Supporting information

Probing the effects of heterocyclic functionality in [(benzene)Ru(TsDPENR)Cl] catalysts for Asymmetric Transfer Hydrogenation

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Asymmetric catalysis, transfer hydrogenation, heterocycle, TsDPEN, ruthenium

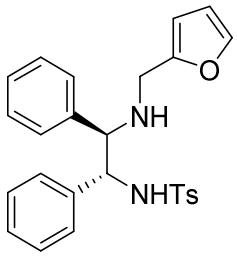
Contents

General Experimental.

General; Solvents and reagents for the synthesis of complexes and catalytic reactions were degassed prior to use and all reactions were carried out under either a nitrogen or argon atmosphere. All heated experiments were conducted using thermostatically controlled oil baths. Reactions were monitored by TLC using aluminum backed silica gel 60 (F254) plates, visualized using UV 254 nm and phosphomolybdic acid (PMA), potassium permanganate or vanillin dips as appropriate. Flash column chromatography was carried out routinely using 60 micrometer silica gel. Reagents were used as received from commercial sources unless otherwise stated. ^{1}H NMR spectra were recorded on a Bruker DPX (300, 400 or 500 MHz) spectrometer. Chemical shifts are reported in δ units, parts per million relative to the singlet at 7.26 ppm for chloroform and 0.00 ppm for TMS. Coupling constants (J) are measured in Hertz. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR Golden Gate. Mass spectra were recorded on a Bruker Esquire2000 or a Bruker MicroTOF mass spectrometer. Melting points were recorded on a Stuart Scientific SMP 1 instrument and are uncorrected. GC analysis was performed using a Hewlett Packard 5890. Dry solvents were purchased and used as received. HPLC analyses on a Hewlett-Packard 1050 instrument. Optical rotations were measured on an AA-1000 polarimeter.

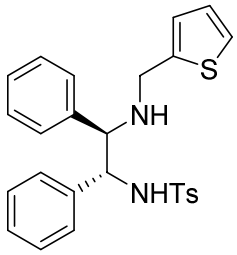
Experimental Procedures for ligands and complexes.

(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(furan-2-ylmethyl)amino]ethyl}-4-methylbenzene sulfonamide (6).



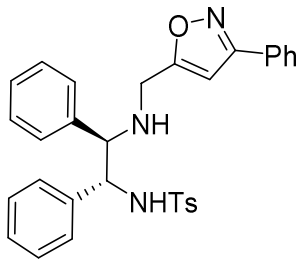
To a solution of (*R,R)*TsDPEN (500 mg, 1.36 mmol) in dry DCM (20 mL) with 4 Å molecular sieves was added dropwise a solution of 2-furaldehyde (130 mg, 1.36 mmol) in dry DCM (10 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in dry THF (8 mL) and cooled to 0 °C followed by dropwise addition of $LiAlH_4$ (2 M in THF, 0.68 mL, 1.36 mmol). After stirring at rt for 72 h the reaction mixture was cooled to 0 °C and quenched by slow addition of EtOAc. Sat. Rochelle salt solution (15 mL) was added and left to stir at rt for 30 min. Following extraction with EtOAc (3 × 15 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (10 – 20% EtOAc in Pet. Ether) afforded the pure product as an off-white solid (523 mg, 1.17 mmol, 86%); Mp 128.4 – 129.9 °C $[\alpha]_D^{22}$ -41.7 (*c* 0.05 in $CHCl_3$), ν_{max} 3298, 3061, 3029, 2916, 2847, 1599, 1505, 1493, 1454, 1373, 1354; δ_H (500 MHz, $CDCl_3$) 7.35 (2 H, d, *J* 8.1, Ts-ArH), 7.30 (1 H, m, 5'-furan), 7.17 – 7.11 (3 H, m, ArH) 7.10 – 7.02 (4 H, m, ArH), 7.00 (2 H, d, *J* 8.1,Ts-ArH), 6.97 (2 H, m, ArH), 6.92 (2 H, t, *J* 7.0, ArH), 6.26 (1 H, m, 4'-furan), 6.00 (1 H, br. s, NH), 5.98 (1 H, d, *J* 3.1, 3'-furan), 4.31 (1 H, dd, *J* 7.3, 2.9 C*H*$NHSO_2$), 3.69 (1 H, d, *J* 7.3, C*H*$NHCH_2$), 3.62 (1 H, d, J_{AB} 14.4, CH_AH_BNH), 3.42 (1 H, d, J_{AB} 14.4, CH_AH_BNH), 2.32 (3 H, s, Ts-CH_3); δ_C (125 MHz, $CDCl_3$) 152.95, 142.70, 141.93, 138.65, 138.29, 137.00, 129.11, 128.41, 127.99, 127.61, 127.58, 127.38, 127.32, 127.08, 110.06, 107.10, 66.51, 62.99, 43.54, 21.43; MS (ESI^+): *m*/*z*, 447.3 $[M + H]^+$; HRMS calcd for $C_{26}H_{27}N_2O_3S$ $[M + H]^+$ 447.1737, found 447.1736 (0.2 ppm error).

(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(thiophen-2-ylmethyl)amino]ethyl}-4-methylbenzene sulphonamide (7).



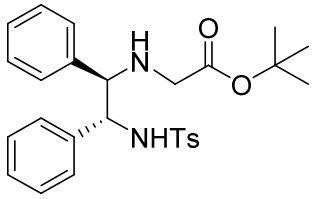
To a solution of (*R*,*R*)TsDPEN (400 mg, 1.09 mmol) in dry DCM (15 mL) with 4 Å molecular sieves was added dropwise a solution of 2-thiophenecarboxaldehyde (123 mg, 1.09 mmol) in dry DCM (6 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in dry THF (10 mL) and cooled to 0 °C followed by dropwise addition of $LiAlH_4$ (2 M in THF, 0.55 mL, 1.10 mmol). After stirring at rt overnight the reaction mixture was cooled to 0°C and quenched by slow addition of EtOAc. Sat. Rochelle salt solution (15 mL) was added and left to stir at rt for 30 min. Following extraction with EtOAc (3 × 15 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (0 – 5% MeOH in DCM) afforded the pure product as an off-white solid (388 mg, 0.840 mmol, 77%); Mp 151.4 – 152.1 °C, $[\alpha]_D^{22}$ -31.0 (*c* 0.05 in $CHCl_3$), ν_{max} 3336, 3299, 3031, 2930, 2841, 1598, 1492, 1440, 1424, 1347, 1328, 1304; δ_H (500 MHz, $CDCl_3$) 7.42 (2 H, d, *J* 8.1, Ts-ArH), 7.25 (1 H, d, *J* 5.0, ArH), 7.21 – 7.16 (3 H, m, ArH) 7.10 – 7.01 (5 H, m, ArH), 6.99 – 6.95 (2 H, m, ArH), 6.95 – 6.90 (3 H, m, ArH), 6.75 (1 H, d, *J* 2.5, ArH), 6.11 (1 H, d *J* 2.5, $NHSO_2$), 4.33 (1 H, dd, *J* 7.9, 2.6, C*H*$NHSO_2$), 3.85 (1 H, d, J_{AB} 14.0, C$H_A$$H_B$NH), 3.75 (1 H, d, *J* 7.9, C*H*$NHCH_2$), 3.64 (1 H, d, *J* 14.0, $CH_A$$H_B$NH), 2.35 (3 H, s, Ts-$CH_3$); δ_C (125 MHz, $CDCl_3$) 143.18, 142.76, 138.54, 138.14, 136.99, 129.13, 128.46, 127.95, 127.71, 127.59, 127.53, 127.33, 127.14, 126.63, 124.97, 124.71, 66.37, 62.97, 45.57, 21.45; MS (ESI^+): *m*/*z*, 463.3 $[M + H]^+$; HRMS calcd for $C_{26}H_{27}N_2O_2S_2$ $[M + H]^+$ 463.1508, found 463.1511 (0.5 ppm error).

***N*-((*R*,*R*)-1,2-Diphenyl-2-(((3-phenylisoxazol-5-yl)methyl)amino)ethyl)-4-methylbenzenesulfonamide (8)**



Propargyl/TsDPEN (405 mg, 1.00 mmol) was added to a solution of N-hydroxybenzimidoyl chloride (156 mg, 1.00 mmol) in DMF (2 mL) with 4 Å molecular sieves. After stirring for 96 h, the molecular sieves were filtered off and water (15 mL) was added. The mixture was extracted with EtOAc (3 x 15 mL) and the combined organic extracts were washed with water (3 x 15 mL). The organic layer was then dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to yield the crude product. Purification by column chromatography in (0 – 30% EtOAc in Pet. Ether) gave the pure product as an off-white solid (416 mg, 0.794 mmol, 79%); Mp 63.6 – 70.4 °C, $[\alpha]_D^{20}$ -43.3 (*c* 0.05 in $CHCl_3$); ν_{max} 3244, 3030, 2920, 1727, 1599, 1579, 1494, 1453, 1442, 1407, 1323 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.76 (2H, m, ArH), 7.49 – 7.44 (3H, m, ArH), 7.37 (2H, d, *J* 8.2, Ts-ArH), 7.19 – 7.15 (3H, m, ArH), 7.11 – 7.02 (5H, m, ArH), 7.00 (2 H, d, *J* 8.2, Ts-ArH) 6.94 (2H, d , *J* 7.2, ArH), 6.24 (1H, s, Isoxazole-H), 5.82 (1H, d, *J* 5.3,$NHSO_2$), 4.40 (1H, t, *J* 6.3, C*H*$NHSO_2$), 3.87 – 3.77 (2H, m, CH_AH_BNH + C*H*$NHCH_2$), 3.65 (1H, d, J_{AB} = 15.5 Hz, CH_AH_BNH), 2.31 (3H, s, Ts-CH_3); δ_C (126 MHz, $CDCl_3$) 171.38, 162.31, 142.91, 138.01, 136.84, 130.02, 129.19, 128.98, 128.92, 128.56, 128.17, 127.92, 127.64, 127.53, 127.27, 127.03, 126.82, 99.93, 66.83, 63.11, 42.38, 21.42; MS (ESI^+): *m*/*z* 524.3 $[M + H]^+$; HRMS calcd for $C_{31}H_{30}N_3O_3S$ $[M + H]^+$ 524.2002, found 524.2003 (0.1 ppm error)

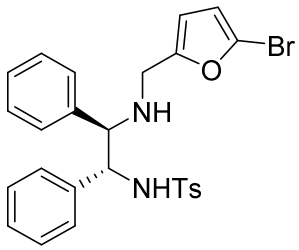
***tert*-Butyl ((*R, R*)-2-((4-methylphenyl)sulfonamido)-1,2-diphenylethyl)glycinate (9)**



tert-Butyl bromoacetate (205 mg, 1.05 mmol, 155 µL) was added dropwise to a stirring mixture of TsDPEN (366 mg, 1.00 mmol) and K_2CO_3 (207 mg, 1.5 mmol) in MeCN (4 mL). After

stirring overnight, the solvent was removed under reduced pressure and the residue dissolved in EtOAc (15 mL) and water (15 mL). The organic layer was separated and the aqueous layer extracted with EtOAC (2 x 15 mL). The organic extracts were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to yield the crude product. Purification by column chromatography (0 – 30% EtOAc in Pet. Ether) gave the pure product as a white solid (340 mg, 0.708 mmol, 71%); Mp 79.4 – 83.2 °C, $[\alpha]_D^{22}$ -18.8 (*c* 0.1 in $CHCl_3$) ν_{max} 3250, 3030, 2979, 2929, 1721, 1599, 1494, 1454, 1368, 1346, 1324 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.40 (2 H, d, *J* 8.1, Ts-ArH), 7.16 – 7.09 (3 H, m, ArH), 7.08 – 7.01 (5 H, m, ArH), 6.98 - 6.94 (2 H, m, ArH), 6.92 (2 H, d, *J* 6.9, ArH), 6.21 (1 H, m, $NHSO_2$), 4.32 (1 H, dd, *J* 7.5, 3.5, C*H*$NHSO_2$), 3.72 (1 H, d, *J* 7.5, C*H*$NHCH_2$), 3.14 (1 H, d, *J* 17.2, CH_AH_BNH), 3.03 (1 H, d, *J* 17.2, CH_AH_BNH), 2.34 (3 H, s, Ts-CH_3), 2.06 (1 H, br. s, NH), 1.41 (9 H, s, 3 x CH_3); δ_C (126 MHz, $CDCl_3$) δ ppm 171.14, 142.67, 138.47, 138.28, 137.17, 129.12, 128.31, 127.97, 127.78, 127.68, 127.44, 127.29, 127.08, 81.46, 67.26, 63.13, 49.04, 28.05, 21.44; MS (ESI^+): *m/z* 481.3 $[M + H]^+$; HRMS calcd for $C_{27}H_{33}N_2O_4S$ $[M + H]^+$ 481.2156, found 481.2155 (0.1 ppm error)

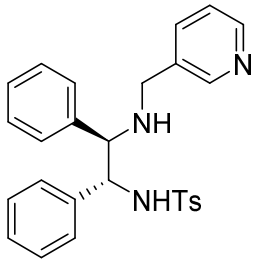
(*R*,*R*)-2-((5-Bromofuran-2-yl)methyl)amino-1,2-diphenylethyl-4-methylbenzenesulfonamide (10)



To a solution of (*R*,*R*)-TsDPEN (500 mg, 1.36 mmol) in dry DCM (20 mL) with 4 Å molecular sieves was added dropwise a solution 5-bromo-2-furaldehyde (238 mg, 1.36 mmol) in dry DCM (10 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in MeOH (15 mL) and $NaBH_4$ (103 mg, 2.72 mmol) was added portionwise. The reaction was stirred at room temperature until the imine had reacted completely. Upon completion, the solvent was removed under reduced pressure and the residue partitioned between EtOAc (10 mL) and water (10 mL). The organic fraction collected and extracted again with EtOAc (2 x 10 mL). Organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography in DCM gave the pure product as a orange solid (368 mg, 0.701 mmol, 52%); Mp 94.7 – 100.2 °C, $[\alpha]_D^{22}$ -41.7 (*c* 0.1 in $CHCl_3$),

ν_{max} 3062, 3031, 1597, 1494, 1454, 1326, 1205, 1185, 1155, 1122 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (2 H, d, *J* 8.1, Ts-ArH), 7.18 - 7.13 (3 H, m, ArH), 7.11 - 7.04 (3 H, m, ArH), 7.02 (2 H, d, *J* 8.1, Ts-ArH), 6.99 - 6.92 (4 H, m, ArH), 6.16 (1 H, d, *J* 3.1, Furan-2'-H), 5.95 (1 H, d, *J* 3.1, Furan-3'-H), 5.93 (1 H, d, *J* 4.4, $NHSO_2$), 4.33 (1 H, dd, *J* 7.2, 4.4, C*H*$NHSO_2$), 3.71 (1 H, d, *J* 7.2, C*H*$NHCH_2$), 3.59 (1 H, d, *J* 14.8, CH_AH_BNH) 3.41 (1 H, d, *J* 14.8, CH_AH_BNH) 2.34 (3 H, s, Ts-CH_3), 1.78 (1 H, br. s, N*H*CH_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.07, 142.76, 138.41, 138.17, 136.95, 129.14, 128.44, 128.06, 127.68, 127.54, 127.42, 127.30, 127.06, 120.77, 111.68, 109.94, 66.48, 62.95, 43.57, 21.44; MS (ESI^+): *m*/*z* 525.2 [M + H]$^+$; HRMS calcd for $C_{26}H_{26}BrN_2O_3S$ [M + H]$^+$ 525.0842, found 525.0847 (1.0 ppm error)

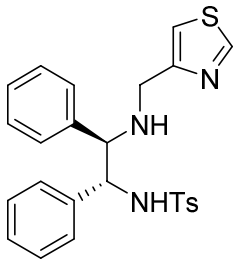
(1*R*,2*R*)-*N*-{1,2-diphenyl-2-[(pyridin-3-ylmethyl)amino]ethyl}-4-methylbenzene sulfonamide (11).



To a solution of (*R*,*R*)TsDPEN (366 mg, 1.00 mmol) in dry DCM (15 mL) with 4 Å molecular sieves was added dropwise a solution pyridine-3-carboxaldehyde (107 mg, 1.00 mmol) in dry DCM (5 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in dry THF (7 mL) and cooled to 0 °C followed by dropwise addition of $LiAlH_4$ (2 M in THF, 0.5 mL, 1.00 mmol). After stirring at rt for 5 hours the reaction mixture was cooled to 0°C and quenched by slow addition of EtOAc. Sat. Rochelle salt solution (12 mL) was added and left to stir at rt for 30 min. Following extraction with EtOAc (3 × 10 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (0 – 30 % EtOAc in DCM) afforded the pure product as an off-white solid (185 mg, 0.405 mmol, 40%) Mp 160.5 – 161.0 °C $[\alpha]_D^{22}$ -20.7 (*c* 0.05 in $CHCl_3$), ν_{max} 3312, 3031, 2923, 2854, 2793, 1597, 1584, 1494, 1475, 1450, 1425, 1349, 1327; δ_H (500 MHz, $CDCl_3$) 8.52 (1 H, d, *J* 3.8, 6'py-H), 8.36 (1 H, s, 2'py-H), 7.56 (1 H, d, *J* 7.7, 5'py-H), 7.37 (2 H, d, *J* 8.2, ArH), 7.26 (1 H, dd, *J* 7.7, 5.0, 4'py-H), 7.22 – 7.16 (4 H, m, ArH), 7.08 (1 H, d, *J* 7.2, ArH), 7.06 – 6.96 (6H, m, ArH), 6.90 (2 H, d, *J* 7.2, ArH), 6.02 (1 H, br. s, CH_2N*H*), 4.42

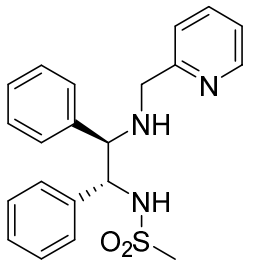
– 4.32 (1 H, m, PhC*H*NH), 3.71 (1 H, d, *J* 7.8, PhC*H*NHSO$_2$), 3.66 (1 H, d, J_{AB} 13.6, CH_AH$_B$NH), 3.46 (1 H, d, J_{AB} 13.6, CH$_A$$H_B$NH), 2.33 (3 H, s, Ts-CH$_3$); δ_C(125 MHz, CDCl$_3$) 149.59, 148.73, 142.84, 138.47, 137.96, 136.93, 135.75, 134.75, 129.12, 128.53, 128.01, 127.80, 127.60, 127.41, 127.06, 123.51, 66.85, 48.26, 21.43; MS (ESI$^+$): *m*/*z*, 458.3 [M + H]$^+$; HRMS calcd for $C_{27}H_{28}N_3O_2S$ [M + H]$^+$ 458.1897, found 458.1891 (1.3 ppm error);

(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(thiazol-4-ylmethyl)amino]ethyl}-4-methylbenzene sulphonamide (12)



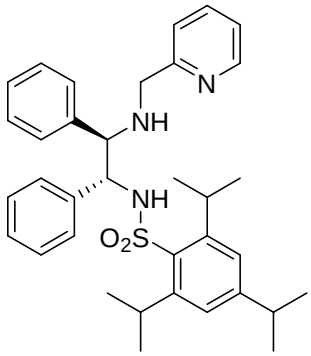
To a solution of (*R*,*R*)TsDPEN (366 mg, 1.00 mmol) in dry DCM (15 mL) with 4 Å molecular sieves was added dropwise a solution thiazole-4-carboxaldehyde (113 mg, 1.00 mmol) in dry DCM (5 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in dry THF (8 mL) and cooled to 0 °C followed by dropwise addition of $LiAlH_4$ (2 M in THF, 0.5 mL, 1.00 mmol). After stirring at rt for 5 hours the reaction mixture was cooled to 0°C and quenched by slow addition of EtOAc. Sat. Rochelle salt solution (12 mL) was added and left to stir at rt for 30 min. Following extraction with EtOAc (3 × 10 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (3% MeOH in DCM) afforded the pure product as a yellow solid (120 mg, 0.259 mmol, 26%) Mp 67.8 – 72.4 °C, $[\alpha]_D^{22}$ -29.3 (*c* 0.05 in CHCl$_3$), ν_{max} 3243, 3062, 3029, 2919, 1598, 1493, 1453, 1409, 1322, 1184, 1153, 1090, 1027; δ_H (500 MHz, CDCl$_3$) 8.75 (1 H, s, 2'-thiazole-H), 7.40 (2 H, d, *J* 8.2, ArH), 7.18 – 7.13 (3 H, m, ArH), 7.11- 6.98 (9 H, m, ArH), 6.95 (2 H, d, *J* 7.0, ArH),), 6.28 (1 H, br. s, CH$_2$N*H*), 4.38 (1 H, d, *J* 7.5 PhC*H*NH), 3.82 (1 H, d, J_{AB} 14.2, CH_AH$_B$NH), 3.78 (1 H, d, *J* 7.5, PhC*H*NHSO$_2$), 3.68 (1 H, d, J_{AB} 14.2, CH$_A$$H_B$NH), 2.35 (3 H, s, Ts-CH$_3$); δ_C(125 MHz, CDCl$_3$) 155.80, 153.01, 142.71, 138.73, 138.31, 137.06, 129.12, 128.39, 127.97, 127.63, 127.45, 127.32, 127.08, 114.46, 67.12, 63.08, 46.80, 21.44; MS (ESI$^+$): *m*/*z*, 464.2 [M + H]$^+$; HRMS calcd for $C_{25}H_{26}N_3O_2S_2$ [M + H]$^+$ 464.1461, found 464.1463 (0.4 ppm error).

(1*R*,2*R*)-*N*-1,2-Diphenyl-2-((pyridin-2-ylmethyl)amino)ethyl)-methanesulfonamide (13)



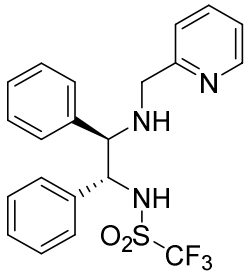
To a solution of (*R*,*R*)-MsDPEN (300 mg, 1.03 mmol) in dry DCM (15 mL) with 4 Å molecular sieves was added dropwise a solution of 2-pyridinecarboxaldehyde (111 mg, 1.03 mmol) in dry DCM (6 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in dry THF (10 mL) and cooled to 0 °C followed by dropwise addition of $LiAlH_4$ (2 M in THF, 0.52 mL, 1.04 mmol). After stirring at rt for 5 hours the reaction mixture was cooled to 0°C and quenched by slow addition of EtOAc. Sat. Rochelle salt solution (15 mL) was added and left to stir at rt for 45 min. Following extraction with EtOAc (3 × 15 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (0 – 2% MeOH in DCM) afforded the pure product as a yellow solid (233 mg, 0.611 mmol, 59%); Mp 52.6 – 54.0 °C, $[\alpha]_D^{22}$ -3.7 (*c* 0.05 in $CHCl_3$), ν_{max} 3287, 3063, 3026, 2933, 1590, 1570, 1493, 1454, 1433, 1316, 1200, 1143; δ_H (500 MHz, $CDCl_3$) 8.53 (1 H, d, *J* 4.4, 6'-pyH), 7.62 (1 H, t, *J* 7.7, 4'-pyH), 7.25 – 7.09 (12 H, m, ArH) 6.84 – 6.67 (2 H, m, ArH), 4.57 (1 H, d, *J* 7.9 C*H*NHSO$_2$), 3.88 – 3.84 (2 H, m, C*H*NHCH$_2$ + C*H*$_A$H$_B$NH), 3.67 (1 H, d J_{AB} 14.8, CH$_A$*H*$_B$NH), 2.38 (3 H, s, Ms-CH$_3$); δ_C(125 MHz, $CDCl_3$) 158.99, 149.14, 139.33, 138.87, 136.55, 128.47, 128.45, 127.86, 127.81, 127.76, 127.63, 122.18, 122.08, 67.05, 63.33, 51.99, 41.32; MS (ESI$^+$): *m*/*z*, 382.2 $[M + H]^+$; HRMS calcd for $C_{21}H_{24}N_3O_2S$ $[M + H]^+$ 382.1584, found 382.1586 (0.7 ppm error).

(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(pyridin-2-ylmethyl)amino]ethyl}-2,4,6-triisopropylbenzenesulfonamide (14)



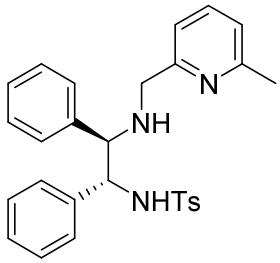
To a solution of (*R*,*R*)TrisDPEN (479 mg, 1.00 mmol) in dry DCM (14 mL) with 4 Å molecular sieves was added dropwise a solution of 2-pyridinecarboxaldehyde (107 mg, 1.00 mmol) in dry DCM (5 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in dry THF (10 mL) and cooled to 0 °C followed by dropwise addition of $LiAlH_4$ (2 M in THF, 0.5 mL, 1.00 mmol). After stirring at rt for 5 hours the reaction mixture was cooled to 0°C and quenched by slow addition of EtOAc. Sat. Rochelle salt solution (12 mL) was added and left to stir at rt for 30 min. Following extraction with EtOAc (3 × 10 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (40% EtOAc in Pet. Ether) afforded the pure product as a white solid (387 mg, 0.680 mmol, 68%) Mp 152.6 – 153.2 °C $[\alpha]_D^{22}$ +10.0 (*c* 0.05 in $CHCl_3$), ν_{max} 3340, 3289, 3061, 3030, 2957, 2928, 2867, 1600, 1569, 1492, 1454, 1432; δ_H (500 MHz, $CDCl_3$) 8.51 (1 H, d, *J* 4.6, 6’ py-H), 7.63 (1 H, td, *J* 7.7, 1.4, 4’ py-H), 7.22 (1 H, d, *J* 7.7, 3’ py-H), 7.17 (1 H, t, *J* 6.1, ArH), 7.14 – 7.09 (3 H, m, ArH), 7.07 (1 H, br. s, $NHSO_2$), 6.98 (2 H, s, tris-3’,5’-H), 6.96 – 6.91 (3 H, m, ArH), 6.87 (2 H, t, *J* 7.4, ArH), 6.75 (2 H, d, 7.4, ArH), 4.51 (1 H, d, *J* 9.3, C*H*$NHSO_2$), 3.99 (2 H, sep, Tris– *o*-C*H*$(CH_3)_2$), 3.83 (1 H, d, J_{AB} 14.8, CH_AH_BNH), 3.69 (1 H, d, J_{AB} 14.8, CH_AH_BNH), 3.64 (1 H, d, *J* 9.3, C*H*$NHCH_2$), 2.83 (1 H, sep, *J* 6.9, Tris – *p*-C*H*$(CH_3)_2$), 1.21 (6 H, d, *J* 6.9, Tris – *p*-CH$(CH_3)_2$), 1.17 (6 H, d, *J* 6.7, Tris-CH_3), 1.04 (6 H, d, *J* 6.7, Tris-CH_3); δ_C(125 MHz, $CDCl_3$) 159.25, 152.27, 149.94, 149.05, 139.30, 138.33, 136.52, 133.74, 128.18, 127.87, 127.68, 127.48, 127.05, 123.21, 122.22, 122.02, 67.93, 63.03, 52.07, 34.12, 29.66, 24.96, 24.70, 23.67, 23.61; MS (ESI^+): *m*/*z*, 570.4 $[M + H]^+$; HRMS calcd for $C_{35}H_{44}N_3O_2S$ $[M + H]^+$ 570.3149, found 570.3148 (0.0 ppm error).

(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(6-methyl-pyridin-2-ylmethyl)amino]ethyl}-1,1,1-trifluoromethanesulfonamide (15)



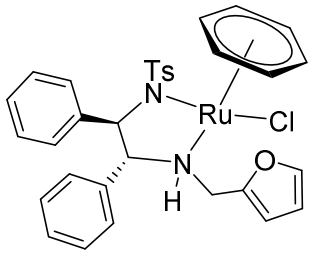
To a solution of (*R*,*R*)TfDPEN (50 mg, 0.15 mmol) in dry DCM (3 mL) with 4 Å molecular sieves was added dropwise 2-pyridinecarboxaldehyde (16 mg, 0.15 mmol) in dry DCM (1 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in dry THF (10 mL) and cooled to 0 °C followed by dropwise addition of $LiAlH_4$ (2 M in THF, 75 µL, 0.15 mmol). After stirring at rt for 5 hours the reaction mixture was cooled to 0°C and quenched by slow addition of EtOAc. Sat. Rochelle salt solution (2 mL) was added and left to stir at rt for 30 min. Following extraction with EtOAc (3 × 3 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (10 – 20% EtOAc in DCM) afforded the pure product as a white solid (30 mg, 0.069 mmol, 46%) Mp 59.2 – 62.0 °C, $[\alpha]_D^{22}$ -62.5 (*c* 0.02 in $CHCl_3$), ν_{max} 3310, 3064, 3031, 2926, 1720, 1656, 1597, 1571, 1454, 1437, 1368, 1272; δ_H (500 MHz, $CDCl_3$) 8.62 (1 H, d, *J* 4.4 6' py-H), 7.68 (1 H, t, *J* 7.40, ArH), 7.30 – 7.24 (2 H, m, ArH), 7.23 – 7.19 (3 H, m, ArH), 7.18 – 7.14 (3 H, m, ArH), 7.13 - 7.02 (5 H, m, ArH), 4.71 (1 H, d, *J* 8.6, C*H*NHTf), 4.04 (1 H, d, *J* 16.6, NHCH_AH_B), 3.82 (1 H, d, *J* 16.6, NHCH_AH_B), 3.78 (1 H, d, *J* 8.6, C*H*NHCH_2); δ_C (125 MHz, $CDCl_3$) 159.05, 148.47, 139.58, 139.07, 137.15, 128.50, 128.20, 127.86, 127.72, 127.66, 127.09, 122.41, 122.37, 119.71 (q, *J* 322 Hz, CF_3), 67.53, 64.71, 50.86; δ_F (376 MHz, $CDCl_3$) -77.14 (3 F, s, CF_3); MS (ESI^+): *m*/*z*, 434.0 $[M - H]^-$; HRMS calcd for $C_{21}H_{21}F_3N_3O_2S$ $[M + H]^+$ 436.1301, found 436.1305 (1.0 ppm error).

(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(6-methyl-pyridin-2-ylmethyl)amino]ethyl}-4-methyl benzenesulfonamide (16)



To a solution of (*R*,*R*)TsDPEN (366 mg, 1.00 mmol) in dry DCM (15 mL) with 4 Å molecular sieves was added dropwise a solution of 6-methylpyridine-2-carboxaldehyde (121 mg, 1.00 mmol) in dry DCM (5 mL). The molecular sieves were filtered off after stirring overnight and the solvent removed under reduced pressure. The residue was dissolved in dry THF (8 mL) and cooled to 0 °C followed by dropwise addition of $LiAlH_4$ (2 M in THF, 0.50 mL, 1.00 mmol). After stirring at rt for 5 hours the reaction mixture was cooled to 0°C and quenched by slow addition of EtOAc. Sat. Rochelle salt solution (12 mL) was added and left to stir at rt for 30 min. Following extraction with EtOAc (3 × 10 mL), the organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography (2% MeOH in DCM) afforded the pure product as an off-white solid (386 mg, 0.819 mmol, 82%); Mp 107.2 – 110.7 °C, $[\alpha]_D^{22}$ -7.3 (*c* 0.05 in $CHCl_3$), ν_{max} 3358, 3338, 3064, 3030, 2924, 2850, 1594, 1578, 1494, 1455, 1435, 1377, 1322, 1290, 1259; δ_H (500 MHz, $CDCl_3$) 7.52 (1 H, t, *J* 7.7, 4'pyH), 7.44 (2 H, d, *J* 8.1, Ts-ArH), 7.17 – 7.10 (3 H, m, ArH), 7.10 – 7.01 (7 H, m, ArH), 7.01 – 6.97 (2 H, m, ArH), 6.96 – 6.90 (4 H, m, ArH), 4.39 (1 H, d, *J* 8.1, PhC*H*NH), 3.78 (1 H, d, J_{AB} 15.2, CH_AH$_B$NH), 3.73 (1 H, d, *J* 8.1, PhC*H*NHSO$_2$), 3.60 (1 H, d, J_{AB} 15.2, CH$_A$*H*$_B$NH), 2.60 (3 H, s, py-CH_3), 2.35 (3 H, s, Ts-CH_3); δ_C(125 MHz, $CDCl_3$) 158.39, 158.09, 142.56, 139.34, 138.74, 137.37, 136.77, 129.09, 128.21, 127.85, 127.81, 127.55, 127.44, 127.15, 127.08, 121.54, 119.06, 67.21, 63.31, 51.74, 24.36, 21.45; MS (ESI$^+$): *m*/*z*, 472.3 $[M + H]^+$; HRMS calcd for $C_{28}H_{30}N_3O_2S$ $[M + H]^+$ 472.2053, found 472.2053 (0.0 ppm error).

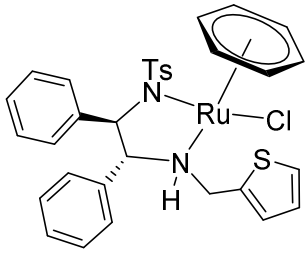
Complex formed from ligand 6. (17)



dr 3:2

To a Schlenk tube charged with benzene ruthenium (II) chloride dimer (56 mg, 0.112 mmol) and **6** (100 mg, 0.224 mmol) in dry 2-propanol (6 mL) was added triethylamine (89 mg, 0.880 mmol, 123 µL). After stirring at 80 °C for 1 h, the solution was allowed to cool to rt and the solvent removed under reduced pressure. The residue was dissolved in $CHCl_3$ (10 mL) and washed with water (10 mL). The organic layer was dried over $MgSO_4$, filtered and solvent removed under reduced pressure to afford the crude mixture. Purification by column chromatography (15% EtOAc in DCM followed by 1-3% MeOH in DCM) afforded the product as a brown solid (75 mg, 0.114 mmol, 51%); Mp 191.2 – 194.5 °C, $[\alpha]_D^{22}$ +100.0 (*c* 0.05 in $CHCl_3$), ν_{max} 3295, 3197, 3061, 3028, 2922, 2871, 1599, 1493, 1453, 1435, 1367, 1329, 1268, 1193, 1148; Major diastereomer: δ_H (500 MHz, $CDCl_3$) 7.41 (1 H, s, ArH), 7.33 – 7.27 (2 H, m, ArH), 7.12 – 7.02 (3 H, m, ArH) 6.92 – 6.82 (3 H, m, ArH), 6.77 – 6.72 (4 H, m, ArH), 6.6 (2 H, d, *J* 7.3 ArH), 6.37 (2 H, s, ArH), 5.70 (6 H, s, benzene), 4.45 (1 H, br, NH), 4.32 – 4.24 (1 H, m, CH_AH$_B$NH), 4.13 (1 H, d *J* 13.7, CH$_A$$H_B$NH), 4.05 (1 H, m, PhC*H*NSO$_2$), 3.84 (1 H, t, *J* 11.6, PhC*H*NH), 2.25 (3 H, s, Ts-CH$_3$); δ_C(125 MHz, $CDCl_3$) 149.38, 141.92, 141.68, 139.49, 139.41, 136.55, 129.86, 128.93, 128.65, 128.02, 127.56, 126.93, 126.71, 126.48, 111.32, 109.39, 84.01, 80.49, 69.66, 51.52, 21.26; Minor diastereomer: δ_H (500 MHz, $CDCl_3$) 7.49 (1 H, s, ArH), 7.36 (1 H, m, ArH), 7.33 – 7.27 (2 H, m, ArH) 7.12 – 7.02 (3 H, m, ArH) 6.82 – 6.80 (3 H, m, ArH), 6.72 – 6.69 (4 H, m, ArH), 6.58 – 6.53 (1 H, m, ArH), 6.41 (1 H, s, ArH), 6.17 (1H, s, ArH), 5.64 (6 H, s, benzene), 5.44 (1H, m, NH), 4.71 (1 H, m, CH$_A$$H_B$NH), 4.39 (1 H, m, PhC*H*NSO$_2$), 4.05 (1 H, m, PhC*H*NH), 3.72 (1 H, d *J* 14.6, CH$_A$$H_B$NH), 2.23 (3 H, s, Ts-CH$_3$)); δ_C(125 MHz, $CDCl_3$) 150.46, 143.08, 142.21, 139.39, 138.44, 136.85, 128.60, 128.35, 128.10, 127.53, 126.71, 126.48, 126.41, 125.96, 111.74, 109.16, 83.72, 74.44, 71.86, 50.02, 21.24; MS (ESI$^+$): *m*/*z*, 625.2 [M – Cl]$^+$; HRMS calcd for $C_{32}H_{31}N_2O_3SRu$ [M – Cl]$^+$ 625.1093, found 625.1095 (1.0 ppm error).

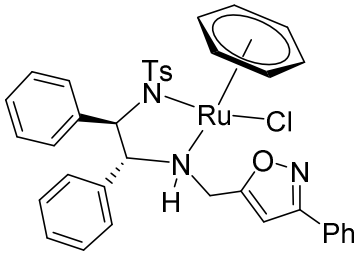
Complex formed from ligand 7. (18)



dr 3:1

To a Schlenk tube charged with benzene ruthenium (II) chloride dimer (56 mg, 0.112 mmol) and **7** (100 mg, 0.216 mmol) in dry 2-propanol (6 mL) was added triethylamine (89 mg, 0.880 mmol, 123 µL). After stirring at 80 °C for 1 h, the solution was allowed to cool to rt and the solvent removed under reduced pressure. The residue was dissolved in $CHCl_3$ (10 mL) and washed with water (10 mL). The organic layer was dried over $MgSO_4$, filtered and solvent removed under reduced pressure to afford the crude mixture. Purification by column chromatography (20% EtOAc in DCM followed by 1-4% MeOH in DCM) afforded the pure product as a brown solid (38 mg, 0.056 mmol, 26%); Mp 151.4 – 152.1 °C, $[\alpha]_D^{22}$ +72.2 (*c* 0.003 in $CHCl_3$), ν_{max} 3293, 3062, 3027, 2923, 2868, 1599, 1493, 1453, 1433, 1379, 1328, 1270, 1197; δ_H (500 MHz, $CDCl_3$) Major diastereomer: 7.27 (1 H, s, ArH), 7.22 (1 H, m, ArH), 7.14 (1 H, ArH), 7.10 – 7.04 (2 H, m, ArH), 7.03 – 6.99 (2 H, m, ArH), 6.95 – 6.89 (1 H, m, ArH), 6.87 - 6.79 (3 H, m, ArH), 6.76 (2 H, d, *J* 7.32, ArH), 6.73 - 6.69 (2 H, m, ArH), 6.60 (2 H, d, *J* 7.5, ArH), 5.66 (6 H, s, benzene), 4.54 – 4.40 (2 H, m, C*H*$_A$H$_B$NH + CH$_A$H$_B$N*H*), 4.31 (1 H, d, *J* 13.7, CH$_A$*H*$_B$NH), 4.10 (1 H, d, *J* 10.8, PhC*H*NSO$_2$), 3.91 - 3.80 (1 H, m, PhC*H*NH), 2.25 (3 H, s, Ts-CH_3); δ_C(125 MHz, $CDCl_3$) 141.94, 139.43, 139.17, 137.93, 136.70, 129.89, 129.05, 128.67, 128.40, 128.01, 127.57, 127.46, 127.05, 126.89, 126.39, 125.09, 84.08, 81.00, 69.59, 54.47, 21.25; MS (ESI$^+$): *m*/*z*, 641.2 $[M - Cl]^+$; HRMS calcd for $C_{32}H_{31}N_2O_2S_2Ru$ $[M - Cl]^+$ 641.0865, found 641.0868 (0.7 ppm error).

Complex formed from ligand 8. (19)

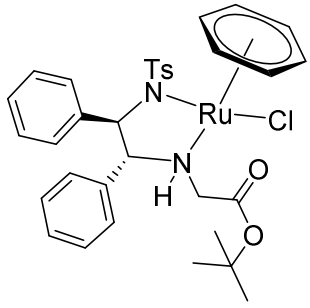


dr 2:1

To a Schlenk tube charged with benzene ruthenium (II) chloride dimer (58 mg, 0.116 mmol) and **8** (120 mg, 0.229 mmol) in PhCl (1.8 mL) was added triethylamine (93 mg, 0.92 mmol,

128 µL). After stirring at 80 °C for 1 h, the solution was allowed to cool to rt and the solvent removed under reduced pressure. The residue was dissolved in $CHCl_3$ (15 mL) and washed with water (15 mL). The organic layer was dried over $MgSO_4$, filtered and solvent removed under reduced pressure to afford the crude mixture. Purification by column chromatography (15% EtOAc in DCM followed by 0-3% MeOH in DCM) afforded the product as a dark brown solid (77 mg, 0.104 mmol, 46%); Mp > 250 ºC (Decomp), $[\alpha]_D^{22}$ +50.0 (*c* 0.002 in $CHCl_3$), ν_{max} 3056, 3029, 1598, 1558, 1493, 1437, 1405, 1374, 1269, 1156, 1127 cm^{-1}; Major: ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.77 (2 H, m ArH), 7.51 - 7.43 (4 H, m, ArH), 7.33 – 7.27 (2 H, m, ArH), 7.11 – 7.06 (3 H, m, ArH), 6.95 – 6.91 (1 H, m, isoxazole-H), 6.86 (2 H, d, *J* 7.8, ArH), 6.83 – 6.78 (2 H, m, ArH), 6.74 (2 H, t, *J* 7.3, ArH), 6.72 – 6.67 (1 H, m, ArH), 6.64 (1 H, d, *J* 7.3, ArH), 5.74 (6 H, s, benzene), 4.58 - 4.41 (2 H, m, C$H_A$$H_B$NH + CHNSO$_2$), 4.12 (1 H, d, *J* 10.68, C$H_A$$H_B$NH), 4.05 – 3.90 (1 H, m, C*H*NHCH$_2$), 2.26 (3 H, s, Ts-CH$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.24, 163.04, 141.65, 139.65, 139.19, 135.97, 130.53, 129.79, 129.12, 128.94, 128.82, 128.14, 128.09, 127.48, 127.08, 126.99, 126.82, 126.57, 102.60, 84.19, 80.83, 69.36, 50.80, 21.27. MS (ESI^+): *m/z* 702.3 $[M - Cl]^+$; HRMS calcd for $C_{37}H_{33}N_3NaO_3RuS$ $[M – HCl + Na]^+$ 724.1178, found 724.1188 (0.0 ppm error)

Complex formed from ligand 9. (20)

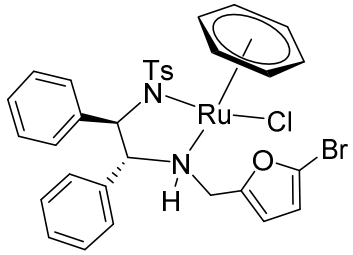


dr 3.5:1

To a Schlenk tube charged with benzene ruthenium (II) chloride dimer (52 mg, 0.104 mmol) and **9** (100 mg, 0.208 mmol) in PhCl (1.5 mL) was added triethylamine (84 mg, 0.832 mmol, 116 µL). After stirring at 80 °C for 1 h, the solution was allowed to cool to rt and the solvent removed under reduced pressure. The residue was dissolved in $CHCl_3$ (10 mL) and washed with water (15 mL). The organic layer was dried over $MgSO_4$, filtered and solvent removed under reduced pressure to afford the crude mixture. Purification by column chromatography (10% EtOAc in DCM followed by 0-3% MeOH in DCM) afforded the product as a dark brown solid (87 mg, 0.125 mmol, 60%); Mp > 250 ºC (Decomp) $[\alpha]_D^{22}$ +631.3 (*c* 0.002 in $CHCl_3$); ν_{max} 3060, 3029, 2978, 2931, 1731, 1636, 1600, 1494, 1454, 1436, 1393 cm^{-1}; Major: ^1H NMR

(500 MHz, $CDCl_3$) δ ppm 7.32 (2 H, d, *J* 8.1, Ts-ArH), 7.16 – 7.05 (4 H, m, ArH), 6.82 (2 H, d, *J* 7.9, ArH), 6.79 - 6.75 (1 H, m, ArH), 6.74 - 6.68 (3 H, m, ArH), 6.64 - 6.54 (2 H, m, ArH), 6.06 – 5.94 (1 H, dd, *J* 11.4, 6.6, NH), 5.83 (6 H, s, benzene), 4.41 (1 H, dd, *J* 18.4, 6.6, C*H*$_A$H$_B$NH), 4.32 (1 H, d, *J* 10.8, CHNSO$_2$), 4.13 (1 H, t, *J* 11.6, C*H*NHCH$_2$), 3.27 (1 H, d, *J* 18.4, CH$_A$*H*$_B$NH), 2.23 (3 H, s, Ts-CH$_3$), 1.44 (9 H, s, 3 x CH$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 170.65, 143.13, 139.40, 138.66, 135.46, 129.82, 128.55, 128.47, 128.44, 128.08, 126.51, 126.49, 125.92, 84.08, 84.03, 73.79, 71.53, 56.57, 27.85, 21.23; MS (ESI$^+$): m/z 659.3 [M – Cl]$^+$; HRMS calcd for $C_{33}H_{37}N_2O_4RuS$ [M – Cl]$^+$ 659.1512, found 659.1526 (0.8 ppm error).

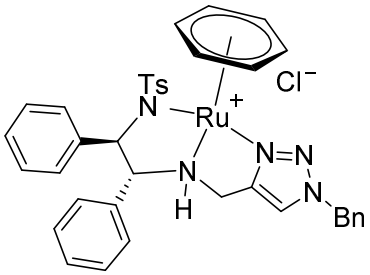
Complex formed from ligand 10. (21)



dr 2:1

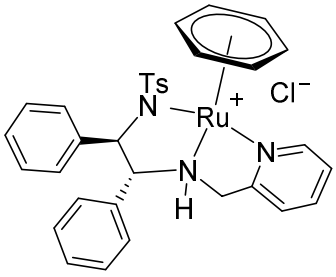
To a Schlenk tube charged with benzene ruthenium (II) chloride dimer (40 mg, 0.081 mmol) and **10** (85 mg, 0.162 mmol) in PhCl (1.2 mL) was added triethylamine (66 mg, 0.65 mmol, 90 µL). After stirring at 85 °C for 1 h, the solution was allowed to cool to rt and the solvent removed under reduced pressure. The residue was dissolved in $CHCl_3$ (10 mL) and washed with water (12 mL). The organic layer was dried over $MgSO_4$, filtered and solvent removed under reduced pressure to afford the crude mixture. Purification by column chromatography (15% EtOAc in DCM followed by 0-3% MeOH in DCM) afforded the product as a brown solid (85 mg, 0.115 mmol, 71%); Mp 185.4 – 189.4 ºC, $[\alpha]_D^{22}$ +100.0 (*c* 0.05 in $CHCl_3$), ν_{max} 3062, 3027, 2919, 2871, 1599, 1494, 1454, 1436, 1398, 1374 cm^{-1}; Major diastereomer; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.34 – 7.28 (2 H, m, ArH), 7.13 – 7.03 (4 H, m, ArH), 6.90 – 6.79 (3 H, m, ArH), 6.78 – 6.66 (3 H, m, ArH), 6.60 (2 H, d, *J* 7.9 Ts-ArH), 6.36 (1 H, m, 3'furan-H), 6.25 (1 H, d, *J* 3.20, 2'furan-H), 5.78 (6 H, s, benzene-H), 4.38 – 4.33 (1 H, m, C*H*$_A$H$_B$NH), 4.16 – 4.11 (1 H, m, CH$_A$*H*$_B$NH), 4.04 (1 H, d, *J* 10.8, C*H*NHCH$_2$), 3.86 – 3.81 (1 H, m, C*H*NSO$_2$), 2.25 (3 H, s, Ts-ArH); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 151.24, 141.57, 139.57, 139.36, 136.30, 129.79, 128.83, 128.63, 128.43, 128.04, 127.55, 126.98, 126.49, 121.33, 112.82, 112.44, 84.17, 80.56, 69.67, 51.60, 21.25; MS (ESI$^+$): *m/z* 703.1 [M + H]$^+$; HRMS calcd for $C_{32}H_{30}BrN_2O_3RuS$ [M – Cl]$^+$ 703.0199, found 703.0202 (0.1 ppm error)

Complex formed from ligand 4. (22)



To a mixture of benzene ruthenium (II) chloride dimer (47 mg, 0.094 mmol) and **4** (100 mg, 0.186 mmol) in dry 2-propanol (5 mL) was added triethylamine (75 mg, 0.744 mmol, 103 µL) and stirred at 80 °C for 1 h. The mixture was allowed to cool to room temperature before removal of the solvent under reduced pressure. The residue was dissolved in chloroform (10 mL) and washed with water (10 mL). The organic layer separated, dried over $MgSO_4$, filtered and the solvent removed to afford the crude product. Purification by column chromatography (5% MeOH in DCM) afforded the pure product as a brown solid (78 mg, 0.104 mmol, 56%) Mp > 200 ºC (Decomp), $[\alpha]_D^{22}$ +71.7 (*c* 0.01 in $CHCl_3$), ν_{max} 3369, 3030, 2865, 1599, 1494, 1452, 1434, 1266, 1130, 1084; δ_H (500 MHz, $CDCl_3$) 10.74 (1 H, br, NH), 7.52 (2 H, d, *J* 7.6, ArH), 7.45 (3 H, t, *J* 7.5, ArH), 7.40 (2 H, d, *J* 7.5, ArH), 7.32 (1 H, s, triazole-H), 7.21 (2 H, t, *J* 7.5, ArH), 7.13 (3 H, m, ArH), 6.85 (2 H, d, *J* 7.0, ArH), 6.78 – 6.70 (5 H, m, ArH), 6.25 (6 H, s, benzene), 5.71 (1H, d, J_{AB} 14.8, Benzyl- CH_AH$_B$), 5.66 (1H, d, J_{AB} 14.8, Benzyl-CH$_A$$H_B$), 4.90 (1 H, dd, *J* 11.8, 3.0, PhC*H*NH), 4.49 (1H, d, *J* 11.8, PhC*H*NTs), 3.78 (1H, m, CH_AH$_B$NH), 3.70 (1H, m, CH$_A$$H_B$NH), 2.20 (3 H, s, tosyl-CH_3); δ_C(125 MHz, $CDCl_3$) 149.30, 141.38, 139.86, 138.90, 133.39, 132.73, 130.50, 129.50, 128.88, 128.62, 128.60, 128.47, 128.15, 127.55, 126.88, 126.59, 119.54, 86.50, 78.82, 62.17, 55.98, 41.73, 21.15; MS (ESI^+): *m*/*z*, 716.3 $[M - Cl]^+$; HRMS calcd for $C_{37}H_{36}N_5O_2SRu$ $[M - Cl]^+$ 716.1628, found 716.1641 (0.5 ppm error).

Complex formed from ligand 5. (23)

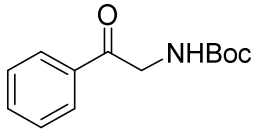


To a mixture of benzene ruthenium (II) chloride dimer (54.7 mg, 0.109 mmol) and **5** (100 mg, 0.218 mmol) in dry 2-propanol (5 mL) was added triethylamine (89 mg, 0.875 mmol, 123 µL)

and stirred at 80 °C for 1 h. The mixture was allowed to cool to room temperature before removal of the solvent under reduced pressure. The residue was dissolved in chloroform (10 mL) and washed with water (10 mL). The organic layer separated, dried over $MgSO_4$, filtered and the solvent removed to afford the crude product. Purification by column chromatography (0 – 10% MeOH in DCM) afforded the pure product as a brown solid (40 mg, 0.059 mmol, 27%) Mp > 200 ºC (Decomp), $[\alpha]_D^{22}$ +71.7 (*c* 0.01 in $CHCl_3$), ν_{max} 3360, 3030, 2873, 1607, 1492, 1451, 1434, 1265, 1128, 1084, 1044; δ_H (500 MHz, $CDCl_3$) 10.45 (1 H, s, NH), 9.54 (1 H, d, *J* 5.5 , 6'-pyH), 7.91 (1 H, t, *J* 7.5, 4'-pyH) 7.49 (1H, t, *J* 6.5, 5'-pyH), 7.37 (2H, d, *J* 7.5, ArH), 7.32 (1 H, d, *J* 7.8, ArH), 7.21 (2 H, t, *J* 7.3, ArH), 7.16 (1 H, t, *J* 7.3, ArH), 7.04 (2 H, d, *J* 8.1, ArH), 6.76 (2H, d, *J* 8.0, ArH), 6.72 (2 H, d, *J* 7.4, ArH), 6.66 (1H, t, *J* 7.1, ArH), 6.59 (2 H, t, *J* 7.4, ArH), 6.26 (6 H, s, benzene), 4.67 (1 H, d, *J* 12.3, PhC*H*NTs), 4.40 (1 H, d, J_{AB} 18.0, CH_AH$_B$NH), 4.08 (1 H, d, J_{AB} 18.0, CH$_A$$H_B$NH), 4.03 (1 H, d, *J* 12.3, NHC*H*Ph), 2.21 (3 H, s, Ts-CH_3); δ_C (125 MHz, $CDCl_3$) 161.92, 155.91, 142.22, 139.73, 139.45, 136.97, 132.73, 130.50, 129.28, 128.84, 128.55, 128.17, 127.23, 126.71, 126.29, 124.57, 120.24, 86.67, 77.56, 62.94, 54.54, 21.15; MS (ESI^+): *m*/*z*, 636.3 $[M - Cl]^+$; HRMS calcd for $C_{33}H_{32}N_3O_2SRu$ $[M - Cl]^+$ 636.1253, found 636.1260 (0.2 ppm error).

Synthesis of ketone substrates where not commercially available:

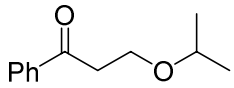
***tert*-Butyl (2-oxo-2-phenylethyl)carbamate**



$NaHCO_3$ (840 mg, 10.0 mmol) was added to a solution of 2-aminoacetophenone hydrochloride (687 mg, 4.00 mmol) in water (14 mL). MeOH (14 mL) and Boc_2O (1.31 g, 6 mmol) were then added to the mixture and left to stir at rt for 20 h. The mixture was then transferred to a conical flask with ice-cold water (55 mL) causing a white precipitate to form. The precipitate was filtered off via Büchner filtration, washed with ice-cold water (2 x 10 mL) and dried under vacuum to give the product (846 mg, 3.60 mmol, 90%); δ_H (300 MHz, $CDCl_3$) 7.98 – 7.94 (2 H, m, ArH) 7.65 – 7.59 (1 H, m, ArH) 7.52 - 7.46 (2 H, m, ArH) 5.55 (1 H, br. s, NH) 4.67 (2 H, d, *J* 4.5, CH_2NH) 1.48 (9 H, s, $(CH_3)_3$); δ_c (101 MHz, $CDCl_3$) δ 194.57, 155.88, 134.67, 134.03, 128.98, 127.93, 79.92, 47.62, 28.47

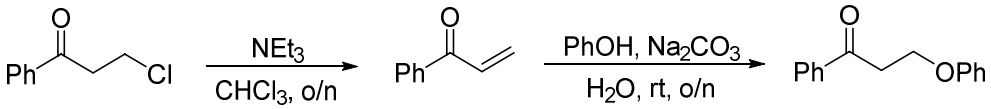
M. C. Myers, J. A. Iera, J. Bang, T. Hara, S. Saito, G. P. Zambetti, D. H. Appella, *J. Am. Chem. Soc.*, 2005, **127**, 6152-6153

3-Isopropoxy-1-phenylpropan-1-one

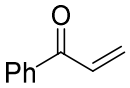


3-Chloropropiophenone (200 mg, 1.19 mmol) was dissolved in 2-propanol (12 mL) and stirred at 80 °C for 48 h. The solution was then cooled to rt and the solvent removed under reduced pressure. The crude product was then purified by column chromatography with gradient elution 0-50% DCM in Pet. ether to give the product as a colourless oil (188 mg, 0.98 mmol, 82%); δ_H (300 MHz, $CDCl_3$) 7.97 (2 H, d, *J* 8.0, ArH), 7.59 - 7.53 (1 H, m, ArH), 7.50 - 7.44 (2 H, m, ArH), 3.86 (2 H, t, *J* 6.7, C*H*$_2$OCH), 3.63 (1 H, spt, *J* 6.2, OC*H*$(CH_3)_2$), 3.25 (2 H, t, *J* 6.7, COC*H*$_2$), 1.16 (6 H, d, *J* 6.2, $(CH_3)_2$); δ_c (101 MHz, $CDCl_3$) 198.80, 137.20, 133.21, 128.68, 128.24, 72.05, 63.52, 39.42, 22.18.

New method. NMR matches *S. Guo, S. Xing, S. Mao, Y. Gao, W. Chen, Y. Wang, *Tetrahedron Lett.*, 2014, **55**, 6718 – 6720.



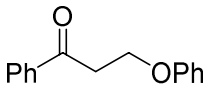
1-Phenylprop-2-en-1-one



Triethylamine (1.69 mL, 12.0 mmol) was added dropwise to a solution of 3-chloropropiophenone (843 mg, 5.00 mmol) in $CHCl_3$ (12 mL). After stirring o/n at rt, the solution was washed with 0.1 M HCl (10 mL), sat. $NaHCO_3$ (10 mL) and water (3 x 10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the product as a clear oil (580 mg, 4.39 mmol, 88%); δ_H (300 MHz, $CDCl_3$) 7.99 - 7.91 (2 H, m, ArH), 7.62 - 7.55 (1 H, m, ArH), 7.53 - 7.44 (2 H, m, ArH), 7.16 (1 H, dd, *J* 17.1, 10.6, COC*H*=CH_2), 6.44 (1 H, dd, *J* 17.1, 1.7, CH=C*H*$_A$H$_B$), 5.94 (1 H, dd, *J* 10.6, 1.7, CH=CH$_A$*H*$_B$)

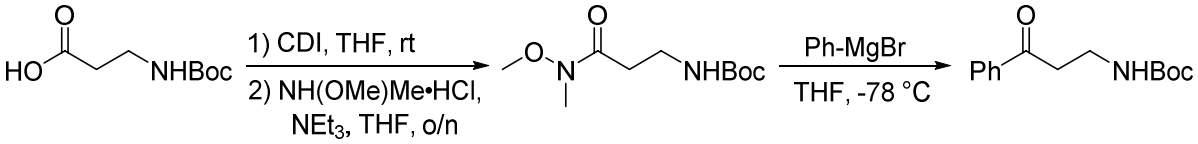
*S. Chanthamath, S. Takaki, K. Shibatomi, S. Iwasa, *Angew. Chem., Int. Ed.*, 2013, **52**, 5818-5821

3-Phenoxy-1-phenylpropan-1-one

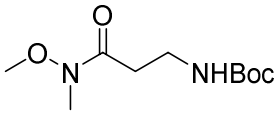


To a stirring solution of 1-phenylprop-2-en-1-one (580 mg, 4.39 mmol) in phenol (413 mg, 4.4 mmol) was added Na_2CO_3 (1.8 mL, 0.05 M aq.). After stirring o/n, water (25 mL) and EtOAc (25 mL) were added and the organic layer extracted. The compound was extracted again from the aqueous extract with EtOAc (2 x 25 mL). Organic extracts were combined, dried over $MgSO_4$, filtered and solvent removed under reduced pressure. The crude product was then purified by column chromatography with gradient elution 0-10% EtOAc in Pet. ether to give the product as a white solid (671 mg, 2.97 mmol, 68%); δ_H (300 MHz, $CDCl_3$) 8.01 (2 H, d, *J* 8.2, ArH), 7.63 - 7.56 (1 H, m, ArH), 7.53 - 7.45 (2 H, m, ArH), 7.33 - 7.26 (2 H, m, ArH), 6.99 – 6.89 (3 H, m, ArH), 4.44 (2 H, t, *J* 6.6, CH_2OPh), 3.48 (2 H, t, *J* 6.65, COCH_2); δ_c (101 MHz, $CDCl_3$) 197.78, 158.75, 136.94, 133.48, 129.60, 128.79, 128.27, 121.04, 114.70, 63.30, 38.30.

*S. Guo, S. Xing, S. Mao, Y. Gao, W. Chen, Y. Wang, *Tetrahedron Lett.*, 2014, **55**, 6718 – 6720

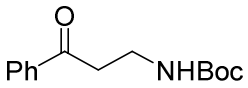


***tert*-Butyl 3-(methoxy(methyl)amino)-3-oxopropylcarbamate.**



To a solution of boc-β-alanine (1.89 g, 10 mmol) in THF (13.5 mL) was added 1,1'-carbonyldiimidazole (1.78 g, 11 mmol) in one portion and stirred at rt for 4 h. Triethylamine (2.23 g, 3.07 mL, 22 mmol) was added to a separate solution containing N,O-dimethylhydroxylamine hydrochloride (1.07 g, 11 mmol) in THF (6 mL) and stirred for 2 h. The Boc-β-alanine containing solution was then added to the second solution. After stirring for 20 h, the mixture was filtered and the solids washed with THF (2 x 7.5 mL). The filtrate was concentrated under reduced pressure and dissolved in DCM (50 mL). The DCM extract washed 0.1 M HCl (20 mL) and water (50 mL). The organic extract was dried over $MgSO_4$, filtered and solvent removed under reduced pressure to give the product as a white solid (2.02 g, 8.70 mmol, 87%); δ_H (400 MHz, $CDCl_3$) 5.22 (1 H, br. s, NH), 3.67 (3 H, s, OCH_3), 3.42 (2 H, d, *J* 5.3, C*H*$_2$NH), 3.18 (3 H, s, NCH_3), 2.64 (2 H, br. s, $COCH_2$), 1.43 (9 H, s, $(CH_3)_3$)
NMR matches, L. Zygalski, C. Middel, K. Harms and U. Koert, Org. Lett. 2018, **20**, 5071-5074.

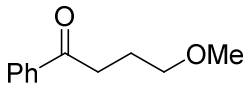
***tert*-Butyl 3-oxo-3-phenylpropylcarbamate**



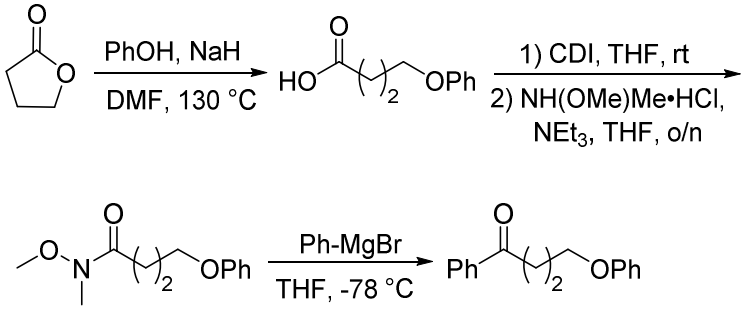
Product from the previous step (2.02 g, 8.70 mmol) was dissolved in dry THF (59 mL) and cooled to -78 °C. Phenylmagnesium bromide (3 M in Et_2O, 6.96 mL, 20.9 mmol) was added dropwise over 30 min to the solution and the mixture was then allowed to warm to rt. After stirring for 2 h, the mixture was cooled to -78 °C and sat. NH_4Cl (100 mL) and EtOAc (100 mL) was added. After warming to rt, the organic extract was collected and the aqueous layer washed with EtOAc (2 x 100 mL). The organic extracts were combined, washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was then purified by column chromatography with gradient elution 0-20% EtOAc in Pet. ether to give product as a white solid (1.585 g, 6.36 mmol, 73%); δ_H (400 MHz, $CDCl_3$) 7.96 (2 H, d, *J* 7.7, ArH), 7.61 - 7.54 (1 H, m, ArH), 7.50 - 7.44 (2 H, m, ArH), 5.14 (1 H, br. s, NH), 3.55

(2 H, d, *J* 5.5, C*H*$_2$NH), 3.25 – 3.16 (2 H, m, COCH$_2$), 1.42 (9 H, s, (CH$_3$)$_3$); δ_c (101 MHz, CDCl$_3$) 199.44, 156.06, 136.70, 133.48, 128.76, 128.11, 79.29, 38.77, 35.55, 28.49.
NMR matches. S. M. Nicolle, W. Lewis, C. J. Hayes and C. J. Moody, *Angew. Chem., Int. Ed.*, 2016, **55**, 3749–3753.

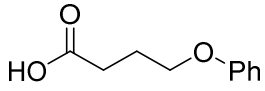
4-Methoxy-1-phenylbutan-1-one



To a solution of cyclopropyl phenyl ketone (1.46 g, 10 mmol) in MeOH (8.5 mL) was added dropwise conc. H_2SO_4 (0.436 mL, 802 mg, 8.18 mmol) and the solution was refluxed. After refluxing for 3 days, 0.1 mL of H_2SO_4 and 2 mL of MeOH was added and refluxed for a further 3 days. The solvent was then removed under reduced pressure and Et_2O (40 mL) and water (60 mL) were then added. The ether layer was separated and the aqueous layer extracted again with Et_2O (2 x 40 mL). The ether layers were combined, washed with sat. $NaHCO_3$ (40 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was then purified by column chromatography with gradient elution 0-5% EtOAc in hexanes to give the product as a clear oil (1.590 g, 8.93 mmol, 89%); δ_H (400 MHz, $CDCl_3$) 7.98 (2 H, d, *J* 7.7, *o*-ArH), 7.60 - 7.52 (1 H, m, *p*-ArH), 7.50 - 7.42 (2 H, m, *m*-ArH) 3.47 (2 H, t, *J* 5.9, C*H*$_2$OCH$_3$), 3.34 (3 H, s, OCH$_3$), 3.08 (2 H, t, *J* 7.2, CH$_2$CO) 2.03 (2 H, quin, *J* 6.5, C*H*$_2$CH$_2$OCH$_3$). δ_c (101 MHz, $CDCl_3$) 200.12, 137.17, 133.10, 128.70, 128.18, 71.92, 58.68, 35.23, 24.29
*W. S. Trahanovsky and N. S. Fox, *J. Am. Chem. Soc.*, 1974, **96**, 7968-7974 (procedure from this, NMR different as CCl_4 referenced). S. Yamaguchi and K. Kabuto, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 3033-3038.



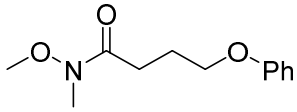
4-Phenoxybutanoic acid



To a suspension of sodium hydride (60% wt, 724 mg, 18.1 mmol) in DMF (18 mL) was added dropwise a solution of phenol (1.69 g, 18.0 mmol) in DMF (9 mL). After stirring for 1h, a solution of γ-butyrolactone (1.50 g, 17.4 mmol) in DMF (9 mL) was added dropwise and the resultant solution was stirred at 130 h for 6.5 h. The solution was cooled to rt and concentrated under reduced pressure. The residue was partitioned between DCM (150 mL) and water (150 mL) and the aqueous layer separated. The organic extract was then washed again with water (2 x 75 mL) and the aqueous extracts were combined and acidified with 1 M HCl (22.5 mL) to a pH of 2. EtOAc (150 mL) was added to the aqueous extract and the organic layer was collected. The aqueous layer was extracted again with EtOAc (2 x 75 mL) and the EtOAc extracts were combined. The EtOAc extract was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography in (0 – 33% EtOAc in hexane) gave the pure product as clear crystals (1.09 g, 6.05 mmol, 35%); δ_H (300 MHz, $CDCl_3$) 7.33 - 7.24 (2 H, m, ArH), 6.99 - 6.85 (3 H, m, ArH), 4.03 (2 H, t, *J* 6.0, C*H*$_2$OPh), 2.60 (2 H, t, *J* 7.2, C*H*$_2$COOH), 2.13 (2 H, quin, *J* 6.6, C*H*$_2$CH$_2$OPh)

Sankyo Company, Limited, EP1471054, **2004**, A1, Location in patent: Page 310-311.

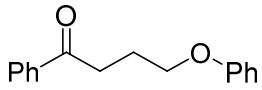
_N_-Methoxy-_N_-methyl-4-phenoxybutanamide



To a solution of 4-phenoxybutanoic acid (1.08 g, 5.99 mmol) in THF (8 mL) was added 1,1'-carbonyldiimidazole (1.07 g, 6.59 mmol) in one portion and stirred at rt for 2 h. Triethylamine (1.46 g, 2.02 mL, 14.5 mmol) was added to a separate solution containing N,O-dimethylhydroxylamine hydrochloride (643 mg, 6.59 mmol) in THF (3.5 mL) and stirred for 2 h. The acid containing solution was then added to the second solution and stirred at rt for 20 h. The solvent was removed under reduce pressure and re-dissolved in DCM (50 mL). The DCM extract was washed with 1 M HCl (15 mL) and water (20 mL). The organic extract was dried over $MgSO_4$, filtered and solvent removed under reduced pressure to give the product as a white solid (1.28 g, 5.72 mmol, 95%); δ_H (300 MHz, $CDCl_3$) 7.34 - 7.20 (2 H, m, ArH), 6.98 - 6.84 (3 H, m, ArH), 4.03 (2 H, t, *J* 6.0 CH_2OPh), 3.68 (3 H, s, OCH_3), 3.19 (3 H, s, NCH_3), 2.65 (2 H, t, *J* 7.1, CH_2CO), 2.13 (2 H, quin, *J* 6.6, C*H*$_2$CH$_2$OPh)

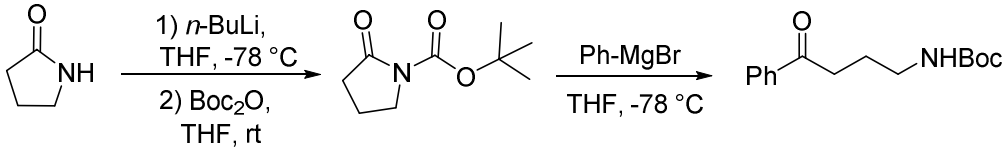
Weinreb amide has previously been made via another route but NMR similar to reference (+0.12 ppm difference) *N. Satyamurthi, J. Singh, I. Singh Aidhen, *Synthesis*, 2000, **3**, 375 – 382

4-Phenoxy-1-phenylbutan-1-one

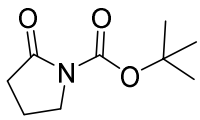


Weinreb amide from the previous step (1.28 g, 5.72 mmol) was dissolved in dry THF (33 mL) and cooled to -78 °C. Phenylmagnesium bromide (3 M in Et_2O, 2.00 mL, 6.00 mmol) was added dropwise over 30 min to the solution and the mixture was then allowed to warm to rt. After stirring for 2 h, the mixture was cooled to -78 °C and sat. NH_4Cl (30 mL) and EtOAc (50 mL) was added. After warming to rt, the organic extract was collected and the aqueous layer washed with EtOAc (2 x 50 mL). The organic extracts were combined, washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was then purified by column chromatography with gradient elution 0-15% EtOAc in Pet. ether to give product xx as a white solid (1.248 g, 5.20 mmol, 91%); δ_H (300 MHz, $CDCl_3$) 7.99 (2 H, d, *J* 8.0, ArH), 7.61 - 7.52 (1 H, m, ArH), 7.51 - 7.41 (2 H, m, ArH), 7.34 - 7.26 (2 H, m, ArH), 7.00 - 6.85 (3 H, m, ArH), 4.08 (2 H, t, J 6.0, $COCH_2$), 3.22 (2 H, t, J 7.0, CH_2OPh), 2.25 (2 H, quin, J 6.6, CH_2CH_2OPh); δ_c (101 MHz, $CDCl_3$) 199.72, 158.98, 137.05, 133.17, 129.57, 128.71, 128.15, 120.81, 114.60, 66.92, 35.07, 23.94; MS (ESI^+): m/z 263.2 $[M+Na^+]^+$, $C_{16}H_{16}NaO_2$ requires 263.1043 found 263.1040 error 0.9 ppm

New route to this compound. *NMR matches P. J. Wagner and H. W. Frerking, *Canadian Journal of Chemistry*, 1995, **73**, 2047-2061



***tert*-Butyl 2-oxopyrrolidine-1-carboxylate**

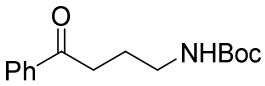


Both products from G. D. Williams, R. A. Pike, C. E. Wade, M. Wills, *Org. Lett.*, 2003, ***5*** (22), 4227–4230.

A solution of 2-pyrrolidinone (851 mg, 10 mmol) in dry THF (20 mL) was cooled to -78 °C. *n*-BuLi (2.5 M in hexanes, 4.8 mL, 12 mmol) was added dropwise to the solution and stirred

at -78 °C for 1 h. A solution of di-*tert*-butyl dicarbonate (2.40 g, 11 mmol) in dry THF (2.5 mL) was added dropwise to the pyrrolidinone containing solution and left to stir for 2 h. The solution was warmed to rt and sat. NH_4Cl (10 mL) and water (10 mL) were added. The organic layer was collected and extracted again with Et_2O (3 x 10 mL). Organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by column chromatography in (20 – 30% EtOAc in Pet. Ether) gave the pure product (1.24 g, 6.70 mmol, 67%); δ_H (300 MHz, $CDCl_3$) 3.74 (2 H, t, *J* 7.2, CH_2NBoc), 2.51 (2 H, t, *J* 8.1, $COCH_2$), 1.99 (2 H, t, *J* 7.5, CH_2CH_2N), 1.53 (9 H, s, $(CH_3)_3$); δ_c (101 MHz, $CDCl_3$) 174.39, 150.33, 82.84, 46.56, 33.05, 28.12, 17.50

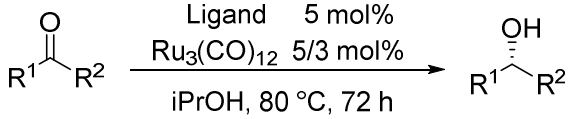
***tert*-Butyl (4-oxo-4-phenylbutyl)carbamate**



A solution of lactam from the previous step (1.24 g, 6.70 mmol) in dry THF (26 mL) was cooled to -78 °C. Phenylmagnesium bromide (3 M in Et_2O, 2.35 mL, 7.05 mmol) was added dropwise over 1 h to the solution and the mixture was then allowed to warm to rt. 2 M HCl was added until the solution reached pH 2 and the mixture was extracted with DCM (3 x 40 mL). Organic extracts were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. Purification by recrystallization in hot Pet. Ether gave the product as yellow crystals (1.16 g, 4.41 mmol, 66%); δ_H (300 MHz, $CDCl_3$) 7.96 (2 H, d, *J* 7.9, ArH), 7.56 (1 H, m, ArH), 7.51 - 7.41 (2 H, m, ArH), 4.64 (1 H, Br. s, NH), 3.29 - 3.16 (2 H, m, CH_2NH), 3.03 (2 H, t, *J* 7.1, $COCH_2$), 1.95 (2 H, quin, *J* 7.1, $CH_2CH_2CH_2$), 1.42 (9 H, s, $(CH_3)_3$); δ_c (101 MHz, $CDCl_3$) δ 199.87, 156.18, 136.93, 133.19, 128.70, 128.14, 79.24, 40.24, 35.84, 28.48, 24.62.

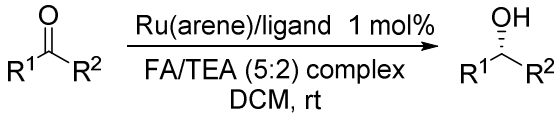
Both products from G. D. Williams, R. A. Pike, C. E. Wade, M. Wills, *Org. Lett.*, 2003, **5**, 4227–4230.

Tridentate ligand reductions (Method A)



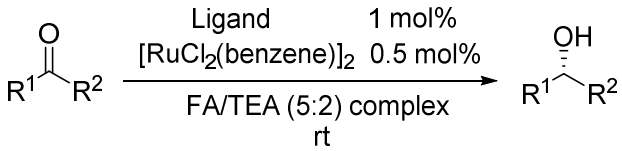
A mixture of ligand (5 mol%) and $Ru_3(CO)_{12}$ (5/3 mol%) in *i*PrOH (10 mL) was stirred at 80 °C under an inert atmosphere for 30 min in a Schlenk tube. Ketone (1 mmol) was then added to the solution and the resulting mixture was stirred at 80 °C for 72 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (0 – 50% EtOAc in Pet. Ether). Enantiomeric excess was determined by GC or chiral HPLC.

Ru(arene)/ligand reductions (Method B)



Catalyst (1 mol%) in FA/TEA 5:2 complex (0.5 mL) was stirred under an inert atmosphere at rt for 15 min. The ketone (1 mmol) in DCM (0.5 mL) was then added to the mixture and stirred at rt. Sat. $NaHCO_3$ (10 mL) was added and the product extracted with EtOAC (10 mL). The aqueous layer was further extracted with EtOAc (2 x 10 mL). Organic fractions were then combined, dried over $MgSO_4$, filtered and the solvent removed under pressure. The crude products were purified by column chromatography (0 – 50% EtOAc in Pet. Ether). Enantiomeric excess was determined by chiral GC or HPLC.

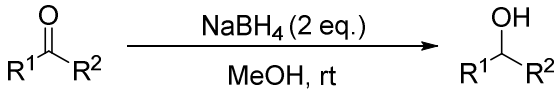
***In situ* procedure (Method C)**



To a Schlenk tube charged with $[RuCl_2(Benzene)]_2$ (2.50 mg, 0.5 mmol) and ligand (1 mmol) was added formic acid/triethylamine 5:2 complex (0.5 mL). After stirring for 30 min, the ketone (1 mmol) was added and left to stir. Upon completion, $NaHCO_3$ (10 ml) was added and the product was extracted with EtOAC (3 x 10 mL). The organic extracts were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude products

were purified by column chromatography (0 – 50% EtOAc in Pet. Ether). Enantiomeric excess was determined by chiral GC or HPLC.

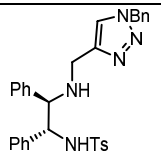
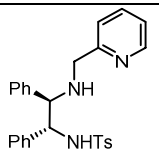
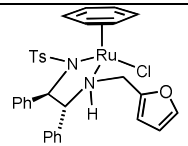
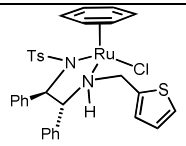
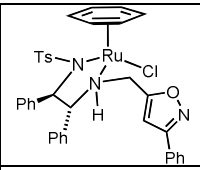
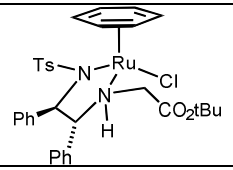
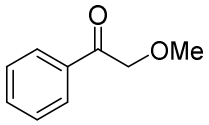
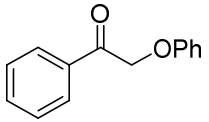
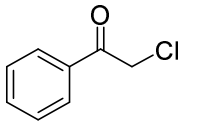
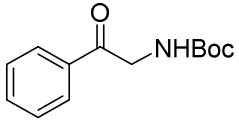
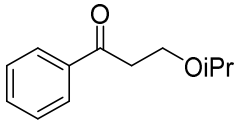
Racemic alcohols procedure.



To a solution of ketone (1 eq.) in MeOH (0.1 M) was added $NaBH_4$ (2 eq.) portion-wise. The solution was stirred at rt until the ketone had consumed. The solvent was then removed under reduced pressure and the residue partitioned between water and EtOAc. The organic extract was collected and the aqueous layer extracted a further 2 times with EtOAc. Organic layers were combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. Products were purified by column chromatography gradient elution 0-40% EtOAc in Pet. ether.

Tables of reduction results.

Table S1: Screening of reductions of substrates to give products 24-35.

						
	Ligand **4**	Ligand **5**	Complex of **6**	Complex of **7**	Complex of **8**	Complex of **9**
Method	**Method A**	**Method A**	**Method B**	**Method B**	**Method B**	**Method B**
Substrate						
	No reduction	No reduction	5 d 84%Y, 94% ee	5 d 41%Y, 91% ee	6 d 74%Y, 92% ee	7 d 79%Y, 91% ee 82% conv
	72h 94%Y, 81%ee Full conv	72h 96% Y , 53% ee Full conv	72h 71%Y, 92%ee Full conv	120h 89%, 94%ee 98% conv	96h 91%, 90%ee Full conv- TLC	6 d 97%Y, 92% ee Full conv
	No reduction (inhibits)	No reduction (inhibits)	96 h 91%Y, 90% ee 99% conv	96 h, 79%Y, 89% ee Full conv-TLC	96 h, 87%Y, 91% ee 99% conv	7 d 86%Y, 91% ee 94% conv
	72h 99%Y, 97%ee Full conv	72h 92%Y, 94%ee Full conv	120h, 94%Y, 97% ee Full conv	120h, 95%Y, 96% ee Full conv	120h, 95%Y, 93% ee Full conv	7 d 91%Y, 95% ee 98% conv
	72h 95%Y, 99% ee Full conv	72h 96%Y, 99% ee Full conv	120h 70%Y, 89% ee 80% conv	132h 45%Y, 92%ee 52% conv	120h 74%Y, 94% ee 87% conv	7 d 41%Y, 96% ee 55% conv

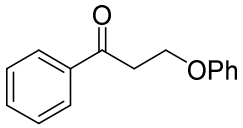
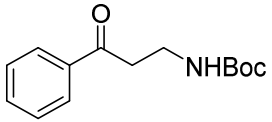
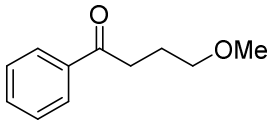
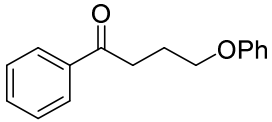
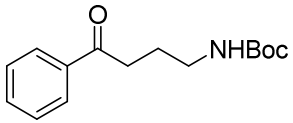
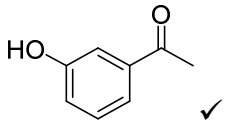
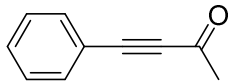
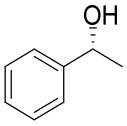
	72h 98%Y, 86%ee Full conv	72h 96%Y, 90%ee Full conv	120h 94%Y, 91%ee 98% conv	120h 41%Y, 87%ee 50% conv	6d 93%Y, 91% ee Full conv	7 d 70%Y, 90% ee 72% conv
	72h 95%Y, 92%ee	72h 88%Y, 91%ee	120h 88%Y, 91%ee 95% conv	120h 41%Y, 91%ee 52% conv	144h 84%Y, 92%ee 85% conv	6 d 92%Y, 96% ee 96% conv
	72h 91%Y, 83%ee 99% conv	72h 89%Y, 89%ee 95% conv	144h 70%Y, 88%ee 89% conv	144h 49%Y, 84%ee 55% conv	168h 57%Y, 90%ee 66% conv	7 d 66%Y, 92% ee 71% conv
	72 h, 98%Y, 90% ee Full conv	72 h, 98%Y, 90% ee Full conv	72 h 93%Y, 90%ee 93% conv	7 d, 61%Y, 87%ee	6 d, 96%Y, 89%ee Full conv	7 d, 48%Y, 93%ee 50% conv
	72h 99%y, 92%ee Full conv	72h 92%y, 91%ee Full conv	80h 92%Y, 93 %ee Full conv	144h 45%Y, 88 %ee 55% conv	144h 73% Y, 76%%ee 77% conv	7 d 45%Y, 90% ee 50% conv
	48h 98%c, 94%ee	48h 99%c, 88%ee	96h 81%Y, 93%ee Full conv	144h 74%Y, 92%ee 94% conv	144h 86%Y, 93%ee 94% conv	4 d 87%Y, 90% ee 99% conv
	No reduction	No reduction	4 d 80%Y, 86%ee	5 d 57%Y, 89%ee	5 d 65%Y, 86%ee	5 d 45%Y, 84% ee 56% conv

Table S2.* Application of *in situ*-formed catalysts to ATH of a range of substituted ketones (*in situ* procedure). Conditions; 1 mol% ligand 6-9/0.5 mol% $[(benzene)RuCl_2]_2$, 5:2 FA:TEA, DCM, [S] = 1M, rt.

Reduction	Time/h	Conv/%	ee /%	*R/S*
36/ Furan **6**	47	99.8	87	*R*
36/ Thio **7**	94	99	87	*R*
36/ Isox **8**	156	99	89	*R*
36/ Ester **9**	96	99	90	*R*
37/ Furan **6**	72	99	57	*R*
37/ Thio **7**	165	99	57	*R*
37/ Isox **8**	185	80	66	*R*
37/ Ester **9**	96	98	61	*R*
38/ Furan **6**	184	91	87	*R*
38/ Thio **7**	200	70	87	*R*
38/ Isox **8**	190	63	87	*R*
38/ Ester **9**	96	51	87	*R*
39/ Furan **6**	164	90	65	*R*
39/ Thio **7**	166	87	66	*R*
39/ Isox **8**	166	63	63	*R*
39/ Ester **9**	164	97	68	*R*
40/ Furan **6**	72	99.6	99	*R*
40/ Thio **7**	96	95	99	*R*
40/ Isox **8**	96	96	99	*R*
40/ Ester **9**	70	99	99	*R*
41/ Furan **6**	96	97	94	*R*
41/ Thio **7**	168	99	93	*R*
41/ Isox **8**	168	99	95	*R*
41/ Ester **9**	72	99	96	*R*

* Acetylcyclohexane was also reduced with the following results: Furan **6**; 144h, 92% conv. 53% ee, Thio **7**; 144h, 75% conv. 35% ee, Isox **8**; 144h, 70% conv. 36% ee, Ester **9** 120h, 98% conv. 48% ee. The product was formed in S configuration in each case.

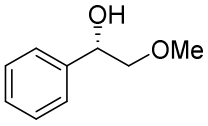
Reduction products



(*R*)-1-Phenylethan-1-ol

Acetophenone (60 mg, 0.50 mmol) and catalyst **17** (3.3 mg, 5.00 μmol) were reacted following method B to give (*R*)-1-phenylethanol as a colourless oil (46 mg, 0.38 mmol, 75%); δ_H (300 MHz, $CDCl_3$) 7.42 - 7.32 (4 H, m, ArH), 7.32 - 7.27 (1 H, m, ArH), 4.90 (1 H, q, *J* 6.4, C*H*OH), 1.94 (1 H, br. s, OH), 1.50 (3 H, d, *J* 6.4, CH_3); δ_C (101 MHz, $CDCl_3$) 145.94, 128.63, 127.60, 125.51, 70.54, 25.28; $[\alpha]^{28}$ +54.3 (*c* 0.25 in $CHCl_3$) 94% ee (*R*), GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 110 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 9.82 min., *R* isomer 15.51 min., *S* isomer 16.50 min.)

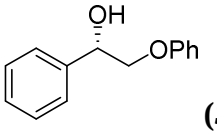
Ref: $[\alpha]^{28}$: +58.1 (0.73 c in CH_2Cl_2) – 96.3% ee (*R*) – R. Soni, K. E. Jolley, G. J. Clarkson, and M. Wills, *Org. Lett.*, 2013, **15**, 5110-5113. NMR in agreement



(*S*)-2-Methoxy-1-phenylethan-1-ol (24)

α-Methoxyacetophenone (50 mg, 0.33 mmol) and ligand **8** (2.4 mg, 3.3 μmol) were reacted following method C to give product **24** as a clear oil (37 mg, 0.24 mmol, 74%); δ_H (300 MHz, $CDCl_3$) 7.42 - 7.30 (5 H, m, ArH), 4.90 (1 H, dd, *J* 8.85, 3.20, C*H*OH), 3.59 - 3.52 (1 H, m, C$H_A$$H_B$OMe), 3.48 - 3.42 (4 H, m, CH_AH_BOMe + OCH_3), 2.73 (1H, br. s, OH); δ_C (101 MHz, $CDCl_3$) 140.36, 128.53, 127.97, 126.26, 78.30, 72.76, 59.14; $[\alpha]_D^{22}$ +45.6 (*c* 0.2 in $CHCl_3$) 92% ee (*S*); HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 254 nm, ketone 12.28 min., *S* isomer 11.55 min., *R* isomer 13.15 min.). The racemic peaks were not quite baseline separated however the resolution for the asymmetric compound was.

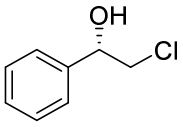
Ref: $[\alpha]_D^{20}$ +33.8 (c 1.3, CH_2Cl_2) 81% ee (*S*) – S. Wei, R. Messerer, S. B. Tsogoeva, *Chem. - Eur. J.*, 2011, **17**, 14380-14384. NMR in agreement



(*S*)-2-Phenoxy-1-phenylethan-1-ol (25)

α-Phenoxyacetophenone (106 mg, 0.50 mmol) and ligand **4** (13.4 mg, 0.025 mmol) were reacted following method A to give product **25** as an off-white solid (101 mg, 0.47 mmol, 94%); δ_H (300 MHz, $CDCl_3$) 7.50 - 7.43 (2 H, m, ArH), 7.40 (2 H, t, J 7.3, ArH), 7.36 - 7.26 (3 H, m, ArH), 7.02 – 6.88 (3 H, m, ArH), 5.13 (1 H, d, *J* 9.0, C*H*OH), 4.16 - 4.07 (1 H, m, C$H_A$$H_B$OPh), 4.06 - 3.96 (1 H, m, C$H_A$$H_B$OPh), 2.76 (1 H, d, *J* 2.2, OH); δ_C (101 MHz, $CDCl_3$) 158.50, 139.77, 129.69, 128.70, 128.31, 126.41, 121.44, 114.77, 73.42, 72.71; $[\alpha]_D^{29}$ +50.4 (*c* 0.2 in $CHCl_3$) 81% ee (*S*), HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 93:7, 1 mL/min, 254 nm, ketone 22.26 min., *S* isomer 35.91 min., *R* isomer 19.84 min.)

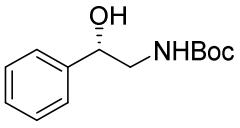
Ref: $[\alpha]_D$ = +56.6 (c = 0.35, $CHCl_3$), 93% ee (*S*) - R. Soni, K. E. Jolley, S. Gosiewska, G. J. Clarkson, Z. Fang, T. H. Hall, B. N. Treloar, R. C. Knighton, and M Wills, *Organometallics*, 2018, **37**, 48-64. NMR in agreement



(*S*)-2-Chloro-1-phenylethan-1-ol (26)

α-Chloroacetophenone (106 mg, 0.33 mmol) and catalyst **19** (2.4 mg, 3.3 µmol) were reacted following method B to give product **26** as a clear oil (45 mg, 0.29 mmol, 87%); δ_H (300 MHz, $CDCl_3$) 7.37(5H, m, ArH), 4.93 (1H, dt, *J* 8.7, 3.3, C*H*OH), 3.77 (1H, dd, *J* 11.2, 8.7, C$H_A$$H_B$Cl), 3.67 (1H, dd, *J* 11.2, 8.3, C$H_A$$H_B$Cl), 2.64 (1H, d, *J* 3.3, CHO*H*); δ_C (101 MHz, $CDCl_3$) 140.03, 128.81, 128.60, 126.18, 74.20, 51.05; $[\alpha]_D^{29}$ +56.3 (*c* 0.2 in $CHCl_3$) 91% ee (*S*); GC analysis (CP-CHIRALSIL-DEX-CB, 25 m x 0.25 mm x 0.25 µm, gas H_2, T = 140 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 1.70 min., *R* isomer 7.91 min., *S* isomer 7.36 min.).

Ref: $[\alpha]^{32}$: +61.8 (0.81 c in $CHCl_3$) – 96.8% ee (*S*) - Rina Soni, Katherine E. Jolley, Guy J. Clarkson, and Martin Wills, *Org. Lett.*, 2013, **15**, 5110-5113. NMR in agreement

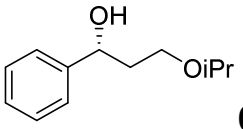


***tert*-Butyl (*S*)-(2-hydroxy-2-phenylethyl)carbamate (27)**

tert-Butyl (2-oxo-2-phenylethyl)carbamate (78 mg, 0.33 mmol) and catalyst **19** (2.4 mg, 3.3 µmol) were reacted following method B to give product **27** as an off-white solid (75 mg, 0.32 mmol, 95%); δ_H (300 MHz, $CDCl_3$) ppm 7.43 - 7.30 (5 H, m, ArH), 4.98 (1 H, Br. s, NH), 4.84 (1 H, d, *J* 3.2, CHOH), 3.54 - 3.46 (1 H, Br. m, C$H_A$$H_B$NH,) 3.32 - 3.23 (1 H, m, C$H_A$$H_B$NH),

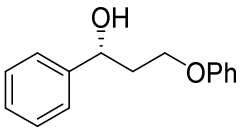
3.14 (1 H, br. s, OH), 1.47 (9 H, s, $(CH_3)_3$); δ_c (101 MHz, $CDCl_3$) 157.14, 141.96, 128.61, 127.90, 126.01, 79.96, 74.06, 48.47, 28.48; $[\alpha]_D^{29}$ +52.5 (*c* 0.2 in $CHCl_3$) 93% ee (*S*); HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 254 nm, ketone 11.70 min., *S* isomer 11.85 min., *R* isomer 13.98 min.)

$[\alpha]_D^{25}$ +45.1 (c 0.6, $CHCl_3$), ee 93 % (*S*) - A. Russo and A. Lattanzi, *Adv. Synth. Catal.*, 2008, **350**, 1991-1995. NMR in agreement. Reference also uses OD-H column (different conditions) where major (i.e. *S*) comes after *R* isomer in chromatogram



(*R*)-3-Isopropoxy-1-phenylpropan-1-ol (28)

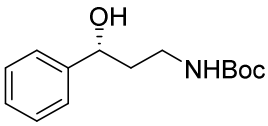
3-Isopropoxy-1-phenylpropan-1-one (64 mg, 0.33 mmol) and catalyst **19** (2.4 mg, 3.3 µmol) were reacted following method B to give product **28** as a colourless oil (48 mg, 0.25 mmol, 74%); ν_{max} 3414, 3062, 3030, 2971, 2926, 2868, 1493, 1453, 1421, 1380 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.39 - 7.31 (4 H, m, ArH), 7.28 - 7.22 (1 H, m), 4.97 - 4.90 (1 H, m, C*H*OH), 3.81 (1 H, d, *J* 2.8, OH), 3.67 - 3.53 (3 H, m, CH_2OCH), 2.06 - 1.92 (2 H, m, CHOHCH_2), 1.21 (3 H, d, *J* 4.4), 1.18 (3 H, d, *J* 4.4); δ_c (101 MHz, $CDCl_3$) 144.64, 128.41, 127.27, 125.82, 74.30, 72.38, 67.01, 38.81, 22.22, 22.13; MS (ESI^+): *m*/*z* 217.2 $[M+Na]^+$; HRMS calcd. for $C_{12}H_{18}NaO_2$ $[M+Na]^+$ 217.1199, found 217.1197 (error 0.9 ppm); $[\alpha]_D^{25}$ +51.66 (*c* 0.05 in $CHCl_3$) 94% ee (*R*); HPLC analysis (CHIRALPAK IA, 250 × 4.6 mm column, hexane/2-propanol 96:4, 0.7mL/min, 254 nm, ketone 7.79 min., *S* isomer 7.60 min., *R* isomer 10.38 min.) D. A. Gandamana, B. Wang, C. Tejo, B. Bolte, F. Gagosz, S. Chiba, *Angew. Chem. Int. Ed.*, **57**, 2018, 6181-6185 (reported recently for racemic without IR) No optical data available



(*R*)-3-Phenoxy-1-phenylpropan-1-ol (29)

3-Phenoxy-1-phenylpropan-1-one (75 mg, 0.33 mmol) and catalyst **19** (2.2 mg, 3.3 µmol) were reacted following method B to give product **29** as a white solid (68 mg, 0.30 mmol, 89%); ν_{max} 3441, 3030, 2949, 2927, 2886, 1599, 1588, 1493, 1476, 1466, 1454 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.43 - 7.34 (4 H, m, ArH), 7.30 (3 H, t, *J* 7.40, ArH) 6.97 (1 H, t, *J* 7.4, ArH), 6.92 (2 H, d, *J* 7.9, ArH), 5.06 – 4.99 (1 H, m, CHOH), 4.22 - 4.15 (1 H, m, CH_AH_BOPh), 4.09 - 4.03 (1 H, m, CH_AH_BOPh), 2.52 (1 H, br. s, OH), 2.32 - 2.14 (2 H, m, CHOHCH_2); δ_c (101 MHz, $CDCl_3$) 158.78, 144.30, 129.63, 128.67, 127.76, 125.91, 121.09, 114.69, 72.32, 65.49, 38.54;

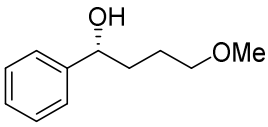
MS (ESI$^+$): *m*/*z* 251.2 [M+Na]$^+$; HRMS calcd. for $C_{15}H_{16}NaO_2$ [M+Na]$^+$ 251.1043, found 251.1041 (error 0.7 ppm); $[\alpha]_D^{25}$ +8.5 (*c* 0.2 in $CHCl_3$) 91% ee (*R*); HPLC analysis (CHIRALCEL OD-H, 250 × 4.6 mm column, hexane/2-propanol 95:5, 0.8 mL/min, 254 nm, ketone 16.72 min., *S* isomer 24.24 min., *R* isomer 22.48 min.). The racemic peaks were not baseline separated however the resolution for the asymmetric compound was almost complete. Known but not fully characterised- No optical data available.



***tert*-Butyl (*R*)-(3-hydroxy-3-phenylpropyl)carbamate (30)**

tert-Butyl (3-oxo-3-phenylpropyl)carbamate (83 mg, 0.33 mmol) and catalyst **19** (2.4 mg, 3.3 µmol) were reacted following method B to give product **30** as a white solid (70 mg, 0.28 mmol, 84%); δ_H (400 MHz, $CDCl_3$) 7.40 - 7.28 (5 H, m, ArH), 4.88 (1 H, br s, NH), 4.75 (1 H, br. s. CHOH), 3.60 - 3.42 (1 H, m, CHOH), 3.24 - 3.08 (2 H, m, C*H*$_2$NH), 1.86 (2 H, d, *J* 5.6 Hz), 1.46 (9 H, s); δ_c (101 MHz, $CDCl_3$) 157.02, 144.41, 128.57, 127.51, 125.77, 79.69, 71.82, 39.76, 37.70, 28.52; $[\alpha]_D^{27}$ +11.3 (*c* 0.3 in $CHCl_3$) 92% ee (*R*); HPLC analysis (CHIRALCEL OD-H, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 254 nm, ketone 9.70 min., *S* isomer 21.82 min., *R* isomer 13.64 min.)

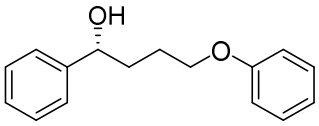
$[\alpha]_D^{20}$ -18.9 (c = 0.4, $CHCl_3$) 98%ee – G. Facchetti, R. Gandolfi, M. Fuse, D. Zerla, E. Cesarotti, M. Pellizzoni and I. Rimoldi, *New J. Chem.*, 2015, **39**, 3792—3800. NMR in agreement



(*R*)-4-Methoxy-1-phenylbutan-1-ol (31)

4-Methoxy-1-phenylbutan-1-one (90 mg, 0.50 mmol) and catalyst **17** (3.2 mg, 5.00 µmol) were reacted following method B to give product **31** as a clear oil (63 mg, 0.35 mmol, 70%); δ_H (400 MHz, $CDCl_3$) 7.40 - 7.30 (4 H, m, ArH), 7.29 - 7.22 (1 H, m, ArH), 4.70 (1 H, br. s, C*H*OH), 3.42 (2 H, t, *J* 5.5, C*H*$_2$OCH$_3$), 3.35 (3 H, s, OCH$_3$), 2.83 (1 H, br. s., OH), 1.91 - 1.80 (2 H, m, C*H*$_2$CHOH), 1.79 - 1.61 (2 H, m, C*H*$_2$CH$_2$OCH$_3$); δ_c (101 MHz, $CDCl_3$) 144.97, 128.50, 127.46, 125.95, 74.29, 72.98, 58.75, 36.80, 26.38; $[\alpha]_D^{25}$ +53.3 (*c* 0.1 in $CHCl_3$) 88% ee (*R*); HPLC analysis (CHIRALPAK IC, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 210 nm, ketone 12.18 min., *S* isomer 16.18 min., *R* isomer 18.51 min.)

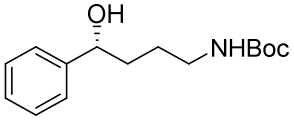
Ref: $[\alpha]_D$ +44.6 (c 0.82, cyclopentane) 84% ee (R) – J. A. Kenny, M. J. Palmer, A. R. C. Smith, T. Walsgrove, M. Wills, Synlett, 1999, 1615–1617. NMR in agreement.



(*R*)-4-phenoxy-1-phenylbutan-1-ol (32)

4-Phenoxy-1-phenylbutan-1-one (120 mg, 0.50 mmol) and catalyst **17** (3.2 mg, 5.00 µmol) were reacted following method B to give product **32** as a clear oil (113 mg, 0.47 mmol, 93%); ν_{max} 3322, 3062, 3030, 2948, 2872, 1599, 1586, 1494, 1472, 1453 cm^{-1}, δ_H (400 MHz, $CDCl_3$) 7.39 – 7.33 (4 H, m, ArH), 7.31 - 7.27 (2 H, m, ArH), 6.94 (1 H, t, *J* 7.5, ArH), 6.89 (2 H, d, *J* 7.5, ArH), 4.78 (1 H, br. s, C*H*OH), 3.99 (2 H, d, *J* 5.4, CH_2OPh), 2.08 (1 H, br. s, OH), 2.00 – 1.80 (4 H, m, CH_2CH_2CH_2O); δ_c (101 MHz, $CDCl_3$) 159.01, 144.69, 129.57, 128.64, 127.74, 126.01, 120.81, 114.63, 74.37, 67.81, 35.89, 25.86; MS (ESI^+): *m*/*z* 265.2 $[M+Na]^+$; HRMS calcd. for $C_{16}H_{18}NaO_2$ $[M+Na]^+$ 265.1199, found 265.1195 (error 1.4 ppm); $[\alpha]_D^{28}$ +35.5 (*c* 0.3 in $CHCl_3$) 90% ee (*R*); HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 90:10, 1 mL/min, 254 nm, ketone 13.83 min., *S* isomer 19.90 min., *R* isomer 28.85 min.)

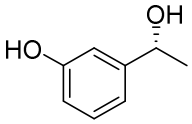
No Data available (Oil so no M.p.)



***tert*-Butyl (*R*)-(4-hydroxy-4-phenylbutyl)carbamate (33)**

tert-Butyl (4-oxo-4-phenylbutyl)carbamate (100 mg, 0.38 mmol) and catalyst **17** (2.5 mg, 3.79 µmol) were reacted following method B to give product **33** as an off-white solid (93 mg, 0.35 mmol, 92%); δ_H (300 MHz, $CDCl_3$) 7.37 - 7.32 (4 H, m, ArH), 7.30 - 7.23 (1 H, m) 4.76 - 4.68 (1 H, m, C*H*OH), 4.54 (1 H, br. s, NH), 3.16 (2 H, d, *J* 6.9, CH_2NH), 2.06 (1 H, br. s., OH) 1.86 - 1.67 (2 H, m, CH_2CHOH), 1.66 - 1.49 (2 H, m, CH_2CH_2NH, overlap H_2O peak), 1.43 (9 H, s, $(CH_3)_3$); δ_c (101 MHz, $CDCl_3$) 156.23, 144.83, 128.60, 127.68, 125.93, 79.28, 74.28, 40.43, 36.15, 28.54, 26.62; $[\alpha]_D^{29}$: +27.6 (*c* 0.2 in $CHCl_3$) 93% ee (*R*); HPLC analysis (CHIRALPAK IA, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 254 nm, ketone 13.86 min., *S* isomer 20.93 min., *R* isomer 26.52 min.)

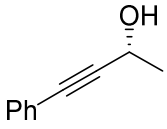
Data in accordance with racemic alcohol; Y. Okamoto, V. Köhler, T. R. Ward, *J. Am. Chem. Soc.* 2016, **138**, 5781-5784. No record of asymmetric alcohol.



(*R*)-3-(1-hydroxyethyl)phenol (34)

3'-Methoxyacetophenone (68 mg, 0.50 mmol) and catalyst **17** (3.3 mg, 5.00 µmol) were reacted following method B to give product **34** as a white solid (56 mg, 0.81 mmol, 81%); δ_H (300 MHz, DMSO-d_6) 9.22 (1 H, s, ArOH), 7.07 (1 H, t, *J* 7.8, ArH) 6.78 - 6.68 (2 H, m, ArH), 6.58 (1 H, d, *J* 8.0, ArH), 5.03 (1 H, d, *J* 3.2, CHO*H*), 4.61 (1 H, t, *J* 5.5, C*H*OH) 1.27 (3 H, d, *J* 6.2, CH_3); δ_C (101 MHz, DMSO-d_6) 157.17, 149.04, 128.89, 115.97, 113.38, 112.19, 68.04, 25.96; $[\alpha]_D^{25}$ +32.5 (*c* 0.1 in MeOH) 93% ee (*R*), HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 93:7, 0.9 mL/min, 220 nm, ketone 11.70 min., *S* isomer 27.94 min., *R* isomer 23.23 min.)

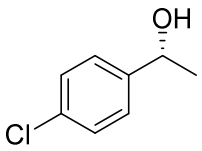
Ref: $[\alpha]^{32}$ +32.0 (*c* 1.00 in MeOH) – 99% ee (*R*) - Fábio D.Nasário, Tarcila Cazetta, Paulo J.S.Moran, J. Augusto R. Rodrigues, *Tetrahedron: Asymmetry*, 2016, **27**, 404-409. NMR in agreement.



(*R*)-4-phenylbut-3-yn-2-ol (35)

4-Phenylbut-3-yn-2-one (72 mg, 0.50 mmol) and catalyst **20** (3.5 mg, 5.00 µmol) were reacted following method B to give product **35** as a clear oil (33 mg, 0.23 mmol, 45%); δ_H (400 MHz, $CDCl_3$) 7.49 - 7.28 (5 H, m, ArH), 4.76 (1 H, d, *J* 6.0, C*H*OH), 1.92 (1 H, br. s, OH), 1.56 (3 H, d, *J* 6.0, CH_3); δ_c (101 MHz, $CDCl_3$) 131.78, 128.50, 128.40, 122.72, 91.10, 84.13, 58.97, 24.51; $[\alpha]_D^{29}$ +25.4 (*c* 0.2 in $CHCl_3$) 84% ee (*R*)**;** HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 90:10, 1 mL/min, 220 nm, Ketone: 6.59 min, *S* isomer: 19.32 min, *R* isomer: 8.12 min)

$[\alpha]^{20}$: +43.8 (1.0 c in Et_2O) 96% ee – Y.-M. Zhang, M.-L. Yuan, W.-P. Liu, J.-H. Xie, *Org. Lett.*, 2018, **20**, 4486-4489. NMR in agreement, HPLC uses same column (different conditions) major peak first (*R*) same.

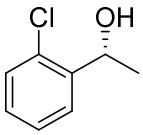


(*R*)-1-(4-Chlorophenyl)ethan-1-ol (36)

4'-Chloroacetophenone (154 mg, 1.00 mmol) and ligand **6** (4.5 mg, 0.01 mmol) were reacted following method C to give product **36** as a yellow oil (140 mg, 0.90 mmol, 90%); δ_H (300

MHz, $CDCl_3$) 7.34 – 7.29 (4 H, m, ArH), 4.93 – 4.84 (1 H, m, C*H*OH), 1.87 1.80 (1 H, br. m, OH), 1.48 (3 H, d, *J* 6.4, CH_3); δ_C (101 MHz, $CDCl_3$) 144.37, 133.19, 128.72, 126.92, 69.86, 25.38; $[\alpha]^{26}$+37.8 (*c* 0.2 in $CHCl_3$) 87% ee (*R*), GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 125 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 14.82 min., *R* isomer 27.56 min., *S* isomer 29.77 min.)

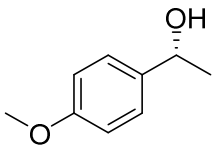
Ref: [α] +51.7 (*c* 0.23 in $CHCl_3$) 94% ee (*R*) – R. Soni, K. E. Jolley, S. Gosiewska, G. J. Clarkson, Z. Fang, T. H. Hall, B. N. Treloar, R. C. Knighton, and M Wills, *Organometallics*, 2018, **37**, 48-64. NMR in agreement



(*R*)-1-(2-Chlorophenyl)ethan-1-ol (37)

2'-Chloroacetophenone (154 mg, 1.00 mmol) and ligand **6** (4.5 mg, 0.01 mmol) were reacted following method C to give product **37** as a yellow oil (132 mg, 0.85 mmol, 85%); δ_H (300 MHz, $CDCl_3$) 7.60 (1 H, d, *J* 7.61, ArH), 7.37 - 7.27 (2 H, m, ArH), 7.24 - 7.16 (1 H, m, ArH), 5.34 - 5.26 (1 H, m, CHOH), 1.97 (1 H, d, *J* 3.2, OH), 1.50 (3 H, d, *J* 6.3, CH_3); δ_C (101 MHz, $CDCl_3$) 143.19, 131.78, 129.53, 128.53, 127.34, 126.54, 67.10, 23.63; $[\alpha]^{28}$ +37.8 (*c* 0.4 in $CHCl_3$) 57% ee (*R*), GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 150 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 6.12 min., *R* isomer 8.84 min., *S* isomer 9.47 min.)

Ref: [α] +64.8 (0.42 c in $CHCl_3$) 88% ee (*R*) – R. Soni, K. E. Jolley, S. Gosiewska, G. J. Clarkson, Z. Fang, T. H. Hall, B. N. Treloar, R. C. Knighton, and M Wills, *Organometallics*, 2018, **37**, 48-64. NMR in agreement

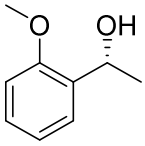


(*R*)-1-(4-Methoxyphenyl)ethan-1-ol (38)

4'-Methoxyacetophenone (150 mg, 1.00 mmol) and ligand **6** (4.5 mg, 0.01 mmol) were reacted following method C to give product **36** as a yellow oil (111 mg, 0.73 mmol, 73%); δ_H (300 MHz, $CDCl_3$) 7.33 - 7.28 (2 H, m, ArH), 6.92 - 6.86 (2 H, m, ArH), 4.86 (1 H, qd, *J* 6.5, 3.6, C*H*OH), 3.81 (3 H, s, OCH_3), 1.73 (1 H, br. s, OH), 1.48 (3 H, d, *J* 6.5, CH_3); δ_C (101 MHz, $CDCl_3$) 159.11, 138.14, 126.79, 113.98, 70.10, 55.42, 25.14; $[\alpha]^{25}$ +49.1 (*c* 0.2 in $CHCl_3$) 87%

ee (*R*), GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 120 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 36.18 min., *R* isomer 39.16 min., *S* isomer 41.02 min.)

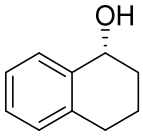
Ref: [α] +58.3 (0.53 c in $CHCl_3$) 96% ee (*R*) – R. Soni, K. E. Jolley, S. Gosiewska, G. J. Clarkson, Z. Fang, T. H. Hall, B. N. Treloar, R. C. Knighton, and M Wills, *Organometallics*, 2018, **37**, 48-64. NMR in agreement



(*R*)-1-(2-Methoxyphenyl)ethan-1-ol (39)

2'-Methoxyacetophenone (150 mg, 1.00 mmol) and ligand **6** (4.5 mg, 0.01 mmol) were reacted following method C to give product **39** as a colourless oil (108 mg, 0.71 mmol, 71%); δ_H (300 MHz, $CDCl_3$) 7.38 (1 H, d, *J* 7.5, ArH), 7.32 - 7.27 (1 H, m, ArH), 7.00 (1 H, t, J *7.5*, ArH), 6.92 (1 H, d, *J* 8.2, ArH), 5.13 (1 H, quin, *J* 6.2, C*H*OH), 3.91 (3 H, s, OCH_3), 2.66 (1 H, d, *J* 5.3, OH), 1.55 (3 H, d, *J* 6.5, CHOHC*H*$_3$); δ_C (101 MHz, $CDCl_3$) 156.69, 133.55, 128.42, 126.22, 120.93, 110.56, 66.67, 55.38, 22.97; $[\alpha]^{25}$ +17.3 (*c* 0.3 in $CHCl_3$) 65% ee (*R*), GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 130 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 16.47 min., *R* 19.07 isomer min., *S* 19.89 isomer min.)

Ref: [α] +16.0 (1.0 c in $CHCl_3$) 66% ee (*R*). Perna, F. M.; Ricci, M. A.; Scilimati, A.; Mena, M. C.; Pisano, I.; Palmieri, L.; Agrimi, G.; Vitale, P. J. Mol. Catal. B: Enzym. 2016, 124, 29−37. NMR in agreement

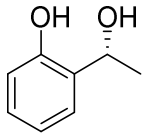


(*R*)-1,2,3,4-Tetrahydronaphthalen-1-ol (40)

Tetralone (146 mg, 1.00 mmol) and ligand **6** (4.5 mg, 0.01 mmol) were reacted following method C to give product **40** as a yellow oil (132 mg, 0.89 mmol, 89%); δ_H (300 MHz, $CDCl_3$)7.48 - 7.41 (1 H, m, ArH), 7.24 - 7.17 (2 H, m, ArH), 7.14 - 7.08 (1 H, m, ArH), 4.84 - 4.75 (1 H, m, C*H*OH), 2.90 - 2.66 (2 H, m), 2.07 – 1.88 (3 H, m), 1.85 - 1.73 (1 H, m), 1.72 - 1.65 (1 H, m); δ_C (101 MHz, $CDCl_3$) 138.93, 137.24, 129.14, 128.78, 127.71, 126.31, 68.28, 32.40, 29.37, 18.92; $[\alpha]^{25}$ -33.1 (*c* 0.4 in $CHCl_3$) 99% ee (*R*), GC analysis (CP-CHIRALSIL-

DEX-CB, 25 m x 0.25 mm x 0.25 μm, gas He, T = 120 °C, P = 12 psi, FID temp 250 °C, injector temp 220 °C, ketone 38.54 min., R isomer 65.74 min., *S* isomer 61.42 min.)

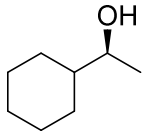
Ref: [α] −34.4 (c 0.57, $CHCl_3$), 99% ee (*R*) – R. Soni, K. E. Jolley, S. Gosiewska, G. J. Clarkson, Z. Fang, T. H. Hall, B. N. Treloar, R. C. Knighton, and M Wills, *Organometallics*, 2018, **37**, 48-64. NMR in agreement



(*R*)-2-(1-hydroxyethyl)phenol (41)

2'-Hydroxyacetophenone (136 mg, 1.00 mmol) and ligand **6** (4.5 mg, 0.01 mmol) were reacted following method C to give product **41** as a colourless oil (125 mg, 0.91 mmol, 91%); δ_H (300 MHz, $CDCl_3$) 7.91 (1 H, s, ArOH), 7.23 - 7.15 (1 H, m, ArH), 7.00 (1 H, dd, *J* 7.5, 1.3, ArH), 6.92 - 6.81 (2 H, m, ArH), 5.10 (1 H, d, *J* 4.5, C*H*OH), 2.43 (1 H, br. s, CHO*H*), 1.61 (3 H, d, *J* 6.6, CH_3); δ_C (101 MHz, $CDCl_3$) 155.46, 129.05, 128.55, 126.60, 120.04, 117.19, 71.69, 23.54; $[\alpha]_D^{19}$ +13.8 (*c* 0.2 in $CHCl_3$) 94% ee (*R*), GC analysis (CP-CHIRALSIL-DEX-CB, 25 m x 0.25 mm x 0.25 μm, gas He, T = 150 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 3.26 min., *R* isomer 15.02 min., *S* isomer 17.40 min.)

Ref: $[\alpha]^{32}$: +22.3 (0.65 c in CH_2Cl_2) – 98.8% ee (*R*) - Rina Soni, Katherine E. Jolley, Guy J. Clarkson, and Martin Wills, *Org. Lett.*, 2013, **15**, 5110-5113. NMR in agreement



(*S*)-1-Cyclohexylethan-1-ol (acetylcyclohexane)

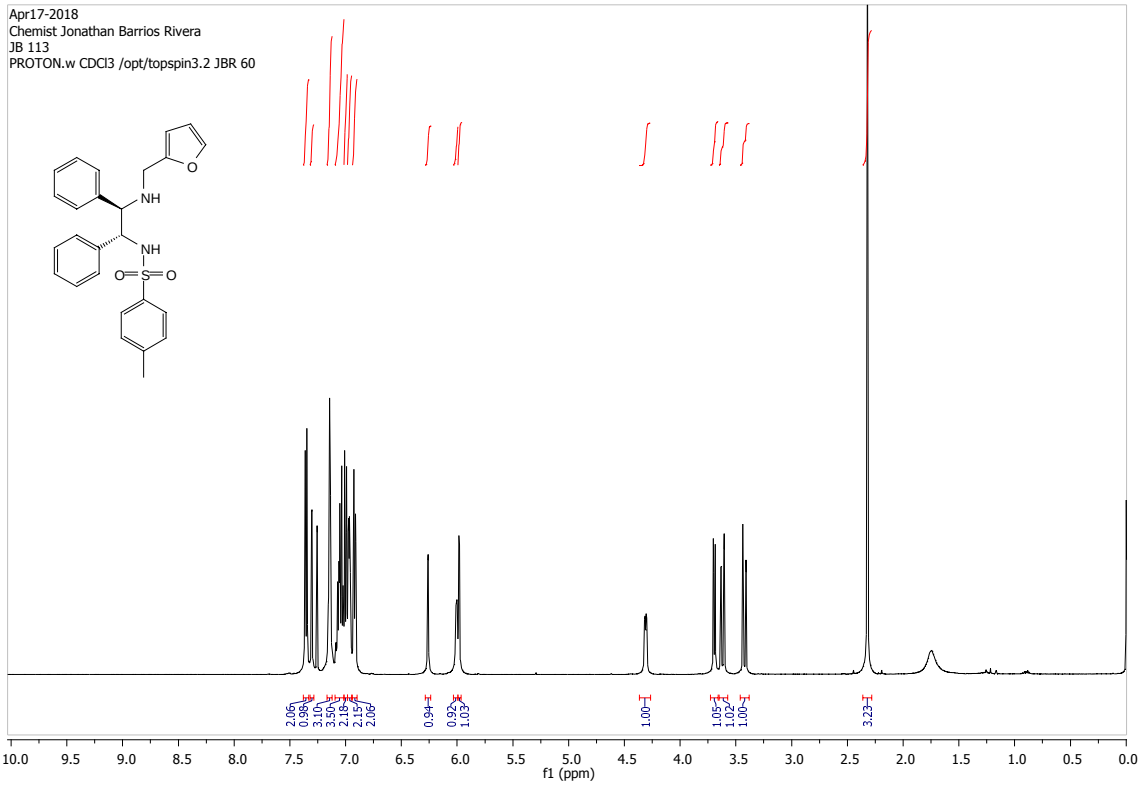
Cyclohexyl methyl ketone (126 mg, 1.00 mmol) and ligand **6** (4.5 mg, 0.01 mmol) were reacted following method C to give (*S*)-1-cyclohexylethan-1-ol as a colourless oil (108 mg, 0.84 mmol, 84%); δ_H (300 MHz, $CDCl_3$) ppm 3.55 (1 H, t, *J* 6.0, C*H*OH), 1.90 - 1.61 (5 H, m), 1.34 - 1.12 (8 H, m), 1,08 – 0.92 (2 H, m); δ_C (101 MHz, $CDCl_3$) δ 72.34, 45.25, 28.83, 28.49, 26.64, 26.36, 26.26, 20.50; $[\alpha]_D^{25}$ +1.13 (*c* 0.2 in $CHCl_3$) 53% ee (*S*); GC analysis of (*S*)-1-cyclohexylethyl acetate (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas hydrogen, T = 92 °C, P = 12 psi, FID temp 250 °C, injector temp 220 °C, ketone 19.28 min., *R* isomer 37.37 min., *S* isomer 32.72 min.)

Ref: $[\alpha]_D$ = −1.20 (c 0.57, $CHCl_3$), 71% ee (*R*) - R. Soni, K. E. Jolley, S. Gosiewska, G. J. Clarkson, Z. Fang, T. H. Hall, B. N. Treloar, R. C. Knighton, and M Wills, *Organometallics*, 2018, **37**, 48-64. NMR in agreement

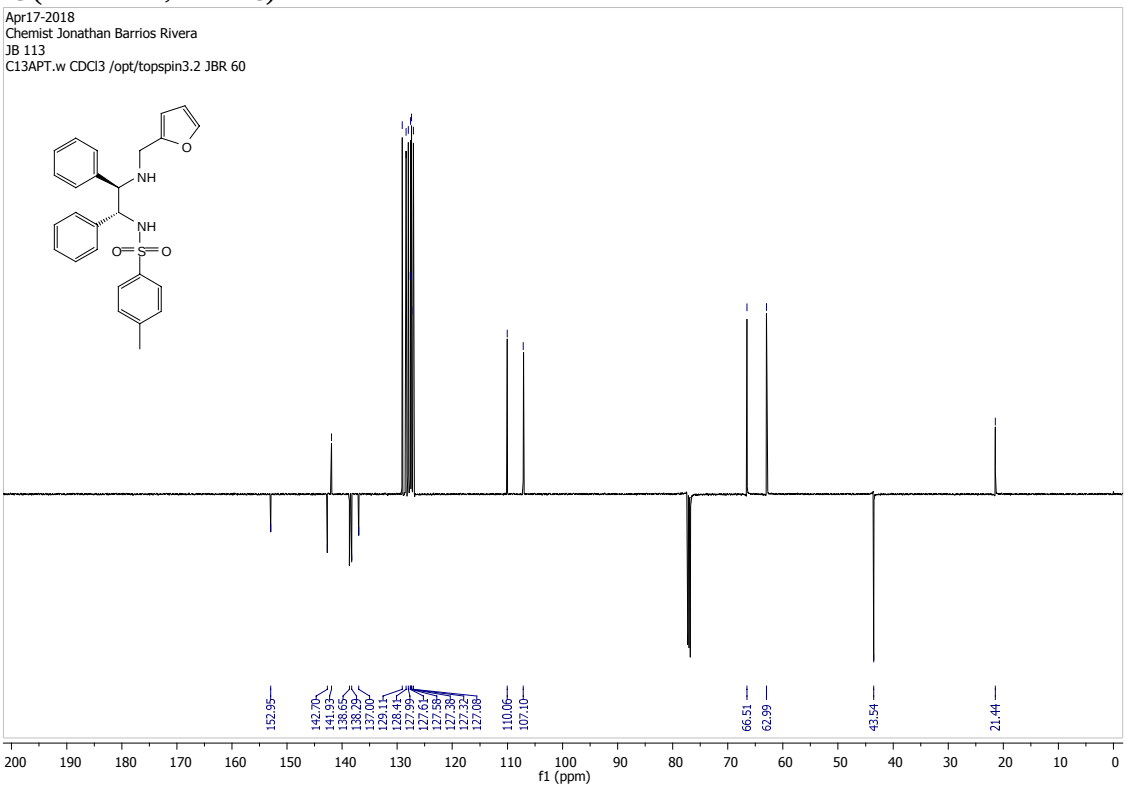
NMR Spectra

(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(furan-2-ylmethyl)amino]ethyl}-4-methylbenzenesulfonamide (6)

δ_H (500 MHz, $CDCl_3$)

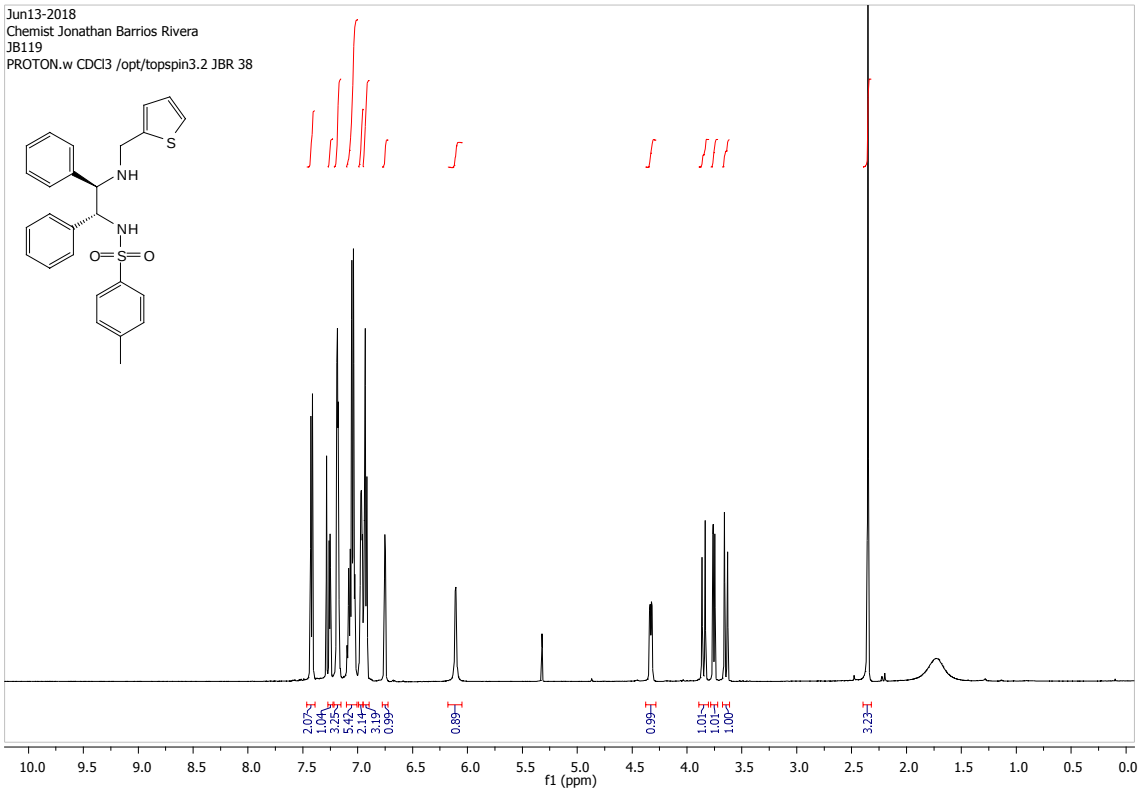


δ_C (125 MHz, $CDCl_3$)

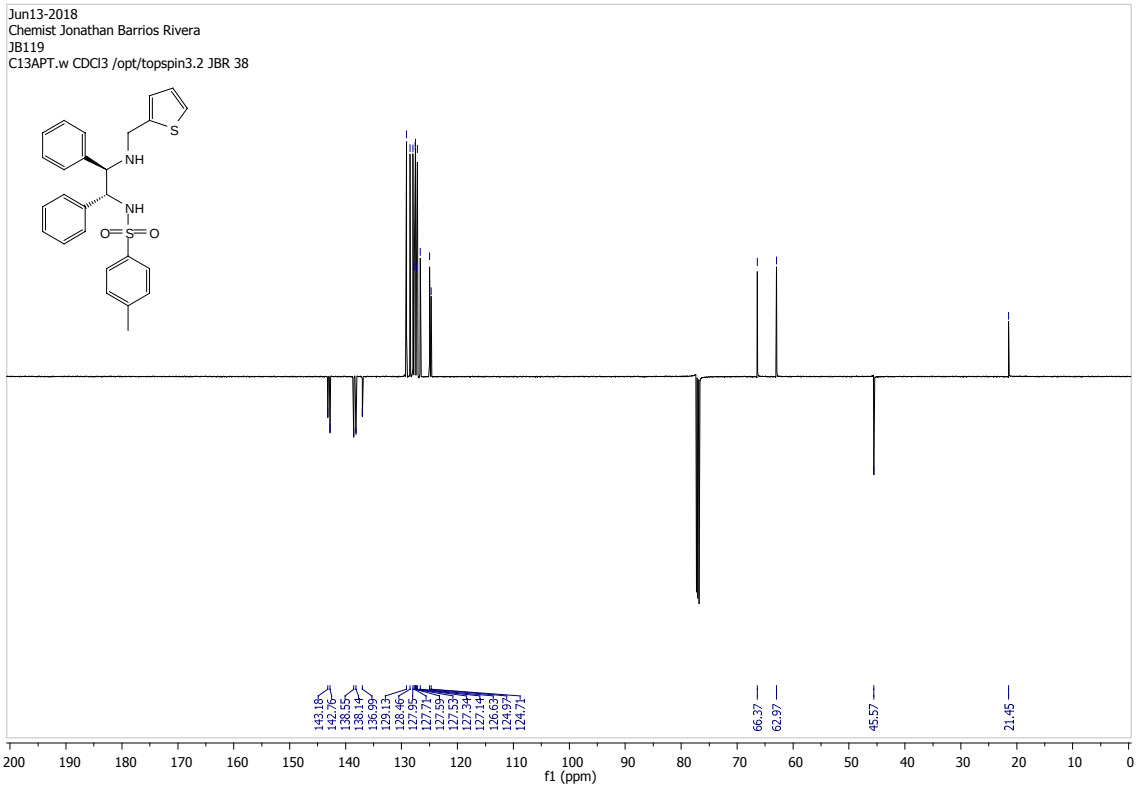


(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(thiophen-2-ylmethyl)amino]ethyl}-4-methylbenzenesulfonamide (7)

δ_H (500 MHz, $CDCl_3$)

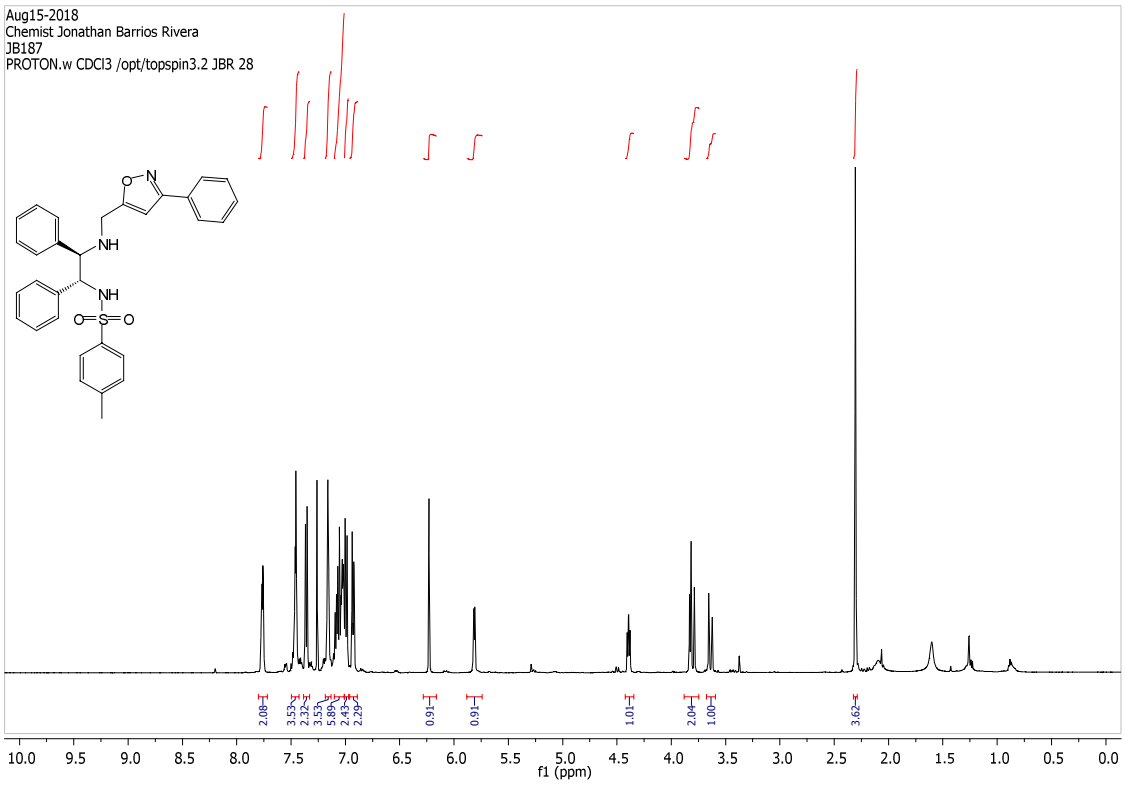


δ_C (125 MHz, $CDCl_3$)

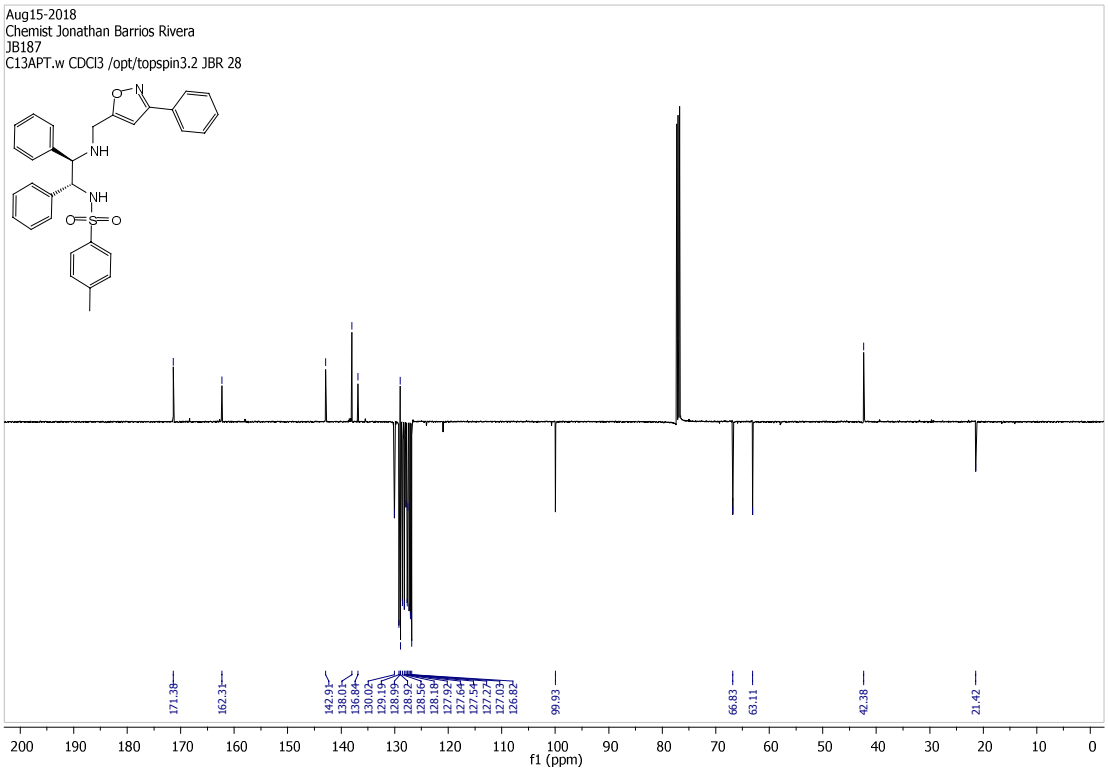


_N_-((_R_,_R_)-1,2-Diphenyl-2-(((3-phenylisoxazol-5-yl)methyl)amino)ethyl)-4-methylbenzenesulfonamide (8)

δ_H (500 MHz, $CDCl_3$)

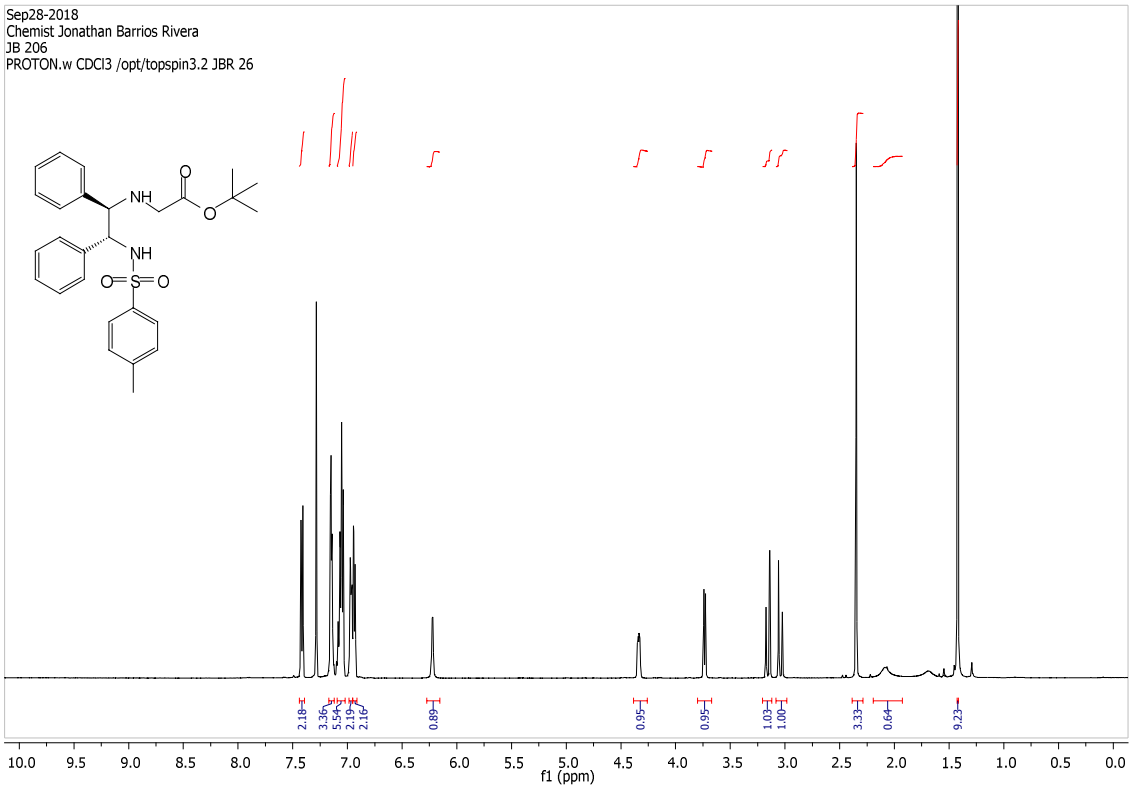


δ_C (126 MHz, $CDCl_3$)

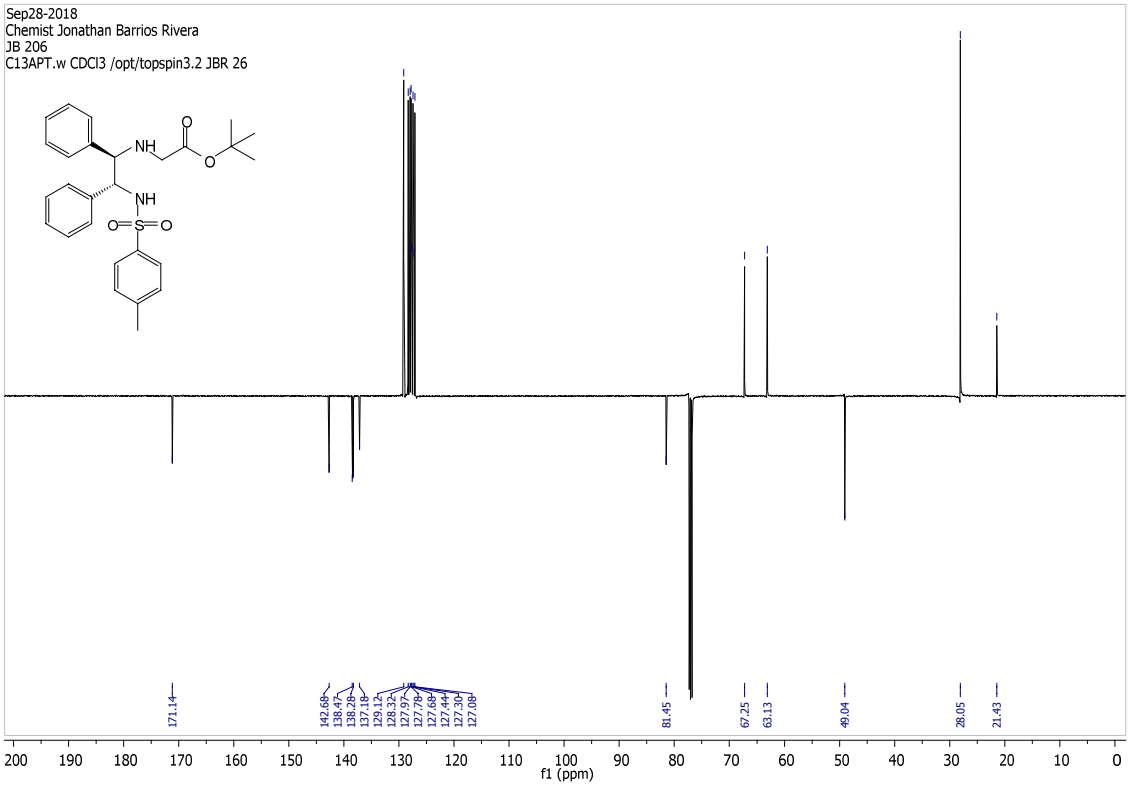


tert-Butyl ((_R_, _R_)-2-((4-methylphenyl)sulfonamido)-1,2-diphenylethyl)glycinate (9)

δ_H (500 MHz, $CDCl_3$)

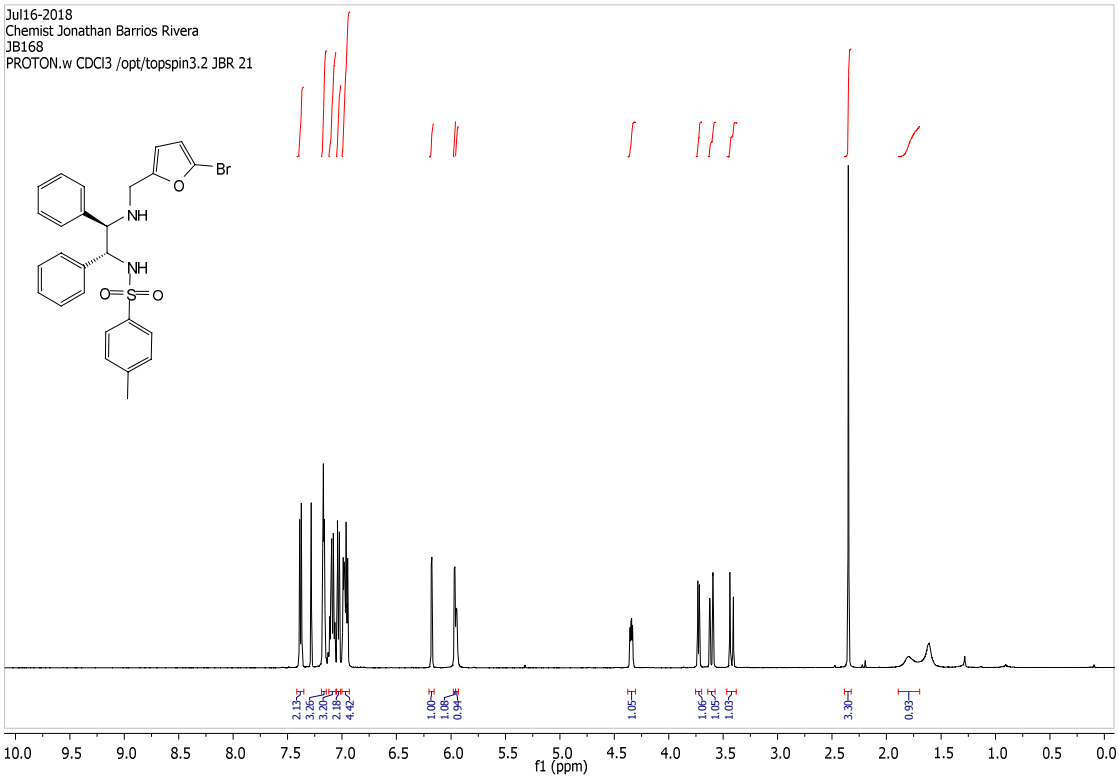


δ_C (126 MHz, $CDCl_3$)

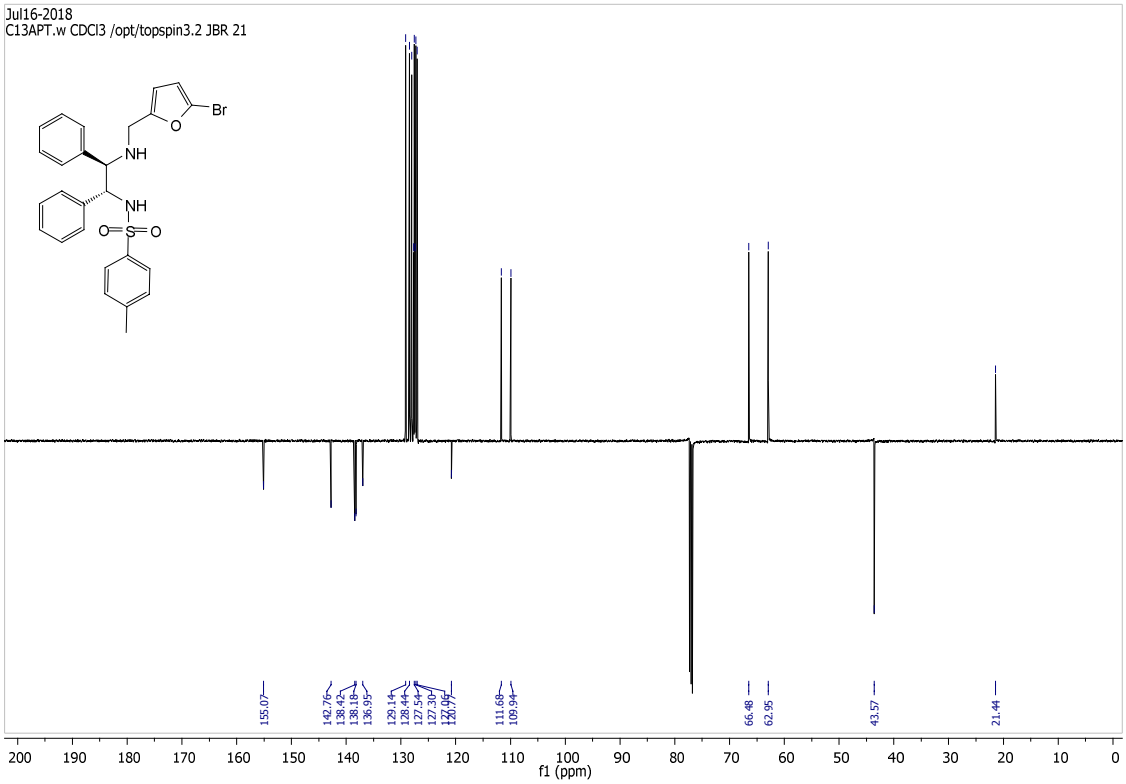


(*R*,*R*)-2-((5-Bromofuran-2-yl)methyl)amino-1,2-diphenylethyl-4-methylbenzenesulfonamide (10)

δ_H (500 MHz, $CDCl_3$)

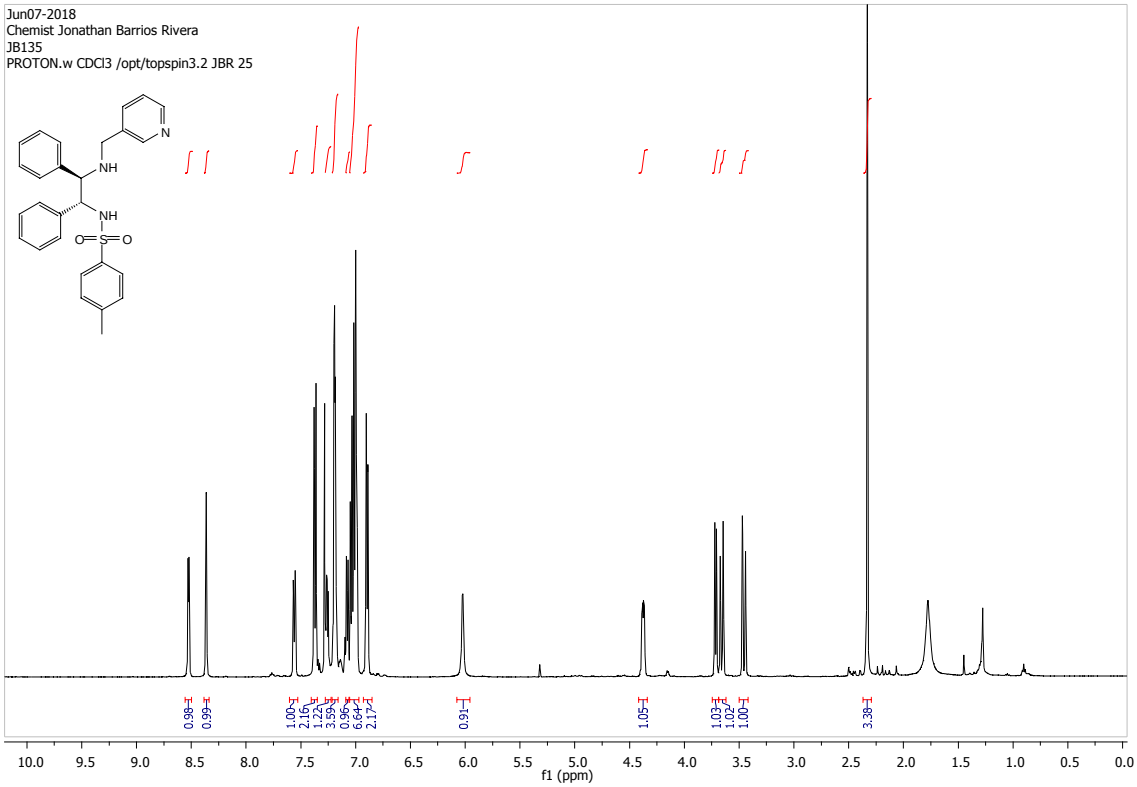


δ_C (126 MHz, $CDCl_3$)

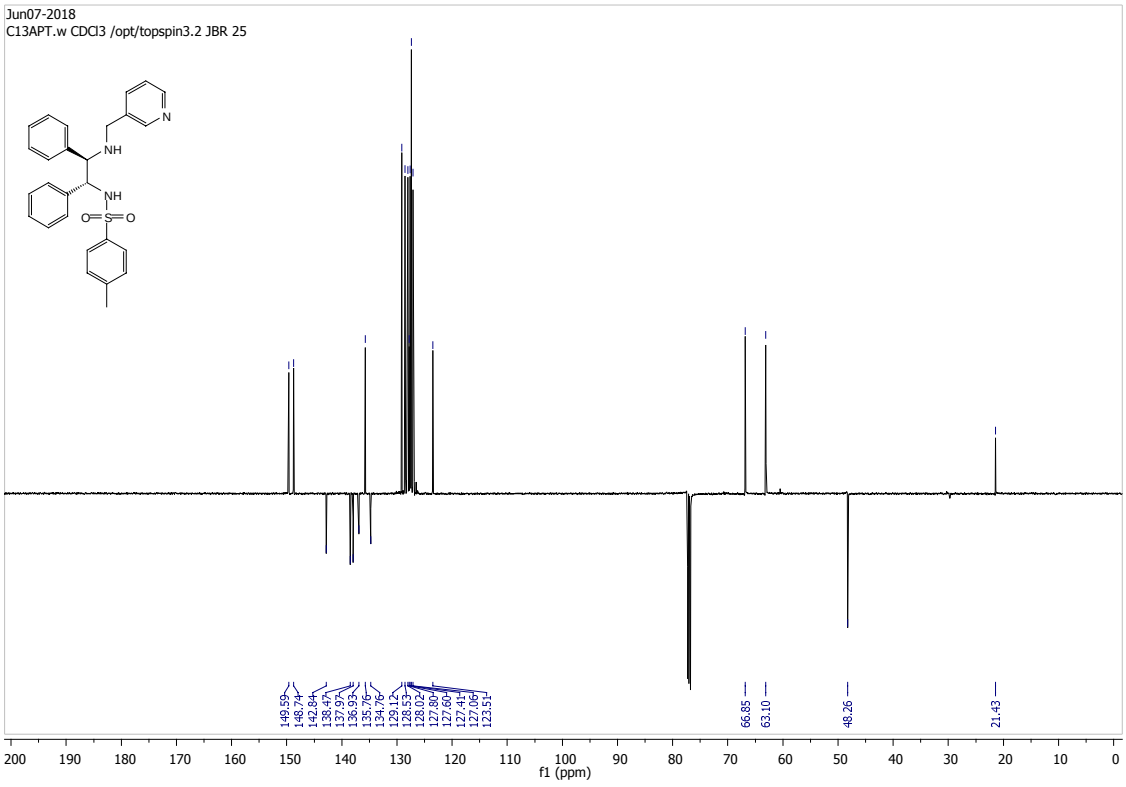


(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(pyridin-3-ylmethyl)amino]ethyl}-4-methylbenzenesulfonamide (11)

δ_H (500 MHz, $CDCl_3$)

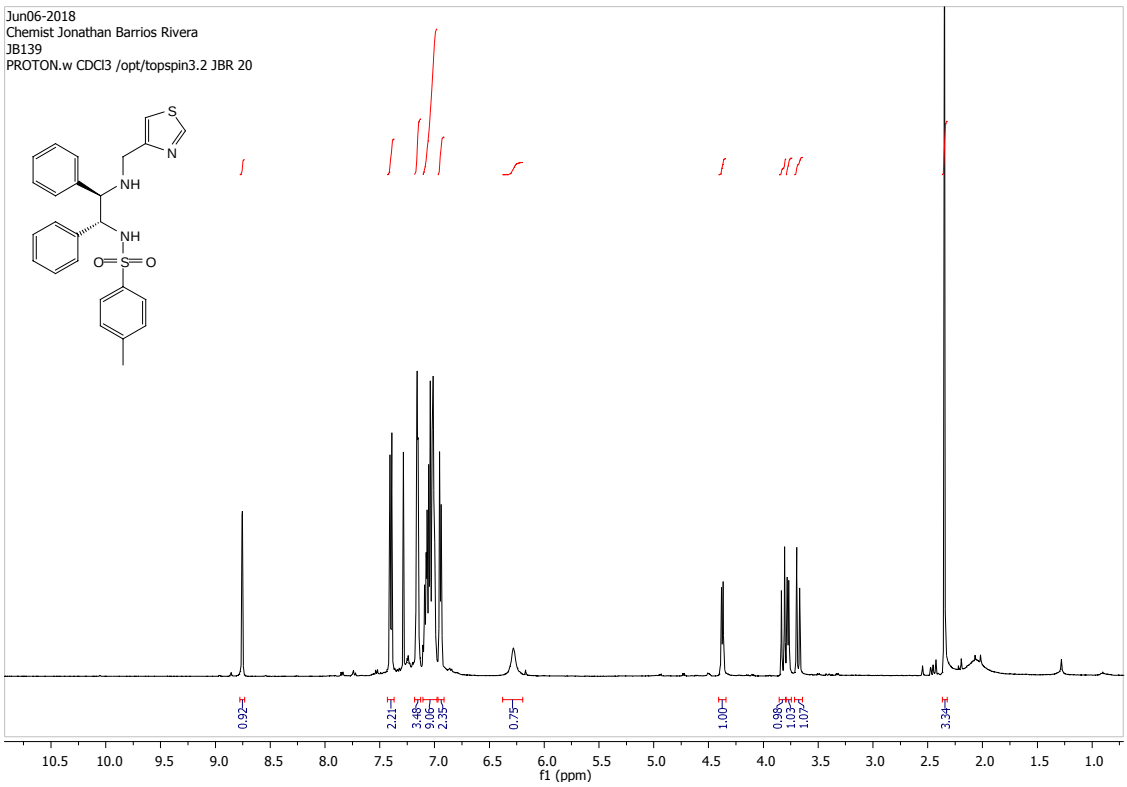


δ_C (125 MHz, $CDCl_3$)

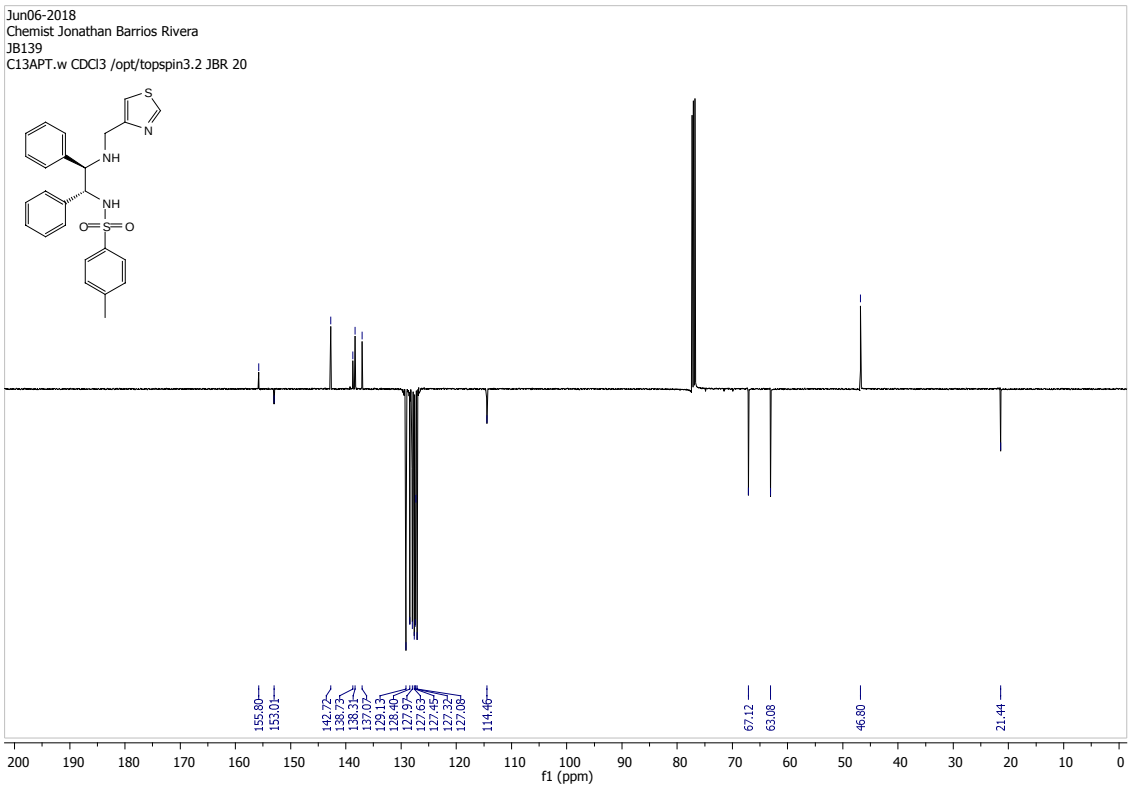


(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(thiazol-4-ylmethyl)amino]ethyl}-4-methylbenzenesulfonamide (12)

δ_H (500 MHz, $CDCl_3$)

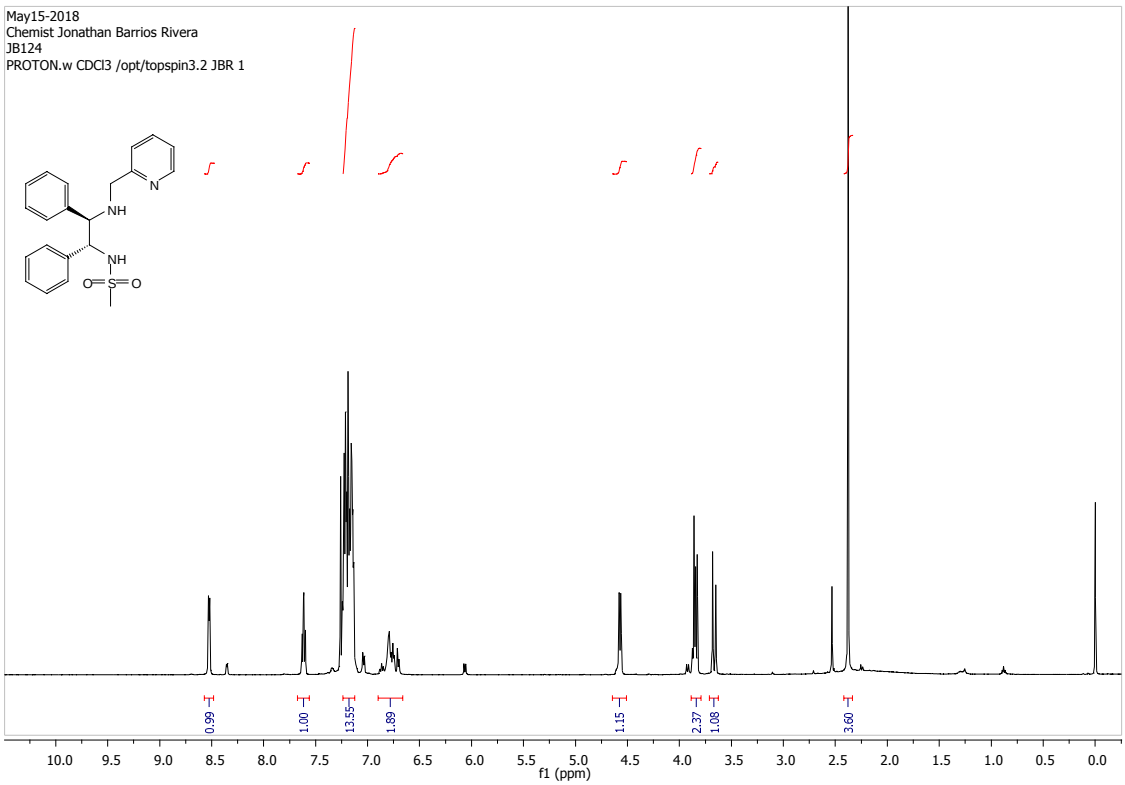


^{13}C NMR δ_C (125 MHz, $CDCl_3$)

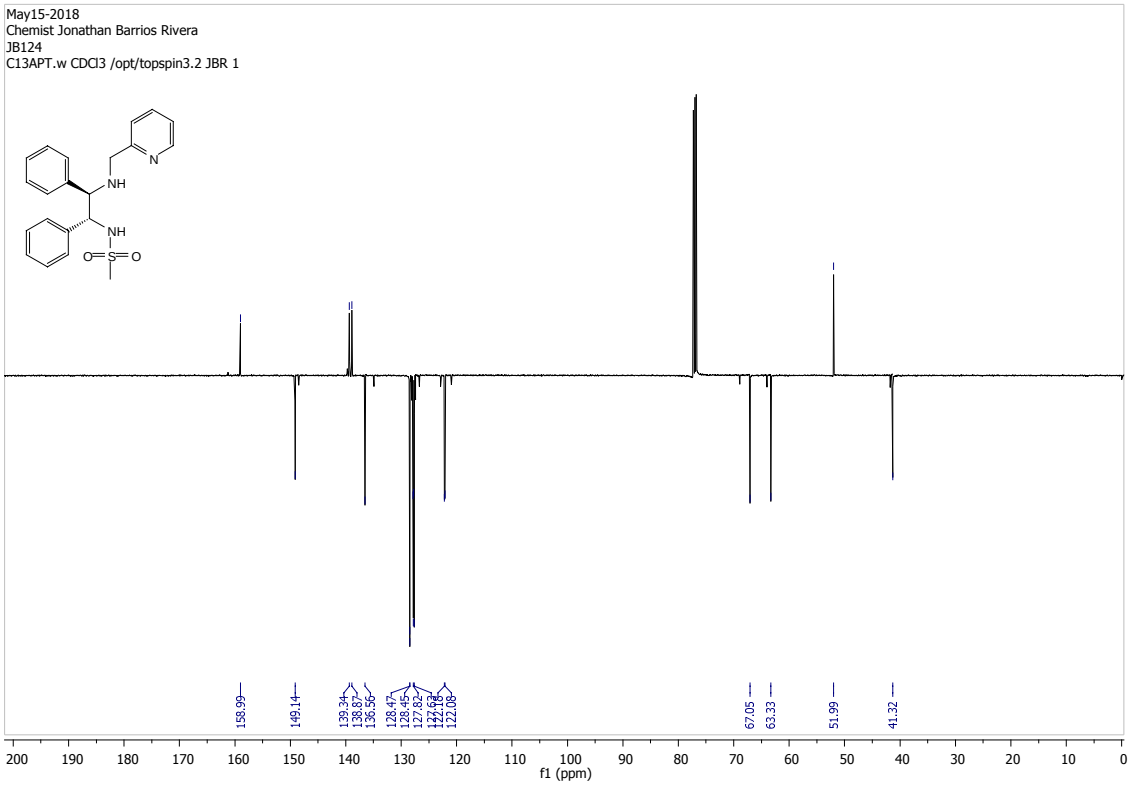


(1*R*,2*R*)-*N*-1,2-Diphenyl-2-((pyridin-2-ylmethyl)amino)ethylmethanesulfonamide (13)

δ_H (500 MHz, $CDCl_3$)

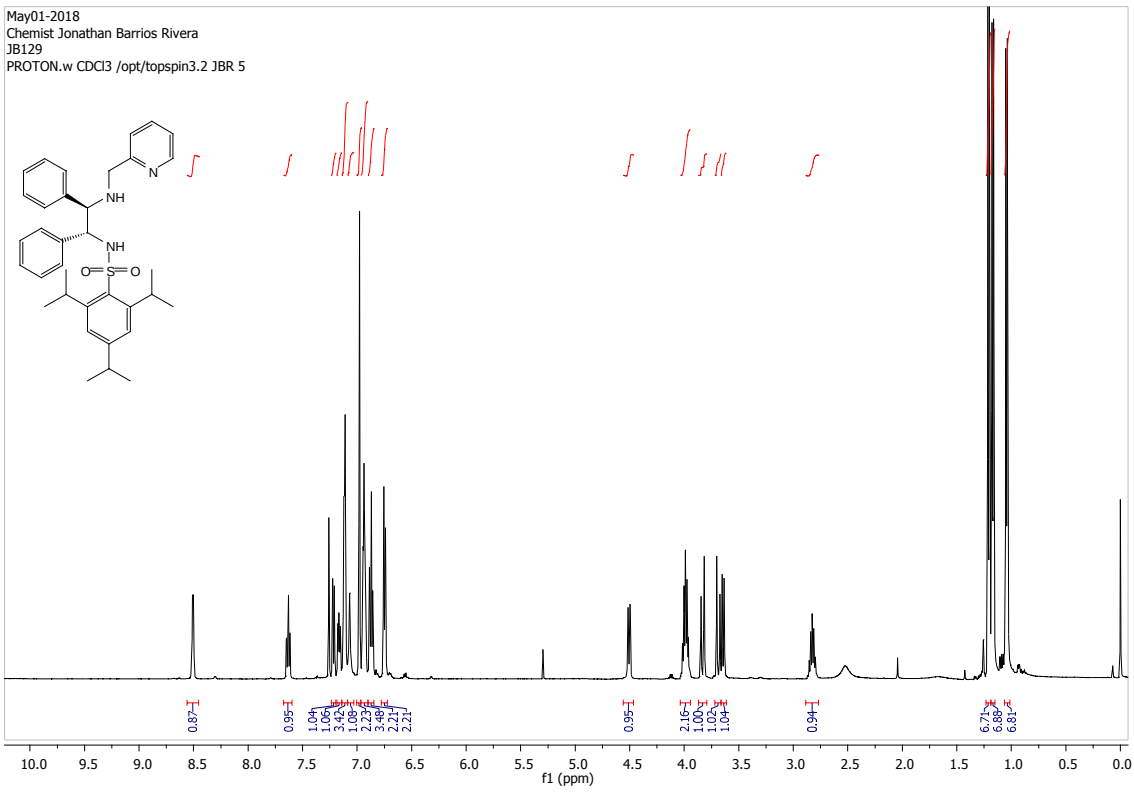


δ_C (125 MHz, $CDCl_3$)

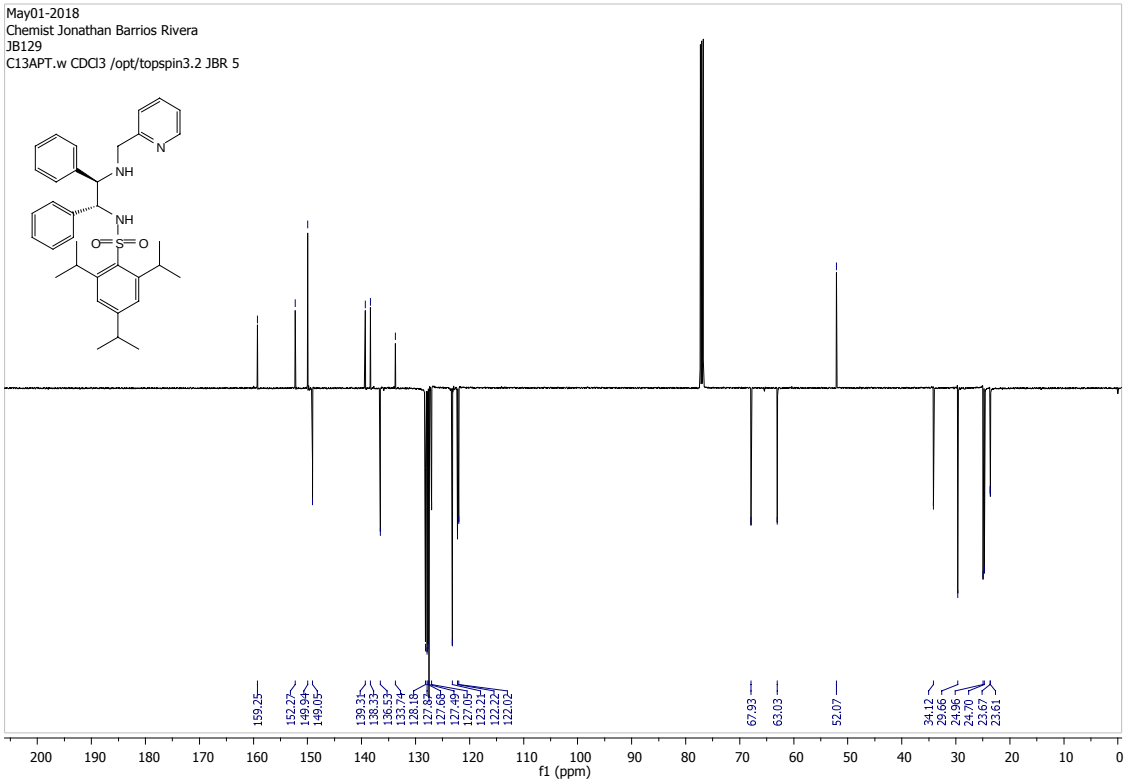


(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(pyridin-2-ylmethyl)amino]ethyl}-2,4,6-triisopropylbenzenesulfonamide (14)

δ_H (500 MHz, $CDCl_3$)

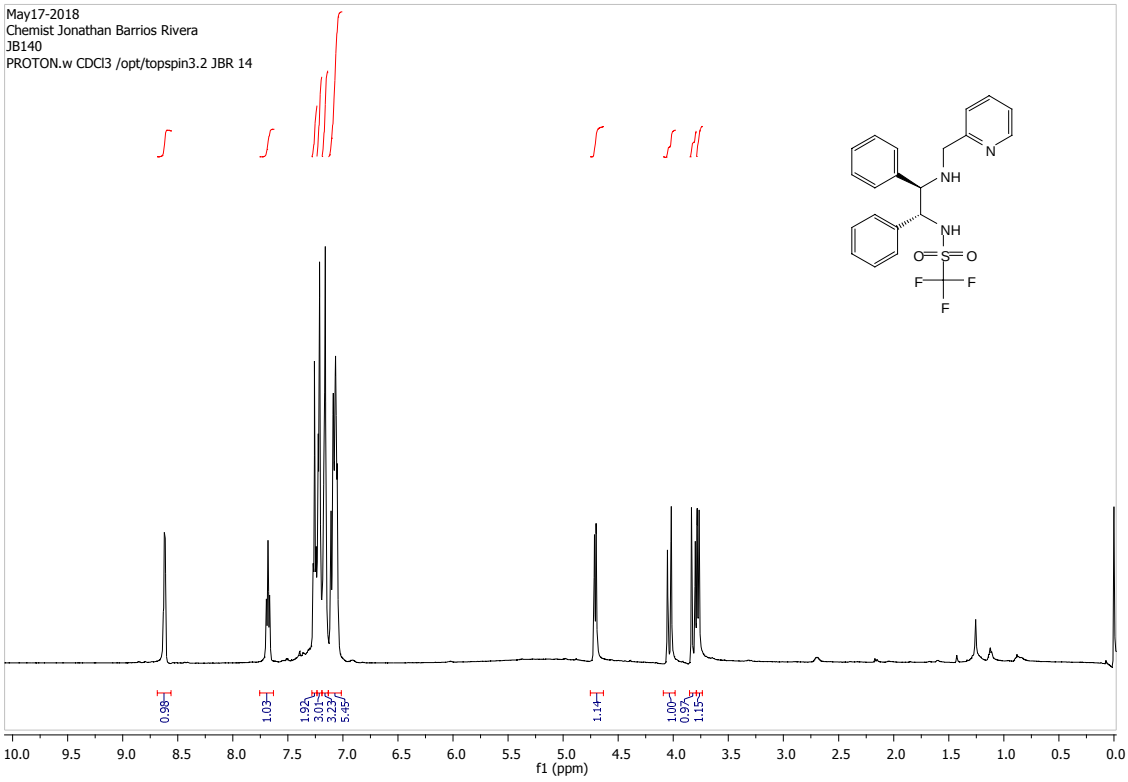


δ_C (125 MHz, $CDCl_3$)

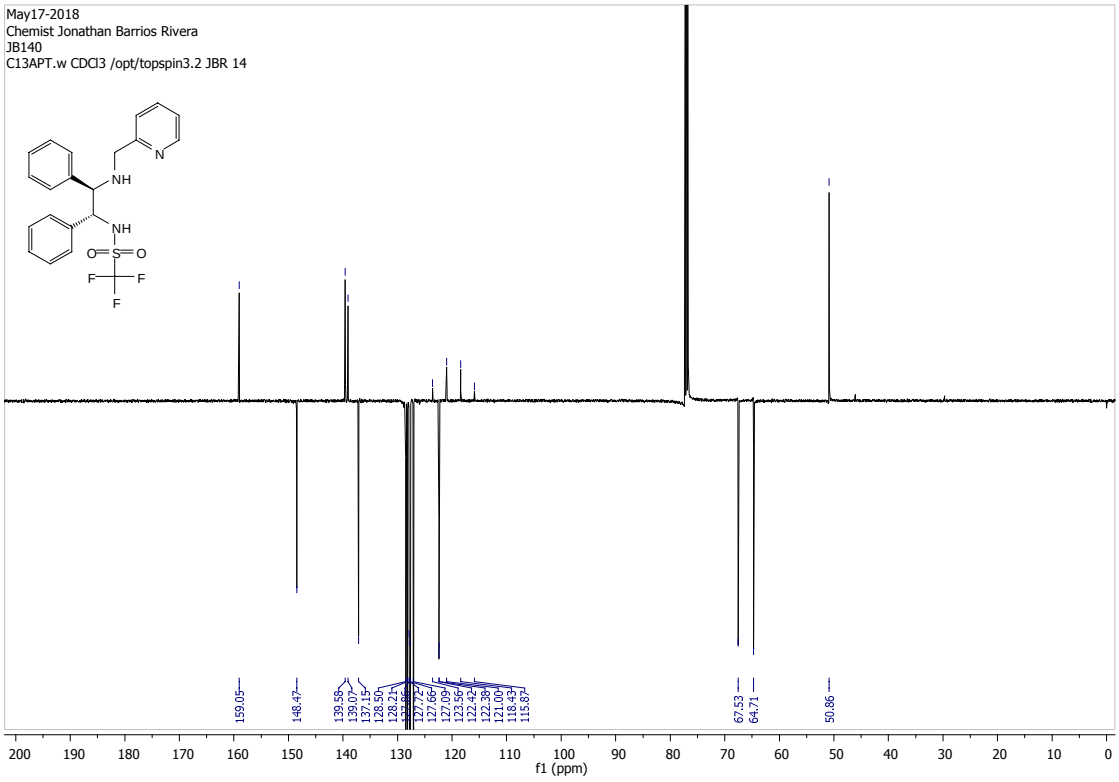


(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(6-methyl-pyridin-2-ylmethyl)amino]ethyl}-1,1,1-trifluoromethanesulfonamide (15)

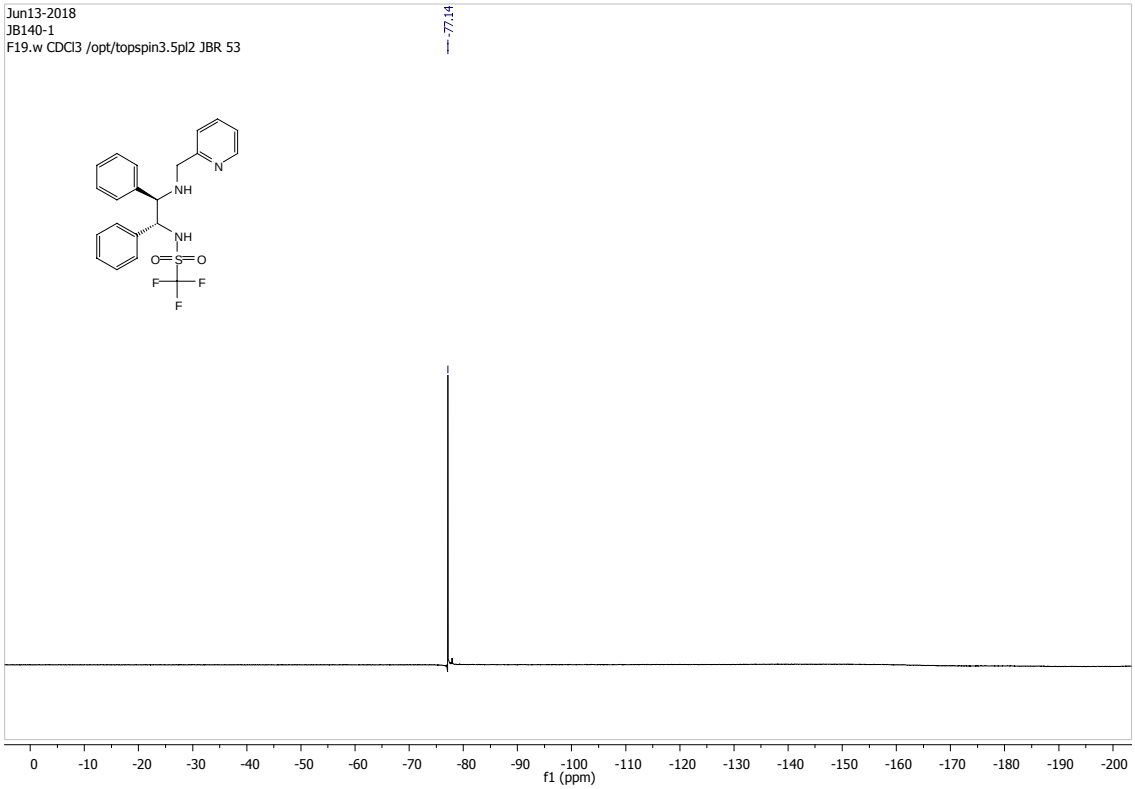
δ_H (500 MHz, $CDCl_3$)



δ_C (125 MHz, $CDCl_3$)

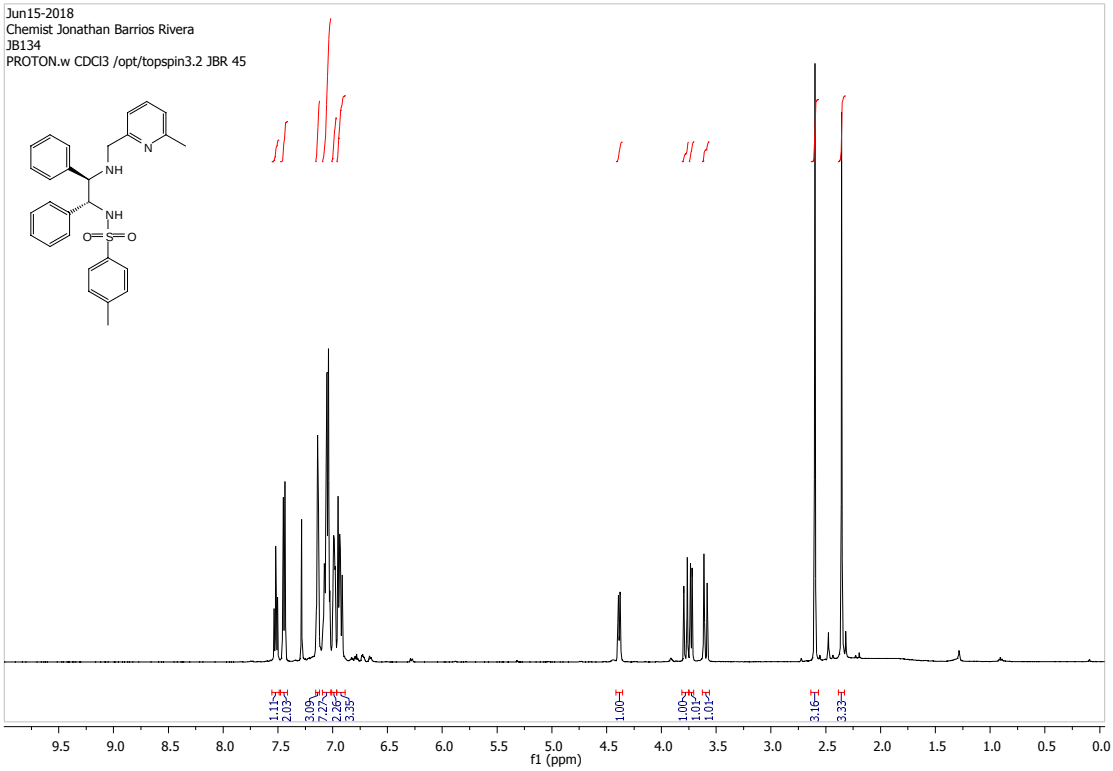


δ_F (376 MHz, $CDCl_3$)

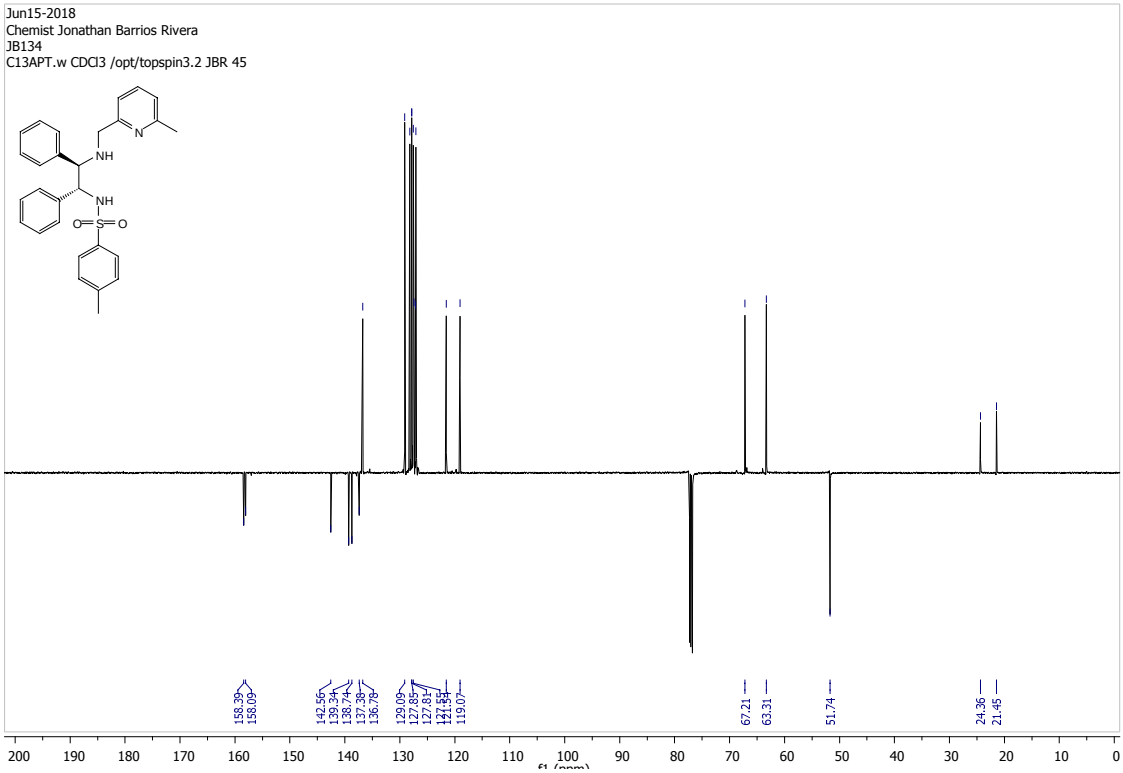


(1*R*,2*R*)-*N*-{1,2-Diphenyl-2-[(6-methyl-pyridin-2-ylmethyl)amino]ethyl}-4-methylbenzenesulfonamide (16)

δ_H (500 MHz, $CDCl_3$)

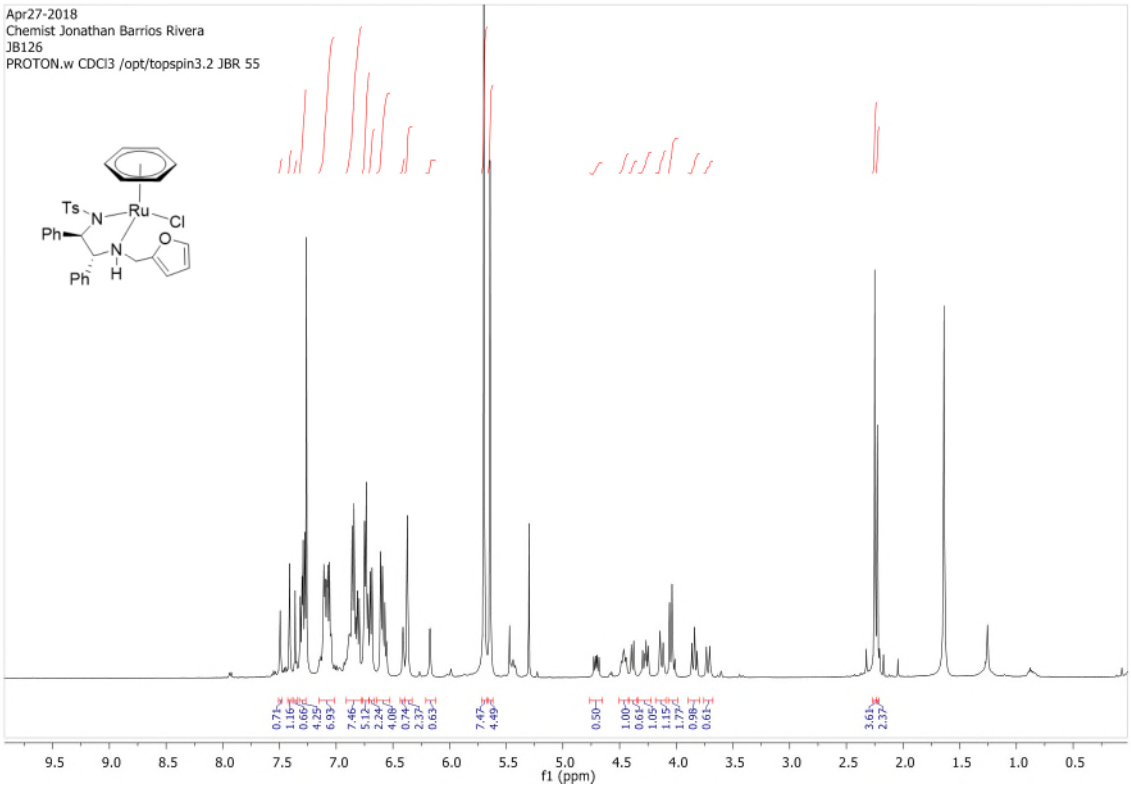


δ_C (125 MHz, $CDCl_3$)

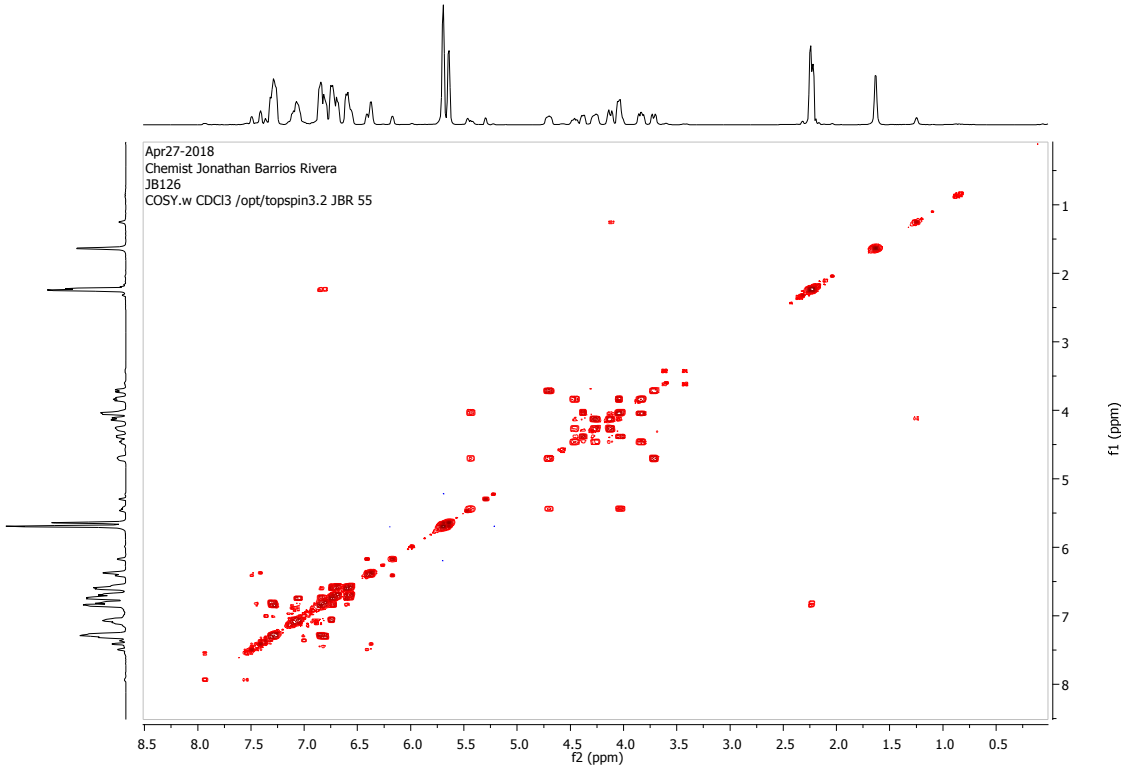


Complex formed from ligand 6 (17)

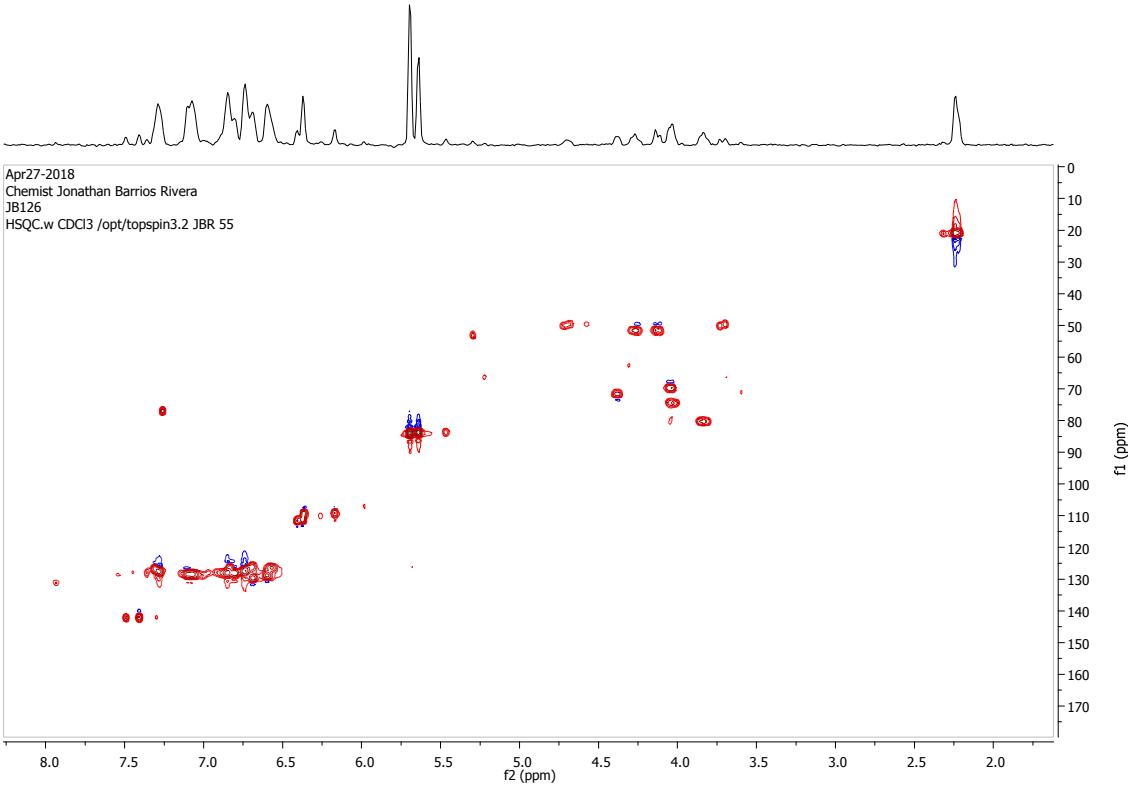
^{1}H NMR δ_H (500 MHz, $CDCl_3$)



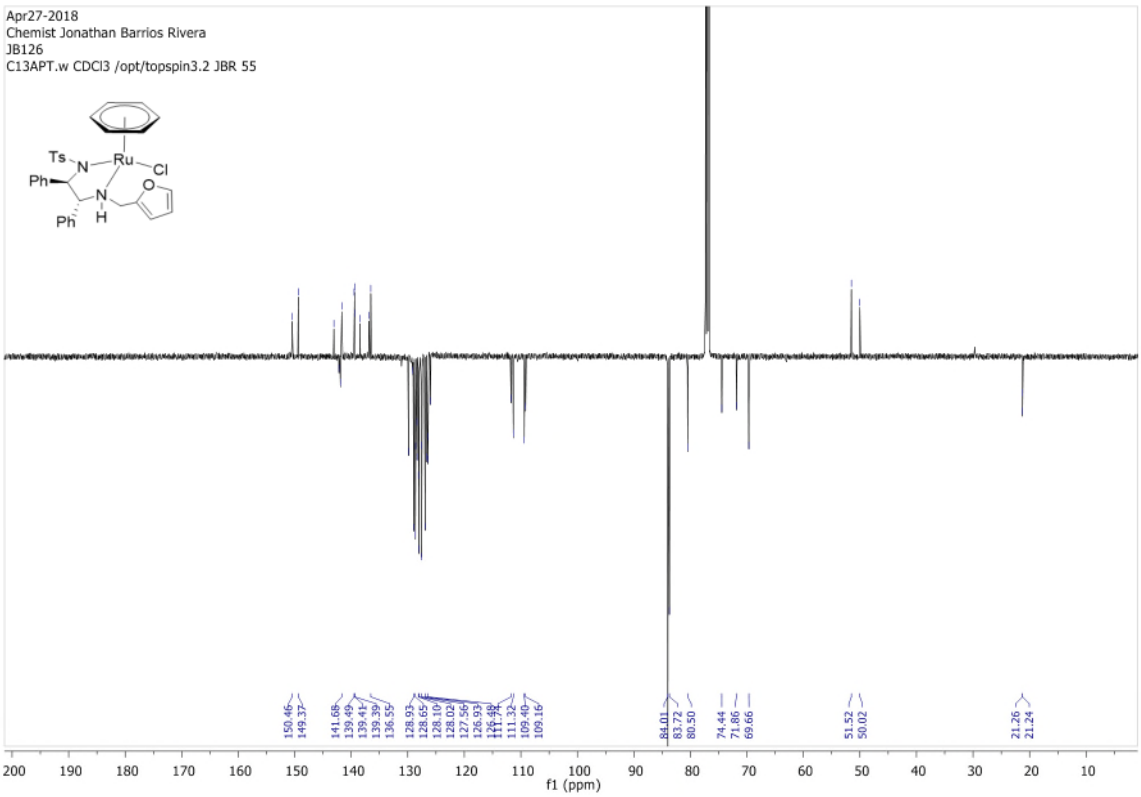
COSY


Apr27-2018
Chemist Jonathan Barrios Rivera
JB126
COSY.w CDCl3 /opt/topspin3.2 JBR 55
f1 (ppm)
f2 (ppm)

HSQC

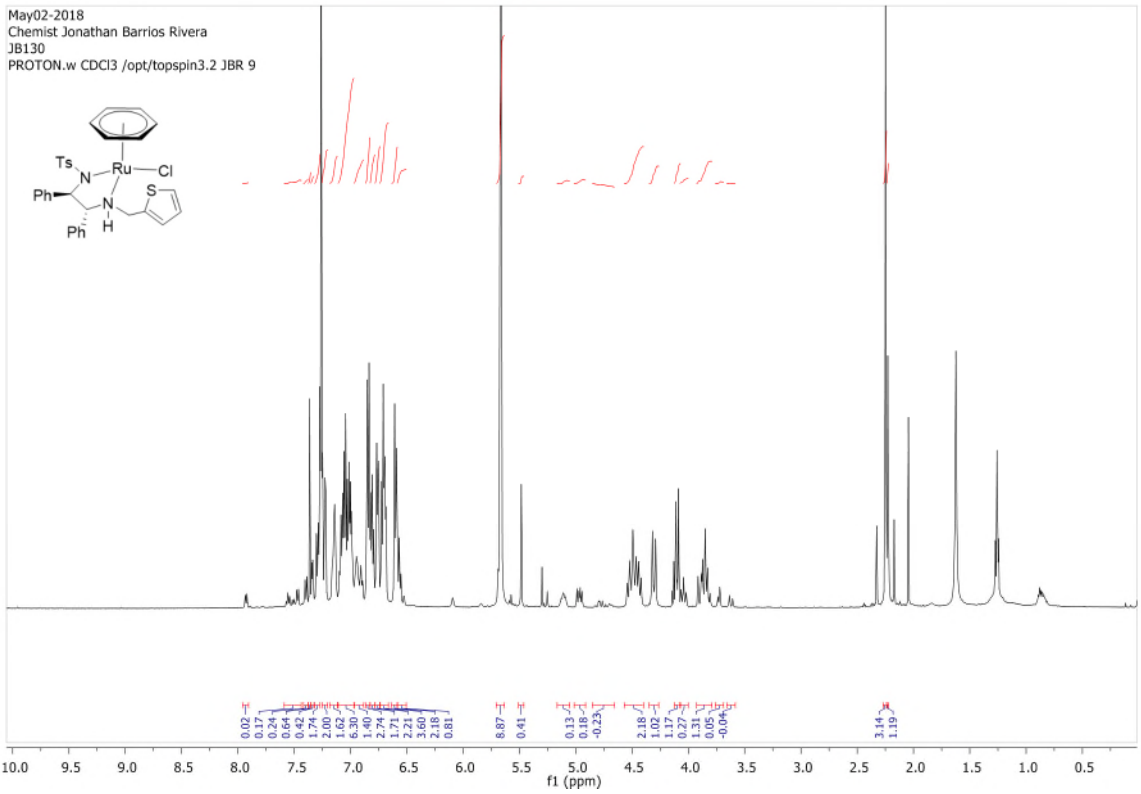

Apr27-2018
Chemist Jonathan Barrios Rivera
JB126
HSQC.w CDCl3 /opt/topspin3.2 JBR 55
f1 (ppm)
f2 (ppm)

δ_C (125 MHz, $CDCl_3$)

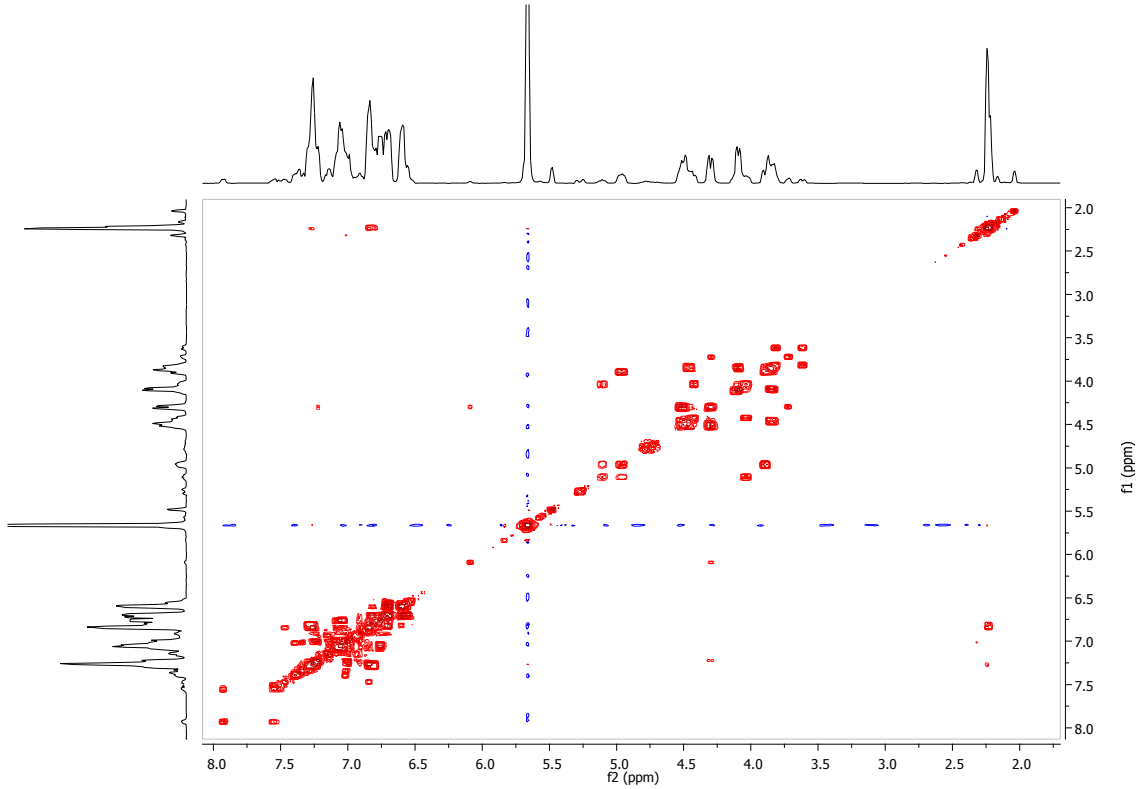


Complex formed from ligand 7 (18)

^{1}H NMR δ_H (500 MHz, $CDCl_3$)



COSY


f2 (ppm)
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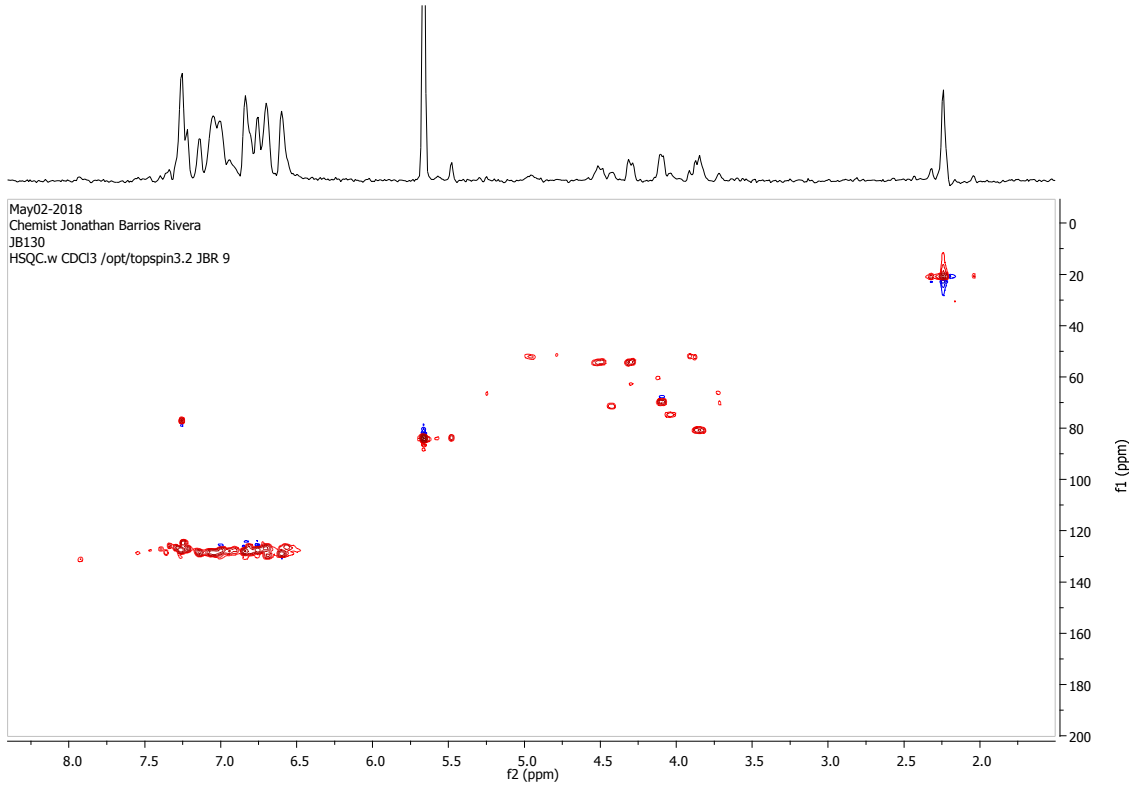
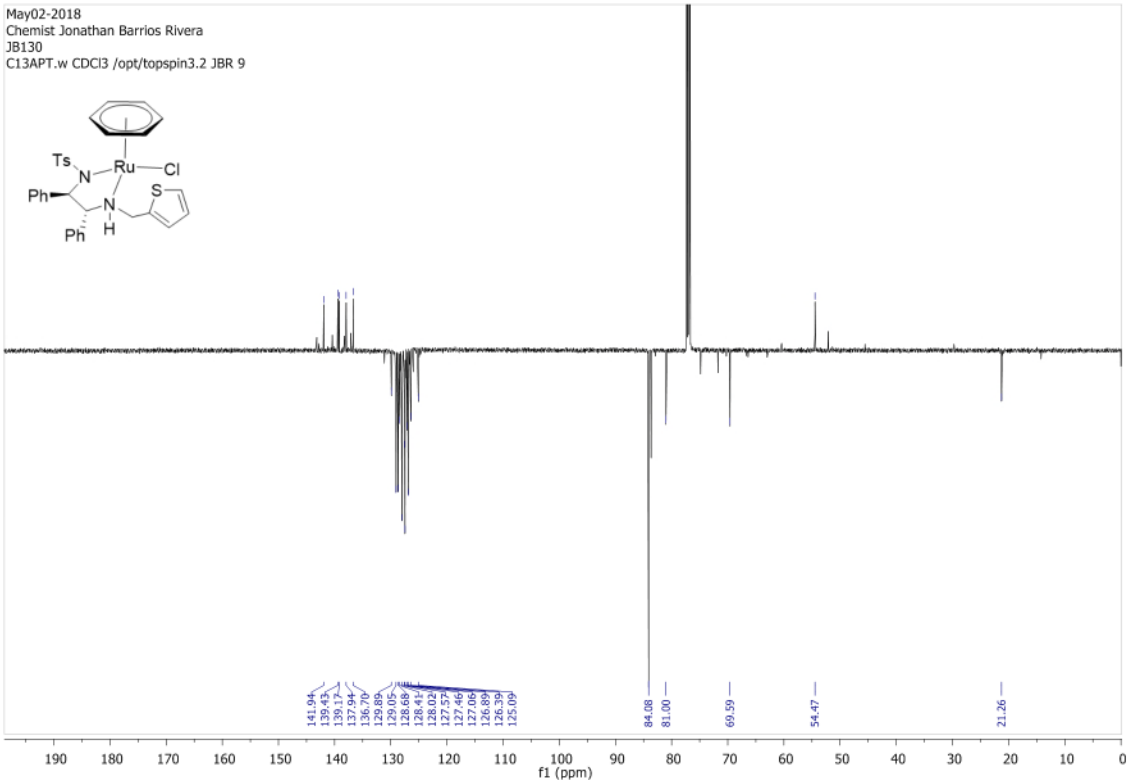
HSQC

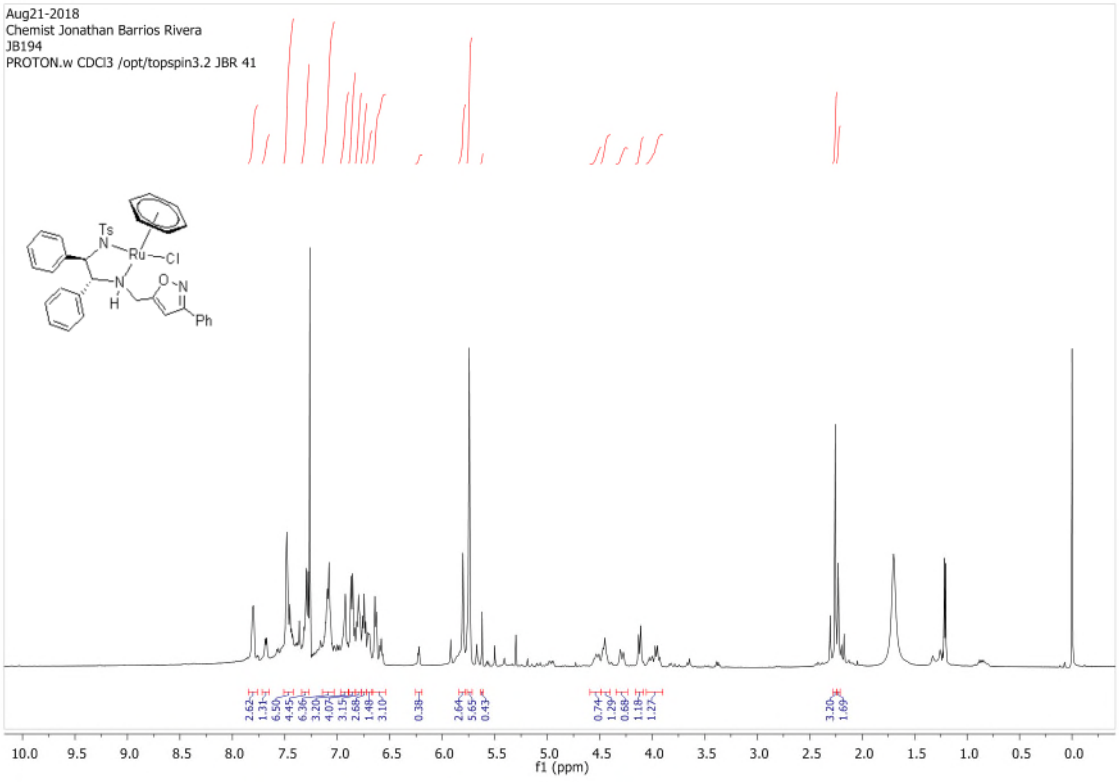

May02-2018
Chemist Jonathan Barrios Rivera
JB130
HSQC.w CDCl3 /opt/topspin3.2 JBR 9
f2 (ppm)
f1 (ppm)

^{13}C NMR δ_C (125 MHz, $CDCl_3$)

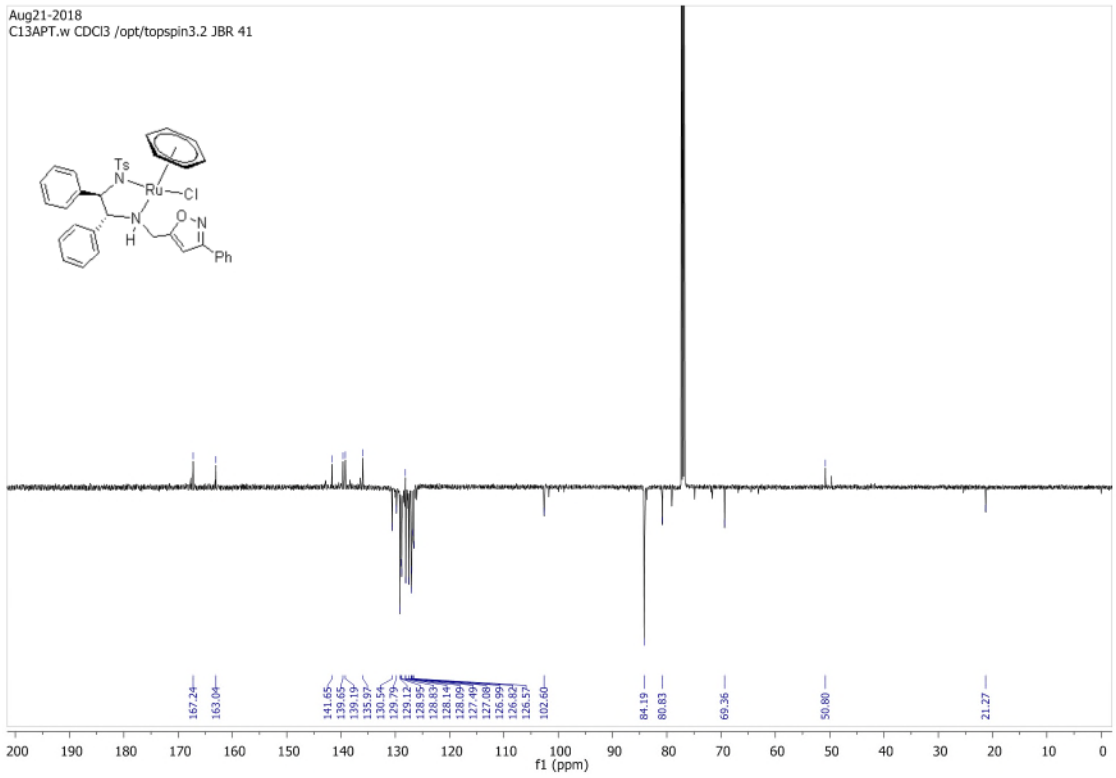


Complex formed from ligand 8 (19)

^{1}H (500 MHz, $CDCl_3$)

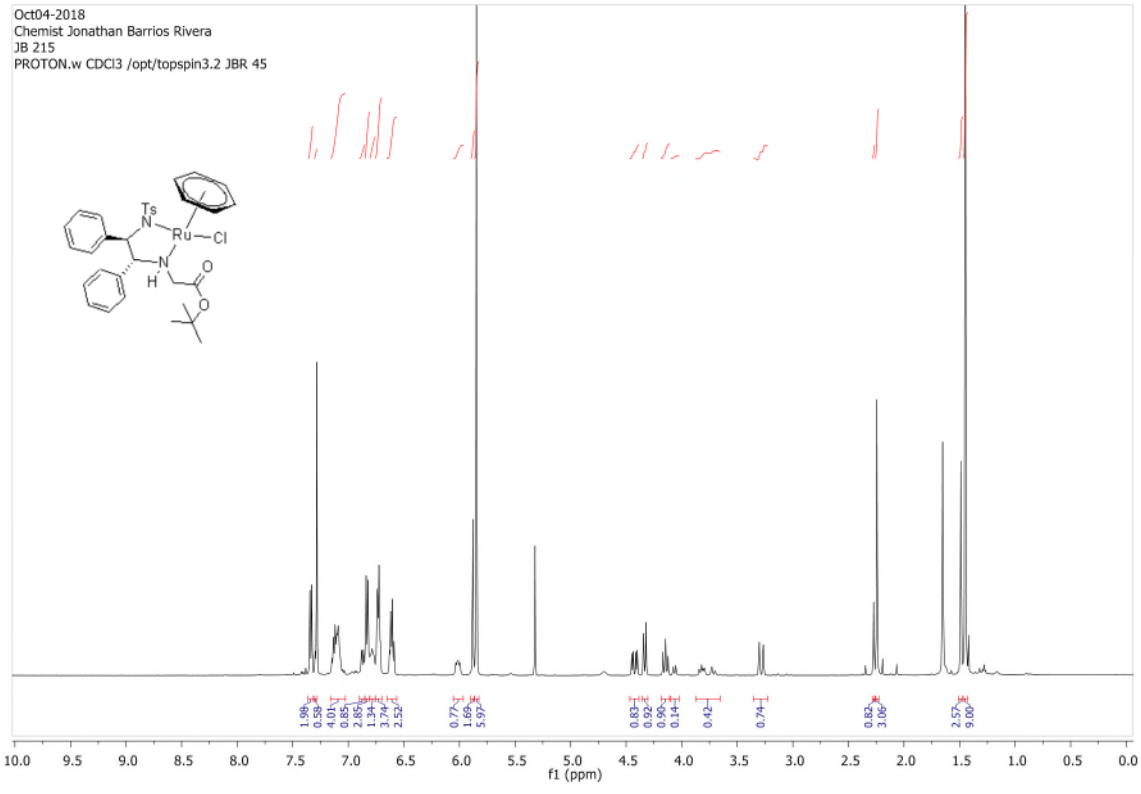


δ_C (126 MHz, $CDCl_3$)

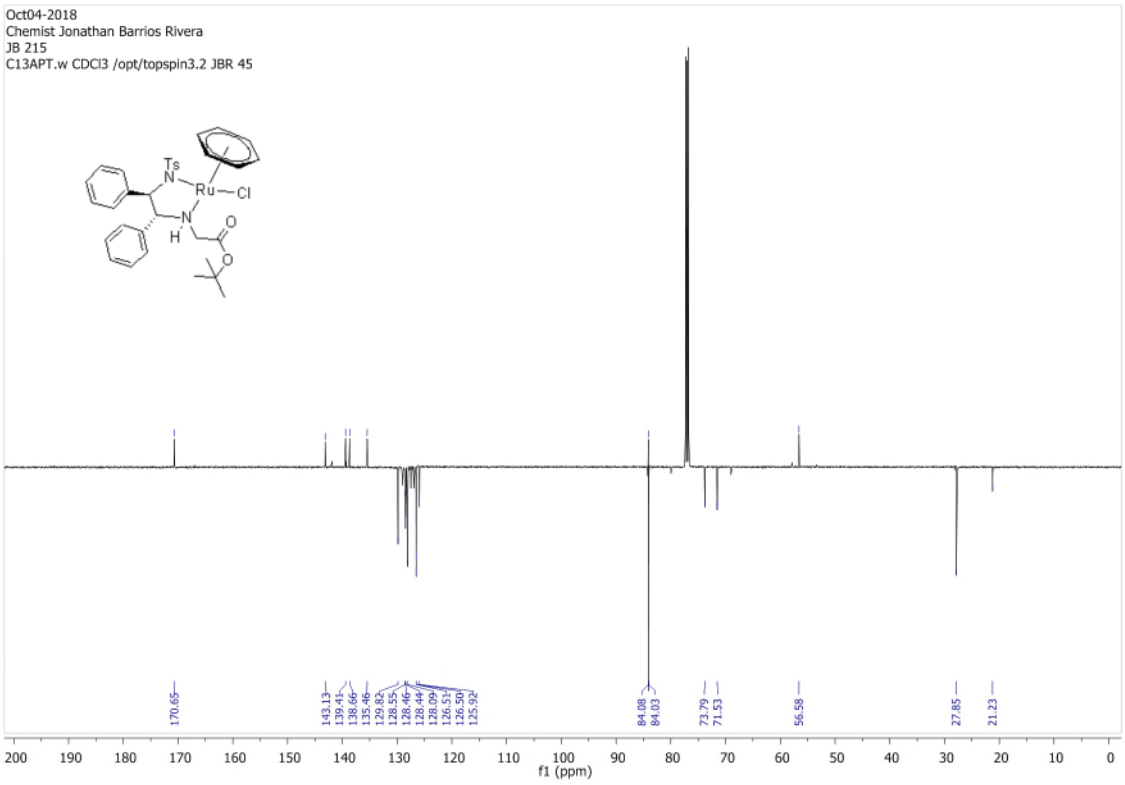


Complex formed from ligand 9 (20)

δ_H (500 MHz, $CDCl_3$)

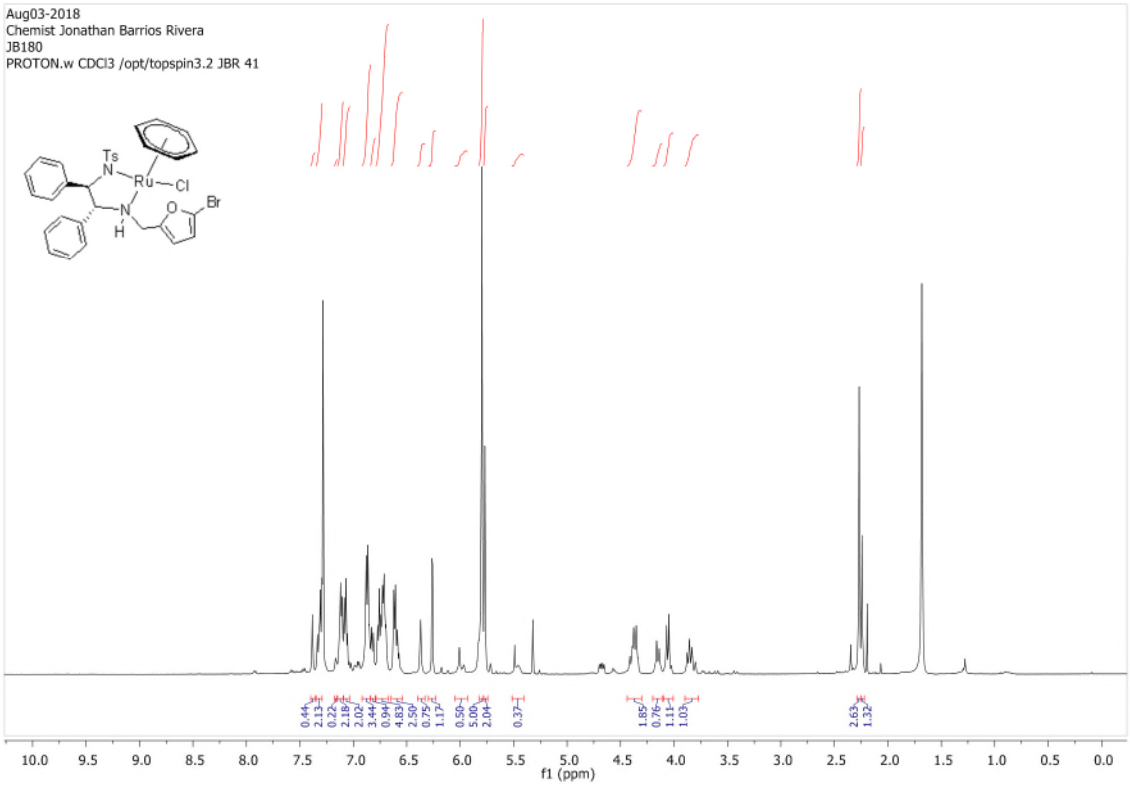


δ_C (126 MHz, $CDCl_3$)

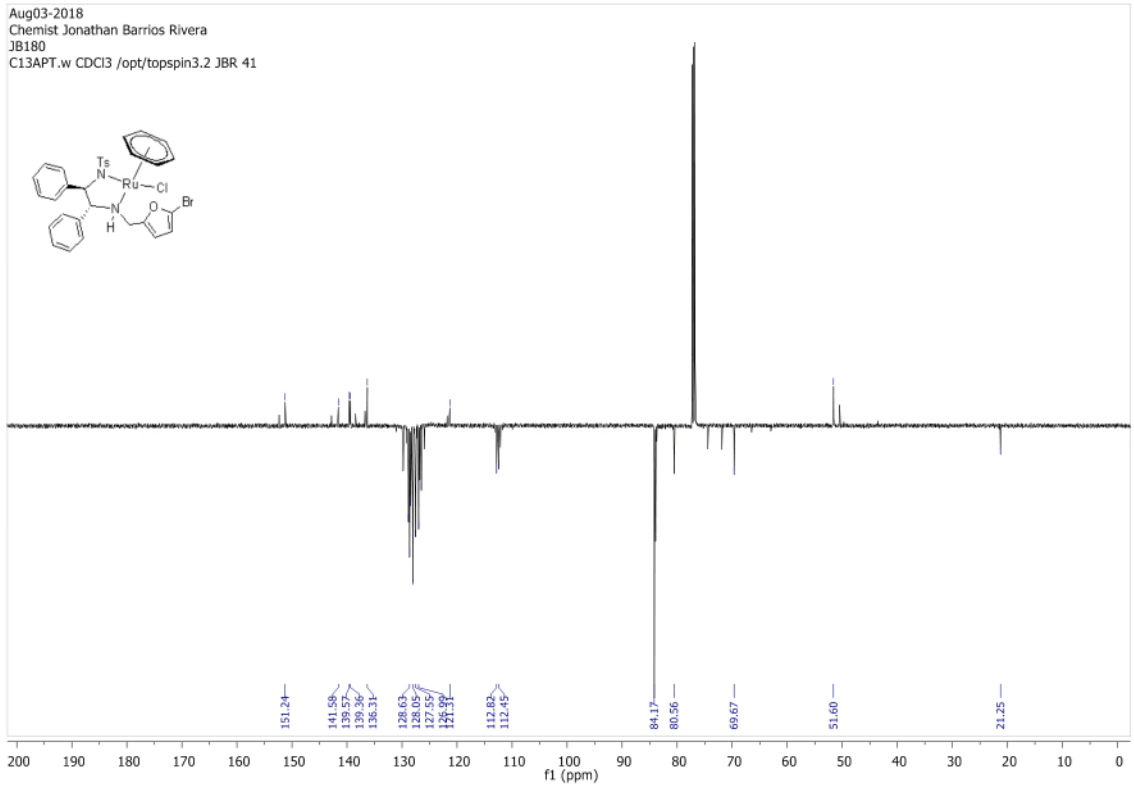


Complex formed from ligand 10 (21)

δ_H (500 MHz, $CDCl_3$)

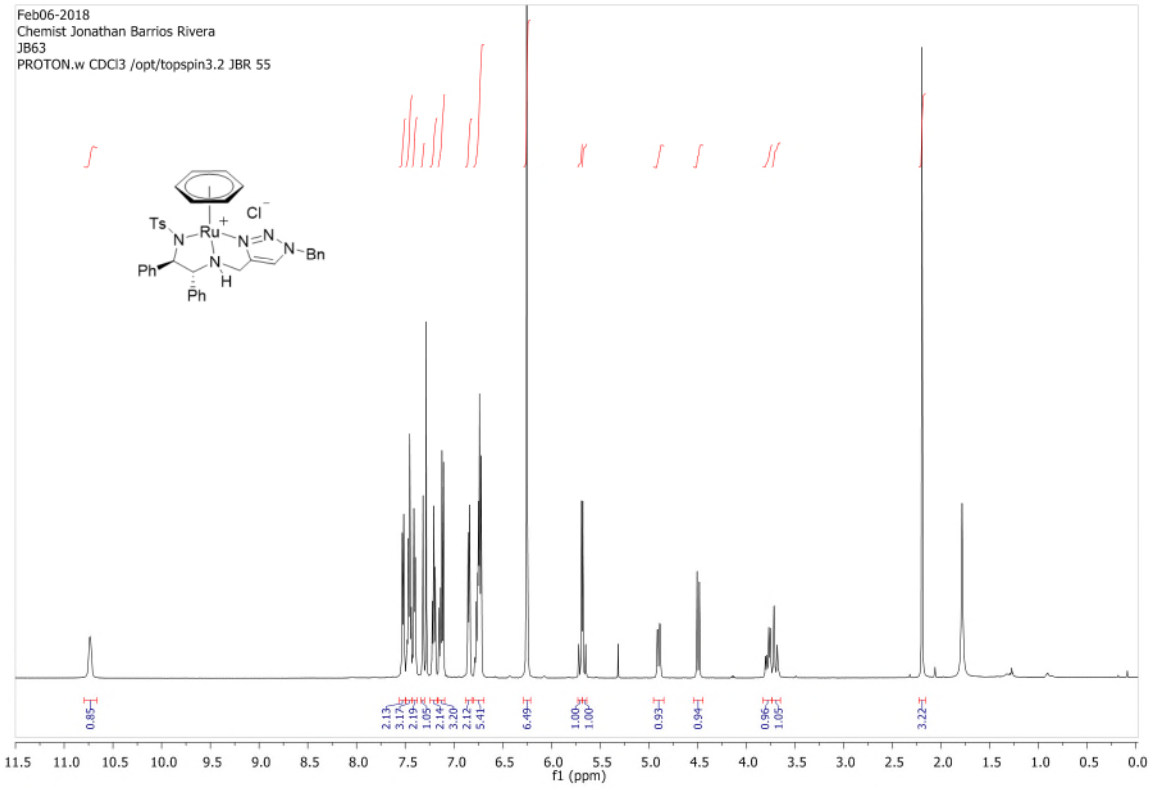


δ_C (126 MHz, $CDCl_3$)

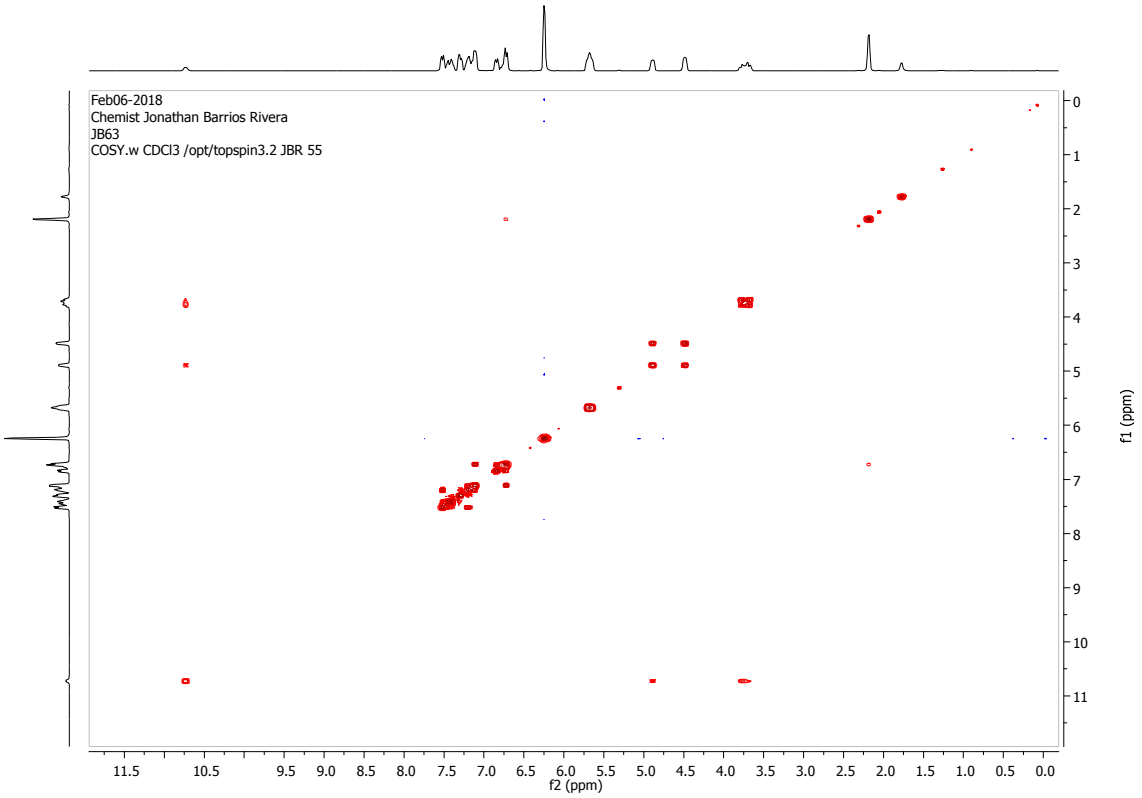


Complex from ligand 4 (22)

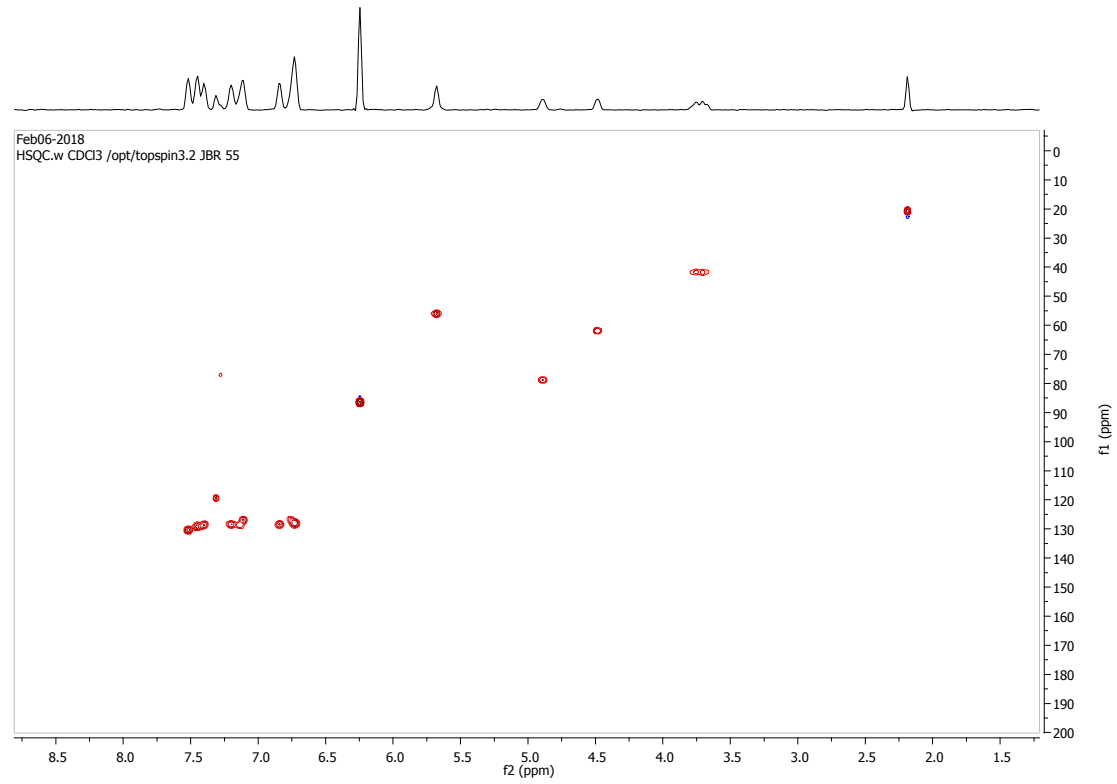
δ_H (500 MHz, $CDCl_3$)



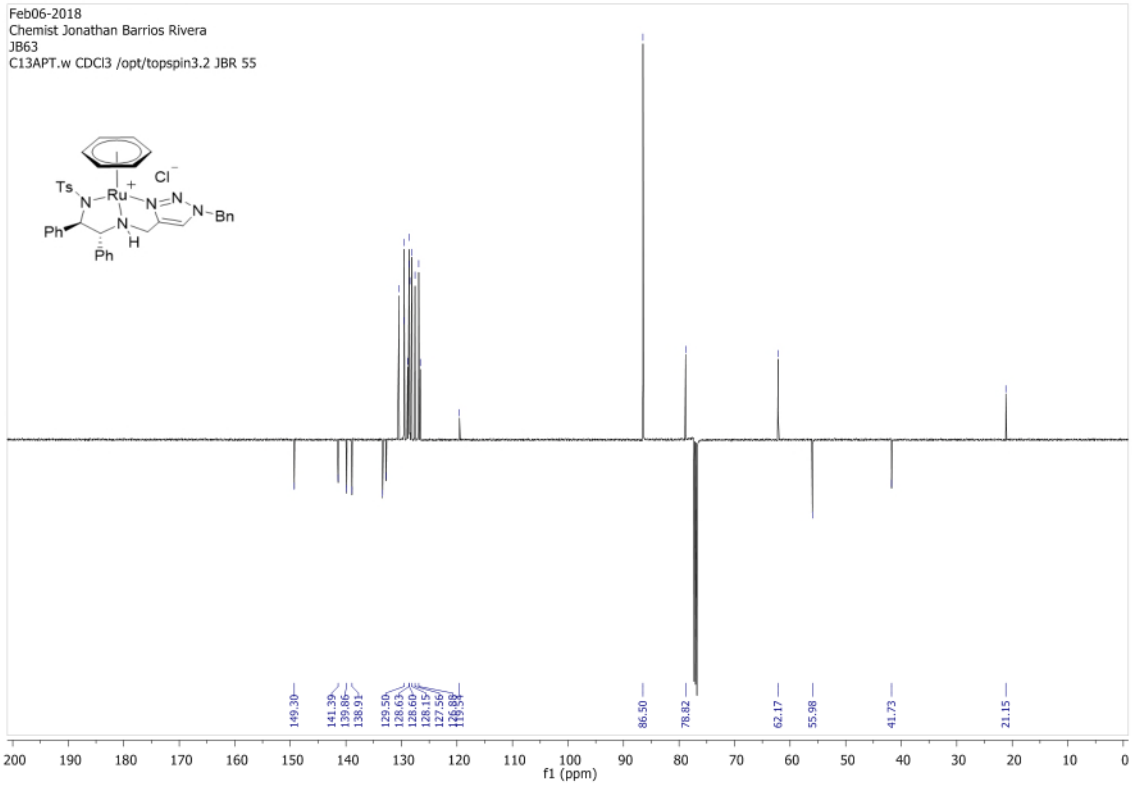
COSY (500 MHz, $CDCl_3$)



HSQC

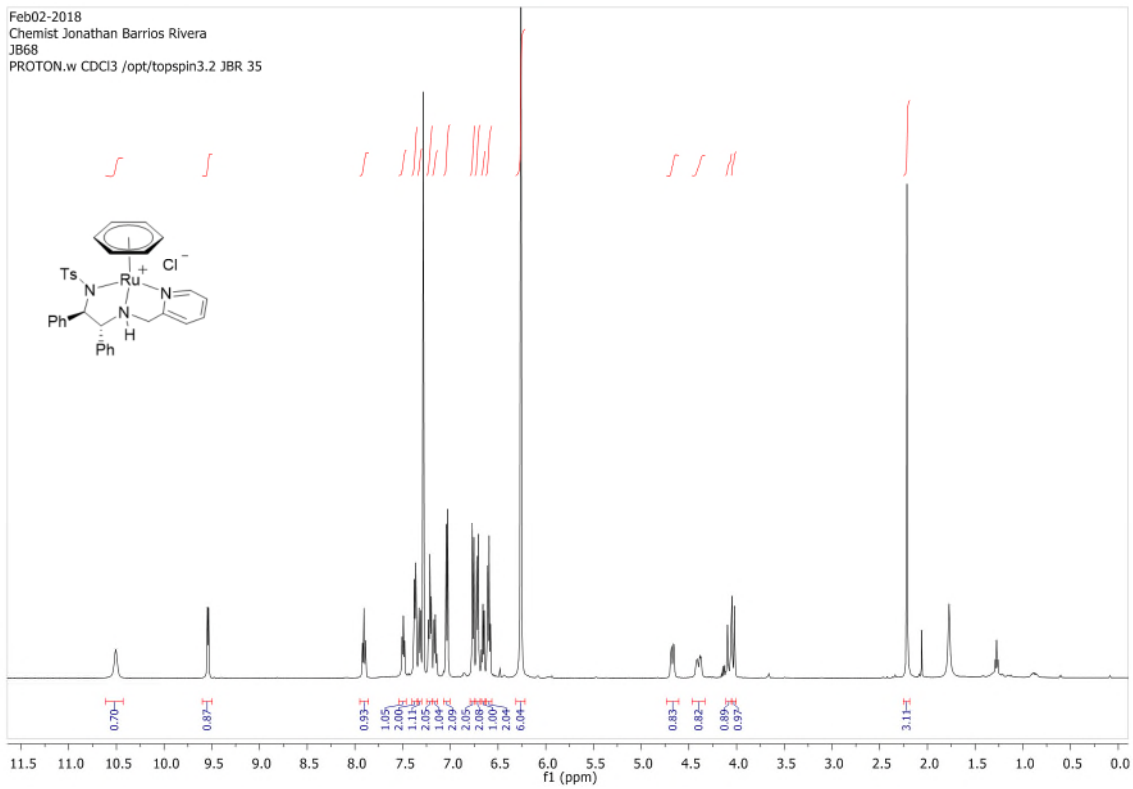


δ_C (125 MHz, $CDCl_3$)

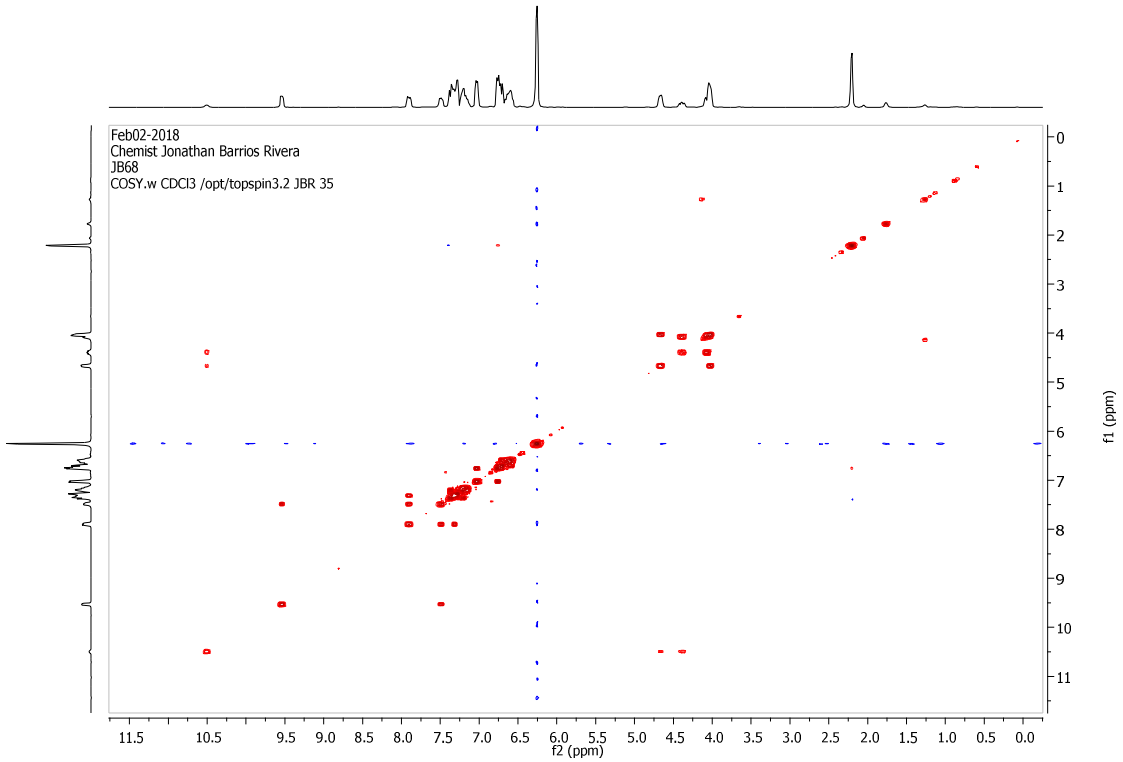


Complex from ligand 5 (23)

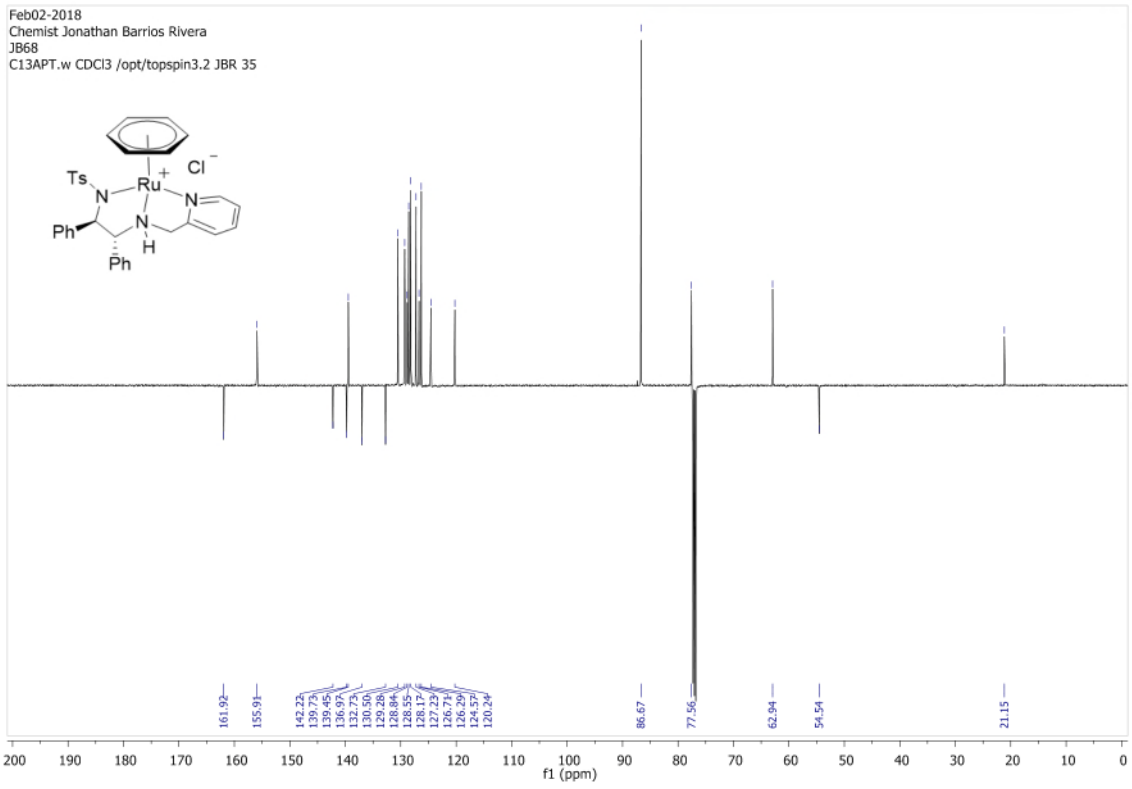
^1H NMR δ_H (500 MHz, $CDCl_3$)



COSY

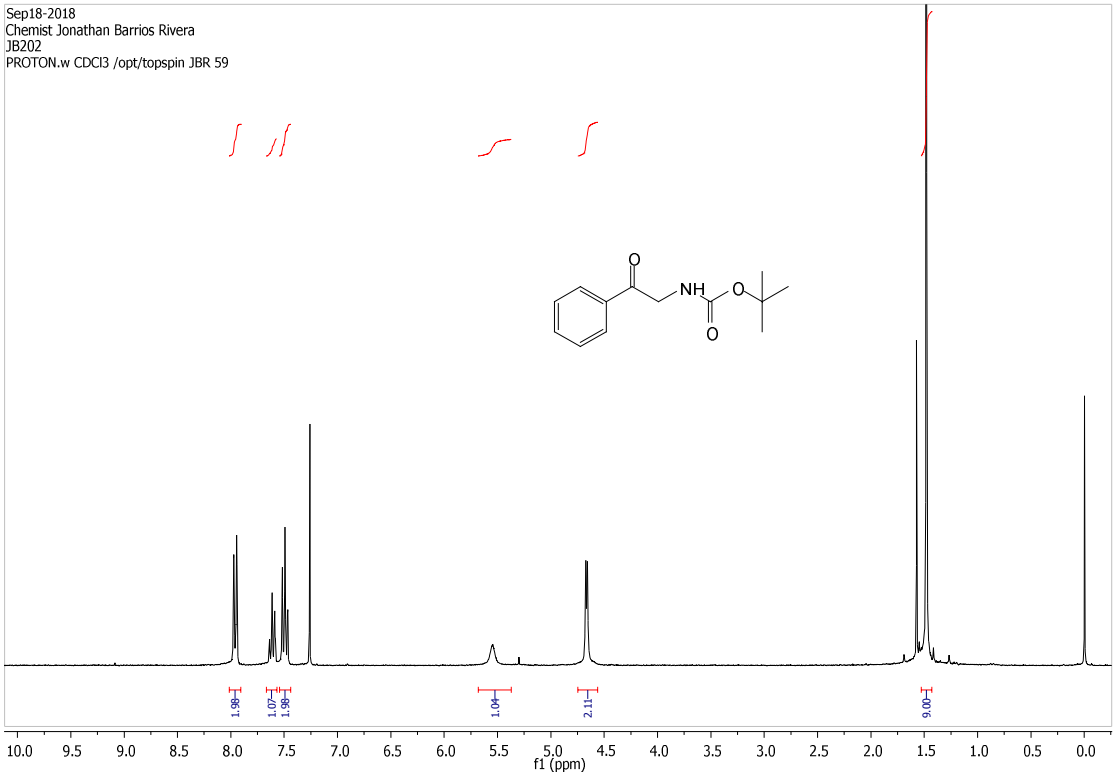


^{13}C NMR δ_C (125 MHz, $CDCl_3$)



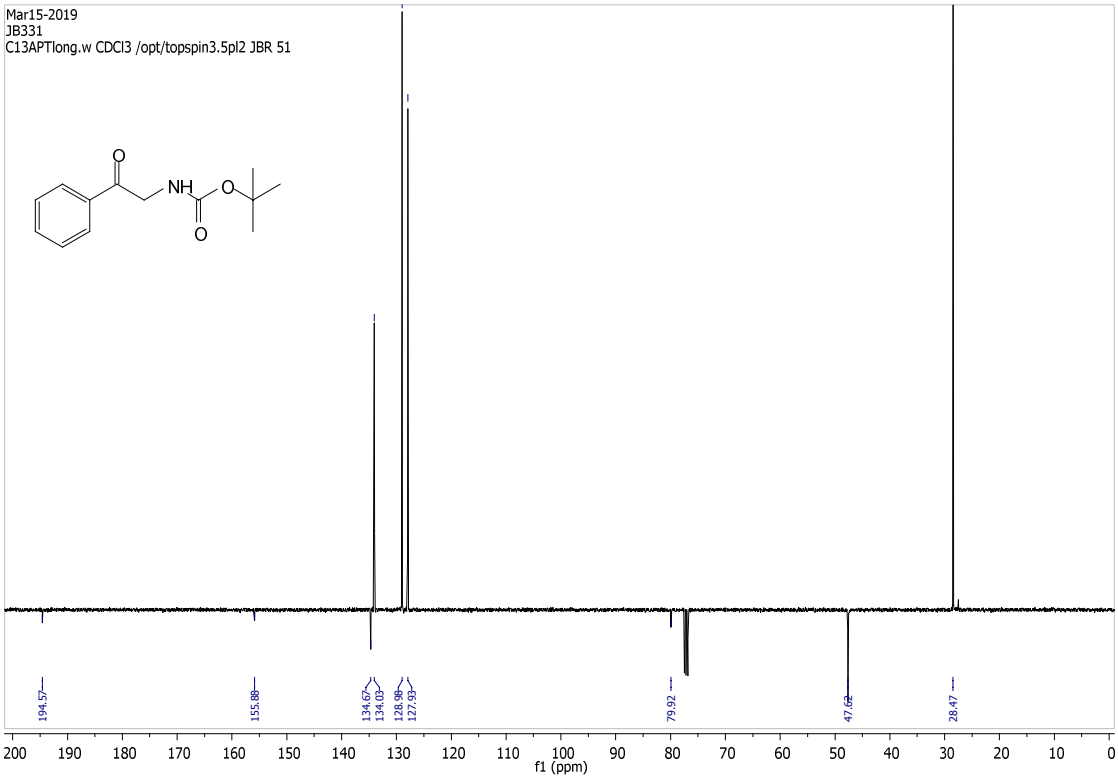
tert-Butyl (2-oxo-2-phenylethyl)carbamate

δ_H (300 MHz, $CDCl_3$)



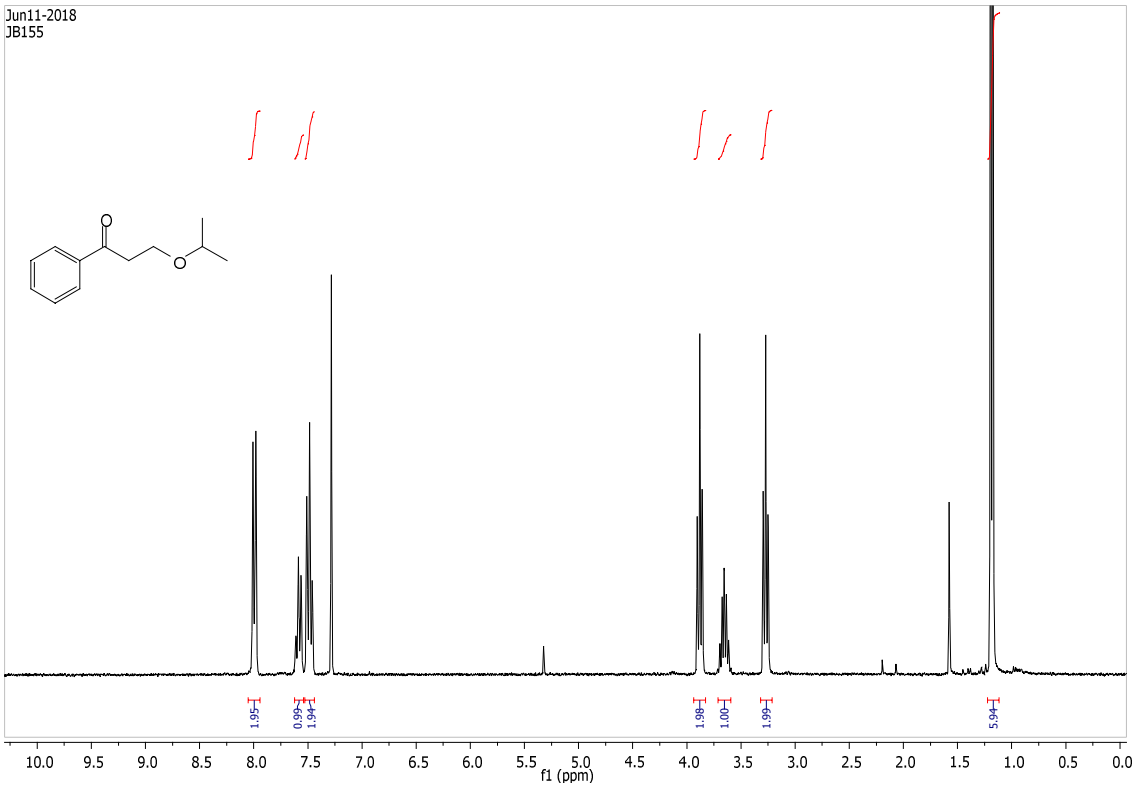
tert-Butyl (2-oxo-2-phenylethyl)carbamate

δ_C (101 MHz, $CDCl_3$)



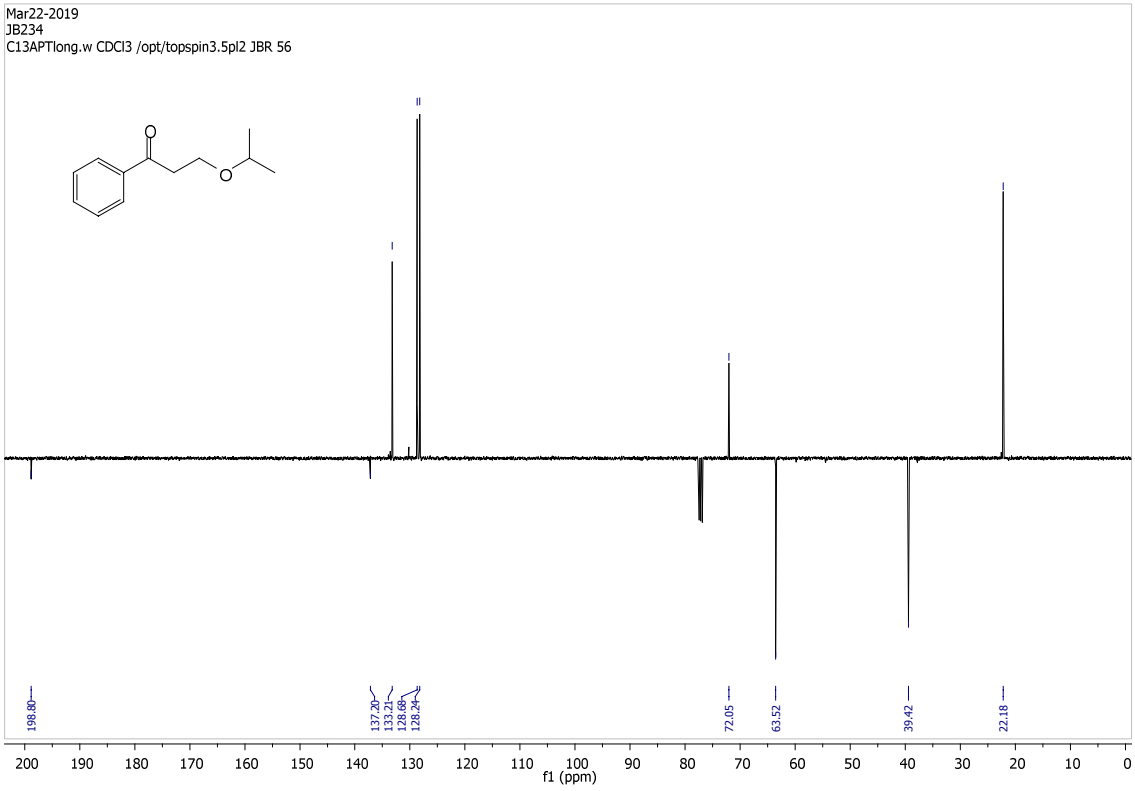
3-Isopropoxy-1-phenylpropan-1-one

δ_H (300 MHz, $CDCl_3$)



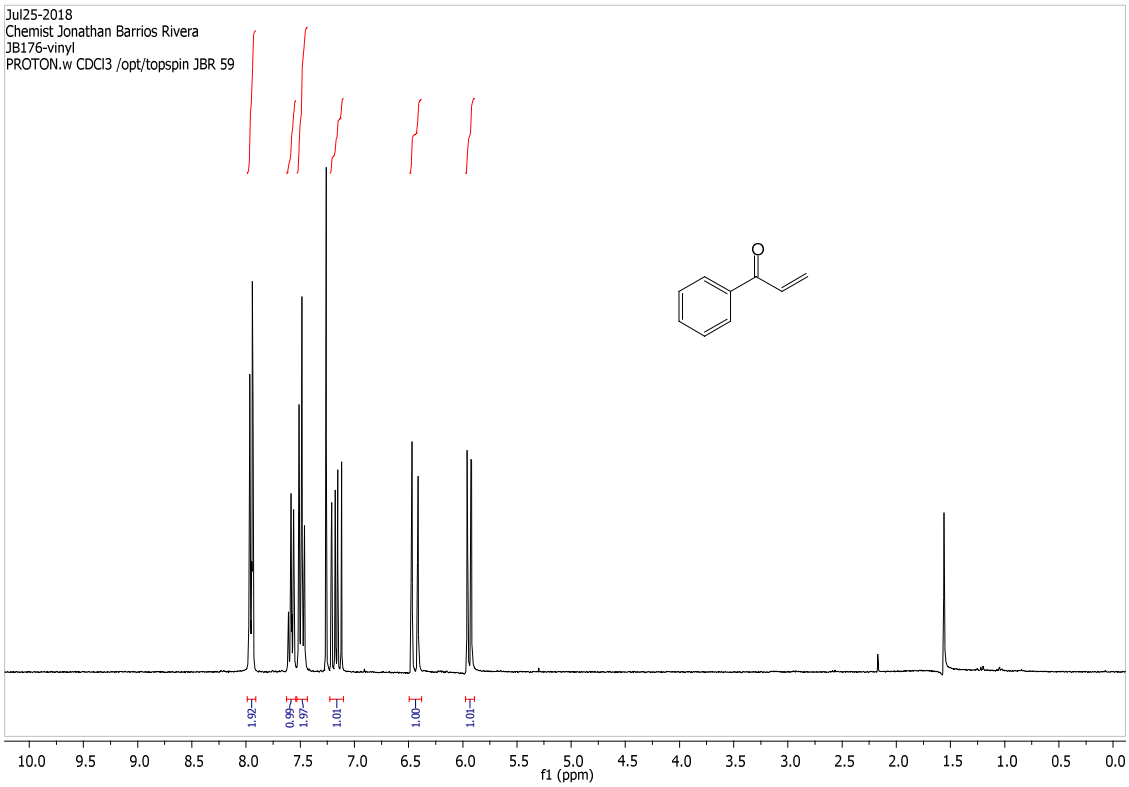
3-Isopropoxy-1-phenylpropan-1-one

δ_C (101 MHz, $CDCl_3$)



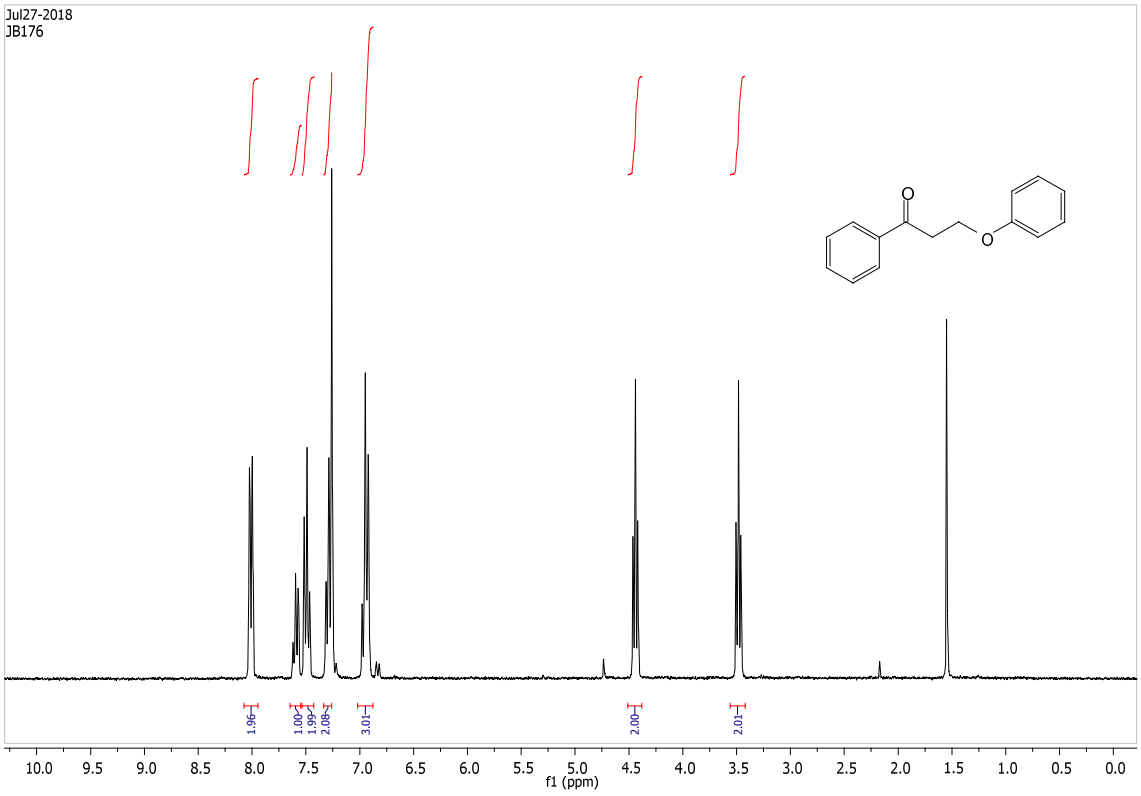
1-Phenylprop-2-en-1-one

δ_H (300 MHz, $CDCl_3$)



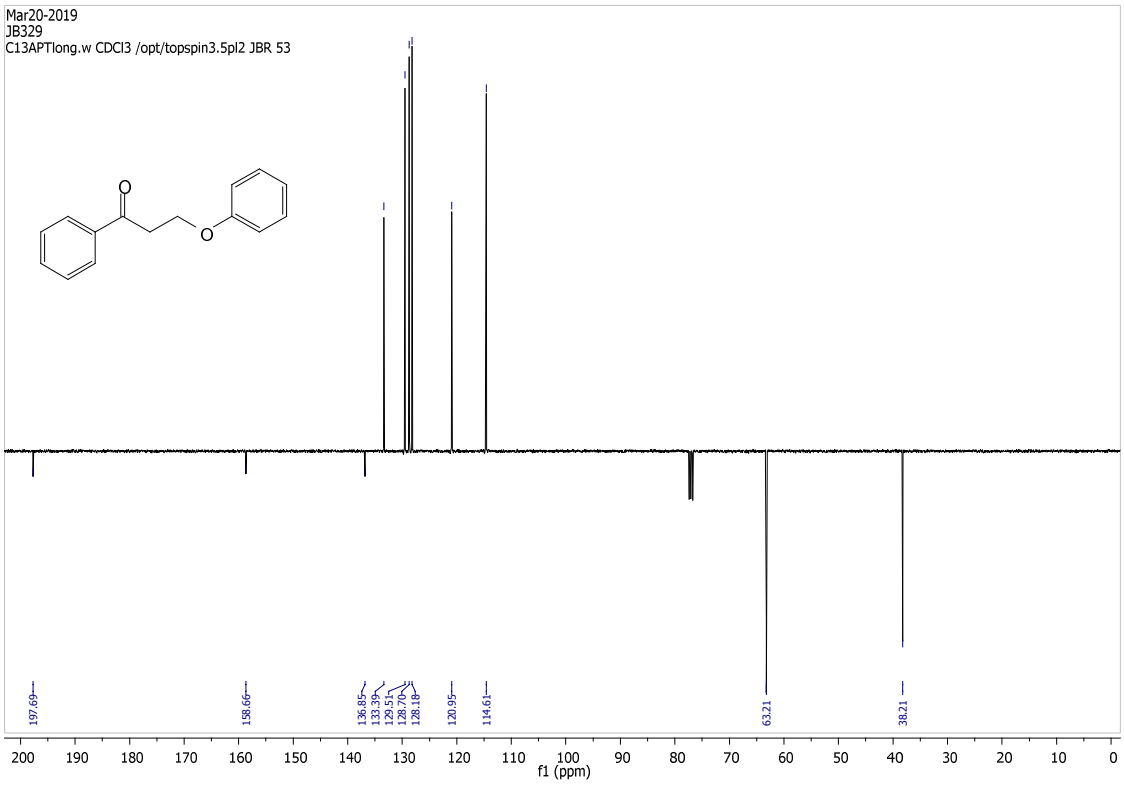
3-Phenoxy-1-phenylpropan-1-one

δ_H (300 MHz, $CDCl_3$)



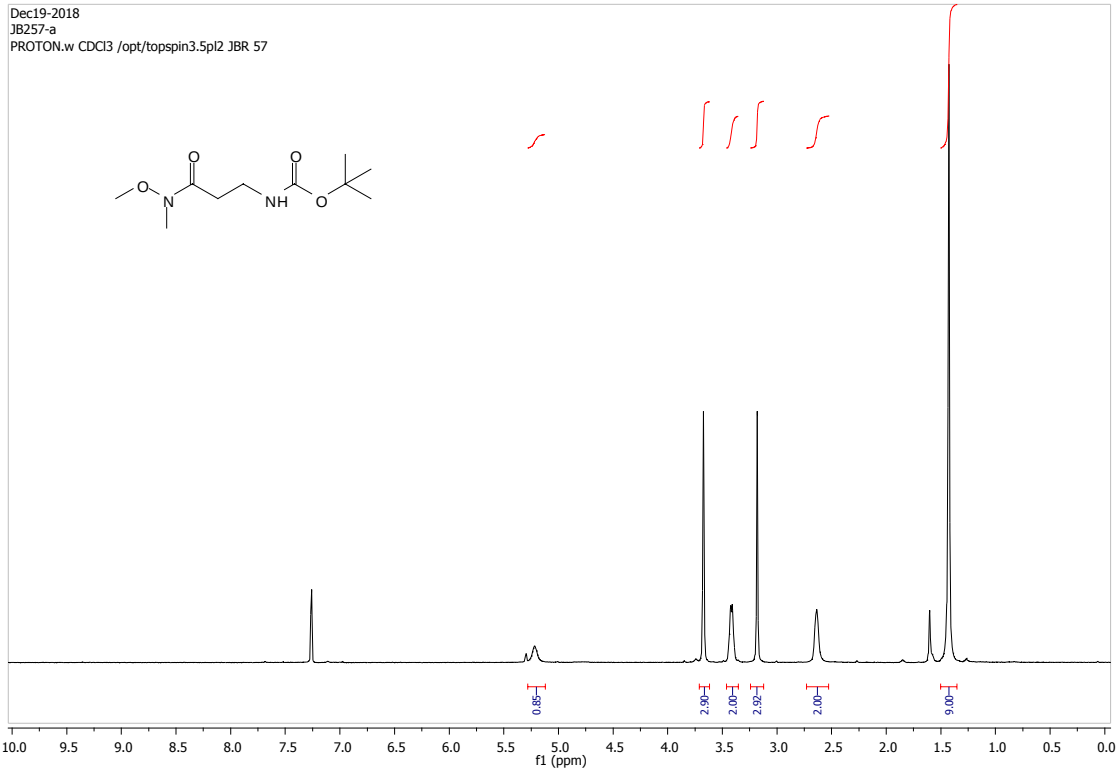
3-Phenoxy-1-phenylpropan-1-one

δ_C (101 MHz, $CDCl_3$)



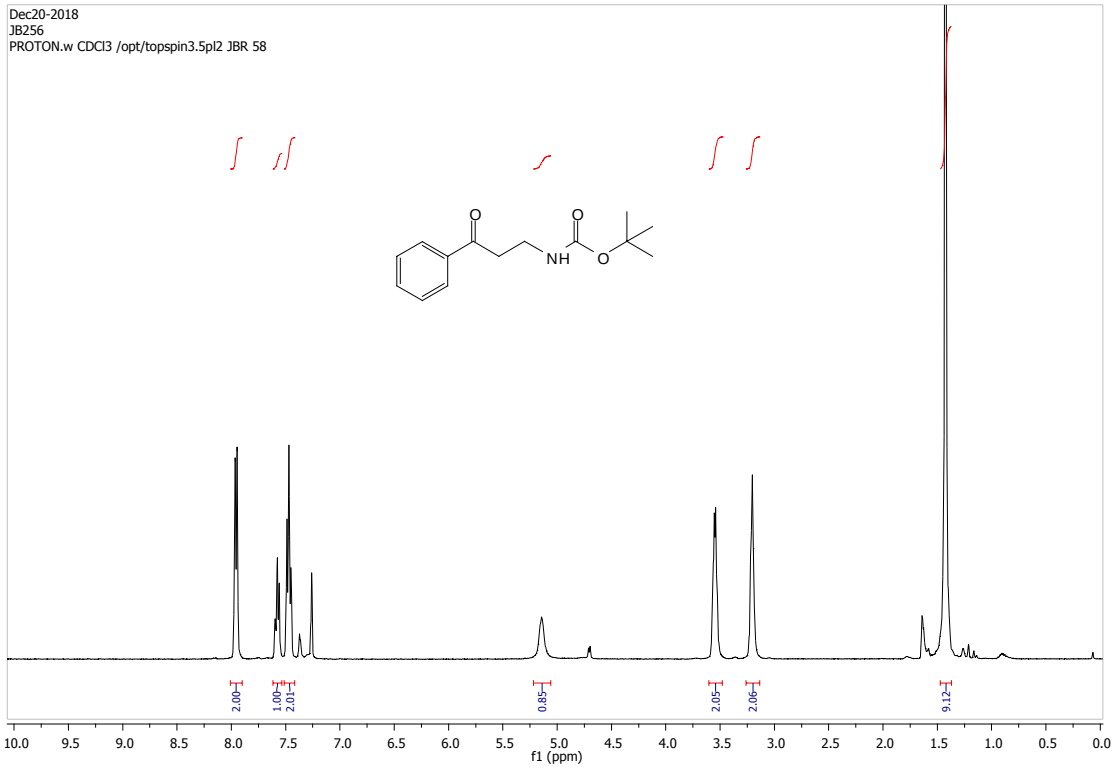
tert-Butyl 3-(methoxy(methyl)amino)-3-oxopropylcarbamate

δ_H (400 MHz, $CDCl_3$)



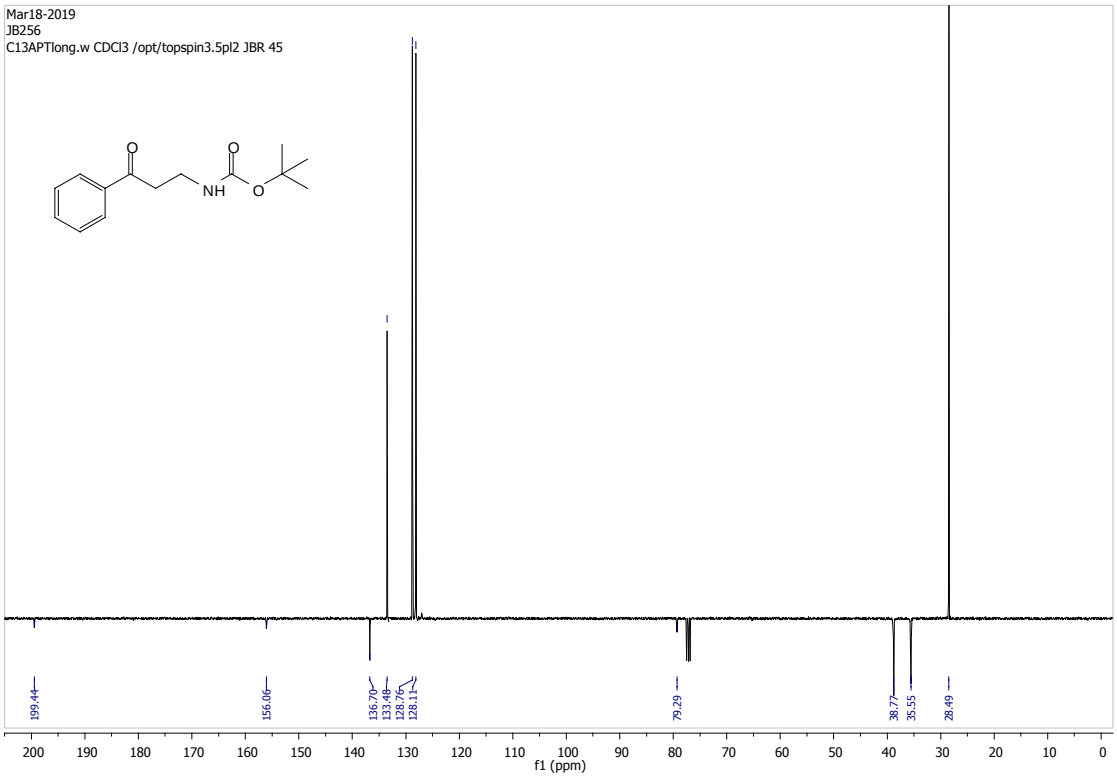
***tert*-Butyl 3-oxo-3-phenylpropylcarbamate**

δ_H (400 MHz, $CDCl_3$)



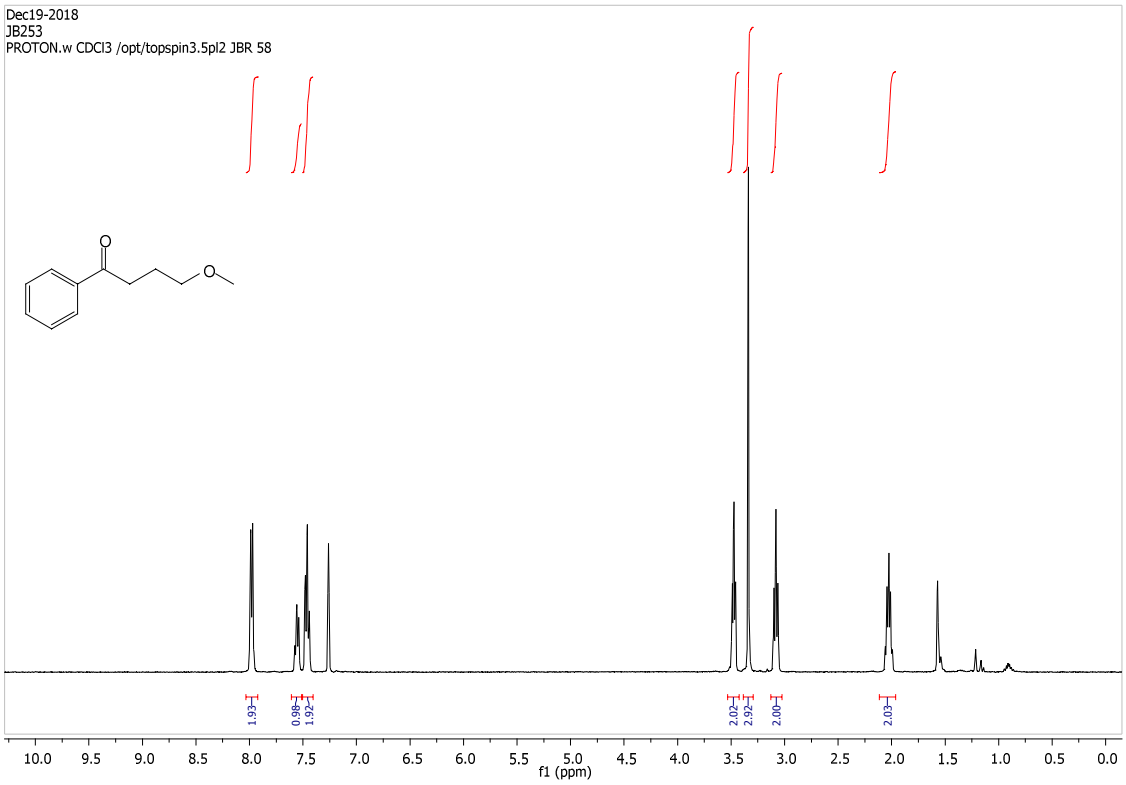
tert-Butyl 3-oxo-3-phenylpropylcarbamate

δ_C (101 MHz, $CDCl_3$)



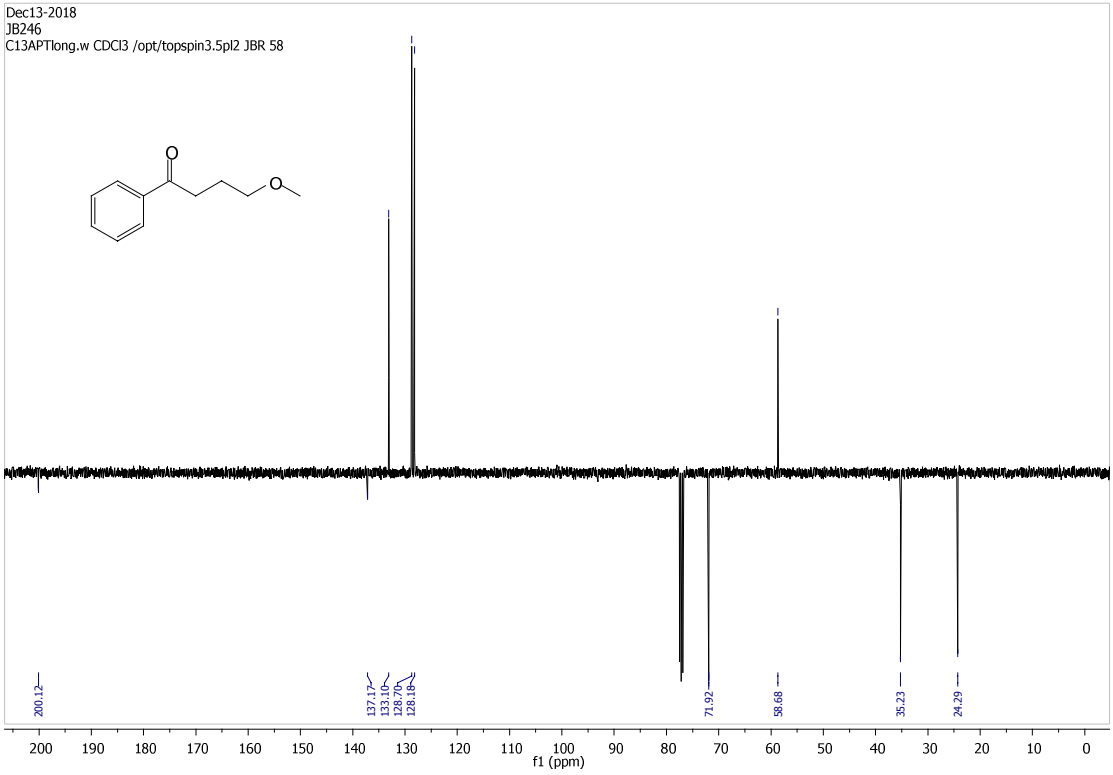
4-Methoxy-1-phenylbutan-1-one

δ_H (400 MHz, $CDCl_3$)



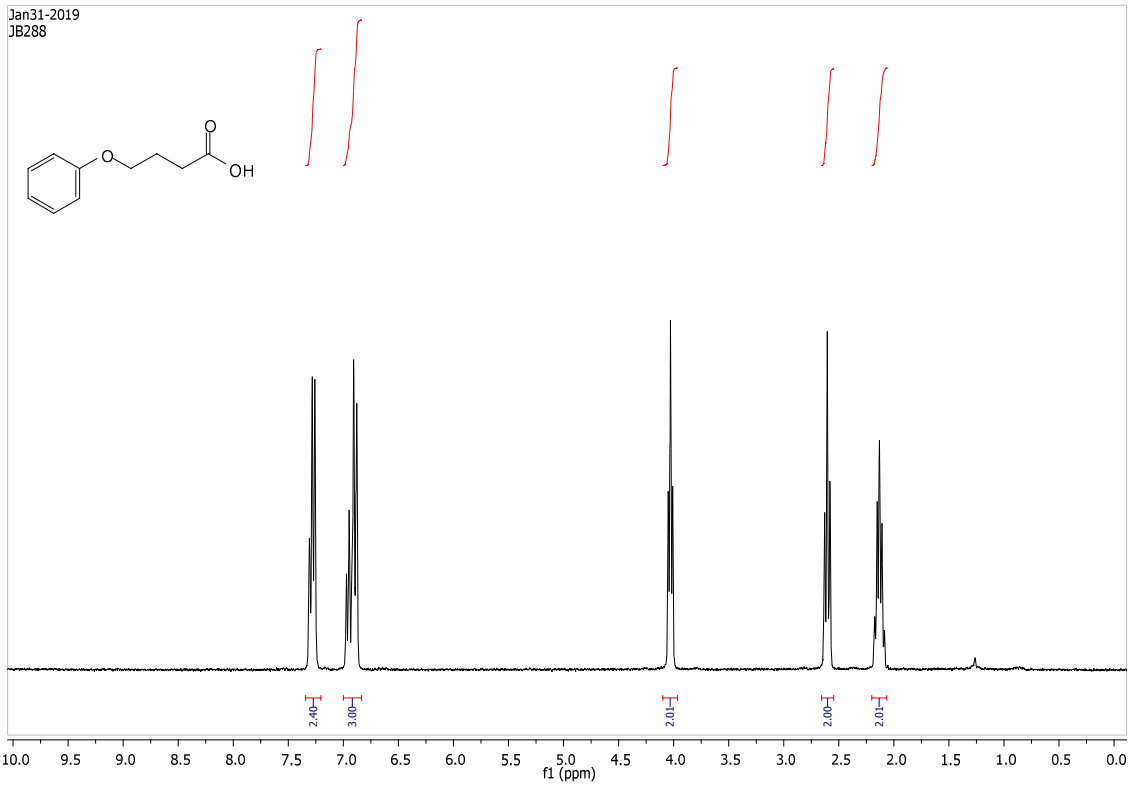
4-Methoxy-1-phenylbutan-1-one

δ_C (101 MHz, $CDCl_3$)



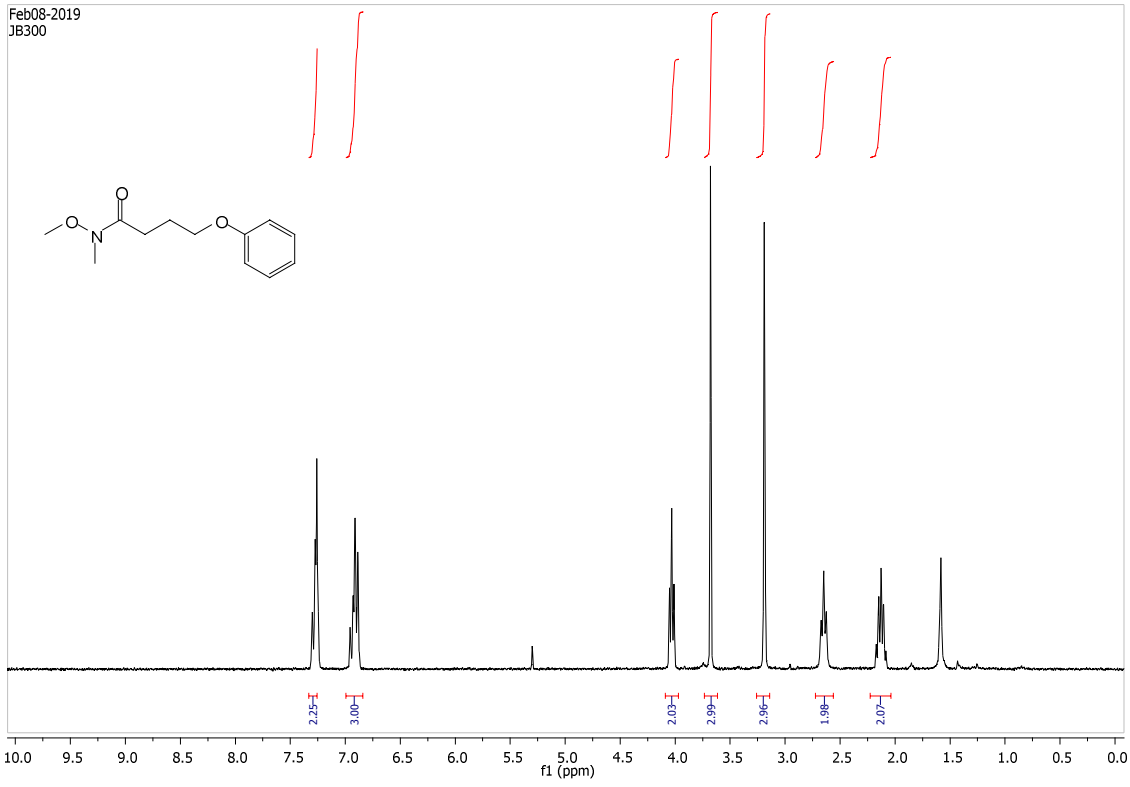
4-Phenoxybutanoic acid

δ_H (300 MHz, $CDCl_3$)



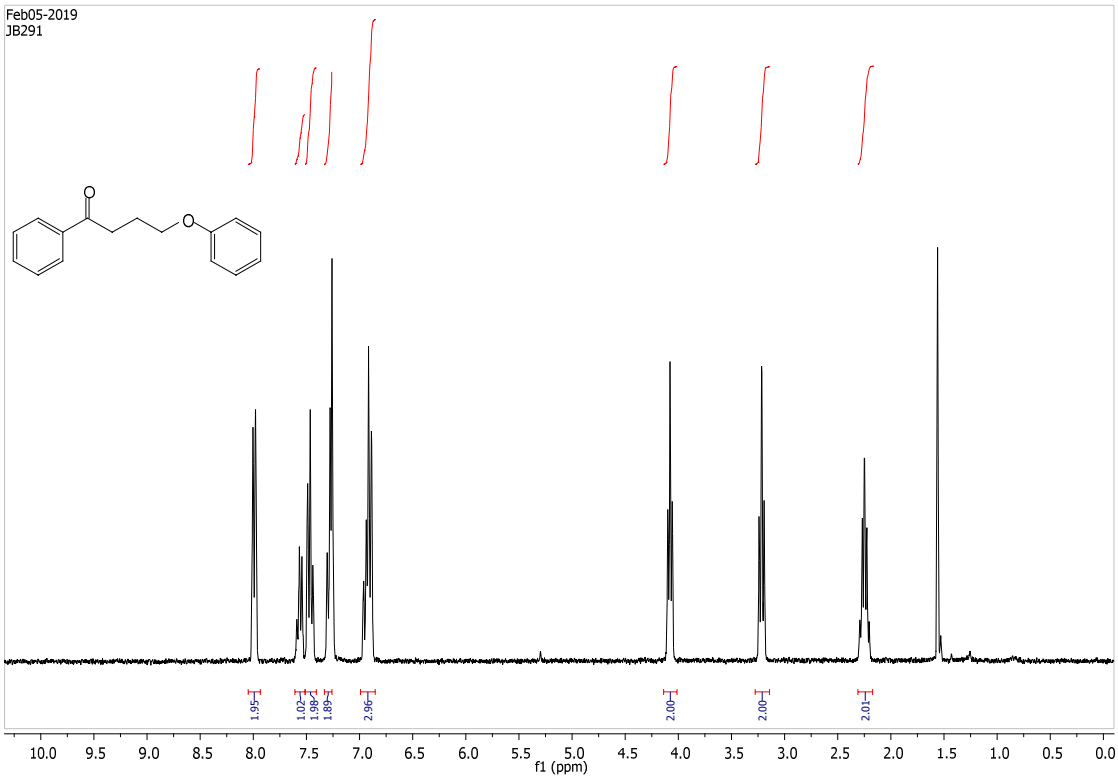
***N*-Methoxy-*N*-methyl-4-phenoxybutanamide**

δ_H (300 MHz, $CDCl_3$)



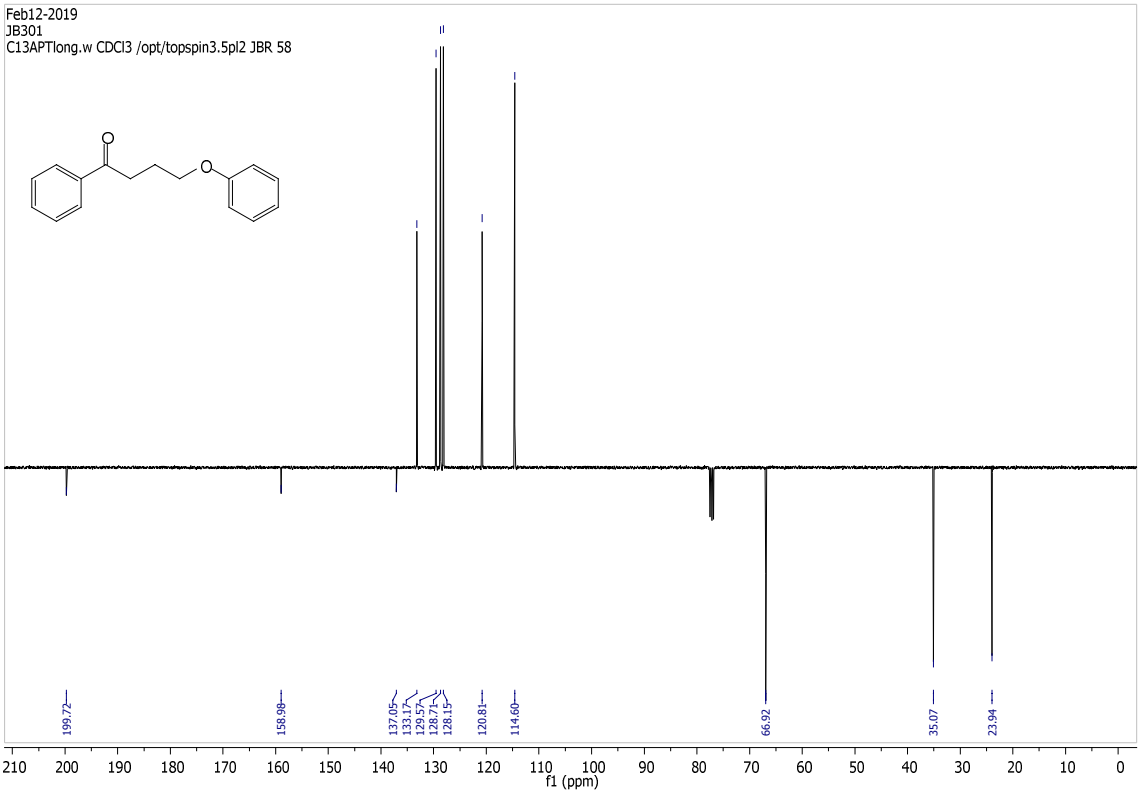
4-Phenoxy-1-phenylbutan-1-one

δ_H (300 MHz, $CDCl_3$)



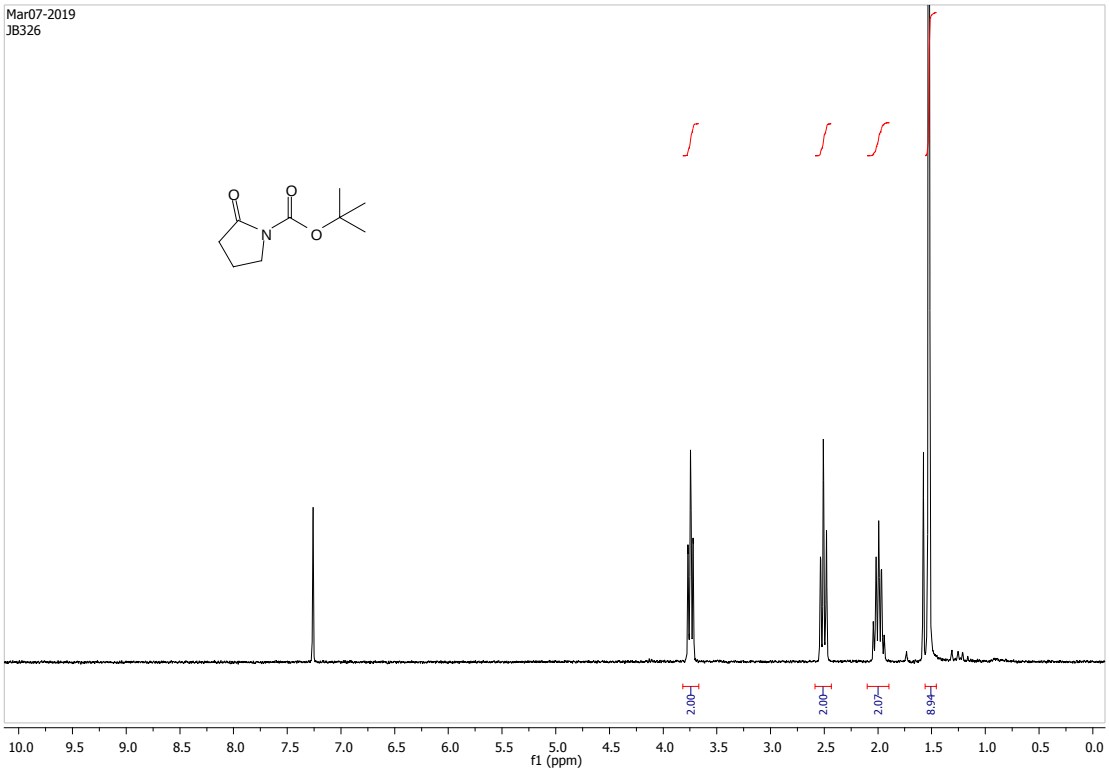
4-Phenoxy-1-phenylbutan-1-one

δ_C (101 MHz, $CDCl_3$)



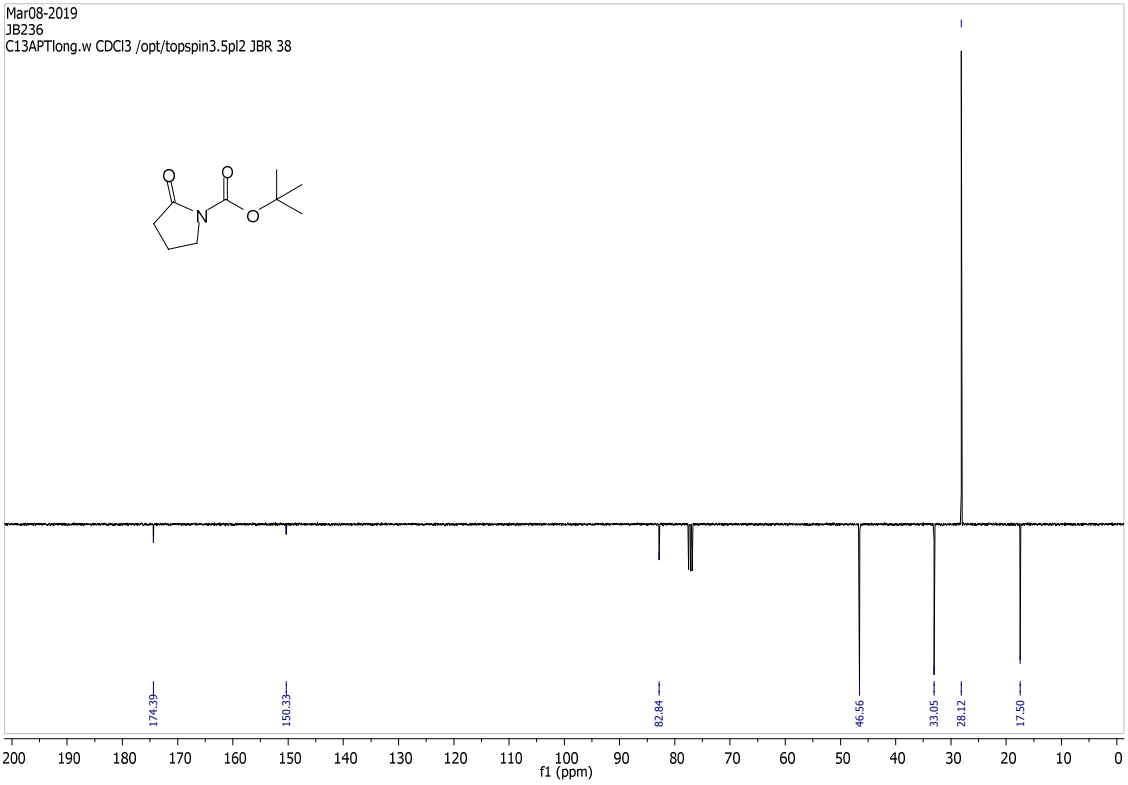
tert-Butyl 2-oxopyrrolidine-1-carboxylate

δ_H (300 MHz, $CDCl_3$)



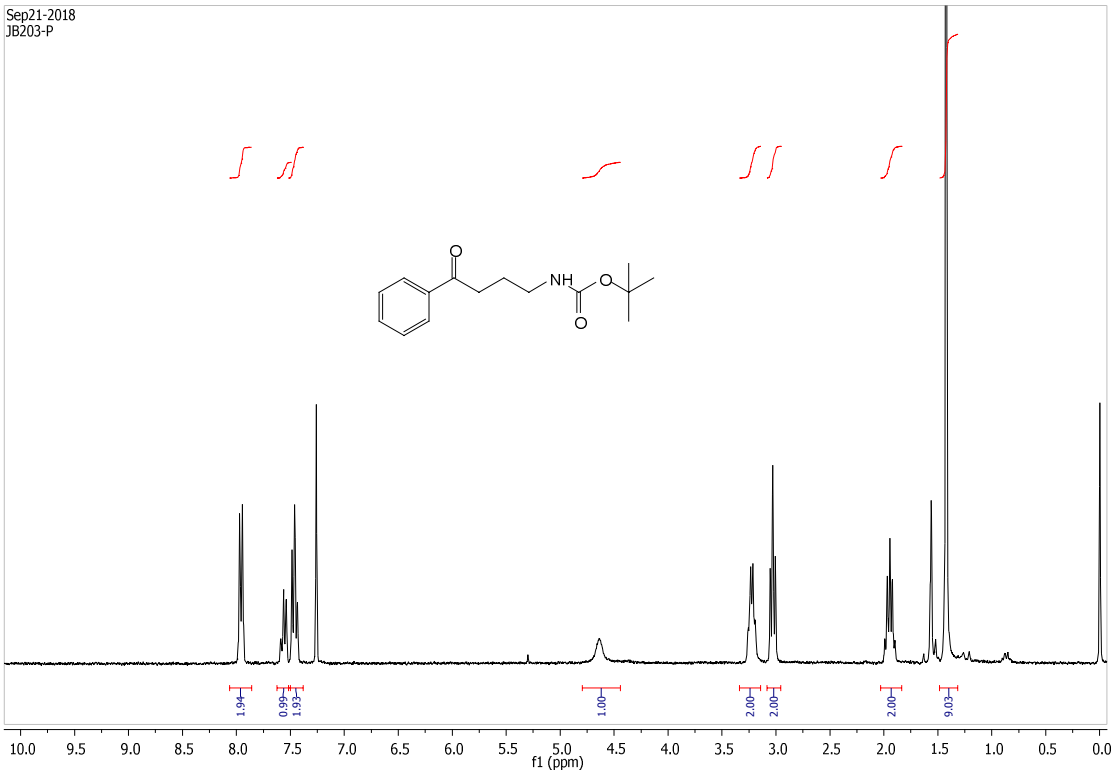
tert-Butyl 2-oxopyrrolidine-1-carboxylate

δ_C (101 MHz, $CDCl_3$)



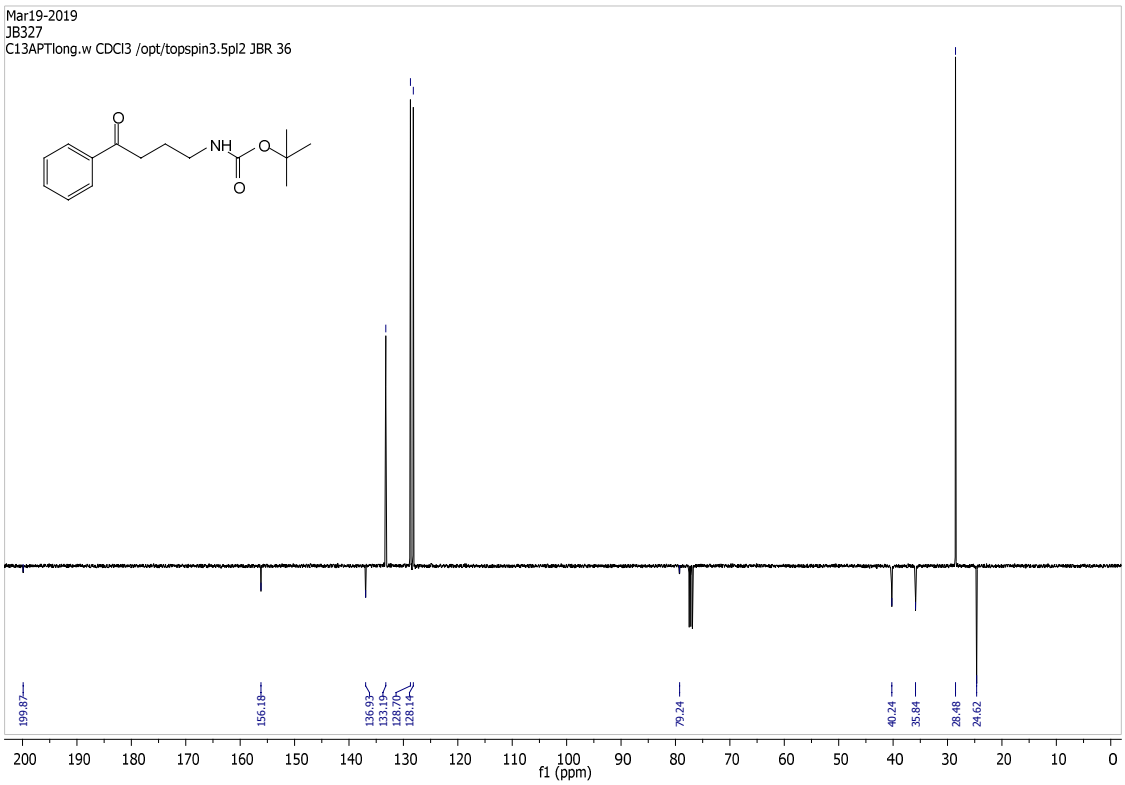
tert-Butyl (4-oxo-4-phenylbutyl)carbamate

δ_H (300 MHz, $CDCl_3$)



tert-Butyl (4-oxo-4-phenylbutyl)carbamate

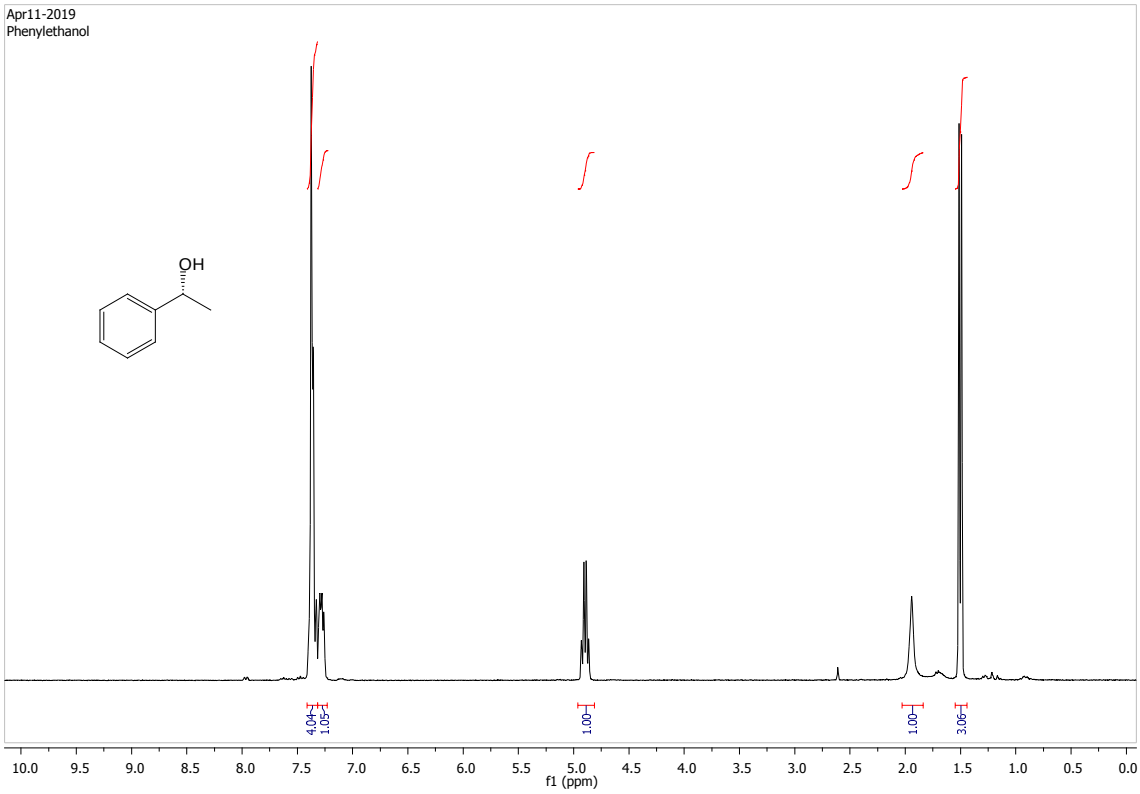
δ_C (101 MHz, $CDCl_3$)



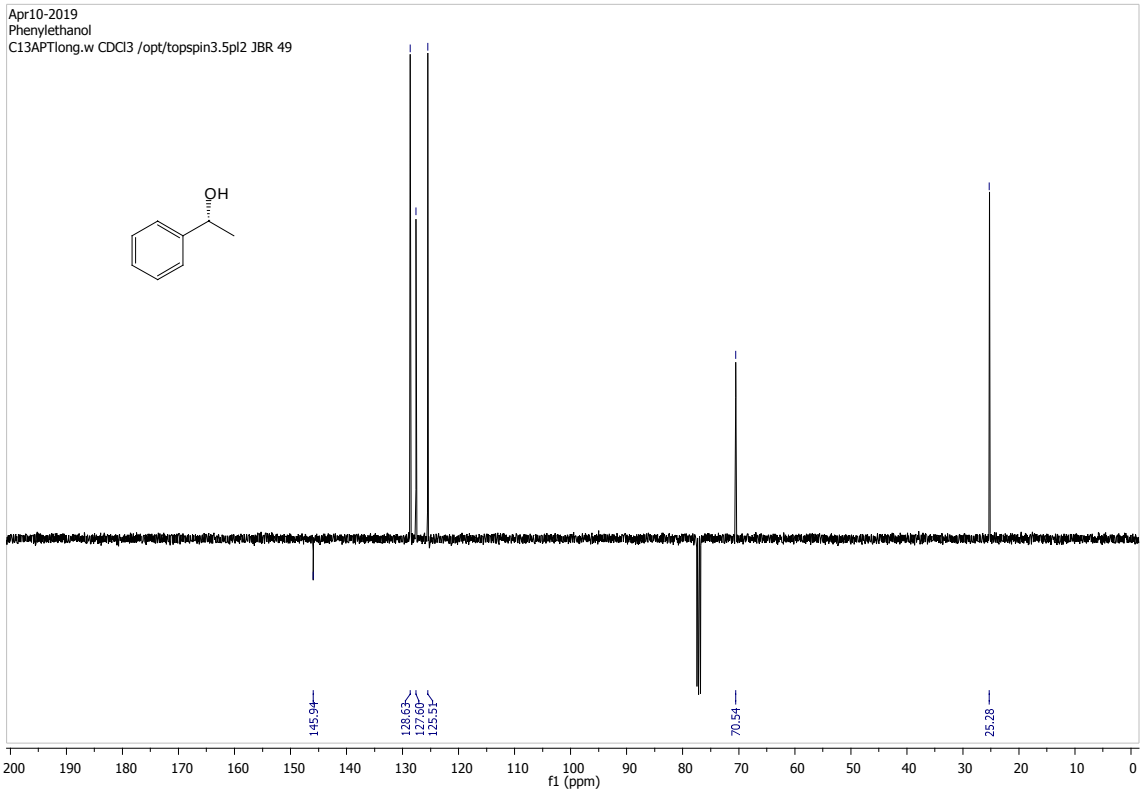
Reduction products NMR

(*R*)-1-Phenylethan-1-ol

δ_H (300 MHz, $CDCl_3$)

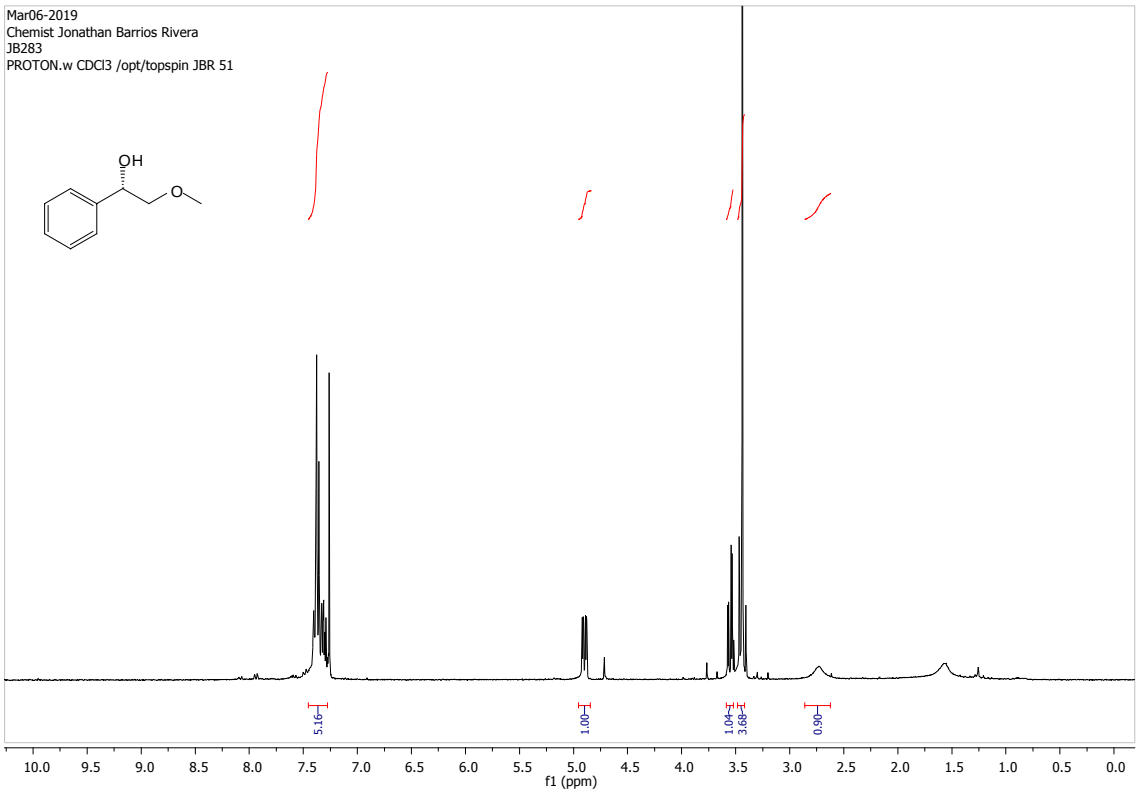


δ_C (101 MHz, $CDCl_3$)

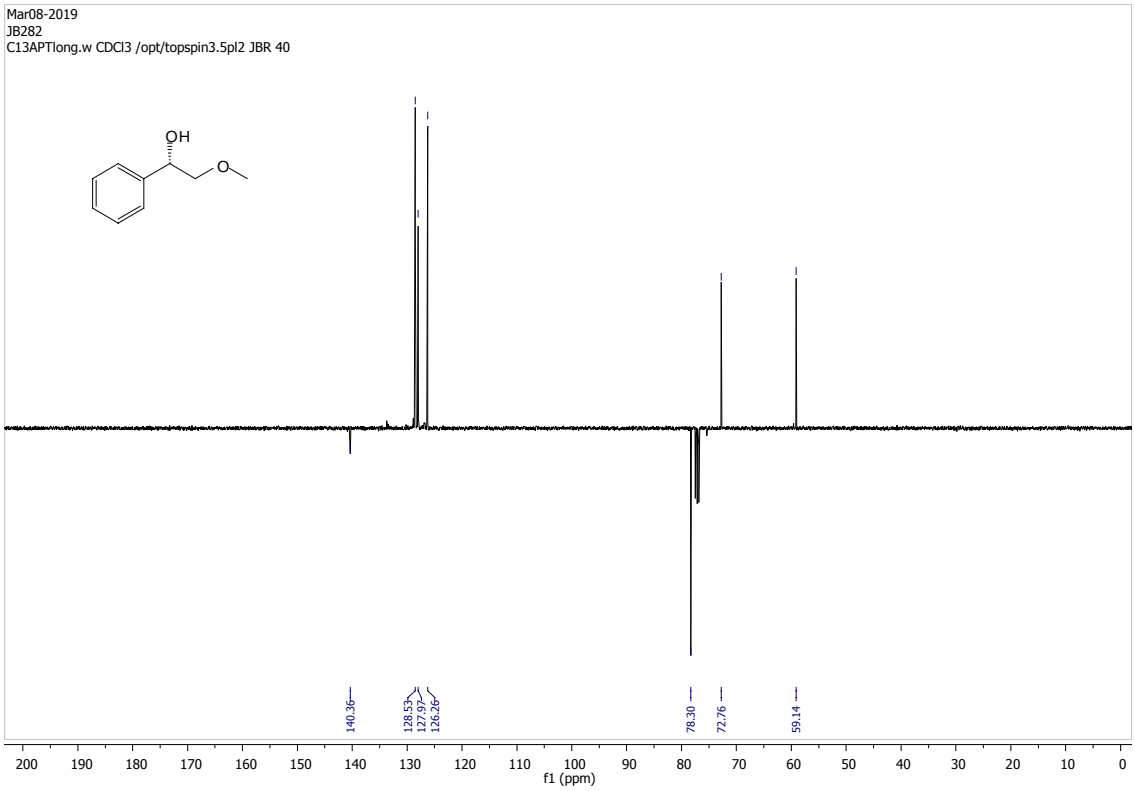


(*S*)-2-Methoxy-1-phenylethan-1-ol (24)

δ_H (300 MHz, $CDCl_3$)

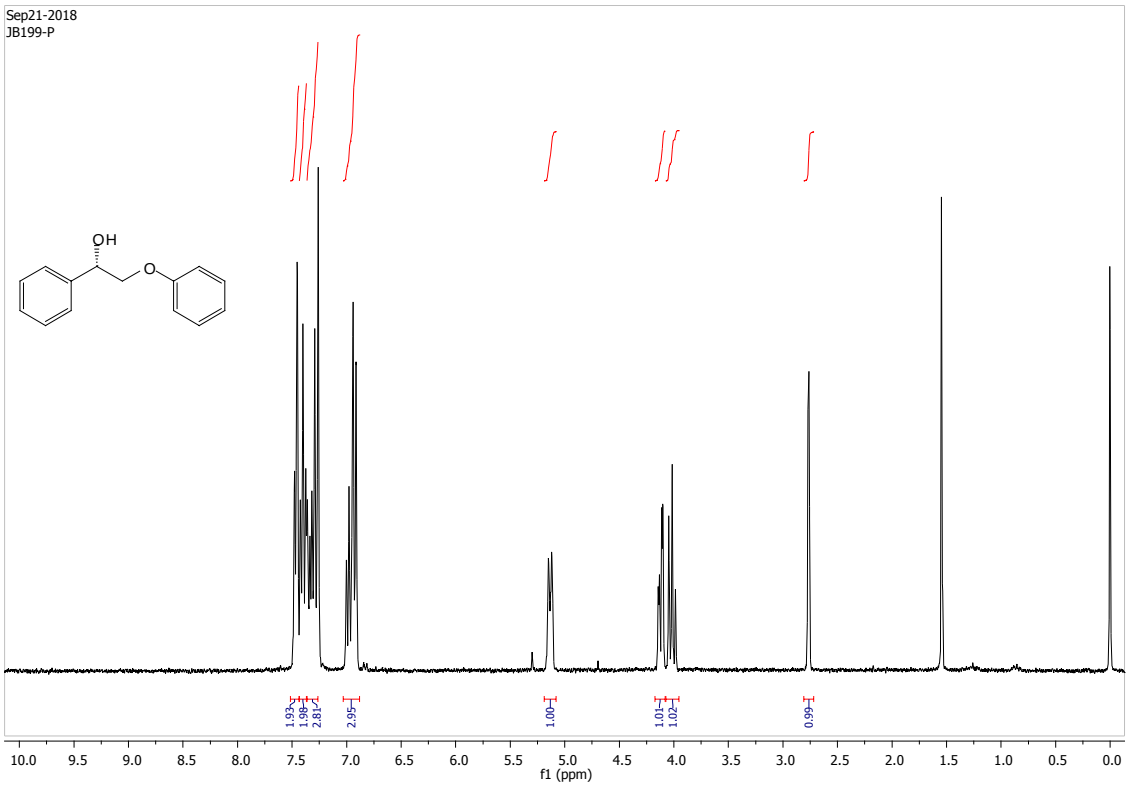


δ_C (101 MHz, $CDCl_3$)

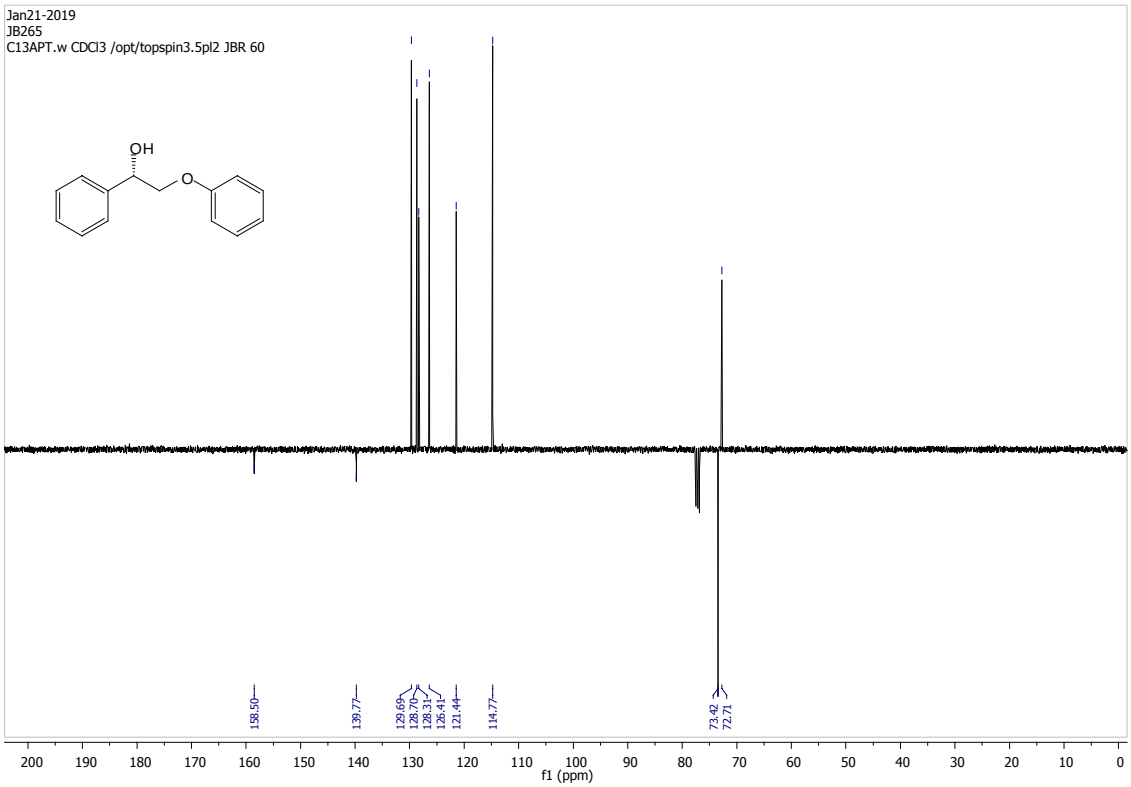


(*S*)-2-Phenoxy-1-phenylethan-1-ol (25)

δ_H (300 MHz, $CDCl_3$)

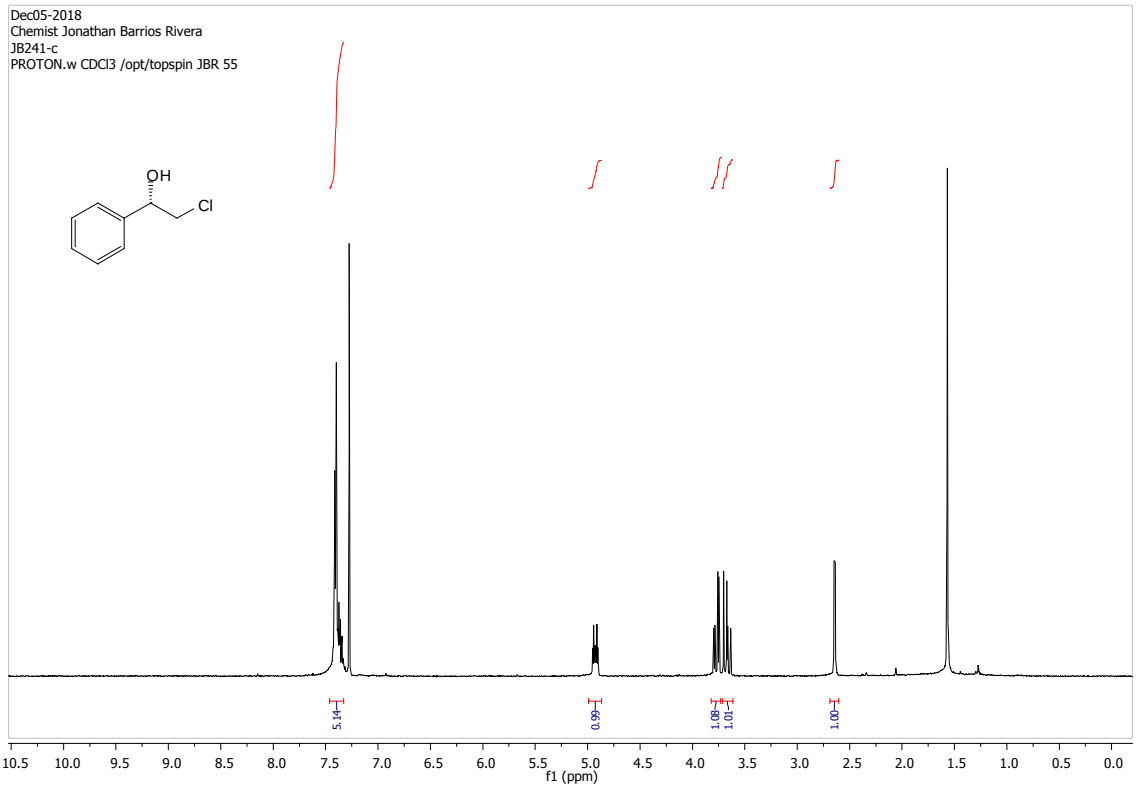


δ_C (101 MHz, $CDCl_3$)

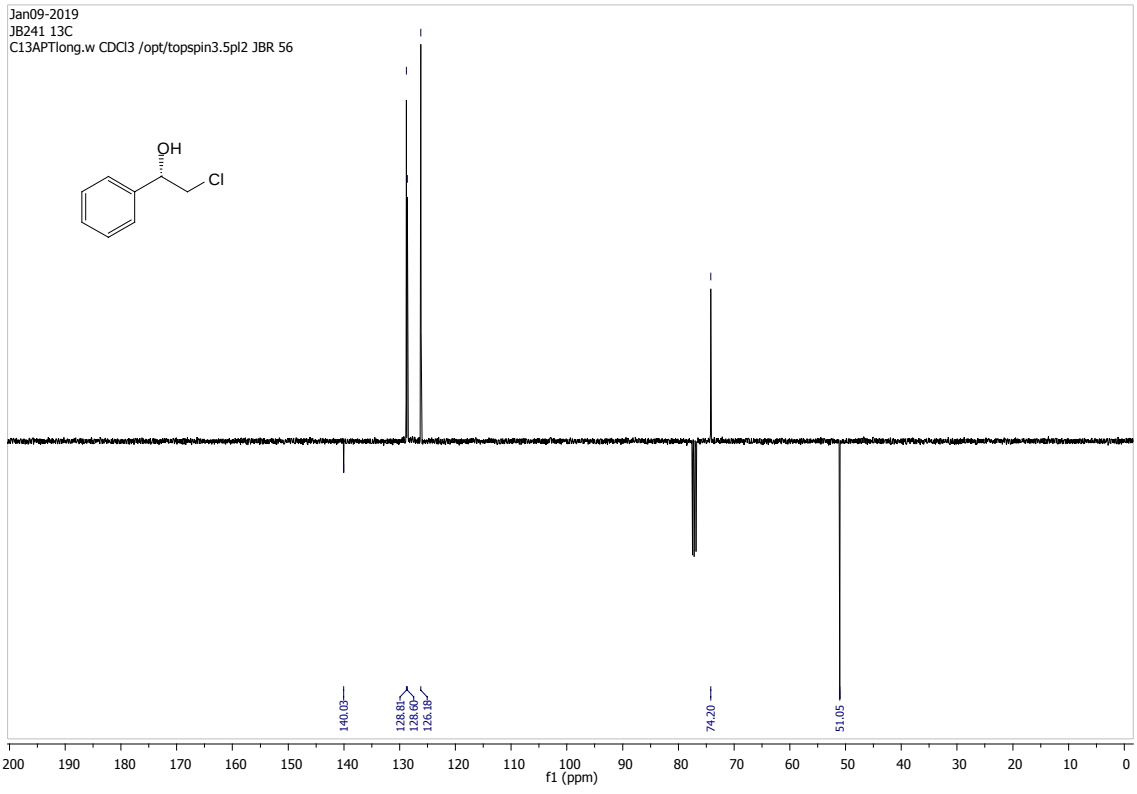


(*S*)-2-Chloro-1-phenylethan-1-ol (26)

δ_H (300 MHz, $CDCl_3$)

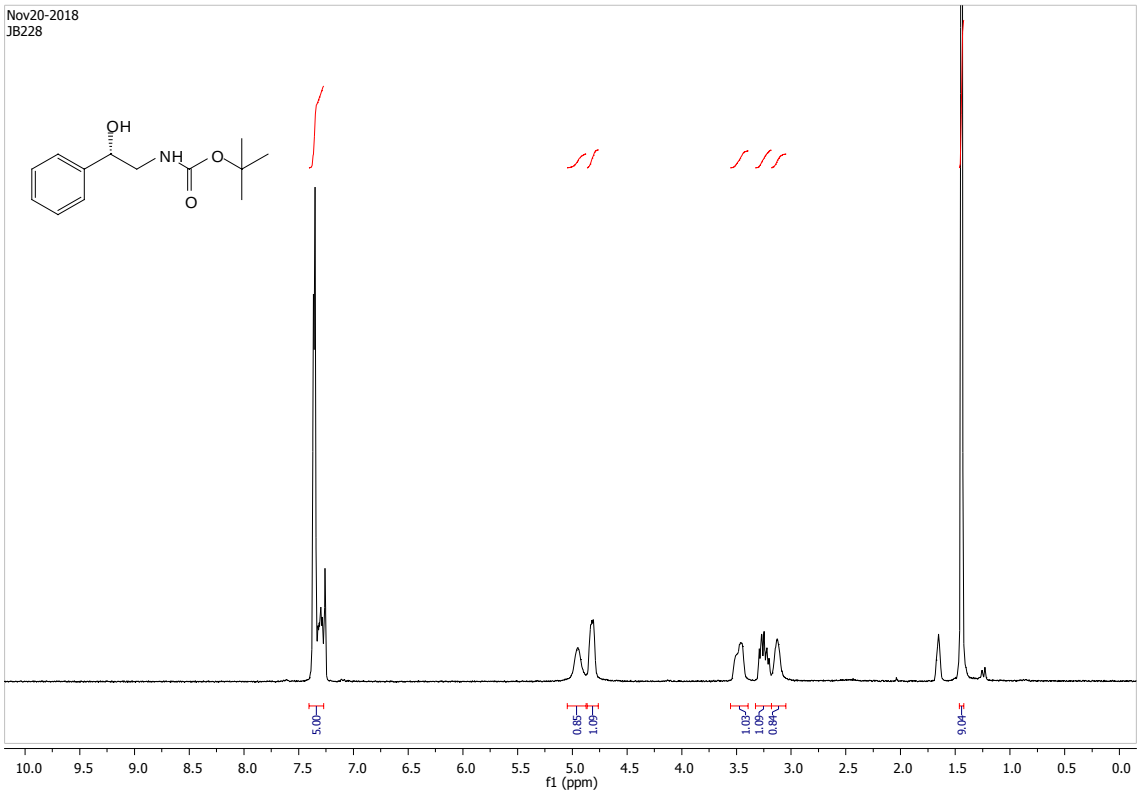


δ_C (101 MHz, $CDCl_3$)

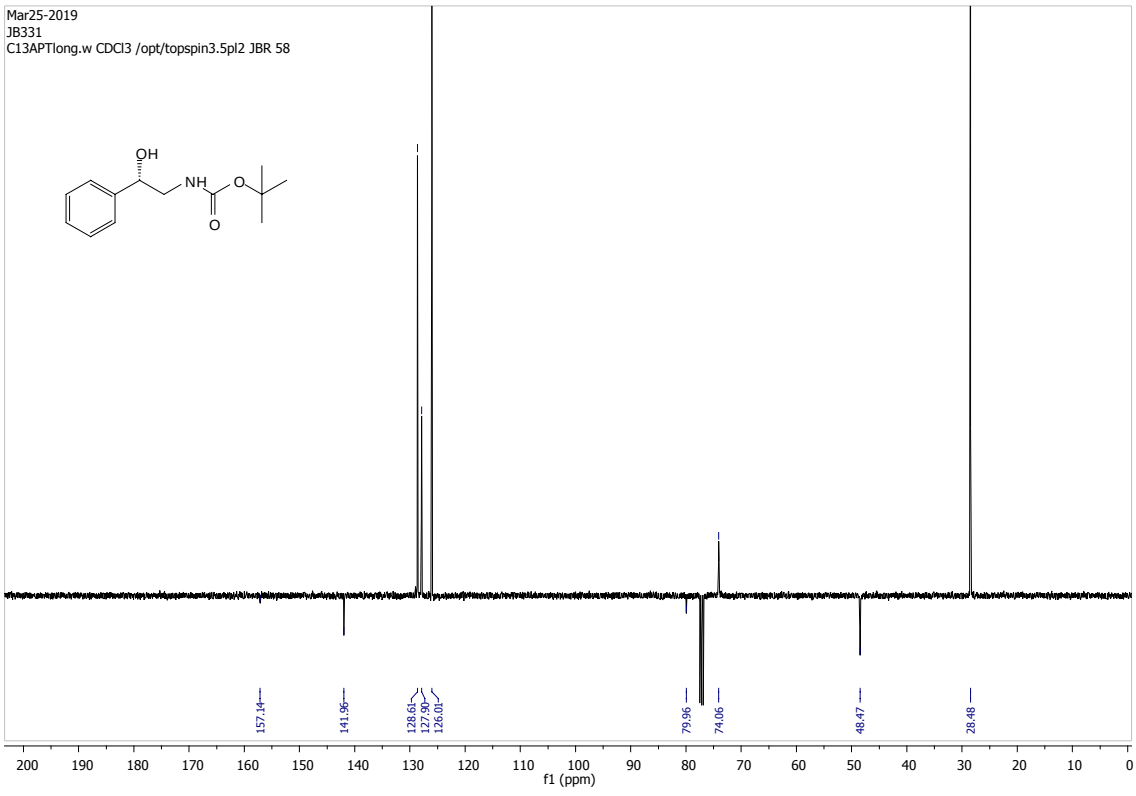


tert-Butyl (*S*)-(2-hydroxy-2-phenylethyl)carbamate (27)

δ_H (300 MHz, $CDCl_3$)

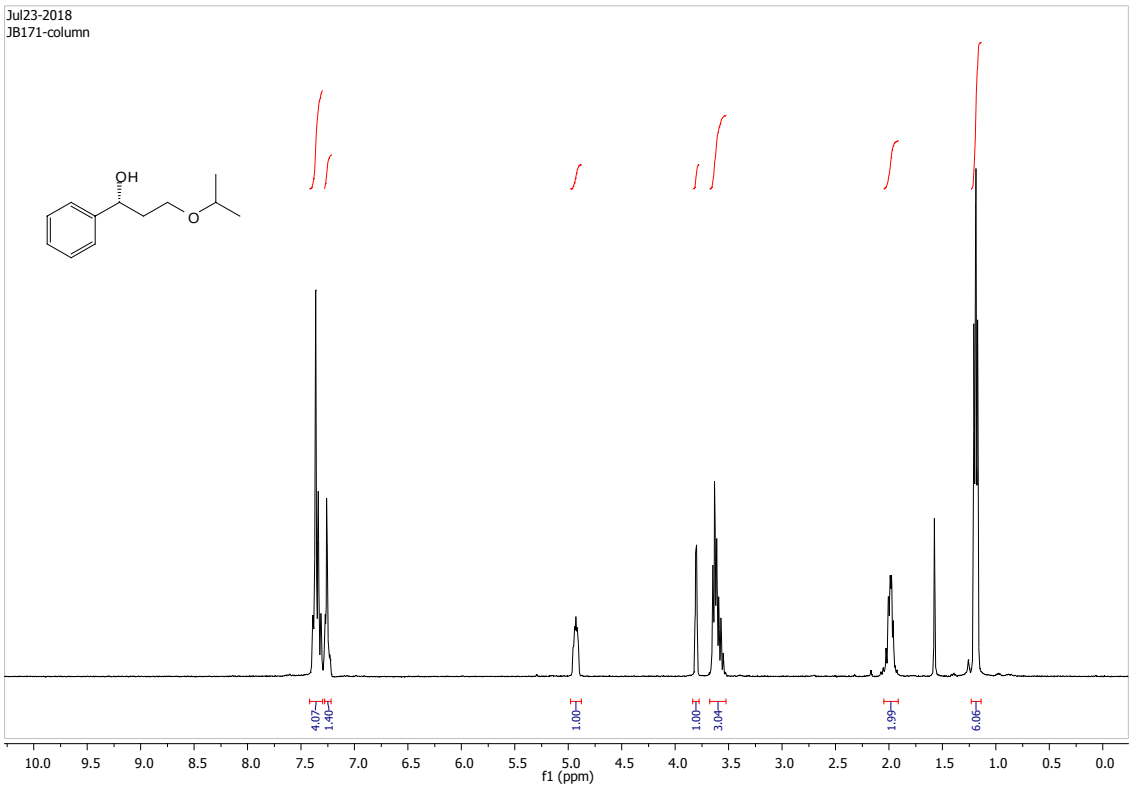


δ_C (101 MHz, $CDCl_3$)

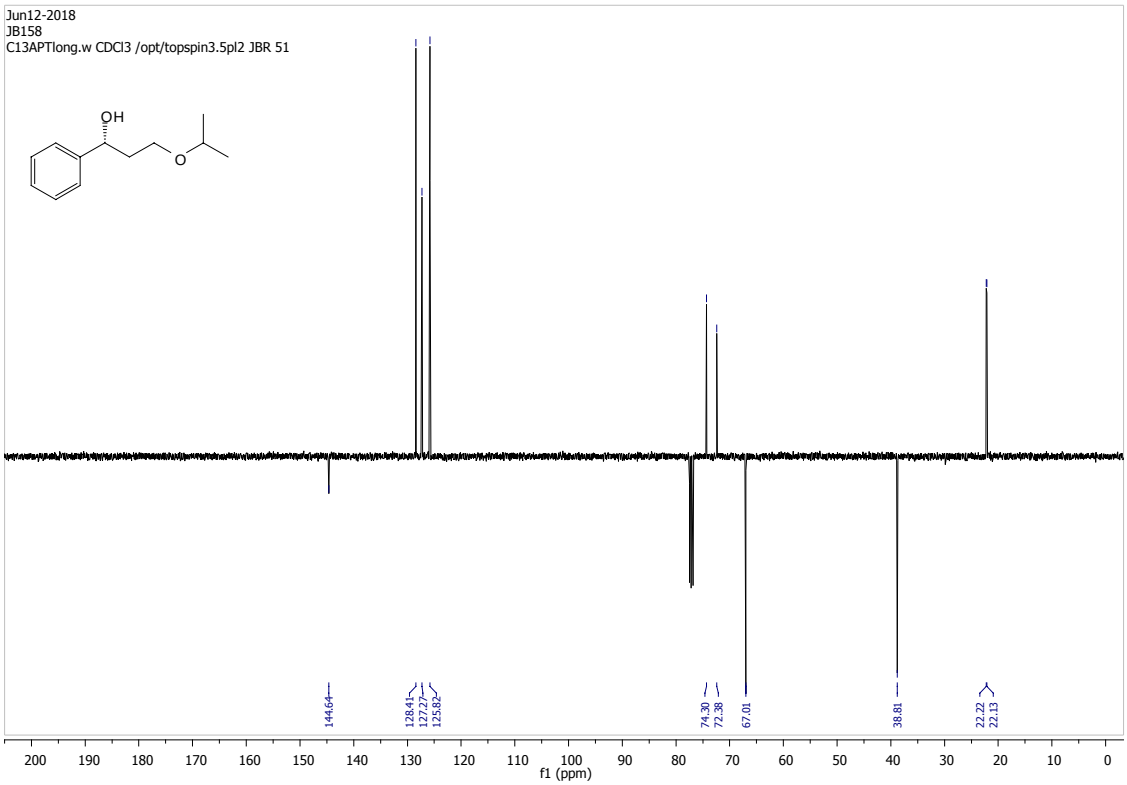


(*R*)-3-Isopropoxy-1-phenylpropan-1-ol (28)

δ_H (300 MHz, $CDCl_3$)

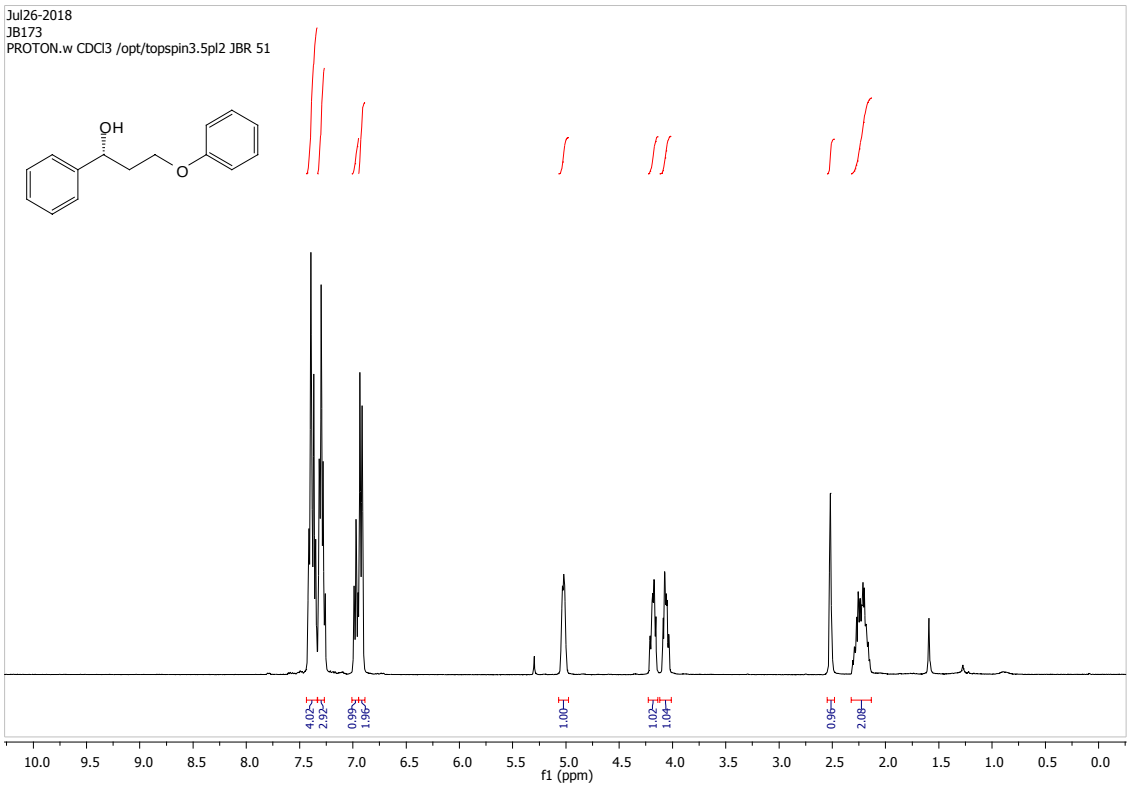


δ_C (101 MHz, $CDCl_3$)

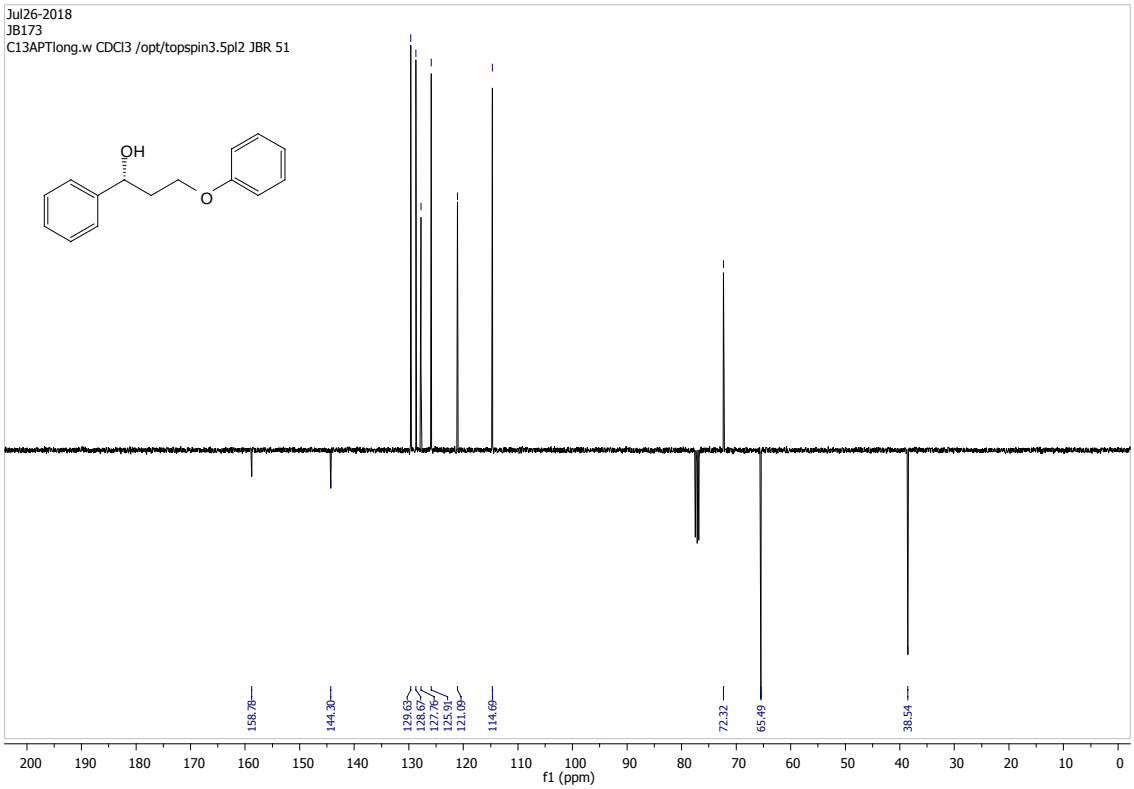


(*R*)-3-Phenoxy-1-phenylpropan-1-ol (29)

δ_H (400 MHz, $CDCl_3$)

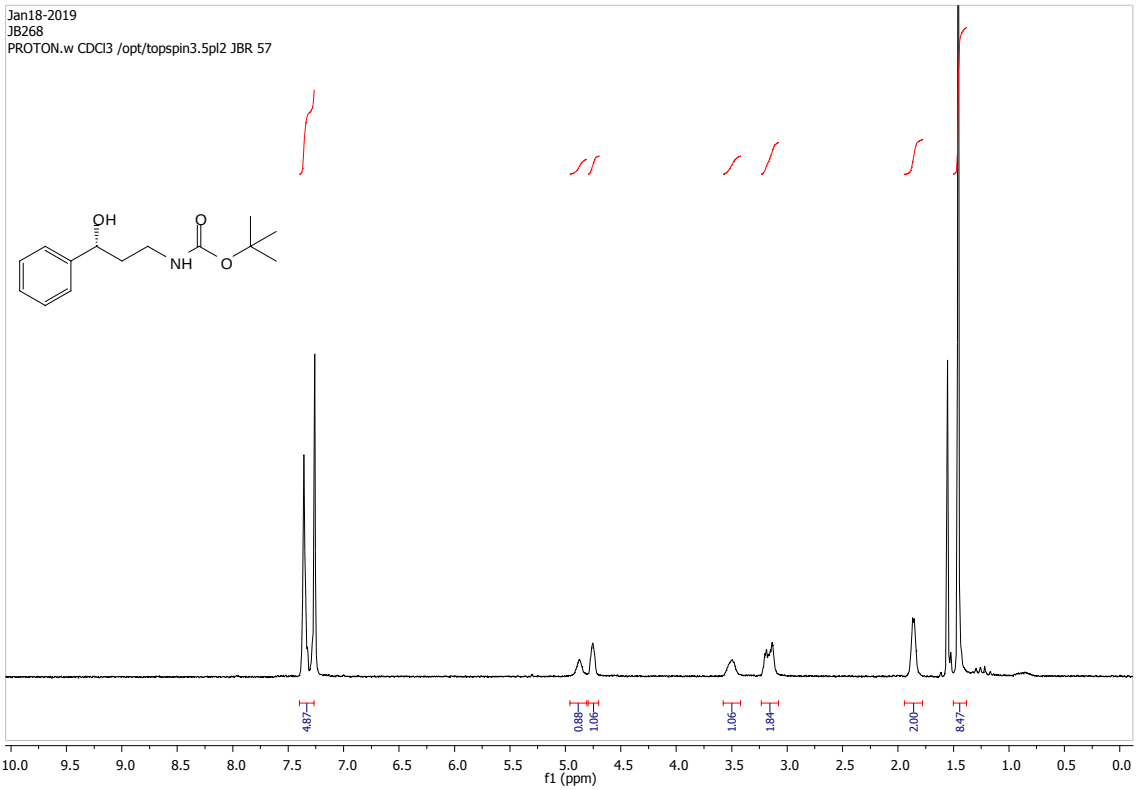


δ_C (101 MHz, $CDCl_3$)

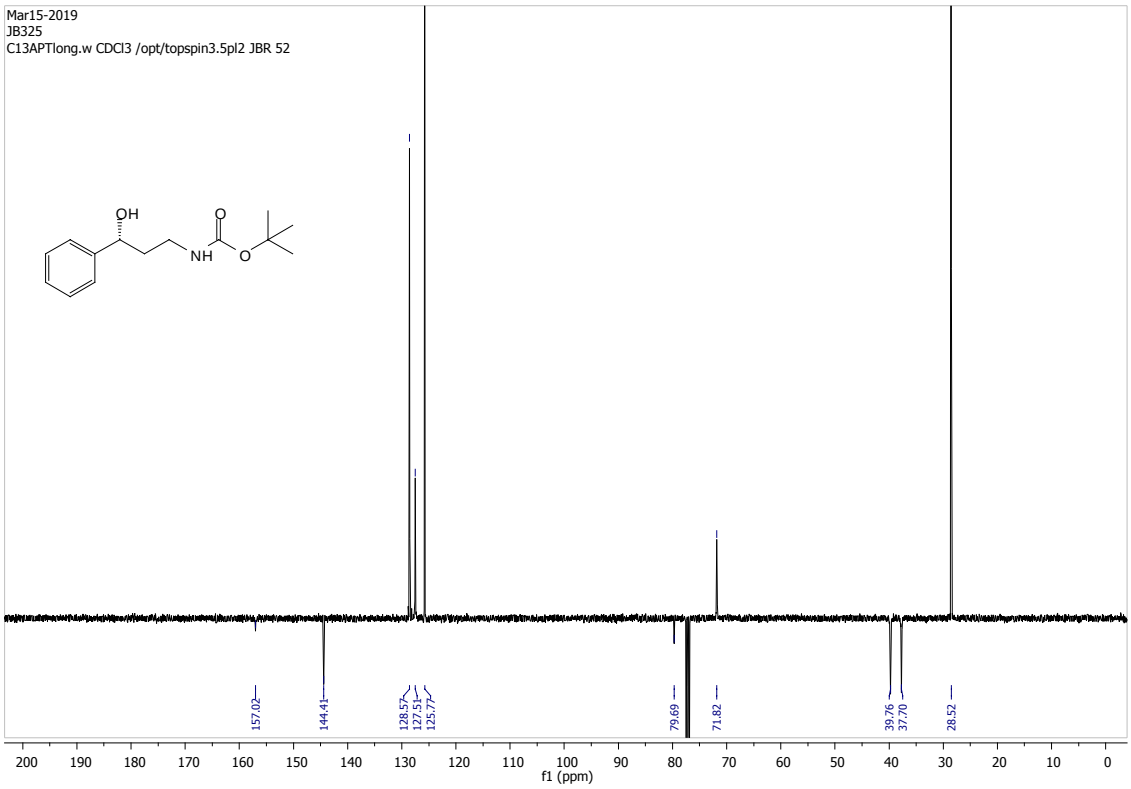


tert-Butyl (*R*)-(3-hydroxy-3-phenylpropyl)carbamate (30)

δ_H (400 MHz, $CDCl_3$)

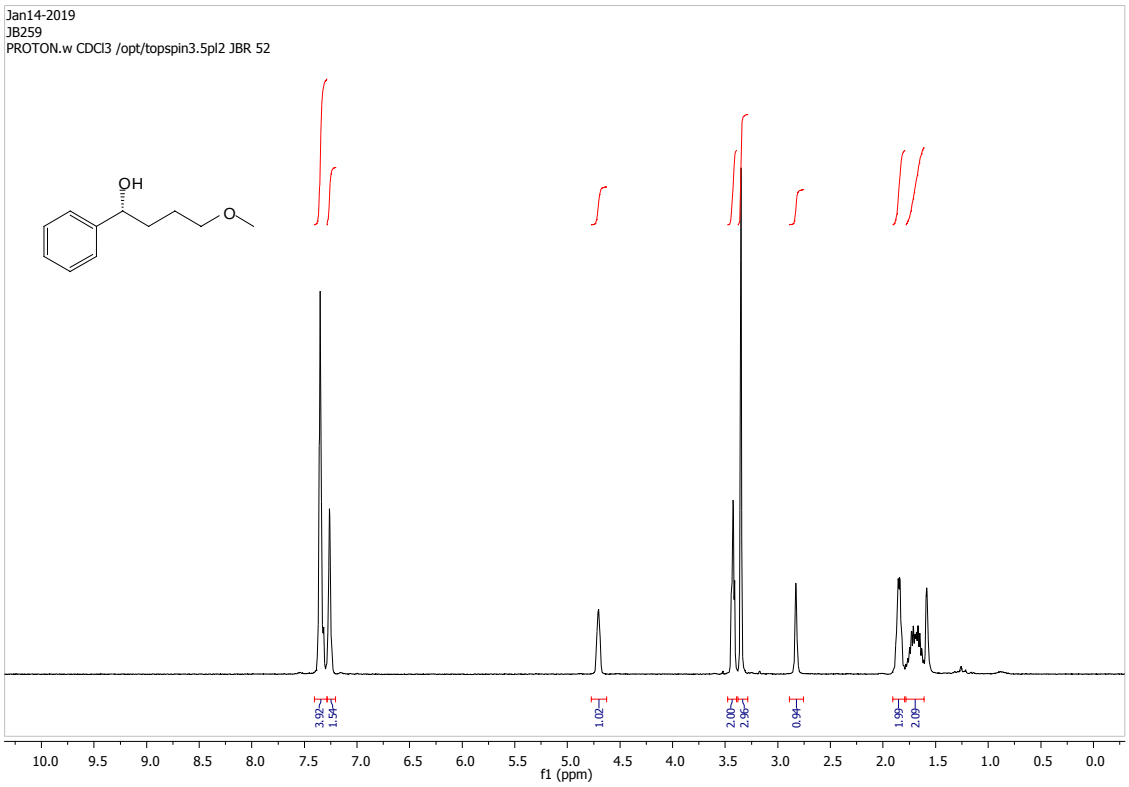


δ_C (101 MHz, $CDCl_3$)

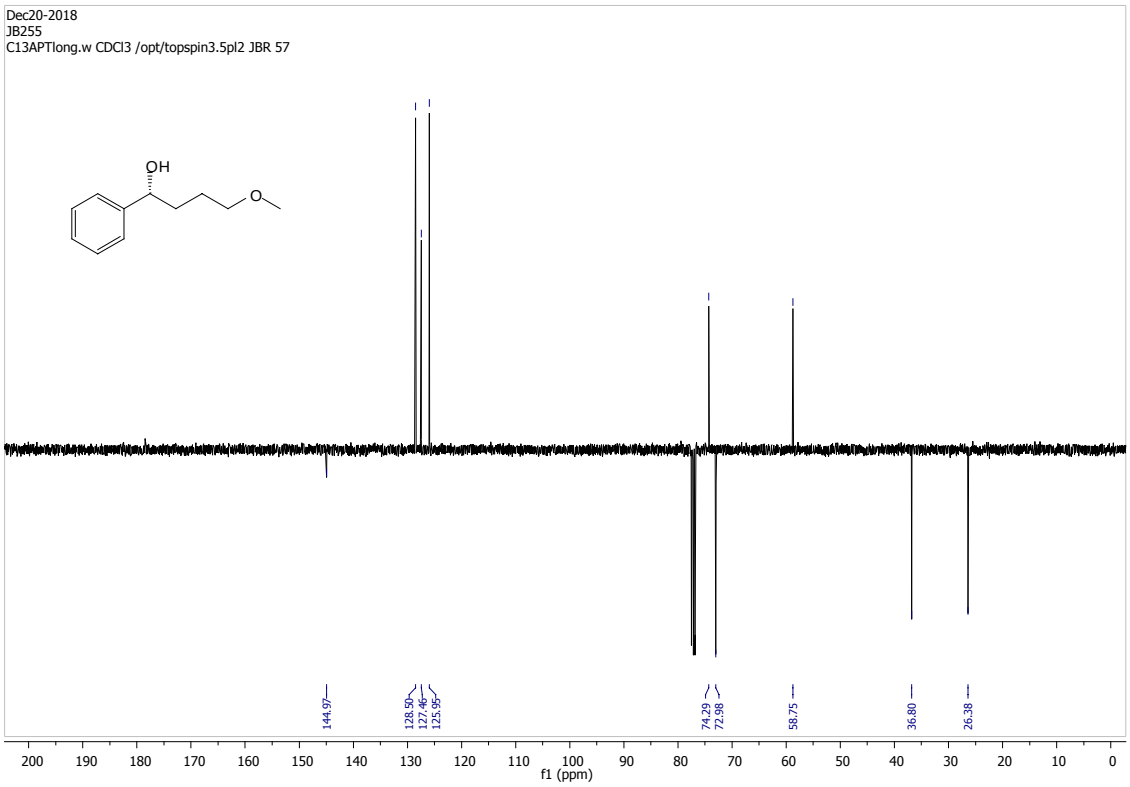


(*R*)-4-Methoxy-1-phenylbutan-1-ol (31)

δ_H (400 MHz, $CDCl_3$)

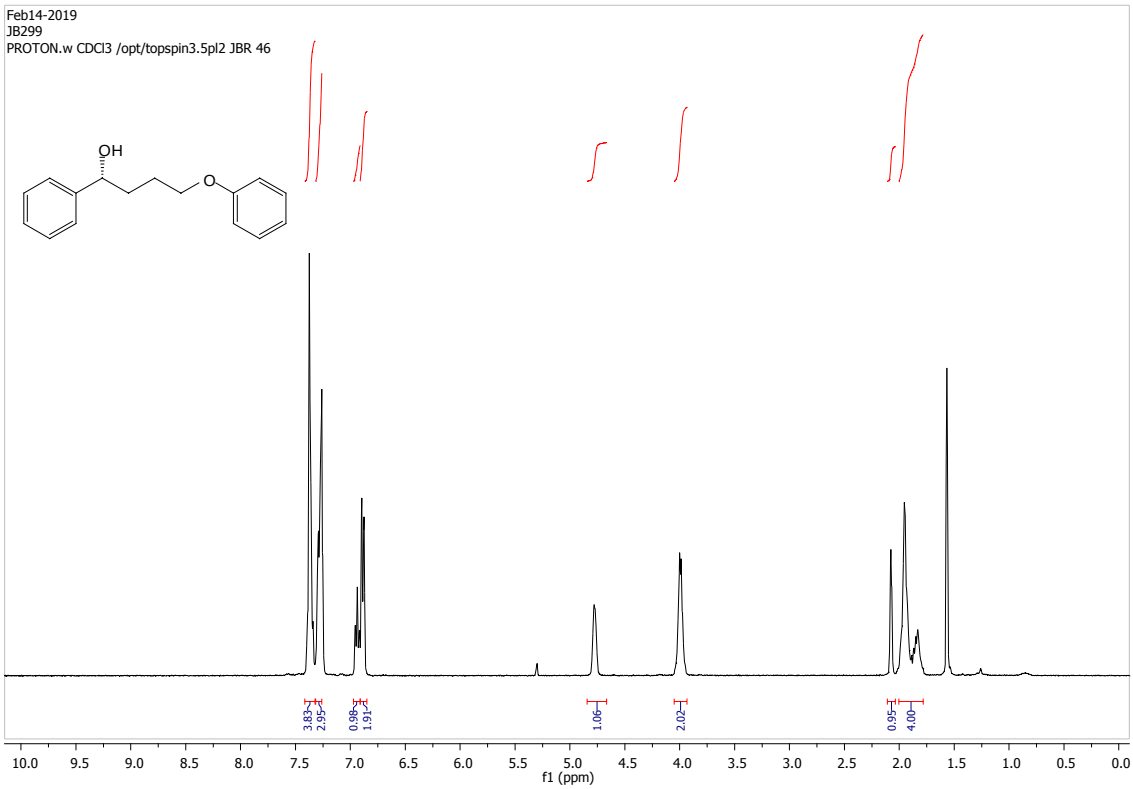


δ_C (101 MHz, $CDCl_3$)

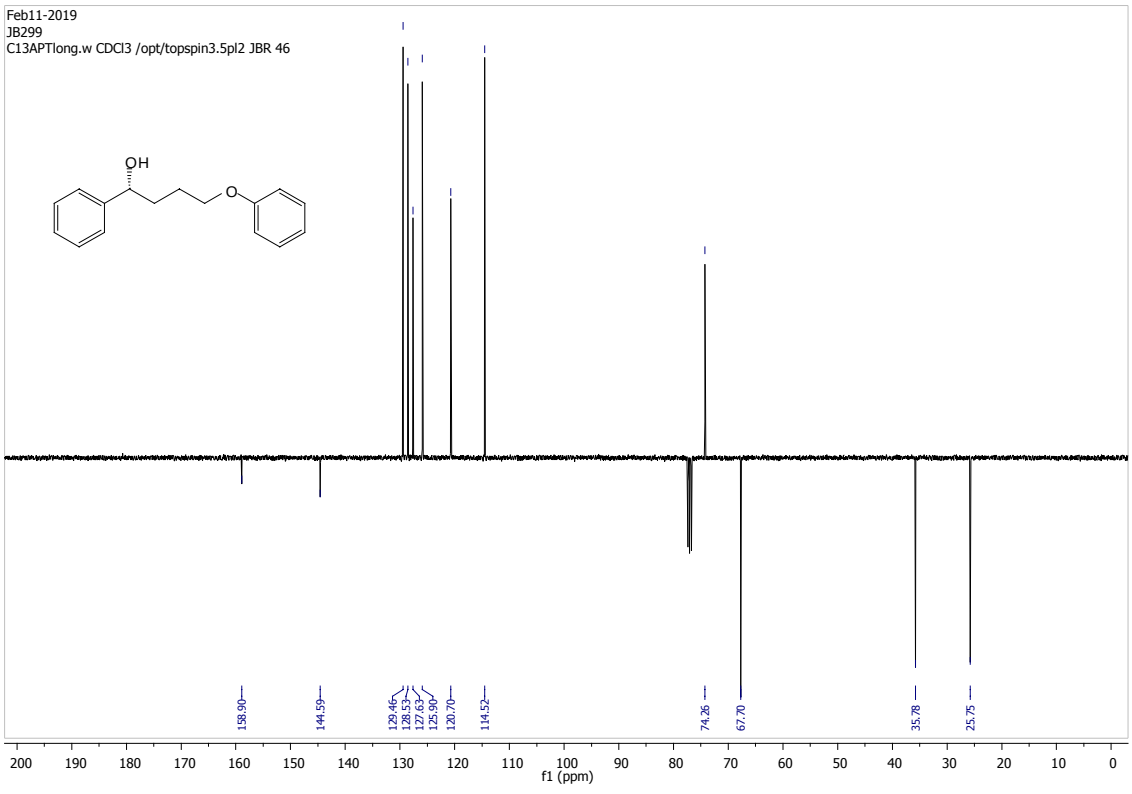


(*R*)-4-phenoxy-1-phenylbutan-1-ol (32)

δ_H (400 MHz, $CDCl_3$)

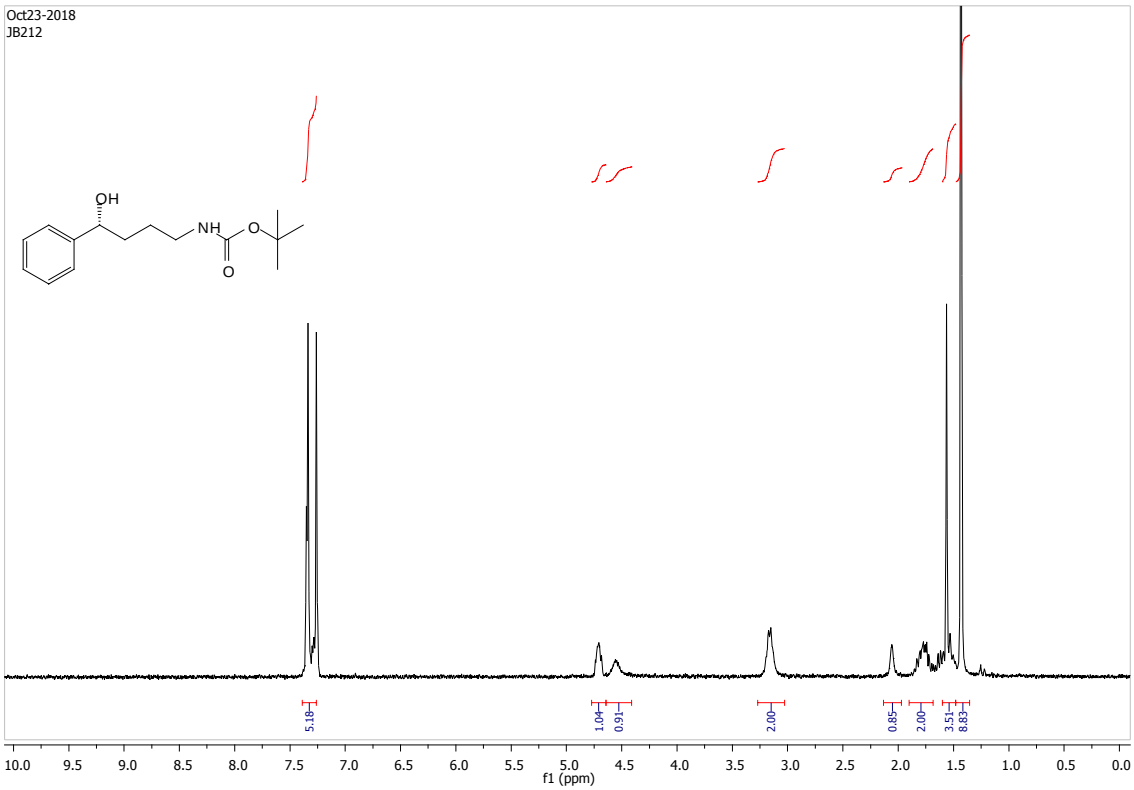


δ_C (101 MHz, $CDCl_3$)

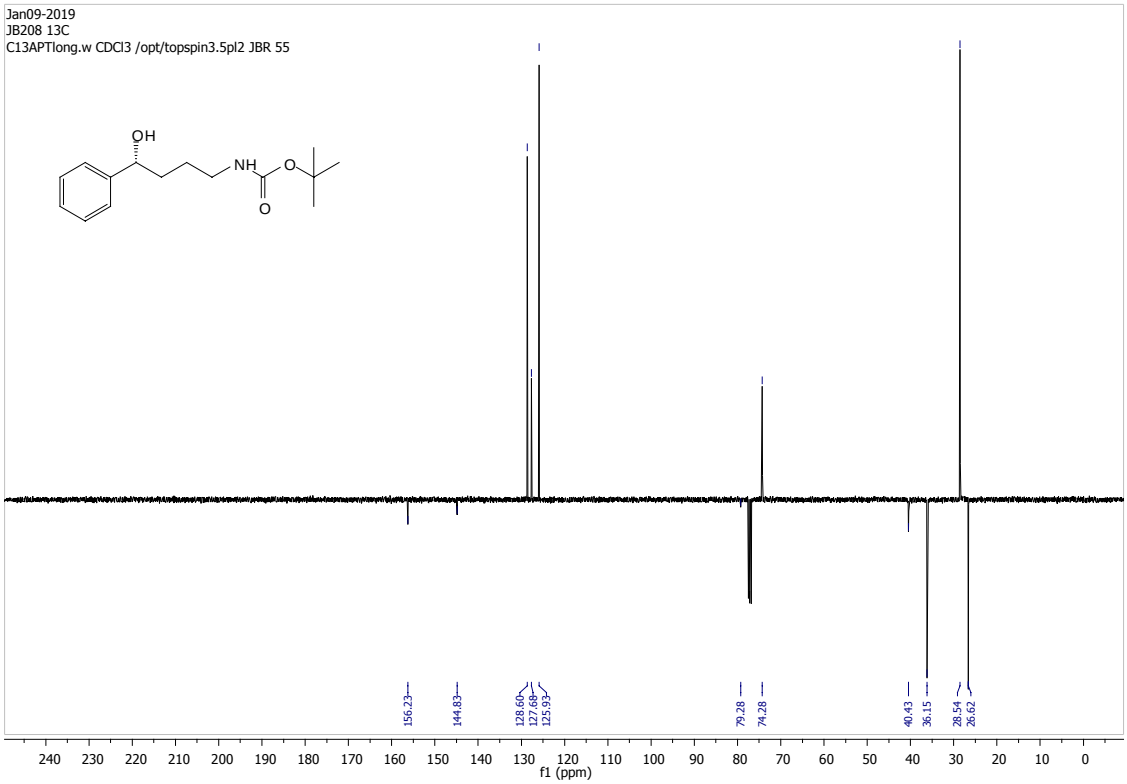


tert-Butyl (*R*)-(4-hydroxy-4-phenylbutyl)carbamate (33)

δ_H (300 MHz, $CDCl_3$)

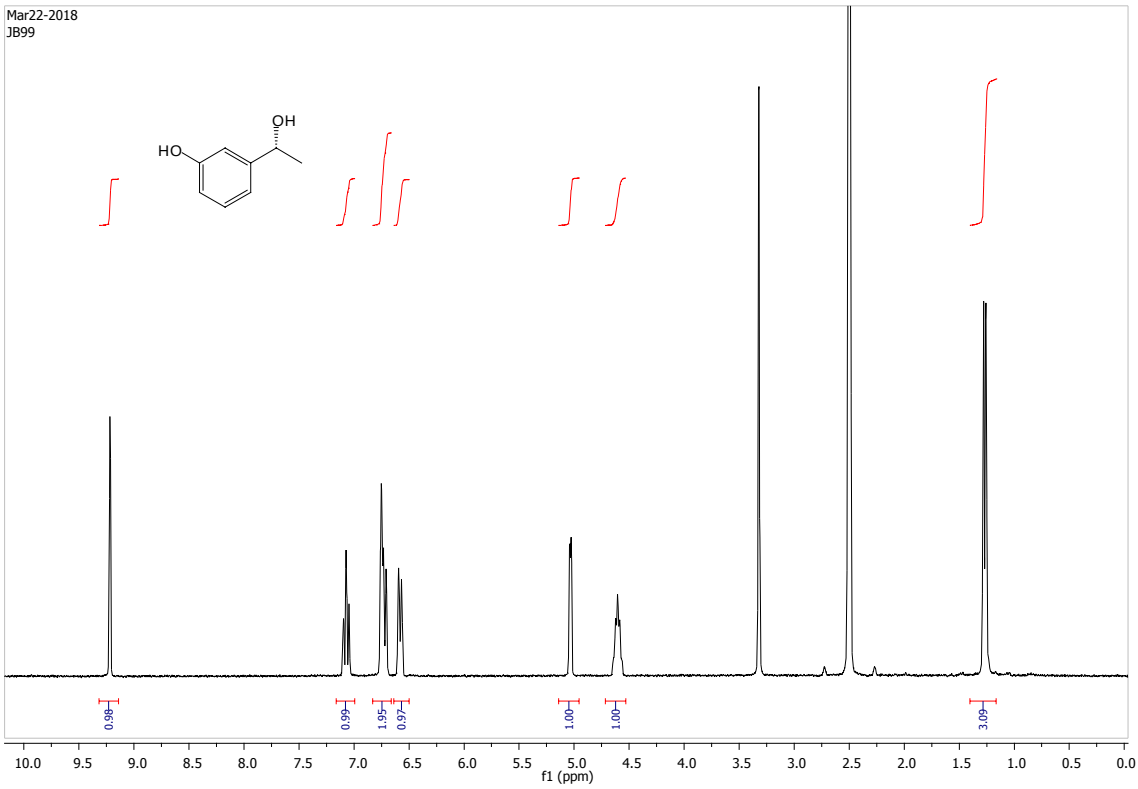


δ_C (101 MHz, $CDCl_3$)

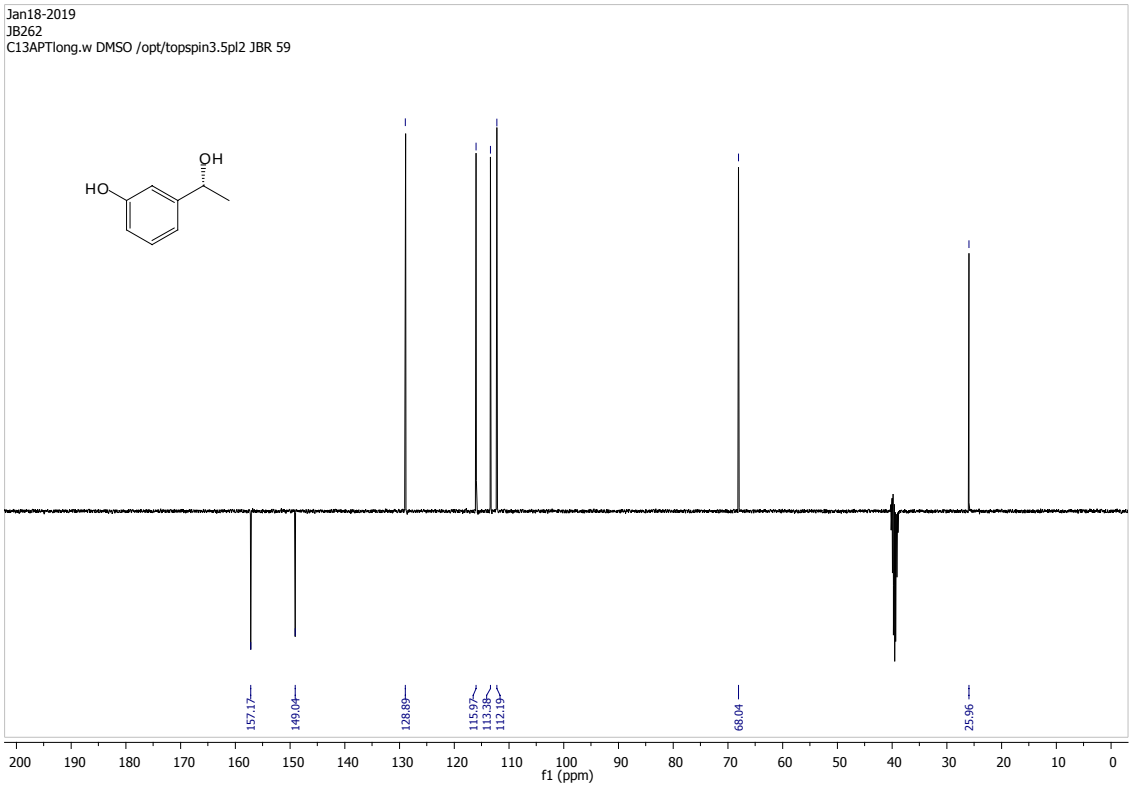


(*R*)-3-(1-hydroxyethyl)phenol (34)

δ_H (300 MHz, DMSO-d$_6$)

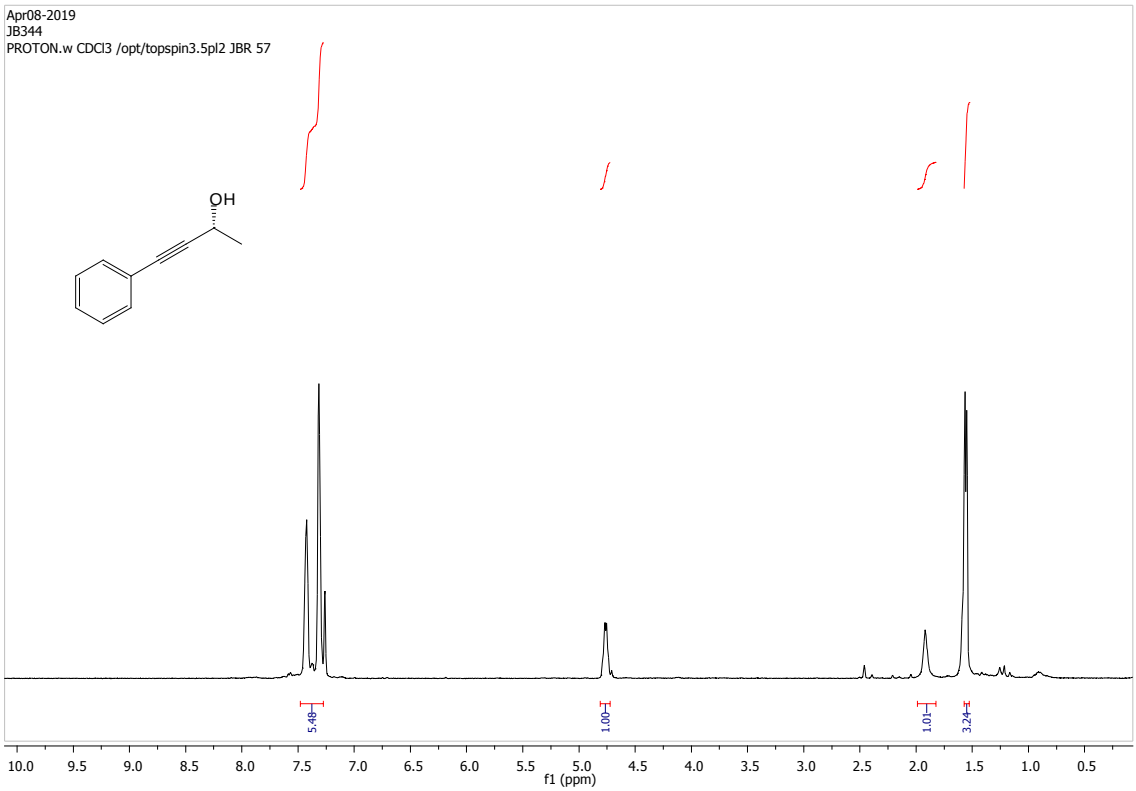


δ_C (101 MHz, DMSO-d$_6$)

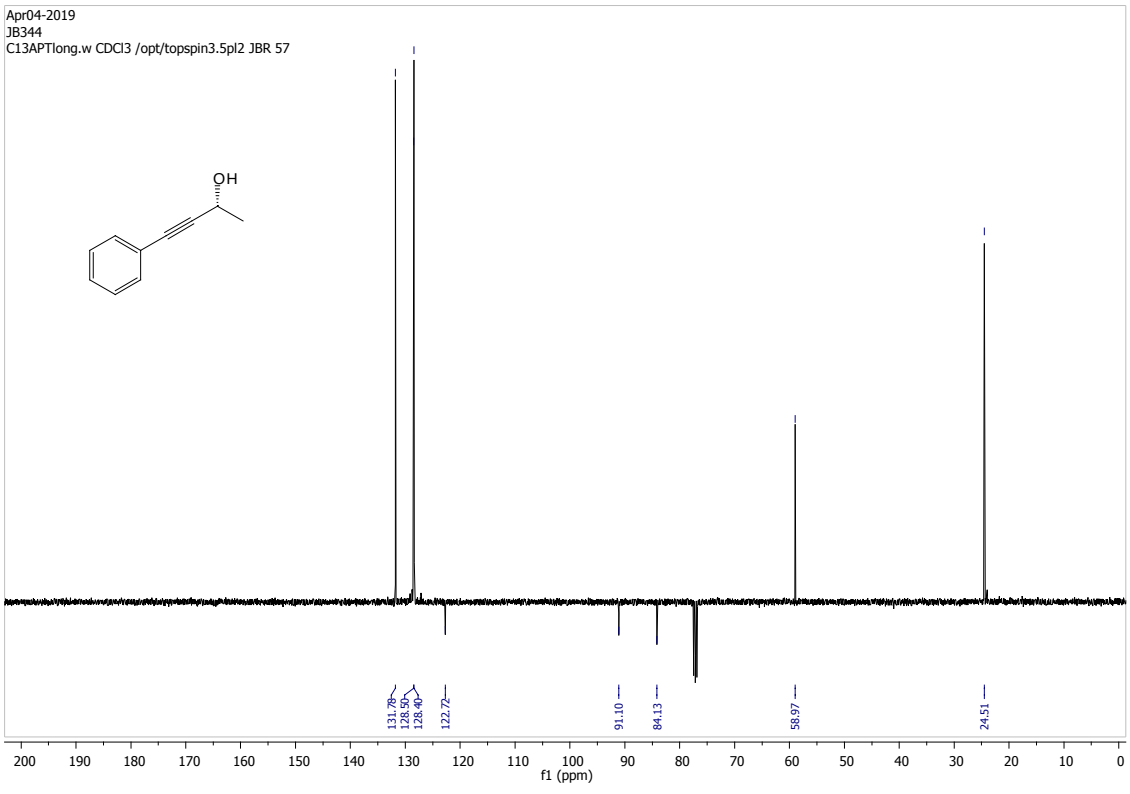


(*R*)-4-phenylbut-3-yn-2-ol (35)

δ_H (400 MHz, $CDCl_3$)

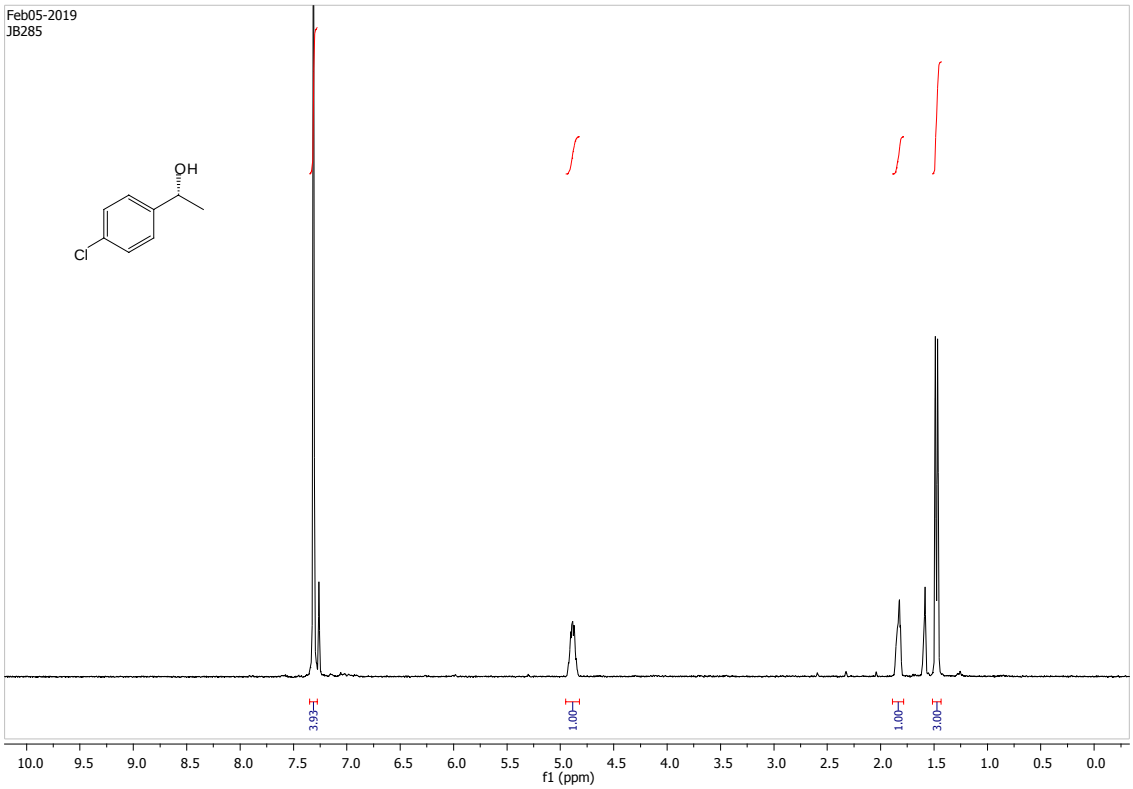


δ_C (101 MHz, $CDCl_3$)

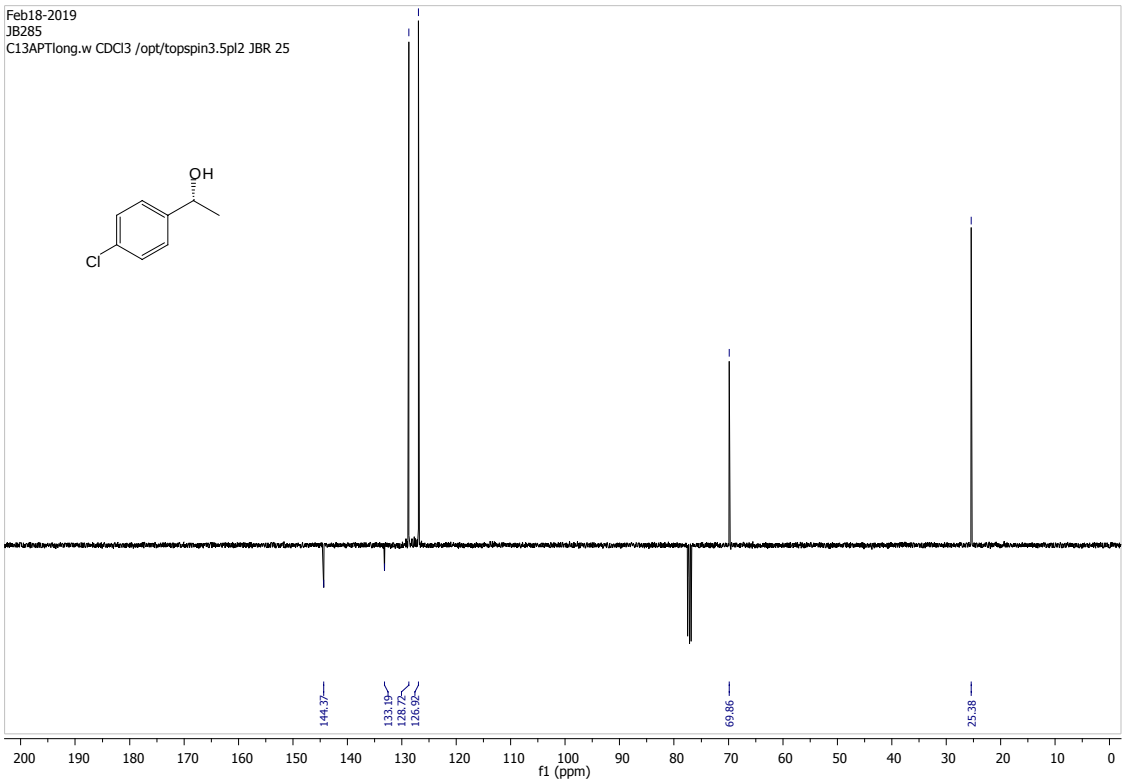


(*R*)-1-(4-Chlorophenyl)ethan-1-ol (36)

δ_H (300 MHz, $CDCl_3$)

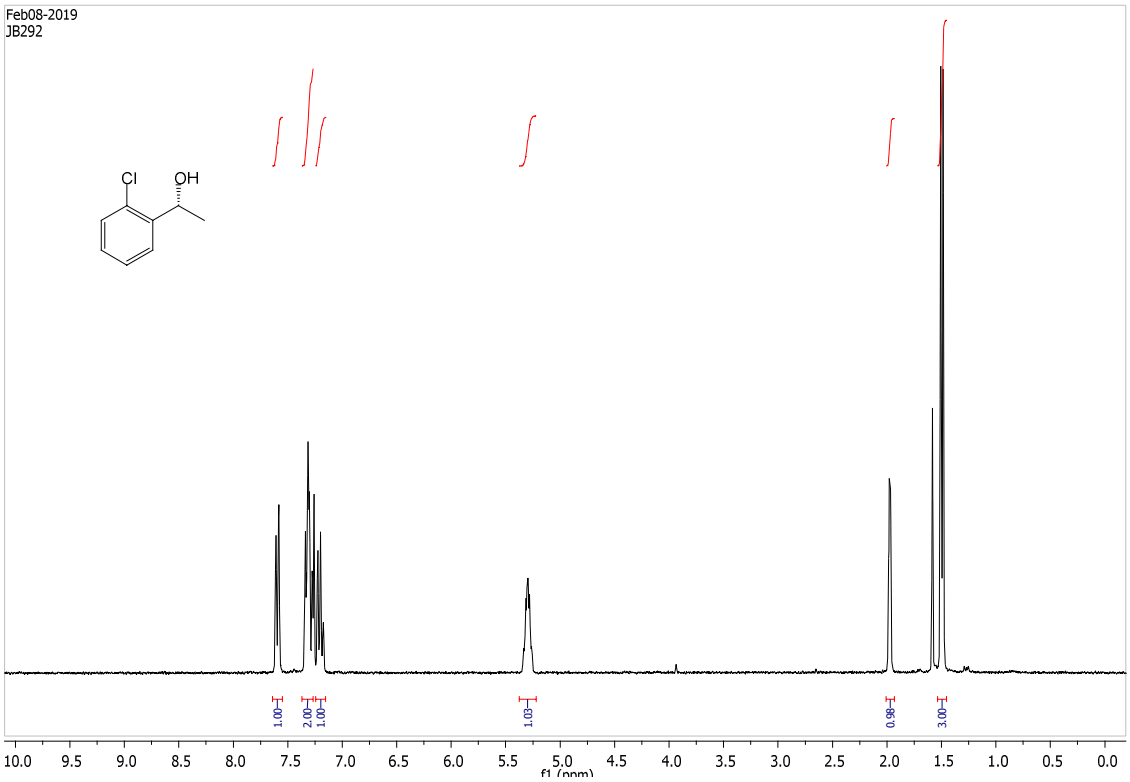


δ_C (101 MHz, $CDCl_3$)

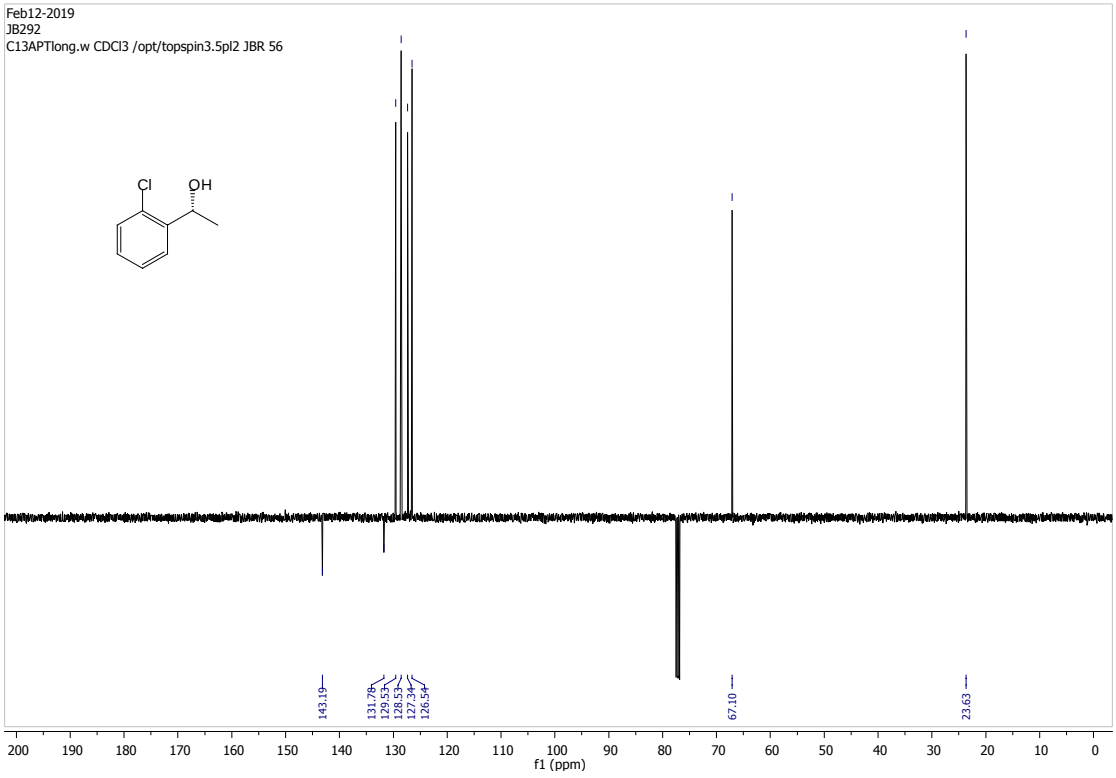


(*R*)-1-(2-Chlorophenyl)ethan-1-ol (37)

δ_H (300 MHz, $CDCl_3$)

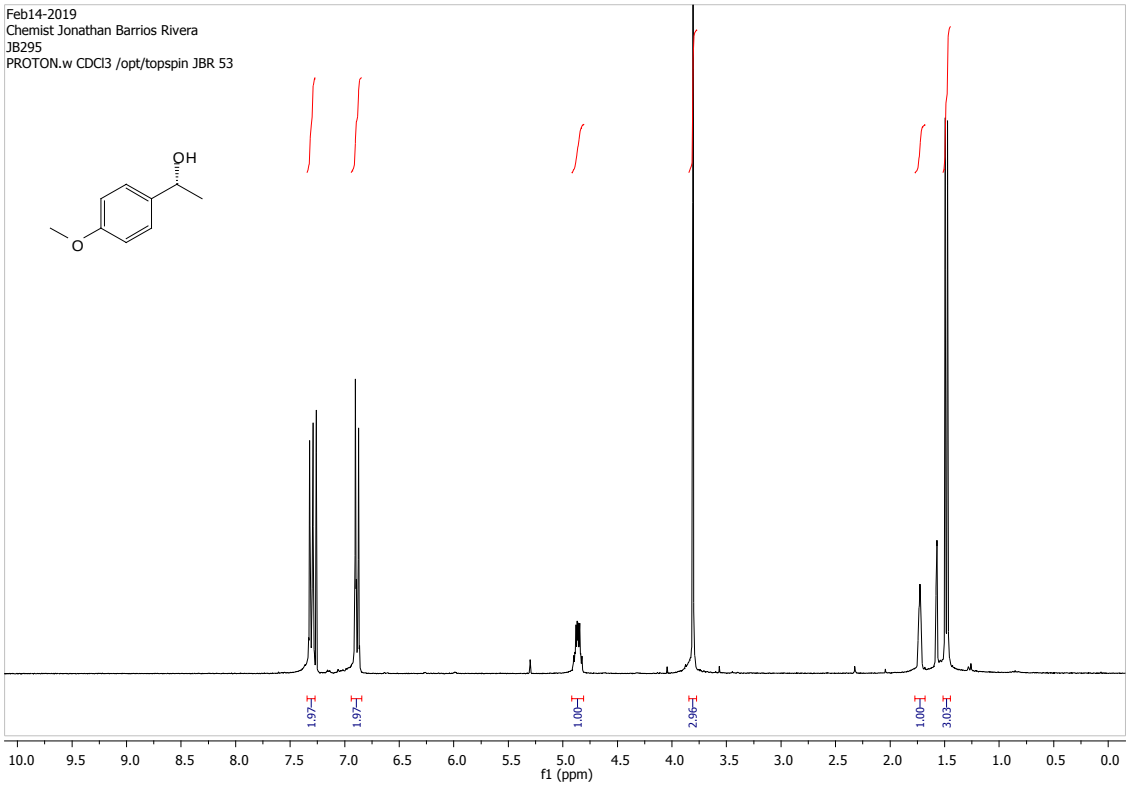


δ_C (101 MHz, $CDCl_3$)

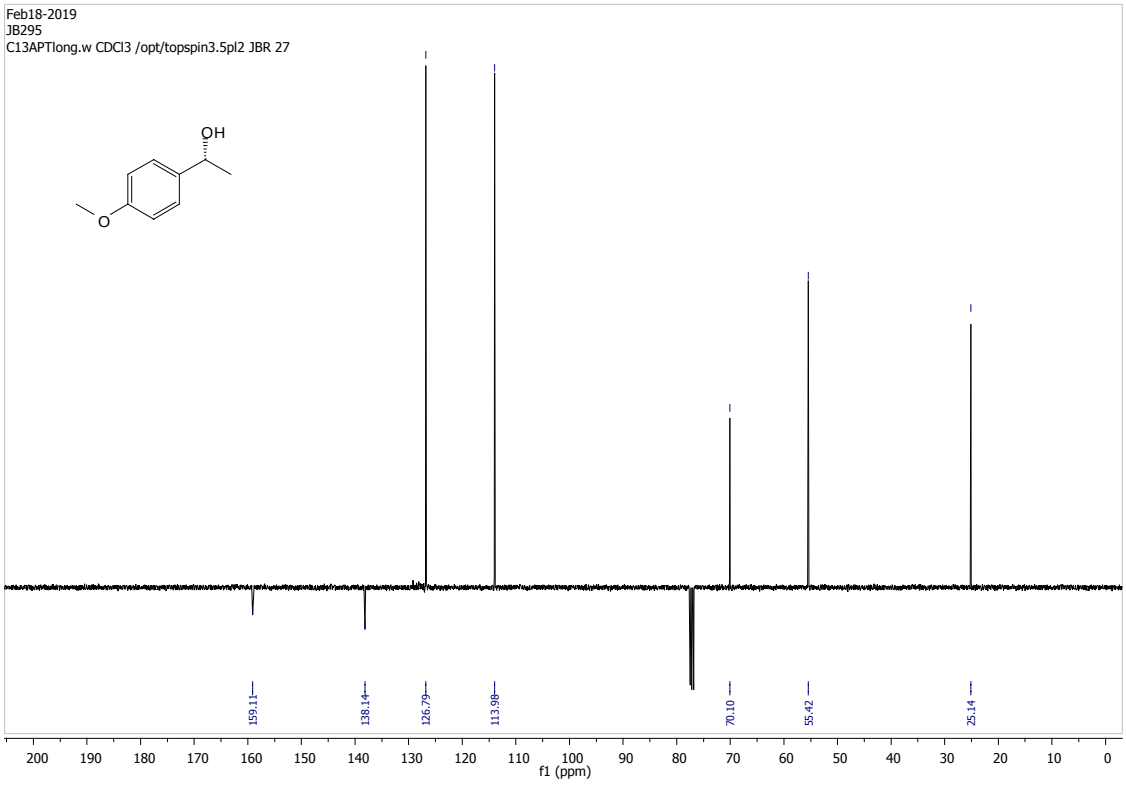


(*R*)-1-(4-Methoxyphenyl)ethan-1-ol (38)

^{1}H (300 MHz, $CDCl_3$)

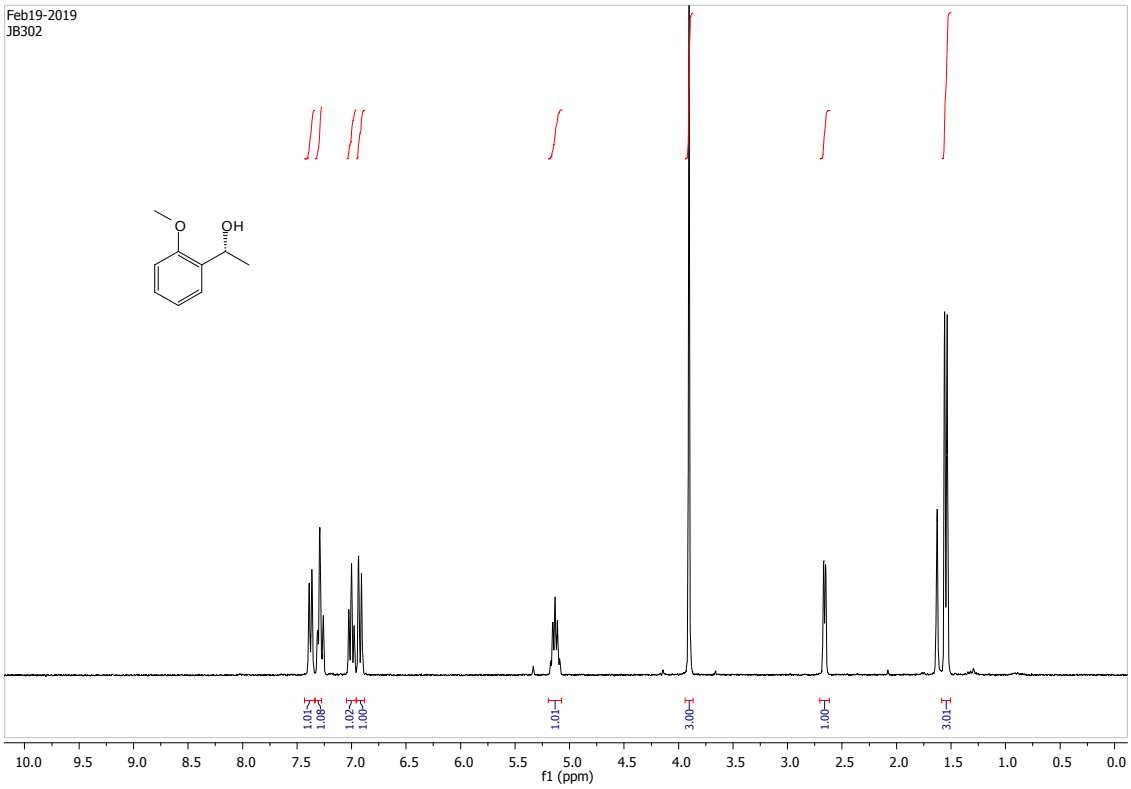


^{13}C (101 MHz, $CDCl_3$)

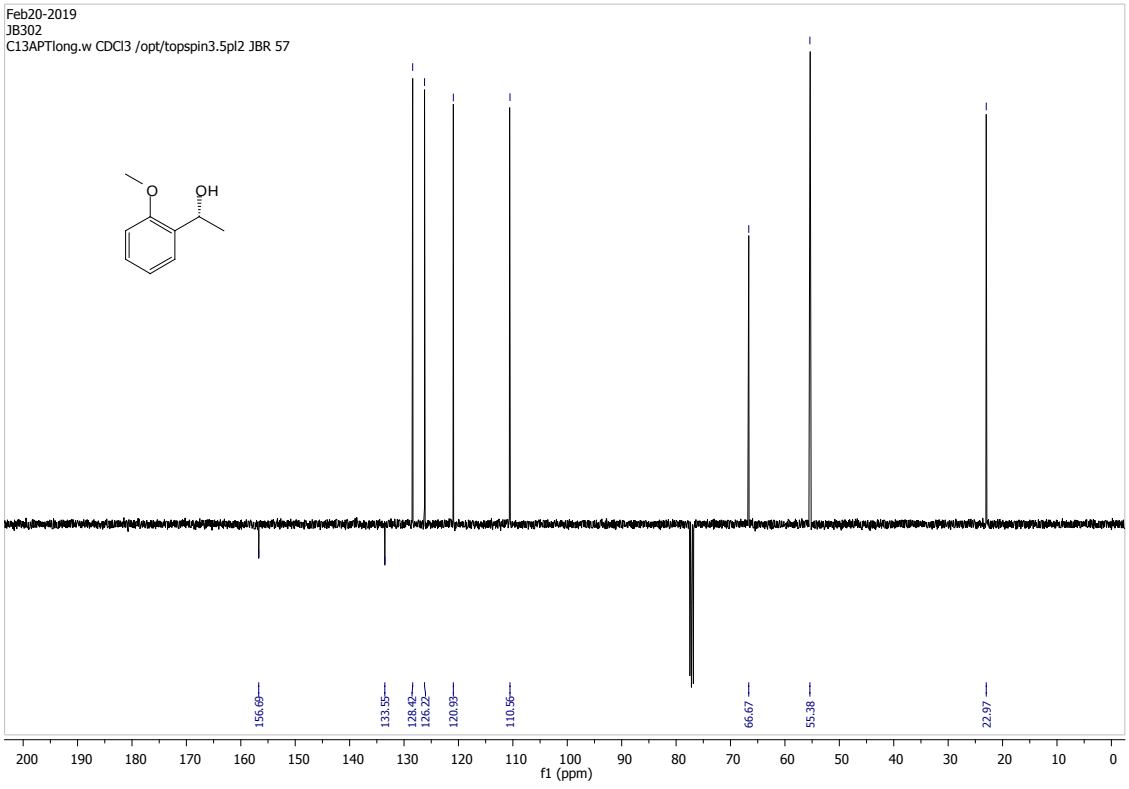


(*R*)-1-(2-Methoxyphenyl)ethan-1-ol (39)

δ_H (300 MHz, $CDCl_3$)

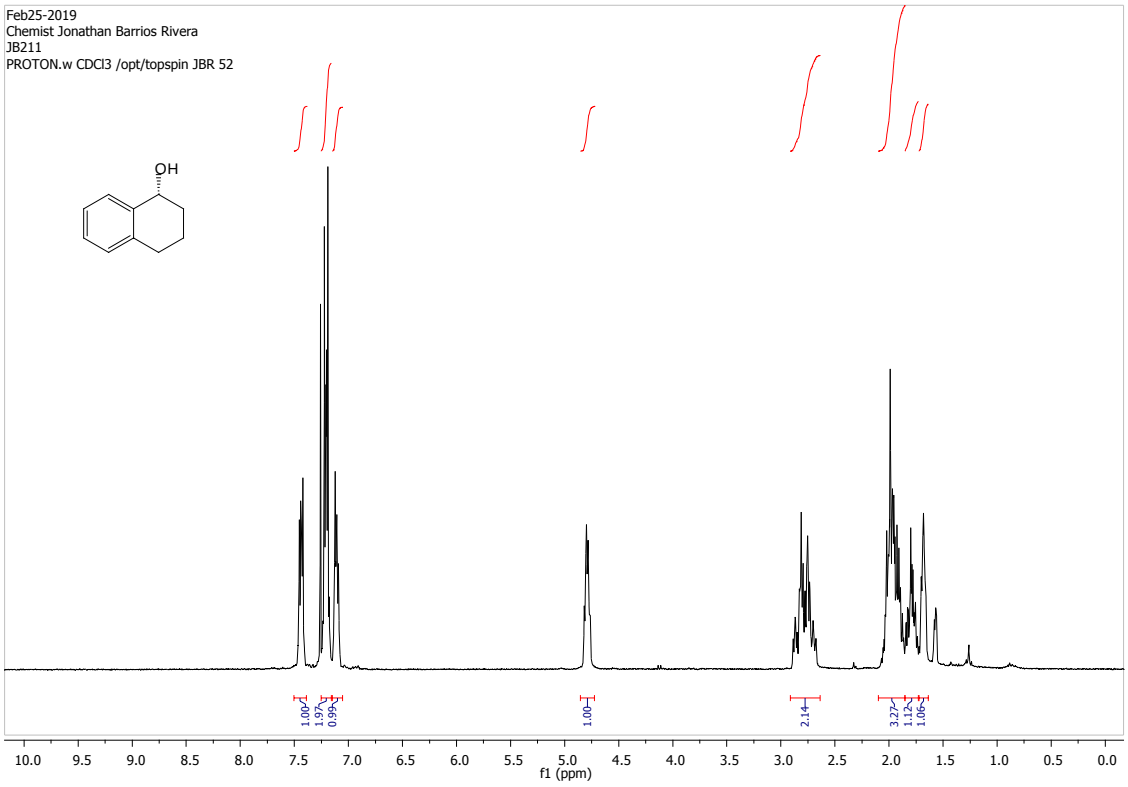


δ_C (101 MHz, $CDCl_3$)

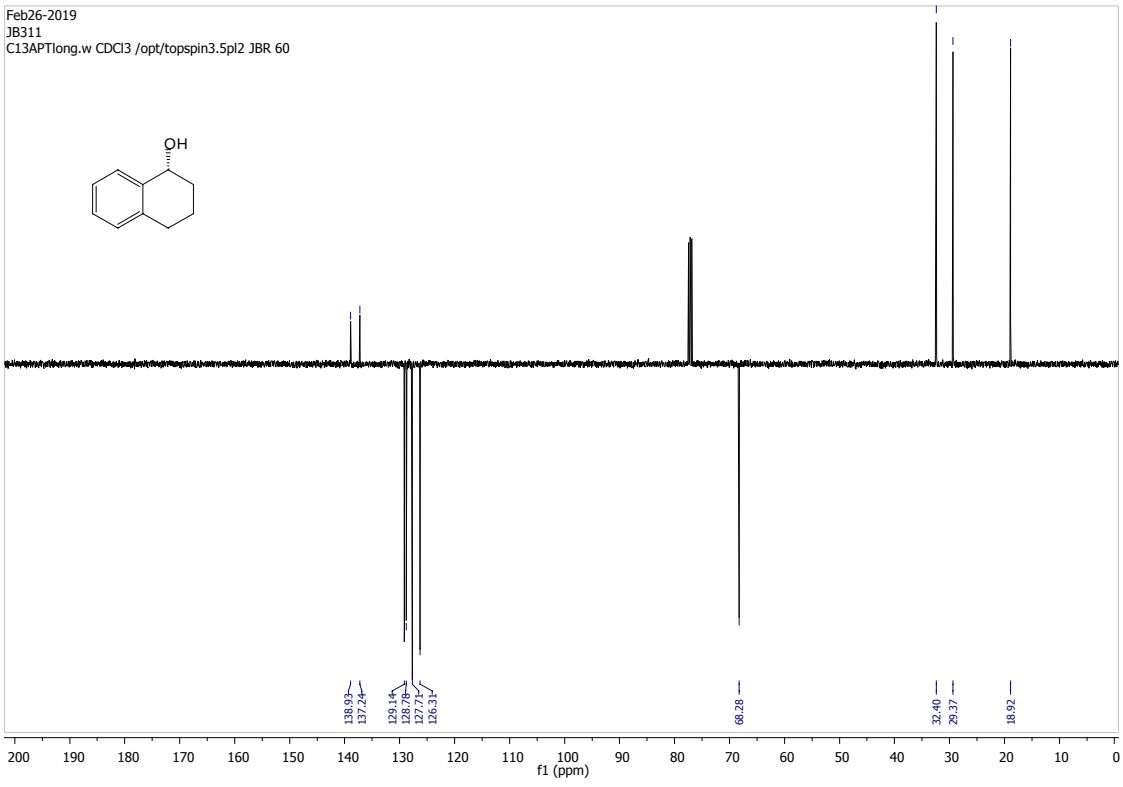


(*R*)-1,2,3,4-Tetrahydronaphthalen-1-ol (40)

δ_H (300 MHz, $CDCl_3$)

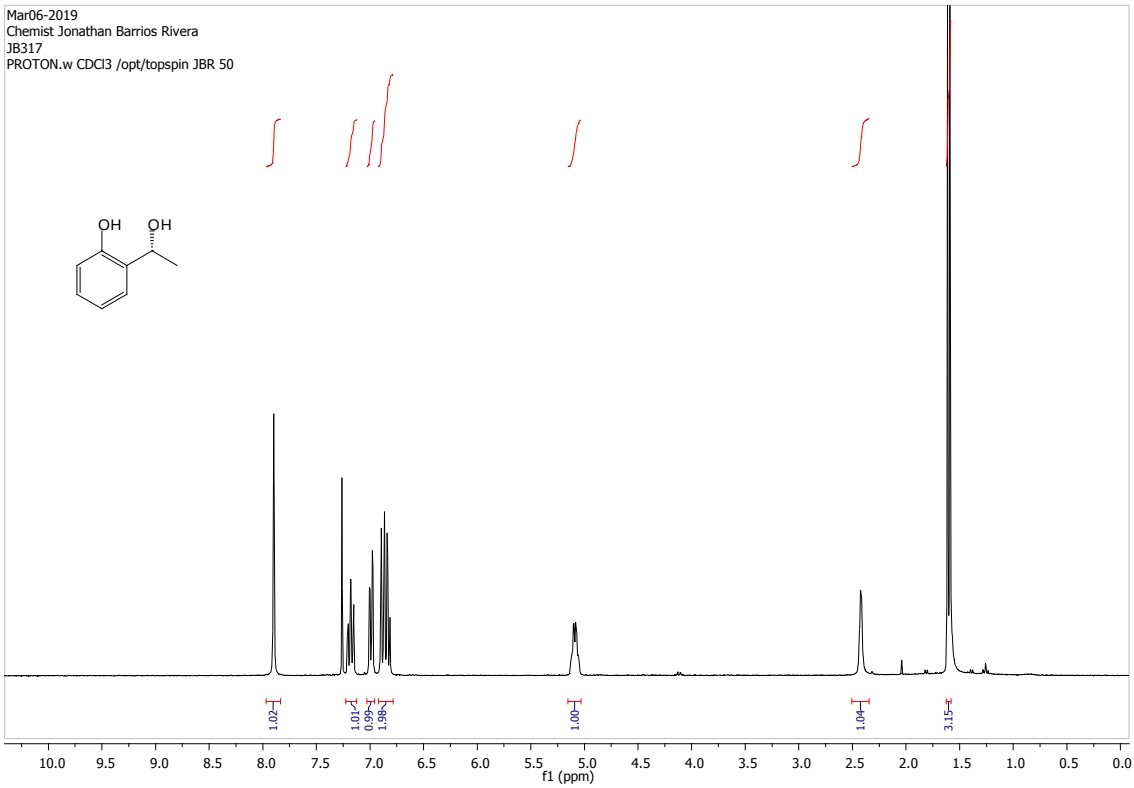


δ_C (101 MHz, $CDCl_3$)

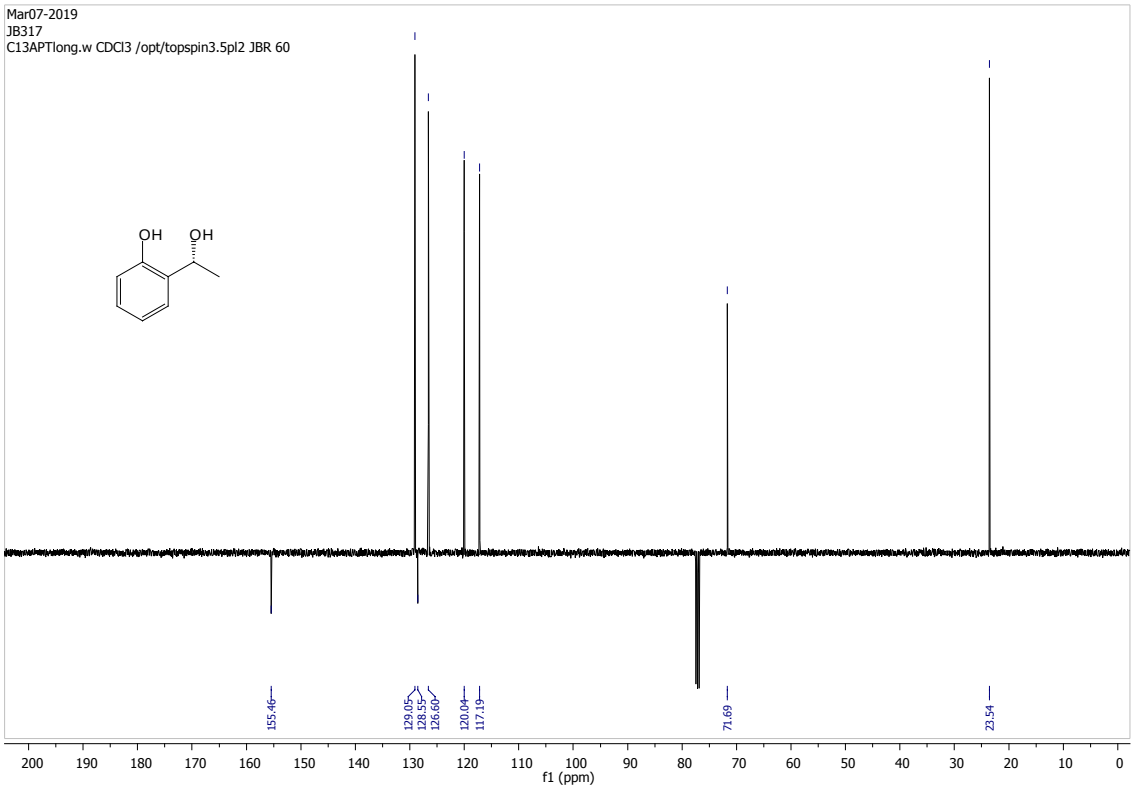


(*R*)-2-(1-hydroxyethyl)phenol (41)

δ_H (300 MHz, $CDCl_3$)

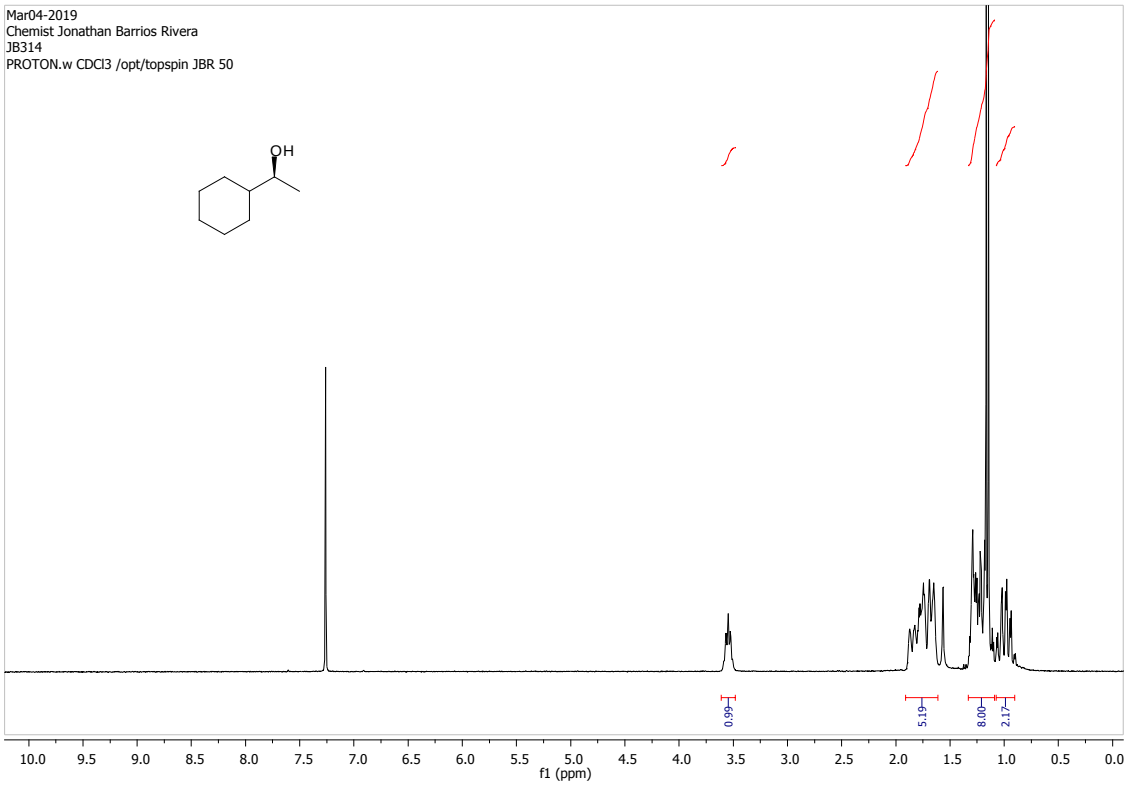


δ_C (101 MHz, $CDCl_3$)

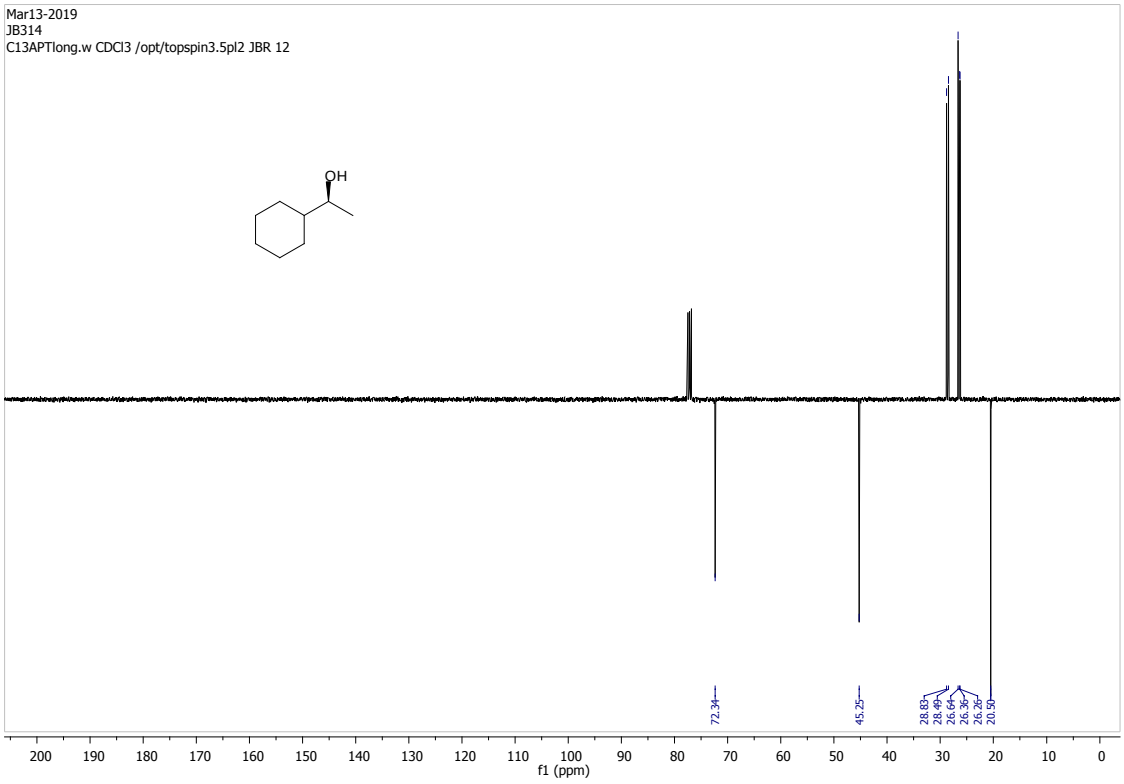


(*S*)-1-Cyclohexylethan-1-ol (acetylcyclohexane)

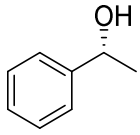
δ_H (300 MHz, $CDCl_3$)



δ_C (101 MHz, $CDCl_3$)

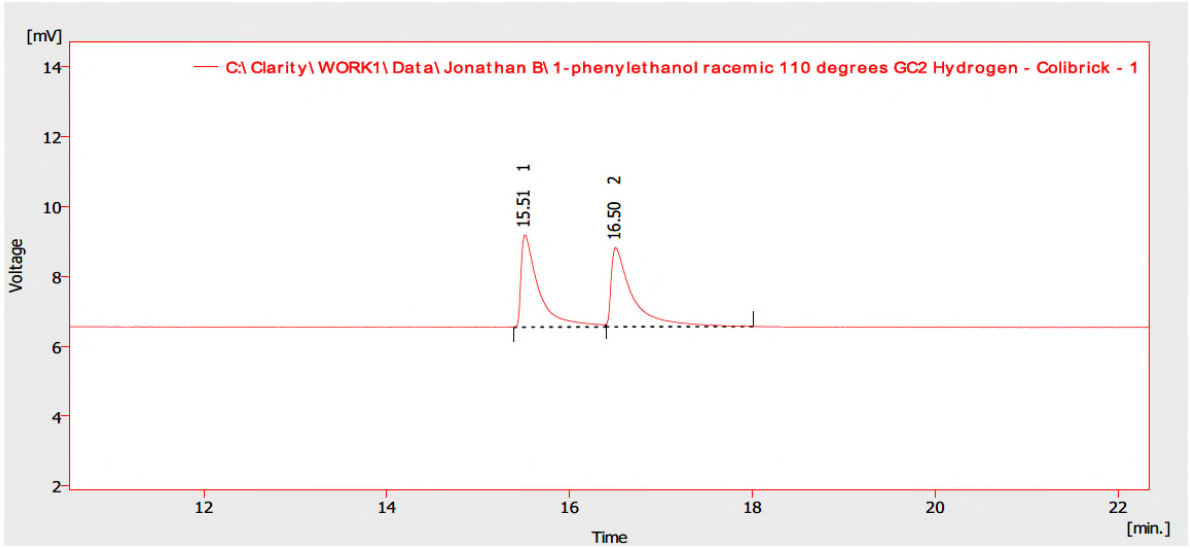


HPLC and GC Spectra for ee determination.



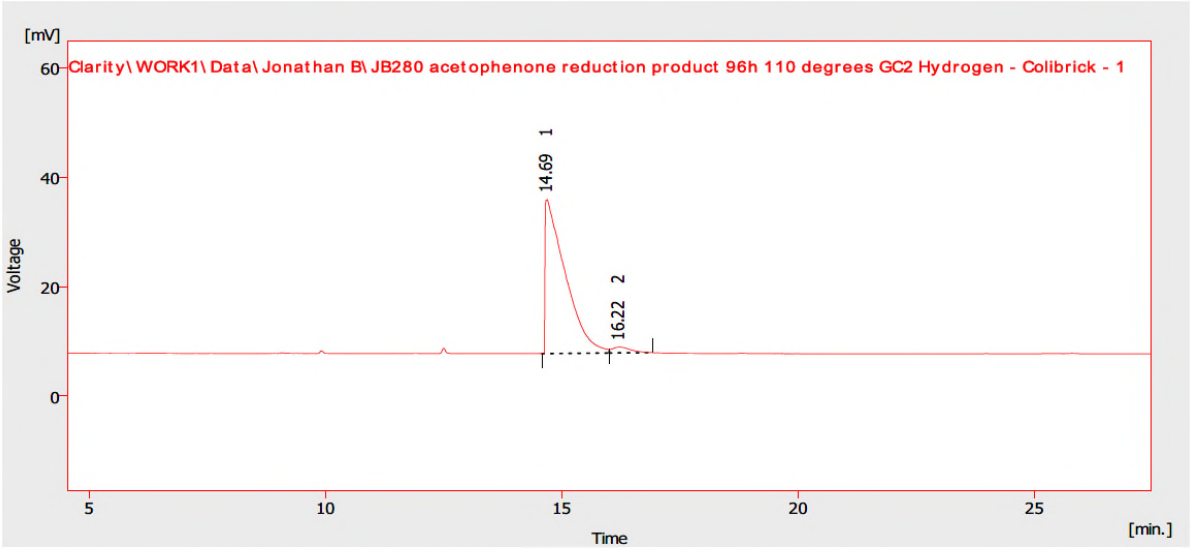
(*R*)-1-Phenylethanol

GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 110 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 9.82 min., *R* isomer 15.51 min., *S* isomer 16.50 min.)



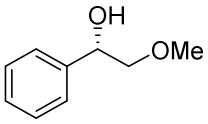
Result Table (Uncal - C:\Clarity\WORK1\Data\Jonathan B\1-phenylethanol racemic 110 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	15.512	35.775	2.636	49.2	53.7	0.18	
2	16.504	36.919	2.273	50.8	46.3	0.20	
	Total	72.694	4.909	100.0	100.0		



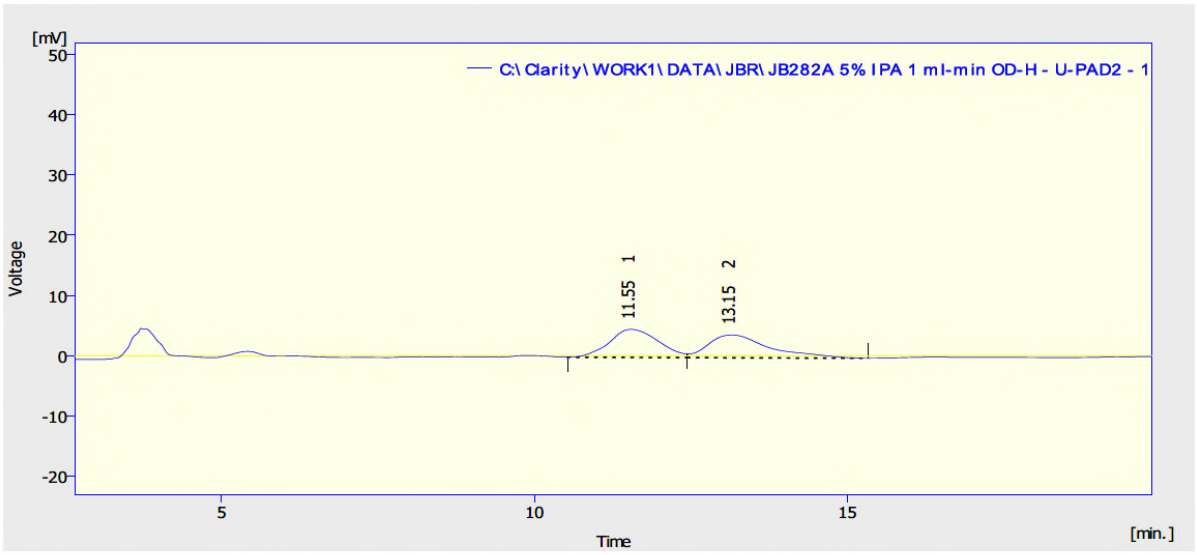
Result Table (Uncal - C:\Clarity\WORK1\Data\Jonathan B\JB280 acetophenone reduction product 96h 110 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.692	837.414	28.151	96.6	96.3	0.45	
2	16.220	29.741	1.072	3.4	3.7	0.48	
	Total	867.154	29.223	100.0	100.0		



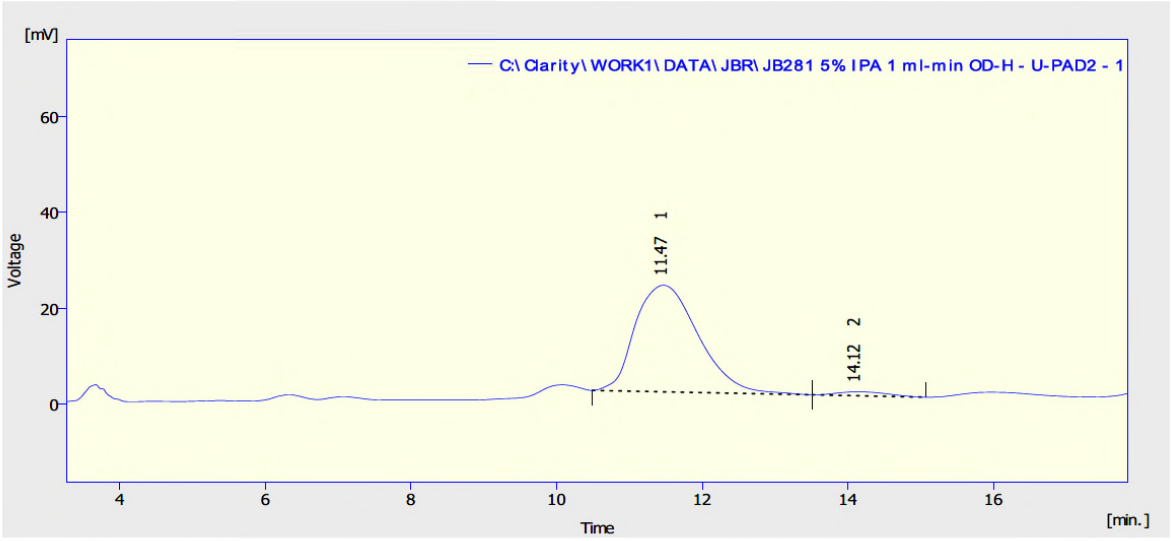
(*S*)-2-methoxy-1-phenylethan-1-ol (24)

HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 254 nm, ketone 12.28 min., *S* isomer 11.55 min., *R* isomer 13.15 min.)



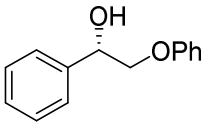
Result Table (Uncal - C:|Clarity|WORK1|DATA|JBR|JB282A 5%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.548	254.791	4.663	49.6	55.1	0.86	
2	13.152	258.690	3.799	50.4	44.9	0.96	
	Total	513.481	8.462	100.0	100.0		



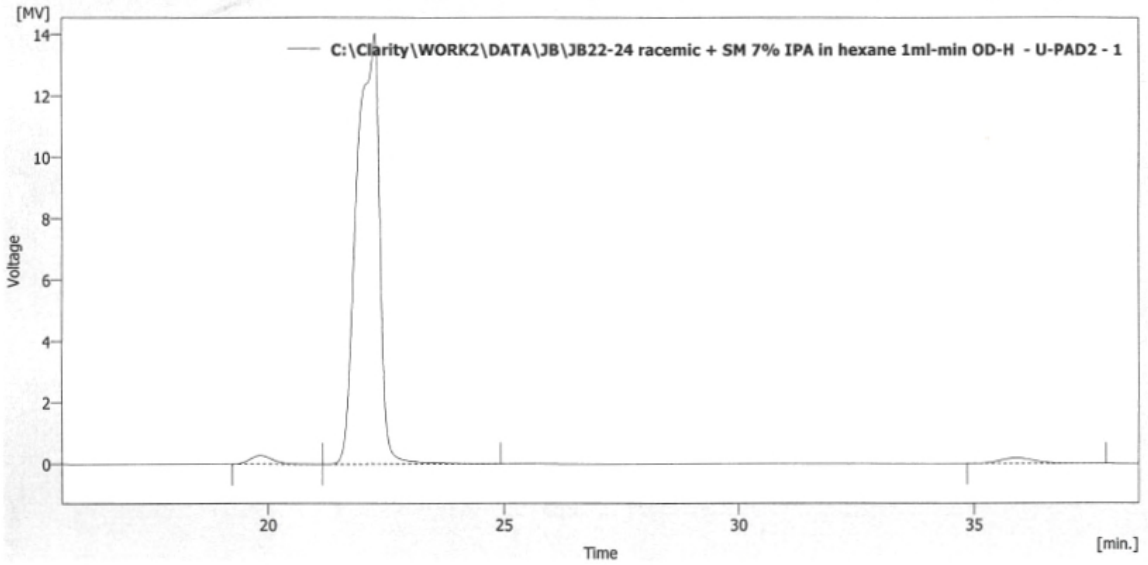
Result Table (Uncal - C:|Clarity|WORK1|DATA|JBR|JB281 5%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.472	1343.463	22.291	97.1	96.4	0.95	
2	14.124	39.849	0.825	2.9	3.6	0.78	
	Total	1383.312	23.116	100.0	100.0		



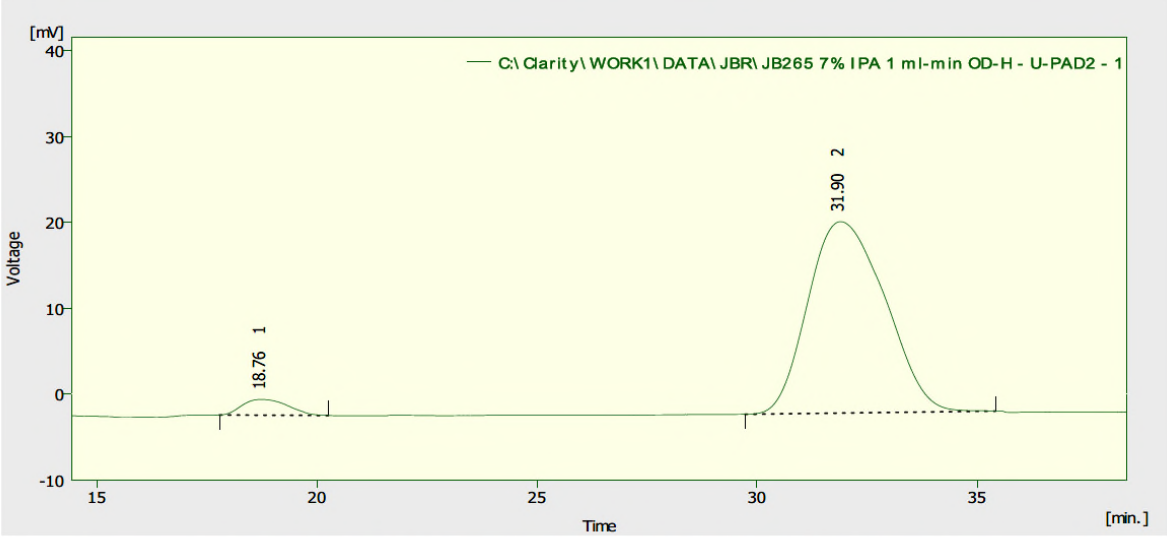
(*S*)-2-phenoxy-1-phenylethan-1-ol (25)

HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 93:7, 1 mL/min, 254 nm, ketone 22.26 min., *S* isomer 35.91 min., *R* isomer 19.84 min.)



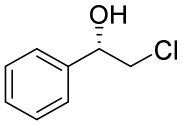
Result Table (Uncal - C:\Clarity\WORK2\DATA\JB\JB22-24 racemic + SM 7% IPA in hexane 1ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	19.836	95.973	2.792	2.0	1.9	0.53	
2	22.256	4670.063	140.303	96.0	96.8	0.56	
3	35.908	96.234	1.832	2.0	1.3	0.81	
	Total	4862.271	144.928	100.0	100.0		



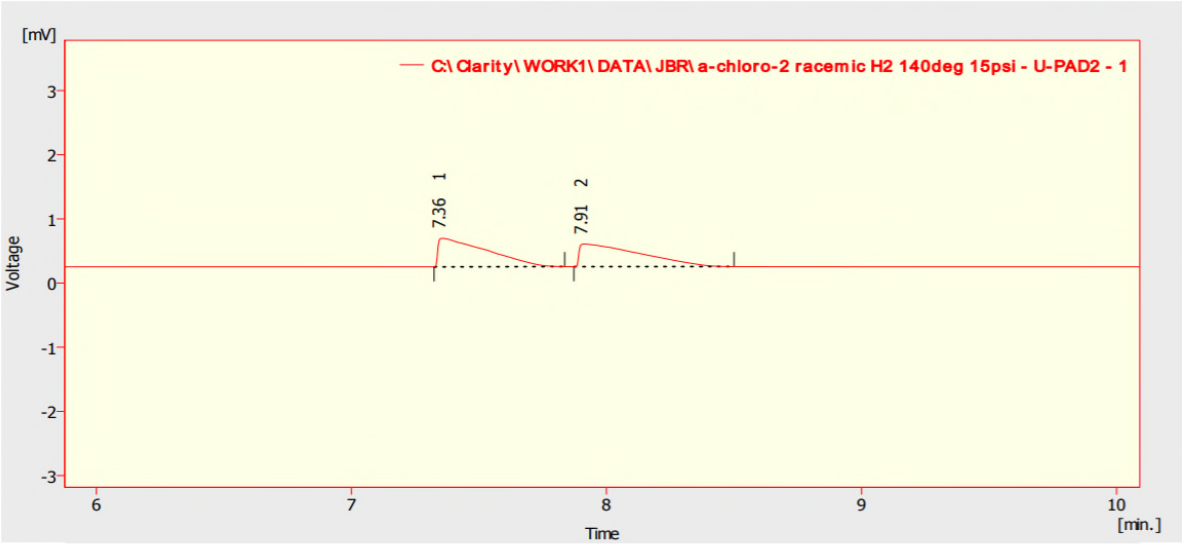
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB265 7%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	18.756	132.468	1.838	4.7	7.6	1.19	
2	31.900	2715.890	22.296	95.3	92.4	2.01	
	Total	2848.358	24.134	100.0	100.0		



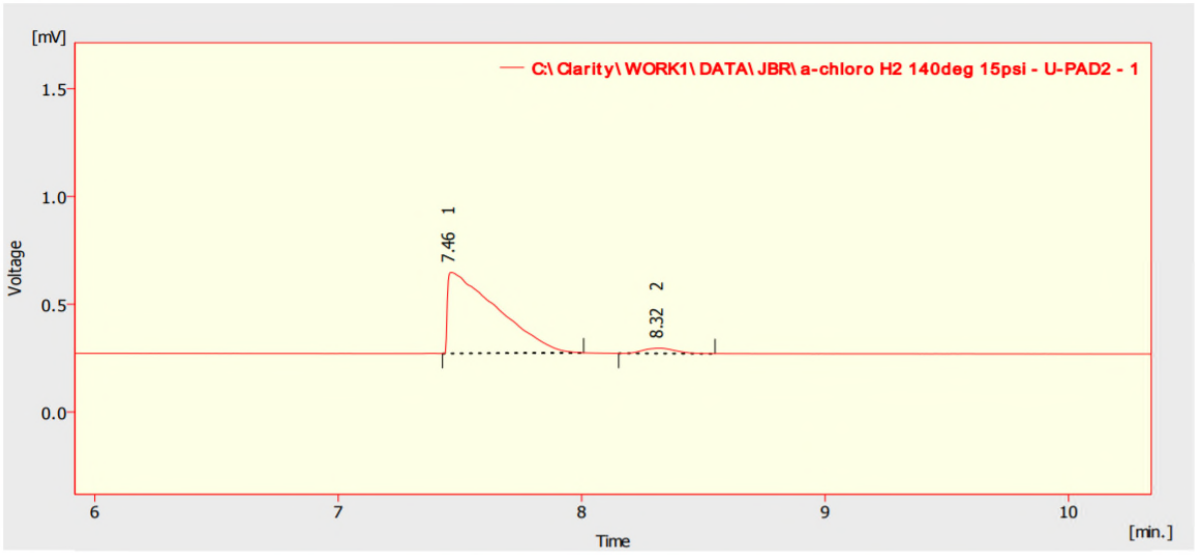
(*S*)-2-Chloro-1-phenylethan-1-ol (26)

GC analysis (CP-CHIRALSIL-DEX-CB, 25 m x 0.25 mm x 0.25 µm, gas H_2, T = 140 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 1.70 min., *R* isomer 7.91 min., *S* isomer 7.36 min.)



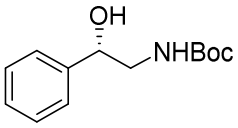
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\a-chloro-2 racemic H2 140deg 15psi - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.356	58.947	4.433	50.0	55.7	0.22	
2	7.912	58.836	3.522	50.0	44.3	0.28	
	Total	117.783	7.954	100.0	100.0		



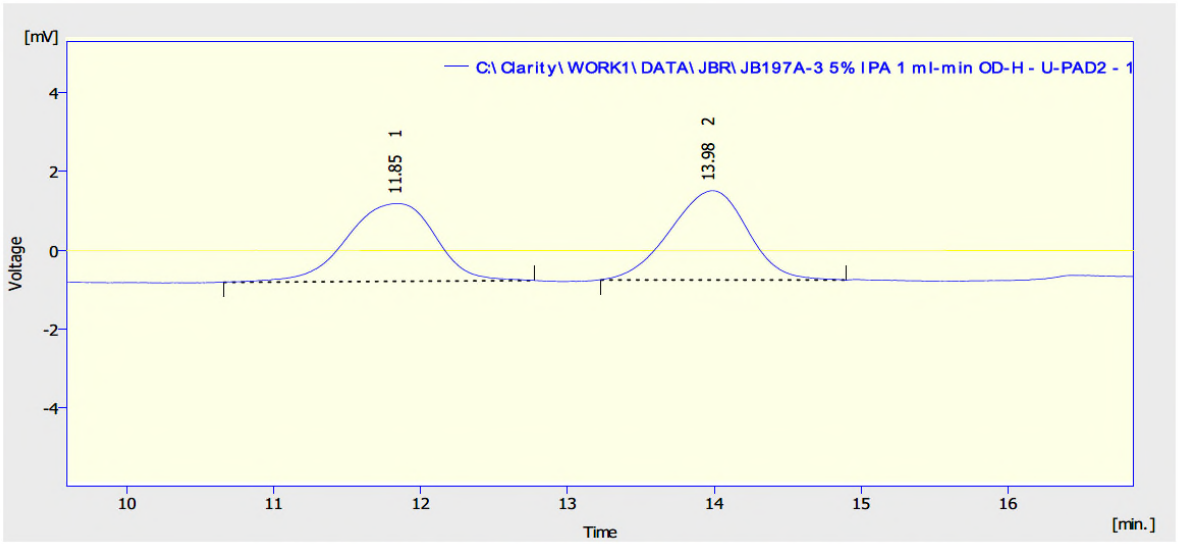
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\a-chloro H2 140deg 15psi - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.464	53.115	3.766	96.0	93.9	0.23	
2	8.320	2.215	0.244	4.0	6.1	0.15	
	Total	55.330	4.011	100.0	100.0		



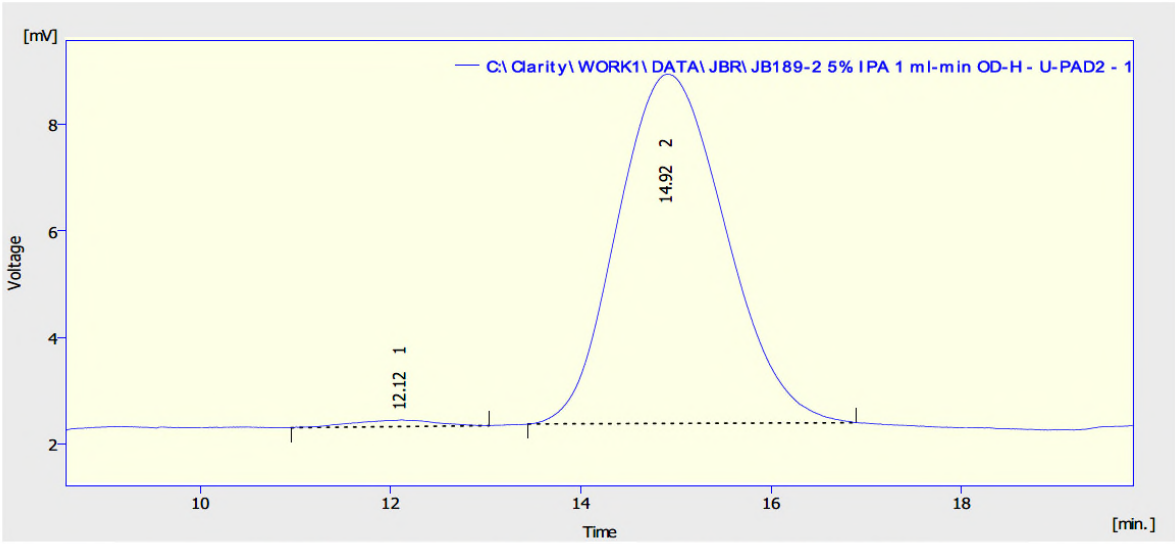
tert-Butyl (_S_)-(2-hydroxy-2-phenylethyl)carbamate (27)

HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 254 nm, ketone 11.70 min., *S* isomer 11.85 min., *R* isomer 13.98 min.)



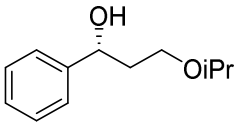
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB197A-3 5%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	11.848	82.974	1.974	50.0	46.6	0.66	
2	13.980	83.122	2.266	50.0	53.4	0.58	
	Total	166.095	4.241	100.0	100.0		



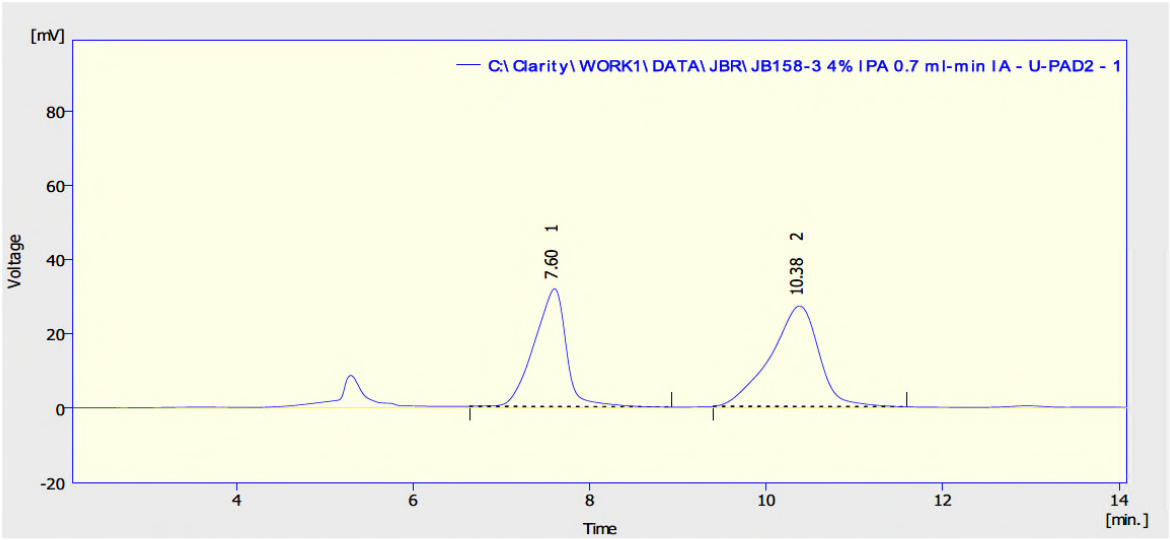
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB189-2 5%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.124	7.590	0.128	1.5	1.9	0.95	
2	14.924	515.672	6.560	98.5	98.1	1.26	
	Total	523.262	6.688	100.0	100.0		



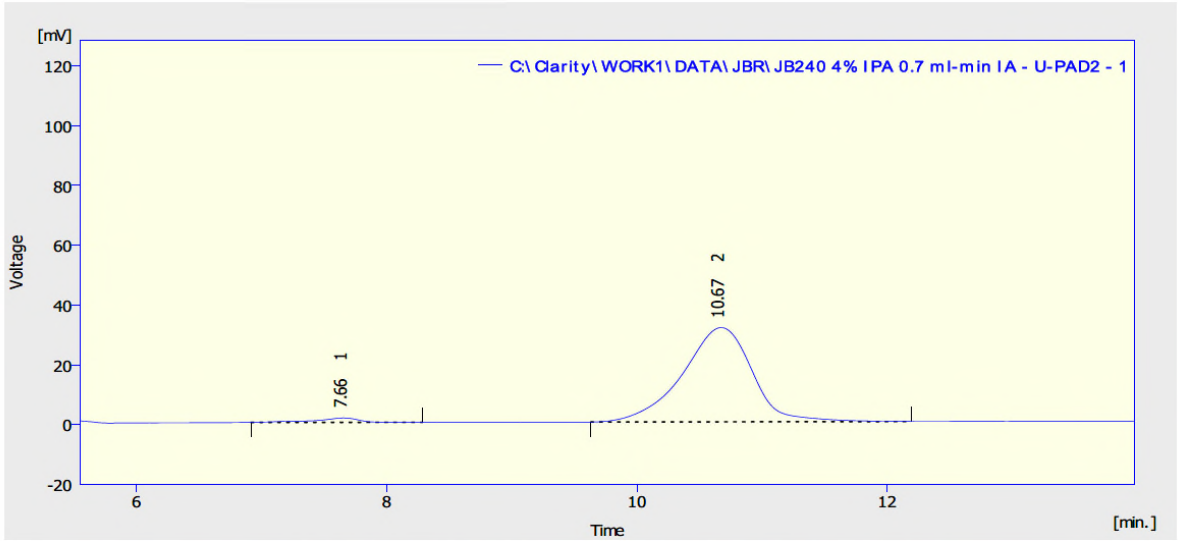
(*R*)-3-isopropoxy-1-phenylpropan-1-ol (28)

HPLC analysis (CHIRALPAK IA, 250 × 4.6 mm column, hexane/2-propanol 96:4, 0.7mL/min, 254 nm, ketone 7.79 min., *S* isomer 7.60 min., *R* isomer 10.38 min.)



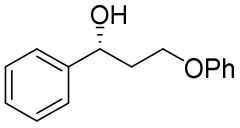
Result Table (Uncal - C:|Clarity|WORK1|DATA|JBR|JB158-3 4%IPA 0.7 ml-min IA - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.600	803.521	31.732	43.7	54.0	0.38	
2	10.380	1036.523	27.083	56.3	46.0	0.56	
	Total	1840.045	58.815	100.0	100.0		



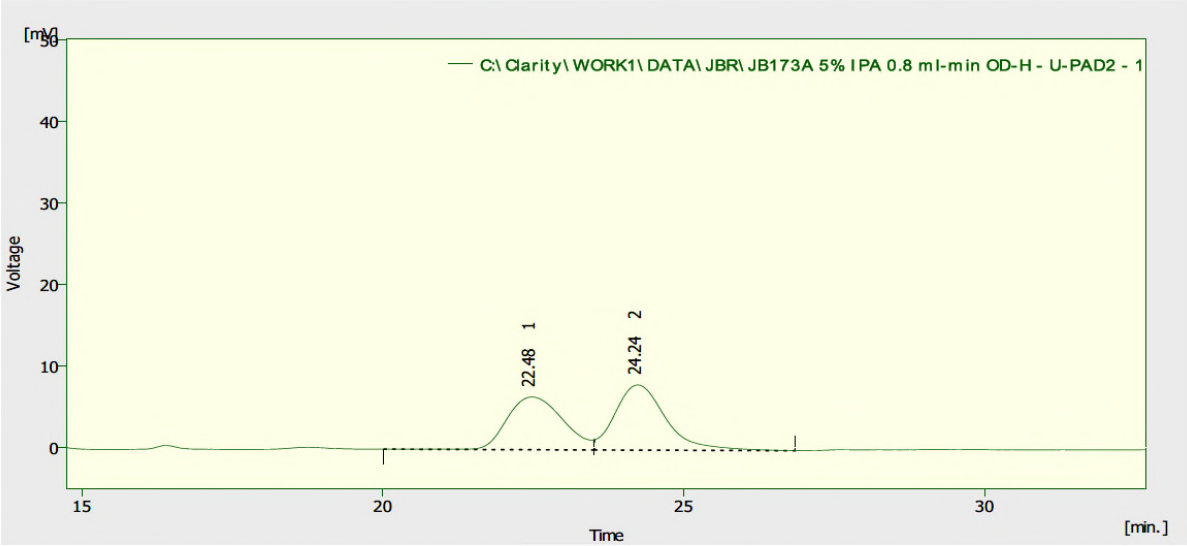
Result Table (Uncal - C:|Clarity|WORK1|DATA|JBR|JB240 4%IPA 0.7 ml-min IA - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.656	34.750	1.470	2.8	4.5	0.30	
2	10.672	1218.478	31.535	97.2	95.5	0.58	
	Total	1253.228	33.005	100.0	100.0		



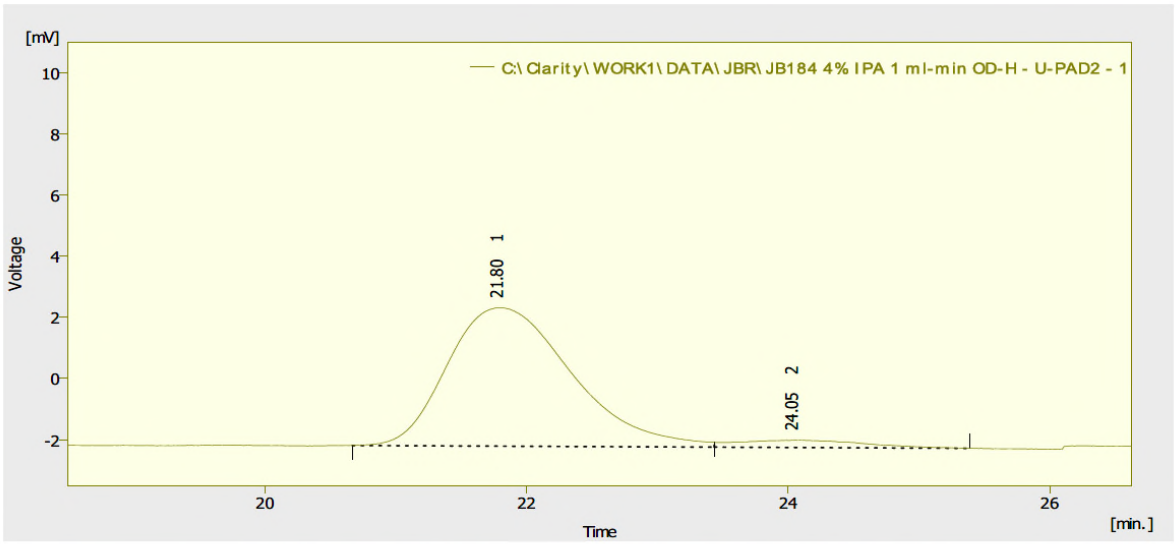
(*R*)-3-phenoxy-1-phenylpropan-1-ol (29)

HPLC analysis (CHIRALCEL OD-H, 250 × 4.6 mm column, hexane/2-propanol 95:5, 0.8 mL/min, 254 nm, ketone 16.72 min., *S* isomer 24.24 min., *R* isomer 22.48 min.)



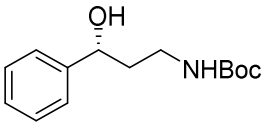
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB173A 5%IPA 0.8 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	22.476	415.836	6.452	47.1	44.7	1.04	
2	24.240	466.872	7.984	52.9	55.3	0.88	
	Total	882.709	14.436	100.0	100.0		



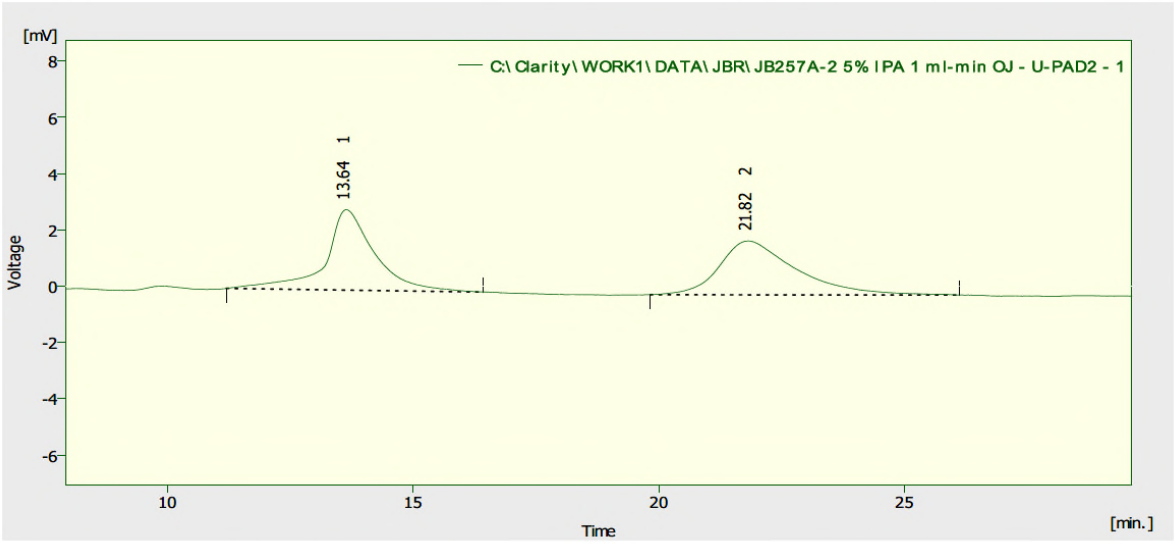
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB184 4%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	21.796	298.895	4.530	94.8	95.0	1.02	
2	24.052	16.324	0.239	5.2	5.0	1.18	
	Total	315.220	4.770	100.0	100.0		



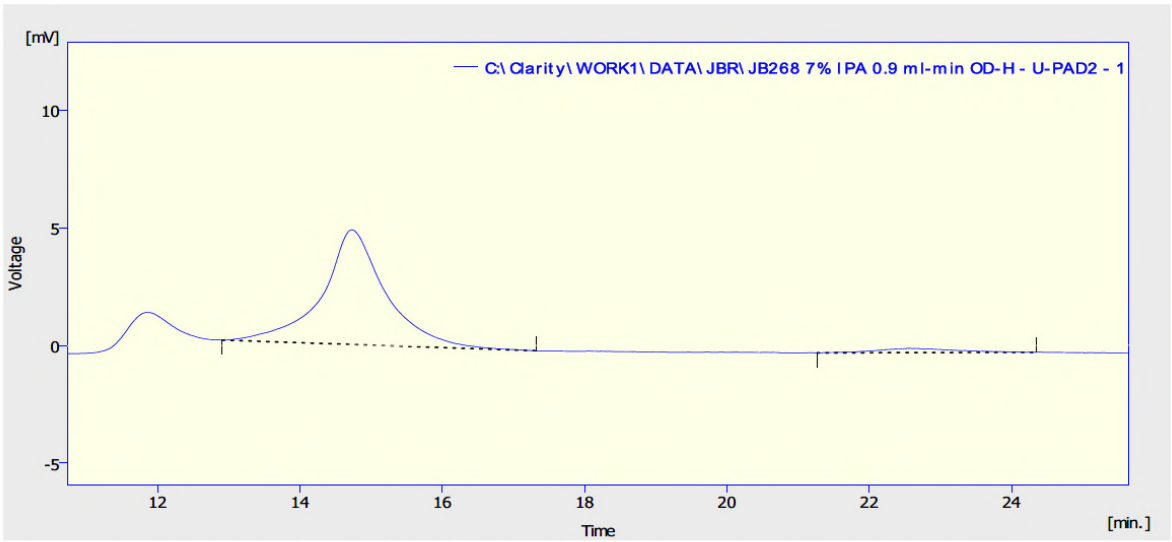
***tert*-Butyl (*R*)-(3-hydroxy-3-phenylpropyl)carbamate (30)**

HPLC analysis (CHIRALCEL OD-H, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 254 nm, ketone 9.70 min., *S* isomer 21.82 min., *R* isomer 13.64 min.)



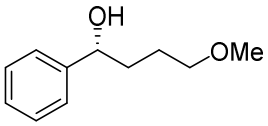
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB257A-2 5%IPA 1 ml-min OJ - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	13.644	200.330	2.863	49.0	59.9	0.85	
2	21.824	208.380	1.914	51.0	40.1	1.56	
	Total	408.710	4.777	100.0	100.0		



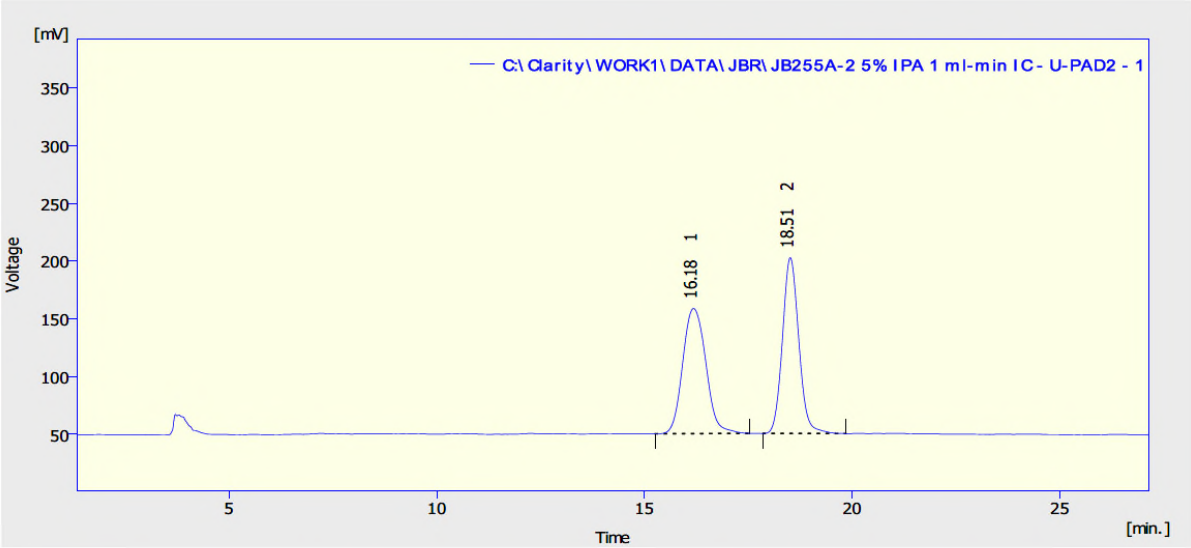
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB268 7%IPA 0.9 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.728	302.317	4.878	95.5	96.3	0.78	
2	22.536	14.084	0.185	4.5	3.7	1.14	
	Total	316.401	5.063	100.0	100.0		



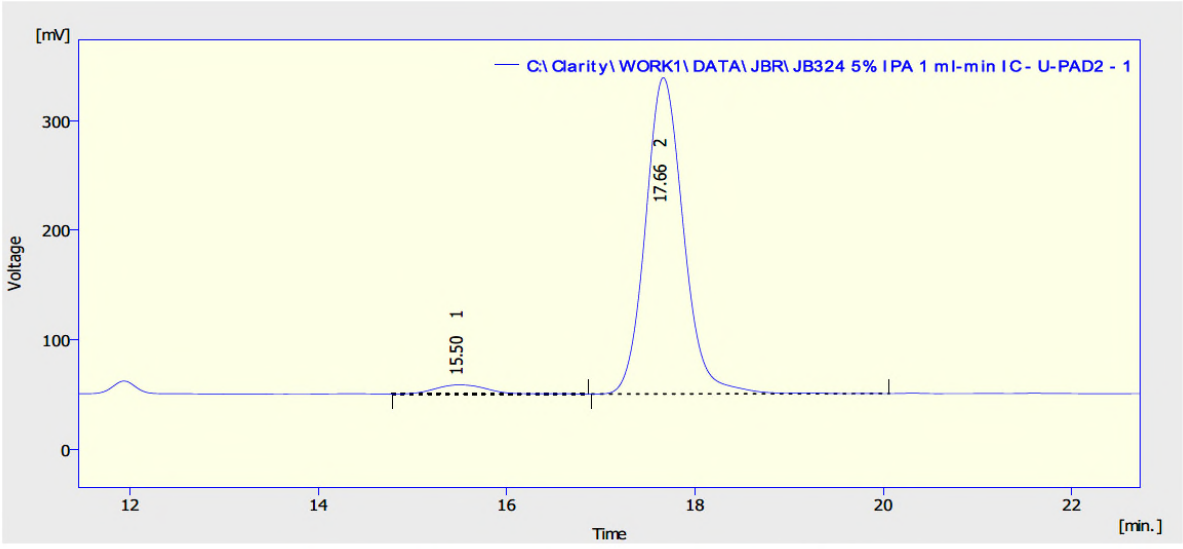
(*R*)-4-Methoxy-1-phenylbutan-1-ol (31)

HPLC analysis (CHIRALPAK IC, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 210 nm, ketone 12.18 min., *S* isomer 16.18 min., *R* isomer 18.51 min.)



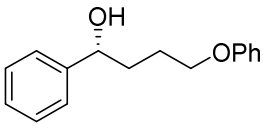
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB255A-2 5%IPA 1 ml-min IC - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	16.184	4200.208	108.454	50.2	41.6	0.61	
2	18.512	4166.373	152.396	49.8	58.4	0.42	
	Total	8366.581	260.850	100.0	100.0		



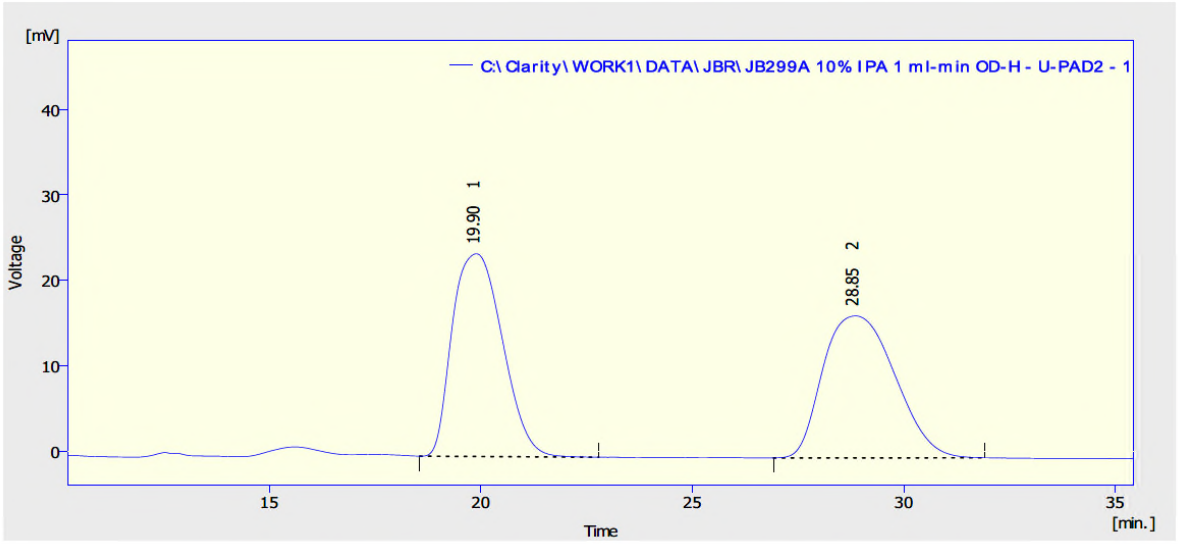
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB324 5%IPA 1 ml-min IC - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	15.500	326.478	8.361	3.9	2.8	0.61	
2	17.664	8100.575	288.920	96.1	97.2	0.43	
	Total	8427.053	297.281	100.0	100.0		



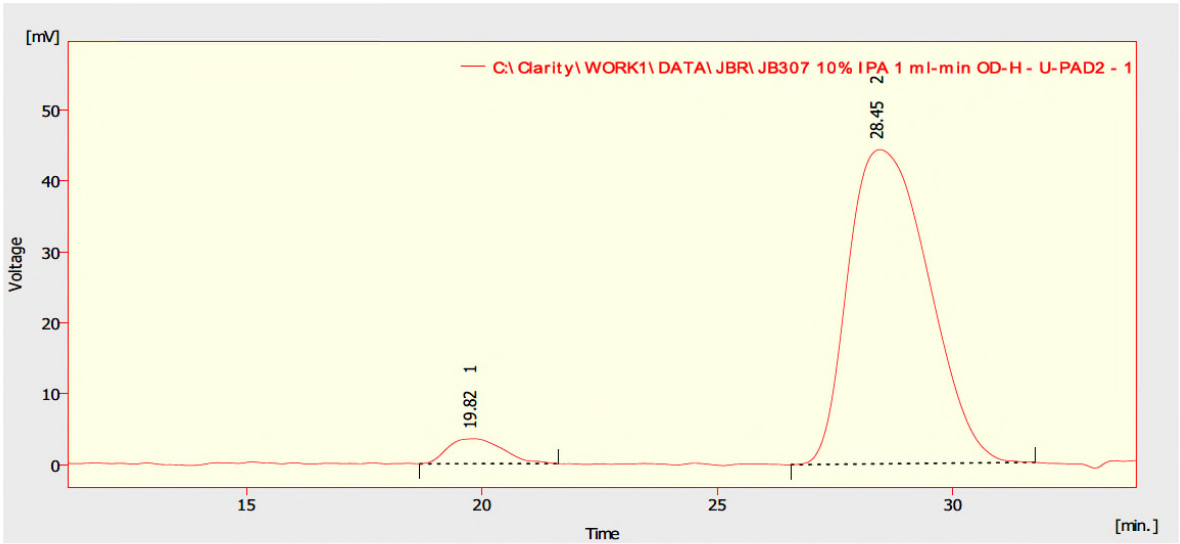
(*R*)-4-phenoxy-1-phenylbutan-1-ol (32)

HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 90:10, 1 mL/min, 254 nm, ketone 13.83 min., *S* isomer 19.90 min., *R* isomer 28.85 min.)



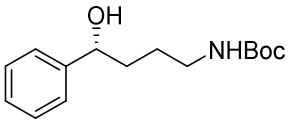
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB299A 10%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	19.896	1956.343	23.750	49.9	58.8	1.34	
2	28.852	1964.721	16.636	50.1	41.2	1.93	
	Total	3921.065	40.385	100.0	100.0		



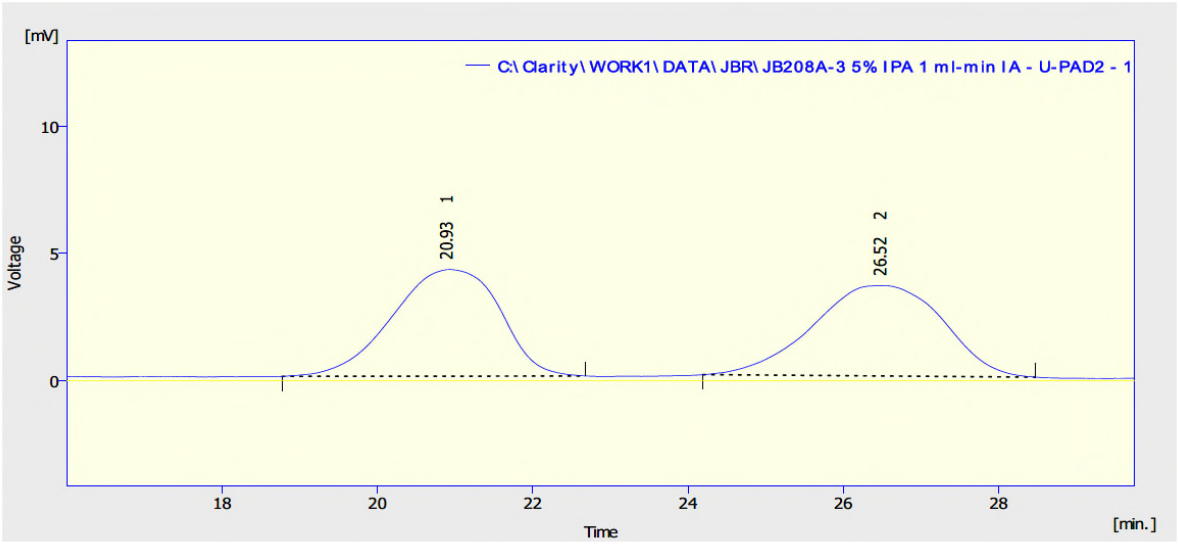
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB307 10%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	19.816	287.214	3.531	5.2	7.4	1.33	
2	28.448	5266.324	44.316	94.8	92.6	1.94	
	Total	5553.538	47.847	100.0	100.0		



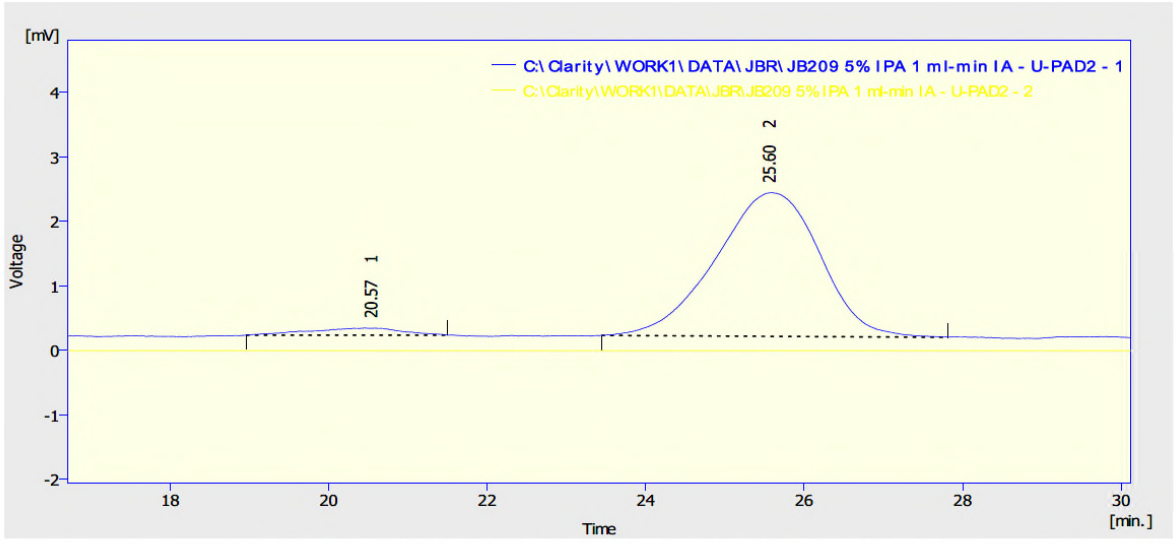
tert-Butyl (_R_)-(4-hydroxy-4-phenylbutyl)carbamate (33)

HPLC analysis (CHIRALPAK IA, 250 × 4.6 mm column, hexane/2-propanol 95:5, 1 mL/min, 254 nm, ketone 13.86 min., *S* isomer 20.93 min., *R* isomer 26.52 min.)



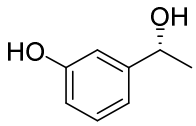
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB208A-3 5%IPA 1 ml-min IA - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	20.928	404.260	4.201	49.5	54.1	1.55	
2	26.516	413.221	3.562	50.5	45.9	1.86	
	Total	817.480	7.763	100.0	100.0		



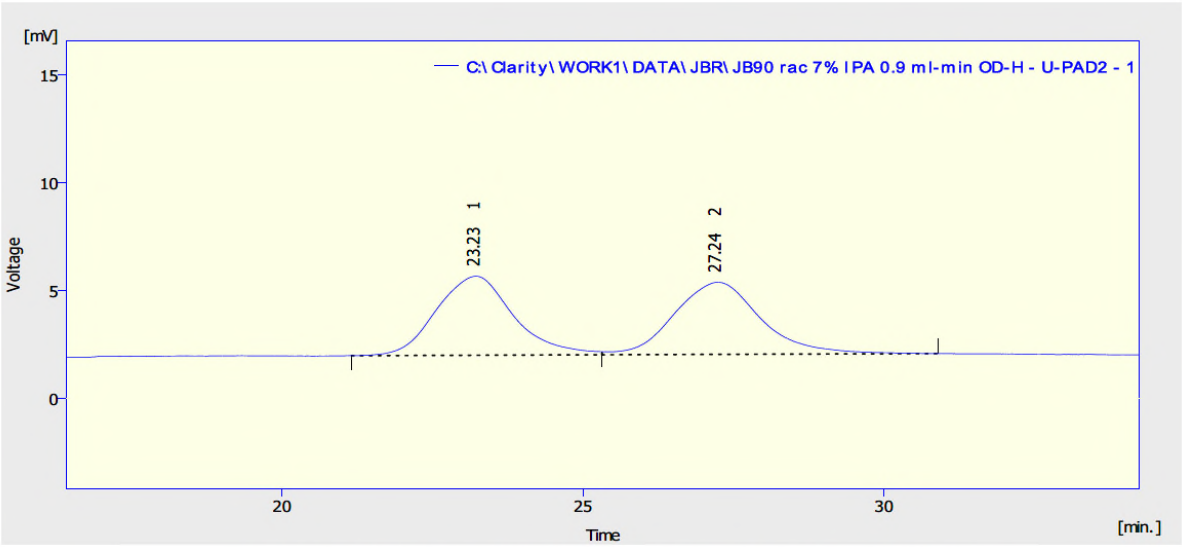
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB209 5%IPA 1 ml-min IA - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	20.572	8.947	0.111	4.2	4.7	1.35	
2	25.600	203.815	2.230	95.8	95.3	1.43	
	Total	212.762	2.341	100.0	100.0		



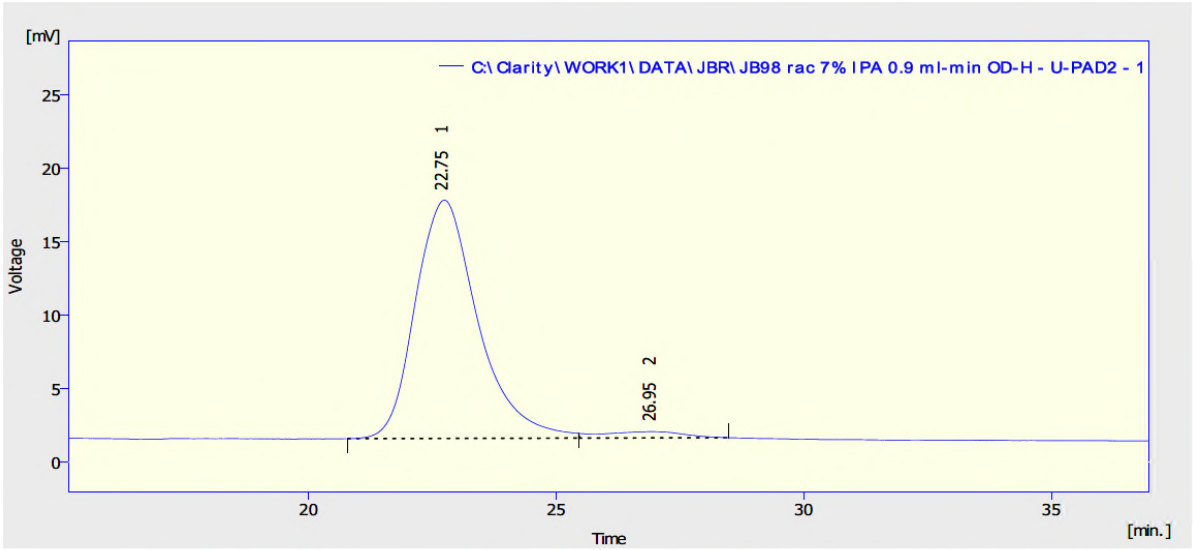
(*R*)-3-(1-hydroxyethyl)phenol (34)

HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 93:7, 0.9 mL/min, 220 nm, ketone 11.70 min., *S* isomer 27.94 min., *R* isomer 23.23 min.)



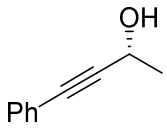
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB90 rac 7%IPA 0.9 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	23.232	326.613	3.665	49.5	52.3	1.36	
2	27.240	333.633	3.344	50.5	47.7	1.50	
	Total	660.246	7.008	100.0	100.0		



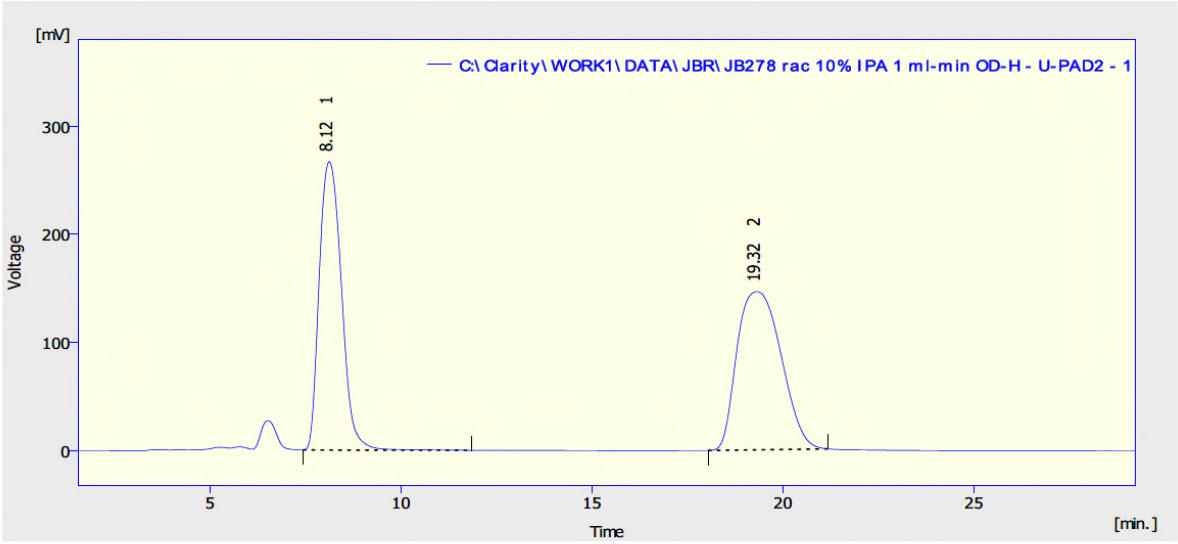
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB98 rac 7%IPA 0.9 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	22.748	1424.056	16.200	96.7	97.4	1.32	
2	26.948	49.213	0.429	3.3	2.6	2.20	
	Total	1473.270	16.629	100.0	100.0		



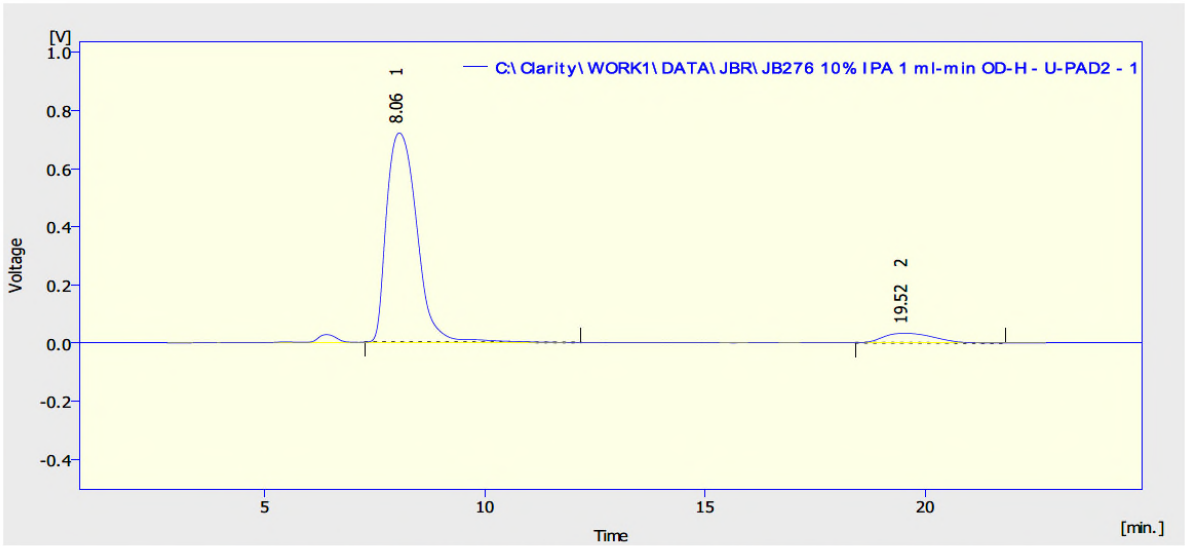
(*R*)-4-phenylbut-3-yn-2-ol (35)

HPLC analysis (Chiralcel OD-H, 250 × 4.6 mm column, hexane/2-propanol 90:10, 1 mL/min, 220 nm, Ketone: 6.59 min, *S* isomer: 19.32 min, *R* isomer: 8.12 min)



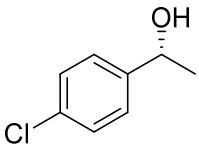
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB278 rac 10%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.120	10816.474	266.903	47.9	64.6	0.65	
2	19.316	11753.323	146.328	52.1	35.4	1.32	
	Total	22569.797	413.230	100.0	100.0		



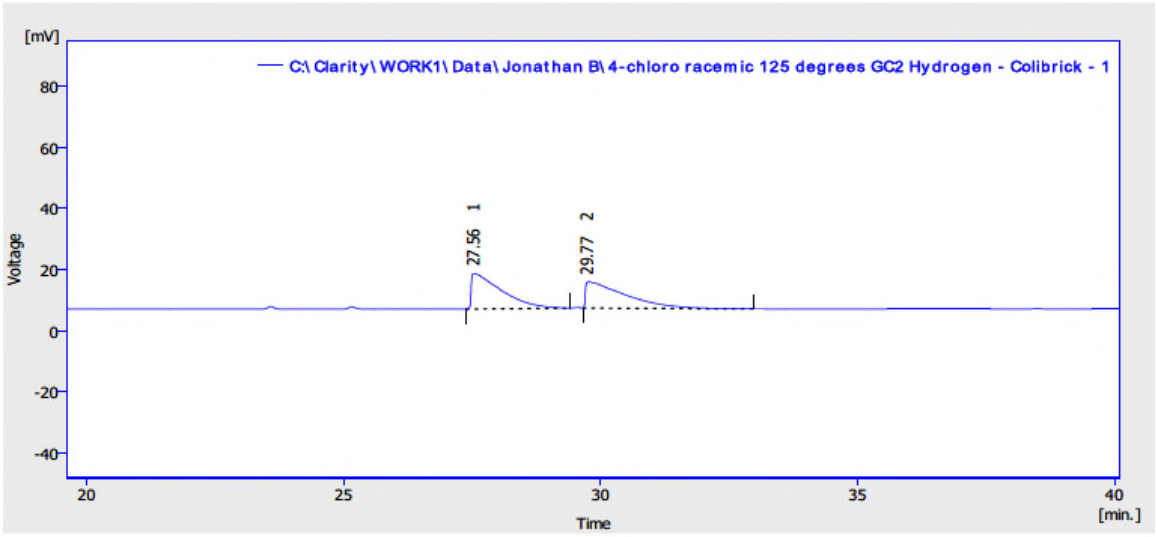
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB276 10%IPA 1 ml-min OD-H - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.056	34519.769	719.883	93.0	95.7	0.76	
2	19.516	2587.695	32.600	7.0	4.3	1.30	
	Total	37107.464	752.482	100.0	100.0		



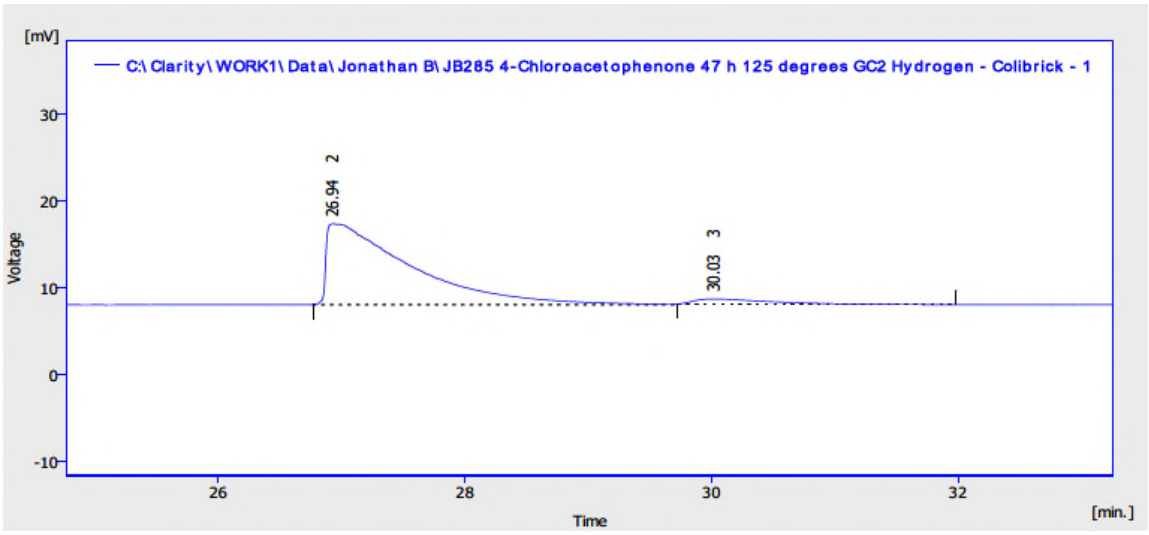
(*R*)-1-(4-Chlorophenyl)ethan-1-ol (36)

GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 125 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 14.82 min., *R* isomer 27.56 min., *S* isomer 29.77 min.)



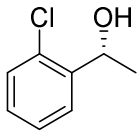
Result Table (Uncal - C:\|Clarity\|WORK1\|Data\|Jonathan B\|4-chloro racemic 125 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	27.560	476.778	11.691	50.5	57.4	0.62	
2	29.768	466.557	8.674	49.5	42.6	0.78	
	Total	943.336	20.365	100.0	100.0		



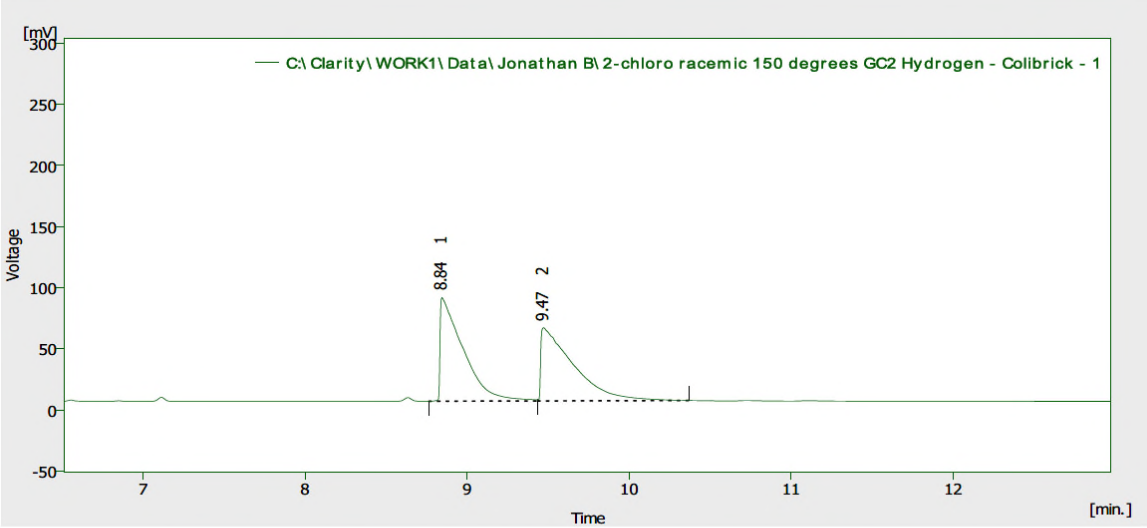
Result Table (Uncal - C:\|Clarity\|WORK1\|Data\|Jonathan B\|JB285 4-Chloroacetophenone 47 h 125 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	14.816	1.153	0.181	0.2	1.8	0.10	
2	26.936	444.714	9.340	93.3	91.7	0.66	
3	30.028	30.922	0.666	6.5	6.5	0.68	
	Total	476.789	10.187	100.0	100.0		



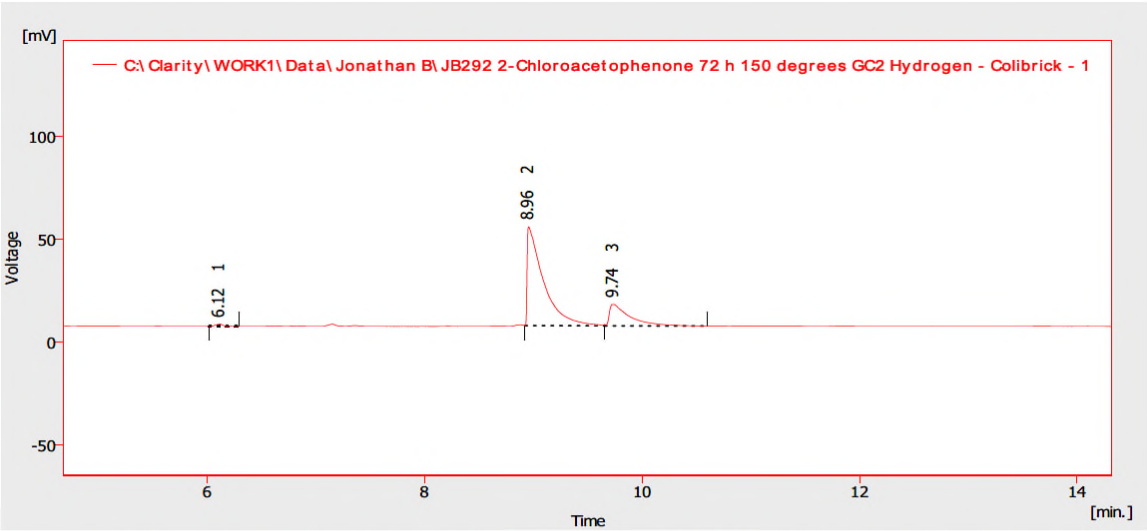
(*R*)-1-(2-Chlorophenyl)ethan-1-ol (37)

GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 150 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 6.12 min., *R* isomer 8.84 min., *S* isomer 9.47 min.)



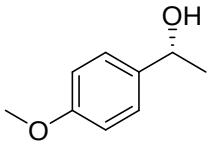
Result Table (Uncal - C:\|Clarity\|WORK1\|Data\|Jonathan B\|2-chloro racemic 150 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	8.844	834.783	84.780	50.1	58.6	0.15	
2	9.472	832.314	59.883	49.9	41.4	0.20	
	Total	1667.097	144.663	100.0	100.0		



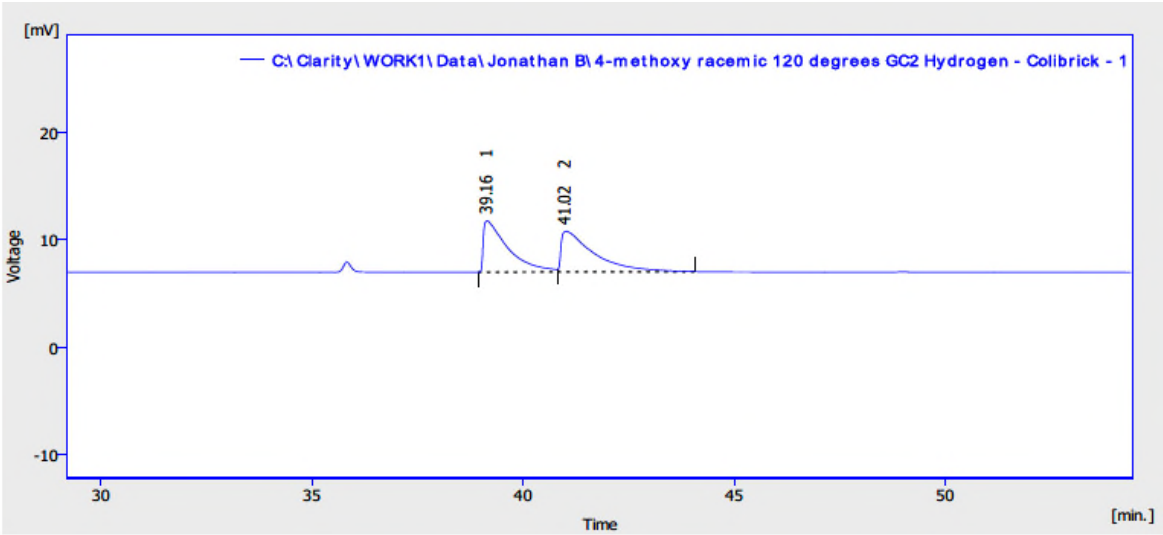
Result Table (Uncal - C:\|Clarity\|WORK1\|Data\|Jonathan B\|JB292 2-Chloroacetophenone 72 h 150 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.116	4.752	1.071	0.7	1.8	0.08	
2	8.956	500.035	48.099	78.0	80.6	0.14	
3	9.736	136.484	10.483	21.3	17.6	0.17	
	Total	641.272	59.653	100.0	100.0		



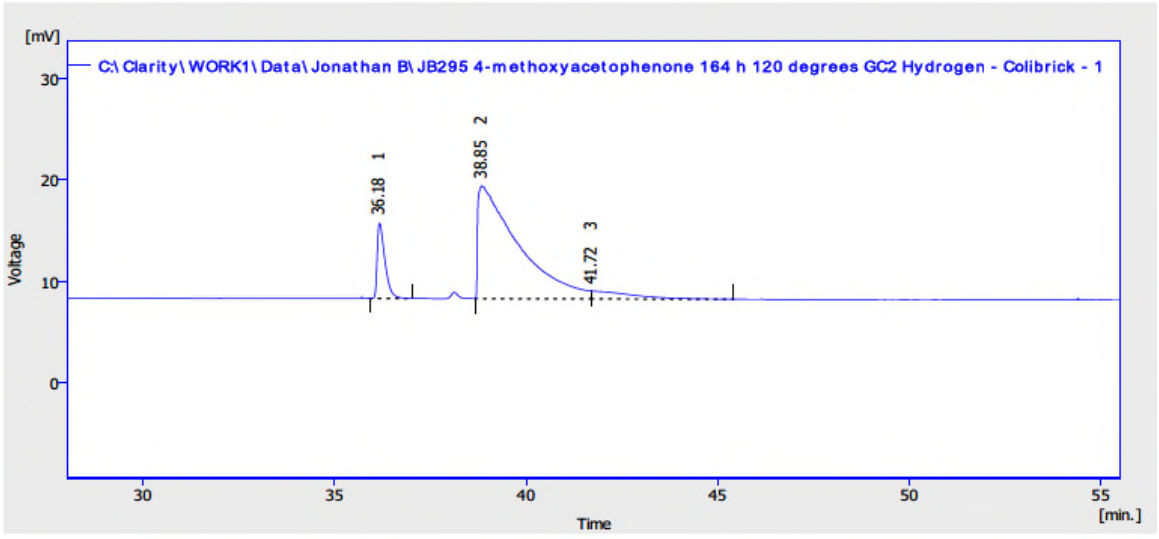
(*R*)-1-(4-Methoxyphenyl)ethan-1-ol (38)

GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 120 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 36.18 min., *R* isomer 39.16 min., *S* isomer 41.02 min.)



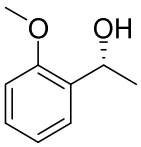
Result Table (Uncal - C:\Clarity\WORK1\Data\Jonathan B\4-methoxy racemic 120 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	39.164	194.334	4.814	48.7	55.8	0.56	
2	41.016	204.501	3.814	51.3	44.2	0.74	
	Total	398.835	8.628	100.0	100.0		



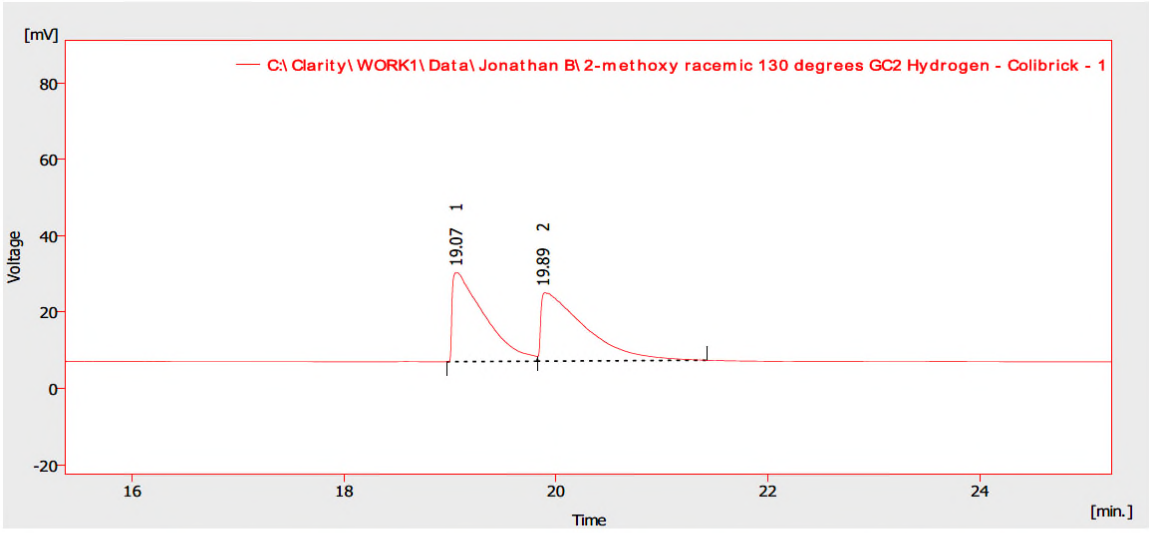
Result Table (Uncal - C:\Clarity\WORK1\Data\Jonathan B\JB295 4-methoxyacetophenone 164 h 120 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	36.176	104.272	7.514	10.7	38.7	0.21	
2	38.848	812.616	11.127	83.5	57.3	1.03	
3	41.716	56.412	0.769	5.8	4.0	1.06	
	Total	973.299	19.410	100.0	100.0		



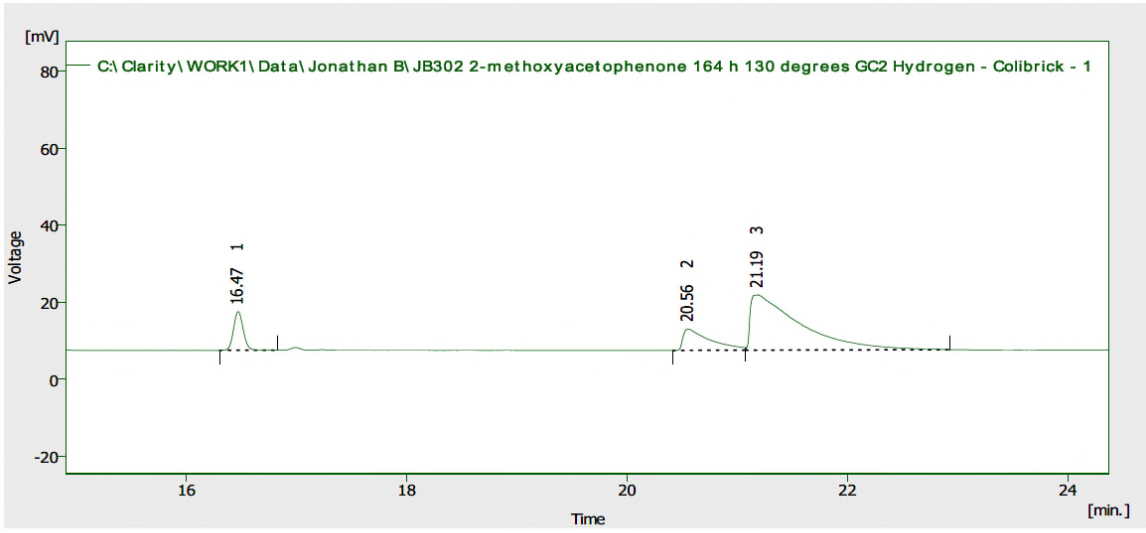
(*R*)-1-(2-Methoxyphenyl)ethan-1-ol (39)

GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas H_2, T = 130 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 16.47 min., *R* 19.07 isomer min., *S* 19.89 isomer min.)



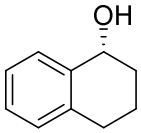
Result Table (Uncal - C:\Clarity\WORK1\Data\Jonathan B\2-methoxy racemic 130 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	19.072	495.469	23.302	48.9	56.5	0.33	
2	19.892	517.550	17.932	51.1	43.5	0.42	
	Total	1013.019	41.234	100.0	100.0		



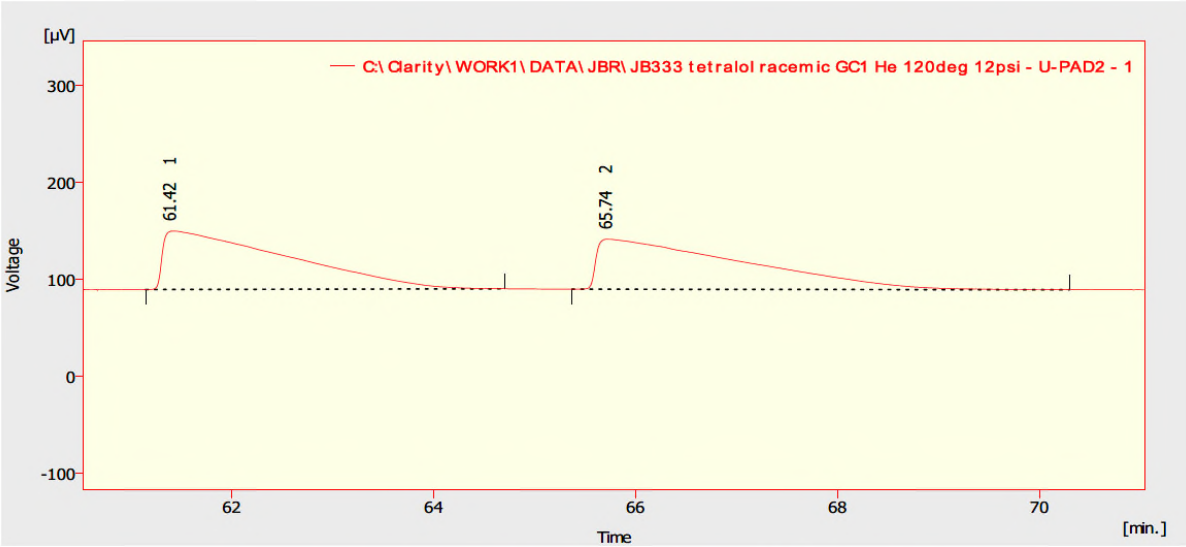
Result Table (Uncal - C:\Clarity\WORK1\Data\Jonathan B\JB302 2-methoxyacetophenone 164 h 130 degrees GC2 Hydrogen - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	16.468	61.298	10.022	10.1	33.5	0.10	
2	20.556	94.348	5.544	15.5	18.5	0.25	
3	21.188	451.145	14.364	74.3	48.0	0.45	
	Total	606.790	29.930	100.0	100.0		



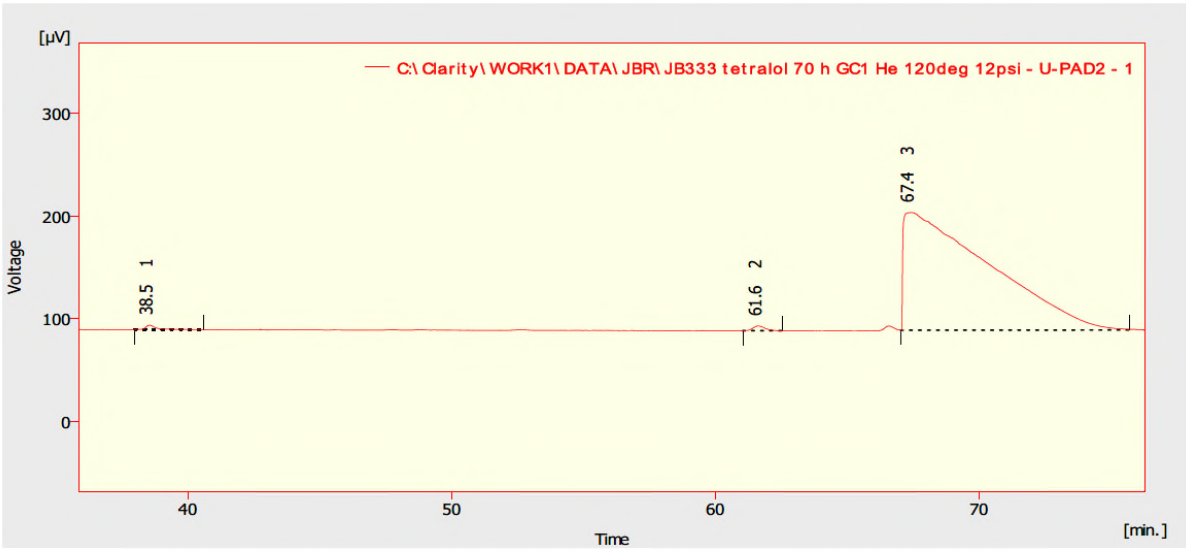
(*R*)-1,2,3,4-Tetrahydronaphthalen-1-ol (40)

GC analysis (CP-CHIRALSIL-DEX-CB, 25 m x 0.25 mm x 0.25 µm, gas He, T = 120 °C, P = 12 psi, FID temp 250 °C, injector temp 220 °C, ketone 38.54 min., *R* isomer 65.74 min., *S* isomer 61.42 min.)



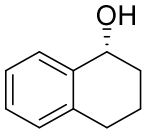
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB333 tetralol racemic GC1 He 120deg 12psi - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	61.416	51.651	0.602	50.0	53.9	1.41	
2	65.736	51.723	0.516	50.0	46.1	1.60	
	Total	103.373	1.118	100.0	100.0		



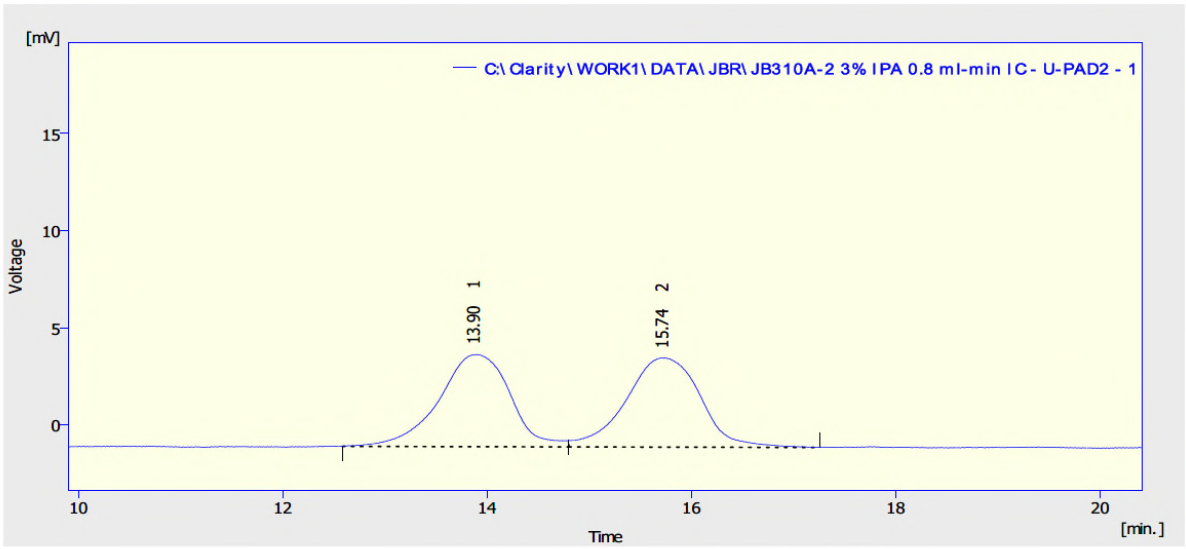
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB333 tetralol 70 h GC1 He 120deg 12psi - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	38.540	1.287	0.043	0.5	3.5	0.36	
2	61.636	1.488	0.048	0.6	3.9	0.48	
3	67.404	260.294	1.150	98.9	92.7	3.67	
	Total	263.069	1.241	100.0	100.0		



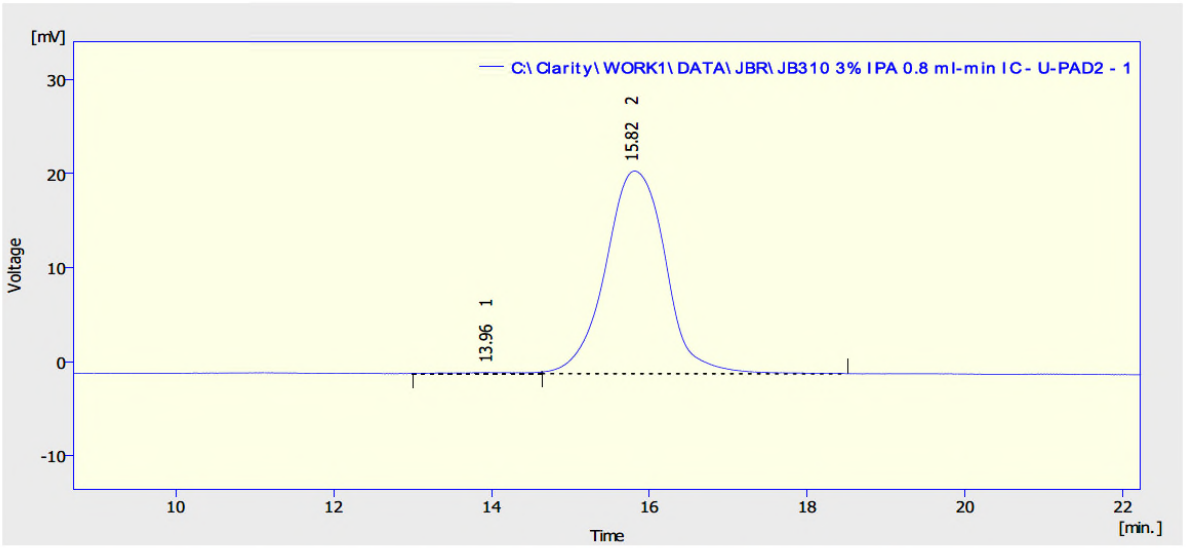
(*R*)-1,2,3,4-tetrahydronaphthalen-1-ol (40)

HPLC analysis (CHIRALPAK IC, 250 × 4.6 mm column, hexane/2-propanol 97:3, 0.8mL/min, 254 nm, ketone 17.52 min., *S* isomer 13.90 min., *R* isomer 15.74 min.)



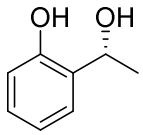
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB310A-2 3%IPA 0.8 ml-min IC - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	13.896	230.194	4.747	49.7	50.8	0.73	
2	15.744	232.529	4.598	50.3	49.2	0.78	
	Total	462.724	9.346	100.0	100.0		



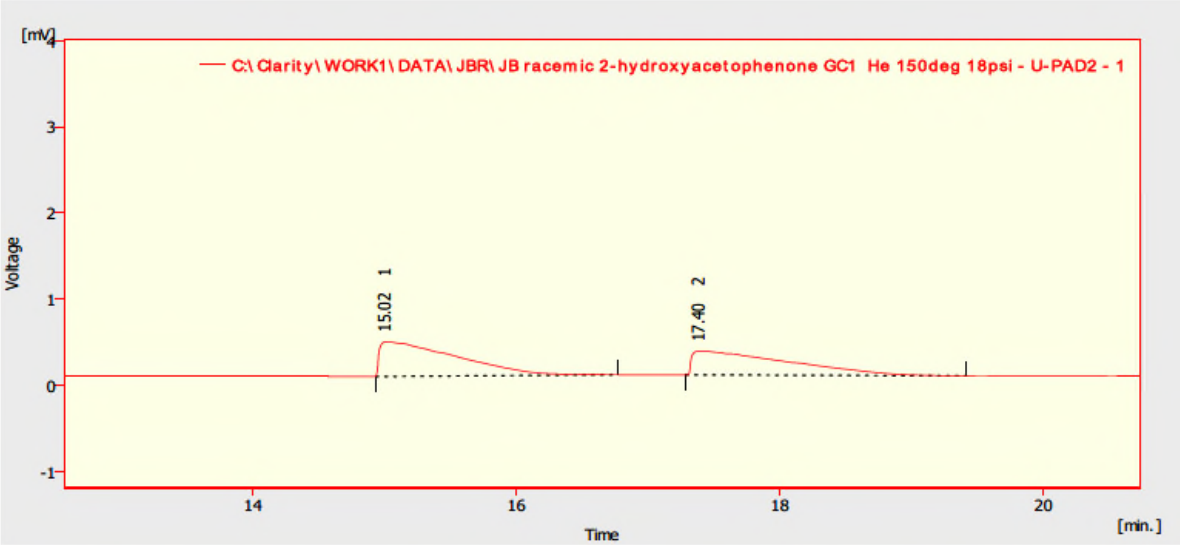
Result Table (Uncal - C:\Clarity\WORK1\DATA\JBR\JB310 3%IPA 0.8 ml-min IC - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	13.964	8.144	0.124	0.7	0.6	0.96	
2	15.816	1139.400	21.562	99.3	99.4	0.81	
	Total	1147.544	21.687	100.0	100.0		



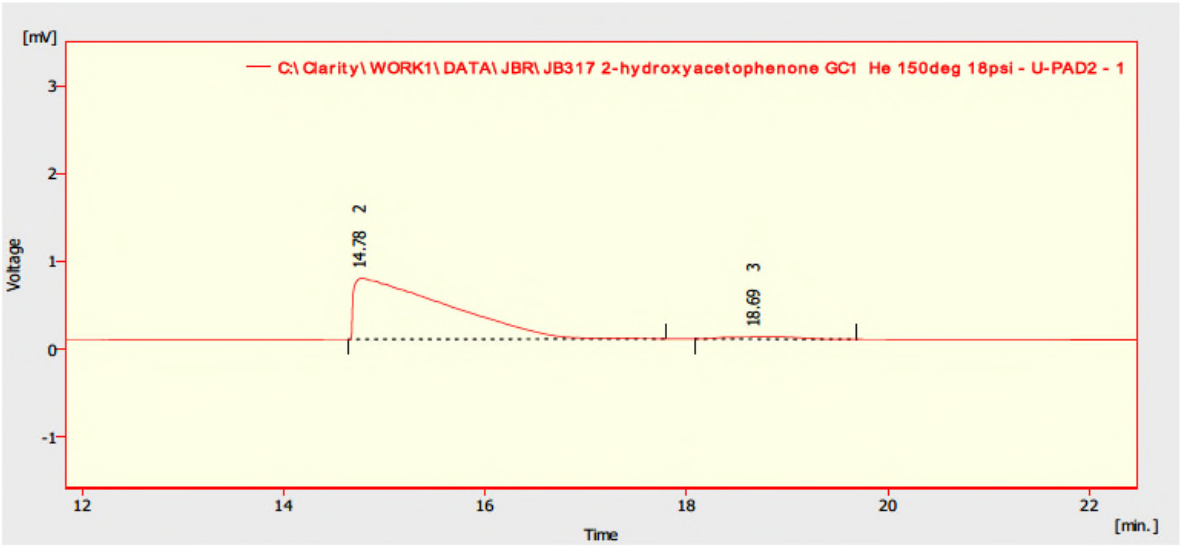
(*R*)-2-(1-Hydroxyethyl)phenol (41)

GC analysis (CP-CHIRALSIL-DEX-CB, 25 m x 0.25 mm x 0.25 µm, gas He, T = 150 °C, P = 15 psi, FID temp 250 °C, injector temp 220 °C, ketone 3.26 min., *R* isomer 15.02 min., *S* isomer 17.40 min.)



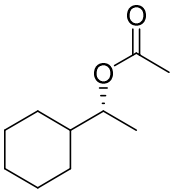
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB racemic 2-hydroxyacetophenone GC1 He 150deg 18psi - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	15.020	164.267	4.055	53.7	59.7	0.67	
2	17.404	141.840	2.738	46.3	40.3	0.84	
	Total	306.107	6.793	100.0	100.0		



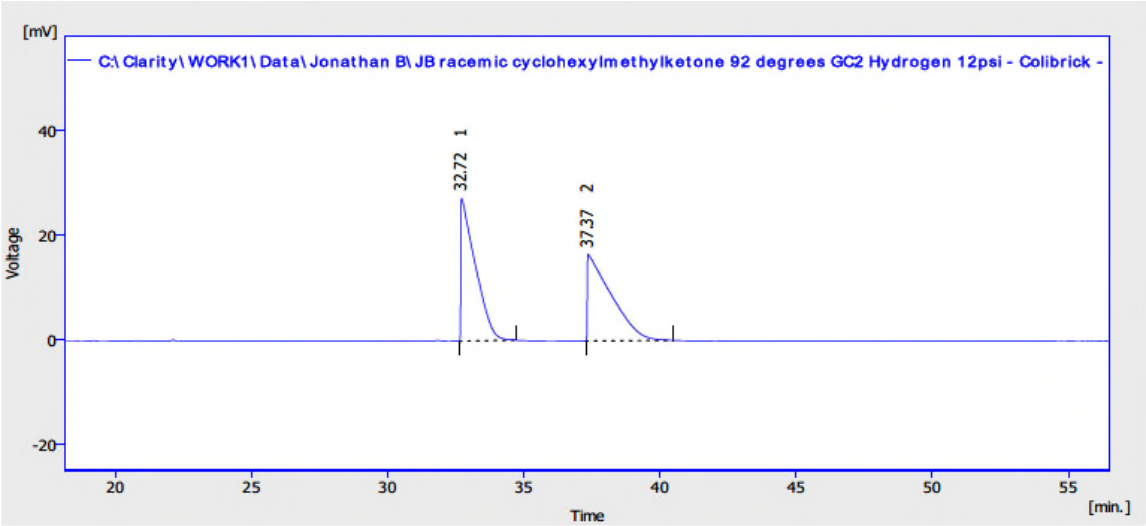
Result Table (Uncal - C:\|Clarity\|WORK1\|DATA\|JBR\|JB317 2-hydroxyacetophenone GC1 He 150deg 18psi - U-PAD2 - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	3.264	13.089	2.688	2.8	27.2	0.06	
2	14.784	449.883	6.959	94.6	70.4	1.05	
3	18.692	12.531	0.234	2.6	2.4	0.89	
	Total	475.502	9.881	100.0	100.0		



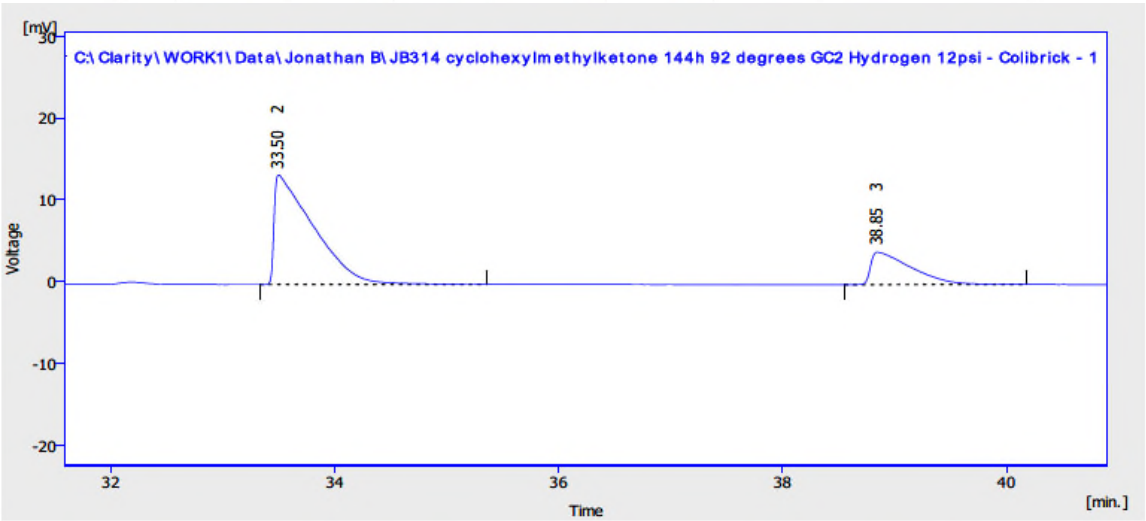
(*R*)-1-Cyclohexylethyl acetate (acetylcyclohexane)

GC analysis (CHROMPAC CYCLODEXTRIN-β-236M-19, 50 m × 0.25 mm × 0.25 μm, gas hydrogen, T = 92 °C, P = 12 psi, FID temp 250 °C, injector temp 220 °C, ketone 19.28 min., *R* isomer 37.37 min., *S* isomer 32.72 min.)



Result Table (Uncal - C:\|Clarity\|WORK1\|Data\|Jonathan B\|JB racemic cyclohexylmethylketone 92 degrees GC2 Hydrogen 12psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	32.716	1006.498	27.433	50.0	62.3	0.58	
2	37.368	1005.365	16.626	50.0	37.7	0.94	
	Total	2011.862	44.059	100.0	100.0		



Result Table (Uncal - C:\|Clarity\|WORK1\|Data\|Jonathan B\|JB314 cyclohexylmethylketone 144h 92 degrees GC2 Hydrogen 12psi - Colibrick - 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	19.276	35.245	3.211	7.6	15.6	0.18	
2	33.500	326.865	13.384	70.8	65.1	0.38	
3	38.852	99.266	3.980	21.5	19.3	0.39	
	Total	461.375	20.575	100.0	100.0		