Electronic Supplementary Material (ESI) for Chemical Communications

NHC–Cu(I) Catalyzed Asymmetric Conjugate Silyl transfer to Unsaturated Lactones: Application in Kinetic Resolution

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Contents

General Experimental

All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents, unless stated otherwise. THF was distilled from sodium / benzophenone. Dichloromethane was distilled from CaH_2.

^{1}H NMR and ^{13}C NMR were recorded using 300, 400 and 500 MHz spectrometers, with chemical shift values being reported in ppm relative to residual chloroform (δ_H = 7.27 or δ_C = 77.2) as internal standards. All coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained using positive and negative electrospray (ES±) or gas chromatography (GC) methodology. Infra-red spectra were recorded as evaporated films or neat using a FT/IR spectrometer. Column chromatography was carried out using 35 – 70 m, 60A silica gel. Routine TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. Plates were viewed using a 254 mm ultraviolet lamp and dipped in aqueous potassium permanganate or *p*-anisaldehyde.

Chiral HPLC was carried out with Chiralcel OD-H, Chiralpak AD-H or Chiralpak IA columns, as indicated.

Selectivity values were calculated using[1]:

$$s = \frac{\ln[1 - C(1 + ee)]}{\ln[1 - C(1 - ee)]}$$

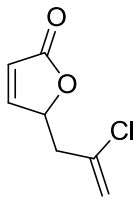
Reagents were either purchased directly from commercial suppliers or prepared according to literature procedures.

$PhMe_2SiB(pin)$ was prepared using a literature procedure.[2] 2-Chloro-3-iodoprop-1-ene was prepared using a literature method.[3] (Furan-2-yloxy)trimethylsilane was distilled before use.

Substrates:

Furan-2(5H)-one and 5,6-dihydro-2H-pyran-2-one were purchased from commercial suppliers, and used as received. 6,7-Dihydrooxepin-2(5H)-one, [4] (Z)-5,6,7,8-tetrahydro-2H-oxocin-2-one, [5] benzo[b]oxepin-2(5H)-one,[6] 5-methylfuran-2(5H)-one,[7] 5-ethylfuran-2(5H)-one,[8] 5-butylfuran-2(5H)-one, [9] 5-pentylfuran-2(5H)-one,[8] 5-allylfuran-2(5H)-one, [10] 5-phenylfuran-2(5H)-one[8] and 5-benzylfuran-2(5H)-one[8] were prepared using literature procedures.

5-(2-Chloroallyl)furan-2(5H)-one



To a stirred solution of silver triflate (2.14 g, 8.32 mmol, 1.3 equiv) in CH_2Cl_2 (15 mL), was added (furan-2-yloxy)trimethylsilane (1.08 mL, 6.40 mmol, 1 equiv) and 2-chloro-3-iodoprop-1-ene (1.67 g, 8.32 mmol, 1.3 equiv) at –78 °C and left to warm to room temperature and stirred overnight. The crude mixture was then vacuum filtered through celite. Concentration *in vacuo* and separation by column chromatography (silica gel, 15 % EtOAc in hexanes) gave the title compound as a dark brown oil (512 mg, 3.24 mmol, 51 %).

MS (ES^+) *m/z*: 158 ($M+H^+$); HRMS calcd for $C_7H_8O_2Cl$: 159.0208. Found: 159.0208; ν_{max} (thin film/cm^{-1}): 2959, 2932, 1739, 1717, 1427, 1246, 1148, 1119, 1065; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.71 (1 H, dd, *J* = 14.8, 6.3 Hz, C*H*$_2$), 2.81 (1 H, dd, *J* = 14.2, 6.9 Hz, C*H*$_2$), 5.29 - 5.36 (2 H, m, CCl=C*H*$_2$), 5.37 (1 H, m, CHO), 6.18 (1 H, dd, *J* = 5.7, 1.9 Hz, CH=C*H*C=O), 7.55 (1 H, dd, *J*=5.7, 1.6 Hz, C*H*=CHC=O); ^{13}C NMR (126 MHz, $CDCl_3$) δ 43.0 (CH_2), 80.1 (CHO), 116.8 (CCl=*C*H$_2$), 122.2 (CH=*C*HC=O), 135.6 (*C*Cl=CH_2), 155.0 (*C*H=CHC=O), 172.4 (C=O).

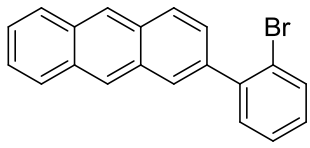
Ligands:

L1-8 were prepared using literature routes.[11,12]

Representative procedure for the synthesis of imidazolinium salts:

Representative Suzuki procedure:

2-(2-Bromophenyl)anthracene



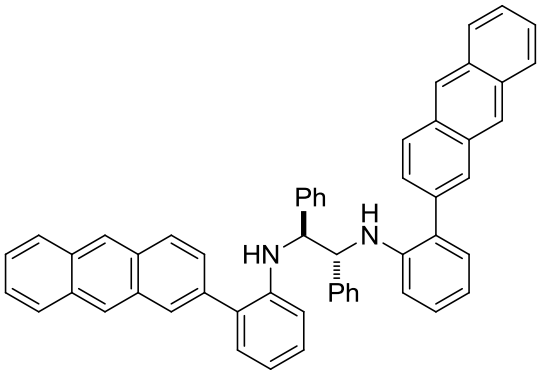
Bromo-2-iodobenzene (1.27 g, 4.50 mmol, 1 equiv), anthracen-2-ylboronic acid (1.0 g, 4.50 mmol, 1 equiv), K_2CO_3 (1.24 g, 9.01 mmol, 2 equiv) and $Pd(PPh_3)_4$ (156 mg, 0.135 mmol, 3 mol %) were placed in a microwave vial and capped. Toluene (5 mL) and H_2O (5 mL) were added and the reaction mixture was irradiated in a microwave reactor at 150 °C for 3 hours. The solution was allowed to

cool, the organic layer was then dried (Na_2CO_3) and concentrated *in vacuo*. The crude mixture was then purified by column chromatography (silica gel, hexanes) to yield 2-(2-bromophenyl)anthracene as a cream solid (1.29 g, 3.87 mmol, 86 %).

MS (ES^+) *m/z*: 333 ($M+H^+$); HRMS calcd for $C_{20}H_{13}Br$: 332.0195. Found: 332.0183; ν_{max} (thin film/cm^{-1}): 3052, 3018, 2963, 2926, 1673, 1624, 1591, 1560, 1528, 1469, 1452, 1437, 1422, 1360, 1327, 1312, 1285, 1274, 1248, 1216, 1157, 1117, 1023, 1011; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.24 - 7.31 (2 H, m, Ar*H*), 7.43 (1 H, td, *J* = 7.3, 1.1 Hz, Ar*H*), 7.47 - 7.49 (1 H, m, Ar*H*) 7.50 (1 H, d, *J* = 3.2 Hz, Ar*H*), 7.57 (1 H, dd, *J* = 8.8, 1.6 Hz, Ar*H*), 7.74 (1 H, dd, *J* = 8.1, 0.9 Hz, Ar*H*), 7.97 - 8.10 (4 H, m, Ar*H*), 8.46 (2 H, s, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.5 (Ar CH), 126.1 (Ar CH), 126.6 (Ar CH), 127.4 (Ar CH), 127.5 (Ar CH), 127.6 (Ar CH), 128.2 (Ar CH), 128.2 (Ar CH), 128.3 (Ar CH), 128.9 (Ar CH), 130.8 (Ar C), 131.3 (Ar C), 131.5 (Ar CH), 132.0 (Ar C), 133.2 (Ar CH); mp 138.6 °C (hexane/CH_2Cl_2).

Representative Buchwald-Hartwig procedure:

(1*R*,2*S*)-*N*1,*N*2-*bis*(2-(Anthracen-2-yl)phenyl)-1,2-diphenylethane-1,2-diamine

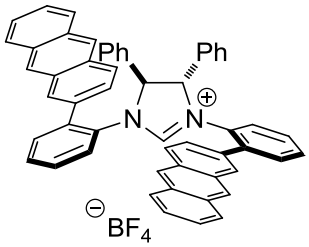


2-(2-Bromophenyl)anthracene (1.29 g, 3.87 mmol, 2.2 equiv), (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine (374 mg, 1.76 mmol, 1 equiv), NaOBu-*t* (372 mg, 3.87 mmol, 2.2 equiv), *rac*-BINAP (219 mg, 0.352 mmol 20 % mol) and $Pd(dba)_2$ (101 mg, 0.176 mmol, 10 % mol) were added to a microwave vial and the vial was capped. The vial was then evacuated and backfilled with argon three times. α, α, α-Trifluorotoluene (10 mL) was then added and the reaction mixture irradiated in a microwave reactor at 110 °C for 6 hours. The reaction mixture was allowed to cool, filtered through a plug of celite and then concentrated *in vacuo*. The crude mixture was then purified by column chromatography (silica gel, 5 % EtOAc in Hexanes) to afford (1*S*,2*S*)-*N*1,*N*2-*bis*(2-(anthracen-2-yl)phenyl)-1,2-diphenylethane-1,2-diamine as a thick yellow oil (757 mg, 1.056 mmol, 60 %).

MS (ES^+) *m/z*: 717 ($M+H^+$); HRMS calcd for $C_{54}H_{41}N_2$: 717.3265. Found: 717.3271; $[\alpha]_D^{25}$ = -117.3 (c = 1 in $CHCl_3$); ν_{max} (thin film/cm^{-1}): 3408, 3050, 3021, 2955, 2924, 2854, 1626, 1600, 1578, 1502, 1452, 1306, 1275, 1215, 1160, 1132, 1068, 1025; ^1H NMR (300 MHz, $CDCl_3$) δ ppm 4.6 (2 H, s, C*H*C*H*), 6.2 (2 H, d, *J* = 7.2 Hz, Ar*H*), 6.7 (2 H, t, *J* = 7.3 Hz, Ar*H*), 6.8 - 6.9 (4 H, m, Ar*H*), 6.9 - 7.0 (6 H, m, Ar*H*), 7.0 - 7.1 (2 H, m, Ar*H*), 7.1 (2 H, dd, *J* = 7.3, 1.5 Hz, Ar*H*), 7.3 (2 H, d, *J* = 8.9 Hz, Ar*H*), 7.5 - 7.6 (4 H, m, Ar*H*), 7.8 (2 H, s, Ar*H*), 8.0 (2 H, d, *J* = 8.7 Hz, Ar*H*), 8.0 - 8.1 (4 H, m, Ar*H*), 8.4 (2 H, s, Ar*H*), 8.5 (2 H, s, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.9 (CH), 125.6 (Ar C), 125.7 (Ar C), 126.2 (Ar C), 126.4 (Ar C), 126.7 (Ar C), 127.3 (Ar C), 127.5 (Ar C), 128.2 (Ar C), 128.3 (Ar C), 128.5 (Ar C), 128.5 (Ar C), 128.5 (Ar C), 129.9 (Ar C), 130.7 (Ar C), 131.8 (Ar C), 131.9 (Ar C), 132.0 (Ar C).

Representative cyclization procedure:

(4*S*,5*S*)-1,3-*bis*(2-(Anthracen-2-yl)phenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate

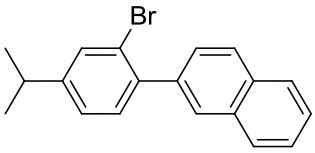


(1*S*,2*S*)-*N*1,*N*2-*bis*(2-(Anthracen-2-yl)phenyl)-1,2-diphenylethane-1,2-diamine (757 mg, 1.06 mmol, 1 equiv), NH_4BF_4 (166 mg, 1.58 mmol, 1.5 equiv) and triethyl orthoformate (2.34 mL) were heated to 130 °C for 4 hours with stirring. The reaction mixture was concentrated *in vacuo* and purified by column chromatography (silica gel, 80 % EtOAc in hexanes) to afford (4*S*,5*S*)-1,3-*bis*(2-(anthracen-2-yl)phenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate (**L10**) as a yellow solid, which was then triturated with CH_2Cl_2/Hexane to give a cream-white solid (766 mg, 0.940 mmol, 89 %).

MS (ES^+) *m/z*: 728 ($M-BF_4+H^+$); HRMS calcd for $C_{55}H_{39}N_2$: 727.3108. Found: 727.3109; $[\alpha]_D^{28}$ = 50.5 (c = 1 in $CHCl_3$); ν_{max} (thin film/cm^{-1}): 3058, 2961, 2924, 2853, 1731, 1672, 1597, 1573, 1530, 1495, 1456, 1304, 1265, 1217, 1185, 1158, 1057; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 4.63 (2 H, s, C*H*C*H*), 6.44 (4 H, d, *J* = 7.6 Hz, Ar*H*), 6.66 (4 H, t, *J* = 7.3 Hz, Ar*H*), 6.91 (2 H, t, *J* = 7.6 Hz, Ar*H*), 7.25 - 7.35 (6 H, m, Ar*H*), 7.40 - 7.47 (4 H, m, Ar*H*), 7.54 - 7.59 (4 H, m, Ar*H*), 8.05 - 8.10 (4 H, m, Ar*H*), 8.11 - 8.18 (4 H, m, Ar*H*), 8.48 (2 H, s, Ar*H*), 8.68 (2 H, br. s, Ar*H*), 9.39 (1 H, s, N=C*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 75.1 (CH), 126.1 (Ar CH), 126.3 (Ar C), 126.4 (Ar CH), 127.1 (Ar CH), 127.7 (Ar CH), 128.2 (Ar CH), 128.3 (Ar CH), 128.5 (Ar CH), 128.8 (Ar CH), 129.3 (Ar CH), 129.5 (Ar CH), 129.6 (Ar CH), 130.0 (Ar CH), 130.6 (Ar C),

131.2 (Ar CH), 131.2 (Ar C), 131.7 (Ar C), 132.2 (Ar C), 132.4 (Ar C), 133.6 (Ar C), 134.5 (Ar C), 137.8 (Ar C), 157.4 (N=C); mp 190.4 °C (hexane/CH_2Cl_2).

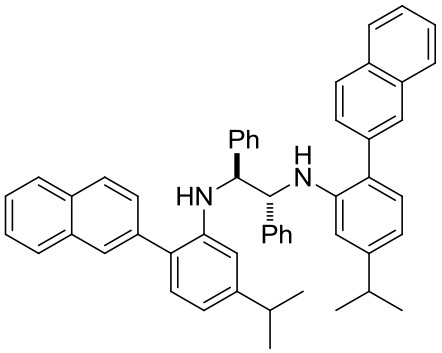
2-(2-Bromo-4-isopropylphenyl)naphthalene



Prepared according to the representative Suzuki procedure.

MS (ES^+) *m/z*: 324 (M); HRMS calcd for $C_{19}H_{17}Br$: 324.0508. Found: 324.0504; ν_{max} (thin film/cm^{-1}): 3053, 2958, 2924, 2866, 1909, 1602, 1490, 1459, 1397, 1362, 1345, 1325, 1268, 1208, 1191, 1129, 1055, 1020, 1012; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.41 (6 H, d, *J* = 7.0 Hz, ArCH(CH_3)$_2$), 3.03 (1 H, spt, *J* = 6.9 Hz, ArC*H*(CH_3)$_2$), 7.34 (1 H ,dd, *J* = 7.8, 1.6 Hz, Ar*H*), 7.45 (1 H, d, *J* = 7.9 Hz, Ar*H*), 7.60 (2 H, dd, *J* = 6.2, 3.4 Hz, Ar*H*), 7.69 (2 H, dd, *J* = 8.7, 1.5 Hz, Ar*H*) 7.93 - 8.02 (4 H, m, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.8 (CH_3), 33.6 (Ar*C*H(CH_3)), 122.6 (Ar C), 125.6 (Ar CH), 126.1 (Ar CH), 126.1 (Ar CH), 127.2 (Ar CH), 127.6 (Ar CH), 127.7 (Ar CH), 128.1 (Ar CH), 128.2 (Ar CH), 131.1 (Ar CH), 131.4 (Ar CH), 132.5 (Ar C), 133.0 (Ar C), 138.6 (Ar C), 139.8 (Ar C), 149.9 (Ar C); mp 78.8 °C (hexane).

(1*R*,2*S*)-*N*1,*N*2-*bis*(5-Isopropyl-2-(naphthalen-2-yl)phenyl)-1,2-diphenylethane-1,2-diamine

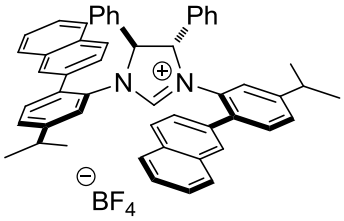


Prepared according to the representative Buchwald-Hartwig procedure.

MS (ES^+) *m/z*: 701 ($M+H^+$); HRMS calcd for $C_{52}H_{49}N_2$: 791.3891. Found: 701.3885; $[\alpha]_D^{28}$ = -190.1 (c = 1 in $CHCl_3$); ν_{max} (thin film/cm^{-1}): 3056, 3028, 2957, 2929, 2865, 2241, 2165, 1733, 1717, 1699, 1684, 1653, 1636, 1609, 1566, 1541, 1520, 1507, 1499, 1456, 1424, 1362, 1344, 1298, 1271, 1197, 1271, 1197, 1142, 1129; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.96 (6 H, d, *J* = 6.8 Hz, ArCH(CH_3)$_2$), 1.01 (6 H, d, *J* = 6.8 Hz, ArCH(CH_3)$_2$), 2.60 (2 H, spt, *J* = 6.8 Hz, ArC*H*(CH_3)$_2$), 4.54 (2 H, s, C*H*C*H*), 6.10 (2 H, br. s., N*H*), 6.58 (2 H, d, *J*=7.7 Hz, Ar*H*), 6.86 - 7.11 (4 H, m, Ar*H*), 7.32 (2 H, d, *J* = 8.3 Hz, Ar*H*), 7.50 - 7.59 (4

H, m, Ar*H*), 7.63 (2 H, s, Ar*H*), 7.73 - 7.83 (4 H, m, Ar*H*), 7.86 - 7.95 (2 H, m, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4 (ArCH(CH_3)$_2$), 23.9 (ArCH(CH_3)$_2$), 33.8 (ArCH(CH_3)$_2$), 63.7 (CH), 110.5 (Ar C), 115.4 (Ar C), 126.0 (Ar CH), 126.2 (Ar CH), 126.6 (Ar CH), 127.3 (Ar CH), 127.7 (Ar CH), 127.8 (Ar CH), 128.0 (Ar CH), 128.4 (Ar CH), 128.4 (Ar CH), 129.7 (Ar CH), 132.4 (Ar C), 133.8 (Ar C), 136.6 (Ar C), 139.6 (Ar C), 143.6 (Ar C), 149.1 (Ar C).

(4*S*,5*S*)-1,3-*bis*(2-(Anthracen-2-yl)phenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate (L9)



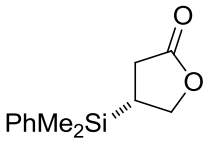
Prepared according to the representative cyclization procedure.

MS (ES$^+$) *m/z*: 711 (M-BF_4). HRMS calcd for $C_{53}H_{47}N_2$: 711.3734. Found: 711.3739; $[\alpha]_D^{28}$ = -117.3 (c = 1 in $CHCl_3$); ν_{max} (thin film/cm^{-1}): 3036, 2961, 2928, 2871, 1623, 1605, 1660, 1497, 1457, 1415, 1375, 1338, 1280, 1215, 1054; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.11 (6 H, d, *J* = 6.6 Hz, ArCH(CH_3)$_2$), 1.15 (6 H, d, *J* = 6.9 Hz, ArCH(CH_3)$_2$), 2.83 (2 H, spt, *J* = 6.6 Hz, ArCH(CH_3)$_2$), 4.57 (2 H, s, C*H*C*H*), 6.32 (4 H, d, *J* = 7.9 Hz, Ar*H*), 6.76 (4 H, t, *J* = 7.6 Hz, Ar*H*), 6.86 (2 H, br. s, Ar*H*), 7.07 (2 H, t, *J* = 7.3 Hz, Ar*H*), 7.21 (4 H, apparent q, *J* = 7.6 Hz, Ar*H*), 7.48 (2 H, d, *J* = 7.9 Hz, Ar*H*), 7.64 - 7.71 (4 H, m, Ar*H*), 7.96 - 8.04 (6 H, m, Ar*H*), 8.12 (2 H, d, *J* = 8.8 Hz, Ar*H*), 9.24 (1 H, br. s, N=C*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.0 (ArCH(CH_3)$_2$), 23.8 (ArCH(CH_3)$_2$), 33.4 (ArCH(CH_3)$_2$), 75.2 (CH), 127.0 (Ar CH), 127.0 (Ar CH), 127.2 (Ar CH), 127.8 (Ar CH), 127.9 (Ar CH), 128.1 (Ar CH), 128.5 (Ar CH), 128.6 (Ar CH), 128.8 (Ar CH), 129.0 (Ar CH), 129.7 (Ar C), 131.0 (Ar CH), 131.3 (Ar C), 132.8 (Ar C), 133.5 (Ar C), 133.8 (Ar C), 135.3 (Ar C), 135.8 (Ar C), 150.2 (Ar C), 156.9 (N=C); mp 228.6 °C (hexane/CH_2Cl_2).

Table 3: The products in entries 1 and 2 have been previously reported.[12]

Representative experimental procedure 1 for Cu-catalyzed 1,4-conjugate silyl additions:

(*R*)-4-(Dimethyl(phenyl)silyl)dihydrofuran-2(3H)-one (Table 3, entry 1)[13]



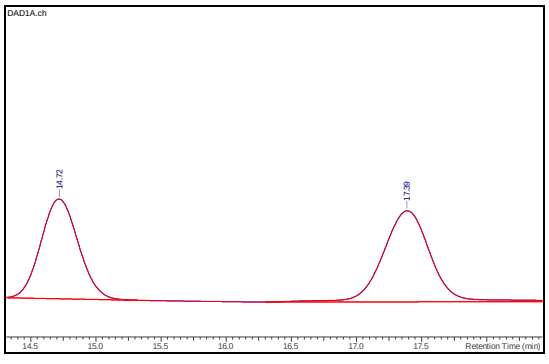
In an oven-dried vial equipped with a stirrer bar, (4*S*,5*S*)-1,3-bis(2-(naphthalen-2-yl)phenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate salt **L8** (7.9 mg, 0.011 mmol, 3.3 mol %), NaOBu-*t* (2.1 mg, 0.022 mmol, 6.6 mol %) and CuCl (1 mg, 0.010 mmol, 3 mol %) were placed and 1.5 mL of THF was added. The solution was allowed to stir for 3 hours at 50 °C under nitrogen and then filtered through a short plug of oven-dried Celite under nitrogen. $PhMe_2SiB(pin)$ (0.1 mL, 0.367 mmol, 1.1 equiv) was added to the filtrate and the reaction stirred for 15 min. The solution was then cooled to –78 °C, and a solution of furan-2(5H)-one (28 mg, 0.334 mmol, 1 equiv) in dry THF (0.5 mL) was added and the mixture was allowed to stir for 3.5 hours at –78 °C, after which the reaction was quenched by the addition of H_2O (0.5 mL) and allowed to warm to room temperature overnight. The aqueous layer was then washed with Et_2O (3 x 2 mL) and dried over $MgSO_4$. Concentration *in vacuo* and separation by column chromatography (silica gel, 20 % EtOAc in hexanes) yielded (*R*)-4-(dimethyl(phenyl)silyl)dihydrofuran-2(3H)-one as a pale yellow oil (62.5 mg, 0.283 mmol, 85 %).

$[\alpha]_D^{28}$ = -6.93 (c = 1 in $CHCl_3$) for a sample of 93:7 er. Lit: $[\alpha]^{20}_D$ = −5.64 (c 0.99, $CHCl_3$) for a sample of >99.5:0.5 er.[12]

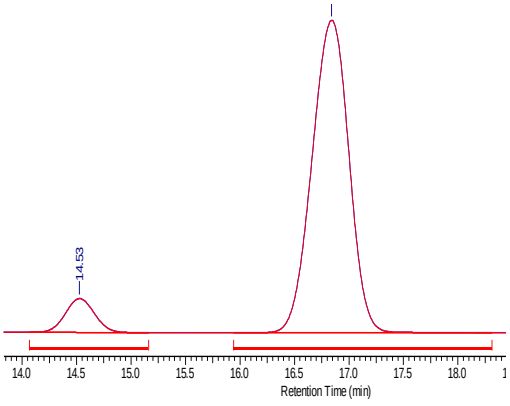
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.37 (3 H, s, SiC*H*$_3$), 0.38 (3 H, s, SiC*H*$_3$), 2.07 (1 H, ddt, *J* = 12.8, 11.3, 8.6 Hz, SiC*H*), 2.30 (1 H, dd, *J* = 17.4, 12.6 Hz, C*H*$_2$C=O), 2.52 (1 H, dd, *J* = 17.4, 8.8 Hz, C*H*$_2$C=O), 4.12 (1 H, dd, *J* = 11.3, 8.8 Hz, C*H*$_2$O), 4.43 (1 H, t, *J* = 8.7 Hz, C*H*$_2$O), 7.38 - 7.50 (5 H, m, Ar*H*).

Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 90 : 10 v / v. Flow: 1 mL / min

Racemate

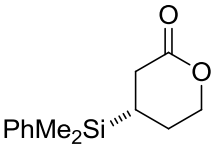


Enantiomerically enriched



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
14.720	11318940	49.950	14.527	2463352	6.976
17.387	11341653	50.050	16.840	30381344	93.024

(*S*)-4-(Dimethyl(phenyl)silyl)tetrahydro-2H-pyran-2-one (Table 3, entry 2)[12]

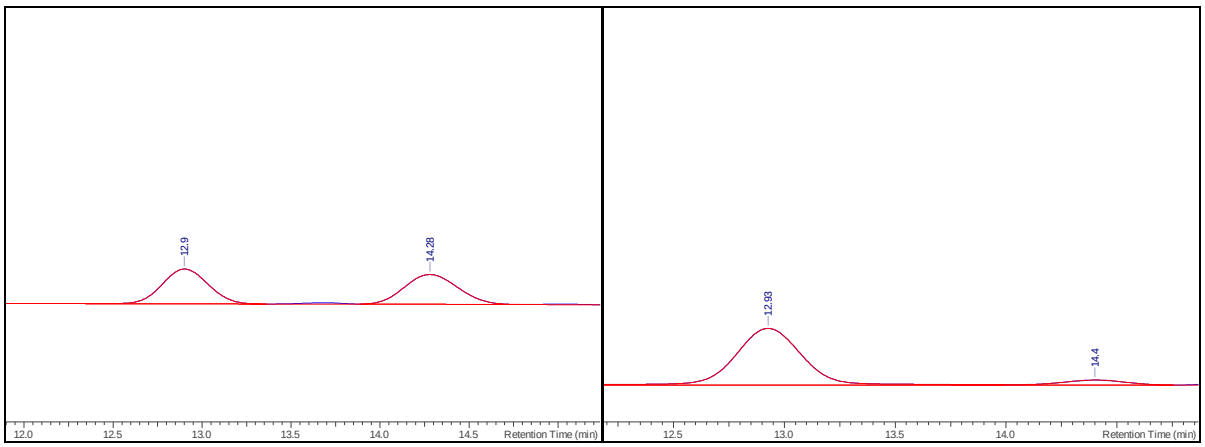


$[\alpha]_D^{28}$ = -23 (c = 1 in $CHCl_3$) for a sample of 92:8 er. Lit: $[\alpha]^{20}_D$ = −36.3 (c 1.0, $CHCl_3$) for a sample of 99:1 er.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.21 (6 H, s, SiC*H*$_3$), 1.22 - 1.34 (1 H, m, C*H*$_2$), 1.47 - 1.59 (1 H, m, C*H*$_2$), 1.68 - 1.77 (1 H, m, SiC*H*), 2.16 (1 H, dd, *J* = 17.3, 12.6 Hz, C*H*$_2$C=O), 2.44 (1 H, ddd, *J* = 17.3, 6.1, 1.5 Hz, C*H*$_2$C=O), 4.13 (1 H, ddd, *J* = 11.1, 9.6, 4.0 Hz, C*H*$_2$O), 4.22 (1 H, dt, *J* = 11.6, 4.5 Hz, C*H*$_2$O), 7.23 - 7.29 (3 H, m, Ar*H*), 7.32 - 7.40 (2 H, m, Ar*H*).

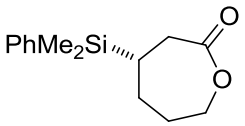
Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 90 : 10 v / v. Flow: 1 mL / min

Racemate *Enantiomerically enriched*



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
12.900	241907	49.950	12.927	4022857	83.998
14.273	244610	50.050	14.400	349814	16.002

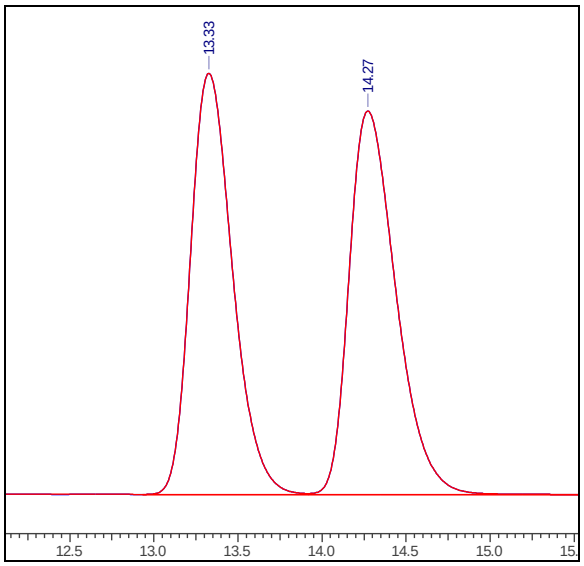
(*S*)-4-(Dimethyl(phenyl)silyl)oxepan-2-one (Table 3, entry 3)

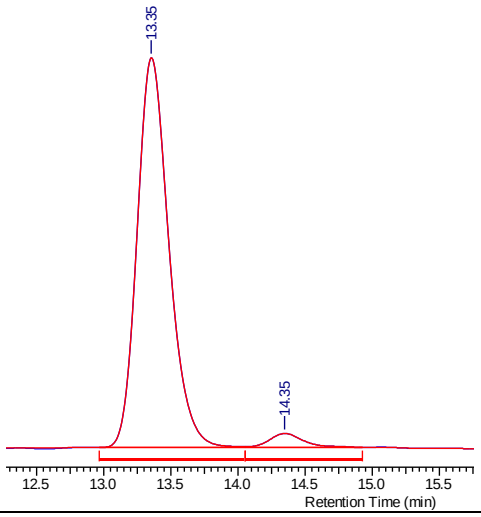


MS (ES^+) *m/z*: 271 ($M+Na^+$). HRMS calcd for $C_{14}H_{20}O_2SiNa$: 271.1125 Found: 271.1120; $[\alpha]_D^{28}$ = 3.1 for a sample of 96.5:3.5 er; ν_{max} (thin film/cm^{-1}): 3069, 3047, 2954, 2927, 2852, 1725, 1475, 1427, 1390, 1361, 1297, 1272, 1251, 1203, 1165, 1111, 1072, 1051; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.34 (3 H, s, SiC*H*$_3$), 0.35 (3 H, s, SiC*H*$_3$), 1.14 (1 H, tdd, *J* = 13.1, 2.5, 1.0 Hz, SiC*H*), 1.31 - 1.44 (1 H, m, SiCHC*H*$_2$), 1.67 - 1.80 (1 H, m, OCH$_2$C*H*$_2$), 1.91 - 2.04 (2 H, m, OCH$_2$C*H*$_2$ and SiCHC*H*$_2$), 2.40 (1 H, dd, *J* = 13.9, 12.1 Hz, C*H*$_2$C=O), 2.67 (1 H, apparent dt, *J* = 13.9, 1.3 Hz, C*H*$_2$C=O), 4.10 (1 H, dd, *J* = 12.6, 10.8 Hz, C*H*$_2$O), 4.27 (1 H, ddt, *J*=12.6, 5.0, 1.3, 1.3 Hz, C*H*$_2$O), 7.35 - 7.42 (3 H, m, Ar*H*), 7.47 - 7.51 (2 H, m, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm -5.3 (Si*C*H$_3$), -5.0 (Si*C*H$_3$), 22.1 (Si*C*H), 29.9 (*C*H$_2$), 30.6 (*C*H$_2$), 35.1 (*C*H$_2$C=O), 69.1 (*C*H$_2$O), 128.0 (Ar CH), 129.5 (Ar CH), 133.9 (Ar CH), 136.1 (Ar C), 176.6 (O=C).

Chiralpak AD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 97 : 3 v / v. Flow: 1 mL / min

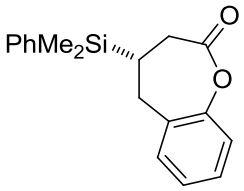
Racemic *Enantiomerically enriched*





Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
13.327	30258060	49.725	13.353	3807258	96.940
14.273	30592936	50.275	14.347	120175	3.060

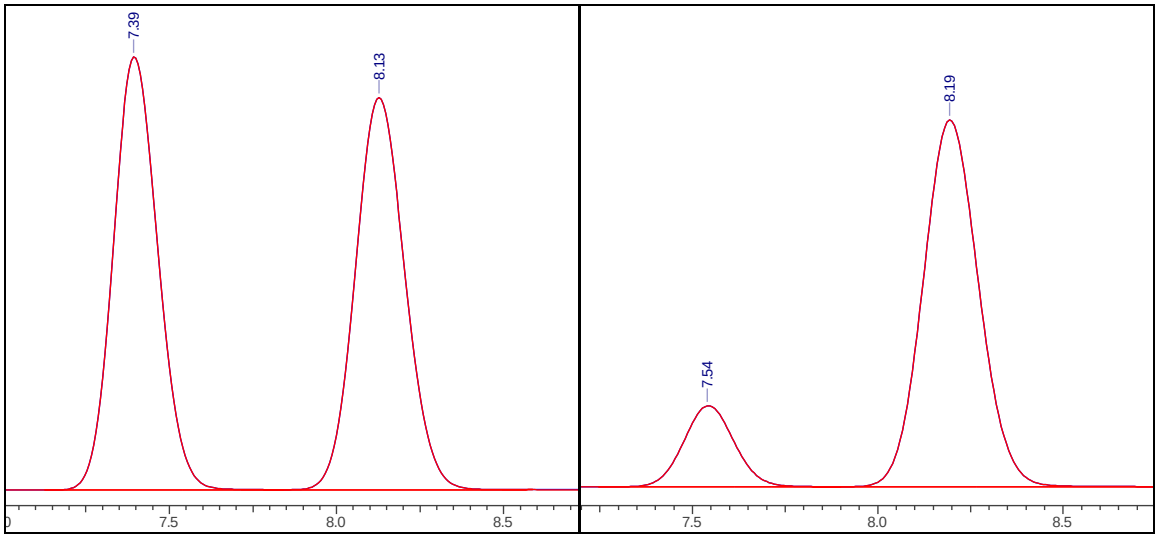
(*S*)-4-(Dimethyl(phenyl)silyl)-4,5-dihydrobenzo[b]oxepin-2(3H)-one (Table 3, entry 5)



MS (ES$^+$) *m/z*: 319 (M+Na). HRMS calcd for $C_{18}H_{20}O_2SiNa$: 319.1125 Found: 319.1121; $[\alpha]_D^{28}$ = 4.4 (c = 1.49 in $CHCl_3$) for a sample of 82:18 er; ν_{max} (thin film/cm^{-1}): 3069, 3047, 3024, 2954, 2925, 2856, 1754, 1608, 1583, 1485, 1457, 1427, 1334, 1312, 1250, 1220, 1185, 1166, 1151, 1112, 1090, 1035; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.3 (3 H, s, SiC*H*$_3$), 0.3 - 0.4 (3 H, s, SiC*H*$_3$), 1.9 (1 H, quin, *J* = 7.9 Hz, SiC*H*), 2.4 - 2.5 (1 H, m, SiCHC*H*$_2$), 2.4 (1 H, t, *J* = 7.7 Hz, SiCHC*H*$_2$), 2.8 (1 H, dd, *J* = 14.1, 6.8 Hz, C*H*$_2$C=O), 3.0 (1 H, dd, *J* = 14.1, 8.3 Hz, C*H*$_2$C=O), 7.0 - 7.2 (3 H, m, Ar*H*), 7.2 - 7.3 (1 H, m, Ar*H*), 7.3 - 7.4 (3 H, m, Ar*H*), 7.5 - 7.6 (2 H, m, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm -4.8 (SiCH$_3$), -4.7 (SiCH$_3$), 26.4 (SiCH), 29.4 (CH$_2$C=O), 32.0 (SiCHCH$_2$), 119.2 (Ar CH), 125.7 (Ar CH), 127.9 (Ar CH), 128.0 (Ar CH), 128.2 (Ar CH), 129.5 (Ar CH), 129.9 (Ar CH), 133.8 (Ar CH), 136.5 (Ar C), 151.8 (Ar C), 172.0 (O=C).

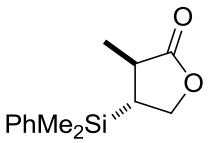
Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 95 : 5 v / v. Flow: 1 mL / min

Racemate *Enantiomerically enriched*



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
7.393	10408488	49.965	7.540	845352	16.765
8.127	10423215	50.035	8.193	4197101	83.235

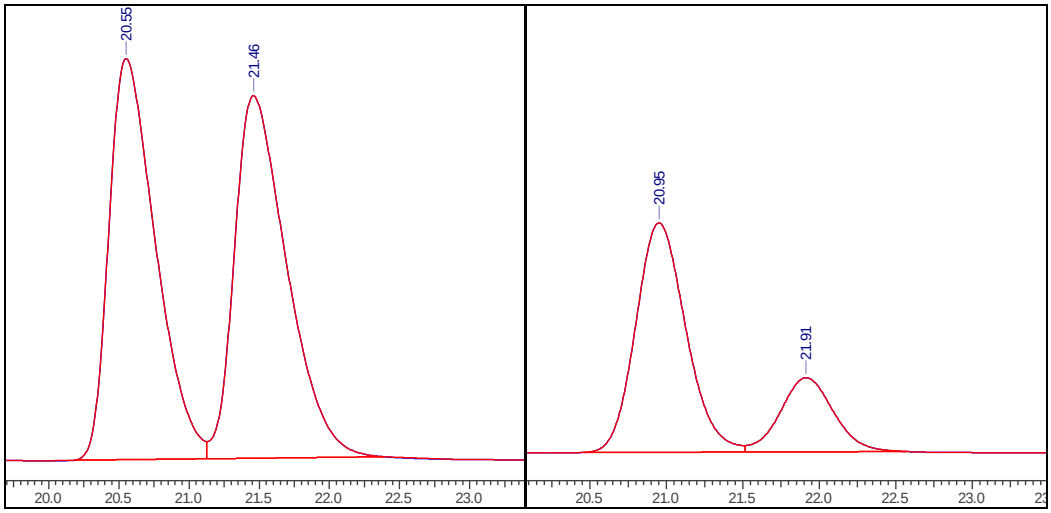
(3*R*,4*R*)-4-(Dimethyl(phenyl)silyl)-3-methyldihydrofuran-2(3H)-one (Table 3 entry 6)



Data for major diastereoisomer: MS (ES$^+$) *m/z*: 257 (M+Na$^+$). HRMS calcd for $C_{13}H_{18}O_2SiNa$: 257.0968. Found: 257.0968; $[\alpha]_D^{28}$= -31.2 for a sample of 77:23 er; ν_{max} (thin film/cm^{-1}): 3070, 3051, 2957, 2933, 2898, 1767, 1455, 1428, 1379, 1296, 1252, 1193, 1169, 1115, 1077, 1051, 1012; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.40 (3 H, s, SiC*H*$_3$), 0.40 (3 H, s, SiC*H*$_3$), 1.19 (3 H, d, *J* = 7.1 Hz, C*H*$_3$), 1.70 (1 H, td, *J* = 12.4, 8.6 Hz, SiC*H*), 2.35 (1 H, dq, *J* = 12.9, 7.1 Hz, C*H*C=O), 3.99 (1 H, dd, *J* = 12.4, 9.1 Hz, C*H*$_2$O), 4.31 (1 H, t, *J* = 8.8 Hz, C*H*$_2$O), 7.42 (2 H, m, Ar*H*), 7.47 - 7.51 (1 H, m, Ar*H*), 7.59 - 7.64 (2 H, m, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm -4.7 (Si*C*H$_3$), -4.6 (Si*C*H$_3$), 15.7 (CH$_3$), 32.0 (Si*C*H), 36.8 (*C*HC=O), 68.7 (CH$_2$O), 128.2 (Ar CH), 129.9 (Ar CH), 133.6 (Ar CH), 135.1 (Ar C), 180.8 (O=C).

Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 99.5 : 0.5 v / v. Flow: 1 mL / min

Racemic *Enantiomerically enriched*

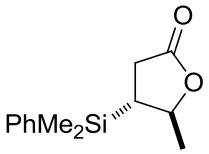


Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
20.553	9157579	50.322	20.953	719590	77.114
21.460	9040316	49.678	21.913	214942	23.886

Table 4: The products in entries 1, 2, 3 and 4 have been previously reported.

Representative experimental procedure 2 for Cu-catalyzed 1,4-conjugate silyl addition with a kinetic resolution:

(4*R*,5*S*)-4-(Dimethyl(phenyl)silyl)-5-methyldihydrofuran-2(3H)-one (Table 4, entry 1)[14]



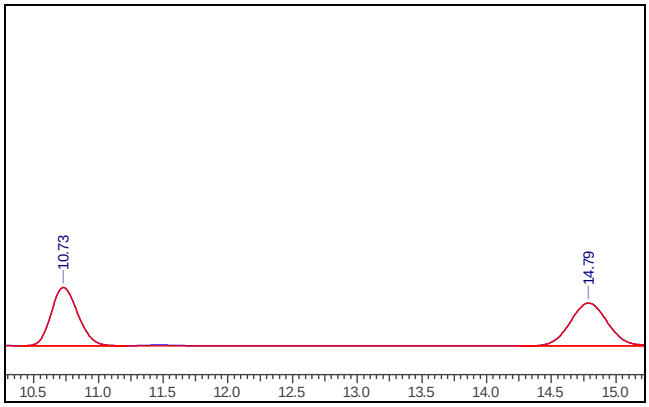
In an oven-dried vial equipped with a stirrer bar, (4*S*,5*S*)-1,3-bis(2-(naphthalen-2-yl)phenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate salt **L8** (7.9 mg, 0.011 mmol, 3.3 mol %), NaOBu-*t* (2.1 mg, 0.022 mmol, 6.6 mol %) and CuCl (1 mg, 0.010 mmol, 3 mol %) were placed and 1.5 mL of THF was added. The solution was allowed to stir for 3 hours at 50 °C under nitrogen, it was then filtered through a short plug of oven-dried Celite under nitrogen. $PhMe_2SiB(pin)$ (0.055 mL, 0.200 mmol, 0.6 equiv) was added to the filtrate and the mixture stirred for 15 min. The solution was then cooled to –78 °C, and a solution of 5-methylfuran-2(5H)-one (32.7 mg, 0.334 mmol, 1 equiv) in dry THF (0.5 mL) was added and the mixture was allowed to stir for 7 hours at –78 °C, after which time the reaction was quenched by the addition of H_2O (0.5 mL) and allowed to warm to room temperature overnight. The aqueous layer was then washed with Et_2O (3 x 2 mL) and dried over $MgSO_4$. Concentration *in vacuo* and separation by column chromatography (silica gel, 20 % EtOAc in hexanes) yielded (4*R*,5*S*)-4-(dimethyl(phenyl)silyl)-5-methyldihydrofuran-2(3H)-one as a pale yellow oil (36.0 mg, 0.153 mmol, 46 %).

$[\alpha]_D^{28}$ = -18.5 (c = 3.2 in $CHCl_3$) for a sample of 86:14 er. Lit: $[\alpha]_D^{20}$ = -22 (c = 0.44 in $CHCl_3$) for a sample of 89:11 er. [13]

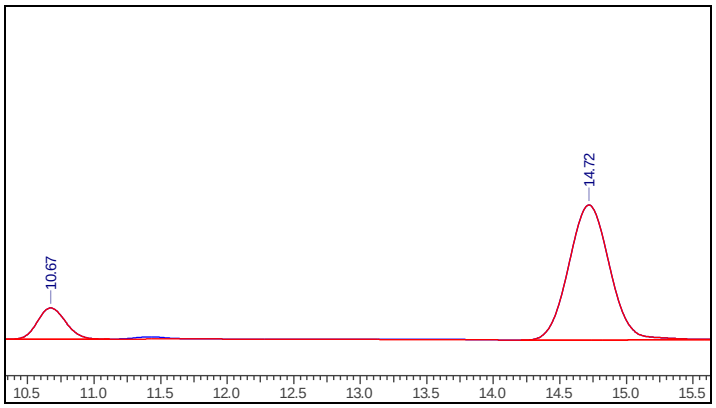
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.39 (3 H, s, SiCH_3), 0.40 (3 H, s, SiCH_3), 1.30 (3 H, d, *J* = 6.0 Hz, CH_3), 1.62 (1 H, ddd, *J* = 12.9, 10.4, 8.8 Hz, SiC*H*), 2.40 (1 H, dd, *J* = 17.7, 12.9 Hz, CH_2C=O), 2.56 (1 H, dd, *J* = 17.7, 8.8 Hz, CH_2C=O), 4.46 (1 H, dq, *J* = 10.4, 6.0 Hz, CH_2O), 7.36 - 7.45 (3 H, m, Ar*H*), 7.46 - 7.52 (2 H, m, Ar*H*).

Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 90 : 10 v /v. Flow: 1 mL / min

Racemate

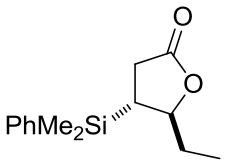


Enantiomerically enriched



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
10.727	4352819	49.098	10.673	2664652	13.977
14.787	4512771	50.902	14.720	16399562	86.023

(4*R*,5*S*)-4-(Dimethyl(phenyl)silyl)-5-ethyldihydrofuran-2(3H)-one (Table 4, entry 2)[15]



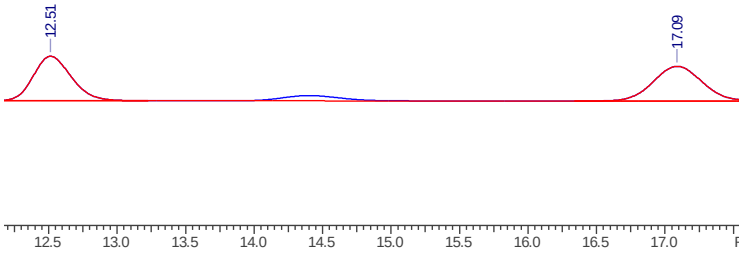
$[\alpha]_D^{28}$ = -25.0 (c = 1.67 in $CHCl_3$) for a sample of 90:10 er. Lit: $[\alpha]_D^{25}$ = 31.8 (c = 0.66 in $CHCl_3$) for a sample of the opposite enantiomer in 99:1 er. [14]

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.38 (3 H, s, SiCH_3), 0.39 (3 H, s, SiCH_3), 0.97 (3 H, t, *J* = 7.4 Hz, CH_3), 1.50 (1 H, m, CH_2), 1.56 - 1.64 (1 H, m, CH_2), 1.69 (1 H, dt, *J* = 12.1, 9.6 Hz, SiC*H*), 2.39 (1 H, dd, *J* =

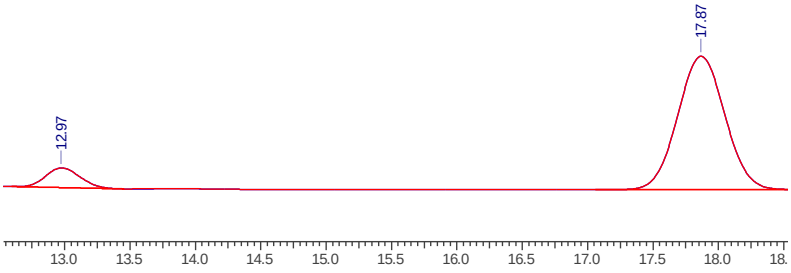
17.8, 12.1 Hz, CH_2C=O), 2.57 (1 H, dd, *J* = 17.7, 9.5 Hz, CH_2C=O), 4.31 (1 H, ddd, *J* = 9.8, 7.9, 3.2 Hz, C*H*O), 7.37 - 7.44 (3 H, m, Ar*H*), 7.46 - 7.50 (2 H, m, Ar*H*).

Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 95 : 5 v / v. Flow: 1 mL / min

Racemate

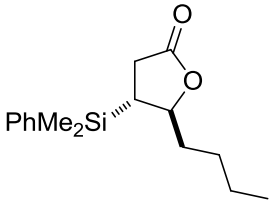


Enantiomerically enriched



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
12.513	1006430	50.305	12.973	780559	9.905
17.087	994211	49.695	17.867	7099897	90.095

(4*R*,5*S*)-5-Butyl-4-(dimethyl(phenyl)silyl)dihydrofuran-2(3H)-one (Table 4, entry 3)[14]

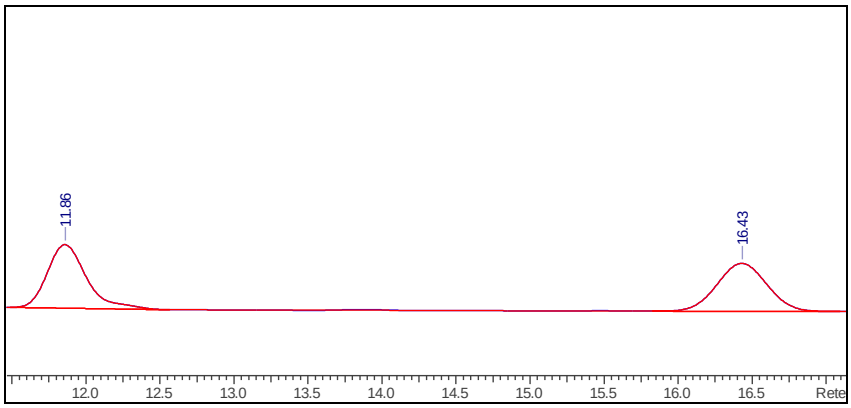


$[\alpha]_D^{30}$ = -4.54 (c = 1.35 in $CHCl_3$) for a sample of 91:9 er.

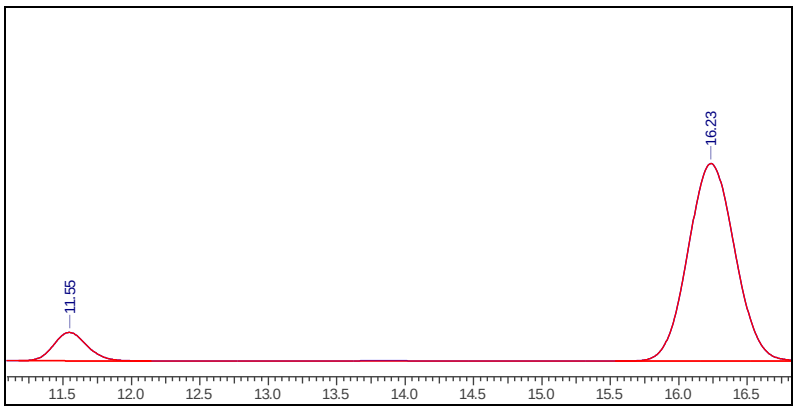
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.39 (3 H, s, SiC*H*$_3$), 0.42 (3 H, s, SiC*H*$_3$), 0.85 (3 H, t, *J* = 7.3 Hz, C*H*$_3$), 1.20 - 1.36 (4 H, m, C*H*$_2$), 1.41 - 1.52 (2 H, m, C*H*$_2$), 1.67 (1 H, dt, *J* = 12.3, 9.6 Hz, SiC*H*), 2.38 (1 H, dd, *J* = 17.7, 12.3 Hz, C*H*$_2$C=O), 2.56 (1 H, dd, *J* = 17.7, 9.1 Hz, C*H*$_2$C=O), 4.31 - 4.38 (1 H, m, C*H*O), 7.38 - 7.44 (3 H, m, Ar*H*), 7.46 - 7.50 (1 H, m, Ar*H*), 7.59 - 7.63 (1 H, m, Ar*H*).

Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 95 : 5 v / v. Flow: 1 mL / min

Racemate

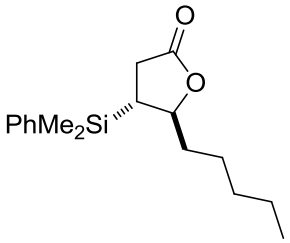


Enantiomerically enriched



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
11.856	9474256	49.478	11.547	1196107	9.344
16.427	9676054	50.515	16.233	11604609	90.656

(4*R*,5*S*)-4-(Dimethyl(phenyl)silyl)-5-pentyldihydrofuran-2(3H)-one (Table 4, entry 4)[14]

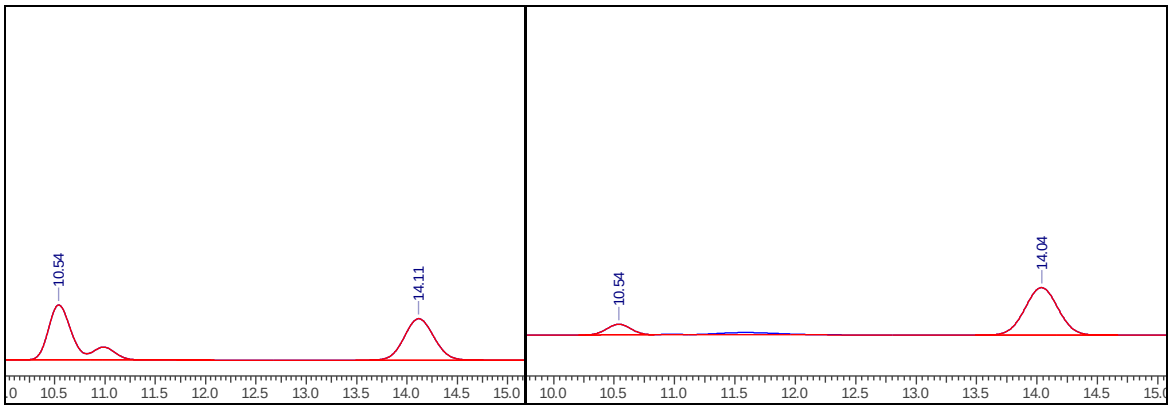


$[\alpha]_D^{28}$ = -22.5 (c = 0.38 in $CHCl_3$) for a sample of 86:14 er. Lit: $[\alpha]_D^{25}$ = 45.1 (c = 0.82 in $CHCl_3$) for a sample of the opposite enantiomer in 99:1 er.[14]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.38 (3 H, s, SiC*H*$_3$), 0.39 (3 H, s, SiC*H*$_3$), 0.87 (3 H, t, *J* = 6.6 Hz, C*H*$_3$), 1.11 - 1.36 (6 H, m, 3 x C*H*$_2$), 1.39 - 1.57 (2 H, m, C*H*$_2$), 1.67 (1 H, dt, *J*=12.1, 9.6 Hz, SiC*H*), 2.38 (1 H, dd, *J* = 17.5, 12.1 Hz, C*H*$_2$C=O), 2.56 (1 H, dd, *J* = 17.5, 9.2 Hz, C*H*$_2$C=O), 4.28 - 4.41 (1 H, m, C*H*O), 7.34 - 7.45 (3 H, m, Ar*H*), 7.45 - 7.52 (2 H, m, Ar*H*).

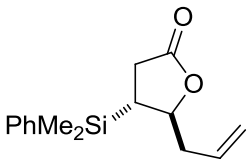
Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent hexane : *iso*-propanol 95 : 5 v / v. Flow: 1 mL / min

Racemate *Enantiomerically enriched*



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
11.540	9884405	49.817	10.540	176513	14.369
14.109	9957071	50.183	14.040	1044390	85.631

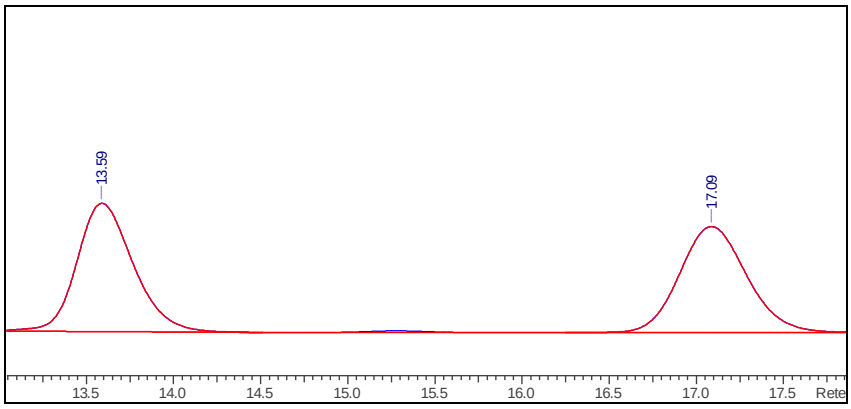
(4*R*,5*S*)-5-Allyl-4-(dimethyl(phenyl)silyl)dihydrofuran-2(3H)-one (Table 4, entry 5)



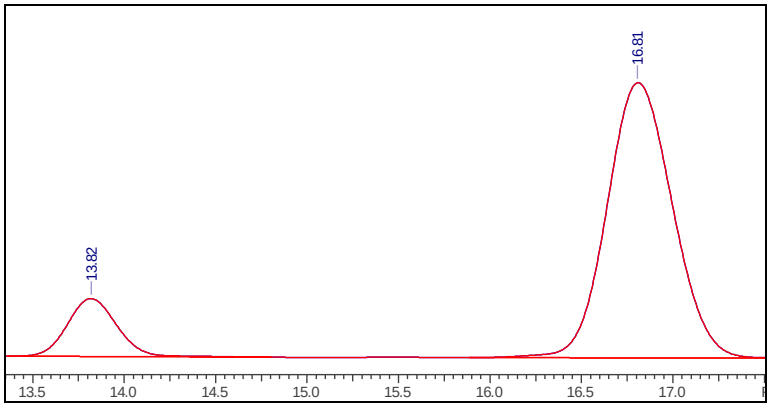
MS (ES^+) *m/z*: 283 (M+Na). HRMS calcd for $C_{15}H_{20}O_2SiNa$: 283.1125. Found: 283.1122; $[\alpha]_D^{28}$ = -15.3 (c = 1.58 in $CHCl_3$) for a sample of 84:16 er; ν_{max} (thin film/cm^{-1}): 3072, 3050, 3011, 2956, 1773, 1428, 1367, 1351, 1253, 1206, 1171, 1149, 1114, 1080, 1044, 1024; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.39 (3 H, s, SiCH_3), 0.40 (3 H, s, SiCH_3), 1.75 (1 H, dt, *J* = 12.0, 9.8 Hz, SiC*H*), 2.15 (1 H, dt, *J* = 14.8, 7.3 Hz, CH_2), 2.33 - 2.39 (1 H, m, CH_2), 2.39 (1 H, dd, *J* = 17.7, 12.0 Hz, CH_2C=O), 2.57 (1 H, dd, *J* = 17.7, 9.5 Hz, CH_2C=O), 4.43 (1 H, ddd, *J* = 10.1, 6.6, 3.5 Hz, C*H*O), 5.00 (1 H, dq, *J* = 17.0, 1.6 Hz, C=CH_2 *trans*), 5.10 (1 H, dt, *J* = 10.4, 0.9 Hz, CH=CH_2 *cis*), 5.76 (1 H, ddt, *J* = 17.3, 10.1, 6.9 Hz, C*H*=CH_2), 7.38 - 7.44 (3 H, m, Ar*H*), 7.47 - 7.51 (2 H, m, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ -5.0 (Si*C*H_3), -4.4 (Si*C*H_3), 27.7 (SiCH), 31.7 (*C*H_2C=O), 39.4 (CH_2), 82.6 (CHO), 118.7 (HC=*C*H_2), 128.2 (Ar CH), 129.9 (Ar CH), 132.5 (H*C*=CH_2), 133.7 (Ar CH), 135.2 (Ar C), 177.1 (O=C).

Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 95 : 5 v / v. Flow: 1 mL / min

Racemic

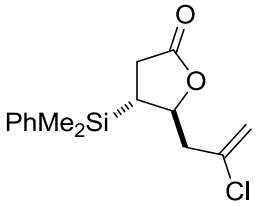


Enantiomerically enriched



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
13.587	7312011	50.473	13.820	741064	15.715
17.087	7174991	49.527	16.807	3974583	84.285

(4*R*,5*S*)-5-(2-Chloroallyl)-4-(dimethyl(phenyl)silyl)dihydrofuran-2(3H)-one (Table 4, entry 6)

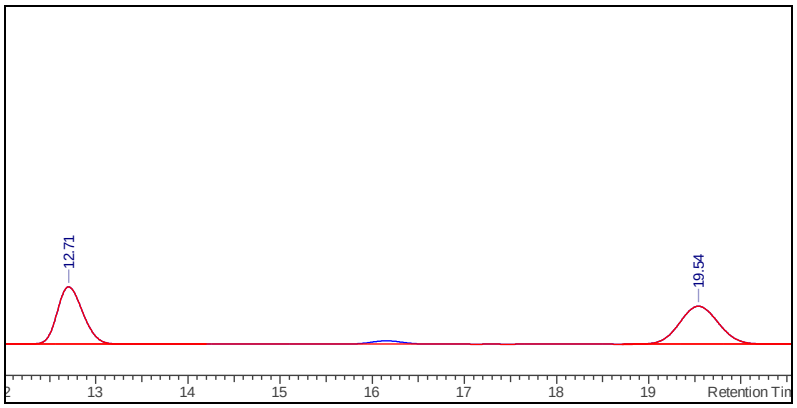


MS (ES^+) *m/z*: 317 (M+Na) HRMS calcd for $C_{15}H19O_2SiNa$: 317.0736. Found: 317.0724; $[\alpha]_D^{28}$ = -19.3 (c = 1.17 in $CHCl_3$) for a sample of 89:11 er; ν_{max} (thin film/cm^{-1}): 2956, 1772, 1639, 1427, 1352, 1253, 1206, 1176, 1115, 1022; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.41 (3 H, s, SiC*H*$_3$), 0.43 (3 H, s, SiC*H*$_3$), 1.70 (1 H, dt, *J* = 12.0, 9.6 Hz, SiC*H*), 2.35 - 2.48 (1 H, m, C*H*$_2$) 2.41 (1 H, dd, *J* = 17.7, 11.9 Hz, C*H*$_2$C=O), 2.54 (1 H, dd, *J* = 14.9, 8.6 Hz, C*H*$_2$), 2.60 (1 H, dd, *J* = 17.7, 9.6 Hz, C*H*$_2$C=O), 4.67 (1 H, ddd, *J* = 9.9, 8.6, 2.8 Hz, C*H*O), 5.24 (2 H, apparent dd, *J* = 15.4, 1.3 Hz, C=C*H*$_2$), 7.38 - 7.45 (3 H, m, Ar*H*), 7.48 - 7.53 (2 H, m, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ -5.0 (Si*C*H$_3$), -4.4 (Si*C*H$_3$), 28.4 (SiCH), 31.6 (*C*H$_2$C=O), 45.5 (CH$_2$), 79.8 (CHO), 115.6 (CCl=*C*H$_2$), 128.3 (Ar CH), 130.1 (Ar CH), 133.8 (Ar CH), 134.8 (Ar C), 137.1 (*C*Cl=CH$_2$), 176.5 (O=C).

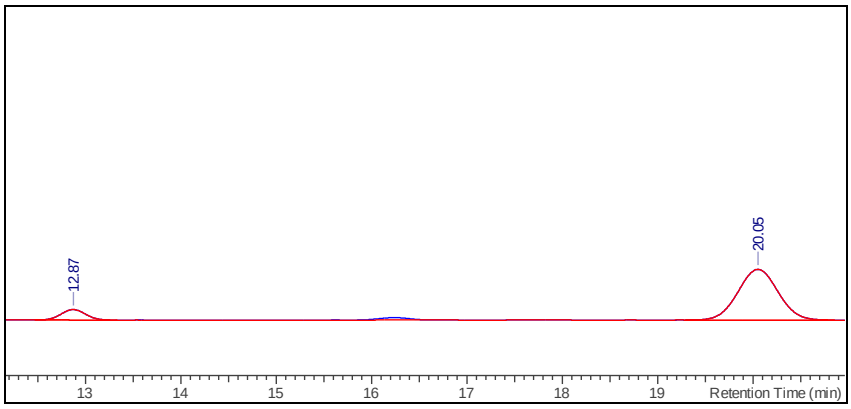
Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : *iso*-propanol 90 : 10 v/v

Flow: 1 mL / min

Racemate

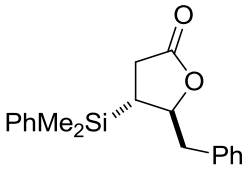


Enantiomerically enriched



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
12.707	9237386	49.919	12.873	82347	11.267
19.540	9267400	50.081	20.053	648546	88.733

(4*R*,5*S*)-5-Benzyl-4-(dimethyl(phenyl)silyl)dihydrofuran-2(3H)-one (Table 4, entry 7)

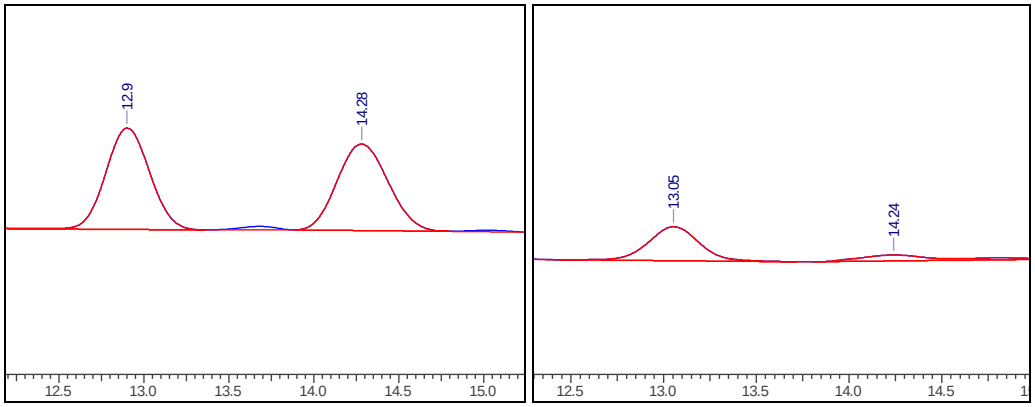


MS (ES^+) *m/z*: 333 (M+Na). HRMS calcd for $C_{19}H_{22}O_2SiNa$: 333.1281. Found: 333.1285; $[\alpha]_D^{28}$ = -20.1 (c = 1.33 in $CHCl_3$) for a sample of 86:14 er; ν_{max} (thin film/cm^{-1}): 3068, 3029, 2955, 2919, 2866, 1770, 1604, 1495, 1455, 1427, 1352, 1252, 1204, 1148, 1114, 1073, 1047, 1018; ^1H NMR (300 MHz, $CDCl_3$)

δ ppm 0.39 (6 H, s, Si(C*H*$_3$)$_2$), 1.73 (1 H, dt, *J* = 11.3, 9.6 Hz, SiC*H*), 2.36 (1 H, dd, *J* = 17.9, 11.5 Hz, C*H*$_2$C=O), 2.51 (1 H, dd, *J* = 17.9, 10.0 Hz, C*H*$_2$C=O), 2.71 (1 H, dd, *J* = 14.3, 7.3 Hz, C*H*$_2$Ph), 2.85 (1 H, dd, *J* = 14.3, 3.2 Hz, C*H*$_2$Ph), 4.59 (1 H, ddd, *J* = 9.5, 7.1, 3.4 Hz, C*H*O), 7.04 - 7.11 (2 H, m, Ar*H*), 7.21 - 7.31 (3 H, m, Ar*H*), 7.38 - 7.46 (3 H, m, Ar*H*), 7.47 - 7.55 (2 H, m, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.1 (SiCH$_3$), -4.3 (SiCH$_3$), 27.7 (SiCH), 31.6 (CH$_2$C=O), 41.7 (CH$_2$Ph), 83.5 (CHO), 126.8 (Ar CH), 127.9 (Ar CH), 128.3 (Ar CH), 128.4 (Ar CH), 129.6 (Ar CH), 130.0 (Ar CH), 133.0 (Ar CH), 133.8 (Ar CH), 135.3 (Ar C), 136.5 (Ar C), 176.9 (O=C).

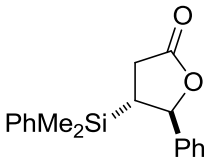
Chiralcel OD-H column, 28 °C, λ = 220 nm. Eluent: hexane : ethanol 95 : 5 v / v. Flow: 1 mL / min

Racemate *Enantiomerically enriched*



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
12.900	6804310	50.010	13.048	8614486	86.175
14.280	6801497	49.990	14.243	1402358	13.825

(4*R*,5*S*)-4-(Dimethyl(phenyl)silyl)-5-phenyldihydrofuran-2(3H)-one (Table 4 entry 8)

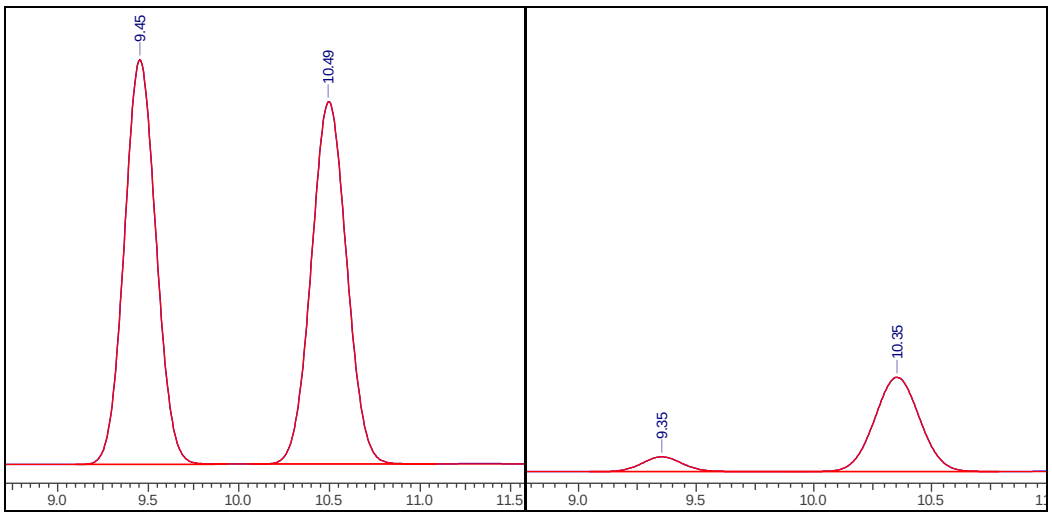


MS (ES$^+$) *m/z*: 319 (M+Na$^+$). HRMS calcd for $C_{18}H_{20}O_2SiNa$: 319.1125. Found: 319.1120; $[\alpha]_D^{28}$ = -20.9 (c = 1.55 in $CHCl_3$) for a sample of 88.5:11.5 er; ν_{max} (thin film/cm^{-1}): 3068, 3017, 2955, 2923, 2854, 1773, 1648, 1619, 1497, 1457, 1427, 1373, 1251, 1219, 1205, 1164, 1113, 1048, 1023; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.23 (3 H, s, SiC*H*$_3$), 0.26 (3 H, s, SiC*H*$_3$), 2.09 (1 H, ddd, *J* = 12.3, 10.1, 8.8 Hz, SiC*H*),

2.51 (1 H, dd, *J* = 17.3, 12.3 Hz, C*H*$_2$C=O), 2.69 (1 H, dd, *J* = 17.3, 8.8 Hz, C*H*$_2$C=O), 5.21 (1 H, d, *J* = 10.4 Hz, C*H*O), 7.27 (2 H, m, Ar*H*), 7.32 - 7.44 (6 H, m, Ar*H*), 7.58 - 7.63 (2 H, m, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm -4.7 (Si*C*H$_3$), -4.3 (Si*C*H$_3$), 32.4 (*C*H$_2$C=O), 32.7 (SiCH), 85.0 (CHO), 126.8 (Ar CH), 127.9 (Ar C), 128.2 (Ar CH), 128.6 (Ar CH), 129.0 (Ar CH), 133.0 (Ar CH), 133.8 (Ar CH), 135.0 (Ar C), 176.9 (O=C).

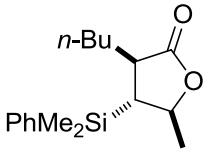
Chiralpak IA column, 28 °C, λ = 220 nm. Eluent hexane: ethanol 97 : 3 v / v. Flow: 0.85 mL / min

Racemic *Enantiomerically enriched*



Retention time (min)	Area [mAU*s]	Area [%]	Retention time (min)	Area [mAU*s]	Area [%]
9.446	1006430	50.305	9.354	1021759	11.432
10.491	994211	49.695	10.348	7863102	88.568

(3*S*,4*R*,5*S*)-3-Butyl-4-(dimethyl(phenyl)silyl)-5-methyldihydrofuran-2(3H)-one[16]



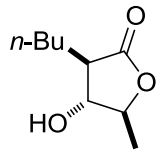
To a stirred solution of diisopropylamine (0.036 mL, 0.256 mmol, 1.5 equiv) in dry THF (0.12 mL) at –78 °C, was added n-BuLi (0.18 mL, 1.44 M, 1.5 equiv) dropwise, and the mixture stirred for 1 h. To

the resulting LDA solution, (4*R*,5*S*)-4-(dimethyl(phenyl)silyl)-5-methyldihydrofuran-2(3H)-one (40 mg, 0.171 mmol, 1 equiv) in dry THF (0.12 mL) was added dropwise and stirred for 1.5 hours at –78 °C. A solution of n-BuI (0.058 mL, 0.512 mmol, 3 equiv) in DMPU (0.03 mL) was then added dropwise at –78 °C. The reaction was then allowed to warm to room temperature overnight and quenched with saturated NH_4Cl solution (1 mL) at 0 °C. The aqueous layer was then extracted with Et_2O (3 x 2 mL) and dried over $NaSO_4$. Concentration *in vacuo* and separation by column chromatography (silica gel, 10 % EtOAc in hexanes) yielded the title compound as a pale yellow oil (36.2 mg, 0.125 mmol, 73 %).

The spectroscopic data was in agreement with the literature other than: $[\alpha]_D^{25}$ = -11.53 (c = 2 in $CHCl_3$) for a sample of 89:11 er, Lit: $[\alpha]_D^{25}$ = -9.48 (c = 3.13 in $CHCl_3$) for a sample of 85:15 er.[15]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.4 (6 H, s, SiC*H*$_3$), 0.8 (3 H, t, *J* = 7.0 Hz, CH_2CH_3), 1.1 - 1.2 (3 H, m, C*H*$_2$), 1.3 (3 H, d, *J* = 6.0 Hz, C*H*$_3$), 1.3 - 1.4 (2 H, m, C*H*$_2$), 1.4 (1 H, dd, *J* = 12.1, 10.2 Hz, SiC*H*), 1.5 - 1.7 (1 H, m, C*H*$_2$), 2.5 (1 H, ddd, *J* = 12.0, 6.4, 4.1 Hz, C*H*C=O), 4.4 (1 H, dq, *J* = 10.0, 6.0 Hz, C*H*O), 7.3 - 7.4 (3 H, m, Ar*H*), 7.5 - 7.6 (2 H, m, Ar*H*).

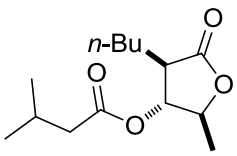
(3*R*,4*R*,5*S*)-3-Butyl-4-hydroxy-5-methyldihydrofuran-2(3H)-one[17]



The spectroscopic data was in agreement with the literature other than: $[\alpha]_D^{25}$ = -12.8 (c = 2 in $CHCl_3$) for a sample of 89:11 er, Lit: $[\alpha]_D^{22}$ = -16.0 (c = 1.0 in $CHCl_3$) for a sample of >98.5:1.5 er.[16]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 0.92 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 1.21 - 1.69 (5 H, m, C*H*$_2$), 1.46 (3 H, d, *J* = 6.2 Hz, CHOC*H*$_3$), 1.79 - 1.95 (1 H, m, C*H*$_2$), 2.29 (1 H, br. S, O*H*), 2.57 (1 H, ddd, *J* = 8.7, 7.3, 5.7 Hz, C*H*C=O), 3.85 (1 H, dd, *J* = 8.7, 7.2 Hz, C*H*OH), 4.16 - 4.27 (1 H, m, C*H*O).

(2*S*,3*R*,4*R*)-4-Butyl-2-methyl-5-oxotetrahydrofuran-3-yl 3-methylbutanoate[16]



The spectroscopic data was in agreement with the literature other than: $[\alpha]_D^{28}$ = 5.65 (c = 1.25 in $CHCl_3$) for a sample of 89:11 er, Lit: $[\alpha]_D^{25}$ = 11.8 (c = 1.2 in $CHCl_3$) for a sample of >98.5:1.5 er.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.92 (3 H, t, *J* = 7.1 Hz, CH_2CH_3), 0.99 (6 H, d, *J* = 6.6 Hz, $CH(CH_3)_2$), 1.28 - 1.46 (4 H, m, CH_2), 1.48 (3 H, d, *J* = 6.6 Hz, $CHOCH_3$), 1.61 - 1.70 (1 H, m, CH_2), 1.81 - 1.92 (1 H, m, CH_2), 2.05 - 2.18 (1 H, m, $CH(CH_3)_2$), 2.24 (2 H, d, *J* = 7.1 Hz, $CH_2C{=}O$), 2.69 (1 H, dt, *J* = 8.3, 5.8 Hz, $CHC{=}O$), 4.37 (1 H, qd, *J* = 6.6, 4.5 Hz, $CHOCH_3$), 4.95 (1 H, dd, *J* = 5.8, 4.8 Hz $CHOC{=}O$).

^{1}H NMR and ^{13}C NMR Spectra

500 MHz $CDCl_3$

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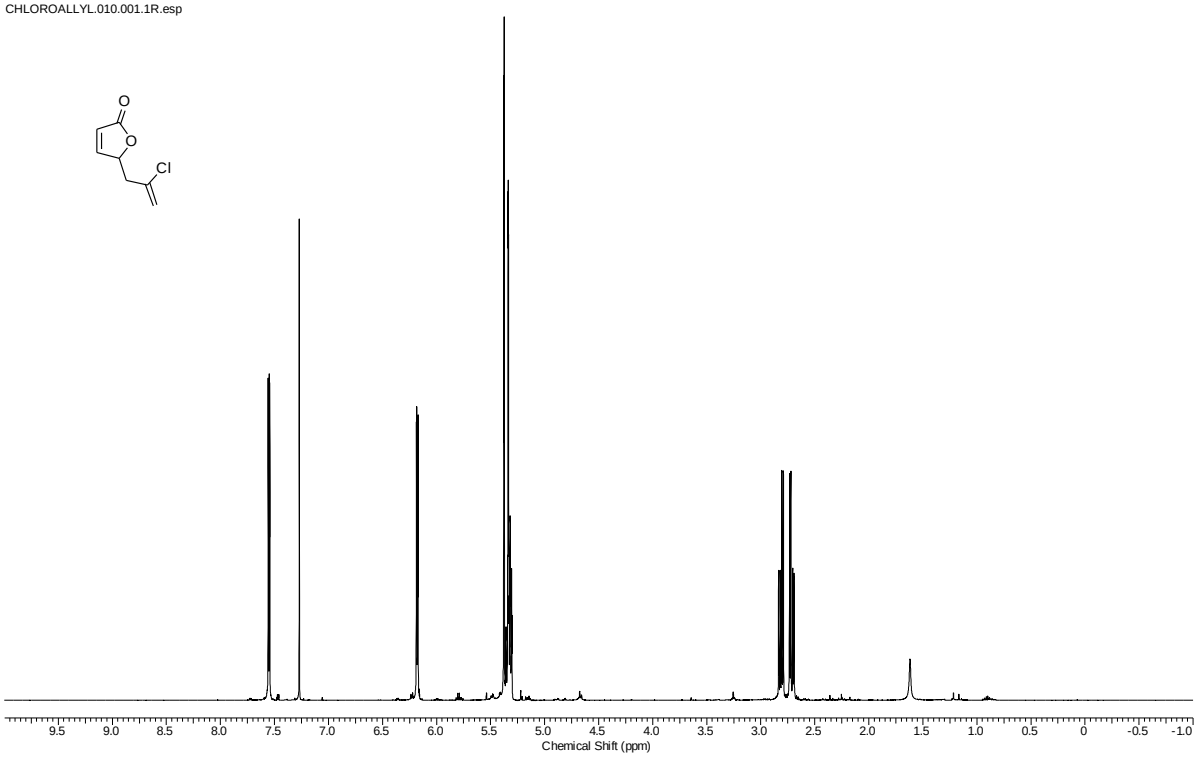
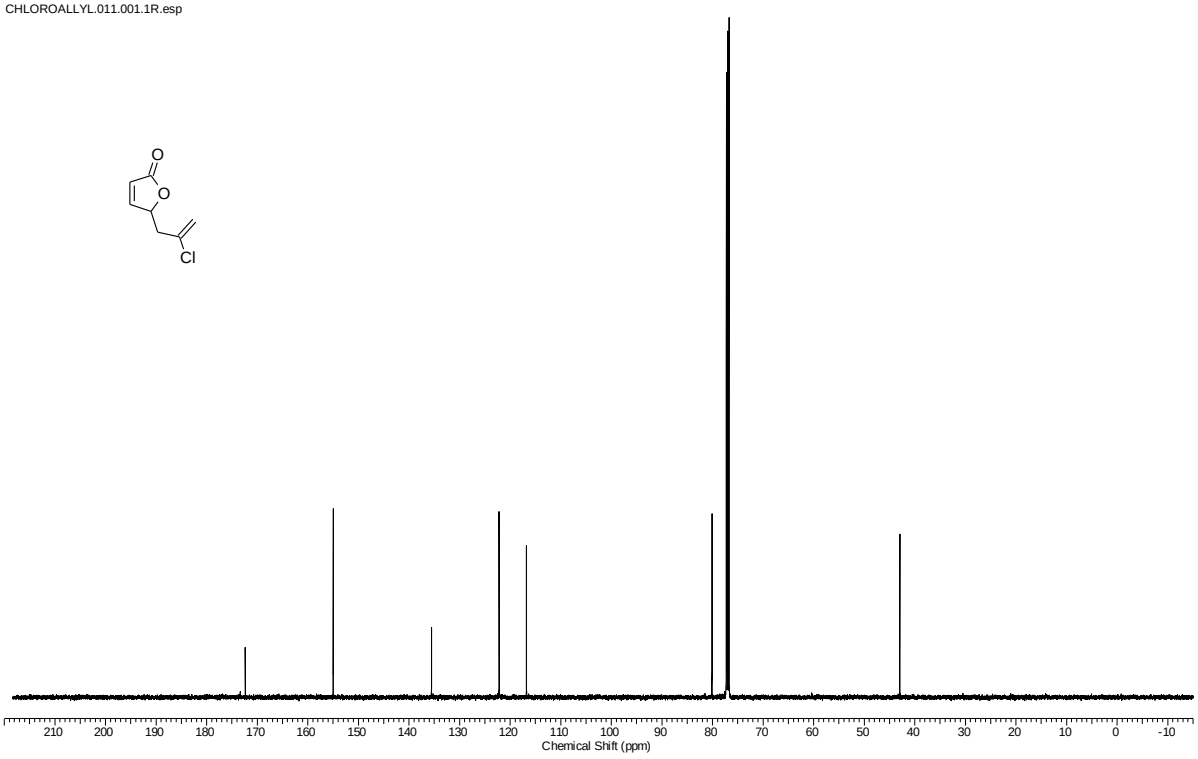


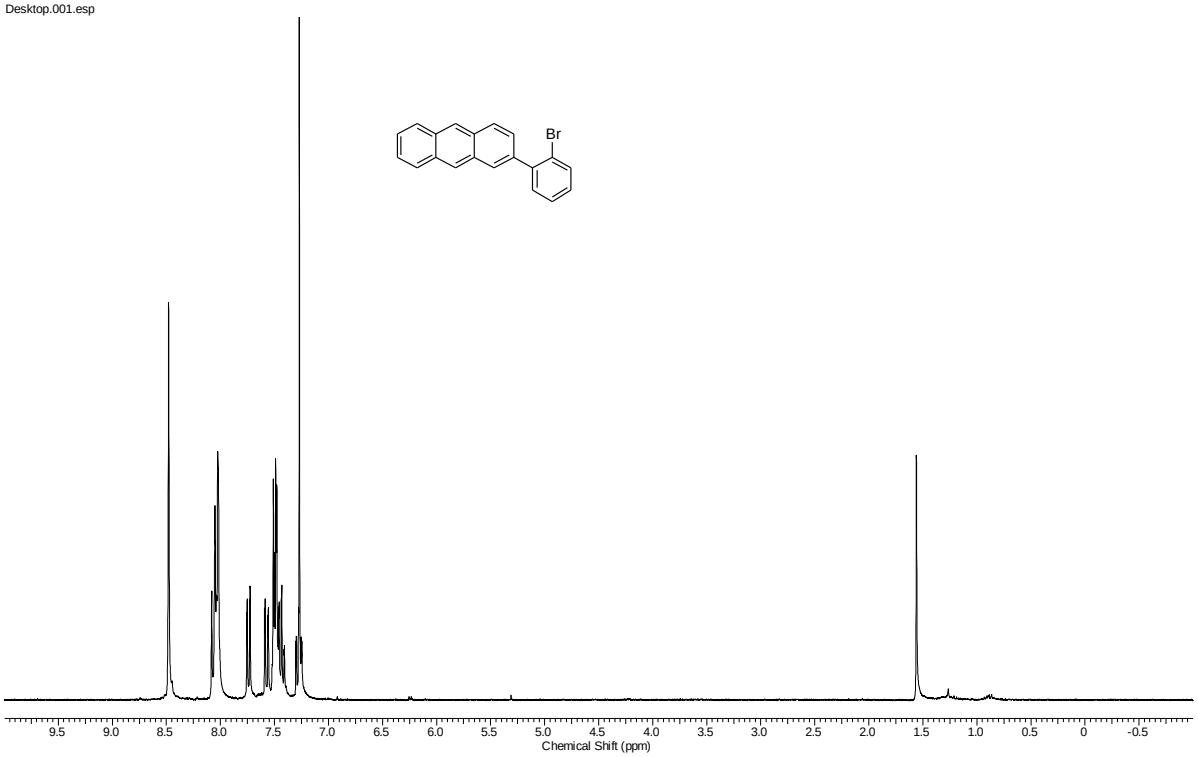
126 MHz $CDCl_3$

CHLOROALLYL.011.001.1R.esp



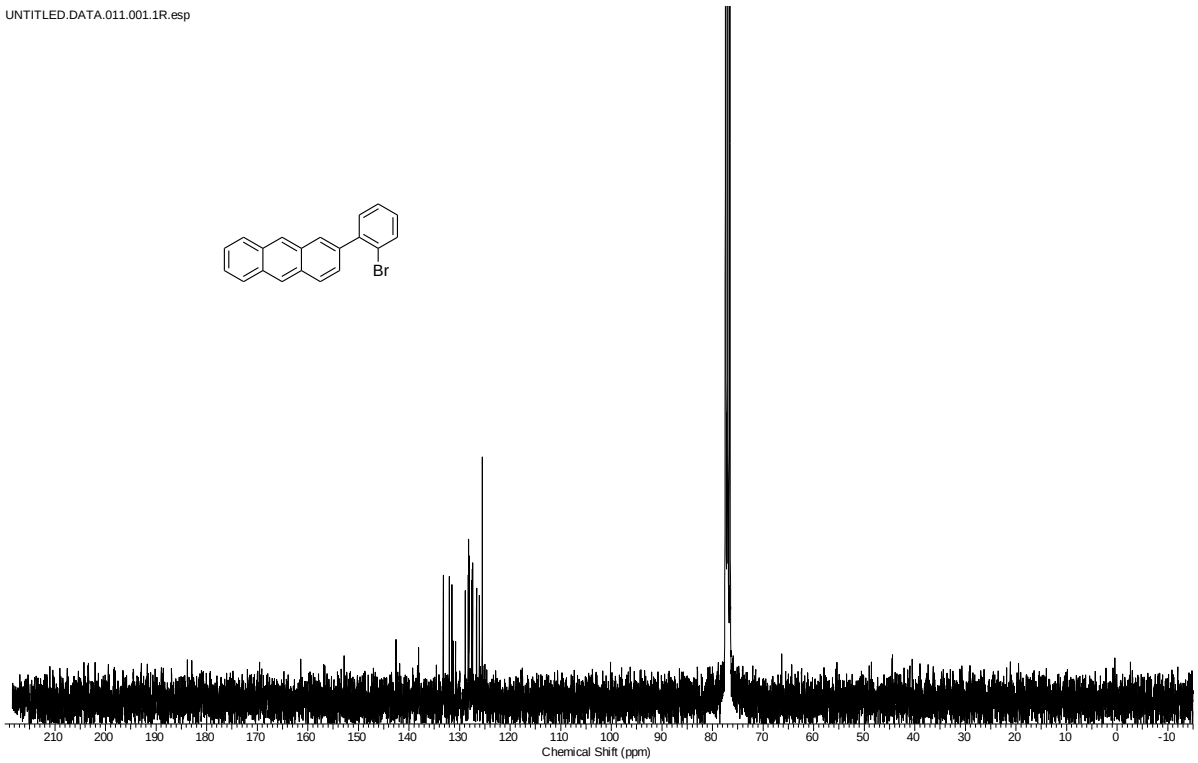
300 MHz $CDCl_3$

Desktop.001.esp



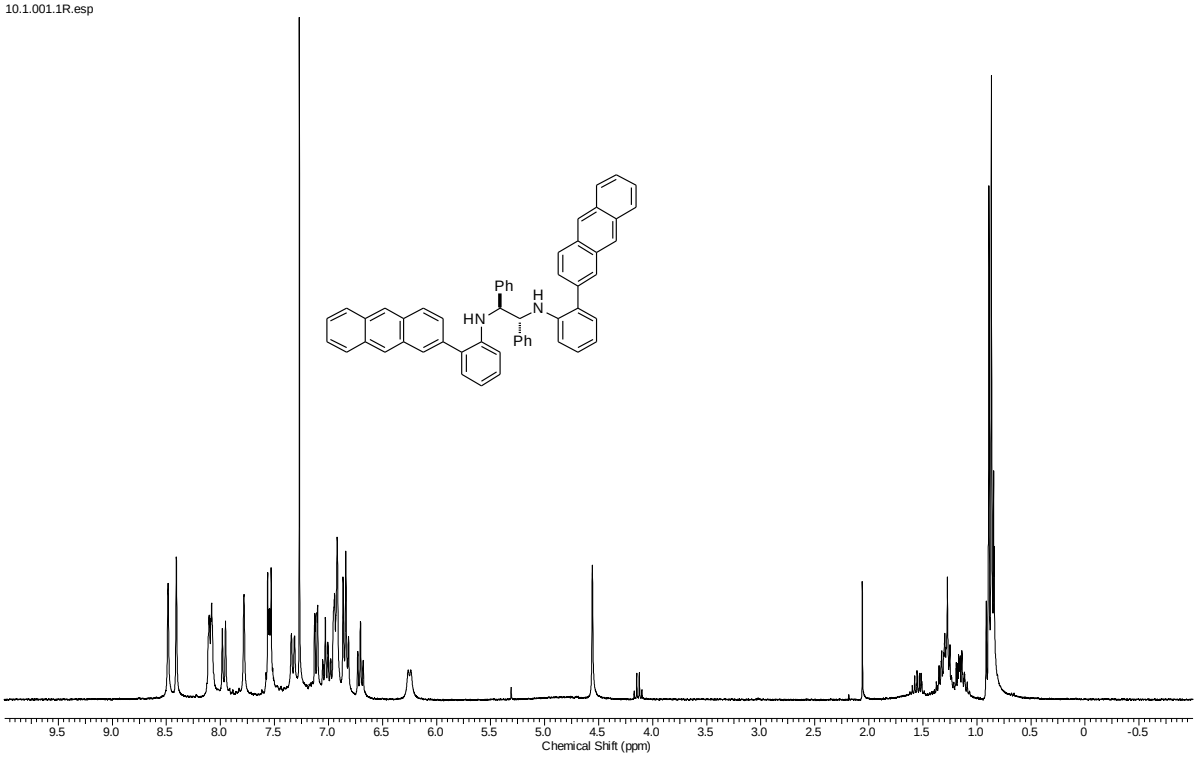
75 MHz $CDCl_3$

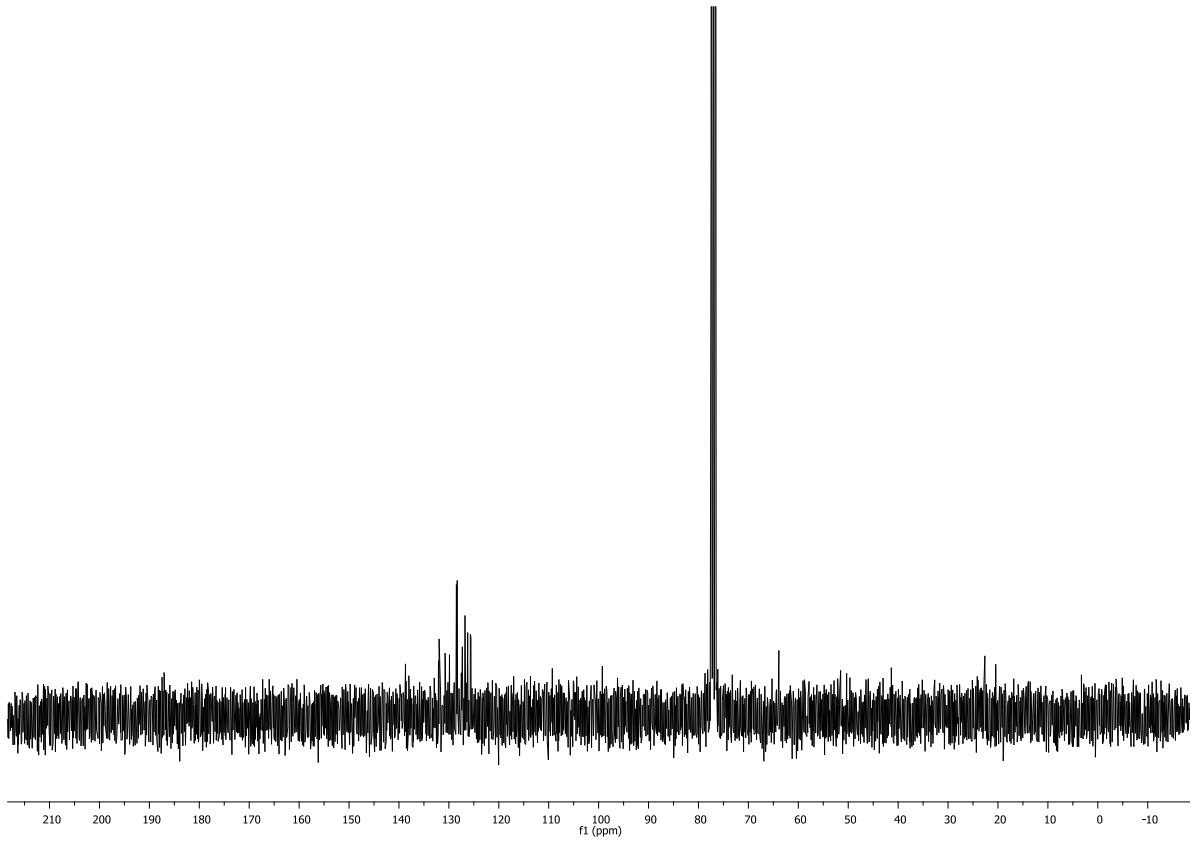
UNTITLED.DATA.011.001.1R.esp



300 MHz $CDCl_3$

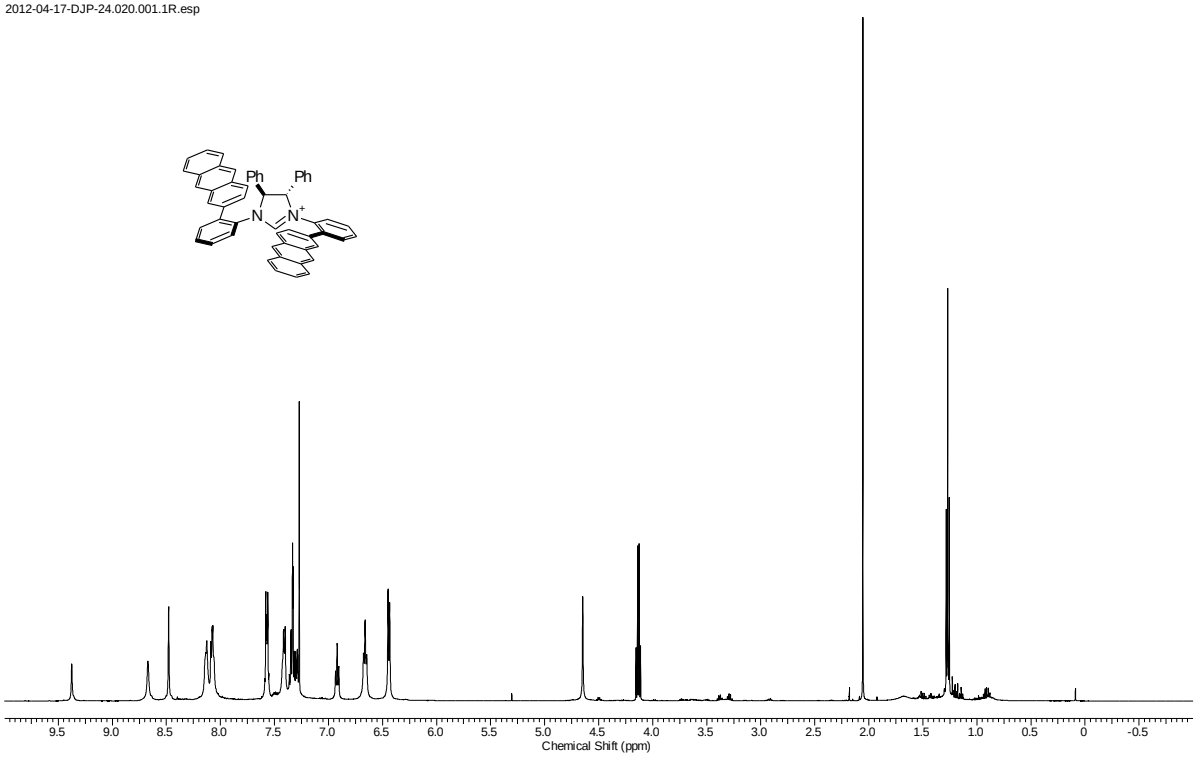
10.1.001.1R.esp





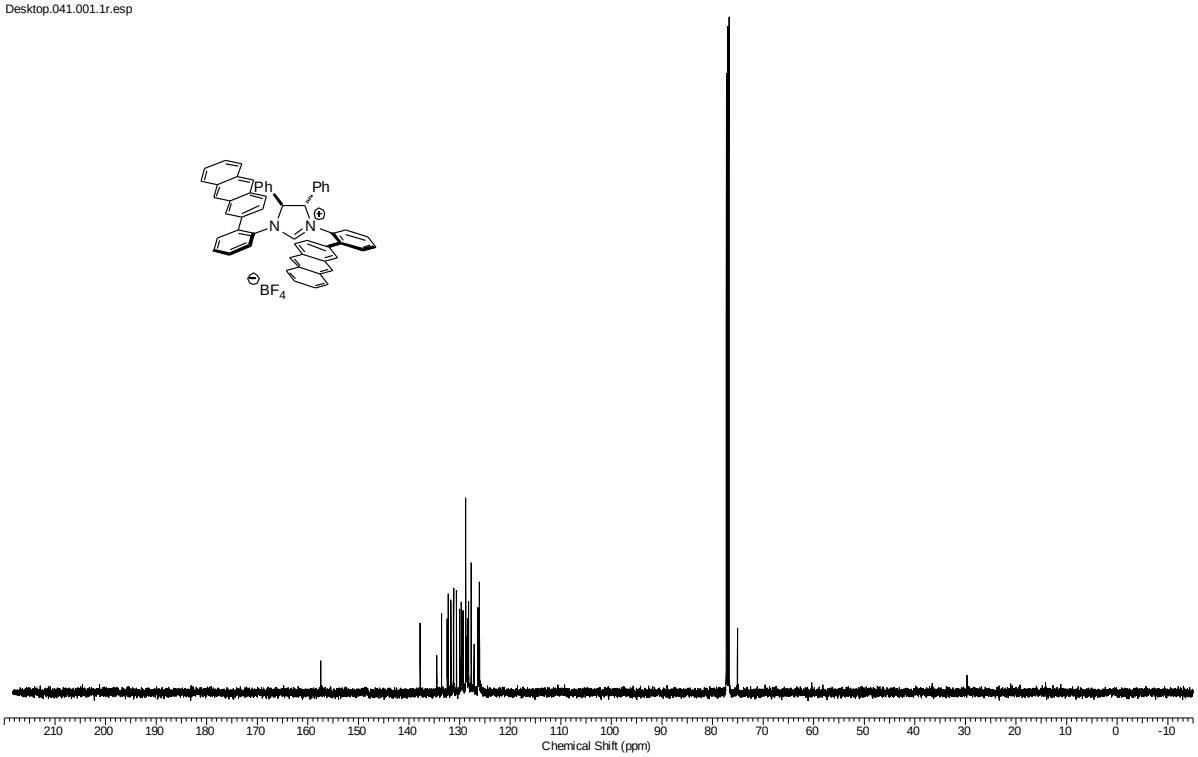
500 MHz $CDCl_3$

2012-04-17-DJP-24.020.001.1R.esp



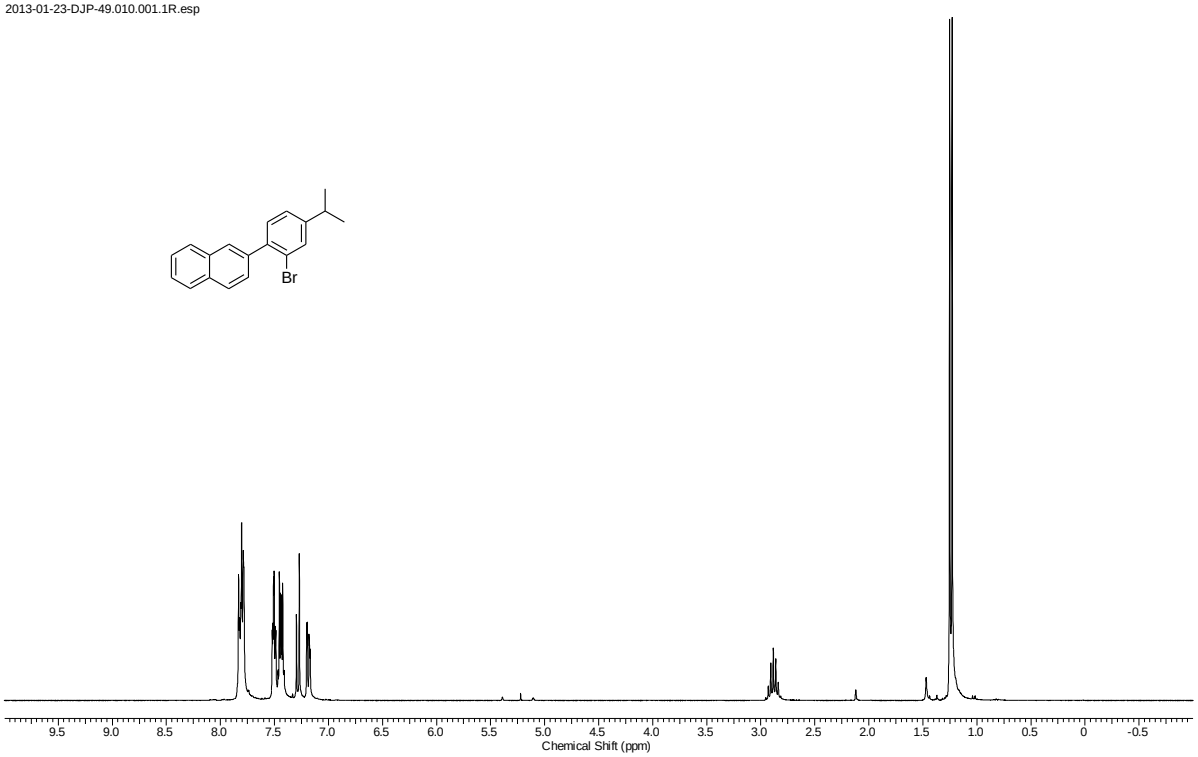
75 MHz $CDCl_3$

Desktop.041.001.1r.esp



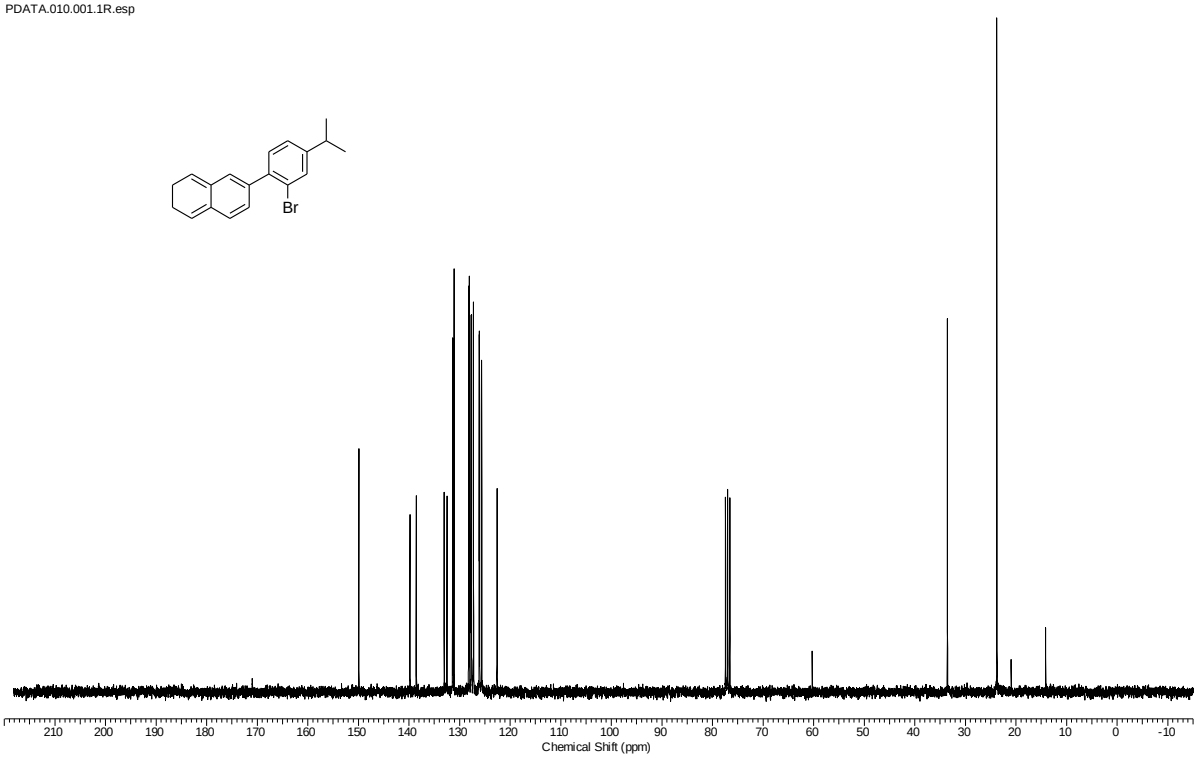
300 MHz $CDCl_3$

2013-01-23-DJP-49.010.001.1R.esp



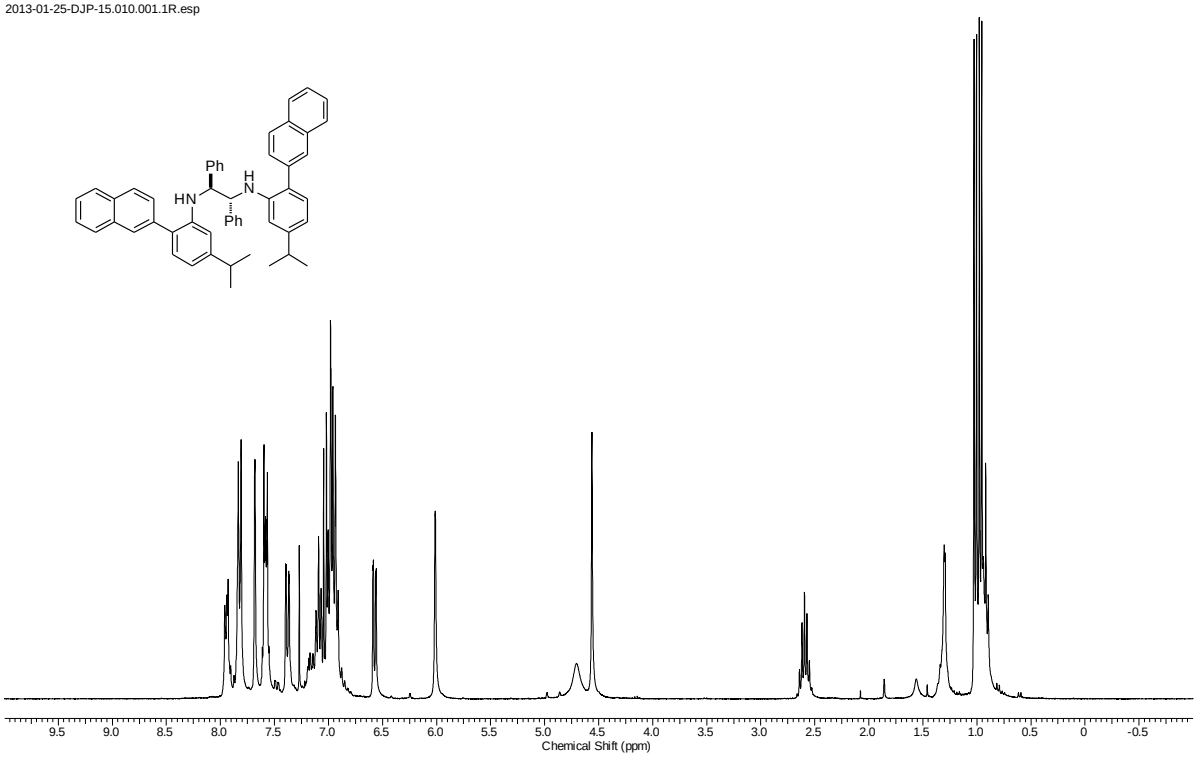
75 MHz $CDCl_3$

PDATA.010.001.1R.esp



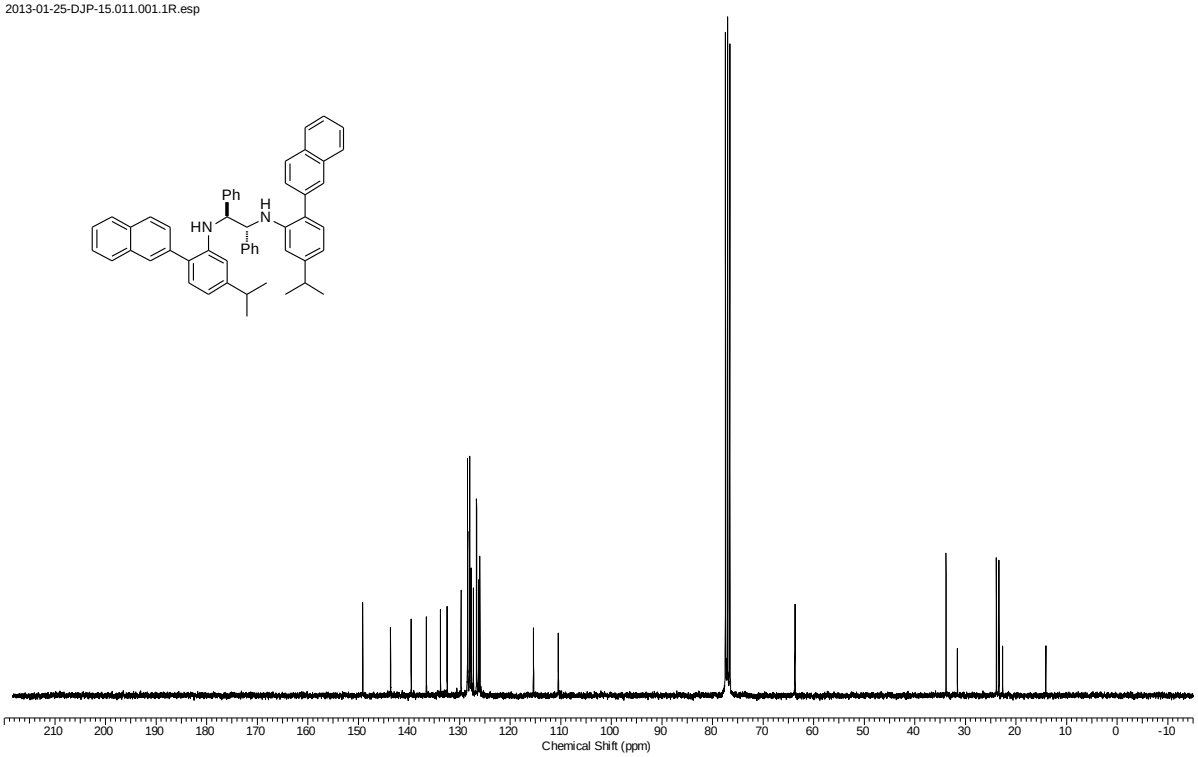
300 MHz $CDCl_3$

2013-01-25-DJP-15.010.001.1R.esp



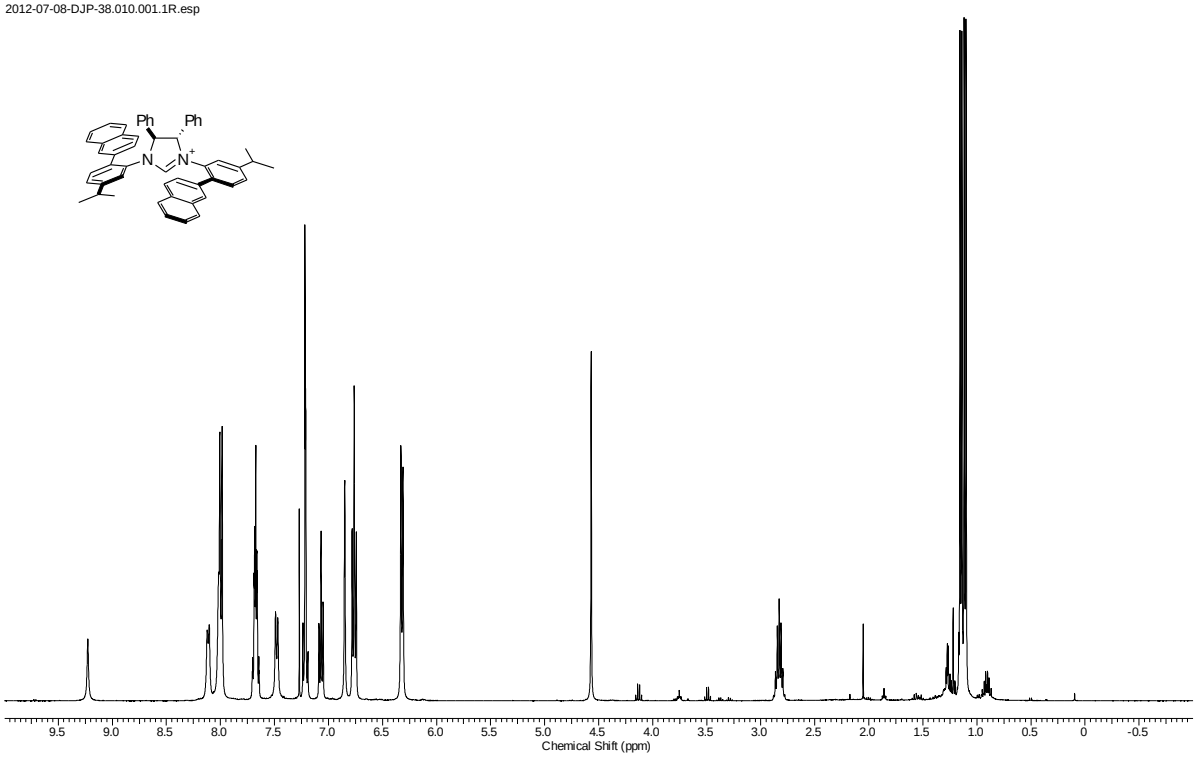
75 MHz $CDCl_3$

2013-01-25-DJP-15.011.001.1R.esp



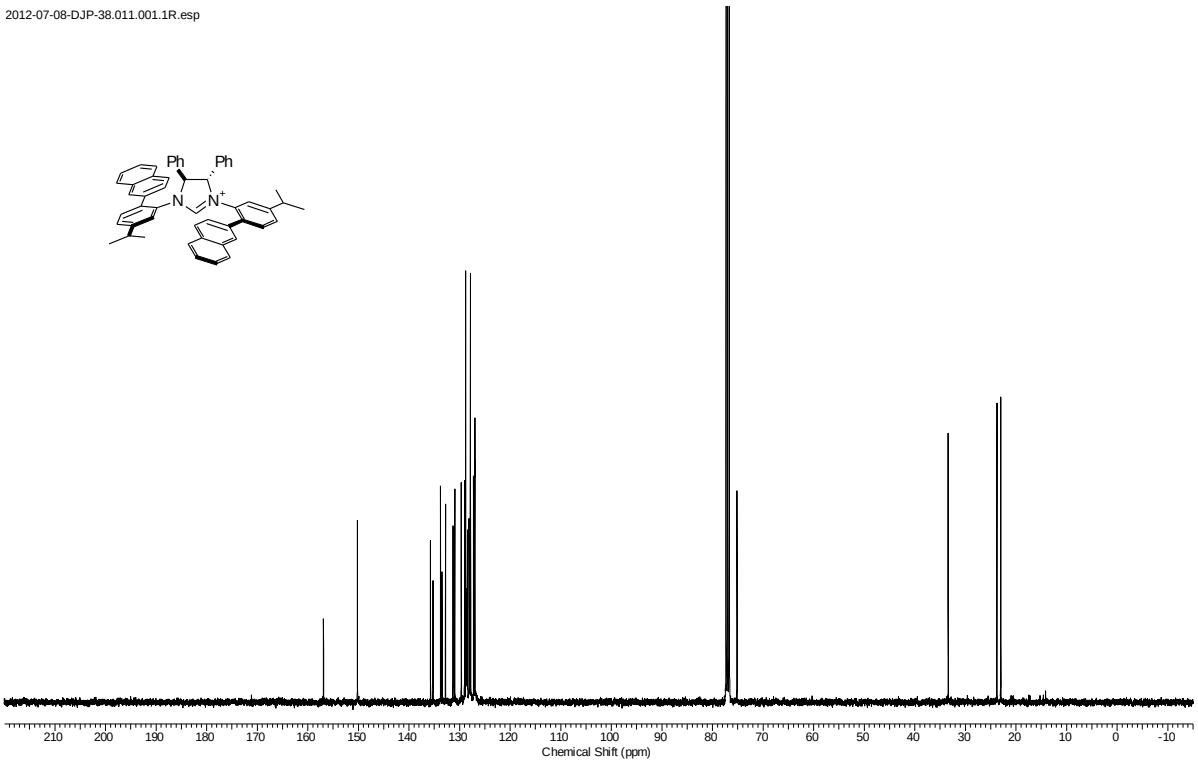
400 MHz $CDCl_3$

2012-07-08-DJP-38.010.001.1R.esp



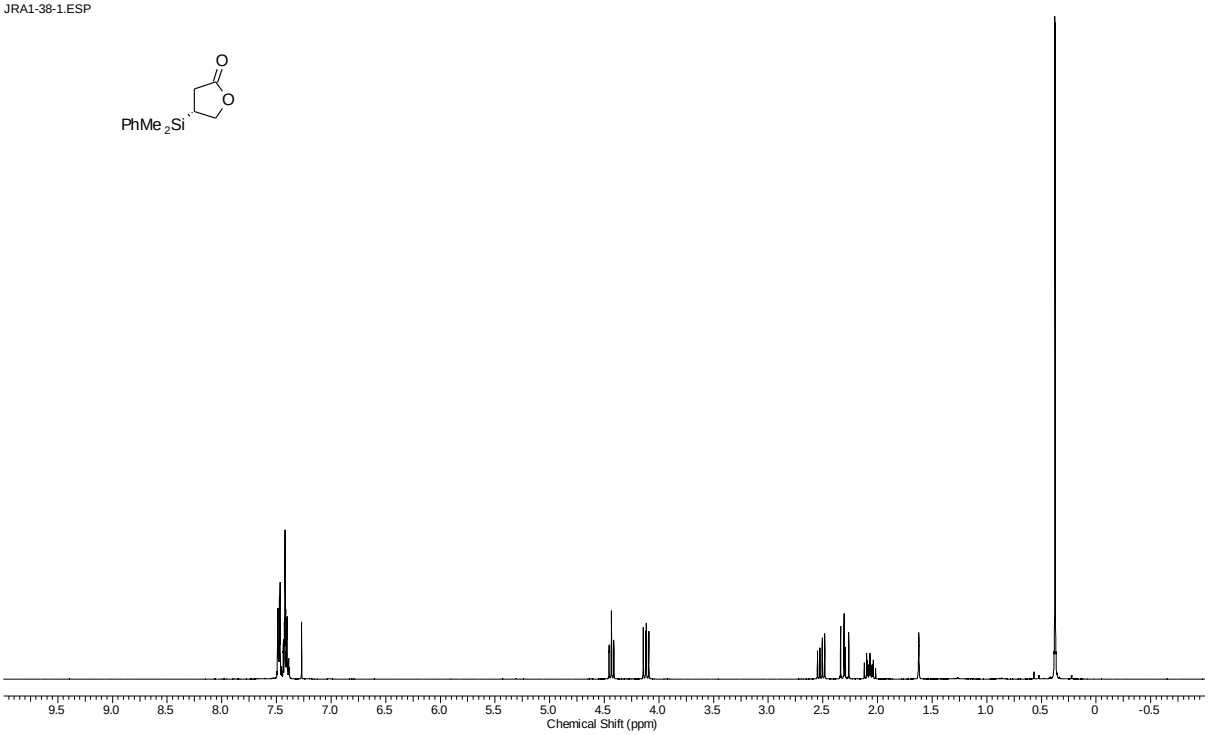
101 MHz $CDCl_3$

2012-07-08-DJP-38.011.001.1R.esp



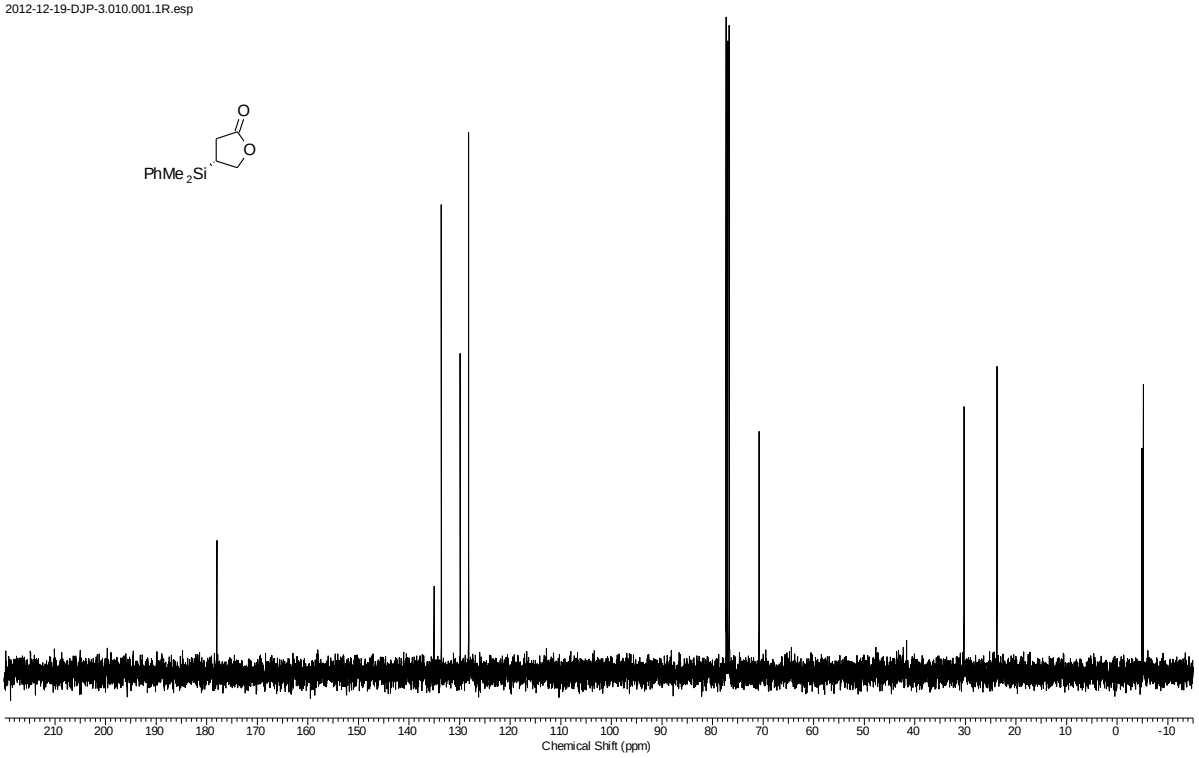
400 MHz $CDCl_3$

JRA1-38-1.ESP



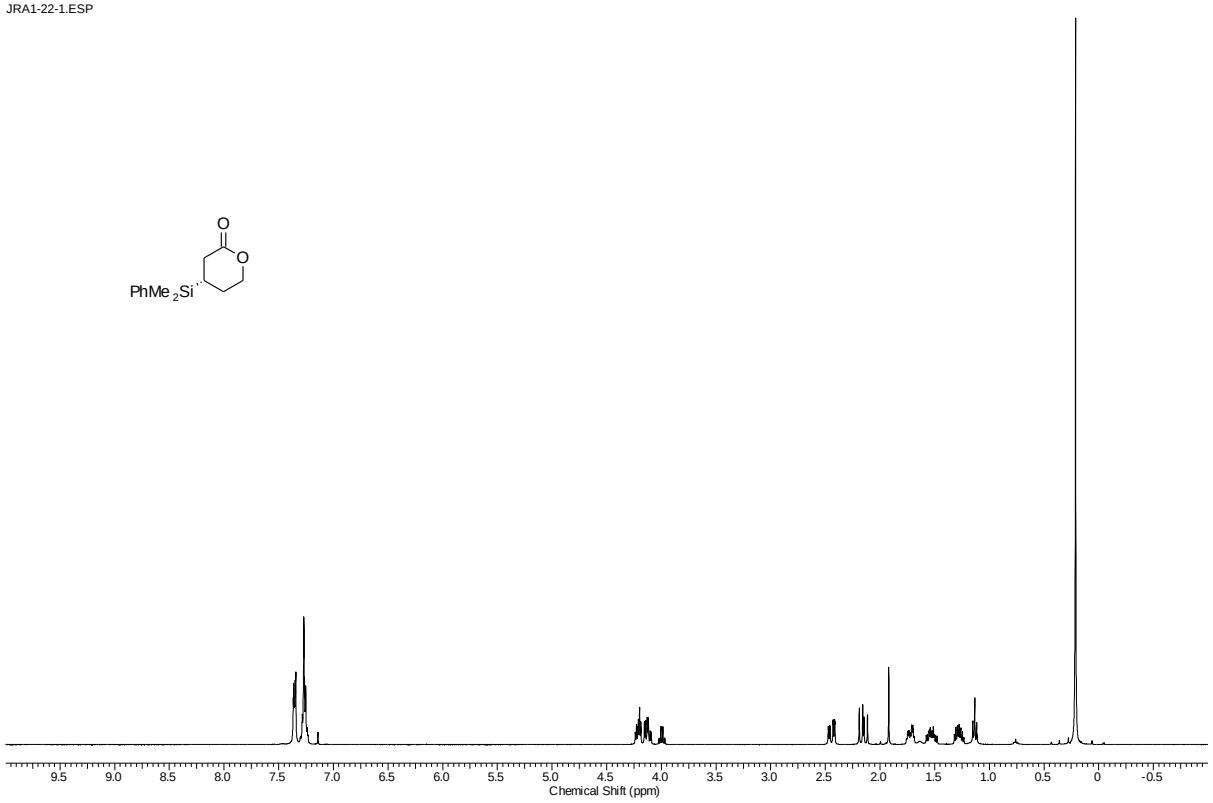
101 MHz $CDCl_3$

2012-12-19-DJP-3.010.001.1R.esp



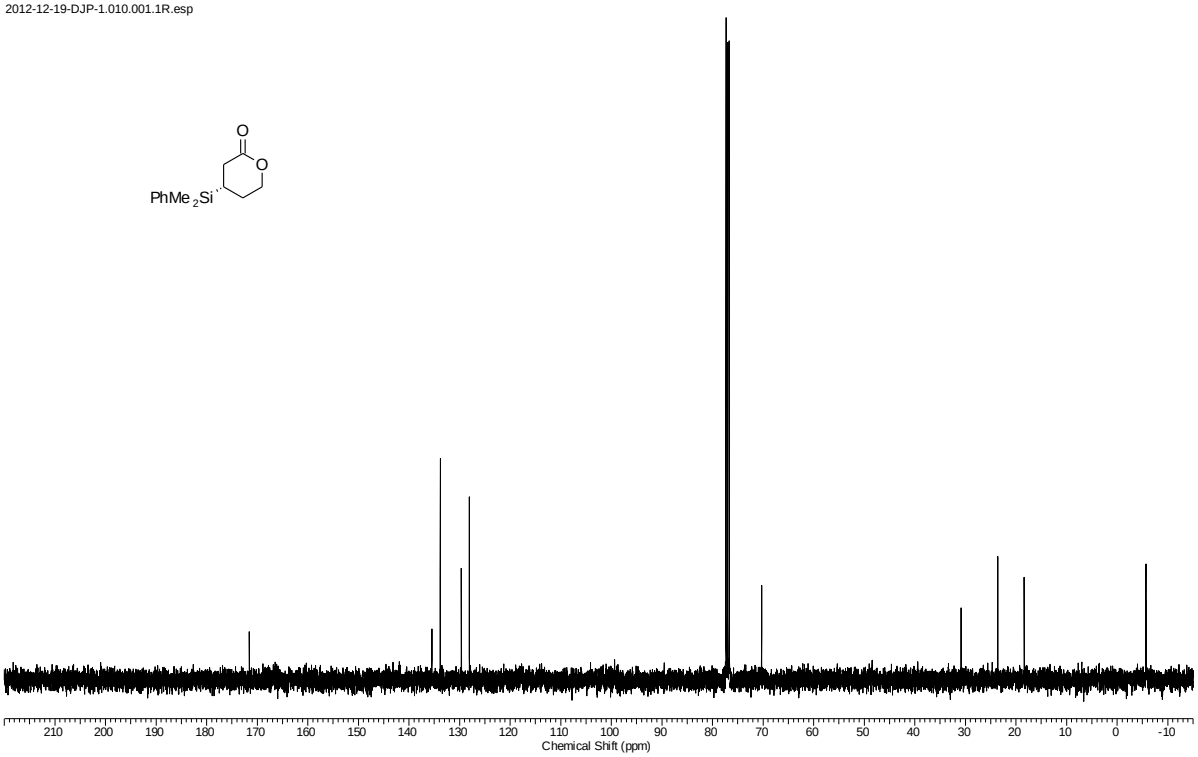
500 MHz $CDCl_3$

JRA1-22-1.ESP



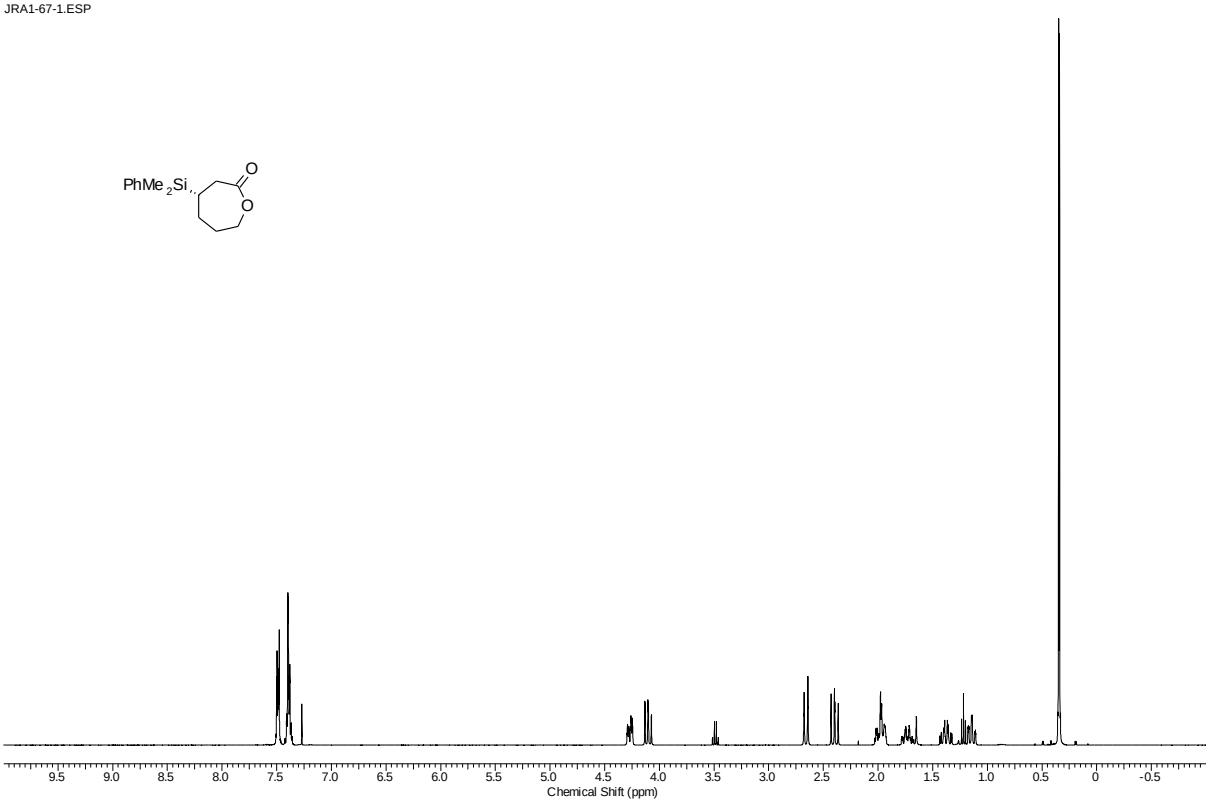
101 MHz $CDCl_3$

2012-12-19-DJP-1.010.001.1R.esp



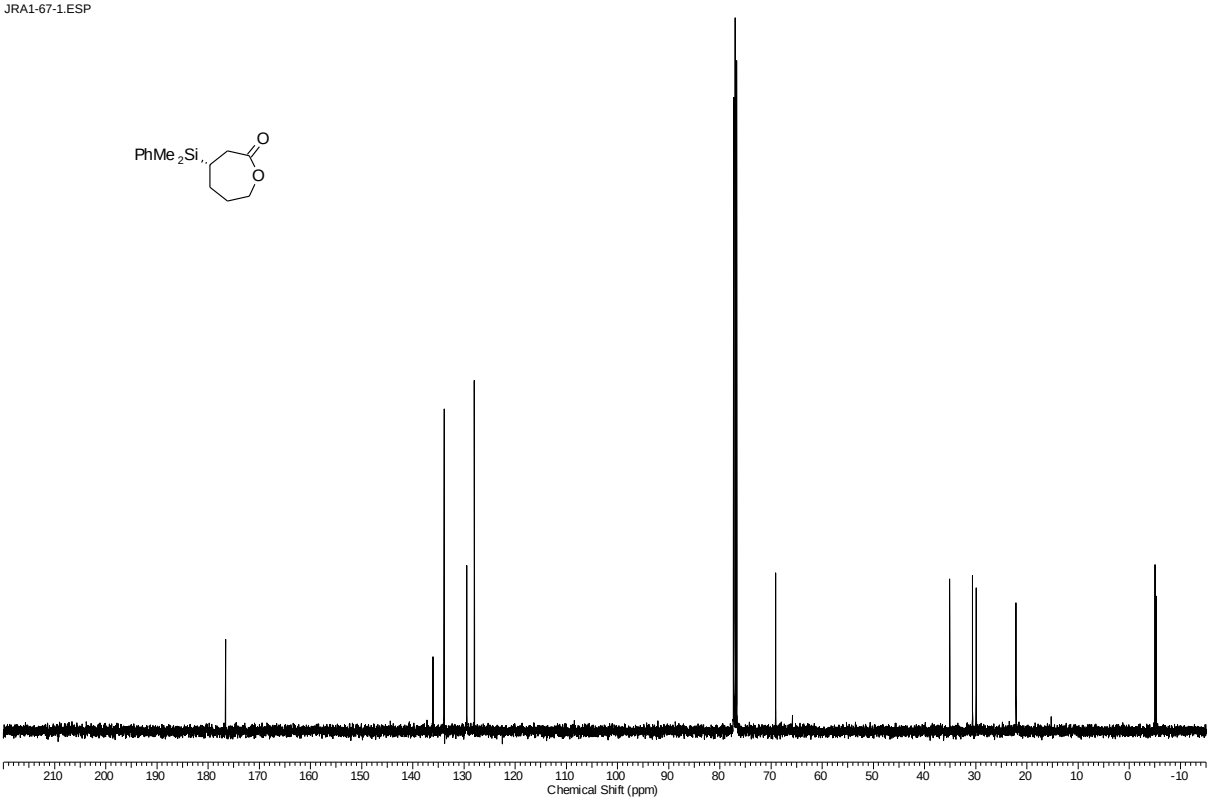
400 MHz $CDCl_3$

JRA1-67-1.ESP



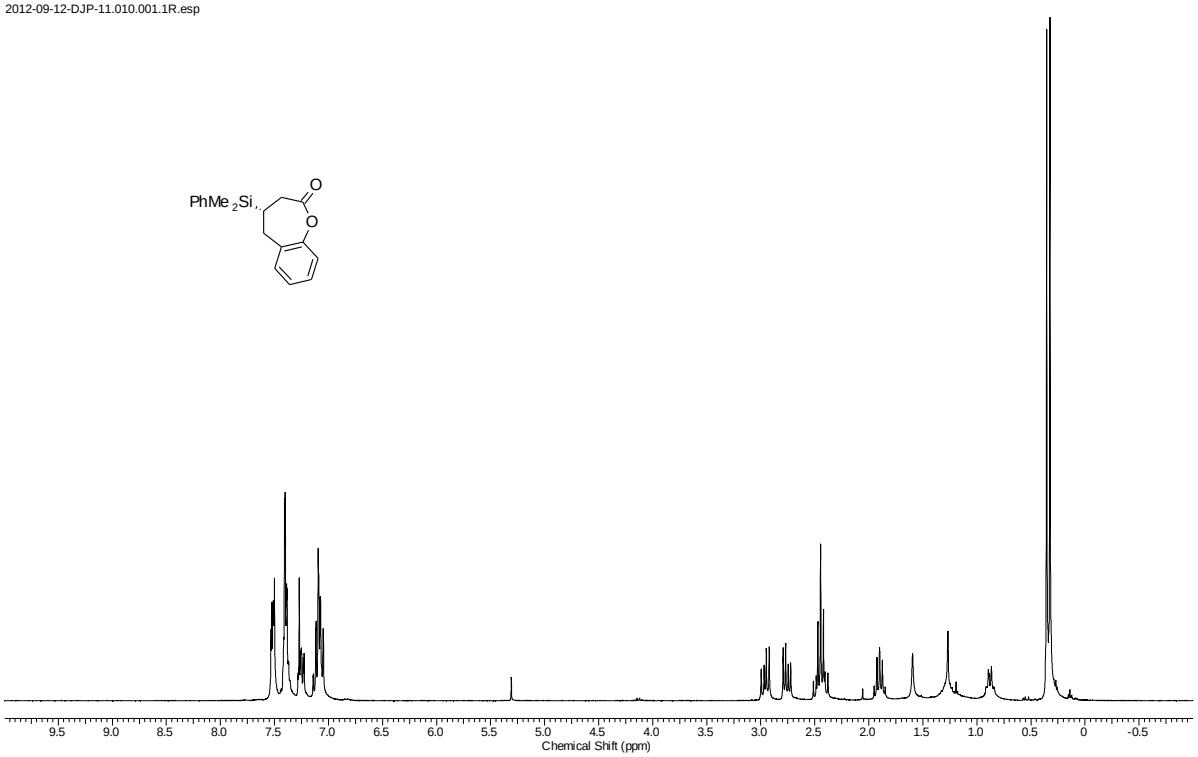
101 MHz $CDCl_3$

JRA1-67-1.ESP



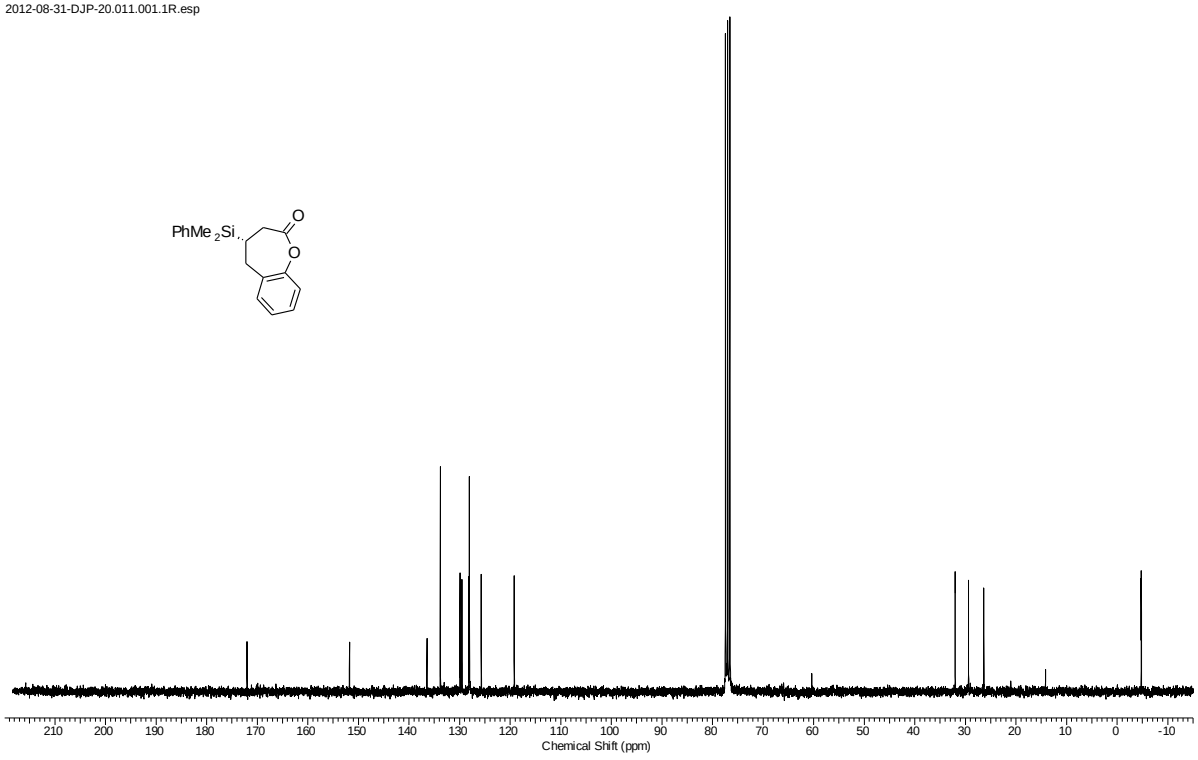
300 MHz $CDCl_3$

2012-09-12-DJP-11.010.001.1R.esp



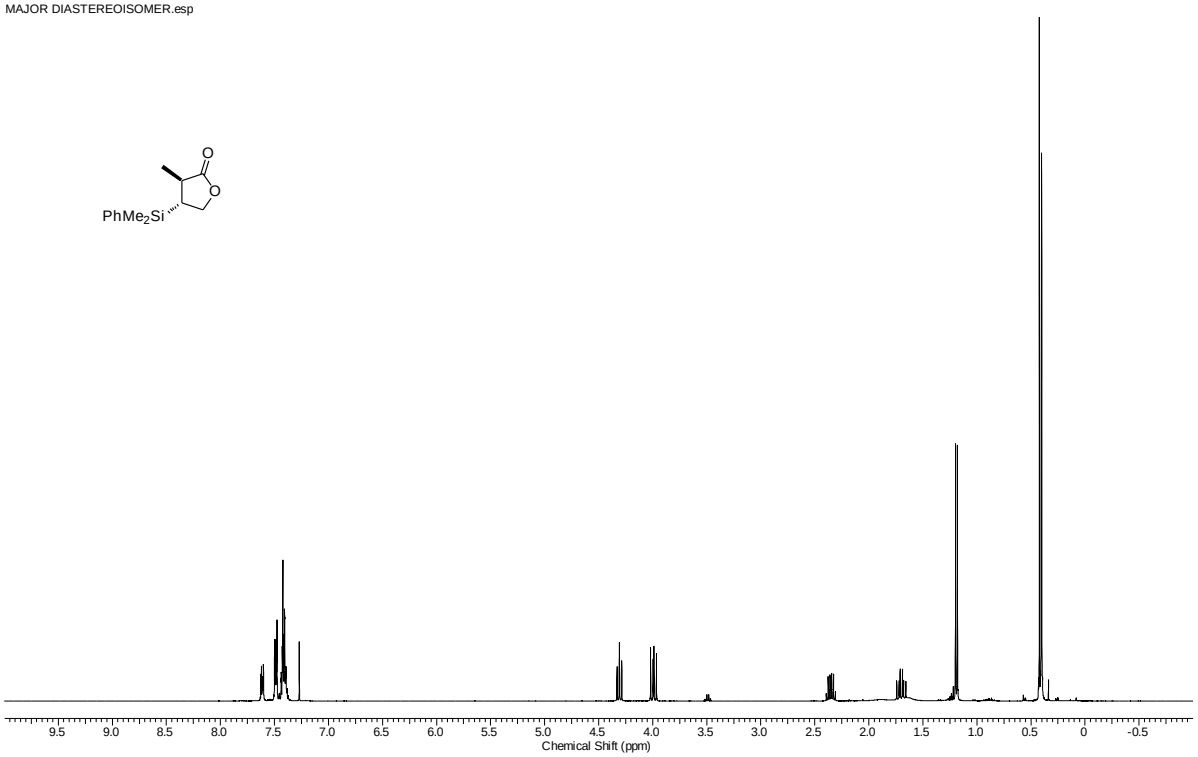
75 MHz $CDCl_3$

2012-08-31-DJP-20.011.001.1R.esp



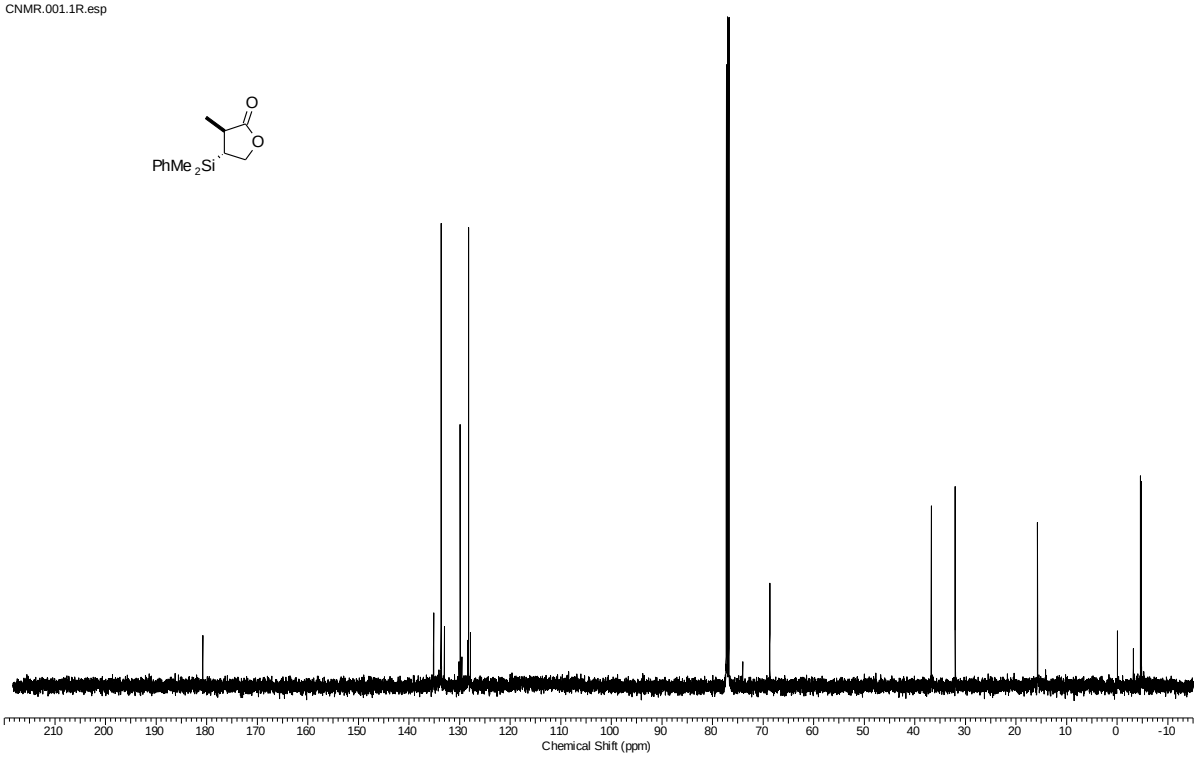
300 MHz $CDCl_3$

MAJOR DIASTEREOISOMER.esp



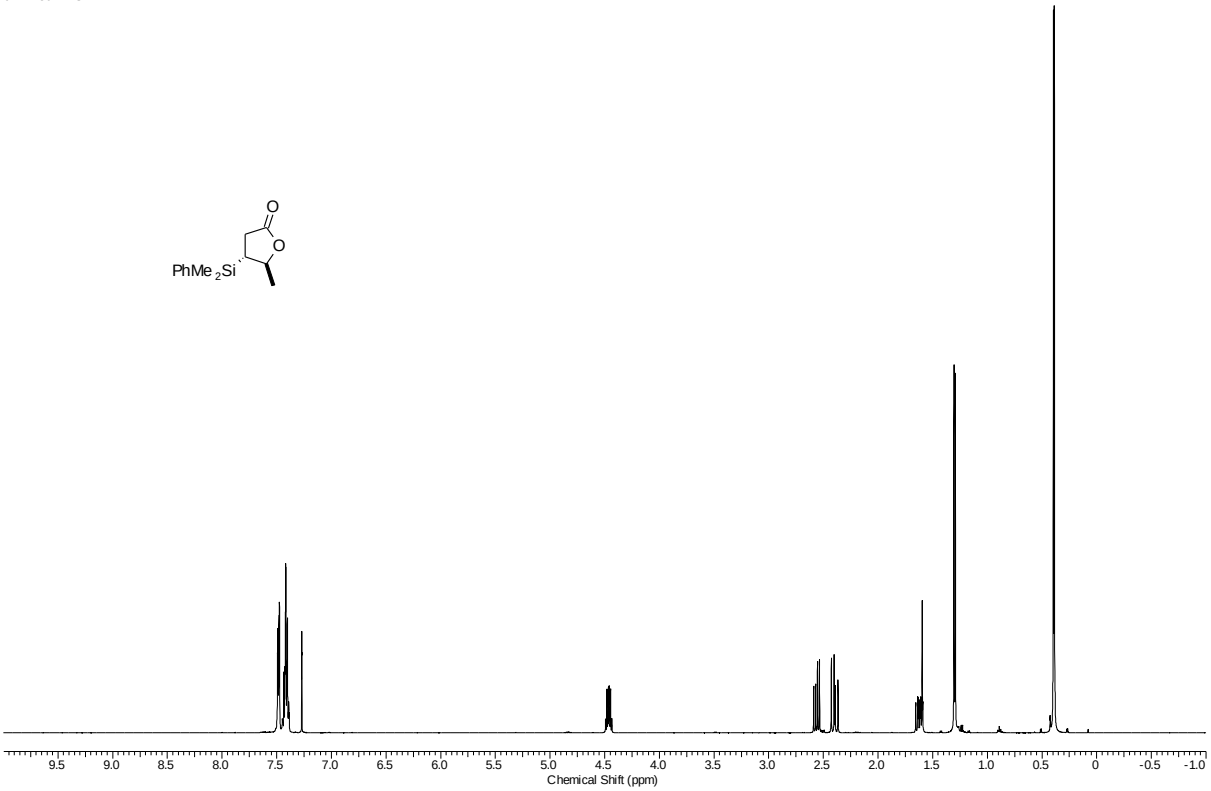
126 MHz $CDCl_3$

CNMR.001.1R.esp



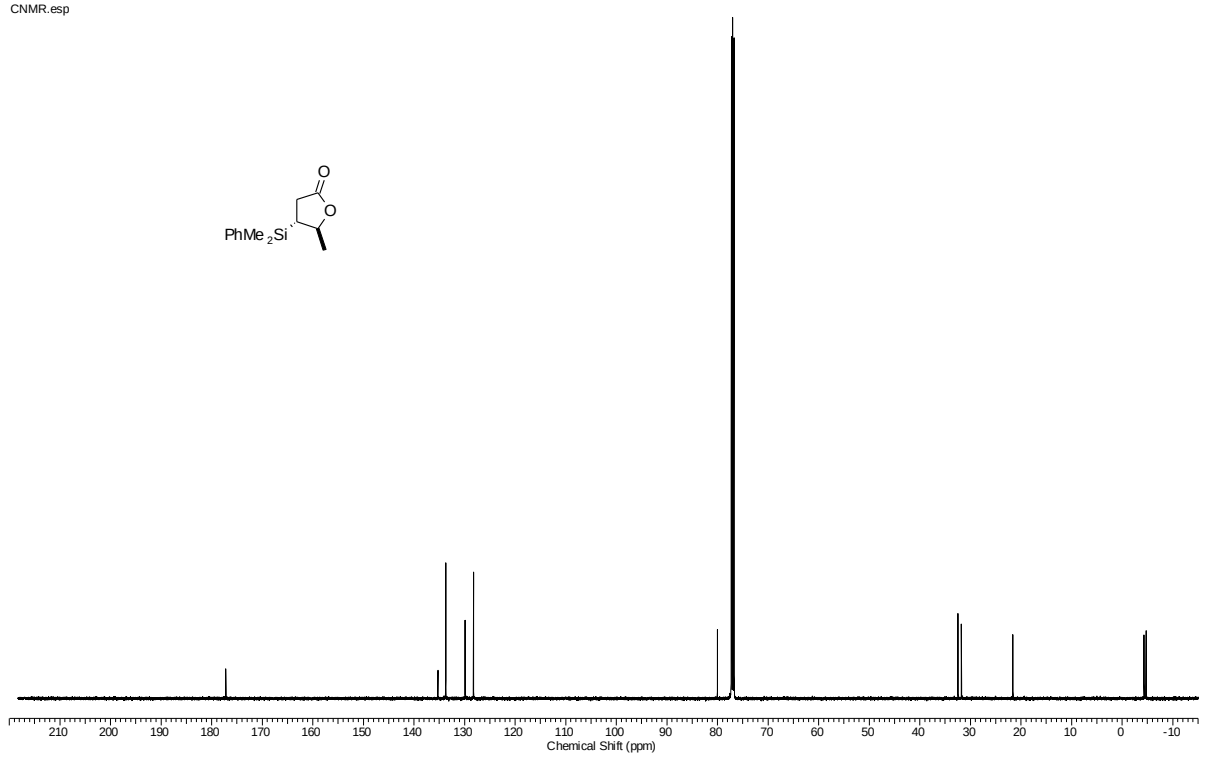
500 MHz $CDCl_3$

JRA2-50-1.ESP



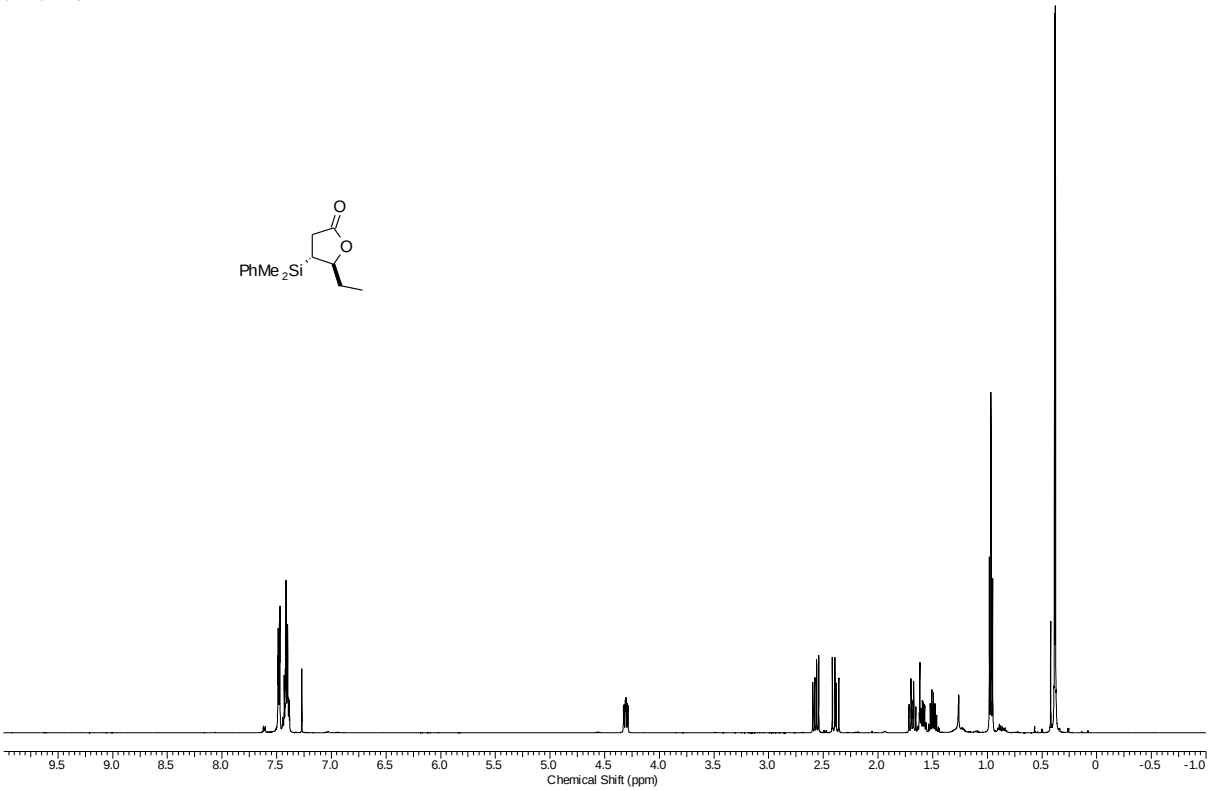
75 MHz $CDCl_3$

CNMR.esp



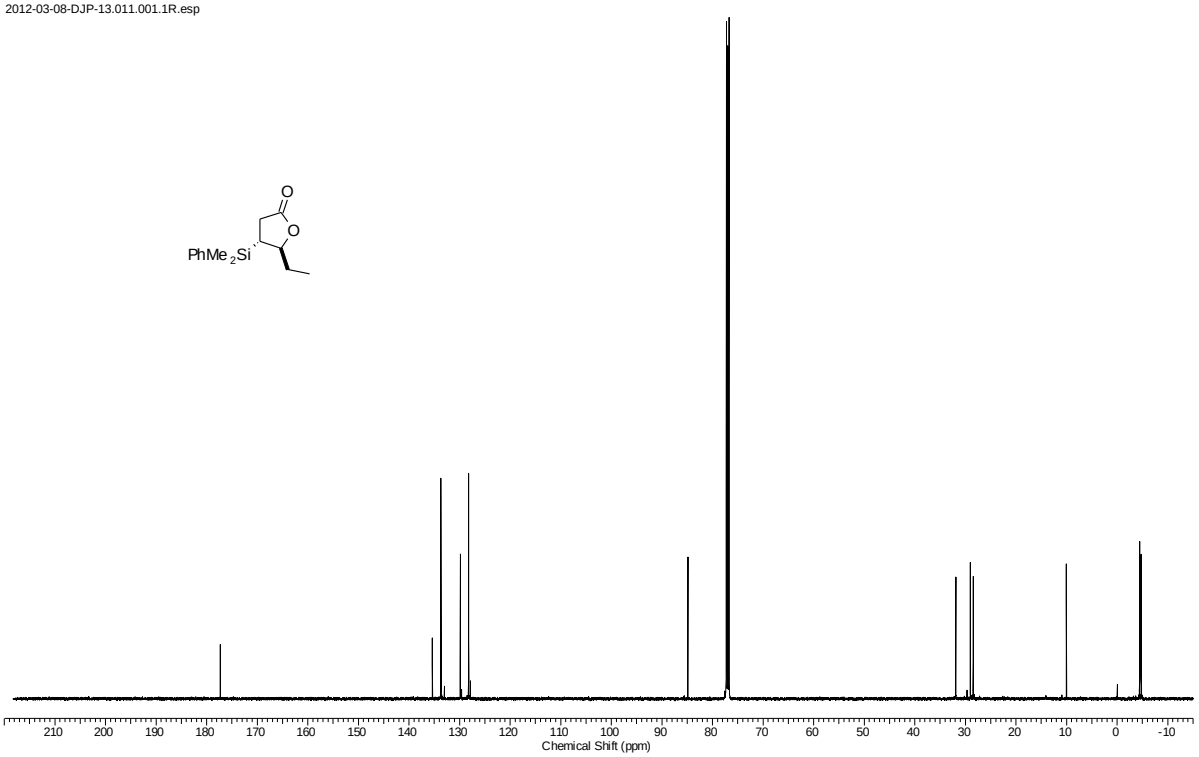
500 MHz $CDCl_3$

JRA2-94-1.ESP



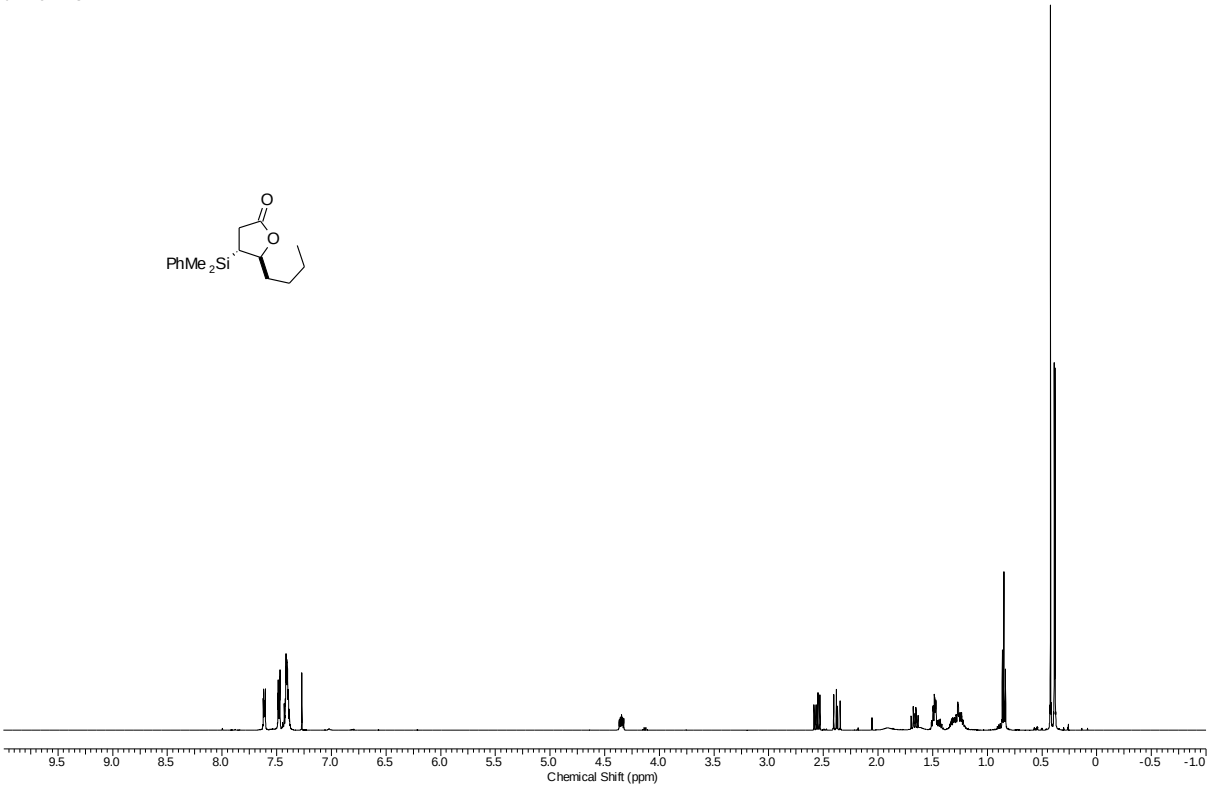
75 MHz $CDCl_3$

2012-03-08-DJP-13.011.001.1R.esp



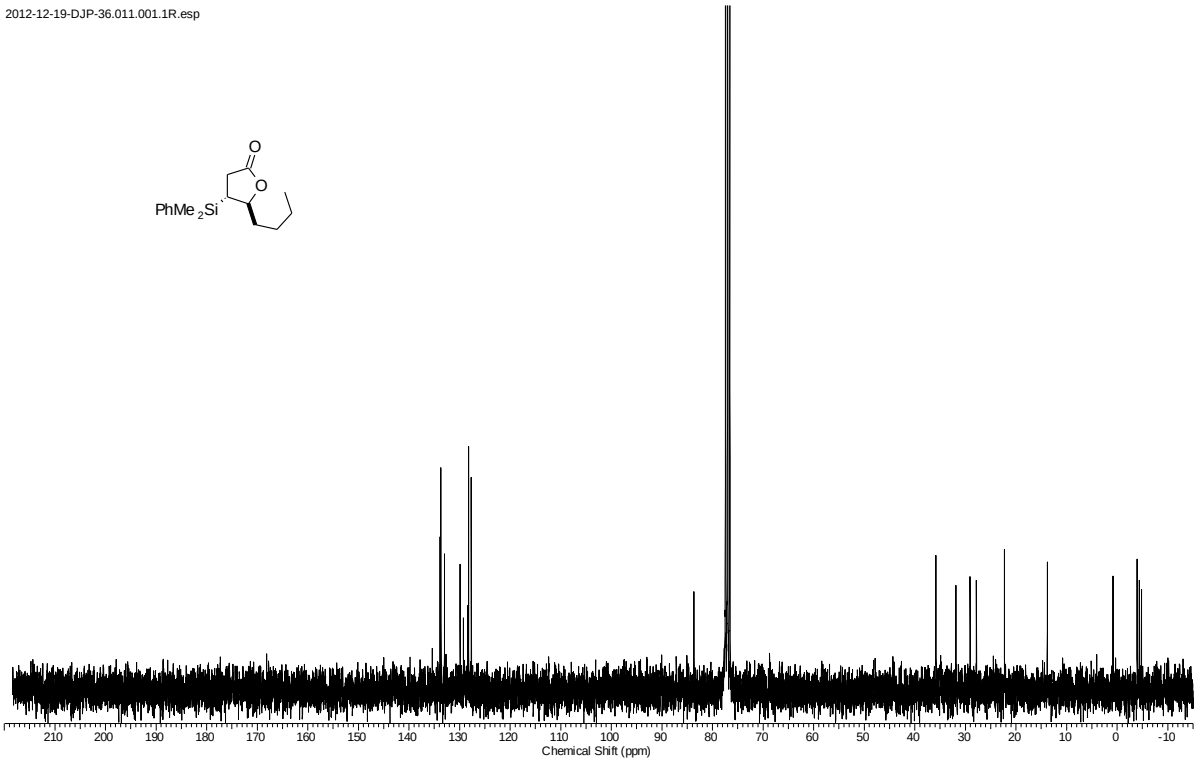
500 MHz $CDCl_3$

JRA2-84-1.ESP



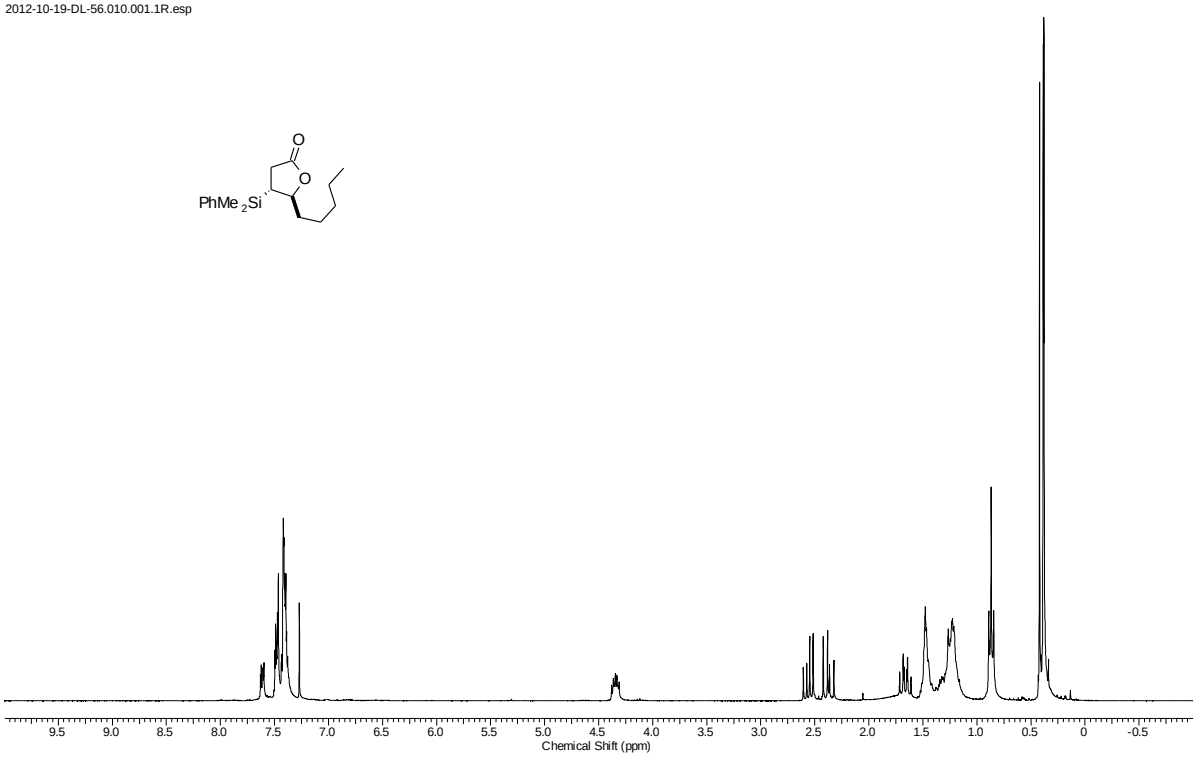
75 MHz $CDCl_3$

2012-12-19-DJP-36.011.001.1R.esp



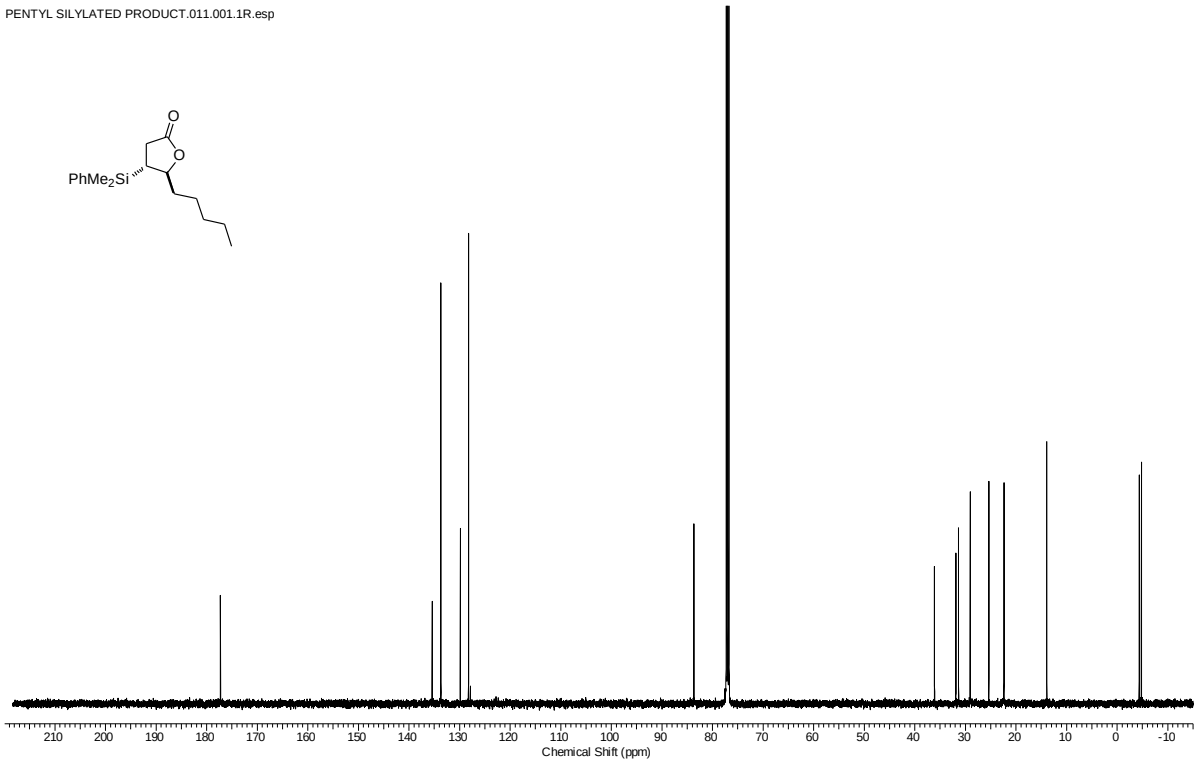
300 MHz $CDCl_3$

2012-10-19-DL-56.010.001.1R.esp



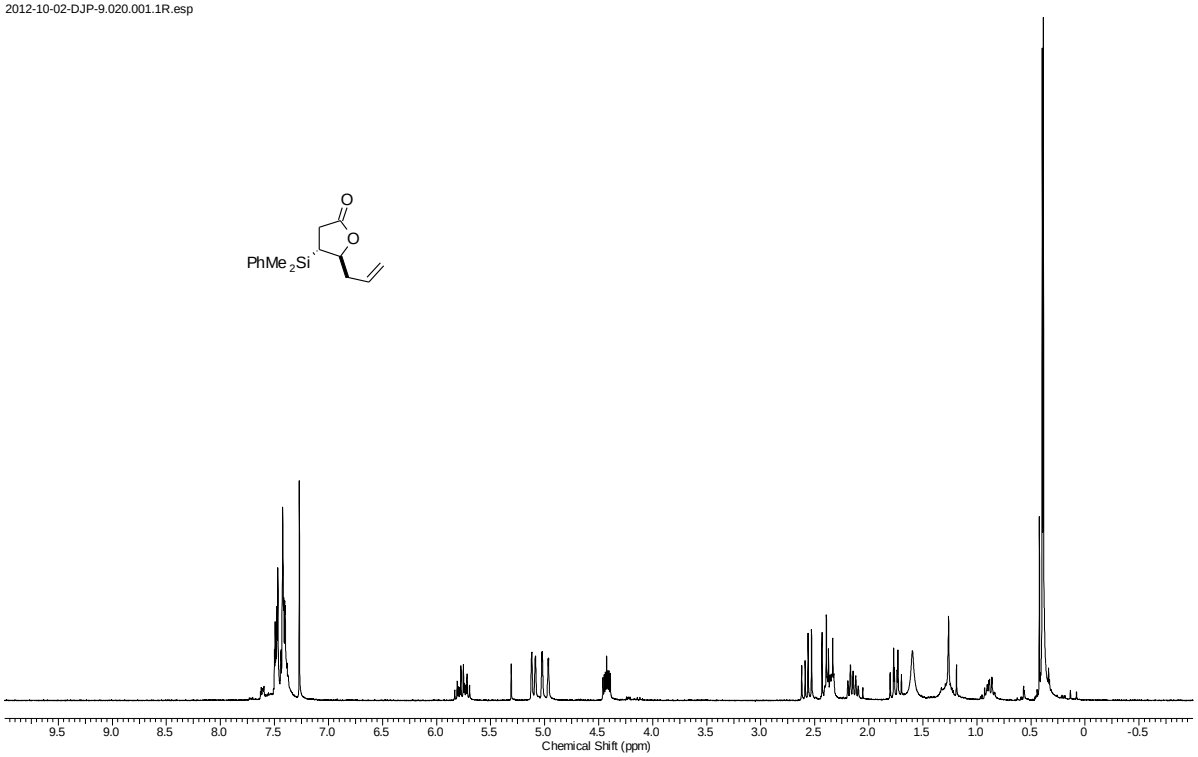
126 MHz $CDCl_3$

PENTYL SILYLATED PRODUCT.011.001.1R.esp



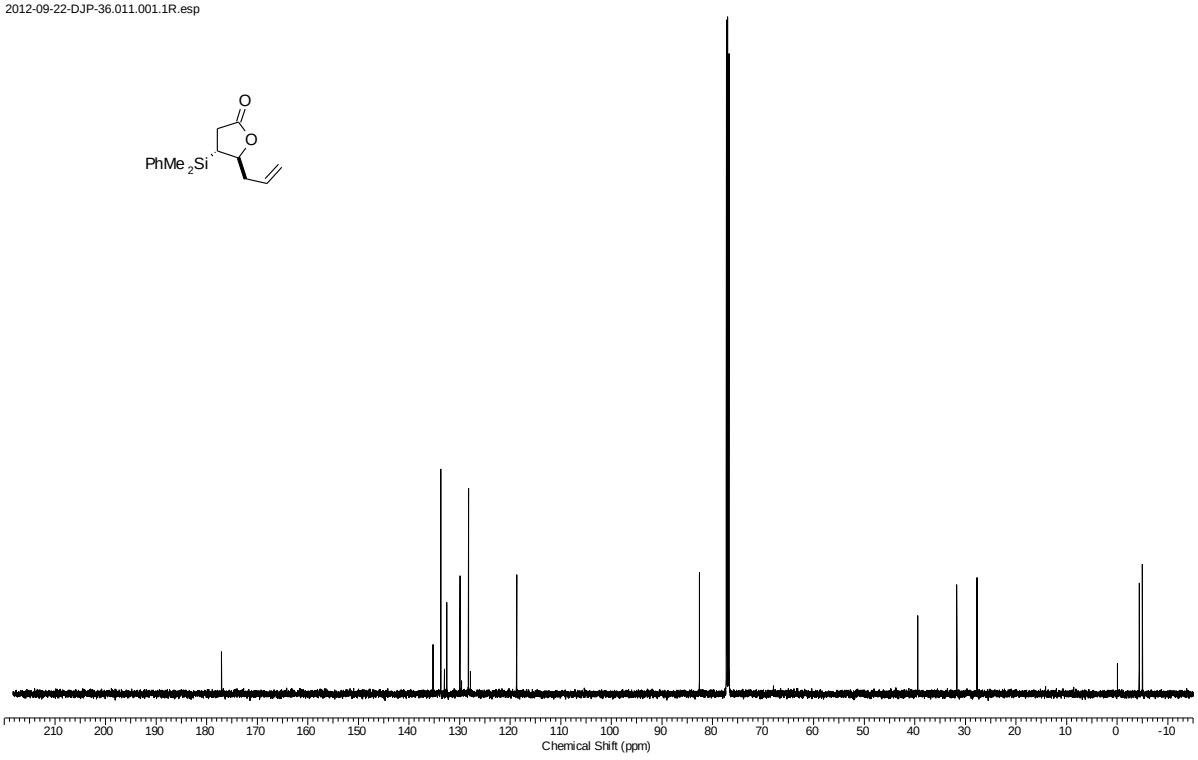
300 MHz $CDCl_3$

2012-10-02-DJP-9.020.001.1R.esp



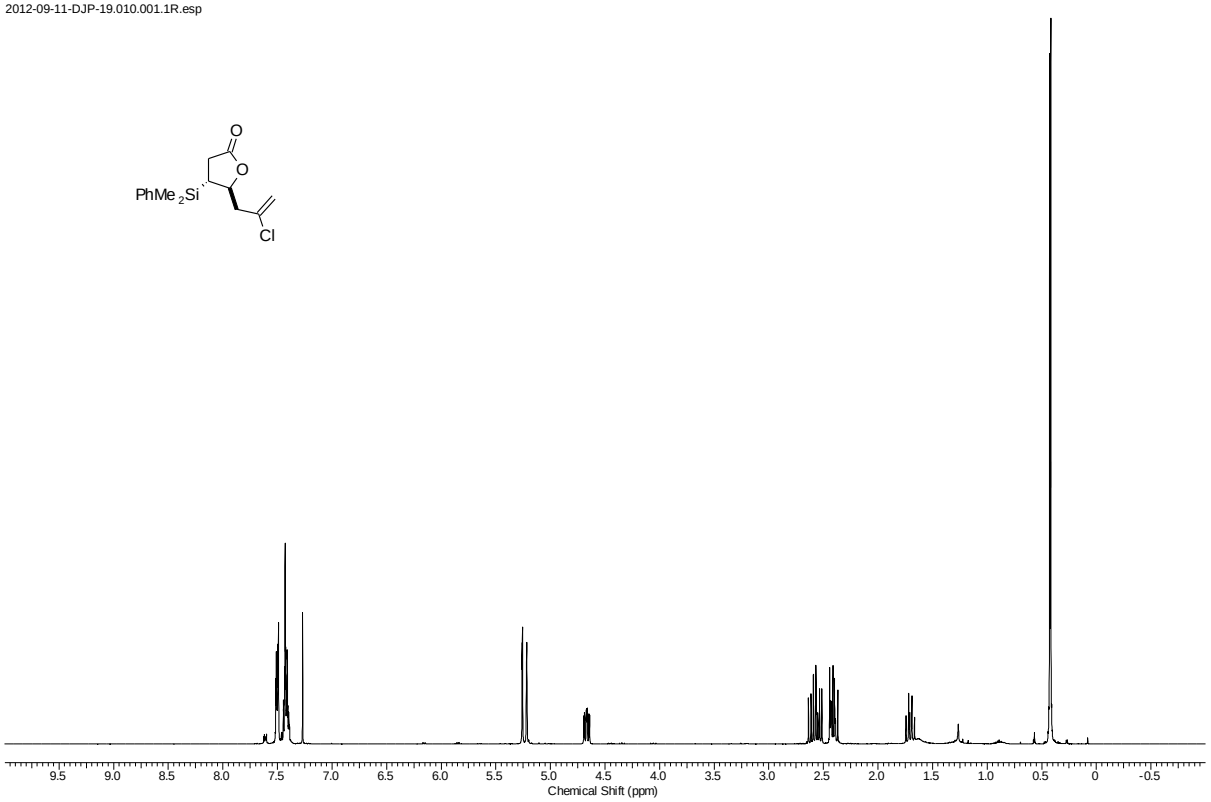
126 MHz $CDCl_3$

2012-09-22-DJP-36.011.001.1R.esp



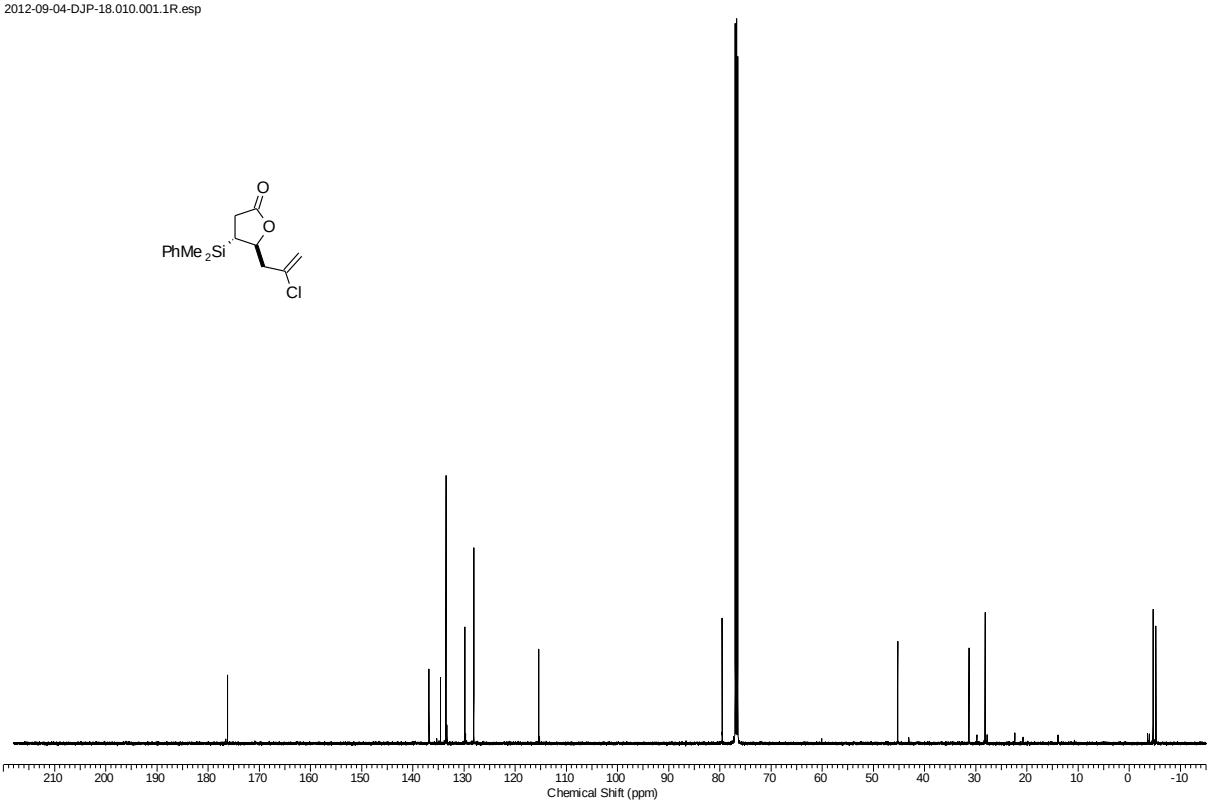
400 MHz $CDCl_3$

2012-09-11-DJP-19.010.001.1R.esp



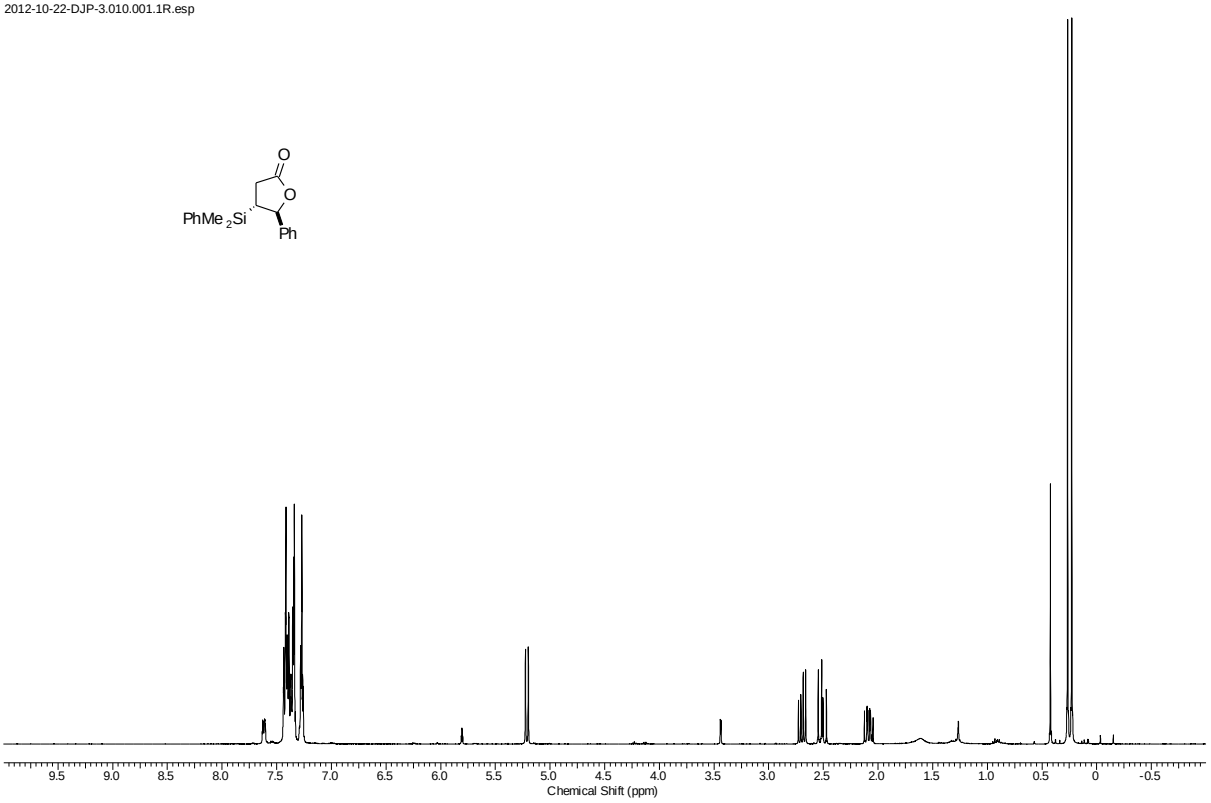
126 MHz $CDCl_3$

2012-09-04-DJP-18.010.001.1R.esp



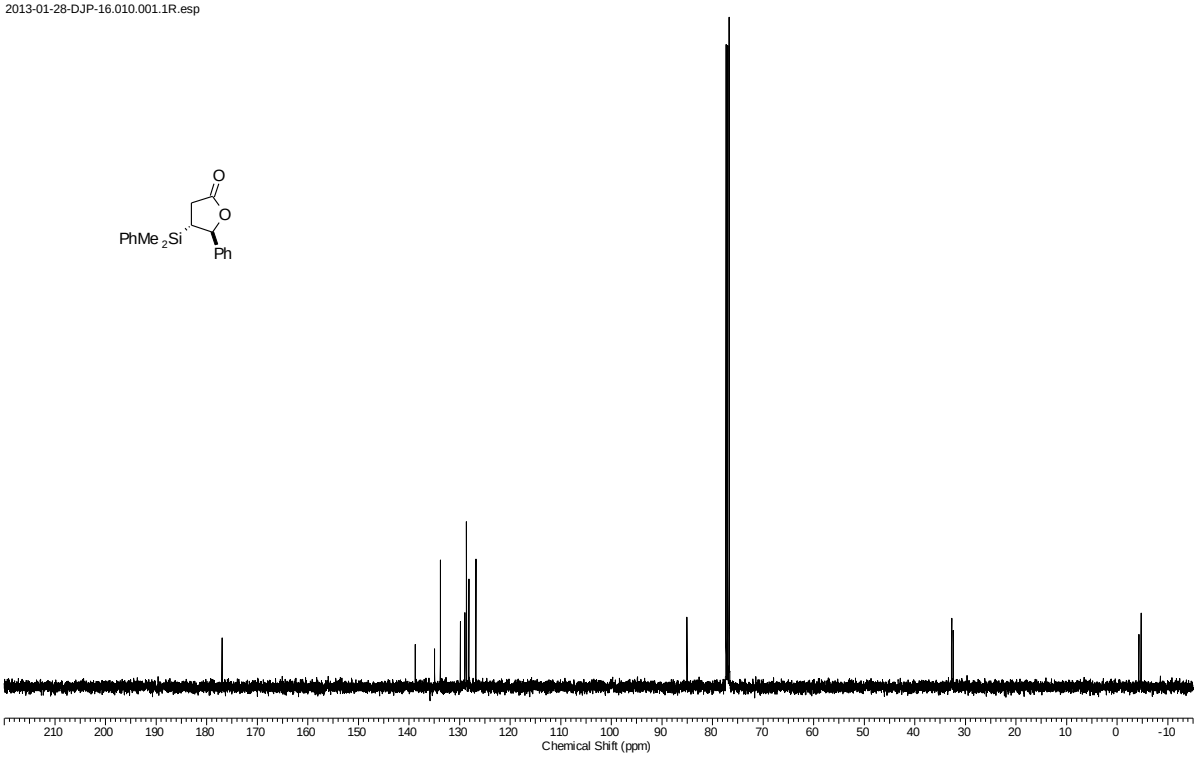
400 MHz $CDCl_3$

2012-10-22-DJP-3.010.001.1R.esp



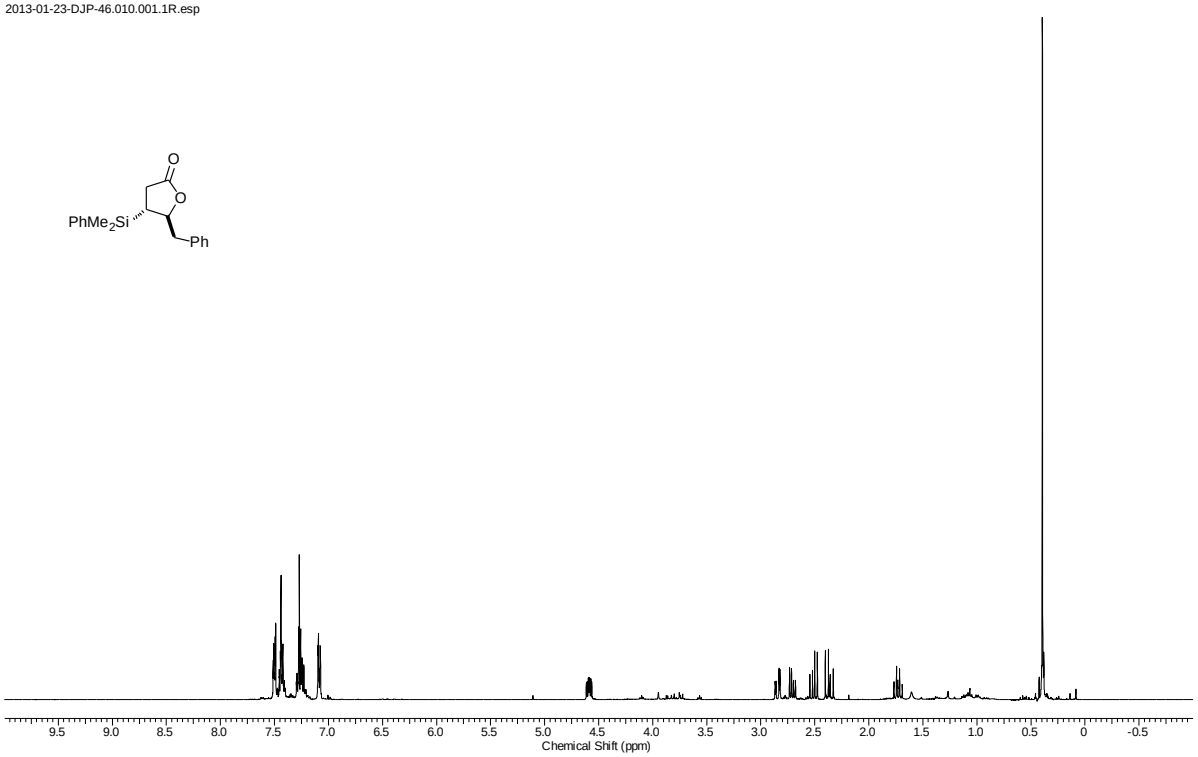
101 MHz $CDCl_3$

2013-01-28-DJP-16.010.001.1R.esp



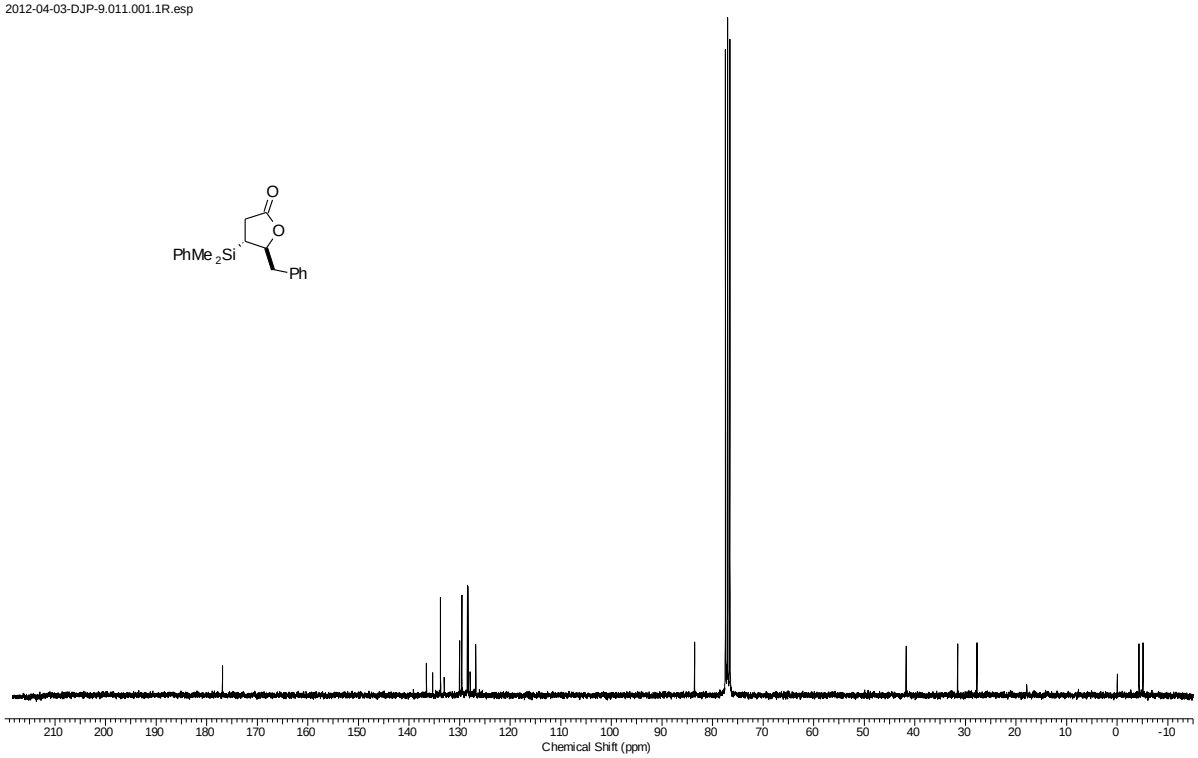
400 MHz $CDCl_3$

2013-01-23-DJP-46.010.001.1R.esp



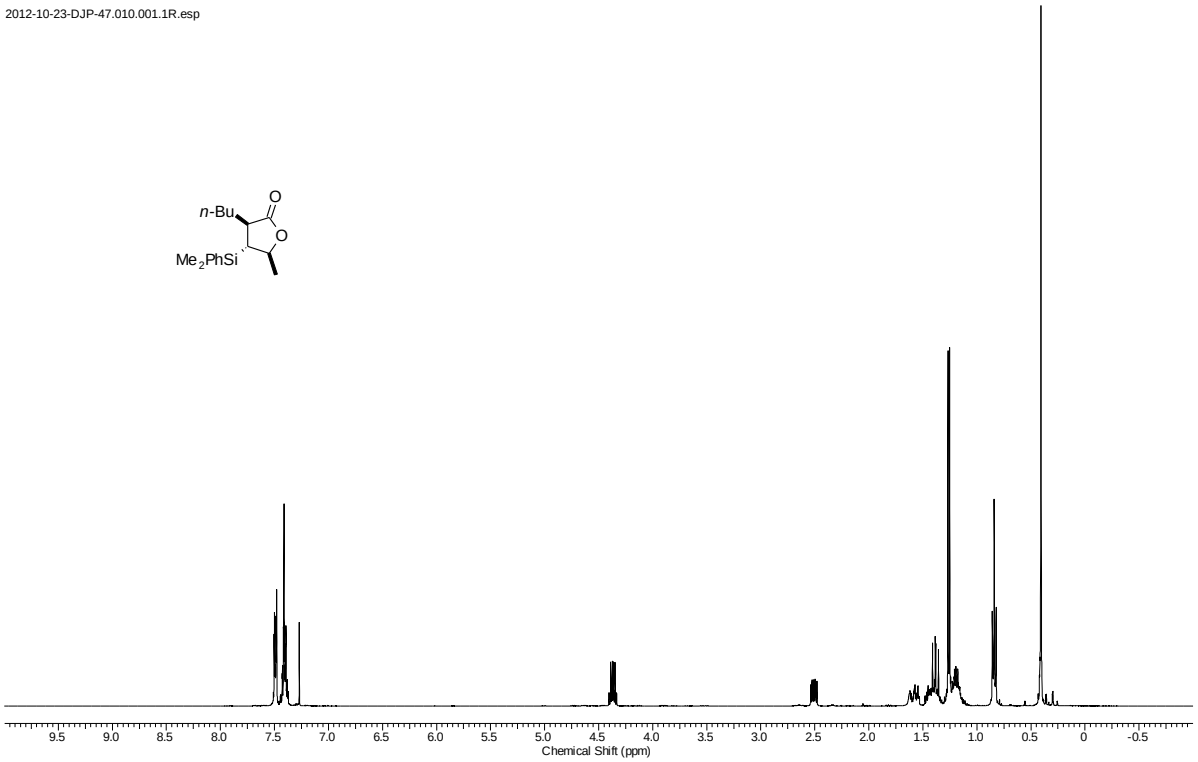
75 MHz $CDCl_3$

2012-04-03-DJP-9.011.001.1R.esp



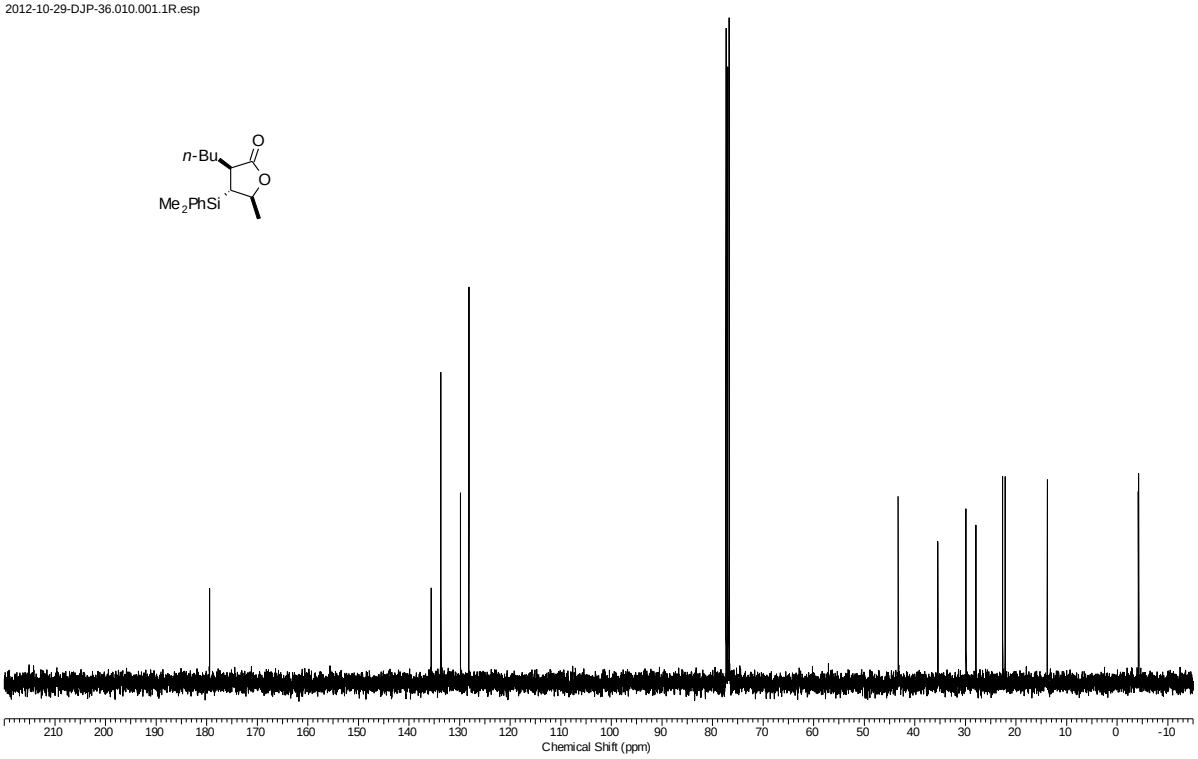
400 MHz $CDCl_3$

2012-10-23-DJP-47.010.001.1R.esp



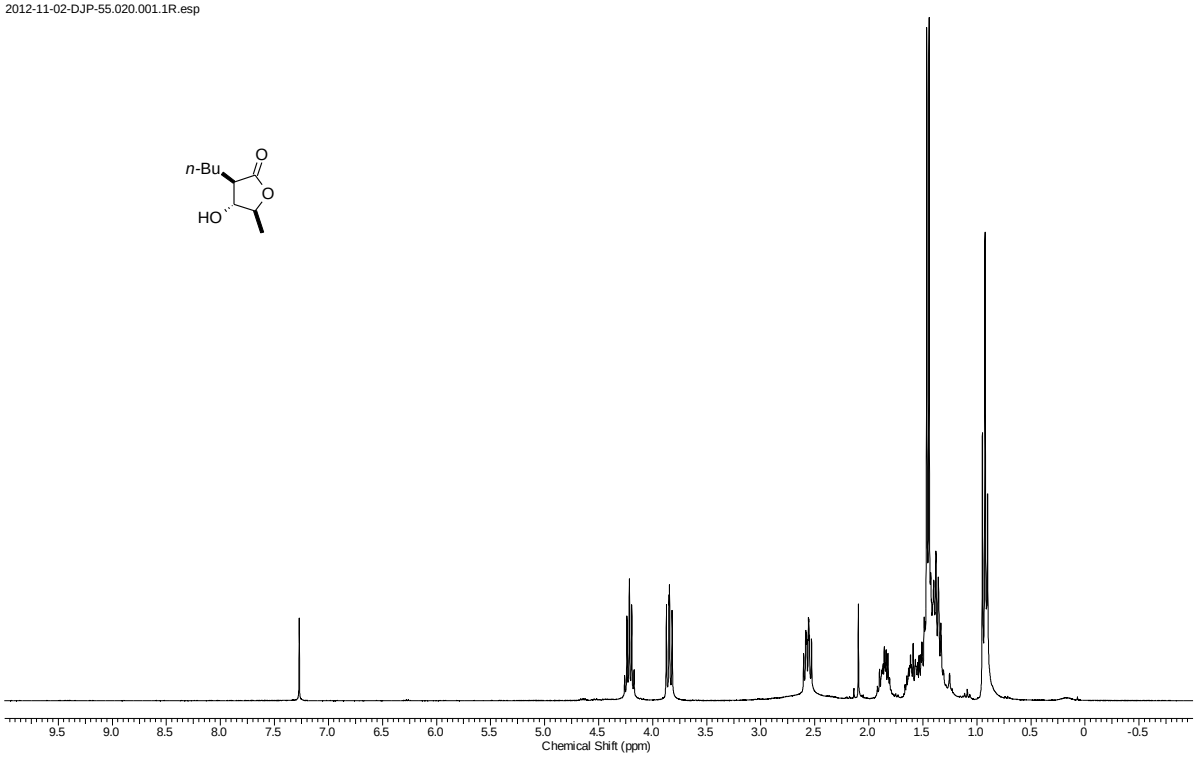
101 MHz $CDCl_3$

2012-10-29-DJP-36.010.001.1R.esp



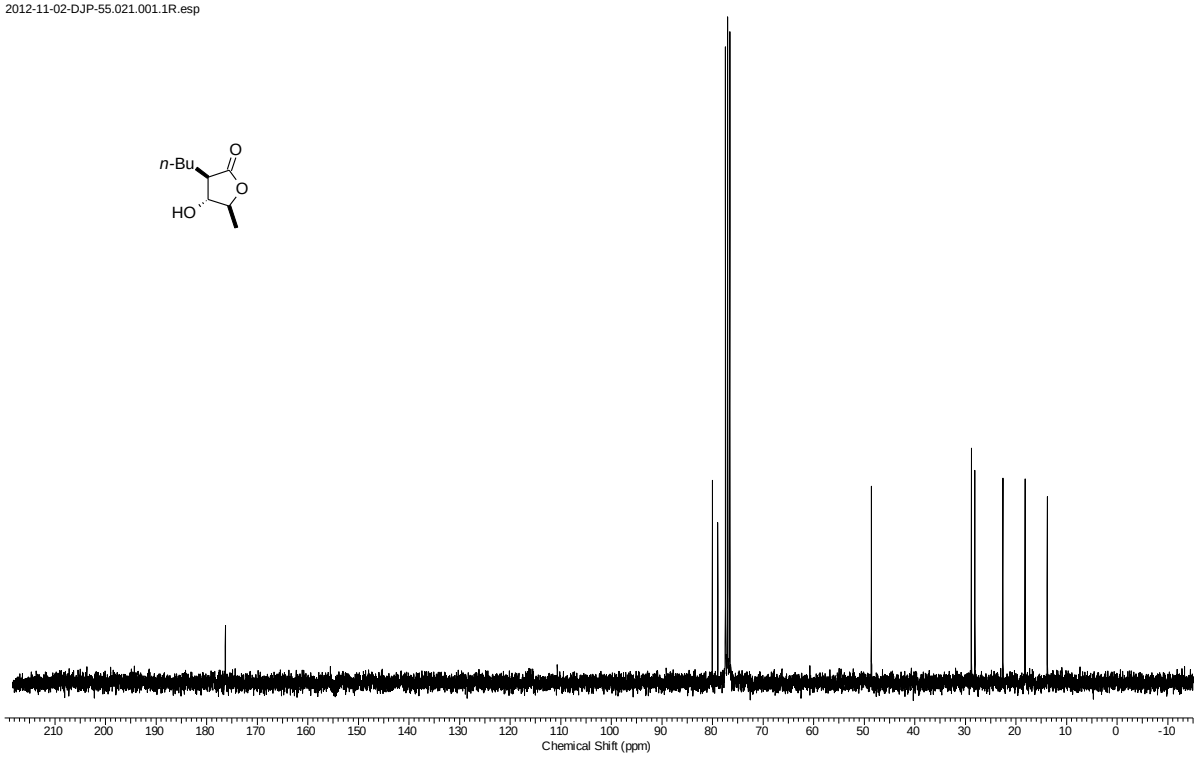
300 MHz $CDCl_3$

2012-11-02-DJP-55.020.001.1R.esp



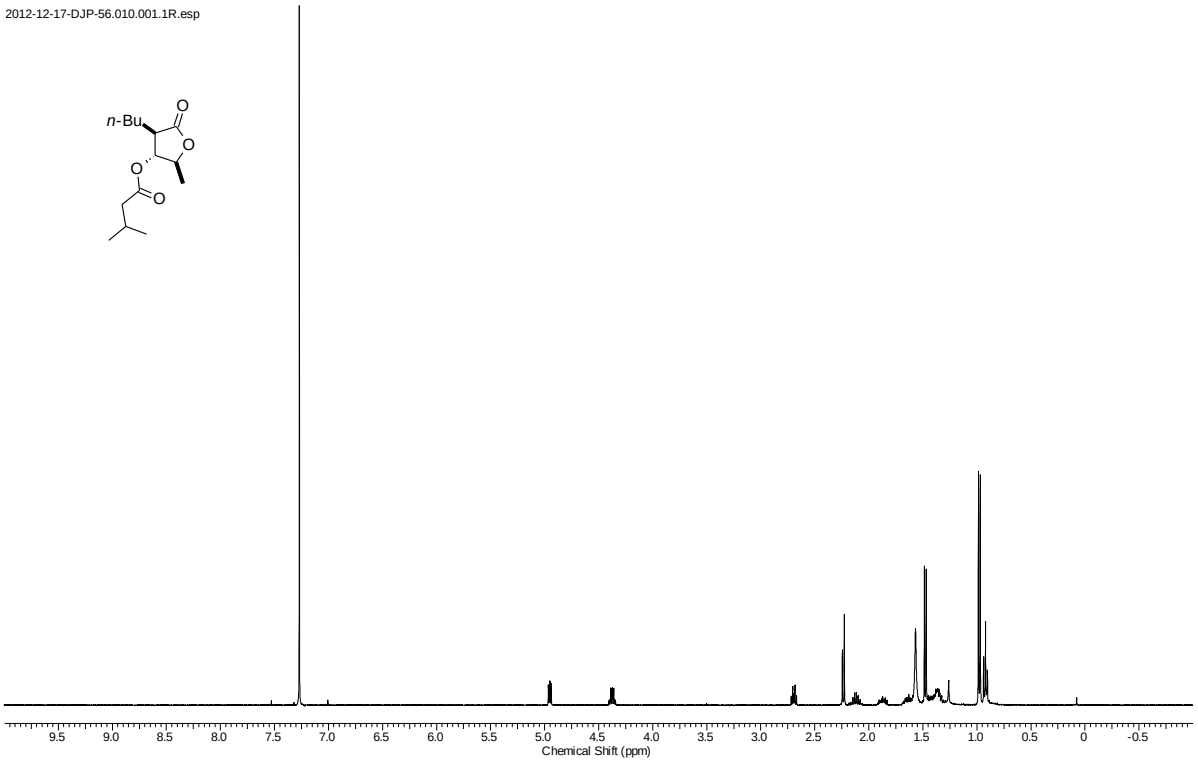
75 MHz $CDCl_3$

2012-11-02-DJP-55.021.001.1R.esp



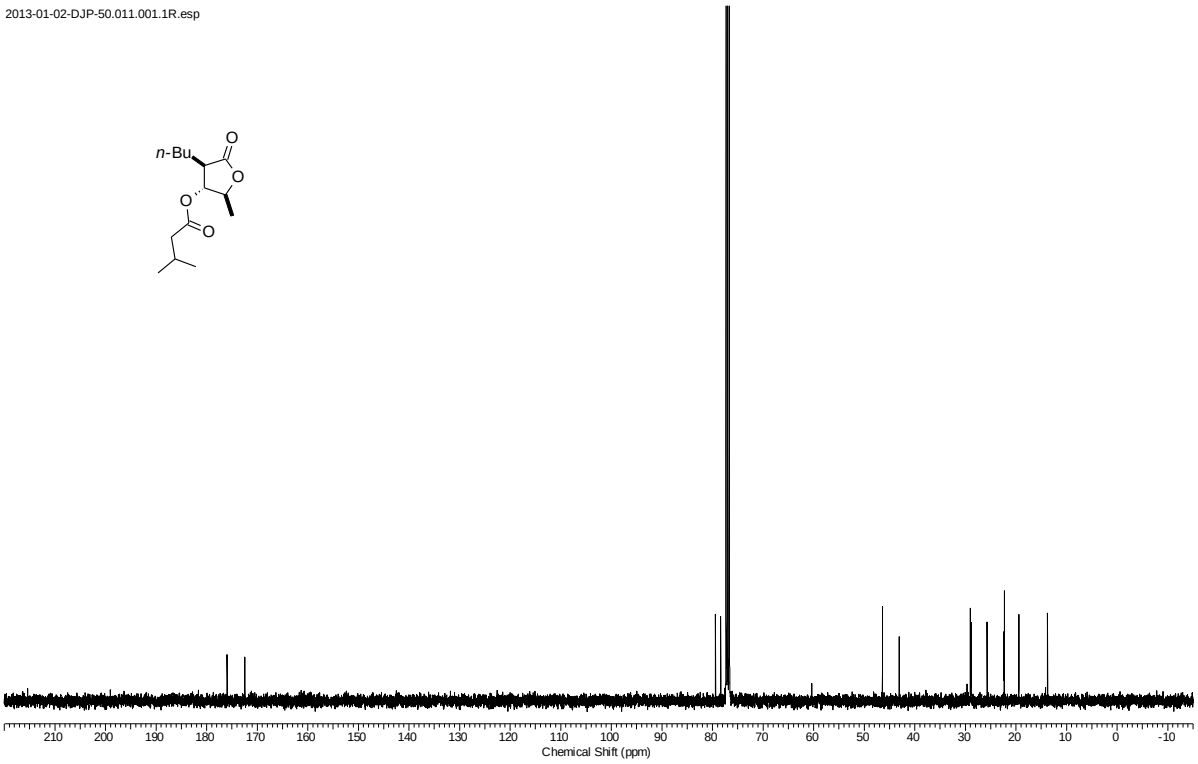
400 MHz $CDCl_3$

2012-12-17-DJP-56.010.001.1R.esp



101 MHz $CDCl_3$

2013-01-02-DJP-50.011.001.1R.esp



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