(8)-S(3)	1.596(7)	F(9)-S(3)	1.570(7)
F(10)-S(3)	1.568(7)	F(11)-S(3)	1.577(6)
F(12)-S(4)	1.553(7)	F(13)-S(4)	1.575(8)
F(14)-S(4)	1.539(10)	F(15)-S(4)	1.580(7)
F(16)-S(4)	1.578(9)	F(17)-S(5)	1.577(4)
F(18)-S(5)	1.583(5)	F(19)-S(5)	1.584(5)
F(20)-S(5)	1.579(5)	F(21)-S(5)	1.564(5)
F(22)-S(6)	1.570(5)	F(23)-S(6)	1.576(5)
F(24)-S(6)	1.596(5)	F(25)-S(6)	1.590(5)
F(26)-S(6)	1.583(5)	F(27)-S(7)	1.578(8)
F(28)-S(7)	1.645(12)	F(29)-S(7)	1.570(12)
F(30)-S(7)	1.587(14)	F(31)-S(7)	1.583(14)
F(32)-S(8)	1.571(5)	F(33)-S(8)	1.577(5)
F(34)-S(8)	1.592(5)	F(35)-S(8)	1.583(5)
F(36)-S(8)	1.573(5)	F(37)-S(9)	1.575(5)
F(38)-S(9)	1.581(5)	F(39)-S(9)	1.587(5)
F(40)-S(9)	1.565(5)	F(41)-S(9)	1.573(5)

F(42)-S(10)	1.574(5)	F(43)-S(10)	1.583(5)
F(44)-S(10)	1.573(5)	F(45)-S(10)	1.576(5)
F(46)-S(10)	1.584(5)	Cl(1)-Cl(2)	1.63(6)
Cl(3)-Cl(4)	2.41(3)	Cl(5)-Cl(6)	0.71(2)
Cl(6)-Cl(7)	2.24(3)	Cl(7)-Cl(8)	0.69(2)
Cl(9)-Cl(12)	1.41(3)	Cl(10)-Cl(11)	0.901(18)
Cl(10)-Cl(12)	2.46(3)	Cl(11)-Cl(12)	2.00(3)

F(2)-C(1)-F(1)	113.0(14)	F(2)-C(1)-F(3)	110.8(12)
F(1)-C(1)-F(3)	108.4(11)	F(2)-C(1)-S(1A)	109.9(9)
F(1)-C(1)-S(1A)	107.5(9)	F(3)-C(1)-S(1A)	107.0(10)
F(6)-C(2)-F(4)	115(2)	F(6)-C(2)-F(5)	114(2)
F(4)-C(2)-F(5)	111(2)	F(6)-C(2)-S(2A)	107(2)
F(4)-C(2)-S(2A)	106(2)	F(5)-C(2)-S(2A)	102(2)
C(4)-C(3)-O(1)	119.5(6)	C(4)-C(3)-C(12)	123.6(7)
O(1)-C(3)-C(12)	117.0(6)	C(3)-C(4)-C(5)	119.7(6)
C(3)-C(4)-C(20)	120.2(6)	C(5)-C(4)-C(20)	119.9(6)
C(6)-C(5)-C(10)	119.4(6)	C(6)-C(5)-C(4)	123.2(6)
C(10)-C(5)-C(4)	117.3(6)	C(7)-C(6)-C(5)	120.6(7)
C(6)-C(7)-C(8)	120.6(7)	C(9)-C(8)-C(7)	119.8(7)
C(8)-C(9)-C(10)	121.4(7)	C(11)-C(10)-C(9)	121.6(6)
C(11)-C(10)-C(5)	120.1(6)	C(9)-C(10)-C(5)	118.2(6)
C(12)-C(11)-C(10)	123.0(6)	C(11)-C(12)-C(3)	116.2(7)
C(11)-C(12)-C(13)	120.3(7)	C(3)-C(12)-C(13)	123.5(6)
C(18)-C(13)-C(14)	118.5(7)	C(18)-C(13)-C(12)	121.3(7)
C(14)-C(13)-C(12)	120.1(7)	C(15)-C(14)-C(13)	119.3(8)
C(14)-C(15)-C(16)	122.8(8)	C(14)-C(15)-S(3)	118.9(7)
C(16)-C(15)-S(3)	118.3(6)	C(15)-C(16)-C(17)	117.7(8)
C(18)-C(17)-C(16)	120.9(8)	C(18)-C(17)-S(4)	120.4(7)
C(16)-C(17)-S(4)	118.7(7)	C(17)-C(18)-C(13)	120.7(8)
C(20)-C(19)-O(2)	119.0(6)	C(20)-C(19)-C(28)	123.6(6)
O(2)-C(19)-C(28)	117.4(5)	C(19)-C(20)-C(21)	117.8(6)
C(19)-C(20)-C(4)	119.4(6)	C(21)-C(20)-C(4)	122.7(6)
C(22)-C(21)-C(26)	118.2(6)	C(22)-C(21)-C(20)	122.5(6)
C(26)-C(21)-C(20)	119.3(6)	C(23)-C(22)-C(21)	121.5(7)
C(22)-C(23)-C(24)	119.3(7)	C(25)-C(24)-C(23)	121.3(7)
C(24)-C(25)-C(26)	120.4(7)	C(25)-C(26)-C(27)	121.5(6)
C(25)-C(26)-C(21)	119.2(6)	C(27)-C(26)-C(21)	119.3(6)
C(28)-C(27)-C(26)	121.2(6)	C(27)-C(28)-C(19)	118.3(6)

C(27)-C(28)-C(29)	120.2(6)	C(19)-C(28)-C(29)	120.9(6)
C(30)-C(29)-C(34)	119.1(6)	C(30)-C(29)-C(28)	121.4(6)
C(34)-C(29)-C(28)	118.9(6)	C(29)-C(30)-C(31)	120.0(6)
C(30)-C(31)-C(32)	120.8(6)	C(30)-C(31)-S(5)	121.1(5)
C(32)-C(31)-S(5)	118.1(5)	C(33)-C(32)-C(31)	118.3(7)
C(34)-C(33)-C(32)	120.8(7)	C(34)-C(33)-S(6)	120.7(5)
C(32)-C(33)-S(6)	118.4(6)	C(33)-C(34)-C(29)	121.2(6)
C(36)-C(35)-C(44)	123.3(6)	C(36)-C(35)-O(3)	118.2(6)
C(44)-C(35)-O(3)	118.4(6)	C(35)-C(36)-C(37)	118.8(7)
C(35)-C(36)-C(52)	119.4(6)	C(37)-C(36)-C(52)	121.5(7)
C(42)-C(37)-C(38)	119.1(7)	C(42)-C(37)-C(36)	118.5(7)
C(38)-C(37)-C(36)	122.2(7)	C(39)-C(38)-C(37)	119.3(8)
C(38)-C(39)-C(40)	121.2(8)	C(41)-C(40)-C(39)	120.8(8)
C(40)-C(41)-C(42)	121.1(8)	C(43)-C(42)-C(41)	121.8(7)
C(43)-C(42)-C(37)	119.9(7)	C(41)-C(42)-C(37)	118.3(7)
C(44)-C(43)-C(42)	121.8(7)	C(43)-C(44)-C(35)	117.3(7)
C(43)-C(44)-C(45)	119.0(7)	C(35)-C(44)-C(45)	123.6(7)
C(46)-C(45)-C(50)	119.7(8)	C(46)-C(45)-C(44)	120.4(7)
C(50)-C(45)-C(44)	119.9(7)	C(45)-C(46)-C(47)	120.4(9)
C(48)-C(47)-C(46)	120.5(9)	C(48)-C(47)-S(7)	119.8(7)
C(46)-C(47)-S(7)	119.7(8)	C(49)-C(48)-C(47)	118.4(8)
C(48)-C(49)-C(50)	122.3(8)	C(48)-C(49)-S(8)	119.5(6)
C(50)-C(49)-S(8)	118.2(6)	C(49)-C(50)-C(45)	118.7(7)
C(52)-C(51)-O(4)	118.0(6)	C(52)-C(51)-C(60)	123.1(7)
O(4)-C(51)-C(60)	118.8(6)	C(51)-C(52)-C(53)	117.9(6)
C(51)-C(52)-C(36)	119.7(7)	C(53)-C(52)-C(36)	122.4(6)
C(52)-C(53)-C(54)	121.5(7)	C(52)-C(53)-C(58)	119.5(6)
C(54)-C(53)-C(58)	118.9(7)	C(55)-C(54)-C(53)	120.1(7)
C(56)-C(55)-C(54)	119.7(7)	C(57)-C(56)-C(55)	121.6(7)
C(56)-C(57)-C(58)	120.5(7)	C(59)-C(58)-C(57)	122.8(6)
C(59)-C(58)-C(53)	118.2(6)	C(57)-C(58)-C(53)	119.0(7)
C(60)-C(59)-C(58)	122.9(7)	C(59)-C(60)-C(51)	117.4(6)
C(59)-C(60)-C(61)	121.5(6)	C(51)-C(60)-C(61)	120.8(6)
C(66)-C(61)-C(62)	120.3(7)	C(66)-C(61)-C(60)	120.7(6)
C(62)-C(61)-C(60)	118.7(6)	C(63)-C(62)-C(61)	119.9(6)
C(62)-C(63)-C(64)	122.3(6)	C(62)-C(63)-S(9)	118.9(5)
C(64)-C(63)-S(9)	118.7(5)	C(63)-C(64)-C(65)	116.5(7)
C(64)-C(65)-C(66)	123.0(7)	C(64)-C(65)-S(10)	117.2(5)
C(66)-C(65)-S(10)	119.7(5)	C(61)-C(66)-C(65)	117.9(7)

C(67)-C(68)-Cl(10)	96(3)	C(70)-C(71)-C(72)	116(3)
C(70)-C(71)-C(69)	115(3)	C(72)-C(71)-C(69)	102(3)
C(71)-C(72)-C(73)	117(2)	C(71)-C(72)-C(96)	173(3)
C(73)-C(72)-C(96)	56(2)	C(72)-C(73)-C(78)	121(2)
C(72)-C(73)-C(96)	78(2)	C(78)-C(73)-C(96)	46(2)
C(81)-C(74)-Cl(6)	78(3)	C(81)-C(74)-C(99)	135(5)
Cl(6)-C(74)-C(99)	72(4)	C(81)-C(74)-Cl(5)	88(3)
C(99)-C(74)-Cl(5)	77(4)	C(81)-C(74)-Cl(7)	55(2)
Cl(6)-C(74)-Cl(7)	87(2)	C(99)-C(74)-Cl(7)	90(4)
Cl(5)-C(74)-Cl(7)	109.3(19)	C(81)-C(74)-Cl(8)	71(2)
Cl(6)-C(74)-Cl(8)	105(2)	C(99)-C(74)-Cl(8)	84(4)
Cl(5)-C(74)-Cl(8)	127(2)	C(87)-C(76)-C(75)	79(10)
Cl(1)-C(77)-Cl(2)	102(6)	C(96)-C(78)-C(73)	67(3)
C(86)-C(80)-C(81)	93(6)	C(74)-C(81)-Cl(7)	85(3)
C(74)-C(81)-Cl(6)	58(2)	Cl(7)-C(81)-Cl(6)	91(2)
C(74)-C(81)-C(80)	145(4)	Cl(7)-C(81)-C(80)	121(3)
Cl(6)-C(81)-C(80)	96(2)	C(74)-C(81)-Cl(8)	74(2)
Cl(6)-C(81)-Cl(8)	97.5(19)	C(80)-C(81)-Cl(8)	137(3)
C(74)-C(81)-Cl(5)	58(2)	Cl(7)-C(81)-Cl(5)	108.4(19)
C(80)-C(81)-Cl(5)	90(2)	Cl(8)-C(81)-Cl(5)	112.5(17)
C(85)-C(82)-C(89)	85(4)	C(88)-C(83)-C(85)	66(7)
C(88)-C(83)-C(89)	150(10)	C(85)-C(83)-C(89)	139(10)
C(88)-C(83)-C(82)	120(8)	C(85)-C(83)-C(82)	62(5)
C(89)-C(83)-C(82)	78(6)	C(88)-C(83)-C(84)	45(4)
C(85)-C(83)-C(84)	108(7)	C(89)-C(83)-C(84)	105(7)
C(82)-C(83)-C(84)	138(5)	C(88)-C(84)-C(79)	144(6)
C(79)-C(84)-C(83)	170(6)	C(83)-C(85)-C(88)	54(5)
C(83)-C(85)-C(82)	76(6)	C(88)-C(85)-C(82)	123(5)
C(83)-C(85)-C(90)	99(6)	C(88)-C(85)-C(90)	123(5)
C(82)-C(85)-C(90)	87(4)	C(80)-C(86)-Cl(5)	94(6)
C(76)-C(87)-C(75)	71(10)	C(83)-C(88)-C(85)	60(5)
C(83)-C(88)-C(84)	99(7)	C(85)-C(88)-C(84)	152(6)
C(83)-C(89)-C(82)	60(5)	C(94)-C(91)-C(92)	54(5)
C(94)-C(91)-C(97)	135(8)	C(92)-C(91)-C(97)	81(6)
C(94)-C(91)-C(95)	102(7)	C(92)-C(91)-C(95)	49(4)
C(94)-C(92)-C(98)	146(8)	C(94)-C(92)-C(95)	126(6)
C(94)-C(92)-C(91)	51(5)	C(98)-C(92)-C(91)	114(7)
C(95)-C(92)-C(91)	77(5)	C(94)-C(92)-C(93)	98(5)
C(98)-C(92)-C(93)	58(6)	C(95)-C(92)-C(93)	89(4)

C(91)-C(92)-C(93)	113(6)	C(98)-C(93)-C(92)	47(5)
C(91)-C(94)-C(92)	75(6)	C(98)-C(95)-C(97)	167(10)
C(98)-C(95)-Cl(2)	64(8)	C(97)-C(95)-Cl(2)	108(6)
C(98)-C(95)-C(92)	67(8)	C(97)-C(95)-C(92)	113(6)
Cl(2)-C(95)-C(92)	117(5)	C(98)-C(95)-C(91)	115(9)
C(97)-C(95)-C(91)	70(5)	Cl(2)-C(95)-C(91)	165(5)
C(92)-C(95)-C(91)	54(4)	C(78)-C(96)-C(73)	66(3)
C(78)-C(96)-C(72)	110(4)	C(73)-C(96)-C(72)	46.1(17)
C(95)-C(97)-C(91)	71(6)	C(91)-C(97)-Cl(2)	106(6)
C(95)-C(98)-Cl(2)	68(9)	C(95)-C(98)-C(92)	72(8)
Cl(2)-C(98)-C(92)	123(10)	C(95)-C(98)-C(93)	123(10)
Cl(2)-C(98)-C(93)	161(10)	C(92)-C(98)-C(93)	75(8)
C(74)-C(99)-Cl(6)	51(3)	C(74)-C(99)-Cl(5)	57(4)
P(2)-N(1)-P(1)	157.1(5)	S(1A)-N(2A)-P(1)	133.1(5)
S(1B)-N(2B)-P(1)	171.2(9)	S(2A)-N(3A)-P(2)	142.2(7)
S(2B)-N(3B)-P(2)	164.4(12)	C(3)-O(1)-P(1)	120.9(4)
C(19)-O(2)-P(1)	116.1(4)	C(35)-O(3)-P(2)	119.2(5)
C(51)-O(4)-P(2)	115.8(4)	N(1)-P(1)-N(2B)	113.6(4)
N(1)-P(1)-N(2A)	113.6(4)	N(1)-P(1)-O(1)	106.3(3)
N(2B)-P(1)-O(1)	112.5(4)	N(2A)-P(1)-O(1)	112.5(4)
N(1)-P(1)-O(2)	112.2(3)	N(2B)-P(1)-O(2)	107.9(3)
N(2A)-P(1)-O(2)	107.9(3)	O(1)-P(1)-O(2)	104.1(3)
N(1)-P(2)-N(3B)	123.0(4)	N(1)-P(2)-N(3A)	123.0(4)
N(1)-P(2)-O(3)	106.3(3)	N(3B)-P(2)-O(3)	107.3(4)
N(3A)-P(2)-O(3)	107.3(4)	N(1)-P(2)-O(4)	110.6(3)
N(3B)-P(2)-O(4)	104.0(4)	N(3A)-P(2)-O(4)	104.0(4)
O(3)-P(2)-O(4)	104.3(3)	O(6)-S(1A)-O(5)	117.8(5)
O(6)-S(1A)-N(2A)	113.8(4)	O(5)-S(1A)-N(2A)	110.9(5)
O(6)-S(1A)-C(1)	105.4(6)	O(5)-S(1A)-C(1)	103.4(6)
N(2A)-S(1A)-C(1)	103.6(5)	N(2B)-S(1B)-C(1)	109.1(12)
F(10)-S(3)-F(9)	90.3(4)	F(10)-S(3)-F(7)	87.9(4)
F(9)-S(3)-F(7)	87.8(3)	F(10)-S(3)-F(11)	90.5(4)
F(9)-S(3)-F(11)	175.9(3)	F(7)-S(3)-F(11)	88.2(3)
F(10)-S(3)-F(8)	176.0(3)	F(9)-S(3)-F(8)	89.8(4)
F(7)-S(3)-F(8)	88.0(4)	F(11)-S(3)-F(8)	89.1(4)
F(10)-S(3)-C(15)	92.1(4)	F(9)-S(3)-C(15)	91.9(4)
F(7)-S(3)-C(15)	179.7(4)	F(11)-S(3)-C(15)	92.1(3)
F(8)-S(3)-C(15)	91.9(4)	O(8)-S(2A)-N(3A)	119.4(9)
O(8)-S(2A)-O(7)	123.2(10)	N(3A)-S(2A)-O(7)	110.7(6)

O(8)-S(2A)-C(2)	103.3(13)	N(3A)-S(2A)-C(2)	96.7(8)
O(7)-S(2A)-C(2)	95.5(9)	N(3B)-S(2B)-C(2)	117.3(16)
F(14)-S(4)-F(12)	87.7(5)	F(14)-S(4)-F(13)	88.7(5)
F(12)-S(4)-F(13)	88.8(4)	F(14)-S(4)-F(16)	175.8(5)
F(12)-S(4)-F(16)	88.3(5)	F(13)-S(4)-F(16)	90.0(5)
F(14)-S(4)-F(15)	91.8(5)	F(12)-S(4)-F(15)	87.2(4)
F(13)-S(4)-F(15)	176.0(4)	F(16)-S(4)-F(15)	89.2(4)
F(14)-S(4)-C(17)	92.2(4)	F(12)-S(4)-C(17)	179.4(5)
F(13)-S(4)-C(17)	91.7(4)	F(16)-S(4)-C(17)	91.8(4)
F(15)-S(4)-C(17)	92.2(4)	F(21)-S(5)-F(17)	87.9(3)
F(21)-S(5)-F(20)	90.2(3)	F(17)-S(5)-F(20)	88.0(2)
F(21)-S(5)-F(18)	90.6(3)	F(17)-S(5)-F(18)	88.0(2)
F(20)-S(5)-F(18)	175.8(3)	F(21)-S(5)-F(19)	175.2(2)
F(17)-S(5)-F(19)	87.3(3)	F(20)-S(5)-F(19)	89.5(3)
F(18)-S(5)-F(19)	89.3(3)	F(21)-S(5)-C(31)	92.5(3)
F(17)-S(5)-C(31)	179.5(3)	F(20)-S(5)-C(31)	92.4(3)
F(18)-S(5)-C(31)	91.7(3)	F(19)-S(5)-C(31)	92.3(3)
F(22)-S(6)-F(23)	88.3(3)	F(22)-S(6)-F(26)	87.8(3)
F(23)-S(6)-F(26)	89.9(3)	F(22)-S(6)-F(25)	87.1(3)
F(23)-S(6)-F(25)	175.4(3)	F(26)-S(6)-F(25)	89.7(3)
F(22)-S(6)-F(24)	87.4(3)	F(23)-S(6)-F(24)	90.5(3)
F(26)-S(6)-F(24)	175.2(3)	F(25)-S(6)-F(24)	89.6(3)
F(22)-S(6)-C(33)	179.2(4)	F(23)-S(6)-C(33)	92.5(3)
F(26)-S(6)-C(33)	92.1(3)	F(25)-S(6)-C(33)	92.0(3)
F(24)-S(6)-C(33)	92.6(3)	F(29)-S(7)-F(27)	88.5(6)
F(29)-S(7)-F(31)	177.2(5)	F(27)-S(7)-F(31)	88.7(7)
F(29)-S(7)-F(30)	90.1(6)	F(27)-S(7)-F(30)	87.0(7)
F(31)-S(7)-F(30)	89.6(8)	F(29)-S(7)-F(28)	89.4(7)
F(27)-S(7)-F(28)	90.3(7)	F(31)-S(7)-F(28)	90.8(6)
F(30)-S(7)-F(28)	177.2(5)	F(29)-S(7)-C(47)	92.3(5)
F(27)-S(7)-C(47)	178.1(10)	F(31)-S(7)-C(47)	90.5(5)
F(30)-S(7)-C(47)	91.3(5)	F(28)-S(7)-C(47)	91.4(5)
F(32)-S(8)-F(36)	88.3(3)	F(32)-S(8)-F(33)	88.3(3)
F(36)-S(8)-F(33)	90.7(3)	F(32)-S(8)-F(35)	87.4(3)
F(36)-S(8)-F(35)	89.3(3)	F(33)-S(8)-F(35)	175.7(3)
F(32)-S(8)-F(34)	87.6(3)	F(36)-S(8)-F(34)	175.9(3)
F(33)-S(8)-F(34)	89.8(3)	F(35)-S(8)-F(34)	89.9(3)
F(32)-S(8)-C(49)	179.6(4)	F(36)-S(8)-C(49)	92.0(3)
F(33)-S(8)-C(49)	91.8(3)	F(35)-S(8)-C(49)	92.5(3)

F(34)-S(8)-C(49)	92.1(3)	F(40)-S(9)-F(41)	90.7(3)
F(40)-S(9)-F(37)	88.6(3)	F(41)-S(9)-F(37)	88.7(3)
F(40)-S(9)-F(38)	176.2(3)	F(41)-S(9)-F(38)	89.2(3)
F(37)-S(9)-F(38)	87.6(3)	F(40)-S(9)-F(39)	90.4(3)
F(41)-S(9)-F(39)	176.1(3)	F(37)-S(9)-F(39)	87.6(3)
F(38)-S(9)-F(39)	89.4(3)	F(40)-S(9)-C(63)	92.2(3)
F(41)-S(9)-C(63)	92.0(3)	F(37)-S(9)-C(63)	178.9(3)
F(38)-S(9)-C(63)	91.6(3)	F(39)-S(9)-C(63)	91.7(3)
F(44)-S(10)-F(42)	88.4(3)	F(44)-S(10)-F(45)	89.9(3)
F(42)-S(10)-F(45)	87.2(3)	F(44)-S(10)-F(43)	90.7(3)
F(42)-S(10)-F(43)	88.6(3)	F(45)-S(10)-F(43)	175.8(3)
F(44)-S(10)-F(46)	176.3(3)	F(42)-S(10)-F(46)	87.9(3)
F(45)-S(10)-F(46)	89.8(3)	F(43)-S(10)-F(46)	89.4(3)
F(44)-S(10)-C(65)	91.8(3)	F(42)-S(10)-C(65)	179.0(4)
F(45)-S(10)-C(65)	91.8(3)	F(43)-S(10)-C(65)	92.4(3)
F(46)-S(10)-C(65)	91.9(3)	C(77)-Cl(1)-Cl(2)	53(5)
C(98)-Cl(2)-C(95)	48(6)	C(98)-Cl(2)-C(77)	147(8)
C(95)-Cl(2)-C(77)	125(5)	C(98)-Cl(2)-Cl(1)	161(8)
C(95)-Cl(2)-Cl(1)	117(4)	C(98)-Cl(2)-C(97)	83(7)
C(77)-Cl(2)-C(97)	100(4)	Cl(1)-Cl(2)-C(97)	84(4)
Cl(6)-Cl(5)-C(74)	49(2)	Cl(6)-Cl(5)-C(99)	53(3)
C(74)-Cl(5)-C(99)	46(3)	C(99)-Cl(5)-C(81)	74(3)
Cl(6)-Cl(5)-C(86)	95(4)	C(74)-Cl(5)-C(86)	88(3)
C(99)-Cl(5)-C(86)	134(4)	C(81)-Cl(5)-C(86)	61(3)
Cl(5)-Cl(6)-C(74)	109(3)	Cl(5)-Cl(6)-C(81)	120(3)
Cl(5)-Cl(6)-C(99)	108(4)	C(74)-Cl(6)-C(99)	57(4)
C(81)-Cl(6)-C(99)	95(4)	Cl(5)-Cl(6)-Cl(7)	159(3)
C(74)-Cl(6)-Cl(7)	53.2(16)	C(99)-Cl(6)-Cl(7)	72(4)
Cl(8)-Cl(7)-C(81)	120(3)	Cl(8)-Cl(7)-C(74)	92(3)
Cl(8)-Cl(7)-Cl(6)	124(3)	C(81)-Cl(7)-Cl(6)	47.3(14)
Cl(7)-Cl(8)-C(74)	67(2)	Cl(11)-Cl(10)-C(68)	115(2)
Cl(11)-Cl(10)-Cl(12)	49.7(16)	C(68)-Cl(10)-Cl(12)	69.6(15)
Cl(10)-Cl(11)-Cl(12)	110(2)	Cl(9)-Cl(12)-Cl(11)	100.4(19)
Cl(9)-Cl(12)-Cl(10)	118.6(19)		

Anisotropic displacement parameters (Å^2).

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[\ h^2a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.064(8)	0.109(12)	0.031(7)	0.001(7)	0.005(6)	-0.009(8)
C(2)	0.204(17)	0.197(17)	0.209(17)	-0.002(7)	-0.011(7)	0.015(7)
C(3)	0.031(4)	0.026(4)	0.024(4)	0.004(3)	-0.002(3)	0.000(3)
C(4)	0.025(3)	0.032(4)	0.019(4)	0.003(3)	-0.002(3)	0.000(3)
C(5)	0.025(3)	0.034(4)	0.020(4)	0.006(3)	0.001(3)	-0.001(3)
C(6)	0.034(4)	0.039(4)	0.019(4)	0.002(3)	0.003(3)	-0.001(3)
C(7)	0.038(4)	0.035(4)	0.027(4)	0.000(3)	0.006(3)	-0.011(3)
C(8)	0.034(4)	0.051(5)	0.026(4)	-0.007(3)	0.007(3)	-0.015(4)
C(9)	0.026(4)	0.047(5)	0.019(4)	-0.004(3)	0.006(3)	-0.006(3)
C(10)	0.022(3)	0.038(4)	0.020(4)	0.000(3)	-0.002(3)	-0.001(3)
C(11)	0.019(3)	0.039(4)	0.025(4)	0.004(3)	-0.003(3)	-0.002(3)
C(12)	0.030(4)	0.036(4)	0.024(4)	0.000(3)	0.000(3)	0.002(3)
C(13)	0.035(4)	0.030(4)	0.029(4)	0.002(3)	0.001(3)	0.005(3)
C(14)	0.034(4)	0.041(5)	0.042(5)	-0.003(3)	0.001(3)	0.000(3)
C(15)	0.039(4)	0.038(5)	0.052(6)	-0.006(4)	0.003(4)	0.002(4)
C(16)	0.060(6)	0.032(4)	0.062(6)	0.003(4)	0.017(5)	0.003(4)
C(17)	0.052(5)	0.035(5)	0.059(6)	0.006(4)	0.009(4)	0.005(4)
C(18)	0.047(5)	0.036(4)	0.040(5)	0.003(3)	0.006(4)	0.009(4)
C(19)	0.025(3)	0.028(4)	0.018(3)	-0.001(3)	-0.002(3)	0.001(3)
C(20)	0.024(3)	0.030(4)	0.024(4)	0.003(3)	-0.005(3)	-0.001(3)
C(21)	0.026(3)	0.027(4)	0.028(4)	0.004(3)	-0.004(3)	-0.003(3)
C(22)	0.033(4)	0.039(4)	0.018(4)	0.004(3)	0.002(3)	-0.002(3)
C(23)	0.045(4)	0.047(5)	0.018(4)	-0.002(3)	-0.001(3)	-0.005(4)
C(24)	0.034(4)	0.046(5)	0.030(4)	-0.008(3)	0.010(3)	0.000(4)
C(25)	0.029(4)	0.037(4)	0.031(4)	-0.008(3)	0.005(3)	0.001(3)
C(26)	0.027(3)	0.033(4)	0.023(4)	-0.002(3)	0.004(3)	0.003(3)
C(27)	0.032(4)	0.028(4)	0.025(4)	0.003(3)	-0.007(3)	0.002(3)
C(28)	0.021(3)	0.038(4)	0.016(4)	0.002(3)	0.000(2)	0.003(3)
C(29)	0.023(3)	0.037(4)	0.027(4)	0.002(3)	-0.004(3)	0.005(3)
C(30)	0.026(4)	0.036(4)	0.024(4)	0.003(3)	-0.002(3)	0.003(3)
C(31)	0.022(3)	0.035(4)	0.029(4)	0.001(3)	0.005(3)	0.000(3)
C(32)	0.028(4)	0.047(4)	0.024(4)	0.004(3)	0.000(3)	0.001(3)
C(33)	0.024(4)	0.041(4)	0.028(4)	0.000(3)	0.003(3)	0.003(3)

C(34)	0.023(3)	0.036(4)	0.026(4)	-0.001(3)	-0.002(3)	0.000(3)
C(35)	0.023(3)	0.039(4)	0.027(4)	-0.001(3)	0.003(3)	-0.009(3)
C(36)	0.026(4)	0.034(4)	0.030(4)	0.001(3)	0.000(3)	-0.009(3)
C(37)	0.028(4)	0.046(5)	0.035(4)	-0.001(3)	0.000(3)	-0.002(3)
C(38)	0.034(4)	0.039(4)	0.035(4)	-0.002(3)	0.008(3)	-0.005(3)
C(39)	0.026(4)	0.059(5)	0.045(5)	0.005(4)	0.008(3)	0.000(4)
C(40)	0.037(4)	0.053(5)	0.060(6)	-0.001(4)	0.000(4)	-0.007(4)
C(41)	0.033(4)	0.053(5)	0.042(5)	-0.004(4)	-0.002(4)	-0.008(4)
C(42)	0.028(4)	0.044(5)	0.036(5)	0.000(3)	-0.001(3)	-0.009(3)
C(43)	0.036(4)	0.043(4)	0.038(5)	-0.002(3)	-0.007(3)	-0.008(4)
C(44)	0.035(4)	0.043(4)	0.026(4)	0.002(3)	-0.004(3)	-0.004(3)
C(45)	0.043(4)	0.041(4)	0.025(4)	-0.008(3)	0.001(3)	-0.011(4)
C(46)	0.082(7)	0.065(6)	0.042(6)	-0.015(5)	0.017(5)	-0.025(6)
C(47)	0.095(8)	0.060(6)	0.049(6)	-0.028(5)	0.037(6)	-0.027(6)
C(48)	0.078(7)	0.059(6)	0.046(6)	-0.022(5)	0.020(5)	-0.019(5)
C(49)	0.042(4)	0.041(5)	0.030(4)	-0.001(3)	0.004(3)	-0.003(4)
C(50)	0.031(4)	0.045(4)	0.024(4)	-0.002(3)	0.001(3)	-0.003(3)
C(51)	0.032(4)	0.031(4)	0.023(4)	0.000(3)	0.003(3)	0.000(3)
C(52)	0.030(4)	0.039(4)	0.019(4)	0.002(3)	0.000(3)	-0.003(3)
C(53)	0.023(3)	0.046(4)	0.017(4)	0.002(3)	0.001(3)	-0.004(3)
C(54)	0.027(4)	0.044(4)	0.027(4)	0.003(3)	0.000(3)	0.000(3)
C(55)	0.030(4)	0.056(5)	0.031(4)	0.005(4)	-0.001(3)	0.004(4)
C(56)	0.037(4)	0.039(4)	0.032(4)	-0.001(3)	0.009(3)	0.004(3)
C(57)	0.034(4)	0.035(4)	0.024(4)	0.000(3)	-0.005(3)	0.000(3)
C(58)	0.027(3)	0.035(4)	0.024(4)	-0.002(3)	0.007(3)	-0.004(3)
C(59)	0.031(4)	0.039(4)	0.025(4)	-0.006(3)	-0.004(3)	-0.005(3)
C(60)	0.031(4)	0.028(4)	0.021(4)	0.001(3)	-0.003(3)	0.000(3)
C(61)	0.035(4)	0.026(4)	0.022(4)	-0.002(3)	-0.001(3)	0.002(3)
C(62)	0.032(4)	0.035(4)	0.026(4)	-0.007(3)	-0.003(3)	-0.008(3)
C(63)	0.034(4)	0.024(4)	0.024(4)	-0.004(3)	0.000(3)	-0.001(3)
C(64)	0.045(4)	0.034(4)	0.025(4)	0.000(3)	0.000(3)	0.005(3)
C(65)	0.042(4)	0.024(4)	0.026(4)	0.003(3)	-0.005(3)	-0.004(3)
C(66)	0.034(4)	0.036(4)	0.026(4)	0.002(3)	-0.004(3)	-0.001(3)
N(1)	0.019(3)	0.050(4)	0.040(4)	-0.010(3)	-0.005(3)	-0.007(3)
N(2A)	0.058(4)	0.039(4)	0.047(5)	-0.016(3)	0.018(3)	0.008(3)
N(2B)	0.058(4)	0.039(4)	0.047(5)	-0.016(3)	0.018(3)	0.008(3)
N(3A)	0.083(6)	0.054(5)	0.062(6)	-0.033(4)	0.011(5)	-0.010(4)
N(3B)	0.083(6)	0.054(5)	0.062(6)	-0.033(4)	0.011(5)	-0.010(4)
O(1)	0.026(2)	0.030(3)	0.041(3)	0.007(2)	-0.007(2)	-0.005(2)

O(2)	0.031(3)	0.028(3)	0.025(3)	-0.001(2)	-0.002(2)	0.006(2)
O(3)	0.023(2)	0.056(3)	0.025(3)	0.005(2)	0.000(2)	-0.005(2)
O(4)	0.031(3)	0.035(3)	0.027(3)	-0.003(2)	-0.002(2)	-0.002(2)
O(5)	0.073(5)	0.062(5)	0.054(5)	-0.023(4)	-0.010(4)	0.044(4)
O(6)	0.031(4)	0.069(5)	0.045(4)	-0.012(4)	0.004(3)	-0.008(3)
O(7)	0.138(9)	0.119(8)	0.100(8)	0.020(7)	0.035(7)	0.046(8)
O(8)	0.197(12)	0.218(13)	0.143(11)	-0.064(10)	-0.025(10)	0.089(10)
F(1)	0.095(6)	0.198(11)	0.028(4)	0.025(5)	0.008(4)	-0.002(7)
F(2)	0.126(7)	0.077(5)	0.065(5)	0.025(4)	-0.020(5)	0.036(5)
F(3)	0.068(5)	0.139(8)	0.040(4)	-0.031(4)	-0.017(3)	0.024(5)
F(4)	0.371(13)	0.350(13)	0.372(13)	-0.008(8)	0.023(8)	0.006(8)
F(5)	0.371(13)	0.350(13)	0.372(13)	-0.008(8)	0.023(8)	0.006(8)
F(6)	0.371(13)	0.350(13)	0.372(13)	-0.008(8)	0.023(8)	0.006(8)
F(7)	0.082(4)	0.070(4)	0.099(5)	-0.030(4)	0.041(4)	0.009(3)
F(8)	0.063(3)	0.058(4)	0.103(5)	0.001(3)	0.024(3)	0.027(3)
F(9)	0.086(4)	0.059(4)	0.095(5)	-0.038(3)	0.029(4)	-0.011(3)
F(10)	0.101(5)	0.080(4)	0.055(4)	-0.012(3)	0.036(3)	0.014(4)
F(11)	0.043(3)	0.062(3)	0.101(5)	-0.021(3)	0.019(3)	-0.002(3)
F(12)	0.172(8)	0.047(4)	0.203(9)	0.051(5)	0.139(8)	0.040(4)
F(13)	0.090(5)	0.053(4)	0.193(9)	0.040(5)	0.083(5)	0.018(3)
F(14)	0.231(10)	0.051(4)	0.085(5)	0.031(4)	0.079(6)	0.031(5)
F(15)	0.128(6)	0.043(3)	0.107(5)	0.024(3)	0.054(5)	0.031(4)
F(16)	0.106(5)	0.048(4)	0.158(7)	-0.015(4)	0.062(5)	-0.020(4)
F(17)	0.015(2)	0.084(3)	0.034(3)	0.000(2)	-0.001(2)	0.001(2)
F(18)	0.027(2)	0.070(3)	0.036(3)	-0.011(2)	0.002(2)	0.009(2)
F(19)	0.029(2)	0.055(3)	0.037(3)	0.013(2)	0.000(2)	-0.007(2)
F(20)	0.029(2)	0.072(3)	0.028(2)	-0.013(2)	0.000(2)	-0.002(2)
F(21)	0.030(2)	0.069(3)	0.040(3)	0.020(2)	-0.002(2)	0.008(2)
F(22)	0.030(2)	0.111(5)	0.032(3)	0.022(3)	0.000(2)	-0.015(3)
F(23)	0.023(2)	0.082(3)	0.034(3)	0.005(2)	0.003(2)	0.006(2)
F(24)	0.036(2)	0.070(3)	0.035(3)	0.010(2)	-0.007(2)	-0.018(2)
F(25)	0.030(2)	0.061(3)	0.034(2)	0.020(2)	-0.007(2)	-0.004(2)
F(26)	0.032(2)	0.080(3)	0.024(2)	-0.004(2)	0.004(2)	-0.006(2)
F(27)	0.372(19)	0.140(8)	0.192(10)	-0.132(8)	0.193(12)	-0.181(11)
F(28)	0.205(10)	0.064(4)	0.130(7)	-0.041(5)	0.103(8)	-0.043(5)
F(29)	0.244(12)	0.059(4)	0.130(7)	-0.031(4)	0.117(8)	-0.058(6)
F(30)	0.208(11)	0.188(10)	0.113(7)	-0.096(7)	0.084(7)	-0.162(9)
F(31)	0.295(15)	0.192(10)	0.093(7)	-0.100(7)	0.092(8)	-0.179(11)
F(32)	0.068(3)	0.047(3)	0.061(3)	-0.002(2)	0.029(3)	-0.005(3)

F(33)	0.053(3)	0.041(3)	0.057(3)	-0.011(2)	0.018(2)	0.005(2)
F(34)	0.072(4)	0.094(4)	0.026(3)	-0.004(3)	0.002(2)	-0.005(3)
F(35)	0.067(3)	0.058(3)	0.050(3)	0.017(2)	0.018(3)	0.024(3)
F(36)	0.047(3)	0.048(3)	0.047(3)	-0.014(2)	0.007(2)	-0.009(2)
F(37)	0.069(3)	0.038(3)	0.061(3)	0.005(2)	0.005(3)	-0.014(2)
F(38)	0.066(3)	0.043(3)	0.032(3)	0.006(2)	0.002(2)	-0.008(2)
F(39)	0.044(3)	0.042(3)	0.059(3)	0.005(2)	0.010(2)	-0.005(2)
F(40)	0.068(3)	0.031(2)	0.043(3)	-0.010(2)	-0.003(2)	-0.012(2)
F(41)	0.061(3)	0.026(2)	0.055(3)	0.000(2)	0.007(2)	0.005(2)
F(42)	0.046(3)	0.050(3)	0.051(3)	0.012(2)	-0.018(2)	-0.016(2)
F(43)	0.050(3)	0.034(2)	0.045(3)	-0.001(2)	-0.011(2)	-0.008(2)
F(44)	0.063(3)	0.056(3)	0.029(3)	0.017(2)	-0.015(2)	-0.019(2)
F(45)	0.042(3)	0.040(3)	0.059(3)	0.006(2)	-0.011(2)	0.003(2)
F(46)	0.038(2)	0.049(3)	0.038(3)	0.013(2)	-0.004(2)	-0.006(2)
P(1)	0.026(1)	0.033(1)	0.029(1)	-0.005(1)	0.002(1)	0.001(1)
P(2)	0.031(1)	0.037(1)	0.029(1)	-0.008(1)	0.000(1)	-0.003(1)
S(1A)	0.034(1)	0.050(1)	0.025(1)	-0.005(1)	-0.002(1)	0.008(1)
S(1B)	0.056(8)	0.088(10)	0.063(9)	-0.022(7)	-0.019(6)	0.020(7)
S(3)	0.057(1)	0.048(1)	0.069(2)	-0.012(1)	0.021(1)	0.004(1)
S(2A)	0.054(2)	0.055(2)	0.093(3)	-0.038(2)	0.008(2)	-0.003(2)
S(2B)	0.114(14)	0.055(8)	0.077(10)	-0.010(7)	0.023(9)	-0.014(8)
S(4)	0.109(2)	0.034(1)	0.117(3)	0.021(2)	0.068(2)	0.016(1)
S(5)	0.022(1)	0.051(1)	0.025(1)	0.001(1)	-0.001(1)	0.002(1)
S(6)	0.023(1)	0.069(1)	0.025(1)	0.007(1)	-0.002(1)	-0.006(1)
S(7)	0.228(5)	0.097(3)	0.110(3)	-0.071(2)	0.107(3)	-0.104(3)
S(8)	0.046(1)	0.038(1)	0.035(1)	0.000(1)	0.007(1)	0.002(1)
S(9)	0.052(1)	0.028(1)	0.039(1)	-0.002(1)	0.003(1)	-0.005(1)
S(10)	0.042(1)	0.036(1)	0.034(1)	0.009(1)	-0.010(1)	-0.005(1)

Hydrogen coordinates and isotropic displacement parameters (Å^2).

	x	y	z	U_{eq}
H(6)	-0.1313	0.2314	0.1820	0.037
H(7)	-0.2371	0.2028	0.1630	0.040
H(8)	-0.3483	0.2297	0.1631	0.044

H(9)	-0.3523	0.2848	0.1762	0.036
H(11)	-0.2908	0.3361	0.1986	0.033
H(14)	-0.2707	0.3777	0.3261	0.047
H(16)	-0.2173	0.4680	0.2504	0.062
H(18)	-0.1140	0.3921	0.1363	0.049
H(22)	-0.0905	0.2697	0.0329	0.036
H(23)	-0.0460	0.2369	-0.0826	0.044
H(24)	0.0552	0.2051	-0.0534	0.044
H(25)	0.1126	0.2072	0.0860	0.039
H(27)	0.1246	0.2306	0.2435	0.034
H(30)	0.1950	0.2676	0.3595	0.035
H(32)	0.1667	0.2474	0.6322	0.039
H(34)	-0.0026	0.2526	0.4609	0.034
H(38)	0.3730	0.3305	0.1275	0.043
H(39)	0.4907	0.3456	0.1043	0.052
H(40)	0.5588	0.3658	0.2254	0.060
H(41)	0.5075	0.3778	0.3643	0.051
H(43)	0.4005	0.3805	0.4642	0.047
H(46)	0.3164	0.4236	0.5097	0.076
H(48)	0.1865	0.4123	0.7343	0.073
H(50)	0.2059	0.3405	0.5463	0.040
H(54)	0.3372	0.2820	0.2662	0.039
H(55)	0.3520	0.2290	0.2129	0.047
H(56)	0.2904	0.2116	0.0811	0.043
H(57)	0.2073	0.2437	0.0099	0.038
H(59)	0.1393	0.2958	0.0050	0.038
H(62)	0.1665	0.3935	0.0465	0.037
H(64)	-0.0115	0.4094	-0.1069	0.042
H(66)	0.0184	0.3229	0.0233	0.038
H(2A)	-0.0204	0.3771	0.4271	0.057
H(2B)	-0.0865	0.3665	0.3770	0.057
H(3A)	0.1802	0.4111	0.3476	0.080
H(3B)	0.0897	0.4079	0.3521	0.080

The structure of **4c** was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0674 [$I > 2\sigma(I)$], wR_2 = 0.1920, 1405 parameters. The trifluoromethyl-sulfonyl-amino group is disordered over the two positions. In addition, the trifluoromethyl-sulfonyl-amino and trifluoromethyl-sulfonyl-phosphazene groups are slightly disordered. The major components (80% occupation) could be located and refined. Only the S atoms of the minor triflate components could be located and refined. All non-H atoms of one of the two trifluoromethyl-sulfonyl-amino/phosphazene groups were refined with anisotropic atomic displacement parameters. The atomic displacement parameters of the F, C and O atoms of the second trifluoromethyl-sulfonyl-amino/phosphazene group were restrained to be isotropic with an effective standard deviation of 0.005, whereby the atomic displacement parameters of the three F atoms were constrained to be equal. For this tri-fluoromethyl-sulfonyl-amino/phosphazene group the respective S...F, C−F and F...F distances were restrained to be equal with an effective standard deviation of 0.02, as were the S−C distances of both trifluoromethyl-sulfonyl-amino/phosphazene groups (total 46 restraints). The solvate (dichloromethane/hexane) region of the crystal was modeled by C and Cl atoms of various occupancies and refined isotropic atomic displacement parameters. A void of 43.95 \%A, close to symmetry elements, remained (0.4 % of the unit cell volume, probe radius 1.2 \%A, grid spacing 0.7 \%A). The H atom attached to the trifluoromethyl-sulfonyl-amino group could not be located and was refined using a riding model, as were the other H atoms in the imidodiphosphorimidate (IDPI). The riding model used C-H distances of 0.95 Å and $U_H = 1.2 \times U_C$ ($CH_{aromatic}$) and 0.88 Å and $U_H = 1.5 \times U_N$ (NH). S = 1.522, residual electron density 0.90 (0.82 Å from F6)/ -0.80 (0.95 from F29) e Å^{-3}. The Flack parameter (Parsons' method: Parsons, Flack and Wagner, *Acta Cryst*. B69 (2013) 249-259) is 0.031(4) [6454 quotients]. **CCDC 1559571**.

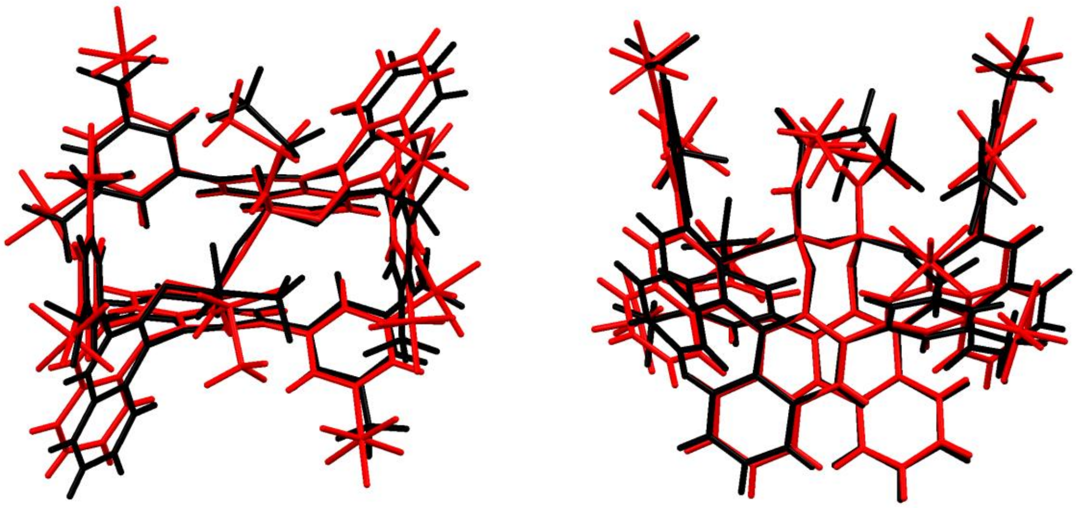
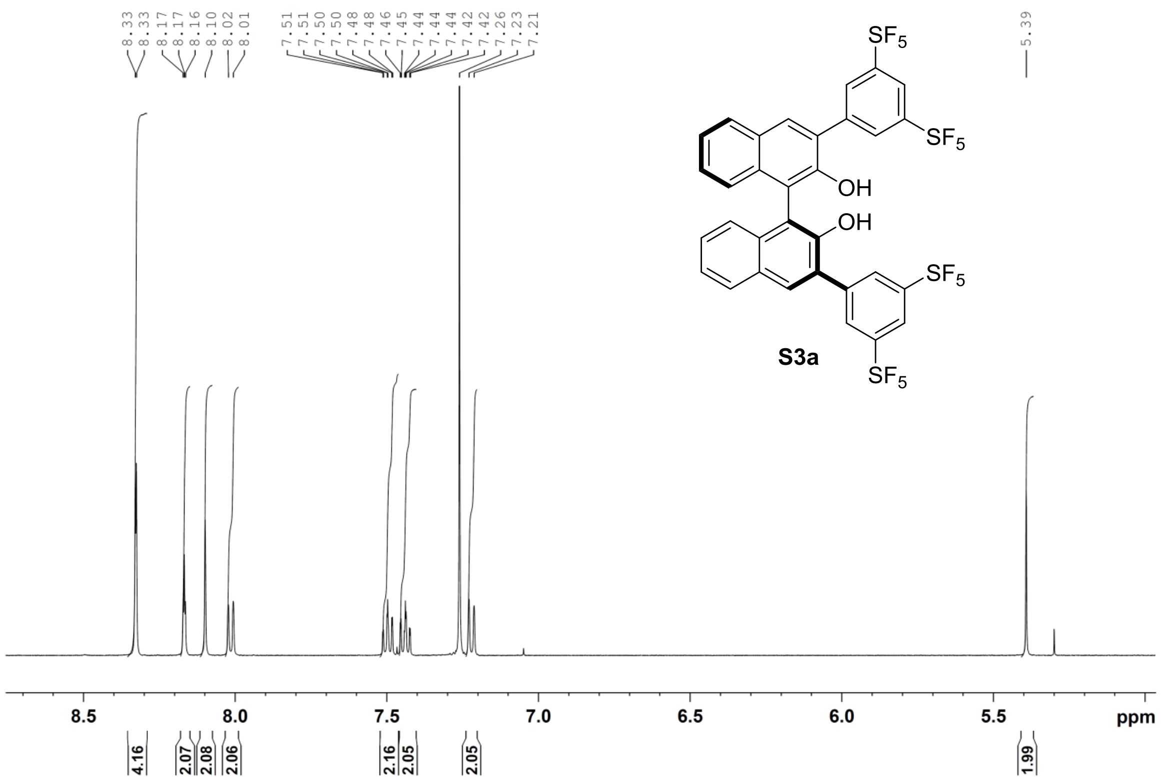


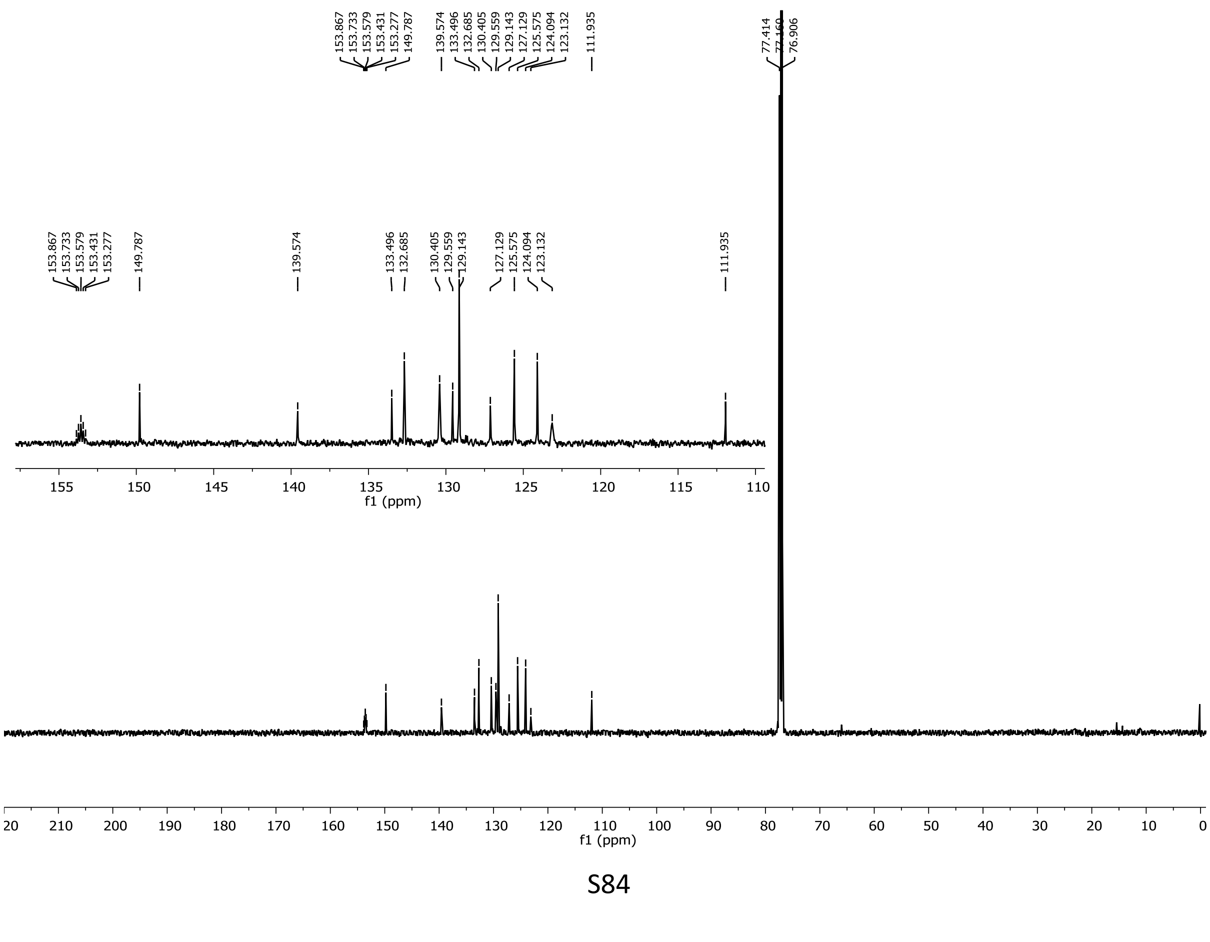
Figure S9. Superposition of the central O_2P-N=PO_2 moieties of **4b** (black, CSD refcode: AWAHIR) and **4c** (red), comparing conformations of the two compounds (left: view from above; right: side view).

Copies of NMR Spectra

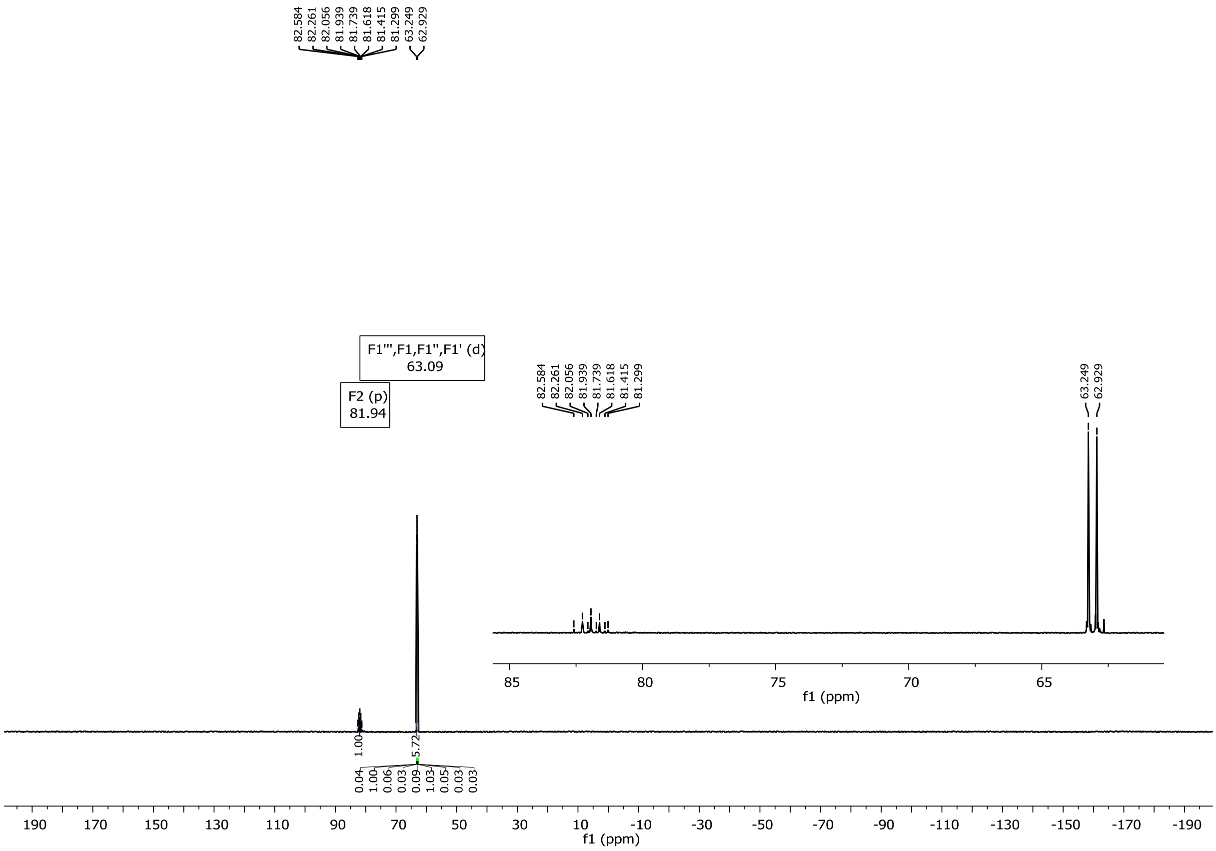
^{1}H NMR (S3a)



^{13}C NMR (S3a)

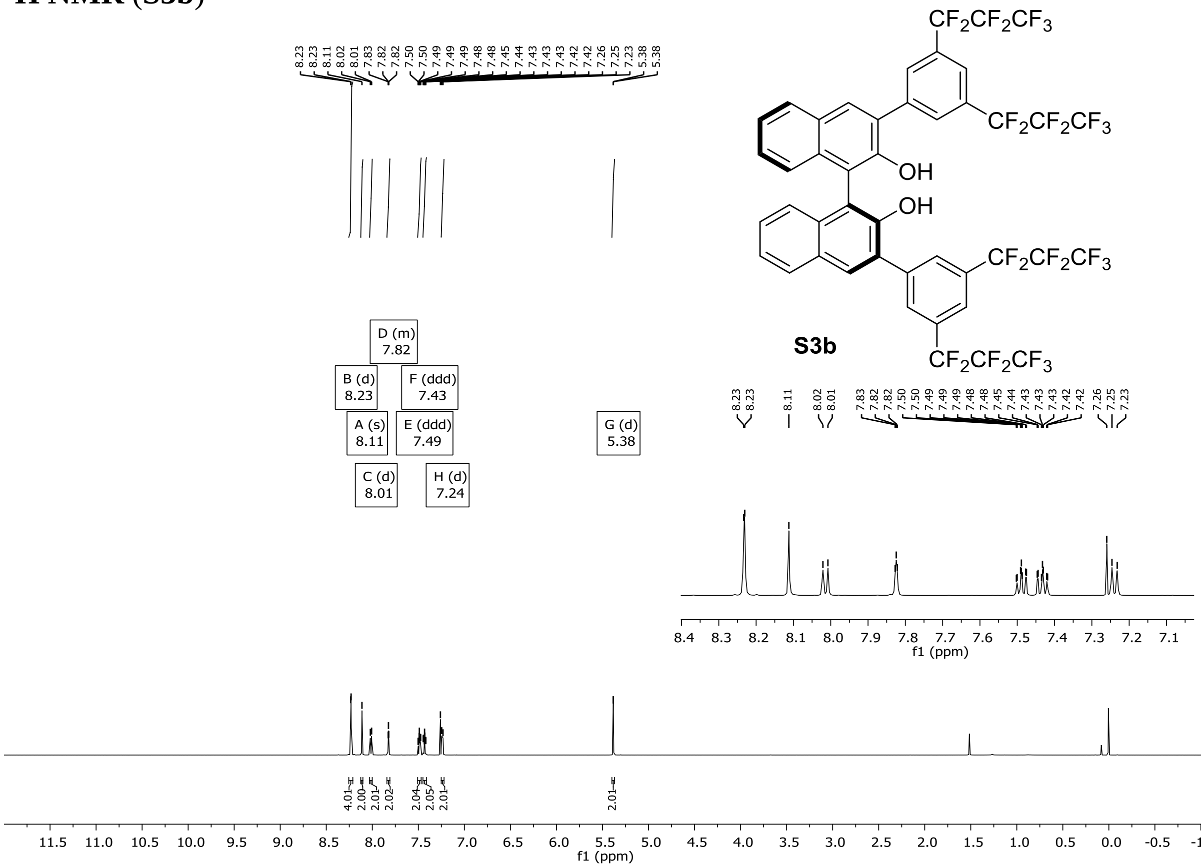


^{19}F NMR (S3a)



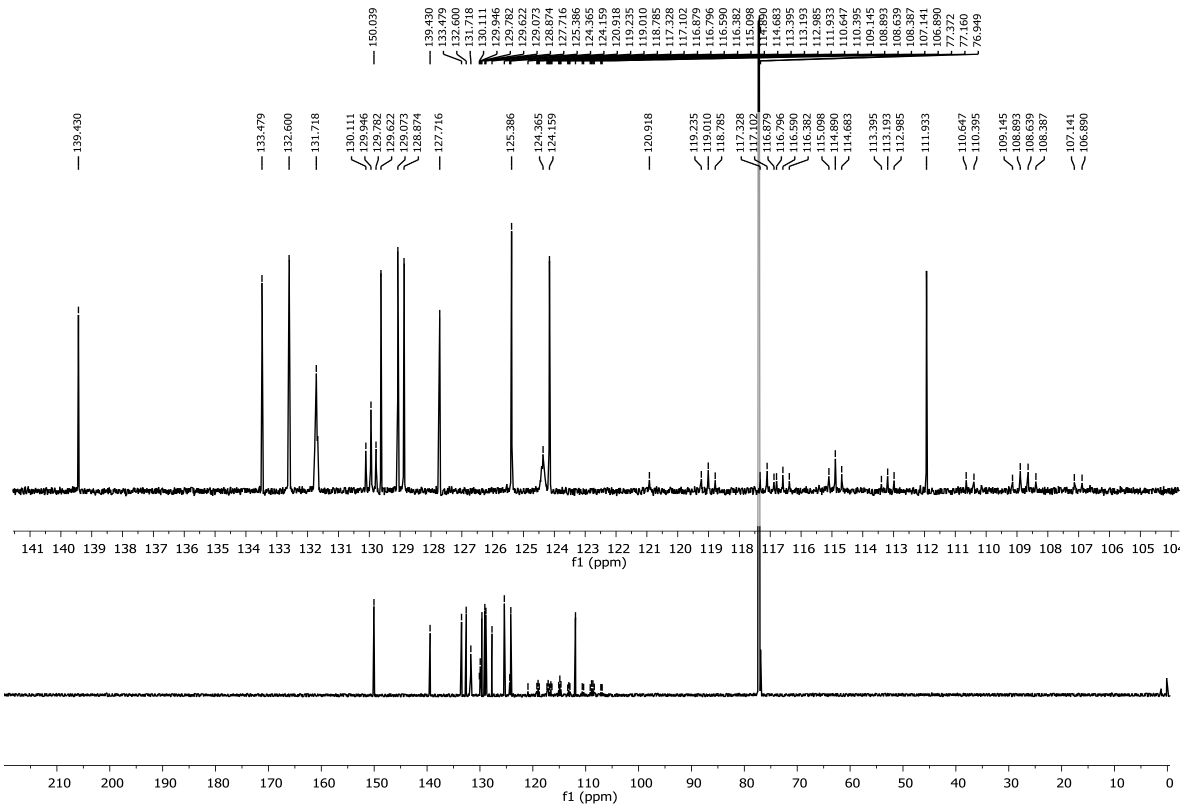
82.584
82.261
82.056
81.939
81.739
81.618
81.415
81.299
63.249
62.929
F1''',F1,F1'',F1' (d)
63.09
F2 (p)
81.94
1.00
5.72
f1 (ppm)

^{1}H NMR (S3b)

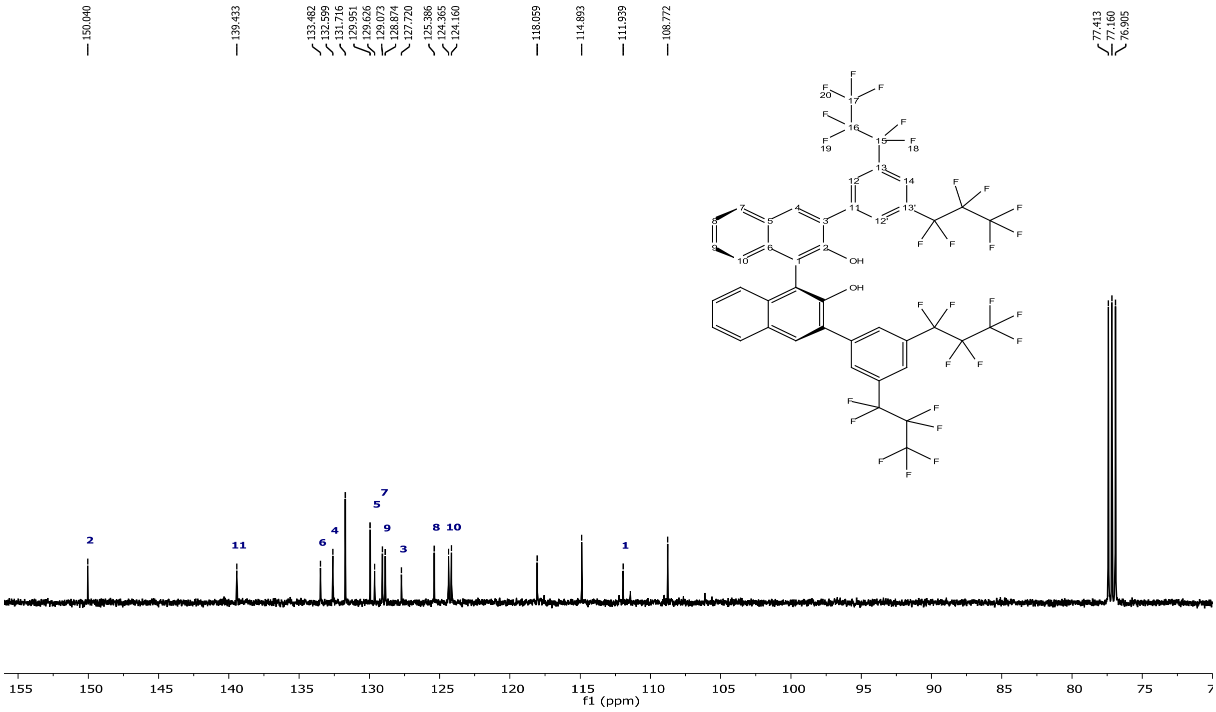


S3b

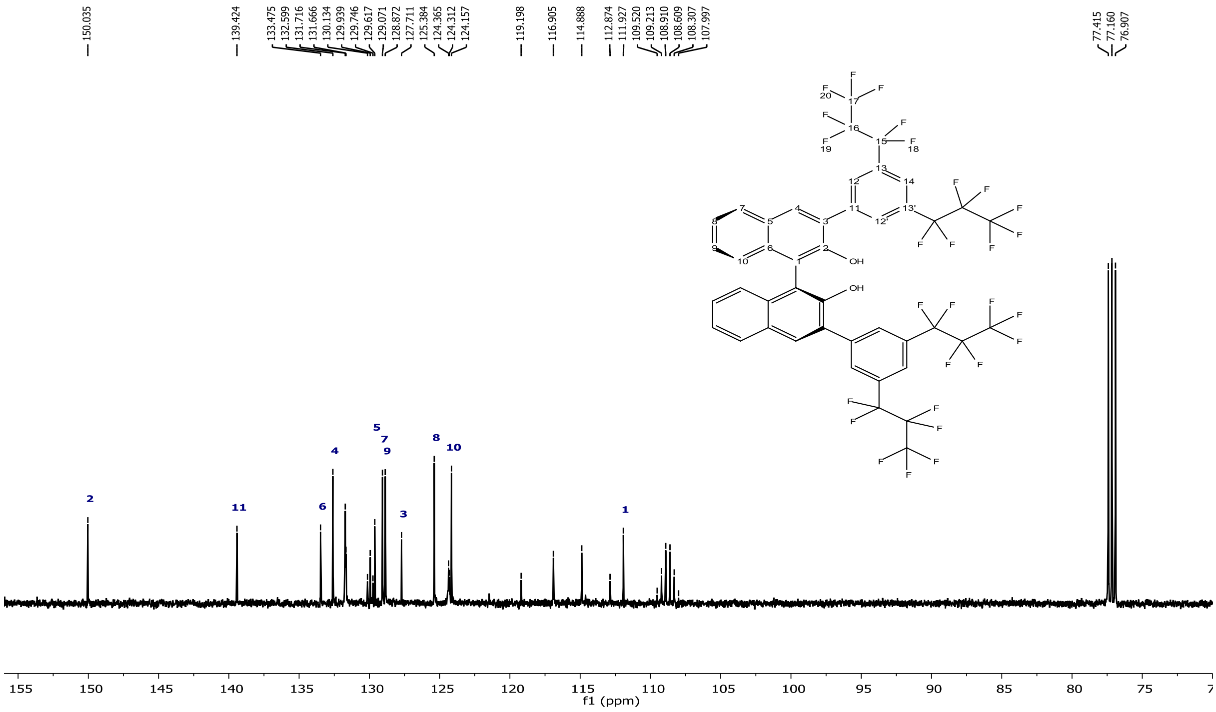
^{13}C NMR (S3b)



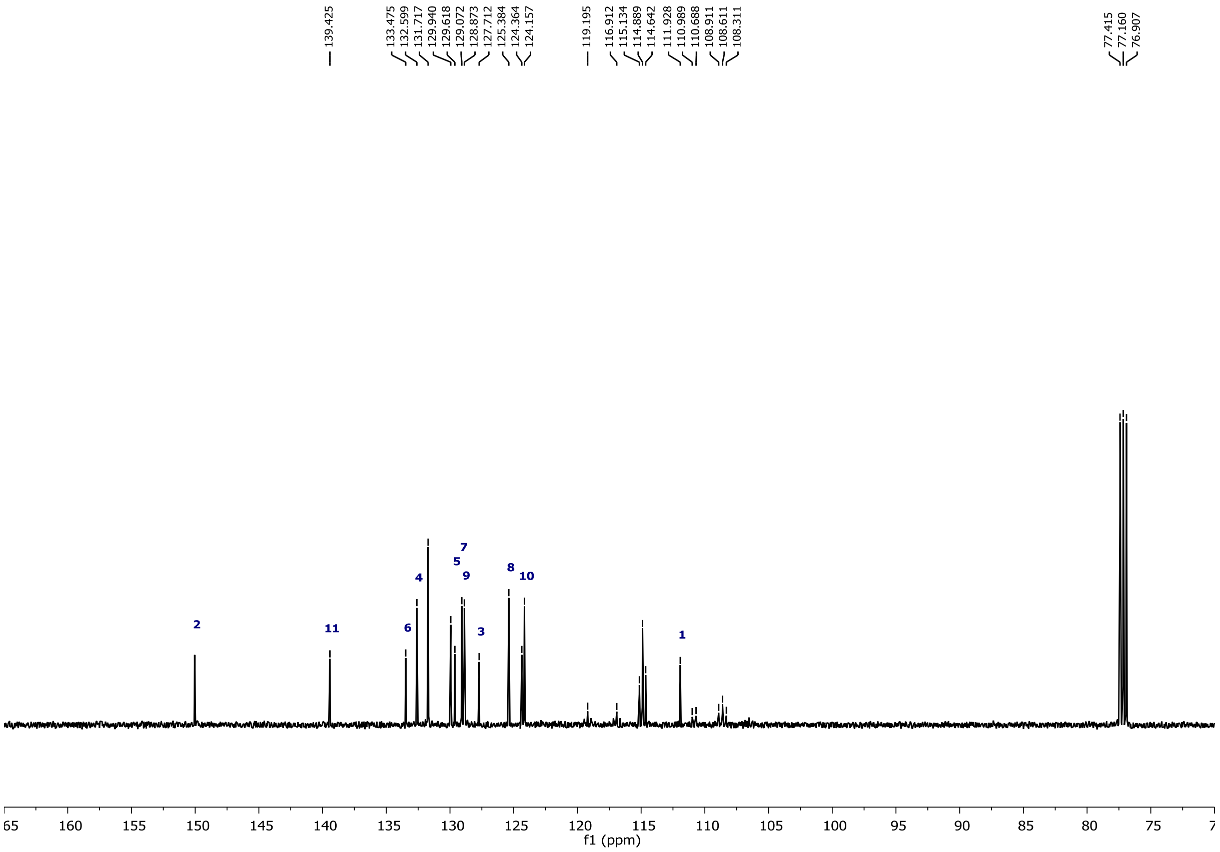
^{13}C NMR (S3b) (^{1}H, ^{19}F decoupled; broadband ^{19}F decoupling)



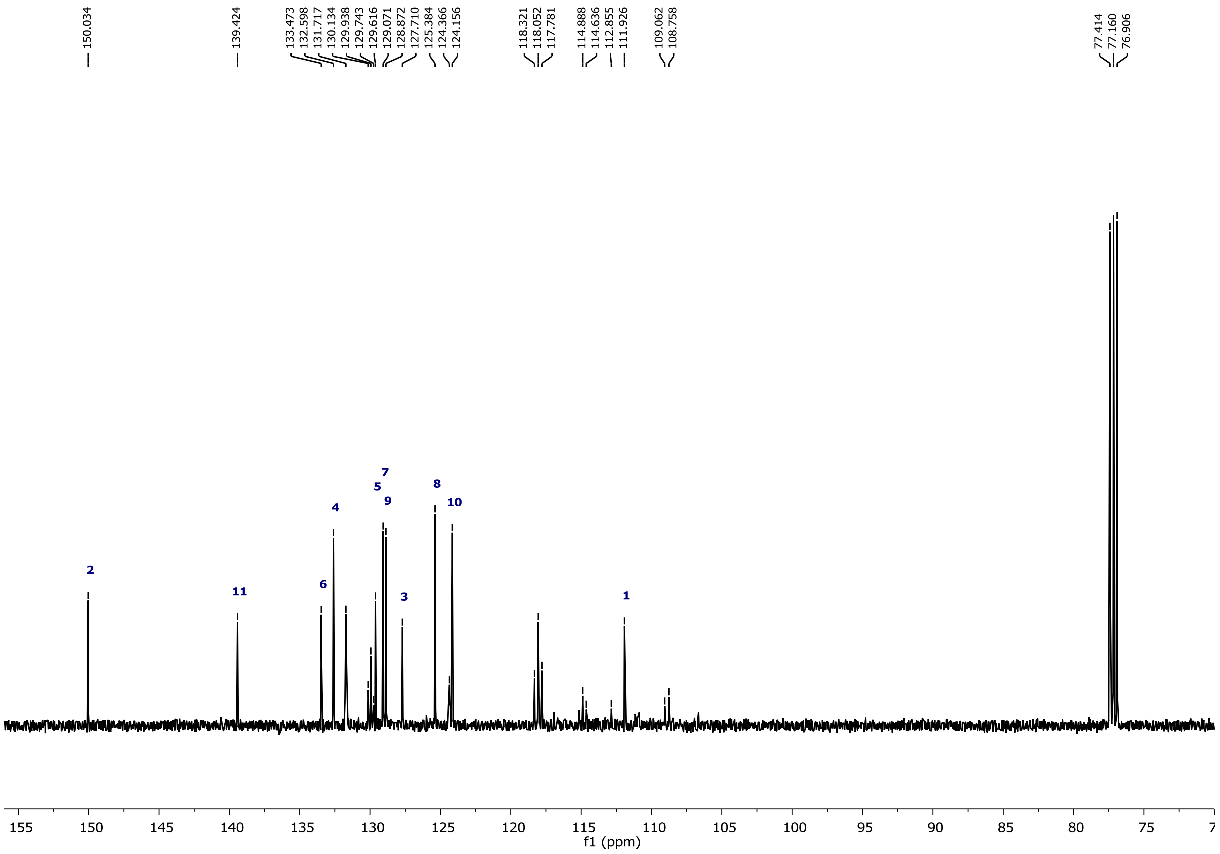
^{13}C NMR (S3b) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling of F19, offset: –126.14)



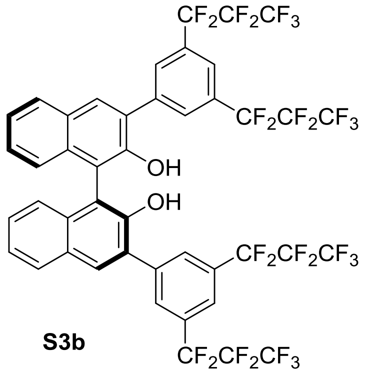
^{13}C NMR (S3b) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling of F18, offset: –111.88)



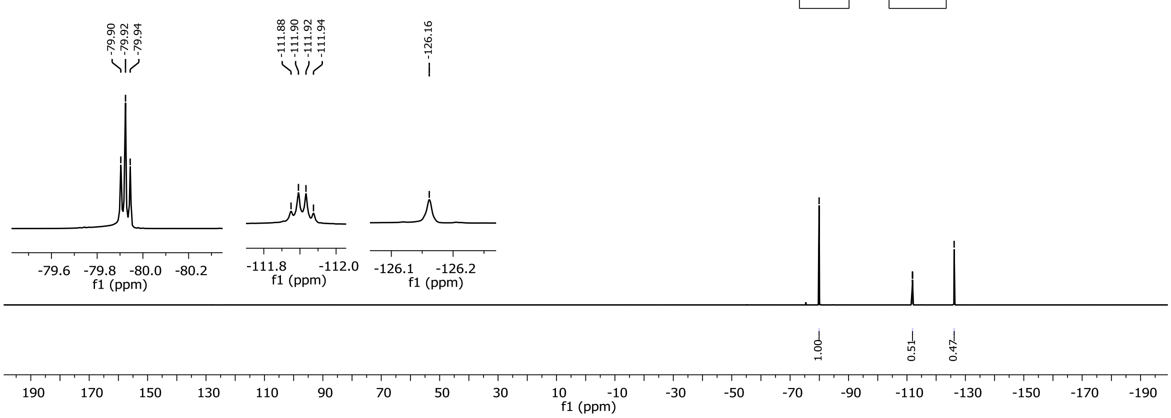
^{13}C NMR (S3b) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling of F20, offset: –79.90)



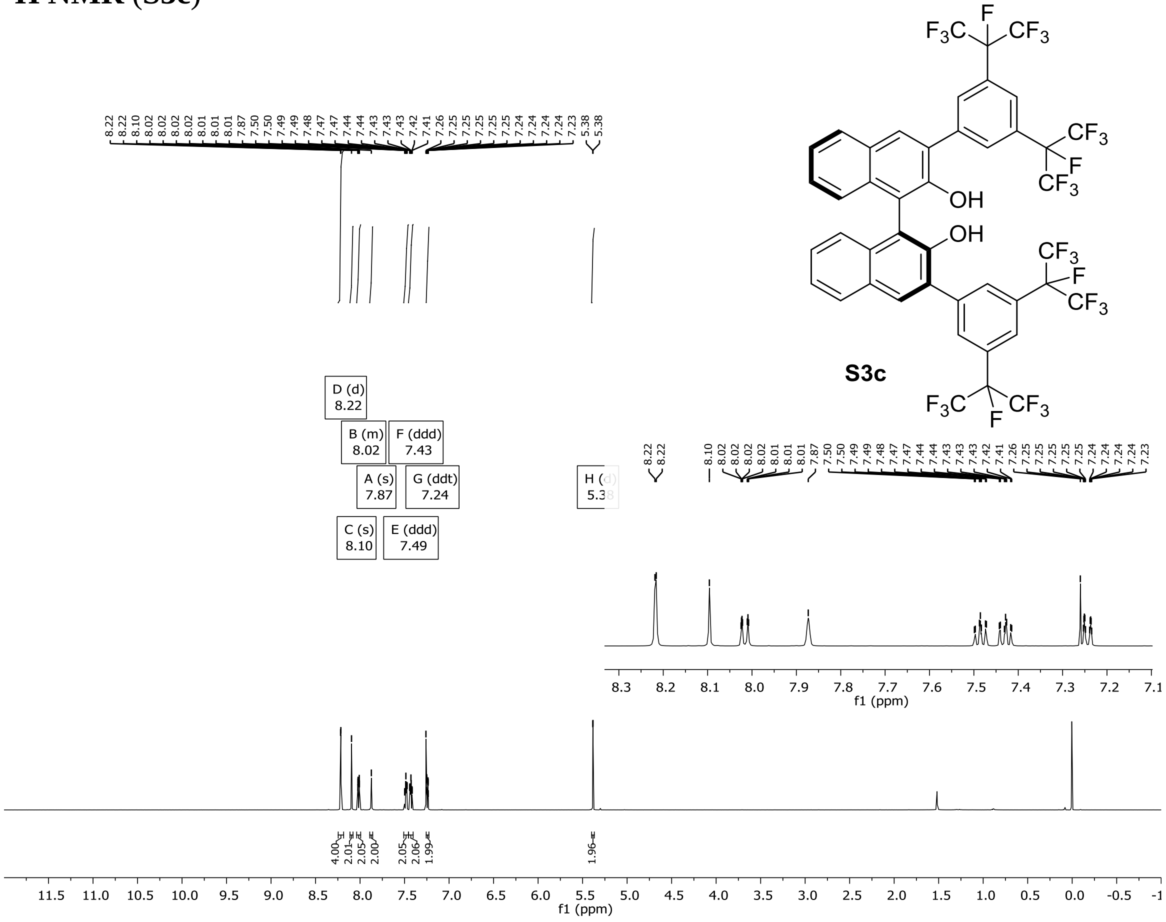
^{19}F NMR (S3b)



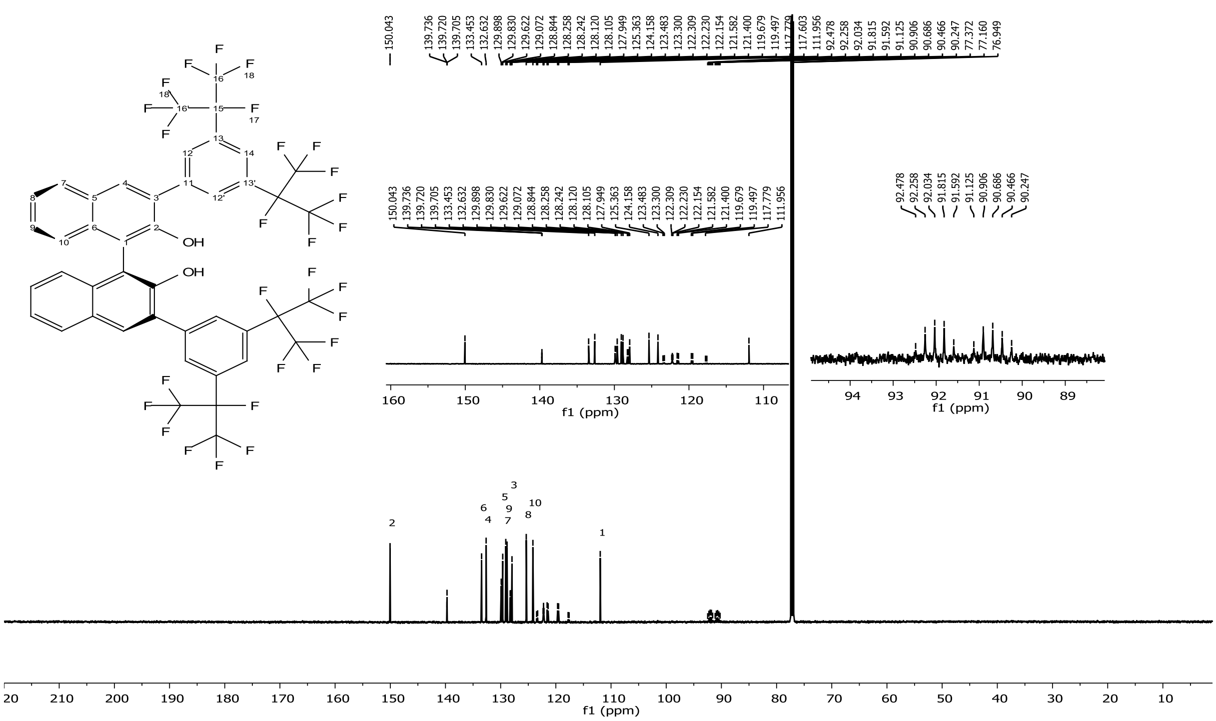
S3b



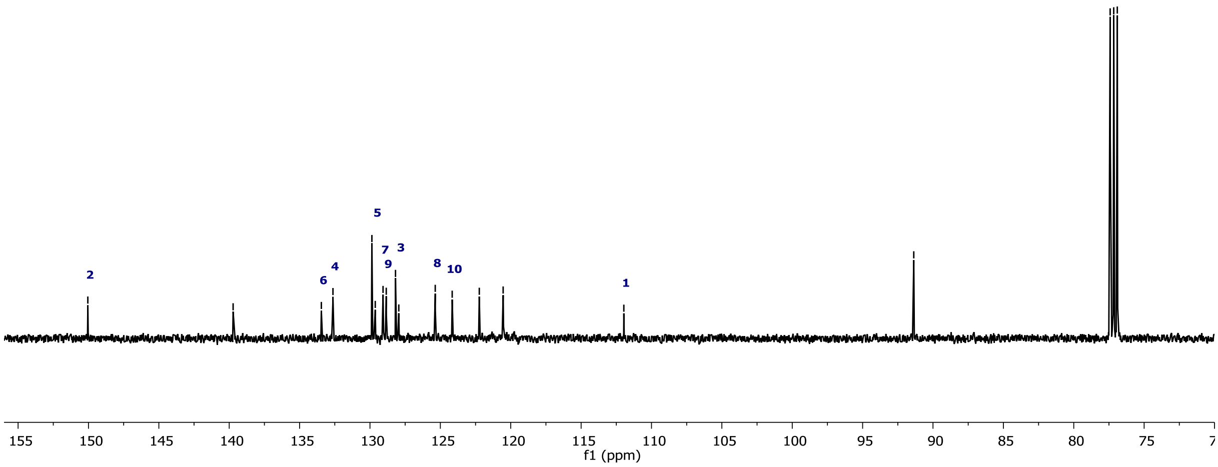
^{1}H NMR (S3c)

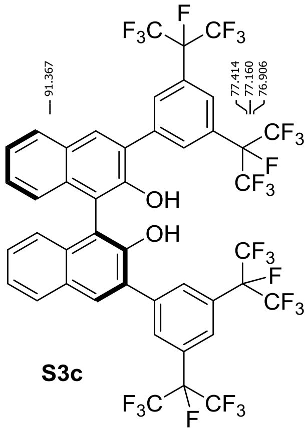


^{13}C NMR (S3c)

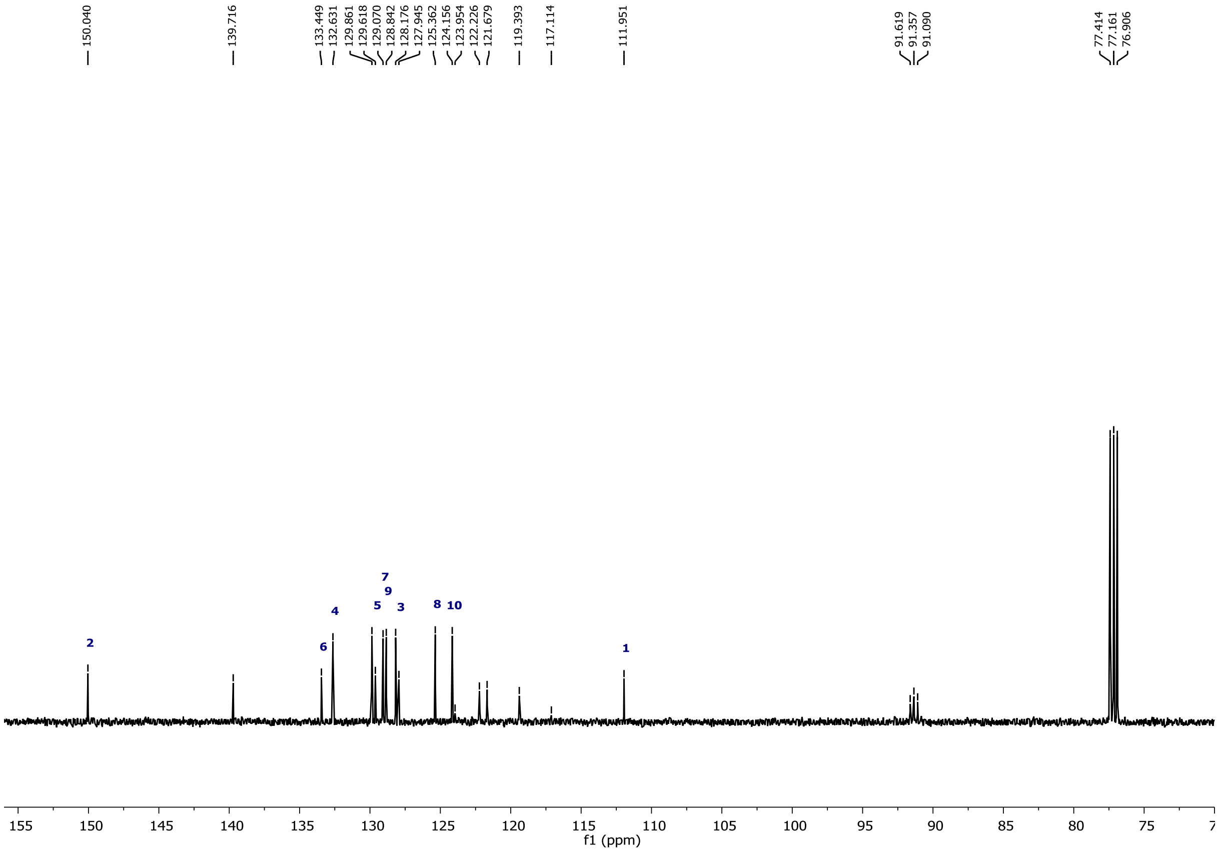


^{13}C NMR (S3c) (^{1}H, ^{19}F decoupled; broadband ^{19}F decoupling)

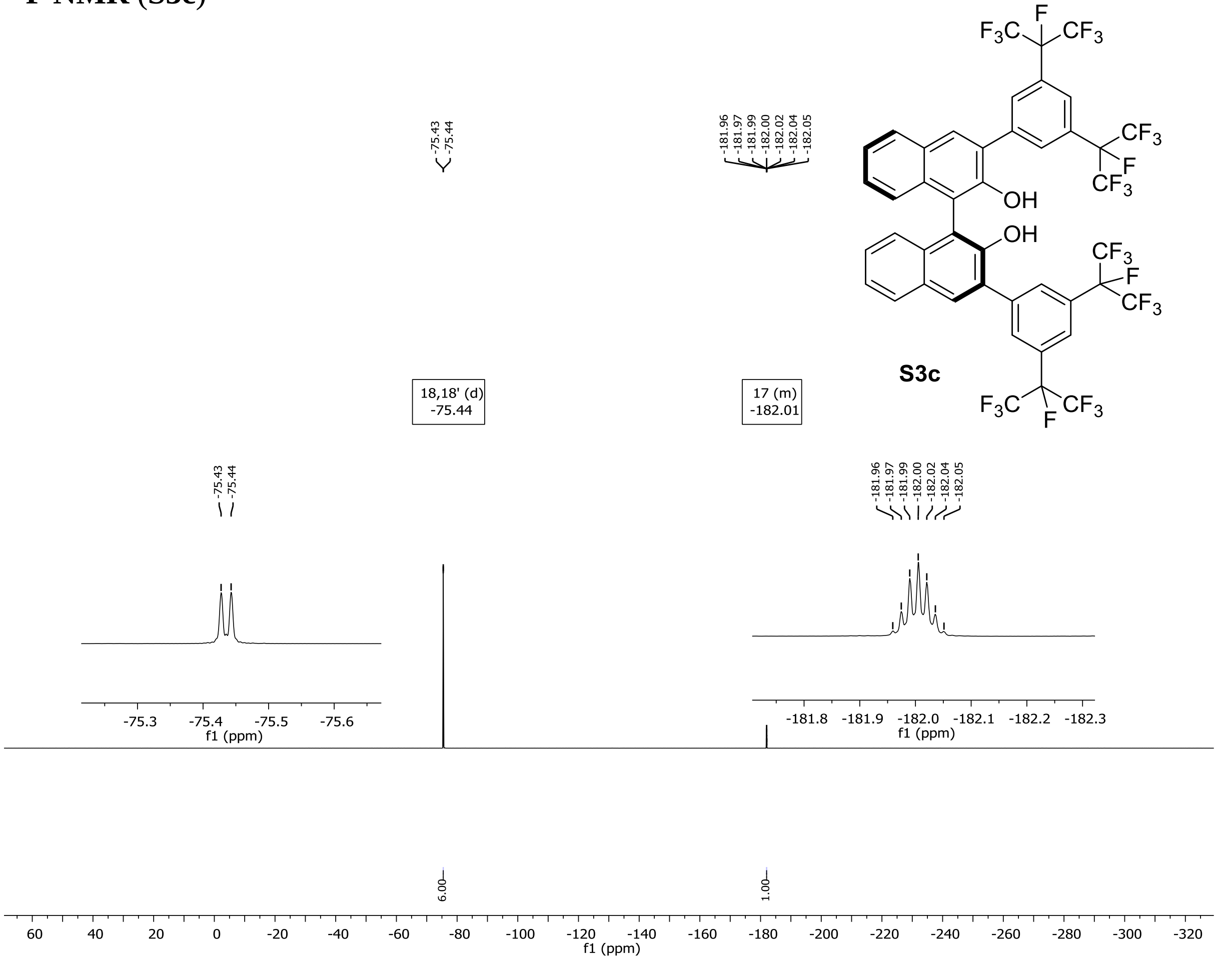




^{13}C NMR (S3c) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling of F17, offset: –182.00)

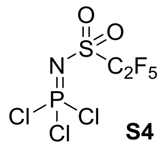


^{19}F NMR (S3c)



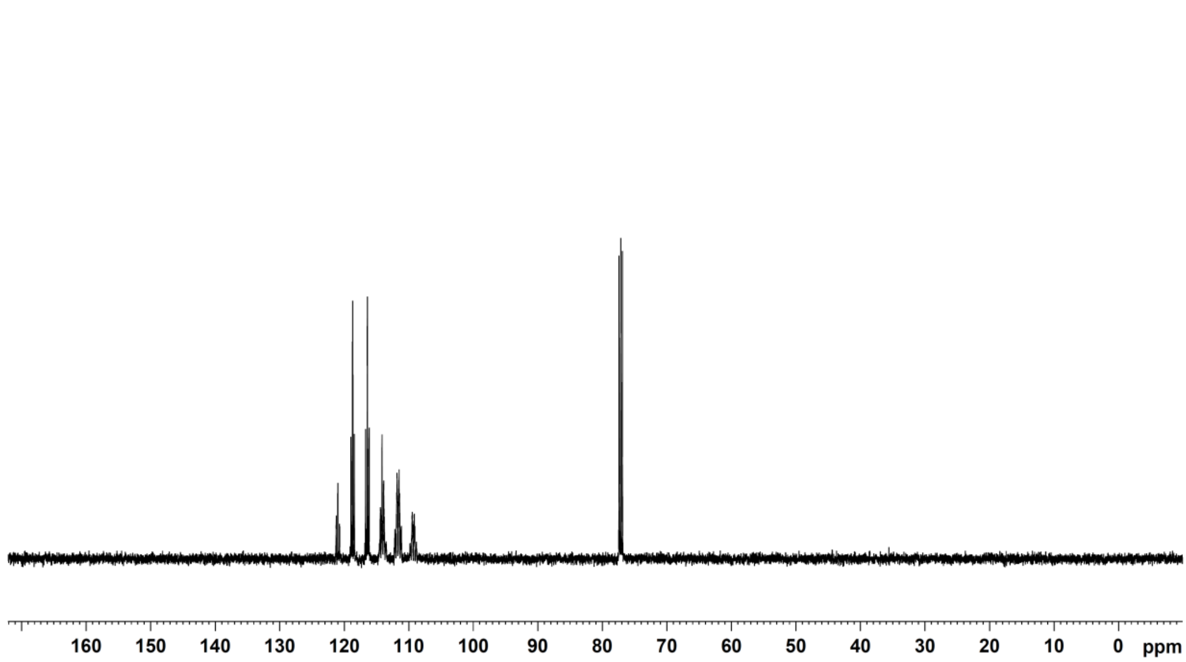
-75.43
-75.44
-181.96
-181.97
-181.99
-182.00
-182.02
-182.04
-182.05
18,18' (d)
-75.44
17 (m)
-182.01
S3c
OH
OH
6.00
1.00
f1 (ppm)

^{13}C NMR (S4)

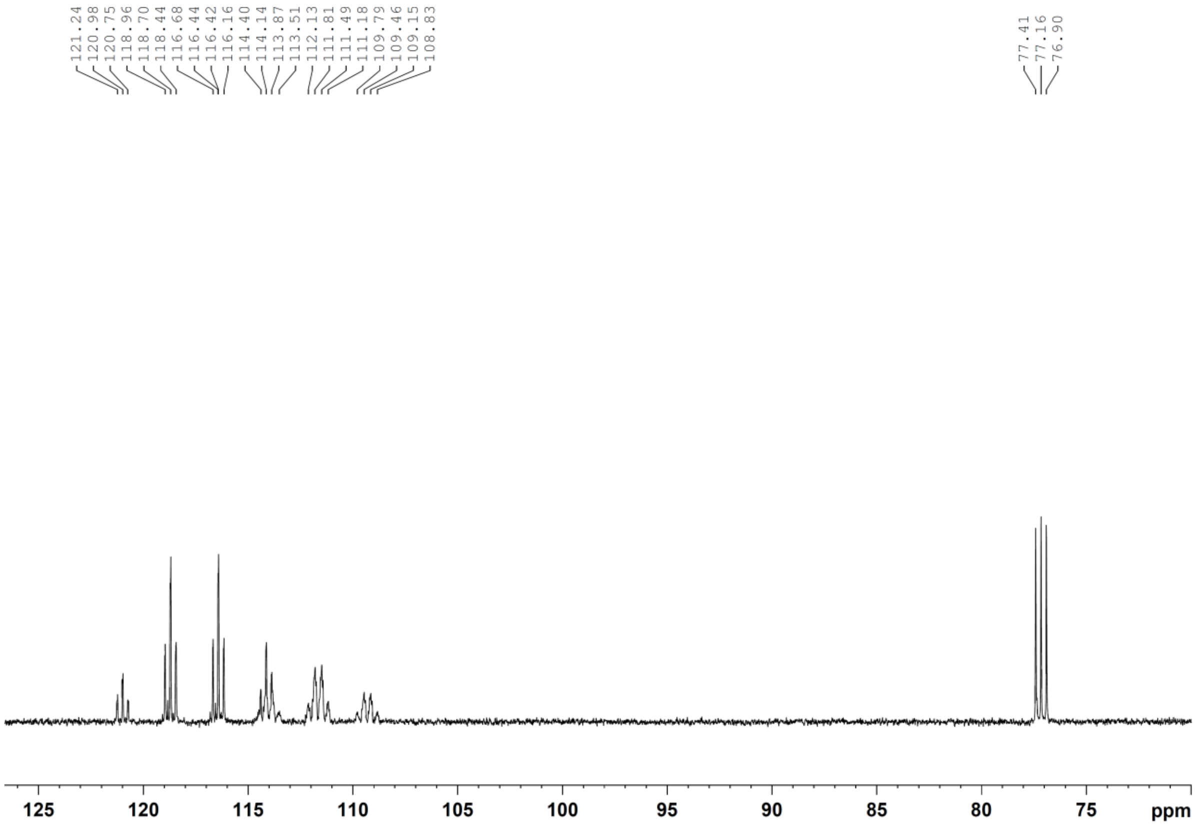


O
O
S
N
C_2F_5
P
Cl
Cl
Cl

S4



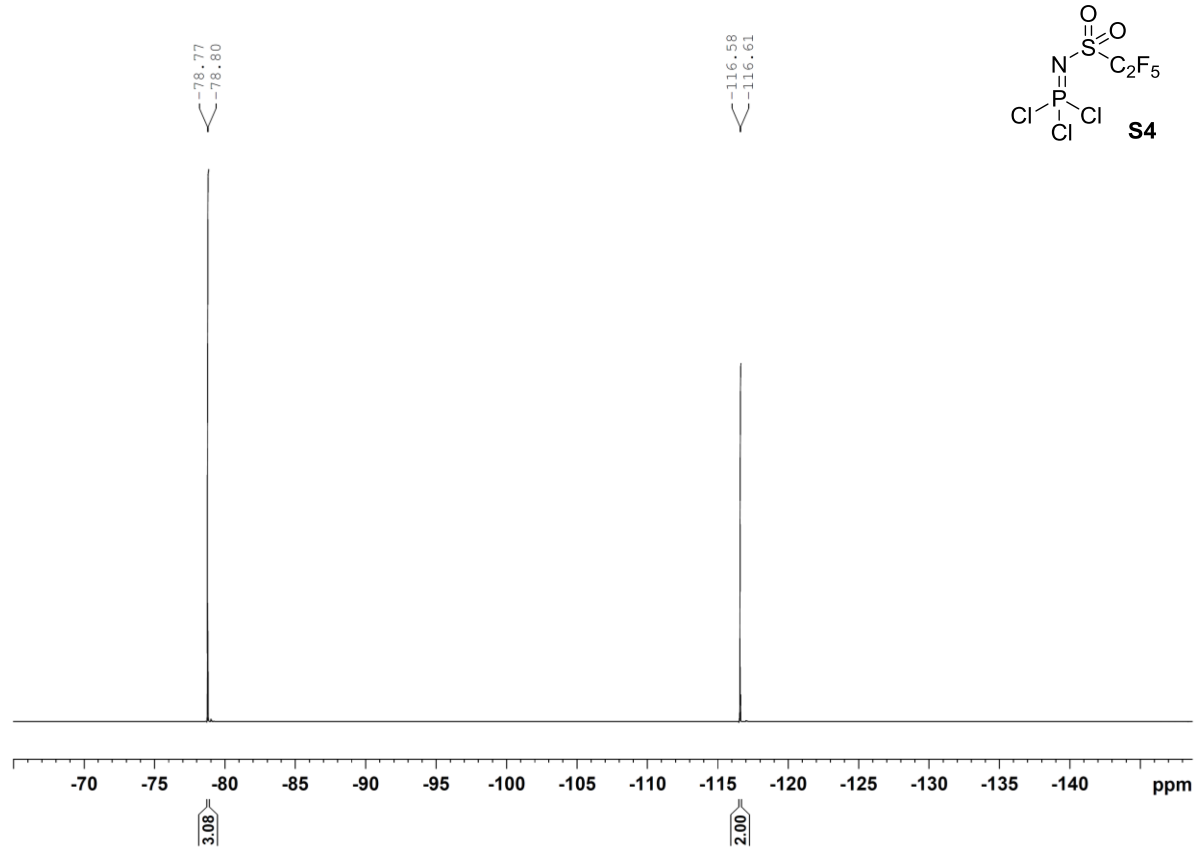
121.24
120.98
120.75
118.96
118.70
118.44
116.68
116.44
116.42
116.16
114.40
114.14
113.87
113.51
112.13
111.81
111.49
111.18
109.79
109.46
109.15
108.83
77.41
77.16
76.90
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



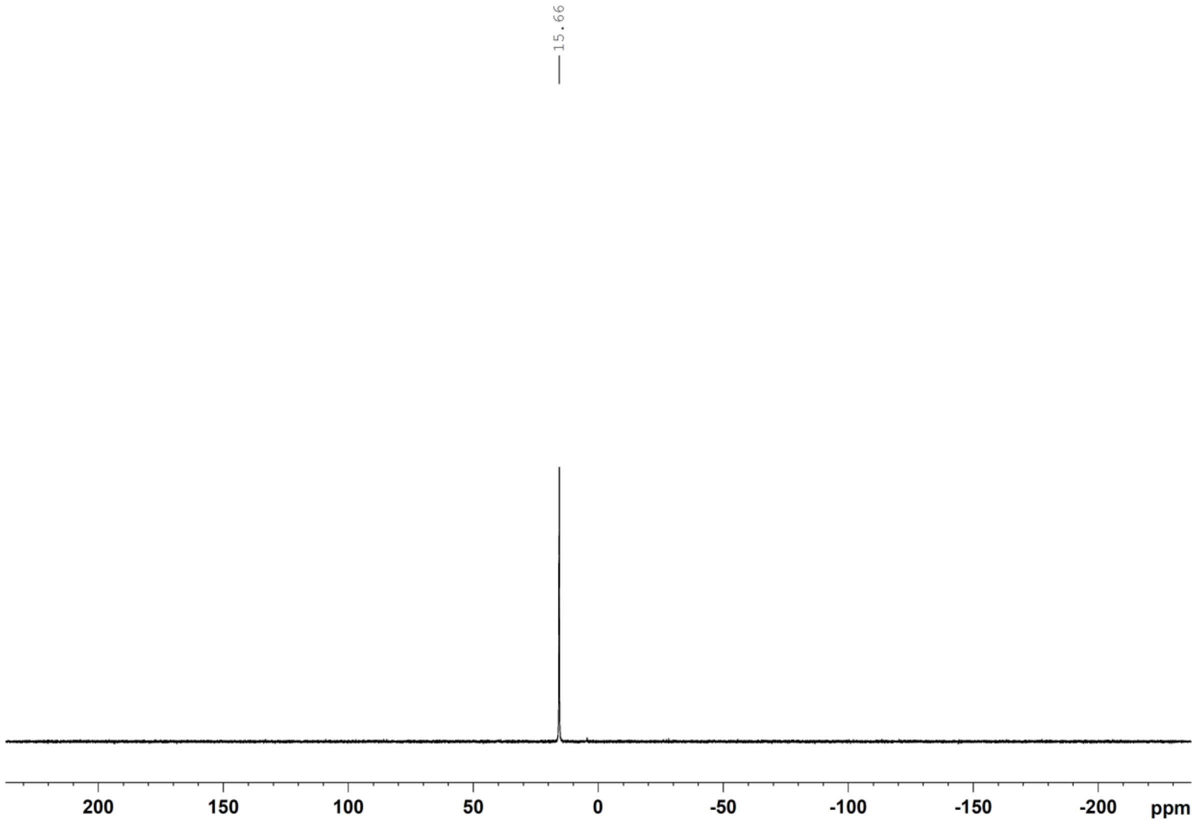
121.24
120.98
120.75
118.96
118.70
118.44
116.68
116.44
116.42
116.16
114.40
114.14
113.87
113.51
112.13
111.81
111.49
111.18
109.79
109.46
109.15
108.83
77.41
77.16
76.90
125 120 115 110 105 100 95 90 85 80 75 ppm

^{19}F NMR (S4)

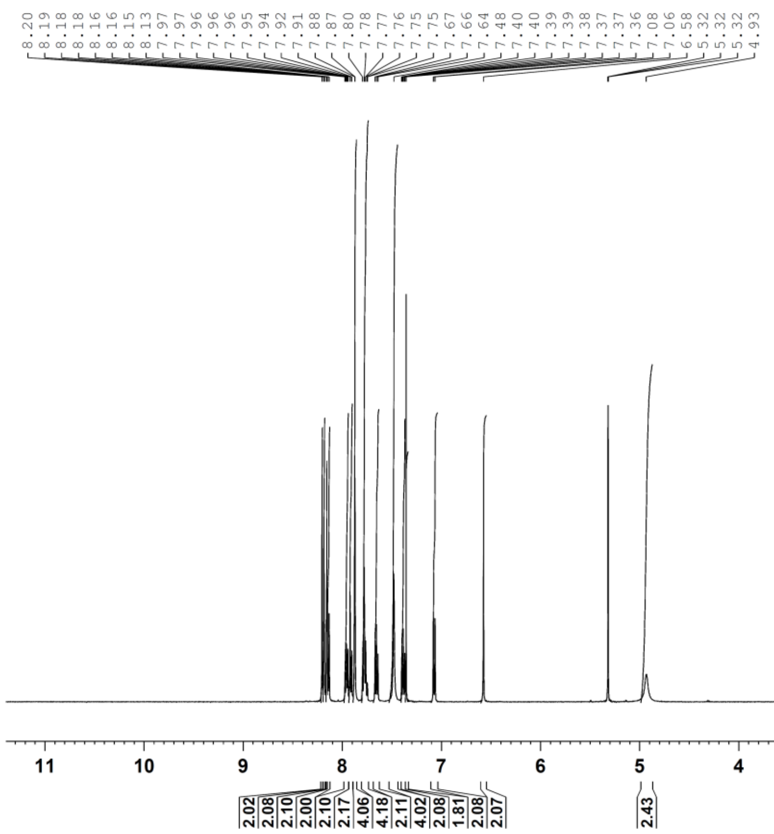
S4

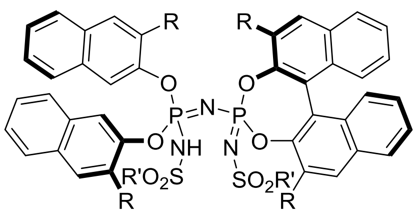


^{31}P NMR (S4)

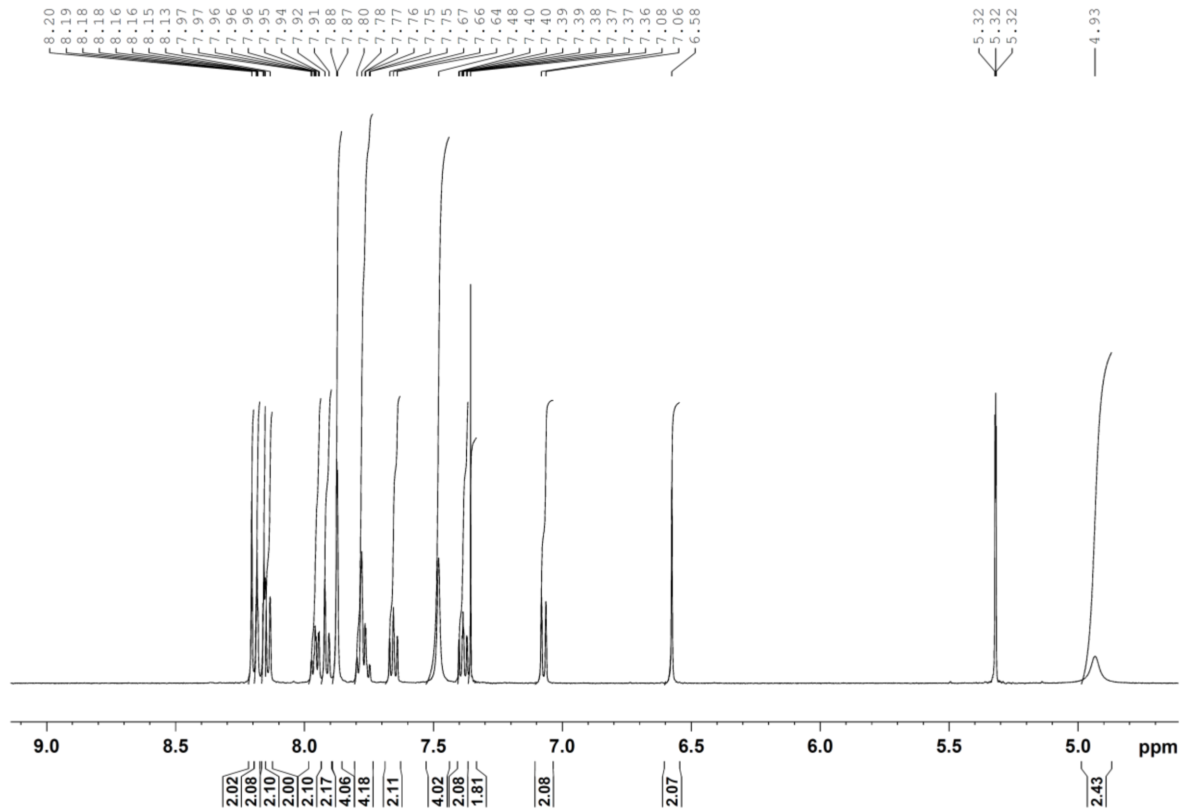


[1]H NMR (4c)

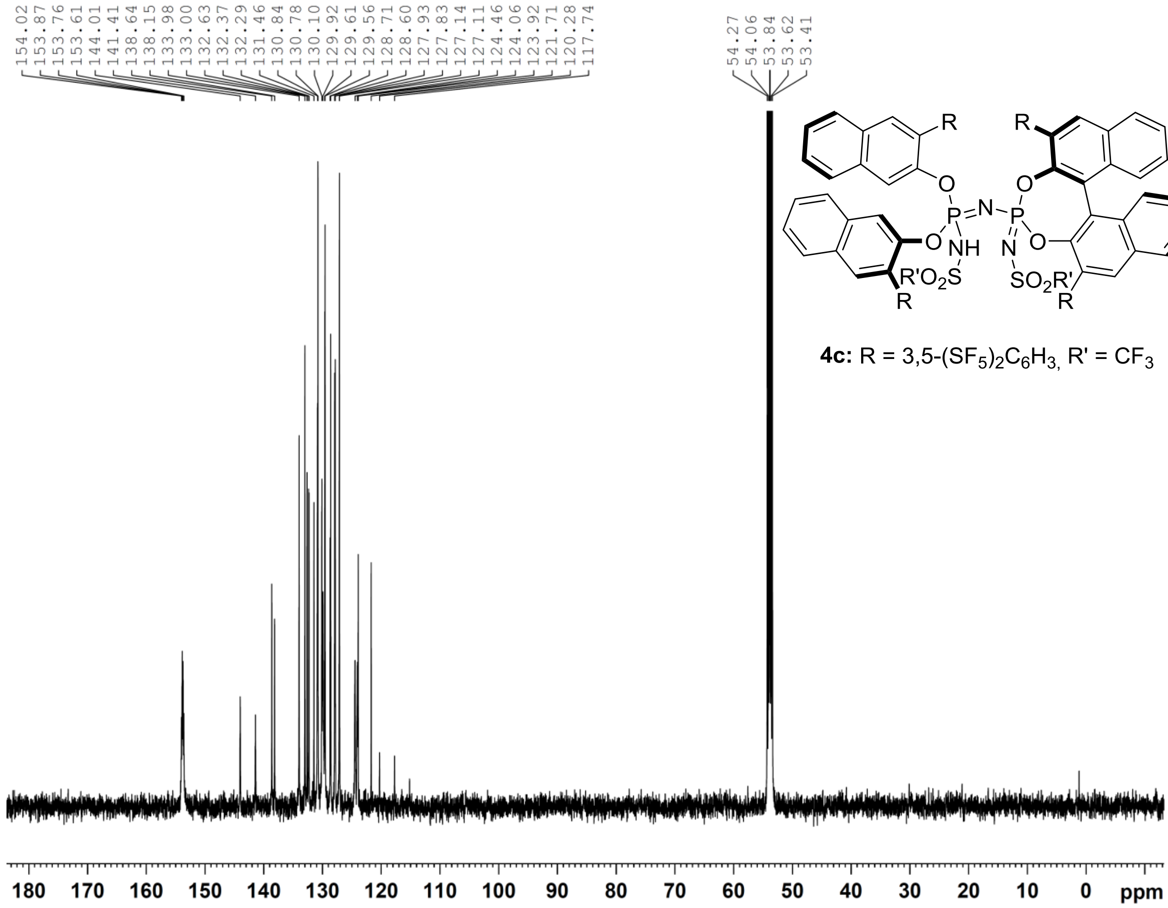




4c: R = 3,5-$(SF_5)_2C_6H_3$, R' = CF_3

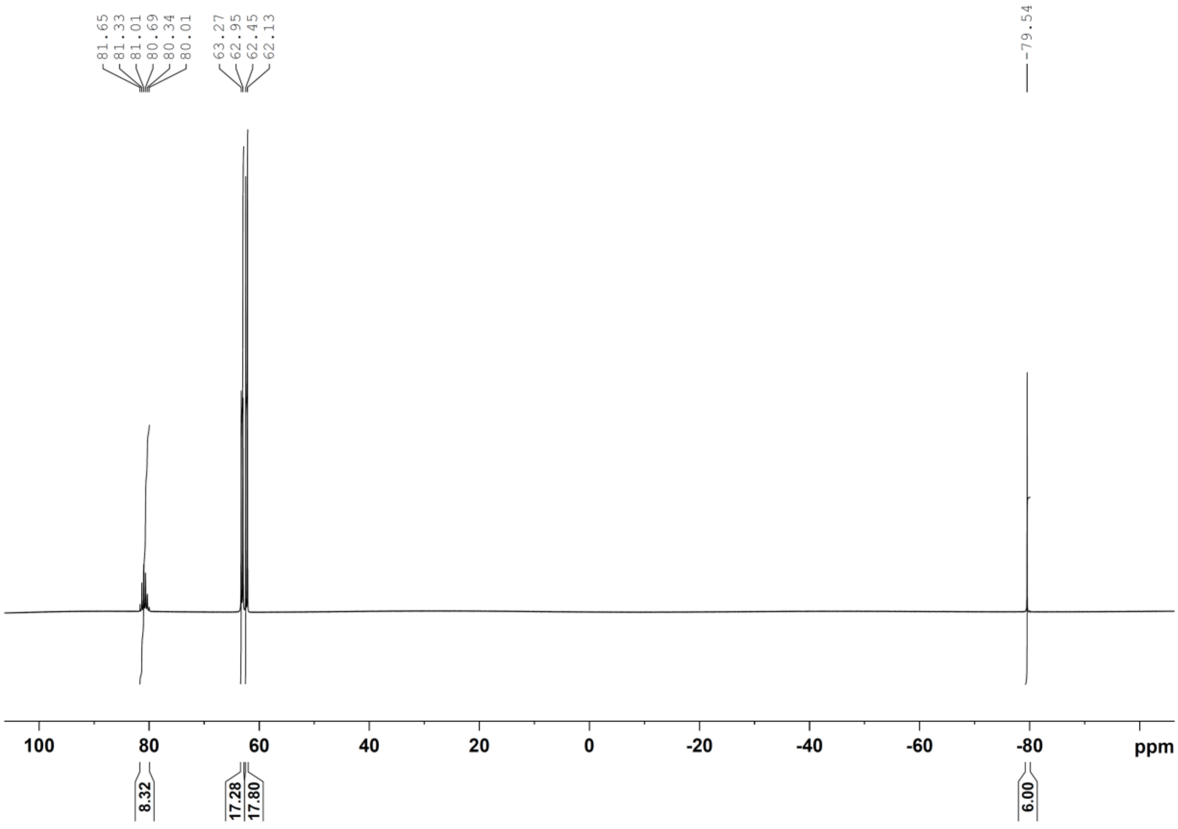


^{13}C NMR (4c)

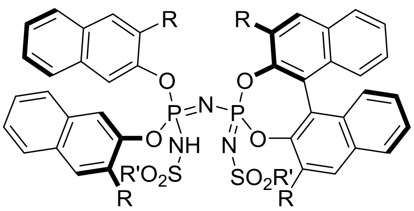


4c: R = 3,5-$(SF_5)_2C_6H_3$, R' = CF_3

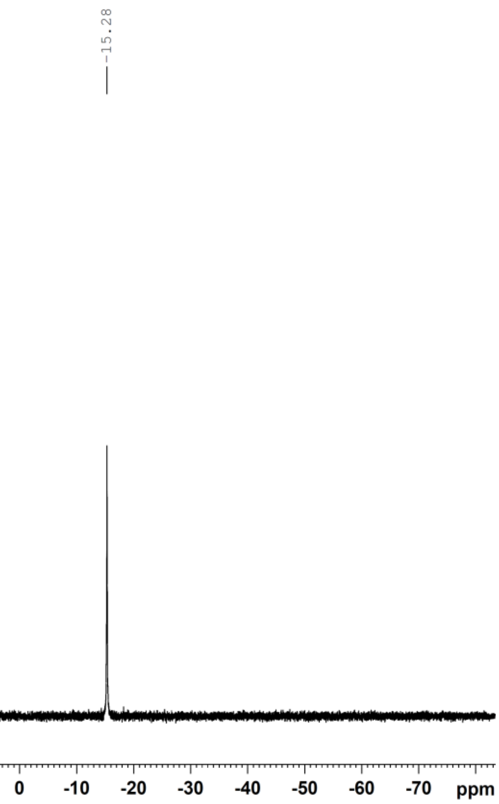
^{9}F NMR (4c)



^{31}P NMR (**4c**)

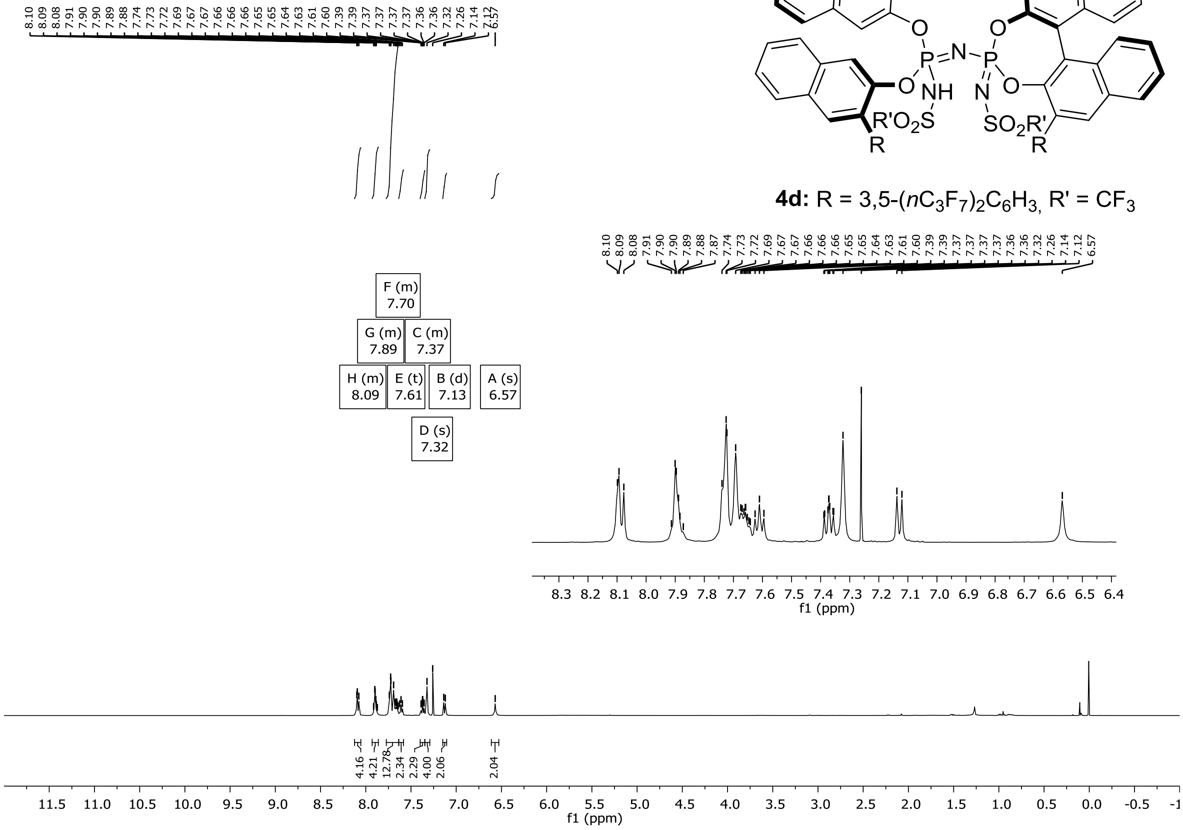


4c: R = 3,5-$(SF_5)_2C_6H_3$, R' = CF_3

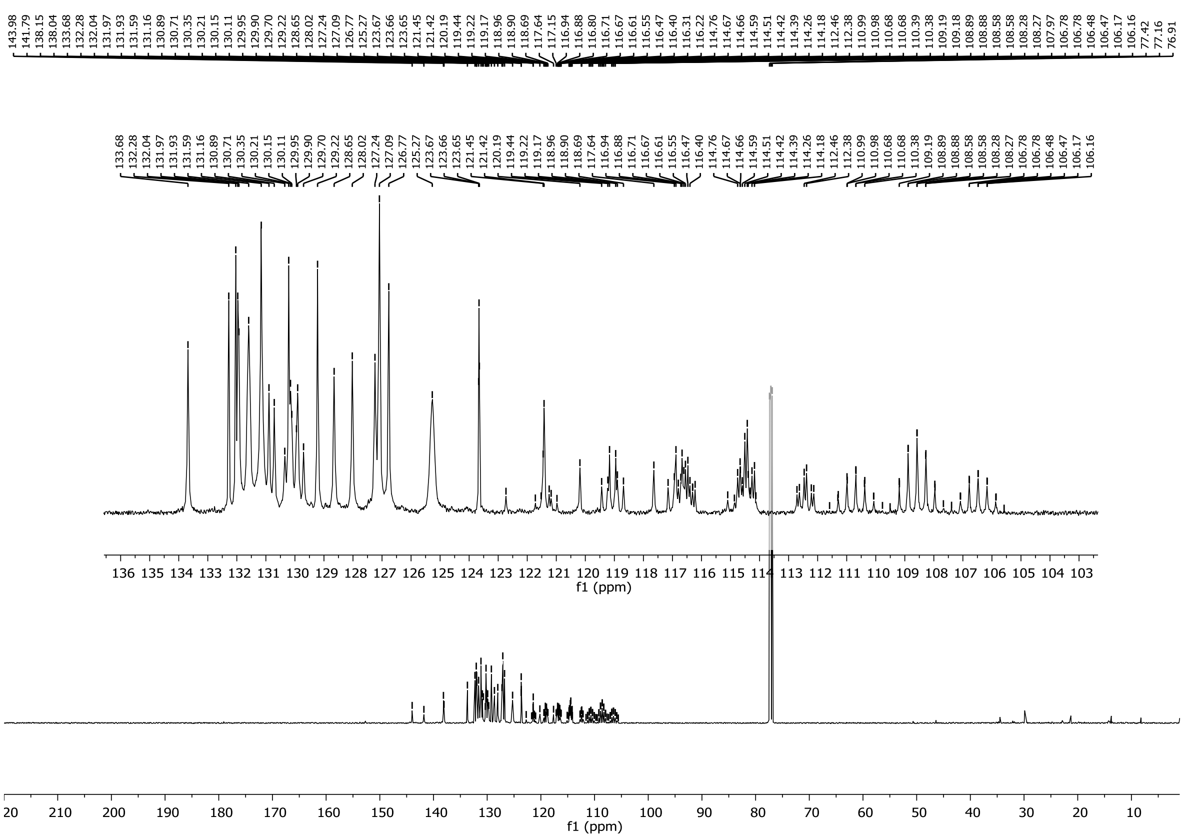


^{1}H NMR (4d)

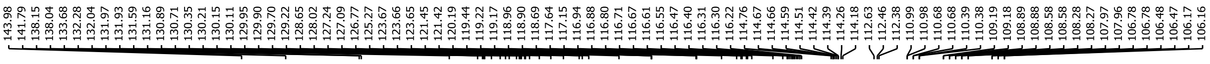
4d: R = 3,5-(nC$_3$F$_7$)$_2$C$_6$H$_3$, R' = CF$_3$

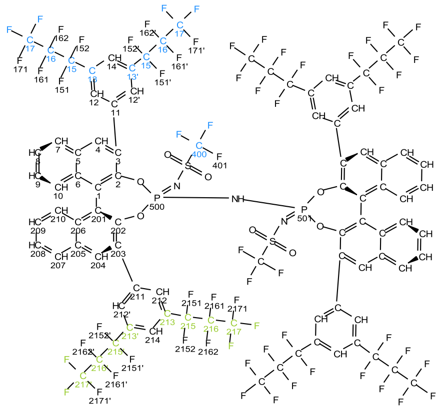


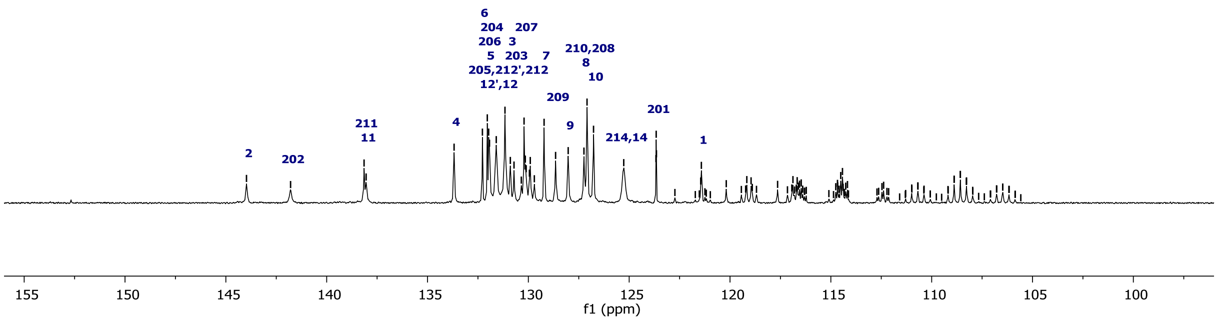
^{13}C NMR (4d)



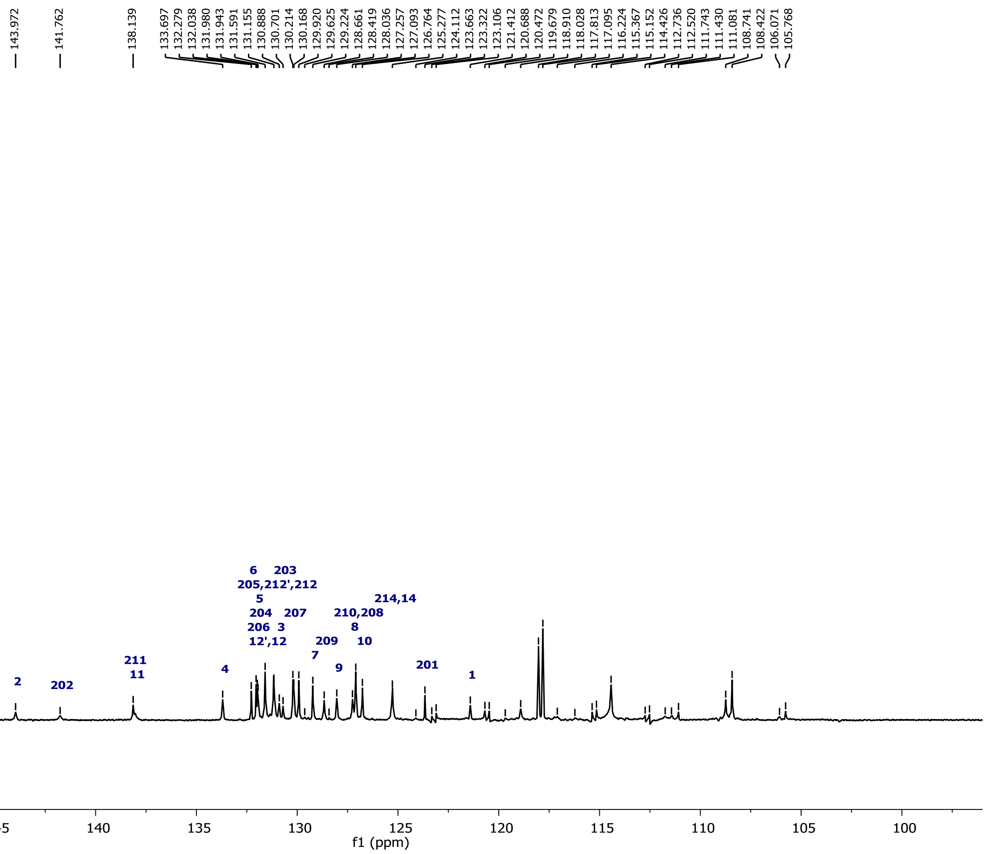
^{13}C NMR (4d)



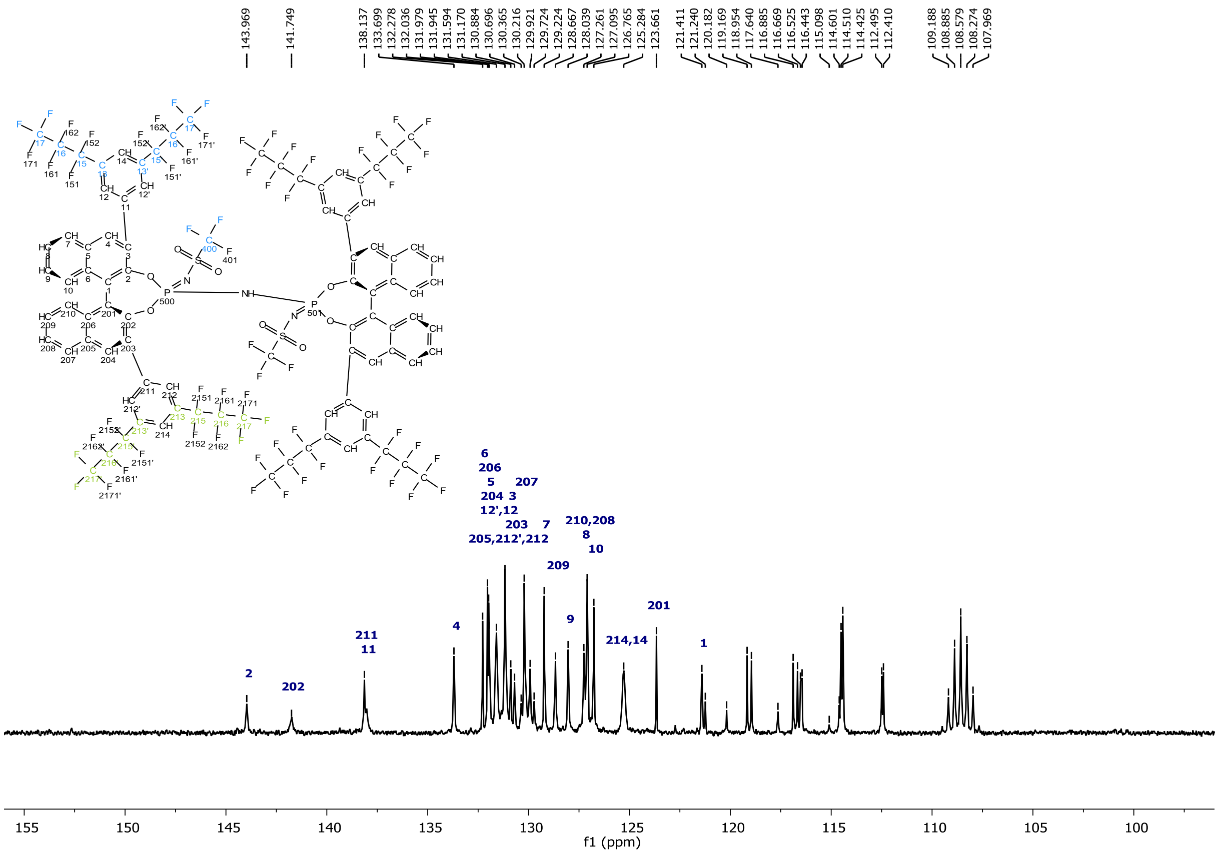




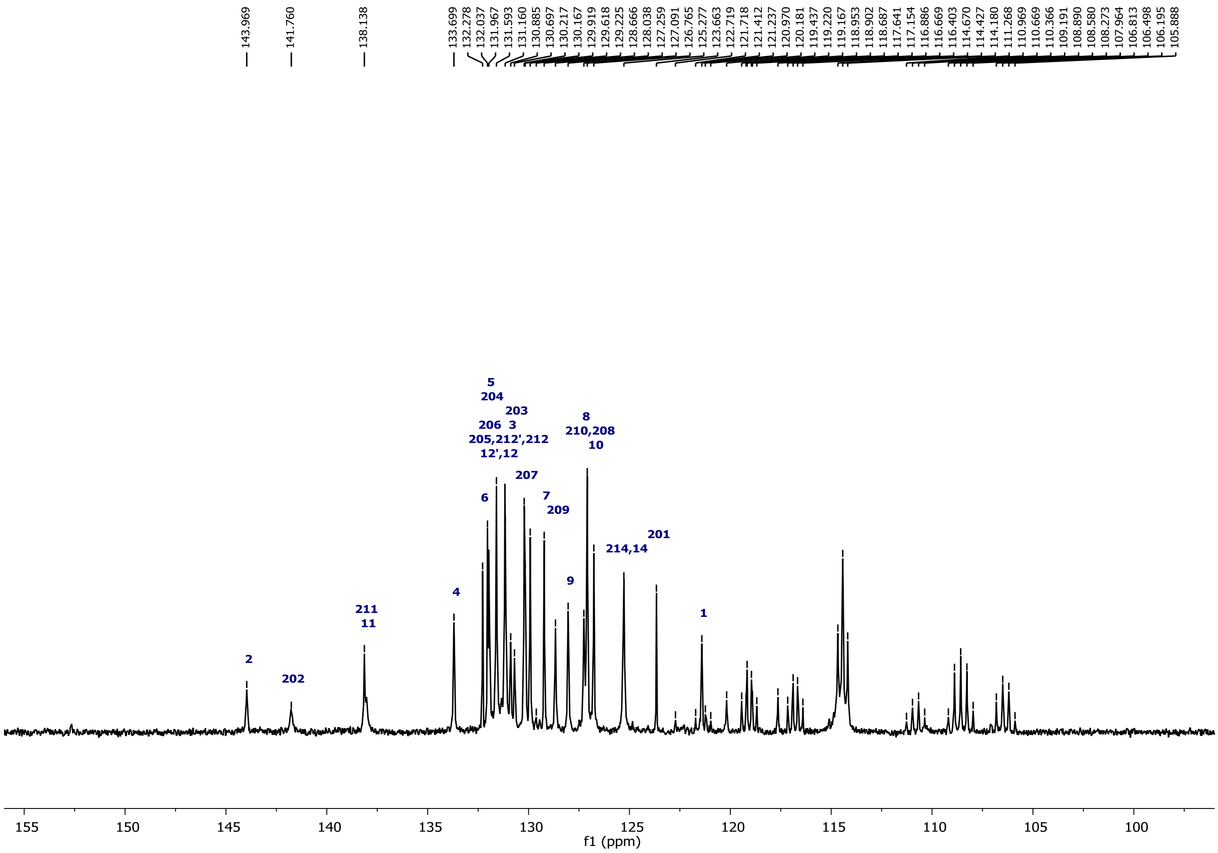
^{13}C NMR (4d) (^{1}H, ^{19}F decoupled; broadband ^{19}F decoupling)



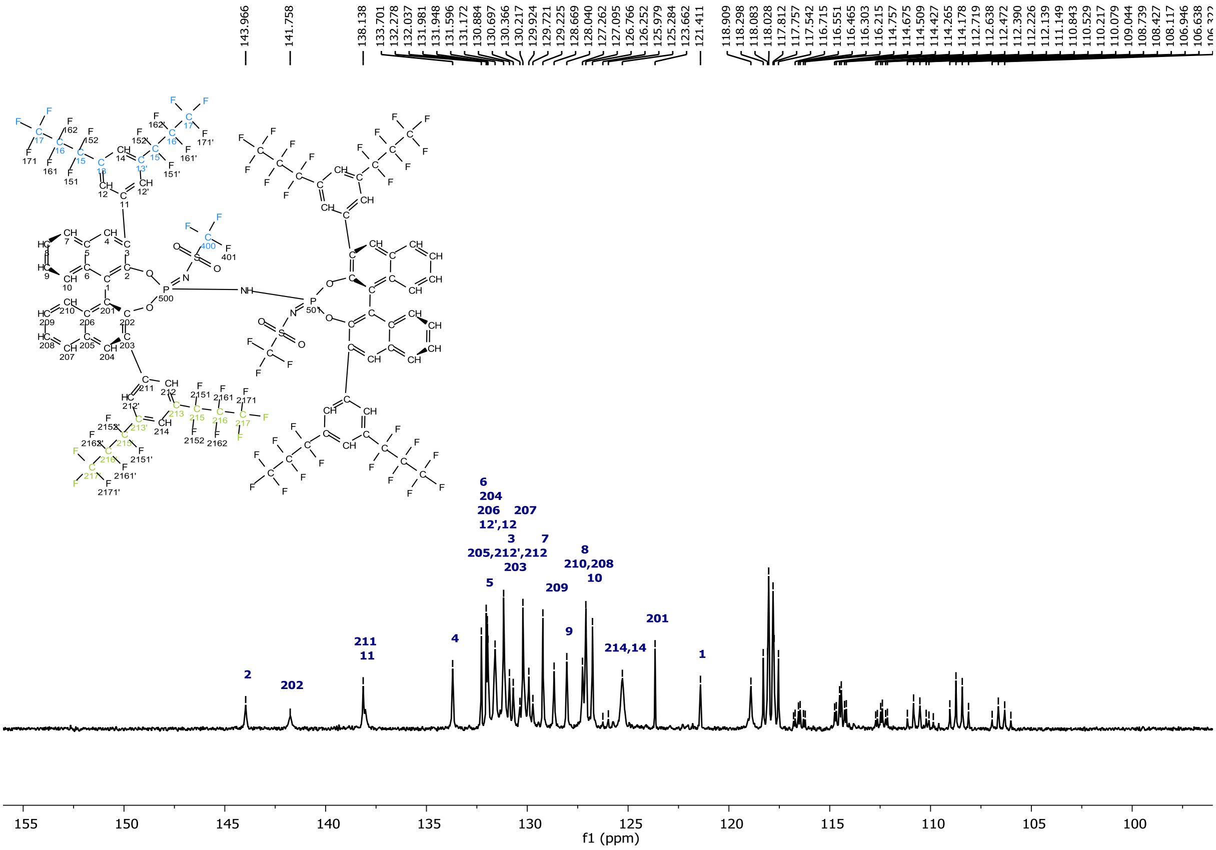
^{13}C NMR (4d) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling for offset δ_F –126.1)



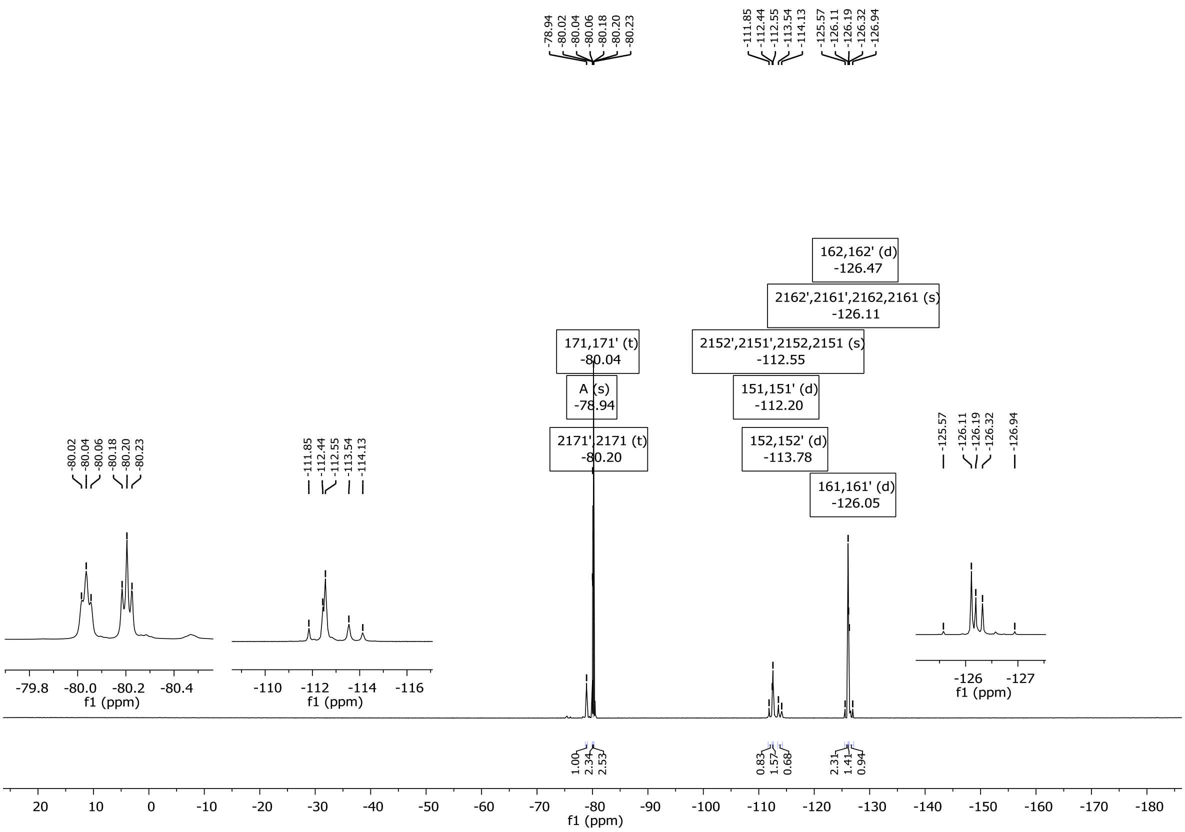
^{13}C NMR (4d) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling for offset δ_F –112.5)



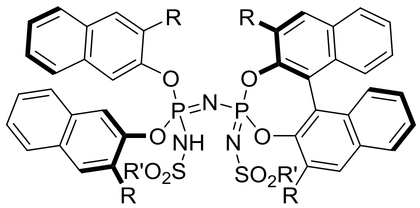
^{13}C NMR (4d) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling for offset δ_F –80.0)



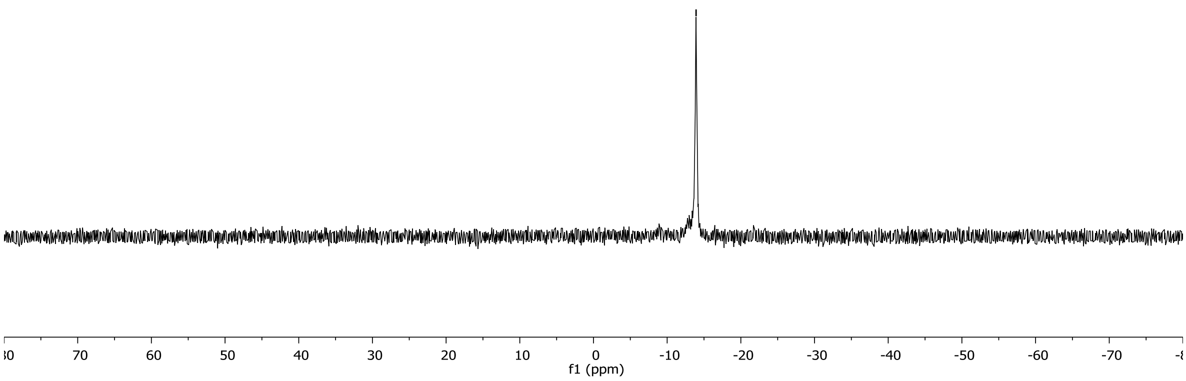
^{19}F NMR (4d)



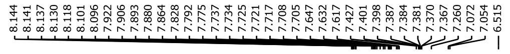
^{31}P NMR (4d)

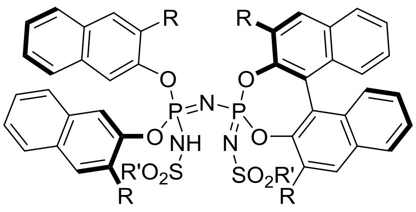


4d: R = 3,5-($n$$C_3F_7$)$_2$$C_6H_3$, R' = CF_3

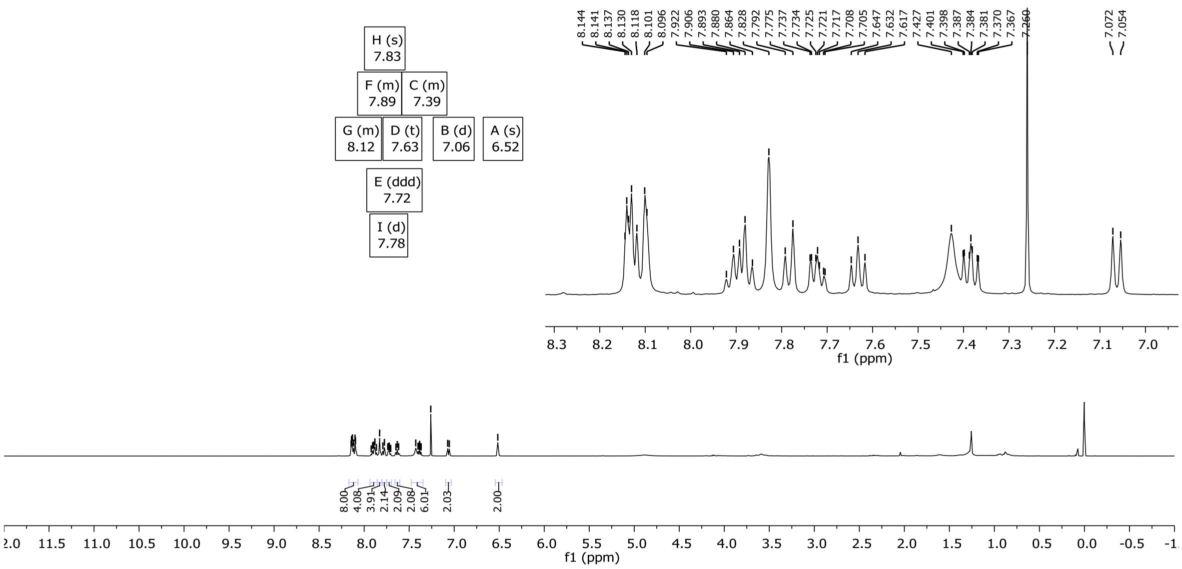


^{1}H NMR (4e)

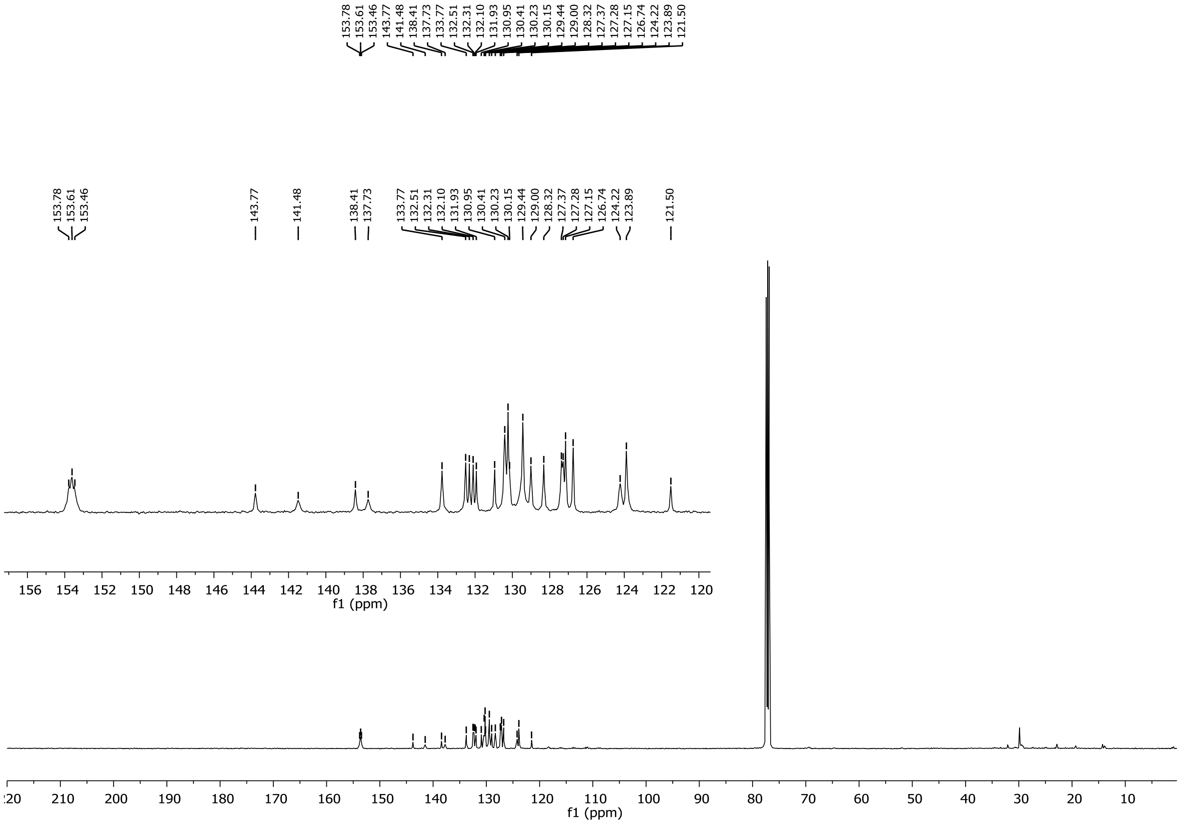




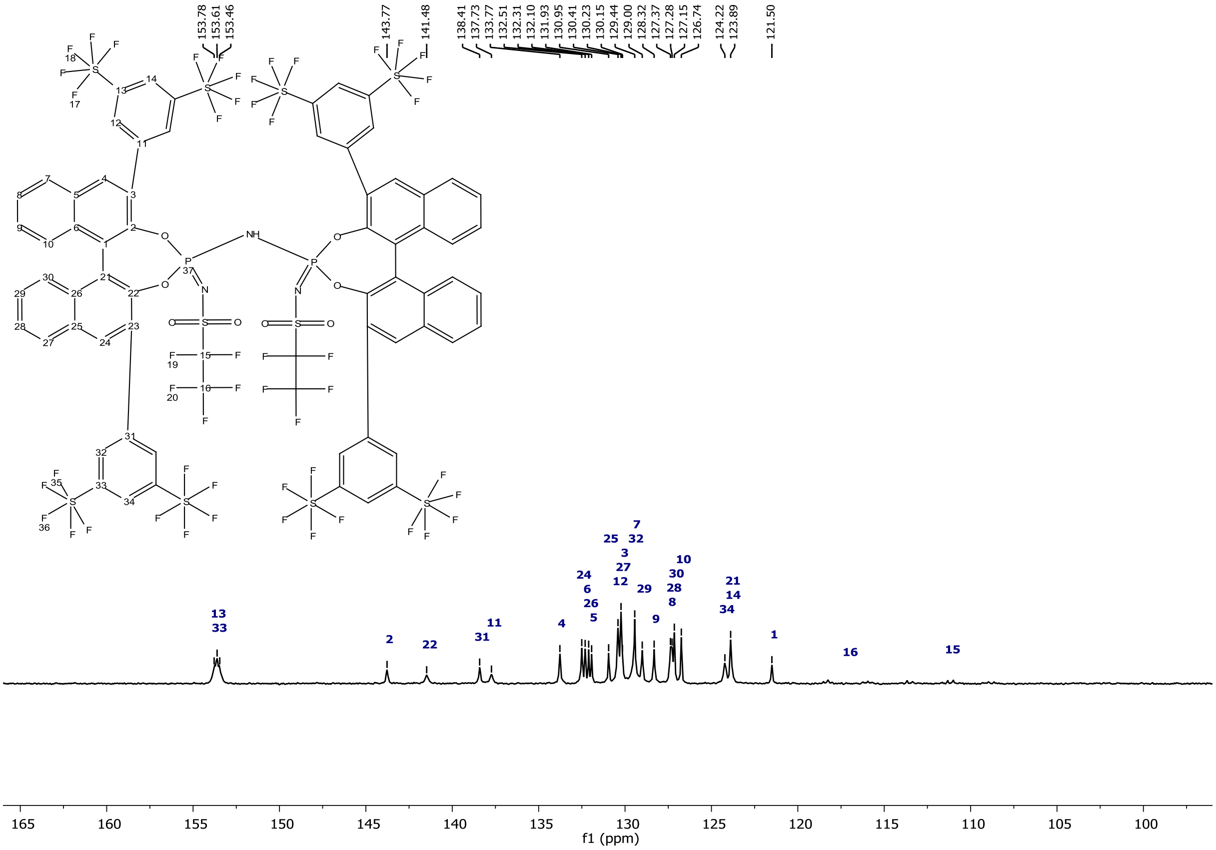
4e: R = 3,5-$(SF_5)_2C_6H_3$, R' = C_2F_5



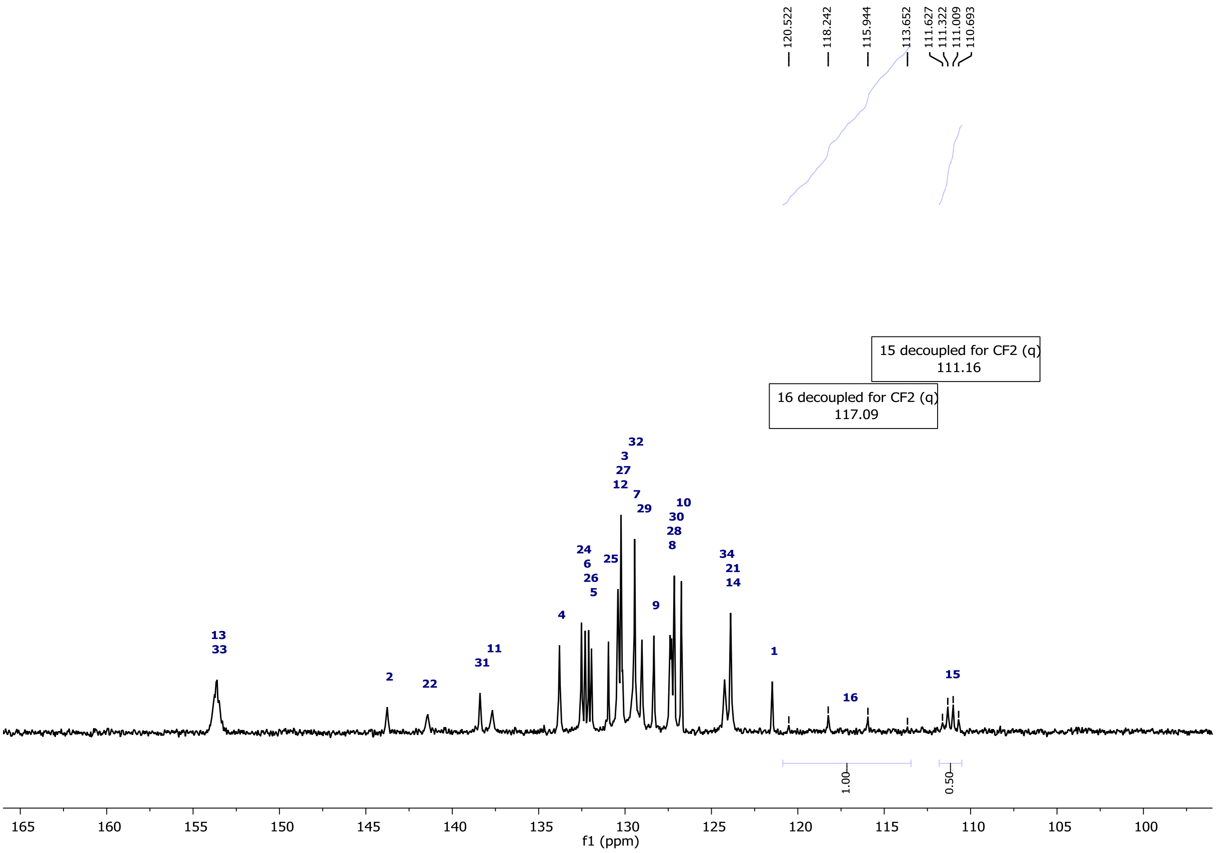
^{13}C NMR (4e)



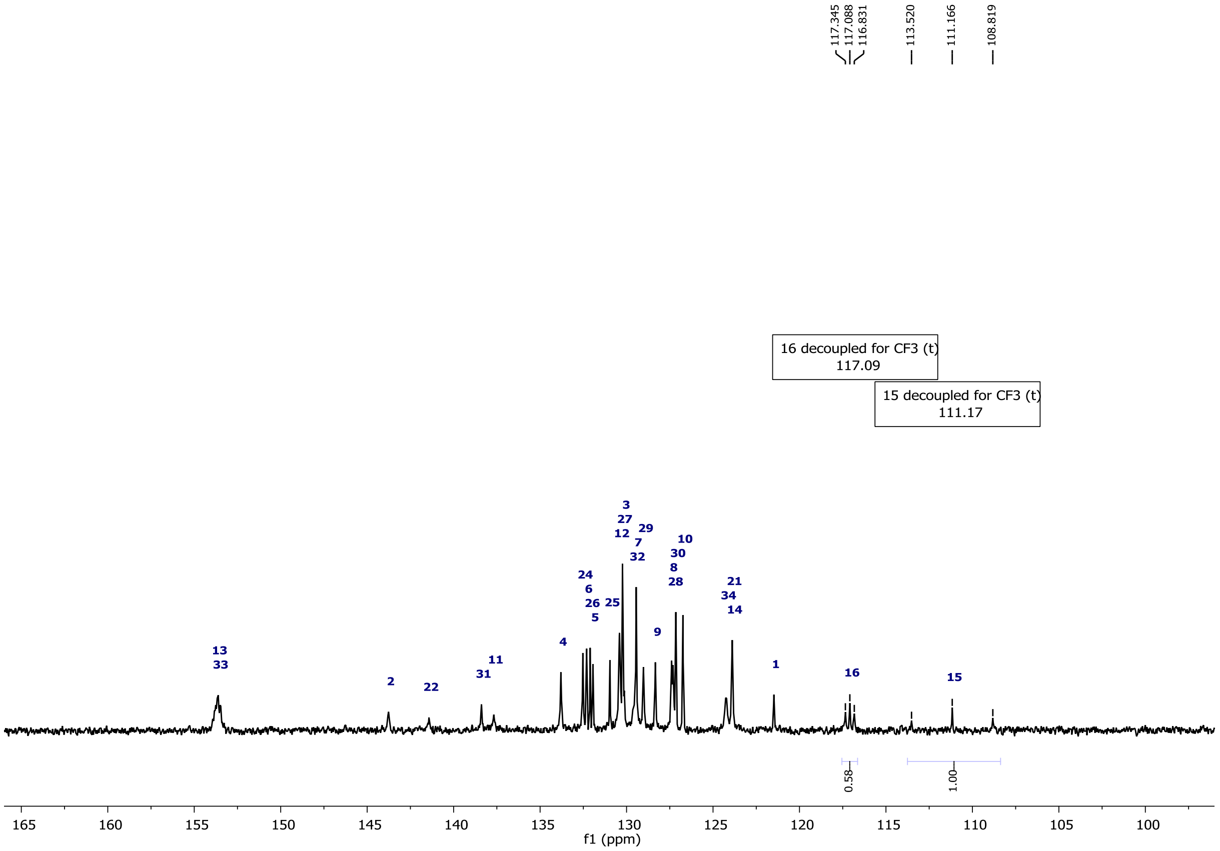
^{13}C NMR (4e)



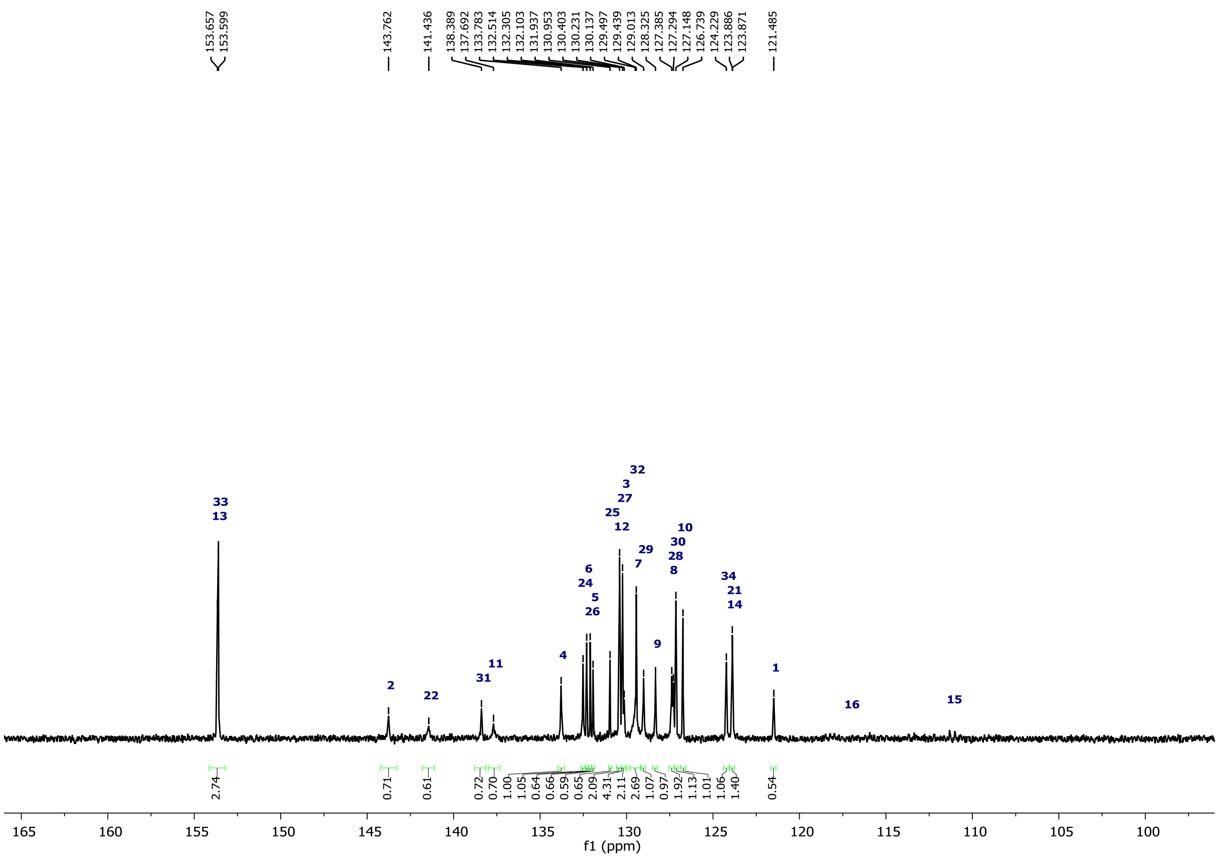
^{13}C NMR (4e) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling for offset δ_F –117.00)



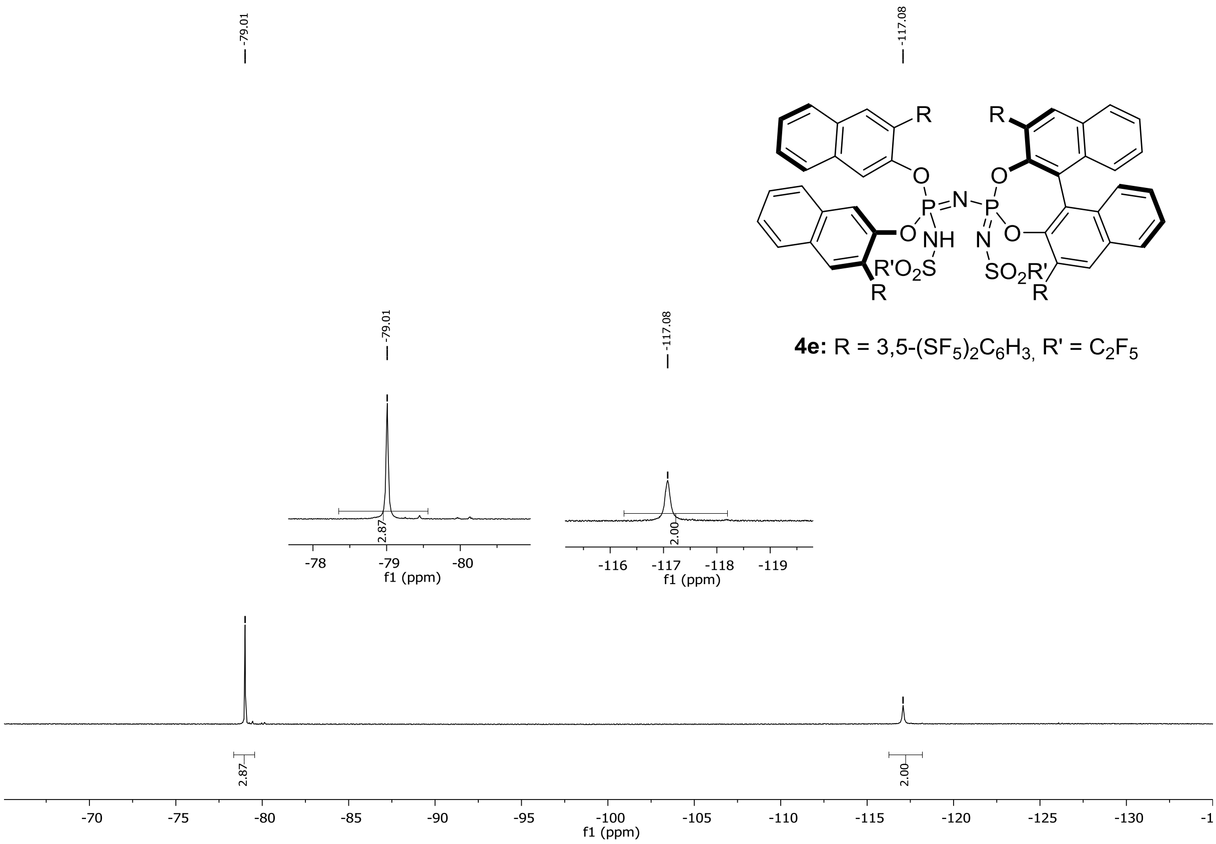
^{13}C NMR (4e) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling for offset δ_F –79.00)



^{13}C NMR (4e) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling for offset δ_F 63.35)

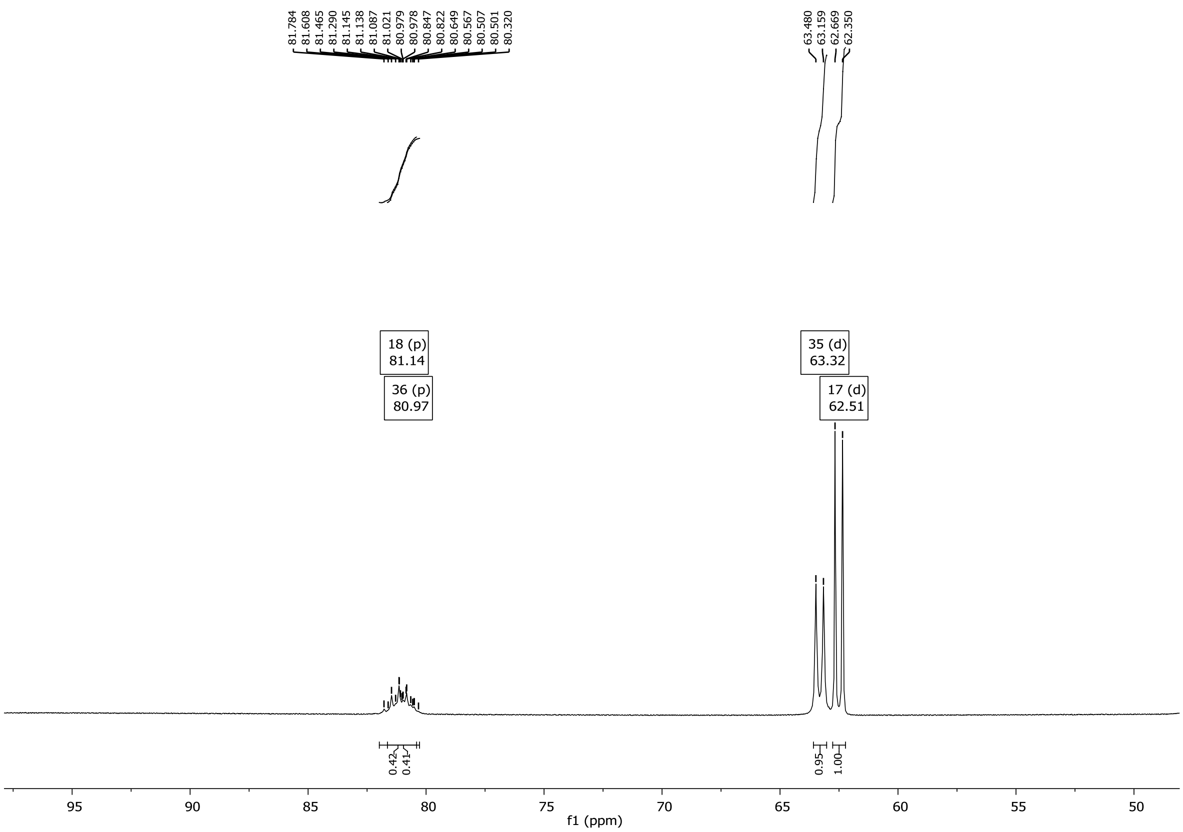


^{19}F NMR (4e)

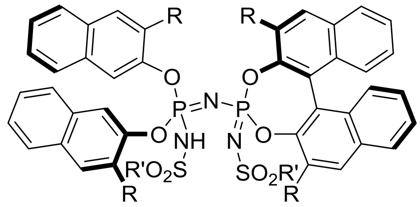


4e: R = 3,5-$(SF_5)_2C_6H_3$, R' = C_2F_5

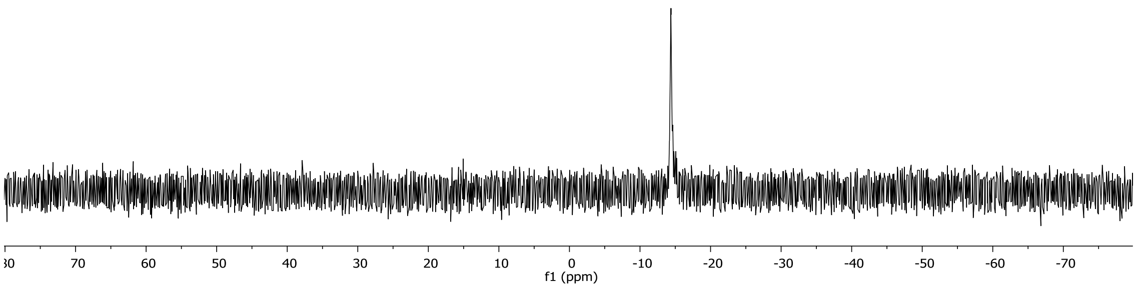
^{19}F NMR (4e)



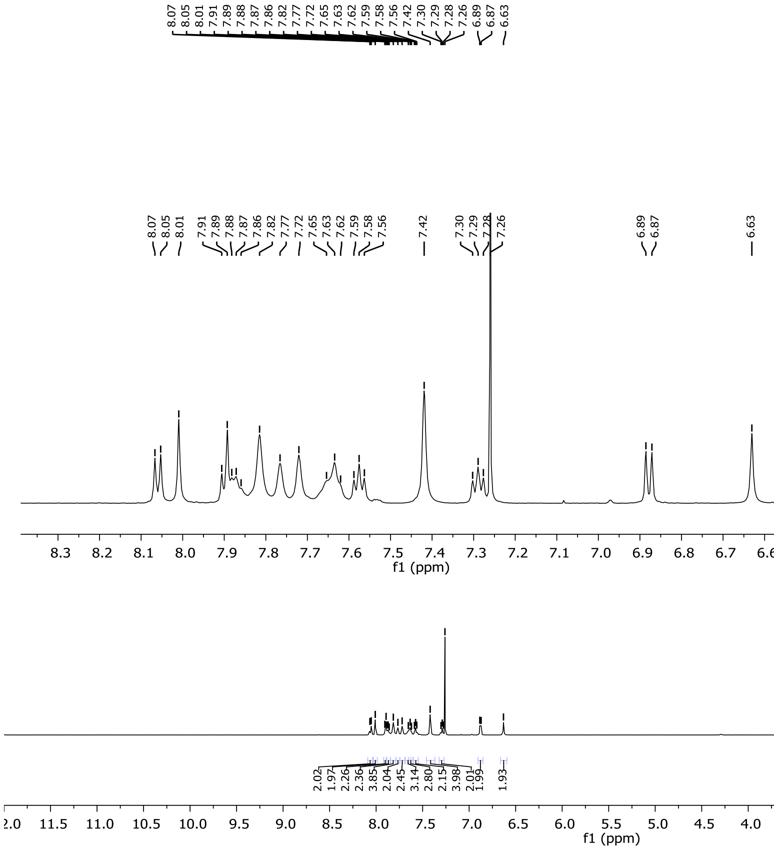
^{31}P NMR (4e)

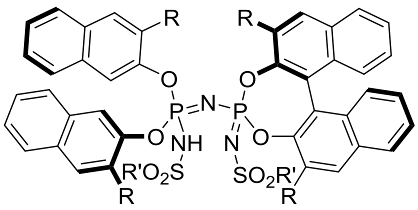


4e: R = 3,5-$(SF_5)_2C_6H_3$, R' = C_2F_5

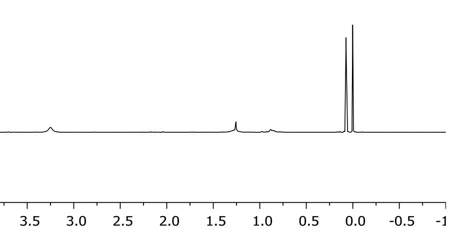


^{1}H NMR (4f)

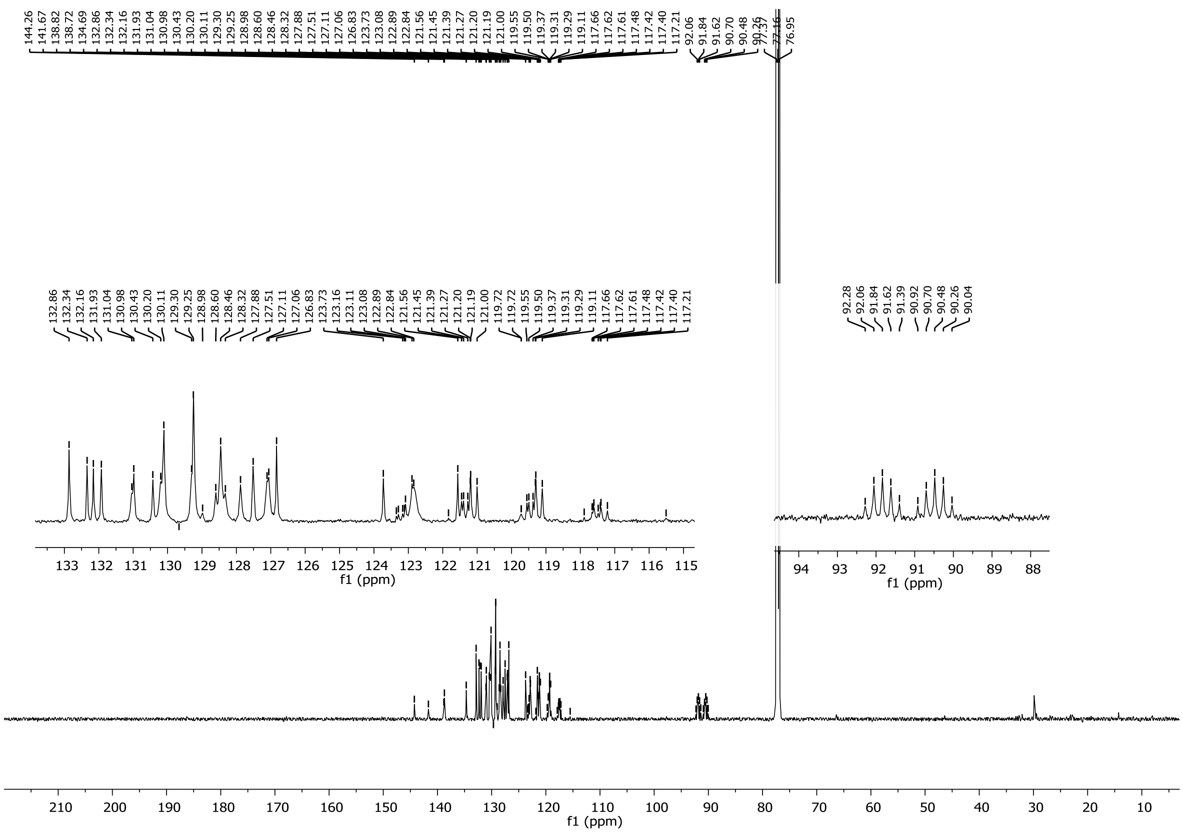




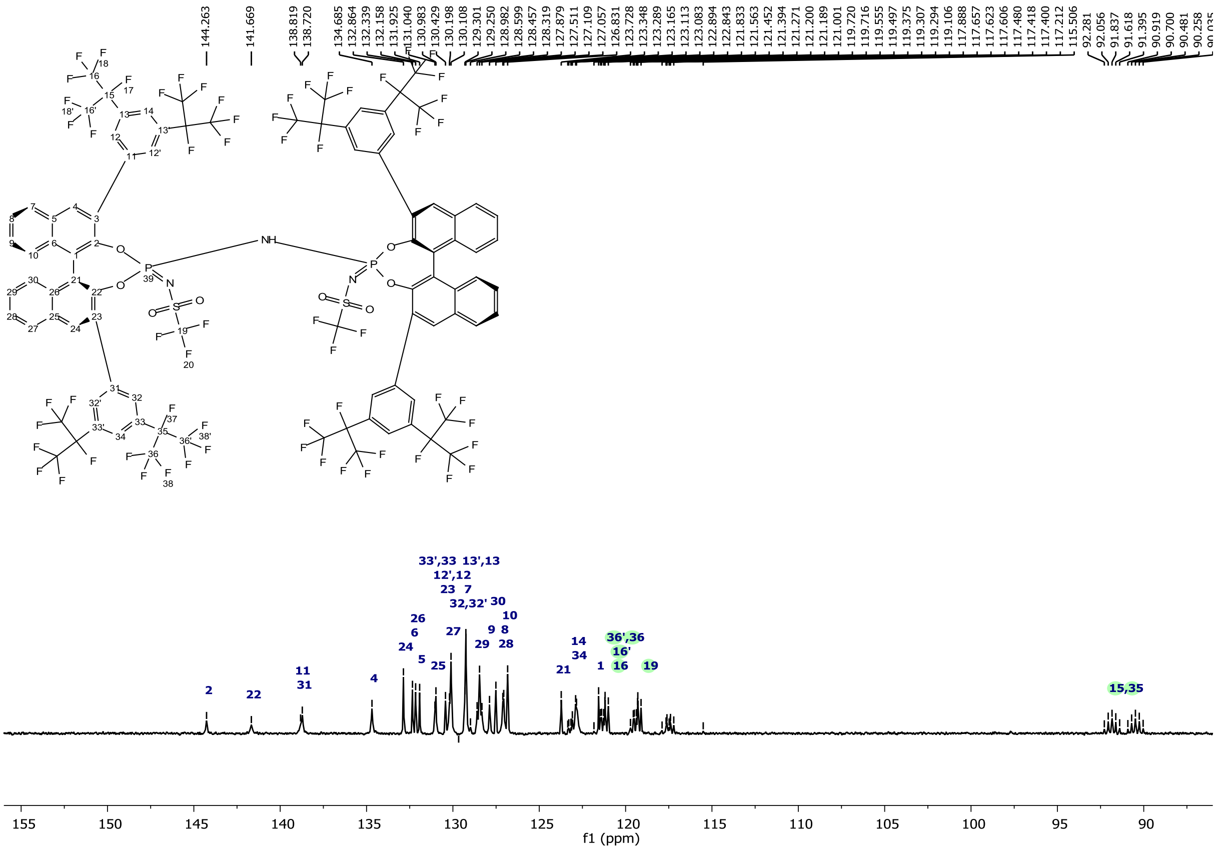
4f: R = 3,5-$(CF(CF_3)_2)_2C_6H_3$, R' = CF_3



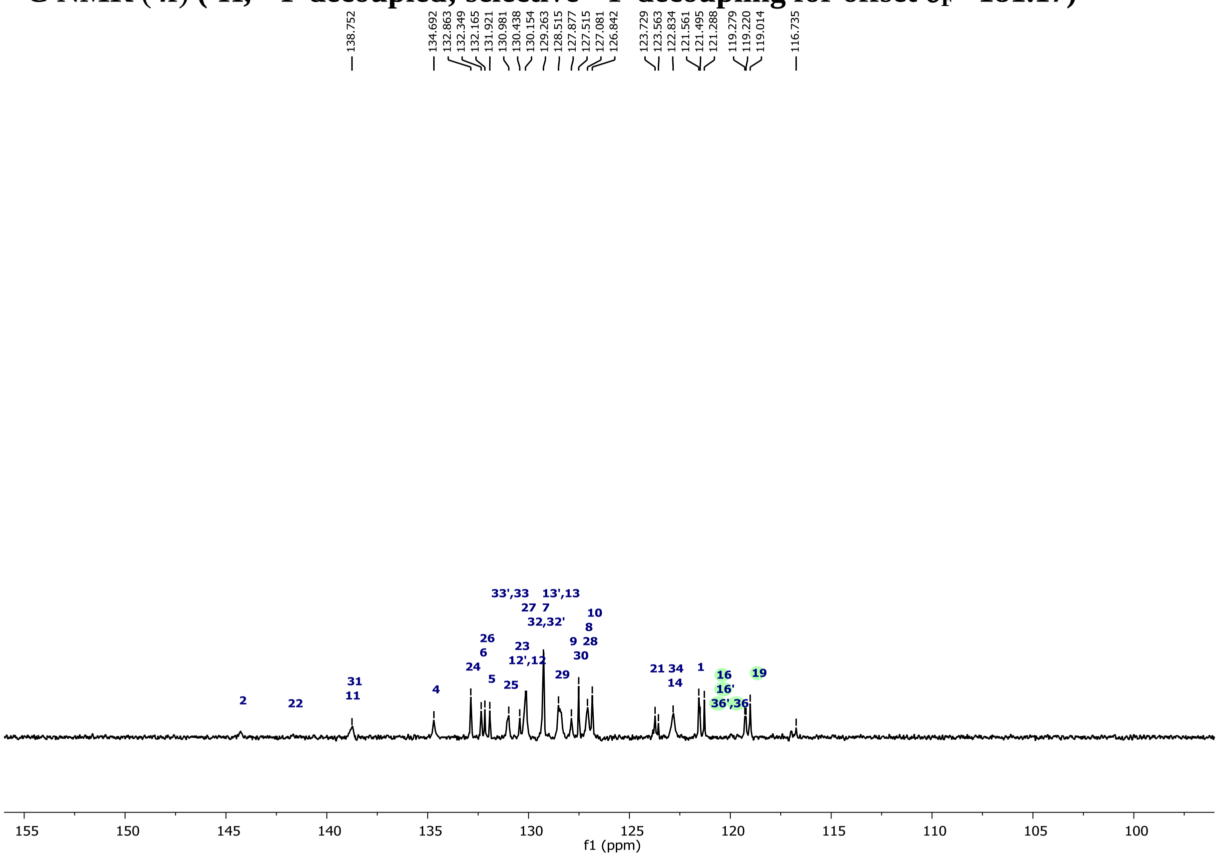
^{13}C NMR (4f)



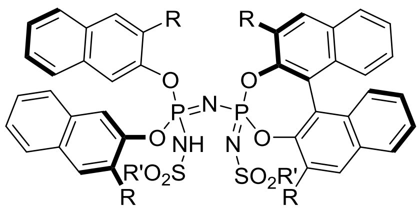
^{13}C NMR (4f)



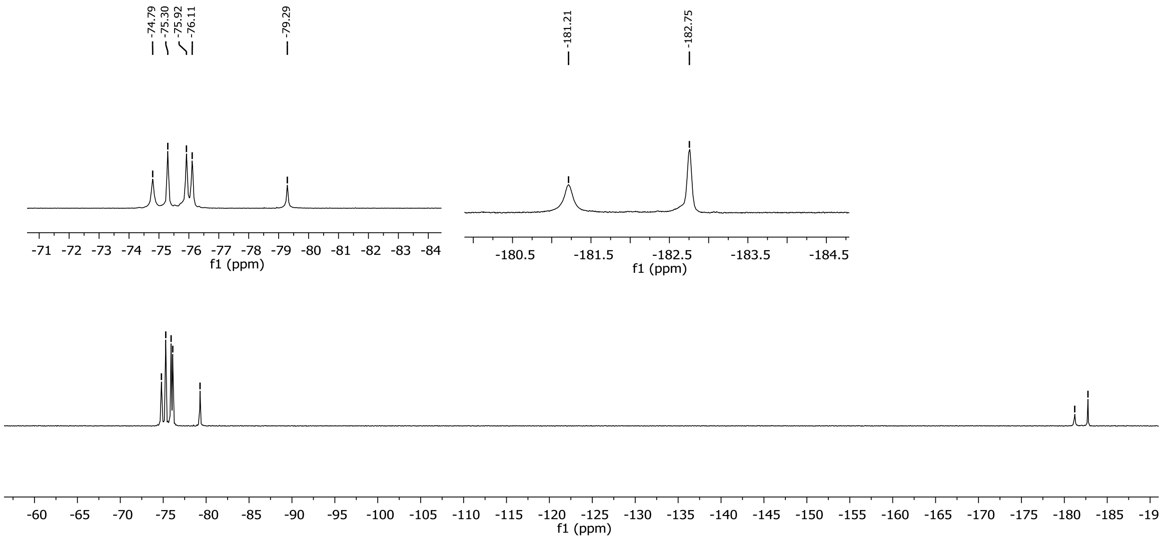
^{13}C NMR (4f) (^{1}H, ^{19}F decoupled; selective ^{19}F decoupling for offset δ_F –181.17)



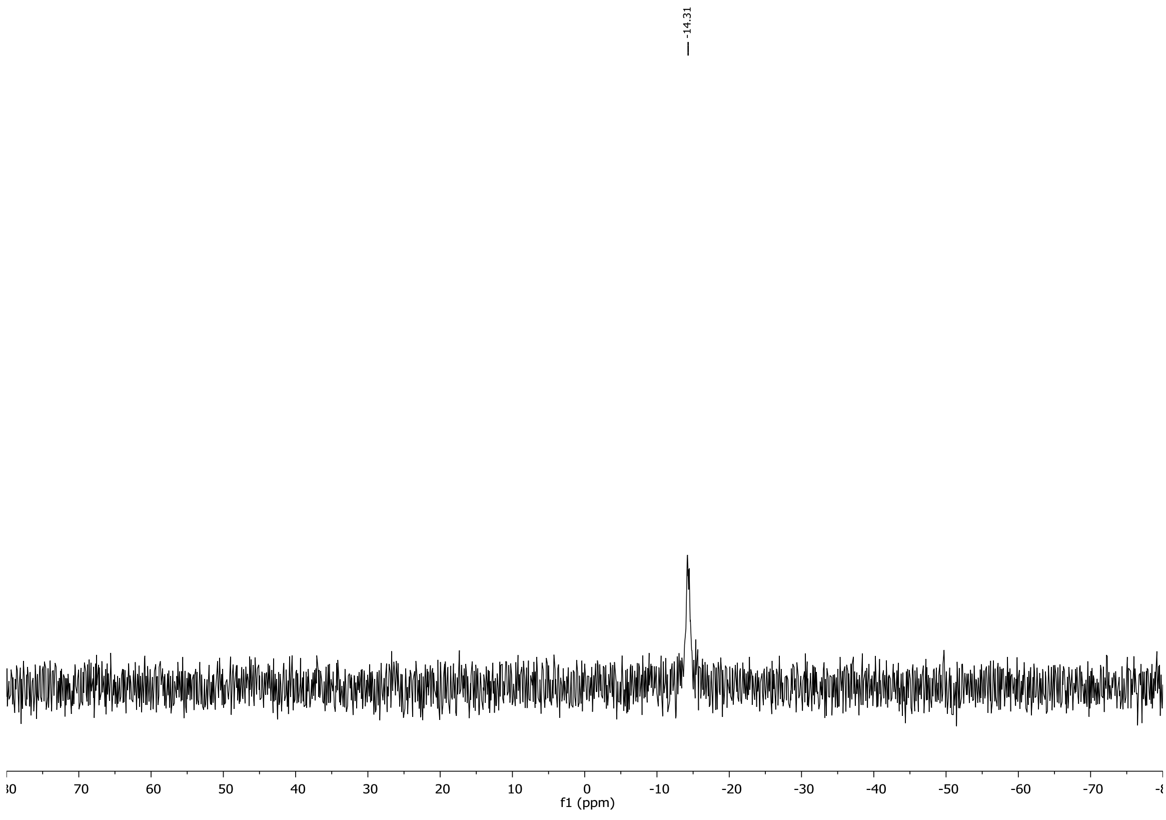
^{19}F NMR (4f)



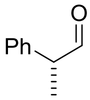
4f: R = 3,5-(CF(CF$_3$)$_2$)$_2$C$_6$H$_3$, R' = CF$_3$



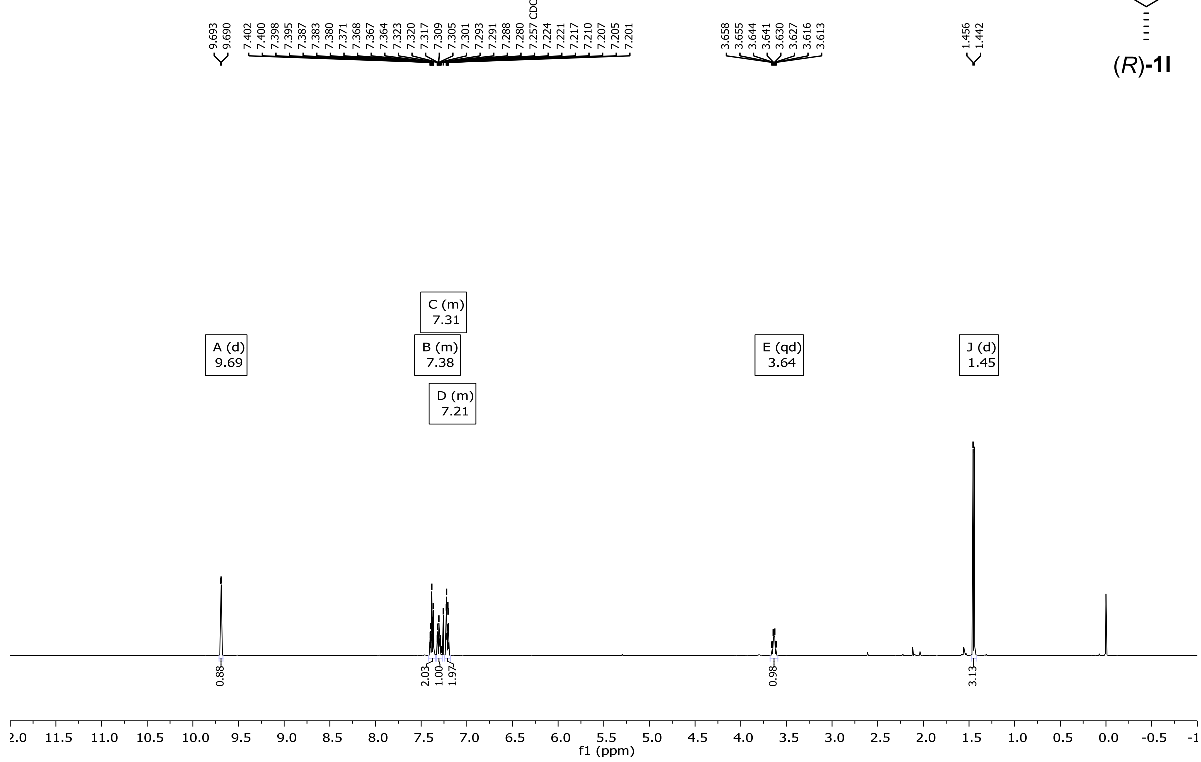
^{31}P NMR (4f)



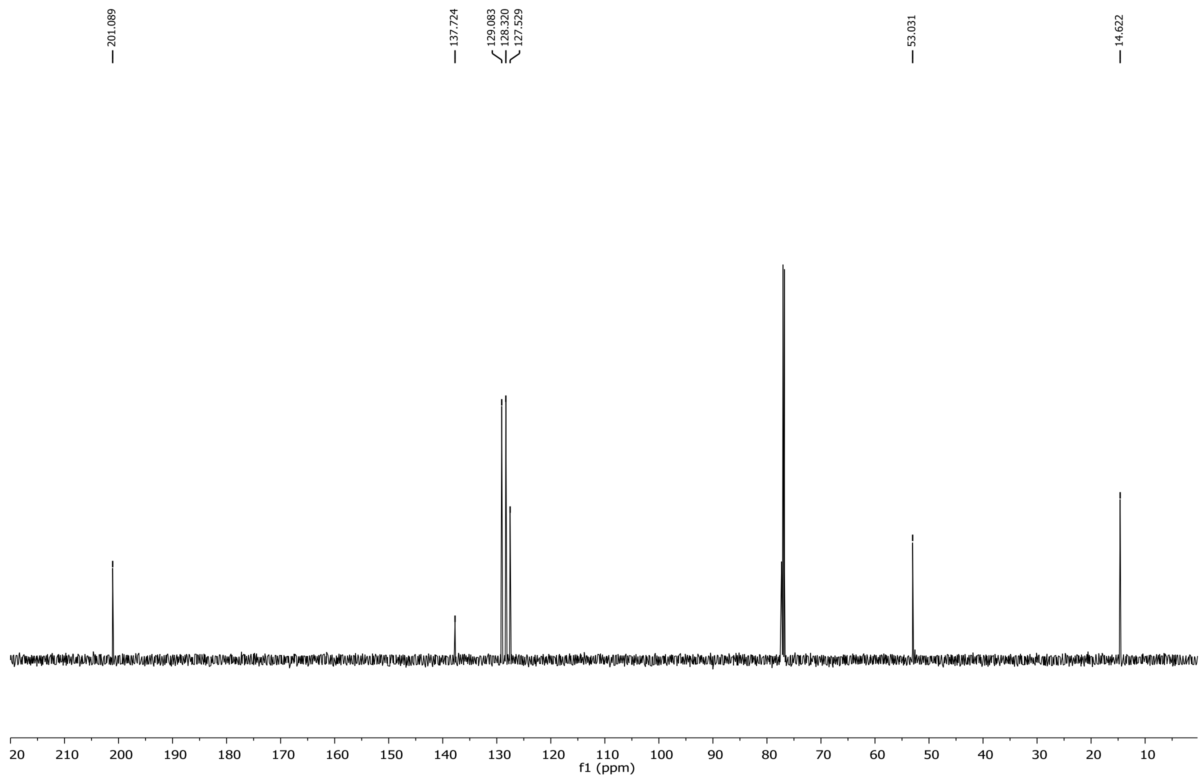
^{1}H NMR ((*R*)-**1l**)



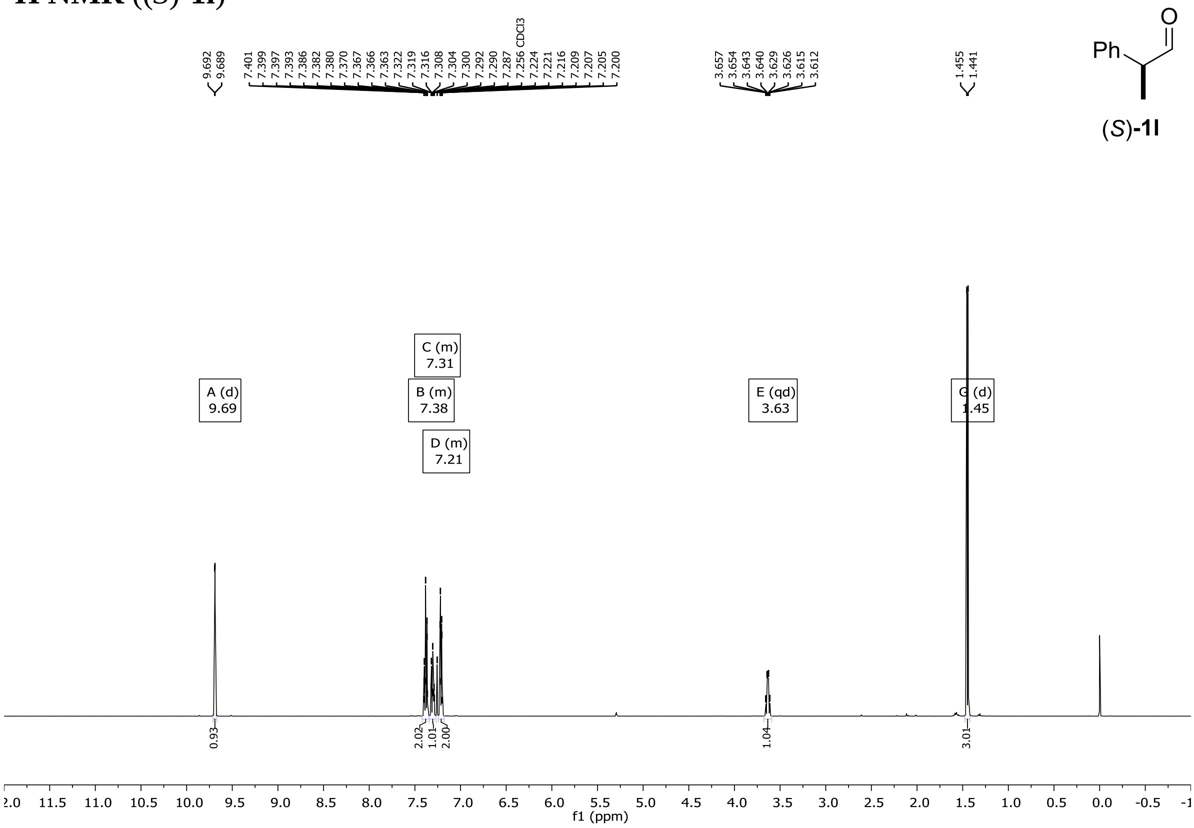
(*R*)-**1l**



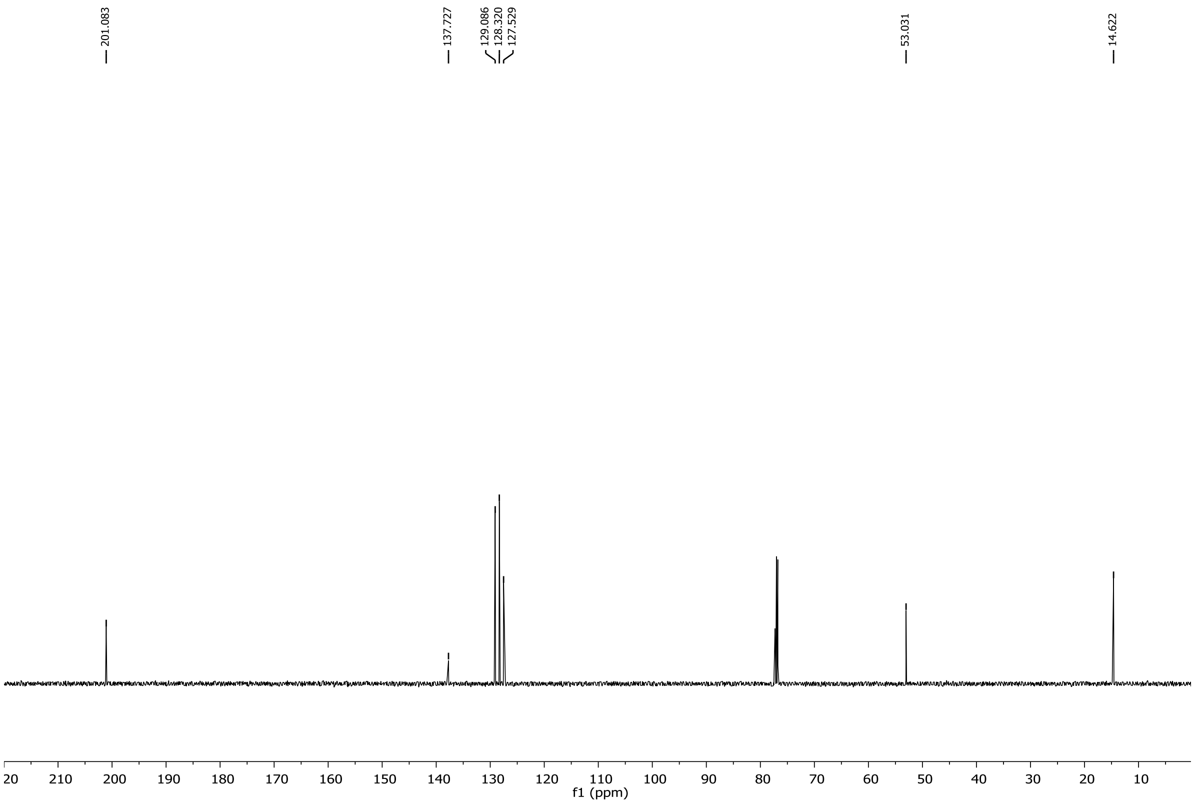
^{13}C NMR ((*R*)-**1l**)



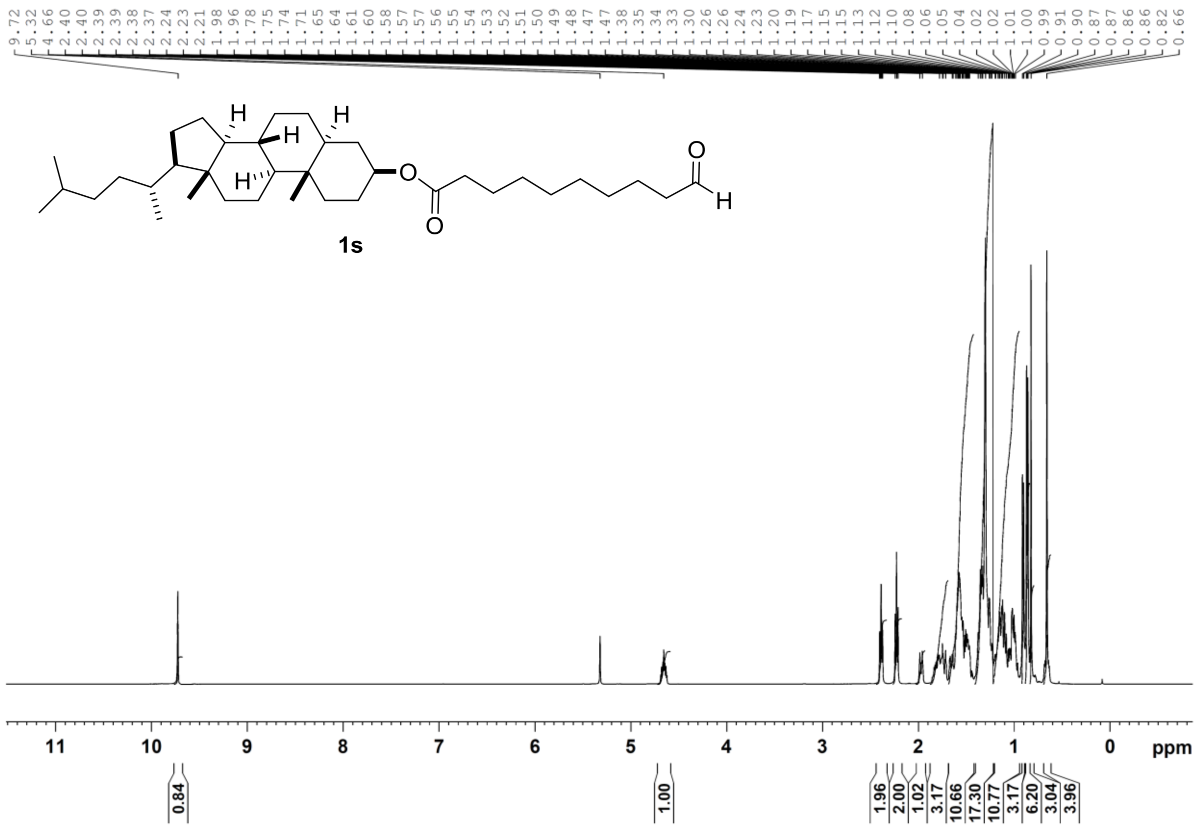
^{1}H NMR ((*S*)-1l)



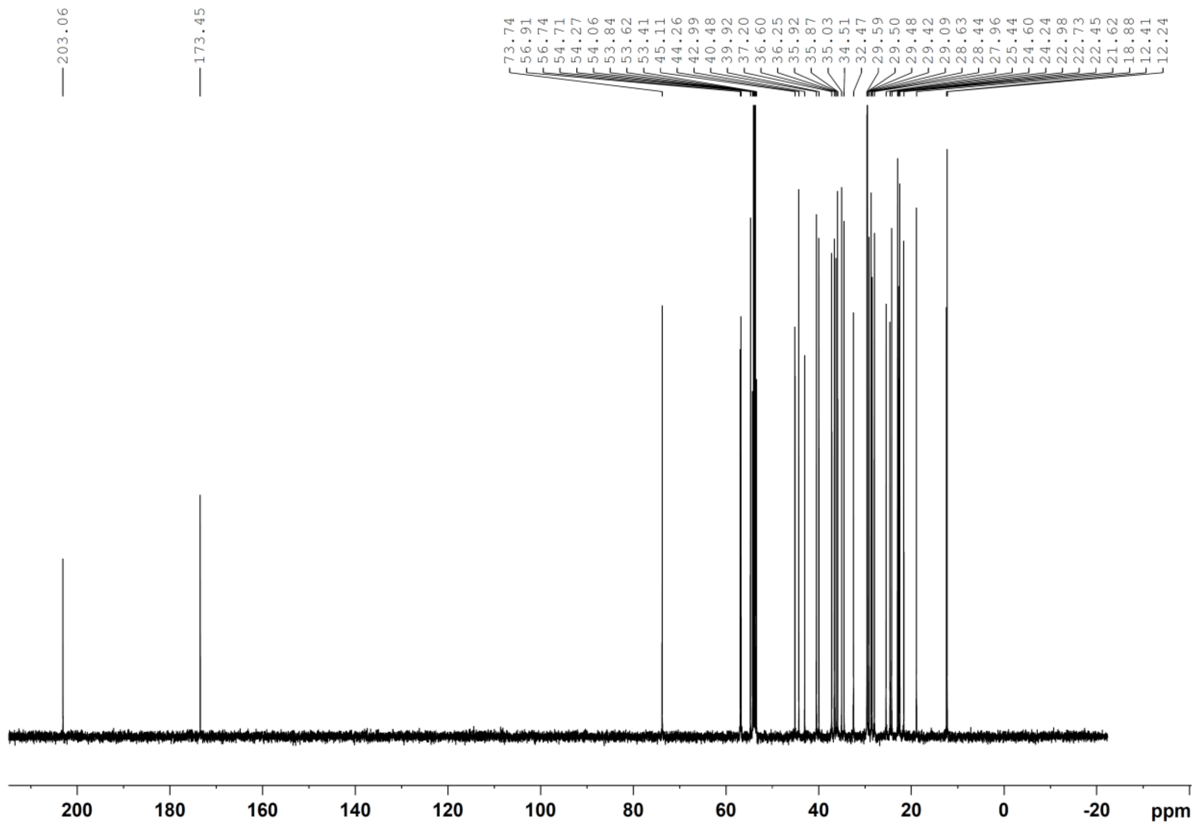
^{13}C NMR ((*S*)-1l)



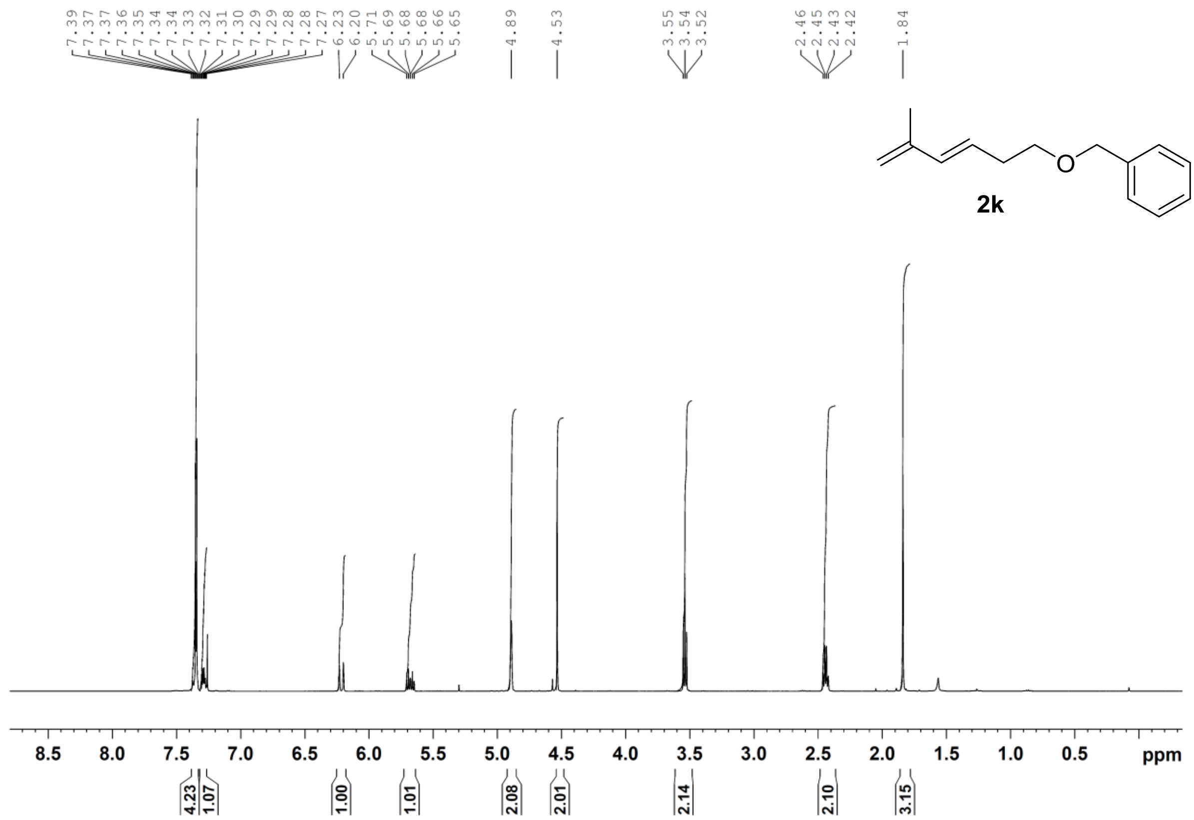
^{1}H NMR (1s)



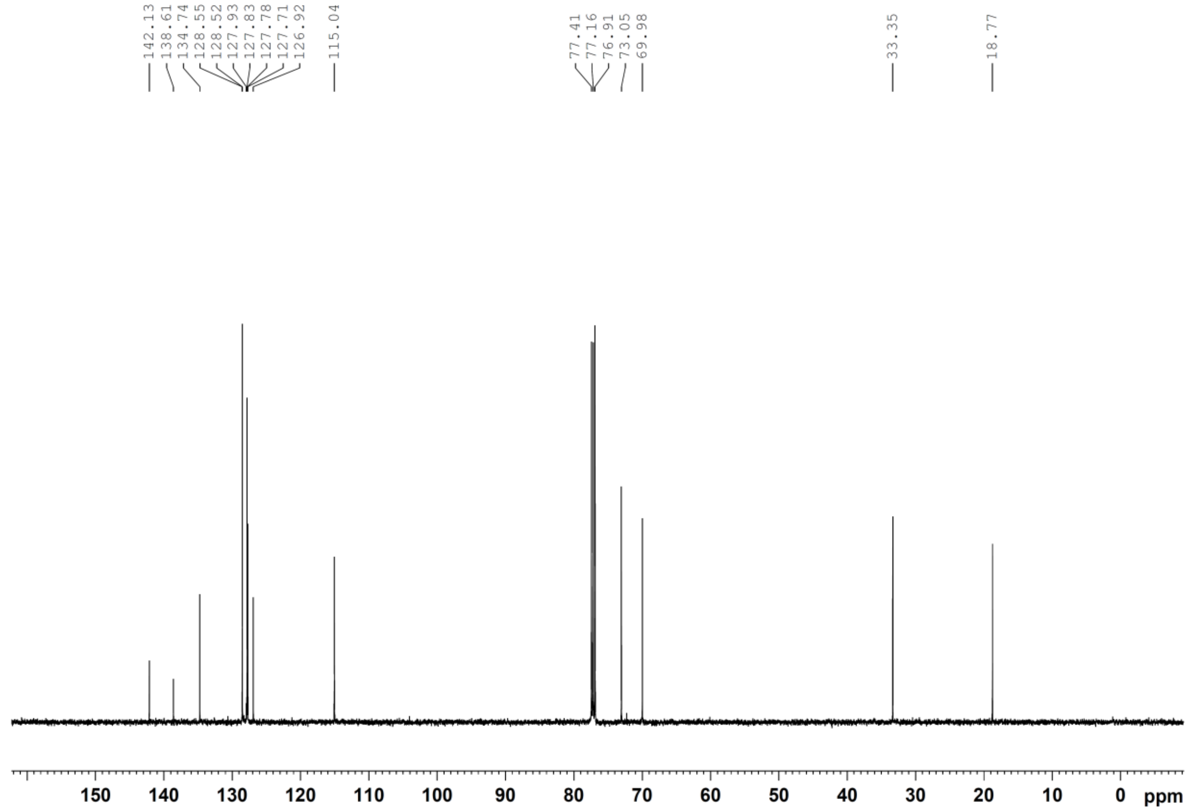
^{13}C NMR (1s)



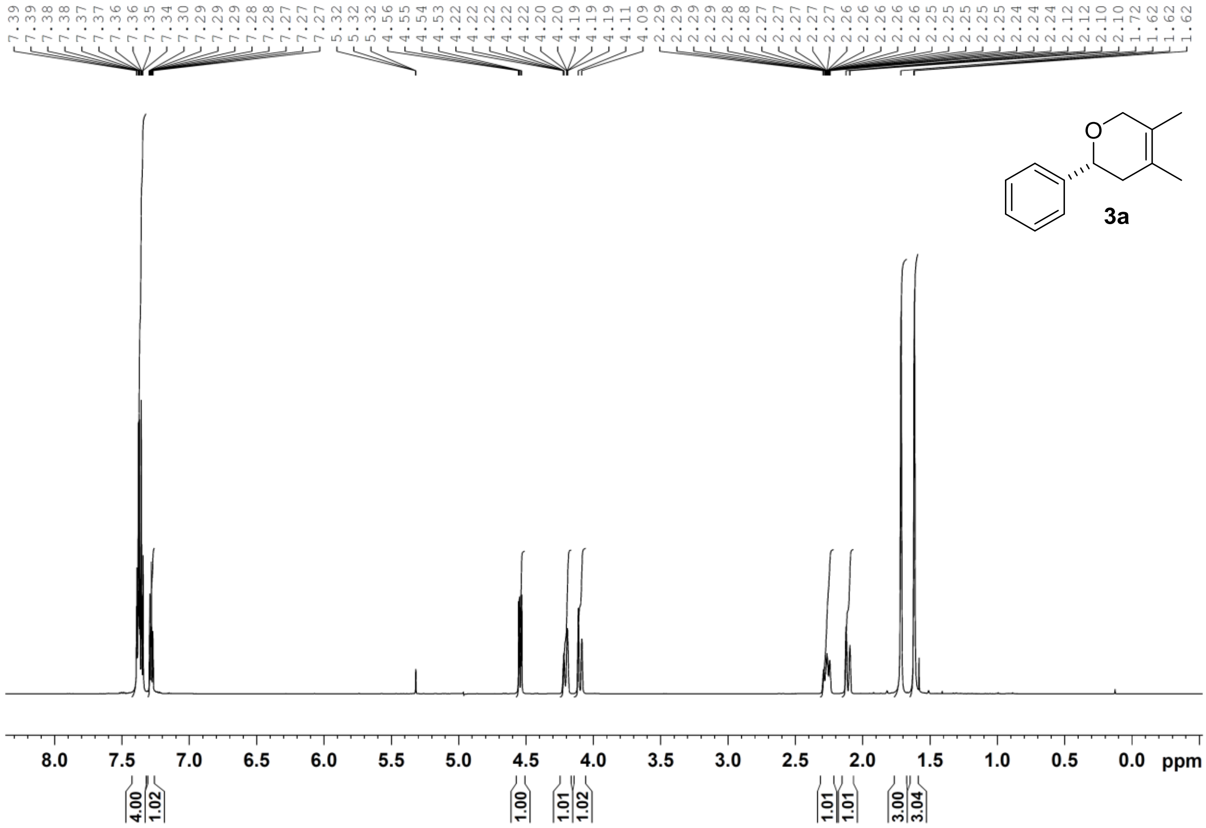
^{1}**H NMR** (**2k**)



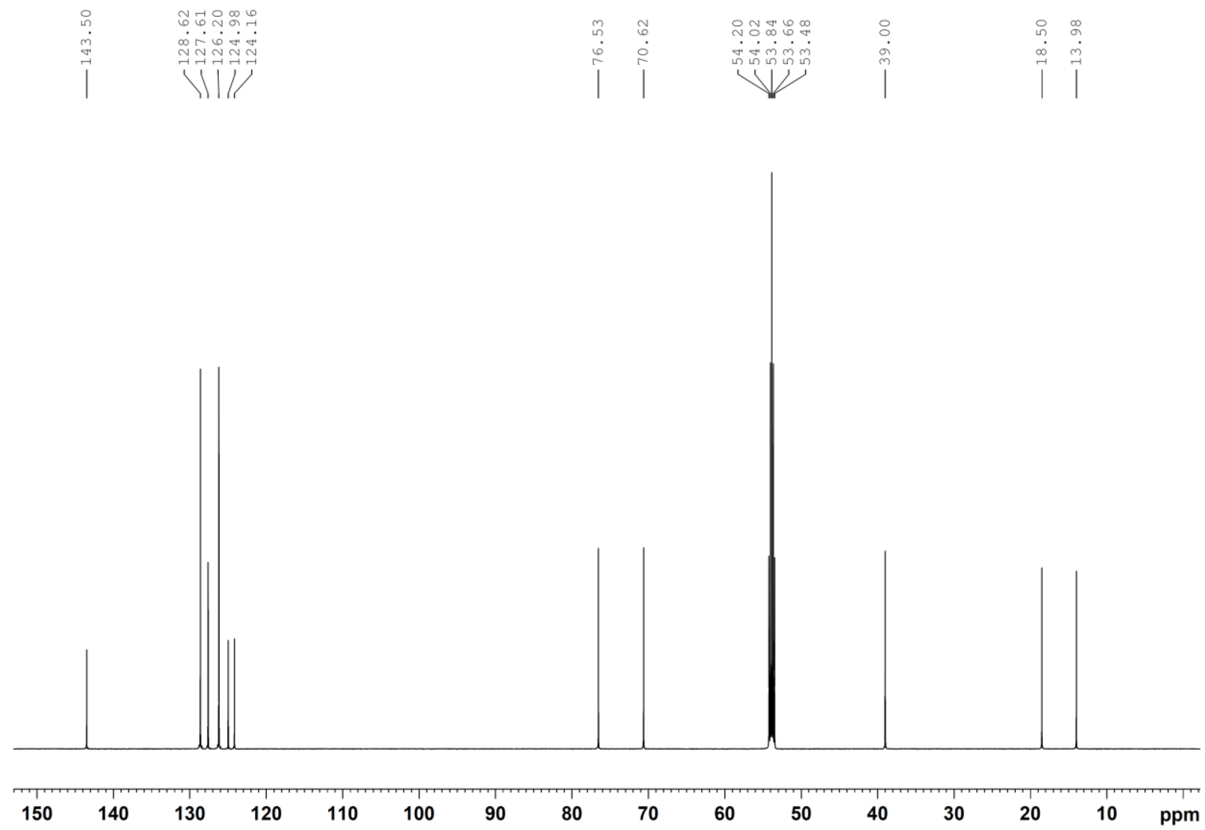
^{13}**C NMR** (**2k**)



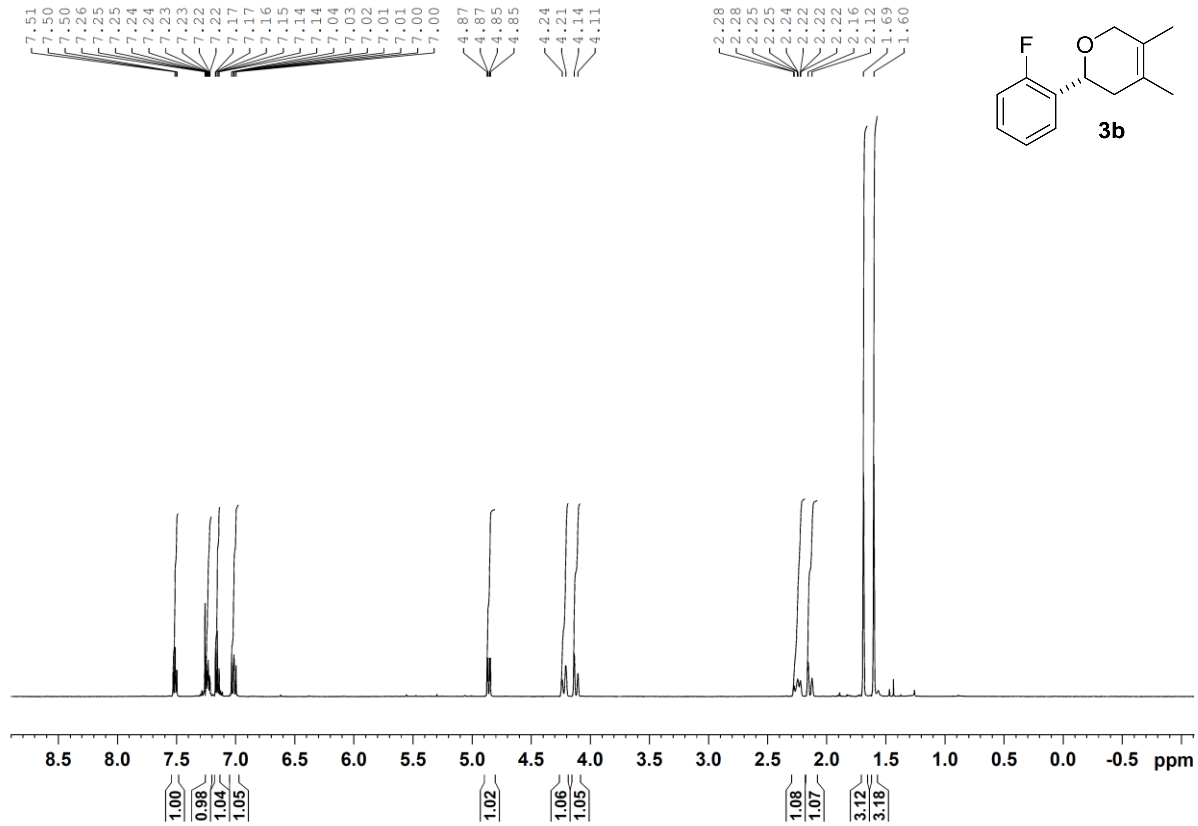
^{1}H NMR (3a)



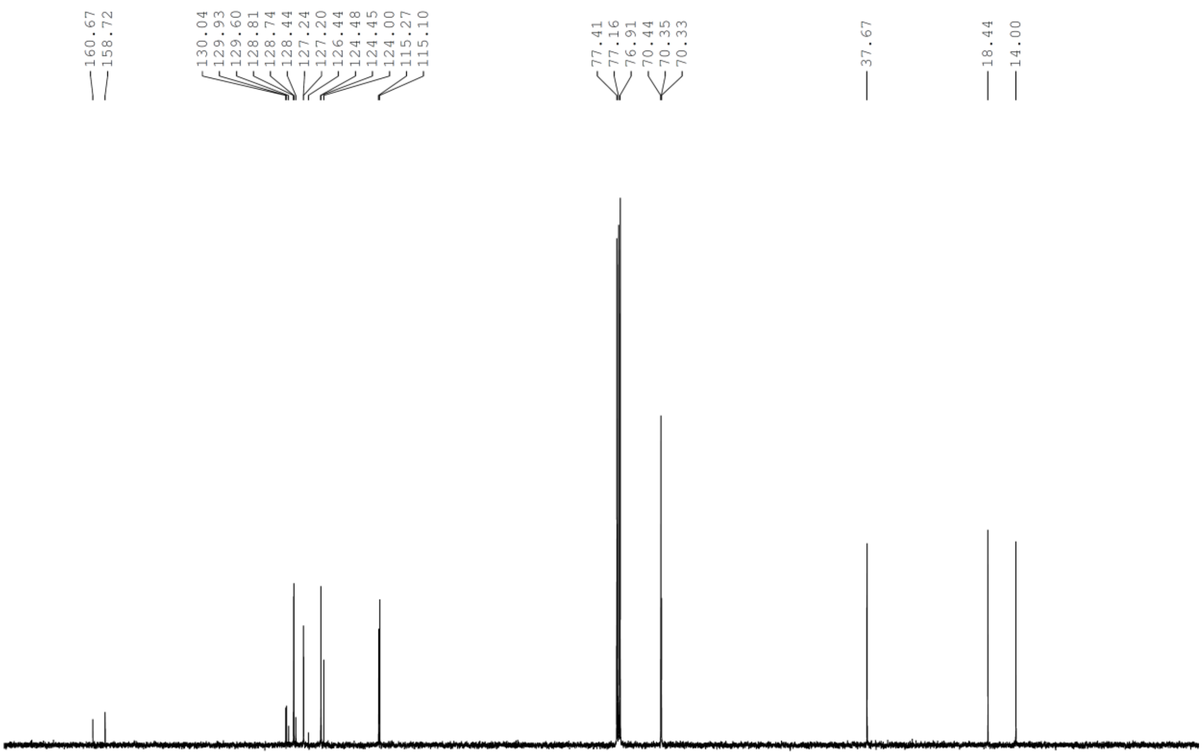
^{13}C NMR (3a)



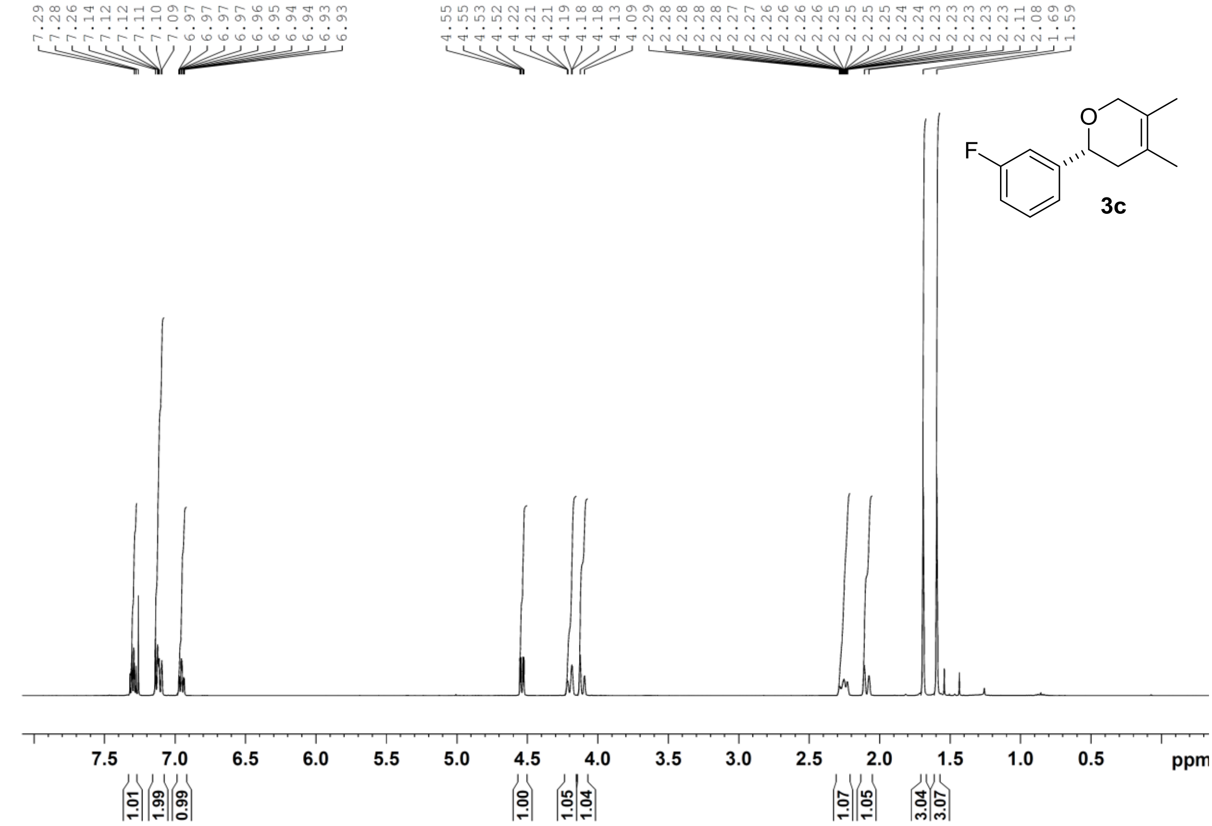
^{1}H NMR (3b)



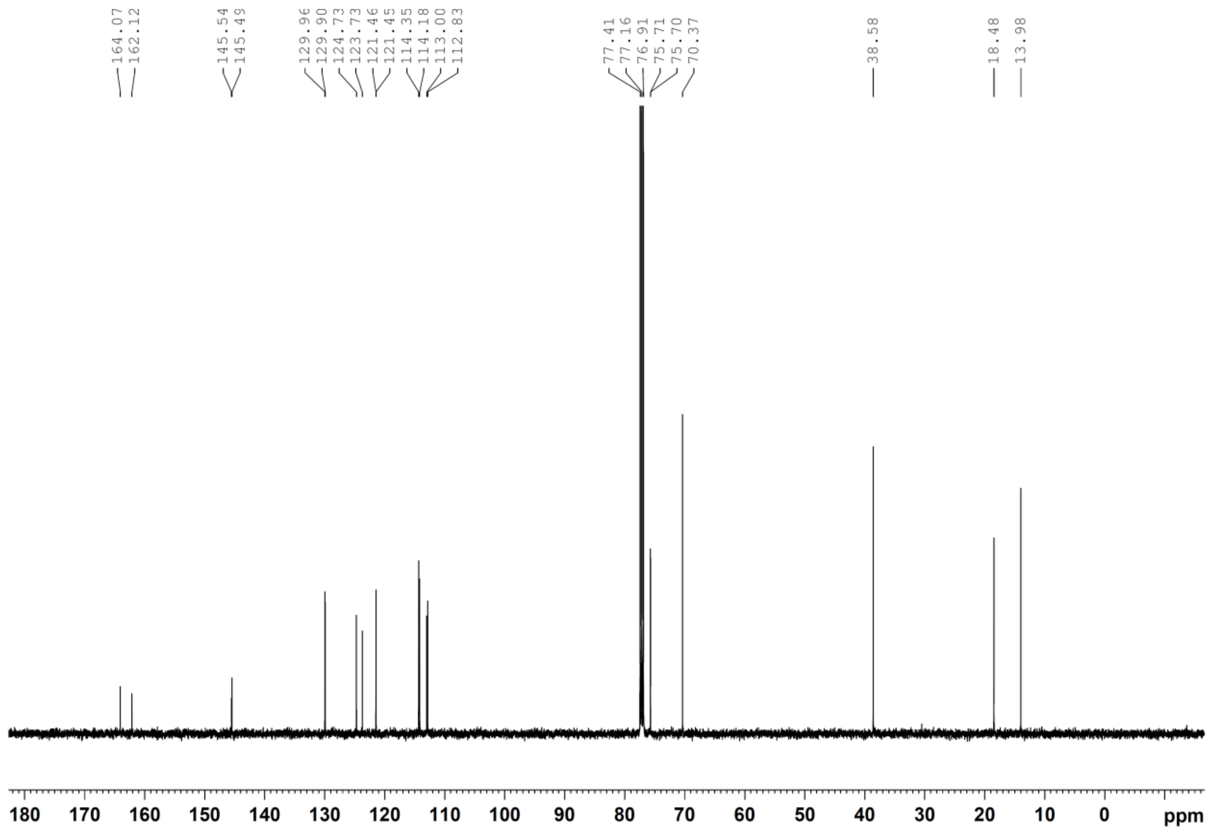
^{13}C NMR (3b)



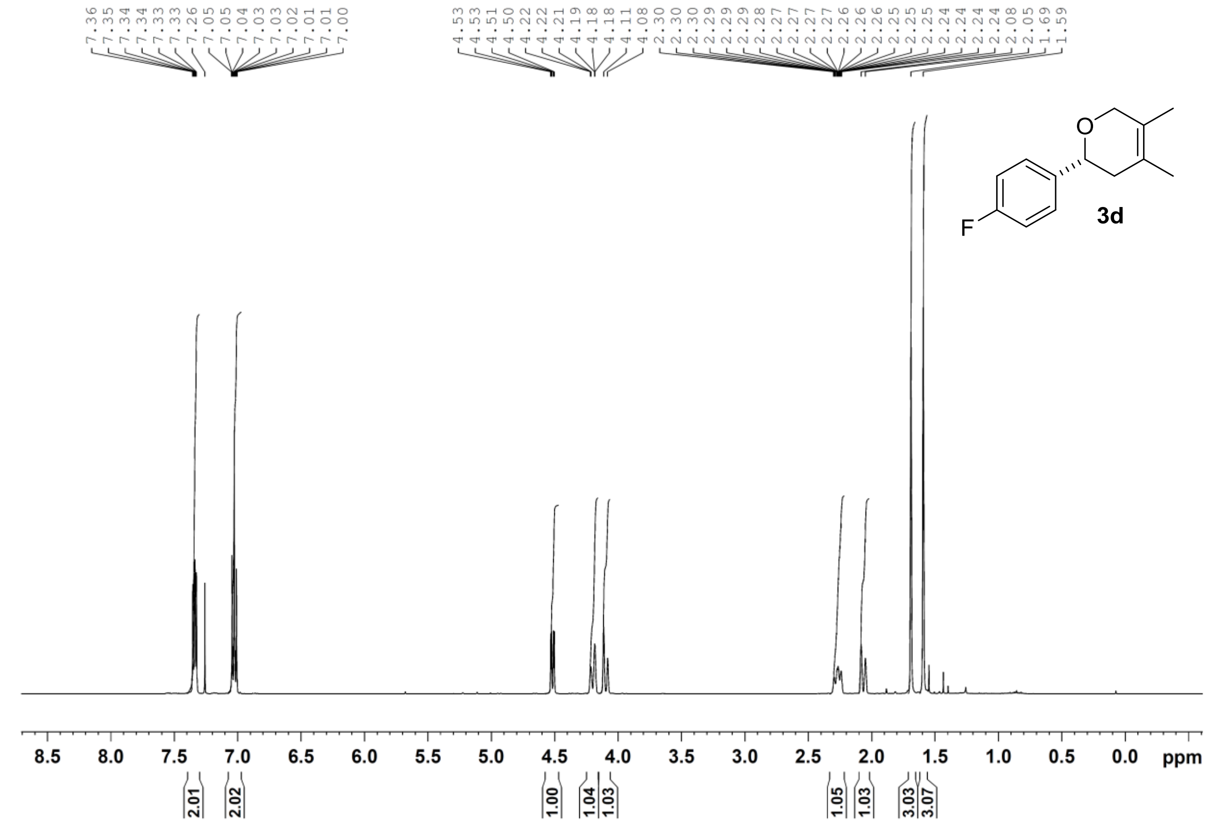
^{1}H NMR (3c)



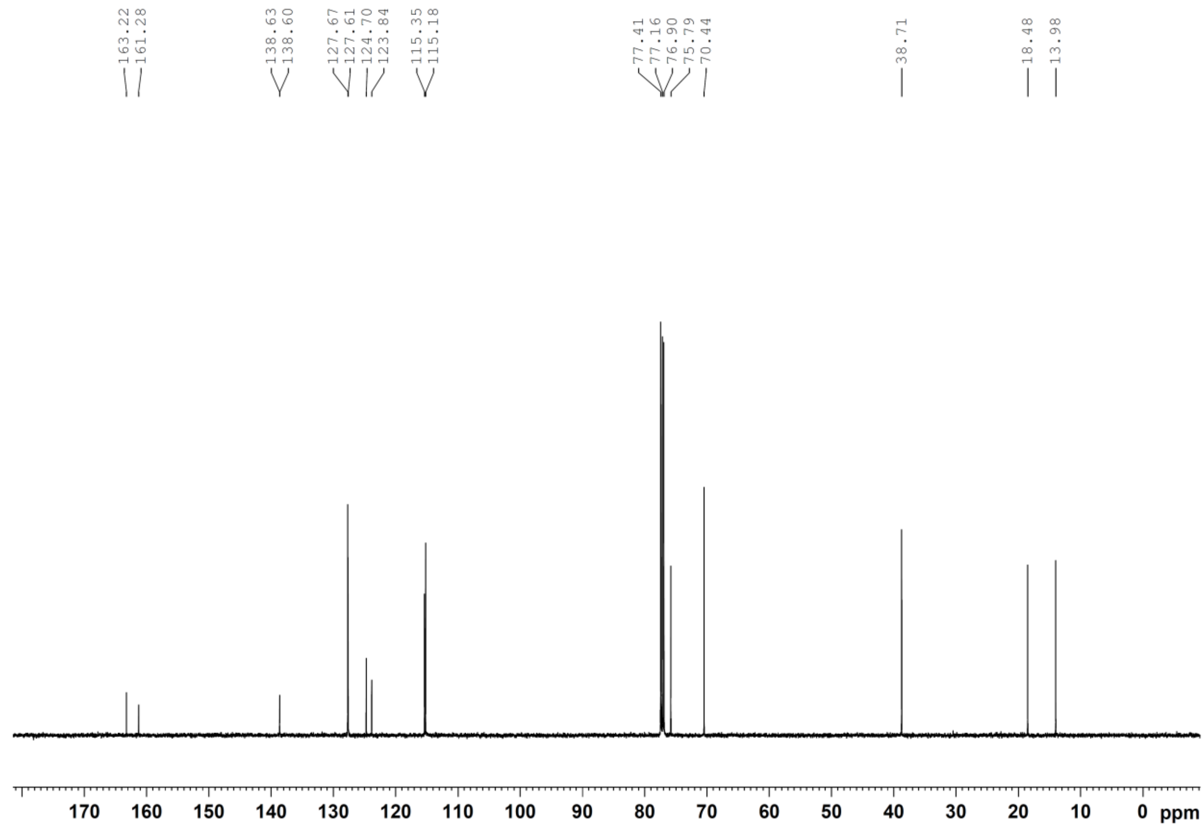
^{13}C NMR (3c)



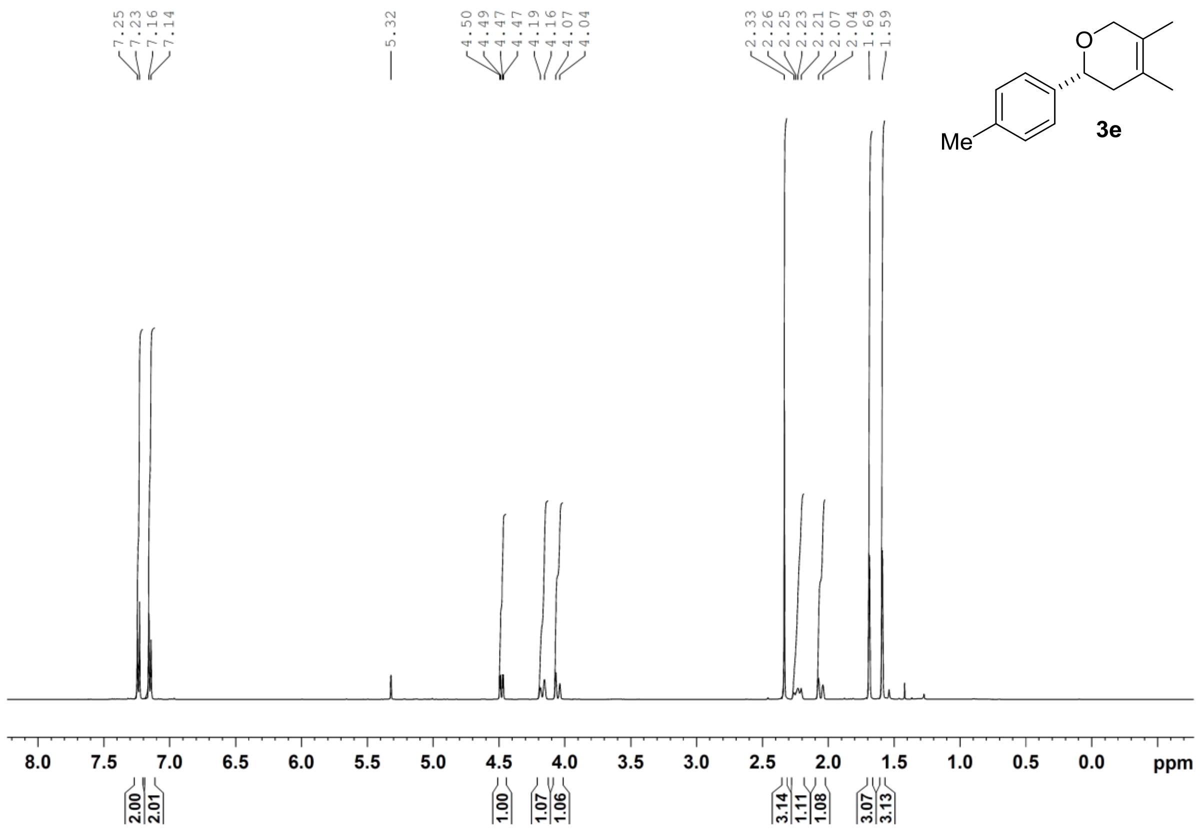
^{1}H NMR (3d)



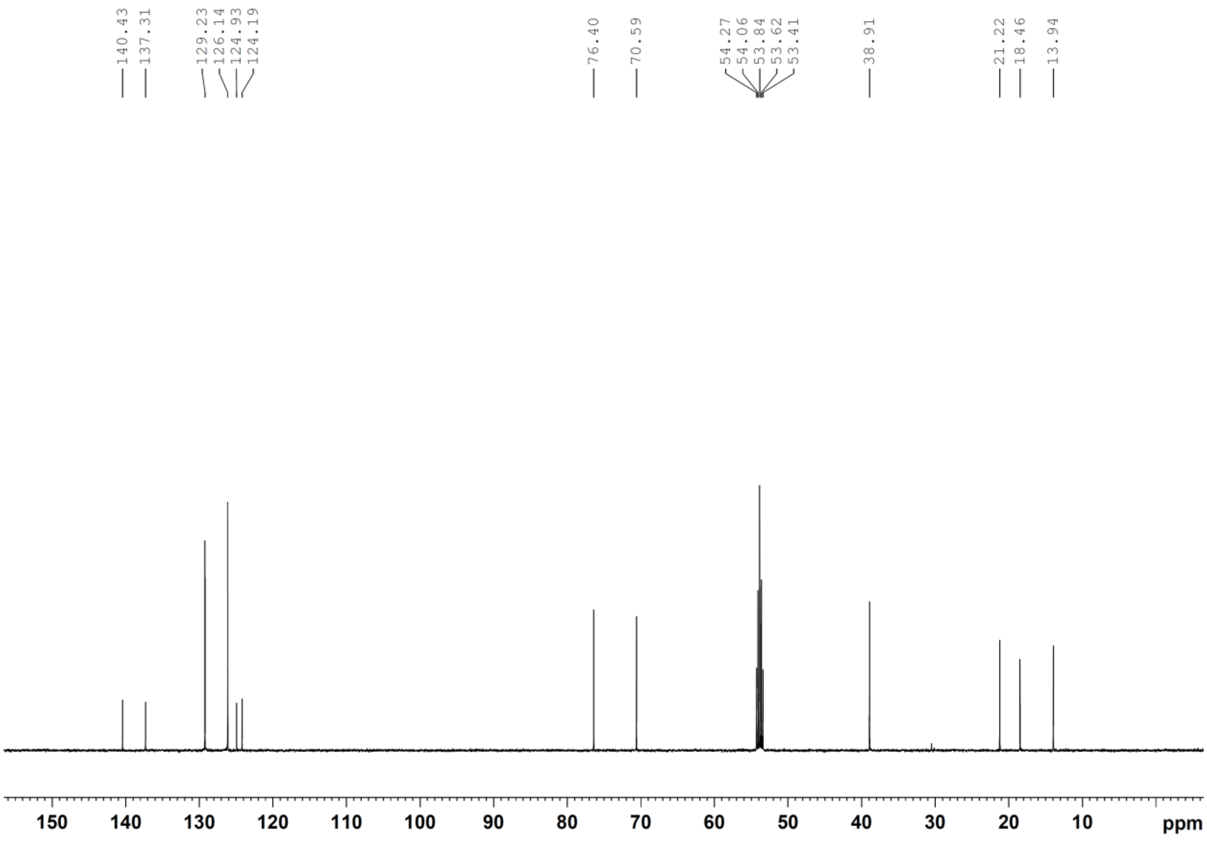
^{13}C NMR (3d)



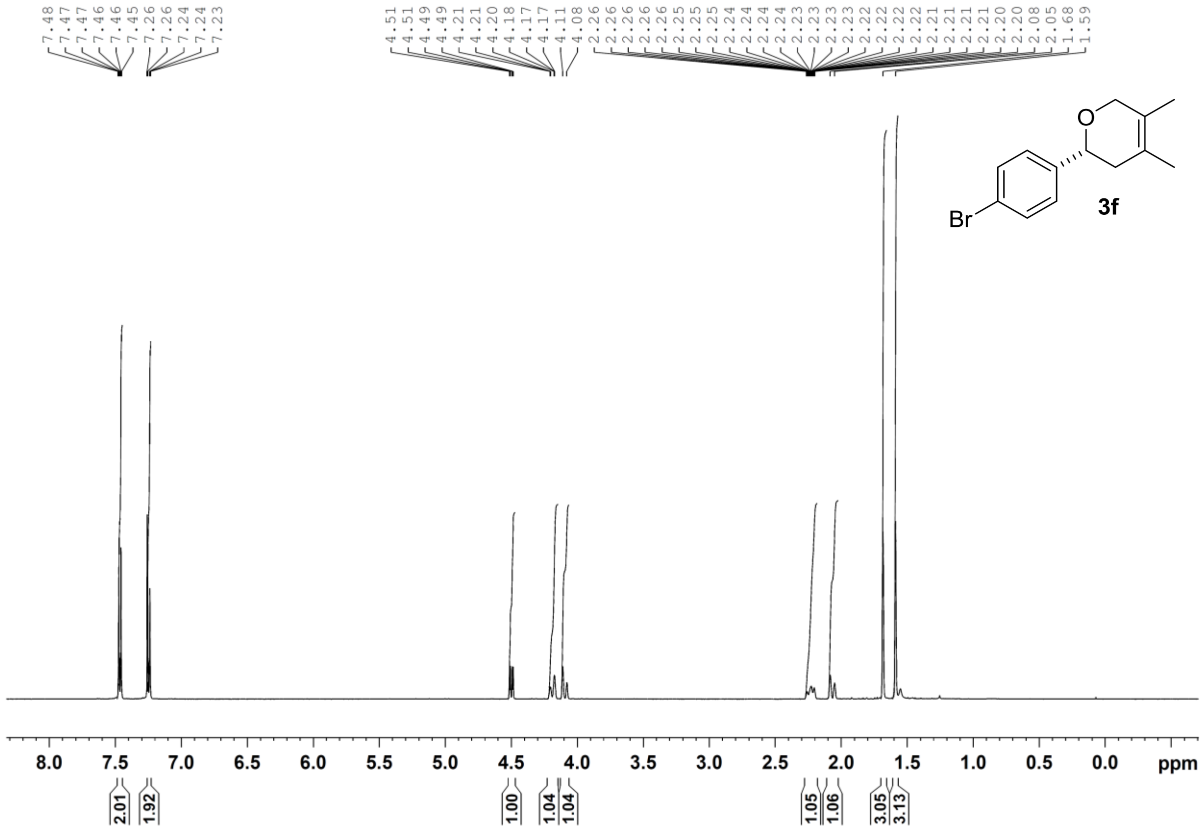
^{1}H NMR (3e)



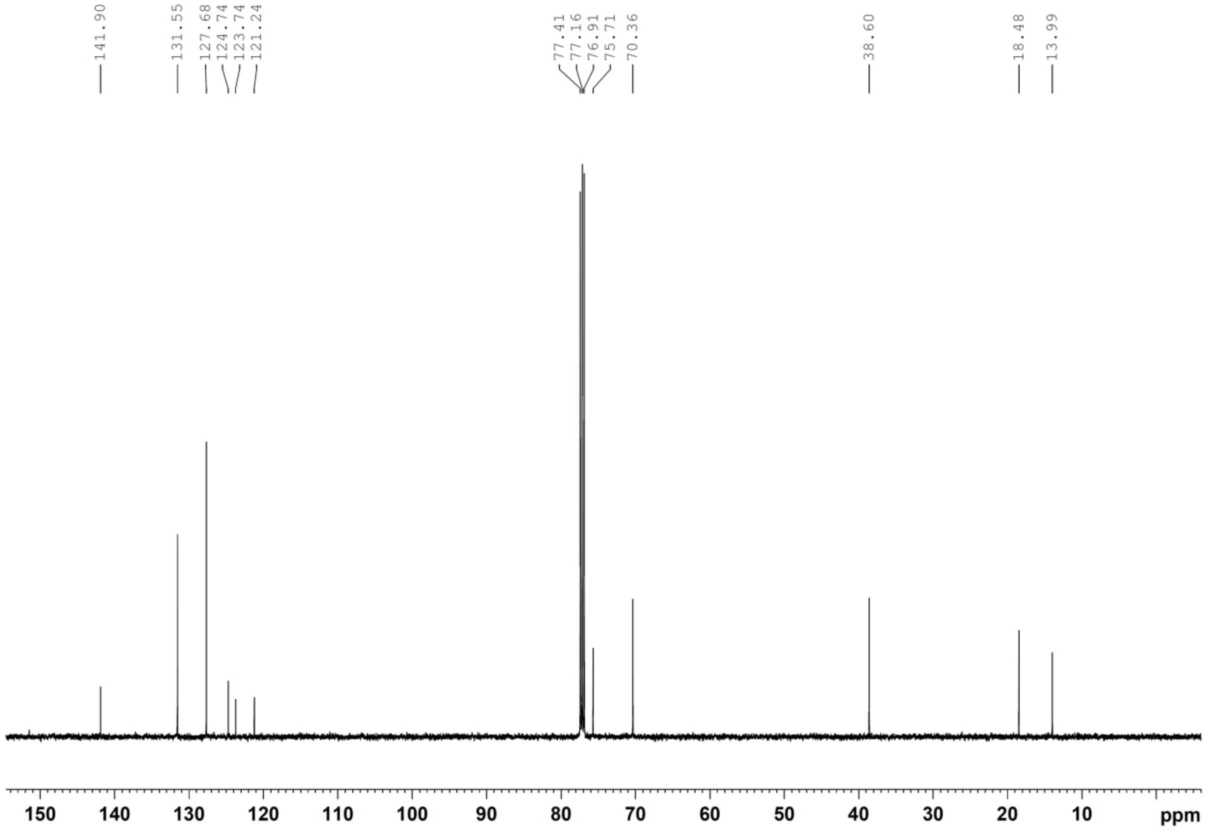
^{13}C NMR (3e)



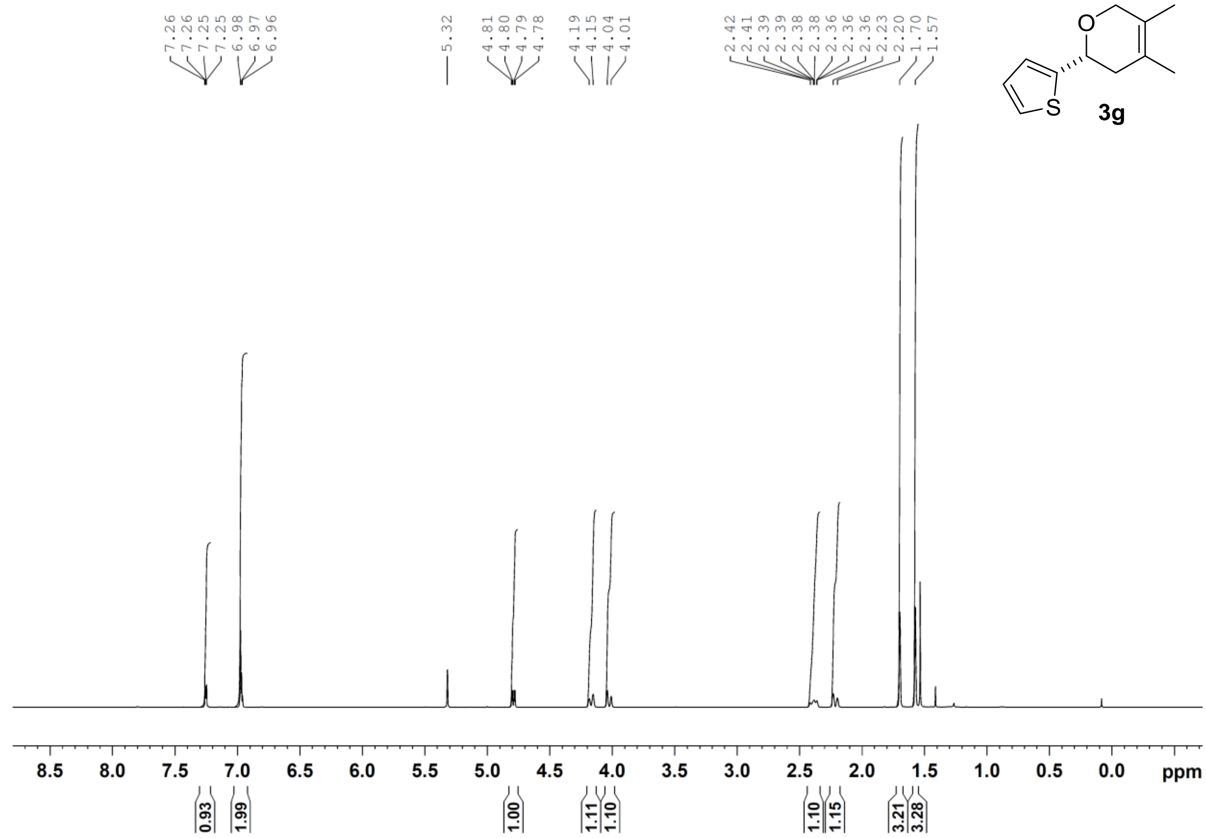
^{1}H NMR (3f)



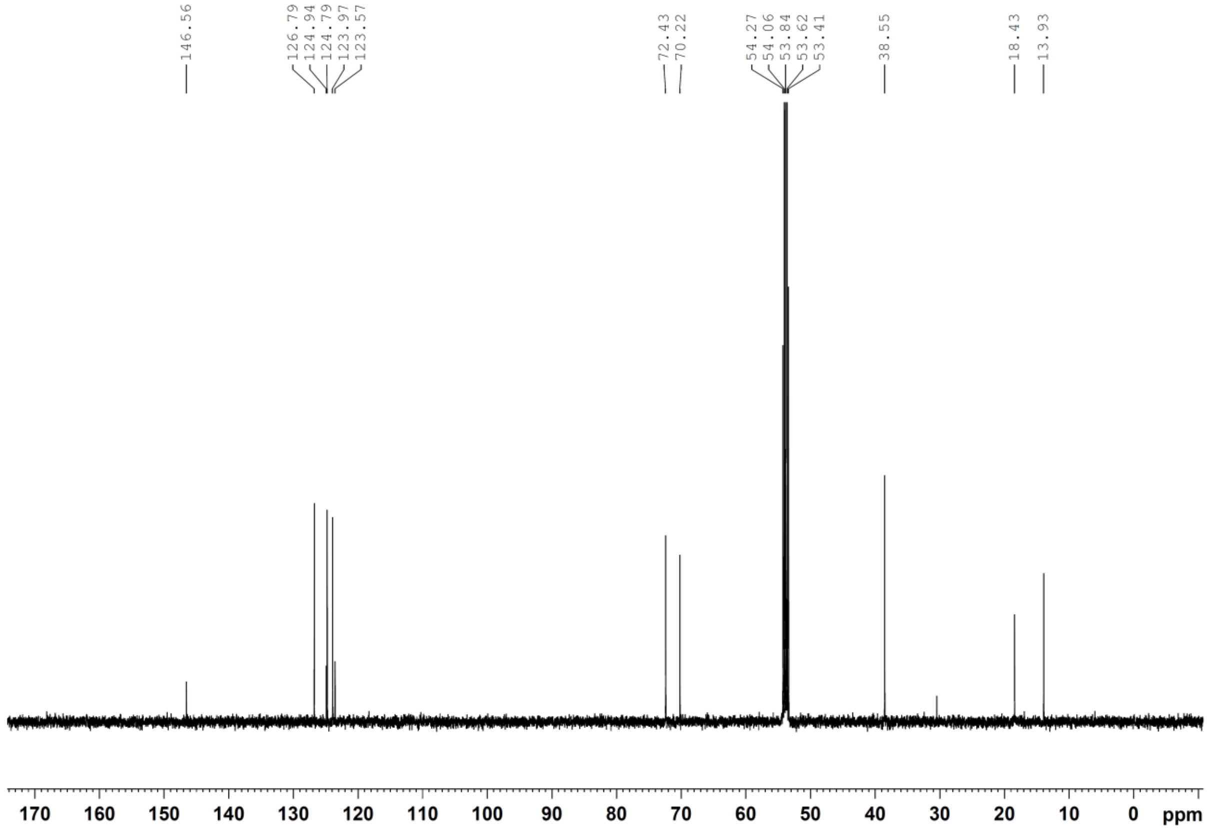
^{13}C NMR (3f)



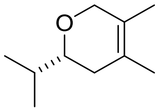
^{1}H NMR (3g)



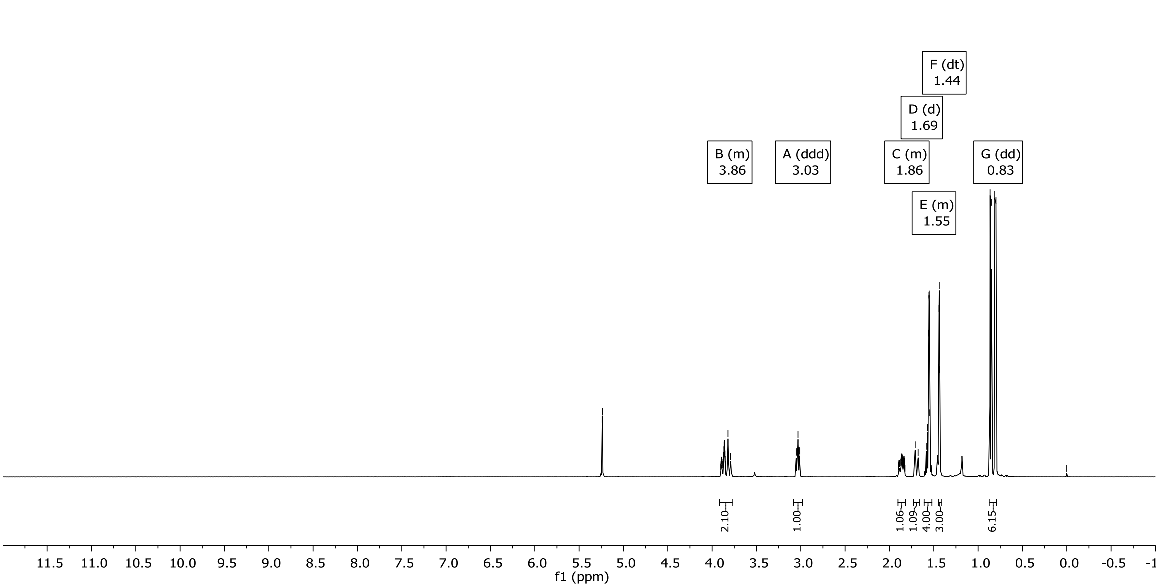
^{13}C NMR (3g)



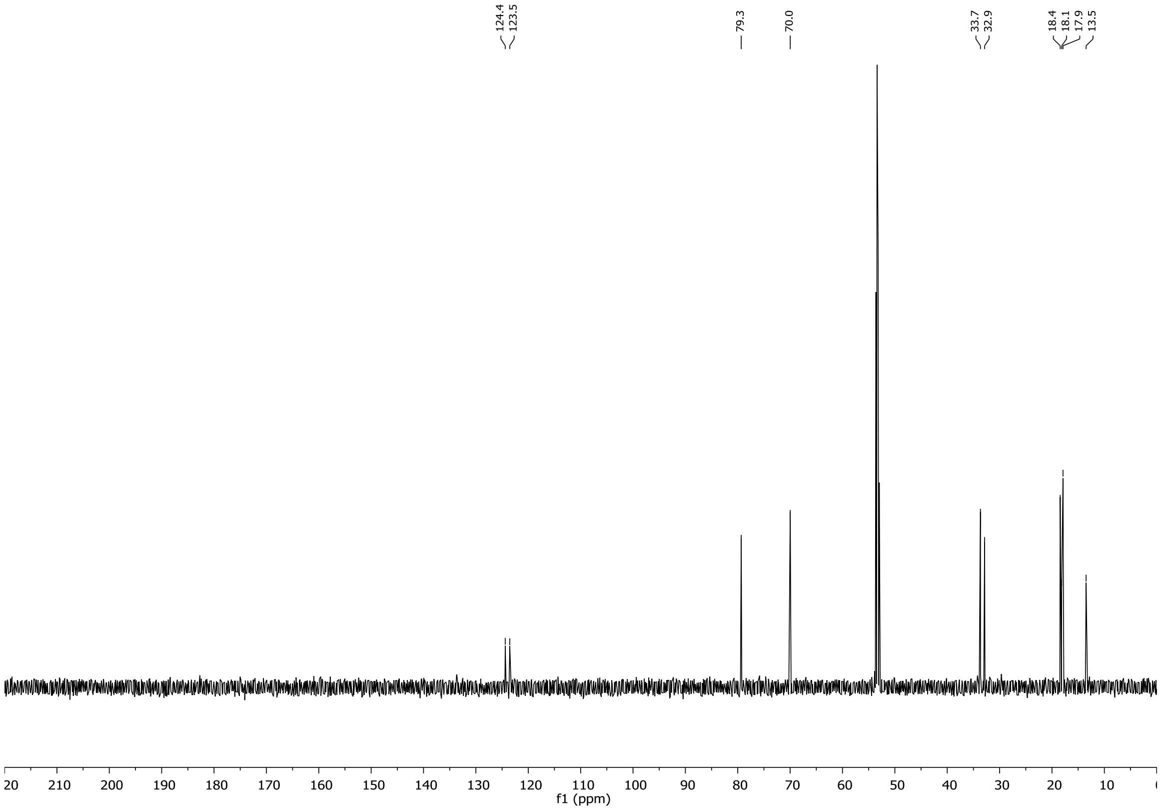
^{1}H NMR (3h)



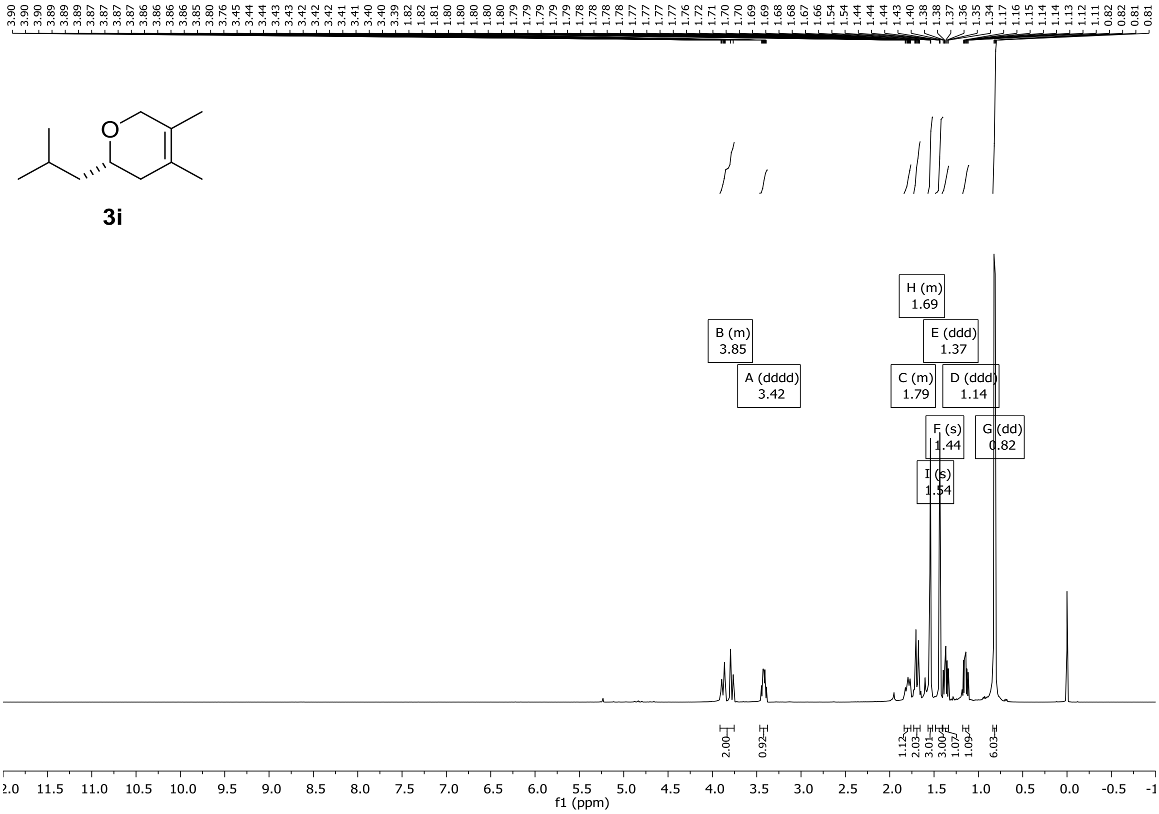
3h



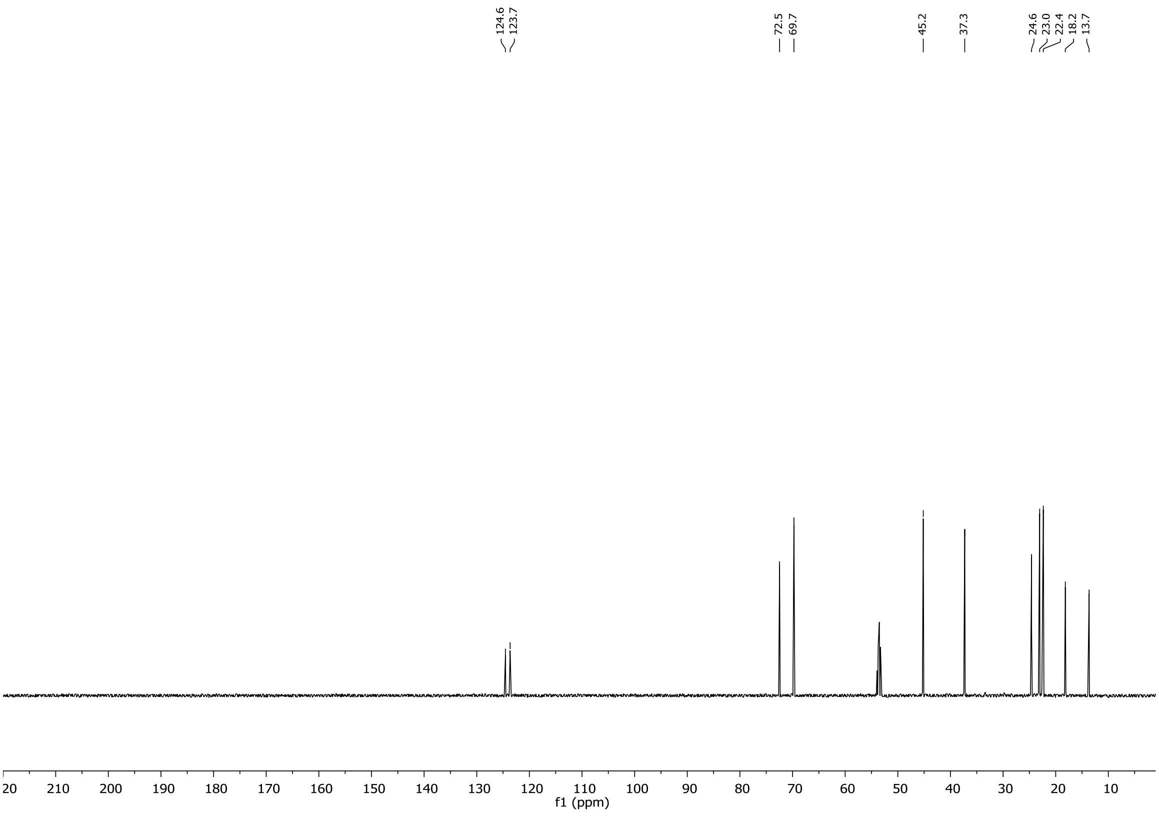
^{13}C NMR (3h)



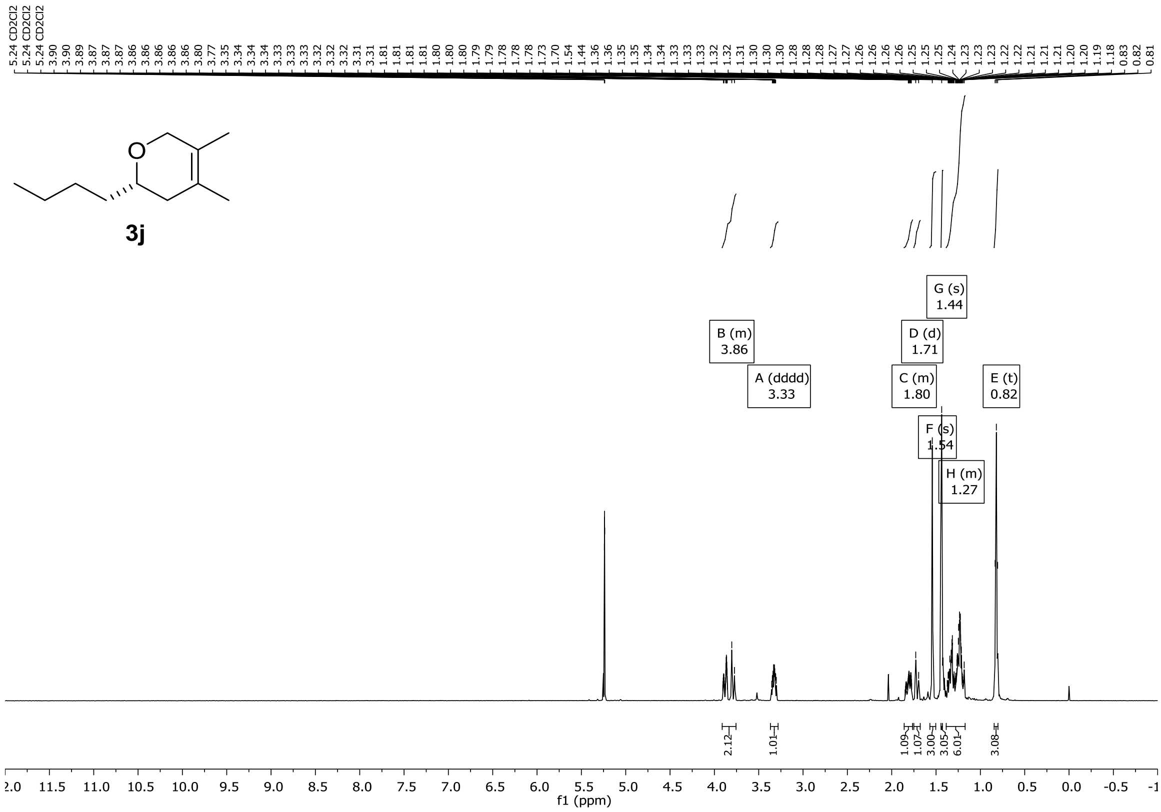
^{1}H NMR (3i)



^{13}C NMR (3i)

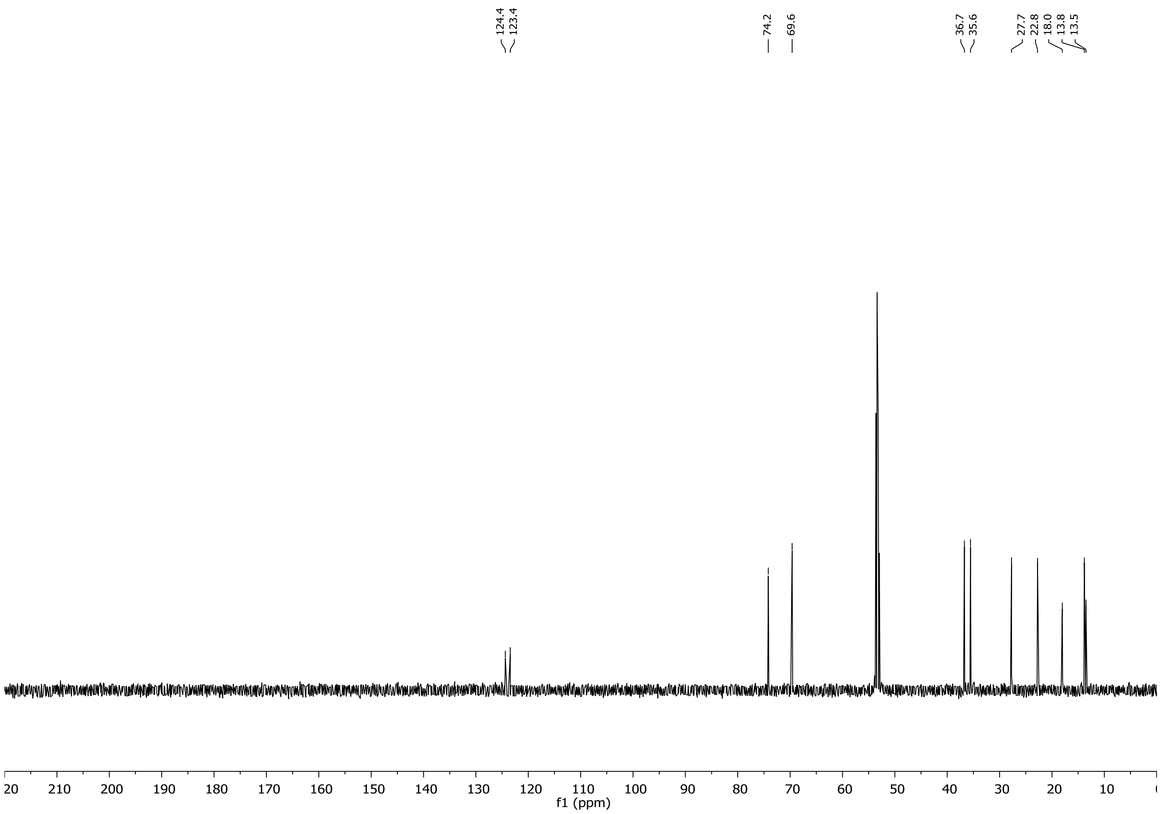


[1]H NMR (3j)

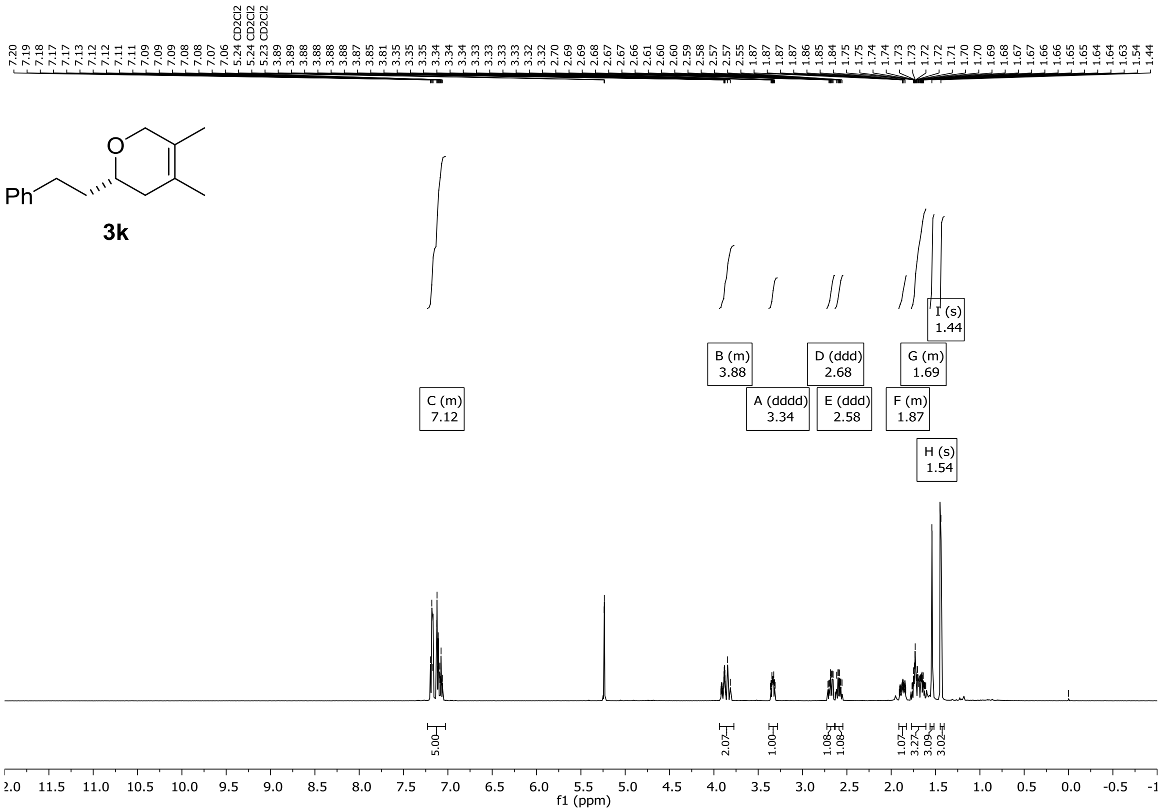


3j

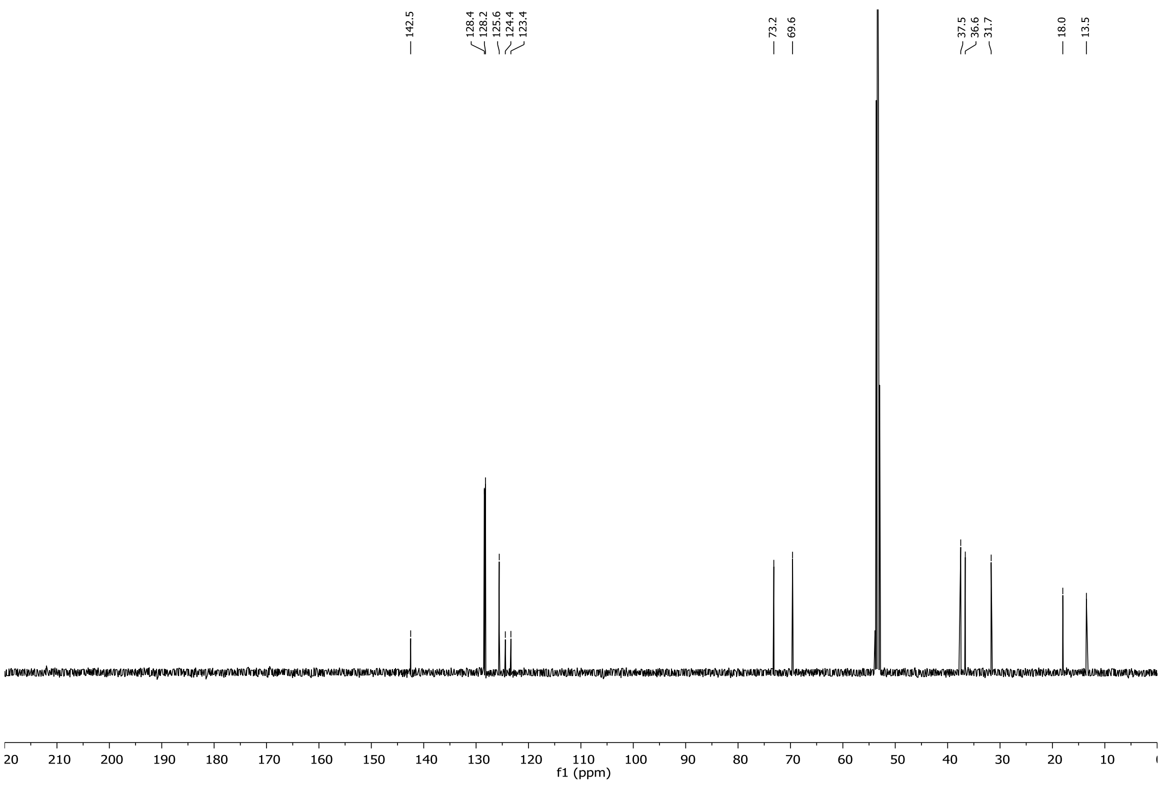
[13]C NMR (3j)

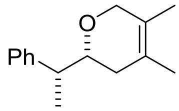


^{1}H NMR (3k)



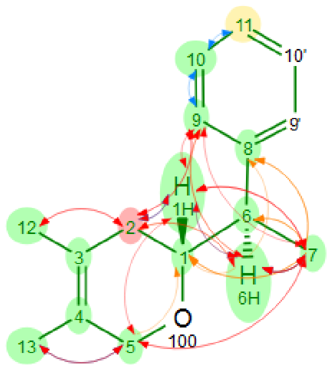
^{13}C NMR (3k)

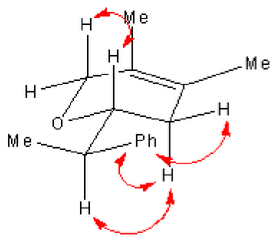


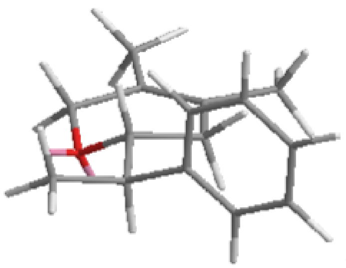


3l

syn, 1R,6R

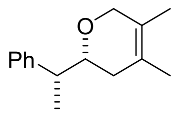




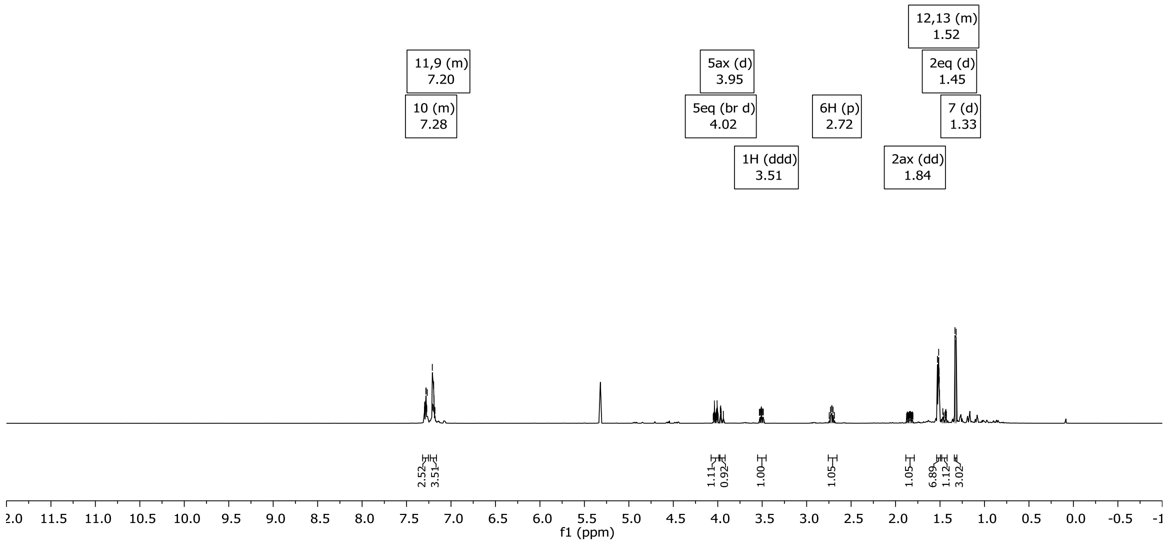


Atom	Chemical Shift	Predicted Shift	Quality	J	COSY	HSQC	HMBC	NOESY
1 C	79.08	81.21	0.67			1H	5ax, 6H, 7	
1H H	3.51	3.95	0.67	10.50(2ax), 3.40(2eq), 8.10(?)	6H, 2ax, 2eq	1		5ax, 7, 2eq, 6H, 9
2 C	35.26	34.46	0.67			2ax, 2eq	6H	
Hax	1.84	1.94, 2.17	-0.39	-17.50(2eq), 10.50(1H)	1H	2		6H, 2eq, 12, 9
Heq	1.45	1.94, 2.17	-0.02	-17.50(2ax), 3.40(1H)	1H	2		1H, 2ax, 12, 9
3 C	124.6	121.15	0.67					
4 C	123.95	123.76	0.67					
5 C	70.37	69.15	0.67			5ax, 5eq		
Hax	3.95	3.99, 4.08	0.56	-15.40(5eq)	13	5	1	13, 7, 1H
Heq	4.02	3.99, 4.08	0.67	-15.40(5ax)	13	5		13, 7
6 C	45.76	39.93	0.67			6H	7	
6H H	2.72	2.93	0.67	7.00(7), 8.10(?)	7, 1H	6	8, 9, 1, 2, 7	1H, 7, 2ax, 9
7 C	18.52	16.47	0.67			7	6H	
H3	1.33	1.34	0.67	7.00(6H)	6H	7	8, 1, 6	5ax, 5eq, 1H, 6H, 9
8 C	144.99	144.51	0.67				6H, 7	
9 C	128.31	126.53	0.67			9	6H	
H	7.2	7.25	0.67		10	9		7, 1H, 6H, 2ax, 2eq
10 C	128.62	128.56	0.67			10		
H	7.28	7.28	0.63		9, 11	10		
11 C	126.59	126.47	0.67			11		
H	7.2	7.22	0.15		10	11		
12 C	18.41	19.13	0.67					
H3	1.52	1.71	0.67					2ax, 2eq
13 C	13.86	16.25	0.67					
H3	1.52	1.76	0.67		5ax, 5eq			5ax, 5eq

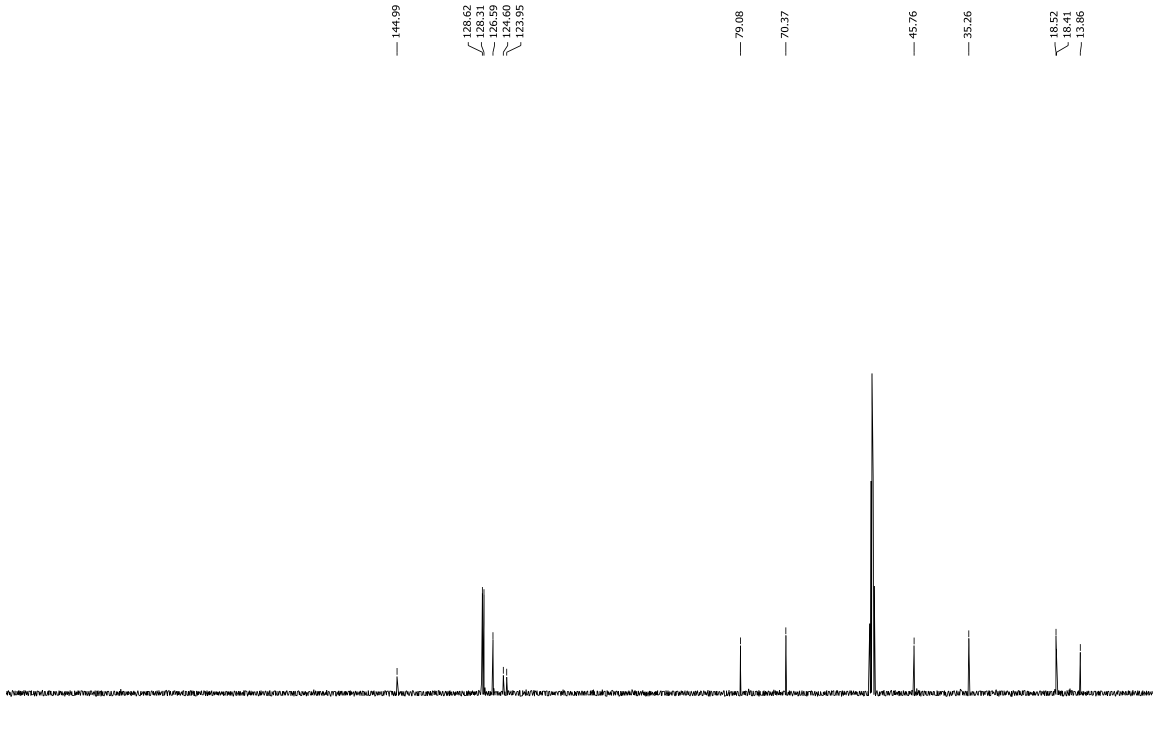
^{1}H NMR (3l)



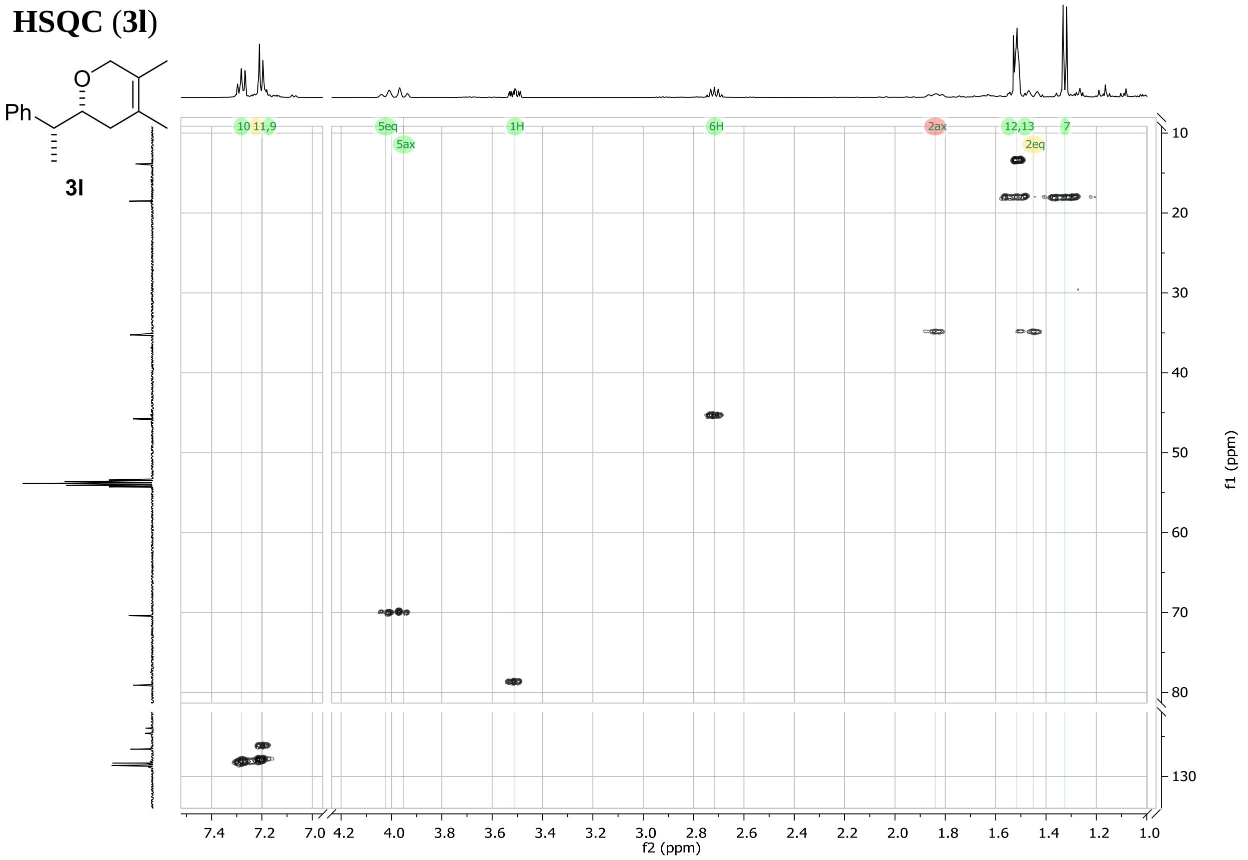
3l



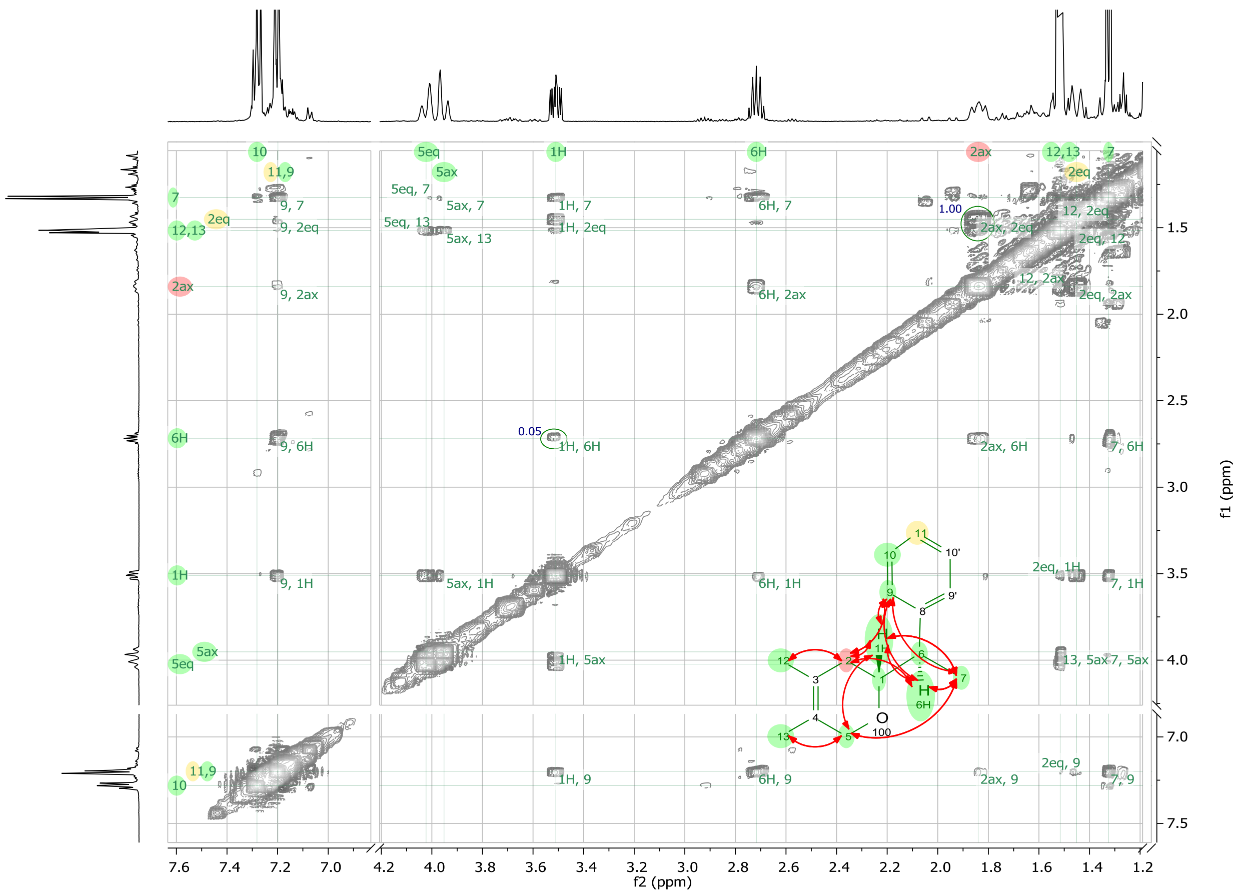
^{13}C NMR (3l)



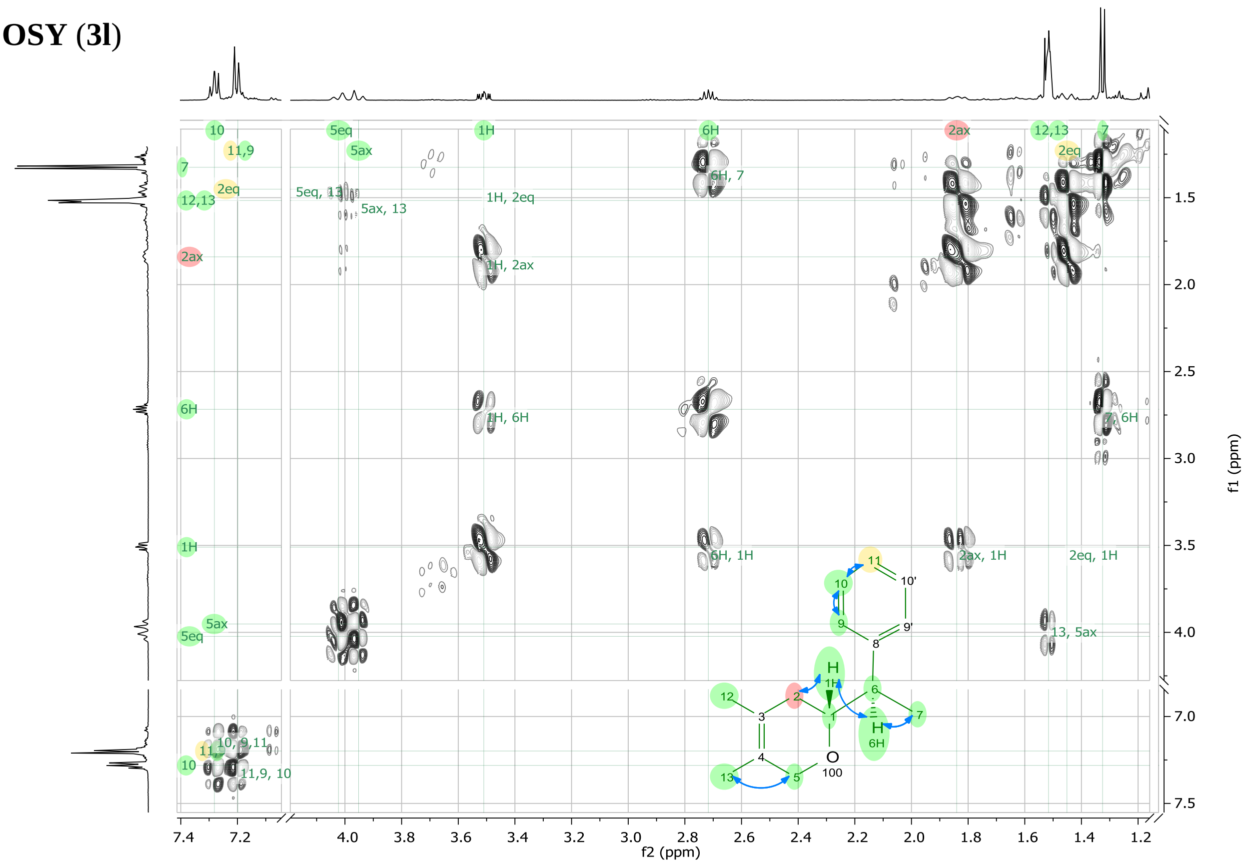
HSQC (3l)



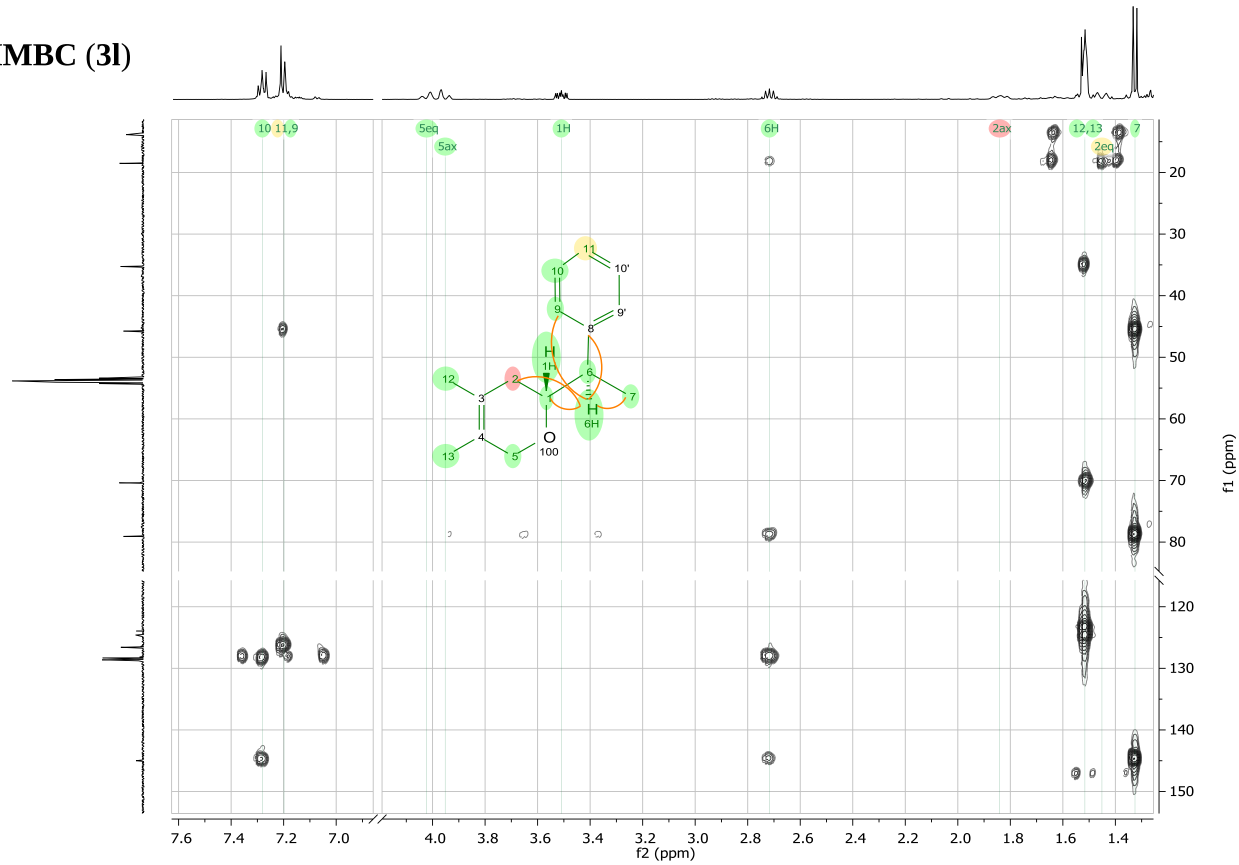
NOESY (3l)

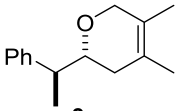


COSY (3l)



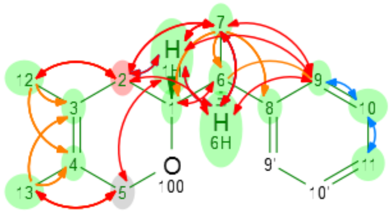
HMBC (3l)

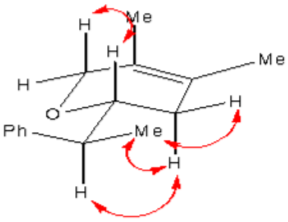




3m

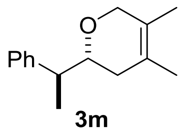
anti, 1R,6S



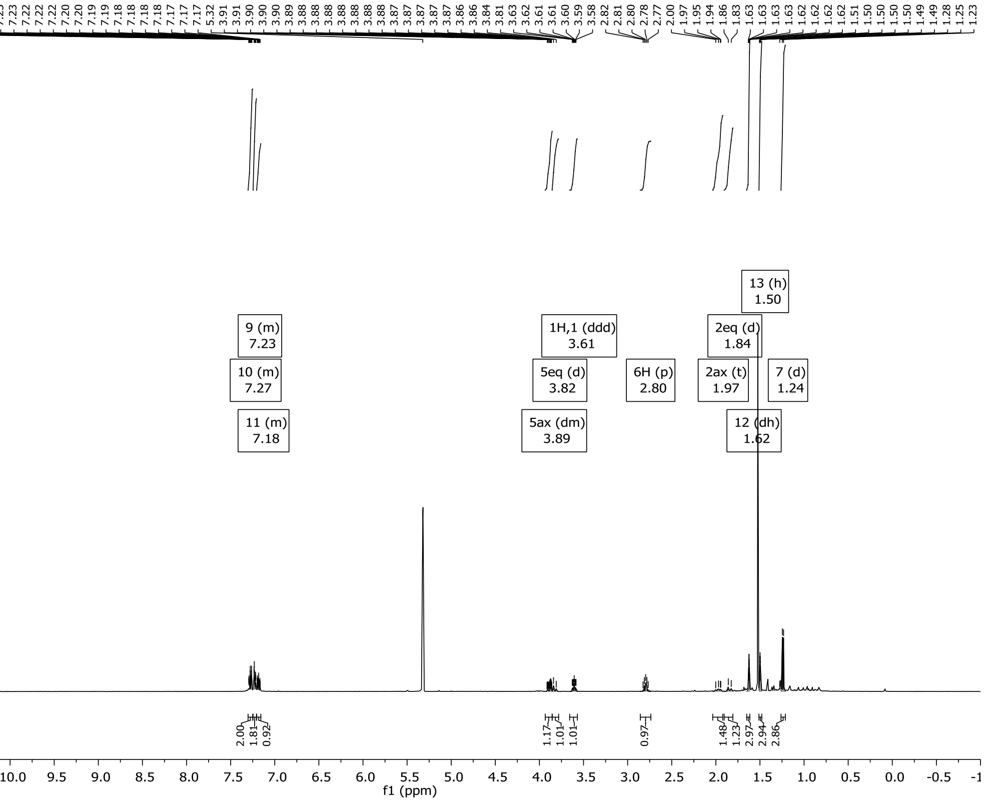


Atom	Chemical Shift	Predicted Shift	Quality	J	COSY	HSQC	HMBC	NOESY
1 C	78.58	81.21	0.67			1H	7	
1H H	3.61	3.93	0.67	10.60(2ax), 3.40(2eq), 7.30(6H)	2eq, 2ax, 6H	1		2eq, 9, 6H, 5ax, 7
2 C	34.66	34.46	0.67			2ax, 2eq	12	
Hax	1.97	1.94, 2.16	-0.43	-16.80(2eq), 10.60(1H)	1H, 2eq	2		12, 6H, 7
Heq	1.84	1.94, 2.16	-0.32	-16.80(2ax), 3.40(1H)	1H, 2ax	2		12, 1H, 7
3 C	124.77	121.15	0.67				13, 12	
4 C	123.76	123.76	0.67				13, 12	
5 C	70.38	69.15	0.67			5ax, 5eq	13	
Hax	3.89	3.99, 4.08	-1	-15.40(5eq)	5eq	5		13, 1H
Heq	3.82	3.99, 4.08	0.31	-15.40(5ax)	5ax	5		13
6 C	45.33	39.93	0.67			6H	7	
6H H	2.8	2.94	0.67	7.20(7), 7.30(1H)	1H, 7	6		9, 2ax, 1H, 7
7 C	18.53	16.47	0.67			7		
H3	1.24	1.34	0.67	7.20(6HH)	6H	7	6, 1, 8	2eq, 9, 2ax, 1H, 6H
8 C	145.41	144.51	0.67				7	
9 C	128.35	126.53	0.67			9	6'	
H	7.23	7.24	0.67		10	9		6H, 1H, 7
10 C	128.42	128.56	0.67			10		
H	7.27	7.28	0.67		9, 11	10		
11 C	126.38	126.47	0.67			11		
H	7.18	7.22	0.62		10	11		
12 C	18.03	19.13	0.67			12		
H3	1.62	1.71	0.67			12	2, 3, 4	2eq, 2ax
13 C	13.87	16.25	0.67			13		
H3	1.5	1.76	0.67			13	3, 4, 5	5ax, 5eq

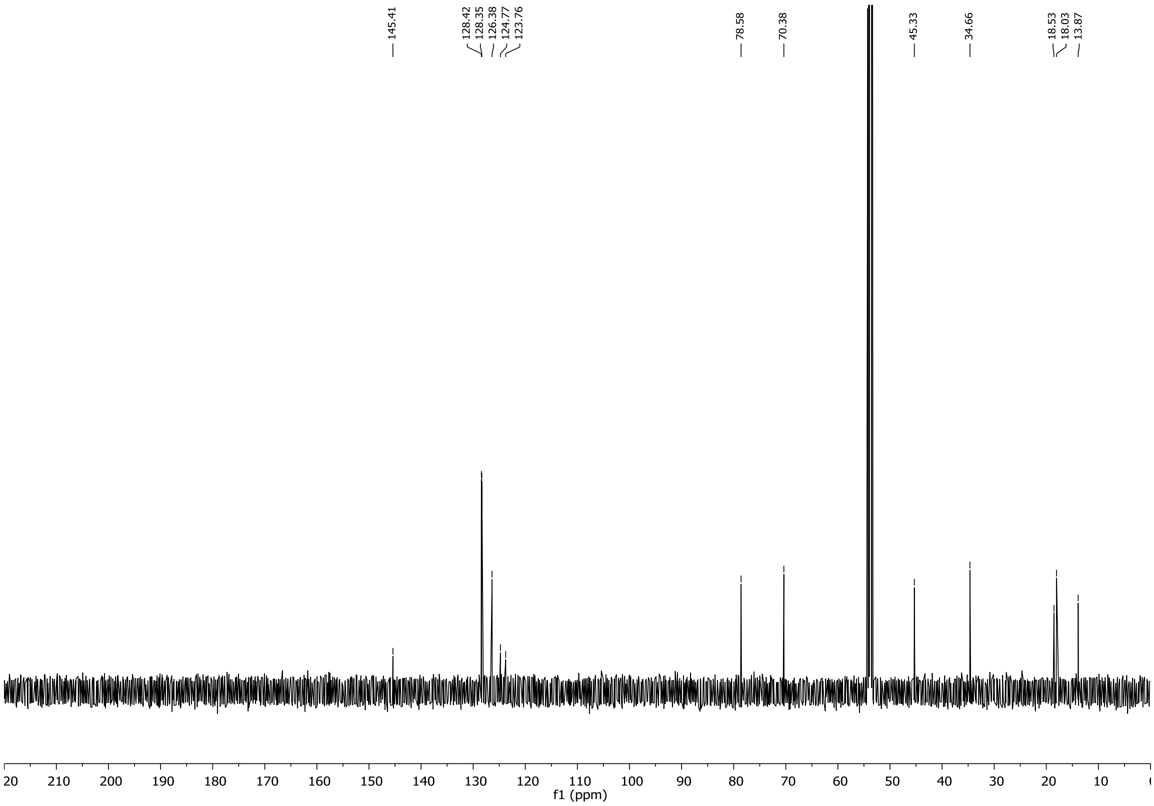
^{1}H NMR (3m)



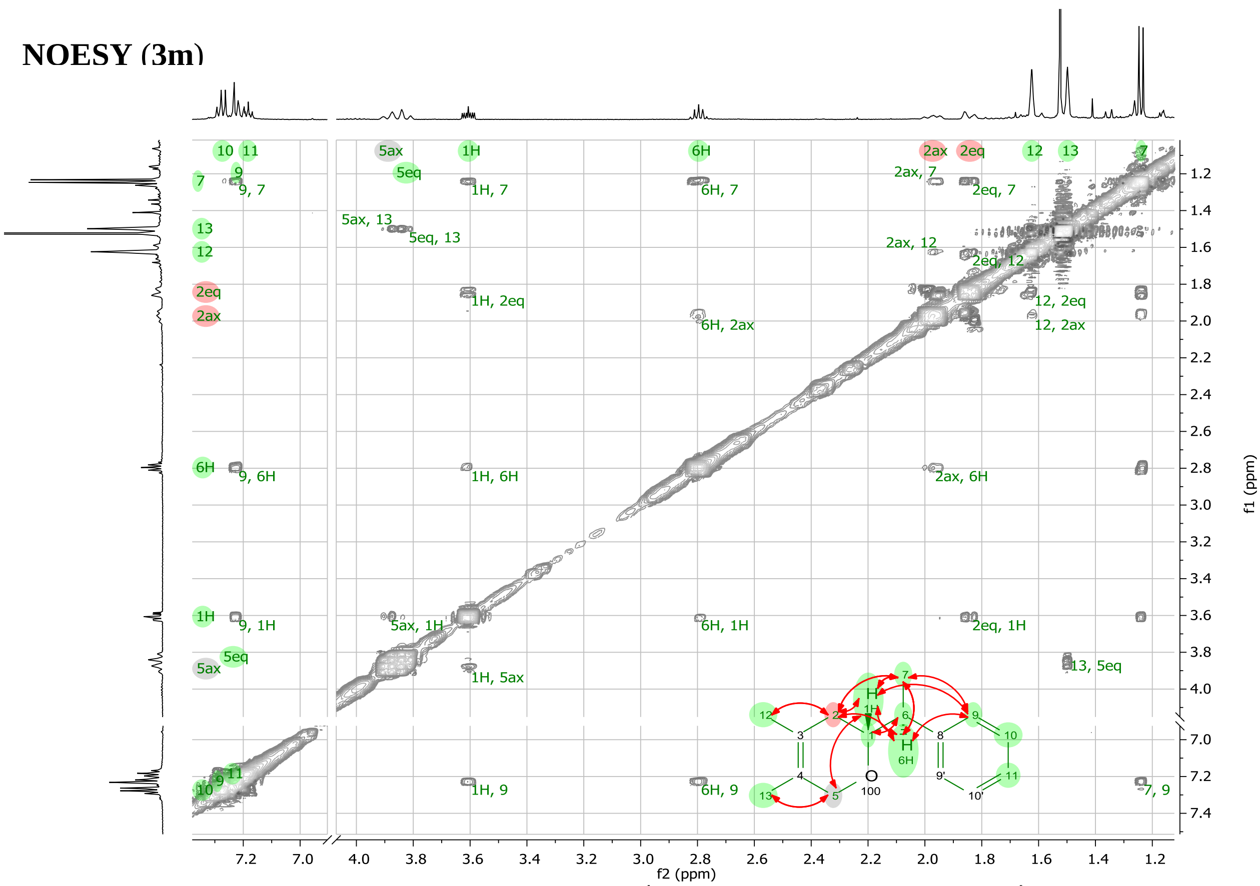
3m



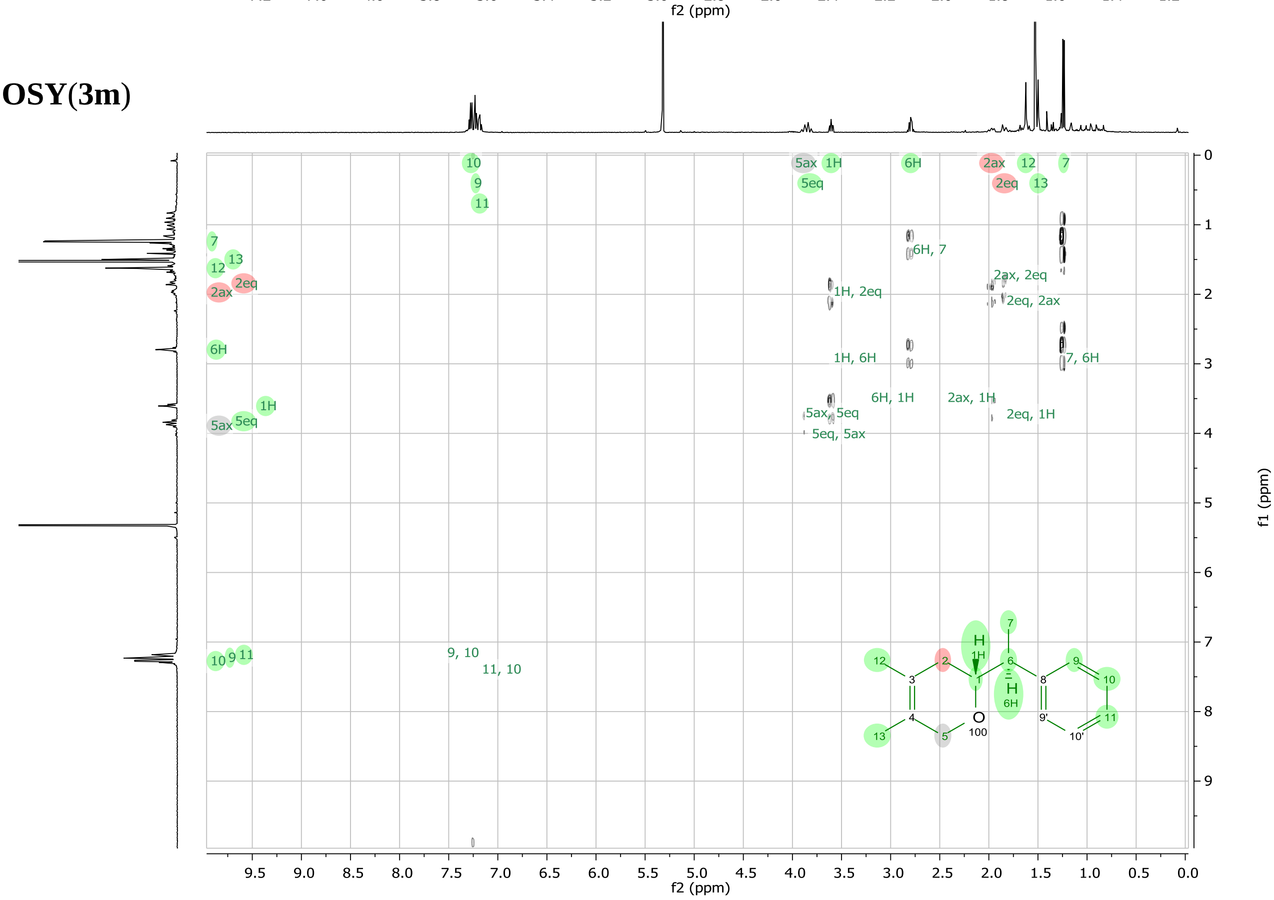
^{13}C NMR (3m)



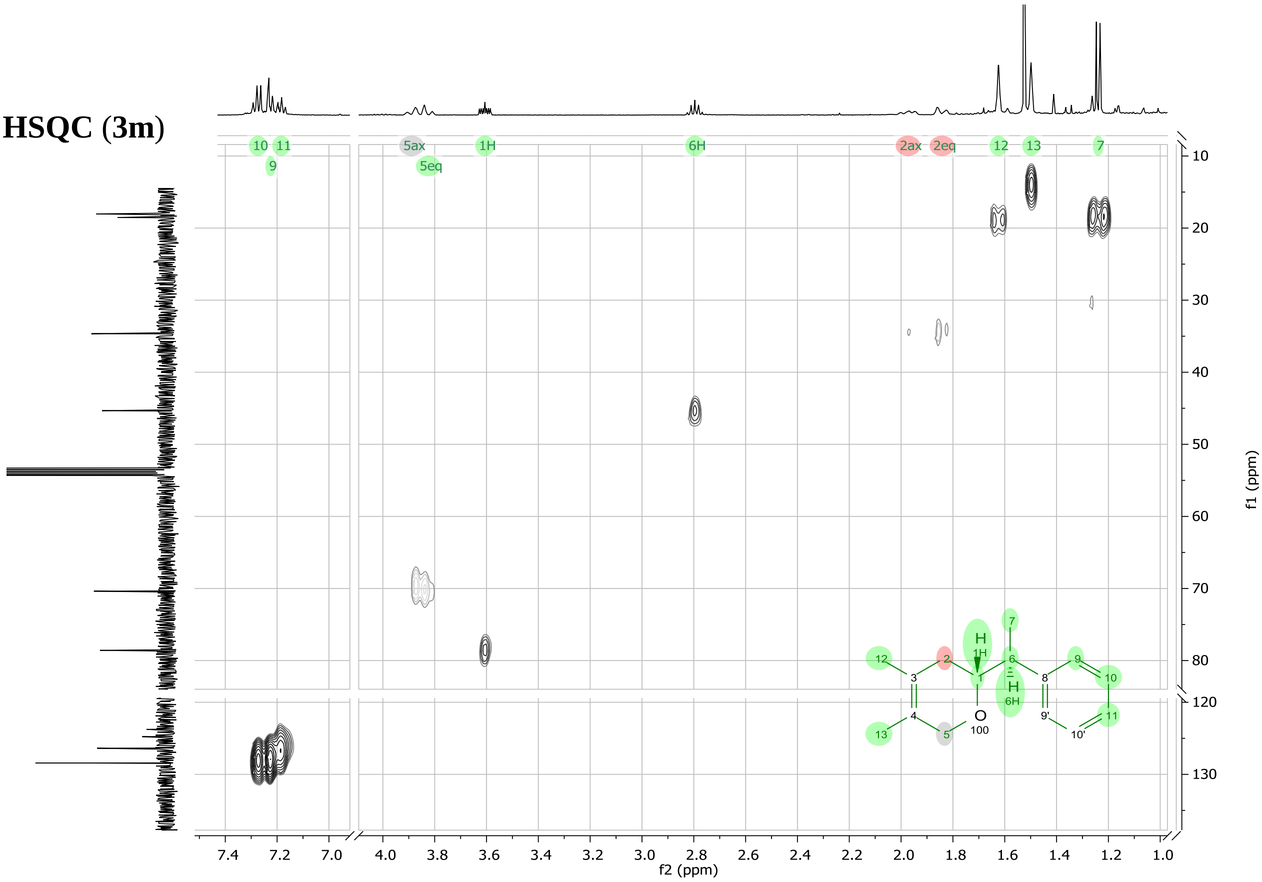
NOESY (3m)



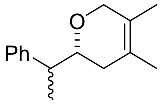
COSY(3m)

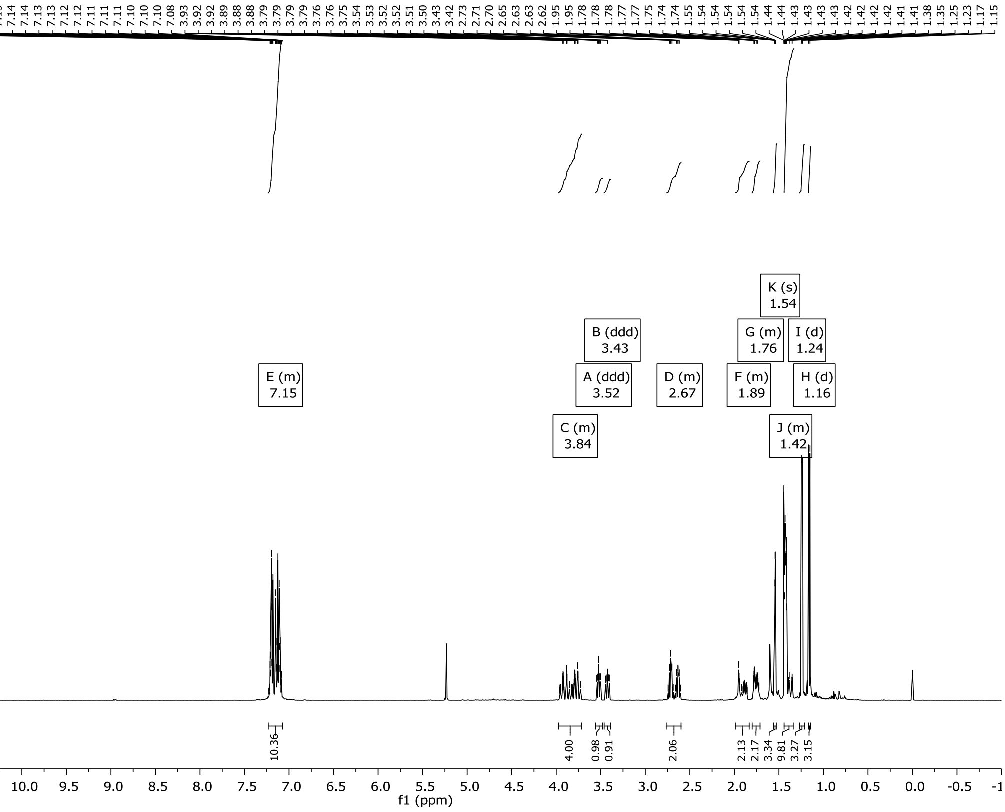


HSQC (3m)

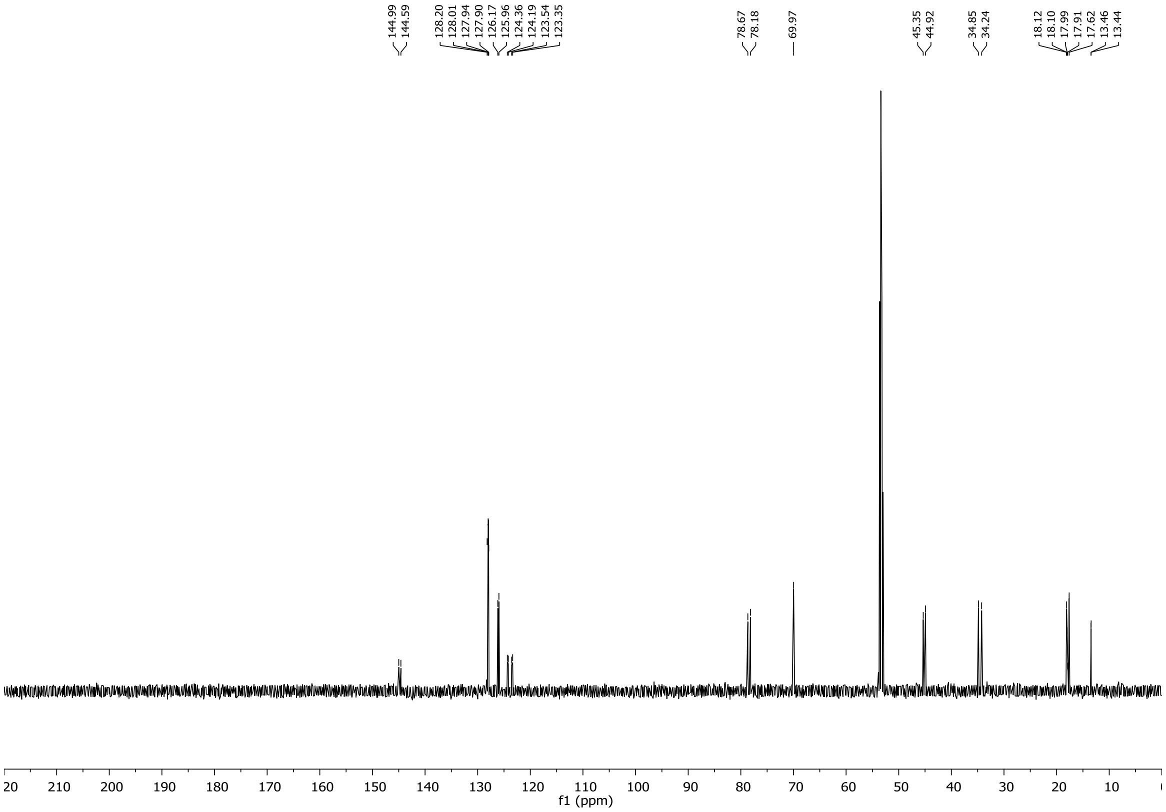


^{1}H NMR (3n)

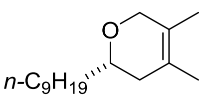




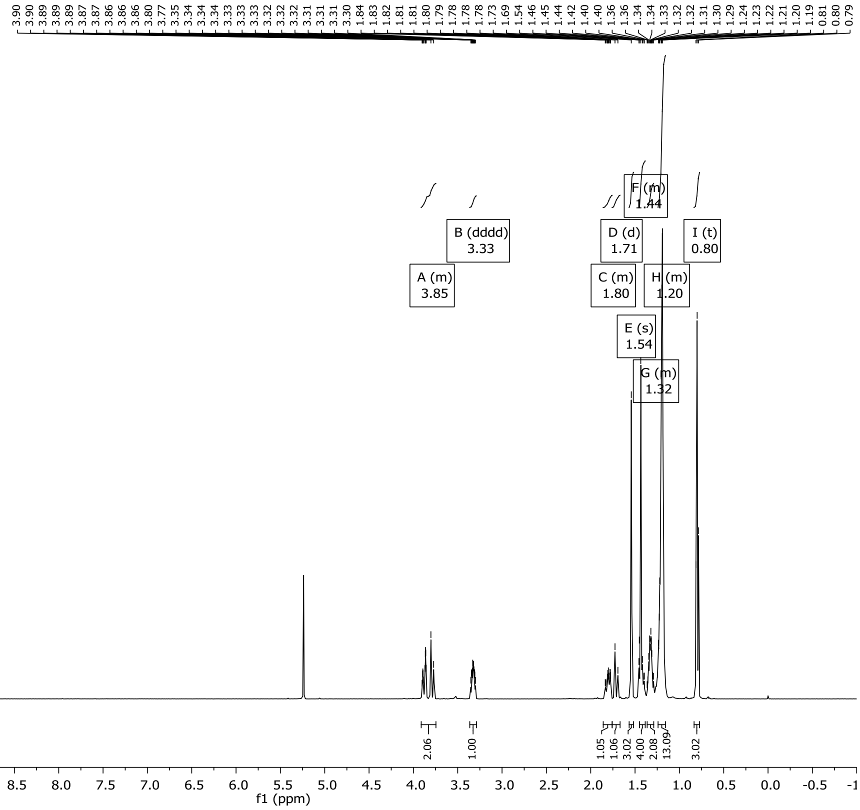
^{13}C NMR (3n)



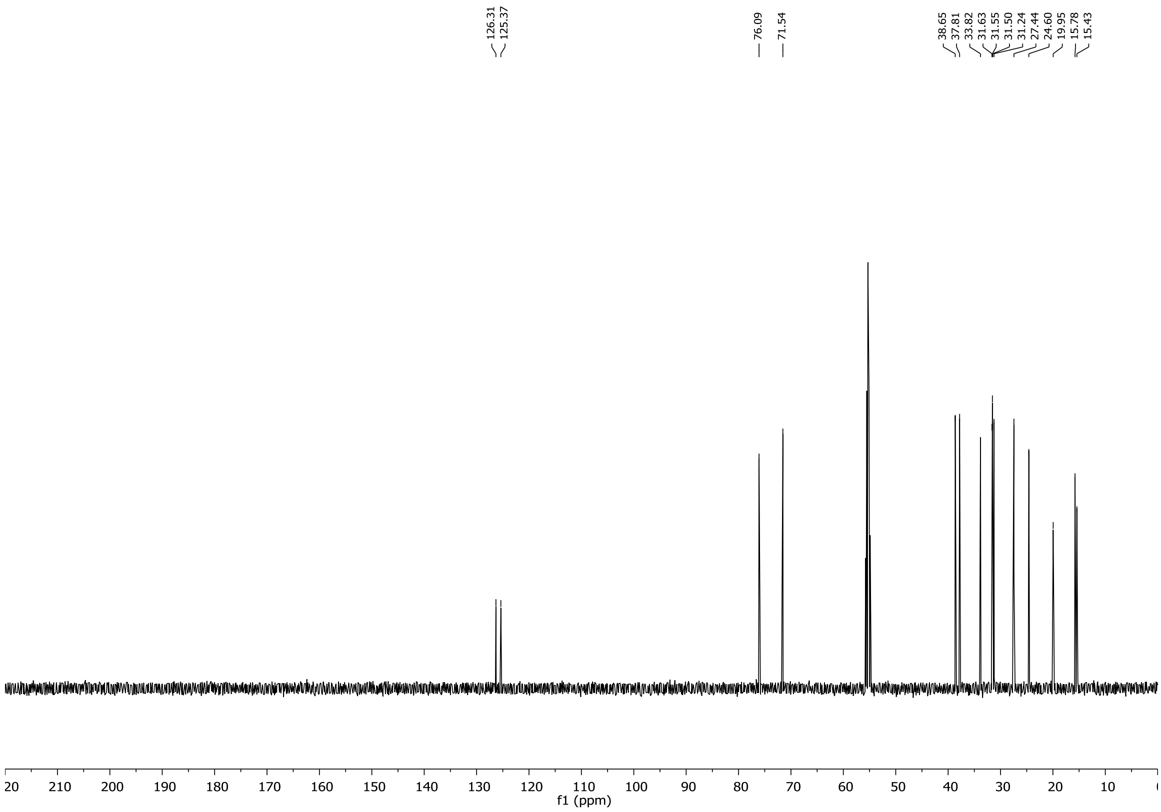
^{1}H NMR (3o)



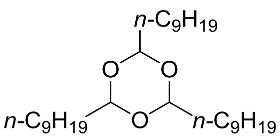
3o



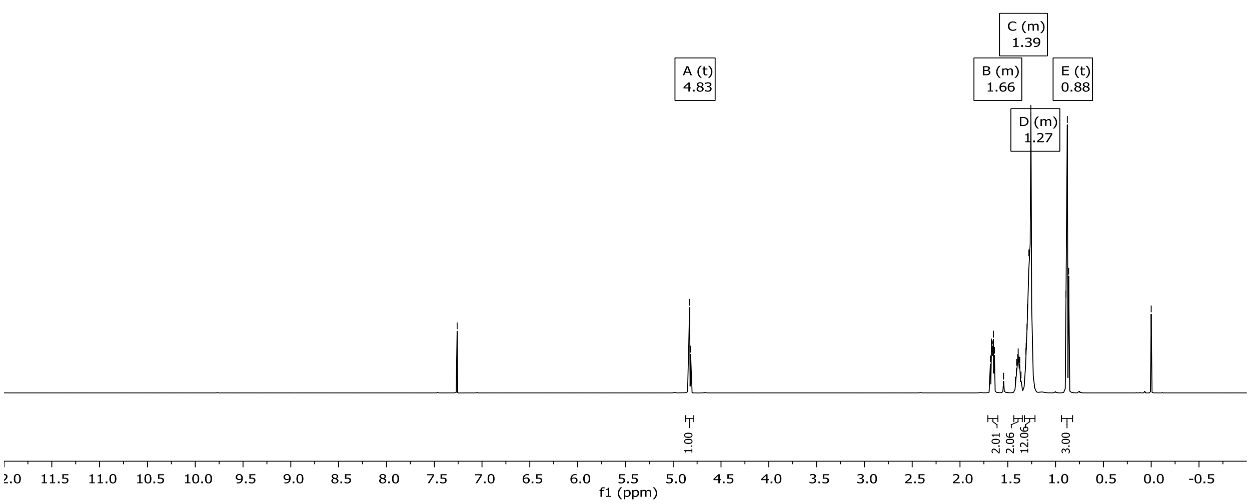
^{13}C NMR (3o)



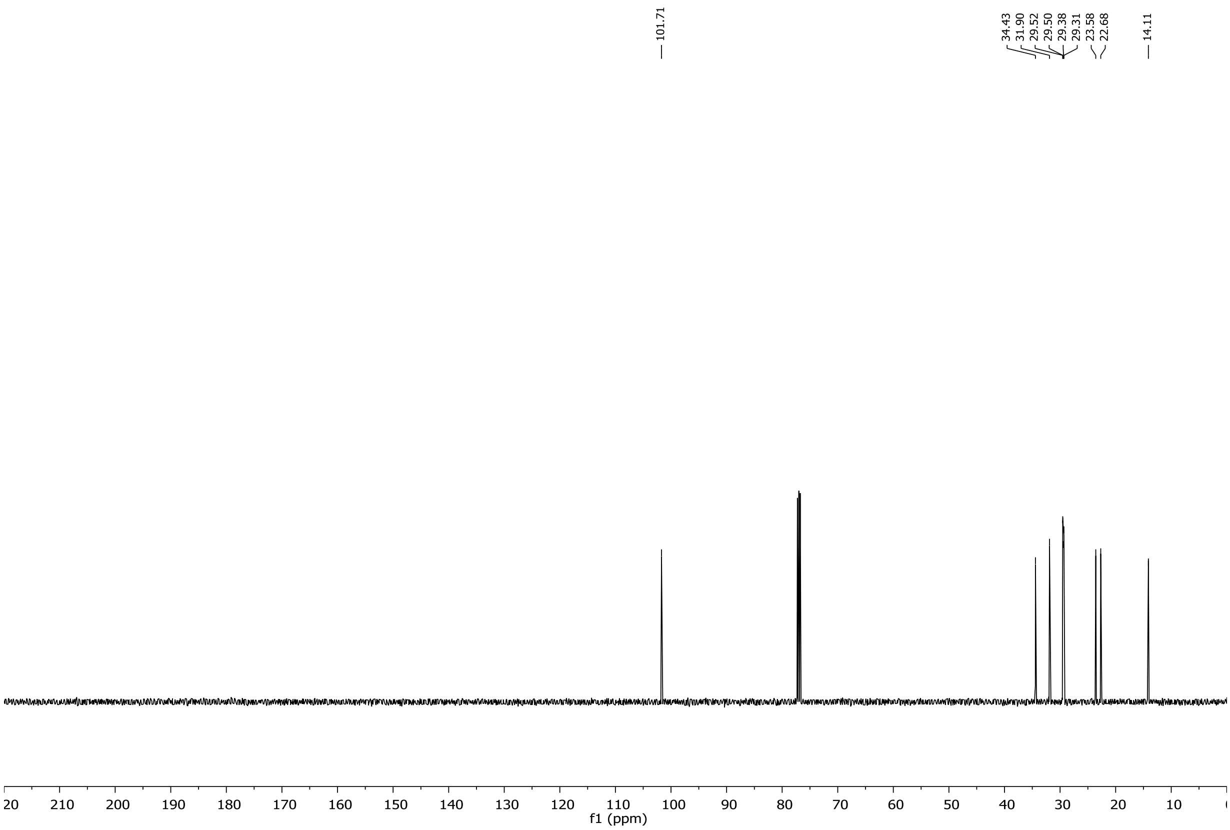
^{1}H NMR (S9)



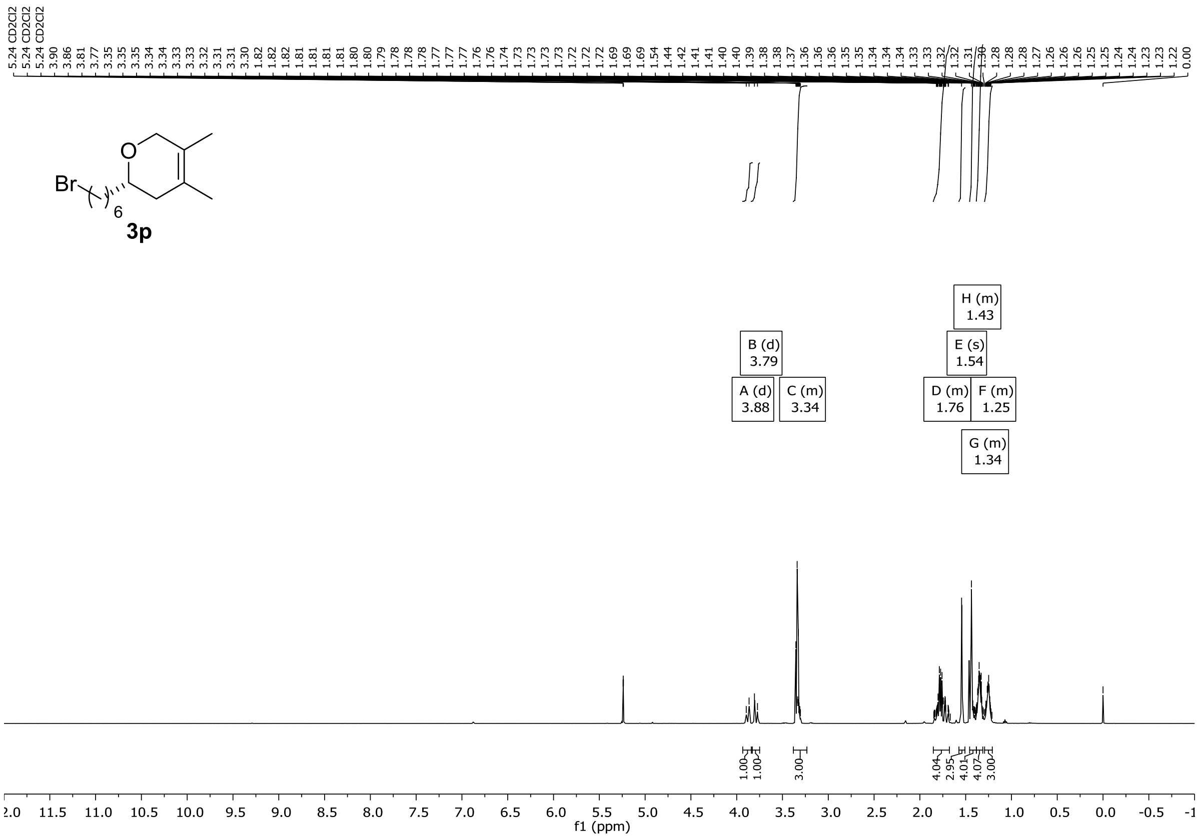
S9



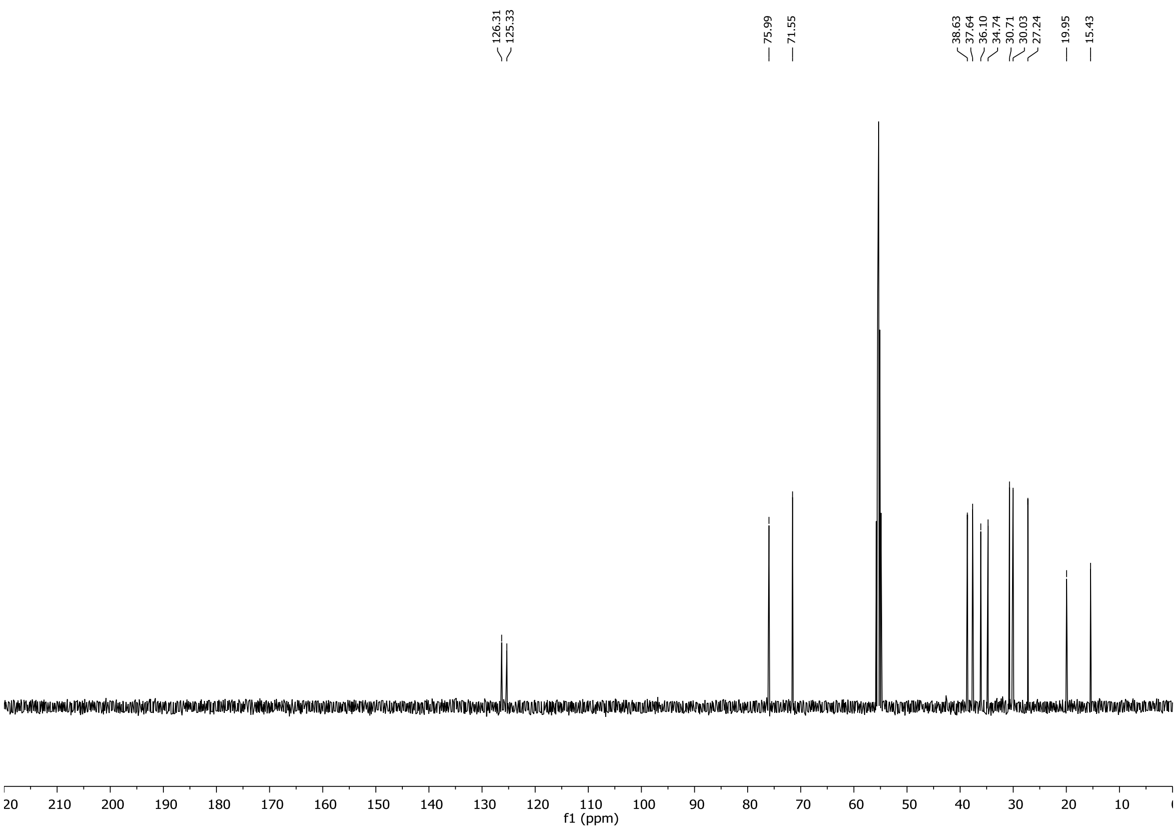
^{13}C NMR (S9)



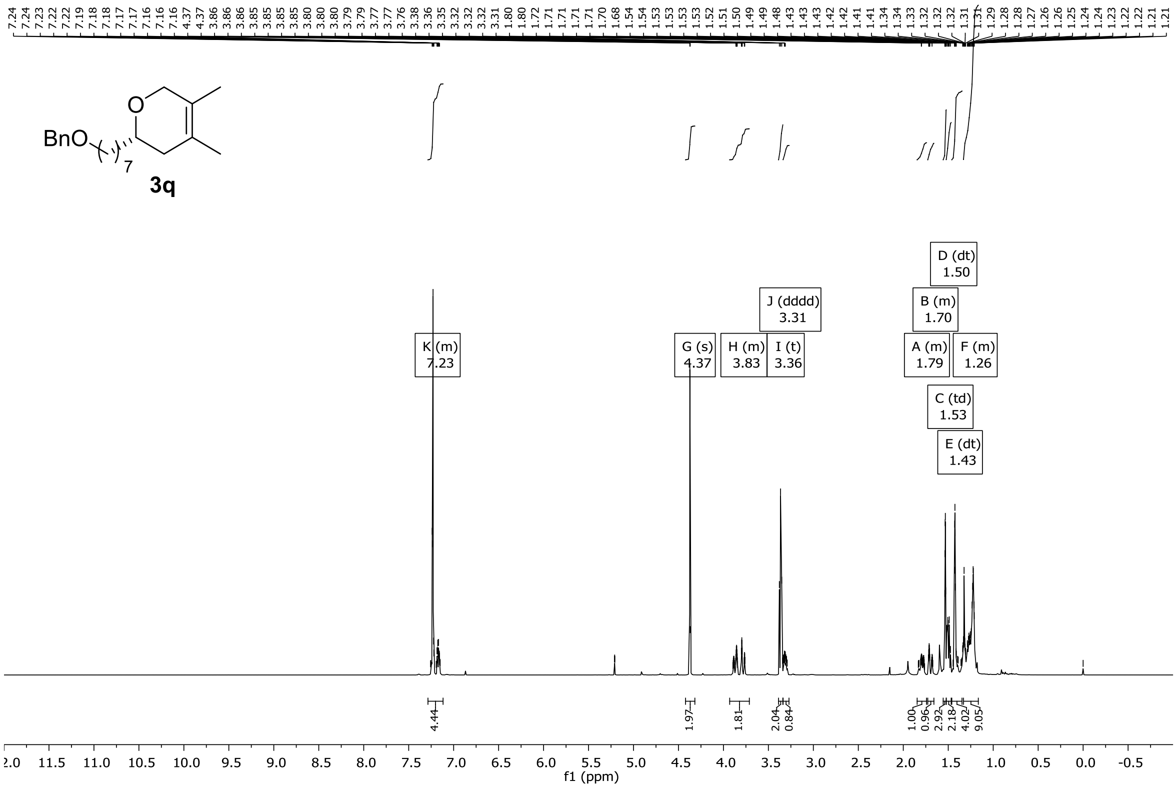
^{1}H NMR (3p)



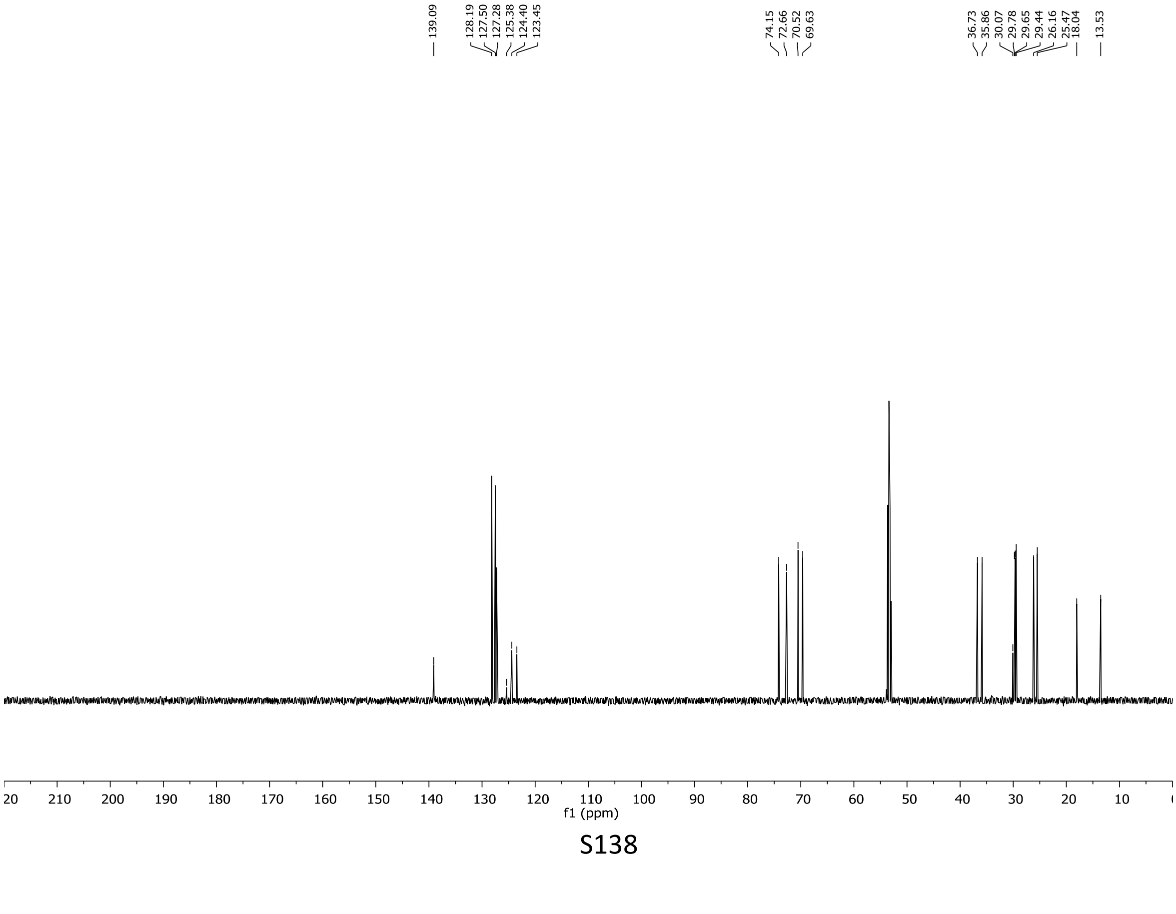
^{13}C NMR (3p)



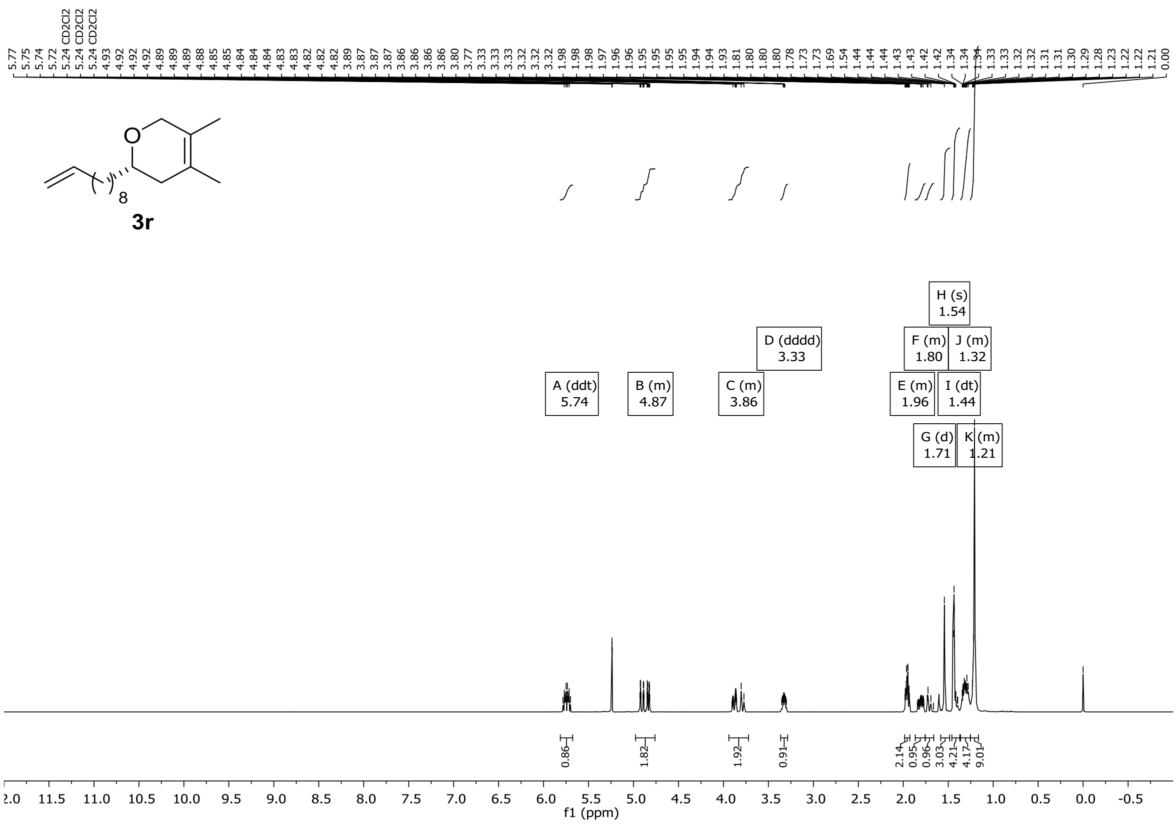
^{1}H NMR (3q)



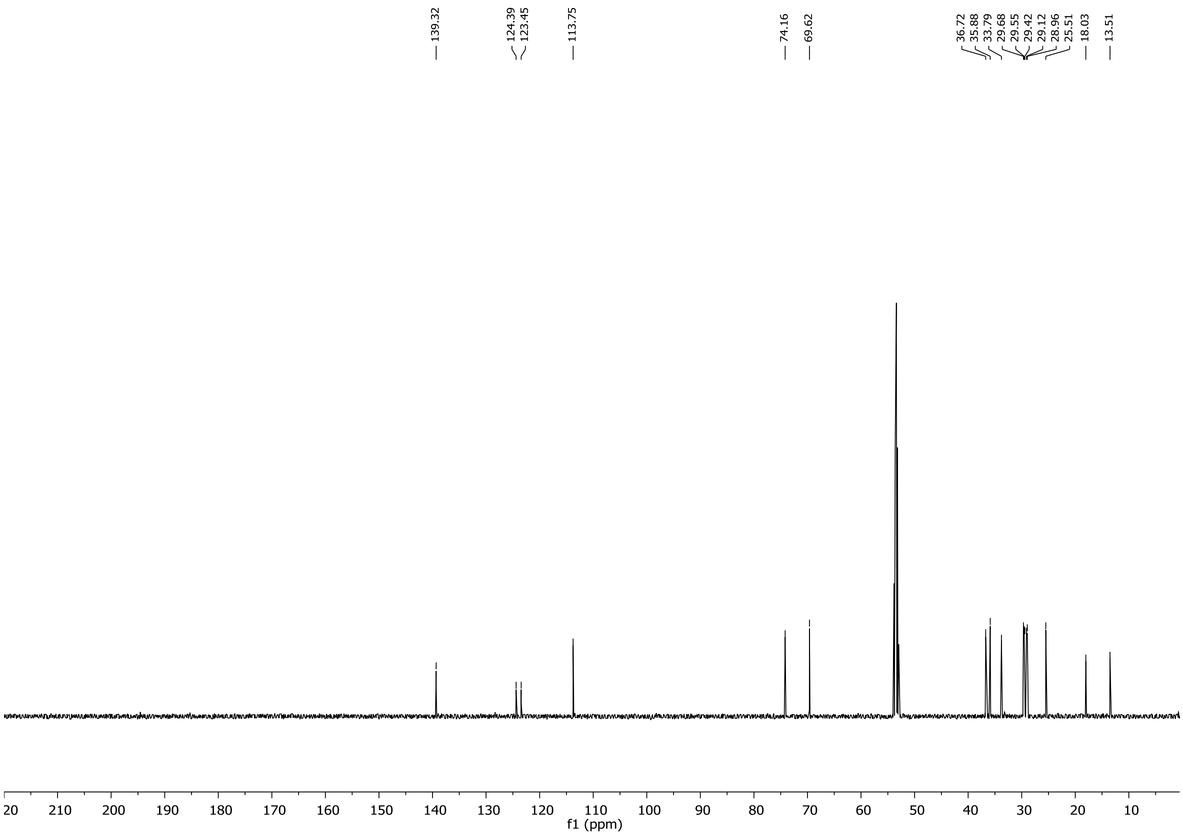
^{13}C NMR (3q)



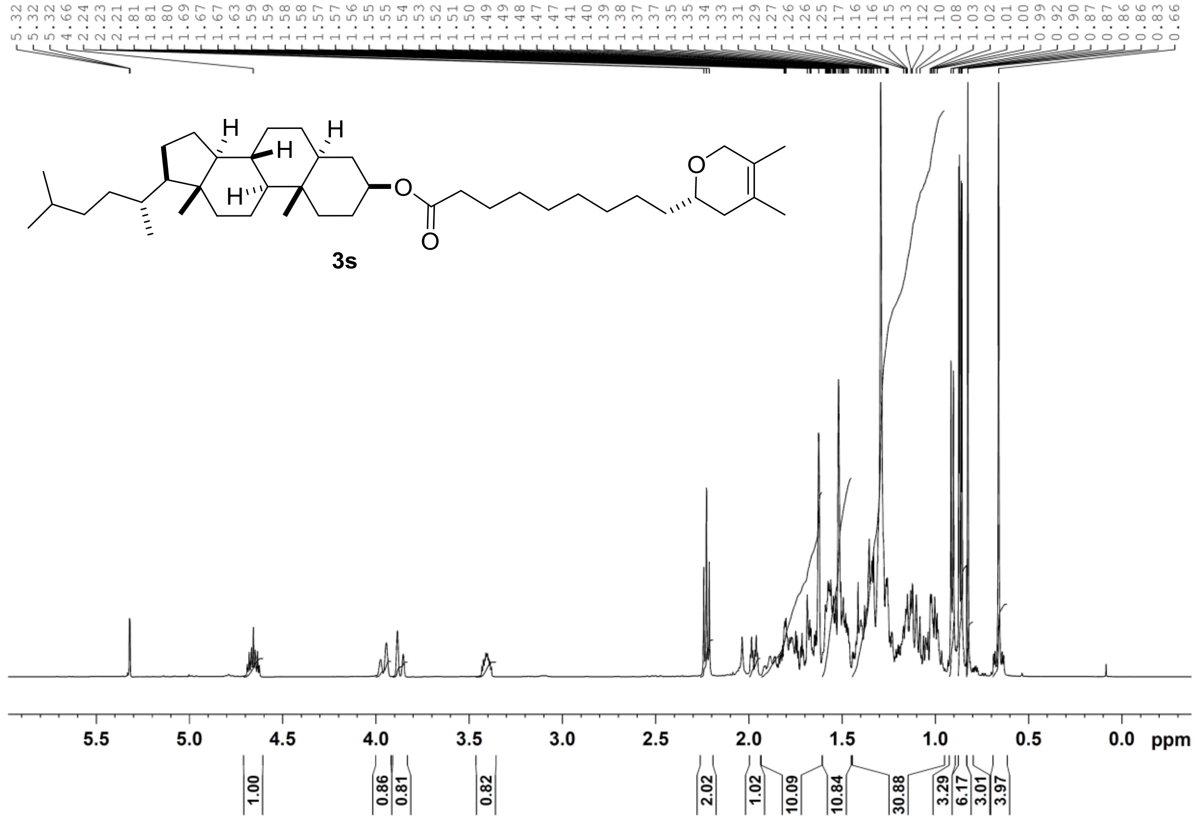
^{1}H NMR (3r)



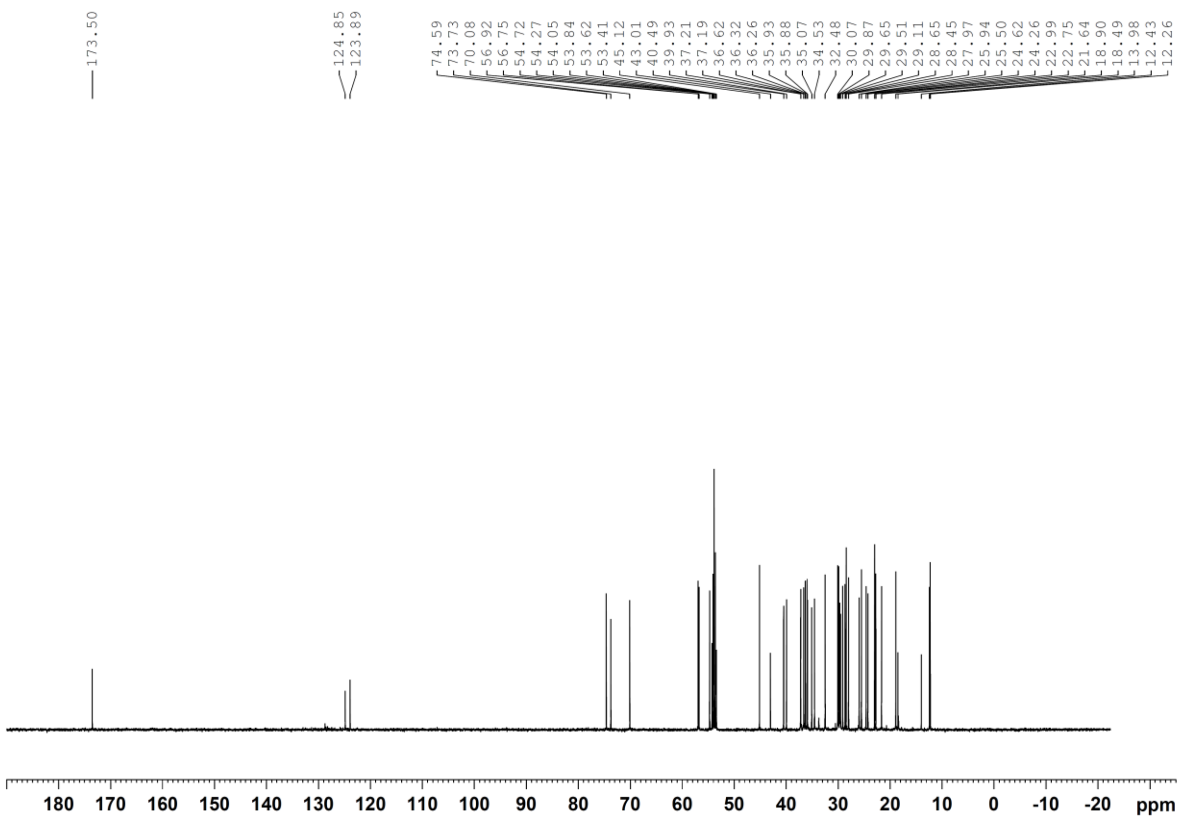
^{13}C NMR (3r)



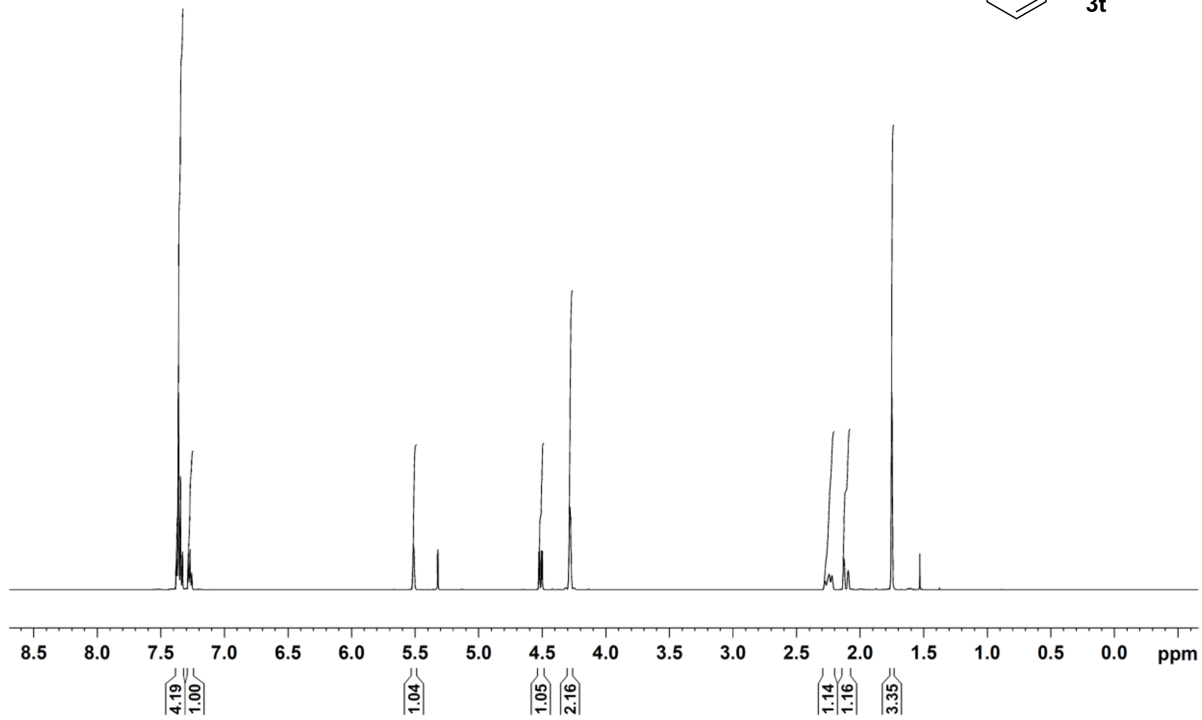
^{1}H NMR (3s)

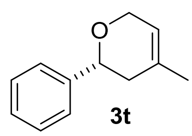


^{13}C NMR (3s)



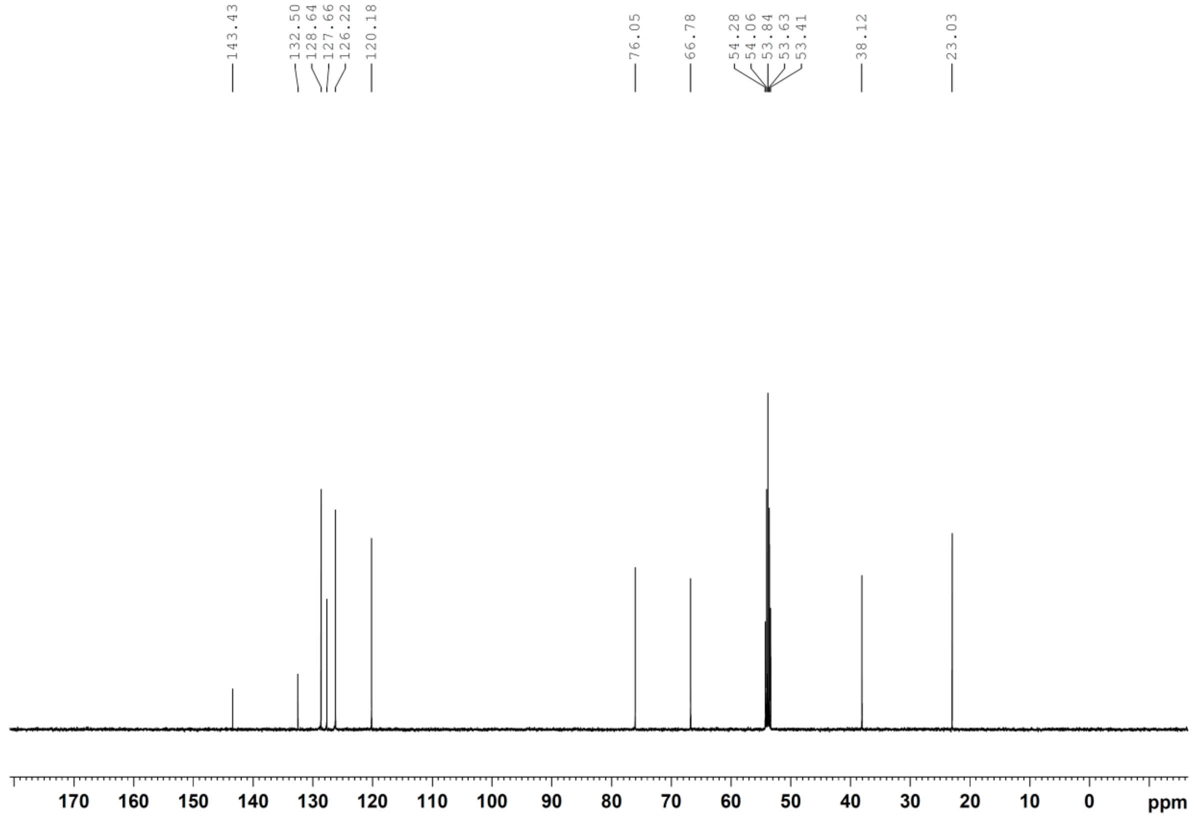
[1]H NMR (3t)



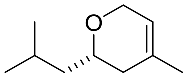


3t

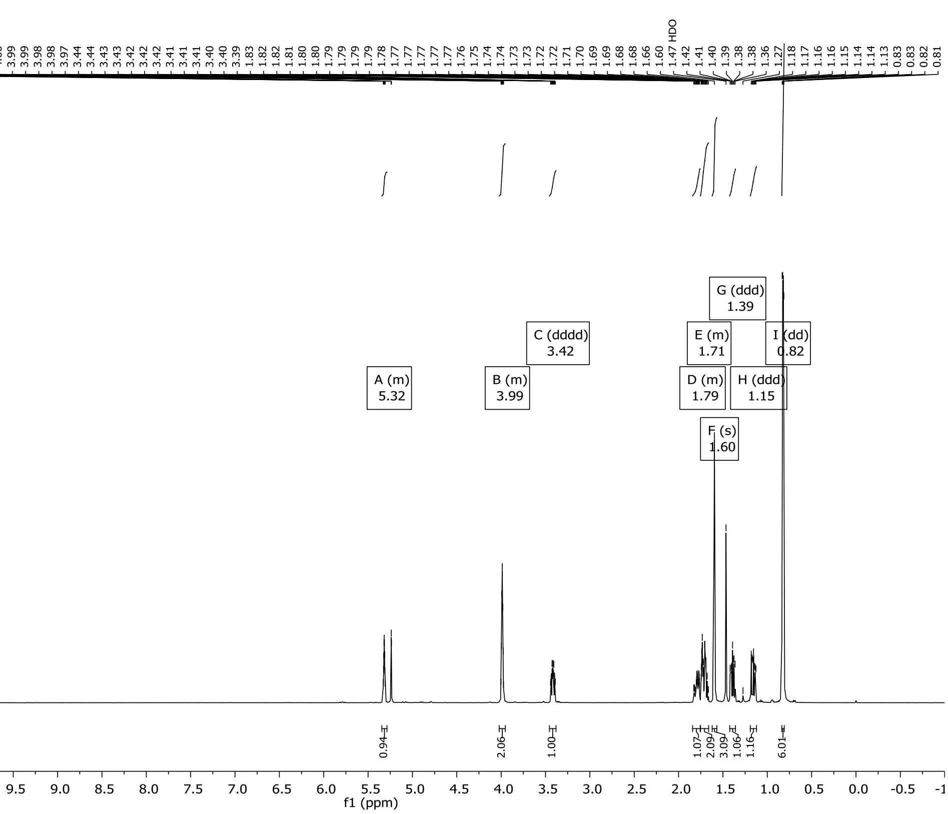
[13]C NMR (3t)



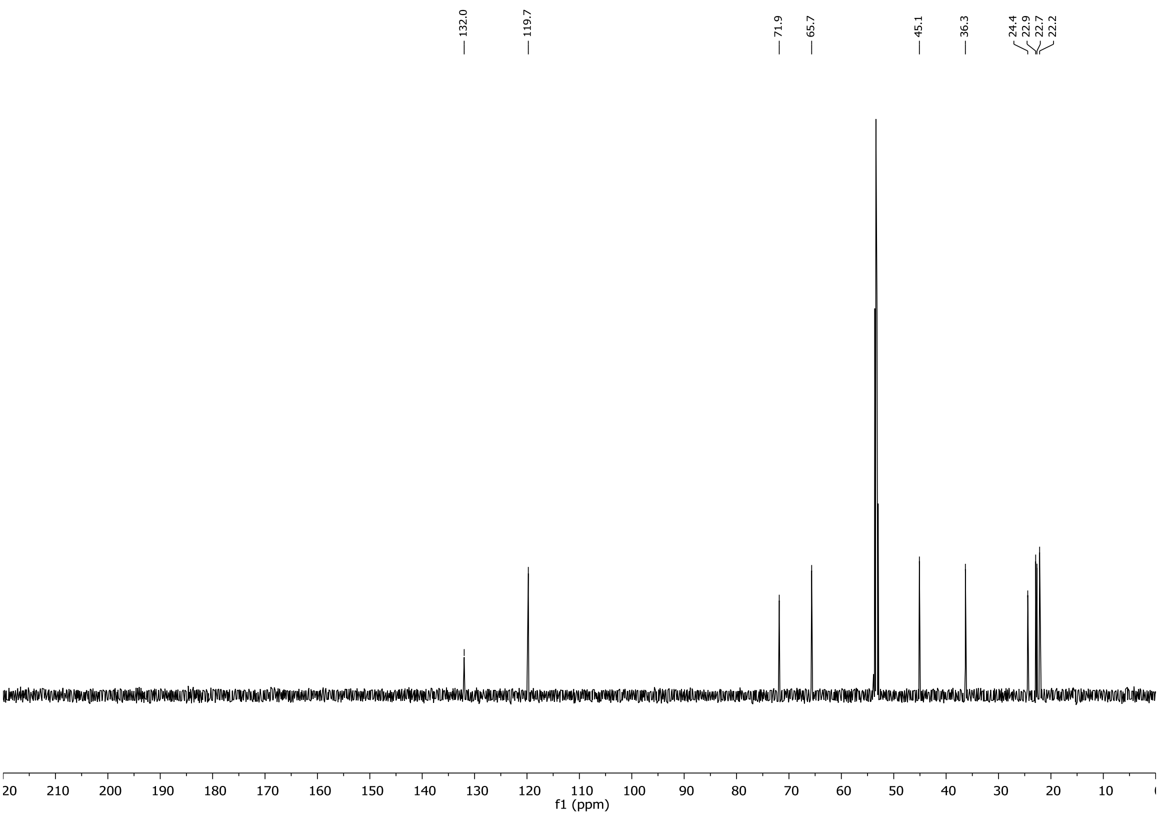
^{1}H NMR (3v)



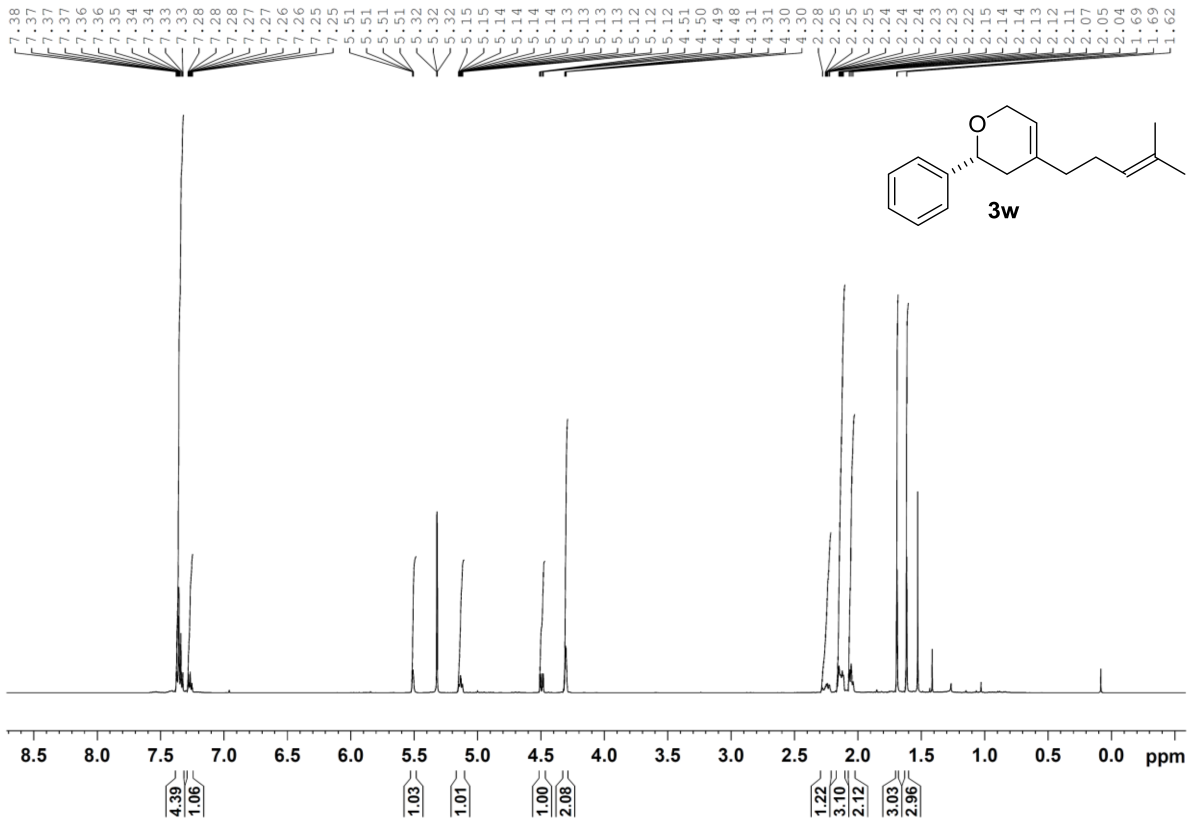
3v



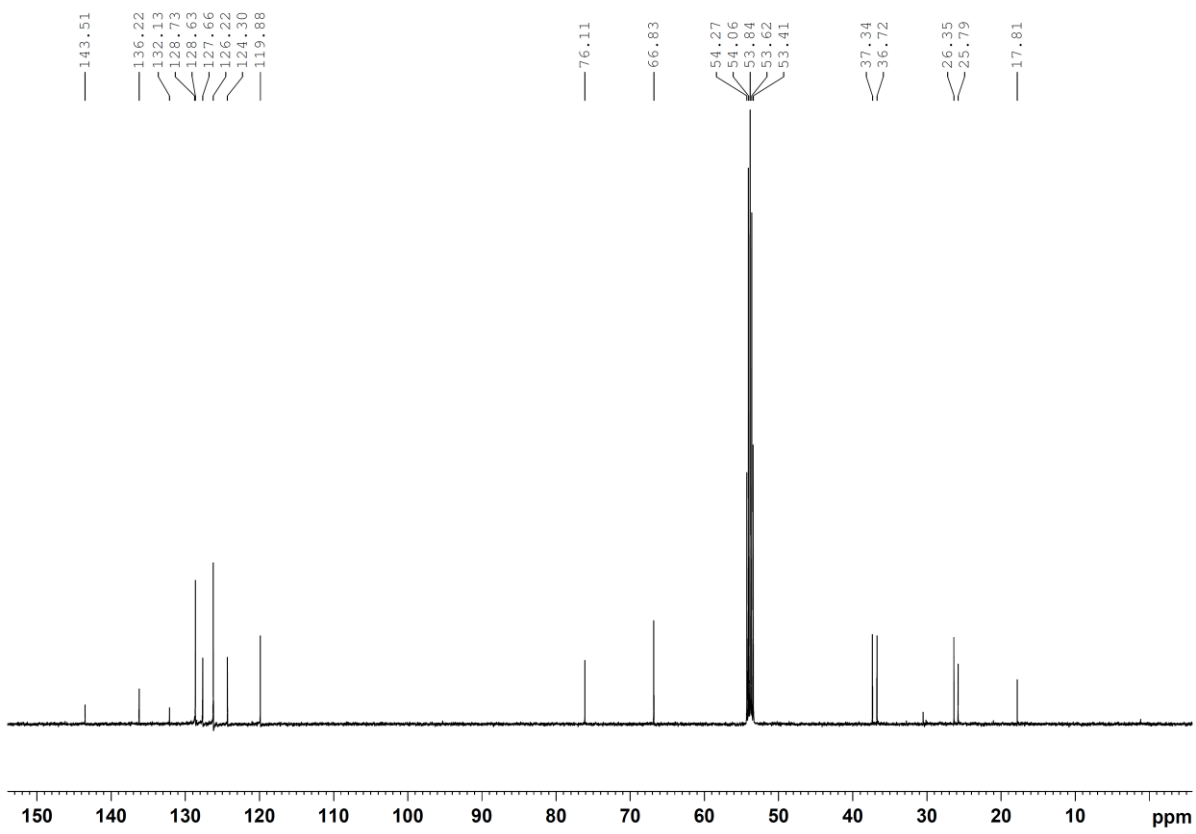
^{13}C NMR (3v)



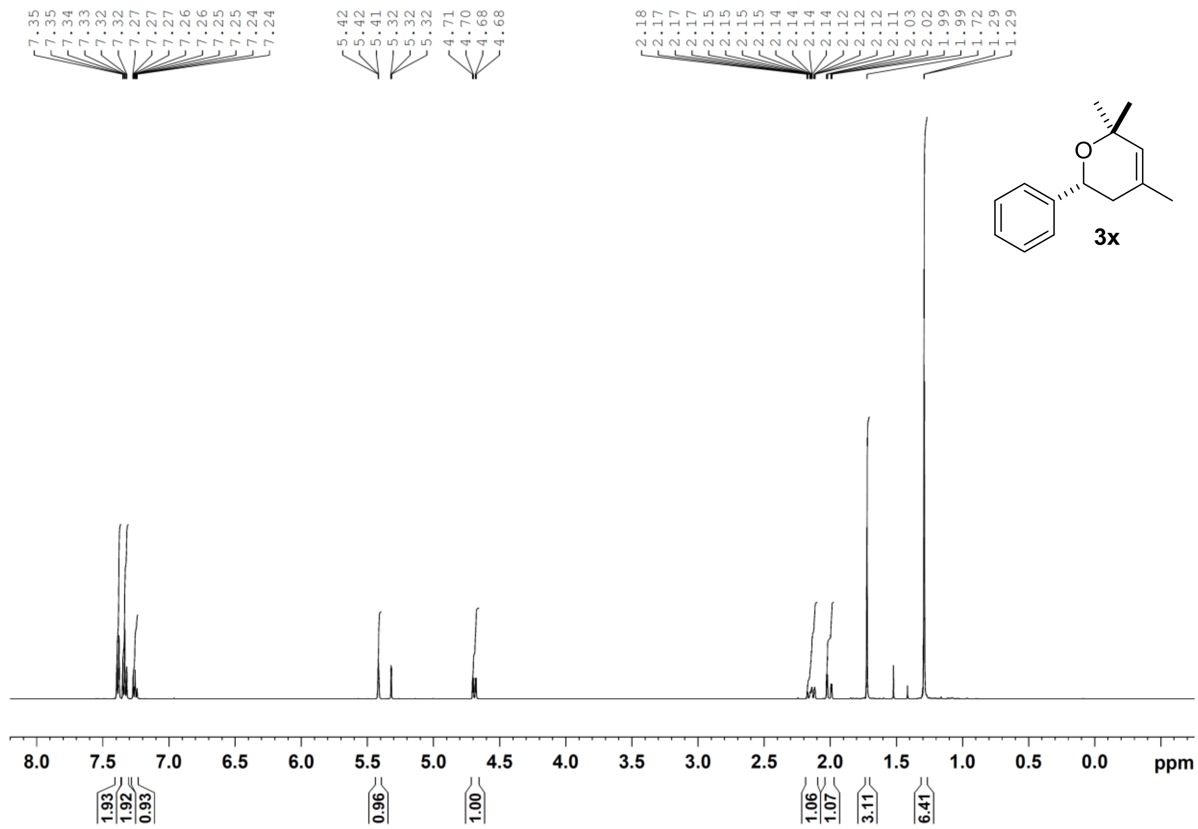
^{1}H NMR (3w)



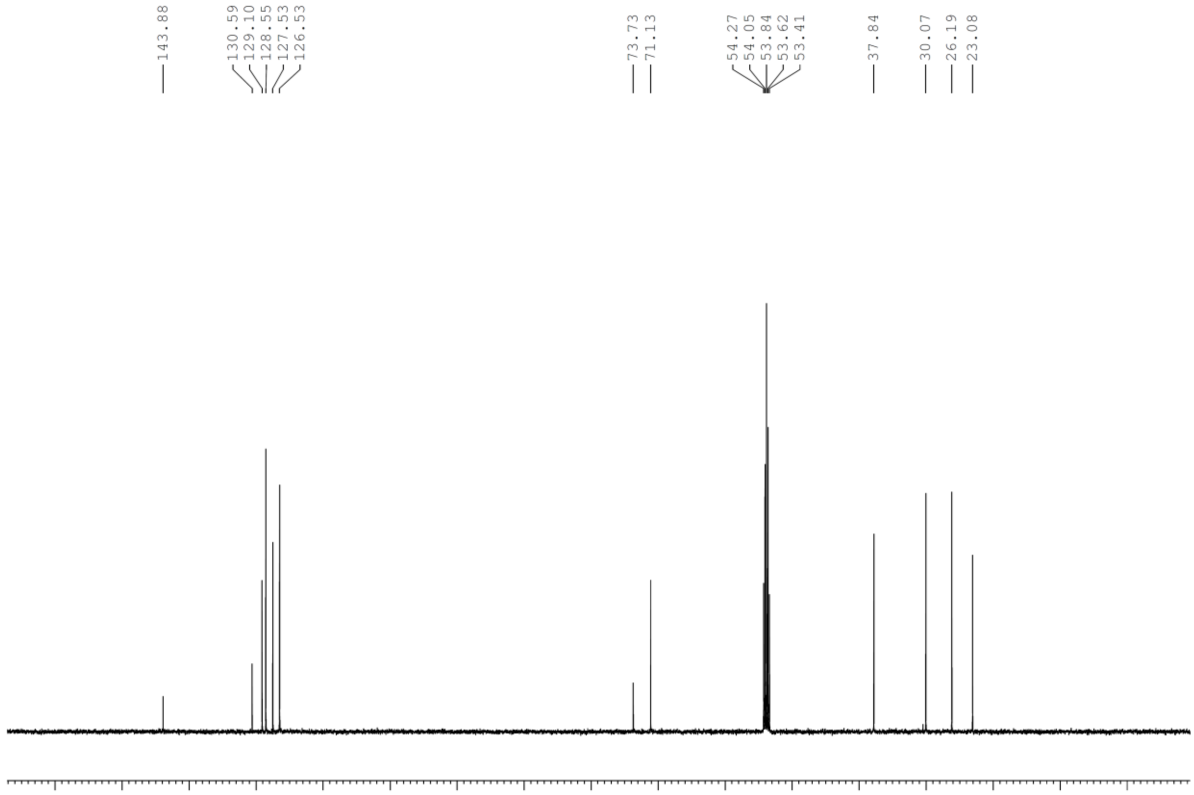
^{13}C NMR (3w)



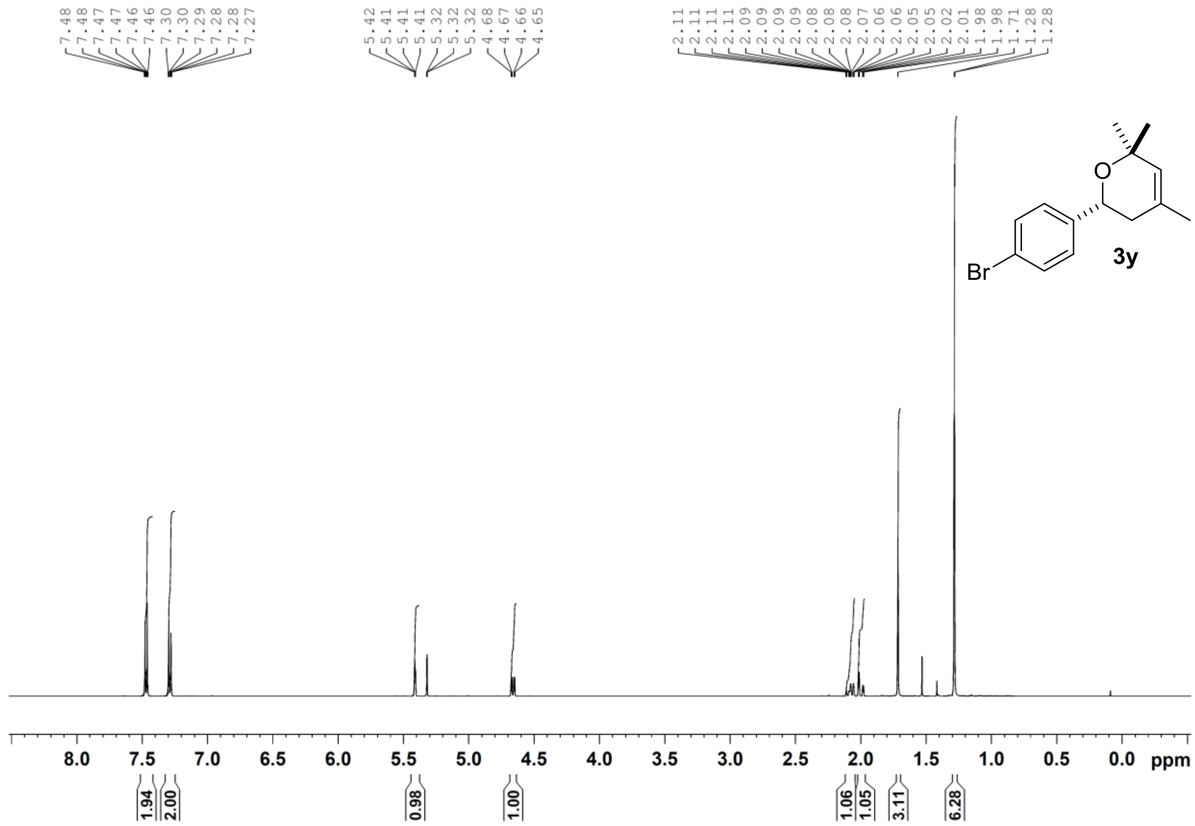
[1]H NMR (3x)



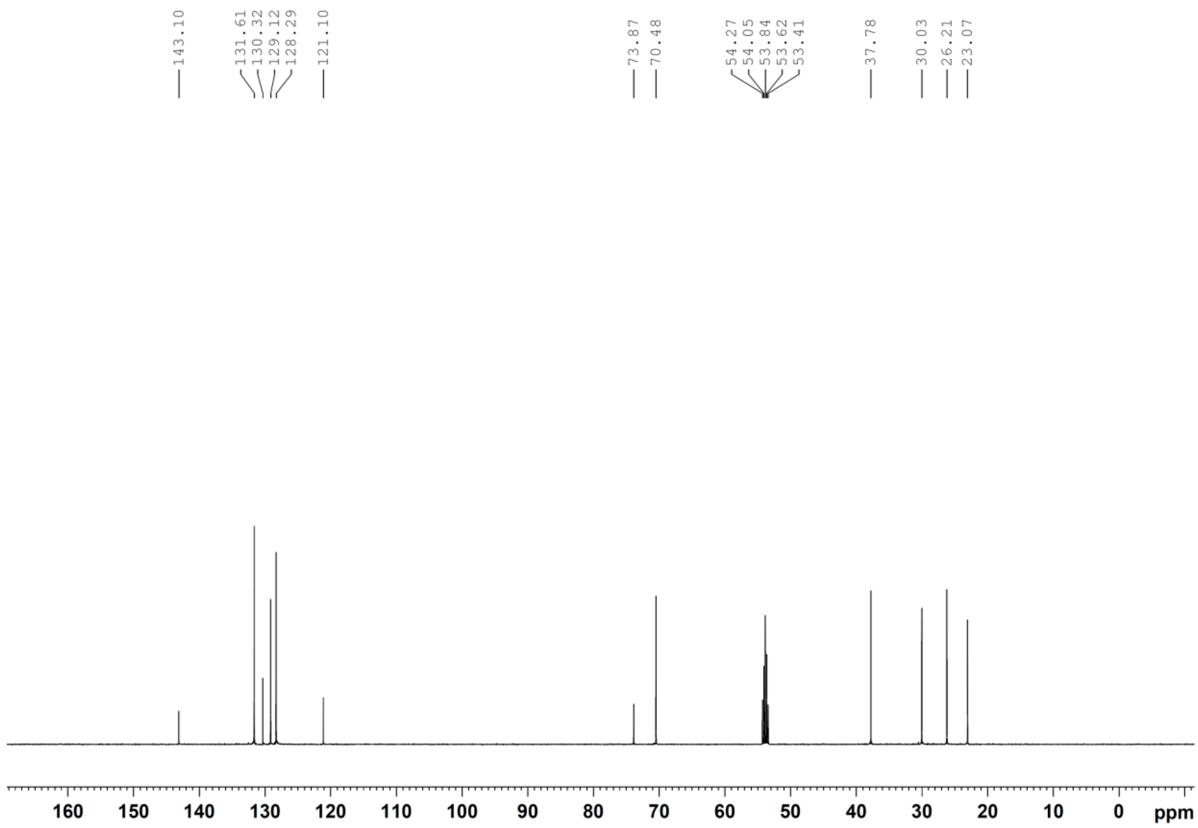
[13]C NMR (3x)



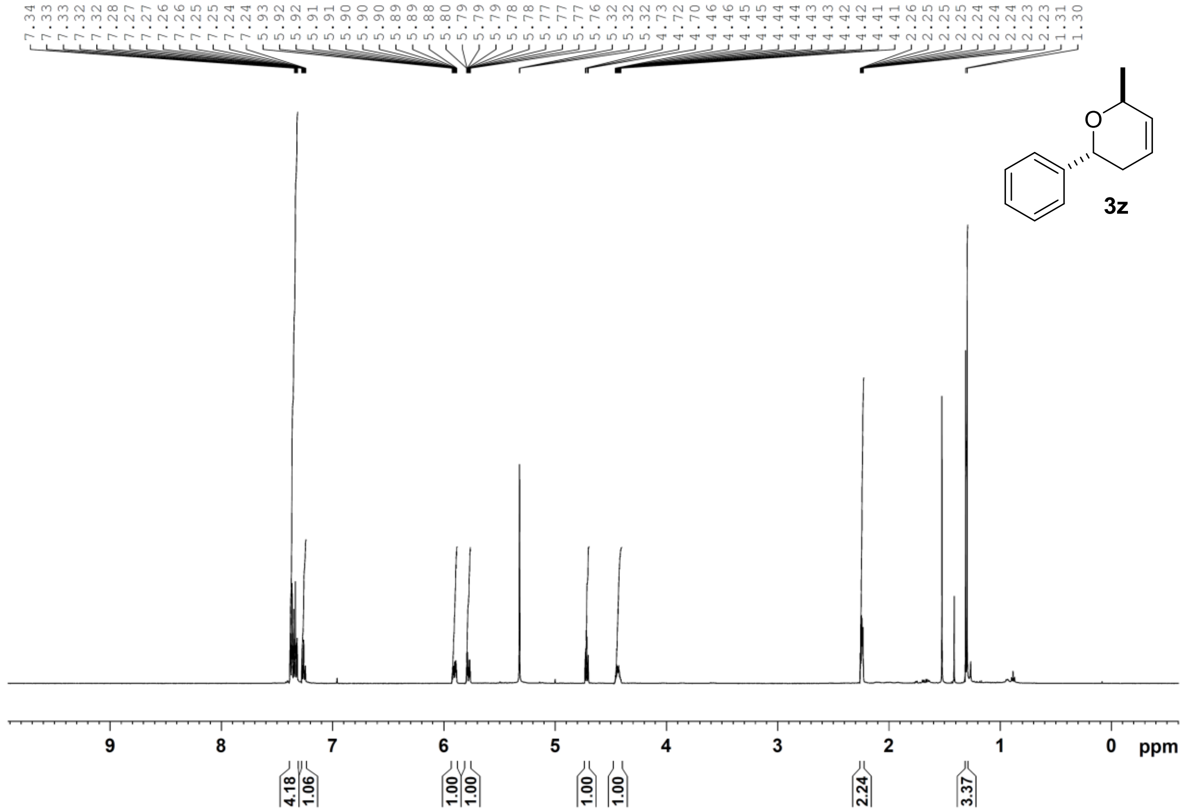
[1]H NMR (3y)



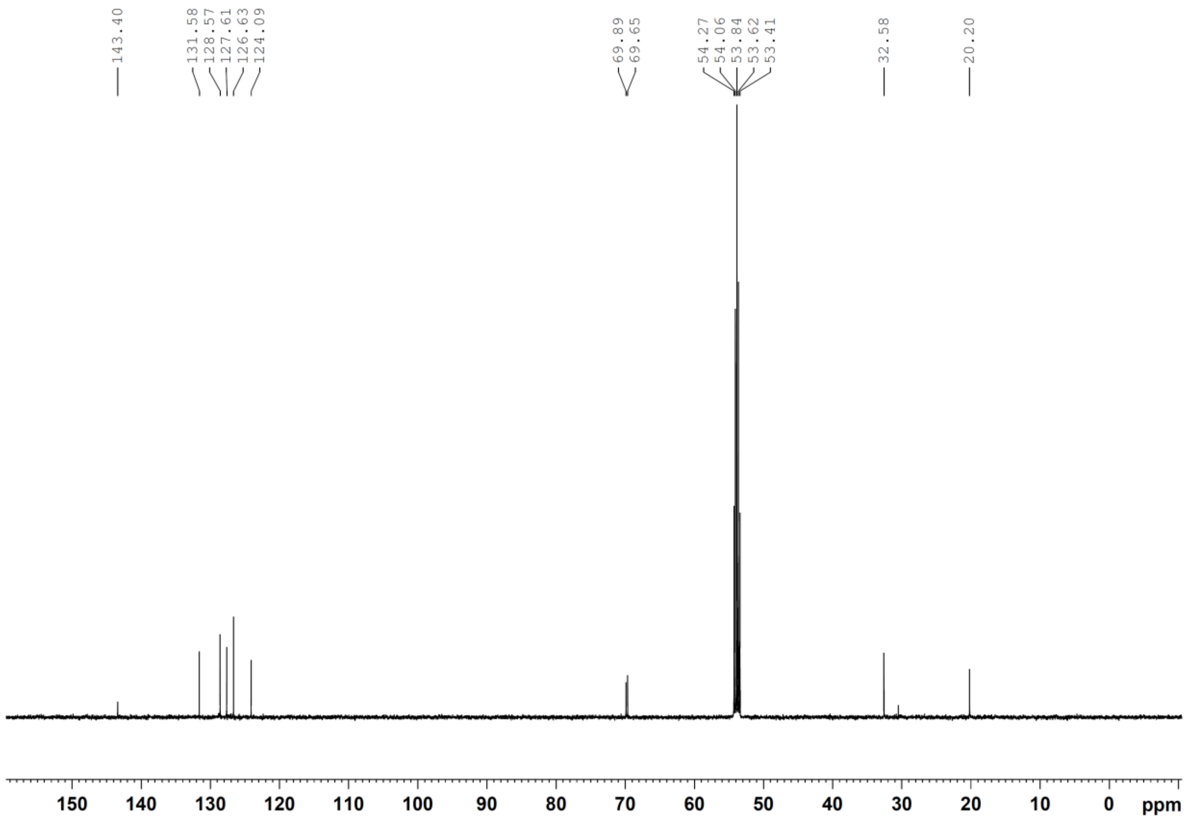
[13]C NMR (3y)



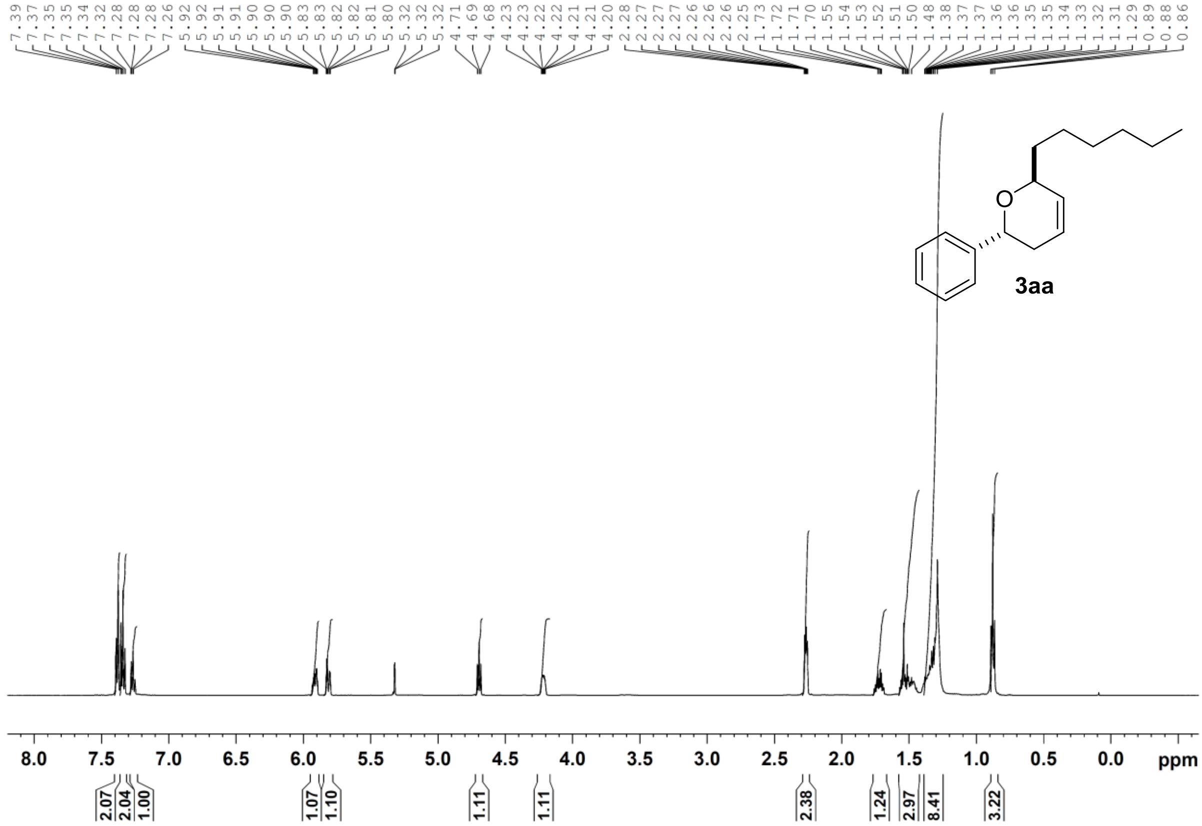
[1]H NMR (3z)



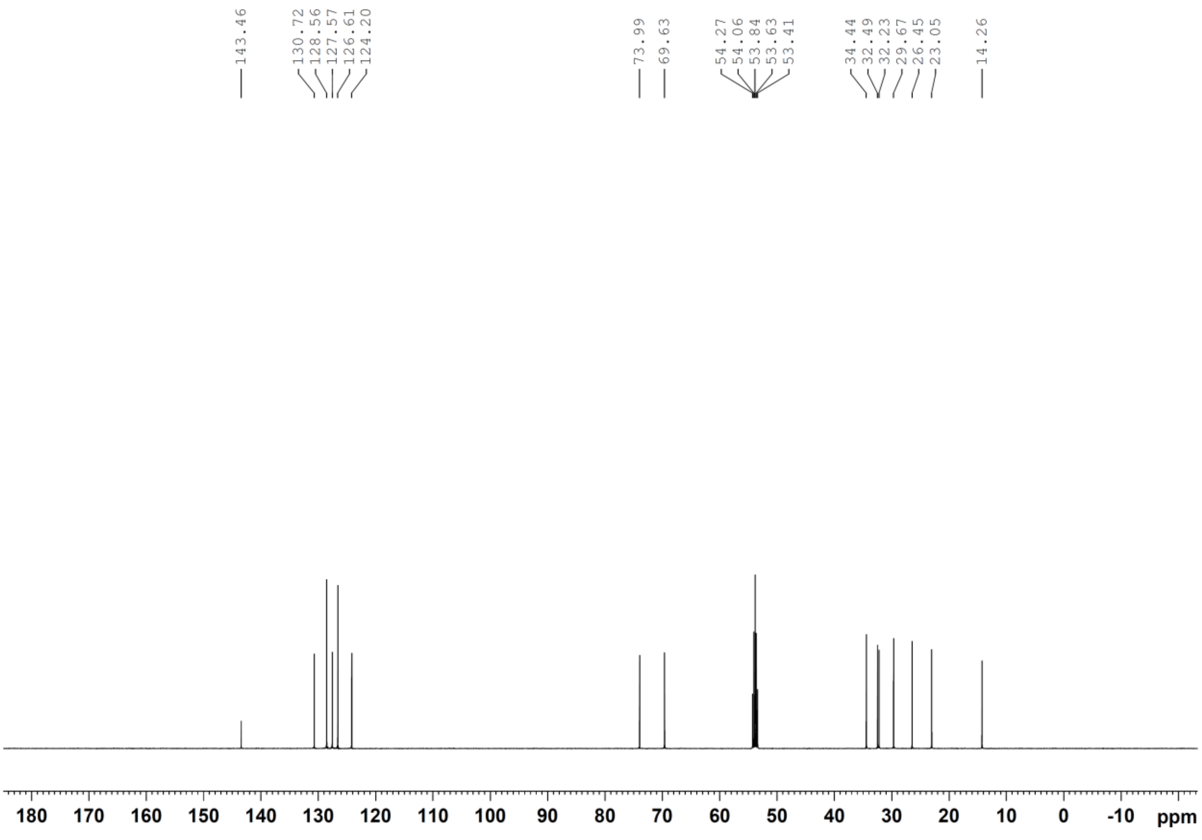
[13]C NMR (3z)



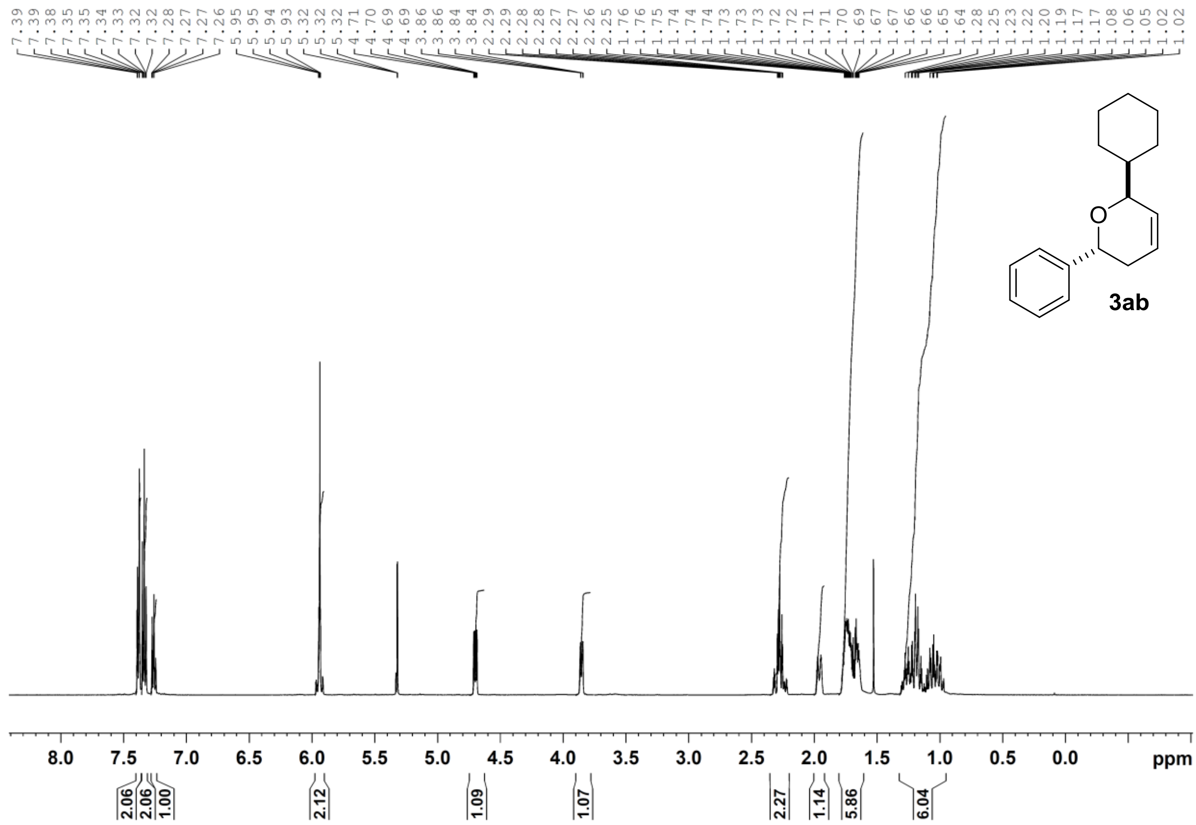
^{1}H NMR (3aa)



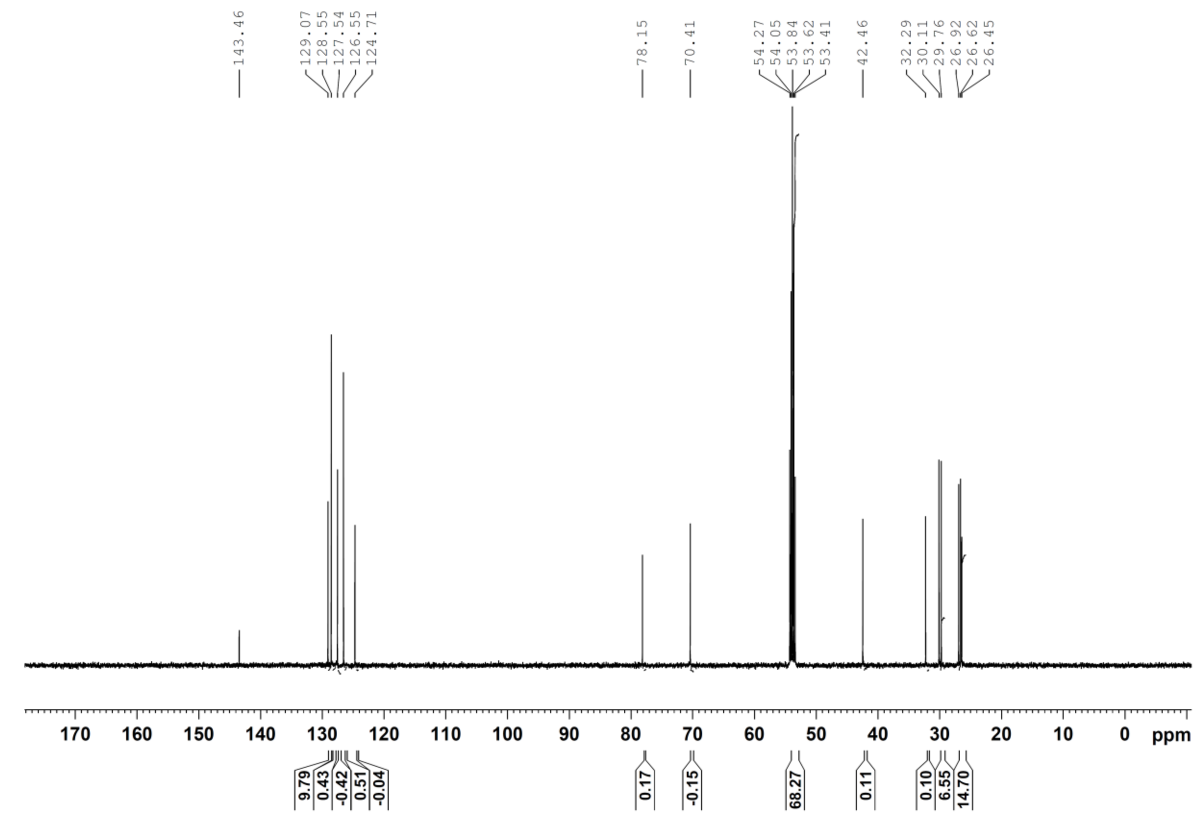
^{13}C NMR (3aa)



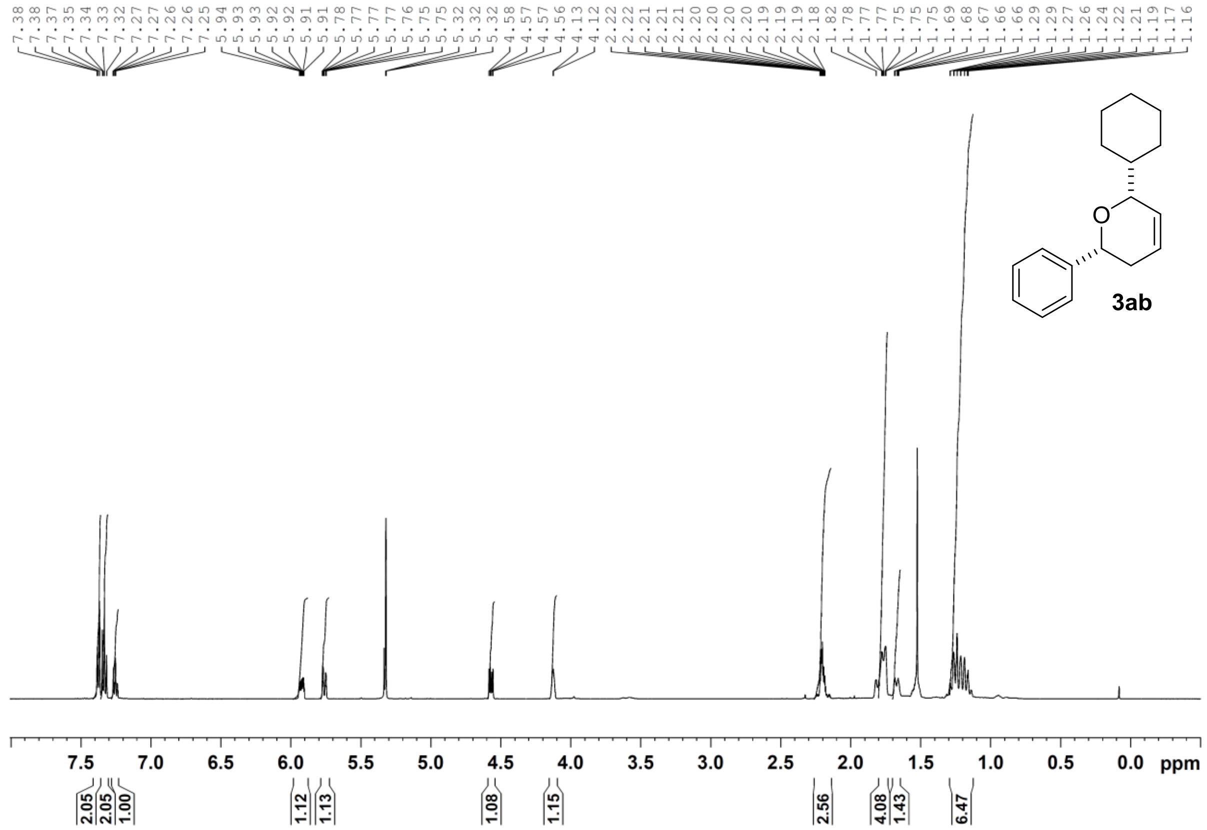
^{1}H NMR (*trans*-**3ab**)



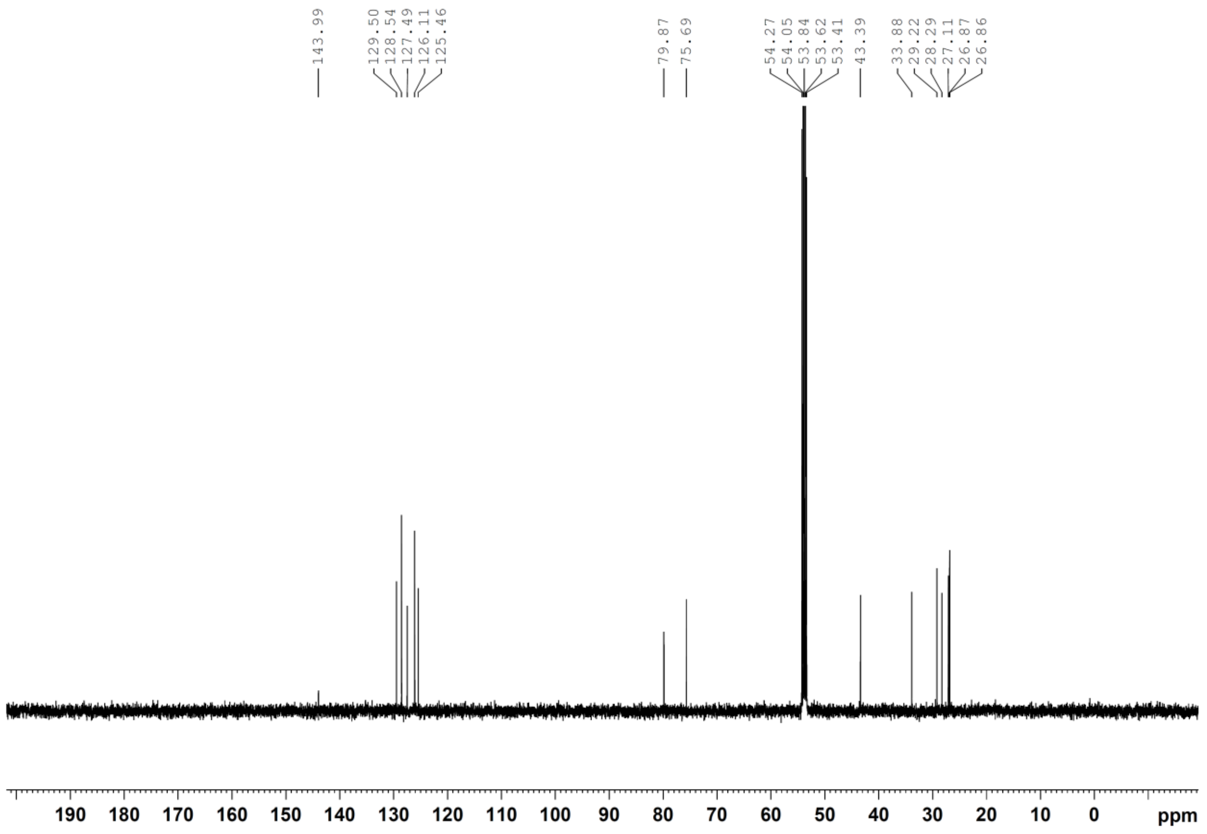
^{13}C NMR (*trans*-**3ab**)



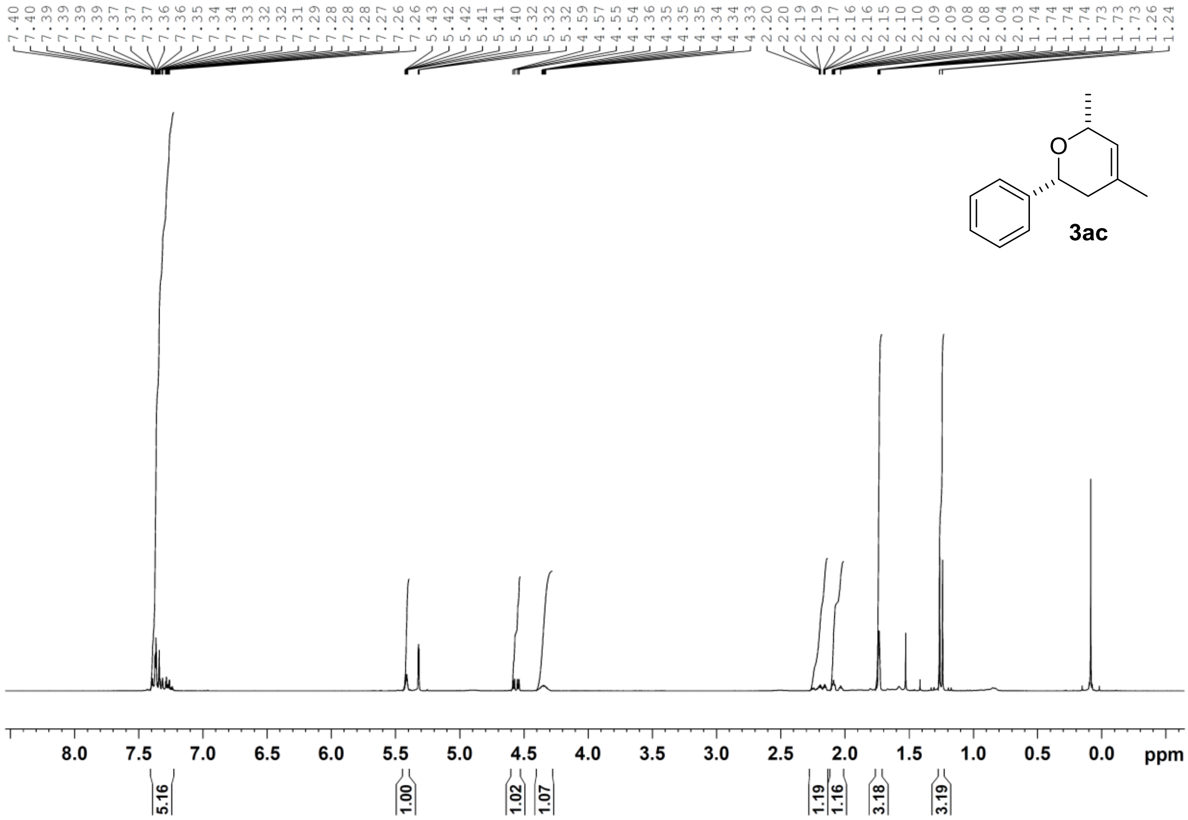
^{1}H NMR (*cis*-**3ab**)



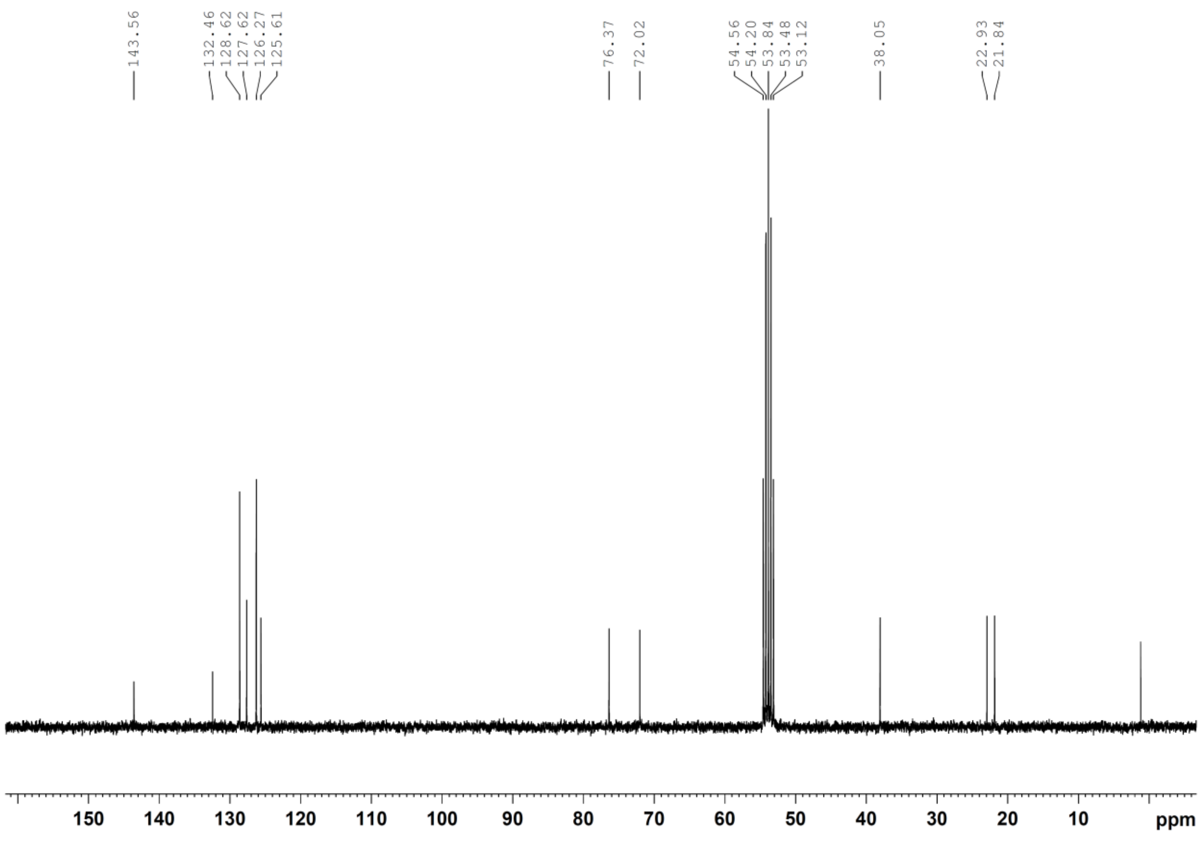
^{13}C NMR (*cis*-**3ab**)



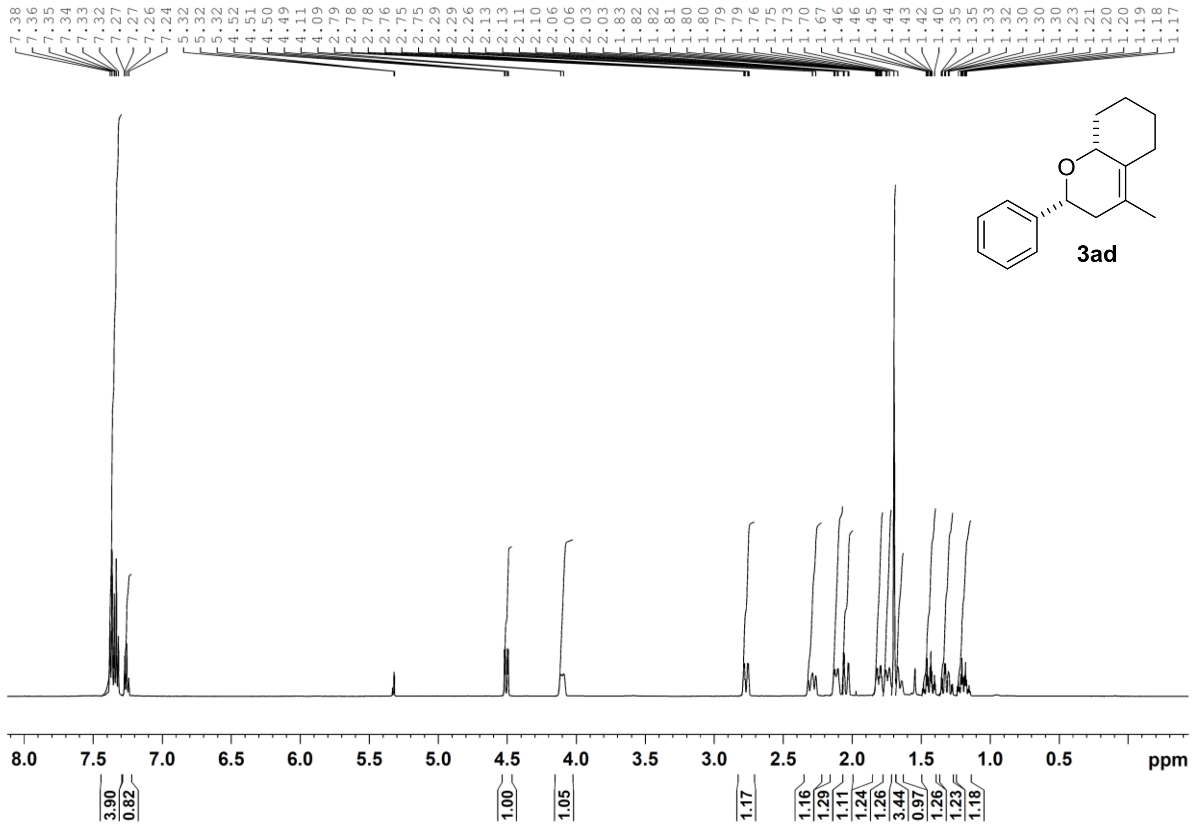
^{1}H NMR (3ac)



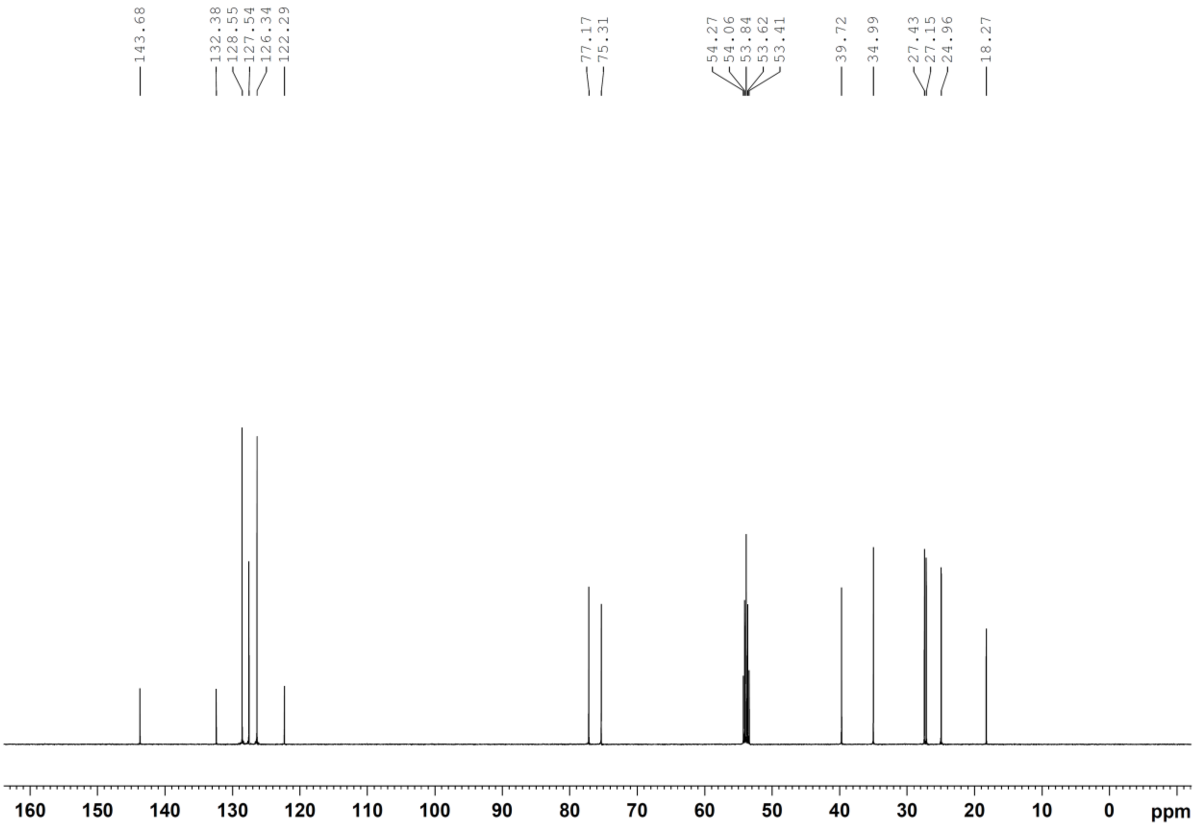
^{13}C NMR (3ac)



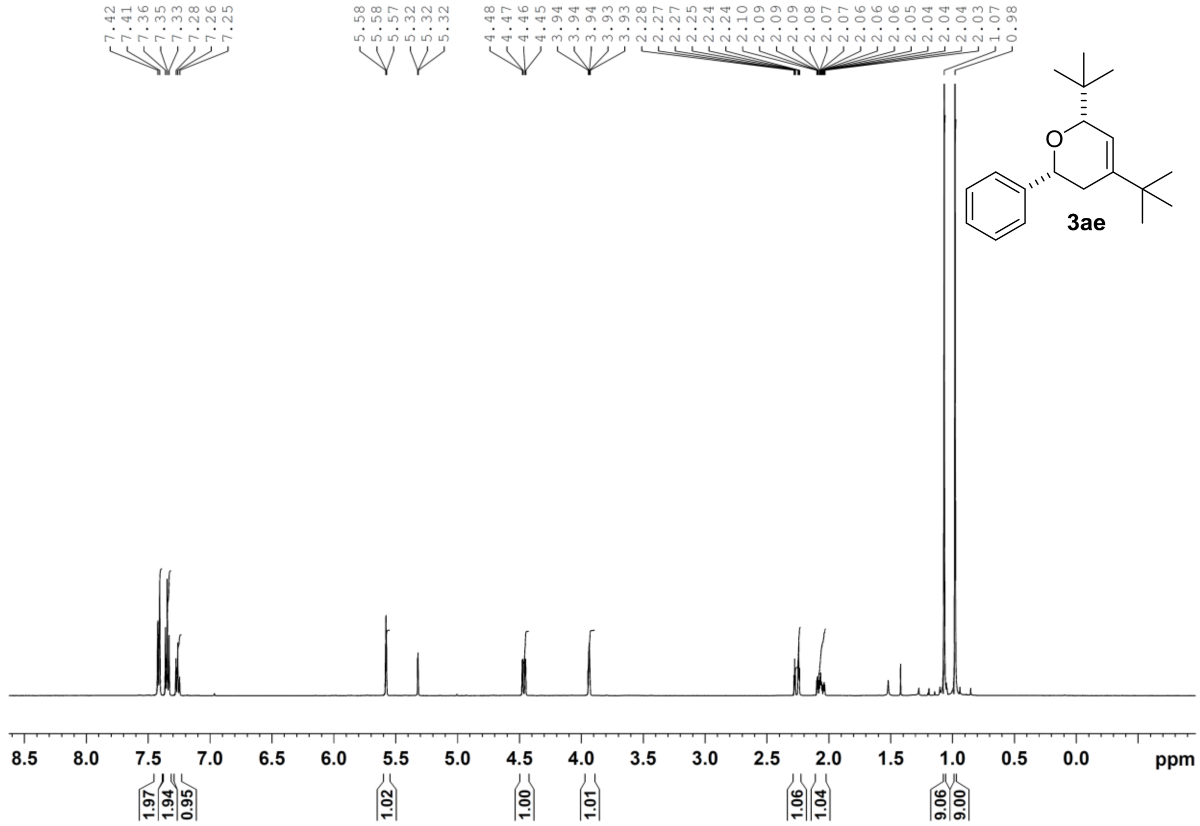
^{1}H NMR (3ad)



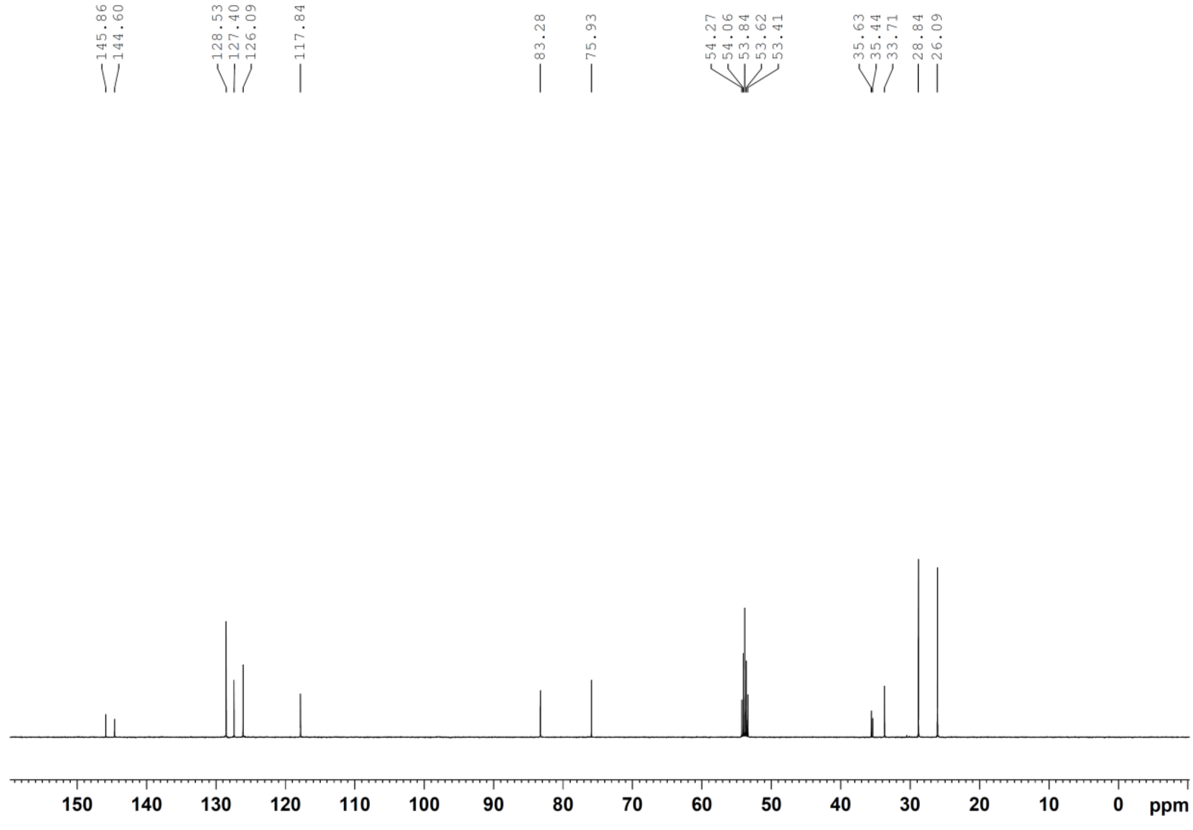
^{13}C NMR (3ad)



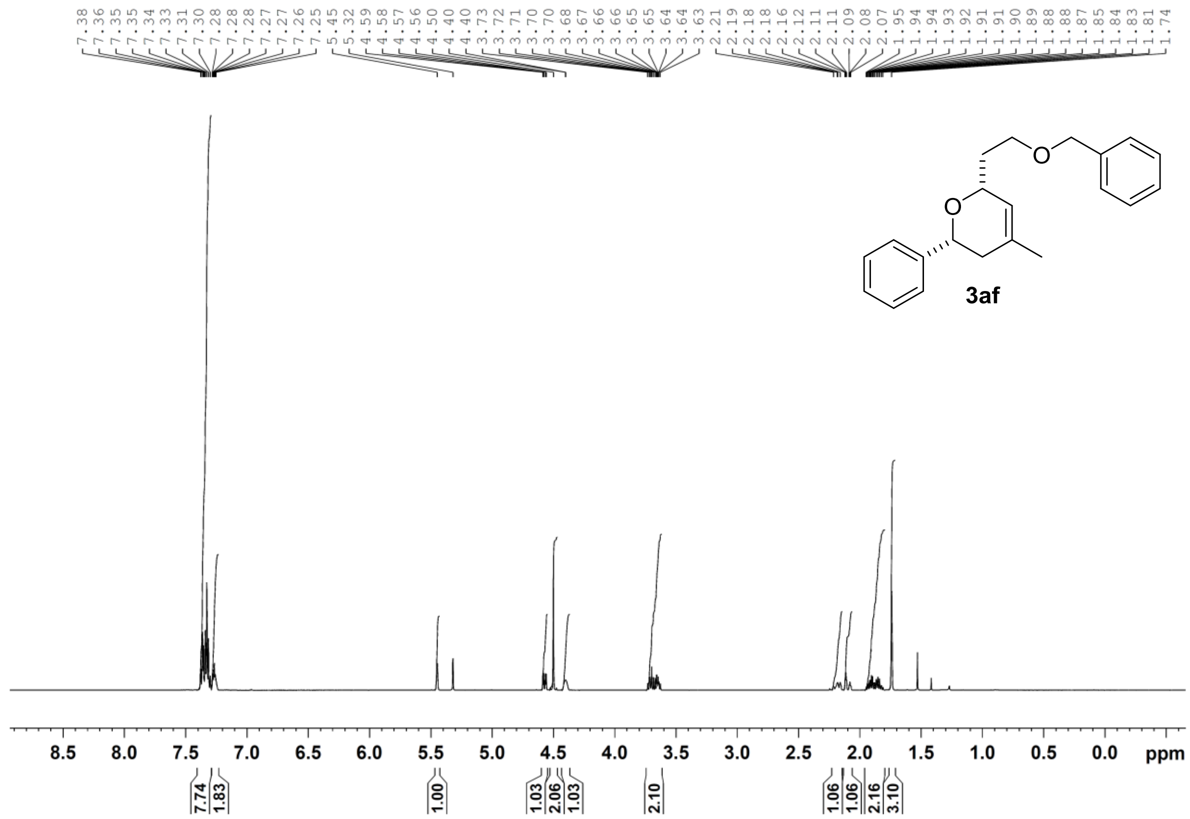
^{1}H NMR (3ae)



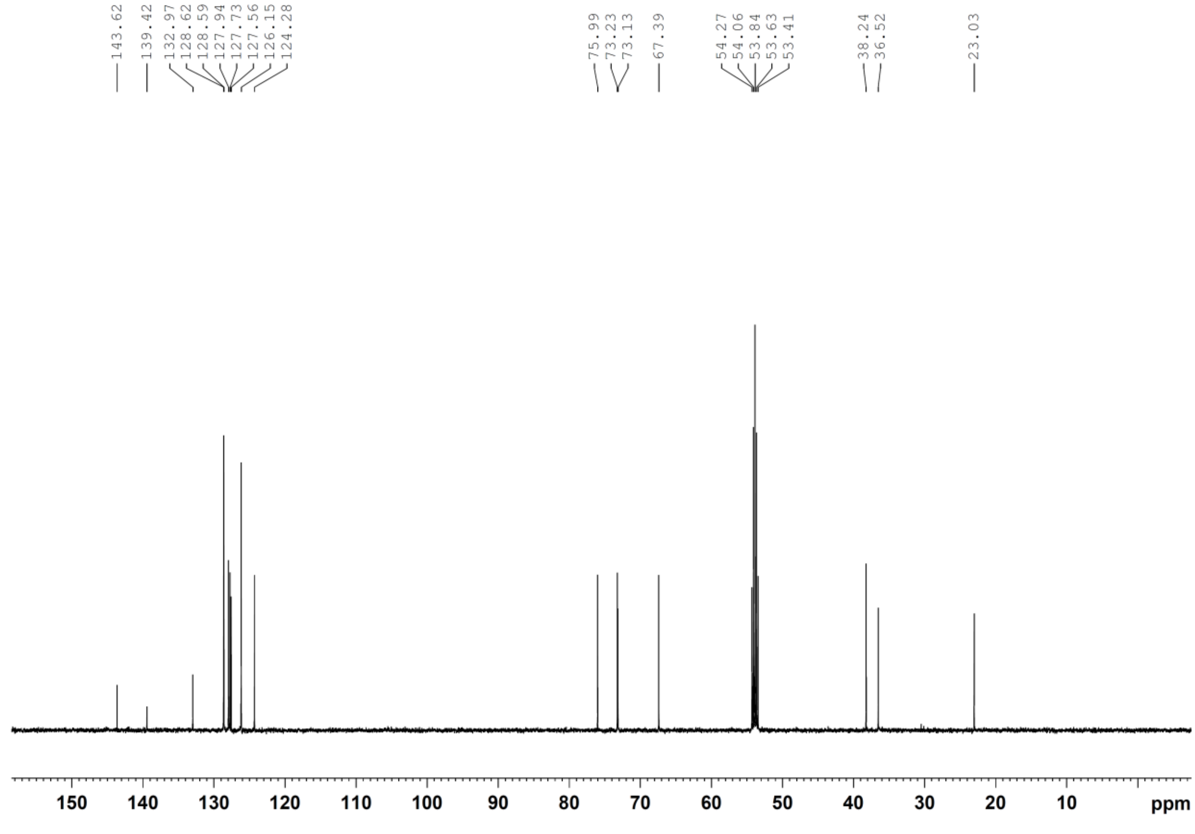
^{13}C NMR (3ae)



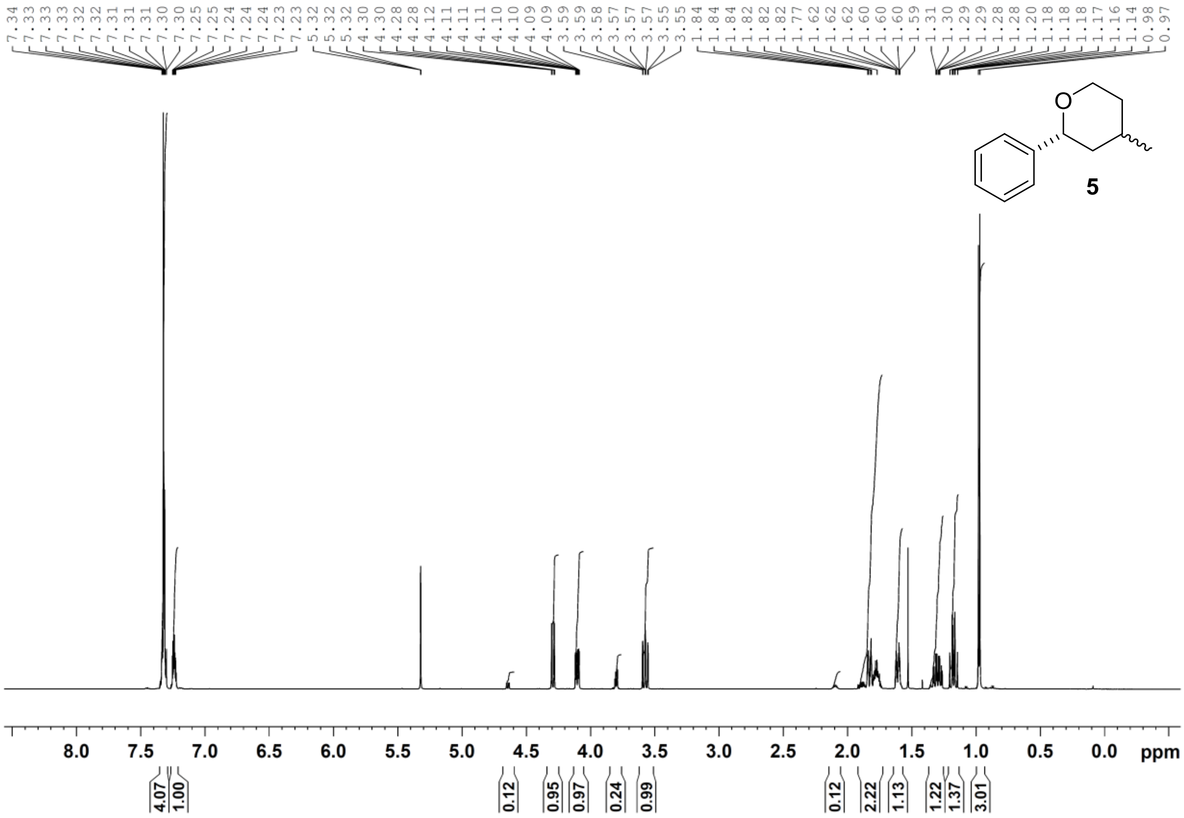
^{1}H NMR (3af)



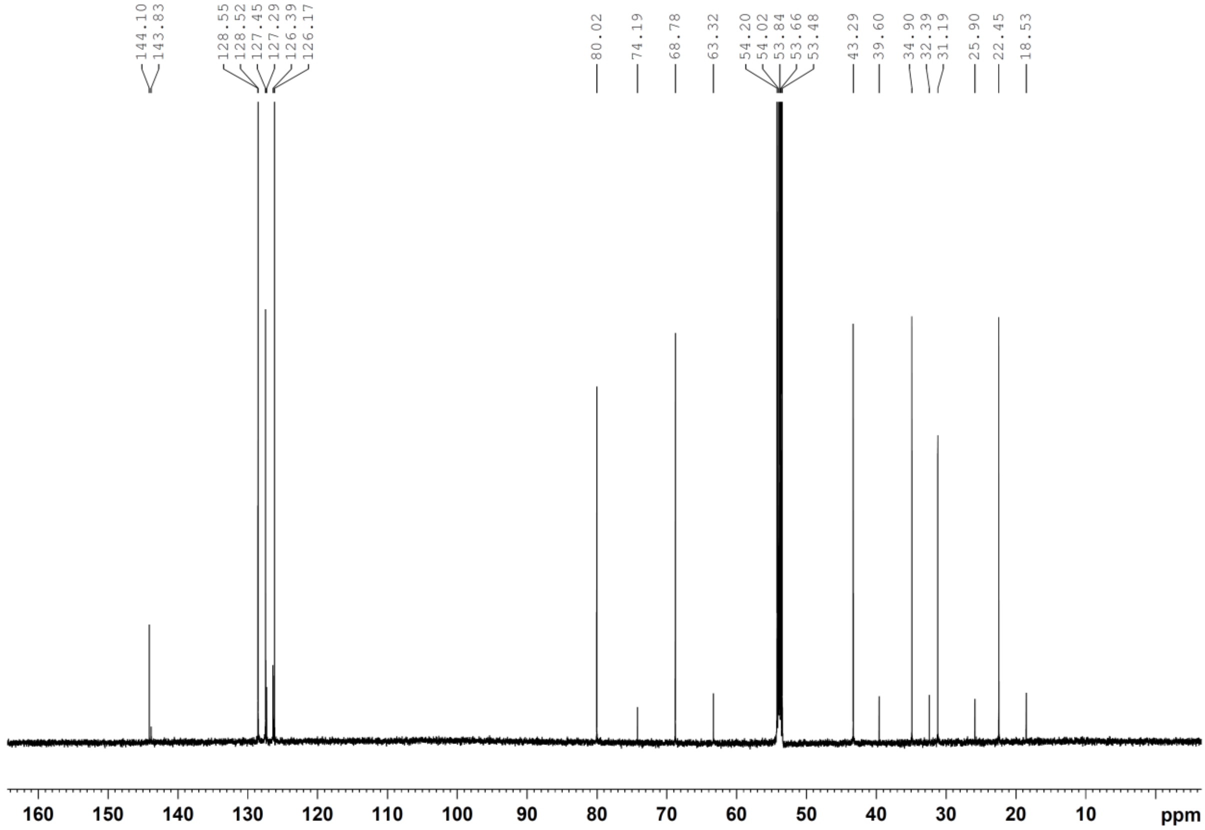
^{13}C NMR (3af)



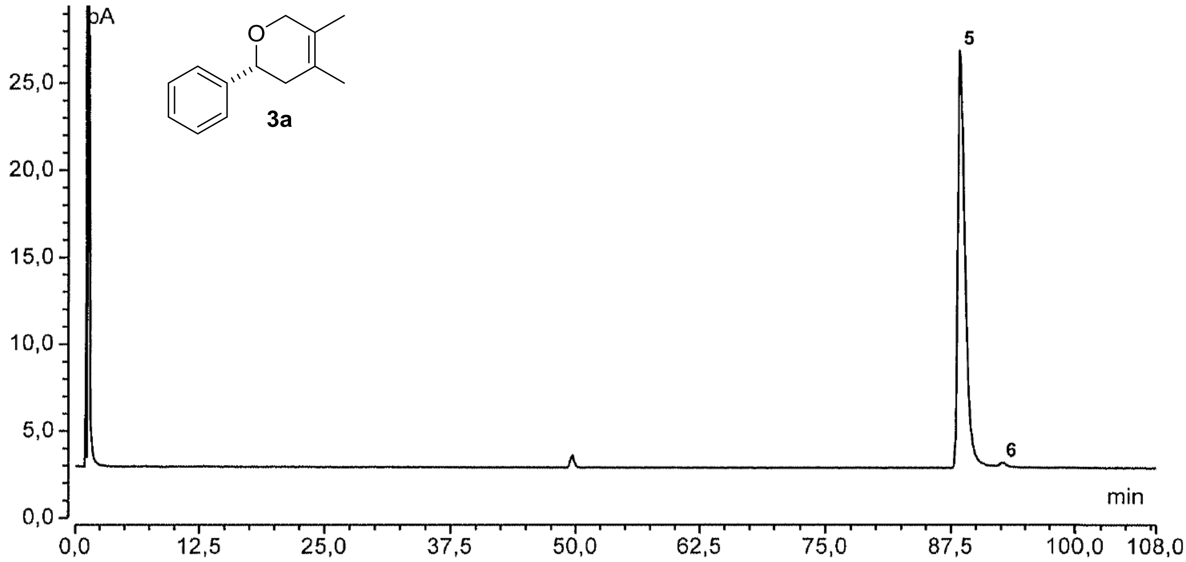
^{1}H NMR (5)



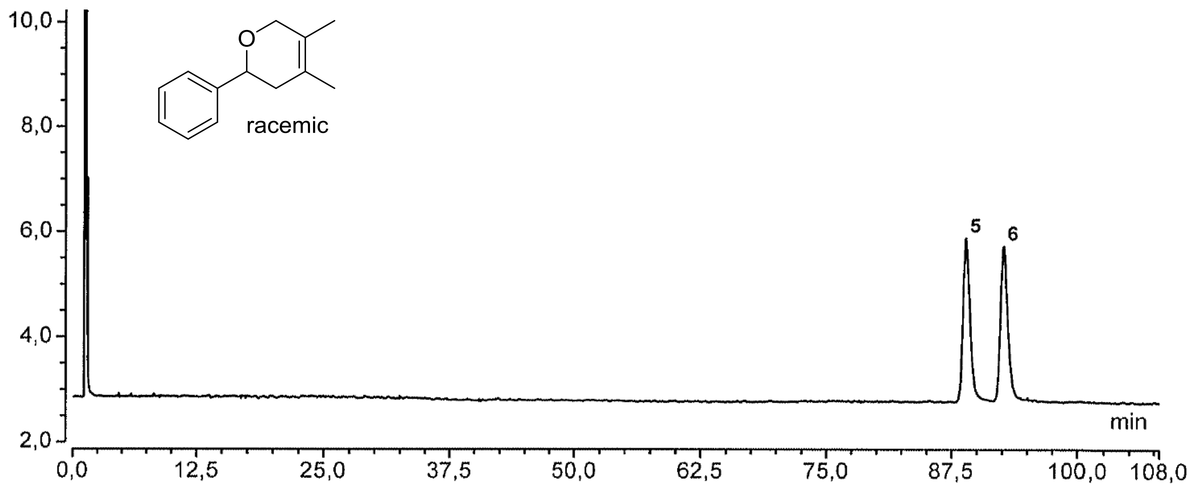
^{13}C NMR (5)



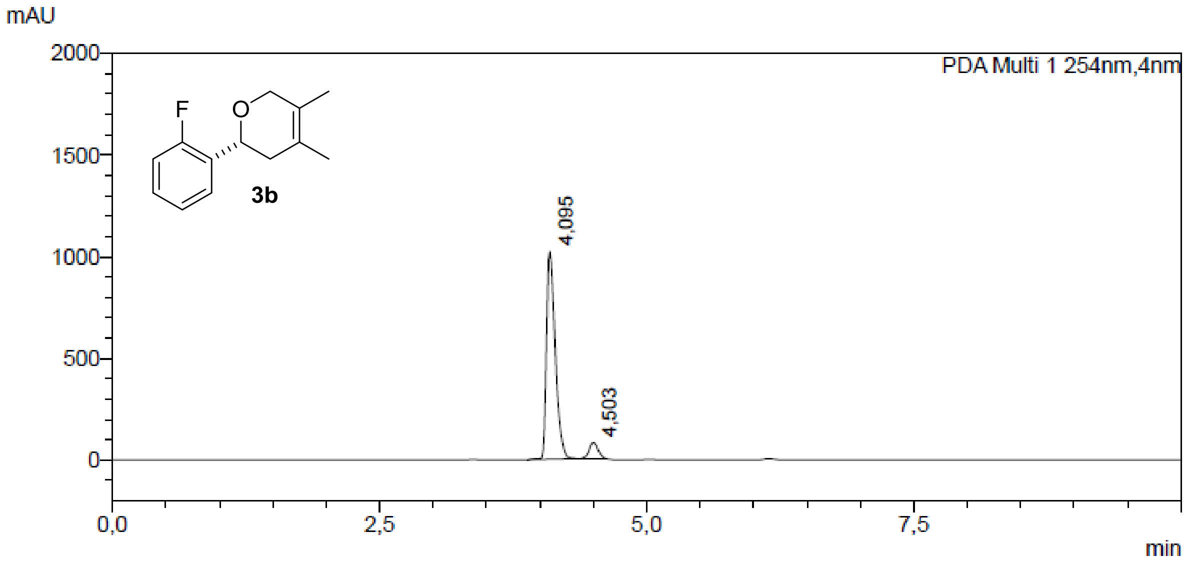
HPLC and GC Traces



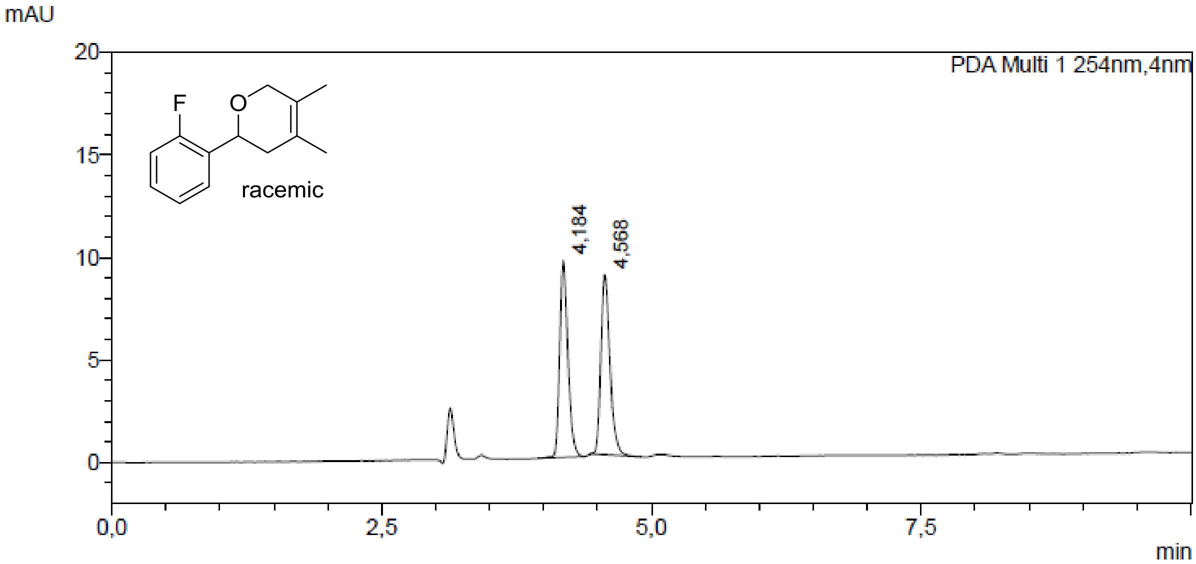
Peak #	Ret. Time/min	Area/%
5	88.43	98.34
6	92.67	1.66



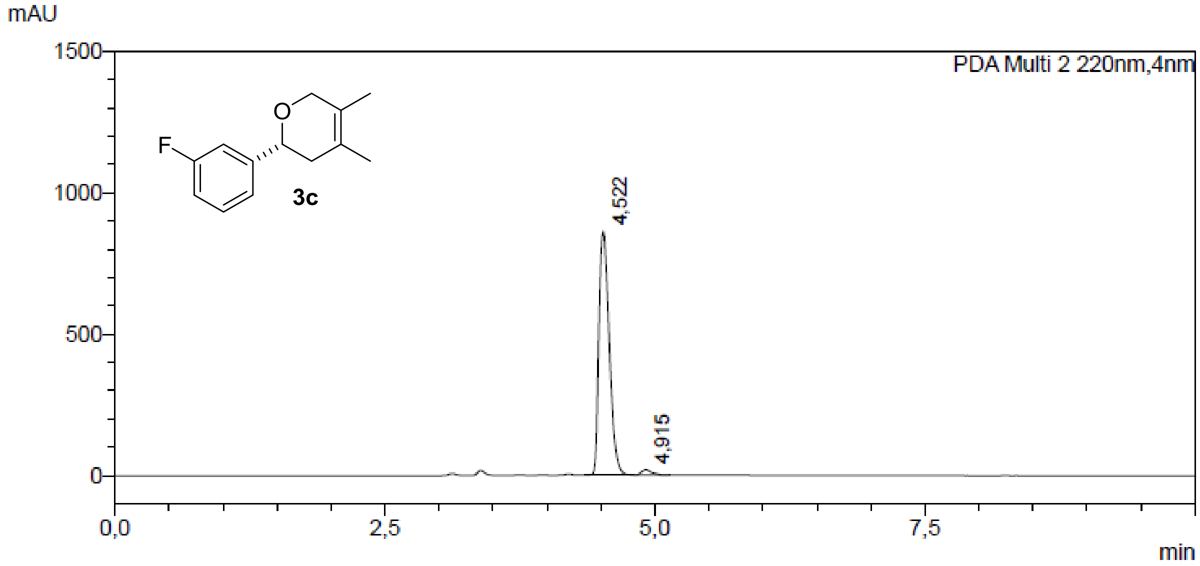
Peak #	Ret. Time/min	Area/%
5	88.95	49.98
6	92.68	50.02



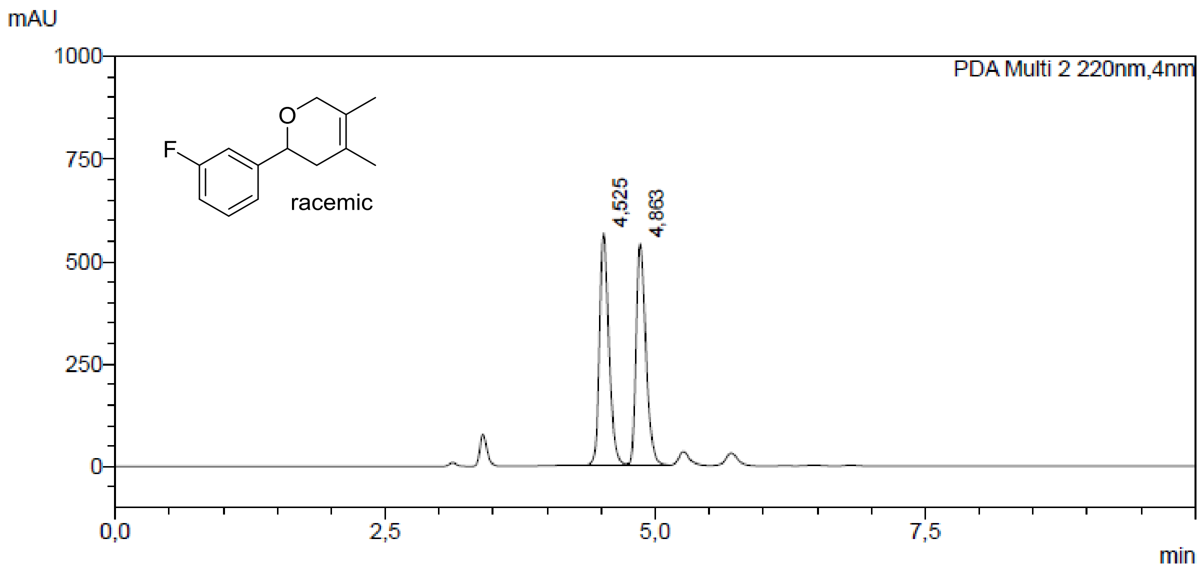
Peak #	Ret. Time/min	Area/%
1	4.10	92.34
2	4.50	7.66



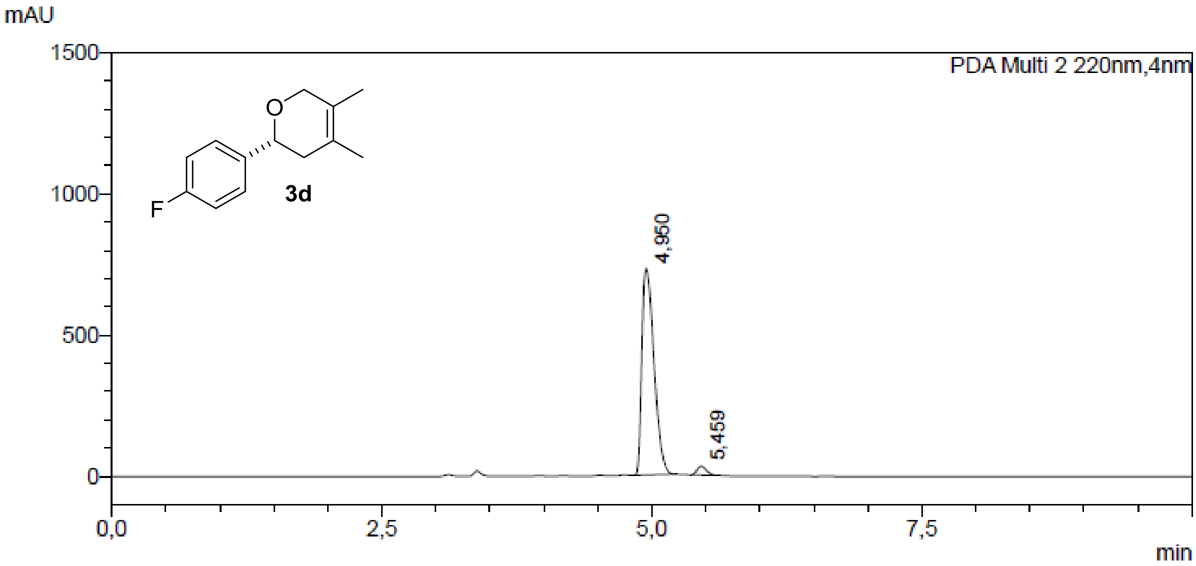
Peak #	Ret. Time/min	Area/%
1	4.18	50.01
2	4.57	49.99



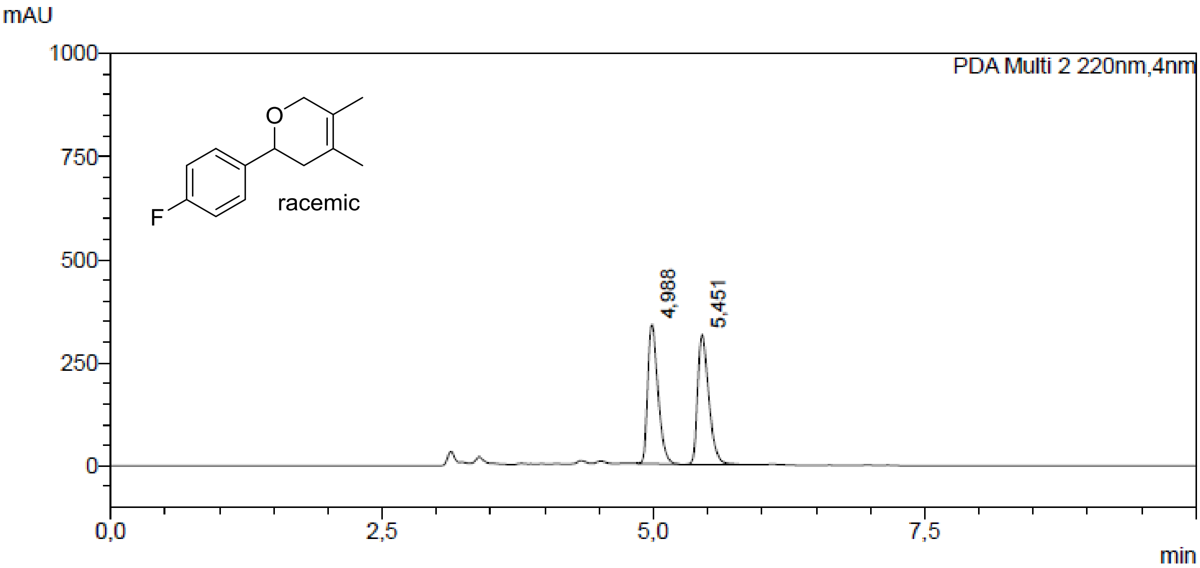
Peak #	Ret. Time/min	Area/%
1	4.52	97.86
2	4.92	2.14



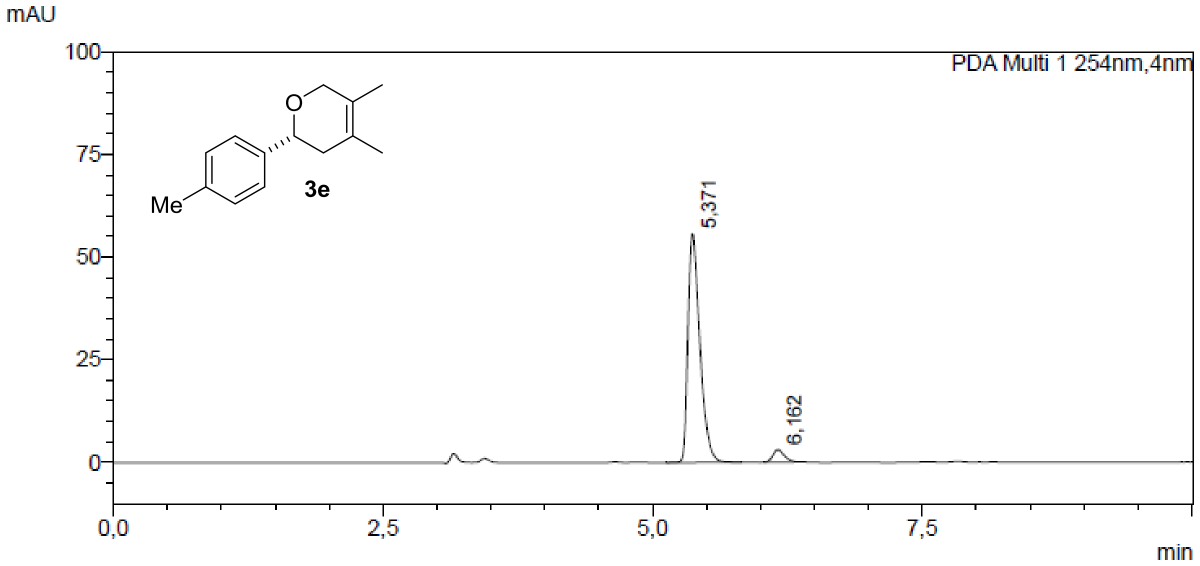
Peak #	Ret. Time/min	Area/%
1	4.53	50.21
2	4.86	49.79



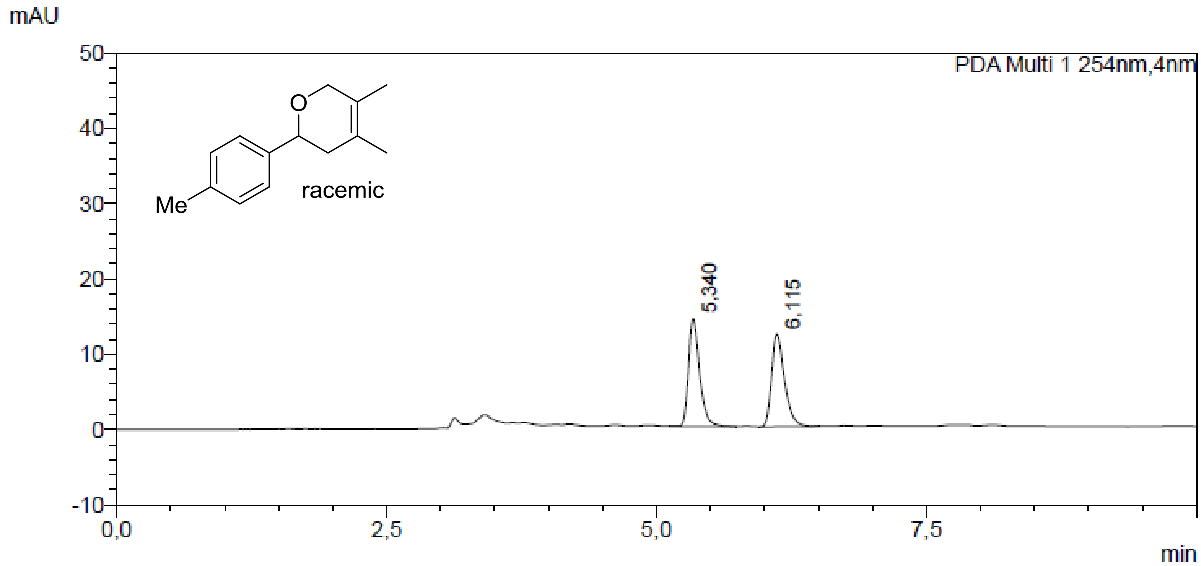
Peak #	Ret. Time/min	Area/%
1	4.95	96.84
2	5.46	3.16



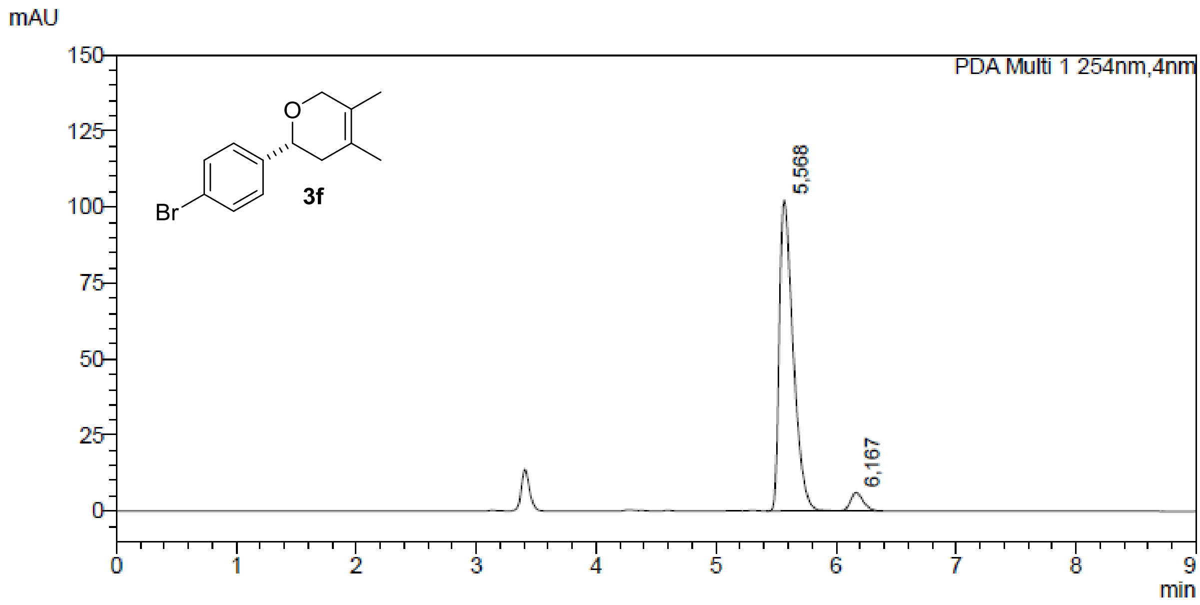
Peak #	Ret. Time/min	Area/%
1	4.99	49.63
2	5.45	50.37



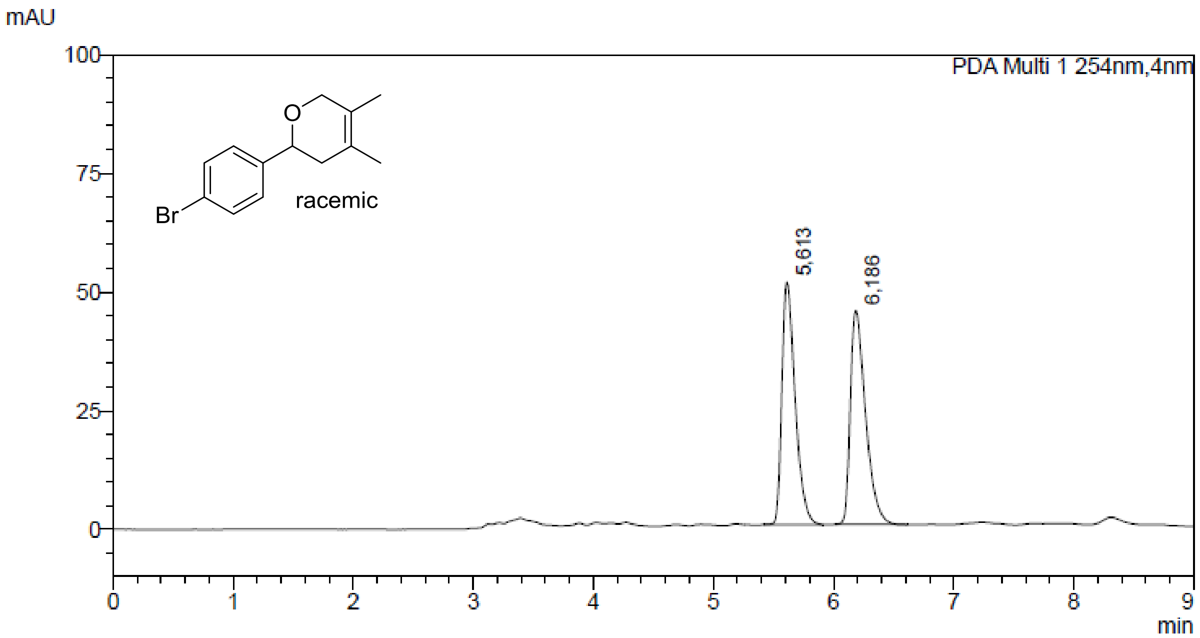
Peak #	Ret. Time/min	Area/%
1	5.37	95.01
2	6.16	4.99



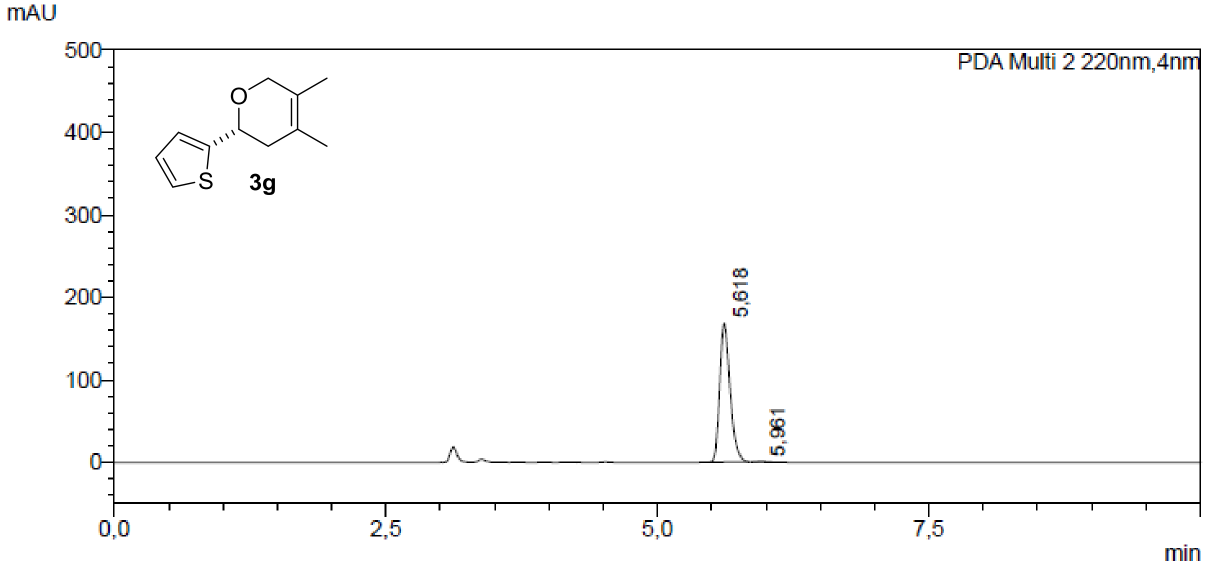
Peak #	Ret. Time/min	Area/%
1	5.34	50.10
2	6.12	49.90



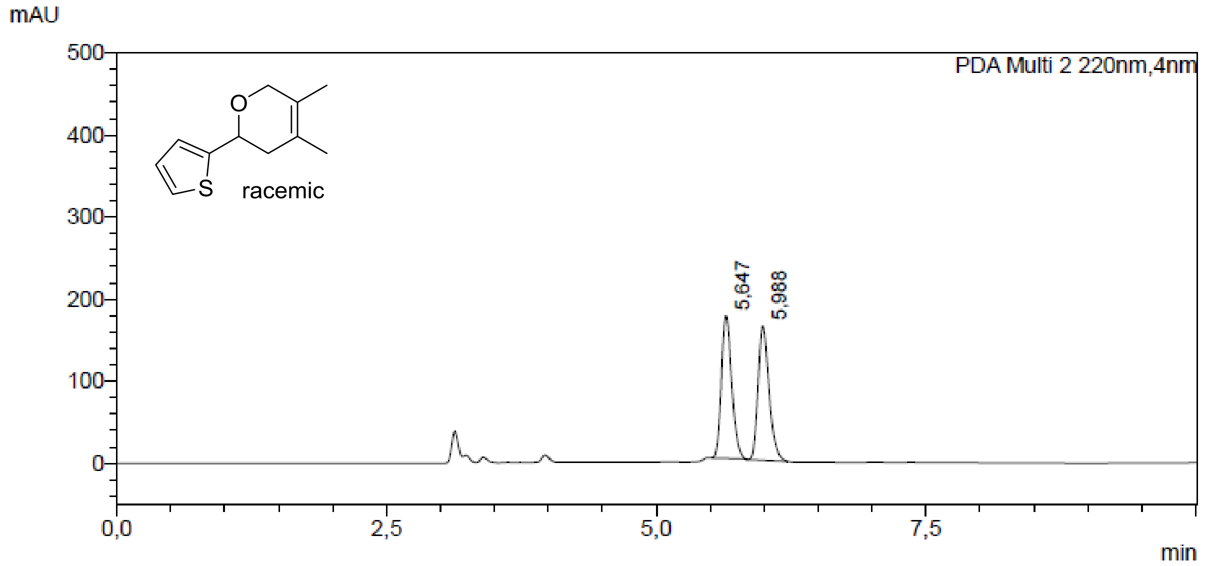
Peak #	Ret. Time/min	Area/%
1	5.57	94.97
2	6.17	5.03



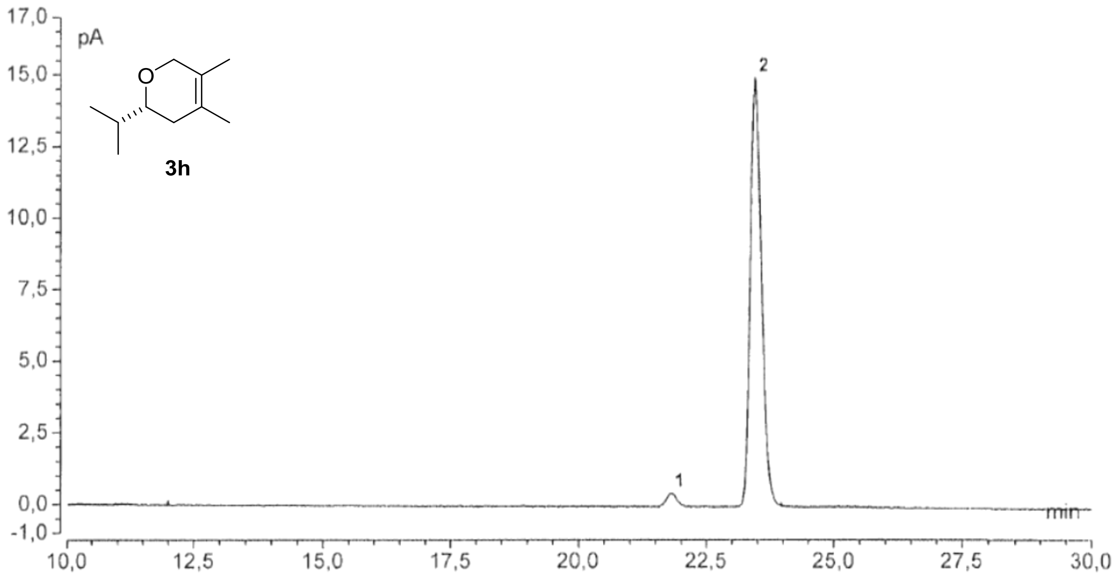
Peak #	Ret. Time/min	Area/%
1	5.61	49.66
2	6.19	50.34



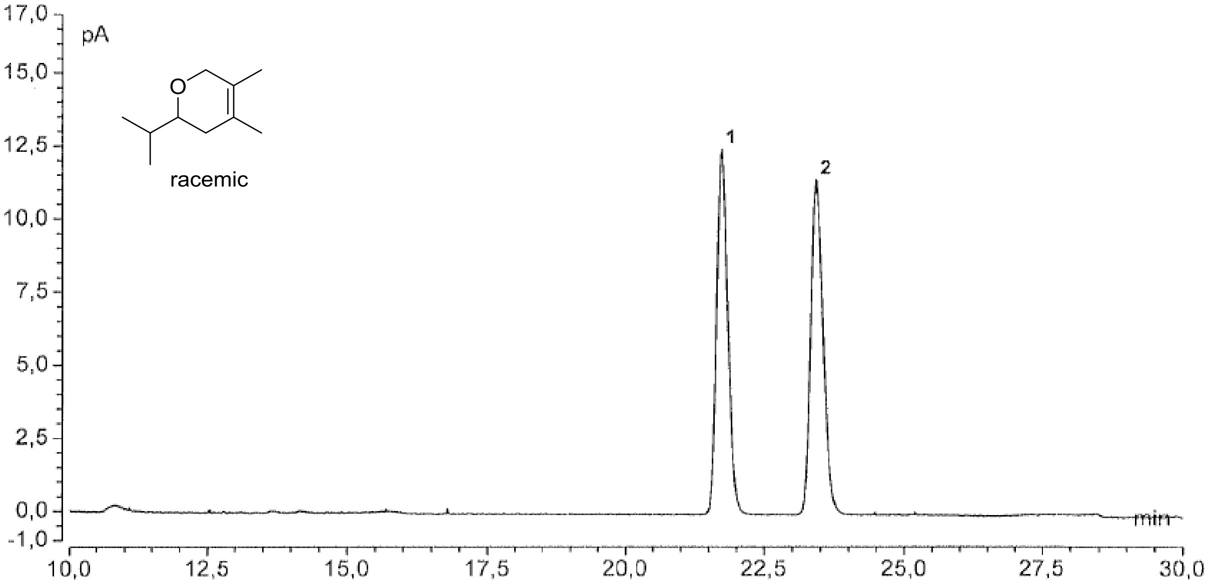
Peak #	Ret. Time/min	Area/%
1	5.52	99.74
2	5.96	0.26



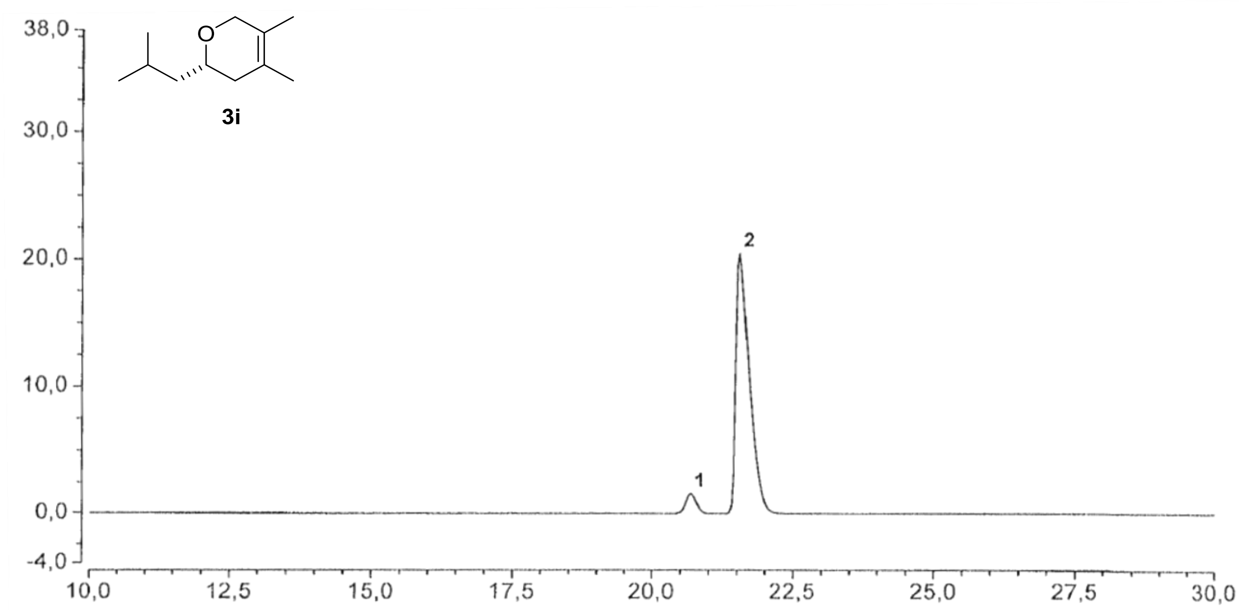
Peak #	Ret. Time/min	Area/%
1	5.65	49.77
2	5.99	50.23



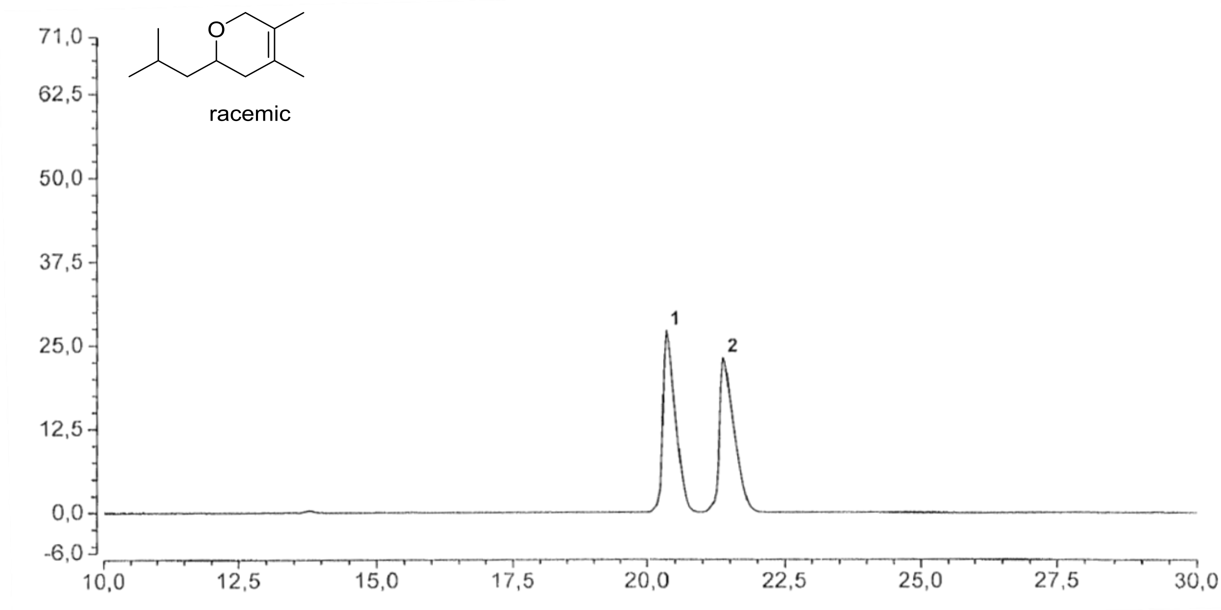
Peak #	Ret. Time/min	Area/%
1	21.81	2.64
2	23.46	97.36



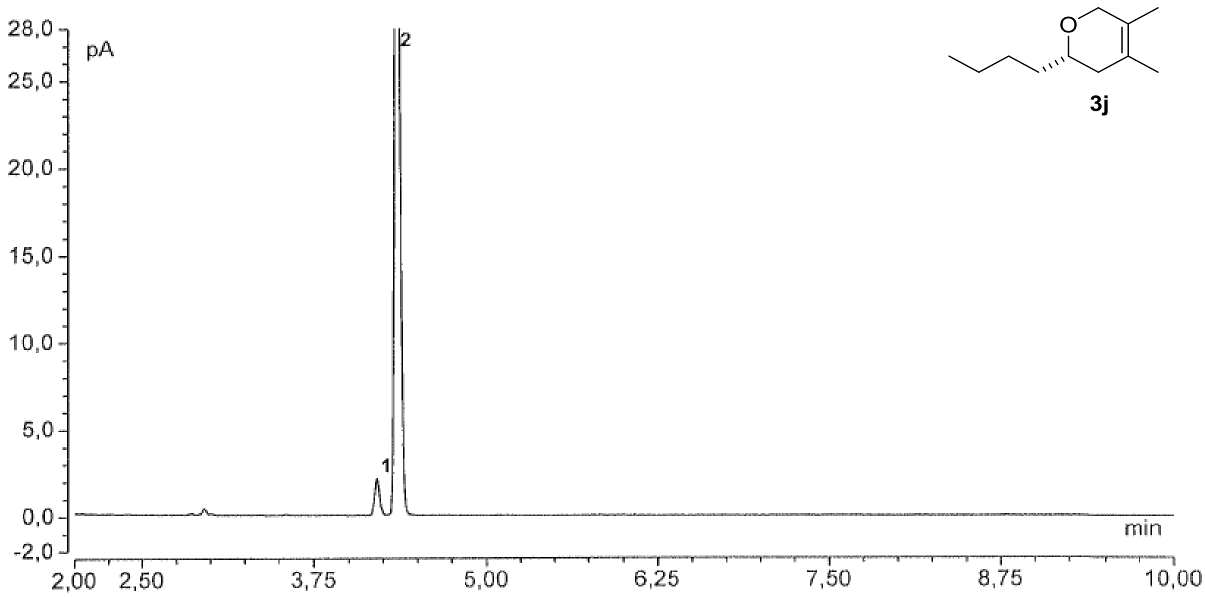
Peak #	Ret. Time/min	Area/%
1	21.75	50.11
2	23.43	49.89



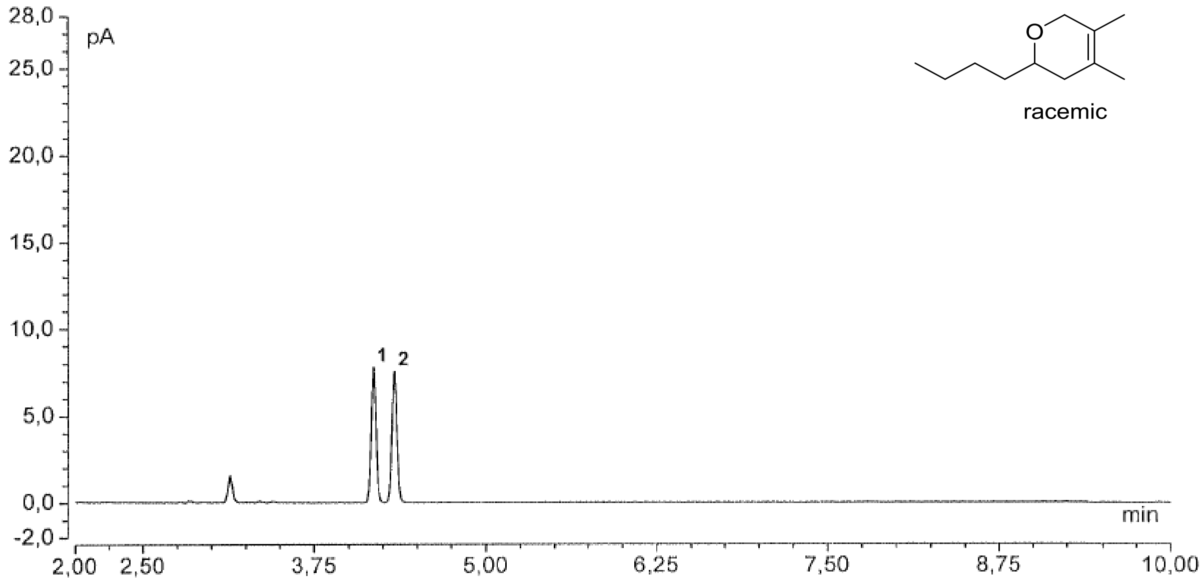
Peak #	Ret. Time/min	Area/%
1	20.68	5.55
2	21.55	94.45



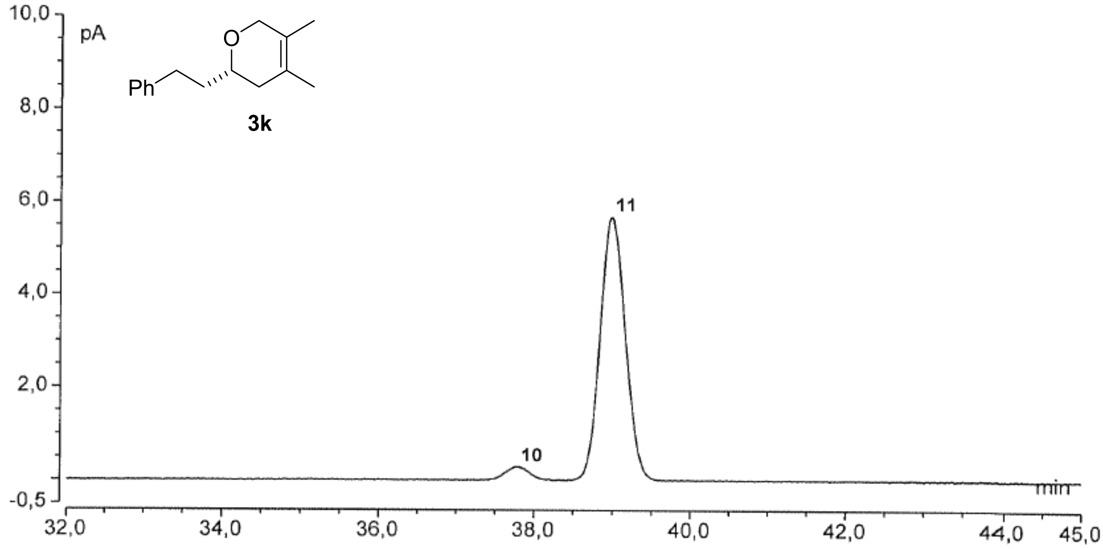
Peak #	Ret. Time/min	Area/%
1	20.34	50.04
2	21.38	49.96



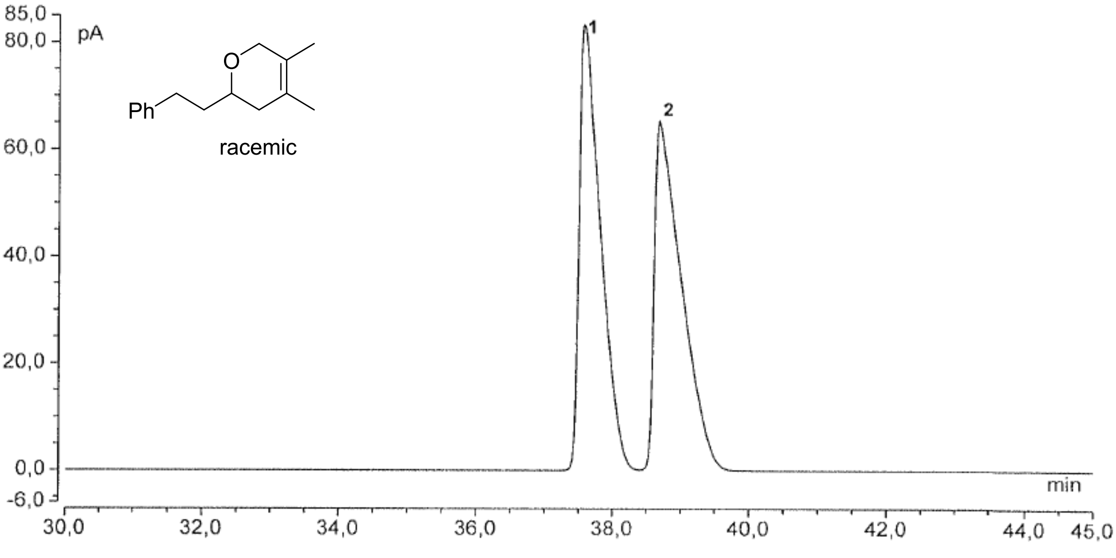
Peak #	Ret. Time/min	Area/%
1	4.21	3.30
2	4.35	96.70



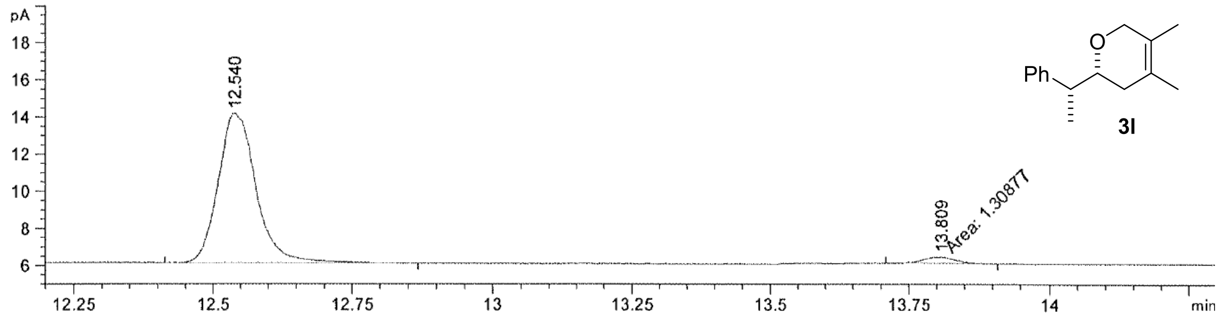
Peak #	Ret. Time/min	Area/%
1	4.18	50.16
2	4.33	49.84



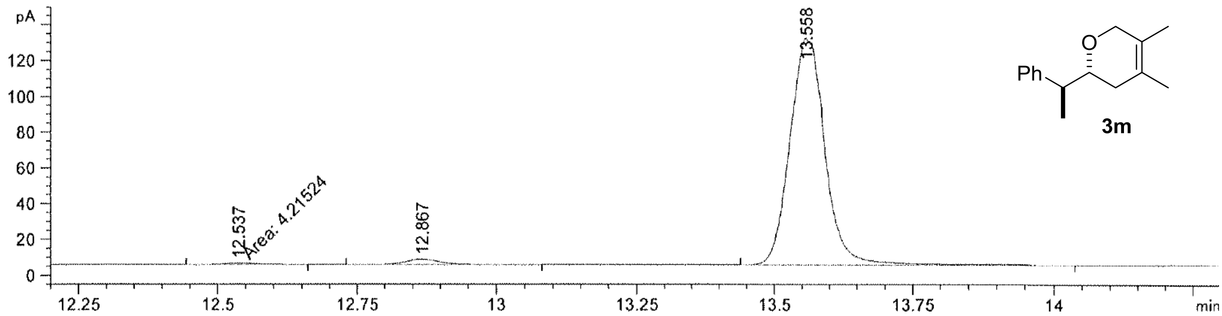
Peak #	Ret. Time/min	Area/%
10	37.79	4.49
11	38.98	95.51



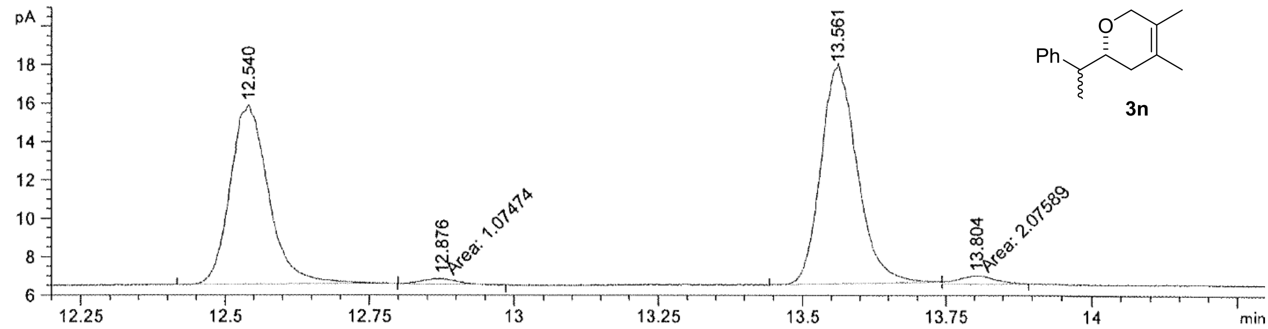
Peak #	Ret. Time/min	Area/%
1	37.59	50.04
2	38.69	49.96



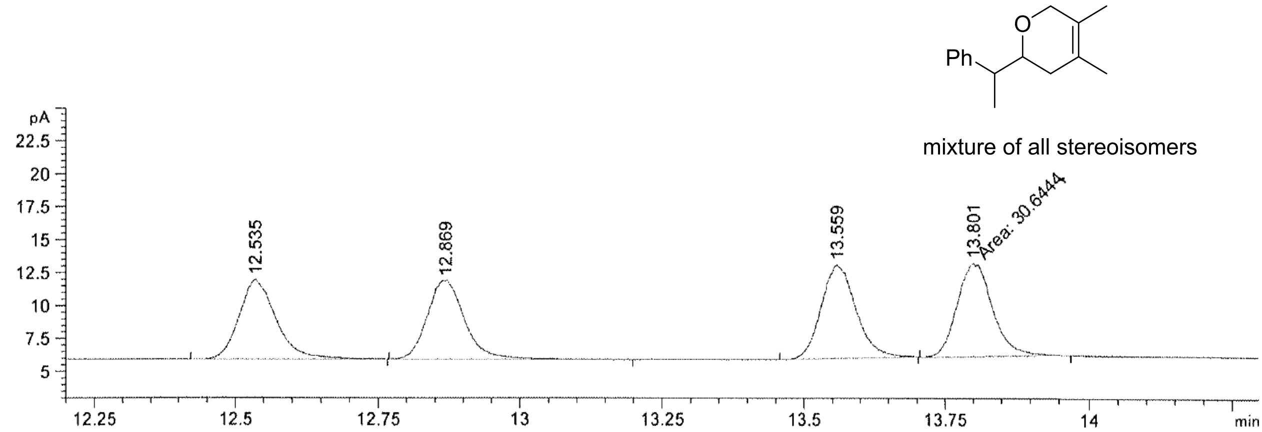
Peak #	Ret. Time/min	Area/%
1	12.54	96.7016
4	13.81	3.2984



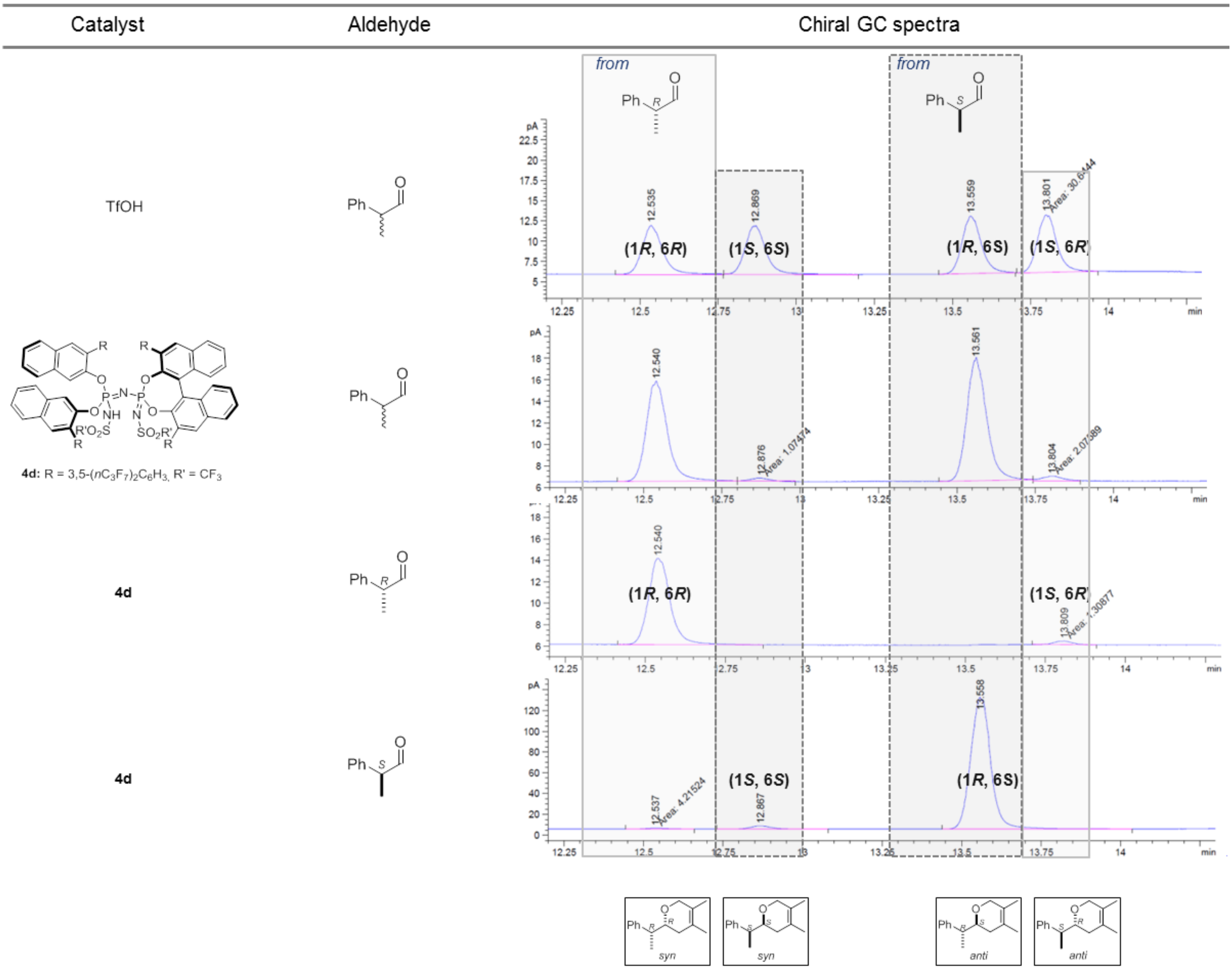
Peak #	Ret. Time/min	Area/%
1	12.54	0.7309
2	12.87	2.4147
3	13.56	96.8544

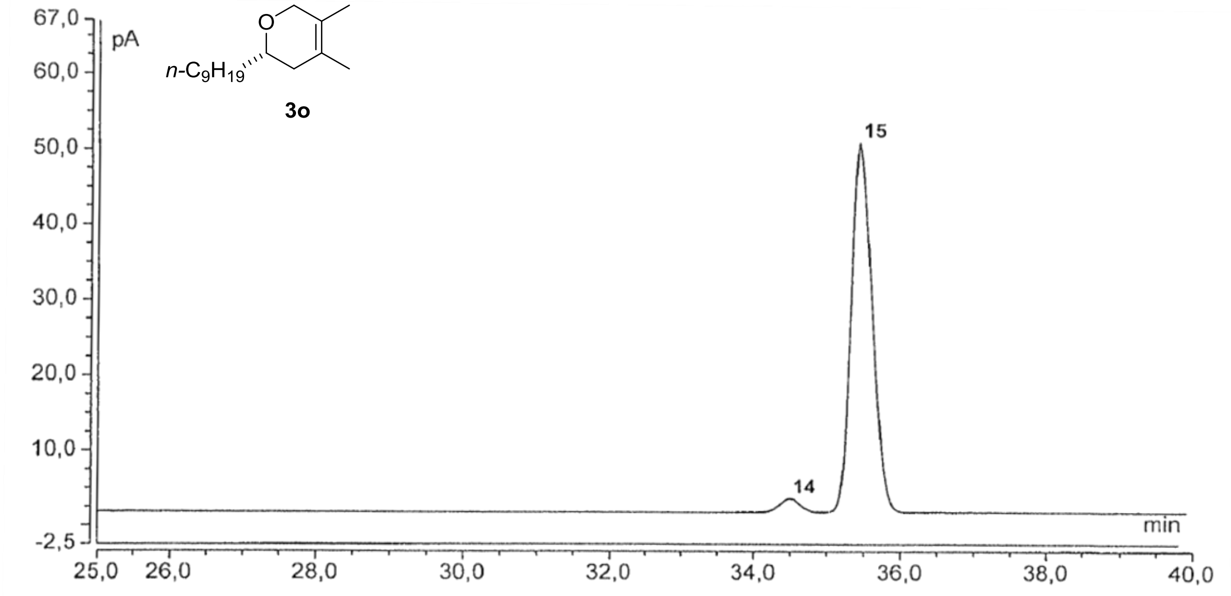


Peak #	Ret. Time/min	Area/%
1	12.54	44.9979
2	12.88	1.1056
3	13.56	51.7611
4	13.80	2.1354

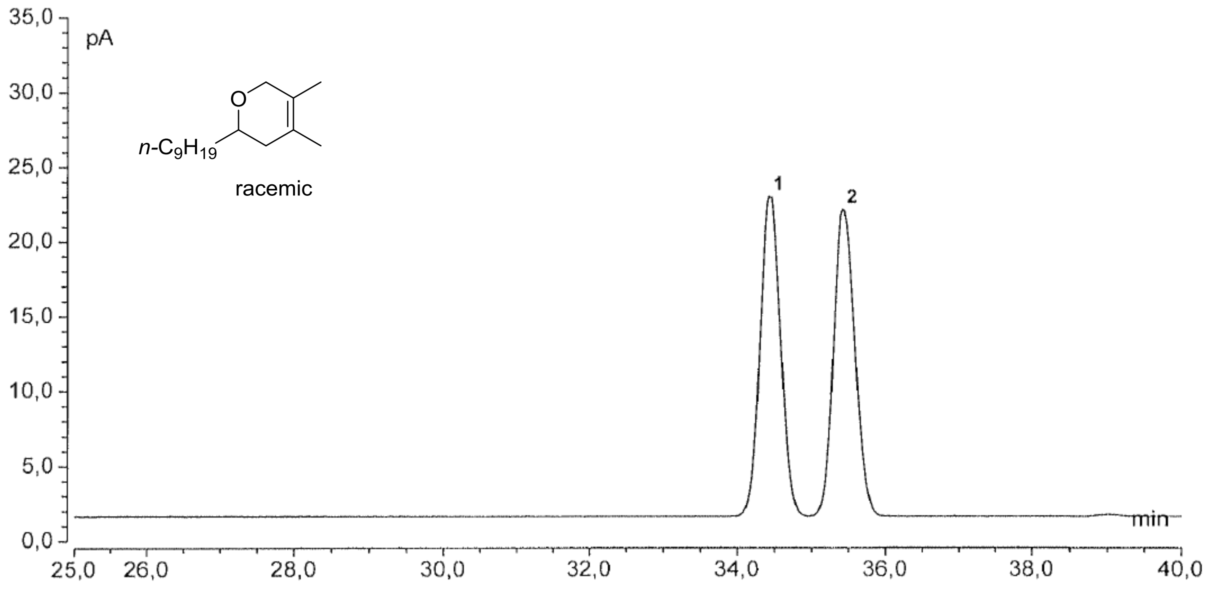


Peak #	Ret. Time/min	Area/%
1	12.54	23.5496
2	12.87	23.6841
3	13.56	26.3370
4	13.80	26.4293

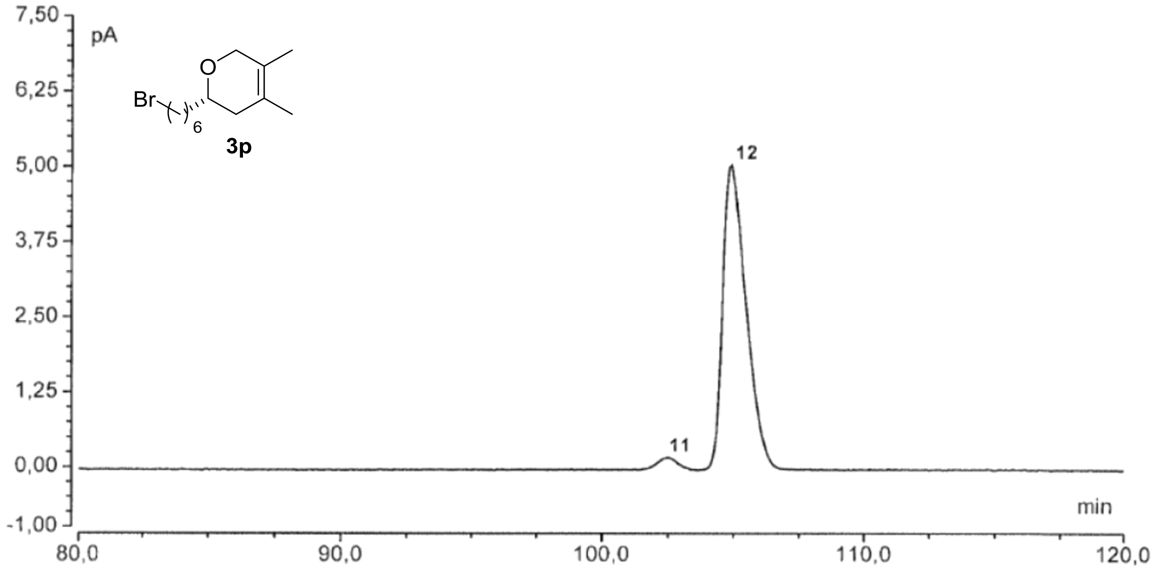




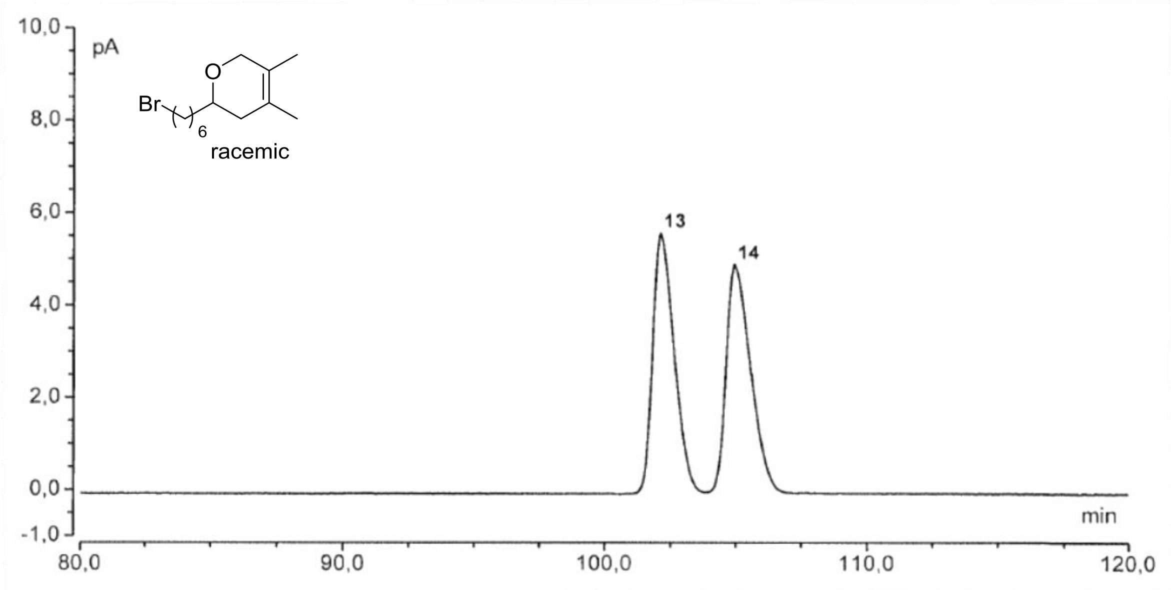
Peak #	Ret. Time/min	Area/%
14	34.49	3.47
15	35.43	96.53



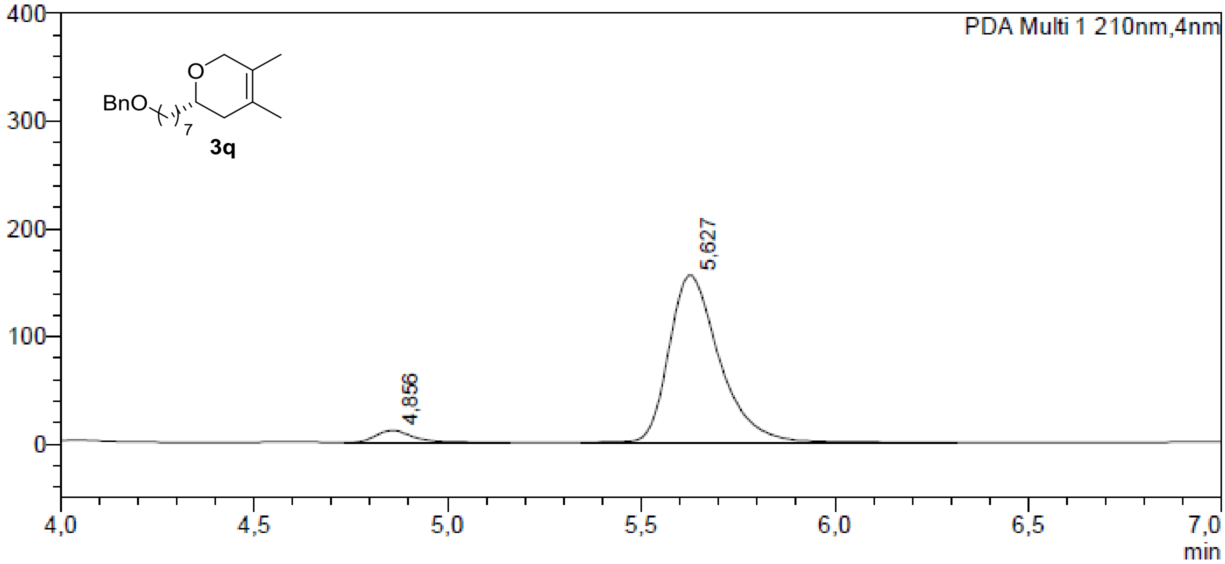
Peak #	Ret. Time/min	Area/%
1	34.45	49.98
2	35.43	50.02



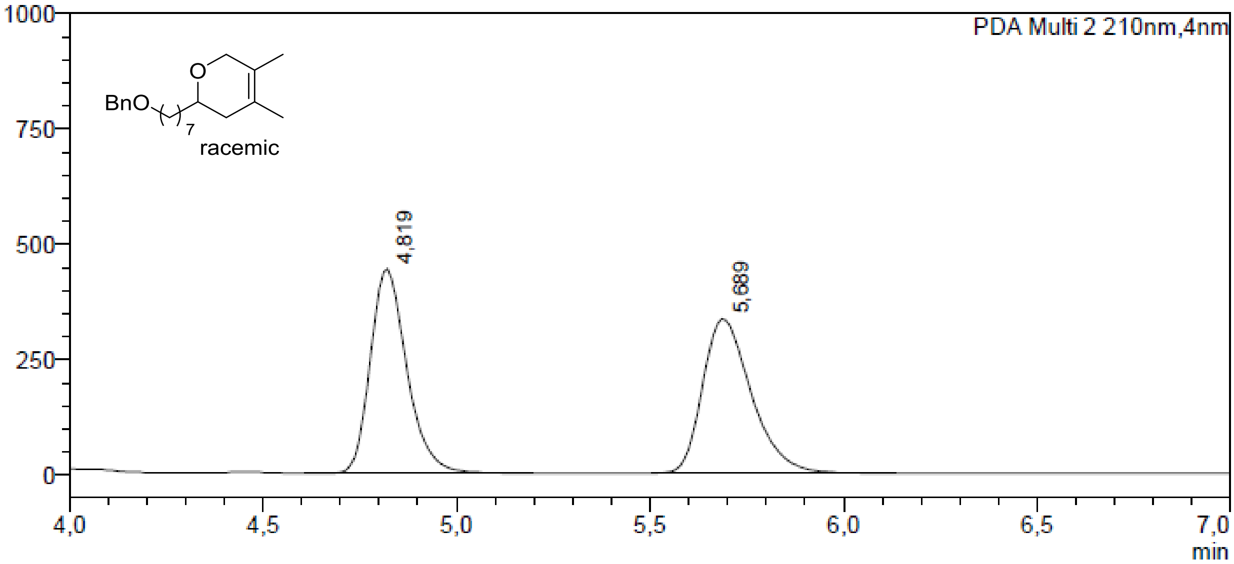
Peak #	Ret. Time/min	Area/%
11	102.41	3.56
12	104.94	96.44



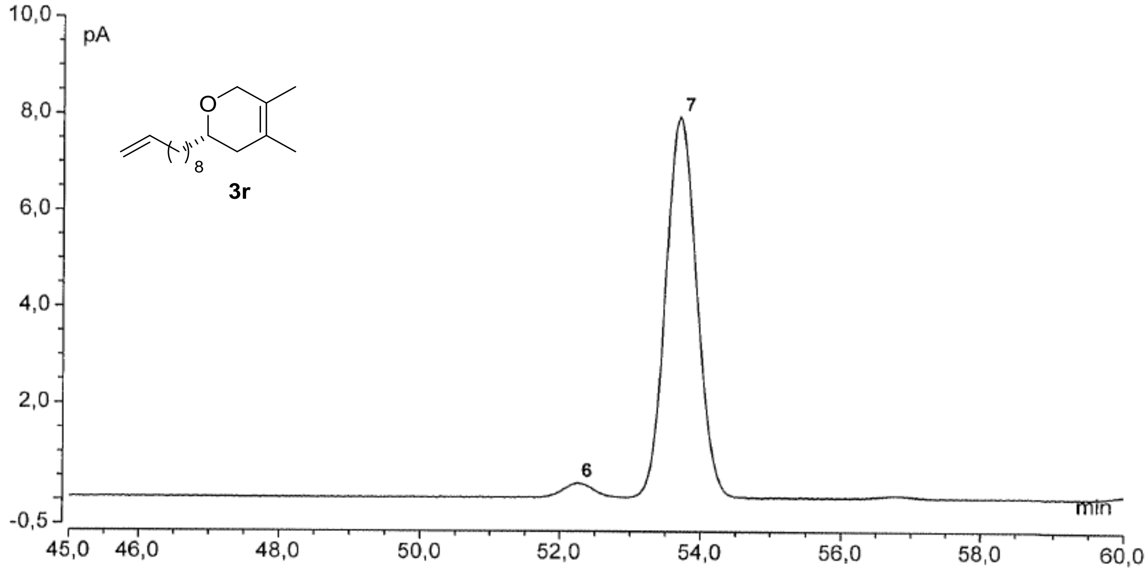
Peak #	Ret. Time/min	Area/%
13	102.11	49.93
14	104.93	50.07



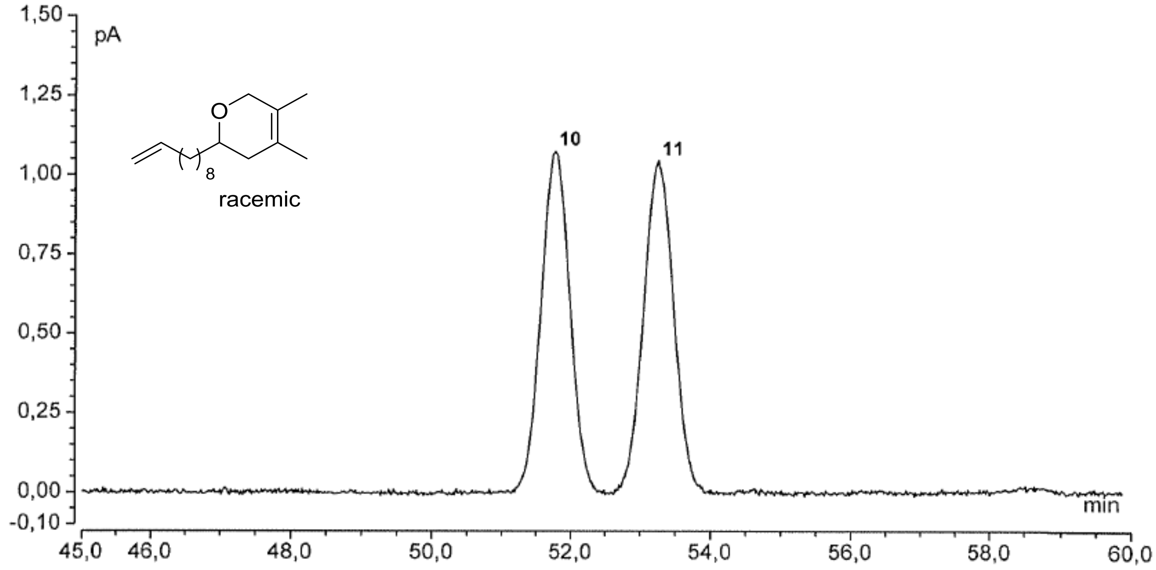
Peak #	Ret. Time/min	Area/%
1	4.86	5.22
2	5.63	94.78



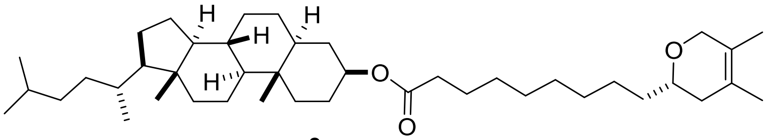
Peak #	Ret. Time/min	Area/%
1	4.82	49.88
2	5.69	50.12



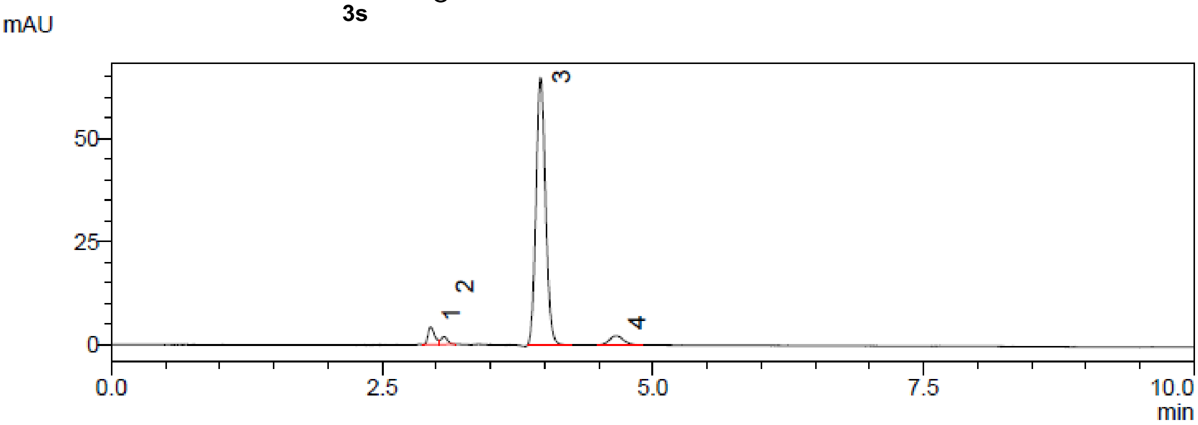
Peak #	Ret. Time/min	Area/%
6	52.26	3.45
7	53.72	96.55



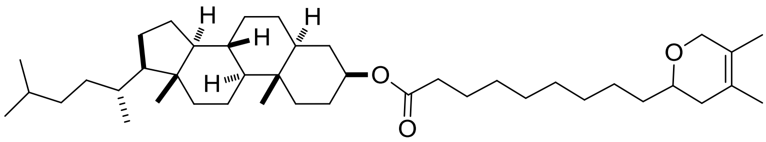
Peak #	Ret. Time/min	Area/%
10	51.78	50.08
11	53.26	49.92

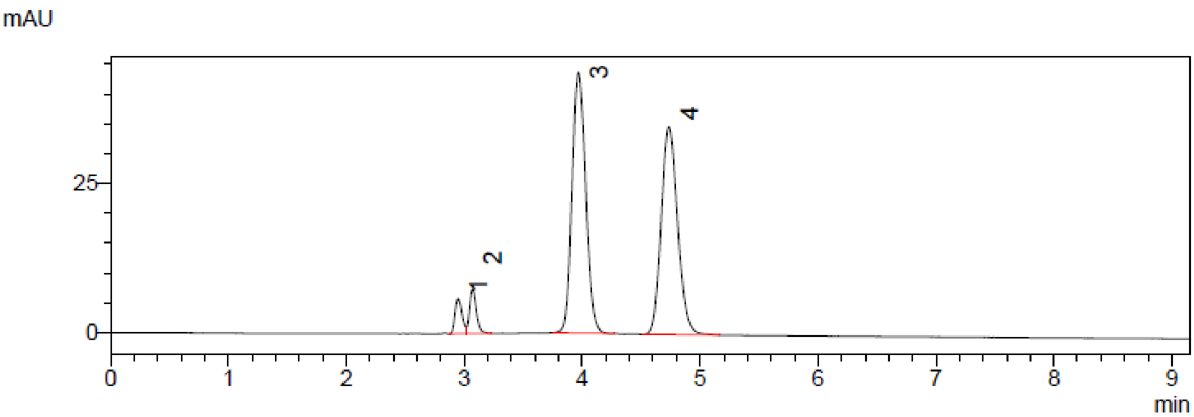


3s

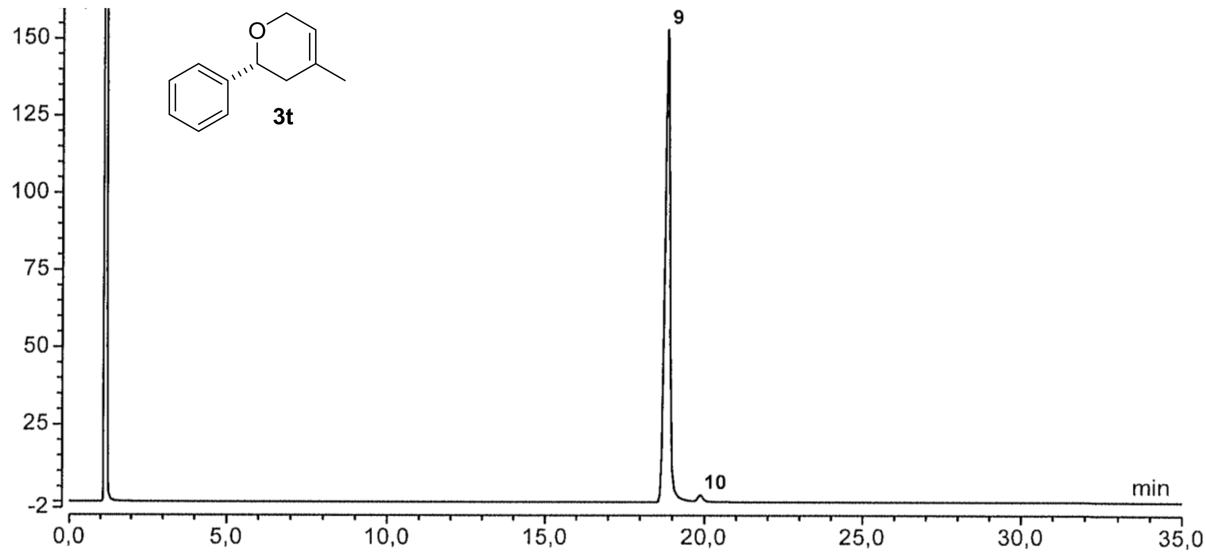


Peak #	Ret. Time/min	Area/%
3	3.96	95.01
4	4.66	4.99

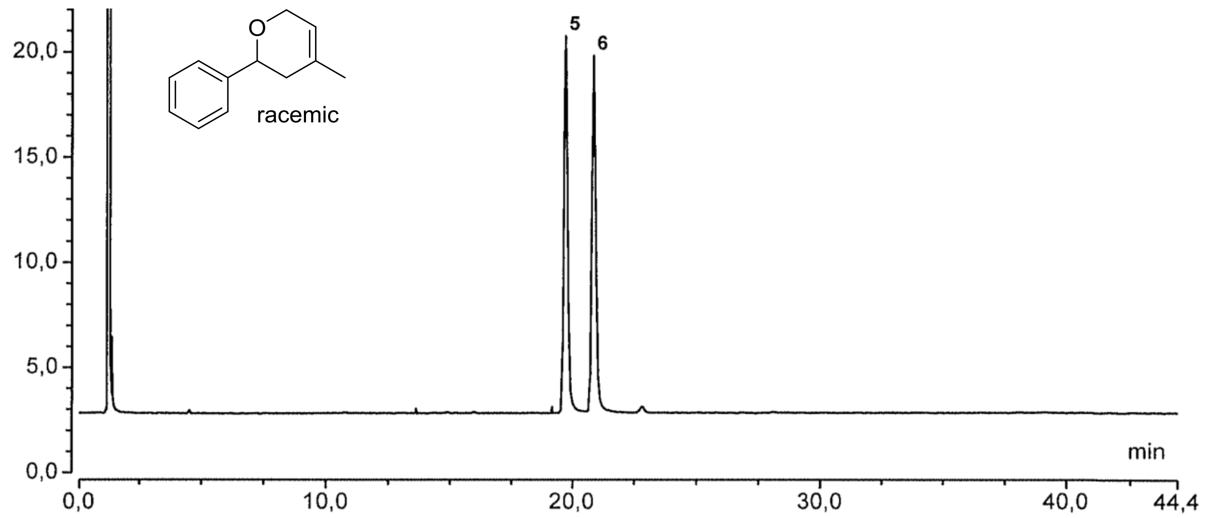




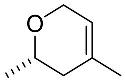
Peak #	Ret. Time/min	Area/%
3	3.97	51.13
4	4.73	48.87



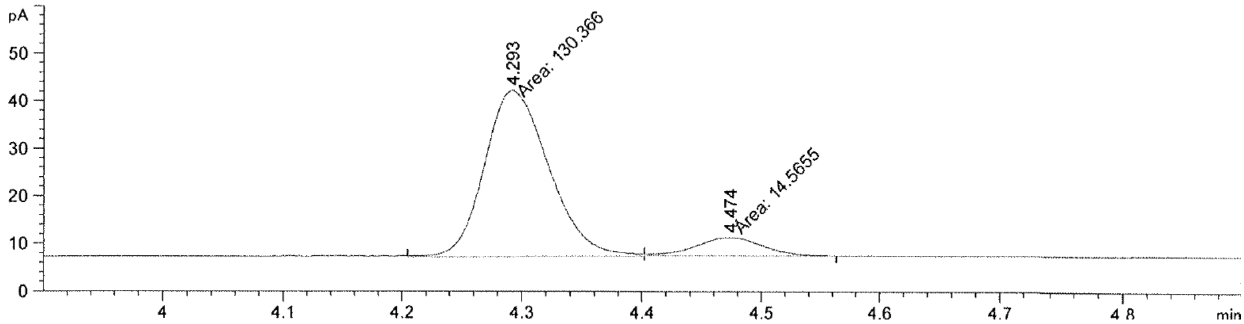
Peak #	Ret. Time/min	Area/%
9	18.86	98.00
10	19.87	2.00



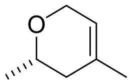
Peak #	Ret. Time/min	Area/%
5	19.72	49.79
6	20.87	50.21



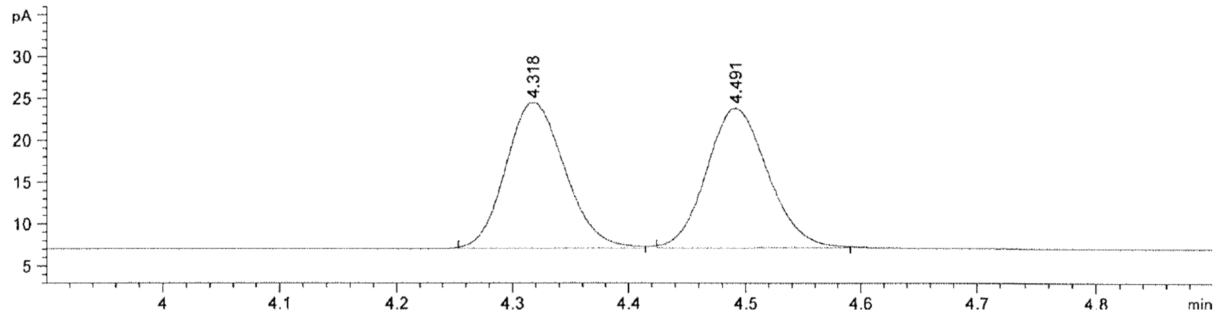
3u



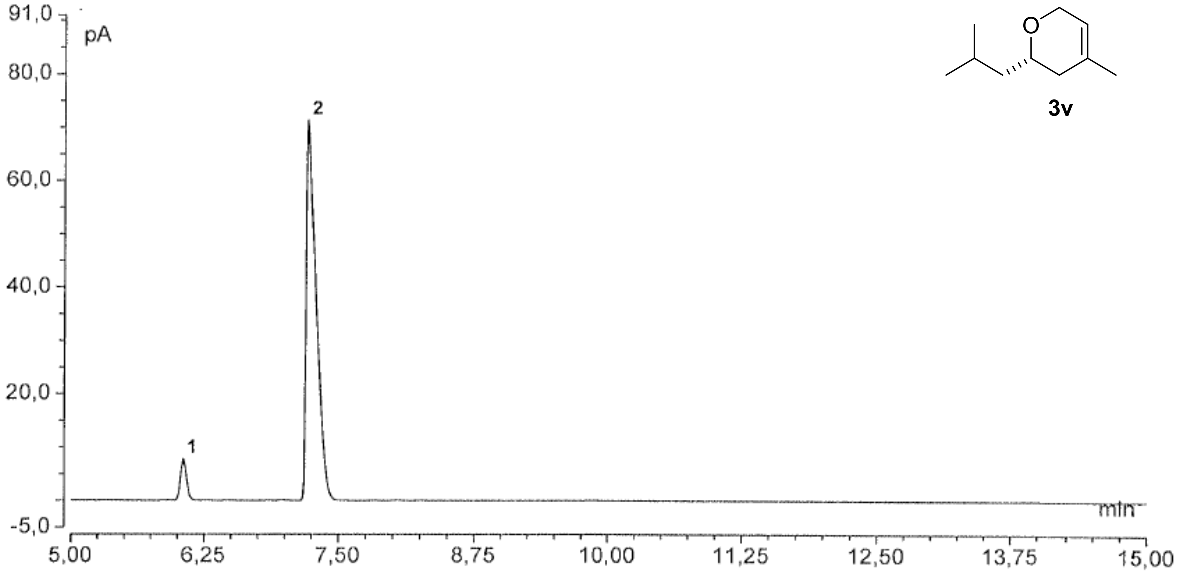
Peak #	Ret. Time/min	Area/%
1	4.29	89.95
2	4.47	10.05



racemic

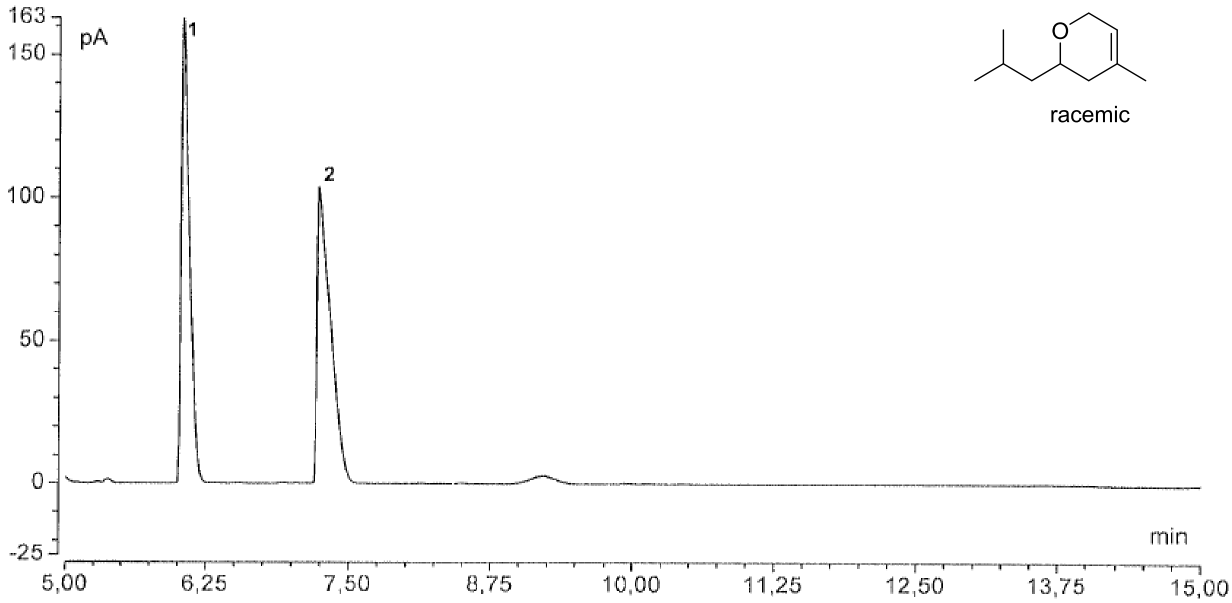


Peak #	Ret. Time/min	Area/%
1	4.32	50.01
2	4.49	49.99



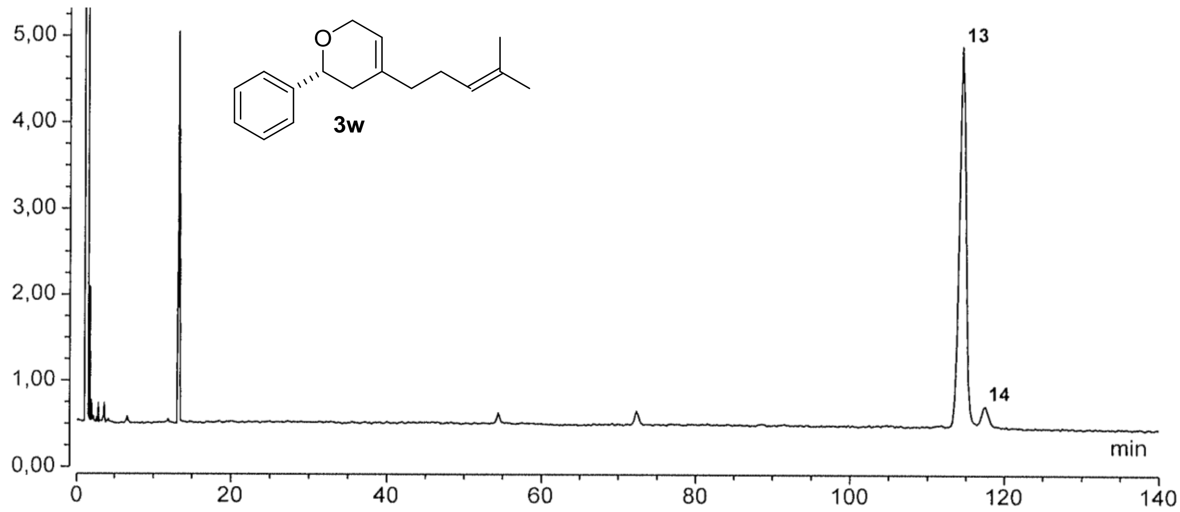
3v

Peak #	Ret. Time/min	Area/%
1	6.06	5.92
2	7.22	94.08

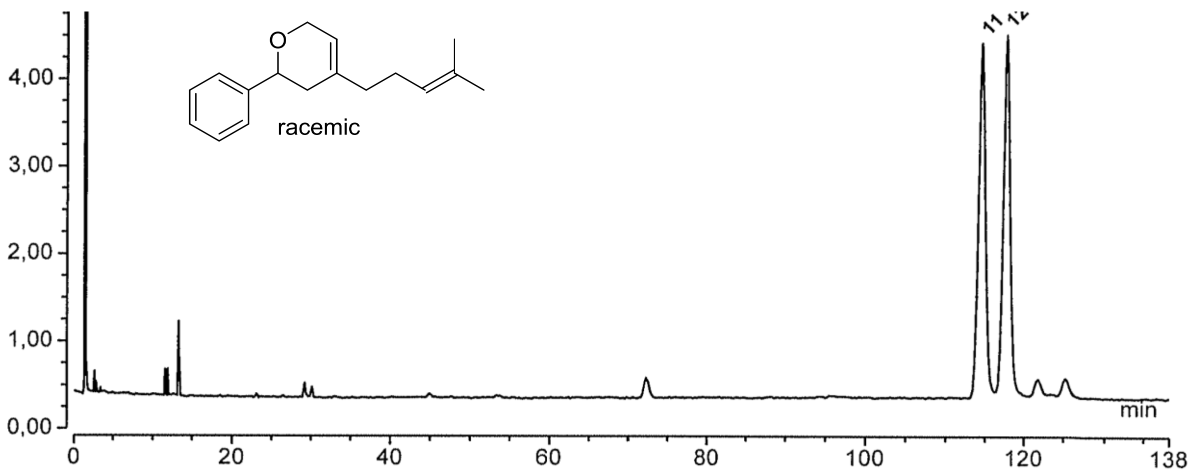


racemic

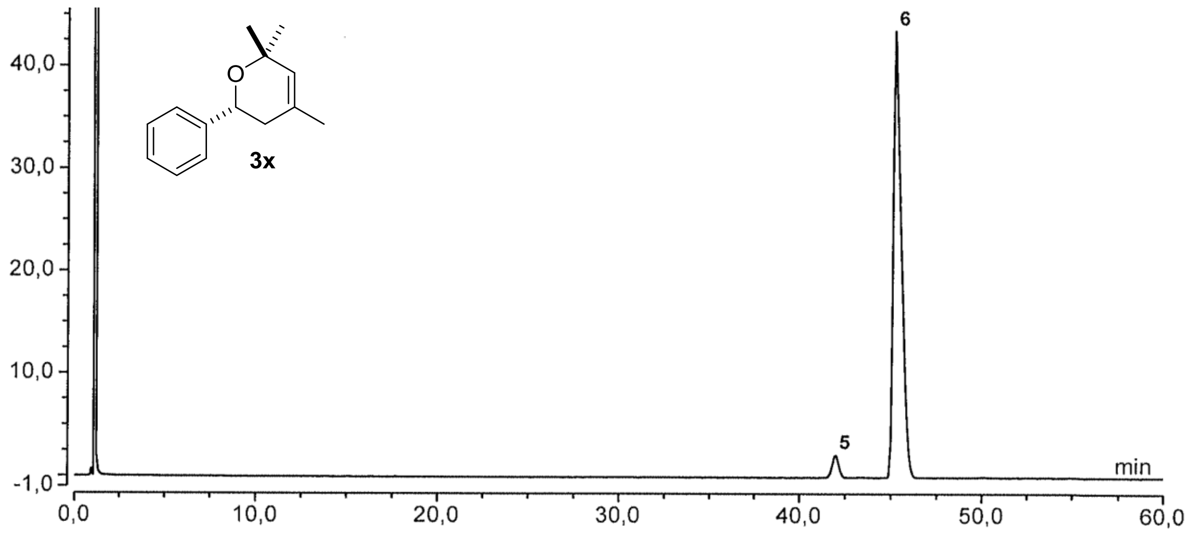
Peak #	Ret. Time/min	Area/%
1	6.04	50.15
2	7.24	49.85



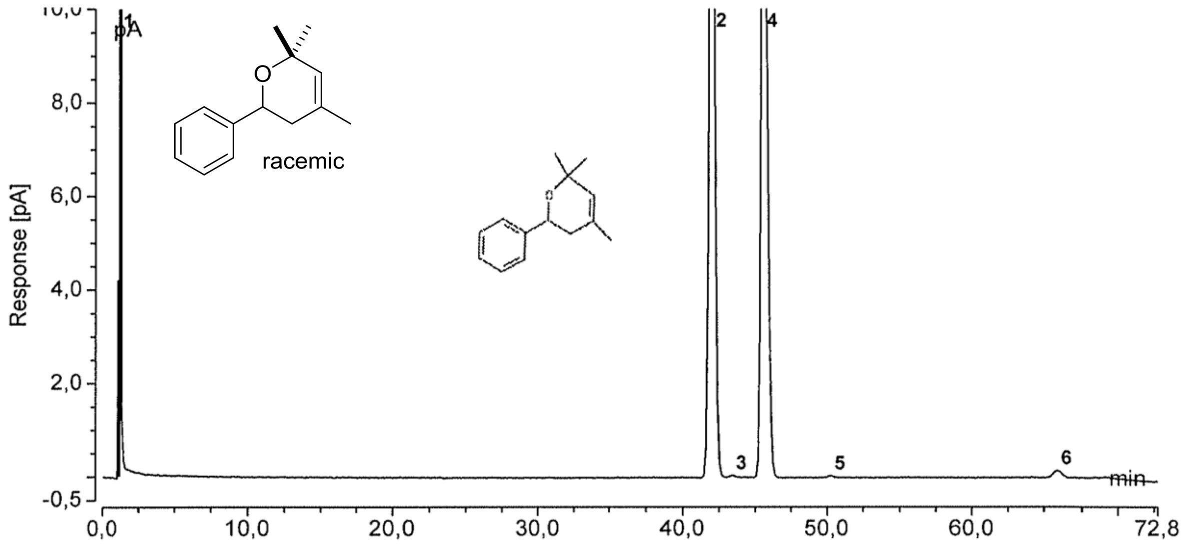
Peak #	Ret. Time/min	Area/%
13	114.52	95.98
14	117.41	4.02



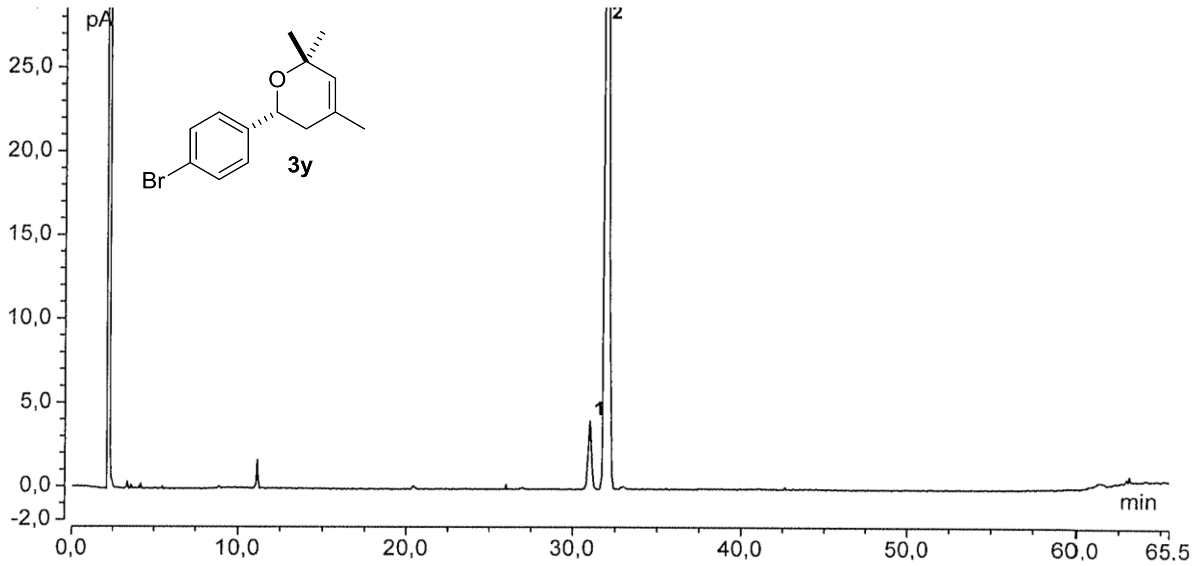
Peak #	Ret. Time/min	Area/%
11	114.68	49.64
12	117.84	50.36



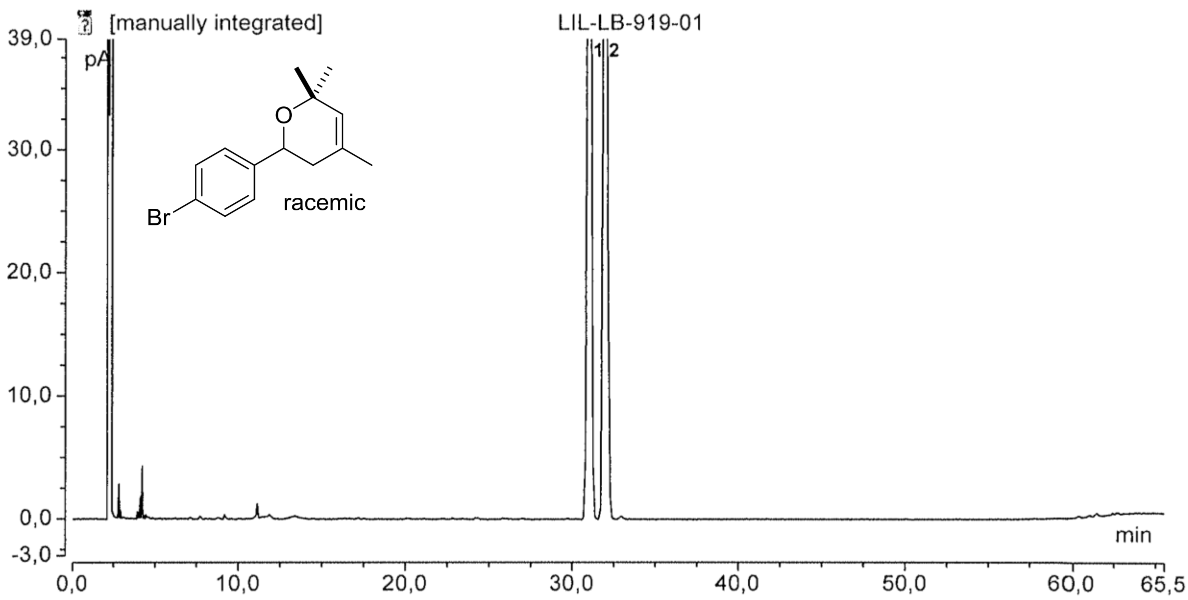
Peak #	Ret. Time/min	Area/%
5	41.98	3.95
6	45.20	96.05



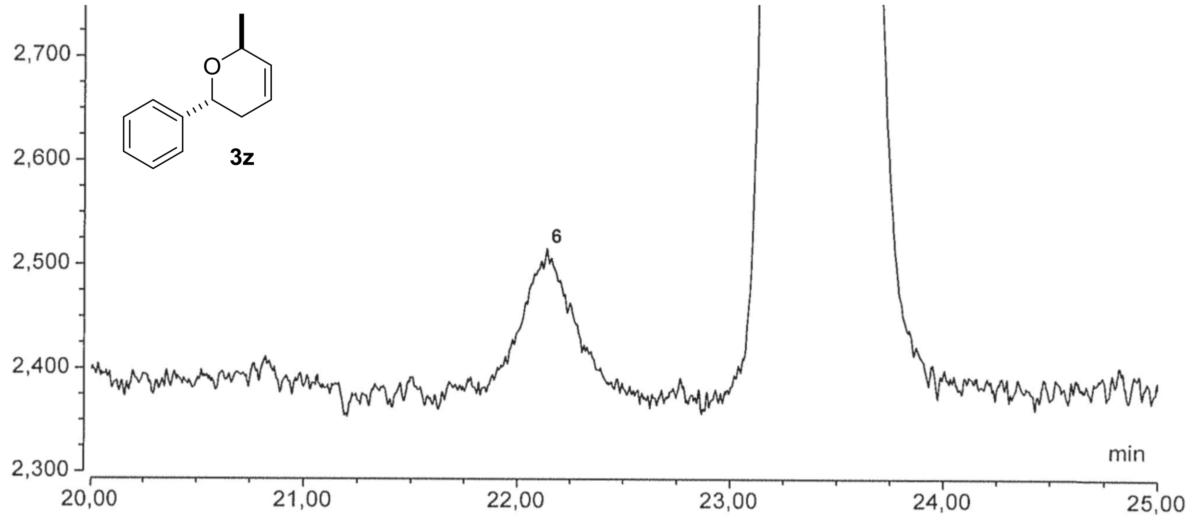
Peak #	Ret. Time/min	Area/%
2	42.01	49.96
4	45.60	50.04



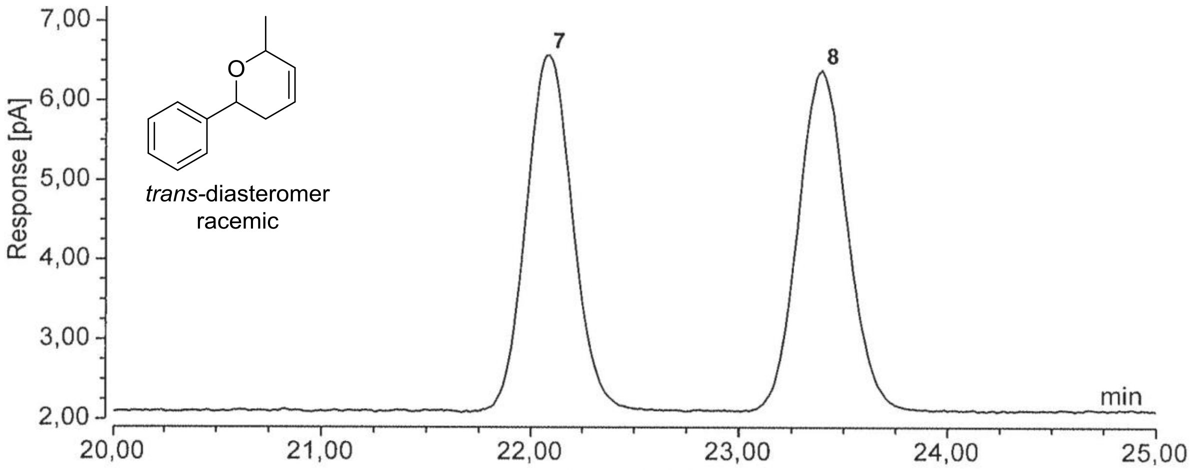
Peak #	Ret. Time/min	Area/%
1	31.01	4.94
2	31.97	95.06



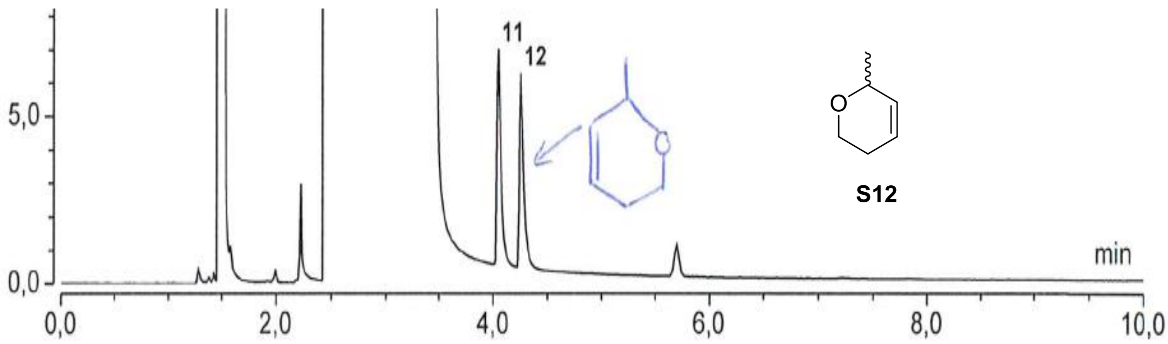
Peak #	Ret. Time/min	Area/%
1	31.04	50.02
2	31.97	49.98



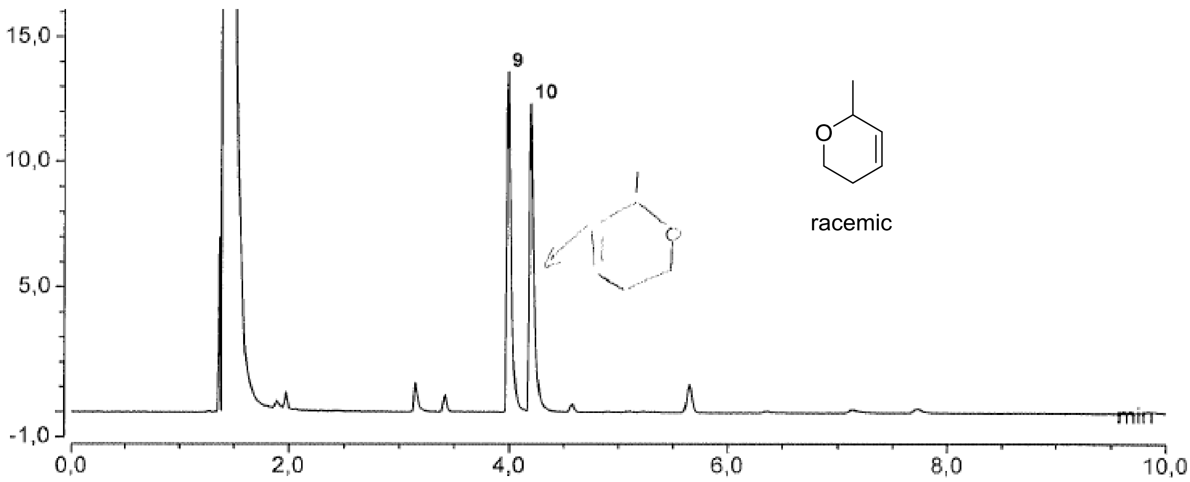
Peak #	Ret. Time/min	Area/%
6	22.14	1.01
7	23.39	98.99



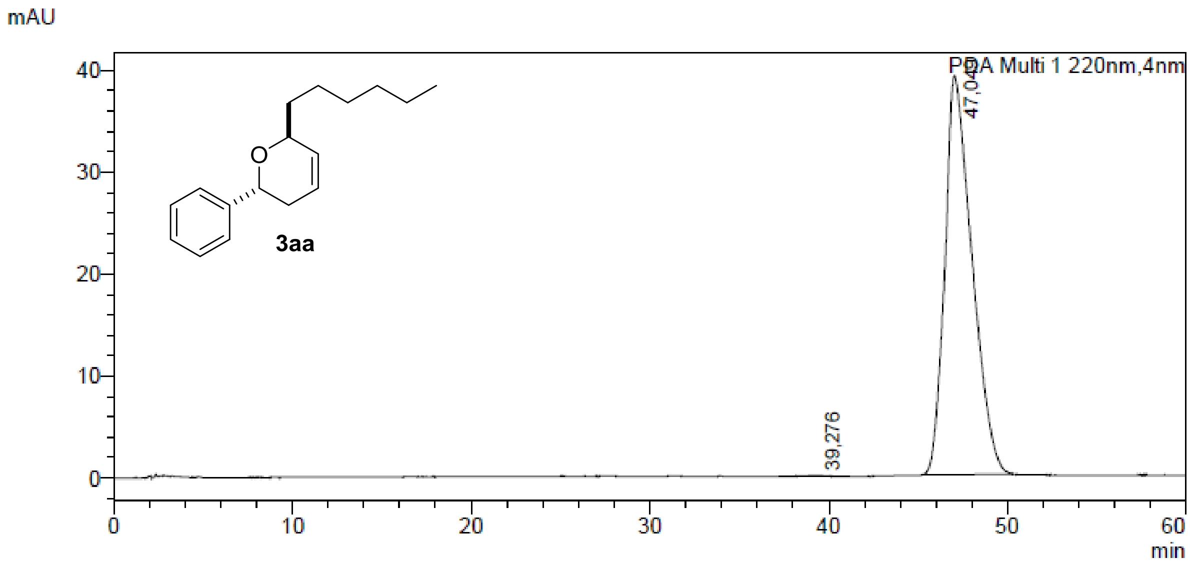
Peak #	Ret. Time/min	Area/%
7	22.09	49.95
8	23.40	50.05



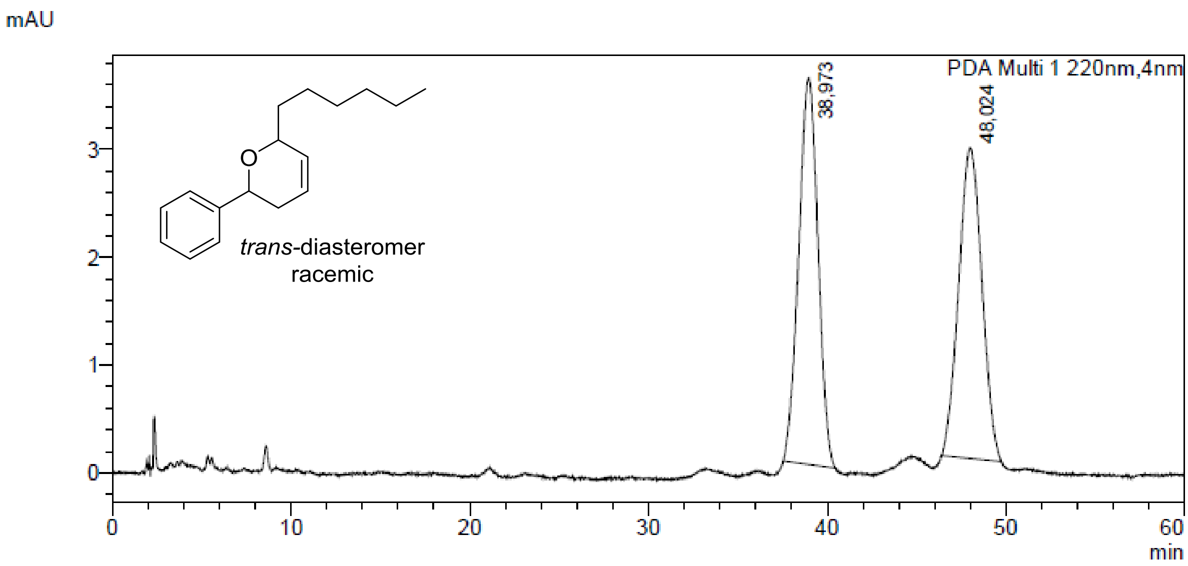
Peak #	Ret. Time/min	Area/%
11	4.05	50.29
12	4.25	49.71



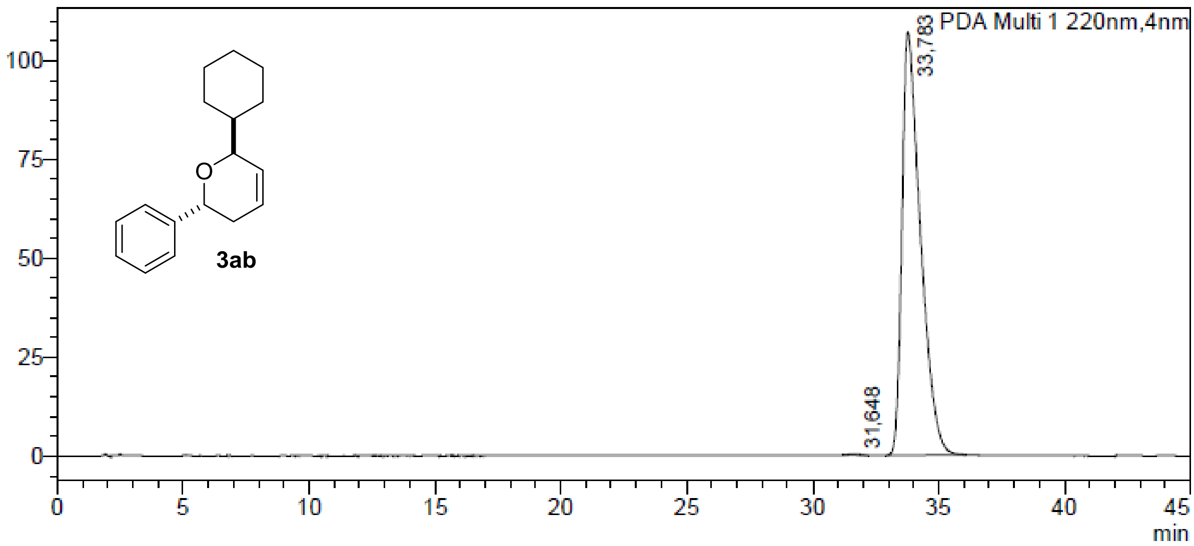
Peak #	Ret. Time/min	Area/%
9	3.99	49.64
10	4.19	50.36



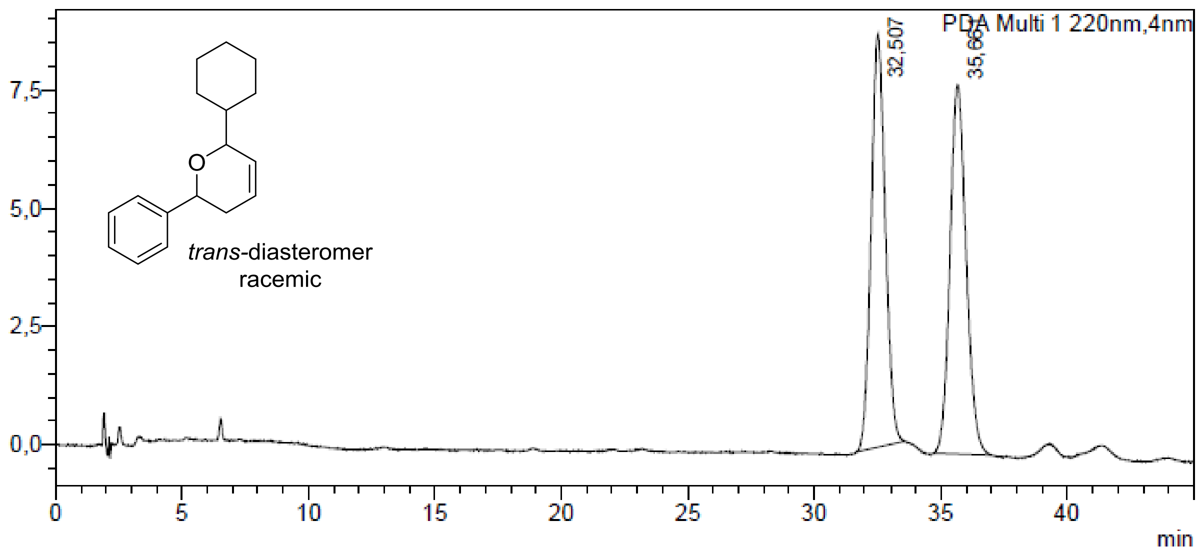
Peak #	Ret. Time/min	Area/%
1	39.28	0.21
2	47.05	99.79



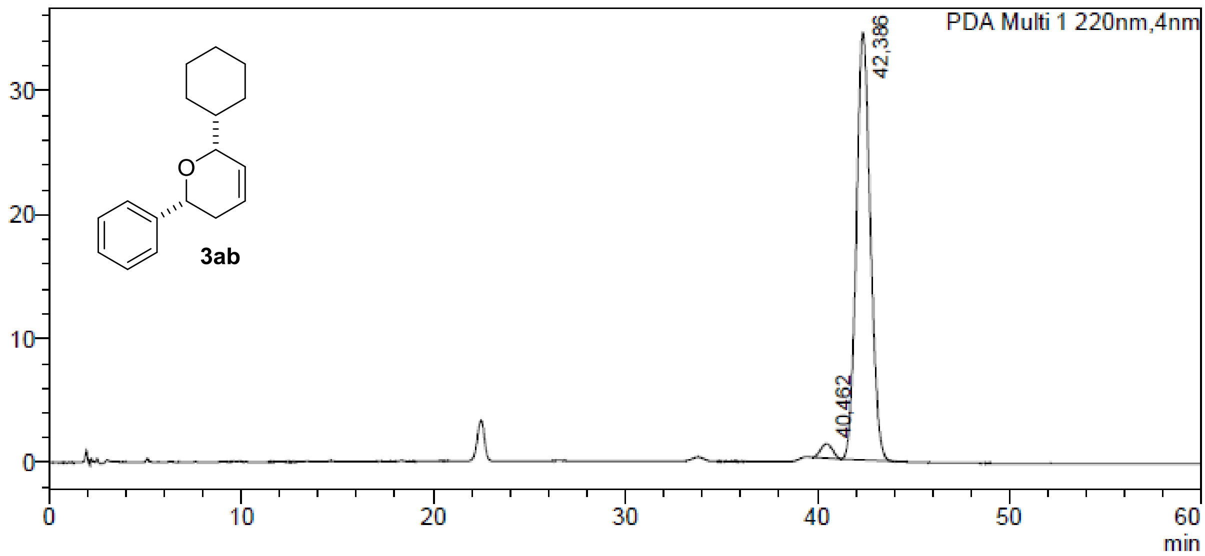
Peak #	Ret. Time/min	Area/%
1	38.97	50.78
2	48.02	49.22



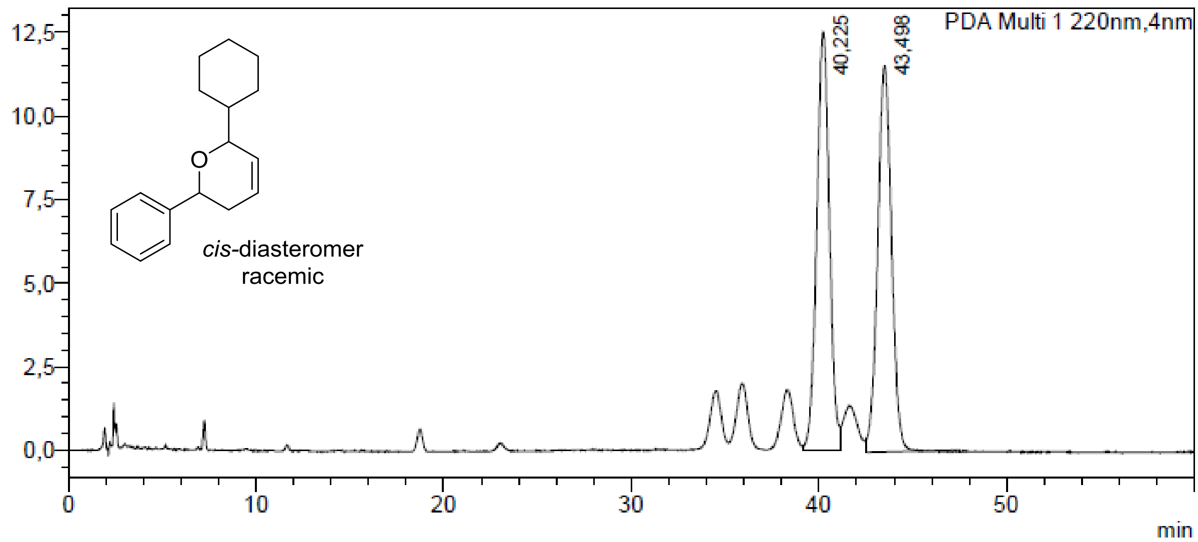
Peak #	Ret. Time/min	Area/%
1	31.65	0.18
2	33.78	99.82



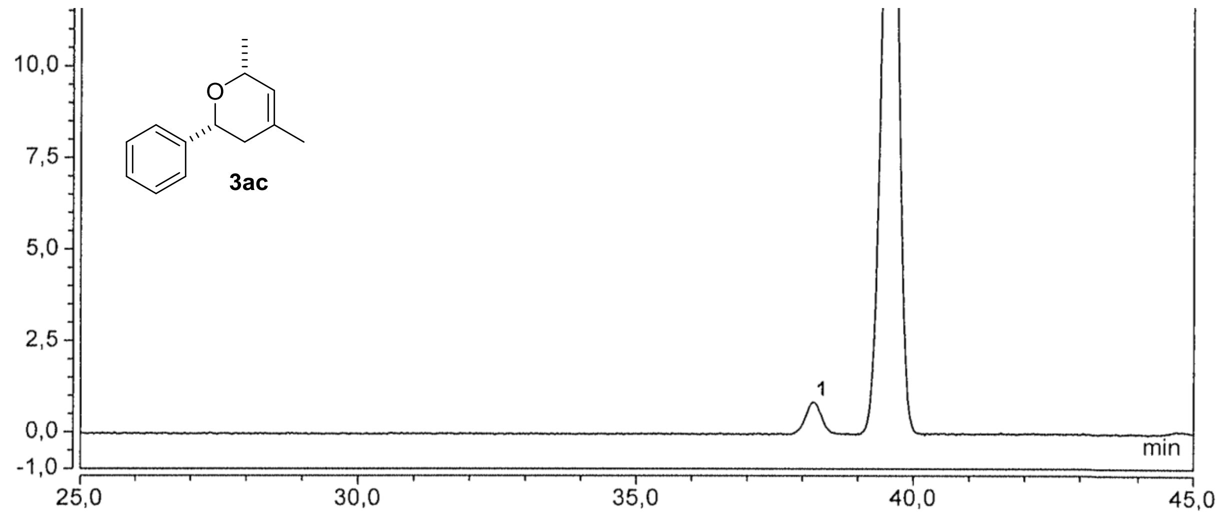
Peak #	Ret. Time/min	Area/%
1	32.51	49.50
2	35.66	50.50



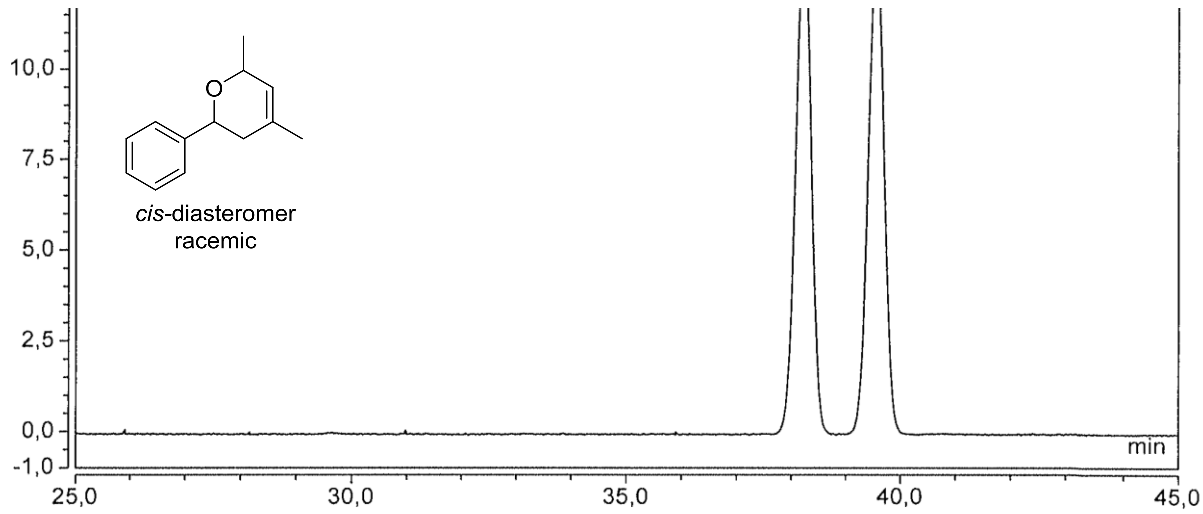
Peak #	Ret. Time/min	Area/%
1	40.46	2.72
2	42.39	97.28



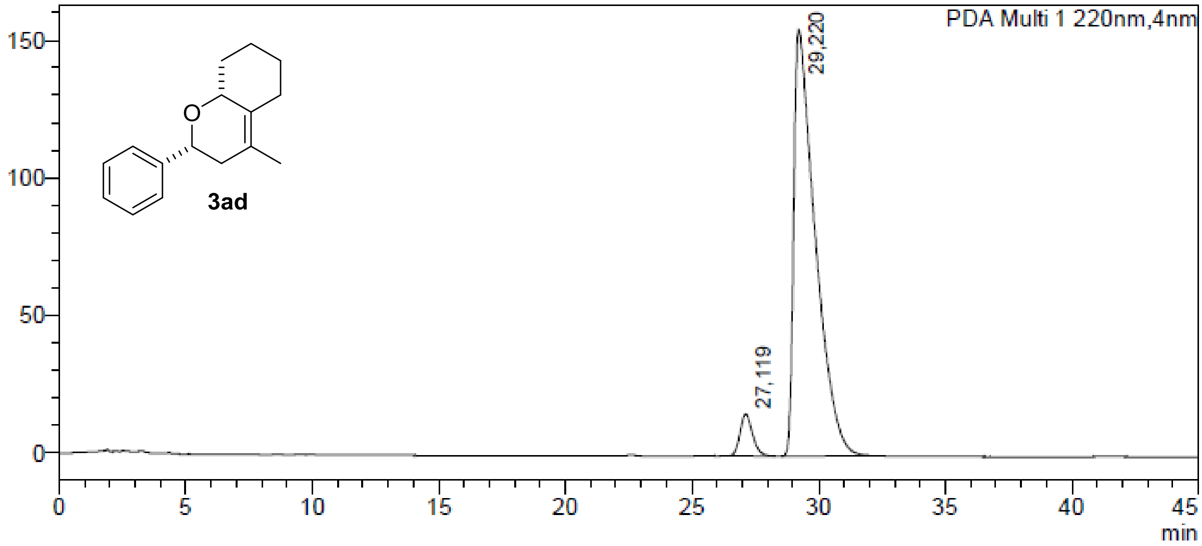
Peak #	Ret. Time/min	Area/%
1	40.23	49.95
2	43.50	50.05



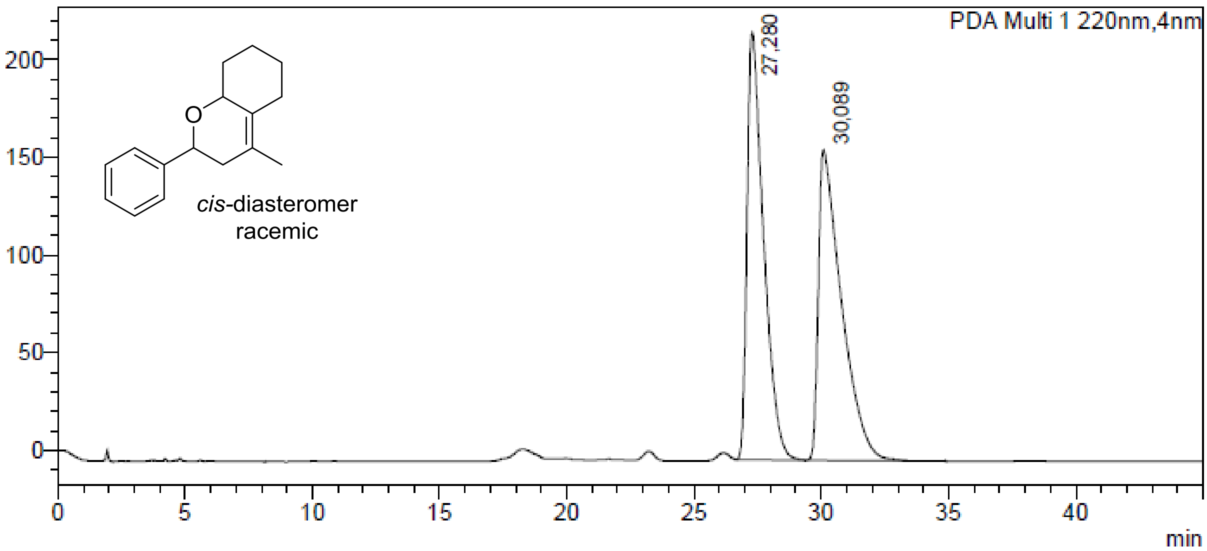
Peak #	Ret. Time/min	Area/%
1	38.19	3.95
2	39.59	96.05



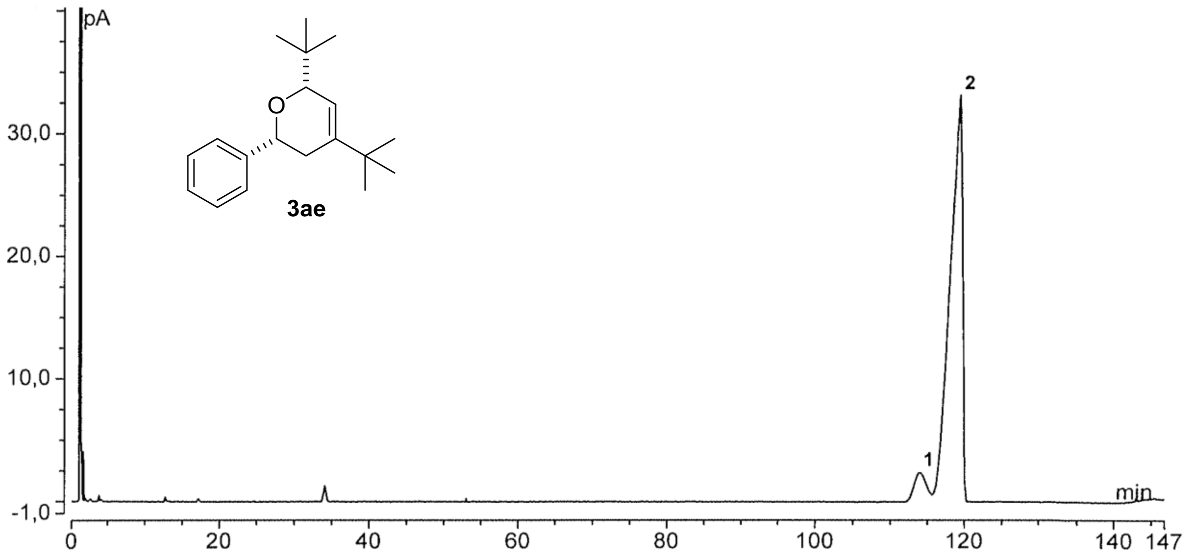
Peak #	Ret. Time/min	Area/%
1	38.24	49.93
2	39.57	50.07



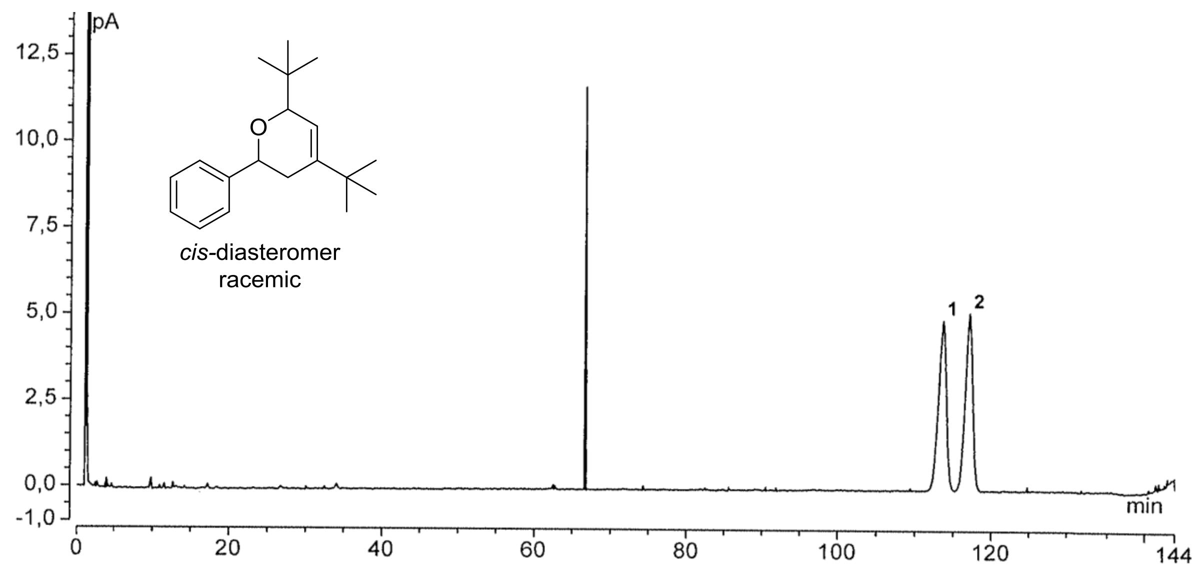
Peak #	Ret. Time/min	Area/%
1	27.12	5.40
2	29.22	94.60



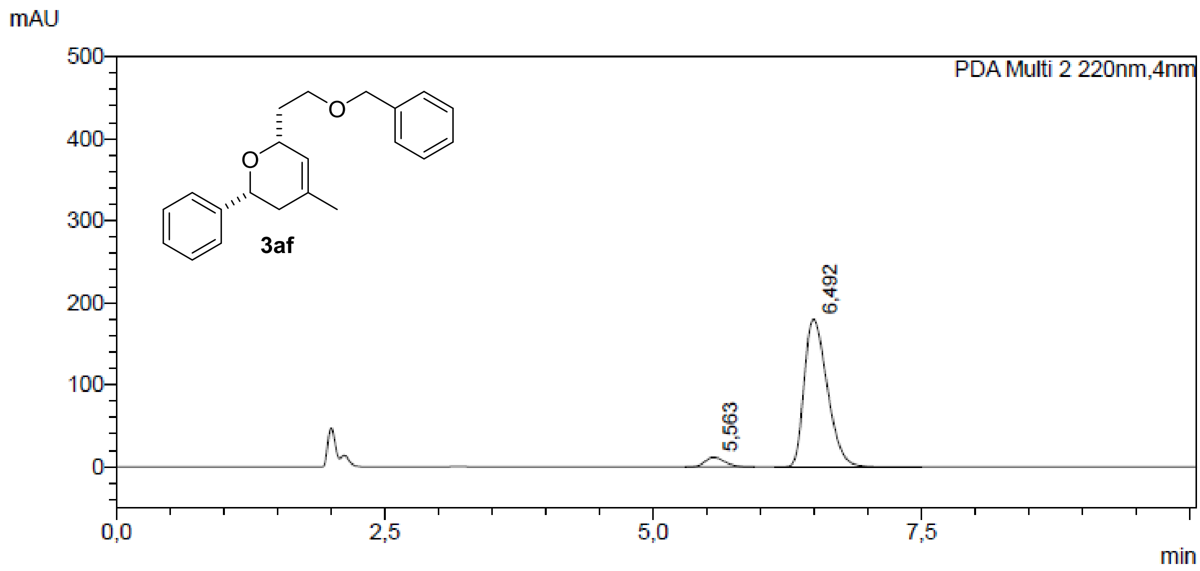
Peak #	Ret. Time/min	Area/%
1	27.28	49.68
2	30.09	50.32



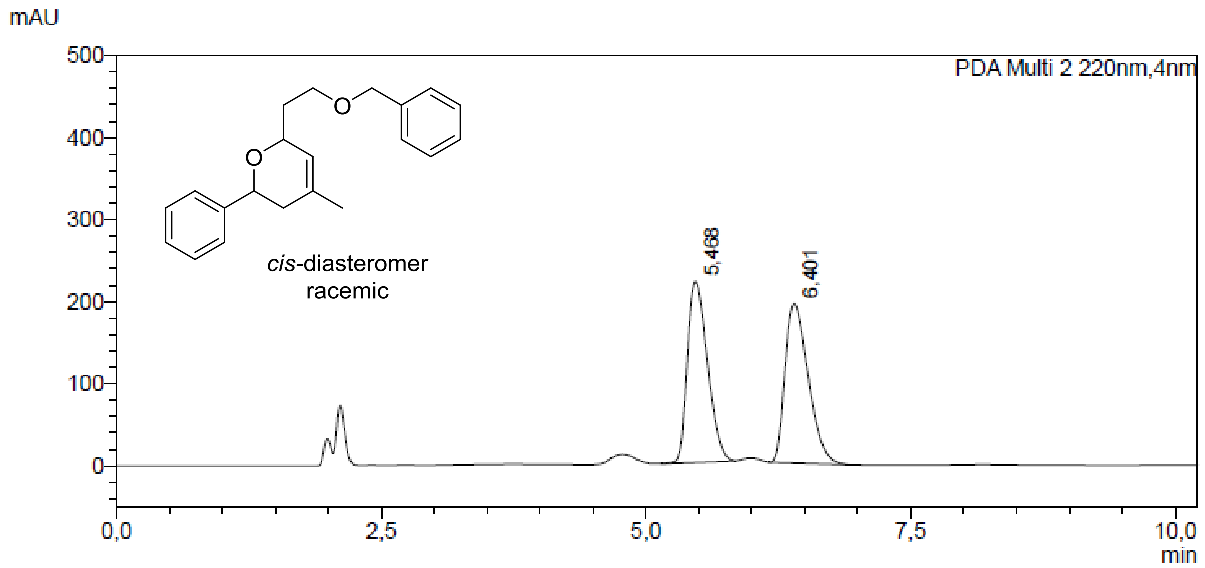
Peak #	Ret. Time/min	Area/%
1	113.99	5.33
2	119.57	94.67



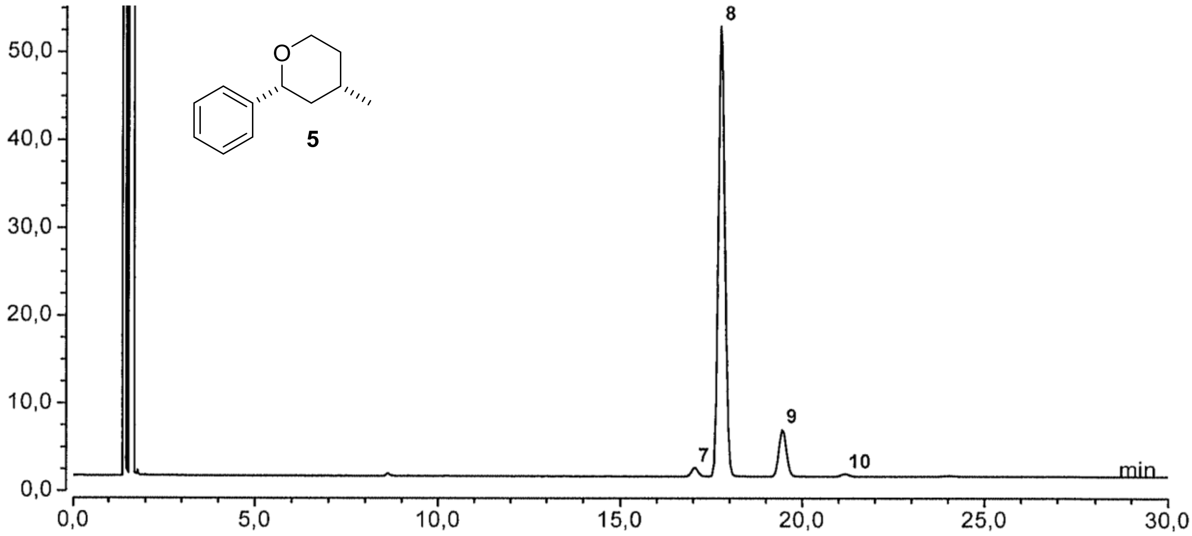
Peak #	Ret. Time/min	Area/%
1	113.62	50.06
2	117.09	49.94



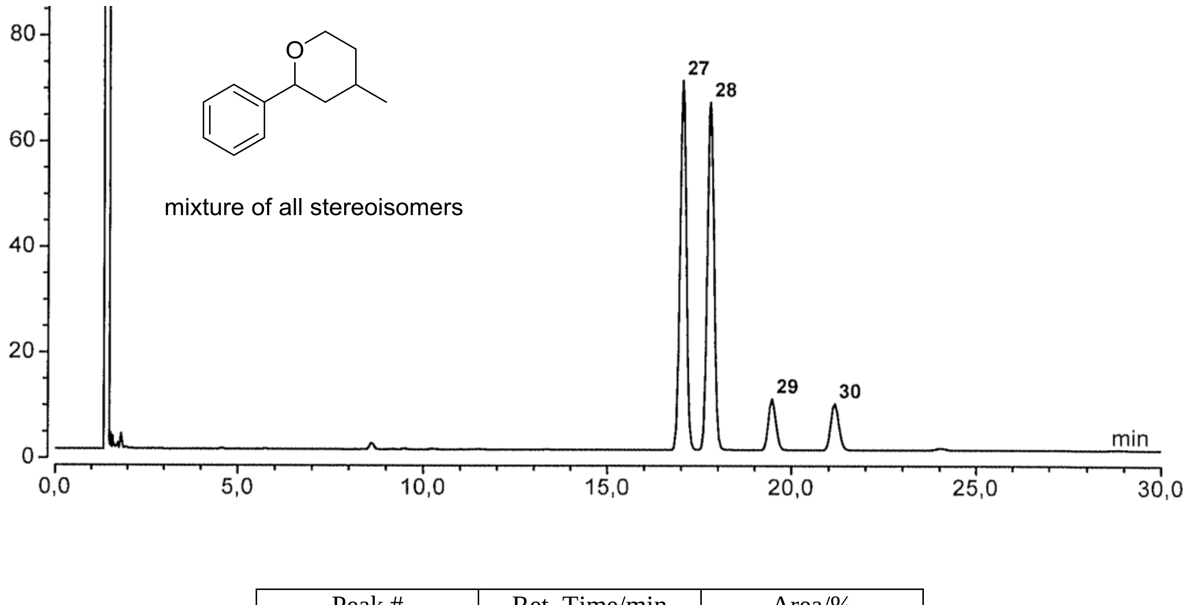
Peak #	Ret. Time/min	Area/%
1	5.56	5.15
2	6.49	94.85



Peak #	Ret. Time/min	Area/%
1	5.47	49.61
2	6.40	50.39



Peak #	Ret. Time/min	Area/%
7	17.04	1.66
8	17.76	87.56
9	19.45	10.18
10	21.17	0.59



Peak #	Ret. Time/min	Area/%
27	17.04	43.05
28	17.79	43.13
29	19.47	6.92
30	21.17	6.90

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